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Rhenium-catalyzed synthesis of naphthalene derivatives via insertion of aldehydes into a C–H bond

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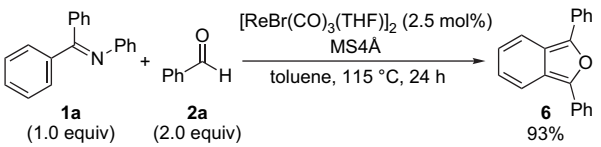
Dedicated to Professor Hisashi Yamamoto in recognition of his significant contribution to modern synthetic organic chemistry

Abstract—A rhenium complex, $[ReBr(CO)_3(THF)]_2$, catalyzed reactions of aromatic ketimines and aldehydes with dienophiles, followed by dehydration, to give naphthalene derivatives in good to excellent yields. This reaction proceeds via C–H bond activation, insertion of an aldehyde, intramolecular nucleophilic cyclization, reductive elimination, elimination of aniline and Diels–Alder reaction. After dehydration, naphthalene derivatives were formed.

1. Introduction

Naphthalene derivatives are useful compounds because, for example, they are partial structures of bioactive molecules[1] and liquid crystals.[2] Various methods have been reported for the transition metal-catalyzed or -mediated synthesis of naphthalene derivatives including gold-catalyzed [4+2] cycloaddition of *o*-alkynylbenzaldehydes with alkynes,[3] palladium-catalyzed [2+2+2] cocycloaddition of arynes and diynes,[4] ruthenium-catalyzed aromatization of aromatic enynes,[5] ruthenium-catalyzed cyclization of iodoalkyne-epoxide functionalities,[6] and Diels–Alder reaction of pentacarbonylbenzopyranylidenetungsten(0) complexes with electron-rich alkenes.[7] One way to improve the previous syntheses is to construct the naphthalene skeleton using a method based on C–H bond activation.[8,9] If this can be achieved, it would offer an efficient and useful way to synthesize naphthalene derivatives. In 2006, we reported on the synthesis of isobenzofuran derivatives via C–H bond activation (Eq. 1), and these compounds can be trapped easily by dienophiles via a Diels–Alder reaction.[9e] The Diels–Alder adducts can be converted easily to naphthalene derivatives via dehydration under acidic conditions.[10]



(1)

We report herein the rhenium-catalyzed synthesis of naphthalene derivatives by the reactions of aromatic ketimines and aldehydes with olefins via C–H bond activation.

2. Results and discussion

Treatment of aromatic ketimine **1a** (0.50 mmol), benzaldehyde **2a** (1.00 mmol), and cyclooctene **3a** with a catalytic amount of $[ReBr(CO)_3(THF)]_2$ (2.5 mol %) in toluene at 115 °C for 24 h, followed by treatment with acetic acid and sulfuric acid at 25 °C for 1.5 h gave naphthalene derivative **4a** in 53% yield (Eq. 2). When this reaction was carried out in the presence of molecular sieves (4 Å), the yield of the naphthalene **4a** increased to 73% (Eq. 2). However, this reaction did not proceed in the presence of transition-metal complexes, which are usually employed as catalysts for C–H bond activation and successive insertion of unsaturated molecules: $Ru_3(CO)_{12}$, $RuH_2(CO)(PPh_3)_3$, and $RhCl(PPh_3)_3$.

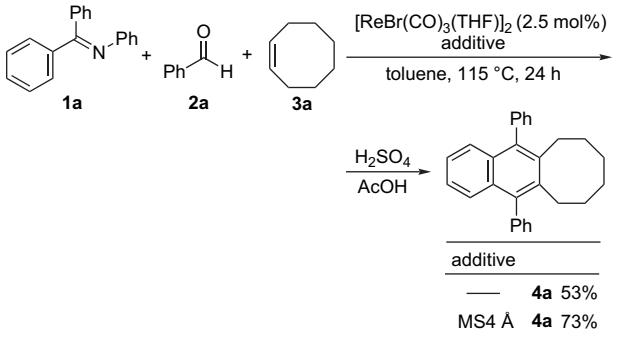


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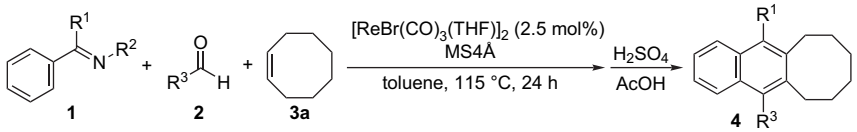
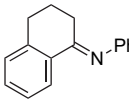
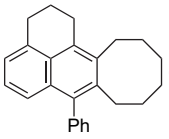
Table 1. Reactions between ketimines, aldehydes and cyclooctene[a]



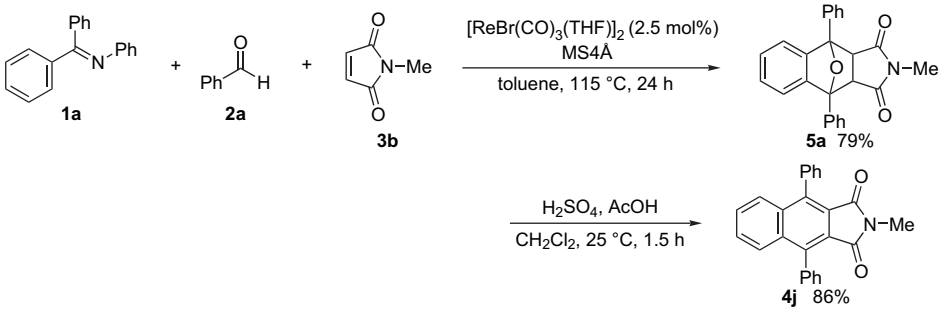
Entry	R^1	R^2	R^3	Product	Yield[b] (%)
1	Ph	$PhCH_2$ **1b**	Ph **2a**	**4a**	75
2		Ph **1c**	Ph **2a**	**4b**	67
3	 **1d**		Ph **2a**	 **4c**	79
4	Ph	Ph **1a**	*p*-$(MeO)C_6H_4$ **2b**	**4d**	66
5	Ph	Ph **1a**	*p*-MeC_6H_4 **2c**	**4e**	72
6	Ph	Ph **1a**	*p*-$CF_3C_6H_4$ **2d**	**4f**	88
7	Ph	Ph **1a**	*o*-MeC_6H_4 **2e**	**4g**	74
8	Ph	Ph **1a**	 **2f**	**4b**	76
9[c]	Ph	Ph **1a**	$^nC_8H_{17}$ **2g**	**4h**	35
10[c]	Me	Ph **1e**	Ph **2a**	**4i**	11

[a] **1** (1.0 equiv), **2** (2.0 equiv), **3a** (2.0 equiv).
[b] Isolated yield.
[c] **3a** (10 equiv).

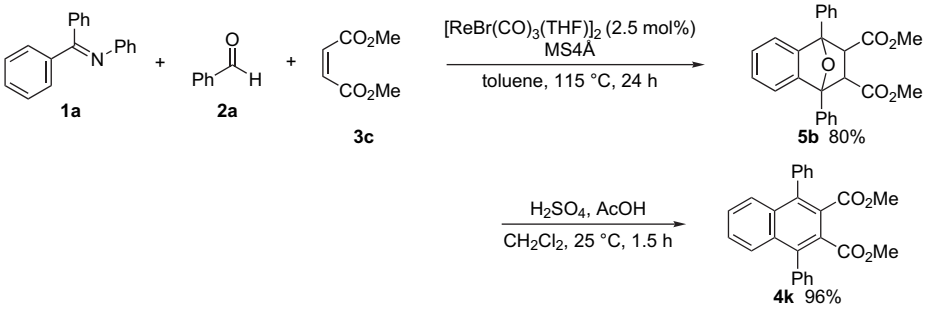
The phenyl group on a nitrogen atom of ketimine **1a** could be replaced by a benzyl group without decreasing the yield of naphthalene **4a** (Table 1, entry 1). By using a ketimine **1c**, which was derived from *trans*-chalcone (benzylideneacetophenone) and aniline, the corresponding naphthalene derivative **4b** was obtained in 67% yield (Table 1, entry 2). Ketimine having an alkyl group at R^1 position, **1d**, also afforded tetracyclic compound **4c** in 79% yield (Table 1, entry 3).

Next, we examined the substituents on the aromatic ring of aldehydes. The treatment of ketimine **1a** with aldehydes having electron-donating groups, such as a *para*-methoxy and *para*-methyl groups, provided the corresponding naphthalenes **4d** and **4e** in 66 and 72% yields, respectively (Table 1, entries 4 and 5). The yield increased and the naphthalene derivative **4f** was obtained in 88% yield with an aldehyde bearing an electron-withdrawing group (Table 1, entry 6). In spite of the bulkiness, *o*-tolualdehyde **2e** afforded the corresponding naphthalene **4g** in 74% yield (Table 1, entry 7). A reaction of **1a** with cinnamaldehyde **2f** also proceeded, and naphthalene derivative **4b** was obtained in 76% yield (Table 1, entry 8); however, a reaction of **1a** with an aliphatic aldehyde, nonanal **2g**, produced naphthalene **4h** in 35% yield (Table 1, entry 9). Another approach to obtain a naphthalene having 1-alkyl-3-phenyl substituents is a reaction between an imine derived from an alkyl phenyl ketone and benzaldehyde. Treatment of a ketimine of acetophenone (R^1=Me) and benzaldehyde with a catalytic amount of $[ReBr(CO)_3(THF)]_2$ gave the desired naphthalene **4i** in 11% yield (Table 1, entry 10).

Several dienophiles could be used in the synthesis of naphthalene derivatives (Eqs. 3 and 4). By the treatment of aromatic ketimine **1a** with benzaldehyde **2a** and maleimide **3b** in the presence of a catalytic amount of $[ReBr(CO)_3(THF)]_2$ and molecular sieves, Diels–Alder adduct **5a** was formed in 79% yield. After isolation, the Diels–Alder adduct **5a** was exposed to acidic conditions, causing dehydrative aromatization. As a result, naphthalene derivative **4j** was obtained in 86% yield (Eq. 3). Dimethyl maleate **3c** also gave the corresponding naphthalene derivative **4k** in good yield (Eq. 4).



(3)



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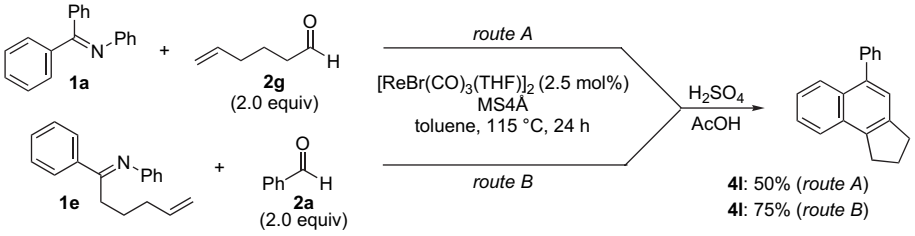

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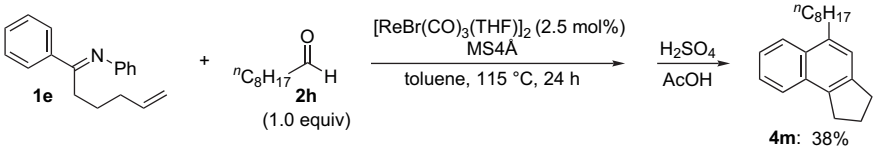
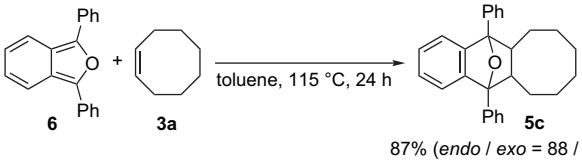


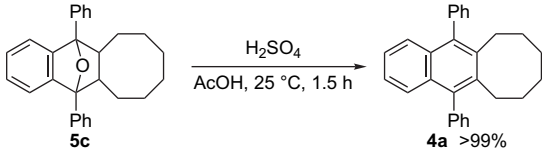
(6)

An aliphatic aldehyde **2g** could be used as the aldehyde component of the naphthalene formation (Eq. 5, route A). In addition, ketimine **1e**, which can isomerize to an enamine, could be employed (Eq. 5, route B). After acidic treatment, routes A and B produced naphthalene derivative **4l** in 50 and 75% yields, respectively (Eq. 5). By the reaction of ketimine **1e** with aliphatic aldehyde **2h**, the corresponding naphthalene derivative **4m** was produced in 38% yield (Eq. 6).

To confirm the reaction mechanism, the following reactions were carried out (Eqs. 7 and 8). The reaction of aromatic ketimine **1a** with benzaldehyde **2a** in the presence of a rhenium catalyst, $[ReBr(CO)_3(THF)]_2$, and molecular sieves gave isobenzofuran **6** in 93% yield (Eq. 1).[11,12] The reactive diene moiety of isobenzofuran can be used for the Diels–Alder reaction.[13] In fact, when a reaction of isobenzofuran **6** was conducted in the presence of cyclooctene **3a**, the Diels–Alder adduct **5c** was produced in 87% yield (*endo*/*exo*= 88/12) (Eq. 7). The formed Diels–Alder adduct **5c** was aromatized without isolation via the ring opening reaction of cyclic ether and the elimination of water by treatment with acetic acid and sulfuric acid at 25 °C for 1.5 h.[14] The reaction produced the corresponding naphthalene derivative **4a** in quantitative yield (Eq. 8).



(7)

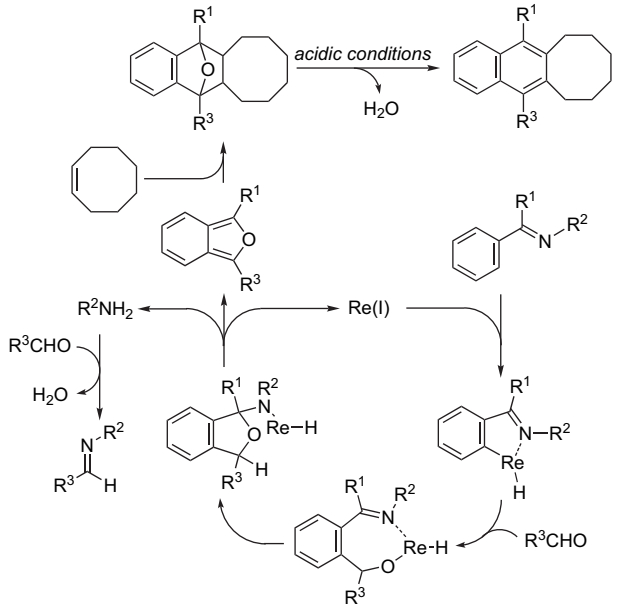


(8)

The proposed reaction mechanism is as follows (Scheme 1): (1) coordination of a nitrogen atom of an imine to a rhenium center; (2) C–H bond activation;[9] (3) insertion of an aldehyde to the rhenium–carbon bond of the aryl-rhenium intermediate; (4) intramolecular nucleophilic attack of the alkoxy-rhenium moiety to a carbon atom of the imine; (5) reductive elimination and elimination of aniline; (6) Diels–Alder reaction with a dienophile; (7) dehydration under acidic conditions. Since the formed aniline reacts with the aldehyde, 2 equiv of the aldehyde is necessary to complete the reaction.

3. Conclusion

In conclusion, we have succeeded in the synthesis of naphthalene derivatives by the reactions of aromatic ketimines and aldehydes with dienophiles, in the presence of a $[ReBr(CO)_3(THF)]_2$ catalyst, followed by dehydration. This reaction proceeds via C–H bond activation, insertion of an aldehyde, intramolecular nucleophilic cyclization, reductive elimination, elimination of aniline, a Diels–Alder reaction, and successive dehydration. By using this reaction, such substituents as aryl, alkenyl, alkyl, ester, and imide groups can be introduced to the naphthalene frameworks. We hope that this method will become a useful tool to synthesize substituted naphthalene derivatives.



Scheme 1. Proposed mechanism of the formation of naphthalene derivatives.

4. Experimental

4.1. General

All reactions were carried out in dry solvent under an argon atmosphere. Toluene was purchased from Wako Pure Chemical Industries and was dried and degassed before use. $[ReBr(CO)_3(THF)]_2$ was prepared by heating a THF solution of $ReBr(CO)_5$ at reflux temperature for 16 h and recrystallized. Ketimines were prepared by condensation of the corresponding ketones with the corresponding amines in the presence of molecular sieves (4 Å) in toluene at 100 °C for 10 h, and were used after distillation or recrystallization. Aldehydes and cyclooctene were purchased from Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co. and Aldrich Co., and used after distillation. Molecular sieves (4 Å, powder) were used after vacuum drying at 150 °C for 5 h. *N*-Methyl maleimide and dimethyl maleate were purchased from Tokyo Kasei Kogyo Co. and Nacalai Tesque Co., and used as received.

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. IR spectra were recorded on a Nicolet Protégé 460.

1,3-Diphenylisobenzofuran **6** is already known and commercially available. The structure of the reaction product was determined by comparing the spectrum data of the product with that of **6**.

4.1.1. Synthesis of naphthalene derivatives by one-pot reaction. A mixture of aromatic ketimine **1** (0.500 mmol), aldehyde **2** (1.00 mmol), cyclooctene **3a** (110 mg, 1.00 mmol), molecular sieves (4 Å, 200 mg), $[ReBr(CO)_3(THF)]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was stirred at 115 °C for 24 h. Then, acetic acid (3.0 mL) and sulfuric acid (1.0 mL) were added, and the mixture was stirred at room temperature for 1.5 h. The crude product was extracted with hexane and purified by column chromatography on silica gel to give naphthalene derivative **4**.

4.1.1.1. 5,12-Diphenyl-6,7,8,9,10,11-hexahydrocycloocta[*b*]naphthalene (4a). ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (m, 4H), 1.51 (m, 4H), 2.82 (t, J=6.0 Hz, 4H), 7.21–7.24 (m, 4H), 7.32–7.35 (m, 4H), 7.43–7.47 (m, 2H), 7.49–7.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 29.3, 31.4, 124.5, 126.3, 126.8, 128.1, 128.2, 130.4, 131.8; IR (Nujol, ν/cm^{-1}) 1599 (w), 1558 (w), 1505 (w), 1457 (s), 1377 (s), 1351 (m), 1072 (m), 1029 (m), 1005 (m), 941 (m), 764 (s), 742 (s), 703 (s), 685 (m), 665 (m). Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.56; H, 7.30.

4.1.1.2. 5-Phenyl-12-styryl-6,7,8,9,10,11-hexahydrocycloocta[*b*]naphthalene (4b). ^1H NMR (400 MHz, $CDCl_3$) δ 1.38–1.47 (m, 6H), 1.74 (m, 2H), 2.75 (m, 2H), 3.08 (m, 2H), 6.76 (d, J=16.8 Hz, 1H), 7.17–7.32 (m, 6H), 7.35–7.40 (m, 3H), 7.42–7.46 (m, 2H), 7.51 (d, J=16.5 Hz, 1H), 7.56–7.58 (m, 2H), 8.18 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 26.5, 29.1, 29.2, 30.5, 31.5, 124.7, 124.7, 125.7, 126.4, 126.6, 126.8, 126.8, 127.6, 128.1, 128.7, 130.3, 130.9, 132.2, 133.5, 135.6, 137.4, 137.6, 137.8, 137.8, 140.6; IR (Nujol, ν/cm^{-1}) 3060 (w), 3024 (w), 1599 (w), 1487 (m), 1449 (s), 1376 (m), 1072 (w), 1033 (w), 967 (m), 909 (w), 767 (s), 754 (m), 704 (m), 692 (s), 666 (w). Anal. Calcd for $C_{30}H_{28}$: C, 92.74; H, 7.26. Found: C, 92.85; H, 7.38.

4.1.1.3. 2,3,8,9,10,11,12,13-Octahydro-7-phenyl-1*H*-cycloocta[*a*]phenalene (4c). ^1H NMR (400 MHz, $CDCl_3$) δ 1.39–1.47 (m, 6H), 1.74–1.77 (m, 2H), 2.09–2.16 (m, 2H), 2.73–2.76 (m, 2H), 3.03–3.06 (m, 2H), 3.08–3.11 (m, 2H), 3.15–3.19 (m, 2H), 7.00–7.03 (m, 1H), 7.11–7.13 (m, 2H), 7.24–7.26 (m, 1H), 7.38–7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 26.3, 26.6, 27.6, 28.2, 29.5, 29.9, 31.5, 31.6, 123.1, 124.1, 124.8, 126.6, 128.1, 128.8, 130.4, 132.0, 132.2, 135.7, 136.4, 137.5, 141.2; IR (Nujol, ν/cm^{-1}) 1653 (m), 1558 (m), 1540 (w), 1506 (w), 1487 (w), 1457 (s), 1376 (s), 1339 (m), 1325 (m), 1204 (m), 1056 (m), 762 (m), 702 (s). Anal. Calcd for $C_{29}H_{30}O$: C, 91.97; H, 8.03. Found: C, 92.17; H, 8.12.

4.1.1.4. 5-(4-Methoxy-phenyl)-12-phenyl-6,7,8,9,10,11-hexahydro-cycloocta[*b*]naphthalene (4d). ^1H NMR (400 MHz, $CDCl_3$) δ 1.33–1.57 (m, 8H), 2.75–2.85 (m, 4H), 3.92 (s, 3H), 7.02–7.07 (m, 2H), 7.18–7.35 (m, 8H), 7.41–7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 29.3, 29.3, 31.4, 31.5, 55.3, 113.5, 124.5, 126.3, 126.4, 126.8, 128.1, 130.4, 131.8, 132.2, 137.7, 137.9, 138.2, 140.7, 158.4; IR (Nujol, ν/cm^{-1}) 1608 (m), 1512 (s), 1457 (s), 1376 (m), 1285 (w), 1244 (s), 1173 (m), 1033 (m), 765 (m), 731 (w), 704 (w). Anal. Calcd for $C_{29}H_{28}O$: C, 88.73; H, 7.19. Found: C, 88.96; H, 7.28.

4.1.1.5. 5-Phenyl-12-*p*-tolyl-6,7,8,9,10,11-hexahydrocycloocta[*b*]naphthalene (4e). ^1H NMR (400 MHz, $CDCl_3$) δ 1.31–1.61 (m, 8H), 2.48 (s, 3H), 2.77–2.81 (m, 4H), 7.16–7.28 (m, 6H), 7.28–7.36 (m, 4H), 7.41–7.54 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 26.3, 29.3, 31.4, 31.5, 124.5, 126.3, 126.4, 126.8, 128.1, 128.8, 130.2, 130.4, 131.7, 131.9, 136.3, 137.5, 137.6, 137.8, 138.0, 140.7; IR (Nujol, ν/cm^{-1}) 1513 (w), 1502 (w), 1463 (s), 1376 (s), 1035 (w), 1005 (w), 809 (m), 777 (w), 763 (s), 748 (m), 702 (s), 685 (w). Anal. Calcd for $C_{29}H_{28}$: C, 92.50; H, 7.50. Found: C, 92.60; H, 7.45.

4.1.1.6. 5-Phenyl-12-(4-trifluoromethyl-phenyl)-6,7,8,9,10,11-hexahydro-cycloocta[*b*]naphthalene (4f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33–1.59 (m, 8H), 2.74–2.81 (m, 4H), 7.11–7.14 (m, 1H), 7.21–7.25 (m, 3H), 7.31–7.33 (m, 2H), 7.43–7.53 (m, 5H), 7.86 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 26.3, 29.3, 31.3, 31.4, 31.4, 124.8, 124.9, 125.2, 125.7, 126.6, 127.0, 127.4, 128.2, 130.3, 130.8, 131.3, 131.8, 136.5, 137.6, 137.7, 138.7, 140.4, 144.7; IR (Nujol, ν/cm^{-1}) 1616 (w), 1456 (m), 1376 (w), 1324 (s), 1165 (m), 1121 (s), 1105 (w), 1066 (m). Anal. Calcd for $C_{29}H_{25}F_3$: C, 80.91; H, 5.85. Found: C, 80.97; H, 5.83.

4.1.1.7. 5-Phenyl-12-*o*-tolyl-6,7,8,9,10,11-hexahydro-cycloocta[*b*]naphthalene (4g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21–1.50 (m, 8H), 1.96 (s, 3H), 2.59–2.70 (m, 1H), 2.78–2.89 (m, 3H), 7.12–7.15 (m, 1H), 7.19–7.26 (m, 4H), 7.31–7.37 (m, 5H), 7.45–7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 26.4, 29.2, 29.3, 30.5, 31.4, 124.5, 124.7, 125.6, 125.7, 126.5, 126.8, 127.2, 128.0, 128.2, 129.9, 130.3, 130.6, 130.7, 131.0, 131.9, 137.0, 137.1, 137.3, 137.8, 137.9, 139.8, 140.7; IR (Nujol, ν/cm^{-1}) 2360 (w), 2341 (w), 1652 (w), 1558 (w), 1506 (w), 1457 (s), 1377 (s), 762 (w), 742 (w), 703 (m). Anal. Calcd for $C_{29}H_{28}$: C, 92.50; H, 7.50. Found: C, 92.56; H, 7.52.

4.1.1.8. 5-Octyl-12-phenyl-6,7,8,9,10,11-hexahydro-cycloocta[*b*]naphthalene (4h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01–1.15 (m, 3H), 1.40–1.70 (m, 14H), 1.70–1.84 (m, 2H), 1.84–2.09 (m, 2H), 7.37–7.47 (m, 4H), 7.56–7.65 (m, 4H), 8.21 (d, J=8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 26.4, 26.5, 28.0, 29.1, 29.4, 29.5, 29.7, 30.6, 31.0, 31.3, 31.6, 32.0, 123.7, 124.2, 126.6, 127.2, 128.0, 130.4, 130.6, 132.3, 135.2, 136.7, 137.0, 137.8, 141.0; IR (Nujol, ν/cm^{-1}) 1600 (w), 1506 (w), 1493 (m), 1467 (s), 1377 (m), 1077 (m), 1033 (m), 887 (w), 761 (s), 703 (s), 688 (w). Anal. Calcd for $C_{30}H_{38}$: C, 90.39; H, 9.61. Found: C, 90.35; H, 9.88.

4.1.1.9. 5-Methyl-12-phenyl-6,7,8,9,10,11-hexahydro-cycloocta[*b*]naphthalene (4i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22–1.47 (m, 6H), 1.62–1.80 (m, 2H), 2.65 (s, 3H), 2.66–2.77 (m, 2H), 3.00–3.10 (m, 2H), 7.11–7.23 (m, 4H), 7.30–7.47 (m, 4H), 7.99 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 26.3, 26.4, 28.3, 29.8, 30.2, 31.7, 123.7, 124.3, 124.7, 126.7, 127.1, 128.1, 130.0, 130.4, 131.4, 131.9, 136.5, 137.5, 137.9, 140.9; IR (Nujol, ν/cm^{-1}) 1575 (w), 1493 (w), 1463 (s), 1378 (m), 1147 (w), 1071 (w), 1027 (w), 752 (s), 703 (s), 644 (w); HRMS calcd for $C_{23}H_{24}$: 300.1878. Found: 300.1883.

4.1.1.10. 5,5a,6,7,8,9,10,11,11a,12-Decahydro-5,12-diphenyl-5,12-epoxycycloocta[*b*]naphthalene (5c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.46–0.54 (m, 2H), 1.29–1.38 (m, 2H), 1.42–1.62 (m, 8H), 2.95–3.01 (m, 2H), 7.04 (dd, J=5.3, 3.0 Hz, 2H), 7.21 (dd, J=5.3, 3.0 Hz, 2H), 7.36–7.45 (m, 6H), 7.66 (d, J=6.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 26.2, 30.4, 46.8, 91.4, 121.3, 126.1, 128.3, 128.4, 128.6, 137.3, 146.8; IR (Nujol, ν/cm^{-1}) 3055 (w), 1734 (w), 1700 (w), 1684 (w), 1635 (w), 1601 (w), 1521 (w), 1506 (w), 1445 (s), 1364 (m), 1315 (m), 1015 (m), 979 (m), 972 (m), 771 (m), 753 (s), 798 (s), 666 (m), 642 (m). Anal. Calcd for $C_{28}H_{28}O$: C, 88.38; H, 7.42. Found: C, 88.18; H, 7.33.

4.1.2. Synthesis of naphthalene derivatives via isolation of Diels–Alder adduct. A mixture of benzhydrylidene-phenyl-amine **1a** (129 mg, 0.500 mmol), benzaldehyde **2a** (106 mg, 1.00 mmol), olefin **3** (0.600 mmol), molecular sieves (4 Å, 200 mg), $[ReBr(CO)_3(THF)]_2$ (10.6 mg, 0.0125 mmol), and toluene (2.0 mL) was stirred at 115 °C for 24 h. The Diels–Alder adduct **5** was isolated by column chromatography on silica gel. Then, dichloromethane (3.0 mL), acetic acid (3.0 mL), and sulfuric acid (1.0 mL) were added to the Diels–Alder adduct **5**, and the mixture was stirred at room temperature for 1.5 h. The crude product was extracted with dichloromethane and purified by column chromatography on silica gel to give naphthalene derivative **4**.

4.1.2.1. 2-Methyl-4,9-diphenyl-benzo[*f*]isoindole-1,3-dione (4j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05–3.08 (m, 3H), 7.42–7.49 (m, 4H), 7.55–7.63 (m, 8H), 7.81–7.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 123.8, 128.2, 128.4, 128.5, 128.7, 129.7, 134.7, 135.4, 139.4, 167.4; IR (Nujol, ν/cm^{-1}) 1761 (m), 1734 (m), 1714 (s), 1608 (w), 1518 (w), 1462 (s), 1442 (s), 1375 (s), 1255 (w), 1235 (m), 1048 (w), 1008 (m), 779 (m), 762 (m), 739 (m), 727 (w), 670 (w), 661 (w). Anal. Calcd for $C_{25}H_{17}NO_2$: C, 82.63; H, 4.72; N, 3.85. Found: C, 82.37; H, 4.92; N, 3.75.

4.1.2.2. 1,4-Diphenyl-naphthalene-2,3-dicarboxylic acid dimethyl ester (4k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 6H), 7.35–7.42 (m, 4H), 7.42–7.53 (m, 8H), 7.62–7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 127.4, 127.6, 127.8, 128.0, 128.7, 129.9, 132.7, 137.5, 139.1, 168.8; IR (Nujol, ν/cm^{-1}) 1736 (s), 1703 (w), 1459 (m), 1436 (m), 1405 (w), 1377 (m), 1357 (w), 1235 (s), 1171 (w), 1133 (m), 983 (w), 858 (w), 777 (m), 727 (m), 703 (m). Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.84; H, 5.19.

4.1.2.3. 3a,4,9,9a-tetrahydro-2-methyl-4,9-diphenyl-4,9-epoxybenzo[*f*]isoindole-1,3-dione (5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 6H), 4.08 (s, 2H), 6.93–6.99 (m, 2H), 7.13–7.18 (m, 2H), 7.42–7.48 (m, 2H), 7.48–7.56 (m, 4H), 8.00–8.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 54.3, 90.3, 120.5, 127.1, 128.0, 128.6, 128.6; IR (Nujol, ν/cm^{-1}) 1769 (m), 1700 (s), 1500 (w), 1457 (m), 1437 (m), 1378 (w), 1354 (w), 1312 (m), 1295 (m), 1280 (w), 1127 (m), 1006 (s), 968 (w), 940 (w), 911 (m), 810 (w), 774 (s), 759 (s), 732 (m), 702 (s), 658 (m).

4.1.2.4. 1,8-Diphenyl-11-oxa-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-9,10-dicarboxylic acid dimethyl ester (5b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 6H), 4.15 (s, 2H), 7.18–7.28 (m, 4H), 7.39–7.49 (m, 6H), 7.69–7.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 54.2, 121.9,

125.3, 126.8, 127.2, 128.3, 128.5, 136.5, 145.4, 170.1; IR (Nujol, ν/cm^{-1}) 1763 (m), 1745 (s), 1730 (s), 1661 (w), 1595 (w), 1459 (s), 1377 (s), 1340 (w), 1303 (w), 1271 (m), 1199 (s), 1161 (m), 1023 (w), 1004 (m), 984 (m), 939 (m), 912 (w), 761 (m), 740 (w), 700 (m), 646 (w).

4.1.3. Synthesis of naphthalene derivatives via intramolecular Diels–Alder reaction. A mixture of aromatic ketimine **1** (0.500 mmol), aldehyde **2** (1.00 mmol), molecular sieves (4 Å, 200 mg), $[ReBr(CO)_3(THF)]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was stirred at 115 °C for 24 h. Then, acetic acid (3.0 mL) and sulfuric acid (1.0 mL) were added, and the mixture was stirred at room temperature for 1.5 h. The crude product was extracted with hexane and purified by column chromatography on silica gel to give naphthalene derivative **4**.

4.1.3.1. 5-Phenyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (4l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (tt, J=7.5, 7.5 Hz, 2H), 3.17 (t, J=7.4 Hz, 2H), 3.34 (t, J=7.4 Hz, 2H), 7.37–7.45 (m, 3H), 7.50–7.54 (m, 5H), 7.87–7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 31.3, 33.9, 124.4, 124.6, 124.8, 125.8, 126.7, 127.0, 128.2, 130.2, 130.6, 139.0, 131.1, 140.4, 141.3; IR (Nujol, ν/cm^{-1}) 1591 (m), 1573 (w), 1493 (m), 1461 (s), 1439 (s), 1395 (w), 1377 (m), 1344 (w), 1075 (m), 1031 (m), 883 (m), 785 (m), 760 (s), 705 (s). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.55; H, 6.54.

4.1.3.2. 5-Octyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (4m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91–0.95 (m, 3H), 1.23–1.58 (m, 10H), 1.78 (tt, J=7.8, 7.5 Hz, 2H), 2.26 (tt, J=7.5, 7.5 Hz, 2H), 3.07 (t, J=7.8 Hz, 2H), 3.12 (t, J=7.5 Hz, 2H), 3.27 (t, J=7.5 Hz, 2H), 7.30 (m, 1H), 7.43–7.55 (m, 2H), 7.83 (d, J=7.5 Hz, 2H), 8.06 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 24.4, 29.3, 29.6, 31.1, 31.2, 31.9, 33.4, 33.9, 123.3, 124.4, 124.5, 125.0, 125.3, 130.8, 130.8, 137.4, 137.7, 140.5; IR (Nujol, ν/cm^{-1}) 1594 (w), 1515 (w), 1464 (s), 1377 (m), 1029 (w), 875 (w), 754 (m), 722 (w). Anal. Calcd for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 89.87; H, 10.00.

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