Selected Paper

# Synthesis of 1-Azaazulenes from Cycloheptatrienylmethyl Ketone *O*-Pentafluorobenzoyloximes by Palladium-Catalyzed Cyclization and Oxidation

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Various 1-azaazulenes are synthesized from cycloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes by treatment with a catalytic amount of $Pd(dba)_2$–*t*-$Bu_3P$ (dba = dibenzylideneacetone) and triethylamine in the presence of MS 4A via alkylideneaminopalladium(II) intermediates generated by oxidative addition of the oximes to a Pd(0) complex.

Azaazulenes are a class of compounds that have been receiving continual interest from chemists, particularly as regards their relationship to the chemistry of azulenes as nonbenzenoid aromatics.[1] Among the azaazulene derivatives, 1-azaazulenes have attracted much attention from the viewpoints of their physical properties and pharmacological activities. For example, it has recently become apparent that 1-azaazulene derivatives exhibit inhibitory activities on histamine release[2] and are useful for treating diseases caused or exacerbated by unregulated p38 mitogen-activated protein (MAP) kinase or tumor necrosis factor (TNF)-alpha activity.[3] Abe et al. reported that ethyl 2-dimethylamino-7*H*-1,7-diazaindeno[1,2-*e*]azulene-3-carboxylate strongly intercalated to calf-thymus DNA and 12-mer DNA.[4] Furthermore, 1-azaazulenium salts are applied to organic pigments contained in the optical recording media such as CD or DVD[5] (Fig. 1).

While many groups have researched the synthesis of 1-azaazulene derivatives,[6] in most cases, tropone derivatives were used as the starting materials. For example, Nozoe and Seto et al. developed a synthetic method for 1-azaazulene derivatives using 2-aminotropones.[6b,c] Nitta et al. reported that the reaction of *N*-vinyliminophosphoranes with tropone derivatives resulted in the formation of 1-azaazulene ring systems.[6d] Tropone derivatives, however, are very expensive and difficult to prepare. Accordingly, it is desired to develop new synthetic routes towards 1-azaazulene derivatives using more easily available reagents.

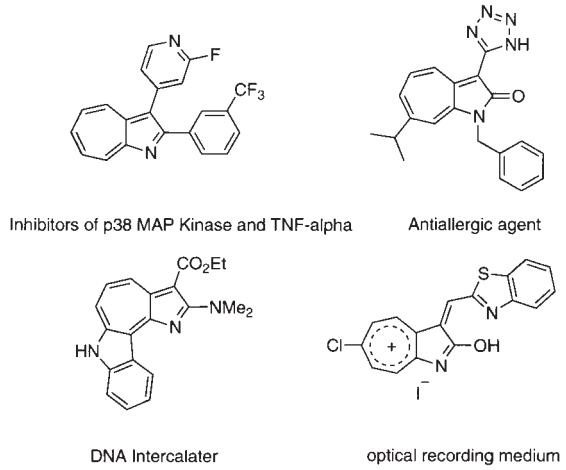
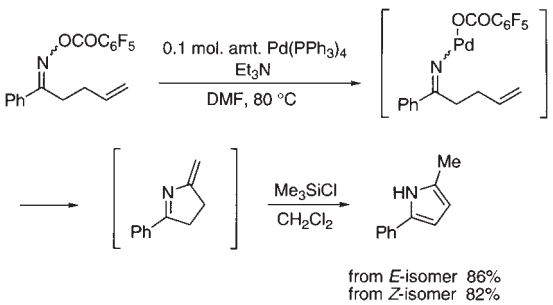



Fig. 1. Various 1-azaazulene derivatives.

We have reported the oxidative addition of oxime derivatives to palladium(0) complexes to generate alkylideneaminopalladium(II) species.[7] This process was applied to the transformation of olefinic ketone *O*-pentafluorobenzoyloximes to various aza-heterocycles,[7a] such as pyrrole,[7b,c] pyridine,[7d] isoquinoline,[7d] and spiroimine[7e,f] via the intramolecular Heck-type reaction (amino-Heck reaction). This amino-Heck reaction is not affected by the geometry of oximes, probably due to the linear-like structures of the alkylideneaminometal species.[8] Both *E* and *Z* $\gamma,\delta$-unsaturated ketone oximes cyclize to pyrroles in good yields (Eq. 1).[7b,c]




(1)

The amino-Heck reaction was expected to be applicable to the synthesis of 1-azaazulenes from cycloheptatrienylmethyl ketone oximes, and we communicated a novel method of 1-azaazulene synthesis by a palladium(0)-catalyzed cyclization of cycloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes via their alkylideneaminopalladium species.[9] This article presents a full account of this catalytic method.

## Results and Discussion

**Synthetic Plan.** The outline of our strategy towards 1-azaazulenes based on the amino-Heck reaction is depicted in

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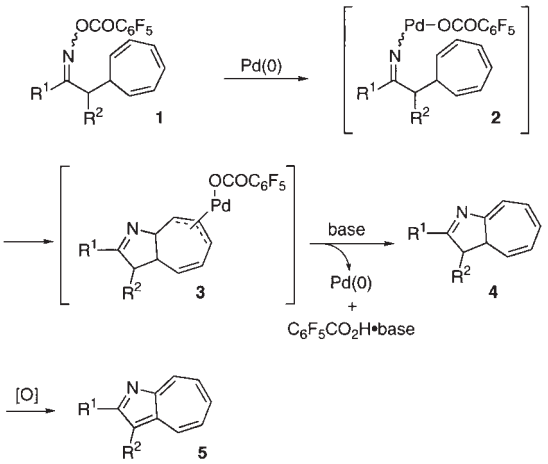
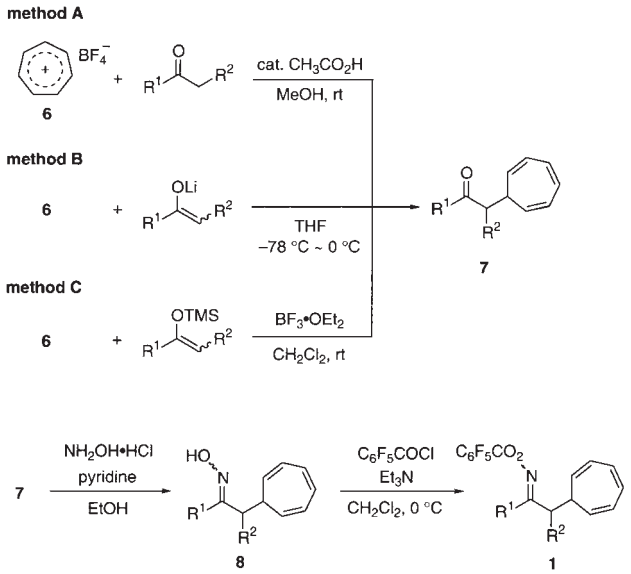


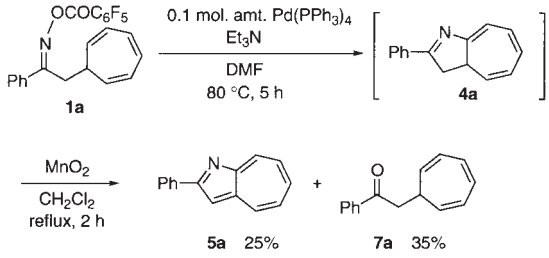

Scheme 1. Synthesis of 1-azaazulene via the amino-Heck reaction.




Scheme 2. Preparation of cycloheptatrienylmethyl ketone oximes.

Scheme 1. The oxidative addition of cyloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes **1** and a Pd(0) complex would generate alkylideneaminopalladium(II) species **2**, which cyclize to 3,4-dihydro-1-azaazulenes **4** via the formation of $\pi$-allylpalladium intermediate **3** and the successive hydropalladium(II) elimination. Then, 1-azaazulenes **5** were envisaged from 3,4-dihydro-1-azaazulenes **4** by oxidation.

**Preparation of Cycloheptatrienylmethyl Ketone *O*-Pentafluorobenzoyloximes.** Cycloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes **1** were prepared from the corresponding cycloheptatrienylmethyl ketones **7** by the oximation and the *O*-pentafluorobenzoylation. Ketones **7** were prepared by the three methods depicted in Scheme 2 from tropylium tetrafluoroborate (**6**) which was commercially available and easily accessible.[10] Reingold et al. reported the acid-catalyzed synthesis of cycloheptatrienylmethyl ketones **7** from tropylium tetrafluoroborate (**6**) and ketones (method A).[11] Other preparations of ketones **7** were achieved by the reaction of **6** with lithium enolates (method B) or with silyl enol ethers in the presence of a Lewis acid (method C).



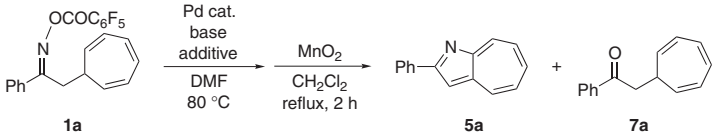

Scheme 3. Synthesis of 1-azaazulene **5a** from oxime **1a**.

**Reaction of 2-Cycloheptatrienyl-1-phenylethanone *O*-Pentafluorobenzoyloxime and Palladium(0) Complex.** As a model compound, 2-cycloheptatrienyl-1-phenylethanone *O*-pentafluorobenzoyloxime (**1a**) was chosen. The amino-Heck reaction was examined in the presence of palladium(0) catalysts and bases. At first, the reaction was carried out at 80 °C with 0.1 mol. amt. $Pd(PPh_3)_4$ and $Et_3N$ in DMF, which were the optimal reaction conditions for the previous pyrrole synthesis.[7b,c] It took 5 h to consume **1a**; after a usual work up, $^1$H NMR of the crude mixture exhibited the formation of 3,3a-dihydro-2-phenyl-1-azaazulene (**4a**), a small amount of the isomers of **4a**,[12] 2-phenyl-1-azaazulene (**5a**), and ketone **7a**. Successive treatment of the crude mixture with $MnO_2$ gave 1-azaazulene **5a** and ketone **7a** in 25% and 35% yields, respectively[13] (Scheme 3).

The amino-Heck reaction of **1a** was screened under various reaction conditions concerning additives, palladium catalysts, ligands, and bases, as shown in Table 1. Addition of MS 4A was effective to accelerate the reaction and increase the yield of 1-azaazulene **5a**, as was also observed in the previous synthesis of spiroimines (entry 2).[7e,f] When $Pd(dba)_2$ (dba = dibenzylideneacetone) and $t$-$Bu_3P$[14,15] were employed as palladium catalysts, the reaction was finished within 0.5 h. After the oxidation, the yield of 1-azaazulene **5a** was improved to 78% and the formation of ketone **7a** was effectively suppressed (entry 5). Several bases were examined, but no remarkable influence was observed on the product yields except for DBU (entries 7–10).

Various 1-azaazulenes were prepared by the amino-Heck reaction with a catalytic amount of $Pd(dba)_2$–$t$-$Bu_3P$, $Et_3N$, and MS 4A; the results are summarized in Table 2. In the reaction of **1b** having a bulky *tert*-butyl group as $R^1$ at 80 °C, it took 4.5 h to consume the starting material **1b**; the desired 1-azaazulene **5b** was obtained in 64% yield (entry 2). At a higher temperature (110 °C), the reaction was accelerated and the yield of **5b** was improved to 84% (entry 3). The oximes having secondary alkyl groups as $R^1$ such as isopropyl **1c** and cyclopropyl groups **1d** cyclized more effectively at 80 °C to give the corresponding 1-azaazulenes **5c** and **d** in good yields (entries 4–7). In contrast, 2-methyl-1-azaazulene (**5e**) was obtained in low yield (entries 8, 9), due to the unstability of **5e** under the reaction conditions.[16] $\alpha,\beta$-Unsaturated ketone oxime **1f** having a styryl group was converted to 2-styryl-1-azaazulene (**5f**) in 68% yield (entry 10), while the oxime **1g** of *p*-methoxystyryl group was converted to 1-azaazulene **5g** in low yield (entry 11). 2,3-Disubstituted 1-azaazulenes **5h–j** were prepared in moderate yields at 110 °C from $\alpha$-substituted cycloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes **1h–j** (entries 12–14). In the reaction of **1i**, 55% yield of 1-azaazulene **5i** was obtained with 3,3a-dihy-

Table 1. Optimization of Pd-Catalyzed Cyclization of Oxime **1a**

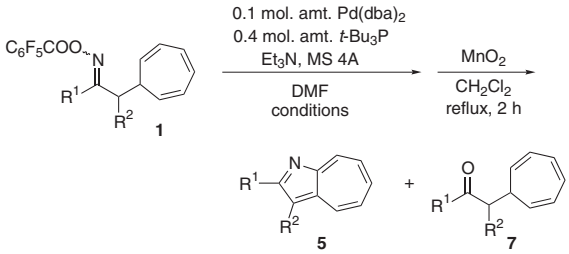


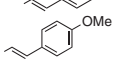

**1a** **5a** **7a**

| Entry | Pd cat. (0.1 mol. amt.) | Base (3 mol. amt.) | Additive | Time/h | Yield/%[a] | |
|---|---|---|---|---|---|---|
| | | | | | **5a** | **7a** |
| 1 | $Pd(PPh_3)_4$ | $Et_3N$ | none | 5 | 25 | 35 |
| 2 | $Pd(PPh_3)_4$ | $Et_3N$ | MS 4A | 1.5 | 61 | 11 |
| 3 | $Pd(dba)_2$ + 2 dppf | $Et_3N$ | MS 4A | 2 | 54 | 34 |
| 4 | $PdCl_2$(dppf) + dppf | $Et_3N$ | MS 4A | 5.5[b] | 19 | 17 |
| **5** | **$Pd(dba)_2$ + 4 *t*-$Bu_3P$** | **$Et_3N$** | **MS 4A** | **0.5** | **78 (84)**[c] | **5 (6)**[c] |
| 6 | $Pd(dba)_2$ + 4 (*o*-tol)$_3$P | $Et_3N$ | MS 4A | 1 | (56)[c] | (14)[c] |
| 7 | $Pd(dba)_2$ + 4 *t*-$Bu_3P$ | DBU | MS 4A | 1 | 7 | 12 |
| 8 | $Pd(dba)_2$ + 4 *t*-$Bu_3P$ | $K_2CO_3$ | MS 4A | 0.8 | 70 | 9 |
| 9 | $Pd(dba)_2$ + 4 *t*-$Bu_3P$ | $Cs_2CO_3$ | MS 4A | 1 | 54 | 15 |
| 10 | $Pd(dba)_2$ + 4 *t*-$Bu_3P$ | $K_3PO_4$ | MS 4A | 1 | 74 | 8 |

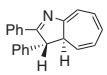
a) Isolated yield. b) 80 °C, 3 h, then 110 °C, 2.5 h. c) $^1$H NMR yield determined with anthracene as an internal standard.

Table 2. Synthesis of 1-Azaazulene **5** from Oxime **1** by Amino-Heck Reaction




| Entry | Oxime | | | Conditions | | Yield/%[a] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | **1** | *T*/°C | Time/h | **5** | | **7** | |
| 1 | Ph | H | **1a** | 80 | 0.5 | **5a** | 78 | **7a** | 5 |
| 2 | *t*-Bu | H | **1b** | 80 | 4.5 | **5b** | 64 | **7b** | 5 |
| 3 | *t*-Bu | H | **1b** | 110 | 0.5 | **5b** | 84 | **7b** | 0 |
| 4 | *iso*-Pr | H | **1c** | 80 | 1 | **5c** | 62 | **7c** | 4 |
| 5 | *iso*-Pr | H | **1c** | 110 | 0.3 | **5c** | 53 | **7c** | trace |
| 6 | *cyclo*-Pr | H | **1d** | 80 | 1.5 | **5d** | 63 | **7d** | 5 |
| 7 | *cyclo*-Pr | H | **1d** | 110 | 0.3 | **5d** | 51 | **7d** | 3 |
| 8 | Me | H | **1e** | 80 | 1.5 | **5e** | 11 | **7e** | 23 |
| 9 | Me | H | **1e** | 110 | 0.3 | **5e** | 27 | **7e** | 9 |
| 10 |  | H | **1f** | 80 | 1 | **5f** | 68 | **7f** | 2 |
| 11 |  | H | **1g** | 110 | 0.3 | **5g** | 35 | **7g** | 0 |
| 12 | Ph | Me | **1h** | 110 | 0.5 | **5h** | 52 | **7h** | 0 |
| 13[b] | Ph | Ph | **1i** | 110 | 0.5 | **5i** | 55 | **7i** | 4 |
| 14 | Et | Me | **1j** | 110 | 0.5 | **5j** | 42 | **7j** | 0 |

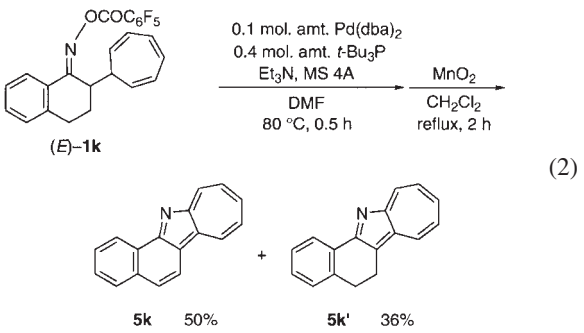
a) Isolated yield. b) **4i** was obtained in 21% yield.




**4i**

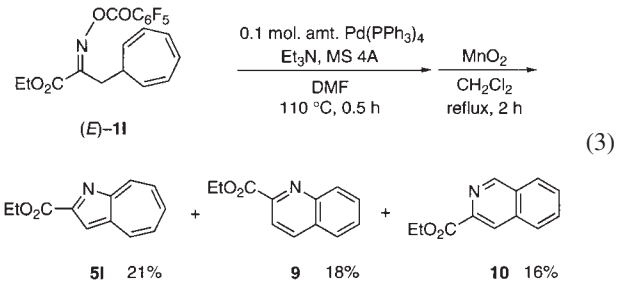
dro-1-azaazulene **4i** in 21% yield; **4i** could not be oxidized by $MnO_2$ (entry 13).[17]

This method can be applied to the synthesis of polycyclic azaazulene derivatives. 2-(Cyclohepta-2,4,6-trienyl)-3,4-dihydronaphthalen-1(2*H*)-one (*E*)-*O*-pentafluorobenzoyloxime (**1k**) cyclized to benzo[*g*]cyclohepta[*b*]indole (**5k**) and 5,6-dihydrobenzo[*g*]cyclohepta[*b*]indole (**5k′**) in 50% and 36% yields respectively (Eq. 2).




(2)

From the oxime of $\alpha$-keto ester **1l**, 21% yield of 1-azaazulene **5l** was obtained with quinoline **9** and isoquinoline **10** in 18% and 16% yields, respectively (Eq. 3).[18]

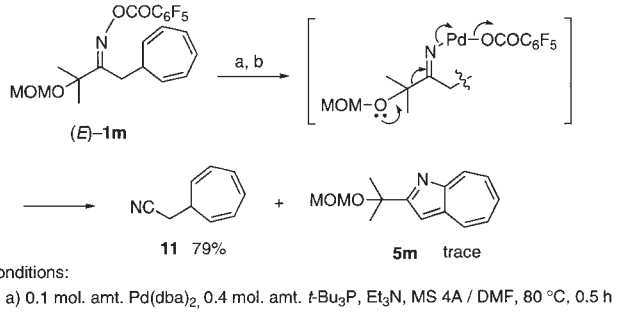



(3)

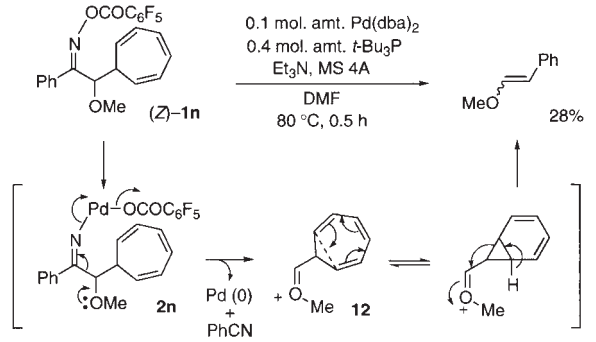
**Nitrile Formation.** Various 1-azaazulenes were thus prepared from cycloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes by the palladium-catalyzed amino-Heck reaction and the successive oxidation, whereas some oximes such as $\alpha$-alkoxy ketoxime and alkynyl ketoxime were transformed to nitriles under the catalytic conditions. From the $\alpha$-methoxymethoxy ketone (*E*)-*O*-pentafluorobenzoyloxime **1m**, nitrile **11** was obtained in 79% yield. Because the nitrile did not form without the Pd(0) catalyst, the fragmentation maybe proceed via an alkylideneaminopalladium intermediate (Scheme 4).

A similar fragmentation was observed in the case of $\alpha$-methoxy ketone (*Z*)-*O*-pentafluorobenzoyloxime **1n** to give 1-methoxy-2-phenylethene in 28% yield, as shown in Scheme 5. From alkylideneaminopalladium(II) intermediate **2n**, the fragmentation reaction occurred to generate oxonium cation intermediate **12**; 1-methoxy-2-phenylethene was then formed via successive rearrangement.[19]

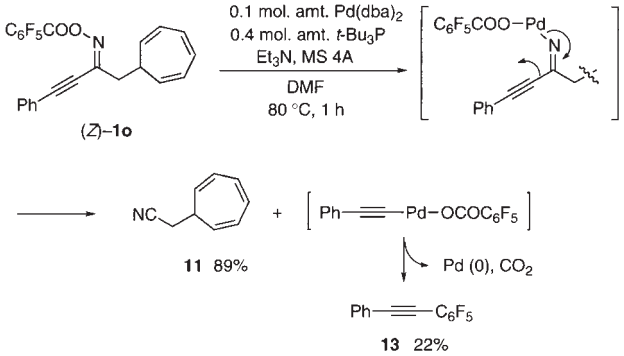
Alkynyl ketone (*Z*)-*O*-pentafluorobenzoyloxime **1o** also gave nitrile **11** and 2-pentafluorophenyl-1-phenylacetylene (**13**) in 89% and 22% yields, respectively. Formation of pentafluorophenylacetylene **13** suggested that nitrile **11** was formed by the elimination[20] of alkynyl group from alkylideneaminopalladium intermediate and successive decarboxylation[21] and reductive elimination pathways (Scheme 6).




Scheme 4.




Scheme 5.




Scheme 6.

In conclusion, various 1-azaazulenes were synthesized from cycloheptatrienylmethyl ketone *O*-pentafluorobenzoyloximes by the palladium-catalyzed amino-Heck reaction and the successive $MnO_2$ oxidation. The reaction proceeds smoothly by the treatment with a catalytic amount of $Pd(dba)_2$–*t*-$Bu_3P$, $Et_3N$, and MS 4A via the formation of alkylideneaminopalladium(II) intermediates. Furthermore, nitriles were formed catalytically from $\alpha$-alkoxy ketone oxime and alkynyl ketone oxime derivatives by fragmentation.

## Experimental

**General.** $^1$H NMR (500 and 270 MHz) spectra were recorded on Bruker DRX 500, Bruker AVANCE 500, and JEOL AL 270 spectrometers in $CDCl_3$ [using tetramethylsilane (for $^1$H, $\delta = 0$) as internal standard], $C_6D_6$ [using $C_6HD_5$ (for $^1$H, $\delta = 7.15$) as internal standard], or DMSO-$d_6$ [using DMSO-$d_5$ (for $^1$H, $\delta = 2.49$) as internal standard]. $^{13}$C NMR (125 and 67.5 MHz) spectra were recorded on Bruker DRX 500, Bruker AVANCE 500, and JEOL AL 270 spectrometers in $CDCl_3$ [using $CDCl_3$ (for $^{13}$C, $\delta = 77.0$) as internal standard], $C_6D_6$ [using $C_6D_6$ (for $^{13}$C, $\delta = 128.0$) as internal standard], or DMSO-$d_6$ [using DMSO-$d_6$ (for $^{13}$C, $\delta = 39.70$) as internal standard]. $^{19}$F NMR (470 MHz) spectra were recorded on Bruker AVANCE 500 spectrometers in $CDCl_3$ [using $C_6F_6$ (for $^{19}$F, $\delta = 0$) as internal standard]. IR spectra were recorded on a Horiba FT 300-S by ATR method. High-resolution mass spectra were obtained with a JEOL MS-700P mass spectrometer. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Flash column chromatography was performed on silica gel [Fuji Silysia Silica gel PSQ-100B and Kanto Chemical Silica

gel 60N (spherical, neutral)] and preparative thin-layer chromatography was carried out using Wakogel B-5F. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure from $P_2O_5$ and then from $CaH_2$, and stored over molecular sieves 4A under an argon atmosphere. Dichloromethane was distilled from $P_2O_5$ and then from $CaH_2$, and stored over molecular sieves 4A. Triethylamine was distilled from $CaH_2$ and stored over KOH. Pentafluorobenzoyl chloride was purchased from Tokyo Chemical Industry and was used without purification.

**General Procedure for the Synthesis of Cycloheptatrienylmethyl Ketones 7. Method A:**[11] Preparation of **7a** is described below as a typical procedure. A solution of tropylium tetrafluoroborate (**6**) (3.10 g, 17.4 mmol) and acetophenone (1.76 g, 14.6 mmol) in methanol (25 mL) containing 10 drops of acetic acid was stirred at reflux temperature for 3 h. The reaction was quenched by water, and organic materials were extracted three times with ethyl acetate. The combined extracts were washed with sat. $NaHCO_3$ aq. and brine, and then, dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 96/4) to give 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (**7a**) (2.50 g, 68%).

**Method B:** Preparation of **7k** is described below as a typical procedure. To an ice cold solution of diisopropylamine (2.6 mL, 19 mmol) in THF (22 mL) was added butyllithium in hexanes (1.55 M, 9.9 mL, 15 mmol); the mixture was stirred at the same temperature for 30 min. After cooling to −78 °C, a solution of $\alpha$-tetralone (2.03 g, 13.9 mmol) in THF (14 mL) was slowly added to the mixture. After stirring at the same temperature for 50 min, the THF solution was transferred via cannular to a suspension of tropylium tetrafluoroborate (**6**) (3.05 g, 17.1 mmol) in THF (34 mL) at −78 °C. The reaction mixture was warmed to room temperature over 1.5 h, and then the reaction was quenched with sat. $NH_4Cl$ aq. Organic materials were extracted three times with ethyl acetate, and the combined extracts were washed with brine. The ethyl acetate solution was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 95/5) to give 2-(cyclohepta-2,4,6-trienyl)-3,4-dihydronaphthalen-1(2*H*)-one (**7k**) (2.22 g, 68%).

**Method C:** Preparation of **7l** is described below as a typical procedure. To an ice cold solution of tropylium tetrafluoroborate (**6**) (1.95 g, 10.9 mmol) and ethyl 2-trimethylsiloxyacrylate[22] (2.25 g, 12.1 mmol) in dichloromethane (25 mL) was added a solution of $BF_3 \cdot Et_2O$ (1.87 g, 13.1 mmol) in dichloromethane (5 mL). After stirring at room temperature for 2 h, the reaction was quenched with water, and organic materials were extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 90/10) to give ethyl 3-(cyclohepta-2,4,6-trienyl)propionate (**7l**) (911 mg, 40%).

**Spectral Data.** 2-(Cyclohepta-2,4,6-trienyl)-1-phenylethanone (**7a**) and 1-(cyclohepta-2,4,6-trienyl)propan-2-one (**7e**) are known compounds, and their spectral data are in good agreement with those of authentic samples.[11]

**1-(Cyclohepta-2,4,6-trienyl)-3,3-dimethylbutan-2-one (7b):** Prepared by method B in 30% yield; Colorless oil; IR (ZnSe) 2954, 2879, 1700, 1465, 1403, 1365, 1207, 1120, 989, 752, 690 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.18 (9H, s), 2.38 (1H, tt, $J$ = 6.2, 7.1 Hz), 2.84 (2H, d, $J$ = 7.1 Hz), 5.18 (2H, dd, $J$ = 6.2, 9.0 Hz), 6.15–6.19 (2H, m), 6.60–6.65 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 26.3, 34.2, 39.3, 44.1, 125.0, 125.6, 130.8, 214.3; Anal. Found: C, 81.82; H, 9.57%. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53%.

**1-(Cyclohepta-2,4,6-trienyl)-3-methylbutan-2-one (7c):** Prepared by method B in 50% yield; Colorless oil; IR (ZnSe) 2969, 1710, 1465, 1363, 1095, 1035, 744, 711 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.10 (6H, d, $J$ = 7.0 Hz), 2.33 (1H, tt, $J$ = 6.0, 7.0 Hz), 2.60 (1H, septet, $J$ = 7.0 Hz), 2.81 (2H, d, $J$ = 7.0 Hz), 5.17 (2H, dd, $J$ = 6.0, 9.0 Hz), 6.16–6.19 (2H, m), 6.61–6.66 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.1, 34.3, 40.8, 43.2, 125.1, 125.3, 130.9, 213.3; Anal. Found: C, 81.62; H, 9.12%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

**2-(Cyclohepta-2,4,6-trienyl)-1-cyclopropylethanone (7d):** Prepared by method B in 38% yield; Colorless oil; IR (ZnSe) 3012, 1698, 1390, 1195, 1062, 1022, 900, 744, 703 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.86 (2H, td, $J$ = 4.0, 6.0 Hz), 1.03 (2H, td, $J$ = 4.0, 7.5 Hz), 1.93 (1H, tt, $J$ = 5.2, 7.8 Hz), 2.30 (1H, tt, $J$ = 6.0, 7.5 Hz), 2.92 (2H, d, $J$ = 7.8 Hz), 5.19 (2H, dd, $J$ = 5.2, 8.8 Hz), 6.16–6.22 (2H, m), 6.62–6.67 (2H, m); $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 10.7, 20.6, 34.6, 46.5, 125.1, 125.2, 131.0, 209.4; Anal. Found: C, 82.43; H, 8.12%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

**1-(Cyclohepta-2,4,6-trienyl)-4-phenylbut-3-en-2-one (7f):** Prepared by method B in 34% yield; Pale yellow oil; IR (ZnSe) 3012, 1687, 1660, 1448, 1365, 1332, 1178, 1062, 975, 744, 688 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.39 (1H, tt, $J$ = 5.9, 7.5 Hz), 3.04 (2H, d, $J$ = 7.5 Hz), 5.25 (2H, dd, $J$ = 5.9, 9.0 Hz), 6.19–6.22 (2H, m), 6.65–6.67 (2H, m), 6.75 (1H, d, $J$ = 16.2 Hz), 7.38–7.41 (3H, m), 7.52–7.55 (2H, m), 7.57 (1H, d, $J$ = 16.2 Hz); $^{13}C$ NMR (125 MHz, $C_6D_6$) $\delta$ 35.2, 44.1, 125.3, 125.8, 126.5, 128.4, 128.9, 130.2, 131.1, 135.0, 141.9, 197.1; HRMS(EI$^+$) Found: $m/z$ 236.1228. Calcd for $C_{17}H_{16}O$: $M^+$, 236.1201.

**1-(Cyclohepta-2,4,6-trienyl)-4-(4-methoxyphenyl)but-3-en-2-one (7g):** Prepared by method B in 36% yield; Colorless crystals; mp 98–99 °C; IR (ZnSe) 3004, 2931, 1652, 1598, 1509, 1421, 1249, 1174, 1024, 968, 842, 696 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 2.38 (1H, tt, $J$ = 5.6, 7.2 Hz), 3.01 (2H, d, $J$ = 7.2 Hz), 3.84 (3H, s), 5.25 (2H, dd, $J$ = 5.6 8.9 Hz), 6.17–6.23 (2H, m), 6.64 (1H, d, $J$ = 15.9 Hz), 6.66–6.70 (2H, m), 6.91 (2H, d, $J$ = 8.6 Hz), 7.50 (2H, d, $J$ = 8.6 Hz), 7.53 (1H, d, $J$ = 15.9 Hz); $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 35.0, 43.7, 55.4, 114.4, 124.0, 125.1, 125.3, 127.1, 130.0, 131.0, 142.6, 161.6, 198.7; Anal. Found: C, 80.97; H, 6.94%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

**2-(Cyclohepta-2,4,6-trienyl)-1-phenylpropan-1-one (7h):** Prepared by method B in 50% yield; Colorless oil; IR (ZnSe) 3014, 1677, 1446, 1222, 1180, 968, 686 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.29 (3H, d, $J$ = 7.0 Hz), 2.35 (1H, ddd, $J$ = 6.2, 6.3, 9.2 Hz), 3.83 (1H, qd, $J$ = 7.0, 9.2 Hz), 5.24 (1H, dd, $J$ = 6.2, 9.5 Hz), 5.38 (1H, dd, $J$ = 6.3, 9.5 Hz), 6.14 (1H, dd, $J$ = 5.0, 9.5 Hz), 6.27 (1H, dd, $J$ = 4.9, 9.5 Hz), 6.62–6.68 (2H, m), 7.47 (2H, dd, $J$ = 7.4, 7.9 Hz), 7.57 (1H, tt, $J$ = 1.3, 7.4 Hz), 7.95 (2H, dd, $J$ = 1.3, 7.9 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 15.8, 41.6, 41.7, 123.1, 125.0, 125.2, 125.6, 128.3, 128.7, 130.8, 130.9, 133.0, 136.8, 203.5; Anal. Found: C, 85.90; H, 7.43%. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%.

**2-(Cyclohepta-2,4,6-trienyl)-1,2-diphenylethanone (7i):** Prepared by method A in 59% yield; Colorless needles; mp 116–118 °C; IR (ZnSe) 3018, 1677, 1569, 1579, 1492, 1446, 1274, 1218, 1176, 983, 754, 692, 653 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$

3.08 (1H, ddd, $J = 6.4$, 6.7, 11.1 Hz), 4.84 (1H, d, $J = 11.1$ Hz), 5.16 (1H, dd, $J = 6.7$, 9.6 Hz), 5.36 (1H, dd, $J = 6.4$, 9.5 Hz), 6.13–6.20 (2H, m), 6.67–6.69 (2H, m), 7.19–7.23 (1H, m), 7.26–7.31 (4H, m), 7.39 (2H, dd, $J = 7.5$, 7.9 Hz), 7.49 (1H, tt, $J = 1.2$, 7.4 Hz), 7.95 (2H, d, $J = 8.4$ Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 42.2, 53.7, 123.6, 125.3, 125.8 (overlapped), 127.3, 128.5, 128.6, 128.8, 128.9, 130.7, 130.9, 133.0, 137.0, 137.3, 199.1; Anal. Found: C, 87.84; H, 6.54%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

**2-(Cyclohepta-2,4,6-trienyl)pentan-3-one (7j):** Prepared by method A in 58% yield; Colorless oil; IR (ZnSe) 3016, 2973, 1712, 1600, 1457, 1376, 1106, 971, 744, 707 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.04 (3H, dd, $J = 7.3$, 7.3 Hz), 1.08 (3H, d, $J = 7.0$ Hz), 2.04 (1H, ddd, $J = 6.1$, 6.2, 9.4 Hz), 2.40 (1H, qd, $J = 7.3$, 17.8 Hz), 2.46 (1H, qd, $J = 7.3$, 17.8 Hz), 2.87 (1H, qd, $J = 7.0$, 9.4 Hz), 5.17 (1H, dd, $J = 6.1$, 9.4 Hz), 5.23 (1H, dd, $J = 6.2$, 9.4 Hz), 6.18 (1H, ddd, $J = 2.5$, 3.2, 9.4 Hz), 6.24 (1H, ddd, $J = 2.4$, 3.2, 9.4 Hz), 6.63–6.68 (2H, m); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 7.6, 14.7, 34.4, 41.2, 47.6, 122.9, 124.2, 125.2, 125.5, 130.85, 130.87, 214.4; Anal. Found: C, 81.60; H, 9.29%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

**2-(Cyclohepta-2,4,6-trienyl)-3,4-dihydronaphthalen-1(2*H*)-one (7k):** Colorless oil; IR (ZnSe) 3019, 2933, 2836, 1675, 1598, 1455, 1361, 1224, 1029, 900, 792, 700 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.14–2.21 (2H, m), 2.32–2.38 (1H, m), 2.89–2.93 (1H, m), 2.99–3.02 (2H, m), 5.31 (1H, dd, $J = 6.0$, 9.4 Hz), 5.45 (1H, dd, $J = 5.9$, 9.4 Hz), 6.20–6.26 (2H, m), 6.63–6.68 (2H, m), 7.22 (1H, d, $J = 7.6$ Hz), 7.29 (1H, dd, $J = 7.4$, 7.6 Hz), 7.45 (1H, dd, $J = 7.4$, 7.8 Hz), 8.02 (1H, d, $J = 7.8$ Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 26.2, 28.1, 38.7, 49.1, 122.8, 124.5 (overlapped), 125.2, 126.6, 127.4, 128.6, 130.6, 131.1, 132.7, 133.2, 143.6, 199.3; Anal. Found: C, 86.10; H, 6.95%. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82%.

**Ethyl 3-(Cyclohepta-2,4,6-trienyl)propionate (7l):** Colorless oil; IR (ZnSe) 3014, 1747, 1731, 1446, 1398, 1276, 1052, 852, 707 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.37 (3H, t, $J = 7.3$ Hz), 2.39 (1H, tt, $J = 6.0$, 7.3 Hz), 3.19 (2H, d, $J = 7.3$ Hz), 4.32 (2H, q, $J = 7.3$ Hz), 5.20 (2H, dd, $J = 6.0$, 9.3 Hz), 6.19–6.24 (2H, m), 6.64–6.68 (2H, m); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 13.9, 33.7, 42.1, 62.5, 124.3, 125.5, 131.0, 160.9, 193.2; Anal. Found: C, 69.74; H, 6.99%. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%.

**1-(Cyclohepta-2,4,6-trienyl)-3-methoxymethoxy-3-methylbutan-2-one (7m):** Prepared by method B in 34% yield; Colorless oil; IR (ZnSe) 2987, 2935, 1716, 1463, 1400, 1361, 1143, 1025, 919, 707 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.36 (6H, s), 2.32 (1H, tt, $J = 5.9$, 7.3 Hz), 3.01 (2H, d, $J = 7.3$ Hz), 3.38 (3H, s), 4.72 (2H, s), 5.19 (2H, dd, $J = 5.9$, 9.2 Hz), 6.16–6.20 (2H, m), 6.62–6.65 (2H, m); $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ 23.6, 34.1, 39.4, 55.5, 82.1, 92.1, 125.0, 125.5, 130.9, 212.0; Anal. Found: C, 71.05; H, 8.68%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

**2-(Cyclohepta-2,4,6-trienyl)-2-methoxy-1-phenylethanone (7n):** Prepared by method B in 58% yield; Pale yellow oil; IR (ZnSe) 3021, 2362, 1689, 1596, 1448, 1199, 1133, 744, 703 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.24 (1H, ddd, $J = 5.6$, 5.7, 6.8 Hz), 3.46 (3H, s), 4.78 (1H, d, $J = 6.8$ Hz), 5.28 (1H, dd, $J = 5.7$, 9.4 Hz), 5.47 (1H, dd, $J = 5.6$, 9.5 Hz), 6.19 (1H, $J = 4.9$, 9.4 Hz), 6.22 (1H, dd, $J = 4.9$, 9.5 Hz), 6.57–6.63 (2H, m), 7.44 (2H, dd, $J = 7.4$, 7.8 Hz), 7.56 (1H, t, $J = 7.4$ Hz), 8.02 (2H, d, $J = 7.8$ Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 41.9, 58.2, 84.9, 121.1, 121.5, 122.5, 125.6, 128.60, 128.66, 130.7, 131.2, 133.5, 135.3, 199.3; Anal. Found: C, 79.82; H, 6.83%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

**4-(Cyclohepta-2,4,6-trienylmethyl)-1-phenylbut-1-yn-3-one (7o):** Prepared by method B in 40% yield; Pale yellow oil; IR (ZnSe) 3014, 2198, 1664, 1488, 1398, 1116, 1066, 757, 688 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.45 (1H, td, $J = 5.8$, 7.5 Hz), 3.02 (2H, d, $J = 7.5$ Hz), 5.25 (2H, dd, $J = 5.8$, 9.1 Hz), 6.21–6.25 (2H, m), 6.68–6.69 (2H, m), 7.38 (2H, dd, $J = 7.3$, 7.6 Hz), 7.45 (1H, t, $J = 7.6$ Hz), 7.55 (2H, dd, $J = 7.3$ Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 34.8, 48.2, 87.9, 91.2, 119.8, 124.5, 125.4, 128.6, 130.8, 131.1, 133.1, 186.5; HRMS(EI$^+$) Found: $m/z$ 234.1017. Calcd for $C_{17}H_{14}O$: M$^+$, 234.1045.

**General Procedure for the Preparation of Cycloheptatrienylmethyl Ketone Oximes 8.** To a solution of 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (**7a**) (1.86 g, 8.82 mmol) and pyridine (1.1 mL, 14 mmol) in ethanol (15 mL) was added hydroxylamine hydrochloride (0.92 g, 13 mmol); the mixture was stirred at 60 °C for 12 h. After the reaction was quenched with water, the mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine. The solution was dried over anhydrous sodium sulfate, and ethyl acetate was removed in vacuo. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 75/25) to give 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (*E*)-oxime (**8a**) (1.88 g, 95%).

**Spectral Data. 2-(Cyclohepta-2,4,6-trienyl)-1-phenylethanone (*E*)-Oxime (8a):** White powder; mp 134–135 °C; IR (KBr) 3199, 3018, 1496, 1444, 1398, 1321, 1085, 998, 931, 767, 698 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.97 (1H, tt, $J = 5.5$, 8.1 Hz), 3.28 (2H, d, $J = 8.1$ Hz), 5.26 (2H, dd, $J = 5.5$, 9.1 Hz), 6.11–6.13 (2H, m), 6.54–6.59 (2H, m), 7.34–7.36 (3H, m), 7.55–7.58 (2H, m), 8.88 (1H, brs); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.9, 36.9, 125.1, 125.3, 126.4, 128.6, 129.2, 131.0, 135.6, 158.4; Anal. Found: C, 80.02; H, 6.81; N, 6.18%. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22%.

**1-(Cyclohepta-2,4,6-trienyl)-3,3-dimethylbutan-2-one (*E*)-Oxime (8b):** Prepared as above in 89% yield; White powder; mp 90–92 °C; IR (ZnSe) 3226, 2965, 1467, 1392, 1207, 1126, 1031, 929, 773, 690 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.13 (9H, s), 1.99 (1H, tt, $J = 5.7$, 7.6 Hz), 2.85 (2H, d, $J = 7.6$ Hz), 5.35 (2H, dd, $J = 5.7$, 9.0 Hz), 6.14–6.18 (2H, m), 6.62–6.67 (2H, m), 9.34 (1H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.4, 28.7, 37.5, 37.6, 124.4, 126.3, 130.9, 165.6; Anal. Found: C, 75.85; H, 9.49; N, 6.73%. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82%.

**1-(Cyclohepta-2,4,6-trienyl)-3-methylbutan-2-one Oxime (8c):** Prepared as above in 94% yield; *E*:*Z* = 3:1 mixture; Colorless oil; IR (ZnSe) 3270, 2964, 1756, 1700, 1652, 1457, 1365, 1240, 944, 746, 703 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.07 (1.5H, d, $J = 7.1$ Hz), 1.09 (4.5H, d, $J = 6.9$ Hz), 1.96 (0.75H, tt, $J = 5.6$, 8.2 Hz), 2.03 (0.25H, tt, $J = 5.5$, 7.8 Hz), 2.43 (0.75H, septet, $J = 6.9$ Hz), 2.58 (0.5H, d, $J = 7.8$ Hz), 2.84 (1.5H, d, $J = 8.2$ Hz), 3.41 (0.25H, septet, $J = 7.1$ Hz), 5.19 (0.5H, dd, $J = 5.5$, 9.1 Hz), 5.25 (1.5H, dd, $J = 5.6$, 9.1 Hz), 6.16–6.19 (2H, m), 6.62–6.68 (2H, m); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 18.8, 20.3, 26.4, 29.4, 32.8, 33.8, 35.6, 36.5, 124.6, 124.9, 125.7, 126.0, 130.9, 131.0, 163.3, 164.0; Anal. Found: C, 75.20; H, 8.93; N, 7.24%. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32%.

**2-(Cyclohepta-2,4,6-trienyl)-1-cyclopropylethanone Oxime (8d):** Prepared as above in 96% yield; *E*:*Z* = 4:1 mixture; Colorless oil; IR (ZnSe) 3259, 3010, 1643, 1438, 1398, 1240, 1024, 943, 696 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.65–0.73 (3.6H, m), 0.84–0.86 (0.4H, m), 1.38 (0.8H, tt, $J = 5.3$, 7.9 Hz), 1.98 (0.2H, tt, $J = 5.6$, 7.6 Hz), 2.05 (0.8H, tt, $J = 5.5$, 8.1 Hz), 2.23

(0.4H, d, $J = 7.6$ Hz), 2.31 (0.2H, tt, $J = 5.5$, 8.5 Hz), 2.86 (1.6H, d, $J = 8.1$ Hz), 5.18 (0.4H, dd, $J = 5.6$, 9.0 Hz), 5.27 (1.6H, dd, $J = 5.5$, 9.0 Hz), 6.15–6.20 (2H, m), 6.63–6.65 (0.4H, m), 6.66–6.70 (1.6H, m), 8.12 (0.8H, br), 8.39 (0.2H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 4.8 (overlapped), 5.8 (overlapped), 8.6, 13.9, 31.4, 32.5, 35.8, 36.5, 124.7, 124.8, 125.7 (overlapped), 130.9, 131.0, 159.2, 160.8; Anal. Found: C, 76.03; H, 8.03; N, 7.36%. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40%.

**1-(Cyclohepta-2,4,6-trienyl)propan-2-one Oxime (8e):** Prepared as above in 99% yield; Colorless oil; IR (ZnSe) 3226, 2910, 1668, 1430, 1367, 1162, 1041, 952, 707, 686 cm$^{-1}$; (*E*)-isomer $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.85 (3H, s), 1.92 (1H, tt, $J = 5.5$, 7.9 Hz), 2.61 (2H, d, $J = 7.9$ Hz), 5.18 (2H, dd, $J = 5.5$, 9.0 Hz), 6.17–6.19 (2H, m), 6.65–6.67 (2H, m), 9.31 (1H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 13.4, 35.8, 39.1, 125.0, 125.1, 130.9, 157.0; (*Z*)-isomer $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.85 (3H, s), 1.91 (1H, tt, $J = 5.5$, 8.2 Hz), 2.86 (2H, d, $J = 8.2$ Hz), 5.22 (2H, dd, $J = 5.5$, 9.0 Hz), 6.17–6.21 (2H, m), 6.66–6.68 (2H, m), 9.44 (1H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 19.7, 31.5, 36.0, 125.0, 125.3, 131.0, 157.2; Anal. Found: C, 73.44; H, 8.07; N, 8.41%. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58%.

**1-(Cycloheptatrienyl)-4-phenylbut-3-en-2-one Oxime (8f):** Prepared as above in 87% yield; *E*:*Z* = 3:1 mixture; Colorless needles; mp 114–115 °C; IR (ZnSe) 3172, 3016, 2861, 1621, 1446, 1259, 1207, 750, 696 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.09 (0.25H, tt, $J = 5.5$, 7.8 Hz), 2.15 (0.75H, tt, $J = 5.6$, 8.2 Hz), 2.92 (0.5H, d, $J = 7.8$ Hz), 3.12 (1.5H, d, $J = 8.2$ Hz), 5.29 (0.5H, dd, $J = 5.5$, 9.2 Hz), 5.36 (1.5H, dd, $J = 5.6$, 9.2 Hz), 6.17–6.19 (2H, m, overlapped), 6.62–6.67 (2H, m), 6.80 (0.75H, d, $J = 16.5$ Hz), 6.87 (0.75H, d, $J = 16.5$ Hz), 6.93 (0.25H, d, $J = 16.8$ Hz), 7.25–7.36 (3H, m), 7.44 (1.5H, d, $J = 7.7$ Hz), 7.51 (0.5H, d, $J = 7.4$ Hz), 7.53 (0.25H, d, $J = 16.8$ Hz), 9.40 (1H, br); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 26.8, 33.9, 36.7, 37.1, 116.6, 124.6, 124.9, 125.7, 126.2, 126.4, 126.9, 127.3, 128.3, 128.9, 129.02, 129.05, 131.0, 131.1, 131.6, 134.1, 136.4, 136.5, 152.5, 156.7; Anal. Found: C, 81.36; H, 7.00; N, 5.51%. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57%.

**1-(Cyclohepta-2,4,6-trienyl)-4-(4-methoxyphenyl)but-3-en-2-one Oxime (8g):** Prepared as above in 93% yield; *E*:*Z* = 3:1 mixture; White powder; mp 126–127 °C; IR (ZnSe) 3170, 3012, 1602, 1509, 1245, 1174, 1031, 964, 696 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.05–2.15 (1H, m), 2.90 (0.5H, d, $J = 7.8$ Hz), 3.09 (1.5H, d, $J = 8.1$ Hz), 3.81 (2.25H, s), 3.82 (0.75H, s), 5.28 (0.5H, dd, $J = 5.4$, 9.1 Hz), 5.35 (1.5H, dd, $J = 5.5$, 9.1 Hz), 6.17–6.19 (2H, m), 6.63–6.65 (2H, m), 6.67 (0.75H, d, $J = 16.6$ Hz), 6.81 (0.75H, d, $J = 16.6$ Hz), 6.85–6.89 (2.25H, m), 7.36–7.40 (1.75H, m), 7.46 (0.5H, d, $J = 8.7$ Hz), 9.25 (0.25H, br), 9.40 (0.75H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 27.1, 34.2, 36.7, 37.2, 55.3 (overlapped), 113.9, 114.1, 122.9 (overlapped), 124.8, 125.1, 125.4, 125.6, 128.2, 128.9, 129.0, 131.0, 131.1, 132.9 (overlapped), 135.4, 154.7, 158.6, 159.9, 160.4; Anal. Found: C, 76.67; H, 6.91; N, 4.86%. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98%.

**2-(Cyclohepta-2,4,6-trienyl)-1-phenylpropan-1-one Oxime (8h):** Prepared as above in 98% yield; *E*:*Z* = 1:1 mixture; Colorless oil; IR (ZnSe) 3249, 3016, 1635, 1496, 1442, 1376, 1307, 948, 916, 769 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.24 (1.5H, d, $J = 6.9$ Hz), 1.29 (1.5H, d, $J = 7.0$ Hz), 1.65 (0.5H, ddd, $J = 5.8$, 5.8, 9.8 Hz), 1.90 (0.5H, ddd, $J = 5.8$, 5.8, 11.5 Hz), 3.04 (0.5H, qd, $J = 6.9$, 9.8 Hz), 3.89 (0.5H, qd, $J = 7.0$, 11.5 Hz), 5.23–5.29 (1.5H, m), 5.41 (0.5H, dd, $J = 5.8$, 9.3 Hz), 6.14 (0.5H, dd, $J = 5.0$, 9.3 Hz), 6.62–6.67 (2H, m), 6.80 (0.75H, d, $J = 16.5$ Hz), 6.87 (0.75H, d, $J = 16.5$ Hz), 6.20–6.25 (1.5H, m), 6.61–6.68 (2H, m), 7.19 (1H, d, $J = 8.2$ Hz), 7.25–7.39 (4H, m), 8.25 (0.5H, br), 8.81 (0.5H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 15.5, 16.2, 35.4, 41.80, 41.83, 42.4, 123.4 (overlapped), 124.5, 124.6, 124.7, 124.8 (overlapped), 125.0, 127.4, 127.8, 128.1, 128.2, 128.5, 128.6, 130.7, 130.85, 130.98, 130.9, 133.0, 135.7, 162.1, 163.2; Anal. Found: C, 80.13; H, 7.01; N, 5.65%. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85%.

**2-(Cyclohepta-2,4,6-trienyl)-1,2-diphenylethanone Oxime (8i):** Prepared as above in 96% yield; *E*:*Z* = 1:1 mixture; White solid; mp 136–138 °C; IR (ZnSe) 3261, 3059, 3022, 2871, 1601, 1495, 1452, 1442, 1301, 1070, 947, 746, 696 cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-$d_6$, 50 °C) $\delta$ 2.29 (0.5H, ddd, $J = 5.6$, 6.0, 12.3 Hz), 2.33 (0.5H, ddd, $J = 5.6$, 5.7, 11.7 Hz), 4.14 (0.5H, d, $J = 11.7$ Hz), 5.01 (0.5H, dd, $J = 6.0$, 9.4 Hz), 5.12 (0.5H, dd, $J = 5.6$, 9.2 Hz), 5.24 (0.5H, dd, $J = 5.7$, 9.3 Hz), 5.35 (0.5H, d, $J = 12.3$ Hz), 5.48 (0.5H, dd, $J = 5.6$, 9.2 Hz), 6.02 (0.5H, dd, $J = 5.4$, 9.4 Hz), 6.16 (0.5H, dd, $J = 5.4$, 9.3 Hz), 6.19 (0.5H, dd, $J = 5.2$, 9.2 Hz), 6.25 (0.5H, dd, $J = 5.6$, 9.2 Hz), 6.59–6.71 (2H, m), 6.99–7.00 (1H, m), 7.07 (1H, d, $J = 7.1$ Hz), 7.13 (1H, d, $J = 7.1$ Hz), 7.17–7.30 (7H, m), 10.73 (0.5H, brs), 11.39 (0.5H, brs); $^{13}$C NMR (125 MHz, DMSO-$d_6$, 50 °C) $\delta$ 39.1, 41.3, 44.0, 52.1, 116.8, 117.4, 117.62, 117.65, 117.7, 118.1, 118.2, 119.2, 119.7, 120.66 (overlapped), 120.71, 120.8, 120.9, 121.2. 121.3, 121.4, 121.6, 121.7, 123.3, 123.47, 123.52, 123.7, 127.3, 128.4, 131.3, 132.0, 147.2, 148.6; Anal. Found: C, 80.13; H, 7.01; N, 5.65%. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65%.

**2-(Cyclohepta-2,4,6-trienyl)pentan-3-one Oxime (8j):** Prepared as above in 96% yield; *E*:*Z* = 4:1 mixture; Colorless oil; IR (ZnSe) 3239, 2969, 1648, 1457, 1376, 1087, 950, 929, 707 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.086 (0.6H, dd, $J = 7.3$, 7.3 Hz), 1.093 (2.4H, dd, $J = 7.6$, 7.6 Hz), 1.18 (0.6H, d, $J = 7.0$ Hz), 1.23 (2.4H, d, $J = 6.9$ Hz), 1.48 (0.2H, ddd, $J = 5.7$, 5.7, 11.6 Hz), 1.66 (0.8H, ddd, $J = 5.8$, 5.8, 10.3 Hz), 2.06–2.14 (0.4H, m), 2.17 (0.8H, qd, $J = 7.6$, 12.9 Hz), 2.32 (0.8H, qd, $J = 7.6$, 12.9 Hz), 2.75 (0.8H, qd, $J = 6.9$, 10.3 Hz), 3.81 (0.2H, qd, $J = 7.0$, 11.6 Hz), 5.14 (0.2H, dd, $J = 5.7$, 9.3 Hz), 5.22–5.25 (1.8H, m), 6.15–6.18 (1H, m), 6.22–6.26 (1H, m), 6.65–6.72 (2H, m); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 10.2, 10.4, 15.3, 16.1, 19.5, 22.8, 33.9, 41.3, 41.9, 42.2, 123.6, 124.1, 124.4, 124.5, 124.7, 124.8, 125.0, 125.1, 130.7 (overlapped), 130.9, 131.0, 164.0, 164.9; Anal. Found: C, 75.17; H, 8.96; N, 7.29%. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32%.

**2-(Cyclohepta-2,4,6-trienyl)-3,4-dihydronaphthalen-1(2*H*)-one (*E*)-Oxime (8k):** Prepared as above in 95% yield; Colorless needles; mp 164–165 °C; IR (ZnSe) 3226, 3014, 2931, 2362, 1625, 1596, 1486, 1454, 1396, 1317, 1078, 954, 742, 696 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.63 (1H, ddd, $J = 5.4$, 5.6, 11.5 Hz), 2.03 (1H, dddd, $J = 3.6$, 6.2, 11.7, 13.8 Hz), 2.33 (1H, dddd, $J = 2.6$, 3.4, 5.5, 13.8 Hz), 2.67–2.79 (2H, m), 4.13 (1H, ddd, $J = 3.4$, 3.6, 11.5 Hz), 5.30 (1H, dd, $J = 5.6$, 9.3 Hz), 5.53 (1H, dd, $J = 5.4$, 9.3 Hz), 6.13 (1H, dd, $J = 5.3$, 9.3 Hz), 6.24 (1H, dd, $J = 5.3$, 9.3 Hz), 6.58 (1H, dd, $J = 5.3$, 10.8 Hz), 6.62 (1H, dd, $J = 5.3$, 10.8 Hz), 7.07 (1H, d, $J = 7.7$ Hz), 7.16 (1H, dd, $J = 7.5$, 7.7 Hz), 7.23 (1H, dd, $J = 7.5$, 7.9 Hz), 7.84 (1H, d, $J = 7.9$ Hz), 8.19 (1H, br); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 24.1, 24.2, 33.2, 38.7, 122.9, 124.7, 124.9, 125.17, 125.21, 126.3, 128.9, 129.3, 129.9, 130.5, 131.3, 138.1, 158.0; Anal. Found: C, 81.30; H, 6.93; N, 5.47%. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57%.

**Ethyl 3-(Cyclohepta-2,4,6-trienyl)-2-hydroxyiminopropio-**

**nate (8l):** Prepared as above in 95% yield; Colorless oil; IR (ZnSe) 3226, 3014, 1716, 1432, 1307, 1288, 1180, 1128, 1014, 705 $cm^{-1}$; (*E*)-isomer $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.33 (3H, t, $J = 7.2$ Hz), 2.06 (1H, tt, $J = 5.5$, 8.0 Hz), 3.07 (2H, d, $J = 8.0$ Hz), 4.29 (2H, q, $J = 7.2$ Hz), 5.25 (2H, dd, $J = 5.5$, 9.1 Hz), 6.15–6.17 (2H, m), 6.62–6.67 (2H, m), 10.0 (1H, br); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 14.0, 27.8, 36.7, 61.9, 124.9, 125.1, 131.0, 151.2, 163.5; (*Z*)-isomer $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.32 (3H, t, $J = 6.8$ Hz), 2.02 (1H, tt, $J = 5.6$, 7.8 Hz), 2.84 (2H, d, $J = 7.8$ Hz), 4.31 (2H, q, $J = 6.8$ Hz), 5.22 (2H, dd, $J = 5.6$, 9.3 Hz), 6.16–6.22 (2H, m), 6.63–6.68 (2H, m), 11.3 (1H, brs); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 13.9, 34.3, 36.1, 62.0, 124.7, 125.1, 131.0, 147.5, 163.4; Anal. Found: C, 64.92; H, 6.79; N, 6.23%. Calcd for $C_{12}H_{15}NO_3$: C, 65.15; H, 6.83; N, 6.33%.

**1-(Cyclohepta-2,4,6-trienyl)-3-methoxymethoxy-3-methylbutan-2-one (*E*)-Oxime (8m):** Prepared as above in 93% yield; Colorless oil; IR (ZnSe) 3351, 2985, 2937, 1436, 1380, 1143, 1083, 1029, 944, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $C_6D_6$) $\delta$ 1.38 (6H, s), 2.27 (1H, tt, $J = 5.5$, 7.9 Hz), 2.98 (2H, d, $J = 7.9$ Hz), 3.10 (3H, s), 4.49 (2H, s), 5.41 (2H, dd, $J = 5.5$, 9.0 Hz), 6.07–6.10 (2H, m), 6.51–6.53 (2H, m), 9.45 (1H, brs); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 26.1, 28.7, 38.0, 55.1, 78.6, 91.9, 124.7, 126.5, 131.2, 162.4; Anal. Found: C, 66.75; H, 8.33; N, 5.32%. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57%.

**2-(Cyclohepta-2,4,6-trienyl)-2-methoxy-1-phenylethanone Oxime (8n):** Prepared as above in 86% yield; Colorless crystals; mp 165–166 °C; IR (ZnSe) 3272, 2929, 1490, 1440, 1336, 1124, 1106, 1068, 941, 927, 763, 694, 582 $cm^{-1}$; (*E*)-isomer $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.81 (1H, ddd, $J = 5.5$, 5.8, 10.1 Hz), 3.55 (3H, s), 4.19 (1H, d, $J = 10.1$ Hz), 5.15 (1H, dd, $J = 5.8$, 9.4 Hz), 5.39 (1H, dd, $J = 5.5$, 9.4 Hz), 6.16–6.21 (2H, m), 6.53 (1H, dd, $J = 5.2$, 10.9 Hz), 6.57 (1H, dd, $J = 5.4$, 10.9 Hz), 7.32–7.36 (5H, m), 8.71 (1H, brs); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 41.7, 57.3, 84.4, 120.7, 123.4, 125.2, 125.7, 128.02, 128.04, 129.0, 130.4, 130.6, 131.2, 156.8; (*Z*)-isomer $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.05 (1H, ddd, $J = 5.5$, 5.8, 10.7 Hz), 3.50 (3H, s), 5.11 (1H, dd, $J = 5.8$, 9.5 Hz), 5.47 (1H, d, $J = 10.7$ Hz), 5.48 (1H, dd, $J = 5.5$, 9.4 Hz), 6.12 (1H, dd, $J = 5.5$, 9.5 Hz), 6.25 (1H, dd, $J = 5.5$, 9.4 Hz), 6.53 (1H, dd, $J = 5.5$, 11.0 Hz), 6.61 (1H, dd, $J = 5.5$, 11.0 Hz), 7.29–7.36 (3H, m), 7.64–7.67 (2H, m), 9.30 (1H, brs); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 42.3, 57.8, 75.3, 120.0, 124.0, 125.3, 126.0, 127.8, 128.3, 129.2, 130.8, 131.1, 133.4, 158.1; Anal. Found: C, 75.03; H, 6.74; N, 5.61%. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%.

**4-(Cyclohepta-2,4,6-trienyl)-1-phenylbut-1-yn-3-one Oxime (8o):** *E*:*Z* = 2:3 mixture; Pale yellow oil; IR (ZnSe) 3247, 3172, 3014, 2856, 2217, 1608, 1490, 1442, 1313, 1149, 1020, 987, 755, 707 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.18–2.22 (1H, m), 2.83 (1.2H, d, $J = 7.8$ Hz), 2.99 (0.8H, d, $J = 8.0$ Hz), 5.27–5.32 (2H, m), 6.21–6.23 (2H, m), 6.66–6.70 (2H, m), 7.25–7.38 (3H, m), 7.44 (0.8H, d, $J = 7.0$ Hz), 7.50 (1.2H, d, $J = 7.0$ Hz), 9.14 (0.6 H, brs), 9.32 (0.4H, brs); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 31.9, 36.4, 36.6, 37.3, 79.6, 84.2, 92.0, 101.0, 121.4, 121.8, 124.9, 125.1, 125.2, 125.3, 128.3, 128.4, 129.1, 129.5, 131.0 (overlapped), 131.9, 132.1, 141.9, 146.3.

**General Procedure for the Preparation of Cycloheptatrienylmethyl Ketone *O*-Pentafluorobenzoyloximes 1.** To 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (*E*)-oxime (**8a**) (819 mg, 3.64 mmol) and triethylamine (1.00 mL, 7.17 mmol) in dichloromethane (20 mL), a solution of pentafluorobenzoyl chloride (1.07 g, 4.64 mmol) in dichloromethane (5 mL) was slowly added at 0 °C, and this mixture was stirred at the same temperature for 15 min. After the reaction was quenched with water, the mixture was extracted three times with ethyl acetate, and the combined extracts were washed with sat. $NaHCO_3$ aq. and brine. The solution was dried over anhydrous sodium sulfate, and ethyl acetate was removed in vacuo. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 95/5) to give 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (*E*)-*O*-pentafluorobenzoyloxime (**1a**) (1.43 g, 95%).

**Spectral Data. 2-(Cyclohepta-2,4,6-trienyl)-1-phenylethanone (*E*)-*O*-Pentafluorobenzoyloxime (1a):** Prepared as above in 95% yield; White powder; mp 88–89 °C; IR (KBr) 3021, 1766, 1650, 1527, 1494, 1332, 1199, 1002, 887, 788, 701, 615 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.99 (1H, tt, $J = 5.6$, 8.1 Hz), 3.29 (2H, d, $J = 8.1$ Hz), 5.15 (2H, dd, $J = 5.6$, 9.2 Hz), 6.10–6.14 (2H, m), 6.50–6.55 (2H, m), 7.35–7.46 (3H, m), 7.65–7.68 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 31.2, 36.8, 106.9–107.2 (m), 123.8, 125.6, 127.5, 128.7, 130.9, 131.0, 133.0, 137.8 (m, d, $J = 254$ Hz), 143.5 (m, d, $J = 254$ Hz), 145.4 (m, d, $J = 253$ Hz), 156.4, 167.5; Anal. Found: C, 63.19; H, 3.50; N, 3.36%. Calcd for $C_{22}H_{14}F_5NO_2$: C, 63.01; H, 3.37; N, 3.34%.

**1-(Cyclohepta-2,4,6-trienyl)-3,3-dimethylbutan-2-one (*E*)-*O*-Pentafluorobenzoyloxime (1b):** Prepared as above in 99% yield; White powder; mp 73–74 °C; IR (ZnSe) 2971, 2362, 1762, 1652, 1496, 1322, 1187, 993, 856, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.23 (9H, s), 1.96 (1H, tt, $J = 6.0$, 7.6 Hz), 2.88 (2H, d, $J = 7.6$ Hz), 5.19 (2H, dd, $J = 6.0$, 9.1 Hz), 6.12–6.15 (2H, m), 6.63–6.64 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 28.1, 31.1, 37.4, 38.8, 107.4–107.7 (m), 124.7, 124.9, 131.0, 137.6 (m, d, $J = 254$ Hz), 143.2 (m, d, $J = 258$ Hz), 145.1 (m, d, $J = 256$ Hz), 156.7, 175.6; Anal. Found: C, 60.03; H, 4.58; N, 3.50%. Calcd for $C_{20}H_{18}F_5NO_2$: C, 60.15; H, 4.54; N, 3.51%.

**1-(Cyclohepta-2,4,6-trienyl)-3-methylbutan-2-one *O*-Pentafluorobenzoyloxime (1c):** Prepared as above in 98% yield; *E*:*Z* = 2:1 mixture; Colorless oil; IR (ZnSe) 2973, 1760, 1652, 1502, 1326, 1195, 1091, 997, 896, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.10 (2H, d, $J = 7.1$ Hz), 1.20 (4H, d, $J = 6.9$ Hz), 2.03 (0.67H, tt, $J = 5.8$, 8.1 Hz), 2.09 (0.33H, tt, $J = 5.7$, 7.8 Hz), 2.64 (0.67H, septet, $J = 6.9$ Hz), 2.74 (0.66H, d, $J = 7.8$ Hz), 2.86 (1.34H, d, $J = 8.1$ Hz), 3.32 (0.33H, septet, $J = 7.1$ Hz), 5.17 (1.34H, dd, $J = 5.8$, 9.1 Hz), 5.22 (0.66H, dd, $J = 5.7$, 9.1 Hz), 6.16–6.21 (2H, m), 6.64–6.67 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 18.9, 20.0, 29.2, 31.4, 33.7, 33.9, 35.4, 36.4, 107.2–107.7 (m, overlapped), 124.2, 124.9, 125.0, 125.5, 130.9, 131.1, 136.6–136.8 and 138.6–138.8 (m, d, overlapped), 142.2–142.4, 143.9–144.4, and 146.0–146.3 (m, overlapped), 156.7, 157.4, 173.5, 174.1; Anal. Found: C, 59.35; H, 4.33; N, 3.63%. Calcd for $C_{19}H_{16}F_5NO_2$: C, 59.22; H, 4.19; N, 3.64%.

**2-(Cyclohepta-2,4,6-trienyl)-1-cyclopropylethanone *O*-Pentafluorobenzoyloxime (1d):** Prepared as above in 98% yield; *E*:*Z* = 5:3 mixture; Colorless oil; IR (ZnSe) 3016, 1758, 1506, 1421, 1326, 1201, 1095, 1002, 869, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.81–0.85 (0.74H, m), 0.85–0.89 (1.26H, m), 0.96–1.00 (0.74H, m), 1.01–1.04 (1.26H, m), 1.54 (0.63H, tt, $J = 5.0$, 8.2 Hz), 2.04 (0.37H, tt, $J = 5.7$, 7.7 Hz), 2.14 (0.63H, tt, $J = 5.9$, 8.1 Hz), 2.26 (0.37H, tt, $J = 5.2$, 8.5 Hz), 2.37 (0.74H, d, $J = 7.7$ Hz), 2.90 (1.26H, d, $J = 8.1$ Hz), 5.20 (1.26H, dd, $J = 5.9$, 9.3 Hz), 5.23 (0.74H, dd, $J = 5.7$, 9.3 Hz), 6.16–6.22 (2H, m), 6.63–6.65 (0.74H, m), 6.66–6.69 (1.26H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 6.3 (overlapped), 7.7 (overlapped), 10.4, 14.1, 32.0, 33.5, 35.8, 36.3, 107.0–107.2 (m), 107.3–107.6 (m), 124.2, 124.8, 125.0, 125.4, 130.9, 131.1, 136.5–136.8 and 138.5–138.8 (m, d, overlapped), 142.1–142.3, 144.0–144.4, and

146.2–146.4 (m, overlapped), 156.4, 157.2, 169.9, 171.6; Anal. Found: C, 59.31; H, 3.78; N, 3.61%. Calcd for $C_{19}H_{14}F_5NO_2$: C, 59.53; H, 3.68; N, 3.65%.

**1-(Cyclohepta-2,4,6-trienyl)propan-2-one (*E*)-*O*-Pentafluorobenzoyloxime (1e):** Prepared as above in 92% yield; Colorless oil; IR (ZnSe) 3018, 1760, 1652, 1523, 1506, 1421, 1326, 1197, 1093, 1002, 873, 713 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.96 (1H, tt, $J = 5.5$, 8.0 Hz), 2.01 (3H, s), 2.80 (2H, d, $J = 8.0$ Hz), 5.22 (2H, dd, $J = 5.5$, 9.1 Hz), 6.19–6.26 (2H, m), 6.66–6.71 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 15.7, 35.7, 38.6, 107.0–107.3 (m), 124.0, 125.4, 131.1, 137.7 (m, d, $J = 254$ Hz), 143.3 (m, d, $J = 259$ Hz), 145.4 (m, d, $J = 252$ Hz), 156.7, 167.6; Anal. Found: C, 57.33; H, 3.53; N, 3.92%. Calcd for $C_{17}H_{12}F_5NO_2$: C, 57.15; H, 3.39; N, 3.92%.

**1-(Cyclohepta-2,4,6-trienyl)-4-phenylbut-3-en-2-one *O*-Pentafluorobenzoyloxime (1f):** Prepared as above in 95% yield; *E*:*Z* = 4:1 mixture; White powder; mp 156–157 °C, dec.; IR (ZnSe) 3018, 1754, 1650, 1625, 1492, 1322, 1186, 1000, 869, 690 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.08 (0.2H, tt, $J = 5.6$, 7.9 Hz), 2.22 (0.8H, tt, $J = 5.9$, 8.1 Hz), 3.10 (0.4H, d, $J = 7.9$ Hz), 3.13 (1.6H, d, $J = 8.1$ Hz), 5.27 (1.6H, dd, $J = 5.9$, 9.1 Hz), 5.32 (0.4H, dd, $J = 5.6$, 9.2 Hz), 6.19–6.22 (2H, m, overlapped), 6.63–6.65 (2H, m, overlapped), 6.96 (0.8H, d, $J = 16.5$ Hz), 7.08 (0.2H, d, $J = 16.6$ Hz), 7.13 (0.8H, d, $J = 16.5$ Hz), 7.31–7.40 (3.2H, m, overlapped), 7.48–7.51 (2H, m, overlapped); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 29.1, 33.8, 37.0, 37.2, 106.6–106.9 (m, overlapped), 115.5, 122.4, 124.0, 124.6, 125.1, 125.7, 127.4, 127.9, 128.9, 129.0, 129.7, 130.3, 131.1, 131.2, 134.9, 135.2, 136.6–136.9 and 138.7–138.9 (m, d, overlapped), 139.0, 140.7, 142.5–142.7, 144.5–144.7, and 146.5–146.7 (m, overlapped), 156.4, 156.8, 163.0, 166.3; Anal. Found: C, 64.81; H, 3.77; N, 3.06%. Calcd for $C_{24}H_{16}F_5NO_2$: C, 64.72; H, 3.62; N, 3.14%.

**1-(Cyclohepta-2,4,6-trienyl)-4-(4-methoxyphenyl)but-3-en-2-one (*E*)-*O*-Pentafuluorobenzoyloxime (1g):** Prepared as above in 95% yield; White powder; IR (ZnSe) 3023, 1754, 1648, 1602, 1488, 1243, 1184, 1002, 910, 829, 698 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.21 (1H, tt, $J = 5.8$, 8.1 Hz), 3.10 (2H, d, $J = 8.1$ Hz), 3.83 (3H, s), 5.26 (2H, dd, $J = 5.8$, 9.1 Hz), 6.18–6.22 (2H, m), 6.61–6.65 (2H, m), 6.82 (1H, d, $J = 16.4$ Hz), 6.90 (2H, d, $J = 8.8$ Hz), 7.08 (1H, d, $J = 16.4$ Hz), 7.43 (2H, d, $J = 8.8$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 29.1, 37.3, 55.4, 106.8–107.0 (m), 114.1, 120.1, 124.2, 125.7, 128.1, 128.8, 131.1, 137.8 (m, d, $J = 254$ Hz), 138.6, 143.5 (m, d, $J = 253$ Hz), 145.5 (m, d, $J = 258$ Hz), 156.4, 160.9, 166.6; Anal. Found: C, 62.93; H, 3.92; N, 2.84%. Calcd for $C_{25}H_{18}F_5NO_3$: C, 63.16; H, 3.82; N, 2.95%.

**2-(Cyclohepta-2,4,6-trienyl)-1-phenylpropan-1-one *O*-Pentafluorobenzoyloxime (1h):** Prepared as above in 89% yield; *E*:*Z* = 1:1 mixture; Colorless oil; IR (ZnSe) 3018, 2362, 1762, 1652, 1498, 1324, 1191, 993, 862, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.31 (1.5H, d, $J = 6.9$ Hz), 1.34 (1.5H, d, $J = 7.0$ Hz), 1.67 (0.5H, ddd, $J = 5.9$, 6.0, 10.6 Hz), 1.87 (0.5H, ddd, $J = 5.8$, 6.0, 11.5 Hz), 3.30 (0.5H, qd, $J = 6.9$, 10.6 Hz), 3.81 (0.5H, qd, $J = 7.0$, 11.5 Hz), 5.17 (0.5H, dd, $J = 6.0$, 9.3 Hz), 5.24 (0.5H, dd, $J = 6.0$, 9.4 Hz), 5.27 (0.5H, dd, $J = 5.8$, 9.4 Hz), 5.48 (0.5H, dd, $J = 5.9$, 9.3 Hz), 6.17 (0.5H, dd, $J = 5.5$, 9.3 Hz), 6.25 (1H, dd, $J = 5.4$, 9.4 Hz), 6.29 (0.5H, dd, $J = 5.2$, 9.3 Hz), 6.57–6.70 (2H, m), 7.08–7.11 (1H, m), 7.32–7.45 (4H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 15.8, 15.9, 38.0, 41.5, 42.0, 42.1, 106.9–107.2 (m, overlapped), 122.5, 123.2, 123.4, 123.9, 124.7, 125.0, 125.4, 125.5, 125.6, 126.5, 126.8, 128.0, 128.1, 128.3, 128.4, 128.8, 129.2, 130.0, 130.3, 130.85, 130.89, 130.94, 130.99, 131.6, 133.0, 136.5–136.9 and 138.5–138.9 (m, d, overlapped), 142.2–142.4, 144.2–144.5, and 146.2–146.4 (m, overlapped), 156.5, 156.9, 172.6, 172.7; Anal. Found: C, 63.56; H, 3.73; N, 3.21%. Calcd for $C_{23}H_{16}F_5NO_2$: C, 63.74; H, 3.72; N, 3.23%.

**2-(Cyclohepta-2,4,6-trienyl)-1,2-diphenylethanone *O*-Pentafluorobenzoyloxime (1i):** Prepared as above in 99% yield; *E*:*Z* = 1:1 mixture; White amorphous material; IR (ZnSe) 3021, 1762, 1652, 1496, 1324, 1189, 1002, 873, 698 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.19 (0.5H, ddd, $J = 5.7$, 5.9, 12.3 Hz), 2.45 (0.5H, ddd, $J = 6.0$, 6.1, 12.3 Hz), 4.39 (0.5H, d, $J = 12.3$ Hz), 5.05 (0.5H, dd, $J = 6.1$, 9.4 Hz), 5.12 (0.5H, dd, $J = 5.7$, 9.3 Hz), 5.33 (0.5H, dd, $J = 5.9$, 9.3 Hz), 5.35 (0.5H, d, $J = 12.3$ Hz), 5.68 (0.5H, dd, $J = 6.0$, 9.4 Hz), 6.14 (0.5H, dd, $J = 5.6$, 9.4 Hz), 6.18 (0.5H, dd, $J = 4.8$, 9.3 Hz), 6.32 (0.5H, dd, $J = 4.8$, 9.3 Hz), 6.39 (0.5H, dd, $J = 5.6$, 9.4 Hz), 6.65–6.75 (3H, m), 6.97–6.98 (1H, m), 7.12–7.15 (2H, m), 7.18–7.21 (2H, m), 7.27–7.33 (4H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 41.9, 42.6, 50.2, 55.1, 104.5–104.7 (m, overlapped), 118.6, 119.80, 119.83, 120.5, 121.3, 121.4, 121.5, 122.2, 122.7, 123.76, 123.79 (overlapped), 123.9, 124.5, 124.7, 124.8, 124.99, 125.1, 125.3, 125.7, 126.56, 126.58, 126.8, 127.0, 127.3, 127.6, 131.1, 131.5, 132.8 (m, d, $J = 234$ Hz), 133.1 (m, d, $J = 234$ Hz), 138.1 (m, d, $J = 238$ Hz), 138.4 (m, d, $J = 238$ Hz), 139.8 (m, d, $J = 237$ Hz), 140.1 (m, d, $J = 237$ Hz), 150.3, 150.7, 163.0, 163.2; Anal. Found: C, 67.80; H, 3.79; N, 2.89%. Calcd for $C_{28}H_{18}F_5NO_2$: C, 67.88; H, 3.66; N, 2.83%.

**2-(Cyclohepta-2,4,6-trienyl)pentan-3-one *O*-Pentafluorobenzoyloxime (1j):** Prepared as above in 94% yield; *E*:*Z* = 4:1 mixture; Colorless oil; IR (ZnSe) 2977, 1756, 1652, 1496, 1322, 1182, 1089, 995, 856, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.11 (2.4H, dd, $J = 7.6$, 7.6 Hz), 1.20 (0.6H, dd, $J = 7.3$, 7.3 Hz), 1.23 (0.6H, d, $J = 7.0$ Hz), 1.32 (2.4H, d, $J = 6.9$ Hz), 1.59 (0.2H, ddd, $J = 5.9$, 5.9, 11.6 Hz), 1.68 (0.8H, ddd, $J = 5.9$, 6.0, 10.7 Hz), 2.17–2.39 (2H, m), 3.03 (0.8H, qd, $J = 6.9$, 10.7 Hz), 3.62 (0.2H, qd, $J = 7.0$, 11.6 Hz), 5.04 (0.2H, dd, $J = 5.9$, 9.2 Hz), 5.20 (0.2H, dd, $J = 5.6$, 9.3 Hz), 5.24 (0.8H, dd, $J = 5.9$, 8.9 Hz), 5.26 (0.8H, dd, $J = 6.0$, 8.8 Hz), 6.18–6.22 (1H, m), 6.25–6.29 (1H, m), 6.65–6.72 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 10.3, 10.9, 15.6, 16.0, 21.0, 13.8, 36.9, 41.4, 41.7, 41.8, 107.2–107.3 (m, overlapped), 122.6, 122.8, 122.9, 123.7, 124.8 (overlapped), 125.4, 125.5, 130.90 (overlapped), 130.94, 130.99, 136.6–136.7 and 138.6–138.8 (m, d, overlapped), 142.2–142.3, 144.2–144.3, and 146.2–146.3 (m, overlapped), 156.9 (overlapped), 174.7, 175.2; Anal. Found: C, 59.34; H, 4.35; N, 3.59%. Calcd for $C_{19}H_{16}F_5NO_2$: C, 59.22; H, 4.19; N, 3.64%.

**2-(Cyclohepta-2,4,6-trienyl)-3,4-dihydronaphthalen-1(2*H*)-one (*E*)-*O*-Pentafluorobenzoyloxime (1k):** Prepared as above in 95% yield; White powder; mp 137–138 °C; IR (ZnSe) 2937, 1758, 1650, 1590, 1494, 1326, 1191, 1000, 919, 862, 700 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.76 (1H, td, $J = 5.9$, 11.6 Hz), 2.05–2.13 (1H, m), 2.34–2.40 (1H, m), 2.73–2.84 (2H, m), 3.97 (1H, ddd, $J = 3.4$, 3.4, 11.6 Hz), 5.28 (2H, dd, $J = 5.9$, 9.2 Hz), 6.14 (1H, dd, $J = 5.7$, 9.2 Hz), 6.27 (1H, dd, $J = 5.6$, 9.2 Hz), 6.52 (1H, dd, $J = 5.7$, 11.0 Hz), 6.62 (1H, dd, $J = 5.6$, 11.0 Hz), 7.11 (1H, d, $J = 7.7$ Hz), 7.21 (1H, dd, $J = 7.5$, 7.7 Hz), 7.34 (1H, dd, $J = 7.5$, 7.8 Hz), 8.05 (1H, d, $J = 7.8$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 23.7, 24.0, 35.7, 38.0, 106.9–107.2 (m), 121.9, 122.7, 125.7, 125.9, 126.6, 126.7, 127.5, 129.0, 130.7, 131.2, 131.3, 137.8 (m, d, $J = 254$ Hz), 139.4, 143.4 (m, d, $J = 254$ Hz), 145.4 (m, d, $J = 252$ Hz), 156.6, 166.6; Anal. Found: C, 64.65;

H, 3.81; N, 3.05%. Calcd for $C_{24}H_{16}F_5NO_2$: C, 64.72; H, 3.62; N, 3.14%.

**Ethyl 3-(Cyclohepta-2,4,6-trienyl)-2-[(*E*)-pentafluorobenzoyloxyimino]propionate (1l):** Prepared as above in 91% yield; Colorless oil; IR (ZnSe) 3018, 1772, 1727, 1650, 1496, 1322, 1176, 1000, 867, 703 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.38 (3H, t, $J = 7.1$ Hz), 2.17 (1H, tt, $J = 5.5$, 8.1 Hz), 3.11 (2H, d, $J = 8.1$ Hz), 4.38 (2H, q, $J = 7.1$ Hz), 5.22 (2H, dd, $J = 5.5$, 9.3 Hz), 6.17–6.21 (2H, m), 6.61–6.66 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 28.5, 42.5, 48.0, 71.1, 108.25–108.5 (m), 123.6, 125.6, 130.2, 136.1 (m, d, $J = 224$ Hz), 141.3 (m, d, $J = 226$ Hz), 142.9 (m, d, $J = 224$ Hz), 151.4, 155.9, 157.3; Anal. Found: C, 54.78; H, 3.60; N, 3.41%. Calcd for $C_{19}H_{14}F_5NO_4$: C, 54.95; H, 3.40; N, 3.37%.

**1-(Cyclohepta-2,4,6-trienyl)-3-methoxymethoxy-3-methylbutan-2-one (*E*)-*O*-Pentafluorobenzoyloxime (1m):** Prepared as above in 89% yield; Colorless oil; IR (ZnSe) 3019, 1741, 1652, 1525, 1496, 1328, 1205, 1002, 921, 688 $cm^{-1}$; $^1H$ NMR (500 MHz, $C_6D_6$) $\delta$ 1.41 (6H, s), 2.23 (1H, td, $J = 5.6$, 7.8 Hz), 2.96 (2H, d, $J = 7.8$ Hz), 3.06 (3H, s), 4.43 (2H, s), 5.24 (2H, dd, $J = 5.6$, 9.1 Hz), 6.04–6.08 (2H, m), 6.48–6.50 (2H, m); $^{13}C$ NMR (125 MHz, $C_6D_6$) $\delta$ 25.9, 30.9, 37.7, 55.3, 78.9, 91.7, 107.3–107.5 (m), 125.0, 125.2, 131.3, 137.6 (m, d, $J = 252$ Hz), 143.5 (m, d, $J = 253$ Hz), 145.4 (m, d, $J = 255$ Hz), 155.9, 173.1.

**2-(Cyclohepta-2,4,6-trienyl)-2-methoxy-1-phenylethanone (*Z*)-*O*-Pentafluorobenzoyloxime (1n):** Prepared as above in 99% yield; Colorless oil; IR (ZnSe) 3021, 2830, 1762, 1652, 1496, 1324, 1184, 1081, 993, 933, 871, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.80 (1H, ddd, $J = 5.5$, 5.9, 10.3 Hz), 3.64 (3H, s), 4.45 (1H, d, $J = 10.3$ Hz), 5.19 (1H, dd, $J = 5.9$, 9.4 Hz), 5.39 (1H, dd, $J = 5.5$, 9.4 Hz), 6.21–6.24 (2H, m), 6.55 (1H, dd, $J = 5.3$, 11.0 Hz), 6.59 (1H, dd, $J = 5.4$, 11.0 Hz), 7.24–7.26 (2H, m), 7.32–7.38 (3H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 41.7, 57.9, 83.8, 106.5–106.8 (m), 119.6, 122.7, 125.5, 126.3, 127.4, 128.1, 129.4, 129.8, 130.7, 131.4, 137.7 (m, d, $J = 252$ Hz), 143.5 (m, d, $J = 259$ Hz), 145.4 (m, d, $J = 252$ Hz), 156.6, 166.8; Anal. Found: C, 61.23; H, 3.81; N, 3.08%. Calcd for $C_{23}H_{16}F_5NO_3$: C, 61.47; H, 3.59; N, 3.12%.

**4-(Cyclohepta-2,4,6-trienylmethyl)-1-phenylbut-1-yn-3-one (*Z*)-*O*-Pentafluorobenzoyloxime (1o):** Prepared as above in 89% yield from **2o** (2 steps); Colorless needles; mp 126–128 °C; IR (ZnSe) 3016, 2362, 2206, 1760, 1652, 1496, 1324, 1201, 1180, 1089, 1002, 885, 759, 690 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.25, (1H, td, $J = 5.6$, 7.8 Hz), 3.00 (2H, d, $J = 7.8$ Hz), 5.31 (2H, dd, $J = 5.6$, 9.1 Hz), 6.23–6.28 (2H, m), 6.67–6.71 (2H, m), 7.36 (2H, dd, $J = 7.0$, 7.5 Hz), 7.43 (1H, t, $J = 7.5$ Hz), 7.45 (2H, d, $J = 7.0$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 36.6, 37.3, 79.0, 104.0, 106.5–106.7 (m), 120.5, 124.1, 125.5, 128.6, 130.5, 131.2, 132.4, 137.8 (m, d, $J = 254$ Hz), 143.6 (m, d, $J = 259$ Hz), 145.7 (m, d, $J = 259$ Hz), 151.6, 156.4; Anal. Found: C, 65.07; H, 3.26; N, 3.05%. Calcd for $C_{24}H_{14}F_5NO_2$: C, 65.02; H, 3.18; N, 3.16%.

**General Procedure for the Synthesis of 1-Azaazulenes 5.** Into a flask containing MS 4A (363 mg) was added a solution of 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (*Z*)-*O*-pentafluorobenzoyloxime (**1a**) (150 mg, 0.358 mmol) in DMF (18 mL) under an argon atmosphere; the mixture was stirred at room temperature for 1 h. To the mixture was added $Pd(dba)_2$ (21.2 mg, 0.036 mmol), *t*-$Bu_3P$ in toluene (1 g/mL, 0.029 mL, 0.014 mmol), and triethylamine (0.15 mL, 1.1 mmol). This mixture was then heated to 80 °C for 30 min. After cooling to 0 °C, the mixture was filtered through a celite pad, and water was added. Organic materials were extracted three times with ether, and the combined extracts were washed successively with water three times and with brine. The ether solution was dried over anhydrous magnesium sulfate; then the ether was removed in vacuo. The crude products were dissolved in dichloromethane (5.0 mL), and $MnO_2$ (932 mg, 10.7 mmol) was added to the solution. The mixture was stirred at the reflux temperature for 2 h and then filtered through a celite pad. The dichloromethane was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel: benzene/acetone/triethylamine = 95:5:1) to give 2-(cyclohepta-2,4,6-trienyl)-1-phenylethanone (**7a**) (3.8 mg, 5%) and the mixture of 2-phenyl-1-azaazulene (**5a**) and *t*-butylphosphine oxide. Finally, the mixture was purified by column chromatography on Sephadex™ LH-20 to give 2-phenyl-1-azaazulene (**5a**) (57.2 mg, 78%).

**Spectral Data. 2-Phenyl-1-azaazulene (5a):** Red powder; mp 158–159 °C; IR (ZnSe) 3388, 3019, 1573, 1508, 1436, 1214, 1025, 769, 752 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.45 (1H, tt, $J = 1.5$, 7.3 Hz), 7.52 (2H, dd, $J = 7.3$, 7.7 Hz), 7.59 (1H, dd, $J = 9.9$, 10.1 Hz), 7.73 (1H, dd, $J = 9.0$, 9.5 Hz), 7.76 (1H, s), 7.78 (1H, dd, $J = 9.0$, 10.1 Hz), 8.32 (2H, dd, $J = 1.5$, 7.7 Hz), 8.50 (1H, d, $J = 9.8$ Hz), 8.66 (1H, d, $J = 9.5$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 110.7, 128.1, 128.8, 128.9, 129.6, 129.9, 134.6, 135.2, 135.3, 136.6, 148.0, 158.7, 167.2; Anal. Found: C, 87.78; H, 5.51; N, 6.70%. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82%.

**2-Phenyl-3,3a-dihydrocyclohepta[*b*]pyrrole (4a):** Yellow oil; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 3.09–3.14 (2H, m), 3.72 (1H, dd, $J = 11.6$, 19.6 Hz), 5.30 (1H, dd, $J = 3.3$, 9.6 Hz), 6.12 (1H, ddd, $J = 2.0$, 6.0, 9.6 Hz), 6.36 (1H, dd, $J = 6.0$, 10.8 Hz), 6.52–6.59 (2H, m), 7.42–7.50 (3H, m), 7.95 (2H, d, $J = 6.9$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 38.9, 43.3, 115.6, 124.2, 126.8, 128.1, 128.8, 130.0, 131.7, 134.2, 155.3, 157.5, 178.6.

**2-*tert*-Butyl-1-azaazulene (5b):** Red oil; IR (ZnSe) 2956, 1583, 1482, 1434, 1405, 1319, 1228, 1008, 929, 794, 748, 717 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.54 (9H, s), 7.29 (1H, s), 7.57 (1H, dd, $J = 9.6$, 9.7 Hz), 7.70 (1H, dd, $J = 9.6$, 9.7 Hz), 7.77 (1H, dd, $J = 9.6$, 9.9 Hz), 8.44 (1H, d, $J = 9.9$ Hz), 8.62 (1H, d, $J = 9.6$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 30.4, 34.9, 110.4, 128.2, 128.8, 133.8, 134.4, 136.0, 147.5, 157.7, 182.2; HRMS(FAB$^+$) Found: $m/z$ 186.1300. Calcd for $C_{13}H_{16}N$: $(M + H)^+$, 186.1283.

**2-Isopropyl-1-azaazulene (5c):** Red oil; IR (ZnSe) 3365, 2960, 1720, 1583, 1481, 1438, 1334, 1012, 794, 746, 586 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.49 (6H, d, 6.8 Hz), 3.45 (1H, septet, $J = 6.8$ Hz), 7.24 (1H, s), 7.58 (1H, dd, $J = 9.8$, 9.8 Hz), 7.70 (1H, dd, $J = 9.5$, 9.8 Hz), 7.77 (1H, dd, $J = 9.3$, 9.5 Hz), 8.44 (1H, d, $J = 9.8$ Hz), 8.59 (1H, d, $J = 9.3$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 22.6, 31.8, 110.7, 128.3, 129.0, 133.8, 134.2, 136.0, 147.5, 157.7, 179.6; HRMS(FAB$^+$) Found: $m/z$ 172.1138. Calcd for $C_{12}H_{14}N$: $(M + H)^+$, 172.1126.

**2-Cyclopropyl-1-azaazulene (5d):** Red oil; IR (ZnSe) 3370, 3004, 1583, 1538, 1481, 1407, 1375, 1326, 1101, 1022, 933, 865, 790, 744 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.23–1.26 (4H, m), 2.33–2.44 (1H, m), 7.07 (1H, s), 7.48–7.55 (1H, m), 7.60–7.69 (2H, m), 8.30 (1H, d, $J = 9.9$ Hz), 8.43–8.47 (1H, m); $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 11.9, 13.8, 110.5, 128.4, 129.1, 132.5, 132.9, 135.2, 147.4, 158.0, 176.2; Anal. Found: C, 84.88; H, 6.68; N, 8.07%. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28%.

**2-Methyl-1-azaazulene (5e):**[16] Dark purple oil; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 2.83 (3H, s), 7.19 (1H, s), 7.59 (1H, dd, $J = 9.7$, 10.3 Hz), 7.67–7.82 (2H, m), 8.42 (1H, d, $J = 9.72$ Hz), 8.55

(1H, d, $J = 9.45$ Hz).

**2-Styryl-1-azaazulene (5f):** Red powder; mp 138–139 °C; IR (ZnSe) 3374, 3023, 1957, 1830, 1670, 1625, 1587, 1461, 1332, 1214, 970, 800, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.33 (1H, dd, $J = 7.3$, 7.3 Hz), 7.41 (2H, dd, $J = 7.5$, 7.7 Hz), 7.47 (1H, s), 7.53 (1H, d, $J = 16.2$ Hz), 7.54–7.58 (1H, m), 7.66 (2H, d, $J = 7.5$ Hz), 7.70–7.74 (2H, m), 7.89 (1H, d, $J = 16.2$ Hz), 8.41 (1H, d, $J = 9.8$ Hz), 8.55 (1H, d, $J = 10.4$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 112.8, 123.5, 127.3, 128.7, 128.8, 128.9, 129.9, 134.0, 134.5, 136.2, 136.3, 147.6, 158.9, 166.0; HRMS(FAB$^+$) Found: $m/z$ 232.1109. Calcd for $C_{17}H_{14}N$: $(M + H)^+$, 232.1126.

**2-(4-Methoxystyryl)-1-azaazulene (5g):** Red powder; IR (ZnSe) 3355, 2929, 1729, 1625, 1600, 1509, 1440, 1251, 1172, 970, 825 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 3.84 (3H, s), 6.93 (2H, d, $J = 8.7$ Hz), 7.38 (1H, d, $J = 16.1$ Hz), 7.42 (1H, s), 7.51–7.54 (1H, m), 7.59 (2H, d, $J = 8.7$ Hz), 7.65–7.69 (2H, m), 7.85 (1H, d, $J = 16.1$ Hz), 8.36 (1H, d, $J = 9.9$ Hz), 8.51–8.54 (1H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 55.3, 112.5, 114.3, 121.3, 128.8, 128.9, 129.6, 129.9, 133.6, 133.9, 135.7, 136.1, 147.6, 158.9, 160.2, 166.5; HRMS(FAB$^+$) Found: $m/z$ 262.1259. Calcd for $C_{18}H_{16}ON$: $(M + H)^+$, 262.1232.

**2-Phenyl-3-methyl-1-azaazulene (5h):** Purple powder; mp 115–116 °C; IR (ZnSe) 3353, 3052, 1577, 1465, 1417, 1334, 1184, 1120, 987, 698 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 2.73 (3H, s), 7.42–7.61 (4H, m), 7.67 (1H, dd, $J = 9.3$, 9.9 Hz), 7.77 (1H, dd, $J = 9.3$, 9.7 Hz), 8.06 (2H, d, $J = 7.8$ Hz), 8.37 (1H, d, $J = 9.9$ Hz), 8.63 (1H, d, $J = 9.7$ Hz); $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 11.1, 119.5, 127.2, 128.5, 128.7, 128.8, 129.7, 132.9, 135.2, 136.4, 136.6, 145.3, 157.3, 165.9; Anal. Found: C, 86.75; H, 6.21; N, 6.22%. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39%.

**2,3-Diphenyl-1-azaazulene (5i):** Purple powder; mp 121–122 °C; IR (ZnSe) 3374, 3056, 1598, 1579, 1500, 1417, 1330, 1072, 1025, 700 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 7.33–7.57 (9H, m), 7.69–7.86 (4H, m), 8.32 (1H, d, $J = 9.7$ Hz), 8.72 (1H, d, $J = 9.5$ Hz); $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 125.8, 127.2, 128.3, 128.7, 128.8, 129.0, 129.5, 130.0, 130.8, 134.3, 135.0, 135.6, 136.0, 137.3, 145.7, 157.6, 164.5; HRMS(FAB$^+$) Found: $m/z$ 282.1295. Calcd for $C_{21}H_{16}N$: $(M + H)^+$, 282.1283.

**(3*R**, 3a*S**)-2,3-Diphenyl-3,3a-dihydrocyclohepta[*b*]pyrrole (4i):** Yellow oil; IR (ZnSe) 3021, 2362, 1600, 1508, 1490, 1444, 1332, 1166, 1074, 991, 763, 690 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.99–3.01 (1H, m), 4.59 (1H, d, $J = 4.7$ Hz), 5.52 (1H, dd, $J = 3.6$, 9.8 Hz), 6.12 (1H, ddd, $J = 2.1$, 5.9, 9.8 Hz), 6.32 (1H, dd, $J = 5.9$, 11.1 Hz), 6.54 (1H, dd, $J = 6.3$, 11.1 Hz), 6.65 (1H, d, $J = 6.3$ Hz), 7.17–7.35 (8H, m), 7.84 (2H, d, $J = 7.2$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 51.6, 62.4, 116.2, 123.7, 126.5, 127.0, 127.3, 128.4, 128.8, 128.9, 129.1, 129.7, 130.9, 133.2, 142.3, 155.2, 178.6; HRMS(FAB$^+$) Found: $m/z$ 284.1410. Calcd for $C_{21}H_{18}N$: $(M + H)^+$, 284.1439.

**2-Ethyl-3-methyl-1-azaazulene (5j):** Purple oil; IR (ZnSe) 3355, 2967, 1668, 1581, 1479, 1430, 1324, 1062, 937 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.44 (3H, t, $J = 7.6$ Hz), 2.50 (3H, s), 3.11 (2H, q, $J = 7.6$ Hz), 7.52 (1H, dd, $J = 9.7$, 9.8 Hz), 7.52 (1H, dd, $J = 9.8$, 9.9 Hz), 7.71 (1 H, dd, $J = 9.8$, 9.9 Hz), 8.25 (1H, d, $J = 9.9$ Hz), 8.48 (1H, d, $J = 9.7$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 9.3, 13.4, 24.1, 119.7, 126.8, 128.1, 131.6, 133.4, 135.8, 143.9, 157.1, 173.4; HRMS(FAB$^+$) Found: $m/z$ 172.1142. Calcd for $C_{12}H_{14}N$: $(M + H)^+$, 172.1126.

**Benzo[*g*]cyclohepta[*b*]indole (5k):**[23] Purple powder; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.72–7.77 (2H, m), 7.84 (1 H, d, $J = 8.7$ Hz), 7.88 (1H, dd, $J = 9.6$, 9.8 Hz), 7.96 (1H, dd, $J = 9.3$, 9.8 Hz), 8.02 (1H, dd, $J = 9.6$, 10.1 Hz), 8.06 (1H, d, $J = 8.5$ Hz), 8.31 (1H, d, $J = 8.7$ Hz), 8.97 (1H, d, $J = 10.1$ Hz), 9.03 (1H, d, $J = 9.3$ Hz), 9.13 (1H, d, $J = 8.8$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 118.7, 123.0, 123.7, 124.7, 126.5, 127.1, 128.2, 128.4, 128.7, 130.3, 132.2, 135.1, 136.7, 137.2, 142.2, 157.4, 159.7.

**5,6-Dihydrobenzo[*g*]cyclohepta[*b*]indole (5k′):**[24] Purple oil; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 3.17 (2H, t, $J = 7.5$ Hz), 3.24 (2H, t, $J = 7.5$ Hz), 7.32–7.41 (3H, m), 7.50 (1H, dd, $J = 9.4$, 9.9 Hz), 7.62 (1H, dd, $J = 9.6$, 9.9 Hz), 7.69 (1H, dd, $J = 9.4$, 10.0 Hz), 8.26 (1H, d, $J = 10.0$ Hz), 8.37 (1H, d, $J = 7.2$ Hz), 8.57 (1H, d, $J = 9.6$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 20.4, 29.3, 122.5, 125.4, 127.2, 127.5, 128.4, 129.0, 129.9, 131.9, 132.0, 134.4, 136.1, 139.8, 142.1, 159.4, 163.5.

**Ethyl 1-Azaazulene-2-carboxylate (5l):** Red oil; IR (ZnSe) 3029, 2834, 1716, 1585, 1409, 1321, 1211, 1097, 1022, 754 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.50 (3H, t, $J = 7.1$ Hz), 4.57 (2H, q, $J = 7.2$ Hz), 7.66 (1H, dd, $J = 9.7$, 9.8 Hz), 7.88 (1H, dd, $J = 9.9$, 9.9 Hz), 7.99 (1H, s), 8.05 (1H, dd, $J = 9.8$, 9.9 Hz), 8.75 (1H, d, $J = 9.7$ Hz), 8.95 (1H, d, $J = 9.9$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 14.5, 61.6, 116.9, 129.3, 130.1, 139.4, 140.6, 147.0, 156.2, 157.5, 164.3; HRMS(FAB$^+$) Found: $m/z$ 202.0870. Calcd for $C_{12}H_{12}O_2N$: $(M + H)^+$, 202.0868.

**Ethyl Quinoline-2-carboxylate (9):**[25] Colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.50 (3H, t, $J = 7.1$ Hz), 4.57 (2H, d, $J = 7.1$ Hz), 7.66 (1H, dd, $J = 7.9$, 8.1 Hz), 7.80 (1H, dd, $J = 8.1$, 8.5 Hz), 7.89 (1H, d, $J = 7.9$ Hz), 8.20 (1H, dd, $J = 8.5$ Hz), 8.31 (1H, d, $J = 4.6$ Hz), 8.33 (1H, d, $J = 4.6$ Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 14.4, 62.3, 121.0, 127.5, 128.5, 129.3, 130.2, 130.8, 137.2, 147.6, 148.3, 165.5.

**Ethyl Isoquinoline-3-carboxylate (10):**[26] Colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.50 (3H, t, $J = 7.2$ Hz), 4.55 (2H, d, $J = 7.2$ Hz), 7.74–7.82 (2H, m), 7.99 (1H, d, $J = 8.2$ Hz), 8.07 (1H, d, $J = 8.1$ Hz), 8.61 (1H, s), 9.36 (1H, s); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 14.4, 61.9, 124.0, 127.7, 128.0, 129.5, 129.9, 131.1, 135.5, 141.8, 152.7, 165.8.

**1-(Cyclohepta-2,4,6-trienyl)acetonitrile (11):** Pale yellow oil; IR (ZnSe) 3018, 2925, 2242, 1523, 1498, 1423, 1402, 1326, 1193, 1102 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 2.29 (1H, td, $J = 6.0$, 7.2 Hz), 2.61 (2H, d, $J = 7.2$ Hz), 5.29 (2H, dd, $J = 6.0$, 9.2 Hz), 6.27–6.30 (2H, m), 6.67–6.70 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 19.8, 35.3, 118.6, 122.8, 126.4, 131.3; HRMS(EI$^+$) Found: $m/z$ 131.0711. Calcd for $C_9H_9N$: $M^+$, 131.0735.

**2-Pentafluorophenyl-1-phenylacetylene (13):**[27] Colorless needles; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.37–7.43 (3H, m), 7.57–7.59 (2H, m); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 73.0, 100.2–100.3 (m), 101.5, 121.5, 128.5, 129.6, 131.9, 137.7 (m, d, $J = 248$ Hz), 141.4 (m, d, $J = 256$ Hz), 147.2 (m, d, $J = 257$ Hz); $^{19}F$ NMR (470 MHz, $CDCl_3$) $\delta$ −0.13 to −0.06 (2F, m), 8.97 (1F, t, $J = 18.8$ Hz), 25.70–25.78 (2F, m).

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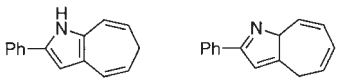
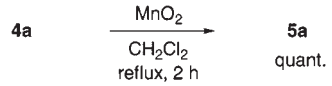
12 The isomerized compounds of **4a**, such as **14** and **15** were detected by $^1$H NMR (Fig. 2).




**14** **15**

Fig. 2. Dihydro-1-azaazulenes.

13 When 3,3a-dihydro-2-phenyl-1-azaazulene (**4a**) treated with $MnO_2$, the oxidation was confirmed to proceed quantitatively (Eq. 4). $MnO_2$ was the most effective oxidant, compared with other oxidants such as $NiO_2$, DDQ, and *p*-chloranil.




(4)

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17 Stereochemistry of **4i** was determined by NOE measurement as shown in Fig. 3.

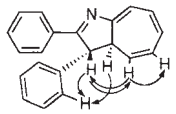


Fig. 3. NOE correlations of **4i**.

18 In this reaction, the combination of $Pd(dba)_2$–*t*-$Bu_3$P was not effective. **5l**, **9**, and **10** were obtained in 5, 10, and 10% yields, respectively.

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