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[2π + 2σ] AND [8π + 2σ] TYPES CYCLOADDITION REACTIONS OF AZA-, THIO-, AND THIAZA-AZULEN-2(1*H*)-ONE DERIVATIVES WITH NAPHTHO[*b*]CYCLOPROPENE: EFFECTS OF SOLVENTS AND YTTERBIUM COMPLEX

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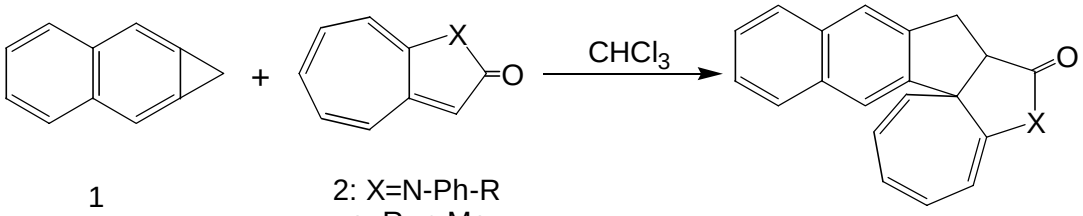
Abstract ---Reactions of naphtho[*b*]cyclopropene with 1-aza- or 1-thiaazulene-2(1*H*)-one derivatives in chloroform under the presence of a catalytic amount of ytterbium complex afforded [2π + 2σ] type cycloaddition products. The analogous reactions of the cyclopropene with a 1-thia-3-azaazulene-2(1*H*)-one derivative gave an [8π + 2σ] type cycloadduct. These reactions were considered to proceed *via* ionic processes, in which the azulene-2(1*H*)-one derivatives played as 2π and 8π components, respectively. On the other hand, reactions of the cyclopropene with 1-azaazulene-2(1*H*)-one derivatives in benzene yielded the another type of [8π + 2σ] type cycloadducts *via* a concerted process.

As menbers of nonbenzenoid aromatic compounds, the chemistry of 1-hetero-azulene-2(1*H*)-one derivatives (**2**,**3**,**6**) have attracted much attention of chemists.[1] The hybridization mode of the heteroatoms in 1-hetero-azulene-2(1*H*)-one derivatives is considered to be sp^2 hybridization to construct longer cyclic conjugated systems. Taking into account the lone pair electrons on the heteroatoms, the 1-hetero-azulene-2(1*H*)-one systems are regarded to have 12 π electrons cyclic cross conjugated systems.

Naphtho[*b*]cyclopropene (**1**) is known to be a reactive species owing to the high strain energy caused by the hindered sp^2 hybridized carbon atoms on the bridgehead positions. Three kinds of reaction paths are considered to be possible for **1**, *i.e.*, a 2π mode, a 2σ mode,[2] and a carbene mode.[3] As a series of our researches on the reactivities of azulene-2(1*H*)-one, we investigated reactions of **1** with **2**,**3**, and **6**. Here, the results are discussed.



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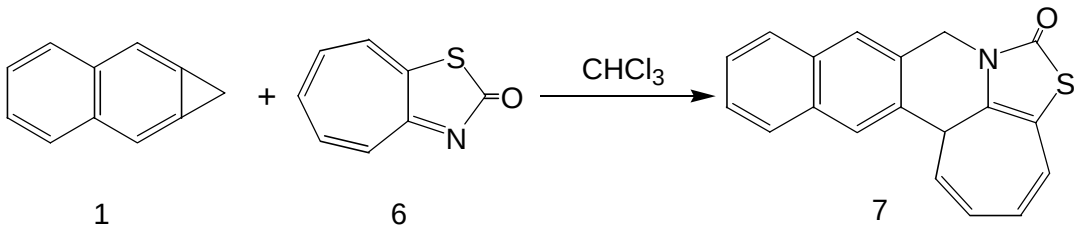
2: X=N-Ph-R
a: R=*p*-Me
b: R=*p*-OMe
c: R=*p*-Cl
3: X=S

4 X=N-Ph-R

5 X=S



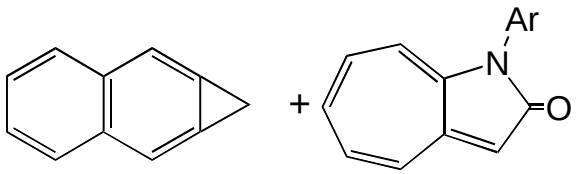
1 6 7

A chloroform solution of *N*-*p*-methylphenyl-1-azaazulene-2(1*H*)-one (**2a**) and an equimolar amount of naphtho[*b*]cyclopropene (**1**) was stirred at 60 ℃ for 3 days. After evaporation of the solvent, the reaction mixture was chromatographed on silica gel to give a [2π + 2σ] type cycloadduct (**4a**) in 15 % yield. A slight improvement in the yield of **4a** was observed by the use of a catalytic amount of ytterbium complex.[4] Thus, a reaction of **1** with **2a** in chloroform under a presence of 3 mol % of $Yb(fod)_3$ afforded **4a** in 23 % yield. Analogous results were obtained in reactions using 1-azaazulene-2(1*H*)-one derivatives (**2b**, **2c**) with a 1-thiaazulene-2(1*H*)-one derivative (**3**). The same type of reaction of 1-thia-3-azaazulene-2(1*H*)-one (**6**) gave another type of [8π + 2σ] type cycloadduct (**7**). In this case, the presence of $Yb(fod)_3$ had no effect on the product yield. These results were summarized in Table 1. The physical properties of **4a-c**, **5**, and **7** are as follow.[5]

Table 1. Product yields in the reactions in chloroform

Azulene-2(1*H*)-one	$Yb(fod)_3$	Products	Yields(%)
2a	No	4a	15
2a	Yes	4a	23
2b	Yes	4b	14
2c	Yes	4c	39
3	Yes	5	30
6	No	7	62
6	Yes	7	60

Another type of reaction was found to proceed by the use of benzene as a solvent. A stirring of a benzene solution of **1** and **2c** at 80 ℃ for 3 days afforded a new type of [8π + 2σ] cycloadduct (**8c**) in 4 % yield together with the above mentioned type [8π + 2σ] cycloadduct (**4c**) in 36 % yield. No improvement was detected by the use of $Yb(fod)_3$. The results of this type of reactions were summarized in Table 2. The physical properties of **8a-c** are as follow.[6] No reaction was proceeded with **3** or **6** in benzene.



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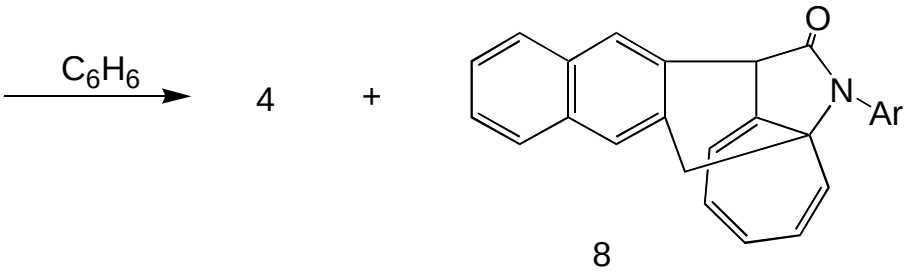

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Table 2. Product yields in the reaction in C_6H_6

Azulene-2(1*H*)-one	$Yb(fod)_3$	Yields(%)	
		8	4
2a	No	22	No
2b	No	35	No
2c	No	4	36
2c	Yes	5	17

The structures of 4 and 5 were deduced on the basis of their spectral properties. MS spectrum showed the molecular weights of **4** and **5** to be those of the 1:1 adducts between the corresponding starting materials. Existences of carbonyl groups were confirmed by IR spectra. ^{1}H NMR spectrum demonstrated existences of naphthalene and 1,7-disubstituted tropylidene moieties. Existences of couplings between the methine and the methylene protons in ^{1}H NMR spectrum suggested the neighborhood of these protons.

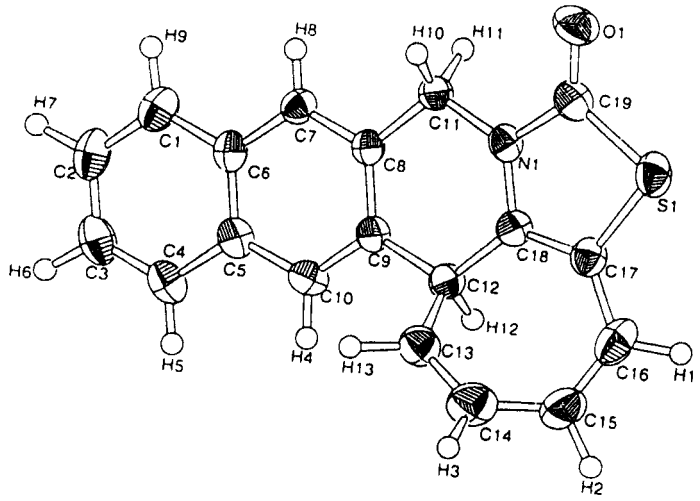


Figure 1. ORTEP drawing of 7

The structure of 7 was decided by the use of a single crystal X- Ray analysis as shown in Figure 1.

The structure of 8 was deduced on the basis of its spectral properties. MS and IR spectram supported the molecular weight and the existence of a carbonyl group. The separation between the methine and the methylene protons was shown by an absence of coupling between these protons in ^{1}H NMR spectrum. The chemical shift of the quaternary carbon (50 ppm) in ^{13}C NMR spectrum suggested this carbon atom to be adjacent to a nitrogen atom.

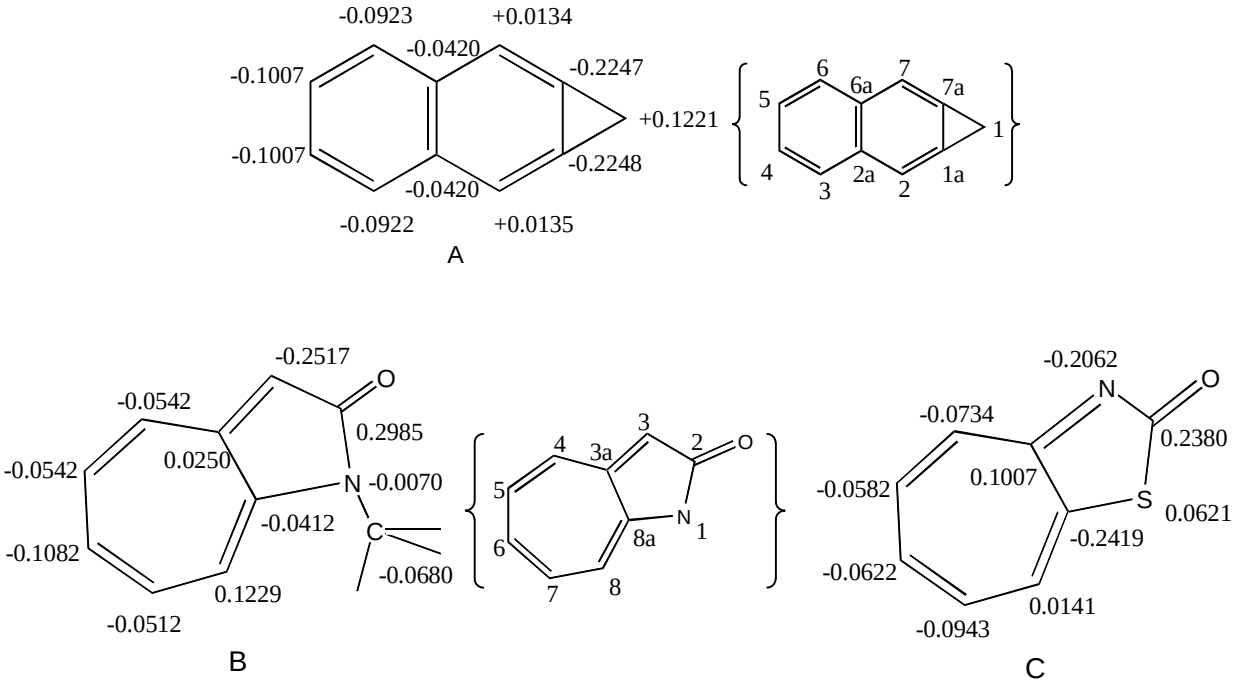
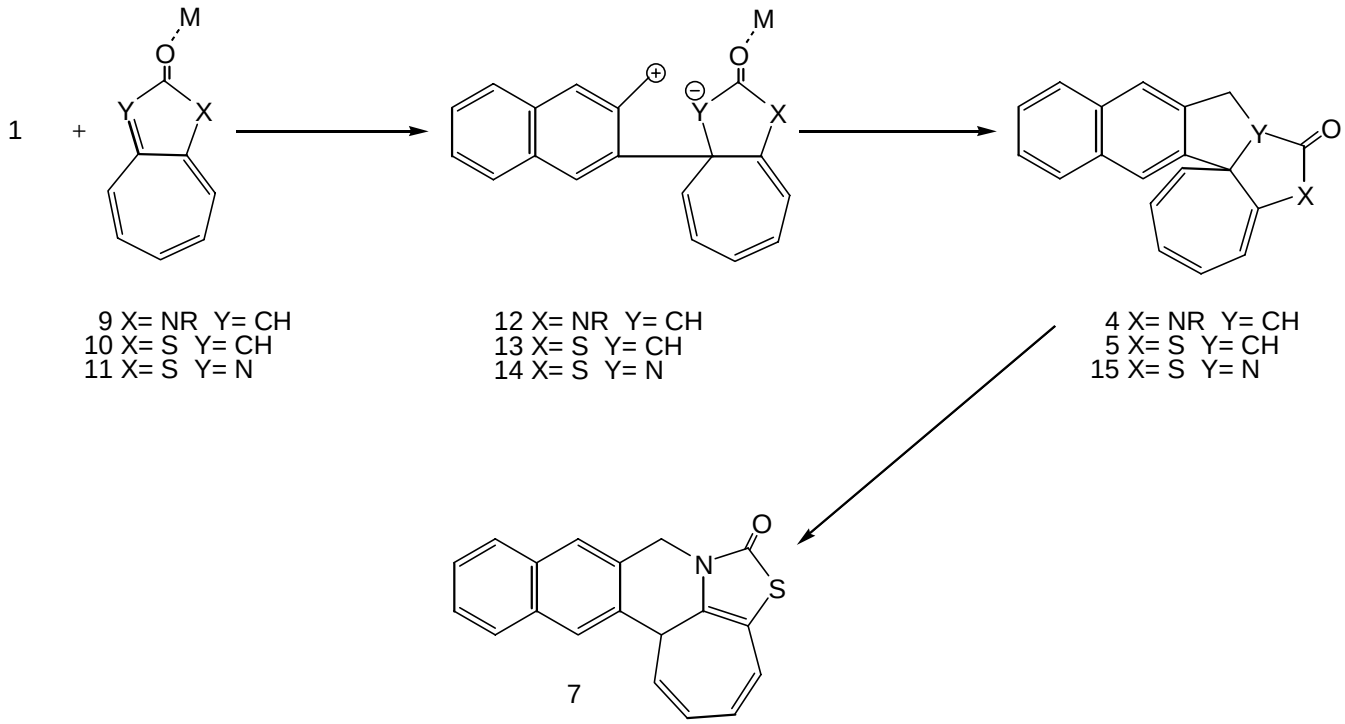


Figure 2

The electron densities were calculated on the essential frameworks corresponding to **1**, **2**, and **6** with PM3 method were shown in the Figure 2 as A, B, and C, respectively. The bridgehead carbon atoms at 3a position of B and C were charged positively.

Considering the activation effect of the ytterbium complex coordinated to the carbonyl group, the reaction mechanism of 1 with 2,3, and 6 are considered to be as follows.



Coordinations of the ytterbium complex to the carbonyl groups of **2**, **3**,and **6** generate the complexes (**9**, **10**, and **11**), respectively. Considering the nucleophilic nature of the bridgehead carbon atoms of **1**, the ionic intermediates (**12**, **13**, and **14**) are thought to be the initial products of the reactions of **1** and the azulene-2(1*H*)-one, respectively. The subsequent ring formation in **12** and **13** can afford the final products **4** and **5**, respectively.

Figure 3 shows a Hammett's plot of the yields of **4** against the substituents on the phenyl group. The electron withdrawing groups seem to give better yields supporting the nucleophilic attack of **1**.

The corresponding ring formation in the ionic intermediate (**14**) forms a cyclic compound (**15**), which is analogous to **4** and **5**. However, under the reaction conditions, **15** seems further to rearrange to form **7**. The driving force of this rearrangement is considered to be a release of the strain energy owing to the spiro-ring in **15** and a construction of a longer conjugation system comparing to that in **15**.

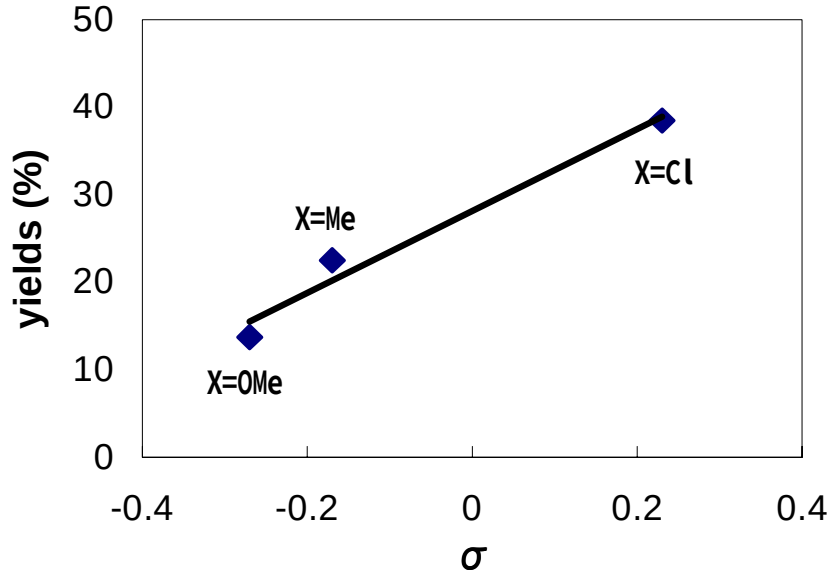
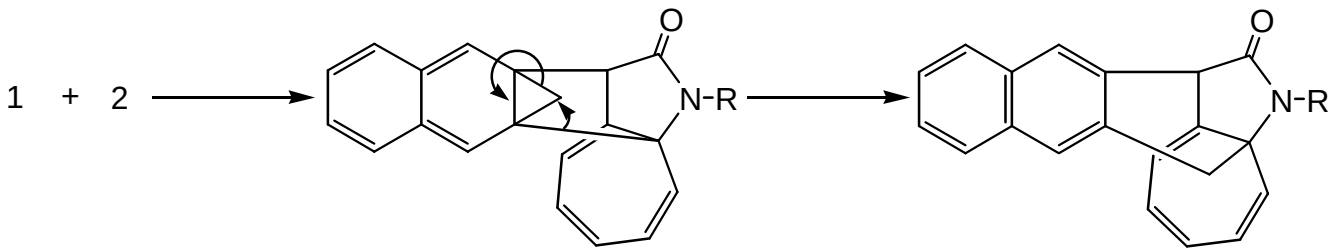


Figure 3. Hammett plot of Hammett's sigma values (σ) vs. yields of 4

The non-polarity of benzene used as the solvent seems to suggest a concerted process for the reaction of 1 and 2 in benzene.[7] An [8π + 2σ] type concerted cycloaddition of 1 and 2 generates an intermediate (16), which then rearranges to form the final product (8), recovering the stability of the aromatic naphthalene moiety.



16 8

Tables 3 and 4 show the orbital energies and the orbital coefficients of HOMO and LUMO of 1 and 2, calculated by PM3 method, respectively.

Table 3. HOMO,LUMO energies and coefficients of 1

	HOMO			LUMO		
	energy (eV)	C_{7a} coefficient	C_{1a} coefficient	energy (eV)	C_{7a} Coefficient	C_{1a} coefficient
1	-8.99	0.296	-0.296	-0.341	-0.280,	-0.280

Table 4. HOMO,LUMO energies and coefficients of 2a-c

	HOMO			LUMO		
	energy (eV)	C_3 Coefficient	C_{8a} coefficient	energy (eV)	C_3 Coefficient	C_{8a} coefficient
2a(Me)	-8.32	-0.422	0.306	-0.983	0.390	-0.345
2b(OMe)	-8.31	-0.414	0.301	-0.978	-0.391	0.345
2c(Cl)	-8.42	0.426	-0.308	-1.08	-0.389	0.345

Figure 4 demonstrates the interactions of the frontier orbital of 1 and 2. The part A in the Figure 4 shows an interaction between the HOMO of 1 and the LUMO of 2, and the part B shows the opposite combination. In the part A, the interactions between the lobes of the molecular orbital at the reaction points are bonding. However in the part B, the corresponding interactions are antibonding. Thus the reaction is considered to proceed through the interaction of the part A.

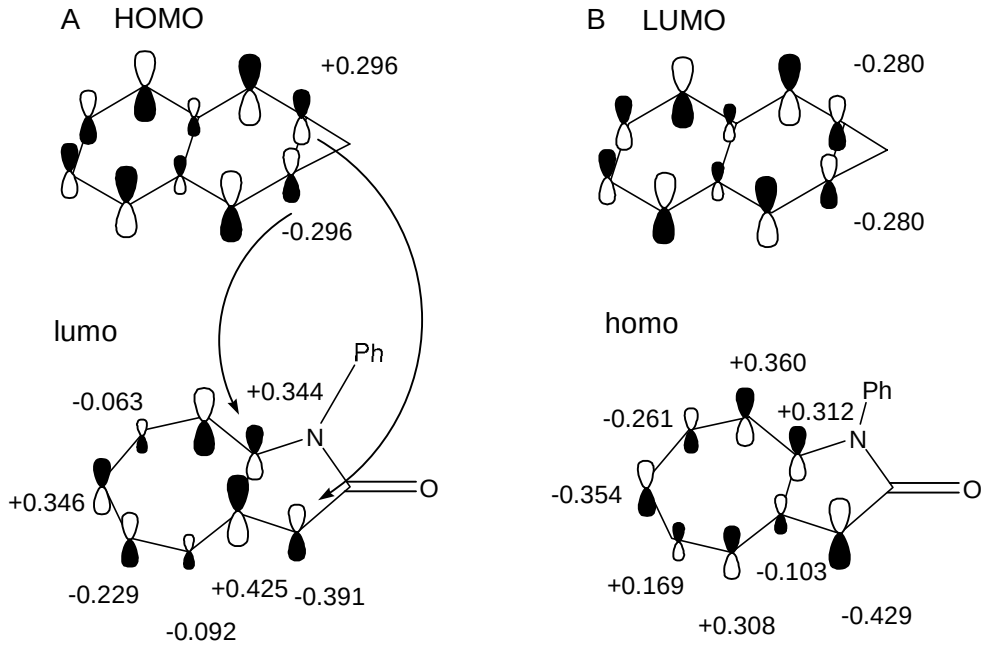


Figure 4

ACKNOLEDGMEMENT

The authors are indebted to Prof. Hideki Masuda of Nagoya institute of technology for his measurement of single crystal X-Ray analysis of the compound (7).

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3. C. Wontrup, C. Mayer, J. Becker, and H. J. Lindler, *Tetrahedron.,* 1985, **41**, 1601.
4. R. Neidlein and Bettina Kr mer, *Chem. Ber.*, 1991, **124**, 353.
5. The physical properties of the products are as follow.

4a: MS m/z (rel intensity)：375 (M^+, 100), 346 (42), 330 (6), 242 (80). IR (KBr) ：3029, 2920, 1726, 1640, 1559, 1512, 1437, 1250, 1209, 754, 718, 683cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm：2.36 (s, CH_3), 3.40(dd, 1H), 3.58-3.72 (m, 2H), 5.57 (d, H_e), 5.73 (d, H_a), 6.17 (dd, H_b), 6.35 (dd, H_c), 6.39 (dd, H_d), 7.00 (br, 2H), 7.20-7.30 (m, 2H), 7.34-7.45 (m, 2H), 7.64 (s, 1H), 7.70 (d, 1H), 7.75 (d, 1H), 8.00 (s, 1H). Coupling constants in Hz: J_{ab}= 10.0, J_{bc}= 6.7, J_{cd}= 11.1, J_{de}= 7.5. ^{13}C NMR ($CDCl_3$) δ ppm：21.0, 32.6, 55.1, 56.6, 101.9, 122.7, 124.3, 124.8, 125.2, 125.9, 126.7, 127.4, 127.5,127.6,127.9,128.1,128.2,128.3,130.3, 132.1, 133.8, 134.2, 137.5,138.8,145.4,147.8,175.4.

4b: MS m/z (rel intensity): 391 (M^+, 100), 362 (46), 346 (5), 242 (80). IR (KBr) ：3015, 2916, 1725, 1638, 1557, 1510, 1441, 1250, 1209, 752, 716, 681cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm：3.39 (dd, 1H), 3.64-3.82 (m, 2H), 3.80 (s, OCH_3), 5.57 (d, H_e), 5.73 (d, H_a), 6.17 (dd, H_b), 6.24 (dd, H_c), 6.39 (dd, H_d), 6.93 (br d, 2H), 7.03 (br, 2H), 7.36-7.41 (m, 2H), 7.64 (s, 1H), 7.70 (d, 1H), 7.75 (d, 1H), 8.00 (s, 1H). Coupling constants in Hz: J_{ab}= 10.5, J_{bc}= 6.4, J_{cd}= 11.0, J_{de}= 7.5. ^{13}C NMR ($CDCl_3$) δ ppm：32.6, 55.1, 55.5, 56.7, 101.9, 114.9, 122.7, 124.3, 124.8,125.2,125.9,126.7,127.3,127.4,127.5, 128.1, 128.1, 129.0, 133.8, 134.2, 137.4, 145.6, 147.7,159.5,175.4.

4c: MS m/z (rel intensity): 395 (M^+, 100), 366 (29), 330 (7), 242 (80). IR (KBr) ：3019, 2911, 1725, 1638, 1557, 1491, 1437, 1250, 1208, 750, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm：3.40(dd, 1H), 3.58-3.72 (m, 2H), 5.57 (d, H_e), 5.73 (d, H_a), 6.18 (dd, H_b), 6.26 (dd, H_c), 6.39 (dd, H_d), 7.08 (br d, 2H), 7.34-7.44 (m, 4H), 7.64 (s, 1H), 7.70 (d, 1H), 7.75 (d, 1H), 8.00 (s, 1H). Coupling constants in Hz: J_{ab}= 10.5, J_{bc}= 6.6, J_{cd}= 11.1, J_{de}= 7.5. ^{13}C NMR ($CDCl_3$) δ ppm：32.5, 55.2, 56.7, 102.0, 122.7, 124.3, 125.2, 126.0, 126.7, 127.4, 127.5, 127.8,

128.1, 129.3, 129.9, 133.2, 133.7, 134.2, 134.6, 137.3, 144.8, 147.4, 175.4.

5: MS m/z (rel intensity): 302 (M^+, 89), 273 (76), 243 (100). IR (KBr): 3019, 1705, 1609, 1499, 1433, 1069, 874, 754, 677 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 3.48 (dd, H_b), 3.54 (d, H_c), 3.63 (d, H_a), 5.58 (dd, H_d), 6.09 (dd, H_e), 6.33 (dd, H_f), 6.51 (dd, H_g), 6.59 (d, H_h), 7.34-7.40 (m, 2H), 7.61 (s, 1H), 7.66-7.74 (m, 2H), 7.87 (s, 1H). Coupling constants in Hz: J_{ab}= 15.3, J_{bc}= 8.1, J_{de}= 10.5, J_{ef}= 6.3, J_{fg}= 10.8, J_{gh}= 7.5. ^{13}C NMR ($CDCl_3$) δ ppm: 32.8, 61.7, 68.8, 120.9, 122.8, 123.3, 125.4, 126.0, 126.6, 127.1, 127.5, 128.0, 128.1, 128.8, 133.5, 134.2, 136.3, 139.8,145.8,172.4.

7: Calcd for $C_{19}H_{13}NOS$: 75.22; H, 4.32; N, 4.62. MS m/z (rel intensity): 303 (M^+, 100), 274 (37), 243 (68). IR (KBr): 3018, 1661, 1586, 1514, 1464, 1313, 1236, 1154,889,750,644 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 3.38 (d, Hc), 4.89 (d, Ha), 5.27 (d, Hb), 5.33 (dd, Hd), 6.28 (ddd, He), 6.62 (dd, Hf), 6.73 (d, Hg), 7.45-7.52 (m, 2H), 7.75 (s, 1H), 7.78-7.85 (m, 2H), 7.89 (s, 1H). Coupling constants in Hz: J_{ab}= 17.4, J_{cd}= 4.9, J_{de}= 9.5, J_{ef}= 5.7, J_{fg}= 11.2. ^{13}C NMR ($CDCl_3$, 200 MHz) δ ppm: 38.0, 44.5, 109.1, 123.1, 124.6 , 125.5, 126.7, 126.8, 126.8, 127.3, 127.6 , 127.6, 127.8, 128.6, 131.0, 132.6, 133.4, 172.4.

6. The physical properties of the products are as follow.

8a: MS m/z (rel intensity): 375 (M^+, 100), 346 (34), 332 (8), 242 (25). IR (KBr): 3049, 1720, 1626, 1512, 1398, 1267, 1213, 746 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 2.37 (s, CH_3), 3.14 (d, H_a), 3.39 (d, H_b), 4.42 (s, 1H), 5.47 (d, H_c), 5.77 (d, H_g), 6.31 (dd, H_f), 6.38 (dd, H_e), 6.47 (dd, H_d), 7.05 (d, 2H), 7.22 (d, 2H), 7.42 (m, 2H), 7.53 (s, 1H), 7.73 (m, 1H), 7.87 (m, 1H), . 8.15 (s, 1H). Coupling constants in Hz: J_{ab}= 19.4, J_{cd}= 6.6, J_{de}= 10.8, J_{ef}= 6.0, J_{fg}= 9.6. ^{13}C NMR ($CDCl_3$) δ ppm: 21.1, 44.7, 50.3, 60.3, 99.8, 122.4, 123.8, 125.2, 125.3, 125.7, 126.9, 127.1, 127.3, 128.1, 128.3, 128.5, 130.0, 132.2, 133.0, 133.7, 137.0, 138.4, 140.2, 143.9, 174.3.

8b: IR (KBr): 3008, 1714, 1608, 1512, 1298, 1249, 1211, 1030, 748 cm^{-1}. ^1H NMR ($CDCl_3$) δ . ppm: 3.09 (d, H_a), 3.38 (d, H_b), 3.80 (s, OCH_3), 4.42 (s, 1H), 5.46 (d, H_c), 5.77 (d, H_g), 6.30 (dd, H_f), 6.38 (dd, H_e), 6.45 (dd, H_d), 6.92 (d, 2H), 7.07 (d, 2H), 7.42 (m, 2H), 7.54 (s, 1H), 7.76 (m, 1H), 7.87 (m, 1H), 8.17(s, 1H). Coupling constants in Hz: J_{ab}= 15.8, J_{cd}= 6.3, J_{de}= 11.0, J_{ef}= 5.8, J_{fg}= 9.6. ^{13}C NMR ($CDCl_3$) δ ppm: 44.8, 50.3, 55.4, 60.3, 99.7, 114.7, 122.4, 123.8, 125.2, 125.3, 125.7, 126.9, 127.3, 127.4, 128.1, 128.4, 128.5, 133.0, 133.7, 137.0,140.2,144.2,159.3,174.3.

8c: MS m/z (rel intensity): 395 (M^+, 100), 366 (16), 242 (16) 241 (16). IR (KBr): 3018, 1722, 1630, 1535, 1491, 1437, 1246, 1211, 748 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 3.09 (d, H_a), 3.38 (d, H_b), 4.42 (s, 1H), 5.47 (d, H_c), 5.77 (d, H_g), 6.31 (dd, H_f), 6.41 (dd, H_e), 6.48 (dd, H_d),

7.13 (d, 2H),7.40 (d, 2H), 7.44 (m, 2H), 7.54 (s, 1H), 7.78 (m, 1H), 7.87 (m, 1H), 8.14 (s, 1H). Coupling constants in Hz: J_{ab}= 15.8, J_{cd}= 6.6, J_{de}= 11.0, J_{ef}= 5.8, J_{fg}= 9.6. ^{13}C NMR ($CDCl_3$) δ ppm: 44.6, 50.3, 56.7, 60.2, 100.0, 122.4, 122.6, 123.7, 123.8, 125.7, 127.0, 127.3, 127.4, 128.0, 128.3, 128.7, 128.8, 129.6, 133.0, 133.3, 133.7, 134.2 , 136.7, 140.0, 143.1,174.1.

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