

[8+2] Cycloadditions of 2,4,6-Cycloheptatriene-1-imines with Chloroketenes: Facile and High-Yield One-Pot Synthesis of 1-Azaazulen-2(1*H*)-ones

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Simple heating of mixtures of *N*-arylcycloheptatriene-1-imines and acyl chlorides in the presence of an excess amount of triethylamine afforded 1-azaazulen-2(1*H*)-ones in high yields. The intermediacy of the [8+2] cycloadducts between the 2,4,6-cycloheptatriene-1-imines and ketenes were confirmed by their isolations. Analogous results were obtained with tropone hydrazones.

1-Azaazulen-2(1*H*)-one derivatives have attracted the attention of chemists not only regarding their utility as synthetic intermediates for 1-azaazulene derivatives,¹⁾ but also due to their own interesting chemical and physical natures.²⁾ Furthermore, the pharmacological activities of 1-azaazulen-2(1*H*)-ones have allowed pharmacologists to study their chemistry extensively,³⁾ including investigations aimed at improving the synthetic methods concerning them.⁴⁾

2,4,6-Cycloheptatriene-1-imines⁵⁾ are known to draw electrons away from the seven-membered ring part toward the external nitrogen atom, resulting in zwitter ionic forms having dipole moments. Molecular-orbital calculations concerning 2,4,6-cycloheptatriene-1-imines have also indicated the existence of a large dipole momentum (3.7 D, 1 Debye = 3.3356 × 10⁻³⁰ C m) and a large charge density (−0.329) on the nitrogen atom.⁶⁾ Consequently, the nitrogen atoms of 2,4,6-cycloheptatriene-1-imines can easily attack electron-deficient olefins: 2,4,6-cycloheptatriene-1-imines react as 8π-components with active acetylenes and cumulenes to give [8+2]-type cycloadducts and with benzoyl isothiocyanate and diphenylnitrileimine to give [8+4]-type cycloadducts.⁷⁾

As a series of studies concerning the reactivities of tropone hydrazone derivatives,⁸⁾ we attempted to use 2,4,6-cycloheptatriene-1-imines and tropone hydrazones in a new procedure for the synthesis of 1-azaazulen-2(1*H*)-ones. We found that the reactions of 2,4,6-cycloheptatriene-1-imines or tropone hydrazones with chloroketenes gave 1-azaazulen-2(1*H*)-ones in high yields. The results are discussed here.

Results and Discussion

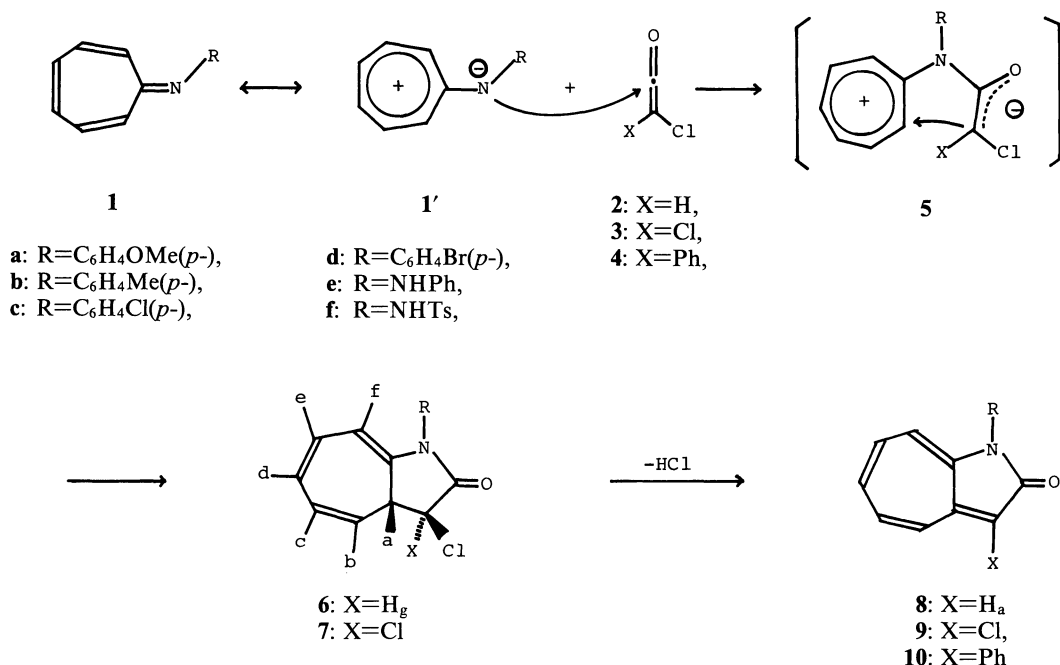
A mixture of *N*-*p*-methoxyphenyl-2,4,6-cycloheptatriene-1-imine (**1a**) and chloroketene (**2**)⁹⁾ in chloroform was heated at 50°C for 72 h in the presence of an excess amount of triethylamine under a nitrogen stream. After the usual workup, the reaction mixtures were separated and purified using column and thin-layer chromatography on silica gel to give 1-*p*-methoxyphenyl-azaazulen-2(1*H*)-one (**8a**) in 73% yield. Under similar

reaction conditions, *N*-*p*-tolyl- (**1b**), *N*-*p*-chlorophenyl- (**1c**), *N*-*p*-bromophenyl- (**1d**) 2,4,6-cycloheptatriene-1-imines and tropone phenylhydrazone (**1e**), tropone tosylhydrazone (**1f**) gave the corresponding 1-azaazulen-2(1*H*)-one derivatives (**8b–f**) in 70–100% yields. Similar reactions using dichloroketene (**3**) and phenylchloroketene (**4**) also gave the corresponding 1-azaazulen-2(1*H*)-ones (**9** and **10**) in 68–100% yields. The intermediates in the formation of 1-azaazulen-2(1*H*)-ones, [8+2]-type cycloadducts (**6** and **7**), could be isolated when the reactions were carried out in the presence of equimolar amounts of the base. The treatments of the [8+2]-type cycloadducts (**6** and **7**) with excess amounts of triethylamine in chloroform at 50°C gave the corresponding 1-azaazulen-2(1*H*)-ones (**8–10**) in quantitative yields. These results are summarized in Table 1.

Table 1. Reaction Conditions and Yields of Products

Iminotropones	Ketenes	Reaction conditions ^{a)}	Products (Yield/%)
1a	2	A	8a (73)
1a	2	B	6a (70), 8a (9)
1b	2	A	8b (75)
1b	2	B	6b (74), 8b (4)
1c	2	A	8c (84)
1c	2	B	6c (76), 8c (10)
1d	2	A	8d (100)
1d	2	B	6d (82), 8d (14)
1d	3	C	9d (100)
1d	4	C	10d (100)
1e	2	A	8e (27)
1e	3	B	9e (68)
1e	4	C	10e (60)
1f	2	A	8f (78)
1f	3	C	7f (23), 9f (72)
1f	4	C	10f (100)

a) A: Mixture of **1**, three equimolar amount of acyl chloride, and excess amount of triethylamine in chloroform was heated at 50°C for 72 h. B: Mixture of **1**, three equimolar amount of acyl chloride, and triethylamine in dry ether was stirred at r. t. for 10 h. C: Mixture of **1**, three equimolar amount of acyl chloride, and excess amount of triethylamine in chloroform was stirred at r. t. for 24–72 h.



Scheme 1.

The structures of **8**, **9**, and **10** were deduced using their spectral properties, and were confirmed by their coincidences to those of the analogous 1-azaazulen-2(1*H*)-ones as follows.^{2,3,4)} The molecular-ion peaks in their high-resolution MS spectra demonstrated that the products were derived from condensation reactions of **1** and ketenes, followed by an elimination of hydrogen chloride. UV spectra showed characteristic patterns¹⁰⁾ as 1-azaazulen-2(1*H*)-ones with maxima at ca. 230, 270, 400, and 415 nm. In the IR spectra, the characteristic absorptions for the carbonyl group of the 1-azaazulen-2(1*H*)-one ring were clearly observed at 1660–1690 cm⁻¹. The ¹H NMR and ¹³C NMR spectra were compatible to the structure of 1-azaazulen-2(1*H*)-ones.

The structures of **6** and **7** were deduced on the basis of their spectral properties as follows. The molecular-ion peaks in their mass spectra demonstrated that the products were 1:1 adducts between **1** and ketenes (**2** or **3**). ¹H NMR and ¹³C NMR spectra indicated the existence of phenyl and 1,7-disubstituted cycloheptatriene moieties.⁷⁾ The assignment of each proton was determined by the use of a double-resonance technique in ¹H NMR spectra. The existence of an amido group was shown by the existence of a strong characteristic absorption band at ca. 1740 cm⁻¹ in the IR spectra.^{7a)} The formation of 1-azaazulen-2(1*H*)-ones (**8**, **9**, **10**) by dehydrochlorinations of **6** and **7** supported the assignment of their structures. The *trans*-configuration between H_a and H_g was confirmed by the coupling constant value (ca. 4 Hz) between these protons.^{7a)}

The reaction is considered to proceed through a nucleophilic attack of the nitrogen atom of **1** to the central

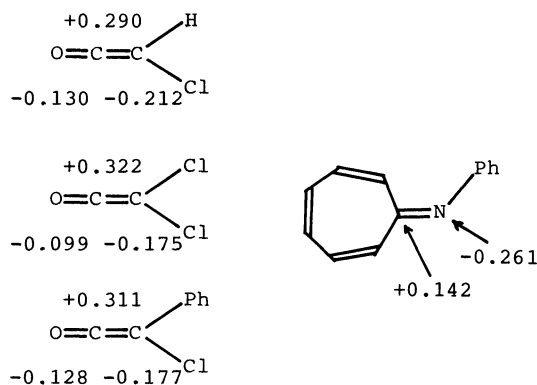


Fig. 1. Values of net atomic charges calculated by MNDO method.

carbon atom of the ketenes to afford an intermediate (**5**), which then cyclizes to give [8+2]-type cycloadducts (**6** and **7**). An analogous reaction mechanism has been proposed by Ciabattini and Cabrion, which concerns the reactions of 2,4,6-cycloheptatriene-1-one and 2,4,6-cycloheptatriene-1-thione, analogues of 2,4,6-cycloheptatriene-1-imine, with chloroketenes to form 2*H*-cyclohepta[*b*]furan-2-one and 2*H*-cyclohepta[*b*]thiophene-2-ones, respectively, via [8+2] cycloadducts, which were not isolated.^{11,12)} The dehydrochlorination of the [8+2]-type cycloadducts (**6** and **7**) by the use of a base afforded 1-azaazulen-2(1*H*)-one derivatives (**8**–**10**).

Molecular orbital calculations¹³⁾ of **1** and chloroketenes using the MNDO method showed the existence of negative charges on the nitrogen atoms of **1** and

positive charges on the central carbon atoms of the ketenes supporting the above mentioned mechanism.

Experimental

The melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and were uncorrected. NMR Spectra were measured with a Hitachi R-90 or a Varian XL-200 spectrometer. IR, UV, and MS spectra were measured with JASCO FT/IR-5300, Hitachi 220A, and Hitachi M-2000S spectrometers, respectively. Wakogel C-200 and Wakogel B5-F were used for column and thin-layer chromatography, respectively.

General Procedure for the Preparation of 8a–d. To a mixture of **1** (0.5 mmol) and triethylamine (3.0 mmol) in chloroform (5 ml) was added a solution of chloroacetyl chloride (1.5 mmol) in chloroform (5 ml) at room temperature under a nitrogen stream. After the addition was completed, the mixture was heated at 50°C for 72 h, poured into water, extracted with dichloromethane, and dried over anhydrous sodium sulfate. After removing the solvent, the residue was chromatographed on silica gel to give **8**.

1-*p*-Methoxyphenyl-1-azaazulen-2(1H)-one (8a): Mp 179–180°C (from ethyl acetate). Found: C, 76.20; H, 5.10; N, 5.60%. Calcd for C₁₆H₁₃NO₂: C, 76.47; H, 5.22; N, 5.57%. MS *m/z* (rel intensity) 251 (M⁺, 57), 236 (23), 178 (40), 165 (44), 156 (95), 149 (100). IR (KBr) 3020, 2950, 1660, 1590, 1550, 1490 cm⁻¹. UV (MeOH) 410 nm (log ε, 3.85), 392 (sh. 3.79), 265 (4.41), 228 (4.29). ¹H NMR (CDCl₃) δ=3.88 (s, Me, 3H), 6.19 (s, H_a), 6.72–7.62 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=55.6, 103.6, 113.0, 114.9, 128.9, 129.6, 131.1, 131.7, 146.1, 159.7, 169.4.

1-*p*-Tolyl-1-azaazulen-2(1H)-one (8b): Mp 116–117°C (from ethyl acetate). Found: C, 81.42; H, 5.48; N, 5.80%. Calcd for C₁₆H₁₃NO: C, 81.68; H, 5.57; N, 5.95%. MS *m/z* (rel intensity) 235 (M⁺, 100), 234 (62), 220 (21), 206 (18), 192 (20), 191 (11), 149 (19). IR (KBr) 3030, 2920, 1680, 1590, 1530, 1520, 1490 cm⁻¹. UV (MeOH) 411 nm (log ε, 3.88), 392 (sh. 3.83), 264 (4.45), 220 (4.21). ¹H NMR (CDCl₃) δ=2.48 (s, Me, 3H), 6.20 (s, H_a), 6.74–7.64 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=21.3, 103.6, 113.0, 128.3, 128.8, 128.9, 130.2, 131.1, 131.7, 138.8, 146.1, 169.3.

1-*p*-Chlorophenyl-1-azaazulen-2(1H)-one (8c): Mp 174–177°C (from ethyl acetate). Found: C, 70.32; H, 3.84; N, 5.43%. Calcd for C₁₅H₁₀NOCl: C, 70.46; H, 3.94; N, 5.48%. MS *m/z* (rel intensity) 255 (M⁺, 100), 254 (53), 226 (14), 220 (15), 192 (35), 167 (24), 149 (46). IR (KBr) 3030, 2920, 1680, 1590, 1540, 1490 cm⁻¹. UV (MeOH) 410 nm (log ε, 3.81), 391 (sh. 3.77), 264 (4.39), 221 (4.19). ¹H NMR (CDCl₃) δ=6.20 (s, H_a), 6.70–7.65 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=103.7, 112.9, 129.1, 129.3, 129.8, 131.1, 132.0, 134.7, 146.5, 165.6.

1-*p*-Bromophenyl-1-azaazulen-2(1H)-one (8d): Mp 192–193°C (from ethyl acetate). Found: C, 59.86; H, 3.30; N, 4.52%. Calcd for C₁₅H₁₀NO: C, 60.02; H, 3.36; N, 4.67%. MS *m/z* (rel intensity) 300 (M⁺, 24), 299 (100), 279 (8), 220 (15), 219 (14), 192 (46). IR (KBr) 3030, 2920, 1680, 1590, 1540, 1500 cm⁻¹. UV (MeOH) 407 nm (log ε, 3.80), 398 (sh. 3.76), 266 (4.37), 229 (4.19). ¹H NMR (CDCl₃) δ=6.20 (s, H_a), 6.70–7.80 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=103.7, 112.9, 129.1, 129.3, 130.2, 131.1, 132.0, 132.8, 133.3, 146.5.

General Procedure of the Preparation of 8e, 8f, 9d–f, and 10d–f. To a solution of **1** (1.0 mmol) and triethylamine (6.0 mmol) in chloroform (5 ml) was added a solution of acyl chloride (3.0 mmol) in chloroform (5 ml) at room temperature under a nitrogen stream. After the addition was completed, the mixture was stirred at room temperature for 24–72 h. The usual reaction-mixture treatment gave the corresponding 1-azaazulen-2(1H)-ones.

1-Anilino-1-azaazulen-2(1H)-one (8e): Mp 256–257°C (decomp) (from ethyl acetate). Found: C, 75.95; H, 4.90; N, 11.61%. Calcd for C₁₅H₁₂N₂O: C, 76.25; H, 5.12; N, 11.86%. MS *m/z* (rel intensity) 236 (M⁺, 56), 202 (36), 145 (22), 129 (47), 117 (100). IR (KBr) 3020, 2950, 1660, 1600, 1530, 1490 cm⁻¹. UV (MeOH) 408 nm (log ε, 3.81), 399 (3.79), 262 (4.49), 234 (4.29). ¹H NMR (CDCl₃) δ=6.21 (s, H_a), 6.55–7.66 (m, olefin and phenyl protons, 10H). ¹³C NMR (CDCl₃) δ=102.0, 112.8, 113.6, 122.0, 129.4, 129.7, 129.8, 131.5, 132.1, 141.6, 141.9.

1-Tosylamino-1-azaazulen-2(1H)-one (8f): Mp 197–198°C (from ethyl acetate). High-resolution MS *m/z* 314.0731. Calcd for C₁₆H₁₄N₂O₃S: M, 314.0724. MS *m/z* (rel intensity) 314 (M⁺, 22), 160 (13), 109 (100), 103 (15). IR (KBr) 3020, 2950, 1680, 1600, 1540, 1490 cm⁻¹. UV (MeOH) 409 nm (log ε, 3.82), 391 (3.82), 265 (4.73), 231 (4.32). ¹H NMR (CDCl₃) δ=2.40 (s, Me, 3H), 5.91 (s, H_a), 7.00–7.72 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=21.8, 100.0, 115.3, 128.5, 129.6, 130.1, 130.8, 132.1, 132.8, 134.0, 145.1, 145.3, 164.8.

3-Chloro-1-*p*-bromophenyl-1-azaazulen-2(1H)-one (9d): Mp 257–258°C (from dichloromethane–hexane). Found: C, 53.96; H, 2.61; N, 4.15%. Calcd for C₁₅H₉NOClBr: C, 53.85; H, 2.71; N, 4.19%. MS *m/z* (rel intensity) 335 (M⁺, 100), 334 (50), 333 (M⁺, 78), 254 (22), 253 (25), 190 (37). IR (KBr) 3030, 2920, 1690, 1590, 1540, 1490 cm⁻¹. UV (MeOH) 419 nm (log ε, 3.95), 405 (3.91), 275 (4.47), 228 (4.32). ¹H NMR (CDCl₃) δ=6.70–7.80 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=113.4, 126.3, 129.9, 130.1, 131.4, 132.5, 132.9.

1-Anilino-3-chloro-1-azaazulen-2(1H)-one (9e): Mp 242–243°C (from ethyl acetate). Found: C, 66.26; H, 4.09; N, 9.95%. Calcd for C₁₅H₁₁N₂OCl: C, 66.55; H, 4.10; N, 10.35%. MS *m/z* (rel intensity) 270 (M⁺, 100), 179 (36), 150 (29). IR (KBr) 3000, 1660, 1600, 1550, 1500 cm⁻¹. UV (MeOH) 419 nm (log ε, 3.81), 396 (3.76), 268 (4.43), 230 (4.28). ¹H NMR (CDCl₃) δ=6.40–7.70 (m, olefin and benzene ring protons, 10H). ¹³C NMR (CDCl₃) δ=113.3, 113.7, 122.3, 126.7, 129.4, 130.4, 131.8, 132.6, 137.5, 142.2, 145.9.

3-Chloro-1-*N*-tosylamino-1-azaazulen-2(1H)-one (9f): Mp 210–213°C (from ethyl acetate). High-resolution MS *m/z* 348.0345. Calcd for C₁₆H₁₃N₂O₃SCl: M, 348.0335. MS *m/z* (rel intensity) 348 (M⁺, 31), 219 (31), 193 (100). IR (KBr) 2950, 1690, 1580, 1480, 1370, 1210, 1160 cm⁻¹. UV (MeOH) 416 nm (log ε, 3.78), 394 (3.77), 272 (4.34), 231 (4.27). ¹H NMR (CDCl₃) δ=2.48 (s, Me, 3H), 7.05–8.20 (m, olefin and benzene ring protons, 9H). ¹³C NMR (CDCl₃) δ=21.8, 115.3, 127.7, 129.5, 130.7, 132.2, 132.5, 134.7.

1-*p*-Bromophenyl-3-phenyl-1-azaazulen-2(1H)-one (10d): Mp 224–225°C (from dichloromethane–hexane). Found: C, 66.98; H, 3.83; N, 3.72%. Calcd for C₂₁H₁₄NOBr: C, 67.04; H, 3.75; N, 3.72%. MS *m/z* (rel intensity) 377 (M⁺, 100), 375 (M⁺, 100), 267 (25), 165 (63), 129 (70). IR (KBr) 3030, 2940, 1660, 1590, 1540, 1490 cm⁻¹. UV (MeOH) 419 nm (log ε, 3.90), 288 (4.26), 241 (4.34). ¹H NMR (CDCl₃) δ=6.70–7.90 (m, olefin

and benzene ring protons, 14H). ^{13}C NMR (CDCl_3) δ =112.7, 127.4, 127.5, 128.6, 129.1, 129.8, 130.3, 131.2, 132.0, 132.7.

1-Anilino-3-phenyl-1-azaazulen-2(1H)-one (10e): Mp 274–275°C (from dichloromethane). Found: C, 80.55; H, 5.06; N, 8.83%. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$: C, 80.75; H, 5.16; N, 8.97%. MS m/z (rel intensity) 312 (M^+ , 100), 221 (39), 220 (88), 165 (70). IR (KBr) 3030, 2920, 1650, 1600, 1540, 1490 cm^{-1} . UV (MeOH) 422 nm ($\log \epsilon$, 4.10), 284 (4.52), 238 (4.58). ^1H NMR (CDCl_3) δ =6.64–8.05 (m, olefin and benzene ring protons, 15H). ^{13}C NMR (CDCl_3) δ =112.5, 113.9, 122.1, 127.5, 128.5, 128.9, 129.2, 130.2, 131.6, 132.0.

3-Phenyl-1-N-tosylamino-1-azaazulen-2(1H)-one (10f): Mp 238–239°C (from dichloromethane–hexane). High-resolution MS: m/z 390.1057. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: M, 390.1037. MS m/z (rel intensity) 390 (M^+ , 58), 235 (100), 221 (58), 152 (85), 124 (77). IR (KBr) 3030, 2920, 1690, 1600, 1540, 1490 cm^{-1} . UV (MeOH) 416 nm ($\log \epsilon$, 3.76), 277 (4.06), 237 (4.28). ^1H NMR (CDCl_3) δ =2.45 (s, Me, 3H), 6.40–8.20 (m, olefin and benzene ring protons, 14H). ^{13}C NMR (CDCl_3) δ =21.9, 113.4, 127.4, 128.1, 128.3, 128.8, 129.5, 130.7, 131.0, 131.2, 131.9, 132.0, 133.5.

General Procedure for the Isolation of 6 and 7. To a mixture of **1** (2.2 mmol) and triethylamine (8.0 mmol) in dry ether (10 ml) was added a solution of acyl chloride (8.0 mmol) in dry ether (5 ml) at room temperature under a nitrogen stream. After the addition was completed, the mixture was stirred at room temperature for 10 h. The usual treatment of the reaction mixture gave **6** or **7**.

6a: Mp 133–135°C (decomp) (from methanol). High-resolution MS: m/z 287.0721. Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2\text{Cl}$: M, 287.0712. MS m/z (rel intensity) 287 (M^+ , 34), 253 (16), 252 (100), 209 (4), 133 (33). IR (KBr) 3020, 2950, 1740, 1640, 1600, 1550, 1490 cm^{-1} . UV (MeOH) 315 nm ($\log \epsilon$, 3.70), 250 (3.77), 221 (4.32). ^1H NMR (C_6D_6) δ =3.21 (s, Me, 3H), 3.23 (m, H_a), 4.28 (d, H_g), 4.70 (dd, H_b), 5.29 (d, H_f), 5.95 (ddm, H_c), 6.04–6.22 (m, $\text{H}_{d,e}$, 2H), 6.60–7.00 (m, benzene ring protons, 4H). Coupling constants in Hz: J_{ab} =4.0, J_{ag} =4.2, J_{bc} =9.5, J_{cd} =5.7, J_{ef} =6.2. ^{13}C NMR (CDCl_3) δ =46.2, 55.5, 57.8, 101.2, 115.0, 115.3, 121.1, 126.0, 128.3, 128.6, 170.7.

6b: Mp 132–134°C (decomp) (from methanol). High-resolution MS: m/z 271.0762. Calcd for $\text{C}_{16}\text{H}_{14}\text{NOCl}$: M, 271.0763. MS m/z (rel intensity) 271 (M^+ , 16), 237 (5), 236 (100), 149 (23), 129 (20). IR (KBr) 3020, 2920, 1740, 1640, 1620, 1550, 1510 cm^{-1} . UV (MeOH) 318 nm ($\log \epsilon$, 3.66), 255 (sh. 3.64), 214 (4.26). ^1H NMR (C_6D_6) δ =2.00 (s, Me, 3H), 3.20 (m, H_a), 4.25 (d, H_g), 4.68 (dd, H_b), 5.29 (d, H_f), 5.94 (ddm, H_c), 6.03–6.20 (m, $\text{H}_{d,e}$, 2H), 6.80–7.00 (m, benzene ring protons, 4H). Coupling constants in Hz: J_{ab} =3.9, J_{ag} =4.3, J_{bc} =9.1, J_{cd} =5.5, J_{ef} =5.8. ^{13}C NMR (CDCl_3) δ =21.2, 46.3, 57.8, 101.2, 121.1, 126.0, 126.8, 128.6, 129.3, 130.4, 170.7.

6c: Mp 156–158°C (decomp) (from methanol). High-resolution MS: m/z 291.0209. Calcd for $\text{C}_{15}\text{H}_{11}\text{NOCl}$: M, 291.0216. MS m/z (rel intensity) 291 (M^+ , 1), 258 (9), 256 (100), 228 (2), 149 (5). IR (KBr) 3030, 2920, 1740, 1640, 1550, 1500, 1490 cm^{-1} . UV (MeOH) 310 nm ($\log \epsilon$, 3.70), 281 (3.73), 220 (4.75). ^1H NMR (C_6D_6) δ =3.10 (m, H_a), 4.17 (d, H_g), 4.61 (dd, H_b), 5.06 (d, H_f), 5.94 (ddm, H_c), 6.02–6.16 (m, $\text{H}_{d,e}$, 2H), 6.60–7.02 (m, benzene ring protons, 4H). Coupling constants in Hz: J_{ab} =4.2, J_{ag} =4.0, J_{bc} =9.6, J_{cd} =5.7, J_{ef} =5.5. ^{13}C NMR (CDCl_3) δ =46.2, 57.5, 101.3, 121.1, 126.4, 128.4, 129.1, 130.0, 170.3.

6d: Mp 162–164°C (decomp) (from methanol). High-

resolution MS: m/z 334.9699. Calcd for $\text{C}_{15}\text{H}_{11}\text{NOClBr}$: M, 334.9712. MS m/z (rel intensity) 335 (M^+ , 15), 302 (100), 300 (97), 220 (5), 192 (13), 149 (76). IR (KBr) 3020, 2920, 1740, 1640, 1620, 1550, 1490 cm^{-1} . UV (MeOH) 310 nm ($\log \epsilon$, 3.90), 273 (3.92), 220 (4.59). ^1H NMR (C_6D_6) δ =3.10 (m, H_a), 4.17 (d, H_g), 4.62 (dd, H_b), 5.06 (d, H_f), 5.94 (ddm, H_c), 6.02–6.18 (m, $\text{H}_{d,e}$, 2H), 6.52–7.00 (m, benzene ring protons, 4H). Coupling constants in Hz: J_{ab} =4.2, J_{ag} =4.1, J_{bc} =9.5, J_{cd} =6.6, J_{ef} =5.6. ^{13}C NMR (CDCl_3) δ =46.2, 57.5, 101.4, 121.1, 126.5, 128.7, 129.1, 129.2, 133.0, 171.4.

7f: Mp 191–193°C (from ethyl acetate). High-resolution MS: m/z 384.0084. Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$: M, 384.0102. MS m/z (rel intensity) 384 (M^+ , 1), 336 (100), 176 (63). IR (KBr) 3200, 3000, 1720, 1650, 1600, 1360, 1170 cm^{-1} . ^1H NMR (CDCl_3) δ =2.45 (s, Me, 3H), 3.60 (bs, H_a), 5.54 (bs, H_b), 6.20–6.60 (m, H_c , H_d , H_e , H_f , 4H), 7.20–7.90 (m, benzene ring protons, 4H).

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