

**A CONVENIENT, ONE-POT AZULENE SYNTHESIS FROM CYCLOHEPTA-
[b]FURAN-2-ONES AND VINYL ETHER AND ITS ANALOGUES. (I)
VINYL ETHYL ETHER, VINYL ACETATES, DIHYDROFURANS, AND
DIHYDROPYRANS AS REAGENT¹**

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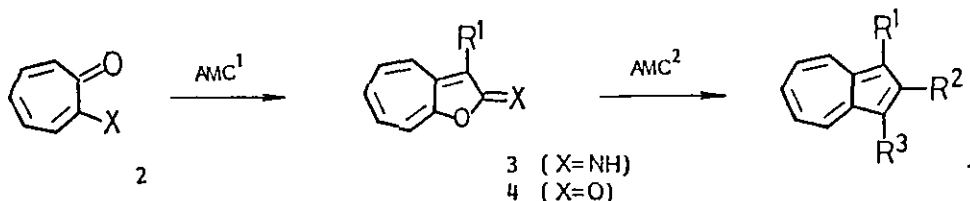
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Abstract - Various functionalized azulene derivatives (more than 40) were synthesized in one-pot and in good yields by the reaction of cyclohepta[b]furan-2-one derivatives with vinyl ethyl ether, vinyl acetate, isopropenyl acetate, dihydropyrans, and dihydrofurans on heating at 160-190 °C in aprotic solvent. Structures of formal cycloadducts in two cases were determined, and a possible pathway of the reaction is discussed.

In 1955, Ziegler and Hafner^{2a} reported the novel azulene synthesis from Zincke's aldehyde and cyclopentadiene, and the method was further developed mainly by Hafner and his coworkers.^{2b} Simultaneously, one of the authors (T.N.) and his coworkers^{3a} found a one-pot synthesis of trisubstituted azulenes (1) starting from a reactive troponoid (2, X=OMe, Cl or OTs and its alkyl derivatives) and active methylene compounds (AMC: malononitril, cyanoacetate, etc.), and this method was also further widened^{3b} by using the reaction of cyclohepta[b]furan-2-imines (3,^{4a} X=NH) and -2-ones (4,^{4b} X=O) with various AMC to afford polysubstituted azulenes (1, R¹=R³=CN, COCH₃, CO₂Et etc., R²=NH₂ or OH etc.).



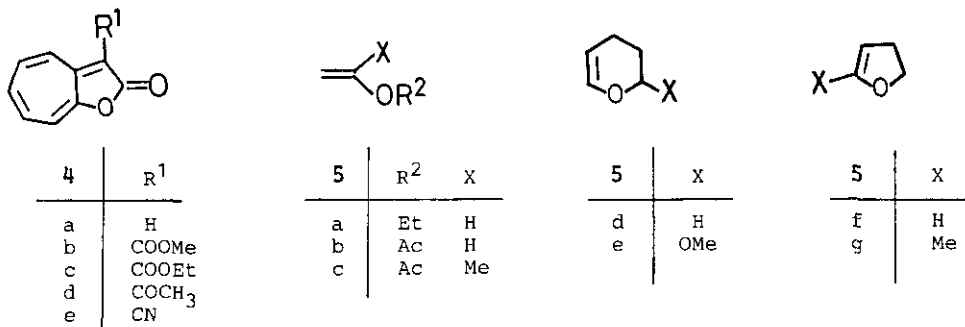
Meanwhile, one of the authors (P.-W. Y.), Yasunami, and Takase^{5a} developed another azulene synthesis, starting from the same furanones (4, X=O) and enamines or their

precursors (aldehydes in the presence of morpholine), and they obtained various azulenes, including polycyclic azulenic hydrocarbons and heterocycle-annulated azulenes.^{5b,6} All of these methods have general wide applications and variously functionalized azulenes have now become very easily available.

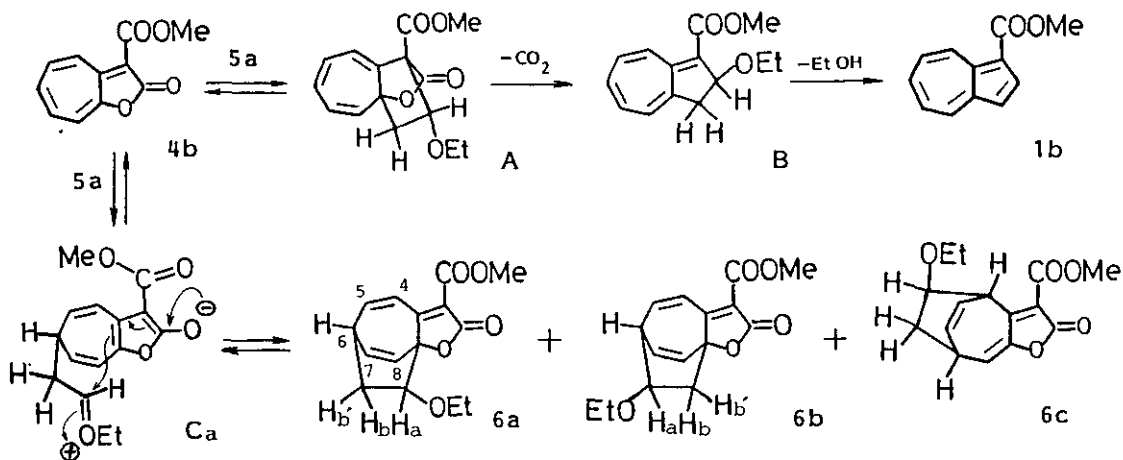
More recently, Daub et al.⁷ reported a synthesis of variously polysubstituted tetrahydroazulene derivatives from 8-methoxyheptafulvenes by the Diels-Alder reaction, which could be easily led to azulenes by DDQ dehydrogenation.

We would now like to describe in this communication another type of a facile one-pot synthesis of variously functionalized azulenes, several of which are very difficult to obtain by any of the known methods.

Generally, cyclohepta[b]furan-2-ones (**4a-e**) were heated with 3-5 equivalents of a reagent [vinyl ether (**5a**), vinyl acetates (**5b,c**) or their cyclic analogues (**5d-g**)] in an aprotic solvent (tetrahydrofuran, acetonitrile, toluene or neat) at 160-190 °C in a Pyrex sealed tube for 20-40 h. After evaporation of the solvent and

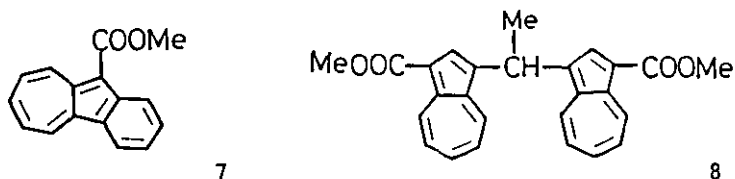


excess reagent, the products were easily separated by silica gel column chromatography (benzene as an eluant) into yellow starting material (**4**), colorless adducts (**6**) and deep-colored azulenes (**1**). Suitable reaction conditions for each reaction were decided by the time-dependent hplc, which showed the formation of several colorless products prior to or along with azulenes (**1**). On continued heating of **4**



Scheme 1.

with an excess reagent at high temperature, especially in a neat state, several minor azulenes were formed as the secondary products, and some alkoxy exchange reactions were also observed between the substrate, azulene and reagent. An example of synthetic procedure is shown below: Upon heating **4b** (0.57 g, 2.8 mmol) and **5a** (1.3 g, 18 mmol) in toluene (0.3 ml) in a sealed tube at 160 °C for 40 h afforded methyl azulene-1-carboxylate (**1b**,⁸ 350 mg, 67%), **6** (150 mg, 20%) as a colorless oil, recovered **4b** (50 mg, 8%), and small amounts of methyl benzo[b]azulene-5-carboxylate (**7**)⁹ and the diazulenylethane derivative **8**.¹⁰ The former (**7**) is presumably produced from three moles of the reagent **5a**, while



the latter **8** is obviously produced from **1b** and acetaldehyde derived from the reagent **5a**.

As azulenes are produced in this reaction only in aprotic solvent at high temperature (and almost no azulenes are formed in alcohol), this azulene formation reaction is believed to proceed via [8+2]cycloadduct (**A**) between the electron deficient polyenoid **4b** and the electron excess polyenophile **5a**, followed by eliminations of CO₂ and ethanol from **B** (Scheme 1).

Colorless products **6**¹¹ were purified by silica gel tlc and their structures were determined on the basis of elemental analysis, CIMS and ¹H nmr as a mixture of three isomeric adducts **6a-c** (C₁₅H₁₆O₅). Structures of two of them were assigned to be formal [4+2]cycloadducts **6a** and **6b** by comparing with ¹H nmr of known [4+2] adduct **10**¹² of dimethylfulvene and **4b**, while the third isomer was presumed to be **6c** (Scheme 1). The toluene solution of the cycloadducts **6a-c** did not produce any azulene on heating at 180 °C, but gave about a 60% yield of azulene **1b** in the presence of an excess (5 mol) of reagent **5a**.

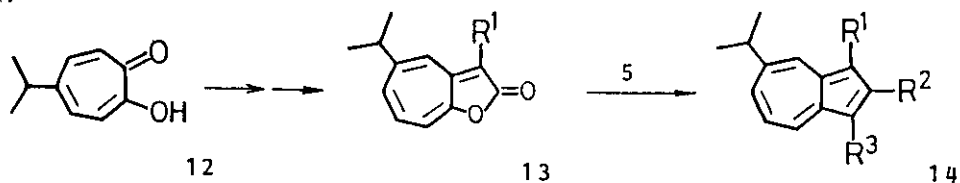
Reaction of **4b** and vinyl acetate (**5b**) afforded the azulene derivative (**1b**) only in 10% yield besides a large amount (80%) of the adduct **11**,¹³ and some unidentified resinous product, and **11** did not give any azulene on heating with the excess reagent.

Therefore we assume that these stable formal cycloadducts **6a-c** are formed via Michael adduct **Ca** and its isomer with subsequent ring closure, and compete with [8+2]cycloadduct **A** that is easily converted into azulenes. We have often

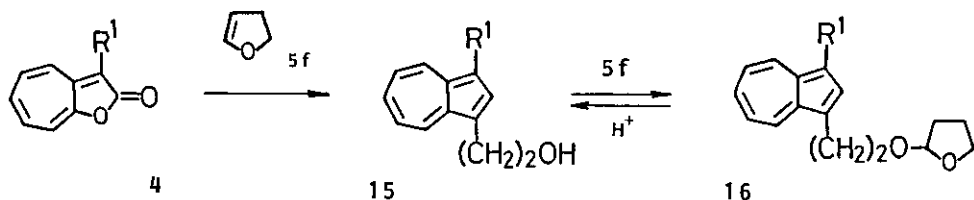


experienced¹⁴ that cyclohepta[b]furan-2-ones afford very easily reversible Michael adducts (mostly at C-6 and C-4) with an active methylene compound as nucleophile prior to azulene formation by the attack of the reagent at C-8a. In this connection, our formal cycloadducts (6) are different from usual concerted [4+2] cycloadduct as referred to by Tian et al.¹⁵ Moreover, the structure of our adducts 6a and 11 is different from those to be anticipated for concerted [4+2] cycloaddition.

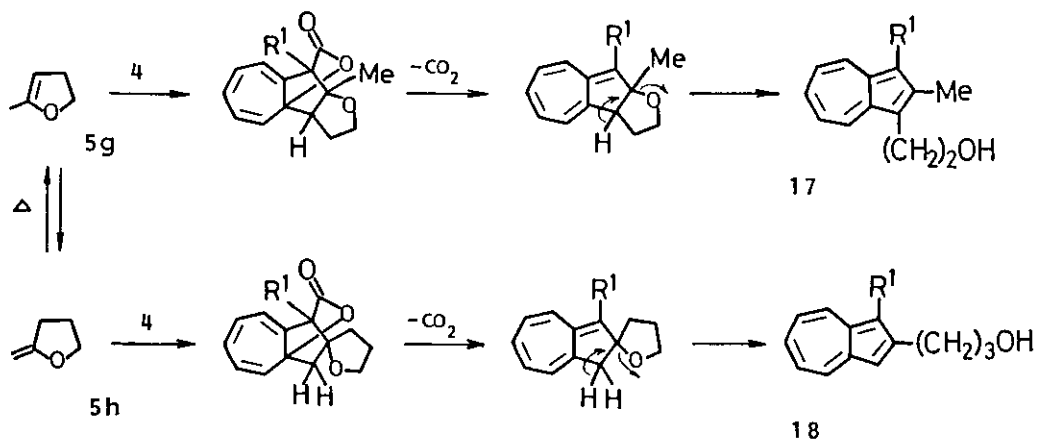
Only 41% of azulene itself (1a) was isolated by the reaction of 4a and 5a, because 1a once formed seems to be further attacked by the reagent to form several green-colored oligomeric compounds as observed by hplc and tlc. Reaction of cyano compound 4e and isopropenyl acetate 5c gave 3-cyano-2-methylazulene (1h) in 60% yield.



Azulene derivatives 14 having an isopropyl group on the seven-membered ring were prepared from γ -thujaplicin (12) via 5-isopropylcyclohepta[b]furan-2-ones (13).



As an extension of the above-mentioned synthesis, we used dihydrofurans (5f,g) and dihydropyrans (5d,e) as reagent, and variously functionalized azulenes were obtained in excellent yields. Azulenes having a primary hydroxyl group (e.g. 15)



Scheme 2.

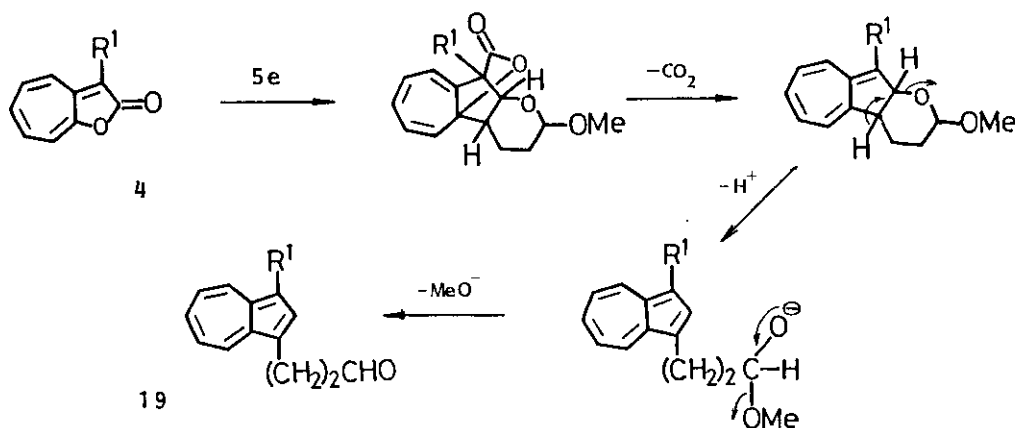
Table. 1 Synthesis of Azulene Derivatives by the Reaction of 4 with 5.

Furanone	Reagent	Azulene			Color Form	mp (°C)	Yield (%)	
		R ¹	R ²	R ³				
4a	5a	1a	H	H	blue violet needles	96-97	41	
4b	5a	1b	COOMe	H	violet oil		74	
4d	5a	1d	COMe	H	violet oil		81	
4e	5a	1e	CN	H	blue violet needles	50-51	63	
4a	5b	1a	H	H	blue violet needles	96-97	14	
4b	5b	1b	COOMe	H	violet oil		10	
4c	5b	1c	COOEt	H	violet oil		18	
4d	5b	1d	COMe	H	violet oil		34	
4e	5b	1e	CN	H	blue violet needles	50-51	11	
4c	5c	1f	COOEt	Me	violet oil		11	
4d	5c	1g	COMe	Me	violet oil		16	
4e	5c	1h	CN	Me	violet needle	109-110	60	
4a	5d	15a	H	H	(CH ₂) ₃ OH	blue oil	19	
4c	5d	15b	COOEt	H	(CH ₂) ₃ OH	blue violet oil	61	
4d	5d	15c ¹⁷	COMe	H	(CH ₂) ₃ OH	violet oil	46	
4e	5d	15d	CN	H	(CH ₂) ₃ OH	blue oil	68	
4a	5f	15e	H	H	(CH ₂) ₂ OH	violet oil	65	
4b	5f	15f ¹⁸	COOMe	H	(CH ₂) ₂ OH	violet oil	62	
4d	5f	15g	COMe	H	(CH ₂) ₂ OH	red violet oil	36	
4e	5f	15h	CN	H	(CH ₂) ₂ OH	violet oil	90	
4a	5g	17a ¹⁹	H	Me	(CH ₂) ₂ OH	blue oil	12	
		18a ²⁰	H	(CH ₂) ₃ OH	H	blue needles	64-65	12
4c	5g	17b	COOEt	Me	(CH ₂) ₂ OH	blue violet needles	76-77	45
		18b	COOEt	(CH ₂) ₃ OH	H	blue violet oil		45
4d	5g	17c	COMe	Me	(CH ₂) ₂ OH	violet oil		54
		18c	COMe	(CH ₂) ₃ OH	H	violet oil		43
4e	5g	17d	CN	Me	(CH ₂) ₂ OH	blue needles	113-114	27
		18d	CN	(CH ₂) ₃ OH	H	violet needles	80-80.5	40
4c	5e	19a	COOEt	H	(CH ₂) ₂ CHO	violet oil		30
4d	5e	19b	COMe	H	(CH ₂) ₂ CHO	red violet oil		25
4e	5e	19c ²¹	CN	H	(CH ₂) ₂ CHO	blue violet needles	87-88	78
13b	5a	14a	COOMe	H	H	blue violet oil		44
13d	5a	14b	COMe	H	H	blue violet oil		51
13e	5a	14c	CN	H	H	blue violet oil		56
13b	5g	14d	COOMe	Me	(CH ₂) ₂ OH	blue violet oil		30
		14e	COOMe	(CH ₂) ₃ OH	H	blue violet needles	43-44	46
13d	5g	14f ²²	COMe	Me	(CH ₂) ₂ OH	blue violet needles	87-88	38
		14g	COMe	(CH ₂) ₃ OH	H	red violet oil		37
13e	5g	14h	CN	Me	(CH ₂) ₂ OH	blue violet oil		34
		14i	CN	(CH ₂) ₃ OH	H	red violet oil		39

on a side chain instantly combine with the reagents (5d,f) to give e.g. 16, which however is easily hydrolyzed to the free alcohol by adding a trace amount of acid (e.g. p-toluenesulfonic acid).

Reaction of 2-methyldihydrofuran (5g) and 4 afforded two isomeric azulenes (17 and 18), because 5g becomes an equilibrium mixture with 5h at high temperature¹⁶ (Scheme 2).

Reaction of 2-methoxydihydropyran (5e) with 4 afforded directly azulenes 19 having a formyl group on a side chain (Scheme 3).



Scheme 3.

Cyclohepta[b]furan-2-one derivatives (4d,e) having an acetyl or cyano group at C-3 position easily give azulene derivatives, and the rate of the reaction and yields of azulenes were approximately in the order of H < CO₂Me < COCH₃ < CN. Yields, structures and properties of various azulenes synthesized by this method are summarized in Table 1.

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- 9) 7: ^1H Nmr (270MHz, CDCl_3) δ =4.08 (3H, s, CH_3), 7.50 (2H, m, H-7,9), 7.54 (1H, td, J=8 and 0.5 Hz, H-2), 7.64 (1H, m, J=11, 8.5, and 1 Hz, H-8), 7.77 (1H, td, J=8 and 0.5 Hz, H-3), 8.43 (1H, td, J=0.5 and 8 Hz, H-1), 8.57 (1H, td, J=0.5 and 8 Hz, H-4), 8.76 (1H, dd, J=8.8 and 1.2 Hz, H-10), and 9.61 (1H, dd, J=11.2 and 1.2 Hz, H-6).
- 10) 8: ^1H Nmr (270MHz, CDCl_3) δ =1.93 (3H, d, J=7.3 Hz, CHCH_3), 3.91 (6H, s, CH_3), 5.31 (1H, q, J=7.3 Hz, CHCH_3), 7.32 (2H, t, J=10 Hz, H-5,5'), 7.49 (2H, t, J=10 Hz, H-7,7'), 7.74 (2H, t, J=10 Hz, H-6,6'), 8.20 (2H, s, H-2,2'), 8.41 (2H, d, J=10 Hz, H-4,4'), and 9.61 (2H, d, J=10 Hz, H-8,8').
- 11) 6a: ^1H Nmr (270MHz, CDCl_3) δ =1.09 (3H, t, J=7 Hz, CH_2CH_3), 1.66 (1H, dd, J=13.4 and 3.1 Hz, H-b'), 2.28 (1H, ddd, J=13.4, 9.6, and 5.5 Hz, H-b), 3.42 (1H, m, H-6), 3.56 (2H, m, CH_2CH_3), 3.89 (3H, s, OMe), 4.14 (1H, dd, J=9.6 and 3.1 Hz, H-a), 6.09 (1H, dd, J=8.8 and 1.0 Hz, H-8), 6.36 (1H, dd, J=8.8 and 7.7 Hz, H-7), 6.97 (1H, dd, J=10.6 and 8.7 Hz, H-5), and 7.26 (1H, dd, J=10.6 and 0.5 Hz, H-4);
- 6b: ^1H Nmr (270MHz, CDCl_3) δ =1.18 (3H, t, J=7 Hz, CH_2CH_3), 1.77 (1H, dd, J=13.1 and 3.8 Hz, H-b'), 2.77 (1H, dd, J=13.1 and 9.4 Hz, H-b), 3.48 (2H, m, CH_2CH_3), 3.84 (1H, m, H-6), 3.88 (3H, s, OMe), 3.95 (1H, m, J=9.4 and 3.8 Hz, H-a), 6.15 (1H, d, J=8.8 Hz, H-8), 6.24 (1H, dd, J=8.8 and 7.1 Hz, H-7), 6.79 (1H, dd, J=10.5 and 9.0 Hz, H-5), 7.33 (1H, d, J=10.5 Hz, H-4).
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- 13) 11: ^1H Nmr (270MHz, CDCl_3) δ =1.59 (1H, ddd, J=14.2, 3.2, and 1 Hz, H-b'), 1.98 (3H, s, COMe), 2.50 (1H, ddd, J=14.2, 10.0, and 5.3 Hz, H-b), 3.46 (1H, m, H-6), 3.91 (3H, s, OMe), 5.41 (1H, dd, J=10.3 and 3.2 Hz, H-a), 6.12 (1H, dd, J=8.6 and 1.5 Hz, H-8), 6.46 (1H, dd, J=8.6 and 7.6 Hz, H-7), 7.00 (1H, dd, J=11.0 and 8.6 Hz, H-5), and 7.29 (1H, dd, J=11.0 and 1.0 Hz, H-4).
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- 17) **15c**: ^1H Nmr (300 MHz, CDCl_3) δ = 2.02 (2H, tt, J = 7 and 6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 2.68 (3H, s, COMe), 3.12 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.72 (2H, t, J = 6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 7.41 (1H, t, J = 10 Hz, H-5), 7.51 (1H, t, J = 10 Hz, H-7), 7.76 (1H, t, J = 10 Hz, H-6), 8.14 (1H, s, H-2), 8.43 (1H, d, J = 10 Hz, H-8), and 9.78 (1H, d, J = 10 Hz, H-4); ^{13}C nmr (75.6 MHz, CDCl_3) δ = 23.2 (t), 29.2 (q), 33.8 (t), 62.3 (t), 123.4 (d), 126.3 (d), 128.9 (d), 129.6 (s), 135.2 (d), 139.1 (d), 139.5 (d), 140.3 (d), 140.4 (d), 141.3 (s), and 195.3 (s).
- 18) **15f**: ^1H Nmr (270 MHz, CDCl_3) δ = 2.20 (1H, br, OH), 3.24 (2H, t, J = 6.6 Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 3.90 (3H, s, OMe), 3.94 (2H, t, J = 6.6 Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 7.34 (1H, t, J = 10 Hz, H-5), 7.42 (1H, t, J = 10 Hz, H-7), 7.70 (1H, t, J = 10 Hz, H-6), 8.23 (1H, s, H-2), 8.39 (1H, d, J = 10 Hz, H-4), and 9.51 (1H, d, J = 10 Hz, H-8); ^{13}C nmr (67.4 MHz, CDCl_3) δ = 30.6 (t), 51.1 (q), 63.3 (t), 115.2 (s), 125.9 (d), 126.2 (s), 127.3 (d), 135.0 (d), 137.4 (d), 139.1 (d), 140.2 (d), 141.1 (s), 141.7 (s), and 165.7 (s).
- 19) **17a**: ^1H Nmr (300 MHz, CDCl_3) δ = 2.69 (3H, s, Me), 3.29 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 3.83 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 7.08 (1H, t, J = 10 Hz, H-5), 7.11 (1H, t, J = 10 Hz, H-7), 7.19 (1H, s, H-3), 7.47 (1H, t, J = 10 Hz, H-6), 8.14 (1H, d, J = 10 Hz, H-8), and 8.23 (1H, d, J = 10 Hz, H-4); ^{13}C nmr (75.6 MHz, CDCl_3) δ = 15.1 (q), 28.9 (t), 63.3 (t), 117.9 (d), 122.2 (d), 122.8 (d), 124.0 (s), 131.7 (d), 134.1 (d), 135.9 (d), 137.6 (s), 140.0 (s) and 149.1 (s).
- 20) **18a**: ^1H Nmr (300 MHz, CDCl_3) δ = 2.07 (2H, tt, J = 7 and 6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.08 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.73 (2H, t, J = 6 Hz, CH_2OH), 7.14 (2H, t, J = 10 Hz, H-5,7), 7.21 (2H, s, H-1,3), 7.50 (1H, t, J = 10 Hz, H-6), 8.19 (2H, d, J = 10 Hz, H-4,8); ^{13}C nmr (75.6 MHz, CDCl_3) δ = 27.4 (t), 33.4 (t), 62.7 (t), 117.2 (d), 123.1 (d), 134.6 (d), 135.7 (d), 140.5 (s), and 154.2 (s).
- 21) **19c**: ^1H Nmr (300 MHz, CDCl_3) δ = 2.92 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{CHO}$), 3.34 (2H, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{CHO}$), 7.46 (2H, t, J = 10 Hz, H-5,7), 7.83 (1H, t, J = 10 Hz, H-6), 7.90 (1H, s, H-2), 8.43 (1H, d, J = 10 Hz, H-8), 8.56 (1H, d, J = 10 Hz, H-4), and 9.85 (1H, s, CHO); ^{13}C nmr (67.8 MHz, CDCl_3) δ = 19.1 (t), 44.3 (t), 96.9 (s), 117.3 (s), 125.9 (d), 126.2 (d), 129.4 (s), 135.5 (d), 136.6 (d), 138.5 (d), 139.6 (d), 143.6 (s), and 199.8 (d).
- 22) **14f**: ^1H Nmr (300 MHz, CDCl_3) δ = 1.35 (6H, d, J = 6.9 Hz, ipr-Me), 2.67 (3H, s, COMe), 2.73 (3H, s, 2-Me), 3.12 (1H, m, J = 6.9 Hz, ipr-CH), 3.24 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 3.79 (2H, t, J = 7 Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 7.31 (1H, t, J = 9.8 Hz, H-5), 7.59 (1H, d, J = 9.8 Hz, H-6), 8.23 (1H, d, J = 9.8 Hz, H-4), and 9.39 (1H, d, J = 1.5 Hz, H-8); ^{13}C nmr (75.6 MHz, CDCl_3) δ = 15.9 (q), 24.6 (q), 28.5 (t), 32.6 (q), 39.1 (d), 63.0 (t), 124.2 (s), 124.3 (s), 126.2 (d), 131.7 (d), 136.2 (d), 136.4 (d), 140.5 (s), 140.6 (s), 149.2 (s), 150.0 (s) and 197.0 (s).

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