Light induced reactions of substituted 1-acetonaphthones with 2-piperidinopropenenitrile. Part III†

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UV excitation ($\lambda \geqslant 280$ nm) of 1-acetonaphthones additionally substituted at C-2 or C-4 in the presence of 2-piperidinopropenenitrile resulted in the occurrence of two types of reactions, photocycloaddition and photosubstitution. Whereas photosubstitution has occurred only in the case of halogen substituents, the formation of [4 + 2]- and [2 + 2]-cycloadducts has been observed, which is dependent on the location of an additional substituent on the ring.

Light induced cycloaddition of captodative olefins[1] to the skeleton of acylnaphthalenes[2–8] and other aromatic compounds[9–15] has been intensively investigated. Recently, we reported the photochemical reactions of substituted 1-acetonaphthones **1a–h** in the presence of a captodative olefin, 2-morpholinopropenenitrile **2a**, to elucidate the effect of the additional substituent on the type of reaction.[16,17] According to our results two types of reactions, (1) *photocycloaddition* and (2) *photosubstitution*, can occur. Whereas, in the case of halogen substituents, their replacement by 2-cyano-2-morpholinovinyl has been observed, addition of **2a** to the 1,2- and 1,4-positions of the naphthalene ring occurred, depending on the location of the additional substituent at the 4- or 2-position, respectively.

Two different intermediates, a diradical and/or an exciplex, are involved in the cycloaddition of captodative olefins to acylnaphthalenes.[2,3] Our earlier results have supported the involvement of the exciplex intermediate rather than the diradical in the reaction with substituted 1-acetonaphthones.[16,17] Since the extent of exciplex formation will be favoured by the better electron-donating ability of olefins, in this work we investigated the photochemical behaviour of **1a–h** in the presence of 2-piperidinopropenenitrile **2b** to find out the effect of the electron donor ability of the piperidino group in comparison to that of the morpholino group on the rate and the stereochemistry of addition.

Results and discussion

Irradiation ($\lambda \geqslant 280$ nm) of an equimolar solution of each of the ketones **1a–h** and **2b** resulted in the occurrence of one or both reactions, *photosubstitution* and *photocycloaddition*, depending on the nature of the additional substituent on the ring. Whereas 4-bromo-1-acetonaphthone **1a** and 4-chloro-1-acetonaphthone **1b** underwent only photosubstitution to give **3b**, and the 4-fluoro-analogue **1c** gave both **3b** and **4e**; irradiation of the other substituted 1-acetonathones **1d–h** resulted in the addition of **2b** to the naphthalene skeleton (Table 1).

† For part II, see ref. 17.

IR, ^{1}H NMR and UV data gave useful information about the structural assignment of the photoproducts. The formation of **3b** was supported by the following observations. (1) The appearance of the CO band at 1680 cm^{-1} in the IR spectrum indicates the conjugation of the CO group. (2) The ^{1}H NMR spectrum shows a signal for the methyl group at 2.75 ppm, which is almost identical to that for the corresponding group in **1a**, **1b** and **1c** at 2.67, 2.53 and 2.73 ppm, respectively; a multiplet at 7.54–8.83 ppm with an overall integration of 6 H for aromatic protons, and the signal for the vinylic proton at 6.60 ppm. (3) Induced bathochromic shift in the UV spectrum by the cross-conjugation of the ring with the additional substituent (substituted ethenyl group) has been observed. These are diagnostic of the structure **3b** and confirm the proposed photosubstitution reaction. Such a reaction has also been observed for photoreactions of **1a–c** in the presence of **2a** and formation of **3a**.[16,17]

The formation of [2 + 2]-cycloadducts **4e–h** has been observed by photoreactions of 4-substituted 1-acetonaphthones **1c**, **1d**, **1f** and **1h**, with fluorine, cyano, methyl, and methoxy groups, respectively. As shown in Table 2, ^{1}H NMR spectra of **4e–h** show the resonance of the acetyl group around 2 ppm, which indicates the attachment of this group to the cyclobutyl ring.[7,16,17] The UV spectra of **4e–h** exhibit intense absorptions ($\varepsilon = 3000$–5000 dm^3 mol^{-1} cm^{-1}) in the region 240–290 nm, consistent with 1,2-adducts with styrene-type conjugation of the benzoid ring and the residual double bond.

Table 1 Photochemical reaction of **1a–h** in the presence of **2b**

	Irrad. time/h	Photosub. yield (%)[a]	Photoadd. [2 + 2] yield (%)[a]	Photoadd. [4 + 2] yield (%)[a]
1a	8	**3b** (13)	—	—
1b	8	**3b** (11)	—	—
1c	15	**3b** (9)	**4e** (12)	—
1d	8	—	**4f** (10)	—
1e	12	—	—	**5c** (7)
1f	8	—	**4g** (9)	—
1g	12	—	—	**6** (8)
1h	8	—	**4h** (12)	—

[a] Isolated yield, based on **1** used.

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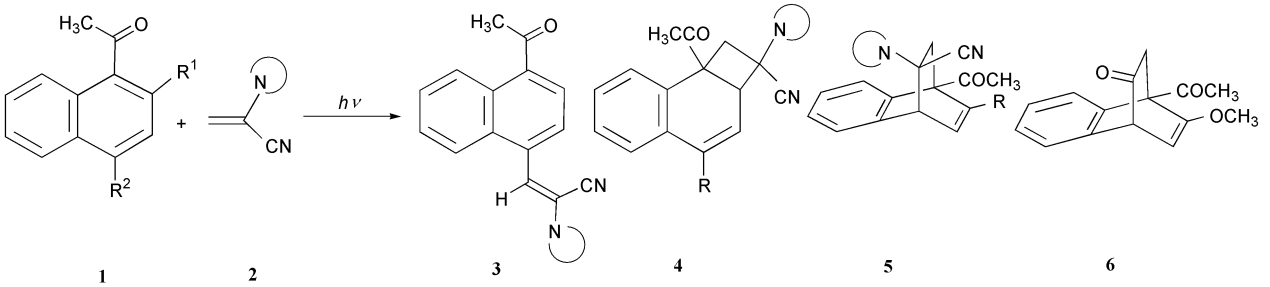


1	R^1	R^2
a	H	Br
b	H	Cl
c	H	F
d	H	CN
e	CH_3	H
f	H	CH_3
g	OCH_3	H
h	H	OCH_3

2	N
a	N O
b	N

3	N
a	N O
b	N

4	R	N
a	F	N O
b	CN	"
c	CH_3	"
d	OCH_3	"
e	F	N
f	CN	"
g	CH_3	"
h	OCH_3	"

5	R	N
a	CH_3	N O
b	OCH_3	"
c	CH_3	N

The *exo* orientation of the piperidino group in the cycloadducts **4e–h** was confirmed by the analysis of the 500 MHz ^{1}H NMR spectrum of compound **4e**. The CH_2 group of the cyclobutyl ring shows two resonances at 3.25 and 2.67 ppm, corresponding to *endo*-1-H and *exo*-1-H, respectively, with a geminal coupling of |12.17 Hz|. The *endo*-1-H should be *cis* to the cyano group, since the anisotropic effect of this group causes a deshielding effect on this proton; therefore, a shift to lower field in comparison with the *exo*-1-H should be expected.[18] On the other hand, the *cis* orientation of the piperidino group with respect to the *exo*-1-H causes a resonance at a higher field. This peak is additionally split by 0.73 Hz owing to a long range (W-type) interaction with 2*a*-H. A four-spin system was also observed for 2*a*-H, 3-H, 4-F and *exo*-1-H. The resonance for 2*a*-H showed a vicinal coupling of 6.31 Hz with 3-H, coupling with 4-F (4.73 Hz) and long-range coupling with *exo*-1-H (0.73 Hz). All these facts confirmed the *exo* orientation of the piperidino group. Such an orientation has also been observed earlier, in the case of **4d** by X-ray crystal structure analysis, by an NOE signal intensity difference determination for **4b**, and also by the analysis of the ^{1}H NMR spectrum of **4a**.[16,17]

Irradiation of **1e** and **1g** with methyl and methoxy groups at the 2-position in the presence of **2b** resulted in the formation of CO deconjugated products, while in the case of **1g** the product was hydrolysed on silica gel and a diketone **6** was formed. The product **6** has been previously obtained on hydrolysis of **5b** following a known procedure.[19] The assignments for **5c** and **6** were achieved by comparison of their spectroscopic data with those obtained for **5a** and **5b** (Table 3). The UV spectrum exhibits absorptions at $\lambda = 242$ ($\varepsilon = 1582$) and 273 nm (683 $dm^3\ mol^{-1}\ cm^{-1}$) for **5c** and $\lambda = 282$ nm ($\varepsilon = 275\ dm^3\ mol^{-1}\ cm^{-1}$) for **6**. This is consistent with formation of the 1,4-adducts with a nonconjugated benzoid ring and the residual double bond. The ^{1}H NMR spectra showed a resonance for the acetyl group at 2.26 and 2.51 ppm for **5c** and **6**, respectively, comparable to the same resonance for **5a** and **5b**. The chemical shifts and couplings for the hydrogens (10-CH_2, 3-H and 4-H) indicate the formation of a 1,4-ethanonaphthalene skeleton.

The preferred *endo* orientation of the amino groups in compounds of type **5** has been firmly established by the crystal structure analysis[2,3] as well as by an NOE signal intensity difference determination experiment.[16,17] Most of the cycloadducts were thermally unstable and underwent retrocleavage to the starting material upon heating. Our new cycloaddition results also support the formation of an exciplex intermediate rather than a diradical intermediate, which we had proposed earlier.[16,17]

The orientation of the olefin in the exciplex intermediate is again affected by the additional substituent. A substituent at the 2-position would lead to an *endo* orientation of the piperidino group, as in **7**, the intermediate of the [4 + 2]-cycloadducts **5**, rather than **8**. Such an orientation facilitates better interaction between the donor group and the electronically excited naphthalene ring. Therefore, this geometry stabilises the exciplex intermediate and favours the formation of the *endo* [4 + 2]-cycloadducts **5**. On the other hand, a substituent in the position 4 would lead to an *exo* orientation of the piperidino group, because of its steric hindrance, as in **9**, which is the intermediate

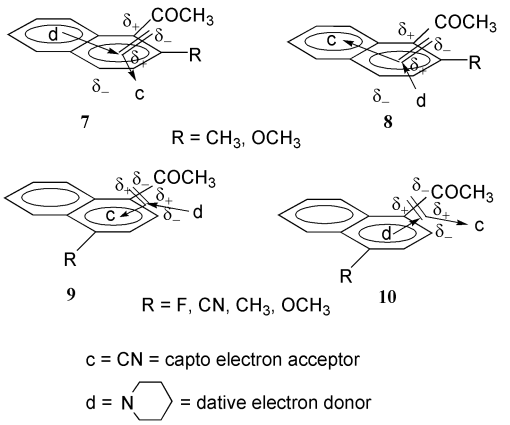
Table 2 Structurally relevant ^{1}H NMR chemical shifts (δ values) and ^{1}H, ^{1}H coupling J (Hz) of **4e–h** in comparison with **4a–d**

		1-CH_2						
	CH_3CO	*exo*-H	*endo*-H	^2J	2*a*-H	3-H	$^3J_{2a,3}$	Ref.
4a	2.04	2.67	3.28	12.17	3.32	5.36	6.30	17
4b	2.00	2.72	3.34	12.2	3.40	6.59	6.15	16
4c	2.22	2.64	3.29	12.07	3.24	5.62	5.61	17
4d	2.00	2.60	3.22	11.95	3.30	4.76	6.41	16
4e	2.03	2.67	3.25	12.17	3.30	5.38	6.31	
4f	1.95	2.68	3.31	12.1	3.28	6.57	7	
4g	1.95	2.62	3.23	12.1	3.10	5.64	7	
4h	1.95	2.55	3.19	12.9	3.34	4.75	6.4	

Table 3 Structurally relevant ^{1}H NMR chemical shifts (δ values) and ^{1}H, ^{1}H coupling J (Hz) of **5a–c** and **6**

		10-CH_2					
	CH_3CO	*endo*-H	*exo*-H	^2J	3-H	4-H	$J_{3,4}$
5a	2.53	1.90	2.20	12.52	—[a]	4.41	6.32
5b	2.53	1.77	2.46	12.9	5.32	4.31	7.16
5c	2.26	1.97	2.69	12.1	—[a]	5.71	5.8
6	2.51	2.15	2.60	18	4.21	5.32	6.4

[a] Overlapped by aromatic hydrogen.



of [2 + 2]-cycloadducts **4**, rather than **10**. This geometry favours the formation of [2 + 2]-cycloadducts **4**.

Conclusion

A comparison of our new results with those obtained with the olefin **2a** indicates that the regio- and also the stereochemistry of addition in both cases are the same. Oxidation potentials of **2a** and **2b** are 1.32 and 1.25 V, respectively.[20] Since yields of photoadditions are low (~10%), we could not observe much difference between the rates of these reactions.

Experimental

General methods

Melting points were determined using a Stuart Scientific SMP2 capillary apparatus and are uncorrected. IR spectra were recorded from KBr discs (unless otherwise mentioned) on Shimadzu IR-435 and Perkin–Elmer 983 instruments. ^{1}H NMR spectra were recorded with Bruker AW 80 (80 MHz), Bruker WM 300 (300 MHz) and Bruker drx 500 (500 MHz) machines. They are reported as follows: chemical shifts δ, [multiplicity, number of protons, coupling constants J (Hz), and assignment]. ^{13}C NMR spectra were recorded with a Bruker drx 500 (125.76 MHz), the DEPT technique was employed for compound **4e**. Mass spectra were obtained on an AMD 604 spectrometer; EI mode at 70 eV (temperature of direct inlet system given), FD mode at 0.005 V and no additional heating of the emitter filament. UV spectra were measured on a Shimadzu UV-160 spectrometer. Microanalysis were carried out with Heraeus CHN-O-RAPID and Carlo Erba 1106 CHN analysers. Preparative layer chromatography (PLC) was carried out on 20 × 20 cm^2 plates, coated with a 1 mm layer of Merck silica gel PF_{254}, prepared by applying the silica as a slurry and drying in air. All irradiations were carried out in a pyrex cell ($\lambda \geqslant 280$ nm) using a 400 W high pressure Hg vapour lamp from NARVA and in the case of **1c** with a 150 W high pressure Hg vapour burner from Philips through a water-cooled immersion well made of Duran glass and cooling of samples by running water.

A solution of 1 mmol of each of the ketones **1a,b,d–h** and **2b** was irradiated in 15 ml dry benzene ($c = 0.067$ M each) and in the case of **1c** in 20 ml acetonitrile ($c = 0.05$ M) and continously purged with a stream of argon for the times given below.

Irradiations

4-Bromo-1-acetonaphthone 1a in the presence of 2-piperidinopropenenitrile 2b. PLC (toluene–ethyl acetate, 7 : 1) of the reaction mixture after 8 h irradiation gave zone 1 ($R_f = 0.65$, 205 mg of **1a**), zone 2 ($R_f = 0.41$, 110 mg of **2b**), and zone 3 ($R_f = 0.35$, 39 mg of **3**; 13% based on **1a** used, 73% based on **1a** consumed). The latter was recrystallised from *n*-hexane–ethyl acetate (10 : 1), m.p. 136–138 °C.

1-[4-(2-Cyano-2-piperidinoethenyl)naphthalenyl]ethanone 3. IR: ν 2225 (CN) and 1680 (CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.71 (m_c, 6 H, 3-, 4- and 5-H of piperidine ring), 2.75 (s, 3 H, COCH3), 3.27 (m_c, 4 H, 2- and 6-H of piperidine ring), 6.60 (s, 1 H, vinylic H), 7.54–8.83 (m, 6 H, aromatic Hs). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 24.06 (N–CH_2–CH_2–CH_2–), 25.39 (CH_3), 30.14 (N–CH_2–CH_2), 49.88 (N–CH_2), 113.84 (CN), 115.44 (vinylic CH), 124.32, 125.23, 126.77, 126.92, 127.02, 128.19 (aromatic C), 128.80 (*C*CN), 130.59 (C-4), 132.43 (C-8*a*), 135.07 (C-4*a*), 137.15 (C-1), 201.69 (CO). EI-MS (145 °C): m/z (%) 304 [M$^+$] (100), 289 [M$^+$ − CH_3] (30), 261 [M$^+$ − $COCH_3$] (40), 247 [M$^+$ − $COCH_3$ − CH_3] (10), 220 [M$^+$ − piperidine] (5), 205 [M$^+$ − piperidine − CH_3] (21), 177 [M$^+$ − piperidine − $COCH_3$] (22), 151 [M$^+$ − piperidine − $COCH_3$ − CN] (26), 135 [**2b**$^+$ − H] (8), 84 [piperidine$^+$] (19). UV ($CHCl_3$): ν_{max} (lg ε) 350 (4.12), 362 nm (4.09). Anal. calc. for $C_{20}H_{20}N_2O$ (304.381): C, 78.92; H, 6.62; N, 9.20%. Found: C, 78.83; H, 6.57; N, 9.14%.

4-Chloro-1-acetonaphthone 1b in the presence of 2b. PLC (toluene–ethyl acetate, 7 : 1) of the reaction mixture after 8 h irradiation gave zone 1 ($R_f = 0.6$, 173 mg of **1b**), zone 2 ($R_f = 0.4$, 95 mg of **2b**), and zone 3 ($R_f = 0.35$, 33 mg of **3**; 11% based on **1b** used, 72% based on **1b** consumed).

4-Fluoro-1-acetonaphthone 1c in the presence of 2b. PLC (toluene–ethyl acetate, 20 : 1) of the reaction mixture after 15 h irradiation gave zone 1 ($R_f = 0.61$, 83 mg of **1c**), zone 2 ($R_f = 0.47$, 27 mg of **2b**), zone 3 ($R_f = 0.40$, 31 mg of **3**; 9% based on **1c** used, 38% based on **1c** consumed), and zone 4 ($R_f = 23$, 40 mg of **4e**; 12% based on **1c** used, 38% based on **1c** consumed). The latter was recrystallised from *n*-hexane–ethyl acetate (10 : 1), m.p. 150–152 °C.

***rel*-(2*R*,2*aS*,8*bS*)-8*b*-Acetyl-4-fluoro-1,2,2*a*,8*b*-tetrahydro-2-piperidinocyclobuta[*a*]naphthalene-2-carbonitrile 4e.** IR: ν 2214 (CN) and 1708 (CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47 (m_c, 2 H, 4-H of piperidine ring), 1.59 (m_c, 4 H, 3- and 5-H of piperidine ring), 2.03 (s, 3 H, $COCH_3$), 2.27 (m_c, 2 H, $CH_{ax}N$), 2.41 (m_c, 2 H, $CH_{eq}N$), 2.67 (dd, 1 H, $^2J = 12.17$ Hz, $^4J_{1,2a} = 0.73$ Hz, *exo*-1-H), 3.25 (d, 1 H, $^2J = 12.17$ Hz, *endo*-1-H), 3.30 (ddd, 1 H, $^3J_{2a,3} = 6.31$ Hz, $^4J_{2a,F} = 4.73$ Hz, $^4J_{2a,exo\text{-}H} = 0.73$ Hz, 2*a*-H), 5.38 (dd, 1 H, $^3J_{3,F} = 12.9$ Hz, $^3J_{3,2a} = 6.31$ Hz, 3-H), 6.70 (m_c, 1 H, 8-H), 7.32 (m_c, 2 H, 6- and 7-H), 7.54 (m_c, 1 H, 5-H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 23.95 (N–CH_2–CH_2–CH_2), 25.10 (CH_3), 25.52 (N–CH_2–CH_2), 43.31 (C-1), 45.88 and 45.95 ($^3J_{C,F} = 8.98$ Hz, C-2*a*), 47.94 (N–CH_2), 48.07 (C-8*b*), 63.99 and 64.02 ($^4J_{C,F} = 4.49$ Hz, C-2), 97.96 and 98.13 ($^2J_{C,F} = 20.45$ Hz, C-3), 116.85 (CN), 122.71 and 122.76 ($^3J_{C,F} = 6.49$ Hz, C-5), 127.25 (C-8*a*), 127.33 and 127.37 ($^4J_{C,F} = 4.49$ Hz, C-6) 128.79 and 130.68 (C-7, C-8), 135.53 and 135.59 ($^2J_{C,F} = 6.48$ Hz, C-4*a*), 158.37 and 160.42 ($^1J_{C,F} = 256.80$ Hz, C-4), 204.78 (CO). EI-MS (125 °C): m/z (%) 323 [M$^+$ − H] (0.01), 297 [M$^+$ − HCN] (0.74), 281 [M$^+$ − $COCH_3$] (7), 197 [M$^+$ − $COCH_3$ − piperidine] (3), 173 [M$^+$ − **2b** − CH_3] (15), 159 (22), 145 [M$^+$ − **2b** − $COCH_3$] (10), 136 [**2b**$^+$] (100). UV ($CHCl_3$): ν_{max} (lg ε) 267 (3.71), 274 nm (3.70). Anal. calc. for $C_{20}H_{21}N_2OF$ (324.396): C, 74.05; H, 6.52; N, 8.64%. Found: C, 74.03; H, 6.54; N, 8.69%.

4-Cyano-1-acetonaphthone 1d in the presence of 2b. PLC (toluene–ethyl acetate, 3 : 1) of the reaction mixture after 8 h irradiation gave zone 1 ($R_f = 0.71$, 170 mg of **1d**), zone 2

($R_f = 0.64$, 114 mg of **2b**), and zone 3 ($R_f = 0.42$, 33 mg of **4f**; 10% based on **1d** used, 78% based on **1d** consumed). The latter was recrystallised from *n*-hexane–ethyl acetate (10 : 1), m.p. 136–137 °C (decomp.).

***rel*-(2*R*,2*aS*,8*bS*)-8*b*-Acetyl-4-cyano-1,2,2*a*,8*b*-tetrahydro-2-piperidinocyclobuta[*a*]naphthalene-2-carbonitrile 4f.** IR: ν 2220 (CN) and 1710 (CO) cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 1.51 (br, 6 H, 3-, 4- and 5-H of piperidine ring), 1.95 (s, 3 H, $COCH_3$), 2.68 (d, 1 H, $^2J = 12.1$ Hz, *exo*-1-H), 2.92 (br d, 4 H, 2- and 6-H of piperidine ring), 3.28 (d, 1 H, $^3J_{2a,3} = 7$ Hz, 2*a*-H), 3.31 (d, 1 H, $^2J = 12.1$ Hz, *endo*-1-H), 6.57 (d, 1 H, $^3J_{2a,3} = 7$ Hz, 3-H), 6.97–7.71 (m, 4 H, aromatic H). EI-MS (150 °C): *m*/*z* (%) 304 [$M^+ - HCN$] (19), 288 [$M^+ - COCH_3$] (0.61), 279 [$M^+ - 2CN$] (0.18), 237 [$M^+ - 2CN - COCH_3$] (3), 195 [$M^+ - 2CN -$ piperidine] (48), 180 [$M^+ - 2CN -$ piperidine $- CH_3$] (100), 152 [$M^+ - 2CN -$ piperidine $- COCH_3$] (27), 136 [**2b**$^+$] (26). UV ($CHCl_3$): ν_{max} (lg ε) 246 (3.66), 286 nm (3.49). Anal. calc. for $C_{21}H_{21}N_3O$ (331.406): C, 76.1; H, 6.4; N, 13.7%. Found: C, 75.7; H, 6.4; N, 13.6%.

2-Methyl-1-acetonaphthone 1e in the presence of 2b. PLC (toluene–ethyl acetate, 3 : 1) of the reaction mixture after 12 h irradiation gave zone 1 ($R_f = 0.78$, 100 mg of **1e**), zone 2 ($R_f = 0.64$, 100 mg of **2b**), and zone 3 ($R_f = 0.49$, 33 mg of **5c**; 7% based on **1e** used, 70% based on **1e** consumed). The latter was recrystallised from *n*-hexane–ethyl acetate (10 : 1), m.p. 136–137 °C (decomp.).

***rel*-(1*S*,4*R*,9*R*)-1-Acetyl-1,4-dihydro-2-methyl-9-piperidino-1,4-ethanonaphthalene-9-carbonitrile 5c.** IR: ν 2220 (CN) and 1710 (CO) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.58 (br, 6 H, 3-, 4- and 5-H of piperidine ring), 1.97 (d, 1 H, $^2J = 12.1$ Hz, *endo*-10-H), 2.01 (s, 3 H, CH_3), 2.26 (s, 3 H, $COCH_3$), 2.40 (m_c, 2 H, $CH_{ax}N$), 2.69 (d, 1 H, $^2J = 12.1$ Hz, *exo*-10-H), 3.25 (m_c, 2 H, $CH_{eq}N$), 5.71 (1 H, $^3J_{3,4} = 5.8$ Hz, 4-H), 6.67–7.25 (m, 5 H, 3-H and aromatic H). EI-MS (155 °C): *m*/*z* (%) 320 [M^+] (0.1), 293 [$M^+ - HCN$] (0.6), 278 [$M^+ - HCN - CH_3$] (2), 277 [$M^+ - COCH_3$] (4), 263 [$M^+ - COCH_3 - CH_3$] (0.6), 250 [$M^+ - HCN - COCH_3$] (1), 184 [$M^+ -$ **2b**] (22), 169 [$M^+ -$ **2b** $- CH_3$] (41), 141 [$M^+ -$ **2b** $- COCH_3$] (13), 136 [**2b**$^+$] (100). UV ($CHCl_3$): ν_{max} (lg ε) 242 (3.20), 273 nm (2.94). Anal. calc. for $C_{21}H_{24}N_2O$ (320.421): C, 78.72; H, 7.55; N, 8.74%. Found: C, 78.84; H, 7.66; N, 8.40%.

4-Methyl-1-acetonaphthone 1f in the presence of 2b. PLC (toluene–ethyl acetate, 3 : 1) of the reaction mixture after 8 h irradiation gave zone 1 ($R_f = 0.72$, 159 mg of **1f**), zone 2 ($R_f = 0.63$, 118 mg of **2b**), and zone 3 ($R_f = 0.47$, 30 mg of **4g**, 9% based on **1f** used, 69% based on **1f** consumed). The latter was recrystallised from *n*-hexane–ethyl acetate (10 : 1), m.p. 143–144 °C (decomp.).

***rel*-(2*R*,2*aS*,8*bS*)-8*b*-Acetyl-4-methyl-1,2,2*a*,8*b*-tetrahydro-2-piperidinocyclobuta[*a*]naphthalene-2-carbonitrile 4g.** IR: ν 2210 (CN) and 1710 (CO) cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 1.50 (br, 6 H, 3-, 4- and 5-H of piperidine ring), 1.95 (s, 3 H, $COCH_3$), 2.07 (s, 3 H, CH_3), 2.32 (b, 4 H, 2- and 6-H of piperidine ring), 2.62 (d, 1 H, $^2J = 12.1$ Hz, *exo*-1-H), 3.10 (d, 1 H, $^3J_{2a,3} = 7$ Hz, 2*a*-H), 3.23 (d, 1 H, $^2J = 12.1$ Hz, *endo*-1-H), 5.64 (d, 1 H, $^3J_{2a,3} = 7$ Hz, 3-H), 6.82–7.26 (m, 4 H, aromatic Hs). EI-MS (120 °C): *m*/*z* (%) 293 [$M^+ - HCN$] (3), 279 [$M^+ - CN - CH_3$] (4), 211 [$M^+ - CN -$ piperidine] (9), 184 [$M^+ -$ **2b**] (42), 169 [$M^+ -$ **2b** $- CH_3$] (100), 141 [$M^+ -$ **2b** $- COCH_3$] (37), 136 [**2b**$^+$] (72). FD-MS (0.005 V): *m*/*z* (%) 320 [M^+] (100), 276 [$M^+ - COCH_3$] (12). UV ($CHCl_3$): ν_{max} (lg ε) 242 (3.45), 270 nm (3.67). Anal. calc. for $C_{21}H_{24}N_2O$ (320.421): C, 78.72; H, 7.55; N, 8.74%. Found: C, 78.78; H, 7.53; N, 8.65%.

2-Methoxy-1-acetonaphthone 1g in the presence of 2b. PLC (toluene–ethyl acetate, 7 : 1) of the reaction mixture after 12 h irradiation gave zone 1 ($R_f = 0.74$, 168 mg of **1g**), zone 2 ($R_f = 0.40$, 100 mg of **2b**), and zone 3 ($R_f = 0.35$, 27 mg of **6** as an oil and 8% based on **1g** used, 70% based on **1g** consumed).

***rel*-(1*R*,4*R*)-1-Acetyl-1,4-dihydro-2-methoxy-1,4-ethanonaphthalene-9-one 6.** IR (film): ν 1714 (br, CO) cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 2.15 (d, 1 H, $^2J = 18$ Hz, *endo*-10-H), 2.51 (s, 3H, $COCH_3$), 2.60 (d, 1 H, $^2J = 18$ Hz, *exo*-10-H), 3.60 (s, 3 H, OCH_3), 4.21 (d, 1 H, $^3J_{3,4} = 6.4$ Hz, 3-H), 5.32 (d, 1 H, $^3J_{3,4} = 6.4$ Hz, 4-H), 7.01–7.30 (m, 4 H, aromatic Hs). UV ($CHCl_3$): ν_{max} (lg ε) 244 (3.0), 270 (2.61), 282 nm (2.44).

4-Methoxy-1-acetonaphthone 1h in the presence of 2b. PLC (toluene–ethyl acetate, 3 : 1) of the reaction mixture after 8 h irradiation gave zone 1 ($R_f = 0.74$, 170 mg of **1h**), zone 2 ($R_f = 0.63$, 110 mg of **2b**), and zone 3 ($R_f = 0.50$, 40 mg of **4h**; 12% based on **1h** used, 79% based on **1h** consumed). The latter was recrystallised from *n*-hexane–ethyl acetate (10 : 1), m.p. 139–140 °C (decomp.).

***rel*-(2*R*,2*aS*,8*bS*)-8*b*-Acetyl-4-methoxy-1,2,2*a*,8*b*-tetrahydro-2-piperidinocyclobuta[*a*]naphthalene-2-carbonitrile 4h.** IR: ν 2220 (CN) and 1705 (CO) cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 1.49 (br d, 6 H, 3-, 4- and 5-H of piperidine ring), 1.95 (s, 3 H, $COCH_3$), 2.31 (br, 4 H, 2- and 6-H of piperidine ring), 2.55 (d, 1 H, $^2J =$ 12.9 Hz, *exo*-1-H), 3.19 (d, 1 H, $^2J = 12.1$ Hz, *endo*-1-H), 3.34 (d, 1 H, $^3J_{2a,3} = 7$ Hz, 2*a*-H), 4.75 (d, 1 H, $^3J_{2a,3} =$ Hz, 3-H), 6.81–7.76 (m, 4 H, aromatic Hs). EI-MS (120 °C): *m*/*z* (%) 309 [$M^+ - HCN$] (0.45), 293 [$M^+ - COCH_3$] (2), 278 [$M^+ - COCH_3 - CH_3$] (1), 266 [$M^+ - COCH_3 - HCN$] (0.57), 262 [$M^+ - COCH_3 - OCH_3$] (0.52), 200 [$M^+ -$ **2b**] (96), 185 [$M^+ -$ **2b** $- CH_3$] (100), 157 [$M^+ -$ **2b** $- COCH_3$] (16), 136 [**2b**$^+$] (12). UV ($CHCl_3$): ν_{max} (lg ε) 246 (3.67), 276 nm (3.69). Anal. calc. for $C_{21}H_{24}N_2O_2$ (336.421): C, 74.97; H, 7.19; N, 8.33%. Found: C, 75.13; H, 7.15; N, 8.34%.

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