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Synthesis and photochromic properties of new spiro[azahomoadamantane-naphthoxazines]

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Abstract

The coupling of various nitrosonaphthols with 4,5-dimethyl-4-azahomoadamantane-4-enium iodide, in the presence of an equimolar amount of triethylamine, affords new spiro[azahomoadamantane-naphthoxazines]. The study of their photochromic properties by flash photolysis shows special features, particularly a hypsochromic shift of the wavelength of absorption of the colored forms, when compared to well known spiro[indoline-naphthoxazines], and also an obvious decrease in the thermal bleaching kinetics. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photochromism; Spirooxazines; Azahomoadamantanes; Flash photolysis; Spectrokinetic parameters

1. Introduction

Spirooxazines undergo photochromism due to a reversible cleavage of the C_{sp^3} –O bond, under UV light. Closed forms of these compounds absorb in the UV range, whereas absorption of the open forms occurs in the visible range (Scheme 1).

Photochromic properties of spiro[indoline-naphthoxazine] **SPO** were first described by Fox in 1961 [1]. However, only during the past decade has this class of compounds been considered for the development of photoresponsive materials (especially in the field of variable optical transmission materials). This had led to many investigations [2–5] and patents [6,7], due to their good fatigue resistance compared to spiropyrans [8]. Further progress towards industrial applications in this area requires optimizing technical properties such as color fastness (e.g. photodegradation).

Our aim was to modify the structure of **SPO**-compounds in order to effect a hypsochromic shift compared to the 1,3,3-trimethylspiro[indoline-naphthoxazine] **SPO**, which turns blue upon irradiation by UV light ($\lambda_{max} = 594$ nm in toluene). Two different approaches were used previously to shift the λ_{max} of the colored form. The first involves the introduction of substituents with strong electronic effects, particularly in the right hand moiety (Scheme 1). In this way, Rickwood et al. [9] achieved a hypsochromic shift in the λ_{max} of the open form, by introducing an electron-donating group in the 6′ position. The second approach to modify the λ_{max} involves the π electron system of the open form

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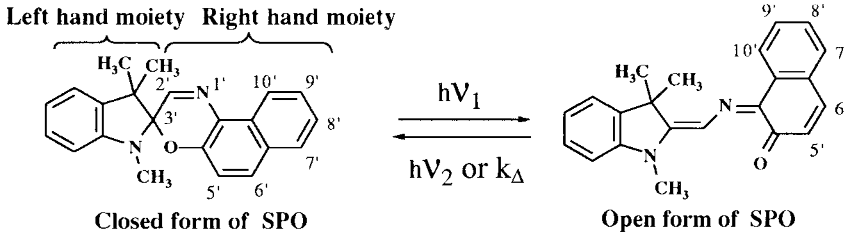

Scheme 1. General photochromic equilibrium in spiro[indoline-naphthoxazine].

because decreasing conjugation usually leads to a hypsochromic shift. For instance, changing the indolinic entity to a piperidine moiety results in a significant hypsochromic shift in the spiropyran [10] series as well as in the spirooxazines [11,12]. Recently synthesized spiro[azabicyclo-naphthoxazines] [13] show a similar effect and this has been attributed to weaker participation of the nitrogen atom in the electron delocalization of the open form [14].

Although a great number of photochromic compounds have been synthesized, molecules that turn red upon UV irradiation are quite rare and are of interest for the design of photochromic lenses. Among the structural modifications that could be carried out on spirooxazines, changes involving the left hand moiety (indolinic part) represents an interesting approach to achieving a blue shift in the λ_{max} of open forms. This idea led to the synthesis of new spiro[azahomoadaman-tane-naphthoxazines] and the assessment of their photochromic properties along with previously reported compounds [10–13].

2. Synthesis

With the above considerations in mind we investigated the synthesis of new photochromic spirooxazines **1** (Fig. 1).

The ammonium salt **4**, a valuable synthon for this synthesis, has been obtained from 2-methyl-2-adamantanol [15], **2**, in two steps, [16], as detailed in Scheme 2

Eneamine **5** was generated in situ from **4** by the action of triethylamine and reacted with nitrosonaphthols to give spirooxazines. The mechanism involved is similar to that previously described for the preparation of spiro[indoline-naphthoxazines] [17], the Fischer's base being replaced by **5**.

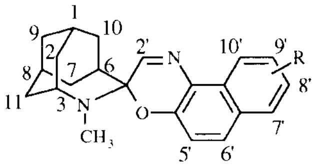

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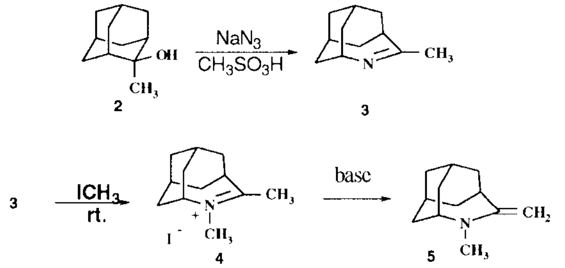
Fig. 1.



Scheme 2.

Various nitrosonaphthols were used to examine the effect of naphthalene substitutions on photochromic properties. Nitrosonaphthol **6** was purchased and compounds **7–9** were prepared from the corresponding hydroxynaphthalenes using previously described [18–20] methods (Fig. 2).

Nitrosonaphthols **12** and **13** were elaborated by an efficient nitrosation method described in a patent [21]. The action of sodium nitrite and sulphuric acid on hydroxynaphthalenes **10** and **11**, led to **12** and **13** with very good yields (Scheme 3) whereas classical nitrosation methods [22,23] failed to produce **13**.

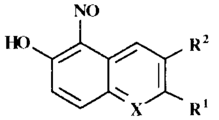
Condensation of the nitrosocompounds (**6–9**, **12** and **13**) with 5-methylene-4-azahomoadamantane **5**, afforded the new spiro[azahomoadamantane-naphthoxazines] **1a–1f**, in yields of 15 to 30% (Fig. 3).

Pure compounds were obtained by flash chromatography followed by a crystallization and were fully characterized by ^{1}H and ^{13}C NMR. Crystallization by slow evaporation of a pentane/ether solution of **1a** afforded crystals suitable for X-ray diffraction [24].

Compound **1a** may be also prepared using 1-amino-2-naphthol in place of 1-nitroso-2-naphthol [25].

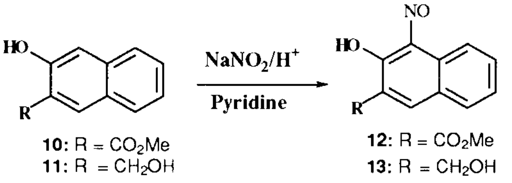
3. Photochromic properties

Photochromic parameters were determined in toluene ($C=2.5\times10^{-5}$ M) at 25°C using a flash photolysis apparatus (power: 60 J, duration: 50 μs) coupled to a Warner–Swasey fast scanning spectrophotometer capable of recording the transient absorption spectrum in the visible region within 1.25 ms [26]. First order rate constants for thermal bleaching (k_{Δ}) were measured by monitoring the decrease in absorbance at the $\lambda_{\max}$ of the open form. The initial absorbance (A_0), namely the colorability, is directly related to the quantum yield of coloration [27].



6: $R^1 = H$, $R^2 = H$, X = CH
7: $R^1 = H$, $R^2 = OMe$, X = CH
8: $R^1 = Br$, $R^2 = H$, X = CH
9: $R^1 = R^2 = H$, X = N

Fig. 2.



Scheme 3.

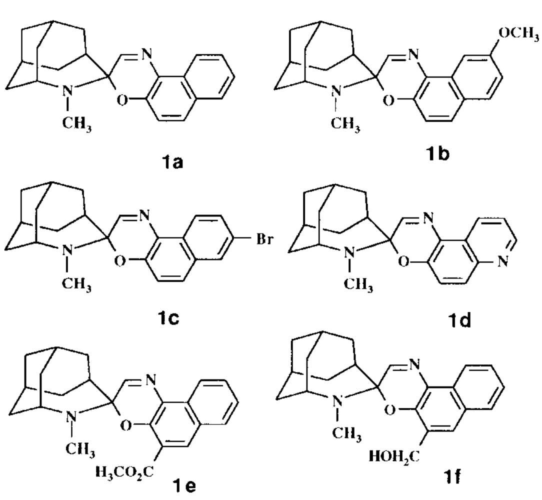


Fig. 3.

$$A_0 = \varepsilon_{MC}\cdot\phi_{col}.k.C_{CF} \quad \text{(for low concentration)}$$

ε_{MC},	molar absorptivity of colored forms
ϕ_{col},	quantum yield of photocoloration
k,	constant including photolysis conditions
C_{CF},	initial concentration of colorless form.

The determination of A_0 allowed us to compare the efficiency of coloration of photochromic compounds under standard experimental conditions.

Photochromic parameters of new spirooxazines **1a–1f**, were compared to spiro[indoline-naphthoxazine] **SPO** analogs, and to related photochromic compounds (**14–16**), in which a saturated *N*-heterocycle is linked to the naphthoxazine unit (Fig. 4).

Photochromic parameters of **14** and **15**, were measured under similar experimental conditions. Corresponding data for photochromic compounds **SPO** and **16** (Fig. 4) were previously reported [28,29] The photochromic parameters of spiro [azahomoadamantane-naphthoxazines] **1a–1f**, **SPO** and **14–16**, are reported in Table 1.

All of the new spirooxazines (**1a–1f**) exhibited photochromic properties in toluene at ambient temperature, showing a hypsochromic shift (5–20 nm) with respect to **SPO**. In all cases, an additional

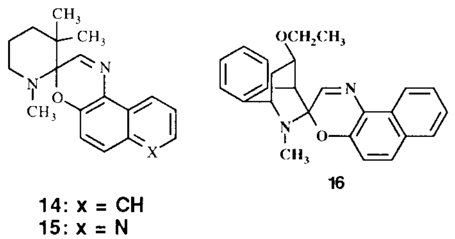


Fig. 4.

Table. 1
Spectrokinetic properties for **1, SPO**, and **14**–**16** (2.5×10^{-5} M in toluene, 25°C).

Compound	$\lambda_{\max}$ (nm)	$k_\Delta(10^3 S^{-1})$	A_0
1a	544e,[a]580	92	0.96
1b	538 ,574	130	0.84
1c	546e, 582	43	0.66
1d	538e, 574	36	1.08
1e	555e, 590	44	1.09
1f	547e, 580	37	0.80
SPO	564e ,594	540	1.08
14	547e, 582	5400	0.44
15	542e, 575	1000	0.46
16	534e, 561	360	1.30

[a] e, shoulder.

shoulder on the blue side of the absorption band appears, and contributes to the pink color observed after irradiation. This behaviour results from a decrease in π electron delocalization in the open form, due to the presence of a saturated heterocycle in place of the indolinic moiety. The blue shifts observed are similar to those in the piperidine series (**14**: 12 nm; **15**: 19 nm), where the conjugation of the π electron system in the open form is weak compared to **SPO**. Nevertheless, among various modifications to the left hand moiety of **SPO**, the most significant hypsochromic shift was observed for compound **16**. Unfortunately, its synthesis is much more difficult than that of **1a–1f**.

The introduction of substituents on the naphthalenic part of the new compounds results in slight variations in the λ_{max} of the open form. For instance, a methoxy group in the 9′-position (**1b**) induces a shift of −6 nm compared to the unsubstituted parent compound. On the other hand, an electron-withdrawing group (e.g. carbomethoxy; **1e**) induces, a 10 nm bathochromic shift. Similar effects were also observed in the spiro[indoline-naphthoxazine] series [14,30].

Concerning fading rates, the linkage of the azahomoadamantane entity on the C_{sp^3}-atom of the photochromic structure, leads to a significant decrease in k_Δ though colorabilities remain very similar to the reference compound **SPO** (k_Δ are 5 to 50 times lower). This effect is particularly interesting for the design of photochromic lenses, giving suitable colorability under sunlight excitation. In contrast, previously described compounds **14,15** present high kinetic values, leading to the lack of perceptible color change at ambient temperature, in toluene. In this case, spectra of the open forms can only be detected on a fast scanning spectrometer.

Colorability of compounds **1a–1f** are comparable to that of **SPO**, whereas in the piperidine series (**14,15**) the colorability is greatly decreased.

4. Conclusion

A family of new spiro[azahomoadamantane-naphthoxazines] shows acceptable range of fading rate constants, good colorability and a hypsochromically shifted λ_{max} in the visible region. Thus, these photochromic compounds are particularly attractive for applications in the field of variable optical transmission materials [31].

5. Experimental

Solvents (SDS Company, France) were used without further purification and were dried over molecular sieves if necessary. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BM 250 spectrometer (250 and 62.5 MHz, respectively, for ^{1}H and ^{13}C) using tetramethylsilane as the internal standard. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. Melting points (°C) were measured in capillary tubes on a Buchi 510 apparatus and are uncorrected. Column liquid chromatography and flash chromatography were performed on silica gel Merck 60 (70–230 mesh) and silica gel Merck 60H (5–50 mesh), respectively. Elemental analysis was performed by the Microanalytical Centre of the University of Aix-Marseille III. The structures of previously reported reaction products were confirmed by ^{1}H NMR and melting point comparisons.

5.1.1. *3-Carbomethoxy-1-nitroso-2-naphthol (**12**).*

At 0°C, 3 ml of an aqueous sodium nitrite solution (20%) was added slowly to a solution of 3-carbomethoxy-2-naphthol (0.6 g, 3 mmol) in 5 ml of pyridine. Then, 10 ml of sulphuric acid (30%)

was added over a period of 30 min. After stirring the mixture 1 h at 0°C, the precipitate was collected by filtration, washed repeatedly with water, and dried to give **12** as a bright yellow powder. Yield 92%, mp 155°C (lit. [32] 153–154°C); δH (DMSO d_6): 3.82 (3H, s, OCH_3); 7.54–7.68 (2H, m; H-6, H-7); 7.79 (1H, dd, *J* 7.2 and 1.3; H-5); 8.31 (1H, s, H-4); 8.31 (1H, sl, H-8).

5.1.2. 3-Hydroxymethyl-1-nitroso-2-naphthol (13).

Using the experimental procedure described above for the preparation of **12**, the nitrosation of 3-hydroxymethyl-2-naphthol (0.52 g, 3 mmol) gave **13** as an orange powder. Yield 90%, mp 138°C; δH ($CDCl_3$): 2.17 (1H, s; CH_2OH); 4.67 (2H, s; CH_2O); 7.48–7.54 (3H, m; H-5, H-6, H-7); 7.75 (1H, s; H-4); 8.29 (1H, s; H-8).

*5.1.3. General method used for the preparation of compounds **1a–1f***

A solution of nitrosonaphthol (5 mmol) in 20 ml of trichloroethylene (except for compound **1f**, for which ethanol was used), compound **4** (5 mmol) and triethylamine (7.5 mmol) was refluxed for 5 h. After evaporation of the solvent, the residue was purified by flash chromatography. Slow evaporation of a solution of the purified product in pentane-ether (95:5) afforded white crystals of **1a–1f**.

*5.1.4. 4-Methylspiro-[4-azahomoadamantane-5,3′-[3H]naphth[2,1-b][1,4]oxazine] (**1a**).*

Purification by liquid column chromatography using a mixture of hexane–ethylacetate (95:5) afforded a 22% yield, mp 108°C (Found: C, 79.46; H, 7.17; N, 8.39. $C_{22}H_{24}N_2O$ requires: C, 79.48; H, 7.28; N, 8.43%); °H ($CDCl_3$): ($CDCl_3$): 1.36–1.45 (1H, m, 1H from CH_2), 1.59 (2H, s broad, CH_2), 1.66–1.95 (7H, m), 2.11 (1H, d, *J* 13.7, 1H from CH_2), 2.39–2.47 (2H, m, 1H from CH_2, 6-H), 2.53 (3H, s, NCH_3), 3.11 (1H, s broad, 3-H), 7.10 (1H, d, *J* 8.8, 5′-H), 7.33 (1H, ddd, *J* 8.2 and 1.1, 8′-H), 7.51 (1H, ddd, *J* 8.2 and 1.1, 9′-H), 7.63 (1H, d, *J* 8.8, 6′-H), 7.67 (1H, s, 2′-H), 7.71 (1H, d, *J* 8.2, 7′-H), 8.46 (1H, d, *J* 8.4, 10′-H); δC ($CDCl_3$); 26.9 (d), 26.9 (d), 30.0 (t), 30.7 (t), 33.5 (t), 36.2 (t), 37.7 (d), 39.7 (q), 39.8 (t), 58.7 (d), 93.8 (s), 117.9 (d), 121.6 (d), 123.6 (s), 123.8 (d), 126.8 (d), 127.8 (d), 129.1 (s), 129.3 (d), 130.8 (s), 144.9 (s), 158.7 (d).

*5.1.5. 9′-Methoxy-4-methylspiro-[4-azahomoadamantane-5,3′-[3H]naphth[2,1-b][1,4]oxazine] (**1b**).*

Purification by liquid column chromatography using a mixture of pentane-ether (90:10)/afforded a 28% yield mp 188°C (Found: C, 76.24; H, 7.28; N, 7.62. $C_{23}H_{26}N_2O_2$ requires C, 76.21; H, 7.23; N, 7.73%); δH ($CDCl_3$): 1.37–1.45 (1H, m, 1H from CH_2), 1.60 (2H, s broad, CH_2), 1.66–1.98 (7H, m), 2.11 (1H, d, *J* 13.7, 1H from CH_2), 2.42–2.47 (2H, m, 1H from CH_2, 6-H), 2.55 (3H, s, NCH_3), 3.12 (1H, s broad, 3-H), 3.96 (3H, s, OCH_3), 6.94 (1H, d, *J* 8.8, 5′-H), 6.99 (1H, dd, *J* 8.9 and 2.6, 8′-H), 7.56 (1H, d, *J* 8.8, 6′-H), 7.61 (1H, d, *J* 8.9, 7′-H), 7.66 (1H, s, 2′-H), 8.46 (1H, d, *J* 2.6, 10′-H); ^{13}C NMR (δ) ($CDCl_3$); 26.7 (d), 26.7 (d), 29.8 (t), 30.5 (t), 33.2 (t), 36.0 (t), 37.5 (d), 39.4 (q), 39.7 (t), 55.2 (q), 58.7 (d), 93.6 (s), 99.6 (d), 114.9 (d), 116.4 (d), 122.8 (s), 124.3 (d), 128.8 (d), 129.2 (d), 132.2 (s), 145.3 (s), 158.2 (d), 158.6 (d).

*5.1.6. 8′-Bromo-4-methylspiro-[4-azahomoadamantane-5,3′-[3H]naphth[2,1-b][1,4]oxazine] (**1c**).*

Purification by liquid column chromatography using a mixture of pentane–ethylacetate (97.5:2.5) afforded an 18% yield, mp 154°C (Found: C, 65.21; H, 5.60; N, 6.65. $C_{22}H_{24}N_2O$ requires: C, 65.25; H, 5.48; N, 6.62%); δH ($CDCl_3$): 1.38–1.45 (1H, m, 1H from CH_2), 1.60 (2H, s broad, CH_2), 1.68–2.00 (7H, m), 2.10 (1H, d, *J* 13.8, 1H from CH_2), 2.40–2.47 (2H, m, 1H from CH_2, 6-H), 2.51 (3H, s, NCH_3), 3.12 (1H, s broad, 3-H), 7.10 (1H, d, *J* 8.8, 5′-H), 7.52 (1H, d, *J* 8.8, 6′-H), 7.58 (1H, d, *J* 8.9, 9′-H), 7.60 (1H, s, 2′-H), 7.86 (1H, s, 7′-H), 8.32 (1H, d, *J* 8.9, 10′-H); δC ($CDCl_3$): 27.0 (d), 27.0 (d), 30.1 (t), 30.8 (t), 33.6 (t), 36.3 (t), 38.1 (d), 39.8 (q), 40.0(t), 58.3 (d), 94.4 (s), 117.7 (s), 119.2 (d), 123.8 (d), 128.0 (s), 128.4 (d), 129.8 (d), 130.1 (d), 130.5 (s), 143.6 (s), 159.1 (d).

*5.1.7. 4-Methylspiro-[4-azahomoadamantane-5,3′-[3H]pyrido[3,2-f][1,4]benzoxazine] (**1d**).*

Purification by liquid column chromatography using a mixture of dichloromethane–ethylacetate (90:10) afforded a 24% yield, mp 101°C. (Found: C, 75.61; H, 6.91; N, 12.68. $C_{21}H_{23}N_3O$ requires C, 75.64; H, 6.95; N, 12.60%); δH ($CDCl_3$) 1.41–2.17 (11H, m), 2.39–2.45 (2H, m), 2.51 (3H, s, NCH_3), 3.14 (1H, s broad, 3-H), 7.31 (1H, d, *J* 9.1, 5′-H),7.41 (1H, dd, *J* 4.7 and 3.1, 9′-H), 7.67 (1H, s, 2′-H), 7.91 (1H, d, *J* 9.1, 6′-H), 8.77 (1H, d, *J* 4.7, 8′-H), 8.79 (1H, dd, *J* 3.5 and 0.5, 10′-H); δC ($CDCl_3$); 26.7 (d), 26.8 (d), 29.9 (t), 30.6 (t), 33.3 (t), 36.0 (t), 38.1 (d), 39.5 (q), 39.8 (t), 58.7 (d), 94.2 (s), 117.9 (d), 121.6 (d), 122.8 (s), 126.0 (s), 130.2 (d), 130.4 (d), 144.1 (s), 145.0 (s), 148.0 (d), 158.8 (d).

5.1.8. 5′-Carbomethoxy-4-methylspiro-[4-azahomo-adamantane-5,3′-[3H]naphth[2,1-b][1,4]oxazine] ***1(e)***

Purification by liquid column chromatography using a mixture of pentane–ether (90:10) afforded a 16% yield, mp 103°C (Found: C, 73.80; H, 6.78; N, 7.24. $C_{24}H_{26}N_2O_3$ requires: C, 73.82; H, 6.71; N, 7.17%); δH ($CDCl_3$): 1.39–1.47 (1H, m, 1H from CH_2), 1.62 (2H, s broad, CH_2), 1.76–1.88 (6H, m), 1.99 (2H, m), 2.28 (1H, d, *J* 13.8), 2.42 (3H, s, NCH_3), 2.65 (1H, d, *J* 12.4), 3.11 (1H, s broad, H-3), 3.96 (3H, s, OCH_3), 7.37 (1H, ddd, *J* 7.6 and 1.1, 8′-H), 7.58 (1H, ddd, *J* 7.6 and 1.1, 9′-H), 7.67 (1H, s, 2′-H), 7.79 (1H, d, *J* 8.1, 7′-H), 8.32 (1H, s, 6′-H), 8.46 (1H, d, *J* 8.4, 10′-H); δC ($CDCl_3$): 26.9 (d), 26.9 (d), 29.9 (t), 30.6 (t), 32.1 (t), 36.1 (t), 36.9 (d), 39.5 (q), 40.1 (t), 52.1 (d), 59.0 (q), 93.5 (s), 119.5 (s), 121.6 (d), 124.0 (s), 124.3 (d), 127.2 (s), 128.7 (d), 128.8 (d), 132.7 (s), 132.8 (d), 144.1 (s), 156.5 (d), 166.3 (s).

5.1.9. 5′-Hydroxymethyl-4-methylspiro-[4-azahomo-adamantane-5,3′-[3H]napht[2,1-b][1,4]oxazine] ***1(f)***

Purification by liquid column chromatography using a mixture of pentane–ether (80:20/afforded a 28% yield, mp 128°C (Found: C, 76.20; H, 7.20; N, 7.62. $C_{23}H_{26}N_2O_2$ requires: C, 76.21; H, 7.23; N, 7.73.%); δH ($CDCl_3$) 1.44–1.52 (1H, m, 1H from CH_2), 1.61 (2H, s broad, CH_2), 1.71–2.42 (11 H, m, 10 H and OH), 2.42 (3H, s, NCH_3), 3.10 (1H, s broad, H-3), 4.83 (1H, d, *J* 13.6, 1H from CH_2O), 4.97 (1H, d, *J* 13.6, 1H from CH_2O), 6.99 (1H, ddd, *J* 7.5 and 1.1, 8′-H), 7.50 (1H, ddd, *J* 7.5 and 1.1, 9′-H), 7.61 (1H, d, *J* 8.1, 7′-H), 7.66 (1H, s, 2′-H), 7.69 (1H, s, 6′-H), 8.46 (1H, d, *J* 8.4, 10′-H); δC ($CDCl_3$): 26.7 (d), 26.8 (d), 29.8 (t), 31.0 (t), 33.5 (t), 33.8 (t), 36.0 (d), 39.3 (t), 39.7 (q), 58.8 (d), 61.5 (t), 93.8 (s), 121.4 (d), 122.4 (s), 123.6 (s), 123.9 (d), 126.6 (d), 126.9 (d), 127.4 (s), 127.7 (d), 130.4 (s), 144.1 (s), 156.6 (d).

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