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Journal of Organometallic Chemistry 692 (2007) 5517–5522
Journal of Organometallic Chemistry
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Note

Easy synthesis of heterocyclic carbene complexes by activation of chalcogenopyrones and benzopyrones to pyrylium salts and subsequent addition of carbanion of methoxy(methyl)pentacarbonyltungsten carbene complex ☆

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Received 28 June 2007; received in revised form 30 August 2007; accepted 30 August 2007
Available online 6 September 2007

Abstract

Methylenechalcogenopyran and benzopyran Fischer carbene complexes are easily obtained from commercially available chalcogenopyrones or benzopyrones and carbanion of methoxy(methyl)carbene tungsten complex. The key of the heterocyclic carbene formation is the activation of the carbonyl group by alkylation with alkyl trifluoromethanesulfonate reagent.

Keywords: Methylenechalcogenopyran and benzopyran carbene complexes; Pyrylium salts; Chalcogenopyrone and benzopyrone

1. Introduction

As their tetrachalcogenofulvene isoelectronic analogues [1], the bichalcogenopyrans form, with various acceptors charge transfer complexes [2] possessing interesting electrical and magnetic properties. However, in comparison with the large studies about the TTF (Tetrathiafulvalene) and related heterocyclic compound chemistry during the past twenty years [1], few works were devoted to electron rich bipyran molecules [3]. Some of us have recently reported on the synthesis of electron rich extended bichalcogenopyrans and benzopyrans bearing methoxy groups in the ethylenic spacer. These compounds were obtained from a Pd° catalytic coupling reaction of α and γ-methylenechalcogenopyran and methylenebenzochalcogenopyran Fischer carbene complexes (Scheme 1) [4]. Most of these complexes, which are the key of the electron rich molecule formation, are synthetized from a condensation reaction between carbanions of Fischer-type carbene complexes [5] and γ-unsubstituted pyrylium salts (Scheme 1) [6].

The second step of this reaction, which implies a hydride departure, requires the use of triphenyl carbenium salt as an oxidant. As the pentacarbonylmetal fragment is sensitive to oxidant reagents, the heterocyclic carbene complexes are isolated in moderate to low yield [6].

Therefore, to tentatively improve the yield, and to obtain carbene complexes with new methylenechalcogenopyran and benzopyran heterocyclic nuclei, we wished to develop an expedient route to these compounds, using commercially available α and γ-chalcogenopyrones and benzopyrones. It is well established that methylation or silylation of the nucleophilic carbonyl oxygen atom of these substrates increases the reactivity towards nucleophile

☆ To the memory of Dr. Pierre GUENOT, Director of the Centre Régional de Mesures Physiques de l'Ouest – Université de Rennes 1.

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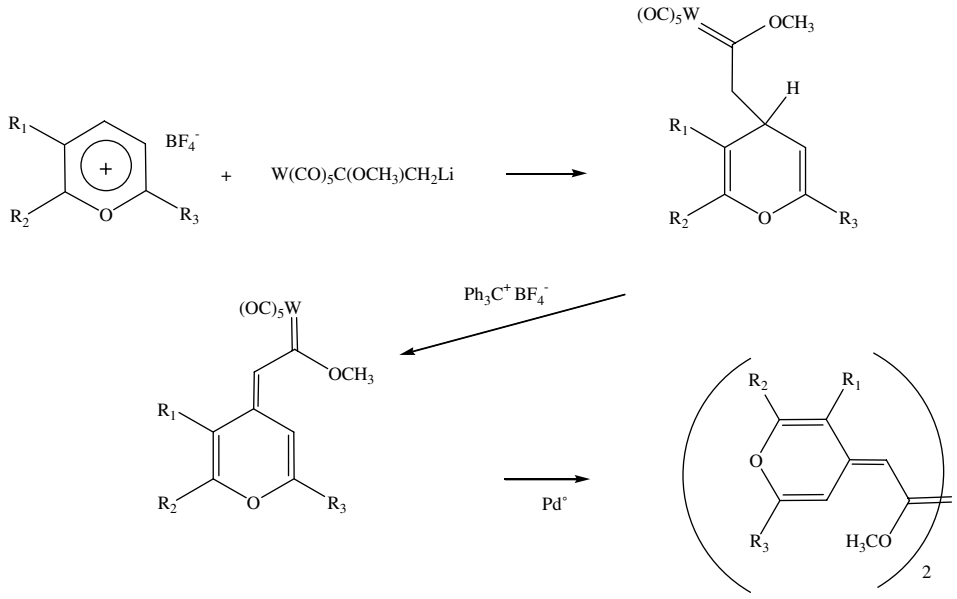
doi:10.1016/j.jorganchem.2007.08.039



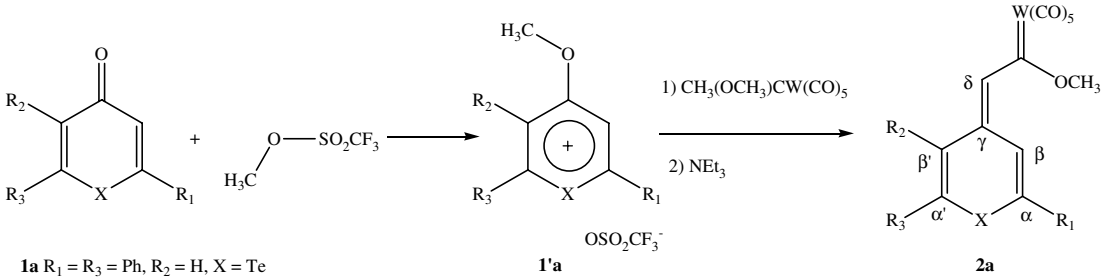
Scheme 1. Access to extended bipyrans from pyrylium salts and carbene complex.

addition, due to the formation of highly electrophilic α or γ-alkoxychalcogenopyrylium and benzopyrylium salts [7]. In this particular case the presence of the leaving alkoxy group should allow the formation of the methylenechalcogenopyran and benzopyran carbene complexes without the oxidation step. Recently, following a similar experimental procedure, we successfully obtained good yield of dithiafulvene carbene complexes from dithiolium salts bearing a leaving thiomethyl group [8].

2. Results and discussion

To test this synthetic methodology in the chalcogenopyrone and chalcogenobenzopyrone series, we first chose to consider the case of 2,6-diphenyltelluropyrone (Scheme 2). Mixing the telluropyrone **1a**, with an excess of methyl trifluoromethanesulfonate in boiling CH_2Cl_2, afforded the 2,6-diphenyl-4-methoxytelluropyran trifluoromethanesulfonate salt **1′a** in 57% yield (white powder). Adding NEt_3 to a THF solution of **1′a** and methoxy(methyl)carbene tungsten complex instantly produced a color change from yellow to blue. After hydrolysis, extraction with ether, and chromatography (silicagel, eluent: ether/petroleum ether) the telluromethylenepyran carbene complex **2a** was isolated (81% yield). The same two-step process was then applied to commercially available 2,6-diphenylthiopyrone **1b**. Unfortunately, isolation of the corresponding 4-methoxythiopyrylium salt was unsuccessful because of the great sensitivity of this compound towards moisture. To overcome this difficulty, a one pot procedure was then attempted. Pyrone **1b** and excess of methyl trifluoromethane sulfonate were heated at 60 °C for 1 h. Excess of the alkylating reagent was removed under vacuum and the solid residue was dissolved in dry THF. The methoxy(methyl)carbene complex and NEt_3 were then added successively. The solution turned blue. After hydrolysis, extraction with ether, and chromatography (silicagel, eluent: ether/petroleum ether), the blue methylenethiopyran carbene complex **2b** was isolated (32% yield).

For comparison purposes, we performed a reaction in THF at −78 °C with the air sensitive 2,6-diphenylthiopyrylium tetrafluoroborate and the carbanion formed by BuLi



1a $R_1 = R_3 = Ph$, $R_2 = H$, X = Te
1b $R_1 = R_3 = Ph$, $R_2 = H$, X = S
1c $R_1 = Ph$, $R_2 = R_3 = (CH)_4$, X = S

1'a

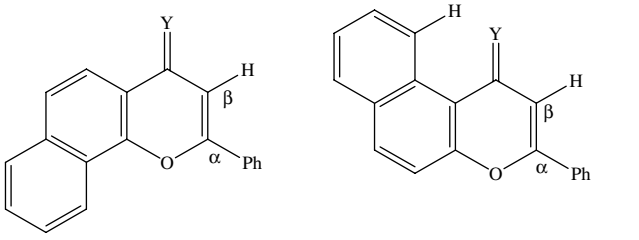
2a
2b
2c

Scheme 2. Chalcogenomethylenepyran and benzomethylenepyran carbene complex formation.

action on the $CH_3(OCH_3)CW(CO)_5$ complex [6]. Subsequent addition of $Ph_3C^+BF_4^-$ salt gave **2b** in very low yield (5%) (Scheme 1). This result emphasized on the efficiency of the pyrone and benzopyrone route.

The ^1H NMR spectra (500 MHz, THF-d_8) of **2a**, **2b** displayed three singlets, characterizing H_β, $H_{\beta'}$ and H_δ. As previously reported for the analogous pyran complex (Scheme 2, $R_1 = Ph$, $R_2 = H$, $R_3 = Ph$, $X = O$) [6], the H_β is more deshielded than the $H_{\beta'}$ due to the presence of the carbene fragment. (δH_β: 8.13 ppm, X = O [6]; **2b**: 8.55 ppm, X = S; **2a:** 8.61 ppm, X = Te; $\delta H_{\beta'}$: 8.09 ppm, X = O [6]; **2b**: 7.34 ppm, X = S; **2a**: 7.34, X = Te).

The reaction was extended to the commercially available 2-phenylthiobenzopyrone **1c** (Scheme 2) and to 2-phenyl α-naphthopyrone **1d** (Fig. 1) without any experimental modification. The expected complexes **2c** (Scheme 2) and **2d** (Fig. 1), in which the carbene fragment is opposite to the fused benzene ring, were obtained in moderate to good yield (**2c**: 43%, **2d**: 61%). The ^1H NMR spectra of **2c** and **2d** confirmed the stereochemistry assignment. The H_β resonates at 8.52 ppm for **2c** and 8.37 ppm for **2d** in accordance with the carbene fragment influence [6]. Adding excess of methyl trifluoromethanesulfonate to the β naphthopyrone **1e** after heating, led to a fluorescent solution characteristic of the presence of the 2-phenyl-4-methoxynaphthopyrylium salt [9]. However, subsequent addition of the methyl(methoxy)carbene tungsten complex and NEt_3 did not give the expected heterocyclic carbene complex **2e** (Fig. 1). It seems that the presence of a benzenic nucleus near the reactive carbon atom prevents, for steric reasons, the carbanion addition. Such limitation of reactivity is not unprecedented [6]. It was previously observed for a γ-unsubstituted pyrylium salt bearing fused saturated carbon rings. The steric influence on the course of the reaction is also exemplified by the chromone case **1f** (Scheme 3). The lack of substituent in the α position dramatically changed the regioselectivity of the carbanion addition. The unsaturated carbene complex **2f**, obtained from carbanion addition onto the heterocyclic α carbon, followed by a ring opening elimination step, was isolated in low yield (28%). In that case, an uncharacterized insoluble precipitate was also formed.

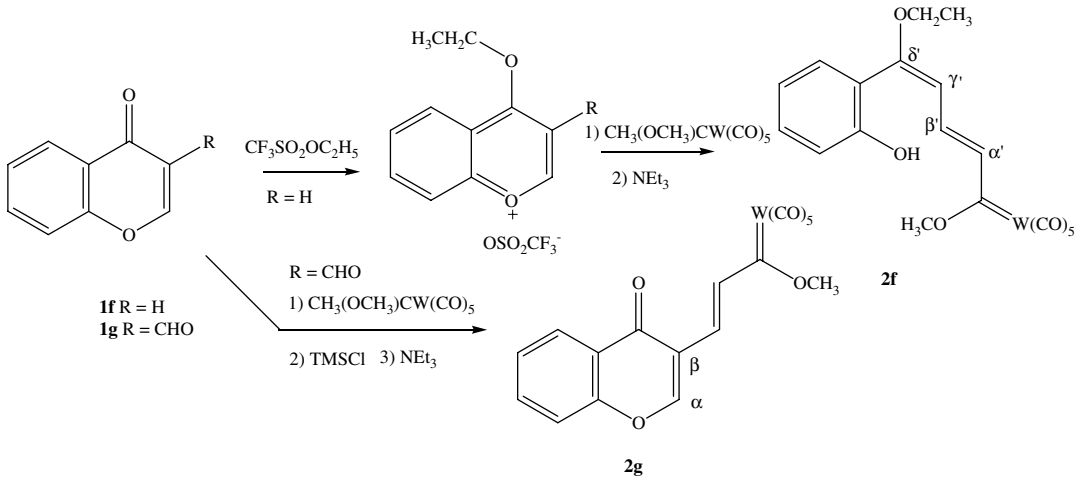


1d, Y = O
2d, Y = CH-C(OCH$_3$)W(CO)$_5$

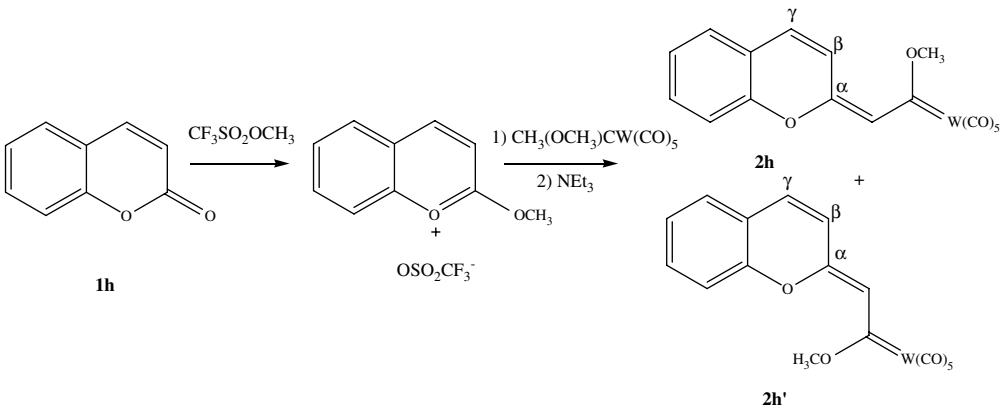
1e, Y = O
2e, Y = CH-C(OCH$_3$)W(CO)$_5$

Fig. 1. α and β naphthopyrones and related carbenes.

The structure of carbene **2f** was confirmed by the ^1H NMR spectrum, which showed a phenolic proton signal at 8.47 ppm (THF_{d8}) and quadruplet–triplet signals characteristic of the ethoxy group [10]. In addition, the alkene hydrogen chemical shift sequence was different from that found for the benzomethylenepyran carbene complexes **2c** and **2d**. In addition, the coupling constant between $H_{\alpha'}$ and $H_{\beta'}$ (14.3 Hz) confirms the trans stereochemistry around the $C_{\alpha'}$ $C_{\beta'}$ double bond. On the other hand, the presence of an aldehyde function in the β position of the benzopyrone **1g** (Scheme 2) seemed to prevent alkylation of the ketone function. Under a prolonged heating influence, a black powder, insoluble in CH_2Cl_2, was only isolated. However, using trimethylsilylchloride (TMSCl) and NEt_3 allowed the formation of the condensation product **2g**, as the result of a reaction between the aldehyde function in **1g** and the carbene carbanion [11]. Finally, we successfully applied the one-pot methylation-carbanion sequences to the coumarin case (Scheme 4). The expected condensation product was isolated as a mixture of isomers



Scheme 3. Reactivity of α-unsubstituted benzopyranones.



Scheme 4. Reactivity of coumarin 1 h.

2h, **2h**′, (60:40%, from ^{1}H NMR spectum, 53% yield). The ^{1}H NMR spectrum of the isomer mixture showed that the alkene β hydrogen is more deshielded for the major isomer (7.69 ppm) than for the minor isomer (6.15 ppm). As exemplified in Scheme 4, in **2h** the β hydrogen is closed to the carbene fragment, which induces a pronounced deshielding effect [6]. It is hardly to be expected that the β hydrogen in **2h** resonates at low field. Consequently structure **2h** was assigned to the major isomer.

3. Conclusion

To summarize, we have described an unprecedented easy access to new heterocyclic methylenechalcogenopyran and methylenechalcogenobenzopyran carbene complexes based on the activation of the commercially available heterocyclic ketones by alkylating reagents and the high reactivity of the intermediate pyrylium salts towards the carbanion of methoxy(methyl)pentacarbonyltungsten carbene. The organometallic carbanion addition was sensitive to the steric strain. For α-substituted heterocycles, γ-addition is observed. After an elimination step, the expected heterocyclic carbene complexes were obtained in moderate to good yield. With unsubstituted benzopyrone **1f**, an α-addition followed by a ring opening step was observed. Finally, this synthetic methodology was successfully applied to the coumarin case.

Pd° self-dimerization of these carbenes should open the route to new extended α and γ-bichalcogenopyrans and benzopyrans.

4. Experimental

General: All preparations involving organometallic methylenepyrans and benzopyrans were carried out in an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard procedure. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or in THF-d_8 on a Brücker spectrometer (500 MHz). Infrared spectra were recorded on a Perkin Elmer spectrometer FTIR-1000 using KBr plates. Elemental Analyses were performed by the Centre Regional de Mesures Physiques de l'Ouest (Université de Rennes 1). Mass spectra were obtained on a high Resolution MS/MS Zab spec Tof micromass (Centre Regional de Mesures Physiques université de Rennes 1). α and γ-pyrones and benzopyrones are commercial products available from Aldrich (except the telluropyrone **1a** [12]).

4.1. General procedure for the preparation of the complexes by activation of the ketone function

Pyrones or benzopyrones were dissolved in an excess of methyl or ethyl trifluoromethanesulfonate (10 equiv.) at 90 °C (water bath). The solution was then heated at 60 °C for 1 h. The excess of the alkylating reagent was removed under vacuum and the obtained solid residue was dissolved in dry THF (10 mL). The methoxy(methyl) carbene complex (1 equiv.) and NEt_3 (2 equiv.) were successively added. The solution turned blue-purple or red. The reaction was monitored by TLC. Cold water was poured into the reaction mixture and the product was extracted with diethyl ether. The extract was dried over magnesium sulfate and the solvent was removed under reduced pressure. After a chromatography on silicagel plates (eluant: petroleum ether/diethylether), the heterocyclic carbene complexes were isolated. For the telluropyrylium **1a** case, the telluropyrylium salt was isolated by adding diethylether in the reaction mixture [9]. In a second step, the telluropyran salt and the carbene were dissolved in THF, followed by NEt_3 addition.

4.2. Synthesis of thiopyran carbene complex *2b* from 2,6-diphenylthiopyrylium tetrafluoroborate salt

At −78 °C, 0.70 mL of a 2.5 M solution of n-BuLi (1.7×10^{-3} mol) were added to a solution of methoxy(methyl)carbene complex (500 mg, 1.3×10^{-3} mol), in dry THF (10 mL), under a N_2 atmosphere. Thiopyrylium salt (1.1 g, 3.3×10^{-3} mol) was then added. The solution was stirred for 1 h at room temperature. Removal of THF, at low pressure, left a dark residue, which was diluted in 20 mL of CH_2Cl_2. Triphenyl carbenium tetra-

fluoroborate (324 mg, 9.8×10^{-4} mol) was then added. Removal of the solvent left a residue, which was subsequently subjected to column chromatography on silicagel using 80/20 v/v petroleum ether/diethyl ether as eluent. Complex **2b** was isolated as purple crystals (44 mg, 5% yield).

4.3. Synthesis of pyran carbene complex 2g from 3-formylchromone

A THF solution made of 3-formyl chromone (454 mg, 2.6×10^{-3} mol), methoxy(methyl)pentacarbonyltungsten carbene complex (1 g, 2.6×10^{-3} mol), trimethylsilylchloride (7.8×10^{-3} mol), and triethylamine (7.8×10^{-3} mol), was stirred at room temperature. The reaction controlled by TLC showed that carbene complex quickly disappeared. Cold water was poured into the orange reaction mixture and the product was extracted with diethylether. The extract was dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographied on silicagel column (Petroleum ether/diethylether 80/20), and **2g** was isolated as red crystals (850 mg, 61% yield).

4.4. Spectroscopic data of carbene complexes

Compound **2a** (Scheme 2): 1028 mg (2×10^{-3} mol) of 4-methoxy-2,6-diphenyltelluropyrylium trifluoromethanesulfonate and 500 mg of methoxy(methyl)pentacarbonylcarbene tungsten complex gave 766 mg of 2a (yield 81%, purple crystals).

^{1}H NMR (THF-d_8, δ (ppm)): 8.61 (s, 1H, H_β), 7.62 (s, 1H, H_δ), 7.61 (m, 4H, H_{Ph}), 7.49 (m, 6H, H_{Ph}), 7.34 (s, 1H, $H_{\beta'}$), 4.58 (s, 3H, OCH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (THF-d_8, δ (ppm)): 292.2 (C(carbene)), 204.9 (CO), 199.4 (CO), 149.6 (C_α), 146.0 ($C_{\alpha'}$), 144.2 (C_δ), 143.7 (C_{Ph}), 143.1 (C_{Ph}), 142.0 (C_γ), 139.9 (C_{Ph}), 130.4 (C_{Ph}), 130.3 (C_{Ph}), 127.7 (C_{Ph}), 127.6 (C_{Ph}), 133.2 ($C_{\beta'}$), 131.3 (C_β), 69.3 (OCH_3). IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 2053, 1979, 1893, 1582, 1570. Anal. Calc. for $C_{25}H_{16}O_6TeW$: C, 41.48; H, 2.23. Found: C, 41.84; H, 2.54%.

Compound **2b** (Scheme 2): 140 mg are obtained from 198 mg of pyrone**1b** (32% yield, purple crystals).

^{1}H NMR (THF-d_8, δ (ppm)): 8.55 (s, 1H, H_β), 7.76 (m, 4H, H_{Ph}), 7.53 (m, 6H, H_{Ph}), 7.35 (s, 1H, H_δ), 7.34 (s, 1H, $H_{\beta'}$), 4.55 (s, 3H, OCH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (THF-d_8, δ (ppm)): 287.1 (C(carbene)), 204.6 (CO), 199.8 (CO), 152.8 (C_α), 150.3 ($C_{\alpha'}$), 139.7 (C_γ), 138.2 (C_{ph}), 137.6 (C_{Ph}), 137.5 (C_δ), 131.6 (C_{Ph}), 131.4 (C_{Ph}), 130.4 (C_{Ph}), 127.4 (C_{Ph}), 127.5 ($C_{\beta'}$), 125.0 (C_β), 68.7 (OCH_3). IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 2054, 1978, 1938, 1895, 1593, 1518. MS (FAB$^+$, $CHCl_3$/CH_3OH, 90/10): m/z (Calc.) ($M^{+\cdot}$) = 629.0255; m/z (Found) ($M^{+\cdot}$) = 629.0221.

Compound **2c** (Scheme 2): 130 mg are obtained from 180 mg of benzopyrone **1c** (yield 43%, purple crystals).

^{1}H NMR (THF-d_8, δ (ppm)): 8.54 (s, 1H, H_β), 8.25 (m, 1H, H_{benzo}), 8.14 (s, 1H, H_δ), 7.76 (m, 2H, H_{Ph}), 7.71 (m, 1H, H_{benzo}), 7.60 (m, 2H, H_{benzo}), 7.52 (m, 3H, H_{Ph}), 4.68 (s, 3H, OCH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (THF-d_8, δ (ppm)): 295.0 (C(carbene)), 204.7 (CO), 199.5 (CO), 148.8 (C_{Ph}), 138.5 (C_α), 137.1 (C_{benzo}), 135.7 (C_{benzo}), 135.2 (C_δ), 131.4 (C_{Ph}), 131.0 (C_{Ph}), 130.2 (C_{benzo}), 130.1 (C_{benzo}), 129.0 (C_γ), 128.4 (C_{benzo}), 127.7 (C_{Ph}), 127.2 (C_{benzo}), 122.8 (C_β), 69.6 (OCH_3). IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 2052, 1970, 1566, 1531, 1487, 1438, 1211. Anal. Calc. for $C_{23}H_{14}O_6SW$: C, 45.87; H, 2.34; S, 5.32. Found: C, 45.89; H, 2.33; S, 5.35%.

Compound **2d** (Fig. 1): 630 mg are obtained from 408 mg of **1d** (yield 66%, purple crystals).

^{1}H NMR (THF-d_8, δ (ppm)): 8.66 (m, 1H, $H_{naphtho}$), 8.37 (s, 1H, H_β), 8.17 (m, 2H, H_{Ph}), 8.06 (d, 1H, $H_{naphtho}$), 8.02 (m, 1H, $H_{naphtho}$), 7.97 (s, 1H, H_δ), 7.93 (d, 1H, ^3J = 9.14 Hz), 7.62 (m, 3H, H_{Ph}), 7.52 (m, 2H, H_{Ph}), 4.69 (s, 3H, OCH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (THF-d_8, δ (ppm)): 291.0 (C(carbene)), 204.6 (CO), 199.8 (CO), 160.1 (C_α), 152.0 ($C_{naphtho}$), 139.3 (C_{Ph}), 136.2 ($C_{naphtho}$), 134.6 ($C_{naphtho}$), 132.3 (C_{Ph}), 130.2 ($C_{naphtho}$); 130.1 (C_{Ph}), 129.7 ($C_{naphtho}$), 129.2 (C_δ), 129.0 ($C_{naphtho}$), 128.6 ($C_{naphtho}$), 127.6 (C_{Ph}), 125.2 ($C_{naphtho}$), 122.9 ($C_{naphtho}$), 120.4 ($C_{naphtho}$) 106.9 (C_β), 67.5 (OCH_3). IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 2053, 1892, 1607, 1556, 1498, 1224. Anal. Calc. for $C_{27}H_{16}O_7W$: C, 50.96; H, 2.53. Found: C, 49.74; H, 2.64%.

Compound **2f** (Scheme 3): 191 mg are obtained from 292 mg of **1f** (yield 28%, red crystals). In this case ethyl trifluoromethanesulfonate was used.

^{1}H NMR (THF-d_8, δ (ppm)): 8.47 (s, 1H, OH), 7.32 (dd, 1H, ^3J = 14.3 Hz, ^3J = 11.6 Hz, $H_{\beta'}$), 7.27 (m, 1H, H_{Ph}), 7.15 (m, 2H, $H_{\alpha'}$ (^3J = 14.3 Hz) and H_{Ph}), 6.86 (m, 1H, H_{Ph}), 6.84 (m, 1H, H_{Ph}), 5.98 (d, 1H, ^3J = 11.6 Hz, $H_{\gamma'}$), 4.36 (s, 3H, OCH_3), 4.11 (q, 2H, OCH_2), 1.27 (t, 3H, CH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (THF-d_8, δ (ppm)): 292.8 (C(carbene)), 204.4 (CO), 199.1 (CO), 172.1 ($C_{\delta'}$), 156.2 (C_{Ph}), 147 ($C_{\beta'}$), 141.4 ($C_{\alpha'}$), 119.0 (C_{Ph}), 116.9 (C_{Ph}), 105.0 ($C_{\gamma'}$), 67.0 (OCH_3), 66.0 (OCH_2), 25.3 (CH_3). IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 3497, 2945, 2063, 1938, 1616, 1588, 1282, 1195, 986. Anal. Calc. for $C_{19}H_{16}OSW$: C, 40.59; H, 2.82. Found: C, 41.03; H, 2.89%.

Compound **2g** (Scheme 3): 850 mg are obtained from 454 mg of **1g** (yield 61%, blue crystals). ^{1}H NMR ($CDCl_3$, δ (ppm)): 8.59 (d, 1H, ^3J = 15.2 Hz, =CH), 8.30 (d, 1H, H_{benzo}), 8.21 (s, 1H, H_α), 7.71 (t, 1H, H_{benzo}), 7.48 (m, 2H, H_{benzo}), 6.99 (d, 1H, J = 15.2 Hz =CH) 4.64 (s, 3H, OCH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (CDCl3, δ (ppm)): 308.3 (C(carbene)), 204.0 (CO), 197.5 (CO), 175.8 (C=O), 157.9 (C_α), 155.2 (C_{benzo}), 145.9 (–CH=), 134.2 (C_{benzo}), 126.5 (C_{benzo}), 126.1 (C_{benzo}), 124.9 (–CH=), 124.1 (C_{benzo}), 119.7 (C_β), 118.2 (C_{benzo}), 69.0 (OCH_3). IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 2066, 1981, 1902, 1643, 1225, 961, 753. MS (LISMS): m/z (Calc.) ($M^{+\cdot}$) = 537.9885; m/z (Found) ($M^{+\cdot}$) = 537.9894.

Compound **2h**, **2h′** mixture of isomers (60/40) (Scheme 4): 540 mg are obtained from 292 mg of coumarin **1h** (yield 53%, red crystals). ^{1}H NMR (THF-d_8, Scheme 3, **2h**, δ (ppm)): 7.74 (d, 1H, $^3J = 10.0$ Hz, Hγ), 7.69 (d, 1H, $^3J = 10.0$ Hz, H_β), 7.59 (m, 1H, H_{Ph}), 7.53 (m, 1H, H_{Ph}), 7.39 (d, 1H, H_{Ph}), 7.26 (s, 1H, CH–C_{carb}), 4.53 (s, 3H, OCH_3). ^{13}C NMR (2D Correlation ^{1}H/^{13}C: HMBC, HMQC) (THF-d_8, **2h**, δ (ppm)): 287.0 (C(carbene)), 204.6 (CO), 199.6 (CO), 156.0 (C_α), 140.2 (C_γ), 133.9 (C_{Ph}), 128.7 (C_{Ph}), 126.1 (C_{Ph}), 124.9 (*C*H–C_{carb}), 122.6 (C_{Ph}), 122.4 (C_{Ph}), 121.1 (C_β), 117.8 (C_{Ph}), 69.0 (OCH_3).

^{1}H NMR (THF-d_8, **2h′**, δ (ppm)): 7.69 (d, 1H, $^3J = 10.0$ Hz, H_γ), 7.59 (m, 1H, H_{Ph}), 7.53 (m, 1H, H_{Ph}), 7.43 (d, 1H, H_{Ph}), 7.32 (m, 1H, H_{Ph}), 6.77 (s, 1H, CH–C_{carb}), 6.75 (d, 1H, $^3J = 10.0$ Hz, H_β), 4.50 (s, 3H, OCH_3).

IR (KBr plate) $\bar{\upsilon}$ (cm^{-1}): 2057, 1894, 1621, 1604, 1555, 1522, 1476. Anal. Calc. for $C_{17}H_{10}O_7W$: C, 40.03; H, 1.98. Found: C, 40.30; H, 2.52%.

Acknowledgement

Financial support by CNRS and by 'Le Conseil Général des Côtes d'Armor et la communauté dagglomération Lannion Trégor' are gratefully acknowledged.

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