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Synthesis of electron donor–acceptor polyunsaturated methylenepyran Fischer type carbene complexes: dynamic ^{1}H-NMR study and solvatochromic properties

F. Robin-Le Guen [a], P. Le Poul [a,1], B. Caro [a,*], R. Pichon [b], N. Kervarec [b]

[a] *Laboratoire de Chimie Organométallique et Biologique, U.M.R. CNRS 6509, I.U.T Lannion, Rue E. Branly, 22300 Lannion, France*
[b] *Service Commun de RMN-RPE, 6 Avenue Le Gorgeu, 29200 Brest, France*

Abstract

Condensation of α and γ methylenepyran aldehydes with the Fischer carbene complexes $(CO)_5M=C(OCH_3)Me$ (M = Cr, W) or $(CO)_5W=C(OCH_3)CH=CH-CH_3$ in the presence of $ClSiMe_3/NEt_3$ yield donor acceptor complexes, in which the electron donating group is connected to the organometallic accepting group by a conjugated ethylenic spacer. ^{1}H- and ^{13}C-NMR studies, suggest that the carbene fragment and the unsaturated chain lie in the same plan, allowing a mesomeric interaction between the oxygen atom of the heterocycle and the metal via the spacer. The positive solvatochromism of the molecules obtained is reported. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to the importance of their physical and chemical properties Fischer type carbene complexes containing an unsaturated side chain have received considerable interest [1]. Very recently unsaturated molecules in which an acceptor amino or methoxypentacarbonyl chromium carbene fragment is linked to an aromatic donor group or an ferrocenyl group via π spacers were synthetized [2]. These so-called 'push pull' molecules have shown to have good non-linear optical properties (NLO). Some of these polarized complexes exhibit in solution large first hyperpolarizability. As ^{1}H- and ^{13}C-NMR studies suggested that the plan containing the carbene fragment and the π system are perpendicular to each other, it was proposed that the non linear response observed is essentially the consequence of the polarization of the unsaturated chain π electrons by the electron

withdrawing inductive effect of the metal carbonyl moiety [2a].

We have reported recently the easy preparation of donor acceptor organometallic compounds by coupling pyrylium salts to carbanions of Fischer type carbene complexes [3] (Scheme 1, $n = 0$, M = Cr or W, Y = OMe or NHEt).

Subsequent insertion of phenylacetylene into the metal–carbon bond has led to new unsaturated Fischer type carbene complexes undirectly stabilized by an heteroatomic group [4] (Scheme 1, $n = 1$ M = W, X = OMe, Y = Ar). These new complexes, which have a pyrylium character, crystallize in a non centrosymmetric space group and exhibit a large negative solvatochromism suggesting that they are good candidates for NLO. This fact and the results of a recent theoretical study, which focus the attention on the importance of pyrylium–methylenepyran duality for NLO purposes [5], encourage us to perform the synthesis of new 'push pull' structure in which a donor α or γ methylenepyran heterocyclic group is connected with the acceptor organometallic fragment by conjugated ethylenic linkages. As the marked differences in the UV–vis spectrum on varying the solvent [6] is a good indicator of

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* Corresponding author. Tel.: +33-2-96485748; fax: +33-2-96485797.

E-mail address: b.caro@iut-lannion.fr (B. Caro).

[1] Present address: Laboratoire de Chimie Organométallique et Biologique, U.M.R. CNRS 6509, Université Catholique de l' Ouest, 22200 Guingamp, France.

the potential NLO efficiency [7], we report the solvatochromic behavior of the molecules obtained. A ^{1}H- and ^{13}C-NMR study, including variable temperature experiments, was also performed to investigate the conformational requirements of these unsaturated π systems.

2. Results and discussion

To obtain the expected 'push pull' structure we chose first to oppose at low temperature (195 K) the carbanion **2a**, produced by *n*-BuLi action on **1a**, to the readily available iminium salt **3a** (X = (CH₃)₂N⁺−) [8].

After hydrolysis and purification by chromatography (silica gel, petroleum ether–diethylether), the intense blue condensation product **4a** was isolated in 28% yield (Scheme 2).

To improve the yield, we tested the modified Peterson procedure, applied by Auman et al. to aromatic

aldehydes and the carbenes **1a** and **1b** [9]. As expected, using the aldehyde **3b** (mixture of isomers) [8] and the carbene **1a** in the presence of triethylamine and trimethylsilylchlorosilane afforded **4a** in 57% yield (Scheme 2).

The reaction was extended without any modification to γ-Methylenepyran aldehyde **3c** (Scheme 3). In this case the unsaturated carbene **4b** was isolated in 65% yield. Subsequent aminolysis of **4b** with piperidine gave **5** (55% yield).

To obtain molecules with more extended π linker, we tried a condensation reaction between the allylic carbanion, corresponding to the propenyl carbene **6**, and the aldehyde **3c** (Scheme 4). Unfortunately an attempt to form the unsaturated carbene **4d**, through the use of *n*-BuLi as base, the carbene **6** and aldehyde **3c** failed.
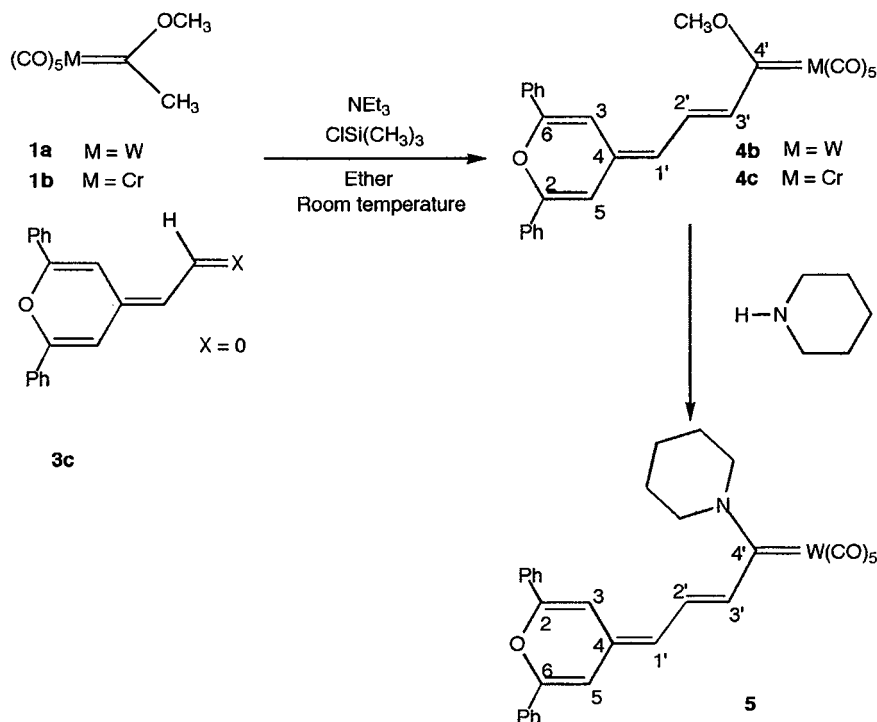
Again the Auman reaction allowed us to isolate the unsaturated carbene complex **4d** in good yield. To the best of our knowledge the use of this synthetic procedure for the condensation of allylic carbanions of Fis-

n = 0　　(M=Cr or W; Y=OMe or NHEt)
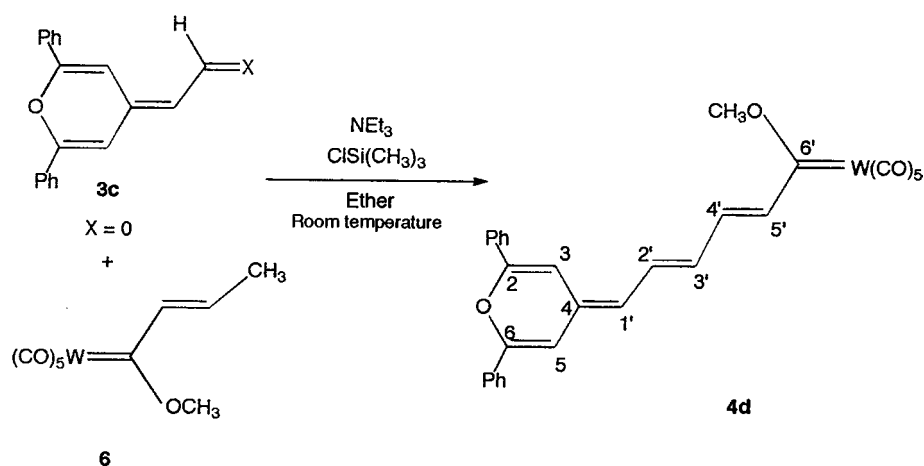
n = 1　　(M=W; X=OMe; Y=Ar)
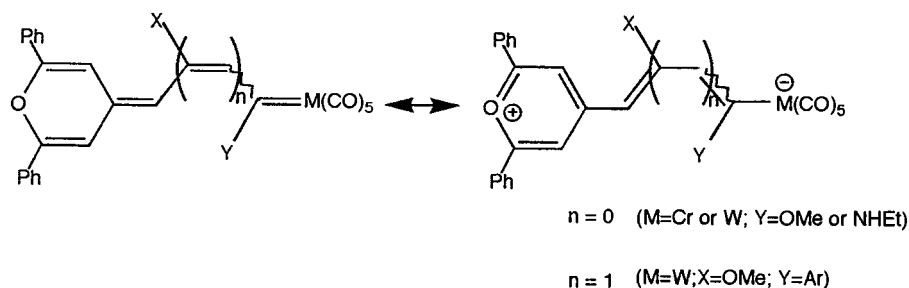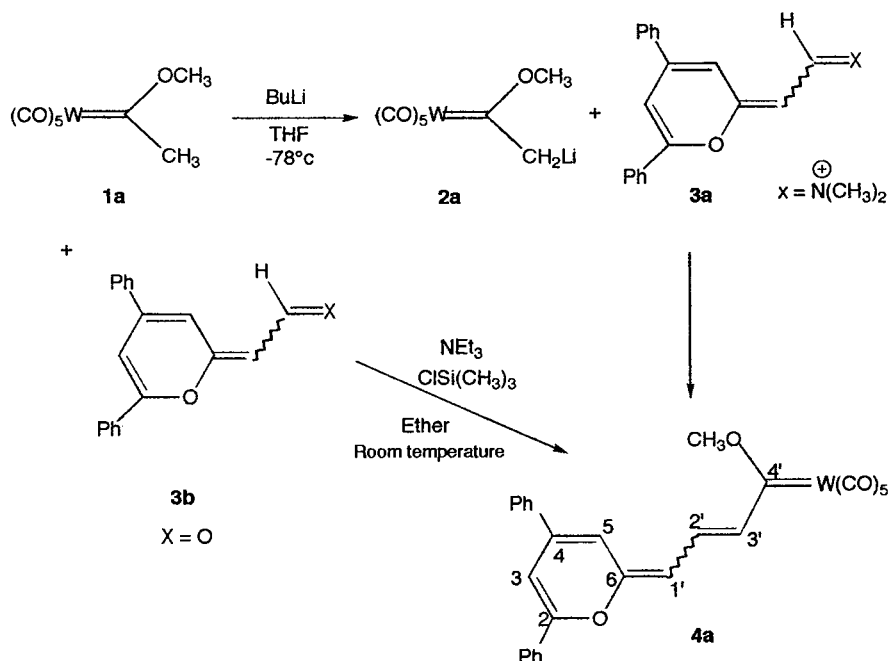
Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

cher type carbene complexes with aldehydes is unprecedented.

Finally, access to the chromium carbene **4c** was achieved by coupling the aldehyde **3c** with the carbene **1b** (57% yield) (Scheme 3).

The new complexes **4a**–**d** and **5** are characterized by FTIR, ^{1}H- and ^{13}C-NMR (including 2D experiments) and mass spectrometry. J_{HH} coupling constants (13.3 Hz (**4a**); 13.4 Hz (**4b**); 13.4Hz (**4c**); 13.0 Hz (**4d**), are consistent with a *trans* configuration for the new carbon–carbon double bonds formed.

The methoxycarbenes **4a**–**d** are deep blue crystals and their solution in CH_2Cl_2 are highly blue colored.

As for similar complexes EHMO calculations have shown that the HOMO is mainly localized on the metal and the LUMO on the unsaturated organic ligand [4], the blue color as attributed to the MLCT transition.

This fact would suggest that a π overlap exists in the ground state between the carbenic fragment and the oxygen atom of methylenepyran group via the spacer. As a consequence the pyrylium resonance structure contributes to a certain extent to the electronic description of the complexes (Scheme 1). These conclusions are in sharp contrast with those proposed by others for monoalkenyl [10] and polyalkenyl [2] methoxy and amino Fischer type carbene complexes in which, in

solution, the predominance of a perpendicular conformation prevents π conjugation between the metal carbonyl carbene fragment and the unsaturated spacer. As a consequence, the MLCT transition has higher energy and as expected for the predominance of the electronic inductive effect, the ^1H and ^{13}C shifts of the α proton and α carbon, directly linked to the carbenic carbon atom appear lowfield from the shifts of the β proton and β carbon. For the methylenepyran complexes reported here, the opposite trend observed, i.e. δ H_α and $C_\alpha < \delta$ H_β and C_β, is indicative again of the predominance of planar conformations which allows a mesomeric interaction between the carbene fragment and the oxygen atom of the methylenepyran group via the spacer. Supplementary information was obtained from variable temperature ^1H-NMR experiments performed on a THF-d_8 solution of **4b**. Lowering the temperature results in a coalescence phenomena ($T_c = 204$ K). At 188 K, indicative of the existence of two conformational isomers, the ^1H-NMR spectrum shows two sets of signals of different intensity. From the chemical shift values and NOE experiments, we attributed this coalescence phenomena to a hindered rotation around the C3′–C4′ bond, allowing at low temperature (188 K) the observation of quasi planar s-*cis*/s-*trans* isomers with a ratio of 83/17%. Similar NMR trends were observed for the chromium carbene complex **4c** ($T_c = 191$ K, 59/41% s-*cis*/s-*trans*) and for the more extended π spacer complex **4d** ($T_c = 208$ K, 77/23% s-*cis*/s-*trans*). These results are in accordance with a previous ^1H-NMR study relative to a β-aminoalkenyl (ethoxycarbene)complex for which the s-*cis*/s-*trans* isomers are detected at 298 K. In this case the intense mesomeric interaction between the amino group and the metal atom in a planar conformation increases the double bond character of the $C_{carbenic}$–$C_{ethylenic}$ bond [11].

It is noteworthy that the presence of the better electron donor amino group in **5** prevents the observation of the coalescence phenomena. Thus, lowering the temperature only changes the high field part of the ^1H-NMR spectrum. This observation is probably due to a dynamic behavior relative to the amino heterocycle.

As for molecular structures with electron donating groups and electron accepting groups linked through some conjugated π electron systems, there is a connection between solvatochromism and NLO properties [7], we have finally investigated the electronic spectra of **4a**–**d** and **5** in two solvents of different polarity.

In Table 1, we have reported the long wavelength absorption band values corresponding to the MLCT transition in DMSO and CCl₄. A positive solvatochromism, i.e. a red shift when the solvent polarity is increased, is observed for **4a**–**d**.

This positive solvatochromism indicates for these complexes an excited state more stabilized than the ground state, due to solvatation by solvents of increasing polarity. An opposite effect (negative solvatochromism) has been found for a similar unsaturated complex than **4b** in which the carbenic carbon bears a phenyl group (Scheme 1, $n = 1$, M = W, X = OMe, Y = Ph) [4]. In this case a strong intramolecular charge transfer occurs and the molecule is much more polarized than **4b** in the ground state (more pyrylium character).

3. Conclusion

In summary, we have described the easy synthesis of electron donor acceptor polyunsaturated methylenepyran Fischer type carbene complexes by coupling carbanions and allylic carbanion of Fisher type carbene complexes with α and γ pyranylideneacetaldehyde. The complexes obtained exhibit in the visible region of the electronic spectrum a strong absorption band corresponding to a MLCT transition. This observation and the results of ^1H-NMR experiments are in favor of the predominance of planar conformations with some ground state contribution for a dipolar resonance form.

Further works are under way to obtain complexes with more extended π linker, and more detailed results concerning the solvatochromic properties of these molecules will be published later.

Table 1
UV–vis data for complexes **4**–**5**

Compounds	λ(DMSO) (nm)	ε(DMSO) (l mol^{-1} cm^{-1})	λ(CCl₄) (nm)	ε(CCl₄) (l mol^{-1} cm^{-1})	$\Delta\lambda = \lambda$(DMSO) $- \lambda$(CCl₄) (nm)
4a	657	18 920	619	12 840	38
4b	590	26 560	569	10 965	21
4c	592	14 440	580	9545	12
4d	653	23 020	594	7610	59
5	442	20 110	460	8500	−18

bottom-border > −18

4. Experimental

4.1. Materials and methods

Synthesis and manipulation were carried out under nitrogen using Schlenk techniques. IR spectra were measured with Perkin–Elmer 1000 FTIR.^{1}H- and ^{13}C-NMR spectra were recorded in THF-d_8 with a Bruker 500, UV–vis absorption spectra were taken on a Secomam 750 spectrophotometer. Mass spectra were performed on MS/MS Zab-Spec TOF micromass.

4.2. Synthesis

4.2.1. (1) General procedure for the synthesis of methoxyalkenylcarbene complexes 4a–d

A solution of the aldehyde 3b or 3c (1.04×10^{-3} mol) with one equivalent of the methoxycarbene 1a, 1b or 6 and three equivalents of $(CH_3)_3SiCl/(C_2H_5)_3N$ in 20 ml of diethylether was stirred at room temperature (r.t.). The reaction controlled by TLC showed quickly disappearance of the starting carbene complex. Water was poured on to the reaction blue 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 chromatographed on silica gel columm (elution:petroleum ether/diethyl ether (80/20%)) afforded, after evaporation of solvent, the condensation products 4a–d.

4.2.2. (2) Procedure using the iminium salt and the carbanion of carbene complexes: synthesis of α-methoxyalkenylcarbene 4a

To a solution of carbanion 2a (8.5×10^{-4} mol) in THF, obtained from the carbene complex 1a and BuLi at $-80°C$ was added one equivalent of the iminium salt 3a at $-80°C$. The blue mixture is warmed up to r.t. After hydrolysis, extraction by diethylether, drying over $MgSO_4$ and purification by silica gel columm, a blue powder of carbene complex 4a was obtained.

4.2.3. (3) Synthesis of aminocarbene complex 5

A solution of methoxyalkenyltungsten carbene 4b (3.13×10^{-4} mol) in 15 ml of diethylether was treated with a large excess of piperidine at $-60°C$ until the solution became red. After flash chromatography on Celite and recrystallization, a red solid 5 was obtained.

4a (28% procedure (2) and 57% yield procedure (1)): two isomers 82/18% at 298 K. ^{1}H-NMR: major δ: 4. 28 (s, 3H, –OCH$_3$); 5.89 (d, 1H, $^3J = 13.3$ Hz, H(1′)); 6.94 (d, 1H, $^3J = 13.3$ Hz, H(3′)); 7.05 (s, 1H, H(5)); 7.26 (s, 1H, H(3)); 8.41 (dd, 1H, $^3J = 13.3$ Hz, $^3J = 13.3$ Hz, H(2′)). Minor δ: 4.30 (s, 3H, –OCH$_3$); 6.12 (d, 1H, $^3J = 13.4$ Hz, H(1′)); 7.05 (d, 1H, $^3J = 13.4$ Hz, H(3′)); 7.26 (s, 1H, H(5)); 7.52 (H(3)); 8.17 (t, 1H, $^3J = 13.4$ Hz, H(2′)). Major + minor δ: 7.51 (m, 12H, H(Ph));

7.82 (m, 4H, H(Ph)); 7.97 (m, 4H, H(Ph)). ^{13}C-NMR: major δ: 67.4 C(OCH$_3$); 104.5 C(3); 105.7 C(1′); 117.7 C(5); 126.5 C(Ph); 127.2 C(Ph); 129.9 C(Ph); 130.0 (Ph); 130.0 C(Ph); 132.4 C(Ph); 135.3 C(3′); 136.5 C(4); 147.3 C(2′); 160.0 C(2); 165.6 C(6); 200.2 C($J_{CW} = 63$ Hz CO); 204.7 C(CO); 285.7 C(4′). Minor δ: 64.6 C(OCH$_3$); 112.6 C(5); 126.4 C(Ph); 127.4 C(Ph); 131.5 C(Ph); 132.2 C(Ph); 149.3 C(2′); 159.8 C(2); 168.1 C(6); C(CO) not observed; 283.7 C(4′). IR (KBr) v (cm^{-1}): 2055, 1920, 1890, 1630, 1562, 1480. MS (FAB, mNBA) m/z (%) = 638.0562 (Calc.); 638.0563 (Found) [M$^+$].

4b (65% yield): ^{1}H-NMR δ: 4.40 (s, 3H, –OCH$_3$); 5.99 (d, 1H, $^3J = 13$ Hz, H(1′)); 7.00 (s, 1H, H(5)); 7.12 (d, 1H, $^3J = 13.4$ Hz, H(3′)); 7.40 (s, 1H, H(3));7.51 (m, 4H, H(Ph)); 8.06 (dd, 1H, $^3J = 13.4$ Hz, $^3J = 13.0$ Hz, H(2′)). ^{13}C-NMR δ: 67.4 C(OCH$_3$); 104.3 C(3); 110.7 C(5); 115.4 C(1′); 126.2 C(Ph); 126.4 C(Ph); 129.9 C(Ph); 131.6 C(Ph); 131.7 C(Ph); 133.0 C(Ph); 132.8 C(Ph); 139.6 C(3′); 142.5 C(2′); 147.5 C(4); 157.3 C(6); 157.6 C(2); 204.7 C (t, $J_{CW} = 61$ Hz, CO); 199.9 C (t, $J_{CW} = 63$ Hz, CO); 289.8 C (t, $J_{CW} = 49$ Hz, 4′).

4b, two isomers 83/17% at 188 K. ^{1}H-NMR δ: major δ: 4.50 (s, 3H, –OCH$_3$); 5.90 (d, 1H, $^3J = 12.7$ Hz, H(1′)); 7.31 (s, 1H, H(5)); 7.61 (m, H(Ph)); 7.44 (d, 1H, $^3J = 13.2$ Hz, H(3′)); 7.80 (s, 1H, H(3)); 7.93 (dd, 1H, $^3J = 13.2$ Hz, $^3J = 12.7$ Hz, H(2′)), 8.13 (m, H(Ph)). Minor δ: 4.08 (s, 3H, –OCH$_3$); 6.40 (d, 1H, $^3J = 12.6$ Hz, H(1′)); 6.93 (d, 1H, $^3J = 12.2$ Hz, H(3′)); 8.70 (dd, 1H, $^3J = 12.2$ Hz, $^3J = 12.6$ Hz, H(2′)). IR (KBr) v (cm^{-1}): 2052, 1890, 1635, 1518, 1491. MS (FAB, mNBA) m/z (%) = 638.0562 (Calc.); 638.0564 (Found) [M$^+$].

4c (60% yield): ^{1}H-NMR δ: 4.46 (s, 3H, –OCH$_3$); 6.01 (d, 1H, $^3J = 12.8$ Hz, H(1′)); 7.03 (d, 1H, $^4J = 1.5$ Hz, H(5)); 7.15 (d, 1H, $^3J = 13,4$ Hz, H(3′)); 7.42 (d, 1H, $^4J = 1.5$ Hz, H(3)); 7.52 (m, 6H, H(Ph)); 7.96 (m, 4H, H(Ph)); 8.02 (dd, 1H, $^3J = 12.8$, $^3J = 13.4$ Hz, H(2′)). ^{13}C-NMR δ: 67.4 C(OCH$_3$); 104.0 C(3); 110.5 C(5); 115.2 C(1′); 126.2 and 126.4 C (m-Ph); 129.8 C(Ph); 131.5 C(Ph); 131.7 C(Ph); 135.5 C(3′); 132.8 C(Ph); 133.0 C(Ph); 147.4 C(4); 141.8 C(2′); 157.2 C(6); 157.5 C(2); 219.4 C(CO); 225.6 C(CO); 313.6 (C4′). IR (KBr) v (cm^{-1}): 2043, 1898, 1654, 1545, 1492, 1210. MS (FAB, mNBA) m/z (%) = 506.0458 (Calc.); 506.0460 (Found) [M$^+$].

4d (55% yield): ^{1}H-NMR δ: 4.47 (s, 3H, OCH$_3$); 5.97 (d, 1H, $^3J = 12.5$ Hz, H(1′)); 6.33 (t, 1H, $^3J = 13$ Hz, H(3′); 6.83 (s, 1H, H(3); 7.21 (d, 1H, $^3J = 14$ Hz, H(5′)); 7.31 (s, 1H, H(5); 7.42 (dd, $^3J = 14$ Hz, $^3J = 13$ Hz, H(4′)); 7.46 (m, 6H, H(Ph)); 7.72 (dd, 1H, $^3J = 12.5$ Hz, $^3J = 13$ Hz, H(2′)); 7.95 (m, 4H, H(Ph)). ^{13}C-NMR δ: 67.5 C(OCH$_3$); 104.0 C(5); 110.0 C(3); 117.5 C(1′); 125.8 C(Ph); 126.1 C(Ph); 127.6 C(3′); 130.9 C(Ph); 131.0 C(Ph); 133.3 C(Ph); 133.5 C(Ph); 139.8 C(4); 142.6 C(5′); 146.0 C(2′); 144.6 C(4′); 155.4 C(6); 155.7 C(2); 199.3 C(CO); 204.7 C(CO); 294.9 C(6′). IR (KBr)

v (cm^{-1}): 2055, 1907, 1651, 1548, 1503. MS (FAB, mNBA) m/z (%) = 664.0719 (Calc.); 664.0723 (Found) [M$^+$].

5 (55% yield): ^{1}H-NMR δ: 1.73–1.92 (m, 6H, CH$_2$); 4.00 (s, 2H, N–CH$_2$); 4.34 (s, 2H, N–CH$_2$); 5.76 (d, 1H, ^3J = 9.4 Hz, H(1′); 6.59 (s, 1H, H(5)); 6.62 (dd, 1H, ^3J = 9.8 Hz, ^3J = 9.4 Hz, H(2′); 6.65 (d, 1H, ^3J = 9.8 Hz, H(3′)); 6.92 (s, 1H, H(3)); 7.42 (m, 6H, H(Ph)); 7.80 (m, 4H, H(Ph)). ^{13}C-NMR δ: 25.5 C(CH$_2$); 28.5 C(CH$_2$); 28.8 C(CH$_2$); 54.5 C(N–CH$_2$); 64.9 C(N–CH$_2$); 102.6 C(3); 108.8 C(5); 114.8 C(1′); 125.3 C(Ph); 125.6 C(Ph); 126.8 C(3′); 129.4 C(Ph); 130.0 C(Ph); 130.3 C(Ph); 133.9 C(Ph); 134.1 C(4); 137.9 C(2′); 152.4 C(6); 153.4(2); 199.8 C (t, J_{WC} = 127.8 Hz, CO); 204.0 C(CO); 244.1 C(4′). IR (KBr) v (cm^{-1}): 2056, 1970, 1916, 1879, 1655, 1506. MS (FAB, mNBA) m/z (%) = 691.1191 (Calc.); 691.1203 (Found) [M$^+$].

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