

Synthesis of bis-2*H* and 4*H*-chalcogenapyrans and benzochalcogenapyrans via Pd⁰ catalyzed dimerization of Fischer type carbene complexes: redox properties and electronic structure of these new extended electron rich molecules

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Abstract—Extended electron rich bis-chalcogenapyrans and bis-benzochalcogenapyrans have been synthesized by Pd⁰ catalyzed dimerization of α - and γ -methylene chalcogenapyran and benzochalcogenapyran Fischer type carbene complexes. Voltammetric studies performed on these molecules show a single two-electron wave around 0 V versus SCE, which is ascribed to the oxidation of the neutral form in radical and dipyrilium cations. DFT calculations show that the oxidation leads to a rotating movement around the central C–C bond and suggest that the solvent plays a major role in the observation of the two one-electron systems. Furthermore, according to the structure, these molecules are likely to be reduced at very low potential ($E = -1.5$ V vs SCE) via a two-electron transfer reaction.

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1. Introduction

The discovery of charge transfer complex (CT) of tetrathiafulvene (TTF) and tetracyanoquinodimethane (TCNQ) as the first organic synthetic metal was the starting point of intense research in the organic conductor area.¹ To make new charge transfer complexes with interesting properties in conductivity and superconductivity, a great variety of molecular and supramolecular structures formed by the association of TTF or dithiafulvene cores and their ‘group 16’ analogs have been synthesized.² Several TTF derivatives have also been studied for their role as donors in active chromophores for third and second order non-linear optics.³ In addition, their redox properties and great stability have found applications in the field of sensors,⁴ organic magnets,⁵ and molecular machines.⁶

Bis-4*H*-chalcogenapyrans **A** and benzochalcogenapyrans **A'**⁷ (Fig. 1), whose electronic molecular properties are analogous to those of the electron donor TTF (14 π -electron system of planar symmetry), have attracted less attention, because the bistiopyran (BTP) forms a less conductive charge transfer complex with TCNQ.⁸ Hybrid electron donors of dithiafulvene and pyran **B** behave similarly (Fig. 1).^{2d,9} Conjugated and highly conjugated **C** (Scheme 1), 4,4'-bis-(4*H*-pyrans and thiopyrans) separated by ethandiyliene groups have also been studied. The voltammetric analysis showed a coalescence of the reversible oxidation waves as the conjugation length is increased (Scheme 1; R=H; **C** gives $C^{+\cdot}$ and $C^{+\cdot}$ gives reversibly C^{2+} in two one-electron waves for $n=0$ and in a single two-electron wave for $n=1, 2$).¹⁰ This behavior was attributed to reduced intramolecular coulombic repulsion in C^{2+} as the length of the unsaturated linkage separating the pyrylium or thiopyrylium rings is extended. Very recently, density functional calculations performed on symmetrical polyconjugated systems (β -carotene and models) indicated a localization of the mono-charges of the dication at each end of the molecule. This charge localization provides additional stabilization by favoring species solvation, leading to potential

Keywords: Fischer type carbene complexes; Bispyrans; Cyclic voltammetry; DFT calculations.

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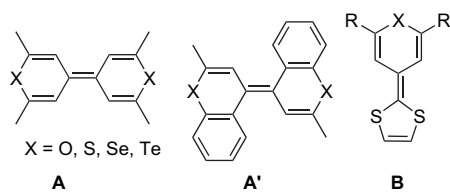


Figure 1. 4*H*-Chalcogenapyrans **A**, benzochalcogenapyrans **A'**, and hybrid electron donors of dithiafulvene and pyran **B**.

inversion (i.e., the $C^{+•} \rightarrow C^{2+}$ reaction is thermodynamically easier than the $C \rightarrow C^{+•}$ reaction). This is well characterized in voltammetry by a single two-electron system. It was suggested that these findings could be applied to the bispyran and bisbenzopyran cases.¹¹

Similar results have been reported for extended TTF derivatives. In several cases, potential inversion is explained by the structural changes between the neutral and oxidized forms. For instance, when the dithiole moieties are attached to the central benzene rings of an anthracene linker, steric repulsions, which decrease the aromaticity of the neutral form **D** (Fig. 2), favor the observation of a single wave.¹² For the same reasons (steric strain in the neutral form) α -thioxanthanyl-4*H*-pyran **E** was reported to exhibit a single reversible two-electron oxidation wave (Fig. 2).¹³

Recently, we have reported an easy access to 'push-pull' γ - and α -methylene chalcogenapyran and benzopyran Fischer type carbene complexes.¹⁴ Higher vinylologues were obtained from a modified Peterson condensation between chalcogenapyranylidene or benzopyranylidene acetaldehyde, and methyl and propenyl (methoxy)pentacarbonyltungsten carbene complexes.¹⁵ The NLO properties of these 'push-pull' molecules have been determined by EFISH measurements. Large positive $\mu\beta$ have been found depending on the chalcogen atom and the length of the unsaturated chain.¹⁶ We anticipated that the self dimerization of these metal carbonyl stabilized carbenes would provide a convenient way to obtain pyran nuclei separated by electron rich polyene linkage.¹⁷ These highly electron rich molecules are likely to be oxidized at low potential (≈ 0 V vs SCE) to form radical and dipyrilium cations, and may be good

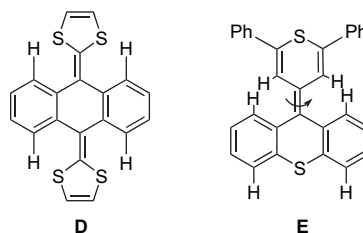


Figure 2. Steric repulsions in polycyclictetrathiafulvene **D** or α -thioxanthanyl-4*H*-pyran **E**.

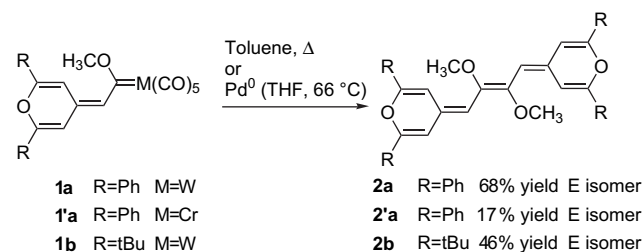
precursors of charge transfer complexes with interesting electric and magnetic properties.

In this paper we have focused on the synthesis and electrochemical properties of these new electron rich molecules. The electronic structure of the neutral, cationic, dicationic, anionic, and dianionic forms have been obtained from DFT calculations. The role of the solvent in the oxidation process has also been investigated.

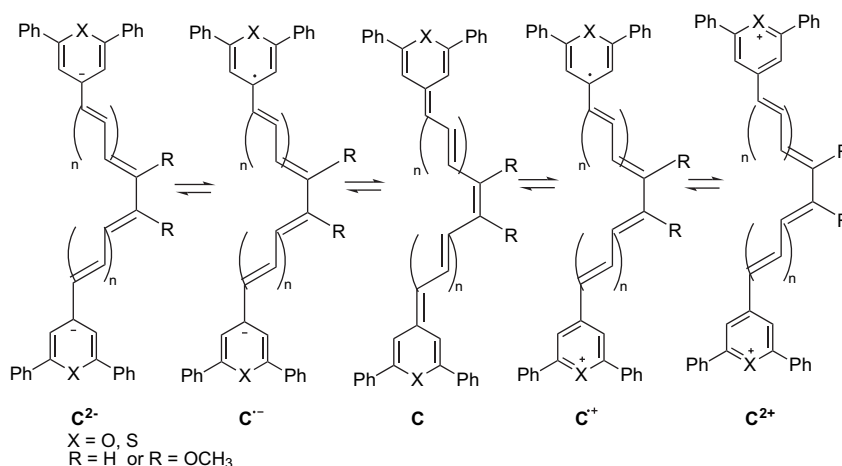
2. Results and discussion

2.1. Synthesis of bis-chalcogenapyran¹⁸

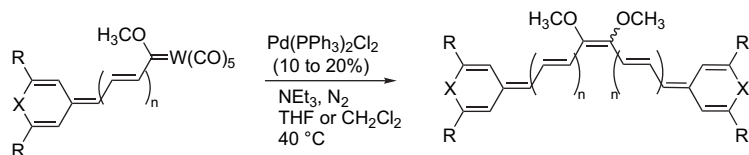
The first attempt of access to bis-4*H*-pyran was carried out by reacting the 2,6-diphenylmethylene pyran carbene complex **1a** in boiling toluene¹⁷ (Scheme 2). Unfortunately the expected product **2a** could not be isolated due to the presence of several other products in the reaction mixture (TLC observation). Our attention was drawn to a recent study of Sierra



Scheme 2. Synthesis of bispyrans **2a** and **2b**.



Scheme 1. Electrochemical oxidation and reduction of 4*H*-chalcogenapyrans.



1c	X=O*	R=Ph	n=1	2c	X=O	R=Ph	n=1	48% yield	E/Z : 90/10%
1d	X=O	R=Ph	n=2	2d	X=O	R=Ph	n=2	60% yield	E isomer
1e	X=O	R=tBu	n=1	2e	X=O	R=tBu	n=1	42% yield	E/Z : 90/10%
1f	X=S	R=Ph	n=1	2f	X=S	R=Ph	n=1	30% yield	E/Z : 90/10%
1g	X=S	R=Ph	n=2	2g	X=S	R=Ph	n=2	60% yield	E/Z : 89/11%
1h	X=Te	R=Ph	n=0	2h	X=Te	R=Ph	n=0	14% yield	E/Z : 80/20%
1i	X=Te	R=Ph	n=1	2i	X=Te	R=Ph	n=1	44% yield	E/Z : 91/9%

* In this case Pd(PPh₃)₄ was used as catalyst (see text)

Scheme 3. Catalyzed dimerization of complexes **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, and **1i**.

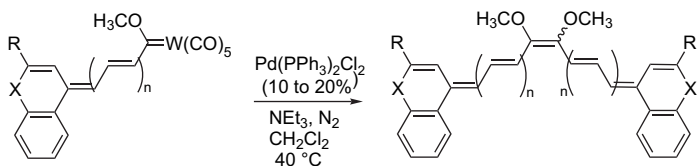
et al., which showed that Pd⁰ complexes or Pd(II) complexes in the presence of triethylamine are efficient catalysts for room temperature self dimerization of aryl substituted and unsaturated Fischer carbene complexes via a mechanism in which a transmetallation (Cr or W to Pd) and the formation of a Pd bis-carbene seem to play a key role.¹⁹

Consequently, carbene **1a** was first reacted in THF at 66 °C with Pd(PPh₃)₄ as catalyst (10% molar ratio). As expected, a rapid reaction occurred leading to the electron rich bispyran **2a** (68% yield: *E* isomer detected by ¹H NMR spectroscopy).

Lower yield of **2a** was obtained from the corresponding chromium carbene complex **1'a** (17% yield, **Scheme 2**).

The tetratertibutylbispyran derivative **2b** was obtained similarly from the carbene **1b**. On the other hand, using Pd(PPh₃)₂Cl₂, N(Et)₃ as a catalytic system, which requires a lower temperature (40 °C in THF), we extended the reaction to higher vinylologues of **1a** and **1b** and to the corresponding thio and telluro heterocyclic tungsten carbene complexes¹⁵ (**Scheme 3**). Bis-4*H*-chalcogenapyrans (**2c–i**) were obtained in low-to-moderate yield. In all cases (except for **1d**, which gave only the isomer), the *E* and *Z* isomers could not be separated.

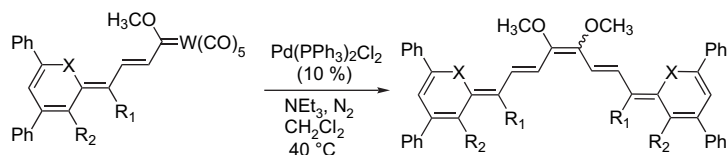
For **1c**, under these conditions, the catalytic dimerization leads to a mixture of the expected bispyran **2c** (two isomers *E/Z*, 90:10) together with a small amount of a product detected by mass spectroscopy analysis (*m/z*: 596.2331).



3a	X=O	R=Ph	n=0	4a	X=O	R=Ph	n=0	90% yield	E isomer
3b	X=O	R=Th	n=0	4b	X=O	R=Th	n=0	85% yield	E isomer
3c	X=O	R=tBu	n=1	4c	X=O	R=tBu	n=1	34% yield	E/Z : 89/11 %
3d	X=O	R=Ph	n=1	4d	X=O	R=Ph	n=1	9% yield	E/Z : 89/11%
3e	X=S	R=Ph	n=1	4e	X=S	R=Ph	n=1	55%yield	E/Z : 87/13%

Ph = Phenyl, Th = Thienyl, tBu = tertibutyl

Scheme 4. Catalyzed dimerization of complexes **3a**, **3b**, **3c**, **3d**, and **3e**.



5a	X=O	R ₁ = R ₂ = -CH ₂ -CH(tBu)-CH ₂ -	6a	X=O	R ₁ = R ₂ = -CH ₂ -CH(tBu)-CH ₂ -	80% yield	E/Z : 94/6%
5b	X=O	R ₁ = R ₂ = H	6b	X=O	R ₁ = R ₂ = H	80% yield	E/Z : 90/10%
5c	X=S	R ₁ = R ₂ = -CH ₂ -CH(tBu)-CH ₂ -	6c	X=O	R ₁ = R ₂ = -CH ₂ -CH(tBu)-CH ₂ -	85% yield	E/Z : 83/17%
5d	X=S	R ₁ = R ₂ = H	6d	X=O	R ₁ = R ₂ = H	61% yield	E/Z : 90/10%

Scheme 5. Catalyzed dimerization of complexes **5a**, **5b**, **5c**, and **5d**.

Table 1. Voltammetric data at 0.02 V s⁻¹ of compounds **4a**, **4c**, **4d**, and **4e**

	X	R	Y=OCH ₃			Y=H	
			<i>n</i>	<i>E</i> ₁ ⁰ /V (Δ <i>E</i> _p /mV)	<i>E</i> ₂ ⁰ /V (Δ <i>E</i> _p /mV)	<i>E</i> ₁ ⁰ /V (Δ <i>E</i> _p /mV)	<i>E</i> ₃ ⁰ /V (Δ <i>E</i> _p /mV)
2a	O	Ph	0	0.07 (47) ^c	^a	0.19 (60) ^d	0.39 (60) ^d
2b	O	<i>t</i> -Bu	0	0.00 (49) ^c	^a		
2c	O	Ph	1	0.07 (47) ^c	^a	0.17 (40) ^d	
2e	O	<i>t</i> -Bu	1	-0.02 (55)	^a		
2f	S	Ph	1	0.02 (67)	-1.71 (233) ^b	0.21 (40) ^d	
2g	S	Ph	2	0.02 (46)	-1.53 (57)	0.19 (50) ^d	
2h	Te	Ph	0	0.12 (73)	-1.61 (110)		
2i	Te	Ph	1	0.14 (50)	-1.46 (48)		

Reference electrode: SCE.

^a Not determined.^b Δ*E*_p at 0.5 V s⁻¹.^c Performed in CH₂Cl₂/NBu₄BF₄, see Ref. 18.^d Δ*E*_p at 0.1 V s⁻¹ from Ref. 10.**Table 2.** Voltammetric data at 0.02 V s⁻¹ of compounds **4a**, **4c**, **4d**, and **4e**

	X	R	Y=OCH ₃			Y=H		
			<i>n</i>	<i>E</i> ₁ ⁰ /V (Δ <i>E</i> _p /mV)	<i>E</i> _{pc} ¹ /V	<i>E</i> _{pc} ² /V	<i>E</i> ₁ ⁰ /V (Δ <i>E</i> _p /mV)	<i>E</i> ₃ ⁰ /V (Δ <i>E</i> _p /mV)
4a	O	Ph	0	0.19 (55)	-1.85 ^a	-1.96	0.31 (60) ^b	0.50 (60) ^b
4c	O	<i>t</i> -Bu	1	0.10 (110)	^a	^a		
4d	O	Ph	1	0.15 (65)	-1.75	-1.91	0.35 (50) ^b	
4e	S	Ph	1	0.16 (59)	-1.64	^a		

Reference electrode: SCE.

^a Not determined.^b Δ*E*_p at 0.1 V s⁻¹ from Ref. 10.

However, pure **2c** was obtained when the reaction was carried out using Pd(PPh₃)₄ as a catalyst (48% yield) isomer (*E/Z*, 90:10).

The reaction was extended, without any modification, to γ -benzopyran carbene complexes **3**. A great variety of unsaturated bis-benzochalcogenapyran were obtained in low-to-good yield (*E* isomer for **4a** and **4b** and mixture of *E* and *Z* isomers for **4c**, **4d**, **4e**) (Scheme 4).

Unsaturated α -methylene carbene complexes behave similarly. Under the influence of Pd(PPh₃)₂Cl₂, N(Et)₃ catalytic system, a good yield of unsaturated bis-2*H*-pyran was isolated as dark crystals (mixture of isomers) (Scheme 5).

It can be noted that the low yield obtained in some cases reflects the difficulty in isolating the corresponding bispyran after work up (see Section 4), due to the great reactivity of some of these compounds to O₂ in the presence of silicagel.¹⁸

2.2. Electrochemical studies

The compounds synthesized in the framework of this study have been investigated under inert atmosphere by cyclic

Table 3. Voltammetric data at 0.02 V s⁻¹ of compounds **6a**, **6b**, and **6c**

	X	<i>E</i> ₁ ⁰ /V (Δ <i>E</i> _p /mV)	<i>E</i> ₂ ⁰ /V (Δ <i>E</i> _p /mV)
6a	O	-0.13 (52)	^a
6b	S	-0.01 (113)	-1.59 (110) ^b
6c	S	-0.02 (48)	-1.64 (167) ^b

Reference electrode: SCE.

^a Not determined.^b Δ*E*_p at 1 V s⁻¹.

voltammetry in CH₂Cl₂ with NBu₄PF₆ as supporting electrolyte. The cyclic voltammetric data (standard potential *E*⁰, cathodic peak potential *E*_{pc}, peak separation Δ*E*_p) of compounds **2**, **4**, and **6** are collated in Tables 1, 2, and 3, respectively. For comparison purpose, values of the equivalent ethandiylidene 2,6-diphenyl-bis-chalcogenapyrans and 2-phenylbisflavenes obtained in similar conditions by Chen et al. appear in Tables 1 and 2 (Y=H).¹⁰

As their ethandiylidene counterparts¹⁰ (Scheme 1, R=H), the bis-4*H* or 2*H*-chalcogenapyrans **2–6**, and chalcogenabenzopyrans **4** (Scheme 1, R=OCH₃) are characterized by a quasi-reversible system (-0.13 V < *E*₁⁰ < +0.19 V vs SCE) (Fig. 3a), which is ascribed to a two-electron transfer reaction as proved by both the peak separation value (Δ*E*_p ≈ 50 mV for most compounds),[‡] and the appearance of two one-electron waves at high scan rate ($\nu > 1$ V s⁻¹) (cf. Fig. 3b).[§] The chalcogenapyrans and benzopyrans in neutral form (**C**) are thus easily oxidized in radical cation **C**^{+•} and dication **C**²⁺ (dichalcogenapyrylium form) as depicted in Scheme 1.

More generally, as shown in Tables 1–4, the standard potential *E*₁⁰ shifts toward negative values when (i) the heavier chalcogen atom (Te) is substituted by oxygen or sulfur atoms,²⁰ (ii) the phenyl group in the 2–6 positions of the heterocycle is substituted by the electron inductive donating *t*-Bu group, and (iii) the less electron rich bisflavene units **4** are substituted by bis-chalcogenapyran moieties **2**.¹⁰ In

[‡] Δ*E*_p = 60 mV for Fc⁺/Fc in the same working conditions.[§] Coulometric experiments have been performed at 25 °C to isolate the dication product. Unfortunately, the instability of the species in the time of the experiment did not allow any characterization.

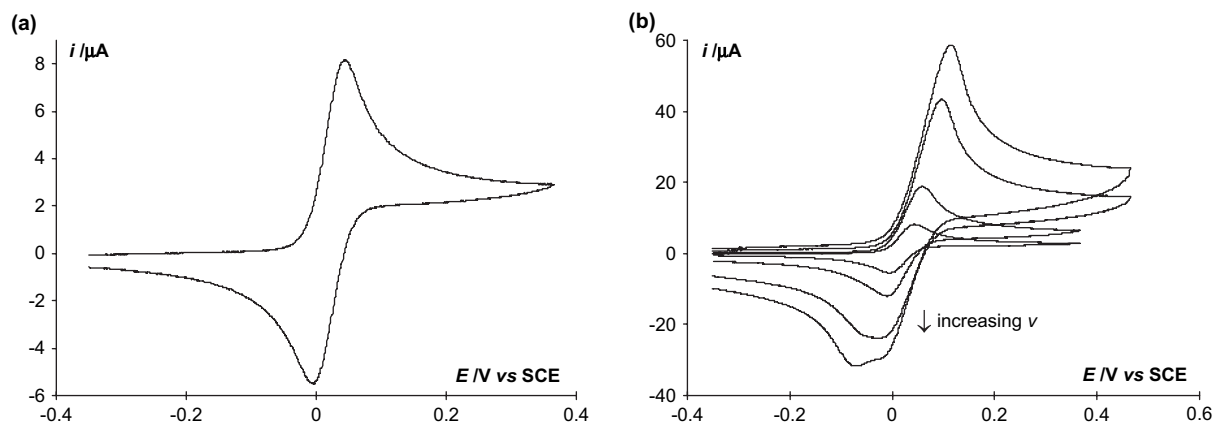


Figure 3. Cyclic voltammogram of **2g** in $\text{CH}_2\text{Cl}_2 + \text{NBu}_4\text{PF}_6$ ($T=293\text{ K}$, $C=0.001\text{ M}$, WE: Pt) at (a) $v=0.02\text{ V s}^{-1}$; (b) $v=0.02; 0.1; 0.5; 1\text{ V s}^{-1}$.

Table 4. Major computed data for $2'\text{c}_0$, $2'\text{c}_0^{+}$, $2'\text{c}_0^{2+}$, $2'\text{c}_0^{-}$, and $2'\text{c}_0^{2-}$ models

	$2'\text{c}_0^{2+}$	$2'\text{c}_0^{+}$	$2'\text{c}_0$	$2'\text{c}_0^{-}$	$2'\text{c}_0^{2-}$
Symmetry	C_2	C_2	C_i	C_2	C_2
First ionization energy (eV)					
In vacuum		8.93	5.69		
In CH_2Cl_2		4.98	4.50		
Electronic affinity (eV)					
In vacuum			0.81	^a	
In CH_2Cl_2			1.71	1.64	
HOMO–LUMO gap (eV)	2.20		1.61		1.55
Bond distances (Å)					
C ₁ –C ₂	1.509	1.450	1.393	1.424	1.451
C ₂ –O(Me)	1.340	1.365	1.401	1.419	1.430
C ₂ –C ₃	1.380	1.401	1.431	1.407	1.390
C ₃ –C ₄	1.440	1.412	1.386	1.411	1.434
C ₄ –C ₅	1.428	1.442	1.458	1.456	1.453
C ₅ –C ₆	1.372	1.361	1.352	1.355	1.363
C ₆ –O ₇	1.346	1.363	1.379	1.403	1.427
O ₇ –C ₈	1.347	1.363	1.380	1.406	1.430
C ₈ –C ₉	1.371	1.360	1.352	1.356	1.365
C ₉ –C ₄	1.428	1.442	1.456	1.451	1.447
O–Me	1.470	1.456	1.442	1.433	1.428

^a No physical meaning (positive HOMO energy).

addition, one observes that the bis-2*H*-chalcogenapyrans are more easily oxidized than the bis-4*H*-counterparts (Table 3).

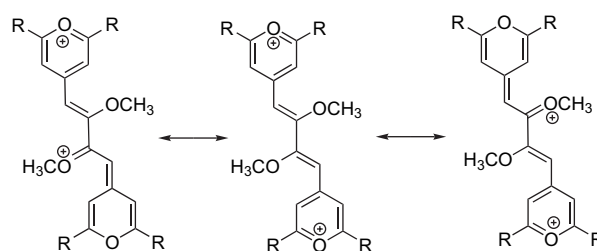


Figure 4. Mesomeric electronic effect for bispyrans 2a^{2+} or 2b^{2+} .

The redox behavior of the newly synthesized chalcogenapyrans (Scheme 1; $\text{R}=\text{OMe}$) differs clearly from that described by Chen et al. (Scheme 1; $\text{R}=\text{H}$) since the presence of two methoxy groups induces lower values for the redox potential E_1^0 and favors the coalescence of the two oxidation steps. Particularly, the decrease in the number of the carbon atoms in the extended conjugation (n) for the methoxy-chalcogenapyrans does not modify the general voltammetric shape, i.e., only single two-electron waves have been observed. This is the main difference with Chen's compounds who found a coalescence of the two oxidation waves from $n \geq 1$.¹⁰ With the absence of a noticeable destabilizing structural effect in the neutral form, such a difference could be explained by the mesomeric electronic influence of the methoxy groups allowing a decrease in the coulombic repulsion in the dicationic form (Fig. 4). However, the weight of methylenepyrans

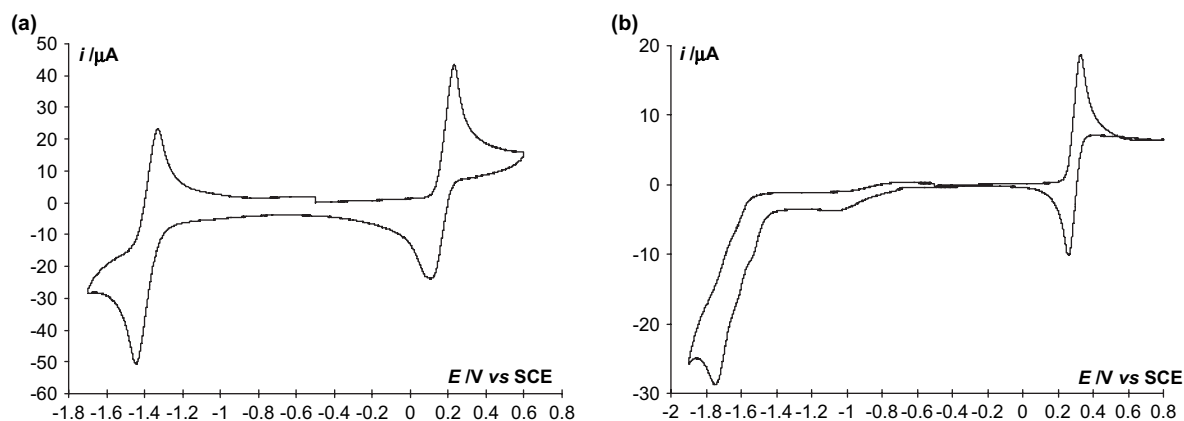


Figure 5. Cyclic voltammogram in $\text{CH}_2\text{Cl}_2 + \text{NBu}_4\text{PF}_6$ ($T=293\text{ K}$, $C=0.001\text{ M}$, WE: Pt) of (a) **2g** ($v=0.5\text{ V s}^{-1}$) and (b) **2d** ($v=0.02\text{ V s}^{-1}$).

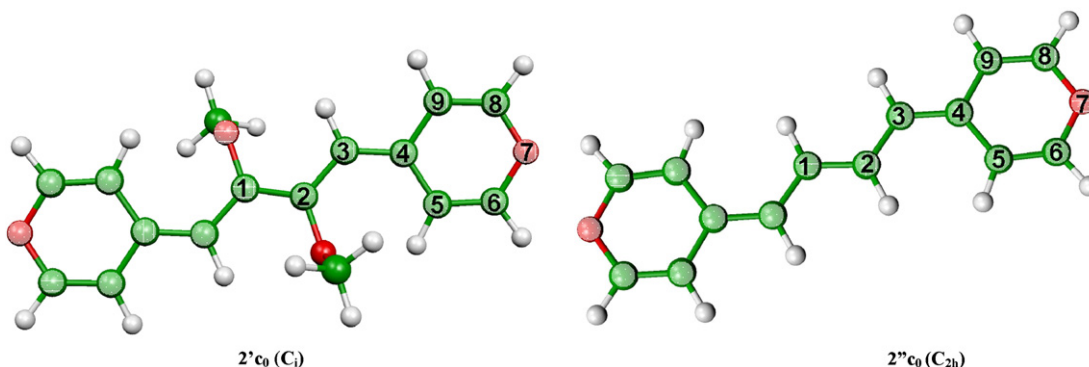


Figure 6. View in projection of $2'c_0$ and $2''c_0$ with atom labeling.

resonance form is probably minimized by the loss of the heterocyclic aromatic character. Consequently, due to this effect, a decisive stabilization of the dicationic form seems unlikely. Probably, solvent effects play a major role.¹¹

Electrochemical studies have also been performed at low cathodic potential down to -2.0 V versus SCE (Tables 1–4). According to the structure of the molecule and to the scan rate, the cyclic voltammograms show for all new compounds electrochemical irreversible (E_{pc}^1 , E_{pc}^2) or quasi-reversible (E_2^0) systems in the -1 V \leftrightarrow -2 V (vs SCE) potential range. The bis-chalcogenopyran **2** and **6** families are characterized by quasi-reversible systems (see Fig. 5a) whereas bis-chalcogenabenzopyran **4** exhibits one or two irreversible peaks (see Fig. 5b). This redox behavior has never been reported so far for other bispyrans and benzopyrans,⁴ and may reflect the reduction of these molecules in monoanion $C^{\cdot-}$ and dianion C^{2-} entities (Scheme 1). These anionic species are likely less thermodynamically stable than the corresponding cations due to their antiaromatic character.²¹

2.3. Theoretical investigation

To obtain more information about the molecular structure, electronic structure, and the electrochemical behavior of the molecules, DFT calculations were performed using a simplified model of **2a** (Scheme 2), in which the phenyl groups have been replaced by hydrogen atoms. Computational details are provided in Section 4. The neutral, cationic, dicationic, anionic, and dianionic forms, which are analogous to **2a** are, respectively, noted $2'c_0$, $2'c_0^+$, $2'c_0^{2+}$, $2'c_0^-$ and $2'c_0^{2-}$ in the followings.

For comparison, the ethandiylidene analogs noted $2''c_0$, $2''c_0^+$, $2''c_0^{2+}$, $2''c_0^-$, and $2''c_0^{2-}$ were also considered. Test calculations on selected examples indicated that for $2'c_0$, the *Z* and *E* isomers have very similar electronic structures and are close in energy, the *E* isomer being the most stable. Therefore, all the geometry optimizations were subsequently carried out assuming the *E* configuration. In this configuration, the highest symmetry possible is C_{2h} and corresponds to a rigorously planar molecule. Two symmetrical out-of-plane deformations lower the symmetry to C_2 or C_i , depending on whether the deformations occur on the same

side (*syn* type) or on opposite sides (*anti* type) of the plane. When these deformations occur, the C_2 and C_i structures were found to be very close in energy (whatever solvent effect is considered or not), except in the case of $2'c_0^+$ where the C_i structure was found to lie 0.4 eV above the C_2 one (see below). Only the structures of lowest energy, characterized as true minima by frequency calculations, are shown here (see Fig. 6 for the atom numbering and Fig. 7 for perspective views of all the optimized species). The most relevant computed data are given in Tables 4 and 5. The reported metrical data correspond to optimizations not considering solvent effect. The inclusion of solvent (CH_2Cl_2) effect in the calculations gave comparable geometries and energy differences between isomers. The ionization potentials and electron affinities are reported with and without solvent effect considered.

Unlike the unsubstituted $2''c_0$ molecule, which is perfectly planar (C_{2h}), $2'c_0$ is found to adopt the lowest C_i symmetry because of the presence of the methoxy groups, which cannot lie in the molecular plane (Fig. 7). As mentioned above, both *anti* (C_i) and *syn* (C_2) conformations of the methyl groups are almost isoenergetic. The MO diagrams of $2'c_0$ and $2''c_0$ are shown in Figure 8. Clearly, their electronic structures are strongly related. They exhibit similar LUMO and high-lying HOMO. These π -type orbitals have their major localization along the carbon chain linking the heterocycles and they have opposite bonding/antibonding character along this chain. Thus, occupying the LUMO or unfilling the HOMO of $2'c_0$ or $2''c_0$ should have similar shortening/lengthening effects on the carbon chain. Reducing $2'c_0$ and $2''c_0$ induces an out-of-plane shifting of the pyran oxygen atoms (Fig. 7), associated with a lengthening of the C–O_{pyr}, C₁–C₂, and C₃–C₄ bonds, whereas the C₂–C₃ bond is shortened. This effect, which is fully consistent with the nature of the LUMO's of $2'c_0$ and $2''c_0$, is of course more important in the dianions than in the monoanions and is associated with a loss of conjugation in the heterocycle. In addition the C₄–C₅ and C₅–C₆ bond lengths (1.453 Å and 1.363 Å in $2'c_0^{2-}$, 1.449 Å and 1.364 Å in $2''c_0^{2-}$) indicate a significant weight of the mesomeric formula in which the negative charge is mainly localized on the carbon 4. Oxidizing $2''c_0$ by one or two electrons maintains the planar C_{2h} structure. The changes in bond lengths (Table 5) are fully consistent with the nature of the HOMO and with the $C^{\cdot+}$ and C^{2+} Lewis formula shown in Scheme 1. The structures of the $2'c_0^+$ and $2'c_0^{2+}$ cations differ significantly from

¹¹ It can be noted that pyrylium salts are reduced reversely or irreversibly in radical and pyranlylidene anions via a two one-electron transfer reaction.

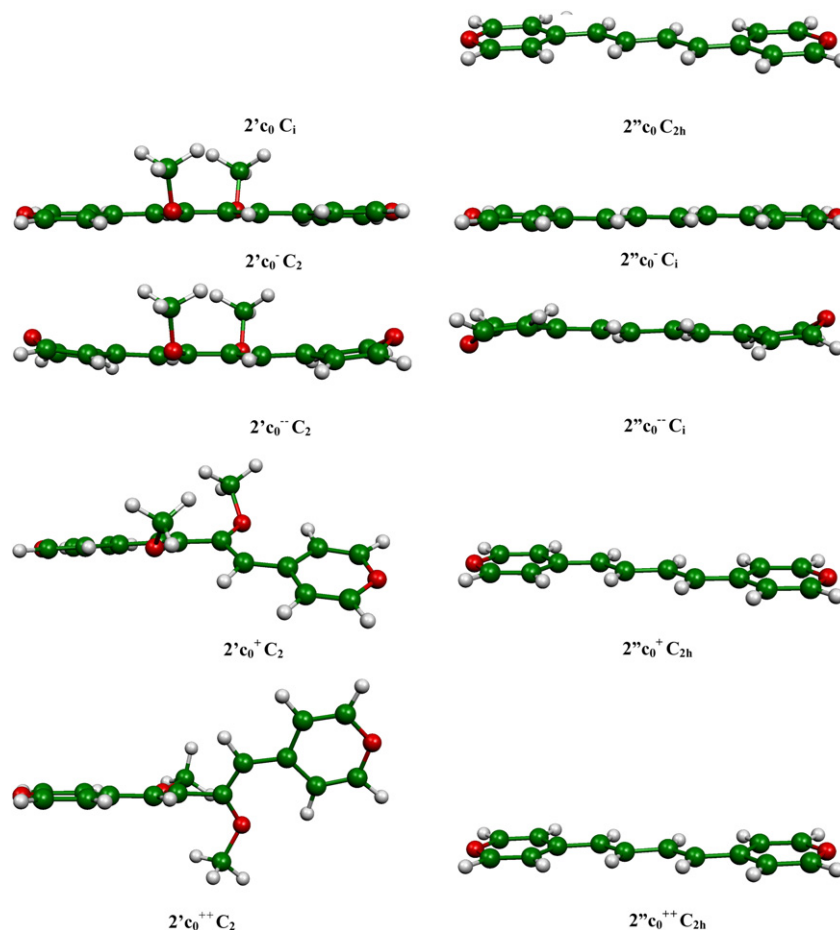


Figure 7. Perspective view of all the optimized species.

those of the cations of $2''\mathbf{c}_0$. They exhibit structures in which both halves of the molecule make angles of 36° and 68° , respectively. Thus, the carbon chains linking the heterocycles are no more planar in these cations. Whereas the C_2 (non-planar) and C_i (near planar) optimized structures are nearly

isoenergetic in the case of the monocation $2'\mathbf{c}_0^{+}$, the C_2 non-planar conformation of $2'\mathbf{c}_0^{2+}$ is 0.4 eV more stable than the near planar one, whether solvent effect is considered or not. Thus, the presence of the methoxy groups in the cations of $2'\mathbf{c}_0$ tends to cancel the π conjugation between both halves

Table 5. Major computed data for $2'\mathbf{c}_0$, $2''\mathbf{c}_0^{+}$, $2'\mathbf{c}_0^{2+}$, $2''\mathbf{c}_0^{-}$, and $2''\mathbf{c}_0^{2-}$ models

	$2'\mathbf{c}_0^{2+}$	$2''\mathbf{c}_0^{+}$	$2'\mathbf{c}_0$	$2''\mathbf{c}_0^{-}$	$2''\mathbf{c}_0^{2-}$
Symmetry	C_{2h}	C_{2h}	C_{2h}	C_i	C_i
First ionization energy (eV)					
In vacuum		9.65	5.79		
In CH_2Cl_2		5.31	4.52		
Electronic affinity (eV)					
In vacuum			1.79	^a	
In CH_2Cl_2			1.29	1.66	
HOMO–LUMO gap (eV)	1.89		1.64		1.56
Bond distances (\AA)					
$\text{C}_1\text{--C}_2$	1.439	1.407	1.380	1.411	1.439
$\text{C}_2\text{--C}_3$	1.371	1.395	1.424	1.405	1.389
$\text{C}_3\text{--C}_4$	1.452	1.416	1.386	1.411	1.437
$\text{C}_4\text{--C}_5$	1.424	1.440	1.457	1.457	1.449
$\text{C}_5\text{--C}_6$	1.374	1.361	1.352	1.354	1.364
$\text{C}_6\text{--O}_7$	1.345	1.362	1.379	1.400	1.424
$\text{O}_7\text{--C}_8$	1.343	1.362	1.382	1.411	1.434
$\text{C}_8\text{--C}_9$	1.375	1.362	1.352	1.359	1.368
$\text{C}_9\text{--C}_4$	1.423	1.438	1.454	1.446	1.444

^a No physical meaning (positive HOMO energy).

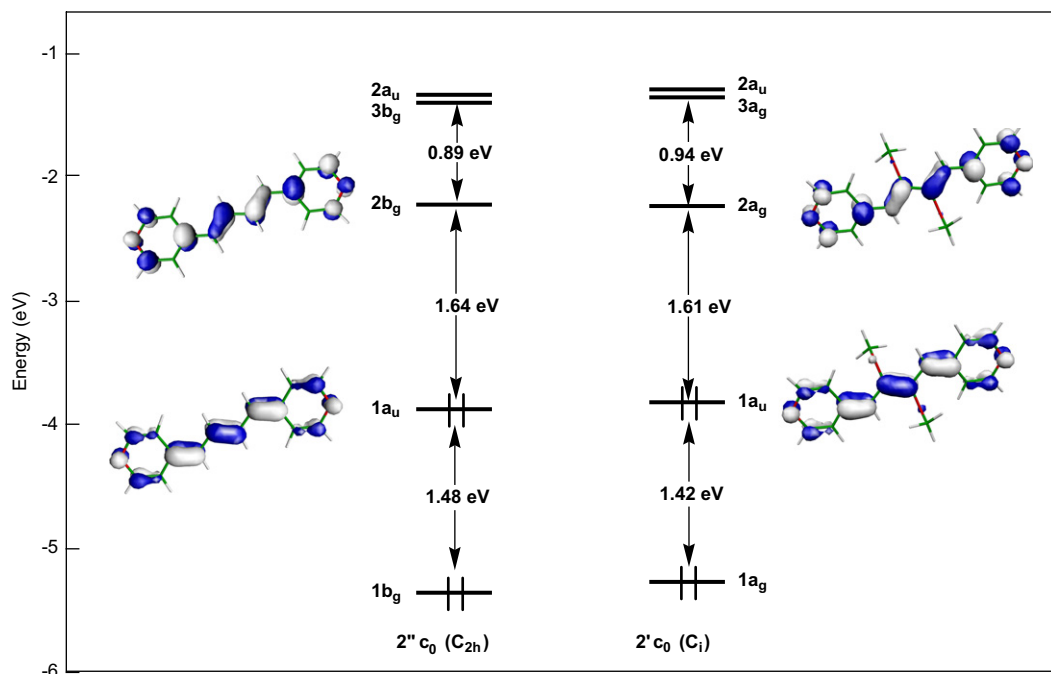


Figure 8. The MO diagrams of the $2'c_0$ and $2''c_0$ models.

of the molecule. Interestingly, the C_1 – C_2 distance is shorter in the cations of $2''c_0$ than in the cations of $2'c_0$. This is due to hyperconjugation (stabilizing σ/π mixing), which is allowed in the non-planar geometries. This involves the oxygen lone pairs of the methoxy groups, as exemplified by the short C–O(Me) bond of 1.340 Å and also by the lengthening and the shortening of the C2–C3 and C3–C4 bonds, respectively, in $2'c_0^{2+}$.

Calculated ionization potentials (IP) indicate that for both $2'c_0$ and $2''c_0$ the second electron is much more difficult to remove than the first one in vacuum (Tables 4 and 5). When solvent effect is introduced in the calculations, the ionization potentials decrease. This lowering is more pronounced for the second IP than for the first one due to a greater stabilization of the dipyrilium forms by the solvent. However, inversion of the values ($IP_2 < IP_1$) is not found. Moreover, due to the electronic influence of the methoxy group, the IP values are smaller and closer for the methoxy molecules. These results agree with those reported by Hapiot et al.¹¹ and show that the solvation effect should be effective for short conjugated molecules. On the other hand, the DFT data do not agree with the different electrochemical behavior of **2a** and its ethandiylidene analog (one two-electron wave for the former and two one-electron waves for the latter).¹⁰ Obviously, the CPM method, which modelizes the solvent as a continuum and cannot consider explicitly molecular interactions with solvent and electrolyte molecules, is not sufficient to rationalize the electrochemical behavior.

The MO diagrams of $2'c_0$ and $2''c_0$ (Fig. 8) show that their LUMOs are rather low lying and separated from the other unoccupied MOs by a significant energy gap. Such a situation suggests that the reduction of $2'c_0$ and $2''c_0$ should lead to stable anionic species. This is in correlation, as reported above, with electrochemical results at very low potential ($\cong -1.5$ V vs SCE) for the bispyran and benzopyran

compounds (Fig. 5). Moreover, the electronic affinities of $2'c_0$ computed with solvent effect considered reveal that it is easier to add the second electron than the first one, in good agreement with the observation for the extended bispyran of a two-electron electrochemical reduction process.

Finally, the UV–vis transition of $2'c_0$ and $2''c_0$ has been calculated using the TDDFT method (see Section 4.2). As expected, in both compounds the allowed transition of lowest energy is the HOMO–LUMO transition. It is isolated in energy from the other transitions and has a large oscillator strength. The corresponding computed wavelengths are 429 nm and 446 nm for $2'c_0$ and $2''c_0$, respectively (in vacuum). These transitions are red-shifted to 474 nm and 484 nm, respectively, when solvent effect is considered. The UV–vis spectrum of **2a** recorded in CH_2Cl_2 shows two close absorption bands of near equal intensity ($\lambda = 502$ nm and 534 nm). Such absorption band morphology exists in the electronic spectrum of an extended bithiopyran synthesized by Chen et al.^{10a}

3. Conclusion

Sierra Pd^0 catalyst of dimerization of Fischer type carbene complexes are very efficient to obtain electron rich molecules, potentially precursor of conducting materials. Extended bis-chalcogenapyrans and bis-benzochalcogenapyrans have been synthesized following this method. Voltammetric studies performed in CH_2Cl_2 show a single two-electron reversible system around 0 V vs SCE, indicating that the formation from the neutral form of the cation radical and dipyrilium cation requires the same energy. DFT calculations suggest that (1) oxidation leads to conformational change, which tends to cancel the conjugation between both halves of the molecule (2) solvent molecules (CH_2Cl_2) should play a major role in the oxidation process

by stabilizing the dication. Moreover, the observation of an electrochemical system at negative potential shows that the neutral form is reducible in anion and dianion. Extension of this synthetic methodology to electron rich extended di-thiafulvene is under investigation in our laboratory.²²

4. Experimental section

4.1. Materials

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from Na/benzophenone under N₂. Chromatographic purification was performed with Silica Gel 60 (0.063–0.200 μm). NMR analyses were carried out using Brücker 400 and 500 MHz spectrometers. IR analyses were recorded on a Perkin–Elmer Spectrum 1000 FTIR spectrophotometer using KBr plates and mass spectroscopy was performed by the Centre Régional de Mesures Physiques de l'Ouest de l'Université de Rennes.

The electrochemical studies of the bispyran derivatives have been performed in a glovebox (O₂<1 ppm, H₂O<1 ppm) with a home-designed 3-electrode cell (WE: Pt, RE: Ag, CE: Cu). The potential of the cell was controlled by a AUTO-LAB PGSTAT 100 (Ecochemie) potentiostat monitored by a computer. The solvent used (CH₂Cl₂) has been distilled over CaH₂ and kept under N₂. The supporting salt, NBu₄PF₆, has been purified, dried under vacuum for 48 h at 100 °C, then kept under N₂ in the glovebox. All experiments have been performed with solutions of 10⁻³ mol L⁻¹ in electroactive species. All potentials have been referred to the SCE by adding low amounts of ferrocene in the electrolytic solution at the end of each experiment ($E^0(\text{Fc}^+/\text{Fc})=+0.4$ V vs SCE in CH₂Cl₂, NBu₄PF₆).

4.2. Computational details

Density functional theory (DFT) calculations were carried out using the Gaussian 03 package.²³ Spin-unrestricted calculations were carried out on all the Odd-electron systems. Full delocalized mix-valence was found for all these species, unlike what has been computed at the UHF level for related bis(tetrathiafulvene) compounds.²⁴ All geometries were optimized at the BP86/6-311G** level.²⁵ Optimizations were carried out both with and without inclusion of solvent effect, which was taken into account within the polarizable continuum model (PCM).²⁶ The value of 8.93 was used for the dielectric constant of dichloromethane. Frequency calculations of vibrational normal modes were computed on all the optimized geometries in vacuum to verify that they are minima. The UV–visible transitions were calculated by means of time-dependent DFT calculations, using the BP86 functional and the 6-311G** basis set, coupled with the PCM model for taking into account solvent effect on the electronic transitions.²⁷ Representation of the orbitals was done using MOLEKEL4.3.²⁸

4.3. General procedure for preparation of bispyrans 2a–i, 4a–e, and 6a–d

In a 100 mL Schlenk, the corresponding Fischer type carbene complexes and Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂+NEt₃

(10% molar) were added successively to 15 mL of freshly distilled THF or CH₂Cl₂, under a stream of nitrogen. The mixture was refluxed. The reaction mixture was monitored by TLC chromatography until complete disappearance of the starting complex. The mixture was cooled to room temperature. When the initial carbene had totally reacted, the mixture was cooled to room temperature, filtered on Celite, diluted with CH₂Cl₂ (10 mL), and washed with de-gassed water (50 mL). The organic phase was dried over MgSO₄, concentrated under vacuum, and the product was isolated by recrystallization in CH₂Cl₂/diethyl ether.

For the bispyran **2a** and **4d** the product was purified by column chromatography (petroleum ether/CH₂Cl₂) under a stream of nitrogen and using de-gassed solvents.

4.3.1. Compound 2a. Yield 68% (*m*=80 mg) from catalyst Pd(PPh₃)₄ and carbene **1a** (*m*=250 mg), FTIR (KBr) $\bar{\nu}$ 1647, 1492, 927, 758, 687 cm⁻¹; UV (CH₂Cl₂) λ_{max} (log ϵ) 502 (4.56), 534 (4.53) nm; ¹H NMR (CDCl₃, 400 MHz) δ 3.67 (s, 6H), 5.81 (s, 2H), 6.41 (d, ⁴*J*=1.6 Hz, 2H), 7.30 (d, ⁴*J*=1.6 Hz, 2H), 7.38 (t, ³*J*=5.7 Hz, 4H), 7.44 (t, ³*J*=7.2 Hz, 8H), 7.75 (d, ³*J*=7.3 Hz, 4H), 7.79 (d, ³*J*=7.3 Hz, 4H); 2D NMR (HMOC, HMBC) (CDCl₃, 125 MHz) δ 60.2, 103.9, 104.1, 109.3, 125.0, 125.5, 129.0, 129.5, 131.0, 149.5, 161.0, 161.0; MS *m/z* calcd for C₄₀H₃₁O₄ 575.2222 (M–H⁺), found 575.2228.

4.3.2. Compound 2b. Yield 46% (*m*=70 mg) from catalyst Pd(PPh₃)₄ and carbene **1b** (*m*=350 mg), FTIR (KBr) $\bar{\nu}$ 2967, 1668, 1480, 1098, 1051, 927, 860, 702 cm⁻¹; ¹H NMR (acetone-*d*₆, 500 MHz) δ 1.16 (m, 36H), 3.44 (s, 6H), 5.47 (s, 2H), 5.61 (s, 2H), 6.45 (s, 2H); 2D NMR (HMOC, HMBC) (acetone-*d*₆, 125 MHz) δ 28.0, 35.5, 59.6, 100.9, 102.8, 106.3, 127.7, 148.3, 161.4, 162.9; MS *m/z* calcd for C₃₂H₄₇O₄ 495.3474 (M–H⁺), found 495.3473.

4.3.3. Compound 2c. Yield 46% (*m*=113 mg) from catalyst Pd(PPh₃)₄ and carbene **1c** (*m*=500 mg), FTIR (KBr) $\bar{\nu}$ 1928, 1652, 1575, 1493, 1233, 1066, 936, 763, 690, 581 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) *E* isomer (90%) δ 7.81 (d, ³*J*=7.1 Hz, 4H), 7.74 (d, ³*J*=7.2 Hz, 4H), 7.36–7.49 (m, 12H), 6.88 (dd, ³*J*=15.3, 12.2 Hz, 2H), 6.77 (s, 2H), 6.42 (d, ³*J*=15.3 Hz, 2H), 6.38 (d, ⁴*J*=1.2 Hz, 2H), 5.85 (d, ³*J*=12.2 Hz, 2H), 3.76 (s, 6H); *Z* isomer (10%) δ 6.93 (m, 2H), 6.36 (m, 2H), 5.80 (m, 2H), 3.83 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) *E* isomer (90%) δ 152.0, 151.0, 148.8, 133.4, 134.1, 130.0, 129.8, 129.0, 124.7, 124.2, 123.5, 118.7, 116.3, 108.8, 102.4, 61.5; *Z* isomer (10%)^{||} δ 146.8, 123.4, 115.9, 60.4; MS *m/z* calcd for C₄₄H₃₆O₄ 628.2614 (M⁺), found 628.2608.

4.3.4. Compound 2d. Yield 60% (*m*=154 mg) from catalyst Pd(PPh₃)₂Cl₂+NEt₃ and carbene **1d** (*m*=500 mg), FTIR (KBr) $\bar{\nu}$ 2936, 2354, 1916, 1652, 1600, 1557, 1494, 1446, 1398, 1346, 1278, 1236, 1157, 1075, 974, 936, 762, 688 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.80 (d, ³*J*=7.2 Hz, 4H), 7.73 (d, ³*J*=7.3 Hz, 4H), 7.36–7.47 (m, 12H), 6.79 (dd, ³*J*=14.0, 12.0 Hz, 2H), 6.74 (d, ⁴*J*=1.1 Hz, 2H), 6.62 (dd, ³*J*=12.0, 11.5 Hz, 2H), 6.44 (d, ³*J*=11.5 Hz,

^{||} Due to the weak quantity of the minor isomer in the mixture, it is not possible to detect all the ¹³C signals.

2H), 6.37 (dd, $^3J=14.0, 12.0$ Hz, 2H), 6.36 (d, $^4J=11$ Hz, 2H), 5.75 (d, $^3J=12.0$ Hz, 2H), 3.69 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 151.0, 149.2, 149.0, 133.5, 133.3, 133.1, 129.9, 129.7, 129.3, 129.0, 128.7, 124.8, 124.4, 120.2, 116.0, 108.7, 102.5, 61.4; MS m/z calcd for $\text{C}_{48}\text{H}_{40}\text{O}_4$ 680.2927 (M^+), found 680.2929.

4.3.5. Compound 2e. Yield 42% ($m=96$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **1e** ($m=500$ mg), FTIR (KBr) $\bar{\nu}$ 2959, 1664, 1582, 1550, 1461, 1399, 1317, 1234, 1099, 1050, 964, 925, 815 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) *E* isomer (89%) δ 6.65 (dd, $^3J=14.0, 12.0$ Hz, 2H), 6.18 (d, $^3J=14.0$ Hz, 2H), 6.00 (d, $^4J=1.8$ Hz, 2H), 5.58 (d, $^4J=1.8$ Hz, 2H), 5.49 (d, $^3J=12.0$ Hz, 2H), 3.58 (s, 6H), 1.20 (s, 18H), 1.17 (s, 18H); *Z* isomer (11%) δ 6.70 (m, 2H), 6.13 (d, $^3J=14.2$ Hz, 2H), 5.99 (d, $^4J=1.8$ Hz, 2H), 5.57 (d, $^4J=1.8$ Hz, 2H), 5.47 (d, $^3J=12.3$ Hz, 2H), 3.65 (s, 6H); ^{13}C NMR ($\text{THF}-d_8$, 125 MHz) *E* isomer (89%) δ 163.4, 162.2, 148.9, 131.1, 124.1, 117.8, 114.5, 105.9, 99.4, 60.8, 36.2, 35.8, 28.1; *Z* isomer (11%) \parallel δ 146.9, 123.8, 118.9, 114.1, 59.6; MS m/z calcd for $\text{C}_{36}\text{H}_{51}\text{O}_4$ 547.3787 ($\text{M}-\text{H}^+$), found 547.3774.

4.3.6. Compound 2f. Yield 30% ($m=76$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **1f** ($m=500$ mg), FTIR (KBr) $\bar{\nu}$ 2925, 2360, 1935, 1616, 1558, 1490, 1233, 1049, 953, 748, 694 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) *E* isomer (90%) δ 7.60 (d, $^3J=7.1$ Hz, 4H), 7.55 (d, $^3J=7.2$ Hz, 4H), 7.36–7.44 (m, 12H), 7.10 (s, 2H), 6.92 (ft, $^3J=13.6$ Hz, 2H), 6.69 (s, 2H), 6.45 (d, $^3J=14.6$ Hz, 2H), 6.05 (d, $^3J=12.5$ Hz, 2H), 3.71 (s, 6H); *Z* isomer (10%) δ 6.67 (s, 2H), 6.39 (d, $^3J=14.3$ Hz, 2H), 6.00 (d, $^3J=12.4$ Hz, 2H), 3.77 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) *E* isomer (90%) δ 149.4, 138.2, 137.8, 136.5, 133.9, 133.5, 129.1, 128.9, 128.8, 128.7, 126.2, 125.9, 125.7, 124.6, 123.3, 120.1, 119.3, 61.7; *Z* isomer (10%) \parallel δ 60.2; MS m/z calcd for $\text{C}_{44}\text{H}_{36}\text{O}_2\text{S}_2$ 660.2157 (M^+), found 660.2156.

4.3.7. Compound 2g. Yield 60% ($m=63$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **1g** ($m=200$ mg), FTIR (KBr) $\bar{\nu}$ 1927, 1614, 1546, 1490, 1444, 1236, 1051, 972, 851, 758, 747, 690 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) *E* isomer (89%) δ 7.68 (d, $^3J=7.5$ Hz, 4H), 7.61 (d, $^3J=7.5$ Hz, 4H), 7.34–7.49 (m, 12H), 7.27 (s, 2H), 7.00 (ft, $^3J=13.5, 13.0$ Hz, 2H), 6.84 (s, 2H), 6.64 (dd, $^3J=14.9, 11.8$ Hz, 2H), 6.47 (d, $^3J=14.9$ Hz, 2H), 6.42 (ft, $^3J=13.9, 11.8$ Hz, 2H), 6.04 (d, $^3J=12.3$ Hz, 2H), 3.63 (s, 6H); *Z* isomer (11%) δ 7.26 (s, 2H), 6.83 (s, 2H), 3.69 (s, 6H); ^{13}C NMR ($\text{THF}-d_8$, 125 MHz) *E* isomer (89%) δ 150.5, 139.0, 138.6, 136.6, 134.3, 134.0, 132.7, 130.7, 120.1, 129.9, 129.6, 126.7, 126.3, 125.9, 121.8, 120.0, 61.4; *Z* isomer (10%) \parallel δ 60.0; MS m/z calcd for $\text{C}_{48}\text{H}_{40}\text{O}_2\text{S}_2$ 712.2470 (M^+), found 712.2470.

4.3.8. Compound 2h. Yield 14% ($m=400$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **1h** ($m=30$ mg), FTIR (KBr) $\bar{\nu}$ 2364, 1933, 1654, 1638, 1590, 1542, 1486, 1440, 1266, 1053, 892, 756, 696 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) *E* isomer (80%) δ 7.98 (s, 2H), 7.37–7.52 (m, 20H), 6.96 (s, 2H), 6.46 (s, 2H), 3.64 (s, 6H); *Z* isomer (20%) δ 8.86 (s, 2H), 7.10 (s, 2H), 5.84 (s, 2H), 3.72 (s, 6H); ^{13}C NMR ($\text{THF}-d_8$, 125 MHz) *E* isomer (80%) δ 152.4, 144.4, 144.0, 143.6, 143.3, 137.2, 133.8, 127.0–130.0,

129.2, 121.2, 60.3; MS m/z calcd for $\text{C}_{40}\text{H}_{32}\text{O}_2$ $^{128}\text{Te}^{130}\text{Te}$ 802.0509 (M^+), found 802.0519.

4.3.9. Compound 2i. Yield 44% ($m=100$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **1i** ($m=400$ mg), FTIR (KBr) $\bar{\nu}$ 2361, 2352, 2326, 1933, 1652, 1591, 1555, 1486, 1441, 1234, 1049, 952, 757, 696 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) *E* isomer (91%) δ 7.30–7.48 (m, 20H), 7.24 (s, 2H), 7.07 (ft, $^3J=13.8, 13.3$ Hz, 2H), 6.78 (s, 2H), 6.55 (d, $^3J=14.6$ Hz, 2H), 6.35 (d, $^3J=12.5$ Hz, 2H), 3.71 (s, 6H); *Z* isomer (9%) δ 6.75 (s, 2H), 6.49 (d, $^3J=13.9$ Hz, 2H), 6.31 (d, $^3J=12.4$ Hz, 2H), 3.77 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) *E* isomer (91%) δ 150.2, 143.1, 142.6, 137.5, 133.4, 132.7, 129.0, 128.6, 128.4, 126.6, 126.4, 125.4, 123.9, 122.1, 61.8; *Z* isomer (9%) \parallel δ 149.9, 60.0; MS m/z calcd for $\text{C}_{44}\text{H}_{36}\text{O}_2$ $^{126}\text{Te}^{128}\text{Te}$ 850.0793 (M^+), found 850.0781.

4.3.10. Compound 4a. Yield 90% ($m=160$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **3a** ($m=400$ mg), FTIR (KBr) $\bar{\nu}$ 1628, 1460, 1300, 1047, 756 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) δ 7.83 (m, 4H), 7.77 (m, 2H), 7.60 (s, 2H), 7.44 (m, 4H), 7.37 (m, 2H), 7.31 (m, 2H), 7.19 (m, 4H), 6.72 (s, 2H), 3.70 (s, 6H); ^{13}C NMR ($\text{THF}-d_8$, 125 MHz) δ 153.0, 151.2, 150.4, 134.6, 129.8, 129.4, 125.6, 125.3, 123.9, 123.5, 118.4, 104.2, 103.7, 60.3; MS m/z calcd for $\text{C}_{36}\text{H}_{28}\text{O}_4$ 524.1988 (M^+), found 524.1988.

4.3.11. Compound 4b. Yield 85% ($m=65$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **3b** ($m=170$ mg), FTIR (KBr) $\bar{\nu}$ 1622, 1461, 1299, 1234, 1124, 1073, 1033, 999, 755, 698 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) δ 7.76 (d, $^3J=7.8$ Hz, 2H), 7.50 (d, $^3J=3.5$ Hz, 2H), 7.47 (d, $^3J=4.8$ Hz, 2H), 7.45 (s, 2H), 7.29 (ft, $^3J=7.4$ Hz, 2H), 7.17 (m, 4H), 7.10 (ft, $^3J=4.5, 4.1$ Hz, 2H), 6.70 (s, 2H), 3.69 (s, 6H); ^{13}C NMR ($\text{THF}-d_8$, 125 MHz) δ 152.8, 151.3, 146.6, 138.5, 129.8, 128.6, 125.4, 125.2, 125.0, 123.7, 123.6, 118.3, 104.1, 103.2, 60.3; MS m/z calcd for $\text{C}_{32}\text{H}_{24}\text{O}_4\text{S}_2$ 536.1116 (M^+), found 536.1121.

4.3.12. Compound 4c. Yield 34% ($m=76$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **3c**, FTIR (KBr) $\bar{\nu}$ 2926, 2362, 2344, 2072, 1934, 1702, 1686, 1648, 1560, 1508, 1460, 1432, 1307, 1233, 1130, 1093, 1048, 954, 935, 856, 826, 748, 692 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) *E* isomer (89%) δ 7.71 (d, $^3J=7.2$ Hz, 2H), 7.22 (ft, $^3J=7.1$ Hz, 2H), 7.08 (ft, $^3J=7.1$ Hz, 2H), 7.01 (d, $^3J=8.1$ Hz, 2H), 6.92 (ft, 2H, $^3J=14.5, 12.2$ Hz), 6.54 (d, $^3J=15.0$ Hz, 2H), 6.72 (d, $^3J=11.8$ Hz, 2H), 6.23 (s, 2H), 3.69 (s, 6H), 1.28 (s, 18H); *Z* isomer (11%) δ 7.66 (d, $^3J=8.2$ Hz, 2H), 7.08 (m, 2H), 6.48 (d, $^3J=11.9$ Hz, 2H), 6.21 (s, 2H), 3.74 (s, 6H), 1.28 (s, 18H); ^{13}C NMR ($\text{THF}-d_8$, 125 MHz) *E* isomer (89%) δ 161.6, 153.1, 150.0, 129.5, 127.6, 124.8, 124.5, 123.5, 123.1, 121.3, 118.0, 114.7, 98.4, 61.3, 28.1; *Z* isomer (11%) \parallel δ 114.3, 59.7; MS m/z calcd for $\text{C}_{36}\text{H}_{40}\text{O}_4$ 536.2927 (M^+), found 536.2930.

4.3.13. Compound 4d. Yield 9% ($m=19$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **3d** ($m=500$ mg), FTIR (KBr) $\bar{\nu}$ 2932, 2359, 1917, 1630, 1606, 1576, 1493, 1462, 1386, 1310, 1233, 1122, 1052, 1006, 947, 907, 848, 818, 764, 747, 687, 637 cm^{-1} ; ^1H NMR ($\text{THF}-d_8$, 500 MHz) *E* isomer (89%) δ 7.89 (m, 4H), 7.79 (dd, $^3J=8.2, 1.3$ Hz, 2H), 7.44 (m, 4H), 7.38 (m, 2H), 7.29 (ftd, $^3J=8.4, 7.0,$

1.3 Hz, 2H), 7.18 (ftd, $^3J=8.2$, 7.0, 1.1 Hz, 2H), 7.14 (m, 2H), 7.13 (ft, $^3J=14.7$, 12.1 Hz, 2H), 7.04 (s, 2H), 6.70 (d, $^3J=12.0$ Hz, 2H), 6.65 (d, $^3J=14.8$ Hz, 2H), 3.75 (s, 6H); Z isomer (11%) δ 7.74 (d, $^3J=6.9$ Hz, 2H), 7.18 (m, 2H), 7.01 (s, 2H), 3.80 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) E isomer (89%) δ 152.8, 150.6, 150.5, 134.4, 129.9, 129.8, 129.3, 127.4, 125.6, 125.2, 124.8, 123.5, 123.2, 122.2, 118.3, 116.5, 101.8, 61.6; Z isomer (11%) $^{\parallel}$ δ 148.4, 60.0; MS m/z calcd for $\text{C}_{40}\text{H}_{32}\text{O}_4$ 576.2301 (M^+), found 576.2300.

4.3.14. Compound 4e. Yield 55% ($m=53$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **3e** ($m=200$ mg), FTIR (KBr) $\bar{\nu}$ 1933, 1597, 1438, 1238, 1054, 950, 909, 748, 688 cm^{-1} ; ^1H NMR (THF- d_8 , 500 MHz) E isomer (87%) δ 7.89 (d, $^3J=7.9$ Hz, 2H), 7.68 (d, $^3J=7.5$ Hz, 4H), 7.37–7.46 (m, 6H), 7.43 (s, 2H), 7.22–7.31 (m, 6H), 7.17 (ft, $^3J=14.0$, 12.8 Hz, 2H), 6.97 (d, $^3J=12.1$ Hz, 2H), 6.73 (d, $^3J=14.7$ Hz, 2H), 3.73 (s, 6H); Z isomer (13%) δ 7.82 (d, $^3J=8.2$ Hz, 2H), 6.89 (d, $^3J=11.3$ Hz, 2H), 6.79 (d, $^3J=14.2$ Hz, 2H), 3.78 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) E isomer (87%) δ 151.0, 139.2, 134.0, 132.3, 132.0, 131.8, 131.4, 129.7, 128.4, 128.2, 127.6, 126.8, 125.3, 125.1, 123.8, 123.6, 119.2, 61.7; Z isomer (13%) $^{\parallel}$ δ 149.1; MS m/z calcd for $\text{C}_{40}\text{H}_{32}\text{O}_2\text{S}_2$ 608.1844 (M^+), found 608.1844.

4.3.15. Compound 6a. Yield 80% ($m=223$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **5a** ($m=500$ mg), FTIR (KBr) $\bar{\nu}$ 2948, 1935, 1595, 1555, 1492, 1449, 1365, 1247, 1146, 1123, 1064, 958, 760, 702 cm^{-1} ; ^1H NMR (THF- d_8 , 500 MHz) E isomer (94%) δ 8.03 (d, $^3J=7.6$ Hz, 4H), 7.30–7.43 (m, 16H), 7.35 (m, 2H), 6.44 (d, $^3J=16.1$ Hz, 2H), 6.32 (s, 2H), 3.77 (s, 6H), 2.79 (d, $^2J=14.8$ Hz, 2H), 2.68 (d, $^2J=13.9$ Hz, 2H), 2.21 (ft, $^3J=14.4$ Hz, 2H), 2.09 (ft, $^3J=13.6$ Hz, 2H), 1.45 (m, 2H), 0.94 (s, 18H); Z isomer (6%) δ 3.82 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) E isomer (94%) δ 152.7, 149.7, 140.2, 134.1, 132.3, 129.7, 129.4, 129.2, 128.3, 127.7, 124.9, 124.6, 123.3, 114.5, 111.3, 104.6, 60.9, 42.9, 29.1, 27.7, 26.8, 26.5; MS m/z calcd for $\text{C}_{58}\text{H}_{60}\text{O}_4$ 820.4492 (M^+), found 820.4476.

4.3.16. Compound 6b. Yield 80% ($m=207$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **5b** ($m=500$ mg), FTIR (KBr) $\bar{\nu}$ 1633, 1592, 1491, 1450, 1372, 1350, 1274, 1236, 1165, 1069, 952, 878, 857, 755, 692 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) E isomer (90%) δ 7.79 (d, $^3J=7.1$ Hz, 4H), 7.52 (d, $^3J=7.4$ Hz, 4H), 7.40–7.47 (m, 12H), 7.01 (ft, $^3J=13.7$, 12.7 Hz, 2H), 6.45 (d, $^3J=15.3$ Hz, 2H), 6.40 (s, 2H), 6.39 (s, 2H), 5.51 (d, $^3J=11.6$ Hz, 2H), 3.77 (s, 6H); Z isomer (10%) δ 7.73 (m, 4H), 7.57 (d, $^3J=7.8$ Hz, 4H), 7.40–7.47 (m, 12H), 6.83 (s, 2H), 6.33 (s, 2H), 5.91 (d, $^3J=12.3$ Hz, 2H), 3.83 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) E isomer (90%) δ 155.2, 152.3, 148.7, 137.1, 134.8, 132.9, 129.5, 128.9, 128.7, 128.4, 125.2, 124.7, 122.0, 118.2, 117.5, 105.8, 100.6, 61.3; Z isomer (10%) $^{\parallel}$ δ 124.7, 125.3, 113.2, 100.3, 60.1; MS m/z calcd for $\text{C}_{44}\text{H}_{36}\text{O}_4$ 628.2614 (M^+), found 628.2624.

4.3.17. Compound 6c. Yield 85% ($m=241$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **5c** ($m=500$ mg), FTIR (KBr) $\bar{\nu}$ 2926, 2072, 1917, 1597, 1477, 1364, 1235, 1054, 1025, 955, 802, 756, 694; ^1H NMR (THF- d_8 , 500 MHz) E isomer (83%) δ 7.60 (d, $^3J=7.6$ Hz, 4H), 7.28–7.42 (m, 6H), 7.12 (d, $^3J=15.2$ Hz, 2H), 6.61 (d,

$^3J=15.2$ Hz, 2H), 6.54 (s, 2H), 3.74 (s, 6H), 2.77 (d, $^2J=14.4$ Hz, 2H), 2.66 (d, $^2J=15.1$ Hz, 2H), 2.20 (ft, $^2J=15.7$ Hz, 2H, $^3J=11.7$ Hz), 1.86 (ft, $^2J=14.1$, 13.3 Hz, 2H), 1.86 (m, 2H), 0.87 (s, 18H); Z isomer (17%) $^{\parallel}$ δ 6.53 (s, 2H), 3.77 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) E isomer (83%) δ 150.6, 143.0, 138.5, 136.2, 135.9, 132.9, 131.4, 131.1, 129.6, 129.4, 129.2, 126.8, 126.6, 125.7, 122.9, 117.6, 68.1, 43.5, 32.9, 31.6, 30.7, 27.3; Z isomer: not detected signals; MS m/z calcd for $\text{C}_{58}\text{H}_{60}\text{O}_2\text{S}_2$ 852.4035 (M^+), found 852.4039.

4.3.18. Compound 6d. Yield 61% ($m=62$ mg) from catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2+\text{NEt}_3$ and carbene **5d** ($m=200$ mg), FTIR (KBr) $\bar{\nu}$ 1931, 1596, 1487, 1443, 1366, 1331, 1235, 1111, 1049, 950, 917, 874, 754, 720, 696, 680, 631 cm^{-1} ; ^1H NMR (THF- d_8 , 500 MHz) E isomer (90%) δ 7.67 (d, $^3J=7.7$ Hz, 4H), 7.57 (d, $^3J=7.8$ Hz, 4H), 7.37–7.49 (m, 12H), 6.88 (s, 2H), 6.72 (ft, $^3J=14.0$, 12.9 Hz, 2H), 6.65 (s, 2H), 6.47 (d, $^3J=14.8$ Hz, 2H), 6.25 (d, $^3J=12.4$ Hz, 2H), 3.68 (s, 6H); Z isomer (10%) $^{\parallel}$ δ 3.72 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) E isomer (90%) δ 150.5, 140.0, 138.2, 138.1, 137.7, 134.7, 130.1, 129.6, 129.5, 128.7, 126.7, 126.6, 126.4, 124.1, 122.1, 121.4, 120.3, 61.5; Z isomer: not detected signals; MS m/z calcd for $\text{C}_{44}\text{H}_{36}\text{O}_2\text{S}_2$ 660.2157 (M^+), found 660.2154.

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Supplementary data

It includes ^1H spectra of compounds **2a–2i**, **4a–4e**, and **6a–6d**, tables of total energies, and atom coordinates for the minimized structures. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.099.

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