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Photochemical functionalization of allyl benzoates by C−H insertion

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ABSTRACT

The photoreactivity of allyl benzoates, containing an electron-rich double bond, has been explored by irradiation at 305 nm in different solvents. Solvent addition products arising from an insertion of the alpha H−C bonds of THF, dioxane, and *i*-PrOH to the allylic double bond was realized. The observed reactivity depended on reaction conditions and substitution pattern of the substrate. A DFT study on this unusual reaction was performed allowing the formulation of two mechanistic pathways.

1. Introduction

The formation of C−C bonds is one of the most important reactions in organic synthesis. Organic chemists have devoted much effort in order to find and develop new and efficient strategies to link organic fragments by thermal processes. In this context, the photochemical approach, despite its great potential, is still an under-explored synthetic methodology. Photoalkylation reactions have been reported so far as radical additions to electron-deficient olefins[1] and the proposed reaction pathway usually involves the photo-generation of radicals by photocatalysts such as aromatic ketones or decatungstate salts.[1,2] In this context, since photoaddition to olefins can be performed under environmentally friendly conditions, photochemical reactions can be considered a ‘green tool’ for the synthetic chemist.[2] Many examples are reported in the literature, mainly belonging to the H−C addition (hydroalkylation reactions) of alkanes, alcohols, amines, and amides to electron-deficient olefins.[1–3] Although ethers have been used less frequently than alcohols as alkylating agents, their photofunctionalization, activated by tetrabutylammonium decatungstate (TBADT),[4] or TiO_2[5] has also been reported. An interesting example of this general approach is the easy regioselective photoalkylation of perfluoroalkylethylenes in an acetone/*i*-PrOH mixture, which occurs with good preparative yields.[6]

This procedure has also been recently employed in the total synthesis of a non-peptidal ligand with high-affinity for the human immunodeficiency virus (HIV) protease inhibitor UIC-94017[7] and in the synthesis of (−)-tetrahydrolipstatin,[8] a potent pancreatic lipase inhibitor. On the other hand, photoaddition reactivity of non-conjugated alkenes and alkenes bearing an electron-donating substituent has been explored in the context of H−X addition (X=O, N, S, etc.)[2] with rare reported examples of hydroalkylation reactions.[9]

Within the framework of our ongoing studies on the photoreactivity of organic compounds[10] we decided to explore the photo-mediated hydroalkylation reactions of electron-rich olefins, such as allyl benzoates.

2. Results and discussion

Preliminary irradiations of allyl benzoate **1a** at different wavelengths (254, 305, or 365 nm) and in different solvents such as acetone, acetonitrile, DCM, cyclohexane, and THF, revealed the formation of photoproducts only in the latter media. Screening of the reaction conditions performed by GC–MS analyses of THF solutions of allyl benzoate after irradiations at different wavelengths, revealed a fast conversion of **1a** at 254 nm, but analyses also showed the presence of several by-products as a consequence of photodegradation due to the use of high energy radiation. On the

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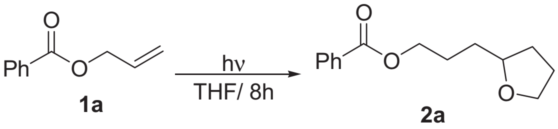
other hand, only trace amounts of photoproducts were revealed after prolonged irradiation at 365 nm. Irradiation at 305 nm allowed good conversion of **1a** and the formation of a main photoproduct with a good compromise between substrate conversion and reaction cleanliness. Thus, preparative scale irradiation of compound **1a** at λ=305 nm for 8 h in THF furnished, after chromatographic separation, compound **2a** in 45% isolated yield, as well as 25% of recovered starting material (Scheme 1).

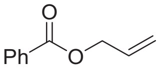
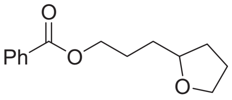
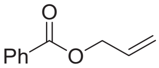
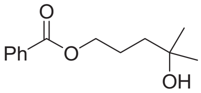
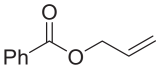
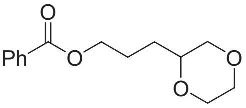
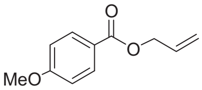
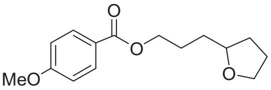
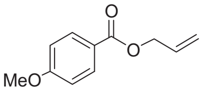
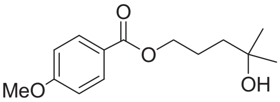
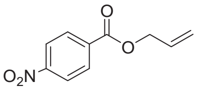
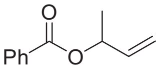
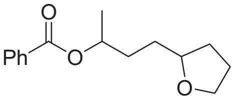
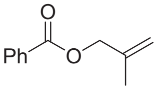
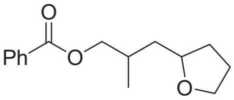
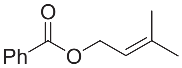
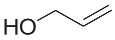
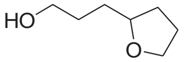


Scheme 1.

Moreover, irradiation performed in freshly distilled THF as well as in commercial THF containing BHT as solvent stabilizer produced similar results. The formation of compound **2a** that can be easily interpreted in terms of an insertion of the α H–C bond of the cyclic ether into the double bond of the allylic moiety, revealed the feasibility of the desired photo-mediated hydroalkylation reactions of electron-rich olefins.

We next preliminarily explored the generality of the reaction performing photoreactions with other solvents and with different allyl derivatives **1** (Table 1). The formation of compound **3a** was observed (35%) during the irradiation of compound **1a** in isopropanol. Interestingly, when compound **1a** was irradiated in dioxane under the same reaction conditions, the solvent addition product **4a** was formed in 39% together with recovered starting material.

Table 1
Products distribution for the irradiation reactions[a]

Starting compound	Solvent	Photoproducts[b] (yield %)
 **1a** (25%)[c]	THF	 **2a** (45 %, 73%[d])
 **1a** (22%)[c]	*i*-PrOH	 **3a** (35%)
 **1a** (19%)[c]	Dioxane	 **4a** (39%)
 **1b** (35%)[c]	THF	 **2b** (39%)
 **1b** (26%)[c]	*i*-PrOH	 **3b** (36%)
 **1c** (11%)[c]	THF	NR[e]
 **1d** (20%)[c]	THF	 **2d** (38%)[f]
 **1e** (18%)[c]	THF	 **2e** (40%)[f]
 **1f** (90%)[c]	THF	NR[e]
 **1g**	THF	 **2g** (8%)

[c] Recovered substrate.
[d] Determined by means of GC–MS.
[f] Sum of diastereoisomers.
[a] Reaction conditions: λ=305 nm, reaction time 8 h.
[b] Isolated yields.
[e] No reaction.

Considering the role of the aromatic moiety, the H–C insertion reaction was not affected by the presence of an electron-donating substituent on the benzoate part of the substrate: irradiation of compound **1b** in THF and *i*-PrOH afforded, respectively, **2b** and **3b** in 39% and 36% yields, values comparable to that obtained for compound **1a**. The presence of an electron-withdrawing group, such as in the case of compound **1c**, did not allow the isolation of addition photoproducts mainly due to the formation of decomposition mixtures.

Concerning the substitution pattern of the allylic moiety, methyl substitution did not affect the formation of the corresponding addition products (see irradiations of compounds **1d** and **1e** in Table 1), while dimethyl substituted substrate **1f** was not able to produce the corresponding insertion product, likely because of steric interactions. Finally, also starting from allylic alcohol **1g** the photoaddition product **2g** was obtained, albeit in very low isolated yield, likely due to its volatility.

As a general comment, the reaction yields are fair to good, considering recovered starting material, but unfortunately are reduced during work-up and purification, due to the volatility of final products, as evidenced in the case of compound **2a**, by observing reaction yield determined by means of GC–MS (see Table 1).

The presence of oxygen in the reaction media did not affect the reactivity since similar results were obtained from irradiations of **1a** in either nitrogen- or oxygen-purged THF solutions. Moreover, the involvement of photoinitiated chain-reaction processes could be excluded since shorter irradiations (30 and 120 min) followed by standing in the dark for 12 h did not result in significant substrate conversion.

Moreover, irradiation performed in the presence of benzophenone as a photocatalyst did not affect the reaction. Finally, irradiations performed in the presence of 10 equiv *E*-piperylene as a triplet quencher did not produce the photoaddition products. On the basis of these results we propose the involvement of a triplet state of the alkene, following a mechanistic pathway different from the common carbon-centered radical conjugate addition mechanism previously reported for electron-poor olefins.[1,2] Since the coupling of experimental data with a theoretical approach has proven successful to unravel competitive photochemical and thermal reaction pathways,[11] we have performed a computational study at the DFT level for the representative system **1a**–THF, both in vacuo and in the mimicked THF solvent. The values of the vertical transition energies of both singlet and triplet states for **1a** and THF, show that only allyl benzoate could be excited under the experimental conditions, with triplet states possibly accessible through an inter-system crossing (isc) (Table 2). The energies calculated along the reaction coordinate, and the geometries of the transition states and intermediates are reported in Table 3, and allowed us to rationalize several aspects of this unusual reactivity.

Table 2
Vertical excitation energies (kJ/mol (nm)) of singlet (S) and triplet (T) states, calculated in THF solution at the TD-DFT level, for **1a** and THF

	1a	THF
S1	393.4 (304.1)	565.2 (211.7)
S2	433.9 (275.7)	623.2 (192.0)
T1	337.9 (354.0)	561.3 (213.1)
T2	391.7 (305.4)	618.9 (193.3)

Table 3
Standard free energy values (ΔG°, kJ/mol) relative to **1a**–THF[a] for singlet and triplet species along the reaction pathway, and activation barriers (Δ$G^{‡}$, kJ/mol) for transition states, relative to the given starting compounds, calculated in vacuo and in THF at 298.15 K

Species	ΔG° in vacuo	ΔG° in THF
1a+THF	0.0	0.0
^{3}[**1a**]+THF	237.5	235.1
^{3}[**2a**]	247.7	242.5
2a	−64.6	−64.6
^{3}[**5**]	211.5	214.5
^{3}[**6**]	220.9	222.1

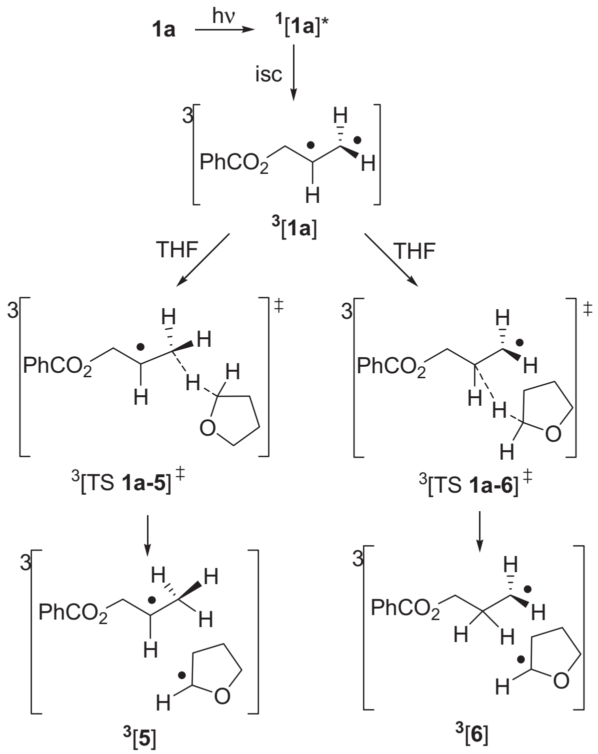
Transition states	ΔG° in vacuo	ΔG° in THF	Δ$G^{‡}$ in vacuo	Δ$G^{‡}$ in THF
^{3}[TS **1a-5**]‡	299.7	299.9	62.2	64.8
^{3}[TS **1a-6**]‡	311.7	311.8	74.2	76.7

[a] The standard free energy values calculated for **1a**+THF at the B3LYP/6-31++G(d,p) level are −769.794273 au in vacuo and −769.802900 au in THF.

From the computational analysis of the PES of the reagents ^{3}[**1a**]+THF, two potentially competitive pathways were evidenced. A favorable pathway, with activation barrier of 64.8 kJ/mol, suggests the possible conversion of ^{3}[**1a**]+THF to intermediate di-radical adduct ^{3}[**5**] (Scheme 2, Fig. 1a) through a hydrogen transfer from the C(2) of THF into the less substituted carbon of the double bond. A less favorable pathway, with activation barrier of 76.7 kJ/mol, leads to intermediate di-radical adduct ^{3}[**6**] (Scheme 2, Fig. 1a) through a hydrogen transfer into the highly substituted carbon of the double bond.

The formation of **2a** can be explained through two alternative or concurrent pathways, both involving the formation of 2′-THF radical. The formation of radical pair ^{3}[**6**], through the thermodynamically less favored pathway, would naturally evolve toward product **2a** by radical coupling and consequential spin multiplicity change (Scheme 3).

On the other hand, the favored formation of radical pair ^{3}[**5**] would need subsequent steps to evolve toward final product **2a**. Indeed, the addition of formed 2′-THF radical into **1a**, in a similar fashion to common carbon-centered radical conjugate additions mechanism, would involve the formation of radical ^{2}[**7**] through the easily accessible transition state ^{2}[TS **1a-5**]‡ (Δ$G^{‡}$=45.6 kJ/mol) (Scheme 4, Table 4, Fig. 1b). Finally, formation of compound **2a** could be ascribed to back hydrogen transfer from the alkyl radical of the ^{3}[**5**] pair. This, could explain why photoinitiated chain-reaction processes were not observed. This, mechanism could be interpreted in terms of a self-catalyzed reaction that represents a new insight into the photohydroalkylation of olefins.



Scheme 2. Proposed mechanism for the formation of triplet adducts.

Despite the fact that formation of radical pair ^{3}[**5**] is more favored, the competitive formation of radical pair ^{3}[**6**] could not be excluded considering the possible involvement of triplet states of higher energy (see T2 in Table 1), by means of direct formation through a forbidden transition or after isc.

3. Conclusions

The photoreactivity of allyl benzoates has been explored by irradiation at 305 nm in different solvents, revealing the feasibility of an unusual photo-mediated hydroalkylation reaction of electron-rich olefins with THF, dioxane, and *i*-PrOH. The observed reactivity depended on reaction conditions and substitution pattern of the substrate. The solvent addition product could be interpreted in terms of an insertion of the α H–C bonds of the solvent into the allylic double bond and was interestingly realized in the absence of additional photocatalysts. Experimental as well computational studies allowed formulation of two concurrent pathways for the photohydroalkylation reaction: a self-catalyzed radical mechanism without chain-reaction propagation and a new mechanism that essentially presents inverted steps with respect to the common carbon-centered radical conjugate additions mechanism, usually invoked for electron-poor olefins.

4. Experimental section

4.1. Instrumentation and chemicals

IR spectra were registered with a Shimadzu FTIR-8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER 300 Avance spectrometer, operating at 300 and 75 MHz, respectively,

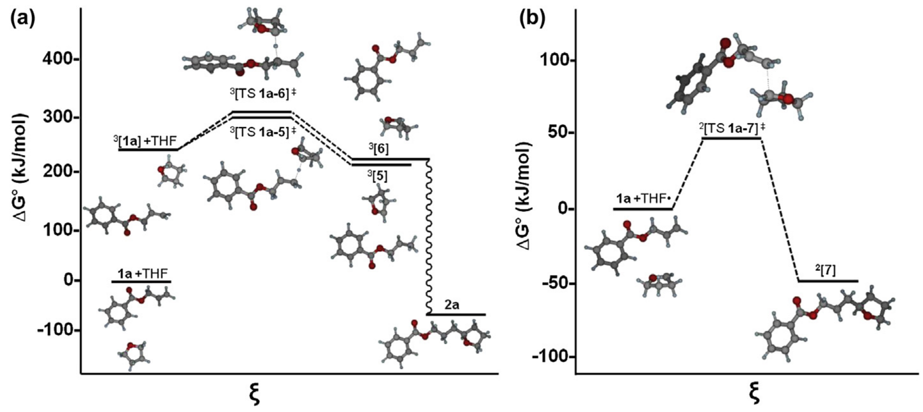
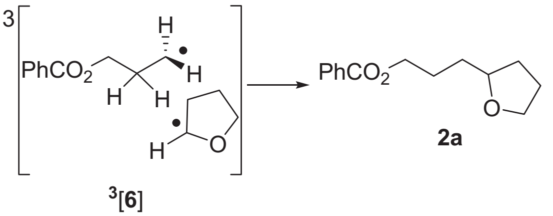
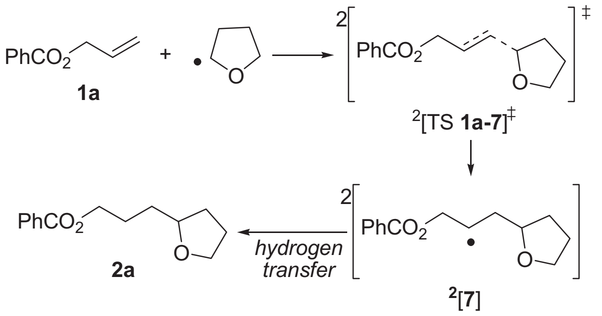


Fig. 1. (a) Standard free energy profiles along the reaction coordinate of **1a** in solution, at 298.15 K. (b) Standard free energy profiles along the reaction coordinate of **1a**—THF• in solution, at 298.15 K.



Scheme 3. Radical coupling for the formation of compound **2a**.



Scheme 4. Proposed mechanism for the formation of compound **2a**.

Table 4

Standard free energy values (ΔG°, kJ/mol), relative to **1a**—THF•[a] for transition states,[b] and product along the reaction pathway, calculated in vacuo and in THF at 298.15 K

Species	ΔG° in vacuo	ΔG° in THF
1a+THF•	0.0	0.0
^{3}[TS **1a-7**]‡	46.2	45.6
^{3}[**7**]	−44.4	−44.6

[a] The standard free energy values calculated for **1a**+THF• at the B3LYP/6-31++G(d,p) level are −769.149619 au in vacuo and −769.158237 au in THF; the thermal correction to the Gibbs free energy is 0.225066 au.

[b] Here the activation free energy, Δ$G^‡$, coincides with the standard free energy of the transition state.

with TMS as an internal standard. GC—MS determinations were carried out on a Shimadzu QP-2010. Flash chromatography was performed by using silica gel (Merck, 0.040—0.063 mm) and mixtures of ethyl acetate and petroleum ether (fraction boiling in the range of 40—60 °C) in various ratios. All solvents and compounds **1a**—**g** were obtained from commercial sources. Compounds **2g**[12] and **3a**[13] had physical characteristics identical to those of the compounds prepared by alternative procedures as reported in the literature.

4.2. General procedure for preparative photochemical reactions

Photochemical reactions were carried out in anhydrous solvent by using a Rayonet RPR-100 photoreactor fitted with 16 Hg lamps irradiating at 305 nm (in 45 mL Pyrex vessels) and a merry-go-round apparatus. In the case of analytical scale photoreactions, qualitative determinations were accomplished by GC—MS analysis. A sample of the substrate (0.4 g) in the appropriate solvent (350 mL), apportioned into nine Pyrex tubes, was irradiated for 8 h. After removal of the solvent, chromatography of the residue returned starting material and gave the following products (yields and recovering of starting materials are reported in Table 1).

*4.2.1. 3-(Tetrahydrofuran-2-yl)propyl benzoate (**2a**).* 260 mg, 45% yield; oil; ^{1}H NMR (CDCl$_3$) 8.05 (dt, J=7.0, 1.5 Hz, 2H, CH arom.), 7.56 (tt, J=7.0, 1.5 Hz, 1H, CH arom.), 7.45 (dt, J=7.0, 1.5 Hz, 2H, CH arom.), 4.36 (t, J=6.3 Hz, 2H, OCH$_2$), 3.87 (m, 2H, OCH$_2$), 3.73 (ddd, J=15.6, 7.5, 6.3 Hz, 1H, OCH), 2.10—1.80 (m, 5H), 1.80—1.60 (m, 2H), 1.50 (m, 1H); ^{13}C NMR (CDCl$_3$) 166.2 (C═O), 132.5 (CH arom.), 130.1 (C arom.), 129.2 (2CH arom.), 128.0 (2CH arom.), 78.5 (OCH), 67.4 (OCH$_2$), 64.6 (OCH$_2$), 31.8 (CH$_2$), 31.1 (CH$_2$), 25.5 (CH$_2$), 25.4 (CH$_2$); IR (liquid film) 2955, 2866, 1718, 1452, 1315, 1275, 1113, 1070, 1026, 712 cm^{-1}; MS m/z 206 ([M—CO]$^+$, 5), 191 (10), 129 (12), 112 (15), 105 (30), 84 (30), 77 (25), 71 (100),43 (25). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74; O, 20.49. Found: C, 71.65; H, 7.60; O, 20.40.

*4.2.2. 3-(1,4-Dioxan-2-yl)propyl benzoate (**4a**).* 241 mg, 39% yield; oil; ^{1}H NMR (CDCl$_3$) 8.00 (br d, J=8.7, 2H, CH arom.), 7.50 (tt, J=8.7, 2.7 Hz, 1H, CH arom.), 7.38 (br t, J=8.7 Hz, 2H, CH arom.), 4.29 (m, 2H, OCH$_2$), 3.74—3.47 (m, 5H, OCH$_2$), 3.24 (br t, J=12.7 Hz, 1H, OCH), 2.03—1.65 (m, 2H), 1.58—1.60 (m, 2H); ^{13}C NMR (CDCl$_3$) 166.4 (C═O), 132.8 (CH arom.), 130.3 (C arom.), 129.5 (2CH arom.), 128.3 (2CH arom.), 74.8 (OCH), 71.1 (OCH$_2$), 66.7 (OCH$_2$), 66.4 (OCH$_2$), 64.7 (OCH$_2$), 28.1 (CH$_2$), 24.5 (CH$_2$); IR (liquid film) 2956, 2852, 1714, 1602, 1451, 1314, 1275, 1099,, 1070, 713 cm^{-1}; MS m/z 219 ([M−1]$^+$, 5), 128 (50), 105 (100), 85 (60), 77 (50), 71 (25), 59 (30), 43 (25). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25; O, 25.57. Found: C, 67.35; H, 7.30; O, 25.30.

*4.2.3. 3-(Tetrahydrofuran-2-yl)propyl 4-methoxybenzoate (**2b**).* 215 mg, 39% yield; oil; ^{1}H NMR (CDCl$_3$) 8.00 (dt, J=9.0, 2.7 Hz, 2H, CH arom.), 6.92 (dt, J=9.0, 2.7 Hz, 2H, CH arom.), 4.34 (t, J=6.5 Hz, 2H, OCH$_2$), 3.89 (m, 2H, OCH$_2$), 3.75 (m, 1H, OCH), 2.10—1.40 (m, 8H); ^{13}C NMR (CDCl$_3$) 166.2 (C═O), 163.1 (C arom.), 131.4 (2 CH arom.), 122.7 (C arom.), 113.4 (2CH arom.), 78.7 (OCH), 67.5 (OCH$_2$), 64.5 (OCH$_2$), 55.2 (OCH$_3$), 31.9 (CH$_2$), 31.2 (CH$_2$), 25.6

(CH_2), 25.5 (CH_2). IR (liquid film) 2956, 2867, 1712, 1607, 1512, 1462, 1316, 1257, 1168, 1102, 1031, 849, 772, 697, 613 cm^{-1}; MS *m*/*z* 236 ($[M-CO]^+$, 5), 221 (5), 152 (20), 135 (70), 112 (25), 84 (100), 77 (20), 71 (70), 43 (30). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63; O, 24.21. Found: C, 67.95; H, 7.60; O, 24.30.

*4.2.4. 4-Hydroxy-4-methylpentyl 4-methoxybenzoate (**3b**).* 189 mg, 36% yield; oil; ^{1}H NMR ($CDCl_3$) 8.00 (dt, *J*=9.0, 2.1 Hz, 2H, CH arom.), 6.92 (dt, *J*=9.0, 2.1 Hz, 1H, CH arom.), 4.32 (t, *J*=6.3 Hz, 2H, OCH_2), 3.86 (s, 3H, OCH_3), 1.56 (t, *J*=6.3 Hz, 2H, CH_2), 1.26 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) 166.3 (C=O), 163.2 (C arom.), 131.5 (2CH arom.), 122.7 (C arom.), 113.5 (2CH arom.), 70.6 (C), 65.0 (OCH_2), 55.3 (OCH_3), 39.9 (CH_2–C), 29.2 ($2CH_3$), 23.8 (CH_2). IR (liquid film) 3400, 2967, 2935, 2843, 1711, 1607, 1512, 1317, 1259, 1169, 1104, 1030, 848, 772, 697, 614 cm^{-1}; MS *m*/*z* 224 ($[M-CO]^+$, 5), 177 (5), 152 (60), 135 (100), 107 (15), 92 (20), 85 (25), 77 (20), 59 (30), 43 (40). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99; O, 25.37. Found: C, 66.60; H, 7.90; O, 25.44.

*4.2.5. 4-(Tetrahydrofuran-2-yl)butan-2-yl benzoate (**2d**).* 214 mg, 38% yield; oil; ^{1}H NMR ($CDCl_3$) 8.05 (dt, *J*=7.0, 1.5 Hz, 2H, CH arom.), 7.50 (tt, *J*=7.0, 1.5 Hz, 1H, CH arom.), 7.40 (br t, *J*=7.0 Hz, 2H, CH arom.), 5.16 (m, 1H, OCH), 3.81 (m, 2H, OCH_2), 3.67 (m, 1H, OCH), 2.00–1.35 (m, 8H), 1.30 (d, *J*=7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) 166.0 (C=O), 132.6 (CH arom.), 130.6 (C arom.), 129.3 (2CH arom.), 128.1 (2CH arom.), 78.9 and 78.6 (OCH), 71.5 and 71.2 (OCH), 67.5 (OCH_2), 32.8 and 32.6 (CH_2), 31.5 and 31.2 (CH_2), 29.5 (CH_2), 25.5 (CH_2), 19.9 (CH_3). IR (liquid film) 2933, 2865, 1714, 1602, 1450, 1313, 1277, 1099, 1070, 1026, 713 cm^{-1}. MS *m*/*z* 220 ($[M-CO]^+$, 5), 105 (40), 84 (55), 77 (25), 71 (100), 43 (25). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12; O, 19.33. Found: C, 72.40; H, 7.98; O, 19.48.

*4.2.6. 3-(Tetrahydrofuran-2-yl)-2-methylpropyl benzoate (**2e**).* 225 mg, 40% yield; oil; ^{1}H NMR ($CDCl_3$) 8.05 (dt, *J*=7.0, 1.5 Hz, 2H, CH arom.), 7.50 (tt, *J*=7.0, 1.5 Hz, 1H, CH arom.), 7.40 (br t, *J*=7.0 Hz, 2H, CH arom.), 4.12 (m, 2H, OCH_2), 3.85 (m, 2H, OCH_2), 3.65 (m, 1H, OCH), 2.16–1.16 (m, 7H), 1.31 (d, *J*=7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) 166.4 (C=O), 132.7 (CH arom.), 130.3 (C arom.), 129.4 (2CH arom.), 128.2 (2CH arom.), 69.9 (OCH), 69.2 (OCH_2), 67.5 and 67.4 (OCH_2), 39.4 and 39.3 (CH_2), 31.9 and 31.7 (CH_2), 30.6 and 30.4 (CH_2), 25.5 and 25.4 (CH_2), 17.6 and 16.8 (CH_3). IR (liquid film) 2874, 1718, 1602, 1451, 1314, 1272, 1176, 1099, 1070, 1027, 712 cm^{-1}. MS *m*/*z* 220 ($[M-CO]^+$, 5), 105 (35), 84 (35), 77 (30), 71 (100), 43 (25). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12; O, 19.33. Found: C, 72.42; H, 8.00; O, 19.55.

4.3. Computational methods

The geometry of the molecular species considered, shown in Schemes 3 and 4, was fully optimized in the singlet or in the triplet spin state, by using the hybrid unrestricted DFT B3LYP functional[14] and the 6-31++G(d,p)[15] basis set. Vertical excitation energies of THF and **1a**, in THF solution, was calculated using the time-dependent DFT (TD-DFT) method,[16] at the same level of theory. Transition-state structures were found by the synchronous transit guided quasi-Newton method.[17] Vibration frequency calculations, within the harmonic approximation, were performed on each optimized structure, to confirm that its energy was a true minimum or a first order saddle point (for transition states) on the potential energy surface. Solvent effects were evaluated by performing single point calculations on the optimized structures, with the implicit THF solvent reproduced by the conductor-like polarized continuum model (CPCM).[18] The standard Gibbs free energy, at 298.15 K, of each energy minimum structure, both in vacuo and in THF solution, was calculated by adding the thermal correction obtained by vibration frequency analysis to the DFT energy calculated both in vacuo and in THF solution. All calculations were performed by the Gaussian 09 program package.[19]

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Supplementary data

NMR spectra of compounds **2**–**4** and coordinates of all computed species. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.05.093. These data include MOL files and InChiKeys of the most important compounds described in this article.

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