

An alternative synthetic path to 1-substituted 2-naphthol

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Electronic Supplementary Information

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General Methods

¹H NMR and ¹³C NMR spectra were recorded on a 200 MHz (products **5** and **7**) and 400 MHz (product **9**) nuclear magnetic resonance spectrometers. In the first case the solvent used was carbon tetrachloride with a capillary tube with deuterated acetone inside, and in the second one the solvent was deuterated acetone. Gas chromatographic analyses were performed on a GC with a flame-ionization detector, using a capillary column (methyl silicone, 30 m length x 0.25 mm internal diameter x 0.25 μm film thickness). The GS/MS analyses were carried out employing a 30 m x 0.12 mm DB-5 MS column. Irradiation was conducted in a reactor equipped with two 400-W lamps emitting maximally at 350 nm (air and water refrigerated). Column chromatography was performed on silica gel (70-270 mesh ASTM).

Materials

Potassium *tert*-butoxide, benzenethiol, 2-naphthalenethiol, benzophenone, naphthalene, chlorobenzene and 1-bromo-2-naphthol were commercially available and used as received.

Dimethylsulfoxide dried with molecular sieves 4A.

Nitromethane distilled at reduced pressure and kept dried with molecular sieves 4A.

2-naphthol distilled at reduced pressure in a Kugelrohr equip.

Diethylphosphite synthesized from PCl₃ and ethanol and distilled at reduced pressure.¹

N,N-di-(*n*-butyl)-*p*-toluenesulfonamide synthesized from *n*-dibutylamine and *p*-toluenesulfonide chloride.²

Experimental Procedures

Photoinduced reactions of anions **1** and **4** in the presence of **2**: The following procedure is representative of all the reactions of **1** with **4**, **6** or sulfur anions in the presence of an electron acceptor. The reactions were carried out in a 50 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 5 mL of dry and degassed dimethylsulfoxide, potassium *tert*-butoxide (1.93 mmol) was added. After total dissolution of the base, 2-naphthol (0.60 mmol), diethylphosphite (1.02 mmol) and *N,N*-di-(*n*-butyl)-*p*-toluenesulfonamide (0.11 mmol) were added. The reaction mixture was irradiated with two 400-W lamps emitting maximally at 350 nm (air and water refrigerated) for 3h. The reaction was quenched with an excess of ammonium nitrate and 30 mL of water were added. After that, it was extracted three times with dichloromethane (portions of 10 mL), and the organic layer obtained was washed twice with water (portions of 15 mL) to eliminate traces of dimethylsulfoxide. The yield of product **5** was quantified by gas chromatography with the internal standard method.

2-Naphthoxide³ and benzenethiolate⁴ anions have very similar oxidation potentials, however, the photoexcitation of the anions (compare entries 1 and 3, Table 2) is required to facilitate the electron transfer. 2-Naphthoxide anion has an absorption maximum at 396 nm in DMSO⁵ and is efficiently excited with the lamps used in this work. On the other hand, benzenethiolate anion has an absorption maximum at 306 nm in DMSO and is not efficiently excited in our system. We also explored the possibility of forming the phenylthiyl radical, using this method; however, we obtained very low performances. In the case of nitromethane anion, it is not excited in our system and is known that it is not a good electron donor with different aromatic and aliphatic halides.⁶

¹ Mc Combie, H.; Saunders, B. C.; Stacy, G. J. *J. Chem. Soc.* **1945**, 380.

² Vogel's, *Practical Organic Chemistry*, 5th. Ed., J. Wiley, New York, **1989**, 1275.

³ Das, T. M.; Neta, P. *J. Phys. Chem. A* **1998**, *102*, 7081.

⁴ Armstrong, D. M.; Sun, Q.; Schuler, R. H. *J. Phys. Chem* **1996**, *100*, 9892.

⁵ Soumillion, J. Ph.; Vandereecken, P.; Van Der Auweraer, M.; Schryver, F. C.; Schanck, A. *J. Am. Chem. Soc.* **1989**, *111*, 2217.

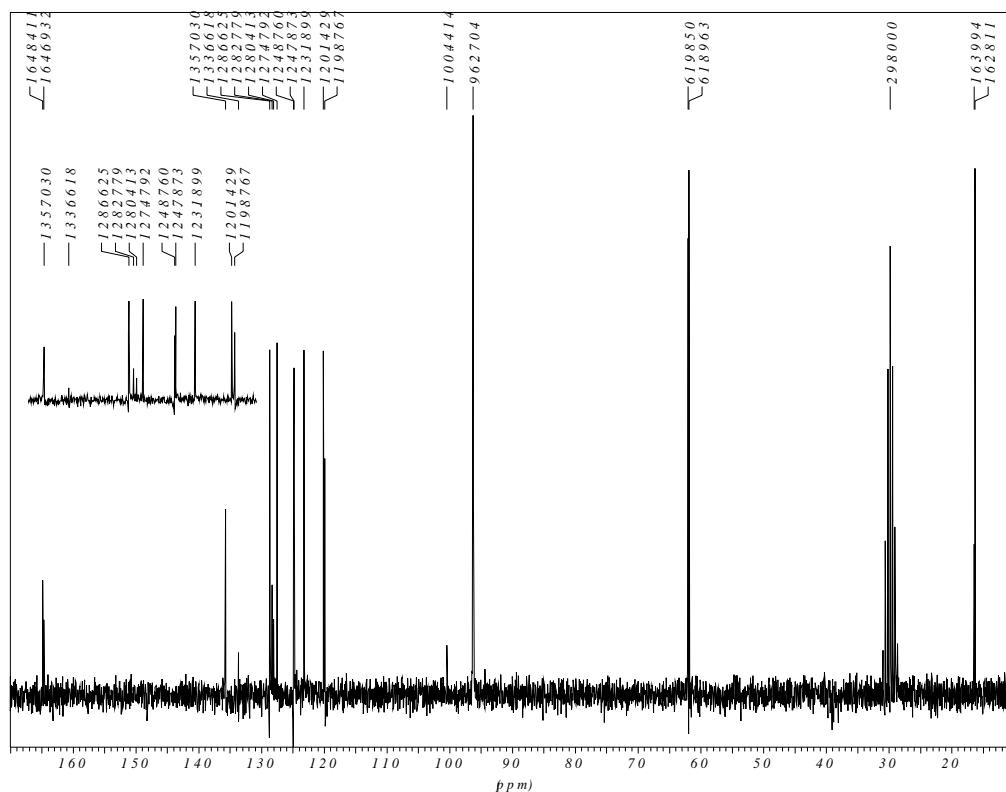
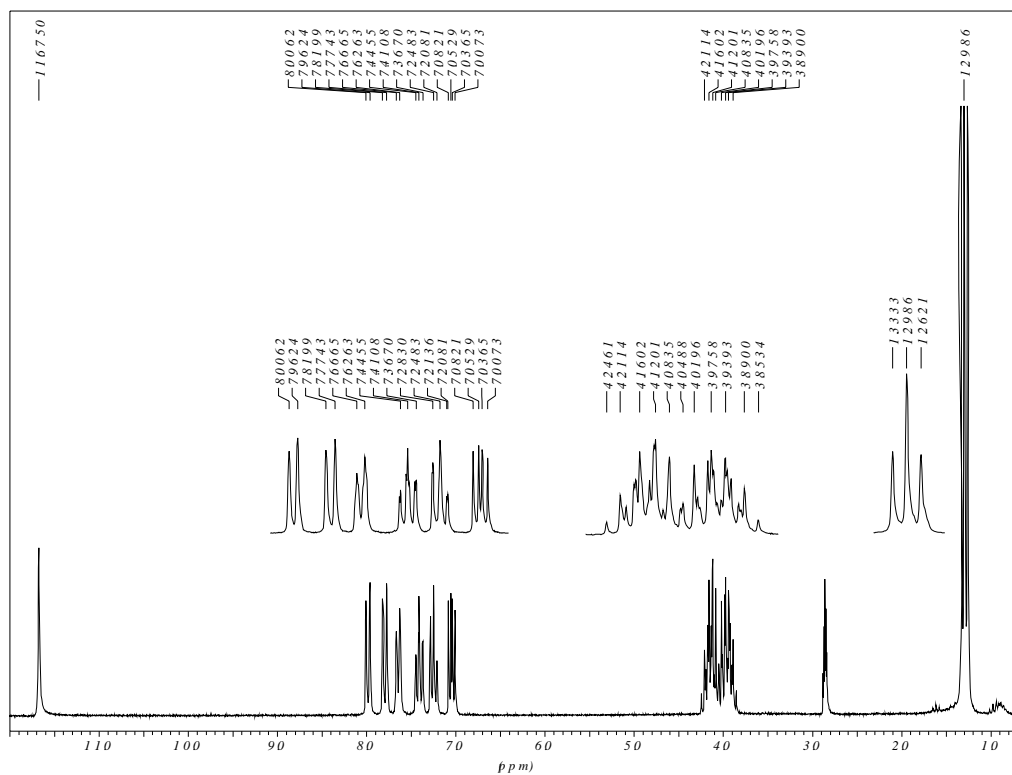
⁶ Rossi, R. A.; Pierini, A. B.; Peññory, A. B. *Chem. Rev.* **2003**, *103*, 71.

Diethyl(2-hydroxy-1-naphthyl)phosphonate 5

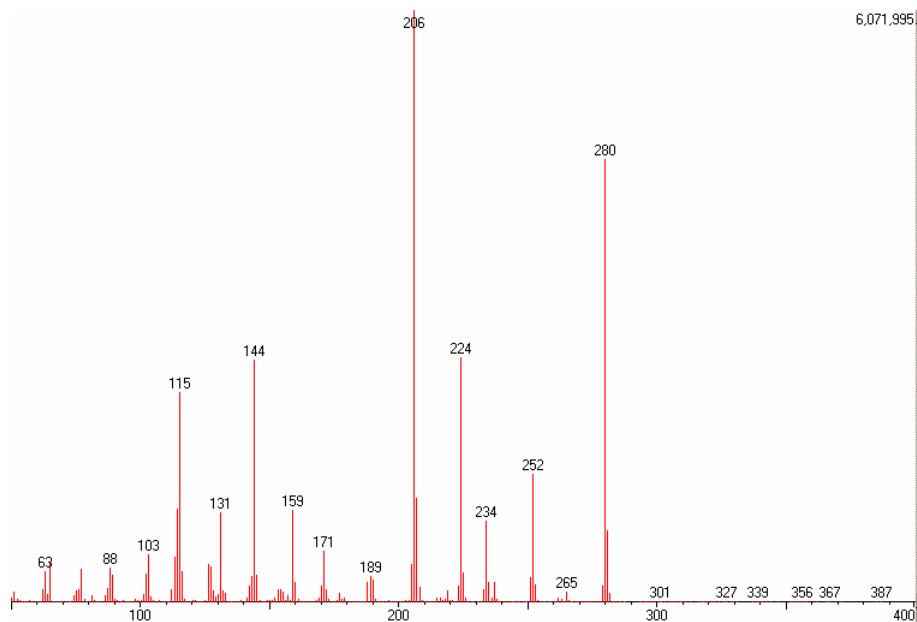
HRMS calculated for $C_{14}H_{17}O_4P$ 280.08645, found 280.08633.

Copies of 1H NMR and ^{13}C spectra

δ_H 1.26-1.33 (6H, t), 3.85-4.25 (4H, m), 7.01-7.08 (1H, dd, $J_1 = 5.84$ Hz $J_2 = 9.12$ Hz), 7.21-7.29 (1H, m), 7.37-7.45 (1H, m), 7.65 (1H, d, $J = 8.04$ Hz), 7.80 (1H, d, $J = 9.12$ Hz), 7.98 (1H, d, $J = 8.76$ Hz), 11.68 (1H, s, OH)



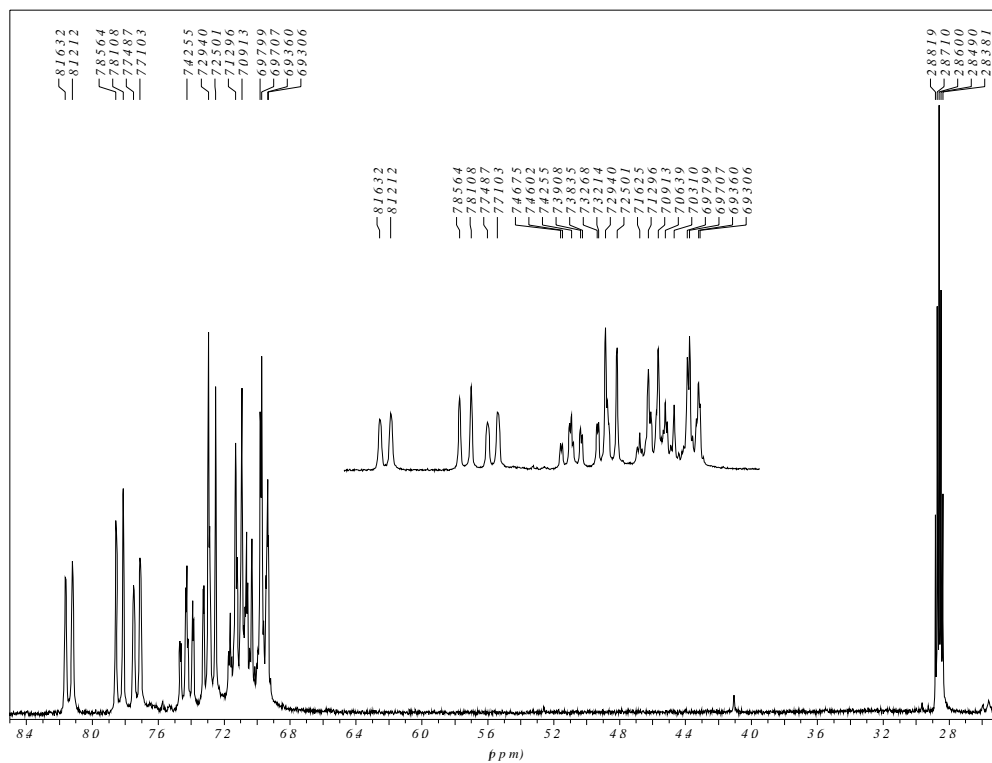
MS (EI = 70eV)

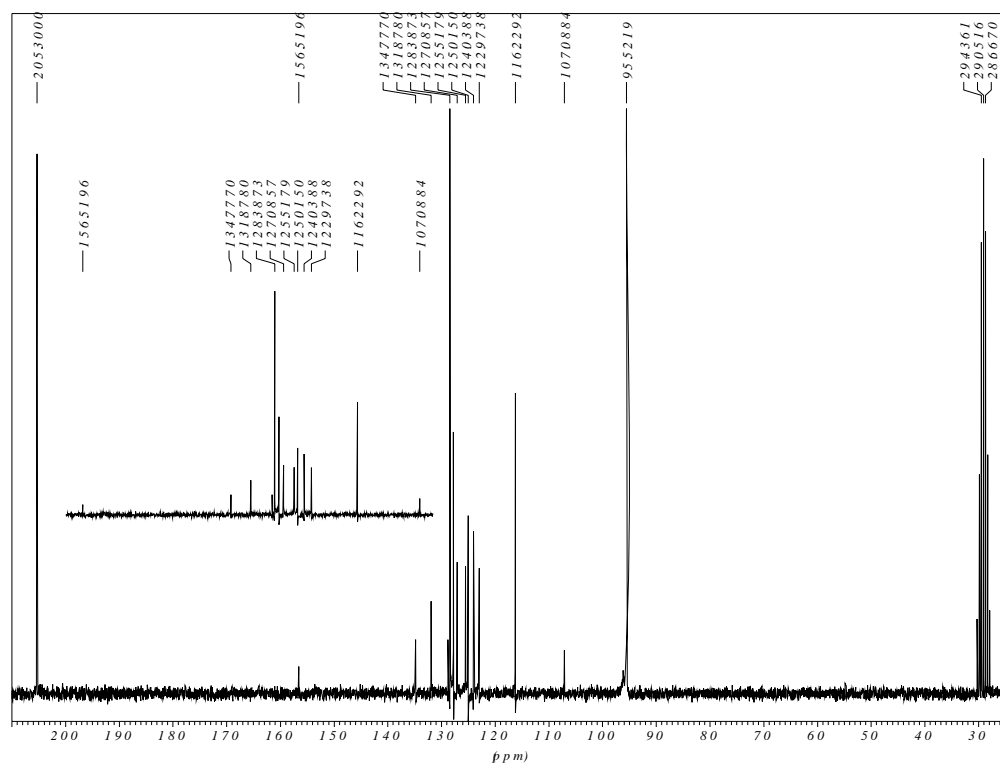


1-(phenylthio)-2-naphthol 7

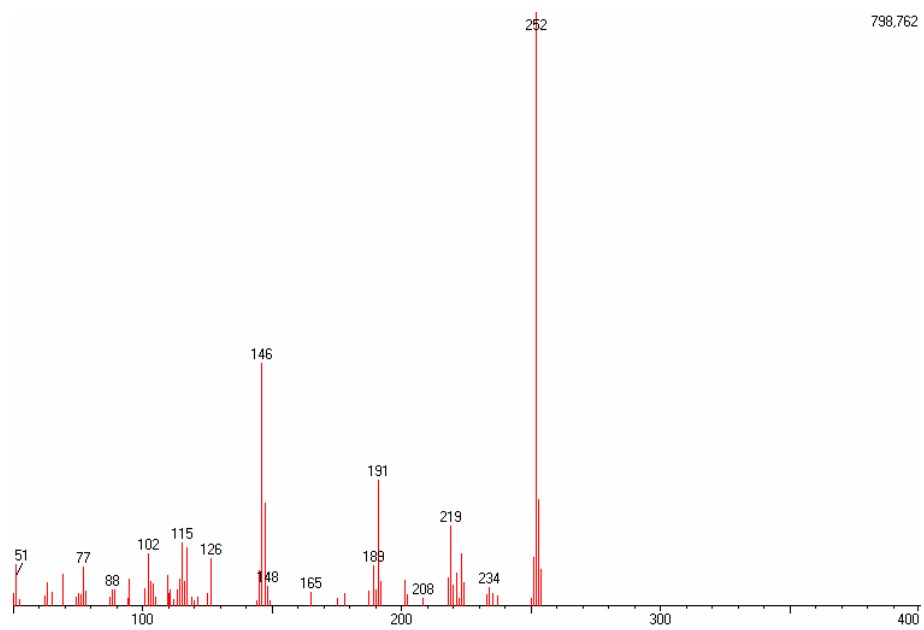
Copies of ^1H NMR and ^{13}C spectra

δ_{H} 6.93-7.17 (6H, m), 7.25-7.33 (2H, m), 7.38-7.47 (1H, m), 7.73 (1H, d, $J = 7.68$ Hz), 7.83 (1H, d, $J = 9.12$ Hz), 8.14 (1H, d, $J = 8.40$ Hz)





MS (EI = 70eV)

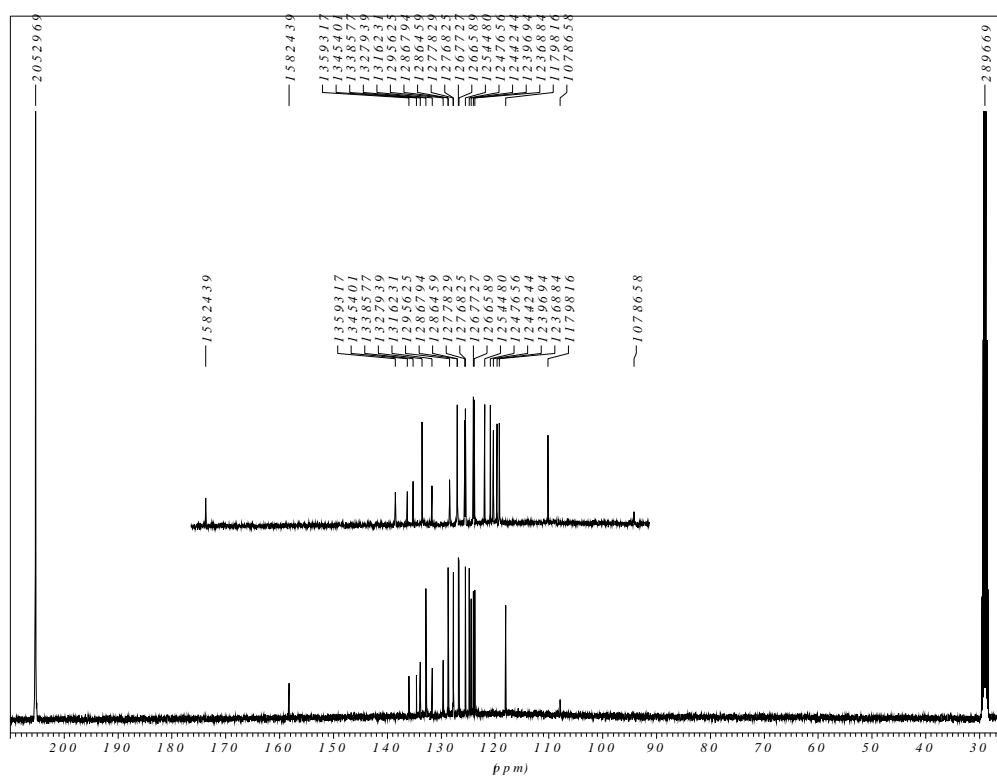
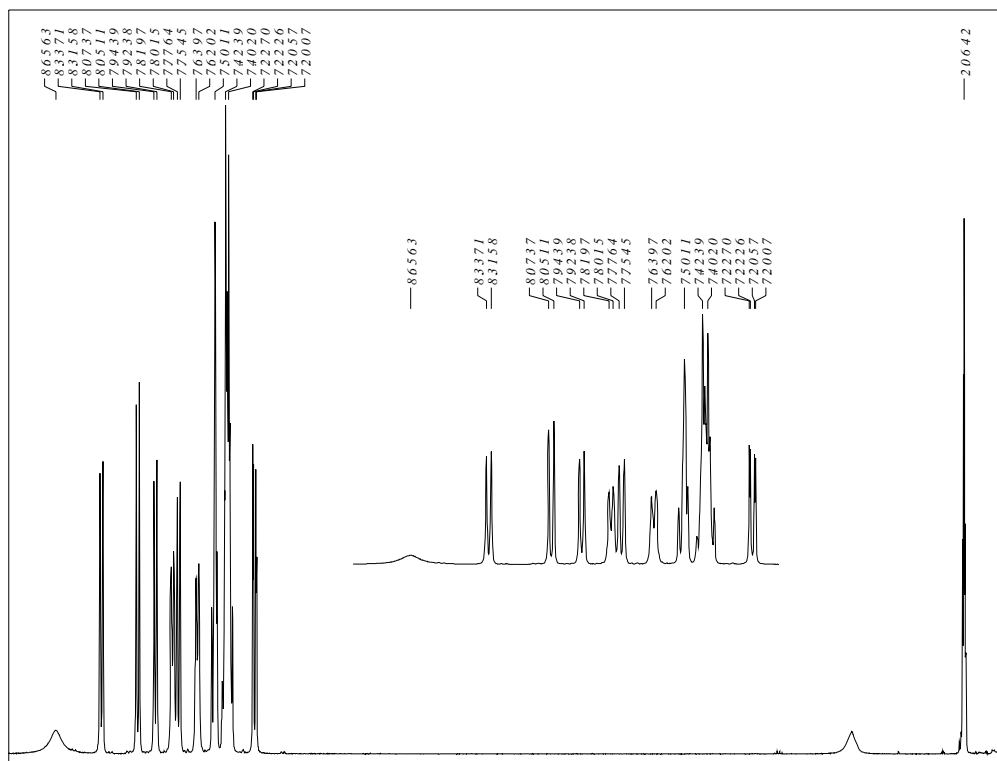


1-(2-naphthylthio)-2-naphthol **9**

1-(2-naphthylthio)-2-naphthol was synthesized by other route from di-(2-naphthyl)-disulfide and 2-naphthol, and isolated from this reaction to verify the proposed structure for **9**.

Copies of ^1H NMR and ^{13}C spectra

δ_{H} 7.20-7.23 (1H, dd, $J_1 = 8.64$ Hz $J_2 = 1.88$ Hz), 7.38-7.45 (4H, m), 7.49-7.52 (2H, m), 7.63 (1H, d, $J = 7.76$ Hz), 7.76 (1H, d, $J = 8.68$ Hz), 7.81 (1H, d, $J = 7.20$ Hz), 7.93 (1H, d, $J = 8.08$ Hz), 8.06 (1H, d, $J = 8.96$ Hz), 8.33 (1H, d, $J = 8.52$ Hz), 8.66 (1H, s, OH)



MS (EI = 70eV)

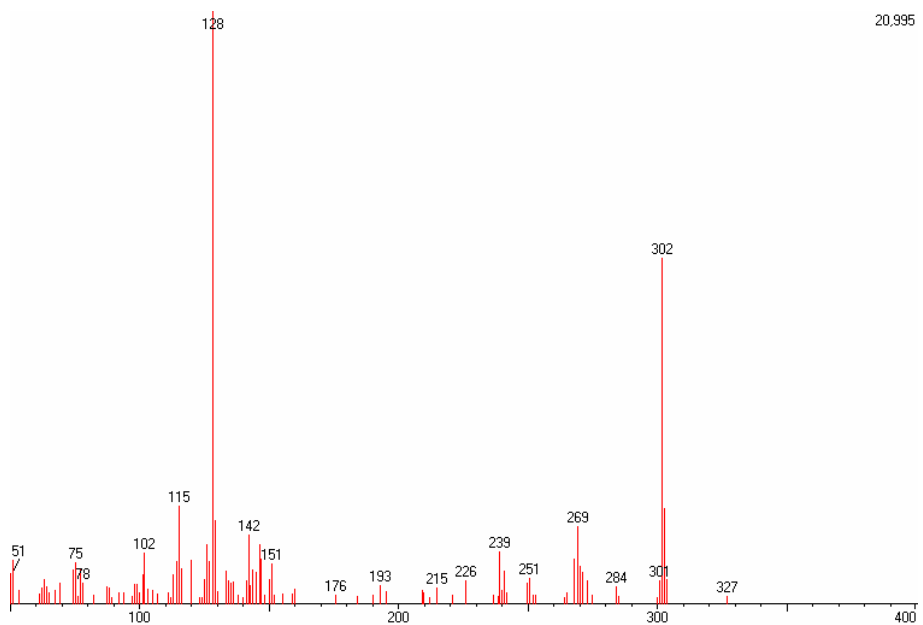


Table of energy differences (kcal/mol) between relevant points of the PES for the coupling of radical **3** with anion **4**.

	DFT B3LYP 6-31+G*	Reaction parameters	Reaction site of radical 3	
			C ₁	O
Energy	Gas fase	ΔE_a^a	-13,51	-13,65
		ΔE_r^b	-23,30	-21,01
	Solvent ^c	ΔE_a^a	0,72	1,46
		ΔE_r^b	-10,23	-4,12
Free energy	Gas fase	ΔG_a^d	-1,05	-1,75
		ΔG_r^e	-10,05	-7,90
	Solvent ^c	ΔG_a^d	13,18	13,36
		ΔG_r^e	3,02	8,99

^a ΔE_a (kcal/mol) = Energy difference between transition states and reactants (radical **3** + anion **4**).

^b ΔE_r (kcal/mol) = Energy difference between radical anions and reactants.

^c Tomasi's polarised continuum model (PCM) for DMSO without geometry optimization.

^d ΔG_a (kcal/mol) = Free energy difference between transition states and reactants. In solvent calculations the energy correction is taken as the same as in gas fase.

^e ΔG_r (kcal/mol) = Free energy difference between radical anions and reactants. In solvent calculations the energy correction is taken as the same as in gas fase.