Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Anions involved in initiation of the thermal induced $S_{RN}1$ reaction for α-arylation of ketones

Daniel A. Caminos*, Marcelo Puiatti, Javier Ivan Bardagí, and Alicia B. Peñéñory

INFIQC, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria,
X5000HUA Córdoba, Argentina,* dcaminos@fcq.unc.edu.ar
www.fcq.unc.edu.ar/infiqc

Contents

Chemicals

Potassium *ter*-butoxide (*t*BuOK), iodobenzene, acetophenone, propiophenone, butyrophenone, BuLi (in hexane), 4-iodo-toluene, bromobenzyl, lithium chloride were all high-purity commercial samples used without further purification. 1,2-di-phenylethanone was synthesized by mw and isolated by chromatography like in our previous works[1,2] DMSO and DMF absolute grade was used without further purification and stored over molecular sieves (4 Å).

General Methods

^{1}H and ^{13}C NMR spectra were recorded at 400.16 and 100.62 MHz respectively on a 400 spectrometer, and all spectra were reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ as solvent. Gas chromatographic analyses were performed with a flame-ionization detector, on 30 m capillary column of a 0.32 mm x 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. GC-MS analyses were performed employing a 25 m x 0.2 mm x 0.33 μm with a 5% phenylpolysiloxane phase column. HRMS spectra were recorded on a GCT Premie orthogonal acceleration time-of-flight (oa-TOF) GC mass spectrometer. Ionization was achieved by electronic impact (70 eV) and detection set up positive mode.

Representative experimental procedure

The reactions were carried out in a 10 mL CEM Discover microwave glass vessel, filled with nitrogen and a magnetic stirrer and 2.5mmol of *t*BuOK. The tube was dried under vacuum, refilled with nitrogen, and then, charged with dried DMSO (2 mL) and degassed. Then 1.5 mmol of the alkyl-phenyl ketone and iodobenzene (0.5 mmol) were then added to the degassed solvent under nitrogen atmosphere. Microwave-induced reactions were performed in a single mode instrument equipped with a noncontact infrared temperature sensor, direct pressure control system and a cooling system by compressed air. The sample vessels were irradiated by a microwave pulse at 100 W for 15 seconds. The temperature was recorded by the internal IR sensor in the bottom of the reactor chamber. After irradiation, the device cooled the tube to 50°C with compressed air above 1 min. (-0.5°C/sec). The average pressure was 1 atm in the vessel during the reaction time. Then, the vessel was removed from the microwave cavity and opened to the atmosphere. The reaction was subsequently quenched by addition of water (10 mL) and NH_4NO_3 in excess, and the mixture was extracted with 10 mL ethyl acetate and water (2× 10 mL). The combined organic extract was dried over anhydrous $CaCl_2$, and complete with ethyl acetate to get 10 mL and the water extract were filled to 100 mL for further quantification. The products were quantified by GC or NMR by the internal standard method or isolated by silica gel chromatography from the crude product reaction mixture. Water layer was recovered to quantify halide ions by potentiometric titration with an $AgNO_3$ standard solution.

Typical mw profile

Figure S1, shows some typical reaction profiles under microwave irradiation of 100 W-15 seconds in a 10 mL vessel with 0.5 mmol PhI and the anion in 2 mL of DMSO under $N_{2(g)}$ atmosphere. In each reaction profile, it can be observed power (W, in green line) and temperature (ºC by IR sensor in red line) and pressure (Bar, blue lines).All parameters were determinated by internal sensors of the CEM Discover reactor. The profiles represents: a) in the coupling reaction of 0.5 mmol PhI, 1.5mmol propiophenone and 2.5 mmol *t*BuOK. b)reaction of 0.5 mmol PhI with dimsyl anion 0.012M; c) reaction of 0.5 mmol PhI with 0.5M *t*BuOK and d) reaction of 0.5 mmol PhI with 0.5 M acetophenone enolate anion in DMSO.

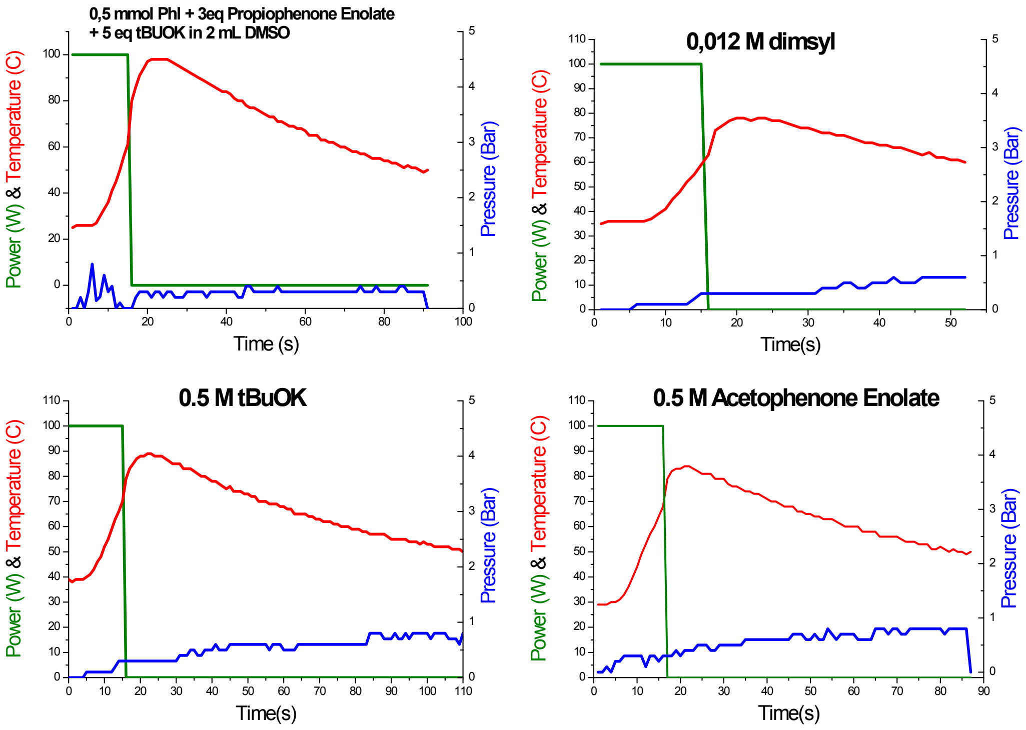
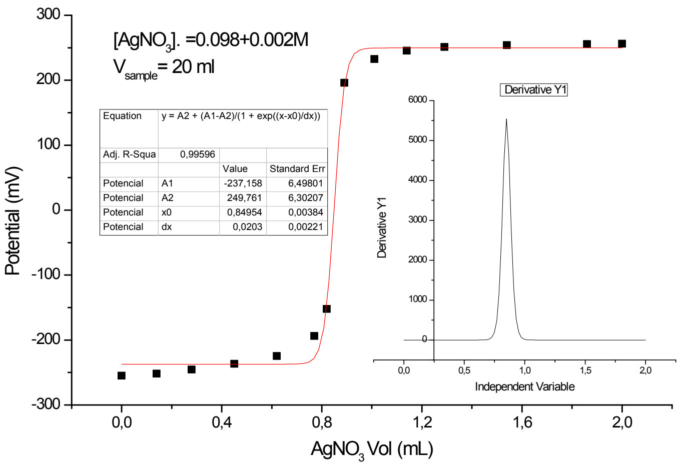


Figure S 1. CEM Discover reactor record the reaction conditions. In each figure, microwave power (green), IR temperature sensor (red) and pressure(blue) profiles for differnet reactions

Iodide quantification by tritation with $AgNO_3$

Water layer from reaction extraction was recovered and completed to 100 mL with distilled MQ water. To quantify halide ions aliquots (10; 20 or 40 mL) of the water solution were transferred in a 100 mL beacker with a magnetic stirrer and sodium thiosulfate and nitric acid was added to reduce all the I_2 to Iodide. Then [$AgNO_3$] 0.098±0.002 M standard solution was added gently and the titration was followed potentiometriclly with an using an Ag/Ag(I) electrode. The Figure S2 shows a typical titration profile. First derivative was used to determinate the equivalent point.



Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Adj. R-Squa	0,99596		
		Value	Standard Err
Potencial	A1	-237,158	6,49801
Potencial	A2	249,761	6,30207
Potencial	x0	0,84954	0,00384
Potencial	dx	0,0203	0,00221

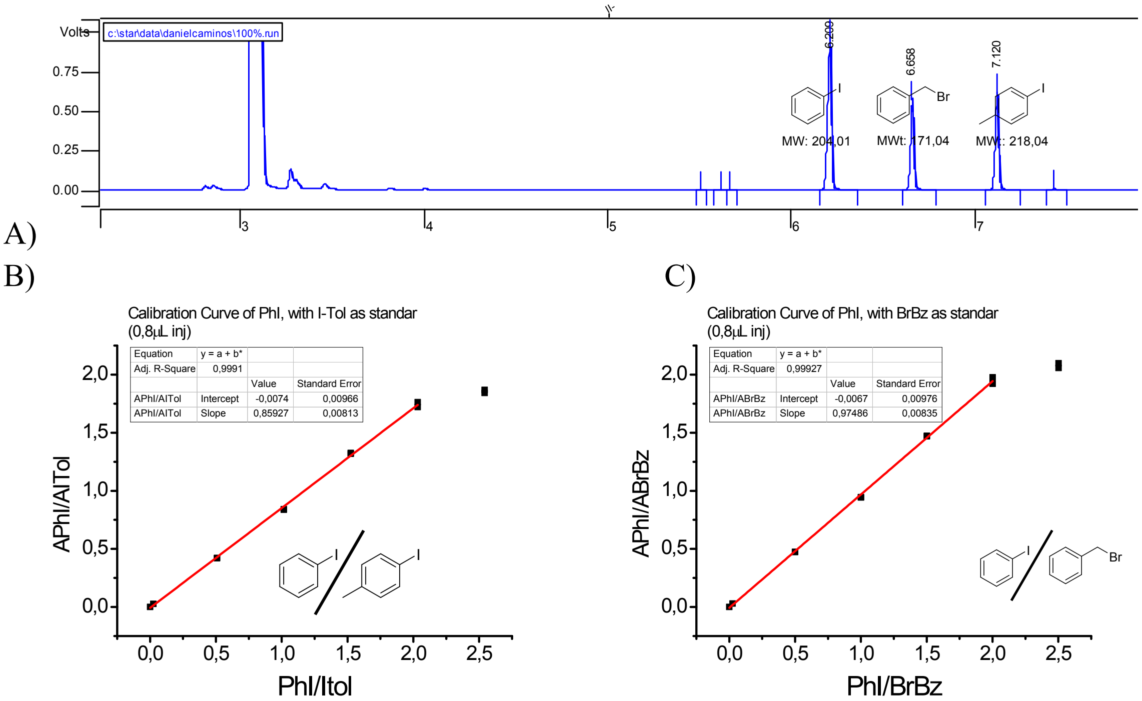
Figure S 2: Tritation profile from water extract from the reaction of 0.5mmol PhI and acetophenone enolate 1.25 M in DMSO (2mL), irradiated by mw 100W-15s., under N2(g) atmosphere.

Calibration curve for PhI

The presence of PhI after microwave reaction was determinate by GC-FID chromatography using an internal standard with both benzyl bromide (BzBr) and I-Toluene. The organic extracts (10 mL) from the reactions with *t*BuOK, were used for this method. Although calibration curves showed a linear fit in the for the two reference compounds, the quantification of the remaining PhI, in each reaction did not have a similar response. (Figure S3). We observe a downward trend but also a great dispersion of data in reference to the potentiometric quantification of the corresponding iodide. Even in the control reactions without *t*BuOK the yield of recovery PhI does not reach the 100%. We think there are a large loss of PhI in the *work up* process. For this reason, we did not use the quantification of PhI for subsequent analysis. Nevertheless, for the quantification, 1 mL aliquot fromthe organic extract was transfer to a 2 mL CG-vial, and then 0.5 mL of double standard solution [BrBz]=0.0506±0.0001 M and [I-tol]= 0.0498 ±0.0001 M was added. All vials were processed by an autosampler CG-FID. The calibration curve was prepared 0%, 5%, 25%, 50%, 75%, 100% and 125% in relation to the 0.5 mmol (100%) of PhI in the organic extract the standar reaction We use a [PhI] =0.0633±0.0003 M according Table S 1 and equation (1)

Table S 1. Calibration curve preparation

	Solutions						
	0%	5%	25%	50%	75%	100%	125%
Standard Solution	500µL// (0.0166±0.005)M·10^{-5} I-tol // (0.01686±0.005)M·10^{-5} BrBzl						
PhI	--	10 µL	200 µL	400 µL	600 µL	800 µL	1000 µL
AcOET	1 mL	0.96 mL	0.8 mL	0.6 mL	0.4 mL	0.2 mL	-
V_F	1.5 mL						
mol PhI (relativ)	0	0.0025	0.0125	0.025	0.0375	0.05	0.0625
mol PhI (real)·10^{-5}	0	0.0633	1.266	2.532	3.798	5.064	6.33
[PhI] 10^{-3}	0	0.422	8.4	16.88	25.32	33.76	42.2



$$\frac{A_{PhI}}{A_{Std}} = F\cdot\frac{mol\ PhI}{mol\ Std} \qquad (1)$$

R^2	F	Ord	range	Std	Inj
0.99984	0.929±0.004	0.003±0.003	0-75%	BrBz	1µL
0.99961	0.837±0.006	0.005±0.005	0-75%	I-Tol	1µL
0.9992	0.975±0.008	0.007±0.009	0-100%	BrBz	0.8µL
0.99911	0.859±0.008	0.007±0.009	0-100%	I-Tol	0.8µL

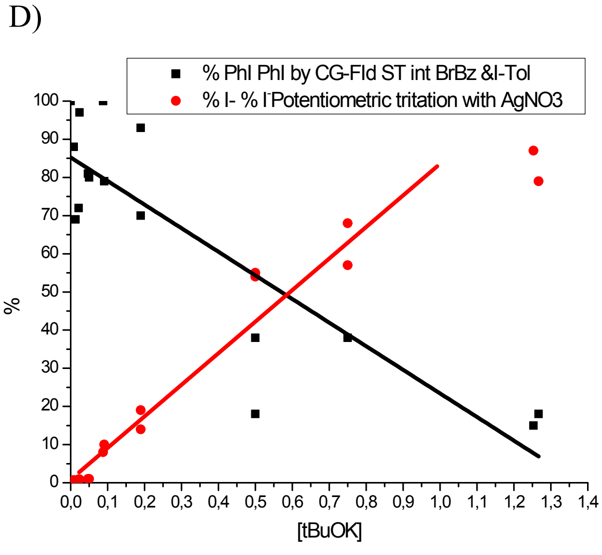
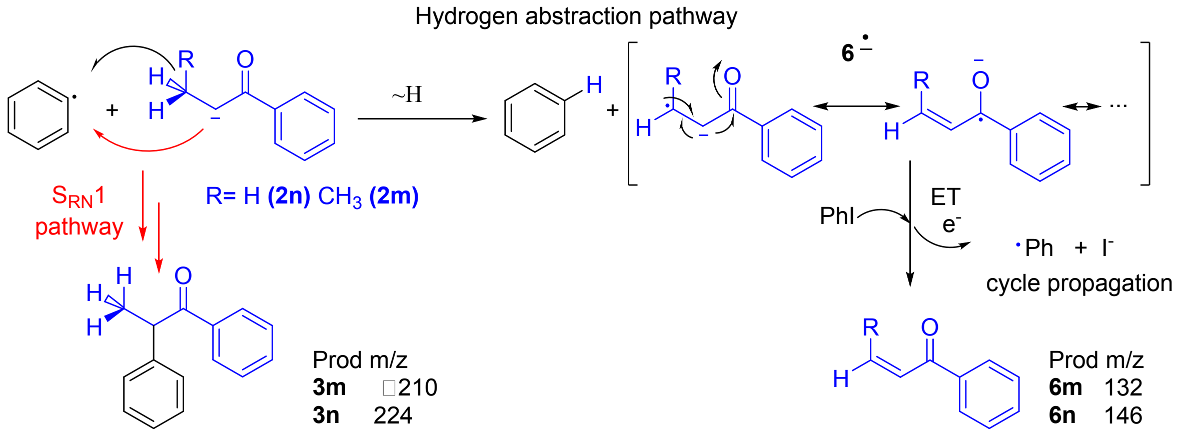


Figure S 3. A) GC-FID Chromatogram for 100 % solution. Calibration cruves for IPh/I-Tol (B), and Iph/BrBz (C). D) Yield quantification of PhI by CG-FID (black) and Iodide (Red) by potentiometric tritation.

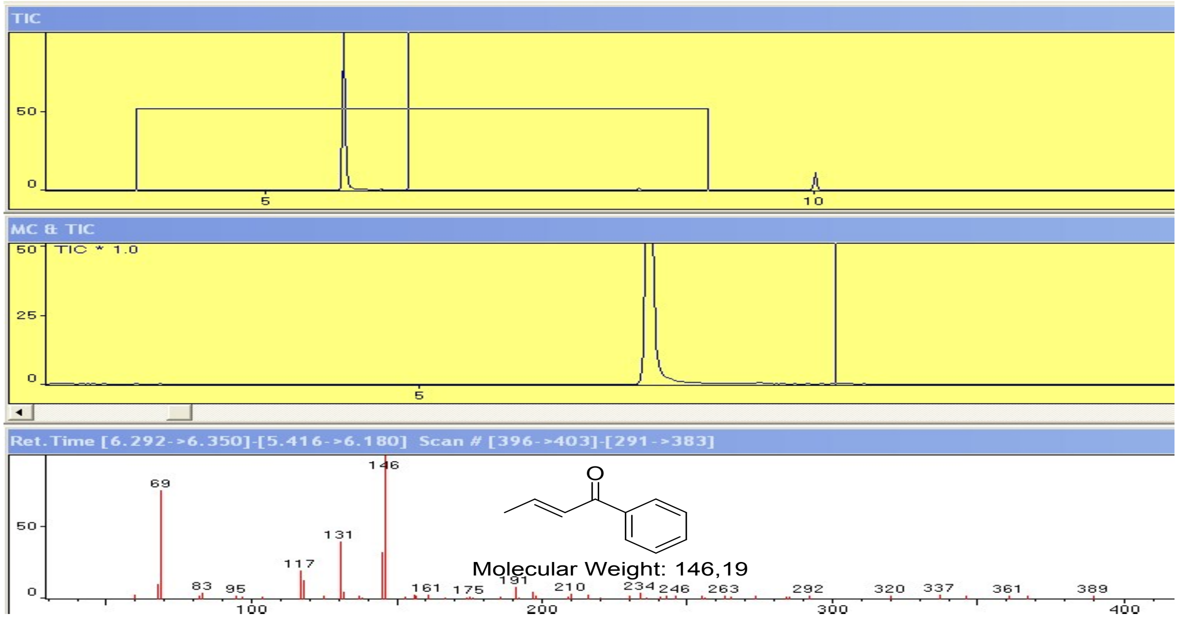
Competition with H_β abstraction

In the case of products **3m** (17%) and **3n** (22%**),** the yields are 50% lower than spected for other acetophenones. (~50 %). [3] This tendency was found by Dell'Erba *et al*, when they use azosulfides (Ar-N=N-StBu) as substrate and the same nucleopyiles **2a**, **2n** and **2m.** In that case, the coupling product yield was 95% **3a**, 60% **3n** and 52% **3m.** This is due to the presence of H_β in the nucleophile. In these cases there is an H abstraction by the $Ph^\bullet$ radical which competes with the coupling reaction by the $S_{RN}1$ mechanims.3 Thus the $Ph^\bullet$ radical is reduced and the new radical anion $\mathbf{6}^{\cdot -}$ is formed. Then, the radical anion $Nu^{\cdot -}$ by an ET to PhI form 2-eneketone and this pathway continues the radical chain Thus a decreasing in the the coupling product yield was found, but without visible effect on yield of dehalogenation, which reaches ~95% (see Scheme S1)



Scheme S 1: Competition phatways in the reaction between Ph radical and enolate nuecleophile with H_β.

Product **6n** was detected in GC-MS analysis (Figure S3). Although product **6m** was not detected in the reaction it is known that 2-eneketone are activated to Michael addition and reaction with the nucleophile (**2m**) will be fast.



4n Fragmentation

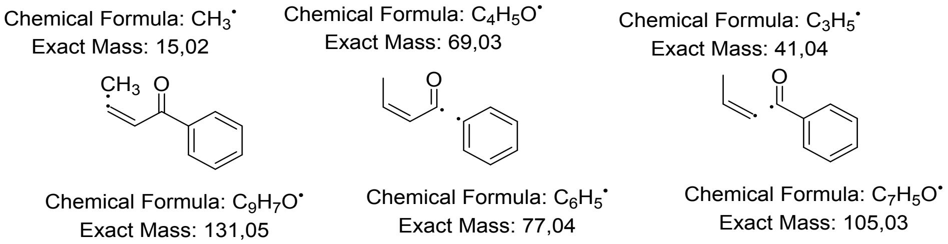


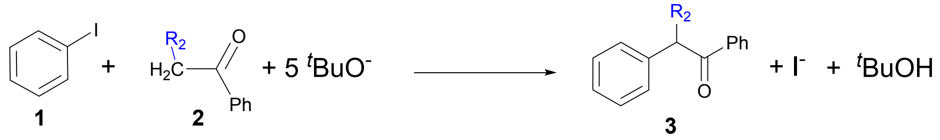
Figure S 4. GC-MS chromatogram from coupling reaction of butyrophenone (2n) and PhI with *t*BuOK in DMSO. Top: full chromatogram, then zoom area and in the bottom area TIC espectrogram and framentation. The (1-phenylbut-2-en-1-one (4n) was detected as trace (t_r= 6.2 min), in a CG-MS analisis of organic extract and identified by their framentation patern.

Coupling Reactions in DMF

Drapeau *et al* published results of a similar to ours reaction, with PhI (1 mmol), 5 eq. of *t*BuOK and 2 eq. of propiophenone (**2m**) as nucleophile in 3 mL of DMF at 60°C giving a 99% yield of **3m** product when it is left 13 h with conventional heating under argon atmosphere. [4] Even the reaction seems effective at room temperature (23ºC) and extending the time reaction to 48 hours. In the case of DMSO as solvent at 60 °C, the yield is less than 1%. In this work a variety of propiophenone derivatives nucleophiles are presented in addition to other ArX (X= I, Br and Cl) and authors claims that the reaction is efficient even with 5 eq DMF or undistilled solvent. In that work from *Dapreau* while a radical mechanism is proposed, similar to our works, the initiation process presented depends on the exclusive participation of DMF in the catalytic cycle. This proposal is supported by computer calculations.

All attempts to reproduce *Drapeau* reactions have so far been unsuccessful (see table S2, entries 5, 9 and 10). In a best attempt, we achieved 50% yield of product **3m** after 13 h at 60ºC in DMF. All reagents and solvents were analyzed by ^1H and ^{13}C-NMR, and contaminants were not detected. The reagents were newly opened and further analyzed by GC-FID and GC-MS, obtaining similar information. The reagents used in further reactions under microwave irradiation and oild bath heating, showed similar results to that already studied (Table 1, **3a**, **3m** and **3n**). It is important to note that commercial *t*BuOK may contain small amounts of KOH and K_2CO_3, which could be affecting the the reaction.[5] In a recent communication, the authors suggest that the previous sublimation of *t*BuOK is crucial to achieve the yields indicated in the article.[6]

Table S 2. Coupling reactions between PhI and enolates anion from achetophenone or propiophenone by mw or oil bath heating



#	*[PhI] M*	*R_2*	*[Anion]M*	*[^{t}BuOK]M*	*heat*	*Atm*	*Solvent*	*Temp. ºC*	*Time*	*% 3*[a]	*%I^-*[b]
1[c]	0.33	CH_2	0.66	1.66	ϕ	Ar	DMF 3mL	60	13h	85	-
2	0.33	CH_2	0.66	1.66	ϕ	Ar	DMF 3mL	60	13h	14 55	82 82
3[c]	0.33	CH_2	0.66	1.66	ϕ	Ar	DMF 3mL	23	48h	85	-
4[c]	0.33	CH_2	0.66	1.66	ϕ	Ar	DMF 3mL	23	72h	99	-
5	0.33	CH_2	0.66	1.66	ϕ	Ar	DMF 3mL	23	72h	0	15
6[c]	0.33	CH_2	0.66	1.66	ϕ	Ar	DMSO 3mL	60	13h	<1	-
7	0.25	CH_2	0.75	1.25	mw	N_2	DMSO 2mL	100	1.5 m	17	96
8[d]	0.25	H	0.75	1.25	mw	N_2	DMF 2mL	70	10 m	7	<10
9[c]	0.33	H	0.66	1.66	ϕ	Ar	DMF 3mL	23	48h	92	-
10	0.33	H	0.66	1.66	ϕ	N_2	DMF 3mL	60	15h	5	66
11	0.33	H	0.66	1.66	ϕ	Ar	DMF 3mL	60	48h	0	5.2
12[d]	0.25	H	0.75	1.25	mw	N_2	DMSO 2mL	80	1.5 m	50	95

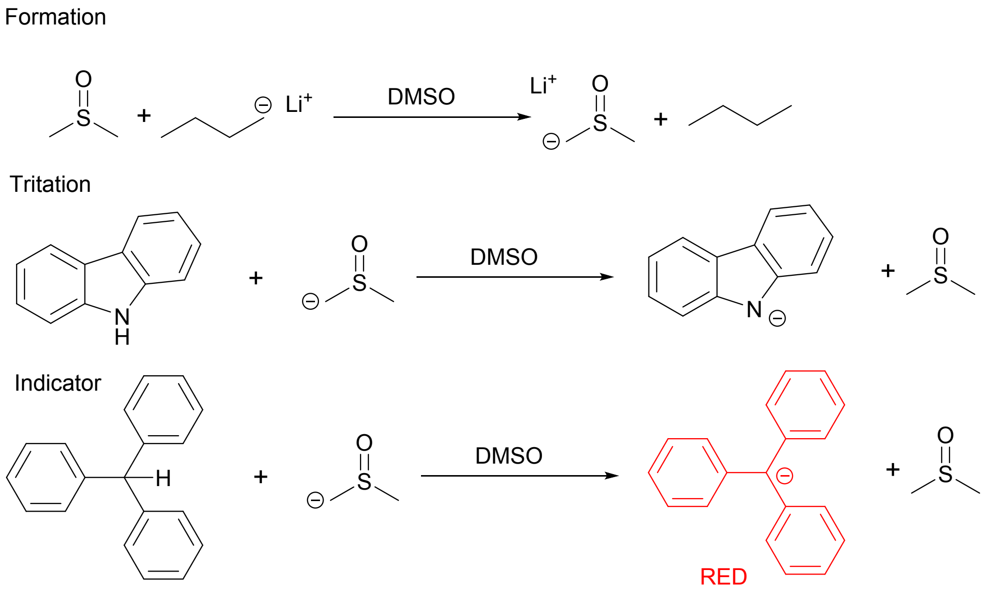
Coupling Reactions between enolates anion from acetophenone or propiophenone and PhI with 5 eq. of *t*BuOK. The reactions were heated in an oil bath (ϕ) or microwave irradiation of 100 W for 15 seconds plus 1 min of cooling (mw) under inert atmosphere ($Ar_{(g)}$ or $N_{2(g)}$). [a] Quantified by NMR with internal standard. [b] Quantified potentiometrically with Ag / Ag (I). [c] According Dapreau et al, ref. 4. [d] According own work, references 1 and 2.

Dimsyl solutions preparation in DMSO

To avoid the effect of $t\mathrm{BuO}^-$, the dimsyl anion was generated by the reaction of DMSO with butyl Lithium (BuLi), as an alternative instead of NaH.[7] The solutions were prepared in a 10 mL sealed vial, filled with nitrogen and a magnetic stirrer. The vials were dried under vacuum, filled with nitrogen, and then charged with dried DMSO (2 mL) and degassed. Then aliquots of BuLi (in hexane) were added. The hexane was evacuated under vacuum slowly to prevent intense bubbling. An aliquot was taken with a syringe and carried to titration vessel or 10 mL CEM Discover microwave glass vessel.

Dimsyl tritation

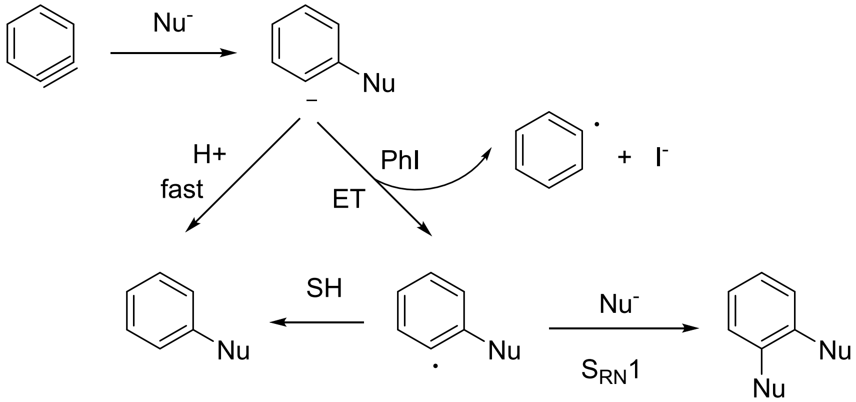
The concentration of dimsyl solutions were determined by titration with carbazole [0,4008M], (pKa = 19.9), using Ph_3CH (pKa = 30) as an indicator. In the Ph_3CH a proton loss forms the red Ph_3C^- anion. Aliquots of the dimsyl solutions were transferred via syringe to a previously dried and degased vial with solid Ph_3CH and the solution turn to an intense red color. Then Carbazole solution was added via syringe to discoloration. The dimsyl solutions obtained were 30 and 85 mM and immediately used in microwave irradiation experiments with PhI.



Scheme S 2:lithium dimsylate formation with BuLi and tritation with carbazole and tri-phenyl metane as indicator.

Initiation by Benzine

Murphy *et al.* propose an initiation via benzine mechanism. (see Scheme S 3), [8] In this case, benzene will act as a diradical that initiates the process. In our previous report, we conducted a test for the benzine mechanism using *p*-iodotoluene, and only found 0.4 % of the *meta* product. With this result we discarded the benzine mechanism as the main contributor to the generation of product **3a**2. But, could this very low amount of benzine, be responsible of the initiation step? The answer should be no because the coupling of benzene with the nucleophile will give an anion not a radical as is pointed out in HAS reactions. A radical formation will implied an ET from a phenyl anion provided that this reaction is faster than the proton abstraction from the solvent which is unlikely. Besides, if this was the case a disubstituted product should be obtained by coupling of the resulted radical with another nucleophile and such a product have not been detected.



Scheme S 3. Benzine mechanism. Benzine couple with the Nu and form an anion. This anion could abstrac H from the solvent or donor an electron to PhI and generate Ph• radical and Ph-Nu radical, wich abstract H from solvet or after coupling with Nu give a disusbtituited product.

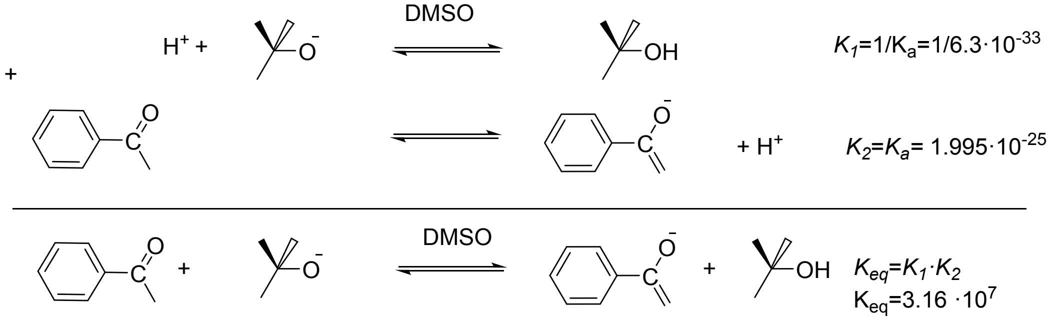
Initiation Experiments: Iodide generation by ET between anion and PhI

To evaluate the initiation step in the reaction we analyze the iodide liberation from the PhI when this reacts only in the presence of one anion specie, like acetopenone enolate, *t*BuO⁻ or the dimsyl. (Scheme S 4) The reactions were carried out in a microwave reactor as described in previous section. In the same way, after completion of the reaction, the vessel was removed from the microwave cavity and opened to the atmosphere, quenched by addition of water (10 mL) and NH_4NO_3 in excess, and the mixture was extracted with 10 mL ethyl acetate and water (2× 10 mL). The combined organic extract was dried over anhydrous $CaCl_2$, and complete with ethyl acetate to get 10 mL and the water extract were filled to 100 mL for further quantification. The products were quantified by GC or NMR by the internal standard method. Water layer was recovered to quantify halide ions by potentiometric titration with an $AgNO_3$ standard solution.

Scheme S 4: Concerted ET from the anion and disiociative C-I bond rupture

Initiation with acetophenone enolate

To prepare the enolate anion we use the pure acetophenone (pKa=24.7)[15] or acetophenone solution 1.03M in desgased DMSO, plus the addition of 0.9 eq. of *t*BuOK (pKa=33.2)[15] in DMSO. The deprotonation of the acetophetone is highly favored by with a $K_{eq=}$ $3.16 \cdot 10^7$. In these conditions, we considered only the enolate anion is present. The reactions were carried out in a 10 mL CEM Discover microwave glass vessel, filled with nitrogen and a magnetic stirrer and the necessary amount of *t*BuOK to get acetophenone enolate concentrations of 0.01; 0.024; 0.044; 0.084; 0.19; 0.49; 0.74 and 1.23 M (see Table S 3). The tube was dried under vacuum, filled with nitrogen, and then charged with dried DMSO (2 mL) and degassed. Then the acetophenone) and iodobenzene (0.5 mmol) were then added to the degassed solvent under nitrogen. Finally the sample vessels were irradiated by microwave at 100 W and, 15 seconds and work up as was mentioned above.



Scheme S 5 Acetophenone Enolate formation by *t*BuOK in DMSO

Table S 3: acetophenone enolate fromation with *t*BuOK in DMSO

#	*tBuOK g*	*tBuOK mmol·*	*Vol µl $^{(a)}$ acetophenone*	*mmol acetofenone*	*[Nu] M*	*%$I^{-(b)}$*	*Temp ºC$^{(c)}$*
1	0.0024	0.02	23*	0.0264	0.01	0	64
2	0.0022	0.02	23*	0.0264	0.098	0	67
3	0.0051	0.045	47*	0.055	0.024	0	63
4	0.0057	0.051	47*	0.055	0.024	0	67
5	0.0097	0.087	88*	0.099	0.044	0	72
6	0.0099	0.088	88*	0.099	0.044	0	66
7	0.0186	0.166	22	0.187	0.084	1.0	75
8	0.0190	0.169	22	0.187	0.085	1.5	73
9	0.0414	0.369	51	0.44	0.18	3.0	76
10	0.0417	0.372	51	0.44	0.19	5.3	76
11	0.1101	0.98	129	1.1	0.49	15.5	84
12	0.1108	0.98	129	1.1	0.49	15.9	80
13	0.1658	1.48	193	1.65	0.74	35	92
15	0.2748	2.45	321	2.75	1.23	80	106
16	0.2775	2.47	321	2.75	1.24	81	106

* From Acetophenone solution 1.0267M in desgased DMSO. Reactions with PhI 0.5mmol and different concentrations of acetophenone enolate ,heated by microwave irradiation of 100 W for 15 seconds in $N_{2(g)}$ atmosphere (a) Experiment were duplicate. (b) Iodine yield (%I^-) determined potentiometrically using an Ag/Ag(I) electrode (c) Temperature ºC determinate by internal IR sensor of the CEM Discover reactor.

Initiation with dimsyl anion

After preparation of the dimsyl solutions in DMSO, aliquots were taken and transfer into 10 mL CEM Discover microwave glass vessel, filled with nitrogen and a magnetic stirrer. The vessel was previously dried under vacuum and filled with nitrogen. Then dried DMSO was added to complete the final 2 ml volume to get dimsyl concentrations of 0.012; 0.025; 0.043 and 0.085 M, and immediately irradiated with a microwave pulse (100W-15 seconds), and posterior work up as was mentioned above for % I^- quantification in water extracts. When the dimsyl concentration increases, also increases viscosity and stirring was difficult. In Figure S 5 it can be seen after the microwave irradiation an irregular heating with superheated areas showing DMSO decomposition and light clear areas.

Table S 4: dimsyl solutions in DMSO

#	[dimsyl] M	I^-%.[a]	T_{max} ºC.[b]
1	0	0	70
2	0.012	15	73
		19	78
3	0.025	15	64
4	0.0425	33	62
5	0.085	28	40

PhI 0.5mmol reactions with different concentrations of dimsyl ion and heated by microwave irradiation of 100 W for 15 seconds in $N_{2(g)}$ atmosphere (a) Iodine yield (%I^-) determined potentiometrically using an Ag/Ag(I) electrode. (b) Temperature ºC determinate by internal IR sensor of the CEM Discover reactor.

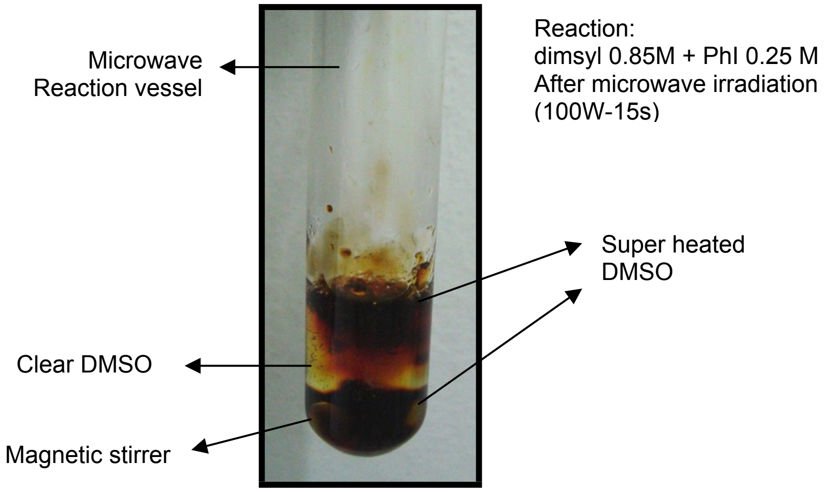
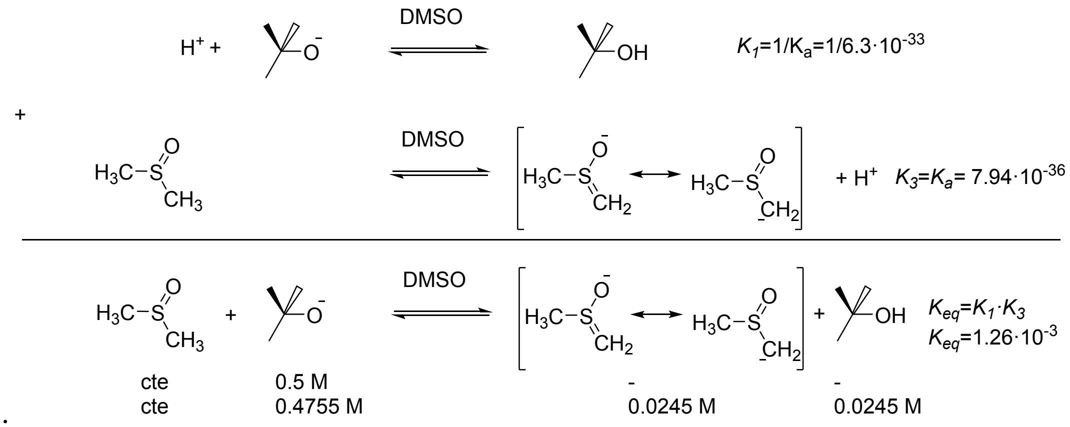


Figure S 5: Reaction vessel of PhI 0.5mmol and dimsyl 0.085M after microwave irradiation of 100 W-15 seconds in $N_{2(g)}$ atmosphere.

Initiation with *t*BuO$^-$

Reactions were carried out in a 10 mL CEM Discover microwave glass vessel, filled with nitrogen and a magnetic stirrer and the necessary amount of the organic base to get *t*BuO$^-$ concentrations of 0.008; 0.013; 0.05; 0.085; 0.19; 0.5 0.75 and 1.25 M. The tube was dried under vacuum, filled with nitrogen, and then charged with dried DMSO (2 mL) and degassed. Then iodobenzene (0.5 mmol) were then added to the degassed solvent under nitrogen. Finally the sample vessels were irradiated by microwave at 100 W for 15 seconds and work up as was mentioned above. The *t*BuO$^-$ anion is in equilibrium with small amount of dimsyl anion. (Scheme S6 and Table S4).



Scheme S 6 Dimsyl formation by *t*BuOK in DMSO

Table S 5 *t*BuOK solutions in DMSO

#(a)	*t*BuOK mass (g)	[*t*BuOK]$_0$ M	[*t*BuOK]$_f$ M	[dimsy]$_f$ M (b)	Temp ºC(c)	%I$^-$(d)	%PhI(e)
1	0	0	0.0023	0	77	0	56
2	0.0019	0.0086	0.0043	0.0063	85	0.7	40
	0.0029	0.013		0.0087	80	0.6	51
3	0.0054	0.0218	0.0091	0.0127	75	0.9	42
	0.0054	0.02411	0.0105	0.0136	79	0.9	56
4	0.0106	0.0415	0.0218	0.0197	71	1	47
	0.0114				74		46
5	0.0198	0.088	0.0564	0.00316	80	8	58
	0.0205	0.091	0.0588	0.0322	79	10	45
6	0.0424	0.19	0.14	**0.05**	82	19	40
	0.0426				81	14	53
7	0.1175	0.5	0.415	**0.085**	89	54	10.4
	0.1182				90	55	22
8	0.1684	0.75	0.644	0.106	99	68	22
	0.1694				87	57	22
9	0.2807	1.25	1.11	0.14	93	81	8.9
	0.2839				91	79	10

Reactions with PhI 0.5mmol and different concentrations of *t*BuOK , heated by microwave irradiation of 100 W for 15 seconds in $N_{2(g)}$ atmosphere. (a) Experiment were duplicate. (b) Equilibrium concentrations calculated with K_{eq}= 1.26·10^{-3} from Scheme S6. (c) Temperature ºC determinate by internal IR sensor of the CEM Discover reactor. (d) Iodine yield (%I$^-$) determined potentiometrically using an Ag/Ag(I) electrode. (e) Yield quantification to PhI by CG with internal standard.

Dimsyl in equilibrium with *t*BuOK

Similar concentration of "*pure"* dimsyl anion and dimsyl in equilibrium with *t*BuOK gave higher deshalogenation yields. In the reaction with PhI and "*pure*" dimsyl solution different coupling byproducts was detected. These compounds could be formed in absence of a better Nu and follows a chain reaction; which increases the final iodide yield. These results seem to indicate that *t*BuO$^-$ do not participate in the initiation but inhibit the action of dimsyl anion but due to the complexity of the experimental conditions its participation could not be totally discarded.

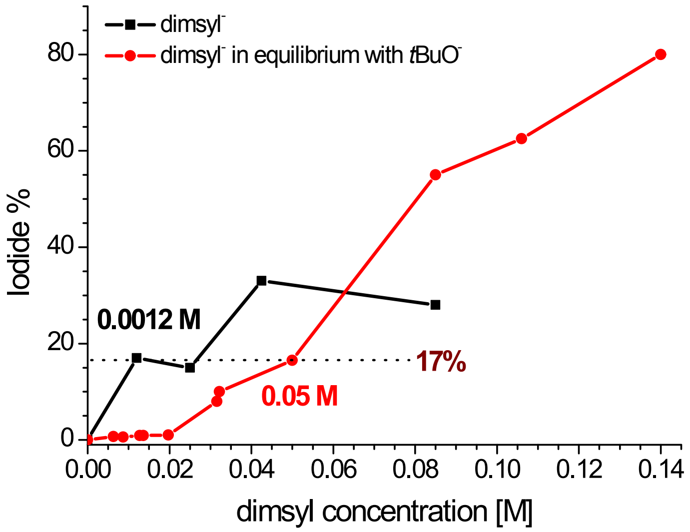


Figure S 6. Comparison between the iodide released by the dimsyl solution in DMSO prepared with *n*BuLi (black) and the dimsyl in equilibrium with the tBuO$^-$ in DMSO (Red). To generate 17% iodide we need a concentration of 0.012 of the "pure" dimsyl and 0.05M of the dimsyl in equilibrium with the tBuOK ~0.14 M. Reactions of PhI 0.25 M with different concentrations of dimsyl (black squares), *t*BuOK (red circles) in DMSO. Heated by microwave irradiation 100w-15s under N_2(g) atmosphere. The yield of iodide anion$^-$ was determined potentiometrically using an Ag/Ag(I) electrode

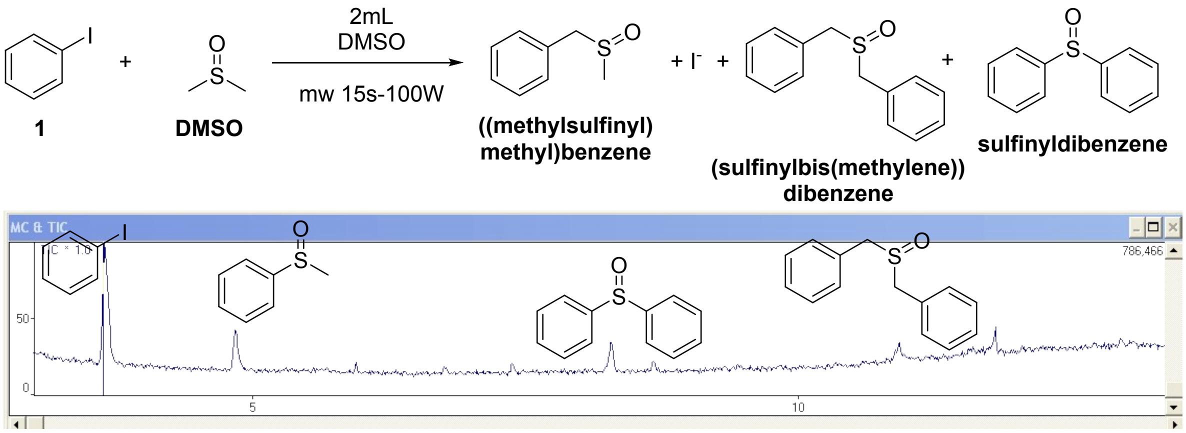


Figure S 7 Reaction of PhI 0.25 M with 0.0425M ofdimsyl. Heated bymicrowave irradiation 100w-15s under N_2(g) atmosphere and GC-MS cromatogram. Different sulfinyl coupling product was detected

Lithiun effect

These dimsyl solutions are difficult to work and in reaction with dimsyl 0.085 M, the mixture was highly viscous, which prevents a uniform heating. This was reflected in the averge temperature reaction vessel only reaches 40º C. (The vessel presents clearly DMSO around a black-brown core, of superheated solution, Figure S5). Some experiments were conducted to analyze the possible effects of this Lithium cation in the experiments with lithium dimsylate. In this case we add 2 eq. of LiCl to 0.5mmol PhI with or whitout *t*BuOK (2 eq) in DMSO and then irradiated by microwave (100W-15s). In the reaction with only LiCl, the inorganic salt produces a heating effect under microwave irradiation, raising the temperature to about 100°C, but not dehalogenation is detected (Table S 6 entry 1 and 2). In addition the GC-MS analysis shows PhI as the only organic compound. While analysis of GC-FID showed similar quantification control values (Table S 6 entry 0) When the *t*BuOK was added 0.5M (with 0.02 dimsyl in equilibrium in DMSO), we observe the same result, only the temperature reaches 80°C (Table S 6 entry 3 and 4). Probably the formation of KCl$_{(DMSO)}$ and Li^{+}-*t*BuO^{-} $_{(DMSO)}$, occur, and the latter remains as an ion pair, not allowing the formation of free dimsyl anion. However it was observed that the dimsyl anion, alone can cause up to almost 30% of the dehalogenation of the substrate, if lithium generates some effect, almost all would be reducing the dimsyl's reactivity.

Table S 6 LiCl effect in the reaction of PhI with *t*BuOK in DMSO

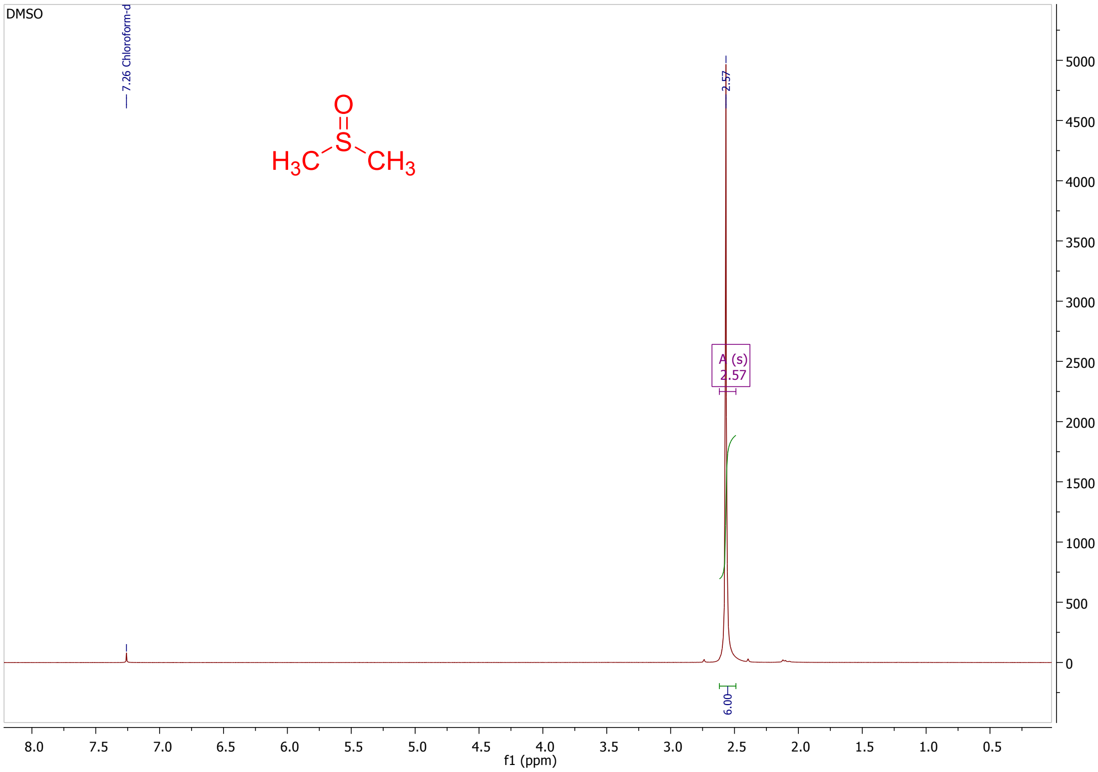
Exp	[tBuOK] M	[dimsyl](a)	[LiCl] M	Temp ºC(b)	%I^{-}(c)	%PhI(d)
0	0	0	0	77	0	56
1	0	0	0.51	101	0	45
2	0	0	0.52	100	0	63
3	0,5058	**0.02**	0.53	85	0	32
4	0,5263		0.57	74	0	53

Reactions of PhI 0.5mmol with LiCl with or without *t*BuOK and heated by microwave irradiation of 100 W for 15 seconds in N$_{2(g)}$ atmosphere. (a) Concentrations calculated with K$_{eq}$= 1.26·10^{-3} from Scheme S2. (b) Temperature ºC determinate by internal IR sensor of the CEM Discover reactor. (c) Iodine yield (%I^{-}) determined potentiometrically using an Ag/Ag(I) electrode. (d) yield quantification to PhI by CG with internal standard.

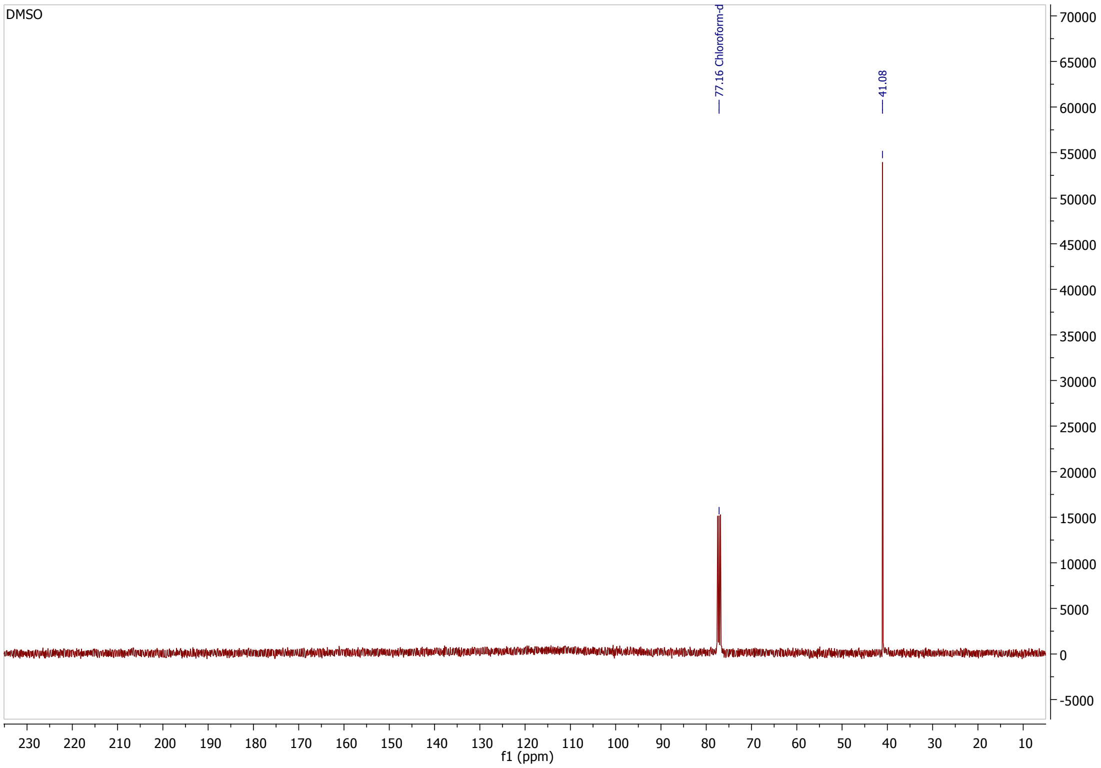
NMR Solvents and reactives

DMSO

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 1H).

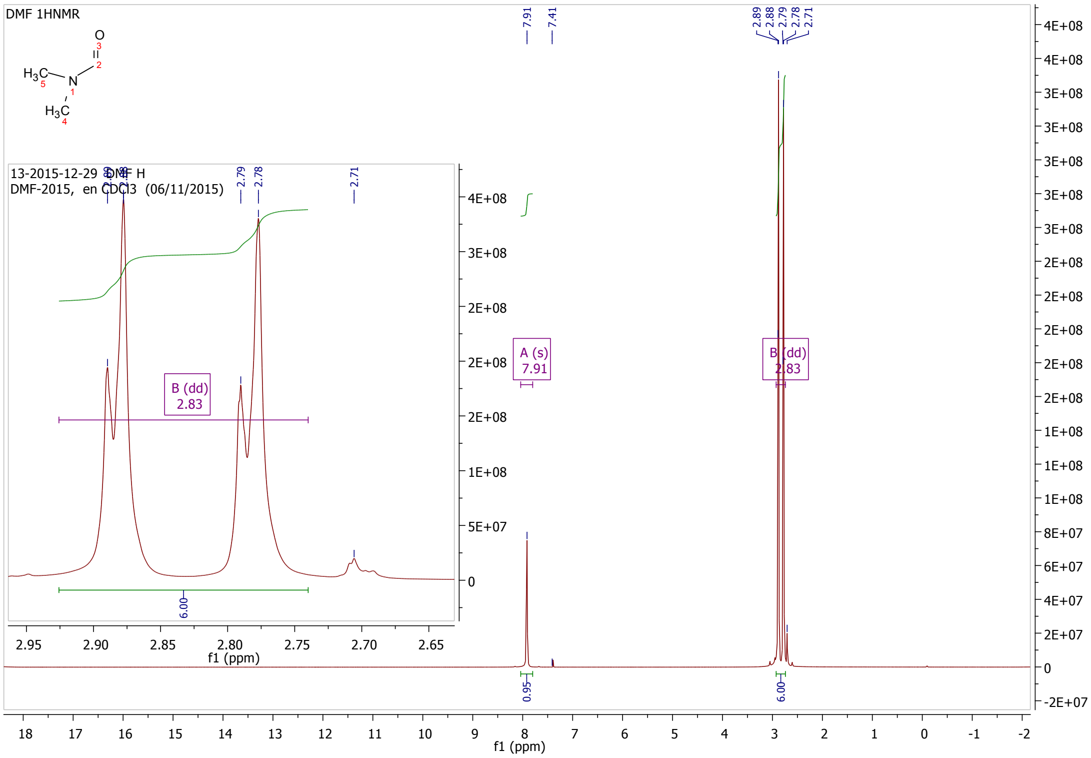


^{13}C NMR (101 MHz, $CDCl_3$) δ 77.16, 41.08.

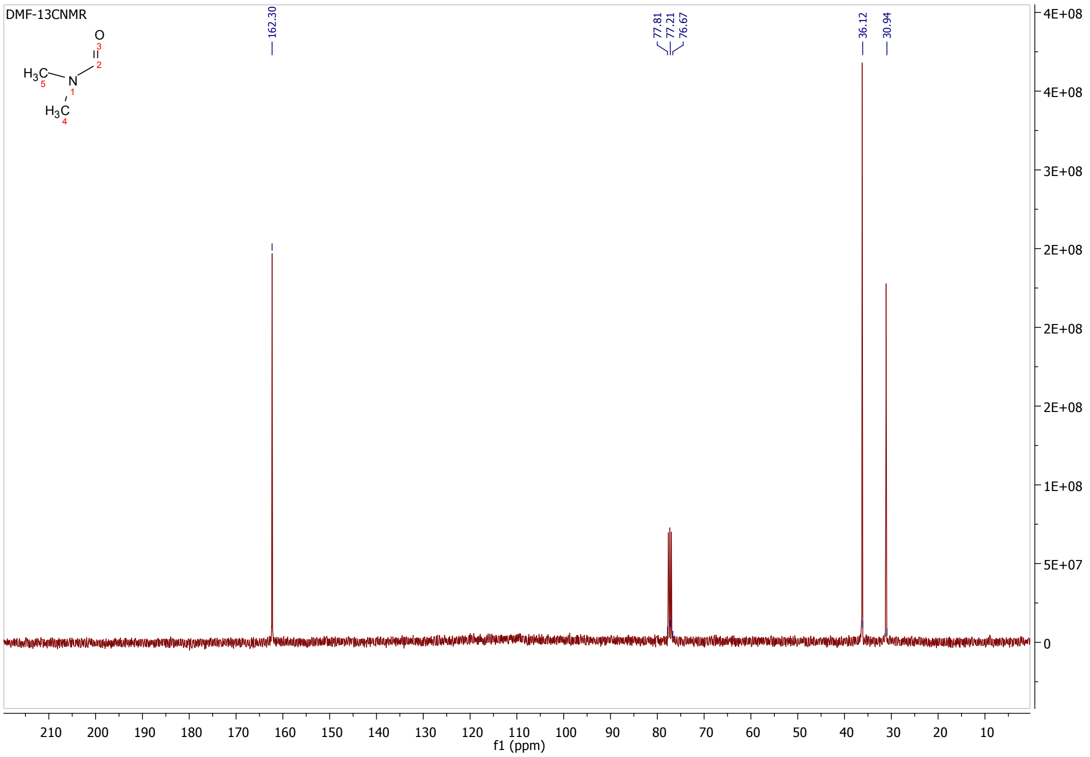


DMF:

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (s, 1H), 2.83 (dd, *J* = 40.0, 5.0 Hz, 6H).

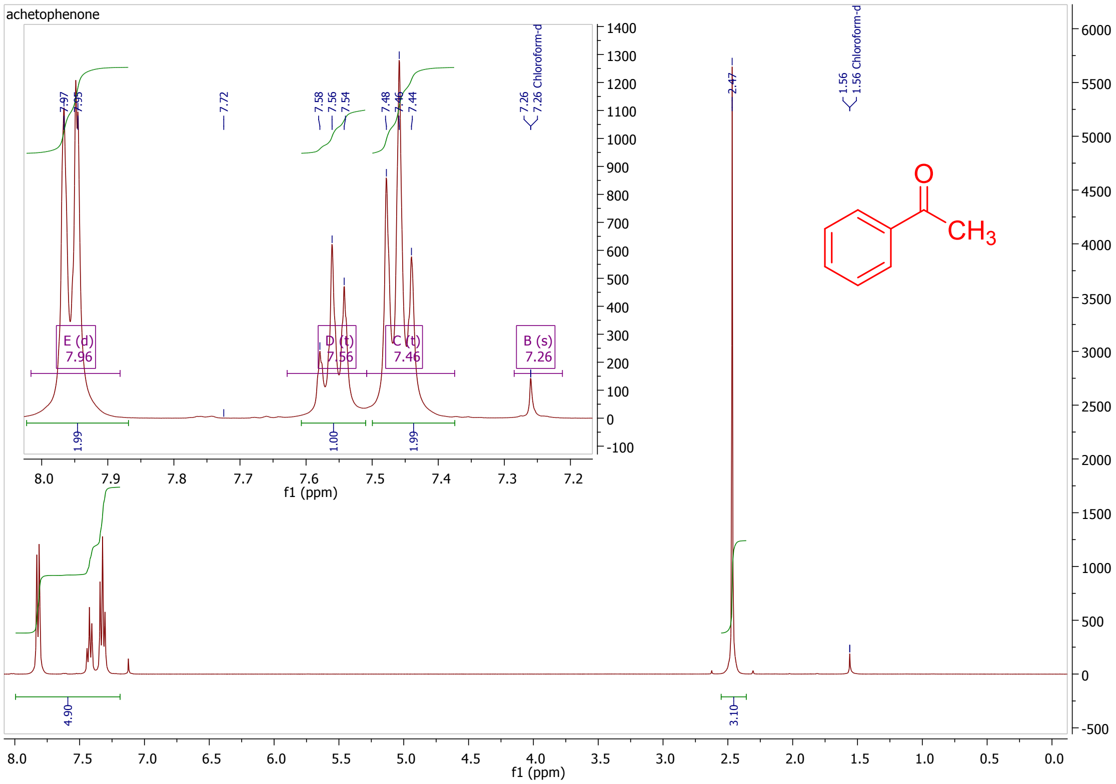


^{13}C NMR (101 MHz, CDCl$_3$) δ 162.30, , 36.12, 30.94. CDCl$_3$ 77.81, 77.21, 76.67

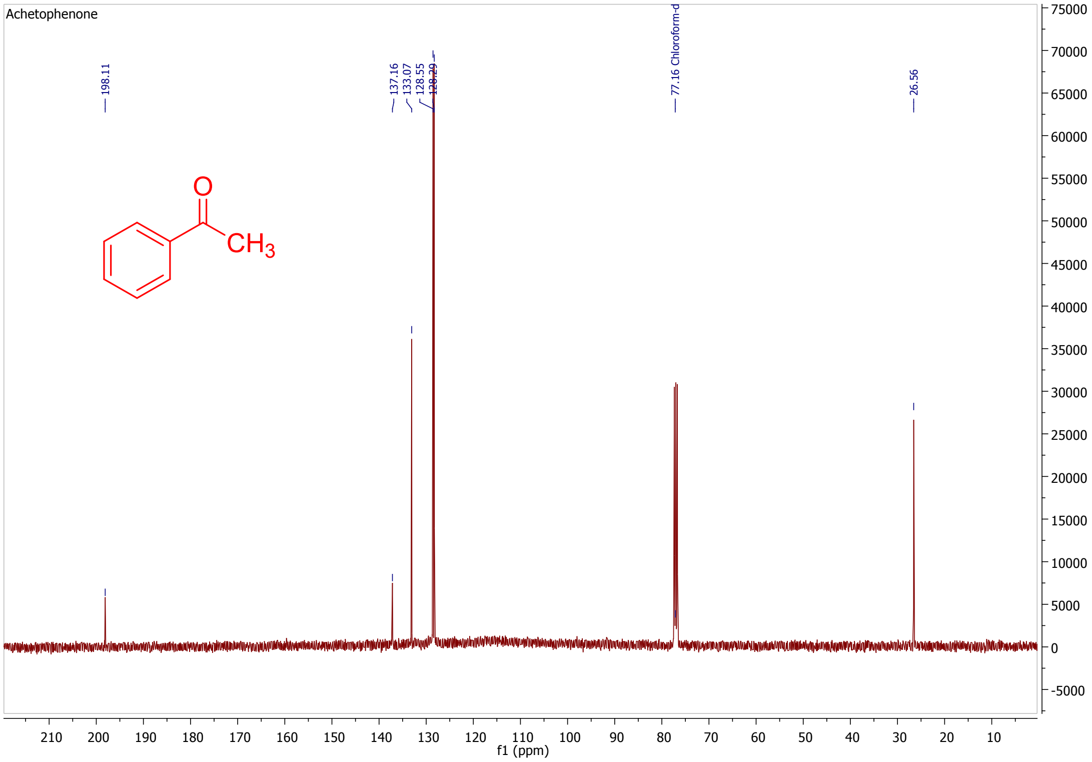


Acetophenone

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.26 (s, $CDCl_3$), 2.60 (s, 3H).

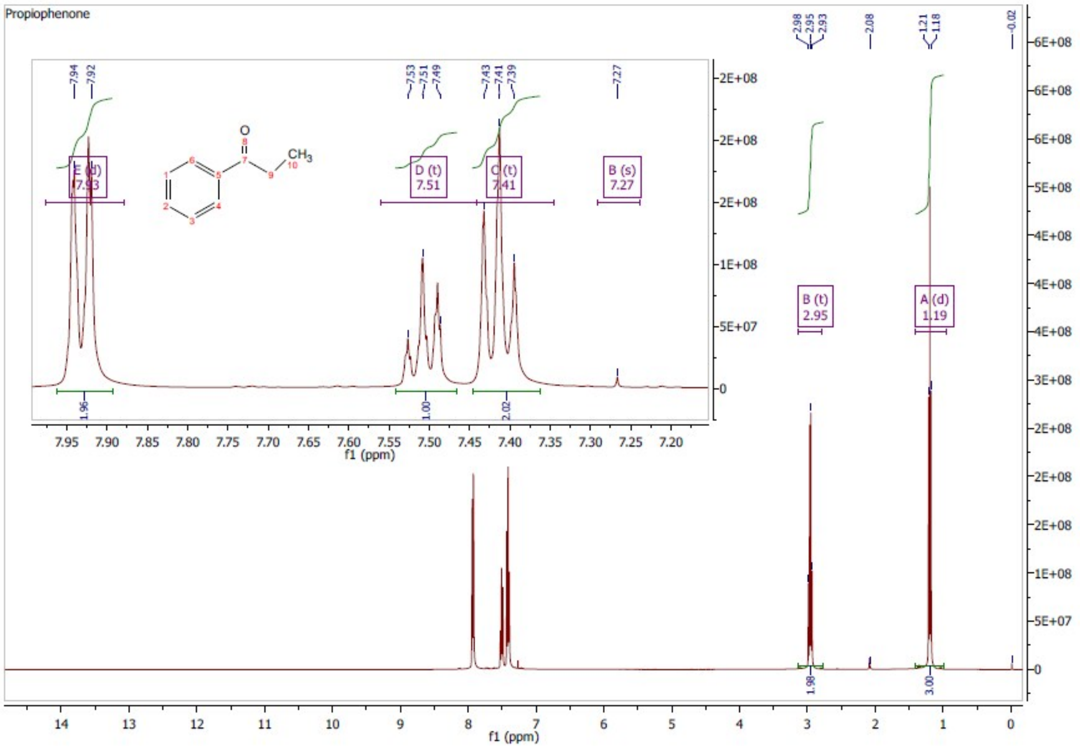


^{13}C NMR (101 MHz, $CDCl_3$) δ 198.11, 137.16, 133.07, 128.55, 128.29, 77.16 ($CDCl_3$), 26.56.

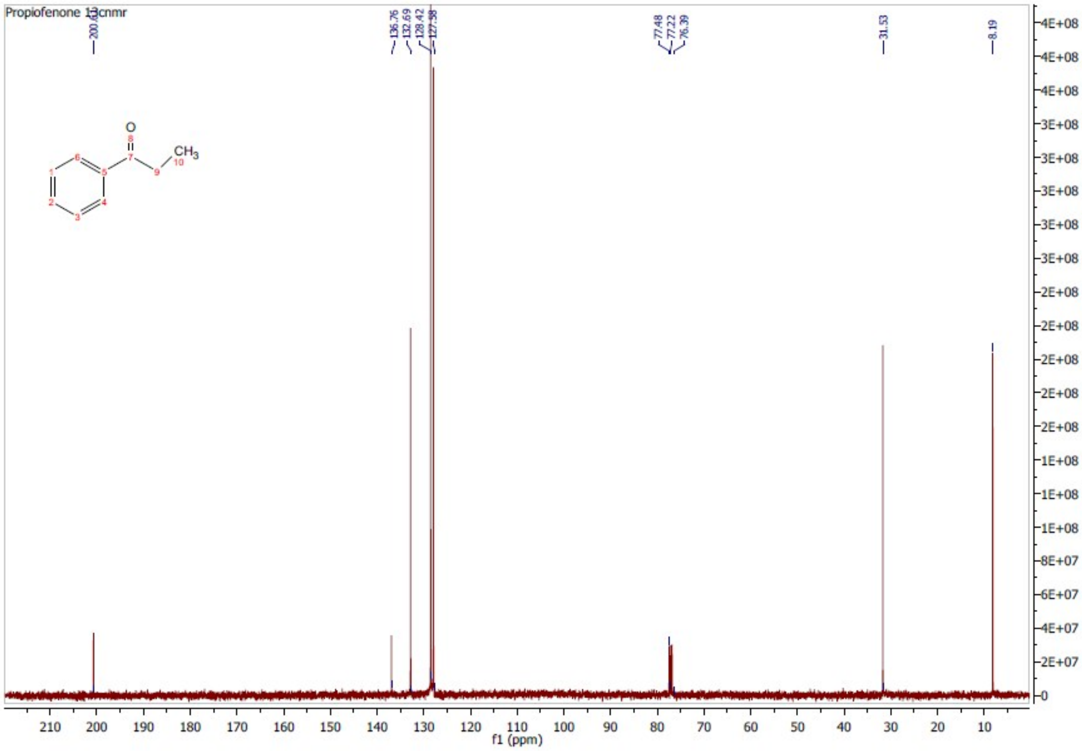


Propiophenone

^{1}H NMR (400 MHz, $CDCl_3$)), δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), δ 2.95 (t, *J* = 10.9 Hz, 2H), 1.19 (d, *J* = 14.5 Hz, 3H 2.08 (s,) 7.27 (s, $CHCl_{3.}$),

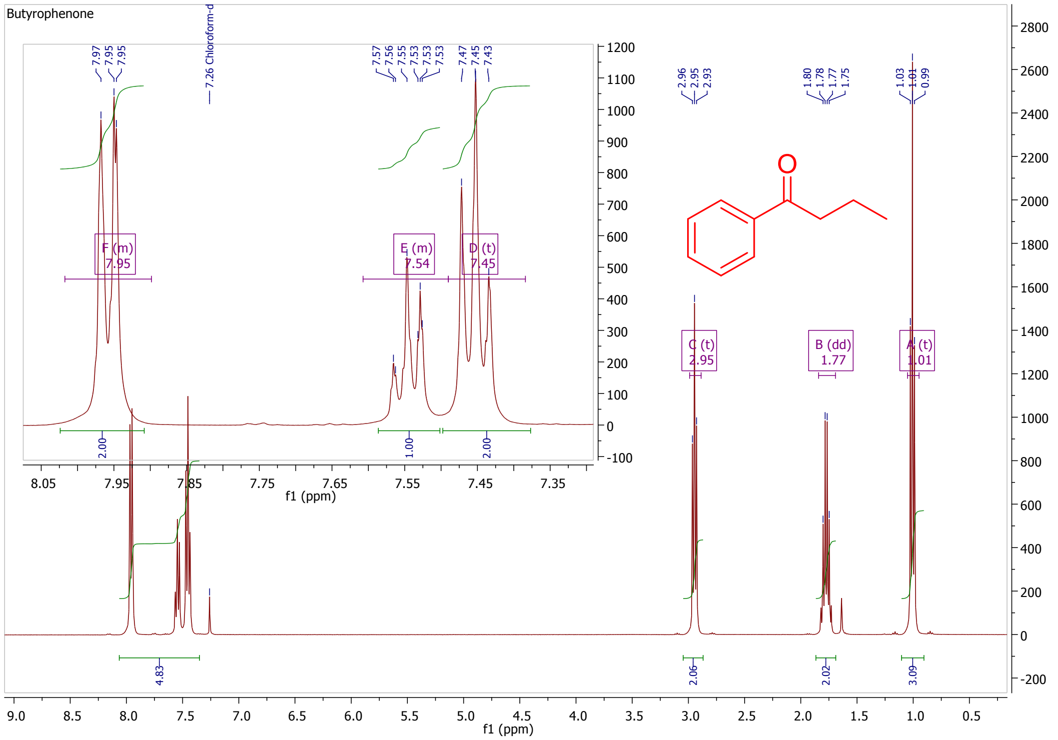


^{13}C NMR (101 MHz, $CDCl_3$) δ 200.61, 136.76, 132.69, 128.42, 127.58, 77.48, 77.22, 76.39, 31.53, 8.19.

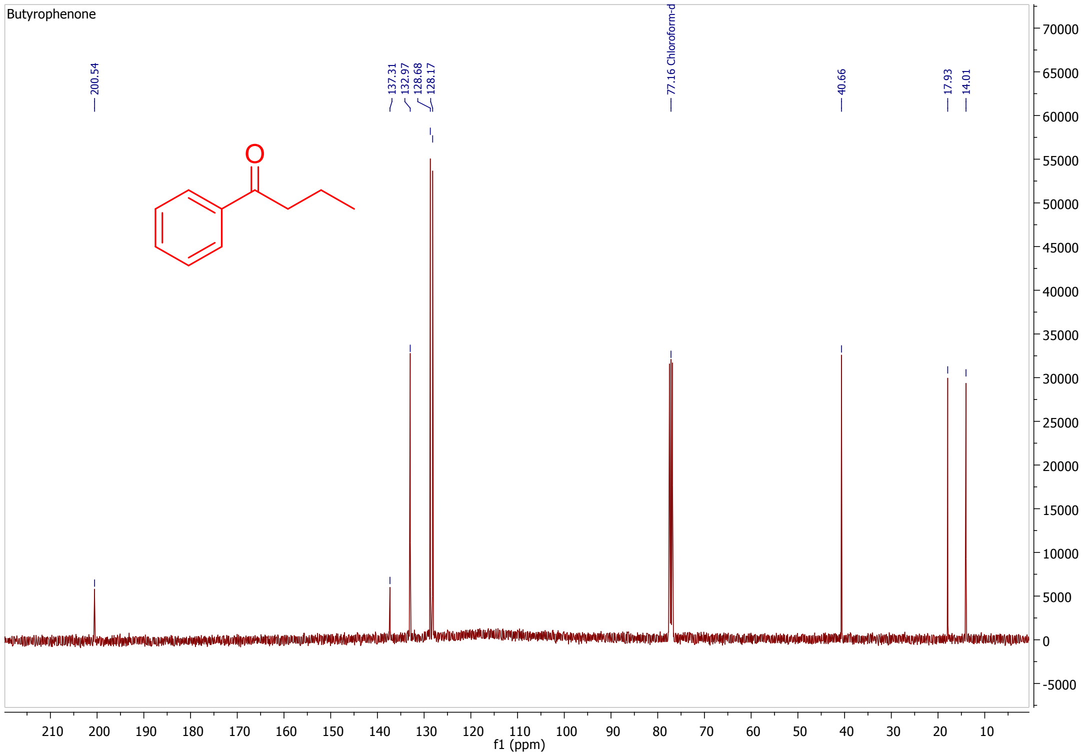


Butyrophenone

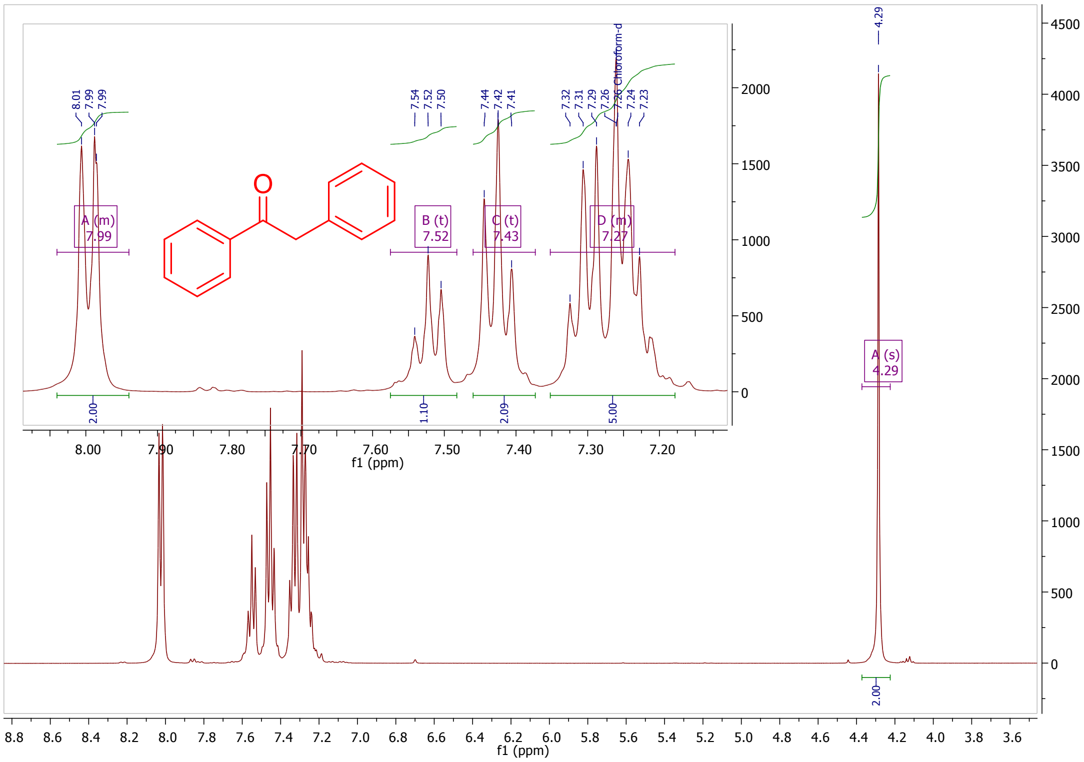
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 2H), 7.61 – 7.49 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.77 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).



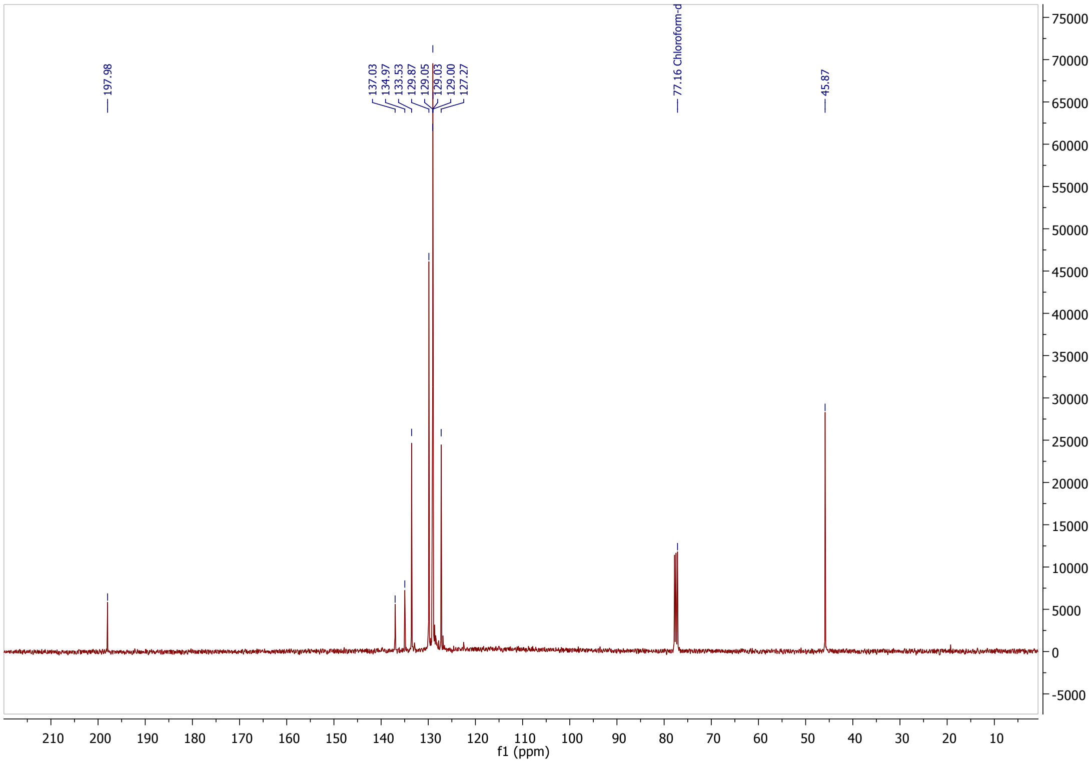
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.54, 137.31, 132.97, 128.68, 128.17, 77.16 ($CDCl_3$), 40.66, 17.93, 14.01.



(3a) 1,2-di-phenylethanone[9,10]: ^{1}H NMR (400 MHz, CDCl3) δ 8.04 – 7.94 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.35 – 7.18 (m, 5H).

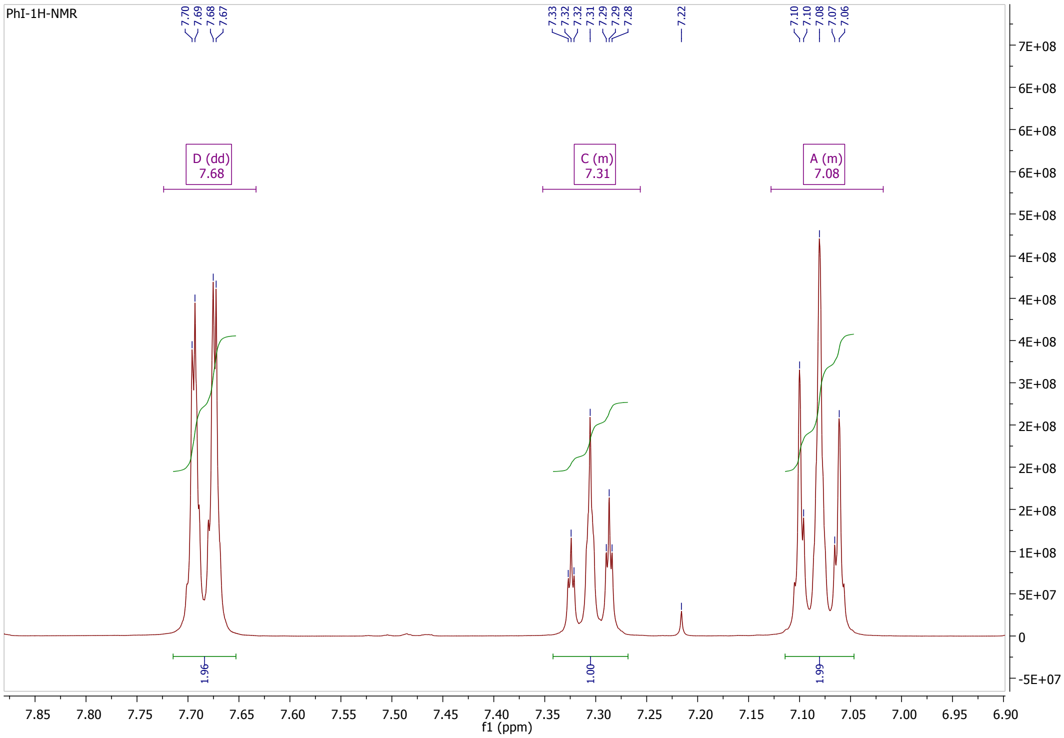


^{13}C NMR (101 MHz, CDCl$_3$) δ 197.98, 137.03, 134.97, 133.53, 129.87, 129.05, 129.03, 129.00, 127.27, 77.16 (chloroform), 45.87.

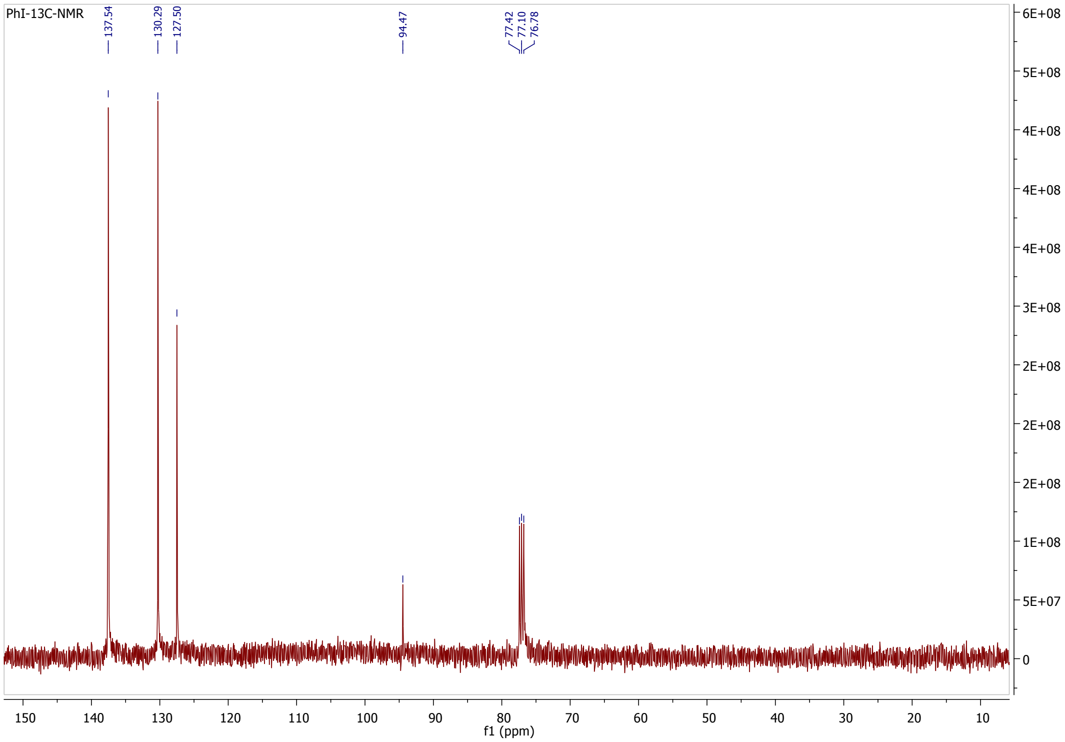


Iodobenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.35 – 7.26 (m, 1H), 7.13 – 7.02 (m, 2H). 7.22 $CHCl_3$.



^{13}C NMR (101 MHz, $CDCl_3$) δ 137.54, 130.29, 127.50, 94.47, $CHCl_3$: 77.42, 77.10, 76.78.

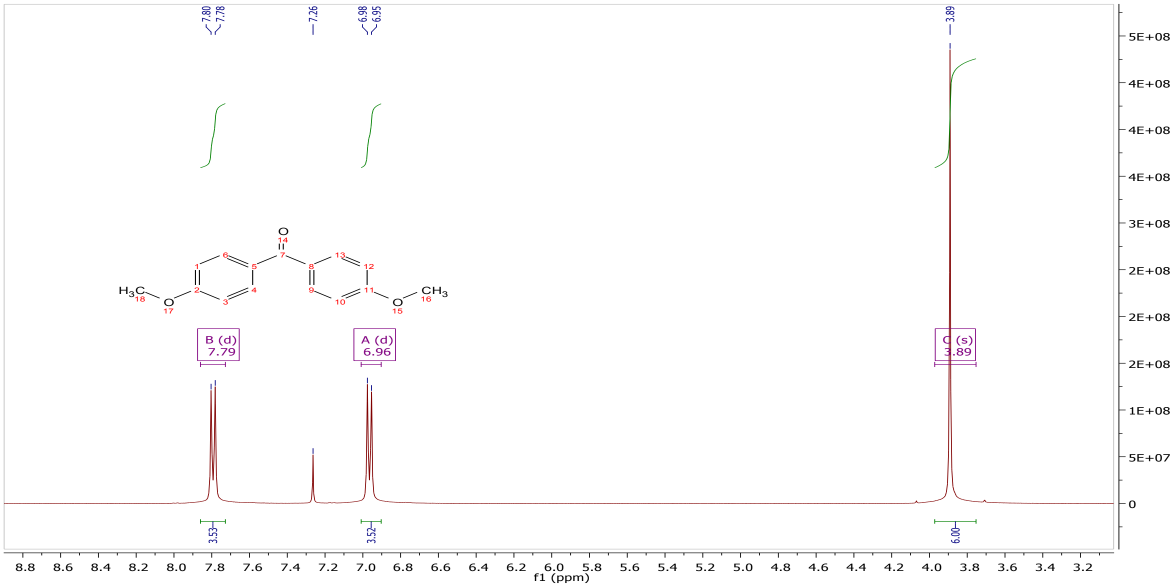


NMR Product identification.

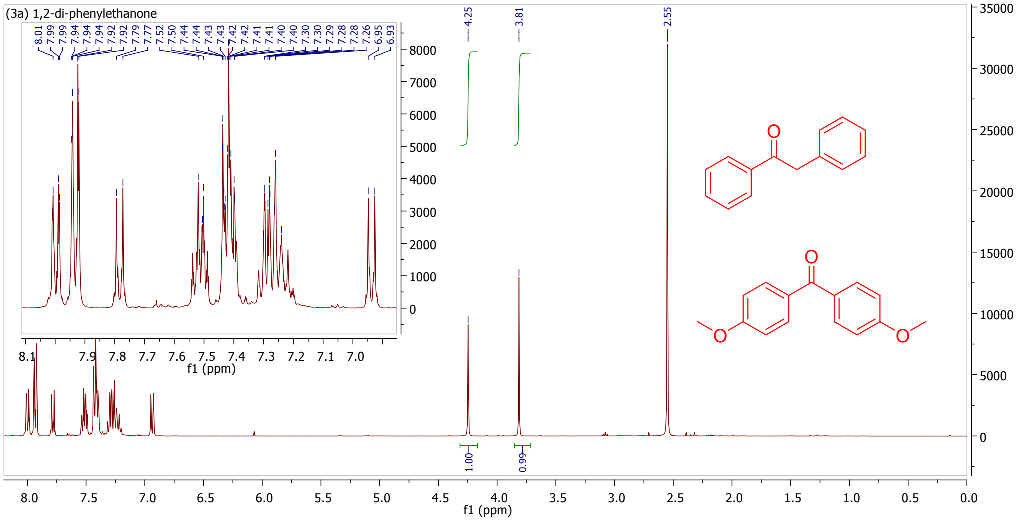
In red lines ^{1}H NMR (400 MHz, $CDCl_3$). Blue line ^{1}H NMR prediction MestreNova v6.02-5475, (C) 2009 Mestrelab research S.L. Predicted spectra shows a slight difference in the chemical shifts with recorded spectra in deuterated chloroform. Predictions and bibliographic data were used for the identification.

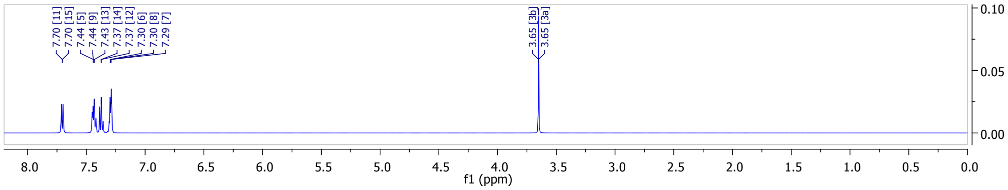
4-4' dimethoxy benzophenone (used for internal standard)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8 Hz, 3H), 6.96 (d, J = 8.8 Hz, 3H), 3.89 (s, 5H).



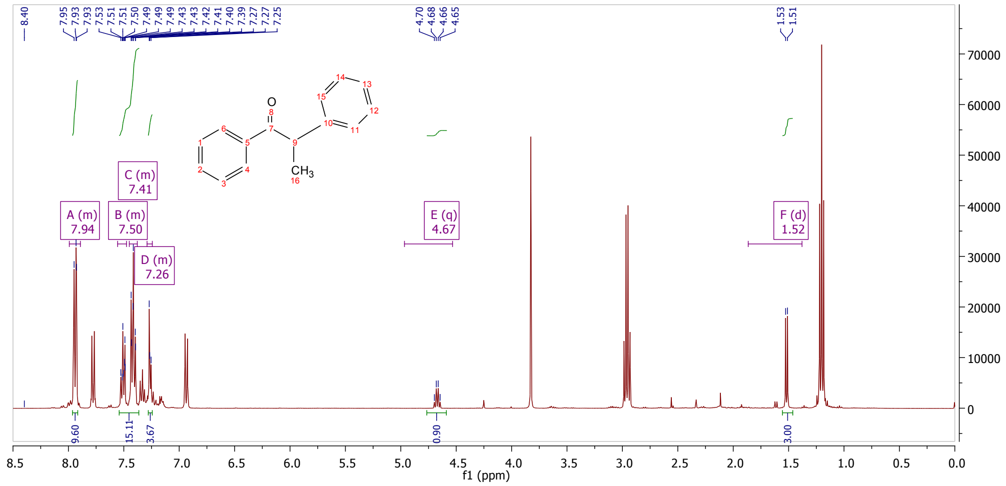
(3a) 1,2-di-phenylethanone[8,11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01, 8.01, 7.99, 7.99, 7.94, 7.94, 7.94, 7.92, 7.92, 7.79, 7.77, 7.52, 7.51, 7.50, 7.50, 7.44, 7.44, 7.43, 7.43, 7.43, 7.42, 7.42, 7.41, 7.41, 7.40, 7.40, 7.30, 7.30, 7.30, 7.29, 7.28, 7.28, 7.26, 7.26, 7.24, 6.95, 6.93, 4.25, 3.81, 2.55.

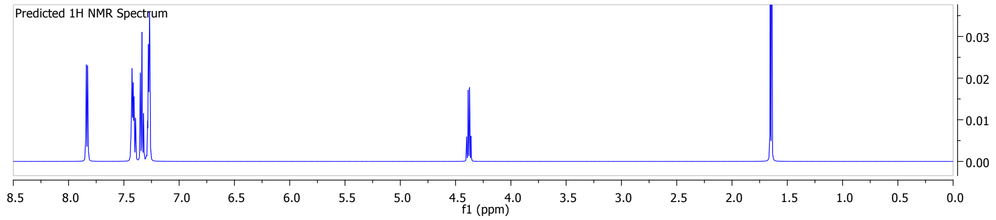




(3m) 1,2-di-phenylpropanone

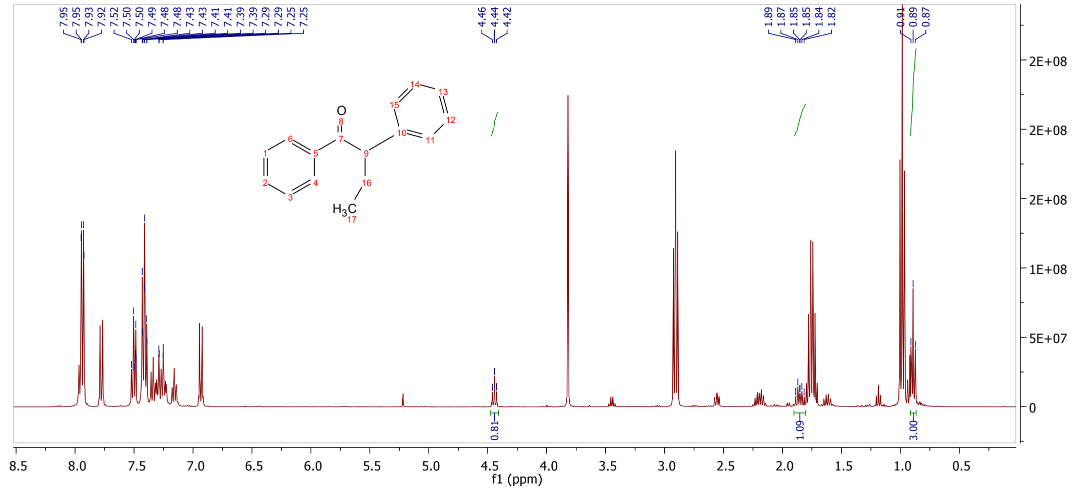
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 – 7.89 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 – 7.38 (m, 3H), 7.29 – 7.24 (m, 3H), 4.67 (q, J = 6.8 Hz, 1H), 1.52 (d, J = 6.9 Hz, 3H).

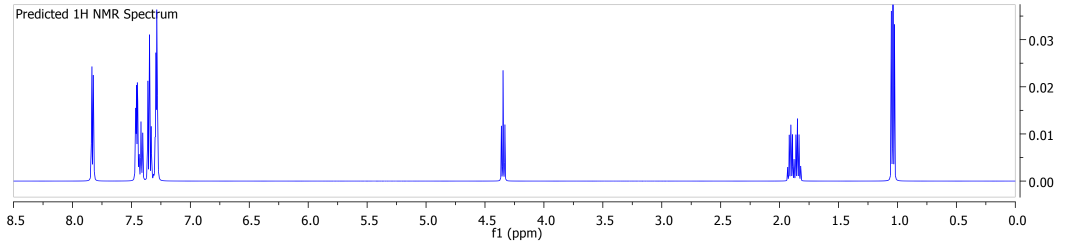




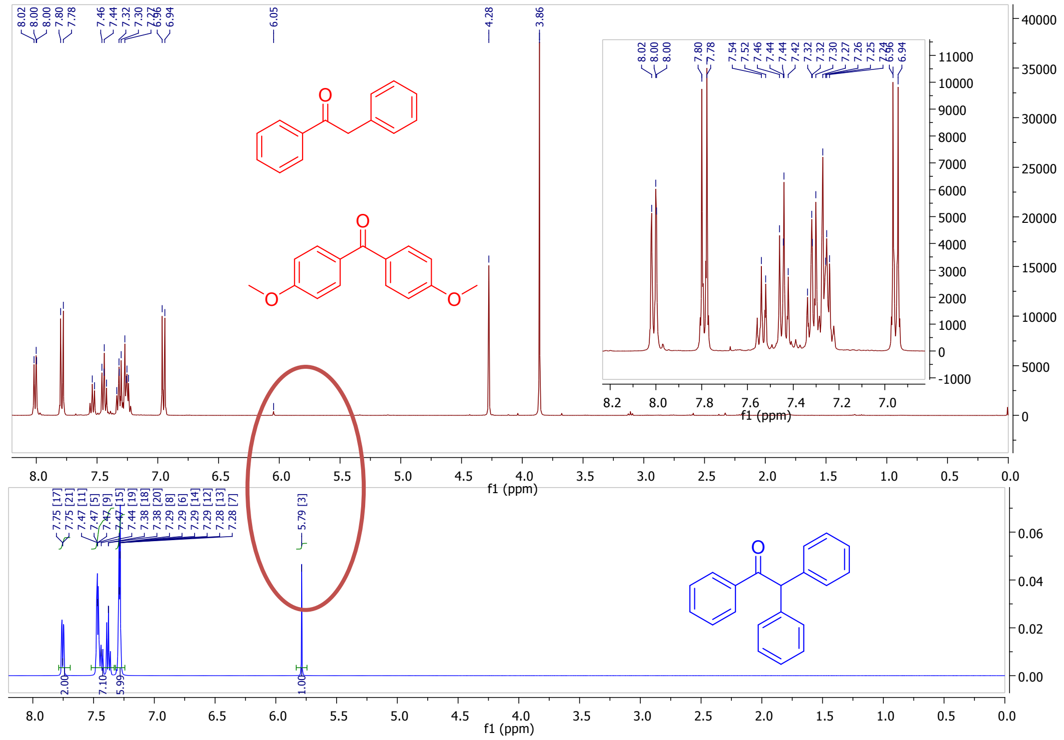
(3n) 1,2-diphenylbutan-1-one

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (dd, J = 8.4, 1.3 Hz, 2H), 7.59 – 7.21 (m, 8H), 4.44 (t, J = 7.3 Hz, 3H), 1.96 – 1.83 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H).





(3o) 1,2,2-triphenylethan-1-one: The signal a δ 5.79 (s) is absent. It was only detected the signals from compounds **3a** and the Standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00, 7.98, 7.78, 7.76, 7.52, 7.50, 7.44, 7.42, 7.41, 7.32, 7.30, 7.29, 7.28, 7.25, 7.24, 7.22, 6.95, 6.93, 4.26, 3.85.



Radical recombination

The spin density maps of the radical dimsyl, enolate **2a** and *t*BuO are presented in Figure S8. In the dimsyl$^\bullet$ and **2a**$^\bullet$ radicals the main spin density is located in the -CH_2 group of the radical, while in the *t*BuO$^\bullet$ over the oxygen atom. Thus, the first two radicals could be expected to be capable of form a dimmer with a new C-C bond.

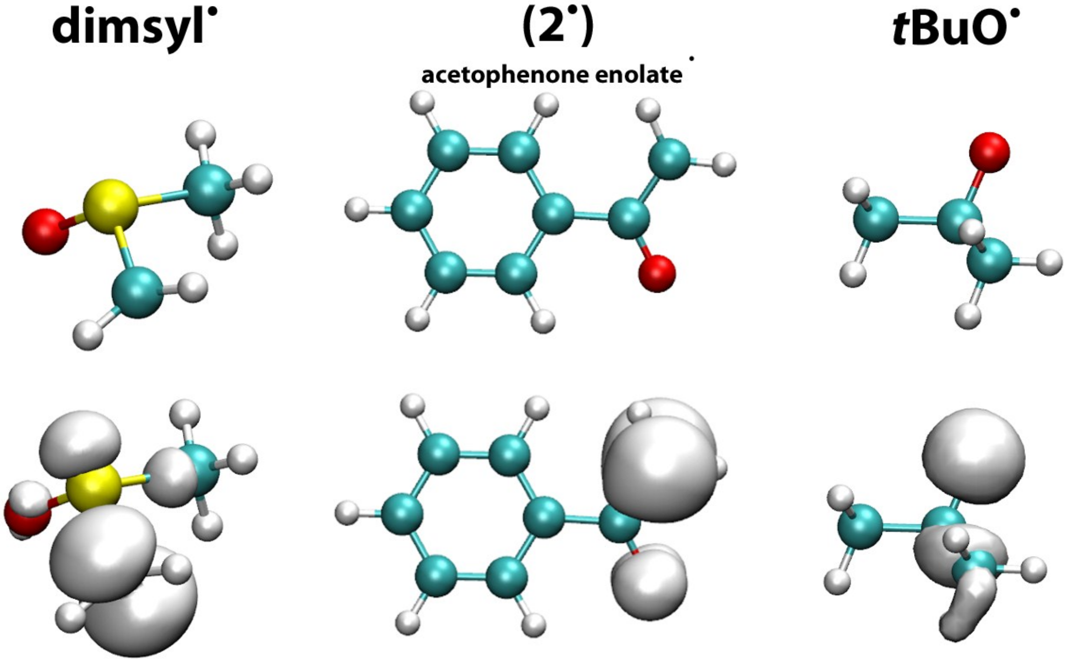
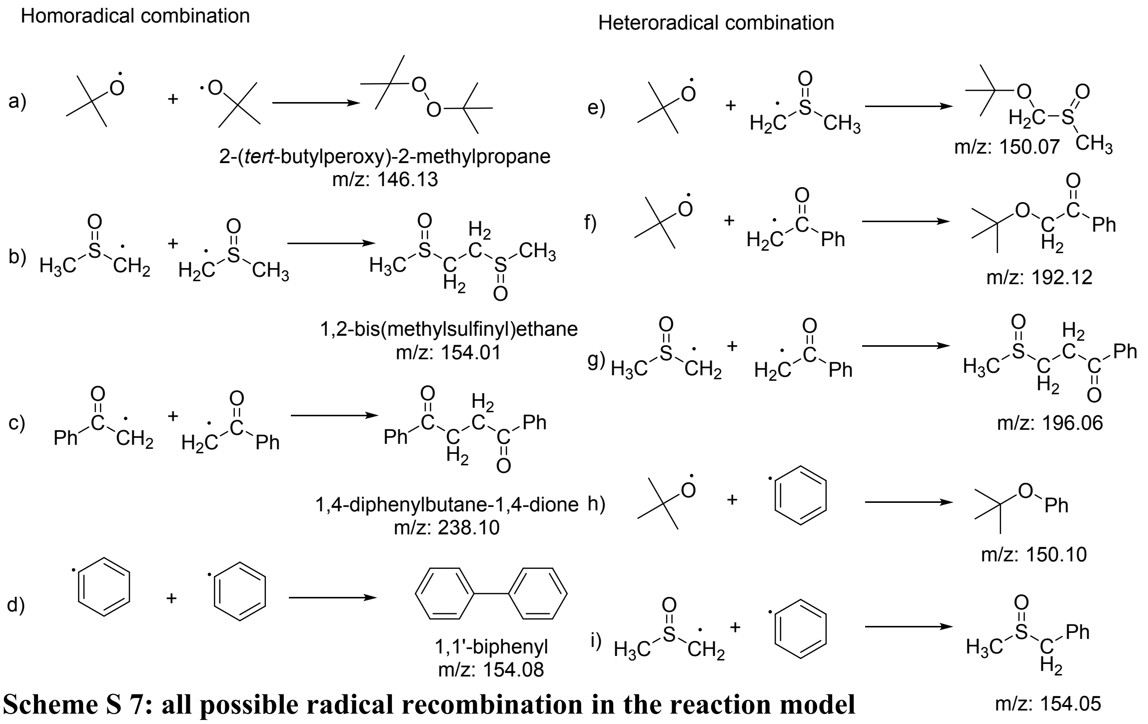
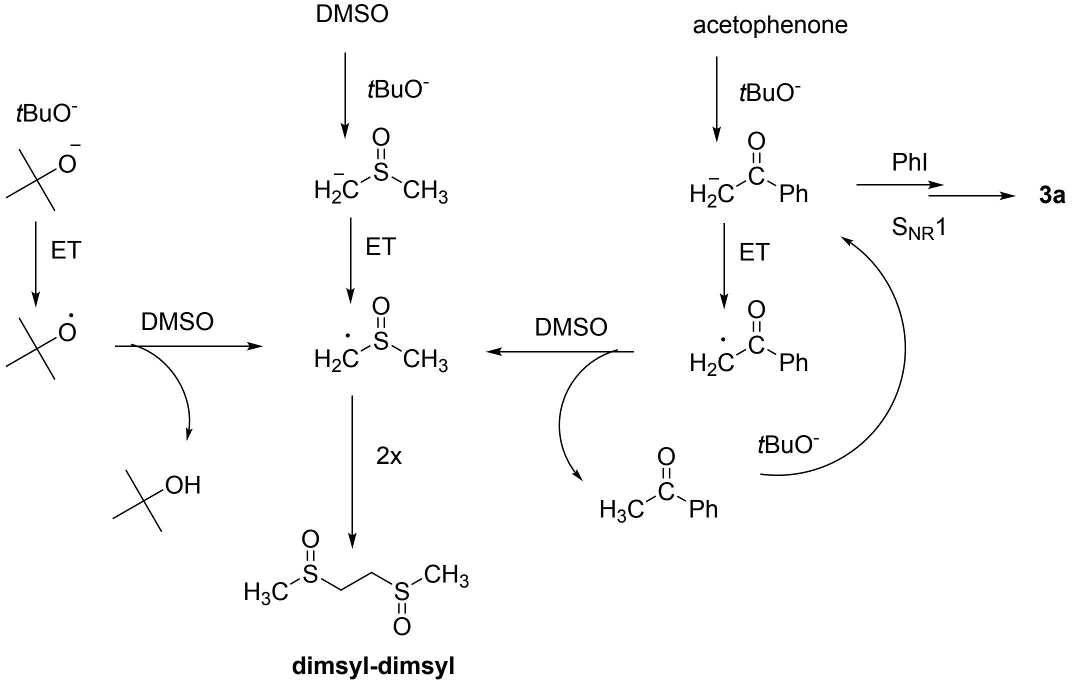


Figure S 8: Up, radical structure and bottom Spin density maps of the calculated species, plotted with an isovalue of 0.005.

Nevertheless, in the model reaction, the radical species are present in a very low concentration. The chances to found another radical to form a new compound as **dimsyl-dimsyl**, **2a-2a** or ***t*BuO-O*t*Bu** homodimmer or dimsyl-2a, *t*BuO-dimsyl or *t*BuO-2a heterodimmer are almost negligible (Scheme S7). Another alternative is hydrogen abstraction from the solvent DMSO to give a new dimsyl radical. In this case, the dimsyl-dimsyl dimmer should be the most likely byproduct to be found in the reaction (Scheme S8). Moreover, in the 0.5 mmol PhI model reaction (or in a 10 mmol scaling reaction), none of these radical recombination species could be detected by GC-MS. Similar situation was found in the reactions with each anion. It is important to mention that the specie *t*BuO-O*t*Bu, is a peroxide and this is highly reactive and incapable of surviving in the reaction or injector conditions in GC-MS.



Scheme S 7: all possible radical recombination in the reaction model



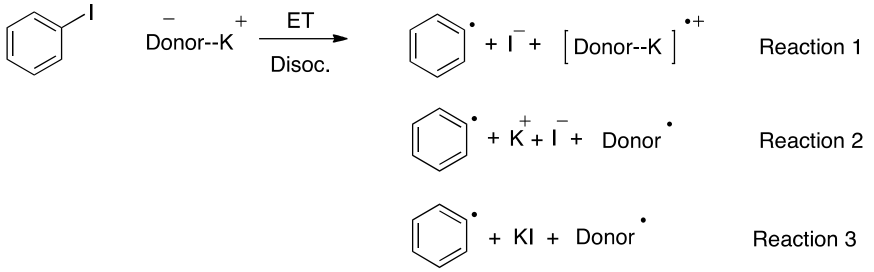
Scheme S 8 dimsyl-dymsil dimmmer formation in the reaction conditions

Computational

Computational studies were carried out using Gaussian 09 package.[12] Calculations were performed with full geometry optimization including in all cases the effect of the solvent (DMSO as polar solvent) through the Tomasi's polarized continuum model (IEFPCM),[13] B3PW91,[14] M062X[15] and PBE0[16] DFT functional and 6-311+G(d,p)[17] as basis set for H, C, N, O and S and MWB46 pseudopotential for I. We checked that the conformations obtained were minima by running frequency calculations. No imaginary vibrational frequencies were found. All energy values include zero point correction.

When computing the ET reaction to Ph-I three reactions were considered being reaction 2 the most favored one (when possible). (Table S7). The values of the most favoured reaction with each donor are included in Table 4 in the article.

Table S7 Oxidation potential and ΔG calculated for the anions presents in the reaction.



Anion/Donor **ET in DMSO as solvent**	**ΔΔEred (V)**	**ΔGET**	**EactET**	**ΔGET**	**EactET**	**ΔGET**	**EactET**
		Reaction 1		**Reaction 2**		**Reaction 3**	
*t*BuOK	0	36.3	42.5	32.8	40	33.6	40.5
Potassium acetophenone enolate	0.31	29.1	37.2	27	35.8	27.8	36.4
Potassium acetone enolate	0.4	27.1	36	25.5	34.9	26.3	35.4
Potassium Dymsilate	0.65	21.3	32.7	20.7	32.4	21.5	32.9
RA intermediate of the reaction	2.36	-18.1	11.6				
ET in DMF as solvent							
*t*BuOK	-0.04	37.2	43	31.0	38.6	32.0	39.3
Anion of DMF	0.97	14	28.2	10.8	26.3	12.1	27.1
DMF-*t*BUOK complex (Ref 22)	0.99	13.4	26.9				
DMF adduct conf. E (Ref 24a)	2.5	-21.4	10.4				
DMF adduct conf. Z (Ref 24a)	2.87	-29.9	7.8				

[a] Computed reduction potentials of the anions at M062X/6-311+G(d,p), with DMSO or DMF as implicit solvent. The energies corresponding to ΔΔEred are in V.[b] Energies of the ET reaction with each donor and PhI ass acceptor, ΔG_{ET} and $Eact_{ET}$ are in kcal/mol..

Ref 22: M. P. Drapeau, I. Fabre, L. Grimaud, I. Ciofini, T. Ollevier, M. Taillefer, *Angew. Chem*. Int. Ed., 2015, **54**, 10587-10591

Ref 24a: J.P. Barham, G. Coulthard , K.J. Emery, E. Doni, F. Cumine, G Nocera, M.P. John L. E. A. Berlouis, T. McGuire. T. Tuttle and J.A. Murphy, *J. Am. Chem. Soc.* 2016, **138**, 7402–7410 DOI: 10.1021/jacs.6b03282

Donor species in DMF

In addition to computing the properties of the electron donors proposed for ET reaction in DMF were calculated, namely, *t*BuOK anion, the anion of DMF, the complex DMF-*tBuOK* recently proposed in reference 4 and the super-electron-donors (SED) proposed in reference 8a. In Table S8 also shows some calculations in DMF as a solvent model. With these results it could also be noted that *t*BuOK is not a great electron donor. It should be underlined that there is not a very important gain in energy when using DMF-anion. According to the energy and parameters computed, the anion of DMF should also be a potential electron donor. However, the solubility of *t*BuOK in DMF is not good and the formation of the anion of DMF is also thermodynamically unfavorable. Two of the last three conditions are not fulfilled in the system used here: fast reaction time during a short period.

Last but not least, it have been proposed that DMF adduct could act as a superelectron donor. However, we must discard its participation in the reactions carried out in DMF under microwave heating since no reaction was observed when we tried the reaction in DMF with *t*BuOK. The conditions that could help the *in situ* formation of the donor are probably not fulfilled with microwave heating, higher temperatures and longer reaction times.

Table S8 Oxidation potentials and ΔG calculated for reactions with the different donors in DMF with B3PW91, M06-2X and PBE0.

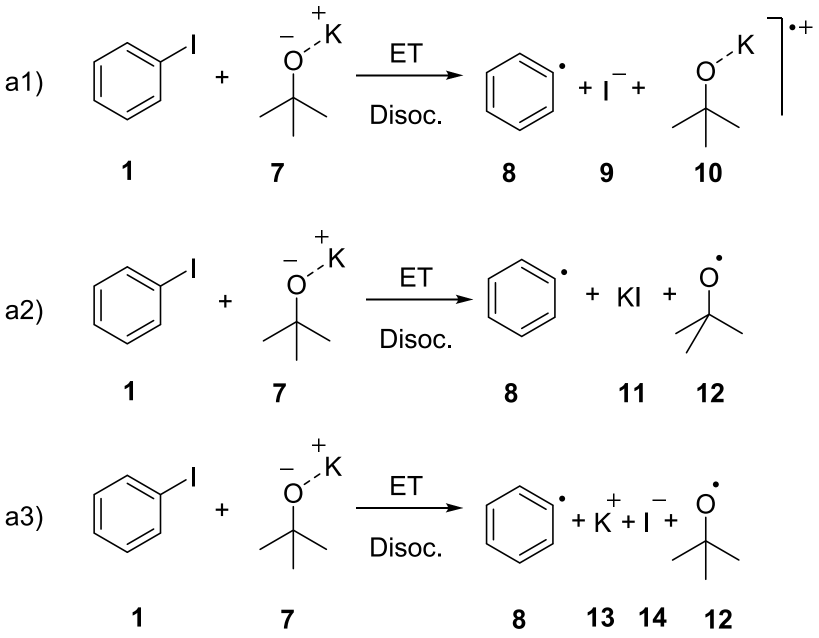
	B3PW91			**M06-2X**			**PBE**		
Anion/Donor	$\Delta\Delta E_{red}$	ΔG_{ET}	E_{act}^{ET}	$\Delta\Delta E_{red}$	ΔG_{ET}	E_{act}^{ET}	$\Delta\Delta E_{red}$	ΔG_{ET}	E_{act}^{ET}
*t*BuOK	-0.02	25.8	33.9	-0.04	30.7	38.4	-0.02	27.07	35.16
Anion of DMF	1.30	-4.7	17.0	0.97	10.5	26.1	1.30	-2.85	18.31
DMF-tBuOK complex (Ref 22)	1.11	3.01	19.8	0.99	13.4	26.9	1.11	5.62	21.66
DMF adduct conf. E (Ref 26a)	2.58	-30.6	6.3	2.50	-21.4	10.4	2.58	-28.24	7.33
DMF adduct conf. Z (Ref 26a)	2.90	-38.4	4.4	2.87	-29.9	7.8	2.90	-35.65	5.39

Computed properties of the anions by DFT with DMSO as an implicit solvent using 6-311+G(d,p) as basis set. $\Delta\Delta E_{red}$ difference in the oxidation potentials of the donors, using the oxidation of tBuOK in DMSO as reference, in V. ΔG_{ET} difference in Gibs energy for the ET reaction with PhI as an acceptor and E_{act}^{ET} the activation energy for ET process $\Delta G^{‡}$ using Saveant's approximation, in kcal/mol

Computed reactions in DMSO

Details of the properties of the species involved in the reactions in DMSO (modeled with IEF-PCM model) and with M062X (grey), B3PW91 (pink) and PBE0 (light blue).

With tBuOK



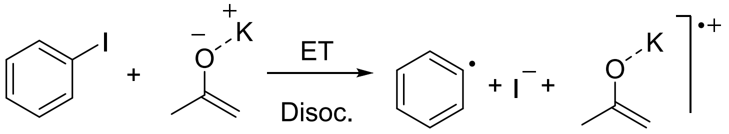
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext	-242.9680853	0.090413	-242.908747
7	*t*BuOK	-833.0123307	0.123063	-832.922965
	Products			
8	Ph-rad	-231.5160036	0.087871	-231.455508
9	Iodide-ext.log	-11.55692124	0	-11.57377
10	*t*BuOK-rad.log	-832.8321329	0.123287	-832.744566
11	KI.log	-611.4313177	0.000233	-611.457111
12	*t*BuO-rad.log	-232.9603113	0.122934	-232.866799
13	K-ext.log	-599.8668896	0	-599.882066
14	Iodide-ext.log	-11.55692124	0	-11.57377

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-243.0534294	0.089826	-242.994731
7	*t*BuOK.log	-832.9997564	0.121866	-832.912077
	Products			
8	Ph-rad.log	-231.5302682	0.087147	-231.470517
9	Iodide-ext.log	-11.6352463	0	-11.652095
10	*t*BuOK -rad-1.log	-832.8245526	0.121786	-832.737097
11	KI.log	-611.4700152	0.000184	-611.496094
12	*t*BuO-rad.log	-232.9916206	0.121565	-232.899581
13	K-ext.log	-599.8300214	0	-599.845197
14	Iodide-ext.log	-11.6352463	0	-11.652095

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-242.8374698	0.090269	-242.778302
7	*t*BuOK.log	-832.6762644	0.122413	-832.58798
	Products			
8	Ph-rad.log	-231.3379239	0.087589	-231.277723
9	Iodide-ext.log	-11.60735678	0	-11.624205
10	*t*BuOK -rad.log	-832.5022187	0.121208	-832.415294
11	KI.log	-611.3143505	0.000156	-611.340554
12	*t*BuOK-rad.log	-232.797905	0.122103	-232.705305
13	K-ext.log	-599.7006036	0	-599.71578
14	Iodide-ext.log	-11.60735678	0	-11.624205

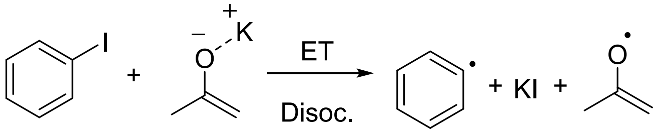
With acetone enolate

b1)



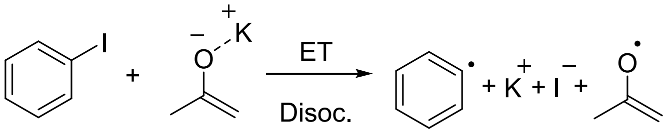
1 **15** **8** **9** **16**

b2)



1 **15** **8** **11** **17**

b3)



1 **15** **8** **13** **14** **17**

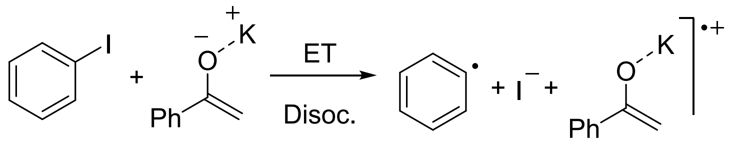
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext	-242.9680853	0.090413	-242.908747
15	Ketone enolate -K.log	-792.5070455	0.072229	-792.466352
	Products			
8	Ph-rad	-231.5160036	0.087871	-231.455508
9	Iodide-ext.log	-11.55692124	0	-11.57377
16	Ketone enolate -rad-K.log	-792.3406564	0.072053	-792.302602
11	KI.log	-611.4313177	0.000233	-611.457111
17	Ketone enolate -rad-ext.log	-192.4659613	0.070889	-192.421908
13	K-ext.log	-599.8668896	0	-599.882066
14	Iodide-ext.log	-11.55692124	0	-11.57377

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-243.0534294	0.089826	-242.994731
15	Ketone enolate-K.log	-792.4812677	0.071497	-792.441581
	Products			
8	Ph-rad.log	-231.5302682	0.087147	-231.470517
9	Iodide-ext.log	-11.6352463	0	-11.652095
16	Ketone enolate-rad-K.log	-792.319385	0.070713	-792.284832
11	KI.log	-611.4700152	0.000184	-611.496094
17	Ketone enolate-rad-ext.log	-192.4844675	0.070213	-192.441143
13	K-ext.log	-599.8300214	0	-599.845197
14	Iodide-ext.log	-11.6352463	0	-11.652095

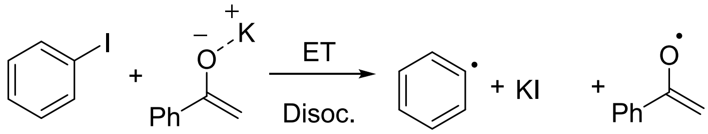
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-242.8374698	0.090269	-242.778302
15	Ketone enolate-K.log	-792.1985464	0.071886	-792.158186
	Products			
8	Ph-rad.log	-231.3379239	0.087589	-231.277723
9	Iodide-ext.log	-11.60735678	0	-11.624205
16	Ketone enolate-rad-K.log	-792.038085	0.071045	-792.00311
11	KI.log	-611.3143505	0.000156	-611.340554
17	Ketone enolate-rad-ext.log	-192.3308783	0.070518	-192.287236
13	K-ext.log	-599.7006036	0	-599.71578
14	Iodide-ext.log	-11.60735678	0	-11.624205

With Acetophenone enolate

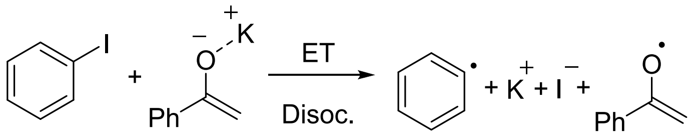
c1)



c2)



c3)



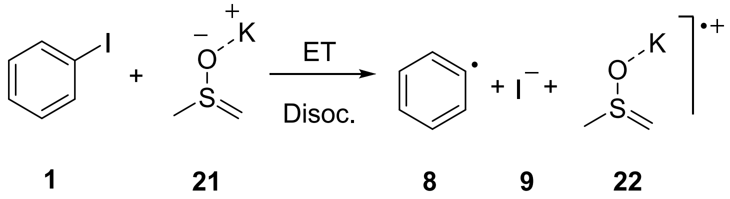
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext	-242.9680853	0.090413	-242.908747
18	acetophenone-anion-K.log	-984.2198362	0.126223	-984.130375
	Products			
8	Ph-rad	-231.5160036	0.087871	-231.455508
9	Iodide-ext.log	-11.55692124	0	-11.57377
19	acetophenone-rad-K.log	-984.0500556	0.12575	-983.963448
11	KI.log	-611.4313177	0.000233	-611.457111
20	acetophenone-rad.log	-384.17593	0.125404	-384.083405
13	K-ext.log	-599.8668896	0	-599.882066
14	Iodide-ext.log	-11.55692124	0	-11.57377

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-243.0534294	0.089826	-242.994731
18	acetophenone-anion-K.log	-984.1888596	0.124979	-984.101525
	Products			
8	Ph-rad.log	-231.5302682	0.087147	-231.470517
9	Iodide-ext.log	-11.6352463	0	-11.652095
19	acetophenone-rad-K.log	-984.0246431	0.124849	-983.939277
11	KI.log	-611.4700152	0.000184	-611.496094
20	acetophenone-rad.log	-384.189981	0.124155	-384.099513
13	K-ext.log	-599.8300214	0	-599.845197
14	Iodide-ext.log	-11.6352463	0	-11.652095

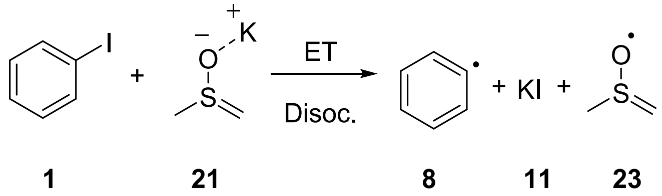
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-242.8374698	0.090269	-242.778302
18	acetophenone-anion-K.log	-983.7573153	0.125677	-983.668884
	Products			
8	Ph-rad.log	-231.3379239	0.087589	-231.277723
9	Iodide-ext.log	-11.60735678	0	-11.624205
19	acetophenone-rad-K.log	-983.5943492	0.125505	-983.508188
11	KI.log	-611.3143505	0.000156	-611.340554
20	acetophenone-rad.log	-383.8874561	0.124796	-383.796335
13	K-ext.log	-599.7006036	0	-599.71578
14	Iodide-ext.log	-11.60735678	0	-11.624205

With potassium dimsylate

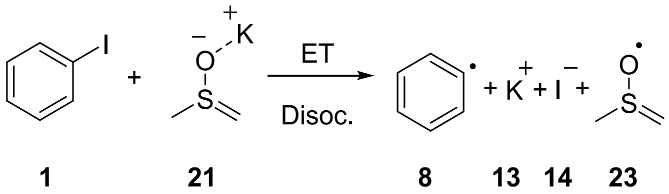
d1)



d2)



d3)

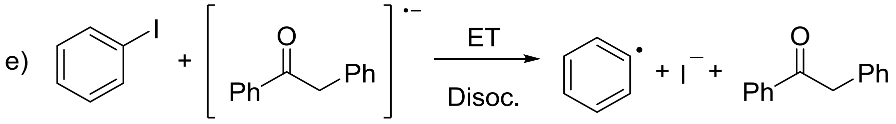


	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext	-242.9680853	0.090413	-242.908747
21	C-K-min3	-1152.524118	0.066296	-1152.490586
	Products			
8	Ph-rad	-231.5160036	0.087871	-231.455508
9	Iodide-ext.log	-11.55692124	0	-11.57377
22	C-K-min3-rad	-1152.367896	0.066282	-1152.336129
11	KI.log	-611.4313177	0.000233	-611.457111
23	dimsyl-rad-ext.log	-552.490132	0.06533	-552.453705
13	K-ext.log	-599.8668896	0	-599.882066
14	Iodide-ext.log	-11.55692124	0	-11.57377

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-243.0534294	0.089826	-242.994731
21	PhI-ext.log	-243.0534294	0.089826	-242.994731
	Products			
8	Ph-rad.log	-231.5302682	0.087147	-231.470517
9	Iodide-ext.log	-11.6352463	0	-11.652095
22	C-K-min3-rad.log	-1152.332758	0.06556	-1152.303054
11	KI.log	-611.4700152	0.000184	-611.496094
23	dimsyl-rad.log	-552.4957603	0.064814	-552.460041
13	K-ext.log	-599.8300214	0	-599.845197
14	Iodide-ext.log	-11.6352463	0	-11.652095

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext.log	-242.8374698	0.090269	-242.778302
21	C-K-min3.log	-1152.126726	0.065991	-1152.093535
	Products	Products		
8	Ph-rad.log	-231.3379239	0.087589	-231.277723
9	Iodide-ext.log	-11.60735678	0	-11.624205
22	C-K-min3-rad.log	-1151.977775	0.065871	-1151.948133
11	KI.log	-611.3143505	0.000156	-611.340554
23	dimsyl-rad.log	-552.2682518	0.065186	-552.232082
13	K-ext.log	-599.7006036	0	-599.71578
14	Iodide-ext.log	-11.60735678	0	-11.624205

$S_{RN}1$ radical anion intermediary $3a^{\cdot -}$



1 **24 or $3a^{\cdot -}$** **8** **9** **3a**

		Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
	Reactants			
1	PhI-ext	-242.9680853	0.090413	-242.908747
24	product-RA-ext.log	-615.9383668	0.217995	-615.761069
	Products			
8	Ph-rad	-231.5160036	0.087871	-231.455508
3a	product-N-ext.gjf.log	-615.8490698	0.220982	-615.669327
9	Iodide-ext.log	-11.55692124	0	-11.57377

		Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
	Reactants			
1	PhI-ext.log	-243.0534294	0.089826	-242.994731
24	product-RA-ext.log	-615.9570213	0.217995	-615.7812485
	Products			
8	Ph-rad.log	-231.5302682	0.087147	-231.470517
3a	product-N-ext.log	-615.8644943	0.219208	615.6864296
9	Iodide-ext.log	-11.6352463	0	--11.652095

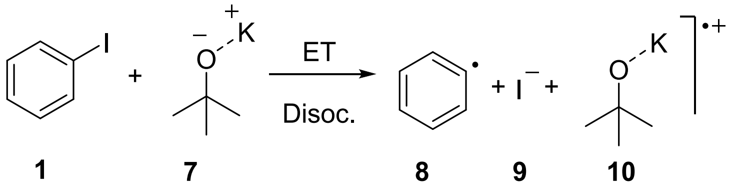
		Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
	Reactants			
1	PhI-ext.log	-242.8374698	0.090269	-242.778302
24	product-RA-ext.log	-615.4658168	0.21695	-615.290044
	Products			
8	Ph-rad.log	-231.3379239	0.087589	-231.277723
3a	product-N-ext.log	-615.3748532	0.220267	-615.195812
9	Iodide-ext.log	-11.60735678	0	-11.624205

Properties in DMF

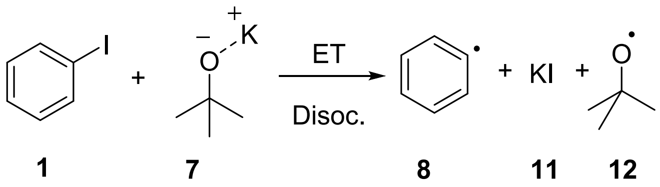
Details of the properties of the species involved in the reactions in DMF (modeled with IEF-PCM model).

With tBuOK

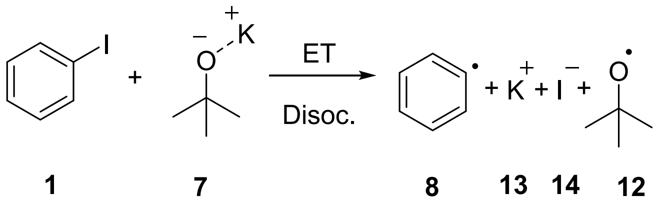
a1)



a2)



a3)

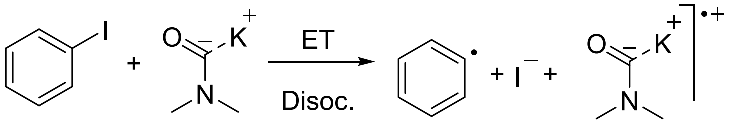


	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.9680459	0.090415	-242.908706
7	*t*BuOK-dmf.log	-833.0119967	0.123074	-832.922596
	Products			
8	Ph-rad-dmf.log	-231.5159695	0.087873	-231.455473
9	Iodide-ext-dmf.log	-11.55638885	0	-11.573237
10	*t*BuOK -rad-dmf.log	-832.8314943	0.122949	-832.743346
11	KI-dmf.log	-611.4308325	0.000236	-611.456609
12	*t*BuO-rad-dmf.log	-232.9635788	0.122861	-232.869754
13	K-ext-dmf.log	-599.8661924	0	-599.881368
14	Iodide-ext-dmf.log	-11.55638885	0	-11.573237

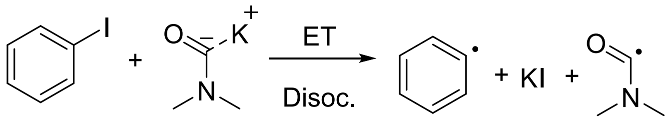
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-243.053392	0.089827	-242.994692
7	*t*BuOK-dmf.log	-832.9994238	0.121874	-832.911708
	Products			
8	Ph-rad-dmf.log	-231.5302353	0.087148	-231.470484
9	Iodide-ext-dmf.log	-11.634711	0	-11.651559
10	*t*BuOK-rad-dmf.log	-832.8234333	0.120863	-832.73813
11	KI-dmf.log	-611.4695099	0.000178	-611.495616
12	*t*BuO-rad-dmf.log	-232.9915322	0.121584	-232.899241
13	K-ext-dmf.log	-599.8293242	0	-599.8445
14	Iodide-ext-dmf.log	-11.634711	0	-11.651559

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.8374315	0.090271	-242.778263
7	*t*BuOK-dmf.log	-832.6759352	0.122423	-832.587633
	Products			
8	Ph-rad-dmf.log	-231.3378903	0.087591	-231.277688
9	Iodide-ext-dmf.log	-11.3923815	0	-11.409884
10	*t*BuOK-rad-dmf.log	-832.5022571	0.122372	-832.414089
11	KI-dmf.log	-611.313857	0.000164	-611.340007
12	*t*BuO-rad-dmf.log	-232.7977306	0.121966	-232.70507
13	K-ext-dmf.log	-599.6999064	0	-599.715082
14	Iodide-ext-dmf.log	-11.60682235	0	-11.623671

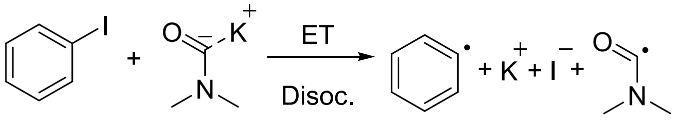
With DMF anion

b1)


1 **25** **8** **9** **26**

b2)


1 **25** **8** **11** **27**

b3)


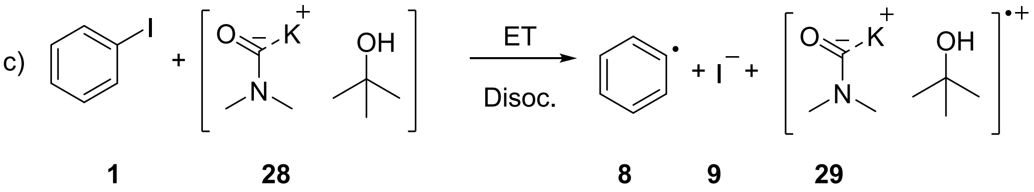
1 **25** **8** **13** **14** **27**

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.9680459	0.090415	-242.908706
25	DMF-K	-847.8372681	0.089674	-847.7814
	Products			
8	Ph-rad-dmf.log	-231.5159695	0.087873	-231.455473
9	Iodide-ext-dmf.log	-11.55638885	0	-11.573237
26	DMF-K-rad.log	-847.6942402	0.091279	-847.639067
11	KI-dmf.log	-611.4308325	0.000236	-611.456609
27	dmf-rad-ext.log	-247.8216025	0.090831	-247.760763
13	K-ext-dmf.log	-599.8661924	0	-599.881368
14	Iodide-ext-dmf.log	-11.55638885	0	-11.573237

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-243.053392	0.089827	-242.994692
25	DMF-K.log	-847.7981959	0.088505	-847.74371
	Products			
8	Ph-rad-dmf.log	-231.5302353	0.087148	-231.470484
9	Iodide-ext-dmf.log	-11.634711	0	-11.651559
26	DMF-K-rad.log	-847.6730752	0.090219	-847.617485
11	KI-dmf.log	-611.4695099	0.000178	-611.495616
27	dmf-rad-ext.log	-247.8397527	0.089808	-247.779801
13	K-ext-dmf.log	-599.8293242	0	-599.8445
14	Iodide-ext-dmf.log	-11.634711	0	-11.651559

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.8374315	0.090271	-242.778263
25	DMF-K.log	-847.4757186	0.089002	-847.420632
	Products			
8	Ph-rad-dmf.log	-231.3378903	0.087591	-231.277688
9	Iodide-ext-dmf.log	-11.6068224	0	-11.623671
26	DMF-K-rad.log	-847.3516878	0.090713	-847.295691
11	KI-dmf.log	-611.313857	0.000164	-611.340007
27	dmf-rad-ext.log	-247.6461612	0.090255	-247.585739
13	K-ext-dmf.log	-599.6999064	0	-599.715082
14	Iodide-ext-dmf.log	-11.60682235	0	-11.623671

With [DMF-tBuOk] complex



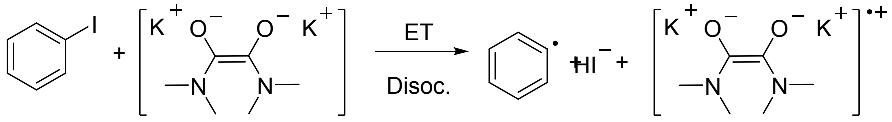
	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.9680459	0.090415	-242.908706
28	taifel	-1081.482854	0.226617	-1081.301519
	Products			
8	Ph-rad-dmf.log	-231.5159695	0.087873	-231.455473
9	Iodide-ext-dmf.log	-11.55638885	0	-11.573237
29	taifel-rad	-1081.342376	0.229303	-1081.160142

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-243.053392	0.089827	-242.994692
28	taifel.log	-1081.47832	0.223515	-1081.300869
	Products			
8	Ph-rad-dmf.log	-231.5302353	0.087148	-231.470484
9	Iodide-ext-dmf.log	-11.634711	0	-11.651559
29	taifel-rad.log	-1081.345073	0.22643	-1081.168713

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.8374315	0.090271	-242.778263
28	taifel.log	-1080.962015	0.224437	-1080.783681
	Products			
8	Ph-rad-dmf.log	-231.3378903	0.087591	-231.277688
9	Iodide-ext-dmf.log	-11.6068224	0	-11.623671
29	taifel-rad.log	-1080.829414	0.227543	-1080.651635

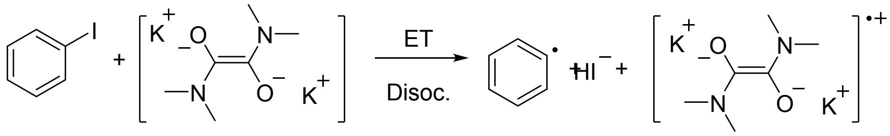
DMF adduct

d1)



1 **30*(E)*** **8** **9** **31*(E)***

d2)



1 **30*(Z)*** **8** **9** **31 *(Z)***

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.9680459	0.090415	-242.908706
30(*E*)	murphy-1	-1695.700677	0.184886	-1695.558896
30(*Z*)	murphy-2	-1695.680807	0.183971	-1695.543263
	Products			
8	Ph-rad-dmf.log	-231.5159695	0.087873	-231.455473
9	Iodide-ext-dmf.log	-11.55638885	0	-11.573237
31(*E*)	murphy-1-RC	-1695.612645	0.185984	-1695.472959
31(*Z*)	murphy-2-RC	-1695.609368	0.185876	-1695.470911

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-243.053392	0.089827	-242.994692
30(*E*)	murphy-1.log	-1695.626017	0.181953	-1695.488292
30(*Z*)	murphy-2.log	-1695.612413	0.181459	-1695.477197
	Products			
8	Ph-rad-dmf.log	-231.5302353	0.087148	-231.470484
9	Iodide-ext-dmf.log	-11.634711	0	-11.651559
31(*E*)	murphy-1-RC.log	-1695.548337	0.184113	-1695.409678
31(*Z*)	murphy-2-RC.log	-1695.546757	0.183693	-1695.410949

	Reactants	Electronic Energy (a.u.)	ZPE (a.u.)	EE + Thermal Free Energy (a.u)
1	PhI-ext-dmf.log	-242.8374315	0.090271	-242.778263
30(*E*)	murphy-1.log	-1694.989704	0.183013	-1694.850766
30(*Z*)	murphy-2.log	-1694.974425	0.18234	-1694.839002
	Products			
8	Ph-rad-dmf.log	-231.3378903	0.087591	-231.277688
9	Iodide-ext-dmf.log	-11.6068224	0	-11.623671
31(*E*)	murphy-1-RC.log	-1694.912609	0.185147	-1694.772669
31(*Z*)	murphy-2-RC.log	-1694.91036	0.184866	-1694.772717

XYZ Coordinates

List of xyz coordinates for the geometries of compounds **1** to **31** minimized with M062X DFT functional, 6-311+G(d,p) basis set in DMSO as solvent (iefpcm). xyz coordinates of the same compounds optimized at B3PW91/ 6-311+G(d,p) and PBE0/6-311+G(d,p) are not included, but will be kindly provided after mail request to: mpuiatti@fcq.unc.edu.ar.

Compund **1**

C	1.396858	-0.006875	0.000000
C	0.007316	0.012672	0.000000
C	-0.704382	1.206277	0.000000
C	-0.000110	2.408202	0.000000
C	1.391287	2.409779	0.000000
C	2.085619	1.204006	0.000000
I	-1.057865	-1.832276	0.000000
H	1.938740	-0.944104	0.000000
H	-1.786988	1.206946	0.000000
H	-0.547382	3.343324	0.000000
H	1.932814	3.347732	0.000000
H	3.169094	1.197615	0.000000

Compound **7**

C	-0.096141	-0.146791	0.168870
C	0.093178	0.141400	1.673462
C	1.608195	0.181203	1.965279
C	-0.487081	1.540571	1.968358
O	-0.528622	-0.818016	2.440272
H	0.326389	-1.127059	-0.072987
H	-1.164140	-0.166760	-0.069908
H	0.386827	0.603826	-0.466508
H	2.049576	-0.797651	1.752966
H	1.771586	0.406376	3.023716
H	2.132496	0.934539	1.367013
H	-0.006910	2.328570	1.377602
H	-0.356955	1.774830	3.029755
H	-1.558915	1.545973	1.746841
K	-1.620153	-2.479257	3.797417

Compound **8**

C	1.401670	-0.016961	0.000000
C	0.029168	0.050521	0.000000
C	-0.715524	1.205401	0.000000
C	-0.005577	2.411368	0.000000
C	1.388023	2.404127	0.000000

C	2.091094	1.200855	0.000000
H	1.933946	-0.961179	0.000000
H	-1.799378	1.194257	0.000000
H	-0.545469	3.351530	0.000000
H	1.929658	3.342265	0.000000
H	3.175244	1.203375	0.000000

Compound **10**

C	-0.123982	-0.190033	0.202974
C	0.145774	0.223705	1.677052
C	1.648414	0.203827	1.962471
C	-0.483278	1.588443	1.963554
O	-0.498093	-0.767479	2.389827
H	0.301746	-1.171936	-0.002946
H	-1.194307	-0.199768	-0.002024
H	0.359526	0.554363	-0.432458
H	2.062496	-0.781097	1.740909
H	1.832725	0.437900	3.012929
H	2.157193	0.949397	1.348487
H	-0.009367	2.356521	1.349426
H	-0.343366	1.851486	3.013984
H	-1.551628	1.566234	1.742879
K	-1.754523	-2.699806	3.735083

Compound **11**

K	-0.643152	0.100000	0.129900
I	2.794152	0.100000	-0.029900

Compound **12**

C	-0.123563	-0.189484	0.203579
C	0.143701	0.220708	1.675266
C	1.647269	0.205703	1.961713
C	-0.481027	1.588226	1.962837
O	-0.499295	-0.769675	2.393923
H	0.300433	-1.172601	-0.001943
H	-1.194292	-0.201535	-0.001164
H	0.357299	0.551177	-0.438241
H	2.064156	-0.777843	1.738318
H	1.830715	0.435776	3.013503
H	2.157332	0.954139	1.351636
H	-0.005038	2.358763	1.352737
H	-0.344563	1.848869	3.014641
H	-1.549275	1.569342	1.740259

Compound **15**

C	0.141370	0.142427	0.018003
C	0.122578	0.400932	1.517229
O	1.030509	-0.208422	2.204992
C	-0.808759	1.265901	2.032733
K	1.944800	1.930295	3.288504
H	-0.890972	1.414569	3.105894
H	-1.533351	1.757046	1.396610
H	-0.624558	0.704755	-0.517989
H	1.124579	0.400954	-0.385532
H	-0.010556	-0.925463	-0.163361

Compound **16**

C	-0.092415	-0.194924	0.275175
C	0.119309	0.780918	1.402639
O	1.054846	0.652566	2.198148
C	-0.799864	1.879201	1.536863
K	2.962437	0.458197	3.915387
H	-1.624103	2.006427	0.848189
H	-0.658745	2.586900	2.342672
H	-1.082460	-0.649169	0.358709
H	-0.055589	0.331051	-0.681698
H	0.672225	-0.968173	0.300997

Compound **17**

C	0.039204	-0.217841	-0.039330
C	0.249046	-0.388121	1.447214
C	1.451405	0.114244	2.052992
O	-0.603979	-0.953554	2.136499
H	1.590464	-0.013560	3.118439
H	2.213848	0.613252	1.471098
H	0.867782	0.296133	-0.523364
H	-0.089703	-1.202537	-0.492599
H	-0.881179	0.345766	-0.203500

Compound **18**

C	-0.079419	-0.218371	0.090585
C	-0.027458	-0.164493	1.487608
C	1.170023	0.091051	2.148593
C	2.342103	0.297239	1.423743
C	2.305927	0.234233	0.033305
C	1.107008	-0.029227	-0.623397

C	-1.357632	-0.489543	-0.675719
C	-2.554377	-0.142776	-0.102825
O	-1.219024	-0.983460	-1.859743
H	-0.926938	-0.342928	2.065540
H	1.190850	0.119076	3.232318
H	3.274714	0.496315	1.938964
H	3.213461	0.388241	-0.540011
H	1.071567	-0.094803	-1.704423
H	-2.613644	0.326252	0.869275
H	-3.485759	-0.381359	-0.606681
K	-2.433210	0.933416	-3.045687

Compound **19**

C	0.781871	0.273425	0.025406
C	1.829746	1.197587	-0.000125
C	3.146431	0.756781	-0.077304
C	3.423276	-0.605633	-0.140019
C	2.381700	-1.531475	-0.113861
C	1.067488	-1.093933	-0.024068
C	-0.647608	0.695623	0.120592
C	-1.032520	2.029729	-0.246652
O	-1.511076	-0.112214	0.487941
H	1.632545	2.260899	0.061568
H	3.955237	1.477212	-0.085682
H	4.449770	-0.946345	-0.206329
H	2.596630	-2.592111	-0.163041
H	0.248585	-1.802611	-0.000055
H	-0.338552	2.748635	-0.655873
H	-2.073736	2.302243	-0.140680
K	-3.808702	-1.172740	1.016632

Compound **20**

C	0.784455	0.273509	0.002804
C	1.833207	1.196393	-0.021106
C	3.151416	0.737355	-0.072902
C	3.415201	-0.628364	-0.102143
C	2.365570	-1.541962	-0.091320
C	1.048453	-1.089093	-0.039782
C	1.498007	2.655794	0.034230
O	0.401040	3.026267	0.461856
C	2.447671	3.623966	-0.443666
H	3.980563	1.434728	-0.067991
H	4.440328	-0.977295	-0.131019

H	2.572469	-2.605164	-0.120690
H	0.229613	-1.798455	-0.032103
H	-0.234469	0.638796	0.048288
H	3.381586	3.348441	-0.911259
H	2.185782	4.670341	-0.363808

Compound **21**

C	-0.039873	-0.028269	-0.046107
S	-0.050180	-0.039989	1.770486
O	1.494970	-0.110729	2.048981
C	-0.638747	1.490184	2.230883
K	1.997158	1.948586	3.524686
H	-1.629179	1.413668	2.669187
H	-0.533728	2.265620	1.471607
H	-1.069900	0.006995	-0.399364
H	0.504968	0.862648	-0.364325
H	0.460151	-0.925720	-0.408952

Compound **22**

C	-0.046059	-0.108340	0.014411
S	0.001452	0.168323	1.802767
O	1.397444	0.701338	2.114080
C	-1.094934	1.519303	1.887880
K	3.364502	1.456571	3.490540
H	-2.087359	1.389701	1.476629
H	-0.885509	2.259176	2.648271
H	-1.069779	-0.350632	-0.268872
H	0.302440	0.797237	-0.479453
H	0.613441	-0.949683	-0.189171

Compound **23**

C	-0.070286	0.081114	-0.065125
S	-0.102261	-0.291008	1.709261
C	1.592239	-0.062959	2.047439
O	-0.409932	-1.774345	1.842277
H	2.031871	0.894877	1.801771
H	2.018789	-0.703226	2.807656
H	0.290686	1.100041	-0.201330
H	0.580804	-0.642106	-0.553815
H	-1.095022	-0.008608	-0.420681

Compound **24**

C	2.846136	0.624948	-0.637748

C	1.627035	0.477822	0.099658
C	1.490789	-0.728474	0.860726
C	2.494540	-1.678150	0.891006
C	3.689723	-1.503208	0.173430
C	3.839062	-0.334308	-0.590931
C	0.616582	1.483267	0.034209
O	0.715338	2.514613	-0.714510
C	-0.638031	1.336689	0.881768
H	0.577151	-0.915036	1.415192
H	2.350174	-2.579395	1.479277
H	4.471028	-2.252672	0.203501
H	4.752411	-0.179862	-1.158233
H	2.977518	1.520853	-1.232954
H	-0.389460	0.974106	1.886367
H	-1.058577	2.338239	1.009746
C	-1.727680	0.437423	0.315695
C	-1.534335	-0.353539	-0.816827
C	-2.558852	-1.163188	-1.306697
C	-3.794639	-1.196253	-0.669727
C	-3.999973	-0.410848	0.463560
C	-2.975557	0.395257	0.947220
H	-0.572029	-0.334421	-1.317174
H	-2.386984	-1.769509	-2.189040
H	-4.590623	-1.825357	-1.050615
H	-4.959173	-0.425266	0.968837
H	-3.142939	1.006786	1.829118

Compound **3a**

C	2.789443	0.593607	-0.662272
C	1.626882	0.455906	0.102265
C	1.461708	-0.674734	0.907342
C	2.447333	-1.654848	0.945668
C	3.603533	-1.509208	0.184319
C	3.774834	-0.383040	-0.619507
C	0.583171	1.527403	0.023711
O	0.724039	2.477217	-0.718771
C	-0.659265	1.402724	0.884886
H	0.563268	-0.804076	1.499394
H	2.312093	-2.530987	1.568180
H	4.371464	-2.273324	0.216461
H	4.675600	-0.270774	-1.210991
H	2.906968	1.473341	-1.283695
H	-0.466032	1.194765	1.941198

H	-1.070396	2.412195	0.817698
C	-1.686204	0.422324	0.343127
C	-1.480029	-0.316347	-0.823030
C	-2.482085	-1.142589	-1.329270
C	-3.713618	-1.224687	-0.689527
C	-3.943935	-0.462194	0.454000
C	-2.942797	0.360928	0.956273
H	-0.532271	-0.257803	-1.349480
H	-2.296742	-1.716988	-2.229741
H	-4.492308	-1.867684	-1.082524
H	-4.906251	-0.506161	0.952653
H	-3.131539	0.958295	1.843108

Calculations in DMF as solvent

Compound **1**

C	1.396842	-0.006860	0.000000
C	0.007319	0.012677	0.000000
C	-0.704362	1.206271	0.000000
C	-0.000096	2.408188	0.000000
C	1.391285	2.409776	0.000000
C	2.085600	1.204011	0.000000
I	-1.057843	-1.832238	0.000000
H	1.938700	-0.944100	0.000000
H	-1.786965	1.206914	0.000000
H	-0.547368	3.343310	0.000000
H	1.932812	3.347729	0.000000
H	3.169075	1.197620	0.000000

Compound **7**

C	-0.096141	-0.146791	0.168870
C	0.093178	0.141400	1.673462
C	1.608195	0.181203	1.965279
C	-0.487081	1.540571	1.968358
O	-0.528622	-0.818016	2.440272
H	0.326389	-1.127059	-0.072987
H	-1.164140	-0.166760	-0.069908
H	0.386827	0.603826	-0.466508
H	2.049576	-0.797651	1.752966
H	1.771586	0.406376	3.023716
H	2.132496	0.934539	1.367013
H	-0.006910	2.328570	1.377602
H	-0.356955	1.774830	3.029755
H	-1.558915	1.545973	1.746841

K	-1.620153	-2.479257	3.797417

Compound **8**

C	1.401660	-0.016943	0.000000
C	0.029168	0.050521	0.000000
C	-0.715503	1.205402	0.000000
C	-0.005566	2.411359	0.000000
C	1.388022	2.404124	0.000000
C	2.091081	1.200859	0.000000
H	1.933916	-0.961170	0.000000
H	-1.799355	1.194235	0.000000
H	-0.545454	3.351523	0.000000
H	1.929656	3.342262	0.000000
H	3.175231	1.203385	0.000000

Compound **10**

C	-0.130468	-0.200287	0.218061
C	0.148888	0.228345	1.685998
C	1.653383	0.211628	1.961532
C	-0.478152	1.595751	1.962940
O	-0.490104	-0.756535	2.412199
H	0.294744	-1.183866	0.018895
H	-1.202188	-0.212579	0.020173
H	0.348096	0.538144	-0.427911
H	2.065647	-0.776608	1.751630
H	1.844703	0.461015	3.007270
H	2.158108	0.948000	1.333106
H	-0.011365	2.356744	1.334527
H	-0.327185	1.871327	3.008700
H	-1.548832	1.570463	1.753996
K	-1.775946	-2.729785	3.661032

Compound **11**

K	-0.641393	0.100000	0.129818
I	2.792393	0.100000	-0.029818

Compound **12**

C	2.048934	-0.727394	-1.274558
C	1.558715	-0.027522	-0.000010
C	-0.005536	0.035891	-0.000025
O	1.904603	1.305622	-0.000051
C	2.048914	-0.727313	1.274590
H	3.144163	-0.723956	-1.305756

	H	1.707483	-1.767787	-1.295317
	H	1.670620	-0.214849	-2.165313
	H	-0.372661	0.546713	-0.894148
	H	-0.372676	0.546761	0.894064
	H	-0.364747	-0.998743	-0.000002
	H	1.670601	-0.214698	2.165306
	H	3.144143	-0.723891	1.305798
	H	1.707446	-1.767698	1.295421
Compound	**25**			
	C	2.323023	-1.047746	0.000034
	H	2.968106	-1.060343	0.885872
	H	1.693647	-1.935268	-0.000003
	H	2.968192	-1.060329	-0.885742
	N	1.467988	0.126938	0.000000
	C	2.161695	1.393547	0.000055
	H	1.423244	2.195099	0.000001
	H	2.800370	1.496698	0.885902
	H	2.800501	1.496699	-0.885697
	C	0.088528	0.084974	-0.000038
	O	-0.430859	-1.071447	-0.000059
	K	-2.661976	0.202647	-0.000115
Compound	**26**			
	C	2.132646	-1.033389	0.006207
	H	2.781167	-1.158160	0.874823
	H	1.329681	-1.765750	0.038319
	H	2.719508	-1.168051	-0.903903
	N	1.553605	0.313082	0.019485
	C	2.482443	1.436481	-0.009199
	H	1.916889	2.365610	0.005706
	H	3.138992	1.393829	0.861601
	H	3.087655	1.391126	-0.916369
	C	0.253136	0.506823	0.049083
	O	-0.669837	-0.268859	0.072719
	K	-3.123425	-1.191273	-0.098263
Compound	**27**			
	C	2.303999	-1.039933	-0.033251
	N	3.166000	-1.056031	1.149749
	C	3.118723	-2.040156	2.030959
	O	2.447304	-3.034819	2.076928
	C	4.083084	0.062534	1.317503
	H	2.919330	-1.028483	-0.935181

H	1.676685	-1.928482	-0.029435
H	1.676067	-0.146799	-0.017270
H	4.656172	-0.080715	2.231320
H	4.763443	0.115551	0.464832
H	3.520962	0.996657	1.382158

Compound **28**

C	-3.631440	-0.500750	0.587630
H	-3.755860	-1.339540	1.281110
H	-3.640350	0.432960	1.145850
H	-4.474570	-0.512200	-0.111820
N	-2.368750	-0.605560	-0.122230
C	-2.190950	-1.807400	-0.905710
H	-1.226790	-1.757840	-1.411730
H	-2.213200	-2.702550	-0.272200
H	-2.982840	-1.907090	-1.657050
C	-1.383430	0.353360	-0.088870
H	0.253720	-0.014030	-0.646070
O	-1.620550	1.389810	0.597440
O	1.265620	-0.054350	-0.867170
C	1.935650	-0.831730	0.120400
C	3.357160	-1.060840	-0.380510
H	3.853520	-0.102530	-0.553350
H	3.939930	-1.628090	0.349810
H	3.340270	-1.617160	-1.320940
C	1.958810	-0.064200	1.446790
H	0.937330	0.166270	1.764230
H	2.441800	-0.647750	2.234950
H	2.513970	0.871850	1.332770
C	1.218090	-2.171230	0.307490
H	1.150110	-2.696740	-0.648820
H	1.758690	-2.804610	1.015850
H	0.204890	-2.011910	0.686490
K	0.512460	2.543310	-0.352580

Compound **29**

C	-3.763590	0.098660	0.771740
H	-3.807070	-0.515010	1.673200
H	-3.557310	1.132480	1.038610
H	-4.717130	0.035960	0.245070
N	-2.692860	-0.393130	-0.100950
C	-2.800090	-1.767120	-0.577180
H	-1.952940	-1.988690	-1.223990

H	-2.802610	-2.453030	0.272450
H	-3.728050	-1.888980	-1.138470
C	-1.661890	0.357640	-0.416620
H	0.598210	-0.244580	-1.128710
O	-1.366500	1.491060	-0.134370
O	1.431980	0.019580	-0.718440
C	1.889870	-1.072170	0.104990
C	3.205940	-0.603350	0.707820
H	3.049090	0.274140	1.339930
H	3.641360	-1.394020	1.321670
H	3.913410	-0.346140	-0.083320
C	0.857360	-1.349120	1.195610
H	-0.079690	-1.709480	0.760170
H	1.224740	-2.113260	1.884440
H	0.650900	-0.437150	1.761600
C	2.095960	-2.302510	-0.772460
H	2.834460	-2.095840	-1.549950
H	2.443920	-3.147010	-0.173490
H	1.155320	-2.590880	-1.251410
K	1.079910	2.630320	-0.121160

Compound **30(E)**

C	-1.607860	-1.470290	1.792280
H	-0.861200	-2.187280	2.170320
H	-1.528400	-0.543380	2.366840
H	-2.604060	-1.890990	1.962510
N	-1.432510	-1.177060	0.376570
C	-1.616200	-2.391700	-0.405820
H	-1.508670	-2.157660	-1.468930
H	-0.886150	-3.173860	-0.147900
H	-2.623290	-2.788280	-0.243930
C	-0.144860	-0.568170	0.123440
O	0.941330	-1.323730	0.352110
K	1.722990	0.523470	1.890910
C	-0.046490	0.737040	-0.317100
N	-1.151170	1.570460	-0.711660
C	-1.348860	2.698150	0.177370
H	-0.380370	3.138950	0.415620
H	-1.967310	3.459990	-0.307880
H	-1.851570	2.401370	1.117400
C	-2.407050	1.000740	-1.150820
H	-3.052830	0.662200	-0.329130
H	-2.944970	1.762050	-1.728960

H	-2.217540	0.141070	-1.795090
O	1.140570	1.332570	-0.424050
K	1.797270	-0.612060	-1.912270

Compound **30(Z)**

C	-1.191380	-2.004090	1.192100
H	-0.296180	-2.641690	1.236160
H	-1.204630	-1.370780	2.082680
H	-2.075450	-2.652770	1.206300
N	-1.204970	-1.160150	0.000060
C	-1.191250	-2.004170	-1.191920
H	-1.204210	-1.370940	-2.082550
H	-0.296110	-2.641890	-1.235670
H	-2.075380	-2.652760	-1.206270
C	-0.053250	-0.242190	0.000100
O	1.146320	-0.823840	-0.000040
C	-0.325500	1.097180	0.000110
N	0.817150	2.016070	0.000510
C	1.613740	1.968470	-1.205950
H	0.965400	2.119180	-2.072230
H	2.357120	2.774520	-1.195990
H	2.137720	1.005930	-1.343980
C	1.614320	1.967190	1.206530
H	2.138290	1.004490	1.343400
H	2.357760	2.773180	1.196900
H	0.966450	2.117140	2.073290
O	-1.509700	1.676440	-0.000470
K	3.445960	-1.147810	-0.000350
K	-3.495910	0.307270	-0.000060

Compound **31 (E)**

C	-0.937152	-1.660006	2.478285
H	-0.385716	-2.598248	2.327712
H	-0.341342	-1.013783	3.119810
H	-1.881788	-1.887972	2.975269
N	-1.229661	-0.986258	1.223580
C	-2.166307	-1.738417	0.393454
H	-2.400818	-1.186191	-0.514012
H	-1.750066	-2.718380	0.118537
H	-3.089054	-1.902663	0.954153
C	-0.125720	-0.384642	0.600136
O	1.041800	-0.549931	1.093511
K	2.214124	1.816164	0.791073

C	-0.271276	0.466117	-0.566590
N	-1.526057	0.893306	-1.022318
C	-2.450857	1.496948	-0.067867
H	-2.448202	0.941851	0.866986
H	-2.180816	2.542978	0.135457
H	-3.459898	1.478013	-0.485819
C	-1.520345	1.581835	-2.302449
H	-2.549979	1.660033	-2.656237
H	-1.098618	2.593429	-2.227989
H	-0.934587	1.020191	-3.027422
O	0.777991	0.785225	-1.223879
K	2.135145	-1.506000	-1.181550

Compound **31** (Z)

C	-1.692251	-1.105394	1.182117
H	-1.084877	-1.535805	1.991116
H	-1.804584	-0.035523	1.349630
H	-2.680073	-1.572549	1.211939
N	-1.080888	-1.345583	-0.128793
C	-0.971149	-2.771672	-0.405310
H	-0.572413	-2.928257	-1.406525
H	-0.315636	-3.286220	0.310048
H	-1.967451	-3.214423	-0.345034
C	0.133917	-0.622054	-0.353828
O	1.201581	-1.248859	-0.627952
C	0.017739	0.814992	-0.337132
N	1.209509	1.564950	-0.345332
C	1.027369	2.999712	-0.486207
H	0.369985	3.215682	-1.326264
H	0.593629	3.454317	0.415658
H	2.002774	3.455191	-0.668163
C	2.221635	1.238482	0.654345
H	3.185557	1.648038	0.343030
H	1.964329	1.672765	1.631892
H	2.315346	0.161129	0.758486
O	-1.102042	1.407152	-0.397559
K	3.448422	-1.973530	-1.409547
K	-2.984119	0.121439	-1.607952

References

1 Soria Castro S. M., Caminos D. A. and. Peñéñory A. B, *RSC Adv*. **2014**, 4, 17490-17497.

2 Daniel A. Caminos, Alexis D. Garro Silvia Soria-Castro, Alicia B. Peñéñory, *RSC Adv*., **2015**, 5, 20058

3 a)Semmelhack, M. F.; Bargar, T.M. *J. Org. Chem.,* , **1977**, 42, (8), 1481-1482. b) Lukach A. E., N. Santiago A., and Rossi R. A., *J. Org. Chem.* **1997**, 62, 4260-4265. c) Dell'Erba C., Novi M., Petrillo G. and Tavani C. *Terrahedron* **1993**, 49(1), 235-242

4 Martin Pichette Drapeau, Indira Fabre, Laurence Grimaud, Ilaria Ciofini, Thierry Ollevier, Marc Taillefer, *Angew. Chem. Int. Ed*., 54, **(2015)** 10587-10591

5 *t*BuOK Product Specification Sigma-Aldrich:
http://www.sigmaaldrich.com/Graphics/COfAInfo/SigmaSAPQM/SPEC/15/156671/156671-BULK_______ALDRICH__.pdf (acceded 03-04-**2017**)

6 : Mack Taillefer, in a personal email comunicaction, 26-11-2016

7 Corey, Chaykovsky. J. Am. Chem. Soc. 1965, 87:6, 1345- 1353

8 J.P. Barham, G. Coulthard , K.J. Emery, E. Doni, F. Cumine, G Nocera, M.P. John L. E. A. Berlouis, T. McGuire. T. Tuttle and J.A. Murphy, *J. Am. Chem. Soc.* 2016, **138**, 7402−7410 DOI: 10.1021/jacs.6b03282

9 J.-C. Hsieh, Y.-C. Chen, A.-Y. Cheng and H.-C. Tseng, Org.Lett., 2012, 14, 1282–1285.

10 Martin Pichette Drapeau, Indira Fabre, Laurence Grimaud, Ilaria Ciofini, Thierry Ollevier, Marc Taillefer, Angew. Chem. Int. Ed., 54, (2015) 10587-10591

11 J.-C. Hsieh, Y.-C. Chen, A.-Y. Cheng and H.-C. Tseng, Org.Lett., 2012, 14, 1282–1285.

12 Gaussian 09, Revision E.01, M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria,; M. A. Robb, J. R. Cheeseman; G. Scalmani, V. Barone,; B. Mennucci,; G. A. Petersson,; H.Nakatsuji; M.Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada,; M. Ehara,; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. A. Jr. Montgomery; J. E. Peralta; F. Ogliaro; M. Bearpark; J. J. Heyd; E. Brothers; K. N. Kudin; V. N. Staroverov; R. Kobayashi; J. Normand; K. Raghavachari; A. Rendell; J. C. Burant; S. S. Iyengar; J.Tomasi; M. Cossi; N. Rega; N. J. Millam; M. Klene; J. E. Knox; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; Ö. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

13 a) J. Tomasi; B. Mennucci; R. Cammi, , Quantum mechanical continuum solvation models. Chem Rev 2005, 105 (8), 2999-3093. b) G. Scalmani; M. J. Frisch , Continuous surface charge polarizable continuum models of solvation. I. General formalism. J Chem Phys 2010, 132 (11), 114110.

---

14 a) J. P. Perdew, in Electronic Structure of Solids ‘91, Ed. P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991. b) J. P. Perdew; Y. Wang, Phys. Rev. B, 1992, 45, 13244-49. c) J. P. Perdew; J. A. Chevary ; S. H. Vosko; K. A. Jackson; M. R. Pederson; D. J. Singh; C. Fiolhais, Phys. Rev. B, 1993, 48, 4978. d) J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B, 1996, 54, 16533-39. e) Burke, J. P.Perdew, and Y. Wang, in Electronic Density Functional Theory: Recent Progress and New Directions, Ed. J. F. Dobson, G. Vignale, and M. P. Das (Plenum, 1998). f) A. D. Becke, J. Chem. Phys., 1993, 98, 5648-52.

[15] a)Y. Zhao and D. G. Truhlar, *J. Phys. Chem.*, **110** (2006) 5121-29. b) Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, **110** (2006) 13126-30.

[16] a) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **77** (1996) 3865-68. b) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **78** (1997) 1396. c) C. Adamo and V. Barone, *J. Chem. Phys.*, **110** (1999) 6158-69.

17 a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., 1980, 72, 650. b) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, J. Comput. Chem., 1983, 4, 294-301.