Part 10: Chemically triggered alkoxyamines C–ON bond homolysis in ionic liquid solvents

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-07-2015-013899.R2
Article Type:	Paper
Date Submitted by the Author:	31-Aug-2015
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Journal Name

ARTICLE

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The homolysis of the C−ON bond of three alkoxyamines - the non-activated alkoxyamine **1**, its *N*-methylated version **2** and its *N*-oxidated version **3** - is investigated in several ionic liquids. These three alkoxyamine were selected as their homolysis is prone to sharp solvent effects. EPR studies on these alkoxyamines in four ionic liquids (IL) afforded results that were similar to those previously published (*Polymer. Chem.*, 2012, **3**, 2901; *J. Org. Chem.* 2012, **77**, 9634). Indeed, the correlations between Reichardt solvent polarity constants E_T^N and log k_d, and those based on the Kalmet-Abboud-Taft relationship did not change significantly when ILs were implemented.

Introduction

Thanks to the pioneering work of Rizzardo and the seminal work of Georges on Nitroxide Mediated Polymerization (NMP),[12] it has quickly grown to become a technique used in many different industries and laboratories for the preparation of new materials.[3,4] NMP is described as a simplified three-stage polymerization process (Fig. 1a),[5,6] based on the kinetic parameters: $k_{d,ds}$, the rate constant of the homolysis of the C−ON bond of the dormant species (ds), which affords nitroxyl and macroalkyl radicals; $k_{c,ds}$, the rate constant of the cross-coupling reaction between nitroxyl and alkyl radicals; k_p, the propagation rate constant; and k_t the termination rate constant. Although the various effects influencing the homolysis rate constants k_d of homolysis of molecular alkoxylamine have been investigated during the last 30 years,[7,8] no investigation on solvent effect of ionic liquids has yet been reported.

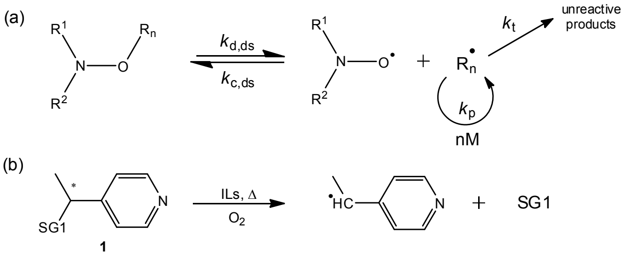

Fig. 1 (a) Simplified scheme for NMP. (b) Conditions for investigation of the C−ON bond homolysis exemplified for **1**.

However, until recently,[9-11] the investigation of the solvent effect on the rate constant $k_{d,ds}$ (or k_d for the molecular alkoxyamine) of the C−ON bond homolysis in alkoxyamines did not arouse much interest.[12-19] In general, a very weak solvent effect was commonly accepted.**5**,**6**,[11,12] However, it has been shown that changing the solvent can significantly affect the fate of NMP experiments; for example, a poor quality bulk NMP of isoprene has been reported whereas a successful one has been reported in 1,4-dioxane or pyridine as solvent.[20,21]

Ionic liquids (ILs) are organic salts (Fig. 2) that are liquid at ambient temperature and exhibit zero vapor pressure.[22] Hence, they are considered as potential solvents for green and environmentally friendly chemical processes, due to their unique combination of low volatility, chemical stability, high conductivity, wide electrochemical range and ability to dissolve organic and inorganic compounds. In the last few years, ionic liquids have been advantageously used for polymer synthesis.[23,24] In 2004, for the first time Zhang *et al.*[25,26] performed NMP of styrene and methyl methacrylate in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]PF_6 (IL 3 in Figure 2) with bimolecular initiation. Control and livingness were not as good as in bulk as larger polydispersities were obtained and the preparation of block copolymers was unsuccessful.[24] At the same time, Ryan *et al.*[27] reported NMP of methyl acrylate at 140° C using 4-oxo-TEMPO as a control agent and AIBN as initiator. M_n increased linearly with monomer conversion and the polydispersity index reached ca. 1.4 in the best case.

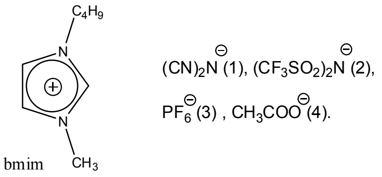

Fig. 2 ILs used for investigation of C−ON bond homolysis.

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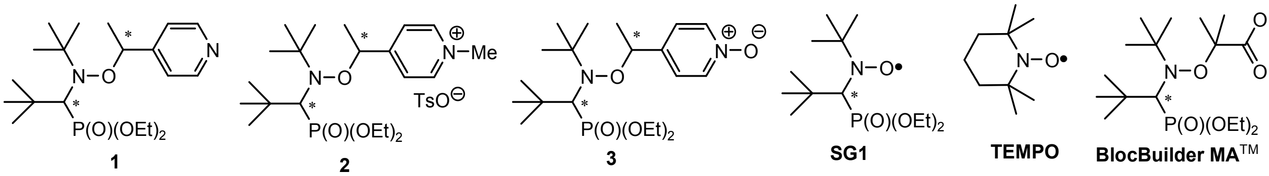

Fig. 3 Alkoxyamines investigated and structures of SG1 and TEMPO nitroxides.

1-Butyl- 3-methyl imidazolium bis(trifluoromethylsulfonyl)imide [bmim]NTf$_2$ (2) was used as the polymerization medium for the SG1-mediated copolymerization of methyl methacrylate with a low percentage of styrene, initiated by the BlocBuilder MA™ alkoxyamine at 90 °C.[28] Importantly, the effect of IL on the C—ON bond homolysis mentioned in the articles cited above has been investigated during NMP experiments meaning that the effect of IL might be biased by antagonistic/synergetic effects of IL occurring in other reactions involved in the NMP process (see Figure 1a)

In this work, we investigated the effect of 4 ILs – 1-butyl-3-methylimidazolium dicyanamide [bmim]DCA (1), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim]NTf$_2$ (2), 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]PF$_6$ (3), 1-butyl-3-methylimidazolium acetate [bmim]Ac (4) – with alkoxyamine **1**, which was non-activated, alkoxyamine **2** which was activated by the *N*-methylation of **1** and alkoxyamine **3** which was activated by *N*-oxidation of **1**. (Fig. 3) These three alkoxyamines were selected as their homolysis is sensitive to solvent effects.[9,10]

Experimental section

Alkoxyamine **1**, **2** and **3** were prepared as previously reported.[29-31] k_d values were measured in four ILs using EPR as previously described.[32] For EPR experiments, alkoxyamines were dissolved in ILs at a concentration of 10^{-4} M, with O_2 as scavenger (Fig. 1b), and the sample was heated to the required temperature in the cavity of the ESR machine. k_d values were given by eqn (1), with C_0 the initial concentration of alkoxyamine and t the time. The activation energies E_a for the C—ON bond homolysis were given by eqn (2), with the frequency factor $A = 2.4 \times 10^{14}$ s^{-1}, the temperature T and the constant $R = 8.314$ J^{-1}·K^{-1}·mol^{-1}.[7,33]

$$\ln Co/(Co - C) = -k_d \cdot t \qquad (1)$$

$$k_d = A \cdot e^{-\frac{Ea}{RT}} \qquad (2)$$

Results and discussion

Alkoxyamine **3** is soluble in the four ILs whereas **1** and **2** are not soluble in [bimAc]. k_d are reported in Table 1. A few examples of semi-log log(C/C_0) *vs*. *t* plot are displayed in Fig. 4 for **1**. Taking into account the solvent effect previously observed with **1** – **3**,[9,10,34] the parameters selected for the correlations (Table 2) are the normalized Reichardt solvent polarity parameter E_T^N, the hydrogen bond donor (HBD) α, the hydrogen bond acceptor (HBA) β, the polarity/polarizability parameter π^*.[22,35-38] For a reliable and quantitative discussion, k_d values were re-estimated at 60 °C as k_d' applying eq. 2.

Table 1 k_d values and activation energies E_a measured in solvents 1-5 and the re-estimated k_d' values at 60°C for *RR/SS* and *RS/SR* diastereoisomers of **1-3**.

	T	(*RR/SS*)-**1**[a]			*T*	(*RS/SR*)-**1**[a]		
Solvent	(°C)	k_d (10^{-4} s^{-1})[b]	E_a (KJ mol^{-1})[c]	k_d' (10^{-5} s^{-1})[d]	(°C)	k_d (10^{-4} s^{-1})[b]	E_a (KJ mol^{-1})[c]	k_d' (10^{-5} s^{-1})[d]
1 ([bmim]DCA)	82	4.8	120.3	2.9	82	4.3	120.6	2.5
2 ([bmim]NTf$_2$)	60	0.5	118.7	5.8	60	0.1	117.1	1.3
3 ([bmim]PF$_6$)	82	7.9	118.8	4.9	82	4.1	120.7	2.5
4 ([bmim]Ac)	--	--	--	--	--	--	--	--
5 *t*-BuPh[e,f]	85	2.5	121.5	1.6	85	2.3	121.8	1.5
6 H_2O/MeOH (*v*/*v* 1:1)[e]	80	5.6	119.4	4.5	80	5.3	119.2	4.8
7 H_2O	--	--	--	--	--	--	--	--
	T	(*RR/SS*)-**2**[a]			*T*	(*RS/SR*)-**2**[a]		
Solvent	(°C)	k_d (10^{-4} s^{-1})[b]	E_a (KJ mol^{-1})[c]	k_d' (10^{-3} s^{-1})[d]	(°C)	k_d (10^{-4} s^{-1})[b]	E_a (KJ mol^{-1})[c]	k_d' (10^{-3} s^{-1})[d]
1	60	19.5	108.7	1.9	58	13.4	109.7	1.3
2	49	6.6	108.3	2.2	58	23.2	107.8	2.6
3	39	0.4	111.3	0.7	58	8.6	110.6	0.9
5[e]	60	7.4	111.6	0.7	60	5.2	112.6	0.6
7[e]	40	4.1	106.5	4.7	40	3.2	107.1	3.8
	T	(*RR/SS*)-**3**[a]			*T*	(*RS/SR*)-**3**[a]		
Solvent	(°C)	k_d (10^{-4} s^{-1})[b]	E_a (KJ mol^{-1})[c]	k_d' (10^{-4} s^{-1})[d]	(°C)	k_d (10^{-4} s^{-1})[b]	E_a (KJ mol^{-1})[c]	k_d' (10^{-4} s^{-1})[d]
1	64	9.6	112.2	5.3	63	7.1	112.7	4.4
2	64	13.9	111.2	7.7	58	9.6	110.3	10.3
3	63	11.9	111.6	6.6	59	6.1	111.8	6.2
4	64	4.5	111.2	6.2	63	4.6	111.7	6.4
5[e]	61	3.7	113.9	3.7	61	4.1	113.6	4.1
7[e]	60	7.0	111.8	7.0	60	7.3	111.7	7.3

[a] Given in ref. 29. [b] Statistical error is less than 10%. [c] Estimated using the average value of $A = 2.4 \times 10^{14}$ s^{-1}. See ref. 33. [d] Estimated using the frequency factor given in footnote *c* combined with the data in the 4th column for the (*RR/SS*) isomer and the 8th column for the (*RS/SR*) isomer. [e] Given in ref. 9,10. [f] *t*-BuPh: *tert*-butylbenzene.

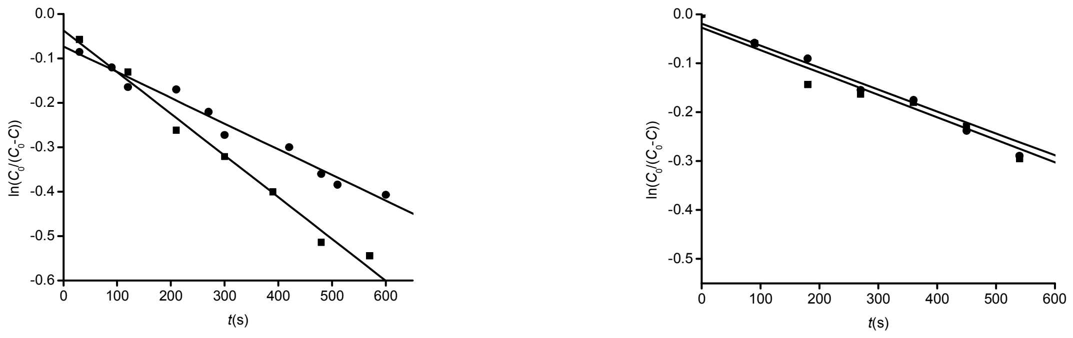

Fig. 4 Plots of ln(C/C_0) *vs.* t for [bmim]DCA (1) (●) and [bmim]PF_6 (3) (■) as solvents for the *RR/SS* (left) and *RS/SR* (right) diastereoisomers of **1** at 82°C.

First, we compared the values of the activation energies of alkoylamines **1**, **2** and **3** obtained in the ionic liquids with those obtained in *tert*-butylbenzene and water as solvents.9[,10] The activations energies measured are of the same size as those reported for conventional solvent.9[,10] That is, E_a values (Table 1) show difference smaller than 3 kJ mol^{-1} between E_a of *tert*-butylbenzene and of water, except for (*RS/SR*)-**1** in [bmim]NTf_2 and for (*SS/RR*)-**2** and (*SR/RS*)-**2** in [bmim]PF_6 and [bmim]NTF_2, respectively, which exhibit differences of 5 kJ mol^{-1}. Nevertheless, this highlights that the use of an ionic liquid has a weak but clear effect on E_a, e.g., a 1.5-fold increase in k_d from [bmim]DCA to water for (*RR/SS*)-**3**, a 3.5-fold increase in k_d from *t*-BuPh to [bmim]NTf_2 for (*RR/SS*)-**1**, and a 7-fold increase in k_d from [bmim]PF_6 to water for (*RR/SS*)-**2**.

Table 2. Values of normalized Reichardt solvent polarity parameter E_T^N, hydrogen bond donor (HBD) α, hydrogen bond acceptor (HBA) β, polarity/ polarizability parameter π*.

Solvent	E_T^N	α	β	π*
1 [bmim]DCA[a]	0.640	0.53	0.57	1.06
2 [bmim]NTf_2[a]	0.645	0.60	0.24	0.97
3 [bmim]PF_6[b]	0.667	0.77	0.41	0.91
4 [bmim]Ac	0.571[c]	0.48 [d]	1.20[d]	0.96[d]
5 *t*-BuPh[e]	0.099	0.00	0.18	0.41
7 H_2O [e]	1.000	1.17	0.47	1.09

[a] see ref. 35 [b] see ref. 22. [c] See ref. 36. [d] see ref. 37. [e] see ref. 9.

Then, the influence of anions of ILs on E_a was compared. In most cases, very little energy change is observed, i.e., 1 - 2 kJ mol^{-1}). Indeed, the largest change was measured for (*RS/SR*)-**1** wherein ΔE_a = 3.6 kJ mol^{-1}, but it is less than 3 kJ mol^{-1} for other alkoxyamines ((*RR/SS*)-**1**-**3**). The counteranions of ionic liquids thus have little influence on the rate of the C−ON bond homolysis.

Thirdly, the different diastereoisomers of alkoyamines **1**, **2** and **3** were compared. For **2**, the diastereomic ratii of the homolysis rate constants $k'_{d,RR/SS}/k'_{d,RS/SR}$ ranged from 0.78 to 1.46. For **3**, these values spanned a smaller range, from 0.74 to 1.20 and for **1**, these values spanned a larger range, from 1.16 to 4.46. However, taking into account the conventional error of *ca.* 1 kJ mol^{-1} for E_a implies that significance occurs for ratii larger than 1.44 and smaller than 0.7. Consequently, these data will not be discussed further, except that the high value of 4.46 in [bmim]NTf_2 (2) for **1** might denote a different solvation process between the two diastereoisomers.

Table 3. Linear correlation $y = a + bx$ for log(k_d' s-^{1}) *vs.* E_T^N in various solvents at 60°C for **1**, **2** and **3** and their subsequent statistical outputs.

alkoxyamine	*y*-intercept[a]	Slope[a]	R^2[b]	*N*[c]	SD[d]	Outliers[e]
(*RR/SS*)-**1**	-4.85 (5)	0.68 (10)	0.77	15	0.10	
(*SR/SR*)-**1**	-4.91 (5)	0.59 (8)	0.85	11	0.08	2
(*RR/SS*)-**2**	-3.15 (11)	0.99 (18)	0.71	13	0.18	3
(*SR/SR*)-**2**	-3.33 (9)	1.04 (14)	0.85	12	0.13	3
(*RR/SS*)-**3**	-3.46 (2)	0.37 (5)	0.79	15	0.05	
(*SR/SR*)-**3**	-3.42 (4)	0.26 (6)	0.69	11	0.06	2

[a] Error given on the last digit. [b] Square of the linear regression coefficient. [c] Number of data. [d] Standard deviation. [e] Previously published outliers are not reported in Fig.5a.

As the non-specific solvent properties (ε_r, *n* and η) were not suitable to describe the reactivity reported, specific parameters such as E_T^N, α and π* were then investigated.
The moderate correlation ($R^2 > 0.7$) obtained for E_T^N suggested the influence of the polarity of the solvent played a role although it did not account for the whole reactivity (Table 3 Fig. 5 top). The positive slopes of the plot of log k_d against E_T^N show that the higher the solvent polarity, the larger k_d, meaning the transition state (TS) or the products were more stabilized than the starting materials for all alkoxyamines.

Solvent effects are often investigated using the Kalmet−Abboud−Taft (KAT) relationships (3).[38]

$$\log k_d' = \log k_{d,0}' + a_1(\pi^* + a_2 \times \delta) + a_3\alpha + a_4\beta \quad (3)$$

Table 4. Coefficients and statistical outputs for eq. 3 for alkoxyamines **1**, **2**, and **3**.

Equation	alkoxyamine	log($k_{d,0}$' s^{-1})[a]	a_1[a]	*t*-test[b]	a_3[a]	*t*-test[b]	R^2 [c]	SD[d]	*N*[e]	*F*-test[f]	Outliers[g]
3a	(*RR/SS*)-**1**	-4.91 (6)	0.39 (11)	99.93	0.24 (8)	99.84	0.77	0.12	14	14	none
3b	(*SR/SR*)-**1**	-4.91 (8)	0.35 (11)	98.03	0.16 (8)	92.53	0.74	0.11	13	10	2
3c	(*RR/SS*)-**2**	-3.09 (15)	0.27 (19)	79.77	0.52 (12)	99.75	0.77	0.18	12	14	3
3d	(*SR/SR*)-**2**	-3.31 (13)	0.36 (17)	93.55	0.46 (11)	99.81	0.78	0.16	14	16	3
3e	(*RR/SS*)-**3**	-3.48 (3)	0.16 (5)	99.95	0.16 (3)	99.98	0.81	0.05	17	29	none

[a] Error given on the last digit. [b] Student *t*-test. [c] Square of regression coefficient. [d] Standard deviation. [e] Number of data. [f] Student-Fischer *F* test given at 99.99% confidence. [g] Previously reported outliers are not reported in Fig. 5b.

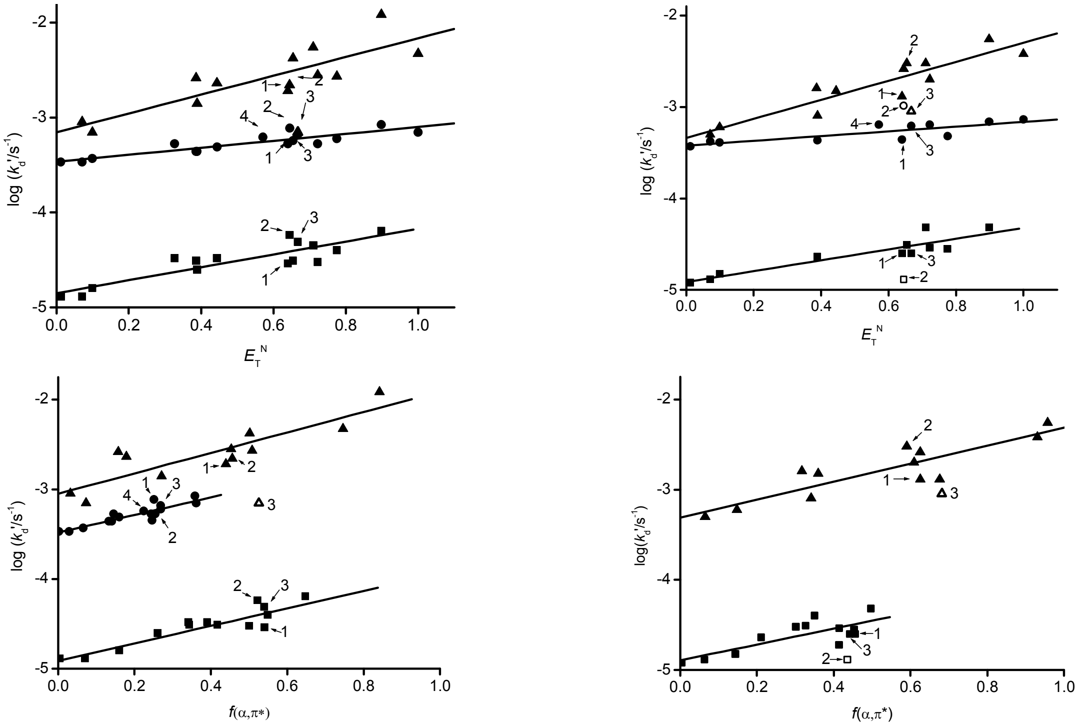

Fig. 5 (top) Linear correlations for log(k_d' s^{-1}) *vs.* E_T^N for the (*RR/SS*) (left) and the (*RS/SR*) (right) diastereoisomers of **1** (■), **2** (●) and **3** (▲) at 60°C in various solvents (see Tables 1 and 2 and ref. 8). (bottom) Plots of the KAT relationships for (*RR/SS*) (left) and (*RS/SR*) (right) diastereoisomers of **1** (■), **2** (●) and **3** (▲). Empty symbols are for outliers ILs. Outliers mentioned in previous work are not reported here.

Statistical analysis showed that β was non significant as **1**, **2** and **3** did not carry "acidic" protons.[§] Correlations were good for **1**, sufficiently good for **3** and moderately good for **2**, as shown with good statistical parameters (Student *t* test and Student-Fischer *F* test Table 4 and Figure 5 bottom). The slopes for π^* and α were positive, implying that k_d' increased with polarity/polarizability and HBD properties of the solvent, and that consequently TS or products were better stabilized than the starting materials.

The implementation of the k_d of ILs did not significantly change coefficients a_1 and a_3, except a_1 in eq. 3b, *i. e.*, $a_1 = 0.35$ against 0.56 previously reported.[9] All comments describing the effects for conventional solvents hold for ILs. That is, TS and products from the homolysis of **1** - **3** are stabilized by the polarity of the solvent (parameter π^*)[9] and the HBD properties of the solvent (parameter α)[9] except that for **2** the parameter α describes the ability of the solvent to dissociate the intimate ion pair in **2**.[10]

Conclusion

Our results show unambiguously that ILs behave as common solvents in the homolysis of alkoxyamines and their effects are merely accounted for by conventional parameters such as E_T^N, α and π^*. In light of our results, the weak effect of ILs on NMP reported previously using poorly solvent sensitive TEMPO based alkoxyamines is not surprising. Assuming that ILs also behave as common solvents when BlocBuilder MA^{TM} is used as initiator/controller, it was possible to determine $k_d = 7.8\ 10^{-3}$ at 70 °C for BlocBuilder MA^{TM} in [bmim]NTf$_2$ (2).[39] This value is close to the one reported in 1,4-dioxan ($k_d = 4.3\ 10^{-4}$ s^{-1} at 70 °C) in which NMP of MMA in the presence of small amount of styrene is successful. Hence, our observations confirm nicely that ILs behave as conventional solvents as quoted by Charleux and coll.:[28] *"the IL did not seem to influence the activation-deactivation mechanism. In other words, one should not expect an improvement in the alkoxyamine dissociation conditions or in the system livingness".*

Acknowledgements

The authors thank Aix-Marseille University, CNRS and ANR (grant: ANR-14-CE06-0023-02), the A*MIDEX project (ANR-11-IDEX-0001-02) funded by the «Investissements d'Avenir» French Government program, managed by the French National Research Agency (ANR), as well as the Fondation ARC pour la recherche sur le cancer (PJA 20141201886) for the financial support. MBI thanks government of Gabon and Campus France for a Ph.D. grant. SRAM thanks the Russian Science Foundation (grant 15-13-20020) for supporting the correlations analysis of this work.

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[§] δ values were tentatively estimated but did not improve at all the KAT correlation.

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