Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

β-Phosphorus Hyperfine Coupling Constant in Nitroxides: 6. Solvent Effect in Non-Cyclic Nitroxides

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Table 1S1. HBD parameter α, intrinsic volume V_X, molar volume V_M, normalized Reichardt solvent polarity parameter E_T^N, cohesive pressure *c*, polarity/polarizability π*, relative dielectric constant ε_r and dipolar moment μ[1-2]

	Solvent[a]	E_T^{N}[b]	*c*[b]	π*[b,d]	α[b,d]	V_X[d]	V_M[c]	ε_r[b,c]	μ[b,c]	*n*	δ	*B*
1	*n*-pentane	0.009	205	-0.15	0.00	81.3	114.52	1.84	0.00	1.3575	0	0
2	*n*-hexane	0.009	225	-0.11	0.00	95.4	130.50	1.88	0.09	1.3749	0	0
3	CHex	0.006	285	0.00	0.00	84.5	108.10	2.02	0.00	1.4262	0	0°
4	*n*-octane	0.012	231	0.01	0.00	123.6	162.56	1.95	0.00	1.3876[e]	0	0
5	benzene	0.111	353	0.55	0.00	71.6	88.85	2.27	0.00	1.5011	1	48
6	toluene	0.099	337	0.49	0.00	85.7	106.24	2.38	0.31	1.4969	1	58
7	*t*-BuPh	0.099	337	0.41	0.00	113.9	154.80	2.37	0.36	1.4927	1	60
8	PhBr	0.182	408	0.77	0.00	89.1	105.03	2.65	1.56	1.5568	1	40
9	Pyridine	0.302	466	0.87	0.00	67.5	80.55	12.91	2.37	1.5102	1	472
10	AcPh	0.306	456	0.68	0.00	101.4	116.30	17.39	2.95	1.5342	1	202
11	*t*-BuPh/CH_2Cl_2										1	
12	CH_2Cl_2	0.309	414	0.73	0.13	49.4	64.00	8.93	1.14	1.4242	0.5	23
13	DCE	0.327	400	0.73	0.00	63.5	80.16	10.36	1.83	1.4448	0.5	40
14	$CHCl_3$	0.259	362	0.69	0.20	61.7	80.50	4.89	1.15	1.4459	0.5	14
15	CCl_4	0.052	310	0.21	0.00	73.9	96.49	2.24	0.00	1.4602	0.5	0
16	DME	0.231	307	0.53	0.00	55.2	104.4	3.5	1.71	1.3796	0	238
17	Et_2O	0.117	251	0.24	0.00	73.1	103.80	4.20	1.15	1.3524	0	271

18	*i*-Pr_2O	0.105	243.5	0.19	0.00	101.3	141.14	3.88	1.22	1.3689	0	293
19	*n*-Bu_2O	0.071	251	0.18	0.00	129.5	169.30	3.08	1.17	1.3992	0	33
20	*t*-BuOMe	0.124								1.3690	0	
21	14D	0.164	388	0.49	0.00	68.1	85.22	2.21	0.45	1.424	0	236
22	THF	0.207	359	0.55	0.00	62.2	81.14	7.58	1.75	1.4072	0	305
23	AcOEt	0.228	331	0.45	0.00	74.7	97.86	6.02	1.78	1.3614	0	164
24	acetone	0.355	488	0.62	0.08	54.7	73.55	20.56	2.69	1.3587	0	193
25	ACN	0.46	581	0.66	0.19	40.4	52.43	35.94	3.92	1.3441	0	178
26	$MeNO_2$	0.481	669	0.75	0.22	42.4	53.64	35.87	3.56	1.3819	0	65
27	DMSO	0.444	708	1	0.00	61.3	71.40	46.45	4.06	1.4793	0	362
28	F	0.775	1568	0.97	0.71	36.5	39.54	109.50	3.37	1.4475	0	270
29	NMF	0.722	910	0.90	0.62	50.6	58.48	182.40	3.86	1.4319	0	287
30	DMF	0.386	581	0.88	0.00	58.1	77.40	36.71	3.82	1.4305	0	294
31	MeOH	0.762	858	0.60	0.98	30.8	40.43	32.66	2.87	1.3284	0	218
32	EtOH	0.654	676	0.54	0.86	44.9	58.41	24.55	1.66	1.3614	0	235
33	TFE	0.898	573	0.73	1.51	41.5	72.40	26.67	2.52	1.2907	0	
34	*i*-PrOH	0.546	558	0.48	0.76	59.0	76.51	19.92	1.66	1.4772	0	236
35	*n*-BuOH	0.586	485	0.47	0.84	73.1	91.53	17.51	1.75	1.3993	0	231
36	*t*-BuOH	0.389	467	0.41	0.42	73.1	93.95	12.47	1.66	1.3877	0	247
37	BnOH	0.608	612.9	0.98	0.60	91.6	103.67	12.70	1.66	1.5404	0	208
38	EG	0.79	1050	0.92	0.90	50.8	56.01	37.70	2.31	1.4318	0	224

39	TEG	0.682	786.4	0.88	0.66	118.9	133.48	23.69	5.58	1.4558	0	260
40	water/MeOH	0.71									0	
41	water	1	2294	1.09	1.17	16.7	18.00	78.36	1.85	1.3330	0	156
42	Tampon	--	--								0	
43	AcOH	0.648	357	0.64	1.12	46.5	57.24	6.15	1.68	1.3719	0	139
44	Et_3N	0.043	231	0.09	0.00	105.4	138.81	2.42	0.66	1.4010	0	650
45	*i*-Pr_2NH	0.145	314						1.15	1.3924	0	
46	*i*-PenOH	0.565	510.8	0.40	0.84	87.2	108.87	15.19	1.82	1.4085	0	227
47	CS_2	0.065	412	0.51	0.00	49.1	60.28	2.64	0.06	1.6275	0	0
48	Mecyc	0.006	255.4		0		127.67	2.02	0	1.4231	0	0
49	PhCl	0.108	383	0.68	0.00	83.9	101.68	5.62	1.69	1.5248	0.5	38

[a] CHex: cyclo-hexane, tBuPh: tert-butylbenzene, PhBr: bromobenzene, AcPh: acetophenone, DCE: 1,2-di-chloroethane, DME: 1,2-dimethoxyethane, 14D: 1,4-dioxane, THF: tetrahydrofurane, AcOEt: ethyl acetate, ACN: acetonitrile, DMSO: dimethylsulfoxide, F: formamide, NMF: N-methylformamide, DMF: N,N-dimethylformamide, TFE: 2,2,2-trifluoroethanol, EG: ethylene glycol, TEG: triethylene glycol, AcOH: acetic acid, i-PenOH: iso-pentanol, Mecyc: methylcyclopentane, PhCl: chlorobenzene. [b] Given in ref. 1. [c] Given in ref. 2. [d] Given in ref. 3. [e] For *n*-heptane.

Table 2SI. Koppel-Palm linear correlations of a_N for **1•** - **7•**.

eq.	nitroxide	*y*-intercept[a]	a_2[a,b]	a_4[a,b]	a_5[a,b]	R^2[c]	N[d]	*F*-test[e]	$w_{f(\varepsilon r)}$[f]	w_E[f]	w_c[f]	outliers
9a	**1•**[g]	14.82 (14)	-[h]	0.056 (2)	-[h]	0.94	41	280	11[i]	89	-[j]	29,39
9b	**2•**[k]	15.09 (44)	-[h]	0.058 (6)	-[h]	0.93	15	82	14[i]	86	-[j]	2,15,26
9c	**3•**	13.49 (2)	-[h]	0.015 (4)[l]	0.0004 (1)	0.94	26	197	-[j]	38	62	14,33,38,39
9d		13.34 (5)	0.50 (16)[m]	-[h]	0.0006 (1)	0.94	26	180	17	-[j]	83	14,33,38,39
9e	**4•**	13.57 (4)	-[h]	0.039 (4)	0.0002 (1)[n]	0.87	36	110	-[j]	79	21	14,31,38
9f		13.38 (7)	0.69 (22)[o]	-[h]	0.0006 (1)	0.87	37	113	24	-[j]	76	14,33,43
9g	**5•**	13.50 (3)	-[h]	0.026 (3)	0.0002 (1)[p]	0.90	39	168	-[j]	72	28	none
9h		13.28 (5)	0.72 (16)	-[h]	0.0005 (1)	0.91	38	183	29	-[j]	71	33,43
9i	**6•**	13.44 (12)	-[h]	0.010 (3)	0.0004 (1)	0.89	37	140	-[j]	32	68	27,33
9j	**7•**	13.41 (4)	-[h]	0.016 (3)	0.0004 (1)	0.90	39	159	-[j]	44	56	none
9k		13.27 (4)	0.52 (13)[q]	-[h]	0.0005 (1)	0.92	38	207	22	-[j]	78	33

[a] Errors are given on the last digit in parentheses. [b] Student *t*-test at 99.99% unless otherwise mentioned. [c] Square of the regression coefficient. [d] Number of data. [e] Student-Fischer *F*-test given at 99.99% unless otherwise mentioned. [f] Weight of each parameter in percent with an error of ± 7% as given by eqs. 17 and 18. [g] Polarizability was the only other parameter affording reliable statistical outputs, i.e., a_1 = 1.61 (50) and t =

99.73%. [h] Not included in the correlation. [i] Given for $f(n^2)$. [j] Not determined. [k] a_1 = -2.39 (1.59) and *t*-test at 84%. Other possibilities were even worse. [l] *t*-test = 99.89%. [m] *t* = 99.44%. [n] *t* = 92.87%. [o] *t* = 99.68%. [p] *t* = 99.90%. [q] *t* = 99.97%.

Table 3SI. Koppel – Palm multiparameter correlations (eq. 10) based on the Kirkwood function of the relative permittivity ε_r, the cohesive pressure (square of the Hildebrand solubility parameter δ_H), and on the molar volume V_M for nitroxides **5•** - **7•**.

eq		$\log a_{P,0}$[a]	b_2[a,b]	b_5[a,b]	b_6[a,b]	R^2[c]	F[d]	N[e]	$w_{f(\varepsilon r)}$[f]	w_c[f]	w_{VM}[f]	outliers
10a	**5•**	49.8 (3)	-4.3 (11)[g]	-0.0020 (4)	-[h]	0.76	55	38	-[i]	-[i]	-[i]	41,44
10b		48.5 (6)	-3.2 (11)[j]	-0.0016 (4)[k]	0.009 (4)[l]	0.80	45	38	31	42	27	41,44
10c	**6•**	46.2 (3)	-2.2 (9)[m]	-0.0017 (3)	-[h]	0.71	45	39	-[i]	-[i]	-[i]	41
10d		45.4 (5)	-1.6 (9)[n]	-0.0015 (4)	0.005 (3)[o]	0.74	33	39	24	54	22	41
10e	**7•**	45.6 (2)	-2.2 (8)[p]	-0.0022 (3)	-[h]	0.79	66	39	-[i]	-[i]	-[i]	41
10f		44.7 (5)	-1.5 (9)[q]	-0.0020 (3)	0.006 (3)[r]	0.81	49	39	18	60	22	41

[a] Errors are given on the last digit in parentheses. [b] Student *t*-test of confidence given at 99.99 % unless otherwise mentioned. [c] Square of the regression coefficient. [d] Student-Fischer *F*-test of reliability given at 99.99% confidence. [e] Number of data. [f] Weight of each parameter in per cent with an error of ± 7% as given by eqs. 17 and 18. [g] t = 99.96%. [h] Not included in the correlation. [i] Not determined. [j] t = 99.40%. [k] t = 99.94%. [l] t = 98.4%. [m] t = 98.60%. [n] t = 94.5%**.** [o] t = 98.20%. [p] t = 99.80%. [q] t = 93.75%. [r] t = 94.70%.

Table 4SI. Kalmet – Aboud – Taft multiparameter correlations (eq. 14) for a_N of nitroxides **1• - 7•** based on the polarity/polarizability parameter π*, the cohesive pressure *c*, and on the Hydrogene Bonding Donor (HBD) parameter α of solvents.

eq.		*y*-intercept[a]	c_1[a,b]	c_3[a,b]	c_5[a,b]	R^2[c]	F[d]	N[e]	w_{π^*}[f]	w_α[f]	w_c[f]	outliers
14a	**1•**	15.20 (3)	0.58 (5)	0.73 (4)	-[g]	0.95	355	41	-[h]	-[h]	-[h]	29,39
14b		15.18 (3)	0.49 (6)	0.68 (4)	0.0002 (6)[i]	0.96	281	41	30	58	12	29,39
14c	**2•**	14.00 (14)	1.05 (20)[j]	1.13 (9)	-[g]	0.96	103	12	-[h]	-[h]	-[h]	2,15,26
14d		14.10 (19)	0.77 (35)[k]	1.01 (15)[l]	0.0002 (2)[m]	0.96	68	12	22	64	12	2,15,26
14e	**3•**	13.49 (4)	0.45 (7)	0.40 (4)	-[g]	0.90	117	28	-[h]	-[h]	-[h]	38,39
14f		13.48 (4)	0.33 (8)[l]	0.44 (6)	0.0002 (1)[n]	0.93	101	28	28	49	23	38,39
14g	**4•**	13.49 (4)	0.47 (6)	0.48 (5)	-[g]	0.84	95	38	-[h]	-[h]	-[h]	33,41
14h		13.56 (4)	0.38 (9)	0.44 (6)	0.0002 (1)[o]	0.87	77	40	31	49	20	none
14i	**5•**	13.50 (2)	0.42 (4)	0.37 (3)	-[g]	0.90	170	38	-[h]	-[h]	-[h]	28,41[p]
14j		13.44 (3)	0.33 (5)	0.33 (4)	0.0002 (1)	0.93	163	40	31	44	25	none
14k	**6•**	13.50 (3)	0.27 (5)	0.30 (4)	-[g]	0.80	70	39	-[h]	-[h]	-[h]	27,41
14l		13.41 (3)	0.13 (5)[q]	0.13 (4)[r]	0.0004 (1)	0.90	103	38	16	20	64	27,33

14m	**7•**	13.44 (3)	0.39 (5)	0.26 (5)	-[g]	0.83	187	39	-[h]	-[h]	-[h]	41
14n		13.38 (3)	0.23 (5)	0.18 (4)	0.0003 (1)	0.92	137	40	27	29	44	none

[a] Errors are given on the last digit in parentheses. [b] Student *t*-test of confidence given at 99.99% unless otherwise mentioned. [c] Square of the regression coefficient. [d] Student-Fischer *F*-test of reliability given at 99.99% confidence. [e] Number of data. [f] Weight of each parameter in percent with an error of ± 7% as given by eqs. 17 and 18. [g] Not used in the correlation. [h] Not determined. [i] t = 99.10%. [j] t = 99.94%. [k] t = 94.10%. [l] t = 99.98%. [m] t = 64.00%. [n] t = 99.00%. [o] t = 98.29%. [p] Same R^2 and F values are observed when 28 and 41 are included except a larger scattering than for the 3-parameter correlation. [q] t = 96.80%. [r] t = 99.60%.

Table 5SI. Kalmet – Aboud – Taft multiparameter correlations (eq. 15) for $a_{\beta,P}$ of nitroxides **1•** - **8•** based on the polarity/polarizability parameter π*, the cohesive pressure *c*, the intrinsic volume V_X, and on the Hydrogen Bonding Donor (HBD) parameter α of solvents.

eq		*y*-intercept[a]	d_1[a,b]	d_3[a,b]	*t*[c]	d_5[a,b]	R^2[d]	*F*[e]	*N*[f]	w_{π^*}[g]	w_α[g]	w_c[g]	outliers
15a	**2•**	40.52 (58)	-9.87 (93)	-12.86 (63)	99.99	-[h]	0.98	297	14	34	66	-[i]	41
15b	**3•**	46.29 (13	-2.07 (30)	0.75 (22)	99.79	-[h]	0.68	25	26	-[i]	-[i]	-[i]	27,30,36,41
15c		46.51 (13)	-1.34 (27)	1.19 (19)	99.99	-0.0014 (13)[j]	0.83	36	26	31	37	32	27,30,36,41
15d	**4•**	49.48 (8)	-1.45 (19)	0.0048 (1241)	3.00	-[h]	0.77	38	26	99	1	-[i]	12-14,24-27,29,30,35,37-39,41
15e		49.62 (7)	-0.99 (16)	-[h]	-[h]	-0.0008 (2)[k]	0.88	84	26	57	-[i]	43	12-14,24-27,29,30,35,37-39,41
15f		49.65 (6)	-1.03 (15)	0.19 (9)	95.00	-0.0009 (2)	0.90	65	26	48	13	39	12-14,24-27,29,30,35,37-39,41
15g	**5•**	48.71 (8)	-1.65 (14)	-1.16 (10)	99.99	-[h]	0.94	230	32	28	72	-[i]	12-14,25,26,28,29,44
15h	**6•**	44.54 (10)	-1.84 (17)	0.08 (13)[l]	49.0	-[h]	0.78	63	38	94	6	-[i]	28,29
15i		45.86 (12)	-1.35 (25)	-[h]	-[h]	-0.0013	0.81	79	39	54	-[i]	46	41
15j	**7•**	55.80 (10)	-1.92 (18)	-0.25 (13)[m]	94.0	-[h]	0.82	82	38	85	15	-[i]	28,29
15k		45.27 (12)	-1.33 (24)	-[h]	-[h]	-0.0018 (3)	0.86	112	39	46	-[i]	54	41

[a] Errors are given on the last digit in parenthesie. [b] Student *t*-test of confidence given at 99.99% unless otherwise mentioned. [c] Student *t*-test. [d] Square of the regression coefficient. [e] Student-Fischer *F*-test of reliability given at 99.99% confidence. [f] Number of data. [g] Weight of each

parameter in percent with an error of ± 7% as given by eqs. 17 and 18. [h] Not used in the correlation. [i] Not determined. [j] t = 99.98%. [k] t = 99.98%. [l] t = 49.00%. [m] t = 94.00%.

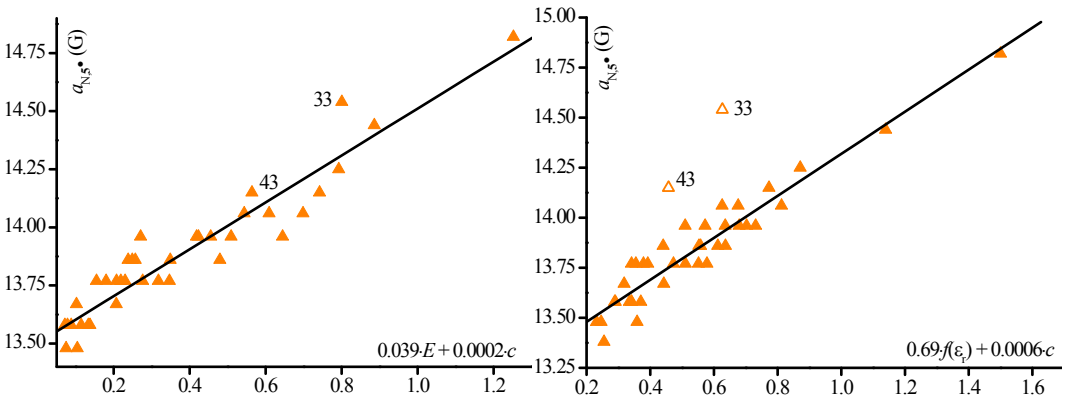


Figure 1SI. Koppel-Palm plots $a_N = f(E,c)$ and $a_N = f(f(\varepsilon_r),c)$ (left and right hand-sides, respectively) for **5•** (□). Empty symbols are for outliers.

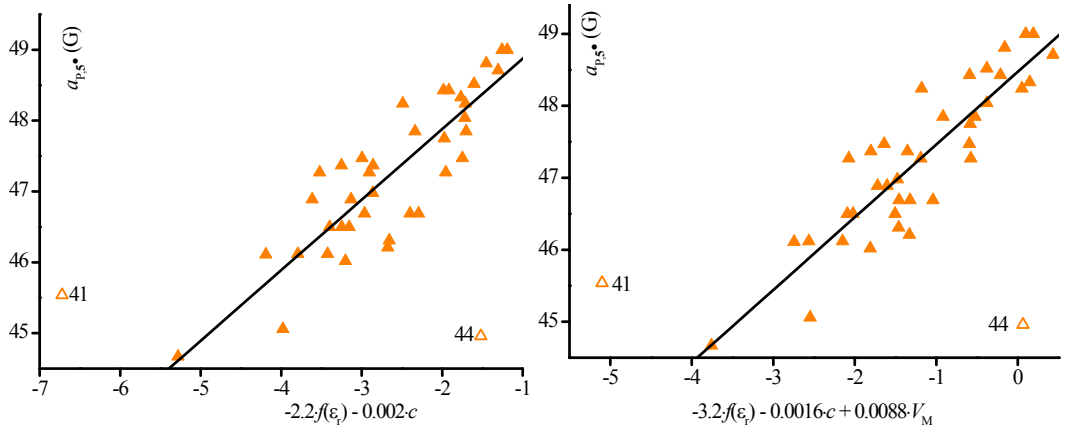
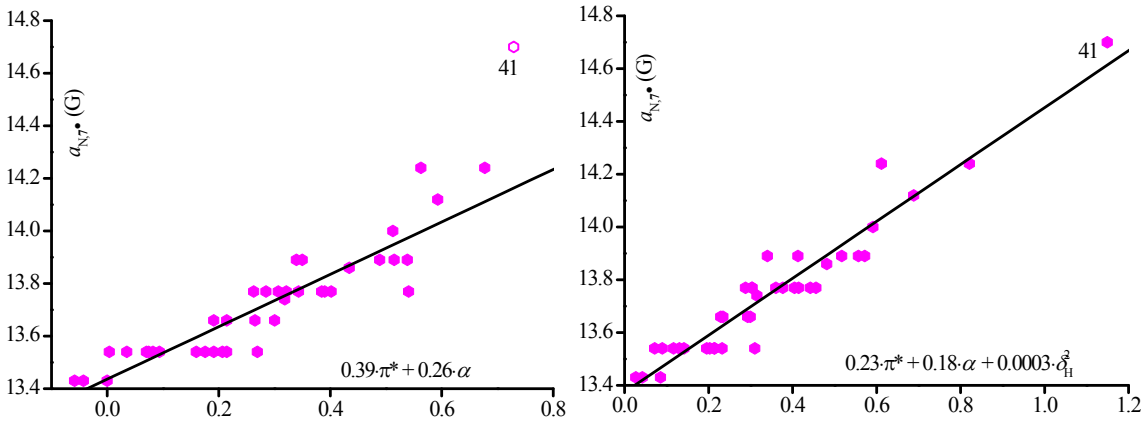
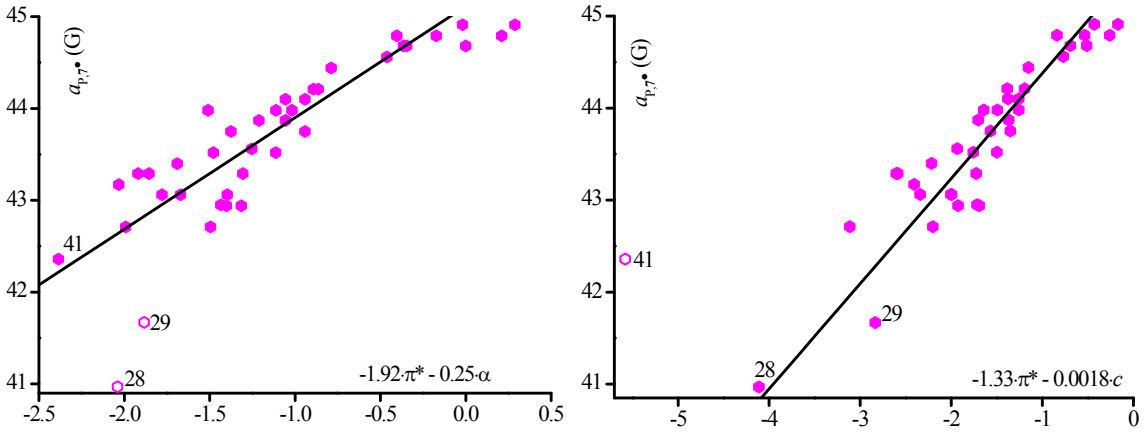


Figure 2SI. Koppel – Palm plots with two (left) and three (right) molecular descriptors for $a_P = f(c,f(\varepsilon_r))$ and $a_P = f(c,f(\varepsilon_r),V_M)$ for **5•** (□). Empty symbols are for outliers.



(a) (b)

Figure 3SI. KAT plots of eqs. 14l (a) and 14m (b) for **7•**.



(a) (b)

Figure 4SI. KAT correlations for **7•** with (a) eq. 15j and (b) eq. 15k. Empty symbols are for outliers.

[1] C. Reichardt, T. Welton, Solvent and Solvent Effect in Organic Chemistry, 4th ed., Wiley-VCH, Weinheim, 2011.

[2] G. E. Zaikov, R. G. Makitra, G. G. Midyana, L. I. Bazylyak, *Influence of the Solvent on Some Radical Reaction* Chemistry Research and Applications Series, Nova Science Publishers Inc., New York, **2010**.