Electronic Supplementary Material (ESI) for RSC Advances.

β-Phosphorus Hyperfine Coupling Constant in Nitroxides: 4. Solvent Effect

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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. Linear relationships $a_N = f(a_{N,1\bullet})$ for **2•** - **7t•** in various solvents (eq. 2).

equation	nitroxide	slope α_1	error[a]	*y*-intercept	error[a]	R^{2b}	N^c	outliers
2a	**2•**	1.19	9	-3.65	140	0.96	10	2,5,6,26,39
2b	**3•**	0.84	4	0.89	75	0.85	38	22,30,39
2c	**4c•**	0.70	3	2.75	47	0.94	40	28,29,35,39
2d	**4t•**	0.72	3	2.10	52	0.92	43	39
2e	**5c•**	0.69	4	3.00	63	0.89	40	31,34,39,44
2f	**5t•**	0.71	3	2.32	51	0.92	42	18,39
2g	**6c•**	0.82	3	0.84	50	0.94	41	16,28,39
2h	**6t•**	0.69	3	2.61	50	0.92	42	28,39
2i	**7t•**	0.60	3	4.00	49	0.85	42	26,39

[a] Error given on the last digit. [b] Square of the regression coefficient. [c] Number of data.

Table 3SI. Linear relationships $a_N = f(a_{N,3\bullet})$ for **4•** - **7t•** in various solvents (eq. 3).

equation	nitroxide	slope α_2	error[a]	*y*-intercept	error[a]	R^{2b}	N^c	outliers
3a	**4c•**	0.77	4	3.05	50	0.94	36	19,28,30,35,45
3b	**4t•**	0.78	4	2.62	56	0.90	40	28
3c	**5c•**	0.72	4	3.78	59	0.90	35	19,28,30,31,44,45
3d	**5t•**	0.75	3	2.96	46	0.94	35	6,18,19,28,30,45
3e	**6c•**	0.87	3	1.56	43	0.96	34	6,15,19,22,28,39,45
3f	**6t•**	0.78	3	2.61	48	0.94	39	28,30
3g	**7t•**	0.66	3	4.21	40	0.94	38	26,28,39

[a] Error given on the last digit. [b] Square of the regression coefficient. [c] Number of data.

Table 4SI. Linear relationships $a_{\beta,P,c} = f(a_{\beta,P,\mathbf{3}\bullet})$ for **4c•** - **6c•** in various solvents (eq. 4).

equation	nitroxide	slope α_3	error[a]	*y*-intercept	error[a]	R^{2b}	N^c	outliers
4a	**4c•**	1.08	3	-7.00	154	0.96	40	29
4b	**5c•**	1.00	4	-3.89	205	0.94	39	5,29
4c	**6c•**	1.00	4	-2.19	185	0.94	40	29

[a] Error given on the last digit. [b] Square of the regression coefficient. [c] Number of data.

Table 5SI. Linear relationships $a_{\beta,P,t} = f(a_{\beta,P,\mathbf{3}\bullet})$ for **4t•** - **7t•** in various solvents (eq. 5).

equation	nitroxide	slope α_4	error[a]	*y*-intercept	error[a]	R^{2b}	N^c	outliers
5a	**4t•**	1.21	4	-9.60	186	0.96	38	29,40,41
5b	**5t•**	1.28	5	-12.41	235	0.96	38	29,40,41
5c	**6t•**	1.50	5	-25.00	257	0.96	38	28,29,41
5d	**7t•**	0.78	4	13.04	174	0.92	39	29,35

[a] Error given on the last digit. [b] Square of the regression coefficient. [c] Number of data.

Table 6SI. Plots $y = f(x)$ for each pair of diastereoisomers (eqs. 6).

equation	*x*-axis	*y*-axis	slope	error[a]	*y*-intercept	error[a]	R^{2b}	N^c	outliers
6a	**4c•**	**4t•**	1.12	3	-1.46	136	0.99	43	41
6b	**5c•**	**5t•**	1.35	4	-10.89	165	0.97	44	5
6c	**6c•**	**6t•**	1.53	5	-22.89	243	0.97	43	28

[a] Error given on the last digit. [b] Square of the regression coefficient. [c] Number of data

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

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
10a	**1•**[g]	14.82 (14)	-[h]	0.056 (2)	-[h]	0.94	41	280	11[i]	89		29,39
10b	**2•**[j]	15.09 (44)	-[h]	0.058 (6)	-[h]	0.93	15	82	14[i]	86		2,15,26
10c	**3•**	13.55 (4)	-[h]	0.017 (6)[k]	0.0006 (1)[l]	0.88	28	95		34	66	14,28
10d	**4c•**	13.46 (2)	-[h]	0.020 (4)	0.0004 (1)	0.91	39	182		48	52	33
10e		13.27 (5)	0.62 (17)[m]	-[h]	0.0006 (1)	0.91	38	176	22		78	33,43
10f	**4t•**	13.12 (3)	-[h]	0.020 (10)	0.0004 (1)	0.90	39	171		48	52	33
10g		12.91 (5)	0.75 (16)	-[h]	0.0006 (1)	0.92	38	197	26		74	33,43
10h	**5c•**	13.43 (3)	-[h]	0.027 (4)	0.0003 (1)[n]	0.89	37	135		62	38	31,44
10i		13.27 (7)	0.48 (22)[o]	-[h]	0.0006 (1)	0.86	36	107	18		82	31,33,43
10j	**5t•**	13.11 (3)	-[h]	0.028 (3)	0.0003 (1)[p]	0.90	38	154		65	35	14,18
10k		12.92 (7)	0.71 (20)[n]	-[h]	0.0005 (1)	0.87	38	115	28		72	33,43
10l	**6c•**	13.34 (3)	-[h]	0.036 (4)	0.0002 (1)[q]	0.90	39	167		78	22	39
10m		13.03 (6)	1.08 (20)	-[h]	0.0006 (1)	0.90	38	165	33		64	33,43
10n	**6t•**	13.09 (3)	-[h]	0.022(4)	0.0004 (1)	0.90	39	160		51	49	33
10o		12.87 (6)	0.73 (13)[r]	-[h]	0.0006 (1)	0.90	38	157	25		75	33,43
10p	**7t•**	13.14 (3)	-[h]	0.024 (3)	0.0002 (1)	0.86	33	96		68	32	none

[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. eqs.18 and 19. [g] Polarizability was the only 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] a_1 = -2.39 (1.59) and *t*-test at 84%. Other possibilities were even worse. [k] t = 98.50%. [l] t = 99.00%. [m] t = 99.92%. [n] *t*-test at 99.94%. [o] t = 96.4%. [p] *t*-test at 99.90%. [q] t = 99.35%. [r] t = 99.98%.

Table 8SI. Koppel – Palm multiparameter correlations (eq. 11) based on the Kirkwood function of the relative permittivity ε_r, the cohesive pressure (square of the Hildebrand solubility parameter δ), and on the molar volume V_M for nitroxides **3•** - **7t•**.

eq	nitroxide	$\log a_{\beta,P,0}$[a]	b_2[a,b]	b_4[a,b]	b_5[a,b]	b_6[a,b]	R^2[c]	F[d]	N[e]	$w_{f(\varepsilon r)}$[f]	w_E[f]	w_c[f]	w_{VM}[f]	outliers
11a	**3•**	50.4 (7)	-6.8 (12)	-[g]	-[g]	0.014 (4)[h]	0.79	62	35	60			40	34
11b	**4c•**	47.8 (7)	-5.8 (12)	-[g]	-0.0019 (5)[i]	0.012 (4)	0.87	82	39	41		34	25	41
11c	**4t•**	52.2 (8)	-5.6 (14)[i]	-[g]	-0.0026 (5)	0.012 (5)[j]	0.86	74	39	36		41	23	41
11d		51.7 (8)	-5.8 (15)[k]	-0.065 (22)[l]	-[g]	0.012 (4)[m]	0.83	57	38	41	32		27	28,29
11e	**5c•**	47.0 (7)	-4.3 (13)[n]	-[g]	-0.0022 (5)[h]	0.009 (4)[o]	0.82	54	39	34		44	22	41
11f	**5t•**	52.7 (7)	-6.1 (13)	-[g]	-0.0029 (5)	0.013(4)[p]	0.90	100	39	35		42	23	41
11g		52.0 (7)	-6.2 (11)	-0.075 (20)[q]	-[g]	0.013 (4)[r]	0.88	82	38	40	34		26	28,29
11h	**6c•**	48.6 (7)	-5.3 (13)[h]	-[g]	-0.0016 (5)[t]	0.009 (4)[u]	0.82	55	39	44		33	23	41
11i	**6t•**	51.8 (11)	-10.4 (18)	-[g]	-0.0009 (5)[w]	0.015 (6)[x]	0.82	54	40	56		19	25	none
11j		51.1 (9)	-8.4 (18)	-0.064 (27)[z]	-[g]	0.014 (5)[aa]	0.84	60	39	48	25		27	29
11k	**7t•**	54.5 (3)	-6.3 (10)	-[g]	-0.0020 (4)	-[g]	0.87	85	28	57		43		31,32,34-36,38,41
11l		53.4 (7)	-5.2 (11)	-[g]	-0.0018 (4)[bb]	0.007 (4)[x]	0.89	63	28	45		38	17	31,32,34-36,38,41

[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.18 and 19. [g] Not included in the correlation. [h] t = 99.90%. [i] t = 99.98%. [j] t = 99.00%. [k] t = 99.96%. [l] t = 99.38%. [m] t = 99.17%. [n] t = 99.80%. [o] t = 97.40%. [p] t = 99.64%. [q] t = 99.92%. [r] t = 99.75%. [s] t = 99.97%. [t] t = 99.95%. [u] t = 97.80%. [y] t = 99.40%. [w] t = 91.70%. [x] t = 98.20%. [y] t = 99.84%. [z] t = 97.70%. [aa] t = 98.60%. [bb] t = 99.96%.

Table 9SI. Kalmet – Aboud – Taft multiparameter correlations (eq. (15)) for a_N of nitroxides **1•** - **7t•** 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
15a	**1•**	15.20 (3)	0.58 (5)	0.73 (4)	-[g]	0.95	355	41				29,39
15b		15.18 (3)	0.49 (6)	0.68 (4)	0.0002 (6)[h]	0.96	281	41	30	58	12	29,39
15c	**2•**	14.00 (14)	1.05 (20)[i]	1.13 (9)	-[g]	0.96	103	12				2,15,26
15d	**3•**	13.57 (4)	0.55 (7)	0.41 (6)	-[g]	0.84	86	35	55	45		41
15e	**4c•**	13.47 (3)	0.45 (6)	0.40 (4)	-[g]	0.87	120	39				41
15f		13.41 (3)	0.29 (6)	0.23 (5)	0.0004 (1)	0.93	167	39	27	26	46	33
15g	**4t•**	13.13 (3)	0.48 (5)	0.39 (4)	-[g]	0.91	173	39				41
15h		13.07 (3)	0.35 (6)	0.34 (4)	0.0003 (1)	0.93	154	40	30	27	43	none
15i	**5c•**	13.40 (4)	0.51 (6)	0.40 (5)	-[g]	0.87	114	37				1,31,41
15j		13.34 (4)	0.36 (6)	0.35 (5)	0.0004 (1)	0.91	117	38	27	36	37	1,31
15k	**5t•**	13.15 (3)	0.44 (6)	0.39 (4)	-[g]	0.87	119	39				41
15l		13.09 (3)	0.33 (7)	0.35 (5)	0.0003 (1)[j]	0.90	108	40	30	37	33	none
15m	**6c•**	13.31 (3)	0.61 (5)	0.46 (4)	-[g]	0.93	240	38				39,41
15n		13.26 (3)	0.51 (6)	0.41 (4)	0.0002 (1)	0.95	227	39	39	42	19	39
15o	**6t•**	13.14 (3)	0.37 (5)	0.43 (4)	-[g]	0.80	141	38				28,41
15p		13.07 (3)	0.26 (7)[k]	0.38 (5)	0.0003 (1)	0.91	123	40	22	45	33	none
15q	**7t•**	13.10 (3)	0.43 (6)	0.41 (4)	-[g]	0.88	132	39	44	56		none
15r		13.09 (2)	0.29 (5)	0.25 (4)	0.0003 (1)	0.94	150	32	29	31	40	26,33

[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.18 and 19. [g] Not used in the correlation. [h] $t = 99.10\%$. [i] $t = 99.94\%$. [j] $t = 99.98\%$. [k] $t = 99.96\%$.

Table 10SI. Kalmet – Aboud – Taft multiparameter correlations (eq. 16) for $a_{\beta,P}$ of nitroxides **2•** - **7t•** 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*[b]	d_5[a,b]	d_6[a,b]	*t*	R^2[c]	*F*[d]	*N*[e]	w_{π^*}[f]	w_α[f]	w_c[f]	w_{VX}[f]	outliers
16a	**2•**	40.52 (58)	-9.87 (93)	-12.86 (63)	99.99	-[g]	-[g]	-[f]	0.98	297	14	34	66			41
16b	**3•**	51.00 (11)	-2.75 (20)	-0.56 (18)	99.55	-[g]	-[g]	-[f]	0.91	146	30	81	19			12,13,25,26,28,31
16c		50.63 (24)	-2.85 (27)	-[g]	-[g]	-[g]	0.005 (2)	95.50	0.95	221	27	88			12	10,12,13,25,26,28,31,32,35
16d	**4c•**	47.74 (16)	-2.80 (28)	-0.88 (21)[h]	99.98	-[g]	-[g]	-[f]	0.85	90	36					25,26,28,29
16e		46.40 (49)	-2.94 (37)	-0.69 (28)[i]	98.30	-[g]	1.60 (47)	99.82	0.84	60	39	57	18		25	41
16f		46.79 (44)	-2.13 (39)	-[g]	-[g]	-0.0020 (4)	1.53 (41)	99.94	0.88	82	39	42		34	24	41
16g	**4t•**	53.39 (13)	-3.61 (24)	-1.10 (17)	99.99	-[g]	-[g]	-[f]	0.93	207	36					25,26,28,29
16h		51.31 (38)	-3.44 (38)	-0.77 (21)[j]	99.91	-[g]	1.15 (36)	99.96	0.91	117	38	63	19		18	28,29
16i	**5c•**	46.94 (13)	-2.63 (22)	0.82 (16)	99.99	-[g]	-[g]	-[f]	0.89	126	35					5,25,26,28,29
16j		46.29 (31)	-2.45 (23)	-0.66 (17)[k]	99.95	-[g]	0.69 (30)	97.10	0.90	97	35	63	23		14	5,25,26,28,29
16k	**5t•**	52.70 (14)	-3.68 (26)	-1.32 (19)	99.99	-[g]	-[g]	-[f]	0.92	200	36					25,26,28,29
16l		51.34 (40)	-3.44 (30)	-0.92 (22)[h]	99.98	-[g]	1.43 (38)	99.94	0.91	121	38	58	21		21	28,29
16m	**6c•**	48.65 (12)	-3.12 (22)	-0.52 (16)[l]	99.75	-[g]	-[g]	-[f]	0.90	149	36					25,26,28,29
16n		47.86 (36)	-3.24 (27)	-0.41 (20)[m]	95.0	-[g]	0.96 (35)	99.00	0.89	96	39	71	12		17	41
16o		48.13 (33)	-2.72 (30)	-[g]	-[g]	-0.0013 (3)[n]	0.90 (31)	99.40	0.91	121	39	59		25	16	41
16p	**6t•**	51.52 (16)	-4.48 (29)	-1.20 (21)	99.99	-[g]	-[g]	-[f]	0.93	217	37					25,26,29
16q		50.78 (40)	-4.26 (30)	-1.02 (22)	99.99	-[g]	0.77 (40)	94.30	0.94	159	37	68	22		10	25,26,29
16r	**7t•**	52•23 (23)	-1.89 (18)	-[g]	-[g]	-[g]	0.007 (2)	99.36	0.87	102	32	77			23	10,12,13,25,26,28,29

[a] Errors are given on the last digit in parenthesis. [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.18 and 19. [g] Not used in the correlation. [h] t = 99.98%. [i] t = 98.30%. [j] t = 99.91%. [k] t = 99.95%. [l] t = 99.75%. [m] t = 95.00%. [n] t = 99.92%.

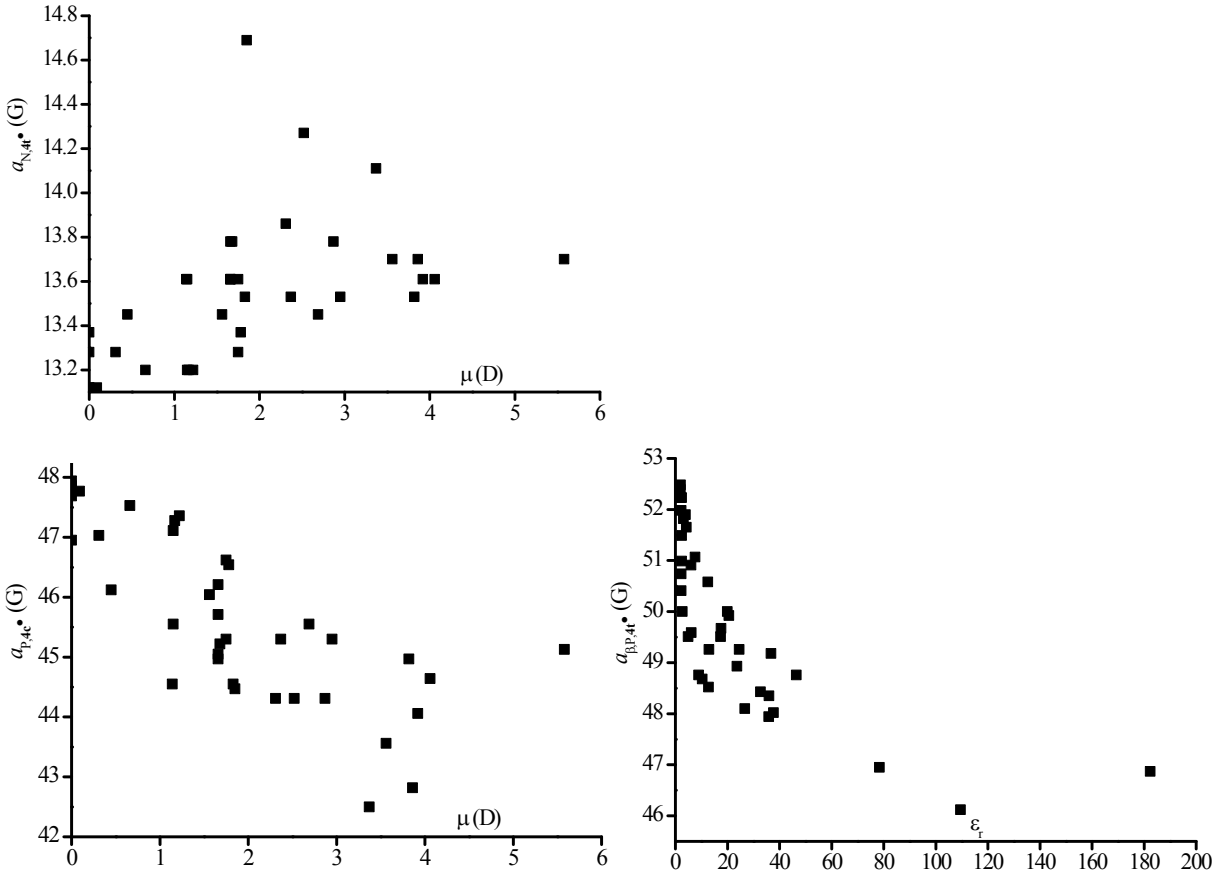
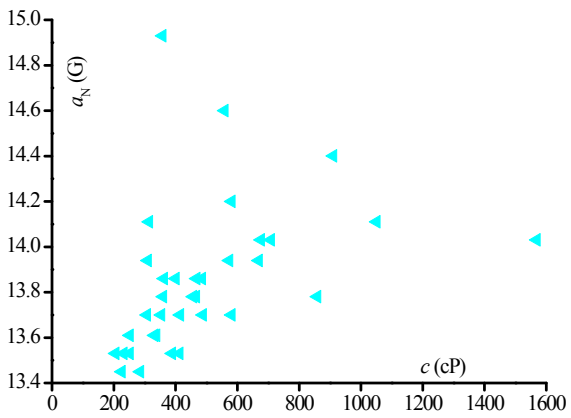
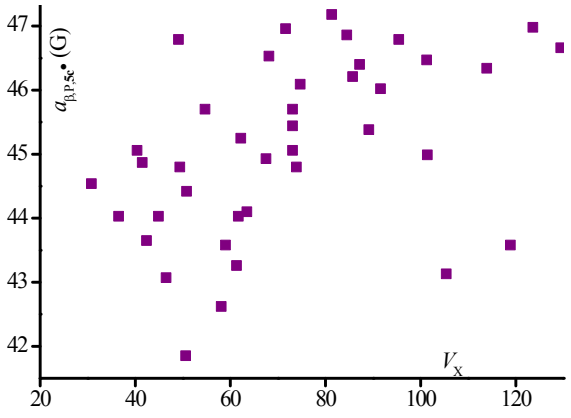
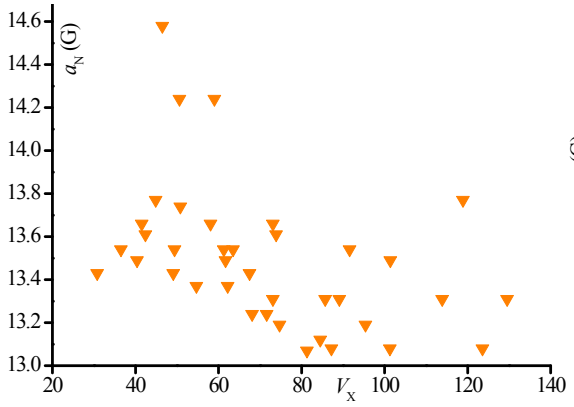
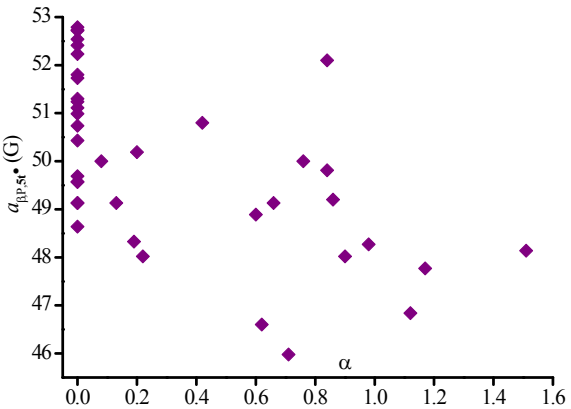


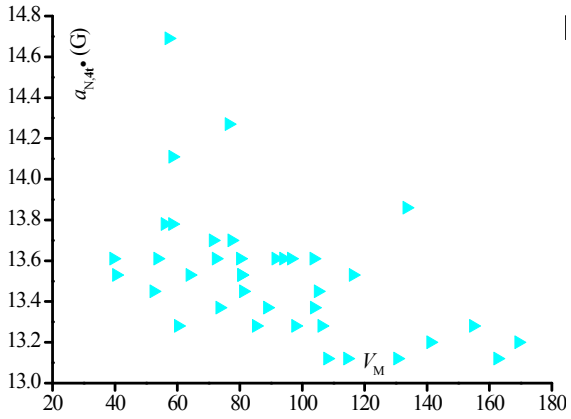
Figure 1SI. Plots a_N *vs* μ for **4t•** (top row), and plots $a_{\beta,P}$ *vs* μ and $a_{\beta,P}$ *vs* ε_r for **4c•** and **4t•**, respectively (bottom row).

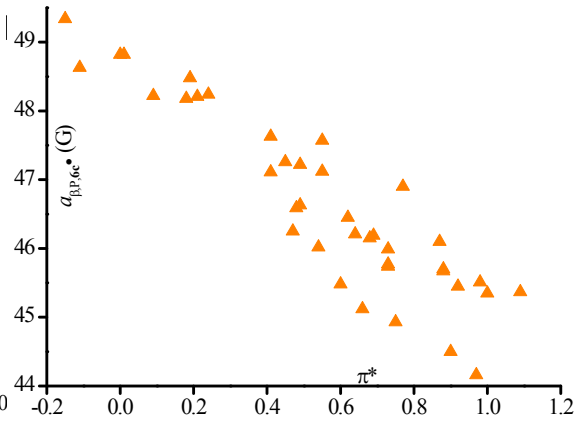

a_N (G)
c (cP)

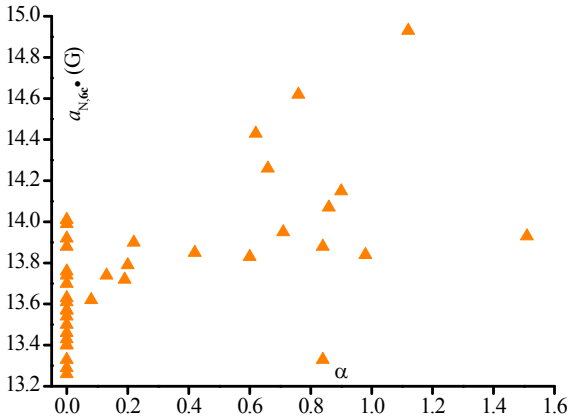

$a_{\beta,P,5\epsilon\bullet}$ (G)
V_X


a_N (G)
V_X


$a_{\beta,P,5t\bullet}$ (G)
α


$a_{N,4t\bullet}$ (G)
V_M


$a_{\beta,P,6\epsilon\bullet}$ (G)
π*


$a_{N,6\epsilon\bullet}$ (G)
α

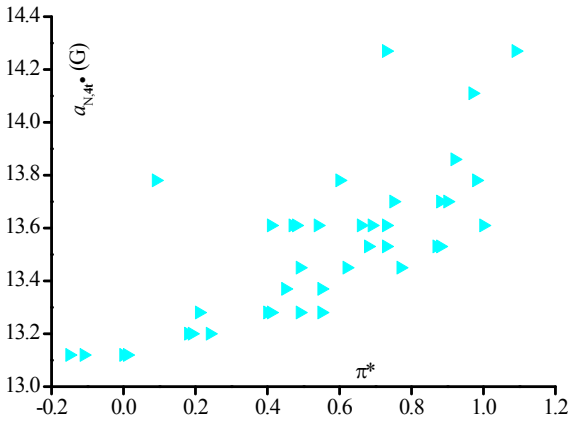


Figure 2SI. Plots a_N against c, V_X (Å), V_M (Å), α and π* (left) for **4c•**, **6t•**, **4c•**, **6c•**, and **4c•** (from top to bottom) and $a_{\beta,P}$ against c, V_X (Å), V_M (Å), α and π* (right) for **5t•**, **5c•**, and **6c•** (from top to bottom).

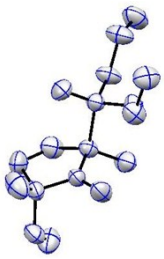


Figure 3SI. ORTEP of **10t•**.

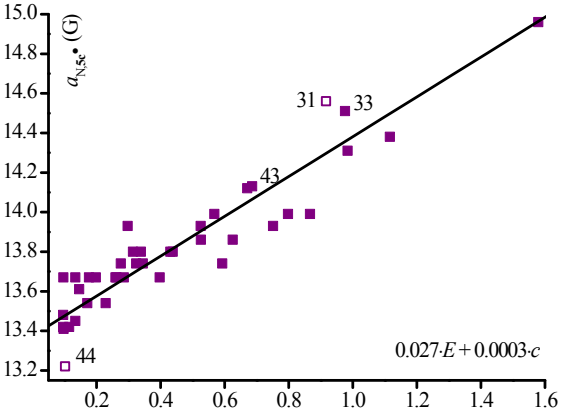


Figure 4SI. Koppel-Palm plots $a_N = f(E,c)$ for **5c•** (○). Empty symbols are for outliers.

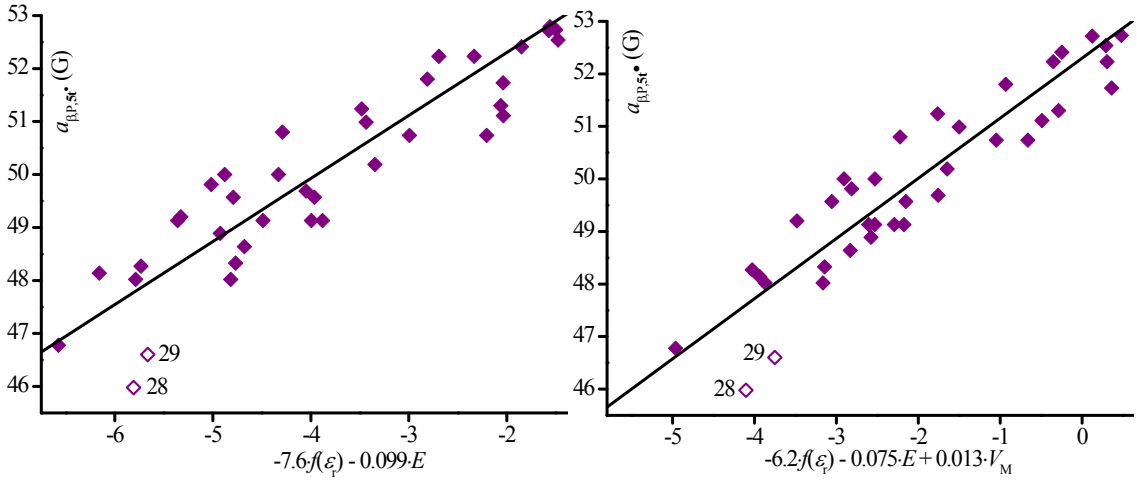


Figure 5SI. Koppel – Palm plots with two (left) and three (right) molecular descriptors for $a_{\beta,P} = f(E,f(\varepsilon_r))$ and for $a_{\beta,P} = f(E,f(\varepsilon_r),V_M)$ for **5t•** (🕘). Empty symbols are for outliers.

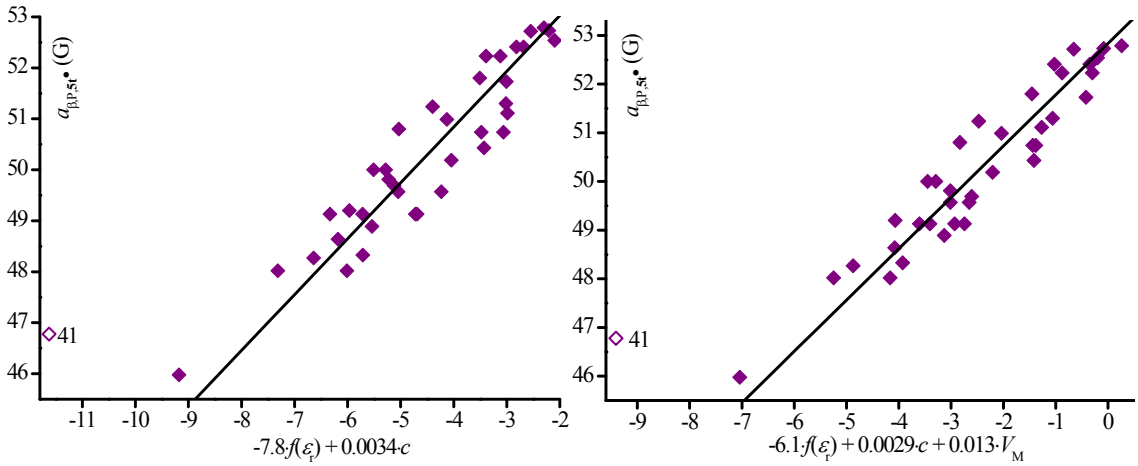
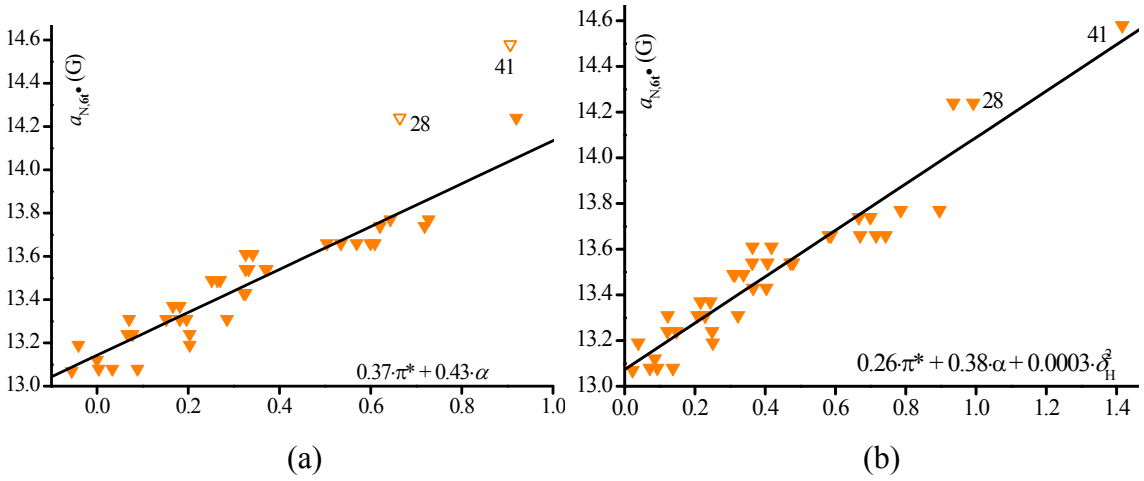
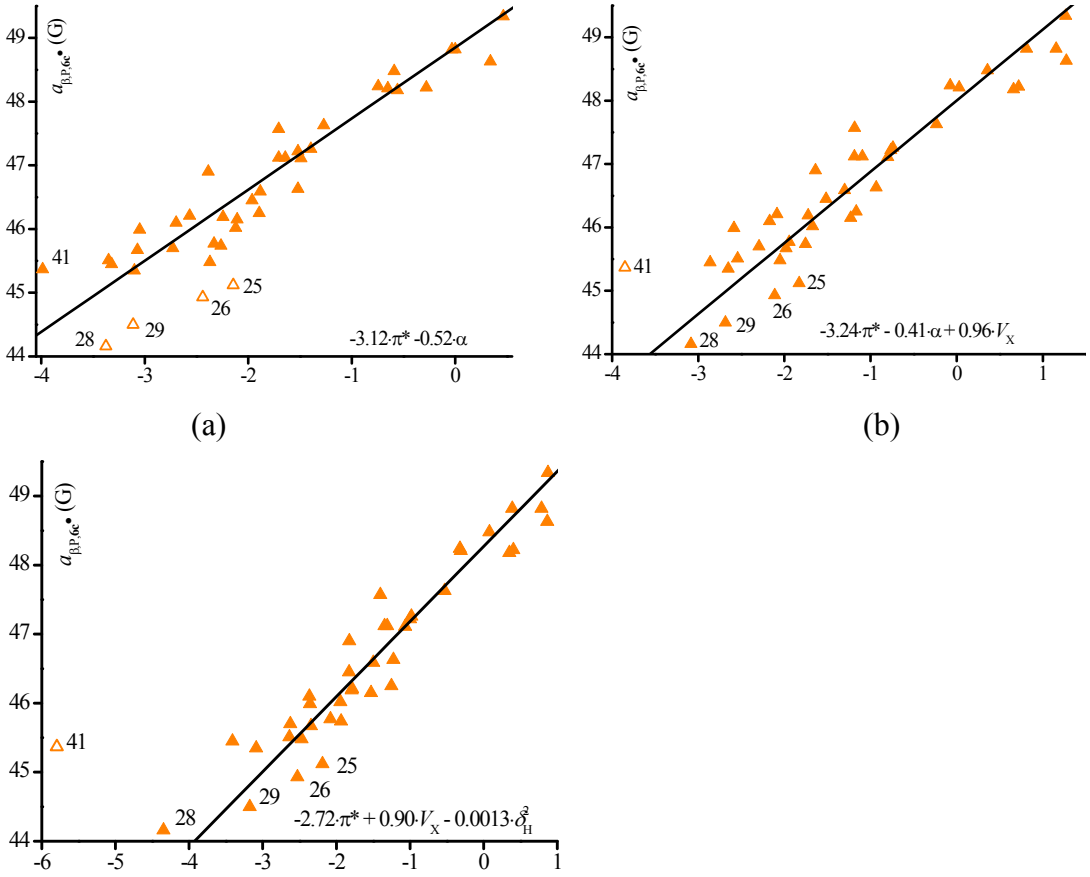


Figure 6SI. Koppel – Palm plots with two (left) and three (right) molecular descriptors for $a_{\beta,P} = f(c,f(\varepsilon_r))$ and $a_{\beta,P} = f(c,f(\varepsilon_r),V_M)$ for **5t•** (🕘). Empty symbols are for outliers.



(a) (b)

Figure 7SI. KAT plots of (a) eqs. 15o (see Table 4SI) and (b) eq. 15i for **6t•**.



(a) (b)

(c)

Figure 8SI. KAT correlations (see Table 10SI) for **6c•** with (a) eq. 16m (b) eq. 16n (c) with eq. 16o. Empty symbols are for outliers.

Preparation of nitroxides

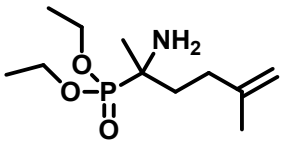
^{1}H nuclear magnetic resonance (NMR) spectra were recorded using an internal deuterium lock at ambient temperatures on the following instruments: Bruker AC400 (400 MHz) and Bruker AC300 (300 MHz). Data are presented as follows: chemical shift (in ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br means the signal is broad, dd = doublet of doublets), coupling constant (*J* in Hz) and integration. ^{31}P NMR spectra were recorded on a Bruker AC300 (122 MHz) and on a Bruker AC400 (162 MHz) spectrometers with complete proton decoupling. Chemical shifts (δ) were reported in ppm using residual non-deuterated solvents as internal reference.[3]

High-resolution mass spectra (HRMS) were performed on a SYNAPT G2 HDMS (Waters) spectrometer equipped with atmospheric pression ionization source (API) pneumatically assisted. Samples were ionized by positive electrospray mode as follows: electrospray tension (ISV): 2800 V ; opening tension (OR): 20 V ; nebulization gas pression (nitrogen): 800 L/h. Low resolution mass spectra were recorded on ion trap AB SCIEX 3200 QTRAP equipped with an electrospray source. The parent ion (M^+, $[M+H]^+$, $[M+Na]^+$ or $[M+NH_4]^+$) is quoted.

Analytical thin layer chromatographies (TLC) were carried out on Merck Kieselgel 60 F254 plates. Flash column chromatographies were carried out on Merck Kieselgel 60 (230-400 mesh). Solvent system: gradients of DCM/MeOH; EtOAc/EtOH.

All experiments were performed under anhydrous conditions and an inert atmosphere of argon and, except where stated, using dried apparatus and employing standard techniques for handling air-sensitive materials. All reagents were weighed and handled in air at room temperature.

For EPR measurements, samples with 0.5 mM concentration of nitroxide were prepared in non-degassed solvents. Experiments were performed indifferently on Elexsys, EMX or ER 100D Bruker machines (a difference smaller than 0.1 G was noticed). EPR spectra were recorded with a gain of 2 10^5 (72 dB for Elexsys), a modulation amplitude of 1.0 G, a sweep width of 150 G, a sweep time of 21 s, and a power of 20 mW as parameters.

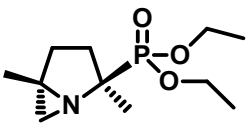


2

5-methylhex-5-en-2-one (2 g, 17.8 mmol) and diethyl phosphite (2.53 mL, 19.6 mmol) were stirred at rt under an ammoniac atmosphere for 16h monitoring by ^{31}P NMR. Then, the mixture was poured in DCM. The solution was acidified with 1M HCl solution and washed with DCM (5 x 50 mL). The aqueous layer was basified with $NaHCO_3$ (≈ pH 8) and then extracted with DCM (5 x 50 mL), the organic layer dried ($MgSO_4$), and the solvent evaporated to afford 3.15 g (71%) of the aminophosphonate **2.** ^1H NMR (300 MHz, $CDCl_3$): δ 4.70 (s, 2H), 4.19-4.10 (m, 4H), 2.27-2.05 (m, 2H), 1.73 (s, 3H), 1.78-1.71 (m, 2H), 1.43 (br s, 2H), 1.33 (t, *J* = 7.1 Hz, 6H), 1.27 (d, *J* = 16 Hz, 3H). ^{31}P NMR (122 MHz, $CDCl_3$): δ 32.3. ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.6 (C), 109.7 (CH_2), 62.2 (d, *J* = 7.7 Hz, CH_2), 62.1 (d, *J* = 7.7 Hz, CH_2), 51.6 (d, *J* = 147 Hz, C), 35.4 (d, *J* = 3.9 Hz, CH_2), 30.8 (d, *J* = 7.2 Hz, CH_2), 22.5 (CH_3), 22.0 (d, *J* = 2.8 Hz, CH_3), 16.5 (d, *J* = 5.5 Hz, 2 CH_3). HRMS (ESI) calc for $C_{11}H_{25}NO_3P^+$: 250.1567 $[M+H]^+$; found: 250.1564.

Synthesis of 3t and 3c:

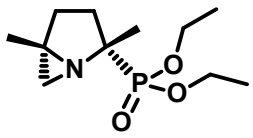
The aminophosphonate **2** (6.5 g, 26.1 mmol) was dissolved in 50 mL DCE, then 100 mL of an aqueous solution of $NaHCO_3$ (13.2 g, 157 mmol) was added. This mixture heated to reflux under argon atmosphere. A solution of I_2 (7.3 g, 28.8 mmol) in 200 mL DCE was added dropwise. The mixture was stirred under reflux for 3 hours. Solid $Na_2S_2O_3$ was added to the reaction mixture and stirred for 30 minutes. The organic phase was decanted and the aqueous phase was extracted with DCM. The organic layers were collected, dried over $MgSO_4$, filtered and evaporated. The crude product was obtained as a mixture of 2 diastereoisomers (ratio 2:1). The two diastereoisomers was separated by column chromatography (DCM/MeOH gradient). Major diastereoisomer **3t**: 3.8 g, minor diastereoisomer **3c**: 1.9 g. Yield 88%.



3t

^1H NMR (400 MHz, $CDCl_3$): δ 4.27-4.11 (m, 4H), 2.22-2.13 (m, 1H), 2.07-1.97 (m, 2H), 1.89 (br s, 1H), 1.48 (br s, 1H), 1.46 (br d, *J* = 2.3 Hz, 1H), 1.36-1.31 (m, 12H). ^{13}C

NMR (75 MHz, $CDCl_3$): δ 65.7 (d, *J* = 167 Hz, C), 62.5 (d, *J* = 7.2 Hz, CH_2),62.2 (d, *J* = 7.2 Hz, CH_2), 48.1 (C), 32.8 (CH_2), 31.4 (d, *J* = 1.1 Hz, CH_2), 30.9 (d, *J* = 14.9 Hz, CH_2), 21.1 (CH_3), 20.0 (d, *J* = 1.1 Hz, CH_3), 16.7 (d, *J* = 5.0 Hz, CH_3), 16.6 (d, *J* = 5.5 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.6. HRMS (ESI) calc for $C_{11}H_{23}NO_3P^+$: 248.1410 $[M+H]^+$; found: 248.1408.

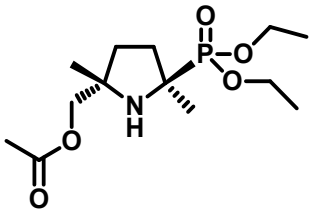


3c

^1H NMR (400 MHz, $CDCl_3$): δ 4.25-4.09 (m, 4H), 2.15-2.05 (m, 2H), 2.03-1.91 (m, 1H), 1.86-1.77 (m, 1H), 1.58-1.53 (m, 2H), 1.37-1.30 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.0 (d, *J* = 158 Hz, C), 62.4 (d, *J* = 6.6 Hz, CH_2),61.9 (d, *J* = 6.6 Hz, CH_2), 46.4 (d, *J* = 13.8 Hz, C), 33.9 (d, *J* = 1.7 Hz, CH_2), 30.3 (d, *J* = 9.9 Hz, CH_2), 29.7 (d, *J* = 5.0 Hz, CH_2), 24.0 (CH_3), 22.0 (CH_3), 16.1 (d, *J* = 5.5 Hz, $2CH_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.2. HRMS (ESI) calc for $C_{11}H_{23}NO_3P^+$: 248.1410 $[M+H]^+$; found: 248.1408.

All the reactions hereafter were performed for the two pure diastereoisomers.

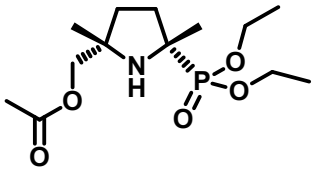
Synthesis of 4t and 4c.



4t

A solution of aziridine **3t** (500 mg, 2.02 mmol) was dissolved in 2 mL of acetic acid. The mixture was stirred overnight at room temperature under argon. Then, the mixture was dissolved in DCM and poured on a saturated solution of $NaHCO_3$. After several extractions with DCM, the organic layer was dried with $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (DCM/MeOH gradient). The acetate **4t** was obtained as a colorless oil (385 mg, yield 62%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.25-4.10 (m, 4H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.85 (d, *J* = 10.8 Hz, 1H), 2.45-2.28 (m, 1H), 2.09 (s, 3H), 1.93-1.55 (m, 4H), 1.40-1.28 (m, 9H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9 (C), 71.0 (d, *J* = 2.2 Hz,CH_2), 62.7 (d, *J* = 7.3 Hz, CH_2), 62.0 (d, *J* =

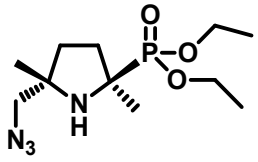
8.1 Hz, C), 61.9 (d, J = 8.1 Hz, CH_2), 60.3 (d, J = 164 Hz, C), 34.4 (d, J = 5.1 Hz, CH_2), 34.1 (CH_2), 25.6 (CH_3), 25.3 (d, J = 8.1 Hz, CH_3), 20.8 (CH_3), 16.5 (d, J = 5.9 Hz, CH_3), 16.4 (d, J = 5.9 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.8. HRMS (ESI) calc for $C_{13}H_{27}NO_5P^+$: 308.1621 $[M+H]^+$; found: 308.1622.



4c

This product was obtained according to the **4t** procedure: aziridin **3c** (500 mg, 2.02 mmol) to acetate **4c** (433 mg, yield 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.3-4.05 (m, 4H), 3.98 (d, J = 10.3 Hz, 1H), 3.77 (d, J = 10.3 Hz, 1H), 2.40-2.25 (m, 1H), 2.06 (s, 3H), 1.98-1.87 (m, 1H), 1.85-1.55 (m, 3H), 1.42 (d, J = 15.6 Hz, 3H), 1.35-1.27 (m, 6H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (C), 70.7 (CH_2), 62.8 (d, J = 7.3 Hz, CH_2), 61.8 (d, J = 8.1 Hz, CH_2), 61.7 (d, J = 9.5 Hz, C), 60.4 (d, J = 172 Hz, C), 34.1 (d, J = 5.9 Hz, CH_2), 33.6 (d, J = 1.5 Hz, CH_2), 26.4 (CH_3), 25.3 (d, J = 8.1 Hz, CH_3), 20.71 (CH_3), 16.4 (d, J = 5.1 Hz, CH_3), 16.3 (d, J = 5.9 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.9. HRMS (ESI) calc for $C_{13}H_{27}NO_5P^+$: 308.1621 $[M+H]^+$; found: 308.1622.

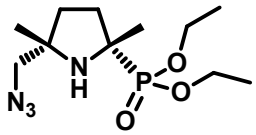
Synthesis of 6t and 6c.



6t

A solution of aziridin **3t** (2.23 g, 9.03 mmol), NaN_3 (3.52 g, 54.2 mmol) and NH_4Cl (2.46 g, 45.1 mmol), in 150 mL CH_3CN was heated for 4 hours at 80 °C. Then, the reaction was diluted with CH_3CN, filtered through Celite and evaporated. The crude product was purified by column chromatography (DCM/MeOH gradient) to obtain 1.97 g of **6t**, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21-4.10 (m, 4H), 3.23 (d, J = 11.8 Hz, 1H), 3.18 (d, J = 12.0 Hz, 1H), 2.41-2.29 (m, 1H), 1.87-1.69 (m, 4H), 1.37 (d, J = 15.5 Hz, 3H), 1.33 (t, J = 7.0 Hz, 6H), 1.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.6 (d, J = 6.1 Hz, C), 62.8 (d, J = 7.7 Hz, CH_2),62.2 (d, J = 7.7 Hz, CH_2), 61.7 (CH_2), 60.7 (d, J = 157 Hz, CH_2), 35.2 (d, J = 5.0 Hz, CH_2), 34.6 (CH_2), 26.4 (CH_3), 25.8 (d, J = 8.3 Hz, CH_3), 16.7 (d, J = 5.0 Hz, CH_3), 16.6 (d, J

= 5.5 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.1. HRMS (ESI) calc for $C_{11}H_{24}N_4O_3P^+$: 291.1581 $[M+H]^+$; found: 291.1580.

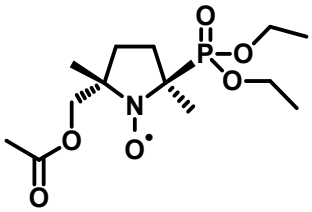


6c

This product was obtained according to the **6t** procedure: aziridin **3c** (1.11 g, 4.49 mmol) to azide **6c** (1.07 g, yield 82 %). ^1H NMR (400 MHz, $CDCl_3$): δ 4.22-4.09 (m, 4H), 3.29 (d, *J* = 11.8 Hz, 1H), 3.14 (d, *J* = 11.8 Hz, 1H), 2.40-2.26 (m, 1H), 1.99-1.90 (m, 1H), 1.80-1.60 (m, 3H), 1.39 (d, *J* = 15.3 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 6H), 1.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.7 (d, *J* = 8.3 Hz, C), 62.7 (d, *J* = 7.7 Hz, CH_2),62.5 (d, *J* = 7.7 Hz, CH_2), 60.9 (d, *J* = 173 Hz, C), 60.82 (CH_2), 35.3 (d, *J* = 5.0 Hz, CH_2), 34.1 (d, *J* = 2.8 Hz, CH_2), 27.0 (d, *J* = 1.1 Hz, CH_3), 25.7 (d, *J* = 7.2 Hz, CH_3), 16.7 (d, *J* = 5.5 Hz, $2CH_3$).^{31}P NMR (162 MHz, $CDCl_3$): δ 29.8. HRMS (ESI) calc for $C_{11}H_{24}N_4O_3P^+$: 291.1581 $[M+H]^+$; found: 291.1580.

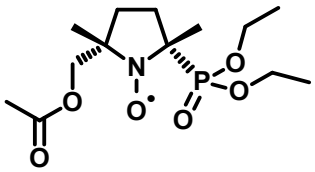
General procedure of secondary amine oxidation to nitroxide

A solution of corresponding secondary amine and *m*-CPBA (1.5 eq) in DCM was stirred 1 hour at 0 °C. Then, the reaction mixture was washed with $Na_2S_2O_3$, $NaHCO_3$. After extraction with DCM, the organic layer was dried with $MgSO_4$. The solvent was evaporated and the crude product was purified by flash chromatography (AcOEt/EtOH gradient).



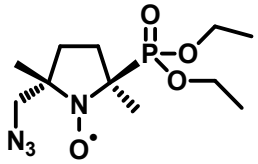
4t•

This product was obtained according to the general procedure of oxidation of amine **4t** (366 mg, 1.20 mmol) to nitroxyde **4t•** (360 mg, yield 94%).HRMS (ESI) calc for $C_{13}H_{26}NO_6P^+$•: 323.1492 $[M+H]^+$; found: 323.1494.



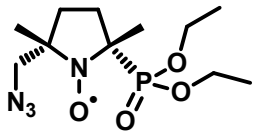
4c•

This product was obtained according to the general procedure of oxidation of amine **4c** (200 mg, 0.65 mmol) to nitroxyde **4c•** (189 mg, yield 90%). HRMS (ESI) calc for $C_{13}H_{26}NO_6P^{+}$•: 323.1492 $[M+H]^{+}$; found: 323.1494.



6t•

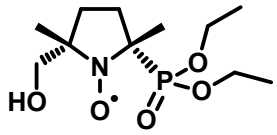
This product was obtained according to the general procedure of oxidation of amine **6t** (800 mg, 2.76 mmol) to nitroxyde **6t•** (404 mg, yield 48%). HRMS (ESI) calc for $C_{11}H_{23}N_4O_4P^{+}$•: 306.1451 $[M+H]^{+}$; found: 306.1451.



6c•

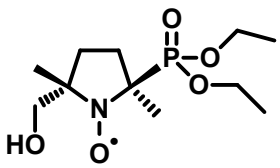
This product was obtained according to the general procedure of oxidation of amine **6c** (500 mg, 1.72 mmol) to nitroxyde **6c•** (268 mg, yield 51%). HRMS (ESI) calc for $C_{11}H_{23}N_4O_4P^{+}$•: 306.1451 $[M+H]^{+}$; found: 306.1451.

Synthesis of 10t• and 10c•



10c•

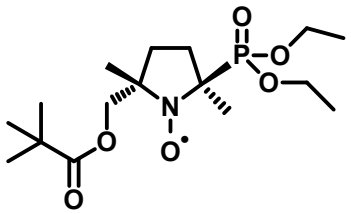
A solution of minor acetate **4c•** (200 mg, 0.621 mmol) in MeOH (5 mL) at O °C was treated with K_2CO_3 (129 mg, 0.931 mmol) and stirred for 1 hour. The mixture was dissolved in DCM and poured on saturated solution of $NaHCO_3$. The organic layer was dried with $MgSO_4$ and concentrated *in vacuo.* Purification by flash chromatography (AcOEt/EtOH gradient) gave the pure product **10c•** as a red oil. (157 mg, 90 %). HRMS (ESI) calc for $C_{11}H_{24}N_4O_5P^{+}$•: 281.1387 $[M+H]^{+}$; found: 281.1384.



10t•

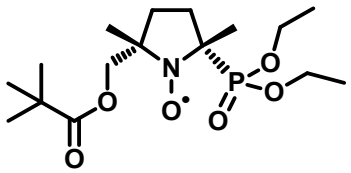
Saponification of **4t•**, flash chromatography and recrystallization from Et_2O gave the pure compound **10t•** as a red crystal. Yield 82% Mp = 63 °C. HRMS (ESI) calc for $C_{11}H_{24}N_4O_5P^+$•: 281.1387 $[M+H]^+$; found: 281.1384. $C_{11}H_{23}NO_5P$• (280.3): calcd. C 47.14, H 8.27, N 5.00; found C 47.05, H 8.41, N 5.07.

Synthesis of 5t• and 5c•



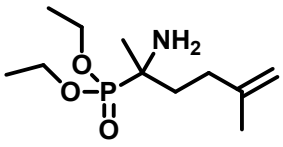
5t•

To a solution of alcohol **10t•** (200 mg, 0.714 mmol) in DCM (3 mL) at room temperature under argon was added Et_3N (288 mg, 2.85 mmol), a catalytic amount of DMAP and pivaloyl chloride (172 mg, 1.43 mmol). The mixture was stirred for 1 day. Then, the mixture was poured on a saturated solution of $NaHCO_3$ and extracted with DCM. The organic layer was dried with $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified by flash chromatography (AcOEt/EtOH gradient) to afford product **5t•**, 203 mg, yield 78%. HRMS (ESI) calc for $C_{16}H_{32}NO_6P^+$•: 365.1962 $[M+H]^+$; found: 365.1962.



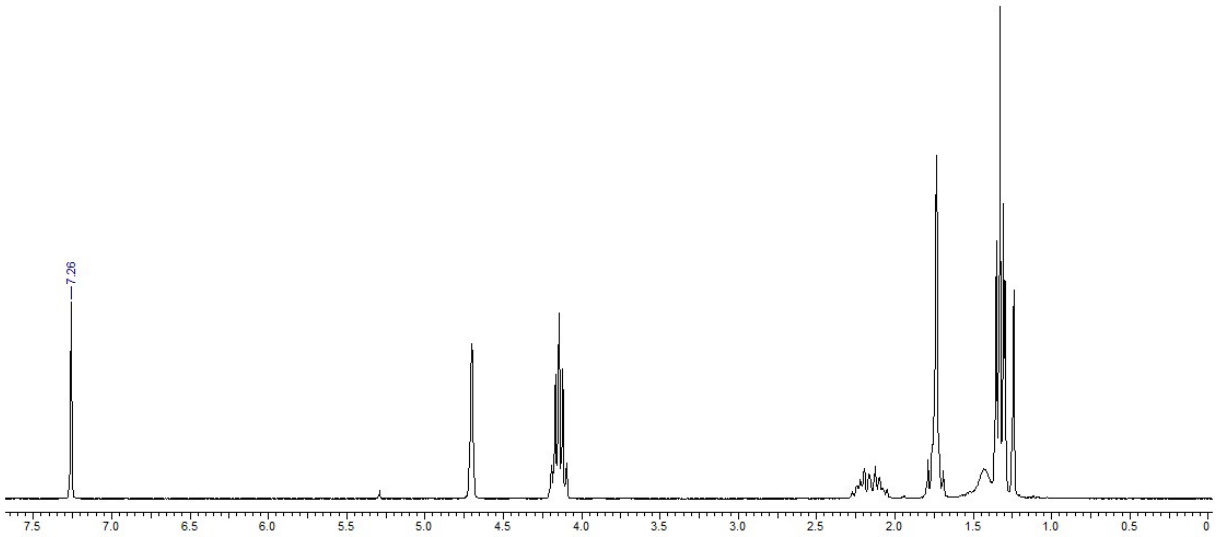
5c•

This compound was obtained using the same procedure: **10c•** (200 mg, 0.714 mmol) to product **5c•** (213 mg, yield 82%). HRMS (ESI) calc for $C_{16}H_{32}NO_6P^+$•: 365.1962 $[M+H]^+$; found: 365.1962.

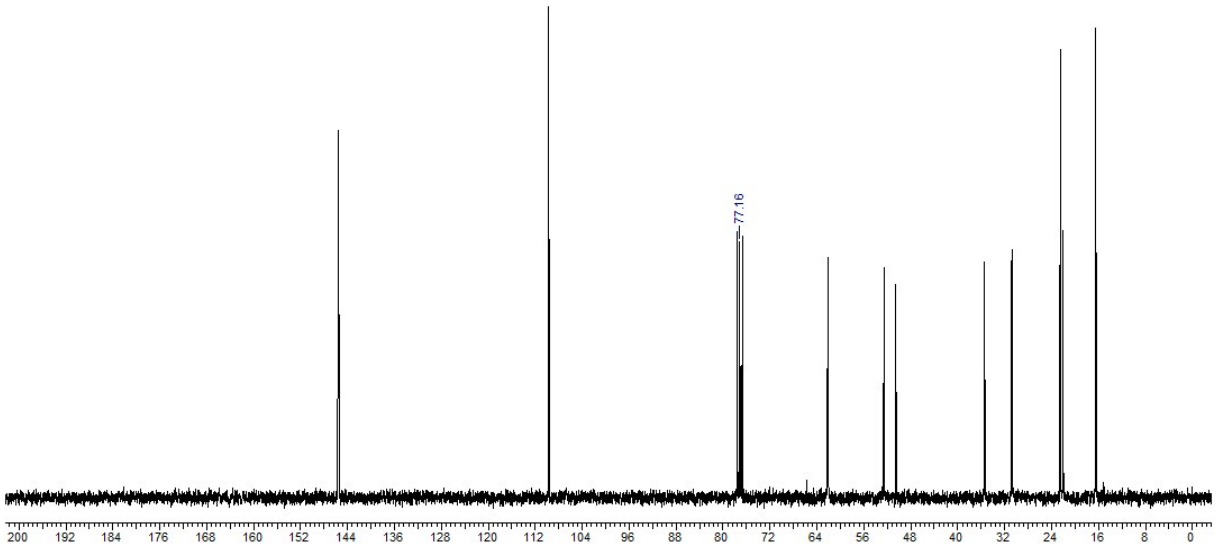


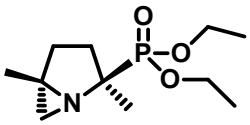
2

^{1}H NMR (300 MHz, $CDCl_3$):



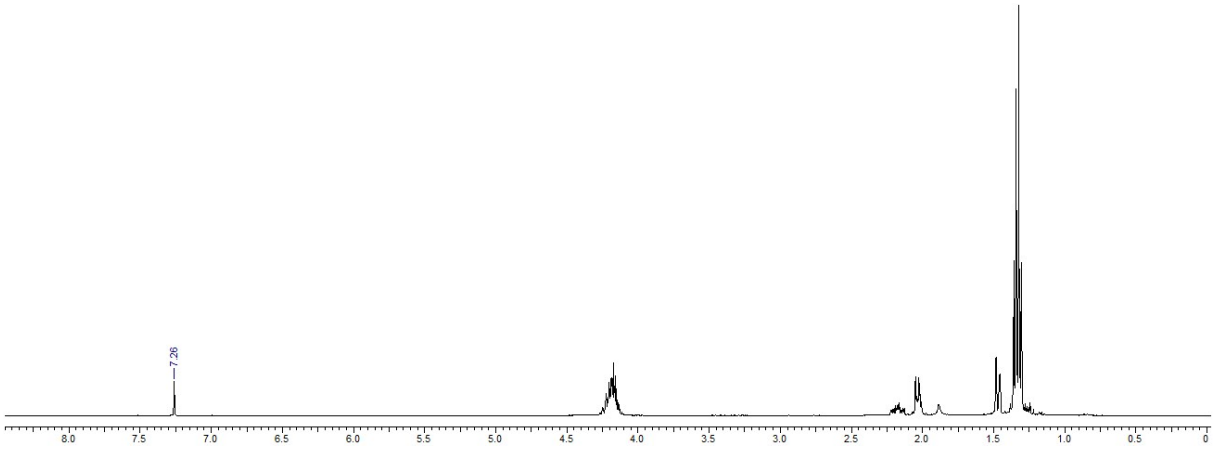
^{13}C NMR (75 MHz, $CDCl_3$):



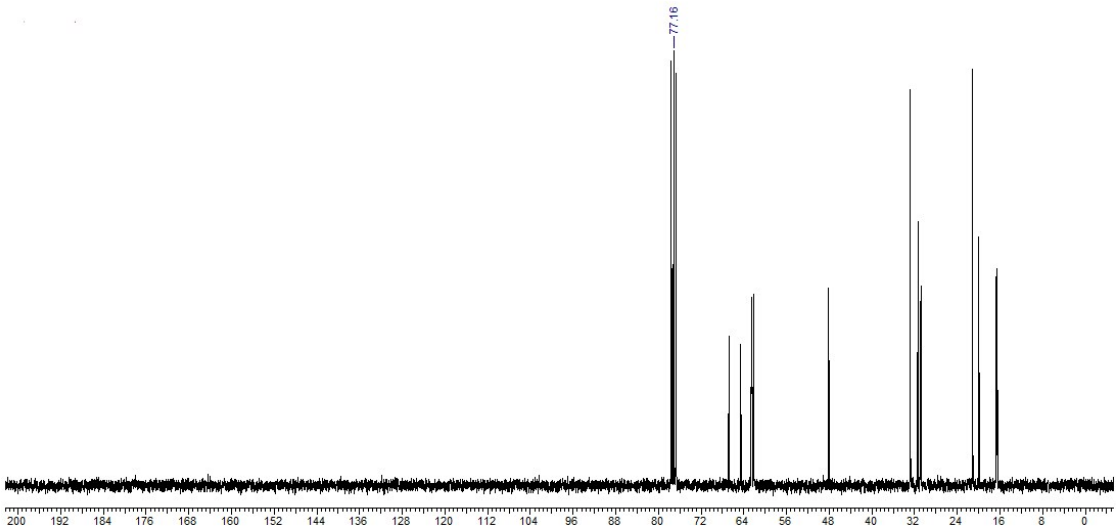


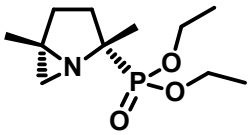
3t :

^{1}H NMR (400 MHz, $CDCl_3$):



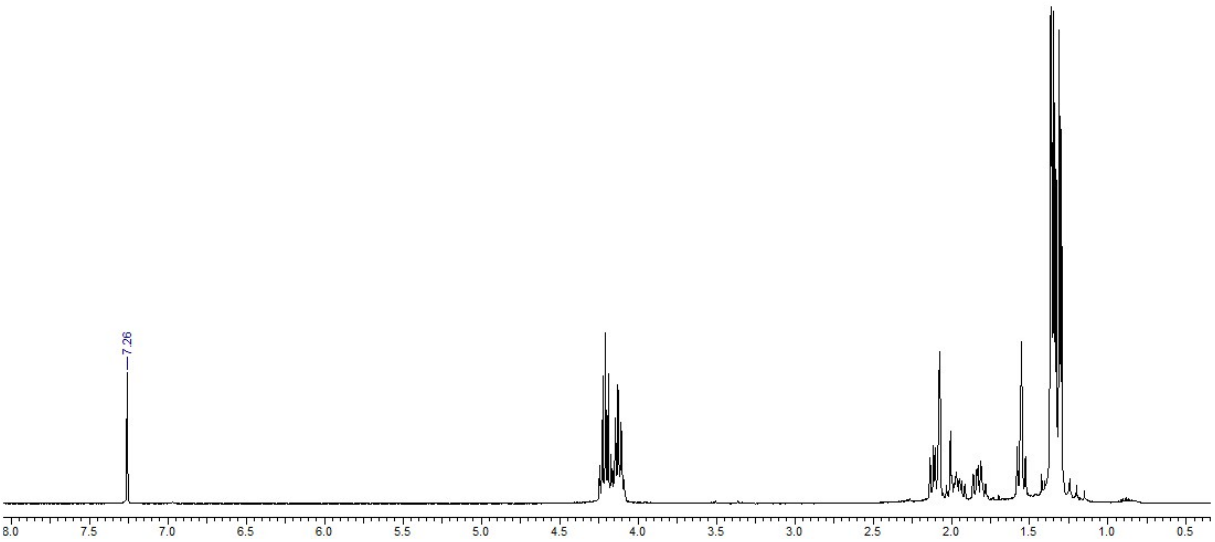
^{13}C NMR (75 MHz, $CDCl_3$):



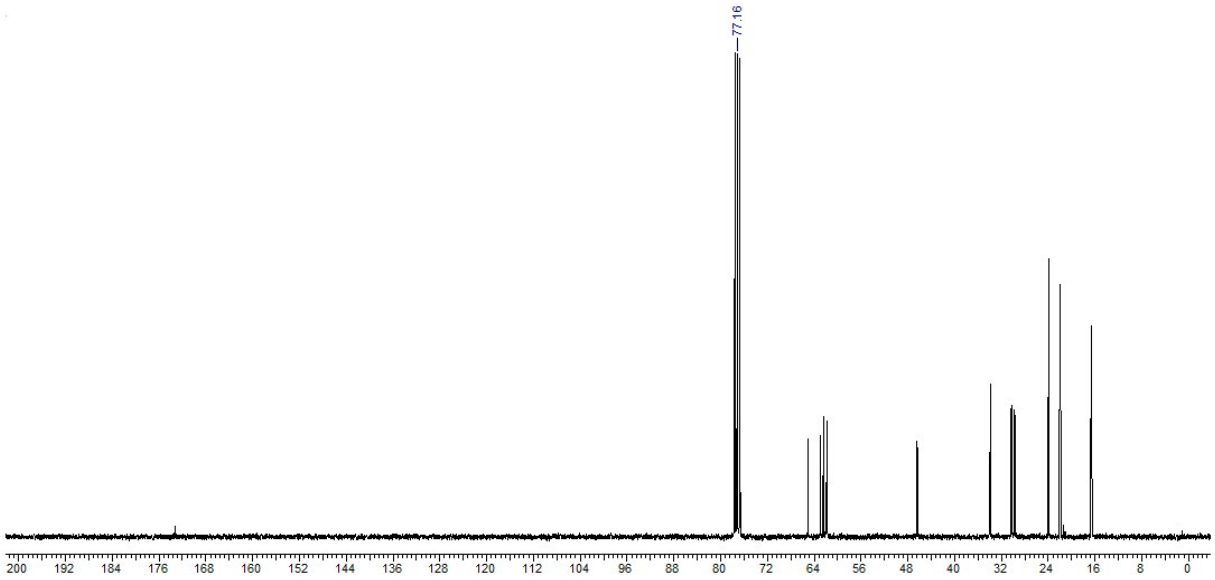


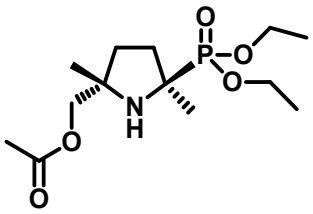
3c :

^{1}H NMR (400 MHz, $CDCl_3$):



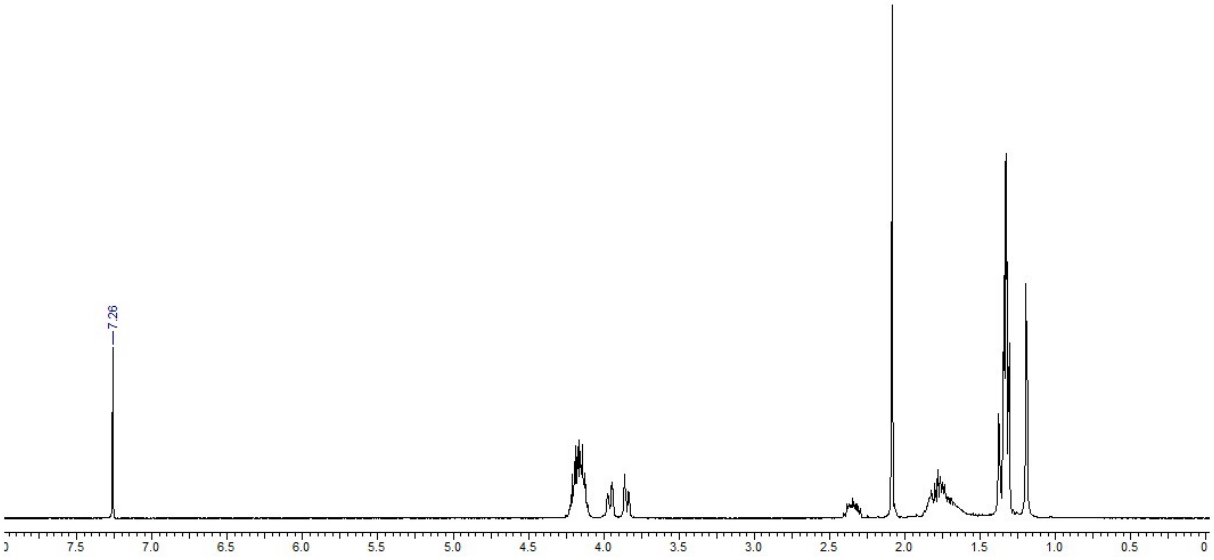
^{13}C NMR (75 MHz, $CDCl_3$):



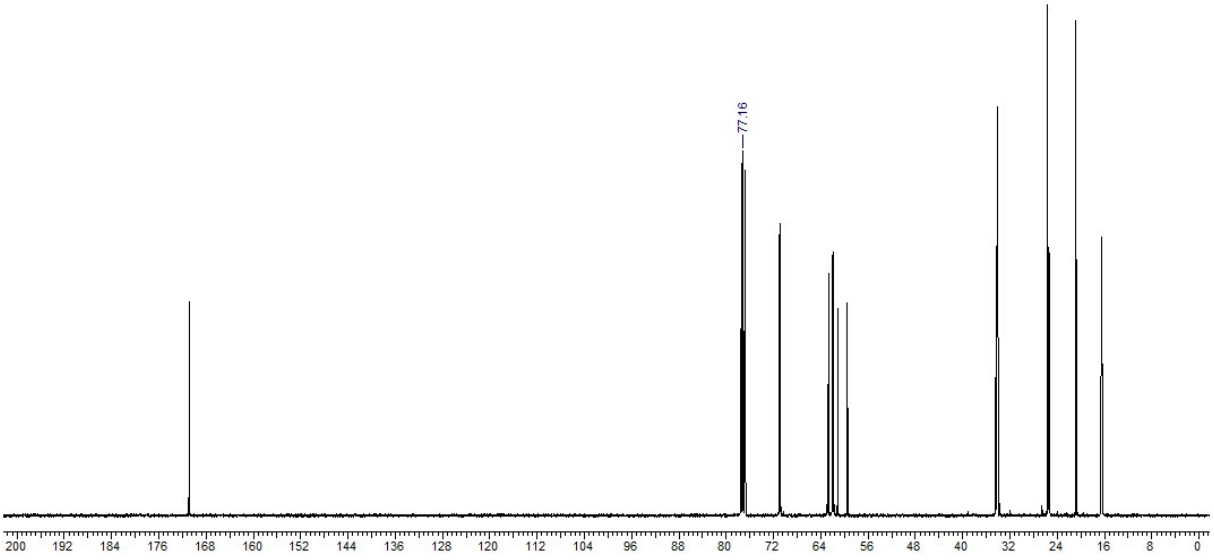


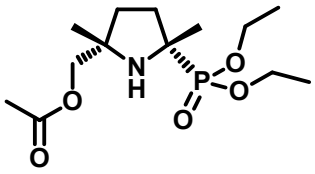
4t :

^{1}H NMR (400 MHz, $CDCl_3$):



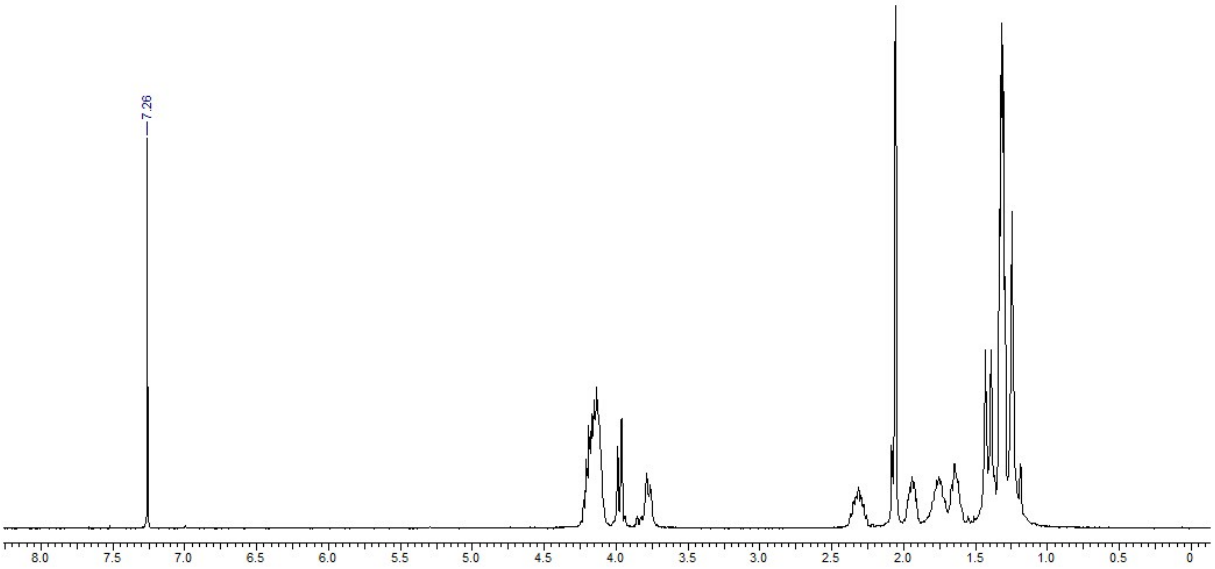
^{13}C NMR (100 MHz, $CDCl_3$):



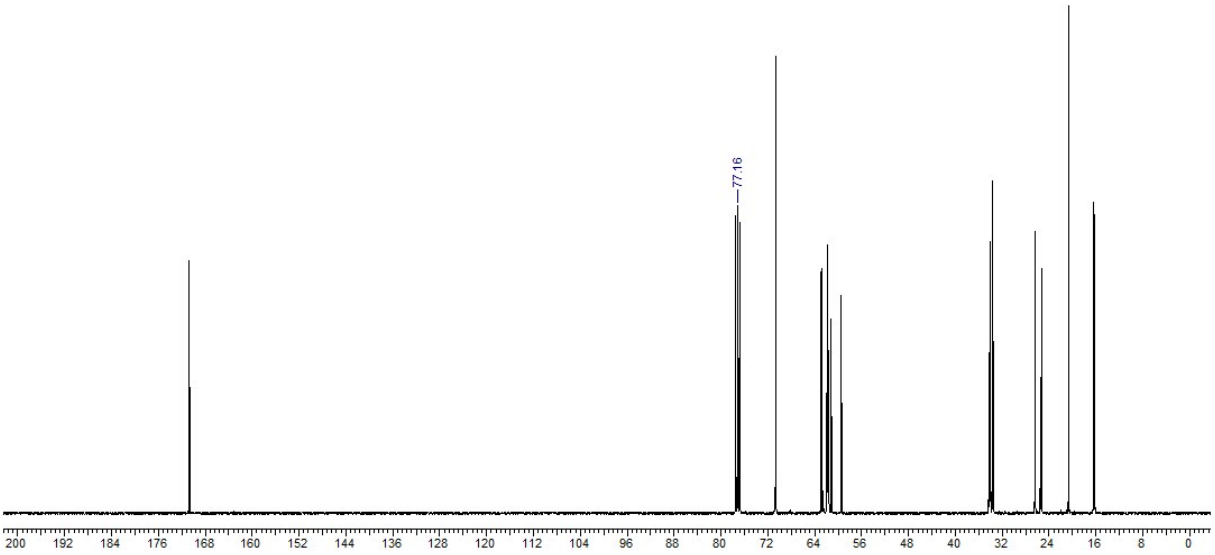


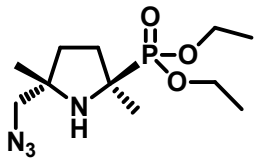
4c:

^{1}H NMR (400 MHz, $CDCl_3$):



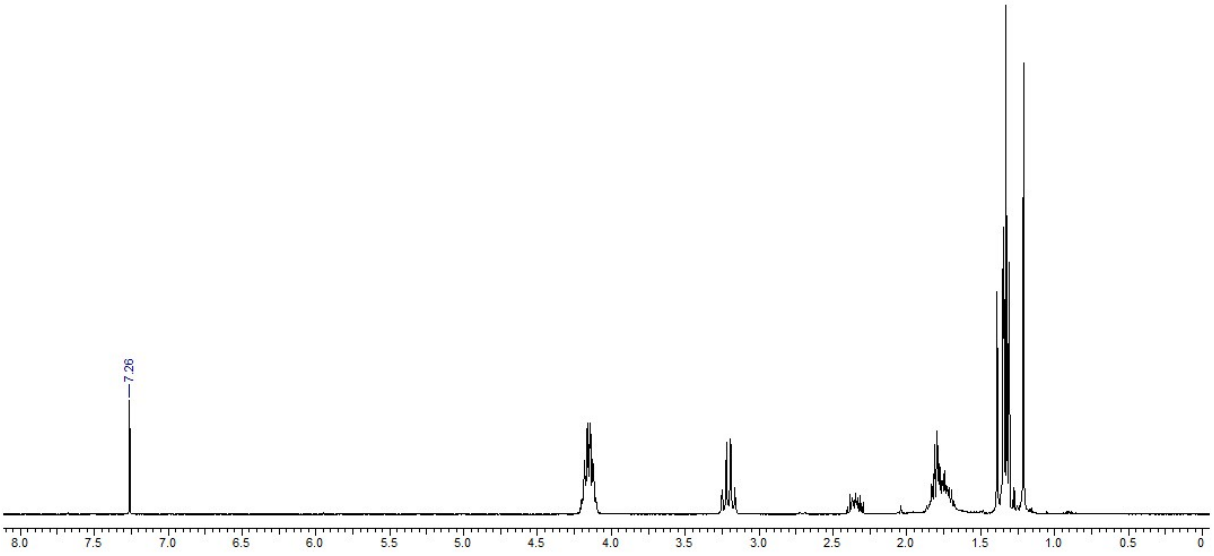
^{13}C NMR (100 MHz, $CDCl_3$):



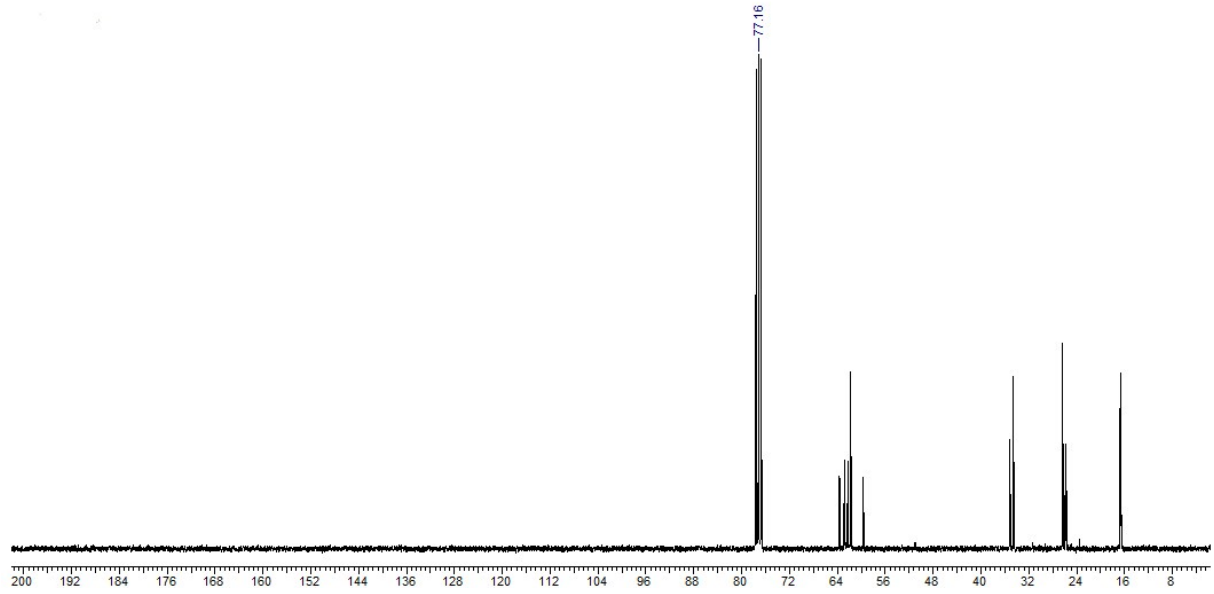


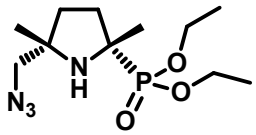
6t:

^{1}H NMR (400 MHz, $CDCl_3$):



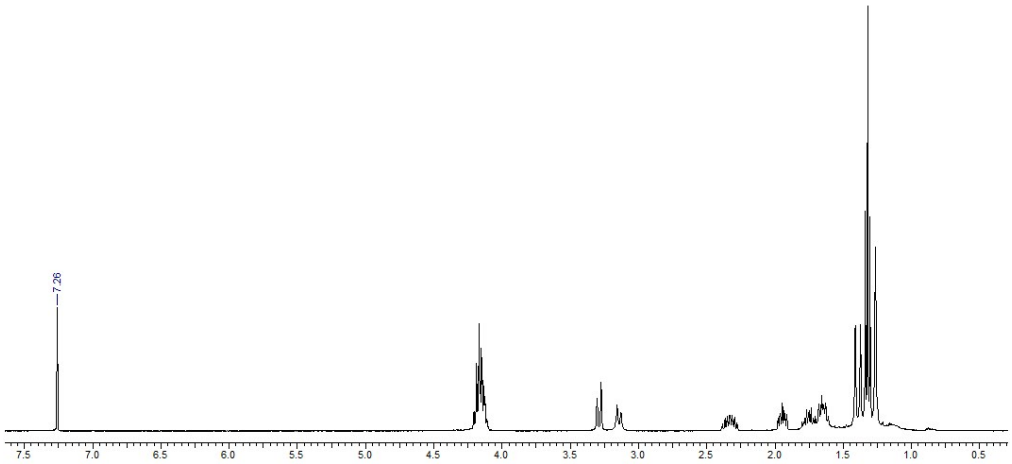
^{13}C NMR (75 MHz, $CDCl_3$):



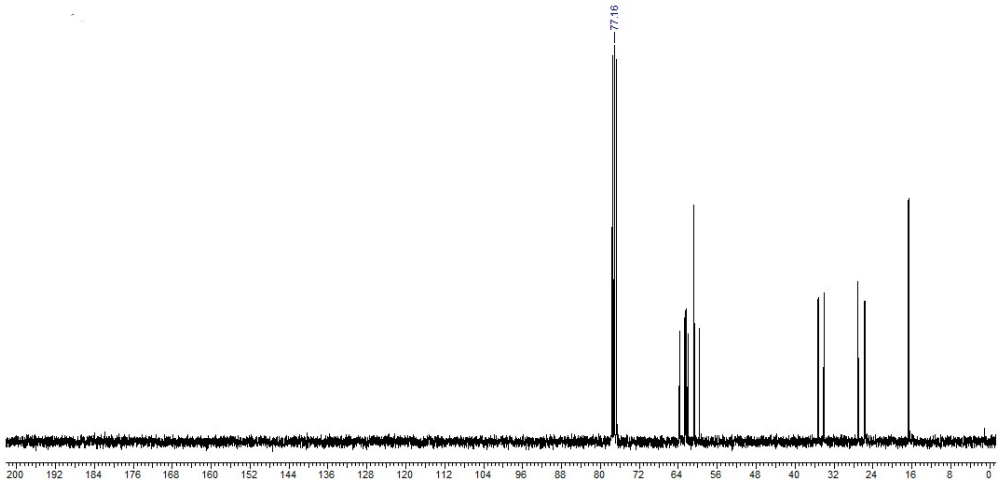


6c:

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



[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**.

[3] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem*., **1997**, *62*, 7512.