

ESI

Table 1 ^{29}Si -NMR chemical shifts of trimethylsilyl esters of sulfonic acid ROSiMe_3

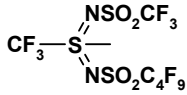
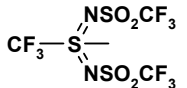
N	R	$\delta_{29\text{Si}}$ (ppm)		-H _o
		Neat	CH_2Cl_2 (50%)	
1	4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$	31.62	32.10	about 6,5-7,5 ⁽¹⁾
2	CH_3SO_2	32.03	32.27	
3	$\text{C}_6\text{H}_5\text{SO}_2$	32.19	32.57	
4	4- $\text{ClC}_6\text{H}_4\text{SO}_2$	33.03	33.40	
5	ClSO_2	44.36	44.12	about 13-15 ⁽²⁾
6	$\text{C}_4\text{F}_9\text{SO}_2$	43.95	44.40	
7	CF_3SO_2	44.10	44.26 (42.00 in CCl_4)	
1b		62.00	61.50	about 24-25
1a		63.51	62.85 (62.00 in CCl_4)	

Diagram 1

^{29}Si -NMR chemical shifts of trimethylsilylesters of phenoles ROSiMe_3 –vs- H_0 values^{1,2}

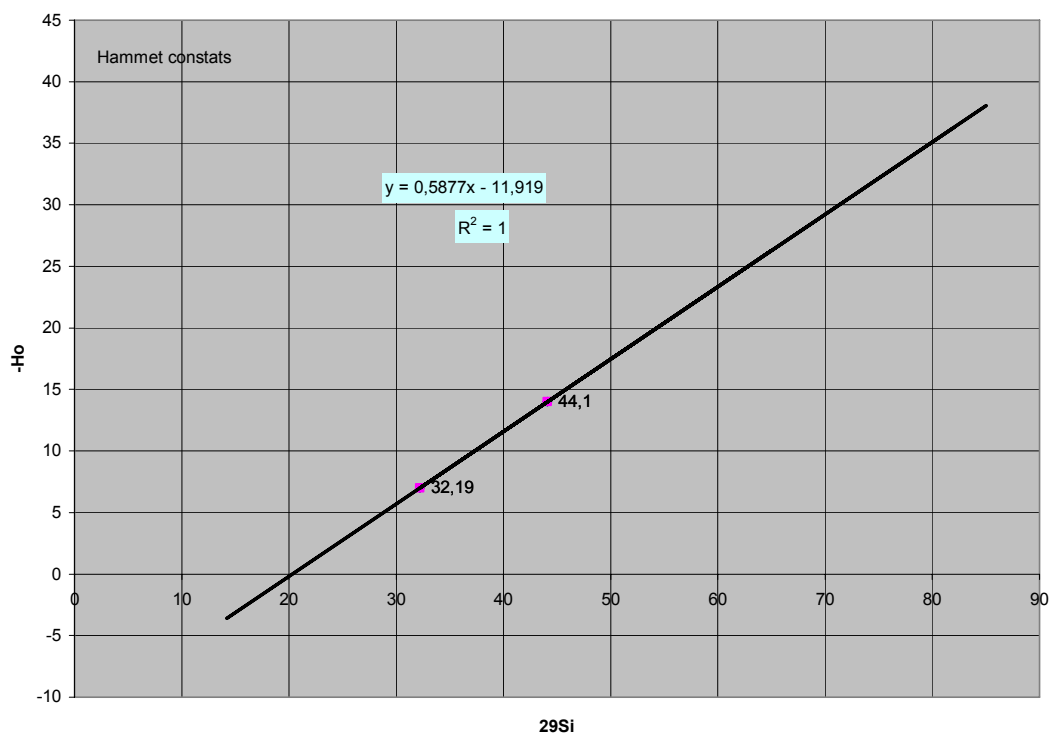


Table 2²⁹Si-NMR chemical shifts of trimethylsilylestere of phenoles ROSiMe₃ –vs- pK_a values³

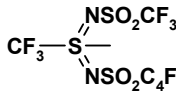
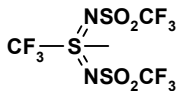
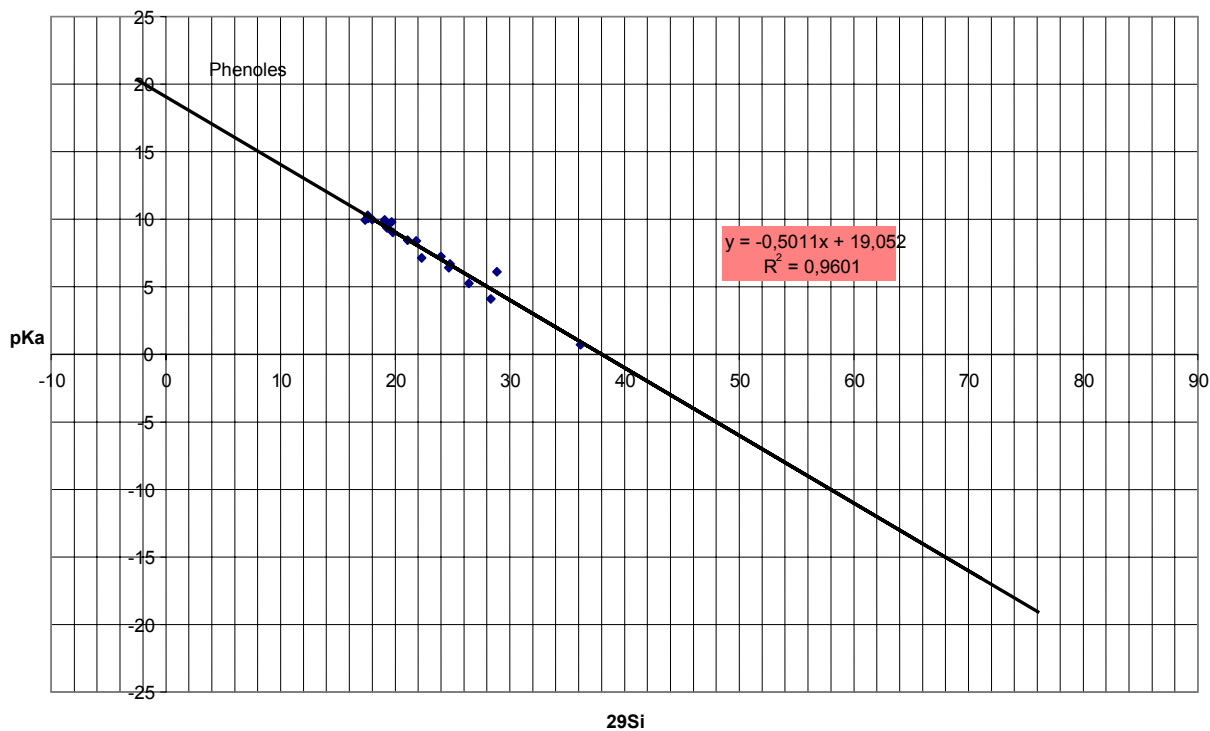
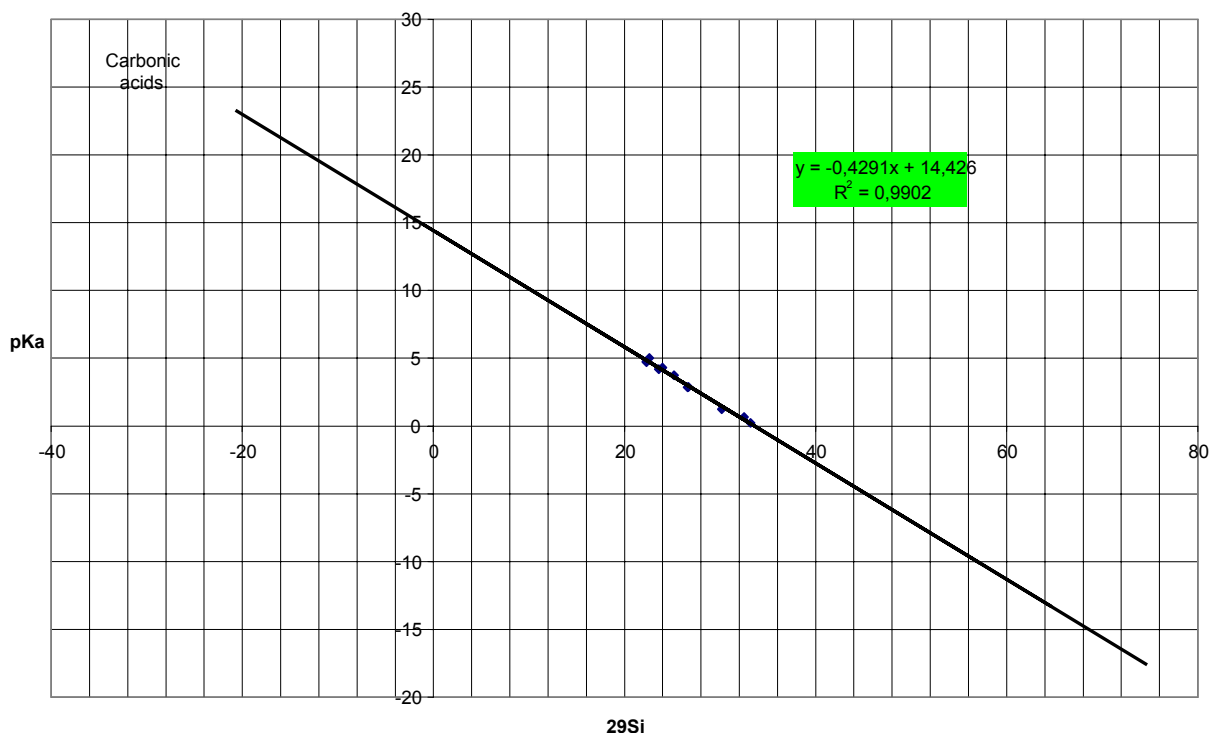
N	R	δ _{29 Si}	pK _a
1	C ₆ H ₅	18,00	9,98
2	2-CH ₃ C ₆ H ₄	17,60	10,28
3	3-CH ₃ C ₆ H ₄	17,64	10,08
4	4-CH ₃ C ₆ H ₄	17,70	10,14
5	4-FC ₆ H ₄	19,10	9,95
6	4-ClC ₆ H ₄	19,30	9,38
7	2-BrC ₆ H ₄	21,10	8,44
8	3-BrC ₆ H ₄	19,80	9,03
9	4-BrC ₆ H ₄	19,30	9,36
10	4-IC ₆ H ₄	19,70	9,81
11	4-(CH ₃)SiOC ₆ H ₄	17,39	9,96
12	2-NO ₂ C ₆ H ₄	24,00	7,23
13	3-NO ₂ C ₆ H ₄	21,86	8,40
14	4-NO ₂ C ₆ H ₄	22,30	7,15
15	2,4,6-Cl ₃ C ₆ H ₂	24,70	6,41
16	2,4,6-Br ₃ C ₆ H ₂	24,80	6,70
17	C ₆ F ₅	28,91	6,10
18	C ₆ Cl ₅	26,45	5,26
19	2,4-(NO ₂) ₂ C ₆ H ₃	28,36	4,11
20	2,4,6(NO ₂) ₃ C ₆ H ₂	36,16	0,71
1b		61,5	about -11.8
1a		62.85	about -12.5

Diagram 2²⁹Si-NMR chemical shifts of trimethylsilylesters of phenoles ROSiMe₃ –vs- pK_a values³**Table 3**²⁹Si-NMR chemical shifts of trimethylsilyl esters of carbonic acids and pK_a values³

N ^o	R	$\delta_{29\text{Si}}$	pK _a
1	C(O)C(CH ₃) ₃	22,6	5,02
2	C(O)CH ₃	22,3	4,76
3	C(O)CH=CHCH ₃	22,3	4,71
4	C(O)CH ₂ C ₆ H ₅	24,0	4,30
5	C(O)C ₆ H ₅	23,6	4,20
6	C(O)H	25,2	3,75
7	C(O)CH ₂ Br	26,7	2,89
8	C(O)CH ₂ Cl	26,6	2,86
9	C(O)CHCl ₂	30,2	1,23
10	C(O)CCl ₃	32,5	0,66
11	C(O)CF ₃	33,2	0,22

1b	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagup \\ \text{CF}_3-\text{S} \\ \diagdown \\ \text{NSO}_2\text{C}_4\text{F}_9 \end{array}$	61,5	about -11,9
1a	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagup \\ \text{CF}_3-\text{S} \\ \diagdown \\ \text{NSO}_2\text{CF}_3 \end{array}$	62,85	about -12,54

Diagram 3²⁹Si-NMR chemical shifts of trimethylsilyl esters of carbonic acids and pK_a values³**Table 4**²⁹Si-NMR chemical shifts of trimethylsilyl esters of an assorted number of acids and pK_a values⁴

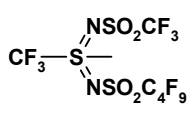
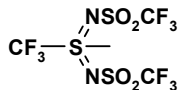
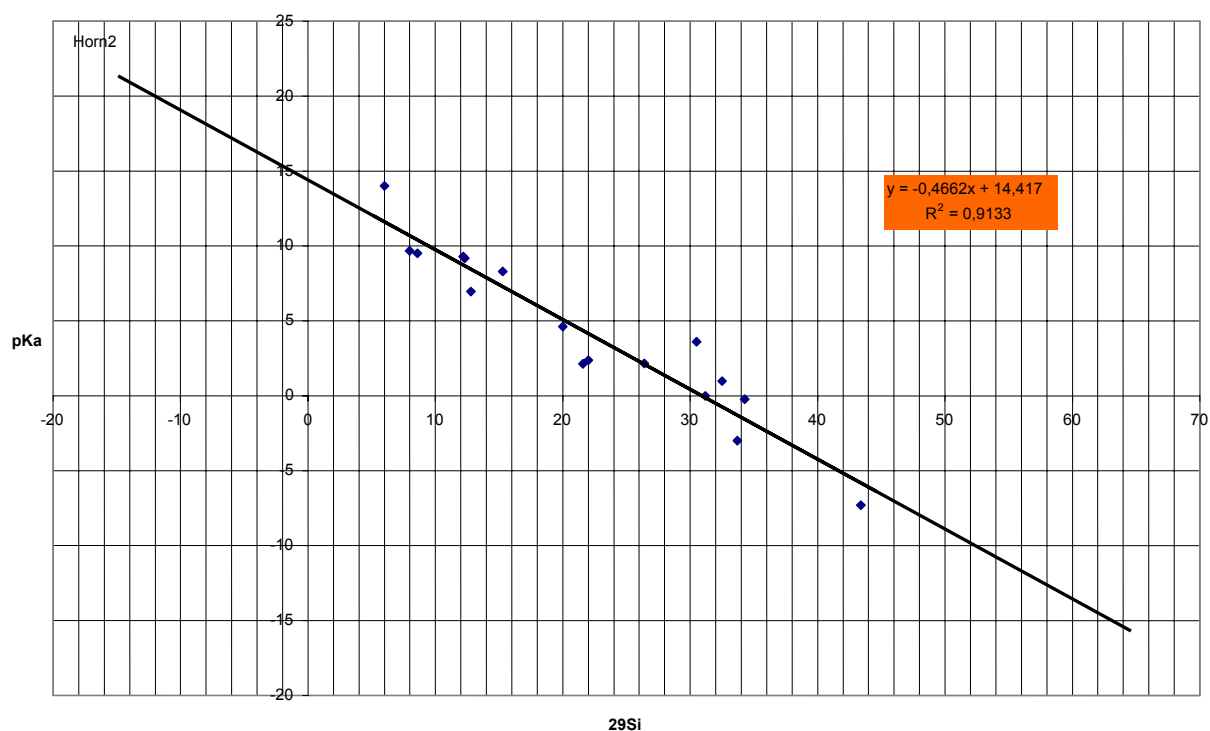
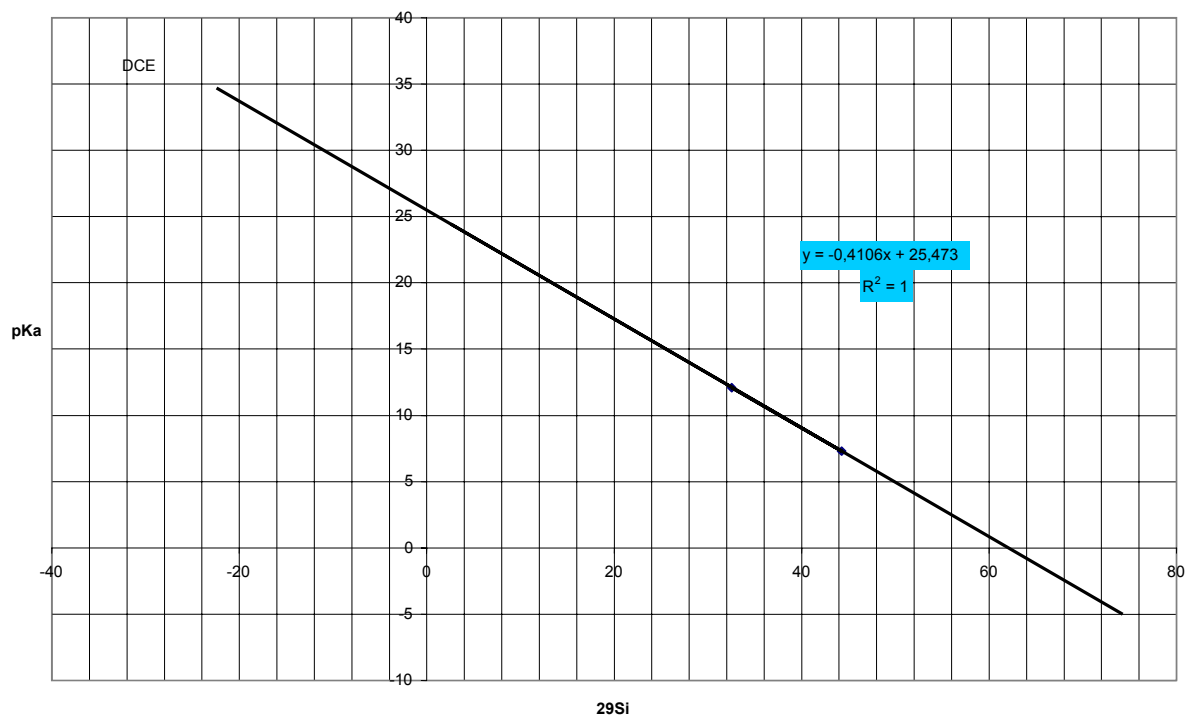
N	Trimehtylsilylesters	$\delta_{29\text{Si}}$	pKa	N	Trimehtylsilylesters	$\delta_{29\text{Si}}$	pKa
1	(CH ₃) ₃ SiO-SO ₂ CF ₃	44,6	-	16	(CH ₃) ₃ SiI	8,6	-9,5
2	[(CH ₃) ₃ Si]ClO ₄	43,4	-7,3	17	[(CH ₃) ₃ Si] ₄ SiO ₄	8,0	9,67
3	(CH ₃) ₃ SiOOCF ₃	34,3	-0,23	18	(CH ₃) ₃ Si(NCO)	7,0	3,54
4	[(CH ₃) ₃ Si] ₂ SO ₄	33,7	-3	19	(CH ₃) ₃ SiOSi(CH ₃) ₃	6,0	13,99
5	(CH ₃) ₃ SiCl	32,5	0,98	20	(CH ₃) ₃ Si(NCS)	5,1	0
6	-[(CH ₃) ₃ SiO-P(O)O] ₃ -	31,2	0	21	(CH ₃) ₃ Si(CN)	12,2	9,28
7	(CH ₃) ₃ SiF	30,5	3,6				
8	(CH ₃) ₃ SiBr	26,4	-2,15				
9	(CH ₃) ₃ SiOOCH ₃	22,0	4,75				
10	[(CH ₃) ₃ SiO] ₂ P(O)CH ₃	21,6	2,38	1b		61,50	-14.25
11	[(CH ₃) ₃ Si] ₃ PO ₄	20,0	2,14				
12	(CH ₃) ₃ SiN ₃	15,3	4,63				
13	(CH ₃) ₃ SiSC ₆ H ₅	15,3	8,3				
14	(CH ₃) ₃ SiSSi(CH ₃) ₃	12,8	6,95	1a		62,85	-14.88
15	[(CH ₃) ₃ SiO] ₃ B	12,3	9,18				

Diagram 4²⁹Si-NMR chemical shifts of trimethylsilyl esters of an assorted number of acids and pK_a values⁴**Table 5**²⁹Si-NMR chemical shifts of trimethylsilyl esters of sulfonic acids in DCE and pK_a values in DCE⁵

N ^o	Trimehtylsilylesters	pKa	δ _{29Si}
1	(CH ₃) ₃ SiO-SO ₂ C ₆ H ₅	12,1	32,57
2	(CH ₃) ₃ SiO-SO ₂ CF ₃	7,3	44,26
1b	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagup \\ \text{CF}_3-\text{S} \\ \diagdown \\ \text{NSO}_2\text{C}_4\text{F}_9 \end{array}$	about - 0,22	61,5
1a	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagup \\ \text{CF}_3-\text{S} \\ \diagdown \\ \text{NSO}_2\text{CF}_3 \end{array}$	about -0,33	62,85

Diagram 5

²⁹Si-NMR chemical shifts of trimethylsilyl esters of sulfonic acids in DCE and pK_a values in DCE ⁵

**Table 6**

²⁹Si-NMR chemical shifts of trimethylsilyl esters of sulphonic acids in AcOH and pK_a values in acetic acid ⁶

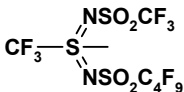
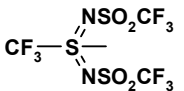
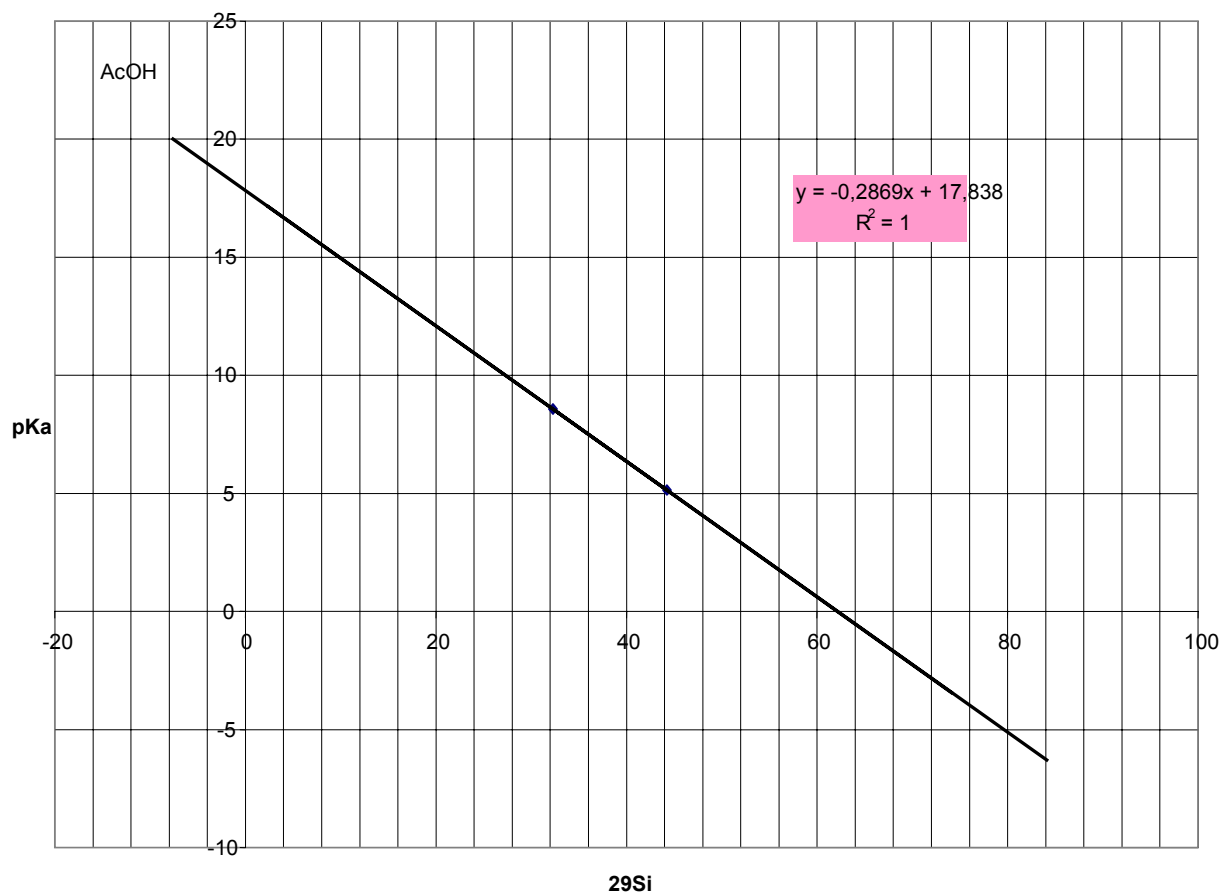
N ^o	Trimehtylsilylesters	pKa	δ _{29Si}
1	(CH ₃) ₃ SiO-SO ₂ C ₆ H ₅	12,1	32,57
2	(CH ₃) ₃ SiO-SO ₂ CF ₃	7,3	44,26
1b		about 0,19	61,5
1a		about -0,19	62,85

Diagram 6

²⁹Si-NMR chemical shifts of trimethylsilyl esters of sulphonic acids in AcOH and pK_a values in acetic acid ⁶

**Table 7**

²⁹Si-NMR chemical shifts of trimethylsilyl esters of sulphonic acids and pK_a values from a linear correlation between free energies of hydrolysis of their methyl esters and acidity. ⁷

N	Trimehtylsilylesters	$\delta_{29\text{Si}}$	pK _a
1	(CH ₃) ₃ SiO-SO ₂ CH ₃	32,27	-1,92
2	(CH ₃) ₃ SiO-SO ₂ C ₆ H ₅	32,57	-2,8
3	(CH ₃) ₃ SiO-SO ₂ C ₆ H ₄ -pBr	33,4	-3,1
4	(CH ₃) ₃ SiO-SO ₂ CF ₃	44,26	-5,9
5	(CH ₃) ₃ SiO-SO ₂ Cl	44,12	-6,0
1b	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagdown \\ \text{CF}_3-\text{S} \\ \diagup \\ \text{NSO}_2\text{C}_4\text{F}_9 \end{array}$	61,5	about -11,07
1a	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagdown \\ \text{CF}_3-\text{S} \\ \diagup \\ \text{NSO}_2\text{CF}_3 \end{array}$	62,85	about -11,5

Diagram 7

^{29}Si -NMR chemical shifts of trimethylsilyl esters of sulphonic acids and pK_a values from a linear correlation between free energies of hydrolysis of their methyl esters and acidity.⁷

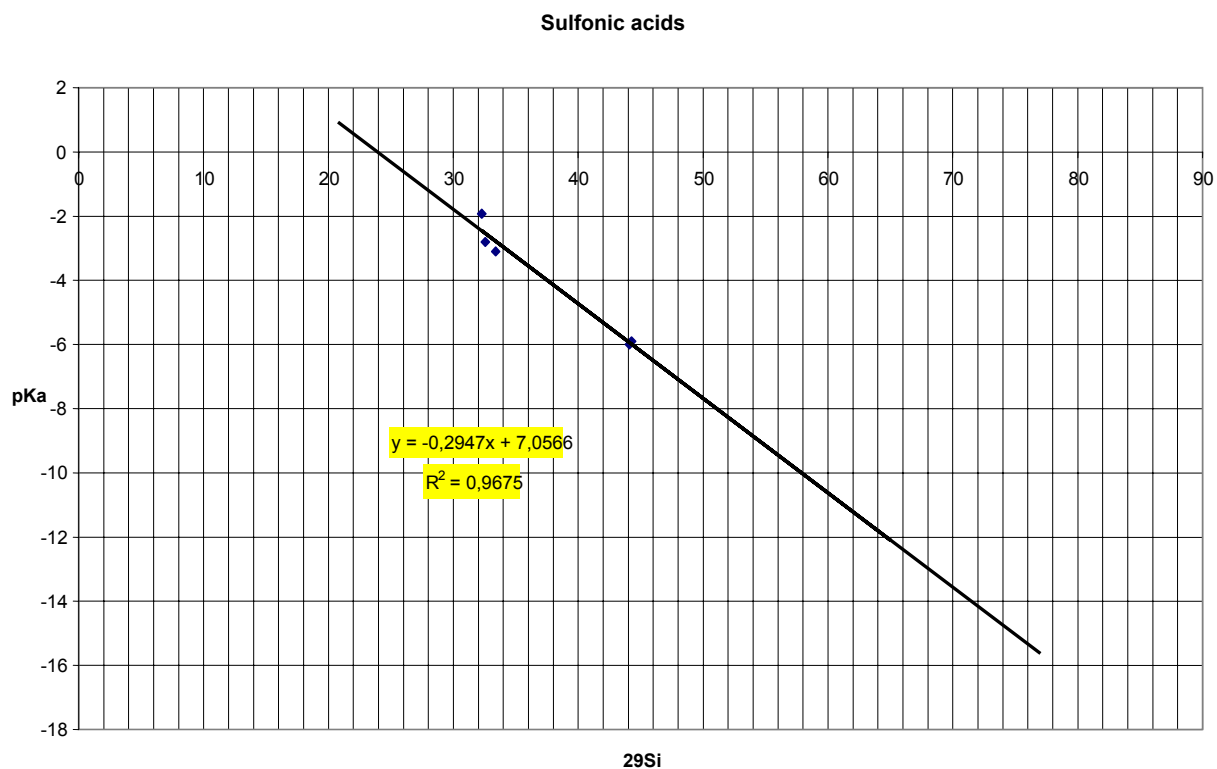
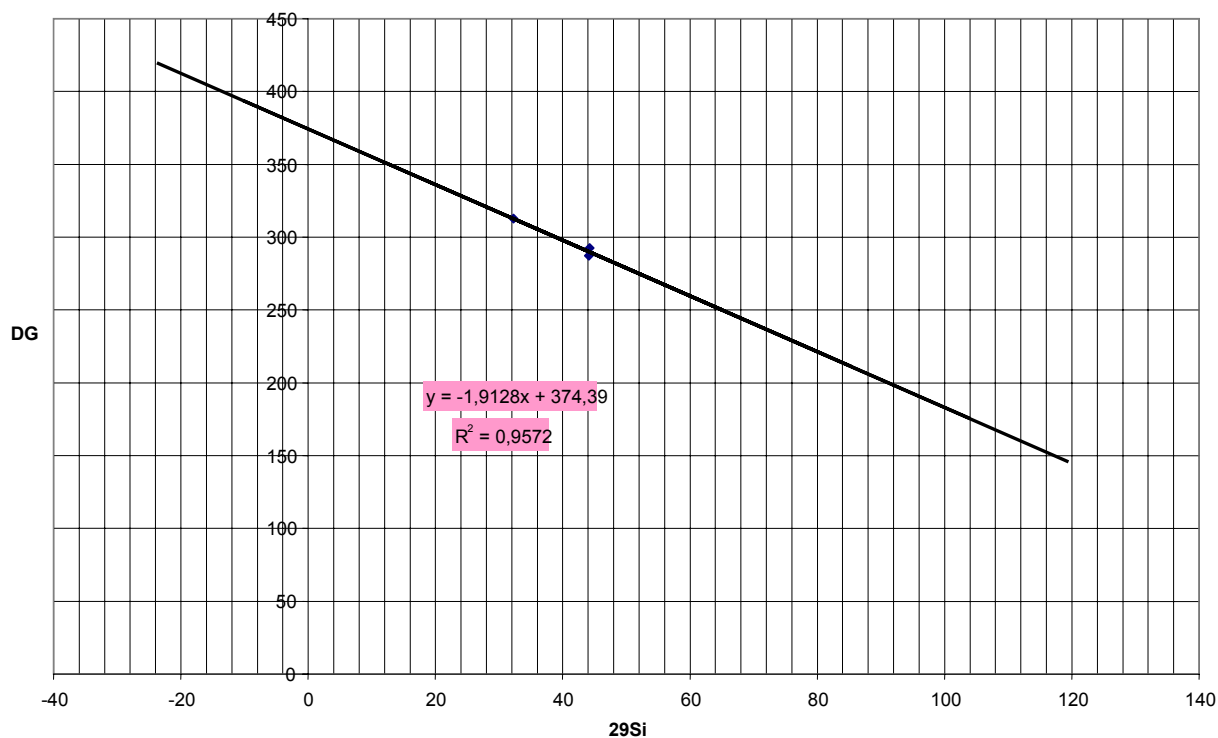


Table 8

²⁹ Si-NMR esters of sulfonic acids	chemical	N	Acid	$\delta_{29\text{ Si}}$	ΔG° , (Kcal/mol)	shifts of trimethylsilyl and ΔG° values ⁸
		1	CH ₃ SO ₂ OH	32,27	312,7	
		2	CF ₃ SO ₂ OH	44,26	292,5	
		3	ClSO ₂ OH	44,12	287,2	
		4	FSO ₃ SbF ₅ H	----	250.5	
		1b	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagup \\ \text{CF}_3-\text{S}-\text{OH} \\ \diagdown \\ \text{NSO}_2\text{C}_4\text{F}_9 \end{array}$	61,5	about 255,8	
		1a	$\begin{array}{c} \text{NSO}_2\text{CF}_3 \\ \diagup \\ \text{CF}_3-\text{S}-\text{OH} \\ \diagdown \\ \text{NSO}_2\text{CF}_3 \end{array}$	62,85	about 252.6	

Diagram 8

²⁹Si-NMR chemical shifts of trimethylsilyl esters of sulfonic acids and ΔG° values⁸



References

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