Supplementary Materials: Metalation Studies on Titanocene Dithiolates

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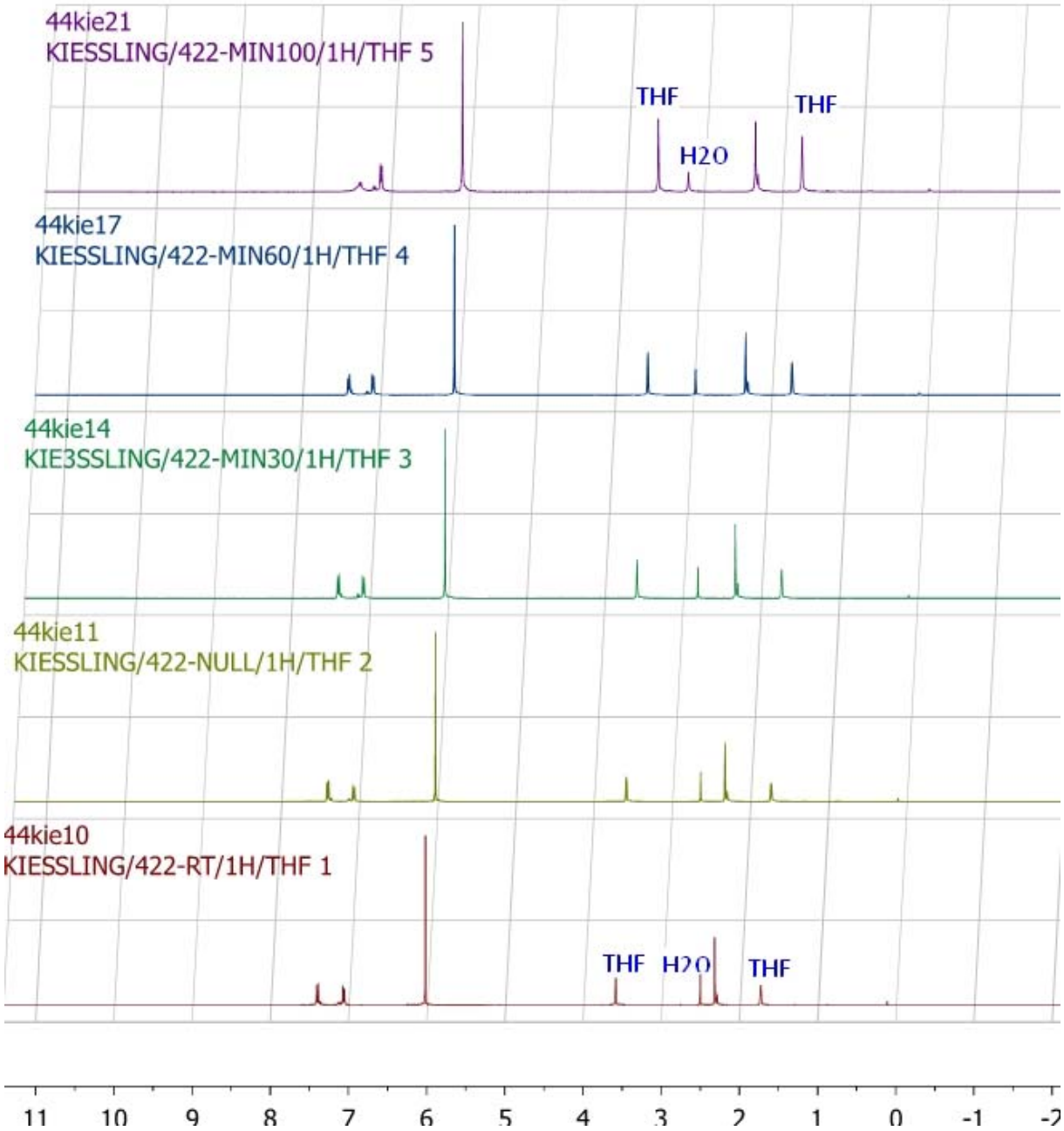


Figure S1: VT-^{1}H-NMR of compound 3a.

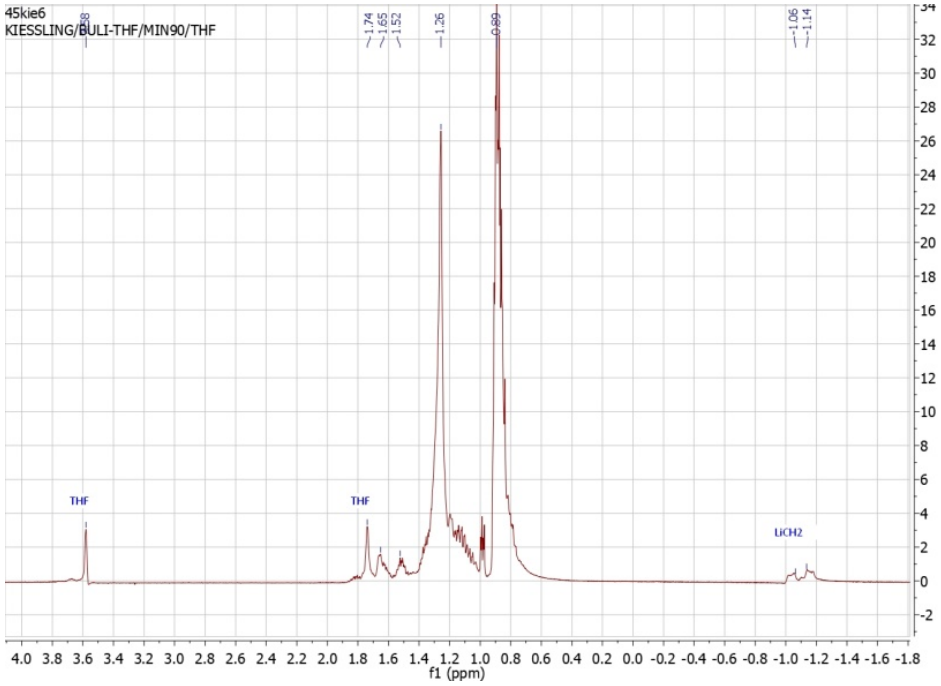


Figure S2: [1]H-NMR of a THF/hexane-solution of n-butyl lithium at −90°C.

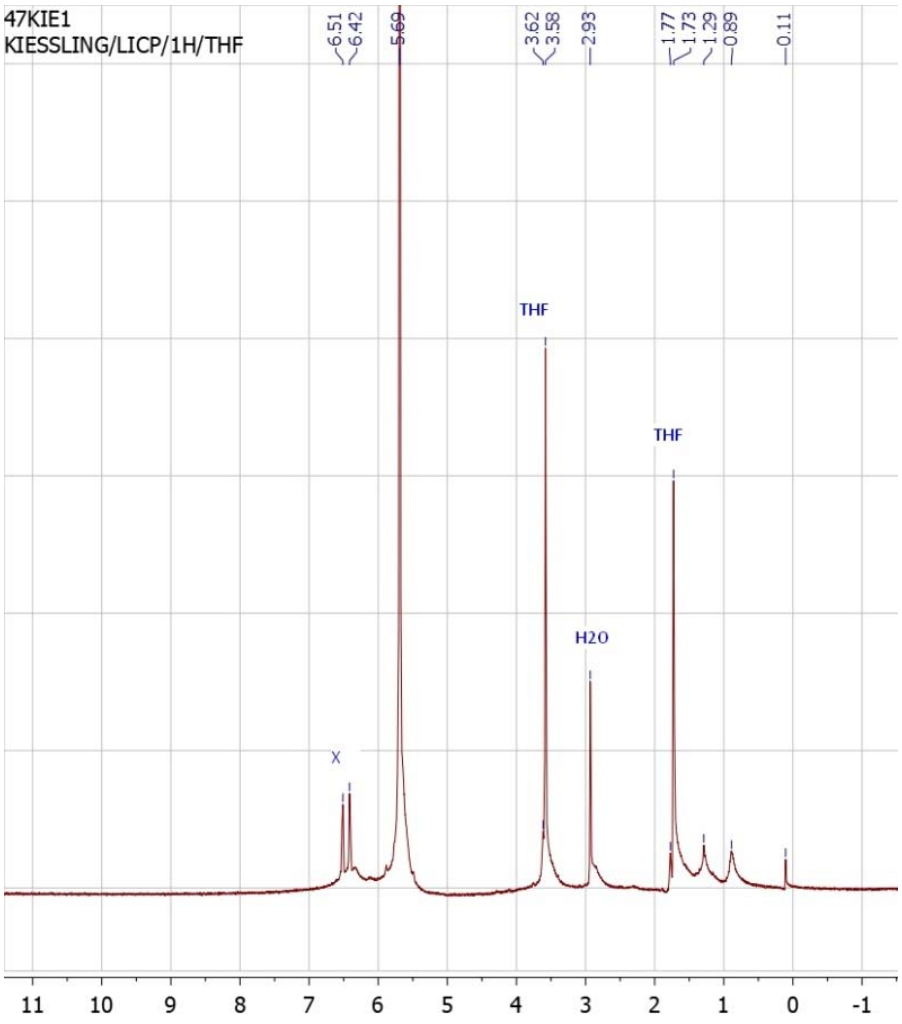


Figure S3:[1]H-NMR of a freshly prepared THF solution of LiC_5H_5 at −80°C.

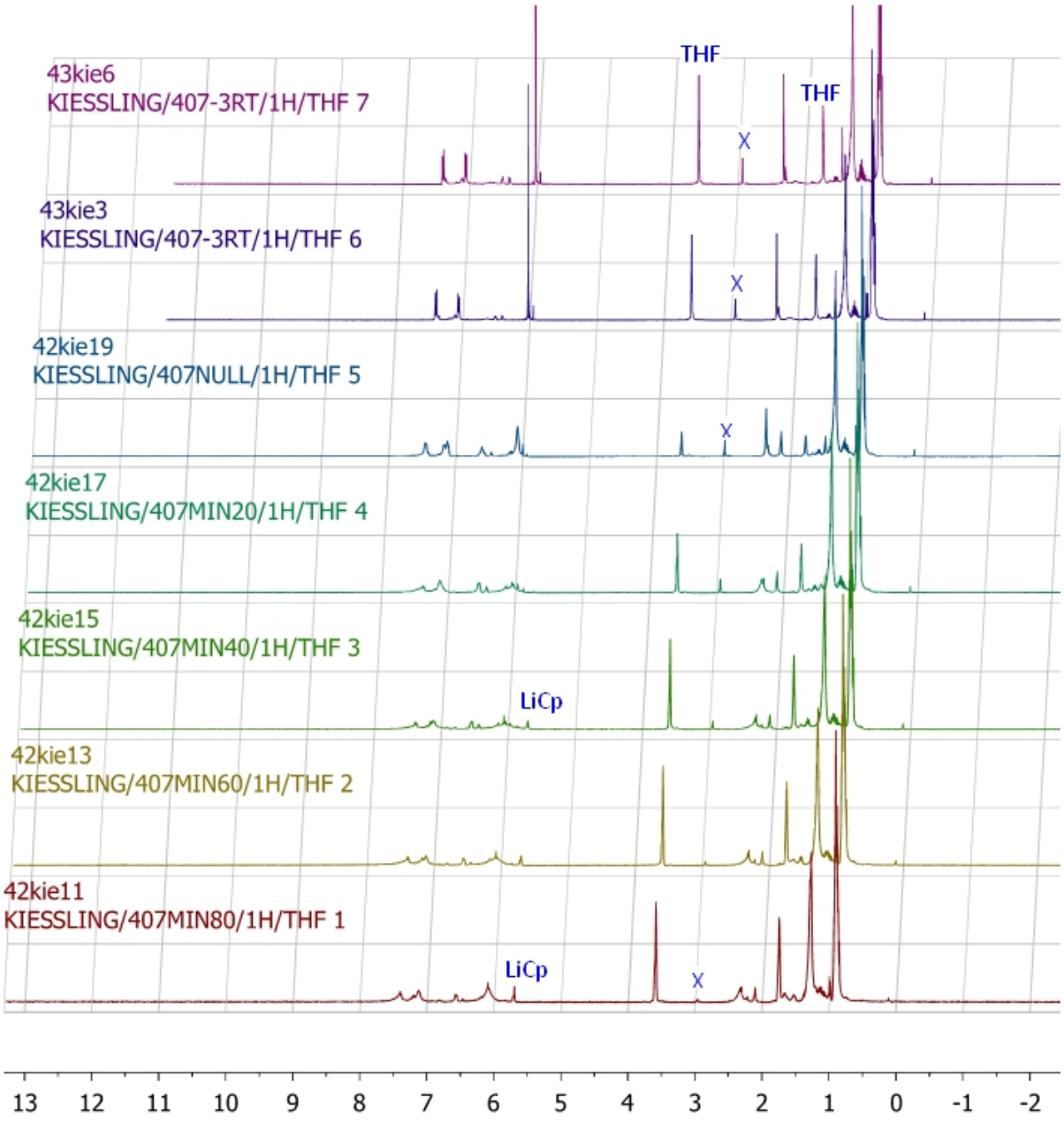


Figure S4: VT-^{1}H-NMR oft the reaction of 3a with 4 eqiv. BuLi in THF, mixed at −120°C. The signal marked with "X" most likely can be assigned to the S$\underline{CH_2}$ group of Tol-S-$CH_2CH_2CH_2CH_3$.

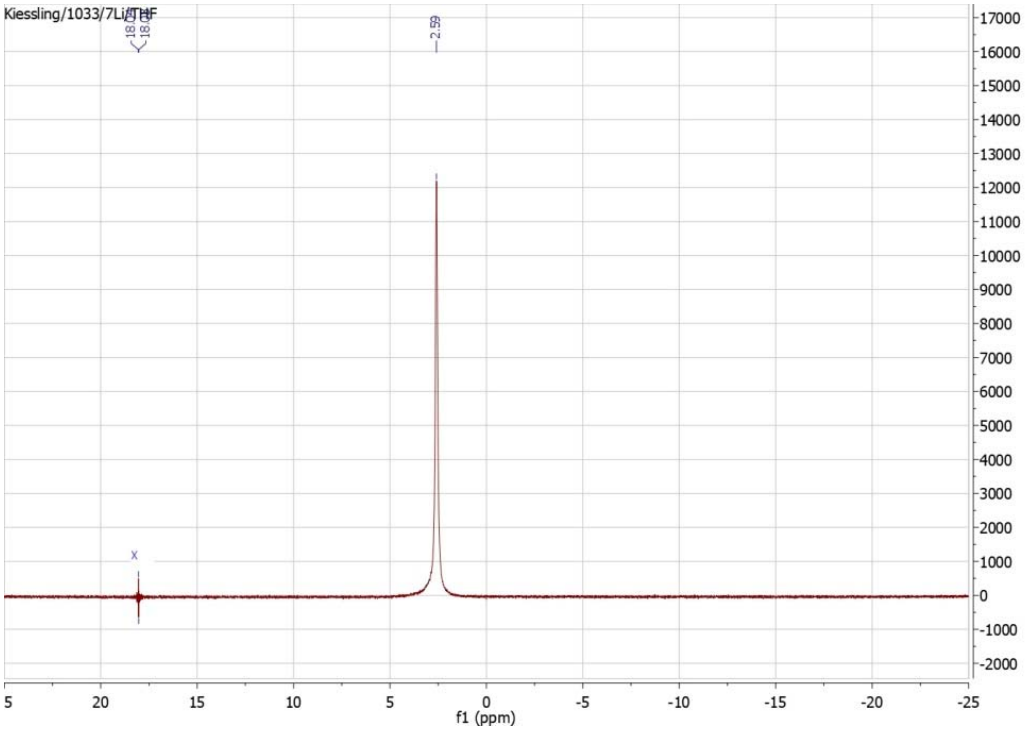


Figure S5: ^{7}Li-NMR of the reaction mixture of 2a with 1.1 equiv BuLi, measured at r.t. The signal marked with "X" is probably an instrument artifact.

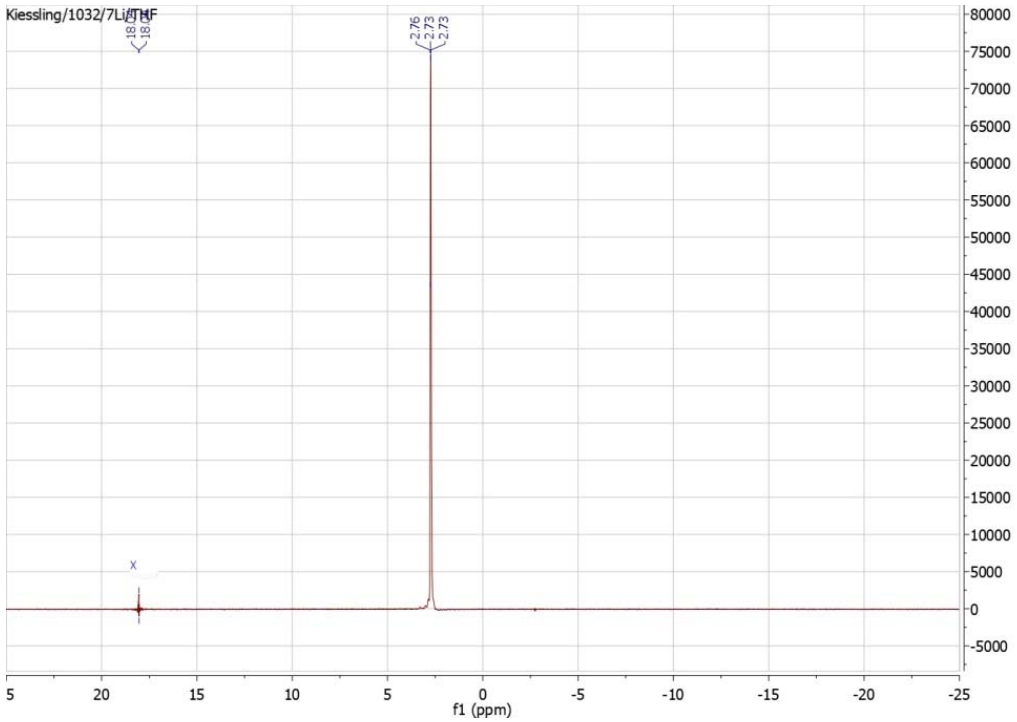


Figure S6: ^{7}Li-NMR of the reaction mixture of 3a with 1.1 equiv BuLi, measured at r.t. The signal marked with "X" is probably an instrument artifact.

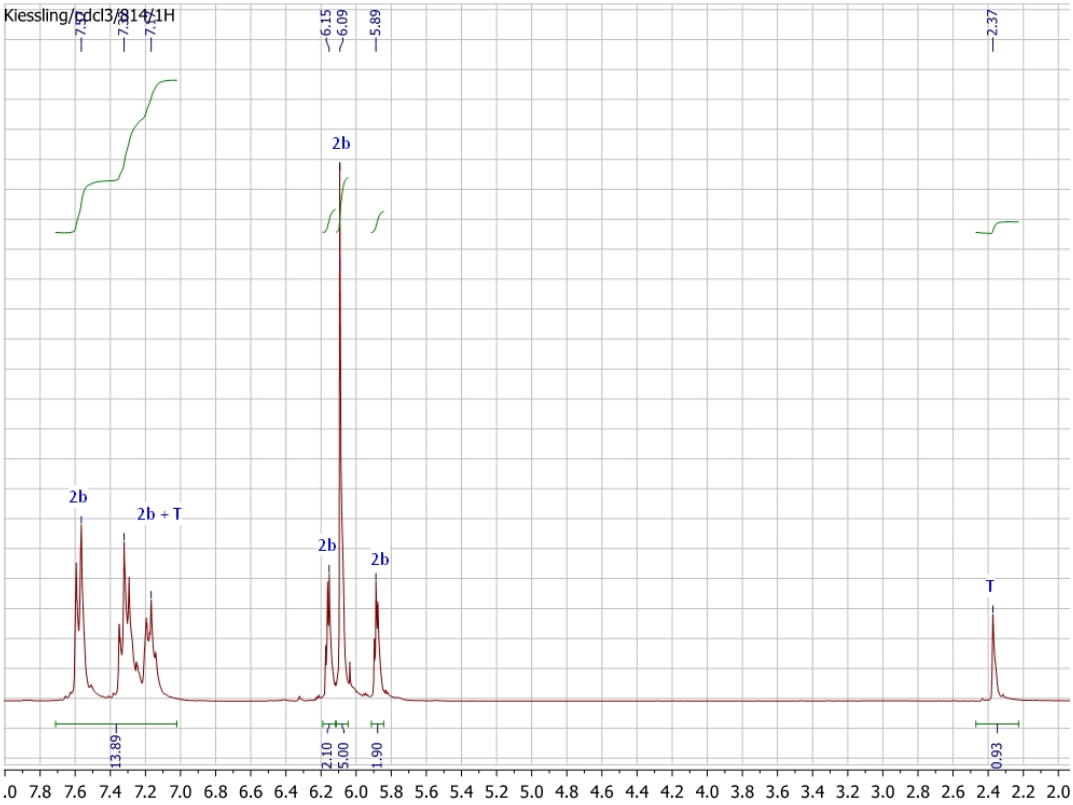


Figure S7: ^{1}H-NMR of 2b in $CDCl_3$. The signals marked with "T" correspond to toluene.

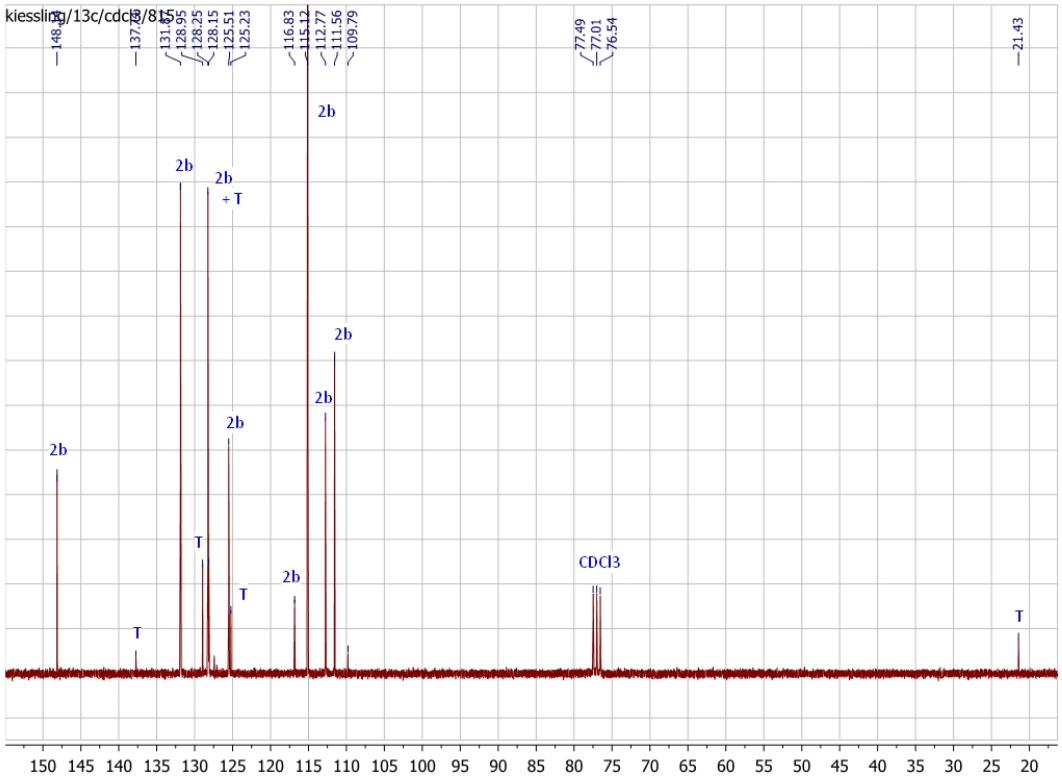


Figure S8: ^{13}C-NMR of 2b in $CDCl_3$. The signals marked with "T" correspond to toluene.

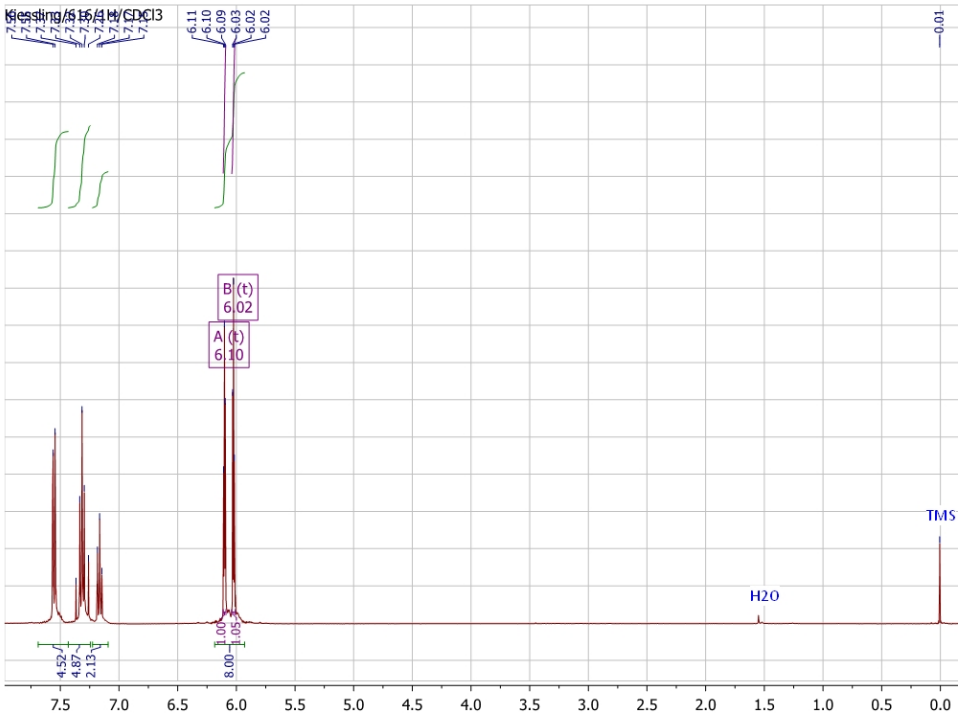


Figure S9: [1]H-NMR of 2c in $CDCl_3$.

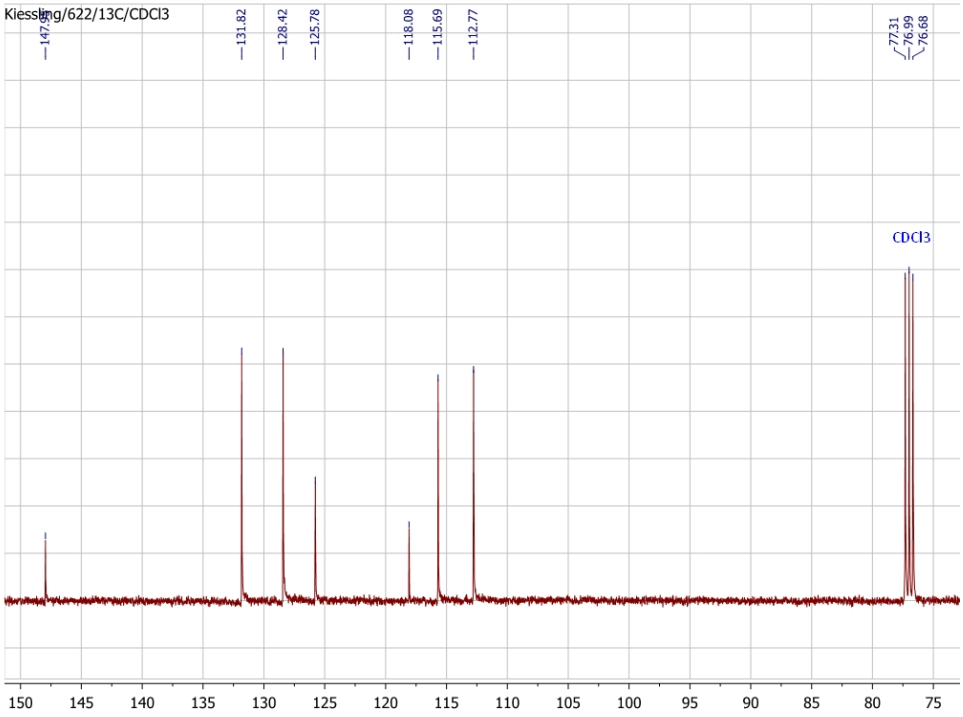


Figure S10: [13]C-NMR of 2c in $CDCl_3$.

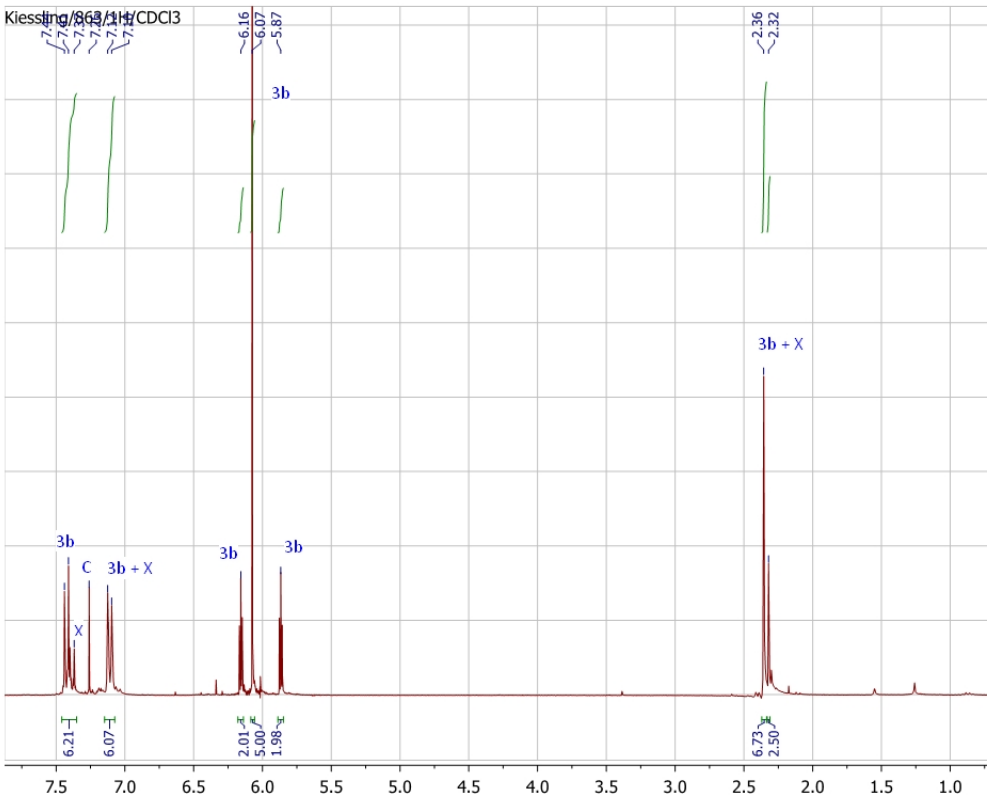


Figure S11: ^{1}H-NMR of 3b in $CDCl_3$. The signal marked with "C" is assigned to $CHCl_3$ solvent; "X" corresponds to an unknown impurity, probably either TolSH or TolSSTol.

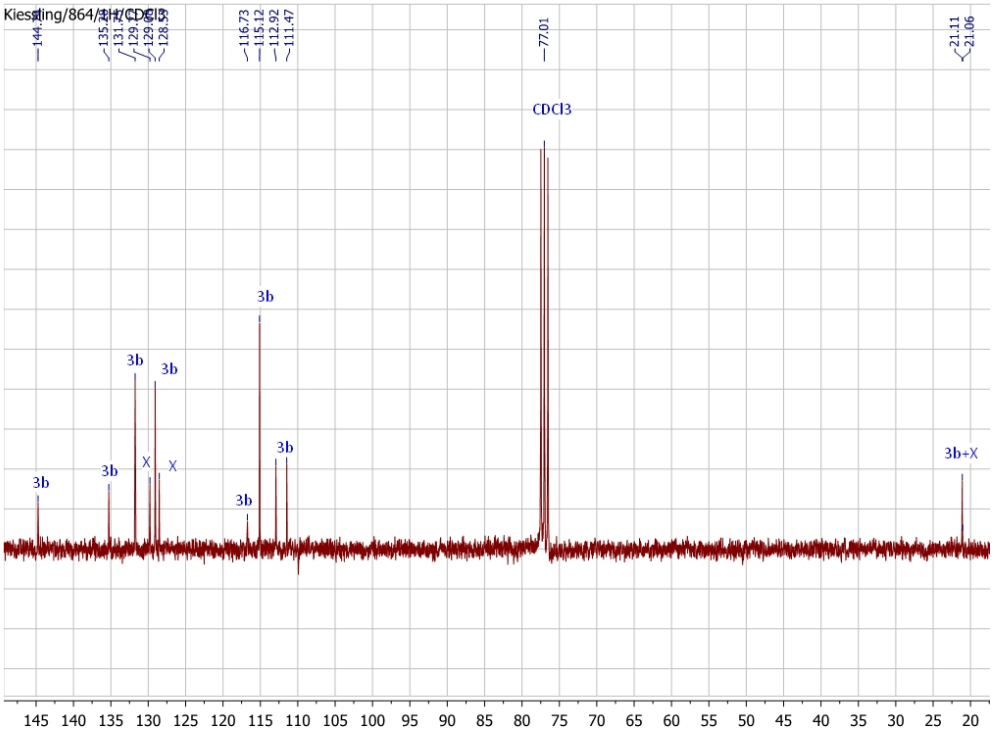


Figure S12: ^{13}C-NMR of 3b in $CDCl_3$. The signals marked with "X" correspond to an unknown impurity probably either TolSH or TolSSTol.

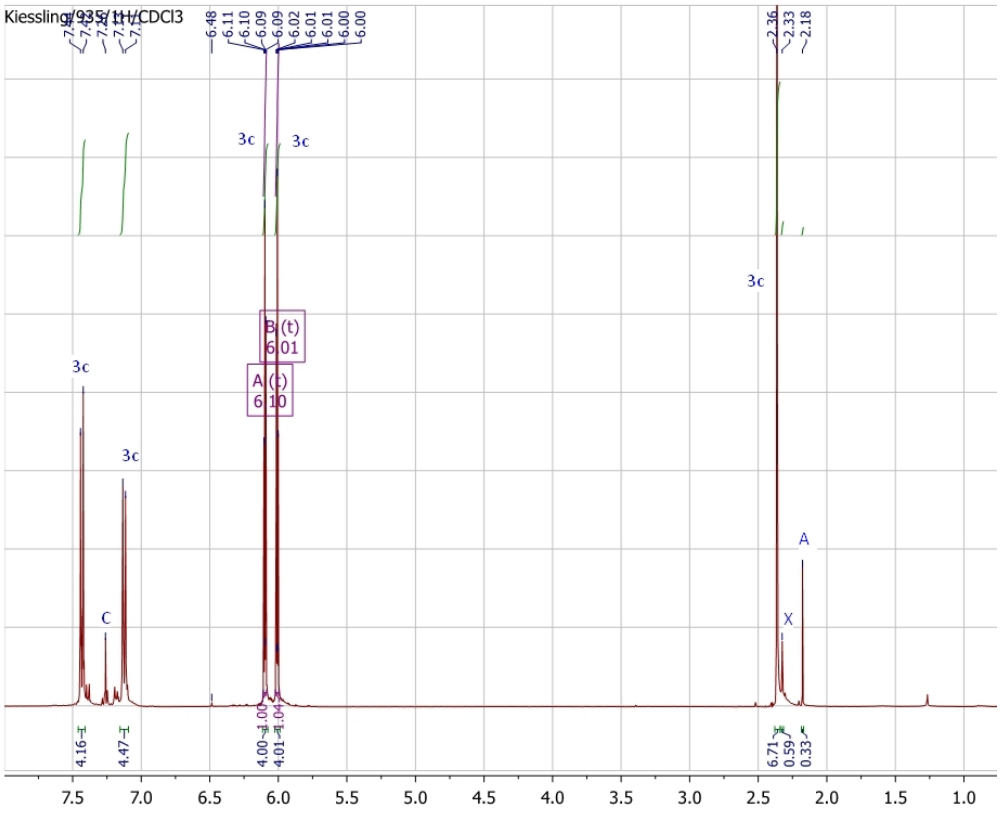


Figure S13: ^{1}H-NMR of 3c in $CDCl_3$. The signal marked with "C" is assigned to $CHCl_3$ solvent, "A" to acetone; "X" corresponds to an unknown impurity, probably either TolSH or TolSSTol.

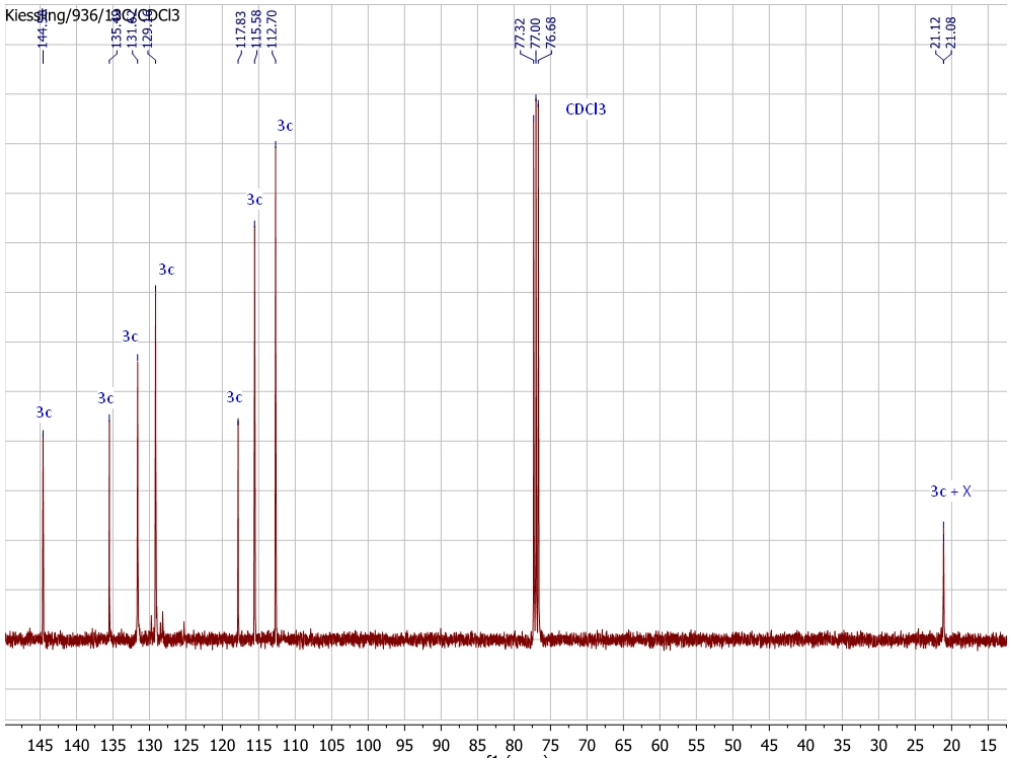


Figure S14: ^{13}C-NMR of 3c in $CDCl_3$. The signal marked with "X" corresponds to an unknown impurity, probably either TolSH or TolSSTol.

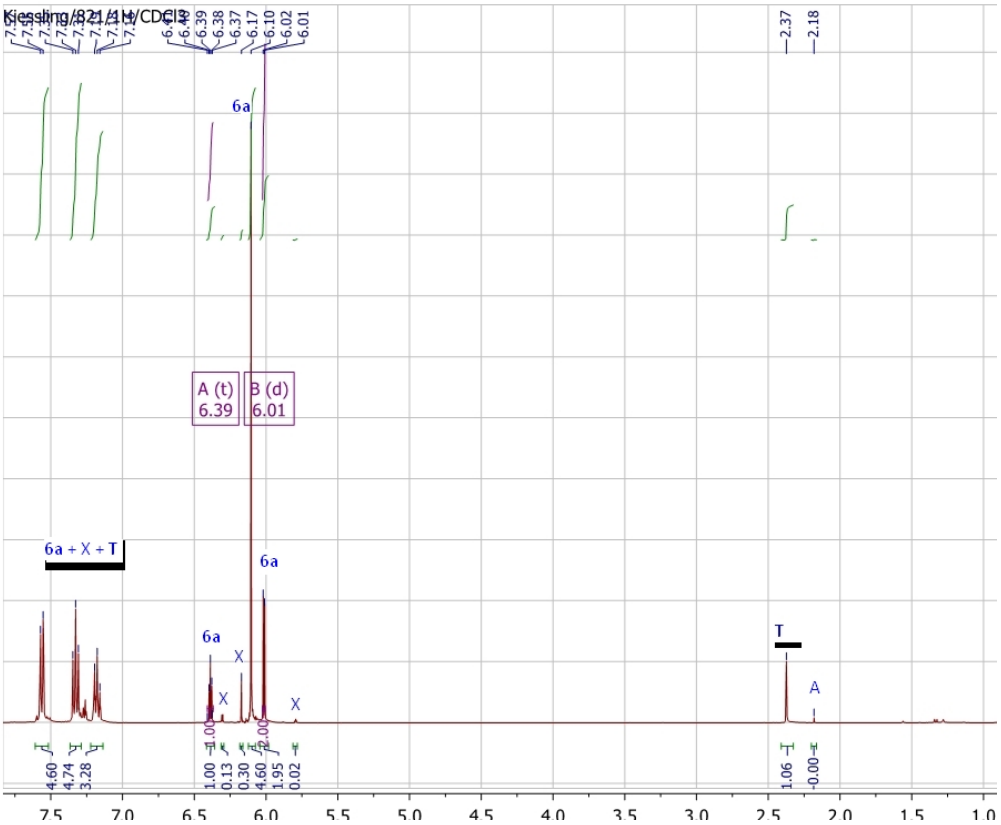


Figure S15: ^{1}H-NMR of 6a in $CDCl_3$. The signals marked with "T" are assigned to toluene residual solvent, "A" to acetone; the signals marked with "X" are most likely from the 1,3-regioisomer of 6a).

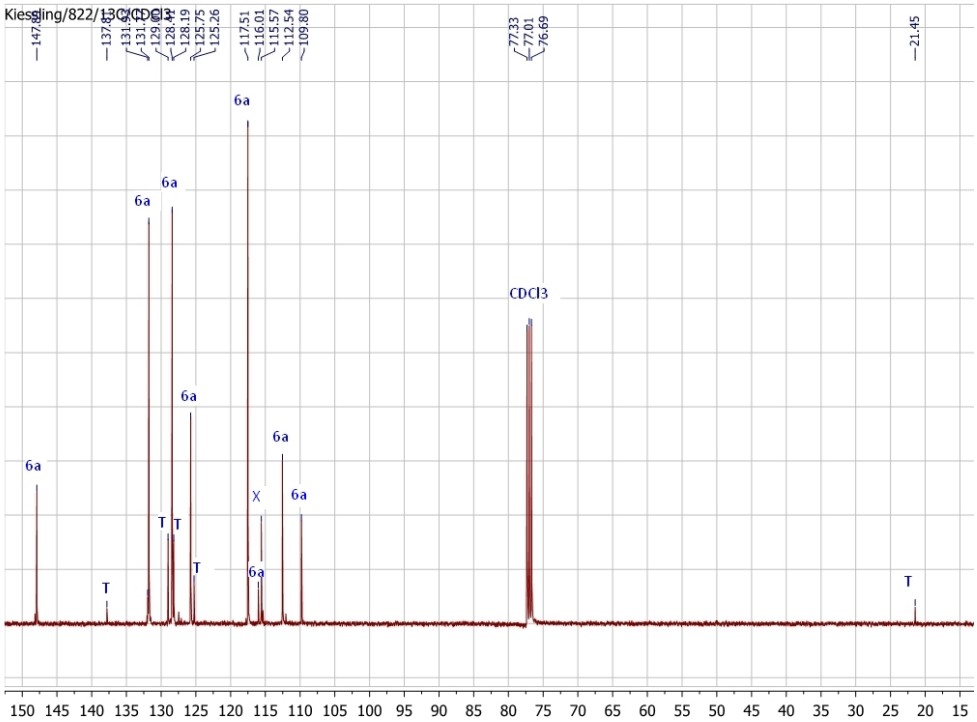


Figure S16: ^{13}C-NMR of 6a in $CDCl_3$. The signals marked with "T" are assigned to toluene residual solvent; the signal marked with "X" is most likely from the 1,3 regioisomer of 6a.

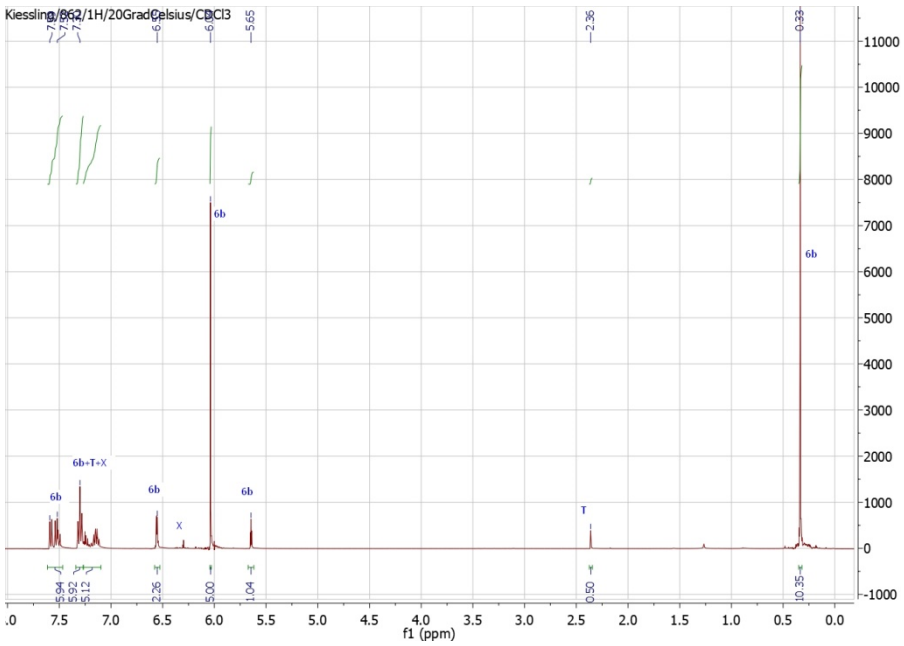


Figure S17: ^{1}H-NMR of 6b in $CDCl_3$. The signals marked with "T" are assigned to toluene residual solvent; the signals marked with "X" are unknown impurities (the signal at ca. 6.3 ppm might be the C_5H_5 signal of $[(C_5H_5)(C_5H_3ClSiMe_3)TiCl(SC_6H_5)]$, the signals between 7.1 and 7.5 ppm might be assigned to residual or liberated PhSH).

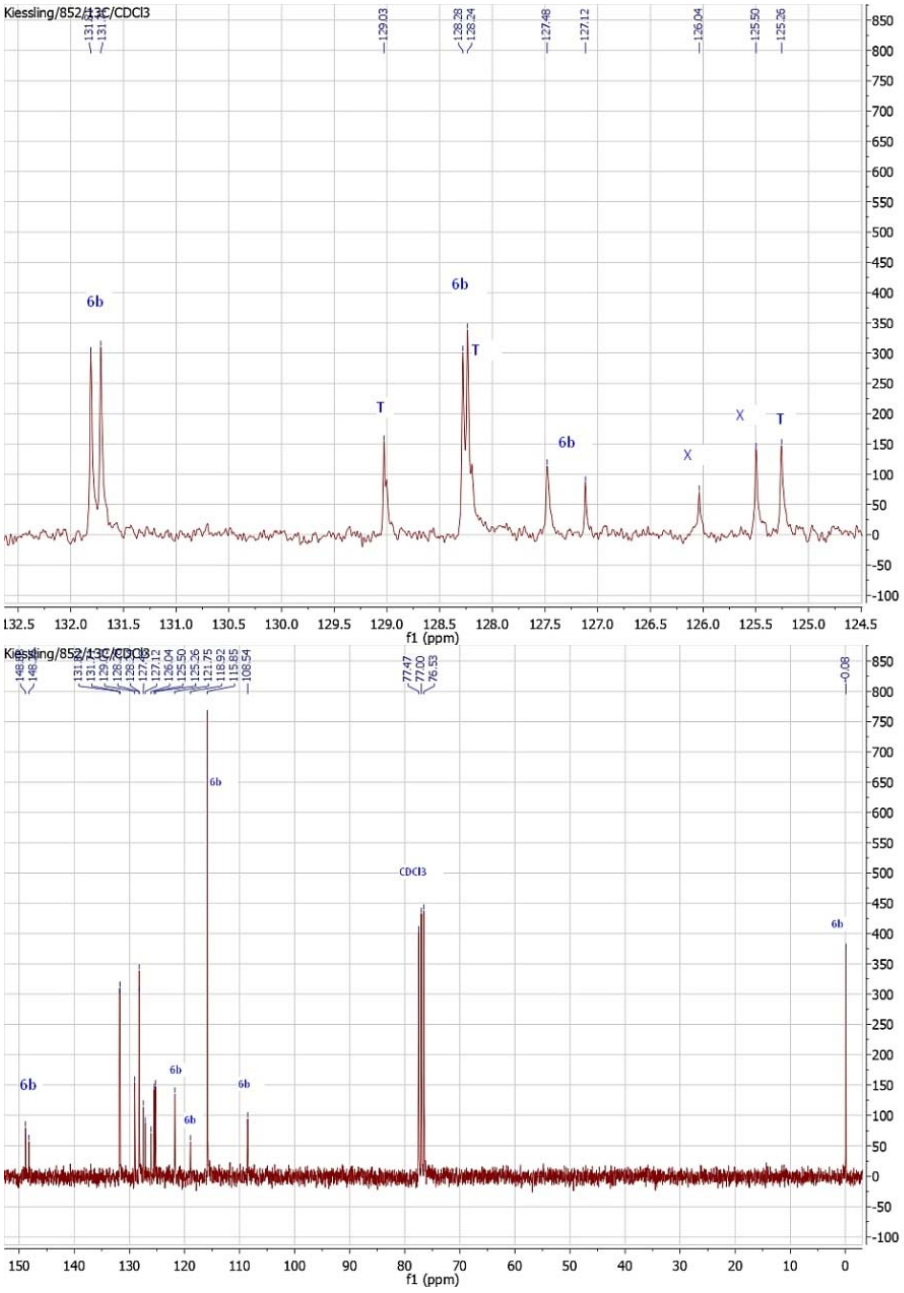


Figure S18: Expanded (top) and full (bottom) ^{13}C-NMR spectrum of 6b in $CDCl_3$. The signals marked with "T" are assigned to toluene residual solvent; the signals marked with "X" are unknown impurities; they might be assigned to residual or liberated PhSH.

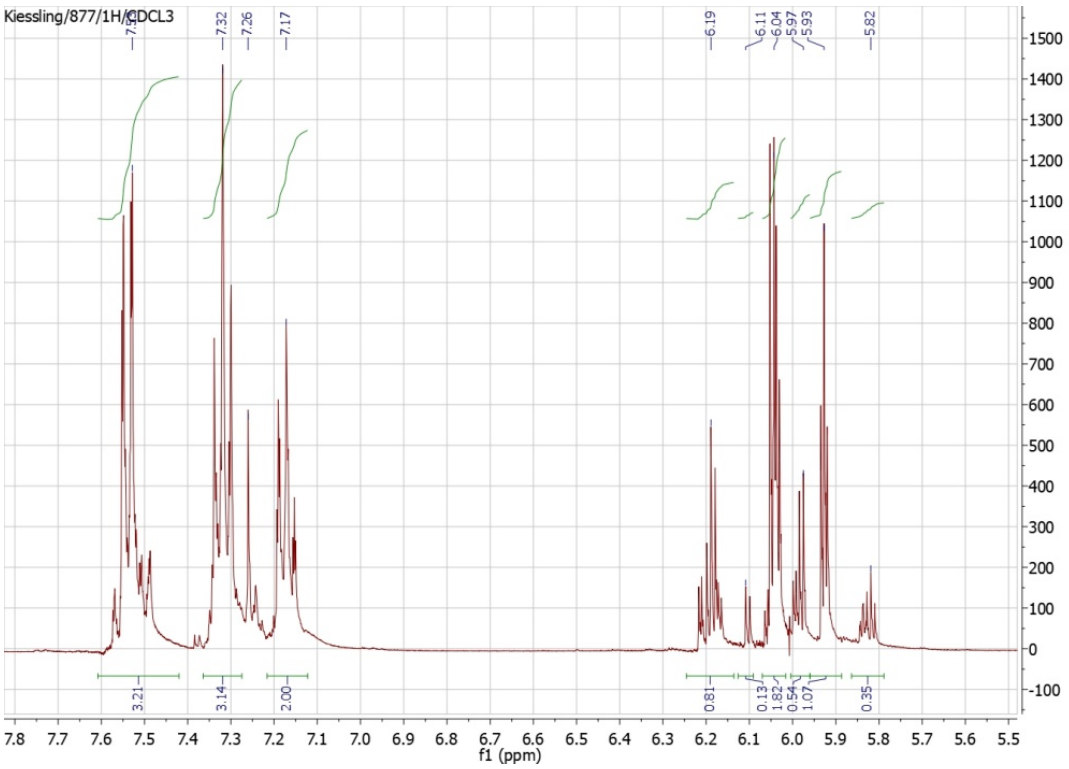


Figure S19: [1]H-NMR spectrum (aromatic region) of the inseparable mixture of 7a and 7b.

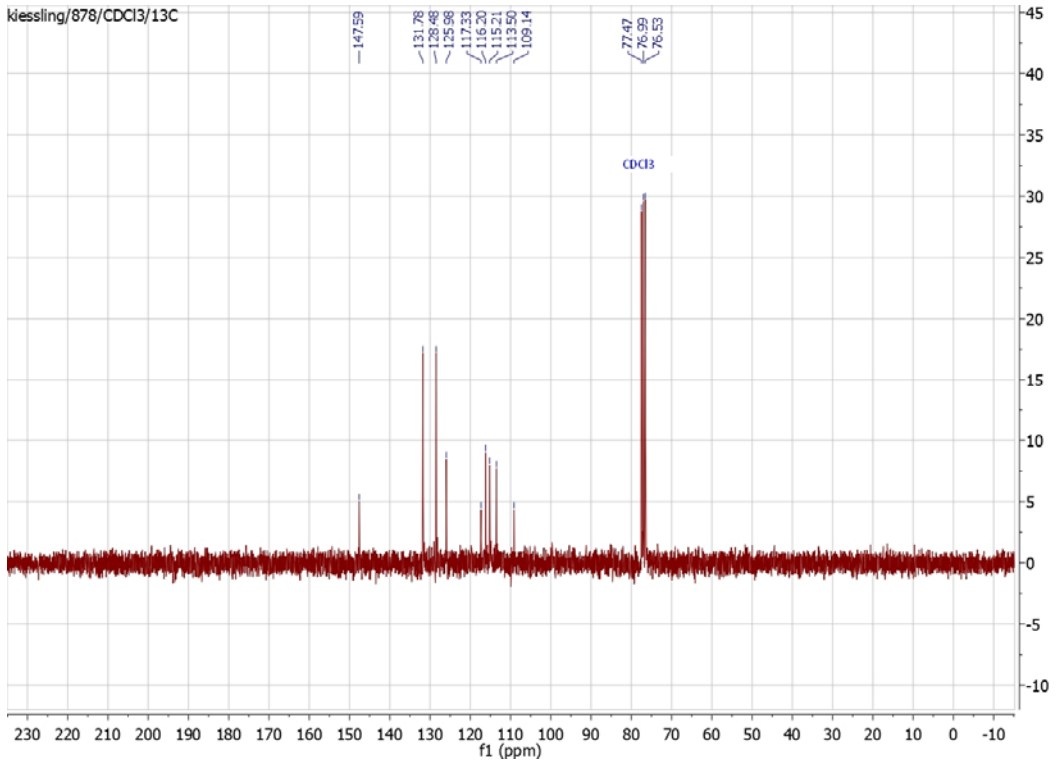


Figure S20: [13]C-NMR spectrum of the inseparable mixture of 7a and 7b.

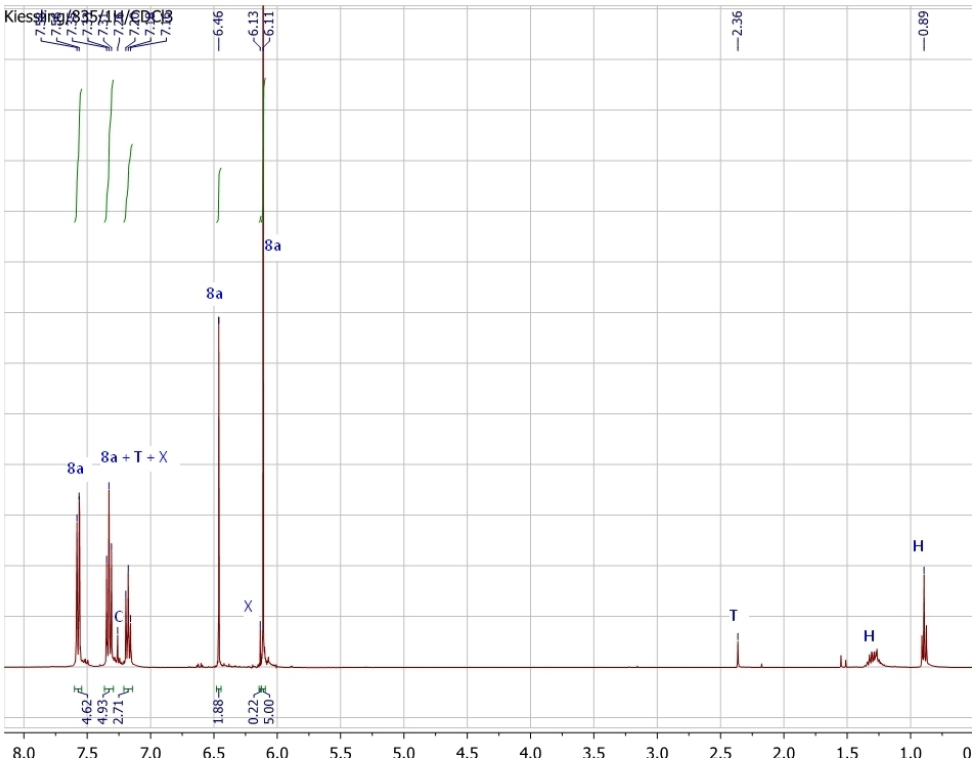


Figure S21: ^{1}H-NMR of 8a in $CDCl_3$. The signals marked with "T" and "H" are assigned to residual toluene and hexane solvent, respectively. The signals marked with"X" are derived from an unknown impurity; the signal at 6.13 ppm can probably be assigned to the 1,2,4-regioisomer of 8a; the signals between 7.1 and 7.5 ppm to residual or liberated PhSH.

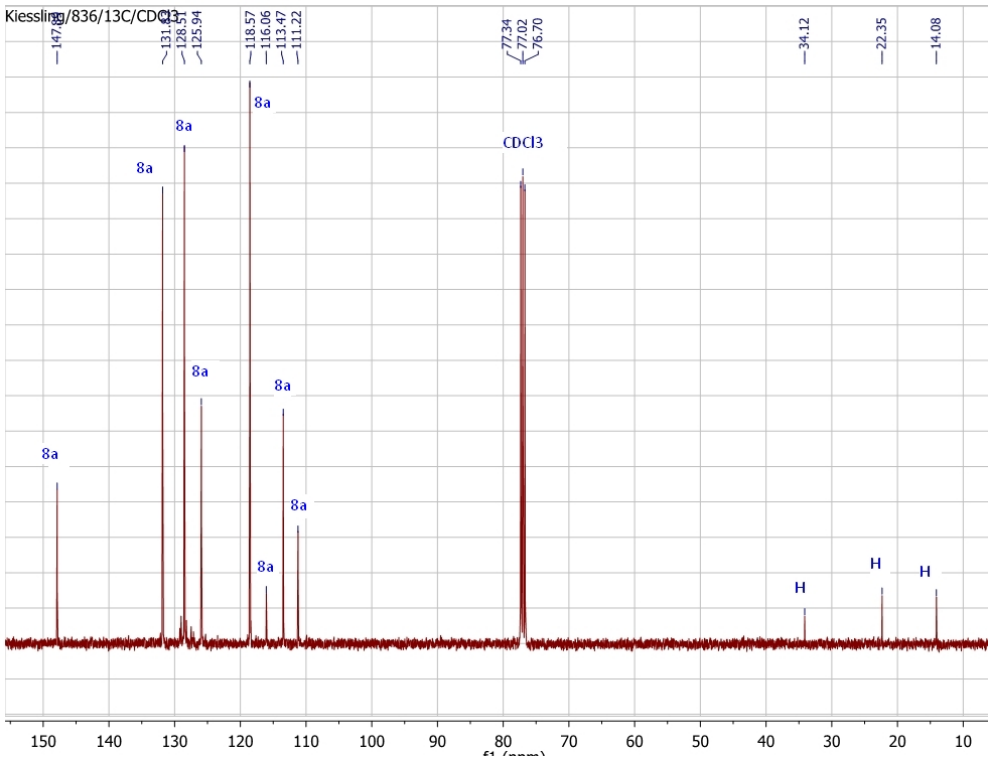


Figure S22: ^{13}C-NMR of 8a in $CDCl_3$. The signals marked with "H" are assigned to residual hexane solvent.

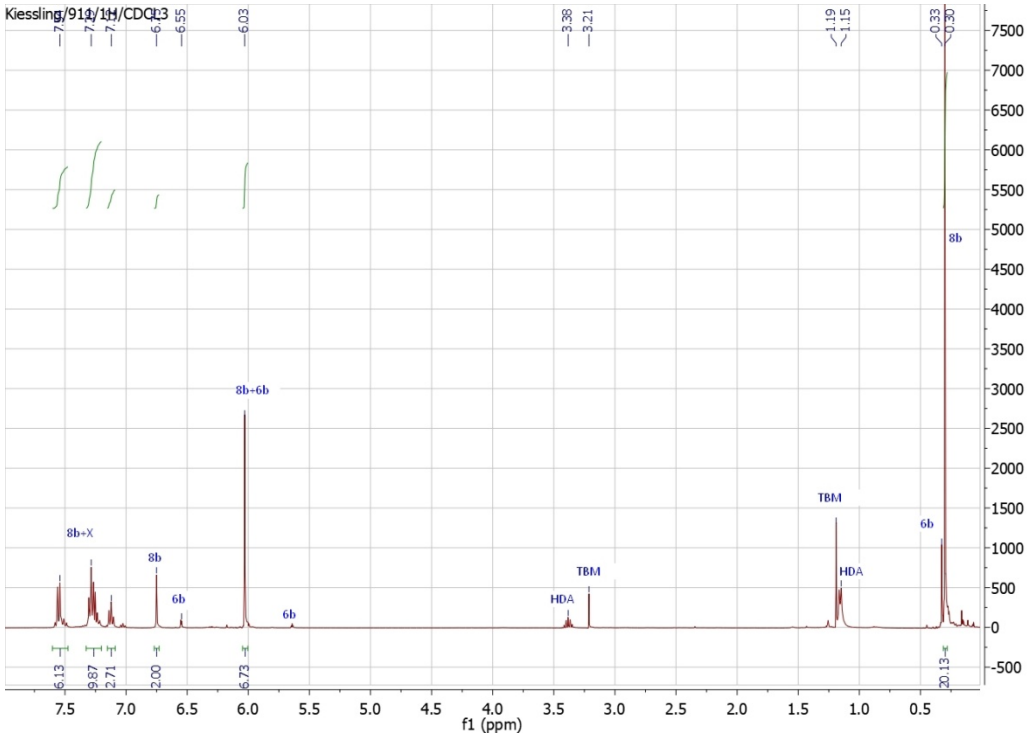


Figure S23: ^{1}H-NMR spectrum of **8b** in $CDCl_3$. The signals marked with "TBM" are assigned to residual tert-butyl-methylether; the signals marked with "HDA" are assigned to residual di-isopropylamine and the ones marked with "X" to an unknown impurity (perhaps residual or liberated PhSH).

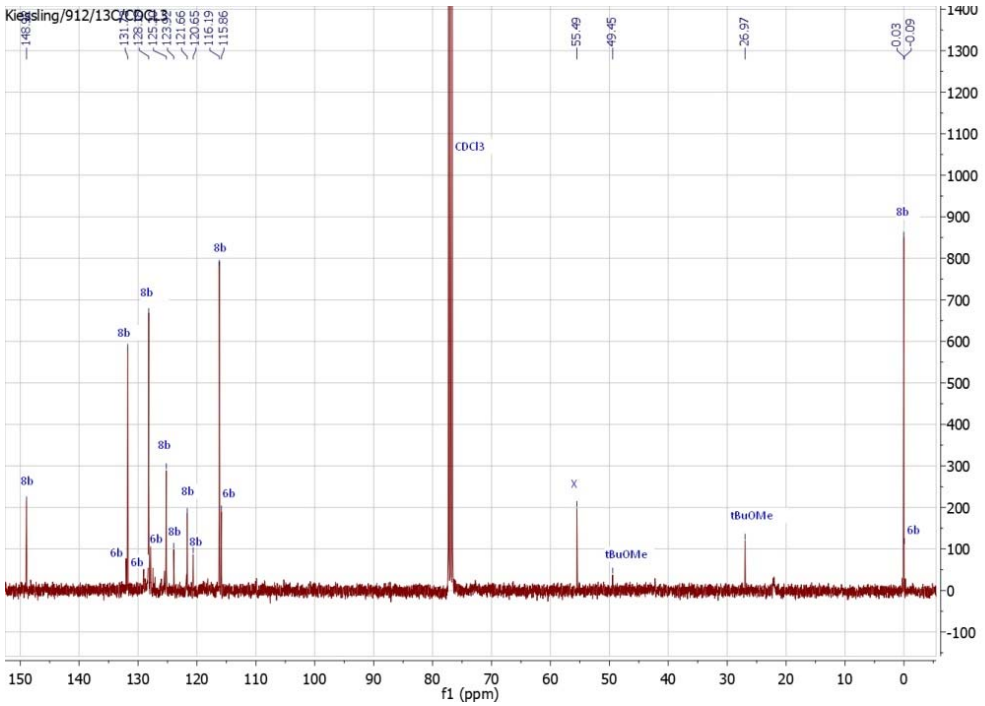
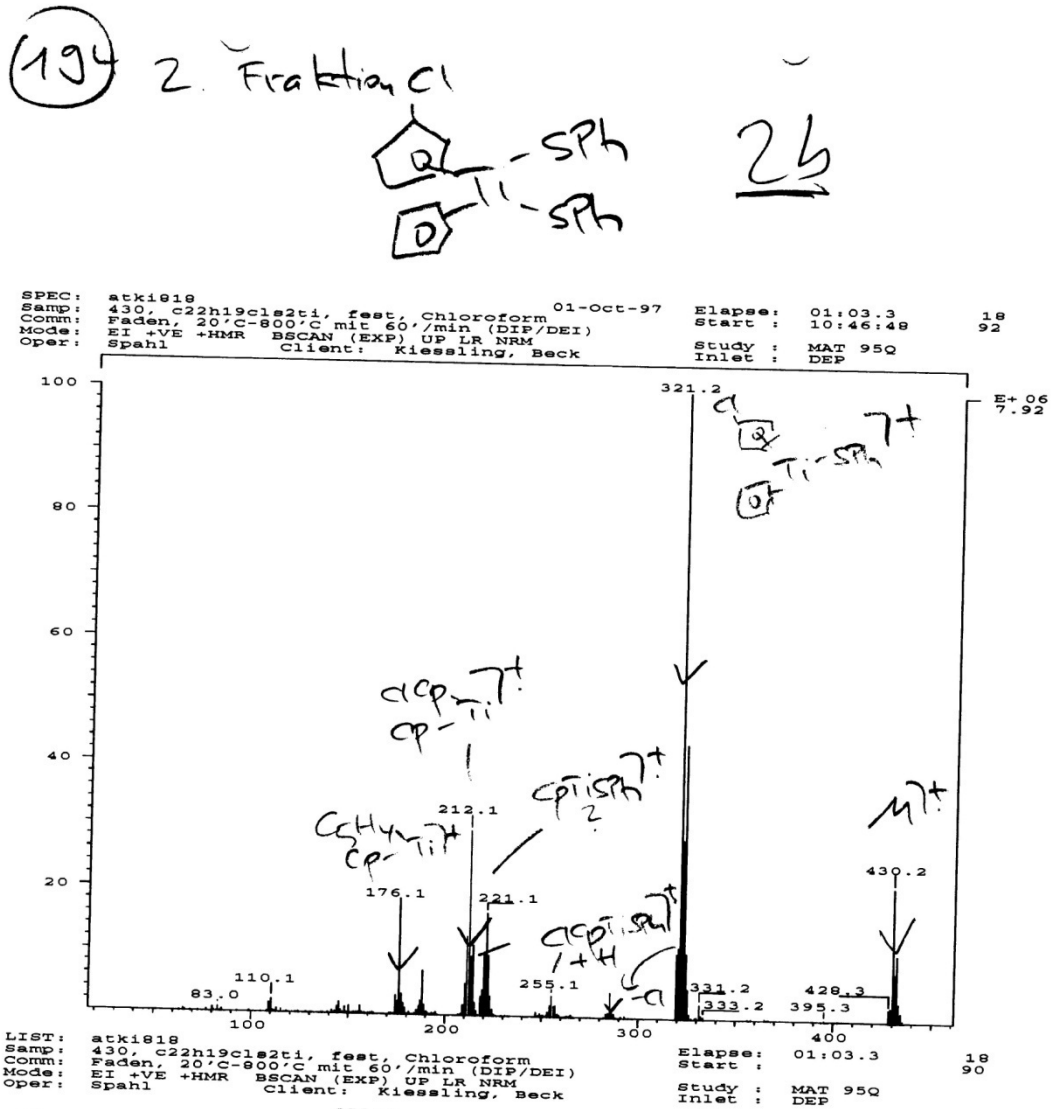


Figure S24: ^{13}C-NMR of 8b in $CDCl_3$. The signal marked with "X" is derived from an unknown impurity.



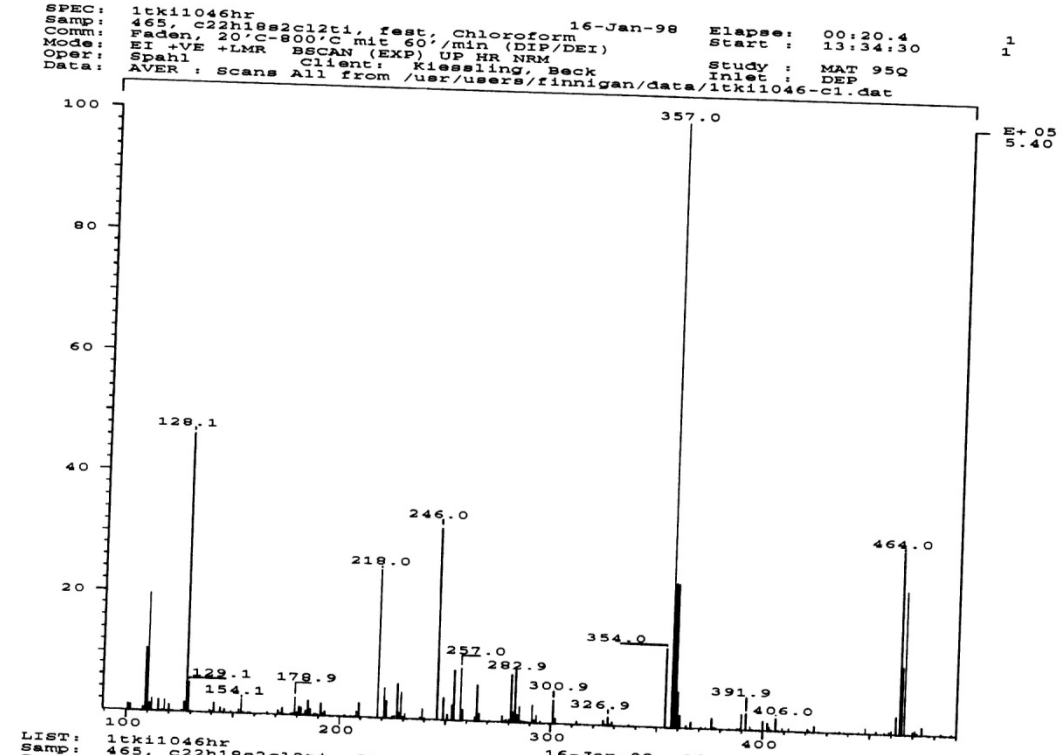
85084

No.	Mass	Intensity	%RA	%RIC	Flags
1	109.1	121997	1.54	0.32	
2	110.1	175319	2.21	0.46	
3	144.1	92932	1.17	0.24	
4	145.1	1412239	1.78	0.37	
5	150.1	98174	1.24	0.26	
6	156.1	95321	1.20	0.25	
7	174.1	238038	3.01	0.63	
8	175.1	173612	2.19	0.46	
9	176.1	14114767	17.87	3.73	
10	177.1	263877	3.33	0.70	
11	178.1	141942	1.79	0.37	
12	186.1	104471	1.32	0.28	
13	187.1	177024	2.24	0.47	
14	188.1	548505	6.93	1.44	
15	189.1	129628	1.64	0.34	
16	209.1	133970	1.69	0.35	
17	210.1	404454	5.11	1.07	
18	211.1	1000666	12.64	2.64	
19	212.1	2320267	29.31	6.11	
20	213.1	744141	9.40	1.96	
21	214.1	885245	11.18	2.33	
22	215.1	162259	2.05	0.43	
23	218.2	249515	3.15	0.66	
24	219.1	324674	4.10	0.86	
25	220.1	803138	10.15	2.12	
26	221.1	1293577	16.34	3.41	
27	222.1	761821	9.62	2.01	
28	223.1	250477	3.16	0.66	
29	224.1	85085	1.07	0.22	
30	254.1	143648	1.81	0.38	
31	255.1	269863	3.41	0.71	
32	256.1	136235	1.72	0.36	
33	257.1	143586	1.81	0.38	
34	285.2	323712	4.09	0.85	
35	286.2	97554	1.23	0.26	
36	319.2	813530	10.28	2.14	
37	320.2	890984	11.26	2.35	
38	321.2	79157778	100.00	20.85	
39	322.2	22366610	28.26	5.89	
40	323.2	34517709	43.61	9.09	
41	324.2	8222091	10.39	2.17	
42	325.2	3727284	4.71	0.98	
43	331.2	1826608	2.31	0.48	
44	428.3	1549399	1.96	0.41	
45	429.2	1840003	2.32	0.48	
46	430.2	16805939	21.24	4.43	
47	431.3	6027757	7.61	1.59	
48	432.2	8361737	10.56	2.20	
49	433.2	2311837	2.92	0.61	
50	434.3	1142427	1.44	0.30	

Figure S25: EI-MS of 2b.

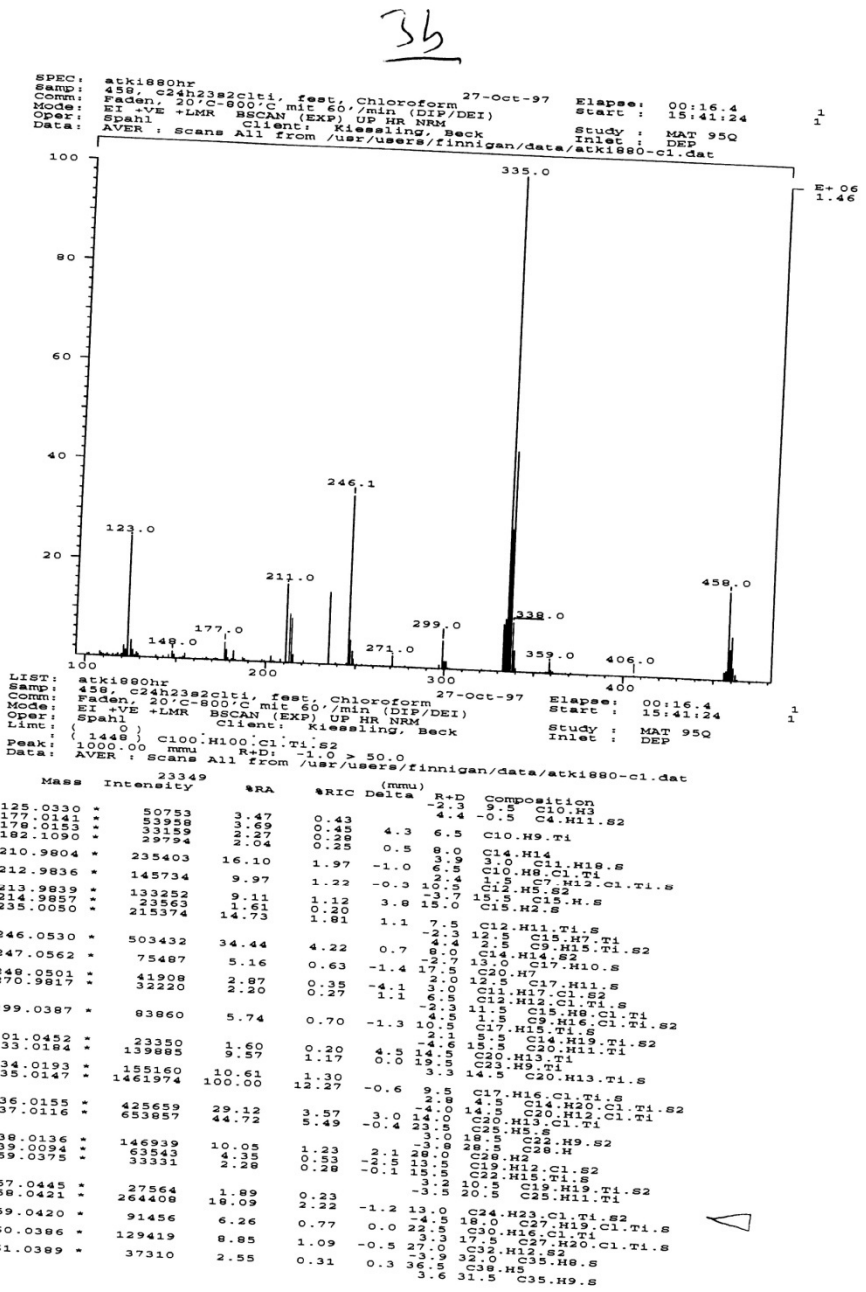
(232) $(CCl_2)Ti(SPh)_2$

2c



Mass	Intensity	%RA	%RIC	Delta (mmu)	R+D	Composition
109.9611 *	105744	13.03	0.98	2.5	5.0	C5.H2.Ti
128.0623 *	249917	30.79	2.31	0.3	7.0	C10.H8
218.0160 *	132219	16.29	1.22	-0.4	3.7 18.0	2.0 C7.H12.S C18.H2
245.9551 *	171730	21.16	1.59	-3.4	3.0 1.0	13.0 C15.H6.S C7.H12.Ti.S.Cl2
353.9813 *	71364	8.79	0.66	-3.0	4.7 9.0	15.0 C15.H2.S2
356.9704 *	540157	66.55	4.99	1.3	13.5	C16.H15.Ti.S2.Cl C19.H11.Ti.Cl2
357.9710 *	128829	15.87	1.19	-3.2	4.7 18.0	8.5 C16.H15.Ti.S.Cl2 C21.H7.S2.Cl
358.9656 *	128212	15.80	1.19	3.2	27.5	C27.Cl
463.9710 *	162995	20.08	1.51	-0.3	13.0 1.1	C22.H18.Ti.S2.Cl2 37.0 C36.S
465.9692 *	127521	15.71	1.18	-1.4	-3.7 18.0 4.5 32.0 27.0 -4.8 32.0	C25.H14.Ti.S.Cl2 C33.H4.S2 C30.H7.S2.Cl C33.H3.S.Cl

Figure S26: HR- EI-MS of 2c.



Mass	Intensity	%RA	%RIC	Delta (mmu)	R+D	Composition
125.0330 *	50753	3.47	0.43		-2.3 9.5	C10.H3
177.0141 *	53958	3.69	0.45		4.4 -0.5	C4.H11.S2
178.0153 *	33159	2.27	0.28	4.3	6.5	C10.H9.Ti
182.1090 *	29794	2.04	0.25	0.5	8.0	C14.H14
210.9804 *	235403	16.10	1.97	-1.0	3.9 3.0	C11.H18.S
212.9836 *	145734	9.97	1.22	-0.3	6.5 2.4 1.5	C10.H8.Cl.Ti C7.H13.Cl.Ti.S
213.9839 *	133252	9.11	1.12	3.8	10.5 -3.7 15.5	C12.H5.S2 C15.H.S
214.9857 *	23563	1.61	0.20		15.0	C15.H2.S
235.0050 *	215374	14.73	1.81	1.1	7.5	C12.H11.Ti.S
246.0530 *	503432	34.44	4.22	0.7	-2.3 12.5 4.4 2.5	C15.H7.Ti C9.H15.Ti.S2
247.0562 *	75487	5.16	0.63	-1.4	8.0 -2.7 13.0	C14.H14.S2 C17.H10.S
248.0501 *	41908	2.87	0.35	-4.1	17.5 2.0 12.5	C20.H7 C17.H11.S
270.9817 *	32220	2.20	0.27	1.1	3.0 6.5	C11.H17.Cl.S2 C12.H12.Cl.Ti.S
299.0387 *	83860	5.74	0.70	-1.3	-2.3 11.5 4.5 1.5 10.5	C15.H8.Cl.Ti C9.H16.Cl.Ti.S2 C17.H15.Ti.S
301.0452 *	23350	1.60	0.20	4.5	2.1 5.5 -4.6 15.5 14.5	C14.H19.Ti.S2 C20.H11.Ti
333.0184 *	139885	9.57	1.17	0.0	19.5	C23.H9.Ti
334.0193 *	155160	10.61	1.30		3.3 14.5	C20.H13.Ti.S
335.0147 *	1461974	100.00	12.27	-0.6	9.5	C17.H16.Cl.Ti.S
336.0155 *	425659	29.12	3.57	3.0	-2.8 4.5 -4.0 14.5 14.0	C14.H20.Cl.Ti.S2 C20.H12.Cl.Ti
337.0116 *	653857	44.72	5.49	-0.4	23.5 3.0	C20.H13.Cl.Ti C25.H5.S
338.0136 *	146939	10.05	1.23	2.1	-3.8 28.5 20.0	C22.H9.S2 C28.H
339.0094 *	63543	4.35	0.53	-2.5	13.5	C20.H2
359.0375 *	33331	2.28	0.28	-0.1	15.5 3.2	C19.H12.Cl.S2 C22.H15.Ti.S
457.0445 *	27564	1.89	0.23		-3.5 10.5 20.5	C19.H19.Ti.S2 C25.H11.Ti
458.0421 *	264408	18.09	2.22	-1.2	13.0 -4.5	C24.H23.Cl.Ti.S2
459.0420 *	91456	6.26	0.77	0.0	18.0 22.5 3.3	C27.H19.Cl.Ti.S C30.H16.Cl.Ti
460.0386 *	129419	8.85	1.09	-0.5	17.5 27.0 -3.9	C27.H20.Cl.Ti.S C32.H12.S2
461.0389 *	37310	2.55	0.31	0.3	32.0 36.5 3.6	C35.H8.S C38.H5 C35.H9.S

Figure S27: HR-EI-MS of 3b.

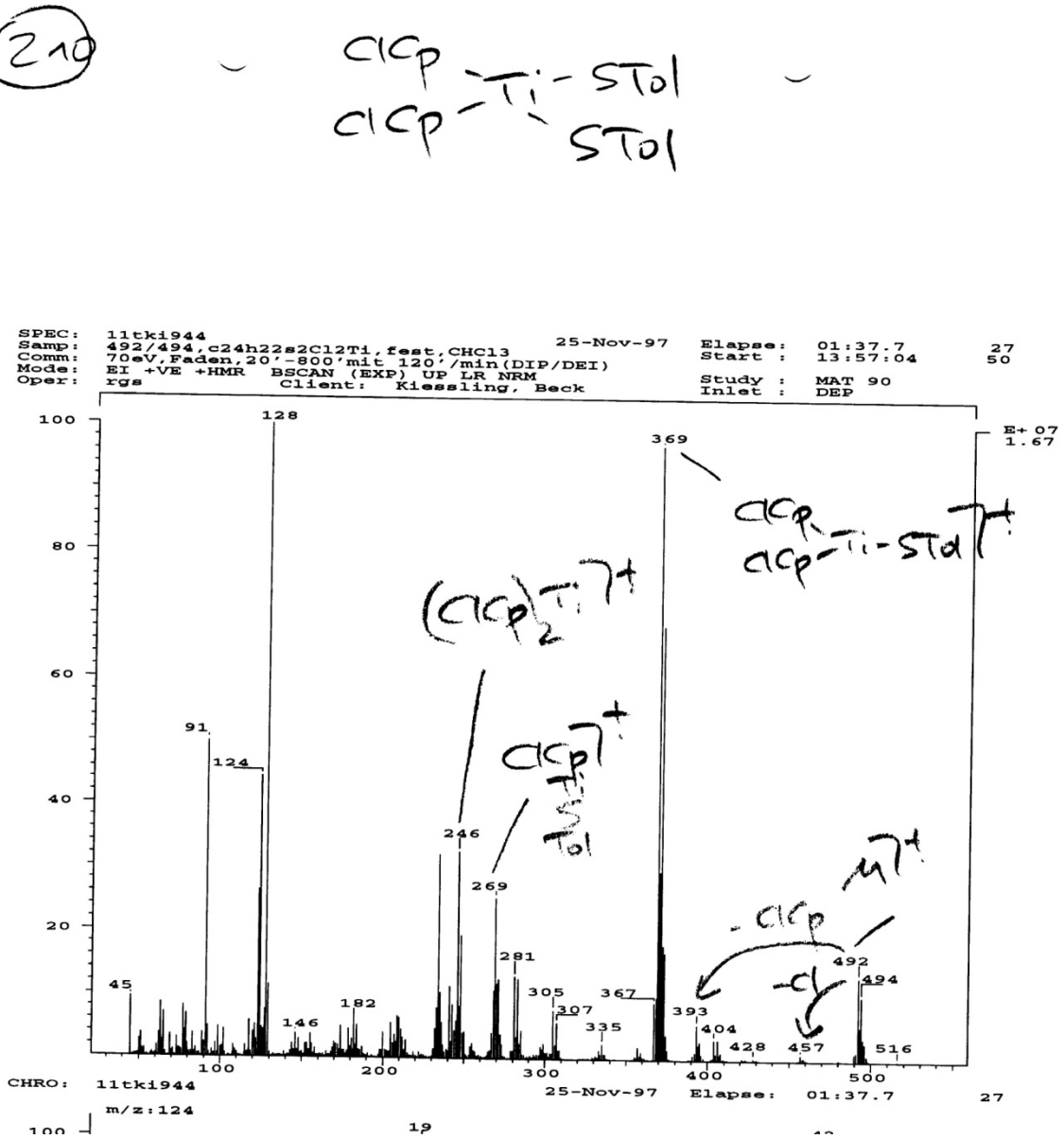
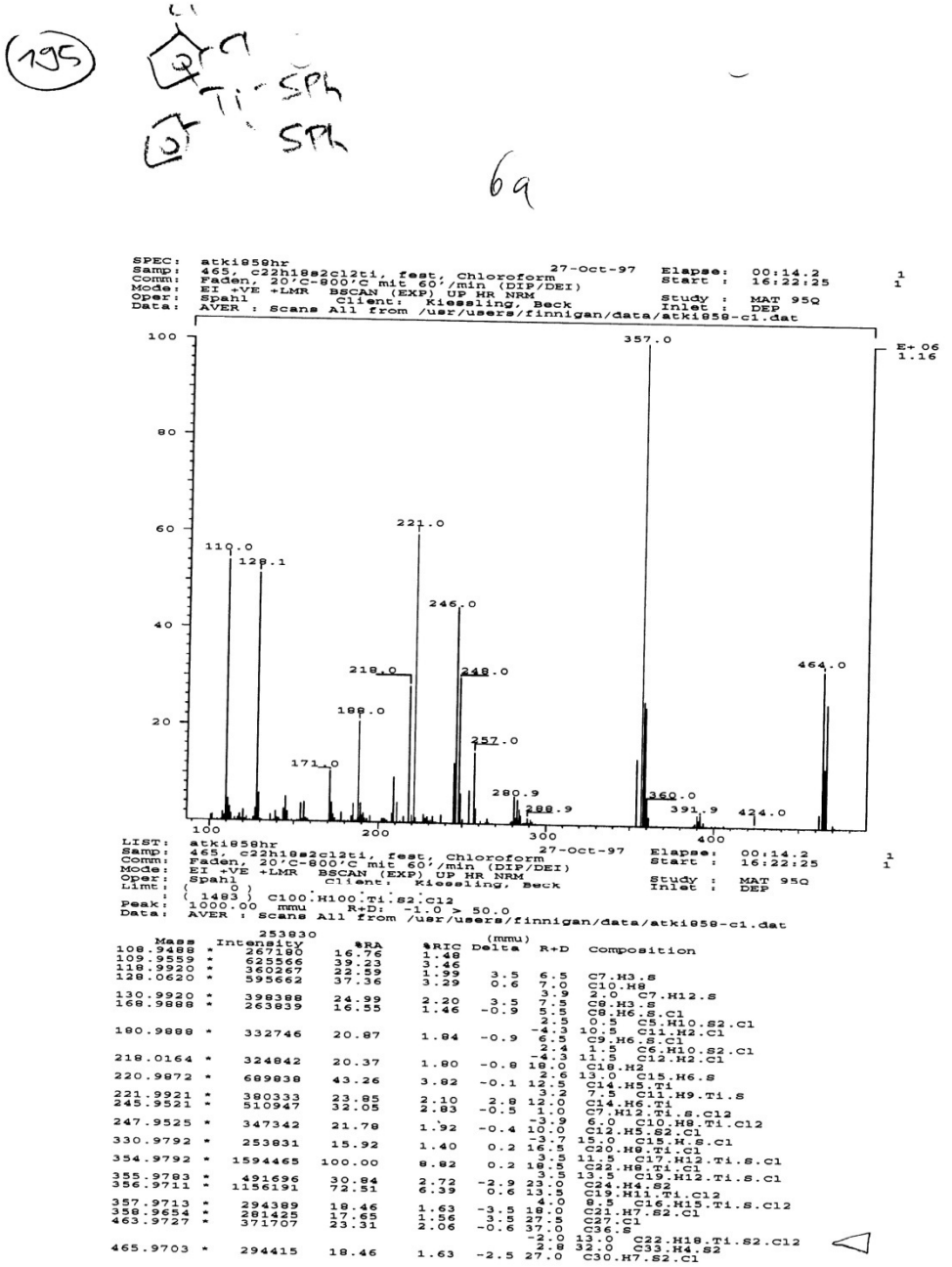
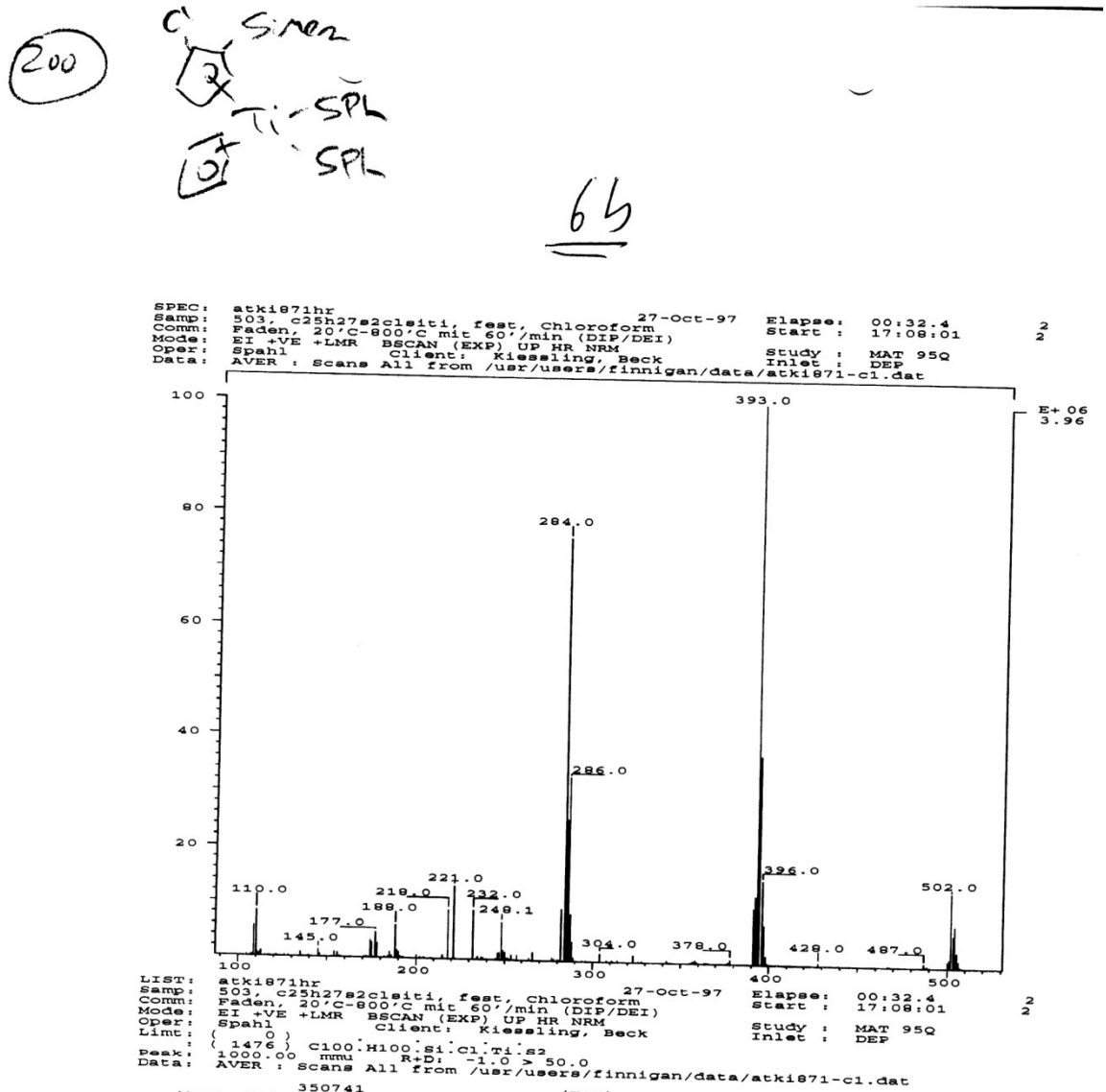


Figure S28: EI-MS of 3c.



Mass	Intensity	%RA	%RIC	(mmu) Delta	R+D	Composition
	253830					
108.9488 *	267180	16.76	1.48			
109.9559 *	625566	39.23	3.46			
118.9920 *	360267	22.59	1.99			
128.0620 *	595662	37.36	3.29	3.5	6.5	C7.H3.S
				0.6	7.0	C10.H8
130.9920 *	398388	24.99	2.20		3.9	2.0 C7.H12.S
168.9888 *	263839	16.55	1.46	3.5	7.5	C8.H3.S
				-0.9	5.5	C8.H6.S.Cl
					2.5	0.5 C5.H10.S2.Cl
180.9888 *	332746	20.87	1.84	-0.9	-4.3	10.5 C11.H2.Cl
					6.5	C9.H6.S.Cl
					2.4	1.5 C6.H10.S2.Cl
218.0164 *	324842	20.37	1.80	-0.8	-4.3	11.5 C12.H2.Cl
					18.0	C18.H2
					2.6	13.0 C15.H6.S
220.9872 *	689838	43.26	3.82	-0.1	12.5	C14.H5.Ti
221.9921 *	380333	23.85	2.10	3.8	7.5	C11.H9.Ti.S
245.9521 *	510947	32.05	2.83	-0.5	12.0	C14.H6.Ti
					1.0	C7.H12.Ti.S.Cl2
247.9525 *	347342	21.78	1.92	-0.4	-3.9	6.0 C10.H8.Ti.Cl2
					10.0	C12.H5.S2.Cl
330.9792 *	253831	15.92	1.40	0.2	-3.7	15.0 C15.H.S.Cl
					16.5	C20.H9.Ti.Cl
354.9792 *	1594465	100.00	8.82	0.2	3.5	11.5 C17.H12.Ti.S.Cl
					18.5	C22.H8.Ti.Cl
355.9783 *	491696	30.84	2.72	-2.9	3.5	13.5 C19.H12.Ti.S.Cl
356.9711 *	1156191	72.51	6.39	0.6	23.0	C24.H4.S2
					13.5	C19.H11.Ti.Cl2
357.9713 *	294389	18.46	1.63	-3.5	4.0	8.5 C16.H15.Ti.S.Cl2
358.9654 *	281425	17.65	1.56	3.5	18.0	C21.H7.S2.Cl
463.9727 *	371707	23.31	2.06	-0.6	27.5	C27.Cl
					37.0	C36.S
					-2.0	13.0 C22.H18.Ti.S2.Cl2
					2.8	32.0 C33.H4.S2
465.9703 *	294415	18.46	1.63	-2.5	27.0	C30.H7.S2.Cl

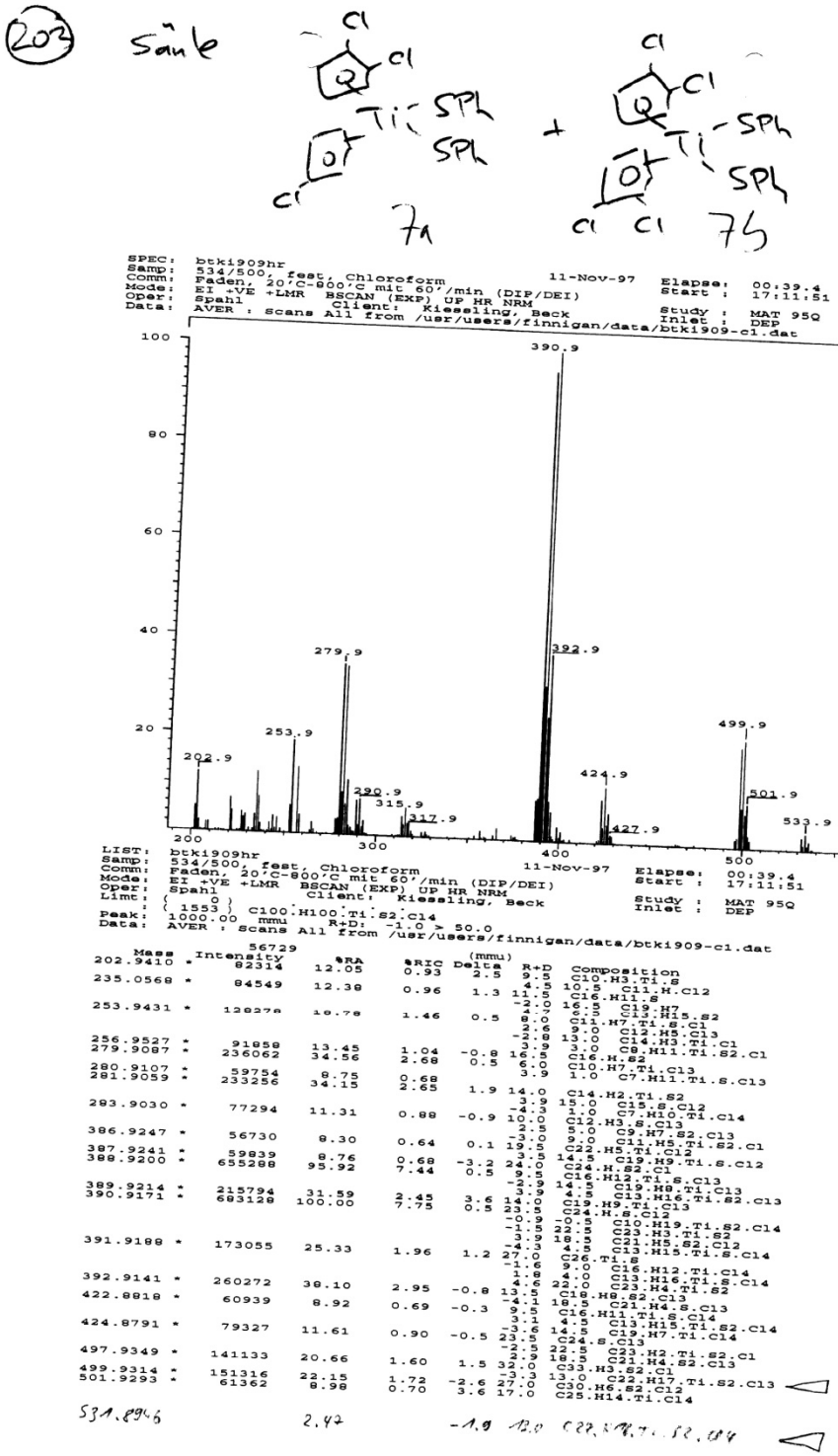
Figure S29: HR-EI-MS of 6a.



350741

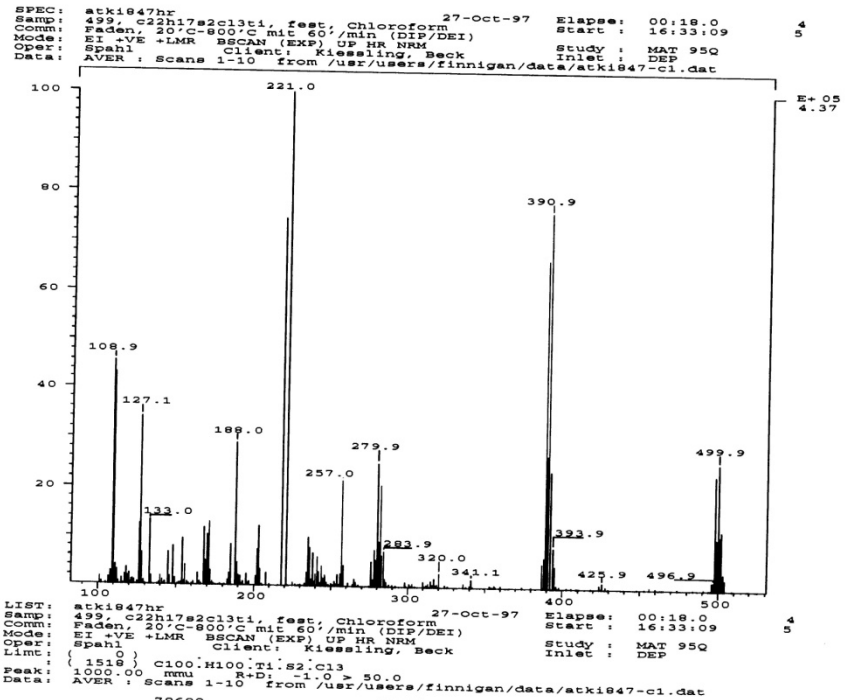
Mass	Intensity	%RA	%RIC	Delta (mmu)	R+D	Composition
176.0108 *	1049264	26.53	3.62	-0.3	7.0	C10.H8.Ti
					0.8	7.0 C9.H8.Si.S
					-2.6	12.0 C12.H4.Si
					3.1	2.0 C7.H12.Ti.S
					4.2	2.0 C6.H12.Si.S2
220.9857 *	518931	13.12	1.79	-0.9	17.5	C16.H.Si
					1.4	12.5 C14.H5.Ti
					2.4	12.5 C13.H5.Si.S
232.0121 *	350742	8.87	1.21	-0.7	4.7	7.5 C11.H9.Ti.S
					9.0	C13.H9.Cl.S
					2.6	4.0 C10.H13.Cl.S2
282.0126 *	369874	9.35	1.28	-1.5	-4.1	14.0 C16.H5.Cl
					7.0	C13.H15.Si.Cl.Ti
283.0119 *	609614	15.39	2.10	-2.5	1.8	2.0 C10.H19.Si.Cl.Ti.S
					6.5	C13.H15.Ti.S2
284.0153 *	2992930	75.66	10.34	-0.3	-4.8	11.5 C15.H11.Si.S2
					11.0	C15.H12.Si.S2
					-1.3	11.0 C16.H12.Ti.S
					-2.0	6.0 C13.H16.Ti.S2
					-3.7	16.0 C10.H8.Si.S
285.0171 *	1007305	25.47	3.48	-1.1	-4.7	16.0 C19.H8.Ti
					20.5	C21.H5.Si
					1.2	15.5 C19.H9.Ti
					2.3	15.5 C10.H9.Si.S
286.0158 *	1304159	32.97	4.50		4.6	10.5 C16.H13.Ti.S
391.0377 *	399923	10.11	1.38	0.5	15.5	C23.H16.Cl.S2
					-2.9	20.5 C26.H12.Cl.S
392.0377 *	480801	12.16	1.66	1.5	4.5	19.5 C25.H15.Si.Ti
					25.0	C29.H9.Cl
					-4.2	5.0 C16.H25.Si.Cl.Ti.S2
393.0347 *	3955560	100.00	13.66	-0.1	4.9	20.0 C26.H13.Cl.S
394.0368 *	1470181	37.17	5.08	-3.9	14.5	C22.H18.Si.Cl.Ti
395.0330 *	1954432	49.41	6.75	1.0	3.3	9.5 C19.H22.Si.Cl.Ti.S
					14.0	C22.H18.Ti.S2
					23.5	C28.H11.Ti
					-1.3	28.5 C30.H7.Si
396.0351 *	593892	15.01	2.05	4.4	2.0	23.5 C27.H11.Si.S
502.0493 *	529732	13.39	1.83	-0.2	4.4	18.5 C25.H15.Ti.S
					28.0	C30.H8.Si
					13.0	C25.H27.Si.Cl.Ti.S2
					-3.6	19.0 C28.H23.Si.Cl.Ti.S

Figure S30: HR-EI-MS of 6b.



Mass	Intensity	%RA	%RIC	Delta (mmu)	R+D	Composition
202.9410 *	82314	12.05	0.93	2.5	9.5	C10.H3.Ti.S
					4.5	10.5 C11.H.Cl2
235.0568 *	84549	12.38	0.96	1.3	11.5	C16.H11.S
					-2.0	16.5 C19.H7
253.9431 *	128278	18.78	1.46	0.5	6.5	C13.H15.S2
					8.0	C11.H7.Ti.S.Cl
					2.6	9.0 C12.H5.Cl3
256.9527 *	91858	13.45			-2.8	13.0 C14.H3.Ti.Cl
279.9087 *	236062	34.56	1.04	-0.8	3.9	3.0 C8.H11.Ti.S2.Cl
			2.68	0.5	16.5	C16.H.S2
280.9107 *	59754	8.75			6.0	C10.H7.Ti.Cl3
281.9059 *	233256	34.15	0.68		3.9	1.0 C7.H11.Ti.S.Cl3
			2.65	1.9	14.0	C14.H2.Ti.S2
283.9030 *	77294	11.31	0.88	-0.9	3.9	15.0 C15.S.Cl2
					-4.3	1.0 C7.H10.Ti.Cl4
					10.0	C12.H3.S.Cl3
386.9247 *	56730	8.30	0.64	0.1	2.5	5.0 C9.H7.S2.Cl3
					-3.0	9.0 C11.H5.Ti.S2.Cl
387.9241 *	59839	8.76	0.68	-3.2	19.5	C22.H5.Ti.Cl2
388.9200 *	655288	95.92	7.44	0.5	3.5	14.5 C19.H9.Ti.S.Cl2
					24.0	C24.H.S2.Cl
					9.5	C16.H12.Ti.S.Cl3
389.9214 *	215794	31.59	2.45	3.6	-2.9	14.5 C19.H8.Ti.Cl3
390.9171 *	683128	100.00	7.75	0.5	3.5	4.5 C13.H16.Ti.S2.Cl3
					14.0	C19.H9.Ti.Cl3
					23.5	C24.H.S.Cl2
					-0.9	-0.5 C10.H19.Ti.S2.Cl4
					-1.5	22.5 C23.H3.Ti.S2
391.9188 *	173055	25.33	1.96	1.2	3.9	18.5 C21.H5.S2.Cl2
					-4.3	4.5 C13.H15.Ti.S.Cl4
					27.0	C26.Ti.S
					-1.6	9.0 C16.H12.Ti.Cl4
392.9141 *	260272	38.10	2.95	-0.8	1.8	4.0 C13.H16.Ti.S.Cl4
					4.6	22.0 C23.H4.Ti.S2
422.8918 *	60939	8.92	0.69	-0.3	13.5	C16.H8.S2.Cl3
					-4.1	18.5 C21.H4.S.Cl3
424.8791 *	79327	11.61	0.90	-0.5	9.5	C16.H11.Ti.S.Cl4
					3.1	4.5 C13.H15.Ti.S2.Cl4
					-3.6	14.5 C19.H7.Ti.Cl4
497.9349 *	141133	20.66	1.60	1.5	23.5	C24.S.Cl3
					-2.5	22.5 C23.H2.Ti.S2.Cl
					2.9	18.5 C21.H4.S2.Cl3
499.9314 *	151316	22.15	1.72	-2.6	32.0	C33.H3.S2.Cl
501.9293 *	61362	8.98	0.70	3.6	-3.3	13.0 C22.H17.Ti.S2.Cl3
					17.0	C25.H14.Ti.Cl4
531.8946		2.42			-1.9	12.0 C22.H7.Ti.S2.Cl4

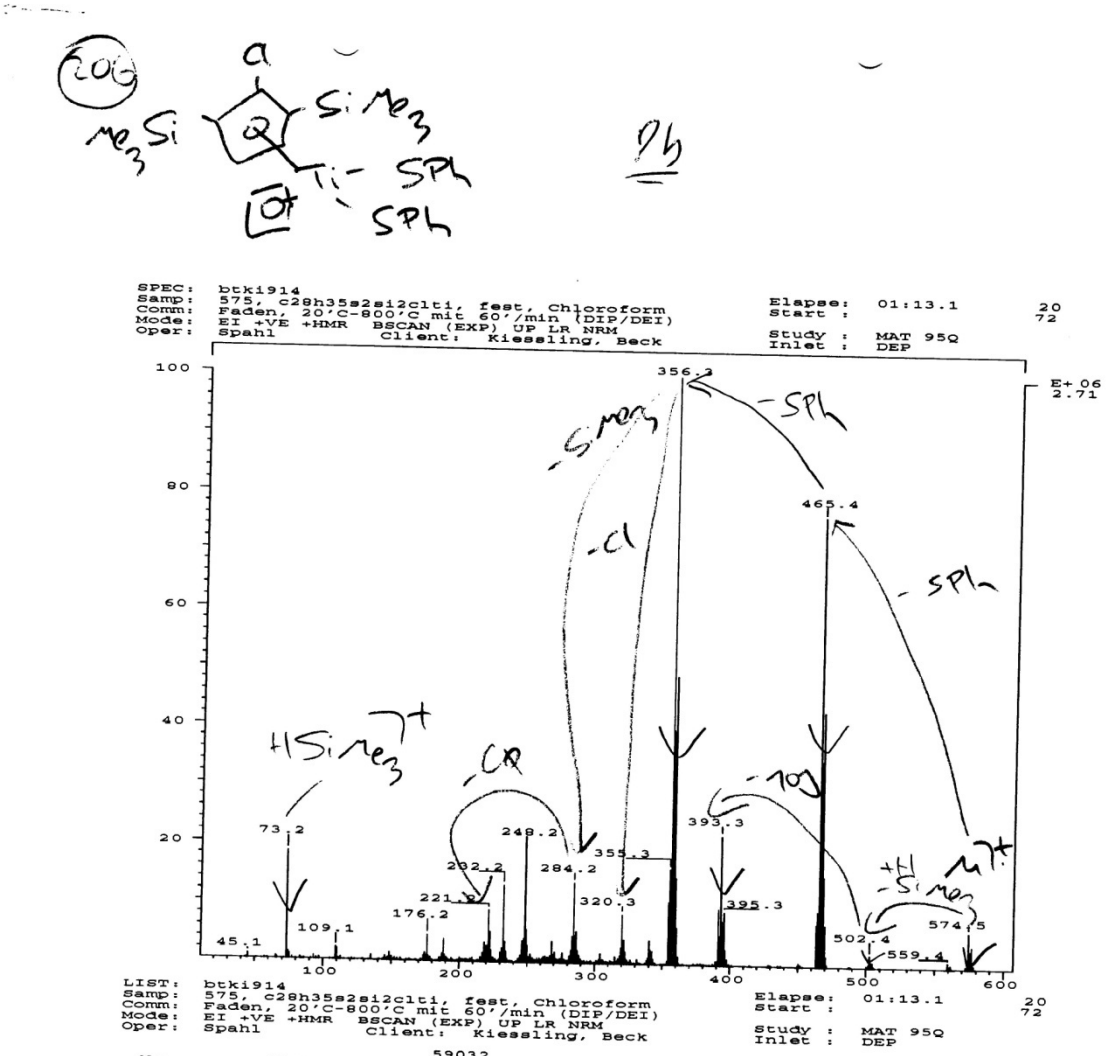
Figure S31: HR-EI-MS of 7a+7b.



78688

Mass		Intensity	%RA	%RIC	Delta (mmu)	R+D	Composition
130.9918	*	330182	75.61	3.59	3.7	4.3	C7.H11.S
168.9888	*	189188	43.32	2.06	-0.9	7.5	C8.H3.S
						5.5	C8.H6.S.Cl
						2.4	0.5 C5.H10.S2.Cl
180.9888	*	255065	58.41	2.77	-1.0	-4.3	10.5 C11.H2.Cl
						6.5	C9.H6.S.Cl
						2.4	1.5 C6.H10.S2.Cl
188.0109	*	126322	28.93	1.37	-0.3	-4.3	11.5 C12.H2.Cl
						8.0	C11.H8.Ti
						3.0	3.0 C8.H12.Ti.S
218.0165	*	325990	74.65	3.54	-0.8	10.0	C10.H2
						2.6	13.0 C15.H6.S
218.9912	*	164936	37.77	1.79		4.1	7.5 C11.H9.Ti.S
219.9935	*	113539	26.00	1.23	-2.1	-1.0	C6.H14.S2.Cl2
220.9863	*	436681	100.00	4.75	0.8	12.5	C14.H5.Ti
						4.1	7.5 C11.H9.Ti.S
221.9901	*	199446	45.67	2.17	4.8	12.0	C14.H6.Ti
222.9864	*	78689	18.02	0.86	-1.6	3.5	C9.H10.Cl3
						-3.7	2.5 C8.H12.Ti.S.Cl
230.9879	*	146736	33.60	1.60	-4.3	0.5	C7.H13.S2.Cl2
242.9956	*	94276	21.59	1.02	-2.1	1.5	C8.H13.S2.Cl2
256.9719	*	93922	21.51	1.02	0.7	2.5	C9.H13.S.Cl3
						-1.4	1.5 C8.H14.Ti.S2.Cl
						-2.7	7.5 C12.H8.Cl3
						-4.8	6.5 C11.H10.Ti.S.Cl
279.9102	*	109642	25.11	1.19	-1.0	6.0	C10.H7.Ti.Cl3
280.9824	*	101789	23.31	1.11	4.6	2.4	1.0 C7.H11.Ti.S.Cl3
281.9050	*	90276	20.67	0.98	2.8	17.5	C19.H5.Ti
						14.0	C14.H2.Ti.S2
316.9820	*	94498	21.64	1.03		4.8	15.0 C15.S.Cl2
330.9792	*	359586	82.35	3.91	0.2	16.5	C20.H8.Ti.Cl
331.9888	*	86497	19.81	0.94	-1.6	3.5	14.5 C17.H12.Ti.S.Cl
						16.0	C20.H9.Ti.Cl
						1.8	11.0 C17.H13.Ti.S.Cl
388.9207	*	290992	66.64	3.16	-0.2	3.8	12.0 C18.H11.Cl3
						9.5	C16.H12.Ti.S.Cl3
						-3.1	4.5 C13.H16.Ti.S2.Cl3
389.9224	*	117362	26.88	1.28	2.5	-3.6	14.5 C19.H8.Ti.Cl3
390.9204	*	331939	76.01	3.61	0.6	14.0	C19.H9.Ti.Cl3
						18.5	C21.H5.S2.Cl2
						-2.8	23.5 C24.H.S.Cl2
391.9208	*	103664	23.74	1.13	-0.8	-4.8	22.5 C23.H3.Ti.S2
						27.0	C26.Ti.S
						2.6	22.0 C23.H4.Ti.S2
						4.6	23.0 C24.H2.S.Cl2
392.9303	*	149334	34.20	1.62	1.0	21.5	C23.H5.Ti.S2
						-2.4	25.5 C26.H.Ti.S
						3.0	22.5 C24.H3.S.Cl2
497.9362	*	101258	23.19	1.10	0.3	32.0	C33.H3.S2.Cl
						-4.5	13.0 C22.H17.Ti.S2.Cl3
499.9333	*	111310	25.49	1.21	-4.5	27.0	C30.H6.S2.Cl2

Figure S32: HR-EI-MS of 8a.



59032

No.	Mass	Intensity	%RA	%RIC	Flags
1	73.2	498758	18.43	2.29	
2	176.2	1218820	4.50	0.56	
3	189.2	1033307	3.81	0.47	
4	218.2	89992	3.33	0.41	
5	220.2	74203	2.74	0.34	
6	221.2	2389566	8.83	1.09	
7	222.2	1406550	5.20	0.64	
8	231.2	63696	2.35	0.29	
9	232.2	3524431	13.03	1.61	
10	233.2	954552	3.53	0.44	
11	246.2	99826	3.69	0.46	
12	247.2	1102880	4.08	0.50	
13	248.2	5593342	20.67	2.56	
14	249.2	1517755	5.61	0.69	
15	250.2	805531	2.98	0.37	
16	268.2	1008881	3.73	0.46	
17	282.2	590333	2.18	0.27	
18	283.2	1252633	4.63	0.57	
19	284.2	3682352	13.61	1.68	
20	285.2	1273733	4.71	0.58	
21	286.2	1479778	5.47	0.68	
22	319.3	74296	2.75	0.34	
23	320.3	2300222	8.50	1.05	
24	321.3	1127933	4.17	0.52	
25	340.3	1126073	4.16	0.51	
26	341.3	67471	2.49	0.31	
27	342.2	61918	2.29	0.28	
28	354.3	2875355	10.63	1.31	
29	355.3	4379225	16.19	2.00	
30	356.3	27056642	100.000	12.36	
31	357.3	10792253	39.89	4.93	
32	358.3	13304662	49.17	6.08	
33	359.3	3985603	14.73	1.82	
34	360.3	1735322	6.41	0.79	
35	391.3	2503133	9.55	1.18	
36	392.3	1360283	5.03	0.62	
37	393.3	5934033	21.93	2.71	
38	394.3	2054533	7.59	0.94	
39	395.3	2481383	9.17	1.13	
40	396.3	727453	2.69	0.33	
41	463.4	1952163	7.22	0.89	
42	464.4	2547153	9.41	1.16	
43	465.4	20660393	76.36	9.44	
44	466.4	9411503	34.78	4.30	
45	467.4	11695663	43.19	5.34	
46	468.3	4128293	15.26	1.89	
47	469.4	1932623	7.14	0.88	
48	574.5	1687243	6.24	0.77	
49	575.5	833543	3.08	0.38	
50	576.5	1025253	3.79	0.47	

Figure S33: EI-MS of 8b.

Table S1: Fragmentation patterns observed in the mass spectra of 2–8.

Compd	M^+	M^+-HCl	M^+-Cp′	M^+-SAr	M^+-SAr-HCl	M^+-2SAr	M^+-2SAr-HCl	$[C_{10}H_8Ti_2(SAr)_2\}^{2+}$	$[C_{10}H_6Cl_2Ti_2(SAr)_2\}^{2+}$	ArS(H)	Ar_2S_2
2b	430.2	395.3	331.2	321.2	285.2	212.1	176.1	221.1	255.1	109/110	218
2c	464.0	(hidden)	365	355.1	(hidden)	246.0	(hidden)	(hidden)	255.0	109/110	218
3b	458.0	–	359.0	335.0	299.0	212.0	176	235	269.0	124	246.1
3c	492.0	457.0	392.9	368.9	(hidden)	246.0	–	235.0	269.0	123/124	246
3c′	404	(hidden)	305	281			–		–		
6a	464.1	–	331.1	355.1	319.1	246.1	210.1	221.1	–	109/110	218
6a′	390.1	–	257.1	281	(hidden)						
6b	502	(487)*	–	393.0	(378)*	284.0	(248)*	221	–	110	218
6b′	428	–	–	319	(304)*						
8a	499.9	–	331	390.9	366	279.9	243.0	221.0	–	110	218
8a′	426.9	–	257	317	(hidden)						
8b	574.5	–	–	465.4	–	356.3	320.3	221.2	–	109	218