SUPPORTING INFORMATION

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1. FIGURES

1.1. NMR Spectra

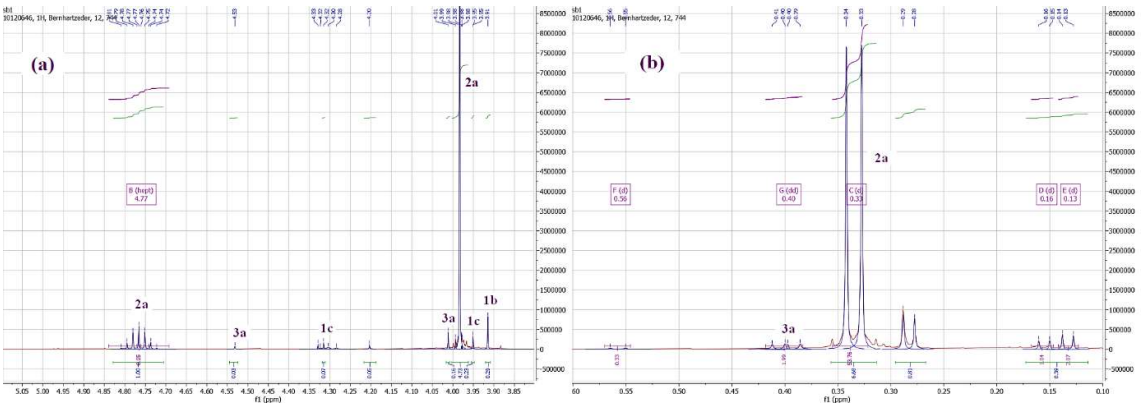


Figure S 1: ^{1}H-NMR (C_6D_6, 270 MHz) of the crude reaction product according section 4.2.1; (a) Cp and Si-H region; (b) Si-CH_3 region

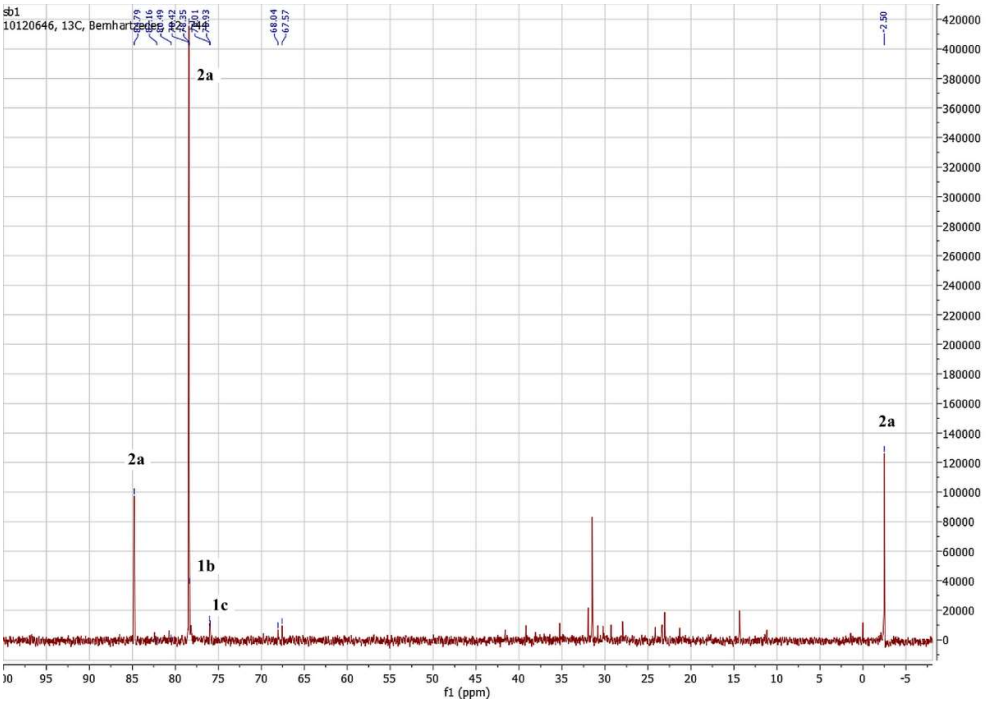


Figure S 2: $^{13}C\{^{1}H\}$-NMR (C_6D_6, 67 MHz) of the crude reaction product according section 4.2.1

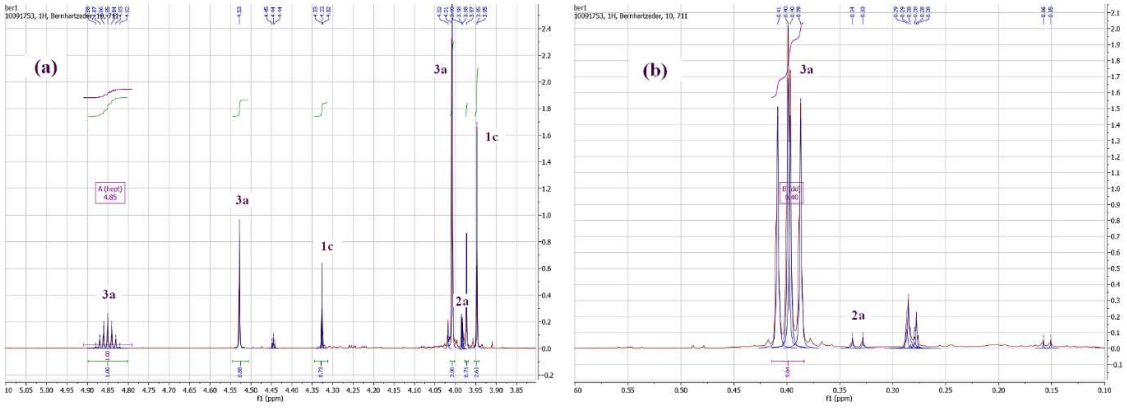


*Figure S 3. ^{1}H-NMR (C_6D_6, 400 MHz) of the crude reaction product obtained from **1c** and 2.5 eq. LiTMP; ; (a) Cp and Si-H region; (b) Si-CH_3 region*

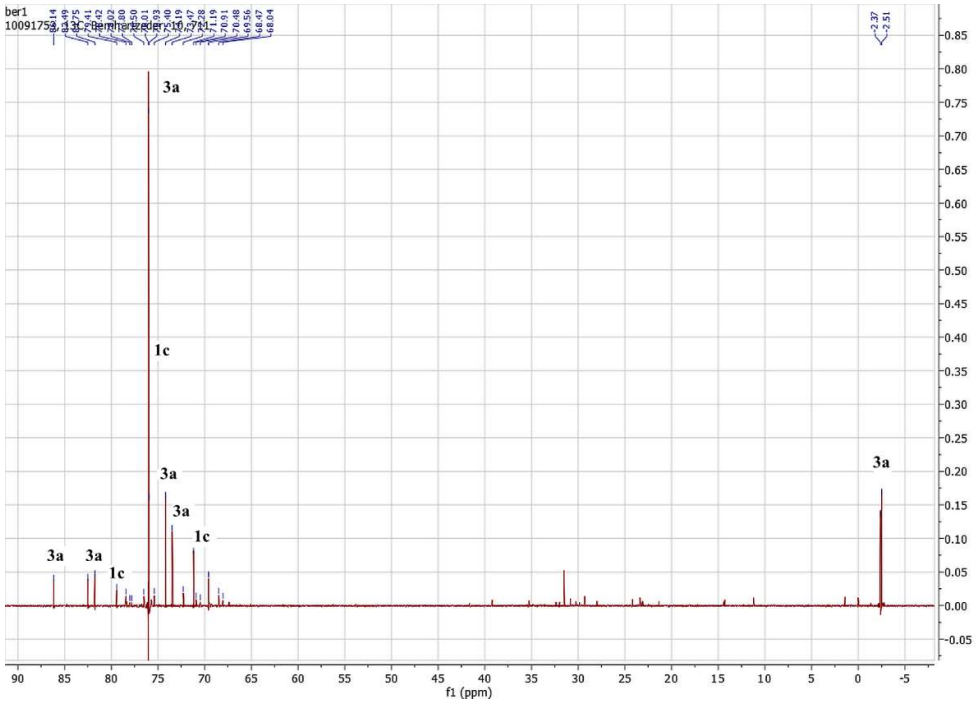


*Figure S 4 ^{13}C{^{1}H}-NMR (C_6D_6, 101 MHz) of the crude reaction product obtained from **1c** and 2.5 eq. LiTMP*

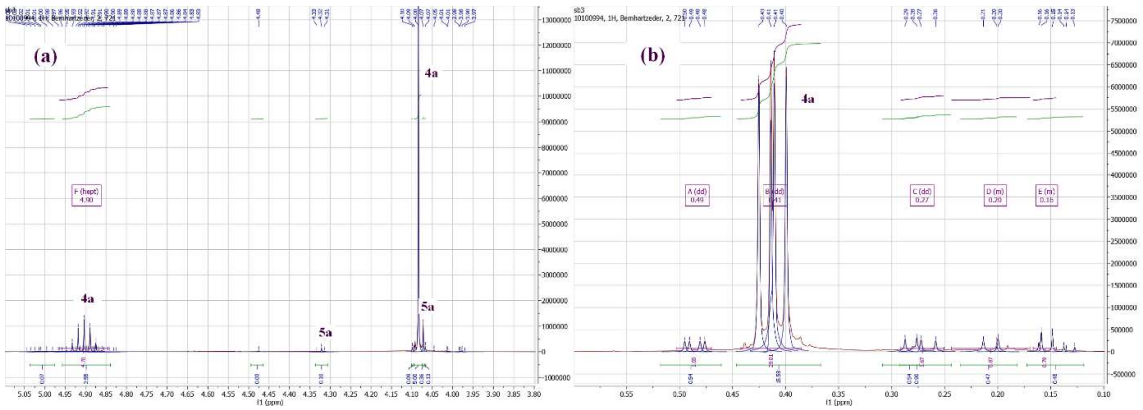


*Figure S 5: ^{1}H-NMR (C_6D_6, 270 MHz) of the crude reaction product obtained from **1c** and 3.5 eq. LiTMP (Section 4.2.2.); ; (a) Cp and Si-H region; (b) Si-CH_3 region*

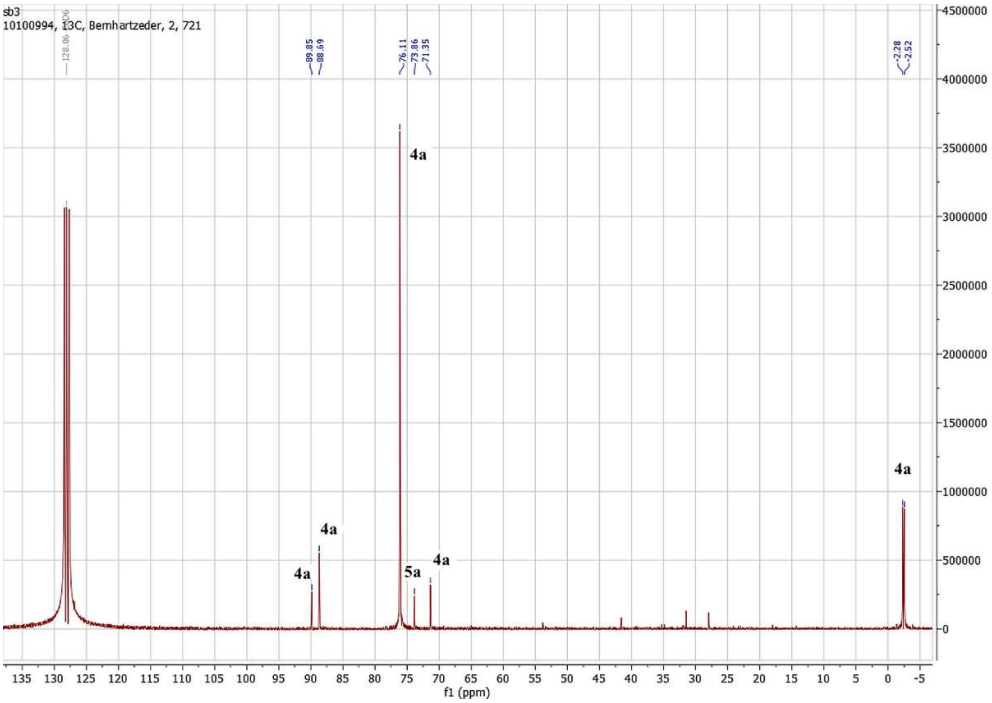


*Figure S 6: $^{13}C\{^1H\}$-NMR (C_6D_6, 67 MHz) of the crude reaction product obtained from **1c** and 3.5 eq. LiTMP (Section 4.2.2.)*

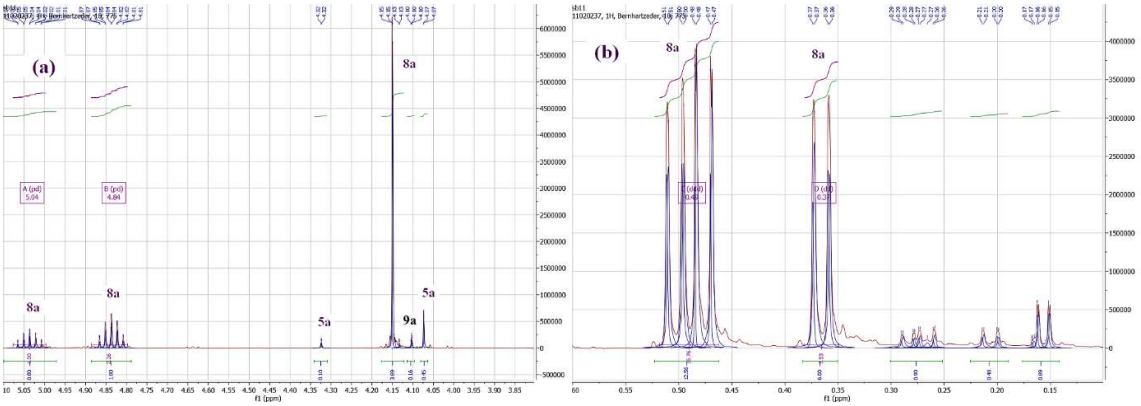


Figure S 7: ^1H-NMR (C_6D_6, 270 MHz) of the crude reaction product obtained acc. Section 4.2.3.; ; (a) Cp and Si-H region; (b) Si-CH_3 region

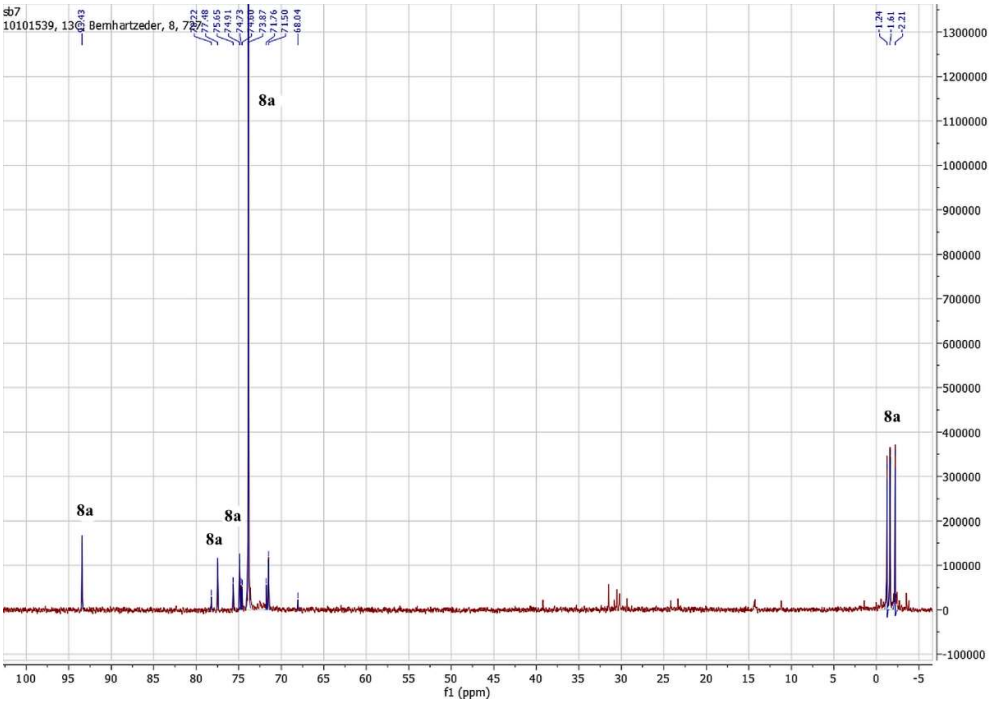


Figure S 8: ^{1}H-NMR (C_6D_6, 270 MHz) of the crude reaction product obtained acc. Section 4.2.3

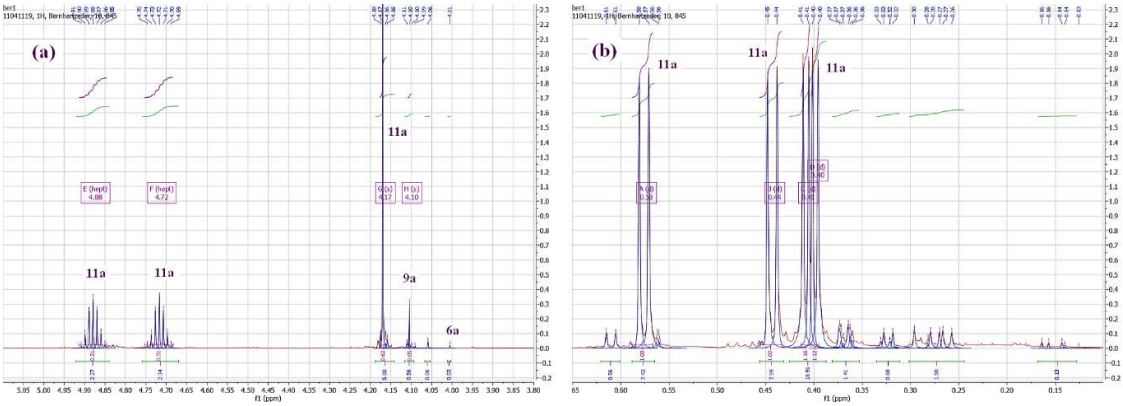


Figure S 9: ^{1}H-NMR (C_6D_6, 400 MHz) of the crude reaction product obtained acc. Section 4.2.4; ; (a) Cp and Si-H region; (b) Si-CH_3 region

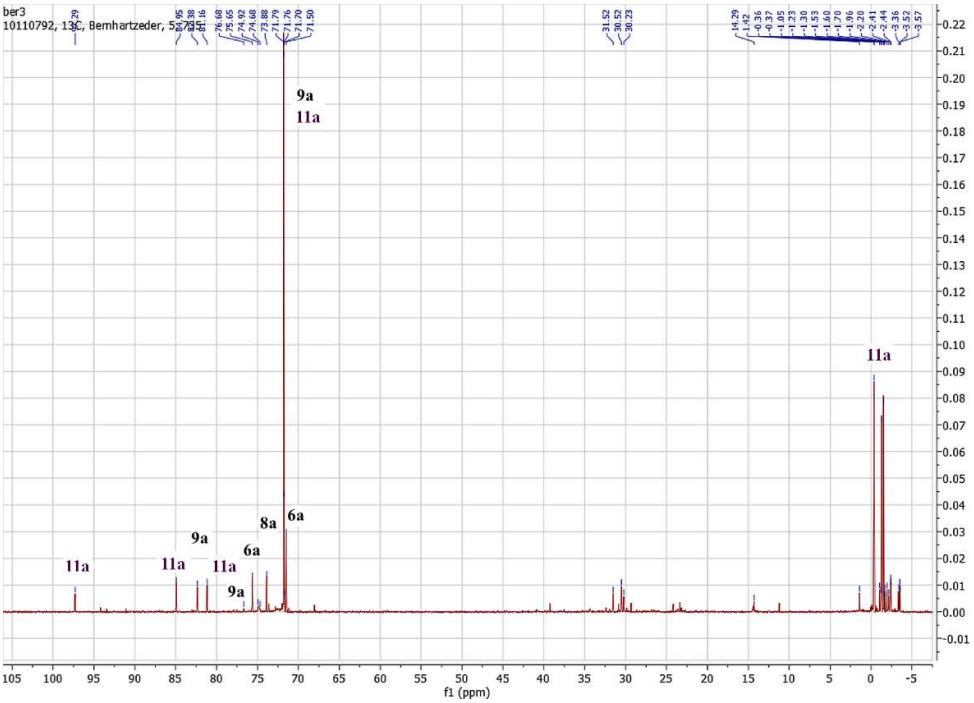


Figure S 10: $^{13}C\{^1H\}$-NMR (C_6D_6, 101 MHz) of the crude reaction product obtained acc. Section 4.2.4

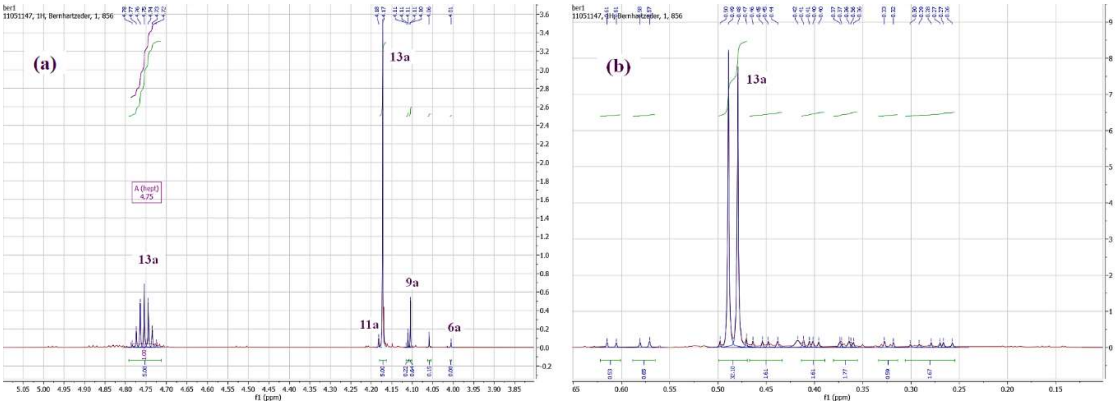


Figure S 11: ^1H-NMR (C_6D_6, 400 MHz) of the crude reaction product obtained acc. Section 4.2.5; ; (a) Cp and Si-H region; (b) Si-CH_3 region

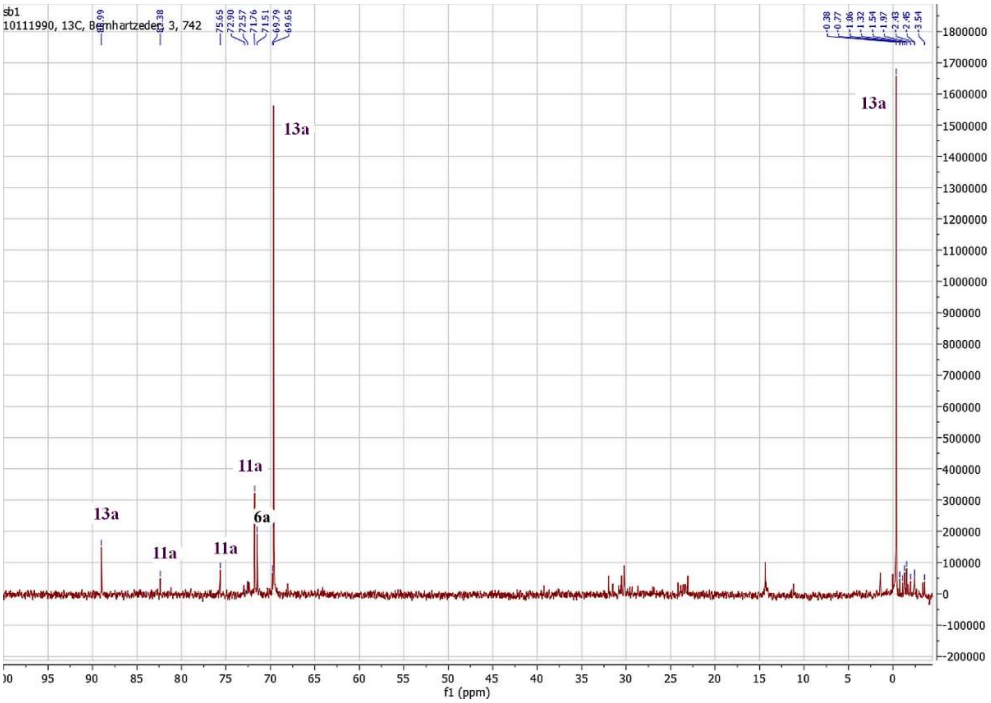


Figure S 12: $^{13}C\{^1H\}$-NMR (C_6D_6, 67 MHz) of the crude reaction product obtained acc. Section 4.2.5

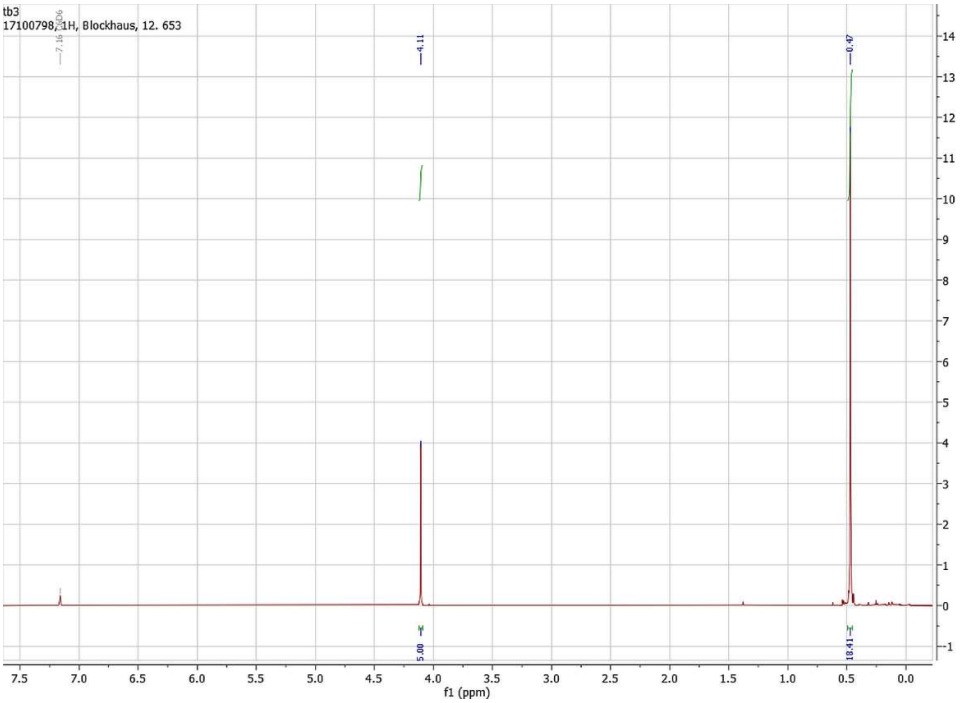


*Figure S 13: ^1H-NMR (C_6D_6, 270 MHz) of compound **4b** (Section 4.2.6)*

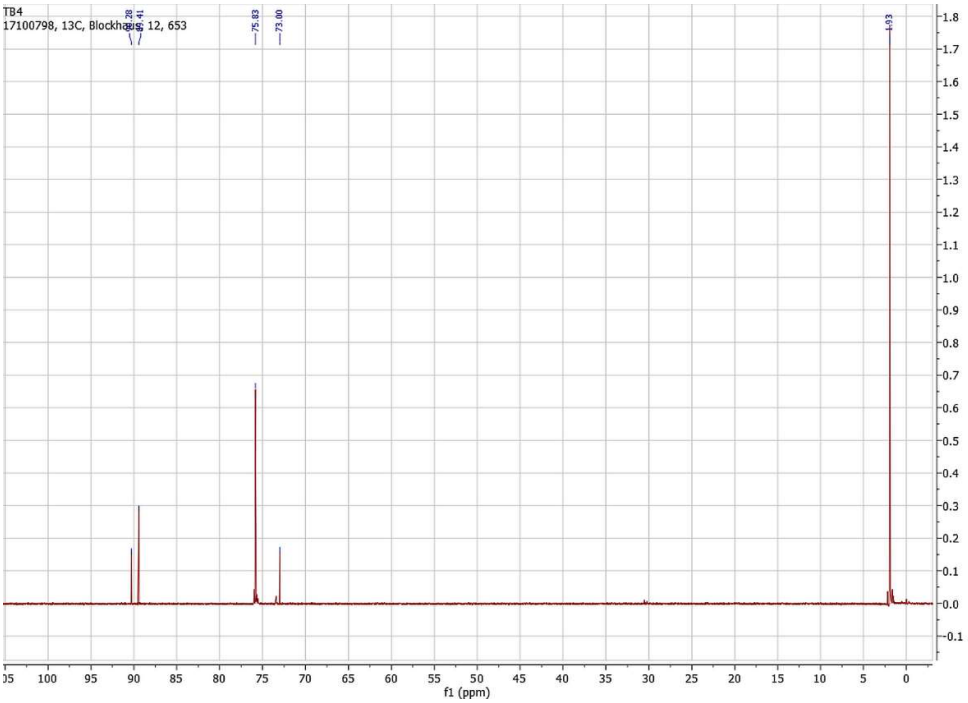


*Figure S 14: $^{13}C\{^1H\}$-NMR (C_6D_6, 67 MHz) of compound **4b (Section 4.2.6.)***

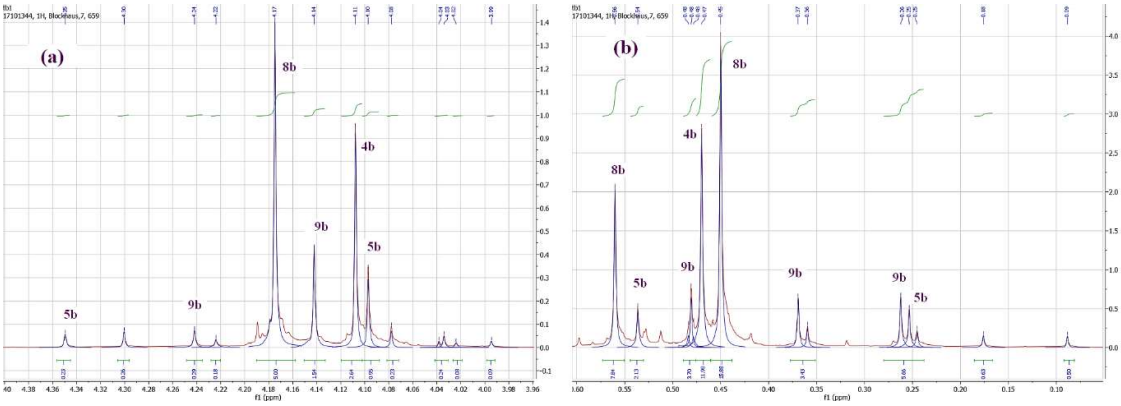


Figure S 15: ^1H-NMR (C_6D_6, 270 MHz) of the crude reaction product obtained acc. Section 4.2.7; ; (a) Cp region; (b) Si-CH_3 region

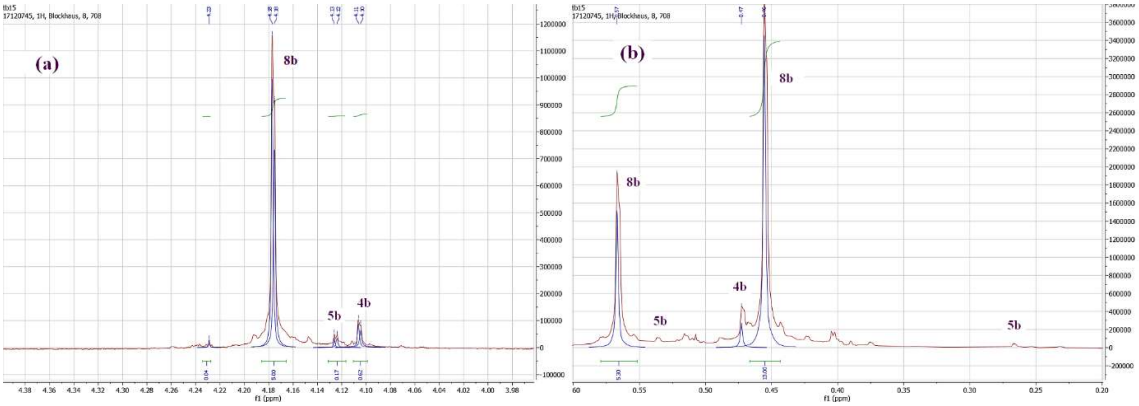


*Figure S 16: ^{1}H-NMR (C_6D_6, 270 MHz) of purified **8b** (section 4.2.7.); ; (a) Cp region; (b) Si-CH_3 region*

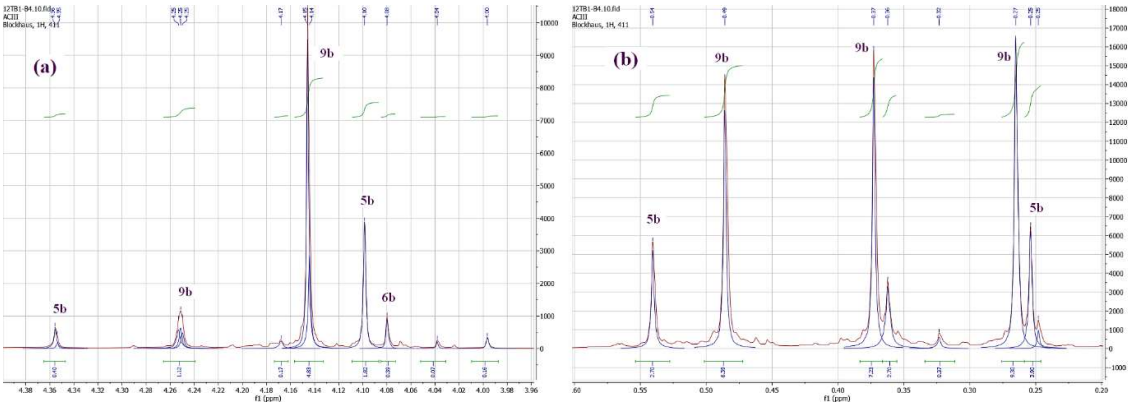


Figure S 17: ^{1}H-NMR (C_6D_6, 400 MHz) of the crude reaction product obtained acc. Section 4.2.8; ; (a) Cp region; (b) Si-CH_3 region

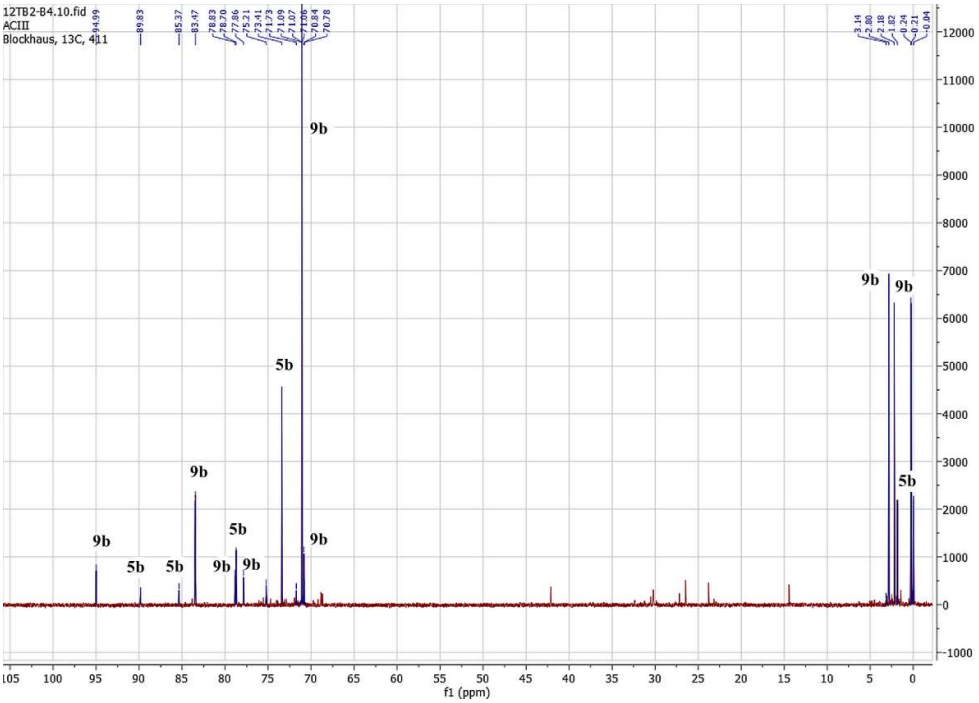


Figure S 18: $^{13}C\{^1H\}$-NMR (C_6D_6, 101 MHz) of the crude reaction product obtained acc. Section 4.2.8

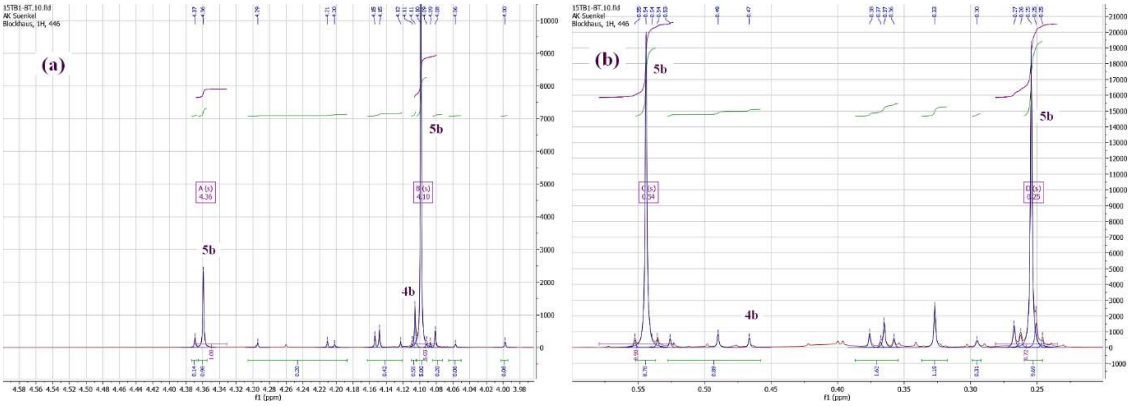


*Figure S 19: ^1H-NMR (C_6D_6, 400 MHz) of **5b** (section 4.2.8); ; (a) Cp region; (b) Si-CH_3 region*

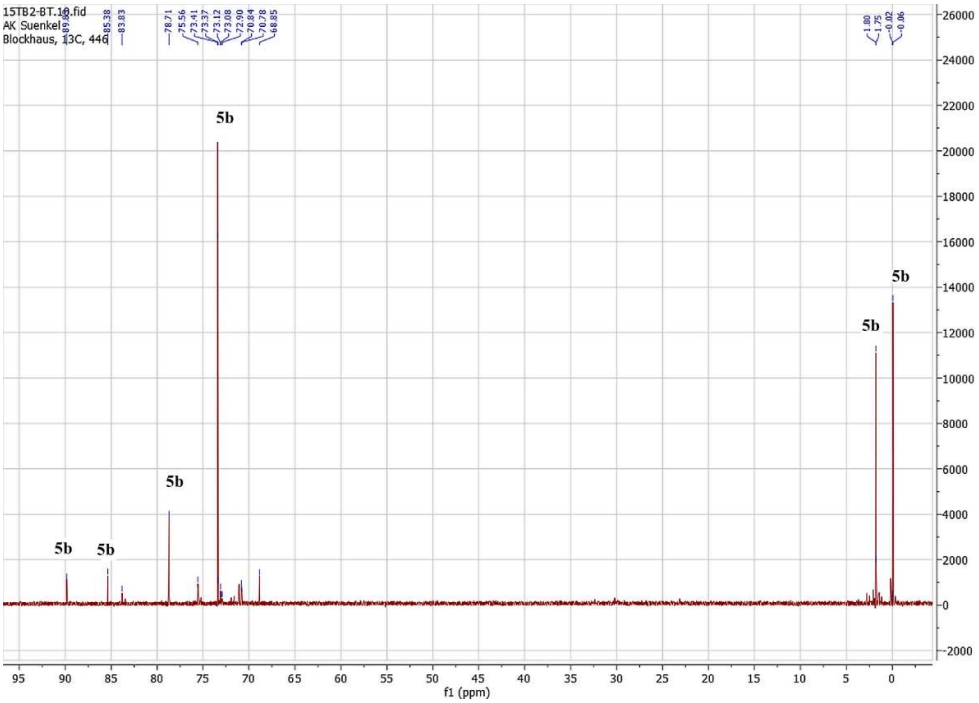


*Figure S 20: $^{13}C\{^1H\}$-NMR (C_6D_6, 101 MHz) of **5b** (section 4.2.8)*

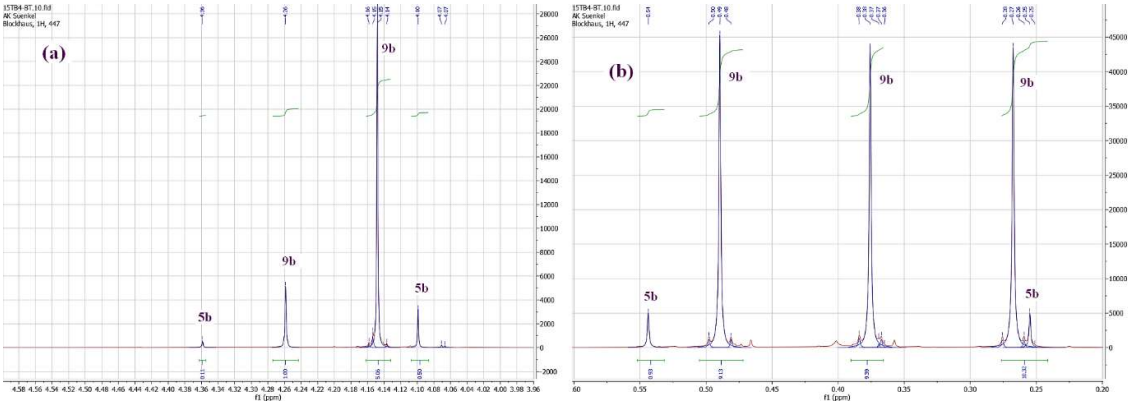


*Figure S 21: ^1H-NMR (C_6D_6, 400 MHz) of **9b** (section 4.2.8); ; (a) Cp region; (b) Si-CH_3 region*

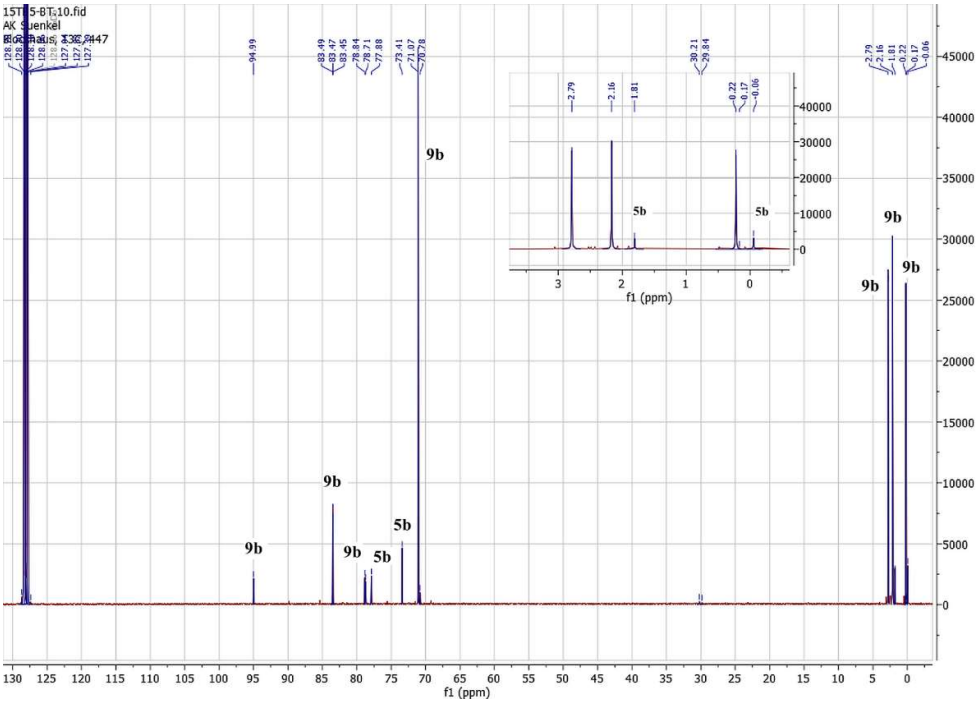


*Figure S 22: $^{13}C\{^1H\}$-NMR (C_6D_6, 101 MHz) of **9b** (section 4.2.8)*

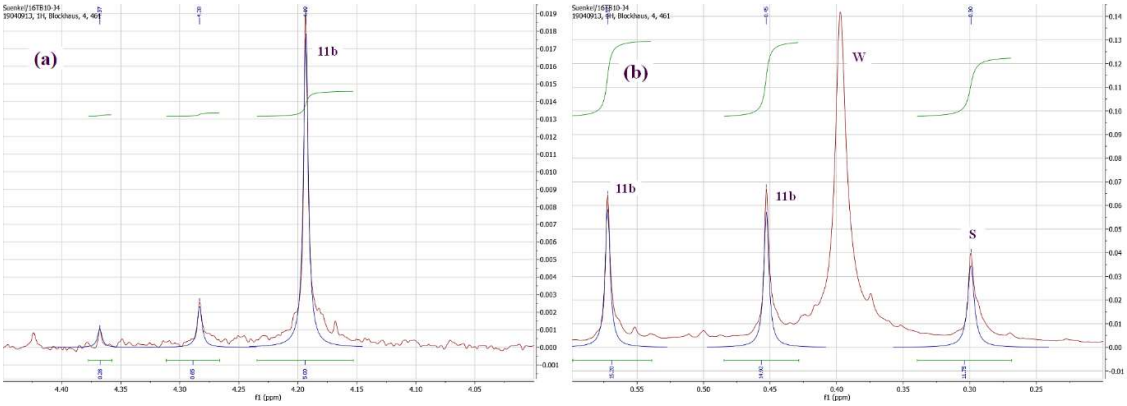


*Figure S 23: ^1H-NMR (C_6D_6, 400 MHz) of **11b** (section 4.2.8); ; (a) Cp region; (b) Si-CH_3 region*

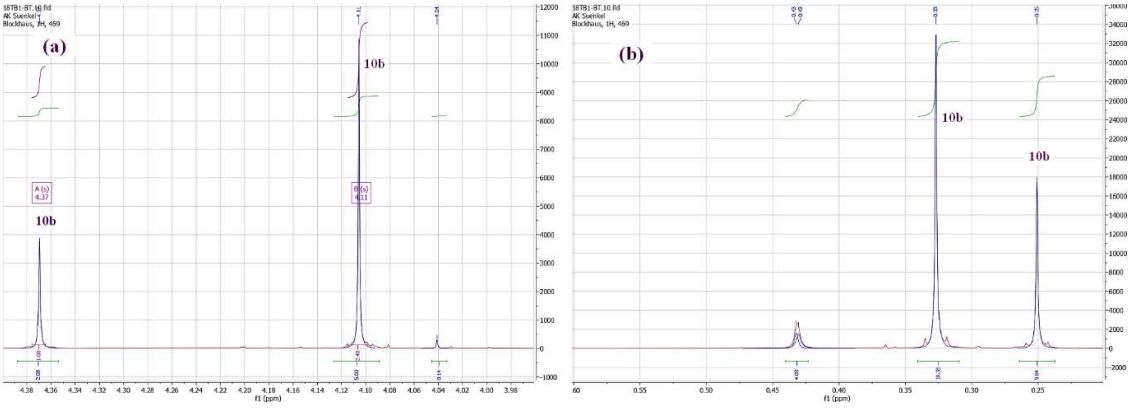


*Figure S 24: ^{1}H-NMR (C_6D_6, 400 MHz) of **10b** (Section 4.2.9); ; (a) Cp region; (b) Si-CH_3 region*

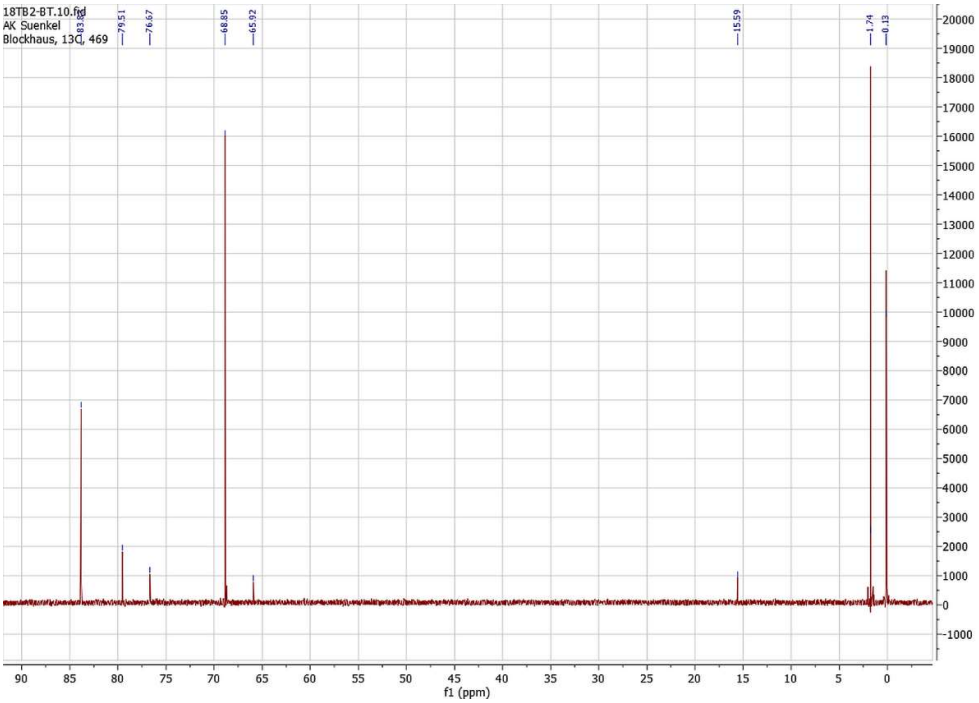


*Figure S 25: $^{13}C\{^{1}H\}$-NMR (C_6D_6, 101 MHz) of **10b** (Section 4.2.9.)*

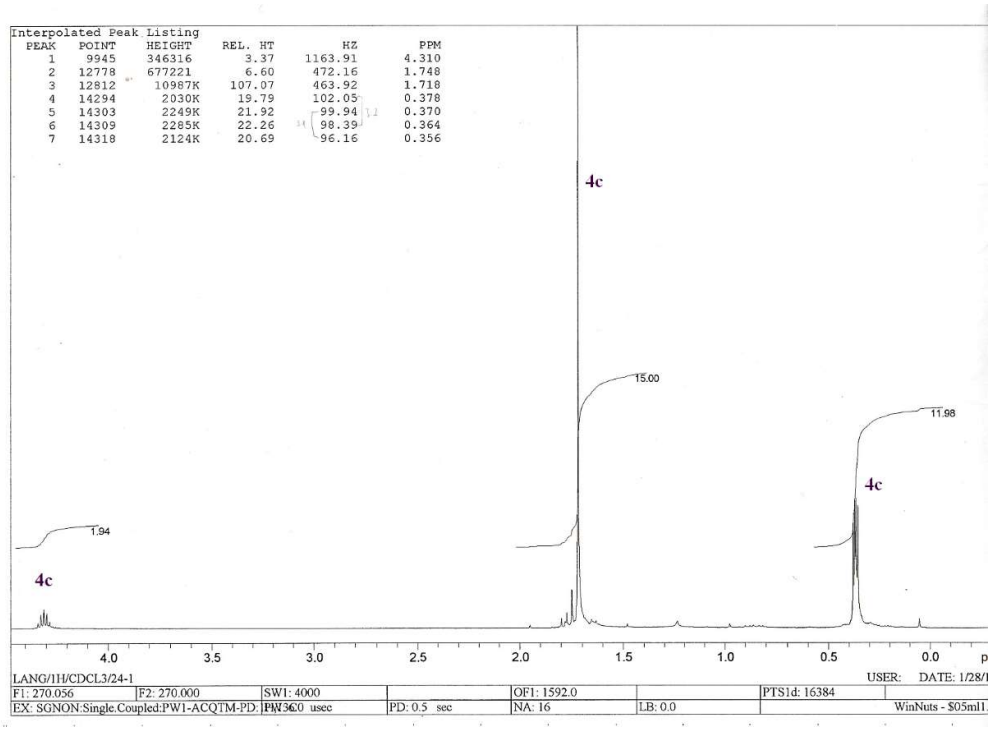


*Figure S 26: ¹H-NMR ($CDCl_3$, 270 MHz) of **4c** (section 4.2.10.)*

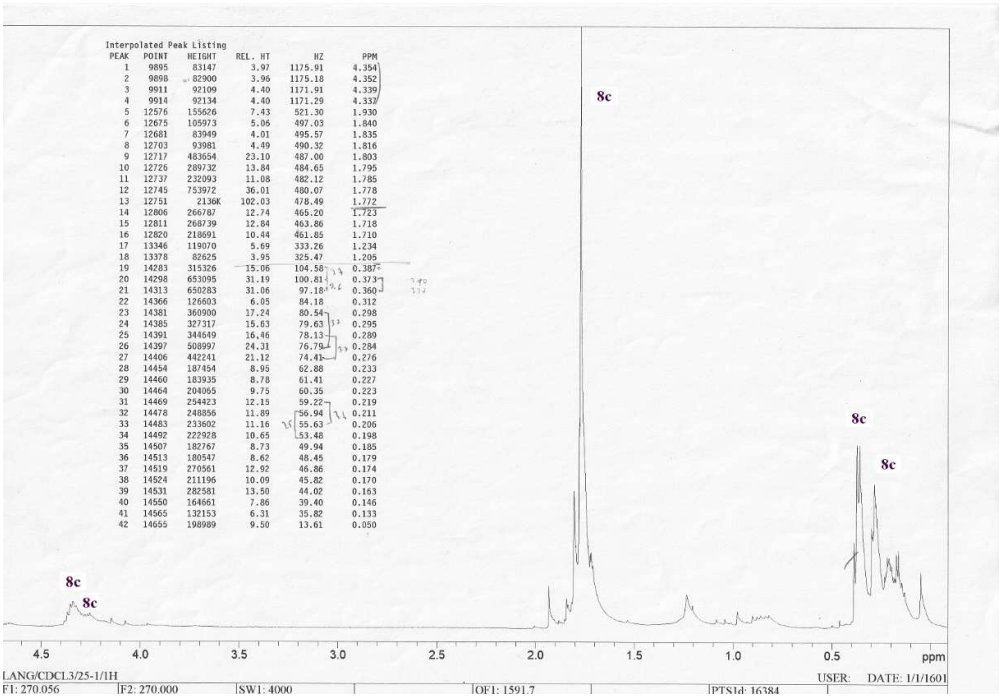


Figure S 27 ¹H-NMR ($CDCl_3$, 270 MHz) of the crude reaction product obtained according section 4.2.11.

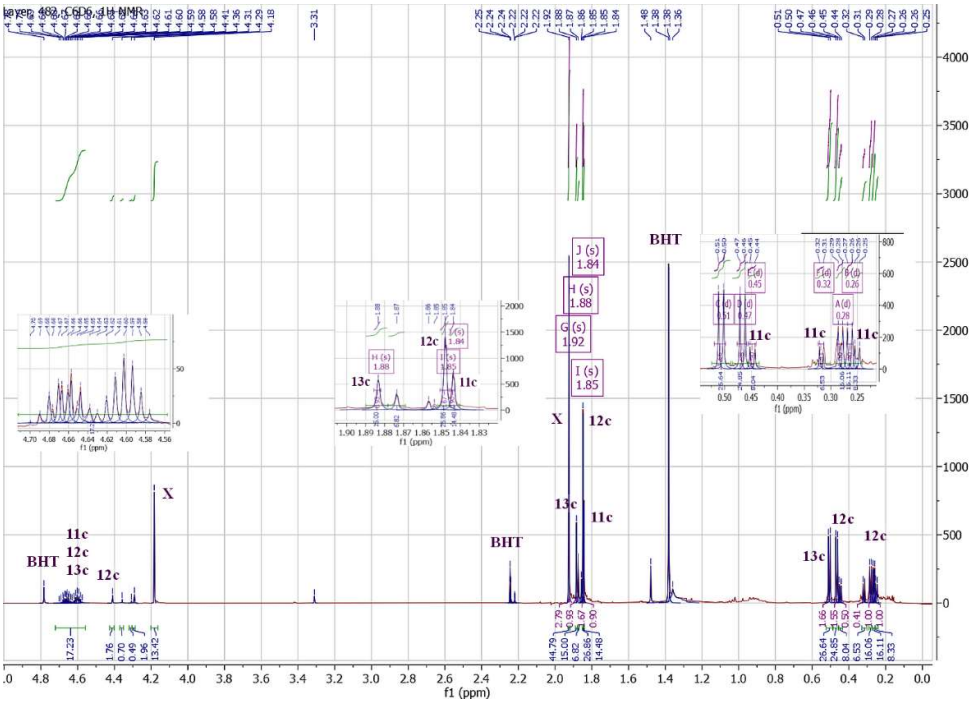


*Figure S 28: ^{1}H-NMR (C_6D_6, 400 MHz) of the crude reaction product obtained according section 4.2.12. Identified „impurities“: BHT (t-Butylhydroxytoluene; stabilizer in THF); X : Cp*Ru(C_5H_5)*

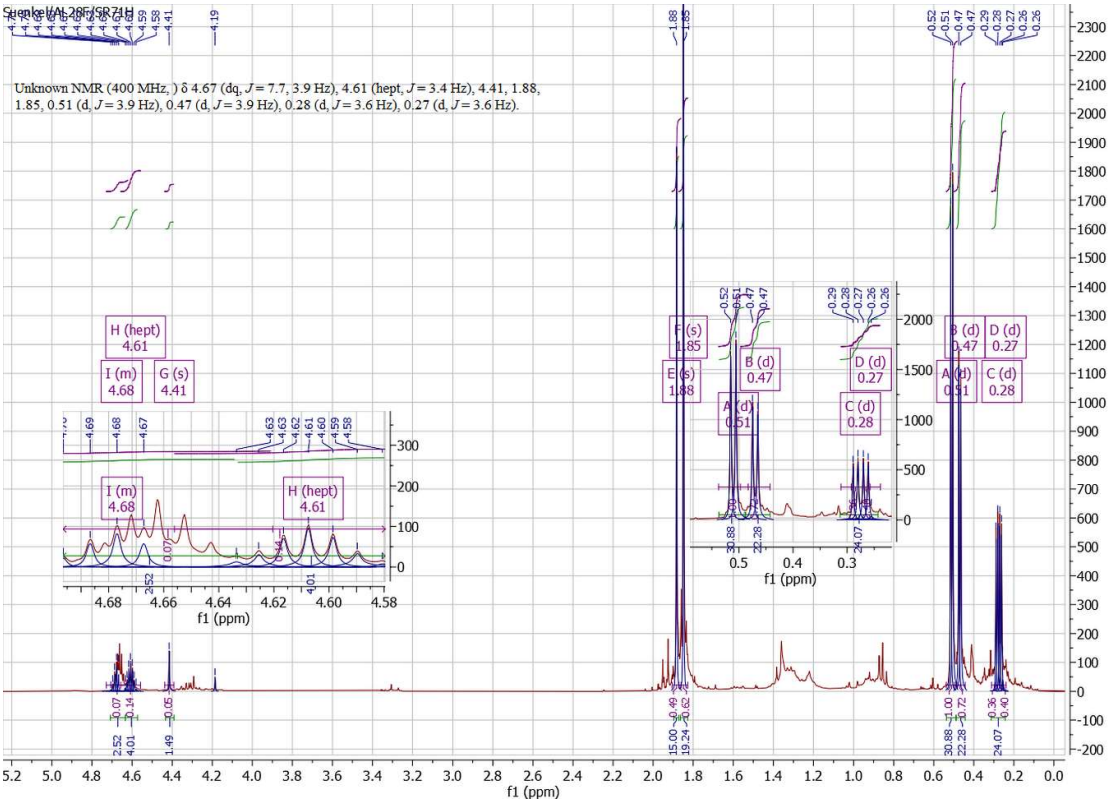


Figure S 29: ^{1}H-NMR (C_6D_6, 400 MHz) of the product of the first purification step (section 4.2.12)

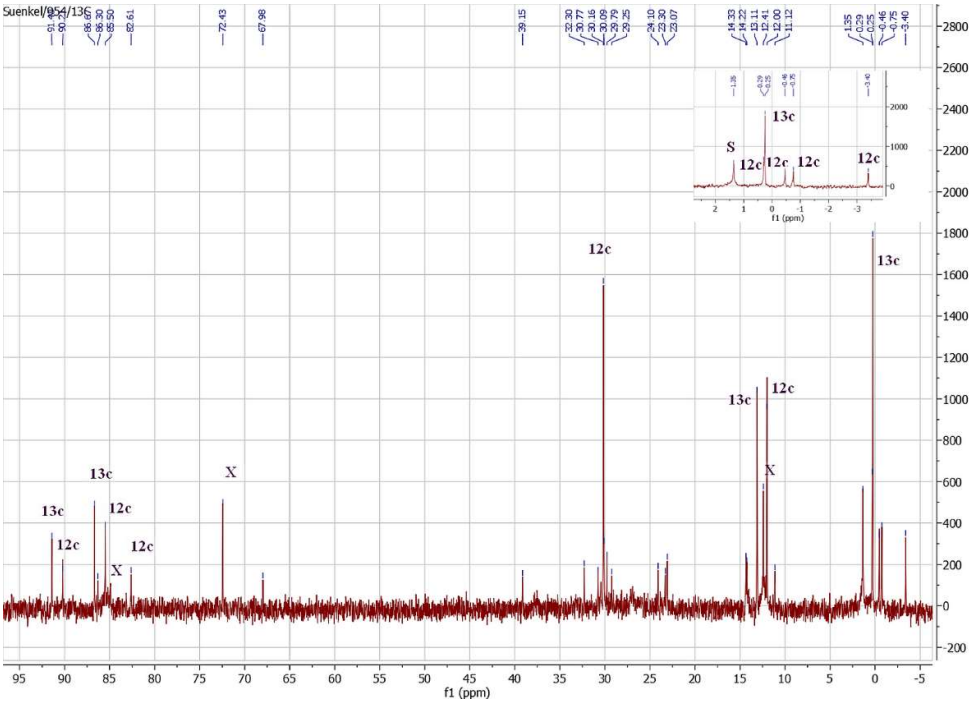


Figure S 30: $^{13}C\{^1H\}$-NMR (C_6D_6, 101 MHz) of the product of the first purification step (section 4.2.12)

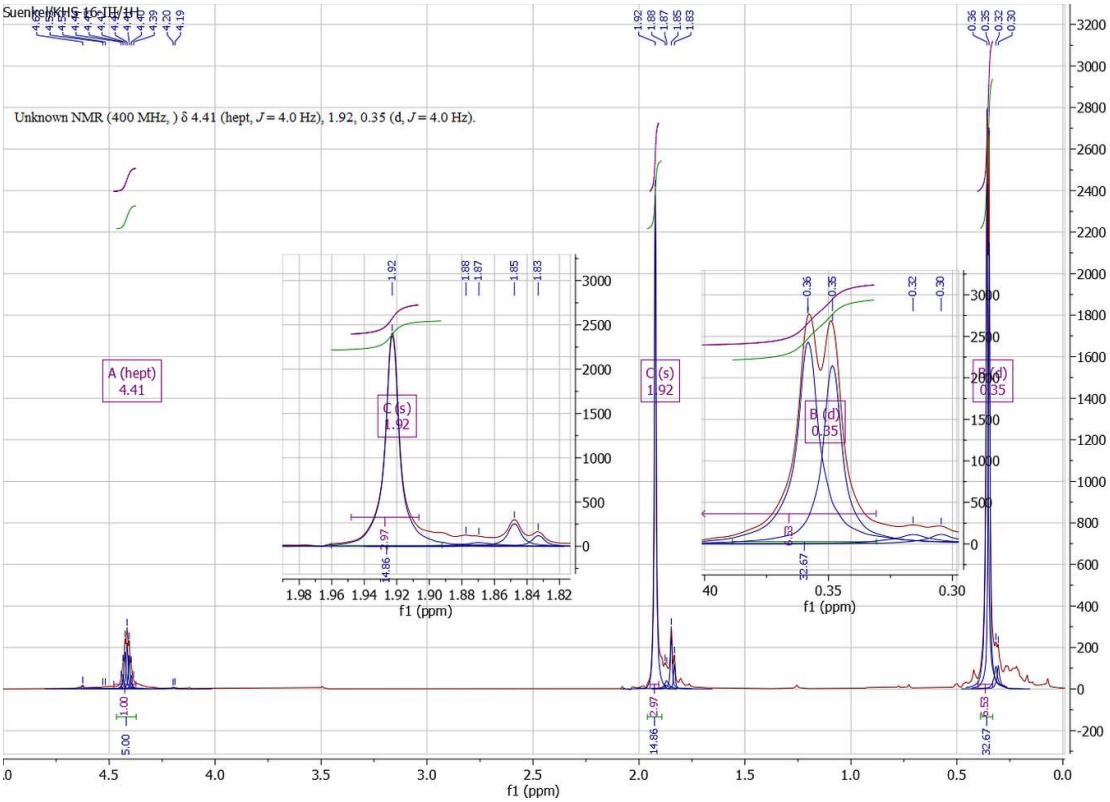


Figure S 31: ^1H-NMR ($CDCl_3$, 270 MHz) of the product of the second purification step (section 4.2.12)

1.2. MASS SPECTRA

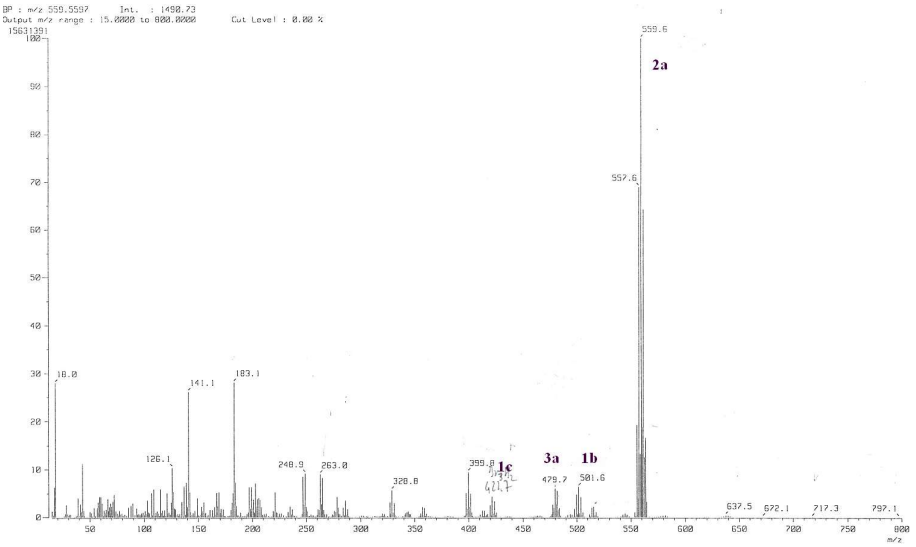


Figure S 32 MS (DEI) of the crude reaction product according section 4.2.1

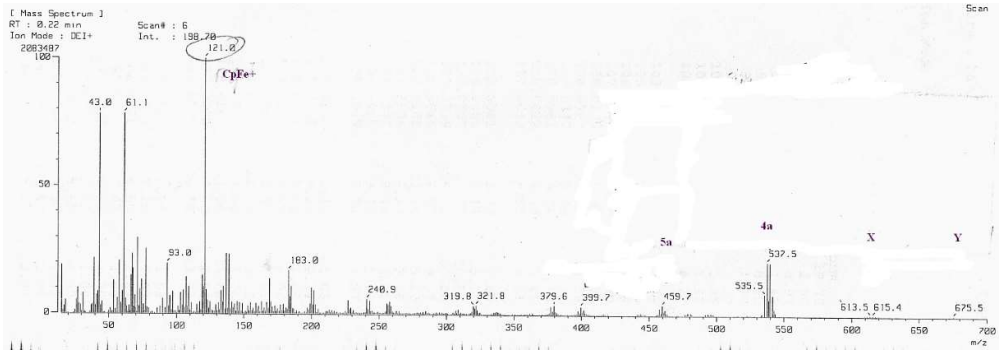


Figure S 33: MS (DEI) of the crude reaction product according section 4.2.2. X = $[FeC_{10}Br_4(SiMe_2H)_2H_4]$, Y= $[FeC_{10}Br_4(SiMe_2H)_3H_3]$

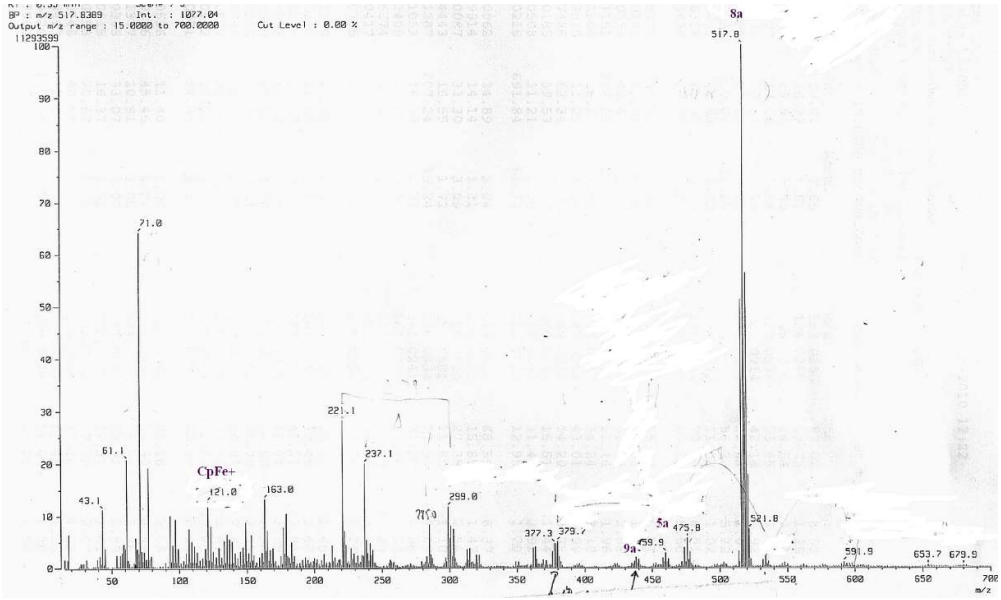


Figure S 34: MS (DEI) of the crude reaction product according section 4.2.3: MS (DIE)

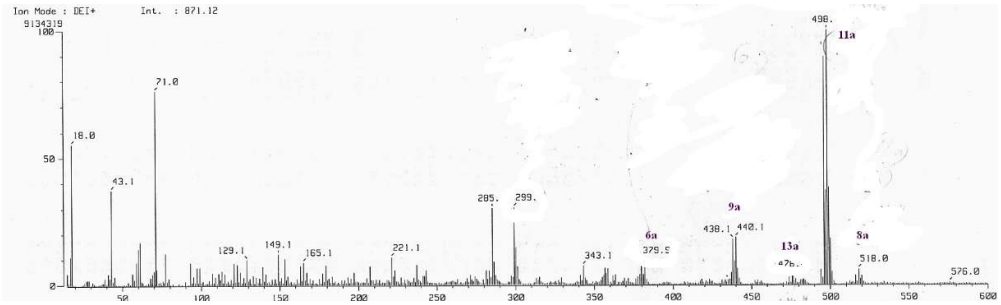


Figure S 35 MS (DEI) of the crude reaction product according section 4.2.4

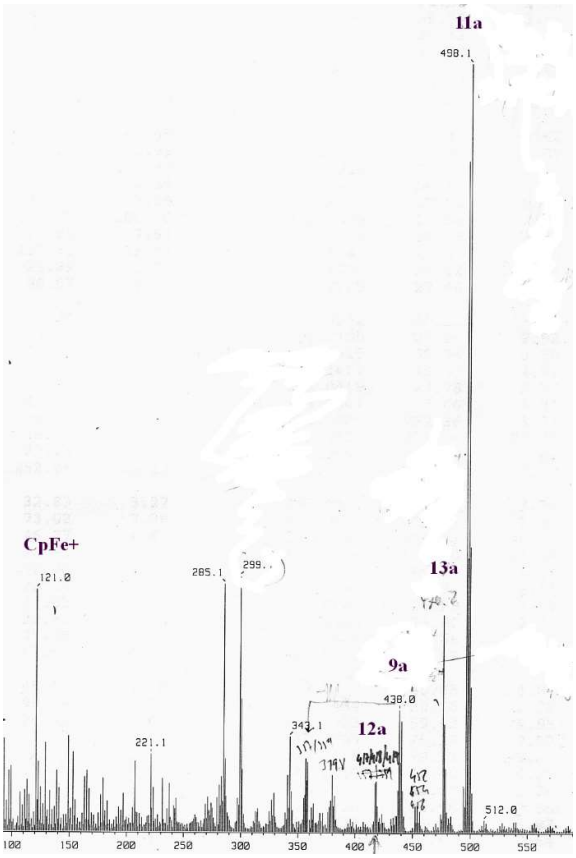


Figure S 36: MS (DEI) of the crude reaction product according section 4.2.5

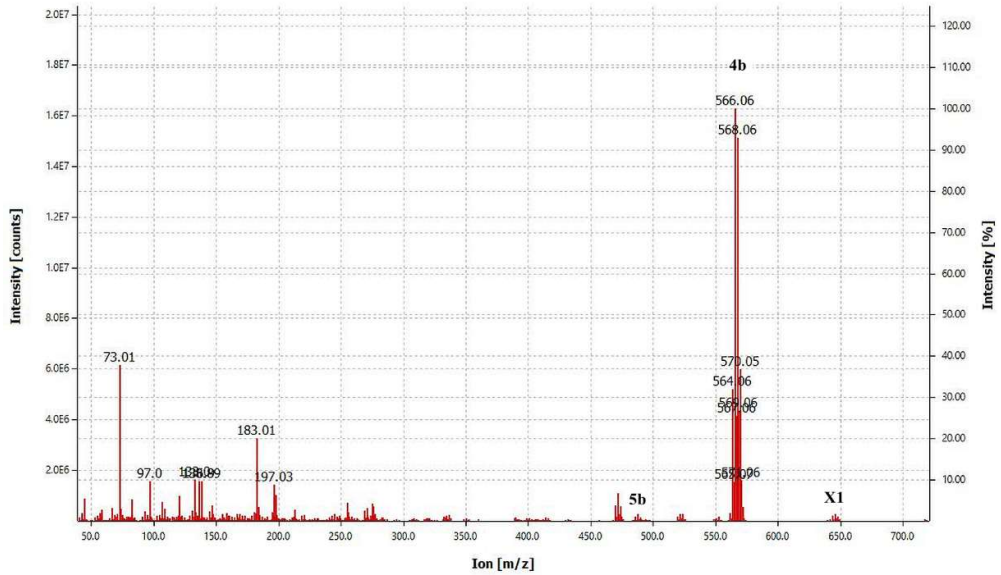


*Figure S 37 MS (EI) of **4b** (Section 4.2.6.). X1 = [$FeC_{10}Br_4(SiMe_3)_2H_4$]*

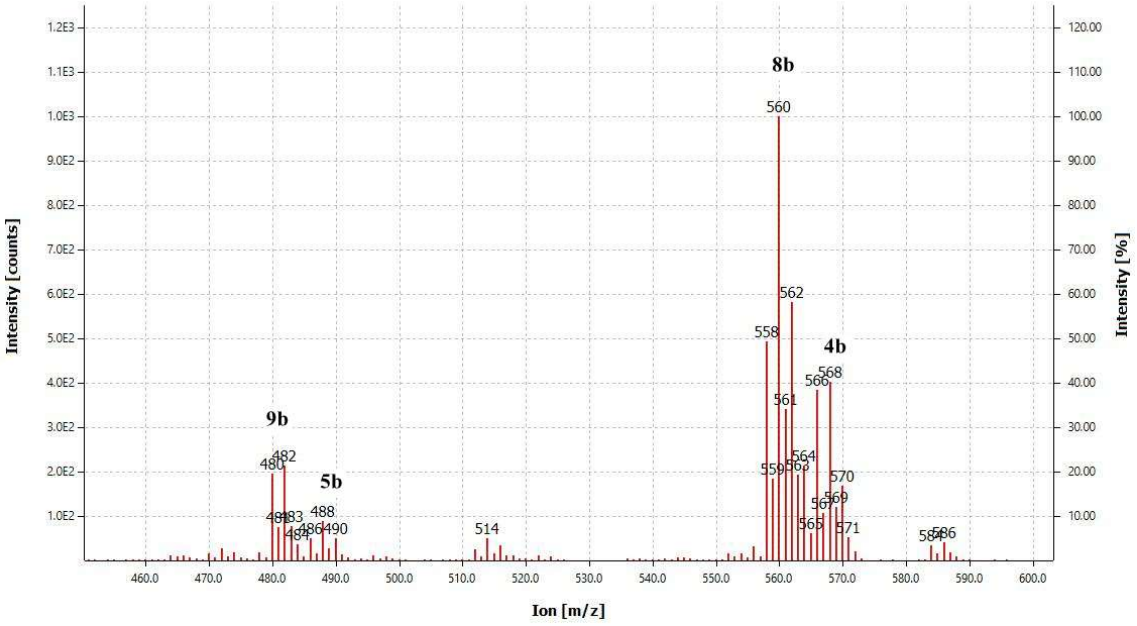


Figure S 38 : MS (EI) of the crude reaction product obtained acc. Section 4.2.7

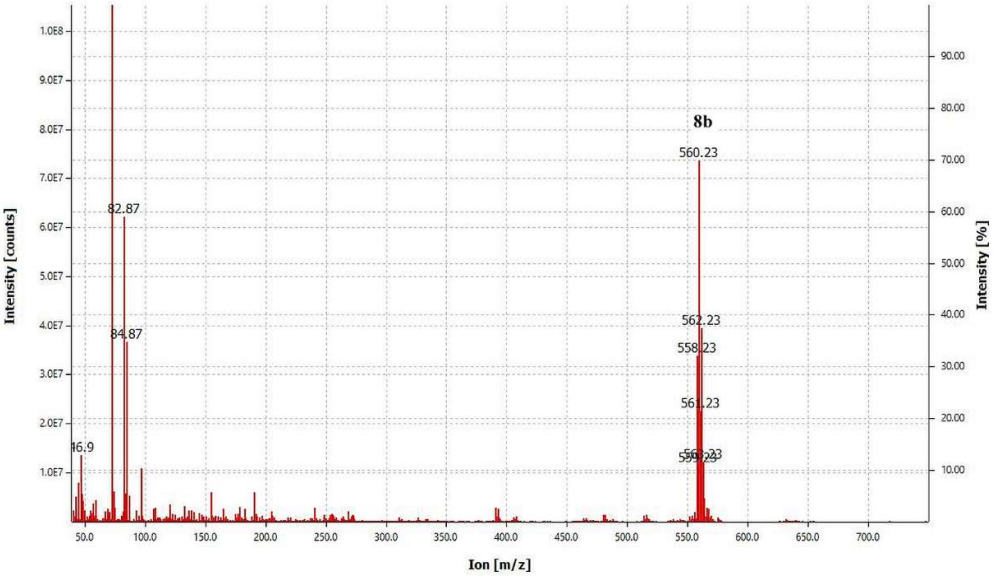


*Figure S 39 : MS (EI) of **8b***

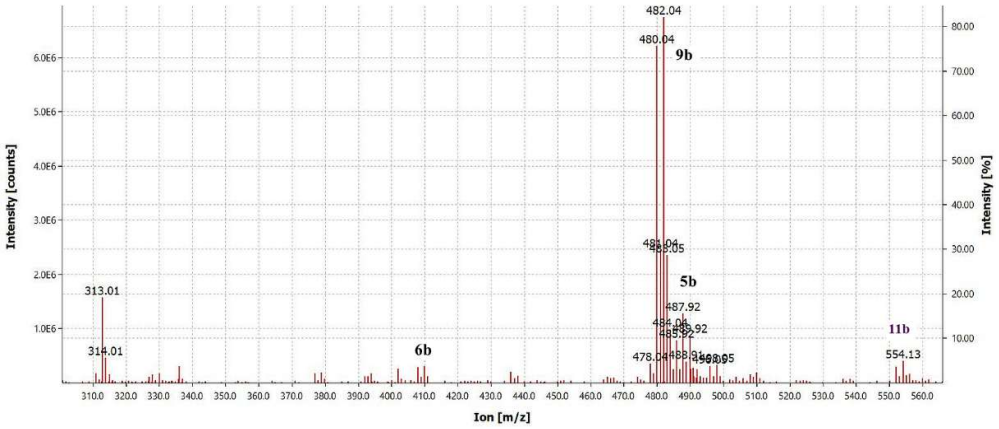


Figure S 40 : MS (EI) : of the crude reaction product obtained acc. Section 4.2.8

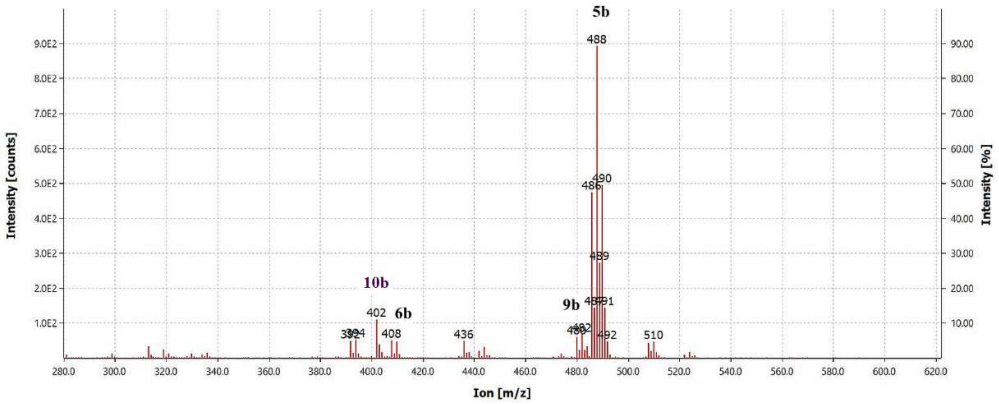


Figure S 41: MS(EI) of the product of the second purification step, fraction F3.2, section 4.2.8.

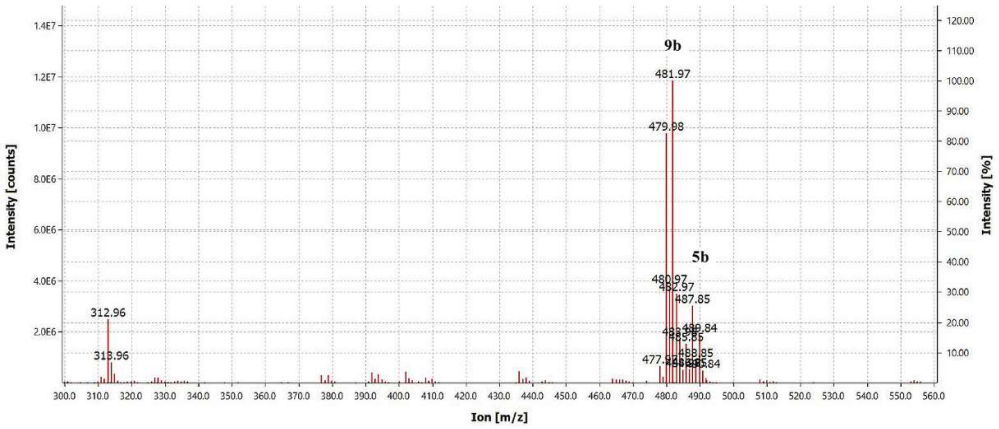


Figure S 42: MS(EI) of the product of the second purification step, fraction F3.3, section 4.2.8.

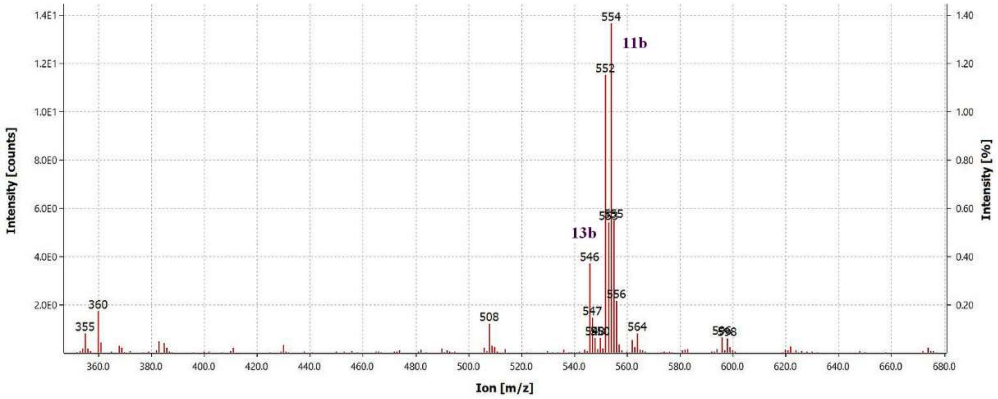


Figure S 43: MS(EI) of the product of the third: MS (EI) purification step, fraction F4.10., section 4.2.8.

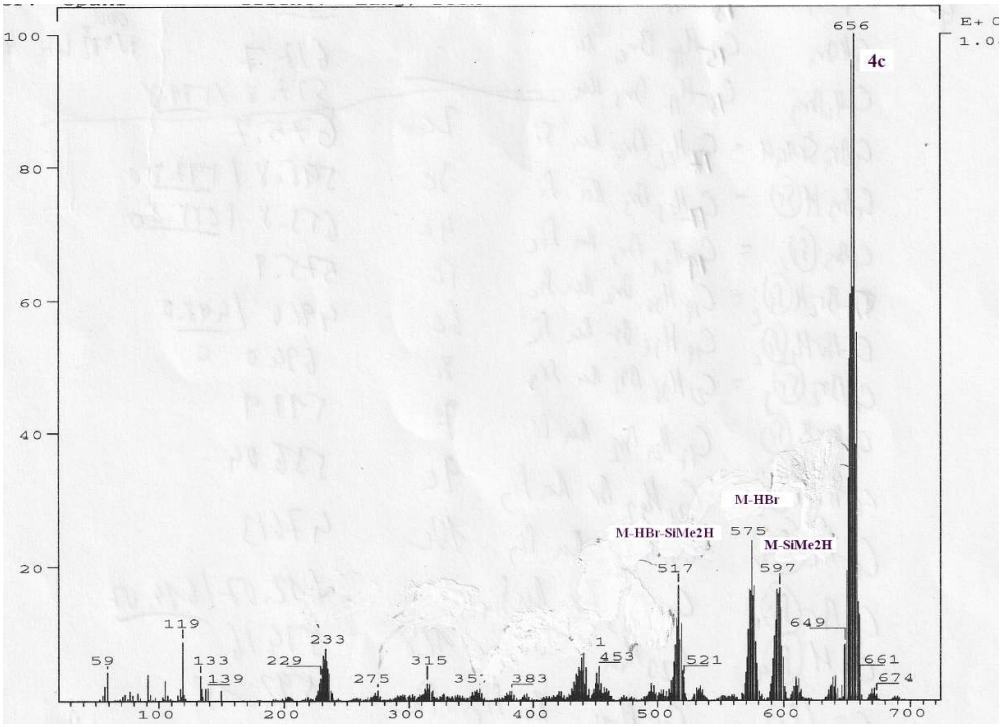


*Figure S 44: MS (EI) of **4c** (Section 4.2.10.)*

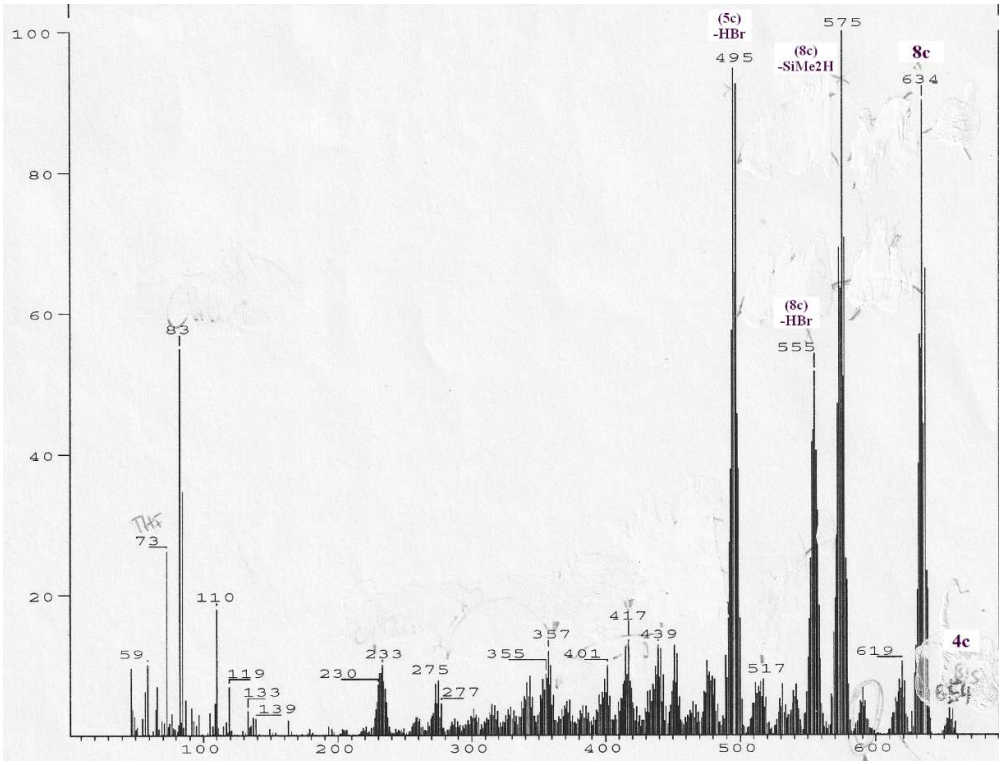


*Figure S 45: MS (EI) of **8c** (Section 4.2.11)*

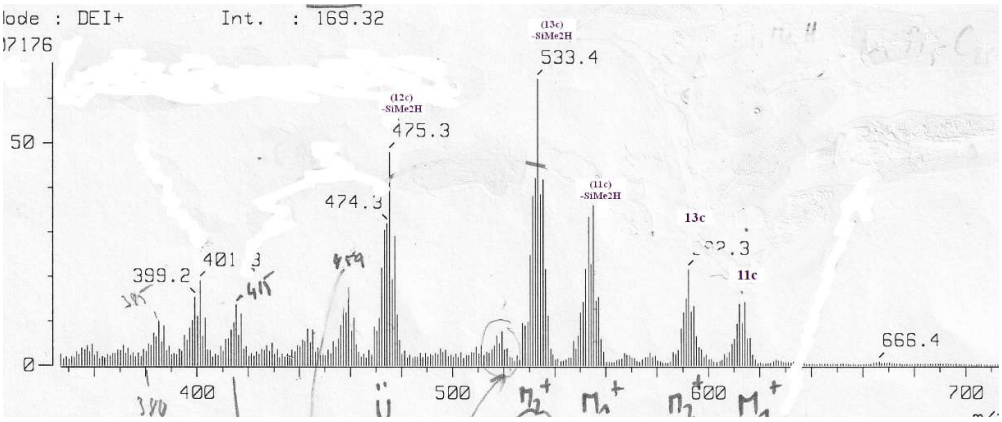


Figure S 46: MS (EI) of the product obtained according section 4.2.12.

1.3. CRYSTALLOGRAPHY

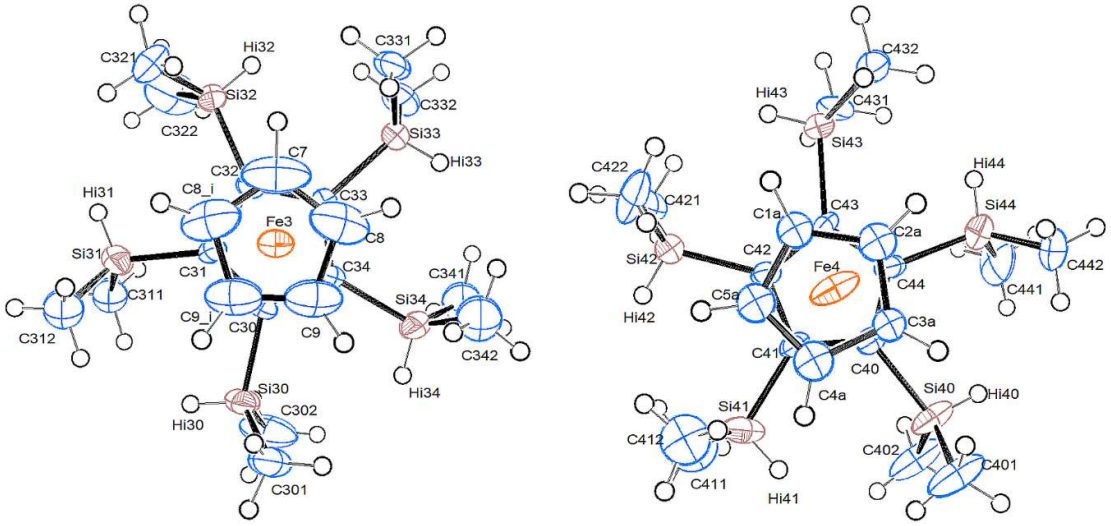


*Figure S 47: ORTEP3 plots of the molecular structure of **13a**, molecules C and D*

2. TABLES

Table S 1 Experimental Details of the Crystal Structure Determinations

Compound	**4b**	**8b**	**13a**
Empirical formula	C_{16} H_{23} Br_3 Fe Si_2	C_{19} H_{32} Br_2 Fe Si_3	C_{120} H_{240} Fe_6 Si_{30}
Formula weight	567.10	560.38	2860.91
Temperature [K]	103(2)	100(2)	173(2)
Crystal system	Monoclinic	Triclinic	Hexagonal
Space group	*P* $2_1/c$	*P* -1	*P* $6_3/m$
Unit cell dimensions			
a [Å].	8.7522(5)	11.4343(4)	33.9541(2)
b	11.5487(8)	14.7364(6)	33.9541(2)
c	20.1992(13)	16.7180(7)	16.95470(10)
α [°]	90	94.226(2)	90
ß	93.828(2)	108.6030(10)	90
γ	90	111.147(2)	120
Volume [$Å^3$]	2037.1(2)	2432.57(17)	16928.0(2)
Z	4	4	4
ρ_{calc} [g/cm^3]	1.849	1.530	1.123
μ [mm^{-1}]	6.737	4.055	0.751
Crystal size [mm^3]	0.040 x 0.030 x 0.030	0.040 x 0.030 x 0.030	0.200 x 0.170 x 0.060
θ range [°]	2.924 – 26.389°.	2.210 – 27.492°.	3.175 – 25.363
Index ranges	-10≤h≤10, -14≤k≤14, -25≤l≤25	-14≤h≤14, -19≤k≤19, -21≤l≤21	-40≤h≤40, -40≤k≤40, -20≤l≤20
Refl. coll.	22467	26247	185175
Indep. Refl. [Rint]	4160 [0.0466]	11062 [0.0369]	10699 [0.0542]
Absorpt. correction		Semi-empirical from equivalents	
Tmax/ Tmin	0.6465/ 0.5818	0.7456 / 0.6650	0.9143 / 0.8388
Data / restr. / param.	4160 / 0 / 205	11062 / 0 / 469	10699 / 283 / 810
GOOF	1.057	1.018	1.028
R1/wR2 [I>2σ(I)]	0.0260/ 0.0442	0.0356/ 0.0759	0.0436/ 0.1127
R1/wR2 (all data)	0.0422/ 0.0499	0.0587/ 0.0830	0.0567/0.1212
Δe max/min [e $Å^{-3}$]	0.496 / -0.497	1.270 / -0.749	0.552/ -0.376
CCDC-#	2407160	2407161	2407162

Table S 2 ^{1}H- and ^{13}C NMR as well as MS data of all identified compounds

comp	^{1}H-NMR [ppm]				^{13}C-NMR [ppm]			MS: M^+	
	δ ($C_5\underline{H}_5$)	δ ($C_5\underline{H}X_n$)	δ (Si-$\underline{H}$)	δ (Si-C$\underline{H}$)	δ ($\underline{C}_5H_5$)	δ ($\underline{C}_5HX_n$)	δ (Si-$\underline{C}$H)	$(m/z)_{calc}$	$(m/z)_{found}$
2a	3.98	–	4.77 h	0.33d	78.4	84.8	-2.5	559.7	559.6
3a	4.01	4.53	4.85 h	0.40dd	76.0	86.1, 82.5, 81.8, 74.2, 73.5	-2.4, -2.5	479.8	479.7
4a	4.08	–	4.90 h	0.41dd	76.1	89.9, 88.7, 71.4	-2.3, -2.5	539.8	539.5
5a	4.07	4.32			73.9	75.7, 71.5		459.9	459.9
6a	4.01				71.5	75.7		382.0	382.1
7a								401.9	401.9[2)]
8a	4.15	–	5.04 h, 4.84 h	0.49ddd, 0.37dd	73.9	93.4, 78.2, 74.9	-1.2, -1.6, -2.2	517.9	517.8
9a	4.10				71.8	81.2, 76.7		440.0	440.1
11a	4.17	–	4.88 h, 4.72 h	0.58d, 0.44d, 0.41d, 0.40d	71.8	97.3, 85.0, 81.2	-0.4, -1.2, -1.5	498.0	498.1
12a								418.1	418.0
13a	4.17	–	4.75 h	0.48d	69.7	89.0	-0.4	476.1	476.2
4b	4.11	–	–	0.47	75.8	90.3, 89.4, 73.0	1.9	567.8	568.1
5b	4.10	4.36	–	0.54s, 0.25s	73.4	89.8, 85.4, 78.7	1.8, 0.0	487.9	488
6b								410.0	410
8b	4.18	–	–	0.57s, 0.46s				560.0	560.2
9b	4.15	4.26	–	0.49s, 0.37s, 0.26s	71.1	95.0, 83.5, 78.8, 77.9, 70.8	2.8, 2.2, 0.2	482.0	482.0
10b	4.11	4.37	–	0.33s, 0.25s	68.9	83.8, 79.5, 76.7	1.7, 0.1	402.1	402
11b	4.19	–	–	0.57s. 0.45s				554.1	554.1
13b								546.2	546
	δ ($C_5\underline{Me}_5$)	δ ($C_5\underline{H}X_n$)	δ (Si-$\underline{H}$)	δ (Si-C$\underline{H}$)	δ ($\underline{C}_5Me_5$)	δ ($\underline{C}_5HX_n$)	δ (Si-$\underline{C}$H)		
4c[1)]	1.74	–	4.31 h	0.38 dd				655.8	656
5c								575.9	495 (M^+-HBr)
8c								634.0	634
11c	1.88				?/-11.97	?	0.30/-0.42/-0.71/-3.65	614.1	614.3
12c	1.85	4.42s	4.68 h (2H)/ 4.61 h (2H)	0.47 d(12H)/ 0.28d (6H)/ 0.27d (6H)	85.5/-12.00	90.2/86.2/82.6	0.29/-0.46/-0.75/-3.4	534.2	475.3 (M^+-$SiMe_2H$)
13c	1.93	–	4.66 h (5H)	0.51 d	86.7/ 13.1	91.4	0.25	592.2	592.3

13c[1)]	1.92 (15H)	–	4.41 h (5H)	0.35 d (30 H)		

1) In $CDCl_3$ 2)Spectrum not shown in the „Figures“ section