Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 379–381

Synthesis and structure of tetrakis[(chloromethyl)dimethylsilylethynyl]silane and -germane

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IR spectra were taken on a Vertex 70 Bruker instrument in KBr. ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{29}Si NMR spectra (79.5 MHz) were registered on a Bruker DRX-400 instrument. Chemical shifts are given relative to TMS. Elemental analysis was done on a Thermo Scientific Flash 2000 automatic CHNS analyzer. Melting points were determined on a Micro-Hot-Stage PolyTherm A device. All solvents were dried and purified by standard procedures.

*Compound **3**:* A flow of dry acetylene was passed through a flask with abs. THF (70 ml), and simultaneously a solution of ethylmagnesium bromide prepared from Mg (2.64 g, 0.11 mol) and EtBr (11.99 g, 0.11 mol) in abs. THF (100 ml) was added at 30 °C dropwise at stirring. After completion, chloro(chloromethyl)dimethylsilane (14.20 g, 0.10 mol) in abs. ether (30 ml) was added dropwise. The mixture was stirred at room temperature for several hours and then decomposed with water and dilute hydrochloric acid. The aqueous layer was separated and extracted three times with ether. The organic layer was combined with ethereal extracts and dried over calcined $CaCl_2$, filtered and washed with ether. The solvent was removed at reduced pressure, and the residue was distilled in vacuum (46°C/50 Torr) to give 8.47 g (64%) of compound **3**. IR, ν, cm^{-1}: 3281, 2968, 2933, 2037, 1396, 1256, 1178, 1105, 1067, 848, 824, 758, 688, 630. ^{1}H NMR, δ, ppm: 0.32 s (6H, Me_2Si), 2.46 s (1H, ≡CH), 2.87 s (2H, CH_2Si). ^{13}C NMR, δ, ppm: –3.46 ($SiMe_2$), 29.58 (CH_2Cl), 86.39 (C≡), 95.07 (HC≡). ^{29}Si NMR, δ: –17.3 ppm. Found, %: C 45.49; H 6.83; Si 21.18; Cl 26.48. C_5H_9SiCl. Calculated: C 45.45; H 6.82; Si 21.21; Cl 26.52.

*Tetrakis[(chloromethyl)dimethylsilylethynyl]silane **4a***: To ethylmagnesium bromide prepared from Mg (2.40 g, 0.10 mol) and EtBr (10.80 g, 0.10 mol) in abs. THF (100 ml), compound **3** (13.26 g, 0.10 mol) was added dropwise at 30 °C, this was stirred at room temperature for 1 h. Then $SiCl_4$ (4.24 g, 0.025 mol) was added dropwise at 30 °C, stirred at room temperature for 1 h. The reaction mixture was treated as above. The solid residue was crystallized from ether to give 11.22 g (81%) of compound **4a**. Colorless crystals, m. p. 188–189 °C. IR, ν, cm^{-1}: 2966, 2927, 2119, 1396, 1255, 1089, 850, 823, 795, 503. 2112. ^{1}H NMR, δ, ppm: 0.36 s (24H, Me_2Si), 2.91 s (8H, CH_2Si). ^{13}C NMR, δ, ppm: –3.66 ($SiMe_2$), 29.41 (CH_2Cl), 105.06 (C≡), 113.87 (C≡). ^{29}Si NMR, δ, ppm: –17.3 ($C_{sp}SiC_{sp3}$),

–100.13 ($C_{sp}SiC_{sp}$). Found, %: C 43.34; H 5.79; Si 25.29; Cl 25.52. $C_{20}H_{32}Si_5Cl_4$. Calculated: C 43.30; H 5.81; Si 25.31; Cl 25.56.

Tetrakis[(chloromethyl)dimethylsilylethynyl]germane ***4b***: To ethylmagnesium bromide prepared from Mg (2.40 g, 0.10 mol) and EtBr (10.80 g, 0.10 mol) in abs. THF (100 ml), compound **3** (13.26 g, 0.10 mol) was added dropwise at 30 °C, and this was stirred at room temperature for 1 h. Then $GeCl_4$ (5.30 g, 0.025 mol) was added dropwise at 30 °C, and this was stirred at room temperature for 1 h. The mixture was treated as above. The solid residue was crystallized from ether to give 10.79 g (72%) of compound **4b**. Colourless crystals, m. p. 196–198 °C. IR, ν, cm^{-1}: 2965, 2941, 2116, 1389, 1252, 1100, 851, 818, 729, 673. ^{1}H NMR, δ, ppm: 0.35 s (24H, Me_2Si), 2.90 s (8H, CH_2Si). ^{13}C NMR, δ, ppm: –3.54 ($SiMe_2$), 29.51 (CH_2Cl), 103.18 (C≡), 111.03 (C≡). ^{29}Si NMR, δ, ppm: –17.4. Found, %: C 40.11; H 5.33; Si 18.73; Ge 12.09; Cl 23.64. $C_{20}H_{32}Si_4GeCl_4$. Calculated: C 40.08; H 5.38; Si 18.75; Ge 12.11; Cl 23.66.

Reaction of compound ***4a*** *with methylamine (a) and ethylenediamine (b) (general procedure).* (*a*) Methylamine (0.22 g, 7.2 mmol) was condensed into the evacuated ampoule containing silane **4a** (0.66 g, 1.2 mmol) in abs. Et_2O (30 ml). The ampoule was sealed and kept at room temperature for 48 h. The formed precipitate was filtered; the solvent was distilled off, the residue was purified by column chromatography. (*b*) The argon filled flask was charged with silane **4a** (0.66, 1.2 mmol) in abs. Et_2O (30 ml) and ethylenediamine (0.29 g ,4.8 mmol), and this was refluxed for 48 h. The formed precipitate was filtered, the residue was treated as above in (*a*).

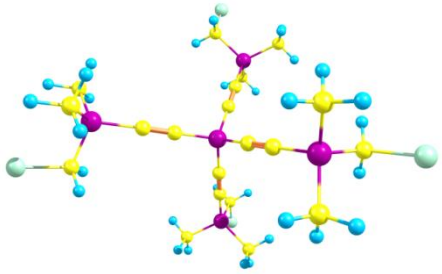
Table S1 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) of $(SiC_5H_8Cl)_4Ge$ and $(SiC_5H_8Cl)_4Si$

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
		$(SiC_5H_8Cl)_4Ge$		
Ge	0.7500	0.2500	0.27003 (6)	0.0341 (2)
Si1	0.45103 (11)	0.27867 (8)	0.02977 (13)	0.0462 (4)
C1A	0.6365 (4)	0.2556 (2)	0.1746 (5)	0.0425 (12)
C2A	0.5651 (4)	0.2649 (2)	0.1151 (5)	0.0452 (13)
C3A	0.3608 (5)	0.3190 (4)	0.1264 (6)	0.076 (2)
H3AA	0.3010	0.3266	0.0834	0.092*
H3AB	0.3475	0.2912	0.1930	0.092*
H3AC	0.3867	0.3604	0.1533	0.092*
C4A	0.4103 (5)	0.1985 (3)	-0.0297 (6)	0.075 (2)
H4AA	0.4609	0.1805	-0.0791	0.090*
H4AB	0.3972	0.1687	0.0342	0.090*
H4AC	0.3514	0.2047	-0.0752	0.090*
C5A	0.4829 (5)	0.3341 (3)	-0.0968 (5)	0.0662 (17)
H5AA	0.5085	0.3756	-0.0672	0.079*
H5AB	0.5334	0.3137	-0.1450	0.079*
Cl1	0.37578 (15)	0.34881 (9)	-0.18340 (16)	0.0830 (6)

Si2	0.72367 (13)	0.44887 (8)	0.51887 (15)	0.0541 (5)
C1B	0.7483 (4)	0.3263 (2)	0.3648 (5)	0.0438 (12)
C2B	0.7379 (4)	0.3751 (3)	0.4243 (5)	0.0513 (14)
C3B	0.6856 (7)	0.5194 (3)	0.4304 (6)	0.102 (3)
H3BA	0.6245	0.5095	0.3917	0.122*
H3BB	0.6771	0.5571	0.4805	0.122*
H3BC	0.7350	0.5287	0.3723	0.122*
C4B	0.8406 (6)	0.4624 (4)	0.5975 (8)	0.105 (3)
H4BA	0.8569	0.4238	0.6424	0.126*
H4BB	0.8919	0.4711	0.5414	0.126*
H4BC	0.8340	0.4995	0.6496	0.126*
C5B	0.6246 (6)	0.4273 (3)	0.6245 (6)	0.078 (2)
H5BA	0.5673	0.4123	0.5813	0.094*
H5BB	0.6466	0.3914	0.6745	0.094*
Cl2	0.5917 (2)	0.49613 (12)	0.7142 (2)	0.1141 (8)
		$(SiC_5H_8Cl)_4Si$		
Si	0.7500	0.2500	0.27107 (7)	0.02976 (19)
Si1	0.45214 (5)	0.27855 (3)	0.03400 (6)	0.04067 (18)
C1A	0.64018 (16)	0.25525 (11)	0.1784 (2)	0.0377 (5)
C2A	0.56736 (18)	0.26474 (12)	0.1190 (2)	0.0427 (5)
C3A	0.3621 (2)	0.31968 (18)	0.1319 (3)	0.0705 (9)
H3AA	0.3003	0.3275	0.0887	0.085*
H3AB	0.3488	0.2912	0.2003	0.085*
H3AC	0.3893	0.3622	0.1588	0.085*
C4A	0.4103 (3)	0.19780 (15)	-0.0237 (3)	0.0669 (8)
H4AA	0.4617	0.1790	-0.0748	0.080*
H4AB	0.3975	0.1675	0.0422	0.080*
H4AC	0.3492	0.2039	-0.0694	0.080*
C5A	0.4839 (2)	0.33467 (15)	-0.0926 (3)	0.0581 (7)
H5AA	0.5097	0.3774	-0.0623	0.070*
H5AB	0.5359	0.3139	-0.1421	0.070*
Cl1	0.37464 (7)	0.34869 (4)	-0.17876 (7)	0.0754 (3)
Si2	0.72482 (6)	0.44745 (3)	0.51701 (7)	0.0481 (2)
C1B	0.74856 (18)	0.32404 (10)	0.3634 (2)	0.0385 (5)
C2B	0.73899 (19)	0.37297 (12)	0.4227 (2)	0.0451 (6)
C3B	0.6869 (3)	0.51879 (16)	0.4274 (3)	0.0895 (12)
H3BA	0.6242	0.5087	0.3876	0.107*
H3BB	0.6781	0.5576	0.4785	0.107*
H3BC	0.7380	0.5282	0.3683	0.107*
C4B	0.8420 (3)	0.4615 (2)	0.5957 (4)	0.0894 (12)
H4BA	0.8588	0.4219	0.6421	0.107*
H4BB	0.8949	0.4703	0.5385	0.107*
H4BC	0.8349	0.4996	0.6486	0.107*
C5B	0.6230 (3)	0.42600 (15)	0.6220 (3)	0.0716 (9)
H5BA	0.5639	0.4117	0.5770	0.086*
H5BB	0.6442	0.3885	0.6726	0.086*
Cl2	0.59174 (9)	0.49526 (6)	0.71273 (10)	0.1039 (4)

Figure S1 Tetrakis[(chloromethyl)dimethylsilylethynyl]silane **4a**

E(MP2/6-311G(d,p) = –4062.814102 a.u., μ = 1.16 D



Standard orientation:

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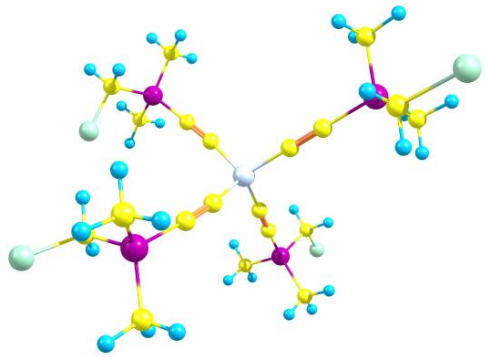
4	6	0	1.394761	0.377725	-1.202041
5	6	0	0.272220	-1.549244	0.762624
6	6	0	2.377409	0.653204	-1.908523
7	6	0	-2.509522	-0.390997	-1.946538
8	6	0	0.493162	-2.597875	1.388869
9	6	0	-0.549513	2.273470	1.805623
10	14	0	3.850117	1.024169	-2.953376
11	14	0	-4.009324	-0.616795	-2.994299
12	14	0	0.817679	-4.135414	2.352742
13	14	0	-0.825822	3.671550	2.975004
14	6	0	-0.362600	3.131150	4.701270
15	6	0	-2.603215	4.231401	2.856325
16	6	0	4.835895	2.398671	-2.162384
17	6	0	3.286670	1.454259	-4.680846
18	6	0	4.851719	-0.579924	-2.968054
19	6	0	-5.449275	-0.698692	-1.771021
20	6	0	-3.865597	-2.222188	-3.936972
21	6	0	-4.199080	0.858228	-4.123375
22	6	0	2.519782	-4.777762	1.932142
23	6	0	-0.524077	-5.382831	1.991873
24	6	0	0.746322	-3.597407	4.164361
25	17	0	1.044736	-4.996550	5.247943
26	17	0	-7.002773	-0.918833	-2.642288
27	17	0	6.337401	-0.384631	-3.955716
28	6	0	0.336312	5.039415	2.379280
29	17	0	0.187624	6.490560	3.424672
30	1	0	-0.481202	3.956450	5.409500
31	1	0	0.677072	2.792982	4.738071
32	1	0	-0.999763	2.303693	5.027452
33	1	0	-2.783793	5.086648	3.514133
34	1	0	-2.851406	4.526297	1.832566
35	1	0	-3.279654	3.422990	3.149486
36	1	0	5.737357	2.612091	-2.744271
37	1	0	5.138285	2.126924	-1.146833
38	1	0	4.238969	3.313776	-2.104730
39	1	0	4.145411	1.643052	-5.331757
40	1	0	2.661174	2.351806	-4.667092
41	1	0	2.699500	0.638943	-5.113427
42	1	0	4.276387	-1.405016	-3.393475
43	1	0	5.158551	-0.867567	-1.960135
44	1	0	-5.525509	0.218598	-1.183180

45	1	0	-5.336221	-1.534947	-1.077717
46	1	0	-4.761839	-2.398544	-4.538982
47	1	0	-3.739178	-3.066036	-3.252448
48	1	0	-3.000673	-2.196738	-4.606517
49	1	0	-5.103656	0.765674	-4.731602
50	1	0	-3.339268	0.939099	-4.795107
51	1	0	-4.265919	1.784917	-3.545964
52	1	0	2.752213	-5.670502	2.520159
53	1	0	3.283418	-4.021975	2.137794
54	1	0	2.578983	-5.039356	0.871429
55	1	0	-0.374242	-6.292817	2.580291
56	1	0	-0.519753	-5.653715	0.931853
57	1	0	-1.510166	-4.975440	2.233313
58	1	0	-0.231628	-3.183115	4.418831
59	1	0	1.501108	-2.839577	4.385201
60	1	0	0.103743	5.342175	1.356038
61	1	0	1.379183	4.716185	2.406320

Figure S2 Tetrakis[(chloromethyl)dimethylsilylethynyl]germane **4b**

E(MP2/6-311G(d,p) = – 5849.164956 a.u., μ = 3.16 D



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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6	6	0	-2.193525	2.476556	0.467727
7	6	0	-2.072818	-2.506990	-0.722012
8	6	0	1.954925	0.519566	-1.972899
9	6	0	1.375450	-0.605626	2.661317
10	14	0	-3.271453	3.959471	0.657194
11	14	0	-3.110366	-3.958580	-1.184363
12	14	0	3.483493	0.771677	-2.971299
13	14	0	2.577963	-0.893263	4.020426
14	6	0	2.831597	-2.726653	4.262948
15	6	0	1.972736	-0.056146	5.581625
16	6	0	-2.947683	4.748644	2.318470
17	6	0	-5.057061	3.455581	0.445396
18	6	0	-2.747509	5.124952	-0.736991
19	6	0	-4.548537	-3.939931	0.043980
20	6	0	-2.107773	-5.521287	-0.985997
21	6	0	-3.742901	-3.734906	-2.926948
22	6	0	3.974024	2.572280	-2.898539

23	6	0	3.201946	0.183628	-4.721368
24	6	0	4.779313	-0.302530	-2.110284
25	17	0	6.371512	-0.142947	-2.923951
26	17	0	-5.666440	-5.307694	-0.273549
27	17	0	-3.713158	6.637109	-0.689398
28	6	0	4.192821	-0.063737	3.482431
29	17	0	4.848101	-0.793517	1.982206
30	1	0	3.183472	-3.197266	3.341425
31	1	0	1.893207	-3.207135	4.555616
32	1	0	3.570738	-2.913301	5.048931
33	1	0	1.824092	1.016080	5.424222
34	1	0	1.016371	-0.484703	5.896349
35	1	0	2.688410	-0.188510	6.399603
36	1	0	-3.550391	5.653326	2.441135
37	1	0	-1.893203	5.020961	2.421282
38	1	0	-3.198739	4.055311	3.126752
39	1	0	-5.715765	4.326143	0.516082
40	1	0	-5.347429	2.740397	1.220810
41	1	0	-5.215414	2.982395	-0.528091
42	1	0	-2.896817	4.666583	-1.716969
43	1	0	-1.694296	5.400882	-0.651139
44	1	0	-5.125309	-3.015609	-0.032019
45	1	0	-4.194682	-4.032804	1.073031
46	1	0	-2.713742	-6.401927	-1.218475
47	1	0	-1.737039	-5.618938	0.038529
48	1	0	-1.244742	-5.509834	-1.658366
49	1	0	-4.392096	-4.567754	-3.212746
50	1	0	-2.908925	-3.690103	-3.633714
51	1	0	-4.313945	-2.806336	-3.018085
52	1	0	4.905010	2.742209	-3.447256
53	1	0	4.122185	2.891618	-1.862801
54	1	0	3.194392	3.200561	-3.339653
55	1	0	4.118064	0.278159	-5.311915
56	1	0	2.419024	0.775931	-5.204389
57	1	0	2.890734	-0.864981	-4.734765
58	1	0	4.498846	-1.357918	-2.134826
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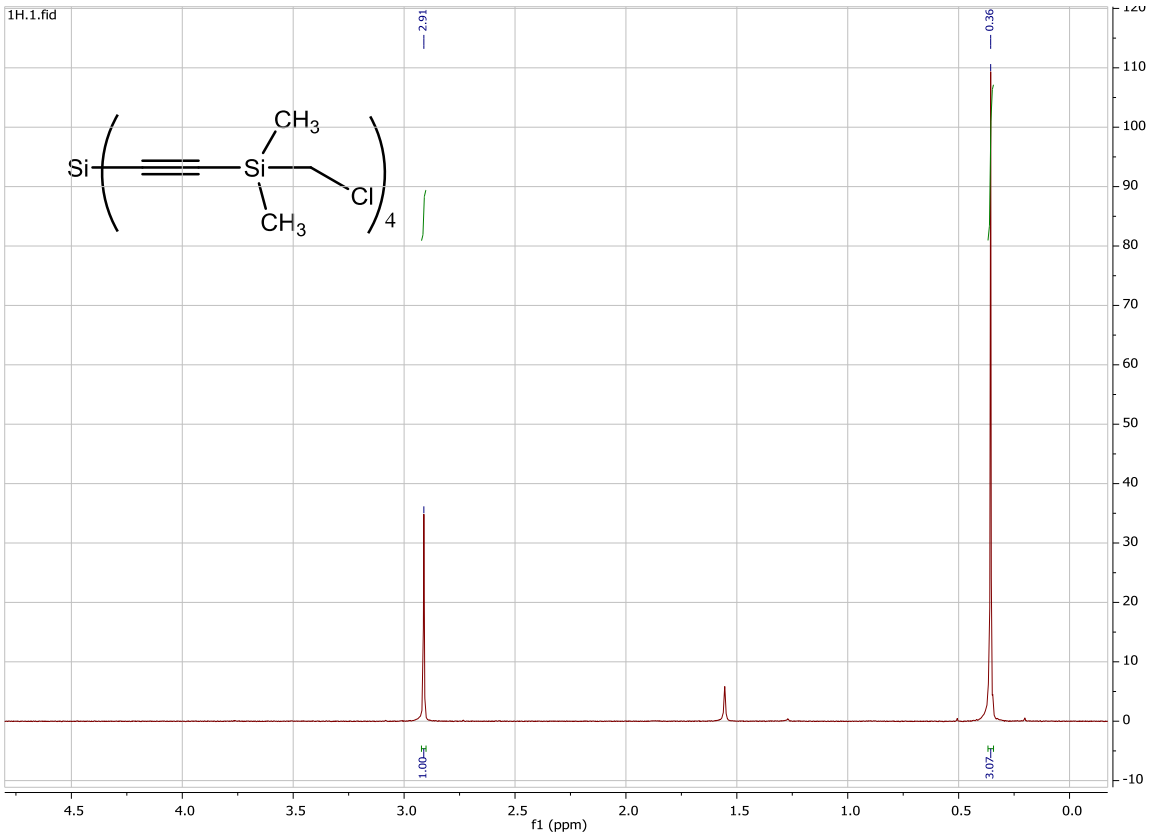


^{1}H NMR of compound **4a**

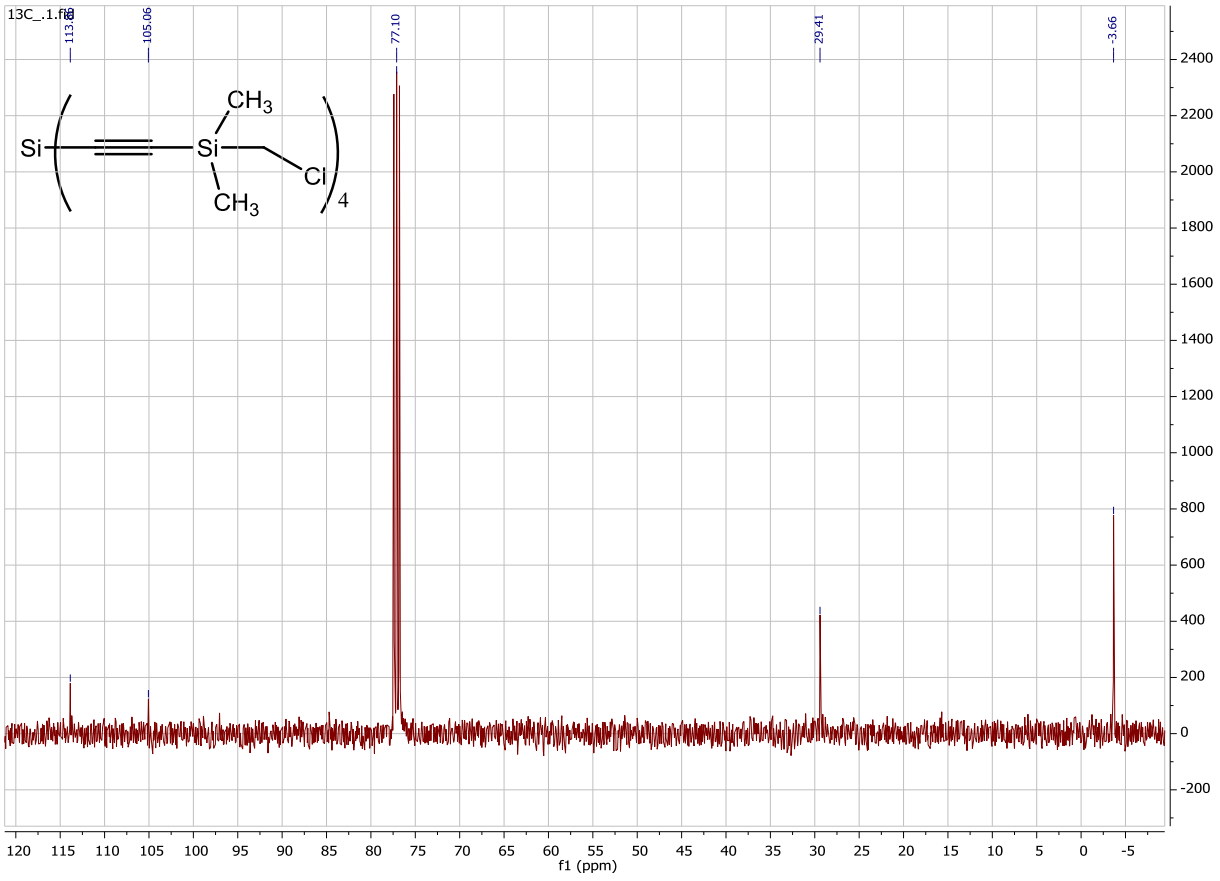
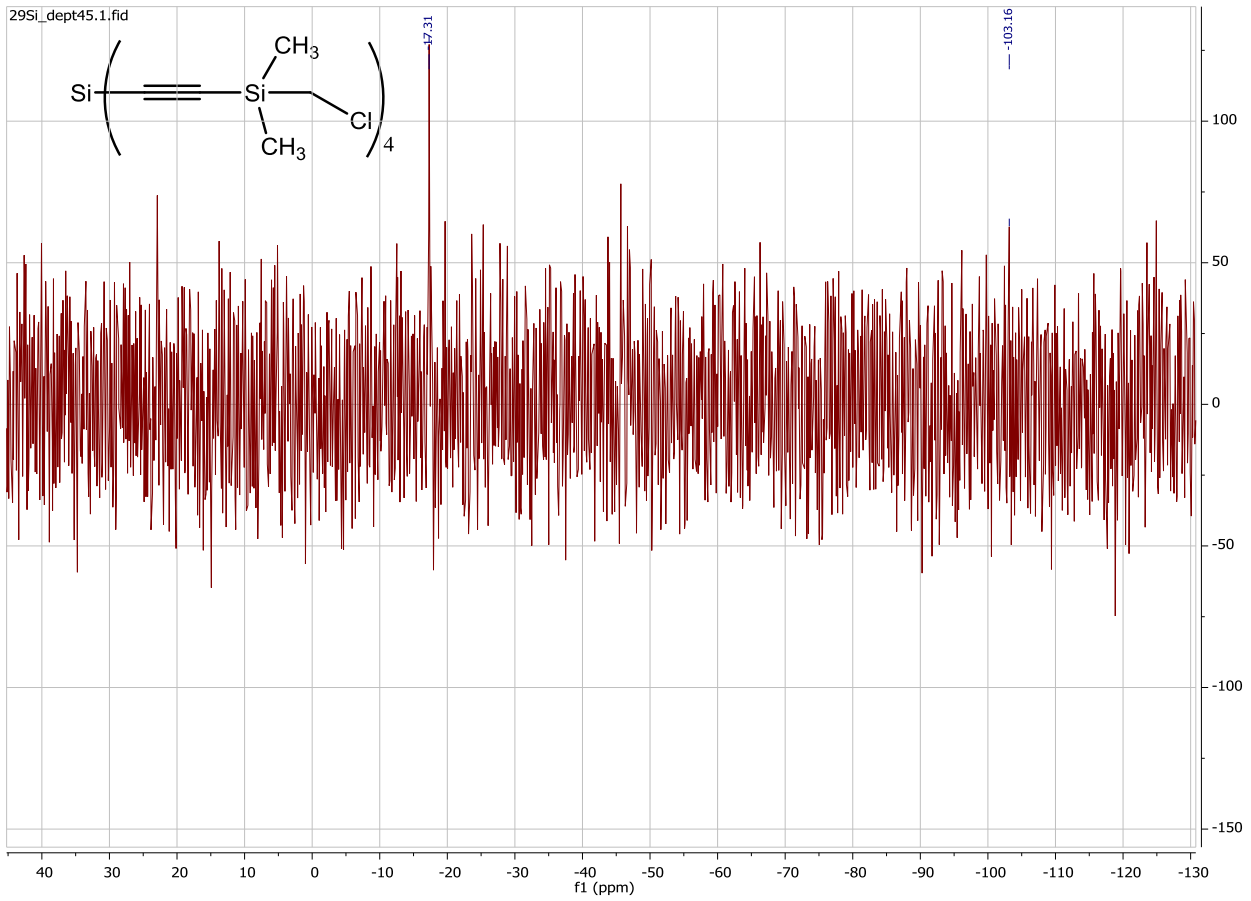
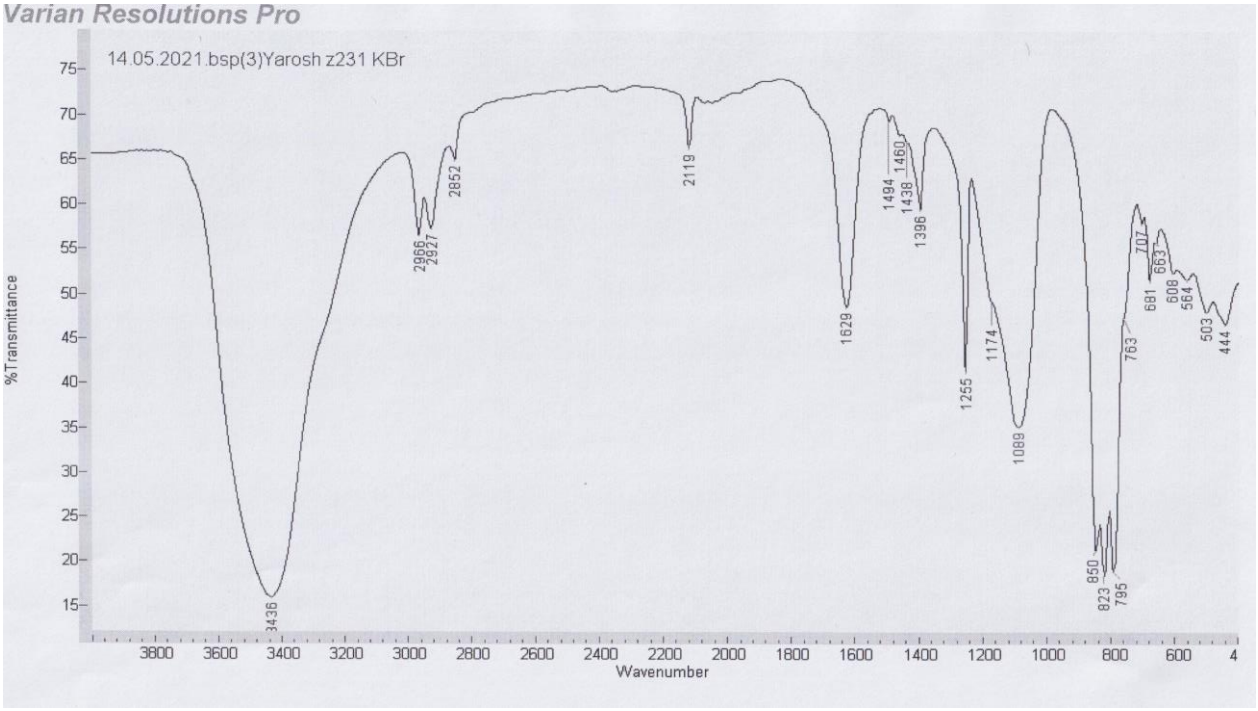


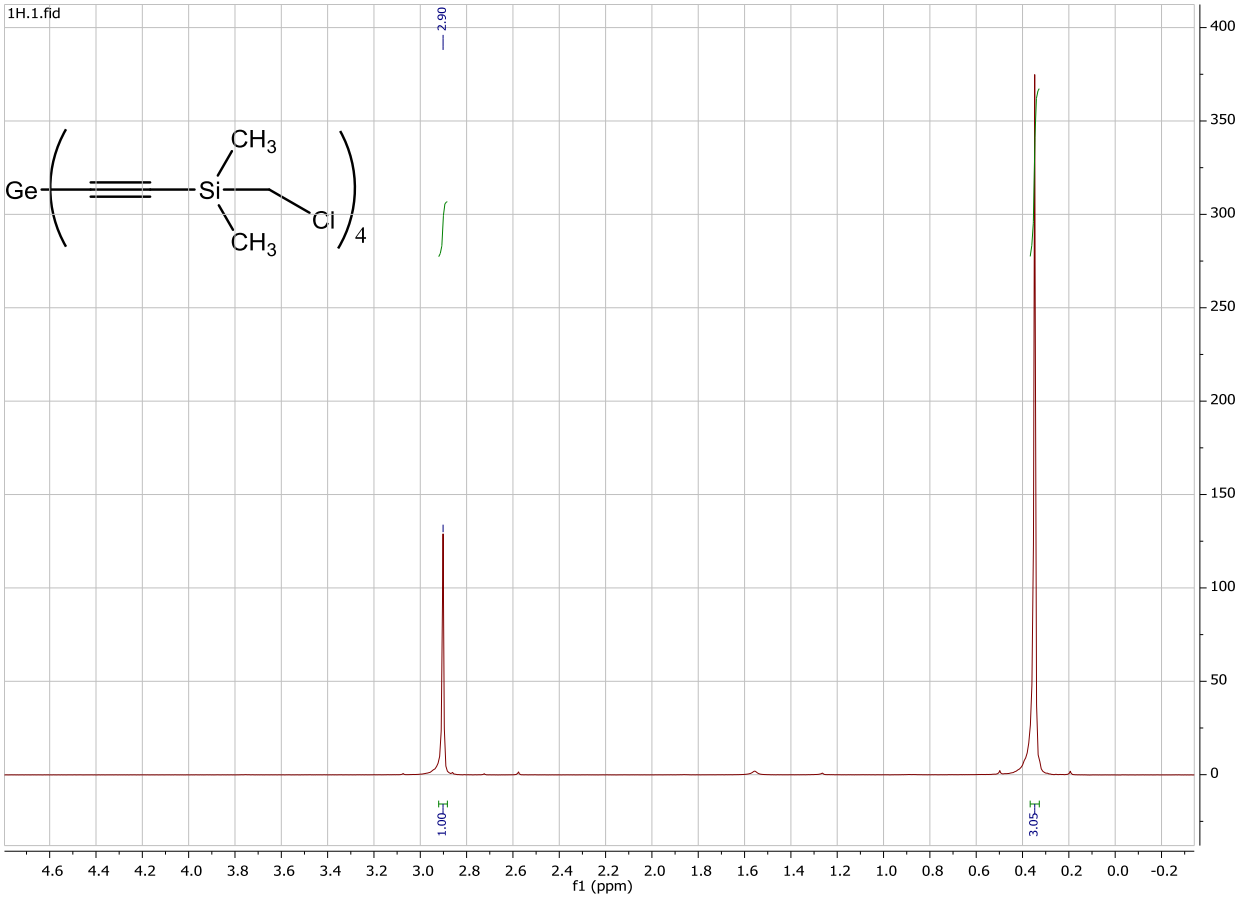
Figure 3. ^{13}C **4a**



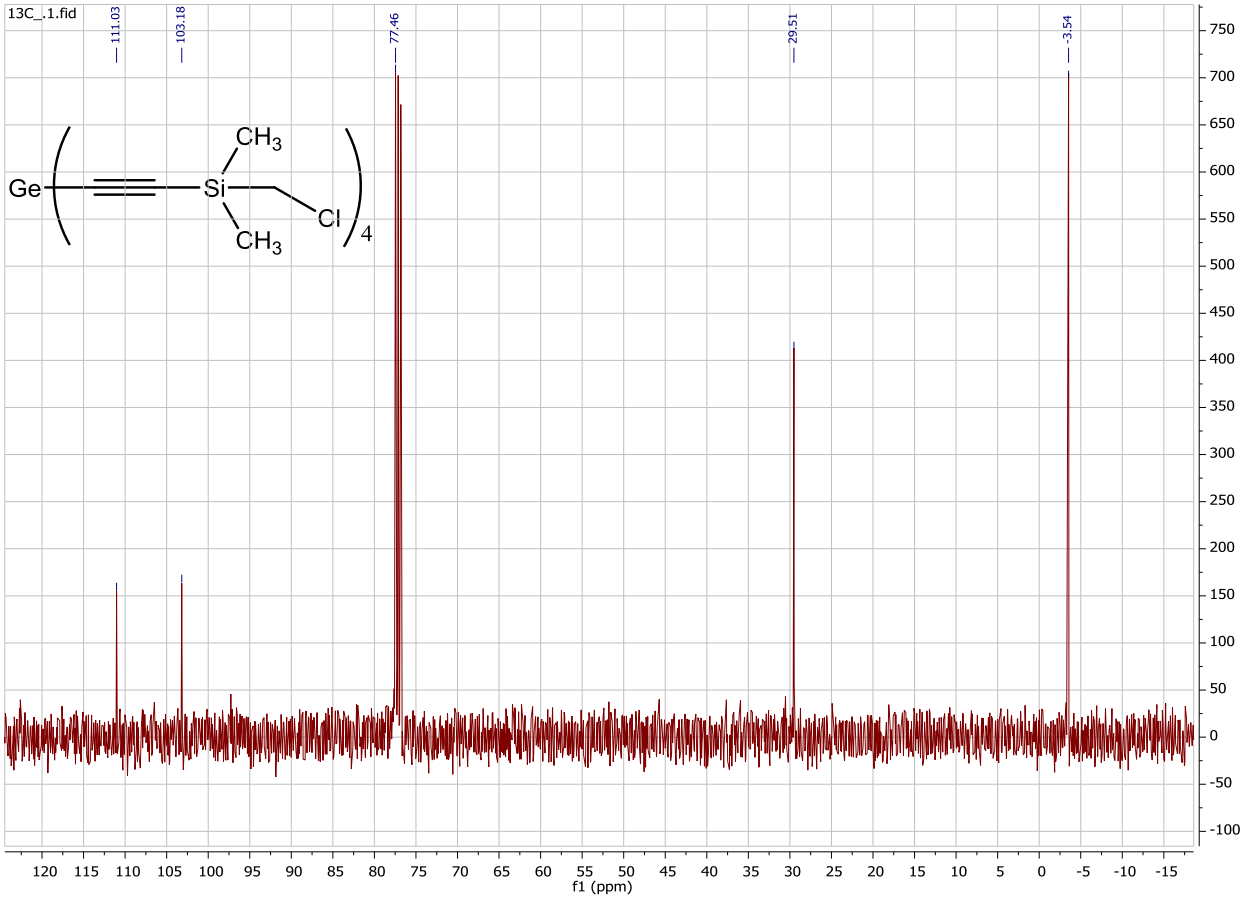
^{29}Si NMR of compound **4a**



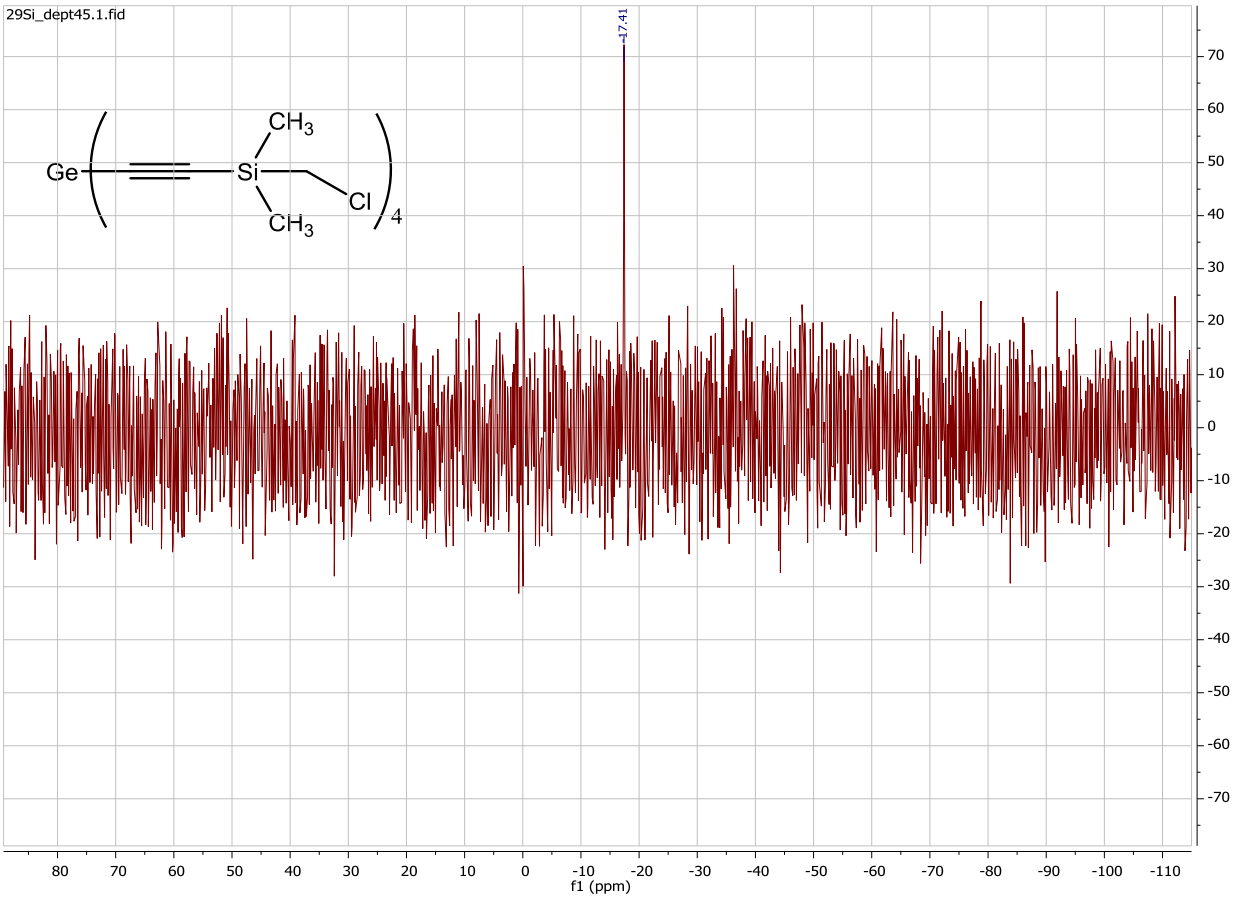
IR of compound **4a**



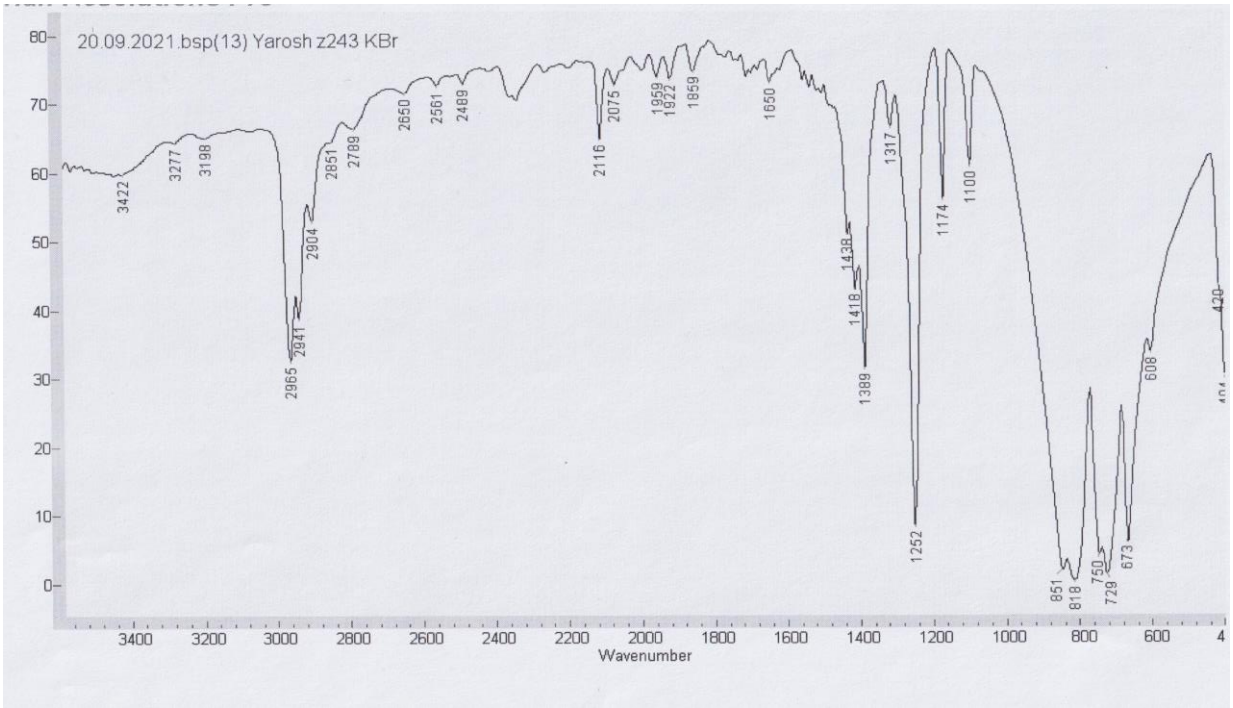
^{1}H NMR of compound **4b**



^{13}C NMR of compound **4b**



^{29}Si NMR of compound **4b**



IR of compound **4a**