Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Facile access to silyl-functionalized N-heterocyclic olefins with $HSiCl_3$

Rajendra S. Ghadwal,*[a] Sven O. Reichmann,[a] Felix Engelhardt,[a] Diego M. Andrada[b] and Gernot Frenking[b]

[a]Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany.[b]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany .

(E-mail: rghadwal@uni-goettingen.de)

Experimental

All syntheses and manipulations were carried out under an inert atmosphere of dry nitrogen or argon gas using glove-box or Schlenk-line techniques. The N-heterocyclic olefins (NHOs) $IPrCH_2$ (**1**) and $SIPrCH_2$ (**2**) ($IPrCH_2$ = {N(2,6-*i*$Pr_2C_6H_3$)CH}$_2$C=CH_2 and $SIPrCH_2$ = {N(2,6-*i*$Pr_2C_6H_3$)-CH_2}$_2$C=CH_2) were prepared[1,2] as reported earlier. C_6D_6 was dried over K-benzophenone ketyl and distilled under dry argon prior to use. All other solvents were dried and purified by a MBRAUN solvent purification system (MB SPS 800). ^{1}H, ^{13}C, and ^{29}C NMR spectra were recorded using a Bruker Avance DPX 300 or Bruker Avance DRX 500 spectrometer. Elemental analyses were performed at the Institut für Anorganische Chemie, Universität Göttingen.

Preparation of $IPrCHSiHCl_2$ (3): To a 100 mL toluene solution of $IPrCH_2$ (**1**) (5.41 g, 13.43 mmol) was added $HSiCl_3$ (0.68 mL, 6.71 mmol) at –78 °C with constant stirring. Resulting suspension was brought to room temperature and further stirred for 4 h. White insoluble precipitate was removed by filtration, washed with 10 mL toluene, and dried under vacuum, which affords compound **5**.[1b] All volatiles from the light yellow filtrate were removed under vacuum to obtained off-white solid. Recrystallization from a 40 mL toluene solution at –30 °C affords colorless crystals of compound **3** (2.96 g, 87 %). Elemental analysis (%) calcd for $C_{28}H_{38}Cl_2N_2Si$: C, 67.04; H, 7.64; N, 5.58; found: C, 67.01; H, 7.63; N, 3.53. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.09 (d, 6H, J = 6.91 Hz, CH*Me*$_2$); 1.13 (d, 6H, J = 6.94 Hz, CH*Me*$_2$); 1.32 (d, 6H, J = 6.89 Hz, CH*Me*$_2$); 1.42 (d, 6H, J = 6.87, Hz CH*Me*$_2$); 2.60 (d, 1H, J = 6.95 Hz, C*H*SiH); 2.94 (q, 2H, J = 6.94 Hz, C*H*Me$_2$); 3.02 (q, 2H, J = 6.92 Hz, C*H*Me$_2$); 4.39 (d, 1H, J = 6.89 Hz, CHSi*H*); 5.87(d, 1H, J = 2.30 Hz, NC*H*); 5.89 (d, 1H, J = 2.15 Hz, NC*H*); 7.08 (m, 4H, *m*-C_6H_3); 7.19 (m, 2H, *p*-C_6H_3). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 22.75, 23.63, 23.96, 24.82 (CH*Me*$_2$); 28.78, 28.80 (*C*HMe$_2$); 48.18 (*C*HSiH); 115.89, 116.61 (N*C*H); 124.80, 125.27 (*m*-C_6H_3); 128.51, 133.99 (*o*-C_6H_3) 130.26, 130.90, (*p*-C_6H_3); 147.98 (*ipso*-C_6H_3) 155.24 (N*C*CH) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 25 °C): δ –9.83 (J_{Si-H} = 291.13 Hz) ppm.

Preparation of $SIPrCHSiHCl_2$ (4): Compound **4** was prepared by a similar method employed for the synthesis of **3** using NHO **2** (2.70 g, 6.67 mmol) and $HSiCl_3$ (0.34 mL, 3.36 mmol). Yield: 1.35 g, 80 %). Elemental analysis (%) calcd for $C_{28}H_{40}Cl_2N_2Si$: C, 66.78; H, 8.01; N, 5.56; found: C, 66.75; H, 7.97; N, 5.55. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.14 (d, 6H, J = 6.92 Hz, CH*Me*$_2$); 1.20 (d, 6H, J = 6.92 Hz, CH*Me*$_2$); 1.36 (d, 6H, J = 6.82 Hz, CH*Me*$_2$); 1.45 (d, 6H, J = 6.83 Hz, CH*Me*$_2$); 2.59 (d, 1H, J = 7.14 Hz, C*H*SiH); 3.18 (m, 4H, C*H*Me$_2$); 3.37(m, 4H, NC*H*$_2$); 4.17 (d, 1H, J = 6.89 Hz, CHSi*H*); 7.09 (m, 4H, *m*-C_6H_3); 7.20 (m, 2H, *p*-C_6H_3). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 22.48, 23.23, 23.43, 24.32 (CH*Me*$_2$); 27.23, 27.45, 27.56 (*C*HMe$_2$); 48.64, 49.27 (N*C*H$_2$); 53.70 (*C*HSiH); 121.80, 122.35, 123.28, 124.10 (*m*-C_6H_3); 128.28, 128.80 (*o*-C_6H_3); 133.29, 134.65 (*p*-C_6H_3); 146.10, 147.39 (*ipso*-C_6H_3); 161.20 (N*C*CH) ppm. ^{29}Si NMR (99 MHz, C_6D_6, 25 °C): δ –7.15 (J_{Si-H} = 295.67 Hz) ppm.

Characterization of compound [***IPrCH$_3$***]***Cl (5):*** Compound **5** was characterized by ^{1}H and ^{13}C NMR spectral study.[1b]

Characterization of compound [S***IPrCH$_3$***]***Cl (6):*** ^{1}H NMR (300 MHz, $CDCl_3$, 25 $^{\circ}$C): δ 1.21 (d, 12H, J = 6.87 Hz, CH*Me*$_2$); 1.28 (d, 6H, J = 6.82 Hz, CH*Me*$_2$); 1.36 (d, 12H, J = 6.70 Hz, CH*Me*$_2$); 1.71 (s, 3H, C*Me*); 2.90 (m, 4H, C*H*Me$_2$); 4.64 (s, 2H, NCH$_2$); 4.69 (s, 2H, NCH$_2$); 7.29 (d, 4H, J = 7.79 Hz, *m*-C$_6$*H*$_3$); 7.49 (t, 2H, J = 7.79 Hz, *p*-C$_6$*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 $^{\circ}$C): δ 12.54 (C*Me*); 23.11, 23.63; 24.28, 24.90 (CH*Me*$_2$); 29.12, 29.14 (*C*HMe$_2$); 53.68 (N*C*H$_2$); 124.44, 125.53, 125.56 (*m*-C$_6$H$_3$); 129.17, 129.33 (*o*-C$_6$H$_3$); 131.61, 131.69 (*p*-C$_6$H$_3$); 146.12 (*ipso*-C$_6$H$_3$); 170.47 (N*C*Me) ppm.

NMR Spectra of the Compounds 3, 4, 5 and 6:

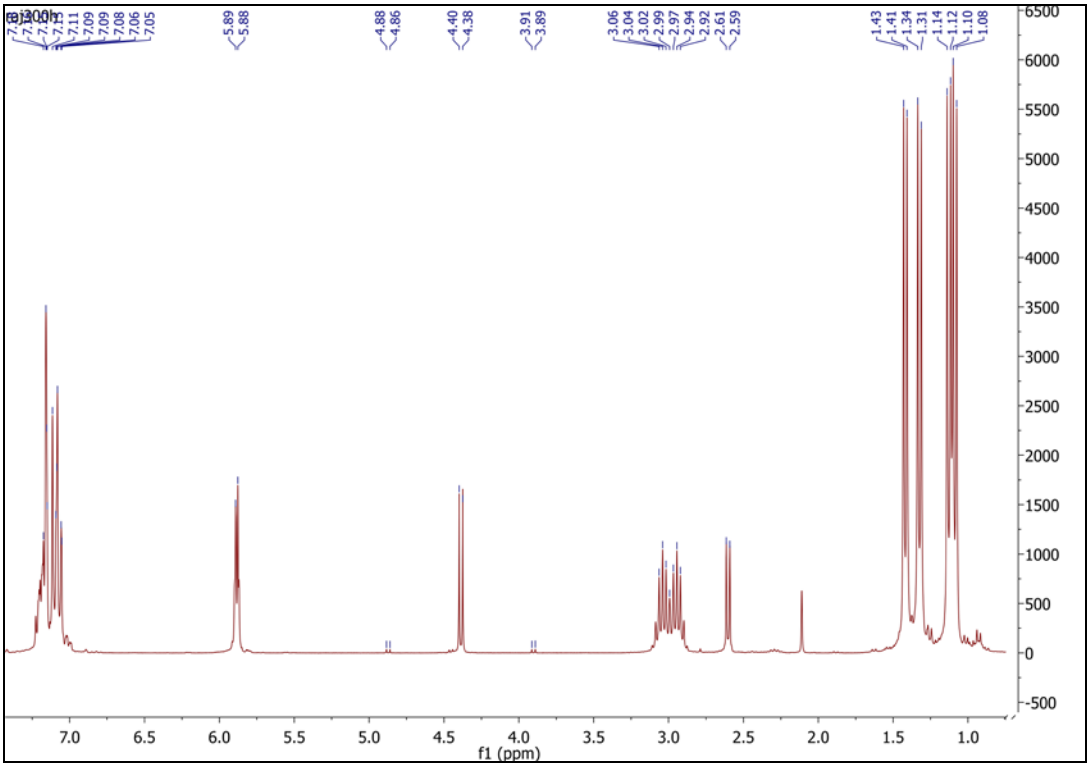

Chart 1: ^{1}H NMR spectrum of compound **3**.

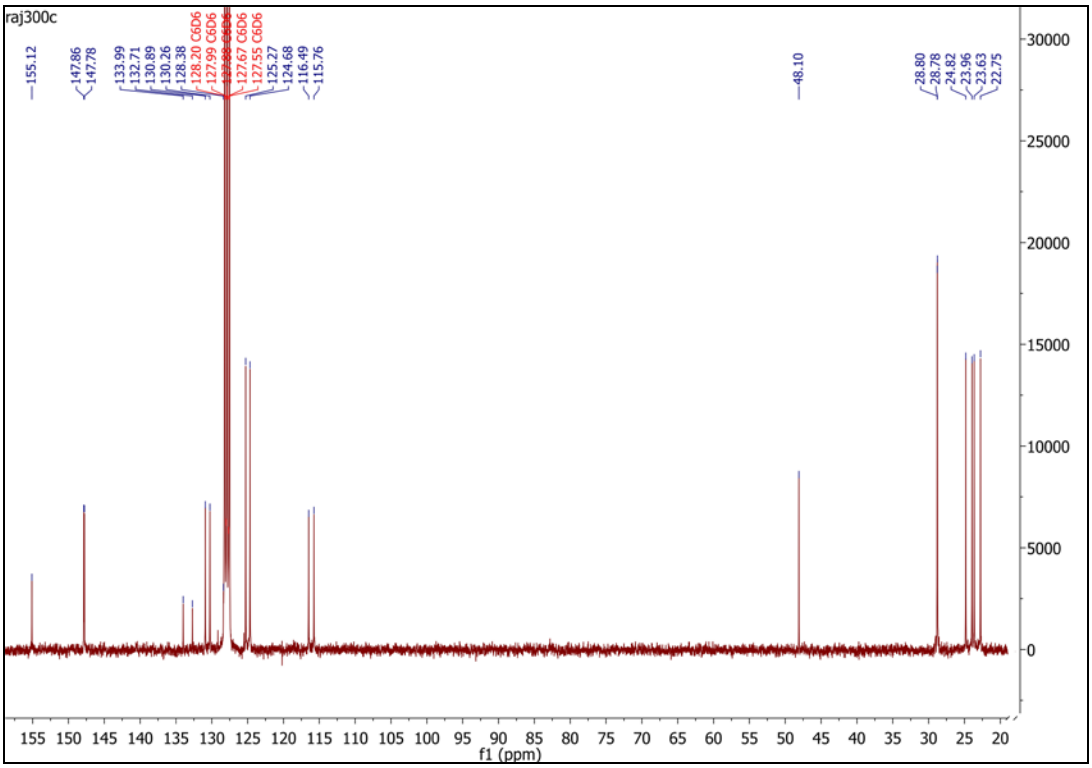

Chart 2: ^{13}C NMR spectrum of compound **3**.

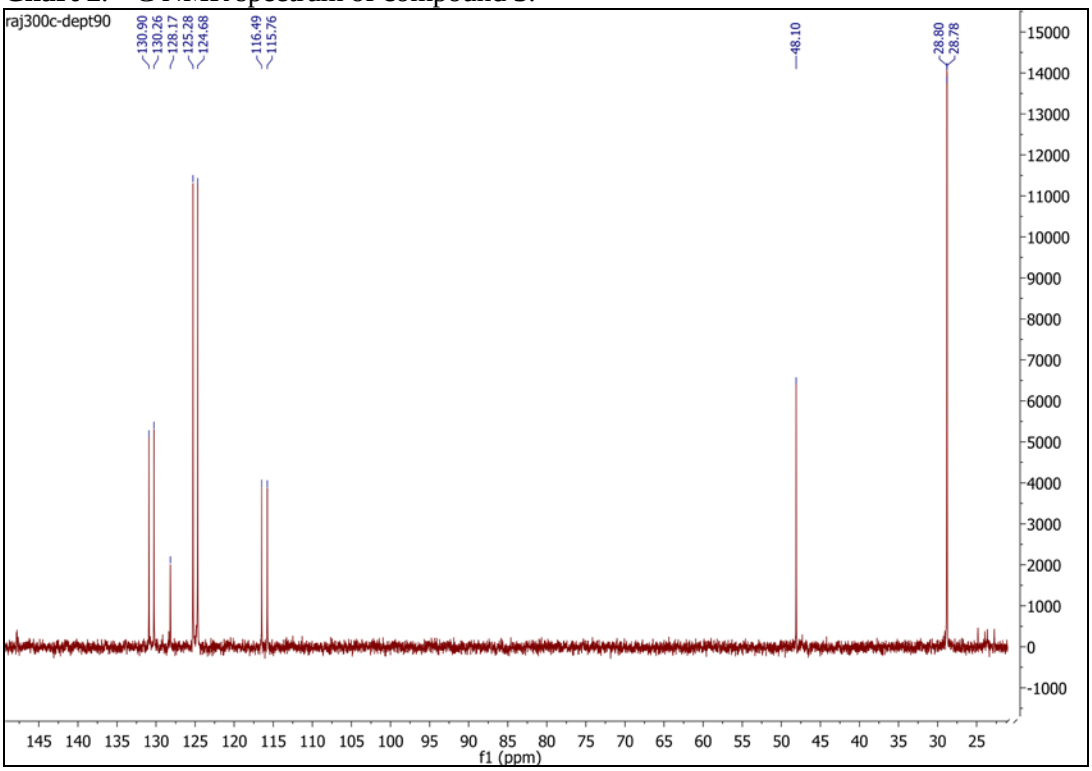

Chart 3: ^{13}C-dept90 NMR spectrum of compound **3**.

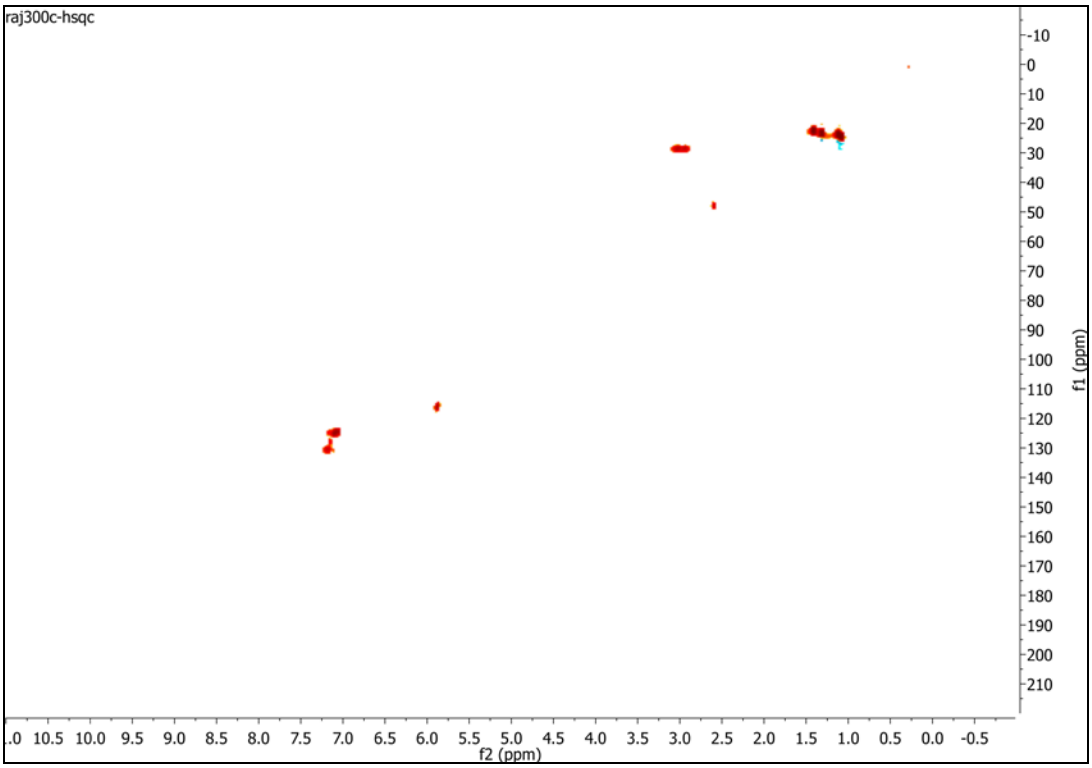

Chart 4: ^{13}C-hsqc NMR spectrum of compound **3**.

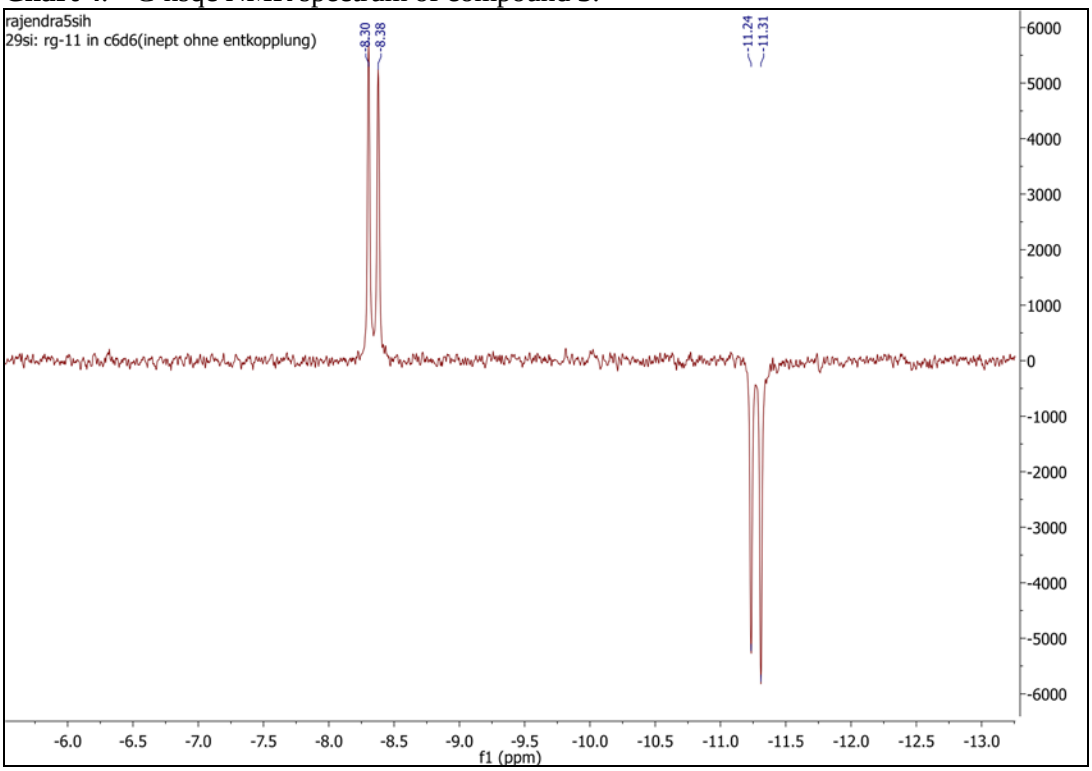

Chart 5: ^{29}Si NMR (INEPT without decoupling) spectrum of compound **3**.

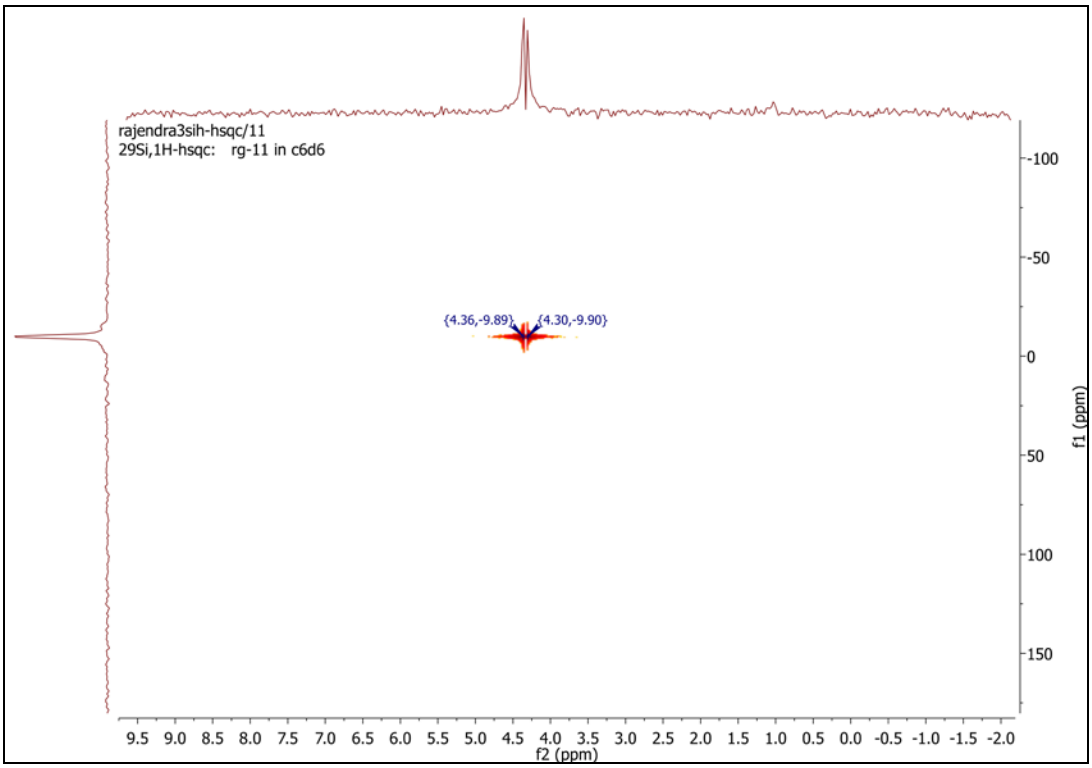

Chart 6: ^{29}Si-^{1}H hsqc NMR spectrum of compound **3**.

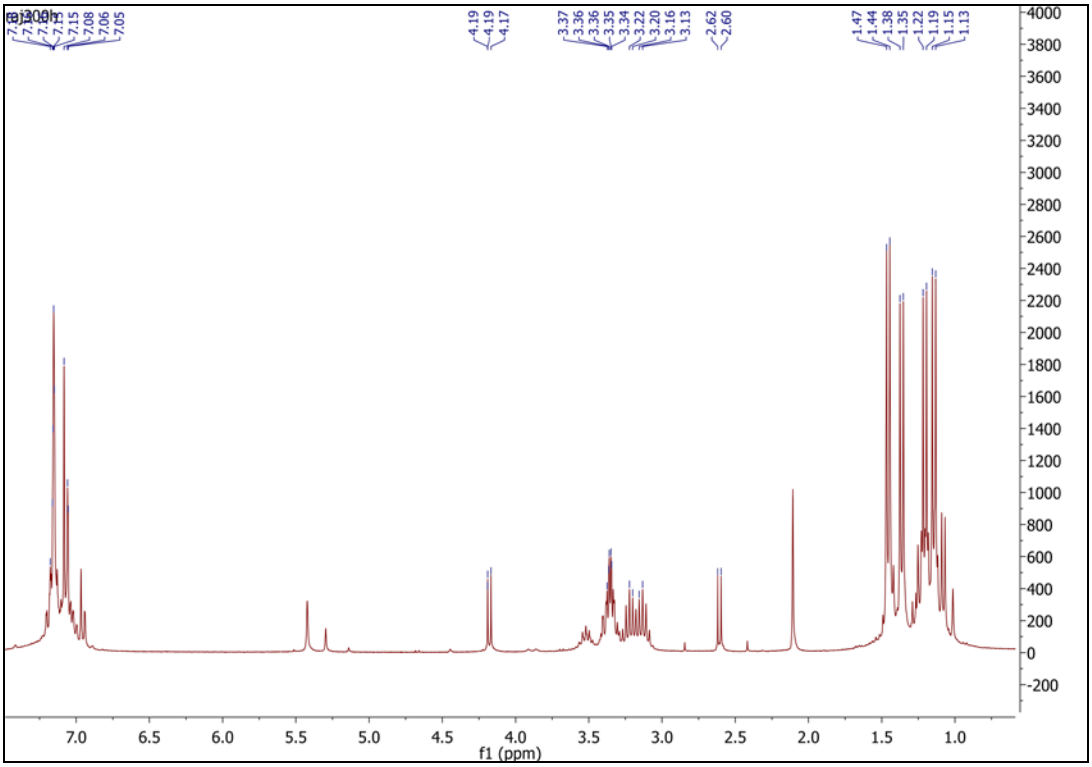

Chart 7: ^{1}H NMR spectrum of compound **4**.

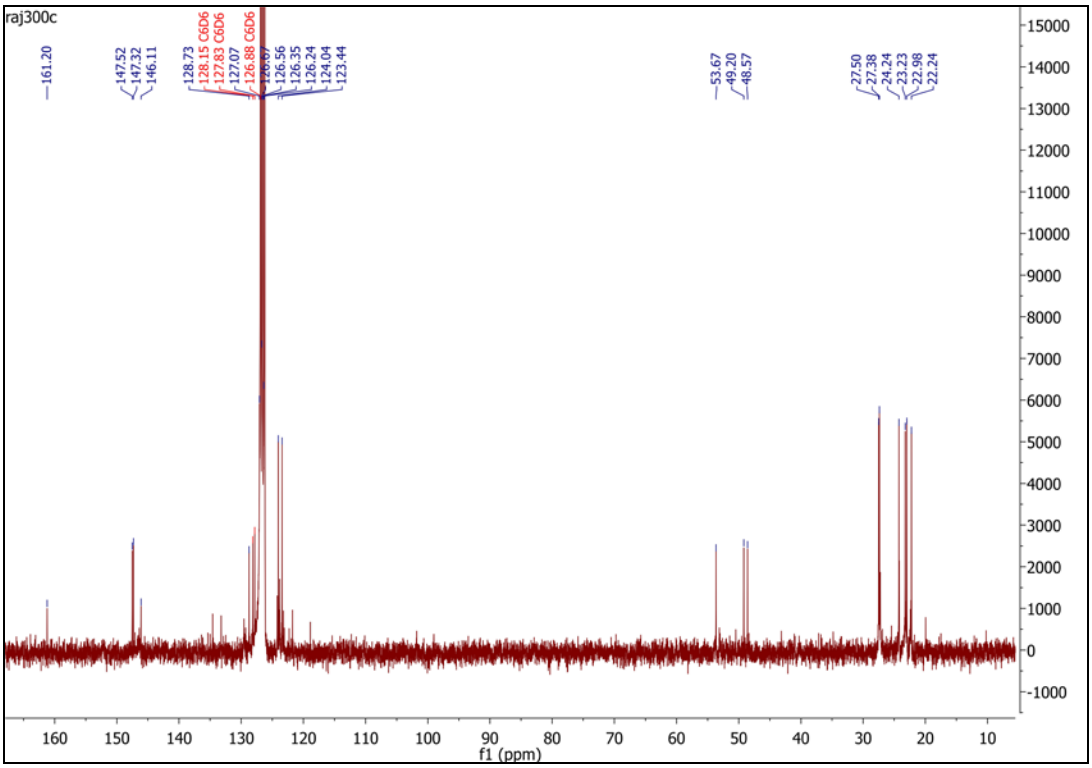

Chart 8: ^{13}C NMR spectrum of compound **4**.

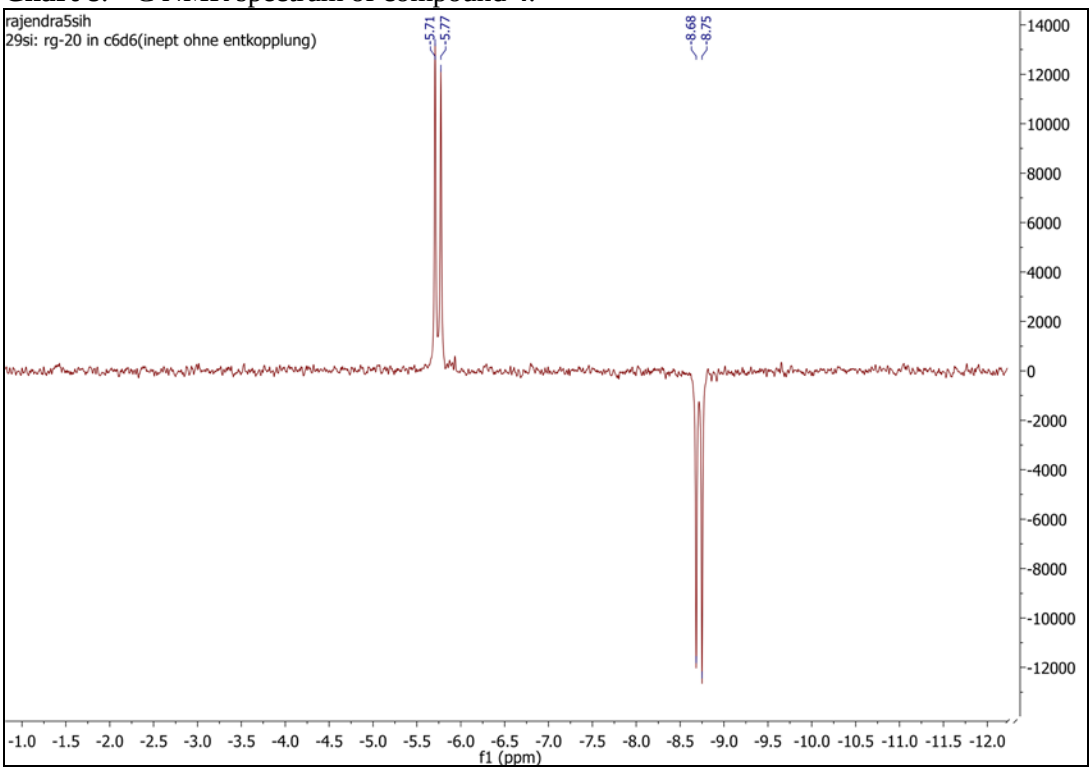

Chart 9: ^{29}Si NMR (INEPT without decoupling) spectrum of compound **4**.

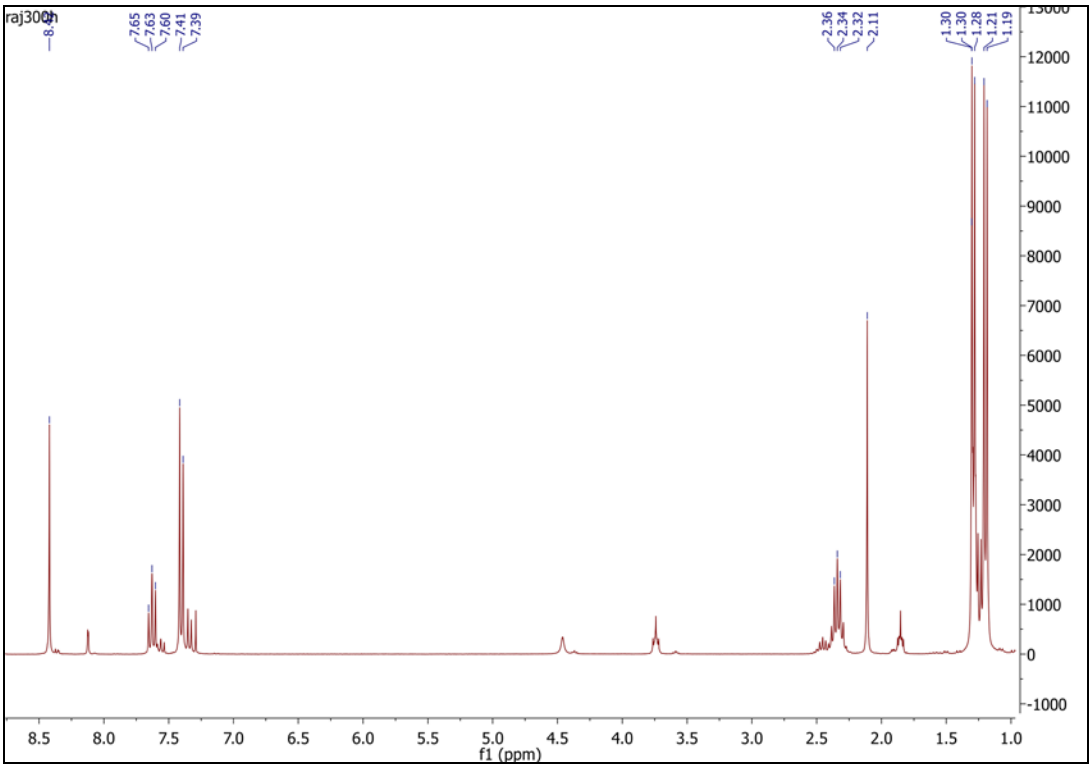

Chart 10: ^{1}H NMR spectrum of compound **5**.

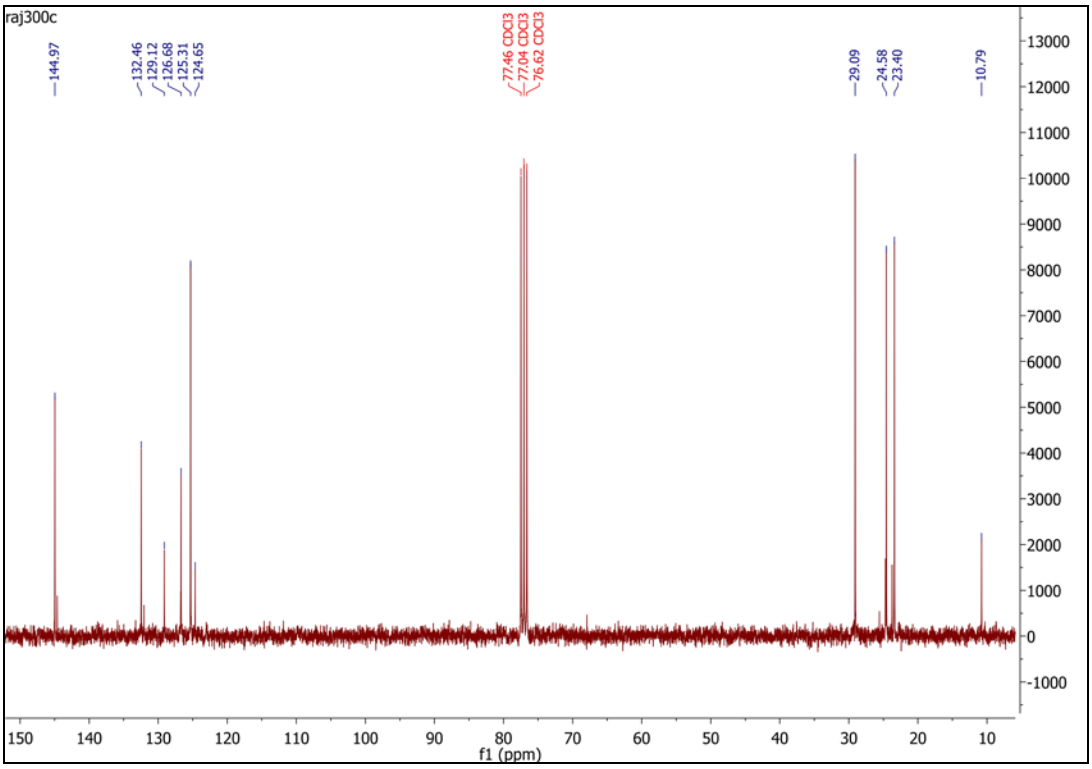

Chart 11: ^{13}C NMR spectrum of compound **5**.

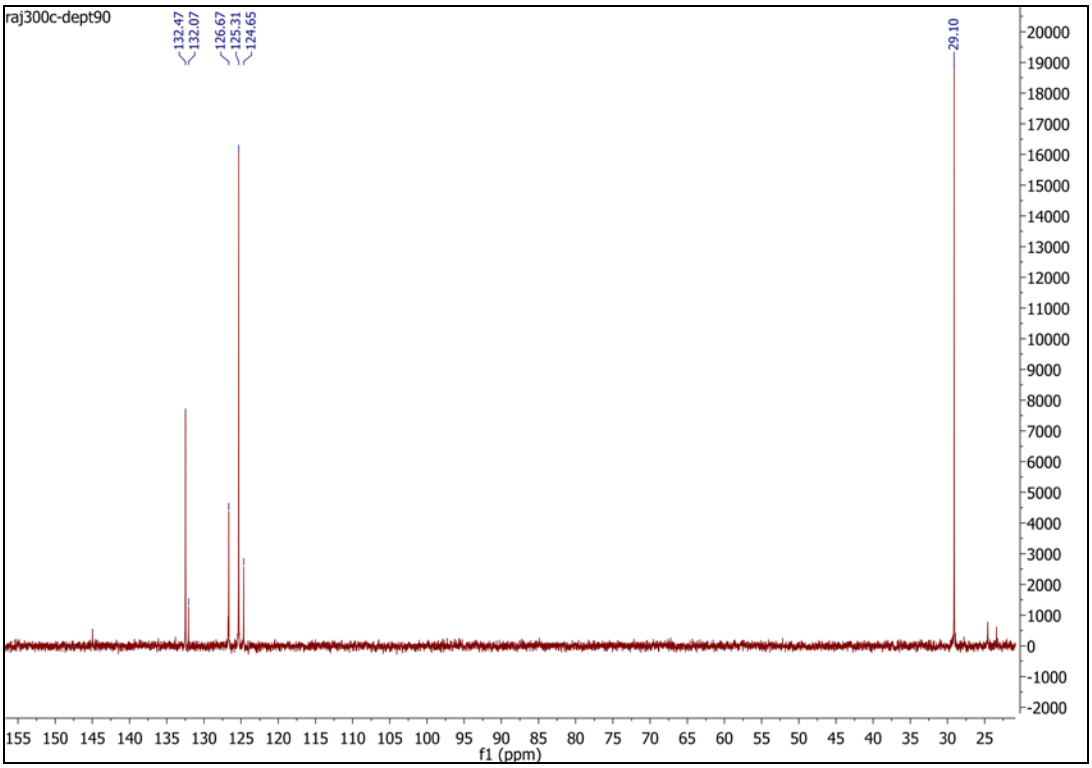

Chart 12: ^{13}C-dept90 NMR spectrum of compound **5**.

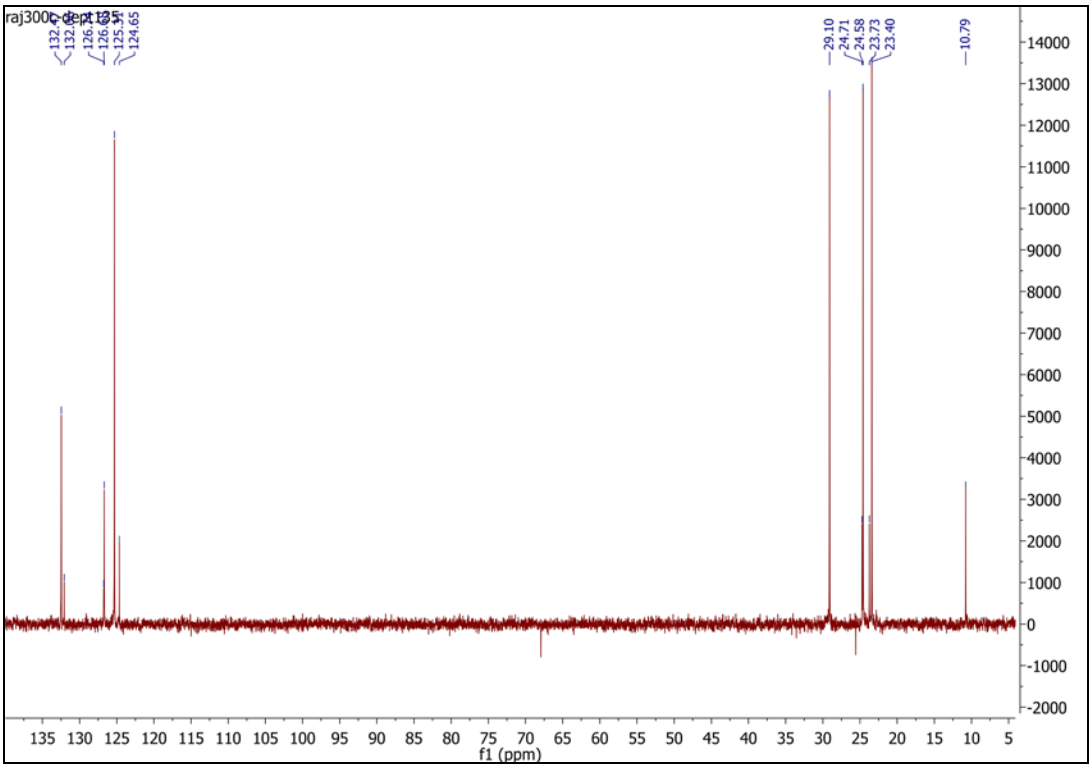

Chart 13: ^{13}C-dept135 NMR spectrum of compound **5**.

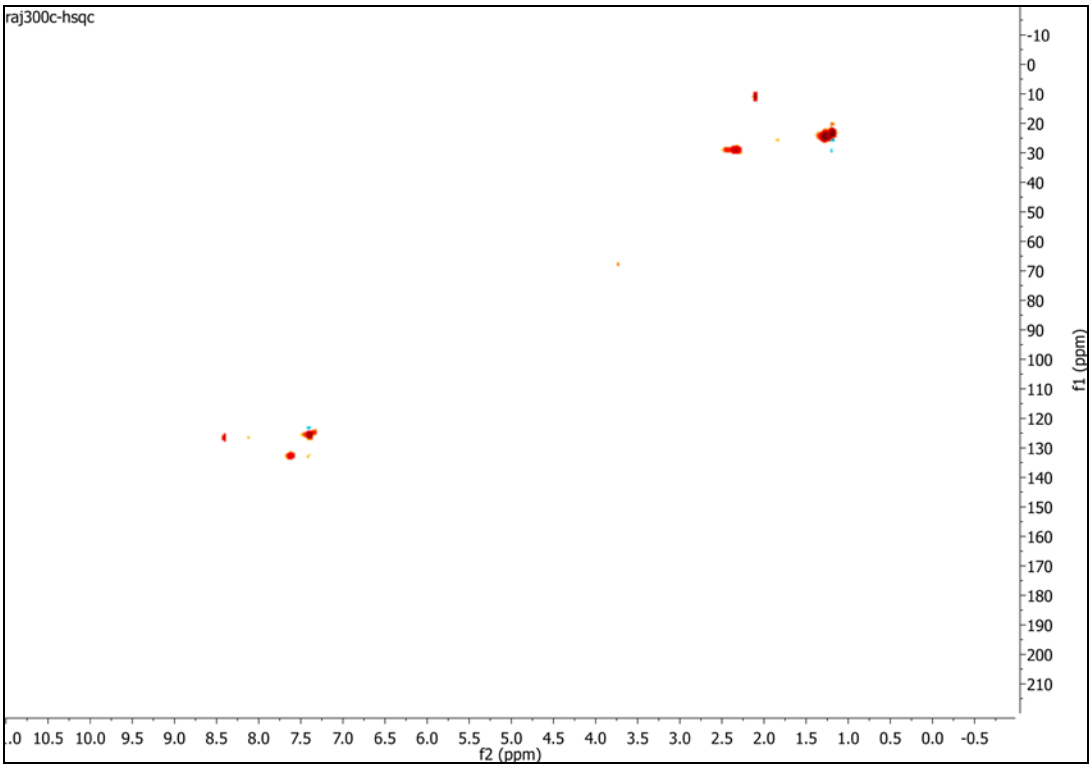

Chart 14: ^{13}C-hsqc NMR spectrum of compound **5**.

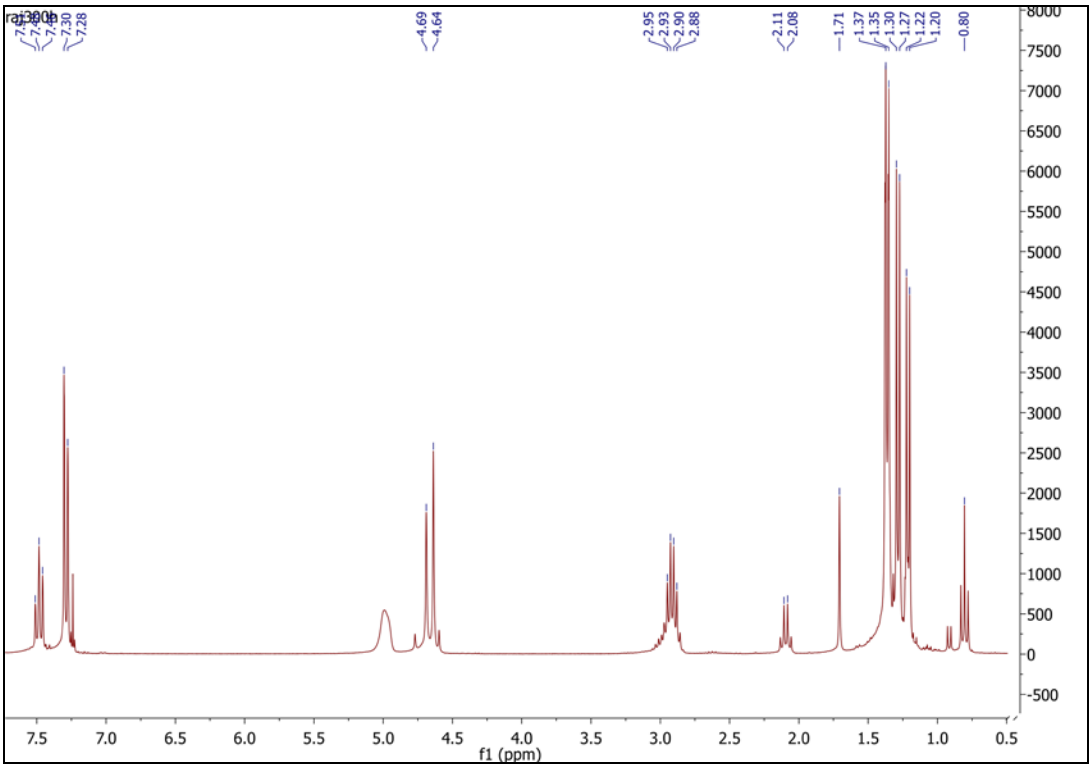

Chart 15: ^{1}H NMR spectrum of compound **6**.

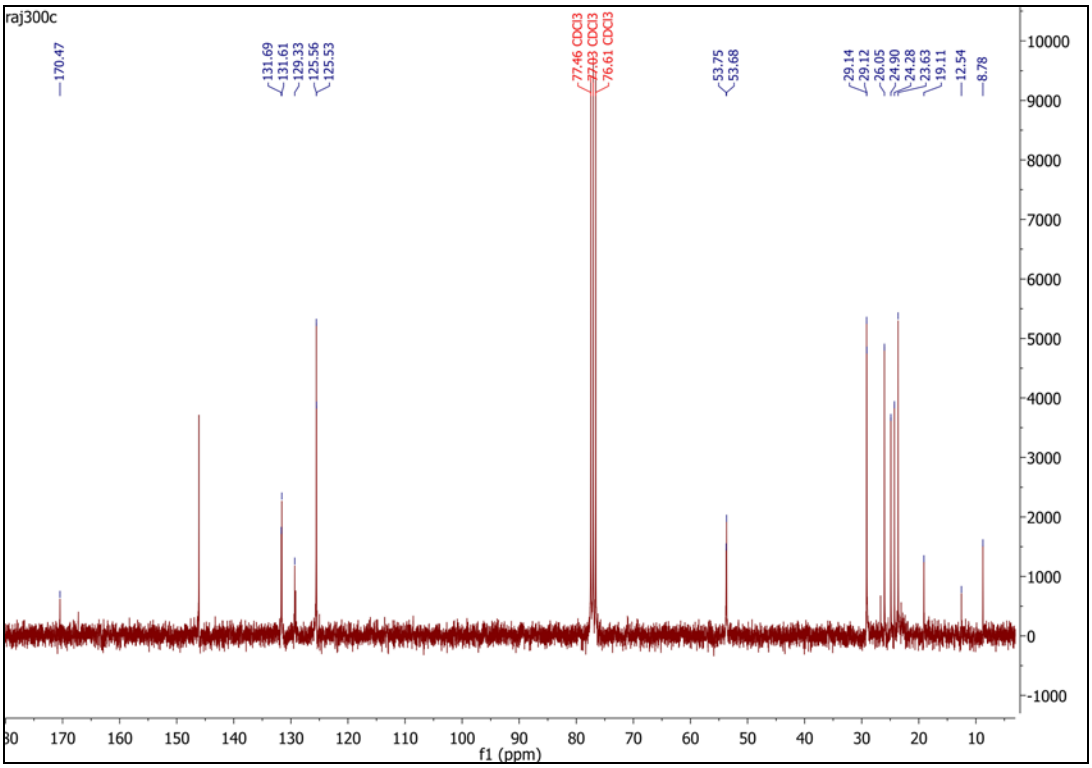

Chart 13: ^{13}C NMR spectrum of compound **6**.

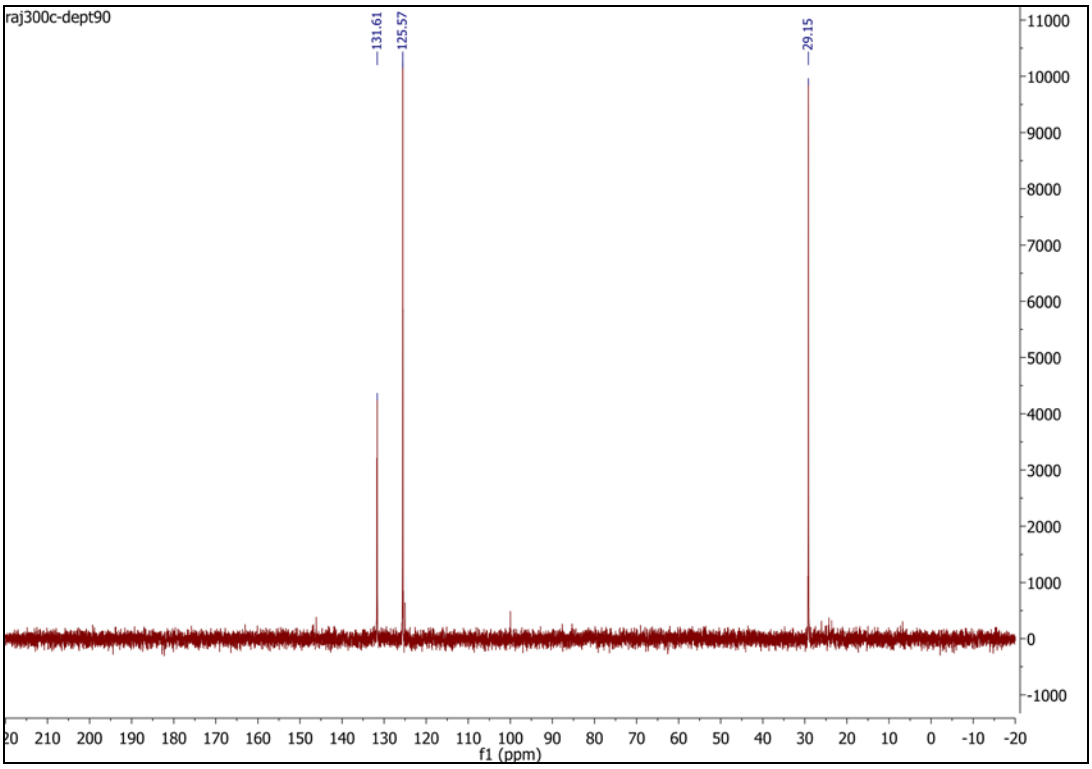

Chart 17: ^{13}C-dept90 NMR spectrum of compound **6**.

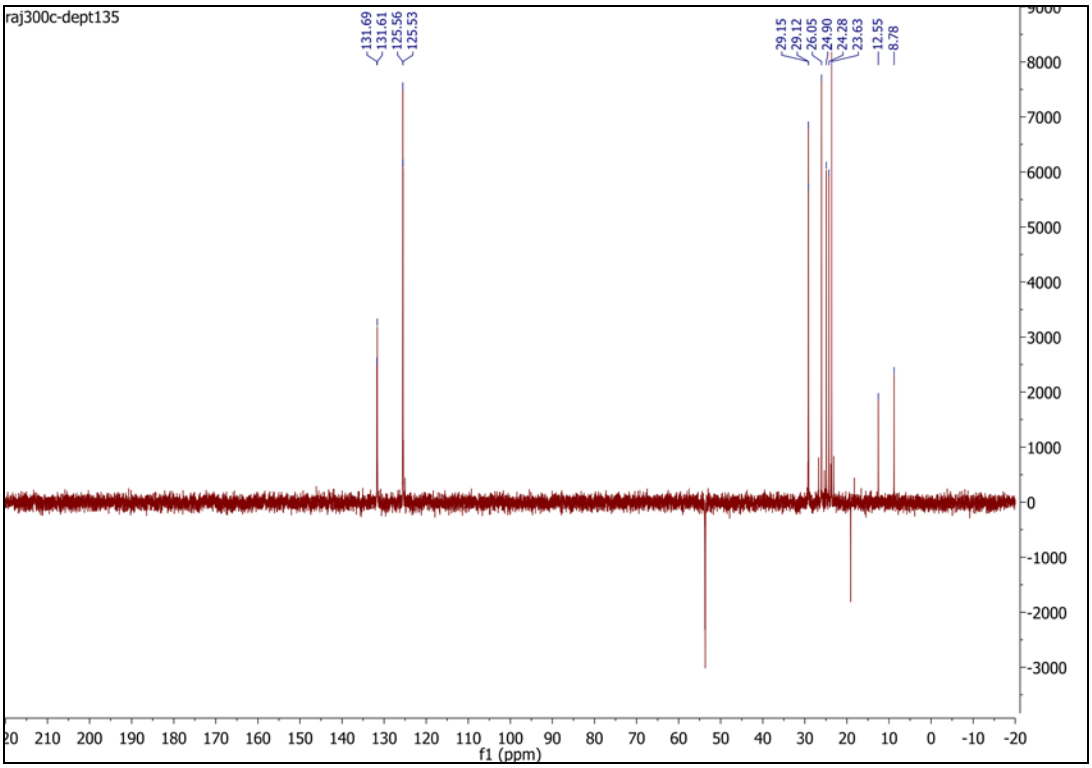

Chart 18: ^{13}C-dept135 NMR spectrum of compound **6**.

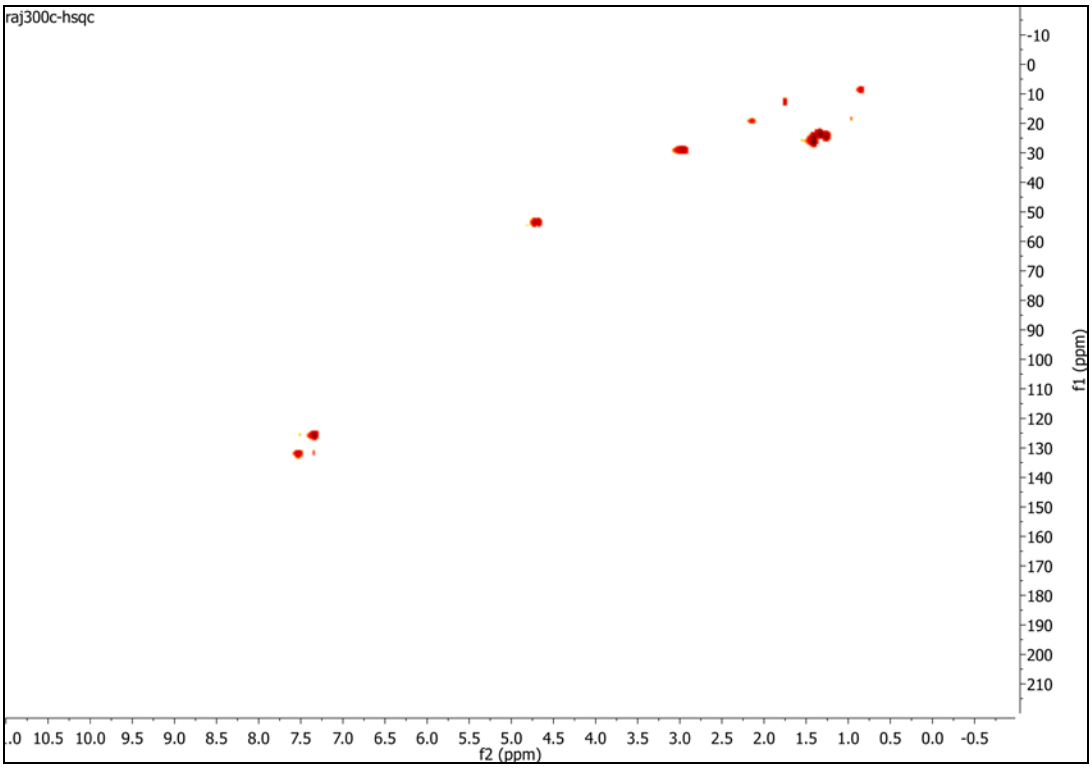

Chart 19: ^{13}C-hsqc NMR spectrum of compound **6**.

X-ray crystallography

Single crystals of **3** for X-ray diffraction study were grown from a saturated benzene solution at room temperature by slow diffusion of *n*-hexane. Crystals of **3** were taken out from the Schlenk flask under argon atmosphere and covered with perfluorated polyether oil on a microscope slide. A suitable crystal was selected using a polarize microscope, mounted on the tip of a MiTeGen© MicroMount, fixed to a goniometer head, and shock cooled by the crystal cooling device. Data were collected on Bruker diffractometer with D8 goniometer and APEXII detector at 100 K (Mo K_α radiation, λ = 71.073 pm; SMART APEX with INCOATEC Mo microsource with INCOATEC Helios mirror optics). The data was integrated with SAINT,[3] and a multi-scan absorption correction with SADABS[4] was applied. The structure was solved by direct methods (SHELXS) and refined on F^2 using the full-matrix least-squares methods of SHELXL.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, except hydrogen H(2) bonded to Si(1), were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. The position of H(2) was derived from the fourier difference density map and refined freely. Crystallographic data has been deposited with the Cambridge Crystallographic Centre. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Table 1. Crystallographic and structure refinement data for compound **3**.

empirical formula	$C_{28}H_{38}Cl_2N_2Si$
CCDC No.	951884
formula weight	501.59
T [K]	296(2)
crystal system	triclinic
space group	$P\bar{1}$
a = 9.4313(9) Å	α = 89.689(2)°
b = 9.5533(9) Å	β = 85.151(2)°
c = 17.2813(16) Å	γ = 63.154(2)°
Volume	1383.3(2) Å^3
Z	2
$\rho_{c\ calcd}$, Mg m^{-3}	1.204
μ, mm^{-1}	0.297
F(000)t	536
θ range for data collection [°]	1.183 to 26.372
no. of reflections collected	23236
no. of independent reflections	5655
Data/restraints/parameters	5655/0/ 310
Goodness-of-fit on F2	1.037
$R1$, $wR2$[$I > 2\sigma(I)$][a]	0.0358, 0.0839
$R1$, $wR2$ (all data)	0.0424, 0.0886
largest diff peak, hole (e Å^{-3})	0.363 and -0.239

Computational details

Theoretical calculations were performed with the GAUSSIAN 09 suite of programs.[6] All geometry optimizations were computed using the functional BP86[7, 8] in combination with the def2-TZVP basis set.[9] The stationary points were located with the Berny algorithm[10] using redundant internal coordinates. Analytical Hessians were computed to determine the nature of stationary points.[11]

Table S2. Cartesian coordinates (in Å) and total BP86/def2-TZVP energies (in au, noncorrected zero-point vibrational energies included) of the calculated species III, **3** and **TSIII→3**.

III

Energy= -1938.0023719

N	-1.345322000000	-1.198063000000	0.303998000000
C	-0.192046000000	-0.639715000000	-0.192616000000
C	-1.030859000000	-2.266488000000	1.143641000000
C	0.321101000000	-2.363038000000	1.182991000000
N	0.838220000000	-1.356951000000	0.366456000000
H	0.971965000000	-3.017658000000	1.748800000000
H	-1.801678000000	-2.816283000000	1.668906000000
C	-2.686391000000	-0.810331000000	-0.030015000000
C	-3.521434000000	-1.745861000000	-0.654935000000
C	-3.155817000000	0.466678000000	0.296145000000
C	-4.838652000000	-1.396057000000	-0.958212000000
C	-4.471501000000	0.809888000000	-0.028396000000
C	-5.313492000000	-0.116813000000	-0.648840000000
H	-3.131867000000	-2.732962000000	-0.911480000000
H	-2.503784000000	1.177086000000	0.808424000000
H	-5.490503000000	-2.121431000000	-1.448129000000
H	-4.836955000000	1.808119000000	0.217281000000
H	-6.341651000000	0.156740000000	-0.892360000000
C	2.235054000000	-1.239872000000	0.051578000000
C	2.908278000000	-0.030273000000	0.240975000000

C	2.907114000000	-2.373575000000	-0.426029000000
C	4.270055000000	0.041268000000	-0.065643000000
C	4.271036000000	-2.292208000000	-0.711582000000
C	4.953382000000	-1.083744000000	-0.534997000000
H	2.376105000000	0.836808000000	0.633650000000
H	2.358724000000	-3.303977000000	-0.585833000000
H	4.794333000000	0.987913000000	0.072800000000
H	4.797142000000	-3.172315000000	-1.085582000000
H	6.018192000000	-1.020071000000	-0.766266000000
C	-0.107829000000	0.476937000000	-1.093744000000
H	-0.940020000000	0.466067000000	-1.809714000000
Si	-0.291195000000	2.395742000000	-0.232117000000
Cl	0.164425000000	1.804679000000	1.859331000000
Cl	1.671742000000	3.134836000000	-0.853297000000
H	0.853610000000	0.504146000000	-1.618530000000

TS(III→3)

Energy= -1937.9293316

N	0.543682000000	-1.634678000000	-0.102821000000
C	-0.434343000000	-0.655870000000	0.037950000000
C	-0.054984000000	-2.877668000000	-0.326944000000
C	-1.398491000000	-2.701086000000	-0.308521000000
N	-1.644727000000	-1.347657000000	-0.088416000000
H	-2.207352000000	-3.406364000000	-0.455790000000
H	0.540836000000	-3.774419000000	-0.441083000000
C	1.948169000000	-1.468698000000	0.076782000000
C	2.449176000000	-0.852658000000	1.232078000000
C	2.822491000000	-1.975746000000	-0.896380000000

C	3.834458000000	-0.739153000000	1.401157000000
C	4.198330000000	-1.863712000000	-0.710364000000
C	4.707736000000	-1.242794000000	0.438484000000
H	1.771206000000	-0.504123000000	2.009797000000
H	2.418097000000	-2.424082000000	-1.805718000000
H	4.222968000000	-0.250059000000	2.295583000000
H	4.877924000000	-2.243334000000	-1.475366000000
H	5.786206000000	-1.148022000000	0.575049000000
C	-2.952371000000	-0.771434000000	-0.063961000000
C	-3.309411000000	0.218051000000	-0.989653000000
C	-3.884612000000	-1.237580000000	0.871275000000
C	-4.602328000000	0.744337000000	-0.967685000000
C	-5.180801000000	-0.715270000000	0.874599000000
C	-5.540146000000	0.278869000000	-0.039290000000
H	-2.579320000000	0.562440000000	-1.723181000000
H	-3.586686000000	-1.996263000000	1.597298000000
H	-4.879811000000	1.515702000000	-1.688049000000
H	-5.906571000000	-1.079097000000	1.604079000000
H	-6.550170000000	0.691971000000	-0.029039000000
C	-0.290138000000	0.720763000000	0.260489000000
H	0.343682000000	1.044724000000	1.619783000000
Si	1.147361000000	1.935121000000	0.528539000000
Cl	2.530089000000	1.895986000000	-1.101141000000
Cl	0.102831000000	3.773121000000	0.294114000000
H	-1.242789000000	1.258667000000	0.235101000000

3

Energy= -1938.0165532

N	0.490521000000	-1.701349000000	-0.191643000000
C	-0.435783000000	-0.664225000000	-0.066128000000
C	-0.167818000000	-2.937554000000	-0.248593000000
C	-1.494202000000	-2.704758000000	-0.145460000000
N	-1.678547000000	-1.318366000000	-0.048000000000
H	-2.336673000000	-3.384060000000	-0.175749000000
H	0.386450000000	-3.862808000000	-0.344401000000
C	1.912751000000	-1.578853000000	-0.134312000000
C	2.531157000000	-1.104838000000	1.029694000000
C	2.682163000000	-1.986311000000	-1.231286000000
C	3.924052000000	-1.022282000000	1.083493000000
C	4.075514000000	-1.914704000000	-1.162313000000
C	4.697814000000	-1.427180000000	-0.008823000000
H	1.920936000000	-0.796404000000	1.879220000000
H	2.184167000000	-2.344389000000	-2.134199000000
H	4.404485000000	-0.641267000000	1.986001000000
H	4.675482000000	-2.229247000000	-2.018250000000
H	5.786254000000	-1.361865000000	0.038527000000
C	-2.959895000000	-0.703624000000	0.033719000000
C	-3.317060000000	0.335888000000	-0.837832000000
C	-3.886778000000	-1.181470000000	0.971635000000
C	-4.594061000000	0.894463000000	-0.759013000000
C	-5.166939000000	-0.626071000000	1.031183000000
C	-5.523256000000	0.416536000000	0.171350000000
H	-2.597280000000	0.695034000000	-1.573746000000
H	-3.595039000000	-1.977061000000	1.659798000000
H	-4.866817000000	1.703037000000	-1.439704000000
H	-5.882812000000	-1.002146000000	1.764531000000
H	-6.520578000000	0.856197000000	0.225902000000

C	-0.235664000000	0.698128000000	0.026082000000
H	-1.149545000000	1.266214000000	0.220252000000
Si	1.200415000000	1.765247000000	-0.208714000000
H	2.322855000000	1.231691000000	-1.018354000000
Cl	0.546201000000	3.505760000000	-1.161729000000
Cl	2.073006000000	2.453814000000	1.574040000000

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