ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Glycidyl Alkoxysilanes Reactivities Towards Simple Nucleophiles in Organic Media for Improved Molecular Structure Definition in Hybrid Materials.

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A. GENERAL INFORMATION

Solvents were purified and dried by standard methods prior to use; alternatively, the MB SPS-800-dry solvent system was used to dry toluene and diethyl ether. Dry dichloromethane was obtained by refluxing solvent on calcium hydride for an hour and distilled under argon. GPTMS (Merck, 97%, 841807.0100), GPTES (Sigma-Aldrich, >97%) and PECS (Sigma-Aldrich, ≈90%) were used without prior purification and stored under argon atmosphere. Solid Lewis acids $ZnCl_2$ and $Cu(BF_4)_2$ were dried by toluene co-evaporation. Glassware used for reaction was either flame dried under vacuum or under argon stream for several minutes. Reactions were carried out under rigorous anhydrous conditions and argon stream/positive pressure of argon. ^1H and ^{13}C NMR spectra were recorded on a *Bruker Avance 300* spectrometer fitted with a 5 mm i.d. BBO probe carefully tuned to the recording frequency of 300.13 MHz (for ^1H) and 75.47 MHz (for ^{13}C), the temperature of the probe was set at room temperature (around 293-294 K), on a *Bruker Avance 400* spectrometer fitted with a 5 mm i.d. BBFO+ probe carefully tuned to the recording frequency of 400.13 MHz (for ^1H) and 100.61 MHz (for ^{13}C), the temperature of the probe was set at 303 K, and on a *Bruker Avance* 500 fitted with a 5 mm i.d. $^{13}C/^1H$ dual cryoprobe carefully tuned to the recording frequency of 500.13 MHz (for ^1H) and 125.76 MHz (for ^{13}C), the temperature of the probe was set at 303 K. The spectra are referenced to the solvent in which they were run (7.26 ppm for ^1H $CDCl_3$ and 77.16 ppm for ^{13}C $CDCl_3$, 4.79 ppm for ^1H D_2O, 3.31 ppm for ^1H CD_3OD and 49.00 ppm for ^{13}C CD_3OD). Chemical shifts ( ) are given in ppm, and coupling constants (*J*) are given in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, sx = sextuplet, sp = septuplet, m = massif and br = broad. All assignments were confirmed with the aid of two-dimensional ^1H, ^1H (COSY), or ^1H, ^{13}C (HSQC, HMBC) experiments using standard pulse programs. All reactions were monitored by TLC on commercially available precoated plates (Kieselgel 60 F254), and the compounds were visualized with $KMnO_4$ solution [$KMnO_4$ (3 g), K_2CO_3 (20 g), NaOH (5% aq.; 5 mL), H_2O (300 mL)] and heating or by UV (254 nm) when possible. Flash column chromatography was carried out using high purity grade (Merck grade 9385) pore size 60Å, 230-400 mesh particle size silica gel (Sigma Aldrich). Combi-Flash chromatography was carried out using Reveleris® X2 Flash Chromatography System with ELSD detection and Reveleris® Flash Cartridges (40 & 20 μm SiO_2). Mobile phases are reported in relative composition (*e.g.* 1:1, PE/AcOEt v/v). Solvents used for chromatography were prior distilled on a Buchi rotavapor R-220-SE. Low resolution mass spectrometry (MS) were recorded on a ThermoFinnigan DSQII quadripolar spectrometer (coupled with a TracUltra GC apparatus) for Chemical Ionization (CI), on a ThermoFinnigan LCQ Advantage spectrometer for ElectroSpray Ionisation (ESI). High resolution mass spectrometry (HRMS) were recorded on a ThermoFinnigan MAT95XL spectrometer (for CI) and on a ThermoFisher Scientific LTQ-Orbitrap spectrometer (for ESI+).

B. LOSS OF MATERIAL DUE TO PURIFICATION ON SILICA-GEL OF ALKOXYSILANES

Firstly, it is worth noting that the reaction crude purification on silica causes a loss of matter due to the hydrolysis and condensation of alkoxysilanes on silica-gel. The less stabilized the silane is, the more material is lost during purification. To support this claim, ideal purifications (*i.e* quick elution, isocratic or gradient) were performed for the pure commercial compounds and the recovery rate was calculated for each (Table 1.).

Table 1. functional alkoxysilane recovery rates after silica-gel chromatography

	Ratio Crude mixture :SiO_2	Recovery rate (%)
GPTMS	1:60	57%
	1:100	18%
GPTES	1:60	80%
	1:100	70%
PECS	1:100	77%

As seen in Table 1, GPTMS recovery rate drops significantly when the silica-gel quantity increase since it is the most sensitive to hydrolysis. In comparison, GPTES recovery rate is fairly high and is not as much affected by the increase of silica-gel. These results are in accordance with the literature that said steric factors exert the greatest effect on the hydrolytic stability of alkoxysilanes.[1–3] To avoid the loss of one or multiple sub-compounds on silica, the reactions were performed on an unusually high scale to yield sufficient crude quantity in view of the purification. Furthermore, after each purification, the representativeness of the isolated species compared to the crude was verified.

(1) Brinker, C. J. Hydrolysis and Condensation of Silicates: Effects on Structure. *J. Non-Cryst. Solids* **1988**, *100* (1–3), 31–50.
(2) Voronkov, M. G.; Yuzhelevskii, Y. A.; Mileshkevich, V. P. The Siloxane Bond and Its Influence on the Structure and Physical Properties of Organosilicon Compounds. *Russ. Chem. Rev.* **1975**, *44* (4), 355.
(3) Arkles, B.; Steinmetz, J. R.; Zazyczny, J.; Mehta, P. Factors Contributing to the Stability of Alkoxysilanes in Aqueous Solution. *J. Adhes. Sci. Technol.* **1992**, *6* (1), 193–206.

C. EXPERIMENTAL PROCEDURES

Procedure for the reaction of *n*-propylamine with GPTMS in THF-d_8 for NMR ^{1}H monitoring

In a dried vial with a septum cap was introduced GPTMS (10 µL, 0.045 mmol, 0.027M, 1 eq), *n*-propylamine (3.7 µL, 0.045 mmol, 0.027M, 1 eq, dried over 3Å molecular sieves) and THF-d_8 (0.6 mL). The mixture was homogenized by manual shaking of the vial and the resulting solution was then removed with a syringe and introduced in a dried NMR tube under argon atmosphere. The NMR tube was then sealed and the reaction monitored by ^{1}H NMR with acquisition at *t* = 0.5h, 1h, 2h, 3h, 24h.

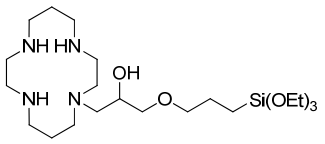
General procedure for the reaction of *n*-butylamine with GPTMS in THF

In a dried 25 mL two-necked round bottom flask equipped with a condenser and under a gentle argon flow was introduced freshly distilled THF (12.5 mL), *n*-butylamine (0.49 mL, 5 mmol, 1 eq, freshly dist. over CaH_2) and GPTMS (2.21 mL, 10 mmol, 2 eq). Then the reaction was heated at 60 °C under positive argon atmosphere and stirring for 48h. The volatiles were evaporated by rotary-evaporation and the residue was dried under high-vacuum to afford 2.29 g of crude mixture.

General procedure for the reaction of *n*-butylamine with GPTMS in solvent-free conditions

In a dried glass tube (20 mm diameter, 150 mm height, magnetic stirring) under a gentle argon flow was introduced *n*-butylamine (0.67 mL, 6.8 mmol, 1 eq, freshly dist. over CaH_2) and GPTMS (3.00 mL, 13.58 mmol, 2 eq). The tube was sealed under argon atmosphere and heated at 70 °C for 48h. After 24h, the mixture was too viscous to be efficiently stirred. After 48h a gel was obtained, fractioned in smaller parts with a spatula, washed with DCM and methanol, and dried as best as possible under high-vacuum to afford 3.5 g of crude. A small quantity of the crude was solubilized in a 0.1M solution of $NaOD/D_2O$ and the resulting solution was analyzed by ^{1}H NMR.

Synthesis of 1-(1,4,8,11-tetraazacyclotetradecan-1-yl)-3-(3-(triethoxysilyl)propoxy)propan-2-ol (3)



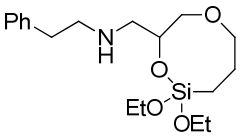
In a dried 25 mL two-necked round bottom flask equipped with a condenser and under a gentle argon flow was introduced cyclam (500 mg, 2.5 mmol, 5 eq) and toluene (6 mL). The suspension was heated at reflux until complete dissolution (clear solution). Then, a solution of GPTES (0.139 mL, 0.5 mmol, 1 eq) in toluene (4 mL) was added dropwise while refluxing. Refluxing was continued for 24 h, after which the reaction mixture was cooled to room temperature and then kept in the freezer overnight. The precipitate of excess cyclam was then removed by filtration and washed with cold toluene. The filtrates were combined and evaporated to dryness by rotary-evaporation and the residue was dried under high-*vacuum* for 2h to afford **3** (257 mg, 0.53 mmol, 106%). The crude purity was satisfactory enough to avoid further purification. ^{1}H NMR (300.16 MHz, $CDCl_3$, 20°C): δ = 3.80(q, *J* = 7.0 Hz, 6H, Si-O-CH_2-CH_3); 3.75-3.68(m, 1H, CH_2-CH-CH_2); 3.47-3.38(m, 3H, CH-CH_2-O-CH_2); 3.31(dd, *J* = 9.6 & 6.3 Hz, CH-CH_2-O-CH_2); 2.94-2.47(m, 16H, CH_2-NH-CH_2 & CH_2-N-CH_2), 2.41(dd, *J* = 14.2 & 2.0 Hz, N-CH_2-CH); 2.06-1.91(m, 1H, N-CH_2-CH_2-CH_2-NH); 1.73-1.62(m, 4H, NH-CH_2-CH_2-CH_2-NH & CH_2-CH_2-Si); 1.55(dt, *J* = 14.5 & 3.7 Hz, 1H, N-CH_2-CH_2-CH_2-NH); 1.21(t, *J* = 7.0 Hz, 9H, Si-O-CH_2-CH_3); 0.67-0.58(m, 2H, CH_2-Si) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ= 73.90(CH-CH_2-O-CH_2); 73.52(CH-CH_2-O-CH_2); 70.26(CH_2-CH-CH_2); 59.65(N-CH_2-CH); 58.48(Si-O-CH_2-CH_3); 58.33 & 58.21(CH_2-N-CH_2); 51.63, 50.63, 50.41, 49.22, 48.65 & 48.09(CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-CH_2-NH-CH_2); 29.07(NH-CH_2-CH_2-CH_2-NH); 26.87(N-CH_2-CH_2-CH_2-NH); 23.07(CH_2-CH_2-Si); 18.44(Si-O-CH_2-CH_3); 6.61(CH_2-Si) ppm. MS (CI): *m/z* (%) 479.3 (100) [*M*+H^+]

General procedure for the reaction of cyclam with GPTMS leading to 1-((2,2-dimethoxy-1,6,2-dioxasilocan-8-yl)methyl)-1,4,8,11-tetraazacyclotetradecane (4) and 1-(1,4,8,11-tetraazacyclotetradecan-1-yl)-3-(3-(trimethoxysilyl)propoxy)propan-2-ol (5)

In a dried 25 mL two-necked round bottom flask equipped with a condenser and under a gentle argon flow was introduced cyclam (500 mg, 2.5 mmol, 5 eq) and toluene (6 mL). The suspension was heated at reflux until complete dissolution (clear solution). Then, a solution of GPTMS (0.110 mL, 0.5 mmol, 1 eq) in toluene (4 mL) was added dropwise while refluxing. Refluxing was continued for 5.5 h, after which the reaction mixture was cooled to room temperature and then kept in the freezer overnight. The precipitate of excess cyclam was then removed by filtration and washed with cold toluene. The filtrates were combined and evaporated to dryness by rotary-evaporation and the residue was dried under high-vacuum to afford 266 mg of a mixture of **4** and **5**. Crude ^{1}H & ^{13}C NMR spectra available in Supporting Information, Figure S9-S10. MS (CI): *m/z* (%) 405.3 (100) [*M*+H$^+$], 437.3 (21) [*M*+H$^+$]. HRMS (ESI): (**4**) *m/z* calcd for $C_{18}H_{41}O_4N_4Si$ [*M*+H$^+$] 405.2892, found 405.2895, (**5**) *m/z* calcd for $C_{19}H_{45}O_5N_4Si$ [*M*+H$^+$] 437.3154, found 437.3154.

Synthesis of *N*-[(2,2-diethoxy-1,6-dioxa-2-silacyclooct-8-yl)methyl]-2-phenylethanamine (6) and *N*-[2-hydroxy-3-[3-(triethoxysilyl)propoxy]propyl]-2-phenylethanamine (7)

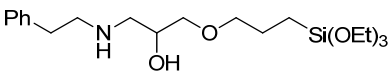
In a dried 25 mL two-necked round bottom flask equipped with a condenser and under a gentle argon flow was introduced phenethylamine (0.315 mL, 2.5 mmol, 5 eq) and toluene (6 mL). Once at reflux, a solution of GPTES (0.139 mL, 0.5 mmol, 1 eq) in toluene (4 mL) was added dropwise while refluxing. Refluxing was continued for 18 h, after which the reaction mixture was evaporated to dryness by rotary-evaporation and the residue was dried under high-vacuum to afford 493 mg of crude. Purification was performed by flash chromatography on a 40g/40µm SiO_2 column with liquid injection and gradient elution (100:0-92:8, $CHCl_3$/MeOH) and yielded **6** (72 mg, 0.204 mmol, 41%) and **7** (29 mg, 0.072 mmol, 15%) as pure colorless oils.



N-[(2,2-diethoxy-1,6-dioxa-2-silacyclooct-8-yl)methyl]-2-phenylethanamine **(6)**

^{1}H NMR (300.16 MHz, $CDCl_3$, 20°C): δ= 7.31-7.24 & 7.23-7.15 (m, 2 & 3H, *phenyl*); 4.20(m, 1H, CH_2-*CH*-CH_2); 3.78(q, *J* = 7.0 Hz, 2H, Si-O-*CH$_2$*-CH_3); 3.71(q, *J* = 7.0 Hz, 2H, Si-O-*CH$_2$*-CH_3); 3.75-3.65(m, 1H, CH-*CH$_2$*-O-CH_2); 3.65-3.57 & 3.54-3.45(m, CH-CH_2-O-*CH$_2$*); 3.23(dd, *J* = 10.9 & 10.3 Hz, 1H, CH-*CH$_2$*-O-CH_2); 2.95-2.75(m, 4H, *CH$_2$*-*CH$_2$*-NH); 2.63(d, *J* = 5.6 Hz, 2H, NH-*CH$_2$*-CH); 1.87-1.62(m, 2H, *CH$_2$*-CH_2-Si); 1.19(dt, *J* = 10.1 & 7.0 Hz, 6H, Si-O-CH_2-*CH$_3$*); 0.72(m, 2H, *CH$_2$*-Si) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ = 140.11, 128.82, 128.57 & 126.27(*phenyl*); 73.84(CH-*CH$_2$*-O-CH_2); 72.53(CH-CH_2-O-*CH$_2$*); 72.19(CH_2-*CH*-CH_2); 58.50 & 58.32(Si-O-*CH$_2$*-CH_3); 51.99(NH-*CH$_2$*-CH); 51.41(CH_2-*CH$_2$*-NH); 36.62(*CH$_2$*-CH_2-NH); 24.25(*CH$_2$*-CH_2-Si); 18.49 & 18.43(Si-O-CH_2-*CH$_3$*); 8.32(*CH$_2$*-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{18}H_{32}NO_4Si$ [*M*+H$^+$] 354.2101, found 354.2095.

N-[2-hydroxy-3-[3-(triethoxysilyl)propoxy]propyl]-2-phenylethanamine **(7)**



^{1}H NMR (300.16 MHz, $CDCl_3$, 20°C): δ= 7.32-7.25 & 7.24-7.16 (m, 2 & 3H, *phenyl*); 3.83(m, 1H, CH_2-*CH*-CH_2); 3.81(q, *J* = 7.0 Hz, 6H, Si-O-*CH$_2$*-CH_3); 3.48-3.35(m, 4H, CH-*CH$_2$*-O-*CH$_2$*); 2.95-2.76(m, 4H, *CH$_2$*-*CH$_2$*-NH); 2.75(dd, *J* = 12.1 & 4.0 Hz, 1H, NH-*CH$_2$*-CH); 2.66 (dd, *J* = 12.1 & 7.9 Hz, 1H, NH-*CH$_2$*-CH); 1.69(m, 2H, *CH$_2$*-CH_2-Si); 1.22(t, *J* = 7.0 Hz, 9H, Si-O-CH_2-*CH$_3$*); 0.63(m, 2H, *CH$_2$*-Si) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ= 139.95, 128.84, 128.62 & 126.33(*phenyl*); 73.79(CH-CH_2-O-*CH$_2$*); 73.43(CH-*CH$_2$*-O-CH_2); 68.87(CH_2-*CH*-CH_2); 58.52(Si-O-*CH$_2$*-CH_3); 52.02(NH-*CH$_2$*-CH); 51.21(CH_2-*CH$_2$*-NH); 36.48(*CH$_2$*-CH_2-NH); 23.09(*CH$_2$*-CH_2-Si); 18.43(Si-O-CH_2-*CH$_3$*); 6.69(*CH$_2$*-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{20}H_{38}NO_5Si$ [*M*+H$^+$] 400.2519, found 400.2511.

General procedure for the reaction of *n*-propanethiol with GPTMS

In a dried 25 mL two-necked round bottom flask equipped with a condenser and under a gentle argon flow was introduced toluene (12.5 mL), *n*-propanethiol (761 mg, 10 mmol, 1 eq) and GPTMS (2.360 g, 10 mmol, 1 eq). The solution was then heated at 60 °C and the reaction monitored by TLC. After 26h and no signs of progression by TLC monitoring, the reaction was stopped and the volatiles removed by rotary-evaporation and dried under high-vacuum to afford 2.42 g of crude mixture. ^{1}H NMR spectrum of the crude mixture was strictly the same as the starting GPTMS.

General procedure for the reaction of *n*-dodecanethiol with GPTMS

In a dried 25 mL two-necked round bottom flask equipped with a condenser and under a gentle argon flow was introduced toluene (12.5 mL), *n*-dodecanethiol (2.024 g, 10 mmol, 1 eq) and GPTMS (2.360 g, 10 mmol, 1 eq). The solution was then heated at toluene reflux and the reaction monitored by TLC. After 21h and no signs of progression by TLC monitoring, the reaction was stopped and the volatiles removed by rotary-evaporation and dried under high-vacuum to afford 4.75 g of crude mixture. ^{1}H NMR spectrum of the crude mixture (Figure S148) was found to be the superposition of the ^{1}H NMR spectrum of the two starting materials and no change was observed.

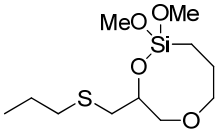
General procedure for the preparation of sodium propylthiolate

In a dried 250 mL round bottom flask under gentle argon flow was degreased NaH (60% in mineral oil, 1.8g, 45 mmol, 0.9 eq) with 5 x 20 mL of hexane (HPLC quality). Toluene (100 mL) was added and the solution was cooled at 0 °C. Then, *n*-propylthiol (4.53 mL, 50 mmol, 1 eq) was very slowly introduced with a syringe. The formation of a white salt was quickly observed. Volatiles (toluene & unreacted *n*-propylthiol) were removed by rotary evaporation to afford sodium propylthiolate as a white salt.

Synthesis of 1-[[(2,2-dimethoxy-1,6-dioxa-2-silacyclooct-8-yl)methyl]thio]propane (8) and 3,3-dimethoxy-2,7-dioxa-11-thia-3-silatetradecan-9-ol (9)

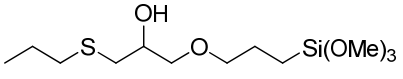
In a dried 10 mL round bottom flask under gentle argon flow was introduced toluene (6.25 mL), sodium propane-1-thiolate (491 mg, 5 mmol, 1 eq) beforehand prepared from propan-1-thiol and NaH, and GPTMS (1.104 mL, 5 mmol, 1 eq). After 3.5h at room temperature, TLC (80:20, PE/AcOEt) indicates that GPTMS was totally converted. The solution was then concentrated by rotary evaporation and dried under high-vacuum to afford 2.16 g. One gram of residue was purified by flash chromatography on a 40g/40µm SiO_2 column with liquid injection and gradient elution (100:0-53:47, PE/AcOEt) and afforded **8** (42 mg, 6.5%) and **9** (50 mg, 6.9%) as pure, colorless oils.

1-[[(2,2-dimethoxy-1,6-dioxa-2-silacyclooct-8-yl)methyl]thio]propane **(8)**



^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ = 4.17(m, 1H, CH_2-*CH*-CH_2); 3.84(dd, *J* = 10.9 & 2.7 Hz, 1H, CH_2-CH-*CH*$_2$-O); 3.65(m, 1H, O-*CH*$_2$-CH_2); 3.58(s, 3H, *CH*$_3$-O-Si); 3.55(s, 3H, *CH*$_3$-O-Si); 3.49(m, 1H, O-*CH*$_2$-CH_2); 3.21(dd, *J* = 10.8 & 9.9 Hz, 1H, CH_2-CH-*CH*$_2$-O); 2.65(dd, *J* = 13.4 & 6.3 Hz, 1H, S-*CH*$_2$-CH-CH_2); 2.55(t, *J* = 7.4 Hz, 2H, CH_3-CH_2-*CH*$_2$-S); 2.54(dd, *J* = 13.0 & 6.7 Hz, 1H, S-*CH*$_2$-CH-CH_2); 1.80(m, 1H, *CH*$_2$-CH_2-Si); 1.71(m, 1H, *CH*$_2$-CH_2-Si); 1.60(sx, *J* = 7.3 Hz, 2H, CH_3-*CH*$_2$-CH_2-S); 0.96(t, *J* = 7.3 Hz, 3H, *CH*$_3$-CH_2-CH_2-S); 0.73(m, 2H, CH_2-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 74.57(CH-*CH*$_2$-O); 72.88(CH_2-*CH*-CH_2); 72.69(CH-CH_2-O-*CH*$_2$); 50.72(*CH*$_3$-O-Si); 50.54(*CH*$_3$-O-Si); 35.33(*CH*$_3$-CH_2); 35.09(S-*CH*$_2$-CH); 24.15(*CH*$_2$-CH_2-Si); 23.13(CH_3-*CH*$_2$); 13.54(CH_2-*CH*$_2$-S); 7.41(*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{11}H_{24}O_4NaSSi$ [*M*+Na^+] 303.10568, found 303.10492.

3,3-dimethoxy-2,7-dioxa-11-thia-3-silatetradecan-9-ol **(9)**

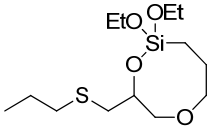


^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ= 3.85(m, 1H, CH_2-*CH*-CH_2); 3.55(s, 9H, *CH*$_3$-O-Si); 3.55(s, 3H, *CH*$_3$-O-Si); 3.51(dd, *J* = 9.6 & 4.0 Hz, 1H, CH_2-CH-*CH*$_2$-O) ; 3.48-3.40(m, 3H, CH-*CH*$_2$-O-*CH*$_2$-CH_2); 2.89(d, *J* = 4.0 Hz, 1H, CH-*OH*); 2.68(dd, *J* = 13.6 & 5.6 Hz, 1H, S-*CH*$_2$-CH-CH_2); 2.59(dd, *J* = 13.6 & 7.0 Hz, 1H, S-*CH*$_2$-CH-CH_2); 2.51(t, *J* = 7.2 Hz, 2H, CH_3-CH_2-*CH*$_2$-S); 1.69(m, 2H, *CH*$_2$-CH_2-Si); 1.60(sx, *J* = 7.3 Hz, 2H, CH_3-*CH*$_2$-CH_2-S); 0.97(t, *J* = 7.3 Hz, 3H, *CH*$_3$-CH_2-CH_2-S); 0.66(m, 2H, CH_2-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 73.53(CH-*CH*$_2$-O); 73.50(O-*CH*$_2$-CH_2); 69.40(CH_2-*CH*-CH_2); 50.65(*CH*$_3$-O-Si); 35.88(S-*CH*$_2$-CH); 34.83(*CH*$_3$-CH_2); 23.14(CH_3-*CH*$_2$); 22.93(*CH*$_2$-CH_2-Si); 13.52(CH_2-*CH*$_2$-S); 5.56(*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_{28}O_5NaSSi$ [*M*+Na^+] 335.13189, found 335.13074.

Synthesis of 1-[[(2,2-diethoxy-1,6-dioxa-2-silacyclooct-8-yl)methyl]thio]propane (10) and 4,4-diethoxy-3,8-dioxa-12-thia-4-silapentadecan-10-ol (11)

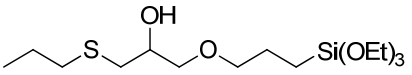
In a dried 10 mL round bottom flask under gentle argon flow was introduced toluene (6.25 mL), sodium propane-1-thiolate (491 mg, 5 mmol, 1 eq) beforehand prepared from propan-1-thiol and NaH, and GPTES (1.33 mL, 5 mmol, 1 eq). After 20h at room temperature, TLC (80:20, PE/AcOEt) indicates that GPTES was totally converted. The solution was then concentrated by rotary evaporation and dried under vacuum to afford 1.49 g. One gram of residue was purified by flash chromatography on a 40g/40µm SiO_2 column with liquid deposition and gradient elution (100:0-87:13, PE/AcOEt) and afforded **10** (16 mg, 1.5%) and **11** (248 mg, 21%) as pure colorless oils.

1-[[(2,2-diethoxy-1,6-dioxa-2-silacyclooct-8-yl)methyl]thio]propane **(10)**



R_f = 0.53 (80:20, PE/AcOEt); ^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ= 4.17(m, 1H, CH_2-*CH*-CH_2); 3.84(q, *J* = 7.1 Hz, 4H, CH_3-*CH*$_2$-O-Si); 3.83(m, 1H, CH_2-CH-*CH*$_2$-O); 3.65(ddd, *J* = 11.6, 8.3 & 3.6 Hz, 1H, O-*CH*$_2$-CH_2); 3.51(ddd, *J* = 10.8, 4.8 & 3.8 Hz , 1H, O-*CH*$_2$-CH_2); 3.22(dd, *J* = 11.0 & 9.8 Hz, 1H, CH_2-CH-*CH*$_2$-O); 2.65(dd, *J* = 13.5 & 6.2 Hz, 1H, S-*CH*$_2$-CH-CH_2); 2.55(t, *J* = 7.3 Hz, 2H, CH_3-CH_2-*CH*$_2$-S); 2.54(dd, *J* = 13.4 & 6.4 Hz, 1H, S-*CH*$_2$-CH-CH_2); 1.80(m, 1H, *CH*$_2$-CH_2-Si); 1.71(m, 1H, *CH*$_2$-CH_2-Si); 1.61(sx, *J* = 7.3 Hz, 2H, CH_3-*CH*$_2$-CH_2-S); 1.24(t, *J* = 7.0 Hz, 3H, *CH*$_3$-CH_2-O-Si); 1.22(t, *J* = 7.0 Hz, 3H, *CH*$_3$-CH_2-O-Si); 0.99(t, *J* = 7.3 Hz, 3H, *CH*$_3$-CH_2-CH_2-S); 0.73(m, 2H, CH_2-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 74.72(CH-*CH*$_2$-O-CH_2); 72.83(CH-CH_2-O-*CH*$_2$); 72.76(CH_2-*CH*-CH_2); 58.57(Si-O-*CH*$_2$-CH_2); 58.44(Si-O-*CH*$_2$-CH_2); 35.35(S-*CH*$_2$-CH_2); 35.19(S-*CH*$_2$-CH); 24.30(*CH*$_2$-CH_2-Si); 23.16(S-CH_2-*CH*$_2$); 18.50(*CH*$_3$-CH_2-O); 18.45(*CH*$_3$-CH_2-O); 13.57(*CH*$_3$-CH_2-CH_2-S); 8.42(*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{28}O_4NaSSi$ [*M*+Na^+] 331.13698, found 331.13617.

4,4-diethoxy-3,8-dioxa-12-thia-4-silapentadecan-10-ol **(11)**



R_f = 0.23 (80:20, PE/AcOEt). ^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ= 3.83(m, 1H, CH_2-*CH*-CH_2); 3.82(t, *J* = 7.0 Hz, 6H, CH_3-*CH*$_2$-O-Si); 3.51(dd, *J* = 9.6 & 4.0 Hz, 1H, CH_2-CH-*CH*$_2$-O); 3.48-3.40(m, 3H, CH-*CH*$_2$-O-*CH*$_2$-CH_2); 2.78(d, *J* = 3.9 Hz, CH-*OH*); 2.65(dd, *J* = 13.6 & 5.6 Hz, 1H, S-*CH*$_2$-CH-CH_2); 2.60(dd, *J* = 13.6 & 7.1 Hz, 1H, S-*CH*$_2$-CH-CH_2); 2.52(t, *J* = 7.3 Hz, 2H, CH_3-CH_2-*CH*$_2$-S); 1.70(m, 2H, *CH*$_2$-CH_2-Si); 1.61(sx, *J* = 7.3 Hz, 2H, CH_3-*CH*$_2$-CH_2-S); 1.22(t, *J* = 7.0 Hz, 6H, *CH*$_3$-CH_2-O-Si); 0.99(t, *J* = 7.3 Hz, 3H, *CH*$_3$-CH_2-CH_2-S); 0.73(m, 2H, CH_2-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ= 73.77(CH-CH_2-O-*CH*$_2$); 73.48(CH-*CH*$_2$-O-CH_2); 69.39(CH_2-*CH*-CH_2); 58.53(CH_3-*CH*$_2$-O); 35.97(S-*CH*$_2$-CH); 34.83(*CH*$_3$-CH_2-O); 23.15(*CH*$_2$-CH_2-Si & S-CH_2-*CH*$_2$); 18.43 (*CH*$_3$-CH_2-O); 13.54(*CH*$_3$-CH_2-CH_2-S); 6.78(*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{15}H_{34}O_5NaSSi$ [*M*+Na^+] 377.17884, found 377.17783.

General procedure for the reaction of sodium azide with glycidyl silanes in methanol

For ^{1}H NMR monitoring and ^{13}C analysis:

In a dried 25 mL two-neck round bottom flask equipped with a condenser and under gentle argon flow was introduced deuterated methanol (7 mL), NaN_3 (0.25 g, 3.85 mmol, 6.7 eq) and the mixture was heated to reflux. Then, a solution of GPTMS (0.136 mL, 0.58 mmol, 1 eq) in deuterated methanol (3 mL) was injected. The mixture was stirred at reflux and the ^{1}H NMR kinetic study was realized by directly sampling 0.6 mL of mixture at *t* = 5 min, 30 min, 1h, 2h, 3h, 5h. The ^{13}C NMR spectrum was acquired on the 5h sample with a 500 MHz NMR spectrometer fitted with a 5 mm i.d. $^{13}C/^{1}H$ dual cryoprobe, probe temperature set at 303 K.

For MS analyses:

In a dried 25 mL two-neck round bottom flask equipped with a condenser and under gentle argon flow was introduced methanol (7 mL, anhydrous, 99.8%, Sigma-Aldrich, Sure/Seal™), NaN_3 (0.25 g, 3.85 mmol, 6.7 eq) and the mixture was heated at reflux. Then, a solution of GPTMS (0.136 mL, 0.58 mmol, 1 eq) in methanol (3 mL, anhydrous, 99.8%, Sigma-Aldrich, Sure/Seal™) was injected. The solution was stirred at reflux for 5h and was directly analyzed by Electrospray Mass Spectrometry (ESI-MS).

General procedure for the reaction of sodium azide with glycidyl silanes in DMF

In a dried 25 mL two-neck round bottom flask equipped with a condenser and under gentle argon flow was introduced DMF (10 mL, anhydrous, 99.8%, Sigma-Aldrich, Sure/Seal™), NaN_3 (0.25 g, 3.85 mmol, 6.7 eq) and the mixture was heated at 70 °C. Then, GPTMS (0.136 mL, 0.58 mmol, 1 eq) was added. The solution was stirred at 70 °C and the ^{1}H NMR kinetic study was realized by directly sampling 0.6 mL of mixture at *t* = 0 min, 5 min, 30 min, 1h, 2h, 3h, 4h, 5h, 6h and the MS analyses were performed on the 6h sample.

General procedures for the reactions of sodium alkoxide on glycidyl alkoxysilanes in THF and under mild conditions

Sodium ethoxide with GPTMS:

In a dried 50 mL round bottom flask under gentle argon flow was introduced freshly distilled THF (16 mL), sodium ethoxide (0.340 g, 5 mmol, 1 eq) and GPTES (1.392 g, 5 mmol, 1 eq). The reaction was left to stir at room temperature under positive argon atmosphere and followed by TLC (60:40, PE/AcOEt). The reaction was stopped after 5 h, the salts were eliminated by filtration under N_2 atmosphere and the solution was concentrated off to afford 714 mg of crude mixture.

Sodium methoxide with GPTES:

In a dried 50 mL round bottom flask under gentle argon flow was introduced freshly distilled THF (16 mL), sodium methoxide (0.270 g, 5 mmol, 1 eq) and GPTMS (1.182 g, 5 mmol, 1 eq). The reaction was left to stir at room temperature under positive argon atmosphere and followed by TLC (60:40, PE/AcOEt). The reaction was stopped after 8 h, the salts were eliminated by filtration under N_2 atmosphere and the solution was concentrated off to afford 992 mg of crude mixture.

Reaction of sodium methoxide with GPTMS in refluxing methanol

In a dried 25 mL two-neck round bottom flask equipped with a condenser and under gentle argon flow was introduced freshly distilled methanol (8.1 mL) and a freshly prepared 0.1M solution of sodium methoxide in methanol (9.05 mL, 0.905 mmol, 1 eq). Then GPTMS (0.200 mL, 0.905 mmol, 1 eq) was injected and the reaction was left refluxing under positive argon atmosphere for 3.5h. The reaction

was then stopped, the salts were eliminated by filtration under N_2 atmosphere and the solution concentrated off to afford 227 mg of crude mixture.

General procedures for the activated reactions of *tert*-butylglycidylether in presence of *n*-propanol leading to 1-(tert-butoxy)-3-propoxypropan-2-ol (12a), 3-(tert-butoxy)-2-propoxypropan-1-ol (12b) and 1-(tert-butoxy)-3-chloropropan-2-ol (12c).

Copper(II) tetrafluoroborate:

In a dried round bottom flask under gentle argon flow was introduced toluene, *tert*-butylglycidylether, propan-1-ol, and then was quickly added dry copper(II) tetrafluoroborate. The reaction was left to stir under positive argon atmosphere and followed by TLC (65:35, PE/AcOEt). After 6h, two compounds (R_f = 0.61, 0.52) began to appear and the reaction was left over-night. The reaction was quenched by addition of water (30 mL), the layers were separated and the aqueous layer extracted with petroleum ether (10 mL x 3). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, concentrated by rotary evaporation and dried under high-*vacuum*. The crude was purified by flash chromatography with silica gel, solid loading, and gradient elution (90:10-80:20, PE/Et_2O).

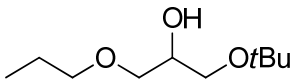
Boron trifluoride diethyl etherate:

In a dried round bottom flask under a gentle argon flow was introduced freshly distilled DCM, *tert*-butylglycidylether, propan-1-ol and then was quickly injected BF_3•Et_2O. The reaction was left to stir under positive argon atmosphere and followed by TLC (65:35, PE/AcOEt). After 4h, *tert*-butylglycidylether (R_f = 0.70) was converted into two compounds (R_f = 0.61 & 0.52 respectively). The reaction was thus quenched by addition of water (30 mL), the layers were separated and the aqueous layer extracted with DCM (10 mL x 3). The combined organic layers were dried over $MgSO_4$, concentrated by rotary evaporation and dried under high-*vacuum*. The crude was purified by combi-flash chromatography with solid loading and gradient elution (96:4-80:20, PE/AcOEt).

Zinc(II) Chloride:

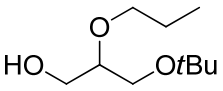
In a dried round bottom flask under a gentle argon flow was introduced freshly distilled DCM, *tert*-butylglycidylether, propan-1-ol, and then was quickly added dry zinc(II) chloride. The reaction was left to stir under positive argon atmosphere and followed by TLC (65:35, PE/AcOEt). After 24h, only traces amount of *tert*-butylglycidylether (R_f = 0.70) was visible on TLC. The reaction was thus quenched by addition of brine (10 mL). The layers were separated and the organic layers were washed with brine (10 mL), water (10 mL), dried over $MgSO_4$, concentrated by rotary evaporation and dried under high-*vacuum*. The crude was purified by combi-flash chromatography with solid loading and isocratic elution (88:12, PE/AcOEt).

1-(tert-butoxy)-3-propoxypropan-2-ol **(12a)**



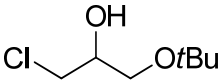
R_f = 0.61 (65:35, PE/AcOEt). ^{1}H NMR (300.16 MHz, $CDCl_3$, 20°C): δ = 3.86(m, 1H, CH_2-CH-CH_2); 3.51-3.33(m, 6H, *CH_2*-O-*CH_2*-CH-*CH_2*-O); 2.53(d, *J* = 4.3 Hz, 1H, CH-*OH*); 1.59(sx, *J* = 7.2 Hz, 2H, CH_3-*CH_2*); 1.19(s, 9H, *CH_3*-C); 0.91(t, *J* = 7.4 Hz, 3H, *CH_3*-CH_2) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ = 73.33(CH_2-O-*CH_2*-CH); 73.27(CH_3-*C*); 72.00(*CH_2*-O-CH_2-CH); 69.94(*CH*-OH); 63.03(CH_2-O-CH_2-CH-*CH_2*-O); 27.63(*CH_3*-C); 22.95(CH_3-*CH_2*); 10.65(*CH_3*-CH_2) ppm. HRMS (ESI): *m/z* calcd for $C_{10}H_{22}O_3Na$ [*M*+Na^+] 213.1467, found 213.1476.

3-(tert-butoxy)-2-propoxypropan-1-ol **(12b)**



R_f = 0.52 (65:35, PE/AcOEt). ^{1}H NMR (300.16 MHz, $CDCl_3$, 20°C): δ = 3.76-3.35(m, 7H, *CH*$_2$-O-*CH*$_2$-*CH*-*CH*$_2$-O); 2.40(t, *J* = 6.2 Hz, 1H, CH-*OH*); 1.59(sx, *J* = 7.3 Hz, 2H, CH_3-*CH*$_2$); 1.18(s, 9H, *CH*$_3$-C); 0.92(t, *J* = 7.4 Hz, 3H, *CH*$_3$-CH_2) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ = 78.52(*CH*-OH); 73.47(CH_3-*C*); 72.11(CH_2-*CH*$_2$-O); 63.62(*CH*$_2$-OH); 62.43(*CH*$_2$-O*t*Bu); 27.50(*CH*$_3$-C); 23.40(CH_3-*CH*$_2$); 10.66(*CH*$_3$-CH_2) ppm. HRMS (ESI): *m/z* calcd for $C_{10}H_{22}O_3Na$ [*M*+Na^+] 213.14612, found 213.14557.

1-(tert-butoxy)-3-chloropropan-2-ol **(12c)**

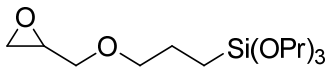


R_f = 0.65 (60:40, PE/AcOEt). ^{1}H NMR (300.16 MHz, $CDCl_3$, 20°C): δ = 3.89(m, 1H, CH_2-CH-CH_2); 3.60(ddd, *J* = 17.9, 11.0 & 5.7 Hz, 2H, Cl-*CH*$_2$-CH); 3.46(d, *J* = 5.0 Hz, 2H, CH-*CH2*-O); 2.60(d, *J* = 6.0 Hz, CH-*OH*); 1.20(s, 9H, *CH3*-C) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ = 73.61(CH_3-*C*); 70.70(*CH*-OH); 62.31(CH-*CH2*-O); 46.00(Cl-*CH*$_2$-CH); 27.60(*CH*$_3$-C) ppm. HRMS (ESI): *m/z* calcd for $C_7H_{15}O_2ClNa$ [*M*+Na^+] 189.0658, found 189.0656.

Synthesis of (3-glycidyloxypropyl)tripropoxysilane (13a), (3-glycidyloxypropyl)methoxydipropoxysilane (13b) & (3-glycidyloxypropyl)dimethoxypropoxysilane (13c)

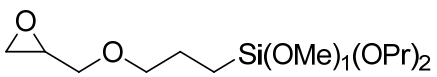
In a dried 50 mL round bottom flask under gentle argon flow was introduced freshly distilled DCM (20 mL), propan-1-ol (3.74 mL, 50 mmol, 5 eq) and GPTMS (2.21 mL, 10 mmol, 1 eq). Then BF_3•Et_2O (37 µL, 0.3 mmol, 0.03eq) was added and the reaction monitored by TLC (80:20, PE/AcOEt). After 1.5h at room temperature, TLC indicate that GPTMS (R_f = 0.31) was totally converted into three compounds (R_f = 0.42; 0.57 & 0.69 respectively). The solution was then concentrated by rotary evaporation and dried under high-*vacuum* to afford 2.76g. One gram of crude was purified by flash chromatography with silica gel as follow: 40 g SiO_2, liquid deposition, isocratic elution (92:8, PE/AcOEt) and afforded five fractions: **13a** (41 mg, pure, colorless oil, 3.5%), mix 11a/11b (154mg, colorless oil), **13b** (107mg, pure, colorless oil, 10.1%), mix 11b/11c (308mg, colorless oil), **13c** (176mg, pure, colorless oil, 18.4%).

(3-glycidyloxypropyl)tripropoxysilane **(13a)**



R_f = 0.69 (80:20, PE/AcOEt). ^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ = 3.69(t, *J* = 6.6 Hz, 6H, Si-O-*CH*$_2$-CH_2); 3.68(dd, *J* = 11.1 & 3.3 Hz, 1H, CH-*CH*$_2$-O); 3.46(m, 2H, CH_2-O-*CH*$_2$-CH_2); 3,39(dd, *J* = 11.5 & 5.6 Hz, 1H, CH-*CH*$_2$-O); 3,13(m, 1H, CH_2-*CH*-CH_2-O); 2.78(dd, *J* = 5.0 & 4.3 Hz, 1H, *CH*$_2$-CH-CH_2-O); 2.60(dd, *J* = 5.0 & 2.7 Hz, 1H, *CH*$_2$-CH-CH_2-O); 1.70(m, 2H, *CH*$_2$-CH_2-Si); 1.57(sx, *J* = 7.0 Hz, 6H, O-CH_2-*CH*$_2$-CH_3); 0.90(t, *J* = 7.4 Hz, 9H, -CH_2-*CH*$_3$); 0.64(m, 2H, CH_2-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 73.99(CH_2-O-*CH*$_2$-CH_2); 71.53(CH-*CH*$_2$-O); 64.56(Si-O-*CH*$_2$-CH_2); 51.01(CH_2-*CH*-CH_2-O); 44.51(*CH*$_2$-CH-CH_2-O); 25.85(O-CH_2-*CH*$_2$-CH_3); 23.21(*CH*$_2$-CH_2-Si); 10.36(CH_2-*CH*$_3$); 6.54(CH_2-*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{15}H_{32}O_5NaSi$ [*M*+Na^+] 343.1917, found 343.1922.

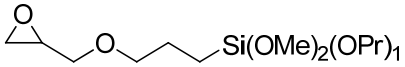
(3-glycidyloxypropyl)methoxydipropoxysilane **(13b)**



R_f = 0.57 (80:20, PE/AcOEt). ^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ = 3.69(t, *J* = 6.7 Hz, 4H, Si-O-*CH*$_2$-CH_2); 3.68(dd, *J* = 11.4 & 3.6 Hz, 1H, CH-*CH*$_2$-O);3.53(s, 3H, Si-O-CH_3); 3.45(m, 2H, CH_2-O-*CH*$_2$-CH_2); 3,38(dd, *J* = 11.6 & 5.8 Hz, 1H, CH-*CH*$_2$-O); 3,13(m, 1H, CH_2-*CH*-CH_2-O); 2.77(dd, *J* = 5.0 & 4.2 Hz, 1H, *CH*$_2$-CH-CH_2-O); 2.60(dd, *J* = 4.7 & 2.6 Hz, 1H, *CH*$_2$-CH-CH_2-O);1.69(m, 2H, *CH*$_2$-CH_2-Si); 1.57(sx, *J* = 7.3 Hz, 6H, O-CH_2-

CH$_2$-CH$_3$); 0.90(t, *J* = 7.4 Hz, 9H, CH$_2$-*CH*$_3$); 0.64(m, 2H, CH$_2$-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 73.85(CH$_2$-O-*CH*$_2$-CH$_2$); 71.50(CH-*CH*$_2$-O); 64.58(Si-O-*CH*$_2$-CH$_2$); 50.98(CH$_2$-*CH*-CH$_2$-O); 50.53(Si-O-*CH*$_3$) 44.45(*CH*$_2$-CH-CH$_2$-O); 25.82(O-CH$_2$-*CH*$_2$-CH$_3$); 23.10(*CH*$_2$-CH$_2$-Si); 10.31(CH$_2$-*CH*$_3$); 6.11(CH$_2$-*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{28}O_5NaSi$ [*M*+Na$^+$] 315.1604, found 315.1606.

(3-glycidyloxypropyl)dimethoxypropoxysilane **(13c)**

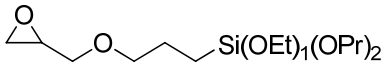


R_f = 0.42 (80:20, PE/AcOEt). ^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): δ= 3.69(t, *J* = 6.7 Hz, 2H, Si-O-*CH*$_2$-CH$_2$); 3.68(dd, *J* = 8.3 & 3.2 Hz, 1H, CH-*CH*$_2$-O); 3.54(s, 6H, Si-O-CH$_3$); 3.45(m, 2H, CH$_2$-O-*CH*$_2$-CH$_2$); 3,38(dd, *J* = 11.4 & 5.7 Hz, 1H, CH-*CH*$_2$-O); 3,13(m, 1H, CH$_2$-*CH*-CH$_2$-O); 2.78(dd, *J* = 5.0 & 4.3 Hz, 1H, *CH*$_2$-CH-CH$_2$-O); 2.59(dd, *J* = 4.9 & 2.7 Hz, 1H, *CH*$_2$-CH-CH$_2$-O); 1.69(m, 2H, *CH*$_2$-CH$_2$-Si); 1.57(sx, *J* = 7.3 Hz, 2H, O-CH$_2$-*CH*$_2$-CH$_3$); 0.90(t, *J* = 7.43 Hz, 3H, CH$_2$-*CH*$_3$); 0.64(m, 2H, CH$_2$-*CH*$_2$-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 73.75(CH$_2$-O-*CH*$_2$-CH$_2$); 71.50(CH-*CH*$_2$-O); 64.62(Si-O-*CH*$_2$-CH$_2$); 50.99(CH$_2$-*CH*-CH$_2$-O); 50.60(Si-O-*CH*$_3$); 44.45(*CH*$_2$-CH-CH$_2$-O); 25.79(O-CH$_2$-*CH*$_2$-CH$_3$); 22.99(*CH*$_2$-CH$_2$-Si); 10.31(CH$_2$-*CH*$_3$); 5.70(CH$_2$-*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{11}H_{24}O_5NaSi$ [*M*+Na$^+$] 287.1291, found 287.1302.

Synthesis of (3-glycidyloxypropyl)tripropoxysilane (13a), (3-glycidyloxypropyl)ethoxydipropoxysilane (14a) & (3-glycidyloxypropyl)diethoxypropoxysilane (14b)

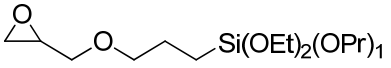
In a dried 50 mL round bottom flask under gentle argon flow was introduced freshly distilled DCM (16 mL), propan-1-ol (1.87 mL, 25 mmol, 5 eq) and GPTES (1.39 mL, 5 mmol, 1 eq). Then BF_3•Et_2O (60 µL, 0.5 mmol, 0.1 eq) was added and the reaction monitored by TLC (90:10, PE/AcOEt). After 22h at room temperature, TLC indicates that GPTES was totally converted into three compounds (R_f = 0.48, 0.38 & 0.32 respectively). The mixture was then washed with brine (2x10 mL) and water (10 mL). The combined aqueous layers were extracted with DCM (10 mL). The combined organic layers were dried over $MgSO_4$, concentrated by rotary evaporation and dried under high-*vacuum* to afford 1.72 g. The residue was purified by combi-flash chromatography on a 120g/40µm SiO_2 column with liquid injection and gradient elution (96:4-90:10, PE/AcOEt) and afforded four fractions: **13a** (61 mg, pure, colorless oil, 4%), **14a** (453 mg, pure, colorless oil, 30%), mix 14a/14b (16mg, mix), **14b** (125 mg, pure, colorless oil, 9%).

(3-glycidyloxypropyl)ethoxydipropoxysilane **(14a)**



R_f = 0.38 (90:10, PE/AcOEt). ^{1}H NMR (300.13 MHz, $CDCl_3$, 20°C): δ = 3.81(q, *J* = 7.0 Hz, 2H, Si-O-*CH*$_2$-CH$_3$); 3.71(dd, *J* = 8.3 & 3.0 Hz, 1H, CH-*CH*$_2$-O-CH$_2$); 3.70(t, *J* = 6.7 Hz, 4H, Si-O-*CH*$_2$-CH$_2$); 3.47(ddd, *J* = 14.7, 9.2 & 6.9 Hz, 2H, CH-CH$_2$-O-*CH*$_2$); 3,38(dd, *J* = 11.4 & 5.7 Hz, 1H, CH-*CH*$_2$-O-CH$_2$); 3,15(m, 1H, CH$_2$-*CH*-CH$_2$); 2.80(dd, *J* = 5.0 & 4.2 Hz, 1H, *CH*$_2$-CH-CH$_2$-O); 2.61(dd, *J* = 5.0 & 2.7 Hz, 1H, *CH*$_2$-CH-CH$_2$-O); 1.71(m, 2H, *CH*$_2$-CH$_2$-Si); 1.57(sx, *J* = 7.0 Hz, 4H, CH$_2$-*CH*$_2$-CH$_3$); 1.22(t, *J* = 7 Hz, 3H, CH$_2$-CH$_2$-*CH*$_3$); 0.90(t, *J* = 7.4 Hz, 6H, O-CH$_2$-*CH*$_3$); 0.64(m, 2H, *CH*$_2$-Si) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ = 73.97(CH-CH$_2$-O-*CH*$_2$); *71.53(*CH-*CH*$_2$-O-CH$_2$); 64.56(Si-O-*CH*$_2$-CH$_2$); 58.52(Si-O-*CH*$_2$-CH$_3$); 51.01(CH$_2$-*CH*-CH$_2$); 44.52(*CH*$_2$-CH-CH$_2$-O); 25.84(CH$_2$-*CH*$_2$-CH$_3$); 23.20(*CH*$_2$-CH$_2$-Si); 18.45(O-CH$_2$-*CH*$_3$); 10.36(CH$_2$-CH$_2$-*CH*$_3$); 6.58(*CH*$_2$-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{14}H_{30}O_5NaSi$ [*M*+Na$^+$] 329.1760, found 329.1746.

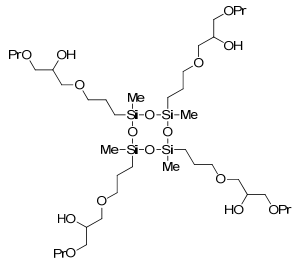
(3-glycidyloxypropyl)diethoxypropoxysilane **(14b)**



R_f = 0.32 (90:10, PE/AcOEt). ^{1}H NMR (300.13 MHz, $CDCl_3$, 20°C): δ = 3.81(q, *J* = 7.0 Hz, 4H, Si-O-*CH*$_2$-CH$_3$); 3.70(t, *J* = 6.7 Hz, 2H, Si-O-*CH*$_2$-CH$_2$); 3.69(dd, *J* = 11.5 & 3.7 Hz, 1H, CH-*CH*$_2$-O-CH$_2$); 3.47(ddd, *J* = 17.3, 9.3 & 6.9 Hz, 2H, CH-CH$_2$-O-*CH*$_2$); 3,38(dd, *J* = 11.5 & 5.7 Hz, 1H, CH-*CH*$_2$-O-CH$_2$); 3,14(m, 1H, CH$_2$-

CH-CH_2); 2.79(dd, *J* = 5.0 & 4.2 Hz, 1H, *CH_2*-CH-CH_2-O); 2.61(dd, *J* = 5.0 & 2.7 Hz, 1H, *CH_2*-CH-CH_2-O); 1.70(m, 2H, *CH_2*-CH_2-Si); 1.57(sx, *J* = 7.1 Hz, 2H, CH_2-*CH_2*-CH_3); 1.22(t, *J* = 7 Hz, 6H, CH_2-CH_2-*CH_3*); 0.90(t, *J* = 7.4 Hz, 3H, O-CH_2-*CH_3*); 0.64(m, 2H, *CH_2*-Si) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 20°C): δ = 73.95(CH-CH_2-O-*CH_2); 71.53(*CH-*CH_2-O-CH_2); 64.56(Si-O-*CH_2*-CH_2); 58.52(Si-O-*CH_2*-CH_3); 51.02(CH_2-*CH*-CH_2); 44.51(*CH_2*-CH-CH_2-O); 25.84(CH_2-*CH_2*-CH_3); 23.18(*CH_2*-CH_2-Si); 18.44(O-CH_2-*CH_3*); 10.36(CH_2-CH_2-*CH_3*); 6.61(*CH_2*-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_{28}O_5NaSi$ [*M*+Na^+] 315.1604, found 315.1616.

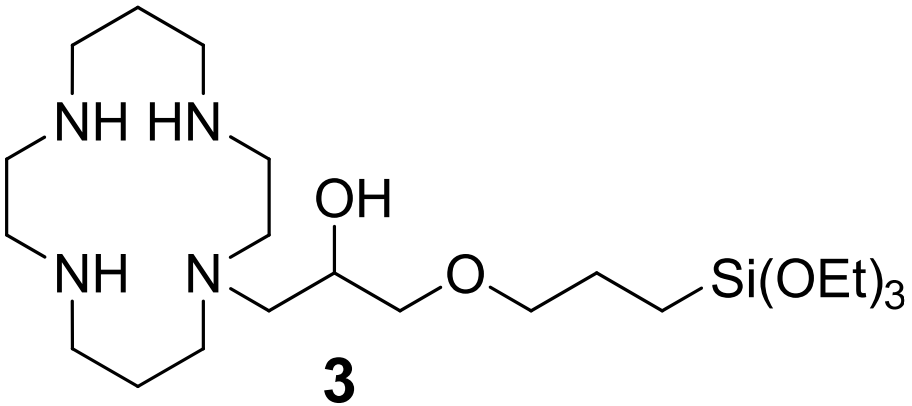
Synthesis of tetrakis(*n*-propoxypropan-2-ol)cyclomethylsiloxane (15)



In a dried 50 mL round bottom flask under gentle argon flow was introduced freshly distilled DCM (16 mL), propan-1-ol (1.87 mL, 25 mmol, 5 eq) and PECS (1.39 mL, 5 mmol, 1 eq). Then BF_3•Et_2O (60 µL, 0.5 mmol, 0.1 eq) was added and the reaction monitored by TLC (98:02, $CHCl_3$/MeOH). After 3h at room temperature, TLC indicates that PECS (R_f = 0.7) was totally converted into two compounds (R_f = 0.26 & 0.09 respectively). The solution was then concentrated by rotary evaporation and was dried under high-*vacuum* to afford 1.17 g. The residue was purified by combi-flash chromatography on a 40g/40µm SiO2 column with liquid injection and gradient elution (98:2-94:06, $CHCl_3$/MeOH) and afforded the tetra substituted cyclosiloxane **15** (1.10 g, 94%) as a pure viscous colorless oil.

R_f = 0.26 (98:02, $CHCl_3$/MeOH). ^{1}H NMR (400.16 MHz, $CDCl_3$, 20°C): GG1-12F1: δ = 3.95(m, 4H, *CH*(OH)); 3.60-3.35(m, 32H, *CH_2*-O-*CH_2*-CH(OH)-*CH_2*-O-*CH_2*); 2.95-2.45(m, 4H, CH(*OH*)); 1.7-1.5(m, 8H, *CH_2*-CH_2-Si); 1.59(sx, *J* = 7.1 Hz, 8H, CH_3-*CH_2*-CH_2-O); 0.91(t, *J* = 7.4 Hz, 12H, *CH_3*-CH_2-CH_2-O); 0.65(m, 8H, *CH_2*-Si); 0.08(s, 12H, *CH_3*-Si) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 20°C): δ = 74.11, 73.37, 72.11 & 72.02(*CH_2*-O-*CH_2*-CH(OH)-*CH_2*-O-*CH_2*), 69.65(*CH*(OH)); 23.23(*CH_2*-CH_2-Si); 22.95(CH_3-*CH_2*-CH_2-O); 13.23(*CH_2*-Si); 10.64(*CH_3*-CH_2-CH_2-O); -0.56(*CH_3*-Si) ppm. HRMS (ESI): *m/z* calcd for $C_{40}H_{88}O_{16}NaSi_4$ [*M*+Na^+] 959.5042, found 959.5043.

D. SPECTROSCOPIC DATA



3

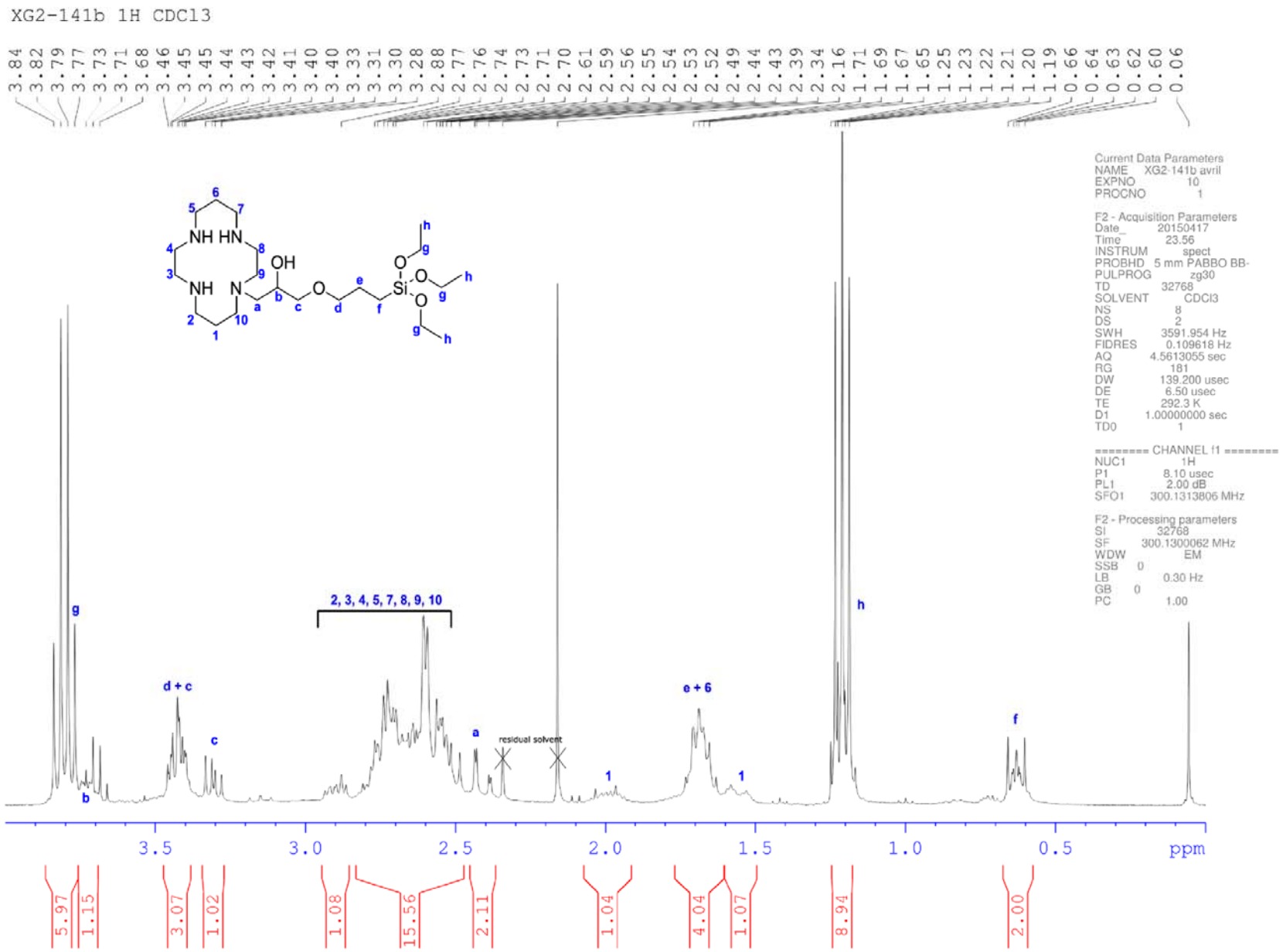


Figure SI_14: ^{1}H NMR spectrum of compound 3

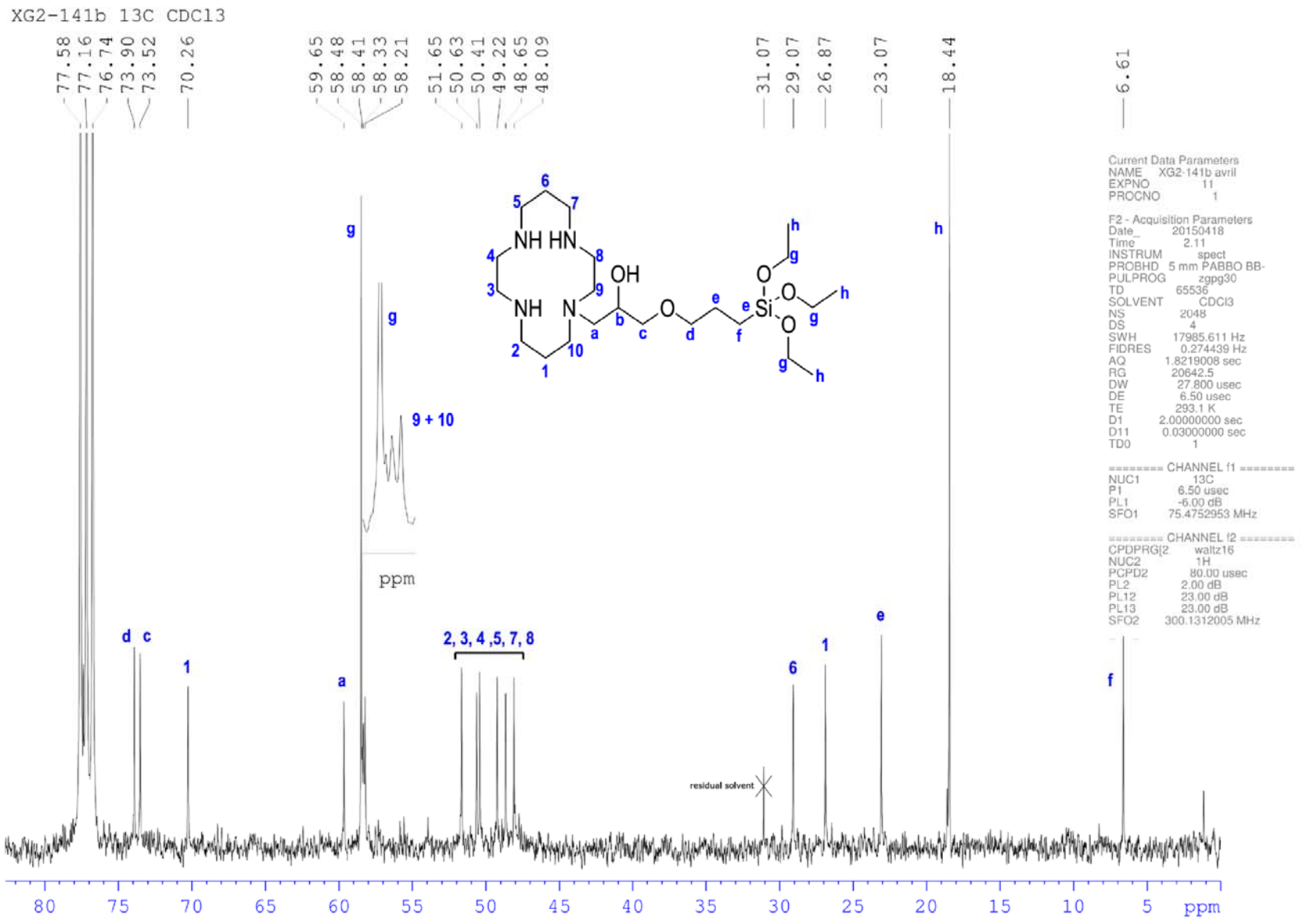


Figure SI_15: ^{13}C NMR spectrum of compound 3

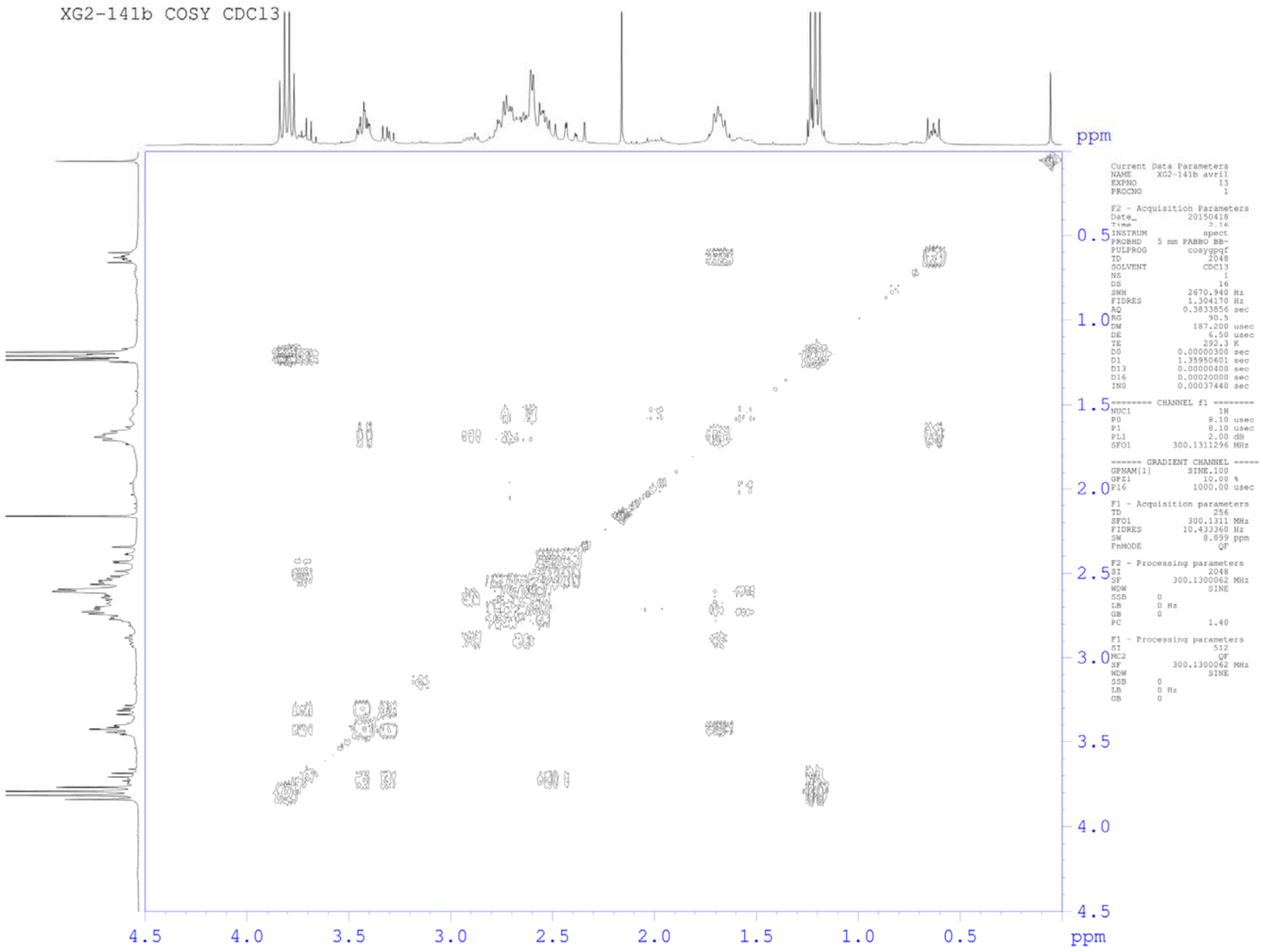


Figure SI_16: ^{1}H -^{1}H COSY of compound 3

SI_17

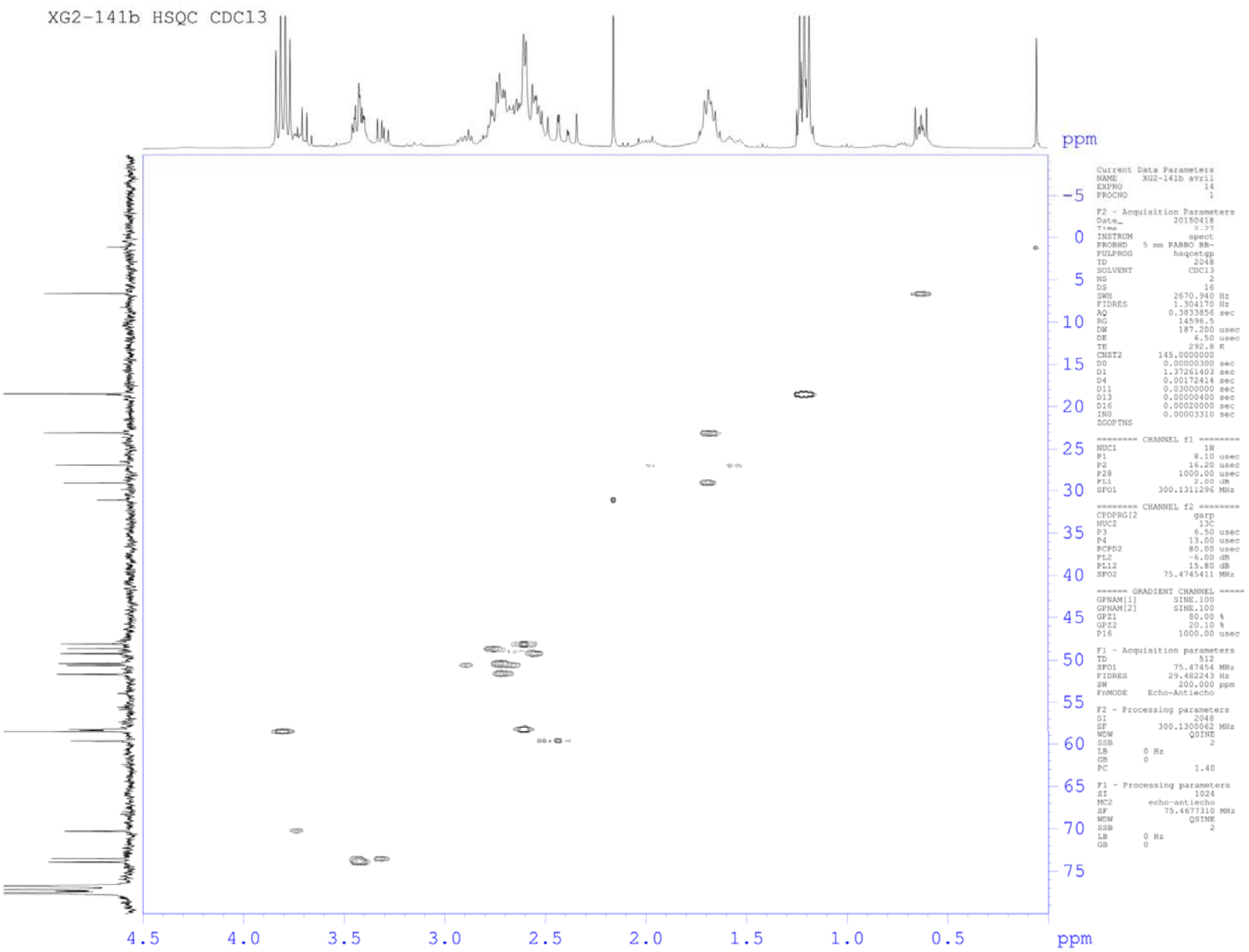


Figure SI_17: HSQC spectrum of compound 3

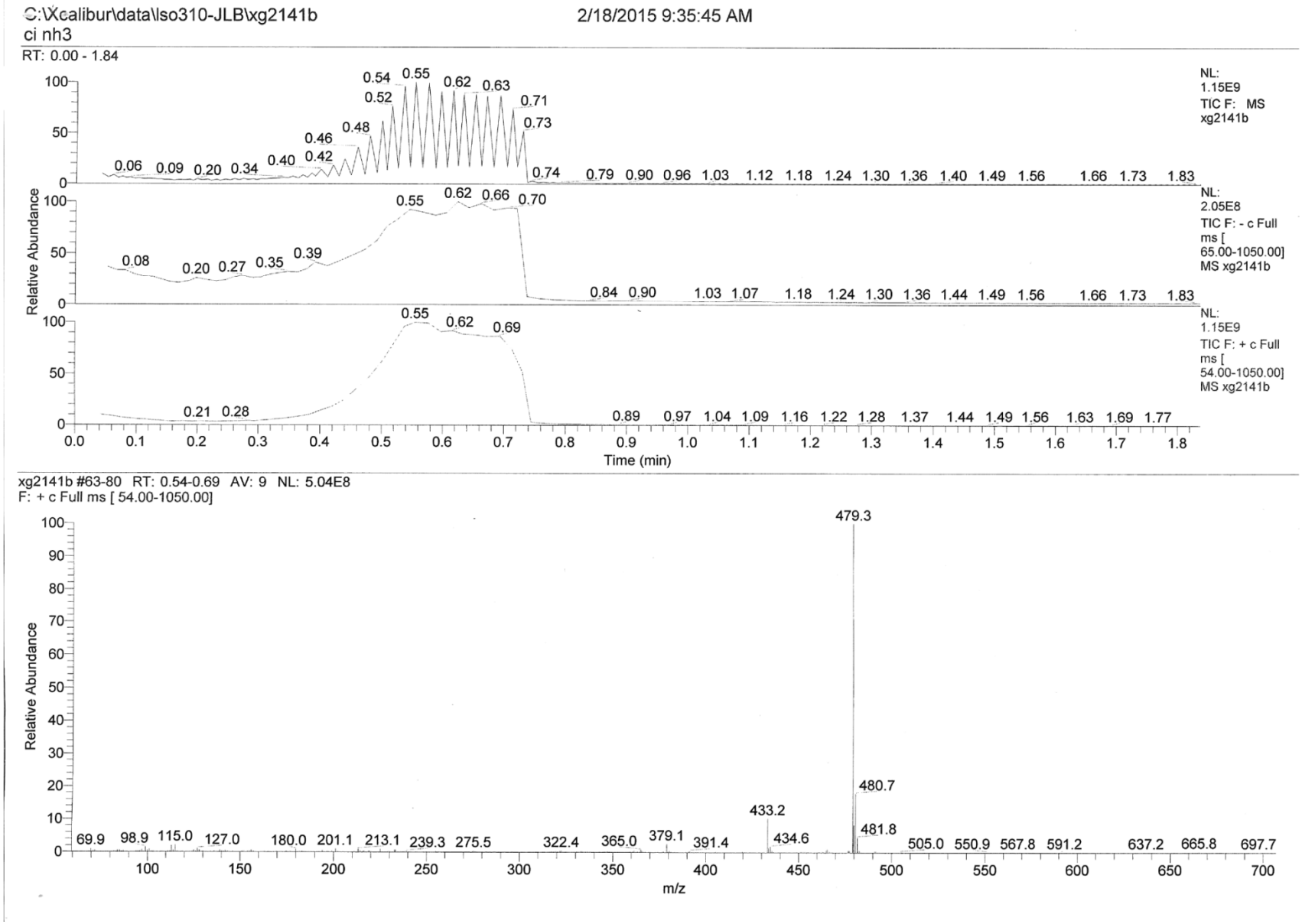
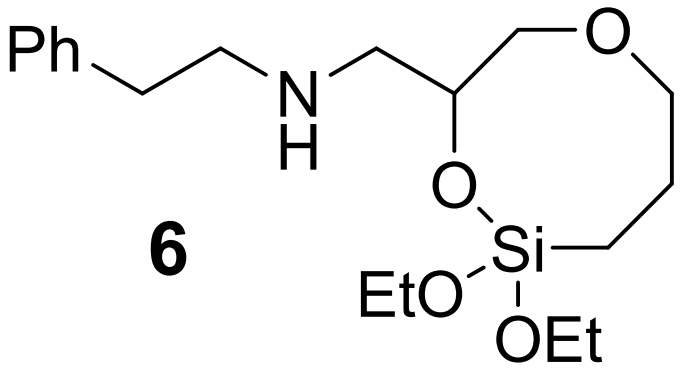


Figure SI_18: CI-MS spectrum of compound 3



6

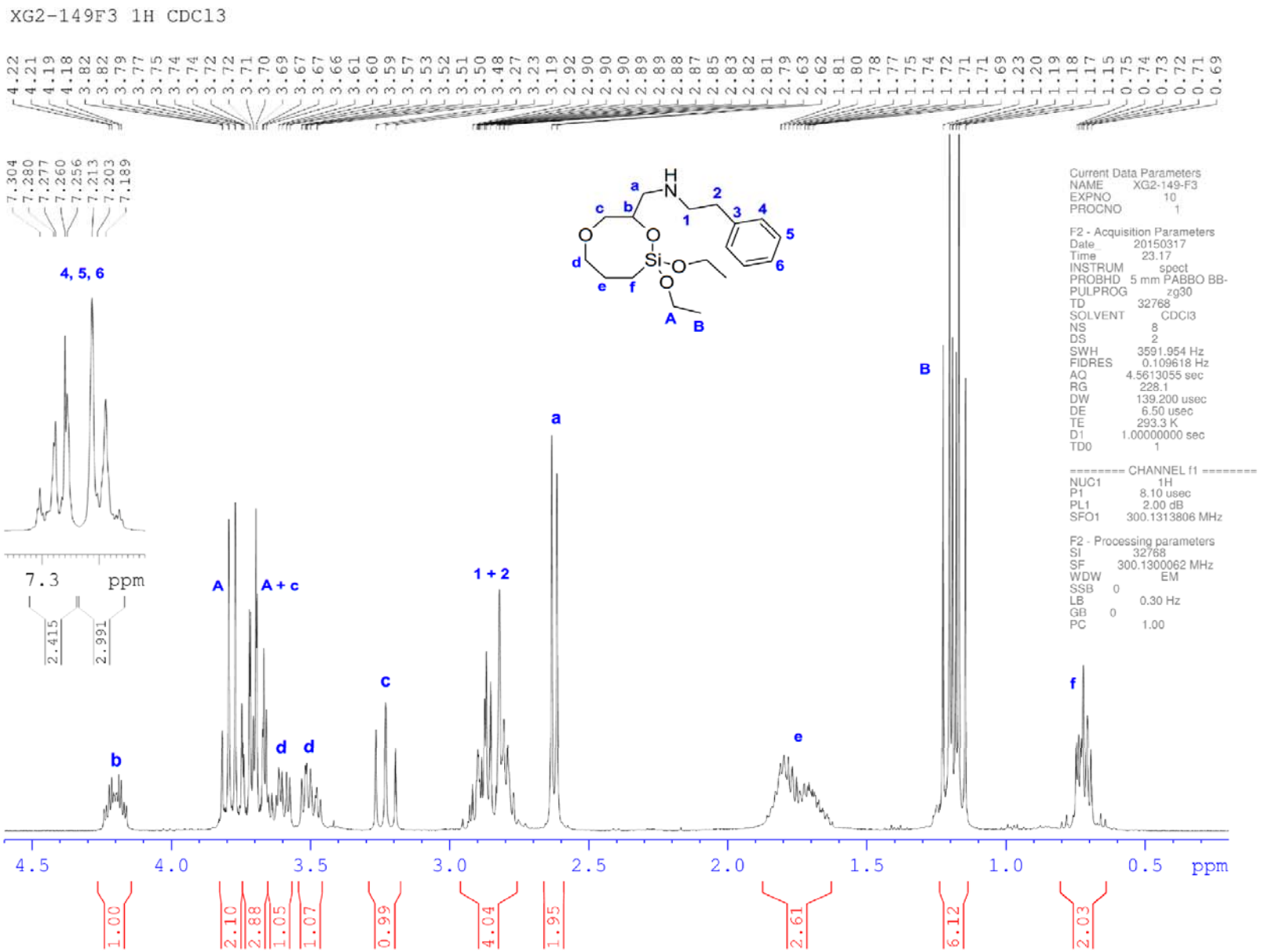


Figure SI_20: ^{1}H NMR spectrum of compound 6

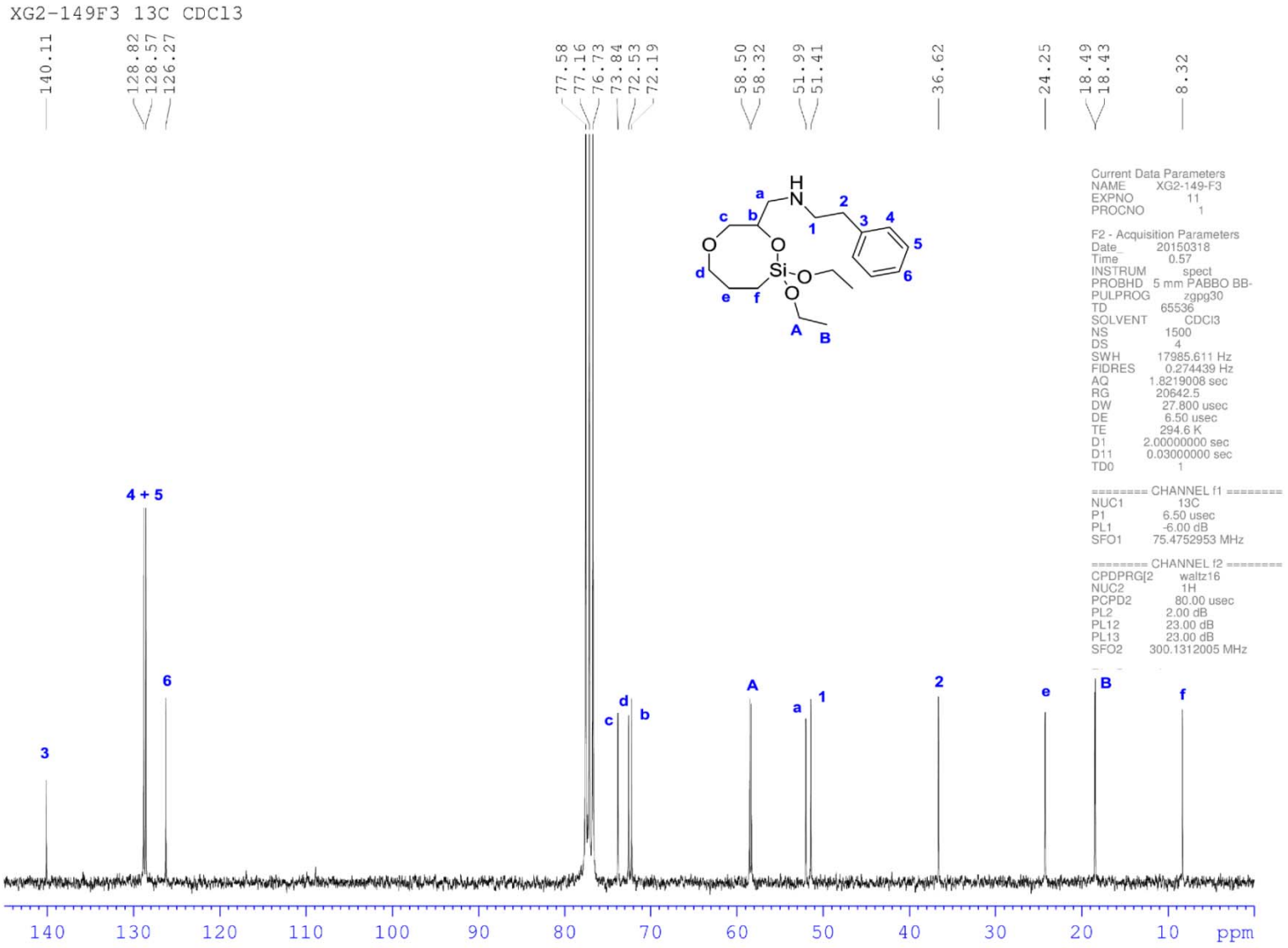


Figure SI_21: ^{13}C NMR spectrum of compound 6

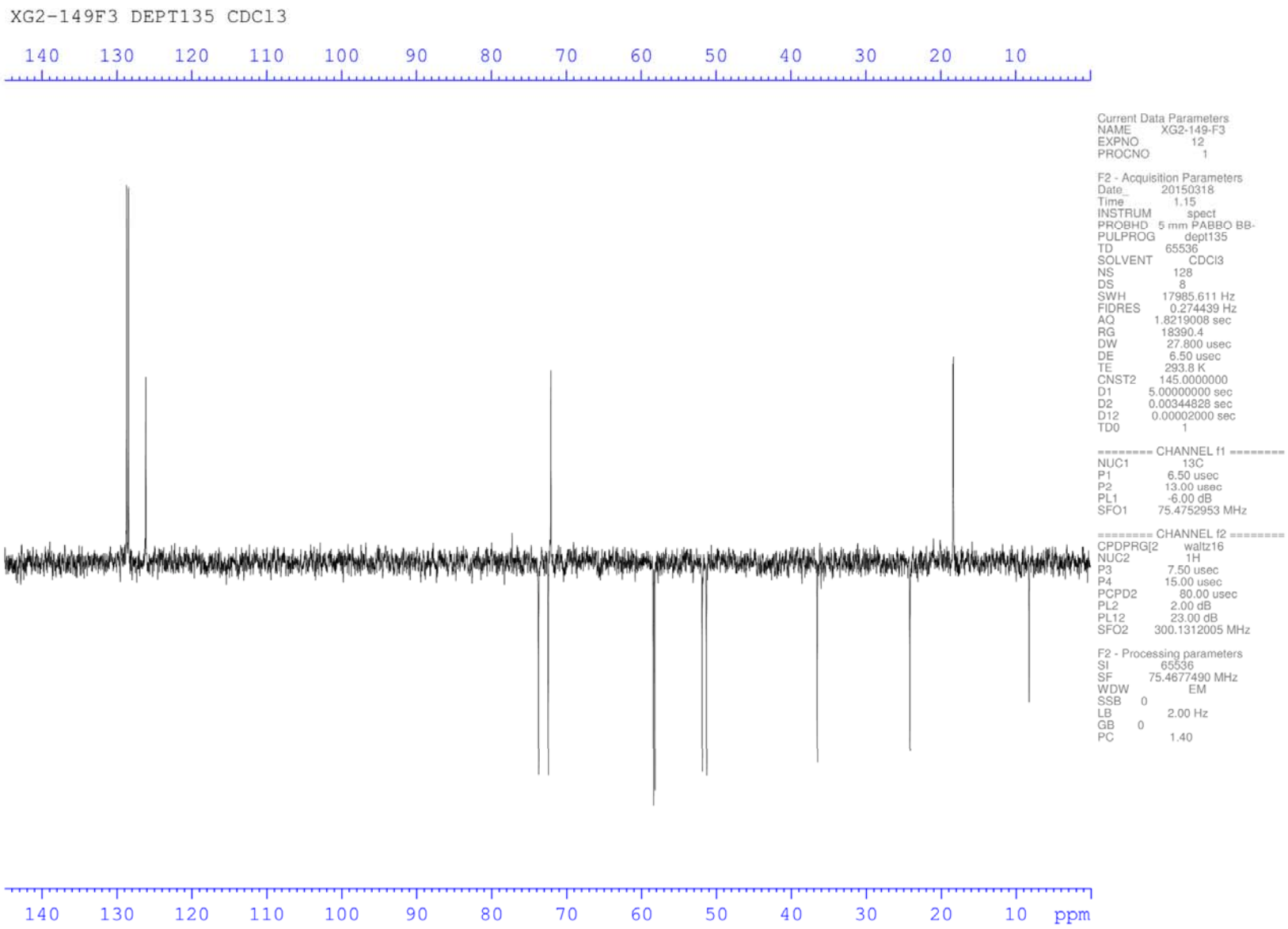


Figure SI_22: DEPT-135 NMR spectrum of compound 6

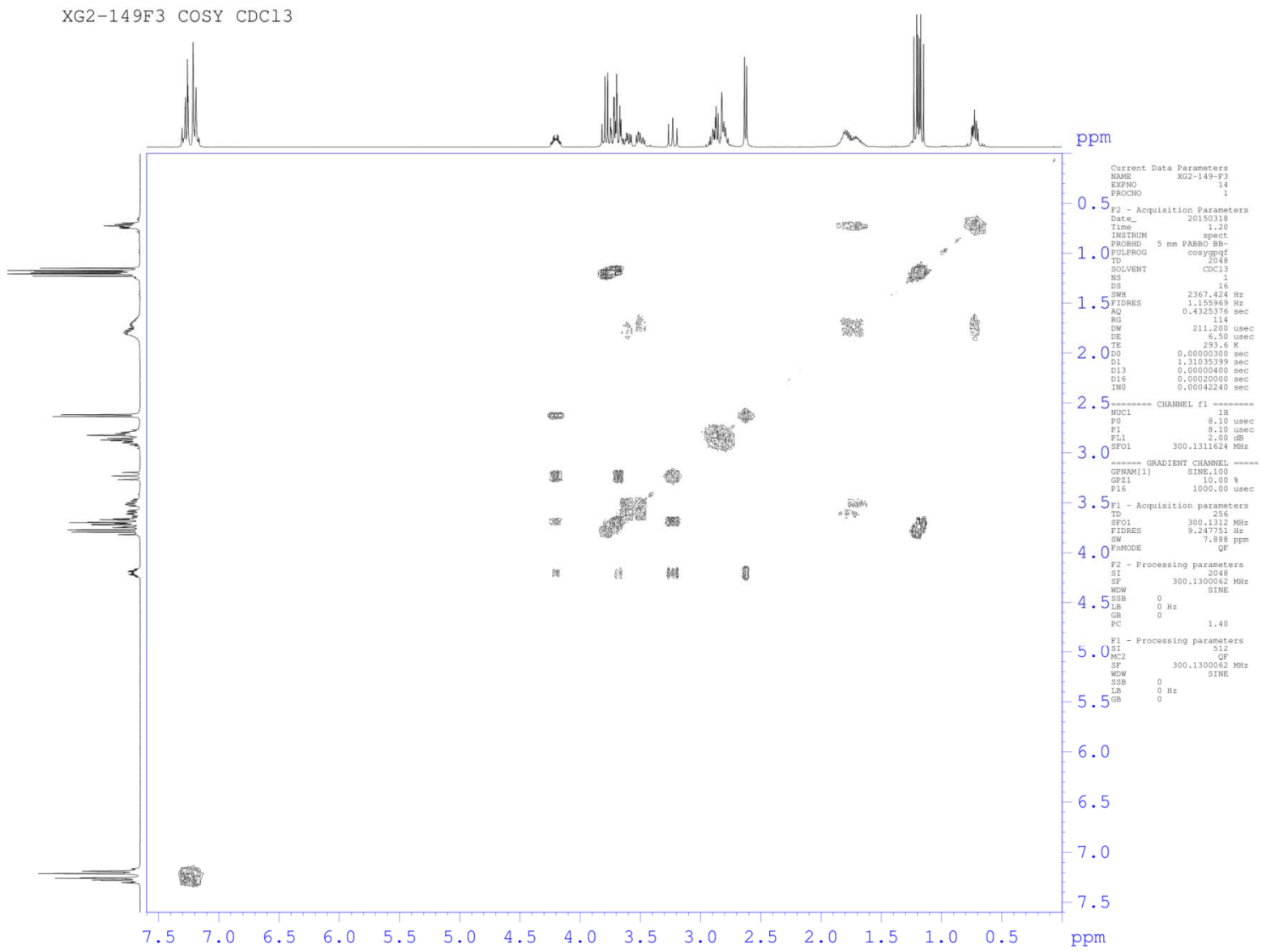


Figure SI_23: ^{1}H-^{1}H COSY of compound 6

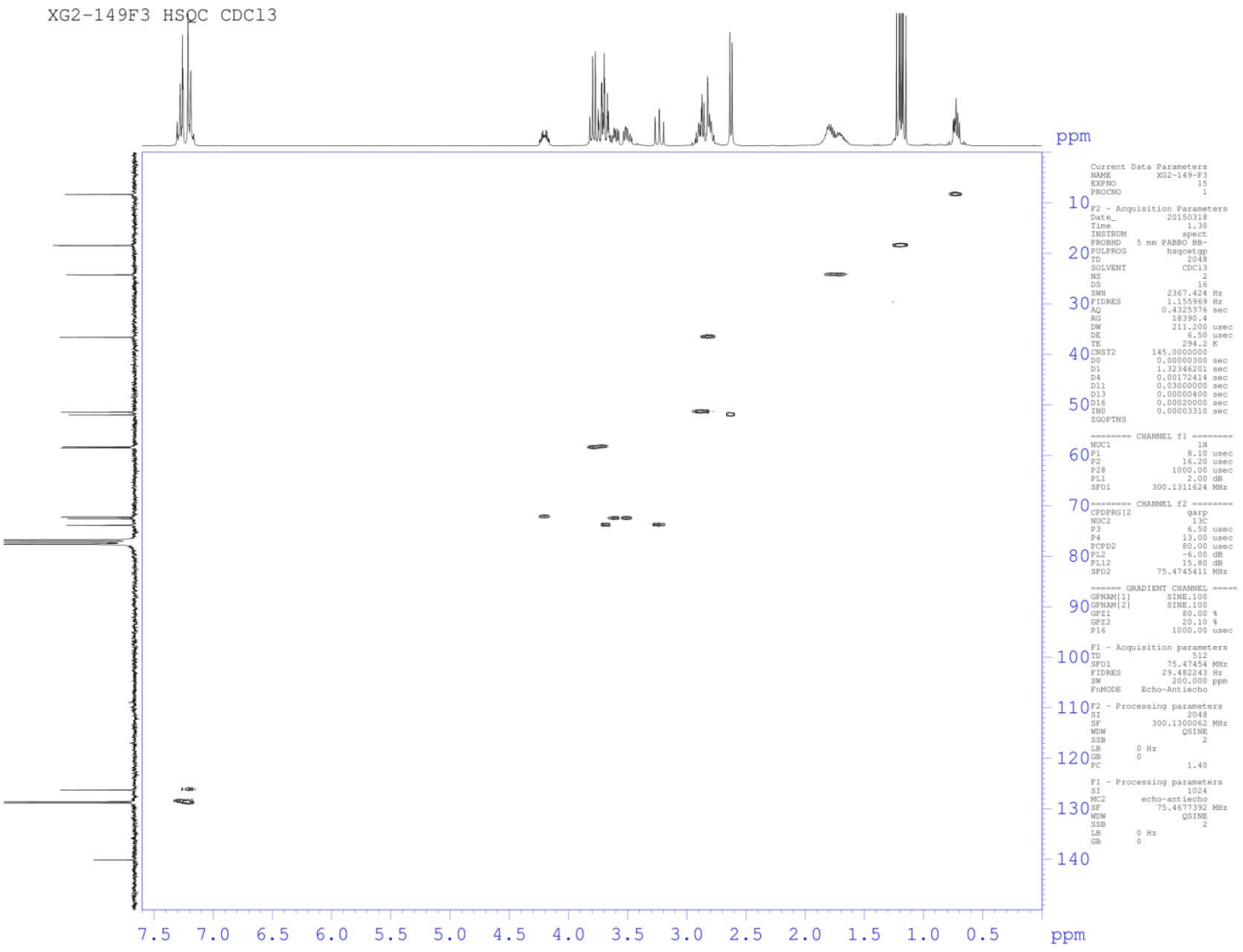


Figure SI_24: HSQC spectrum of compound 6

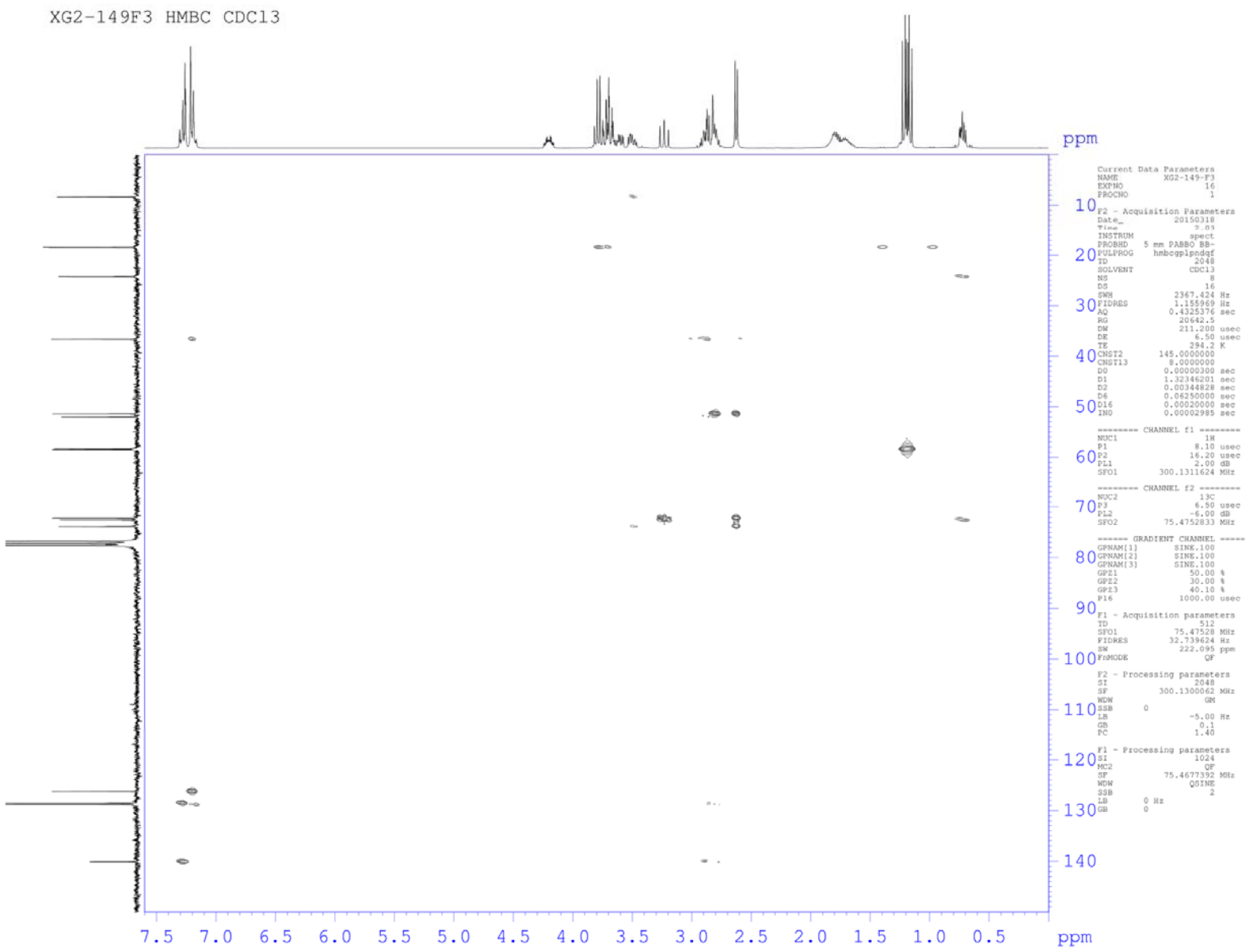


Figure SI_25: HMBC spectrum of compound 6

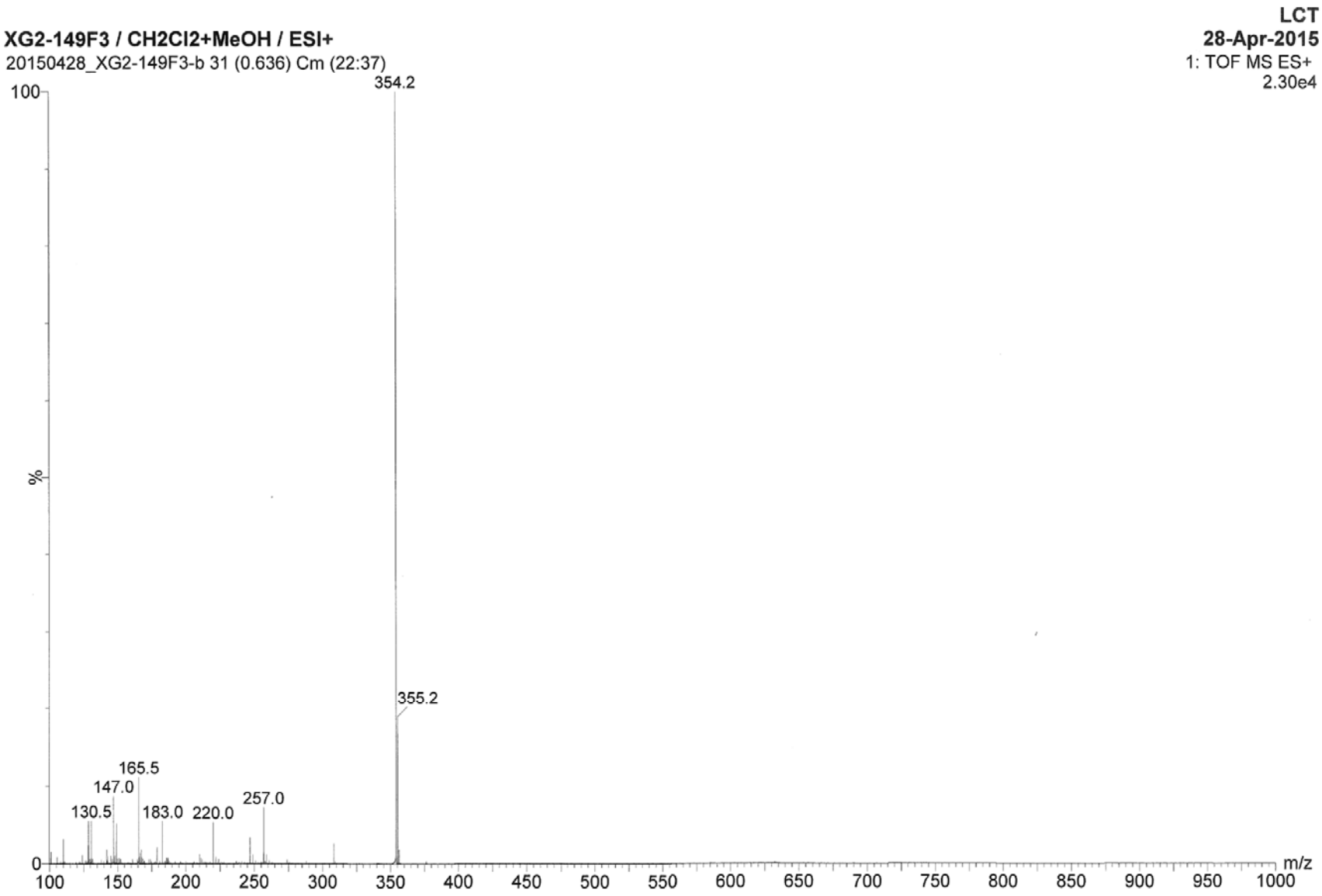


Figure SI_26: HRMS spectrum of compound 6

Elemental Composition Report **Page 1**

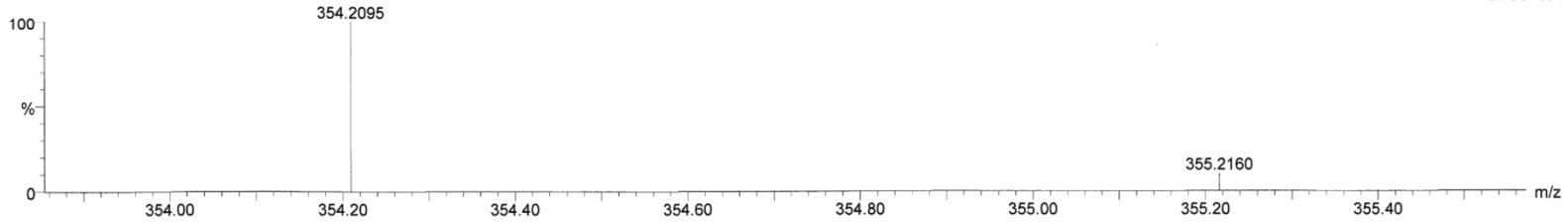
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
179 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-6 O: 0-5 Si: 1-1

LCT
XG2-149F3 / CH2Cl2+MeOH / ESI+
1: TOF MS ES+

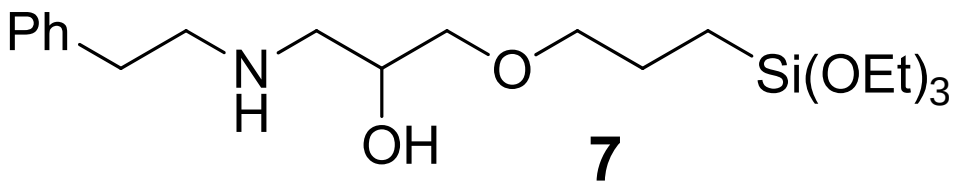
20150428_XG2-149F3 14 (0.285) AM (Cen,13, 80.00, Ar,4100.0,556.28,0.00,LS 10); Cm (6:15)
28-Apr-2015

2.79e+004



Minimum:		5.0	5.0	-1.5		
Maximum:				100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
354.2095	354.2101	-0.6	-1.7	4.5	n/a	C18 H32 N O4 Si

Figure SI_27: HRMS spectrum of compound 6



7

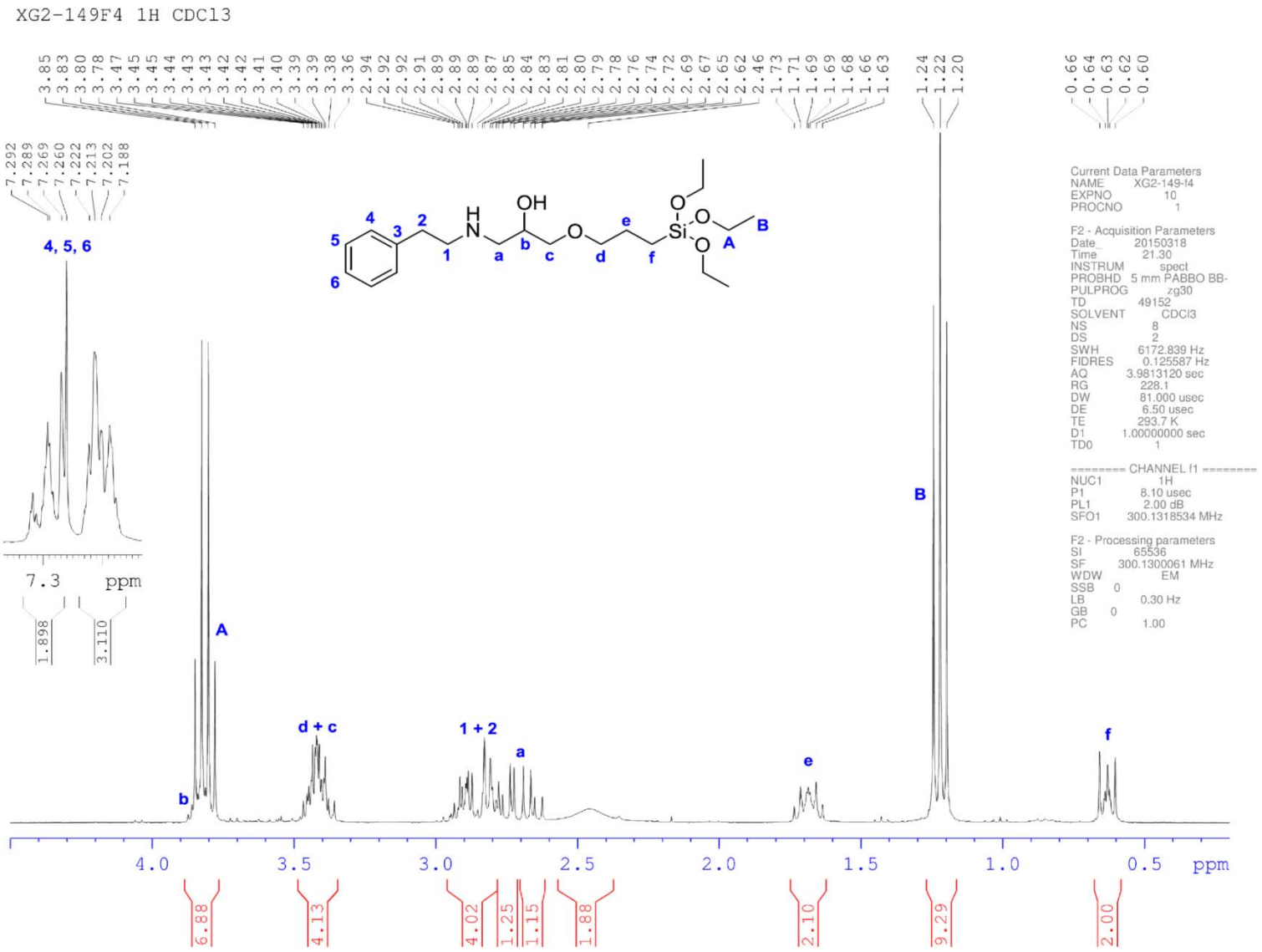


Figure SI_29: ^{1}H NMR spectrum of compound 7

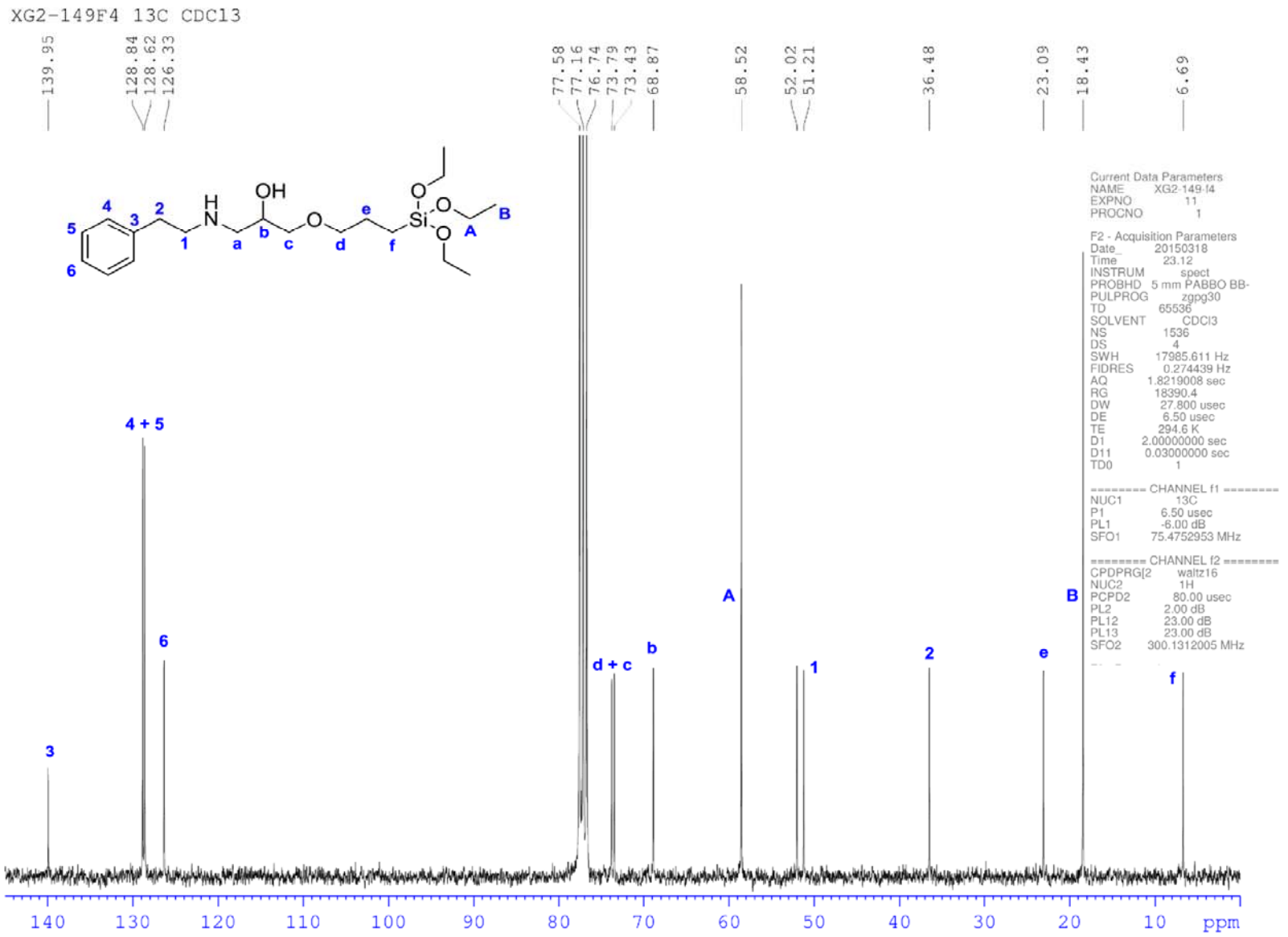


Figure SI_30: ^{13}C NMR spectrum of compound 7

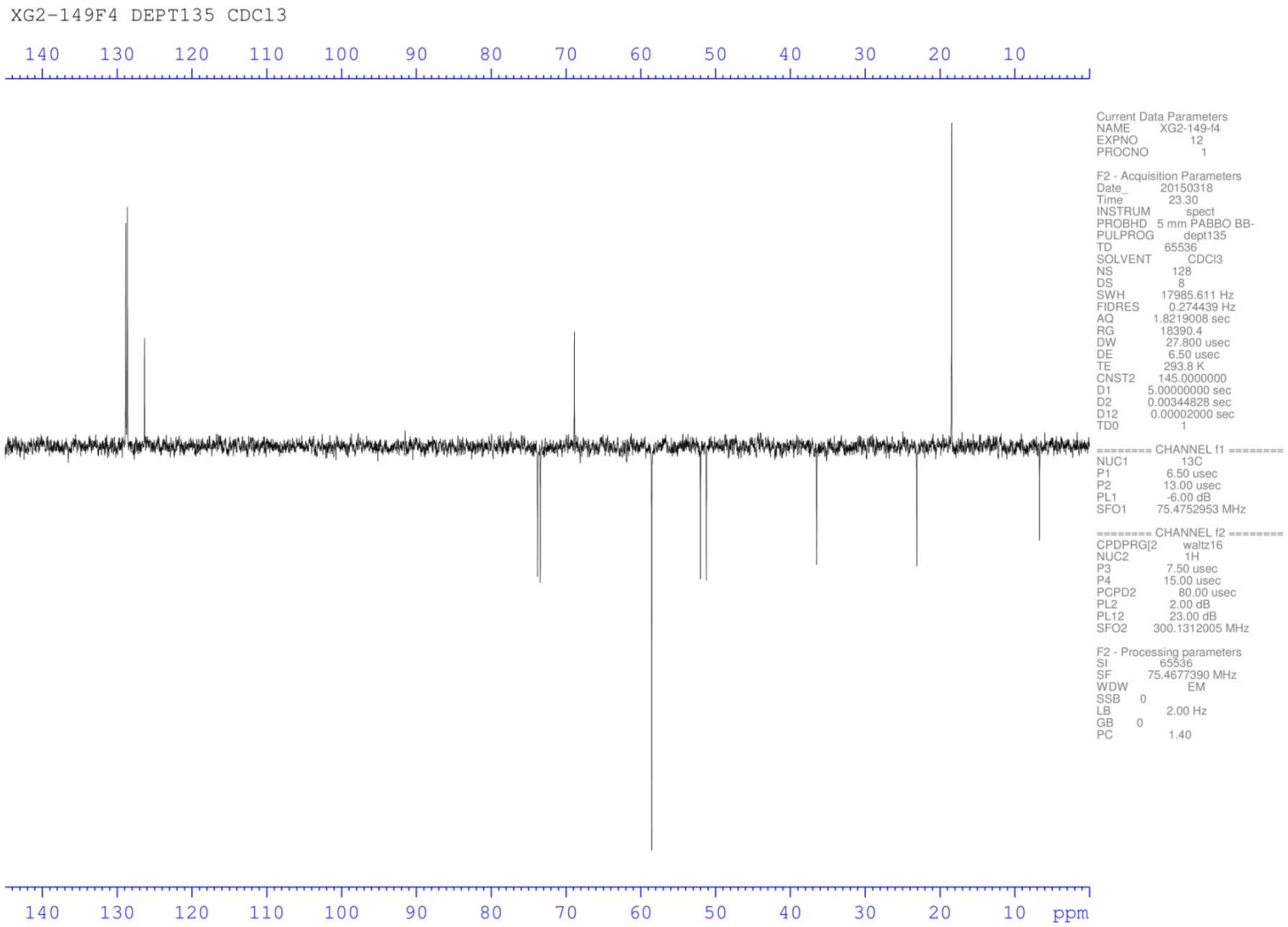


Figure SI_31: DEPT 135 spectrum of compound 7

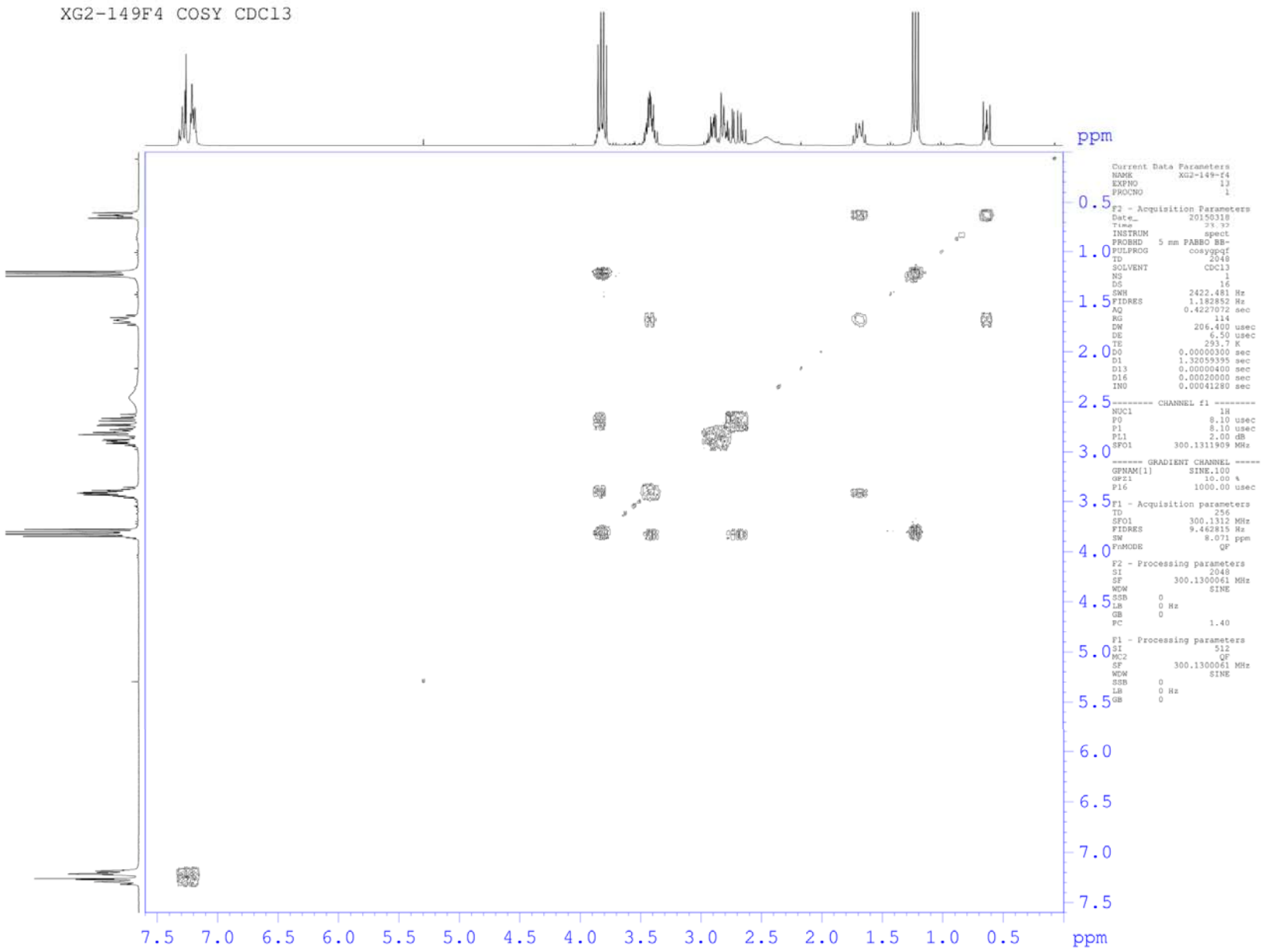


Figure SI_32: ^{1}H ^{1}H COSY spectrum of compound 7

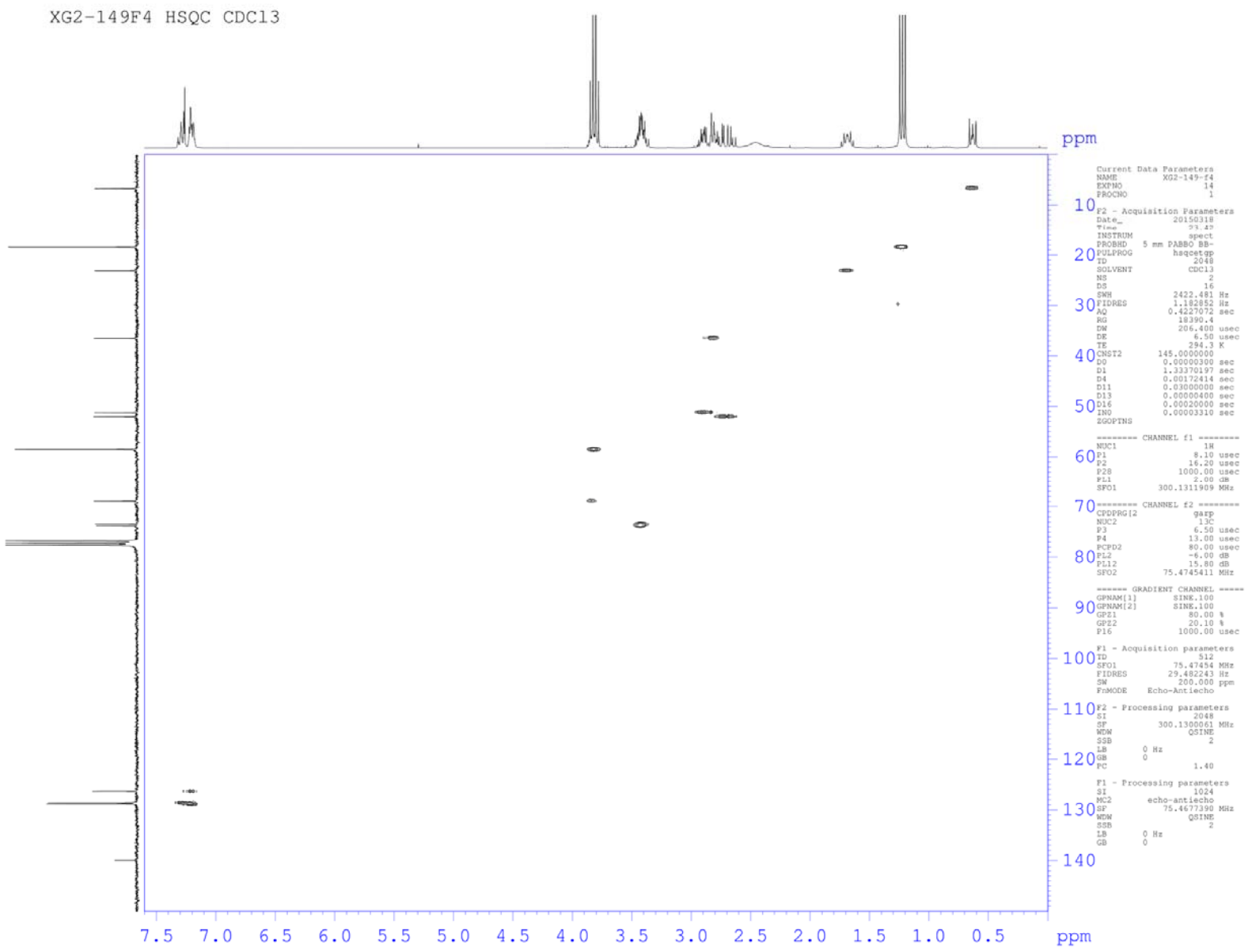


Figure SI_33: HSQC spectrum of compound 7

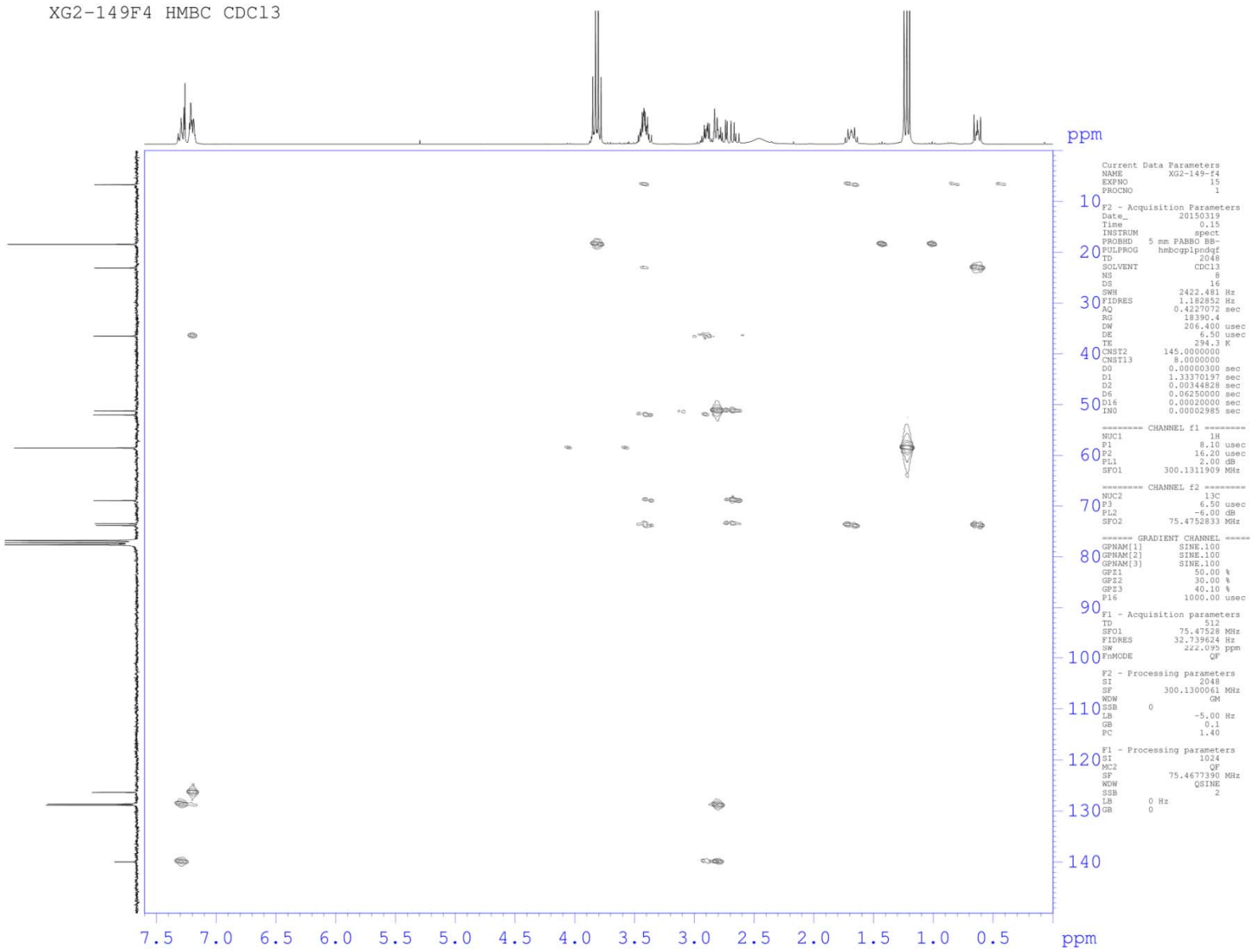


Figure SI_34: HMBC spectrum of compound 7

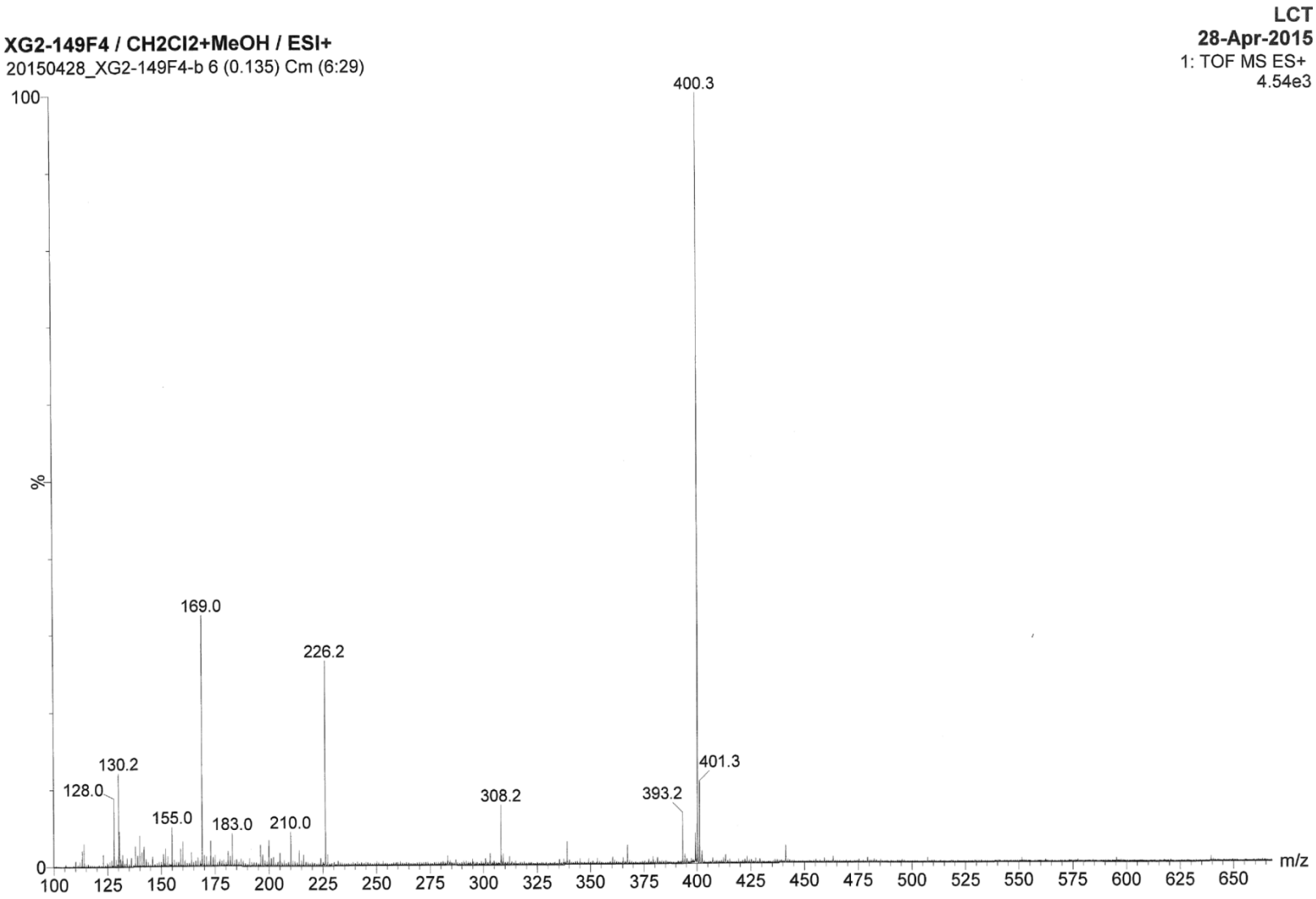


Figure SI_35: ESI-MS spectrum of compound 7

Elemental Composition Report

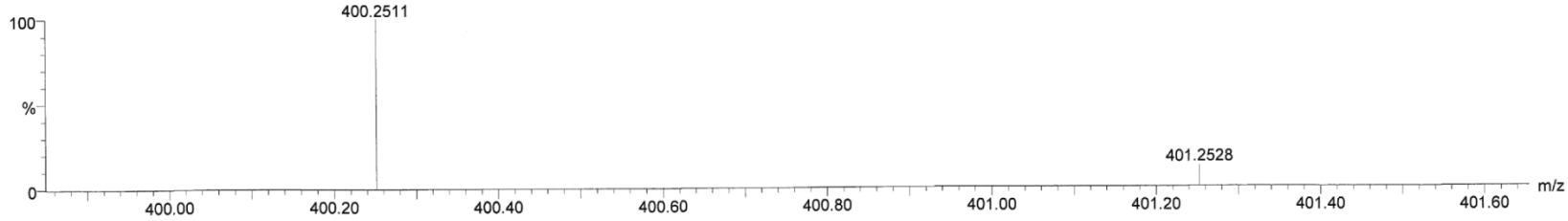
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
202 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-6 O: 0-5 Si: 1-1

LCT
XG2-149F4 / CH2Cl2+MeOH / ESI+
1: TOF MS ES+

20150428_XG2-149F4 25 (0.502) AM (Cen,13, 80.00, Ar,4100.0,556.28,0.00,LS 10); Cm (9:30)
28-Apr-2015

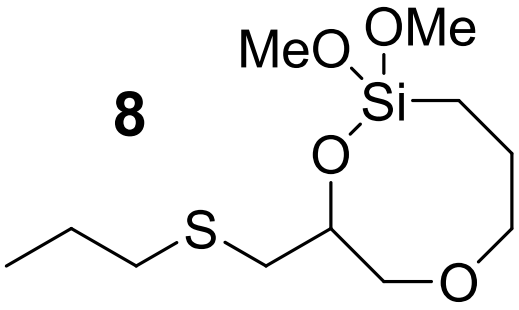
2.65e+004



Minimum:				-1.5		
Maximum:		5.0	5.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
400.2511	400.2519	-0.8	-2.0	3.5	n/a	C20 H38 N O5 Si

Figure SI_36: HRMS spectrum of compound 7

8



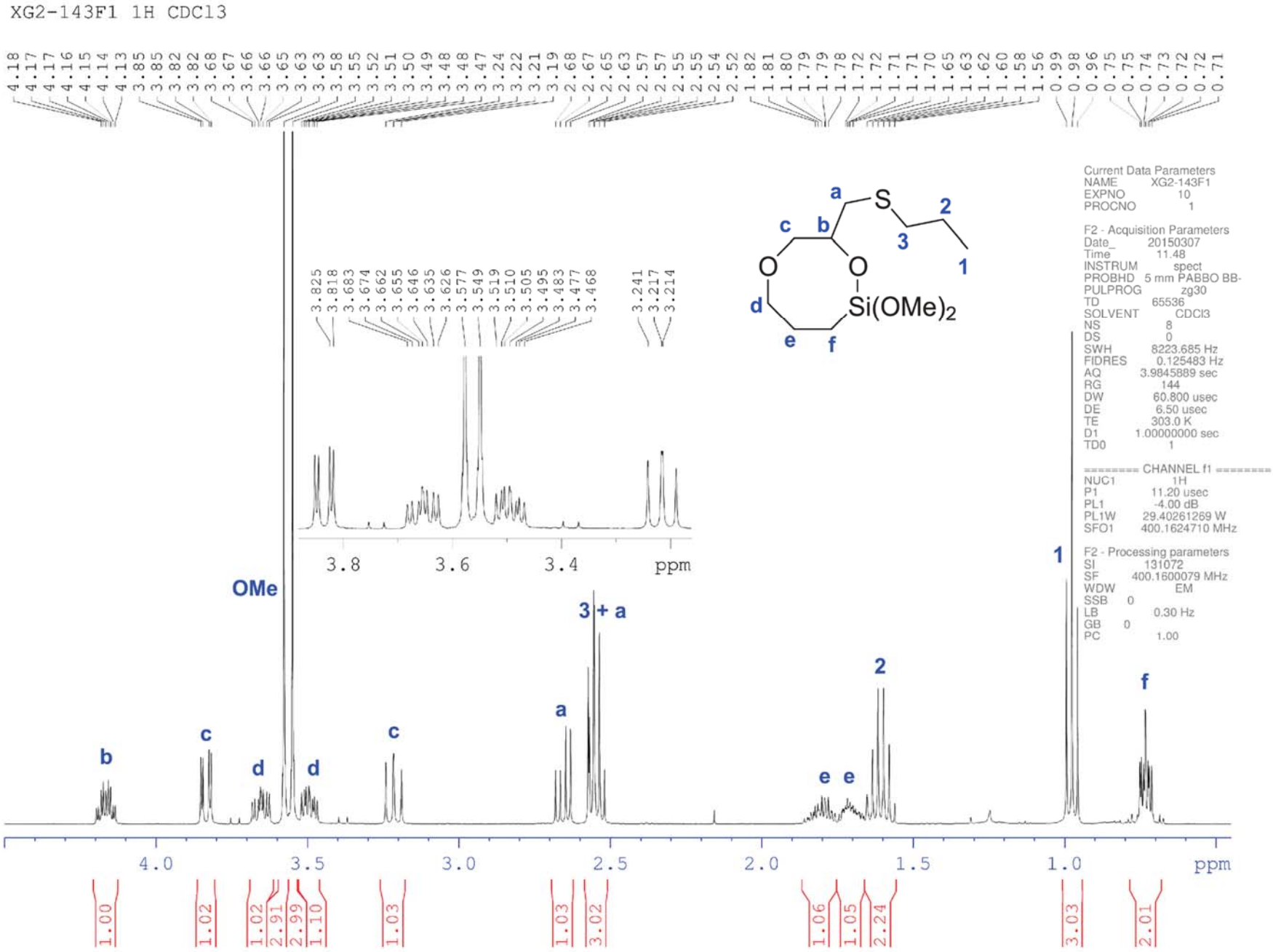


Figure SI_38: ^{1}H NMR spectrum of compound 8

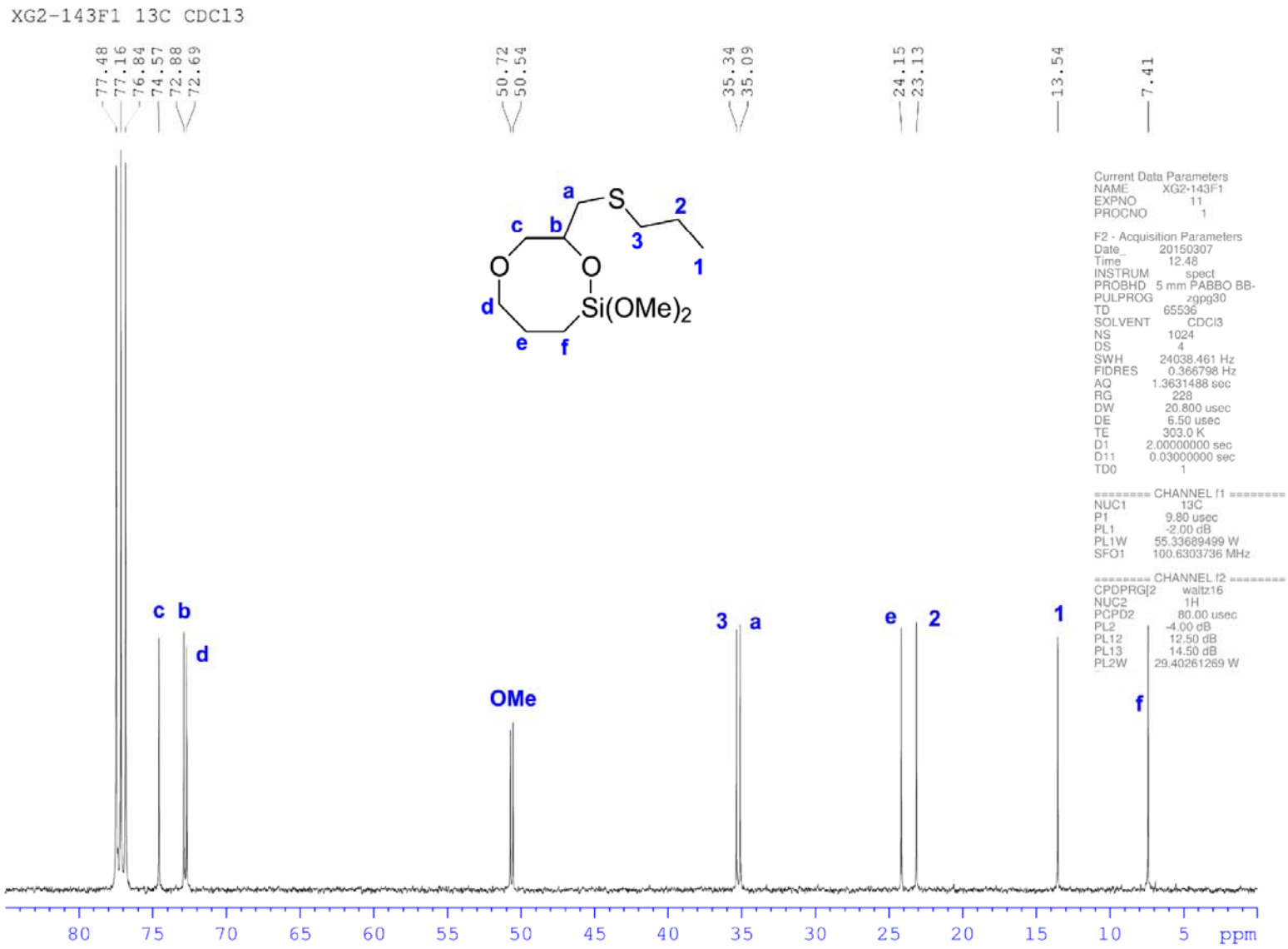


Figure SI_39: ^{13}C NMR spectrum of compound 8

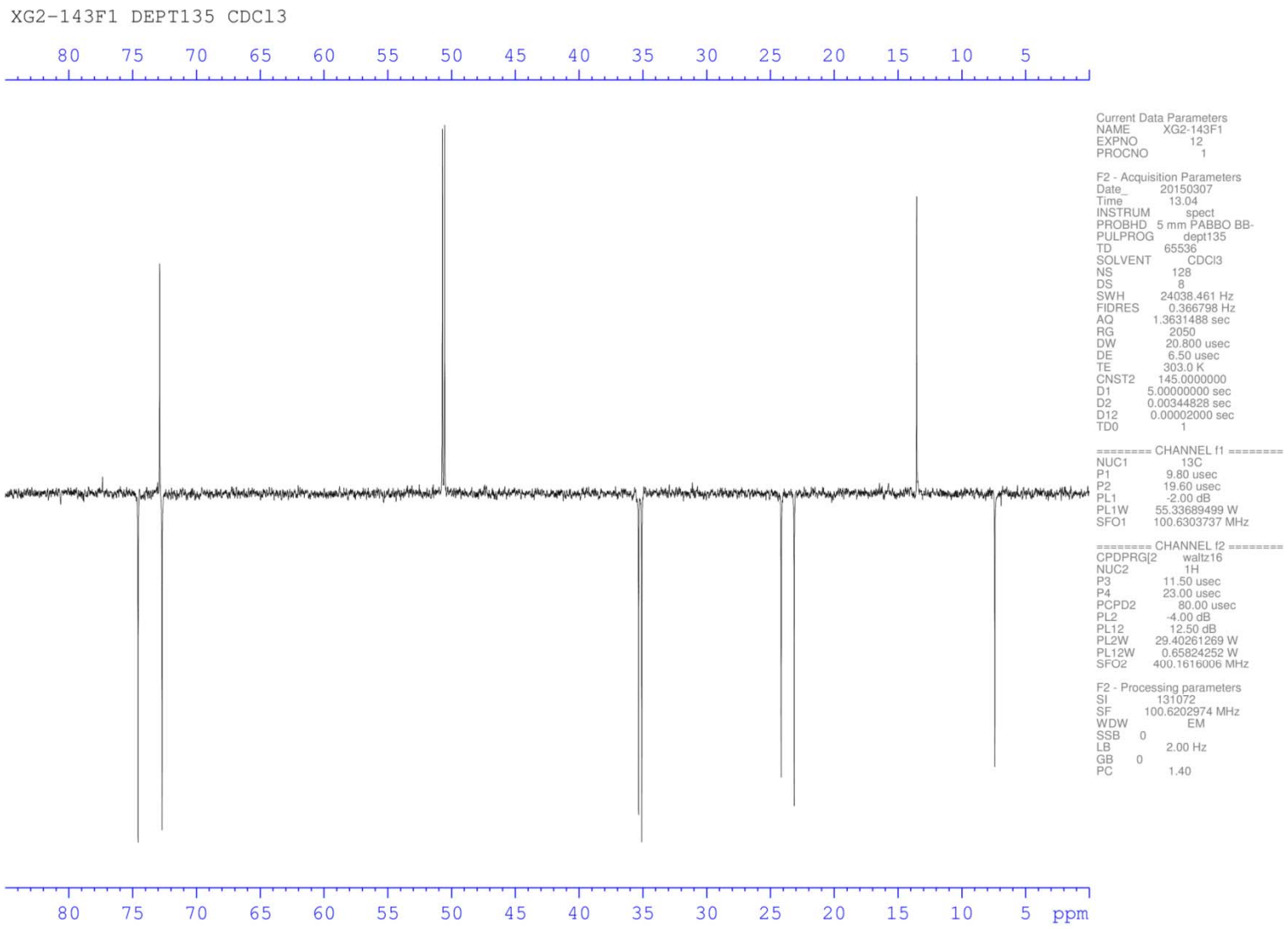


Figure SI_40: DEPT135 spectrum of compound 8

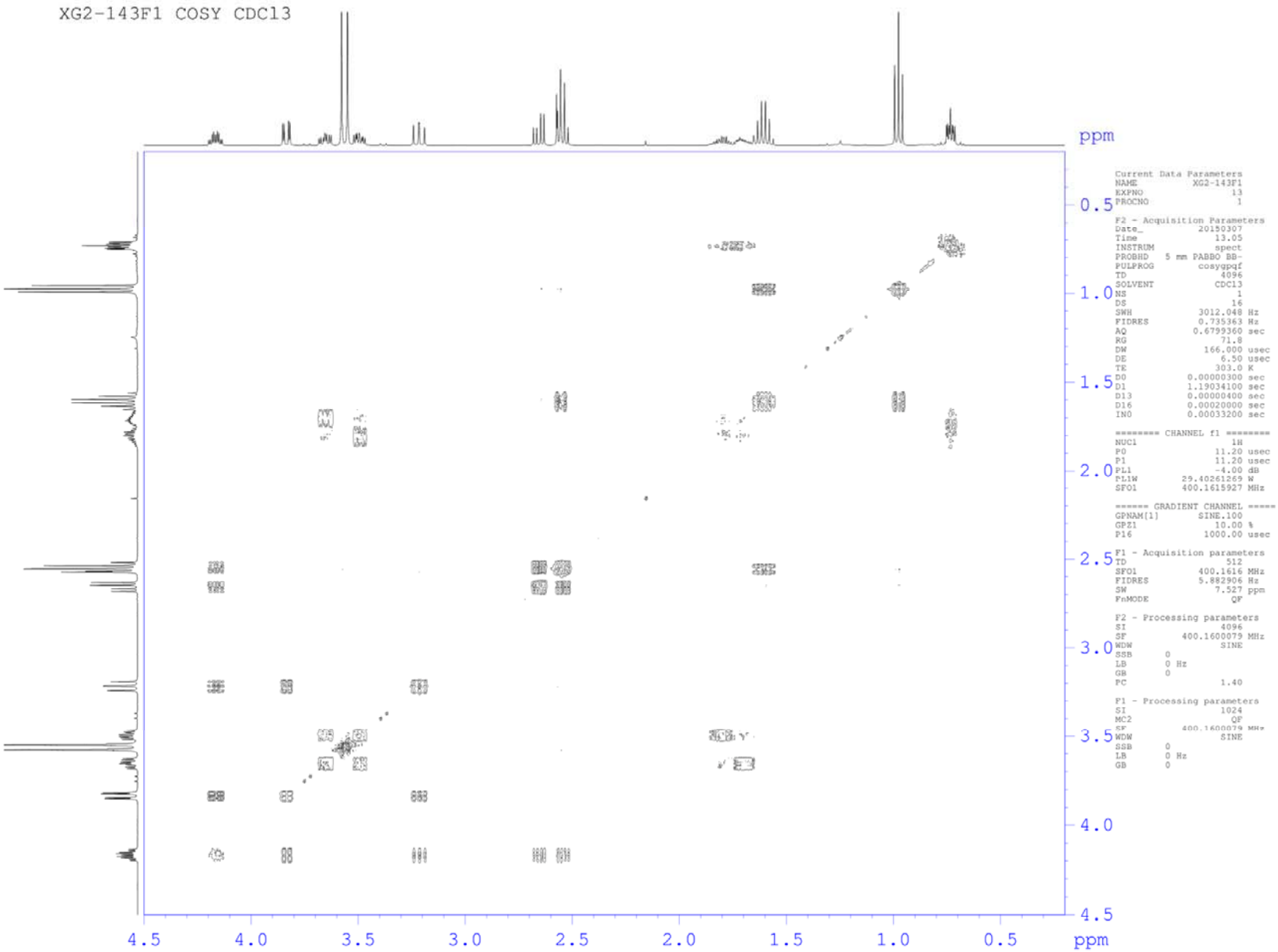


Figure SI_41: ^{1}H-^{1}H COSY spectrum of compound 8

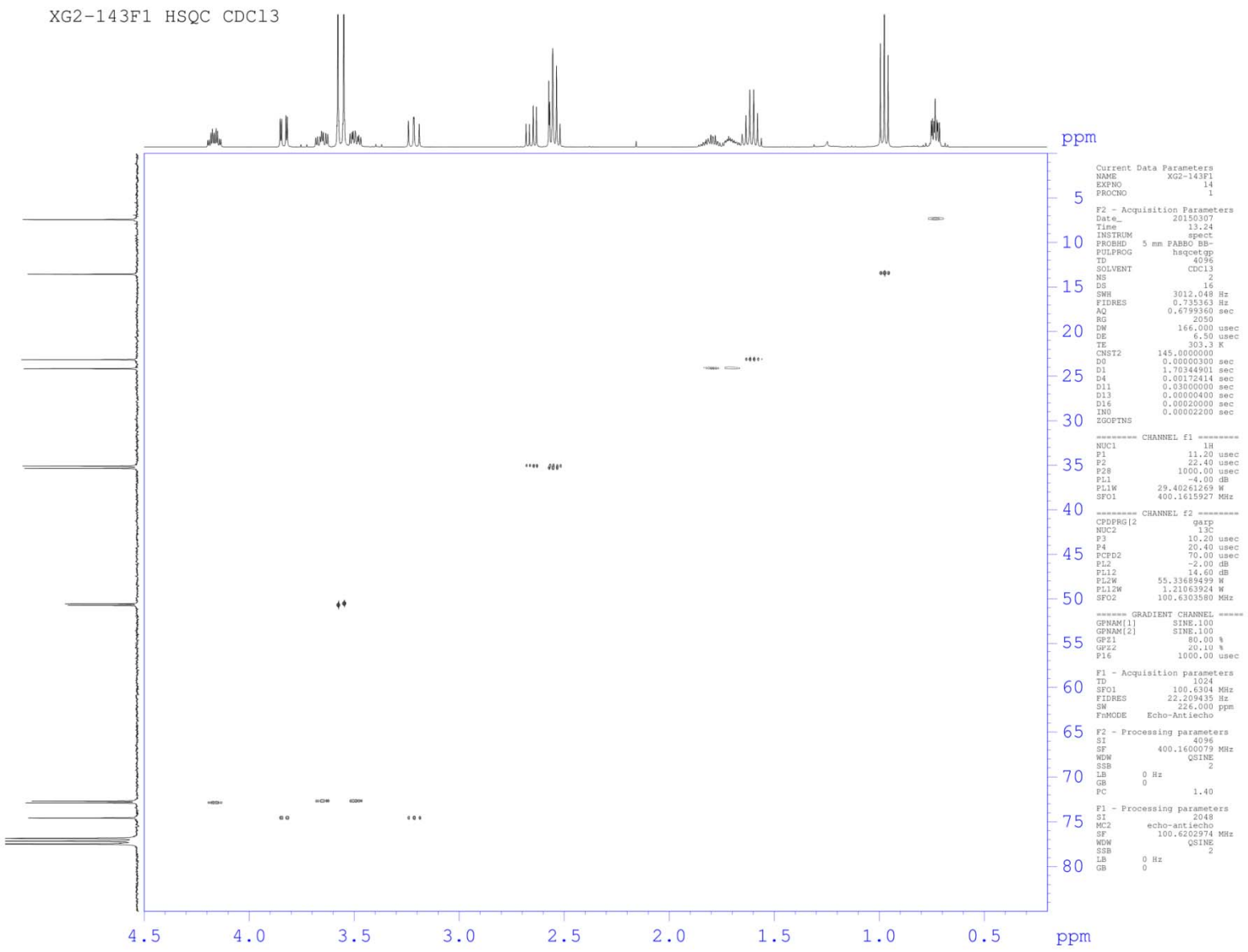


Figure SI_42: HSQC spectrum of compound 8

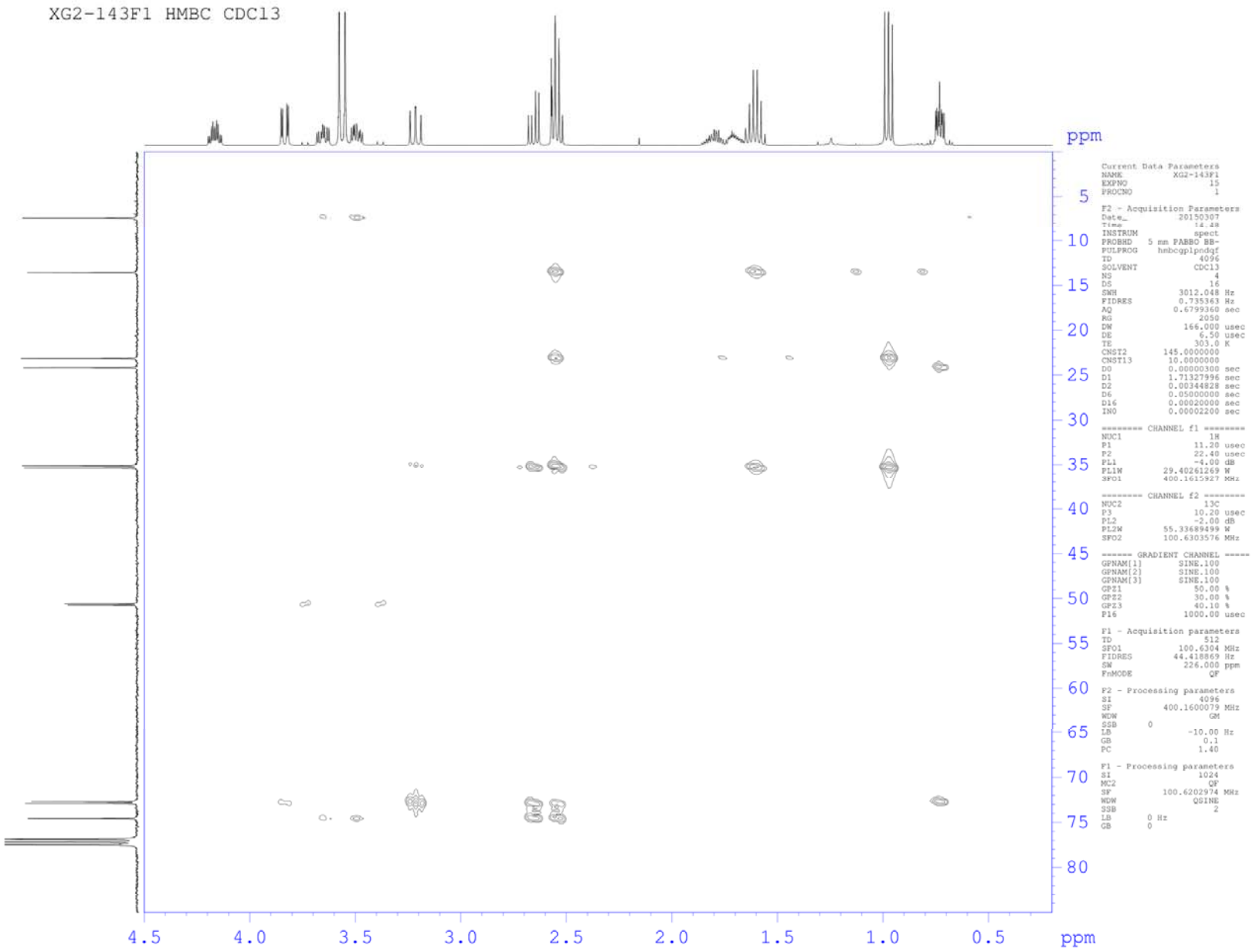


Figure SI_43: HMBC spectrum of compound 8

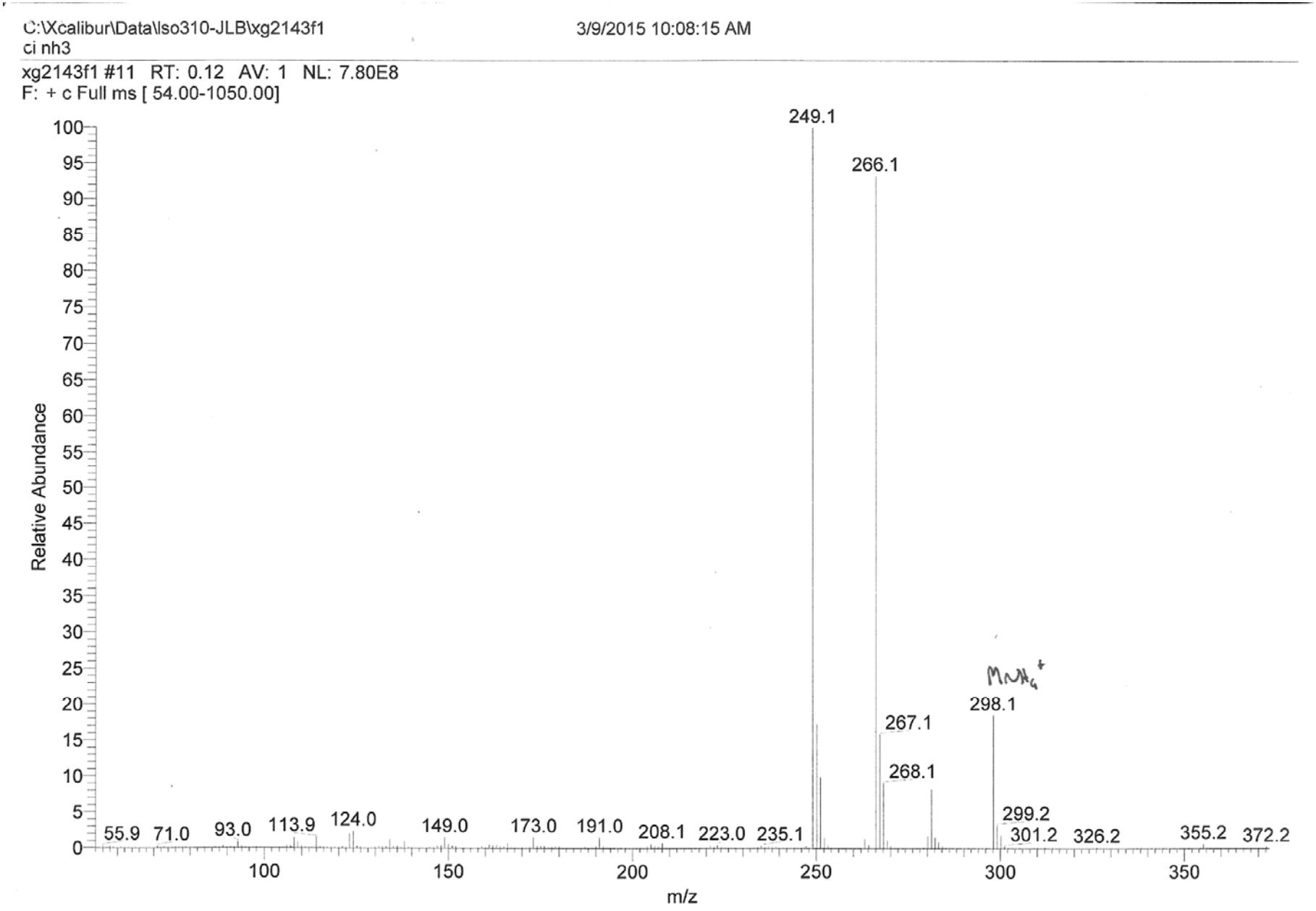
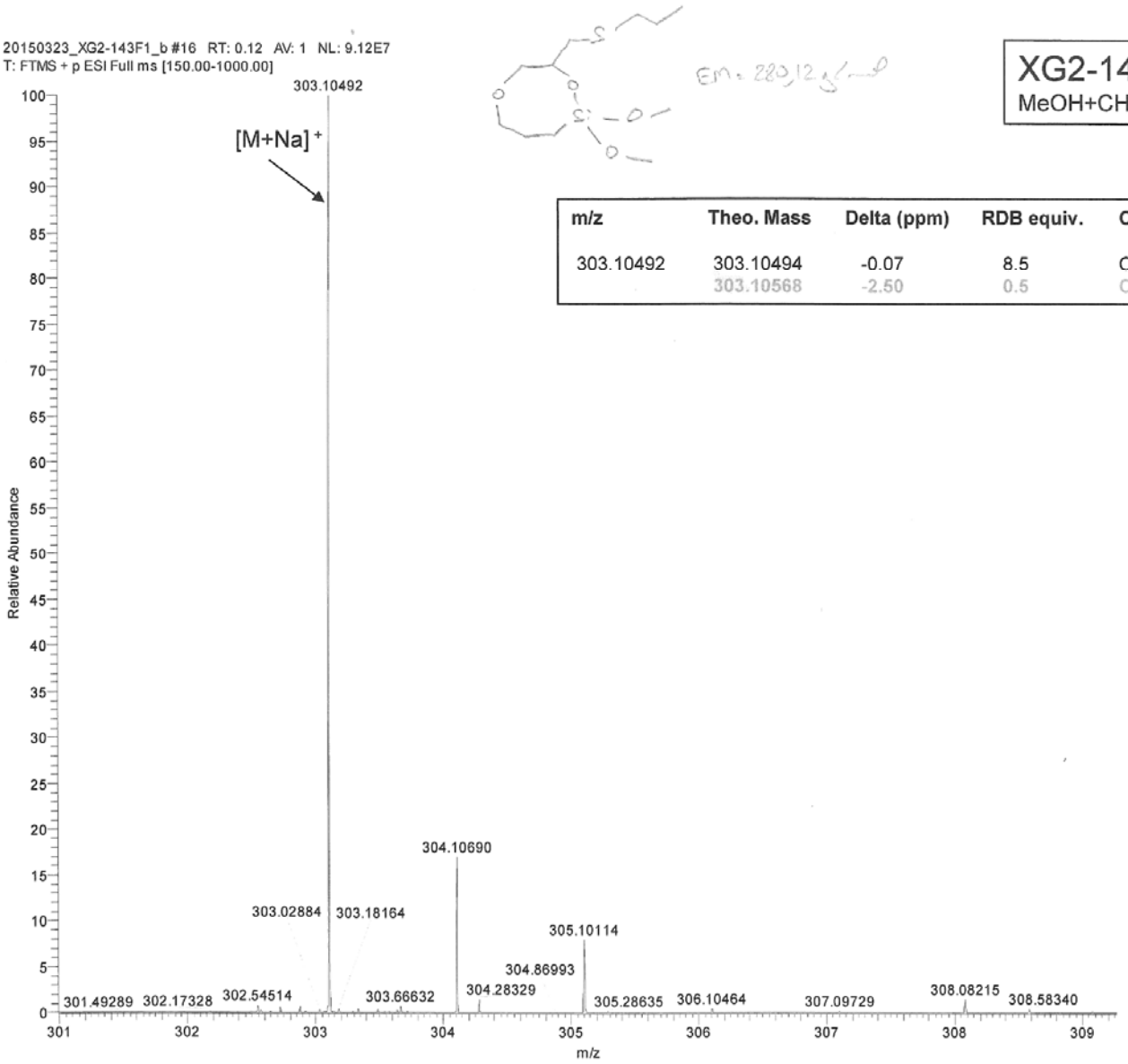


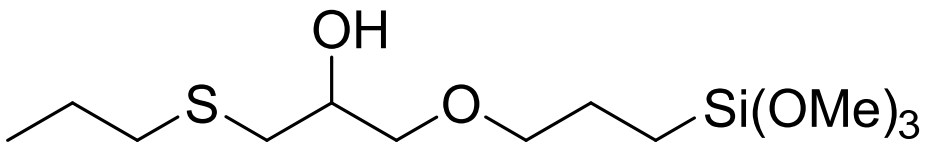
Figure SI_44: CI-MS of compound 8



XG2-143F1 – ESI+
MeOH+CH_2Cl_2

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
303.10492	303.10494	-0.07	8.5	C17 H19 O3 S
	303.10568	-2.50	0.5	C11 H24 O4 Na S Si

Figure SI_45: HRMS of compound 8



9

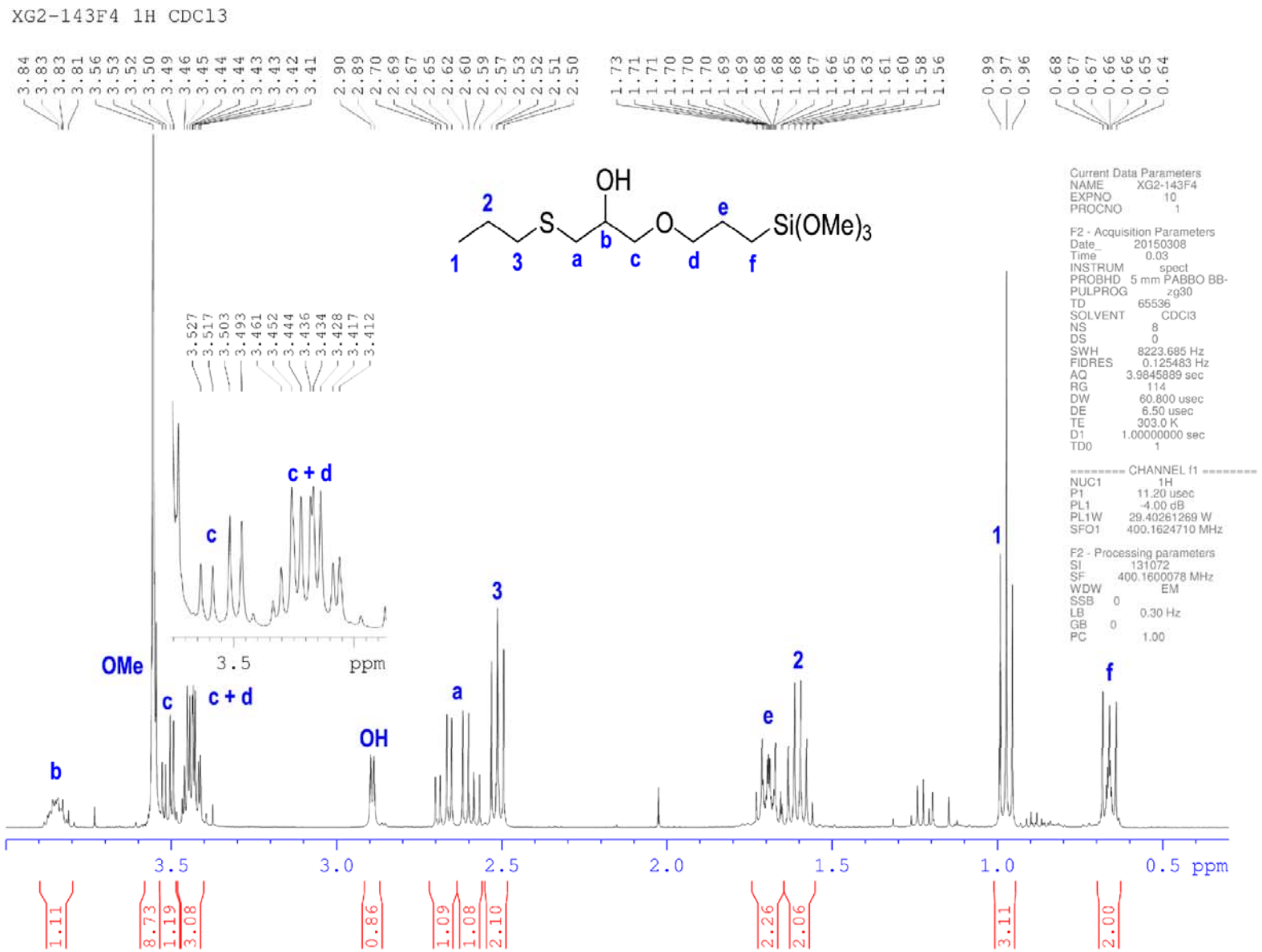


Figure SI_47: ^{1}H NMR spectrum of compound 9

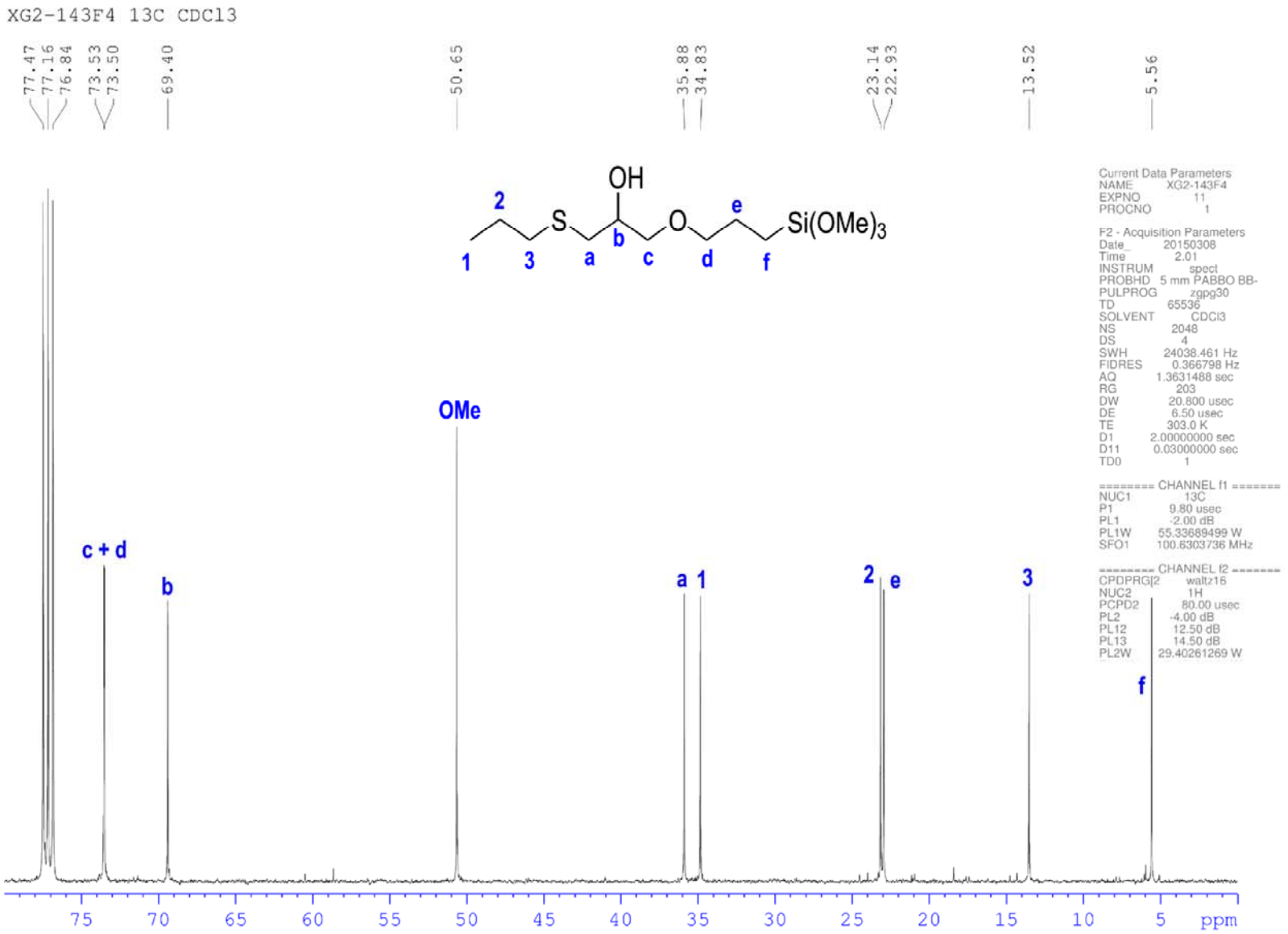


Figure SI_48: ^{13}C NMR spectrum of compound 9

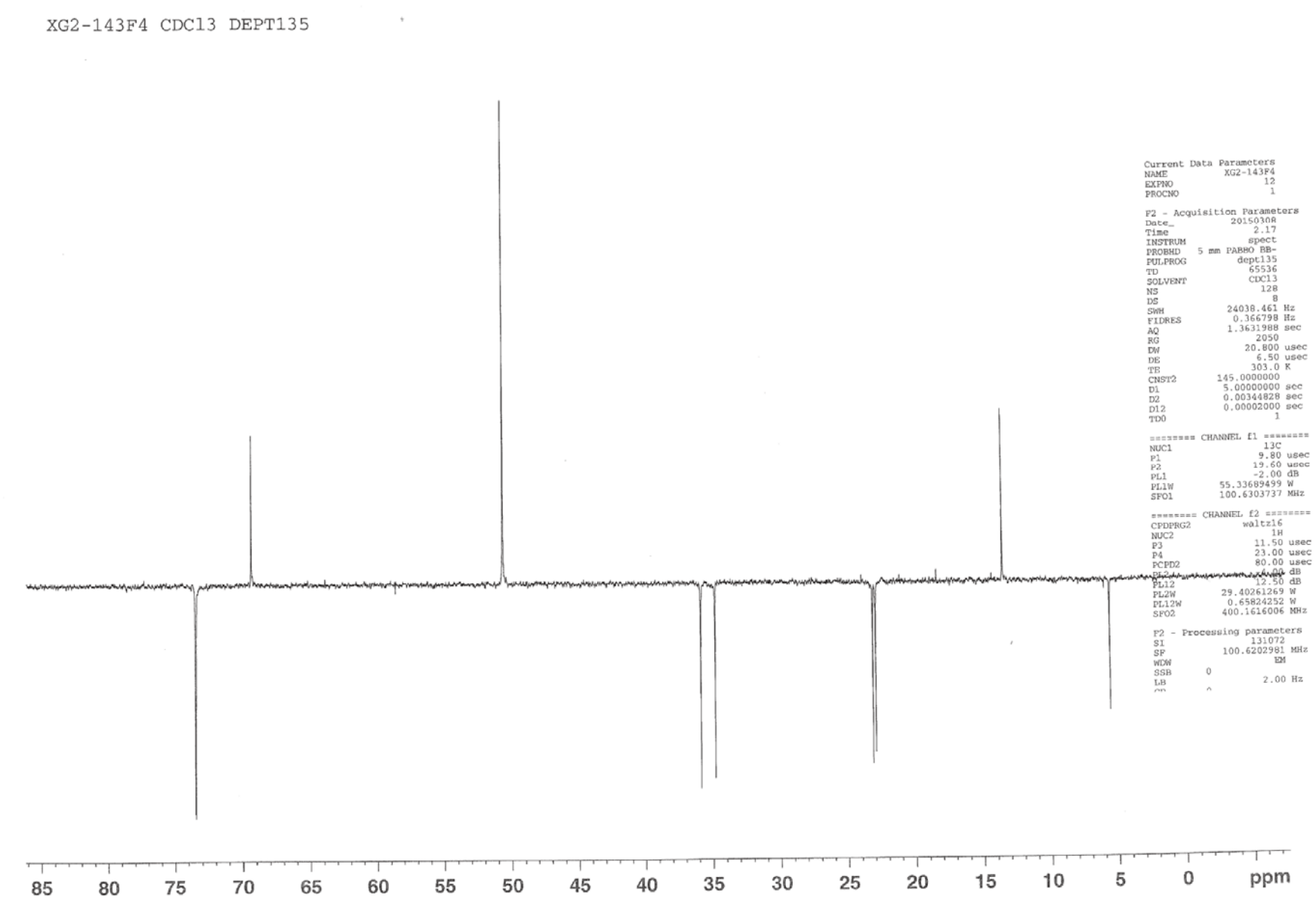


Figure SI_49: DEPT 135 spectrum of compound 9

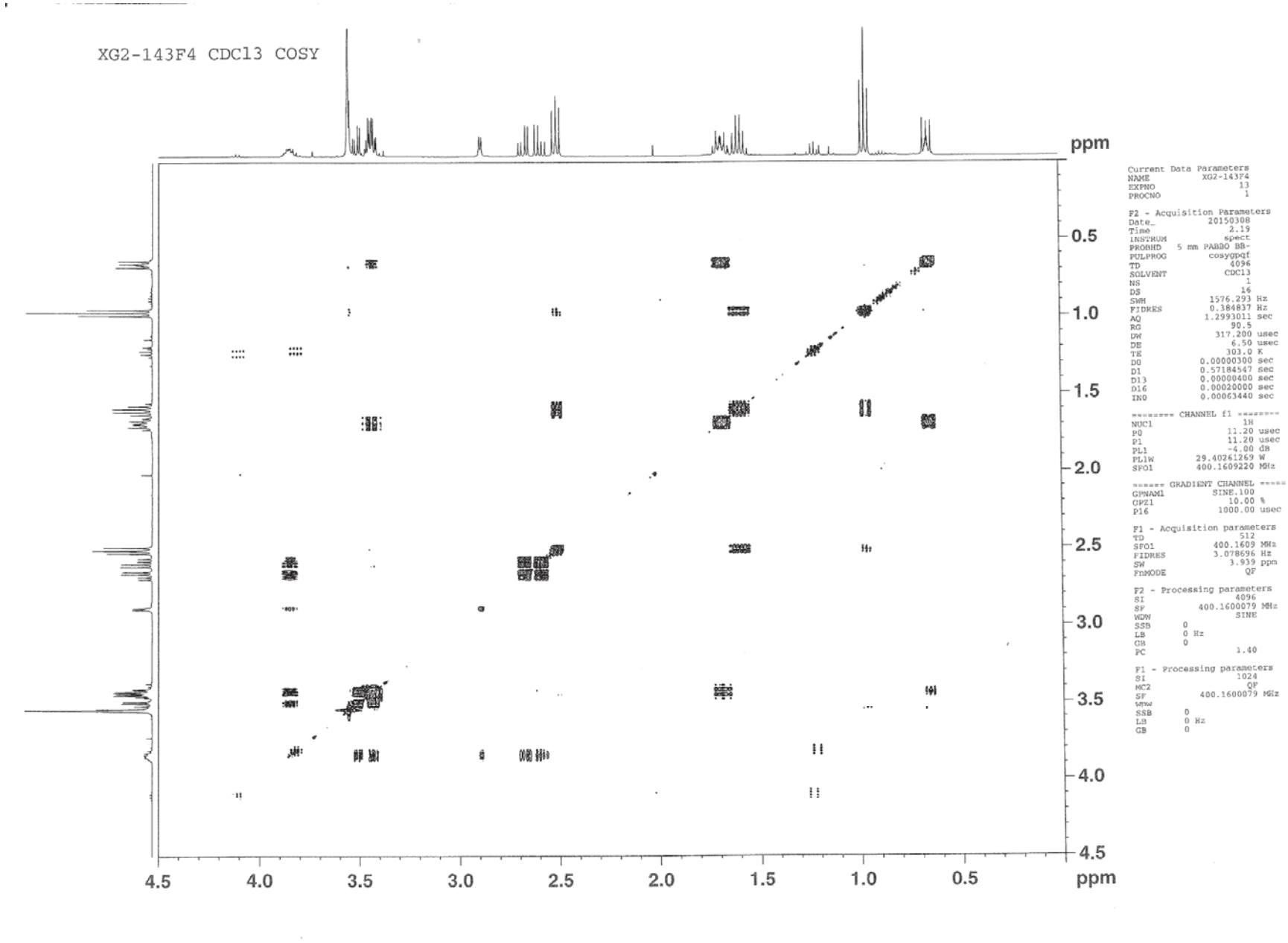


Figure SI_50: ^{1}H-^{1}H COSY spectrum of compound 9

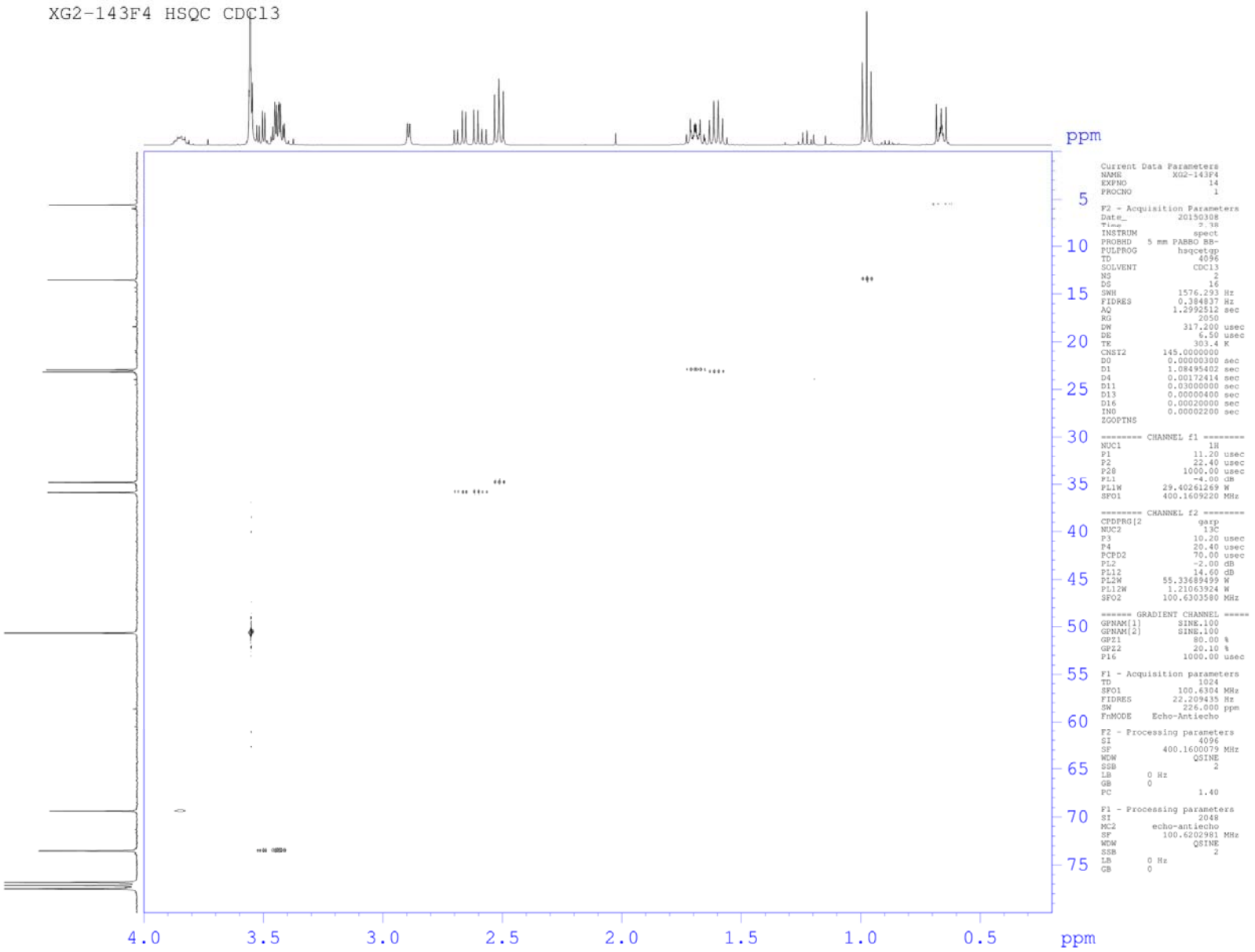


Figure SI_51: HSQC spectrum of compound 9

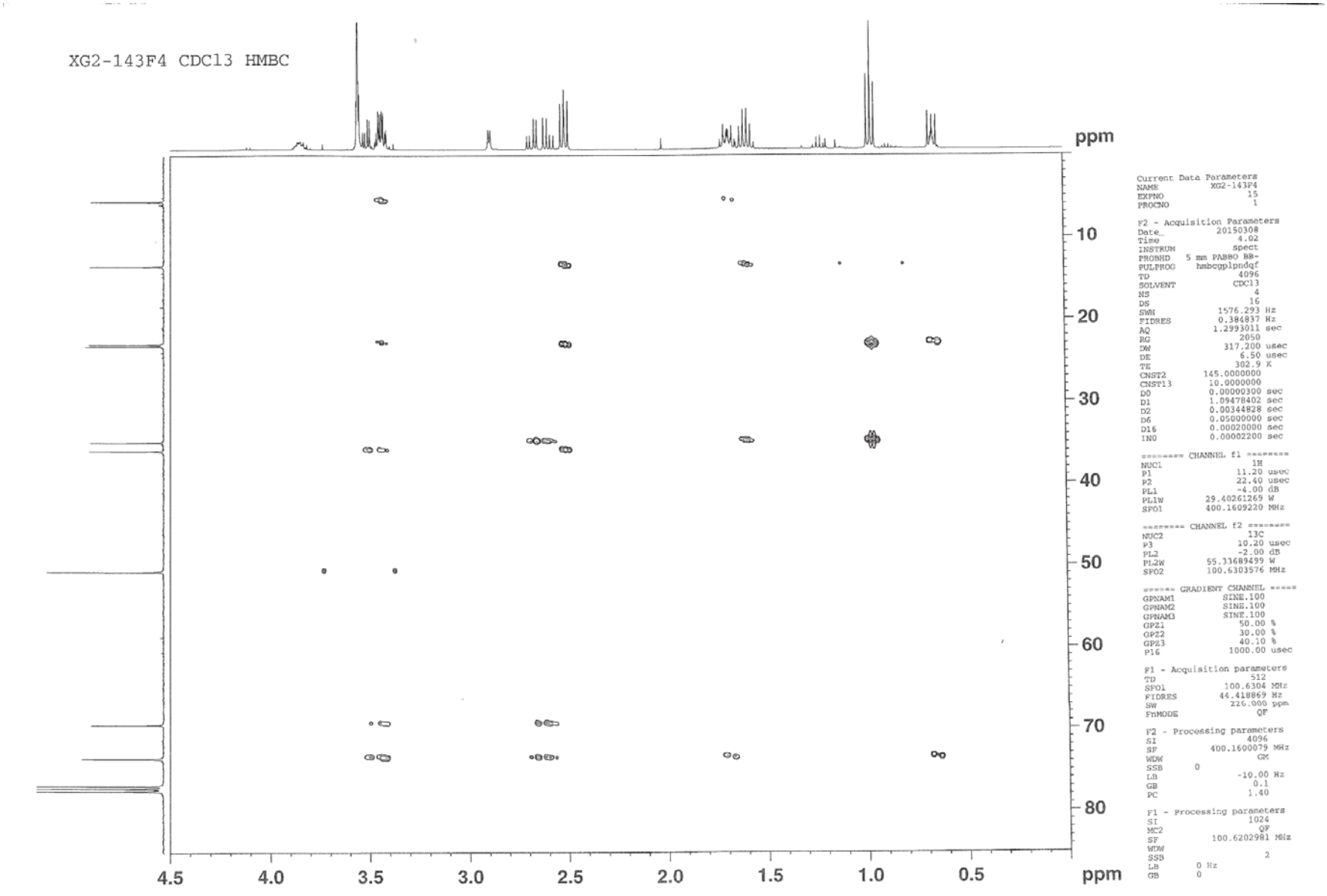


Figure SI_52: HMBC spectrum of compound 9

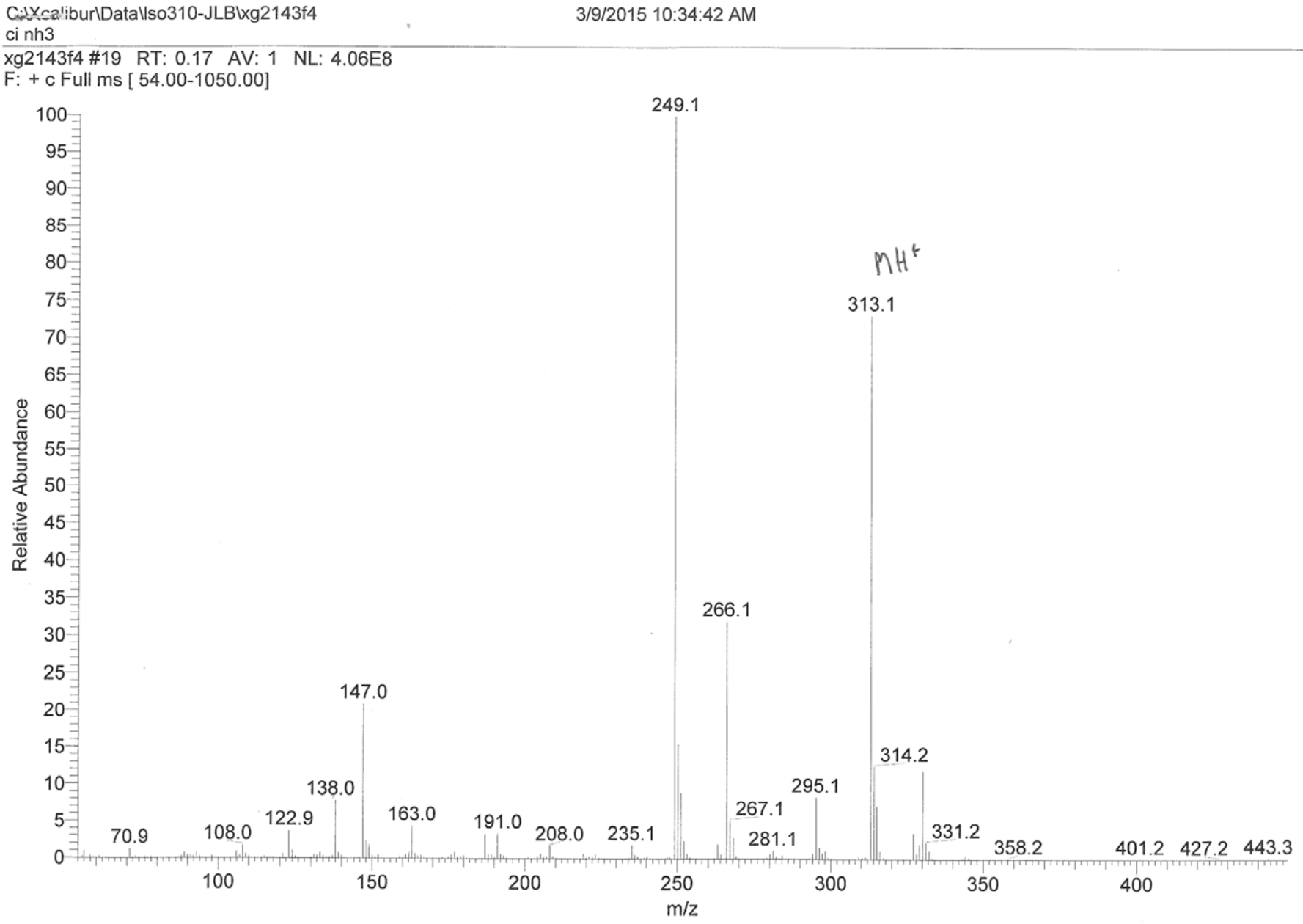
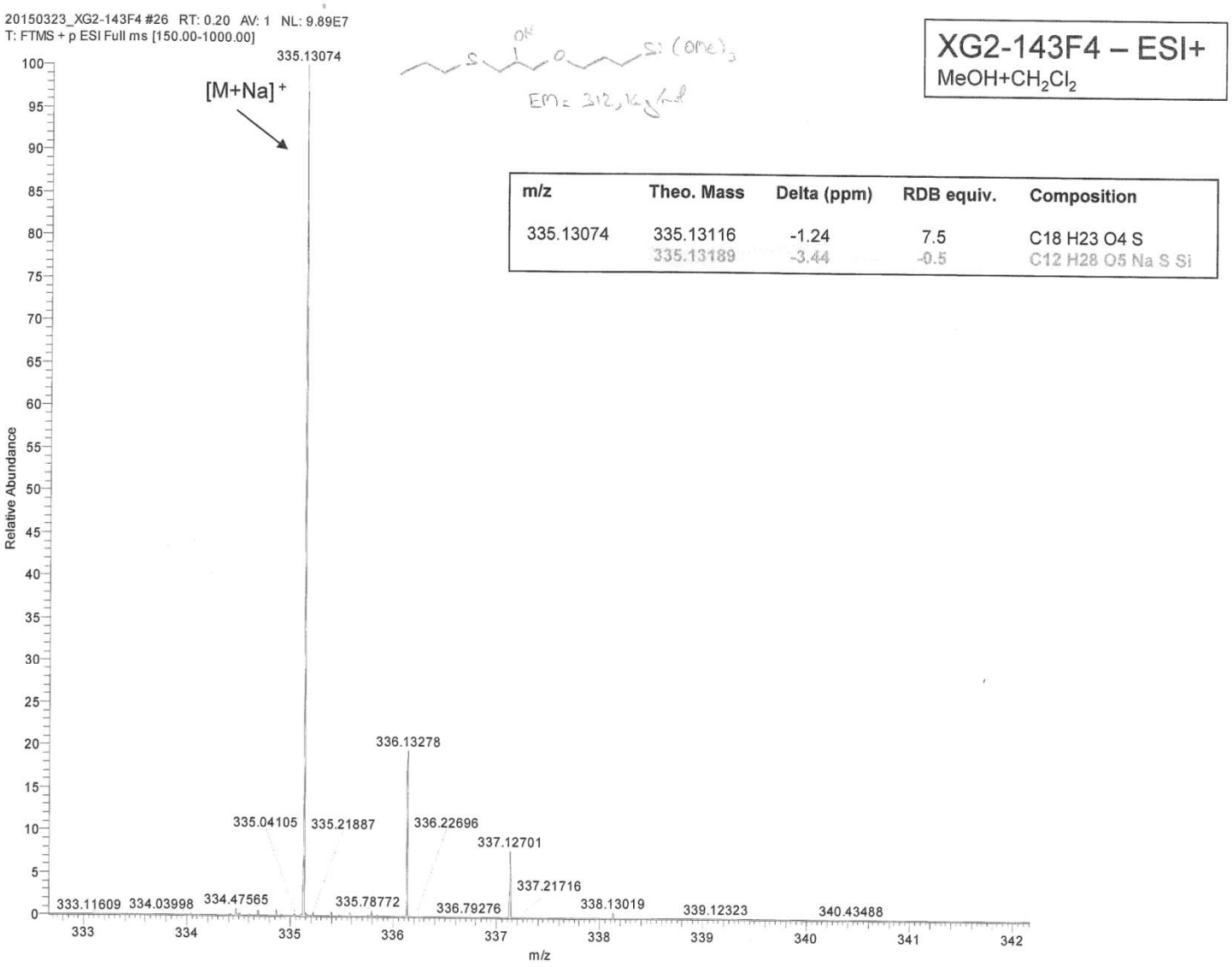


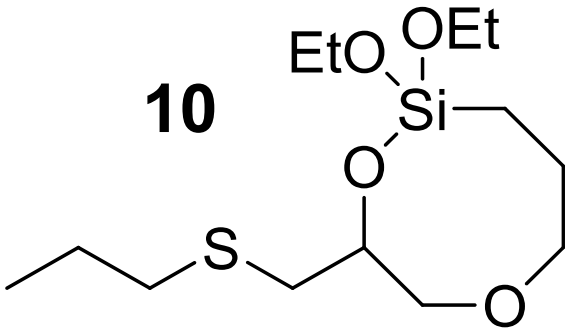
Figure SI_53: CI-MS spectrum of compound 9



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
335.13074	335.13116	-1.24	7.5	C18 H23 O4 S
	335.13189	-3.44	-0.5	C12 H28 O5 Na S Si

Figure SI_54: HRMS of compound 9

10



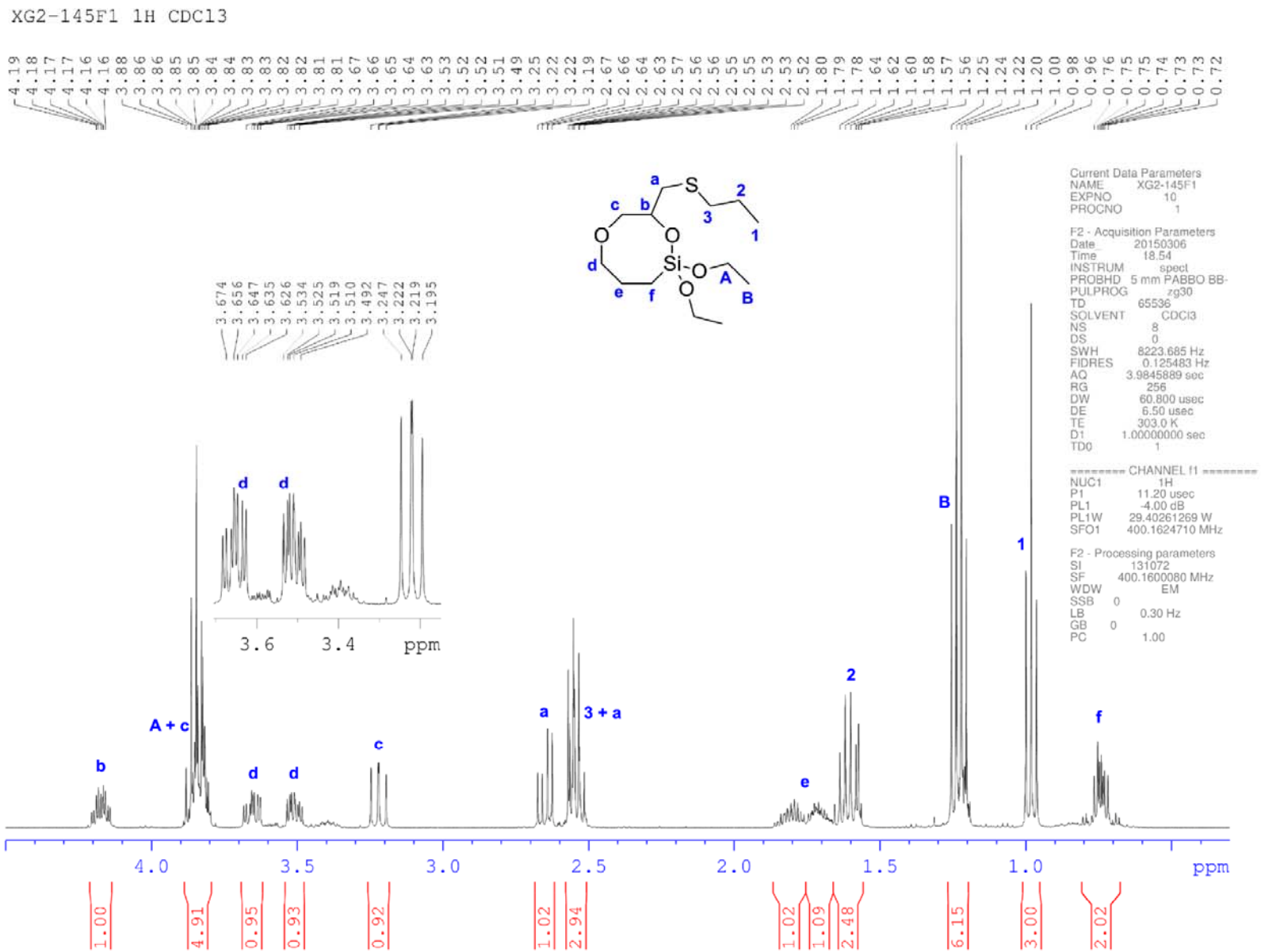


Figure SI_56: ^{1}H NMR spectrum of compound 10

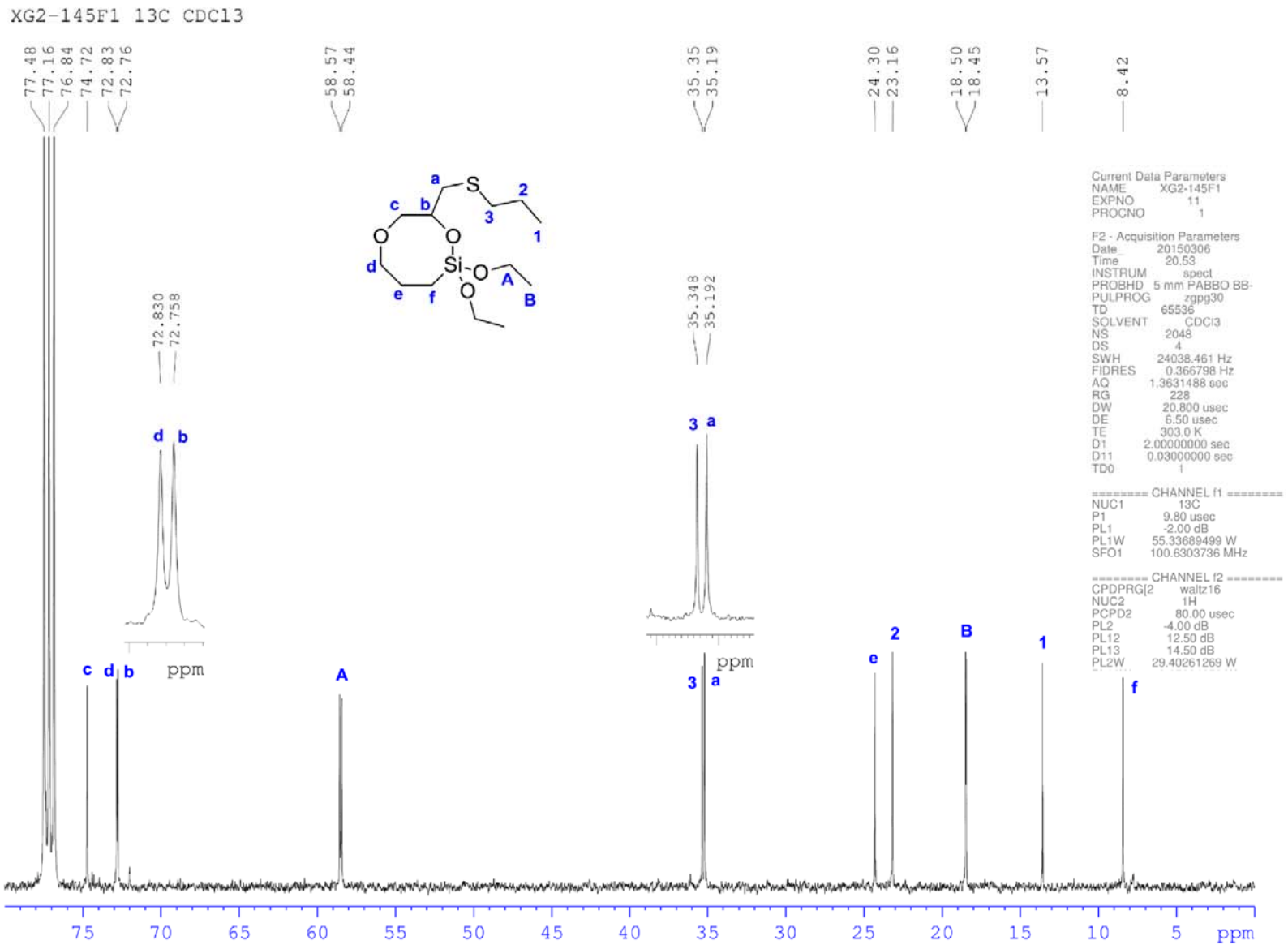


Figure SI_57: ^{13}C NMR spectrum of compound 10

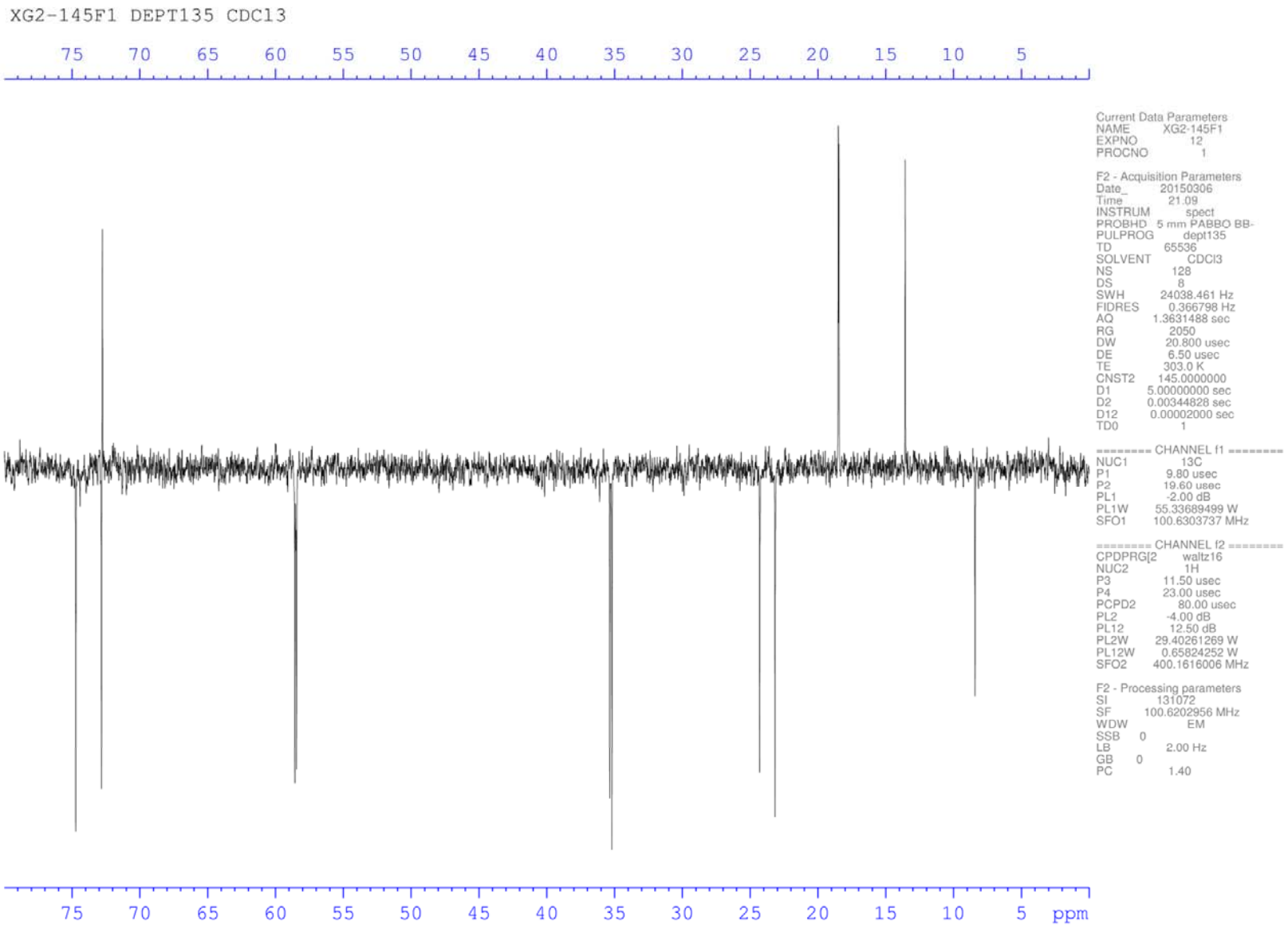


Figure SI_58: DEPT 135 spectrum of compound 10

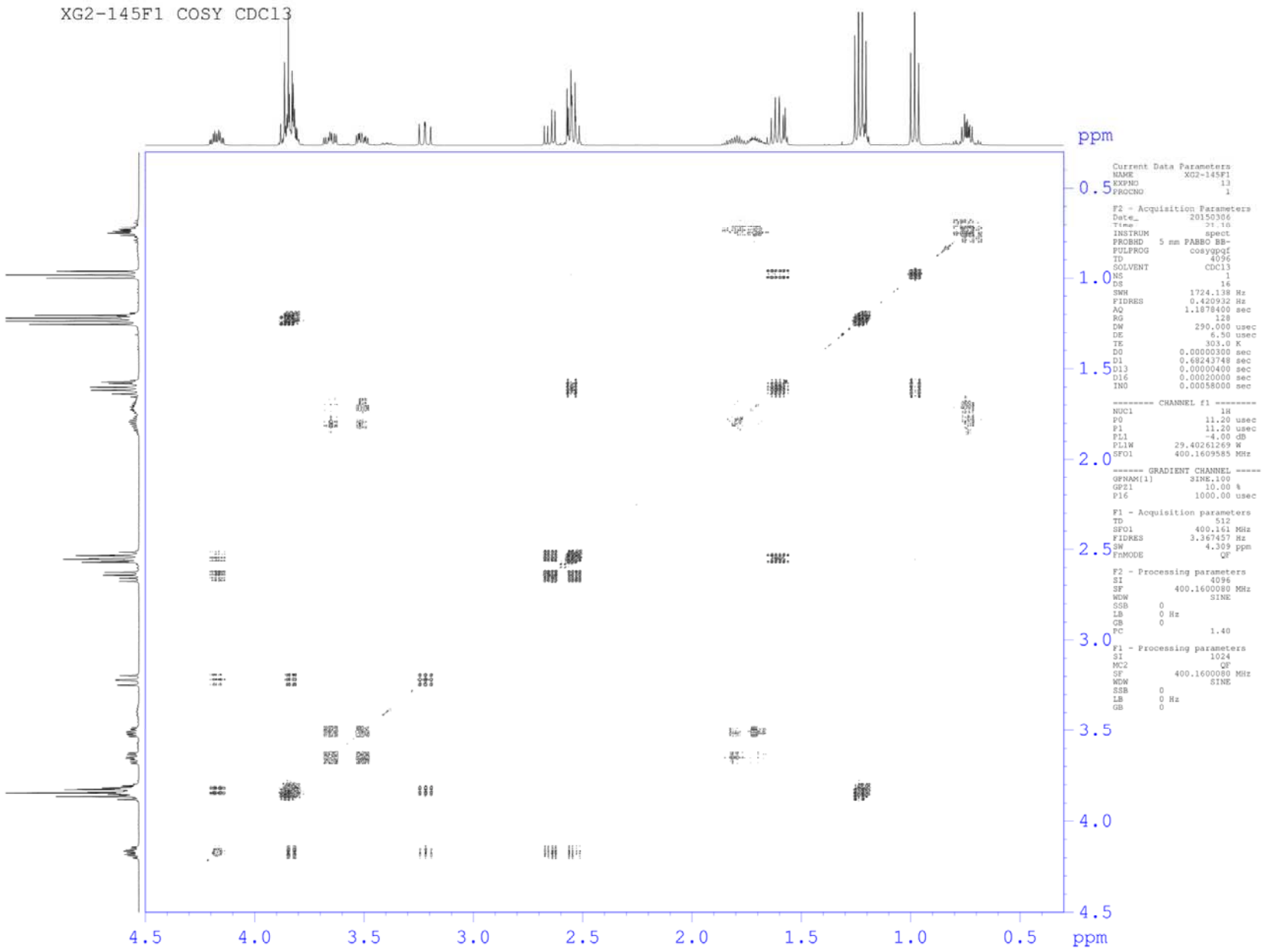


Figure SI_59: ^{1}H-^{1}H NMR spectrum of compound 10

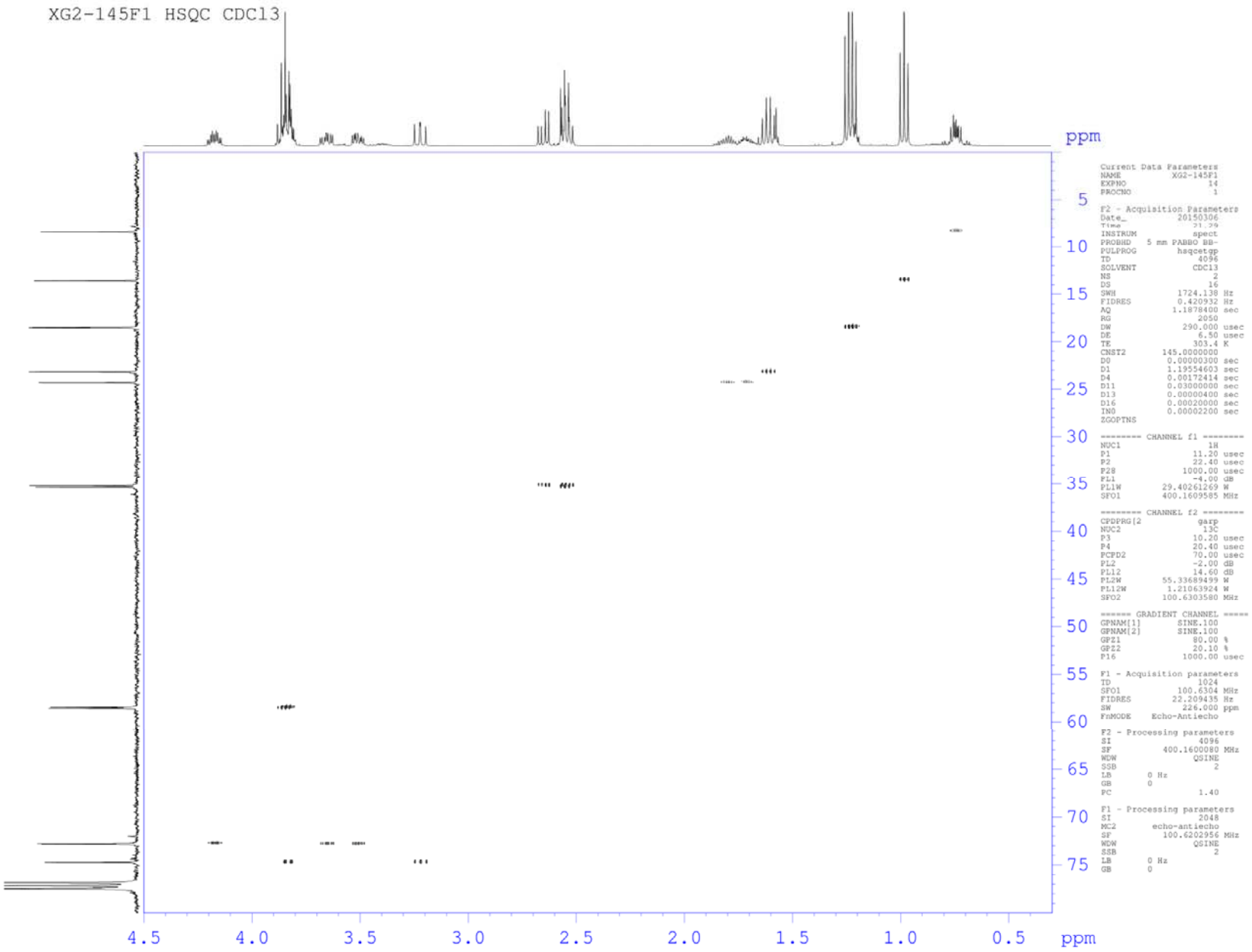


Figure SI_60: HSQC spectrum of compound 10

SI_61

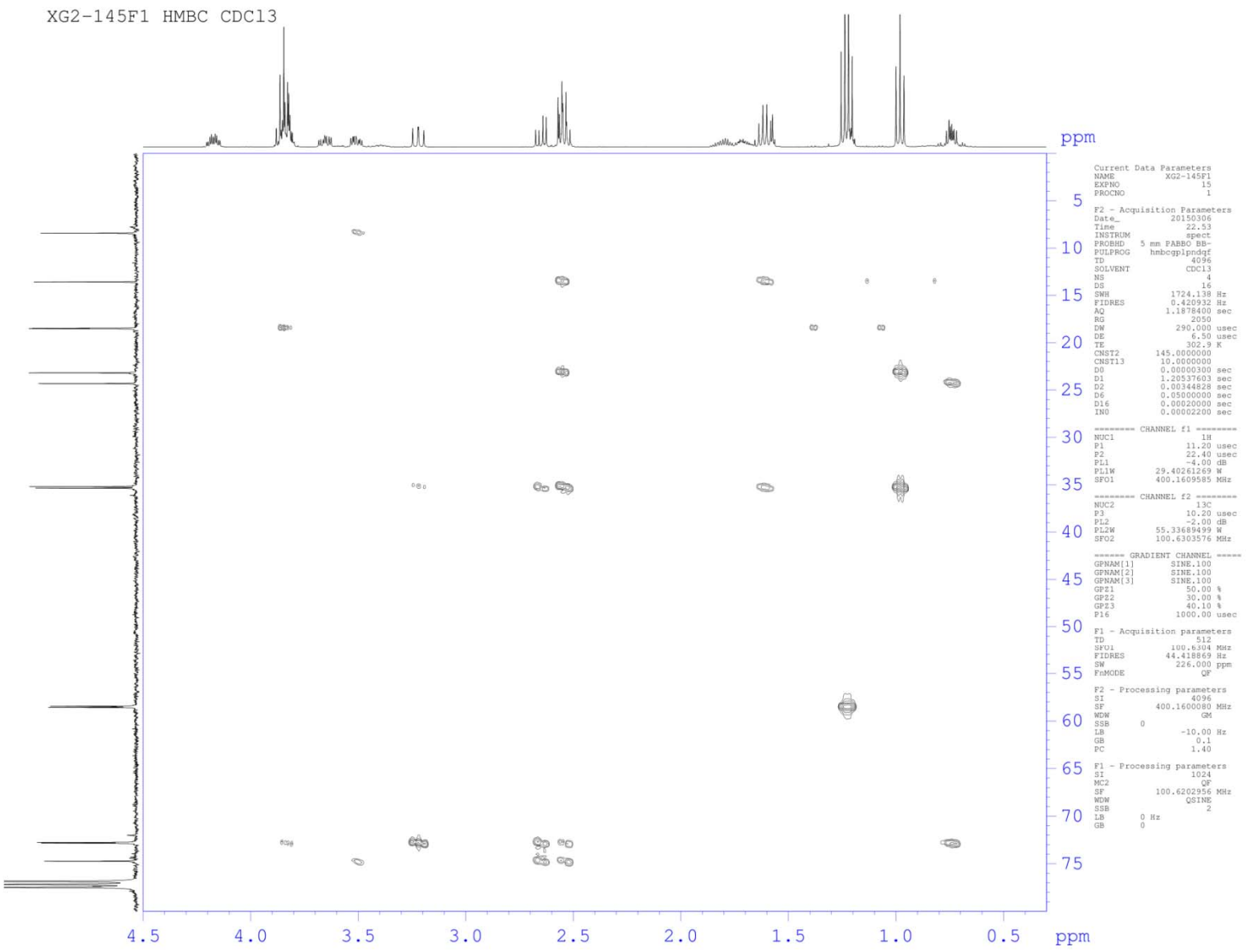


Figure SI_61: HMBC ^{1}H NMR spectrum of compound 10

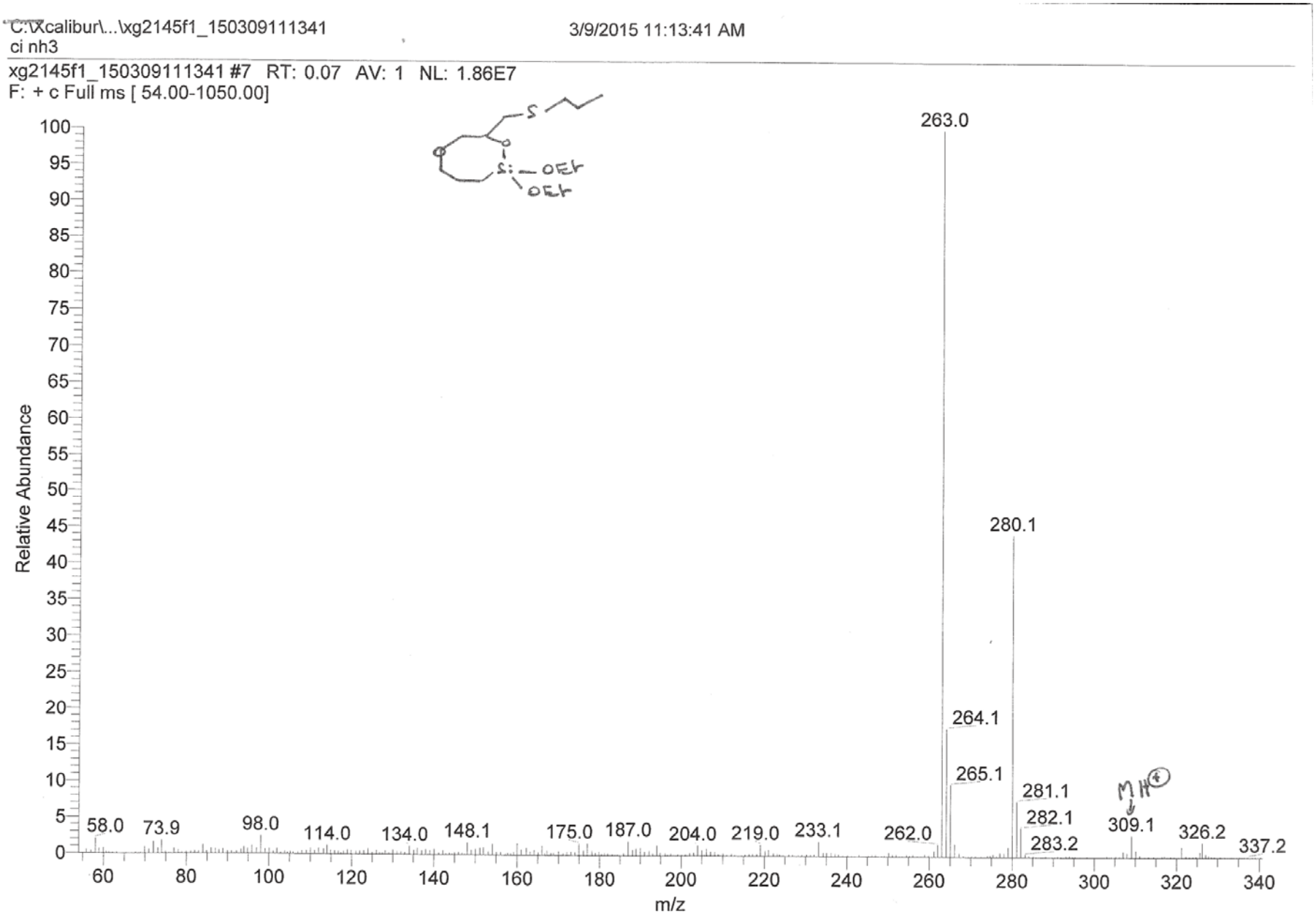
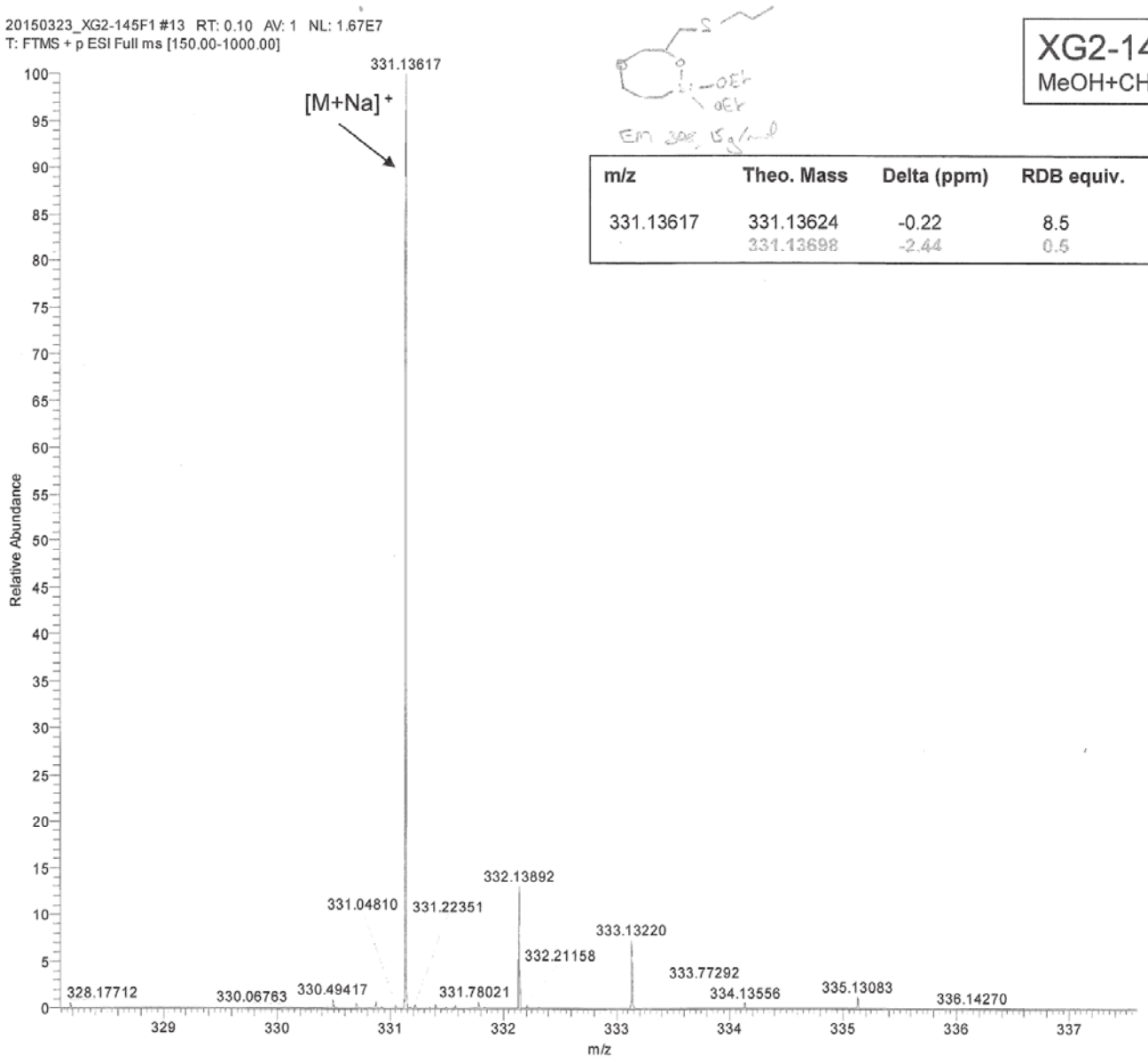


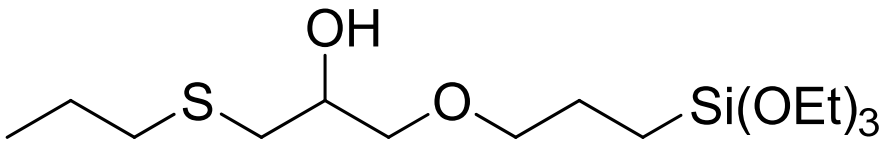
Figure SI_62: CI-MS spectrum of compound 10



XG2-145F1 – ESI+
MeOH+CH_2Cl_2

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
331.13617	331.13624	-0.22	8.5	C19 H23 O3 S
	331.13698	-2.44	0.5	C13 H28 O4 Na S Si

Figure SI_63: HRMS spectrum of compound 10



11

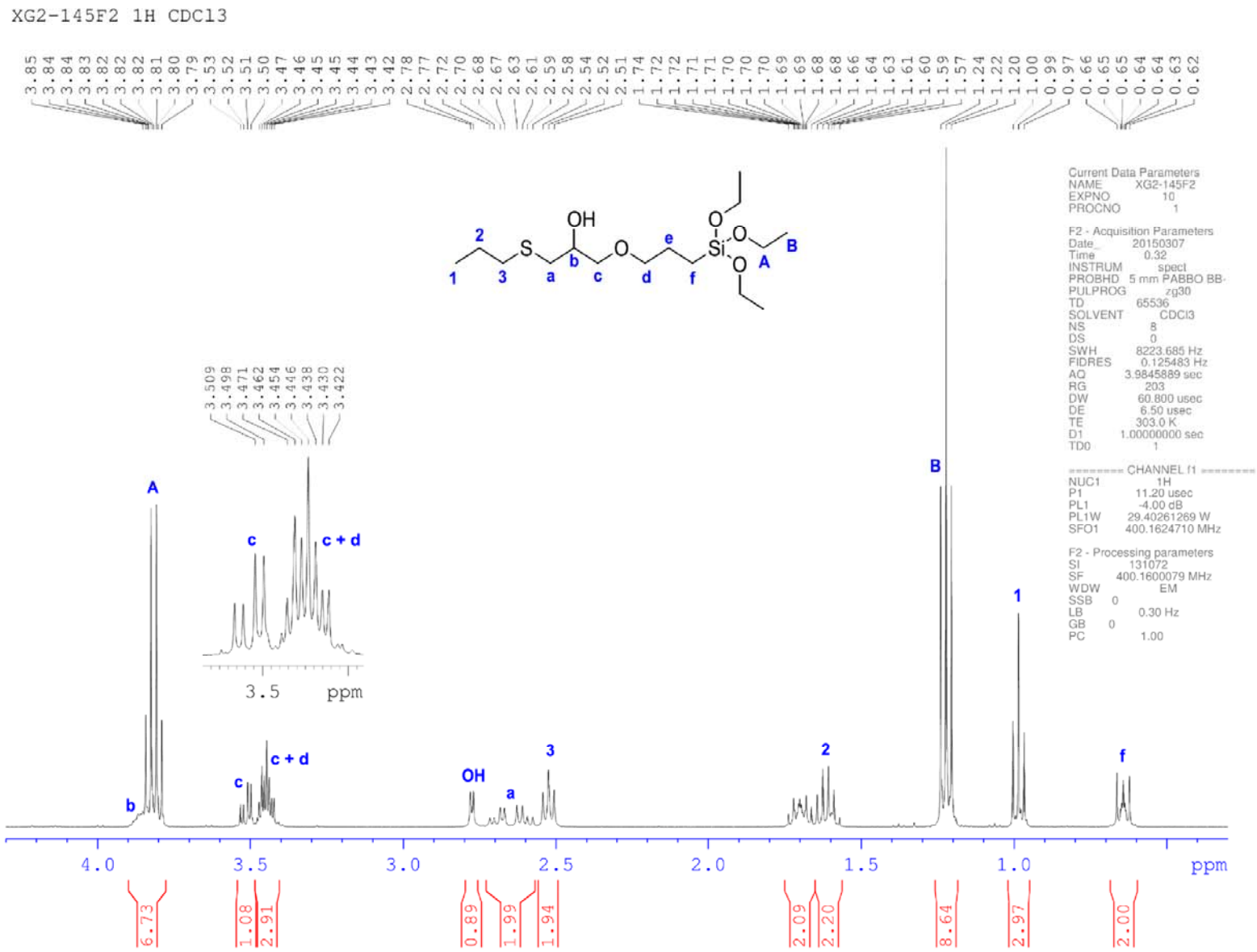


Figure SI_65: ^{1}H NMR spectrum of compound 11

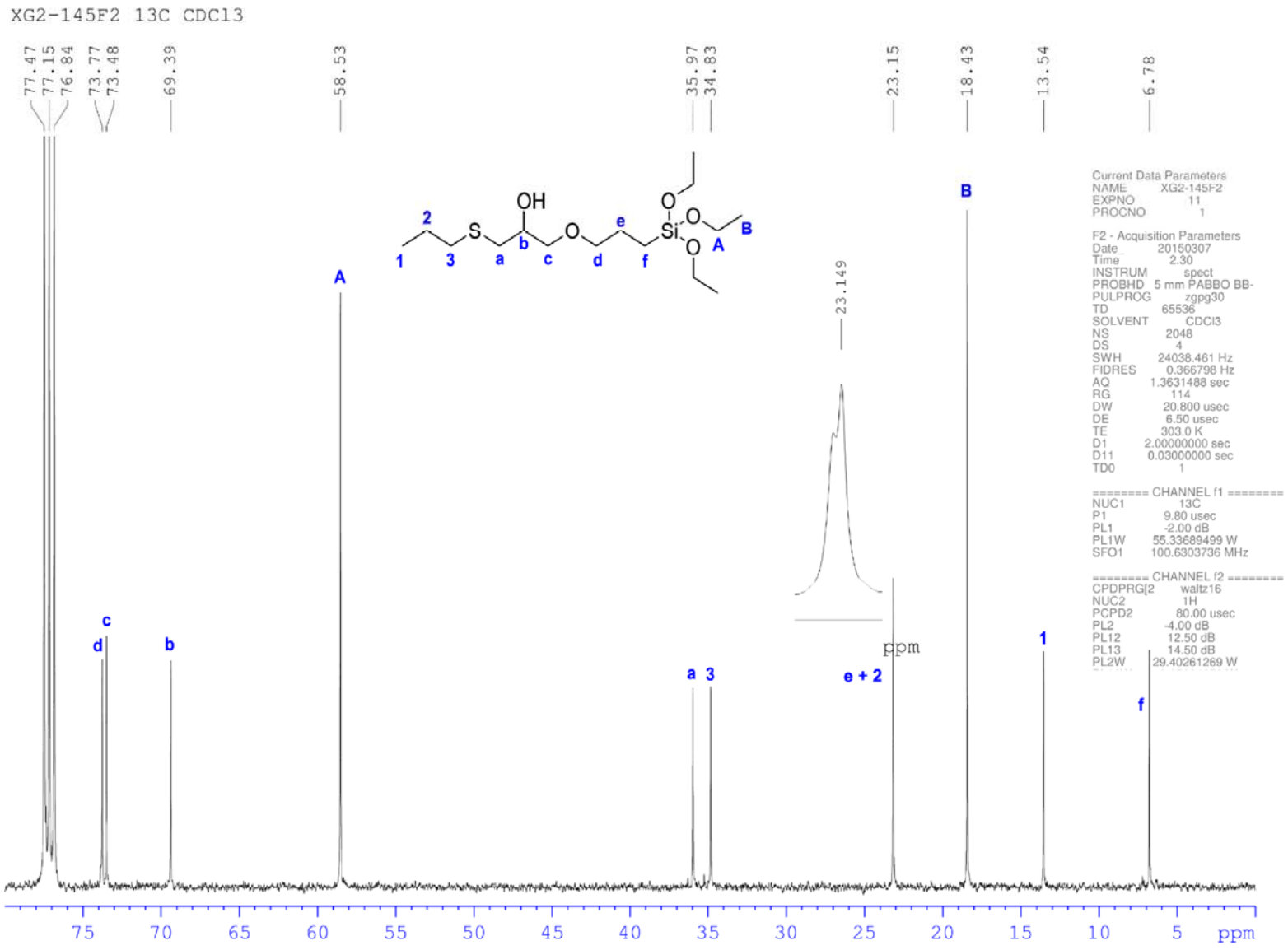


Figure SI_66: ^{13}C NMR spectrum of compound 11

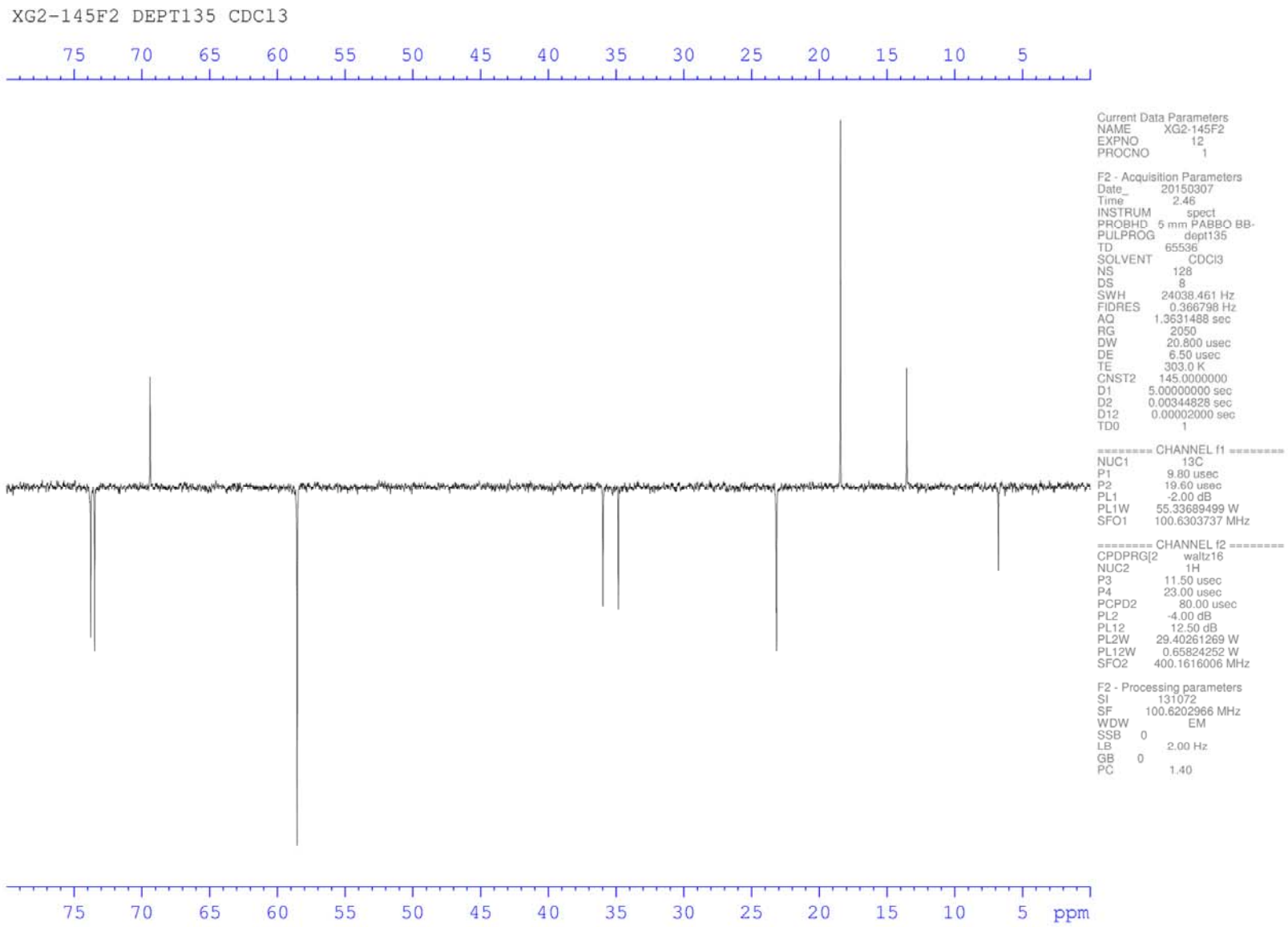


Figure SI_67: DEPT 135 spectrum of compound 11

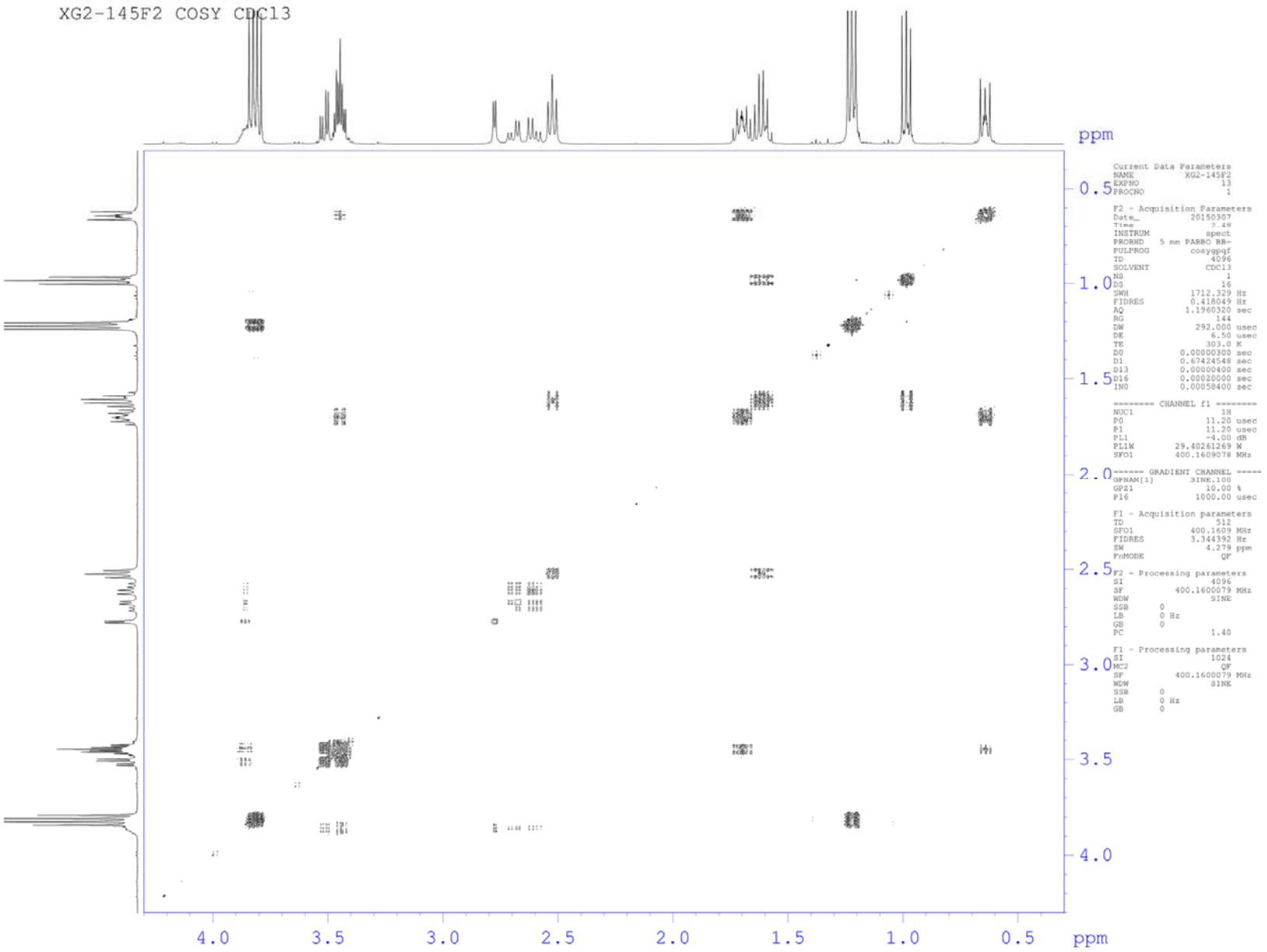


Figure SI_68: ^{1}H ^{1}H COSY spectrum of compound 11

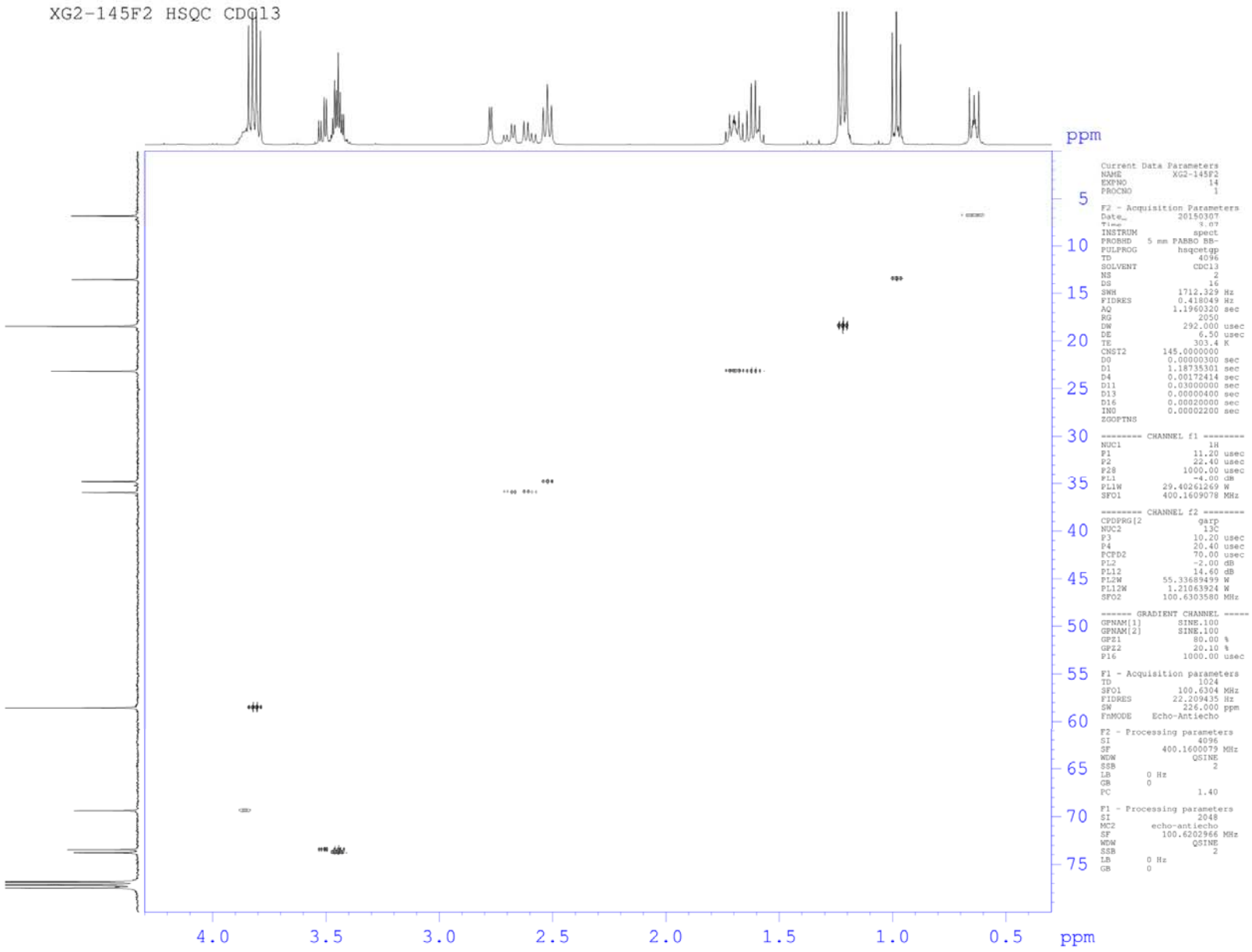


Figure SI_69: HSQC spectrum of compound 11

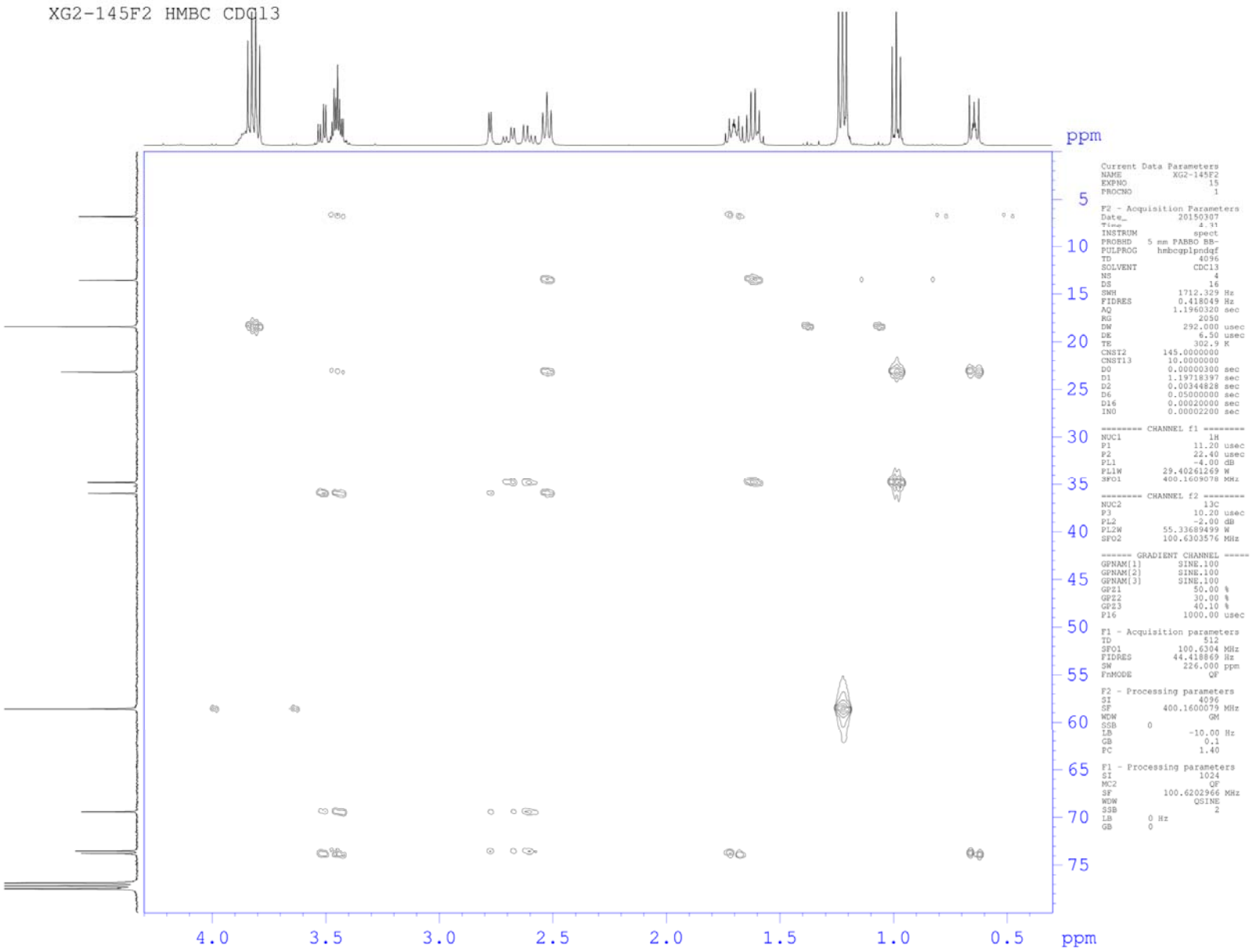


Figure SI_70: HMBC spectrum of compound 11

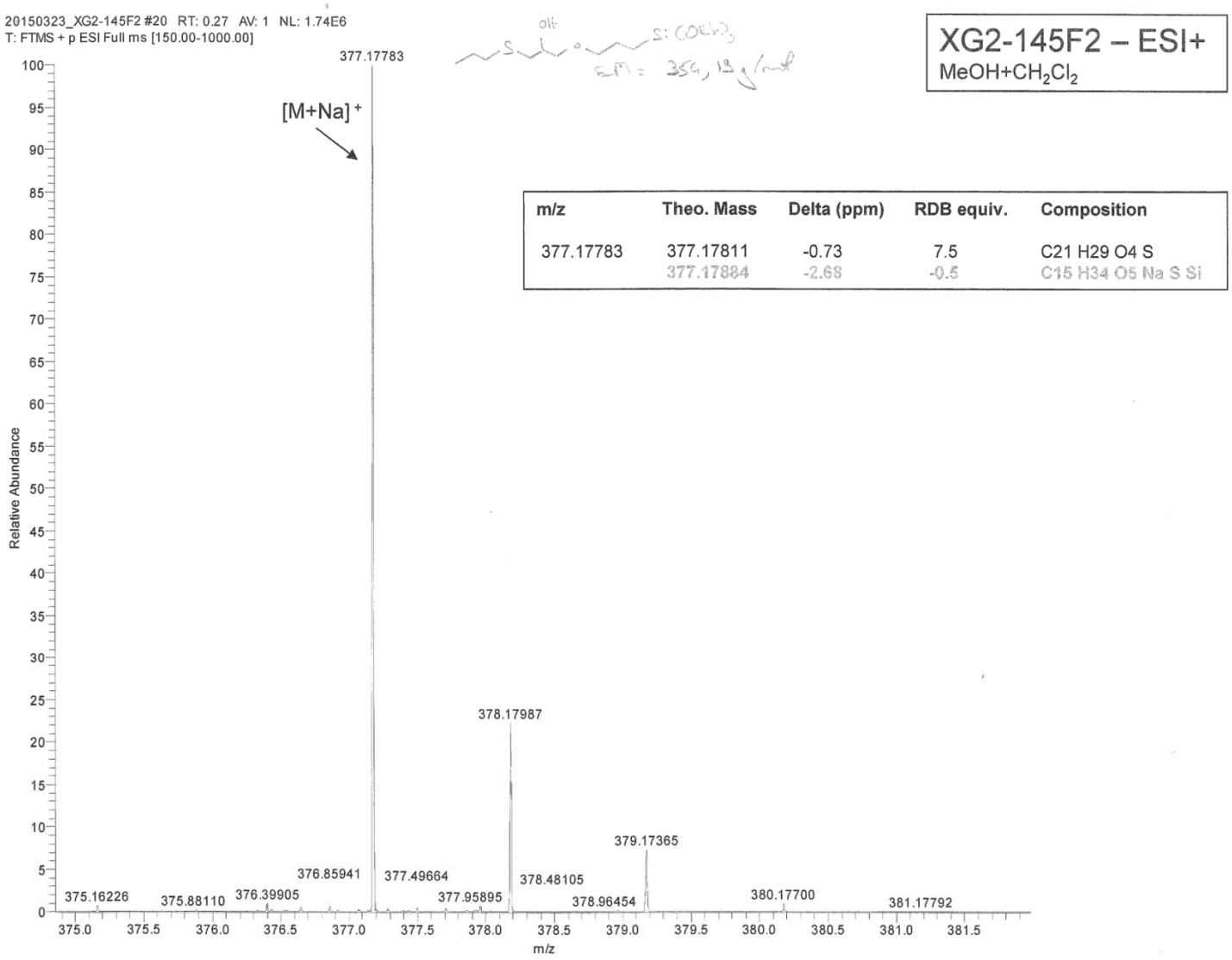
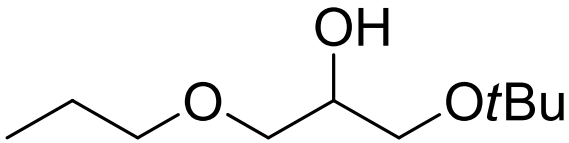


Figure SI_71: HRMS spectrum of compound 11



12a

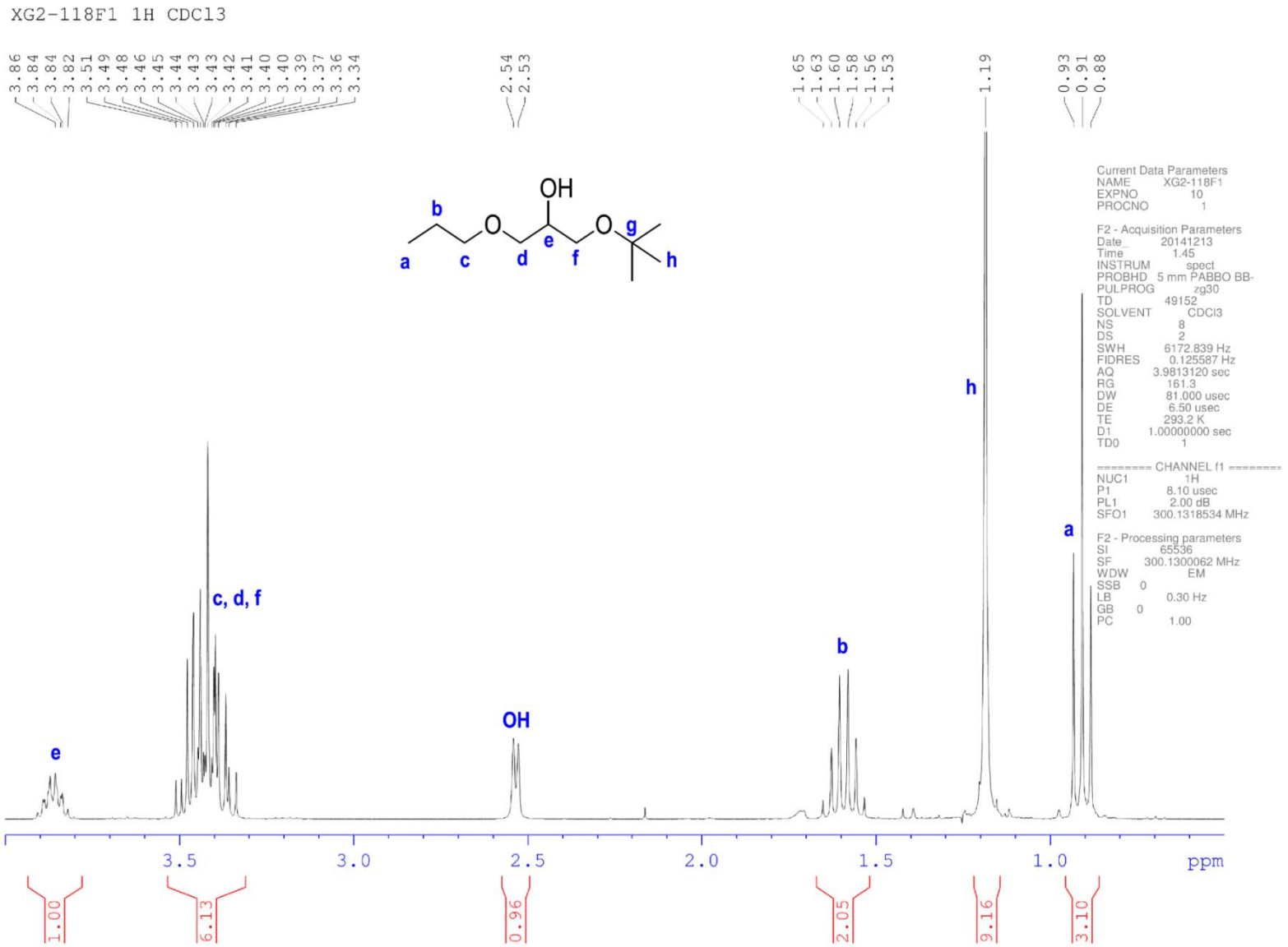


Figure SI_73: ^{1}H NMR spectrum of compound 12a

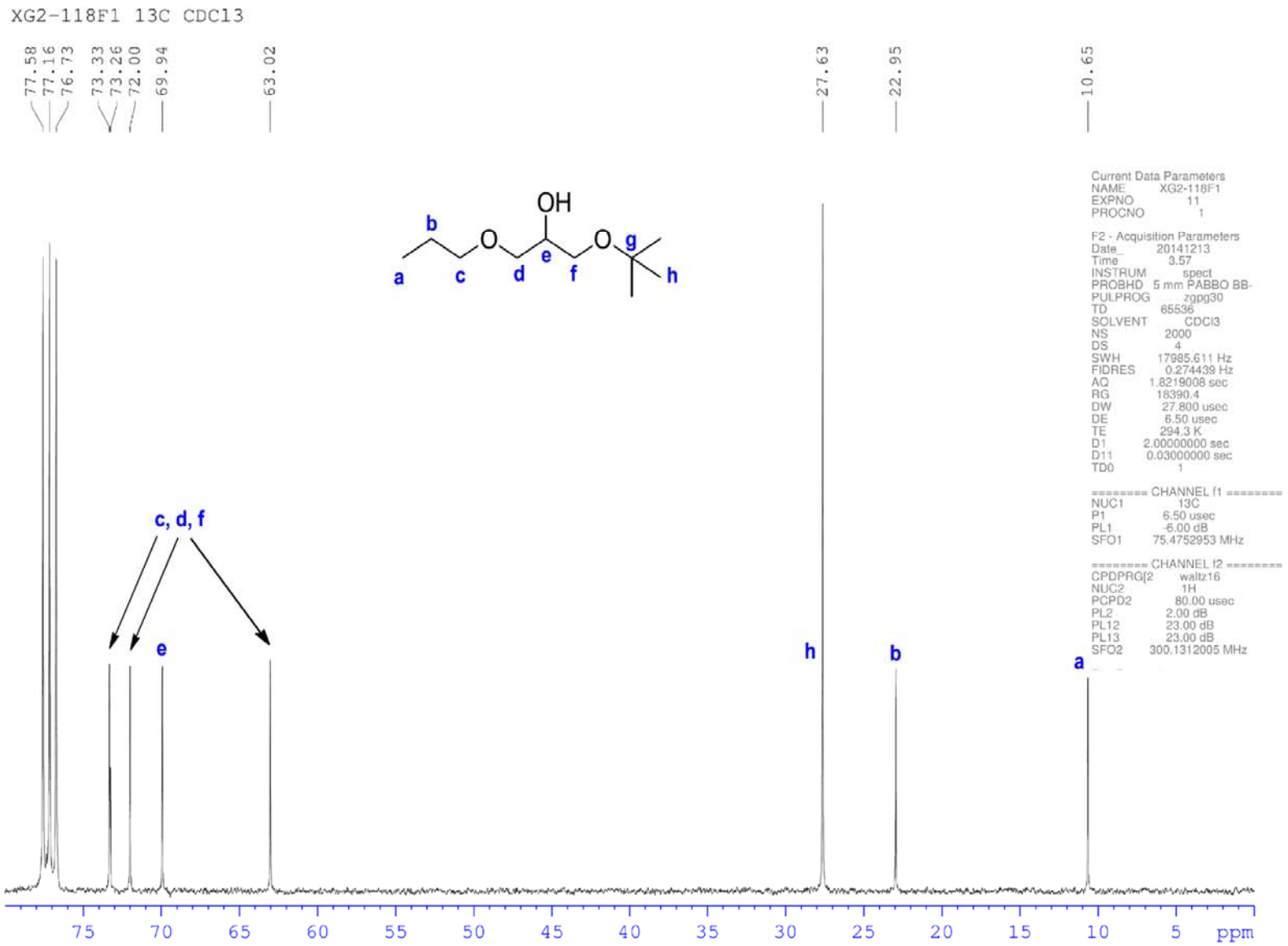


Figure SI_74: ^{13}C NMR spectrum of compound 12a

SI_75

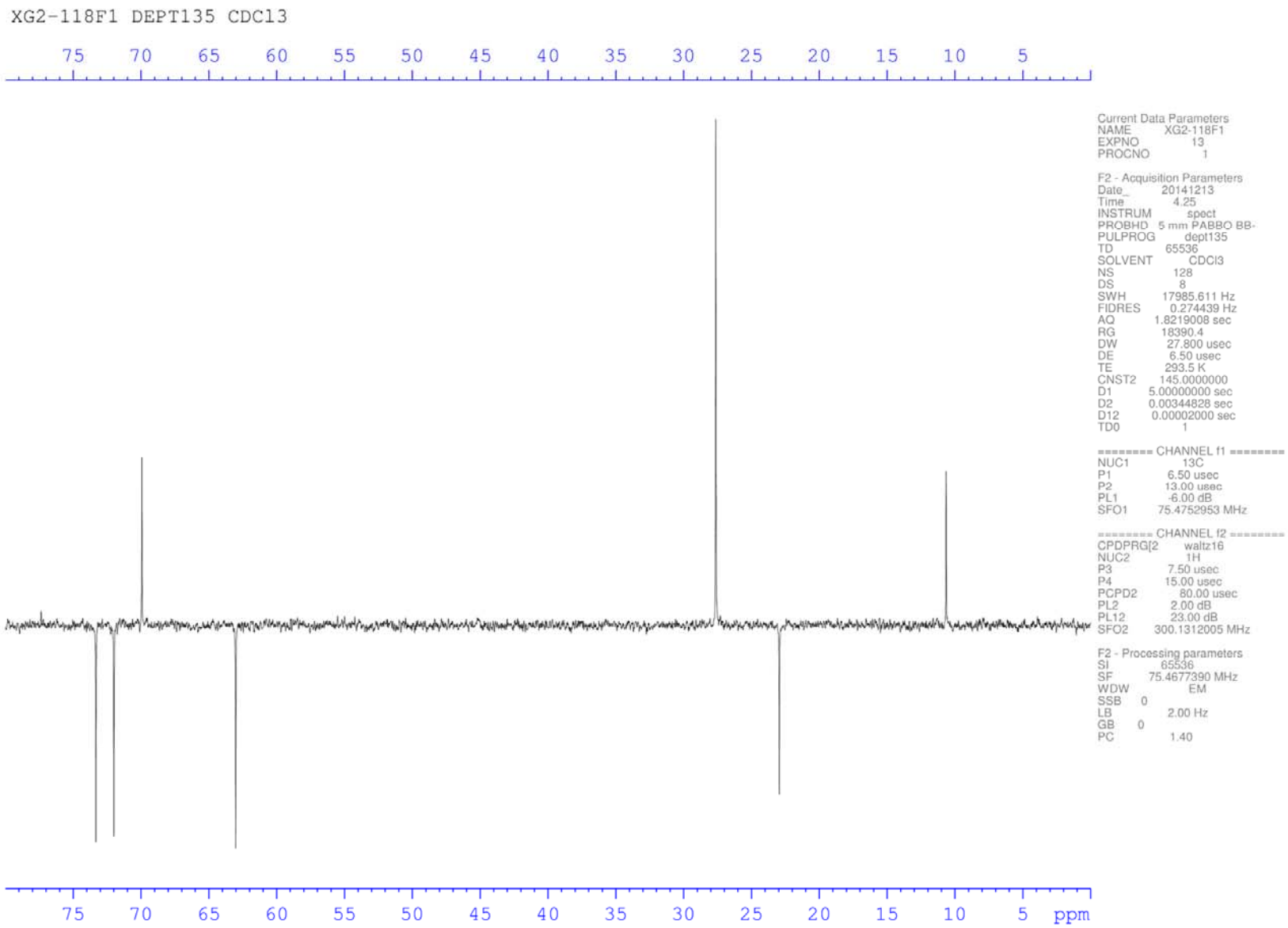


Figure SI_75: DEPT 135 NMR spectrum of compound 12a

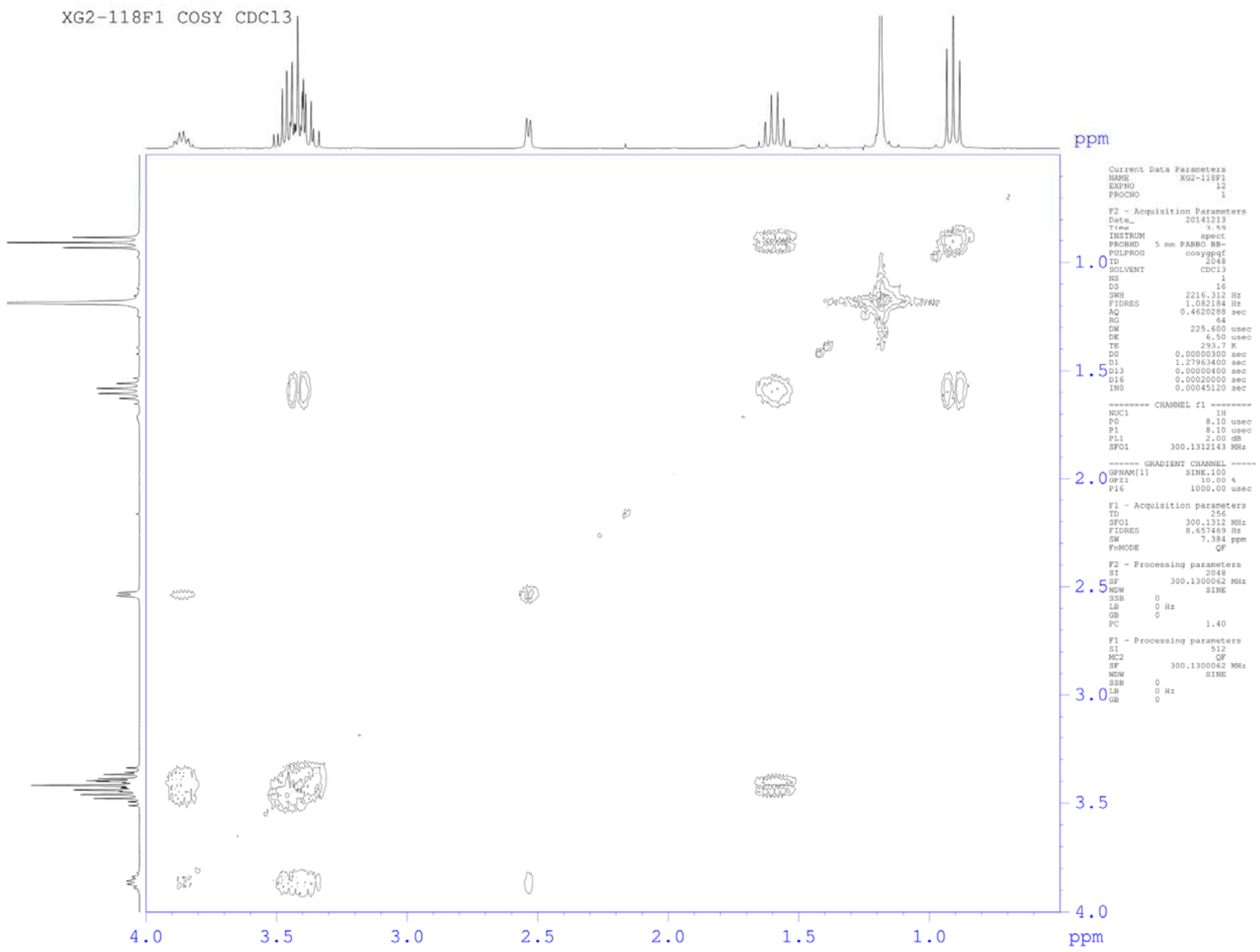


Figure SI_76: H-1H COSY NMR spectrum of compound 12a

SI_77

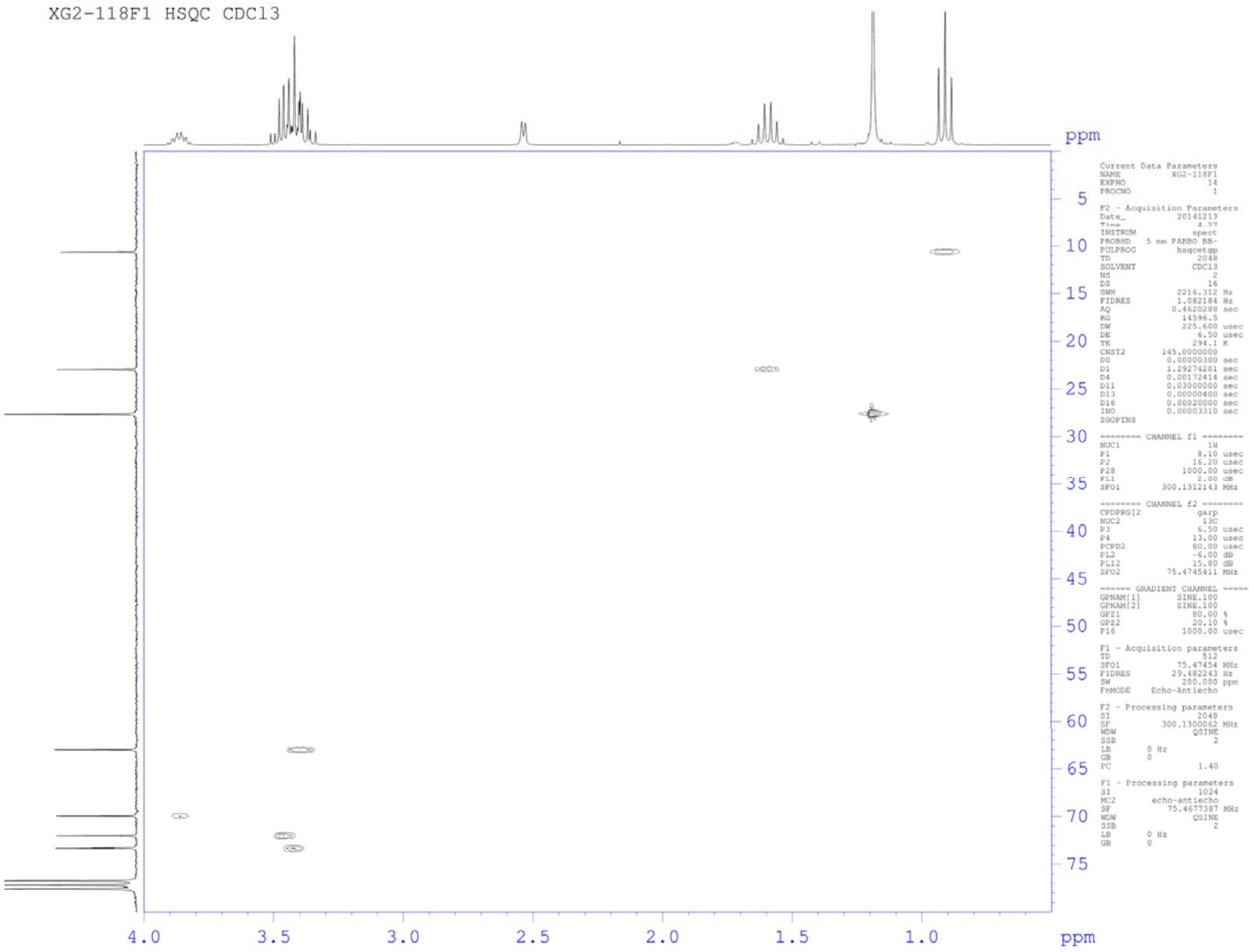


Figure SI_77: HSQC spectrum of compound 12a

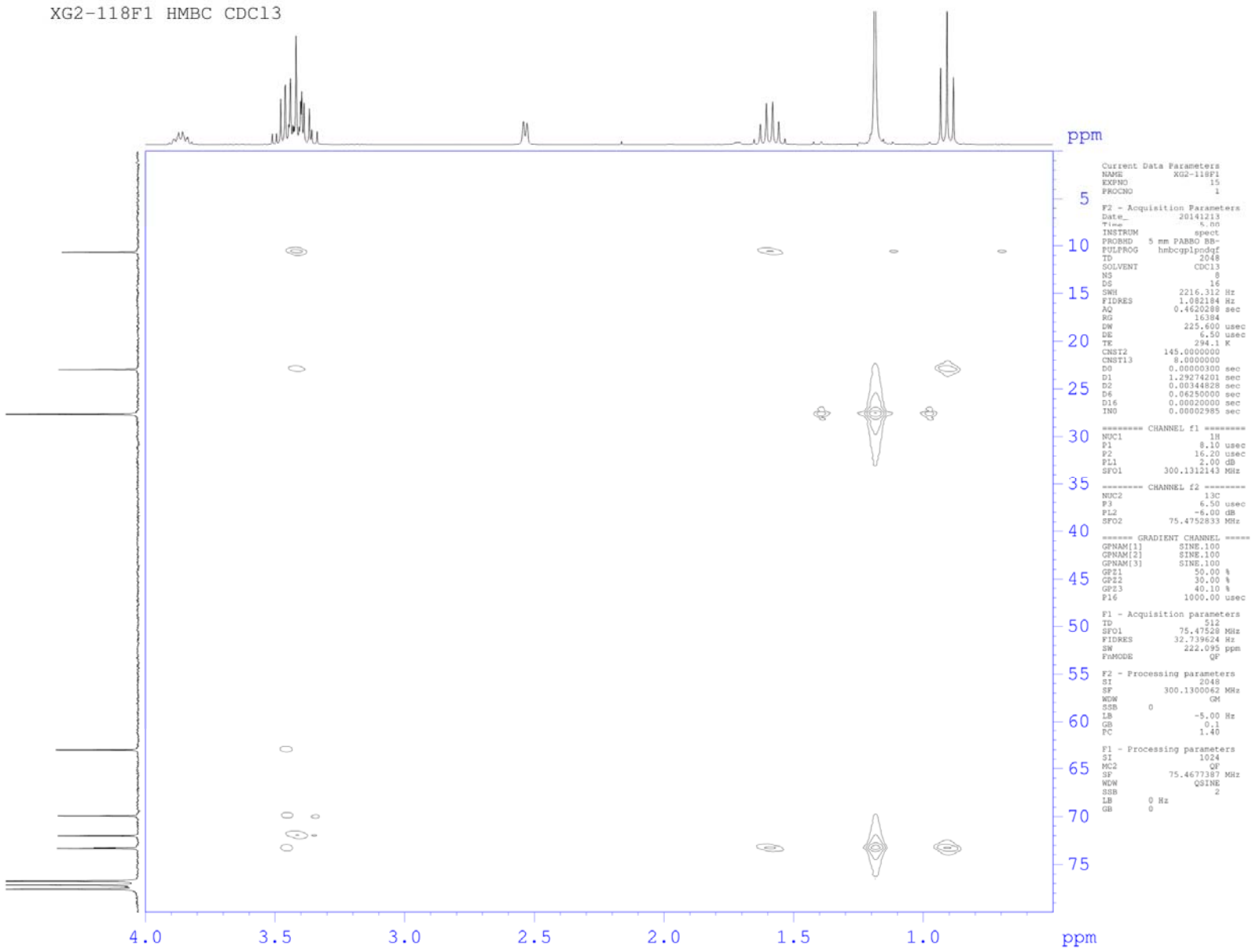


Figure SI_78: HMBC spectrum of compound 12a

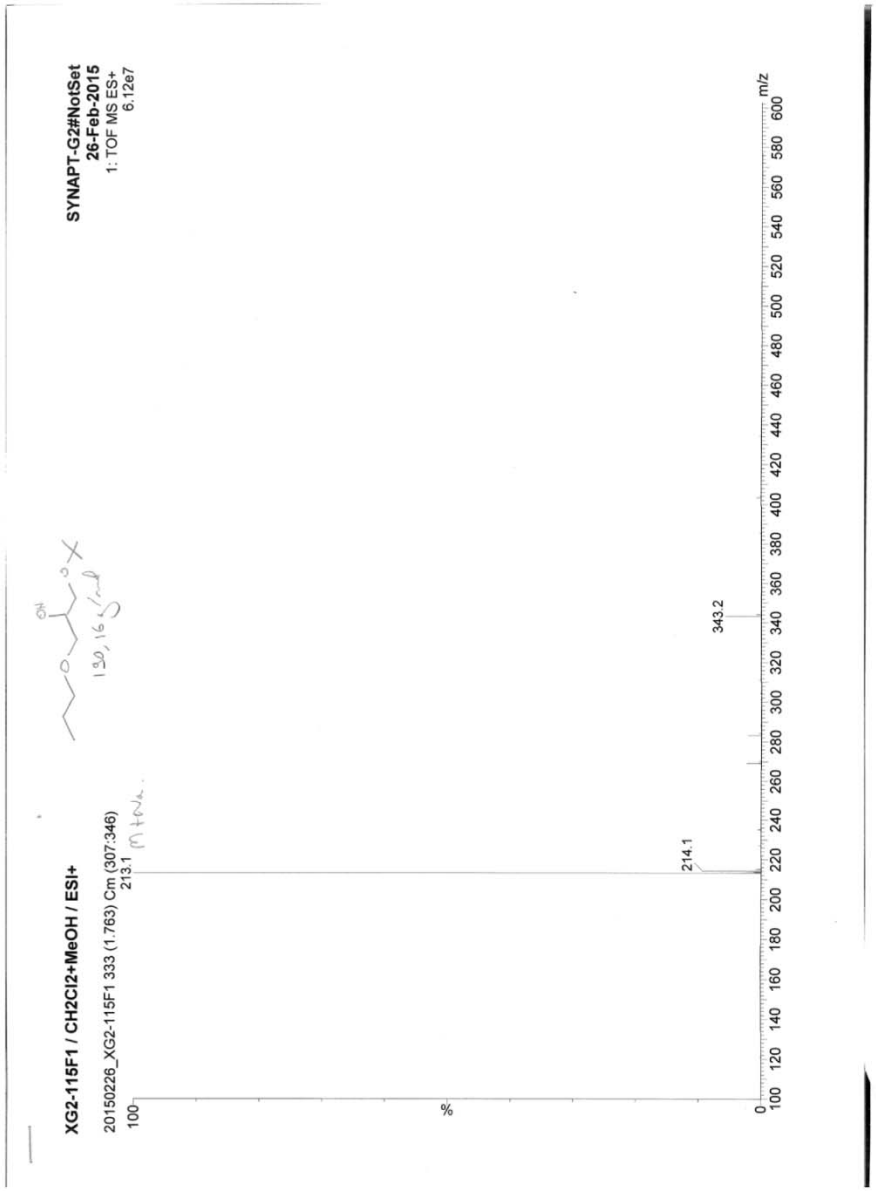
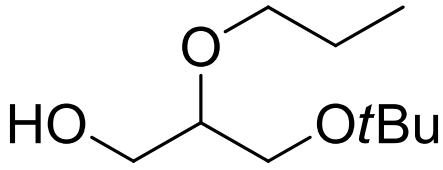


Figure SI_79: ESI-HRMS spectrum of compound 12a



12b

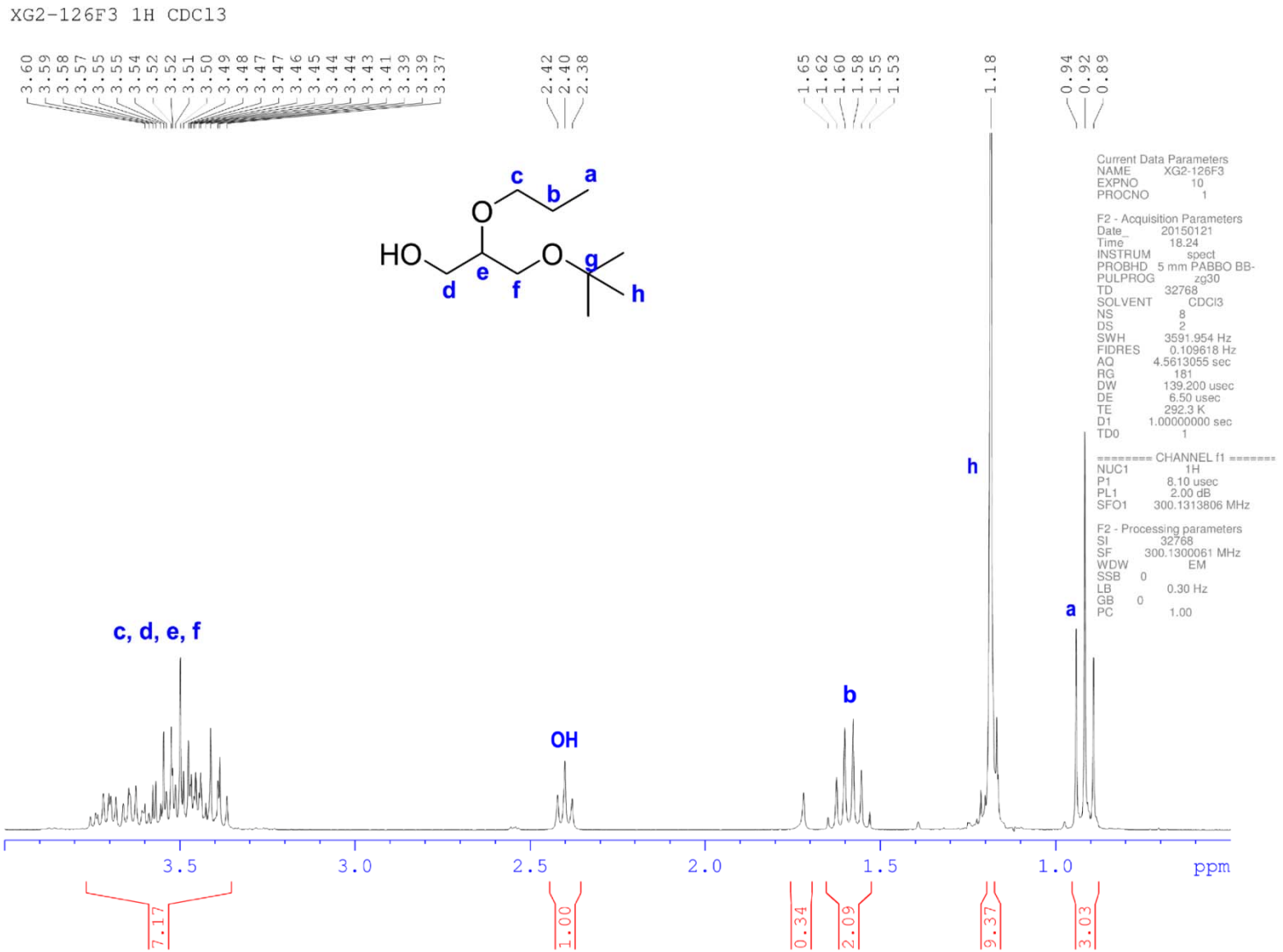


Figure SI_81: ^{1}H NMR spectrum of compound 12b

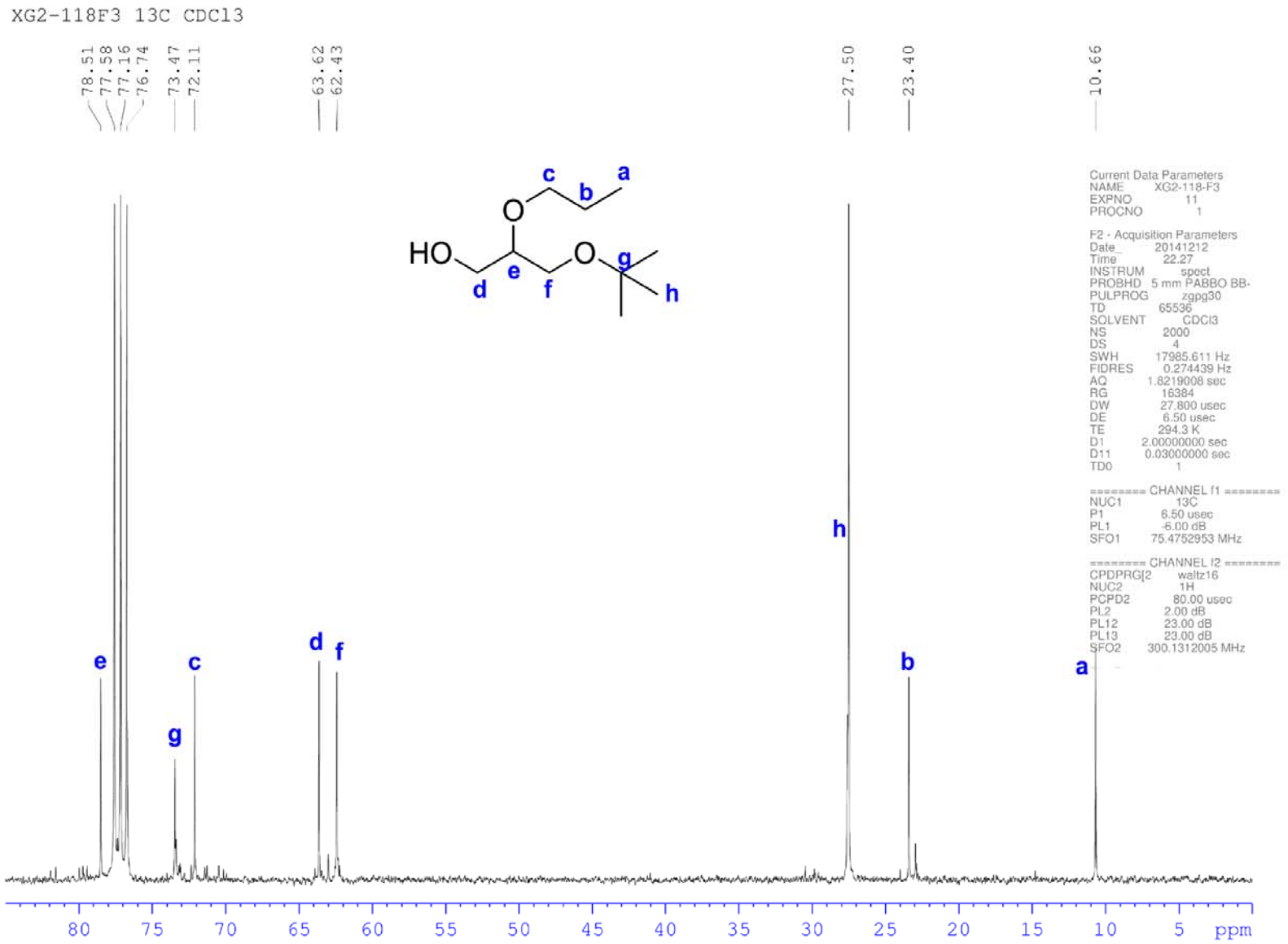


Figure SI_82: ^{13}C NMR spectrum of compound 12b

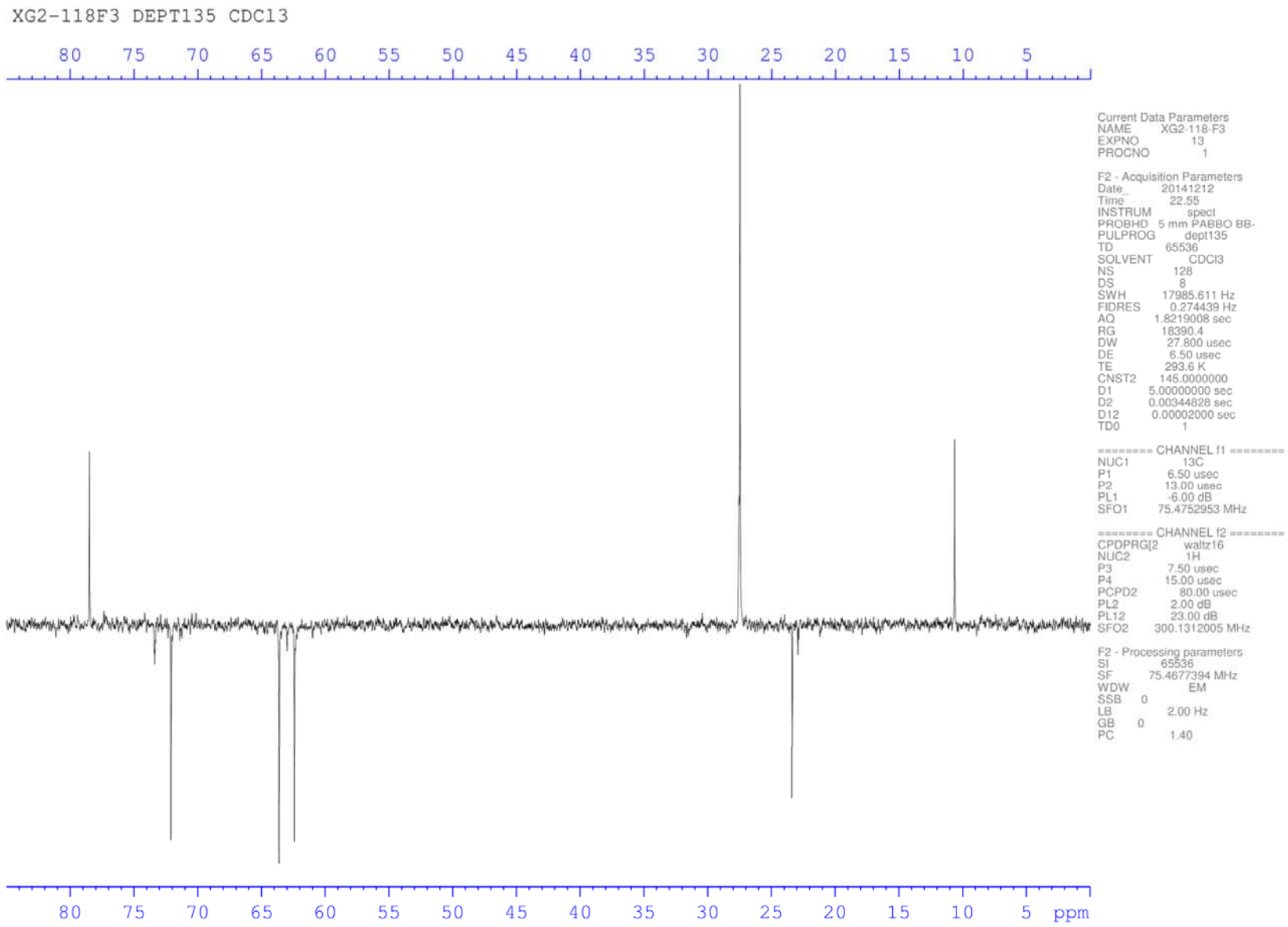


Figure SI_83: DEPT135 NMR spectrum of compound 12b

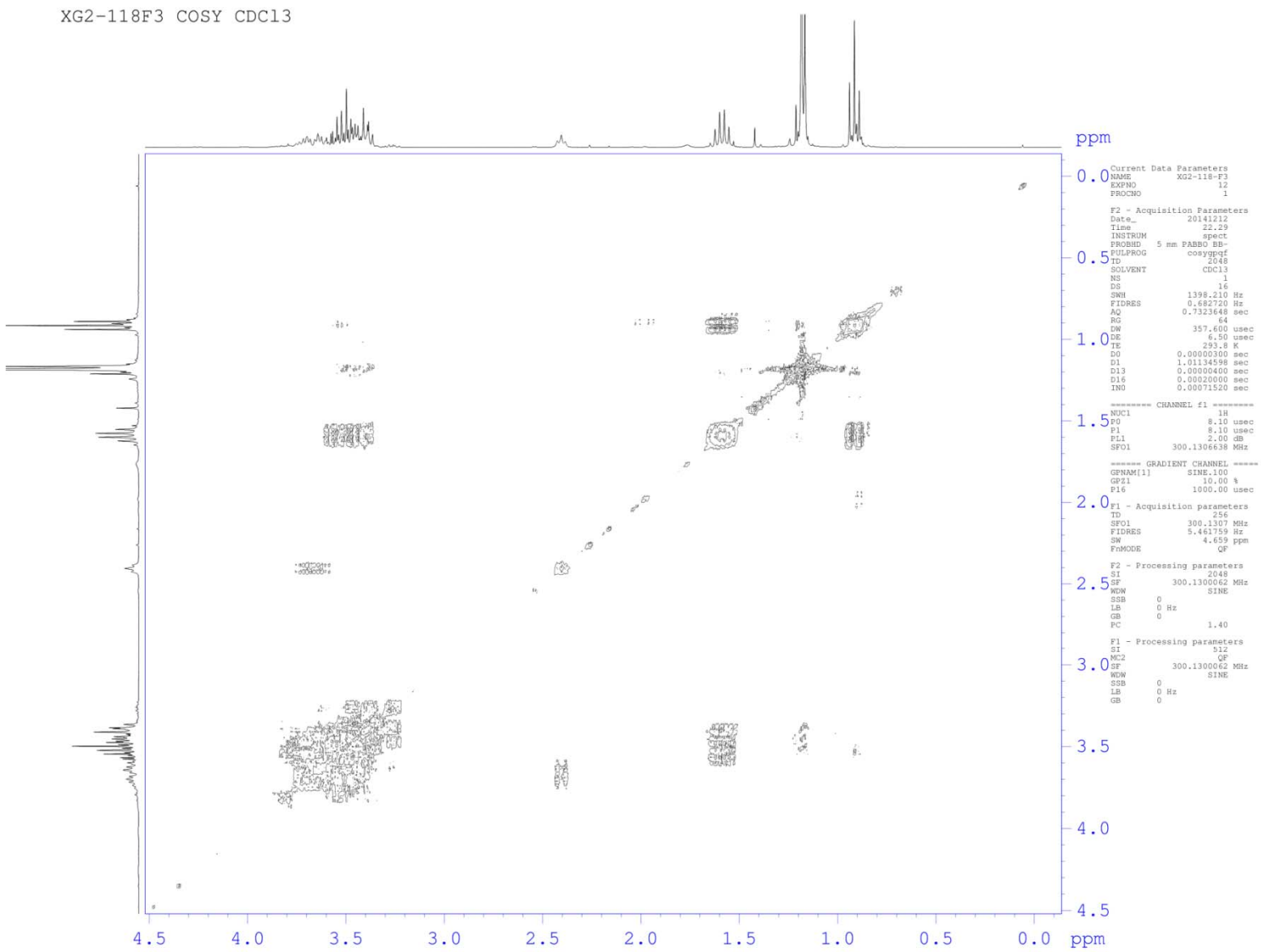


Figure SI_84: 1H-1H NMR spectrum of compound 12b

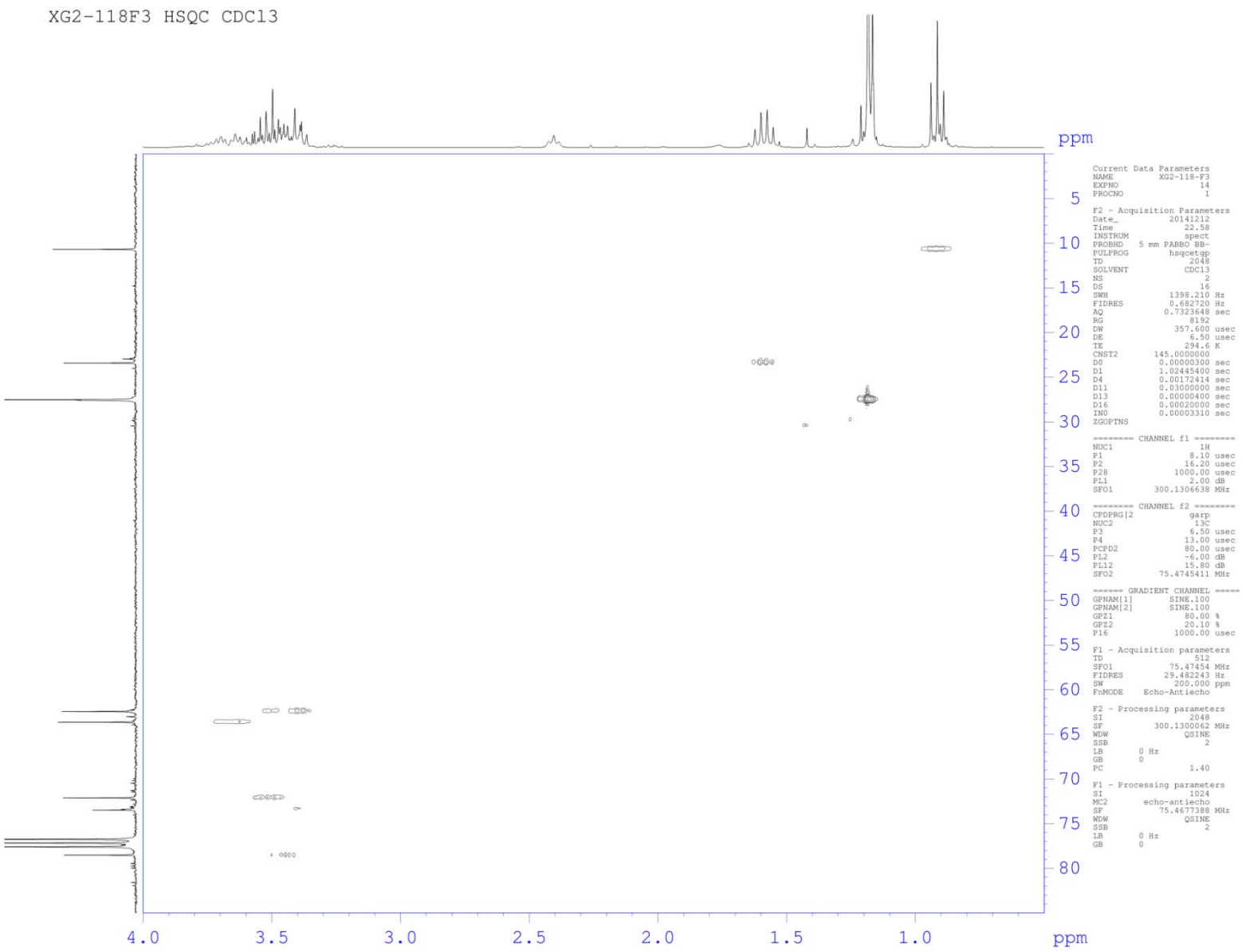


Figure SI_85: HSQC NMR spectrum of compound 12b

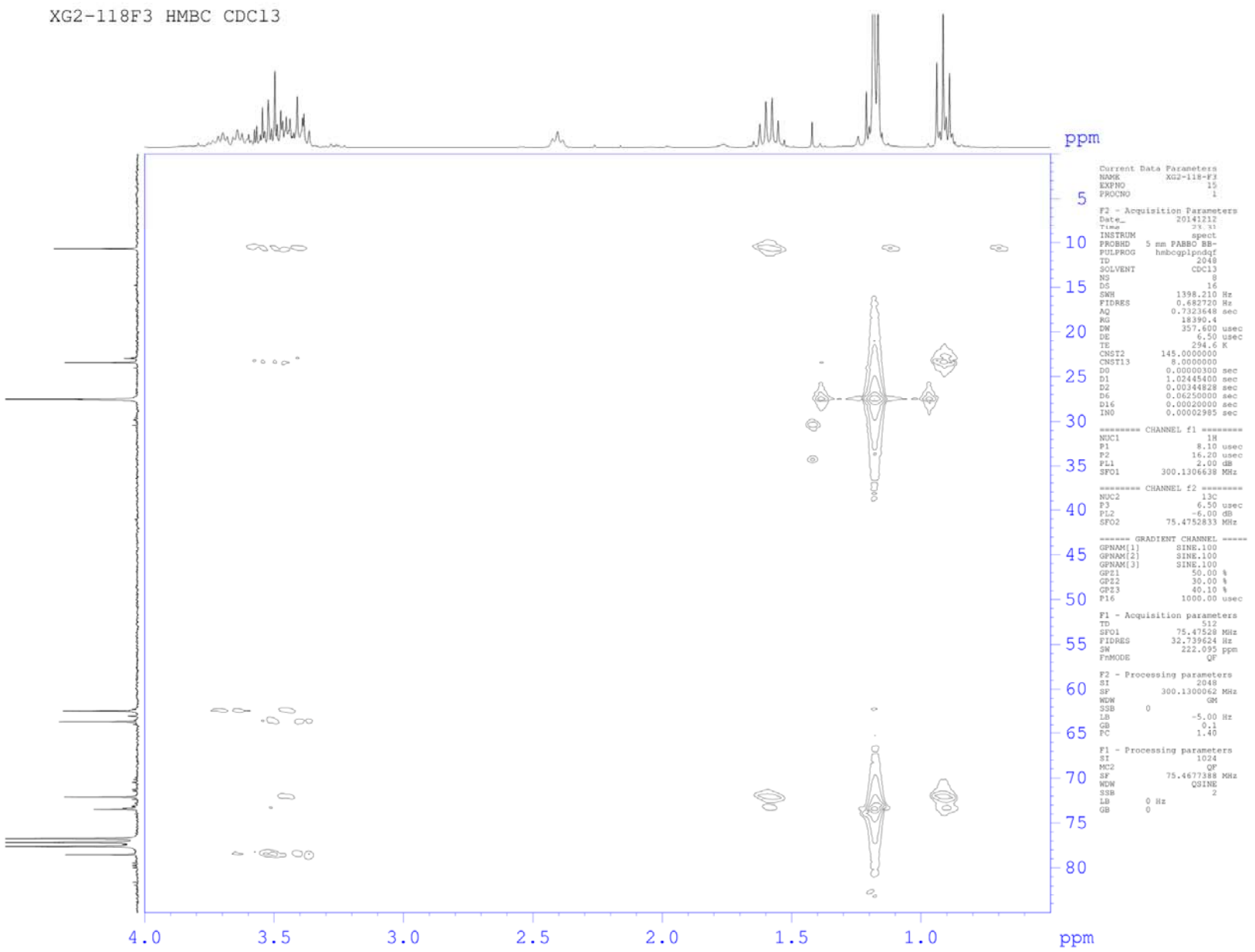
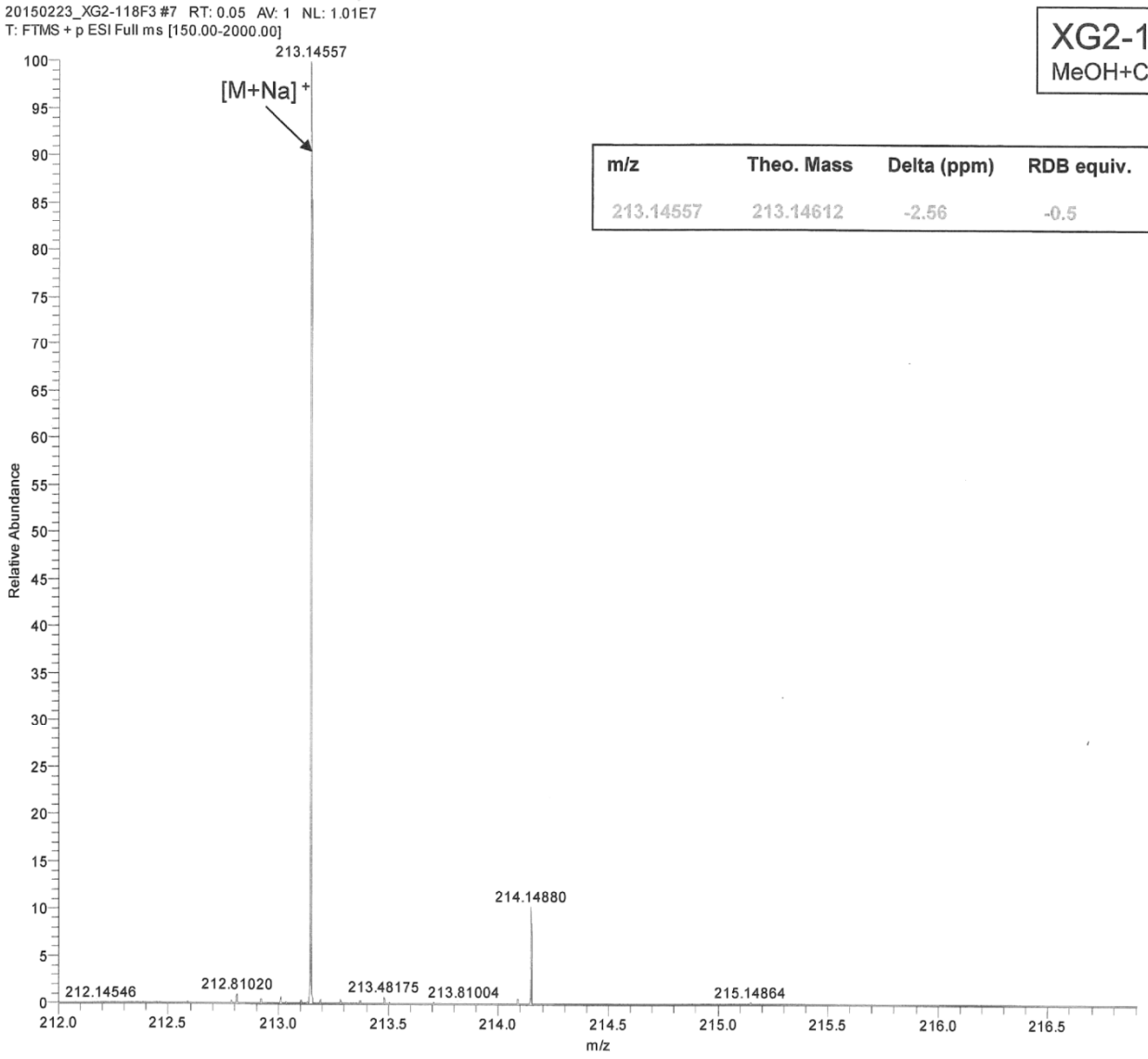


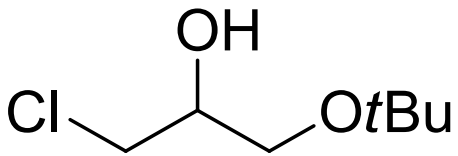
Figure SI_86: HMBC NMR spectrum of compound 12b



XG2-118F3– ESI+
MeOH+CH_2Cl_2

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
213.14557	213.14612	-2.56	-0.5	C10 H22 O3 Na

Figure SI_87: HRMS spectrum of compound 12b



12c

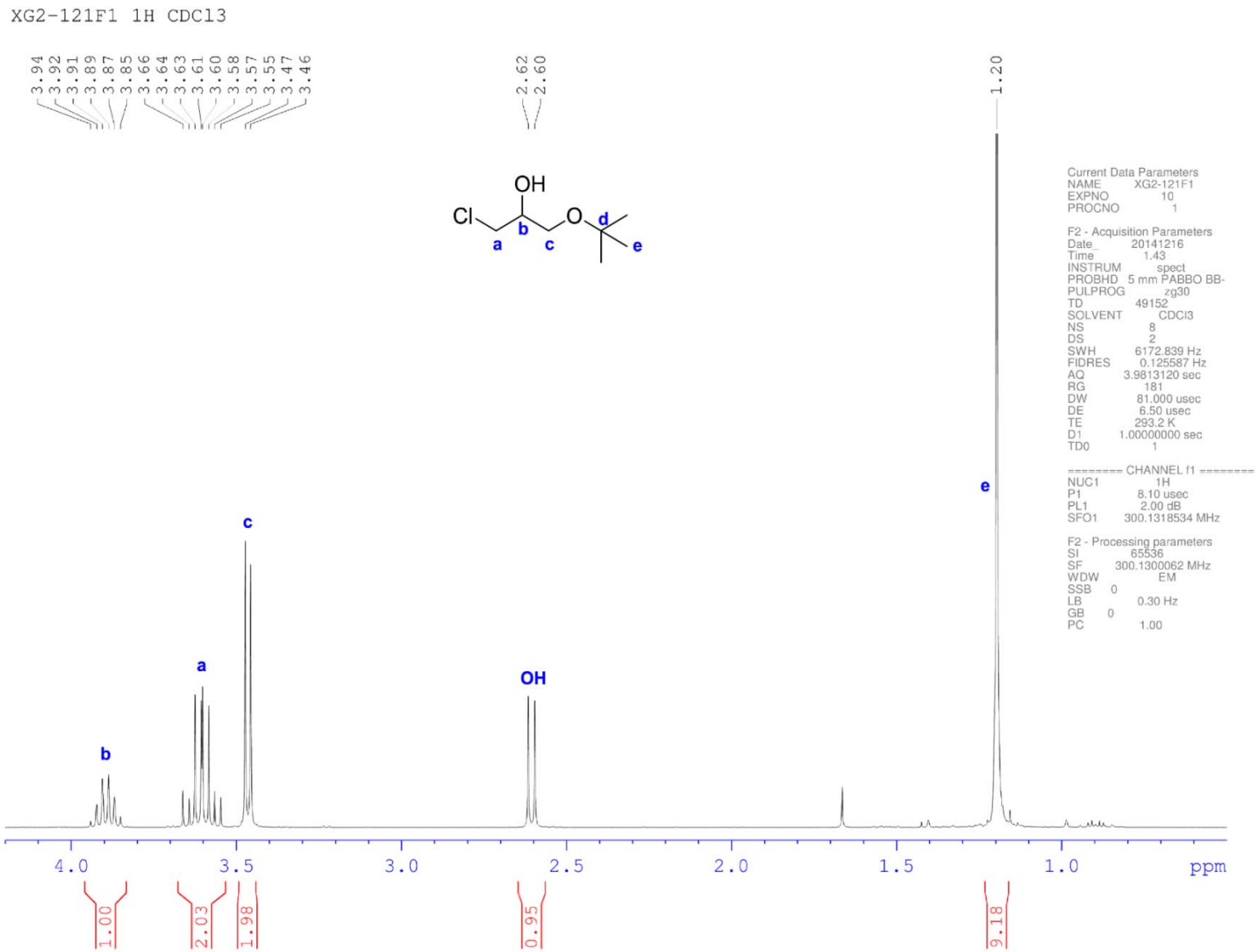


Figure SI_89: ^{1}H NMR spectrum of compound 12c

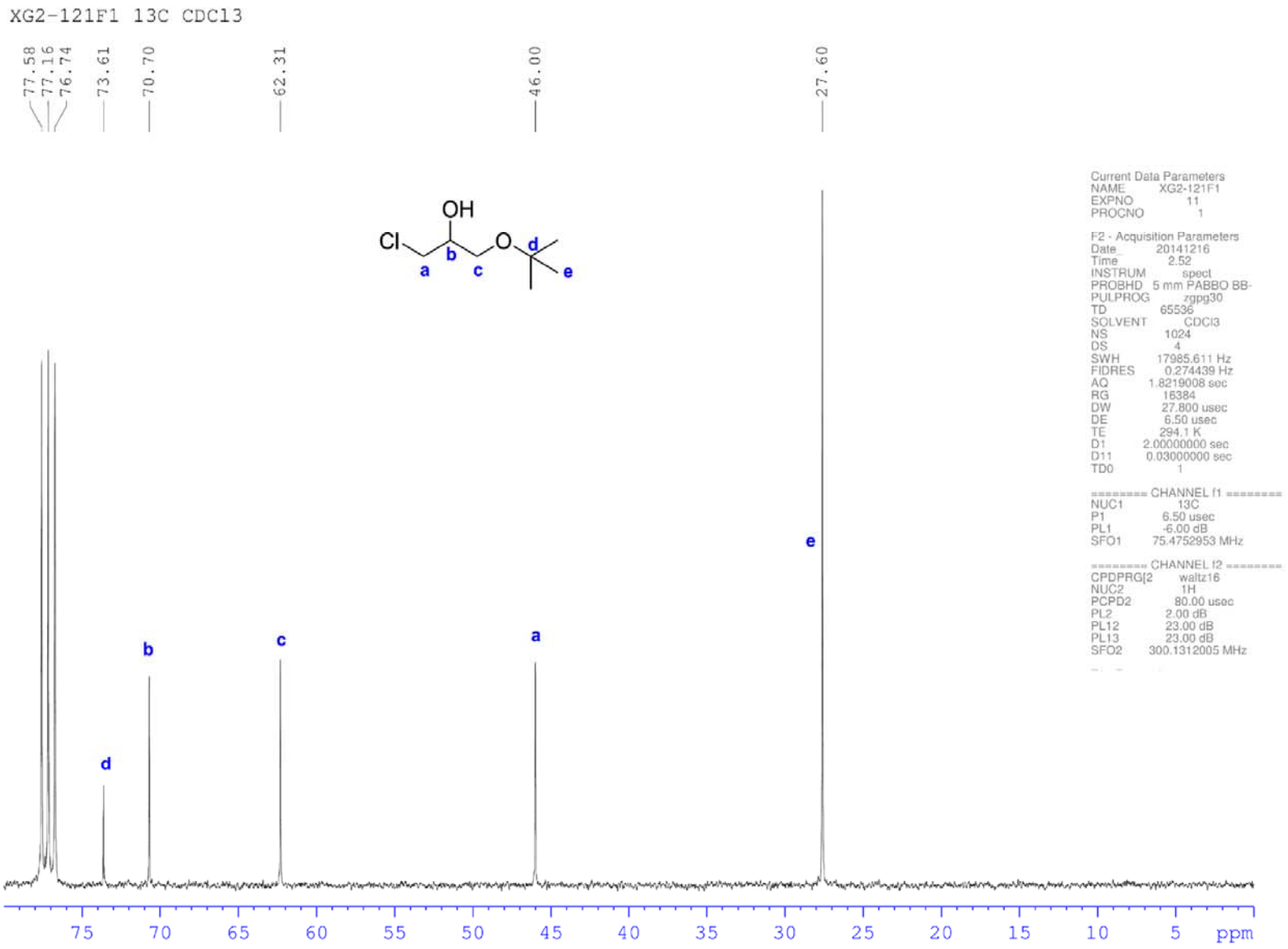


Figure SI_901: ^{13}C NMR spectrum of compound 12c

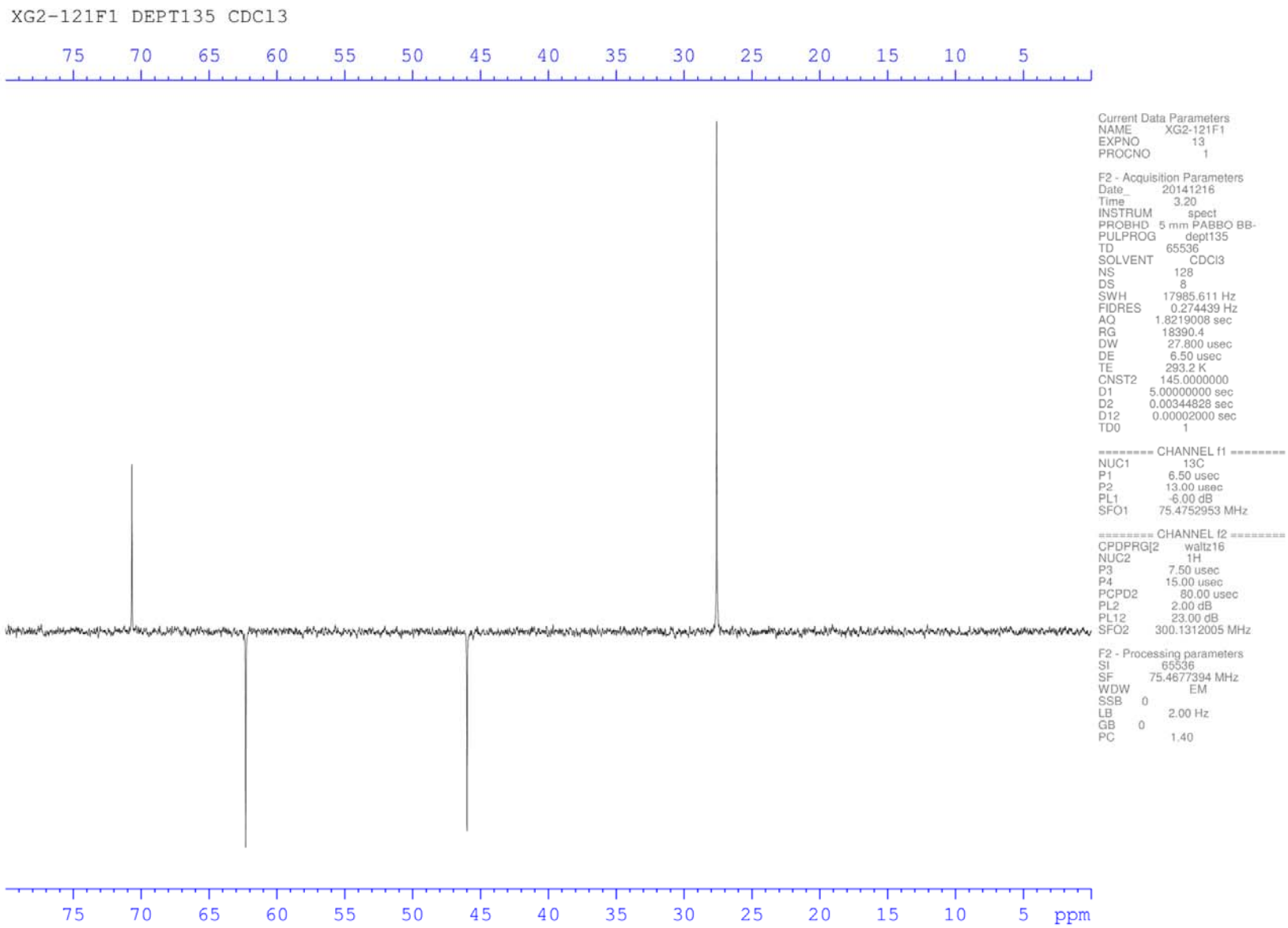


Figure SI_91: DEPT 135 NMR spectrum of compound 12c

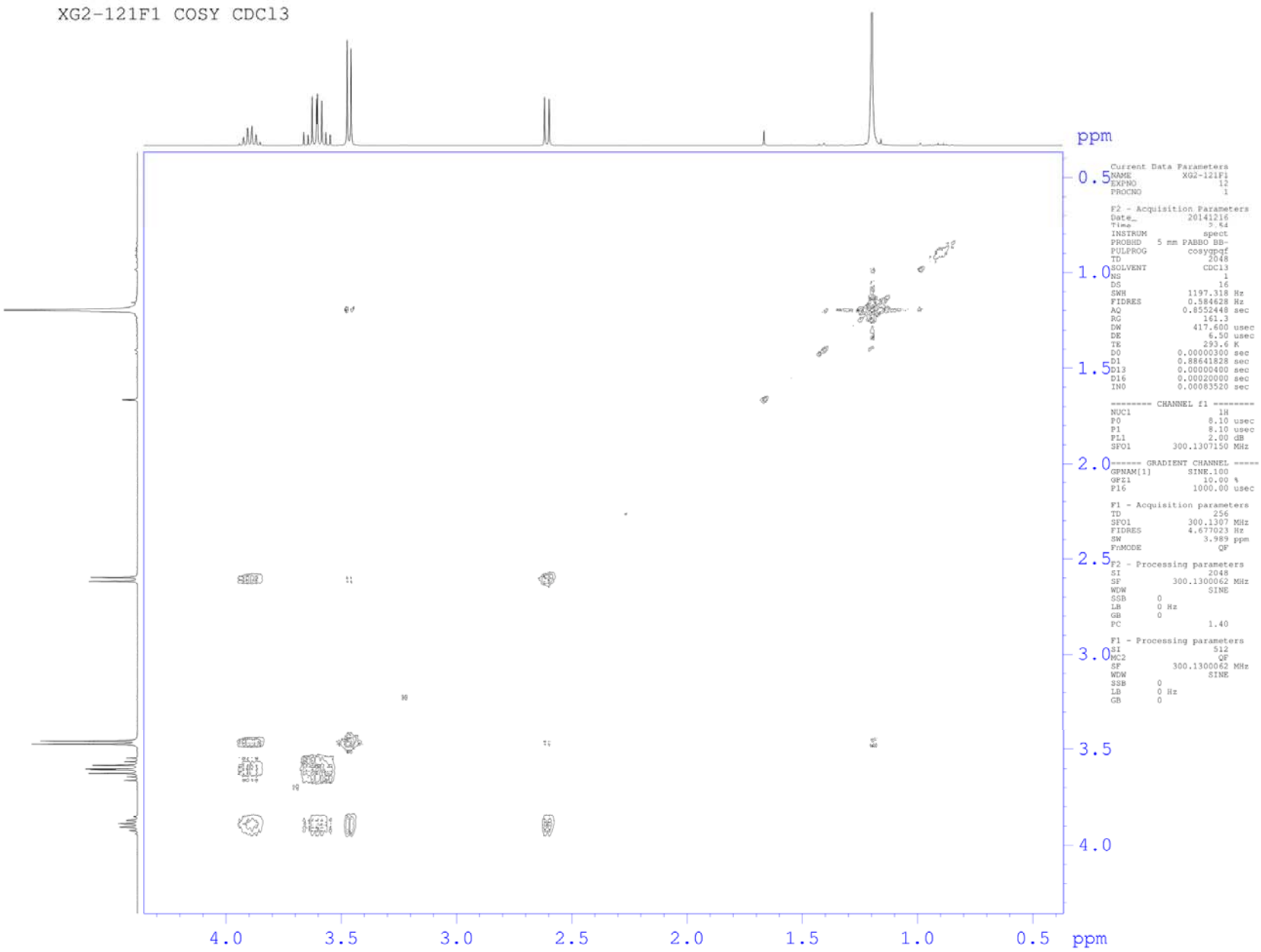


Figure SI_92: COSY NMR spectrum of compound 12c

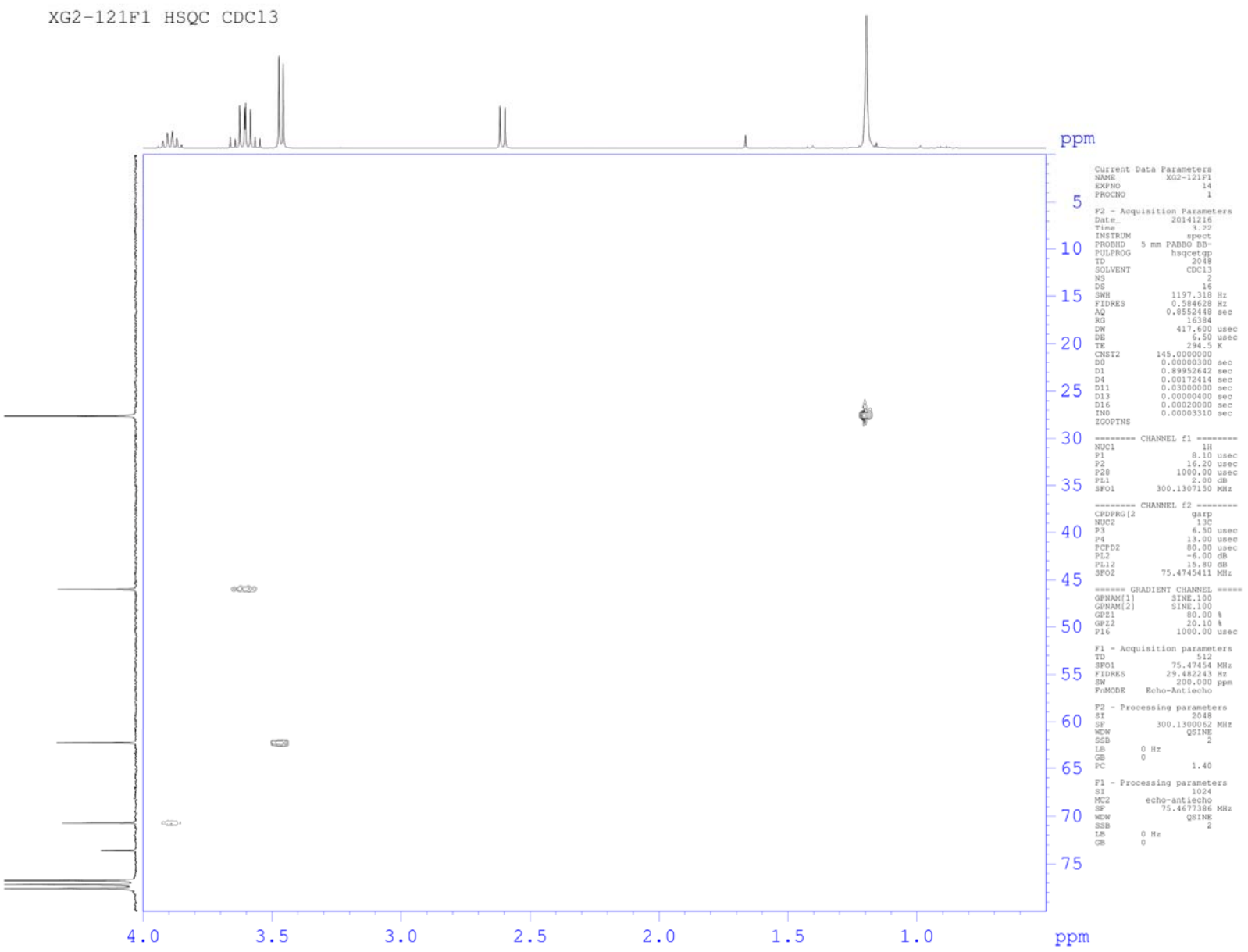


Figure SI_93: HSQC NMR spectrum of compound 12c

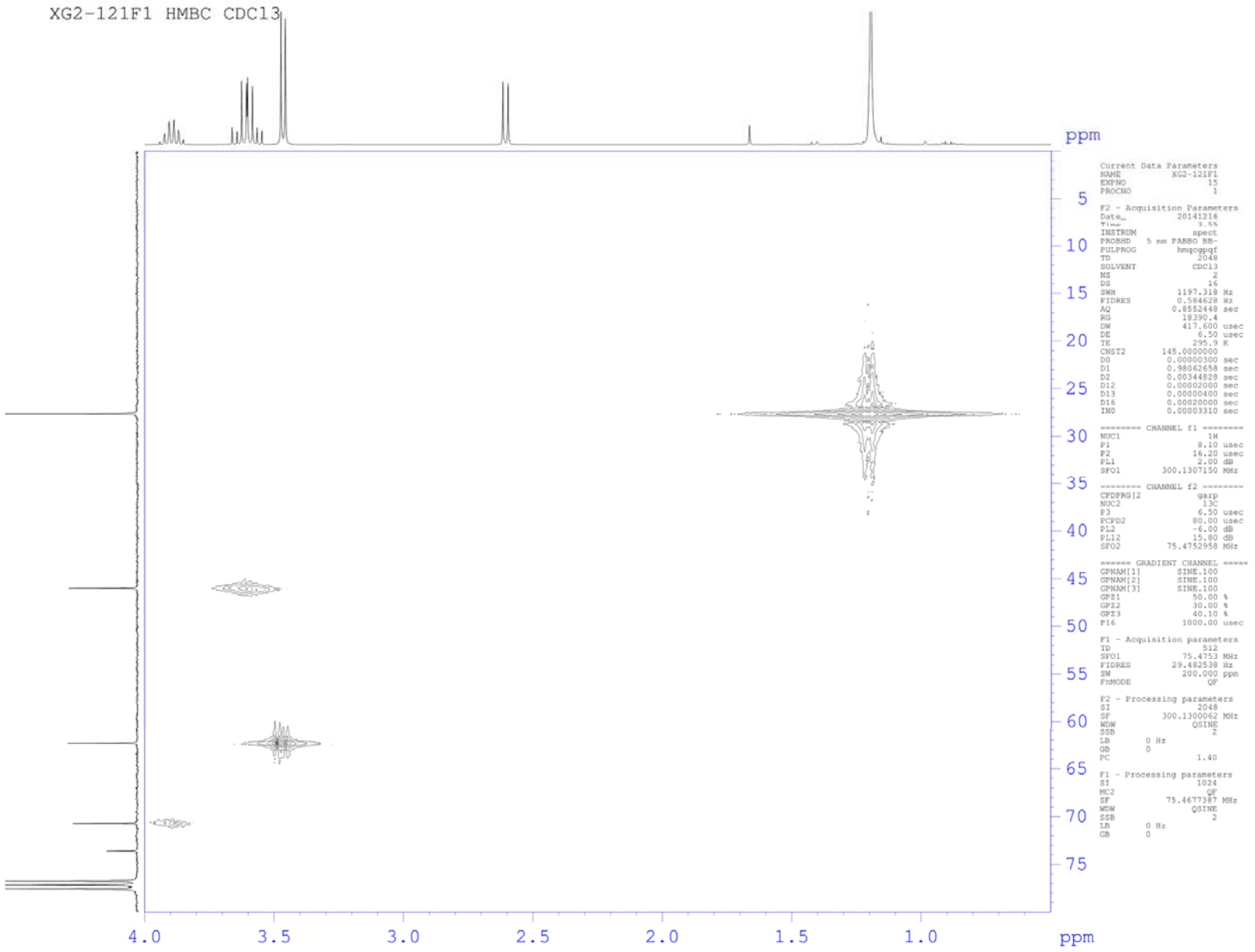


Figure SI_94: HMBC NMR spectrum of compound 12c

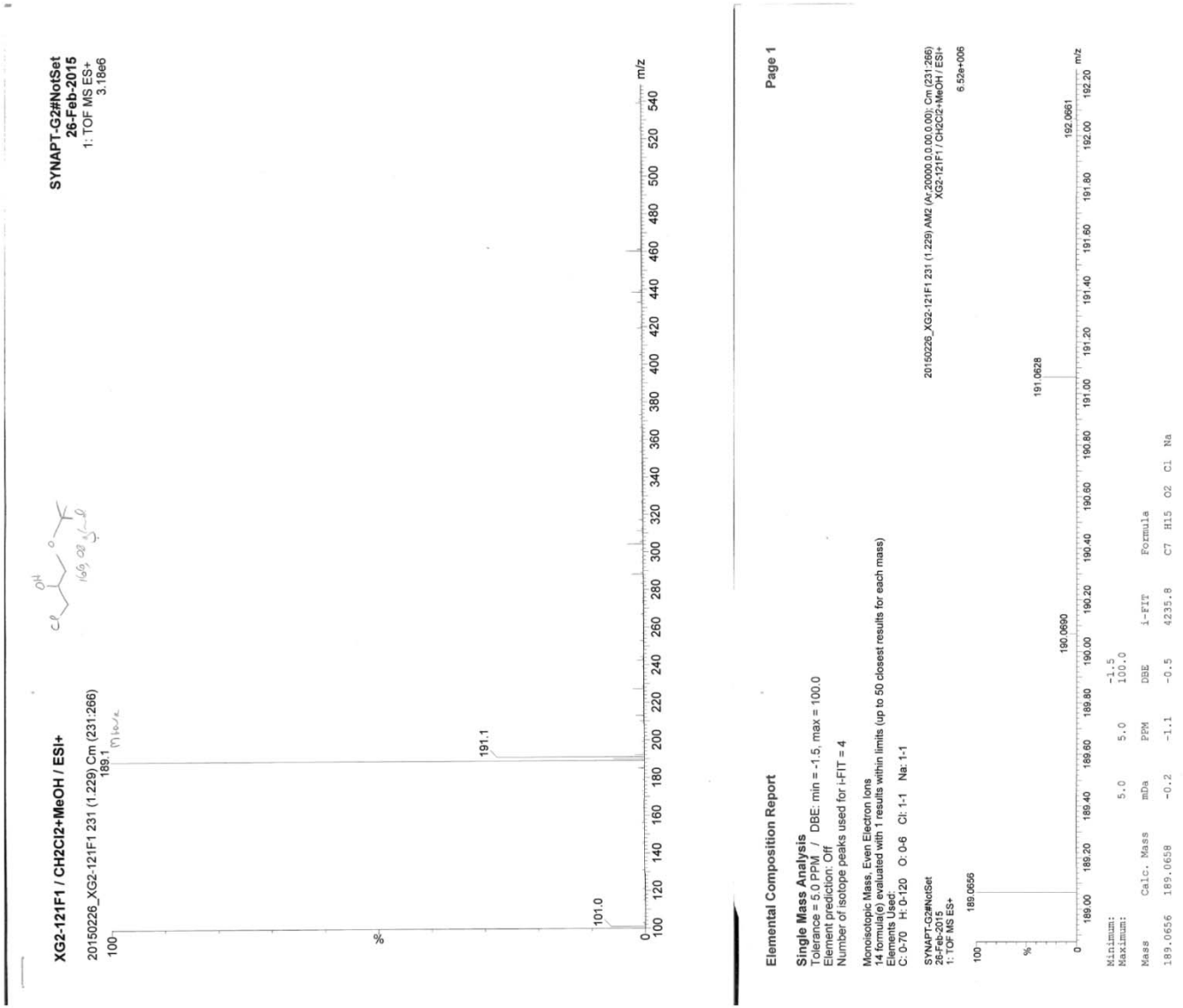
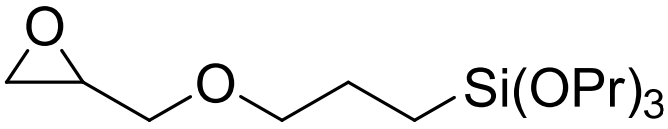


Figure SI_95: ESI HRMS spectrum of compound 12c



13a

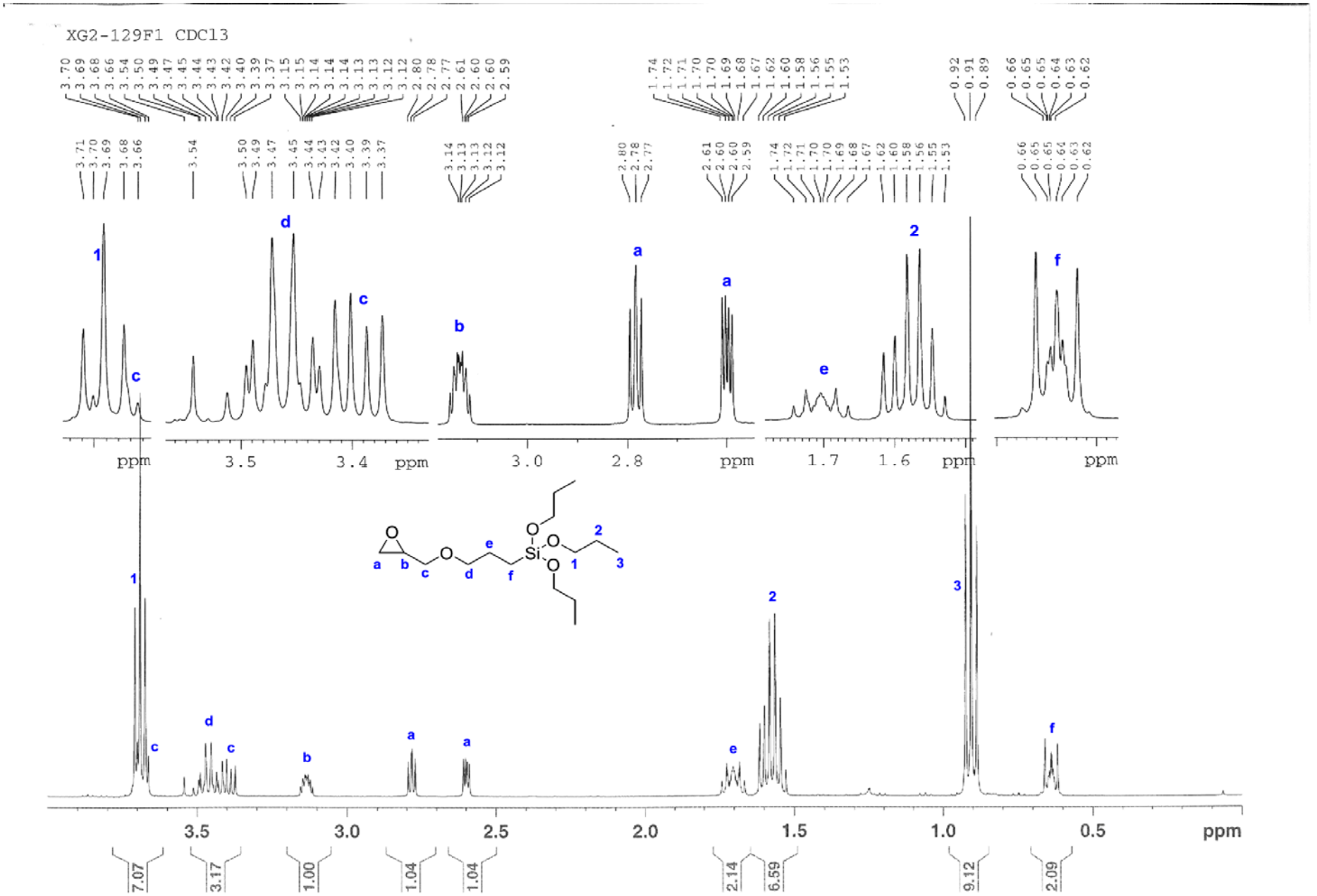


Figure SI_97: ^{1}H NMR spectrum of compound 13a

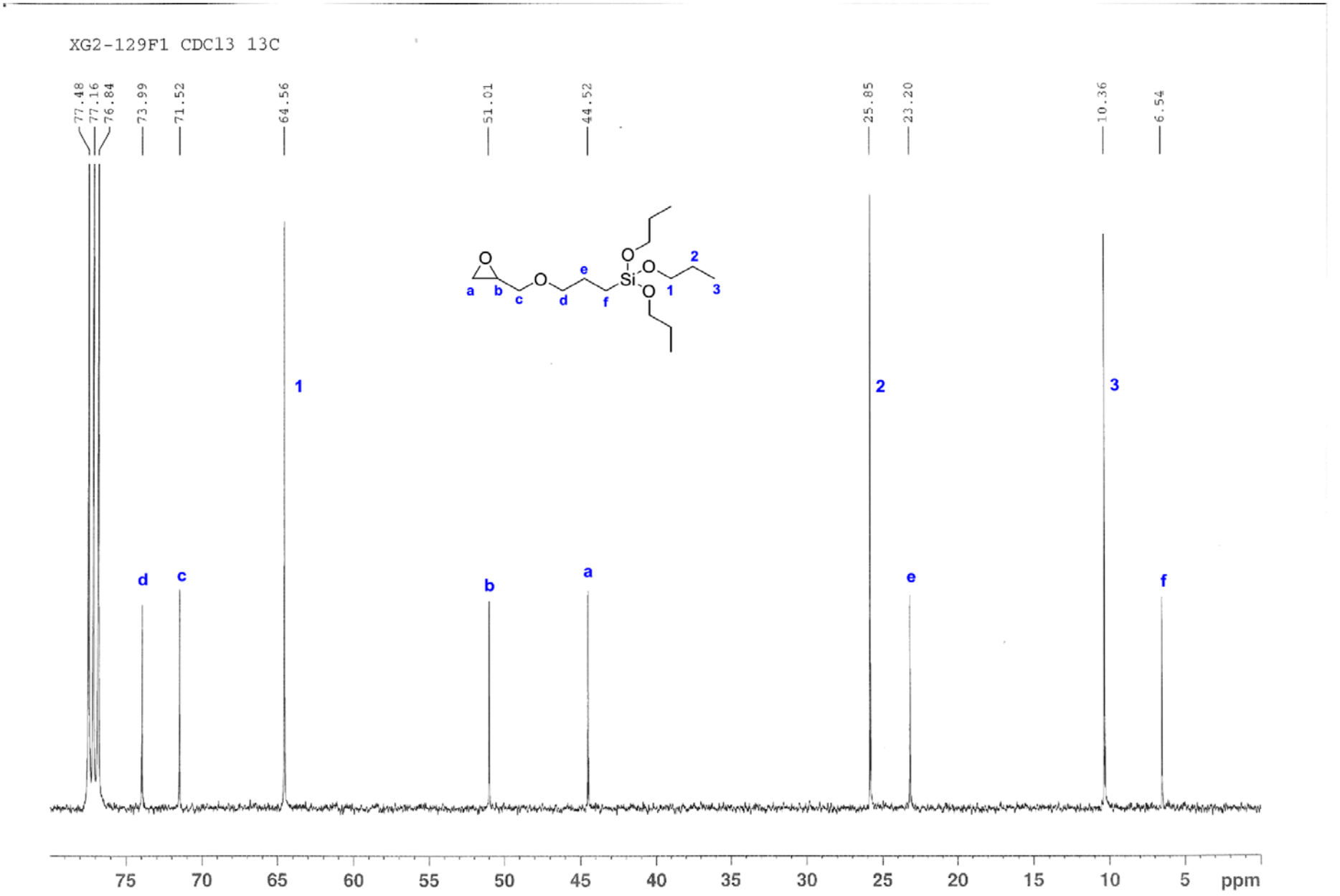


Figure SI_98: ^{13}C NMR spectrum of compound 13a

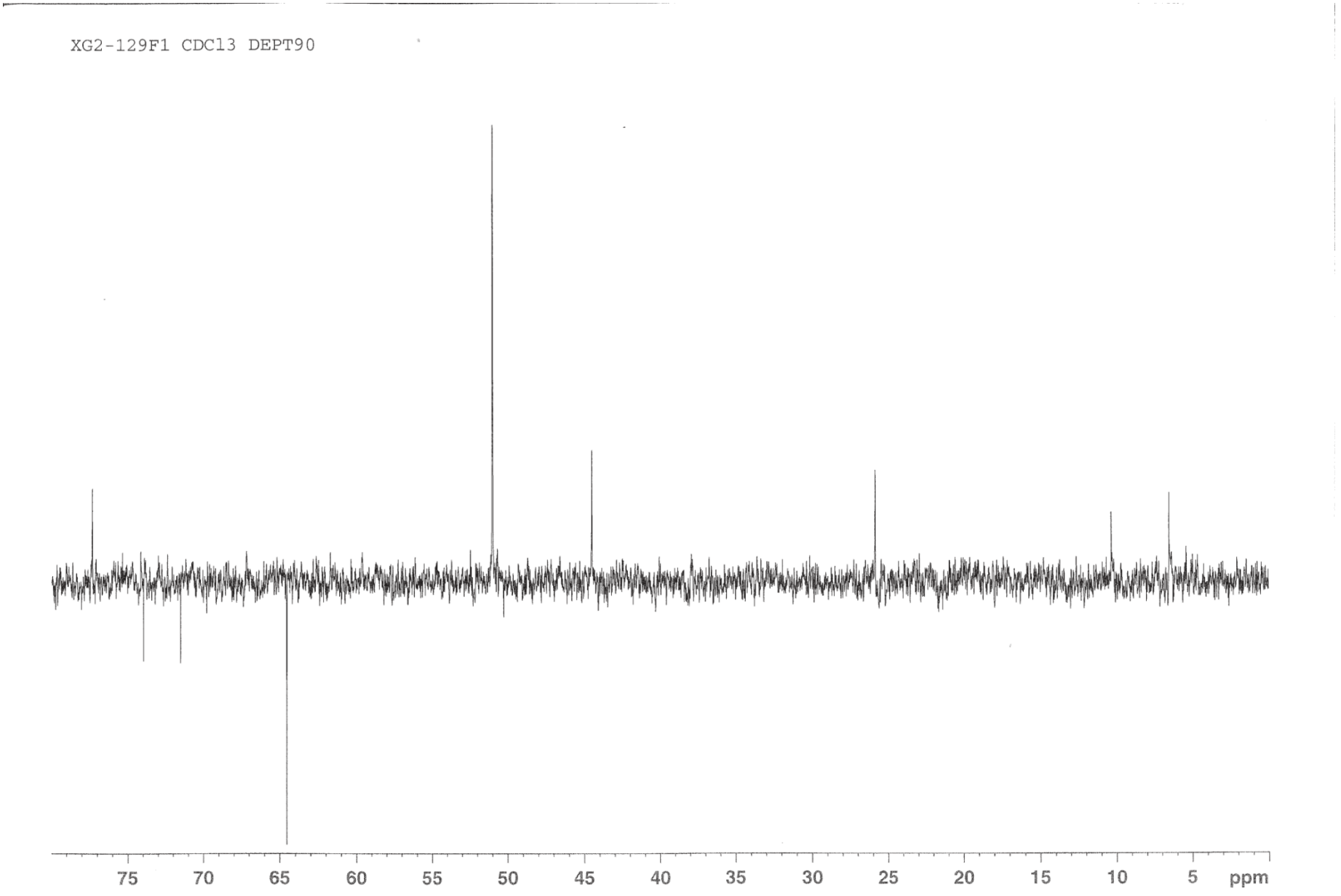


Figure SI_99: DEPT90 NMR spectrum of compound 13a

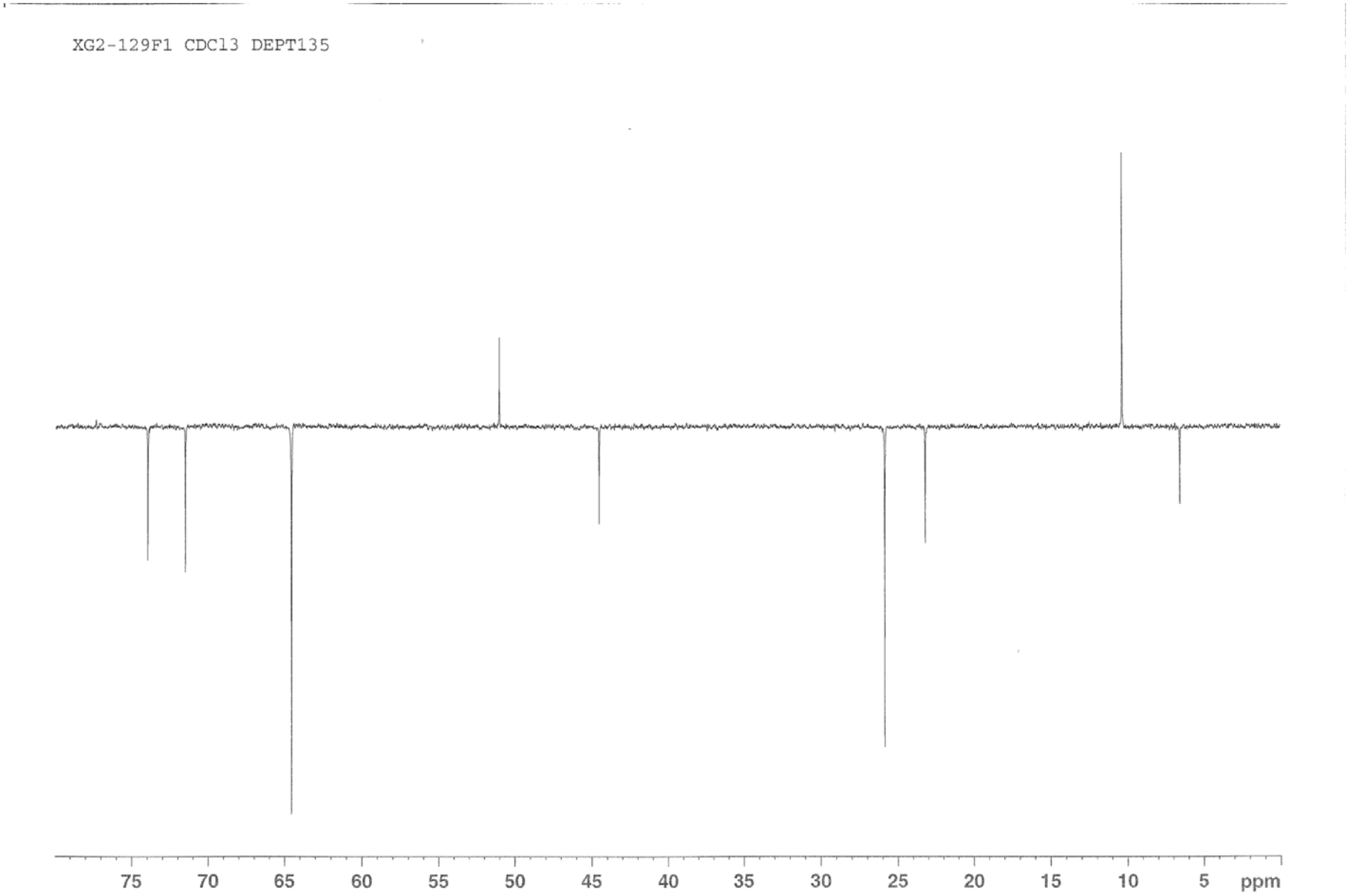


Figure SI_100: DEPT 135 NMR spectrum of compound 13a

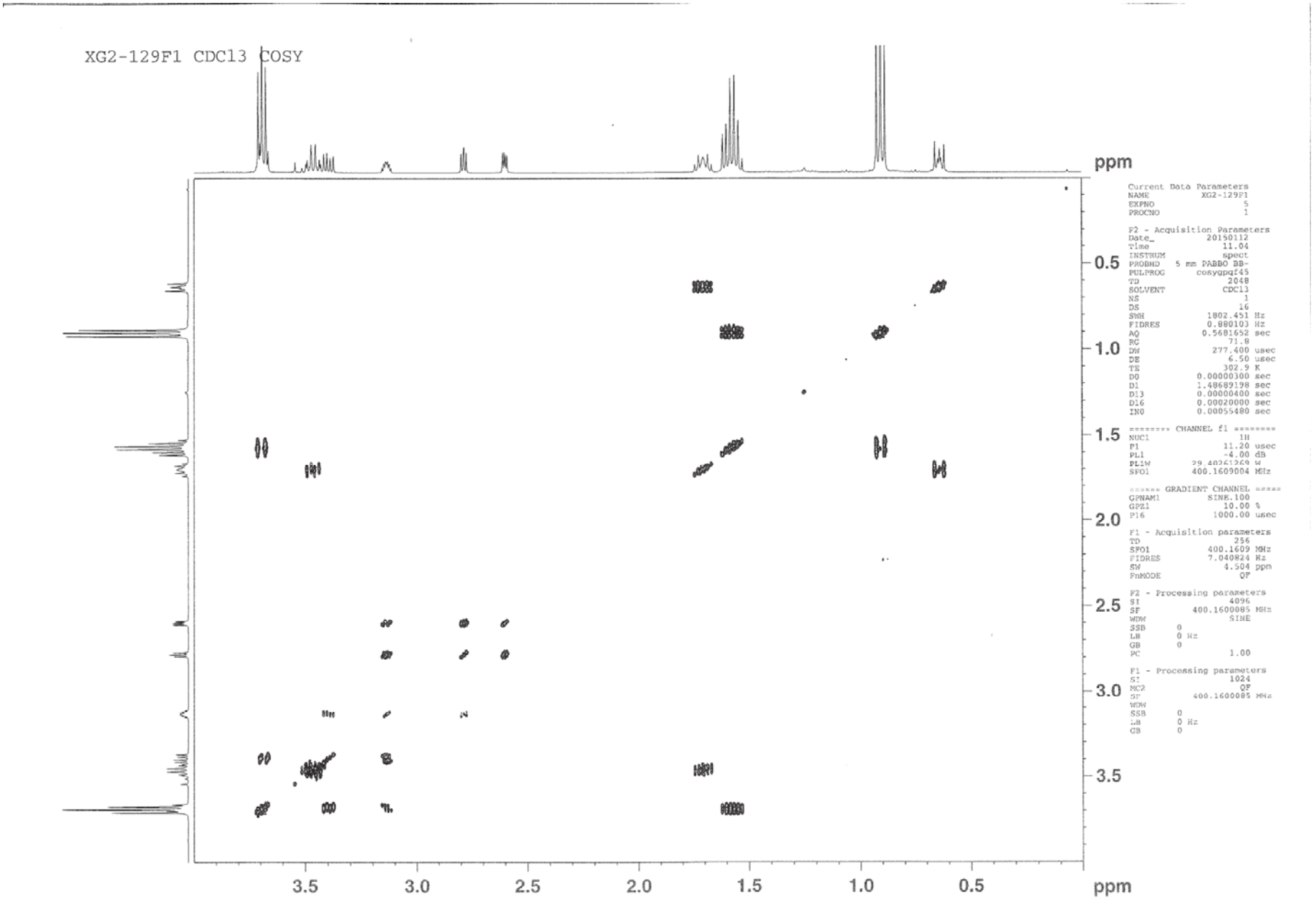


Figure SI_101: ^{1}H-^{1}H COSY NMR spectrum of compound 13a

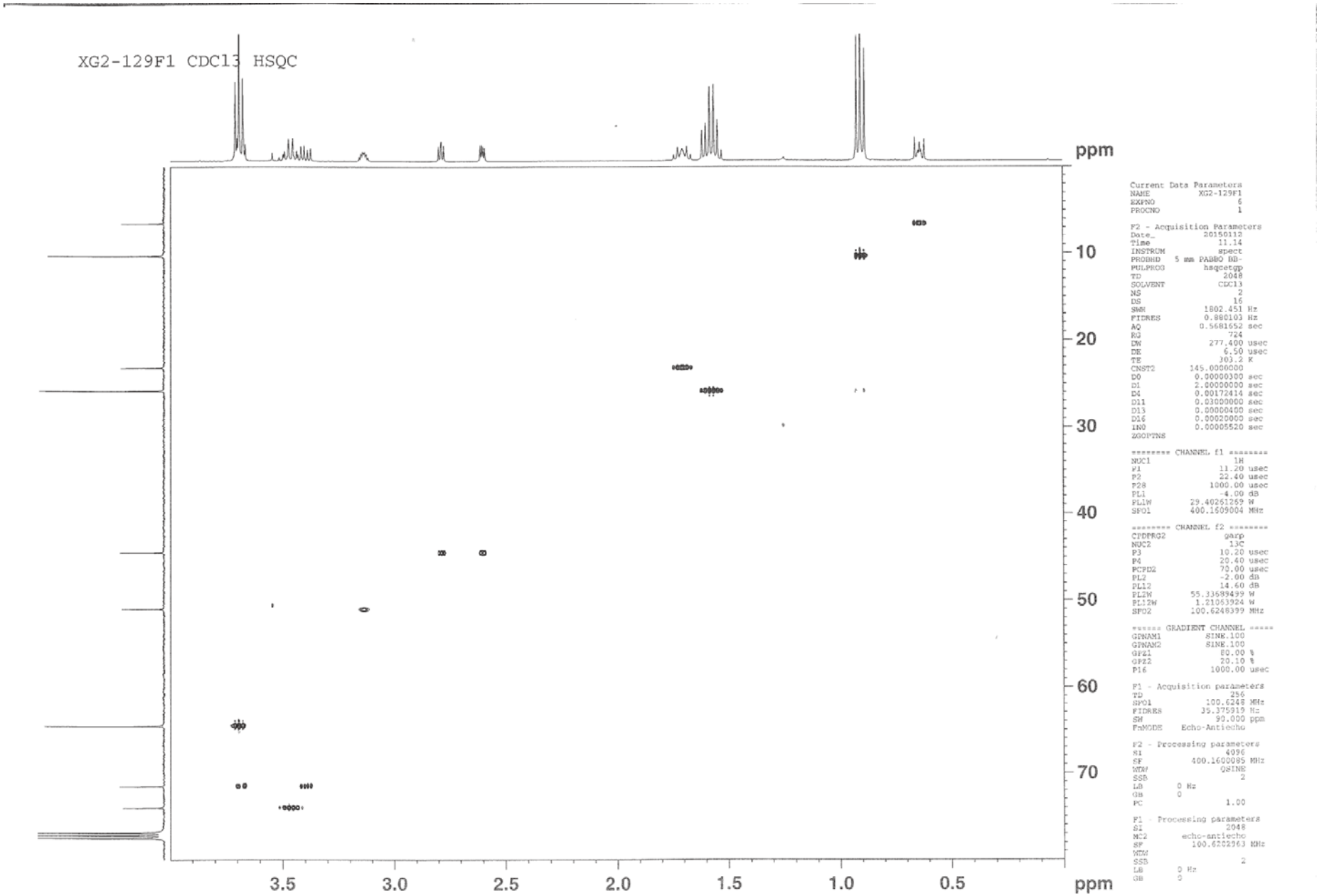


Figure SI_102: HSQC NMR spectrum of compound 13a

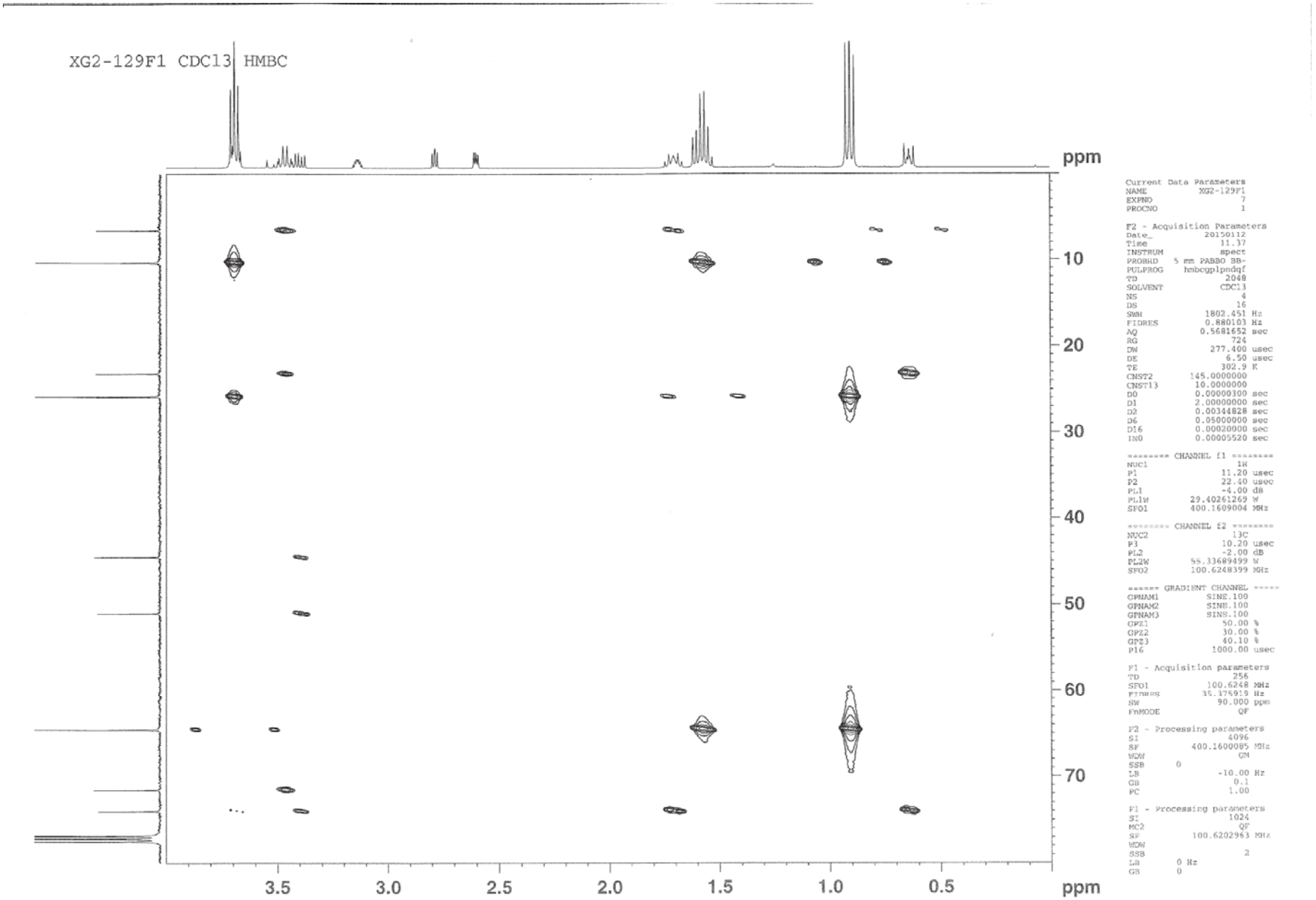


Figure SI_103: HMBC NMR spectrum of compound 13a

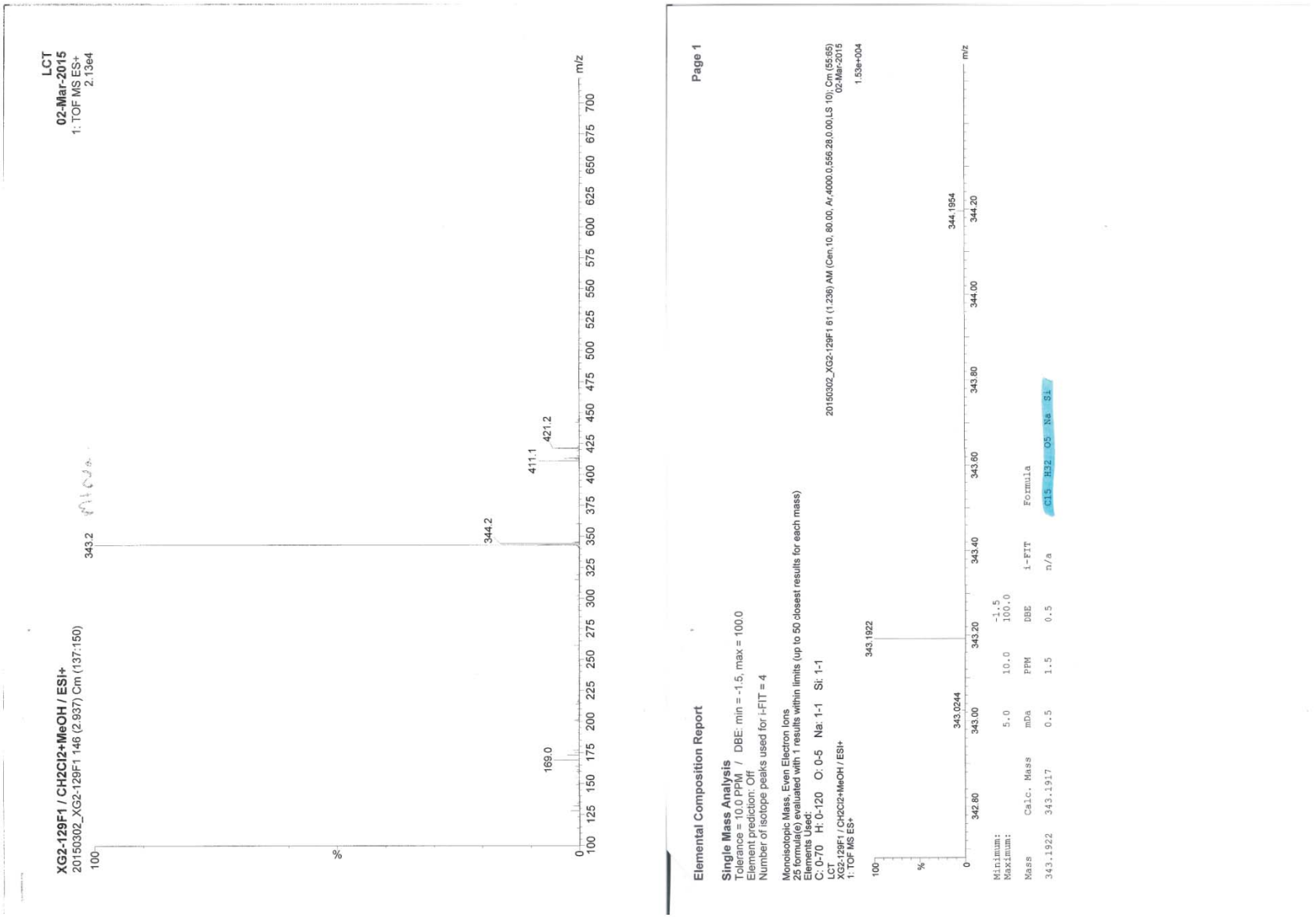
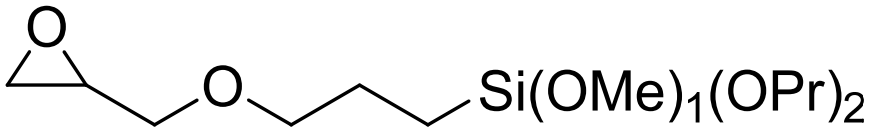


Figure SI_104: ESI HRMS spectrum of compound 13a



13b

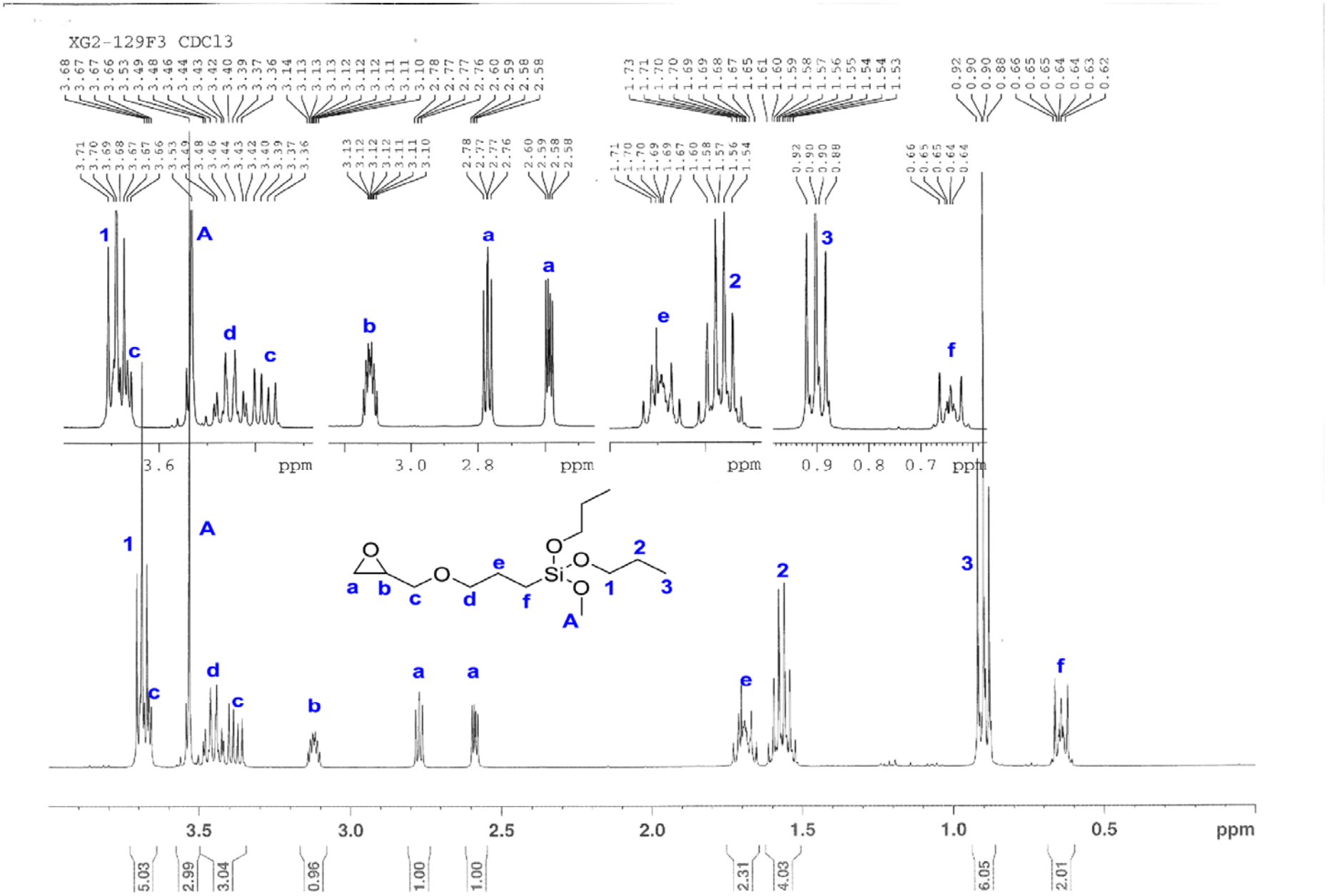


Figure SI_106: ^{1}H NMR spectrum of compound 13b

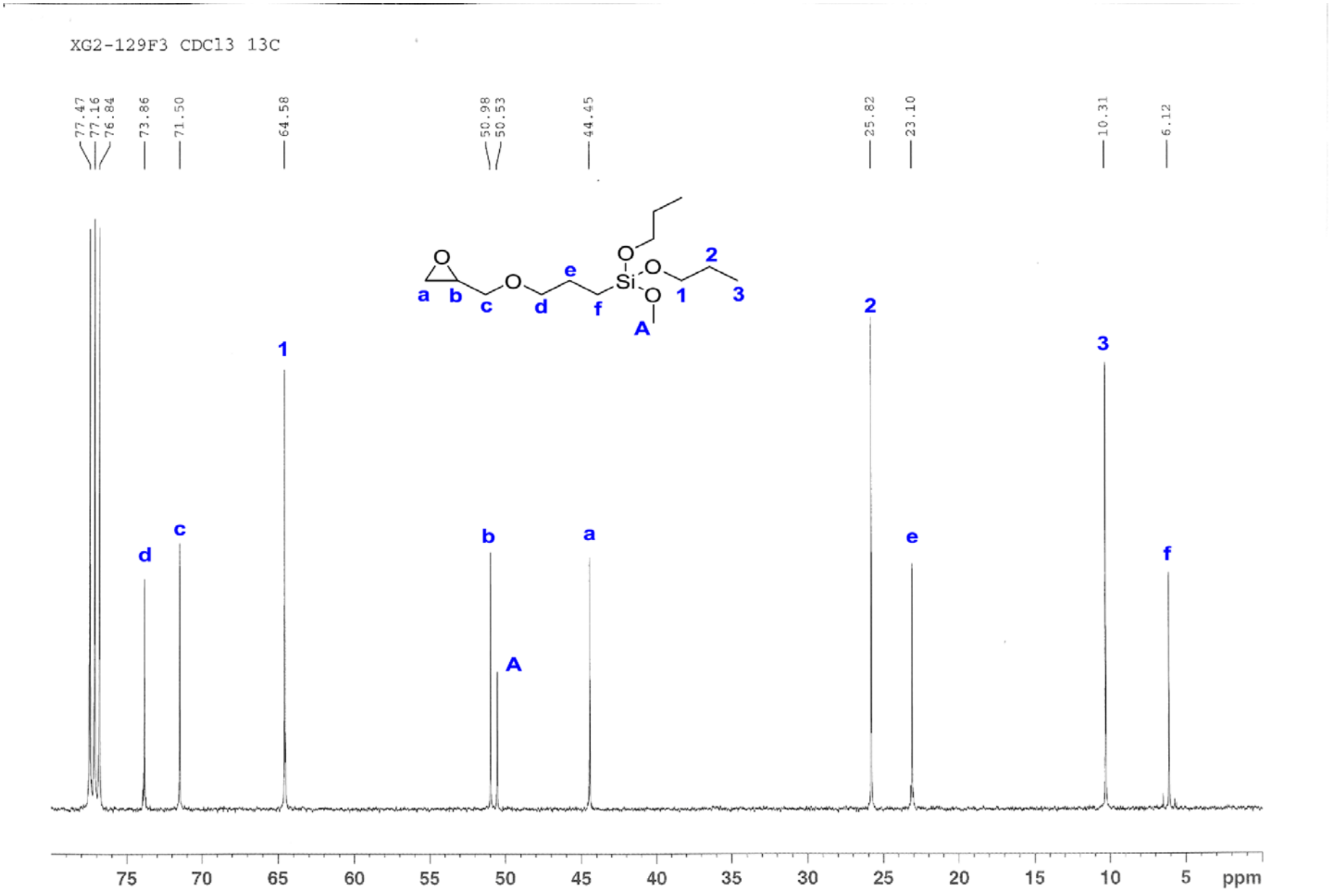


Figure SI_107: ^{13}C NMR spectrum of compound 13b

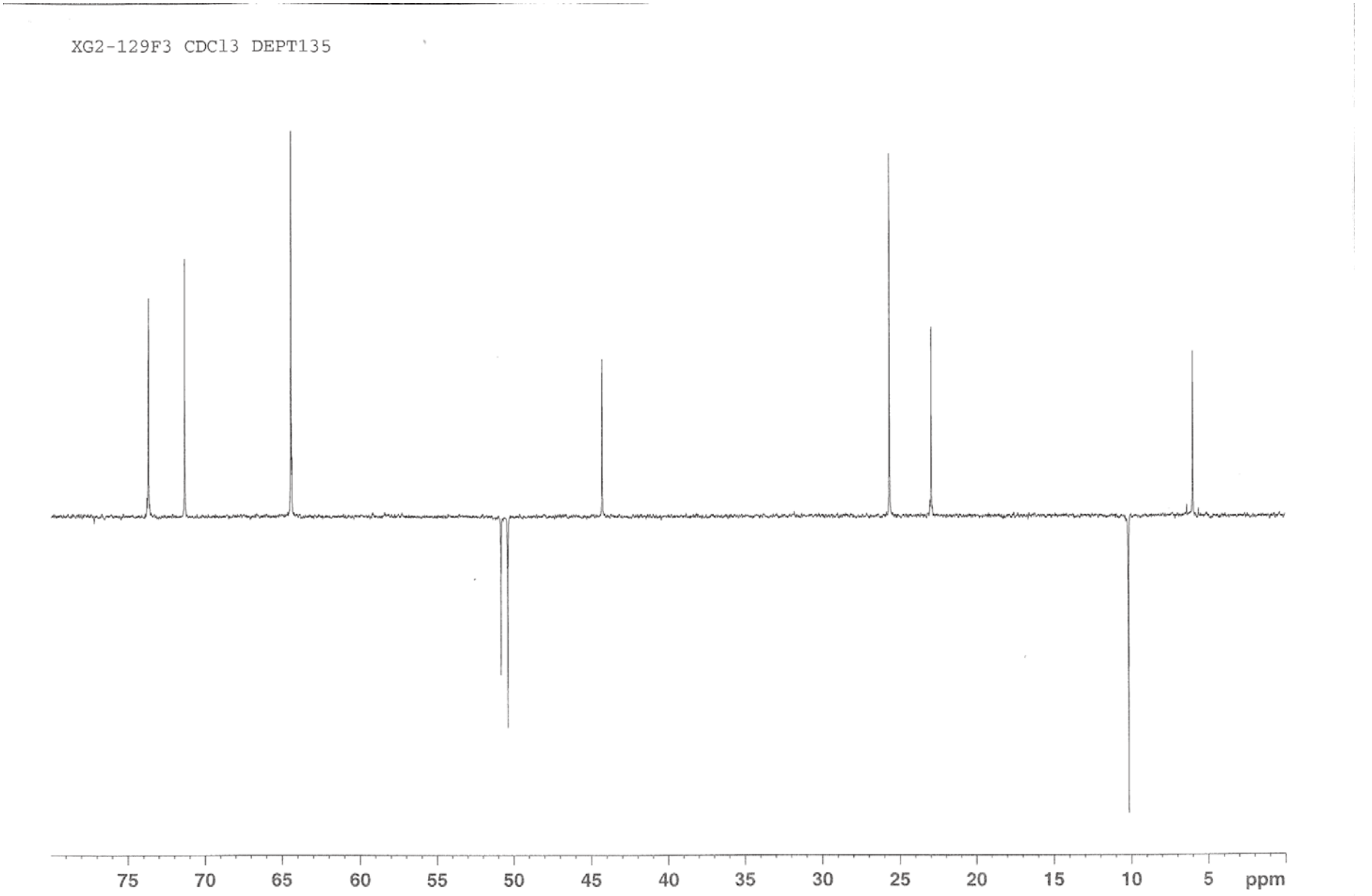


Figure SI_108: DEPT135 NMR spectrum of compound 13b

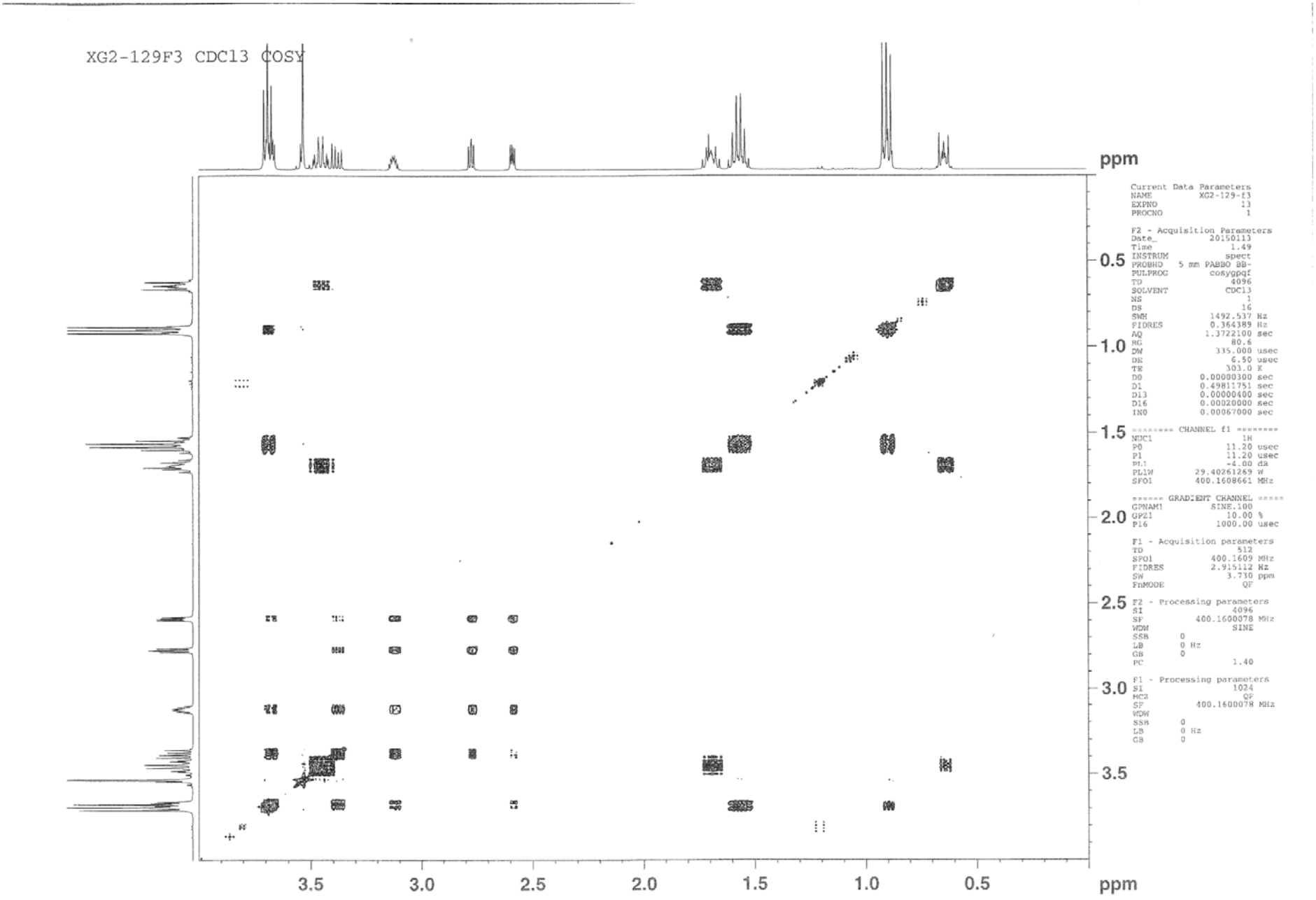


Figure SI_109: ^{1}H-^{1}H COSY NMR spectrum of compound 13b

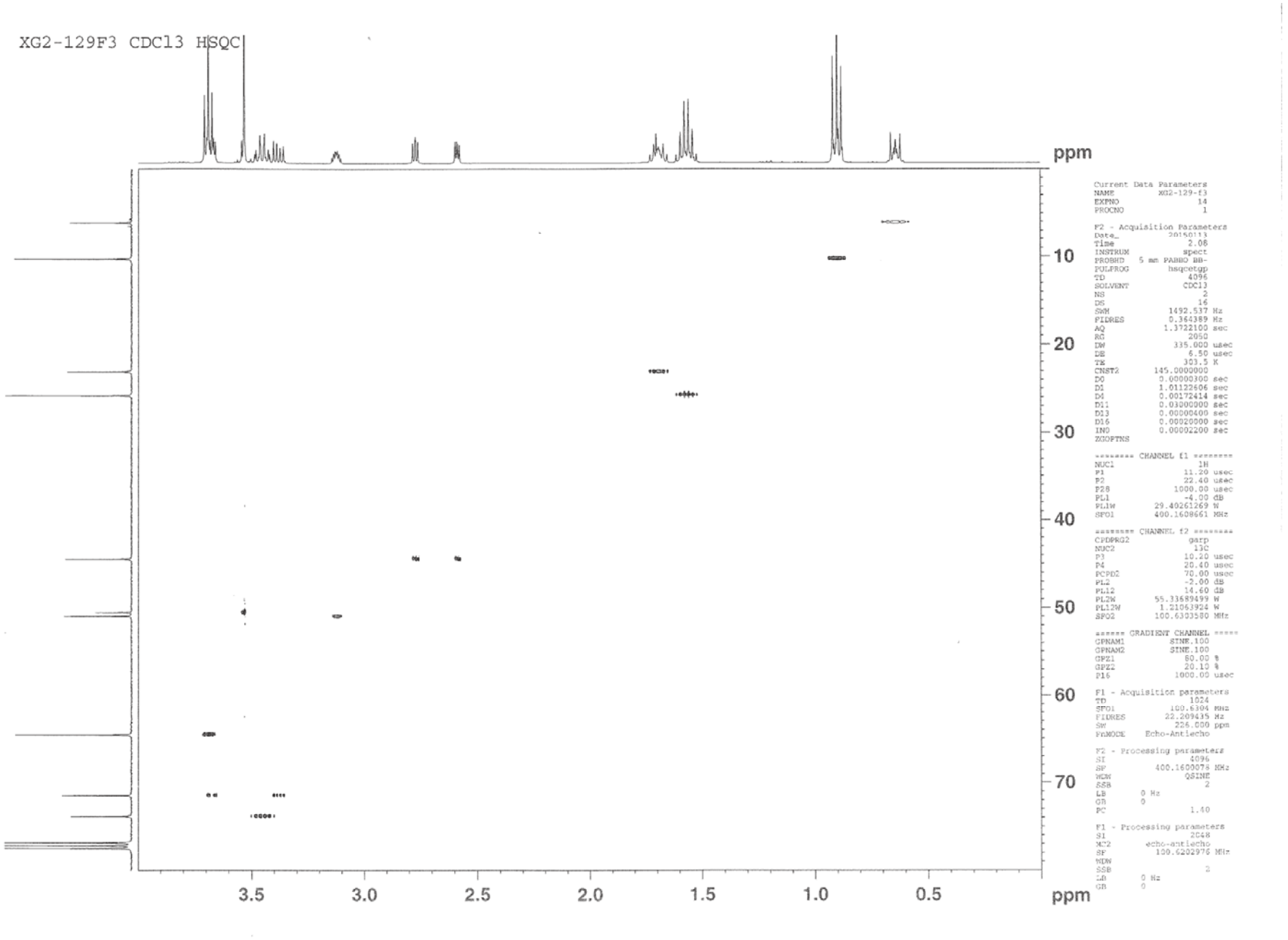


Figure SI_110: HSQC NMR spectrum of compound 13b

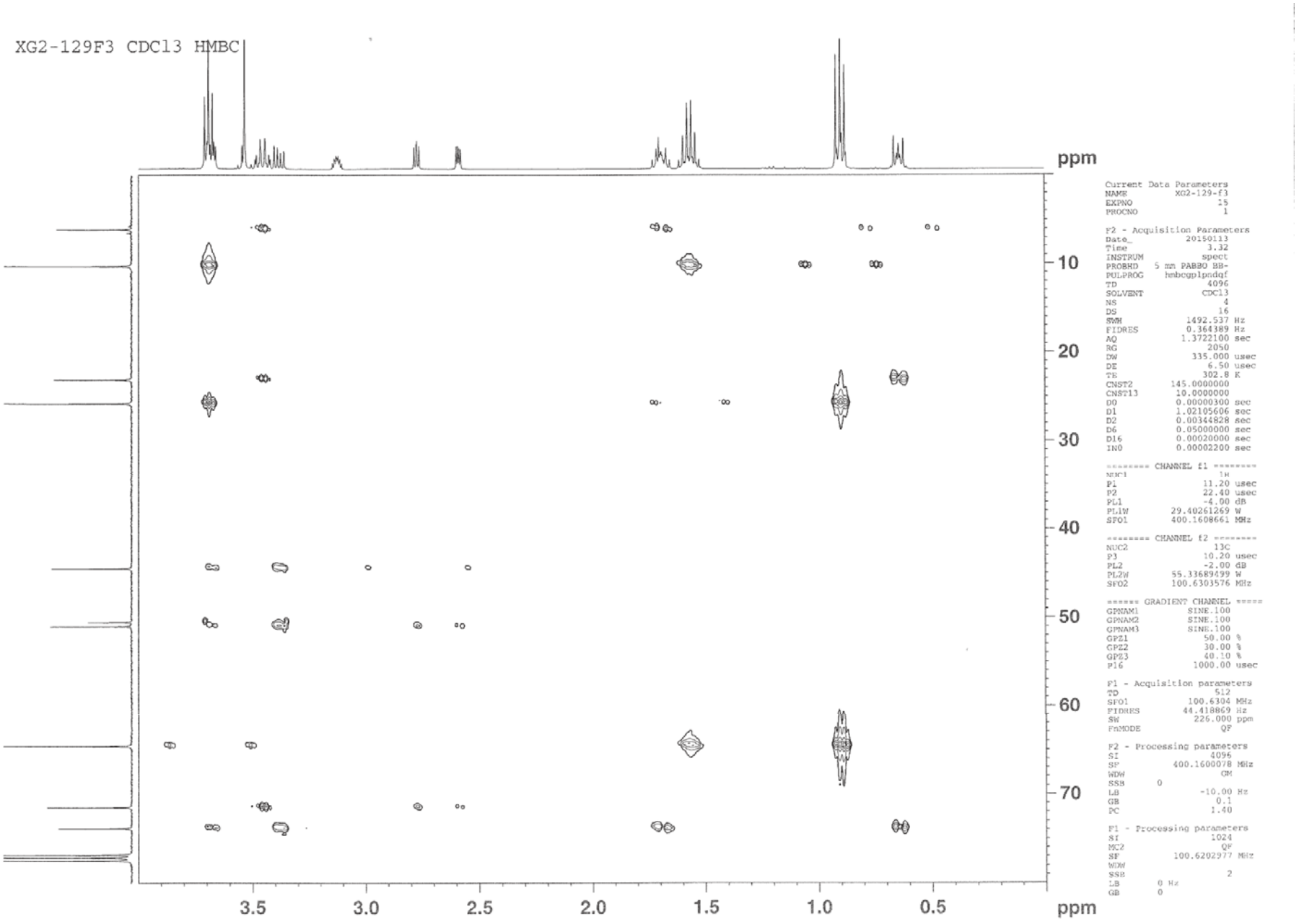


Figure SI_111: HMBC NMR spectrum of compound 13b

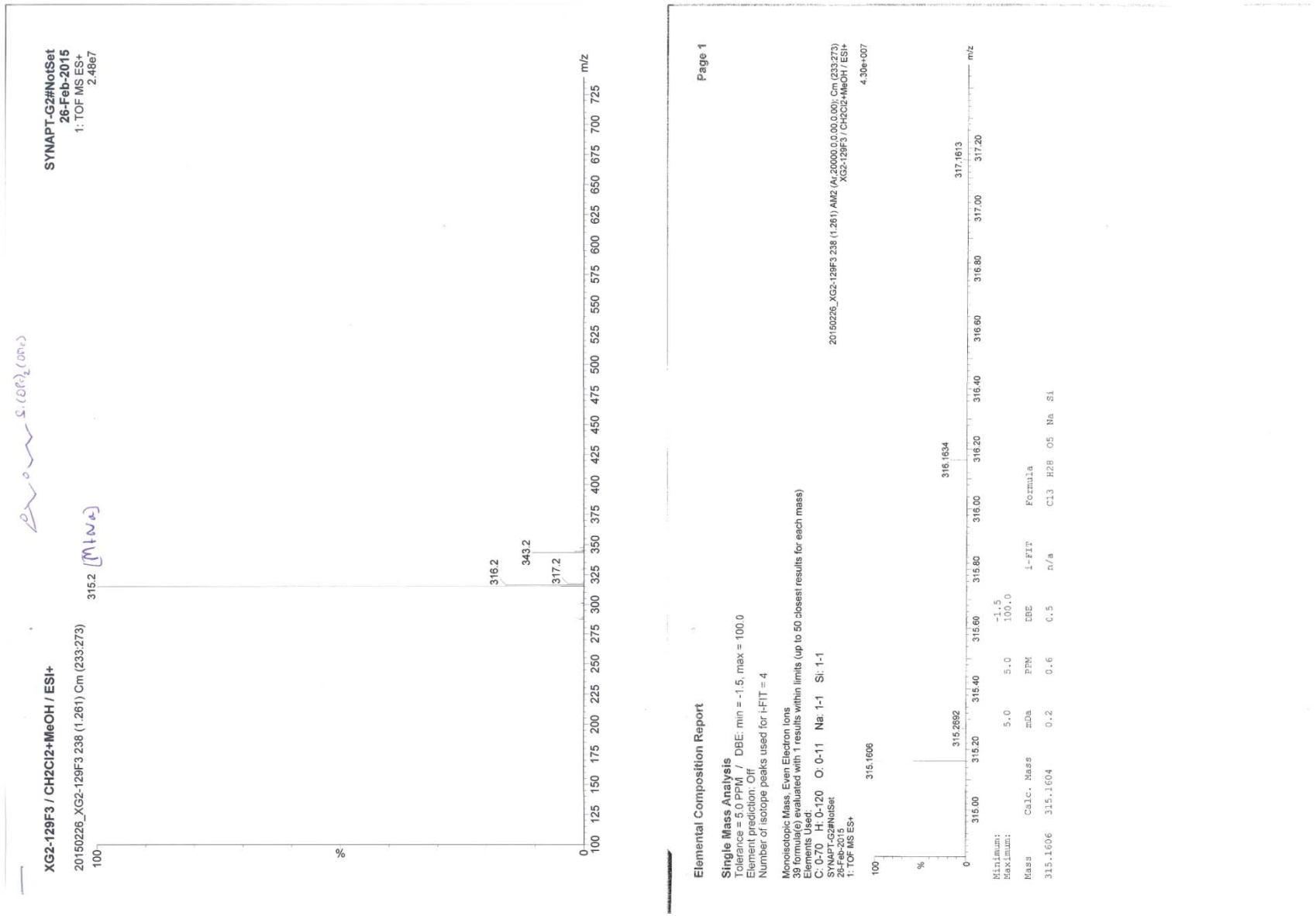
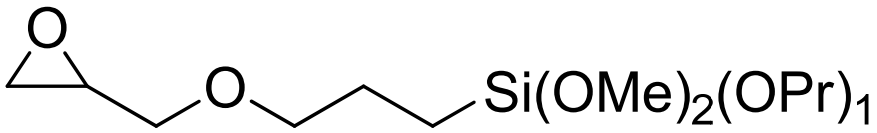


Figure SI_112: ESI-HRMS spectrum of compound 13b



13c

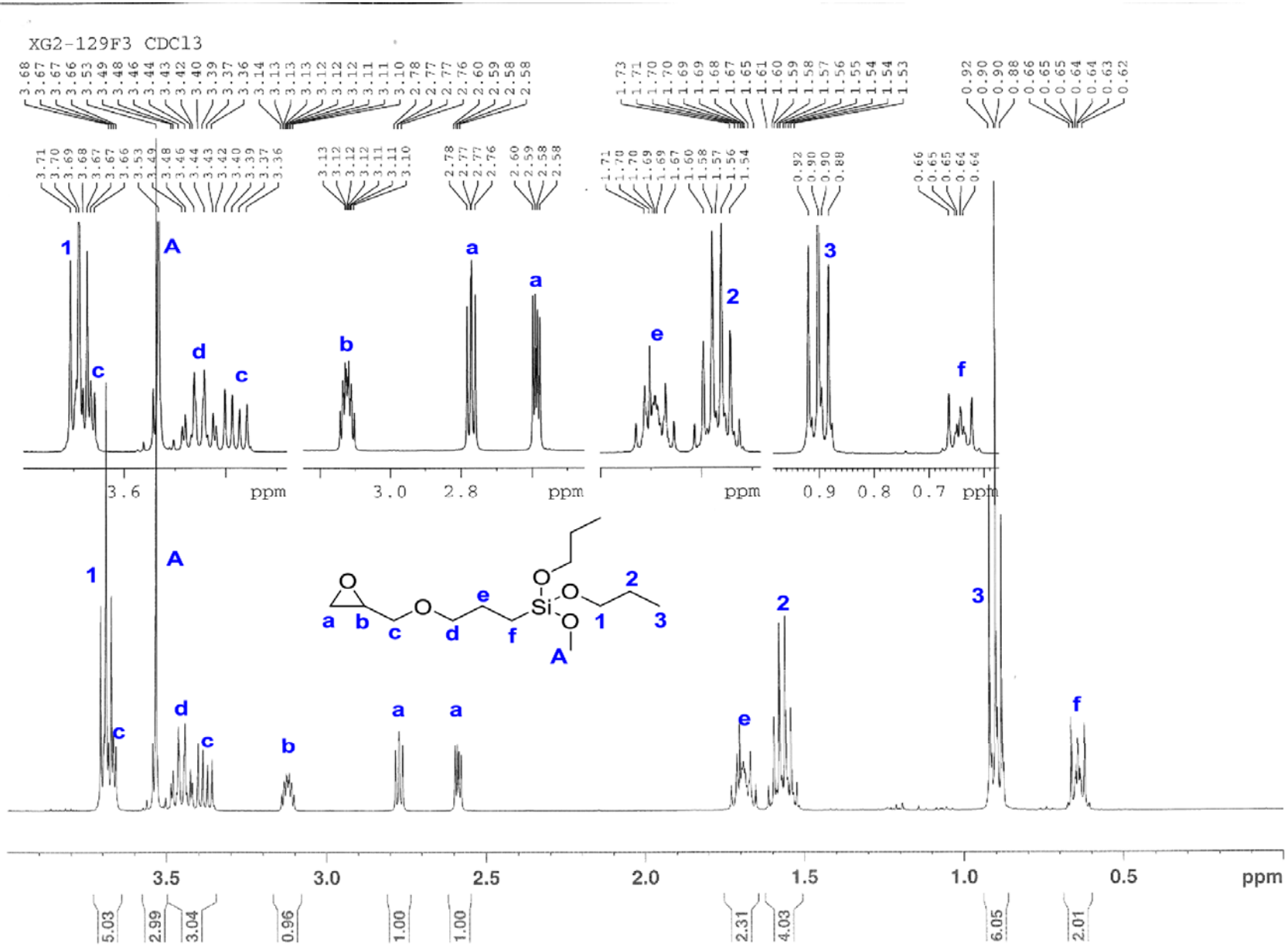


Figure SI_114: ^{1}H NMR spectrum of compound 13c

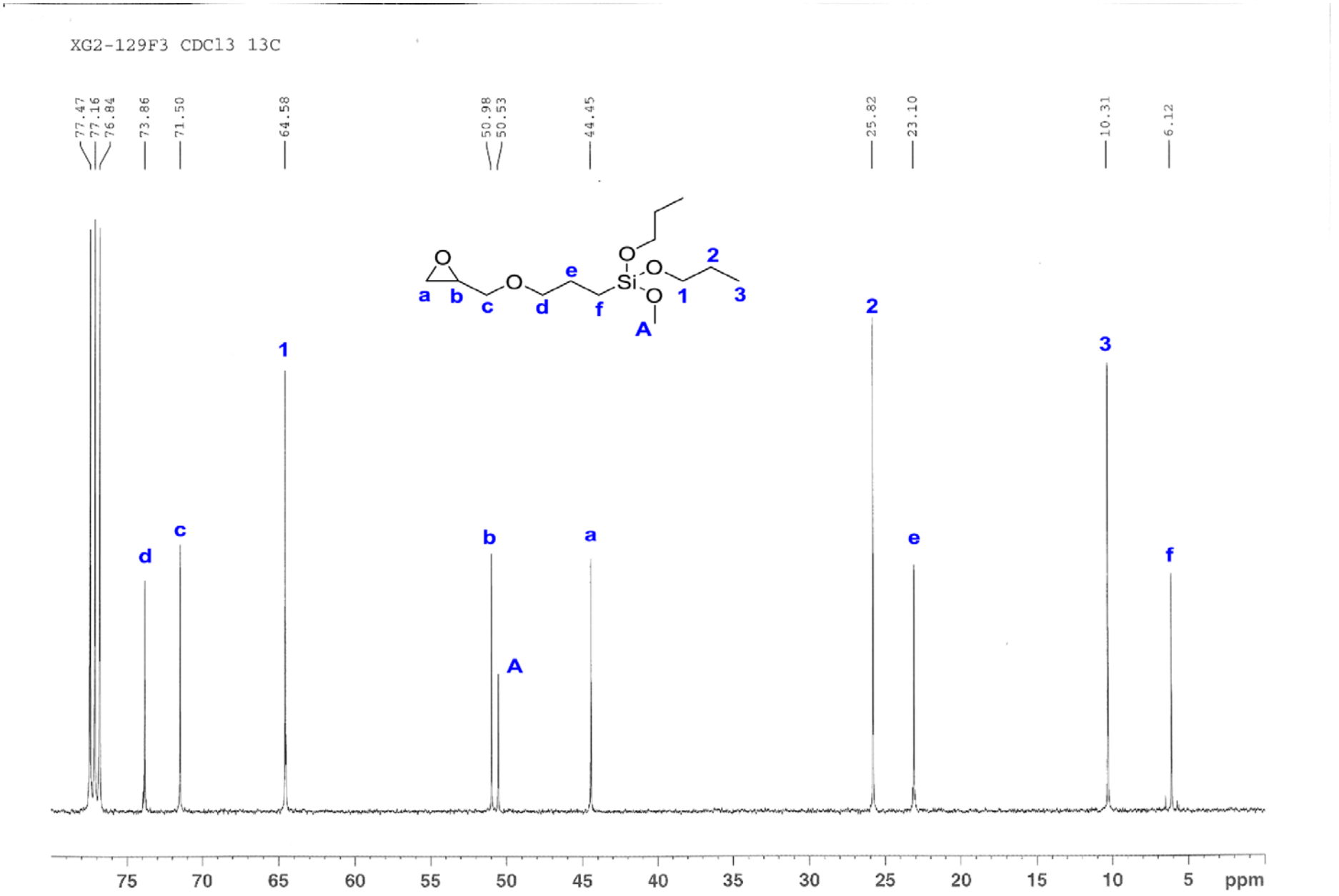


Figure SI_115: ^{13}C NMR spectrum of compound 13c

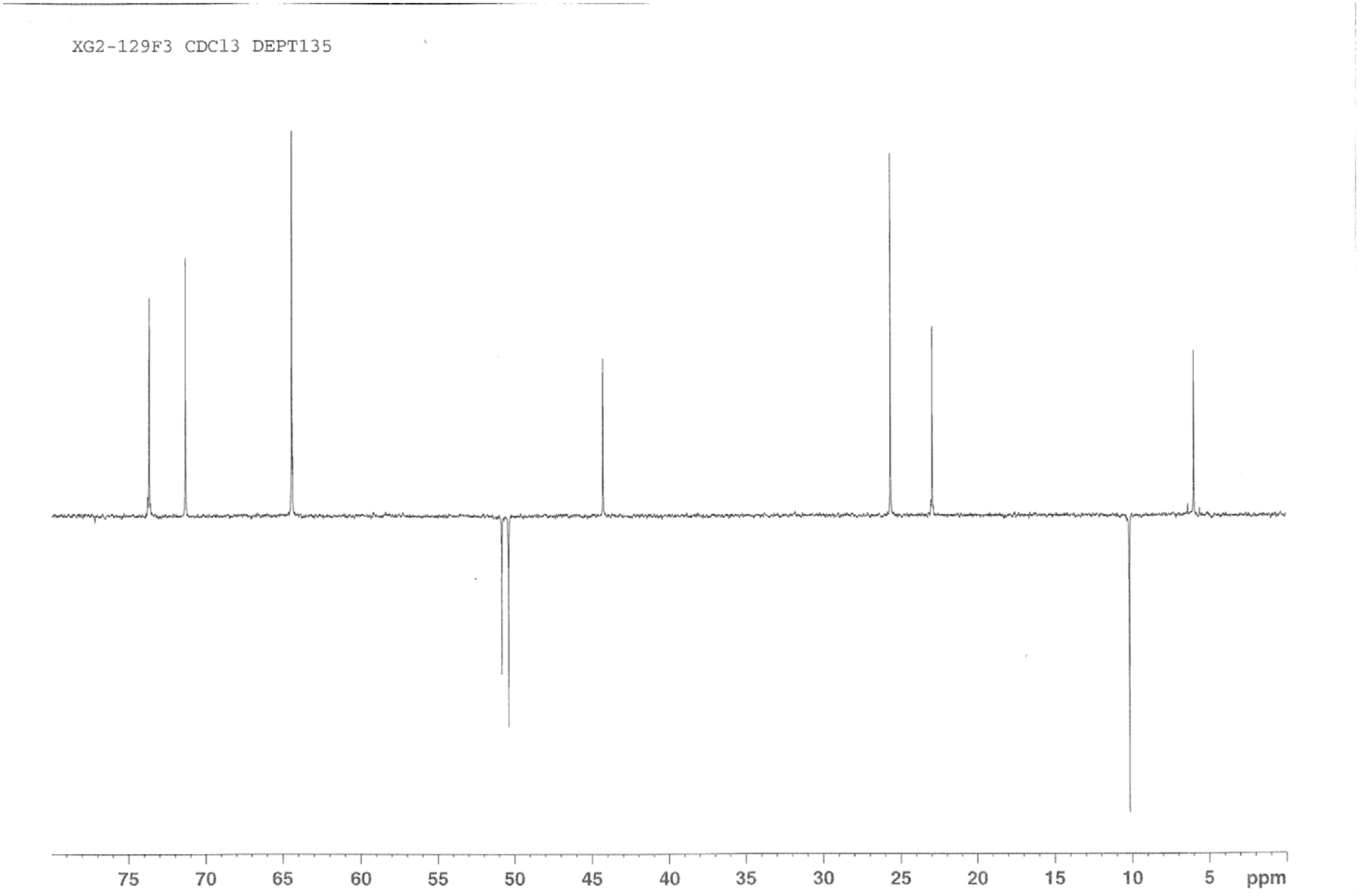


Figure SI_116: DEPT135 NMR spectrum of compound 13c

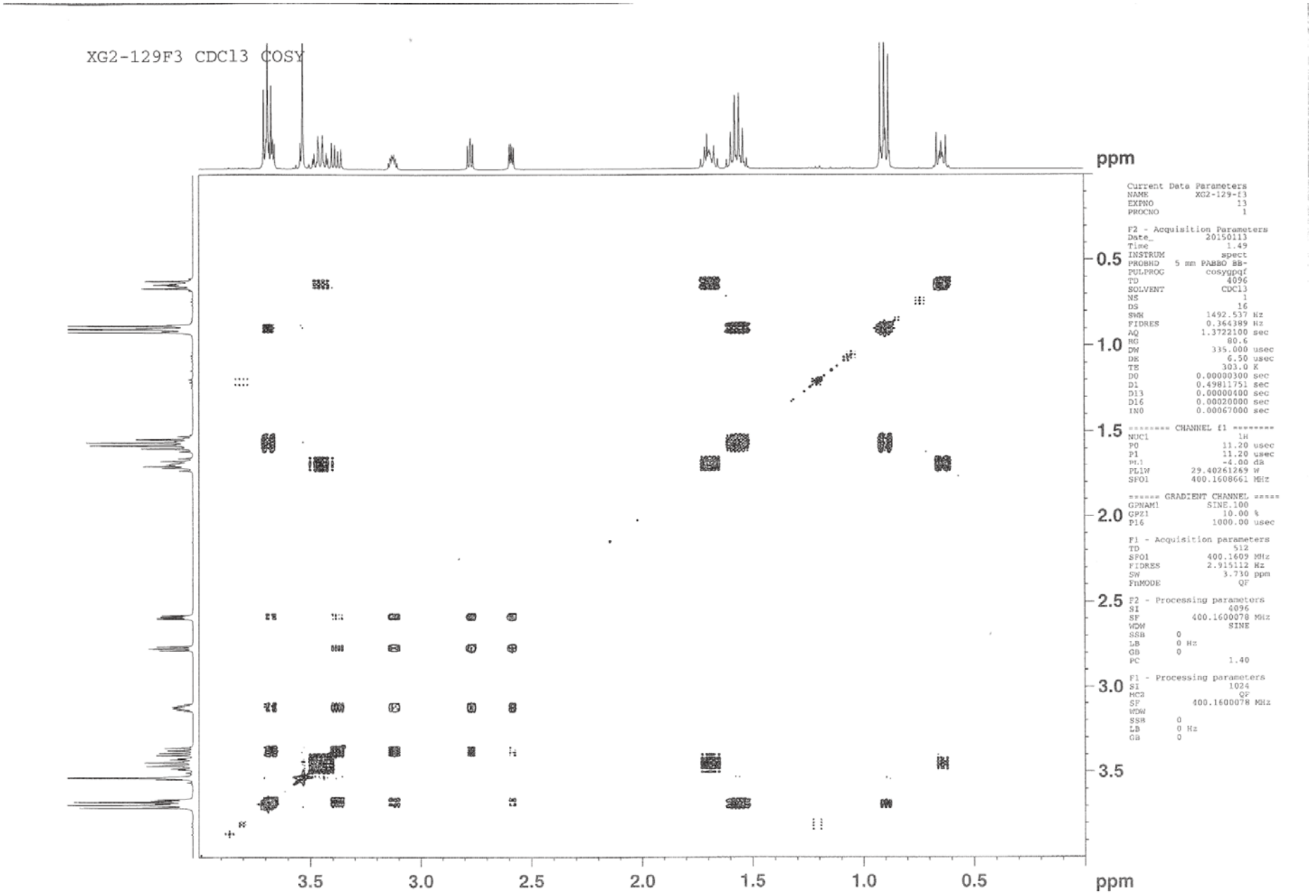


Figure SI_117: ^{1}H-^{1}H COSY NMR spectrum of compound 13c

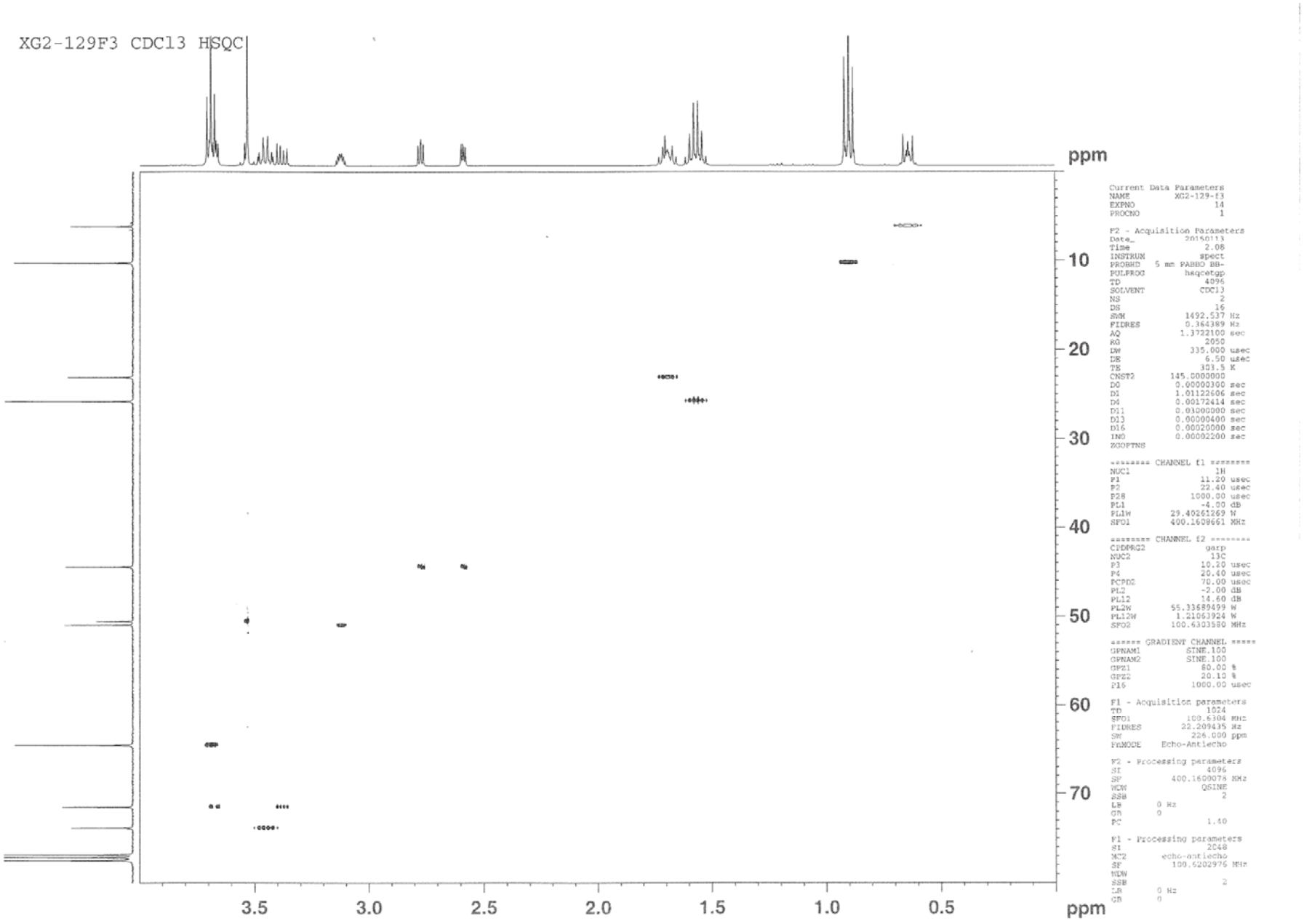


Figure SI_118: HSQC NMR spectrum of compound 13c

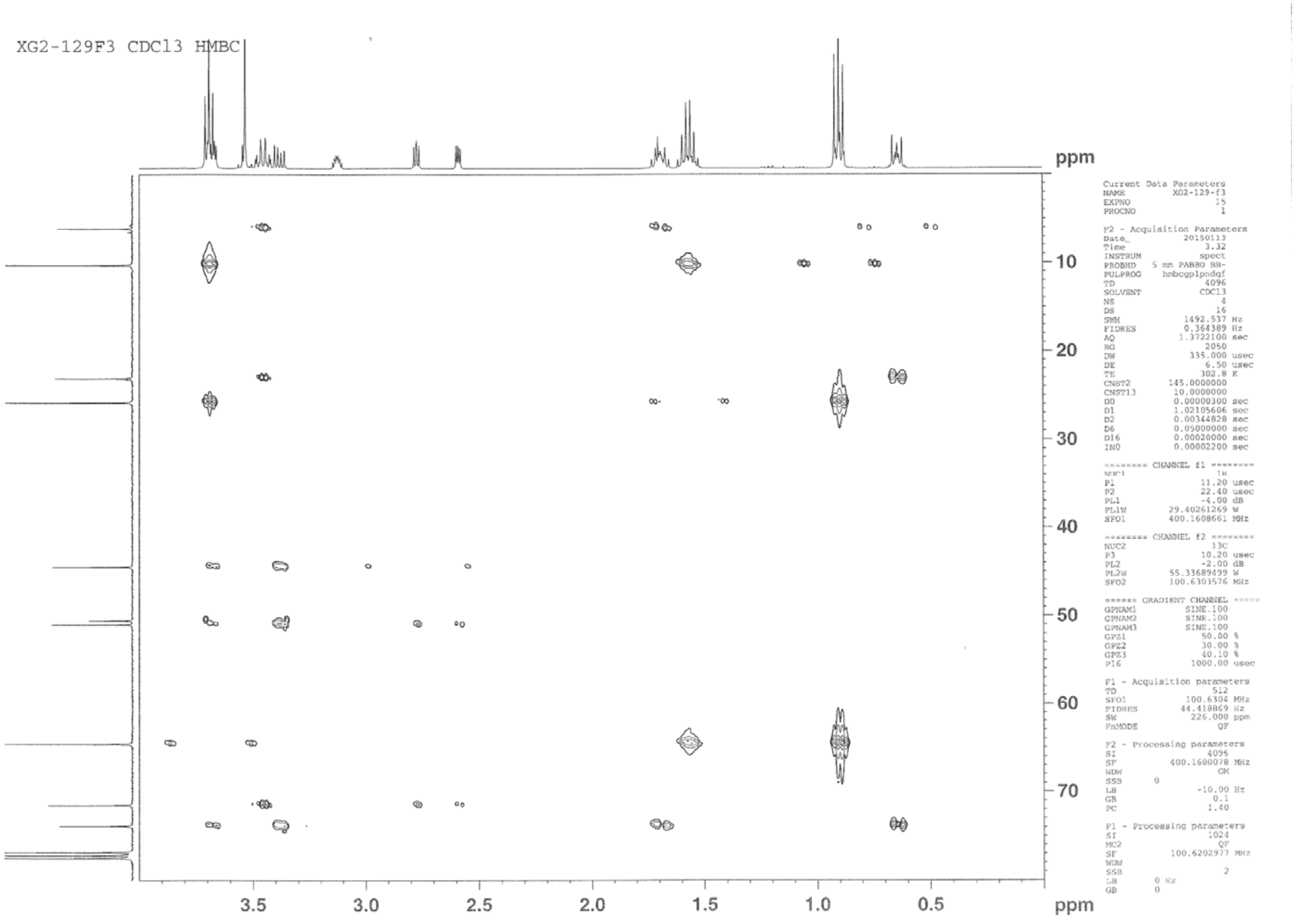


Figure SI_119: HMBC NMR spectrum of compound 13c

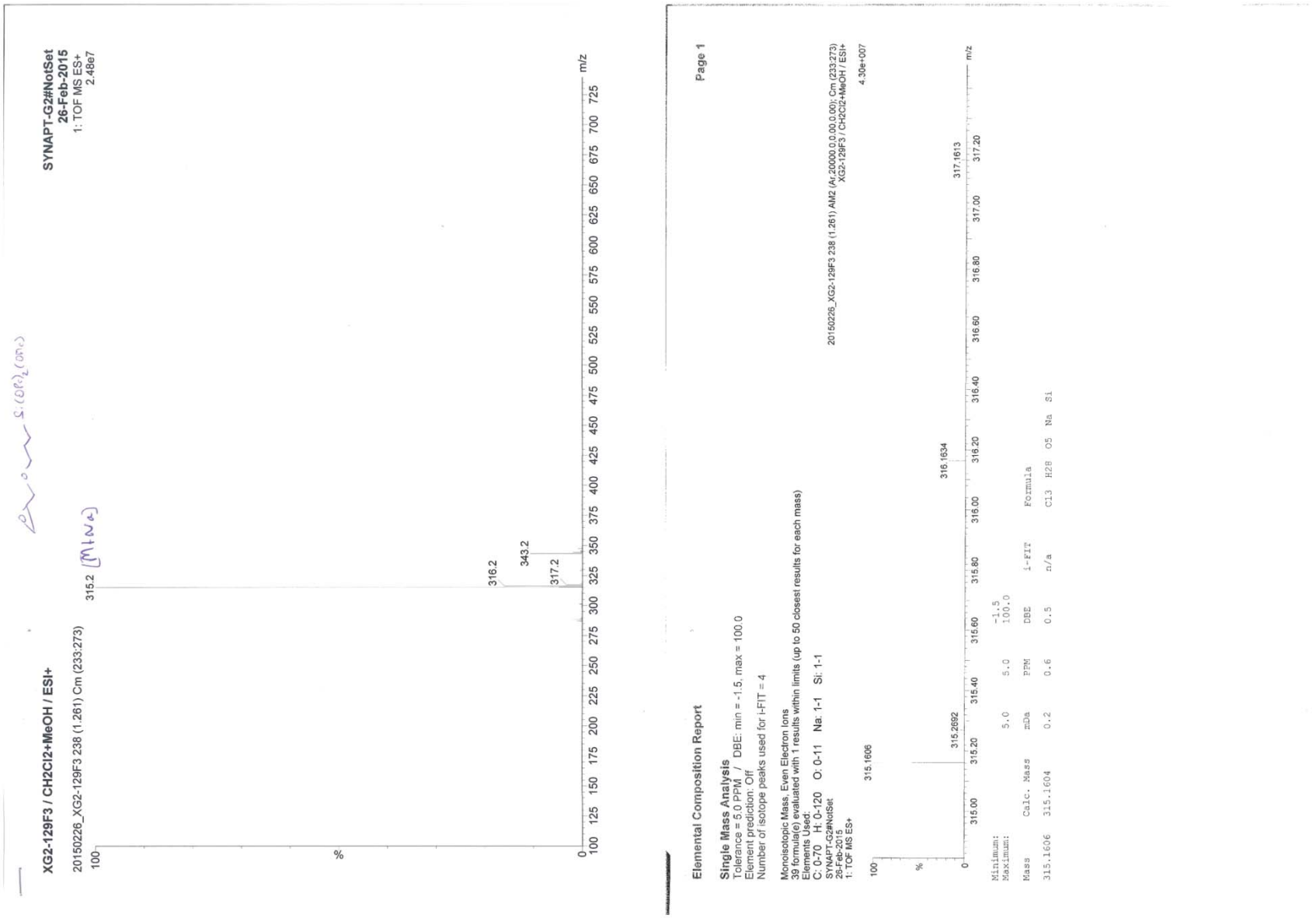
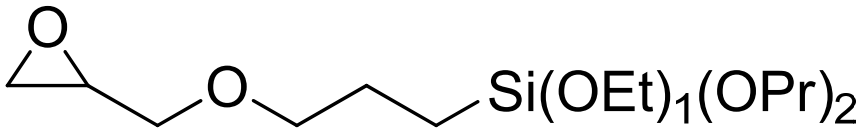


Figure SI_1202: ESI-HRMS NMR spectrum of compound 13c



14a

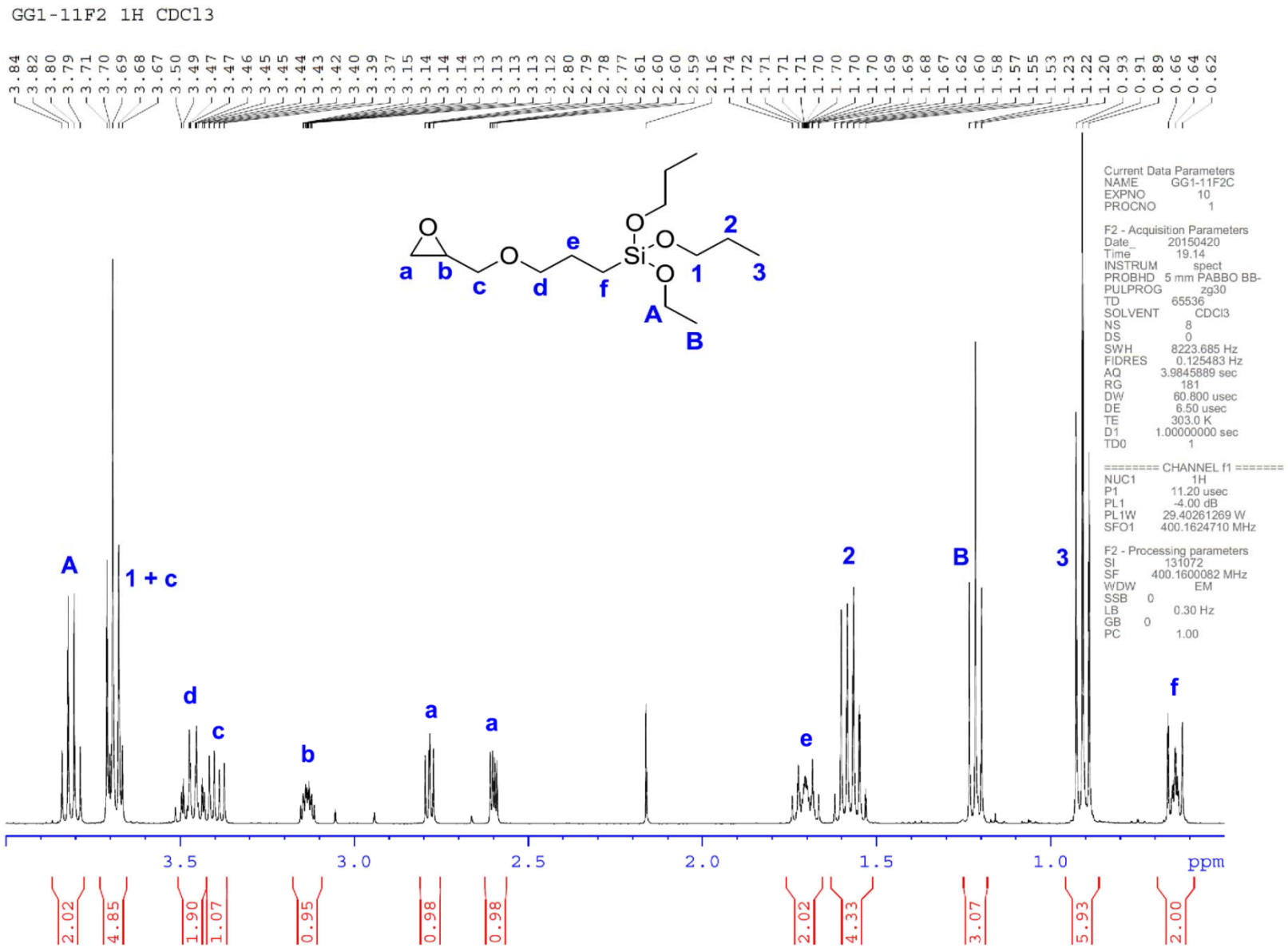


Figure SI_122: ^{1}H NMR spectrum of compound 14a

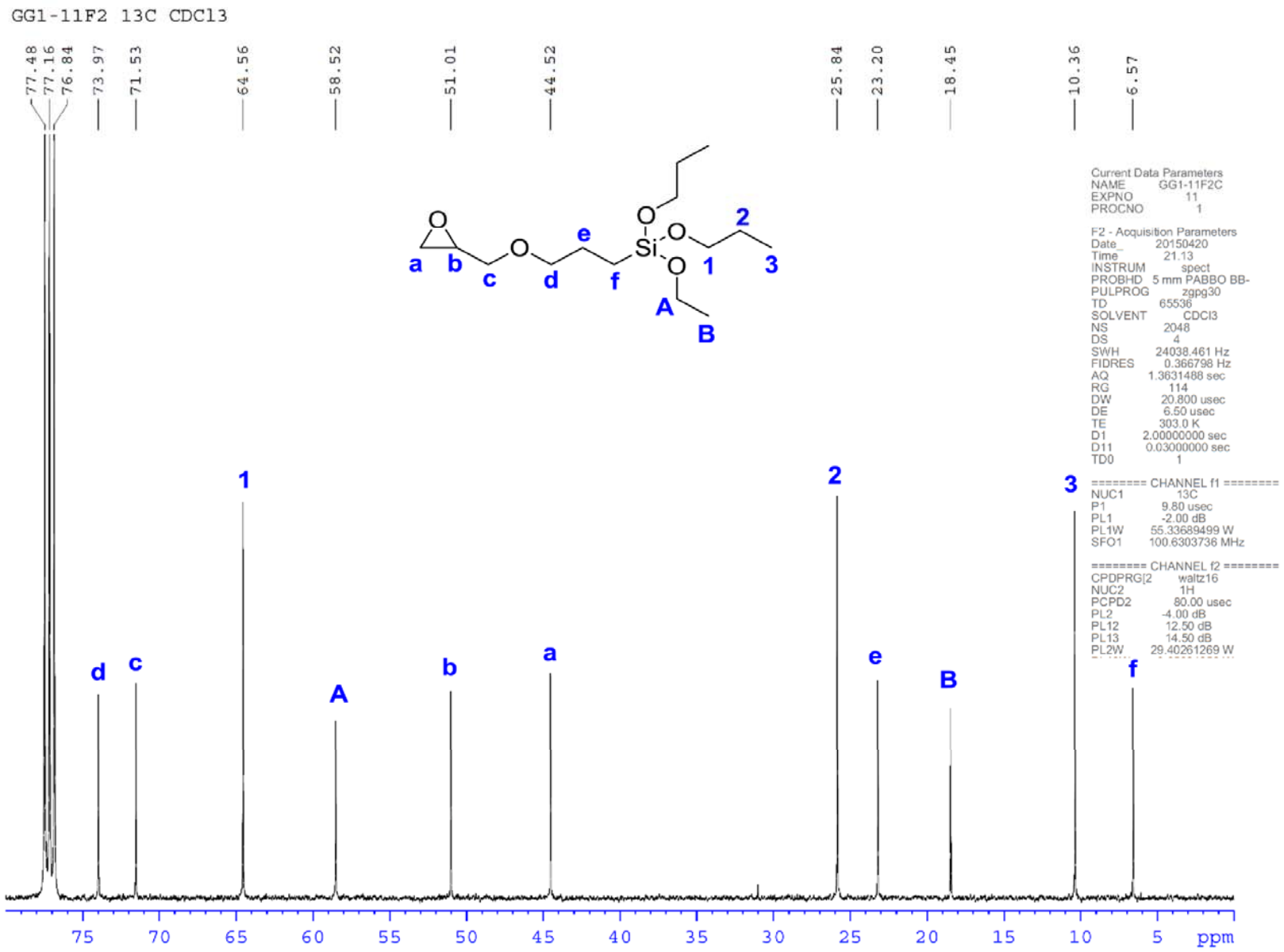


Figure SI_123: ^{13}C NMR spectrum of compound 14a

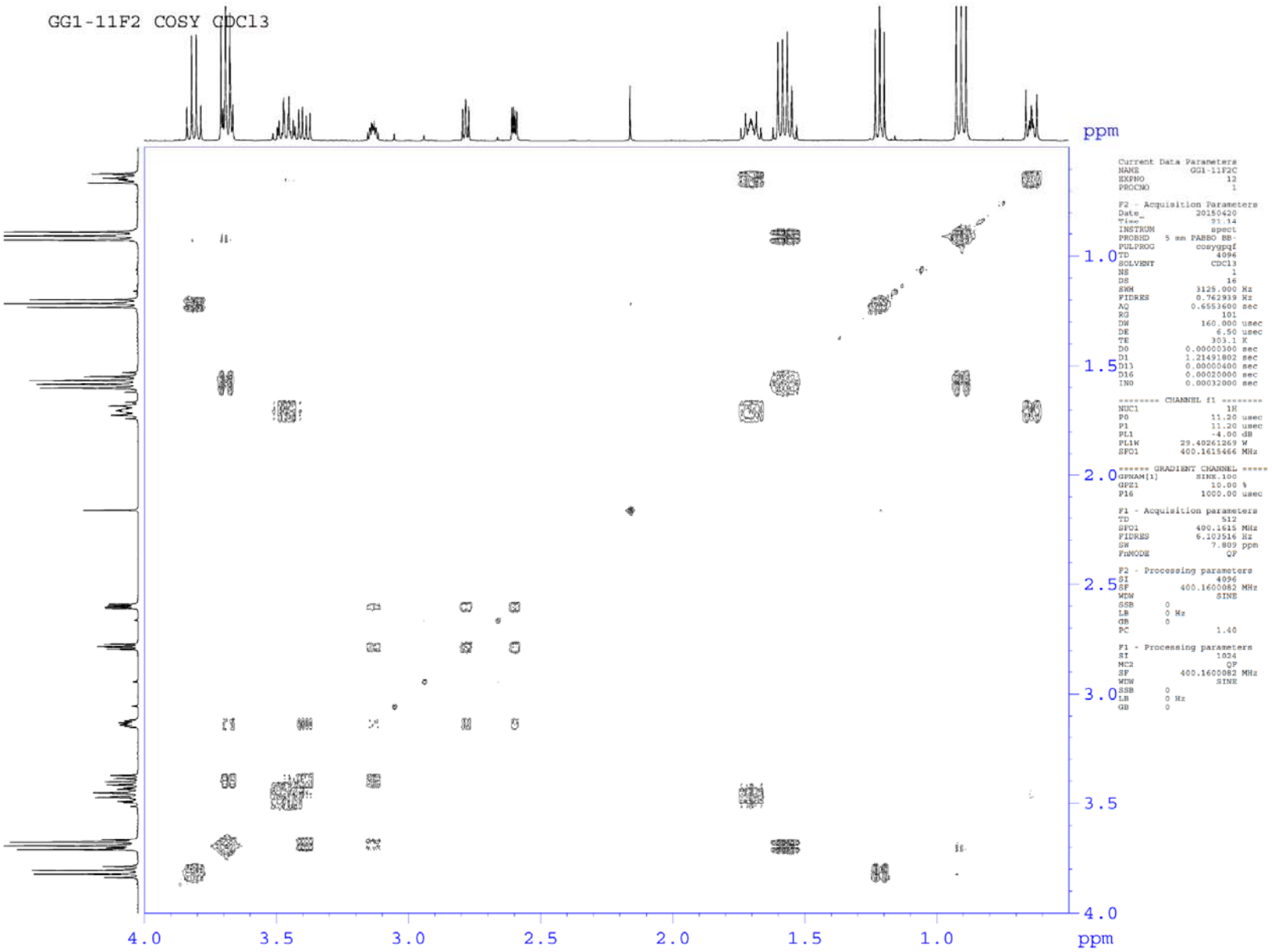


Figure SI_124: ^{1}H-^{1}H COSY NMR spectrum of compound 14a

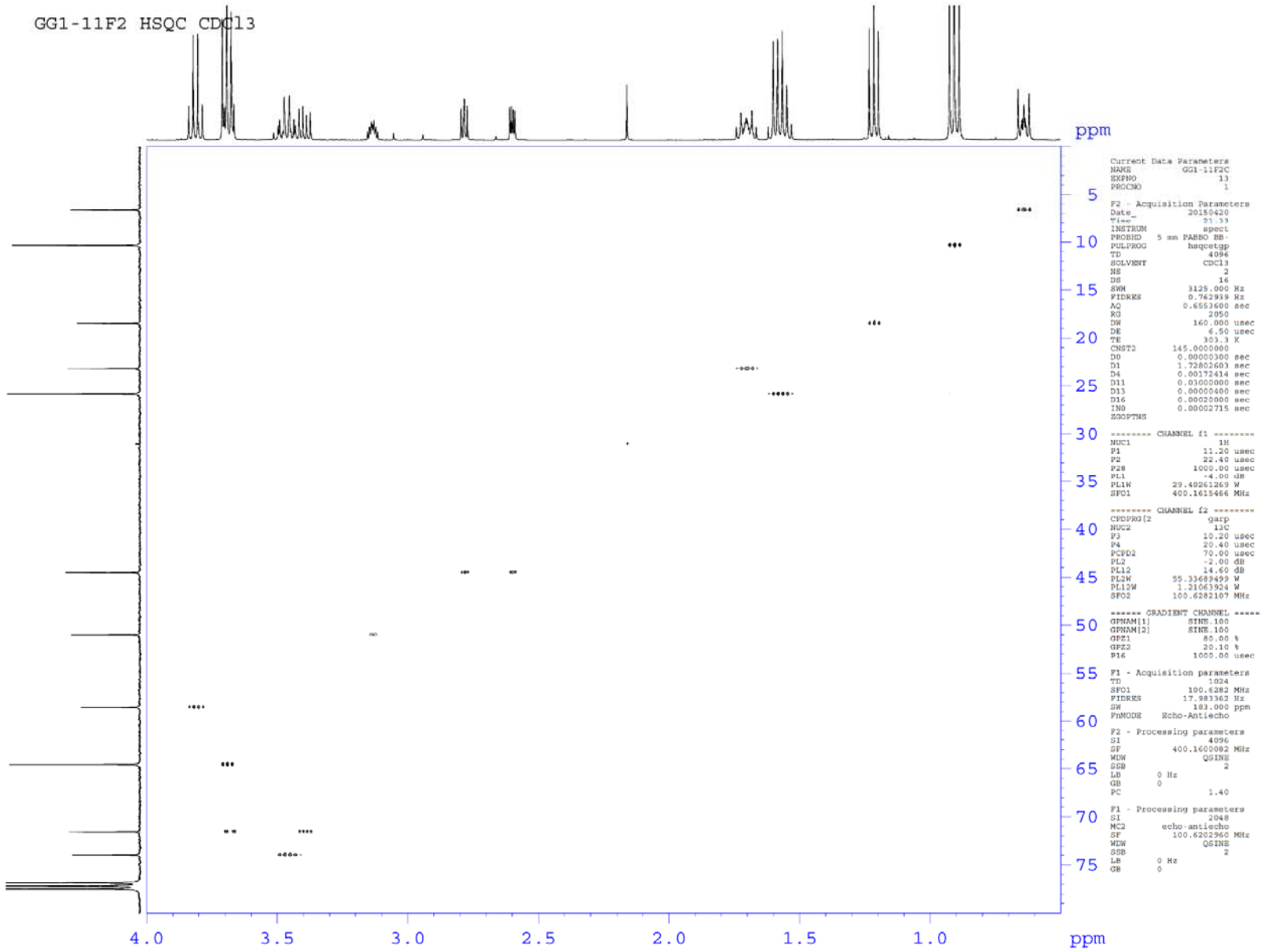


Figure SI_125: HSQC NMR spectrum of compound 14a

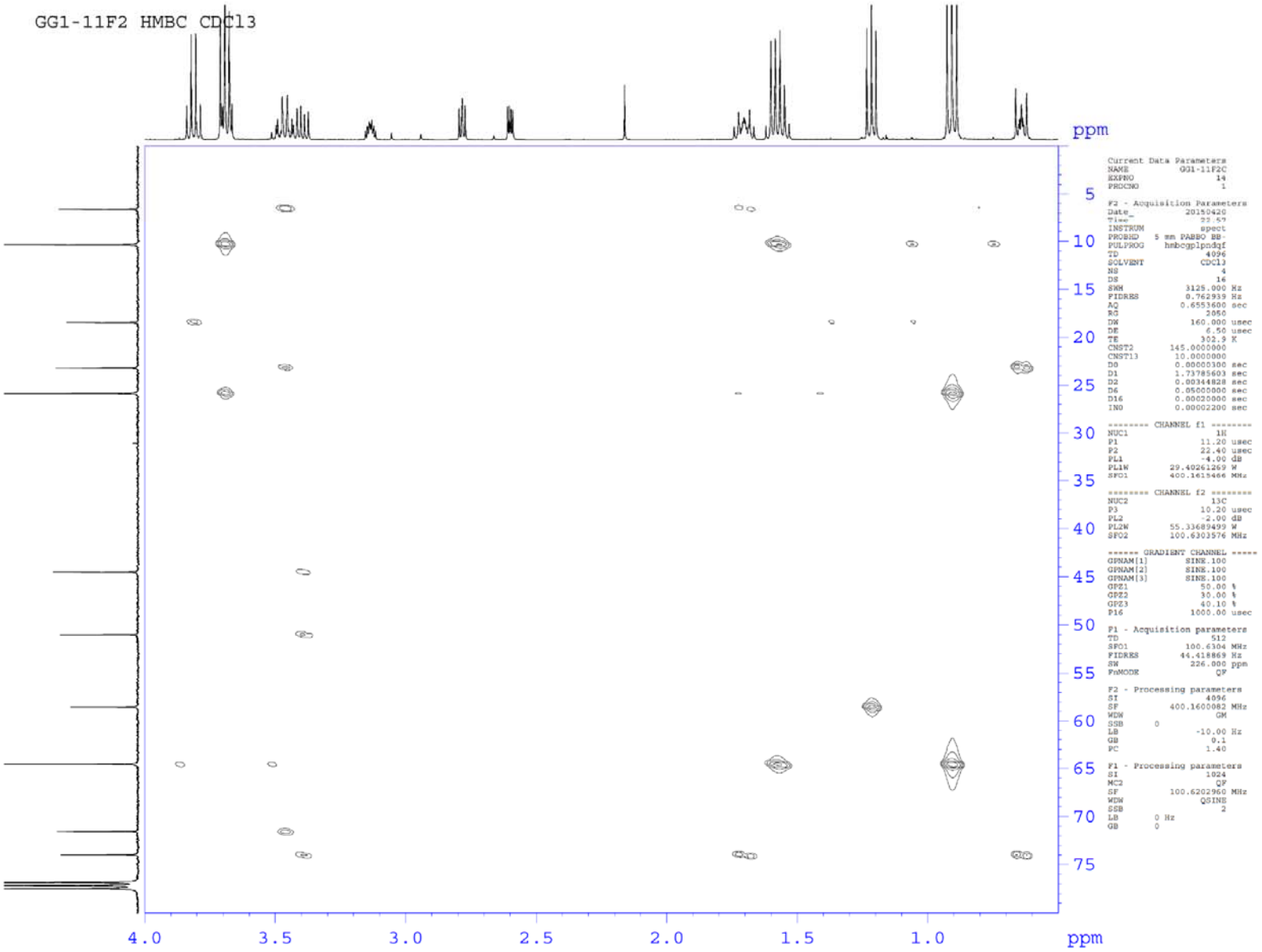


Figure SI_126: HMBC NMR spectrum of compound 14a

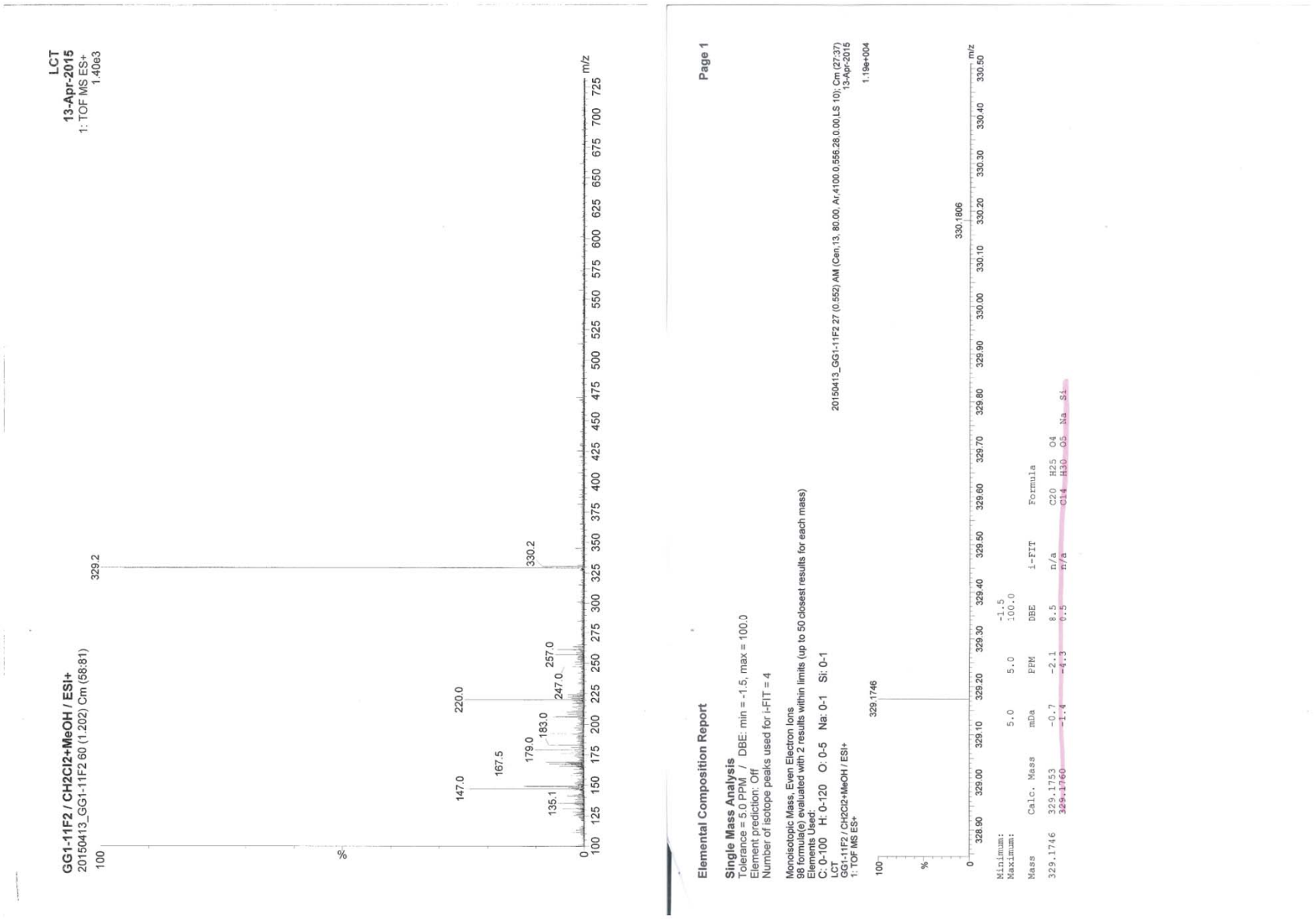
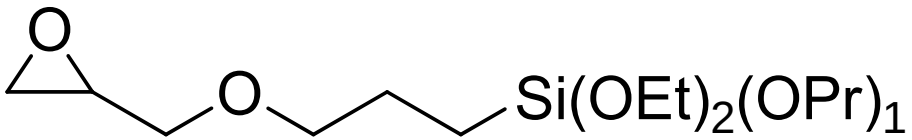


Figure SI_127: ESI HRMS NMR spectrum of compound 14a



14b

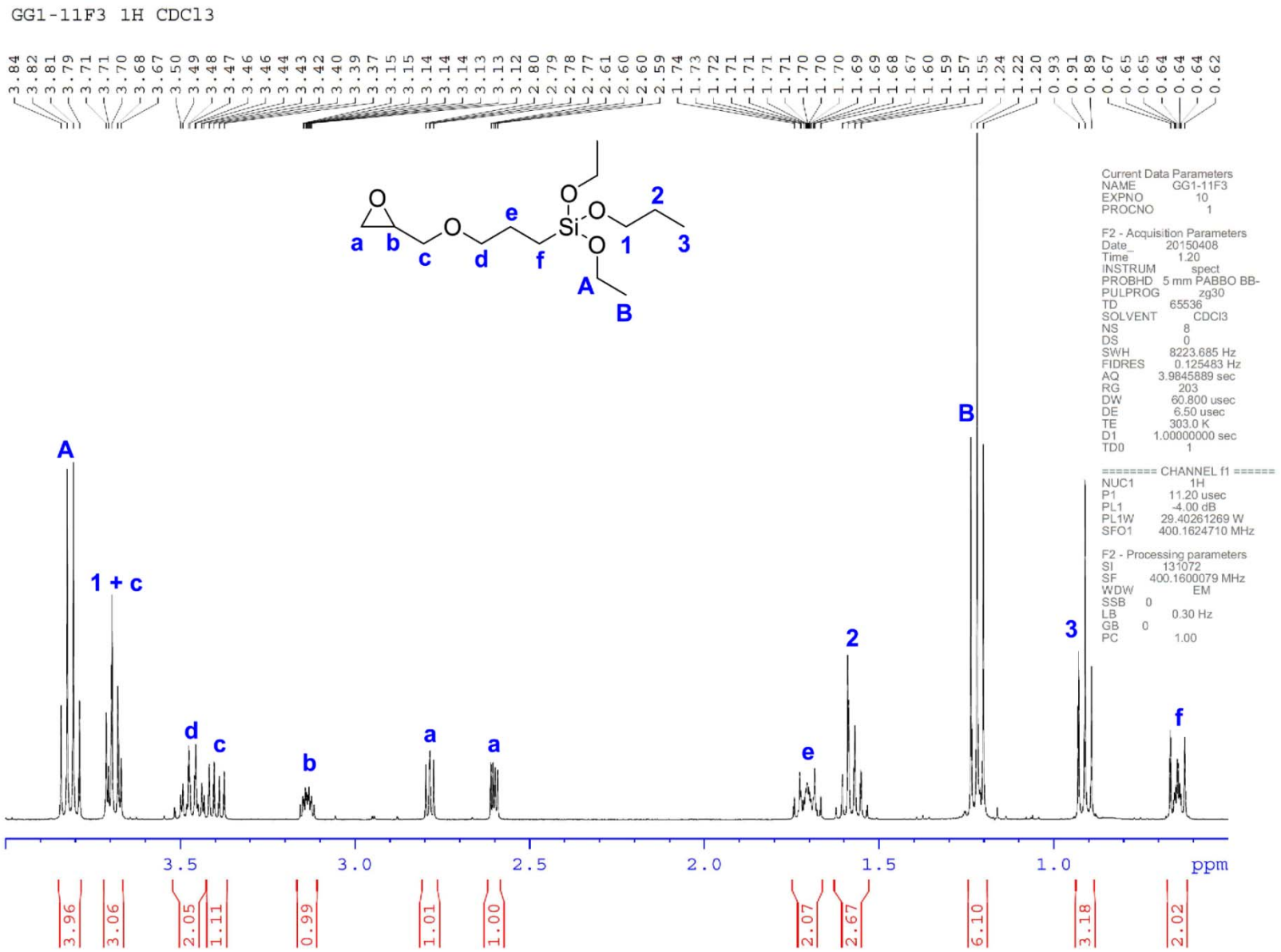


Figure SI_129: ^{1}H-^{1}H NMR spectrum of compound 14b

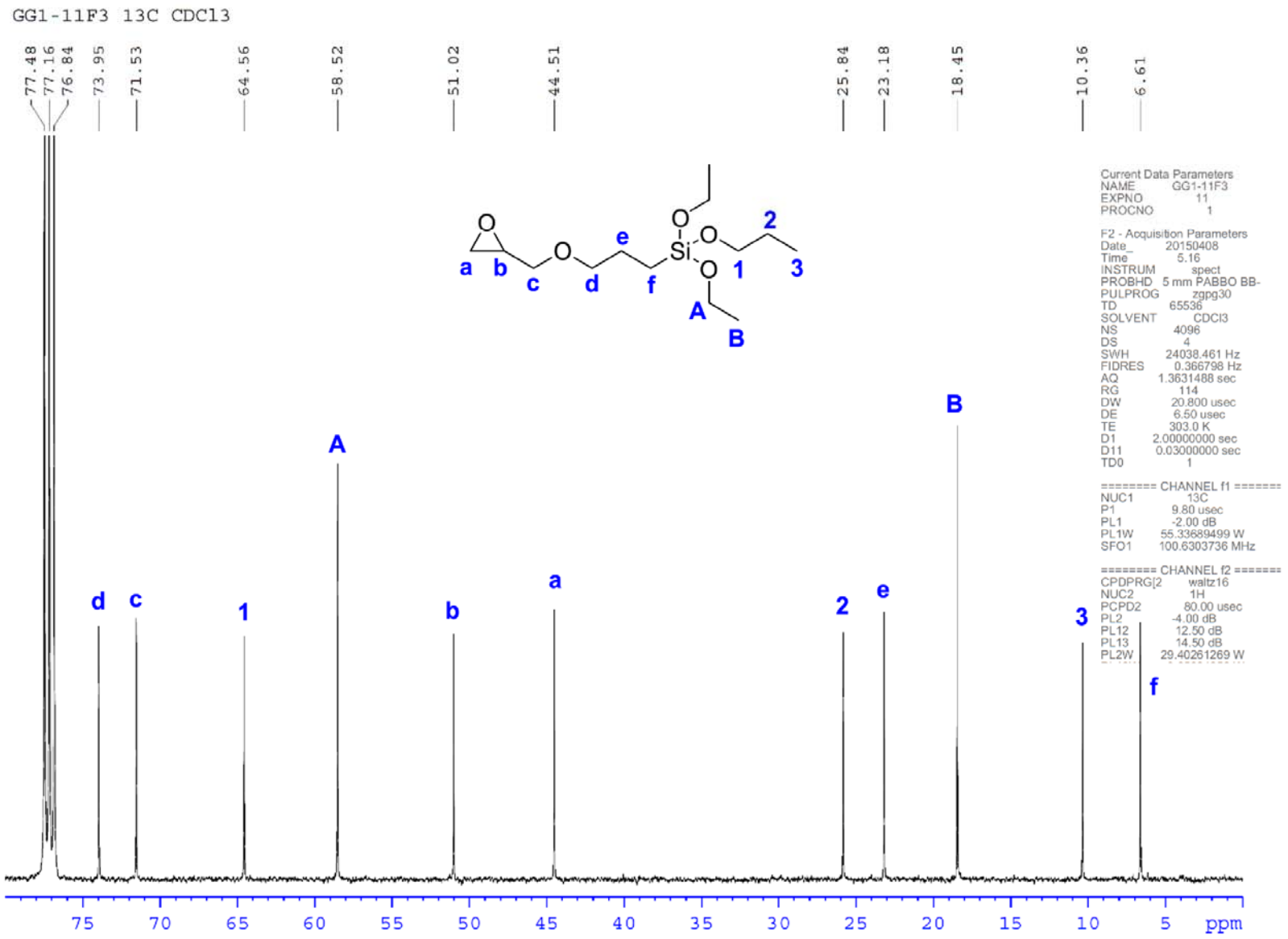


Figure SI_130: ^{13}C NMR spectrum of compound 14b

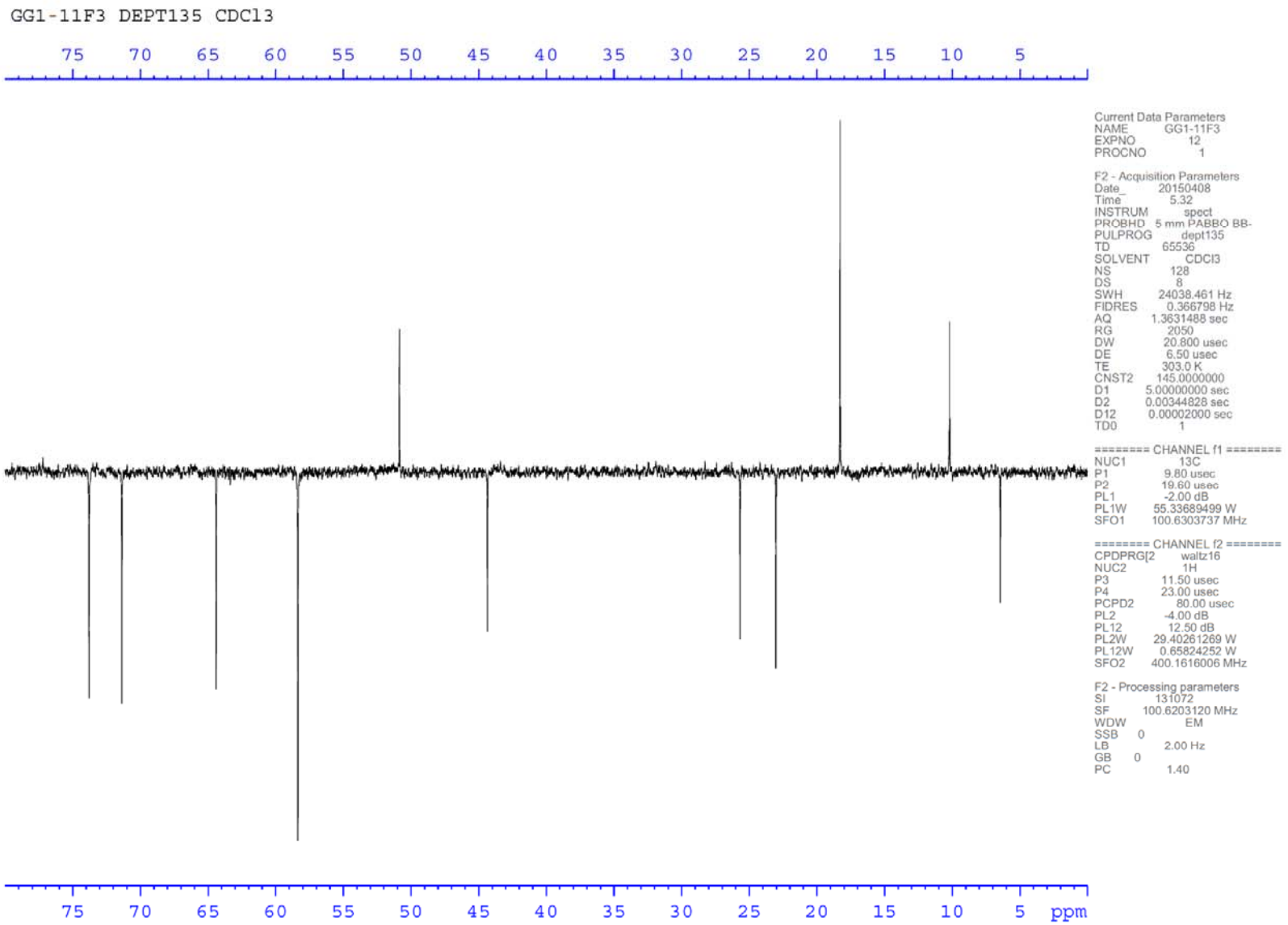


Figure SI_131: DEPT 135 NMR spectrum of compound 14b

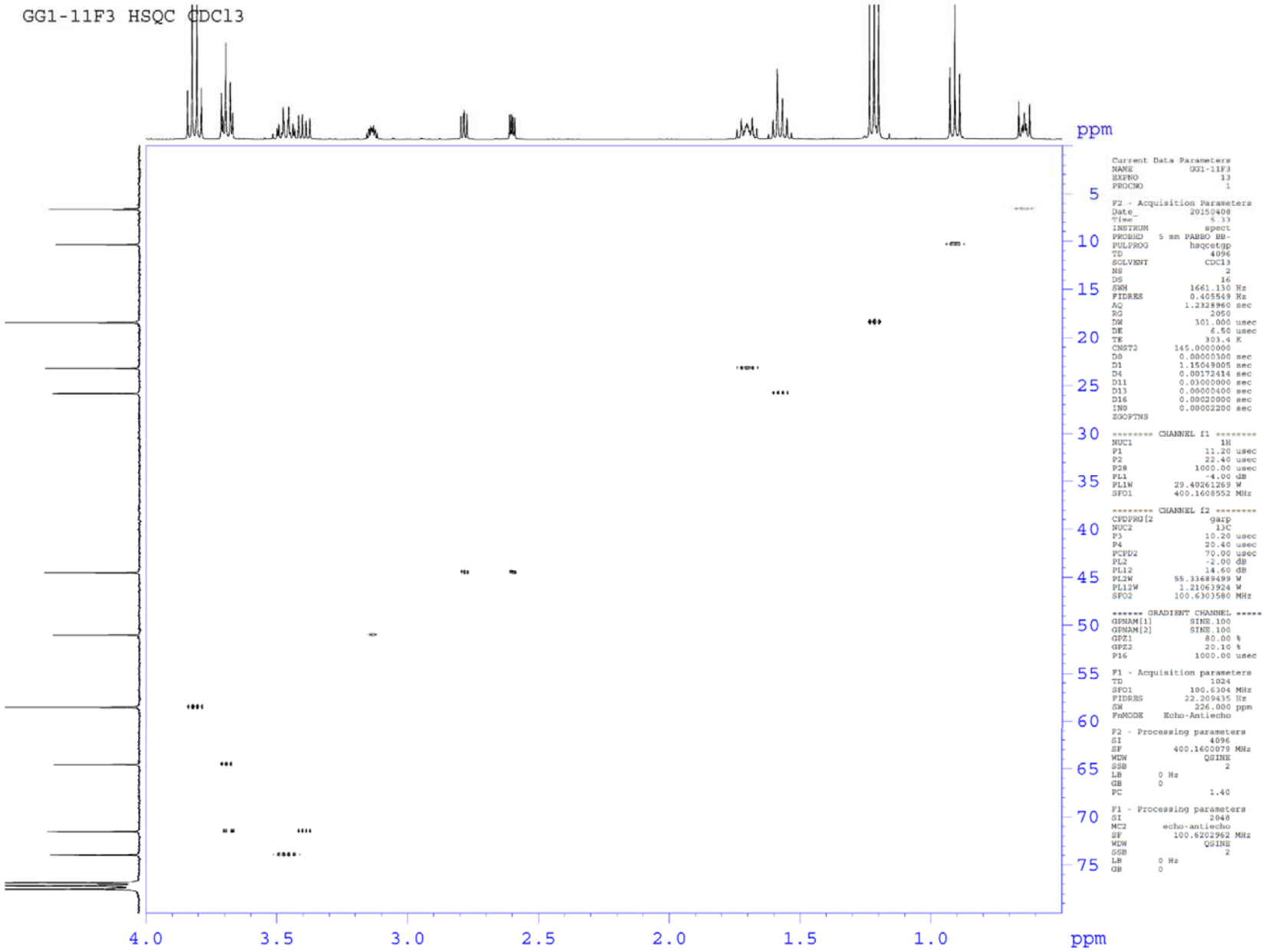


Figure SI_132: HSQC NMR spectrum of compound 14b

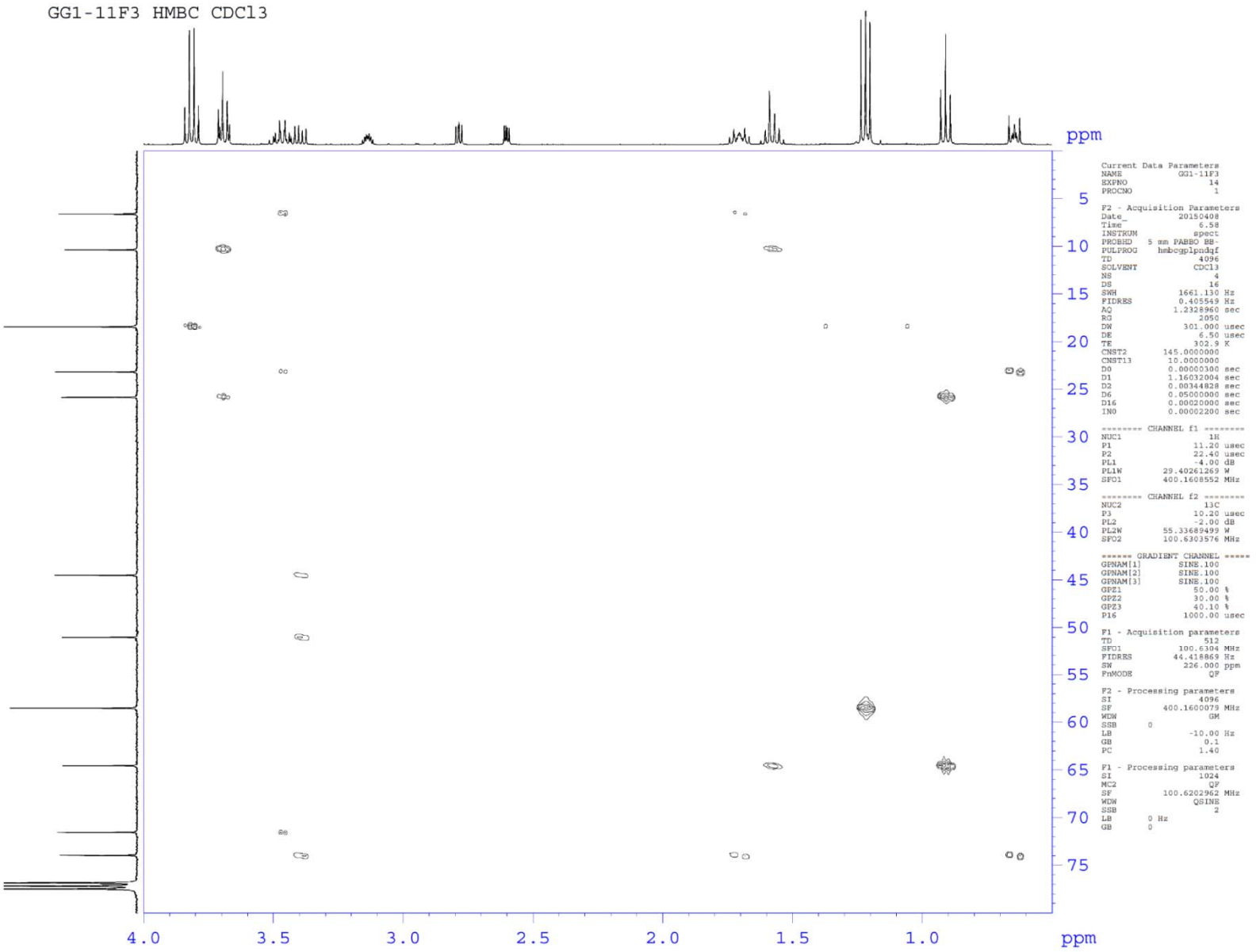


Figure SI_133: HMBC NMR spectrum of compound 14b

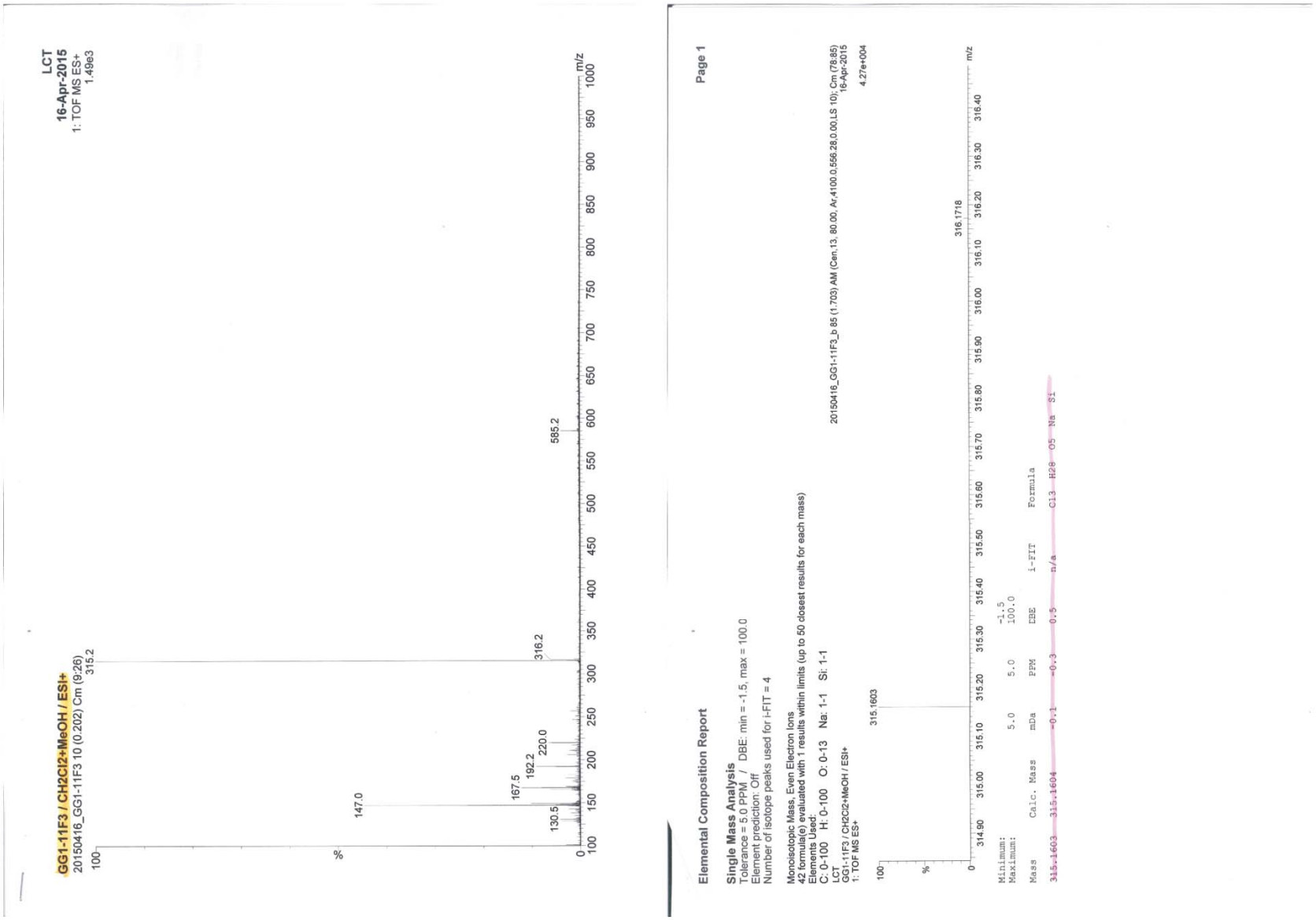
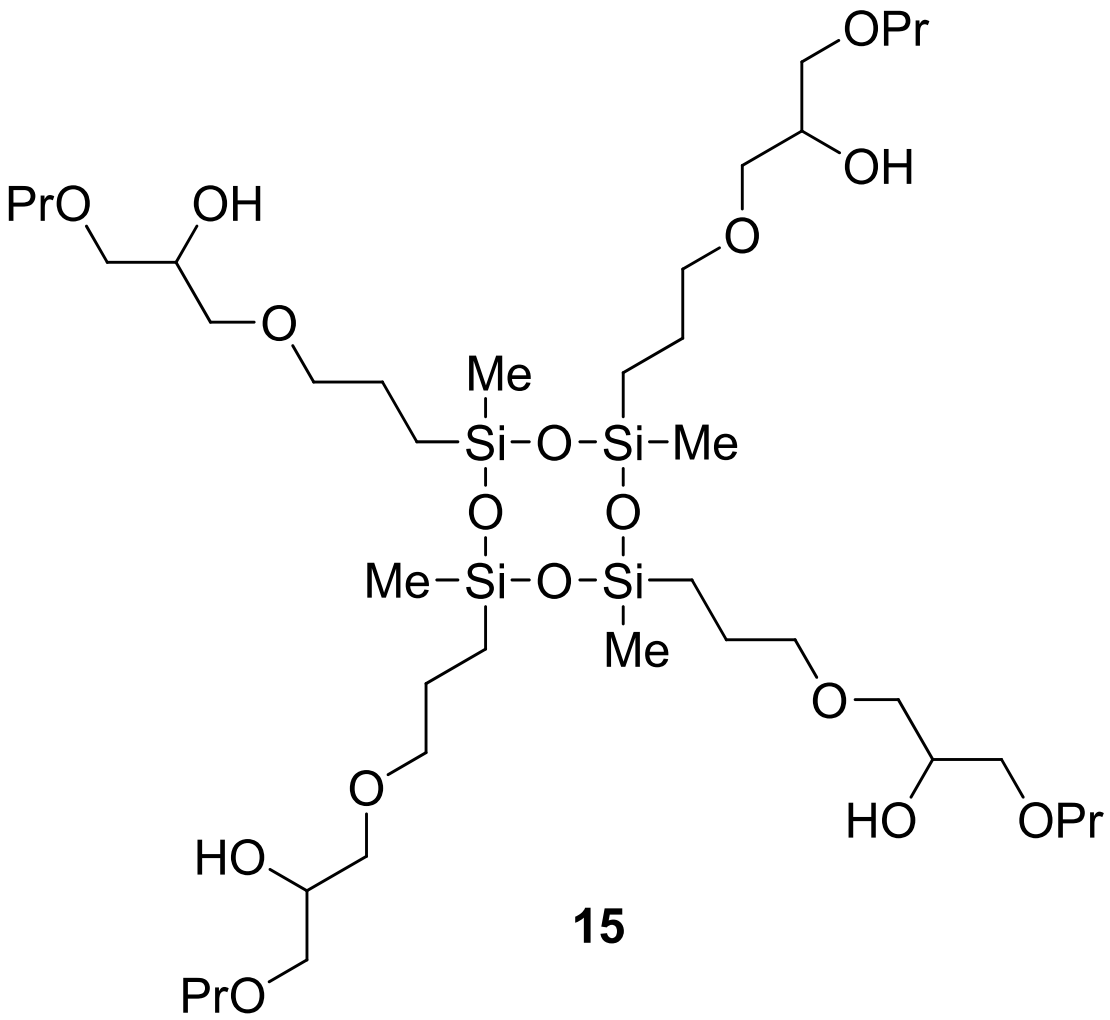


Figure SI_134: ESI HRMS NMR spectrum of compound 14b



15

SI_136

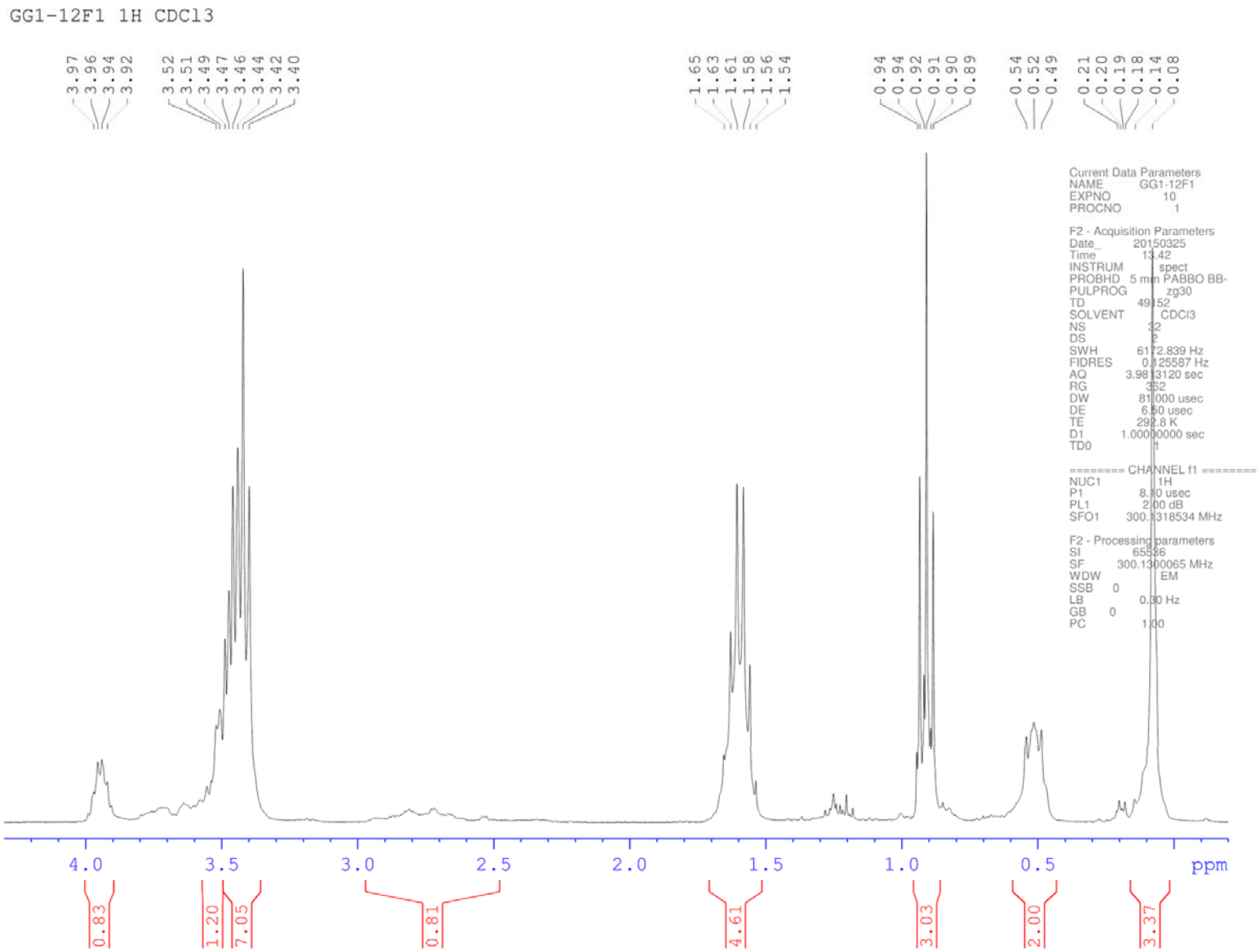


Figure SI_136: ^{1}H NMR spectrum of compound 15

SI_137

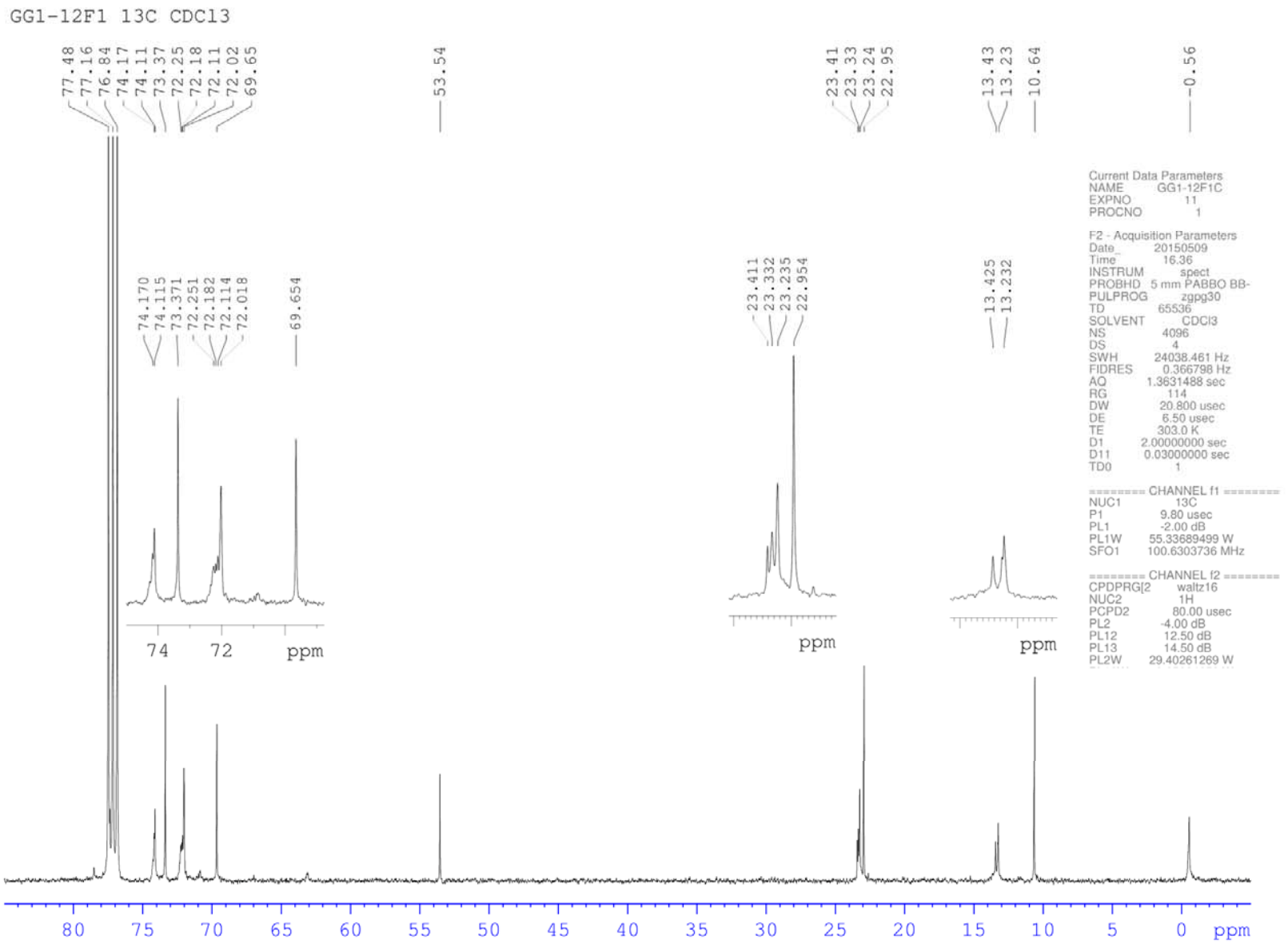


Figure SI_137: ^{13}C NMR spectrum of compound 15

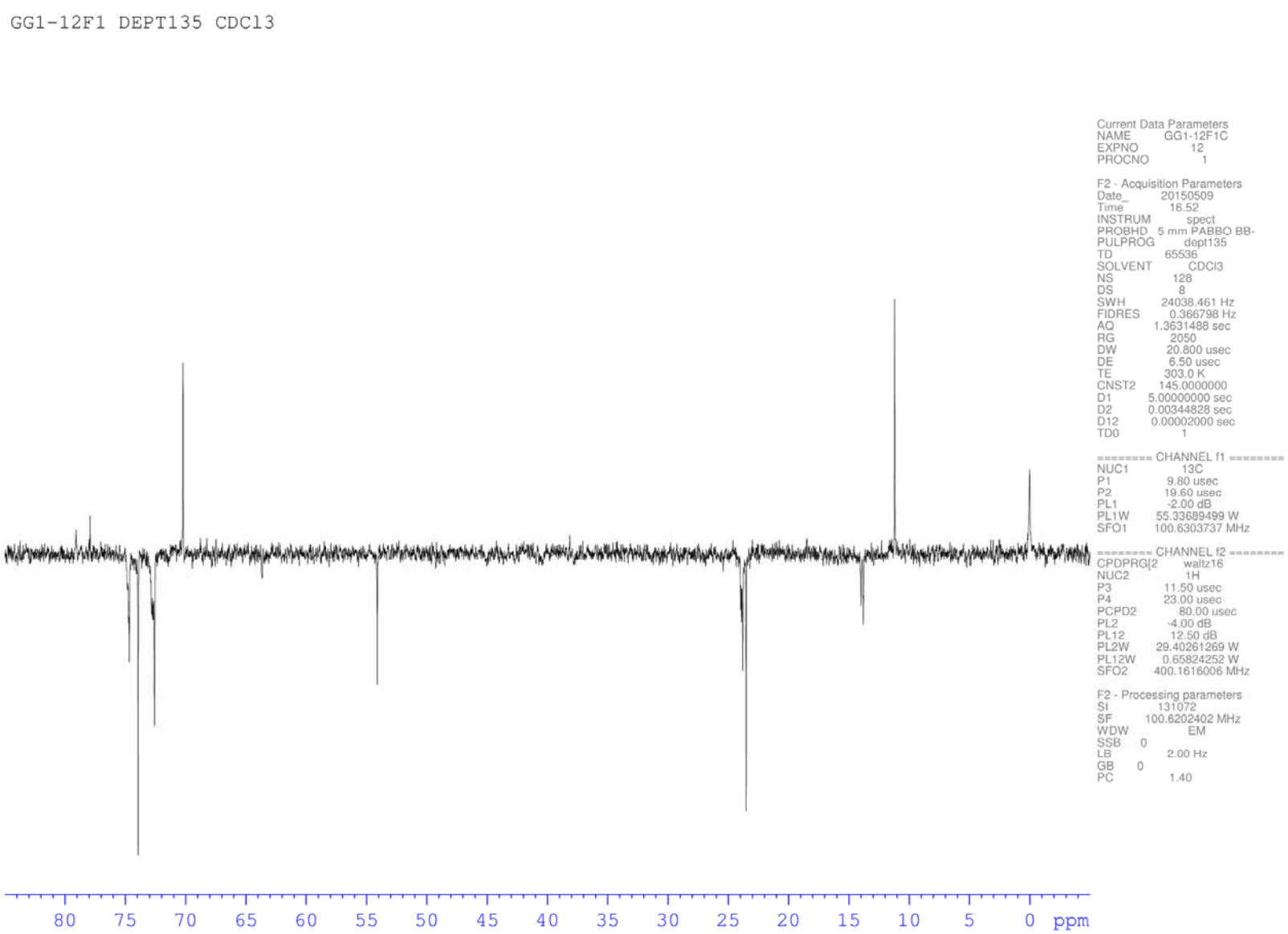


Figure SI_138: DEPT135 NMR spectrum of compound 15

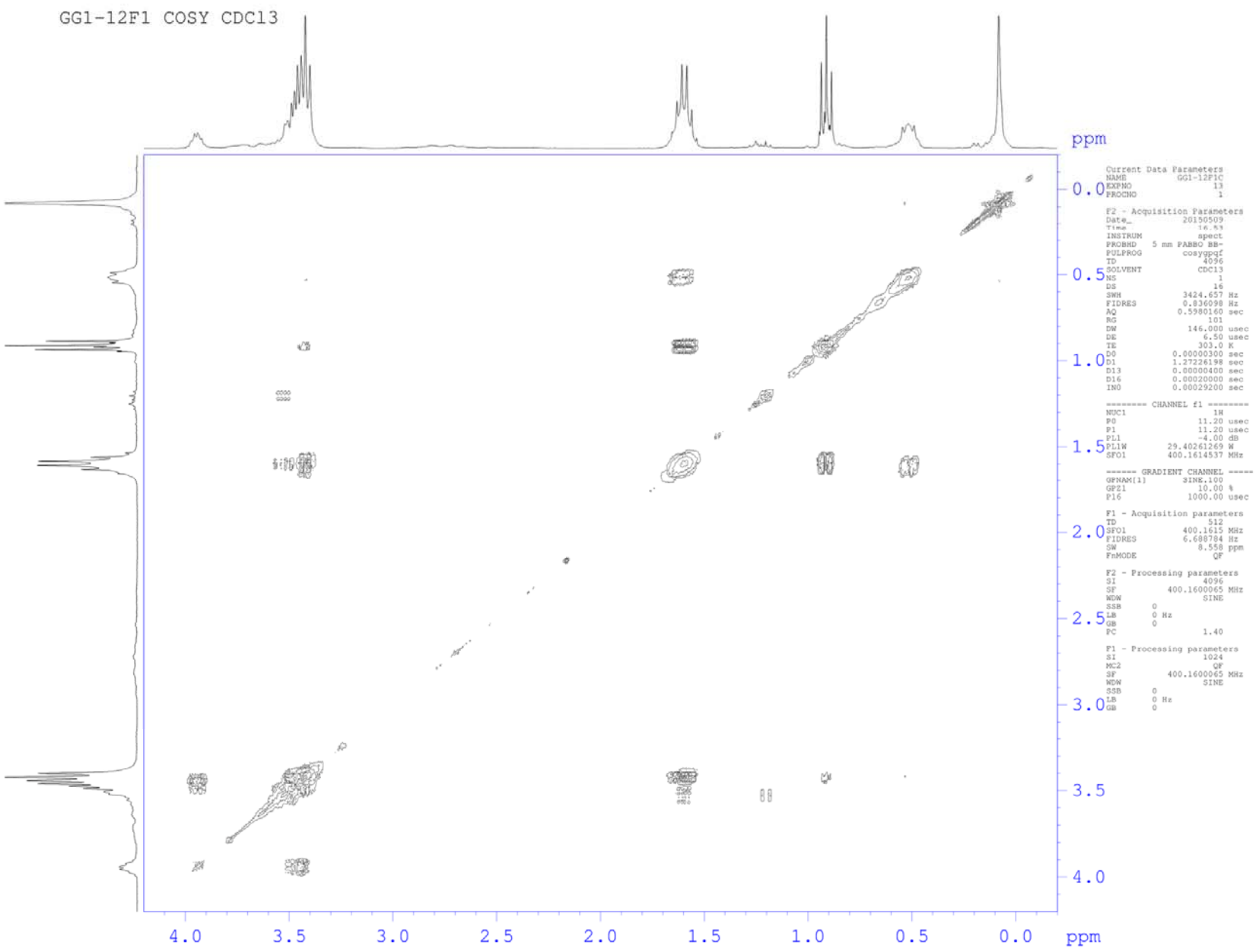


Figure SI_139: ^{1}H-^{1}H NMR spectrum of compound 15

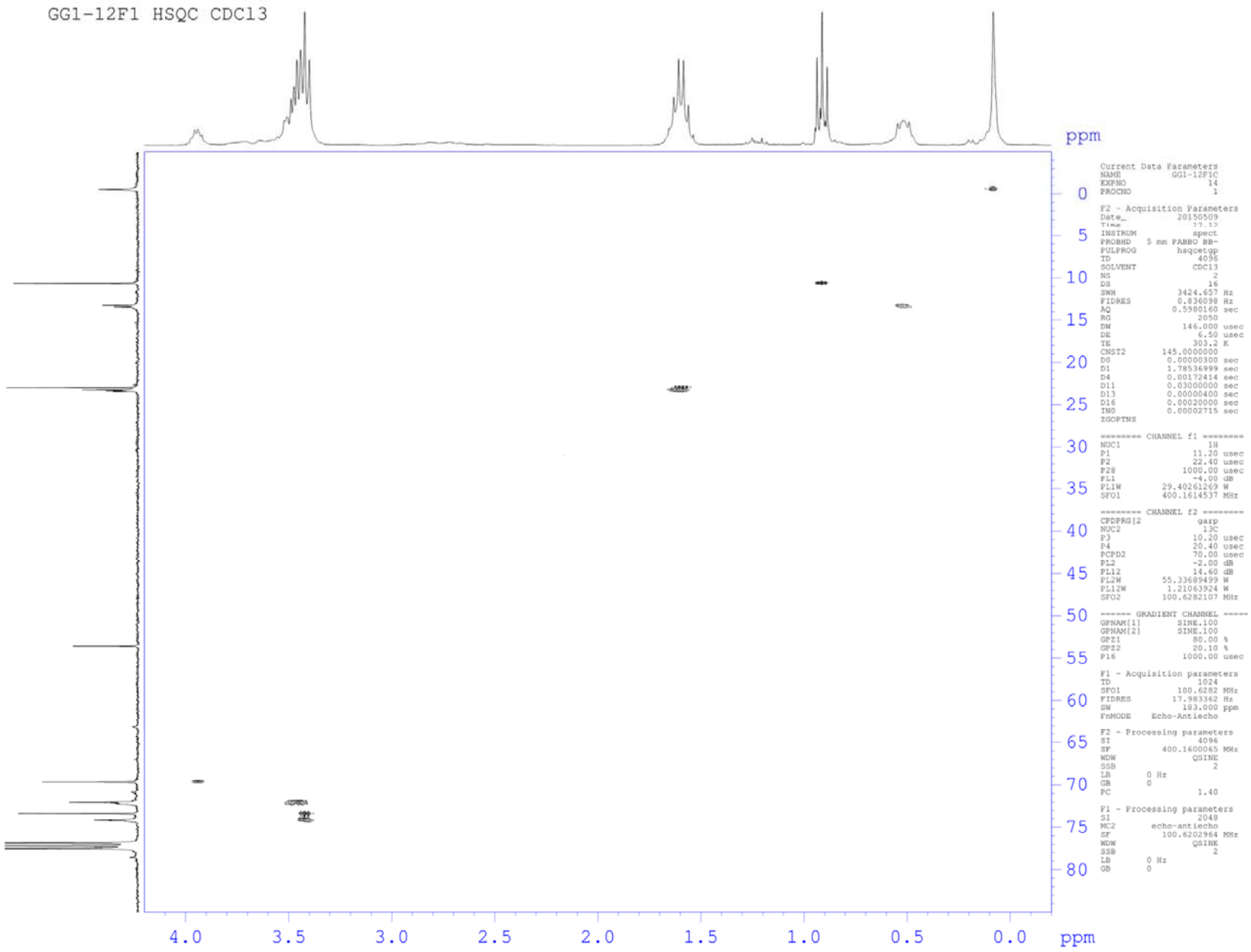


Figure SI_140: HSQC NMR spectrum of compound 15

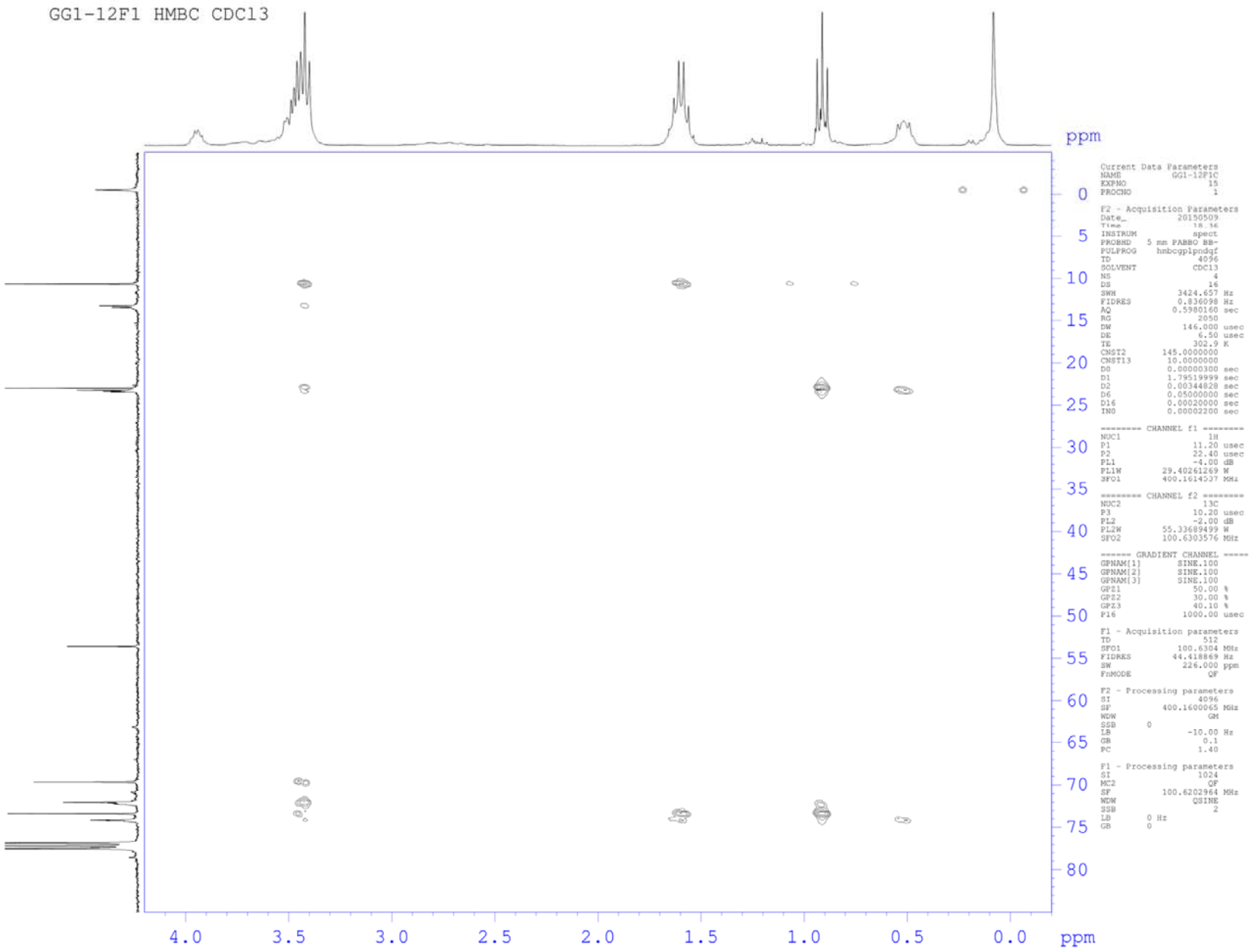


Figure SI_141: HMBC NMR spectrum of compound 15

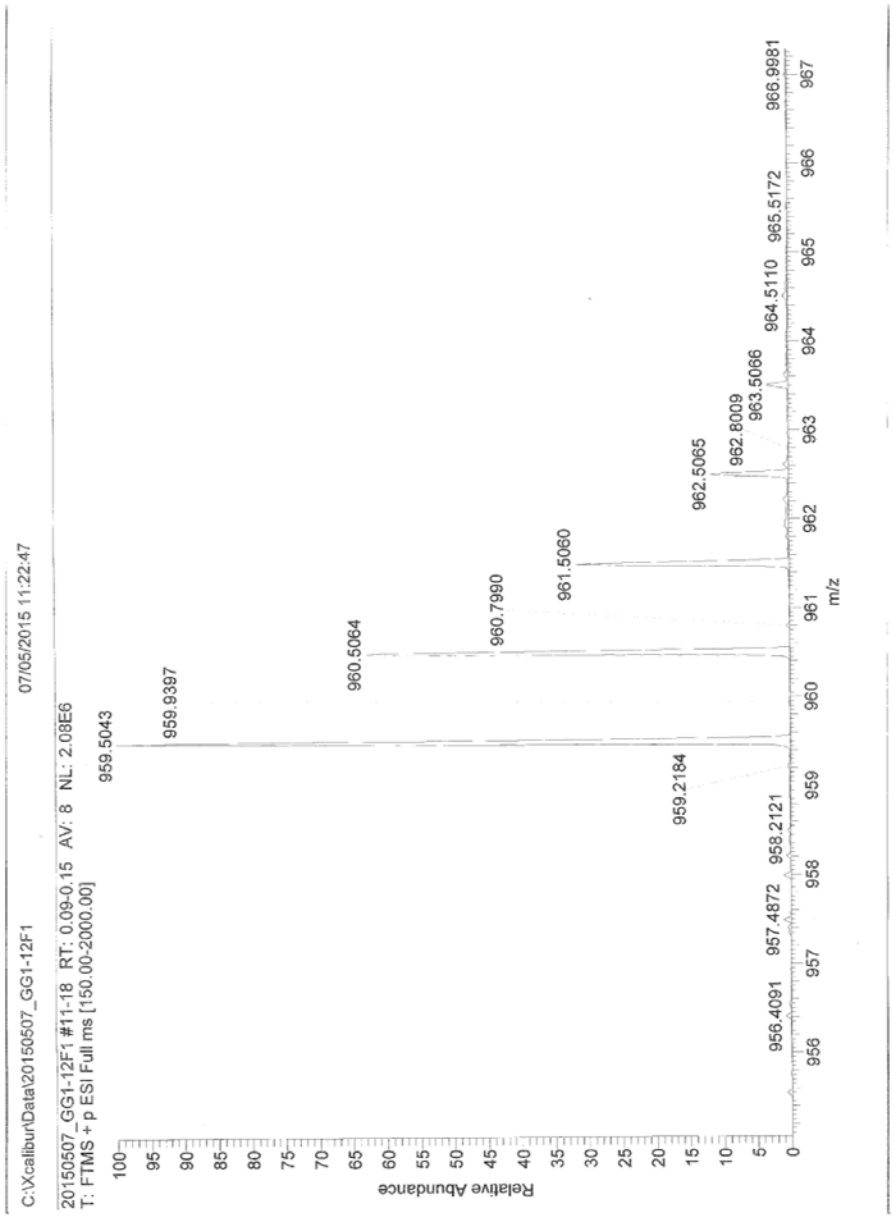


Figure SI_142: HRMS spectrum of compound 15

E. Reference ^{1}H NMR ($CDCl_3$) spectra of GPTMS, GPTES and PECS

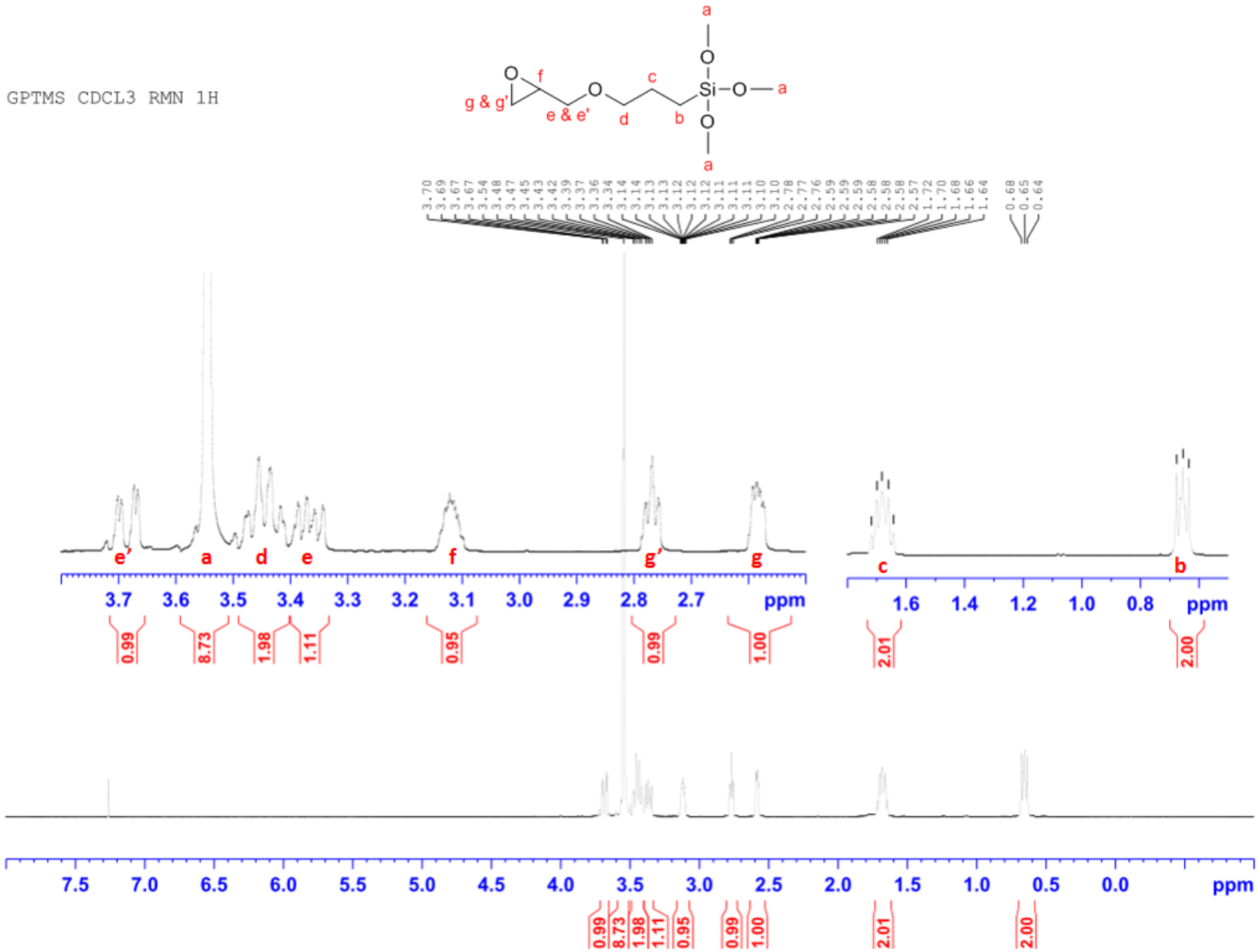


Figure SI_143: ^{1}H NMR spectrum of GPTMS

GPTES CDCL3 RMN 1H

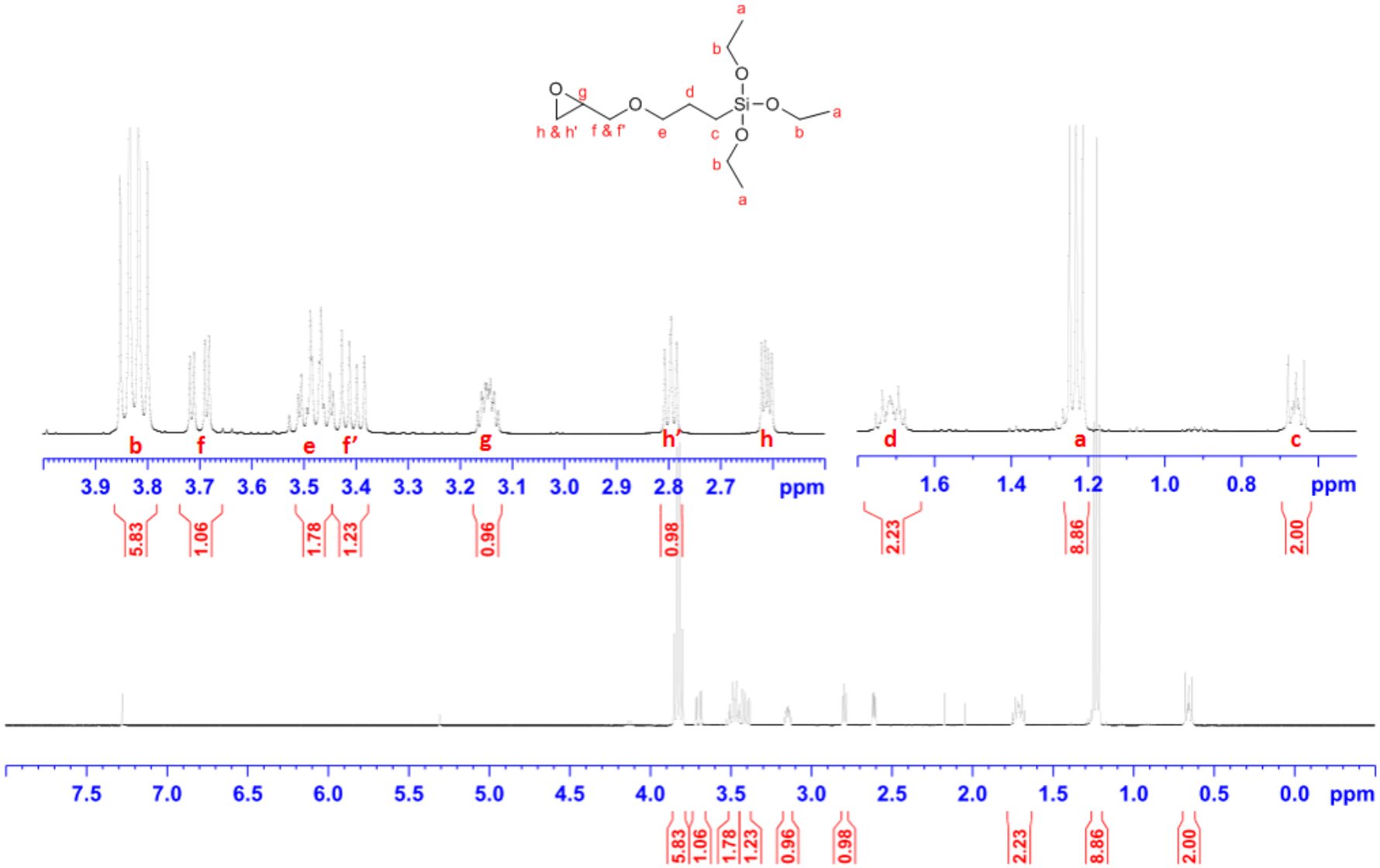


Figure SI_144: ^{1}H NMR spectrum of GPTES

SI_145

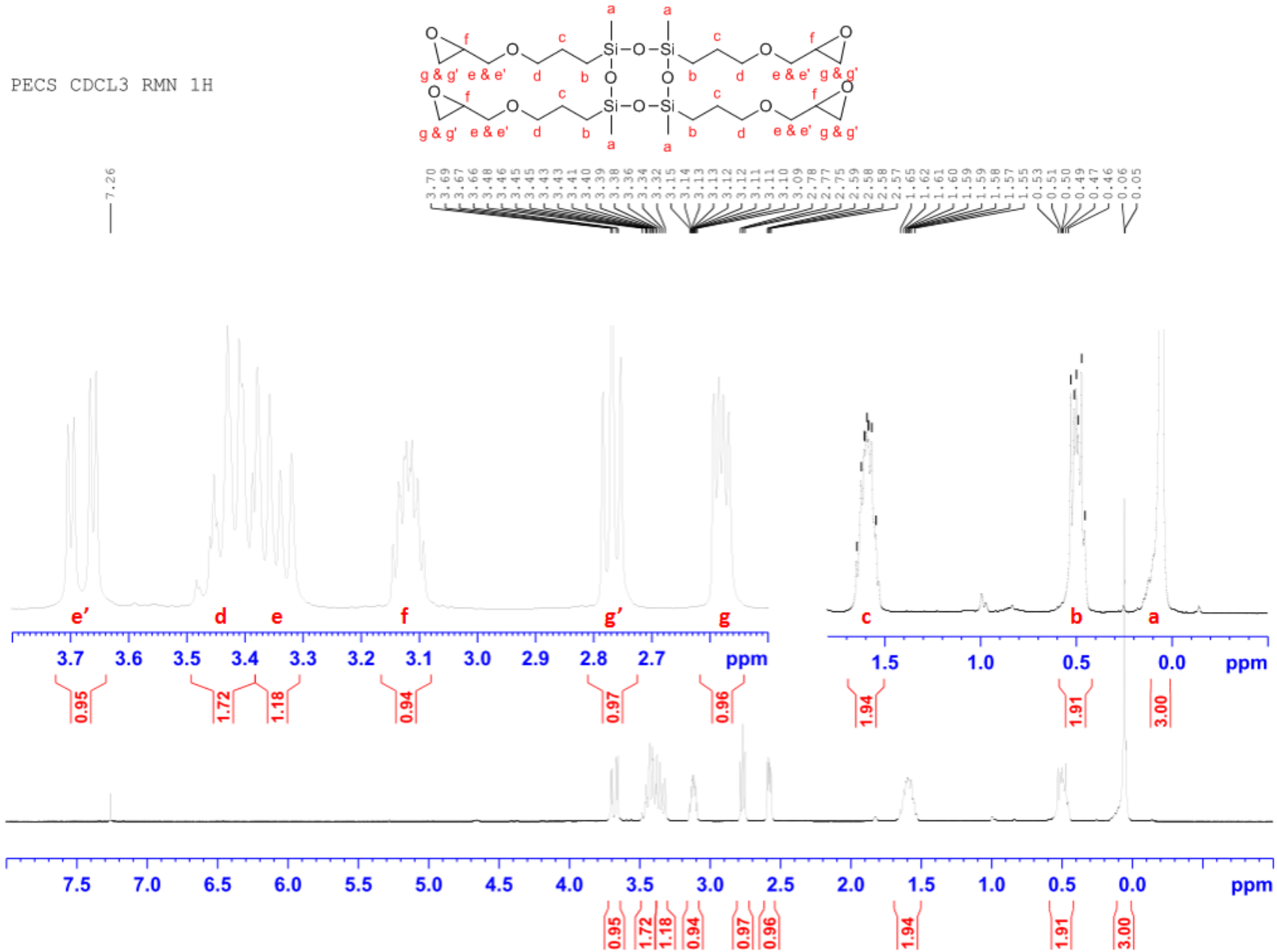


Figure SI_145: ^{1}H NMR spectrum of PECS

E. COMPLEMENTARY SPECTRA CITED IN THE MAIN TEXT

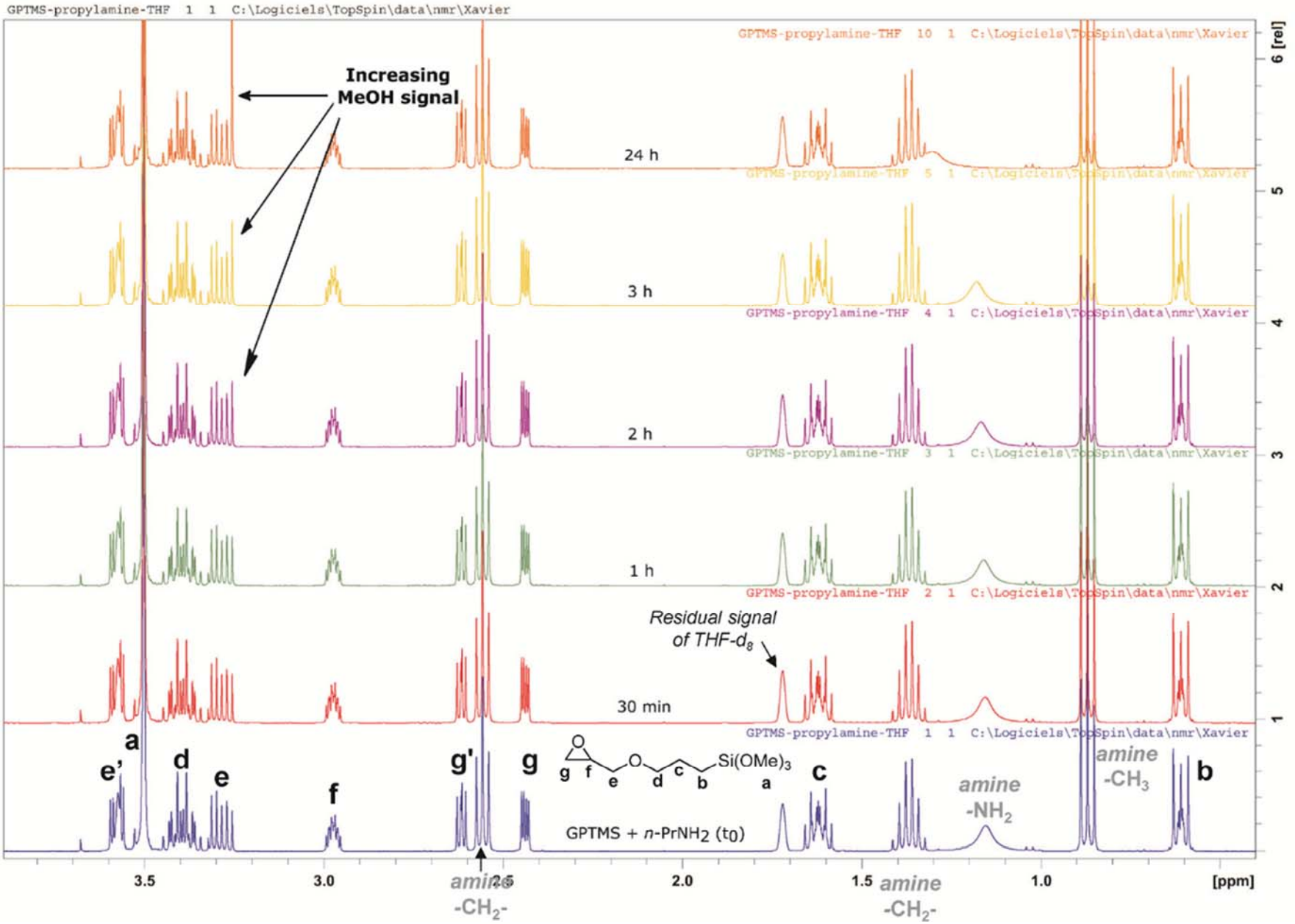


Figure SI_146: ^{1}H NMR monitoring of the reaction between *n*-propylamine and GTPMS in THF-d_8 and at 40 °C.

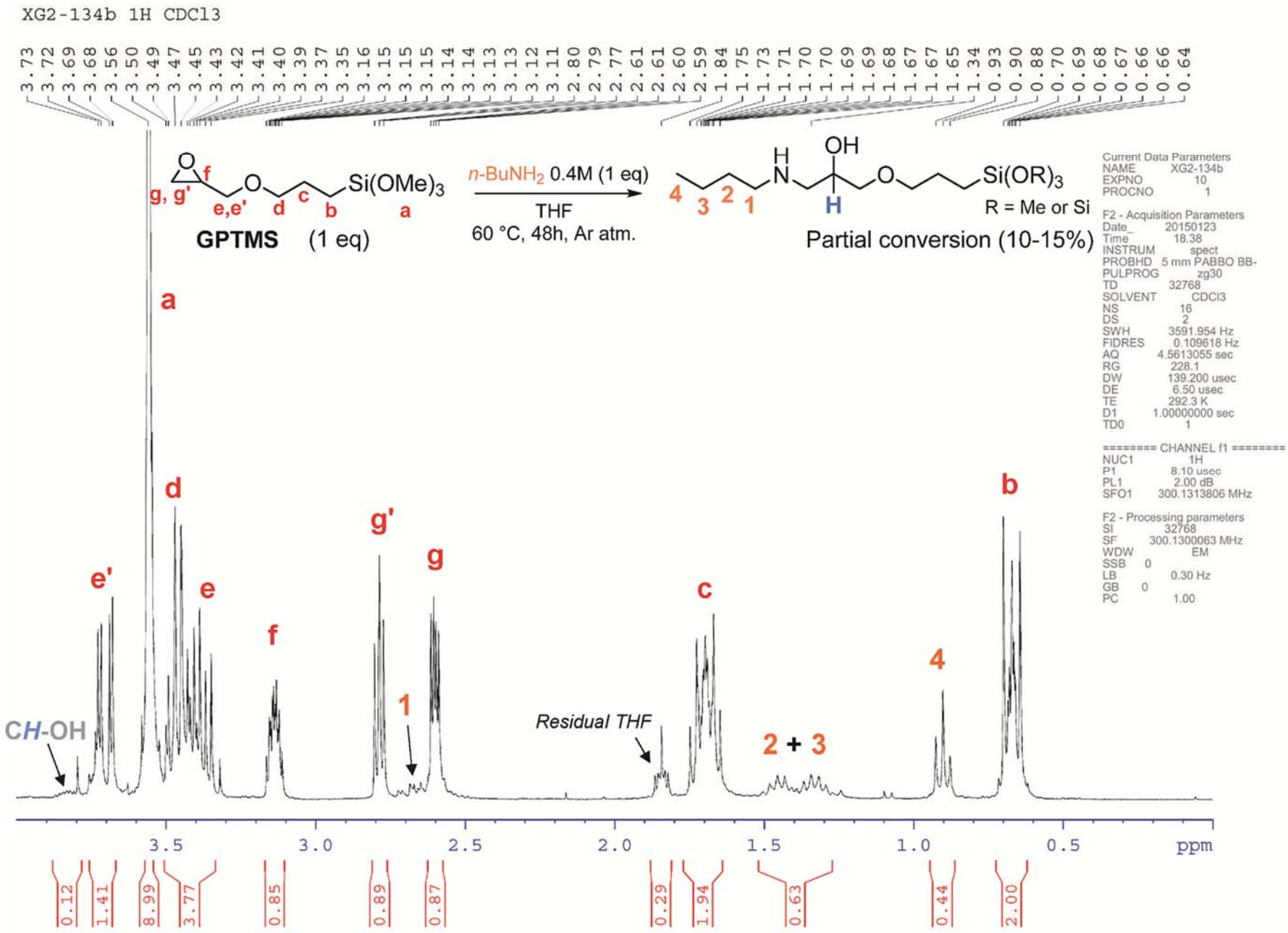


Figure SI_147: ^{1}H NMR spectrum of the crude mixture of the reaction between *n*-butylamine and GPTMS in THF (60 °C, 48h). (Scheme 8 (a.) in article)

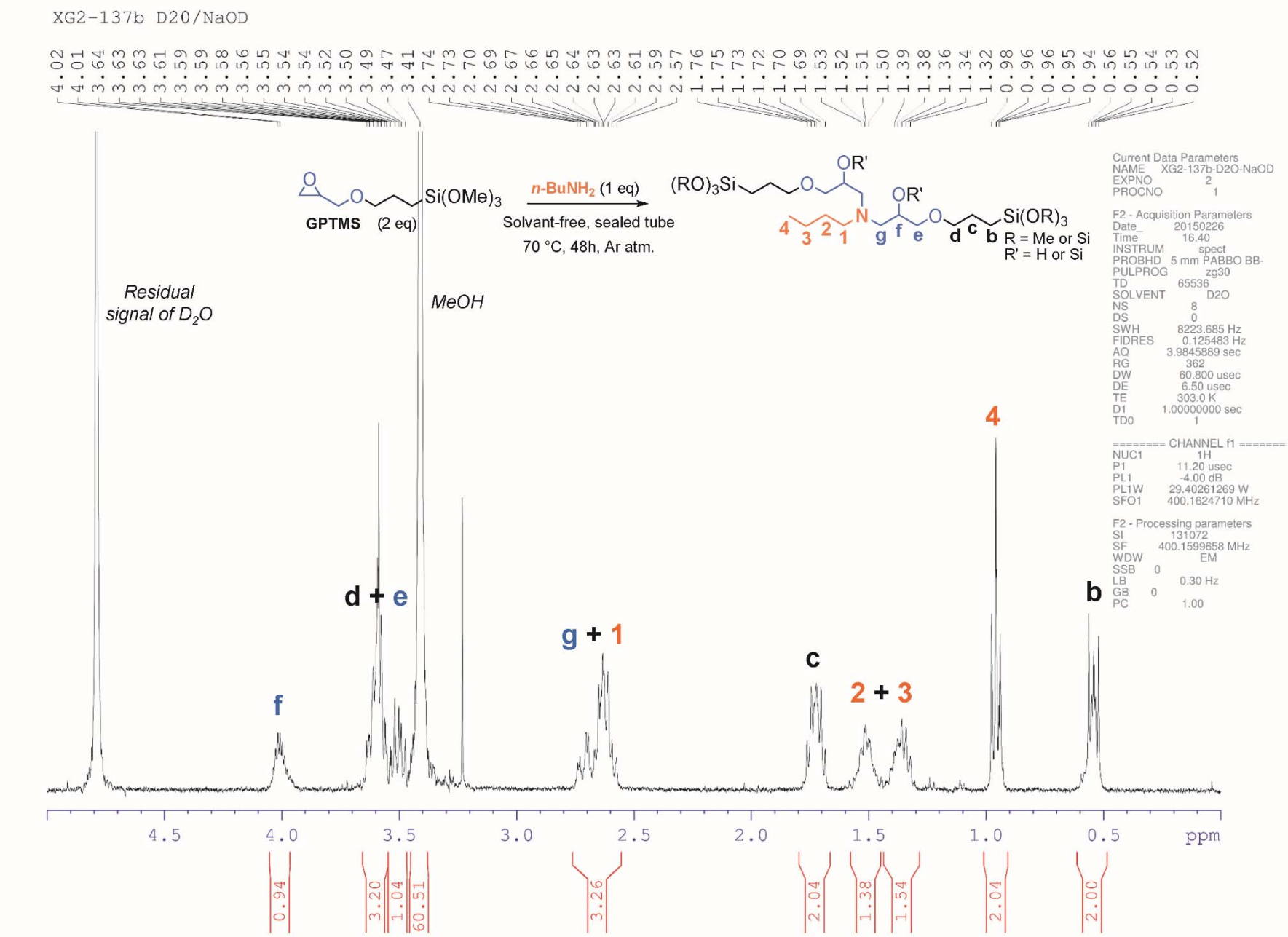


Figure SI_148: ^{1}H NMR spectrum of the dissolved crude material of the reaction between *n*-butylamine and GPTMS in solvent-free conditions (70 °C, 48h).

SI_149

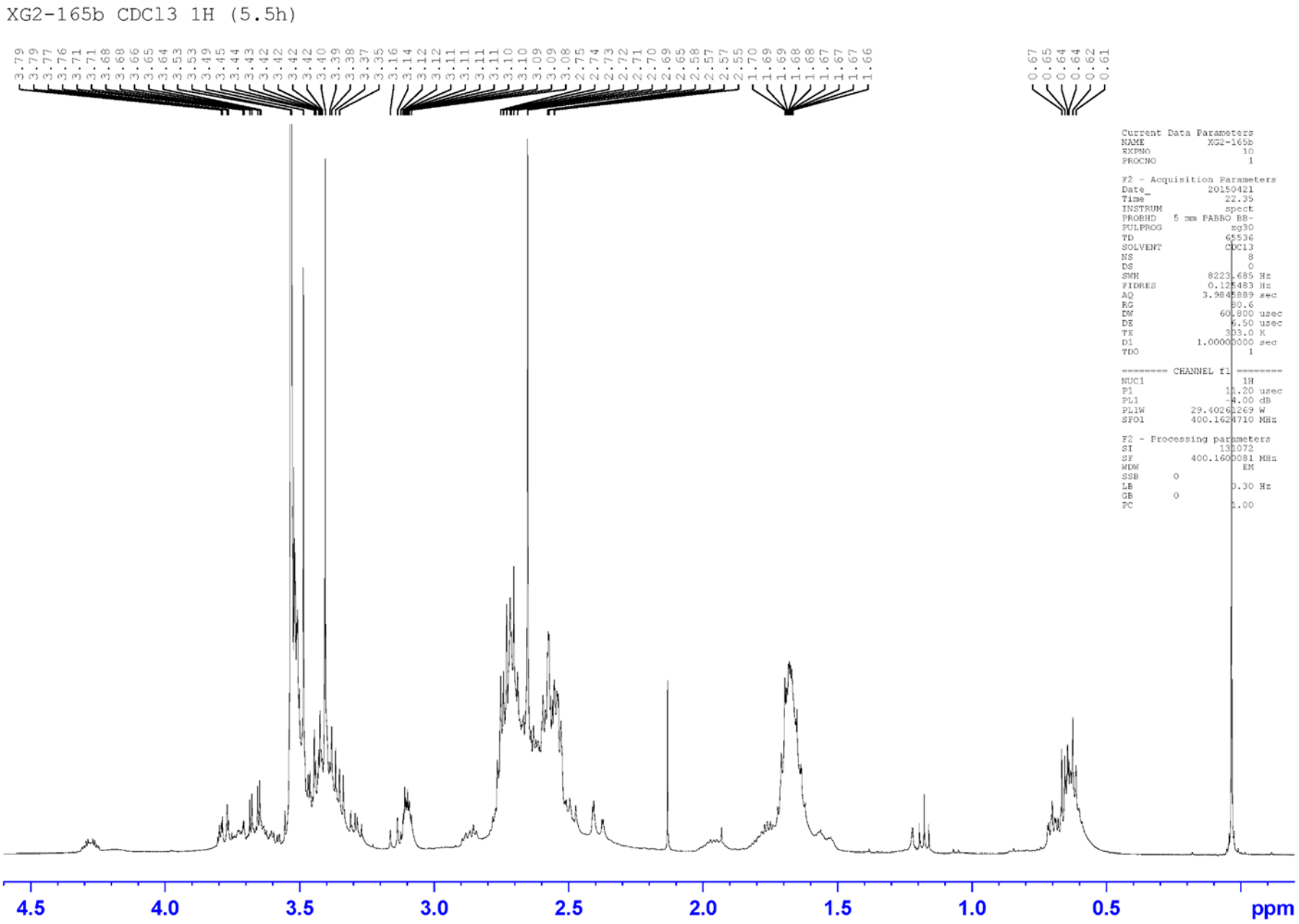


Figure SI_149:. ^{1}H NMR spectrum of the mixture of 4 & 5 issued of the reaction between cyclam and GPTMS in toluene (reflux, 5.5h). (Scheme 3 (b.) in article)

SI_150

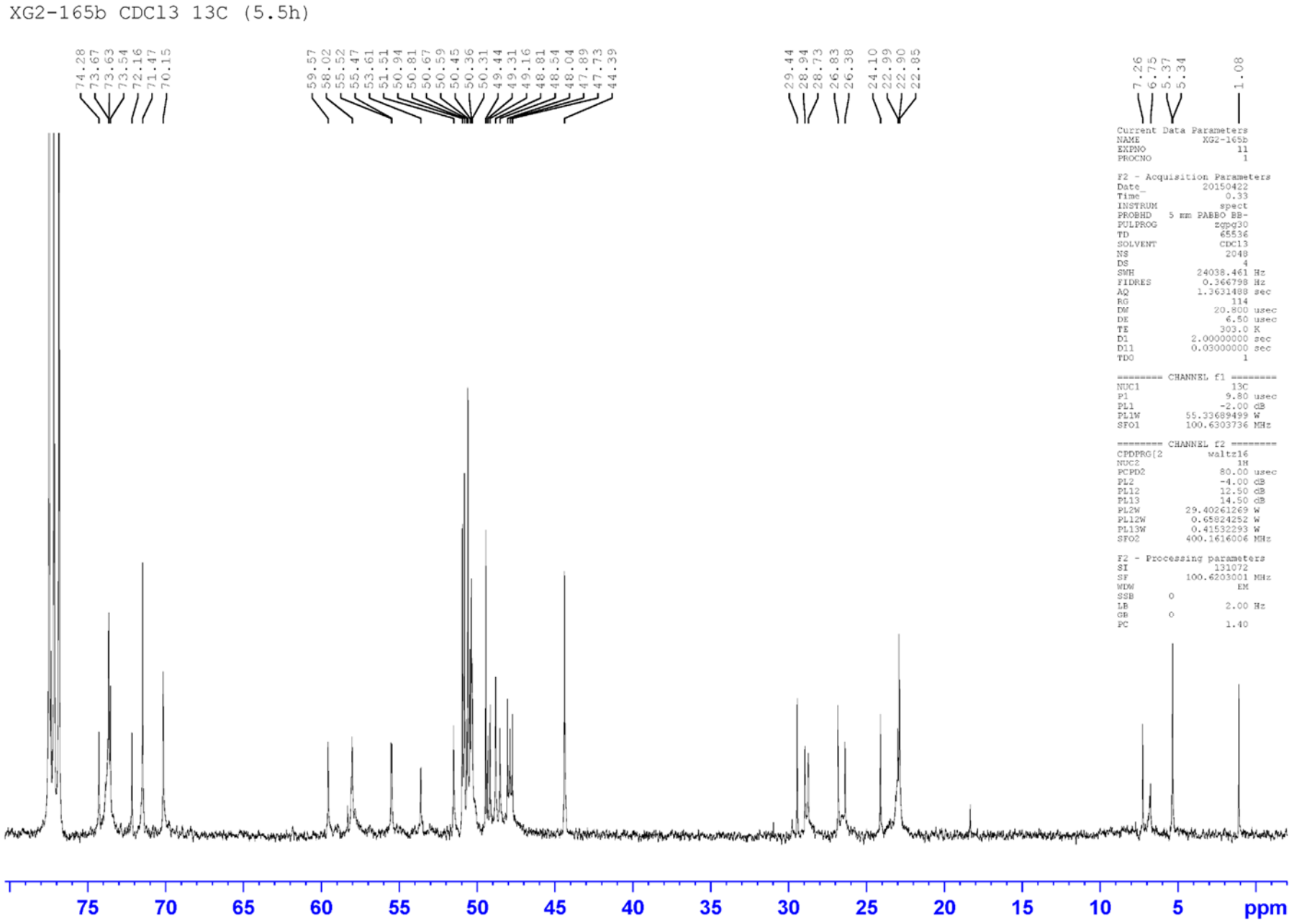


Figure SI_150: ^{13}C NMR spectrum of the mixture of 4 & 5 issued of the reaction between cyclam and GPTMS in toluene (reflux, 5.5h). (Scheme 3 (b.) in article)

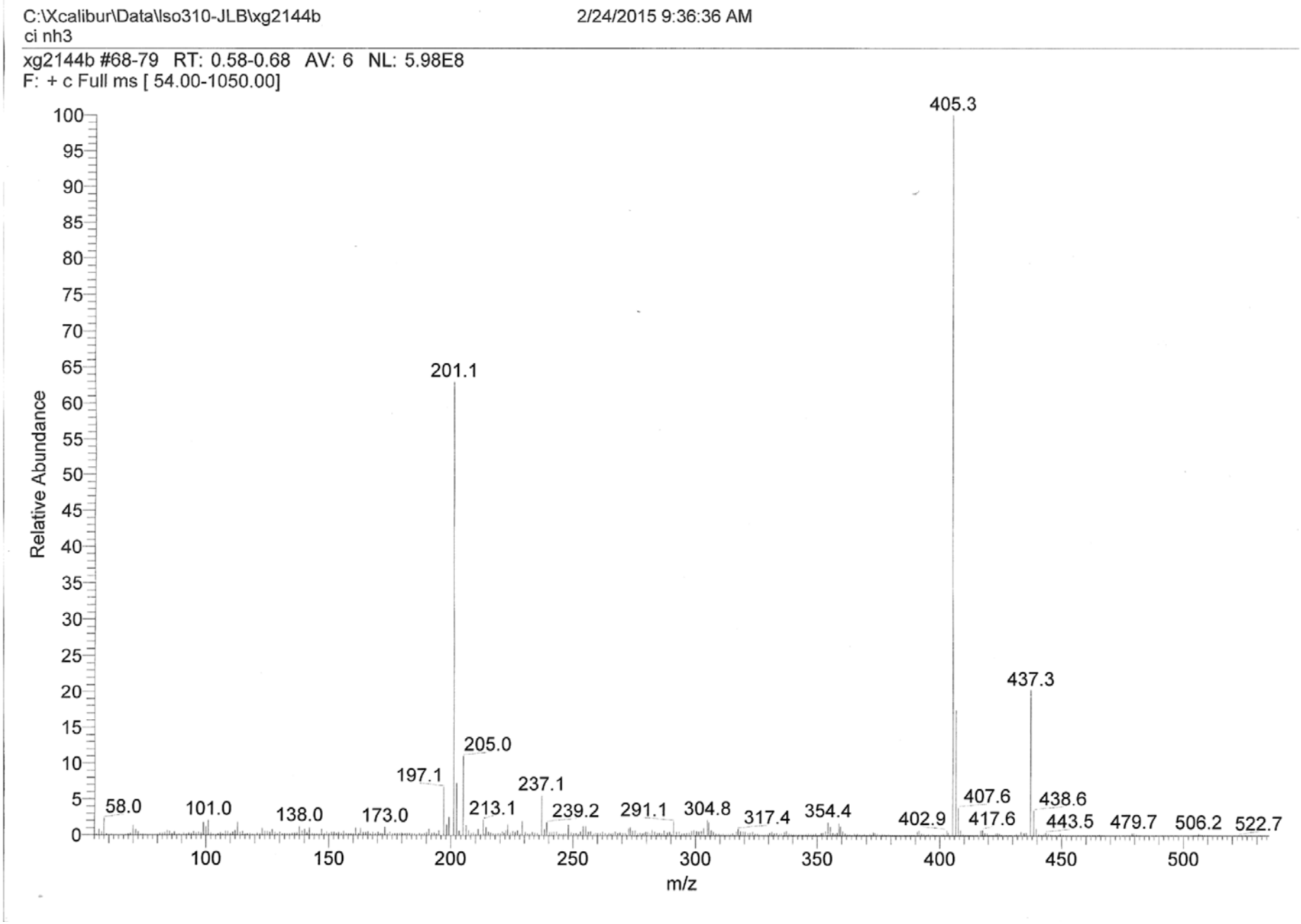
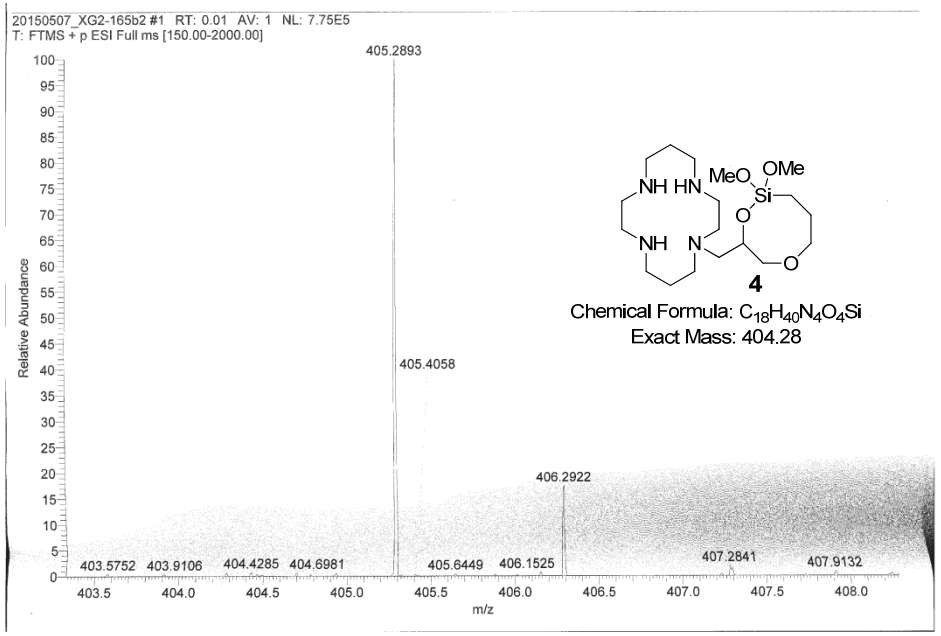
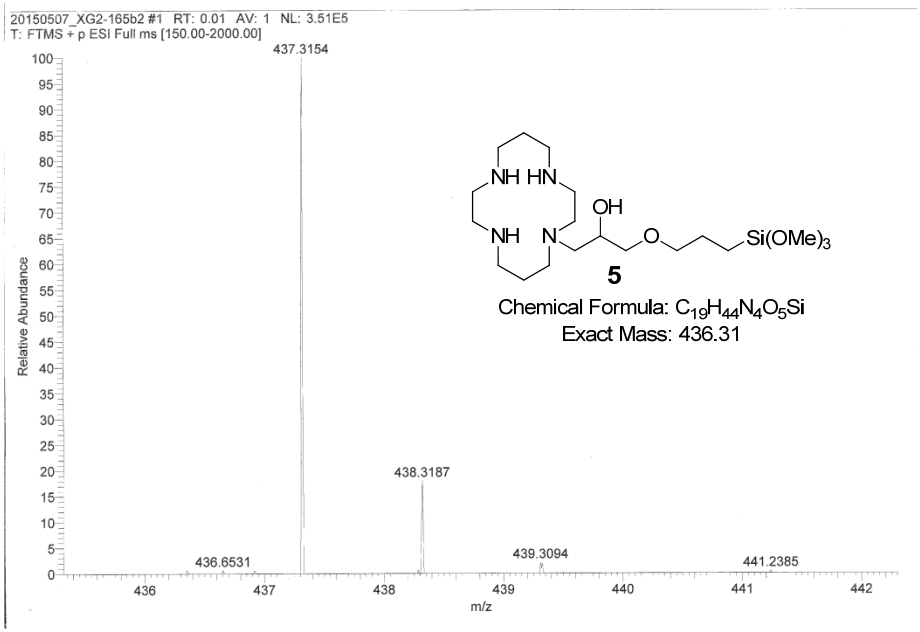


Figure SI_151: MS-CI spectrum of the mixture of 4 & 5 issued of the reaction between cyclam and GPTMS in toluene (reflux, 5.5h). (Scheme 3 (b.) in article)





Elemental compositicn search on mass 405.29

m/z= 400.29-410.29

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
405.2893	405.2894	-0.23	3.0	$C_{19}H_{40}ON_5NaSi$
	405.2892	0.45	1.5	$C_{18}H_{41}O_4N_4Si$
	405.2887	1.58	11.0	$C_{25}H_{35}N_5$
	405.2900	-1.73	10.5	$C_{27}H_{37}ON_2$
	405.2905	-2.85	6.5	$C_{19}H_{37}N_8Si$
	405.2905	-2.87	1.0	$C_{20}H_{43}O_5NSi$
	405.2881	3.08	3.5	$C_{17}H_{38}N_8NaSi$
	405.2908	-3.54	2.5	$C_{21}H_{42}O_2N_2NaSi$
	405.2908	-3.66	-0.5	$C_{14}H_{38}O_4N_8Na$
	405.2878	3.76	2.0	$C_{16}H_{39}O_3N_7Si$
	405.2876	4.21	7.5	$C_{25}H_{38}ON_2Na$
	405.2874	4.88	6.0	$C_{24}H_{39}O_4N$

Elemental compositicn search on mass 437.32

m/z= 432.32-442.32

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
437.3154	437.3154	-0.01	0.5	$C_{19}H_{45}O_5N_4Si$
	437.3156	-0.64	2.0	$C_{20}H_{44}O_2N_5NaSi$
	437.3149	1.05	10.0	$C_{26}H_{39}ON_5$
	437.3163	-2.02	9.5	$C_{28}H_{41}O_2N_2$
	437.3143	2.43	2.5	$C_{18}H_{42}ON_8NaSi$
	437.3140	3.06	1.0	$C_{17}H_{43}O_4N_7Si$
	437.3167	-3.07	5.5	$C_{20}H_{41}ON_8Si$
	437.3167	-3.08	0.0	$C_{21}H_{47}O_6NSi$
	437.3138	3.48	6.5	$C_{26}H_{42}O_2N_2Na$
	437.3170	-3.71	1.5	$C_{22}H_{46}O_3N_2NaSi$
	437.3136	4.10	5.0	$C_{25}H_{43}O_5N$
	437.3136	4.12	10.5	$C_{24}H_{37}N_8$

Figure SI_152: HRMS-ESI spectra of the molecular peaks ([*M*+H$^+$]) of compounds 4 (left) & 5 (right).

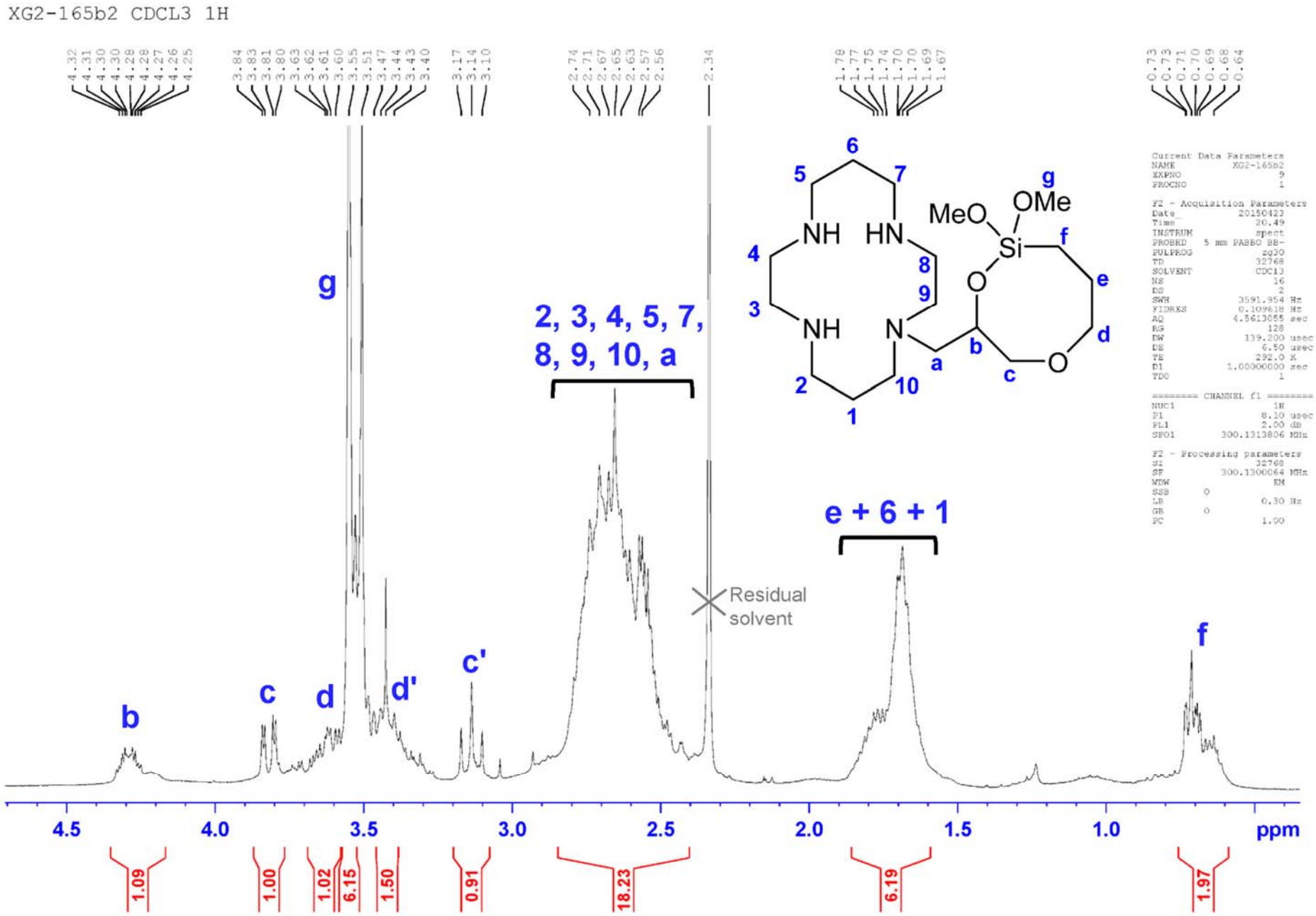


Figure SI_153: ^{1}H NMR spectrum of compound 4

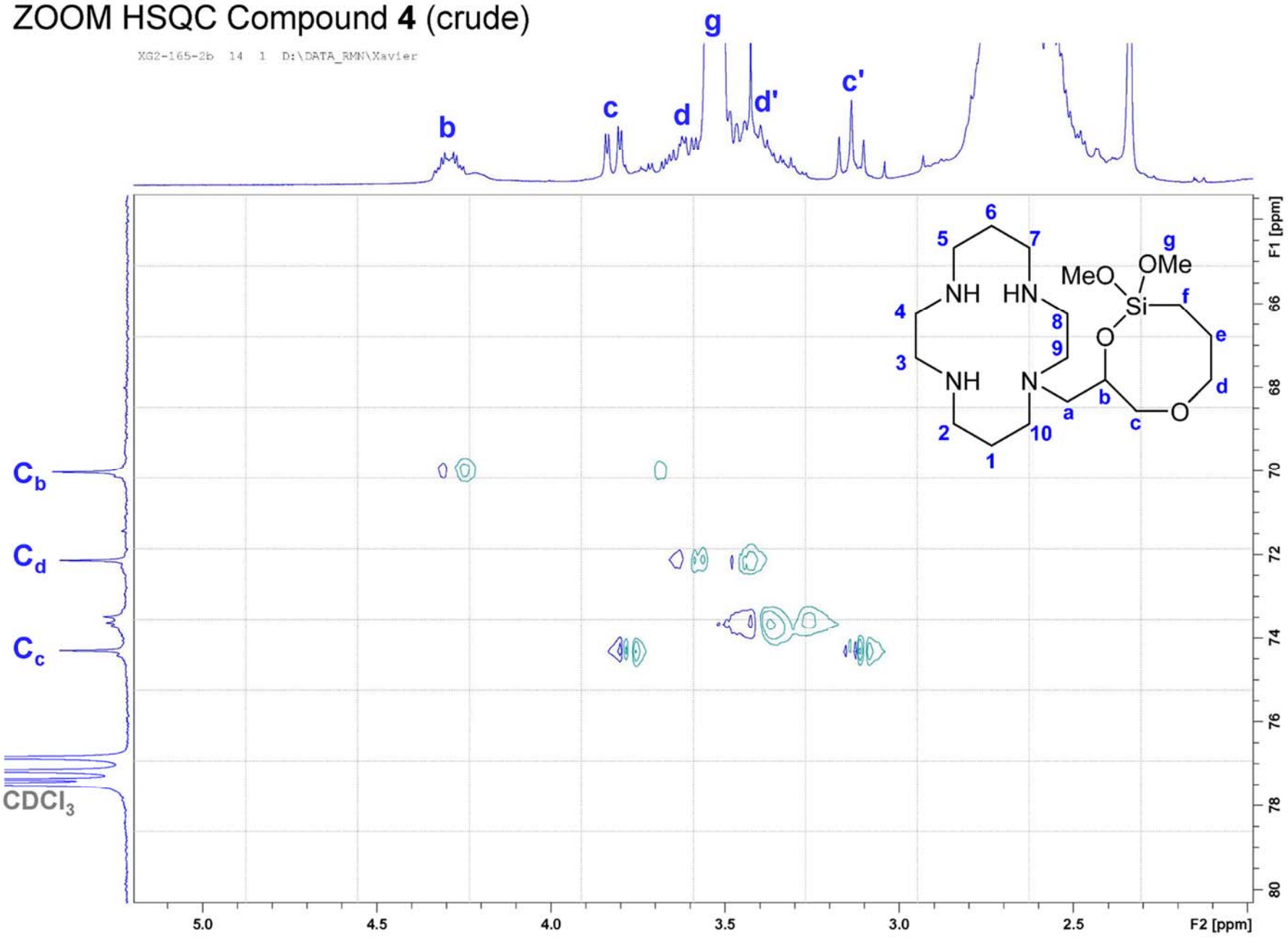


Figure SI_154: HSQC (zoom 2-5 ppm for ^{1}H spectrum; 64-80 ppm for ^{13}C spectrum) of compound 4.

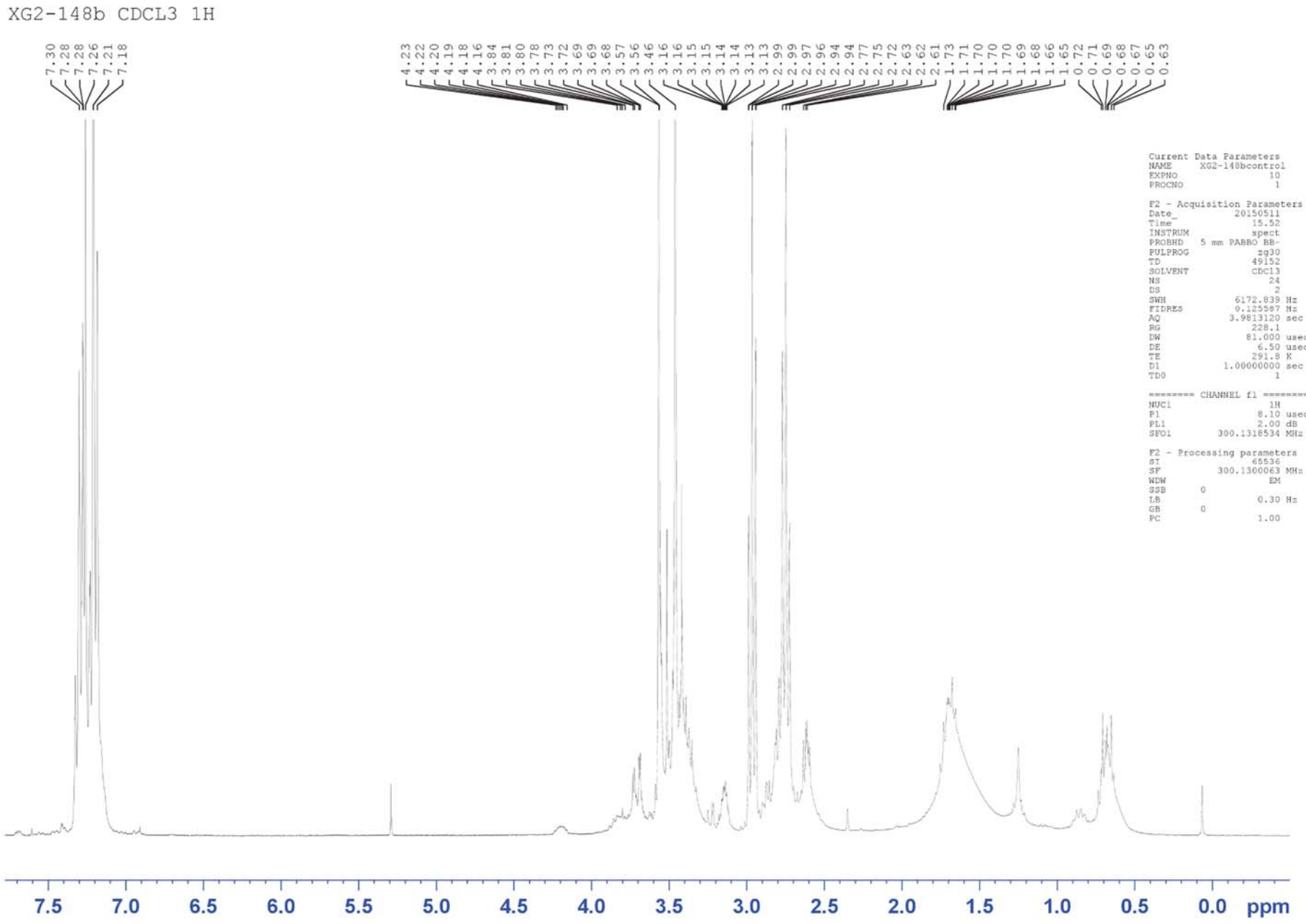


Figure SI_155: ^{1}H NMR spectrum of the crude mixture of the reaction between phenethylamine and GPTMS in toluene (reflux, 3h).

SI_156

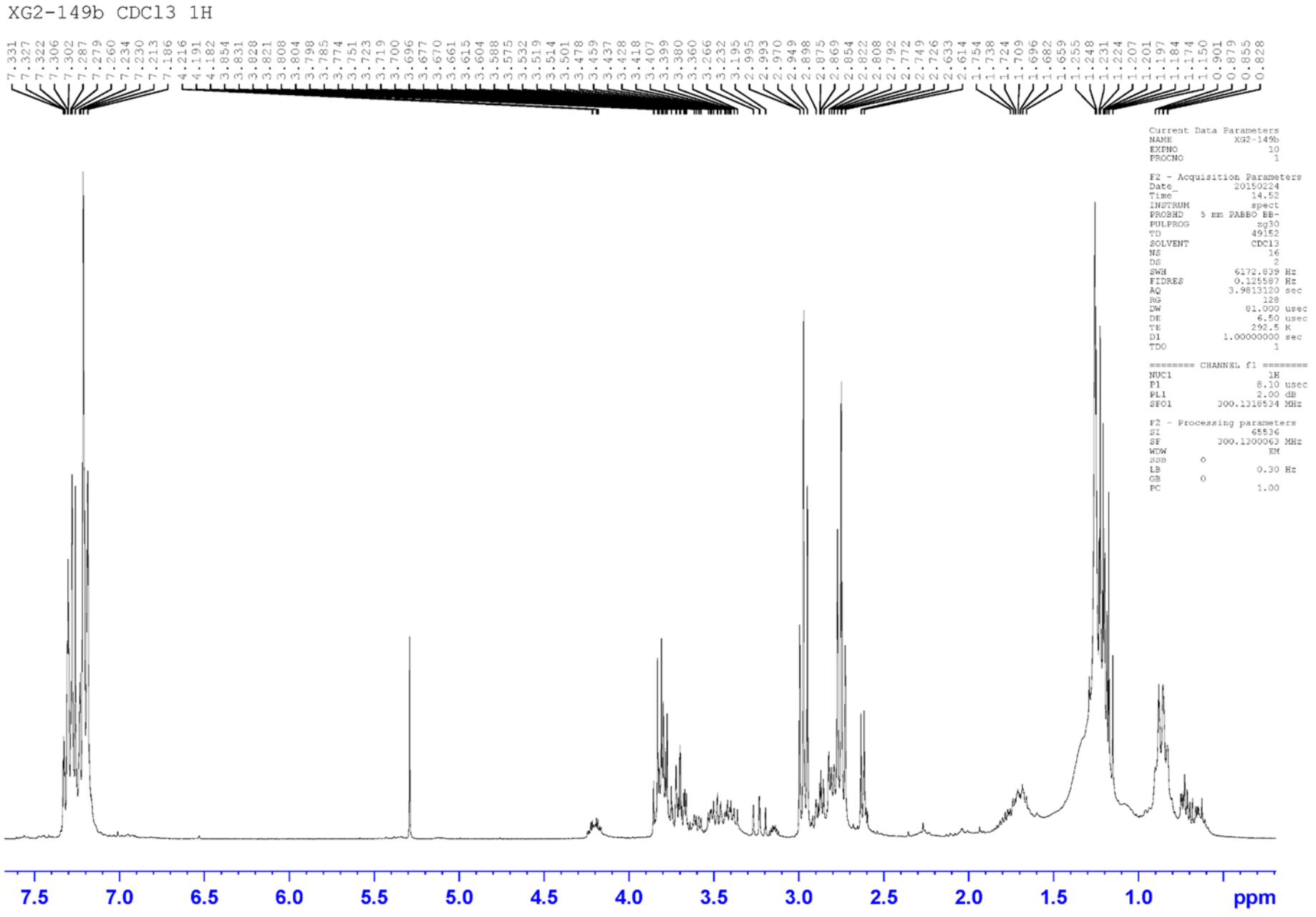


Figure SI_156: ^{1}H NMR spectrum of the crude mixture of the reaction between phenethylamine and GPTES in toluene (reflux, 18h). (Scheme 4. in article)

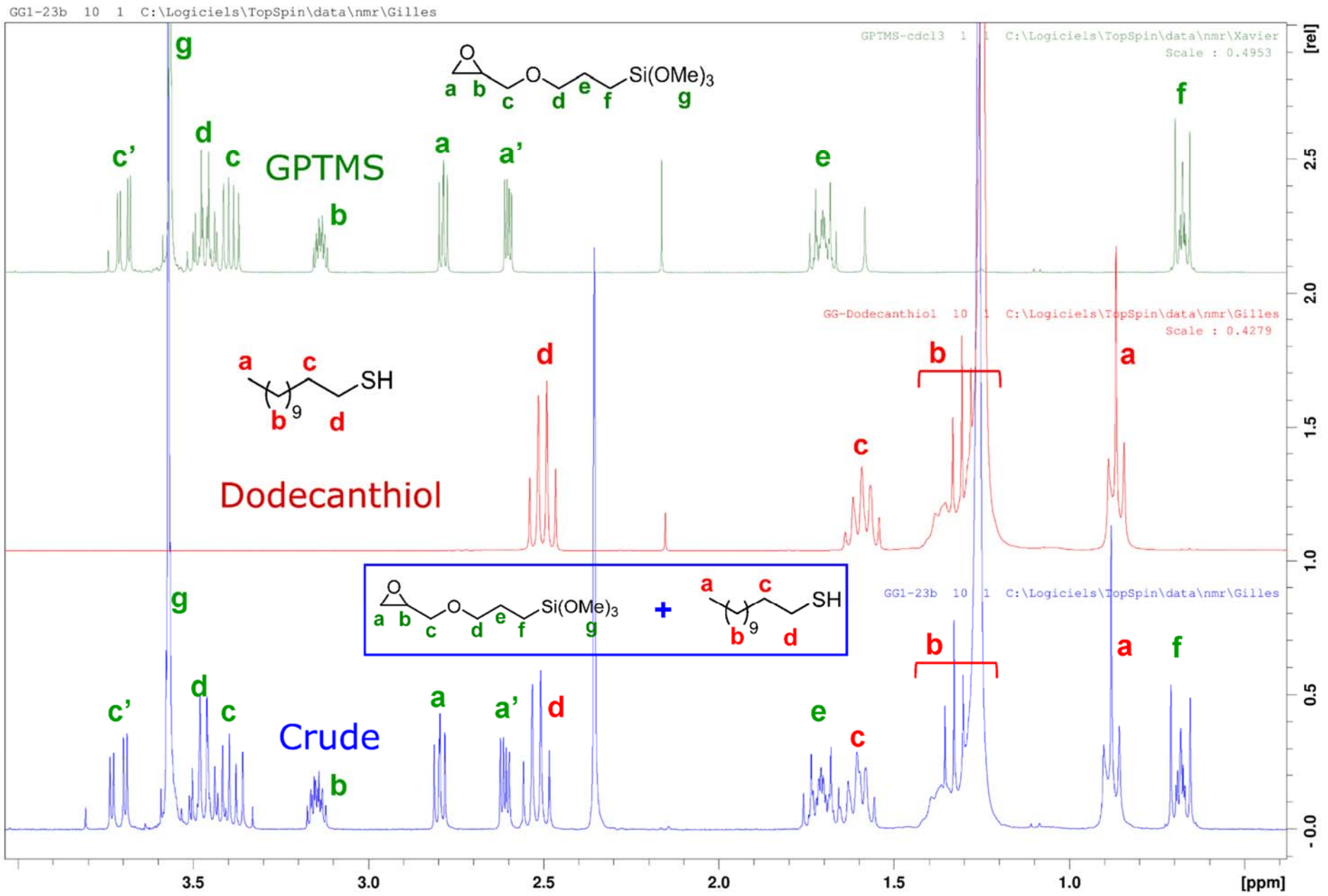


Figure SI_157: Comparison of the ^{1}H NMR spectra of both starting materials, GPTMS (green) and Dodecanthiol (red), with the crude oil (blue) obtained after 21h of reaction in toluene reflux. (Scheme 5. in article)

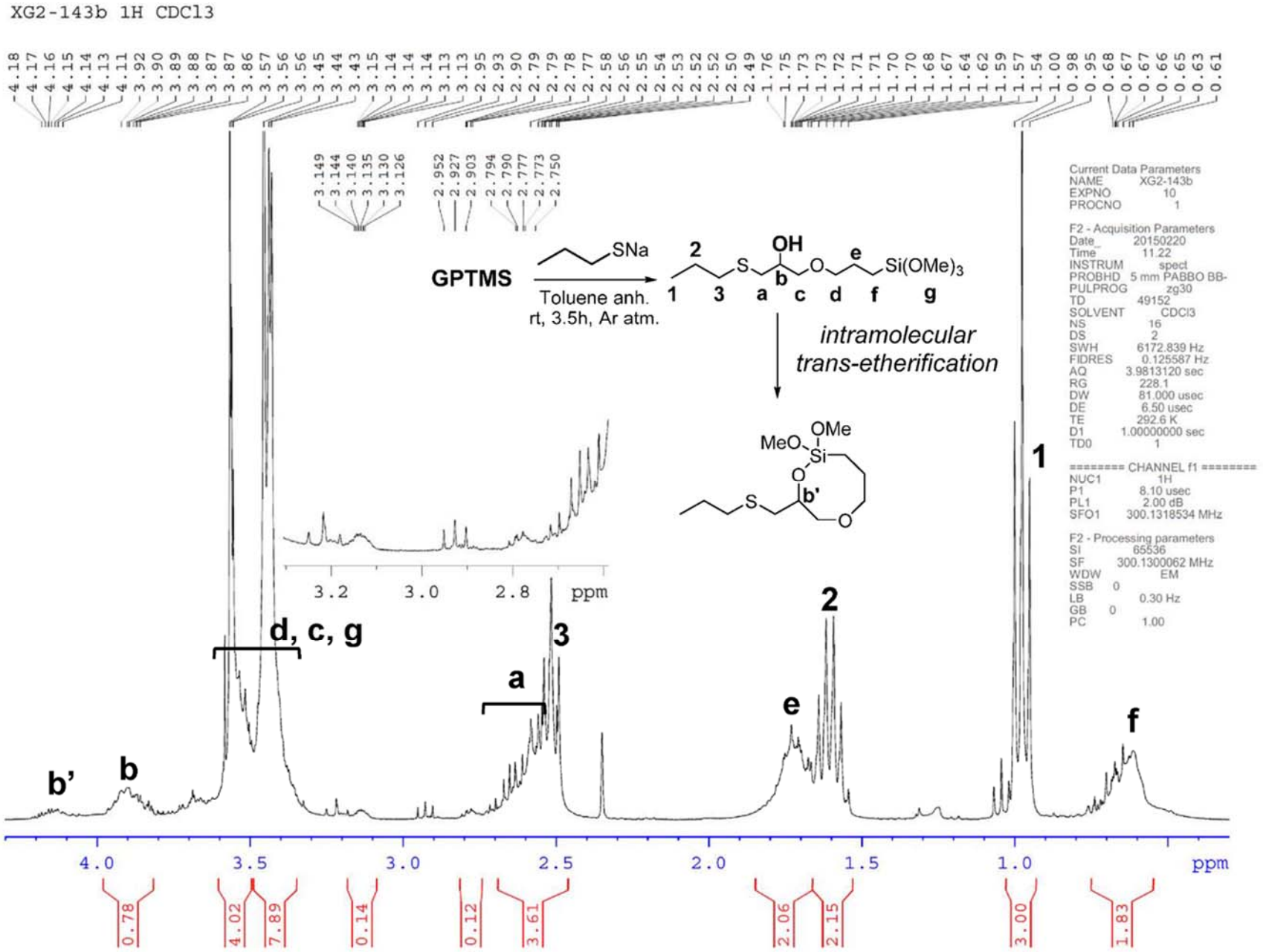


Figure SI_158: ^{1}H NMR spectrum of the crude mixture of the reaction between sodium propylthiolate and GPTMS in toluene (rt, 3.5h). (Scheme 6. in article)

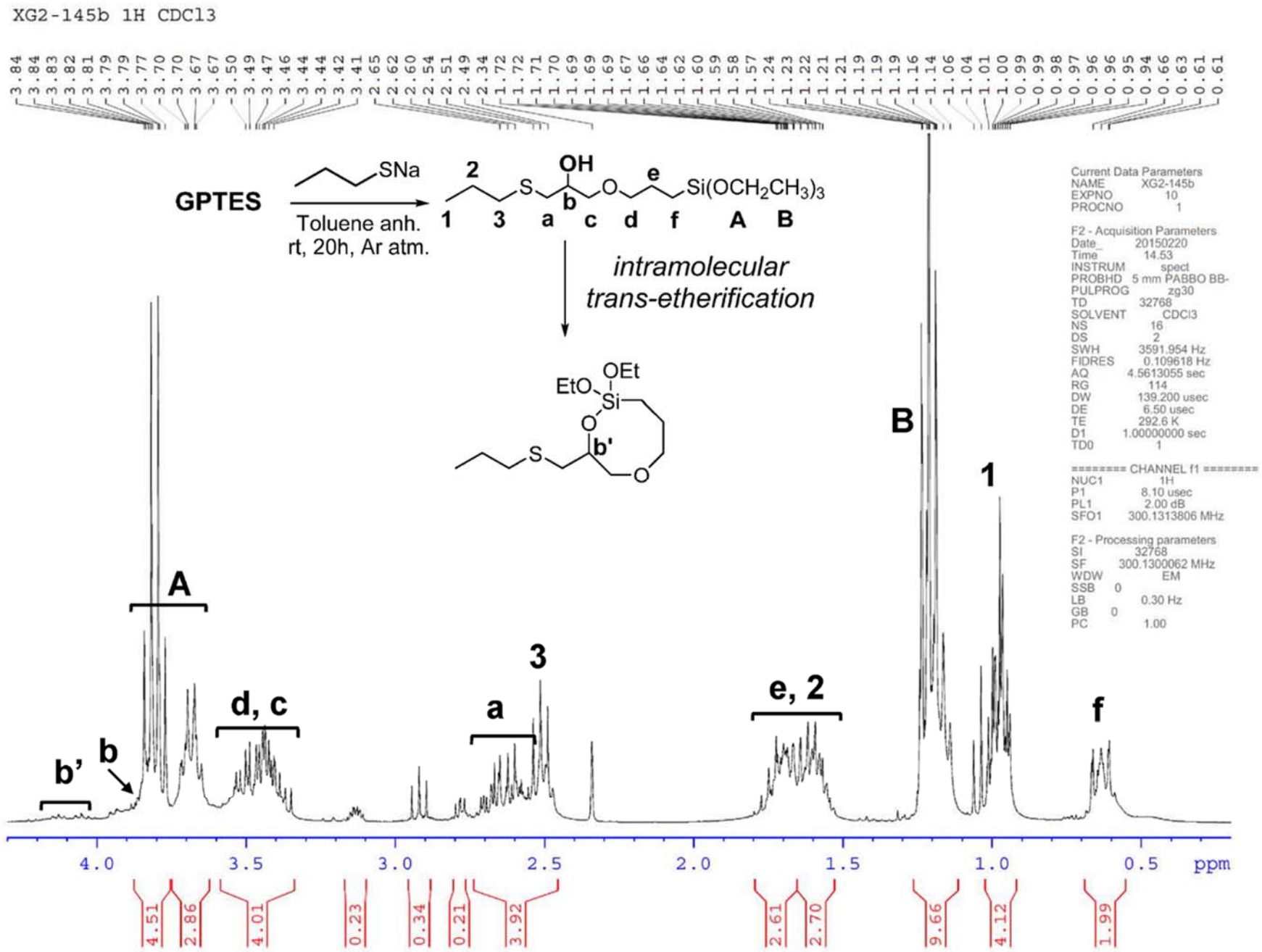


Figure SI_159: ^{1}H NMR spectrum of the crude mixture of the reaction between sodium propylthiolate and GPTES in toluene (rt, 20h). (Scheme 6. in article)

SI_160

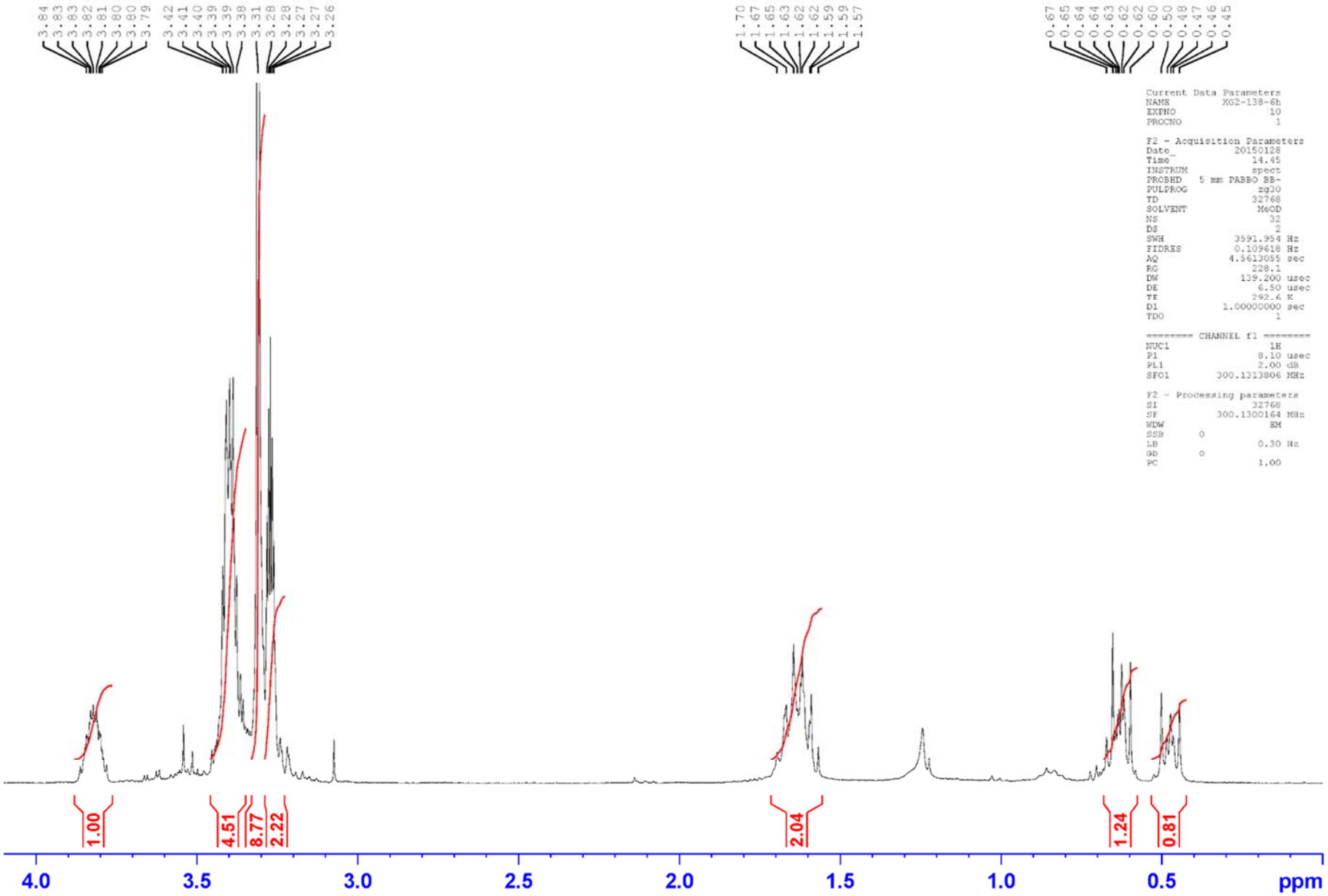


Figure SI_160: ^{1}H NMR spectrum of the reaction mixture after 5h of reaction between NaN_3 (excess) and GPTMS in CD_3OD .

SI_161

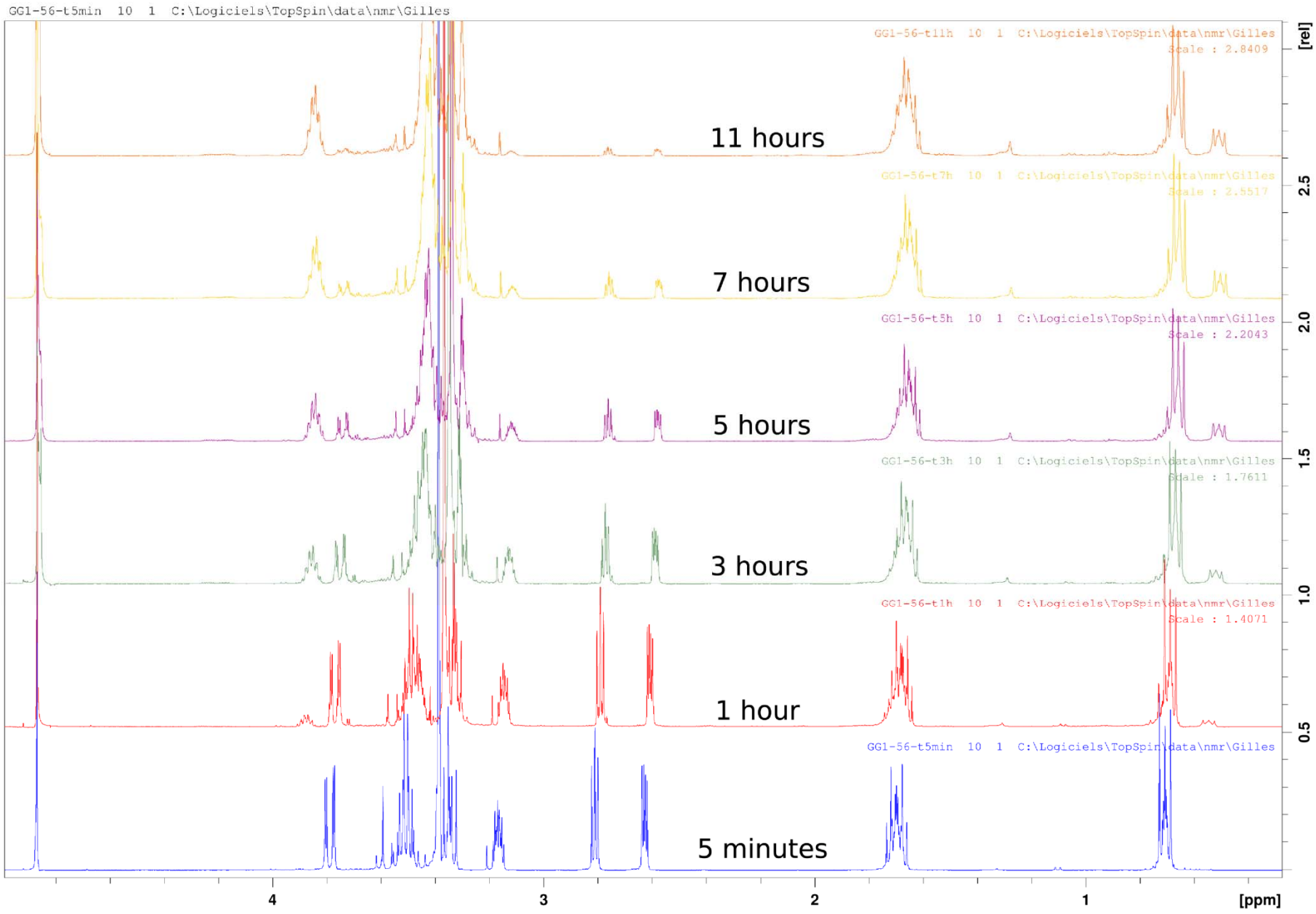


Figure SI_161: ^{1}H NMR monitoring of the reaction between NaN_3 and GTPMS in stoichiometric conditions (CD3OD, 70°C).

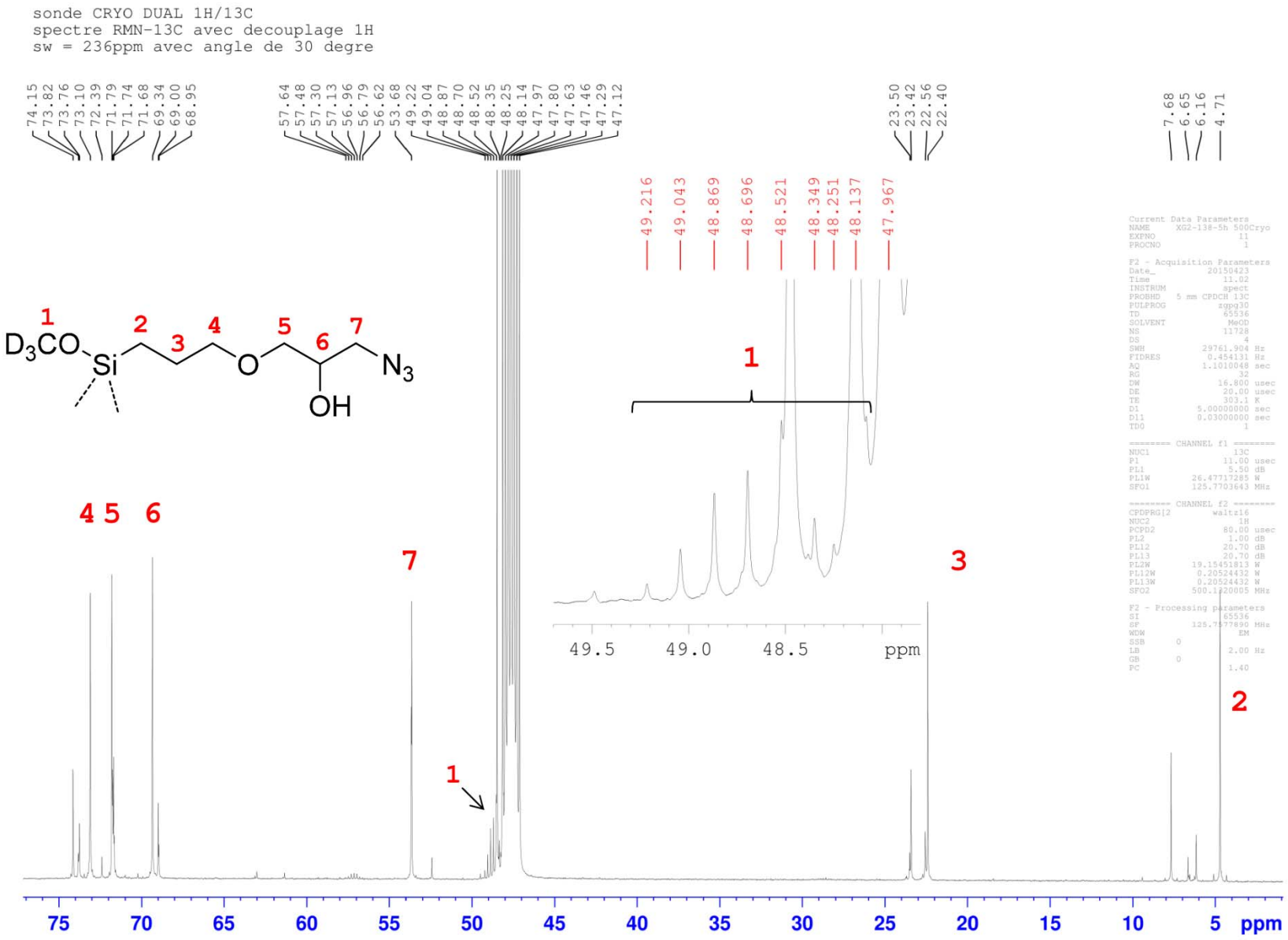


Figure SI_162: ^{13}C NMR spectrum of the crude mixture after 5h of reaction between NaN_3 and GPTMS in refluxing deuterated methanol. (Scheme 7 (a.) in article)

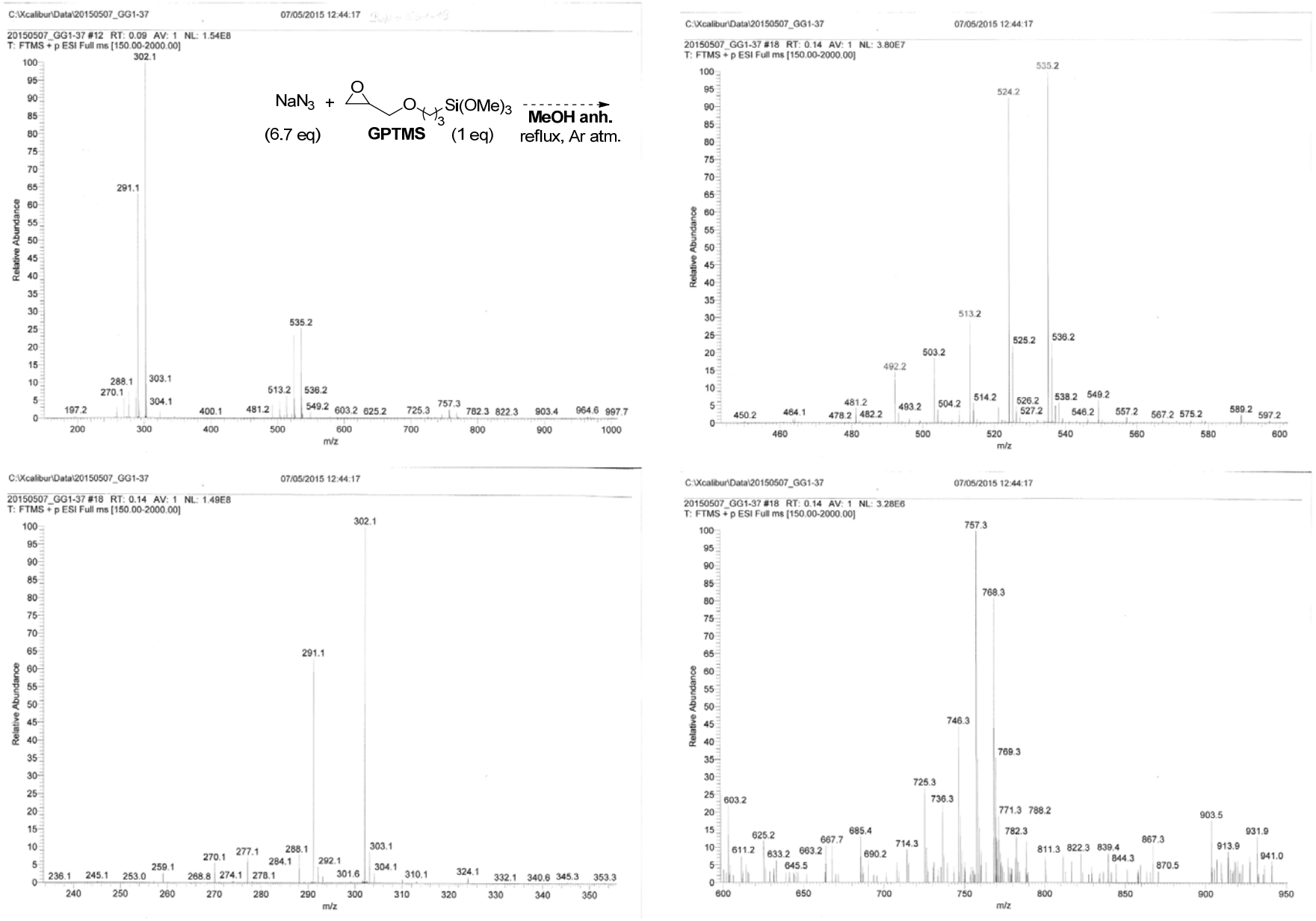
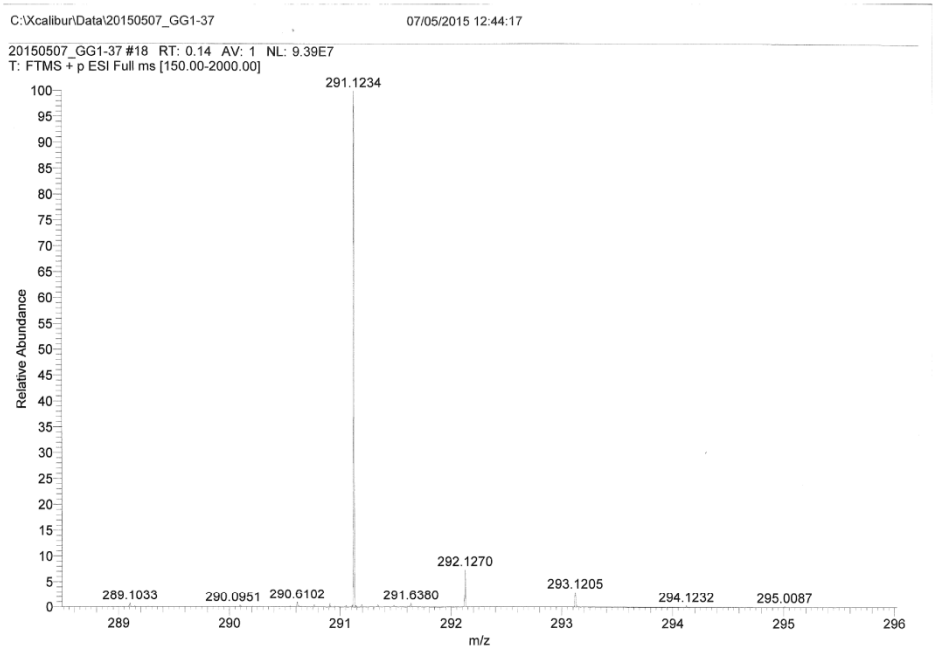


Figure SI_163: Complementary MS-ESI spectra (with zoom) of the crude mixture after 5h of reaction between NaN_3 and GPTMS in refluxing methanol. (Figure 6. in article)



Elemental composition search on mass 291.12

m/z= 286.12-296.12

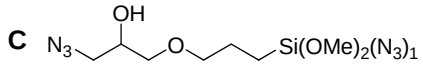
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
291.1234	291.1232	0.87	3.5	$C_8H_{19}O_4N_6Si$
	291.1240	-2.16	12.5	$C_{17}H_{15}ON_4$
	291.1227	2.44	7.5	$C_{16}H_{19}O_5$
	291.1245	-3.72	8.5	$C_9H_{15}N_{10}Si$

Elemental composition search on mass 302.11

m/z= 297.11-307.11

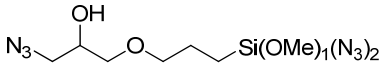
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
302.1142	302.1140	0.60	5.5	$C_7H_{16}O_3N_9Si$
	302.1135	2.11	9.5	$C_{15}H_{16}O_4N_3$
	302.1149	-2.32	14.5	$C_{16}H_{12}N_7$

C



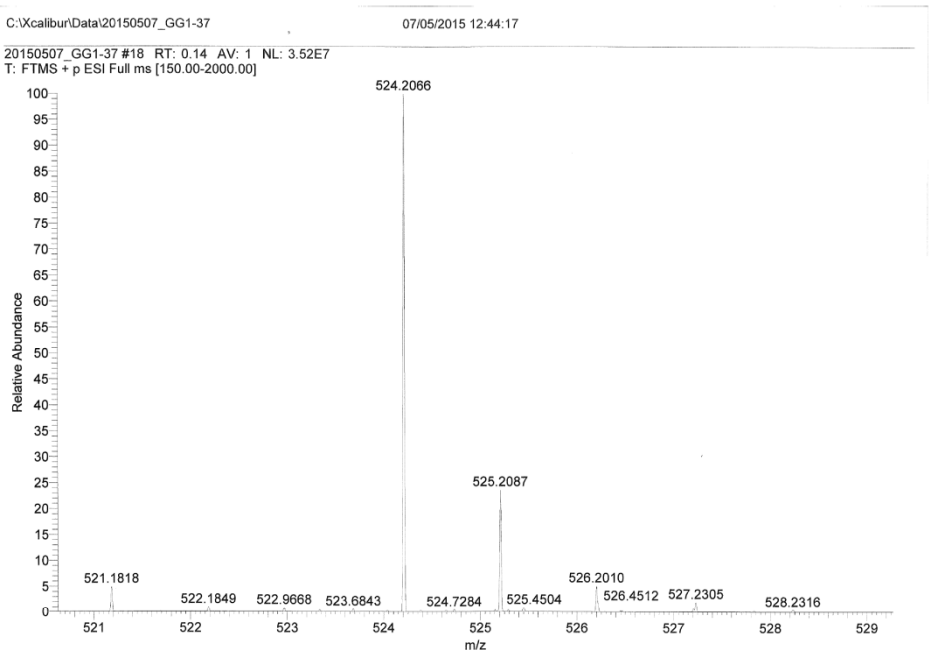
Chemical Formula: $C_8H_{18}N_6O_4Si$
Exact Mass: 290.12

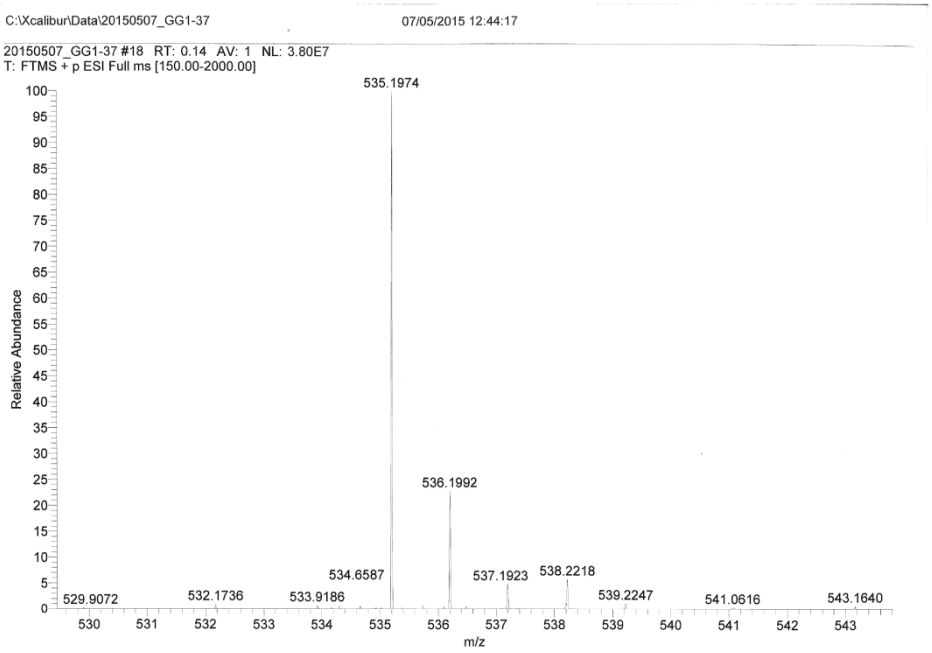
D



Chemical Formula: $C_7H_{15}N_9O_3Si$
Exact Mass: 301.11

Figure SI_164: HRMS-ESI spectra of the molecular peaks ([*M*+H$^+$]) of compounds C (left) & D (right).



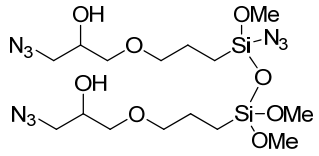


Elemental composition search on mass 524.21

m/z= 519.21-529.21

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
524.2066	524.2066	-0.03	7.0	$C_{16}H_{33}O_5N_{10}NaSi_2$
	524.2066	-0.04	1.5	$C_{17}H_{39}O_{10}N_3NaSi_2$
	524.2063	0.49	0.0	$C_{16}H_{40}O_{13}N_2Si_2$
	524.2063	0.50	5.5	$C_{15}H_{34}O_8N_9Si_2$
	524.2058	1.47	18.0	$C_{29}H_{32}O_2N_4Si_2$
	524.2077	-2.06	5.0	$C_{17}H_{36}O_9N_6Si_2$
	524.2053	2.53	2.0	$C_{15}H_{37}O_9N_6NaSi_2$
	524.2080	-2.59	6.5	$C_{18}H_{35}O_6N_7NaSi_2$
	524.2080	-2.60	1.0	$C_{19}H_{41}O_{11}NaSi_2$
	524.2050	3.05	0.5	$C_{14}H_{38}O_{12}N_5Si_2$
	524.2050	3.06	6.0	$C_{13}H_{32}O_7N_{12}Si_2$
	524.2048	3.49	14.5	$C_{29}H_{35}O_3NNaSi_2$
	524.2045	4.02	13.0	$C_{28}H_{36}O_6Si_2$
	524.2045	4.03	18.5	$C_{27}H_{30}ON_7Si_2$
	524.2090	-4.61	10.0	$C_{18}H_{32}O_5N_{10}Si_2$
	524.2090	-4.62	4.5	$C_{19}H_{38}O_{10}N_3Si_2$

F



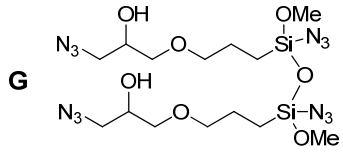
Chemical Formula: $C_{15}H_{33}N_9O_8Si_2$
Exact Mass: 523.20

Elemental composition search on mass 535.20

m/z= 530.20-540.20

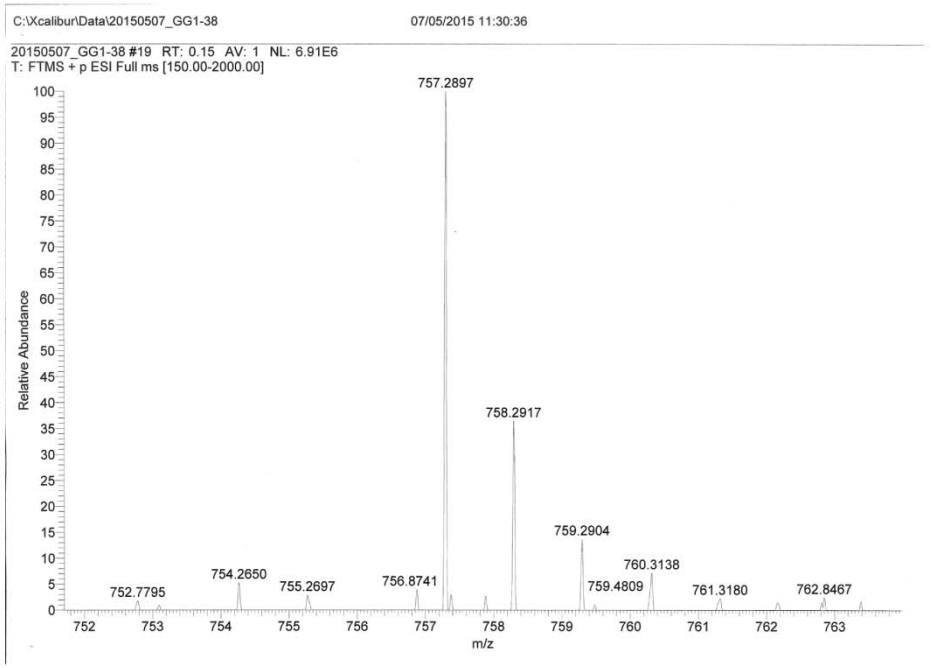
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
535.1974	535.1975	-0.11	3.5	$C_{16}H_{36}O_9N_6NaSi_2$
	535.1972	0.40	2.0	$C_{15}H_{37}O_{12}N_5Si_2$
	535.1972	0.41	7.5	$C_{14}H_{31}O_7N_{12}Si_2$
	535.1969	0.83	16.0	$C_{30}H_{34}O_3NNaSi_2$
	535.1980	-1.15	19.5	$C_{30}H_{31}O_2N_4Si_2$
	535.1967	1.35	14.5	$C_{29}H_{35}O_6Si_2$
	535.1967	1.36	20.0	$C_{28}H_{29}ON_7Si_2$
	535.1985	-2.10	7.0	$C_{16}H_{33}O_8N_9Si_2$
	535.1985	-2.11	1.5	$C_{17}H_{39}O_{13}N_2Si_2$
	535.1961	2.40	4.0	$C_{14}H_{34}O_8N_9NaSi_2$
	535.1988	-2.61	8.5	$C_{17}H_{32}O_5N_{10}NaSi_2$
	535.1988	-2.62	3.0	$C_{18}H_{38}O_{10}N_3NaSi_2$
	535.1958	2.91	2.5	$C_{13}H_{35}O_{11}N_8Si_2$
	535.1956	3.34	16.5	$C_{28}H_{32}O_2N_4NaSi_2$
	535.1953	3.86	15.0	$C_{27}H_{33}O_5N_3Si_2$
	535.1953	3.87	20.5	$C_{26}H_{27}N_{10}Si_2$
	535.1999	-4.61	6.5	$C_{18}H_{35}O_9N_6Si_2$
	535.1948	4.89	-1.0	$C_{13}H_{38}O_{12}N_5NaSi_2$
	535.1948	4.90	4.5	$C_{12}H_{32}O_7N_{12}NaSi_2$

G



Chemical Formula: $C_{14}H_{30}N_{12}O_7Si_2$
Exact Mass: 534.19

Figure SI_165: HRMS-ESI spectra of the molecular peaks ([*M*+H$^+$]) of compounds F (left) & G (right).



Elemental composition search on mass 757.29

m/z= 752.29-762.29

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
757.2897	757.2898	-0.09	3.5	$C_{24}H_{54}O_{14}N_6NaSi_3$
	757.2895	0.28	7.5	$C_{22}H_{49}O_{12}N_{12}Si_3$
	757.2909	-1.50	7.0	$C_{24}H_{51}O_{13}N_9Si_3$
	757.2885	1.68	4.0	$C_{22}H_{52}O_{13}N_9NaSi_3$
	757.2911	-1.86	8.5	$C_{25}H_{50}O_{10}N_{10}NaSi_3$
	757.2911	-1.87	3.0	$C_{26}H_{56}O_{15}N_3NaSi_3$
	757.2922	-3.27	6.5	$C_{26}H_{53}O_{14}N_6Si_3$
	757.2871	3.45	4.5	$C_{20}H_{50}O_{12}N_{12}NaSi_3$
	757.2925	-3.63	8.0	$C_{27}H_{52}O_{11}N_7NaSi_3$
	757.2868	3.82	3.0	$C_{19}H_{51}O_{15}N_{11}Si_3$

I

Chemical Formula: $C_{22}H_{48}N_{12}O_{12}Si_3$
Exact Mass: 756.28

Figure SI_166: HRMS-ESI spectrum of the molecular peaks ([*M*+H$^+$]) of compounds I.

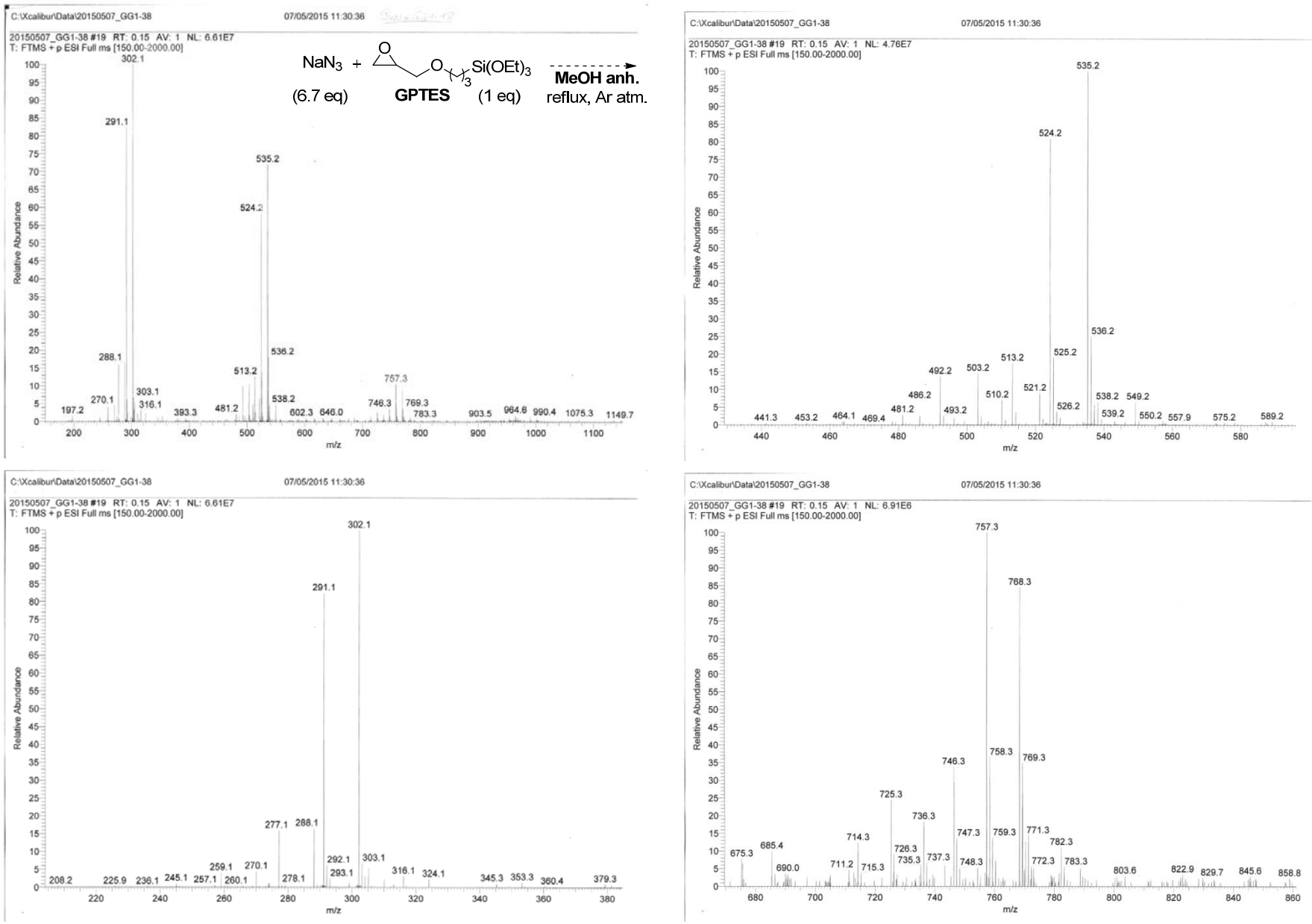


Figure SI_167: MS-ESI spectra (with zoom) of the crude mixture after 5h of reaction between NaN_3 and GPTES in refluxing methanol.

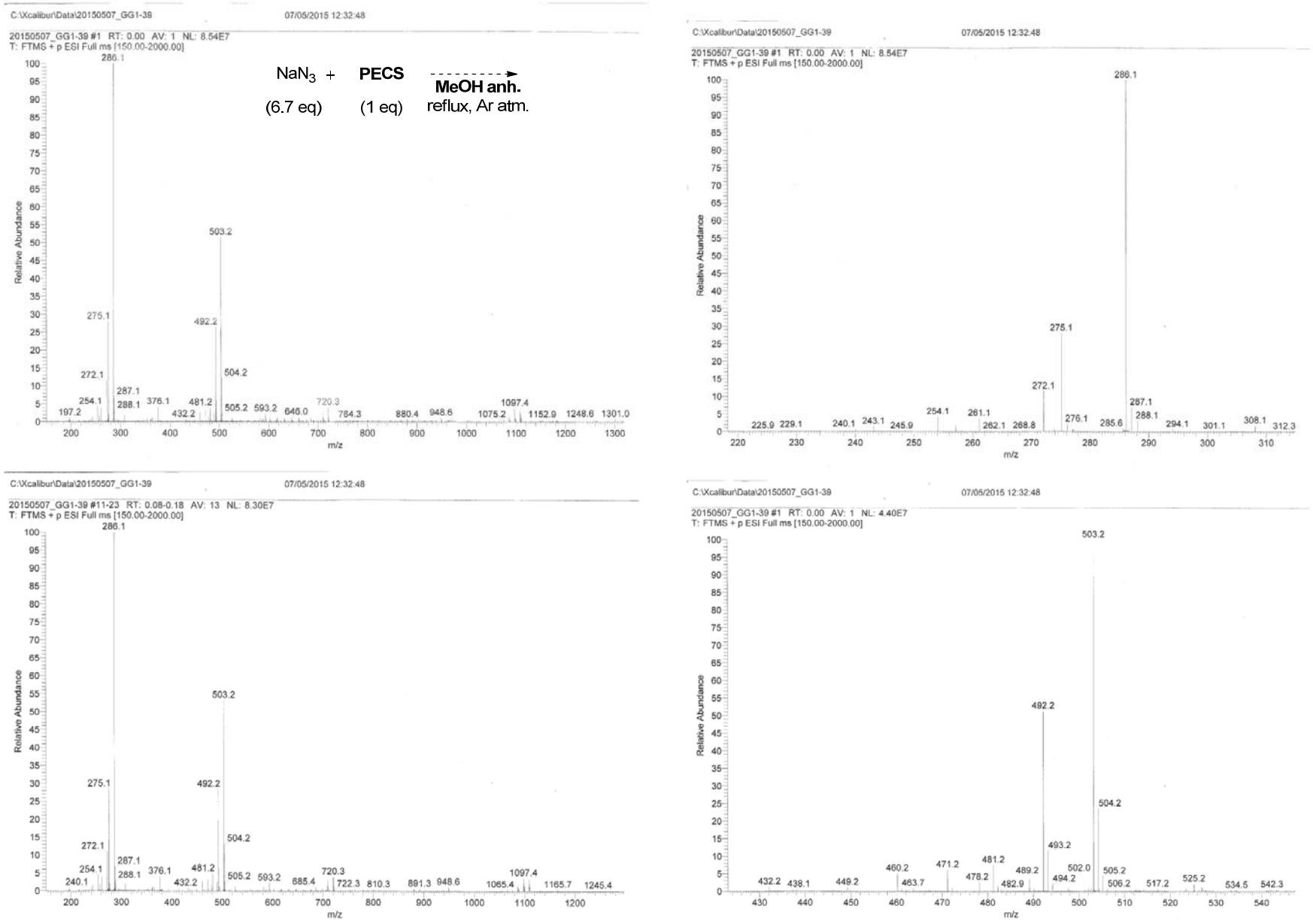
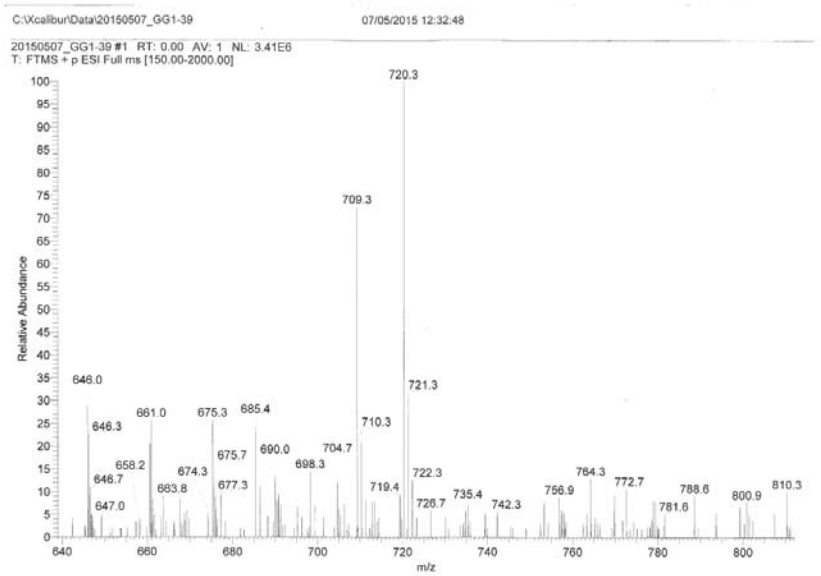
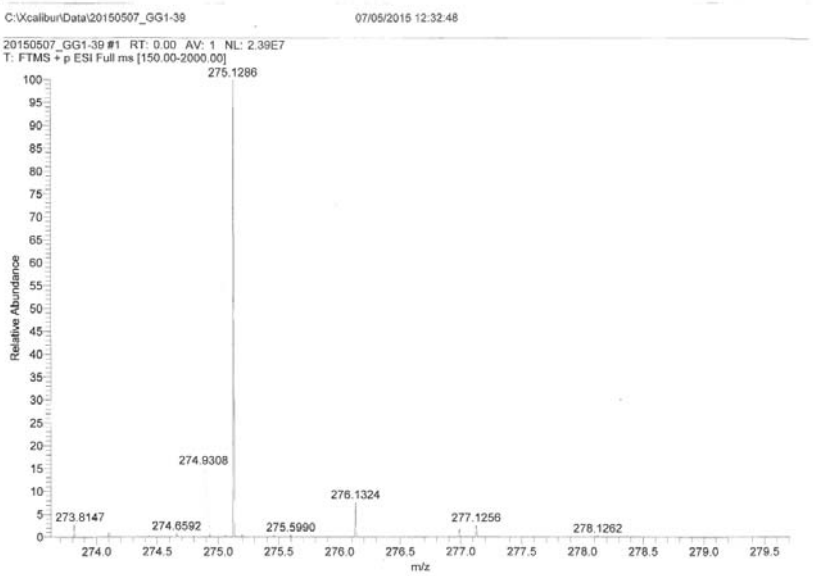
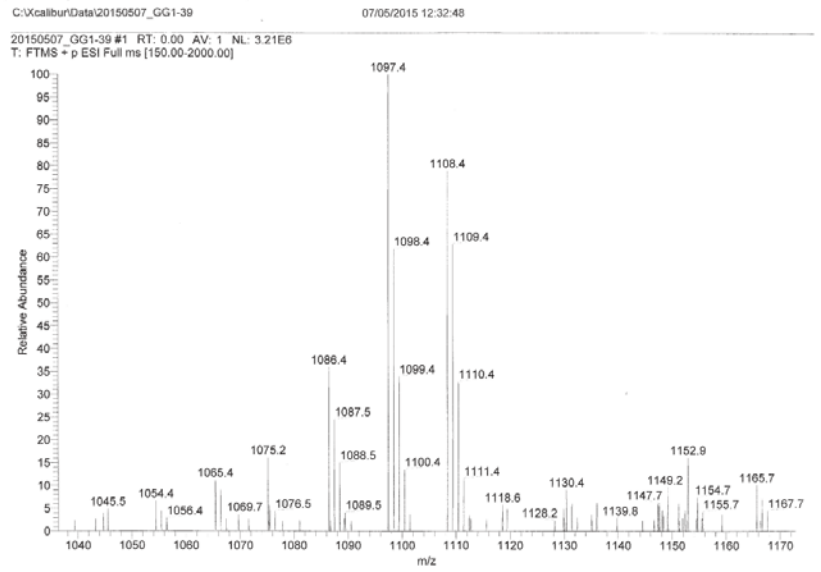


Figure SI_168: MS-ESI spectra (with zoom) of the crude mixture after 5h of reaction between NaN_3 and PECS in refluxing methanol.



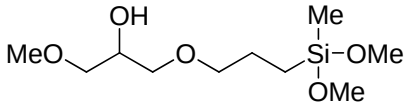




Elemental composition search on mass 275.13

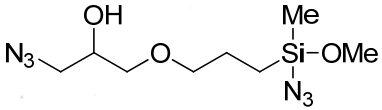
m/z= 270.13-280.13

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
275.1286	275.1285	0.29	-0.5	$C_{10}H_{24}O_5NaSi$
	275.1285	0.30	5.0	$C_9H_{18}N_7NaSi$
	275.1282	1.30	3.5	$C_8H_{19}O_3N_6Si$
	275.1291	-1.90	12.5	$C_{17}H_{15}N_4$
	275.1281	1.96	9.0	$C_{17}H_{19}ONNa$
	275.1278	2.96	7.5	$C_{16}H_{19}O_4$
	275.1296	-3.58	3.0	$C_{10}H_{21}O_4N_3Si$
	275.1296	-3.75	0.0	$C_3H_{17}O_6N_9$
	275.1299	-4.58	4.5	$C_{11}H_{20}ON_4NaSi$
	275.1299	-4.75	1.5	$C_4H_{16}O_3N_{10}Na$



Chemical Formula: $C_{10}H_{24}O_5Si$
Exact Mass: 252.14

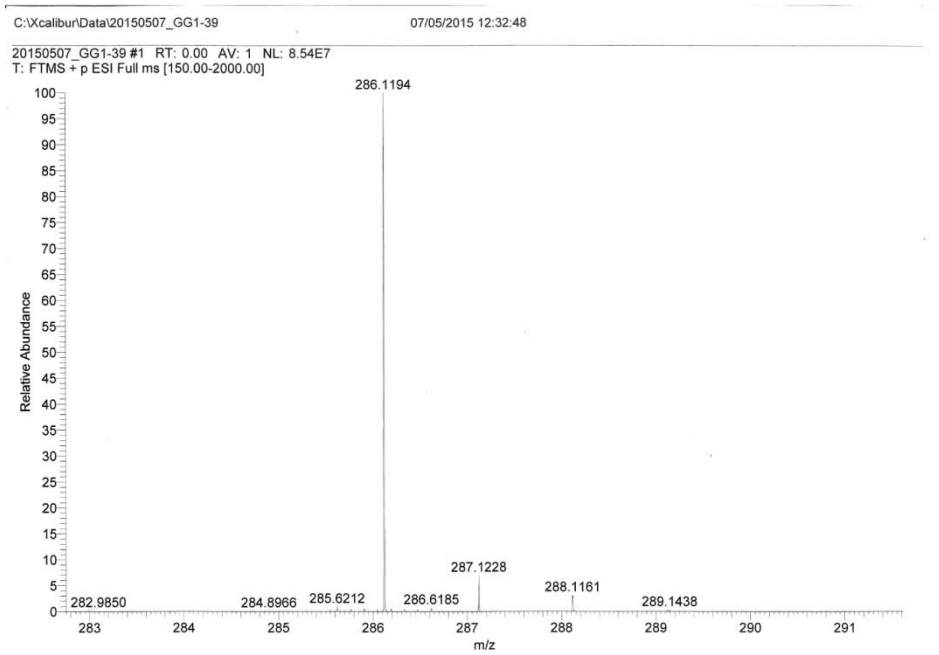
or

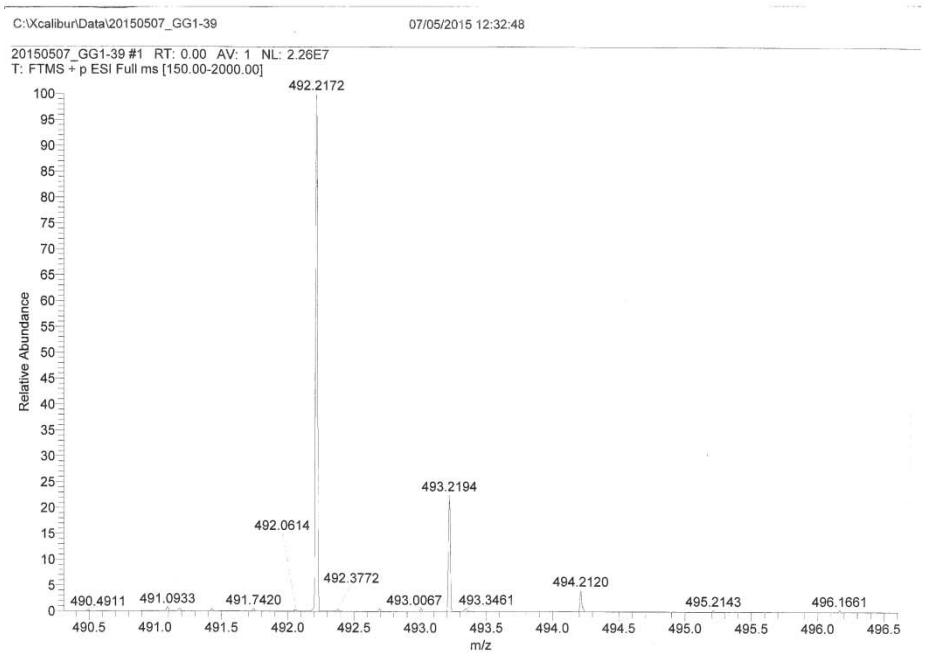


Chemical Formula: $C_8H_{18}N_6O_3Si$
Exact Mass: 274.12

Figure SI_169: MS-ESI zoom spectra (left) and proposed structures for the specie at 275.1286 *m/z*.

SI_170

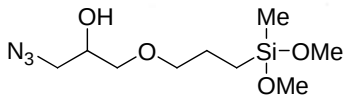




Elemental compositicn search on mass 286.12

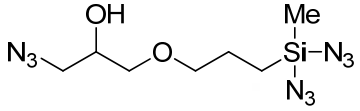
m/z= 281.12-291.12

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
286.1194	286.1194	0.23	1.5	$C_9H_{21}O_4N_3NaSi$
	286.1191	1.05	2.5	$H_{12}O_4N_{15}$
	286.1198	-1.20	0.5	$C_8H_{25}ON_3NaSi_3$
	286.1191	1.21	5.5	$C_7H_{16}O_2N_9Si$
	286.1190	1.37	8.5	$C_{14}H_{20}N_3Si_2$
	286.1186	2.80	9.5	$C_{15}H_{16}O_3N_3$
	286.1202	-2.85	10.5	$C_{18}H_{17}ONNa$
	286.1205	-3.63	7.5	CH_8N_{19}
	286.1207	-4.44	6.5	$C_{10}H_{17}N_7NaSi$
	286.1181	4.45	-0.5	$C_5H_{24}O_3N_5Si_3$
	286.1207	-4.61	3.5	$C_3H_{13}O_2N_{13}Na$



Chemical Formula: $C_9H_{21}N_3O_4Si$
Exact Mass: 263.13

or

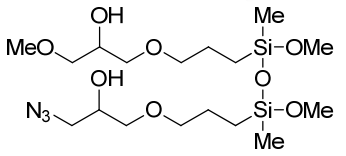


Chemical Formula: $C_7H_{15}N_9O_2Si$
Exact Mass: 285.11

Elemental compositicn search on mass 492.22

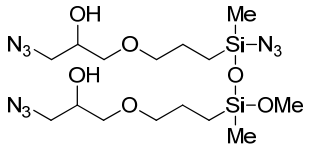
m/z= 487.22-497.22

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
492.2172	492.2174	-0.41	14.5	$C_{24}H_{30}O_3N_7Si$
	492.2174	-0.42	9.0	$C_{25}H_{36}O_8Si$
	492.2174	-0.51	6.0	$C_{18}H_{32}O_{10}N_6$
	492.2168	0.81	1.5	$C_{17}H_{39}O_8N_3NaSi_2$
	492.2168	0.82	7.0	$C_{16}H_{33}O_3N_{10}NaSi_2$
	492.2177	-0.97	16.0	$C_{25}H_{29}N_8NaSi$
	492.2177	-0.98	10.5	$C_{26}H_{35}O_5NNaSi$
	492.2177	-1.07	7.5	$C_{19}H_{31}O_7N_7Na$
	492.2177	-1.08	2.0	$C_{20}H_{37}O_{12}Na$
	492.2179	-1.34	5.0	$C_{17}H_{36}O_7N_6Si_2$
	492.2165	1.37	0.0	$C_{16}H_{40}O_{11}N_2Si_2$
	492.2165	1.38	5.5	$C_{15}H_{34}O_6N_9Si_2$
	492.2164	1.65	2.5	$C_{18}H_{35}O_{11}N_3Na$
	492.2164	1.66	8.0	$C_{17}H_{29}O_6N_{10}Na$
	492.2163	1.75	11.0	$C_{24}H_{33}O_4N_4NaSi$
	492.2181	-1.90	6.5	$C_{18}H_{35}O_4N_7NaSi_2$
	492.2181	-1.91	1.0	$C_{19}H_{41}O_9NaSi_2$
	492.2161	2.20	1.0	$C_{17}H_{36}O_{14}N_2$
	492.2161	2.21	6.5	$C_{16}H_{30}O_9N_9$
	492.2161	2.31	9.5	$C_{23}H_{34}O_7N_3Si$



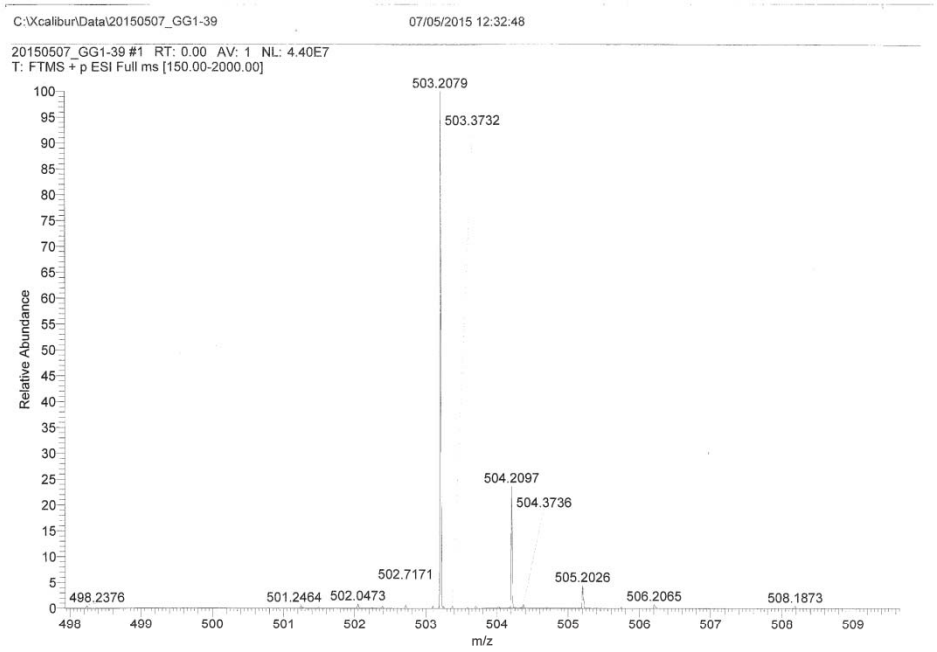
Chemical Formula: $C_{17}H_{39}N_3O_8Si_2$
Exact Mass: 469.23

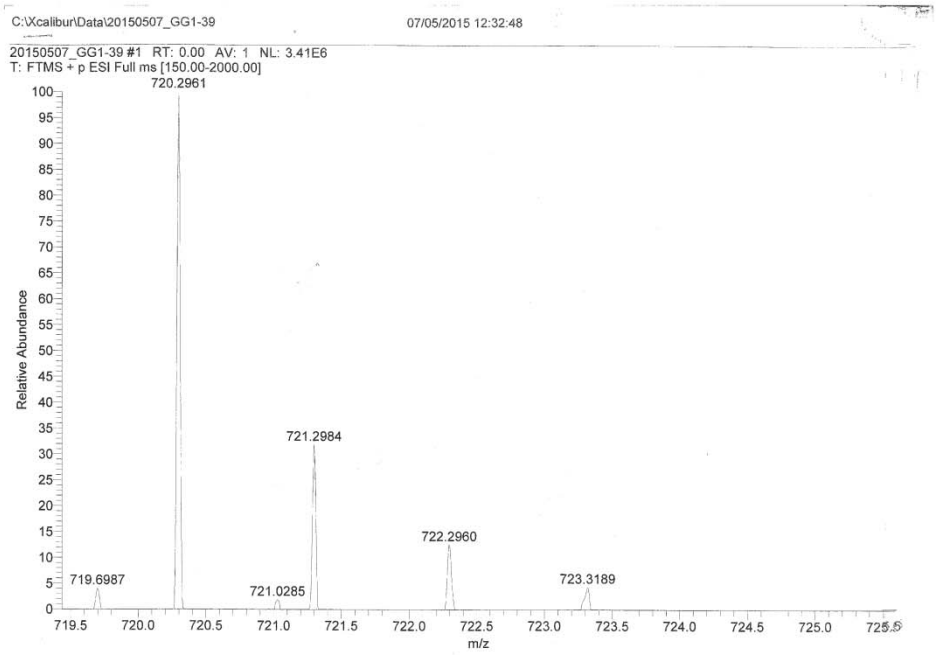
or



Chemical Formula: $C_{15}H_{33}N_9O_6Si_2$
Exact Mass: 491.21

Figure SI_170: Proposed structures for the species at 286.1194 *m/z* (left) and 492.2172 *m/z* (right).

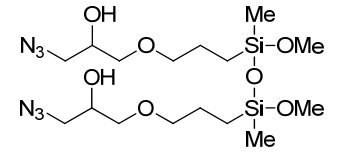




Elemental composition search on mass 503.21

m/z= 498.21-508.21

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
503.2079	503.2082	-0.45	19.5	$C_{30}H_{31}N_4Si_2$
	503.2082	-0.54	16.5	$C_{23}H_{27}O_2N_{10}Si$
	503.2082	-0.55	11.0	$C_{24}H_{33}O_7N_3Si$
	503.2083	-0.65	8.0	$C_{17}H_{29}O_9N_9$
	503.2076	0.65	3.5	$C_{16}H_{36}O_7N_6NaSi_2$ ✓
	503.2083	-0.66	2.5	$C_{18}H_{35}O_{14}N_2$
	503.2085	-1.10	12.5	$C_{25}H_{32}O_4N_4NaSi$
	503.2085	-1.19	9.5	$C_{18}H_{28}O_6N_{10}Na$
	503.2073	1.20	2.0	$C_{15}H_{37}O_{10}N_5Si_2$
	503.2086	-1.20	4.0	$C_{19}H_{34}O_{11}N_3Na$
	503.2087	-1.46	7.0	$C_{16}H_{33}O_6N_9Si_2$
	503.2072	1.47	4.5	$C_{17}H_{32}O_{10}N_6Na$
	503.2087	-1.47	1.5	$C_{17}H_{39}O_{11}N_2Si_2$
	503.2072	1.56	7.5	$C_{24}H_{36}O_8NaSi$
	503.2072	1.57	13.0	$C_{23}H_{30}O_3N_7NaSi$
	503.2071	1.66	16.0	$C_{30}H_{34}ONNaSi_2$
	503.2090	-2.01	8.5	$C_{17}H_{32}O_3N_{10}NaSi_2$
	503.2069	2.01	3.0	$C_{16}H_{33}O_{13}N_5$
	503.2090	-2.02	3.0	$C_{18}H_{38}O_8N_3NaSi_2$
	503.2090	-2.11	0.0	$C_{11}H_{34}O_{10}N_9NaSi$

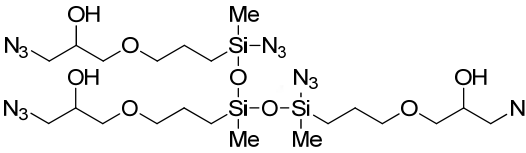


Chemical Formula: $C_{16}H_{36}N_6O_7Si_2$
Exact Mass: 480.22

Elemental composition search on mass 720.30

m/z= 715.30-725.30

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
720.2961	720.2956	0.74	9.5	$C_{21}H_{46}O_8N_{15}Si_3$
	720.2956	0.80	12.5	$C_{28}H_{50}O_6N_9Si_4$
	720.2970	-1.13	3.5	$C_{24}H_{54}O_{14}N_5Si_3$
	720.2951	1.43	16.5	$C_{36}H_{50}O_7N_3Si_3$
	720.2943	2.59	4.5	$C_{20}H_{50}O_{12}N_{11}Si_3$
	720.2942	2.66	7.5	$C_{27}H_{54}O_{10}N_5Si_4$
	720.2982	-2.93	11.5	$C_{32}H_{54}O_8N_3Si_4$
	720.2983	-2.99	8.5	$C_{25}H_{50}O_{10}N_9Si_3$
	720.2991	-4.15	20.5	$C_{41}H_{50}O_5NSi_3$
	720.2929	4.52	2.5	$C_{26}H_{58}O_{14}NSi_4$
	720.2996	-4.85	13.5	$C_{26}H_{46}O_6N_{13}Si_3$



Chemical Formula: $C_{21}H_{46}N_{15}O_8Si_3$
Exact Mass: 720.30

Figure SI_171: Proposed structures for the species at 503.2079 *m/z* (left) and 720.2961 *m/z* (right).

SI_172

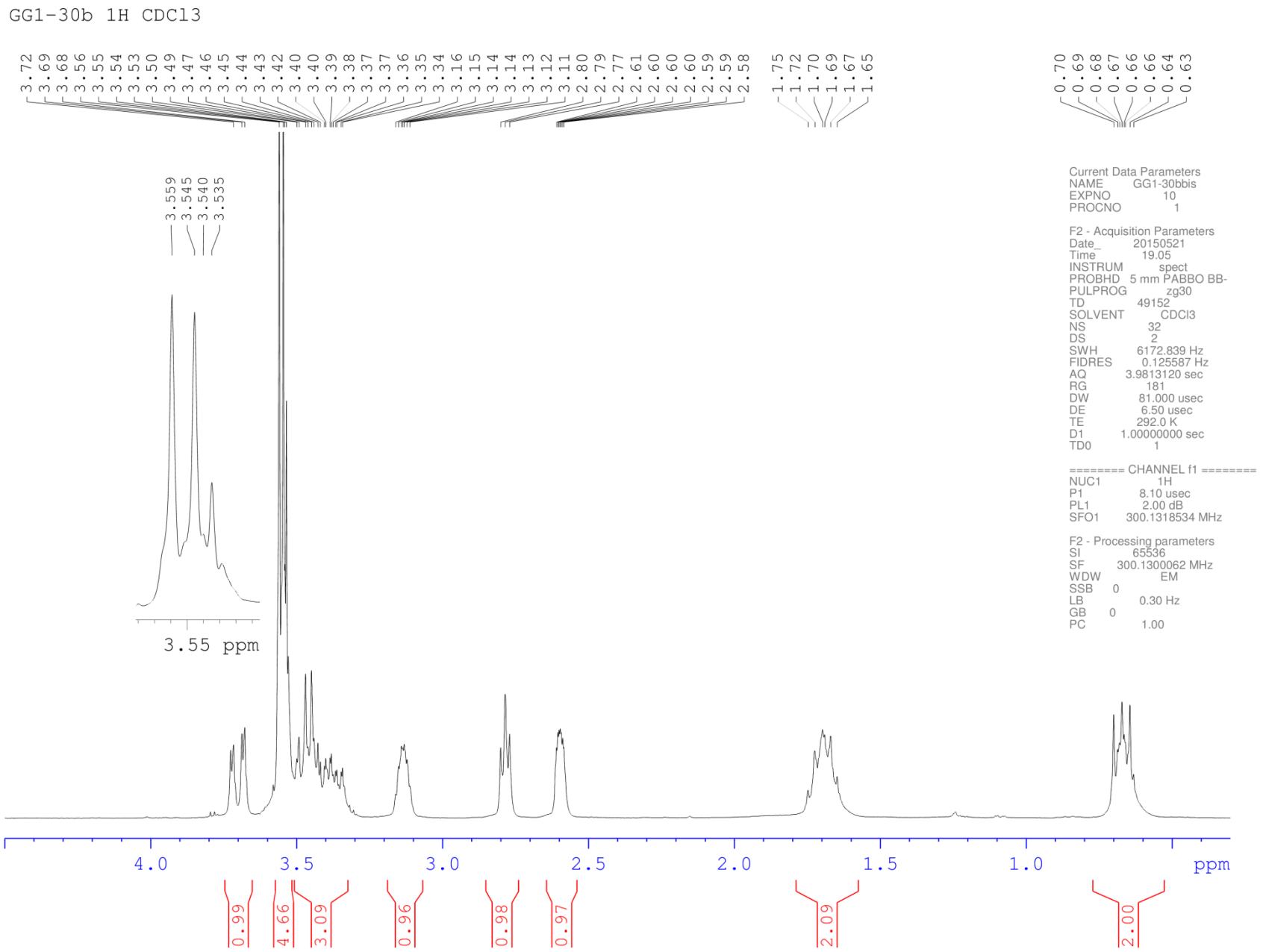


Figure SI_172: ^{1}H NMR spectrum of the crude mixture of the reaction between sodium ethoxide and GPTMS in THF (rt, 5h). (Scheme 8 (a.) in article)

SI_173

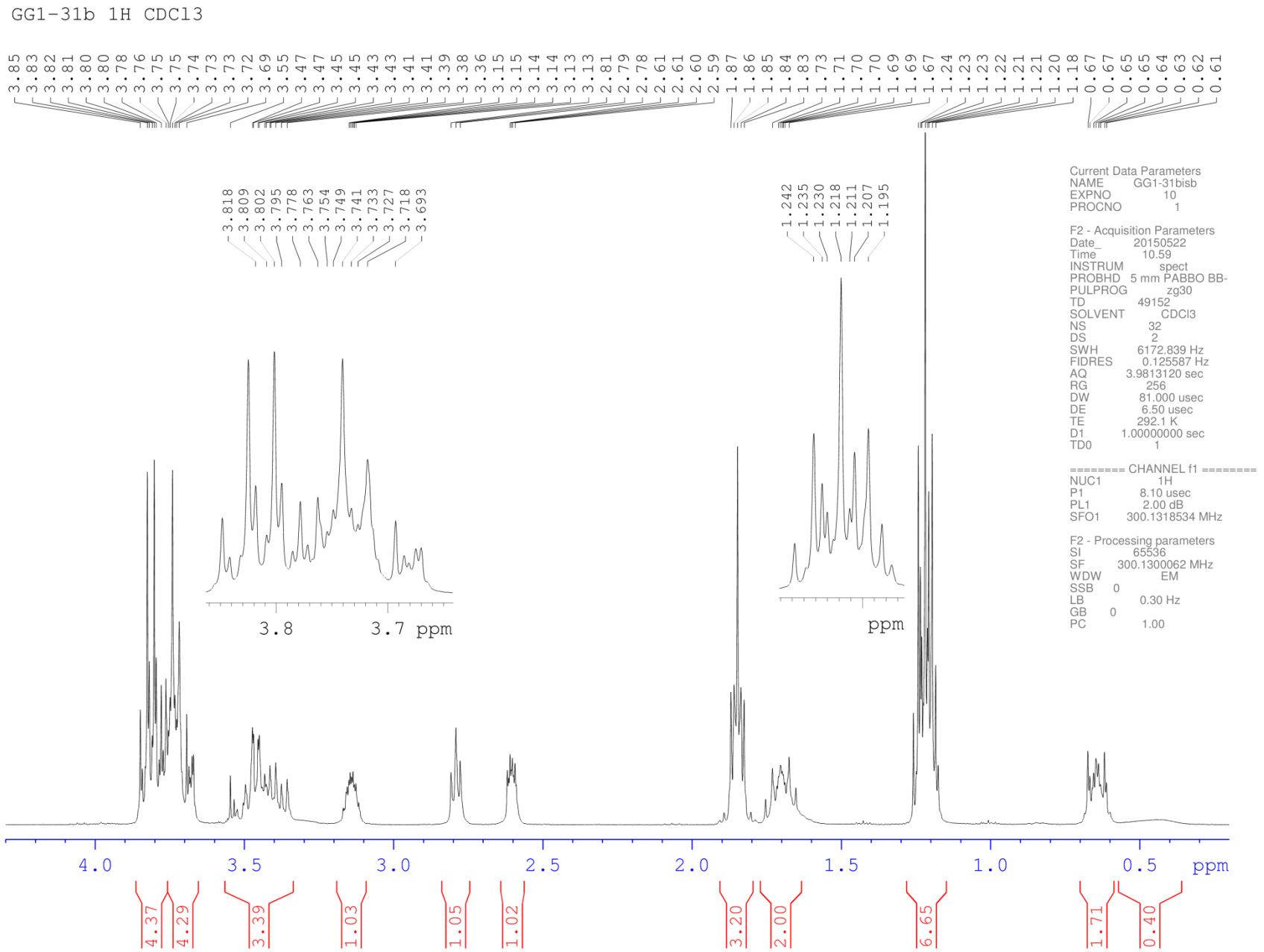


Figure SI_173: ^{1}H NMR spectrum of the crude mixture of the reaction between sodium methoxide and GPTES in THF (rt, 8h). (Scheme 8 (b.) in article)

SI_174

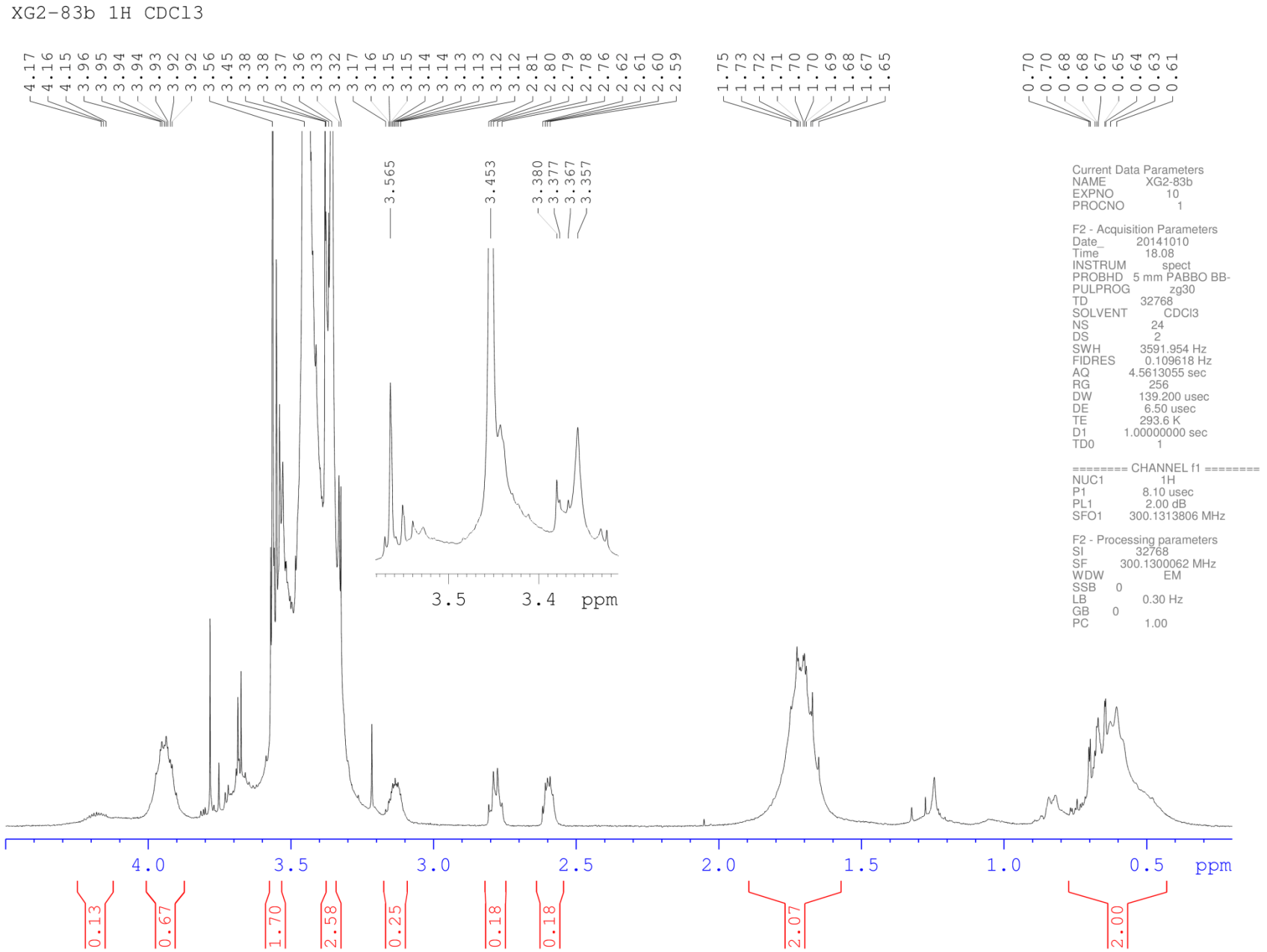


Figure SI_174: ^{1}H NMR spectrum of the crude mixture of the reaction between sodium methoxide and GPTMS in methanol (reflux, 3.5h). (Scheme 8 (c.) in article)

SI_175

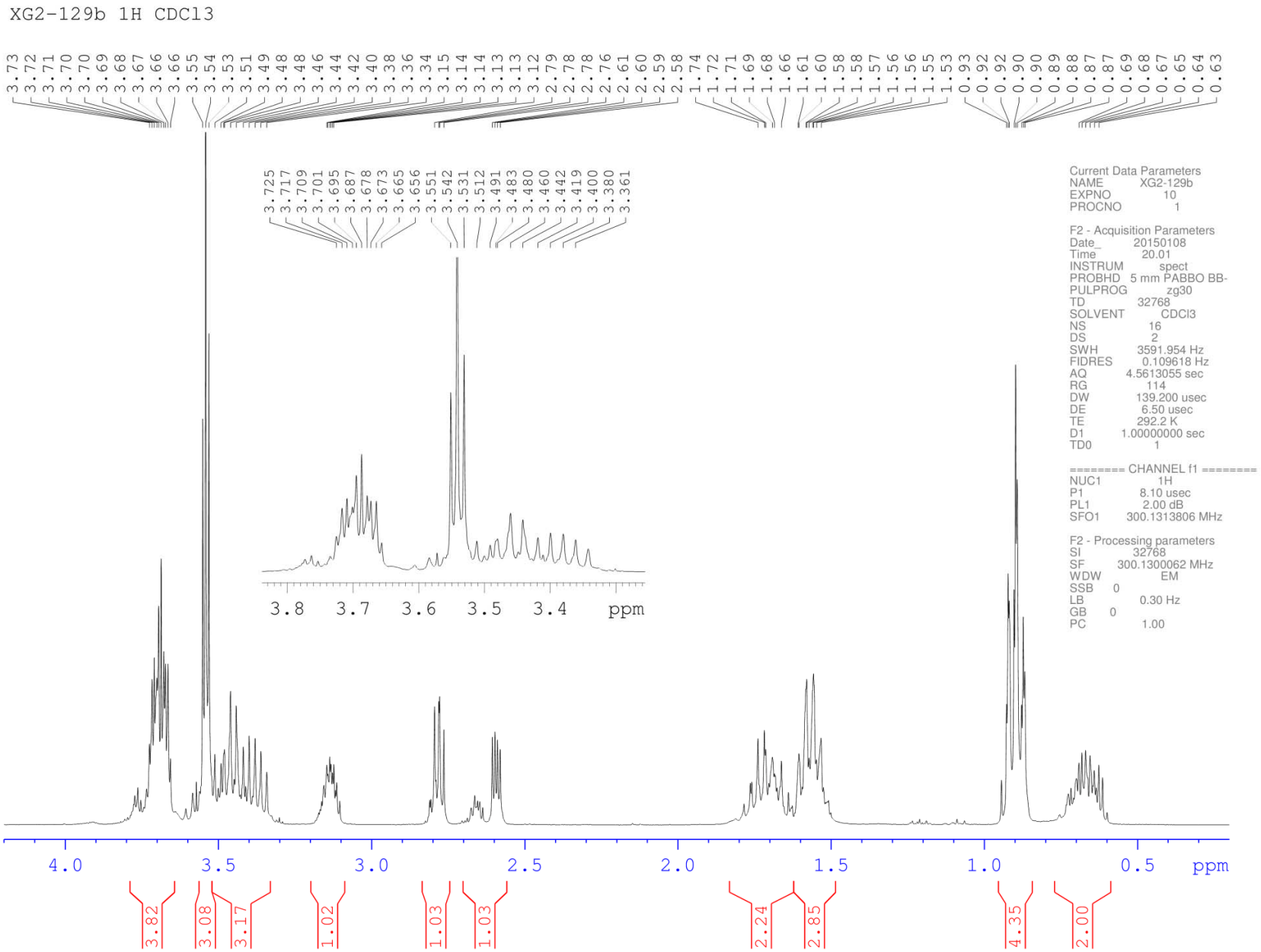


Figure SI_175: ^{1}H NMR spectrum of the crude mixture of the reaction of GPTMS with *n*-propanol in presence of 3 mol% of BF_3•Et_2O (DCM, rt, 1.5h). (Scheme 9. in article)

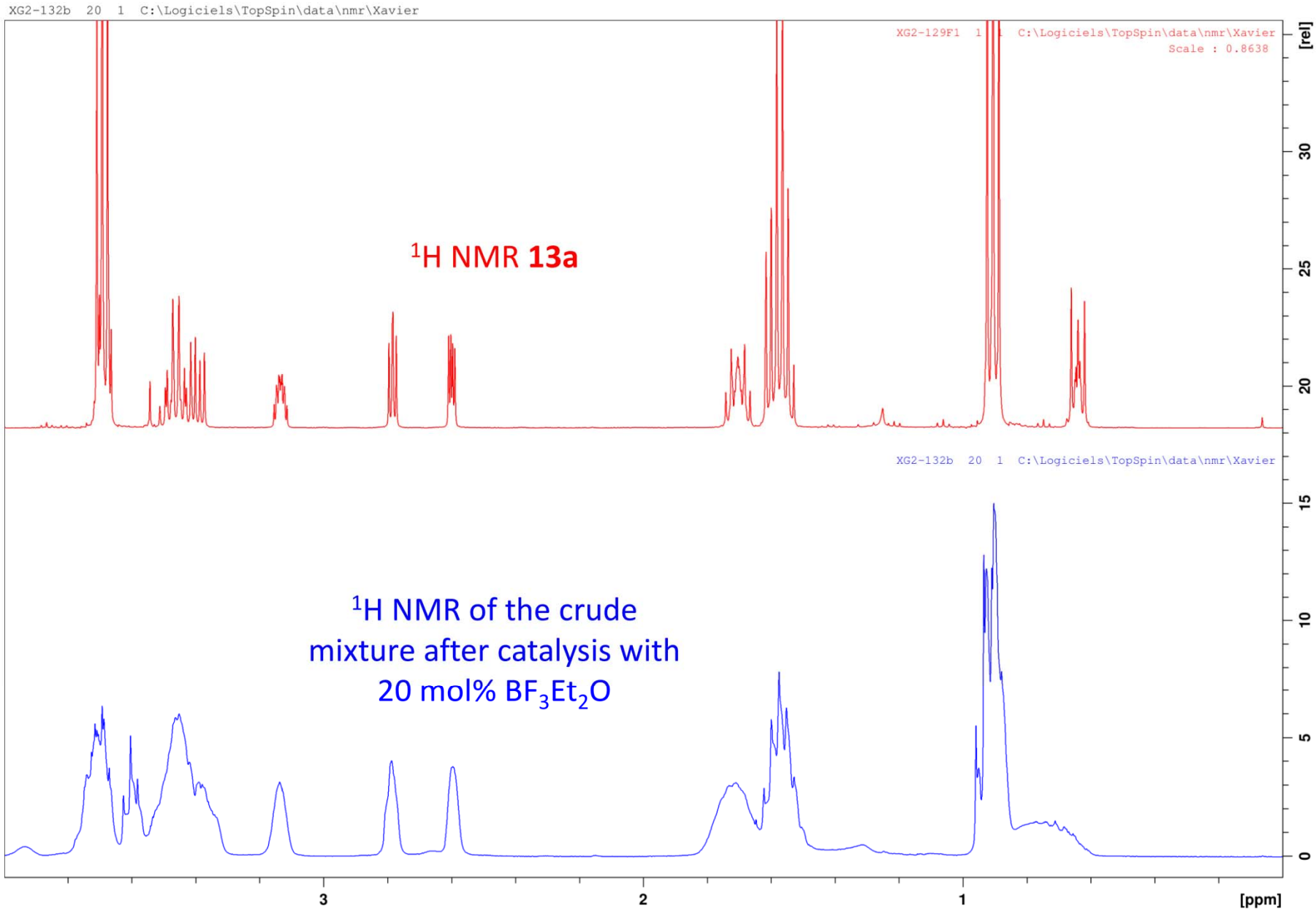


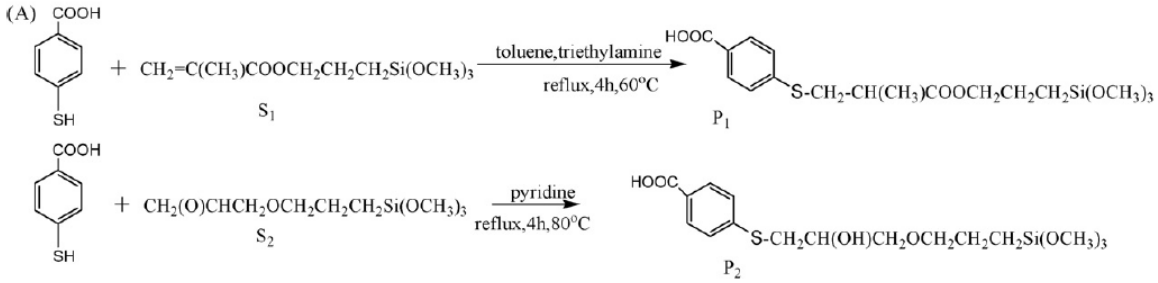
Figure SI_176: Comparison of the ^{1}H NMR spectra of the crude mixture (blue) obtained after the reaction of GPTMS with *n*-propanol in presence of 20mol% of BF_3.Et_2O with the spectra of compound 13a (red).

G. Annex of the article gathering objections and misinterpretations of the literature

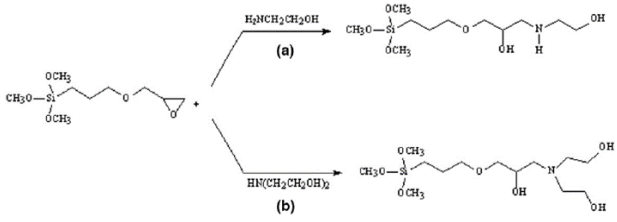
This article aims at exploring the dual reactivity of functional alkoxysilanes and their sensitivity towards reaction conditions. These investigations revealed results that could bring questioning about published work. In our sense, the reactivity of the silicon moiety of functional alkoxysilanes versus the epoxide function has been widely underestimated in various articles describing the reactivity of alkoxysilanes. In fact, such reactions in sol–gel hybrid synthesis using nucleophiles are not well characterized in the literature and can suggest some misinterpretations in some published results. So that, we can contest that some data at the molecular level (NMR for instance) are missing in papers, but these data are clearly essential to conclude to epoxide opening of the glycidyl moiety within glycidylalkoxysilanes. As general statement we can dispute that several misinterpretations are commonly made in the literature. This section is dedicated to describe few of these collected examples from the literature.

- It appeared in the literature that the reaction schemes describing the reactivity of alkoxysilanes with varied nucleophiles give no alteration of the silicon moiety. In the view of our results, it seems complicated to describe selective modification of the epoxide moiety by using alcohols or thiols reactive species.
  Based on our results, these data remain unclear and there is no spectral evidence in these papers showing that the epoxide function and/or the alkoxysilane moiety have/has been modified.

- B. Yan, X.-L. Wang, K. Qian, H.-F. Lu Journal of Photochemistry and Photobiology A: Chemistry 212 (2010) 75–80

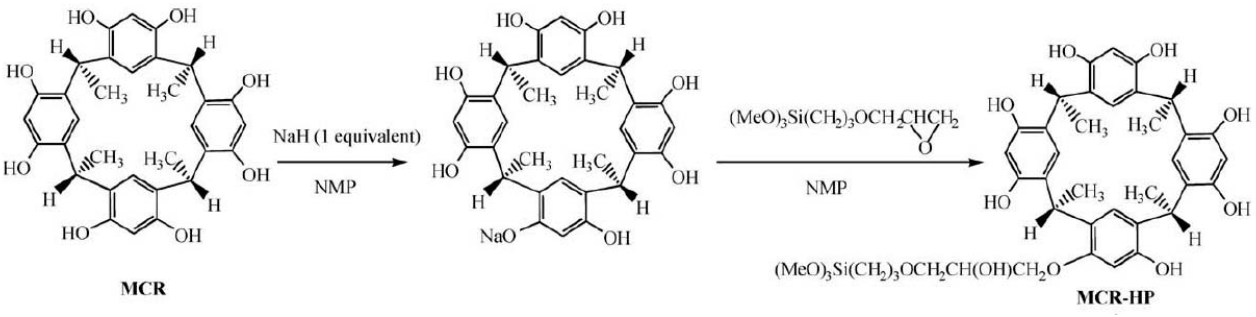


- M. A. Melo Jr., F.J.V.E. Oliveira, C. Airoldi Applied Clay Science 42 (2008) 130–136

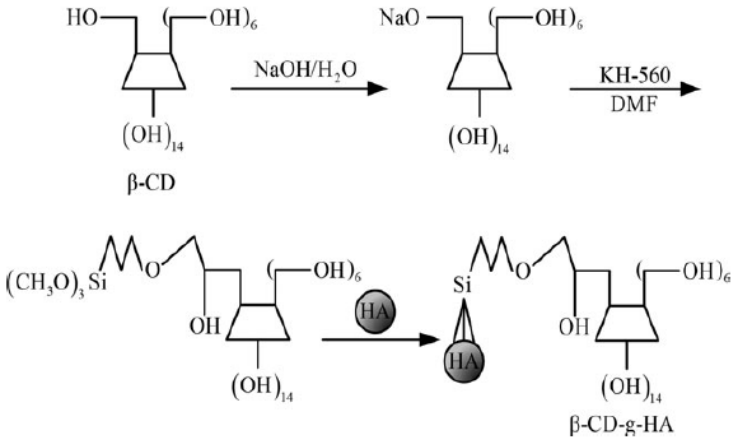


The silylating agents were synthesized by adding, with stirring under a dry nitrogen atmosphere, 2.10 cm^3 (35.0 mmol) of ethanolamine or 3.36 cm^3 (35.0 mmol) of diethanolamine to 7.74 cm^3 (35.0 mmol), of 3-glycidoxypropyltrimethoxysilane dissolved in 100 cm^3 of dry ethanol. To complete the incorporation of these molecules into the epoxide three membered ring, the mixture was left under reflux for 72 h at 323 K.

- H.M. Tan, S.F. Soh, J. Zhao, E.L. Yong, Y. Gong Chirality 23 (2011) E91–E97

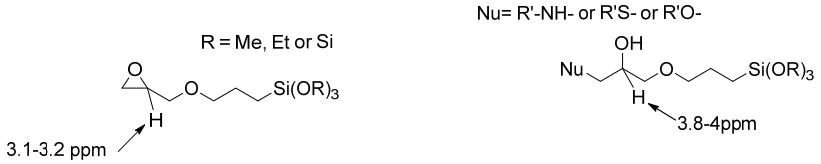


- W. Tang, J. Zhao, B. Sha, H. Liu J. Appl. Polym. Sci. 127, (2013), 2803-2808.



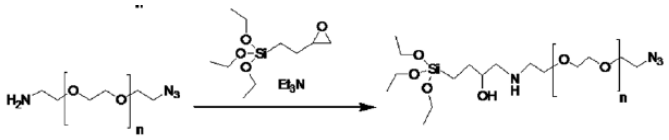
At first, this paper did not write properly the resulting product arising from ring-opening reaction. Only ring opening reaction is described which is not in accordance with the reactivity of alcoolates in presence of GPTMS.

- After exploring intensively the reactivity of alkoxysilanes (GPTMS, GPTES) using various simple nucleophiles, we discuss in our article that the ^{1}H NMR chemical shift relative to the ring opening of the epoxide function of glycidyl moiety is very significant in comparison to the native epoxide. In fact, the ^{1}H NMR chemical shift of C-H epoxide are located at 3.1-3.2ppm whereas the chemical shift of CH for the ring opened compounds are located at 3.8-4.2ppm. In the course of our studies, these information are crucial in order to conclude whether the epoxide is still remaining.



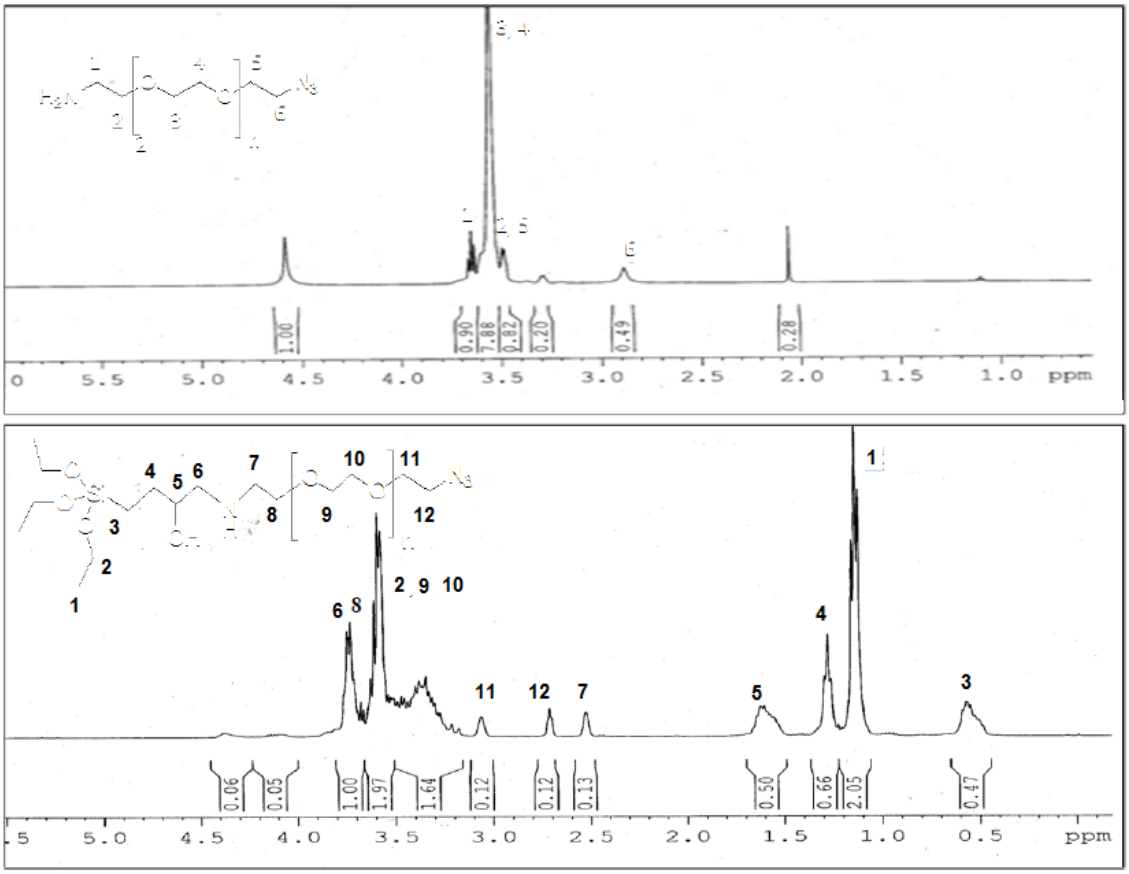
In our model studies, these observations were relatively clear since our resulting compounds displayed NMR data more simple than some of the more sophisticated structures that appear in the literature. Nevertheless, it appeared a collection of published examples where the native epoxide is clearly present in the NMR spectra (when these spectra are available). In our point of view, the following articles revealed misinterpretations regarding the reactivity of the epoxide in presence of nucleophiles. These following examples have been selected because NMR data analysis were provided and could suggest eventual misinterpretations from the authors. In many cases of the literature, the analytical information are not fully provided, so that it is hard to conclude on the ring opening of the epoxide without these NMR data.

- M. Das, D. Bandyopadhyay, R.P. Singh, H. Harde, S. Kumara, S.J. J. Mater. Chem., 2012, 22, 24652



2.2.1.2. Synthesis of azido-terminated PEG silane. For synthesis of azido-terminated PEG silane, α-amino, ω-azido PEG-600 (0.1 mmol) was added to an ethanolic solution of 3-glycidoxypropyltriethoxy-silane (0.09 mmol). Et_3N (0.14 mmol, 20 μl) was added to the solution and the reaction mixture was left to stirring for 12 h.

SI_179

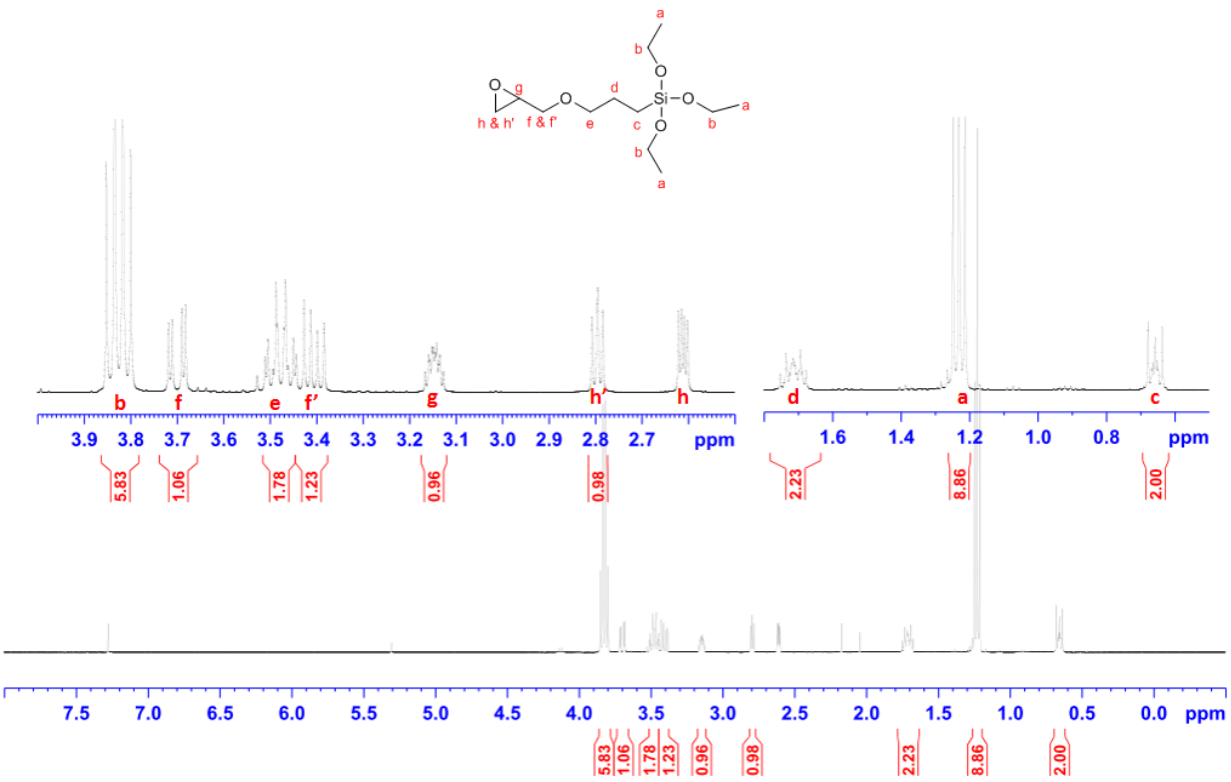


At first, the authors did not describe properly the chemical structures of the GPTES and the proposed resulting compound. As previously mentioned, the chemical shift of the CH(5) resulting from ring opening of the epoxide should be located around 3.8-4.2 ppm. The authors have described this proton-CH(5) at 1.6ppm which could be actually more assigned to the missing protons of the structure as represented as the CH2(d) in the below-described ^{1}H-NMR of GPTES that we provide. After comparison of these ^{1}H-NMR spectra between their structure and the starting material GPTES, the signals H-11, H-12 and H-7 look very similar to the native glycidyl part of the GPTES starting material. So that, these observations could bring questioning about the ring opening of the epoxide function.

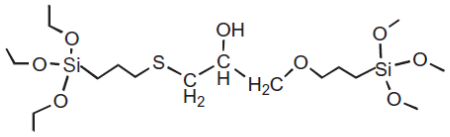
SI_180

[1]H-NMR of assigned GPTES in $CDCl_3$

GPTES CDCL3 RMN 1H



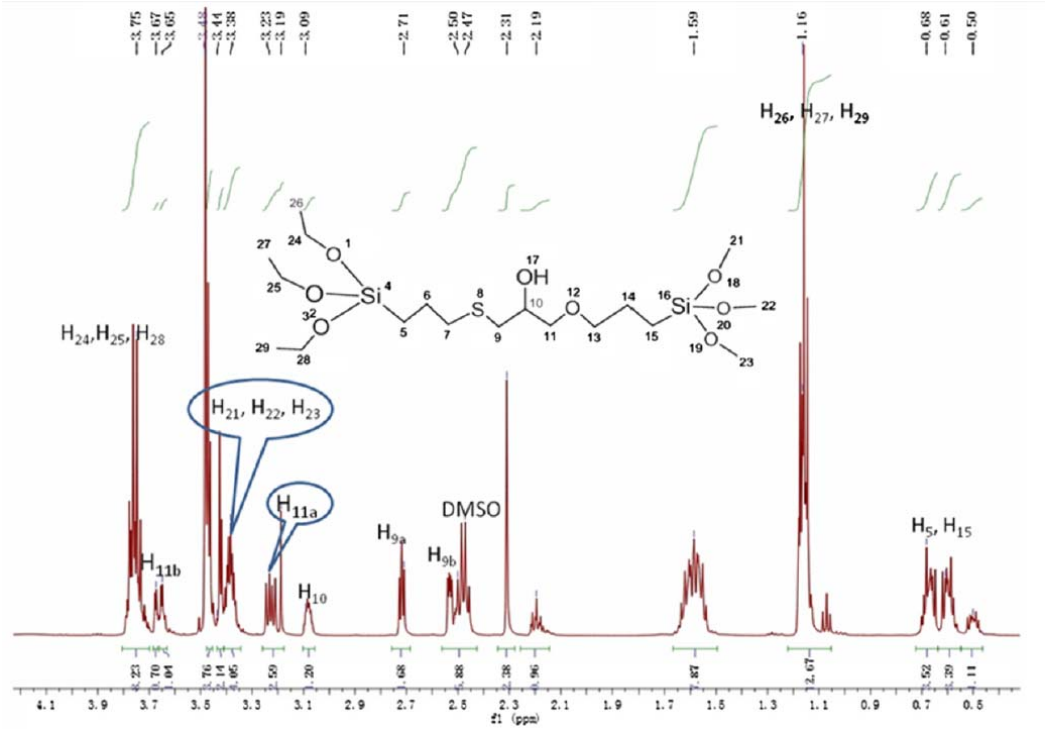
- M.M. Wan, L. Gao, Z. Chen, Y.K. Wang, Y. Wang, J. H. Zhu Microporous and Mesoporous Materials 155 (2012) 24–33.



Scheme 1. The structure of the 1-*O*-[trimethoxysilypropyl]-3-*S*-[triethoxysilypropyl]-2-propanol (M-G).

To prepare the M-G bridge molecule, GPTMS (4.72 g, 20 mmol) was firstly dissolved in toluene with stirring, and then MPTES (4.76 g, 20 mmol) was added into the solution by drops. The mixture was refluxed at 85 °C under nitrogen atmosphere for 24 h.

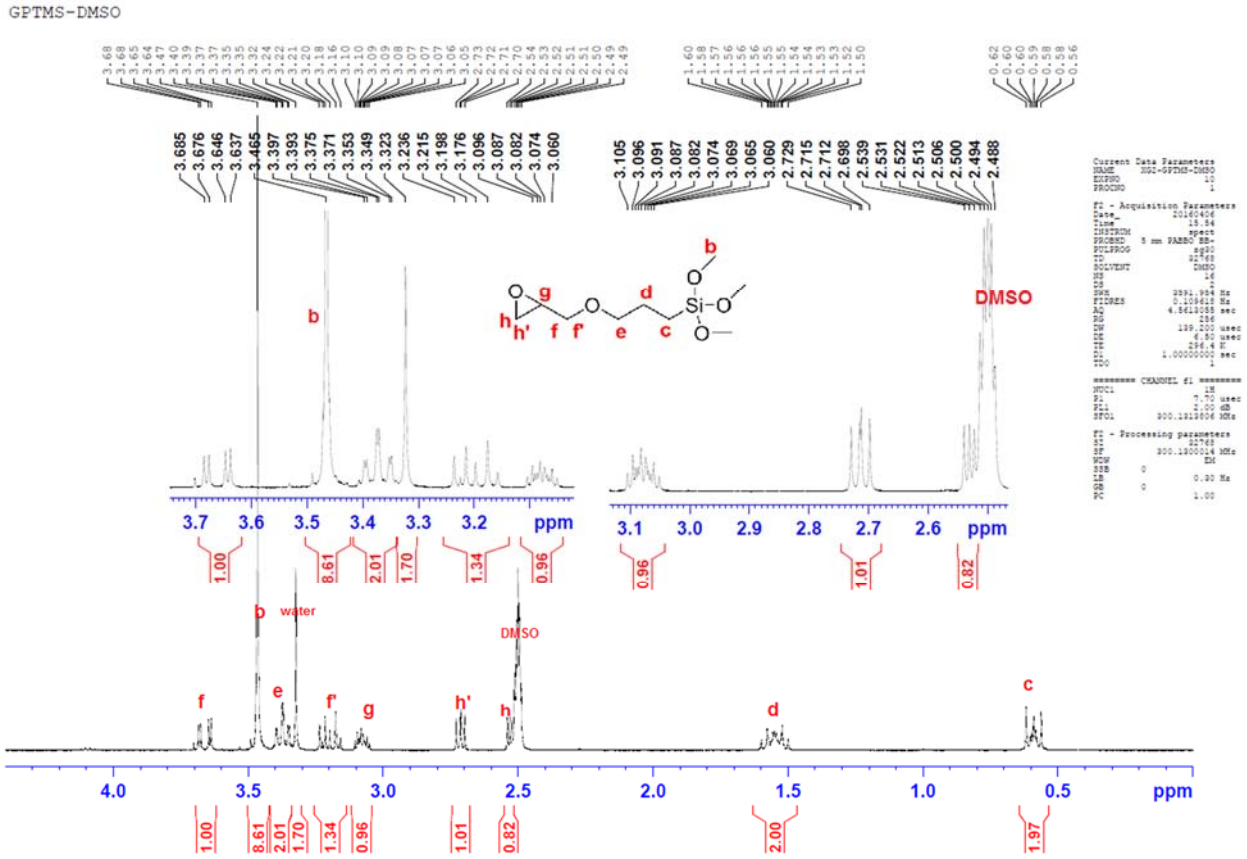
SI_181



Firstly, the attribution for the protons H-21, H-22 and H-23 should be more located at 3.5ppm, whereas this signal at 3.38ppm would fit better with both protons H-13 (as similar as the GPTMS signals labelled H_e– see below). In this cited article, the authors have also assigned the proton (H-10) at 3.1ppm. However, this signal related to the ring opened product should be more shifted at 3.8-4ppm. Actually, in this region (3.8-4.2ppm), there is no evidence of ring-opened product. In consequence, it seems that the ^{1}H NMR signals at 3.1ppm, 2.7ppm and 2.6ppm are more representative of the unmodified glycidyl moiety of GPTMS(H_f, H_g, H_h) (see below for the ^{1}H NMR of the GPTMS in DMSO).

SI_182

[1]H-NMR of assigned GPTMS in DMSO



- M. Arslan, S. Sayin, M. YilmazTetrahedron: Asymmetry 24 (2013) 982–989

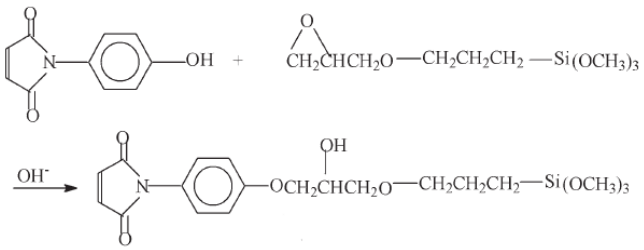
(ii) [3-(2,3-epoxypropoxy)propyl]trimethoxysilane, DMF, 50 °C, 3 h;

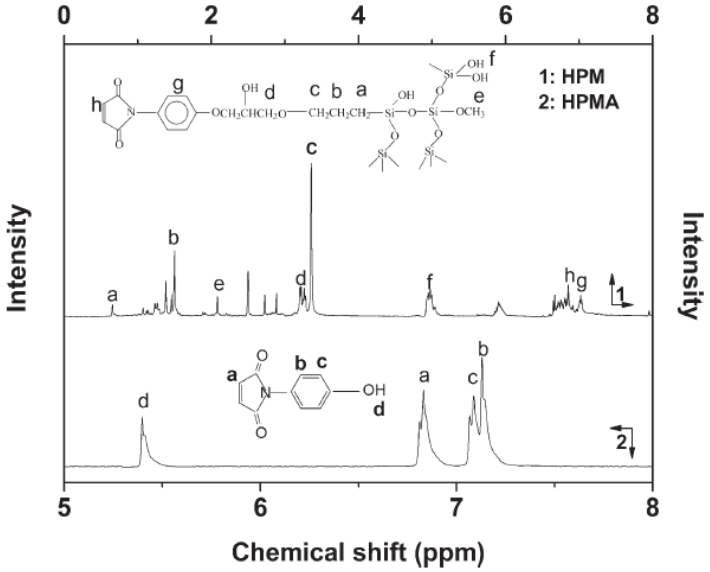
5.3.3. Synthesis of alcohol functionalized β-cyclodextrin (Al-CD) 3

Yield 71.8%, ^{1}H NMR (400 MHz, DMSO): δ (ppm) 2.70 (br, 14H), 2.86 (br, 14H), 3.34–3.26 (m, 42H), 3.70–3.42 (m, 119H), 4.81 (d, 21H, J = 5.48 Hz). ^{13}C NMR (400 MHz, DMSO): δ (ppm) 31.23, 36.24, 60.39, 72.50, 72.89, 73.52, 81.99, 102.40. Anal. Calcd for $C_{126}H_{252}O_{70}Si_7$: C, 49.07; H, 8.24. Found: C, 49.18; H, 8.08.

In this cited article, even if NMR data are provided, the assignment seem incomplete by comparison with the expected structure.

- J.-T. Hu, A. Gu, G. Liang, D. Zhuo, L. Yuan Journal of Applied Polymer Science, 126, (2012) 205–215.





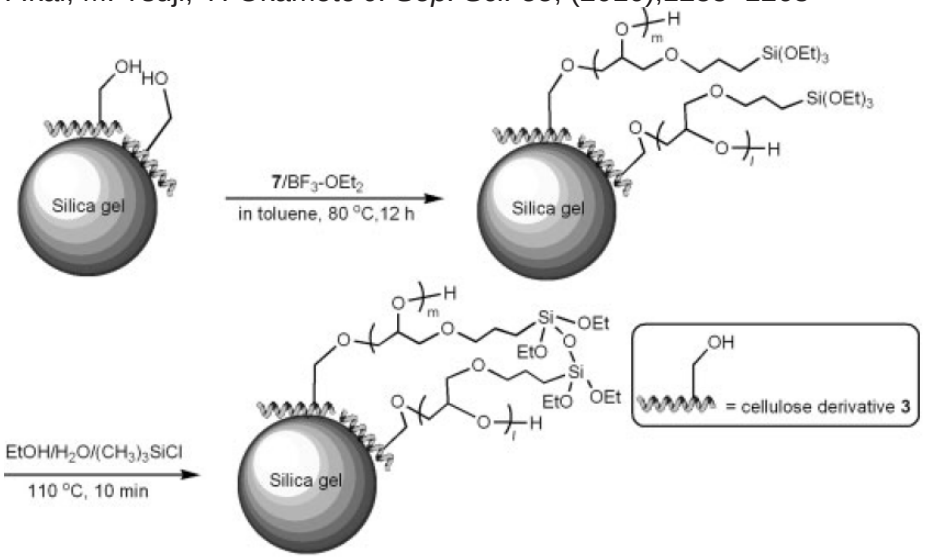
^{1}H-NMR ($\tilde{N}$-dimethylsulfoxide as solvent, ppm): 0.66 (Si—CH_2—); 1.5, 3.4 (—CH_2—CH_2—CH_2—); 3.2 (—O—CH_2); 6.75(—CH=CH— of maleimide ring); 7.02 (aromatic protons).

In this cited article, the NMR assignments are once again incomplete by comparison with the expected structure. Some misinterpretations are also disclosed: the methoxy group H_e should be assigned at 3.3ppm. There is no clear evidence of the C-H proton resulting from ring opening reaction which should be expected at 3.8-4.2 ppm. The unlabeled signals at 2.5; 2.7 and 3.1 ppm could fit with the starting glycidyl moiety of GPTMS.

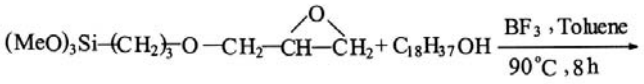
H. Annex of the article: References of the literature being disputed when using BF_3•Et_2O for functionalization of glycidylalkoxysilanes.

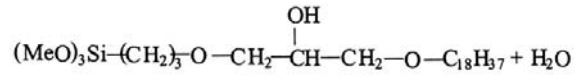
As discussed in the article, the use of $BF_3.Et_2O$ as activator is very common in order to facilitate the ring opening of epoxide function. However, our results strongly suggest that the addition of alcohols nucleophiles in presence of such activator and GPTMS or GPTES reagents results only in trans-etherification reaction on the silicon group. Here are few examples of the literature disclosing ring-opening reaction of glycidylalkoxysilanes:

- S. Tang, T. Ikai, M. Tsuji, Y. Okamoto *J. Sep. Sci. 33*, (2010),1255–1263



- Y. Xin, Z. Rui, L. Guoquan Journal of Liquid Chromatography & Related Technologies *23*, (2000) 1821-1830.





Bonding of the terminal C_{18} chain onto γ-glycidoxypropyltrimethoxysilane was through ring opening reaction then followed by silanization with silica gel as follows: