Bis(N-Heterocyclic Carbene)s Incorporating Silicon in the Ligand Backbone

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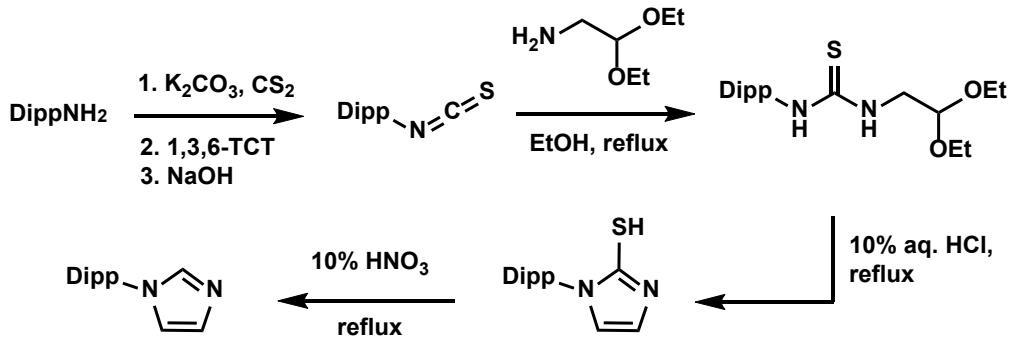
Synthesis of starting materials

Bis(chloromethyl)dimethylsilane and bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane were purchased from Gelest Inc. N-methylimidazole was purchased from Millipore-Sigma. Bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane,[1] N-*iso*-propylimidazole,[2] N-*tert*-butylimidazole,[3] and N-cyclohexylimidazole[4] were synthesized according to literature procedures. Crude N-*iso*-propylimidazole and N-cyclohexylimidazole were purified by flash chromatography (1 : 1 hexanes : ethyl acetate).

Synthesis of bis(iodomethyl)dimethylsilane. To a solution of bis(chloromethyl)dimethylsilane (10.0 g, 0.064 mol) in acetone sodium iodide (38.2 g, 0.255 mmol) was added in one portion. The mixture was then heated to reflux for three hours. After cooling to room temperature, the solids were filtered off and the filtrate was concentrated in vacuo. Diethyl ether (ca. 100 mL) was subsequently added to precipitate remaining salts. After renewed filtration and solvent removal in vacuo, the remaining crude was purified by short-path distillation to yield the product as an orange oil (19.3 g, 0.057 mmol, 89 %). Spectral data matched literature.[5]

Synthesis of N-(2,6-diisopropylphenyl)imidazole.

Scheme S1. Synthetic steps used to prepare N-(2,6-diisopropylphenyl)imidazole.



The target compound was synthesized by adapting a literature procedure[6] according to Scheme S1.

Synthesis of N-(2,6-diisopropylphenyl)isothiocyanate.[7] To a suspension of 2,6-diisopropylaniline (18.3 g, 0.103 mol), K_2CO_3 (28.2 g, 0.204 mol), and dimethylformamide (10 mL) in water (70 mL), CS_2 (10.0 g, 0.131 mol) was added dropwise under vigorous stirring. The mixture was stirred overnight at room temperature. Next day, the orange mixture was cooled to 0ºC, and a solution of cyanuric chloride (9.40 g, 0.051 mol) in dichloromethane (70 mL) was added dropwise (ca. one drop per second) via dropping funnel. The reaction was stirred at room

temperature for four hours and subsequently basified to a pH > 11 with 7M aqueous NaOH. After addition of dichloromethane (150 mL) and water (150 mL) to partition the layers, the organic fraction was separated, washed with water (2 × 100 mL), dried with $MgSO_4$. Solvents were subsequently removed in vacuo and the resulting brown oil was purified via short path distillation to yield the product as a colorless oil (16.2 g, 0.074 mol, 72 %)

Synthesis of N-(2,6-diisopropylphenyl)-2-mercaptoimidazole.[6] N-(2,6-diisopropylphenyl)isothiocyanate (16.2 g, 0.074 mol) was added dropwise to a stirred solution of aminoacetaldehyde diethyl acetal (9.81 g, 0.074 mol) in ethanol (30 mL). The resulting solution was heated to reflux for 1.5 h, cooled to room temperature, and the solvent was removed in vacuo. The residue was suspended in 10% aqueous HCl (150 mL) and heated to reflux for one hour, resulting in formation of a white precipitate. The reaction mixture was cooled in ice for 30 minutes and the product was isolated by vacuum filtration as a white solid (18.2 g, 0.070 mol, 95 %).

Synthesis of N-(2,6-diisopropylphenyl)imidazole.[6] In a 1 L round-bottom flask with a large magnetic stir bar, N-(2,6-diisopropylphenyl)-2-mercaptoimidazole (18.2 g, 0.070 mol) was suspended in 20% aqueous nitric acid. The mixture was heated to reflux until the evolution of brown fumes stopped (ca. 30 minutes). After cooling the mixture to room temperature, water (150 mL) was added, and the product was extracted with ethyl acetate (2 × 150 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo to yield the product as a light-yellow solid (14.6 g, 0.064 mol, 91 %). Spectral data matched literature values.[6]

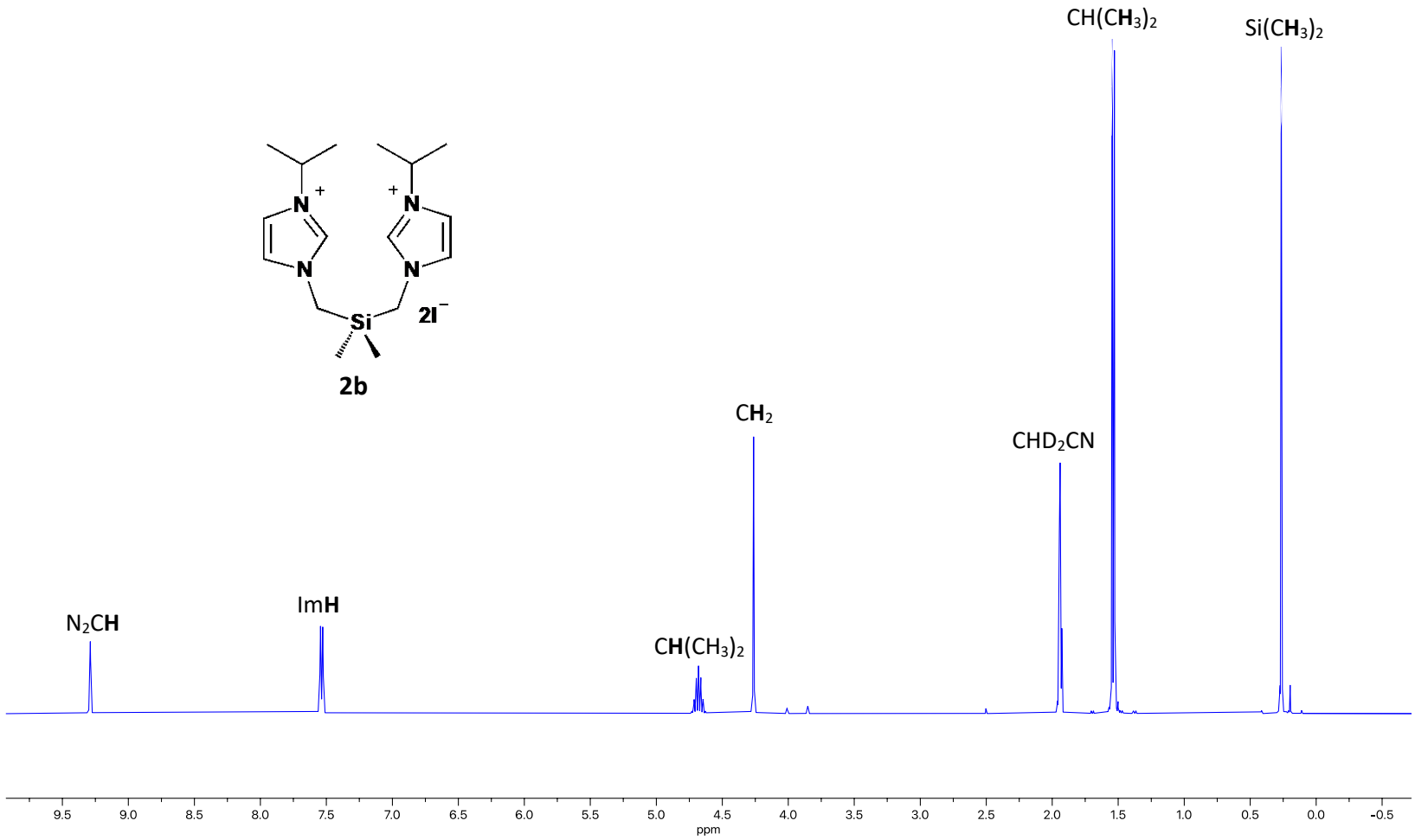


Figure S1. ^{1}H NMR spectrum of **2b** (400MHz, 298K, CD_3CN)

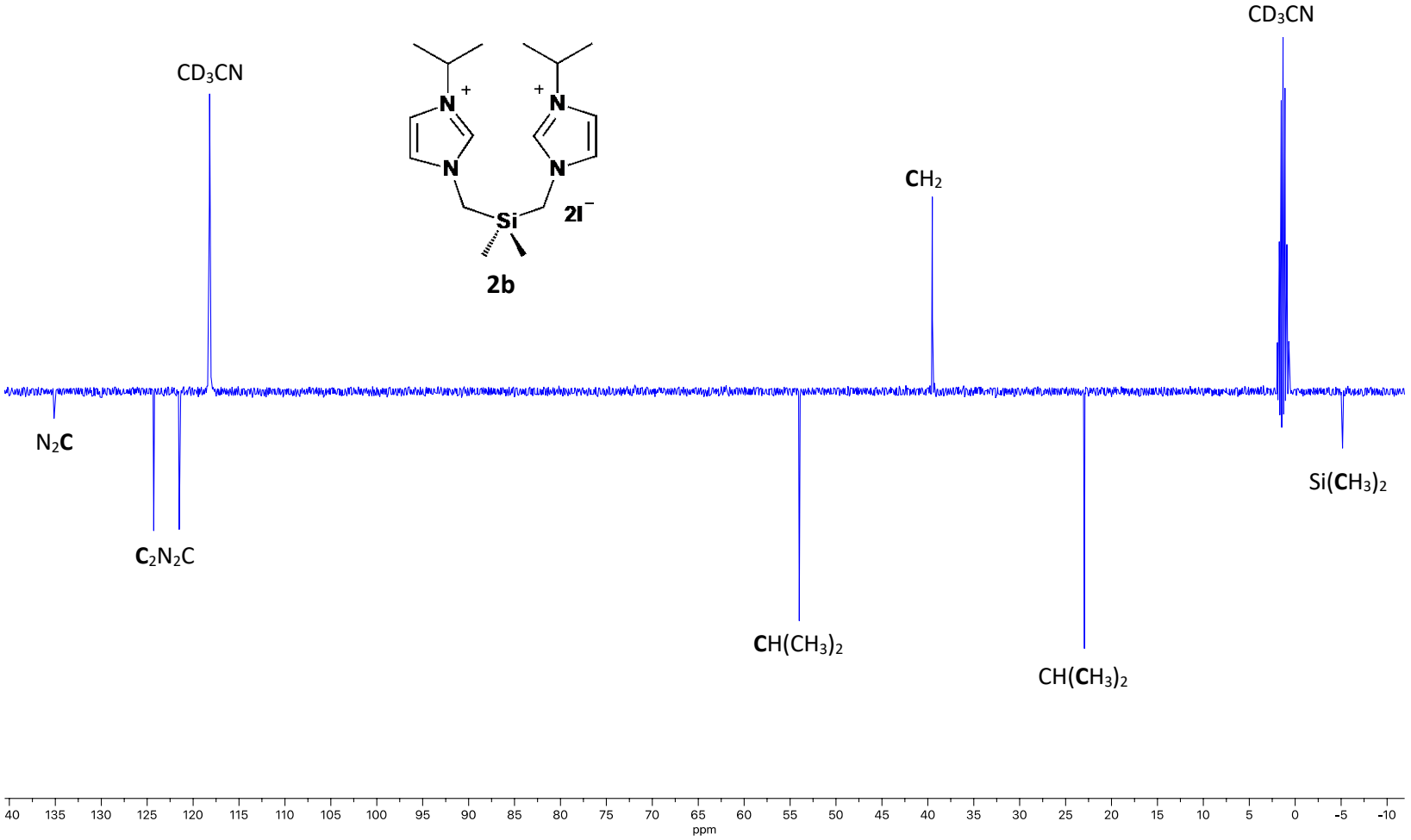


Figure S2. ^{13}C DEPTQ NMR spectrum of **2b** (101MHz, 298K, CD_3CN)

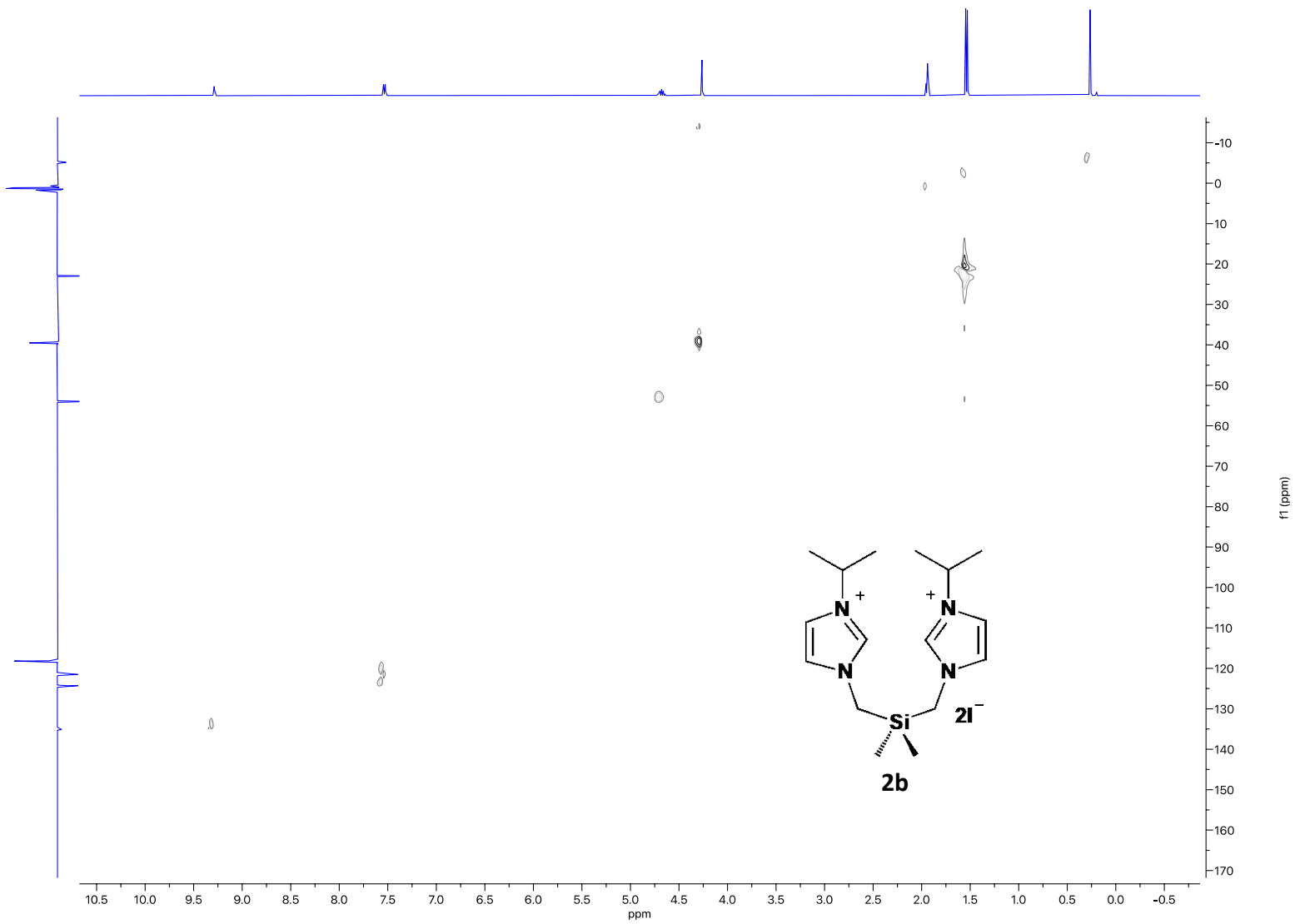


Figure S3. ^{1}H-^{13}C HSQC NMR spectrum of **2b** (400MHz, 298K, CD_3CN)

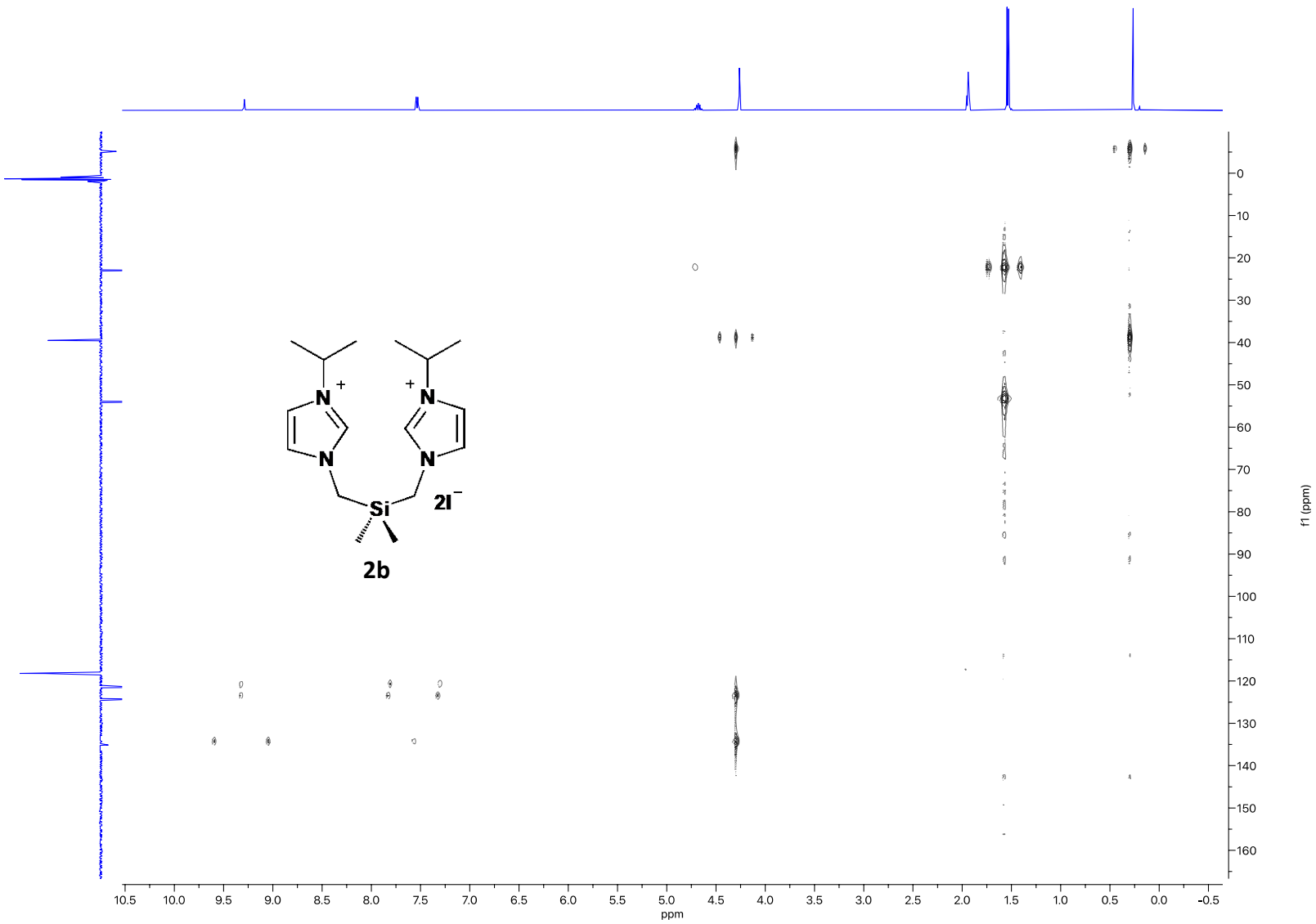


Figure S4. ^{1}H-^{13}C HMBC NMR spectrum of **2b** (400MHz, 298K, CD_3CN)

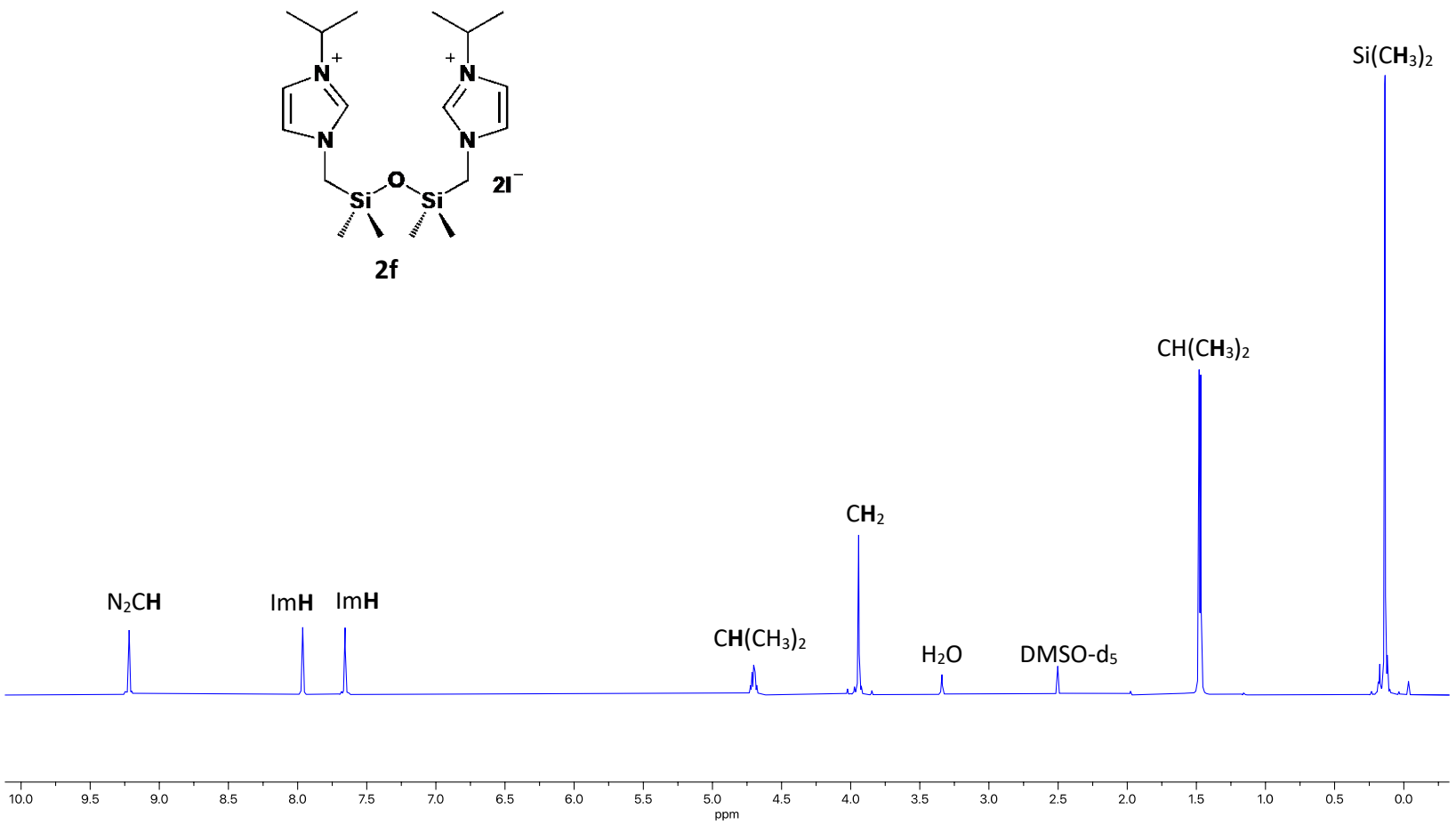


Figure S5. ^{1}H NMR spectrum of **2f** (600MHz, 298K, DMSO-d_6)

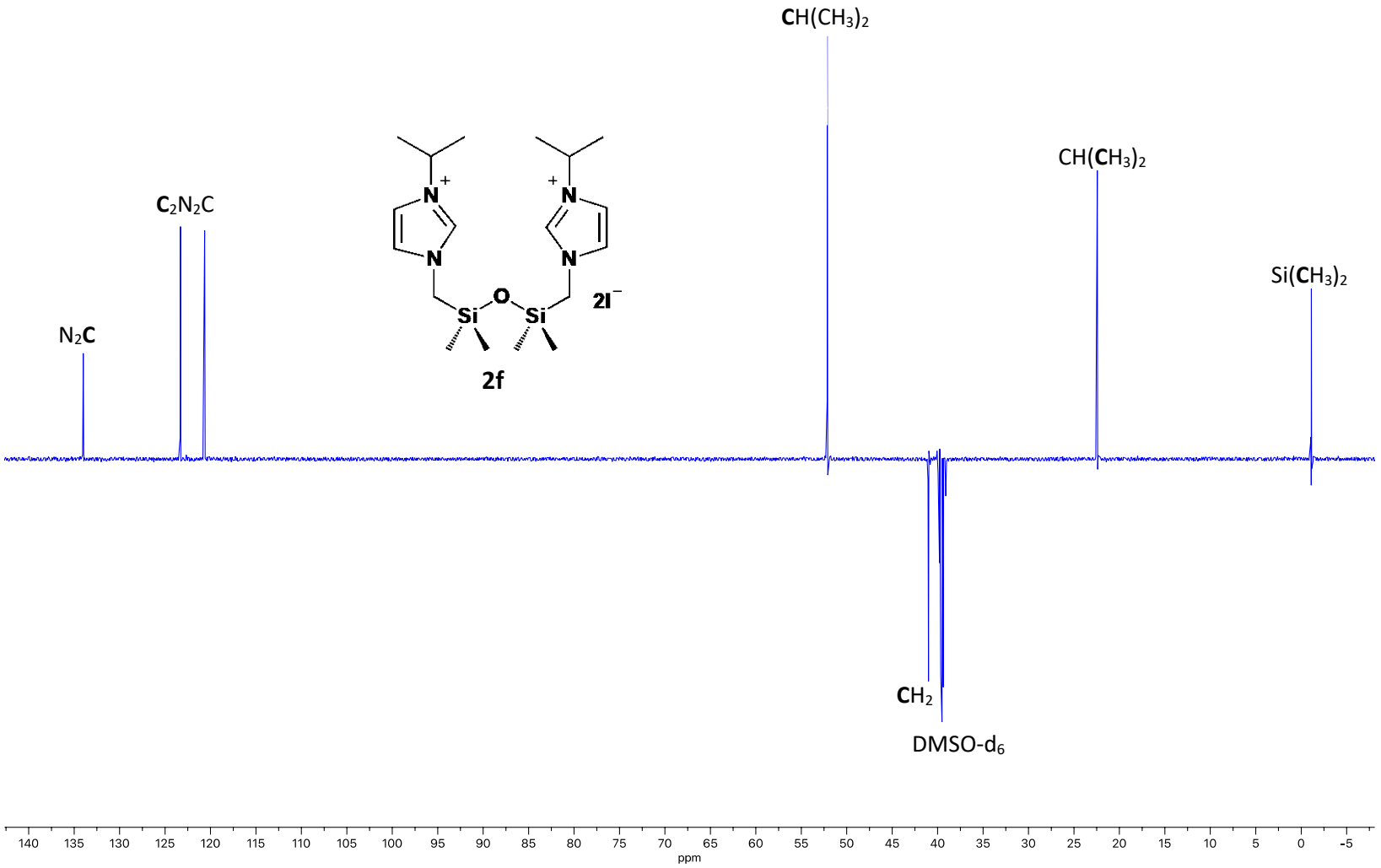


Figure S6. ^{13}C DEPTQ NMR spectrum of **2f** (151MHz, 298K, DMSO-d_6)

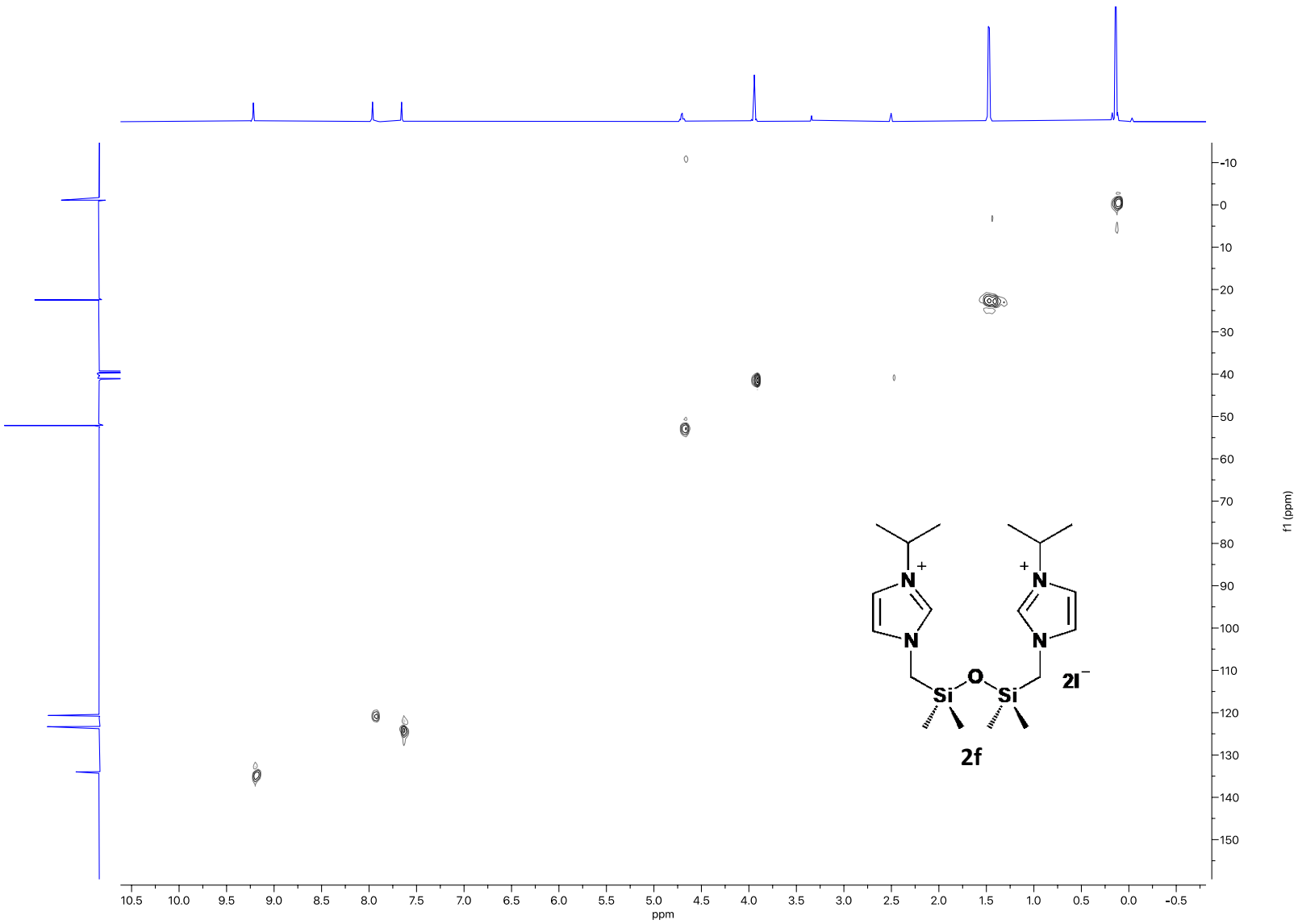


Figure S7. ^{1}H-^{13}C HSQC NMR spectrum of **2f** (600MHz, 298K, DMSO-d_6)

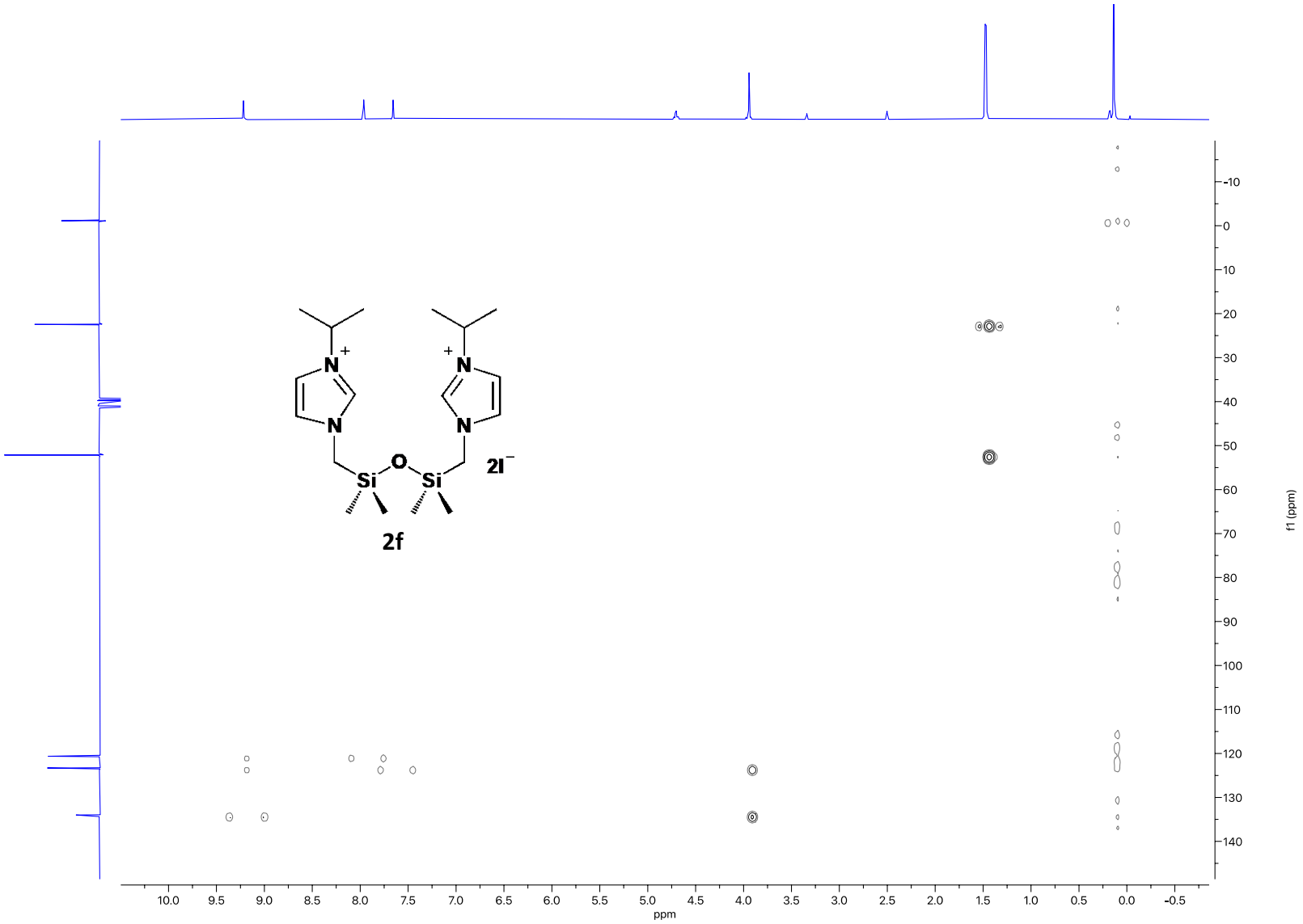


Figure S8. ^{1}H-^{13}C HMBC NMR spectrum of **2f** (600MHz, 298K, DMSO-d_6)

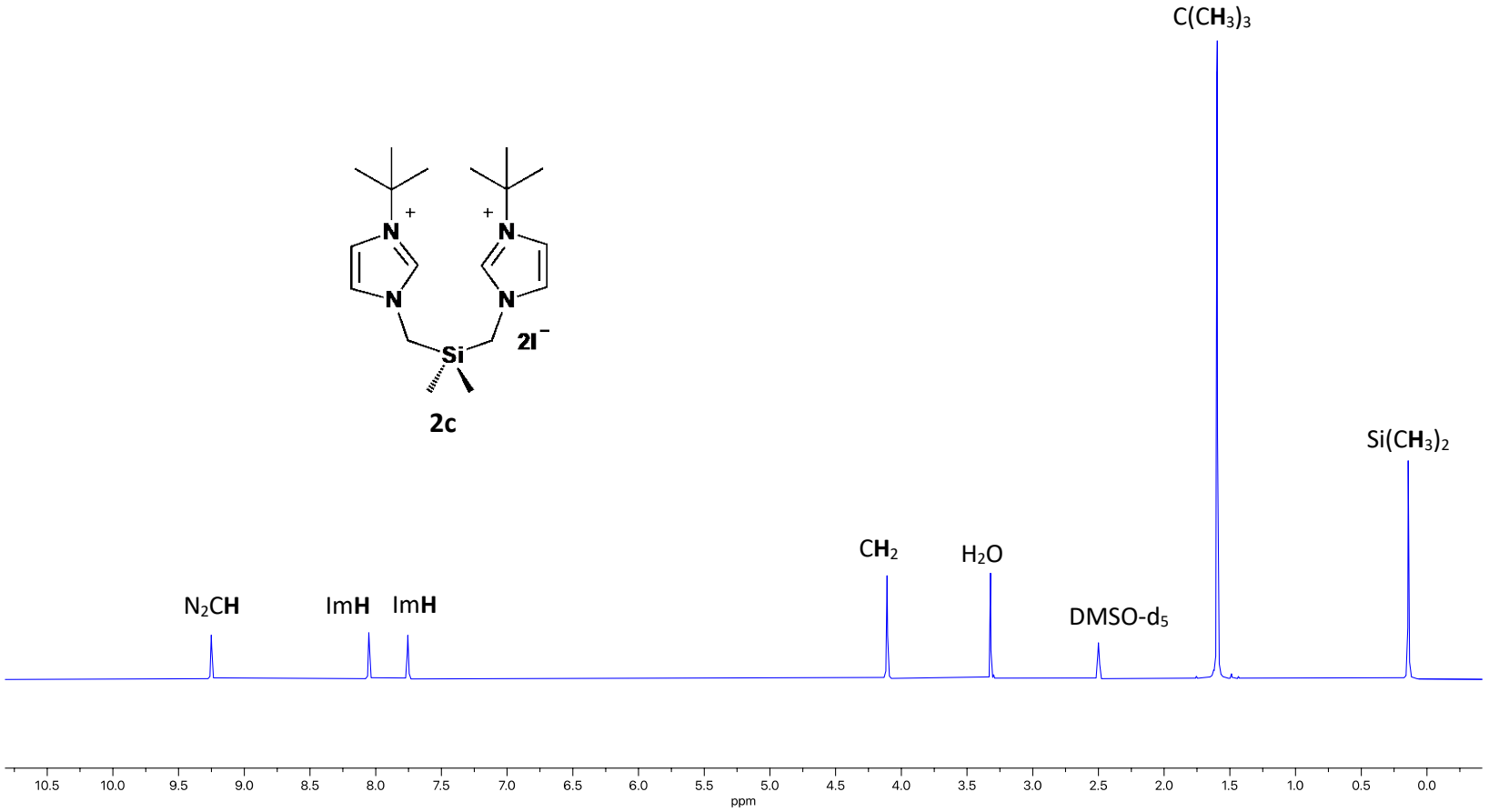


Figure S9. ^{1}H NMR spectrum of **2c** (400MHz, 298K, DMSO-d_6)

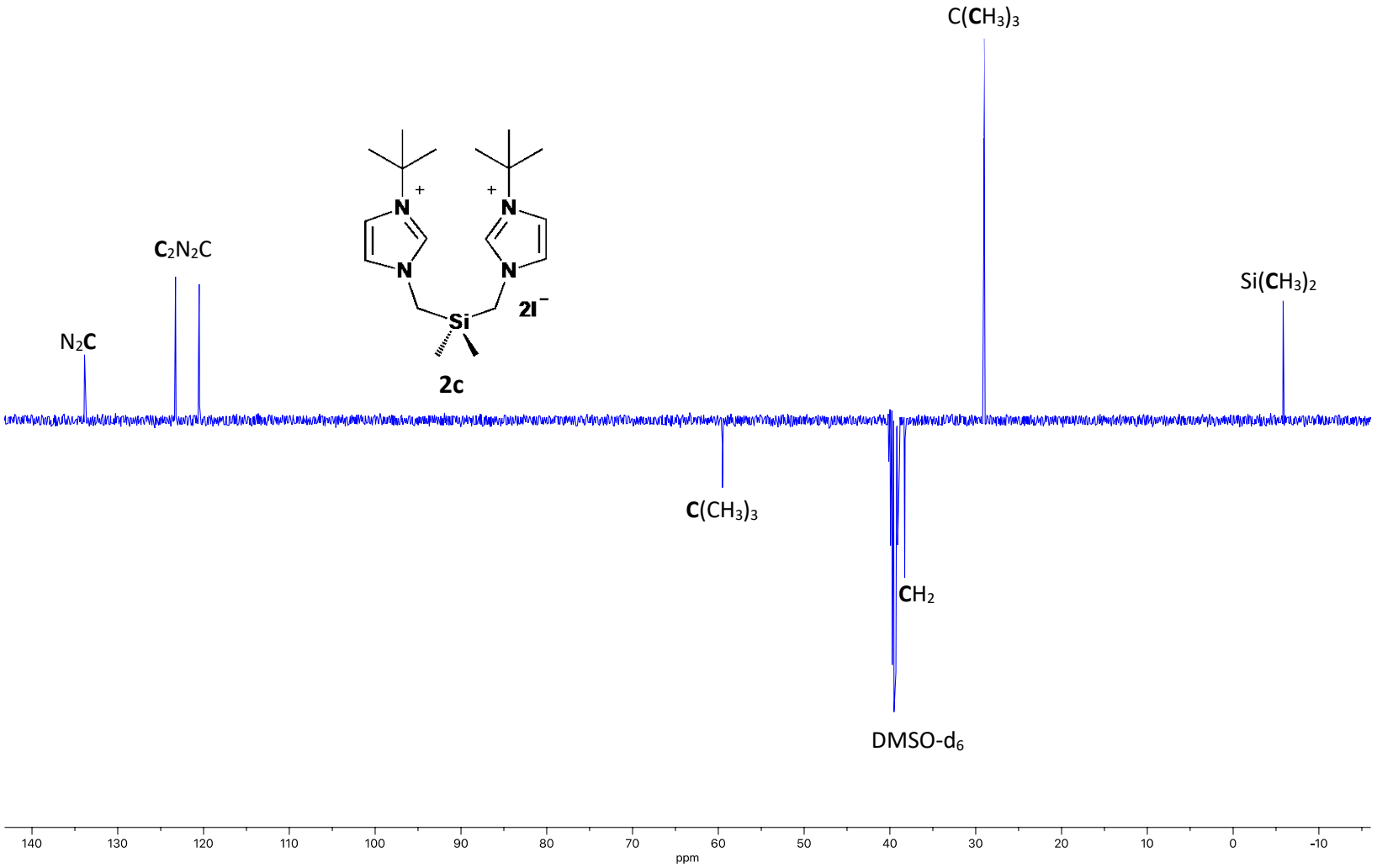


Figure S10. ^{13}C DEPTQ NMR spectrum of **2c** (101MHz, 298K, DMSO-d_6)

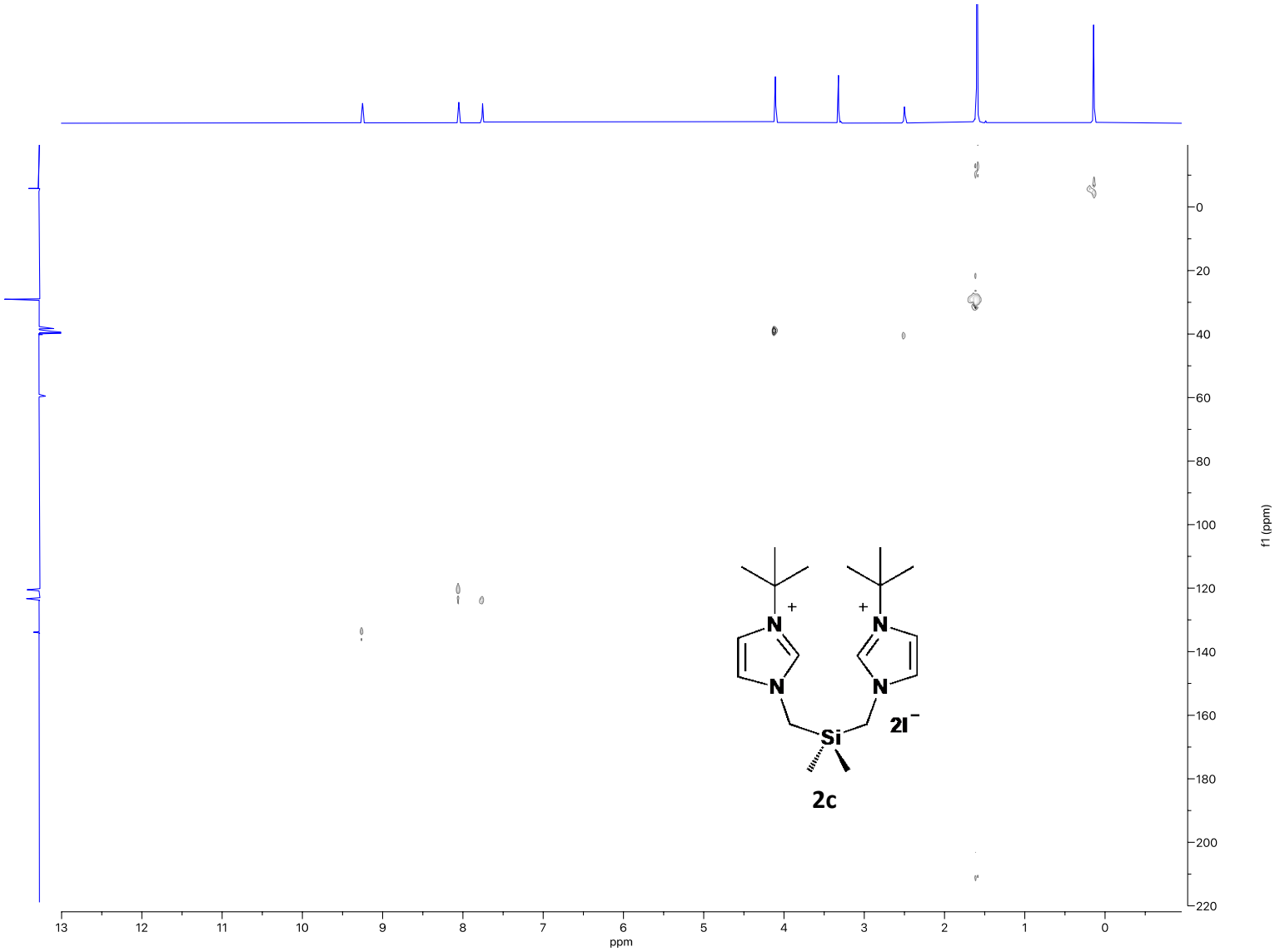


Figure S11. ^{1}H-^{13}C HSQC NMR spectrum of **2c** (400MHz, 298K, DMSO-d_6)

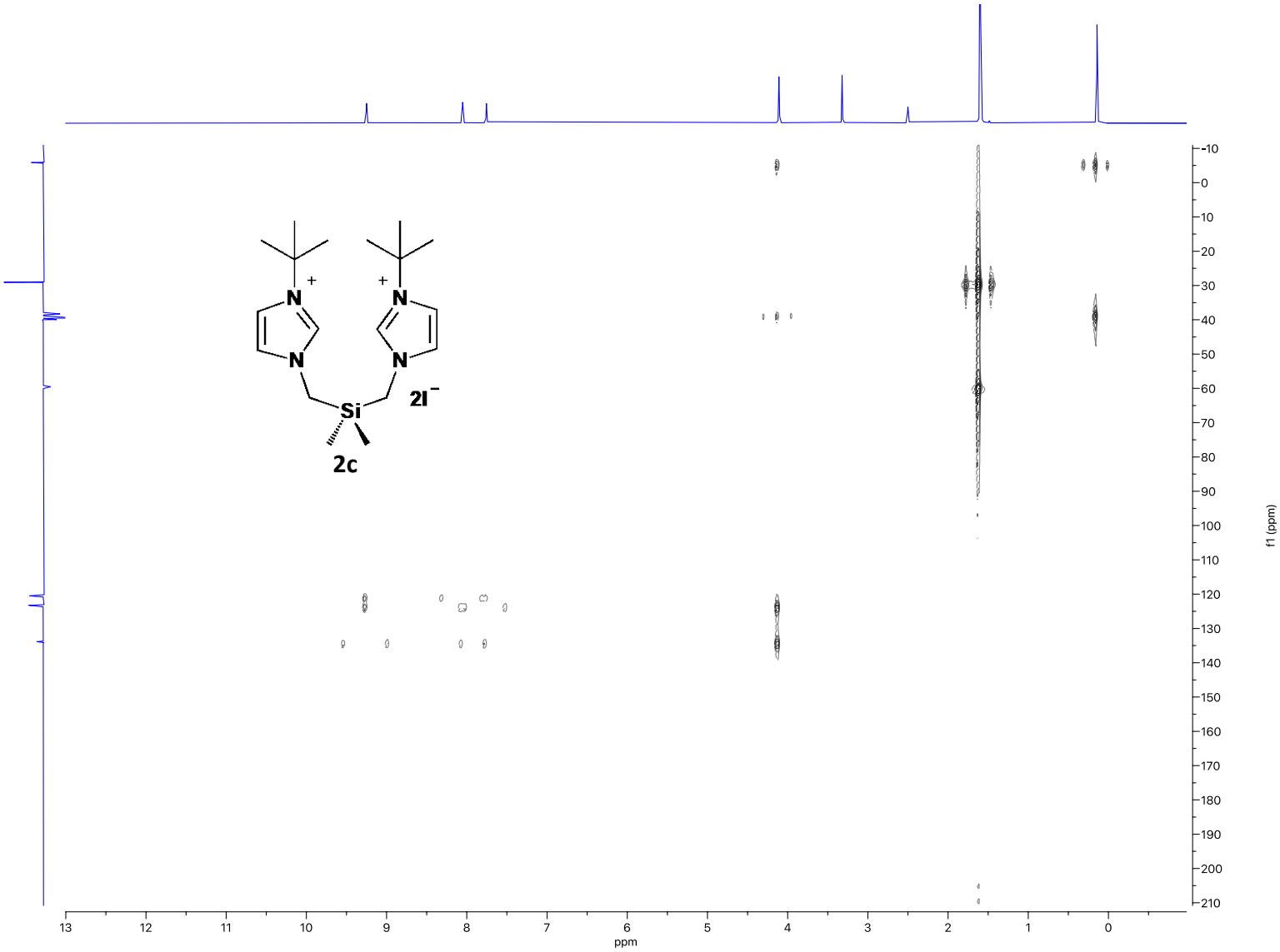


Figure S12. ^{1}H-^{13}C HMBC NMR spectrum of **2c** (400MHz, 298K, DMSO-d_6)

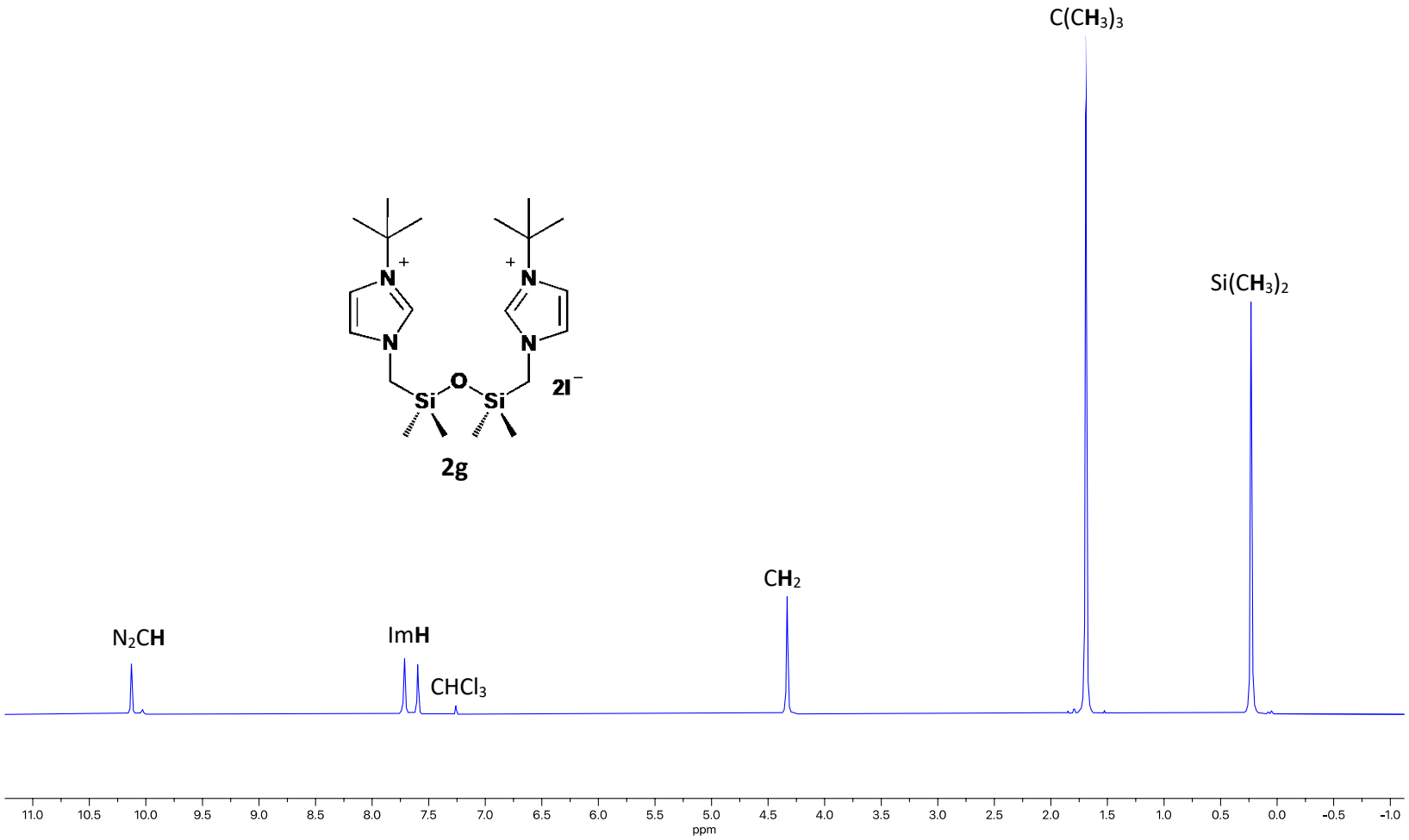


Figure S13. ^{1}H NMR spectrum of **2g** (400MHz, 298K, $CDCl_3$)

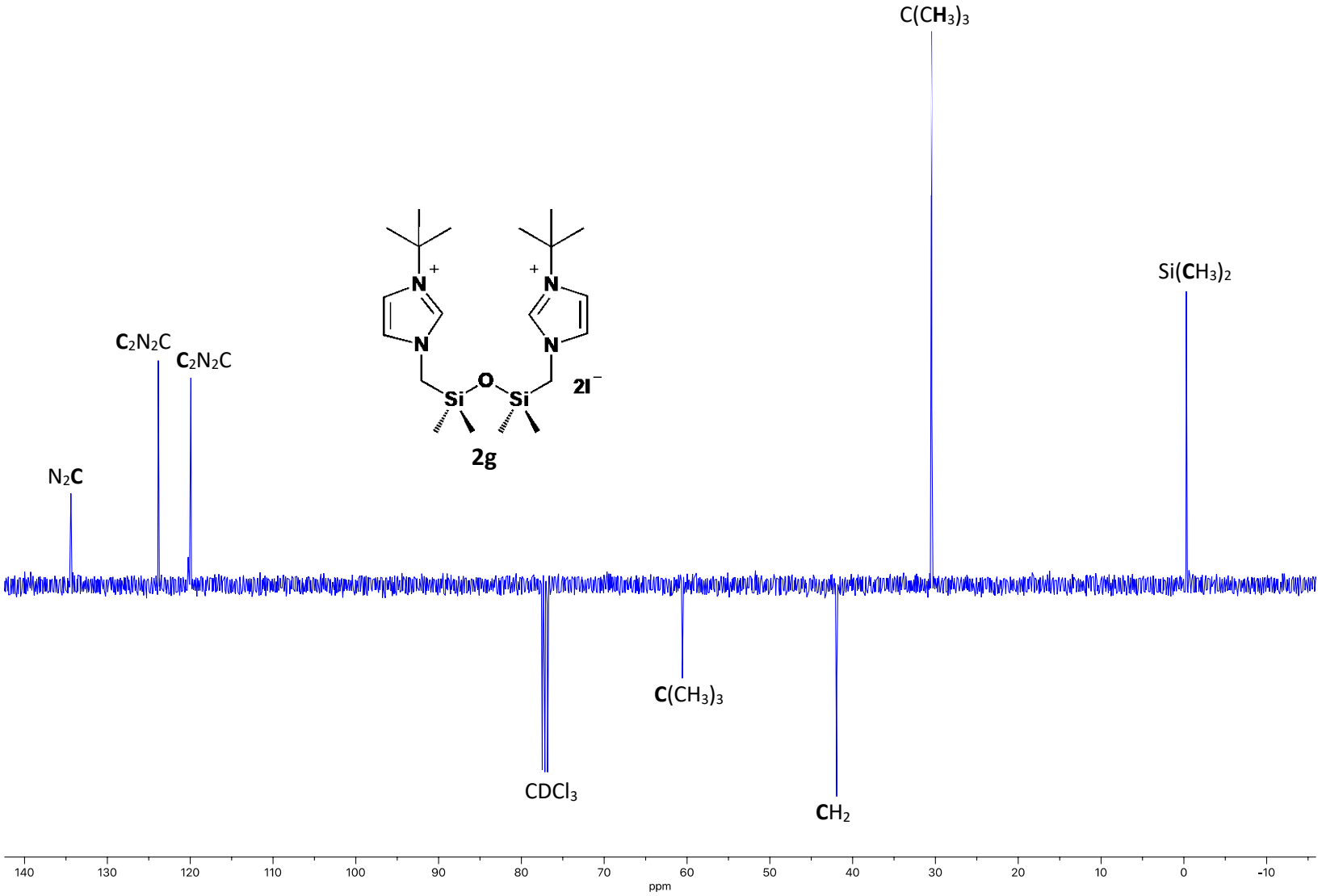


Figure S14. ^{13}C DEPTQ NMR spectrum of **2g** (101MHz, 298K, $CDCl_3$)

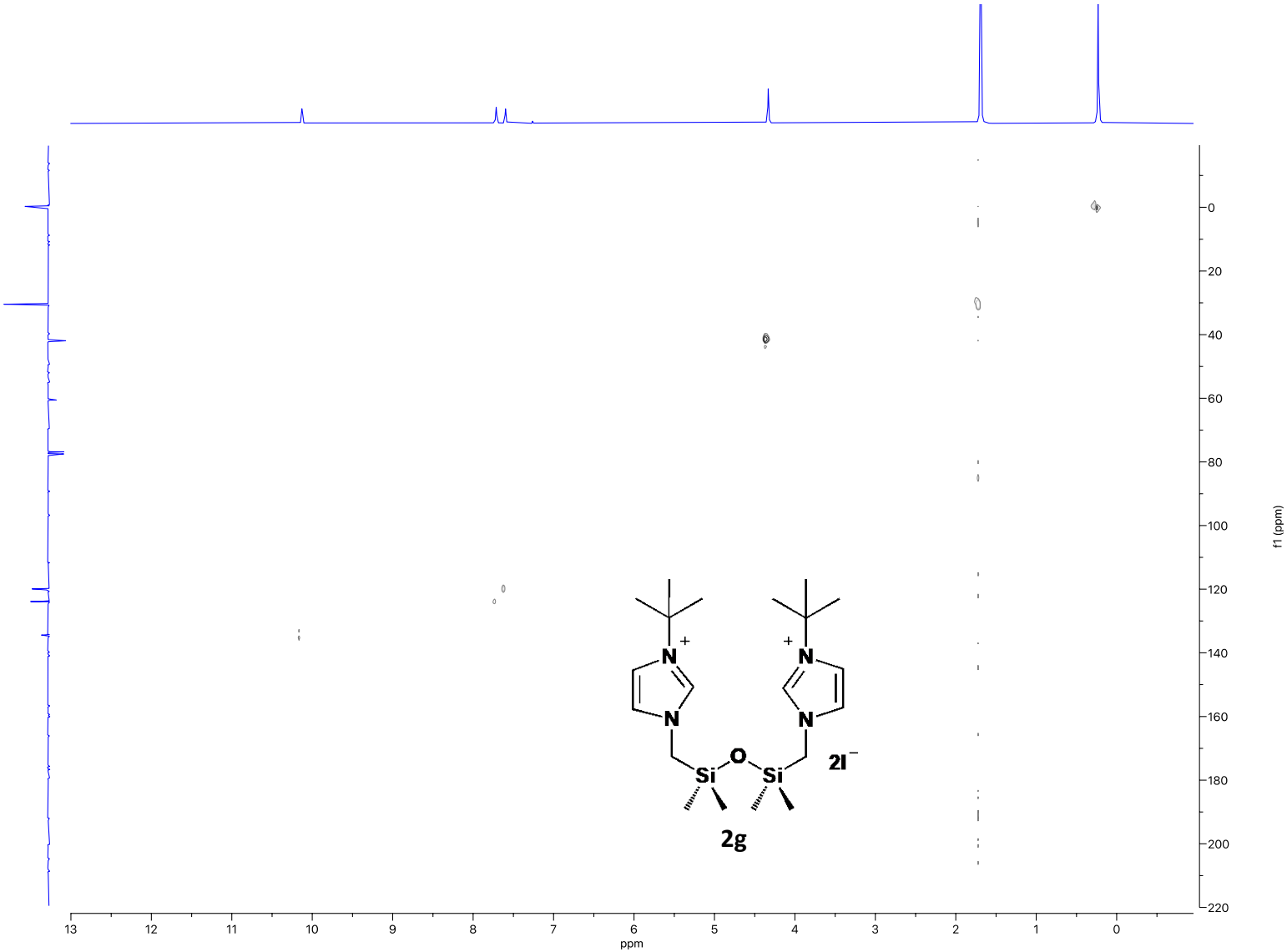


Figure S15. ^{1}H-^{13}C HSQC NMR spectrum of **2g** (400MHz, 298K, $CDCl_3$)

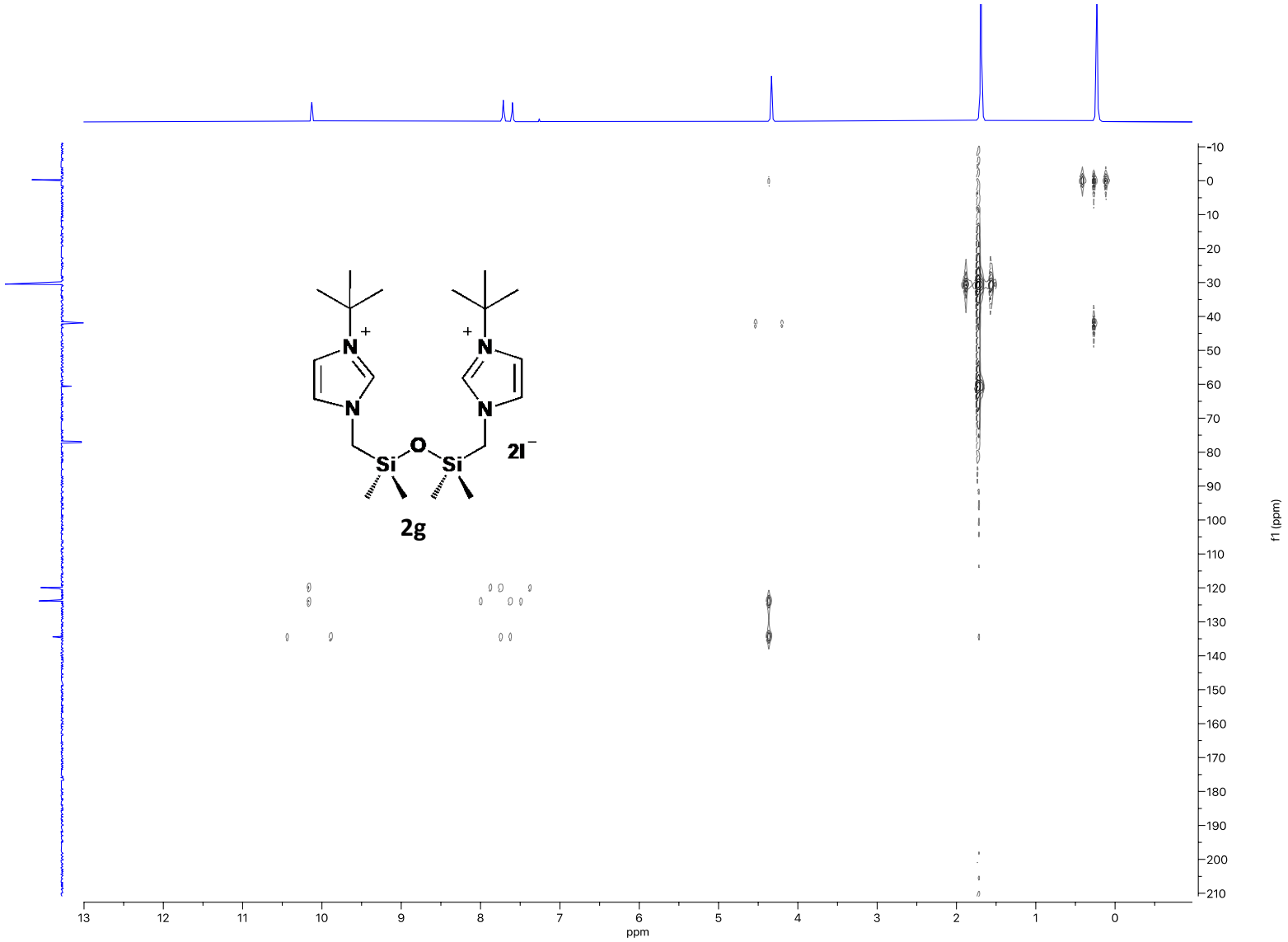


Figure S16. ^{1}H-^{13}C HMBC NMR spectrum of **2g** (400MHz, 298K, $CDCl_3$)

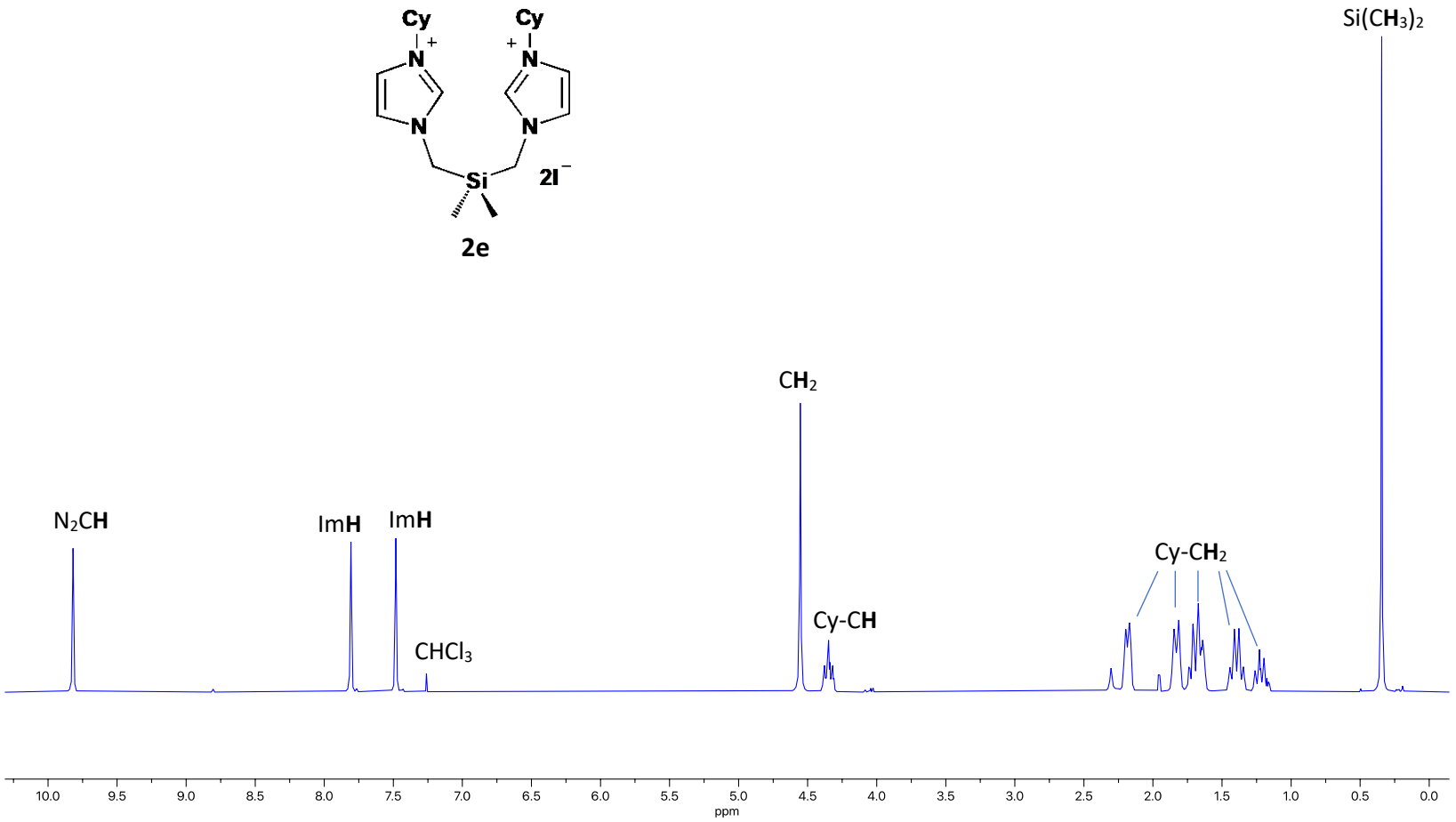


Figure S17. ^{1}H NMR spectrum of **2e** (400MHz, 298K, $CDCl_3$)

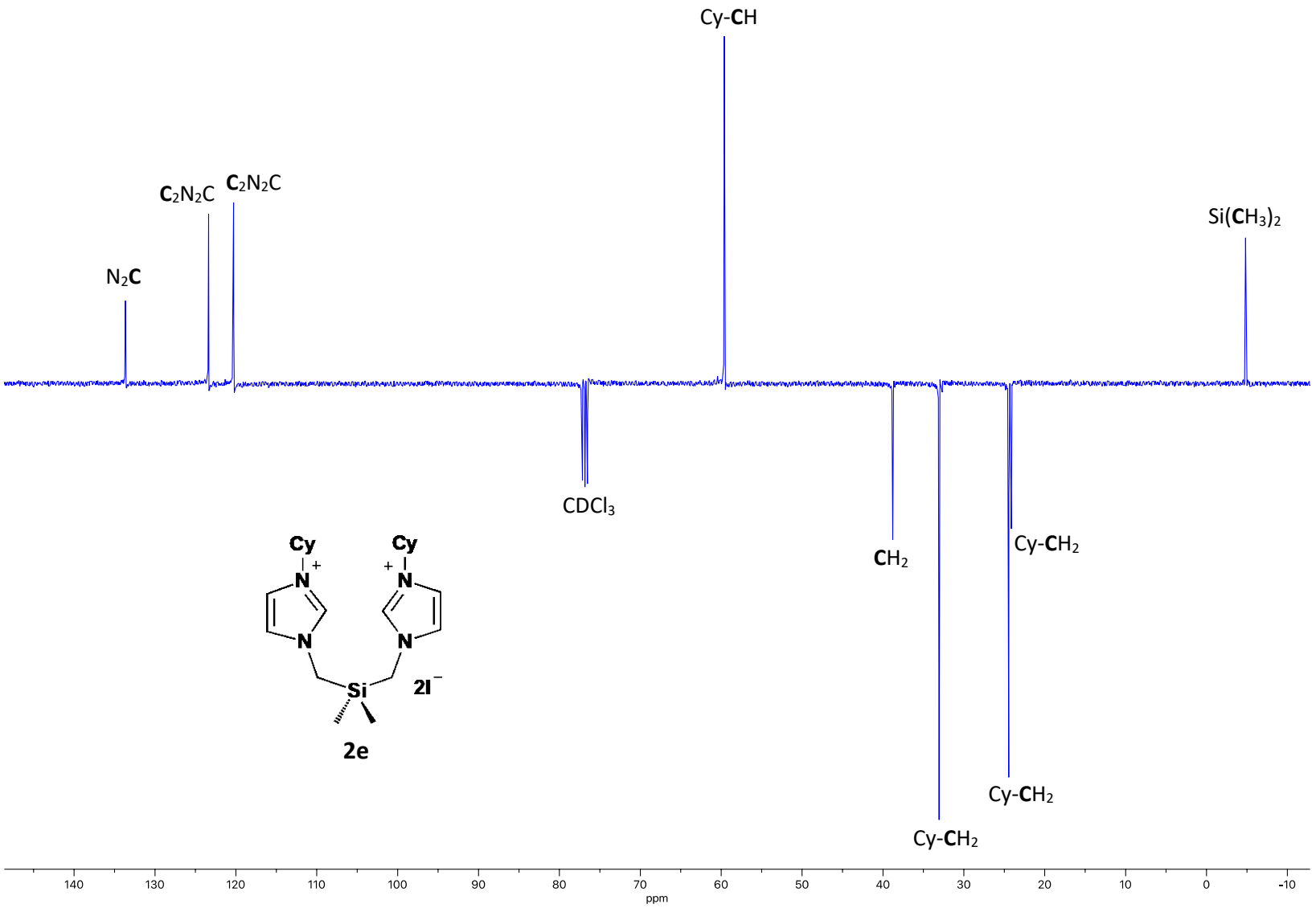


Figure S18. ^{13}C DEPTQ NMR spectrum of **2e** (101MHz, 298K, $CDCl_3$)

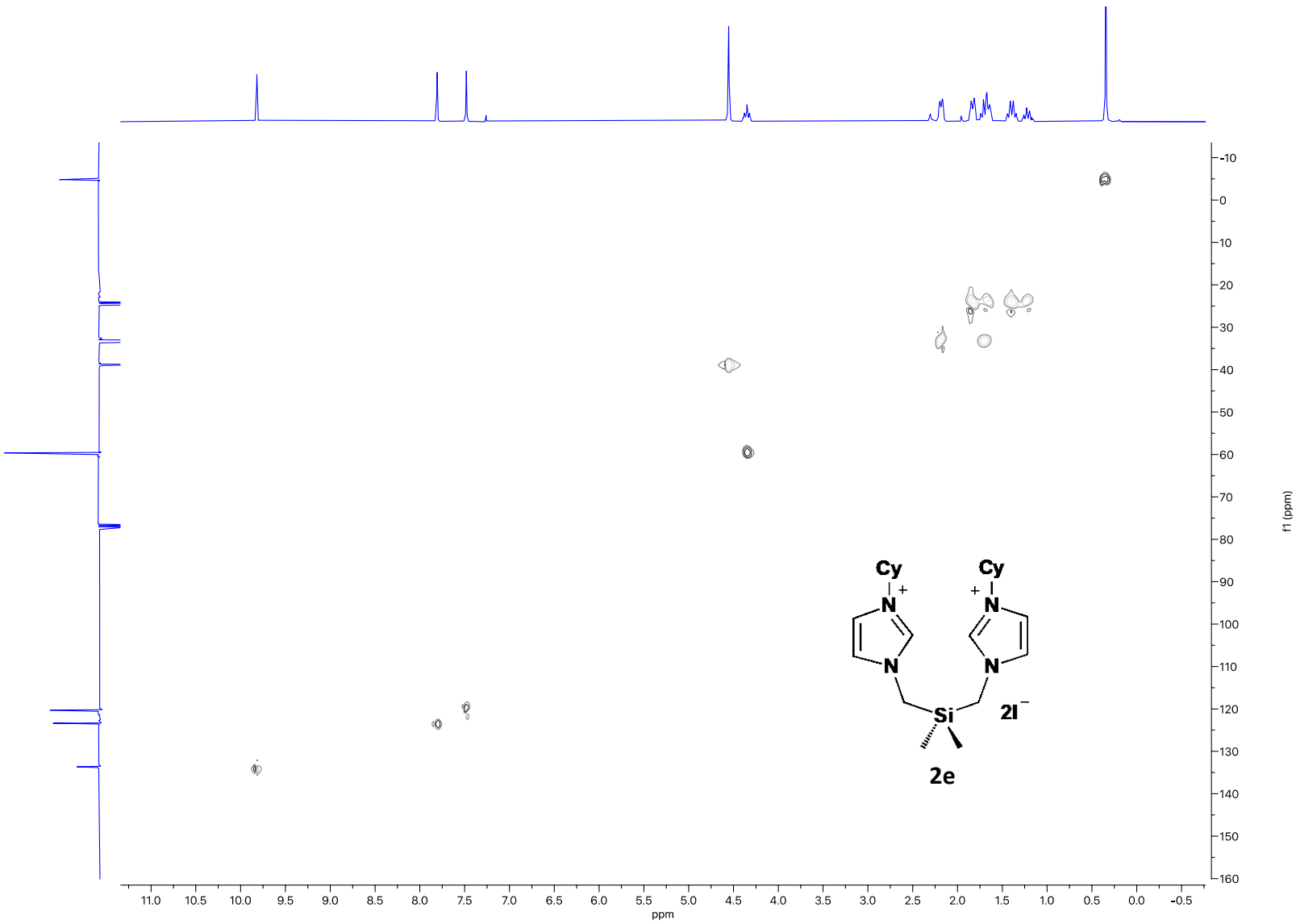


Figure S19. ^{1}H-^{13}C HSQC NMR spectrum of **2e** (400MHz, 298K, $CDCl_3$)

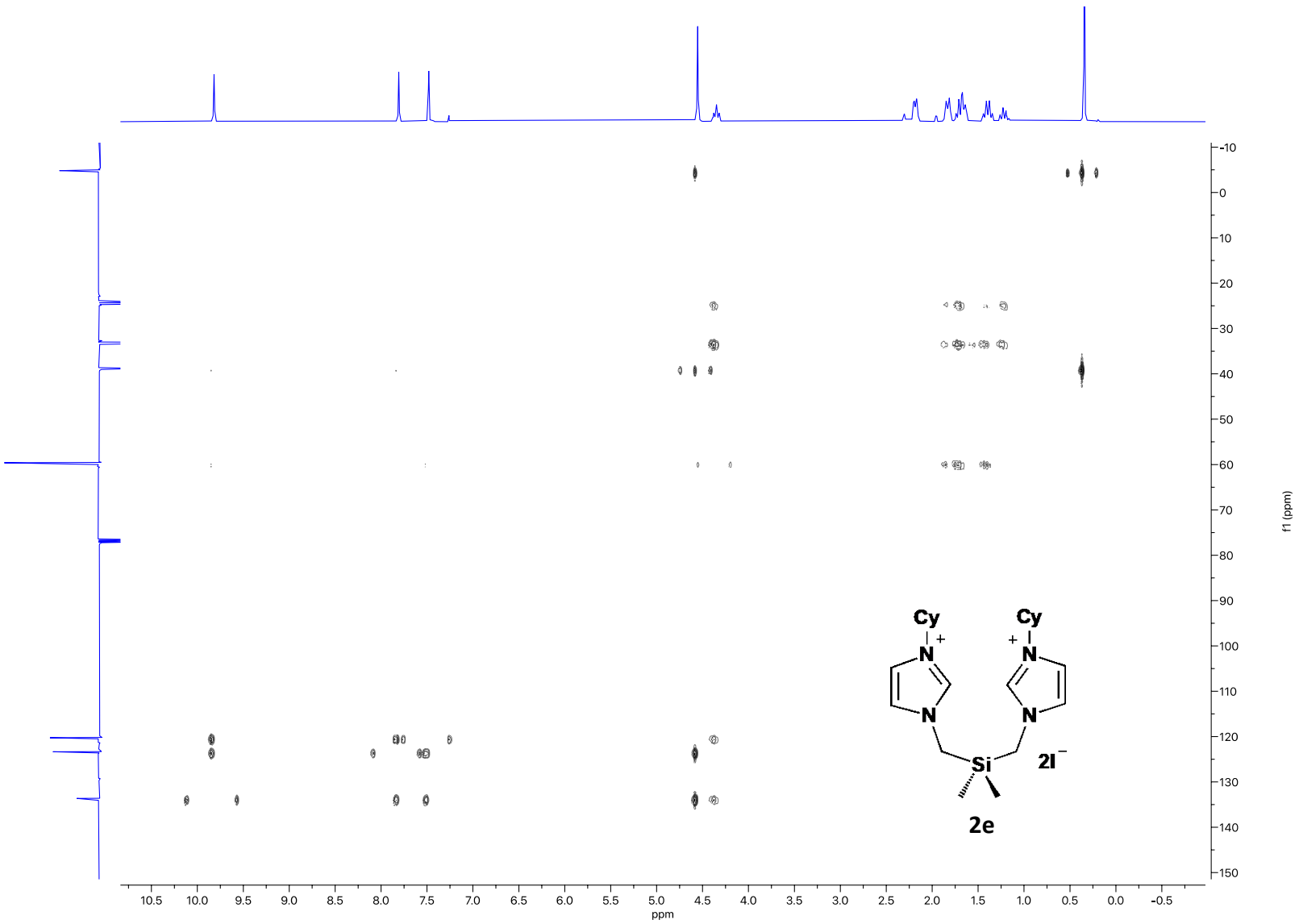


Figure S20. ^{1}H-^{13}C HMBC NMR spectrum of **2e** (400MHz, 298K, $CDCl_3$)

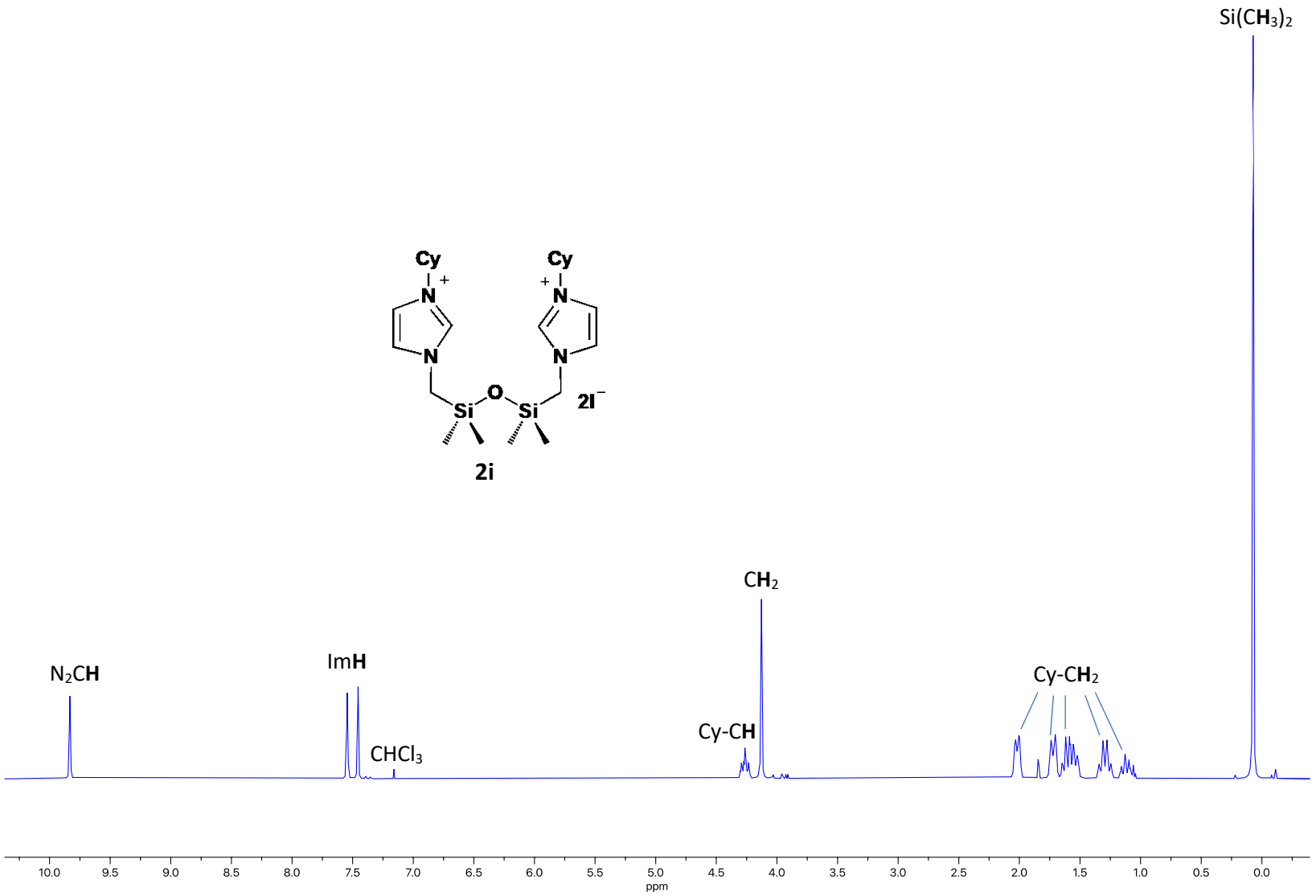


Figure S21. ^{1}H NMR spectrum of **2i** (400MHz, 298K, $CDCl_3$)

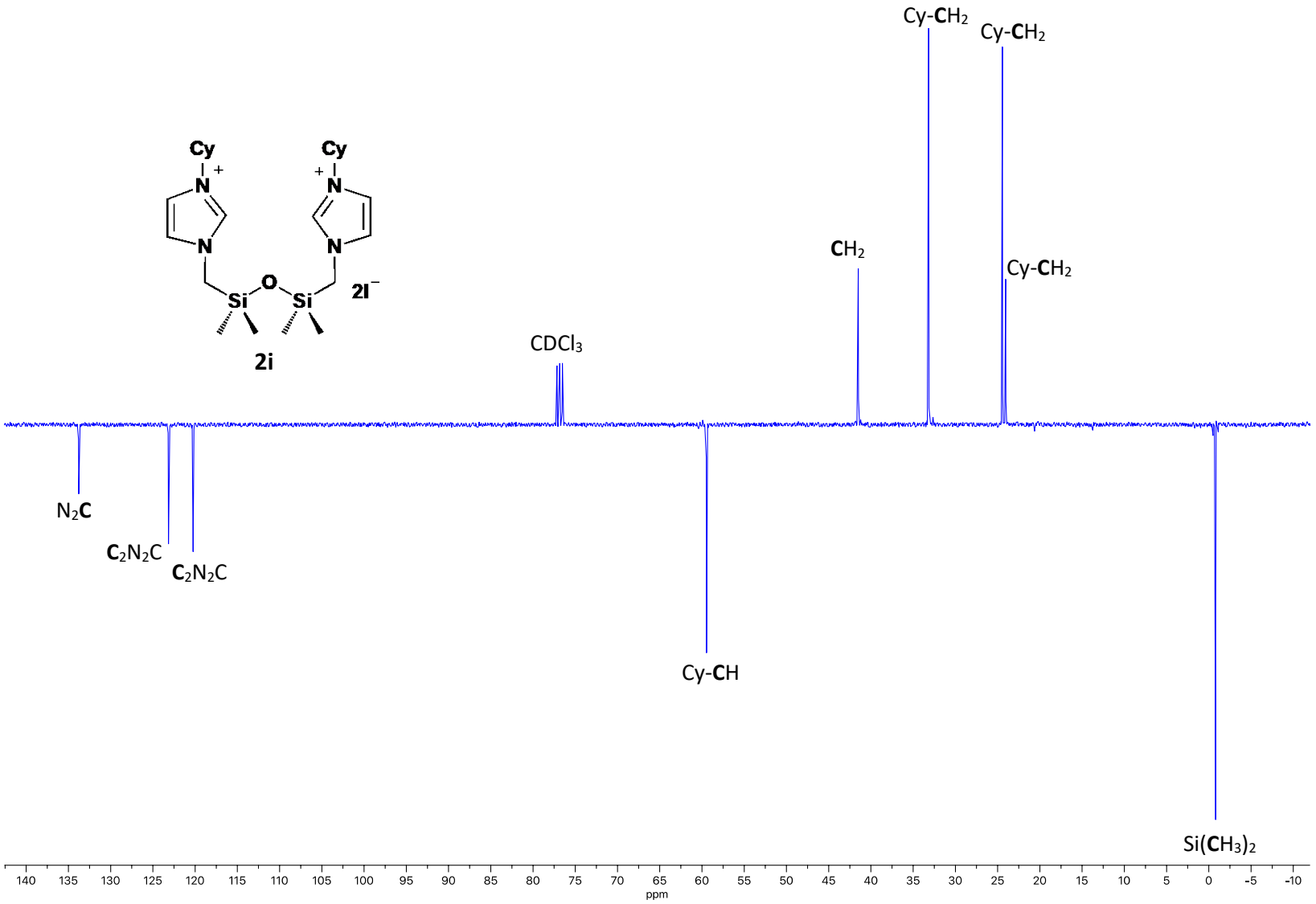


Figure S22. ^{13}C DEPTQ NMR spectrum of **2i** (101MHz, 298K, $CDCl_3$)

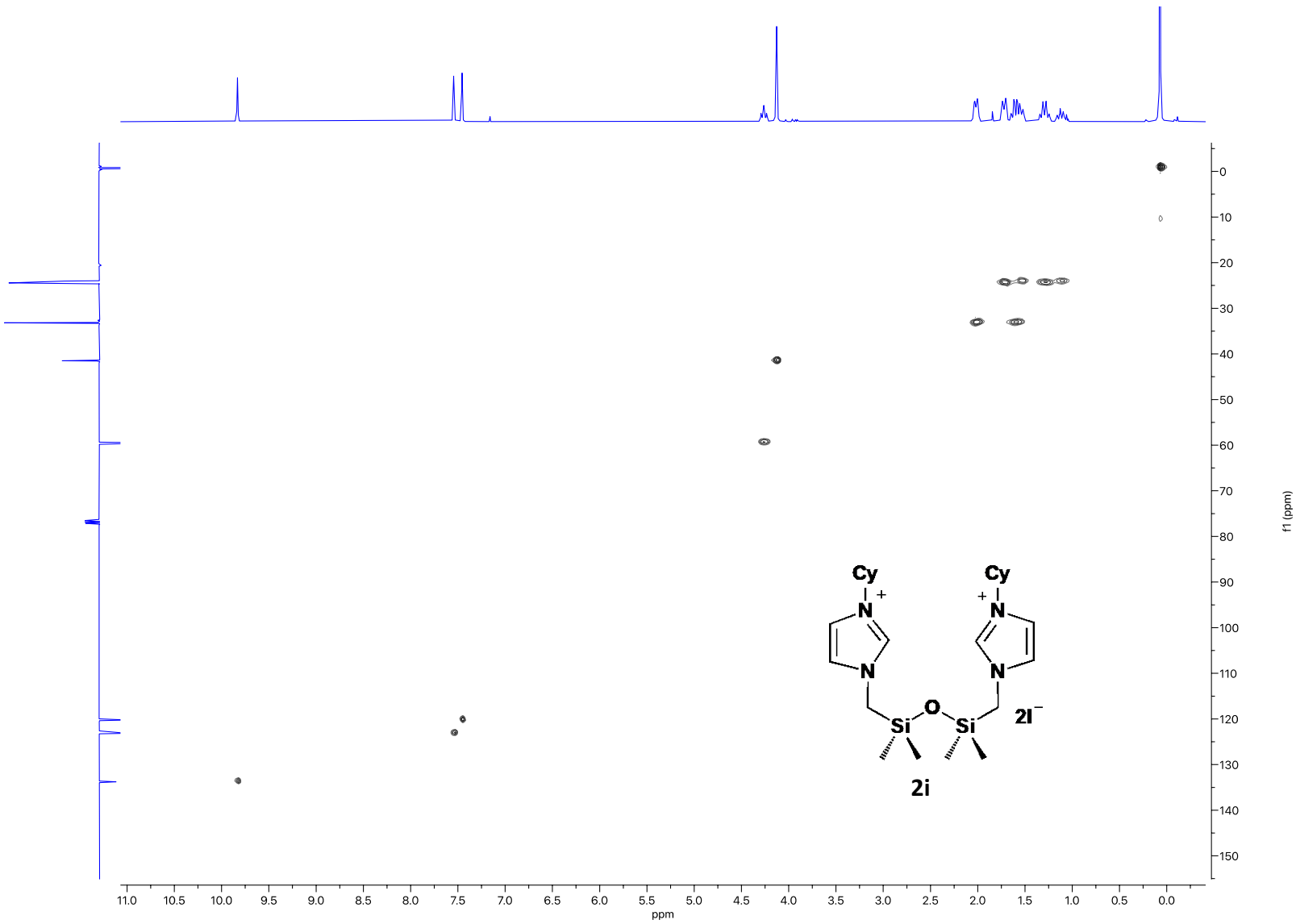


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum of **2i** (400MHz, 298K, $CDCl_3$)

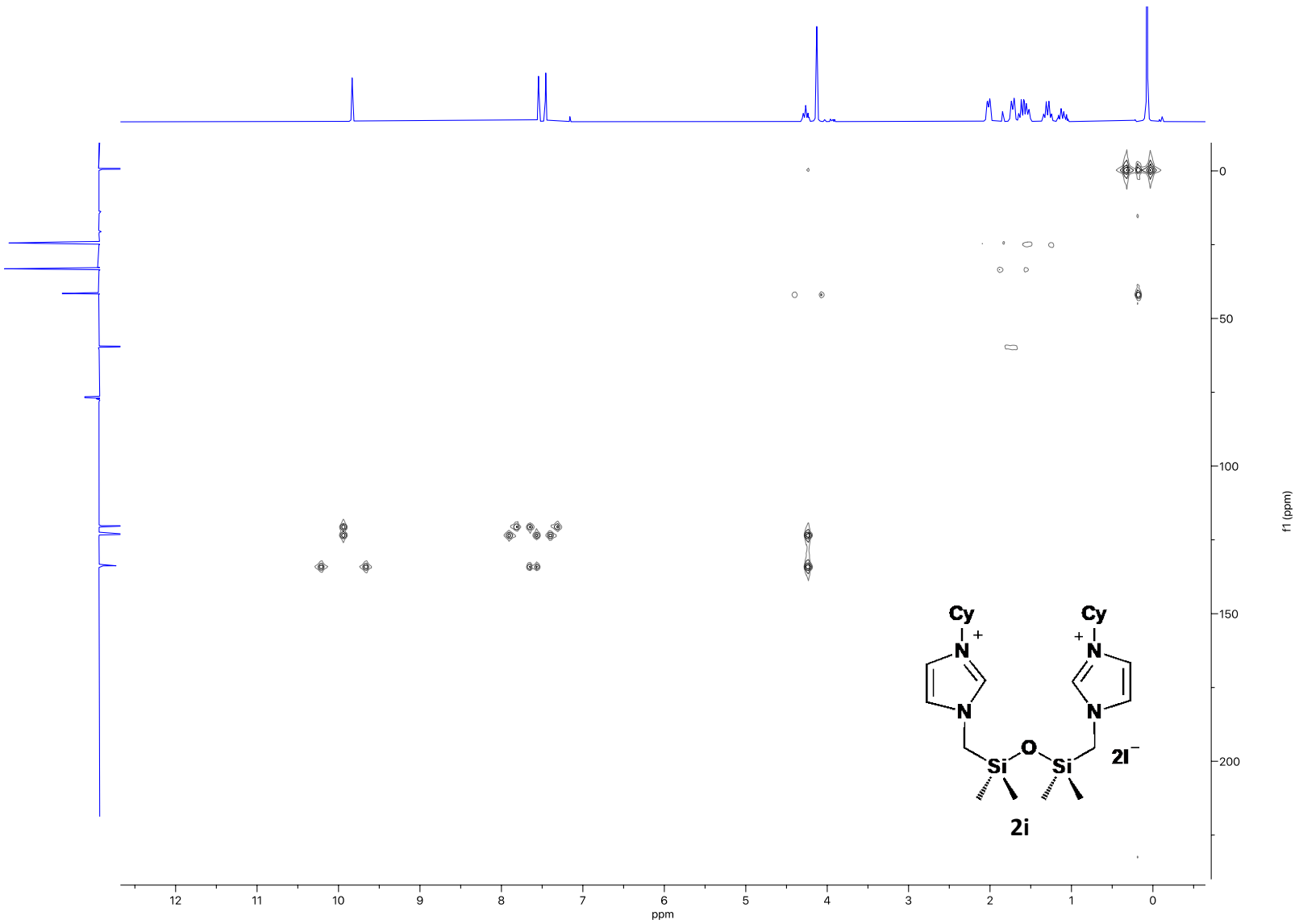


Figure S24. ^{1}H-^{13}C HMBC NMR spectrum of **2i** (400MHz, 298K, $CDCl_3$)

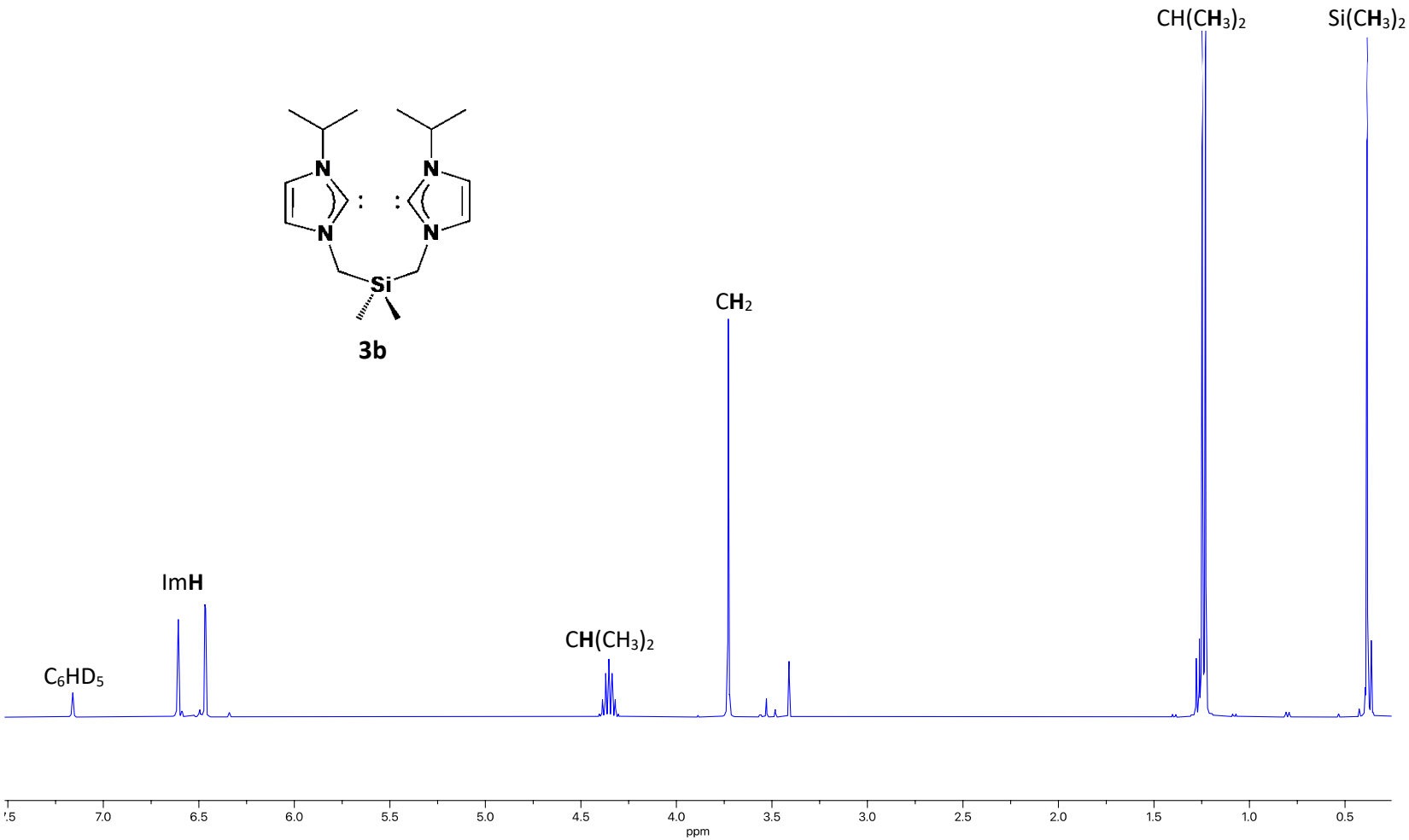


Figure S25. ^{1}H NMR spectrum of **3b** (400MHz, 298K, C_6D_6)

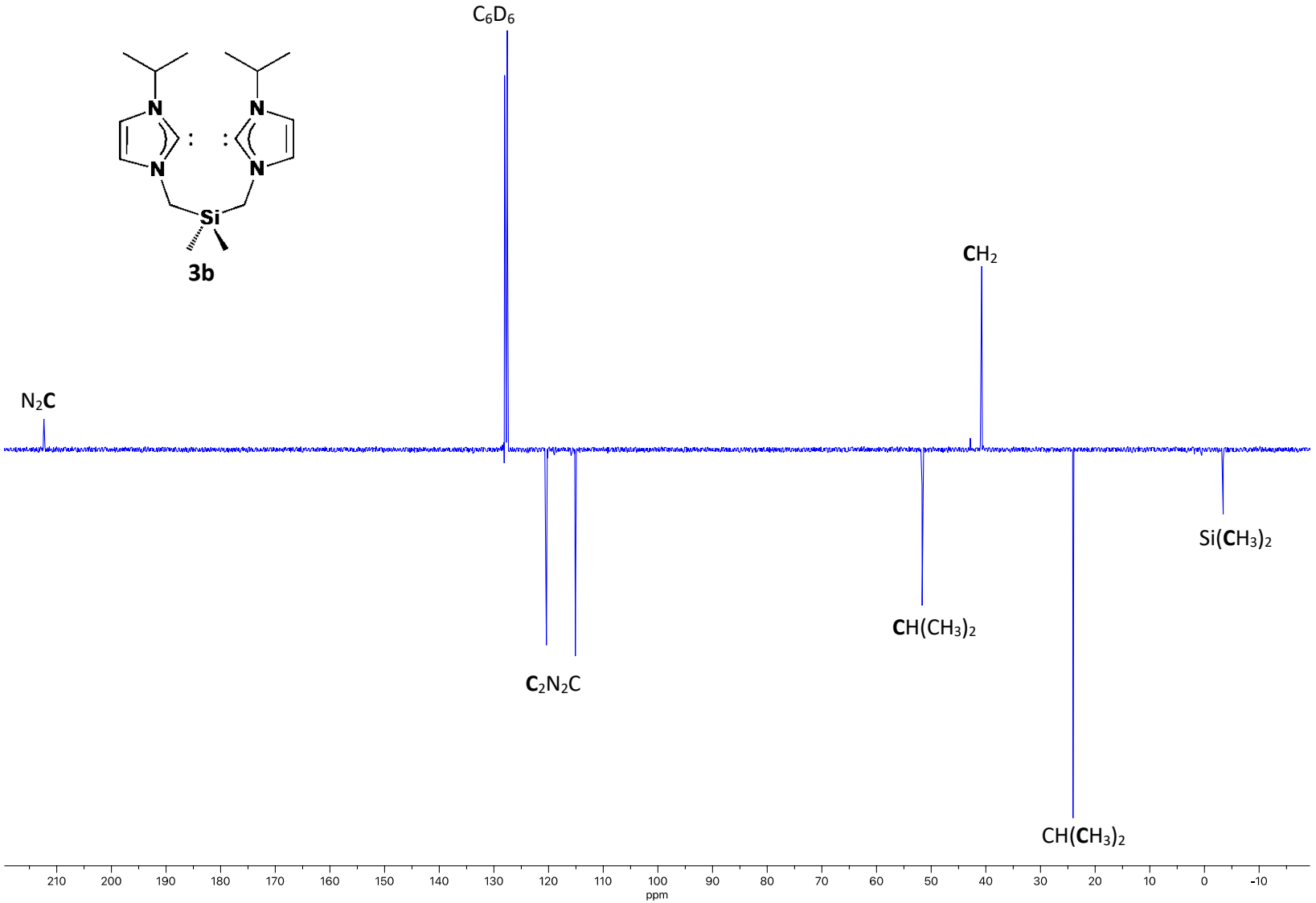


Figure S26. ^{13}C DEPTQ NMR spectrum of **3b** (101MHz, 298K, C_6D_6)

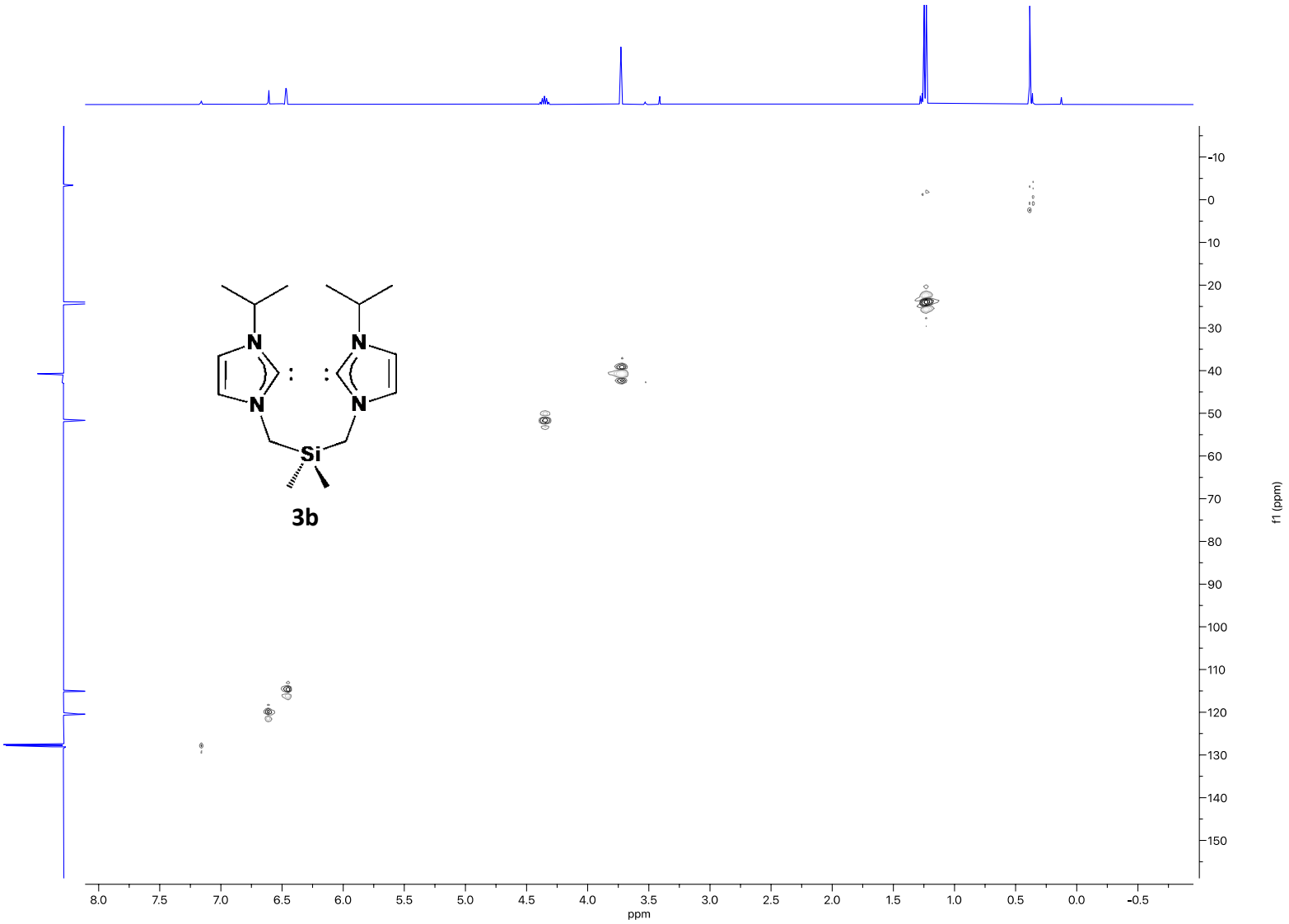


Figure S27. ^{1}H-^{13}C HSQC NMR spectrum of **3b** (400MHz, 298K, C_6D_6)

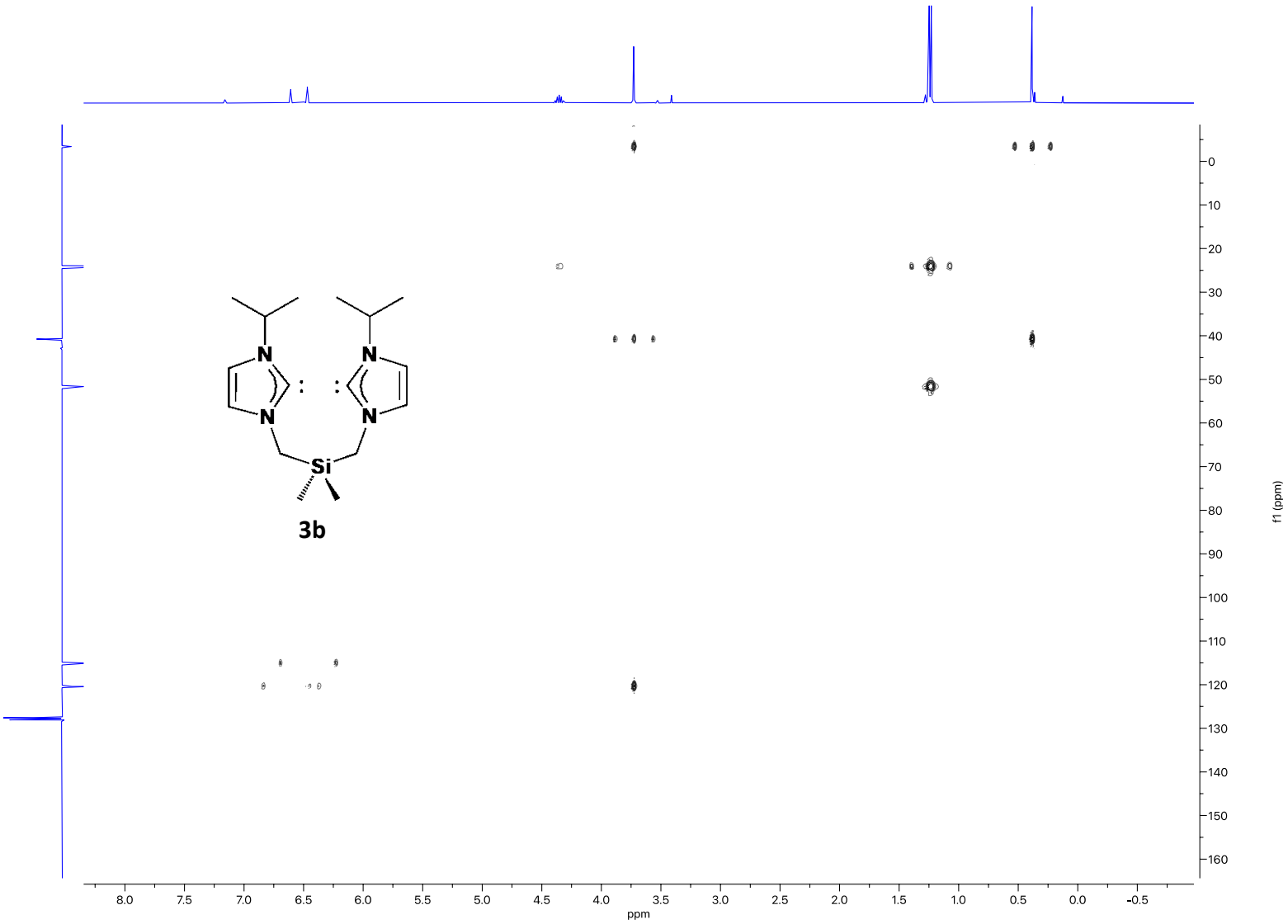


Figure S28. ^{1}H-^{13}C HMBC NMR spectrum of **3b** (400MHz, 298K, C_6D_6)

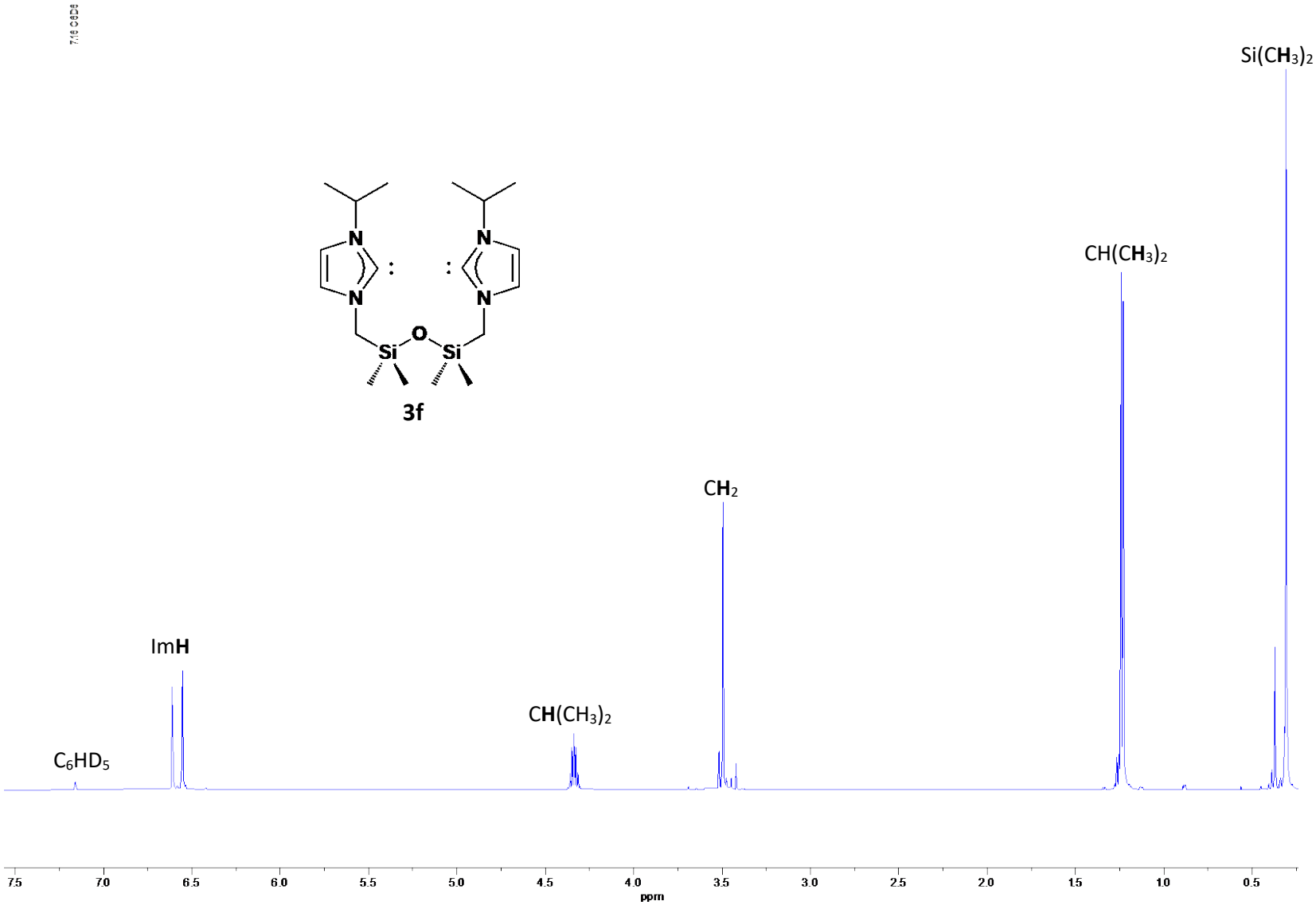


Figure S29. ^{1}H NMR spectrum of **3f** (600MHz, 298K, C_6D_6)

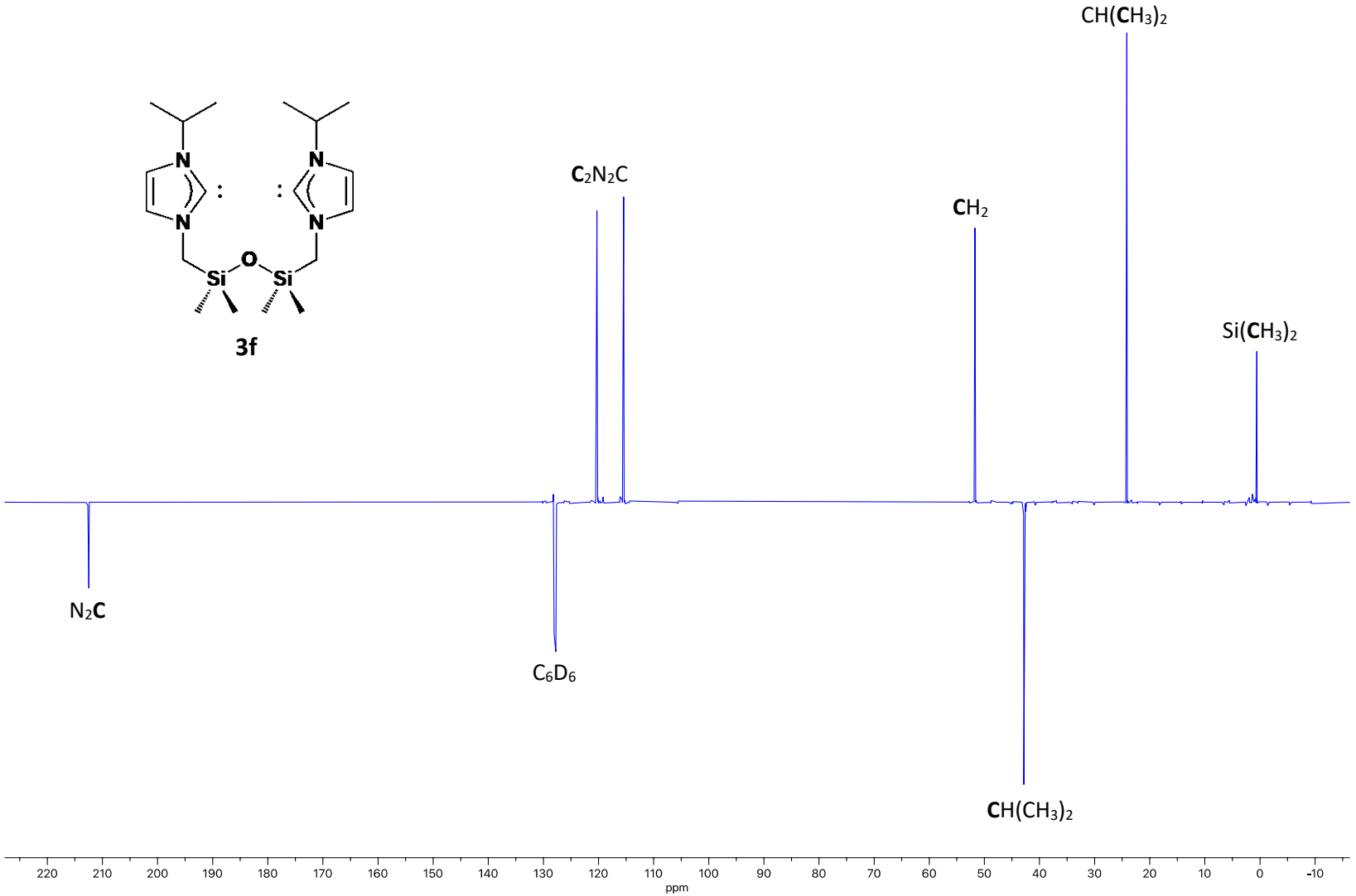


Figure S30. ^{13}C DEPTQ NMR spectrum of **3f** (151MHz, 298K, C_6D_6)

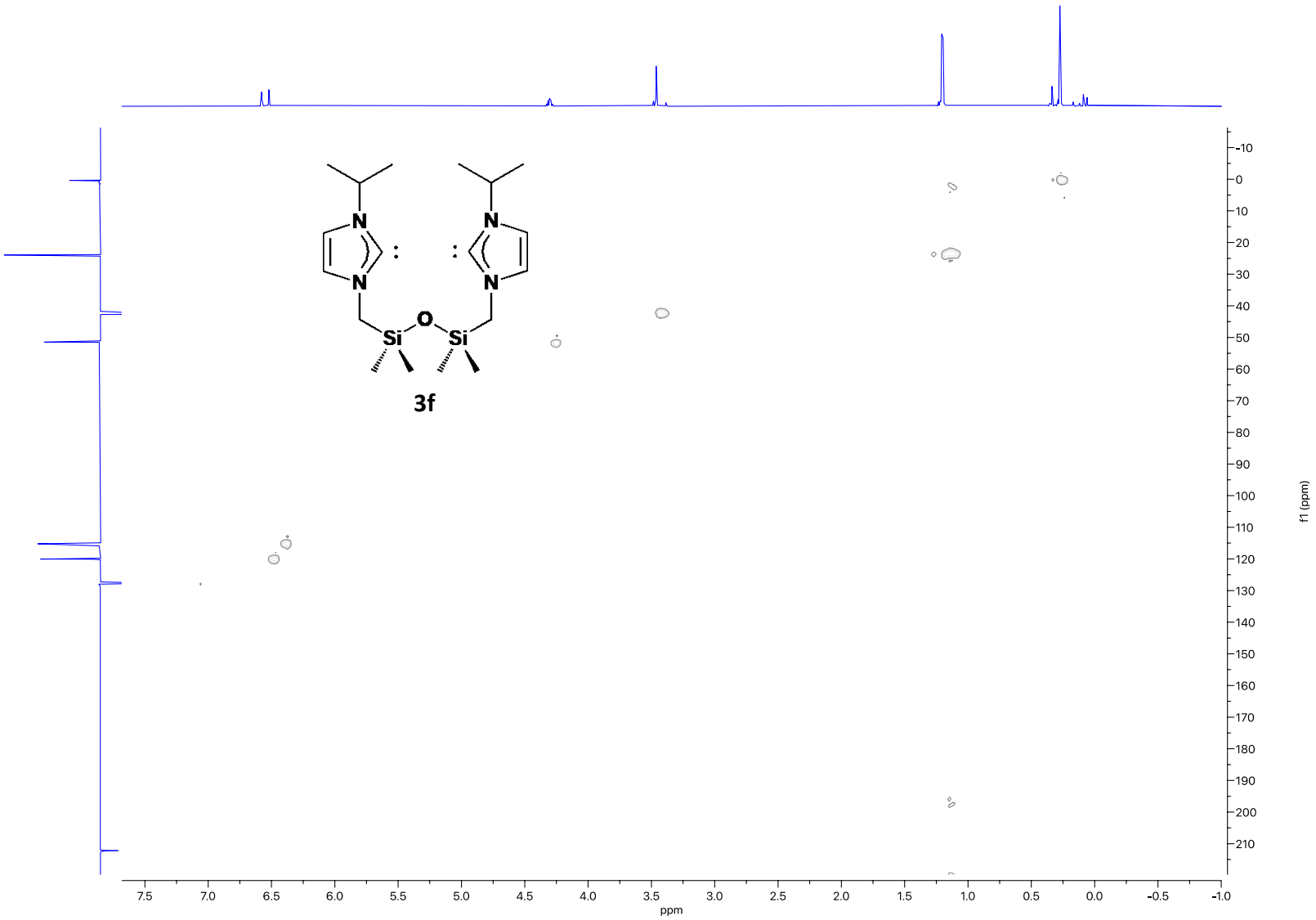


Figure S31. ^{1}H-^{13}C HSQC NMR spectrum of **3f** (600MHz, 298K, C_6D_6)

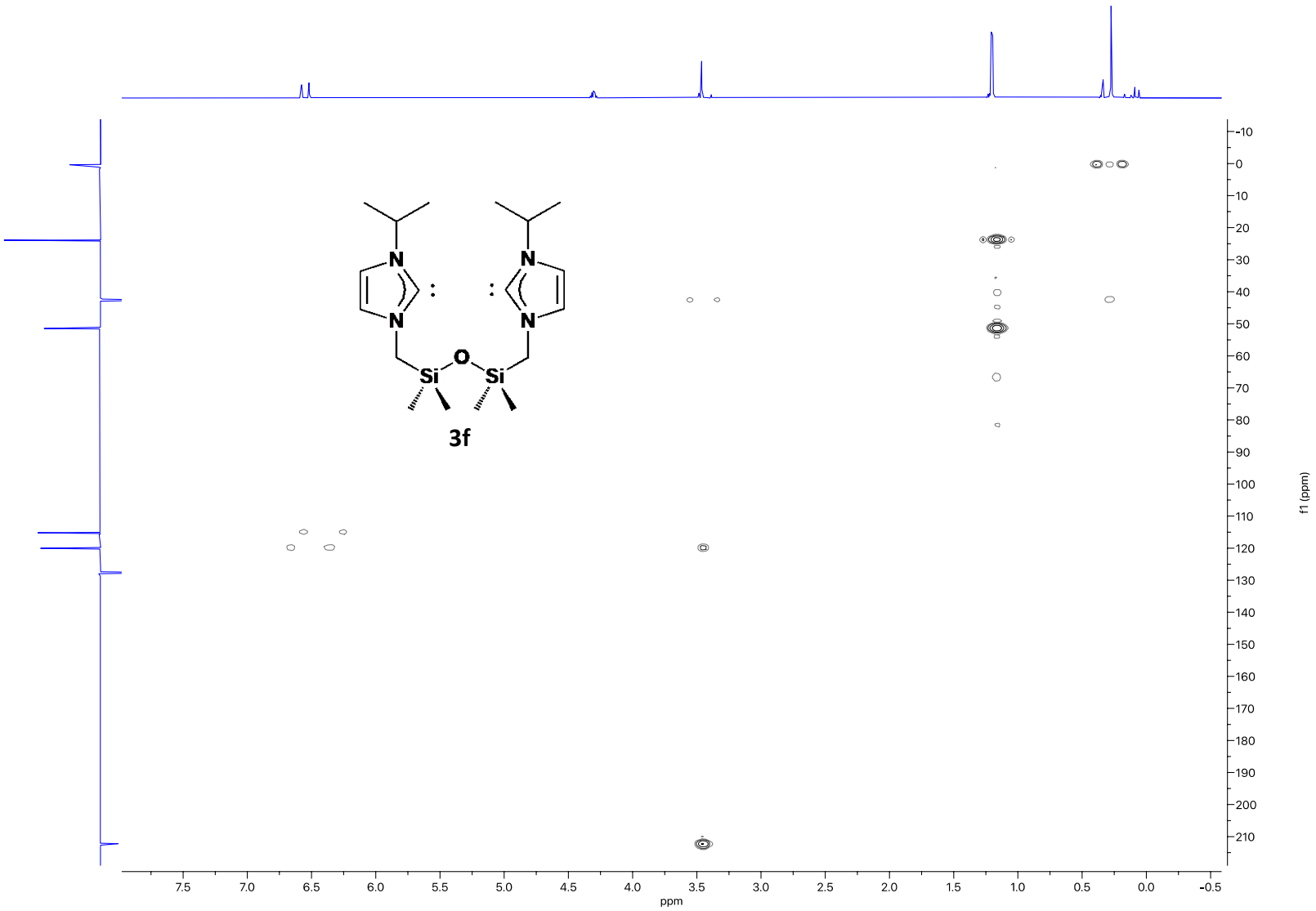
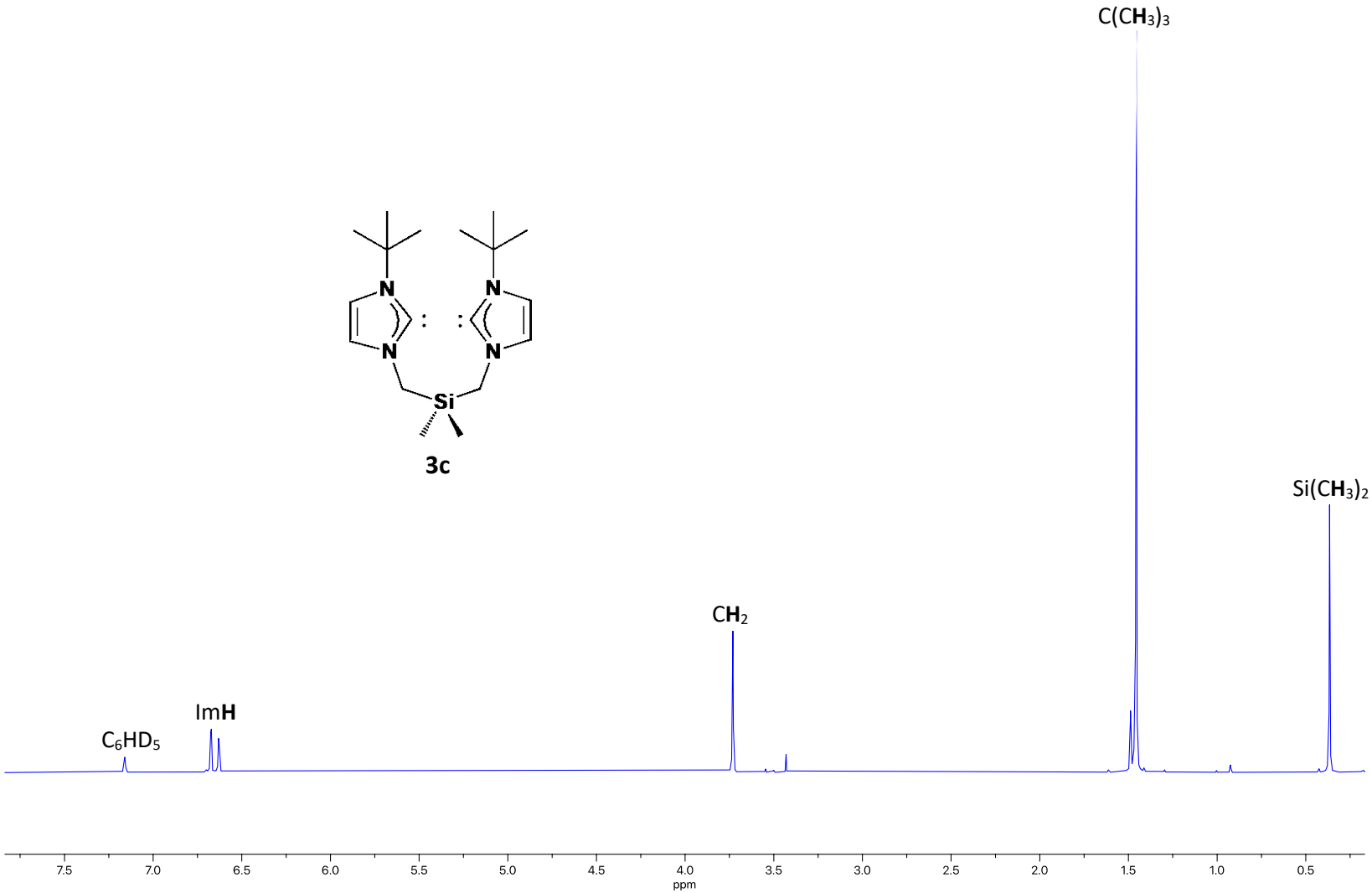


Figure S32. ^{1}H-^{13}C HMBC NMR spectrum of **3f** (600MHz, 298K, C_6D_6)



3c

Figure S33. ^{1}H NMR spectrum of **3c** (400MHz, 298K, C_6D_6)

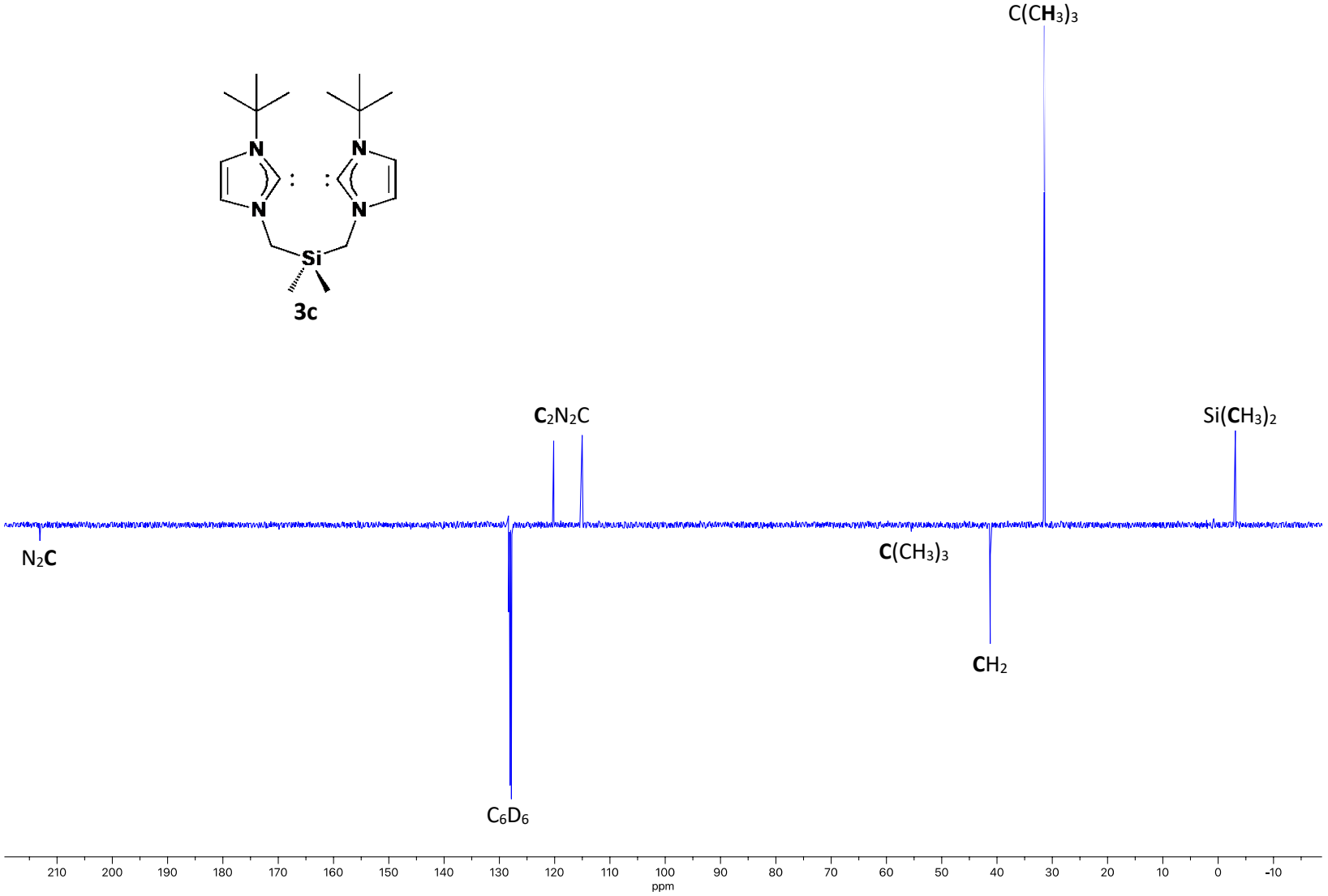


Figure S34. ^{13}C DEPTQ NMR spectrum of **3c** (101MHz, 298K, C_6D_6)

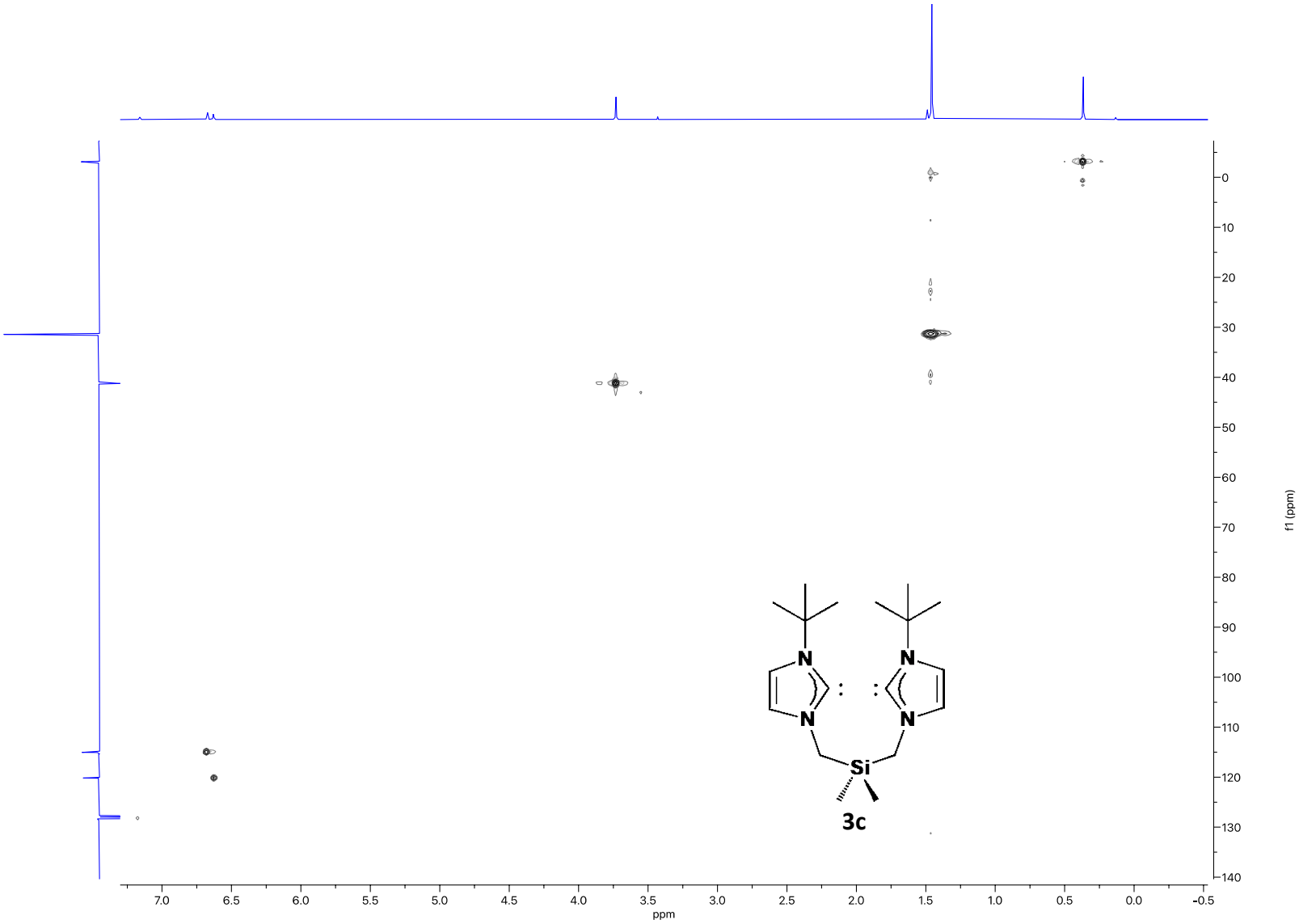


Figure S35. ^{1}H-^{13}C HSQC NMR spectrum of **3c** (400MHz, 298K, C_6D_6)

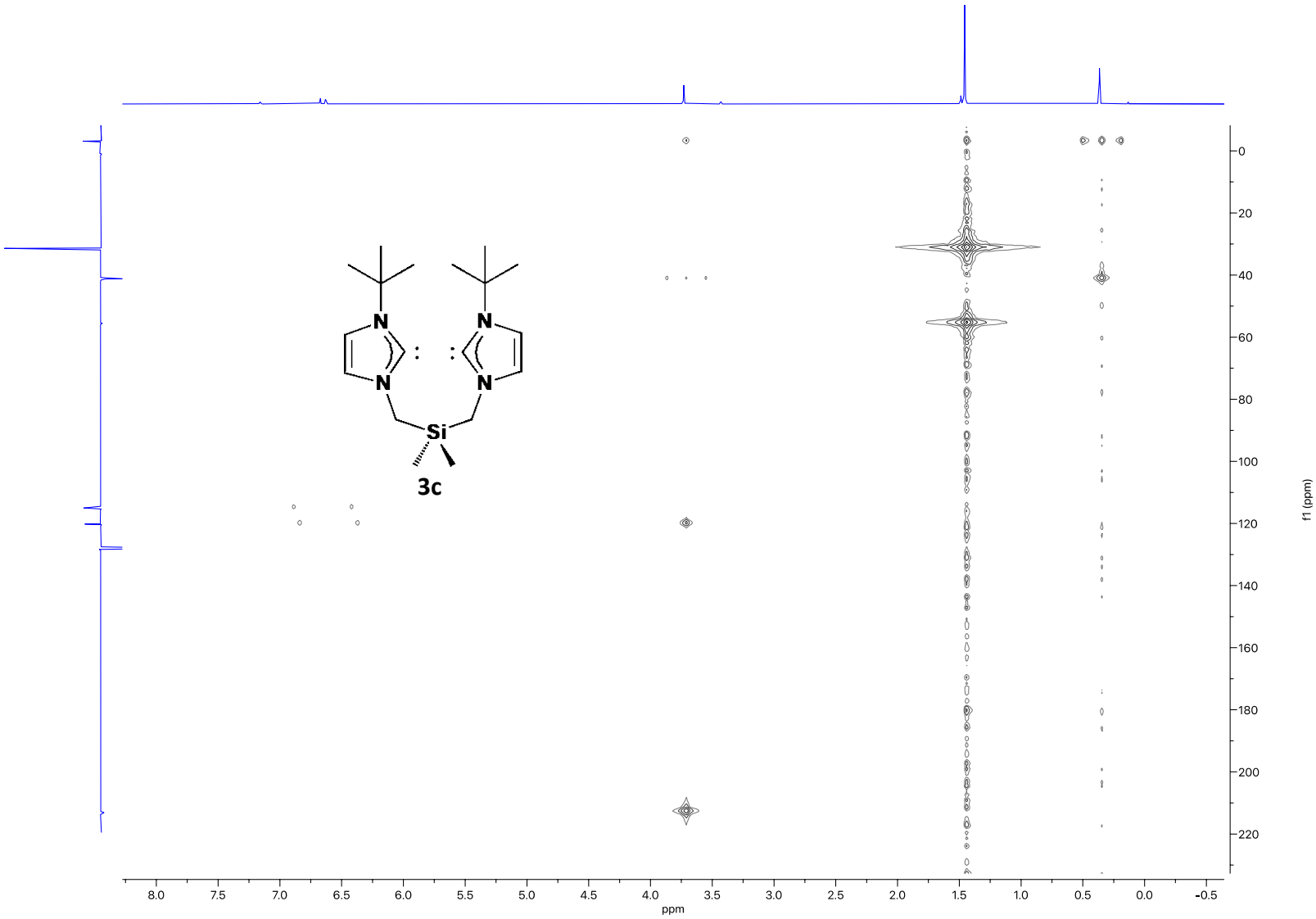
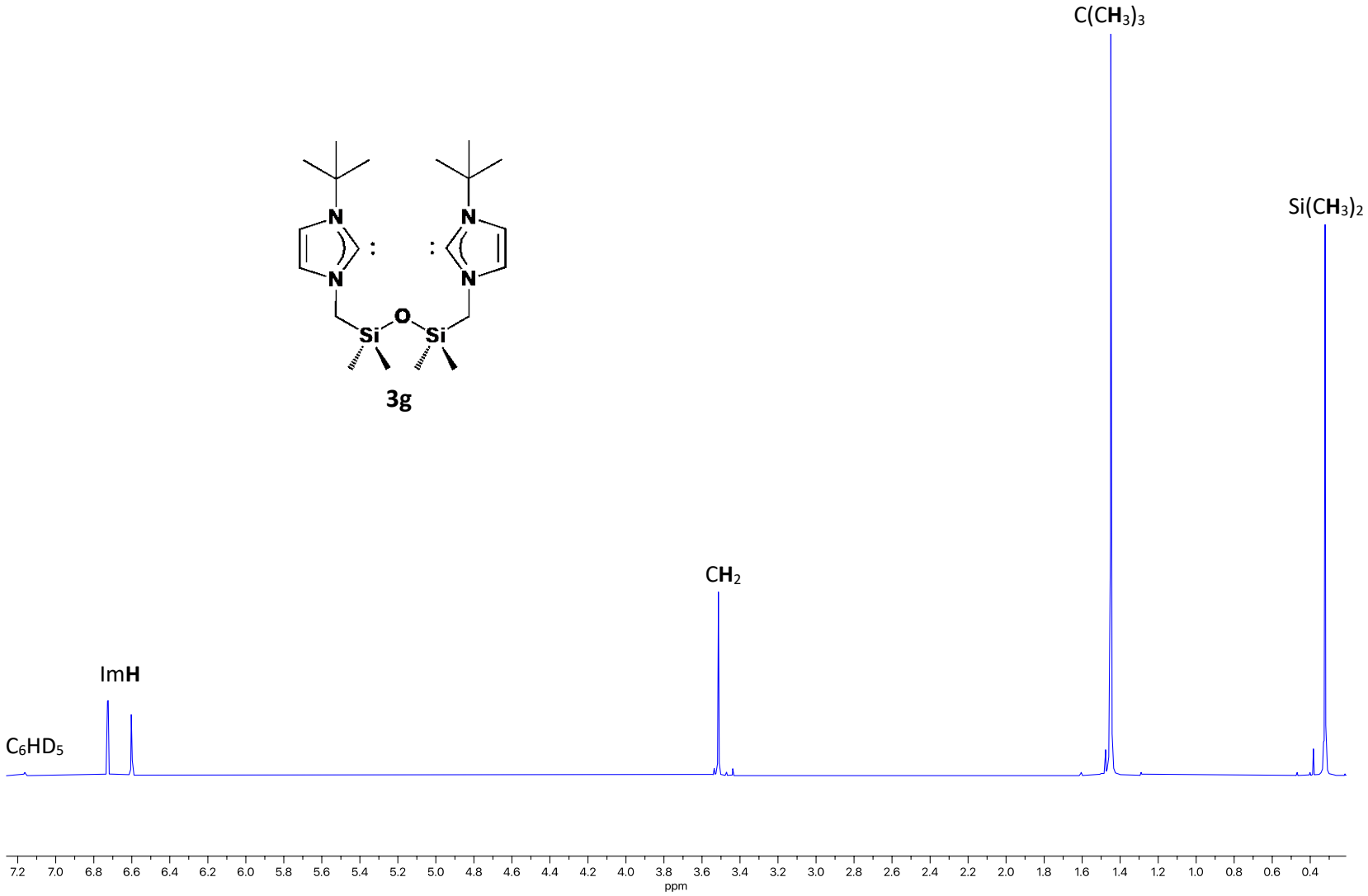


Figure S36. ^{1}H-^{13}C HMBC NMR spectrum of **3c** (400MHz, 298K, C_6D_6)



3g

Figure S37. ^{1}H NMR spectrum of **3g** (400MHz, 298K, C_6D_6)

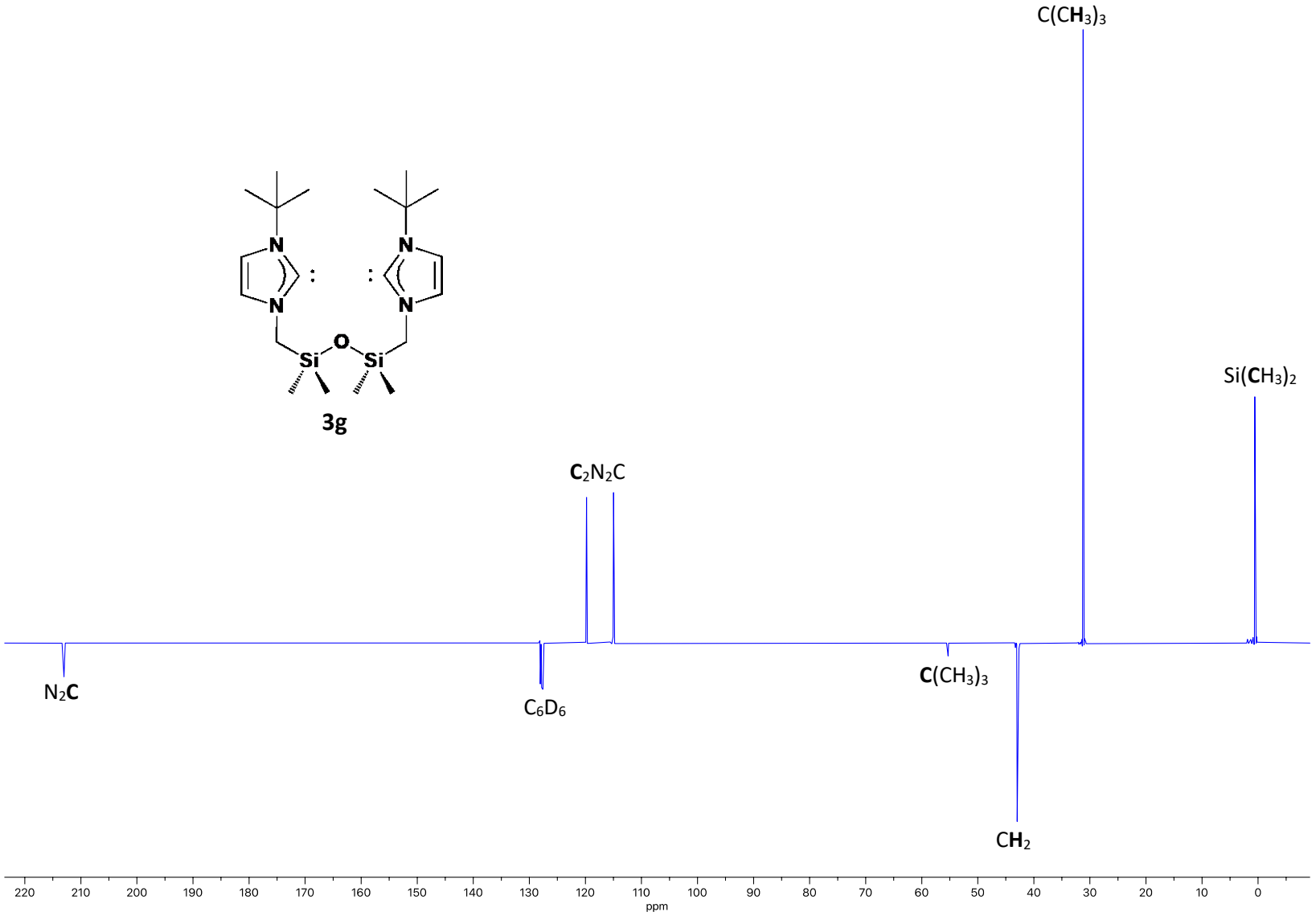


Figure S38. ^{13}C DEPTQ NMR spectrum of **3g** (101MHz, 298K, C_6D_6)

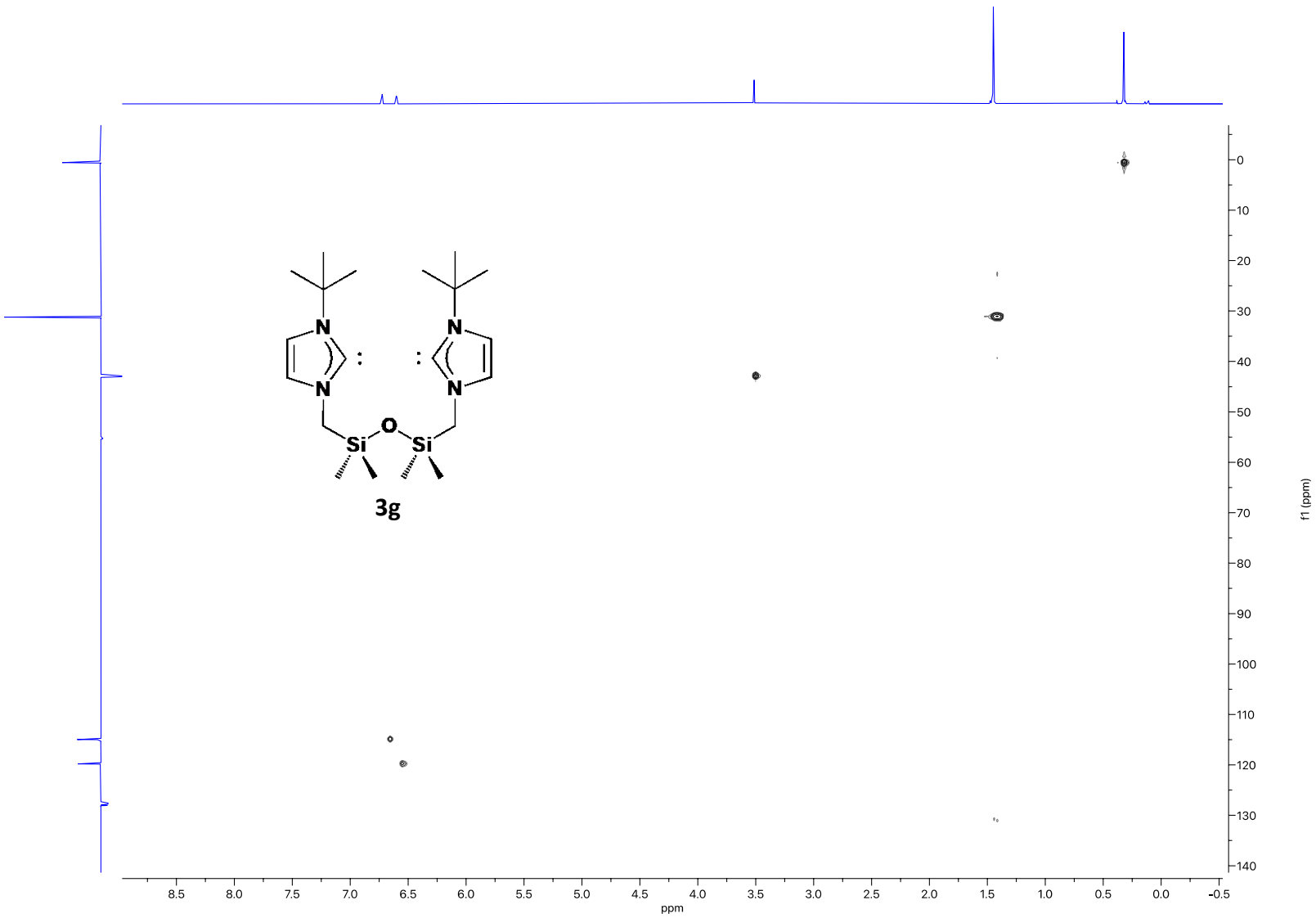


Figure S39. ^{1}H-^{13}C HSQC NMR spectrum of **3g** (400MHz, 298K, C_6D_6)

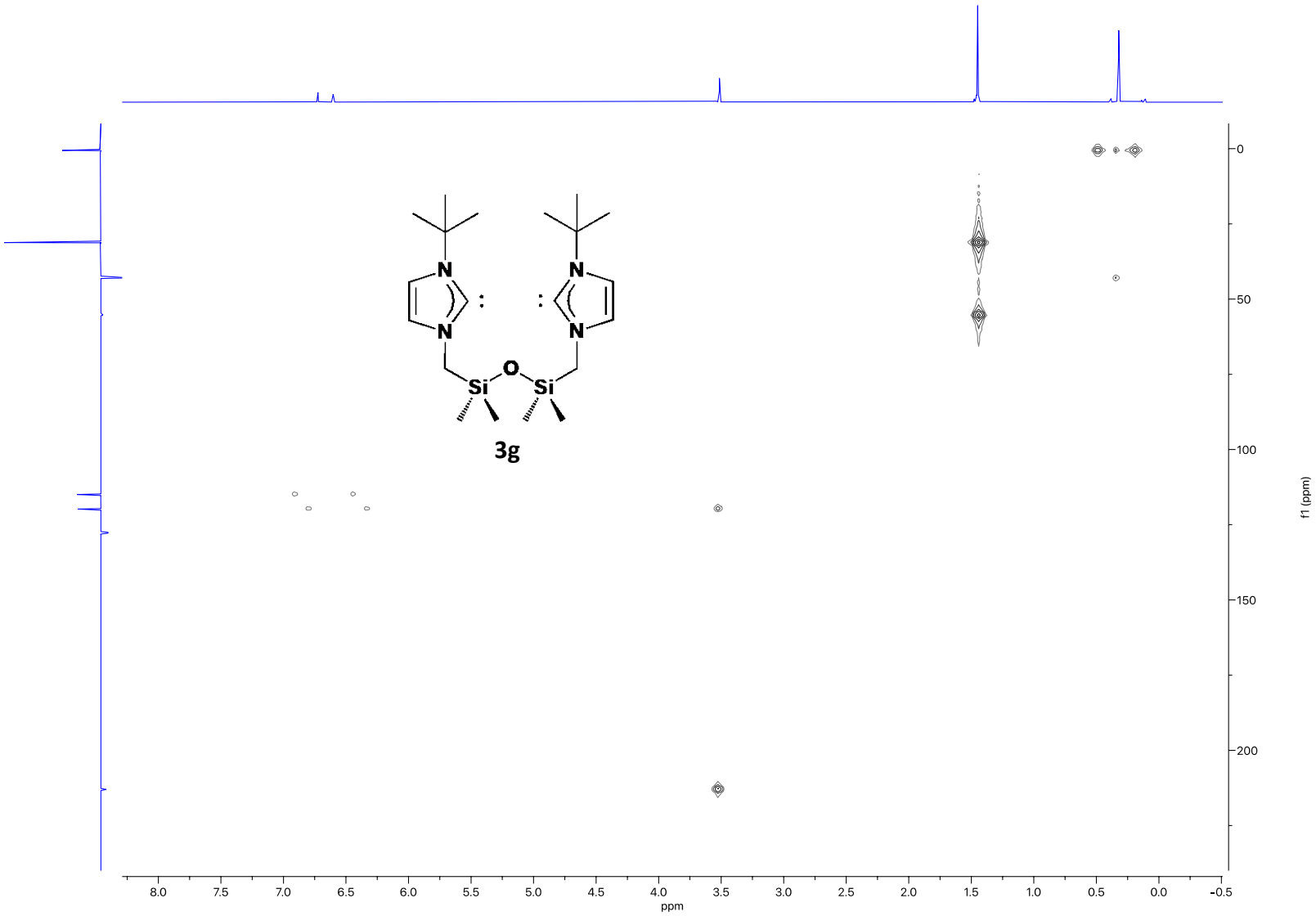


Figure S40. ^{1}H-^{13}C HMBC spectrum of **3g** (400MHz, 298K, C_6D_6)

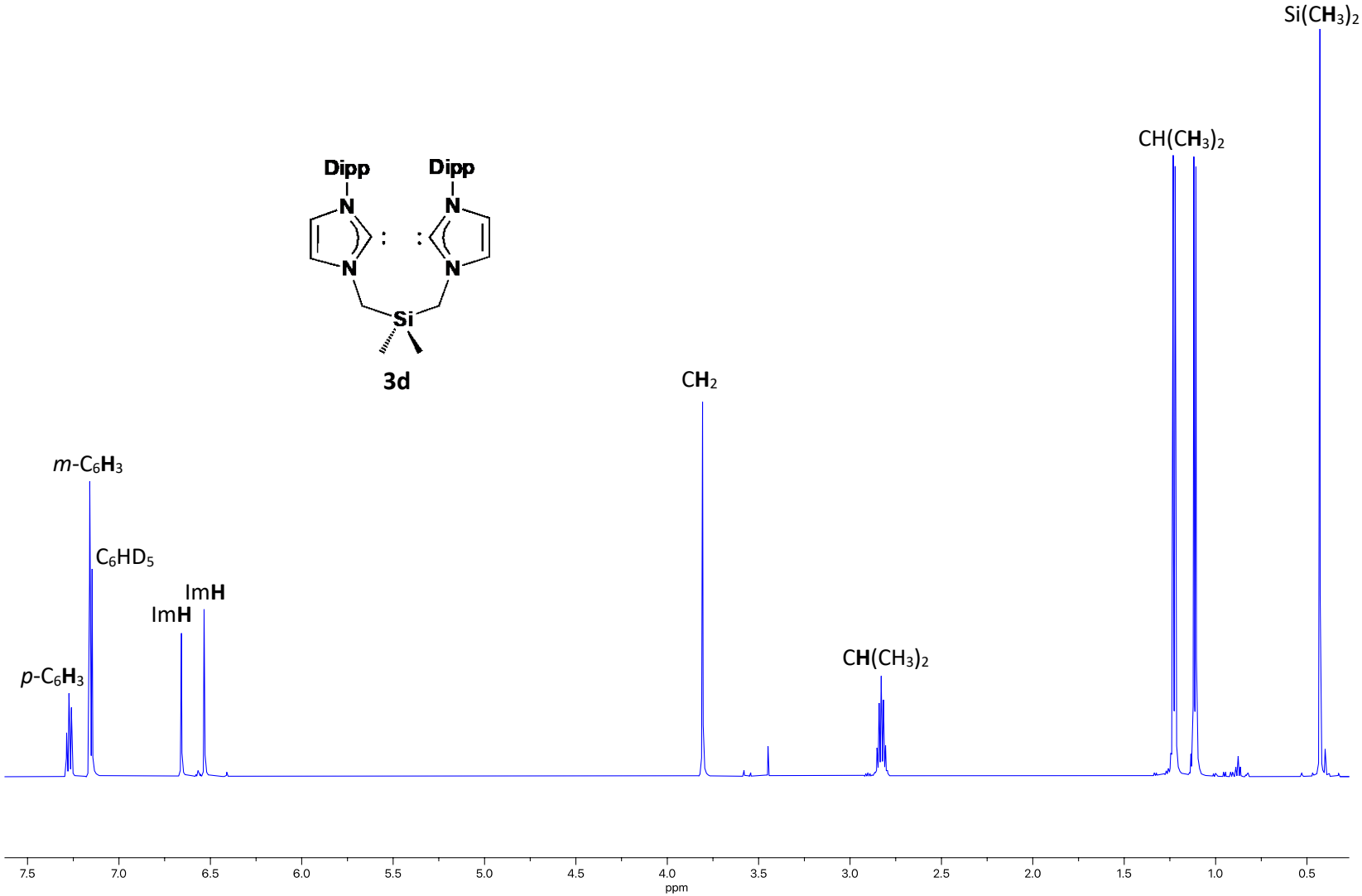


Figure S41. ^{1}H NMR spectrum of **3d** (400MHz, 298K, C_6D_6)

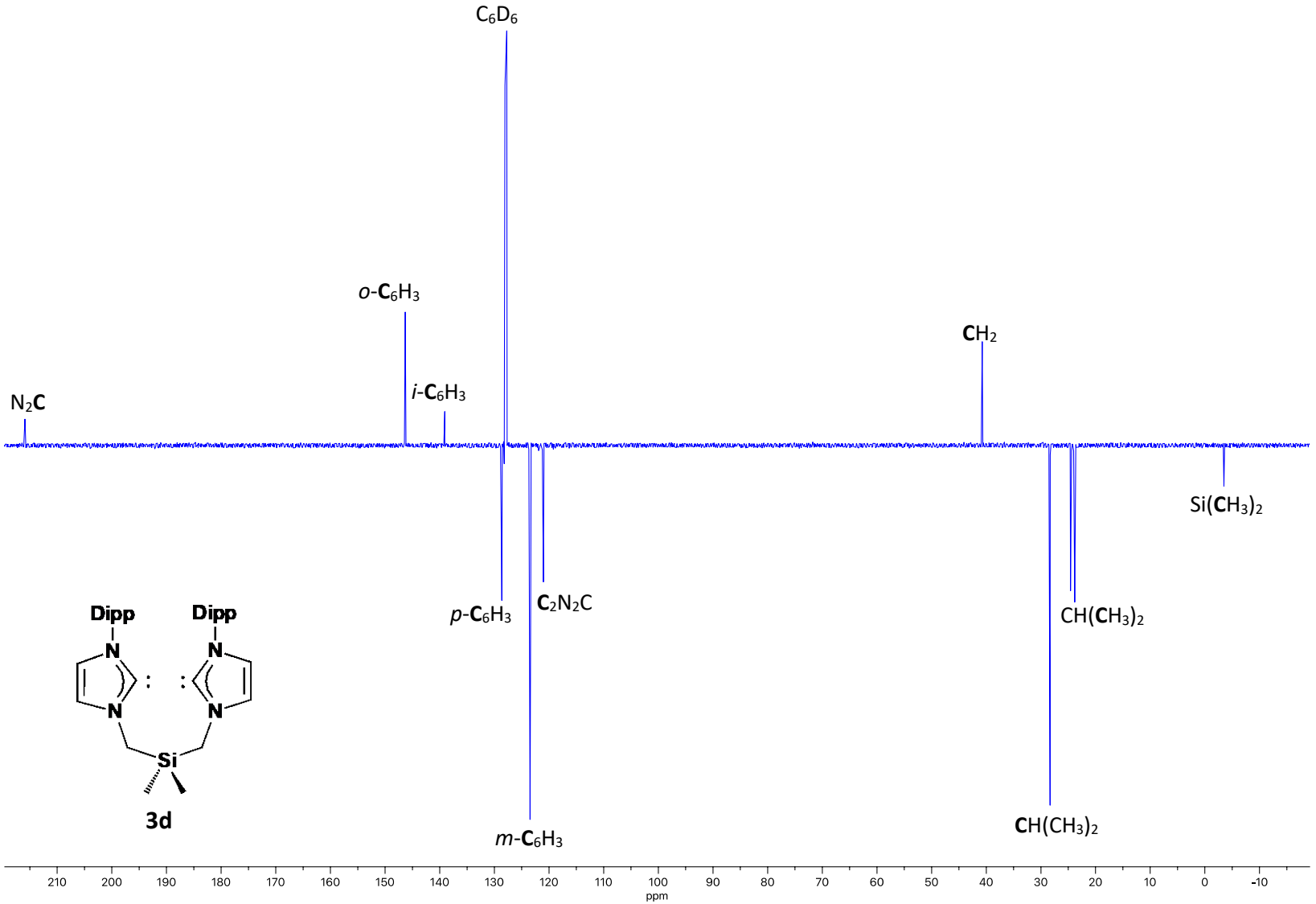


Figure S42. ^{13}C DEPTQ NMR spectrum of **3d** (101MHz, 298K, C_6D_6)

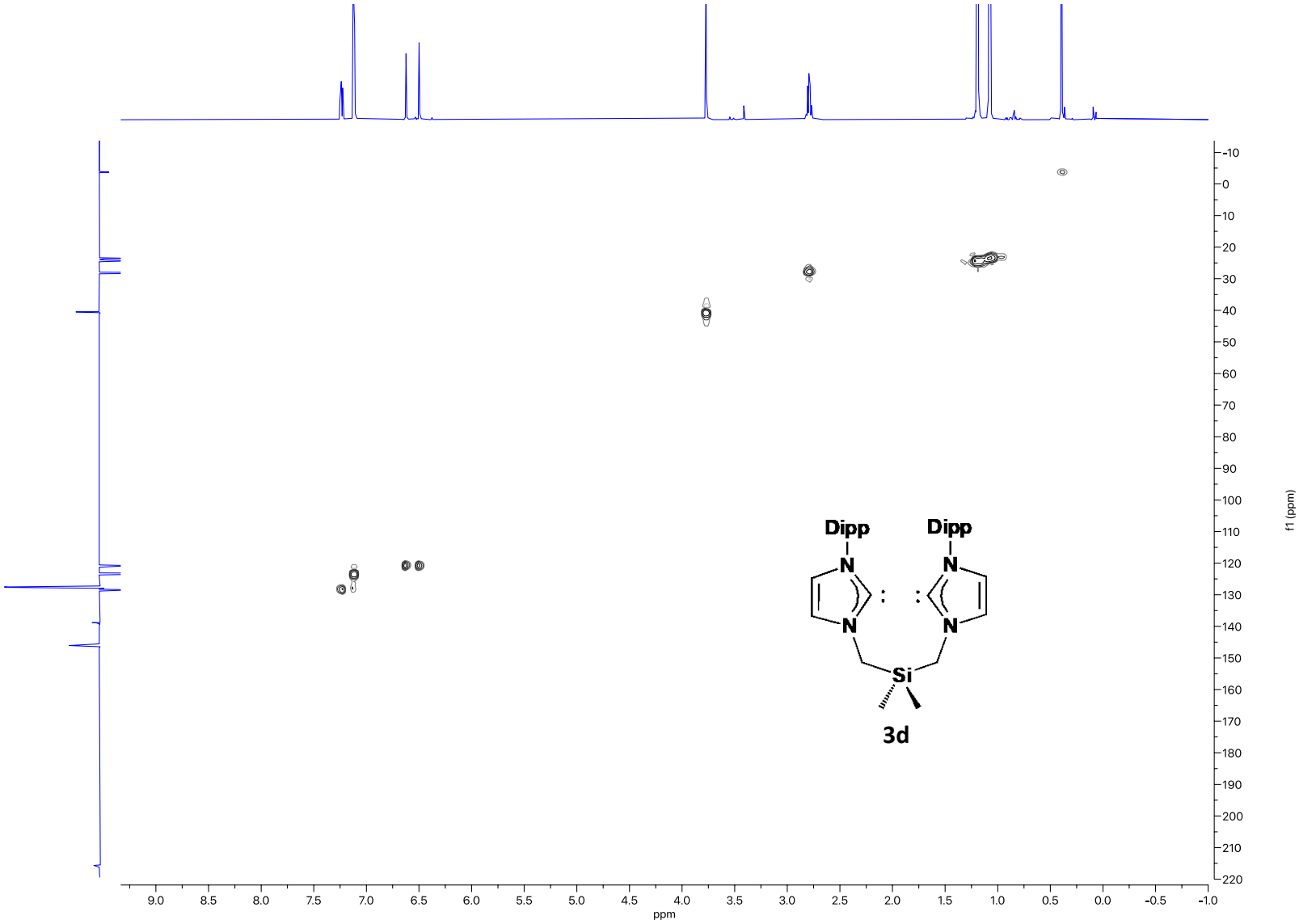


Figure S43. ^{1}H-^{13}C HSQC spectrum of **3d** (400MHz, 298K, C_6D_6)

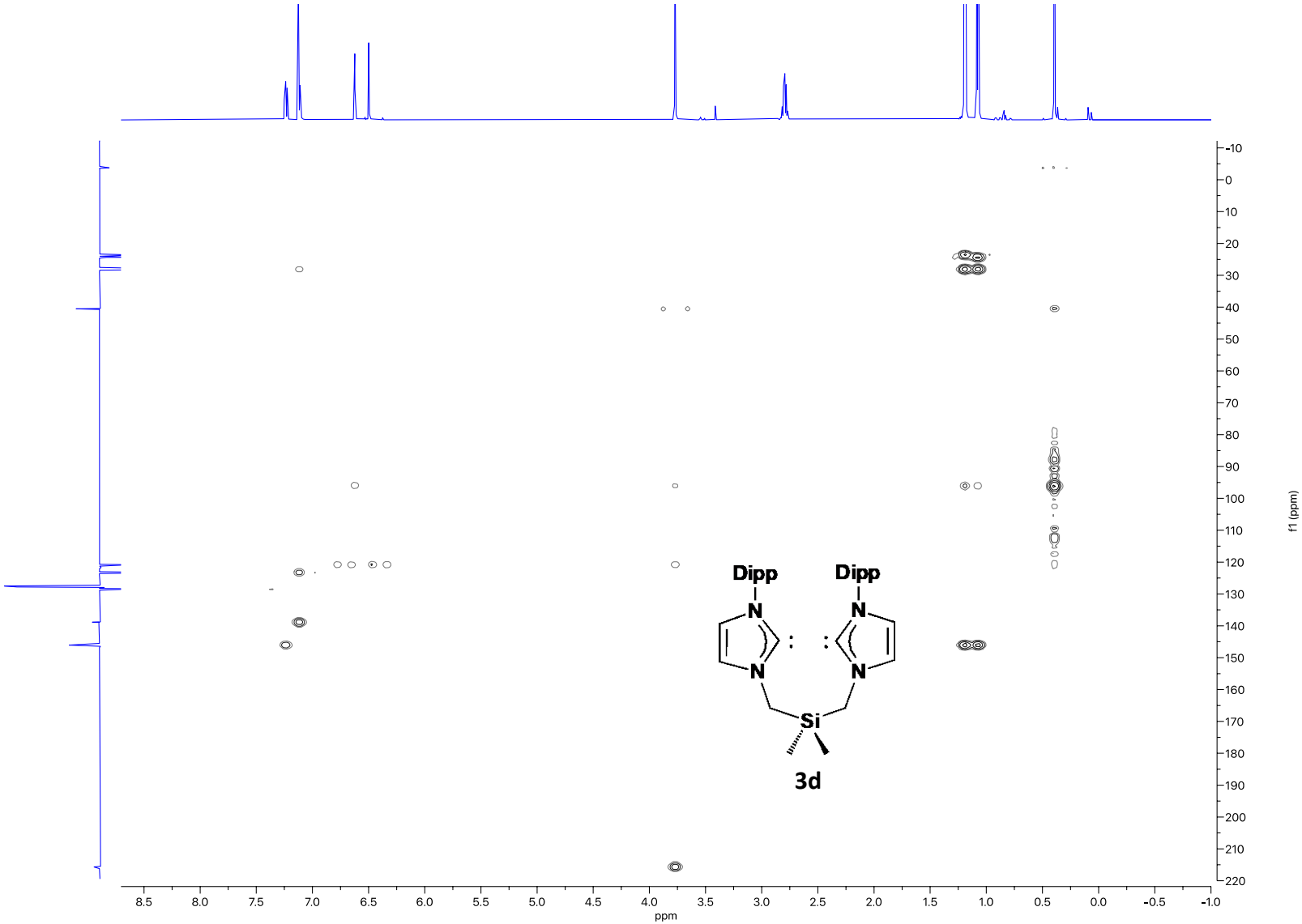


Figure S44. ^{1}H-^{13}C HMBC spectrum of **3d** (400MHz, 298K, C_6D_6)

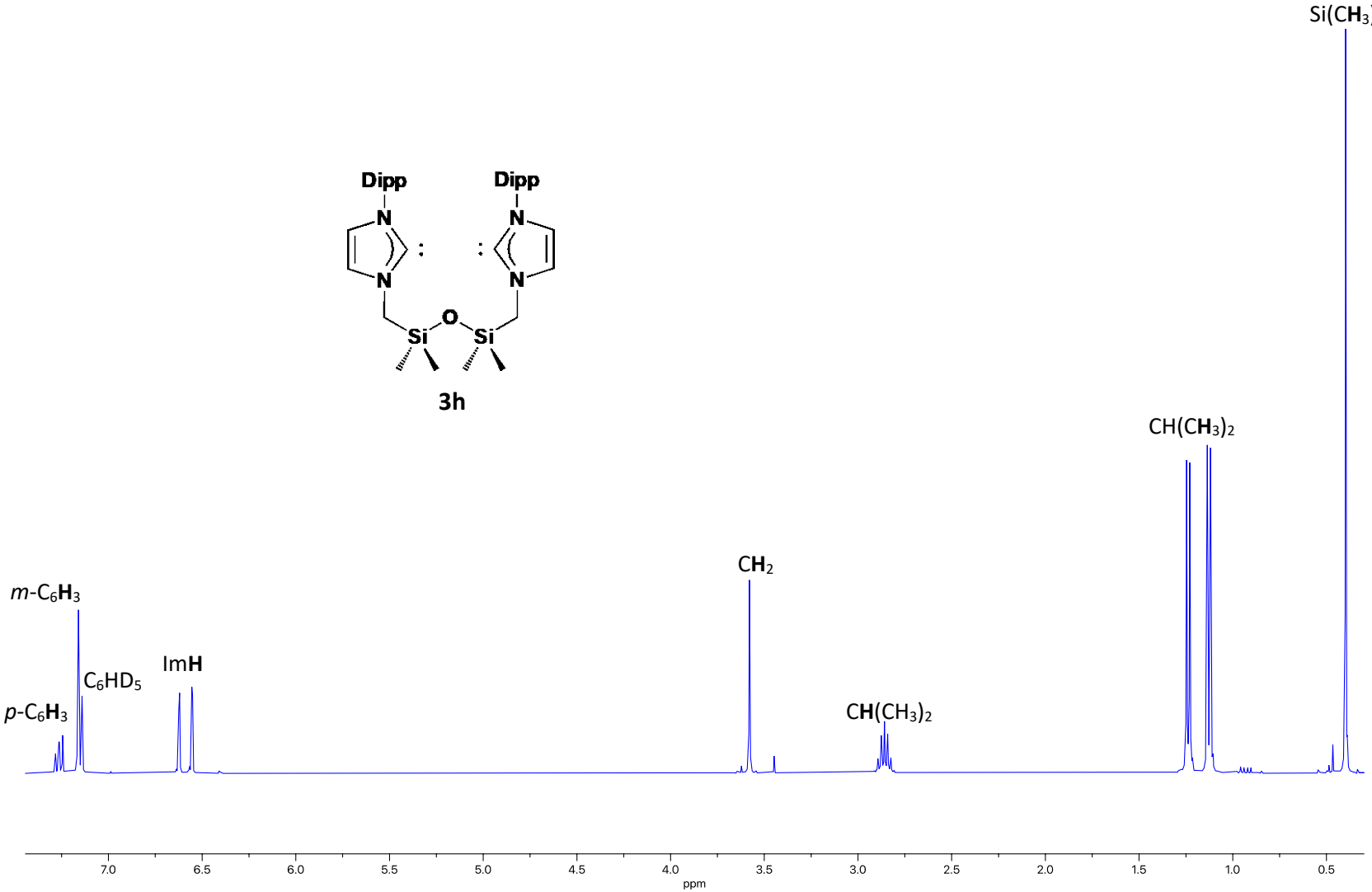


Figure S45. ^{1}H NMR spectrum of **3h** (400MHz, 298K, C_6D_6)

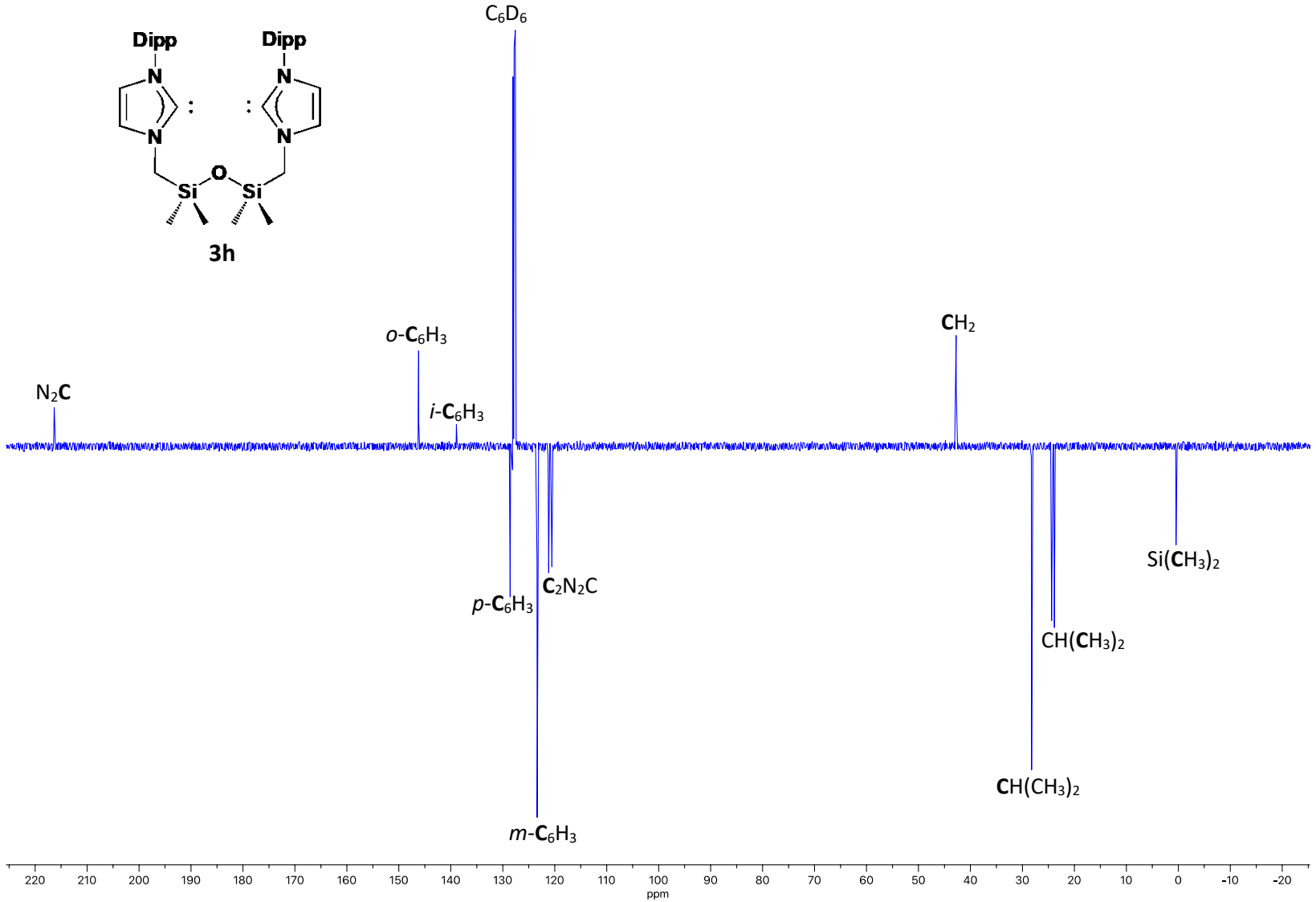


Figure S46. ^{13}C DEPTQ NMR spectrum of **3h** (101MHz, 298K, C_6D_6)

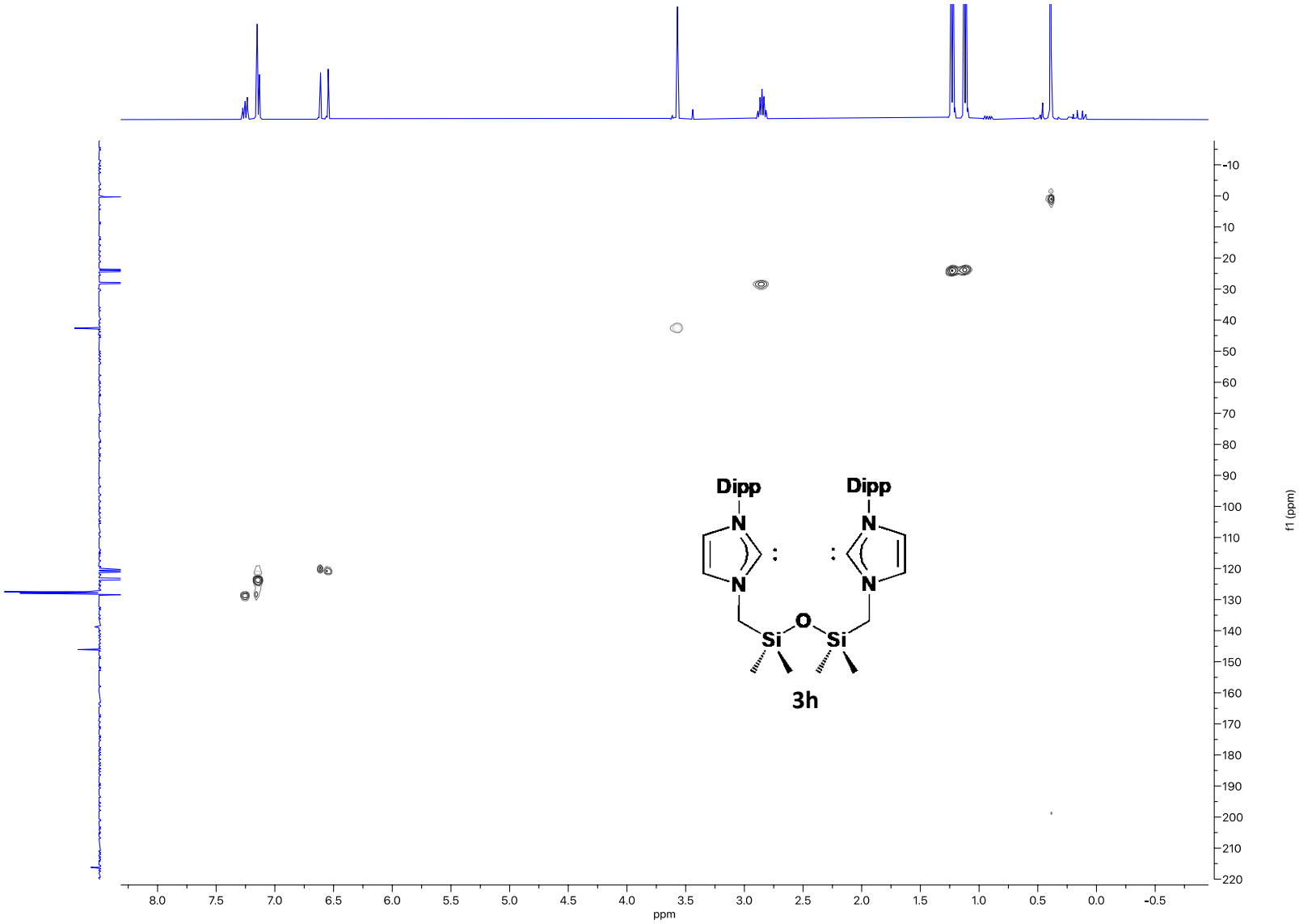


Figure S47. ^{1}H-^{13}C HSQC spectrum of **3h** (400MHz, 298K, C_6D_6)

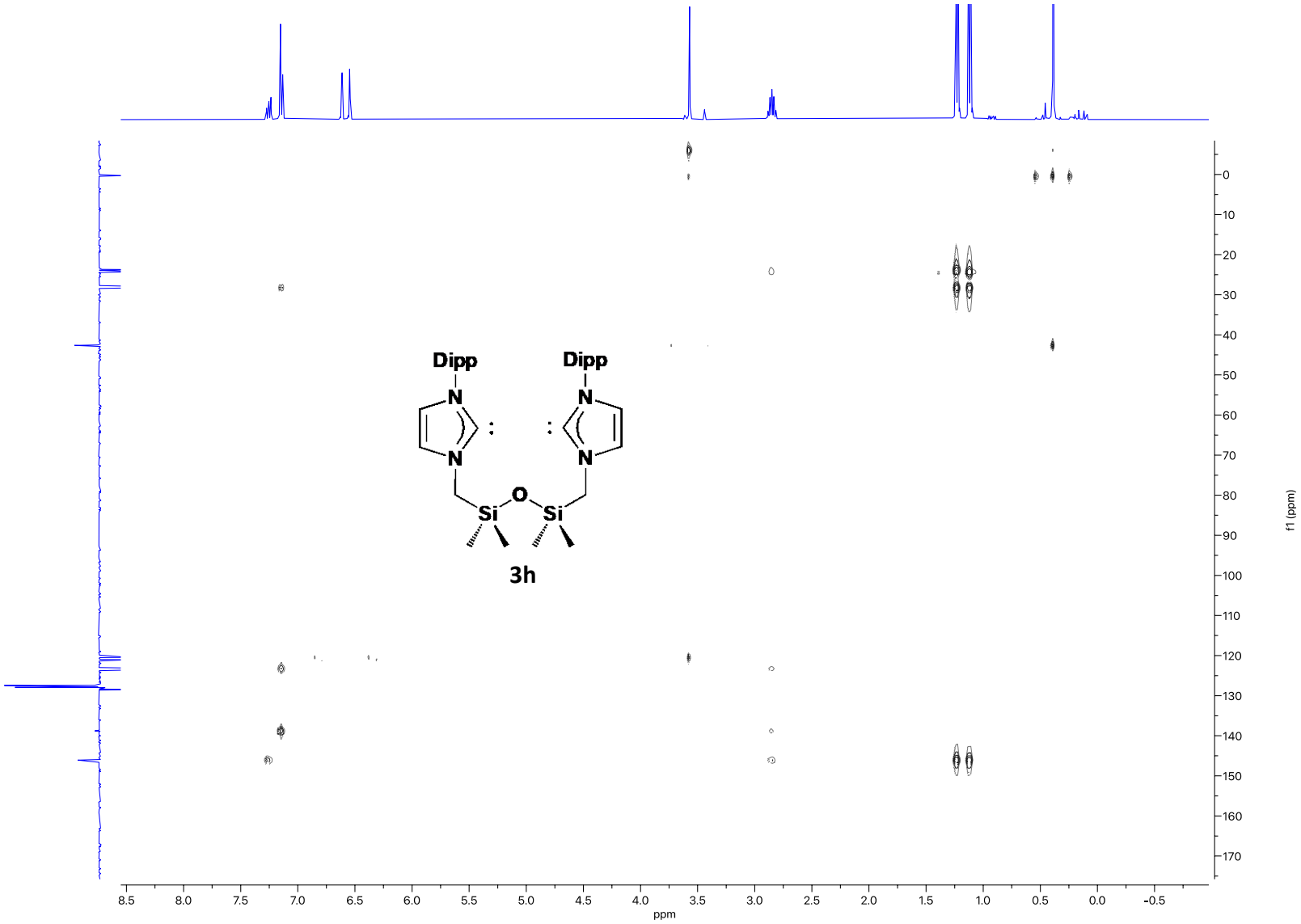


Figure S48. ^{1}H-^{13}C HMBC spectrum of **3h** (400MHz, 298K, C_6D_6)

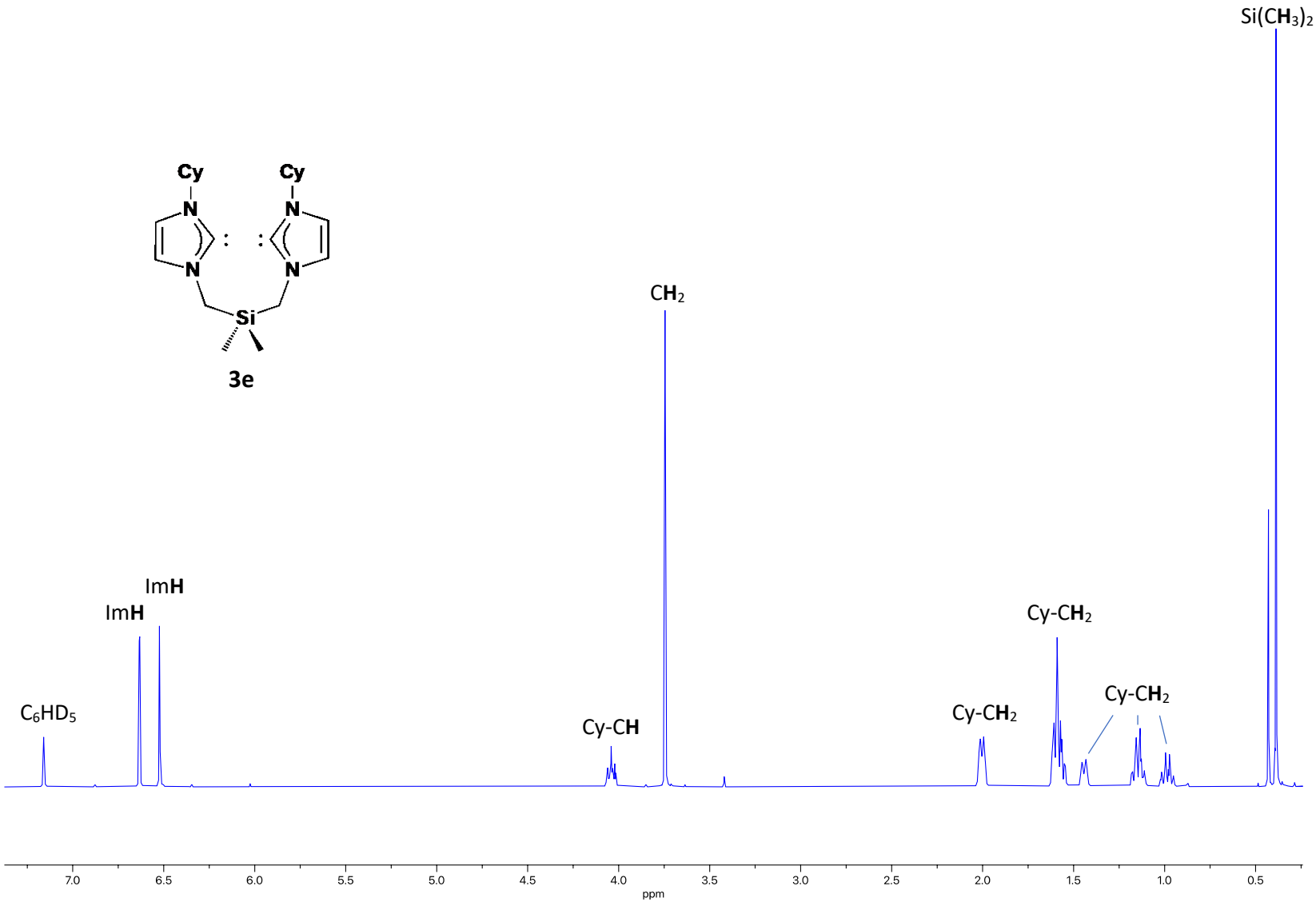


Figure S49. ^{1}H NMR spectrum of **3e** (600MHz, 298K, C_6D_6)

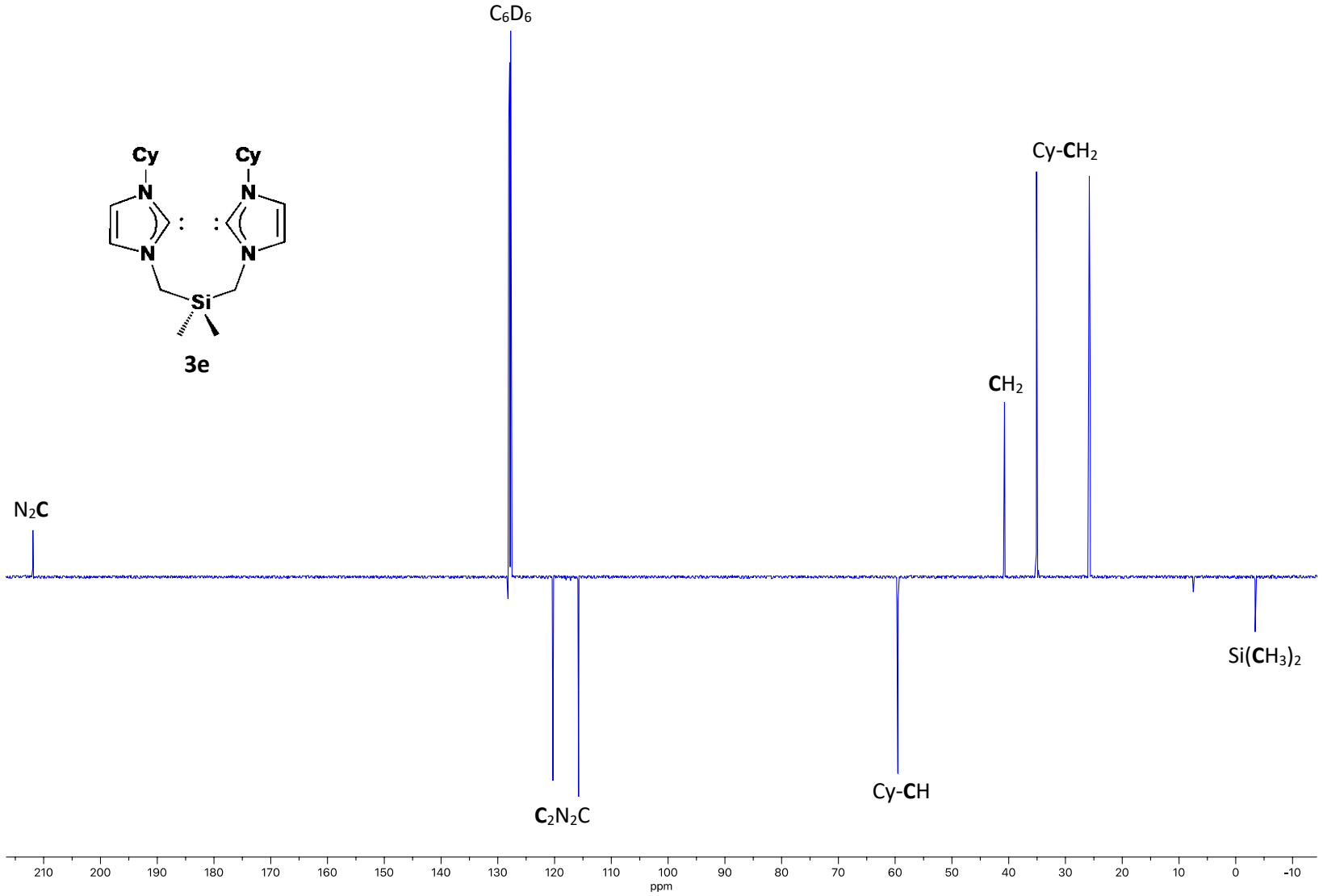


Figure S50. ^{13}C DEPTQ NMR spectrum of **3e** (151MHz, 298K, C_6D_6)

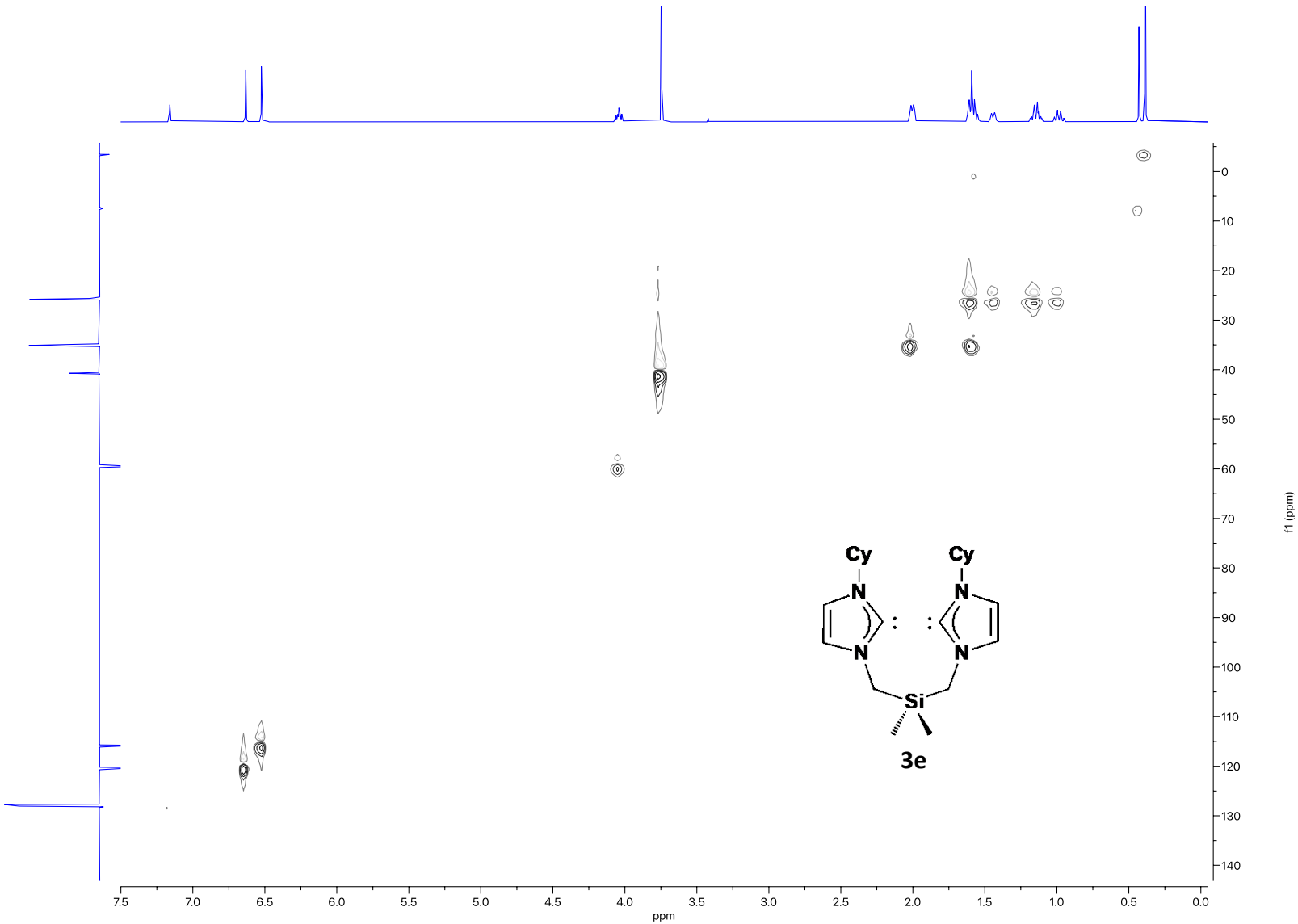


Figure S51. ^{1}H-^{13}C HSQC spectrum of **3e** (600MHz, 298K, C_6D_6)

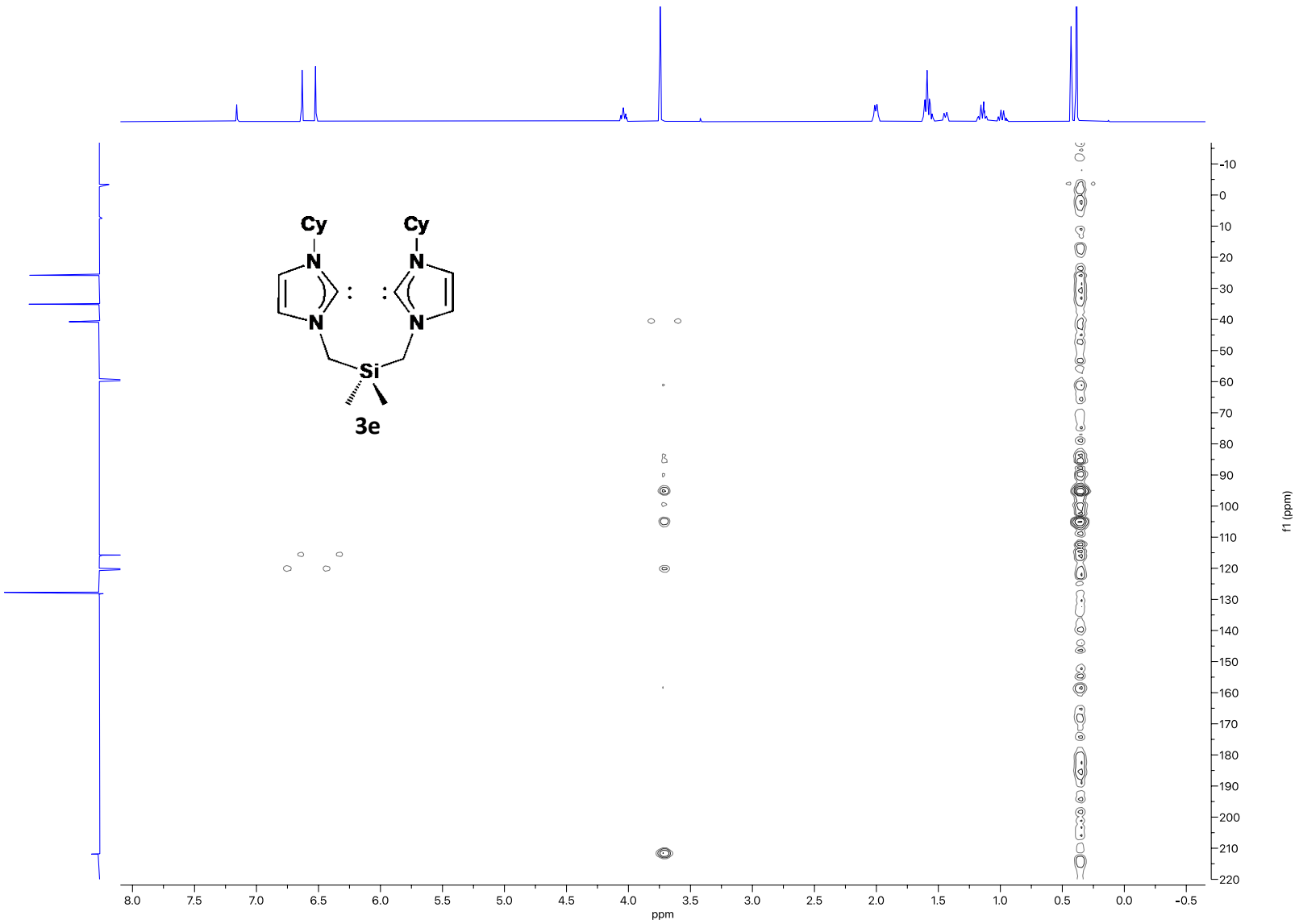


Figure S52. ^{1}H-^{13}C HMBC spectrum of **3e** (600MHz, 298K, C_6D_6)

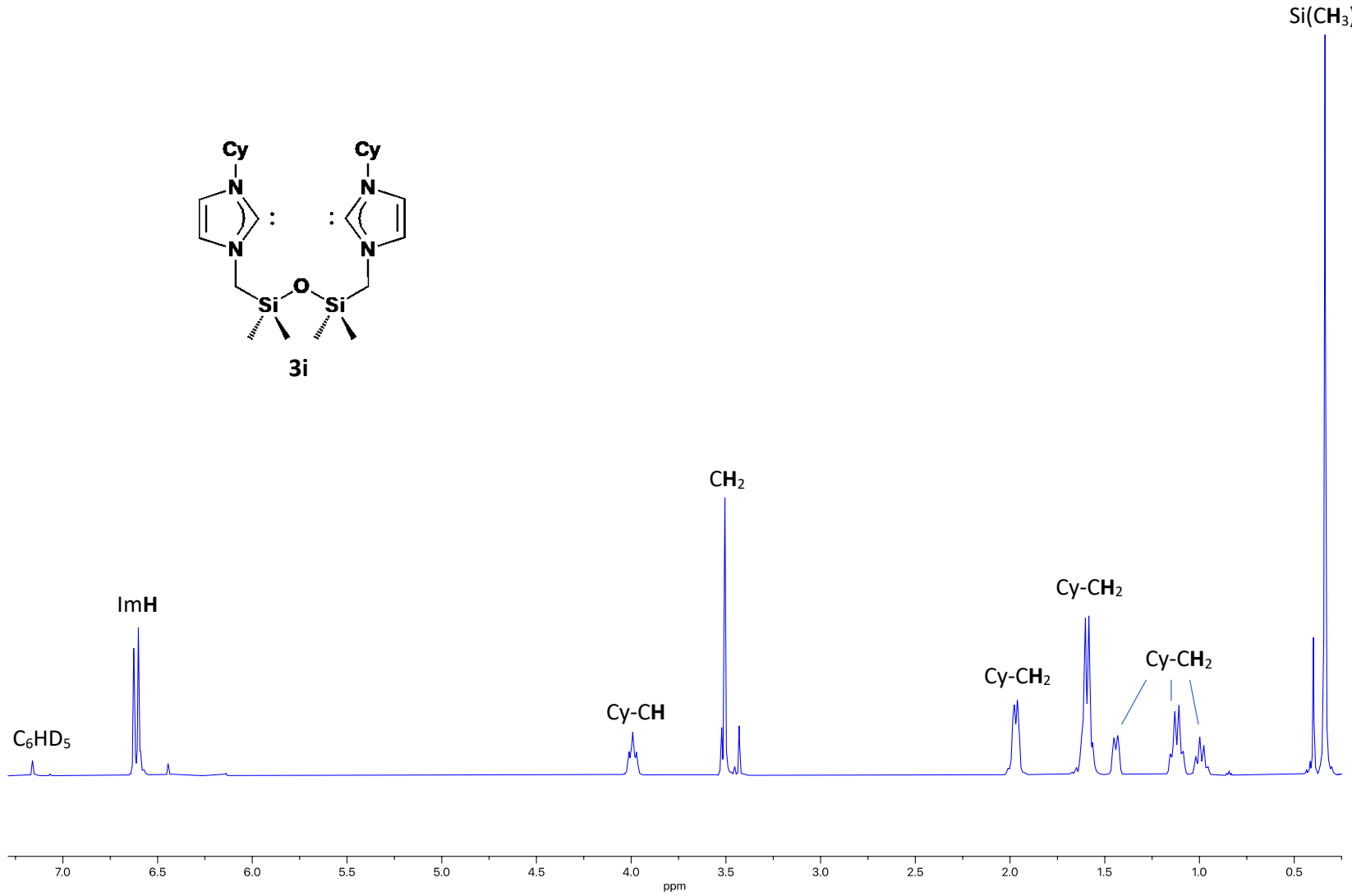


Figure S53. ^{1}H NMR spectrum of **3i** (600MHz, 298K, C_6D_6)

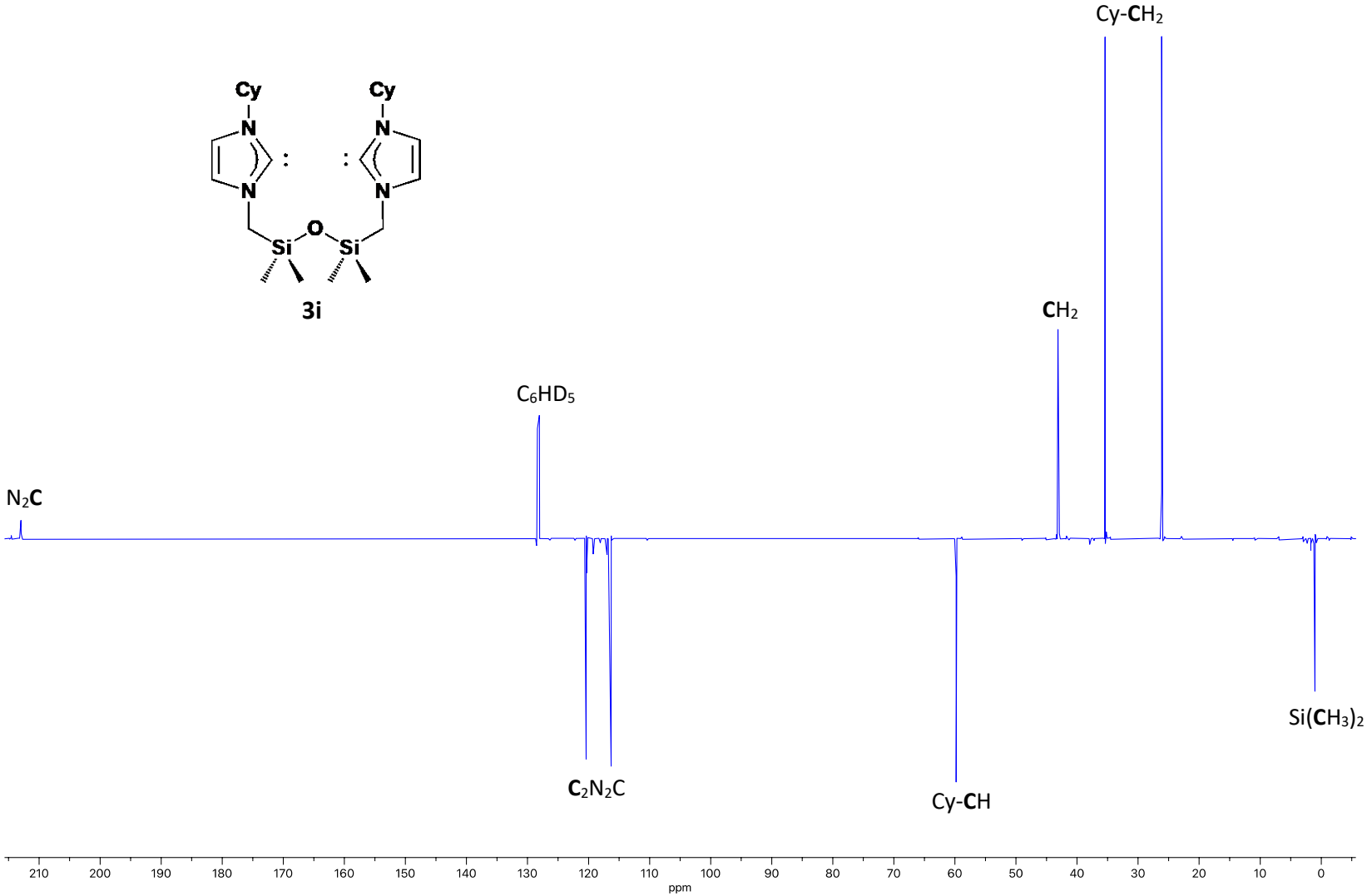


Figure S54. ^{13}C DEPTQ NMR spectrum of **3i** (151MHz, 298K, C_6D_6)

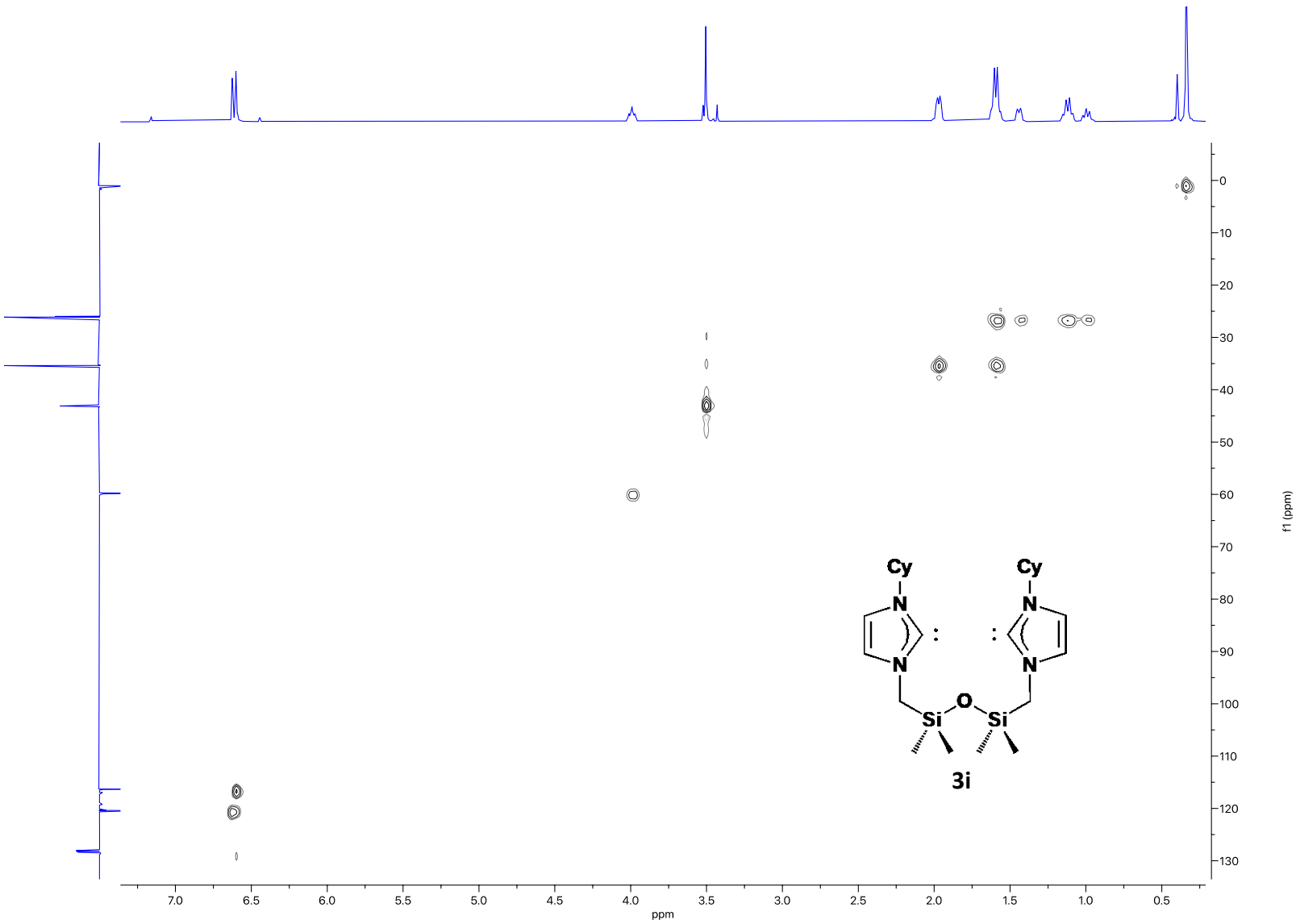


Figure S55. ^{1}H-^{13}C HSQC spectrum of **3i** (600MHz, 298K, C_6D_6)

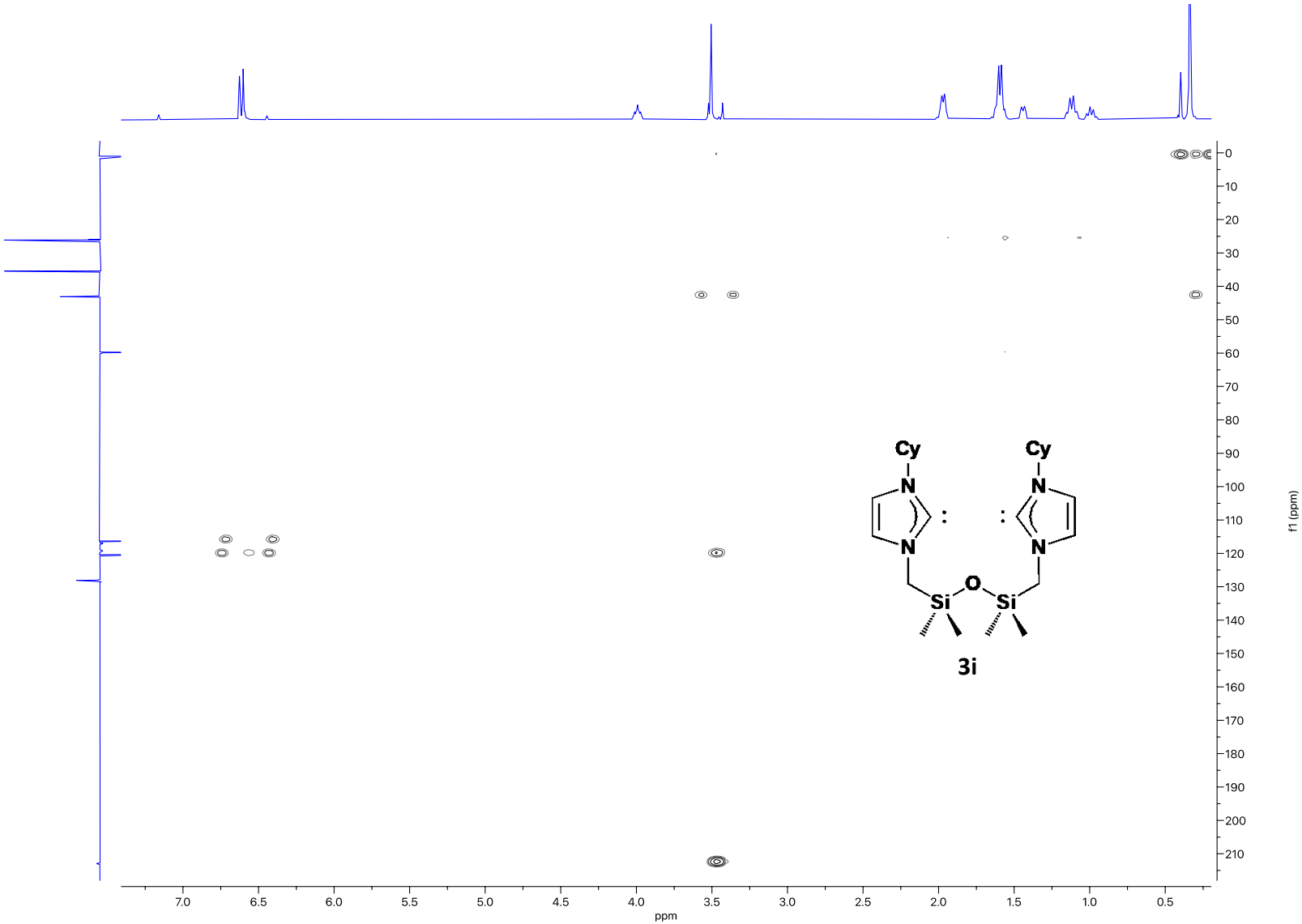


Figure S56. ^{1}H-^{13}C HMBC spectrum of **3i** (600MHz, 298K, C_6D_6)

Table S1. Summary of Crystallographic Data for Compounds **2b**, **2e**, and **2i**.

	2b	**2e**	**2i**
CCDC Deposition #	2279642	2279643	2279641
Formula	$C_{16}H_{30}N_4SiI_2$	$C_{22}H_{38}N_4SiI_2$ +[H_2O]	$C_{24}H_{44}N_4Si_2OI_2$
Formula weight	560.33	658.47	714.61
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/c	C 2/c
a (Å)	9.0436(15)	12.276(2)	17.128(5)
b (Å)	22.182(4)	15.400(3)	21.250(6)
c (Å)	11.772(2)	15.149(2)	12.140(3)
α (º)	90	90	90
β (º)	102.171(3)	100.478(2)	133.535(3)
γ (º)	90	90	90
Volume (Å^3)	2308.4(7)	2816.1(8)	3203.3(15)
Z	4	4	4
Temperature (K)	173	173	173
λ (Å)	0.71073	0.71073	0.71073
ρ(calc) (gcm^{-1})	1.612	1.553	1.482
F(000)	1096.0	1312.0	1432.0
R(int)	0.1335	0.0630	0.0551
μ (mm^{-1})	2.781	2.295	2.060
θ range (º)	3.672 – 55.22	3.374 – 55.068	3.8 – 55.38
Total data	44897	31390	11303
Unique	5344	6470	3669
Completeness (%)	99.6	99.8	98.0
Parameters	214	281	154
R (>2σ)	0.0756	0.0456	0.0358
R_w (all data)	0.1955	0.1429	0.0918
GOF	1.049	1.038	1.022

Deposition Numbers 2279641-2279643 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

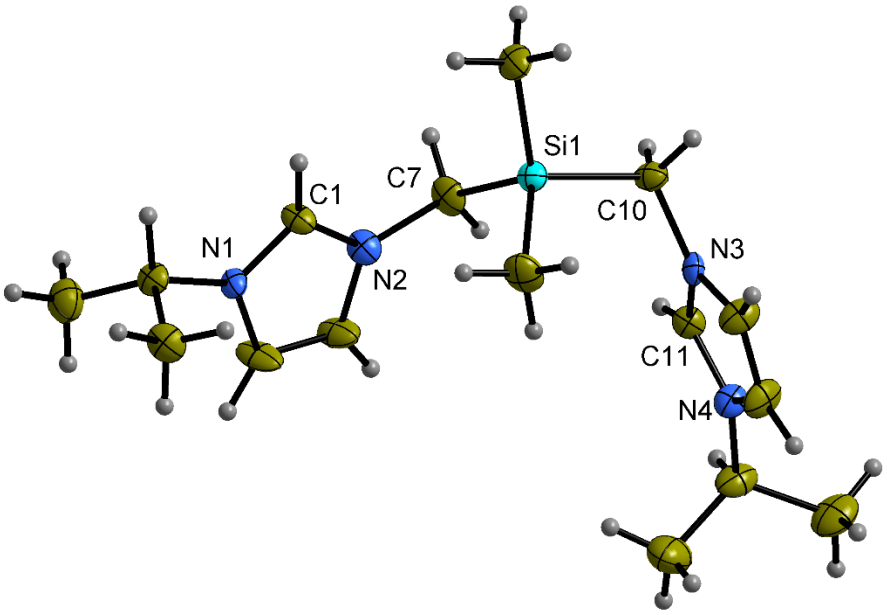


Figure S57. Solid state structure of the dication in **2b** with 50% probability ellipsoids.

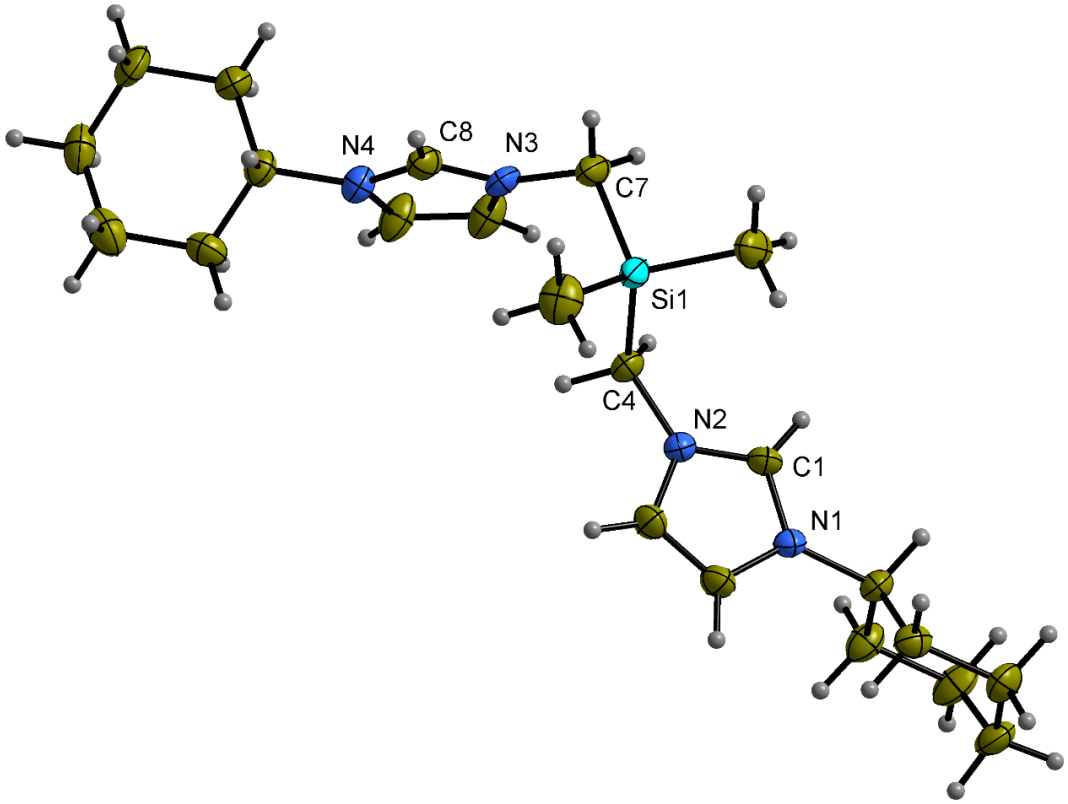


Figure S58. Solid state structure of the dication in **2e** with 50% probability ellipsoids.

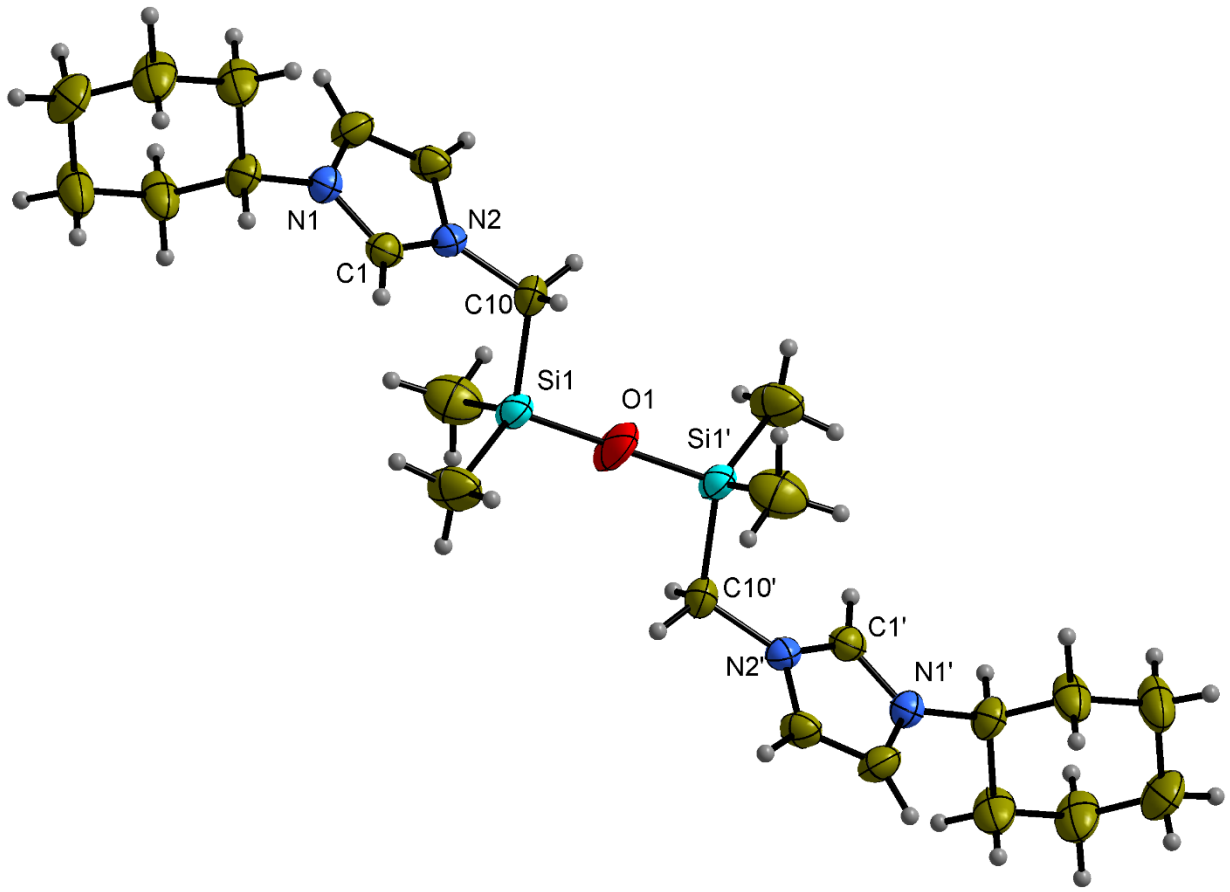


Figure S59. Solid state structure of the dication in **2i** with 50% probability ellipsoids.

References

1 S. Lee, Y. Jeon, Y. Lim, M. A. Hossain, S. Lee, Y. Cho, H. Ju and W. Kim, A new siloxane containing imidazolium iodide as electrolyte for dye-sensitized solar cell, *Electrochim. Acta* 2013, **107**, 675-680.

2 T. Chatterjee, N. T. Kumar and S. K. Das, A planar anthracene-imidazolium/anthracene-benzimidazolium cation system in a spherical polyoxometalate matrix: Synthesis, crystallography and spectroscopy, *Polyhedron*, 2017, **127**, 68-83.

3 S. Sauerbrey, P. K. Majhi, J. Daniels, G. Schnakenburg, G. M. Brändle, K. Scherer and R. Streubel, Synthesis, Structure, and Reactions of 1-tert-Butyl-2-diphenylphosphino-imidazole, *Inorg. Chem*., 2011, **50**, 793-799.

4 R. Martinez, R. Torregrosa, I. M. Pastor and M. Yus, Isoprene as Lithiation Mediator: Synthesis of 2-Substituted 1-Alkylimidazole Derivatives, *Synthesis*, 2012, **44**, 2630-2638.

5 B. Vivet, F. Cavelier and J. Martinez, Synthesis of Silaproline, a New Proline Surrogate, *Eur. J. Org. Chem*., 2000, 807-811.

6 S. Benson, B. Payne and R. M. Waymouth, Synthesis and reactivity of allyl nickel(II) N-heterocyclic carbene enolate complexes, *J. Polym. Sci. A Polym. Chem*., 2007, **45**, 3637-3647.

7 V. Vass, M. Dehmel, F. Lehni and R. Kretschmer, A Facile One-Pot Synthesis of 1,2,3-Tri- and 1,1,2,3-Tetrasubstituted Bis(guanidine)s from Bis(thiourea)s, *Eur. J. Org. Chem*., 2017, 5066-5073.