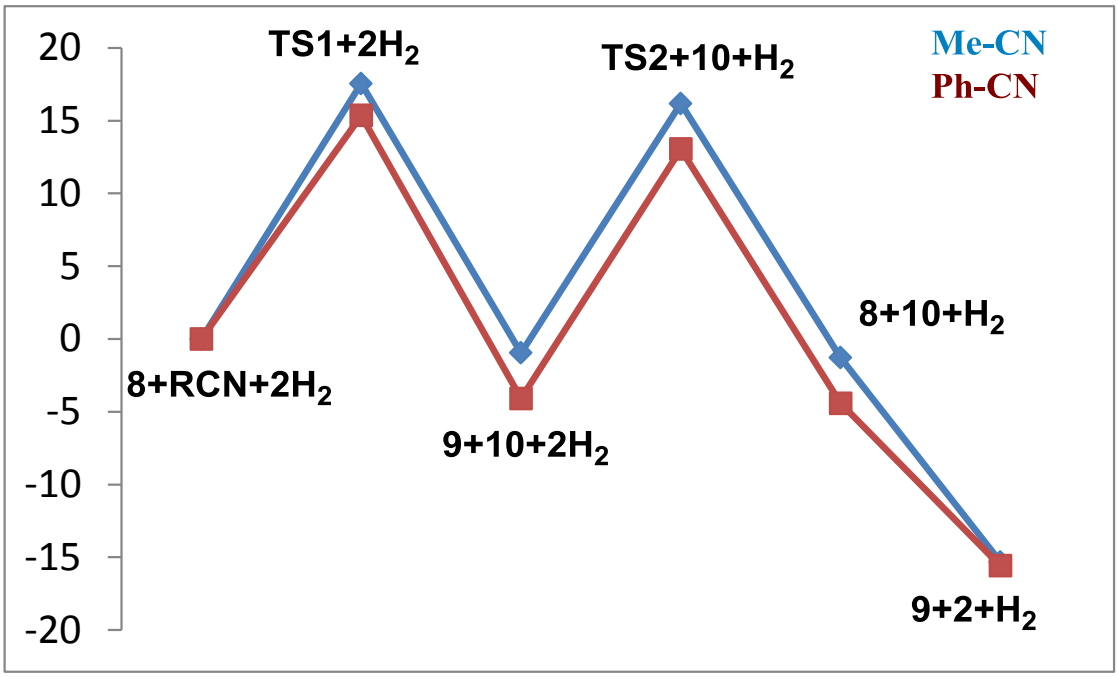
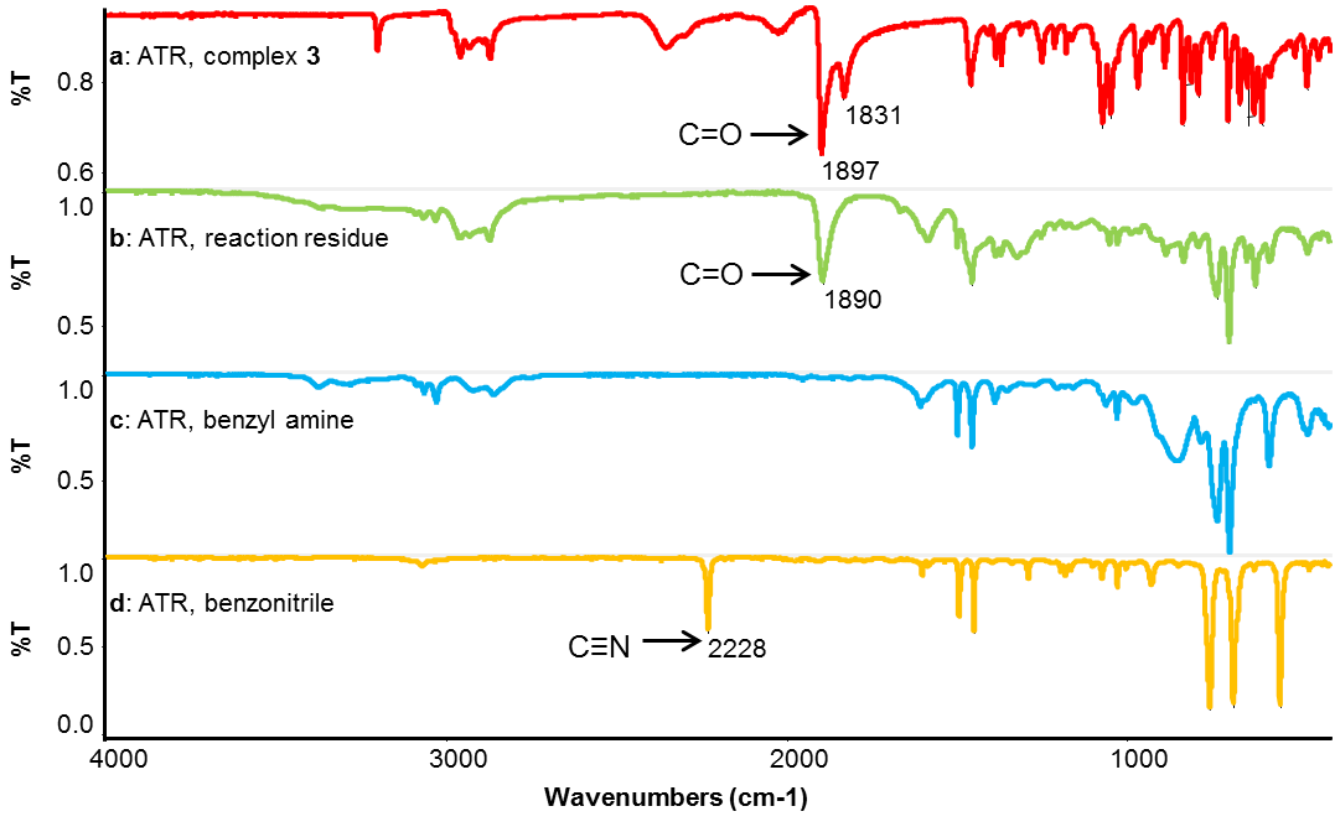
1. Supplementary Figures

1.1 Reaction profile



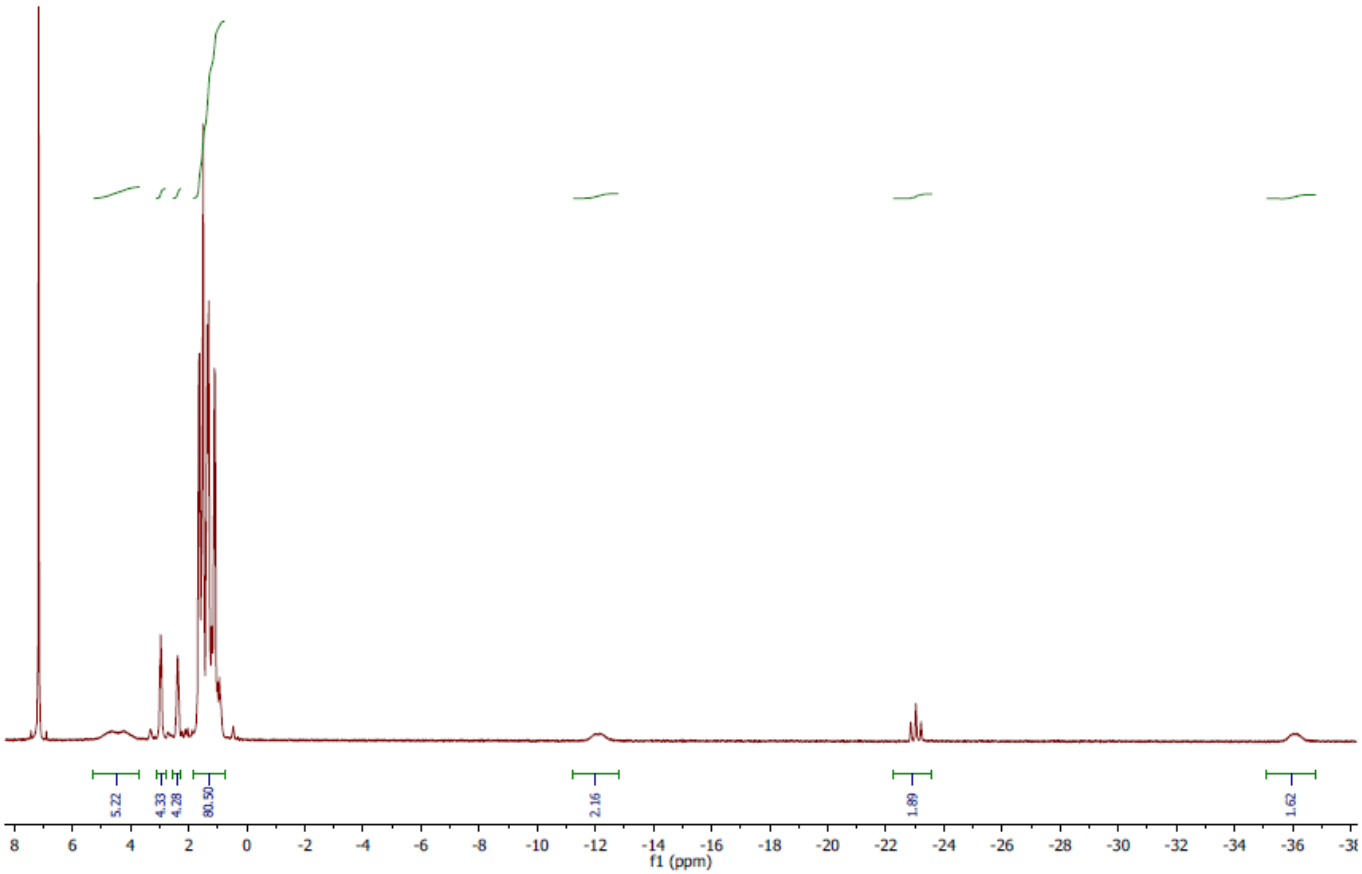
Supplementary Figure 1. Reaction profile for nitrile hydrogenation (kcal/mol).

1.2 IR spectra

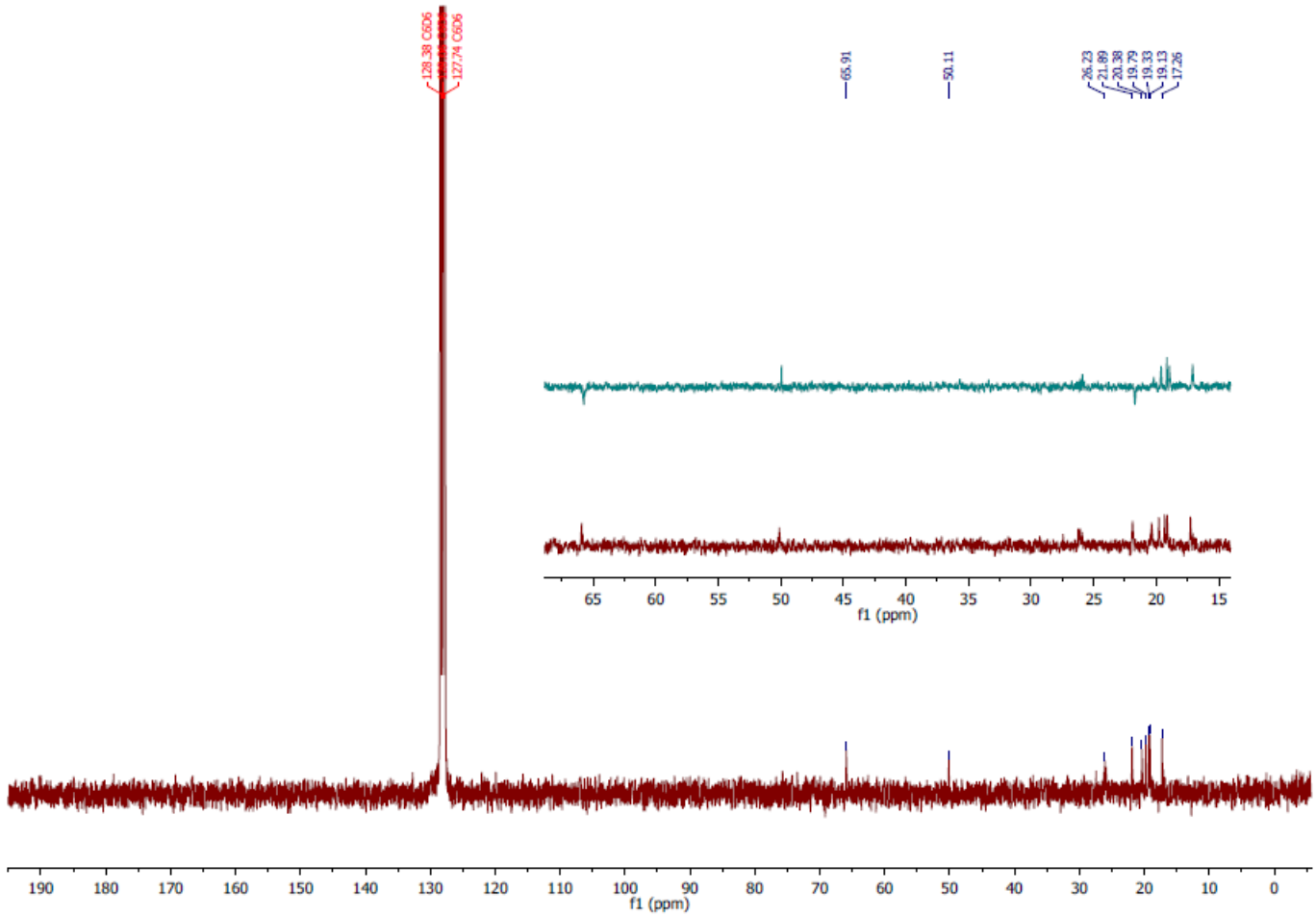


Supplementary Figure 2. ATR-FTIR measurement: a) complex **3**, without solvent; b) reaction residue; c) benzyl amine, pure; d) benzonitrile, pure.

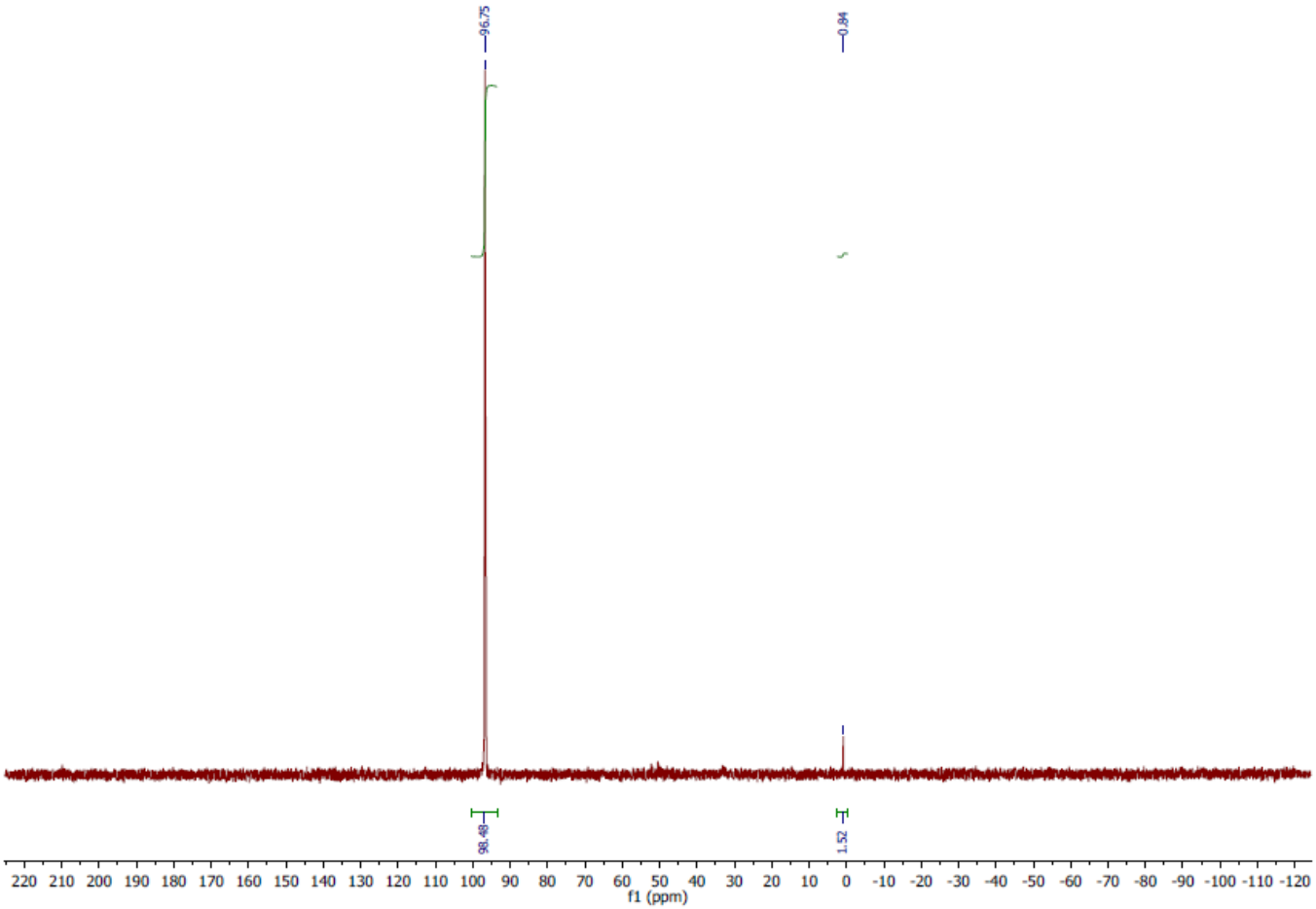
1.3 NMR spectra of Me-3 and intermediates



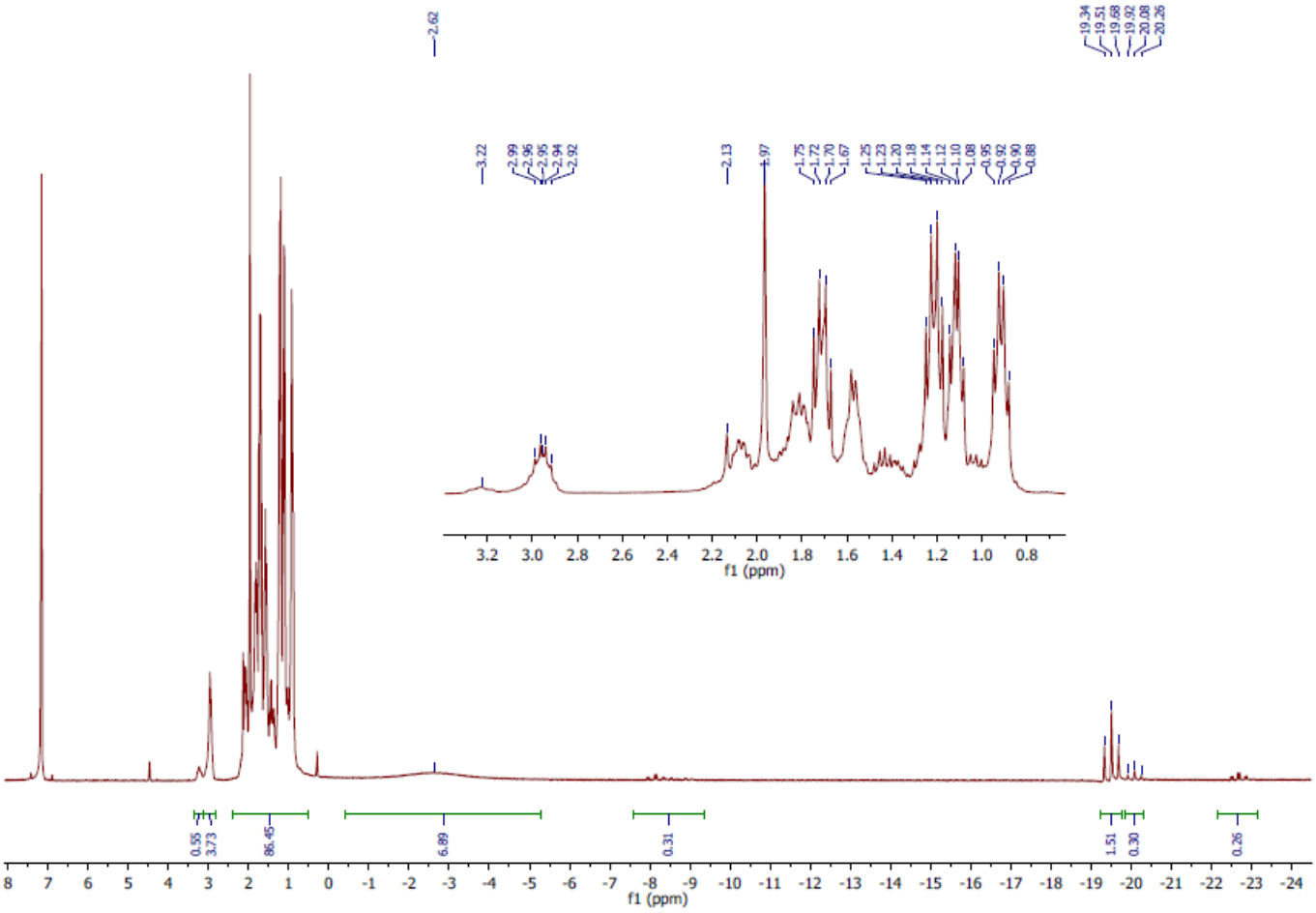
Supplementary Figure 3a. ^{1}H NMR (300.1 MHz) spectrum of {Fe(H)(HBH_3)[(CH_3)N((CH_2CH_2)P($CH(CH_3)_2$)$_2$)$_2$]} (**Me-3**, without CO), C_6D_6.



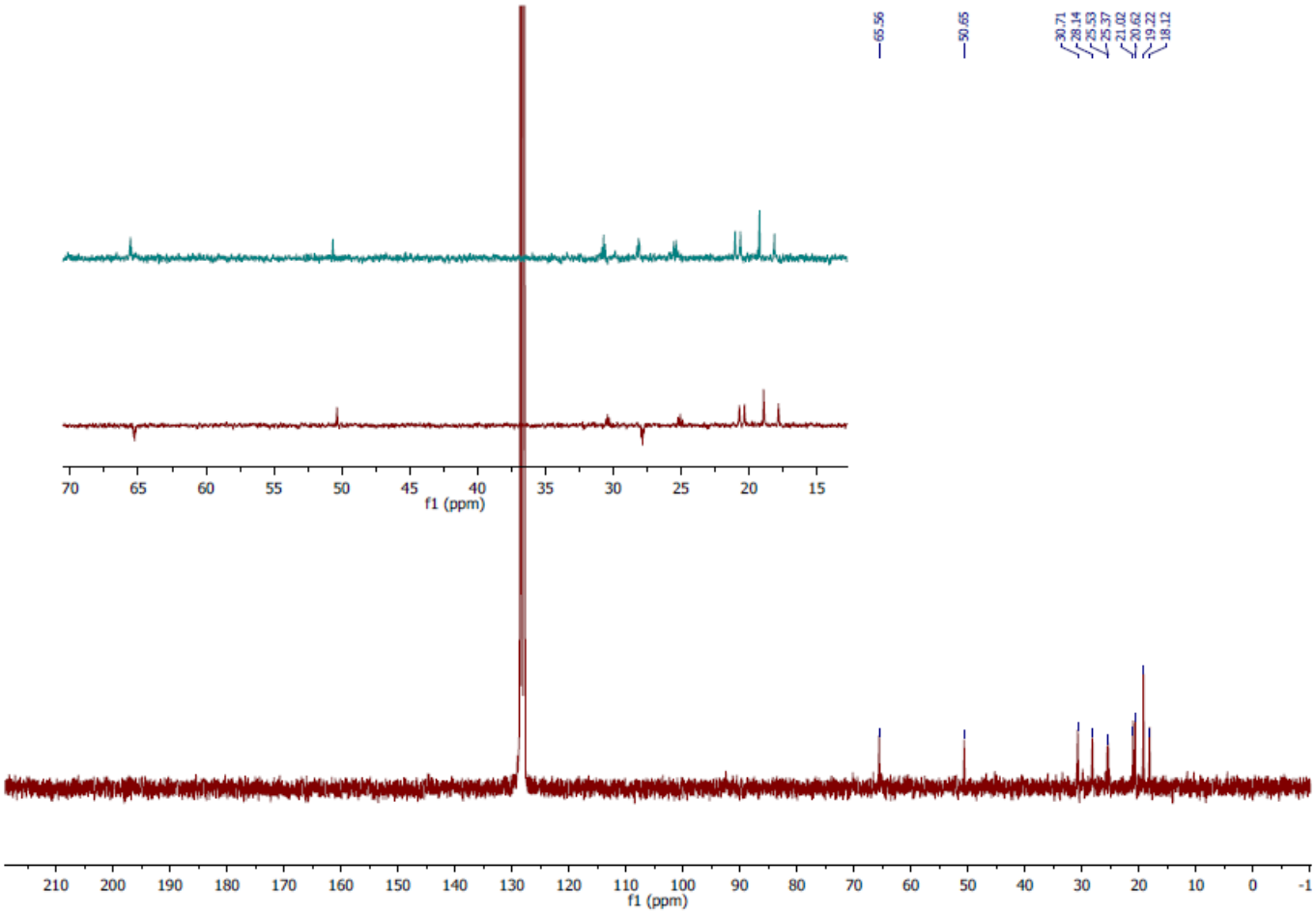
Supplementary Figure 3b. ^{13}C (DEPT) NMR (75.5 MHz) spectra of {Fe(H)(HBH_3)[$(CH_3)N((CH_2CH_2)P(CH(CH_3)_2)_2)_2$]} (**Me-3** without CO), C_6D_6.



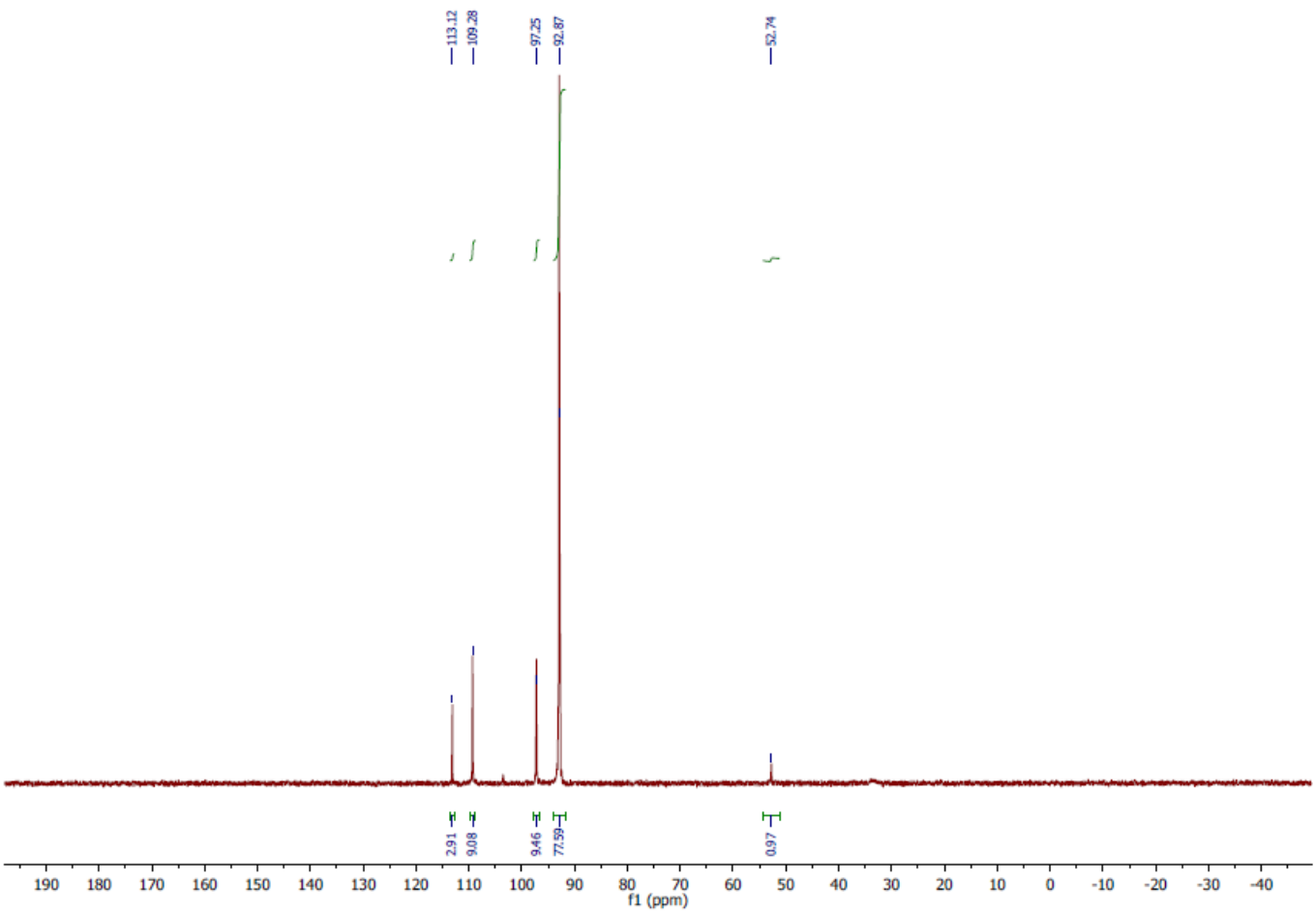
Supplementary Figure 3c. $^{31}P\{^{1}H\}$ NMR (121.0 MHz) spectrum of $[(CH_3)N((CH_2CH_2)P(CH(CH_3)_2)_2)_2]\}$ (**Me-3**, without CO), C_6D_6. The minor peak is due to free ligand $[(CH_3)N((CH_2CH_2)P(CH(CH_3)_2)_2)_2]$.



Supplementary Figure 3d. ^{1}H NMR (300 .1MHz) spectrum of {Fe(H)(HBH_3)(CO)[(CH_3)N((CH_2CH_2)P($CH(CH_3)_2$)$_2$)$_2$]} (**Me-3**), C_6D_6.

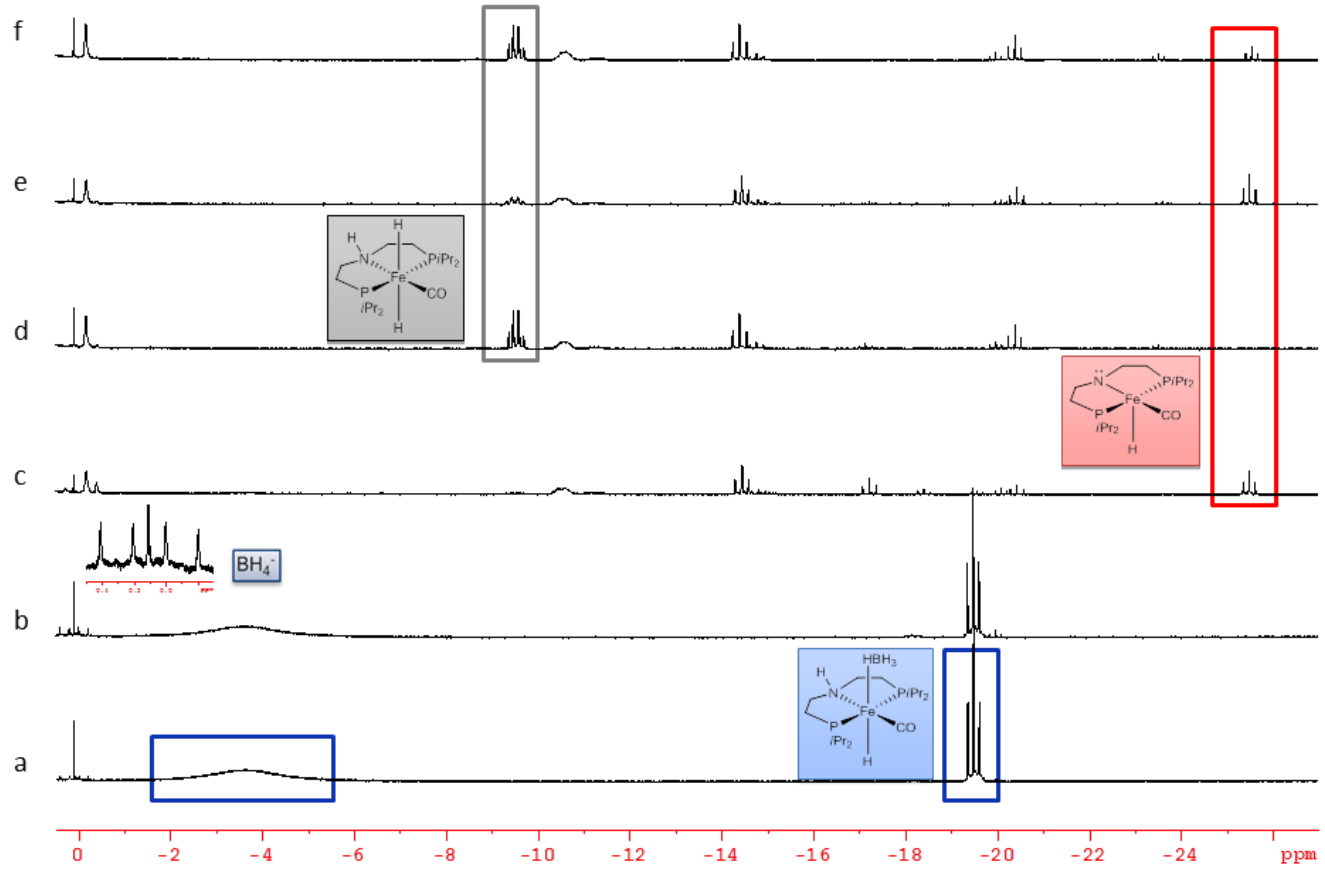


Supplementary Figure 3e. ^{13}C (DEPT) NMR (75.5 MHz) spectra of {Fe(H)(HBH_3)(CO)[$(CH_3)N((CH_2CH_2)P(CH(CH_3)_2)_2)_2$]} (**Me-3**), C_6D_6.

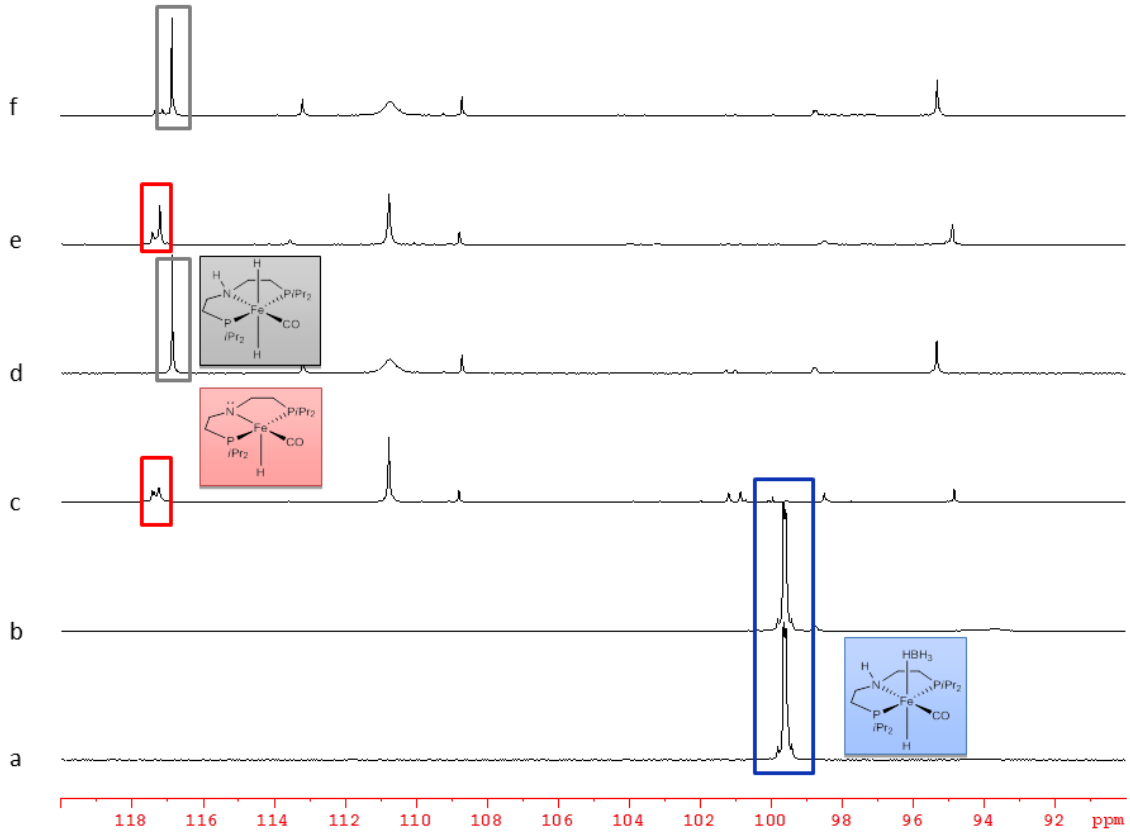


Supplementary Figure 3f. $^{31}P\{^{1}H\}$ NMR (121.0 MHz) spectrum of {Fe(H)(HBH_3)(CO)[(CH_3)N((CH_2CH_2)P($CH(CH_3)_2$)$_2$)$_2$]} (**Me-3**), C_6D_6. Peak at 52.7 ppm is due to oxidised free ligand.

1.4 Detection of species 8 and 9 under catalytic-like conditions



Supplementary Figure 4. ^{1}H NMR (400.1 MHz) spectra (THF-d_8, hydride region) of a solution of **3** and 1.5 eq. PhCN. **Conditions:** Under an argon atmosphere, complex **3** (20 mg, 0.049 mmol) was dissolved in 1 mL THF-d_8 and PhCN (7.6 mg, 0.074 mmol) was added. The resulting yellow orange solution was transferred by means of a gas-tight syringe to a J-Young NMR tube and ^{1}H and ^{31}P NMR spectra were recorded (Supplementary Figures 4 and 5). The relative experimental conditions are reported in the caption of Supplementary Figure 5: only spectra referring to new experimental conditions or showing changes as compared to the one recorded previously are shown.



Supplementary Figure 5. $^{31}P\{^{1}H\}$ NMR (161.9 MHz) spectra (THF-d_8) of a solution of **3** and 1.5 eq. PhCN: residual coupling to hydrides is present for some species.

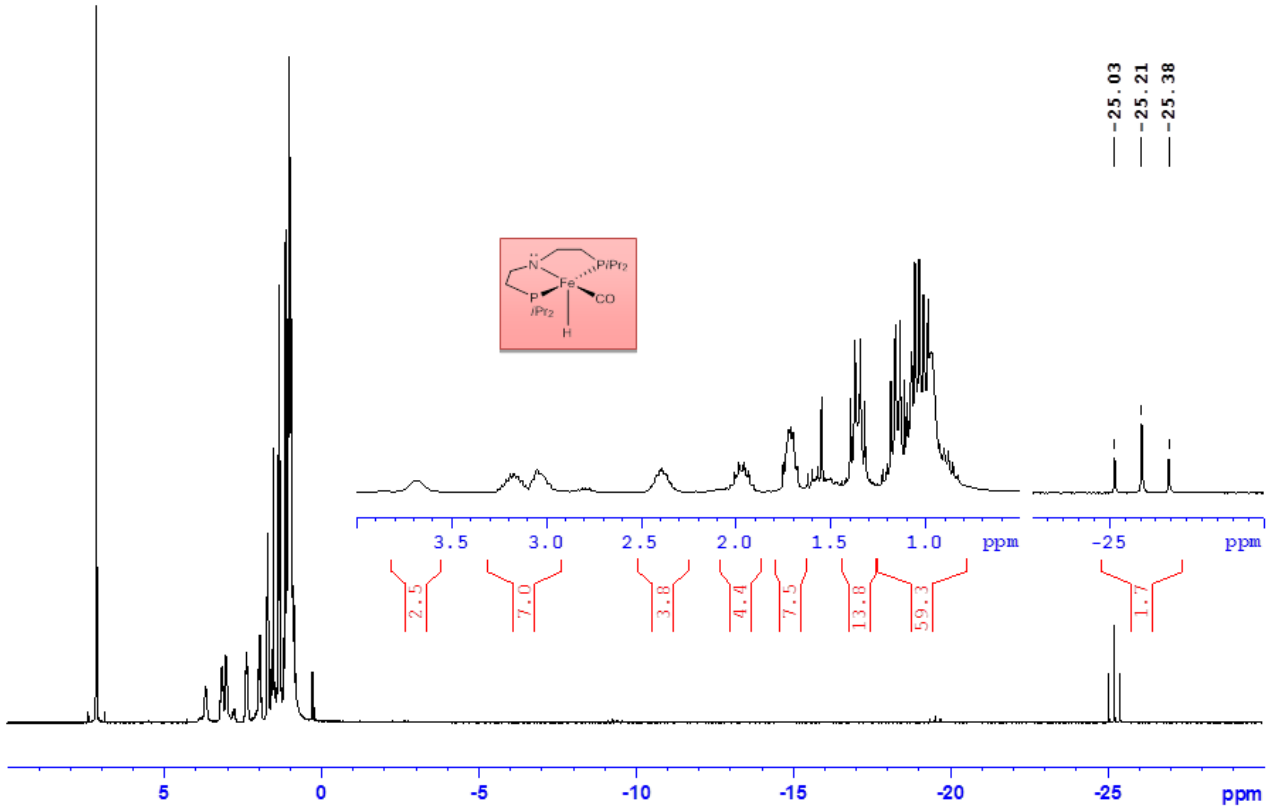
spectra **a**: **room temperature**, reference spectrum, recorded immediately after sample preparation under **argon**; the sample is then heated to 60° C.

spectra **b**: recorded after keeping the sample at **60 °C** for **15 min** under **argon**: the catalyst precursor **3** is no longer present and new hydrides species appear. One has been confidently identified as the amido complex **9** (*vide infra*). No further spectral changes take place after keeping the sample at 60° C for 90 minutes overall. The sample is cooled to room T. The solution color is deep red. Argon is removed after freezing the sample and replaced by hydrogen (1 bar). The sample is intensively shaken to allow for hydrogen diffusion into the solution, which then turns light orange. It is then placed back into the instrument probe for further measurements.

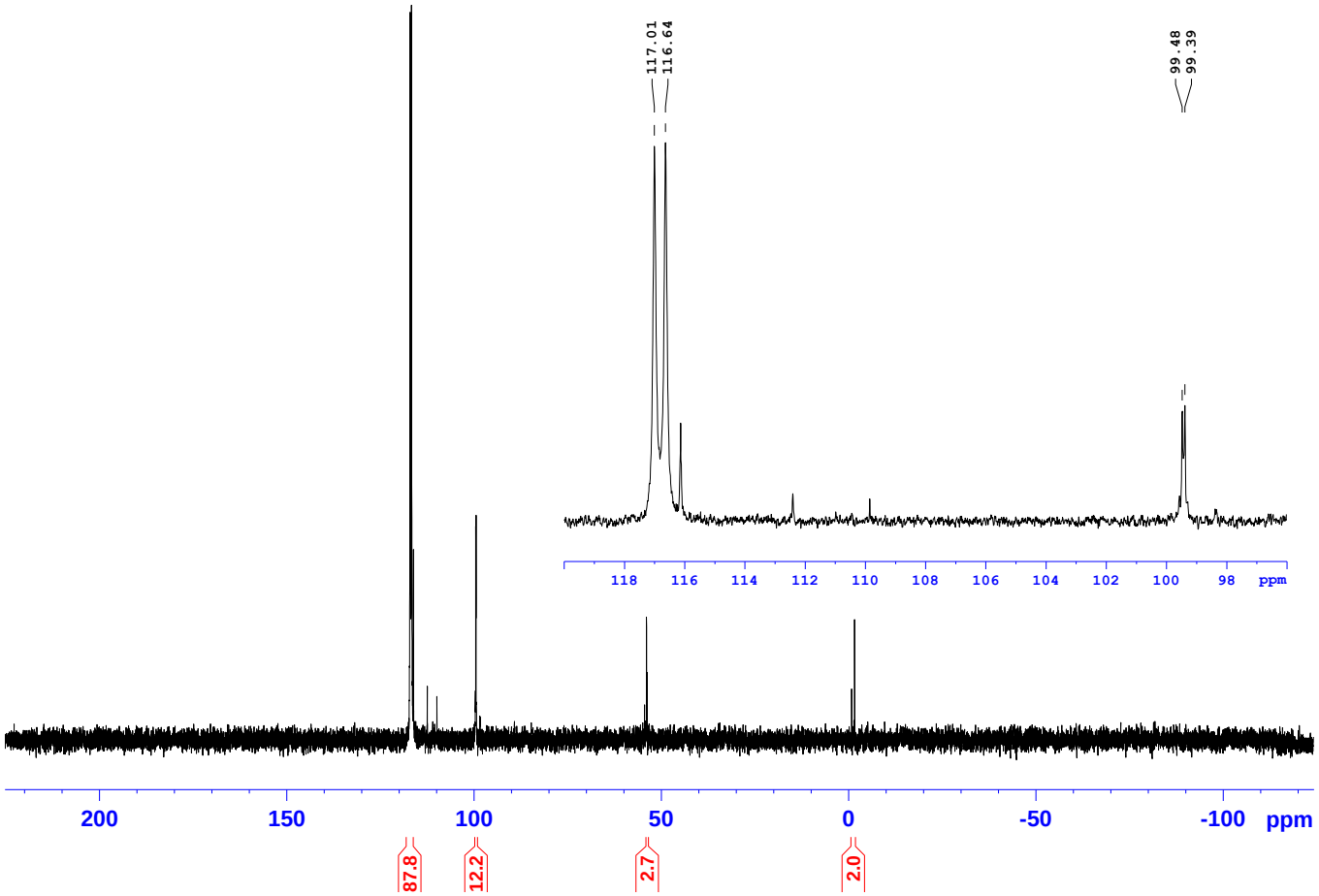
spectra **c**: **room temperature**, under **hydrogen**: the amido complex **9** has disappeared and a new species appears which has been confidently identified as the dihydride **8** (*vide infra*). Other hydride species are unaffected.

spectra **d**: **60 °C**, under **hydrogen**: when the sample is heated up, the amido complex **9** reappears at the expenses of the dihydride **8**. No further spectral changes take place after keeping the sample at 60° C for 90 minutes overall. The sample is therefore cooled down to room T before recording the final spectrum.

spectra **e**: **room temperature**, under **hydrogen**: when the sample is cooled down the relative concentration of the dihydride species **8** increases at the expenses of the amido complex **9**. An equilibrium exists therefore between the two species which is dependent upon temperature and hydrogen concentration.

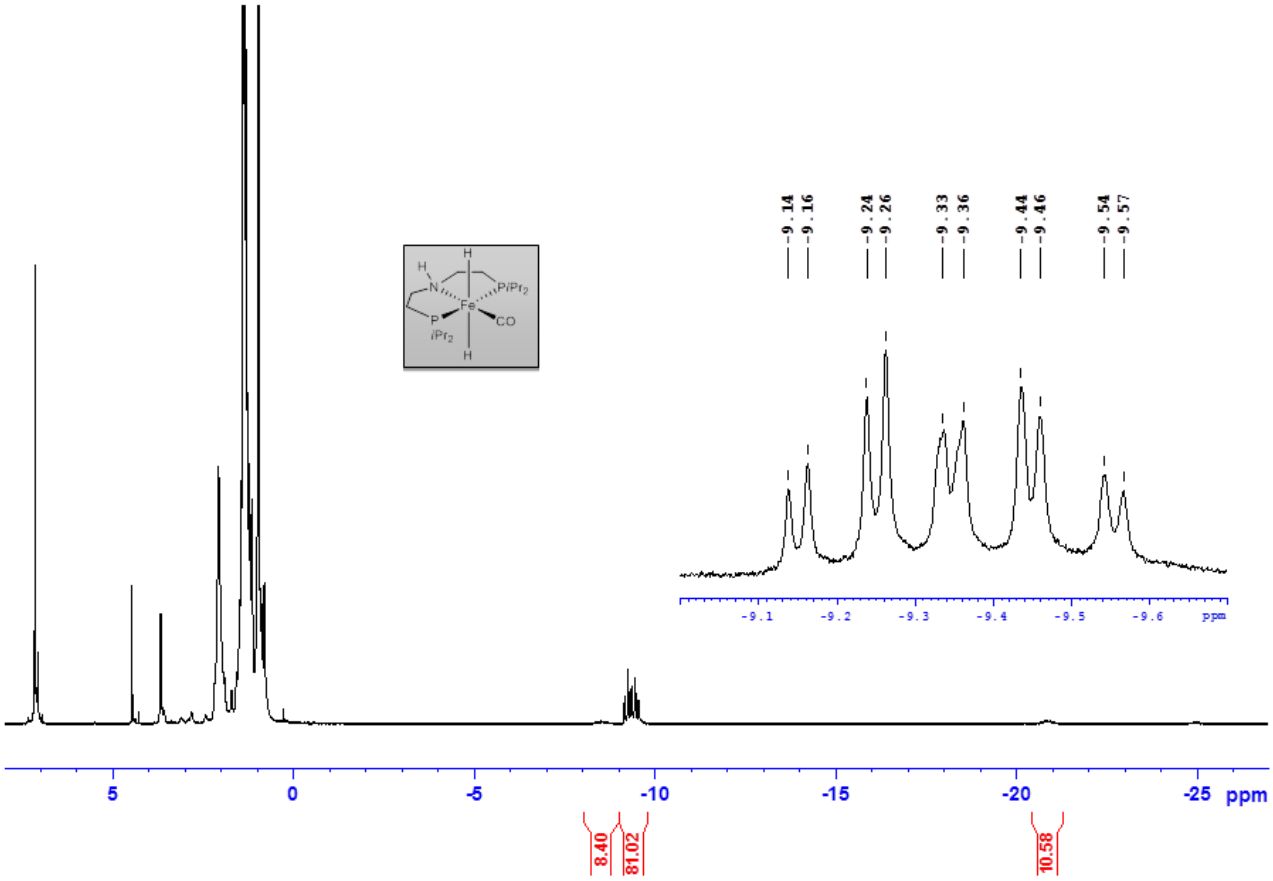


Supplementary Figure 6. ^{1}H NMR (300.1 MHz) spectrum (benzene-d_6) of **9**. **Conditions:** Complex **3** (20 mg, 0.049 mmol) and *t*BuOK (6.6 mg, 0.059 mmol) were dissolved in 2 mL *i*PrOH and the resulting yellow suspension stirred at room temperature for 40 min. The solvent was removed in vacuo and the resulting purple solid was dissolved in 1 mL benzene-d_6. The solution was filtered by means of a syringe PTFE filter and placed in a J-Young NMR tube.

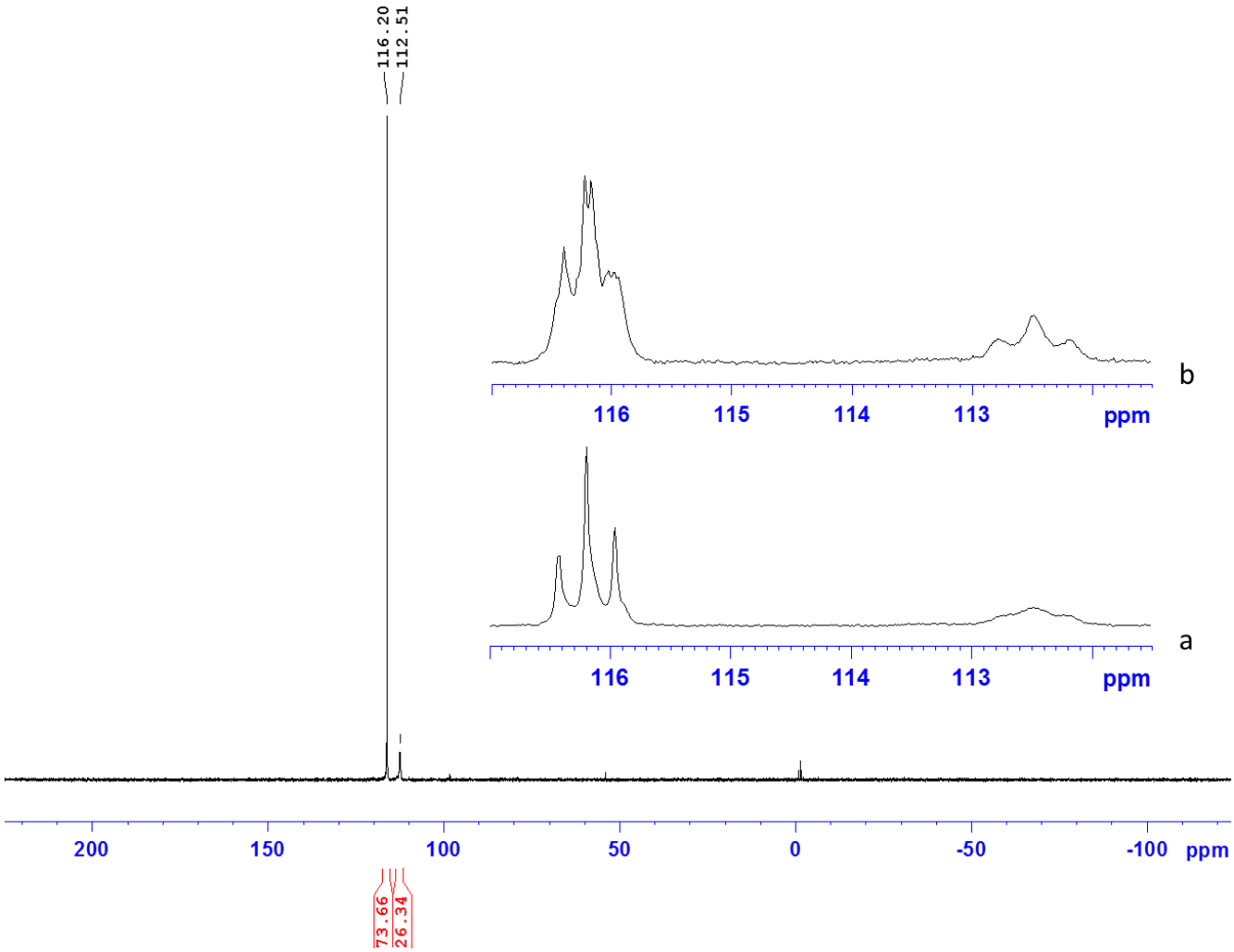


Supplementary Figure 7. $^{31}P\{^{1}H\}$ NMR (121.0 MHz) spectrum (benzene-d_6) of **9**: the peaks relative to the amido complex **9** (δ = 116.8 ppm) and unreacted **3** (δ = 99.4 ppm) appear as doublet due to residual coupling to hydride hydrogens. The spectrum also shows the presence of free ligand (δ = - 1.7 ppm) and free oxidized ligand (δ = 53.9 ppm).

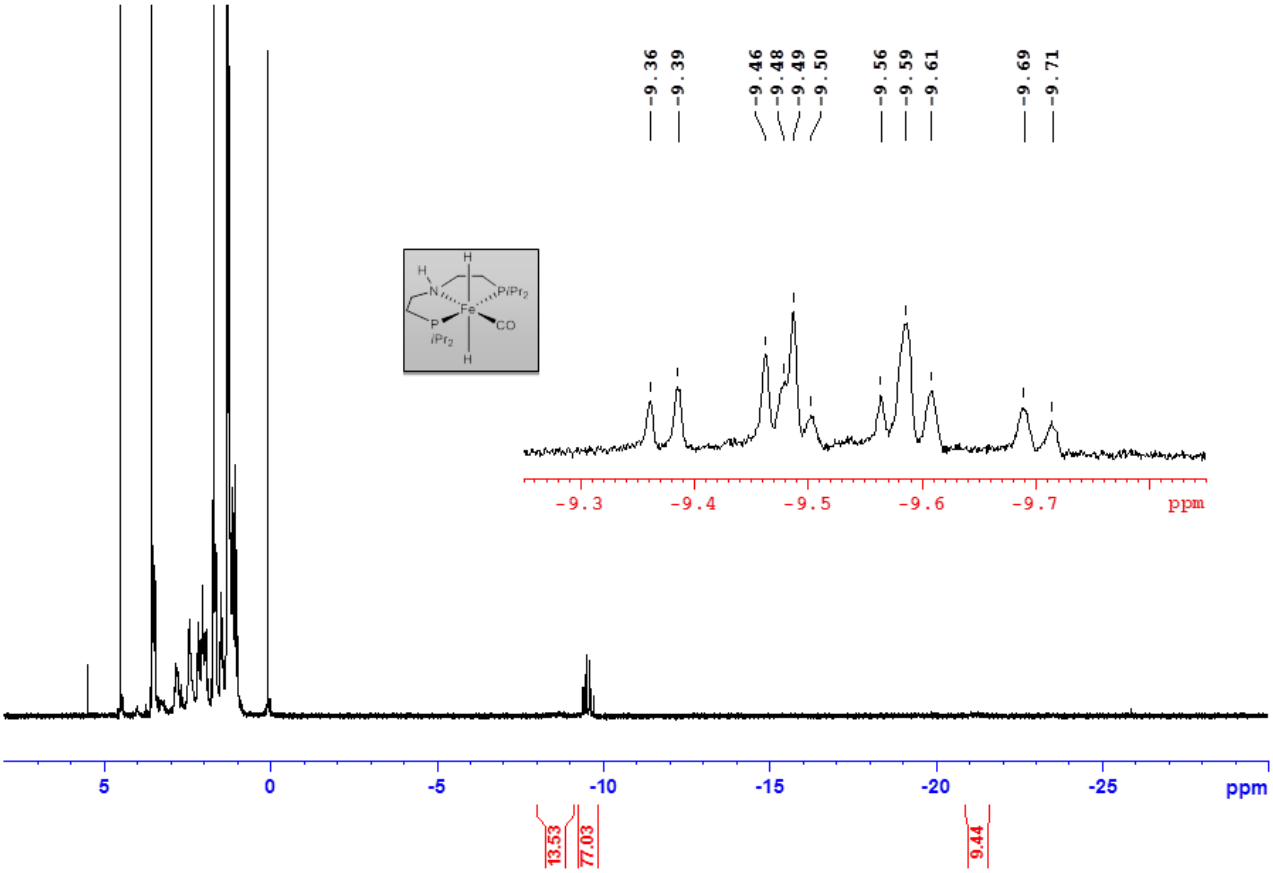
The above sample was subsequently frozen and argon removed under vacuum. Then hydrogen gas was admitted into the NMR tube, the sample was allowed to thaw and then it was shaken intensively until the solution turned light orange.



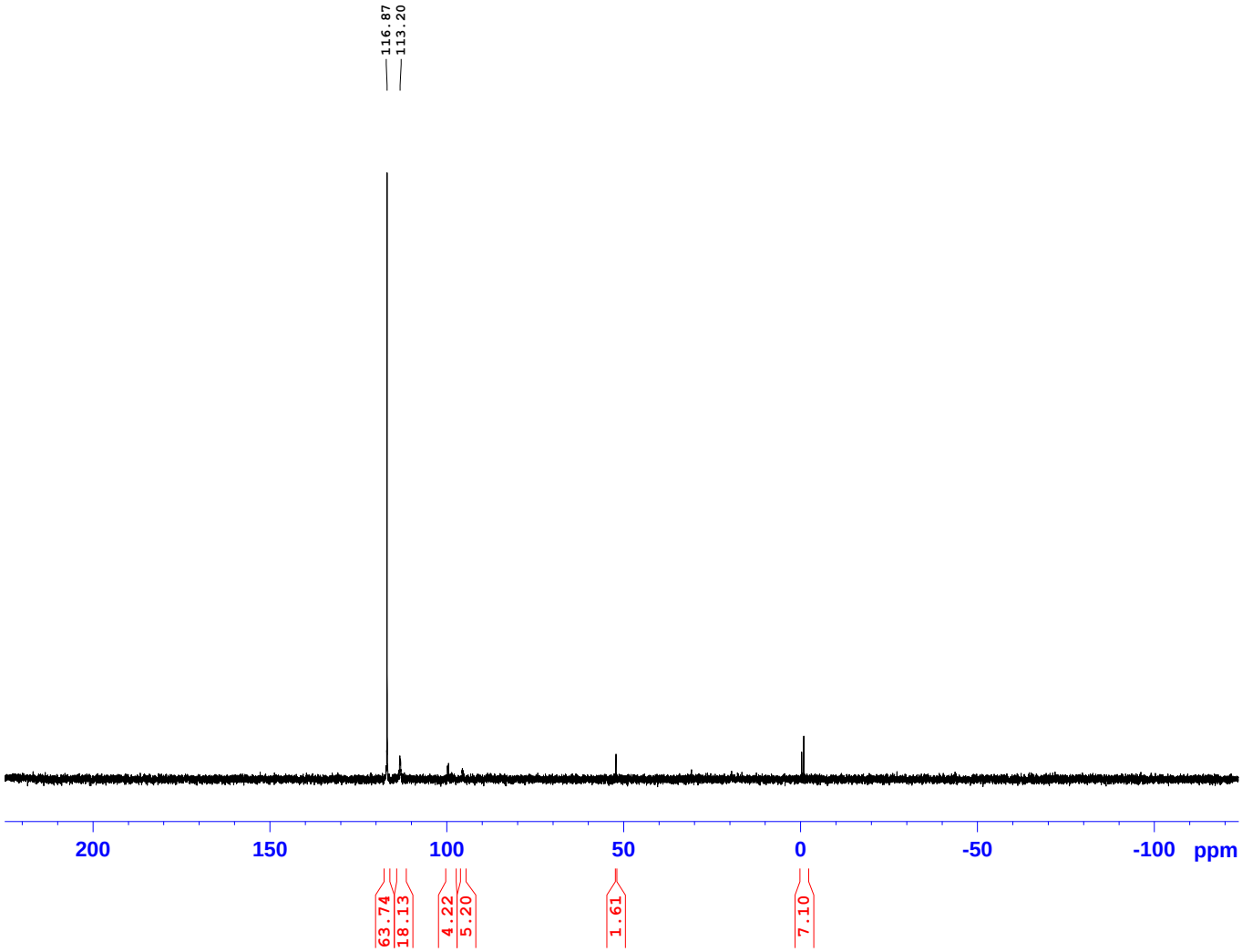
Supplementary Figure 8. ^{1}H NMR (400.1 MHz) spectrum (benzene-d_6) of **8**.



Supplementary Figure 9. $^{31}P\{^{1}H\}$ NMR (161.9 MHz) spectrum (benzene-d_6) of **8**: insert **a** and **b** show the $^{31}P\{^{1}H\}$ NMR spectra, selectively decoupled from ligand hydrogens, showing the residual coupling of the phosphorus atoms to the two hydrides in the molecule. The two spectra have been recorded using different 90° pulse length in order to extend the decoupling frequency range.

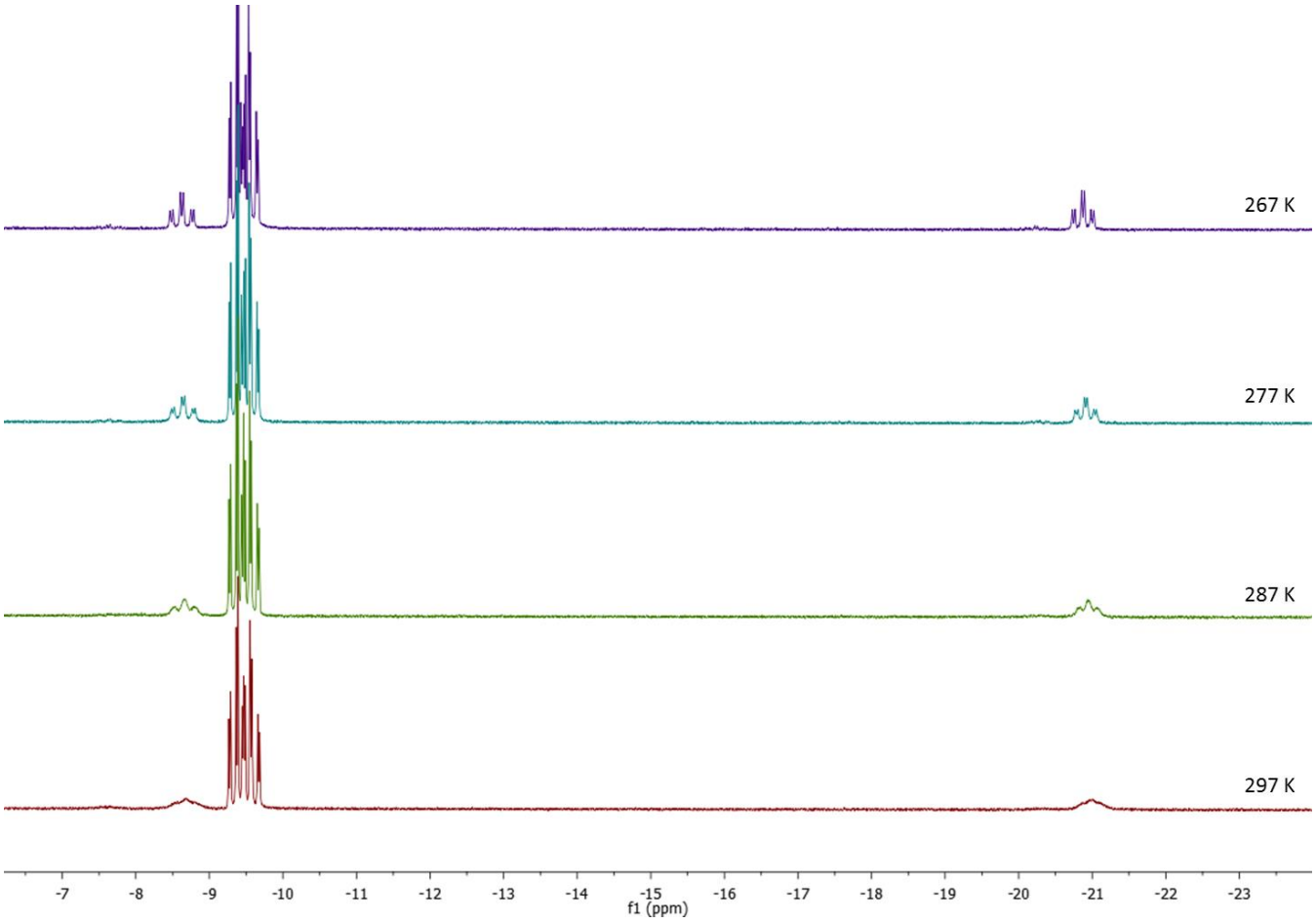


Supplementary Figure 10. ^{1}H NMR (400.1 MHz) spectrum (THF-d_8) of **8**.

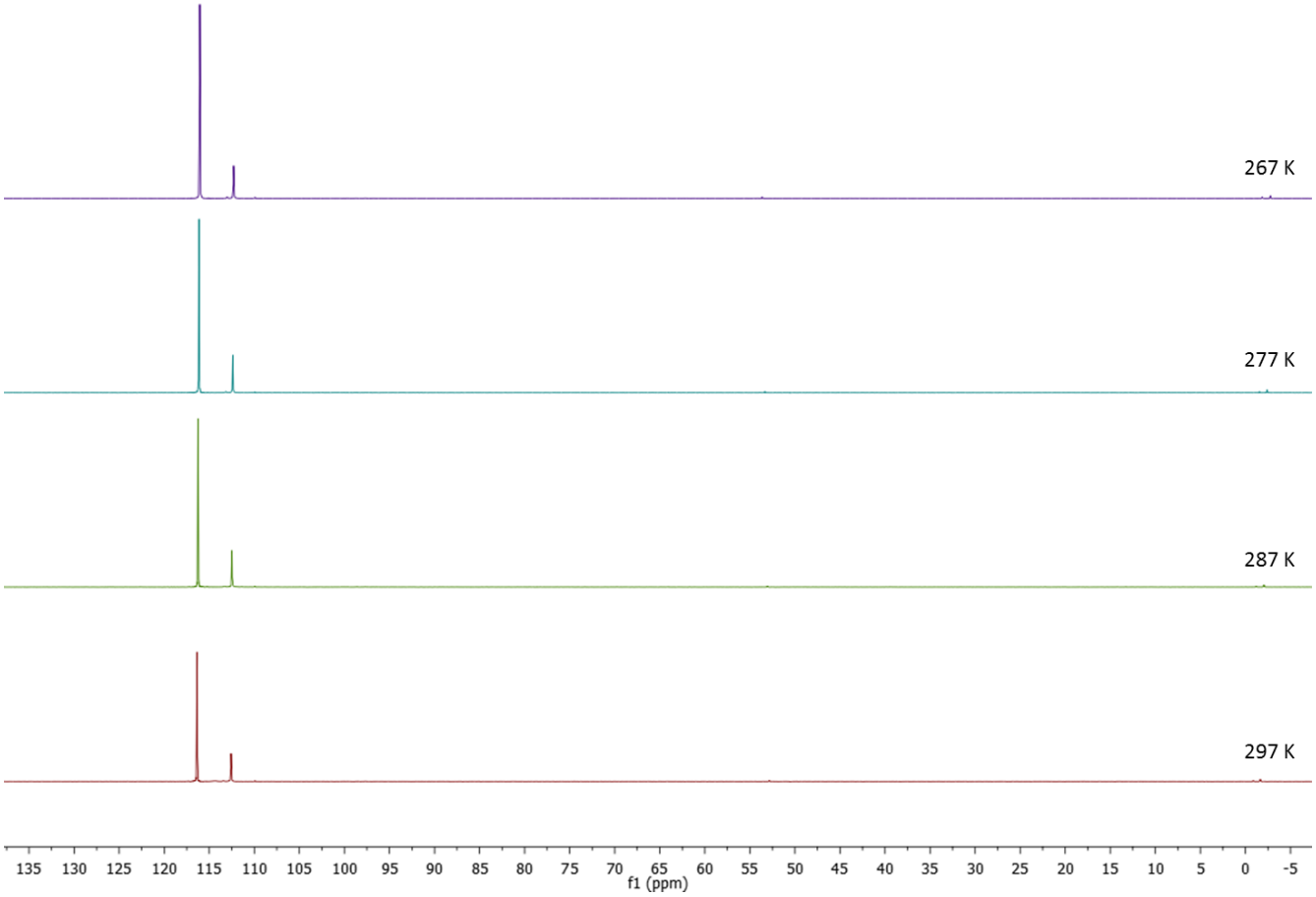


Supplementary Figure 11. $^{31}P\{^{1}H\}$ NMR (161.9 MHz) spectrum (THF-d_8) of **8.**

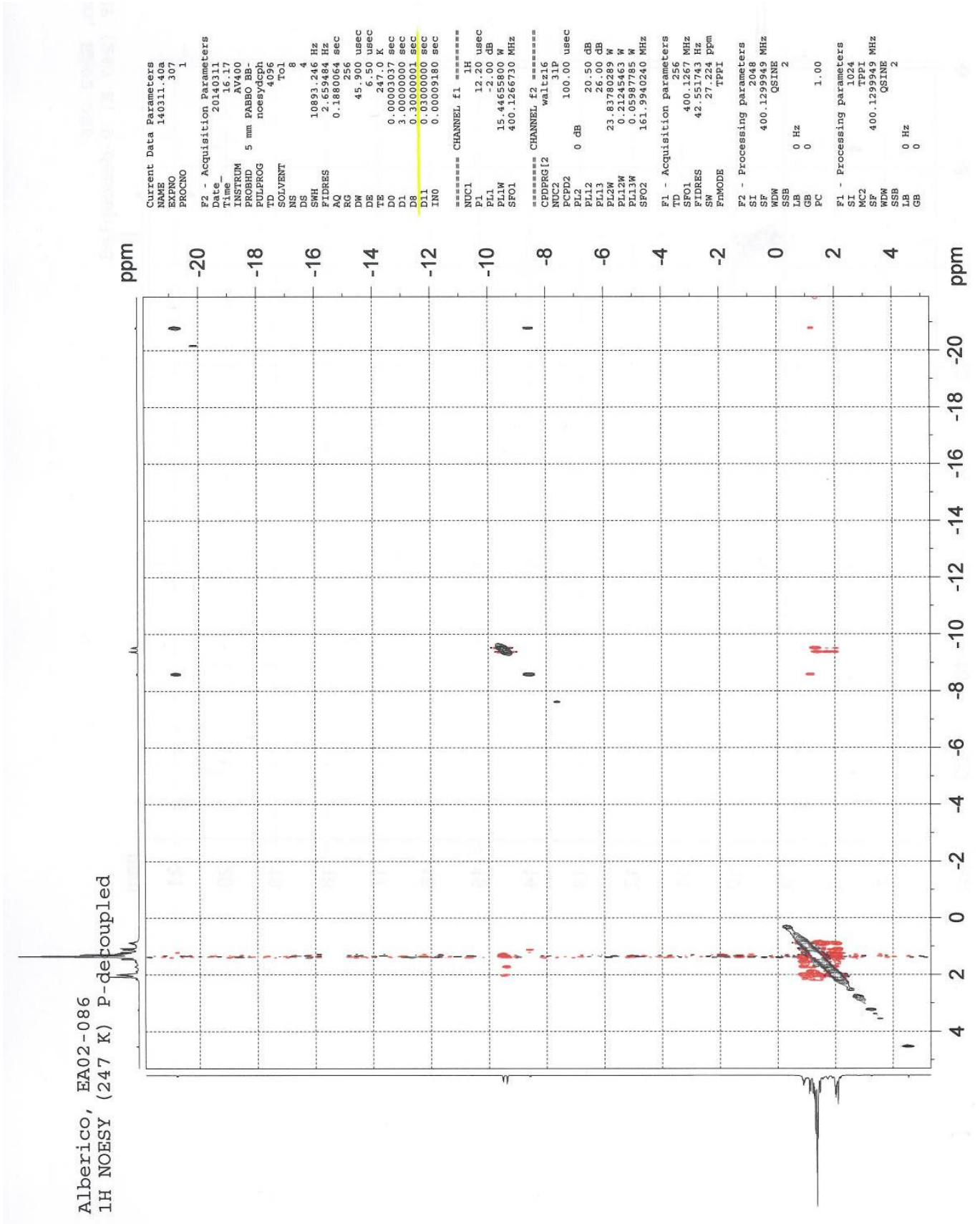
1.5 VT NMR investigations



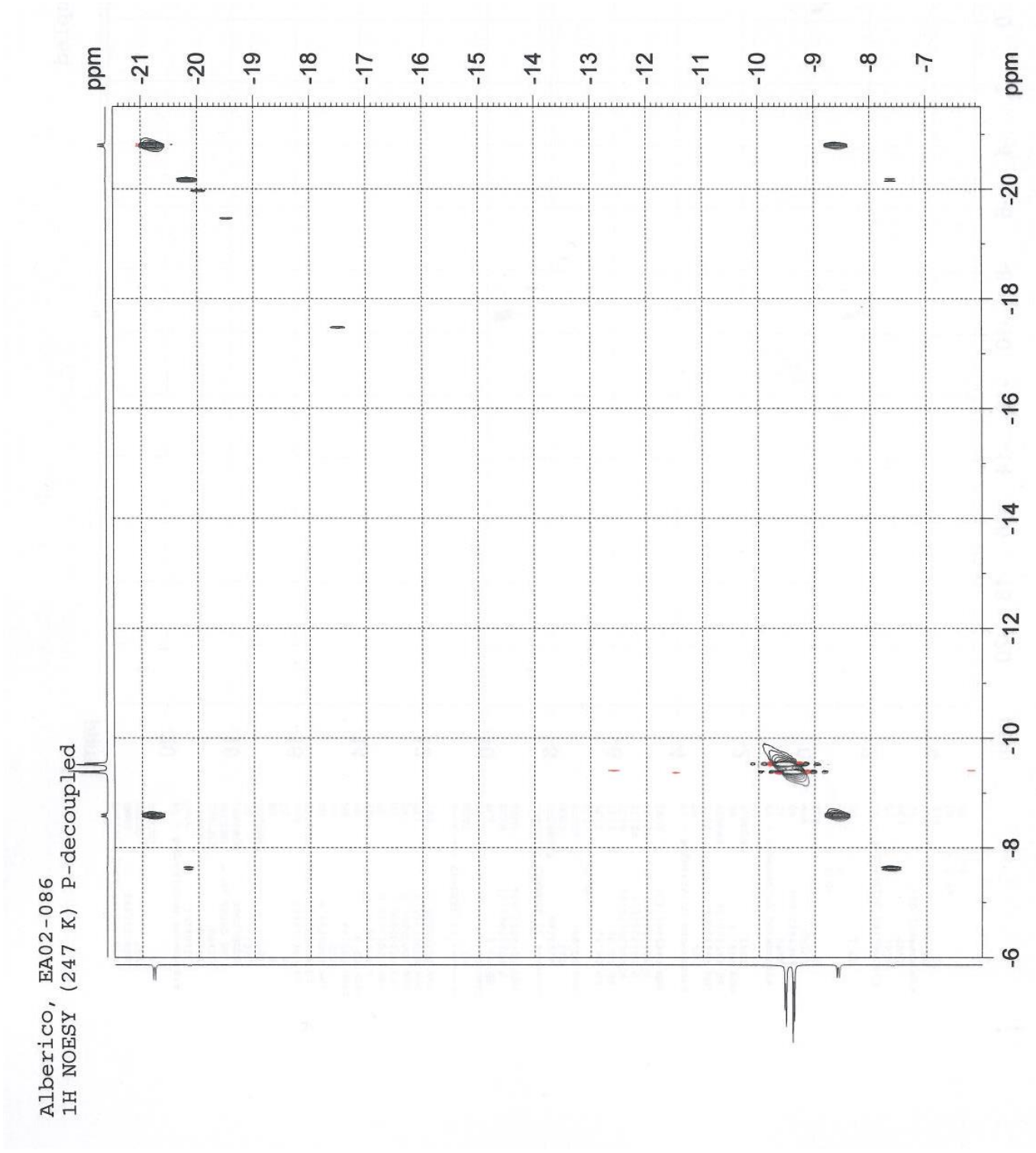
Supplementary Figure 12. Variable temperature. ^{1}H NMR (400.1 MHz) spectrum (toluene-d_8, hydride region) of **8**.



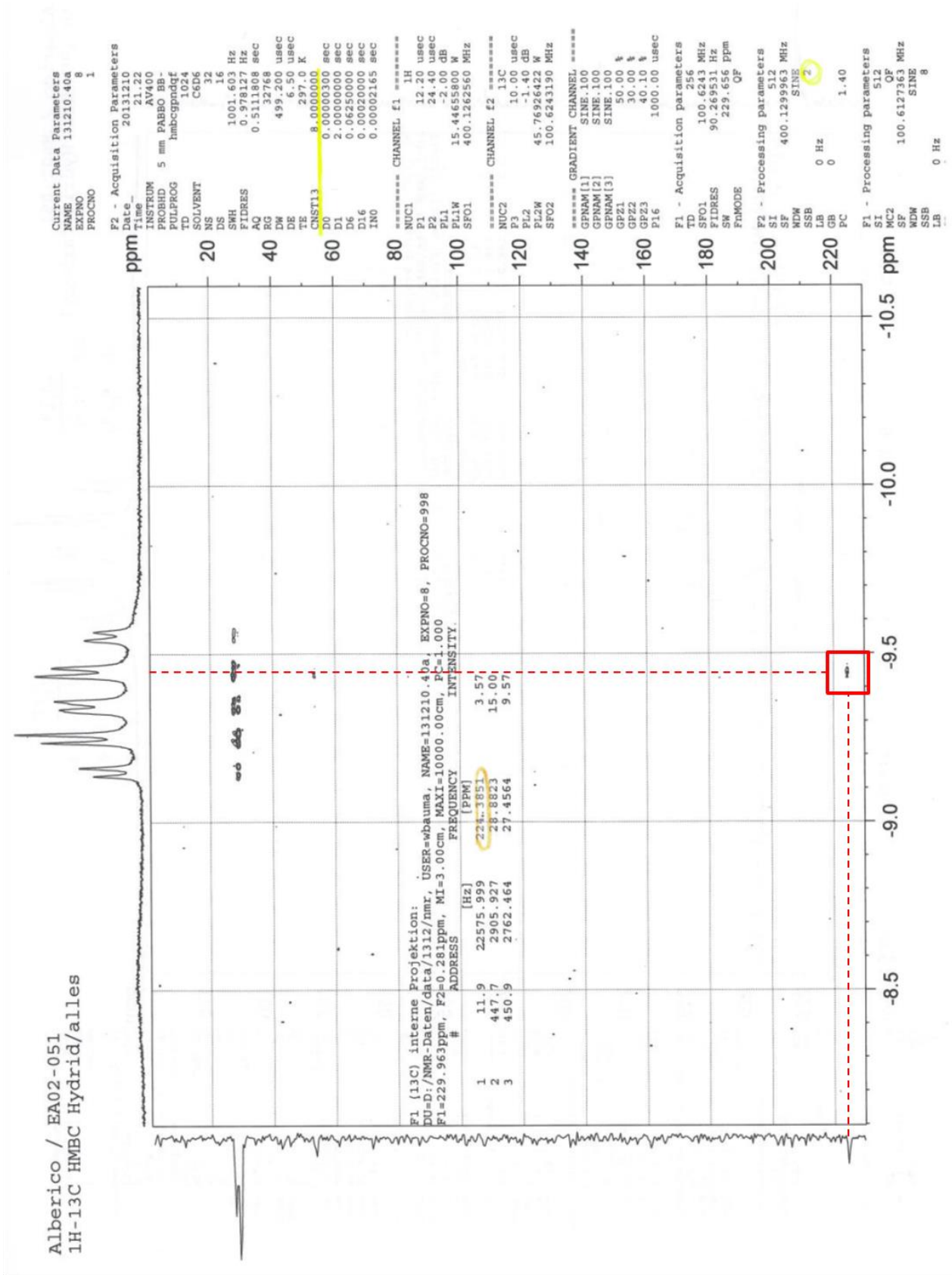
Supplementary Figure 13. Variable temperature $^{31}P\{^{1}H\}$ NMR (161.9 MHz) spectrum (toluene-d_8) of **8**.



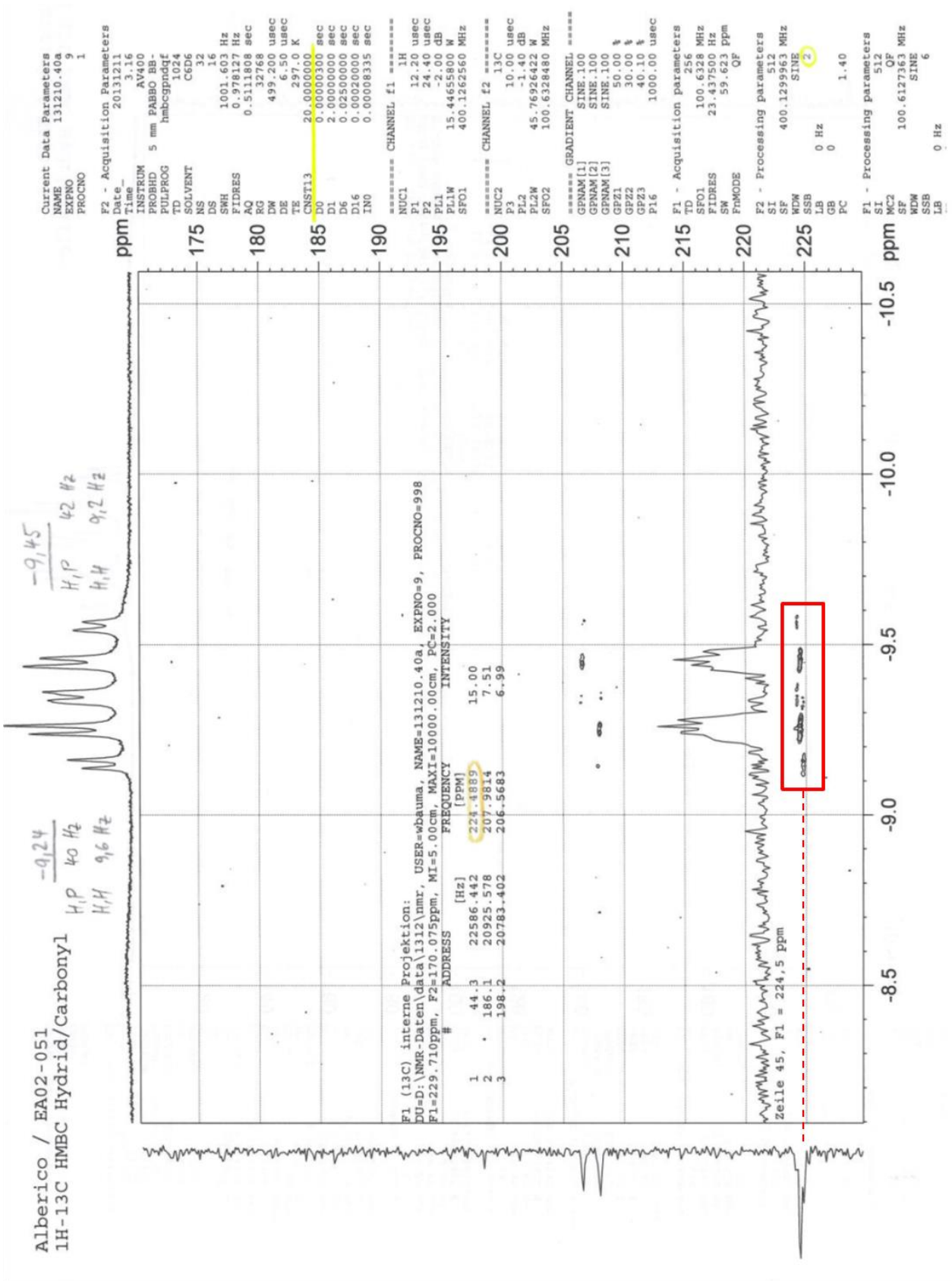
Supplementary Figure 14. $^{1}H\{^{31}P\}$ NOESY NMR (400.1/161.9 MHz) spectrum of **8** (toluene-d_8), at 247 K .



Supplementary Figure 15. $^{1}H\{^{31}P\}$ NOESY NMR (400.1/161.9 MHz) spectrum of **8** (toluene-d_8, hydride region), at 247 K .

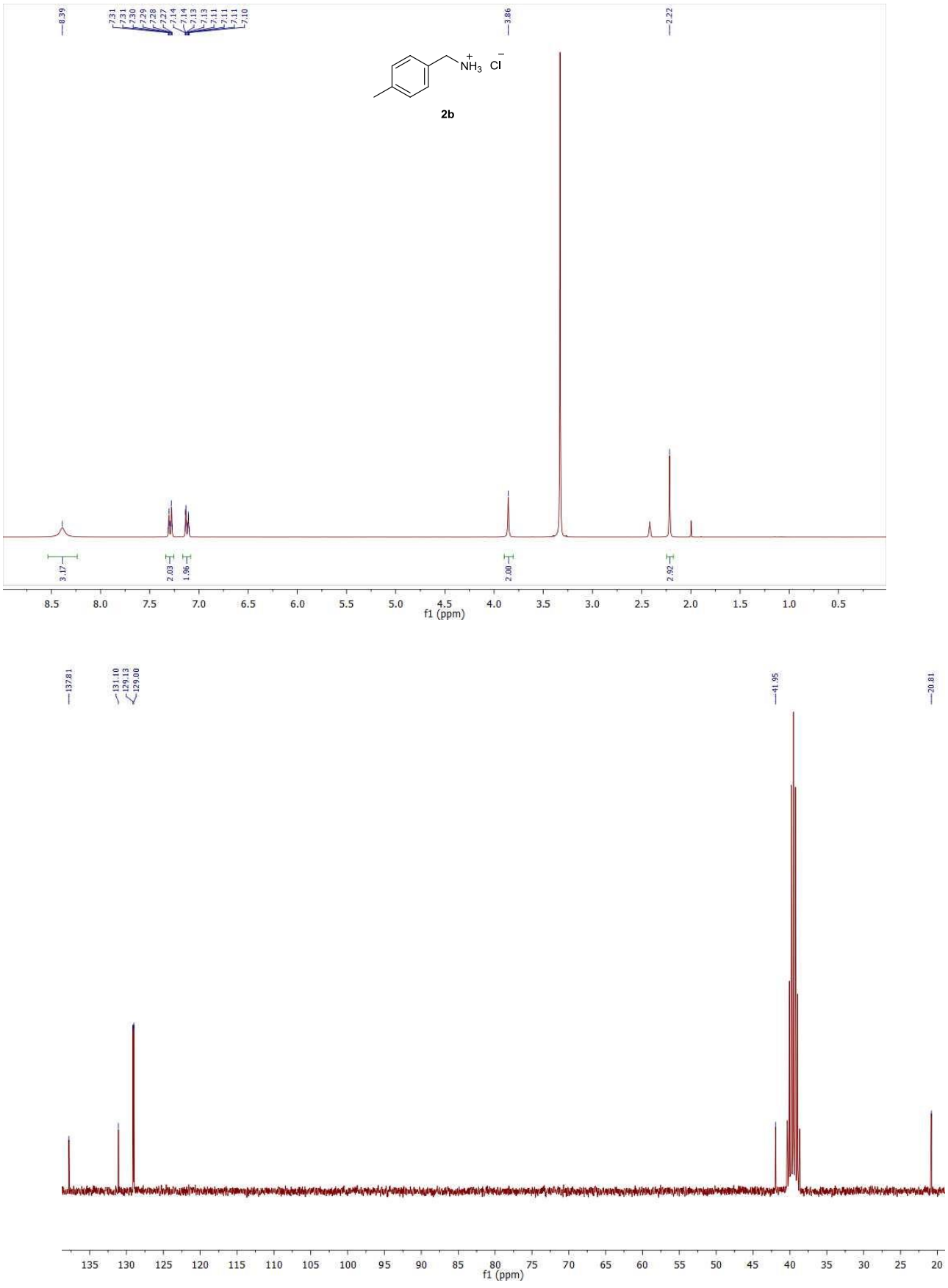


Supplementary Figure 16. ^{1}H-^{13}C HMBC NMR (400.1/100.6 MHz) spectrum of **9** (C_6D_6), hydride region showing the two-bond coupling between the carbon of the coordinated carbonyl group (δ = 224.4 ppm) and the iron hydrides.

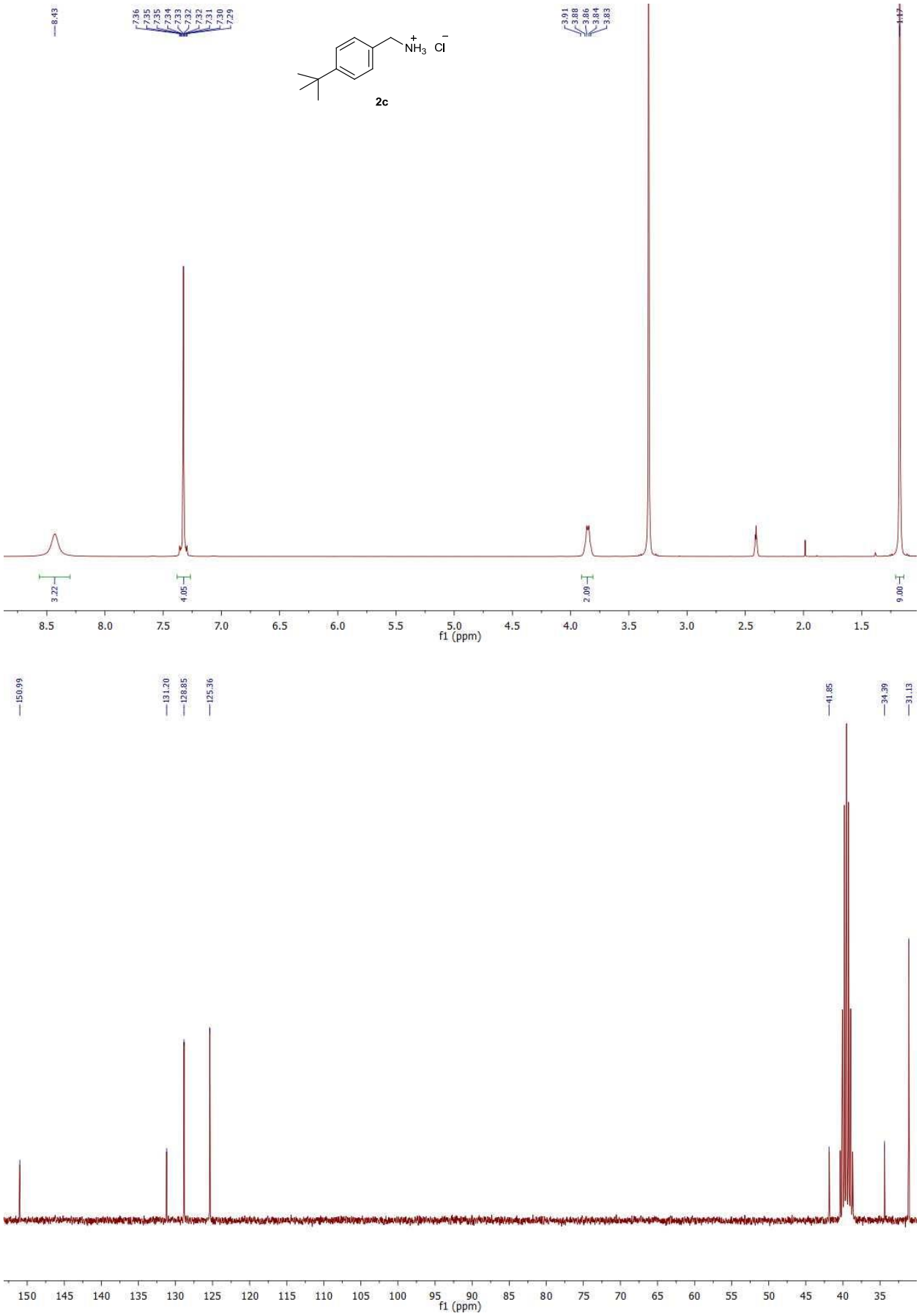


Supplementary Figure 17. ^{1}H-^{13}C HMBC NMR (400.1/100.6 MHz) spectrum (C_6D_6, hydride region). The correlation signals at F2 206.6 ppm and 208.0 are folded (true chemical shifts 27.4 ppm and 28.9 ppm, ligand moiety carbon, see Suppl. Fig. 12).

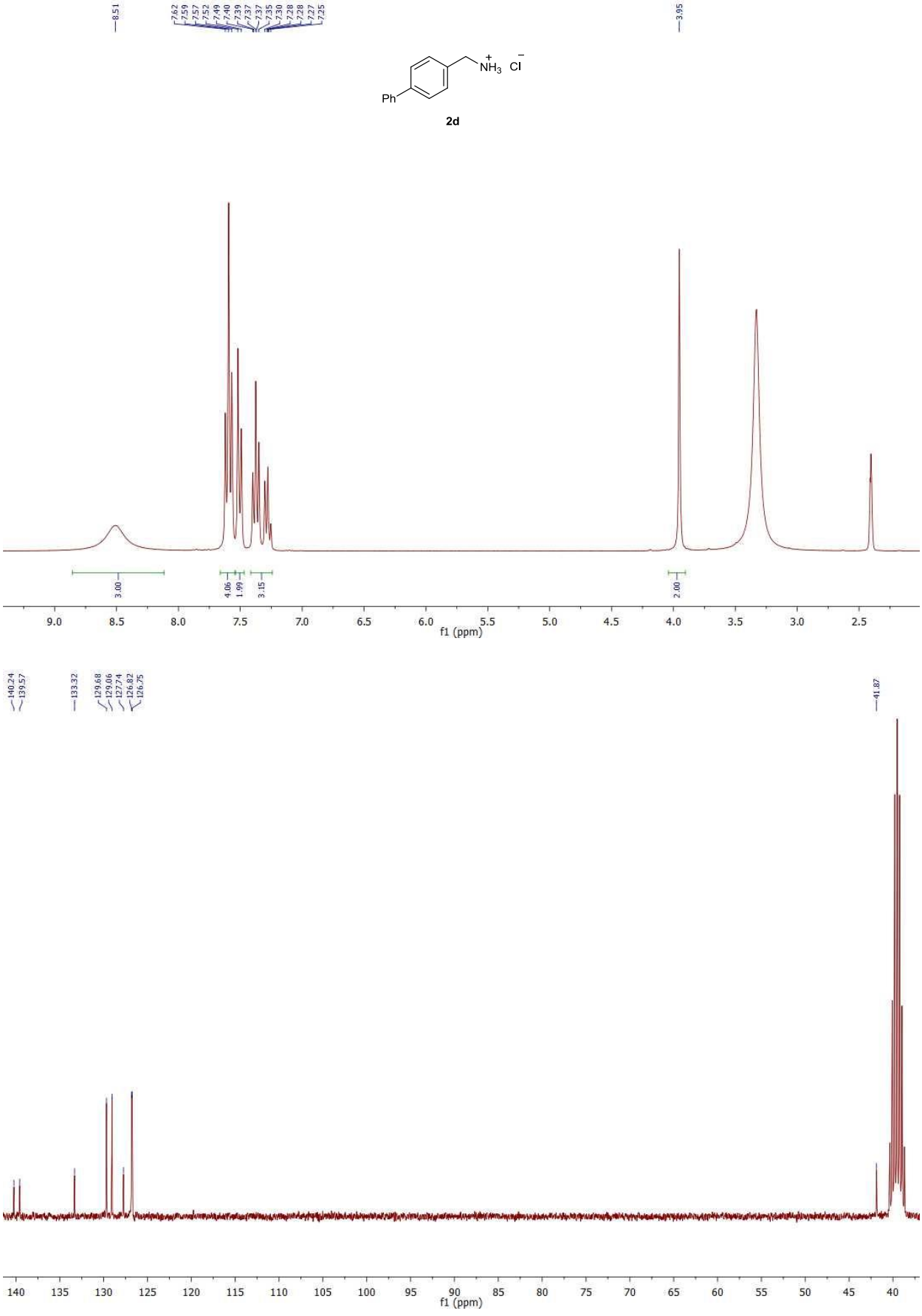
1.6 Selected NMR spectra of isolated HCl products 2, 5, 7



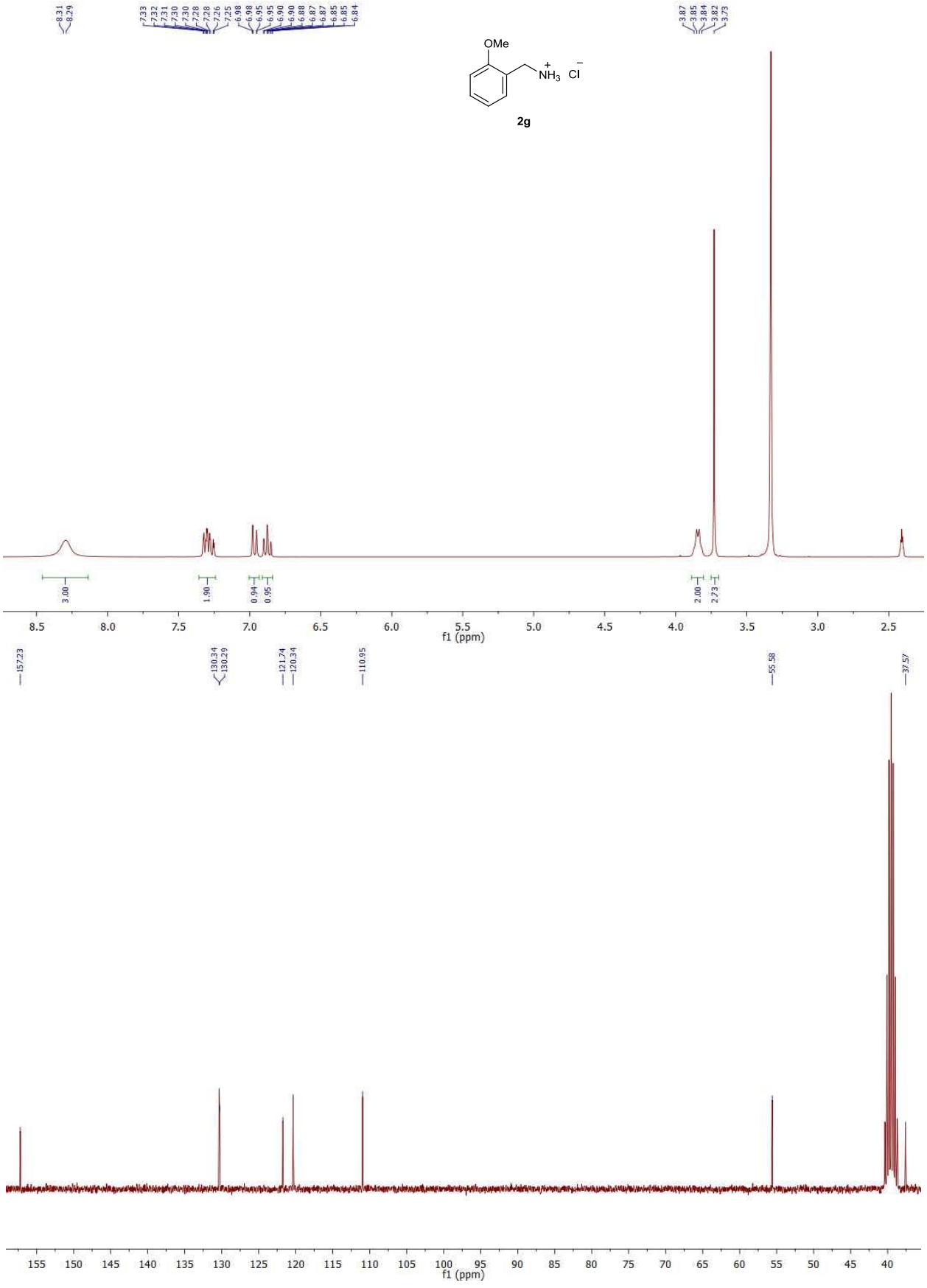
Supplementary Figure 18. ^{1}H and ^{13}C NMR of compound **2b.**



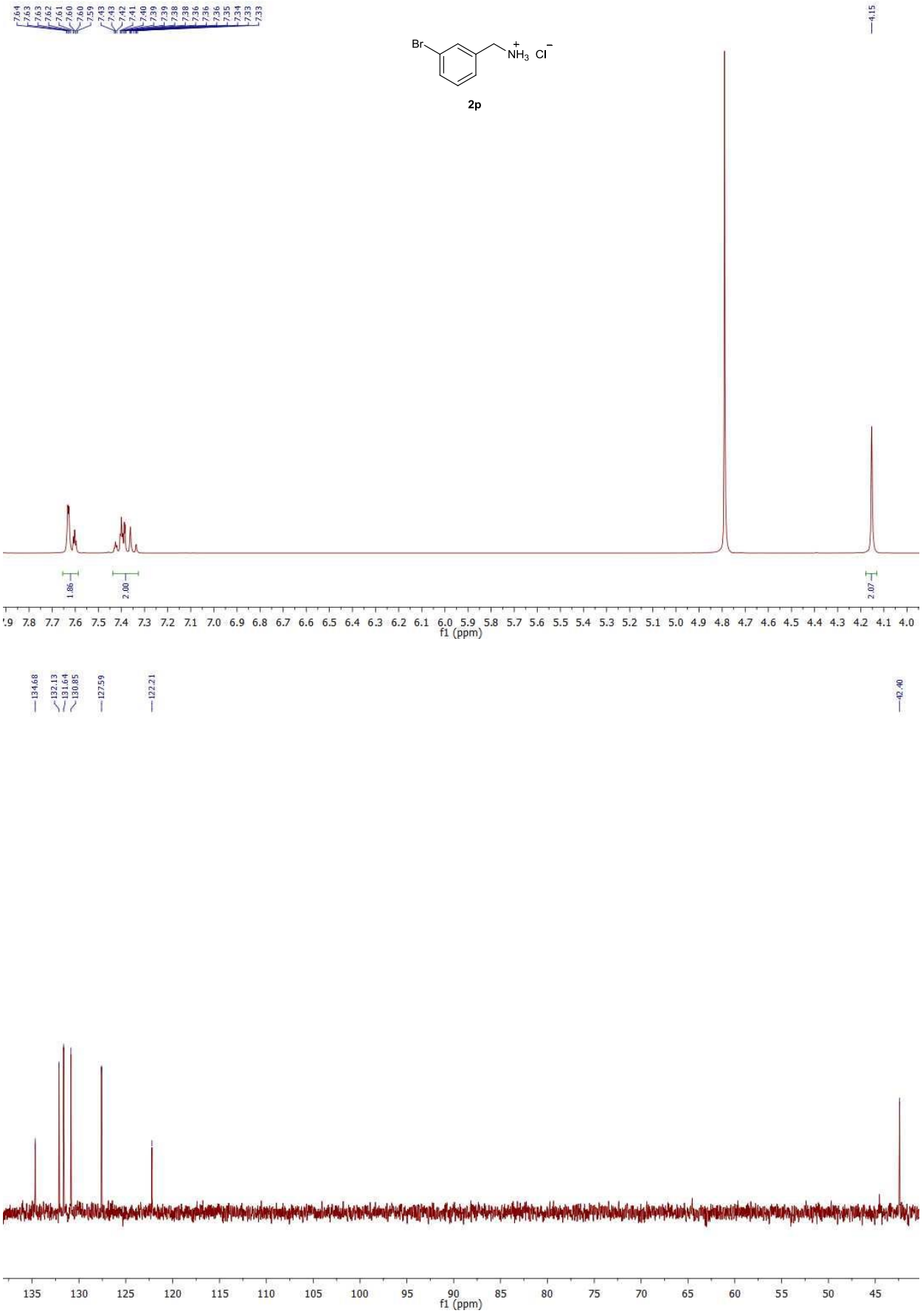
Supplementary Figure 19. ^{1}H and ^{13}C NMR of compound **2c.**



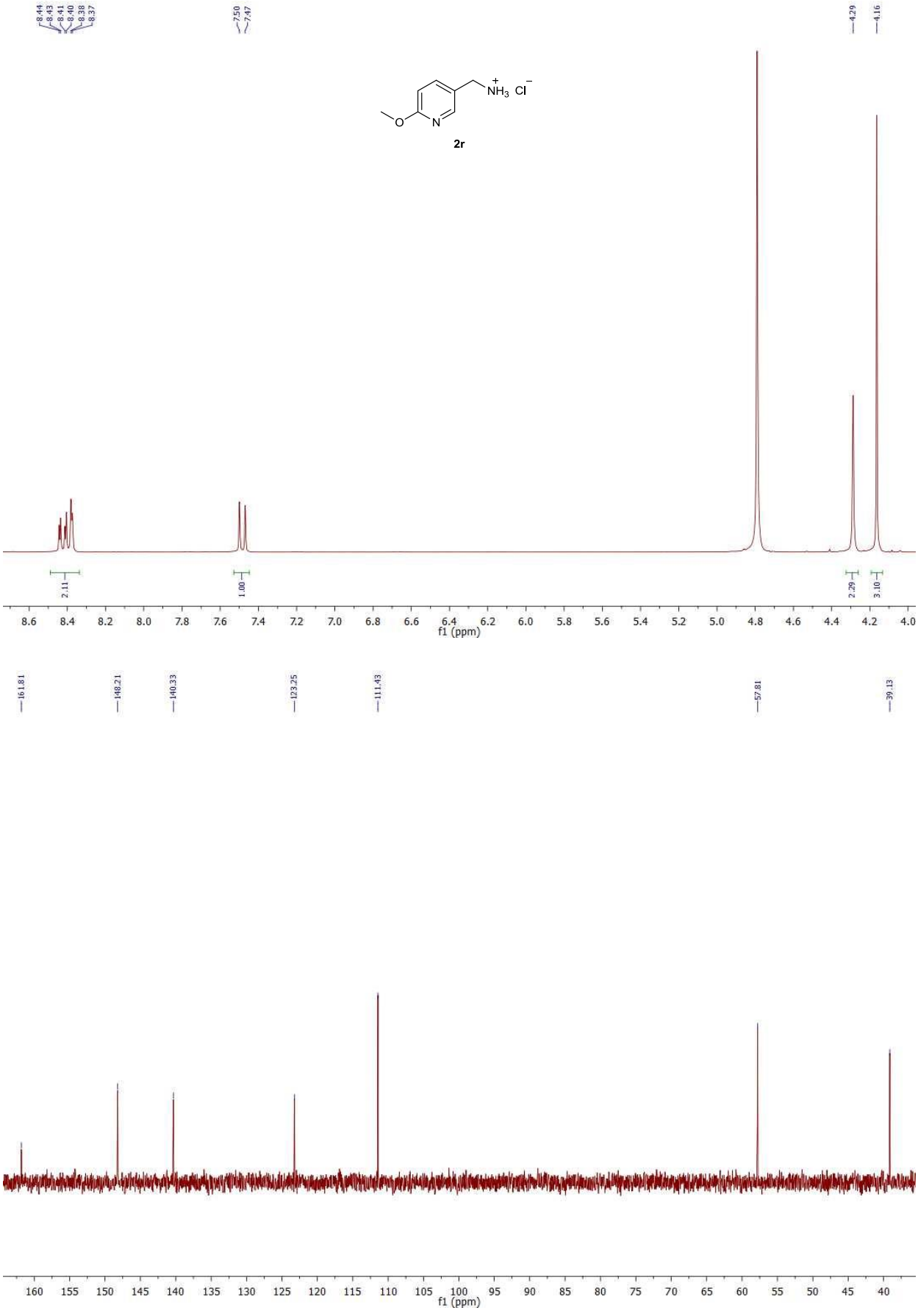
Supplementary Figure 20. ^{1}H and ^{13}C NMR of compound **2d.**



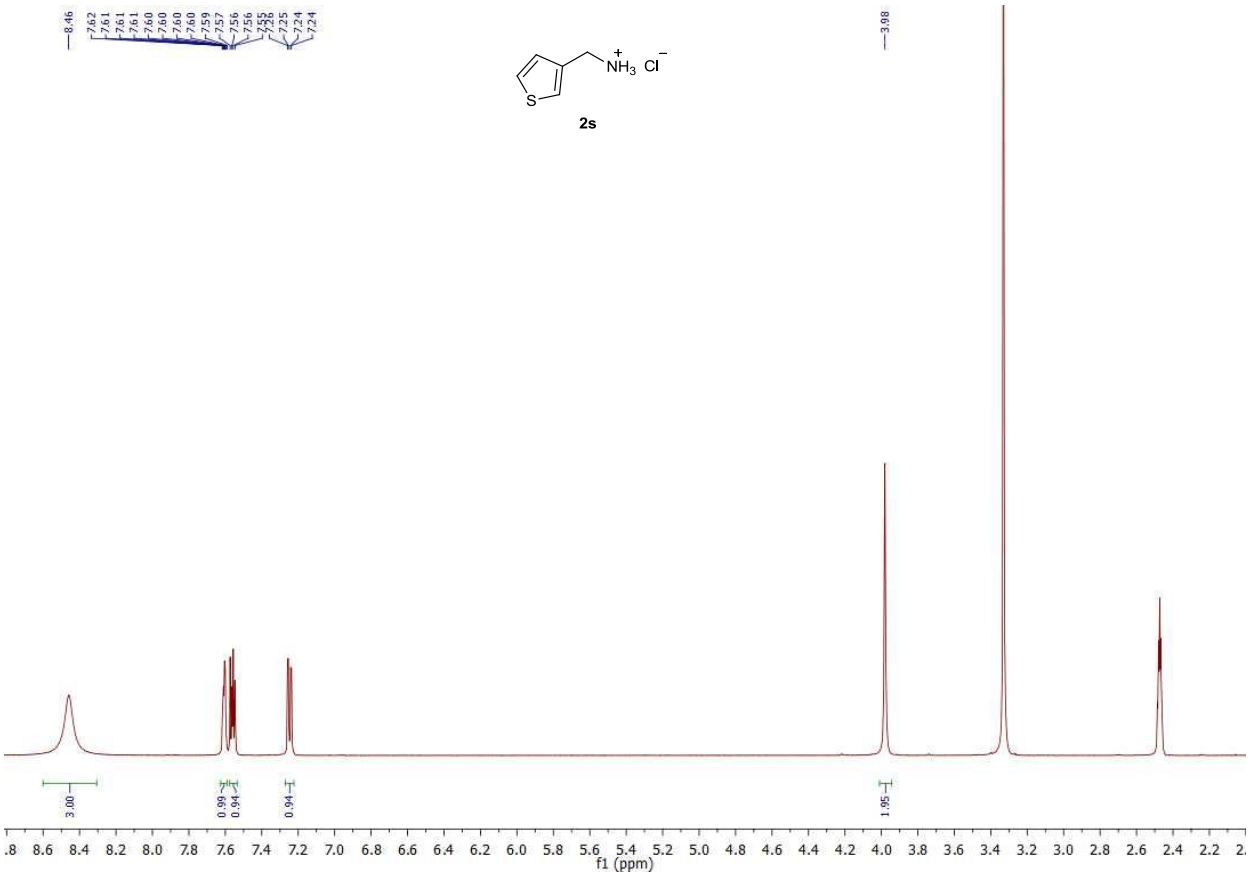
Supplementary Figure 21. ^{1}H and ^{13}C NMR of compound **2g.**

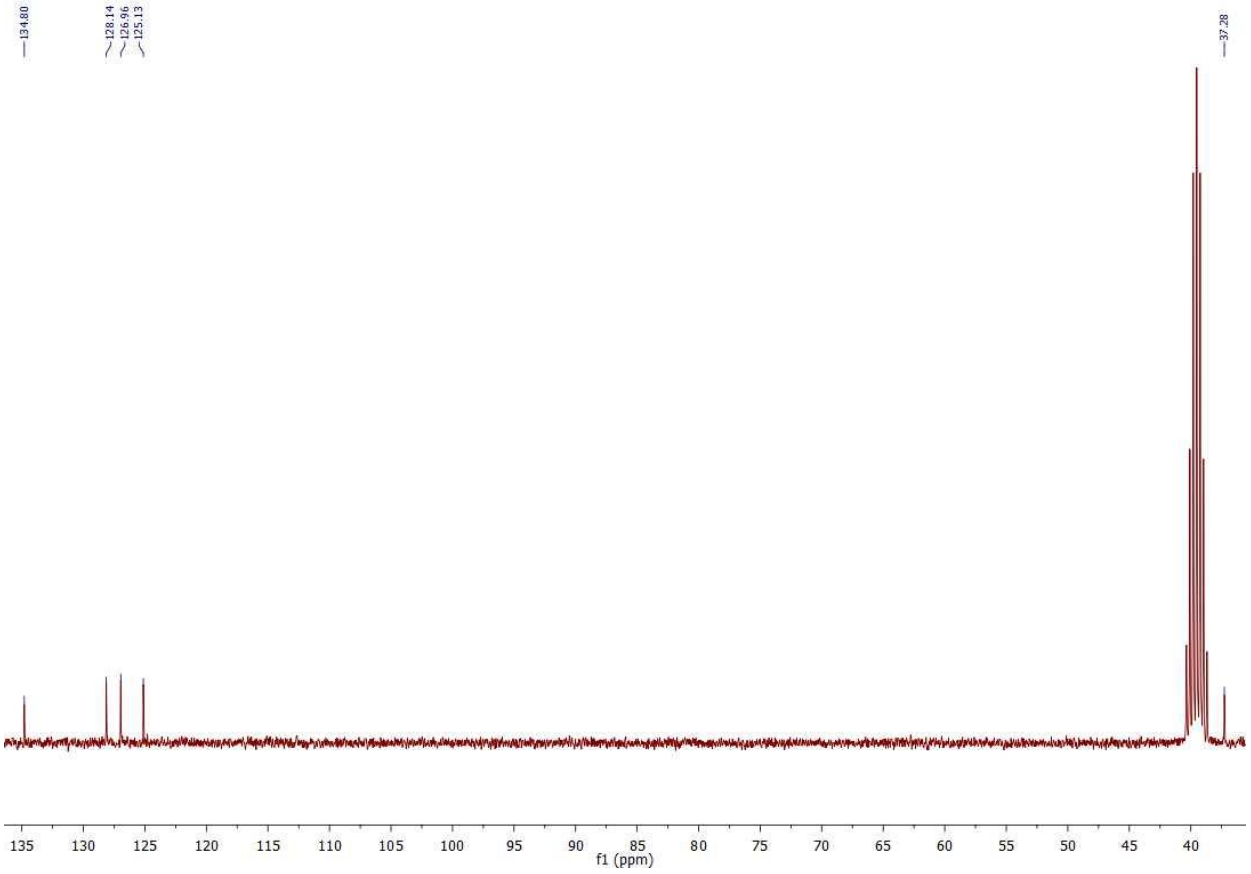


Supplementary Figure 22. ^{1}H and ^{13}C NMR of compound **2p.**

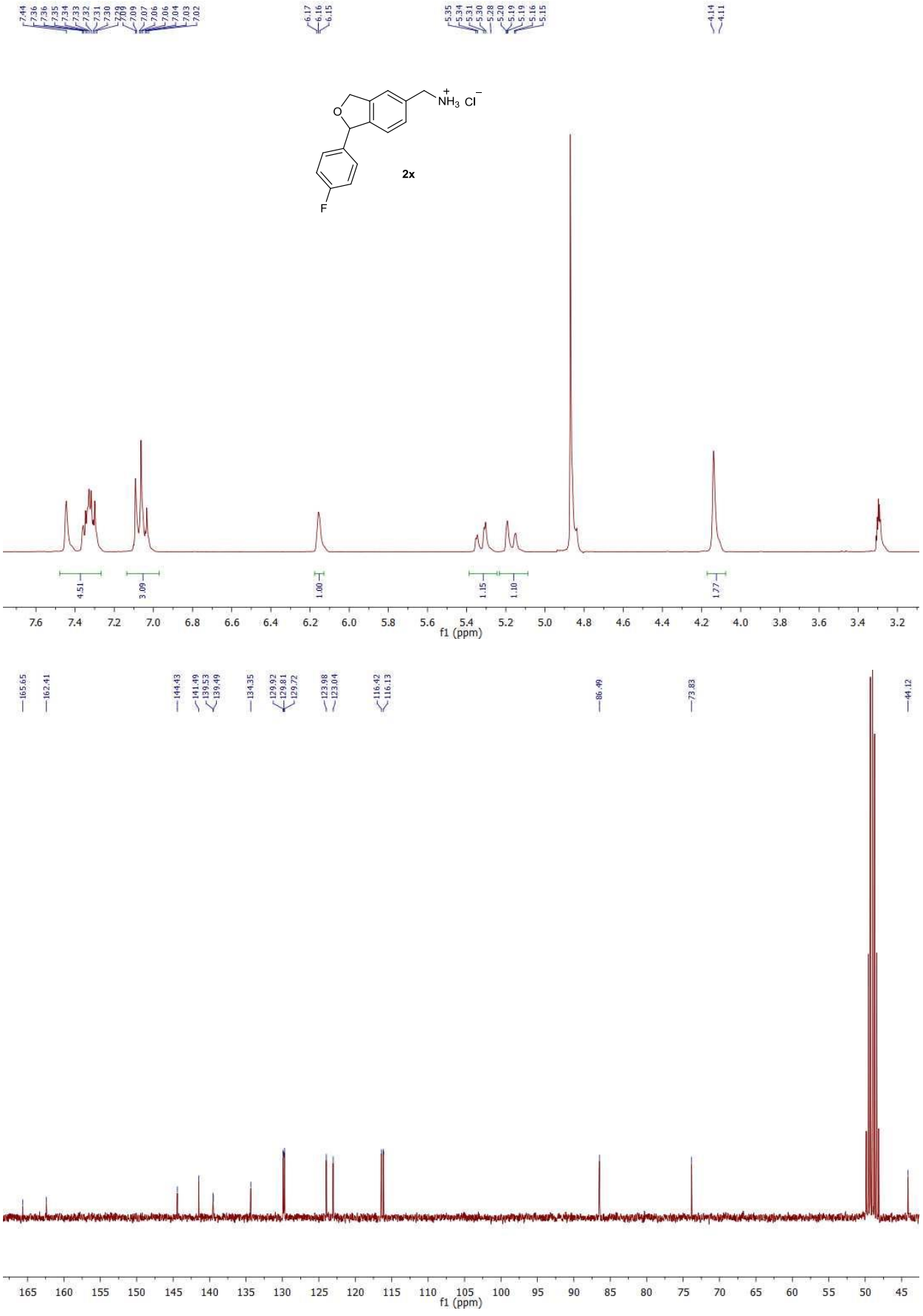


Supplementary Figure 23. ^{1}H and ^{13}C NMR of compound **2r.**

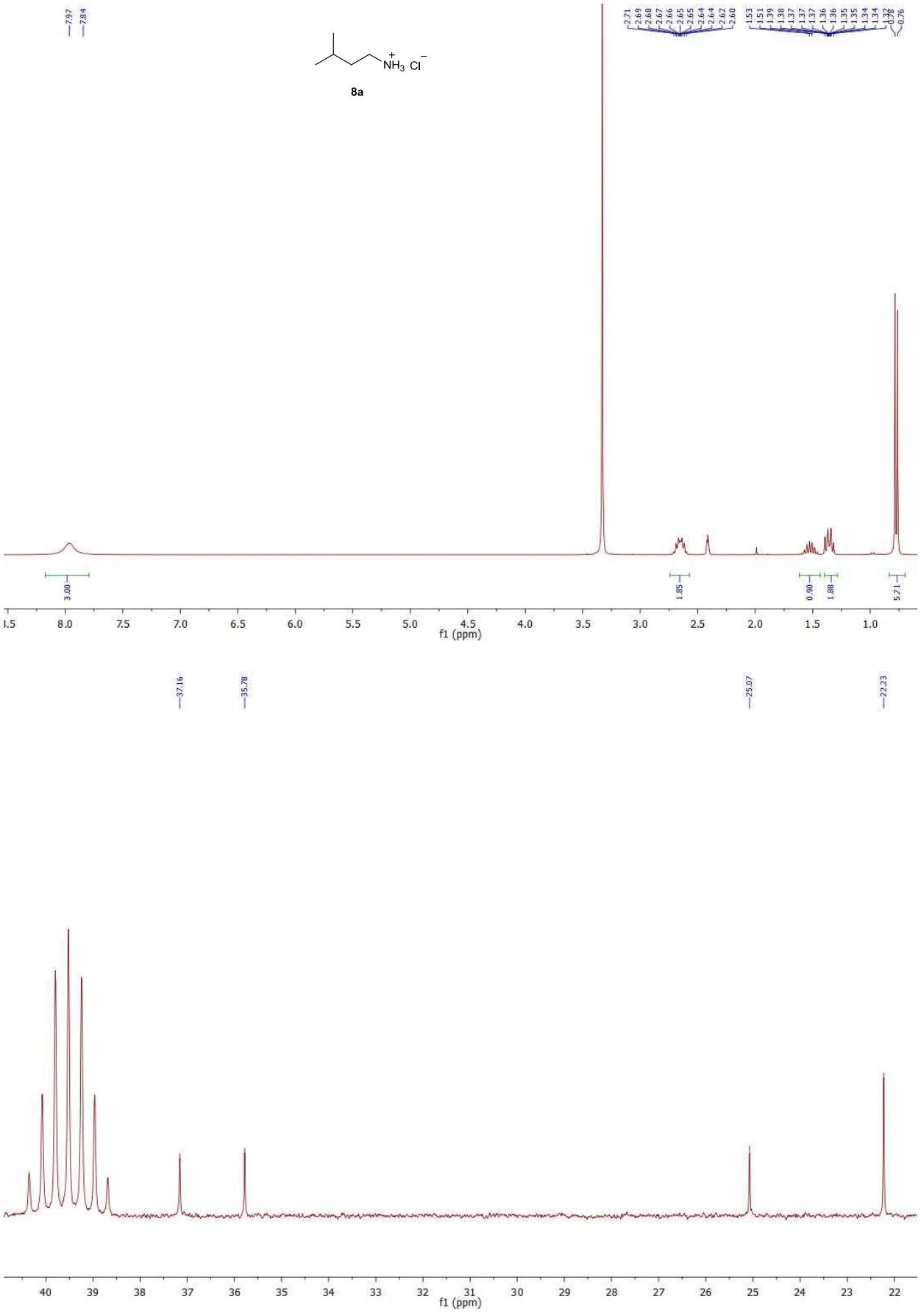




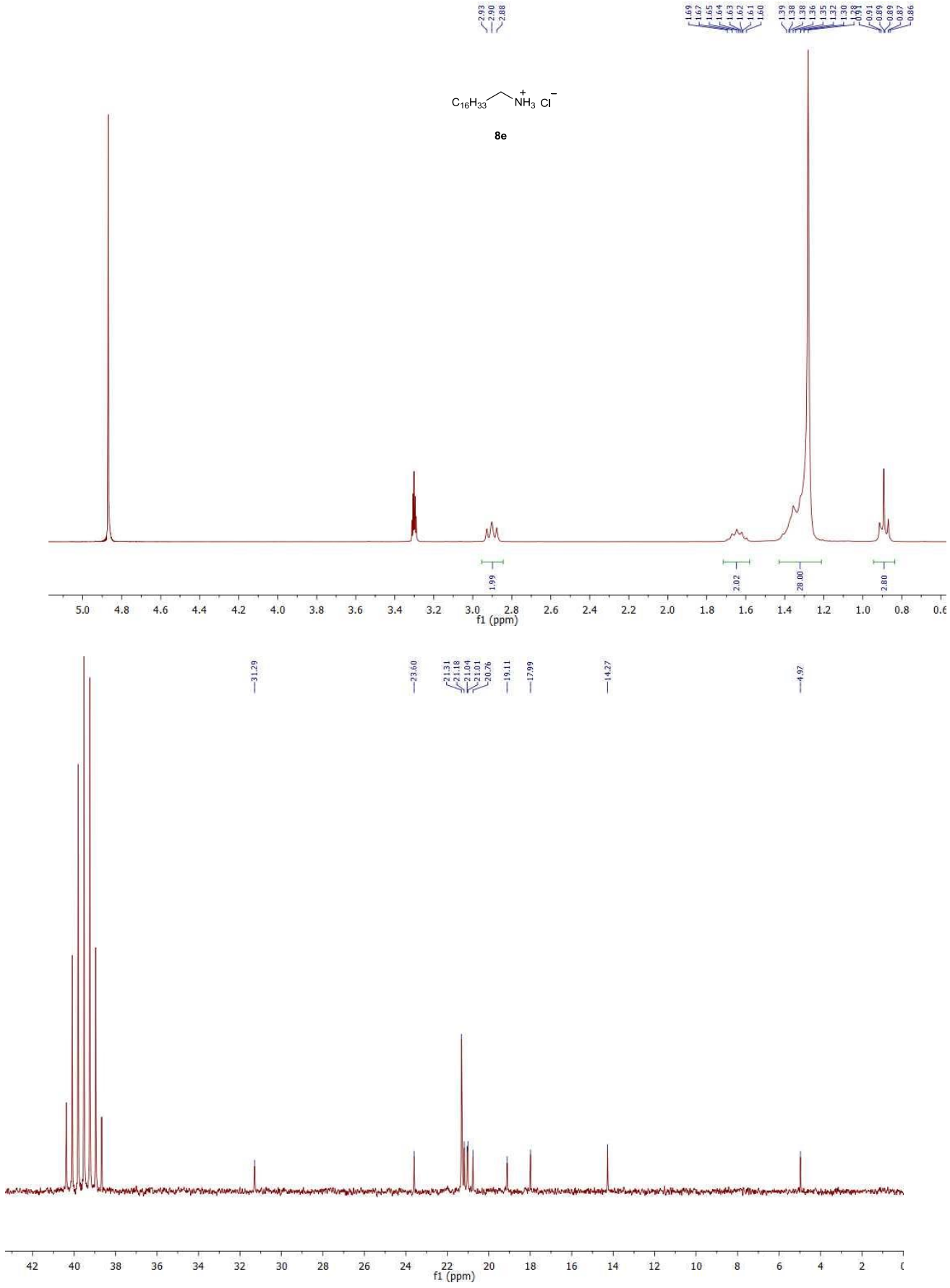
Supplementary Figure 24. ^{1}H and ^{13}C NMR of compound **2s.**



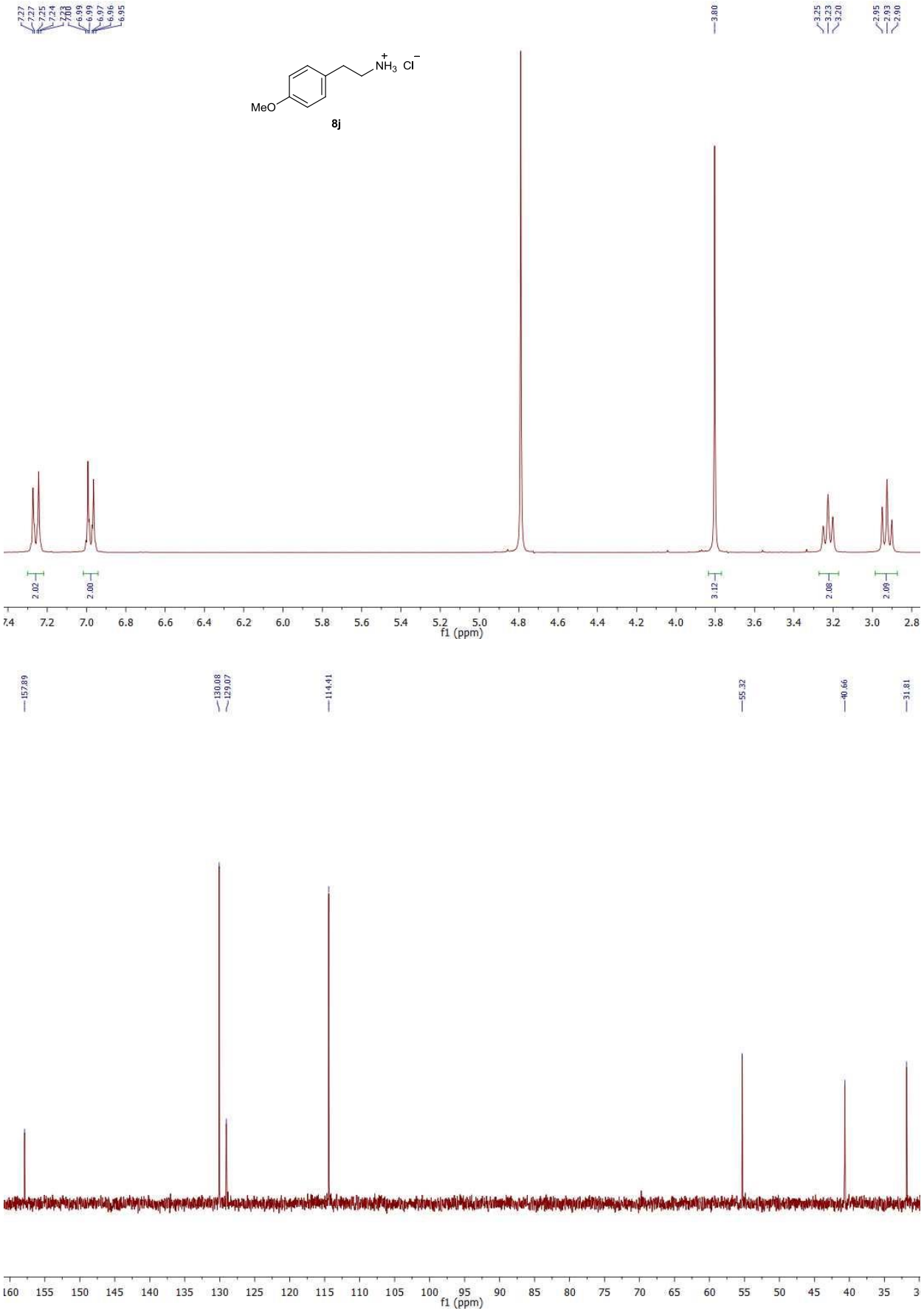
Supplementary Figure 25. ^{1}H and ^{13}C NMR of compound **2x.**



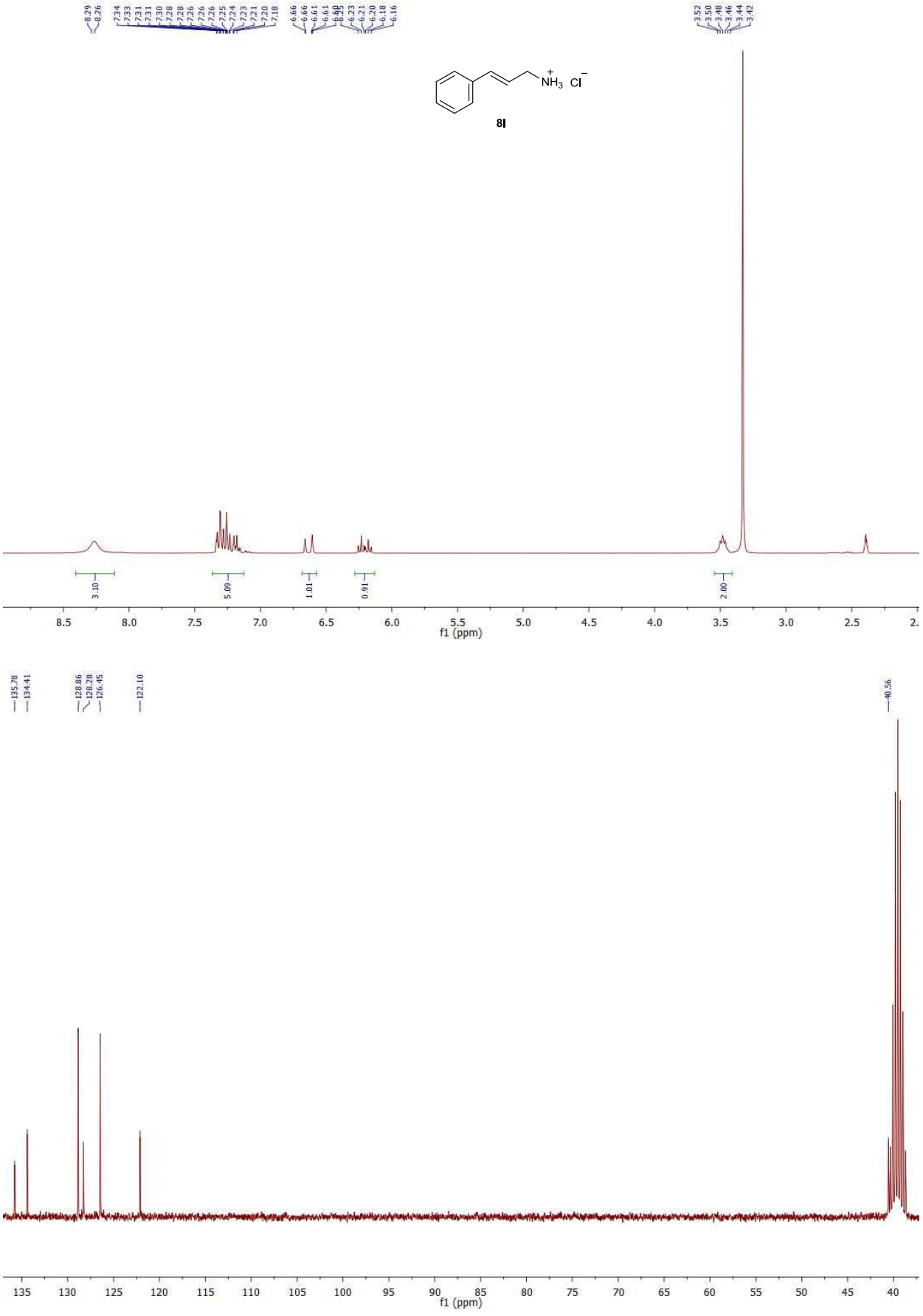
Supplementary Figure 26. ^{1}H and ^{13}C NMR of compound **8a.**



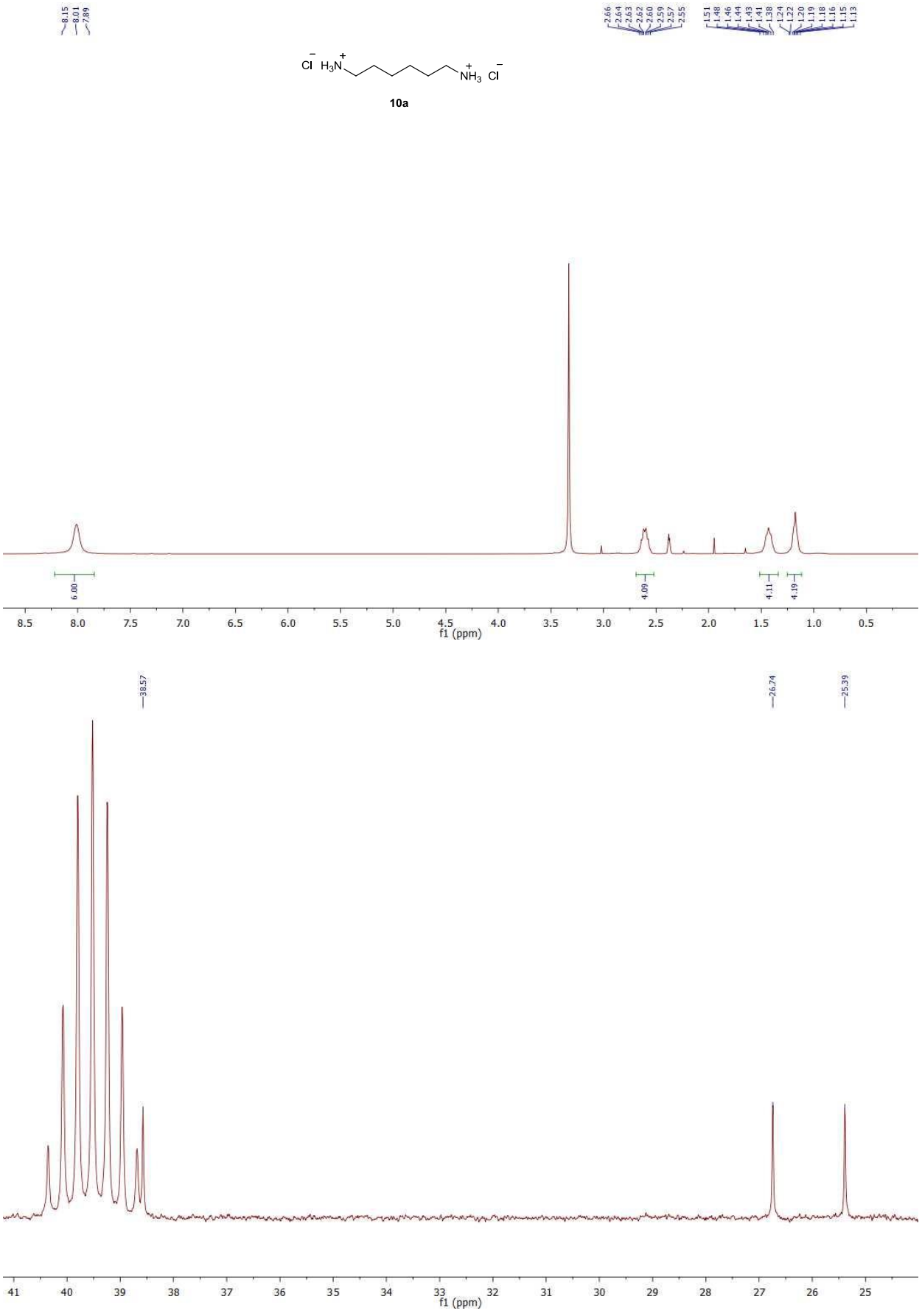
Supplementary Figure 27. ^{1}H and ^{13}C NMR of compound **8e.**



Supplementary Figure 28. ^{1}H and ^{13}C NMR of compound **8j.**



Supplementary Figure 29. ^{1}H and ^{13}C NMR of compound **8l.**



Supplementary Figure 30. ^{1}H and ^{13}C NMR of compound **10a.**

2. Supplementary Methods 1-4

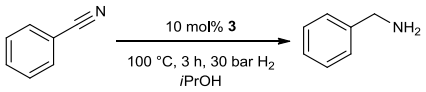
2.1 Computational details

Structure optimizations have been carried out at the B3PW91[71] density functional level of theory with the all-electron TZVP basis set[72] by using the Gaussian09 program package.[73] The B3PW91 functional has been identified suitable for iron carbonyl complexes.[74,75] The optimized geometries are characterized as energy minimums at the potential energy surface from frequency calculations at the same level of theory, i.e.; energy minimum structure has only real frequencies or authentic transition state have only one imaginary vibration mode, which connects the reactant and product. The Gibbs free energies which are used for discussion and comparison are scaled with the thermal correction to Gibbs free energies at 298 K. The bonding patterns of complexes **8** and **9** have been analyzed by using the method of Natural Bond Orbital (NBO) analysis.[76]

2.2 IR details

IR spectra were recorded on an ATR-FTIR spectrometer (Alpha, Bruker). All spectra were measured with 32 scans at 4 cm^{-1} resolution.

For IR investigations, the following reaction was performed before:



Afterwards, the solvent of the reaction mixture was slowly evaporated. The residue was measured to give Supplementary Figure 2b. The complex 3 was measured as a solid (Supplementary Figure 2a). Benzonitrile and benzyl amine were measured purely as reference without any solvent (Supplementary Figure 2c and d). The reaction residue (spectra 2b) shows also full conversion of benzonitrile as the signal at ν = 2228 cm^{-1} was not detected.

2.3 NMR analysis of Me-3 and intermediates

a) Synthesis of [$(CH_3)N((CH_2CH_2)P(CH(CH_3)_2)_2)_2$]

^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.01 (m, 12 H, $^3J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 7.0 Hz, PCH(CH_3)$_2$), 1.04 (m, 12 H, $^3J_{PH}$ = 13.9 Hz, $^3J_{HH}$ = 7.1 Hz, PCH(CH_3)$_2$), 1.57 (m, 4H, $^2J_{PH}$ = 2.8 Hz, PCH_2), 1.59 (m, 4H, $^2J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 7.1 Hz, PCH(CH$_3$)$_2$), 2.20 (s, 3 H, NCH_3), 2.64 (m, 4H, $^3J_{PH}$ = 5.6 Hz, NCH_2); **^{13}C NMR** (100.6 MHz, C_6D_6): δ = 18.99 (d, $^2J_{CP}$ = 9.9 Hz, PCH(*C*H$_3$)$_2$), 20.24 (d, $^1J_{CP}$ = 19.5 Hz, P*C*H$_2$), 20.30 (d, $^2J_{CP}$ = 16.5 Hz, PCH(*C*H$_3$)$_2$), 23.67 (d, $^1J_{CP}$ = 14.0 Hz, P*C*H(CH$_3$)$_2$), 41.75 (s, N(*C*H$_3$)), 56.84 (d, $^2J_{CP}$ = 28.6 Hz, N*C*H$_2$), **^{31}P{^{1}H} NMR** (161.9 MHz, C_6D_6): δ = 1.0 (s, 95.7 %), -11.8 (s, 4.3 %, unknown impurity).

b) Synthesis of {Fe(H)(HBH$_3$)[(CH$_3$)N((CH$_2$CH$_2$)P(CH(CH$_3$)$_2$)$_2$)$_2$]}

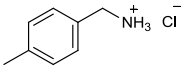
^{1}H NMR (300.1 MHz, C_6D_6): δ = -36.07 (bs, 1 H, Fe*H*HBH$_2$), -23.04 (t, 1 H, Fe*H*, J_{HP} = 53.2 Hz), -12.09 (bs, 1 H, FeH*H*BH$_2$), 0.77-1.49 (overlapped m, 35 H,) 2.38 (m, 2 H), 2.96 (m, 2 H), 4.49 (b, 2 H, FeHHB*H*$_2$) ; **^{13}C NMR** (75.5 MHz, C_6D_6): δ = 17.3 19.1, 19.3, 20.5, 19.8, 21.9, 26.2, 50.1, 65.9; **^{31}P{^{1}H} NMR** (121.0 MHz, C_6D_6): δ = 96.7 (s, 99.6 %), 0.9 (s, 0.4 %, free ligand)

c. Synthesis of {Fe(H)(HBH$_3$)(CO)[(CH$_3$)N((CH$_2$CH$_2$)P(CH(CH$_3$)$_2$)$_2$)$_2$]}

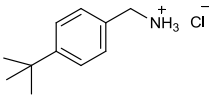
{Fe(H)(HBH$_3$)(CO)[(CH$_3$)N((CH$_2$CH$_2$)P(CH(CH$_3$)$_2$)$_2$)$_2$] (mixture of two isomers, major isomer ~ 90%, minor isomer 10% according to ^{31}P{^{1}H} NMR) Because of extensive overlap only a few peaks could be assigned in the ^{1}H NMR. **^{1}H NMR** (300.1 MHz, C_6D_6): δ = -20.08 (t, 1 H, Fe*H*, J_{HP} = 51.4 Hz, min), -19.51(t, 1 H, Fe*H*, J_{HP} = 52.1 Hz, maj), - 2.62 ppm (b, 4 H, Fe*H*B*H*$_3$, maj + min), 0.88-0.95 (m, PCH(C*H*$_3$)$_2$, maj), 1.08-1.14 (m, PCH(C*H*$_3$)$_2$, maj), 1.18-1.25 (m, PCH(C*H*$_3$)$_2$, maj), 1.67-1.75 (m, PCH(C*H*$_3$)$_2$, maj), 1.97 (s, NC*H*$_3$, maj), 2.13 (s, NC*H*$_3$, min), 2.92-2.99 (m, 2H, maj), 3.22 (b, 2H, min); **^{13}C NMR** (75.5 MHz, C_6D_6): δ (maj) = 18.12, 19.22, 20.62, 21.02, 25.37, 25.53, 28.14, 30.71, 50.65, 65.56 (*The peak of coordinated CO could not be detected, however evidence of its presence was obtained by means of IR*); **^{31}P{^{1}H} NMR** (121.0 MHz, C_6D_6): δ = 92.9 (s, maj); 97.2 (s, min). **IR ATR**: ῡ [cm^{-1}] 2369 (m, ν BH), 2327 (m, ν BH), 2054, (br, ν BH), 1851 (m, ν CO), 1901 (s, ν CO), 1050 (s, δ BH$_3$). **ESI-HRMS** (*m/z, pos*): Calculated for [C17H40FeNP2] 376.198; found: 376.19808 [M-BH$_4$-CO]$^+$.

2.4 Analysis of ^{1}H and ^{13}C NMR spectra

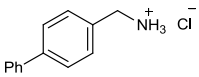
Aromatic and heteroaromatic products 2:



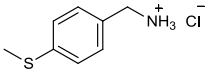
***p*-tolylmethanammonium chloride (2b). ^{1}H NMR** (300.1 MHz, DMSO-d$_6$): δ = 2.22 (s, 3 H), 3.86 (s, 3 H), 7.08-7.16 (m, 2 H), 7.25-7.33 (m, 2 H), 8.39 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d$_6$) δ = 20.8, 42.0, 129.0, 129.1, 131.1, 137.8. **GCMS-EI** (70eV): m/z (%) = 121 (M$^+$, 33), 120 (86), 106 (58), 105 (24), 103 (100), 93 (36), 91 (37), 79 (14), 77 (24), 36 (12). **HRMS** (ESI-TOF, m/z) calcd. for $C_8H_{11}N$ (M+H)$^+$ 122.0964; found 122.0965.



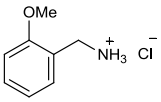
(4-(*tert*-butyl)phenyl)methanammonium chloride (2c). ^{1}H NMR (300.1 MHz, DMSO-d$_6$): δ = 1.17 (s, 9 H), 3.77-3.92 (m, 2 H), 7.29-7.36 (m, 4 H), 8.43 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d$_6$) δ = 31.1, 34.4, 41.9, 125.4, 128.9, 131.2, 151.0. **GCMS-EI** (70eV): m/z (%) = 163 (M$^+$, 6), 162 (18), 148 (44), 132 (13), 131 (13), 115 (10), 106 (100), 91 (21), 79 (11), 77 (12), 30 (17). **HRMS** (EI, m/z) calcd. for $C_{11}H_{17}N$ (M+)$^+$ 164.1434; found 164.1436.



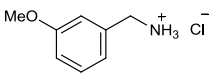
[1,1'-biphenyl]-4-ylmethanammonium chloride (2d). ^{1}H NMR (300.1 MHz, DMSO-d$_6$): δ = 3.95 (s, 2 H), 7.20-7.75 (m, 9 H), 8.51 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d$_6$) δ = 41.9, 126.7, 126.8, 129.1, 129.7, 133.3, 139.6, 140.2. **GCMS-EI** (70eV): m/z (%) = 183 (M$^+$, 56), 182 (100), 167 (31), 166 (78), 165 (51), 155 (39), 154 (26), 153 (41), 152 (60), 151 (18), 128 (13), 115 (14), 106 (38), 77 (27), 63 (11), 51 (13), 30 (22). **HRMS** (EI, m/z) calcd. for $C_{13}H_{12}N$ (M)$^+$ 182.0964; found 182.0963.



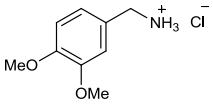
(4-(methylthio)phenyl)methanammonium chloride (2e).[77] **^{1}H NMR** (300.1 MHz, DMSO-d_6): δ = 2.44 (s, 3 H), 4.03 (s, 2 H), 7.23-7.30 (m, 2 H), 7.30-7.38 (m, 2 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 15.2, 127.6, 130.6, 130.8, 141.9.



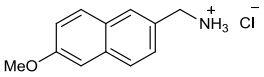
(2-methoxyphenyl)methanammonium chloride (2g). ^{1}H NMR (300.1 MHz, DMSO-d_6): δ = 3.73 (s, 3 H), 3.80-3.89 (m, 2 H), 6.34-6.91 (m, 1 H), 6.94-7.00 (m, 1 H), 7.22-7.36 (m, 2 H), 8.30 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 37.6, 55.6, 111.0, 120.3, 121.7, 130.3, 130.3, 157.2. **GCMS-EI** (70eV): m/z (%) = 137 (M^+, 67), 136 (100), 122 (15), 121 (36), 120 (22), 119 (11), 108 (10), 107 (13), 106 (39), 104 (22), 93 (10), 91 (30), 78 (24), 77 (25), 65 (13), 63 (20), 51 (12), 36 (23). **HRMS** (ESI-TOF, m/z) calcd. for $C_8H_{11}NO$ $(M+H)^+$ 138.0913; found 138.0911.



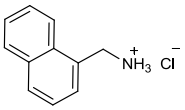
(3-methoxyphenyl)methanammonium chloride (2h). ^{1}H NMR (300.1 MHz, DMSO-d_6): δ = 2.60 (s, 3 H), 2.98-3.10 (m, 2 H), 5.96-6.04 (m, 1 H), 6.09-6.16 (m, 1 H), 6.20-6.27 (m, 1 H), 6.33-6.42 (m, 1 H), 7.65 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 42.1, 55.3, 144.0, 114.5, 121.0, 129.7, 135.6, 159.4. **GCMS-EI** (70eV): m/z (%) = 137 (M^+, 58), 136 (100), 122 (13), 121 (19), 120 (12), 94 (33), 93 (19), 92 (13), 91 (15), 79 (15), 78 (21), 77 (37), 67 (10), 66 (18), 65 (20), 64 (14), 63 (21), 51 (16), 50 (13), 39 (16), 30 (34). **HRMS** (EI, m/z) calcd. for $C_8H_{11}NO$ $(M)^+$ 137.0835; found 137.0831.



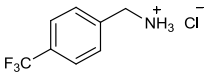
(3,4-dimethoxyphenyl)methanammonium chloride (2i). ^{1}H NMR (300.1 MHz, DMSO-d_6): δ = 3.66 (d, *J* = 6.0 Hz, 6 H), 3.77-3.86 (m, 2 H), 6.81-6.94 (m, 2 H), 7.13-7.18 (m, 1 H), 8.39 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 30.8, 42.1, 44.7, 55.6, 111.6, 113.0, 121.5, 126.4, 148.7, 148.9. **GCMS-EI** (70eV): m/z (%) = 167 (M^+, 53), 166 (46), 152 (14), 151 (27), 150 (11), 139 (10), 137 (14), 136 (100), 124 (23), 121 (11), 109 (13), 107 (17), 93 (11), 92 (16), 80 (18), 79 (17), 77 (14), 65 (15), 53 (10), 51 (15), 30 (16). **HRMS** (EI, m/z) calcd. for $C_9H_{13}NO_2$ $(M)^+$ 167.0941; found 167.0942.



(6-methoxynaphthalen-2-yl)methanammonium chloride (2j). ^{1}H NMR (300.1 MHz, DMSO-d_6): δ = 3.76 (s, 3 H), 4.00 (s, 2 H), 7.08 (dd, *J* = 9.2 Hz, 1 H), 7.20-7.26 (m, 1 H), 7.50 (dd, *J* = 8.5 Hz, 1 H), 7.65-7.78 (m, 2 H), 7.81 (s, 1 H), 8.53 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 42.4, 55.3, 105.9, 119.2, 127.1, 127.2, 128.0, 128.0, 129.2, 129.4, 139.1, 157.7. **GCMS-EI** (70eV): m/z (%) = 188 (11), 187 (M^+, 91), 186 (100), 172 (12), 171 (32), 159 (17), 156 (15), 144 (29), 143 (13), 128 (27), 127 (17), 116 (14), 115 (39), 114 (13). **HRMS** (EI, m/z) calcd. for $C_{12}H_{13}NO$ $(M)^+$ 187.0992; found 187.0993.

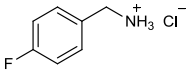


naphthalen-1-ylmethanammonium chloride (2k). ^{1}H NMR (300.1 MHz, DMSO-d_6): δ = 4.44 (m, 2 H), 7.40-7.62 (m, 4 H), 7.84-7.94 (m, 2 H), 8.02-8.09 (m, 1 H), 8.59 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 39.1 (peak from DEPT spectrum), 123.4, 125.3, 126.2, 126.7, 127.2, 128.6, 129.0, 129.9, 130.6, 133.1. **GCMS-EI** (70eV): m/z (%) = 157 (M^+, 80), 156 (100), 129 (52), 128 (46), 127 (32), 126 (14), 115 (15), 77 (13), 30 (10). **HRMS** (EI, m/z) calcd. for $C_{11}H_{10}N$ $(M-H)^+$ 156.0808; found 156.0805.

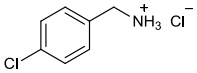


(4-(trifluoromethyl)phenyl)methanammonium (2l). ^{1}H NMR (300.1 MHz, DMSO-d_6): δ = 4.06 (s, 2 H), 7.64-7.80 (m, 4 H), 8.69 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 41.7, 124.2 (q, *J* = 273 Hz),

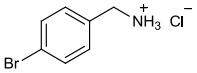
125.4 (q, *J* = 3.6 Hz), 128.9 (q, *J* = 32 Hz), 129.8, 138.8. **GCMS-EI** (70eV): m/z (%) = 175 (M^+, 51), 174 (100), 156 (20), 145 (11), 127 (45), 106 (58), 77 (11), 75 (11), 50 (10), 30 (27). **HRMS** (ESI-TOF, m/z) calcd. for $C_8H_8F_3N$ $(M+H)^+$ 176.0682; found 176.0680.



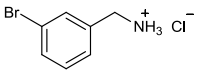
(4-fluorophenyl)methanammonium chloride (2m). **^{1}H NMR** (300.1 MHz, DMSO-d_6): δ = 3.91 (s, 2 H), 7.10-7.25 (m, 2 H), 7.45-7.57 (m, 2 H), 8.56 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 41.4, 115.4 (d, *J* = 10.4 Hz), 130.5 (d, *J* = 3.1 Hz), 131.4 (d, *J* = 8.4 Hz), 162.1 (d, *J* = 122.0 Hz). **GCMS-EI** (70eV): m/z (%) = 125 (M^+, 32), 124 (100), 109 (26), 105 (45), 97 (36), 96 (13), 95 (15), 83 (11), 77 (14), 75 (21), 51 (12), 50 (14), 30 (24). **HRMS** (ESI-TOF, m/z) calcd. for C_7H_8FN $(M+H)^+$ 126.0714; found 126.0712.



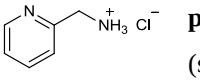
(4-chlorophenyl)methanammonium chloride (2n). **^{1}H NMR** (300.1 MHz, DMSO-d_6): δ = 3.92 (s, 2 H), 7.34-7.94 (m, 4 H), 8.46 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 41.5, 128.6, 131.1, 133.1, 133.2. **GCMS-EI** (70eV): m/z (%) = 142 (15), 141 (M^+, 11), 140 (47), 125 (11), 106 (100), 89 (12), 79 (12), 78 (11), 77 (33), 75 (19), 74 (12), 51 (16), 50 (17), 30 (23). **HRMS** (EI, m/z) calcd. for C_7H_7ClN $(R=NH_2)^+$ 140.0262; found 140.0263.



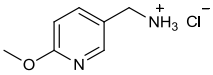
(4-bromophenyl)methanammonium chloride (2o). **^{1}H NMR** (300.1 MHz, DMSO-d_6): δ = 3.91 (s, 2 H), 7.37-7.44 (m, 2 H), 7.49-7.56 (m, 2 H), 8.58 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 41.4, 121.7, 131.3, 131.4, 133.6. **GCMS-EI** (70eV): m/z (%) = 186 (22), 184 (M^+, 23), 106 (100), 89 (10), 79 (14), 78 (15), 77 (23), 75 (10), 51 (12), 50 (16), 30 (17). **HRMS** (ESI-TOF, m/z) calcd. for C_7H_8BrN $(M+H)^+$ 185.9913; found 185.9913.



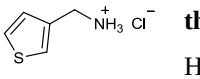
(3-bromophenyl)methanammonium chloride (2p). **^{1}H NMR** (300.1 MHz, D_2O): δ = 4.16 (s, 2 H), 7.31-7.44 (m, 2 H), 7.56-7.69 (m, 2 H). **^{13}C NMR** (75.5 MHz, D_2O): δ = 42.4, 122.2, 127.6, 130.8, 131.6, 132.1, 134.7. **GCMS-EI** (70eV): m/z (%) = 186 (23), 184 (M^+, 24), 106 (100), 79 (13), 78 (12), 77 (22), 50 (10), 30 (13). **HRMS** (ESI-TOF, m/z) calcd. for C_7H_8BrN $(M+H)^+$ 185.9913; found 185.9913.



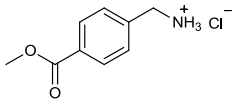
pyridin-2-ylmethanammonium chloride (welches substrat?) (2q). **^{1}H NMR** (300.1 MHz, D_2O) δ = 4.50 (s, 2 H), 7.76-7.90 (m, 2 H), (tt, *J* = 7.9 Hz, *J* = 7.9 Hz, 1 H), 8.73 (dd, *J* = 5.6 Hz, 1 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ = 41.0, 124.8, 124.9, 141.2, 145.7, 151.4. **HRMS** (ESI-TOF, m/z) calcd. for C_7H_8BrN $(M+H)^+$ 109.0760; found 109.0763.



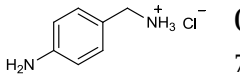
(6-methoxypyridin-3-yl)methanammonium chloride (2r). **^{1}H NMR** (300.1 MHz, D_2O) δ = 4.18 (s, 3 H), 4.30 (s, 2 H), 7.49 (d, *J* = 9.0 Hz, 1 H), 8.32-8.50 (m, 2 H). **^{13}C NMR** (75.5 MHz, D_2O) δ = 39.1, 57.8, 111.4, 123.2, 140.3, 148.2, 161.8. **GCMS-EI** (70eV): m/z (%) = 138 (M^+, 52), 137 (65), 122 (15), 110 (100), 108 (11), 106 (11), 80 (10), 78 (16), 67 (10), 53 (11), 52 (10), 51 (10), 42 (13), 30 (12). **HRMS** (EI, m/z) calcd. for $C_7H_{10}NO$ $(M)^+$ 138.0788; found 138.0786.



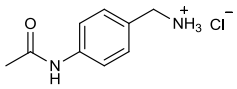
thiophen-3-ylmethanammonium (2t). **^{1}H NMR** (300.1 MHz, D_2O) δ = 3.98 (s, 2 H), 7.25 (dd, *J* = 5.0 Hz, 1 H), 7.54-7.58 (m, 1 H), 7.58-7.63 (m, 1 H), 8.46 (s, 3 H). **^{13}C NMR** (75.5 MHz, D_2O) δ = 37.3, 125.1, 127.0, 128.1, 134.8. **GCMS-EI** (70eV): m/z (%) = 114 (19), 113 (M^+, 100), 112 (79), 97 (30), 85 (52), 69 (13), 45 (20), 39 (13), 38 (10), 36 (20). **HRMS** (EI, m/z) calcd. for C_5H_7NS $(M)^+$ 113.0294; found 113.0290.



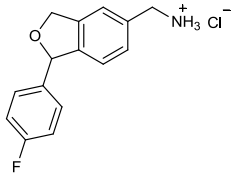
(4-(methoxycarbonyl)phenyl)methanammonium chloride (2u). **^{1}H NMR** (300.1 MHz, D_2O), δ = 3.91 (s, 3H), 4.25 (s, 2H), 7.48-7.60 (m, 2H), 7.98-8.11 (m, 2H) (10% *iso*-propylester present in NMR, signals are not assigned here). **^{13}C NMR** (75.5 MHz, D_2O): δ = 42.6, 52.7, 128.8, 130.0, 137.8, 168.7. NMR shows also *iso*-propylester signals not assigned here. **GCMS-EI** (70eV): m/z (%) = 165 (M^+, 7), 164 (33), 150 (27), 134 (29), 133 (68), 132 (21), 106 (100), 105 (57), 104 (22), 91 (11), 89 (17), 79 (18), 77 (33), 36 (15). **HRMS** (EI, m/z) calcd. for $C_9H_{11}NO_2$ (R=NH_2)$^+$ 164.0706; found 164.0708.



(4-aminophenyl)methanammonium chloride (2v). **^{1}H NMR** (300.1 MHz, D_2O), δ = 4.22 (s, 2 H), 7.42-7.48 (m, 2H), 7.54-7.61 (m, 2H). **^{13}C NMR** (75.5 MHz, D_2O): δ = 42.3, 123.6, 130.6, 130.9, 133.5. **GCMS-EI** (70eV): m/z (%) = 122 (M^+, 89), 121 (100), 16 (68), 94 (40), 93 (14), 78 (16), 77 (22), 65 (10), 63 (15), 36 (16). **HRMS** (EI, m/z) calcd. for $C_7H_{10}BrN$ $(M)^+$ 122.0839; found 122.0835.

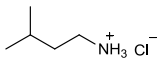


(4-acetamidophenyl)methanammonium chloride (2w).[78] **^{1}H NMR** (300.1 MHz, D_2O), δ = 2.14 (s, 3 H), 4.14 (s, 2 H), 7.40-7.48 (m, 4 H). **^{13}C NMR** (75.5 MHz, D_2O): δ = 22.8, 42.6, 122.2, 129.3, 129.7, 137.6, 173.0.

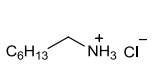


(1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-yl)methanammonium chloride (2x). **^{1}H NMR** (300.1 MHz, MeOD), δ = 4.14 (s, 2 H), 5.09-5.23 (m, 1 H), 5.24-5.39 (m, 1 H), 6.16 (s, 1H), 6.97-7.13 (m, 3 H), 7.27-7.48 (m, 4 H). **^{13}C NMR** (75.5 MHz, MeOD): δ = 44.1, 73.8, 86.5, 116.3 (d, *J* = 22.0 Hz), 123.0, 124.0, 129.7, 129.86 (d, *J* = 8.1 Hz), 134.4, 139.5 (d, *J* = 3.3 Hz), 141.5, 144.4, 164.0 (d, *J* = 122.5 Hz). **HRMS** (EI, m/z) calcd. for $C_{15}H_{13}ONF$ (R=NH_2)$^+$ 242.0976; found 242.0971.

aliphatic products 5:

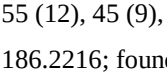


3-methylbutan-1-ammonium chloride (8a). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 0.77 (d, *J* = 6.8 Hz, 6 H), 1.30-1.41 (m, 2 H), 1.45-1.61 (m, 1 H), 2.58-2.72 (m, 2 H), 7.97 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 22.2, 25.1, 35.8, 37.2. **GCMS-EI** (70eV): m/z (%) = 87 (M^+, 3), 70 (6), 55 (4), 44 (6), 42 (6), 41 (10), 39 (10), 30 (100). **HRMS** (ESI-TOF, m/z) calcd. for $C_5H_{13}rN$ $(M+H)^+$ 88.1121; found 88.1125.



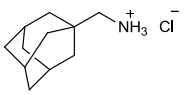
heptan-1-ammonium chloride (8c). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 0.71-0.82 (m, 3 H), 1.08-1.27 (m, 8 H), 138-1.54 (m, 2 H), 2.54-2.70 (m, 2 H), 7.99 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 14.0, 22.0, 25.9, 27.0, 28.3, 31.1, 38.7. **GCMS-EI** (70eV): m/z (%) = 115 (M^+, 1), 86 (3), 56 (4), 55 (5), 45 (5), 44 (7), 43 (6), 42 (6), 41 (14), 39 (9), 30 (100), 29 (10). **HRMS** (ESI-TOF, m/z) calcd. for $C_7H_{17}BrN$ $(M+H)^+$ 116.1434; found 116.1438.

dodecan-1-ammonium chloride (8d). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 0.71-0.81 (m, 3 H), 1.08-1.23 (m, 18 H), 1.38-1.53 (m, 2 H), 2.56-2.71 (m, 2 H), 7.96 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 14.0, 22.1, 25.9, 27.0, 28.6, 28.8, 28.9, 29.0, 29.1, 29.1, 31.4, 38.8. **GCMS-EI** (70eV): m/z (%) = 185 (M^+, 1), 100 (4), 86 (7), 69 (5), 57 (4), 56 (8), 55 (12), 45 (9), 44 (12), 43 (15), 42 (6), 41 (245), 39 (7), 30 (100), 29 (11). **HRMS** (ESI-TOF, m/z) calcd. for $C_{12}H_{27}N$ $(M+H)^+$ 186.2216; found 186.2216.

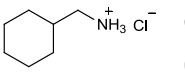


heptadecan-1-ammonium chloride (8e). **^{1}H NMR** (300.1 MHz, MeOD), δ = 0.84-0.94 (m, 3 H), 1.22-1.44 (m, 28 H), 1.57-1.71 (m, 2 H), 2.86-2.94 (m, 2 H). **^{13}C NMR** (75.5 MHz, MeOD): δ = 14.5, 23.7, 27.5, 28.6, 30.2, 30.5, 30.5,

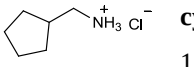
30.7, 30.8 (big peak), 33.1, 40.8. **GCMS-EI** (70eV): m/z (%) = 255 (M^+, 2), 100 (4), 86 (8), 83 (4), 72 (4), 57 (8), 56 (8), 55 (16), 45 (8), 44 (18), 43 (21), 42 (6), 41 (21), 39 (4), 30 (100), 29 (9). **HRMS** (ESI-TOF, m/z) calcd. for $C_{17}H_{37}N$ $(M+H)^+$ 256.2999; found 256.2999.



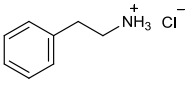
adamantan-1-ylmethanammonium chloride (8f). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 1.39-1.65 (m, 12 H), 1.83-1.91 (m, 3 H), 2.34-2.40, 7.91 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 27.4, 31.6, 36.1, 38.9, 49.9. **GCMS-EI** (70eV): m/z (%) = 165 (M^+, 23), 136 (11), 135 (100), 107 (12), 93 (25), 91 (14), 79 (31), 77 (14), 30 (19). **HRMS** (ESI-TOF, m/z) calcd. for $C_{11}H_{19}N$ $(M+H)^+$ 166.1590; found 166.1590.



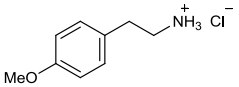
cyclohexylmethanammonium chloride (8g). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 0.74-0.92 (m, 2 H), 0.96-1.20 (m, 3 H), 1.42-1.74 (m, 6 H), 2.46-2.60 (m, 2 H), 8.09 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 25.1, 25.7, 29.8, 35.4, 44.4. **HRMS** (ESI-TOF, m/z) calcd. for $C_7H_{15}N$ $(M+H)^+$ 114.1277; found 114.1278.



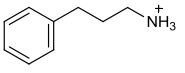
cyclopentylmethanammonium chloride (8h). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 1.03-1.22 (m, 2 H), 1.34-1.57 (m, 4 H), 1.59-1.72 (m, 2 H), 1.93-2.09 (m, 1 H), 2.56-2.69 (m, 2 H), 7.99 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 24.7, 29.9, 37.6, 40.4, 43.6. **GCMS-EI** (70eV): m/z (%) = 99 (M^+, 7), 67 (9), 56 (9), 41 (16), 39 (18), 32 (6), 30 (100). **HRMS** (ESI-TOF, m/z) calcd. for $C_6H_{13}N$ $(M+H)^+$ 100.1121; found 100.1124.



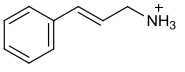
2-phenylethanammonium chloride (8i). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 2.72-2.95 (m, 4 H), 7.06-7.24 (m, 5 H), 8.14 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 33.0, 39.8, 126.7, 128.7, 128.7, 137.5. **GCMS-EI** (70eV): m/z (%) = 121 (M^+, 6), 92 (11), 91 (37), 89 (7), 65 (22), 63 (10), 51 (12), 50 (7), 39 (13), 30 (100). **HRMS** (ESI-TOF, m/z) calcd. for $C_8H_{11}N$ $(M+H)^+$ 122.0964; found 122.0963.



2-(4-methoxyphenyl)ethanammonium chloride (8j). **^{1}H NMR** (300.1 MHz, D_2O), δ = 2.93 (t, *J* = 7.4 Hz, *J* = 7.4 Hz, 2 H), 3.23 (t, *J* = 7.4 Hz, *J* = 7.4 Hz, 2 H), 3.80 (s, 3 H), 6.94-7.02 (m, 2 H), 7.21-7.30 (m, 2 H). **^{13}C NMR** (75.5 MHz, D_2O): δ = 31.8, 40.7, 55.3, 114.4, 129.1, 130.1, 157.9. **GCMS-EI** (70eV): m/z (%) = 151 (M^+, 4), 123 (8), 122 (100), 121 (63), 107 (9), 91 (15), 89 (7), 79 (7), 78 (27), 77 (23), 65 (7), 52 (9), 51 (11), 39 (6), 30 (56). **HRMS** (ESI-TOF, m/z) calcd. for $C_9H_{13}NO$ $(M+H)^+$ 152.1070; found 152.1068.

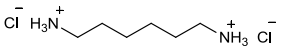


3-phenylpropan-1-ammonium chloride (8k). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 1.69-1.82 (m, 2 H), 2.53 (t, *J* = 7.7 Hz, *J* = 7.7 Hz, 2 H), 2.57-2.70 (m, 2 H), 7.03-7.13 (m, 3 H), 7.14-7.22 (m, 2 H), 8.06 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 28.8, 31.9, 38.3, 126.1, 128.3, 128.5, 141.0. **GCMS-EI** (70eV): m/z (%) = 135 (M^+, 4), 119 (9), 118 (100), 117 (62), 115 (7), 104 (11), 103 (15), 92 (14), 91 (47), 79 (10), 78 (17), 77 (25), 65 (21), 63 (11), 51 (21), 50 (10), 39 (15), 30 (98). **HRMS** (ESI-TOF, m/z) calcd. for $C_9H_{13}N$ $(M+H)^+$ 136.1121; found 136.1124.

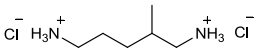


***(E)*-3-phenylprop-2-en-1-ammonium chloride (8l)**. **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ 3.42-3.54 (m, 2 H), 6.13-6.27 (m, 1 H), 6.57-6.94 (m, 1 H), 7.08-7.37 (m, 5 H), 8.26 (s, 3 H). **^{13}C NMR** (75.5 MHz, DMSO-d_6): δ = 40.6, 122.1, 126.5, 128.3, 128.9, 134.4, 135.8. **GCMS-EI** (70eV): m/z (%) = 133 (M^+, 100), 132 (82), 130 (12), 117 (18), 116 (16), 115 (50), 91 (14), 78 (17), 77 (15), 63 (17), 56 (21), 51 (10), 36 (15). **HRMS** (ESI-TOF, m/z) calcd. for $C_9H_{13}N$ $(M+H)^+$ 136.1121; found 136.1124.

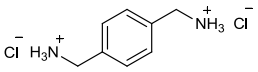
diamine products 7:



hexane-1,6-diammonium chloride (10a). **^{1}H NMR** (300.1 MHz, DMSO-d_6), δ = 1.19-1.29 (m, 4 H), 1.48 (p, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 7.2 Hz, 4 H), 2.62-2.75 (m, 4 H), 7.90 (s, 6 H). **^{13}C NMR** (75.5 MHz, DMSO-$_{d6}$): δ = 25.4, 26.8, 38.6. **GCMS-EI** (70eV): m/z (%) = 117 ($[M+H]^+$, 2), 87 (15), 56 (20), 30 (100). **HRMS** (ESI-TOF, m/z) calcd. for $C_6H_{16}N_2$ $(M+H)^+$ 117.1386; found 117.1390.



2-methylpentane-1,5-diammonium chloride (10b). **^{1}H NMR** (300.1 MHz, D_2O), δ = 0.97 (d, *J* = 6.4 Hz, 3 H), 1.12-1.28 (m, 1 H), 1.64-1.77 (m, 1 H), 1.80-1.96 (m, 3 H), 2.57-2.67 (m, 1 H), 2.84-2.94 (m, 1 H), 3.27-3.40 (m, 2 H). **^{13}C NMR** (75.5 MHz, MeOD): δ = 19.0, 23.4, 30.0, 31.7, 45.1, 51.2.



1,4-phenylenedimethanammonium chloride (10c). **^{1}H NMR** (300.1 MHz, D_2O), δ = 4.20 (s, 4 H), 7.51 (s, 4 H), 7.62-7.67 (m, 2 H), 7.96-8.03 (m, 2 H). **^{13}C NMR** (75.5 MHz, D_2O): δ = 42.6, 129.5, 133.4, 195.8. **GCMS-EI** (70eV): m/z (%) = 135 (M^+, 10), 118 (40), 106 (100), 91 (45), 79 (28), 51 (8).

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