

Supporting Information

for

**New metathesis catalyst bearing chromanyl moieties
at the N-heterocyclic carbene ligand**

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**Experimental procedures of the testing of the new catalyst and copies of ^1H and ^{13}C NMR spectra
of new compounds**

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Testing of the catalyst 9

General CM procedure for allylbenzene and ethyl acrylate (Table 1, entries 1, 2)

- a) To a mixture of allylbenzene (0.2 mmol) and ethyl acrylate (0.4 mmol) in CH₂Cl₂ (1.5 mL) a solution of catalyst **1**, **2**, **3** or **9** (2.5 mol %) in CH₂Cl₂ (0.5 mL) was added. The resulting mixture was stirred at 0 °C under argon atmosphere and controlled by ¹H NMR after 1, 2 and 3 hours.
- b) To a mixture of allylbenzene (0.2 mmol) and ethyl acrylate (0.4 mmol) in CH₂Cl₂ (1.5 mL) a solution of catalyst **3** or **9** (1 mol %) in CH₂Cl₂ (0.5 mL) was added. The resulting mixture was stirred at 0 °C under argon atmosphere and analysed by ¹H NMR after 3 hours.

The spectral data obtained for CM product are consistent with those given in the literature [1].

Yield was determined by comparison of integration of CM product proton signal (dd, 2H) at 3.53 ppm or (dt, 1H) at 5.83 ppm and SM product of allylbenzene ((*E*)-1,4-diphenylbut-2-ene) proton signal (m, 2H) at 5.67–5.71 ppm and/or substrate (allylbenzene, since acrylate was used in excess) proton signal (m, 1H) at 5.81–6.17 ppm. Amount of protons corresponding to these signals was taken into account in the calculations.

General CM procedure for hex-5-enyl acetate and methyl vinyl ketone (Table 1, entry 3)

To a mixture of the hex-5-enyl acetate (0.2 mmol) and methyl vinyl ketone (0.4 mmol) in CH₂Cl₂ (1.5 mL) a solution of catalyst **1**, **2**, **3** or **9** (1 mol %) in CH₂Cl₂ (0.5 mL) was added. The resulting mixture was stirred at 0 °C under argon atmosphere and controlled by ¹H NMR after 3 hours. The spectral data obtained for CM product are consistent with those given in the literature [2].

Yield was determined by comparison of integration of CM product proton signal (dt, 1H) at 6.07 ppm and SM product of hex-5-enyl acetate ((*E*)-dec-5-ene-1,10-diol diacetate) proton signal (m, 2H) at 5.40–5.42 ppm and/or substrate (hex-5-enyl acetate, since ketone was used in excess) proton signal (m, 1H) at 5.74–5.84 ppm. Amount of protons corresponding to these signals was taken into account in the calculations.

General CM procedure for hex-5-enyl acetate and acrylonitrile (Table 1, entry 4)

To a mixture of the hex-5-enyl acetate (0.2 mmol) and acrylonitrile (0.4 mmol) in CH₂Cl₂ (1.5 mL) a solution of catalyst **1**, **2**, **3** or **9** (1 mol %) in CH₂Cl₂ (0.5 mL) was added. The resulting mixture was stirred at 0 °C for 1 h under argon atmosphere and analysed by ¹H NMR. The spectral data obtained for CM product are consistent with those given in the literature [3].

Yield was determined by comparison of integration of CM product proton signal (d, 1H) at 5.35 ppm and SM product of hex-5-enyl acetate ((*E*)-dec-5-ene-1,10-diol diacetate) proton signal (m, 2H) at 5.40–5.42 ppm and/or substrate (hex-5-enyl acetate, since nitrile was used in excess) proton signal (m, 1H) at 5.74–5.84 ppm. Amount of protons corresponding to these signals was taken into account in the calculations.

General CM procedure for selected alkenes with (Z)-but-2-ene-1,4-diol diacetate (Table 2, entries 1–3)

To a mixture of the alkene (0.2 mmol) and (*Z*)-but-2-ene-1,4-diol diacetate (0.4 mmol) in CH₂Cl₂ (1.5 mL) a solution of catalyst **1**, **2** or **9** (2.5 mol %) in CH₂Cl₂ (0.5 mL) was added. The resulting mixture was stirred at 20 °C for 3 h under argon atmosphere. The crude product was

purified by FC (hexane – ethyl acetate v/v 50:1) and analysed by ^1H NMR. The spectral data obtained for CM products are consistent with those given in the literature [4].

General CM procedure for allyloxybenzene and hex-5-enyl acetate (Table 2, entry 4)

To a mixture of the alkenes (0.2 mmol, both) in CH_2Cl_2 (1.5 mL) a solution of catalyst **1**, **2** or **9** (2.5 mol %) in CH_2Cl_2 (0.5 mL) was added. The resulting mixture was stirred at 20 °C for 3 h under argon atmosphere. The crude product was purified by FC (hexane – ethyl acetate v/v 20:1) and analysed by ^1H NMR. The spectral data obtained for CM product are consistent with those given in the literature [4].

General RCM procedure for diethyl diallylmalonate (Table 3, entry 1)

To a solution of the alkene (0.2 mmol) in CH_2Cl_2 (1.5 mL) a solution of catalyst **1**, **2** or **9** (1 mol %) in CH_2Cl_2 (0.5 mL) was added. The resulting mixture was stirred at room temperature for 60 min under argon atmosphere. The crude product was analysed by ^1H NMR. The spectral data obtained for RCM product are consistent with those given in the literature [5].

General RCM procedure for diethyl allylmethylmalonate (Table 3, entry 2)

To a solution of the alkene (0.2 mmol) in CH_2Cl_2 (1.5 mL) a solution of catalyst **1**, **2** or **9** (1 mol %) in CH_2Cl_2 (0.5 mL) was added. The resulting mixture was stirred at room temperature for 60 min under argon atmosphere. The crude product was analysed by ^1H NMR. The spectral data obtained for RCM product are consistent with those given in the literature [5].

General RCM procedure for diethyl dimethylmalonate (Table 3, entry 3)

To a solution of alkene (0.2 mmol) in toluene (2 mL) a solution of catalyst **1**, **2** or **9** (5 mol %) in toluene (1 mL) was added. The resulting mixture was stirred at 80 °C for 16 h under argon atmosphere. The crude product was analysed by ^1H NMR. The spectral data obtained for RCM product are consistent with those given in the literature [5].

General CM procedure for diene and alkene (Table 4, entries 1–4)

To the solution of ethyl (2*E*,4*E/Z*)-3-methylhexa-2,4-dienoate or (2*E*,4*E*)-hexa-2,4-dienoate (0.36 mmol) and a catalyst **1**, **2** or **9** (10 mol %) in dry CH_2Cl_2 or toluene (0.5 mL) the solution of alkene (0.12 mmol) in dry DCM or toluene (0.5 mL) was added dropwise. The reaction mixture was stirred at 45 °C under argon atmosphere for 16 hours. Then the mixture was concentrated in vacuo and purified directly by silica gel chromatography using hexane/ethyl acetate as eluent. The diastereomeric ratio was determined by GC/MS or NMR analysis. The spectral data obtained for compounds: ethyl (2*E*,4*E*)-9-acetoxy-3-methylnona-2,4-dienoate [6] (entry 1, product A), ethyl (2*E*,4*E*)-3-methyl-5-phenylpenta-2,4-dienoate [7] (entry 2, product A), ethyl (2*E*,4*E*)-3-methyl-6-oxohepta-2,4-dienoate [8] (entry 3, product A), ethyl (2*E*,4*E*)-9-acetoxynona-2,4-dienoate [9] (entry 4, product A) and ethyl 7-acetoxyhept-2-enoate [10] (entry 4, product B) are consistent with those given in the literature.

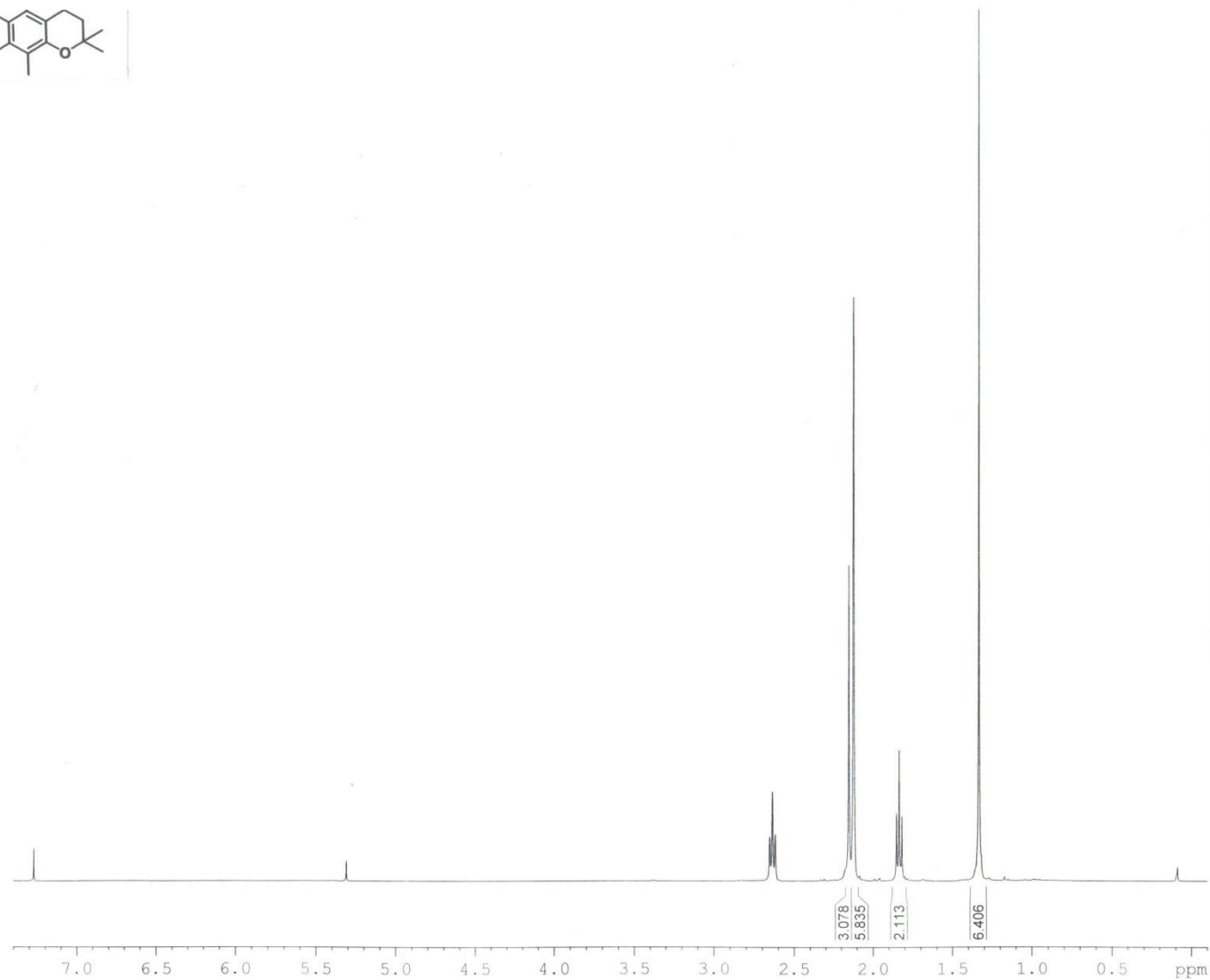
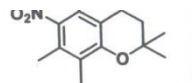
In case of reaction between (2*E*,4*E*)-hexa-2,4-dienoate and hex-5-enyl acetate (entry 4) yield calculated from ^1H NMR spectrum of isolated mixture of inseparable products **A** and **B** by integration of product A proton signal (dd) at 7.26 ppm and product B proton signal (dt) at 6.95 ppm.

General CM procedure for polyene and diene (Scheme 4)

To the solution of a polyene (2.44×10^{-2} mmol) and a catalyst **1**, **2** or **9** (15 mol %) in dry toluene (0.3 mL) ethyl (2*E*,4*Z/E*)-3-methylhexa-2,4-dienoate (9.76×10^{-2} mmol) was added dropwise. The reaction mixture was stirred at room temperature for 96 hours under argon atmosphere. Then the mixture was analysed by HPLC and purified by semipreparative HPLC. The spectral data obtained for CM products: ethyl retinoate and ethyl 12'-apo- β -caroten-12'-oate are consistent with those given in the literature [11].

Copies of NMR spectra of new compounds

¹H NMR spectrum of 6-nitro-2,2,5,7,8-pentamethylchromane (11)



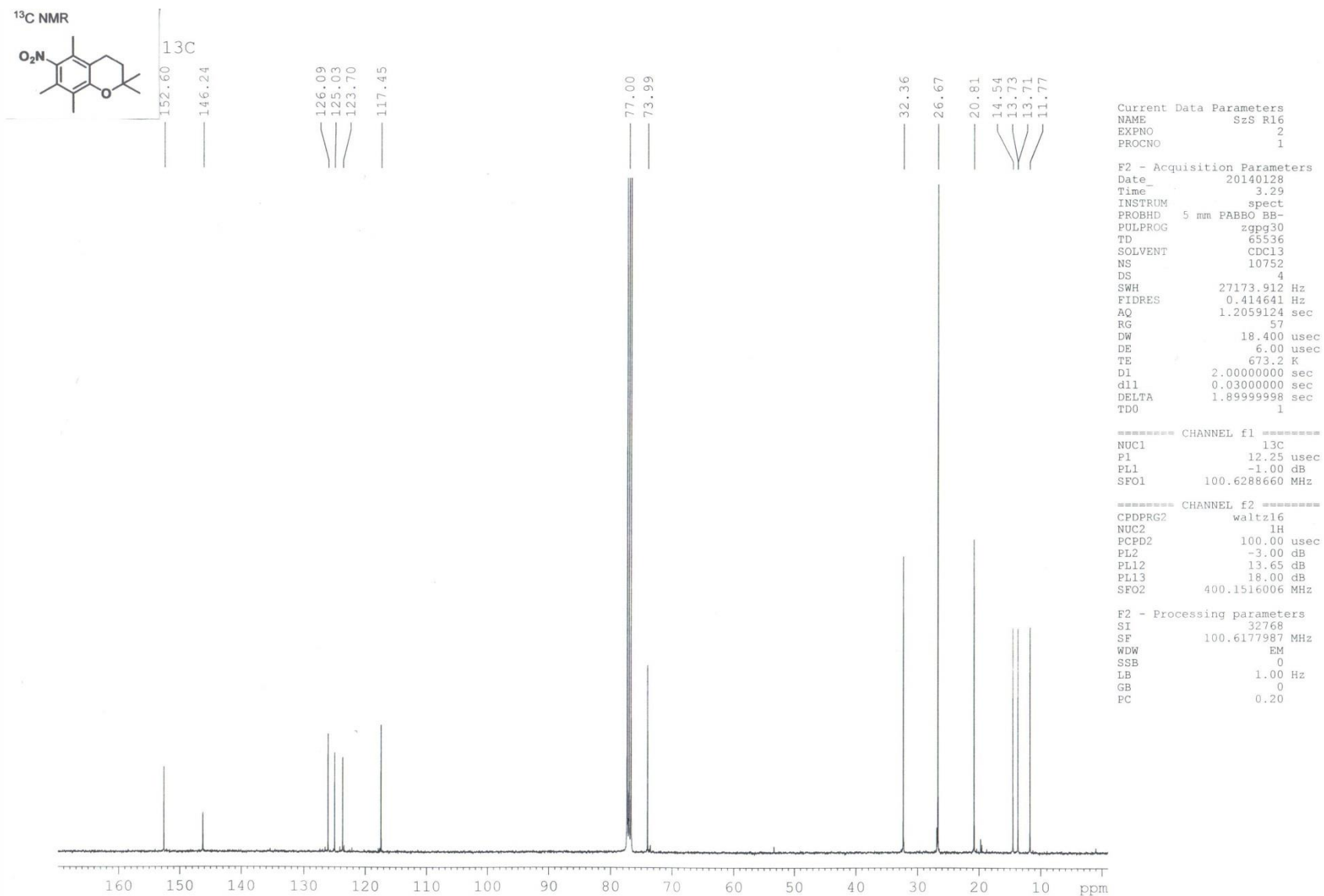
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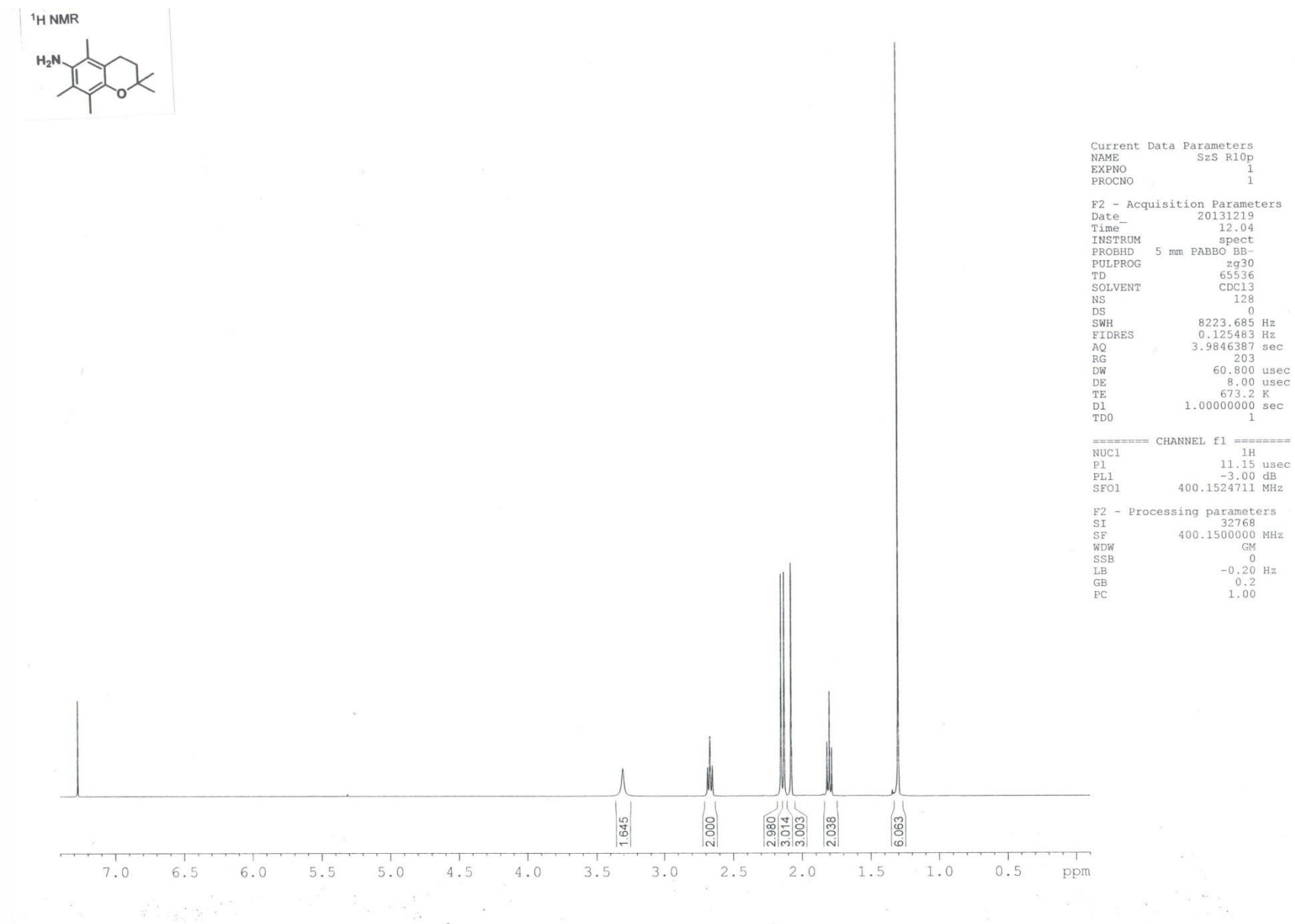
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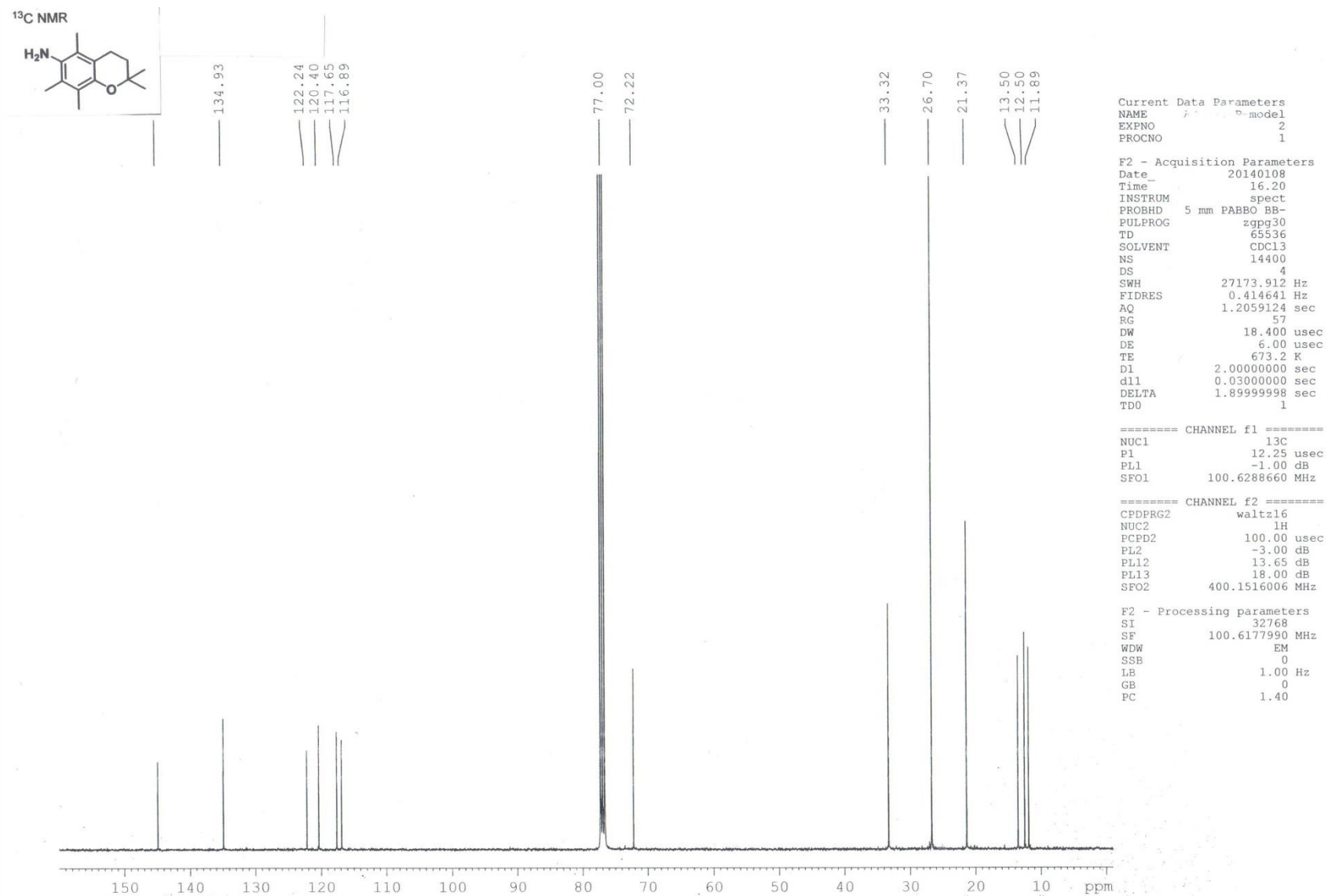
¹³C NMR spectrum of 6-nitro-2,2,5,7,8-pentamethylchromane (11)



¹H NMR spectrum of 2,2,5,7,8-pentamethylchromanyl-6-amine (**12**)

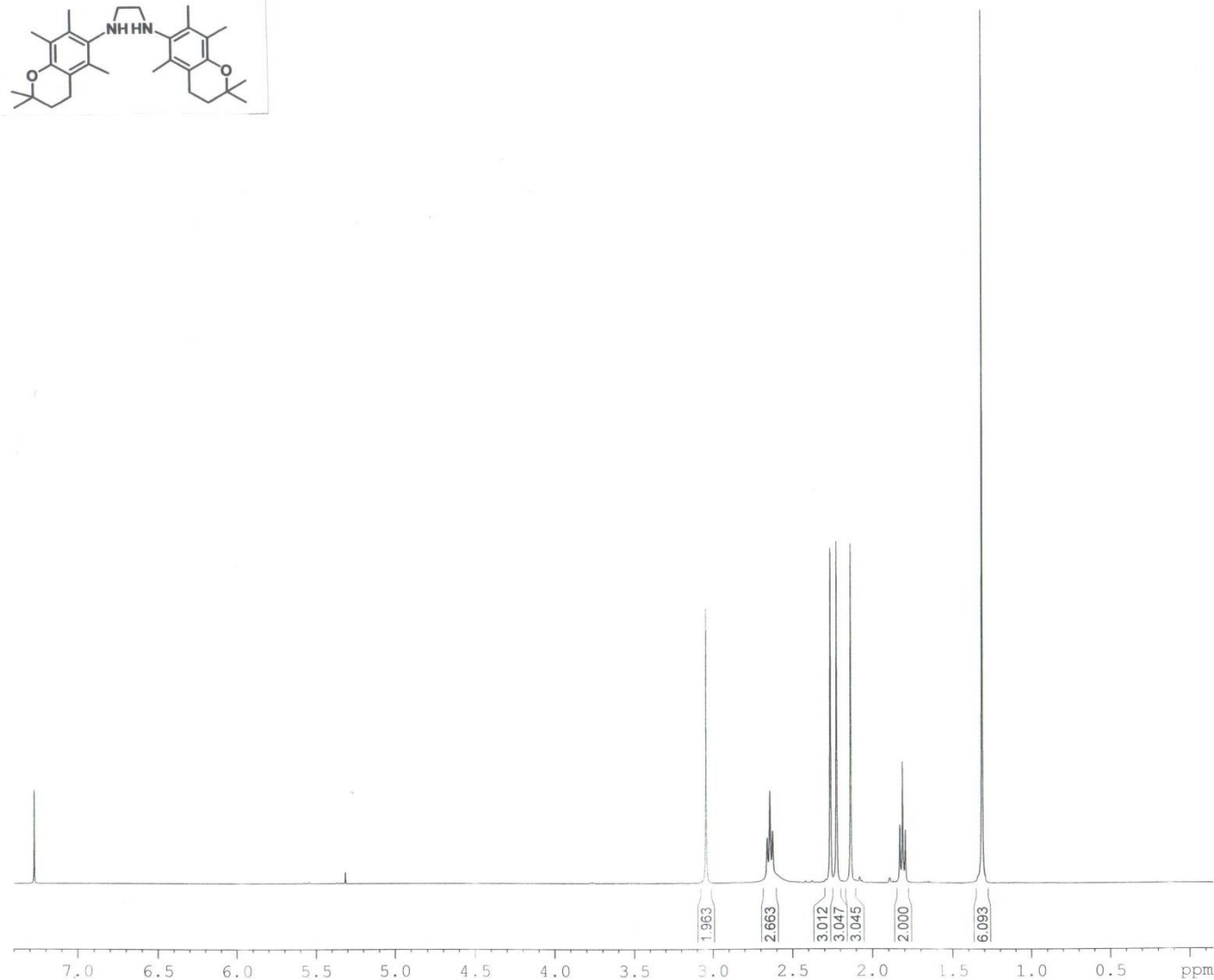
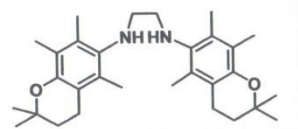


¹³C NMR spectrum of 2,2,5,7,8-pentamethylchromanyl-6-amine (**12**)



¹H NMR spectrum of *N,N*-bis(2,2,5,7,8-pentamethylchroman-6-yl)ethane-1,2-diamine (**13**)

¹H NMR



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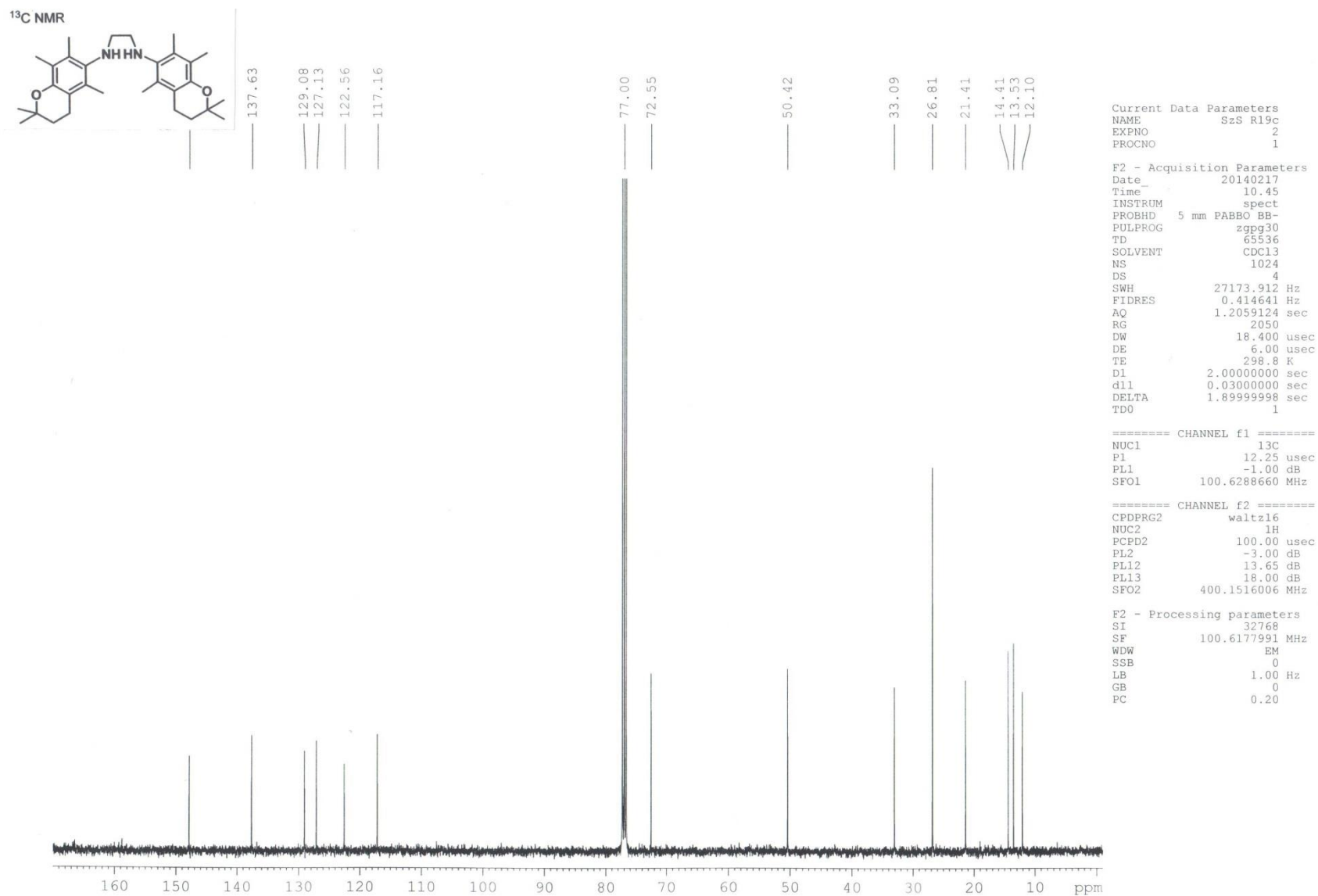
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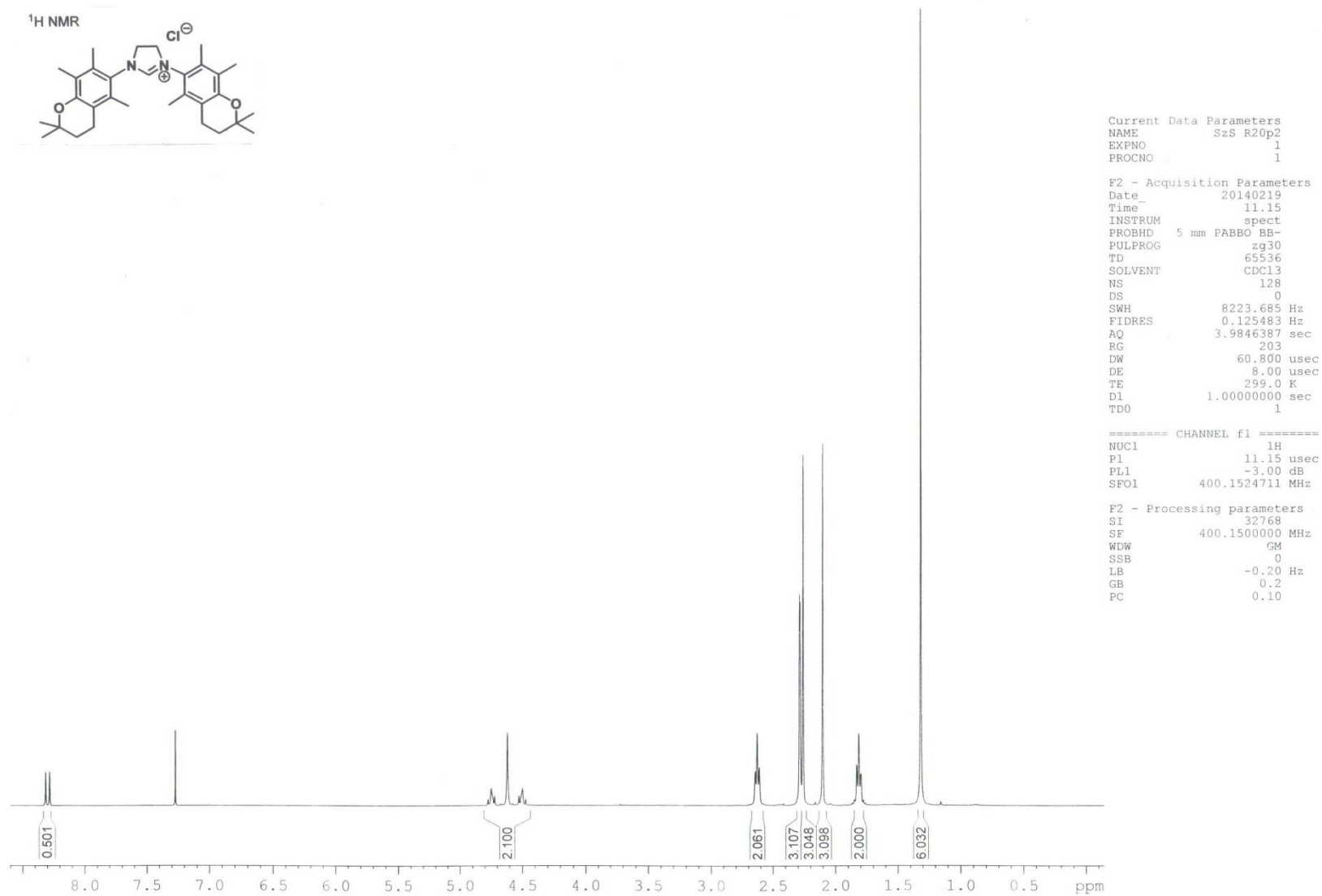
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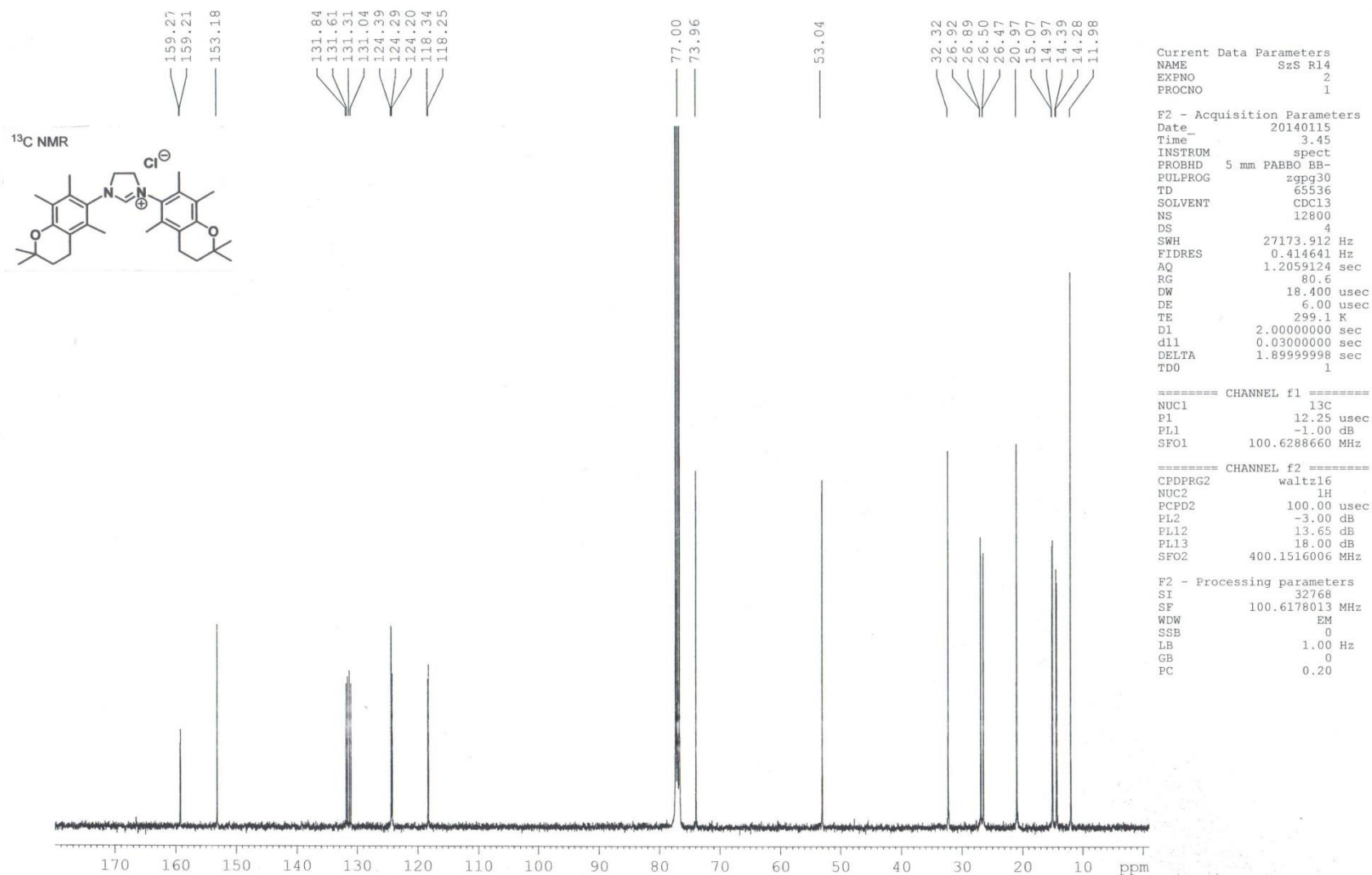
^{13}C NMR spectrum of *N,N*-bis(2,2,5,7,8-pentamethylchroman-6-yl)ethane-1,2-diamine (**13**)



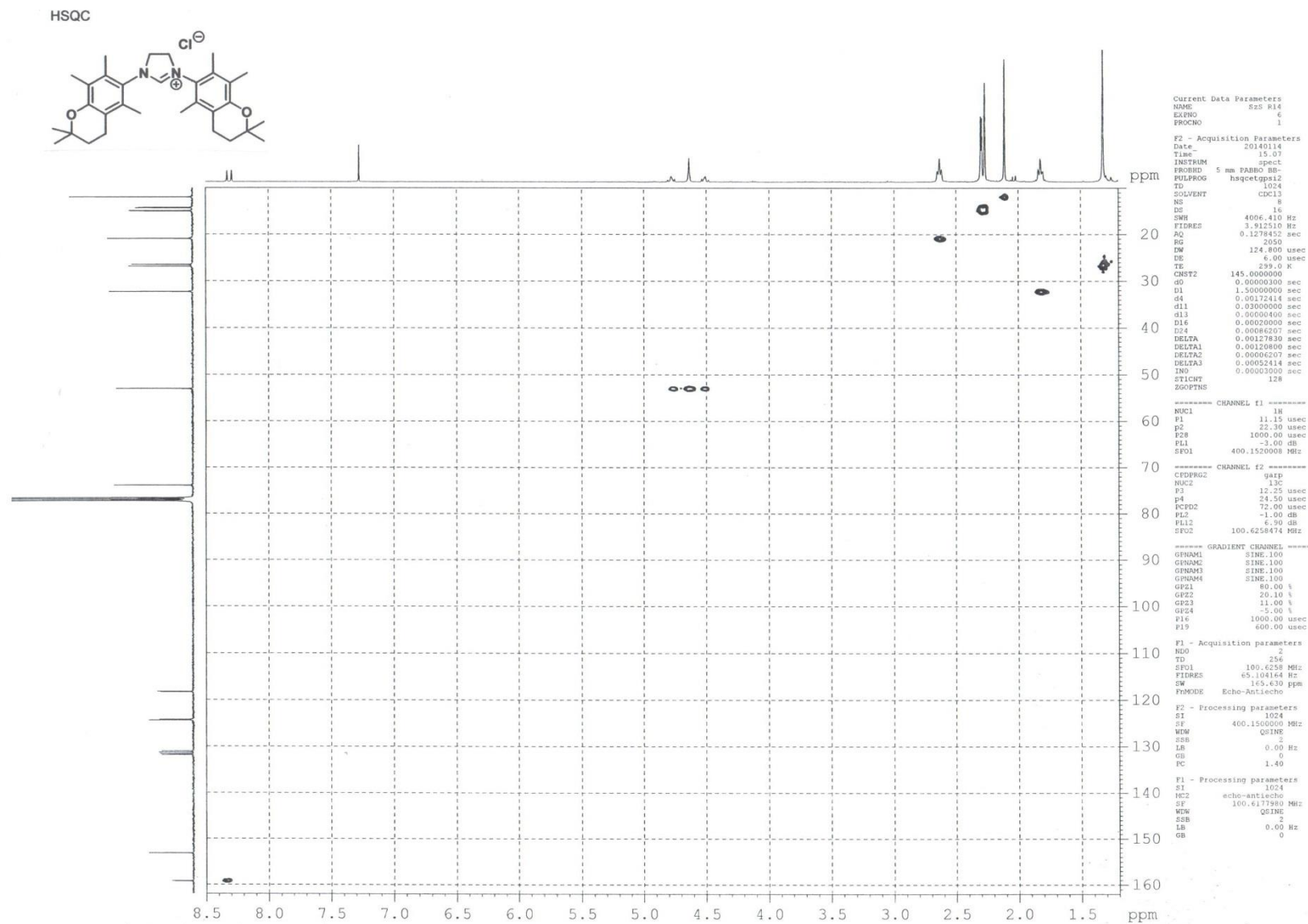
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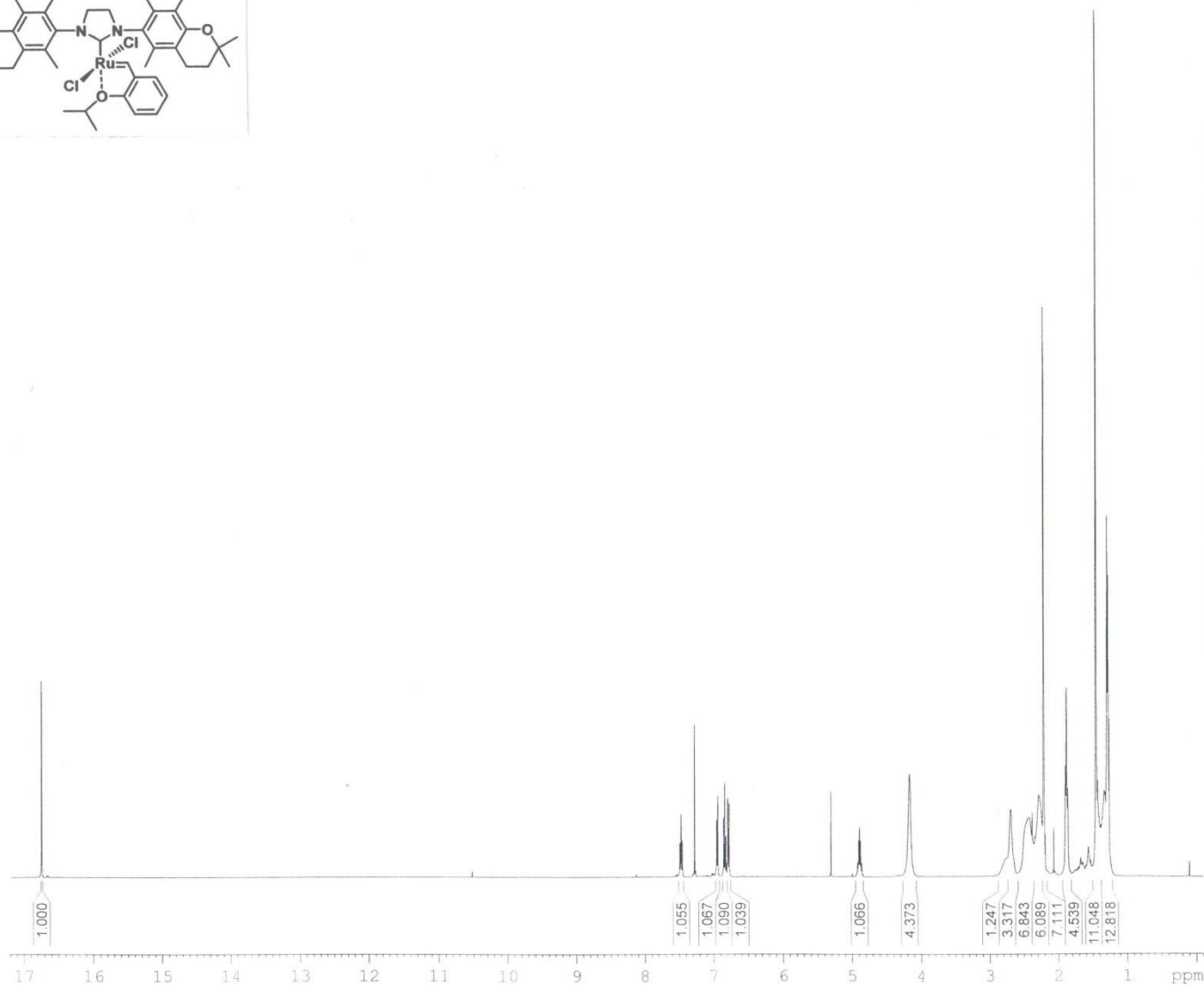
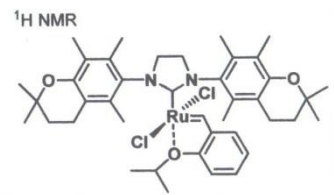
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HSQC spectrum of 1,3-bis(2,2,5,7,8-pentamethylchroman-6-yl)-4,5-dihydro-1H-imidazol-3-ium chloride (**14**)



¹H NMR spectrum of the catalyst **9**



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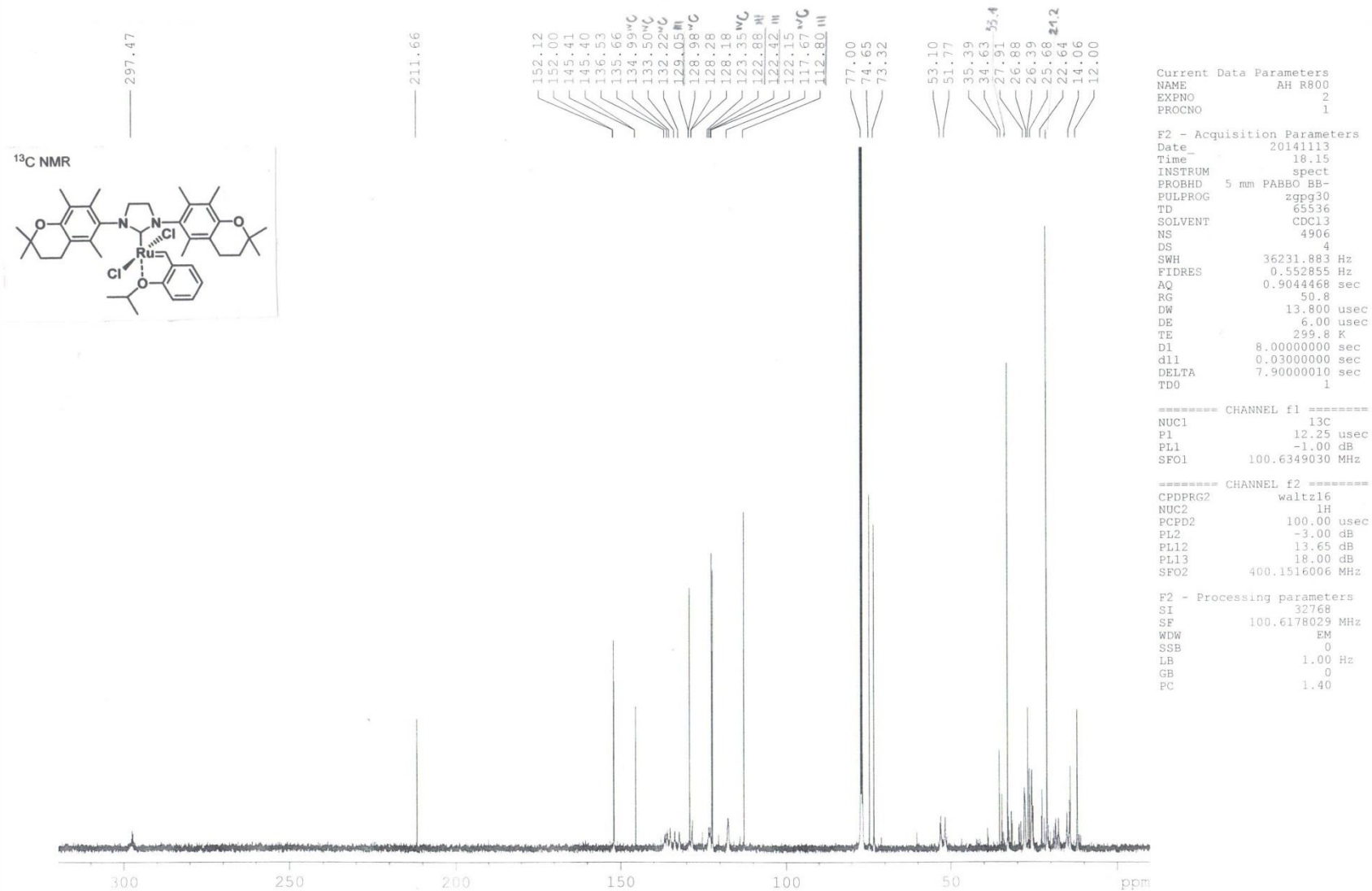
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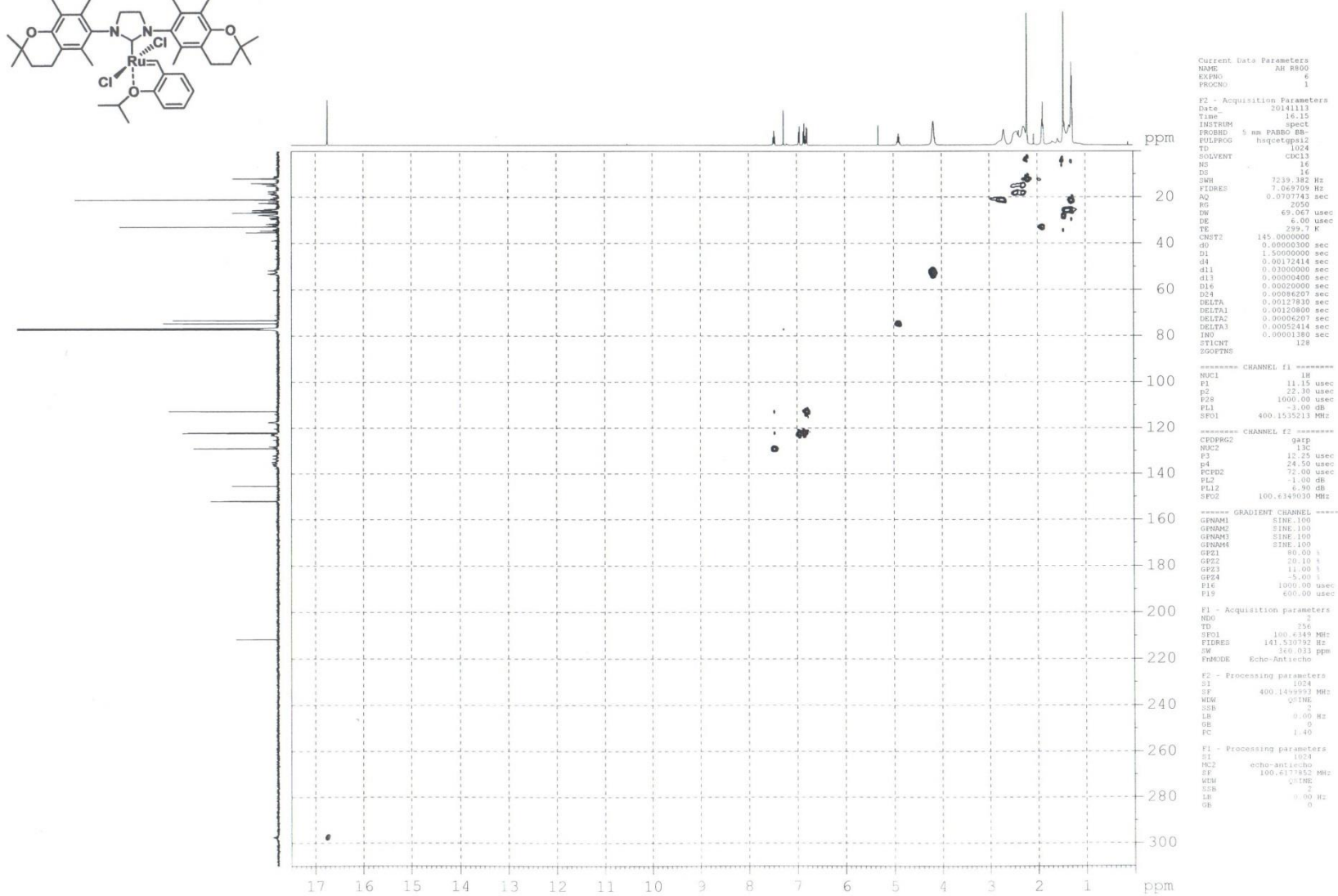
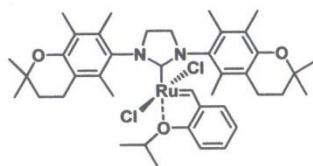
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¹³C NMR spectrum of the catalyst **9**



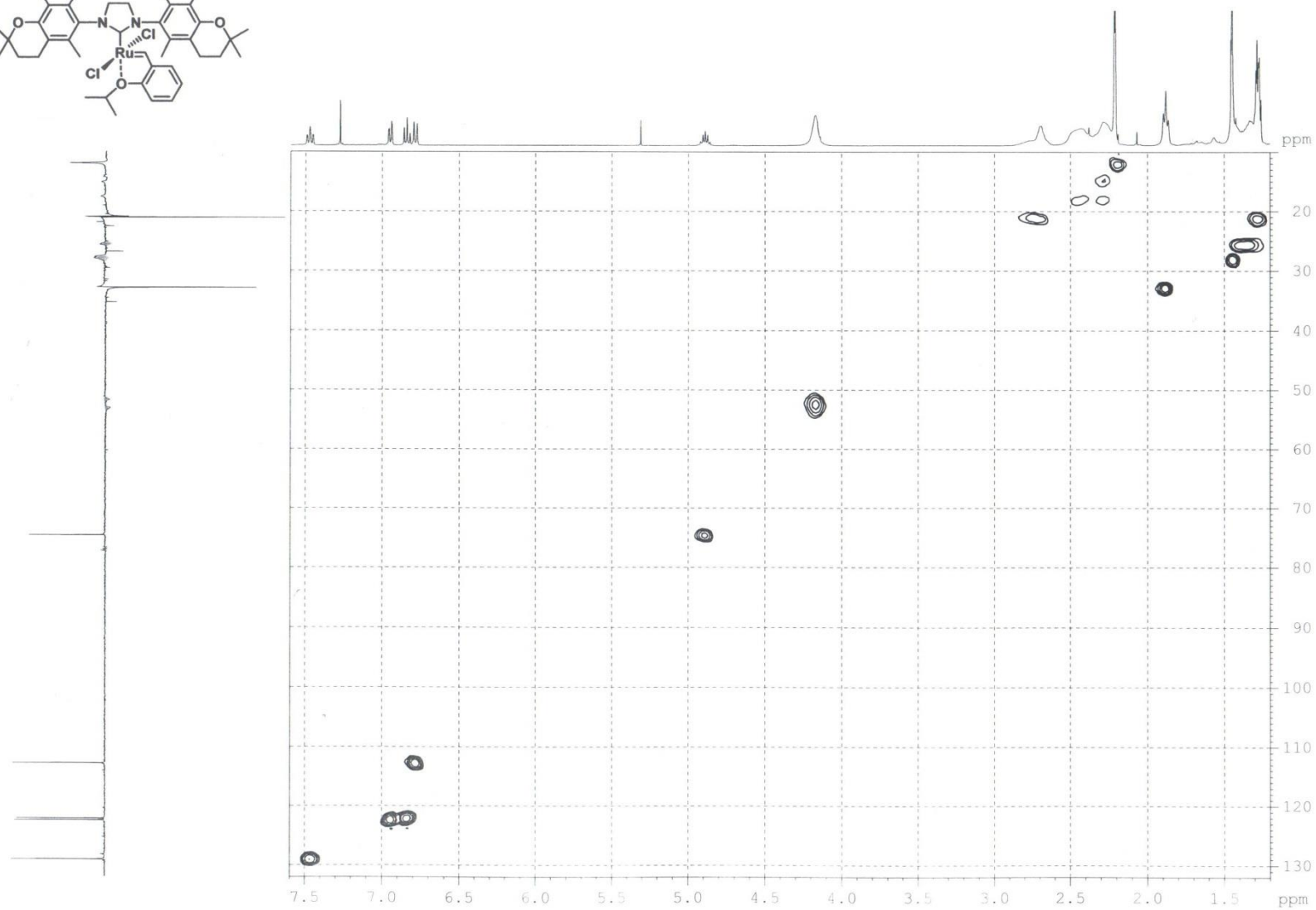
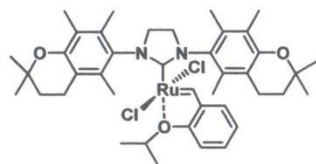
HSQC spectrum of the catalyst **9**

HSQC



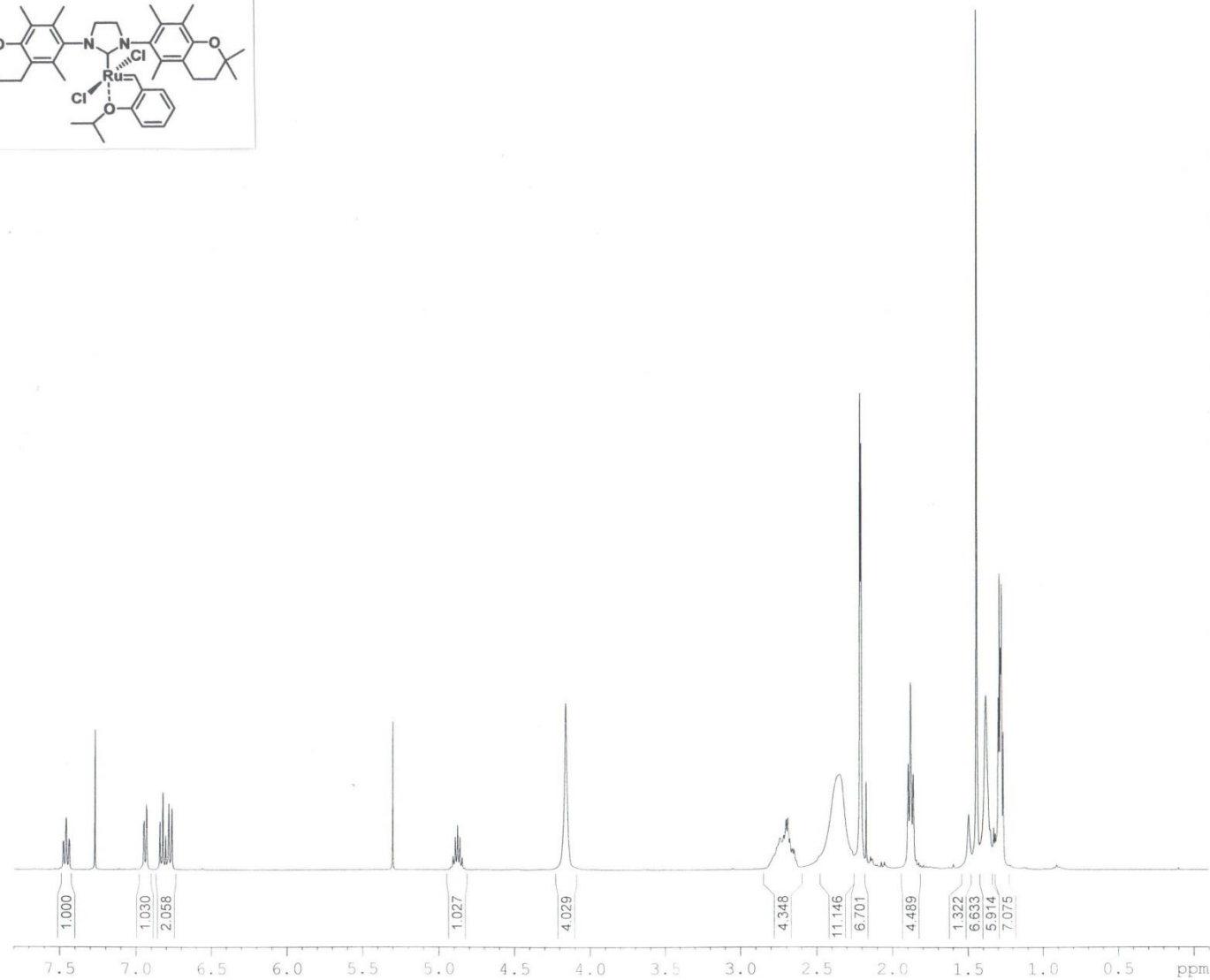
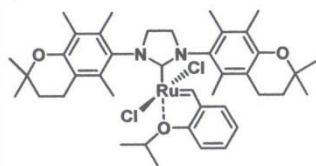
HSQC spectrum of the catalyst **9**

HSQC range ^{13}C to 130 ppm ^1H to 7.5 ppm



¹H NMR spectrum of the catalyst **9**

H NMR range 0-7.5 ppm T = 323K



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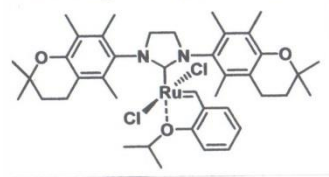
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^{13}C NMR spectrum of the catalyst **9**

^{13}C NMR range 0-220 ppm T = 323K

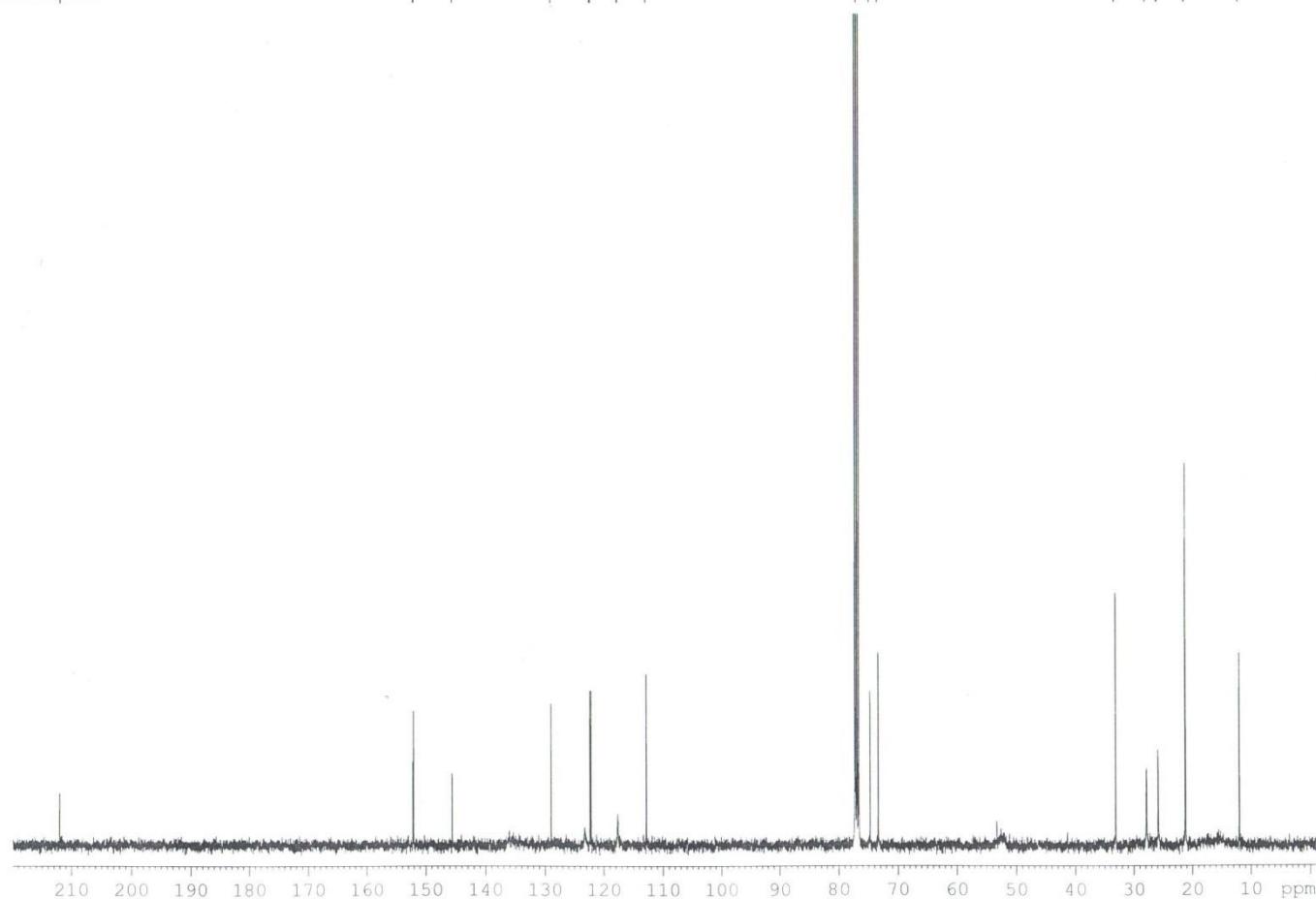


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Current Data Parameters
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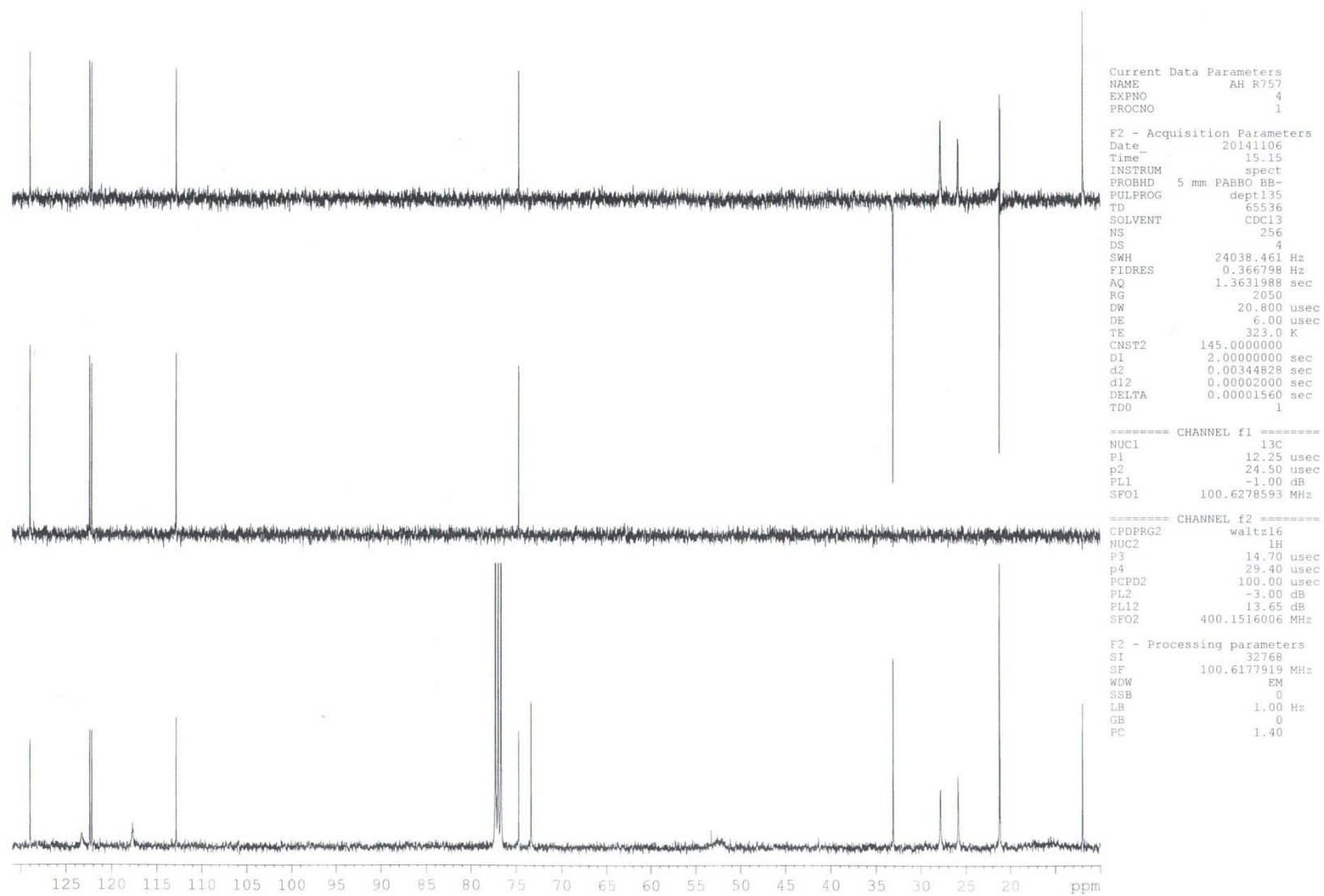
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¹³C DEPT spectrum of the catalyst **9**



References

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