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General methods

All reactions were setup in a glovebox (Vacuum Atmospheres or mBraun) under a nitrogen atmosphere unless otherwise specified. All solvents were purified by passage through solvent purification columns,[1] and further degassed with argon. Ruthenium complex **S1** was obtained from Materia Inc. CAAC salts **9a** – **25a** were prepared according to the methods reported in the literature.[2] CAAC catalysts **9** – **25** were prepared according to the literature procedures already established for previously reported catalysts **10**,[2b] **13**,[2b] **18**,[2b] and **25**.[2c] Methyl oleate was purchased from Nu-Chek-Prep, and subjected to further purification with activated neutral alumina. To activate, neutral alumina was heated to 200 °C for 24 h in a glassware drying oven, was then cooled to room temperature, and added to methyl oleate (1.5 wt%). The methyl oleate was then degassed, and stored over the activated neutral alumina for a minimum of one month before use. Ethylene gas was purchased and used as received from Matheson, and was either Ultra High Purity (99.95%) or Matheson Purity (99.995%). ^{1}H-NMR spectra were acquired at 500 MHz and ^{13}C-NMR spectra at 125 MHz as $CDCl_3$ solutions, on a Varian spectrometer equipped with an AutoX probe. ROESY-AD spectra were acquired at 600 MHz, using standard pulse sequences available in VNMR-J. Gas Chromatographic analyses were conducted using an Agilent 6850 GC equipped with a CTC-PAL autosampler. High-resolution mass spectrometry (HRMS) data was obtained on a JEOL MSRoute mass spectrometer. Elemental analysis was performed by Midwest Microlab, LLC.

General procedure 1: Synthesis of catalysts 9-25

In a glovebox, a vial was charged with dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium(II) (**S1**) (1 equiv), CAAC salt **9a** – **25a** (2.4 equiv), KHMDS (2.8 equiv), and THF (0.03 M). The vial was capped, brought out of the glovebox, and let to stir at room temperature. After 24 hours, the mixture was filtered over a pad of celite, eluted with CH_2Cl_2, and concentrated. The residue was then washed with hexanes, to provide the pure catalyst (**9-25**) as a dark green solid. If desired, the catalyst can be further purified by column chromatography (SiO_2, using 10% EtOAc in hexanes to 25% EtOAc in hexanes).[3]

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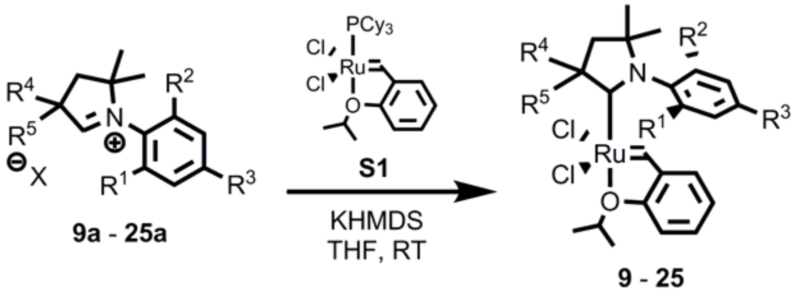
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

[2] a) Lavallo, V. ; Canac, Y. ; Prasang, C. ; Donnadieu, B. ; Bertrand, G. *Angew. Chem.* **2005**, *117*, 5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705. b) Jazzar, R.; Dewhurst, R. D.; Bourg, J. B.; Donnadieu, B.; Canac, Y.; Bertrand, G. *Angew. Chem.* **2007**, *119*, 2957; *Angew. Chem. Int. Ed.* **2007**, *46*, 2899. c) Jazzar, R.; Bourg, J. B.; Dewhurst, R. D.; Donnadieu, B.; Bertrand, G. *J. Org. Chem.* **2007**, *72*, 3492. d) Anderson, D. R.; Lavallo, V.; O`Leary, D. J.; Bertrand, G.; Grubbs, R. H. *Angew. Chem.* **2007**, *119*, 7400; *Angew. Chem. Int. Ed.* **2007**, *46*, 7262. e) Mignani, G.; Pevere, V.; Olivier-Bourbigou, H.; Vallee, C.; Berthod, M.; Citadelle, C. (Rhodia Operations, IFP), WO2010/010290 A1, **2010**.

[3] This is only a necessary purification step for the lower yielding catalysts **9** and **10**. Residual **S1** elutes first as a reddish-brown band, followed by the desired catalyst as a bright green band.



Catalyst 9 (R^1 = Me, R^2 = Et, R^3 = H, R^4 = R^5 = Me)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **9a·PF$_6$** (0.28 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **9** (0.030 g, 15%) as a dark green solid; ^{1}H NMR δ 16.25 (1H, s), 7.52 (1H, m), 7.50 (1H, m), 7.44 (1H, m), 7.28 (1H, m), 6.93 (1H, m), 6.86 (2H, m), 5.17 (1H, m), 2.60 (1H, m), 2.51 (1H, m), 2.29 (3H, s), 2.20 (2H, s), 2.16 (3H, s), 2.06 (3H, s), 1.80 (3H, d, *J* = 6.1 Hz), 1.72 (3H, d, *J* = 6.1 Hz), 1.41 (3H, s), 1.34 (3H, s), 0.89 (3H, t, *J* = 7.4 Hz); ^{13}C NMR δ 286.4, 266.5, 152.4, 144.3, 144.1, 139.5, 138.1, 130.9, 129.7, 128.9, 127.2, 123.8, 122.1, 113.2, 78.7, 75.1, 56.3, 52.2, 30.0, 29.5, 29.4, 28.3, 25.0, 22.3, 22.1, 20.8, 14.7; HRMS (FAB+) 563.1286, $[C_{27}H_{37}RuONCl_2]^+$ requires 563.1296.

Catalyst 11 (R^1 = Me, R^2 = *i*Pr, R^3 = H, R^4 = R^5 = Me)

According to *general procedure 1*: **S1** (0.72 g, 1.2 mmol), **11a·BF$_4$** (0.50 g, 1.4 mmol), and KHMDS (0.34 g, 1.7 mmol) were reacted in THF (40 mL) to provide **11** (0.54 g, 78%) as a dark green solid; ^{1}H NMR δ 16.25 (1H, s), 7.52 (2H, m), 7.47 (1H, m), 7.27 (1H, m), 6.93 (1H, m), 6.84 (2H, m), 5.17 (1H, m), 2.99 (1H, m), 2.28 (3H, s), 2.22 (1H, d, *J* = 12 Hz), 2.18 (1H, d, *J* = 12 Hz), 2.15 (3H, s), 2.07 (3H, s), 1.81 (3H, d, *J* = 6.1 Hz), 1.74 (3H, d, *J* = 6.1 Hz), 1.41 (3H, s), 1.37 (3H, s), 1.28 (3H, d, *J* = 6.6 Hz), 0.69 (3H, d, *J* = 6.6 Hz); ^{13}C NMR δ 297.2, 267.1, 152.6, 148.9, 143.8, 138.4, 138.3, 130.9, 129.7, 129.1, 125.8, 123.8, 122.1, 113.3, 78.4, 75.1, 56.3, 52.1, 29.8, 29.7, 29.6, 28.7, 28.5, 26.3, 24.2, 22.4, 22.1, 21.6; HRMS (FAB+) 577.1468, $[C_{28}H_{39}RuONCl_2]^+$ requires 577.1453.

Catalyst 12 (R^1 = Me, R^2 = *t*Bu, R^3 = H, R^4 = R^5 = Me)

According to *general procedure 1*: **S1** (0.14 g, 0.24 mmol), **12a·BF$_4$** (0.10 g, 0.28 mmol), and KHMDS (0.068 g, 0.34 mmol) were reacted in THF (8 mL) to provide **12** (0.12 g, 86%) as a dark green solid; ^{1}H NMR δ 17.06 (1H, s), 7.70 (1H, m), 7.52 (1H, m), 7.45 (1H, m), 7.24 (1H, m), 6.94 (1H, m), 6.88 (1H, m), 6.85 (1H, m), 5.17 (1H, m), 2.23 (1H, d, *J* = 12 Hz), 2.18 (3H, s), 2.10 (1H, d, *J* = 12 Hz), 1.97 (3H, s), 1.83 (3H, d, *J* = 6.1 Hz), 1.77 (3H, d, *J* = 6.1 Hz), 1.37 (6H, s), 1.34 (9H, s); ^{13}C NMR δ 297.5, 266.1, 152.6, 148.4, 144.3, 138.8, 138.1, 131.0, 130.1, 130.1, 128.2, 123.9, 122.0, 113.4, 79.1, 75.2, 55.5, 52.7, 38.6, 33.8, 32.2, 32.2, 30.9, 28.6, 23.0, 22.5, 22.2 (2C); HRMS (FAB+) 591.1599, $[C_{29}H_{41}RuONCl_2]^+$ requires 591.1609.

Catalyst 14 (R^1 = H, R^2 = *i*Pr, R^3 = H, R^4 = R^5 = Et)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **14a·PF$_6$** (0.29 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **14** (0.080 g, 44%) as a dark green solid; ^{1}H NMR δ 16.03 (1H, s), 7.65 (1H, m), 7.59 (1H, m), 7.53 (1H, m), 7.25 (1H, m), 7.21 (1H, m), 6.94 (1H, m), 6.86 (1H, m), 6.80 (1H, m), 5.12 (1H, m), 3.23 (1H, m), 2.87 (1H, m), 2.64 (1H, m), 2.44 (1H, m), 2.34 (1H, d, *J* = 13 Hz), 2.03 (1H, d, *J* = 13 Hz), 1.89 (1H, m), 1.70 (3H, d, *J* = 6.1 Hz), 1.62 (3H, t, *J* = 7.4 Hz), 1.37 (3H, s), 1.35 (3H, d, *J* = 6.7 Hz), 1.34 (3H, s), 1.09 (3H, t, *J* = 7.4 Hz), 1.04 (3H, d, *J* = 6.7 Hz); ^{13}C NMR δ 301.7, 265.8, 152.7, 148.1, 144.2, 139.7, 131.7, 131.1, 129.4, 127.1, 127.0, 123.8, 122.2, 113.3, 75.3, 74.8, 65.6, 45.0, 33.3, 32.0, 28.6, 28.5, 27.4, 25.1, 23.3, 22.4, 22.4, 14.0, 10.0; HRMS (FAB+) 591.1584, $[C_{29}H_{41}RuONCl_2]^+$ requires 591.1609.

Catalyst 15 (R^1 = R^2 = R^3 = Me, R^4 = R^5 = Et)

According to *general procedure 1*: **S1** (0.21 g, 0.35 mmol), **15a·BF$_4$** (0.25 g, 0.70 mmol), and KHMDS (0.14 g, 0.70 mmol) were reacted in THF (10 mL) to provide **15** (0.10 g, 48%) as a dark green solid; ^{1}H NMR δ 16.41 (1H, s), 7.55 (1H, m), 7.11 (2H, s), 6.95 (1H, m), 6.88 (1H, m), 6.79 (1H, m), 5.12 (1H, m), 2.86 (2H, m), 2.47 (3H, s), 2.19 (6H, s), 2.16 (2H, s), 1.80 (2H, m), 1.68 (6H, d, *J* = 6.1 Hz), 1.52 (6H, t, *J* = 7.4 Hz), 1.36 (6H, s); ^{13}C NMR δ 306.3, 266.7, 152.2, 145.2, 138.5, 138.2 (2C), 138.1, 131.4, 130.5 (2C), 124.4, 122.2, 113.5, 77.8, 74.6, 66.2, 45.5, 29.0 (2C), 27.7 (2C), 22.5 (2C), 21.2, 20.7 (2C), 13.1; HRMS (FAB+) 591.1608, $[C_{29}H_{41}RuONCl_2]^+$ requires 591.1609.

Catalyst 16 (R^1 = Me, R^2 = *i*Pr, R^3 = H, R^4 = R^5 = Et)

According to *general procedure 1*: **S1** (0.21 g, 0.35 mmol), **16a·BF$_4$** (0.26 g, 0.70 mmol), and KHMDS (0.14 g, 0.70 mmol) were reacted in THF (10 mL) to provide **16** (0.17 g, 82%) as a dark green solid; ^{1}H NMR δ 16.45 (1H, s), 7.53 (2H, m), 7.27 (1H, m), 7.26 (1H, m), 6.94 (1H, m), 6.84 (1H, m), 6.76 (1H, m), 5.12 (1H, m), 2.93 (2H, m), 2.86 (1H, m), 2.25 (3H, s), 2.17 (2H, s), 1.87 (1H, m), 1.75 (3H, d, *J* = 6.2 Hz), 1.74 (1H, m), 1.67 (3H, d, *J* = 6.2 Hz), 1.53 (3H, t, *J* = 7.4 Hz), 1.36 (3H, s), 1.31 (3H, s), 1.28 (3H, d, *J* = 6.5 Hz), 0.68 (3H, d, *J* = 6.5 Hz); ^{13}C NMR δ 303.3, 267.3, 152.6, 148.5, 144.2, 138.9, 138.1, 131.4, 129.8, 129.1, 125.8, 124.6, 122.1, 113.5, 77.5, 74.7, 66.1, 45.5, 29.9, 28.6, 28.5, 28.1, 27.8, 26.5, 24.3, 22.8, 22.3, 21.7, 13.1, 13.0; HRMS (FAB+) 605.1751, $[C_{30}H_{43}RuONCl_2]^+$ requires 605.1766.

Catalyst 17 ($R^1 = R^2 = R^3$ = Me, R^4/R^5 = -$(CH_2)_5$-)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **17a·PF$_6$** (0.26 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **17** (0.070 mg, 39%) as a dark green solid; ^{1}H NMR δ 16.35 (1H, s), 7.55 (1H, m), 7.10 (2H, s), 6.93 (1H, m), 6.88 (1H, m), 6.86 (1H, m), 5.16 (1H, m), 3.24 (2H, m), 2.46 (3H, s), 2.29 (2H, s), 2.25 (2H, m), 2.20 (6H, s), 1.93 (2H, m), 1.80 (1H, m), 1.75 (6H, d, *J* = 6.1 Hz), 1.52 (3H, m), 1.40 (6H, s); ^{13}C NMR δ 301.0, 266.3, 152.3, 144.8, 138.5, 138.2 (2C), 137.8, 131.0, 130.5 (2C), 123.9, 122.2, 113.3, 78.6, 74.9, 62.1, 44.9, 35.7 (2C), 29.5 (2C), 25.8, 23.2 (2C), 22.2 (2C), 21.2, 20.8 (2C); HRMS (FAB+) 603.1631, $[C_{30}H_{41}RuONCl_2]^+$ requires 603.1609.

Catalyst 19 ($R^1 = R^2$ = *i*Pr, R^3 = H, R^4 = Me, R^5 = *n*Pr)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **19a·BF$_4$** (0.28 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **19** (0.15 g, 79%) as a dark green solid; ^{1}H NMR δ 16.50 (1H, s), 7.61 (1H, m), 7.50 (1H, m), 7.45 (2H, m), 6.94 (1H, m), 6.83 (1H, m), 6.78 (1H, m), 5.15 (1H, m), 3.02 (2H, m), 2.97 (1H, m), 2.21 (1H, d, *J* = 12 Hz), 2.14 (1H, d, *J* = 12 Hz), 1.97 (1H, m), 1.92 (3H, s), 1.81 (3H, d, *J* = 6.1 Hz), 1.75 (3H, d, *J* = 6.1 Hz), 1.60 (1H, m), 1.37 (3H, s), 1.29 (3H, d, *J* = 6.6 Hz), 1.28 (3H, s), 1.24 (3H, d, *J* = 6.6 Hz), 1.23 (3H, d, *J* = 6.6 Hz), 1.14 (3H, t, *J* = 7.2 Hz), 0.77 (3H, d, *J* = 6.4 Hz), 0.61 (3H, d, *J* = 6.4 Hz); ^{13}C NMR δ 296.3, 267.5, 153.0, 148.6, 148.4, 143.1, 136.7, 130.8, 129.5, 125.9, 125.8, 123.9, 122.0, 113.4, 77.8, 75.0, 60.7, 49.7, 44.3, 31.4, 28.8, 28.6, 28.3, 27.2, 26.4, 25.2, 24.5, 24.4, 22.5, 22.2, 19.9, 14.9; HRMS (FAB+) 633.2080, $[C_{32}H_{47}RuONCl_2]^+$ requires 633.2079.

Catalyst 20 ($R^1 = R^2$ = Et, R^3 = H, R^4/R^5 = bicyclo[3.3.1]nonane)

According to *general procedure 1*: **S1** (0.15 g, 0.25 mmol), **20a·BF$_4$** (0.12 g, 0.30 mmol), and KHMDS (0.070 g, 0.35 mmol) were reacted in THF (10 mL) to provide **20** (0.13 g, 81%) as a dark green solid; ^{1}H NMR δ 16.90 (1H, s), 7.58 (2H, m), 7.46 (2H, m), 6.91 (2H, m), 6.86 (1H, m), 5.05 (1H, m), 3.91 (2H, m), 2.80 (2H, m), 2.52 (4H, m), 2.38 (1H, m), 2.36 (2H, s), 2.30 (2H, m), 2.17 (2H, m), 2.01 (1H, m), 1.99 (2H, m), 1.90 (2H, m), 1.66 (6H, d, *J* = 6.1 Hz), 1.28 (6H, s), 1.00 (6H, t, *J* = 7.4 Hz); ^{13}C

NMR δ 314.5, 271.7, 152.4, 145.6, 143.3 (2C), 140.1, 132.1, 128.9, 126.8 (2C), 125.3, 122.2, 113.8, 76.5, 74.5, 71.5, 48.0, 40.4 (2C), 39.3, 36.7 (2C), 35.3 (2C), 29.2 (2C), 27.7, 27.5, 24.9 (2C), 22.6 (2C), 14.3 (2C); HRMS (FAB+) 669.2066, $[C_{35}H_{47}RuONCl_2]^+$ requires 669.2079.

Catalyst 21 ($R^1 = R^2 = R^3 = Me, R^4 = Me, R^5 = Ph$)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **21a·BF$_4$** (0.28 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **21** (0.055 g, 29%) as a dark green solid. The ^{1}H NMR spectrum shows two diagnostic benzylidene resonances at 17.72 and 16.34 ppm, in a ratio of 2.0:1.0 (due to the presence of conformational and rotational isomers, the ^{1}H- and ^{13}C-spectra of catalyst **21** are highly complex, which precluded further assignment);[4] HRMS (FAB+) 625.1435, $[C_{32}H_{39}RuONCl_2]^+$ requires 625.1453. Elemental analysis (%) C 61.19, H 6.24, N 2.13, $[C_{32}H_{39}RuONCl_2]$ requires C 61.43, H 6.28, N 2.24.

Catalyst 22 ($R^1 = Me, R^2 = Et, R^3 = H, R^4 = Me, R^5 = Ph$)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **22a· BF$_4$** (0.28 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **22** (0.060 g, 32%) as a dark green solid. The ^{1}H NMR spectrum shows two diagnostic benzylidene resonances at 17.71 and 16.32 ppm, in a ratio of 1.0:1.7 (due to the presence of conformational and rotational isomers, the ^{1}H- and ^{13}C-spectra of catalyst **22** are highly complex, which precluded further assignment); [4] HRMS (FAB+) 625.1436, $[C_{32}H_{39}RuONCl_2]^+$ requires 625.1453. Elemental analysis (%) C 61.02, H 6.19, N 1.94, $[C_{32}H_{39}RuONCl_2]$ requires C 61.43, H 6.28, N 2.24.

Catalyst 23 ($R^1 = R^2 = Et, R^3 = H, R^4 = Me, R^5 = Ph$)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **23a·BF$_4$** (0.29 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **23** (0.085 g, 45%) as a dark green solid. The ^{1}H NMR spectrum shows two diagnostic benzylidene resonances at 17.72 and 16.43 ppm, in a ratio of 1.0:3.6. Due to the presence of conformational and rotational isomers, the ^{13}C-spectra of catalyst **23** was highly complex, which precluded further assignment.[4] Although the ^{1}H-spectrum was also complex and exhibited significant line broadening, resonances corresponding to the major benzylidene

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[4] ROESY spectra confirmed that these benzylidene resonances undergo chemical exchange.

were able to be extracted as follows: δ 16.43 (1H), 8.26 (2H), 7.56 (2H), 7.43 (5H), 6.86 (1H), 6.81 (1H), 6.74 (1H), 4.98 (1H), 3.15 (1H), 2.72 (2H), 2.53 (2H), 2.38 (1H), 2.36 (3H), 1.55 (3H), 1.52 (3H), 1.42 (3H), 1.41 (3H), 1.38 (3H), 1.07 (3H), 0.83 (3H); HRMS (FAB+) 639.1598, $[C_{33}H_{41}RuONCl_2]^+$ requires 631.1609. Elemental analysis (%) C 62.46, H 6.41, N 1.94, $[C_{33}H_{41}RuONCl_2]$ requires C 61.96, H 6.46, N 2.19.

Catalyst 24 (R^1 = Me, R^2 = *i*Pr, R^3 = H, R^4 = Me, R^5 = Ph)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **24a·BF$_4$** (0.29 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **24** (0.11 g, 58%) as a dark green solid. The ^{1}H NMR spectrum shows two diagnostic benzylidene resonances at 16.36 and 16.34 ppm, in a ratio of 1.0:2.9. Due to the presence of conformational and rotational isomers, the ^{13}C-spectra of catalyst **24** was highly complex, which precluded further assignment. Although the ^{1}H-spectrum was also complex and exhibited significant line broadening, resonances corresponding to the major benzylidene were able to be extracted as follows: δ 16.34 (1H), 8.24 (2H), 7.51 (5H), 7.38 (1H), 7.29 (1H), 6.85 (1H), 6.80 (1H), 6.74 (1H), 4.93 (1H), 3.18 (1H), 3.09 (1H), 2.37 (1H), 2.31 (3H), 2.25 (3H), 1.61 (3H), 1.52 (3H), 1.36 (3H), 1.34 (3H), 0.84 (3H); HRMS (FAB+) 631.1609, $[C_{33}H_{41}RuONCl_2]^+$ requires 631.1609. Elemental analysis (%) C 62.27, H 6.44, N 2.00, $[C_{33}H_{41}RuONCl_2]$ requires C 61.96, H 6.46, N 2.19.

Catalyst 25 (R^1 = R^2 = *i*Pr, R^3 = H, R^4 = Me, R^5 = Ph)

According to *general procedure 1*: **S1** (0.18 g, 0.30 mmol), **25a·BF$_4$** (0.30 g, 0.70 mmol), and KHMDS (0.17 g, 0.86 mmol) were reacted in THF (10 mL) to provide **25** (0.14 g, 70%) as a dark green solid; ^{1}H NMR δ 16.53 (1H, s), 8.26 (2H, m), 7.63 (1H, m), 7.55 (2H, m), 7.47 (2H, m), 7.44 (1H, m), 7.37 (1H, m), 6.85 (1H, m), 6.78 (1H, m), 6.69 (1H, m), 4.95 (1H, m), 3.15 (1H, d, *J* = 13 Hz), 3.09 (1H, m), 2.99 (1H, m), 2.35 (3H, s), 1.56 (3H, d, *J* = 6.1 Hz), 1.51 (3H, s), 1.41 (3H, d, *J* = 6.1 Hz), 1.40 (3H, s), 1.34 (3H, d, *J* = 6.6 Hz), 1.25 (1H, d, *J* = 6.6 Hz), 0.83 (3H, d, *J* = 6.4 Hz), 0.52 (1H, d, *J* = 6.4 Hz); ^{13}C NMR δ 298.0, 264.8, 153.0, 148.6, 148.4, 143.1, 142.8, 136.9, 131.0, 129.6, 129.4 (2C), 129.2 (2C), 127.5, 126.1, 125.8, 124.1, 121.8, 113.5, 77.6, 74.7, 63.3, 48.3, 29.0, 28.7, 28.3, 27.8, 27.4, 26.4, 24.6, 24.4, 22.7, 22.3; HRMS (FAB+) 668.2027, $[C_{35}H_{46}RuONCl_2]^+$ requires 668.2000.

Determination of Initiation Rates

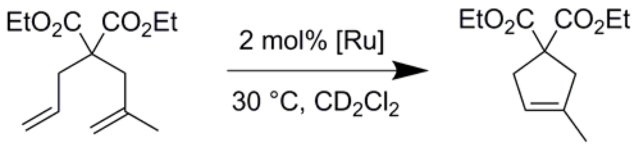
All reactions were set up as described in the literature.[5] In brief, conditions were catalyst (0.003 mmol) and *n*-butylvinylether (0.09 mmol) in C_6D_6 (0.6 mL), at the given temperature.

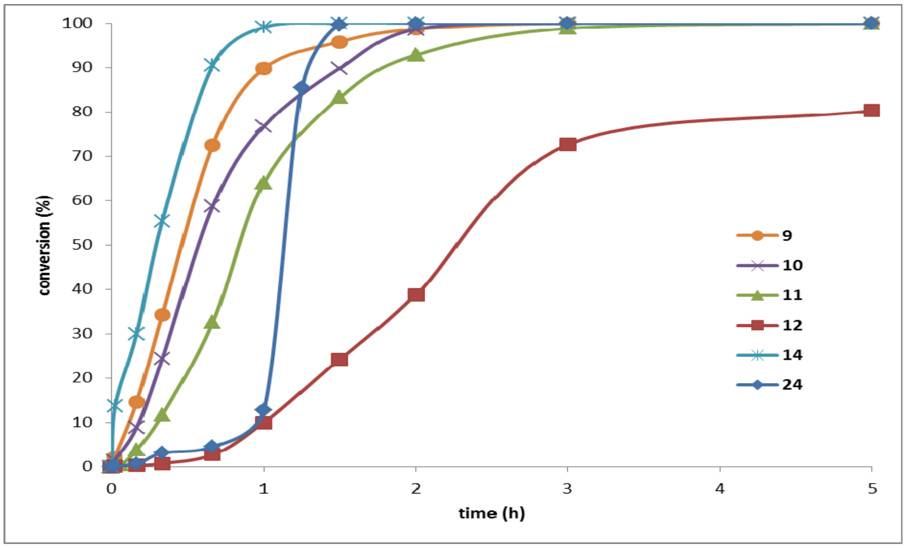
catalyst	temp (°C)	Initiation rate constant, 10^{-3} s^{-1}
9	60	3.2 ± 0.3
10	60	1.3 ± 0.1
11	60	0.29 ± 0.03
12	60	0.24 ± 0.02
13	60	0.0016 ± 0.0002
14	60	>20 [a]
14	30	1.1 ± 0.1
24	60	0.23 ± 0.02

[a] complete initiation had occurred within 90s, and an accurate reading could not be determined via NMR. As such this value represents the theoretical minimum of k_{obs}.

Ring Closing Metathesis Studies

All reactions were setup as in the standardized study, as described in the literature (except 2 mol% catalyst loading was utilized instead of 1 mol%).[6]





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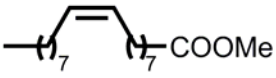
[5] a) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem .Soc.* **2012**, *134*, 693. b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.

[6] Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk T. W.; Grubbs, R. H. *Organometallics.* **2006**, *25*, 5740.

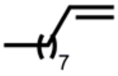
General procedure 2: Ethenolysis of methyl oleate using catalysts 9-25

Reactions were setup analogously to those described in the literature.[7] As a representative procedure for reactions run at 3 ppm, a Fisher-Porter bottle equipped with a stir bar was charged with methyl oleate (15 g, 0.0506 mole) and neat dodecane (0.3 – 0.5 g) as an internal standard in a glovebox. A solution of olefin metathesis catalyst in toluene (0.076 mL, 0.002 M) was then added, The head of the Fisher-Porter bottle was connected via a T-adapter to a pressure gauge and a dip-tube fashioned from 0.17 mm hplc tubing was connectedm to a manual hplc valve. The system was sealed and taken out of the glove box to an ethylene line. The vessel was then purged three times with ethylene, pressurized to 150 psi, and placed in an oil bath at 40 °C. The reaction was monitored by withdrawing samples into 20 mL vials at sequential reaction times via the dip-tube. Immediately after collecting a sample (*ca.* 0.05 mL), it was diluted with hexanes (*ca.*20 mL), then kept in an ice bath until analysis by GC. The samples were analyzed sequentially by GC using an Agilent 6850 system equipped with an HP-1 column (30 m x 0.32 mm) using an oven gradient (60 °C, 2 min; 60 – 250 °C, 21 min) and a flame ionization detector. Response factors were determined for MO (**1**) as well as synthetic samples of **3**, **4**, **3a** and **4a** relative to the internal standard dodecane. A standard mixture of these compounds was used as a calibration standard to confirm consistency of response factors during each analysis run. Representative values for the response factors are shown in the table below.

GC retention times and response factors relative to internal standard (dodecane):



1



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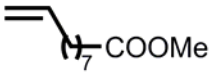

4

3a

4a

Compound	Dodecane	1	3	4	3a	4a
Time (min)	**6.8**	**17.4**	**3.5**	**8.3**	**14.2**	**20.1**
Response Factor	**1.000**	**1.33**	**0.83**	**0.79**	**1.40**	**1.09**

For each timepoint obtained from an ethenolysis reaction, the GC areas of each component of the reaction mixture were converted to the percentages of each component using the response factors above. The turnover numbers for the production of terminal olefins (**3** + **4**) were calculated as follows:

Conversion = 100 – [(final moles **1**) X 100/[initial moles **1**)]
Selectivity = 100 X (moles **3** + **4**)/[(moles **3** + **4**) + (2 X moles **3a** + **4a**)]
Yield = Conversion X Selectivity/100
TON = Yield X (initial moles **1**/moles catalyst)/100

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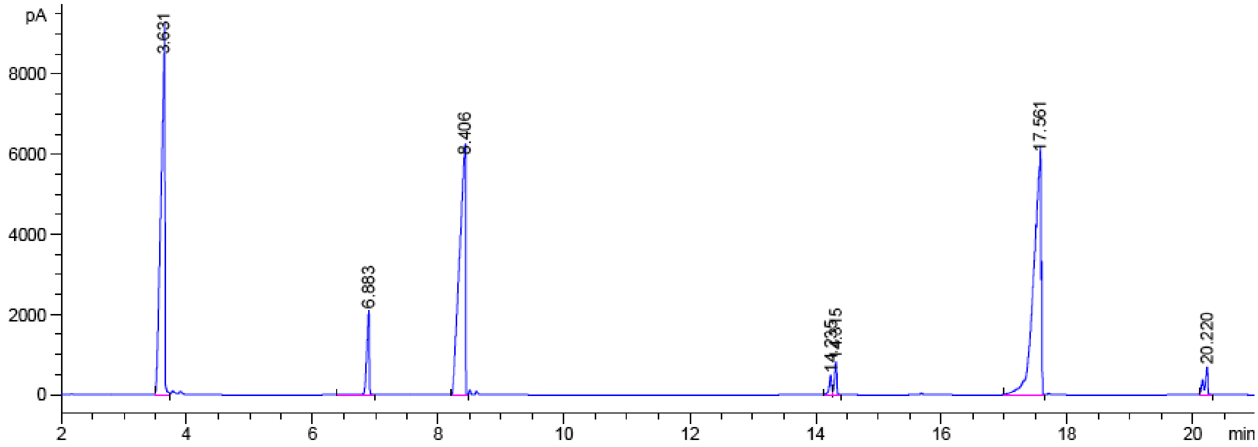
[7] a) Nickel, A.; Ung, T.; Mkrtumyan, G.; Uy, J.; Lee, C.- W.; Stoianova, D.; Papazian, J.; Wei, W.- H.; Mallari, A.; Schrodi, Y.; Pederson, R. L. *Top. Catal.* **2012**, *55*, 518. b) Schrodi, Y.; Ung, T.; Vargas, A.; Mkrtumyan, G.; Lee, C.-W.; Champagne, T. M.; Pederson, R. L.; Hong, S. H. *Clean.* **2008**, *36*, 669.

Example ethenolysis of methyl oleate (1) using 3 ppm catalyst 11 (C_2H_4, 99.95%)

GC Areas for:	Decene (**3**)	dodecane	**4**	**3a**	MO (**1**)	**4a**
Retention Times:	3.5 min	6.8 min	8.3 min	14.2 min	17.4 min	20.1 min
t = 0 min	0.0	2324.1	0.0	0.0	50046.8	0.0
t = 10 min	6369.9	4680.3	6137.3	494.6	88271.1	380.4
t = 20 min	17103.7	4242.6	16471.7	1195.1	61345.2	900.5
t = 30 min	23494.1	4447.0	22815.3	1759.9	60842.8	1422.5
t = 45 min	26489.4	4273.1	25472.7	1941.3	48418.1	1466.7
t = 60 min	37452.0	5613.3	35995.3	2722.8	57701.6	2141.2
t = 80 min	36078.4	5135.9	34673.5	2674.8	50245.9	2117.6
t = 110 min	27171.0	3744.3	26229.7	2077.7	35108.2	1612.0
t = 150 min	41195.0	5626.2	40269.0	3192.5	50647.3	2565.6
t = 210 min	34327.6	4675.0	33616.0	2683.8	40758.2	2059.4
t = 300 min	34618.5	4711.5	33907.8	2683.4	40740.3	2053.4

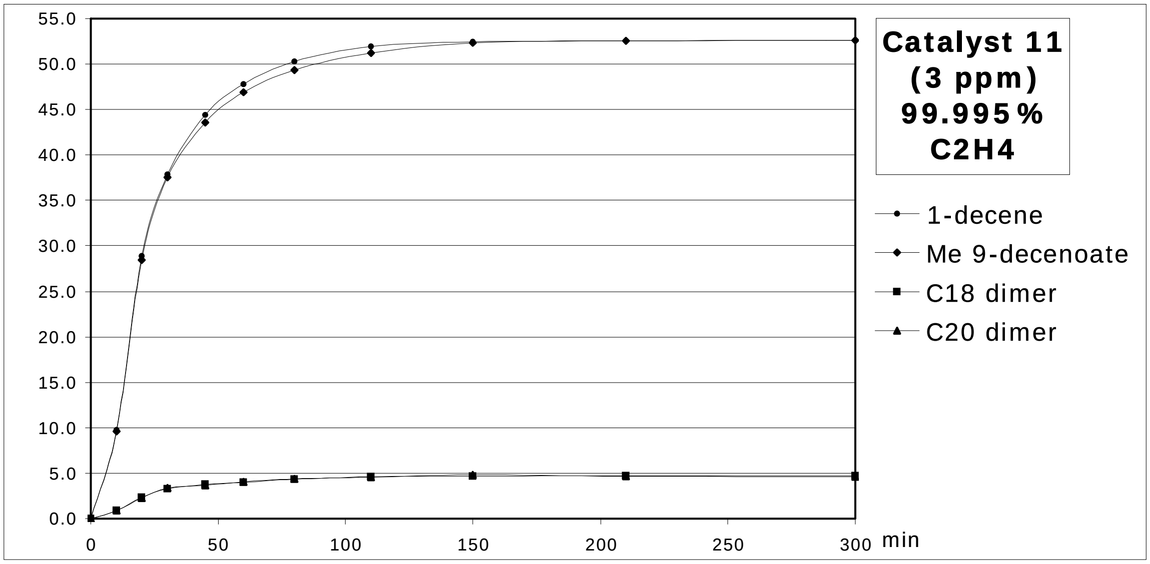
GC trace of ethenolysis of methyl oleate (1) using 3 ppm catalyst 11, at time = 150 min



Contributions of reaction products in ethenolysis of methyl oleate (1) using 3 ppm catalyst 11

GC % Yield	**3**, %	**4**, %	**3a**, %	**1**, %	**4a**, %	total	%conv	% sel.	TON
0	0.0	0.0	0.0	93.2	0.0	93.2	0.0		0
10	9.7	9.6	0.9	81.6	0.9	92.2	10.5	91.8	32553
20	28.9	28.4	2.3	62.6	2.3	93.5	30.9	92.6	96405
30	37.8	37.5	3.3	59.2	3.4	100.2	41.0	91.9	126862
45	44.4	43.6	3.8	49.0	3.6	96.7	47.7	92.2	148132
60	47.8	46.9	4.0	44.5	4.1	95.9	51.4	92.2	159391
80	50.3	49.4	4.3	42.4	4.4	96.5	54.2	92.0	167813
110	52.0	51.2	4.6	40.6	4.6	96.8	56.2	91.8	173737
150	52.4	52.3	4.7	39.0	4.8	96.1	57.1	91.7	176398
210	52.6	52.6	4.7	37.7	4.7	95.0	57.3	91.8	177058
300	52.6	52.6	4.7	37.4	4.6	94.7	57.3	91.9	177193

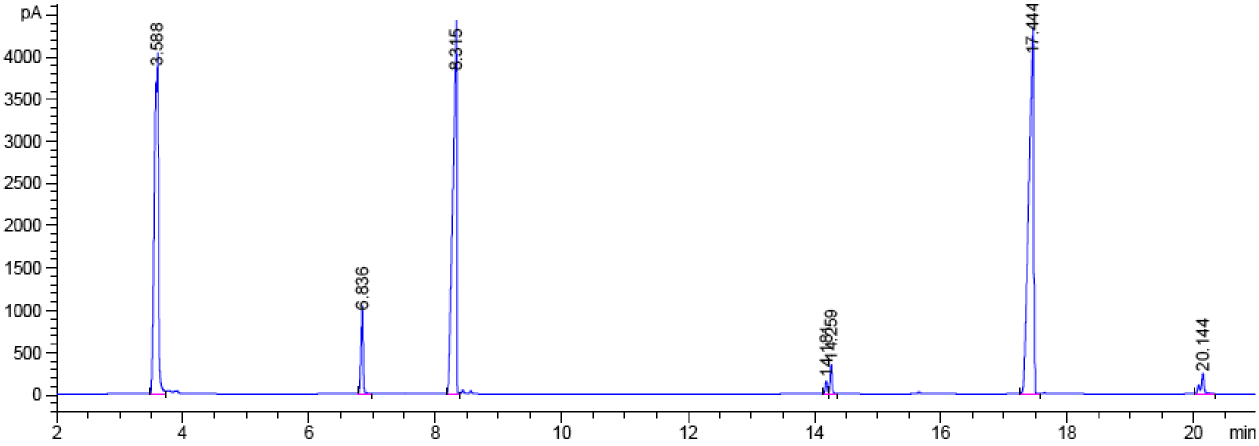
Ethenolysis timecourse plot for catalyst 11, 3 ppm catalyst loading (C_2H_4, 99.95%)



Example ethenolysis of methyl oleate (1) using 3 ppm catalyst 24 (C_2H_4, 99.95%)

GC Areas for:	Decene (**3**)	dodecane	**4**	**3a**	MO (**1**)	**4a**
Retention Times:	3.5 min	6.8 min	8.3 min	14.2 min	17.4 min	20.1 min
t = 0 min	0.0	1260.8	0.0	0.0	30818.8	0.0
t = 10 min	10236.8	2058.6	9870.2	489.3	30166.0	380.5
t = 20 min	13959.8	2050.1	13483.1	721.0	23376.9	556.8
t = 30 min	18933.0	2607.5	18408.5	1042.2	28713.0	822.8
t = 45 min	22842.7	3042.5	22093.3	1255.2	31578.1	1007.4
t = 60 min	13660.9	1803.4	13259.3	765.8	18862.5	617.0
t = 80 min	20192.3	2643.2	19607.8	1136.6	26633.5	891.8
t = 110 min	21474.4	2786.2	20796.2	1216.9	28066.6	961.4
t = 150 min	18706.0	2435.6	18264.1	1064.3	23444.9	826.8
t = 210 min	20533.5	2650.7	19902.7	1164.4	26071.2	923.2
t = 300 min	20537.7	2655.2	19939.7	1176.5	26170.1	927.6

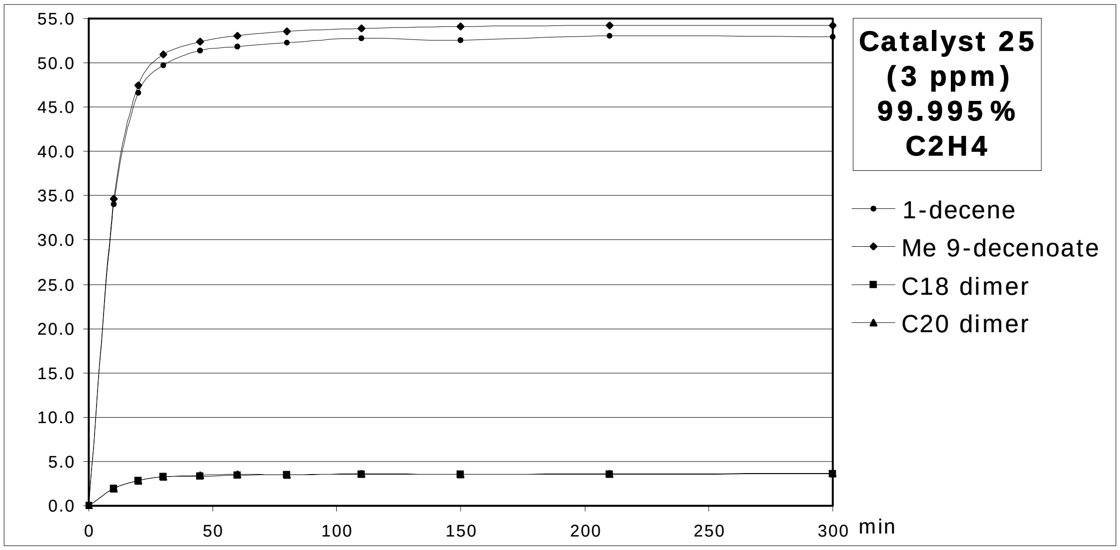
GC trace of ethenolysis of methyl oleate (1) using 3 ppm catalyst 24, at time = 150 min



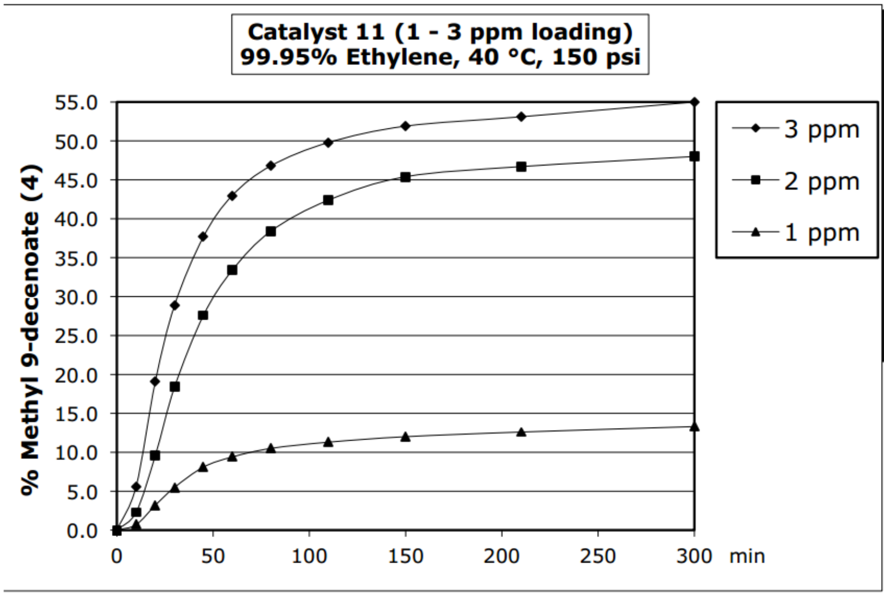
Contributions of reaction products in ethenolysis of methyl oleate (1) using 3 ppm catalyst 24

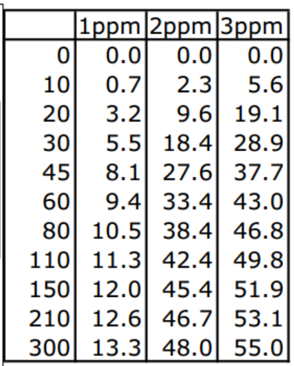
GC % Yield	**3**, %	**4**, %	**3a**, %	**1**, %	**4a**, %	total	%conv	% sel.	TON
0	0.0	0.0	0.0	104.0	0.0	104.0	0.0		0
10	34.0	34.6	1.9	62.3	1.9	98.6	36.3	94.7	115156
20	46.6	47.5	2.9	48.5	2.8	98.4	49.9	94.3	157826
30	49.7	51.0	3.2	46.9	3.3	100.5	53.6	93.9	168861
45	51.4	52.4	3.4	44.2	3.4	99.5	55.3	93.9	174138
60	51.9	53.1	3.5	44.5	3.6	100.5	56.0	93.7	176010
80	52.3	53.5	3.5	42.9	3.5	99.3	56.4	93.8	177545
110	52.8	53.9	3.5	42.9	3.6	99.8	56.9	93.7	178881
150	52.6	54.1	3.6	41.0	3.5	97.9	56.9	93.8	178990
210	53.0	54.2	3.6	41.8	3.6	99.1	57.2	93.7	179867
300	53.0	54.2	3.6	41.9	3.6	99.1	57.2	93.7	179750

Ethenolysis timecourse plot for catalyst 24, 3 ppm catalyst loading (C_2H_4, 99.95%)



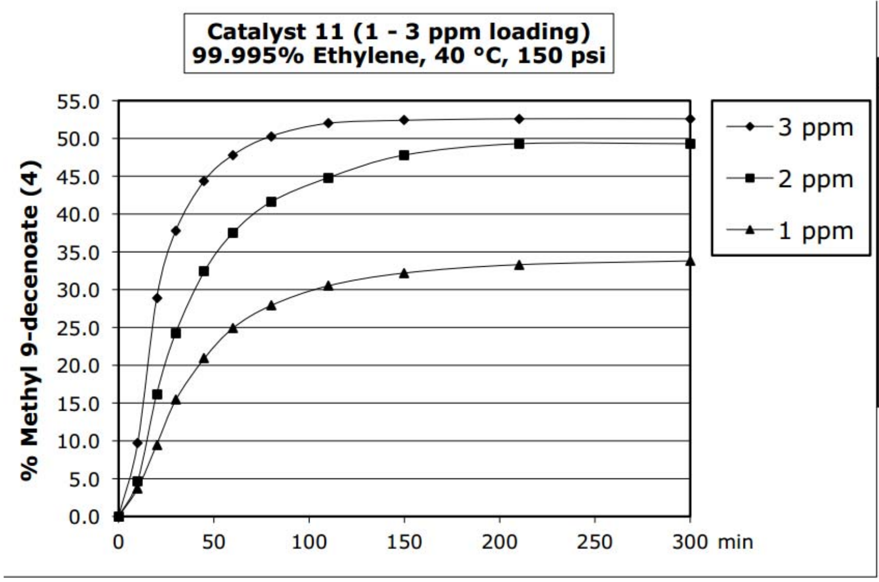
Ethenolysis timecourse plot for catalyst 11, at various catalyst loadings (C_2H_4, 99.95%)

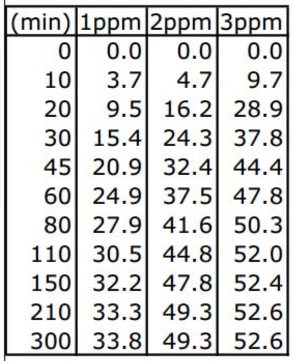




	1ppm	2ppm	3ppm
0	0.0	0.0	0.0
10	0.7	2.3	5.6
20	3.2	9.6	19.1
30	5.5	18.4	28.9
45	8.1	27.6	37.7
60	9.4	33.4	43.0
80	10.5	38.4	46.8
110	11.3	42.4	49.8
150	12.0	45.4	51.9
210	12.6	46.7	53.1
300	13.3	48.0	55.0

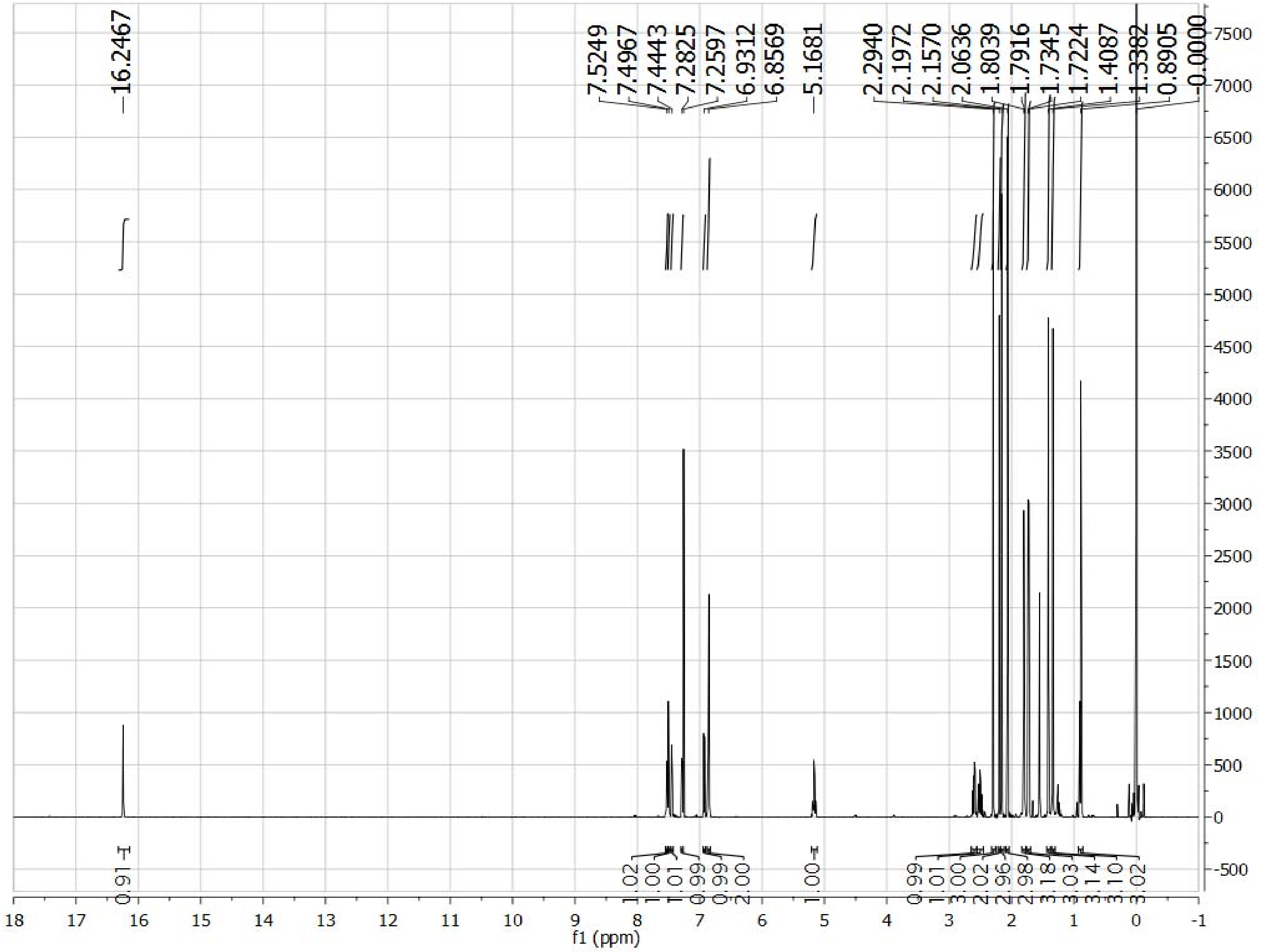
Ethenolysis timecourse plot for catalyst 11, at various catalyst loadings (C_2H_4, 99.995%)



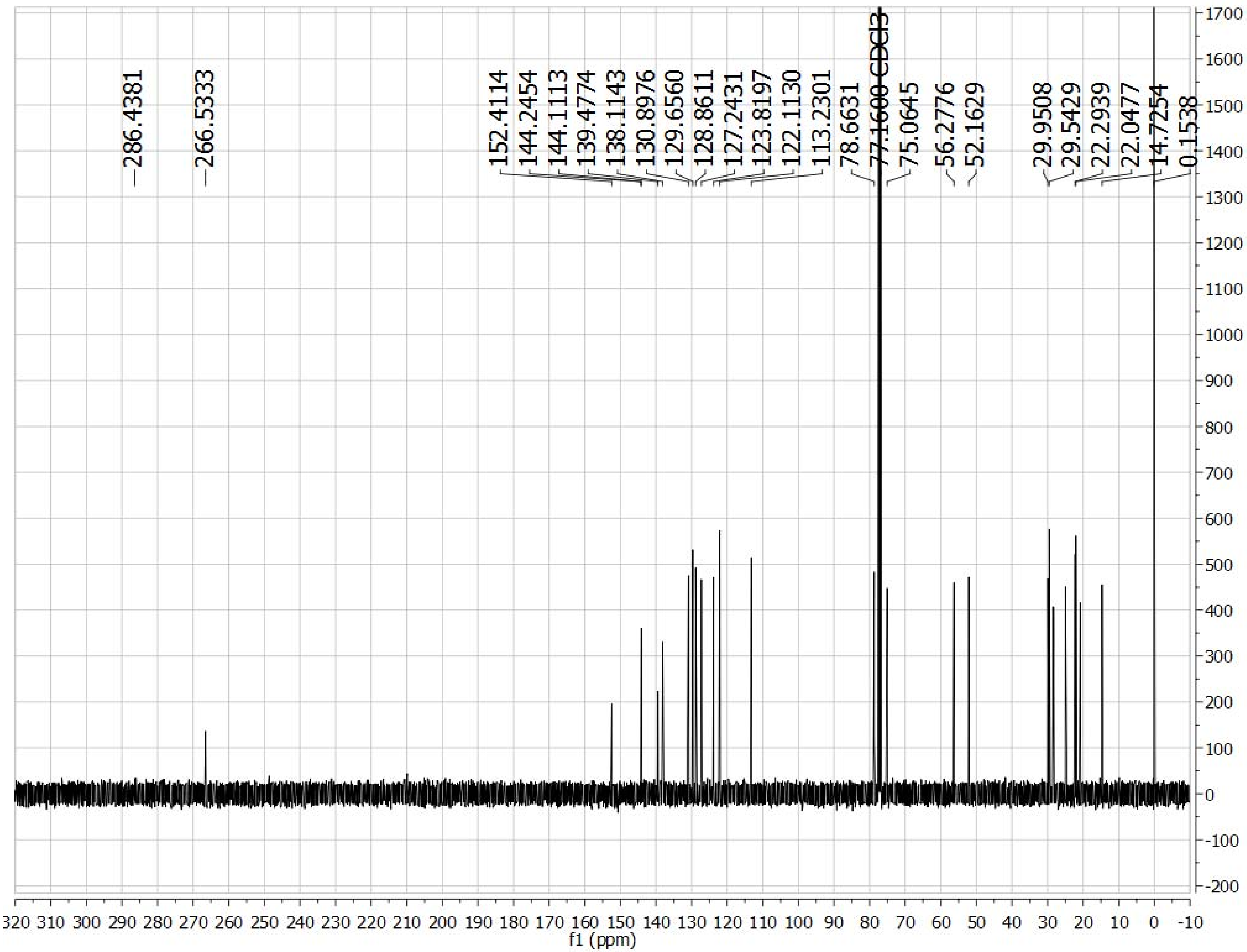


(min)	1ppm	2ppm	3ppm
0	0.0	0.0	0.0
10	3.7	4.7	9.7
20	9.5	16.2	28.9
30	15.4	24.3	37.8
45	20.9	32.4	44.4
60	24.9	37.5	47.8
80	27.9	41.6	50.3
110	30.5	44.8	52.0
150	32.2	47.8	52.4
210	33.3	49.3	52.6
300	33.8	49.3	52.6

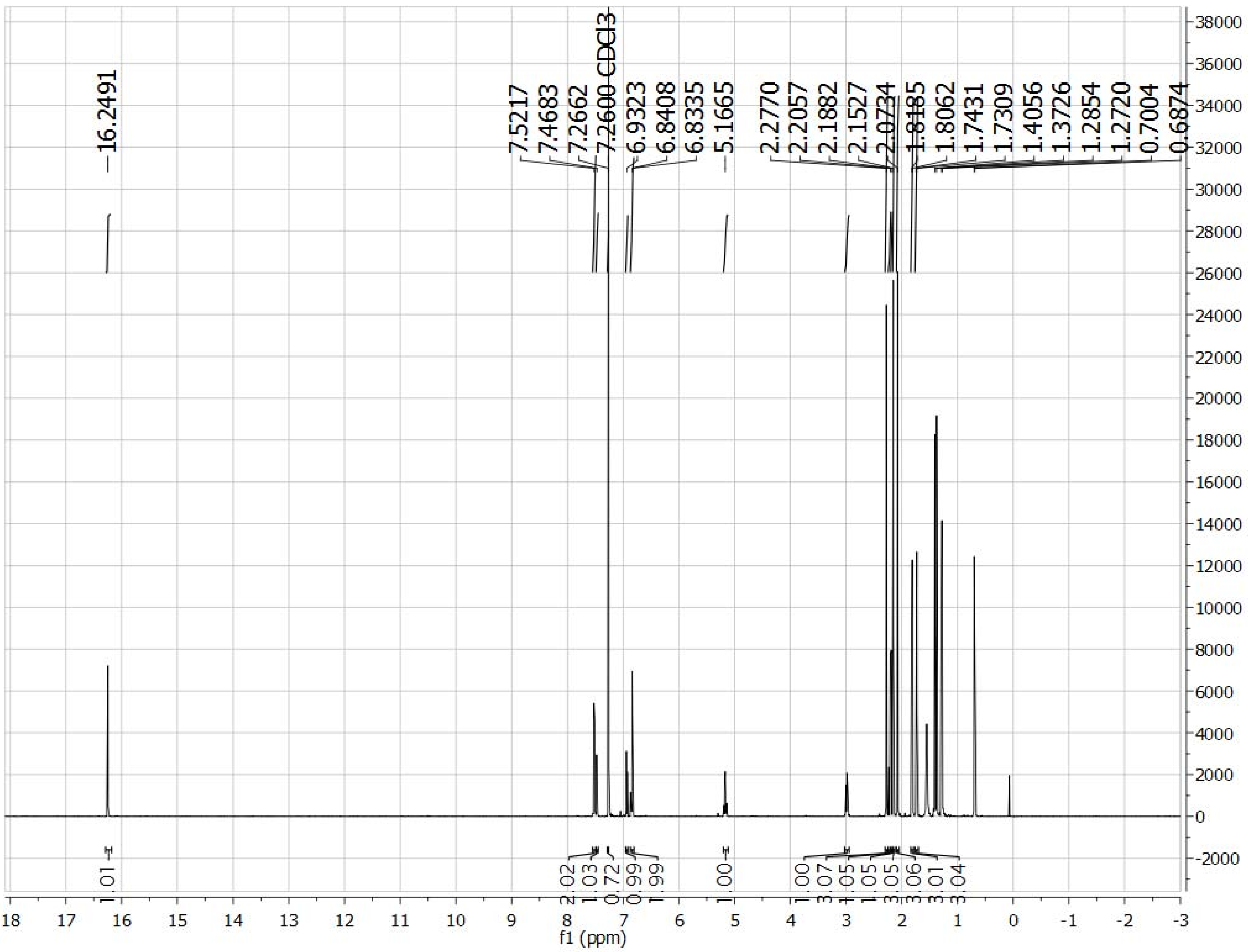
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 9



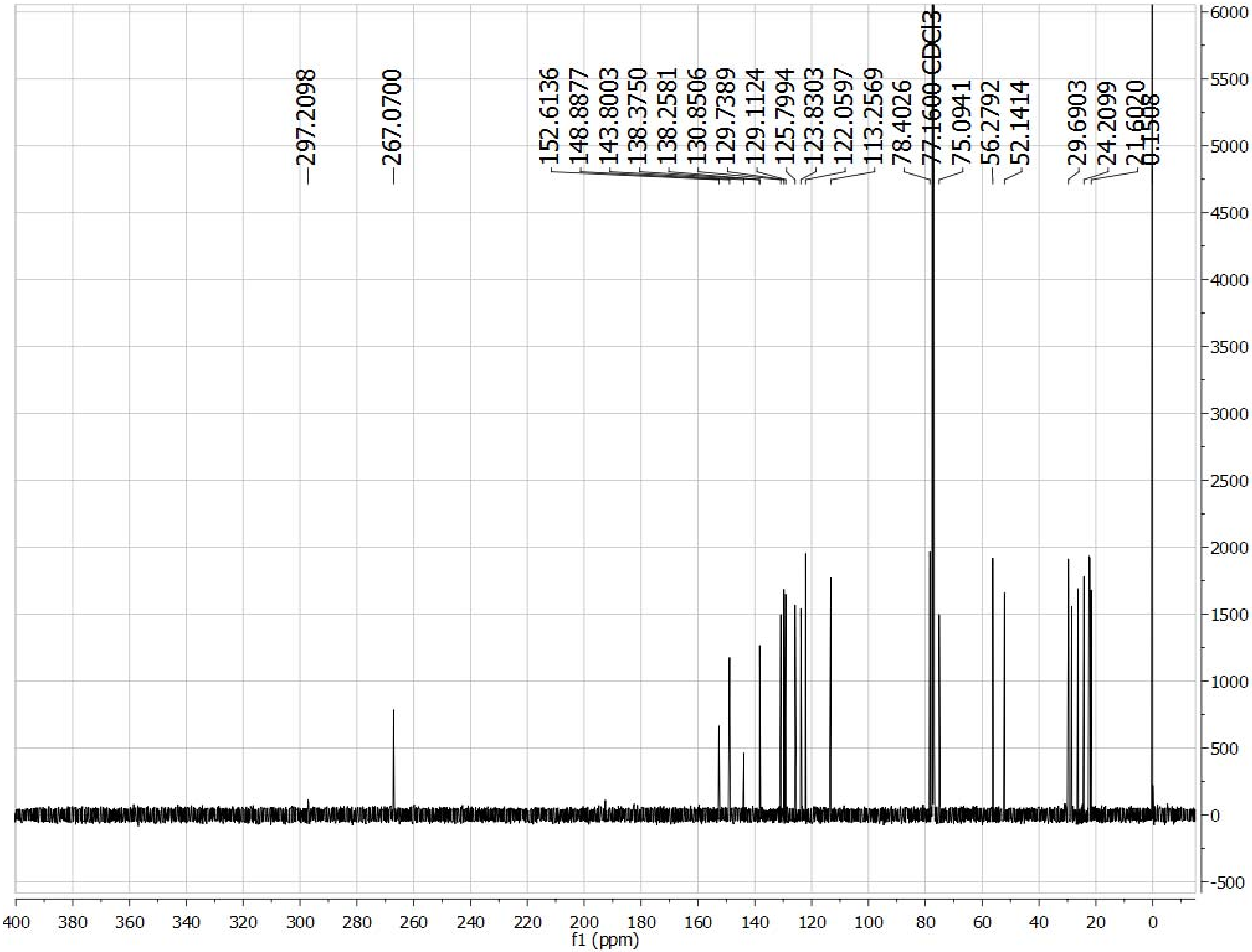
^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of catalyst 9



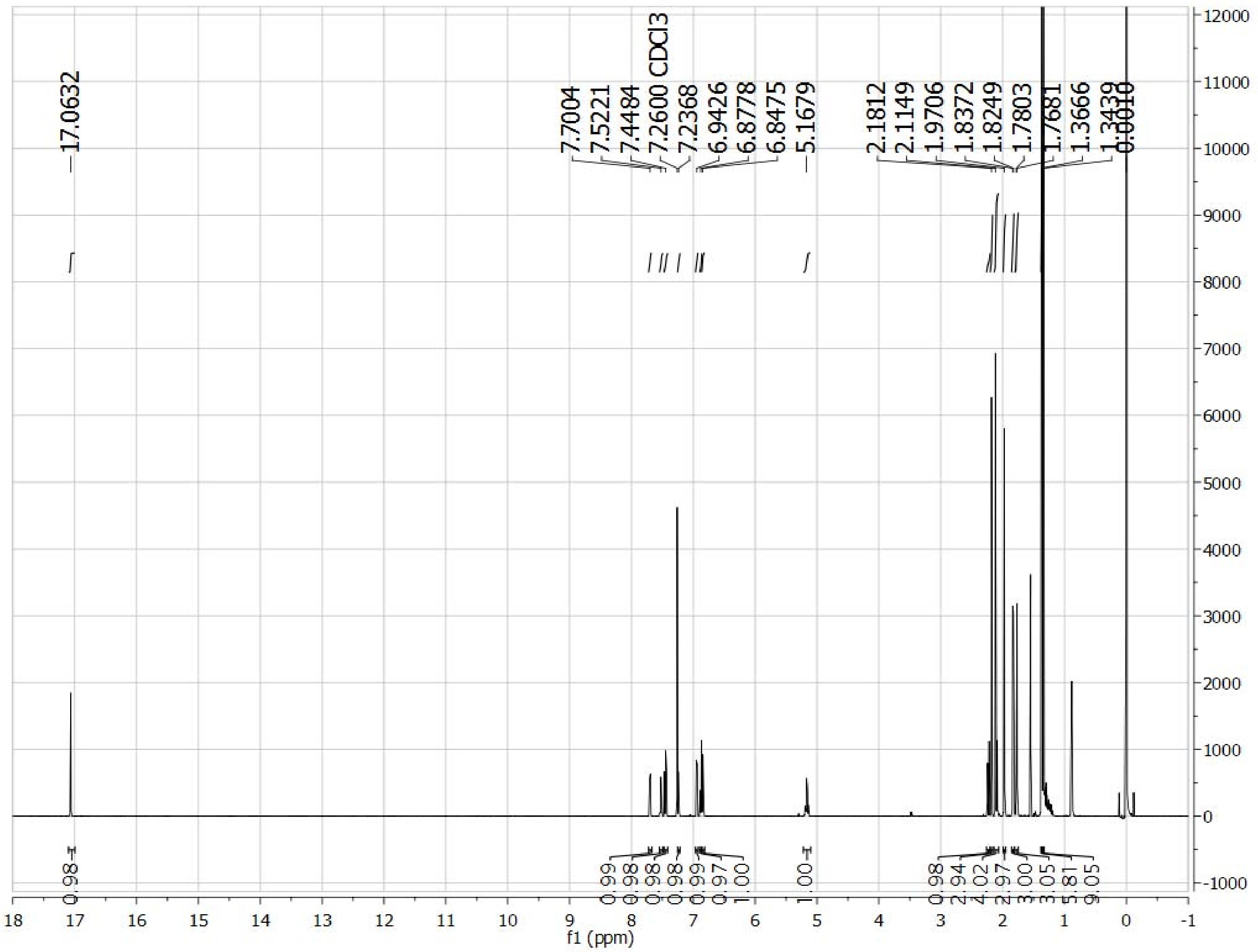
^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of catalyst 11



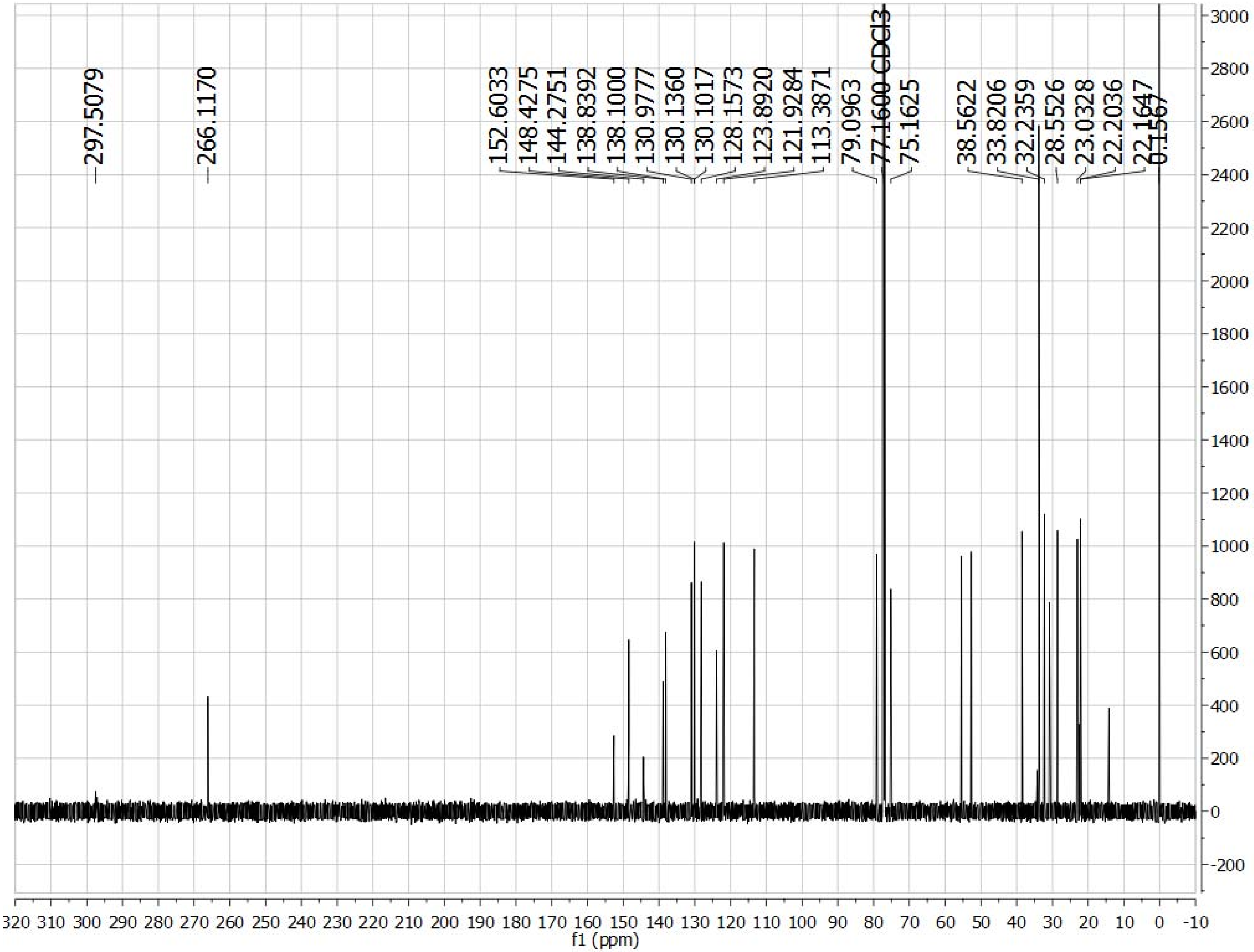
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of catalyst 11



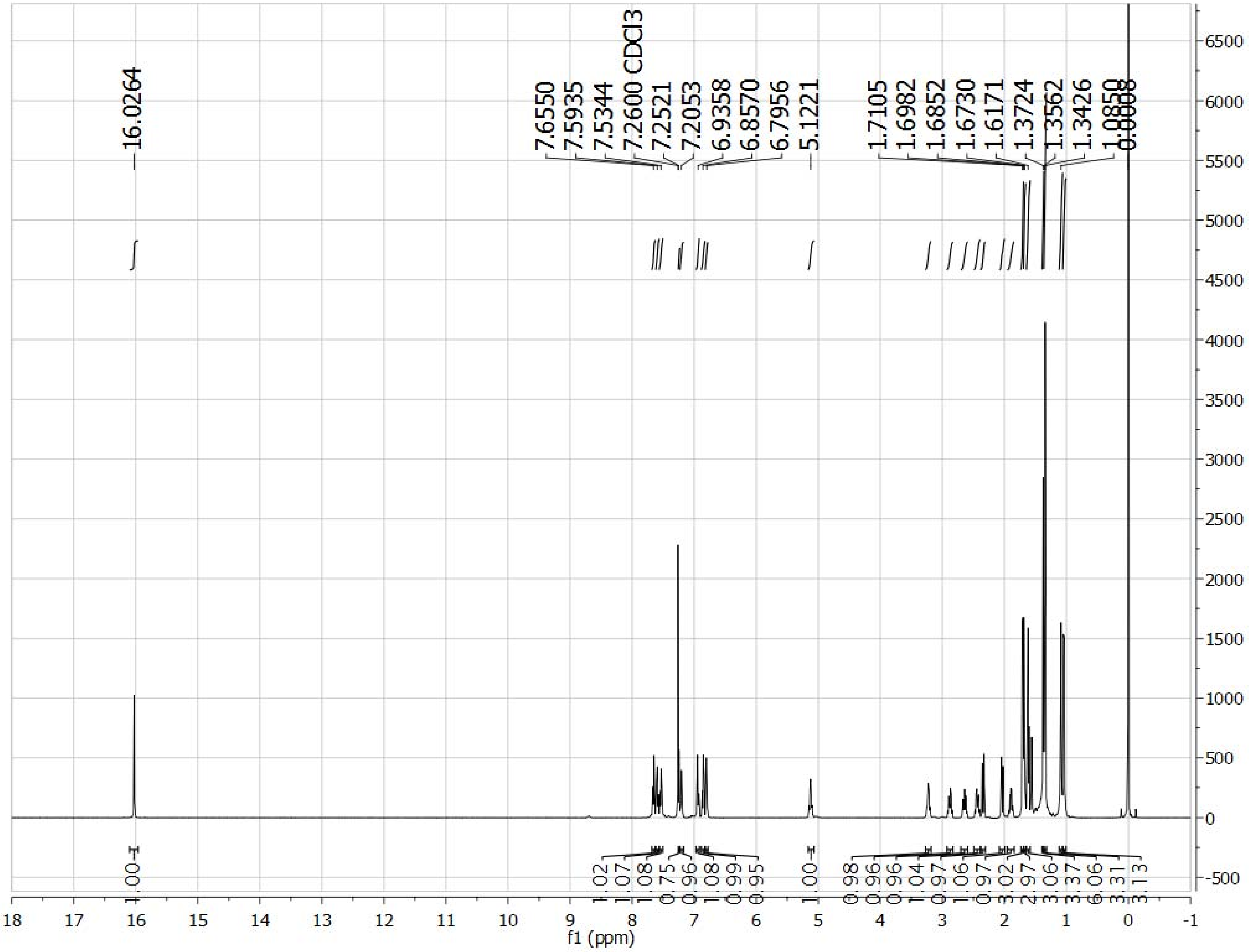
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 12



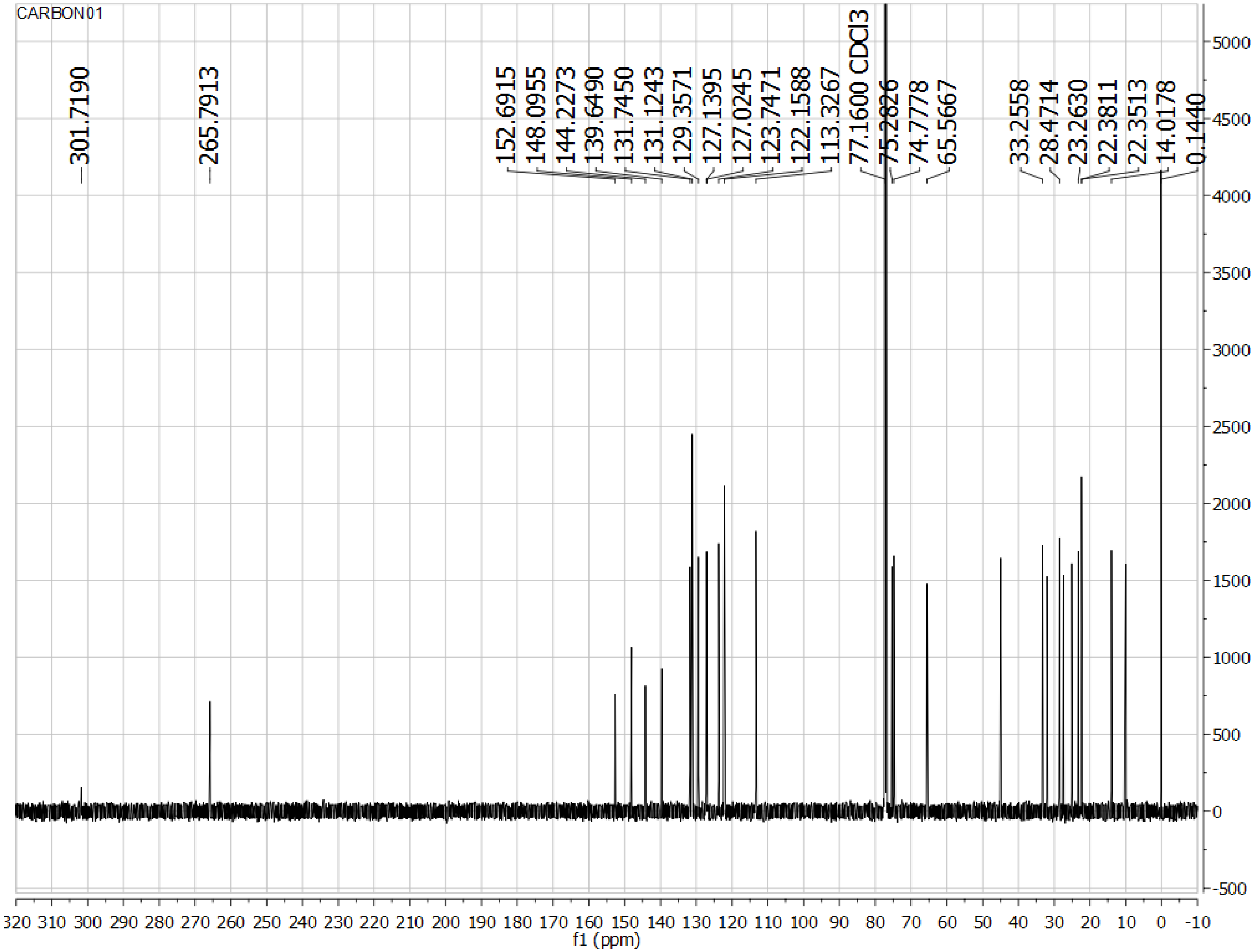
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of catalyst 12



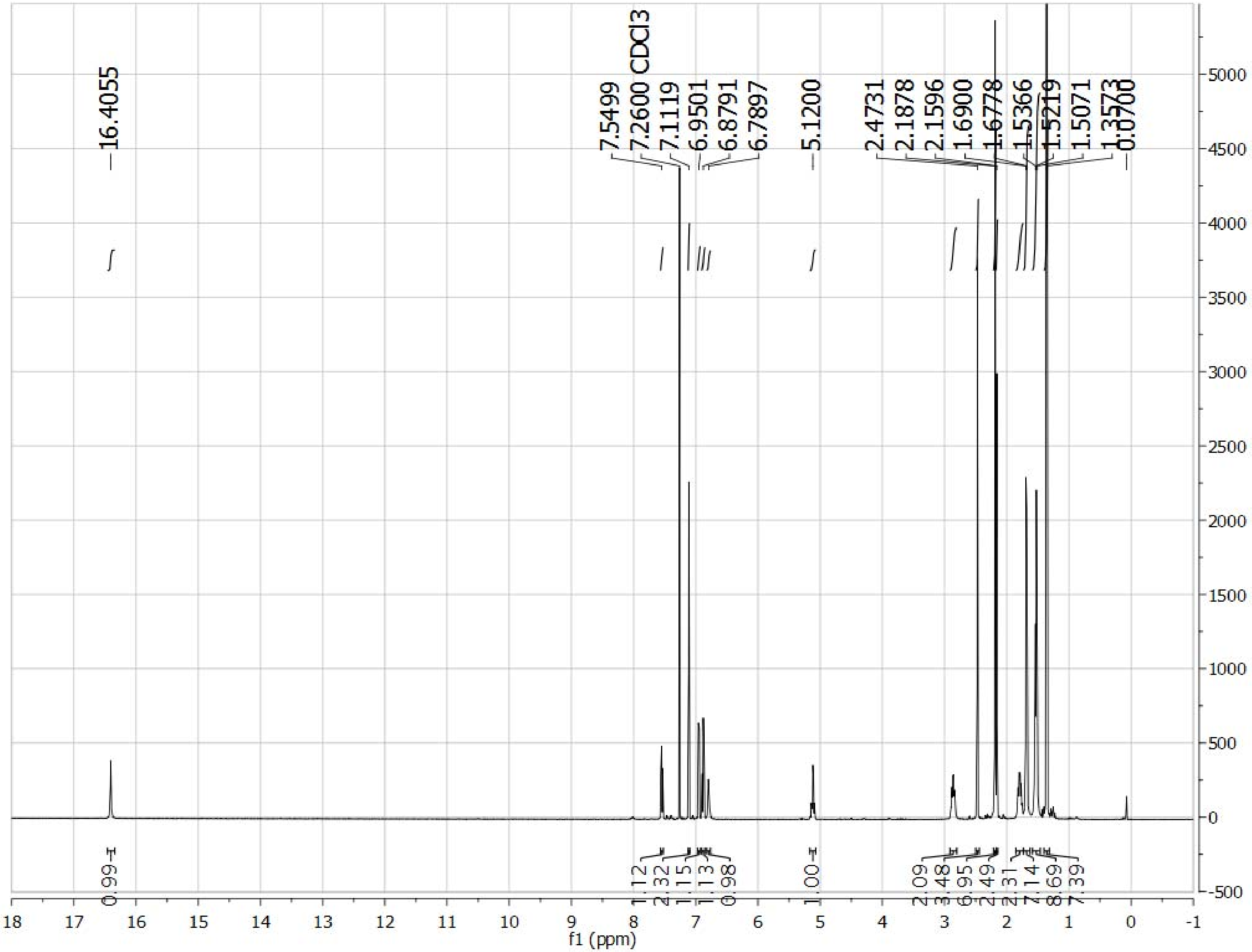
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 14



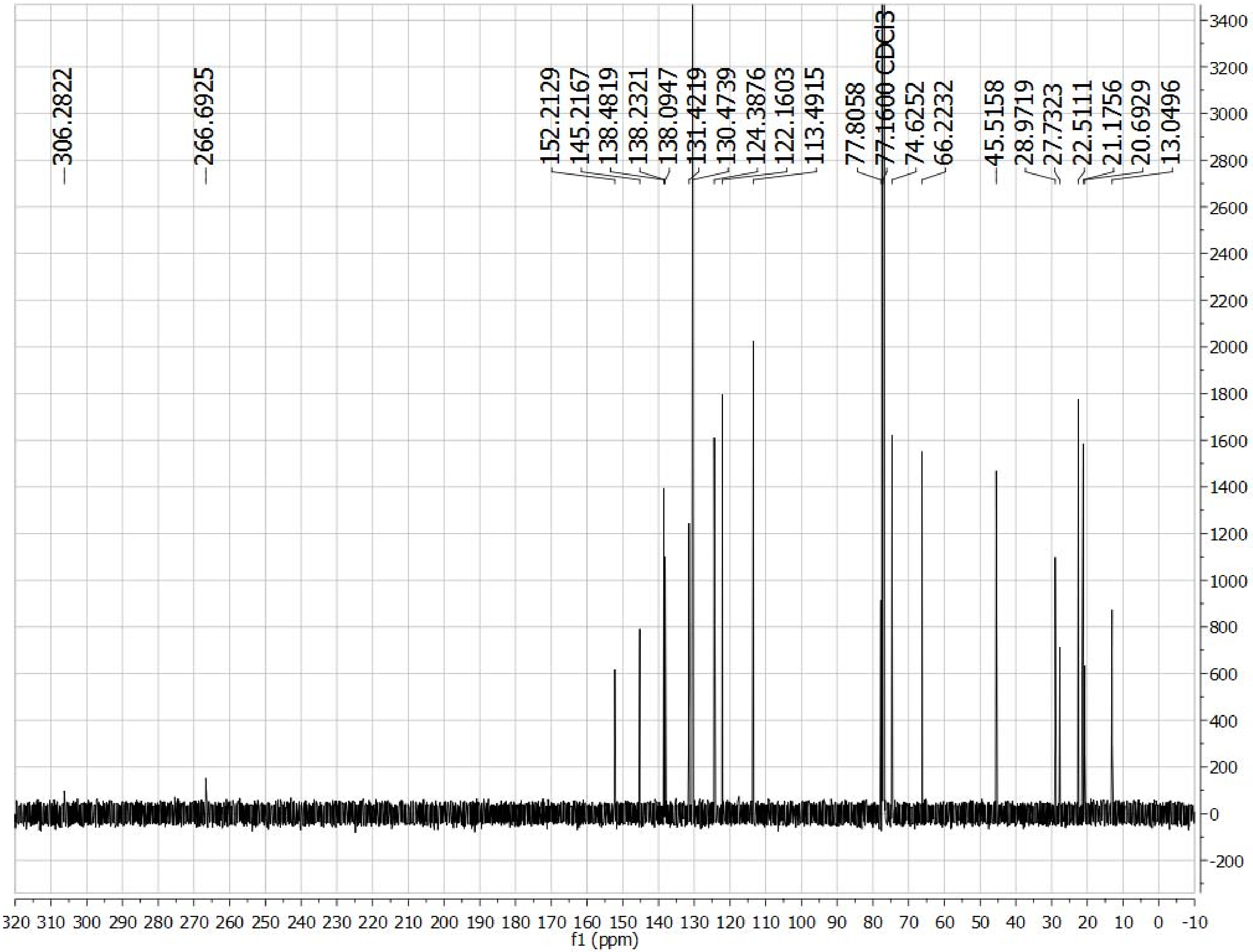
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of catalyst 14



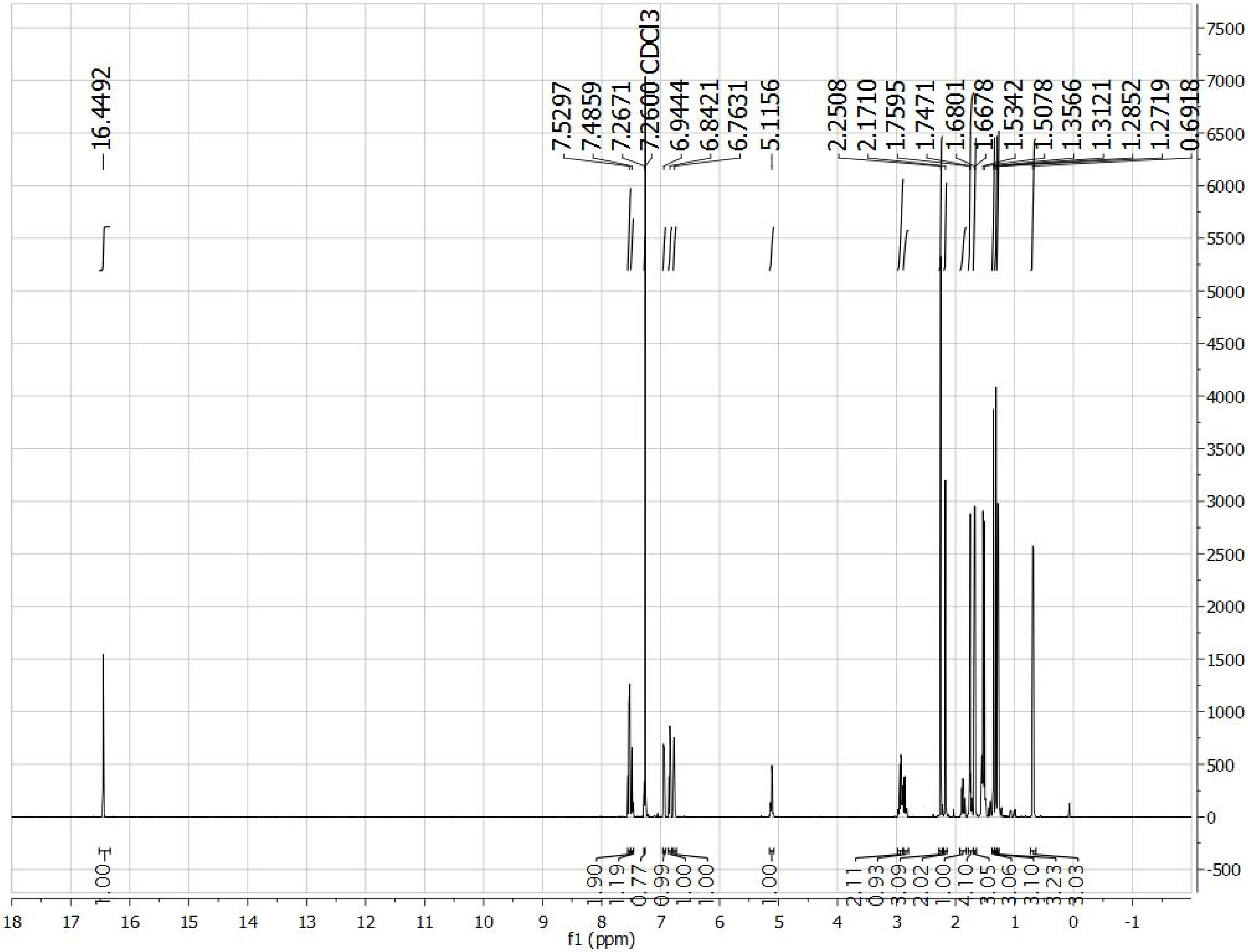
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 15



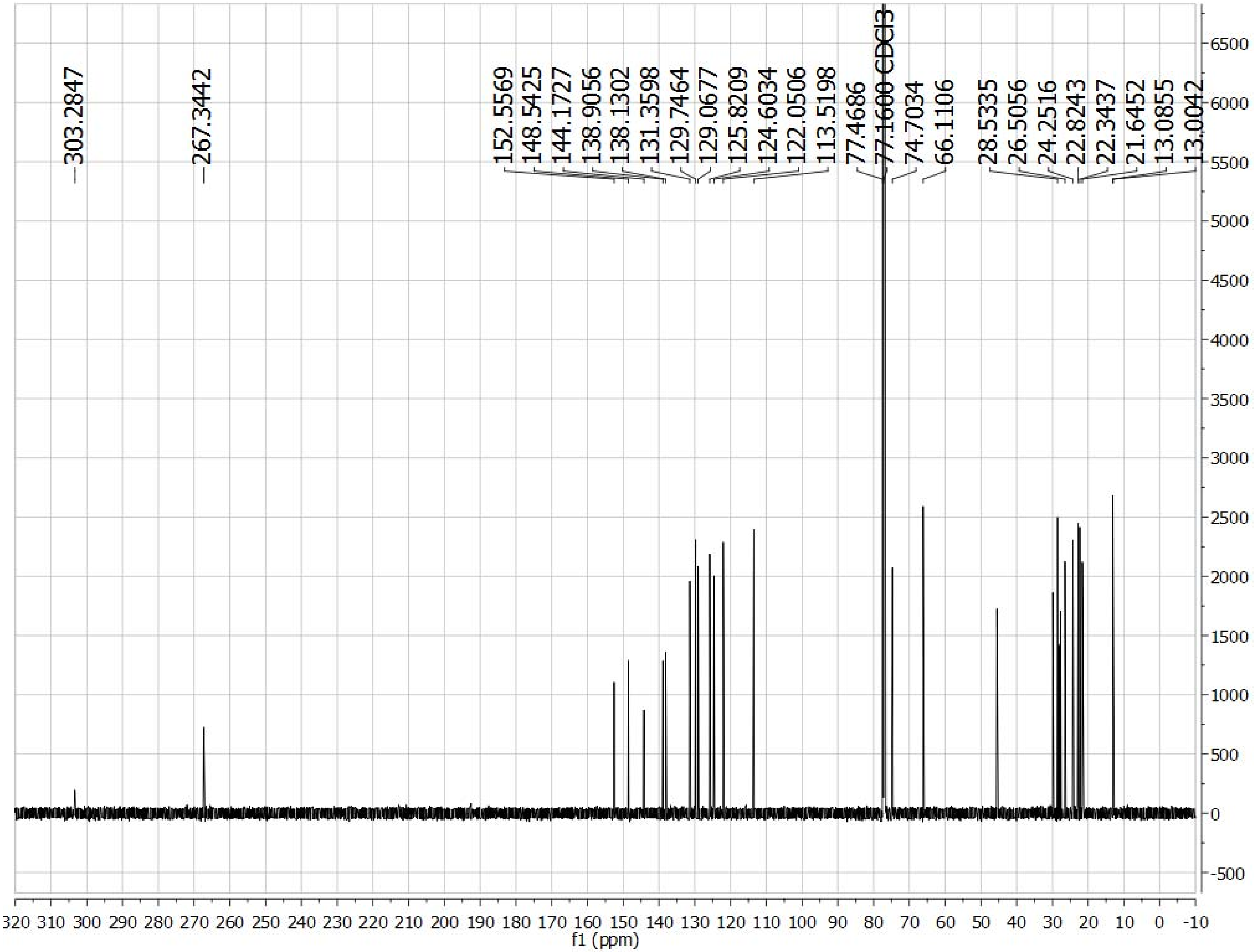
^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of catalyst 15



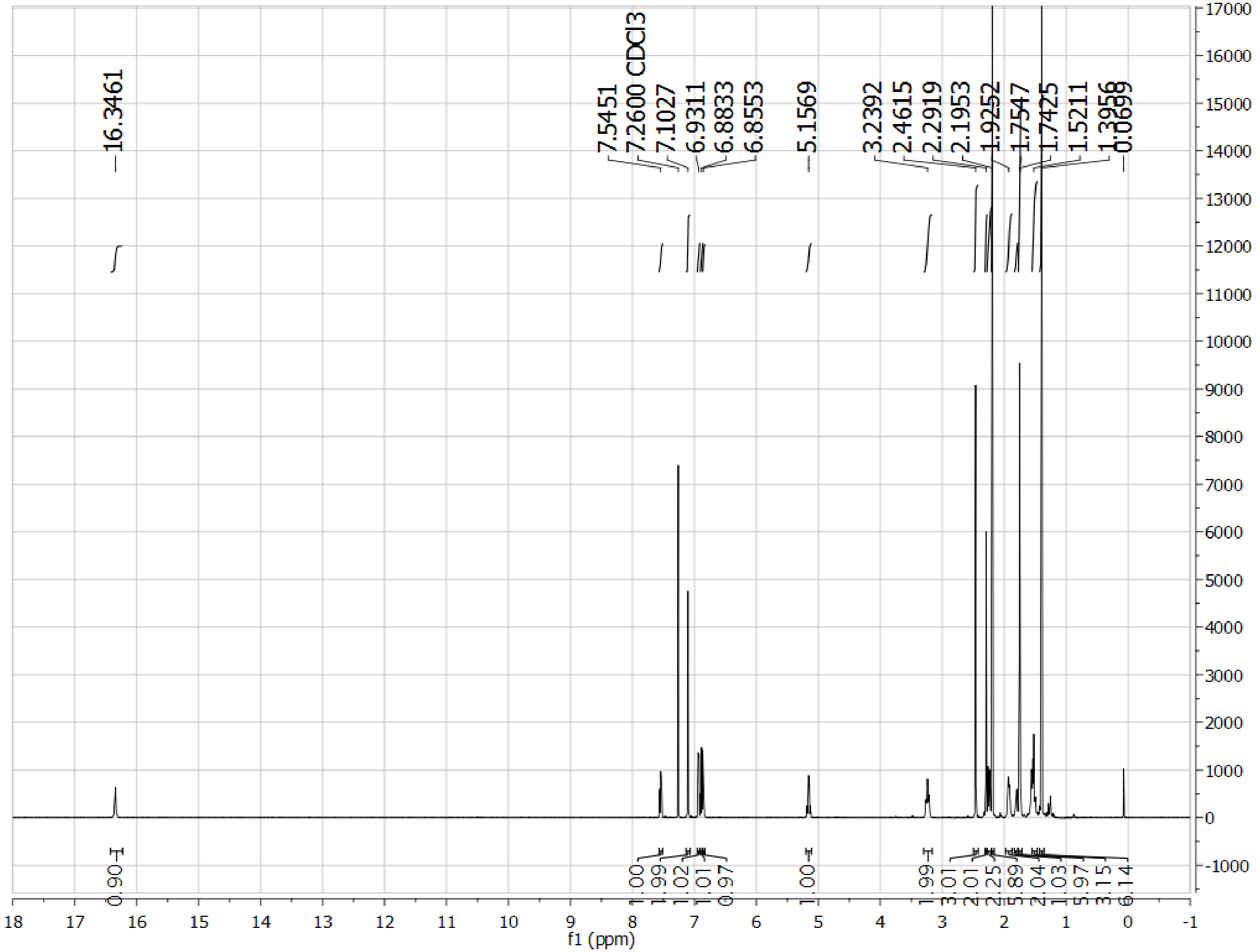
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 16



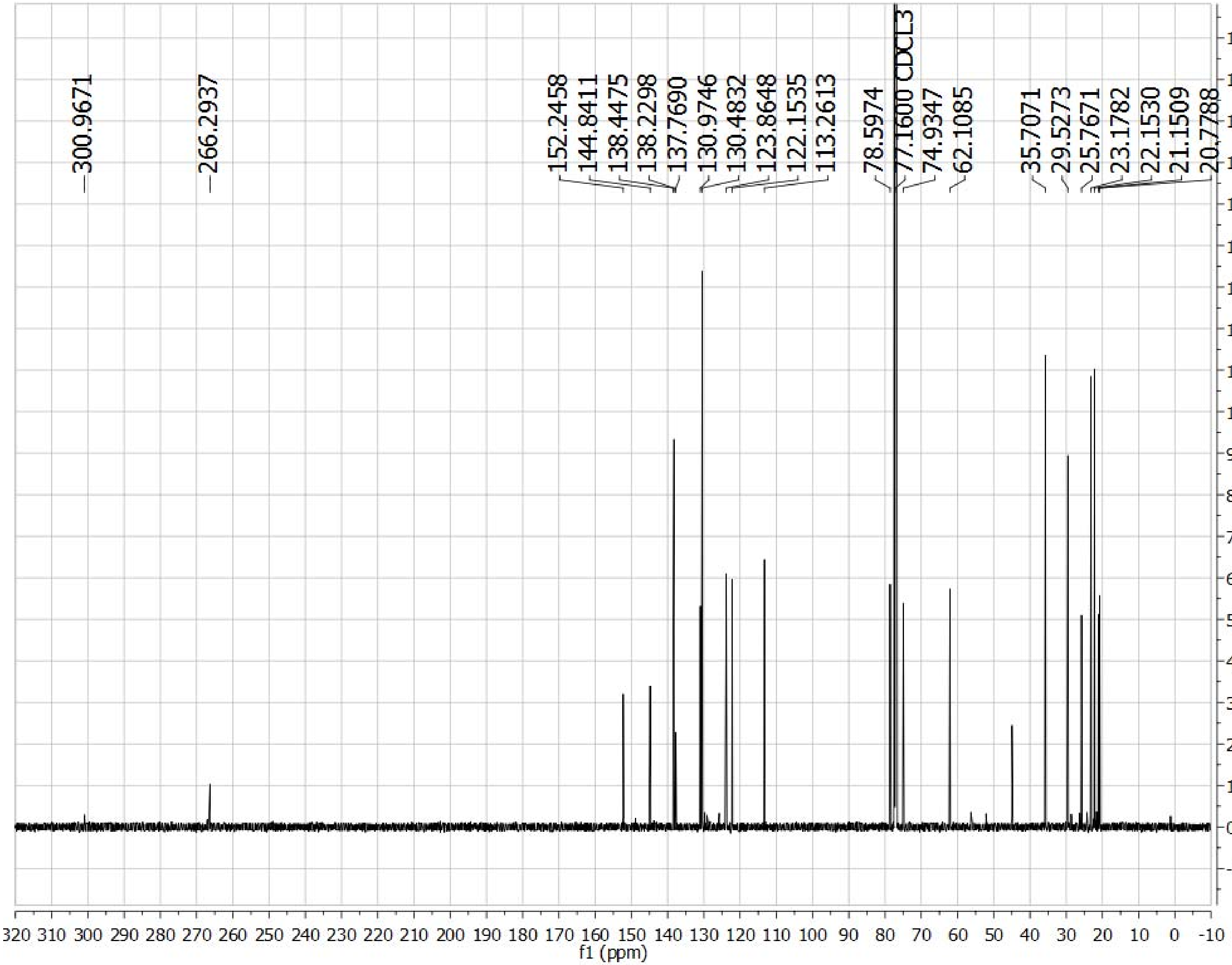
^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of catalyst 16



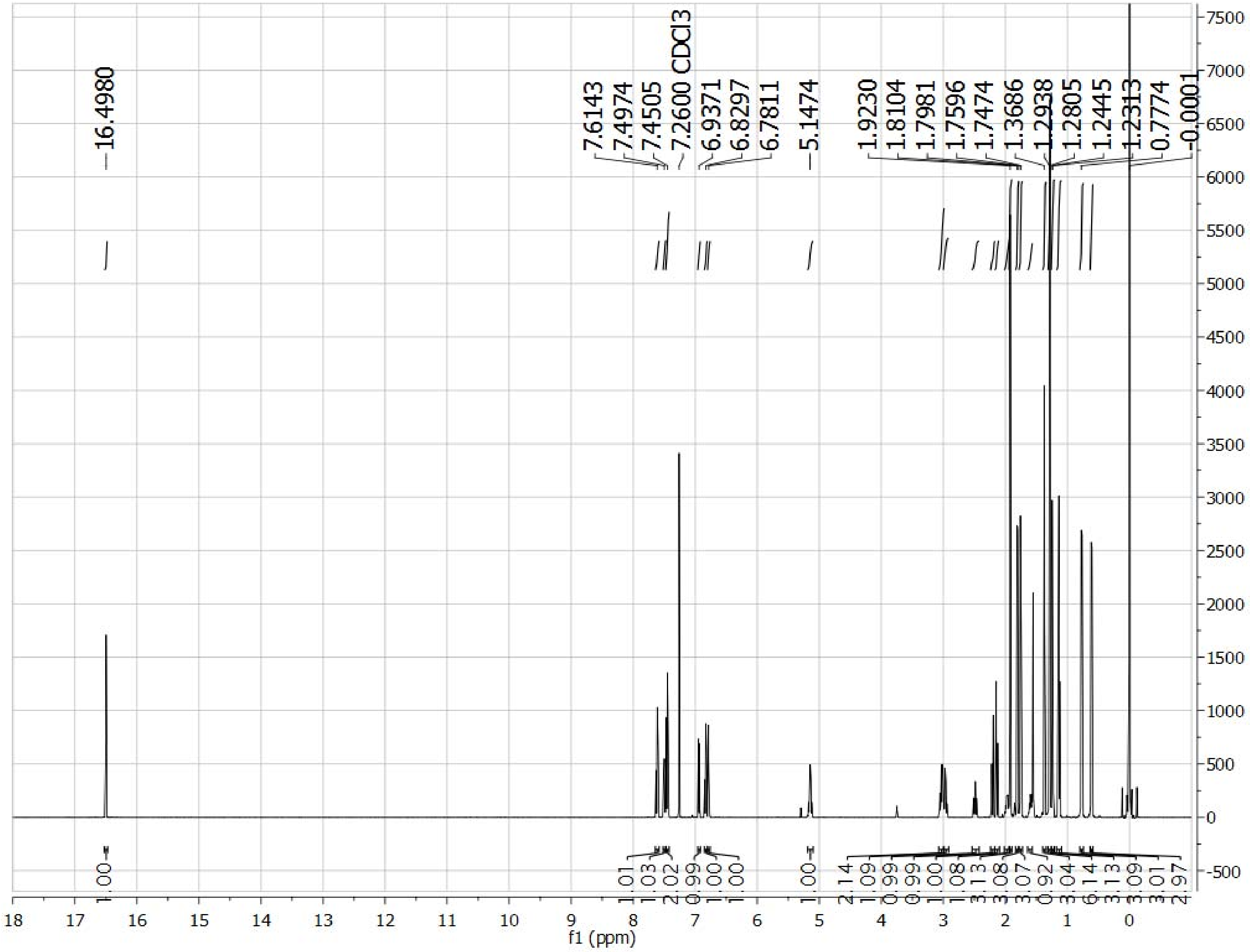
^{1}**H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 17**



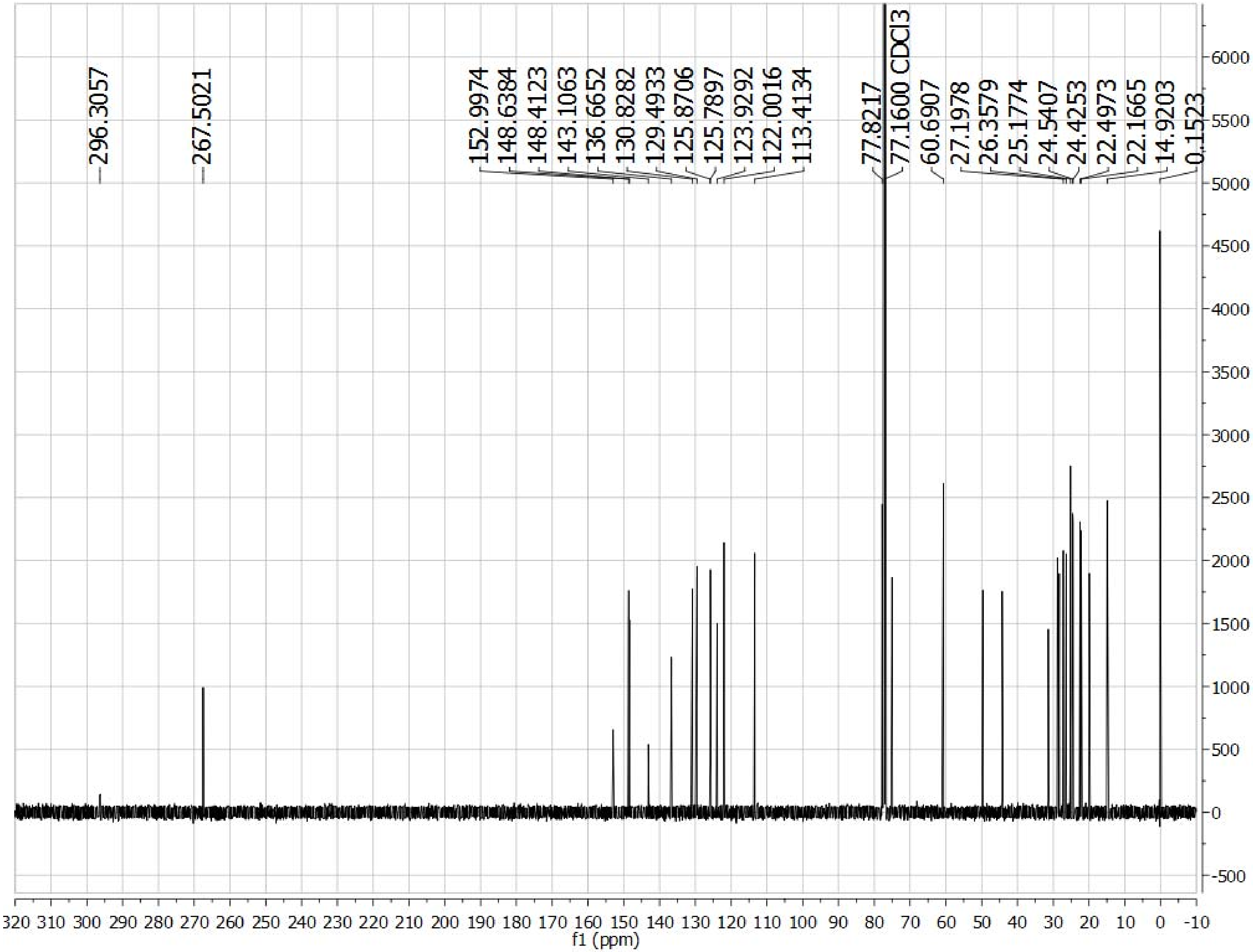
^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of catalyst 17



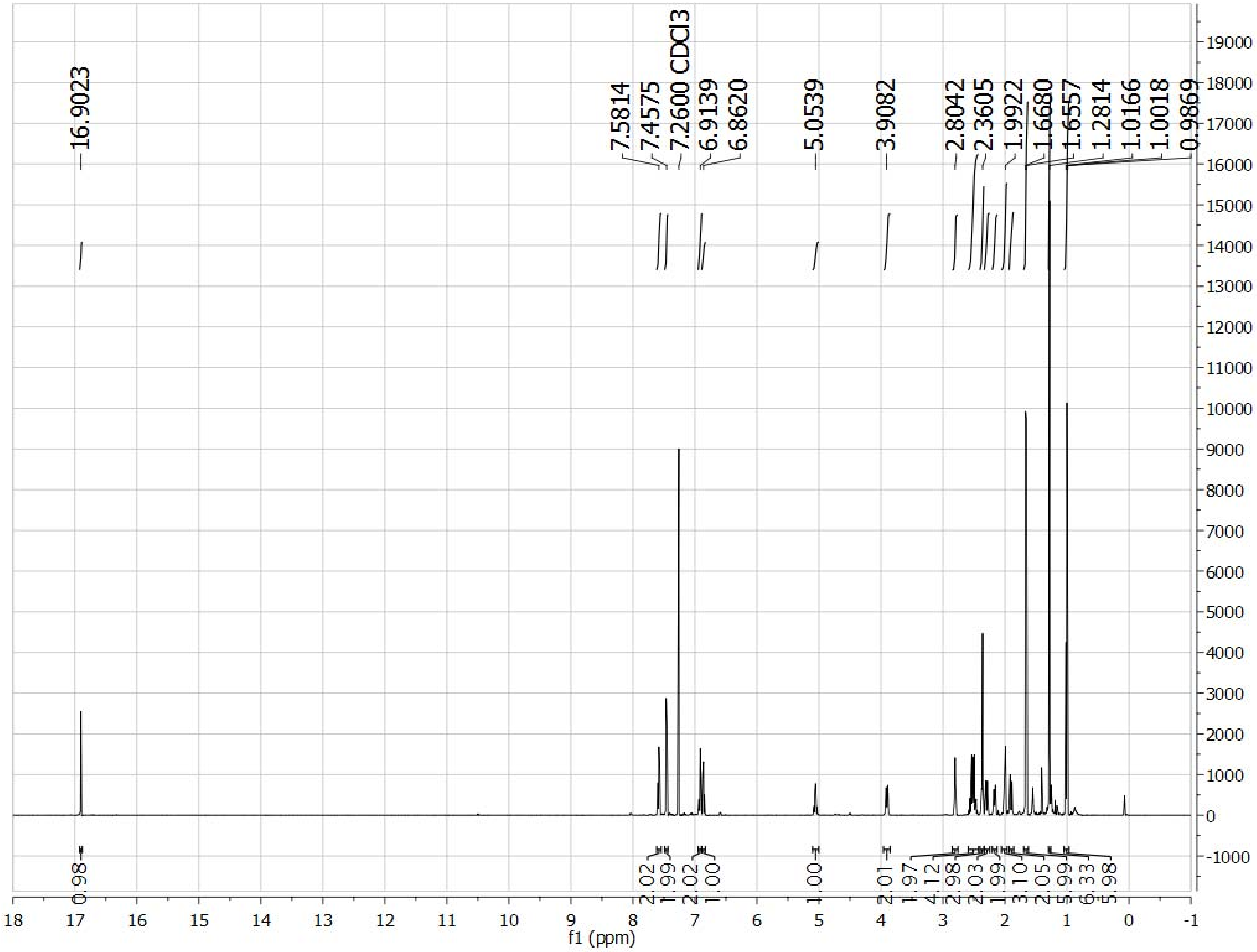
^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of catalyst 19



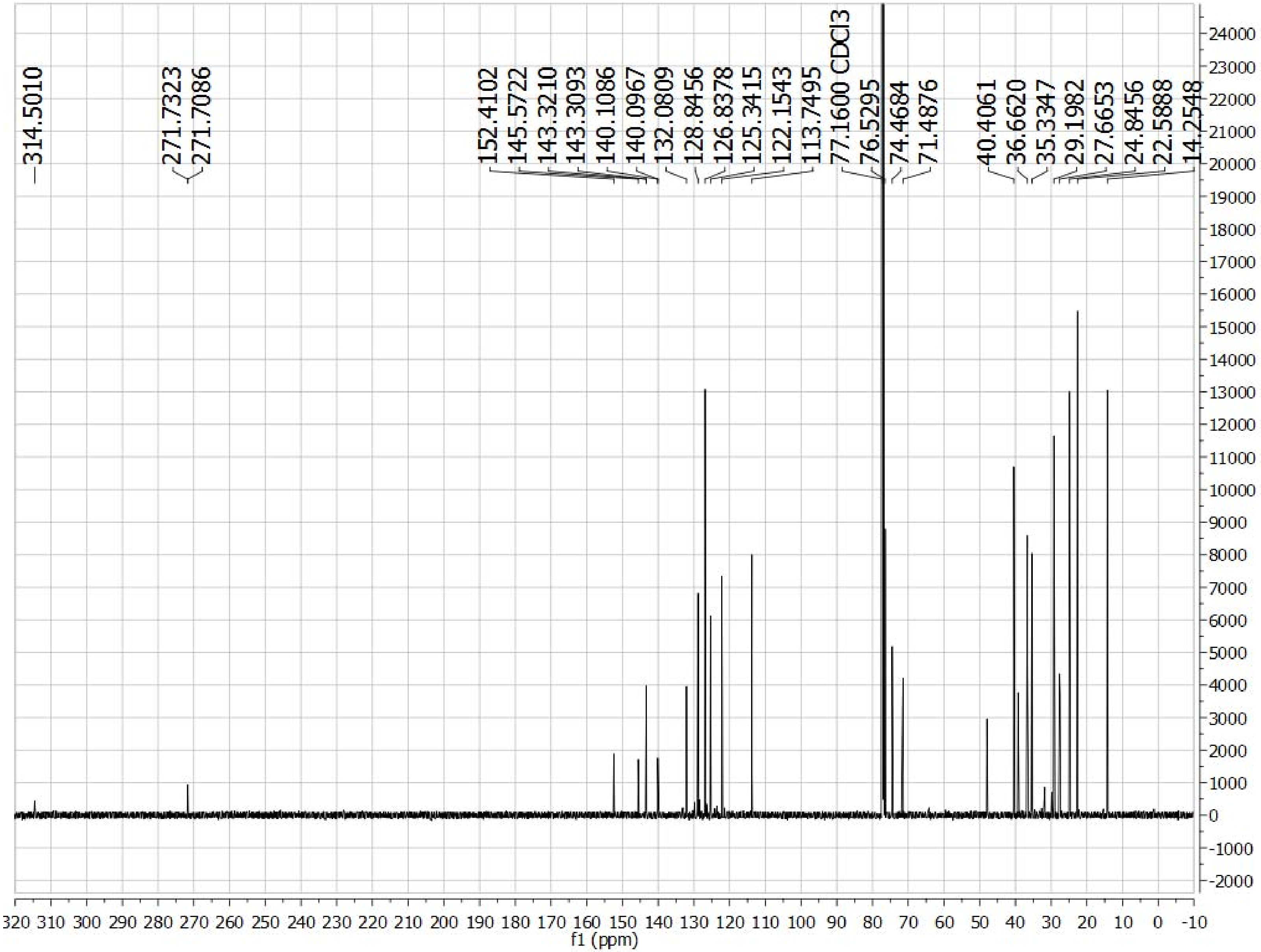
^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of catalyst 19



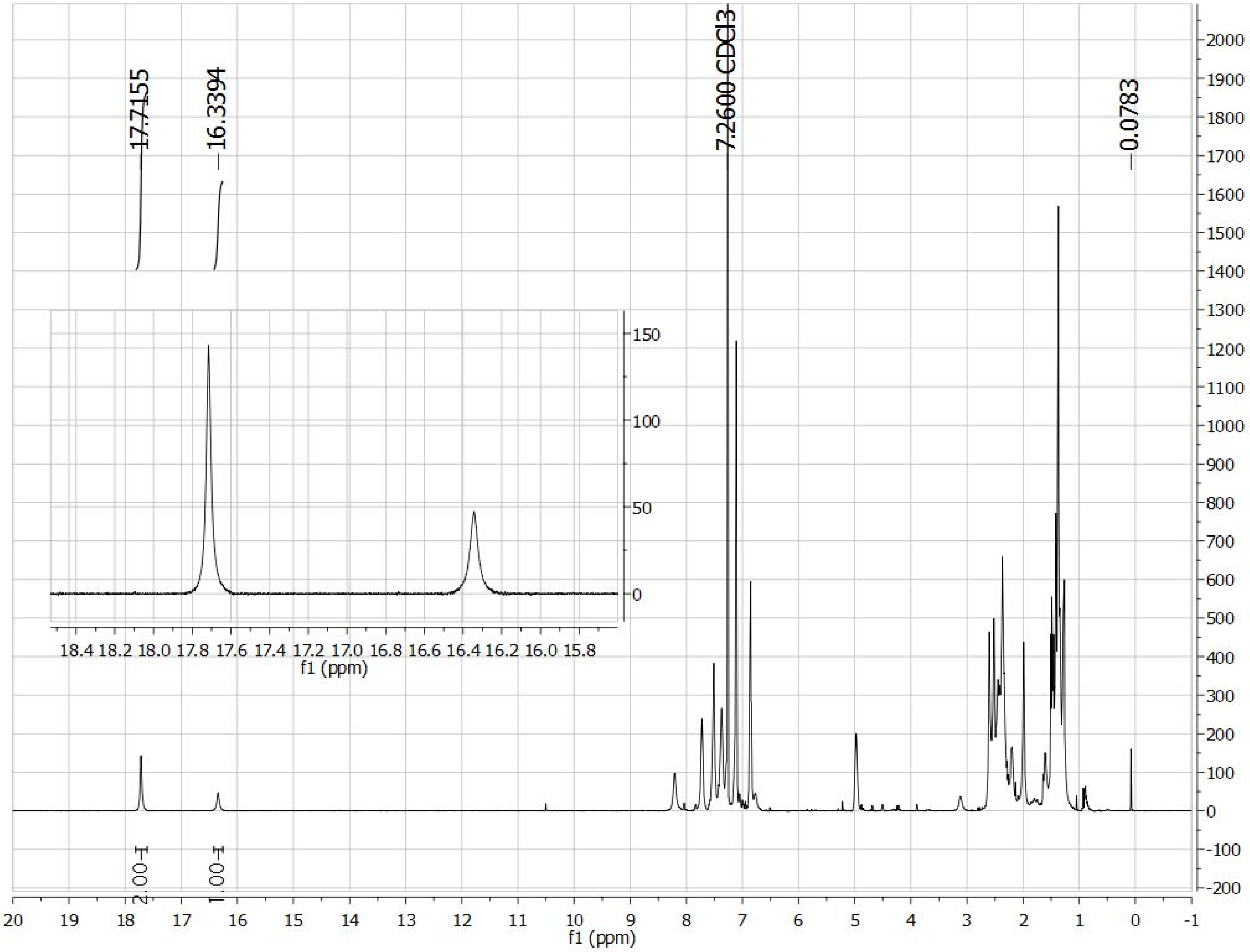
^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of catalyst 20



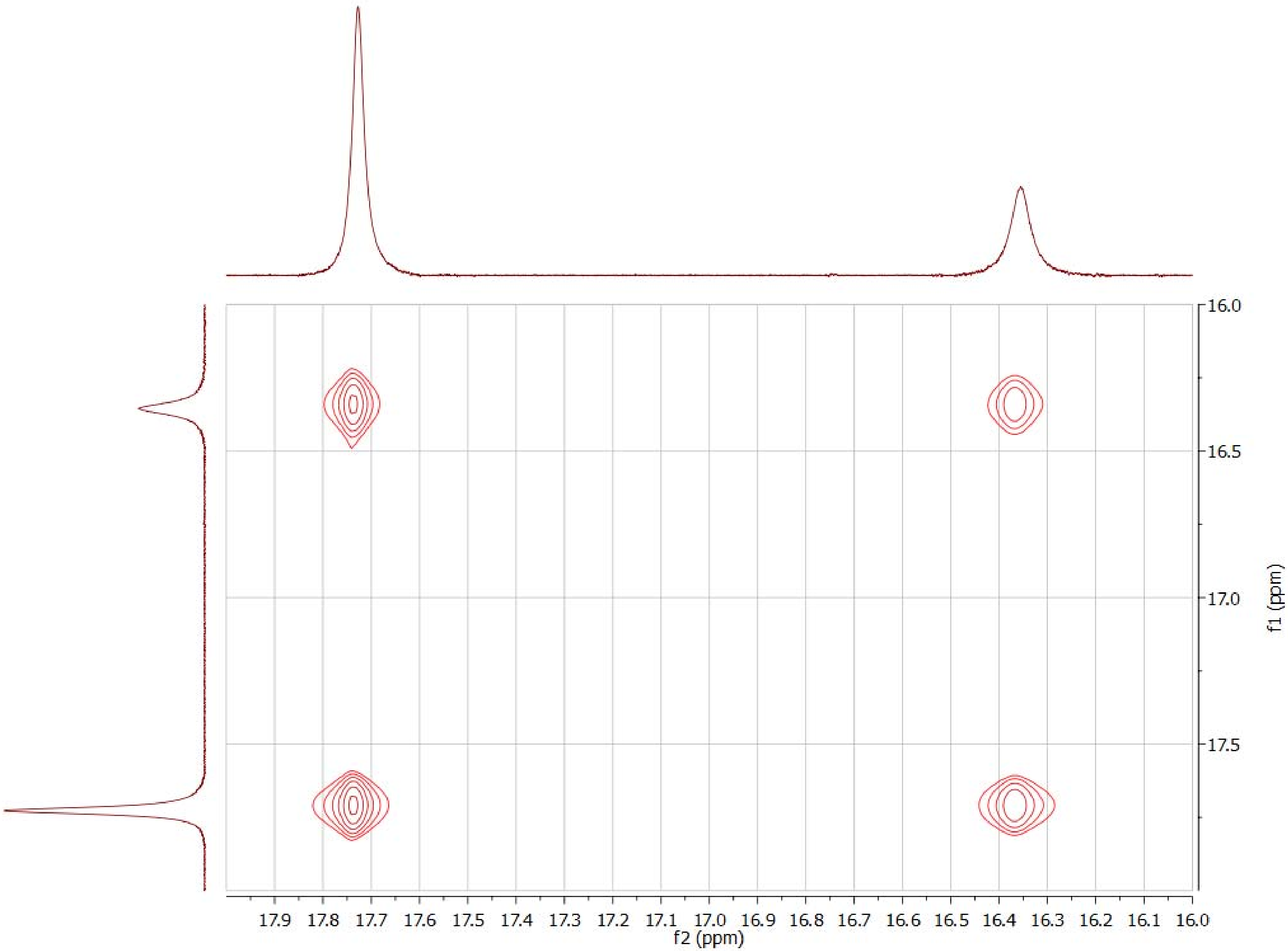
^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of catalyst 20



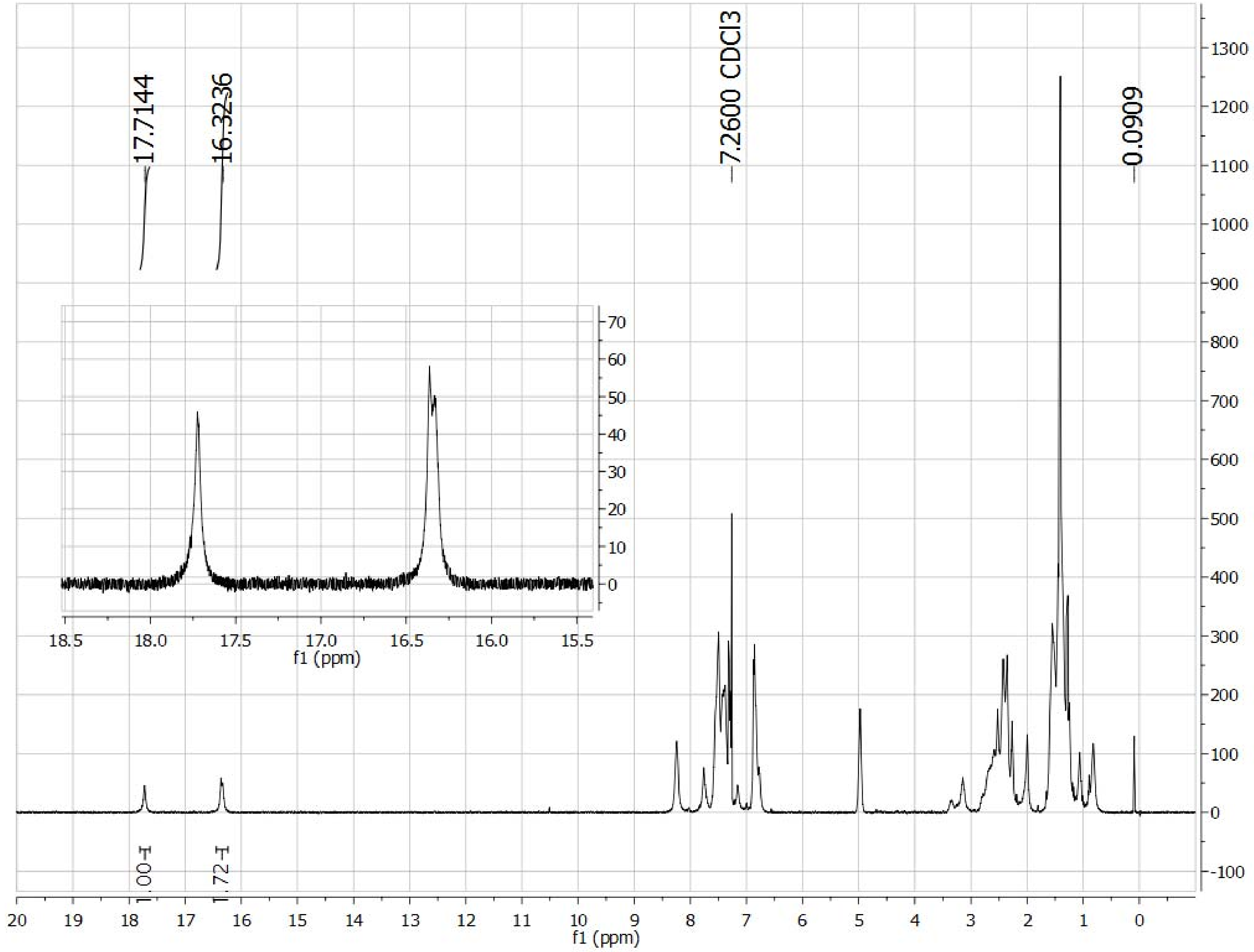
^1H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 21



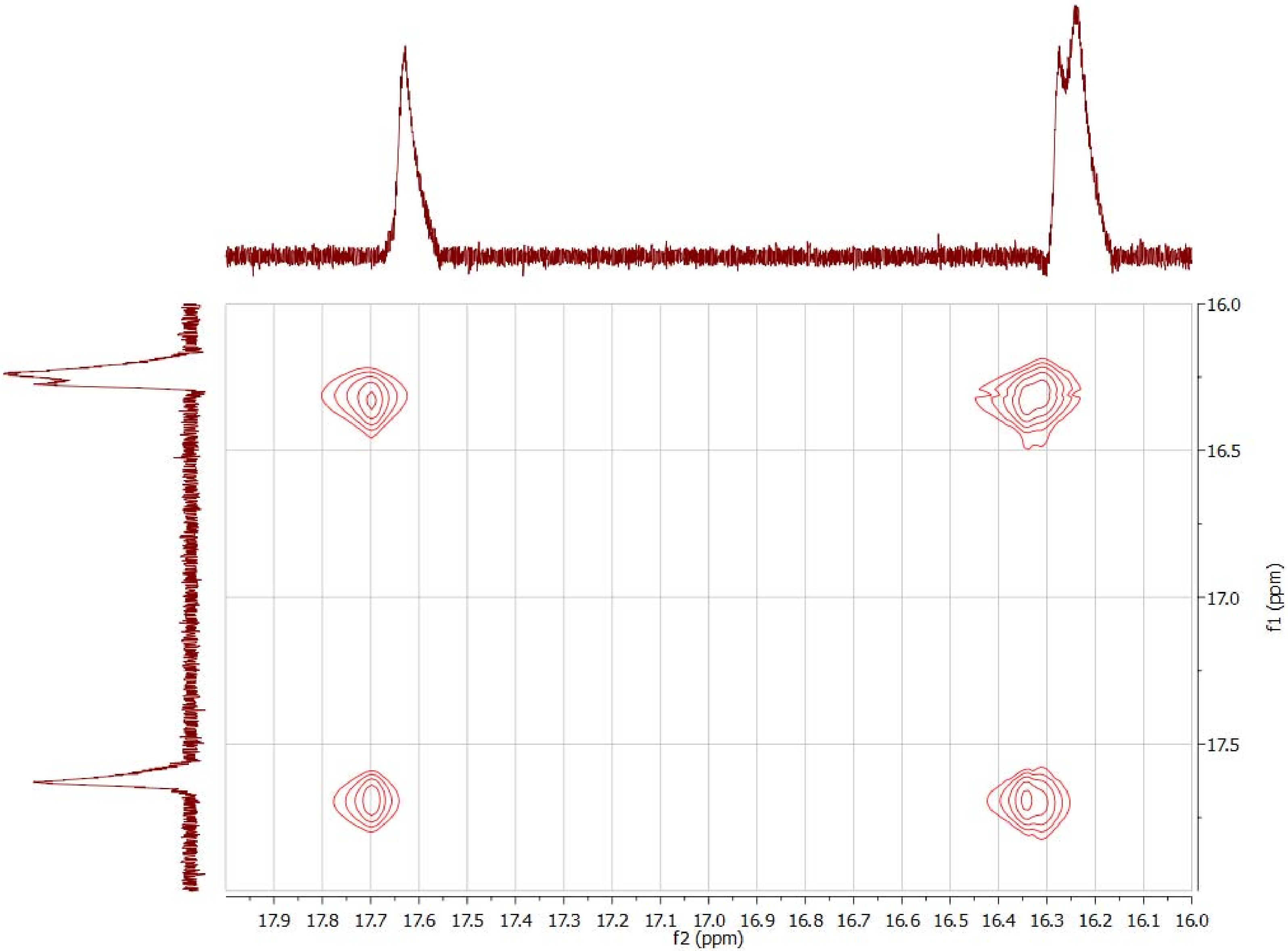
ROESY-AD (600 MHz) spectrum of catalyst 21, showing chemical exchange of the benzylidene protons (16 – 18 ppm)



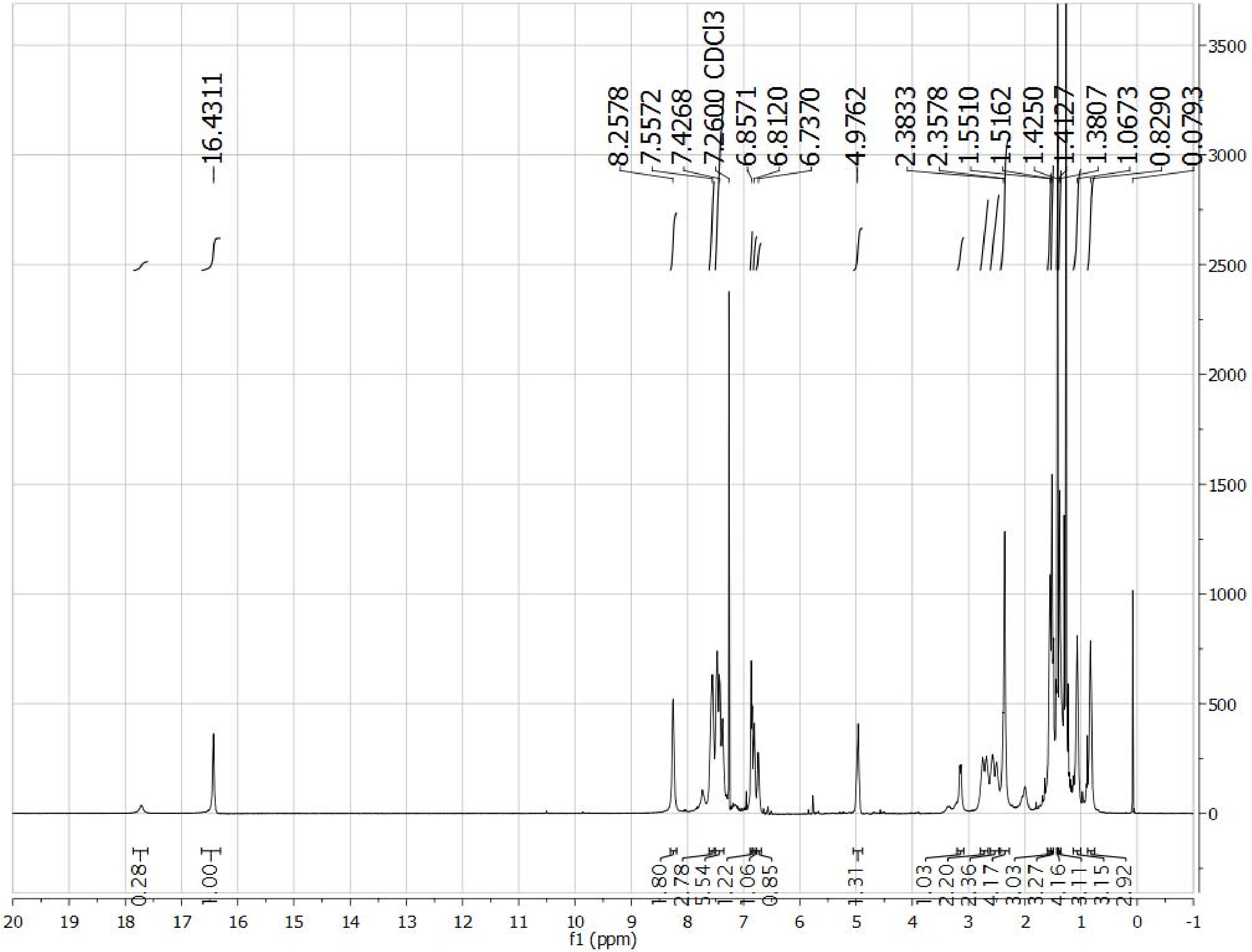
^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of catalyst 22



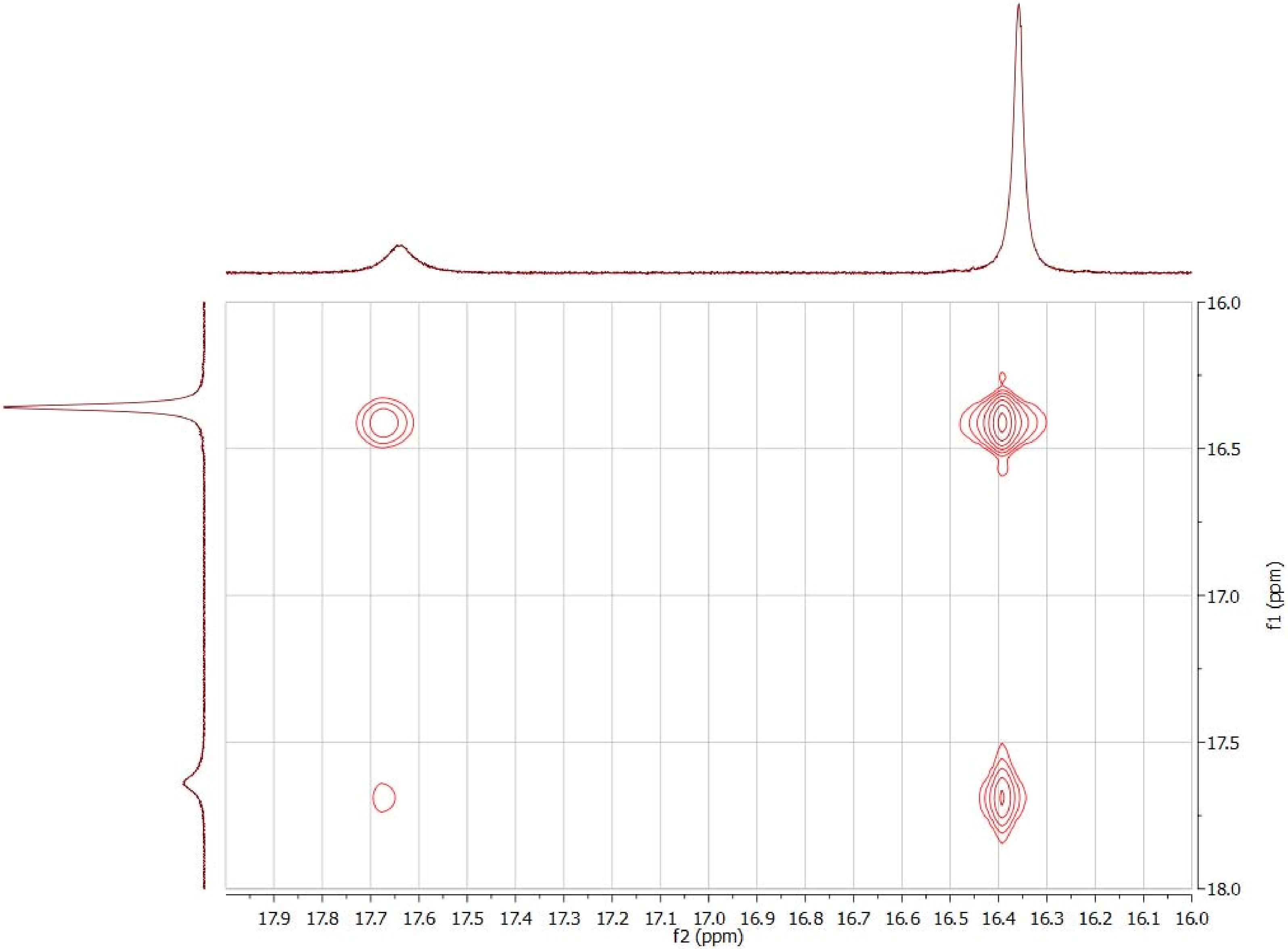
ROESY-AD (600 MHz) spectrum of catalyst 22, showing chemical exchange of the benzylidene protons (16 – 18 ppm)



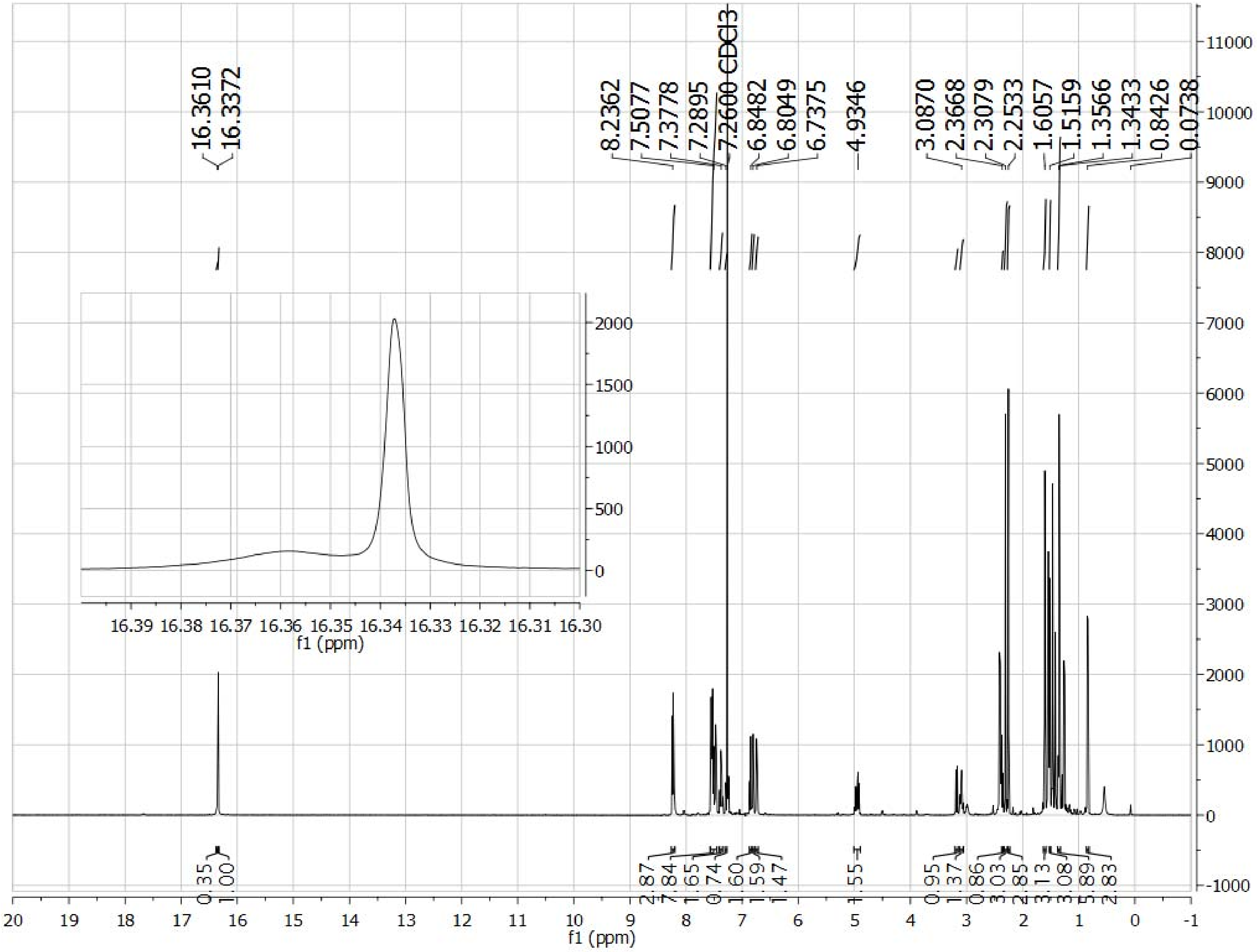
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 23



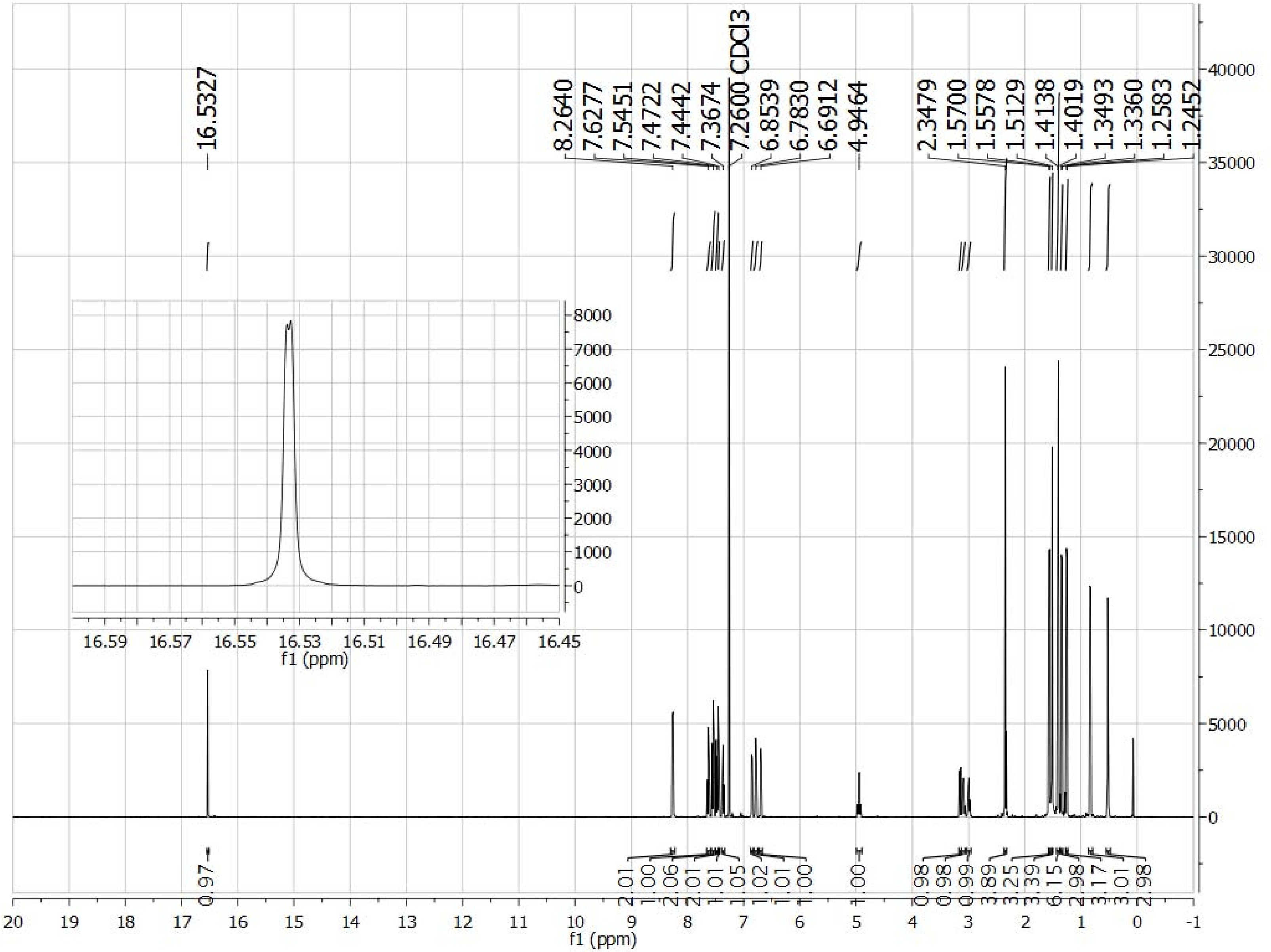
ROESY-AD (600 MHz) spectrum of catalyst 23, showing chemical exchange of the benzylidene protons (16 – 18 ppm)



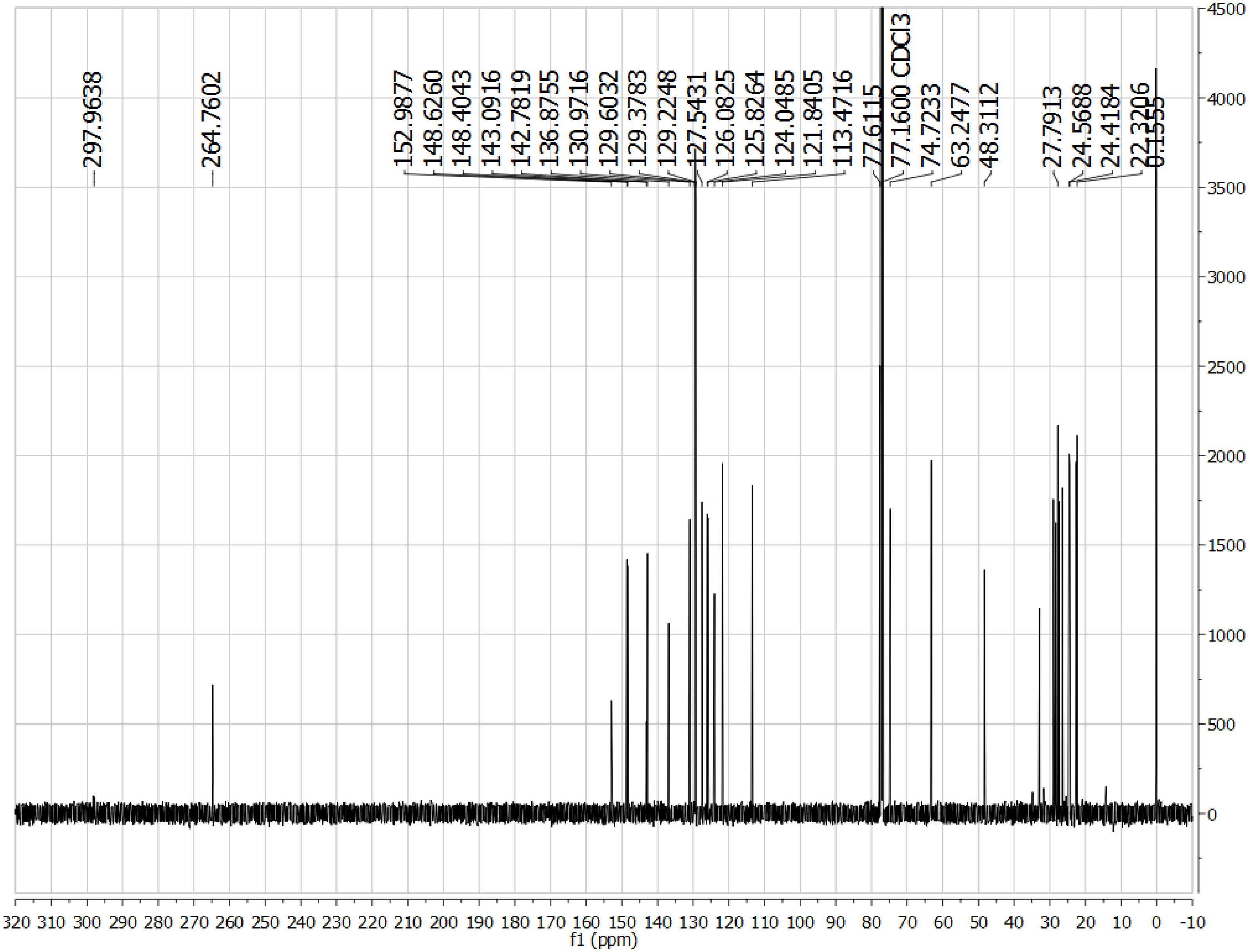
^1H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 24



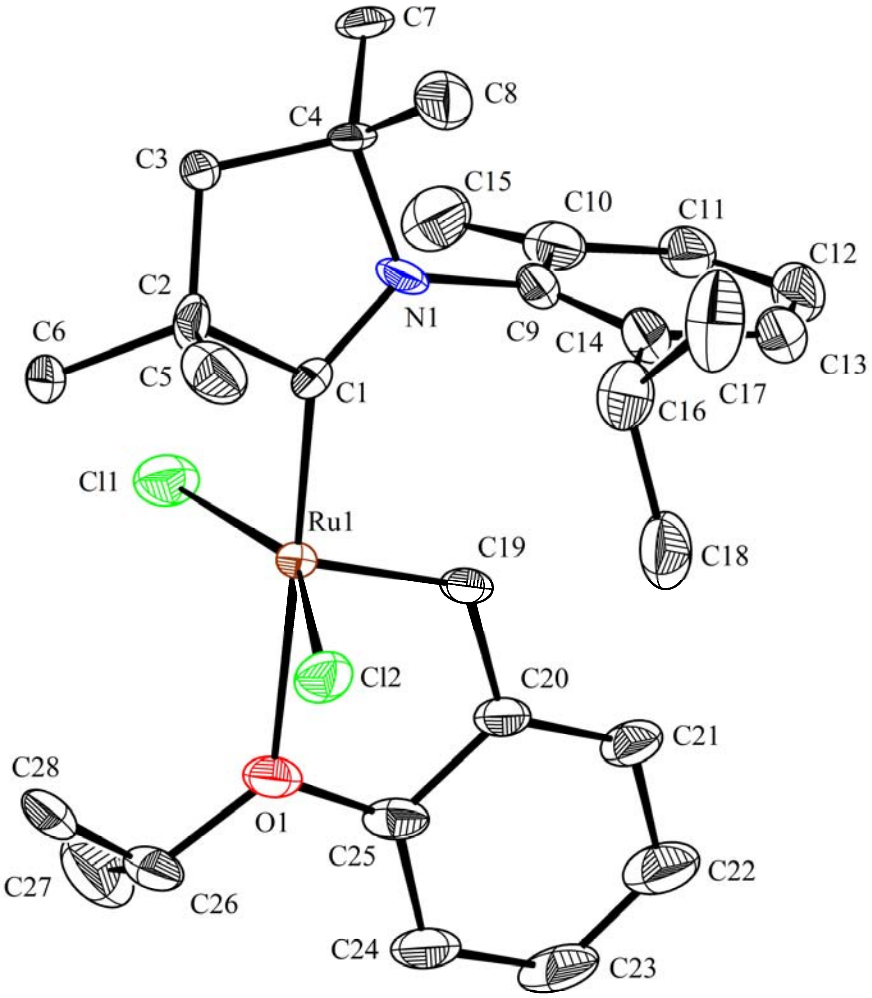
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of catalyst 25



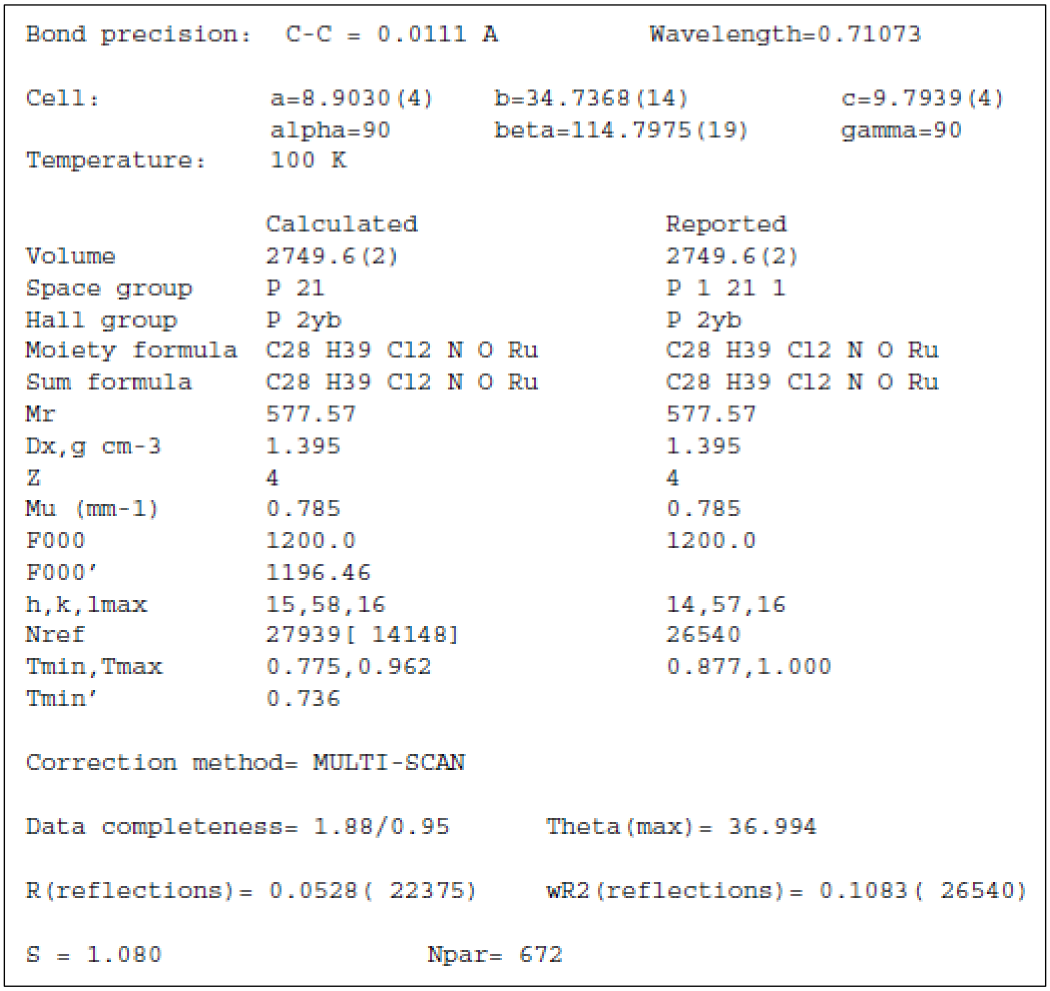
^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of catalyst 25



X-Ray Structure for Catalyst 11 (CCDC 1025991)

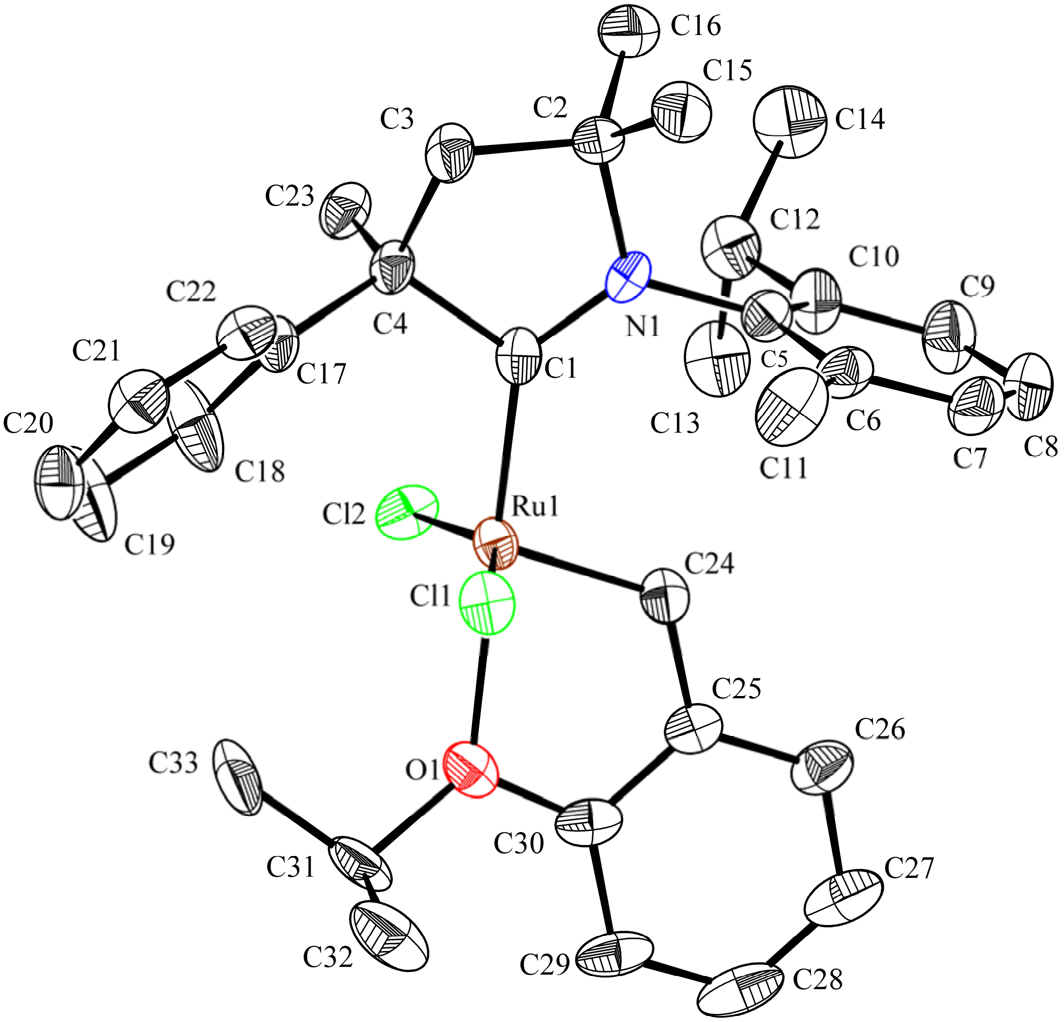


X-Ray Crystallography Data for Catalyst 11 (CCDC 1025991)

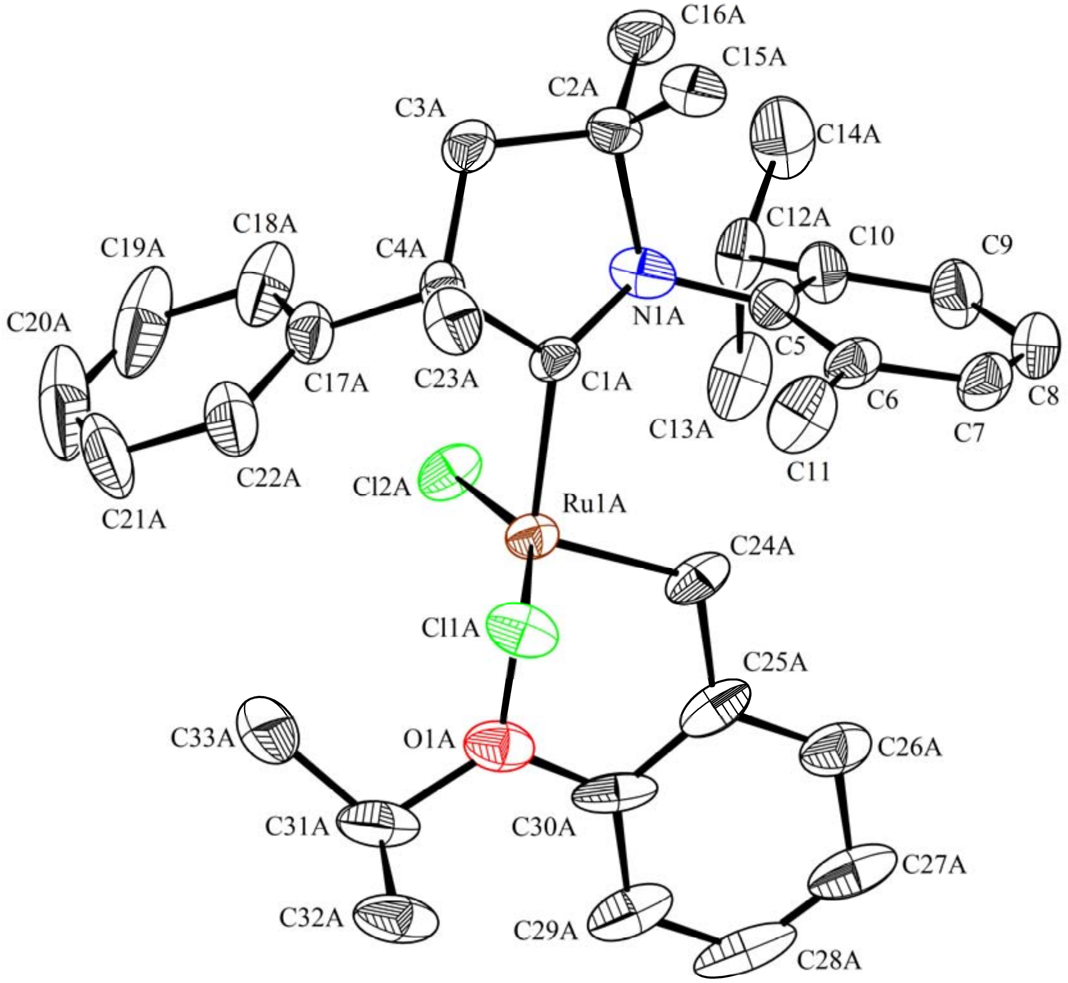


```
Bond precision:   C-C = 0.0111 A          Wavelength=0.71073

Cell:             a=8.9030(4)    b=34.7368(14)          c=9.7939(4)
                  alpha=90       beta=114.7975(19)      gamma=90
Temperature:      100 K

                  Calculated                  Reported
Volume            2749.6(2)                   2749.6(2)
Space group       P 21                        P 1 21 1
Hall group        P 2yb                       P 2yb
Moiety formula    C28 H39 Cl2 N O Ru          C28 H39 Cl2 N O Ru
Sum formula       C28 H39 Cl2 N O Ru          C28 H39 Cl2 N O Ru
Mr                577.57                      577.57
Dx,g cm-3         1.395                       1.395
Z                 4                           4
Mu (mm-1)         0.785                       0.785
F000              1200.0                      1200.0
F000'             1196.46
h,k,lmax          15,58,16                    14,57,16
Nref              27939[ 14148]               26540
Tmin,Tmax         0.775,0.962                 0.877,1.000
Tmin'             0.736

Correction method= MULTI-SCAN

Data completeness= 1.88/0.95       Theta(max)= 36.994

R(reflections)= 0.0528( 22375)     wR2(reflections)= 0.1083( 26540)

S = 1.080                  Npar= 672
```

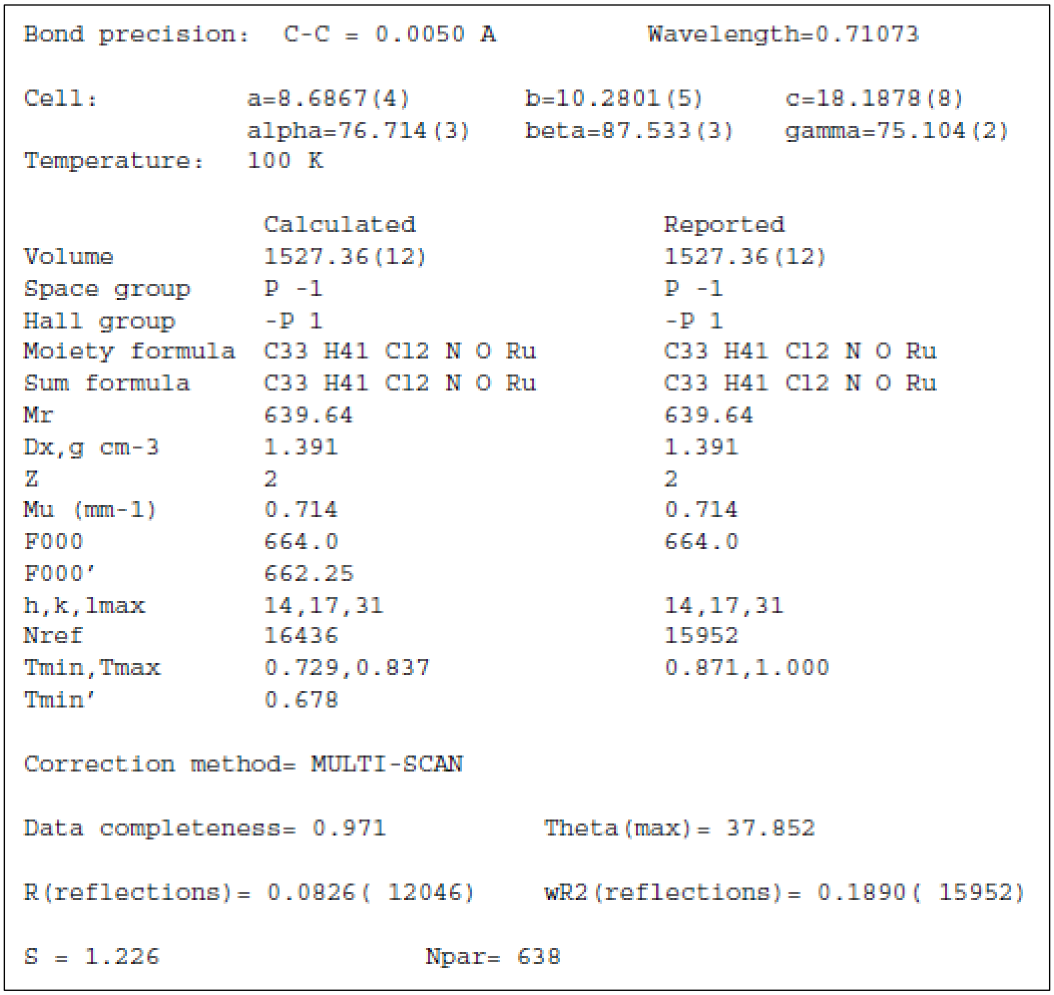
X-Ray Structure for Catalyst 24a (24a:24b, 64:36 ratio) (CCDC 1025992)



X-Ray Structure for Catalyst 24b (24a:24b, 64:36 ratio) (CCDC 1025992)



X-Ray Crystallography Data for Catalyst 24 (CCDC 1025992)



```
Bond precision:   C-C = 0.0050 A          Wavelength=0.71073

Cell:          a=8.6867(4)        b=10.2801(5)      c=18.1878(8)
               alpha=76.714(3)    beta=87.533(3)    gamma=75.104(2)
Temperature:   100 K

                Calculated                Reported
Volume          1527.36(12)               1527.36(12)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C33 H41 Cl2 N O Ru        C33 H41 Cl2 N O Ru
Sum formula     C33 H41 Cl2 N O Ru        C33 H41 Cl2 N O Ru
Mr              639.64                    639.64
Dx,g cm-3       1.391                     1.391
Z               2                         2
Mu (mm-1)       0.714                     0.714
F000            664.0                     664.0
F000'           662.25
h,k,lmax        14,17,31                  14,17,31
Nref            16436                     15952
Tmin,Tmax       0.729,0.837               0.871,1.000
Tmin'           0.678

Correction method= MULTI-SCAN

Data completeness= 0.971          Theta(max)= 37.852

R(reflections)= 0.0826( 12046)    wR2(reflections)= 0.1890( 15952)

S = 1.226                  Npar= 638
```