Easily removable olefin metathesis catalysts

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Contents

1.General

The solvents were dried by distillation over the following drying agents and were transferred under argon: toluene (Na), n-pentane, n-hexane, CH_2Cl_2 (CaH_2). MeOH was dried by stirring over MS 4A for 24h and distilled under argon.

Column chromatography: Merck silica gel 60 (230–400 mesh), Aluminum oxide, activated, neutral, Brockman grade III alumina was generated by mixing 6 % of water (by mass) with neutral, Brockman grade I alumina (~150 mesh).
NMR: Spectra were recorded on Bruker Avance 300 MHz spectrometer in $CDCl_3$, CD_2Cl_2 and D_2O; chemical shifts (δ) are given in parts per milion (ppm) downfield from trimethylsilane as referenced to residual protio solvent peaks, coupling constants (*J*) in Hz.
GC: Trace GC Ultra, Thermo Electron Corporation, HP-5 column.
MS (ESI): Micromass LCT mass spectrometer and LCT PremierXE Waters mass spectrometer. IR: Thermo Nicolet Mattson 300 FT-IR. Indenylidene 1st generation catalyst (**Ind-I**)[1] as well as benzylidene ligands **17**[2] and **18**[3] were synthesized according to the literature method.

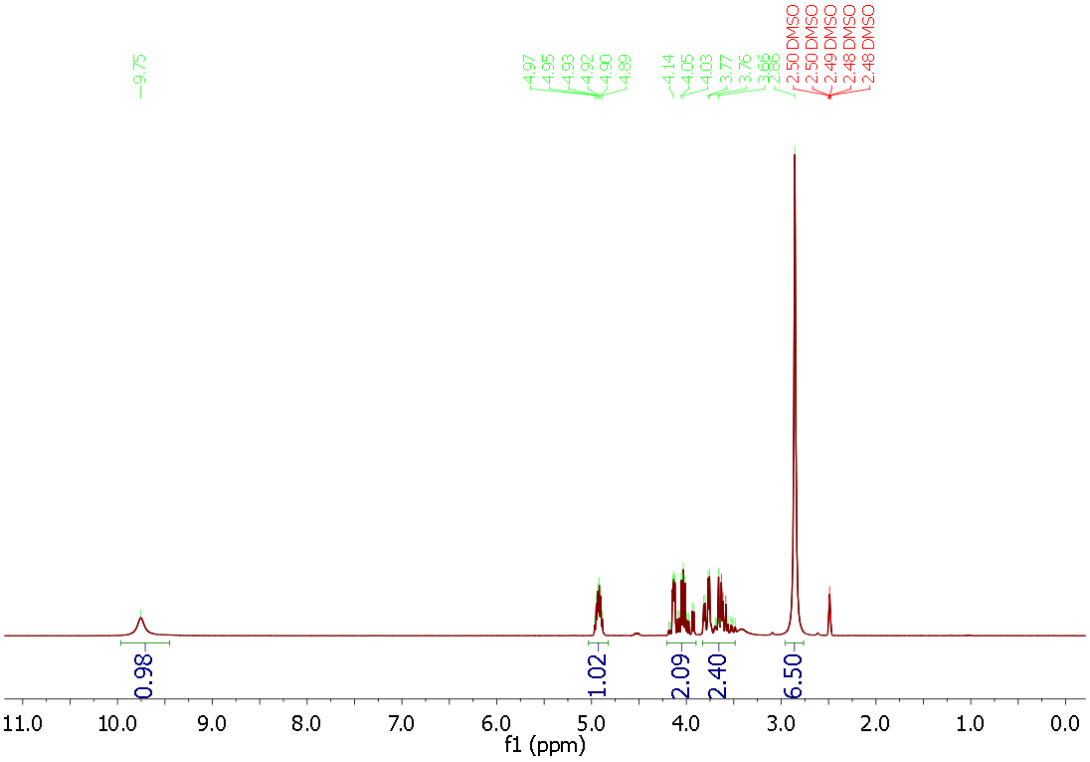
[1] E.A. Shaffer, Ch.-L. Chen, A.M. Beatty, E.J. Valente, H.-J. Schanz, *J. Organomet. Chem.*, **2007**, *692*, 5221-5233.
[2] R.L. Pederson, J.K. Woertink, Ch.M. Haar, D.E. Gindelberger, Y. Schrodi, *PCT Int. Appl.* (2003), WO 2003044060 A2 20030530.
[3] K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem.* **2002**, 114, Nr. 21, 4210-4212.

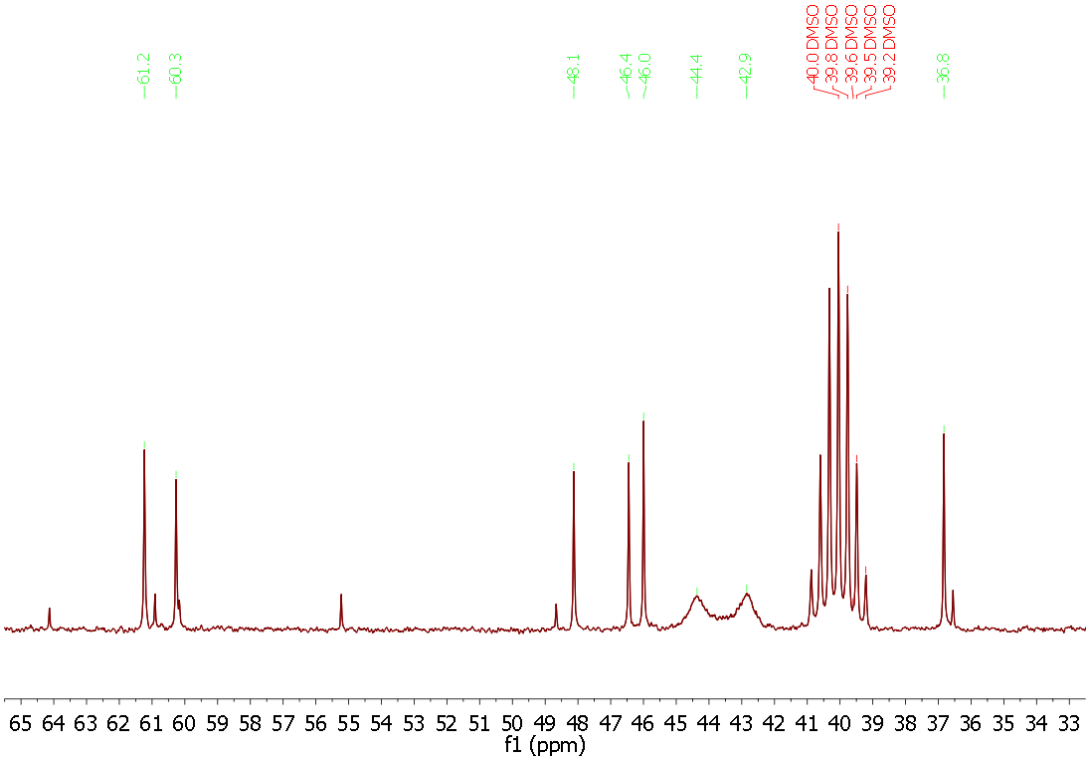
2.Synthesis procedures and analytical data

Synthesis of compound 13

A solution of *N*,*N*-dimethylallylamine (19.4 g, 228 mmol) in water (20 ml) was cooled down to 5 °C and HCl aq (36 %) was added. Mixture was heated up to 50 °C and bromine (23.9 ml, 462 mmol) was slowly added at such a rate that the temperature did not exceed 65 °C. When the addition was completed *iso*-propanol (100 ml) was added and reaction mixture was evaporated to dryness. Recrystallization of crude product from ethanol afforded **13** (42.4 g, 66 %) as a colorless crystals.

^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.75 (bs, 1H), 4.97-4.89 (m, 1H), 4.19-3.92 (m, 2H), 3.82-3.48 (m, 2H), 2.86 (s, 6H). ^{13}C NMR (75.4 MHz, DMSO-d_6). δ ppm: 61.2, 60.3, 48.1, 46.4, 46.0, 44.4, 42.9, 36.8. HRMS (ESI) calc for $C_5H_{11}Br_2N$ ([M+H]$^+$) *m/z* 245.9316 found 245.9312.

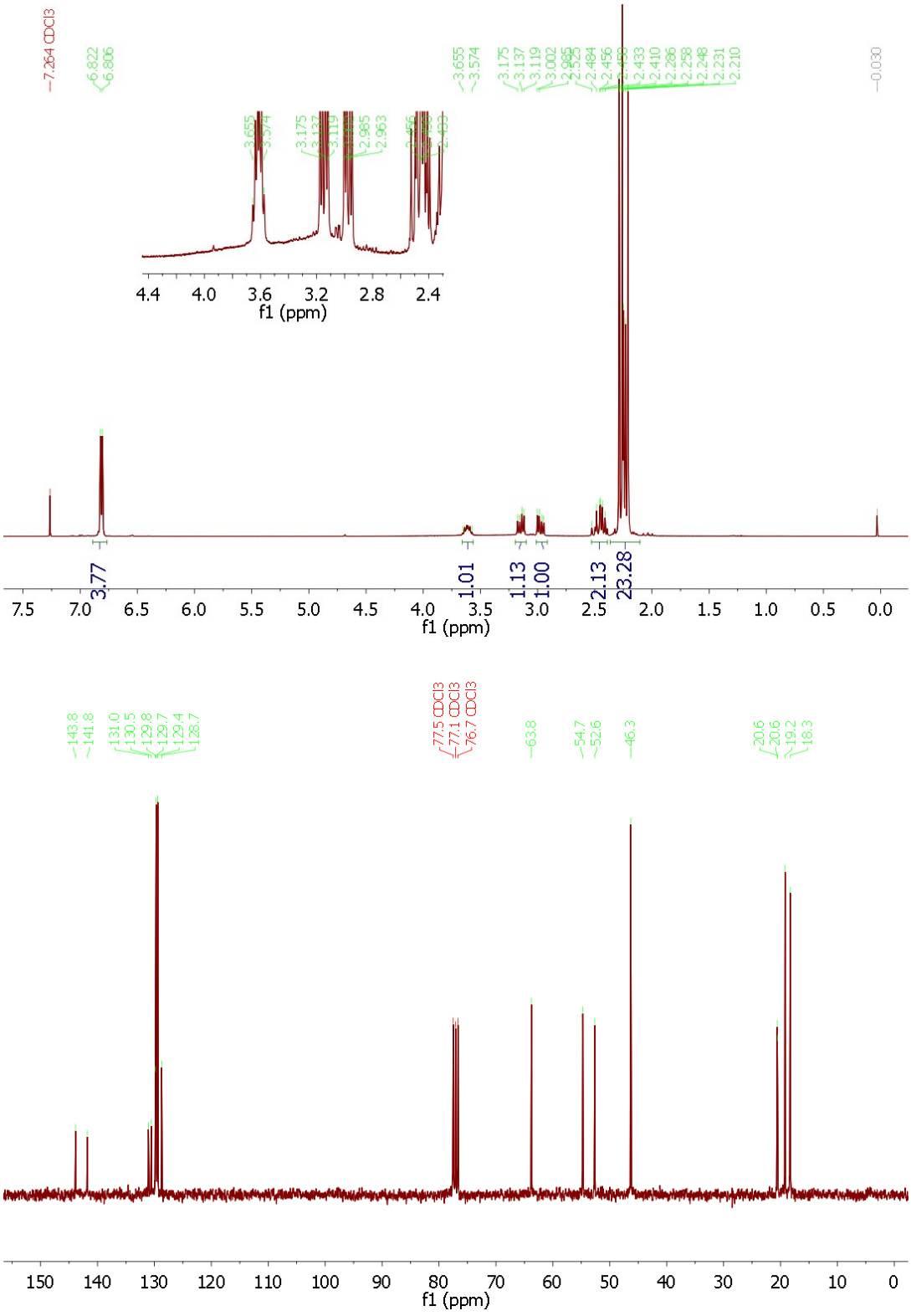




Synthesis of compound 14

Compound **13** (20.0 g, 71.0 mmol) and 2,4,6-trimethylaniline (100.0 ml, 710 mmol) was heated together at 125 ^{o}C for 24 h. Reaction mixture was then cooled down to room temperature and alkalized with sodium hydroxide aq (15 %). Product was extracted with dichloromethane (300 ml). Organic fraction was washed with water (100 ml) and dried with magnesium sulfate. Drying agent was filtered off and solvent was evaporated. Then excess of 2,4,6-trimethylaniline was removed under reduced pressure (3 mbar). Crude product was purified by column chromatography (MeOH/DCM 1/9). Removal of solvents afforded **14** (17.7 g, 70 %) as a light-brown oil.

^{1}H NMR (300 MHz, $CDCl_3$). δ ppm: 6.81-6.78 (m, 4H), 4.20-3.20 (bs, 2H), 3.65-3.57 (m, 1H), 3.14 (dd, J = 5.4 Hz, J = 11.4 Hz, 1H), 2.97 (dd, J = 5.4 Hz, J = 11.4 Hz, 1H), 2.53-2.41 (m, 2H), 2.29-2.21 (m, 24H). ^{13}C NMR(75.4 MHz, $CDCl_3$). δ ppm: 143.8, 141.8, 131.0, 130.5, 129.8, 129.7, 129.4, 128.7, 63.8, 54.7, 52.6, 46.3, 20.6 (d), 19.2, 18.3. HRMS (ESI) calc for $C_{23}H_{35}N_3$ ($[M+H]^+$) *m/z* 354.2909 found 354.2914.

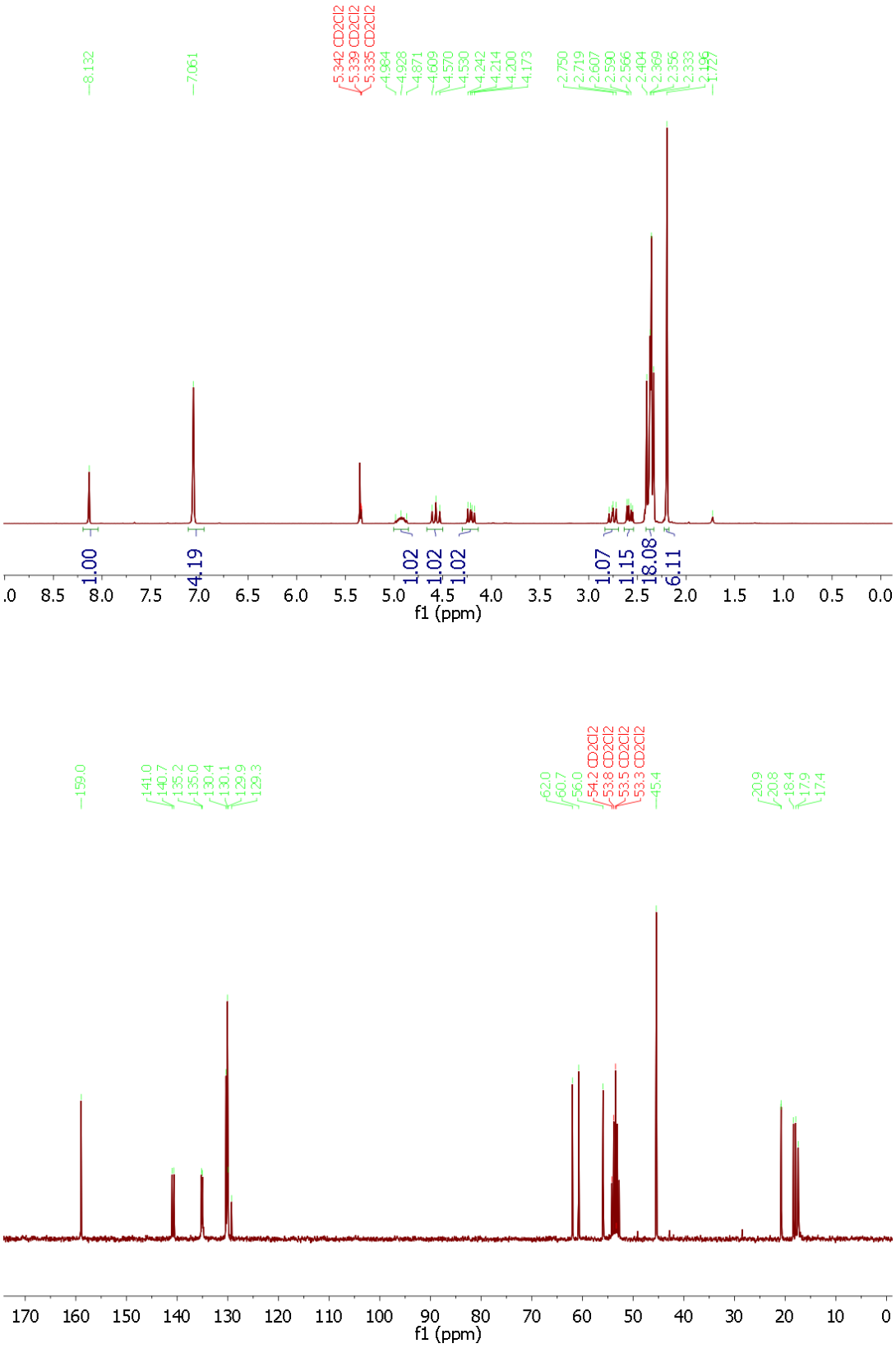


Synthesis of compound 15

Solution of **14** (13.30 g, 37.6 mmol) and ammonium tetrafluoroborate (3.94 g, 37.6 mmol) in triethyl orthoformate (31.3 ml, 188 mmol) was stirred at 120 °C for 3 h. After evaporation of solvents, crude product was purified by recrystallization from dichloromethane/tetrachloromethane mixture to afford **15** (10.60 g, 62 %) as a white crystals.

^{1}H NMR (300 MHz, CD_2Cl_2). δ ppm: 8.13 (s, 1H), 7.06 (s, 4H), 4.98-4.87 (m, 1H), 4.57 (*pseudo*t, 1H), 4.21 (dd, J = 8.1 Hz, J = 12.6 Hz, 1H), 2.76 (dd, J = 9.3 Hz, J = 12.3 Hz, 1H),

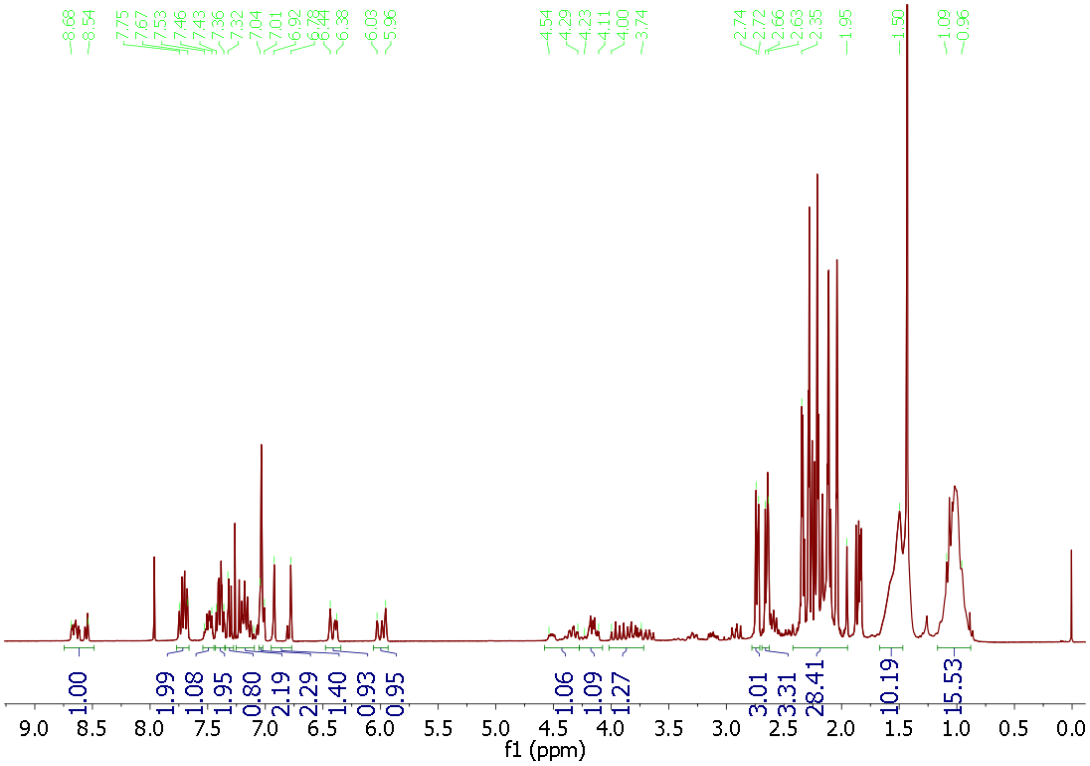
2.57 (dd, J = 5.1 Hz, J = 12.3 Hz, 1H), 2.40-2.33 (m, 18H), 2.20 (s, 6H). ^{13}C NMR(75.4 MHz, $CDCl_3$). δ ppm: 159.0, 141.0, 140.7, 135.2, 135.0, 130.4, 130.1, 129.9, 129.3, 62.0, 60.7, 56.0, 45.4, 20.9, 20.8, 18.4, 17.9, 17.4. HRMS (ESI) calc for $C_{24}H_{33}N_3$ ([M]$^+$) *m/z* 364.2753 found 364.2755.

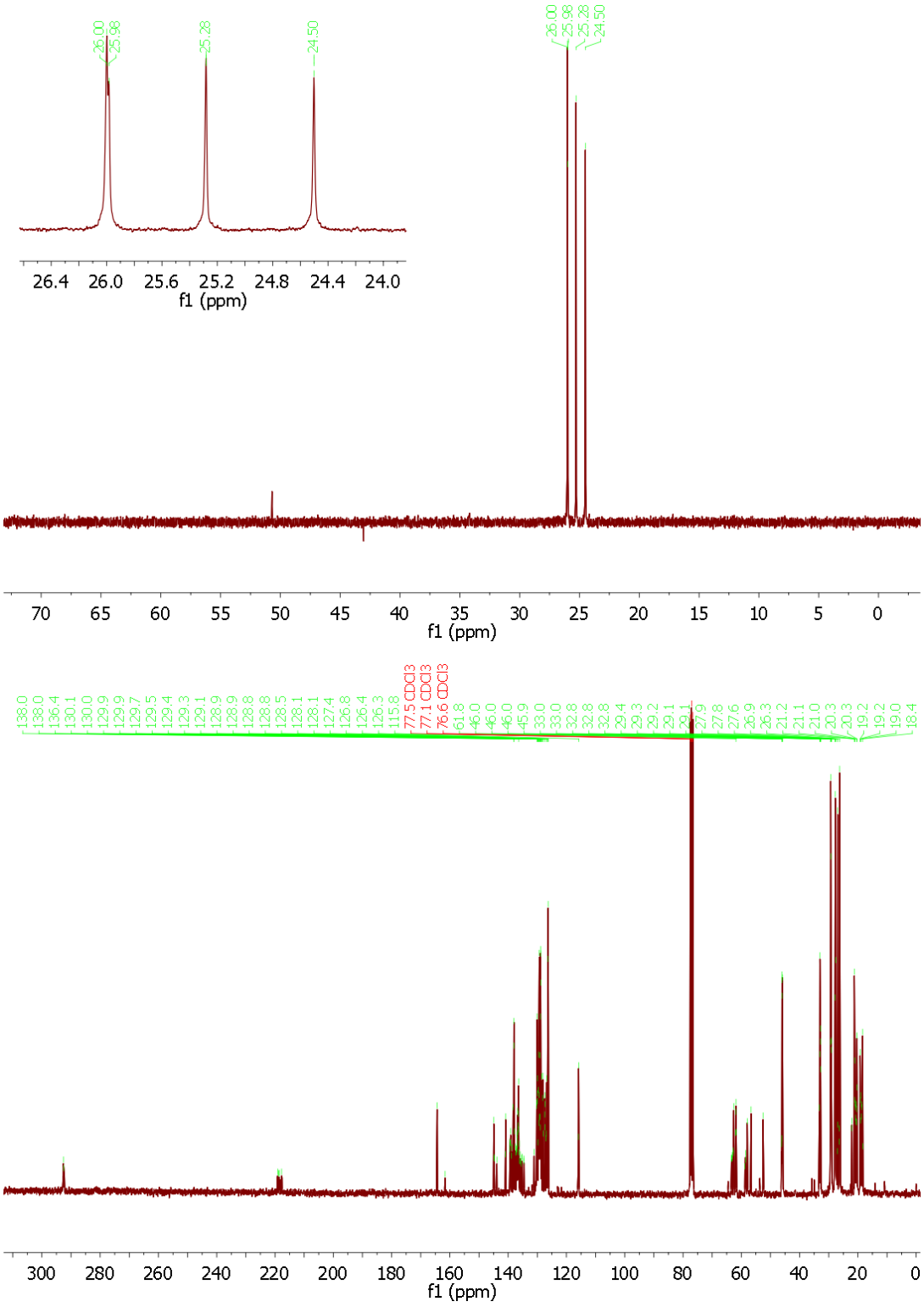


Synthesis of complex 16

Potassium *t*-amylate (1.7 M in toluene, 2.58 ml, 4.39 mmol) was added at room temperature to a suspension of **15** (2.05 g, 4.55 mmol) in dry hexane (40 ml) under argon. Reaction mixture was stirred at room temperature for 1 h, then **Ind-I** (3.00 g, 3.25 mmol) was added and stirring was continued at reflux for 1 h. After cooling down, reaction mixture was filtered through a short pad of silica gel (*c*-hexane/EtOAc 8:2). Solvents were evaporated, crude catalyst was washed with *n*-pentane and dried under vacuum to afford complex **16** (2.71 g, 83 %) as a dark red crystals.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 8.68-8.54 (m, 1H), 7.75-7.67 (m, 2H), 7.53-7.46 (m, 1H), 7.43-7.36 (m, 2H), 7.32-7.10 (m, 3H), 7.04-7.01 (m, 2H), 6.92-6.78 (m, 1H), 6.44-6.38 (m, 1H), 6.03-5.96 (m, 1H), 4.54-4.29 (m, 1H), 4.23-4.11 (m, 1H), 4.00-3.74 (m, 1H), 2.74-2.72 (m, 3H), 2.66-2.63 (m, 3H), 2.35-1.95 (m, 28H), 1.50 (bs, 10H), 1.09-0.96 (m, 15H). ^{31}P NMR (124,5 MHz, $CDCl_3$) δ ppm: 26.00, 25.98, 25.28, 24.50. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 292.7-292.3 (m), 219.3-217.6 (m), 164.4, 161.6, 144.9, 143.9, 140.9, 140.8, 140.5, 139.4, 139.2, 138.9, 138.8, 138.3, 138.0, 137.9, 137.6, 137.4, 137.2, 137.1, 137.0, 136.8, 137.7, 137.5, 136.4, 136.2, 135.9. 131.1, 130.2, 130.1, 129.9, 129.5, 129.4, 128.6, 128.1, 126.6, 126.4, 126.3, 115.9, 115.8, 62.6, 61.9, 61.8, 57.9, 56.7, 52.5, 46.0, 46.9, 29.3-29.2 (m), 27.9, 26.9, 26.3, 21.3-20.2 (m), 19.2-18.4 (m). HRMS (ESI) calc for $C_{57}H_{76}N_3PClRu$ ([M-Cl]$^{+}$) *m/z* 970.4509 found 970.4512.



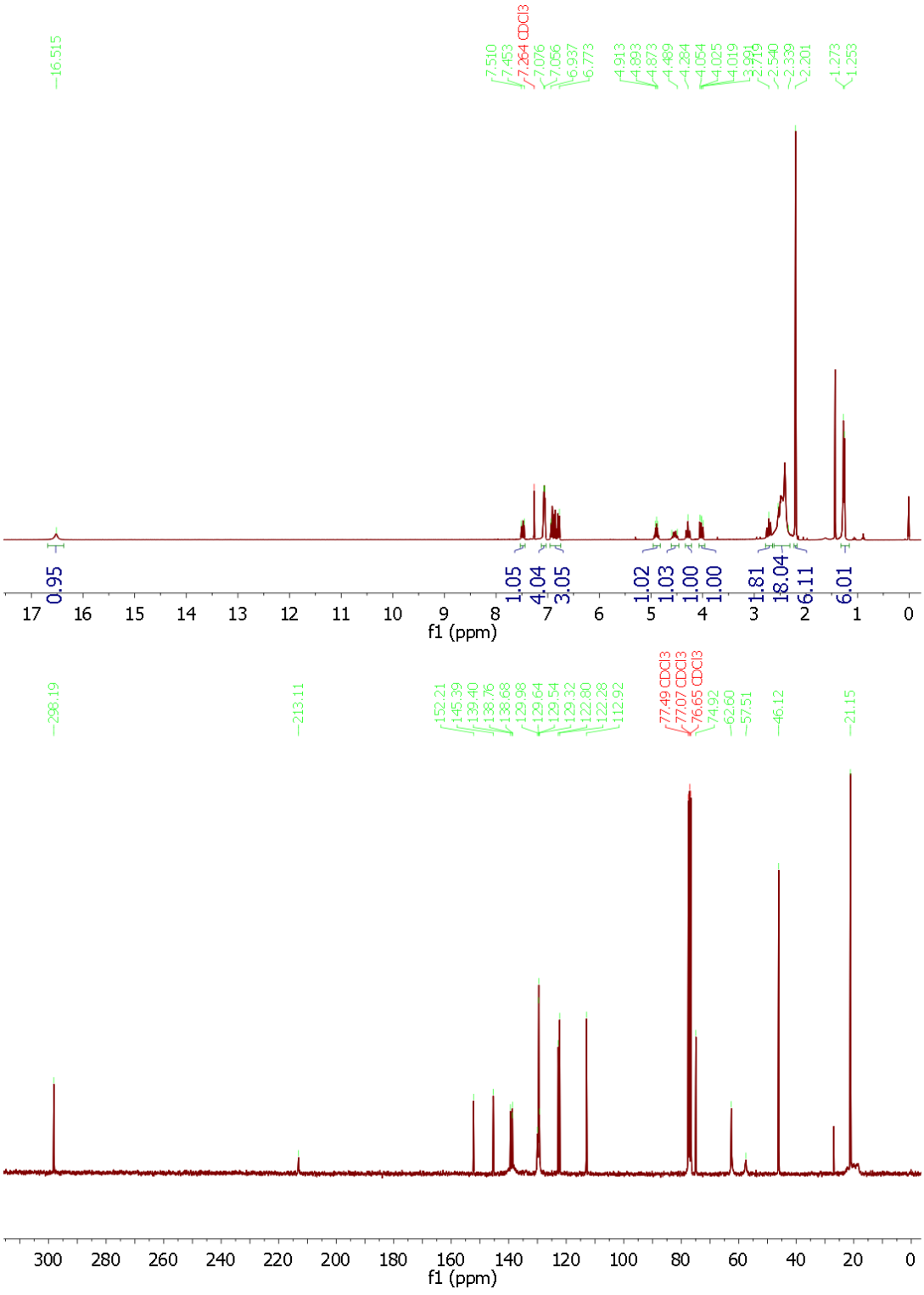


Synthesis of complex 7

Compound **17** (0.15 g, 0.85 mmol) and CuCl (0.11 g, 1.16 mmol) were placed in a Schlenk flask. The flask was filled with argon and then dry toluene (20 ml) was added. Afterwards complex **16** (0.76 g, 0.77 mmol) was added and the resulting solution was stirred at 80 ^{o}C for 20 min. The reaction mixture was cooled down to room temperature and concentrated under vacuum. The resulting material was dissolved in a minimum amount of EtOAc and the insoluble white solid filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuum, and the crude catalyst was purified by flash

chromatography (*c*-hexane/EtOAc 7:3). Removal of solvents afforded complex **7** (0.36 g, 68 %) as a green solid.

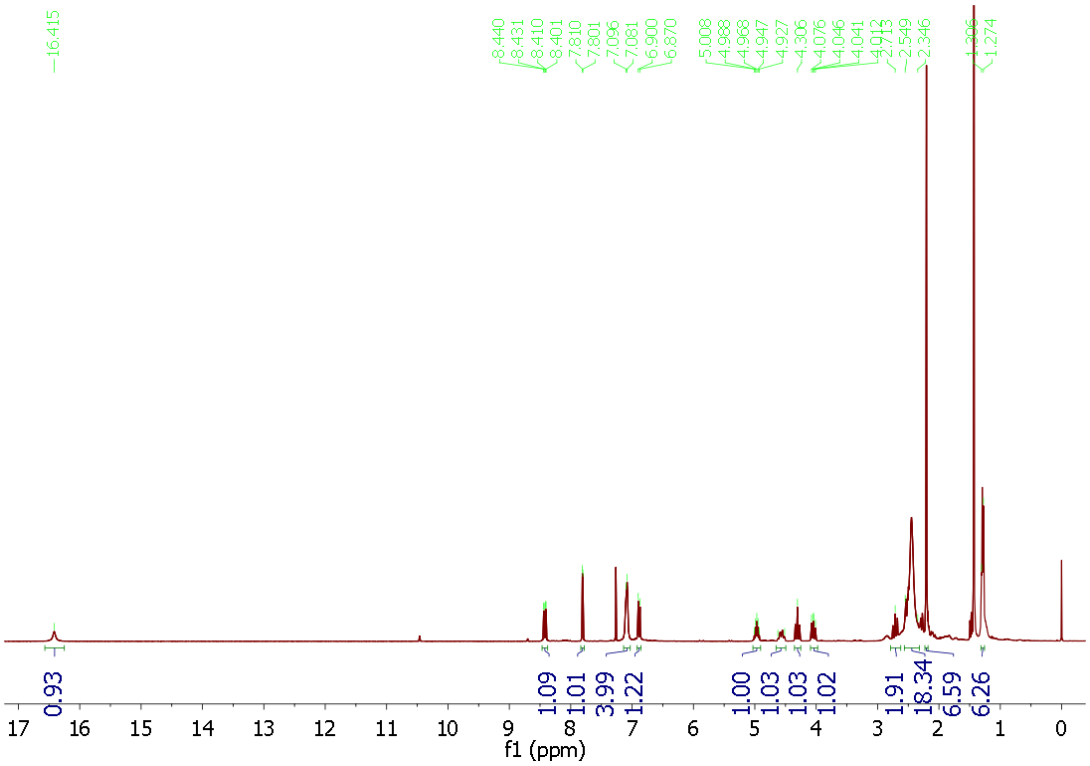
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 16.52 (s, 1H), 7.51-7.45 (m, 1H), 7.08-7.06 (m, 4H), 6.94-6.77 (m, 3H), 4.89 (heptet, *J* = 6.0 Hz, 1H), 4.60-4.49 (m, 1H), 4.28 (*pseudo*t, 1H), 4.02 (dd, *J* = 8.4 Hz, *J* = 10.5 Hz, 1H), 2.72 (*pseudo*t, 2H), 2.54-2.34 (m, 18H), 2.20 (s, 6H), 1.26 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 298.2, 213.1, 152.2, 145.4, 139.4, 138.8, 138.7, 130.0, 129.6, 129.5, 129.3, 122.8, 122.3, 112.9, 74.9, 62.6, 57.5, 46.1, 21.2. HRMS (ESI) calc for $C_{34}H_{45}N_3ONaCl_2Ru$ ([M+Na]$^{+}$) *m/z* 706.1881 found 706.1865.

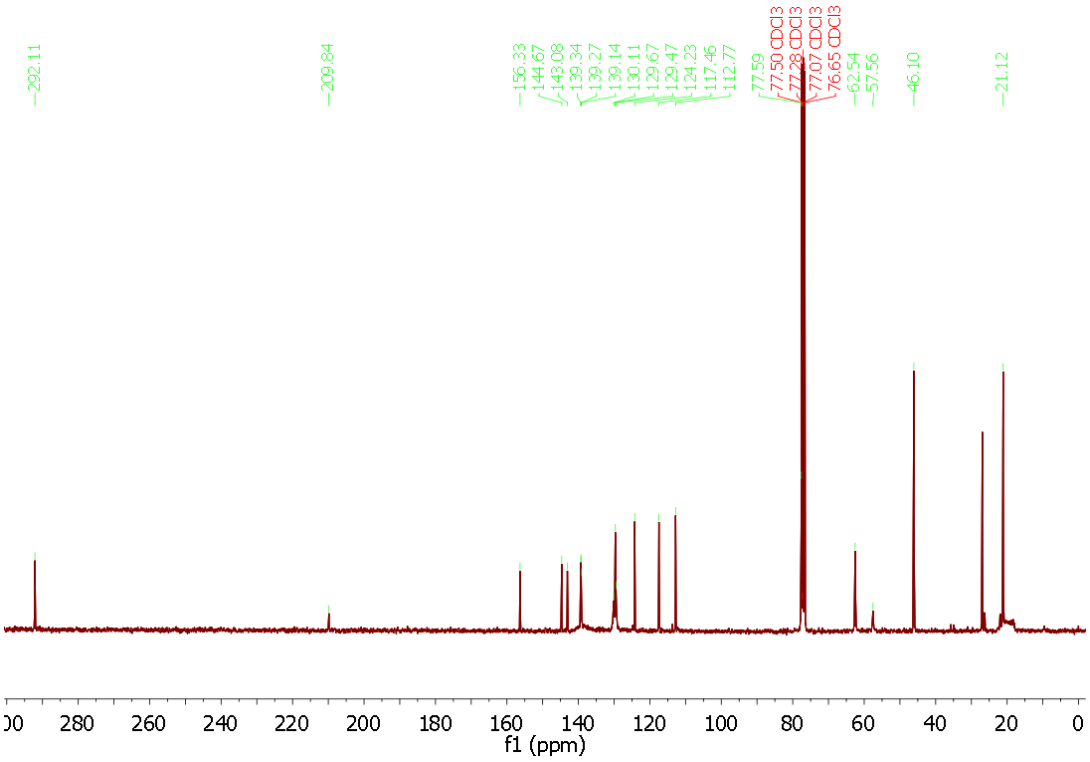


Synthesis of complex 8

Compound **18** (0.146 g, 0.66 mmol) and CuCl (0.089 g, 0.90 mmol) were placed in a Schlenk flask. The flask was filled with argon and then dry toluene (12 ml) was added. Afterwards complex **16** (0.593 g, 0.60 mmol) was added and the resulting solution was stirred at 80 ^{o}C for 20 min. The reaction mixture was cooled down to room temperature and concentrated under vacuum. The resulting material was dissolved in a minimum amount of EtOAc and the insoluble white solid filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuum, and the crude catalyst was purified by flash chromatography (*c*-hexane/EtOAc 7:3). Removal of solvents afforded complex **8** (0.30 g, 69 %) as a green solid.

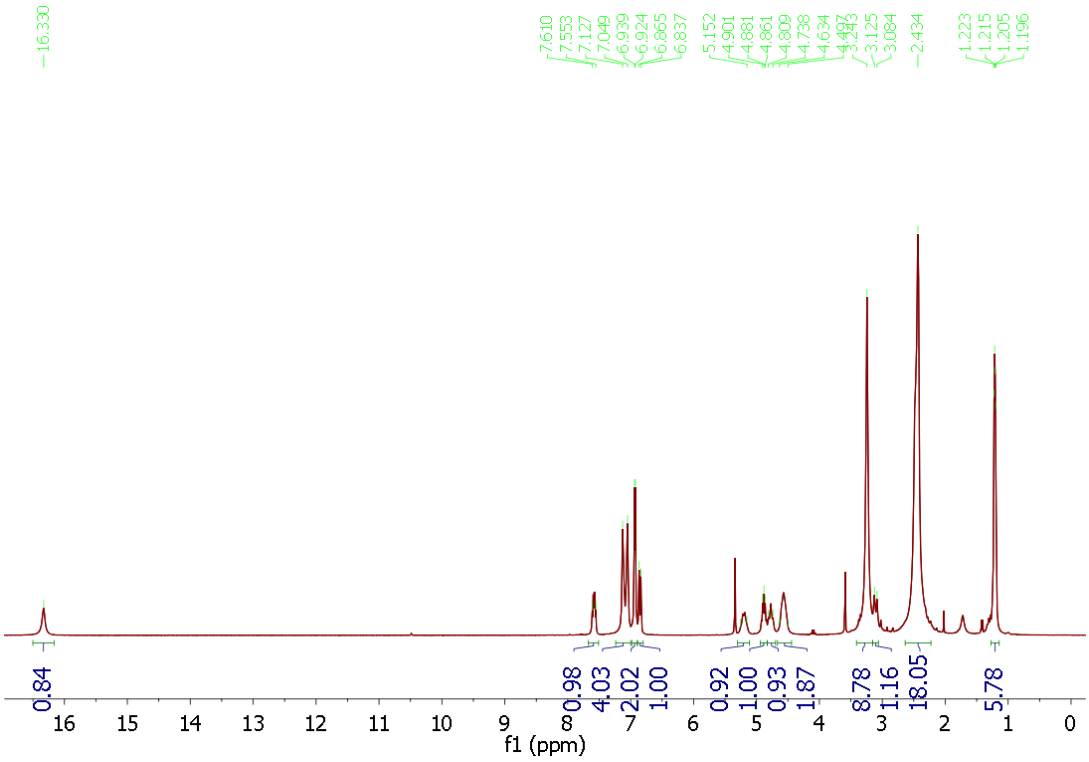
^{1}H (300 MHz, $CDCl_3$) δ ppm: 16.42 (s, 1H), 8.42 (dd, J = 2.7 Hz, J = 9.0 Hz, 1H), 7.80 (d, J = 2.7 Hz, 1H), 7.10-7.00 (m, 4H), 6.88 (d, J = 9.0 Hz, 1H), 4.97 (heptet, J = 6.0 Hz, 1H), 4.62-4.51 (m, 1H), 4.31 (*pseudo*t, 1H), 4.04 (dd, J = 9.0 Hz, J = 10.5 Hz, 1H), 2.71 (*pseudo*t, 2H) 2.55-2.35 (m, 18H), 2.20 (s, 6H), 1.31-1.27 (m, 6H). ^{13}C (75.4 MHz, $CDCl_3$) δ ppm: 292.1, 209.8, 156.3, 144.7, 143.1, 139.34, 139.27, 139.1, 129.7, 129.5, 124.2, 117.5, 112.8, 77.6, 62.5, 57.6, 46.1, 21.1. HRMS (ESI) calcd for $C_{34}H_{40}N_4O_3ClRu$ ([M-Cl]$^{+}$) *m/z* 689.1832 found 689.1838.





Synthesis of complex 9

Complex **7** (0.116 g, 0.17 mmol) was placed under argon in a Schlenk flask and iodomethane (1.06 ml, 17 mmol) was added. Mixture was stirred at room temperature for 5 h. Ethyl acetate was added to a reaction mixture and crude product was filtered off. Next complex was washed with ethyl acetate twice then precipitated from dichloromethane/ethyl acetate mixture, filtered and dried on vacuum to afford **9** (0.138 g, 98 %) as a green solid.
^{1}H (300 MHz, CD_2Cl_2) δ ppm: 16.33 (s, 1H), 7.61-7.53 (m, 1H), 7.13-7.05 (m, 4H), 6.94-6.92 (d, J = 4.5 Hz, 2H), 6.87-6.84 (d, J = 8.4 Hz, 2H), 5.26-5.15 (m, 1H), 4.88 (heptet, J = 6.0 Hz, 1H), 4.81-4.74 (m, 1H), 4.63-4.50 (bs, 2H), 3.24 (s, 9H), 3.10 (d, J = 12.3 Hz, 1H), 2.43 (bs, 18H), 1.21 (dd, J = 2.4 Hz, J = 6.0 Hz 6H). ^{13}C (75.4 MHz, CD_2Cl_2) δ ppm: 296.9, 214.0, 152.2, 145.1, 139.9, 139.7, 139.3, 130.6, 130.1, 129.5, 129.3, 122.5, 122.4, 113.1, 75.4, 67.7, 58.3, 20.9. HRMS (ESI) calcd for $C_{35}H_{48}N_3OCl_2Ru$ ($[M\text{-}I]^+$) *m/z* 698.2218 found 698.2228. IR (KBr) *ν* 3436, 3009, 2977, 1607, 1589, 1487, 1453, 1383, 1259, 1113, 1097, 937, 750.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4.809
4.738
4.634
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3.125
3.084
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1.205
1.196
0.84
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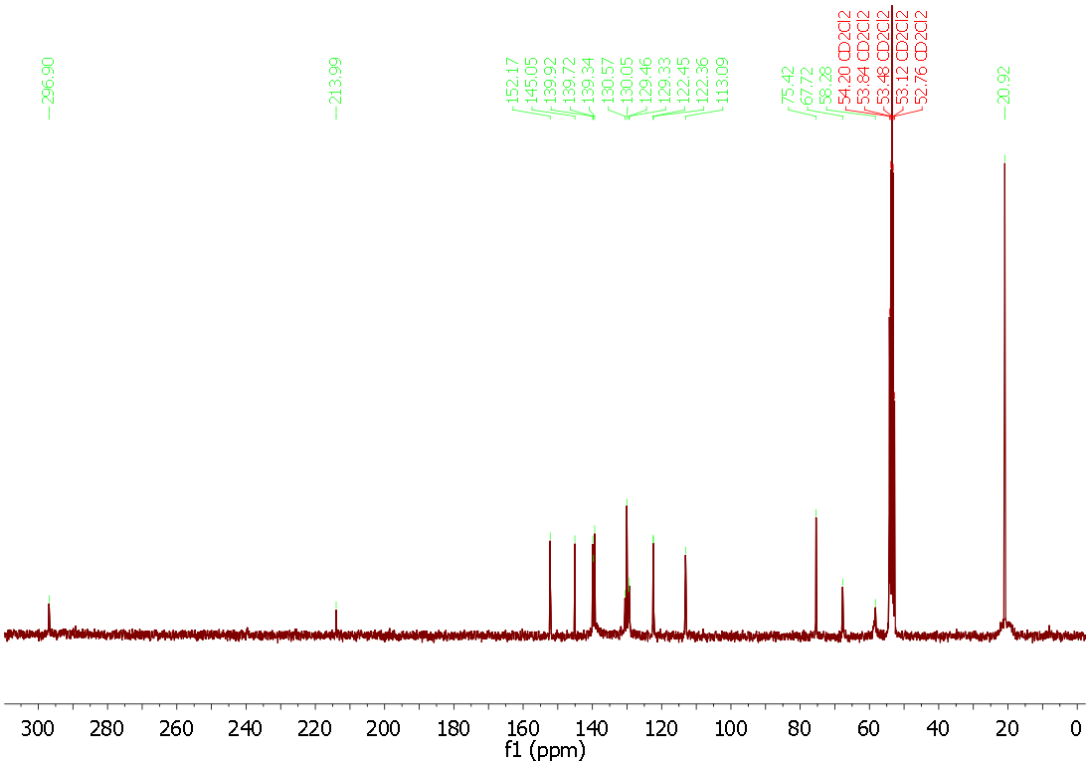
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113.09
75.42
67.72
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53.84 CD2Cl2
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52.76 CD2Cl2
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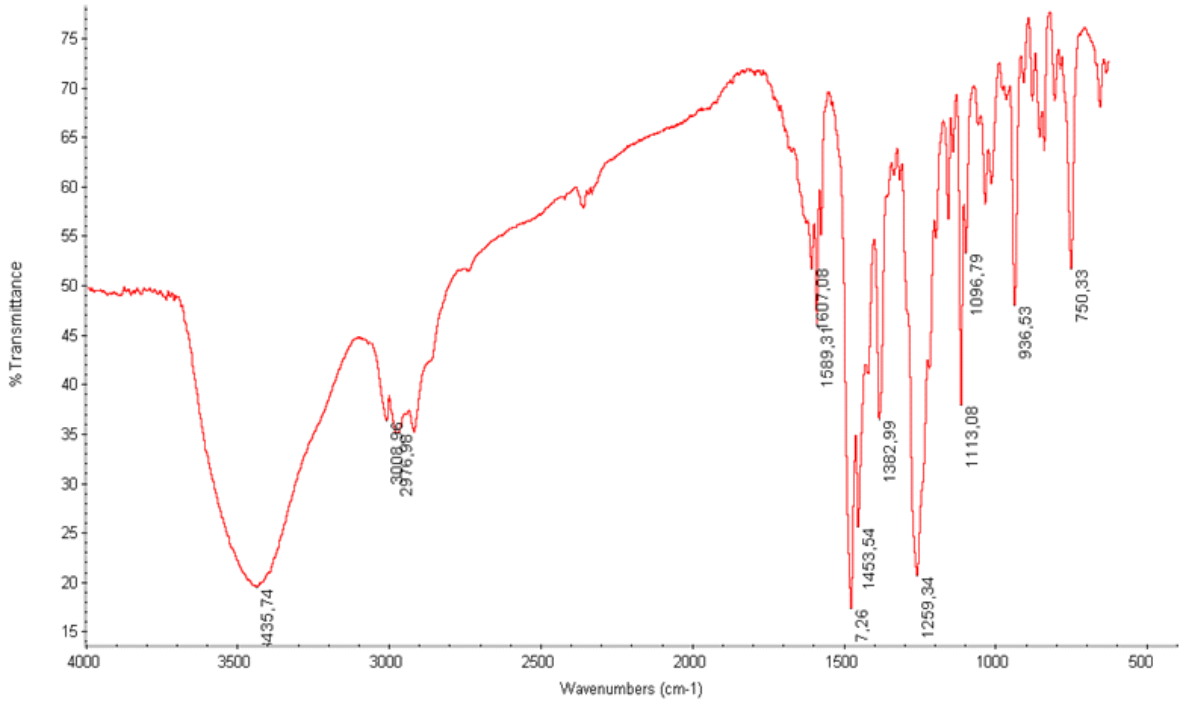
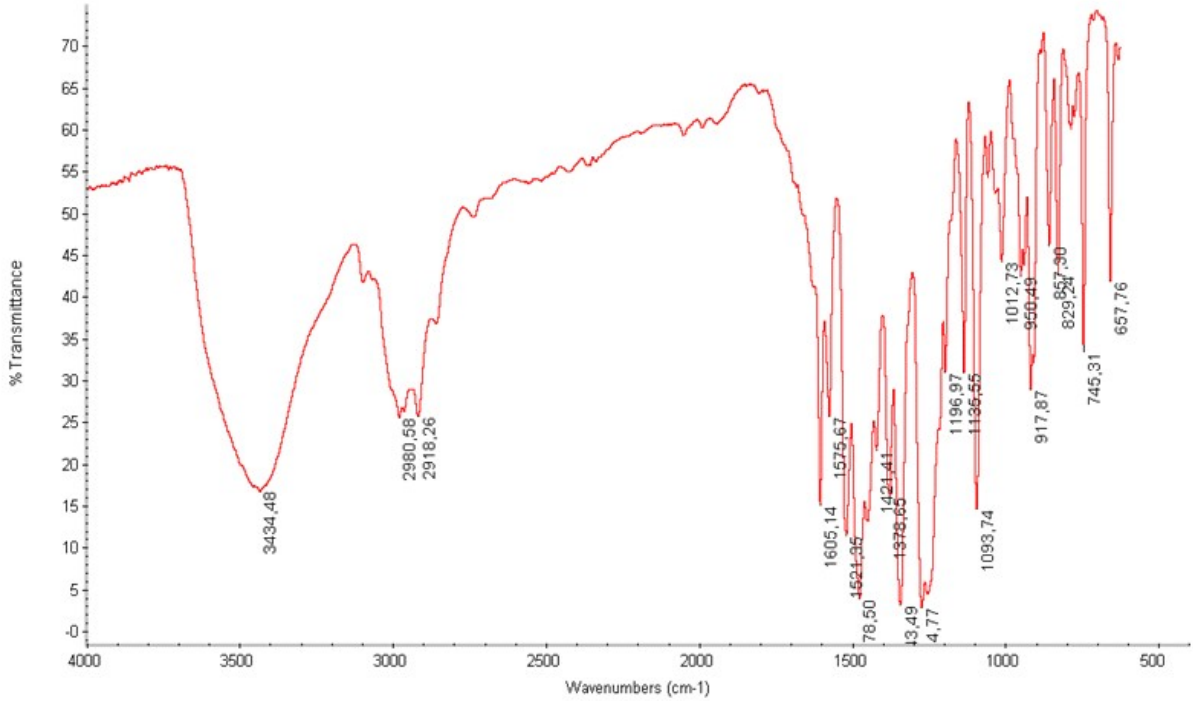
f1 (ppm)



Synthesis of complex 10

The same procedure as described for complex **9** was employed to afford the catalyst **10** as a green solid in 86 % yield.
LRMS (ESI) calcd for $C_{35}H_{47}Cl_2N_4O_3Ru$ ($[M\text{-}I]^+$) *m/z* 743.2 found 743.1; IR (KBr) *v* 3434, 2980, 2919, 1605, 1576, 1521, 1478, 1421, 1379, 1343, 1344, 1197, 1136, 1094, 1013, 950, 917, 857, 829, 745, 658.

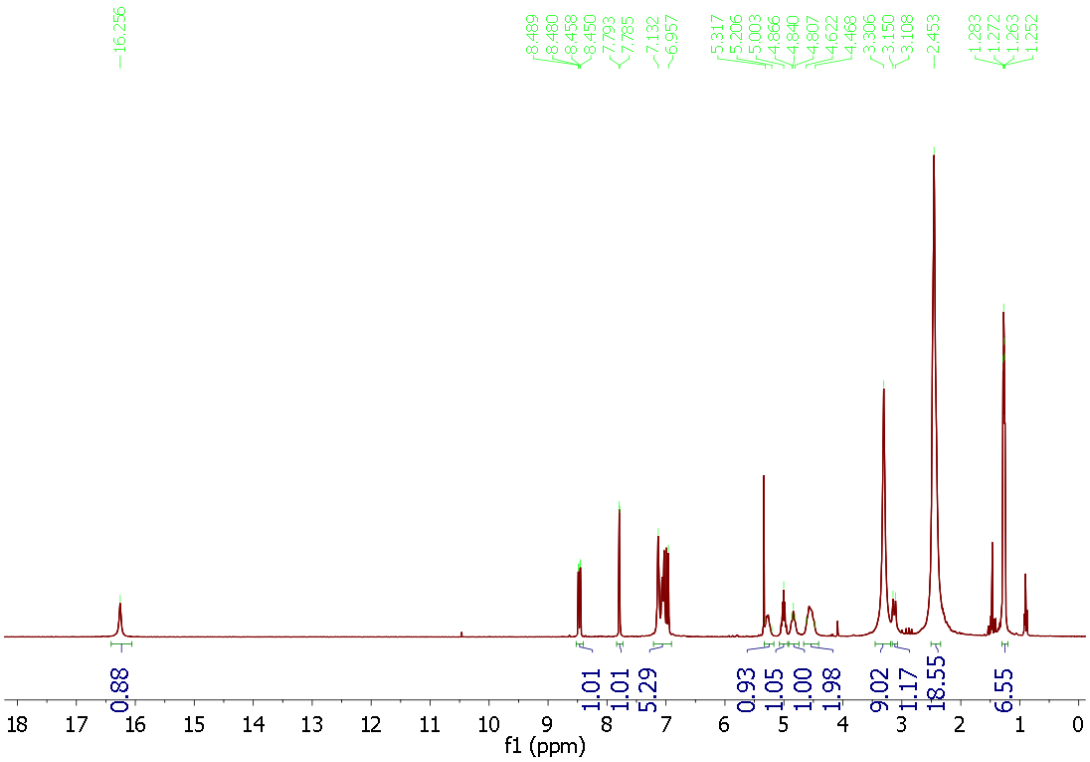


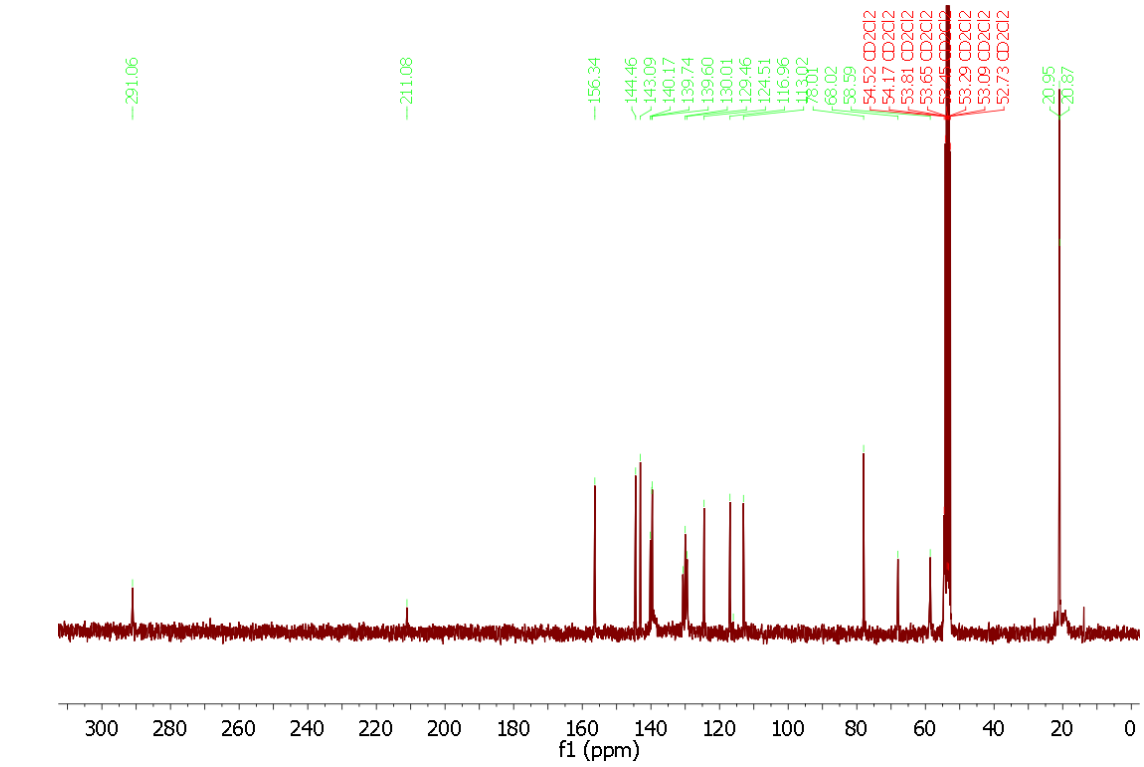
Synthesis of complex 11

Complex **8** (0.50 g, 0.68 mmol) was placed under argon in pressure flask and dry methanol (3 ml) was added. Mixture was cooled down to –30 °C and cold liquid chloromethane (ca 3 ml) was added. Mixture was slowly warmed up to room temperature, then placed in oil bath heated to 50 °C and stirred for 60 h. After that time flask was opened carefully to remove chloromethane and mixture was concentrated. Residue was purified by filtration through a

short plug of aluminium oxide (neutral, Brockman grade I, ethyl acetate/methanol 19:1). Solvents were evaporated, catalyst was washed with ethyl acetate twice and dried on vacuum to afford complex **11** (0.34 g, 64 %) as a green solid. Solubility in neat water: 2 mg/ml.

^{1}H (300 MHz, CD_2Cl_2) δ ppm: 16.26 (s, 1H), 8.47 (dd, J = 2.4 Hz, J = 9.0 Hz, 1H), 7.78 (d, J = 2.4 Hz, 1H), 7.13-6.96 (m, 5H), 5.32-5.21 (m, 1H), 5.00 (heptet, J = 6.0 Hz, 1H), 4.87-4.81 (m, 1H), 4.62-4.47 (m, 2H), 3.31 (s, 9H), 3.13 (d, J = 12.6 Hz, 1H), 2.45 (bs, 18H), 1.28-1.25 (m, 6H). ^{13}C (75.4 MHz, CD_2Cl_2) δ ppm: 291.1, 211.1, 156.3, 144.5, 143.1, 140.2, 139.7, 139.6, 130.6, 130.0, 129.5, 124.5, 117.0, 113.0, 78.0, 68.0, 58.6, 21.0, 20.9. HRMS (ESI) calcd for $C_{35}H_{47}N_4O_3Cl_2Ru$ ([M-Cl]$^+$) *m/z* 743.2069 found 743.2091. IR (KBr) *v* 3402, 2977, 2920, 1605, 1575, 1520, 1478, 1381, 1341, 1292, 1134, 1092, 948, 916, 855, 828, 746, 657.

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143.09
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139.74
139.60
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129.46
124.51
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68.59
54.52 CD2Cl2
54.17 CD2Cl2
53.81 CD2Cl2
53.65 CD2Cl2
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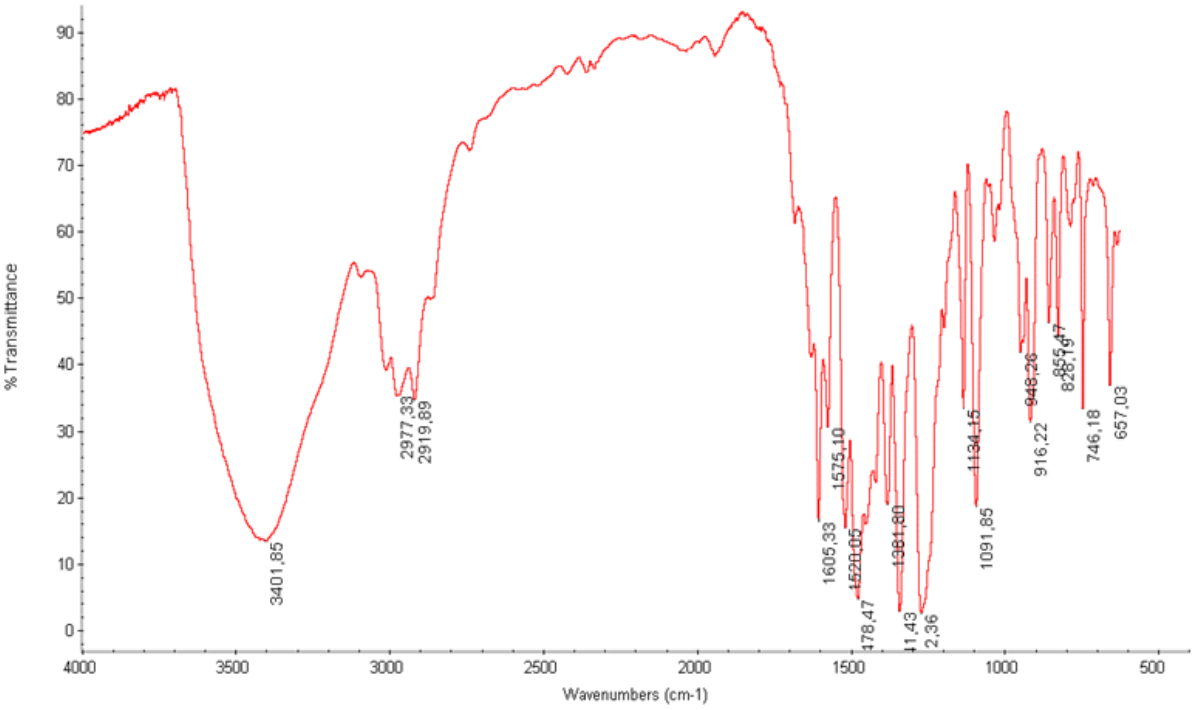
f1 (ppm)


% Transmittance
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2919,89
1605,33
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1381,80
1341,43
1312,36
1134,15
1091,85
948,26
916,22
855,47
828,19
746,18
657,03
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers (cm-1)

3.General procedures for metathesis reactions

Metathesis in DCM – removal of ruthenium-containing impurities by filtration of reaction mixture through silica gel.

Complex **9** (5.21 mg, 1 mol%) was added under argon to a solution of **23** (151 mg, 0.63 mmol) in dichloromethane (12.6 ml). Reaction mixture was stirred at reflux for 4 h then cooled down to room temperature and filtered through a pad of silica gel (1.04 g). Additional portion of DCM (12 ml) was used to remove product from silica gel. DCM was removed on vacuum to give **24** in (129 mg, 97 %) as a colorless oil. Purity of product was determined using GC method, residual ruthenium was measured using ICP MS method.

Metathesis in DCM – removal of ruthenium-containing impurities by extraction with water.

Complex **11** (9.5 mg, 1 mol%) was added under argon to a solution of **23** (293 mg, 1.22 mmol) in dichloromethane (24.4 ml). Reaction mixture was stirred at reflux for 20 minutes then cooled down to room temperature and extracted with water (5 x 15 ml) each time for 10 minutes. After extraction was completed organic fraction was dried with magnesium sulphate. Solvent was removed under vacuum to afford **24** (230 mg, 89 %) as a colorless oil. Purity of product was determined using GC method, residual ruthenium was measured using ICP MS method.

To the combined water fractions silica gel was added and resulted suspension was stirred at room temperature for 10 min. Next crude silica gel was filtered off and residual ruthenium in water was measured using ICP MS method.

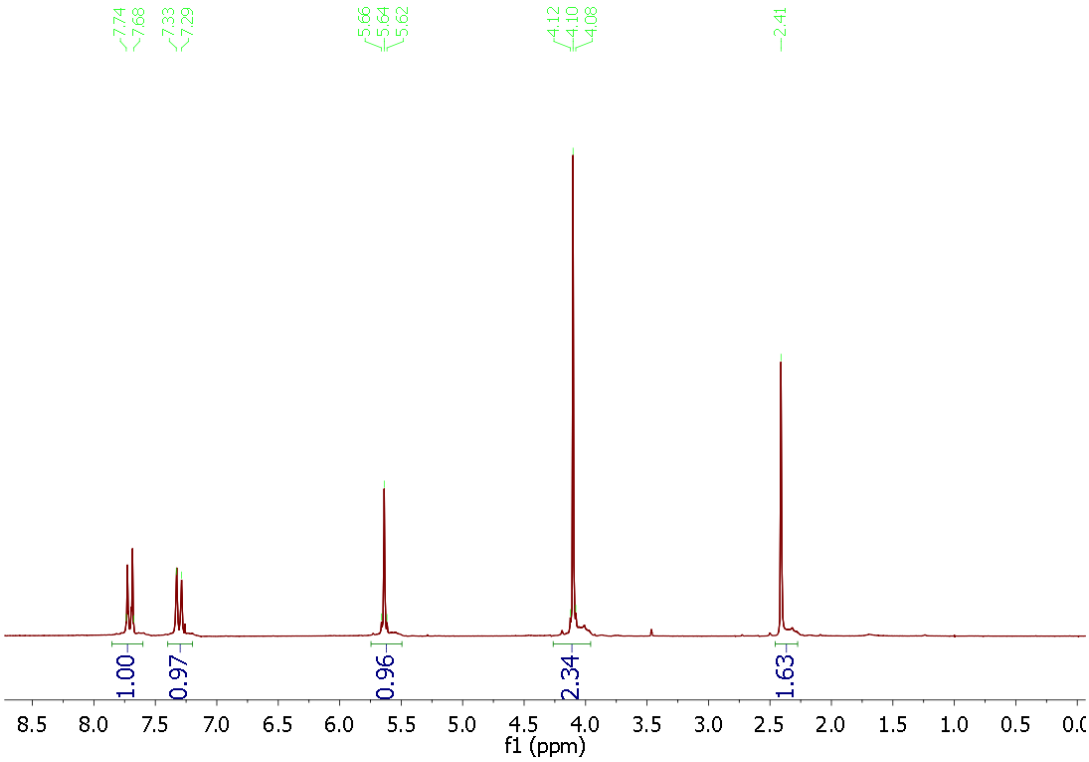
Representative procedure of metathesis in D_2O

Flask equipped with a magnetic stirring bar was charged with substrate ***Z*-38** (29.4 mg, 0.33 mmol) and non-degassed D_2O (1.67 ml). To this solution catalyst **11** was added (1.3 mg, 0.5 mol%). Reaction mixture was stirred at 25 °C for 1 h. Next 0.7 ml of reaction mixture was transferred to an NMR tube. Yield was determined using NMR method.

4.Analytical data of metathesis products

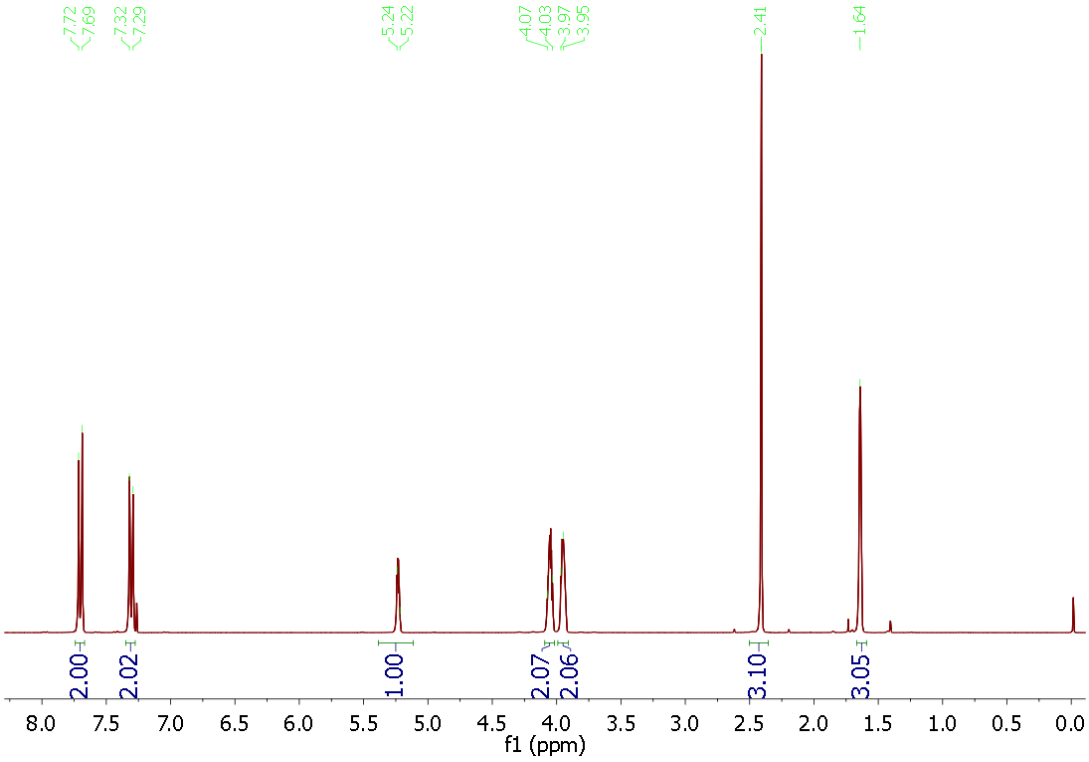
N-Tosyl-2,5-dihydropyrolle (**20**)

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.74-7.68 (m, 2H), 7.33-7.29 (m, 2H), 5.66-5.62 (m, 2H), 4.12-4.08 (m, 4H), 2.41 (s, 3H).



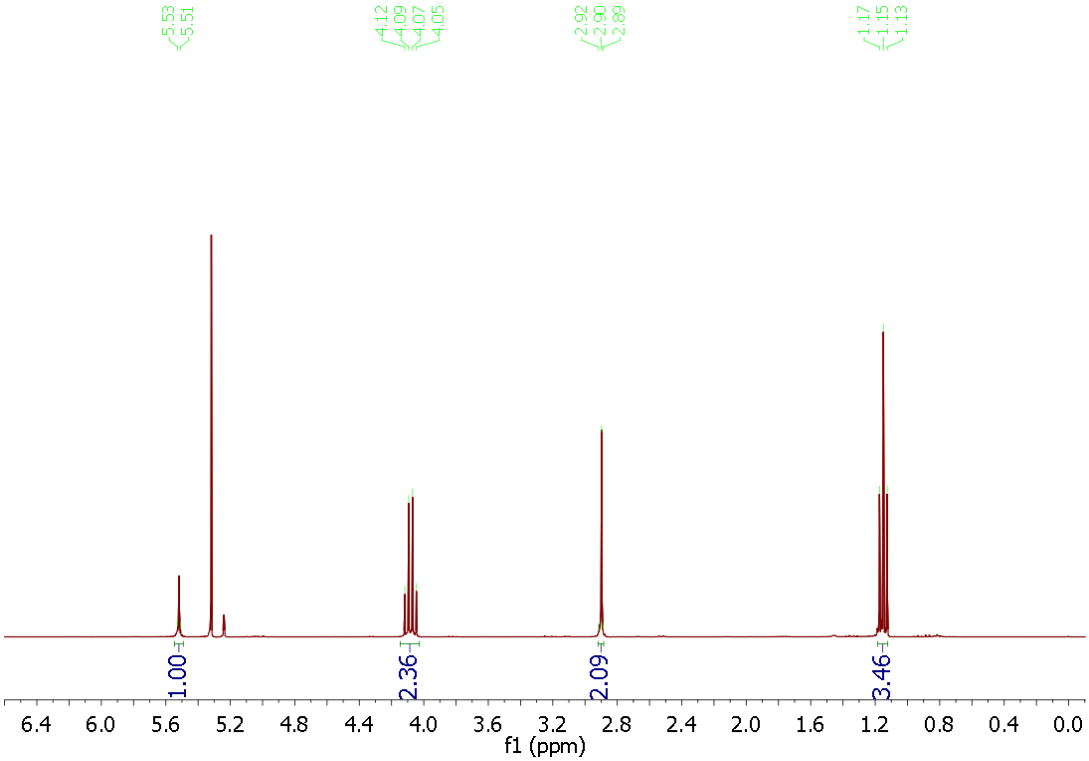
N-Tosyl-3-methyl-2,5-dihydropyrolle (**22**)

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm:7.72-7.69 (m, 2H), 7.32-7.29 (m, 2H), 5.24-5.22 (m, 1H), 4.07-4.03 (m, 2H), 3.97-3.95 (m, 2H), 2.41 (s, 3H), 1.64 (s, 3H).



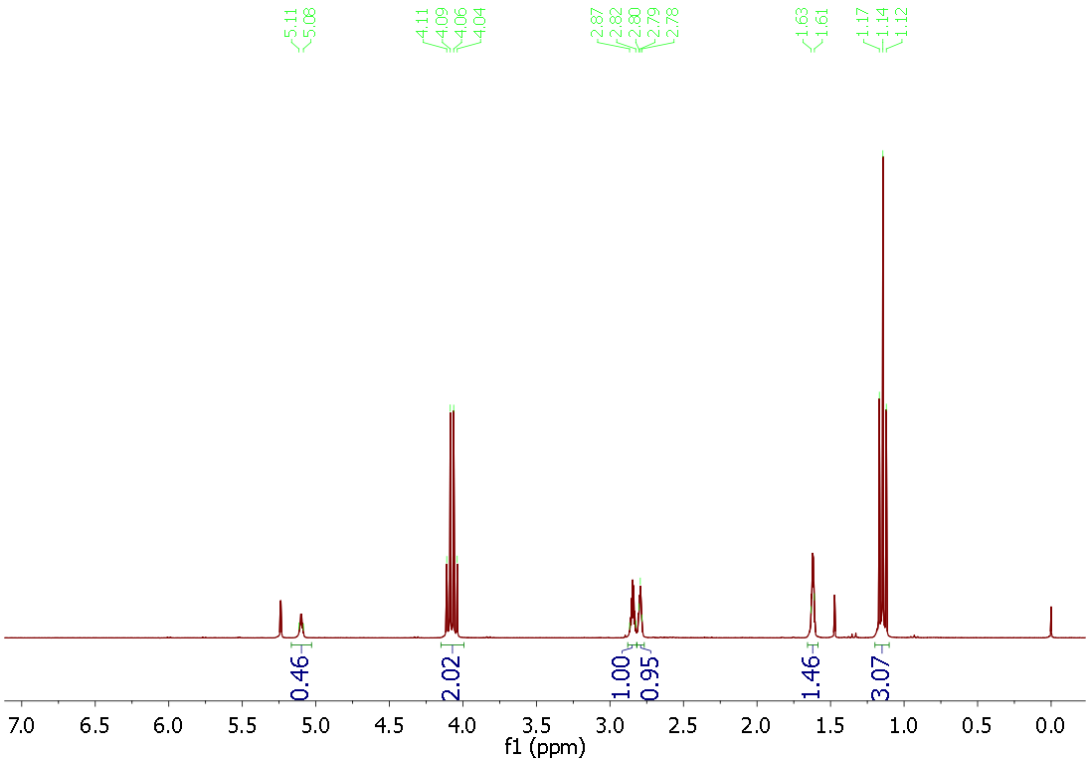
Diethyl 3-cyclopentene-1,1-dicarboxylate (**24**)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.53-5.51 (m, 2H), 4.08 (q, J = 7.2 Hz, 4H), 2.92-2.89 (m, 4H), 1.15 (t, J = 7.2 Hz, 6H).



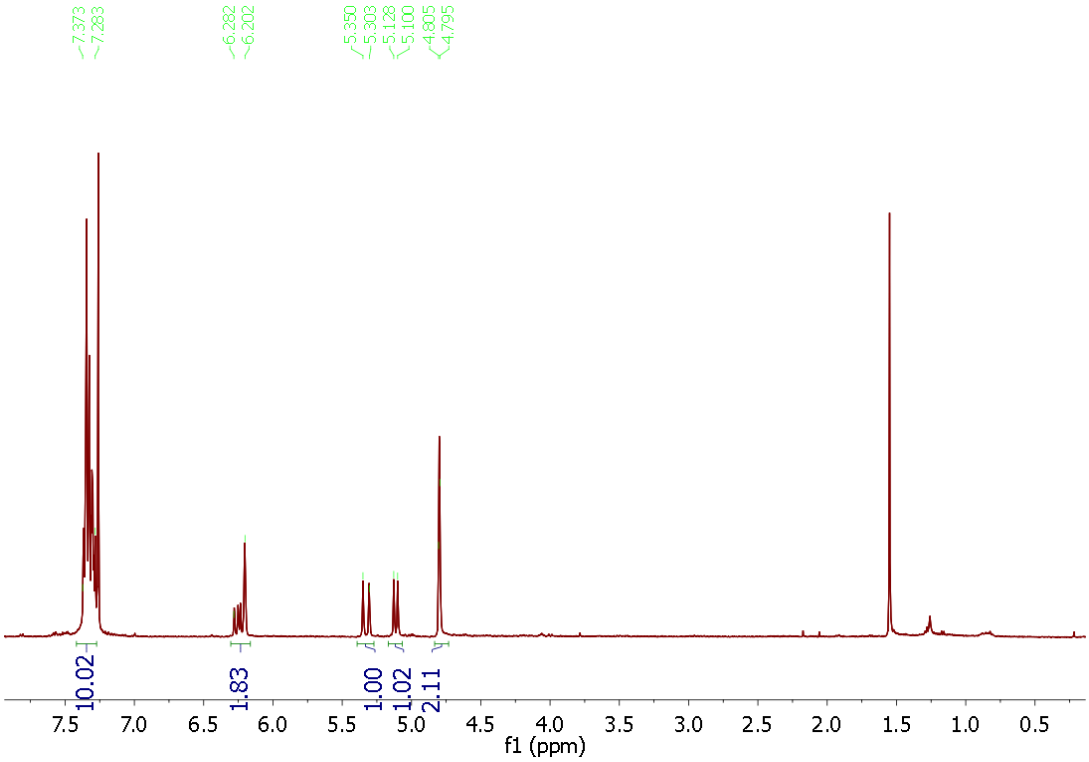
Diethyl 3-methyl-3-cyclopentene-1,1-dicarboxylate (**26**)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.10-5.09 (m, 2H), 4.07 (q, J = 7.2 Hz, 4H), 2.87-2.82 (m, 2H), 2.80-2.78 (m, 2H), 1.63-1.61 (m, 3H), 1.15 (t, J = 7.2 Hz, 6H).



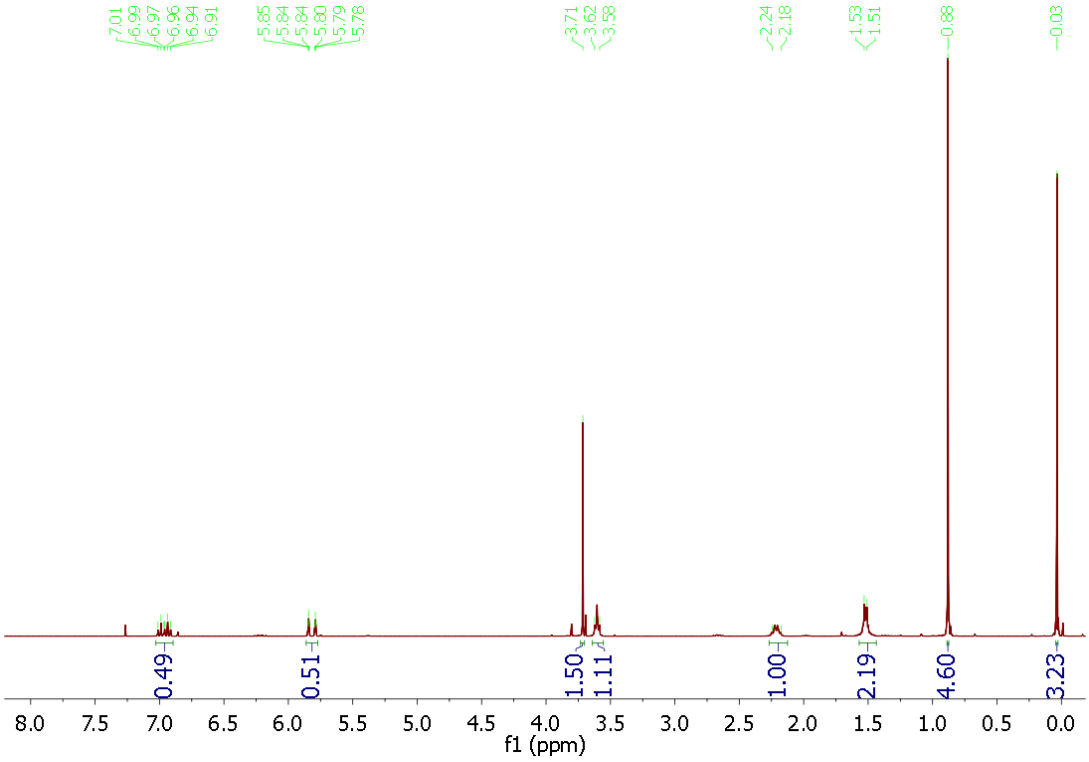
2,2-Diphenyl-3-vinyl-2,5-dihydrofuran (**28**)

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.37–7.28 (m, 10H), 6.28–6.20 (m, 2H), 5.32 (d, J = 14.1, 1H), 5.11 (d, J = 8.4, 1 H), 4.81–4.80 (m, 2H).

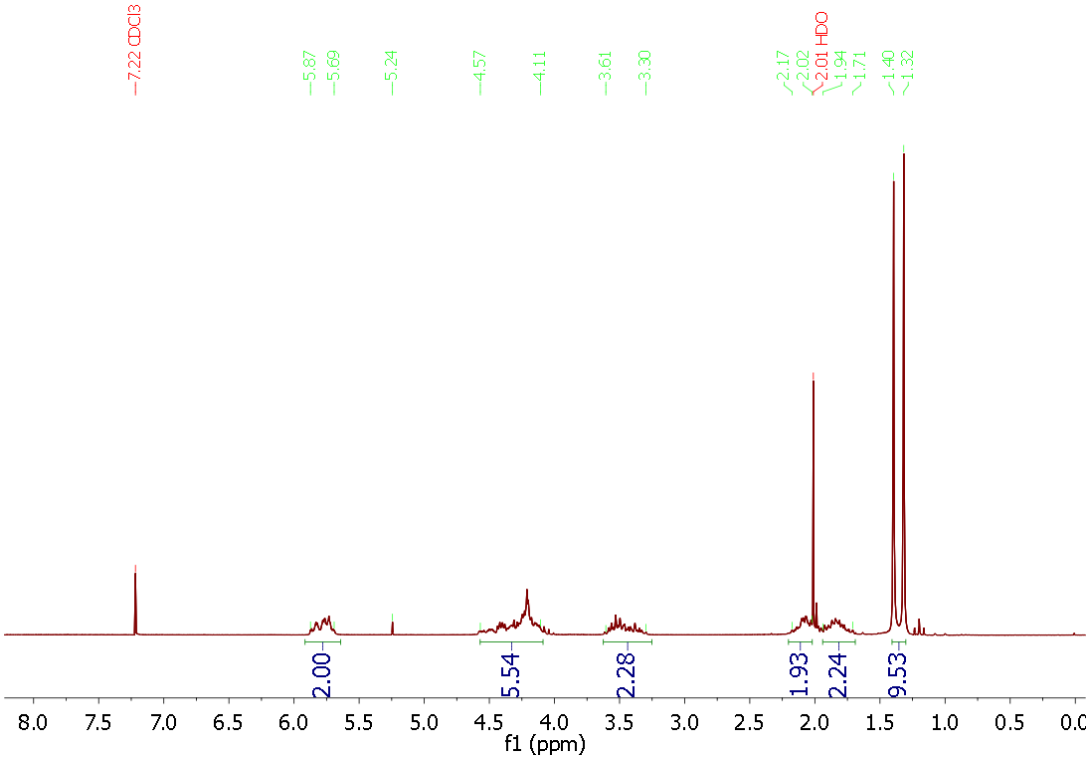


7-(tert-Butyl-dimethyl-silanyloxy)-hept-2-enoic acid methyl ester (**31**)

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 6.96 (dt, J = 6.9 Hz, J = 15.6Hz, 1H), 5.82 (dt, J = 1.8 Hz, J = 15.6Hz , 1H), 3.71 (s, 3H), 3.62-3.58 (m, 2H), 2.24-2.18 (m, 2H), 1.53-1.51 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H).



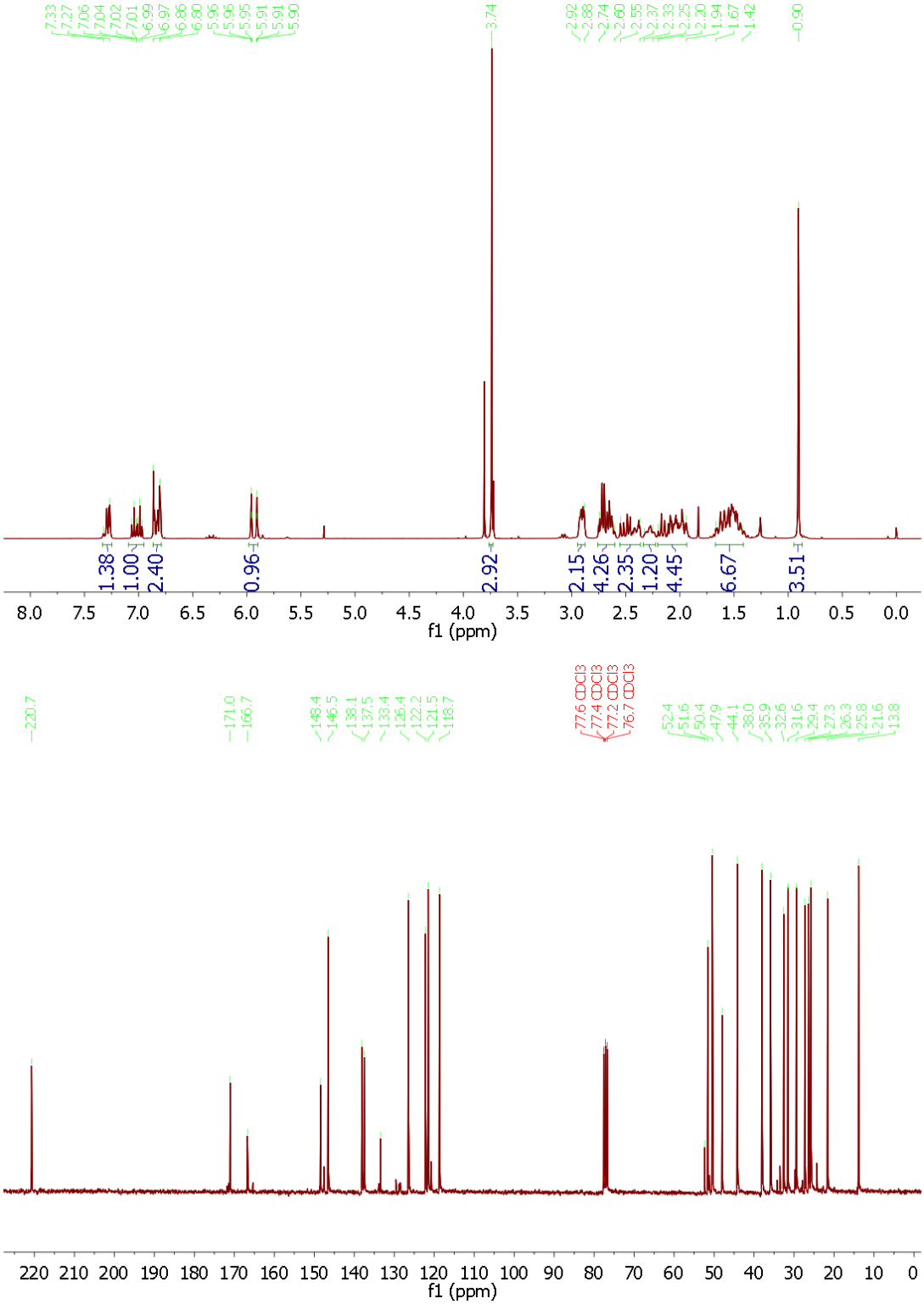
2-(2,5-Dihydropyrrole-1-carbonyl)-pyrrolidine-1-carboxylicacid tert-butyl ester (**33**)
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 5.87-5.69 (m, 2H), 4.57-4.11 (m, 5H), 3.61-3.30 (m, 2H), 2.17-2.02 (m, 2H), 1.94-1.71 (m, 2H), 1.40-1.32 (m, 9H).



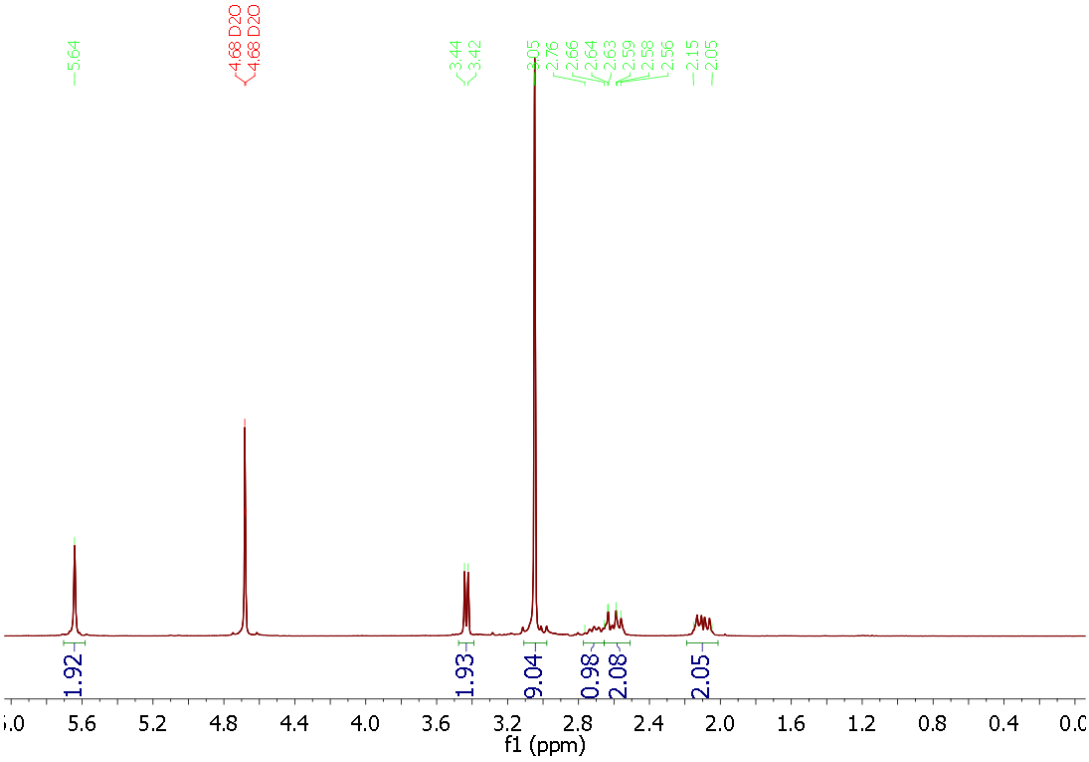
Hex-2-enedioic acid 1-methyl ester 6-(13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl) ester (**35**)

Mixture of *E* and *Z* isomers 9/1, *E* isomer ^{1}H NMR (300 MHz, $CDCl_3$)) δ: 7.33-7.27 (m, 1H), 7.01 (dt, *J* = 6.6 Hz, *J* = 15.9 Hz, 1H), 6.86-6.80 (m, 2H), 5.93 (dt, *J* = 1.5 Hz, *J* = 15.9 Hz, 1H), 3.74 (s, 3H), 2.92-2.88 (m, 2H), 2.74-2.60 (m, 4H), 2.55-2.37 (m, 2H), 2.33-2.25 (m,

1H), 2.20-1.94 (m, 4H), 1.67-1.42 (m, 6H), 0.90 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 220.7, 171.0, 166.7, 148.4, 146.5,138.1, 137.5, 133.4, 126.4, 122.2, 121.5, 118.7, 52.4, 51.6, 50.4, 47.9, 44.1, 38.0, 35.9, 32.6, 31.6, 29.41, 27.3, 26.3, 25.8, 21.6, 13.8. HRMS (ESI) calc for $C_{25}H_{30}O_5Na$ ([M+Na]$^+$) *m/z* 433.1991 found 433.1985.



37: ^{1}H NMR (300 MHz, D_2O) δ ppm: 5.64 (s, 2H), 3.43 (d, 2H, *J* = 6.0Hz), 3.05 (s, 9H), 2.76-2.66 (m, 1H), 2.63-2.56 (m, 2H), 2.15-2.05 (m, 2H).



***E*-38**: ^{1}H NMR (300 MHz, D_2O) δ ppm: 5.78-5.68 (m, 2H), 4.01-3.93 (m, 4H).