Supporting Information

General information....2
Synthesis and Characterization of Rhodium Complexes....3
Optimization of the Reaction Conditions....10
Table S1. Catalyst Screening....11
Optimization on Rh-I-1....14
Table S2. Screening of solvents....14
Table S3. Investigating the water influence....15
Table S4. Varying the solvent volume....15
Table S5. Material of autoclaves....16
Table S6. Temperature effect....16
Table S7. Influence of CO pressure....17
Table S8. Excess of propionic acid....17
Table S9. Reproducibility issue....18
Table S10. Optimization on Rh-I-2....19
Table S11. Optimization of the Reaction with Benzoic Acid (Rh-I-2)....19
Table S12. Optimization on Rh-II-1....20
Table S13. Optimization of the Reaction with Benzoic Acid (Rh-II-1)....20
Table S14. Optimization of the Reaction with *p*-Nitrobenzoic Acid....21
Table S15. Optimization of the Reaction with *p*-dinitrobenzene....21
Reductive Amidation of Aromatic Nitro Compounds....22
References....32
NMR spectra....34

General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker Avance 300, Bruker Avance 400 and Varian Inova-400 spectrometers. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and $^{13}C\{^{1}H\}$ respectively) or DMSO-d_5/d_6 (2.5 and 39.52 ppm for ^{1}H and $^{13}C\{^{1}H\}$ respectively). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = sextet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet; coupling constants are given in Hertz (Hz). NMR yields were calculated using DMF or dinitrobenzene as an internal standard.

Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 gas chromatograph fitted with a flame ionization detector and MS detector. He was used as the carrier gas.

GC settings for the yield determination using FID detector:

Chromatec CR-5MS (30 m, 0.25 mm I.D., 1.0 μm film thickness) capillary columns. The injector temperature was 290 °C, the FID temperature was 250 °C, with a split ratio of 10:1. Column compartment temperature program: 100°C for 2 min, 100→ 290°C at 30 K min^{-1}, 290°C for 3 min. Flow rate 1 ml min^{-1}. Injection volume – 1 μl. Retention time for *p*-nitrotoluene is 4.3 min and 6.0 min for *N*-(*p*-tolyl)propionamide. GC yields were calculated using external calibration.

GC settings for the qualitative analysis using MS detector:

Chromatec CR-5MS (30 meters, 0.25 mm I.D., 1.0 μm film thickness) capillary column. The injector temperature was 290°C, the FID temperature was 250°C, with a split ratio of 40:1. 60°C for 2 min, 60→250°C at 30 K min^{-1}, 250°C for 12 min. Injection volume – 0.2 μl. Flow rate 1 ml min^{-1}. MSD parameters: ion source temperature 200°C, transfer line temperature 290°C.

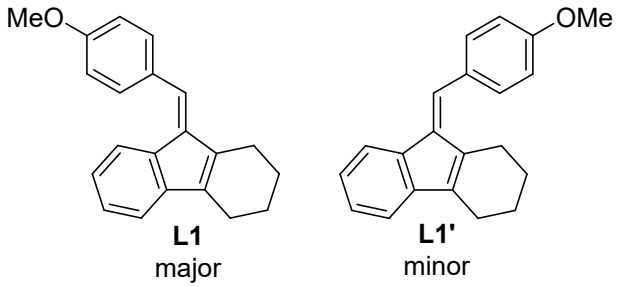
Synthesis and Characterization of Rhodium Complexes

Rh-0-1, Rh-I-6, Rh-I-7, Rh-II-1, Rh-II-2, Rh-III-4 were purchased from Sigma Aldrich.

Rh-III-1 and Rh-III-2 were purchased from ABCR GmbH

Rh-I-5,[1] Rh-I-8,[2] Rh-III-6,[3] Rh-III-7,[3] Rh-III-8, [4] Rh-III-9,[5] Rh-III-12,[5] Rh-III-15[6] were synthesized according to the literature procedures.

Synthesis of THFlu^{PMB} (L1 and L1').



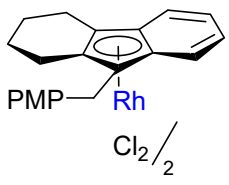
To a solution of 1,2,3,4-tetrahydrofluorene (170 mg, 1.00 mmol, 1 equiv) in 5 ml of THF t-BuONa (96 mg, 1.00 mmol, 1 equiv.) was added and the reaction mixture was stirred at 40 °C for 0.5 h (oil bath). Then p-anysaldehyde (408 mg, 3.00 mmol, 3 equiv.) was added and the reaction was stirred for additional 2 hours. Then AcOH (2ml) was added and the reaction was stirred for 0.5 h. The reaction was cooled, diluted with water and the product was extracted with dichloromethane (2 × 10 mL) and dried with anhydrous sodium sulfate. The solvent was evaporated and the product was purified with column chromatography (SiO_2, 1 × 15 cm). The first colored band eluted with hexane contains the product. Then the product was recrystallized from methanol. The yield of ***L1*** and ***L1'*** is 227 mg (79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 3H), 7.17 (dd appears as t, J = 7.0 Hz, 1H), 7.10 (d, J = 7.0 Hz, 1H), 7.02 (s, 1H), 6.99 – 6.89 (m, 3H), 3.89 – 3.82 (m, 3H), 2.59 – 2.48 (m, 4H), 1.88 – 1.81 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) of **L1** δ 159.5, 131.1, 127.9, 127.6, 124.4, 122.7, 117.4, 113.9, 55.41, 23.1, 22.9, 22.4, 22.2.; of **L1'** δ 55.38, 26.8, 23.8, 23.2, 22.3. Unidentified peaks of **L1** and **L1'** δ 144.8, 140.0, 138.1, 136.6, 134.9, 131.2, 129.5, 127.2, 126.5, 124.7, 118.4, 113.4

HRMS (ESI) m/z calculated for $[M+H]^+$ $C_{21}H_{21}O$ 289.1592; found: 289.1583

Synthesis of [(THFlu^{PMB})RhCl$_2$]$_2$ Rh-III-10



An ethanolic solution (5 mL) of ***(L1*** and ***L1').*** (144 mg, 0.50 mmol, 1 equiv) was added to a solution (5 mL) of $RhCl_3 \cdot 3H_2O$ (132 mg, 0.50 mmol, 1 equiv) in the same solvent, and the reaction mixture was stirred at 80 °C for 16 h (oil bath). The hot solution was poured into hexane, the resulting residue was dried in vacuo and the complex was extracted with dichloromethane (2 × 5 mL). The combined dichloromethane extracts were reduced to the quarter of the volume and the complex was precipitated with 20 ml of hexane. The precipitate was dried

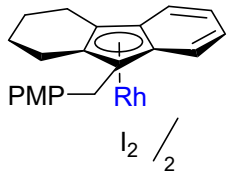
in vacuo and reprecipitated from acetone with Et_2O. The solution was allowed to chill for 30 min in order to achieve total precipitation. Then the red solid was filtered off and dried in vacuo. The yield of ***Rh-III-10*** is 138 mg (60%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (dd appears as t, J = 7.6 Hz, 1H), 7.77 – 7.62 (m, 3H), 7.19 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 8.1 Hz, 2H), 3.76 (dd, J = 119.2, 15.5 Hz, 2H), 3.69 (s, 3H), 2.75 – 2.62 (m, 2H), 2.20 – 2.06 (m, 1H), 1.93 – 1.83 (m, 3H), 1.71 – 1.59 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 158.0, 135.4, 131.9, 129.6, 128.5, 127.0, 123.1, 114.1, 112.8 (d, J = 7.7 Hz), 104.8 (d, J = 6.9 Hz), 97.4 (d, J = 4.6 Hz), 55.0, 39.5, 28.0, 20.6, 20.3, 20.1, 19.8. Several signals of quaternary carbon atoms in the ligand were not observed in ^{13}C{^{1}H} NMR because of their low intensity.

HRMS (ESI) m/z calculated for $[M\text{-}Cl]^+$ $C_{21}H_{21}ORhCl$ 427.0336; found: 427.0332

Synthesis of [(THFlu^{PMB})RhI$_2$]$_2$ Rh-III-11

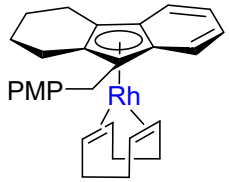


Complex ***Rh-III-10*** (46.5 mg, 0.1 mmol, 1 equiv), anhydrous NaI (300 mg, 2.0 mmol, 20 equiv), and acetone (10 mL) were placed in a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred vigorously at room temperature for 2 days (no inert atmosphere required). The solvent was evaporated in vacuo and the residue was extracted with dichloromethane (5 × 5 mL). The combined solution was dried, the resulting residue was washed with Et_2O (2 × 10 mL). The complex was twice reprecipitated from dichloromethane with hexane. The precipitate was dried. The yield of ***Rh-III-11*** is 49 mg (76%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 – 7.66 (m, 2H), 7.64 – 7.58 (m, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.2 Hz, 2H), 3.94 (dd, J = 115.9, 15.5 Hz, 2H), 3.69 (s, 3H), 3.26 – 3.17 (m, 1H), 2.61 – 2.52 (m, 3H, overlapped with dmso signal), 1.91 – 1.80 (m, 2H), 1.73 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 158.0, 134.4, 131.5, 129.7, 129.3, 127.5, 123.6, 114.2, 112.6 (d, J = 5.6 Hz), 107.4 (d, J = 4.0 Hz), 100.1 (d, J = 4.5 Hz), 84.9 (d, J = 6.9 Hz), 55.0, 29.2, 22.9, 21.1, 21.0, 20.2.
HRMS (ESI) m/z calculated for $[M\text{-}I]^+$ $C_{21}H_{21}ORhI$ 518.9686; found: 518.9682

Synthesis of [(THFlu^{PMB})RhCOD] Rh-I-9



Complex ***Rh-III-10*** (93 mg, 0.2 mmol, 1 equiv), Na_2CO_3 (212 mg, 2.00 mmol, 10 equiv), and COD (44 µL, 0.41 mmol, 2.05 equiv.), ethanol (2 ml) were placed in a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at 80˚C for 4 hours (oil bath). The solvent was removed in vacuo and the residue was extracted with pentane (3 × 10 mL). Then pentane was evaporated and the residue was purified by column chromatography (SiO_2, 1×

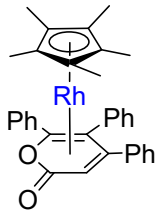
10cm). The complex was eluted with mixture of pentane:dichloromethane (8:1). The yellow band was collected and the solvent was evaporated. The yield of ***Rh-I-9*** is 64 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.94 (m, 5H), 6.75 (d, *J* = 8.1 Hz, 2H), 3.74 (s, 3H), 3.58 – 3.45 (m, 2H), 3.45 – 3.33 (m, 4H), 3.01 – 2.89 (m, 1H), 2.60 – 2.51 (m, 1H), 2.49 – 2.40 (m, 1H), 2.28 – 2.18 (m, 1H), 2.01 – 1.67 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 132.7, 130.2, 129.1, 122.0, 121.2, 118.0, 116.7, 113.8, 110.8 (d, J = 2.7 Hz), 110.3 (d, J = 2.0 Hz), 72.4 (d, J = 13.4 Hz), 71.1 (d, J = 13.7 Hz), 55.3, 31.6, 31.4, 29.1, 24.2, 23.5, 23.3, 20.4. Two signals of quaternary carbon atoms in the indenyl moiety were not observed in ^{13}C{^{1}H} NMR because of their low intensity.

HRMS (ESI) m/z calculated for $[M-H]^+$ $C_{29}H_{32}ORh$ 499.1508; found: 499.1502

Synthesis of [(Cp*)Rh(4,5,6-triphenyl-2H-pyran-2-one)] Rh-I-4



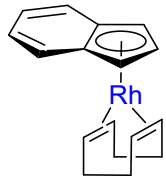
Rh-III-1 (61.8 mg, 0.1 mmol, 1 equiv), AgOAc (66.8 mg, 0.4 mmol, 4.1 equiv), cinnamic acid (29.6 mg, 0.2 mmol, 2 equiv), tolane (36 mg, 0.2 mmol, 2 equiv), and MeOH (2 mL) were placed into the Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 90 °C (an oil bath) for 8 h. After cooling to room temperature, the resulting AgCl was centrifuged, the solvent was removed in vacuo, and the product was isolated by column chromatography on silica (1 × 15 cm) using a mixture of CH_2Cl_2/ hexane (1:1) as an eluent. Evaporation of the first red band gave complex ***Rh-I-4*** as an orange solid. The yield of ***Rh-I-4*** is 89 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 7H), 7.08 – 6.99 (m, 1H), 6.97 – 6.92 (m, 7H), 3.33 (s, 1H), 1.63 (s, 15H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2 (d, J = 10.2 Hz), 138.1, 136.5, 134.0, 131.9, 129.7 (d, J = 7.3 Hz), 129.5, 128.4, 128.3, 128.1, 127.6, 127.5, 127.4, 125.8, 125.7, 125.3, 97.6 (d, J = 5.9 Hz), 54.2 (d, J = 17.5 Hz), 9.5. Several signals of quaternary carbon atoms in the pyrone ligand were not observed in ^{13}C{^{1}H} NMR because of their low intensity.

HRMS (ESI) m/z calculated for $[M+H]^+$ $C_{33}H_{32}O_2Rh$ 563.1451; found: 563.1442

Synthesis of [(Ind)RhCOD] Rh-I-2



Indene (100 mg, 0.58 mmol, 1 equiv) was dissolved in THF (5 mL). The solution was cooled in an ice bath, and BuLi (0.41 mL of 1.4 M solution, 0.58 mmol, 1.03 equiv) was added. Then, complex ***Rh-I-14*** (143 mg, 0.58 mmol, 1 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed in vacuo. The

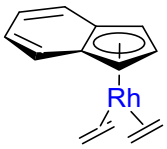
residue was extracted with hexane (2 × 10 mL) and Et_2O (5 mL). The solutions were combined and the solvents were removed in vacuo. The residue was chromatographed on silica (1 × 15 cm) with hexane. The first yellow band was collected, and the solvent was removed in vacuo to give ***Rh-I-2*** as a yellow crystalline solid. The yield of ***Rh-I-2*** is 170 mg (90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 2H), 7.18 – 7.05 (m, 2H), 6.21 – 6.05 (m, 1H), 5.21 (d, J = 2.8 Hz, 2H), 4.02 (s, 4H), 1.95 – 1.69 (m, 8H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 122.4, 119.3, 113.2 (d, J = 2.1 Hz), 92.6 (d, J = 5.2 Hz), 76.1 (d, J = 4.3 Hz), 67.5 (d, J = 13.6 Hz), 31.4

NMR spectra are in agreement with the literature data.[7]

Synthesis of [(Ind)Rh(C_2H_4)$_2$] Rh-I-3



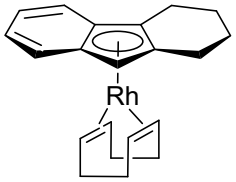
Indene (50 mg, 0.29 mmol, 1 equiv) was dissolved in THF (5 mL). The solution was cooled in an ice bath, and BuLi (0.20 mL of 1.4 M solution, 0.29 mmol, 1.03 equiv) was added. Then, complex $[(C_2H_4)_2RhCl]_2$ (56 mg, 0.29 mmol, 1 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed in vacuo. The residue was extracted with hexane (3 × 10 mL) and Et_2O (2 × 5 mL). The solutions were combined and the solvents were removed in vacuo. The residue was chromatographed on silica (1 × 15 cm) with hexane. The first yellow band was collected, and the solvent was removed in vacuo to give ***Rh-I-3*** as a yellow solid. The yield of ***Rh-I-3*** is 67 mg (85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.22 – 7.11 (m, 2H), 6.27 – 6.11 (m, 1H), 5.13 (d, J = 2.4 Hz, 2H), 2.24 – 1.92 (m, 8H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 123.7, 119.4, 112.0 (d, J = 2.4 Hz), 91.8 (d, J = 5.4 Hz), 78.5 (d, J = 4.2 Hz), 43.9 (d, J = 13.0 Hz)

NMR spectra are in agreement with the literature data. [7]

Synthesis of [(THFlu)RhCOD] Rh-I-1



1,2,3,4-tetrahydrofluorene (100 mg, 0.58 mmol) was dissolved in THF (4 mL) the mixture was cooled with ice bath and BuLi in hexane (0.2 ml of 2.5 M solution, 0.58 mmol) was added dropwise. The reaction mixture was stirred for 5 min, and then ***Rh-I-14*** (123 mg, 0.24 mmol, 0.5 equiv) was added. The reaction mixture was additionally stirred for 1 h, the solvent was removed in vacuo. The residue was chromatographed on SiO_2 (1 × 10 cm) with hexane. A second yellow band was collected and dried to give compound as yellow oily crystals. The yield of ***Rh-I-1*** is 154 mg (70%).

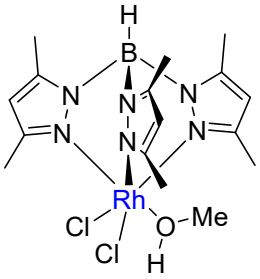
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.1 Hz, 1H), 7.05 – 6.95 (m, 3H), 4.88 (s, 1H), 3.76 – 3.66 (m, 2H), 3.57 – 3.47 (m, 2H), 2.98 – 2.89 (m, 1H), 2.68 – 2.60 (m, 1H), 2.55 (m, J = 15.8, 5.6 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.01 – 1.65 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 121.9, 121.3, 119.4, 116.6, 111.6 (d, J = 5.2 Hz), 111.3 (d, J = 2.2 Hz), 111.2 (d, J = 2.9 Hz), 90.9 (d, J = 3.7 Hz), 72.3 (d, J = 4.7 Hz), 71.5 (d, J = 13.8 Hz), 68.4 (d, J = 13.7 Hz), 31.8, 31.2, 25.6, 23.7, 23.4, 20.6.

HRMS (ESI) m/z calculated for $[M]^+$ $C_{21}H_{25}Rh$ 380.1011; found: 380.1006

NMR spectra are in agreement with the literature data.[8]

Synthesis of $Tp^{Me2}RhCl_2MeOH$ Rh-III-13



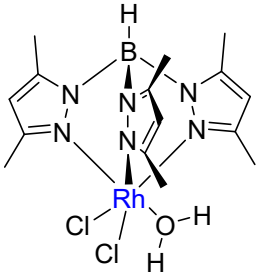
A solution of K[Tp^{Me2}] (336 mg; 1.0 mmol, 1 equiv) in MeOH (5 ml) was added to a solution of $RhCl_3 \cdot 3H_2O$ (263 mg; 1.0 mmol, 1 equiv) in MeOH (2 ml). The reaction mixture was refluxed for 4 h (oil bath). The precipitate was centrifuged off, the solution was concentrated in vacuo until a yellow precipitate began to form. The solution was left overnight at −30 °C. The obtained yellow crystals were filtered off, crushed and dried in vacuo. Compound ***Rh-III-13*** was obtained as a yellow solid. The yield of ***Rh-III-13*** is 301 mg (60%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (q, J = 3.1 Hz, 1H), 6.02 (s, 2H), 5.92 (s, 1H), 3.46 (d, J = 3.6 Hz, 3H), 2.59 (s, 3H), 2.47 (s, 6H), 2.40 (s, 3H), 2.39 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.3, 153.0 (2C), 145.0, 144.6 (2C), 108.8, 108.5 (2C), 50.6, 15.6, 13.9 (2C), 12.3, 12.0 (2C).

NMR spectra are in agreement with the literature data.[9]

Synthesis of $Tp^{Me2}RhCl_2H_2O$ Rh-III-14



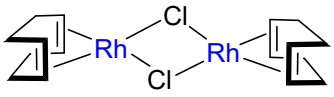
A suspension of complex ***Rh-III-13*** (50 mg, 0.1 mmol) in CH_2Cl_2 (3 ml) with 3 drops of distilled water was stirred overnight on air. The precipitate was centrifuged off and washed with 5 ml of CH_2Cl_2. Compound ***Rh-III-14*** was obtained as a colorless solid. The yield of ***Rh-III-14*** is 46 mg (95%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.63 (s, 2H), 5.97 (s, 2H), 5.91 (s, 1H), 2.59 (s, 3H), 2.48 (s, 6H), 2.39 (s, 2H), 2.38 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 154.9, 153.3 (2C), 144.5, 144.2 (2C), 108.6, 108.4 (2C), 15.7, 14.2 (2C), 12.3, 12.1 (2C).

NMR spectra are in agreement with the literature data. [9]

Synthesis of [CODRhCl]$_2$ Rh-I-12



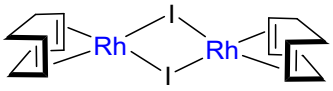
To a suspension of $RhCl_3 \cdot 3H_2O$ (1.0 g, 3.79 mmol, 1 equiv) in 15 ml of ethanol:water (5:1) mixture 1,5-COD (1.3 g, 12.3 mmol, 3.2 equiv) was added. The mixture was refluxed for 10 h (oil bath). Then the reaction was cooled and the orange precipitate was filtered and washed with cooled water and cooled methanol. The precipitate was dried in vacuo. The yield of ***Rh-I-12*** is 840 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 – 4.16 (m, 8H), 2.54 – 2.43 (m, 8H), 1.75 (q, J = 7.7 Hz, 8H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 78.9 (d, J = 14.0 Hz), 31.0

NMR spectra are in agreement with the literature data. [10]

Synthesis of [CODRhI]$_2$ Rh-I-11



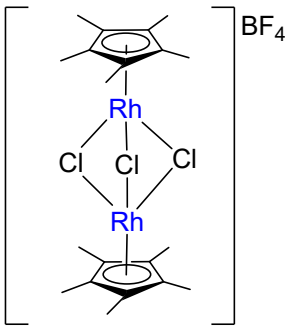
Rh-I-12 (100 mg, 0.2 mmol, 1 equiv), anhydrous NaI (300 mg, 2.0 mmol, 10 equiv), and CH_2Cl_2 (10 mL) were placed in a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred vigorously at room temperature overnight. The solvent was evaporated in vacuo and the residue was extracted with dichloromethane (5 × 5 mL). The combined solution was dried. The yield of ***Rh-I-11*** is 128 mg (95%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 – 4.59 (m, 8H), 2.49 – 2.30 (m, 8H), 1.75 – 1.61 (m, 8H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 79.8 (d, J = 12.8 Hz), 31.4

NMR spectra are in agreement with the literature data.[11]

Synthesis of [Cp*$_2$Rh$_2$Cl$_3$]BF$_4$ Rh-III-3



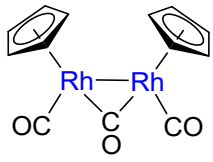
Rh-III-1 (100 mg, 0.16 mmol, 1 equiv), 2M HBF_4 (0.2 ml, 0.4 mmol, 2.5 equiv), and MeOH (2 mL) were placed in a Schlenk tube and were refluxed for 5 minutes. The reaction mixture was then kept at 4°C for 8 hours. The formed crystals were centrifuged off, crushed, washed with MeOH (5 ml) and dried in vacuo. The yield of ***Rh-III-3*** is 84 mg (79%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69 (s, 30H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 96.4 (d, J = 9.1 Hz), 9.7.

NMR spectra are in agreement with the literature data.[12]

Synthesis of $Cp_2Rh_2(CO)_3$ Rh-I-10



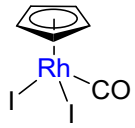
The solution of $CpRh(CO)_2$ (50 mg, 0.22 mmol) in 8 ml of hexane was refluxed under the sun light for 2 days. Then the solvent was evaporated, the residue was was chromatographed (Al_2O_3 1×10cm). The first yellow band, containing unreacted starting compound was eluted with petroleum ether. The second red band was eluted with petroleum ether:Et_2O (4:1) mixture, the solvent was evaporated, giving the product as dark-red powder. The yield of ***Rh-I-10*** is 22 mg (52%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (s, 10H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0 (m, only one signal due to rapid CO exchange), 90.2 (d, J = 2.2 Hz)

NMR spectra are in agreement with the literature data.[13]

Synthesis of $CpRhI_2CO$ Rh-III-5

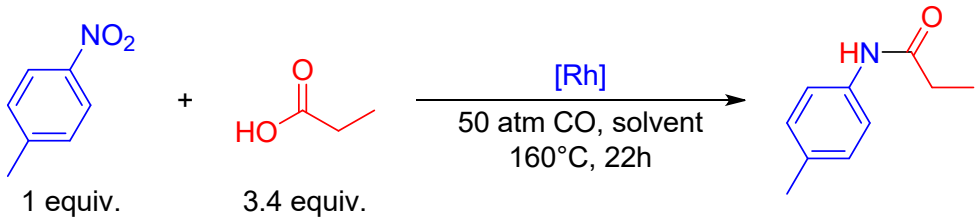


To a solution of ***Rh-I-10*** (30 mg, 0.07 mmol, 1 equiv) in 15 ml of hexane a solution of I_2 (38 mg, 0.14 mmol, 2 equiv) in 15 ml of hot hexane was added. The black precipitate was formed in 5 minutes, it was centrifuged off, washed with hexane (10 ml × 5) and dried in vacuo. The yield of ***Rh-III-5*** is 57 mg (90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (s, 5H)

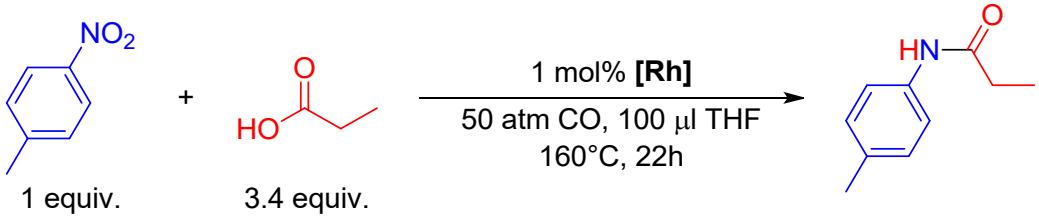
^{13}C NMR (101 MHz, $CDCl_3$) δ 92.3 (d, J = 4.7 Hz). The signal of carbonyl group was not observed in ^{13}C{^{1}H} NMR because of their low intensity.

Optimization of the Reaction Conditions

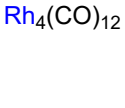


General procedure: Unless otherwise stated, a glass vial in a 10 mL autoclave, was charged with corresponding amount of the catalyst, 4-nitrotoluene (40 mg, 1 equiv., 0.29 mmol), propionic acid (74 µL, 3.4 equiv., 1.00 mmol) and solvent (100 µL). The autoclave was sealed, flushed three times with 10 atm of CO, then charged with the indicated pressure of CO and placed into a preheated oil bath. After 22 hours the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane. The yields were determined by GC using external calibration.

Table S1. Catalyst Screening

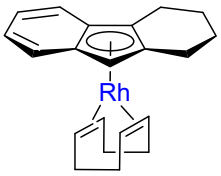


1 equiv. 3.4 equiv.

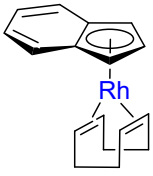


$Rh_4(CO)_{12}$

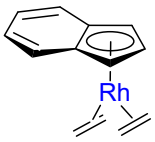
Rh-0-1
24%



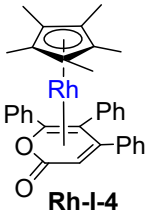
Rh-I-1
96%
64 - 93%[a]



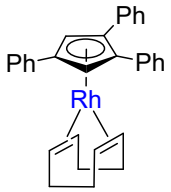
Rh-I-2
75%
62 - 70%[a]



Rh-I-3
82%
23%[a]



Rh-I-4
73%
52%[a]



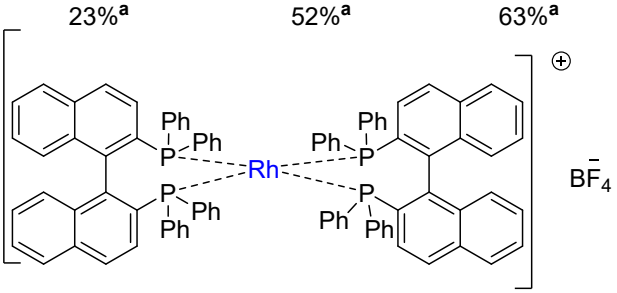
Rh-I-5
92%
63%[a]

$Rh_2(CO)_4Cl_2$

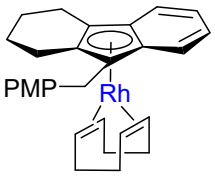
Rh-I-6
24%

$Rh(PPh_3)_2(CO)Cl$

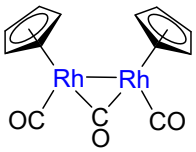
Rh-I-7
19%



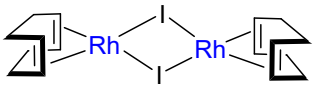
Rh-I-8
30%



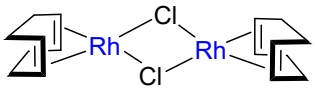
Rh-I-9
89%
65%[a]



Rh-I-10
53%

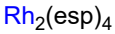


Rh-I-11
64%

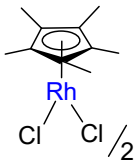


Rh-I-12
36%

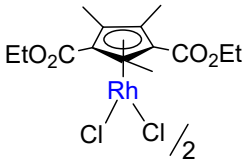
Rh-II-1
88 - 99%



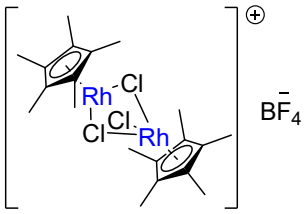
Rh-II-2
100%



Rh-III-1
60%

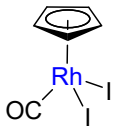


Rh-III-2
67%
42%[a]

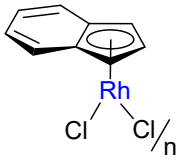


Rh-III-3
42%

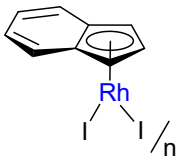
Rh-III-4
15%



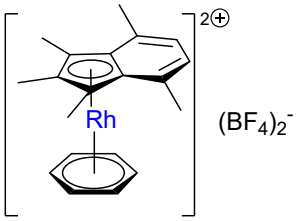
Rh-III-5
67%
20%[a]



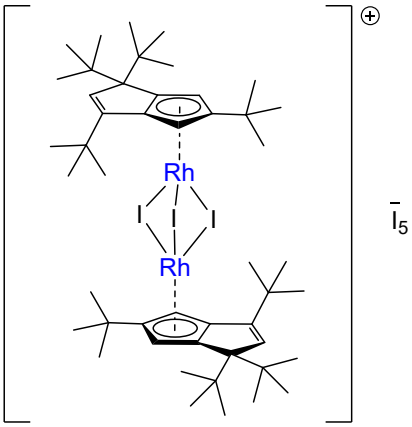
Rh-III-6
11%



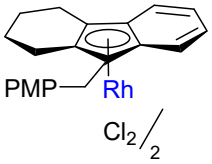
Rh-III-7
51%



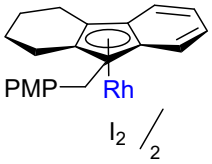
Rh-III-8
32%



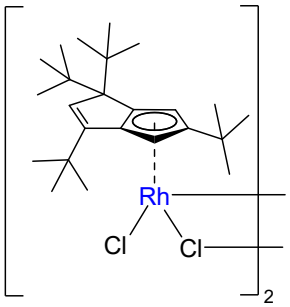
Rh-III-9
28%



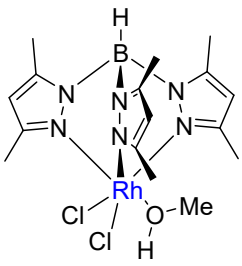
Rh-III-10
19%



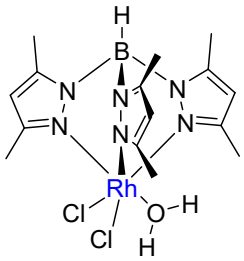
Rh-III-11
53%



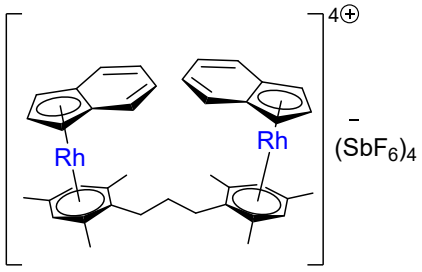
Rh-III-12
19%



Rh-III-13
traces



Rh-III-14
traces



Rh-III-15
53%[b]

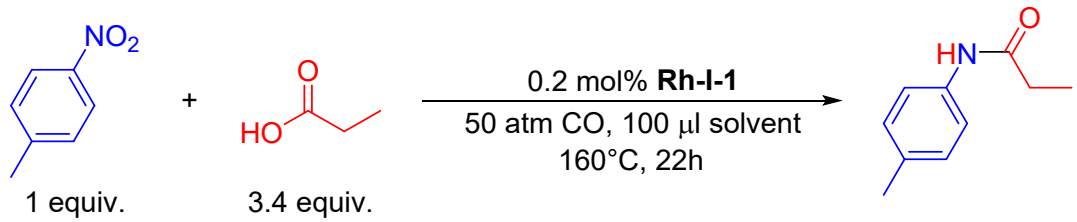
Entry	Catalyst [a]	Yield, %
1	**Rh-0-1**	24
2	**Rh-I-1**	96
3	**Rh-I-1**[b]	64 — 93
4	**Rh-I-2**	75
5	**Rh-I-2**[b]	62— 70
6	**Rh-I-3**	82

7	**Rh-I-3**[b]	23
8	**Rh-I-4**	73
9	**Rh-I-4**[b]	52
10	**Rh-I-5**	92
11	**Rh-I-5**[b]	63
12	**Rh-I-6**	24
13	**Rh-I-7**	19
14	**Rh-I-8**	30
15	**Rh-I-9**	89
16	**Rh-I-9**[b]	65
17	**Rh-I-10**	53
18	**Rh-I-11**	64
19	**Rh-I-12**	36
20	**Rh-II-1**	88 — 99
21	**Rh-II-1**[b]	92 — 93
22	**Rh-II-1**[d]	99
23	**Rh-II-2**	100
24	**Rh-III-1**	60
25	**Rh-III-2**	67
26	**Rh-III-2**[b]	42
27	**Rh-III-3**	42
28	**Rh-III-4**	15
29	**Rh-III-5**	67
30	**Rh-III-5**[b]	20
31	**Rh-III-6**	11
32	**Rh-III-7**	51
33	**Rh-III-8**	32
34	**Rh-III-9**	28
35	**Rh-III-10**	19
36	**Rh-III-11**	53
37	**Rh-III-12**	19
38	**Rh-III-13**	traces
39	**Rh-III-14**	traces
40	**Rh-III-15**[c]	53

[a]The activity of the catalysts was compared at the same amount of rhodium [Rh]. Thus, for dimeric complexes 0.5 mol% of catalyst was used instead of 1.0 mol%, for tetramers - 0.25 mol%, etc.
[b]0.2 mol.% of [Rh] was used.
[c]0.75 mol.% of [Rh]was used.
[d]2 mol.% of [Rh] (1 mol% of rhodium acetate dimer) was used.

Optimization on Rh-I-1

Table S2. Screening of solvents



1 equiv. 3.4 equiv.

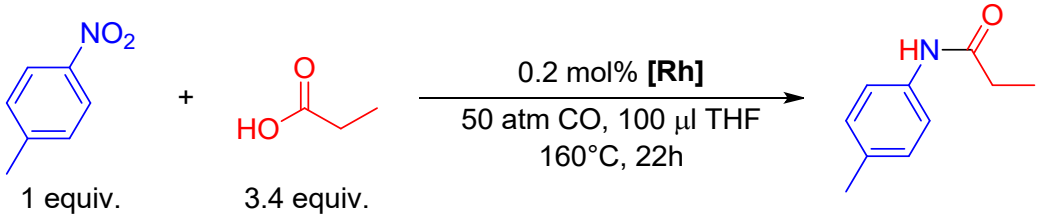
Entry	Solvent	Amount of H_2O	Yield, %[b]
1	**THF**	30 ppm	64 — 93[c]
2	**MTBE**	0.021%	90
3	**^{t}BuOH**	0.1%	84
4	**EtOH**	5.26%	84
5	**neat**	-	61 — 83 [c]
6	**acetone**	0.2%	73
7	**1,4-dioxane**	0.30%	66
8	**MeOH**	0.011%	56
9	**PhMe**	0.012%	54
10	**water**	100%	52
11	**Et_2O**	0.10%	51
12	**petroleum ether**	0.0010%	47
13	**EtOAc**	0.046%	42
14	**PhH**	0.011%	40
15	**MeCN**	0.013%	39
16	**hexane**	0.0024%	30
17	**pentane**	0.0015%	28
18	**$CHCl_3$**	0.05%	11
19	**DCM**	0.0031%	7
20	**DMSO**	0.05%	traces

[a]The water content was measured by Fischer titration

[b]Data from one experiment

[c]Data from more than 10 experiments

Table S3. Investigating the water influence



1 equiv. 3.4 equiv.

Entry	Catalyst	Water loading	Yield, %[b]
1	**Rh-I-5**	-	63 [a]
2		3 equiv.	53 [a]
3	**Rh-I-2**	-	62— 70
4		3 equiv.	67 — 72
5	**Rh-I-1**	-	64 — 93
6		3 equiv.	63 — 78
7[c]		-	1 — 4
9[c]		3 equiv.	11 — 20

[a]Data from one experiment

[b]Data from more than 10 experiments

[c]Reaction lasted for 2h.

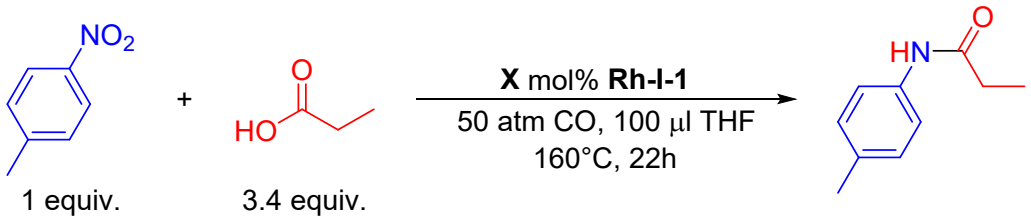
Table S4. Varying the solvent volume

Entry	THF volume, µL	Yield, %[a]
1	0	61 — 83
2	100	64 — 93
3	500	28 — 36[b]

[a]Data from more than 10 experiments

[b]Data from two experiments

Table S5. Material of autoclaves



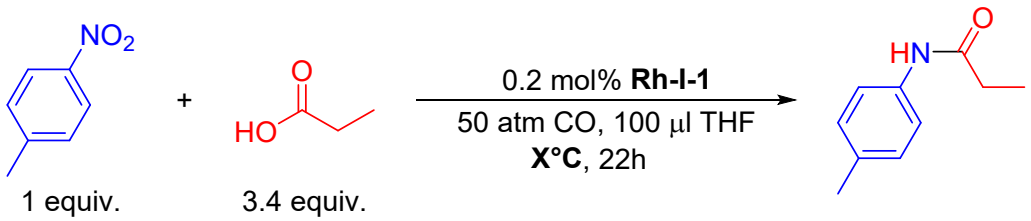
1 equiv. 3.4 equiv.

Entry	Autoclave	Catalyst loading	Yield, % [a]
1	Titanium (10 mL)	0.2	64 — 93
2		1.0	94 — 98[b]
3	Stainless steel (10 mL)	0.2	17 — 91
4		1.0	74 — 94[b]

[a]Data from more than 10 experiments

[b]Data from two experiments

Table S6. Temperature effect



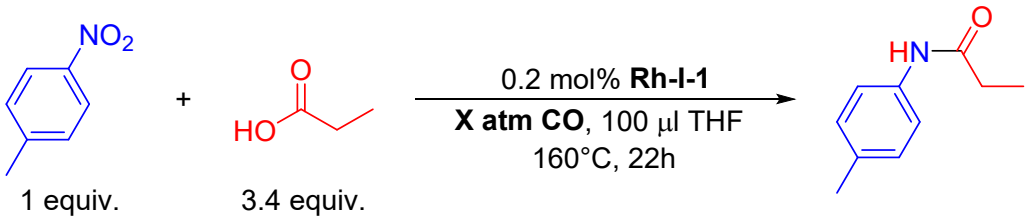
1 equiv. 3.4 equiv.

Entry	t, °C	Yield, % [a]
1	120	7 — 9
2	140	10 — 18
3	160	64 — 93[b]
4	180	75 — 77

[a]Data from two experiments

[b]Data from more than 10 experiments

Table S7. Influence of CO pressure



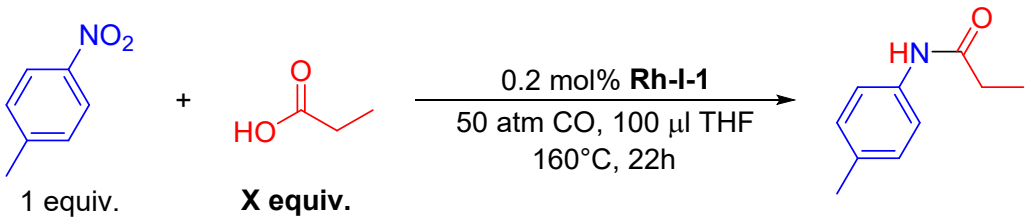
1 equiv. 3.4 equiv.

Entry	CO pressure, atm	Yield, % [a]
1	20	11 — 29
2	30	15 — 35
3	40	33 — 93
4	50	64 — 93[b]

[a]Data from two experiments

[b]Data from more than 10 experiments

Table S8. Excess of propionic acid



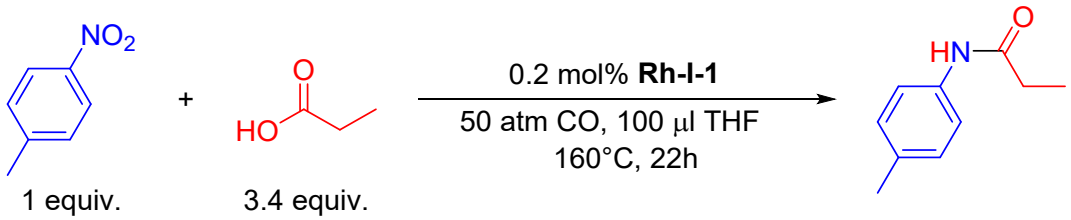
1 equiv. **X equiv.**

Entry	Equiv. of EtCOOH	Yield, % [a]
1	1.5	37 — 70
2	3.4	64 — 93[b]

[a] Data from four experiments.

[b] Data from more than 10 experiments.

Table S9. Reproducibility issue



1 equiv. 3.4 equiv.

Entry	Catalyst	Yield, % [a]
1 [b]	**Rh-I-1**	58
2 [c]		84
3 [b, d]		61
4 [b]	**0.5 mol% Rh-I-2**	56
5 [c]		65
6 [b, d]	**0.25 mol% Rh-I-2**	42

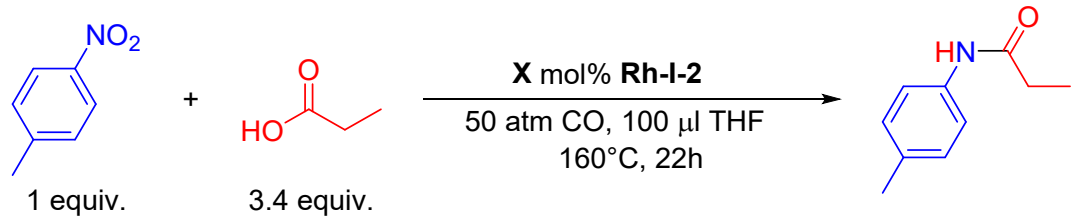
[a] Average value. The reactants were mixed under air and the reactions were carried out in titanium autoclaves.

[b] Approximately 40 minutes between the addition of catalyst to reaction mixture and filling with CO.

[c] Approximately 10 minutes between the addition of catalyst to reaction mixture and filling with CO.

[d] The catalyst was additionally purified under Ar atmosphere and the reactants were mixed in glovebox. Data from one experiment.

Table S10. Optimization on Rh-I-2



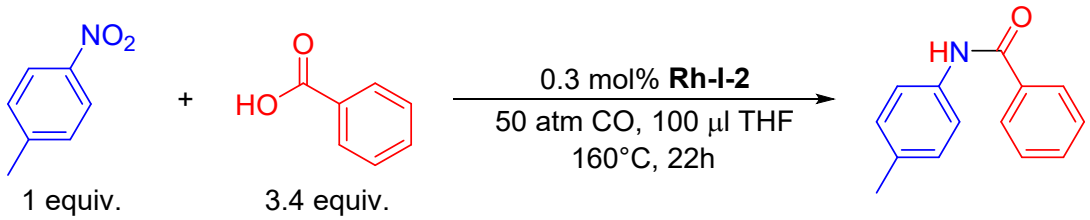
Entry	Rh-I-2 loading, mol%	Altered Parameter	Parameter value	Yield, % [a]
1	**0.3**	**none**		41 — 89
2		**temperature, °C**	140	19 — 26
3 [b]			160	99
4 [b]			180	89
5		**pressure, atm**	30	40 — 66
6		**Excess of EtCOOH, equiv.**	1.5	55 — 65
7			10	58 — 99
8	**0.5**	**none**		48 —93
9		**Excess of EtCOOH, equiv.**	5	37 —80
10			10	39 —92
11 [c]			10	56 —99

[a] Data from 8 experiments.

[b] 72 hours. Data from one experiment.

[c] 48 hours. Data from two experiments.

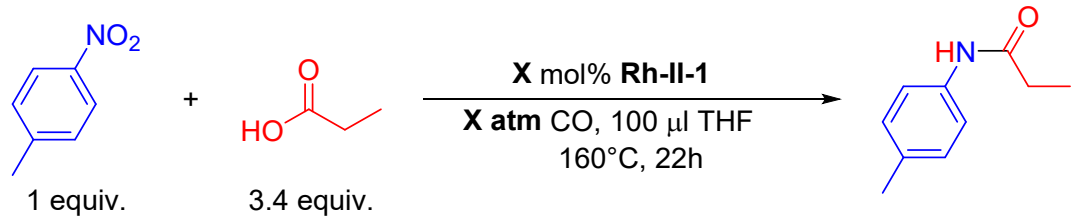
Table S11. Optimization of the Reaction with Benzoic Acid (Rh-I-2)



Entry	Reaction Conditions	Yield, % [a]
1 [b]	**standard**	40
2 [b]	**180°C, 30 atm**	4

[a] Yields were determined by ^{1}H NMR with internal standard. Data from one experiment.

Table S12. Optimization on Rh-II-1



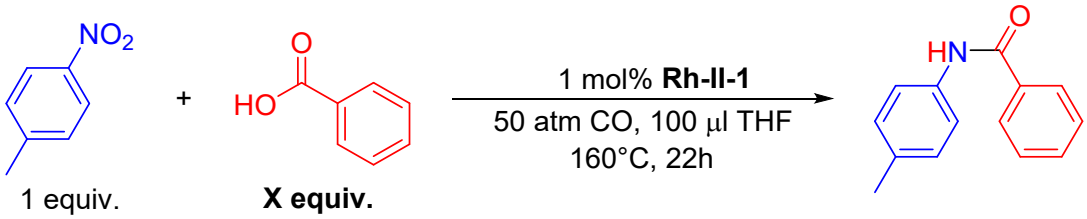
1 equiv. 3.4 equiv.

Entry	Rh-II-1 loading, mol%	Pressure, atm	Yield, % [a]
1	**1**	**50**	99
2		**10**	89 —95
3	**0.5**	**50**	88 — 99[b]
4		**40**	90 — 99
5		**30**	97 — 98
6		**20**	78 — 98
7		**10**	44 — 46
8	**0.2**	**50**	92 —93

[a] Yields were determined by ^{1}H NMR. Data from two experiments.

[b] Data from more than 10 experiments.

Table S13. Optimization of the Reaction with Benzoic Acid (Rh-II-1)



1 equiv. **X equiv.**

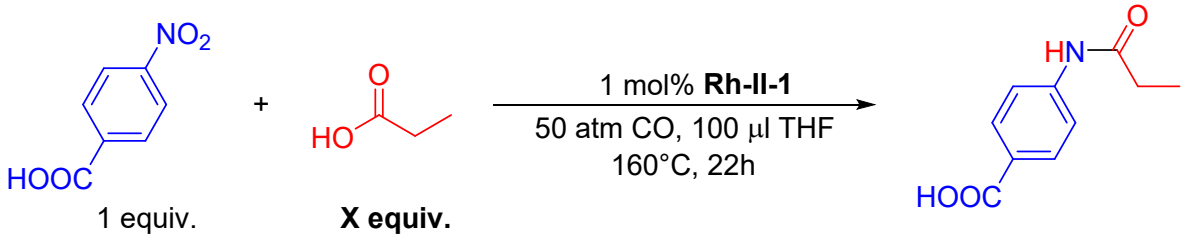
Entry	Excess of PhCOOH, equiv.	Reaction Conditions	Yield, % [a]
1	**1**	**standard**	21 (28% conversion) [b]
2	**3.4**		45 – 50
3		**48h**	40 – 91 [c]
4	**10**		no conversion
5		**300 µl THF**	traces

[a] Yields were determined by ^{1}H NMR. Unless otherwise stated, conversion equals yield. Data from two experiments.

[b] Data from one experiment.

[c] Data from 8 experiments.

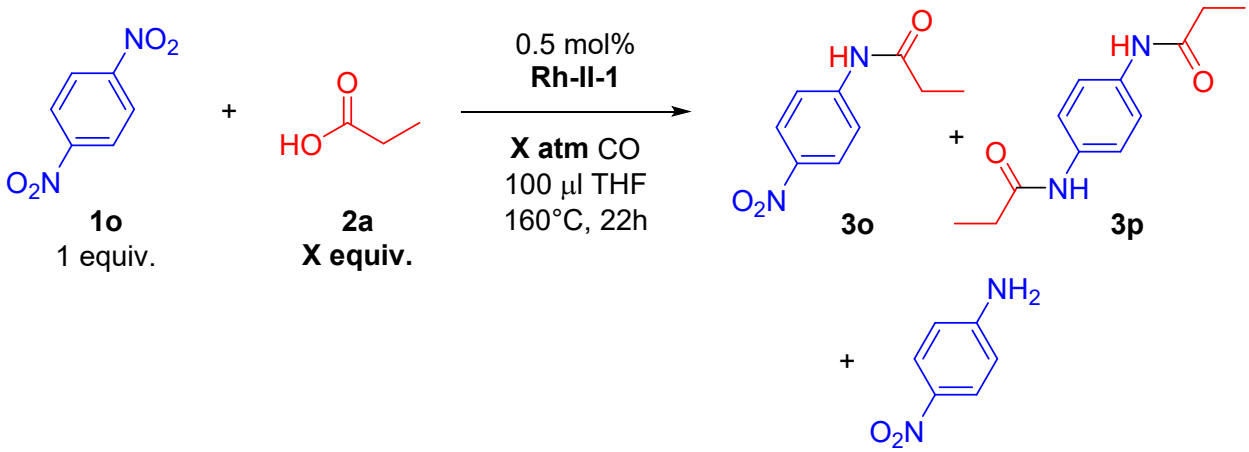
Table S14. Optimization of the Reaction with *p*-Nitrobenzoic Acid



Entry	Excess of EtCOOH, equiv.	Temperature, °C	Yield, % [a]
1	**3.4**	**160**	traces
2		**180**	55
3	**10**	**160**	80
4		**180**	37

[a] Yields were determined by ^{1}H NMR. Data from one experiment.

Table S15. Optimization of the Reaction with *p*-dinitrobenzene

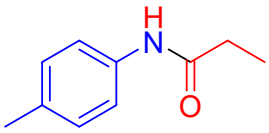


Entry	CO pressure, atm	Excess of EtCOOH, equiv.	Yield of 3o : 3p : 4-nitroaniline, % [a]
1	**30**	**3.4**	58 – 71 : 1 – 6 : 22
2	**50**	**1.5**	66 – 72 : 3 : 16 – 18
3		**3.4**	67 : 2 – 7 : 23 – 24
4		**10**	0 : 99 : 0

[a] Yields were determined by ^{1}H NMR. Data from two experiments.

Reductive Amidation of Aromatic Nitro Compounds

N-(*p*-tolyl)propionamide **(3a)**

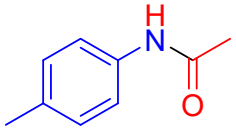


Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (89% yield). The residue was purified using preparative thin layer chromatography in binary system (0.51 in 2:1 Hexane:EtOAc) to afford 36 mg (75%) of the product as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.45 (br.s, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.36 (q, J = 7.7 Hz, 2H), 2.30 (s, 3H), 1.22 (t, J = 7.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 135.6, 133.8, 129.5, 120.1, 30.7, 20.9, 9.9.
NMR spectra are in agreement with the literature data.[14]

Scale-up experiment: rhodium acetate ($Rh_2(OAc)_4$, 16.1 mg, 0.5 mol %, 36.5 μmol), *p*-nitrotoluene (1.0 g, 100 mol %, 7.29 mmol), stirring bar, 2.5 mL of THF and propionic acid (1.85 mL, 340 mol %, 24.8 mmol) were placed into a steel autoclave (100 ml). The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was then heated up to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was diluted with DCM and an aliquot was taken for NMR analysis (87% yield). Then the mixture was filtered through silica gel and the solvents were removed on a rotary evaporator. Using vacuum sublimation, *N*-(*p*-tolyl)propionamide was isolated from the residue in 84% yield (1.0 g) as a white solid.

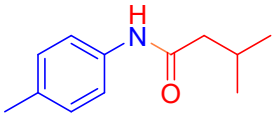
N-(*p*-tolyl)acetamide **(3b)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), acetic acid (57 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (99% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.45 in 5:1 Hexane:EtOAc) to afford 34 mg (78%) of the product as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.47 (br.s, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 2.30 (s, 3H), 2.14 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 135.5, 134.0, 129.5, 120.3, 24.5, 21.0.
NMR spectra are in agreement with the literature data.[15]

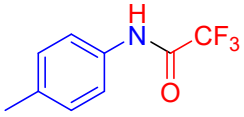
3-methyl-*N*-(*p*-tolyl)butanamide **(3c)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p* -nitrotoluene (40 mg, 100 mol %, 0.29 mmol), isovaleric acid (109 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22 h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (77% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.30 in 5:1 Hexane:EtOAc) to afford 36 mg (64%) of the product as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d overlapped with br.s, J = 8.0 Hz, 3H), 7.10 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H), 2.26 – 2.08 (m, 3H), 0.99 (d, J = 5.5 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 135.5, 133.9, 129.5, 120.2, 47.1, 26.4, 22.6, 21.0.
NMR spectra are in agreement with the literature data.[16]

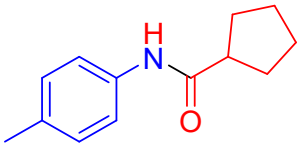
2,2,2-trifluoro-*N*-(*p*-tolyl)acetamide **(3d)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), trifluoroacetic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (99% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.56 in 8:1 Hexane:EtOAc) to afford 34 mg (57%) of the product as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.68 (br.s, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8 (q, J = 37.0 Hz), 136.4, 132.6, 130.0, 120.6, 117.1 (q, J = 288.7 Hz), 21.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -75.72.
NMR spectra are in agreement with the literature data.[17]

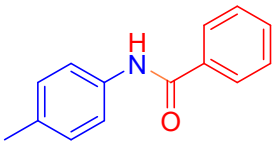
N-(*p*-tolyl)cyclopentanecarboxamide **(3e)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), cyclopentanecarboxylic acid (113 mg, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (99% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.44 in 4:1 Hexane:EtOAc) to afford 52 mg (88%) of the product as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.34 – 7.23 (br.s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 2.66 (p, J = 8.0 Hz, 1H), 2.30 (s, 3H), 2.00 – 1.49 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 135.8, 133.7, 129.5, 119.9, 46.9, 30.7, 26.1, 21.0.
NMR spectra are in agreement with the literature data.[18]

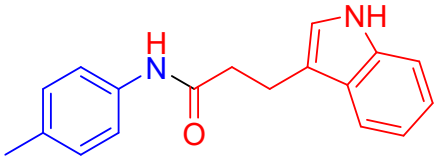
N-(*p*-tolyl)benzamide **(3f)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), benzoic acid (122 mg, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 48h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (72% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.29 in 5:1 Hexane:EtOAc) to afford 34 mg (55%) of the product as white solid (m.p. 159 – 160°C; lit. 156°C[19]).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.83 (br.s, 1H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.57 – 7.49 (m, 3H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 135.5, 135.2, 134.4, 131.9, 129.7, 128.9, 127.1, 120.5, 21.0.
NMR spectra are in agreement with the literature data.[19]

3-(1*H*-indol-3-yl)-*N*-(*p*-tolyl)propanamide **(3g)**

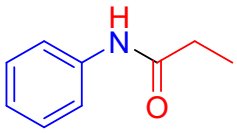


Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), 3-(1*H*-indol-3-yl)propanoic acid (187 mg, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm of CO. The autoclave was placed into an oil bath preheated to 160°C. After 22h, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (99% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.47 in 9:1 DCM:EtOAc) to afford 74 mg (91%) of the product as yellowish solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 7.92 (br.s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.30 – 6.91 (m, 8H), 3.20 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 136.5, 135.3, 134.0, 129.5, 127.2, 122.3, 122.1, 120.1, 119.6, 118.8, 114.9, 111.4, 38.5, 21.4, 21.0.

HRMS (ESI) m/z calculated for $[M+H]^+$ $C_{18}H_{19}N_2O$ 279.1492; found: 279.1493

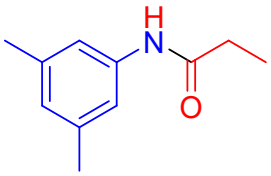
N-phenylpropionamide **(3h)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after nitrobenzene (30 μL, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm of CO. The autoclave was placed into an oil bath preheated to 160°C. After 22h, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR. 99 % yield by NMR. The residue was purified using preparative thin layer chromatography in binary system (Rf 0.43 in 2:1 Hexane:EtOAc) to afford 43 mg (99%) of the product as white solid (m.p. 102 – 104°C; lit. 102.8 – 104.1°C[15]).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.69 (br.s, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.29 (dd appears as t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 2.37 (q, J = 7.5 Hz, 2H), 1.22 (t, J = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 138.2, 129.0, 124.2, 120.1, 30.7, 9.8.
NMR spectra are in agreement with the literature data.[15]

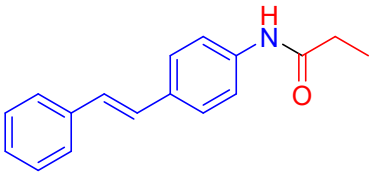
N-(3,5-dimethylphenyl)propionamide **(3i)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after 1,3-dimethyl-5-nitrobenzene (44 mg, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22 h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR. 70% yield by NMR. The residue was purified using preparative thin layer chromatography in binary system (Rf 0.48 in 2:1 Hexane:EtOAc) to afford 33 mg (64%) of the product as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.27 (br.s, 1H), 7.16 (s, 2H), 6.74 (s, 1H), 2.36 (q, J = 7.6 Hz, 2H), 2.27 (s, 6H), 1.23 (t, J = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 138.7, 138.0, 126.0, 117.7, 30.8, 21.4, 9.8.
NMR spectra are in agreement with the literature data.[20]

(E)-*N*-(*p*-styrylphenyl)propionamide **(3j)**

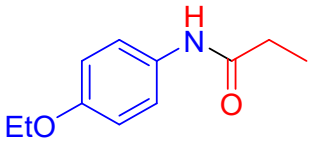


Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *(E)*-1-nitro-4-styrylbenzene (66 mg, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22 h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR. 90% yield by NMR. The residue was purified using preparative thin layer chromatography in binary system (Rf 0.47 in 2:1 Hexane:EtOAc) to afford 60 mg (82%) of the product as white solid (m.p. 218 – 220°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 5H), 7.35 (dd appears as t, J = 7.4 Hz, 2H), 7.29 – 7.15 (m, 3H), 7.08 – 7.03 (m, 2H), 2.41 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 137.5, 133.5, 128.8, 128.1, 128.0, 127.6, 127.3, 126.5, 119.9, 31.0, 9.8. Olefin carbons overlap.

HRMS (ESI) m/z calculated for $[M+H]^+$ $C_{17}H_{18}NO$ 252.1383; found: 252.1387

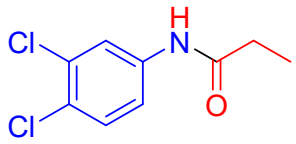
N-(*p*-ethoxyphenyl)propionamide **(3k)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after 1-ethoxy-4-nitrobenzene (49 mg, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22 h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR. 90% yield by NMR. The residue was purified using preparative thin layer chromatography in binary system (0.61 in 2:1 Hexane:EtOAc) to afford 35 mg (62%) of the product as white solid (m.p. 120 – 121°C; lit. 120°C[21]).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.7 Hz, 2H), 7.35 – 7.25 (br.s, 1H), 6.82 (d, J = 8.7 Hz, 2H), 3.99 (q, J = 7.0 Hz, 2H), 2.35 (q, J = 7.6 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 7.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 155.8, 131.1, 121.9, 114.8, 63.8, 30.7, 15.0, 9.9.
NMR spectra are in agreement with the literature data.[22]

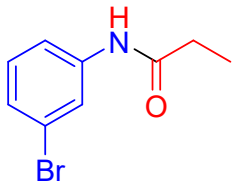
N-(3,4-dichlorophenyl)propionamide **(3l)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after 1,2-dichloro-4-nitrobenzene (56 mg, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (75% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.41 in 2:1 Hexane:EtOAc) to afford 45 mg (71%) of the product as white solid (m.p. 86 – 87°C; lit. 86 – 88°C[23]).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.68 (m, 2H), 7.36 – 7.27 (m, 2H), 2.39 (q, J = 7.5 Hz, 2H), 1.22 (t, J = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 137.6, 132.8, 130.5, 127.4, 121.8, 119.3, 30.7, 9.7.
NMR spectra are in agreement with the literature data.[24]

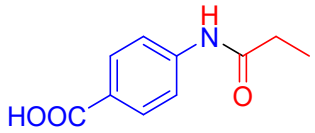
N-(*m*-bromophenyl)propionamide **(3m)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after 1-bromo-3-nitrobenzene (59 mg, 100 mol %, 0.29 mmol), propionic acid (74 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (62% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.48 in 2:1 Hexane:EtOAc) to afford 34 mg (51%) of the product as teal solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 1H), 7.67 – 7.52 (br.s, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.24 – 7.08 (m, 2H), 2.39 (q, J = 7.5 Hz, 2H), 1.22 (t, J = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 139.4, 130.3, 127.2, 123.0, 122.7, 118.5, 30.8, 9.7.
NMR spectra are in agreement with the literature data.[16]

p-propionamidobenzoic acid **(3n)**

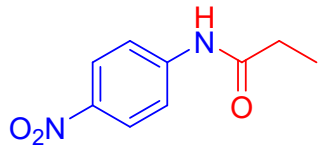


Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 µmol) was placed into a titanium autoclave as an aliquot in 100 µL of THF, after 4-nitrobenzoic acid (49 mg, 100 mol %, 0.29 mmol), propionic acid (218 µL, 1000 mol %, 2.9 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22 h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (80% yield). The residue was purified using preparative flash chromatograph InterChim PuriFlash in binary system (Rf 0.4 in 2:1 Hexane:EtOAc) to afford 41 mg (72%) of the product as white solid.

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.18 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 2.35 (q, J = 7.5 Hz, 2H), 1.08 (t, J = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 167.0, 143.4, 130.4, 124.9, 118.3, 29.7, 9.6.

HRMS (ESI) m/z calculated for $[M+H]^+$ $C_{10}H_{12}NO_3$ 194.0812; found: 194.0812

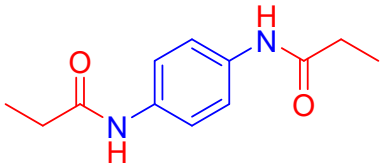
N-(*p*-nitrophenyl)propionamide **(3o)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 µmol) was placed into a titanium autoclave as an aliquot in 100 µL of THF, after *p*-dinitrobenzene (49 mg, 100 mol %, 0.29 mmol), propionic acid (33 µL, 150 mol %, 0.44 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (72% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.5 in 10:1 Hexane:EtOAc) to afford 27 mg (62%) of the product as yellow solid.

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.51 (s, 1H), 8.18 (d, J = 9.3 Hz, 2H), 7.81 (d, J = 9.3 Hz, 2H), 2.38 (q, J = 7.5 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 173.3, 145.7, 142.1, 125.1, 118.7, 29.8, 9.5.
NMR spectra are in agreement with the literature data.[25]

N,N'-(1,4-phenylene)dipropionamide **(3p)**

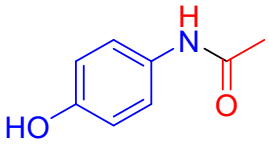


Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-dinitrobenzene (49 mg, 100 mol %, 0.29 mmol), propionic acid (218 μL, 1000 mol %, 2.9 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (99% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.20 in 9:1 DCM:MeOH) to afford 64 mg (99%) of the product as gray solid (m.p. >300°C).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.76 (s, 2H), 7.48 (s, 4H), 2.28 (q, J = 7.6 Hz, 4H), 1.07 (t, J = 7.6 Hz, 6H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 171.6, 134.6, 119.4, 29.4, 9.7.

HRMS (ESI) m/z calculated for $[M+H]^+$ $C_{12}H_{17}N_2O_2$ 221.1285; found: 221.1287

N-(4-hydroxyphenyl)acetamide **(3q)**

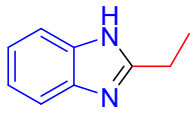


Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 μmol) was placed into a titanium autoclave as an aliquot in 100 μL of THF, after *p*-nitrophenol (40 mg, 100 mol %, 0.29 mmol), acetic acid (57 μL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (83% yield). The residue was purified using preparative flash chromatograph InterChim PuriFlash in DCM – MeOH binary system (gradient 100% DCM to 10% MeOH in DCM for 30 min, Rf 0.5 in 10:1 DCM:MeOH) to afford 36 mg (82%) of the product as white crystals.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 – 9.60 (br.s, 1H), 9.23 – 9.09 (br.s, 1H), 7.34 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.6 Hz, 2H), 1.98 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.7, 153.2, 131.1, 120.9, 115.1, 23.8.

NMR spectra are in agreement with the literature data.[26]

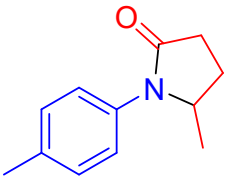
2-ethyl-1*H*-benzo[d]imidazole **(4a)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 µmol) was placed into a titanium autoclave as an aliquot in 100 µL of THF, after 2-nitroaniline (40 mg, 100 mol %, 0.29 mmol), propionic acid (74 µL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22 h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (90% yield). The residue was purified using preparative thin layer chromatography in binary system (Rf 0.28 in 1:2 Hexane:EtOAc) to afford 35 mg (81%) of the product as yellowish solid (m.p. 158 – 160°C; lit. 159 – 160°C[27]).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 – 8.94 (br.s, 1H), 7.68 – 7.40 (m, 2H), 7.32 – 7.10 (m, 2H), 3.00 (q, *J* = 7.7 Hz, 2H), 1.42 (t, *J* = 7.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 138.5, 122.3, 114.7, 22.7, 12.6.
NMR spectra are in agreement with the literature data.[28]

5-methyl-1-(*p*-tolyl)pyrrolidin-2-one **(4b)**



Rhodium acetate ($Rh_2(OAc)_4$, 0.645 mg, 0.5 mol %, 1.5 µmol) was placed into a titanium autoclave as an aliquot in 100 µL of THF, after *p*-nitrotoluene (40 mg, 100 mol %, 0.29 mmol), 4-oxopentanoic acid (101 µL, 340 mol %, 0.99 mmol) were added. The autoclave was sealed, flushed three times with 10 atm of CO, then charged with 50 atm. The autoclave was placed into an oil bath preheated to 160°C. After 22h of reaction time, the autoclave was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2 x 1 mL), solvents were removed on a rotary evaporator, and the residue was analyzed by NMR (99% yield). The residue was purified using preparative thin layer chromatography in binary system (0.39 in 1:1 Hexane:EtOAc) to afford 41 mg (75%) of the product as yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 4H), 4.24 (dt appears as h, *J* = 6.3 Hz, 1H), 2.72 – 2.44 (m, 2H), 2.44 – 2.26 (m, 1H), 2.33 (s, 3H), 1.82 – 1.63 (m, 1H), 1.18 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 135.7, 134.9, 129.6, 124.3, 55.8, 31.3, 26.8, 21.0, 20.2.
NMR spectra are in agreement with the literature data.[29]

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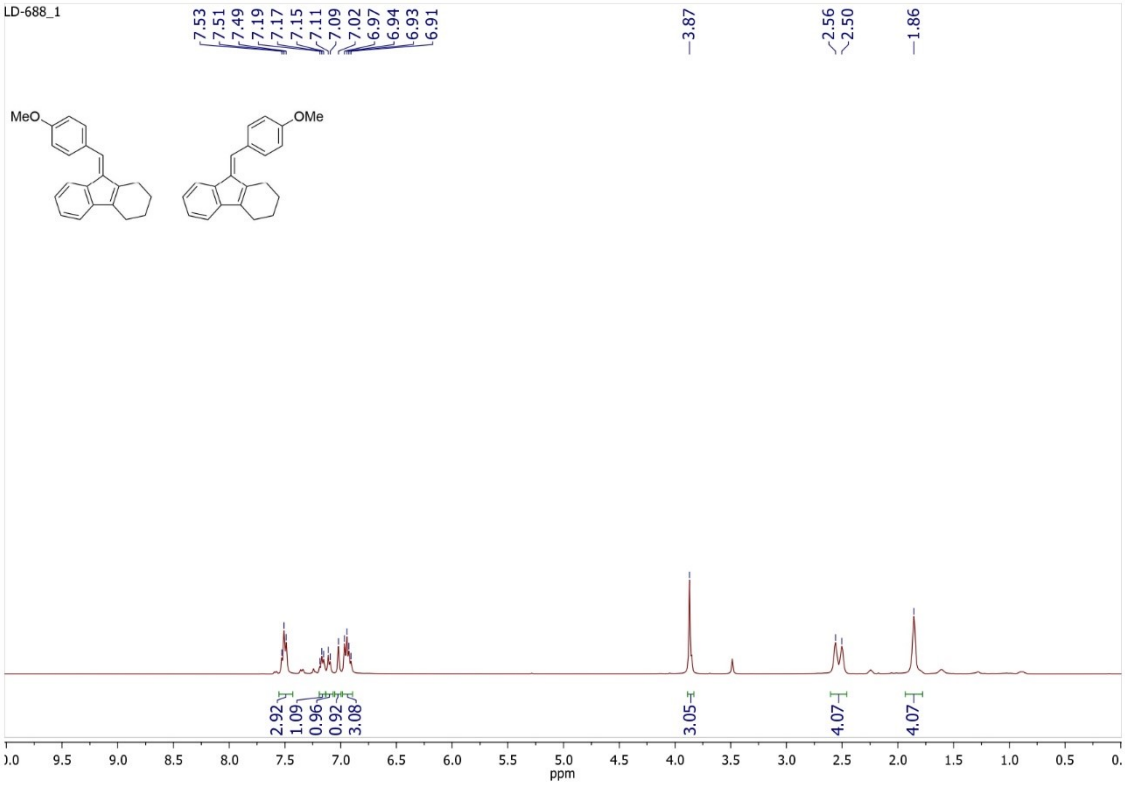
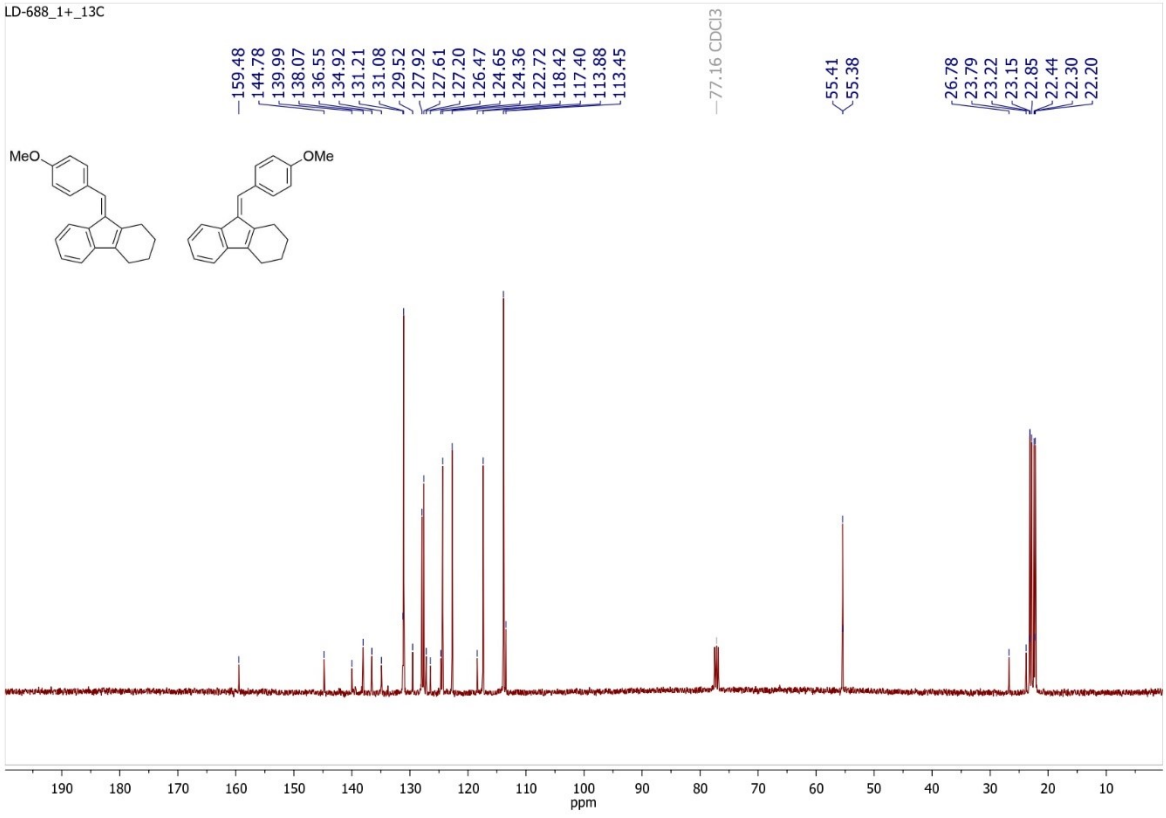
NMR spectra

NMR Spectra of Rhodium Complexes

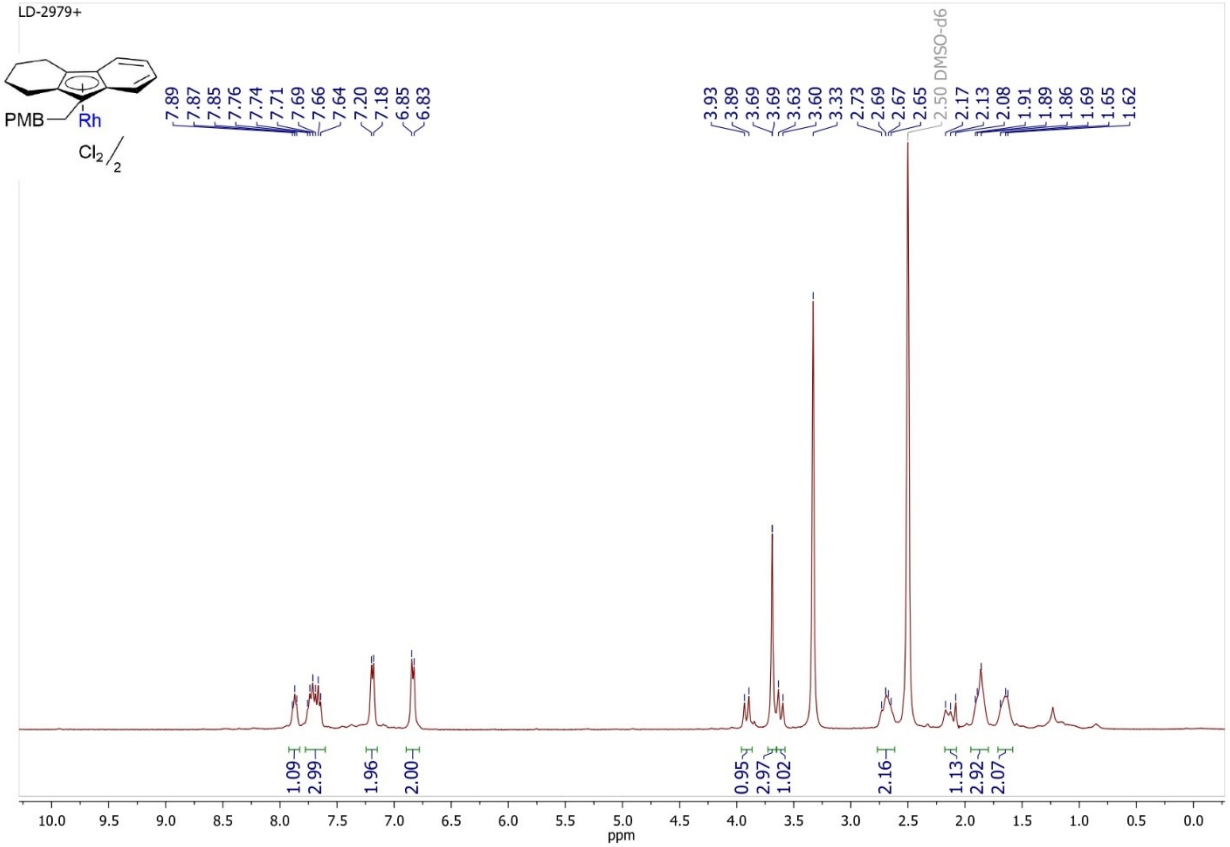
^{1}H NMR (400 MHz) spectrum of ***L1 and L1'*** in $CDCl_3$



$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of ***L1 and L1'*** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of ***Rh-III-10*** in DMSO-d_6



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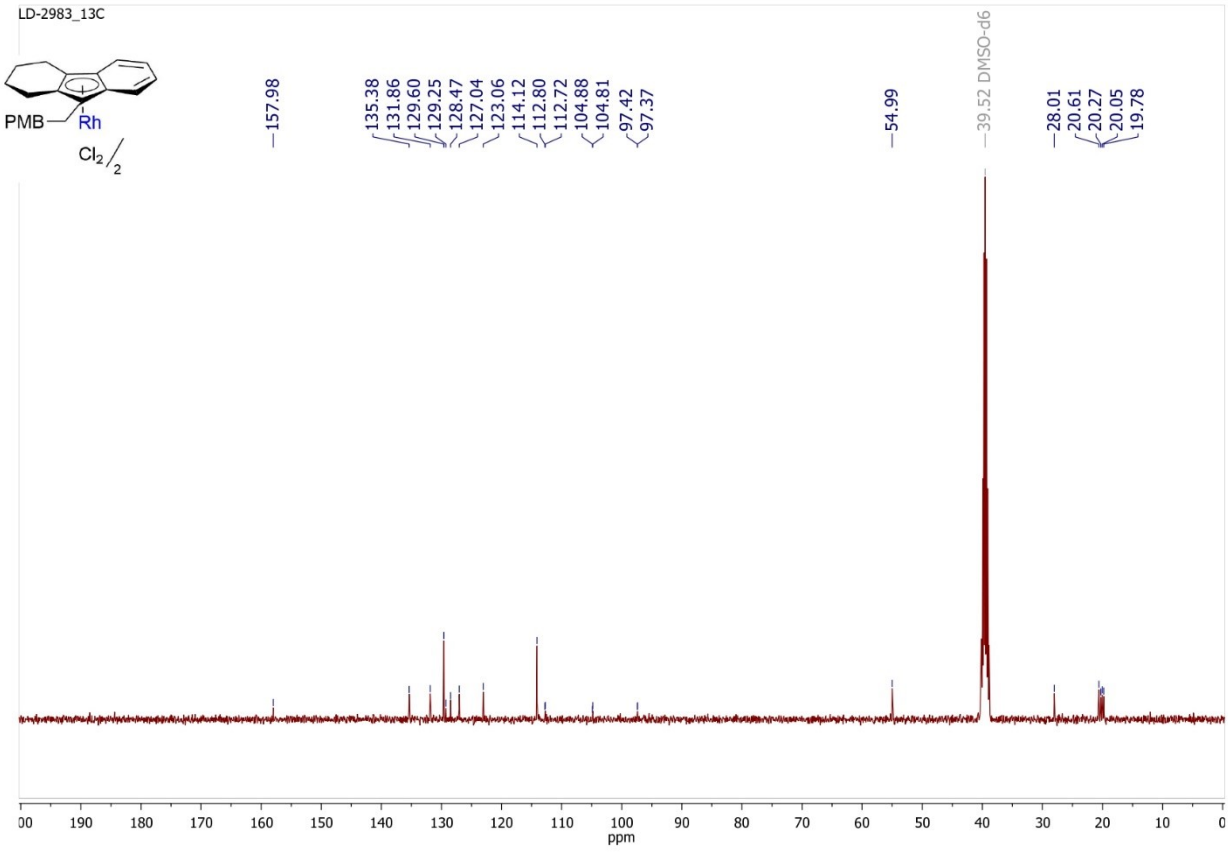

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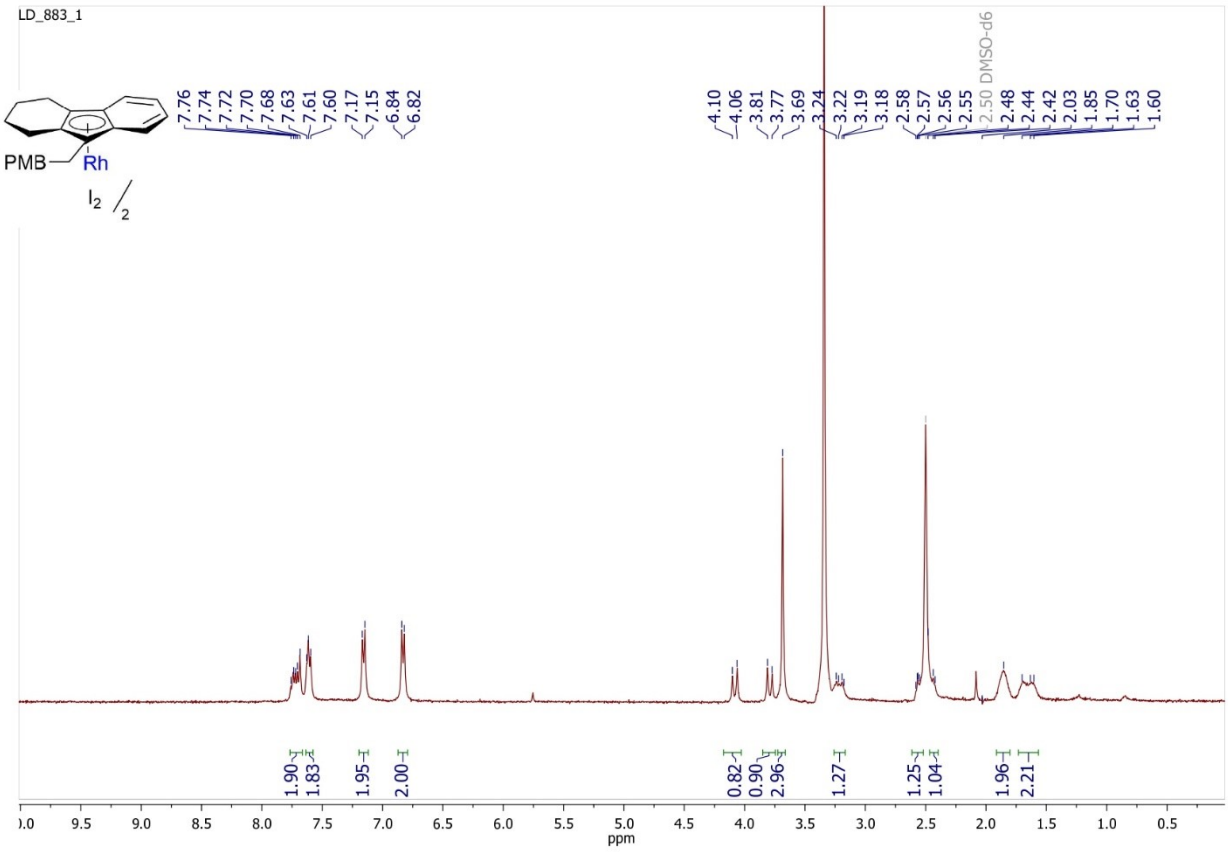

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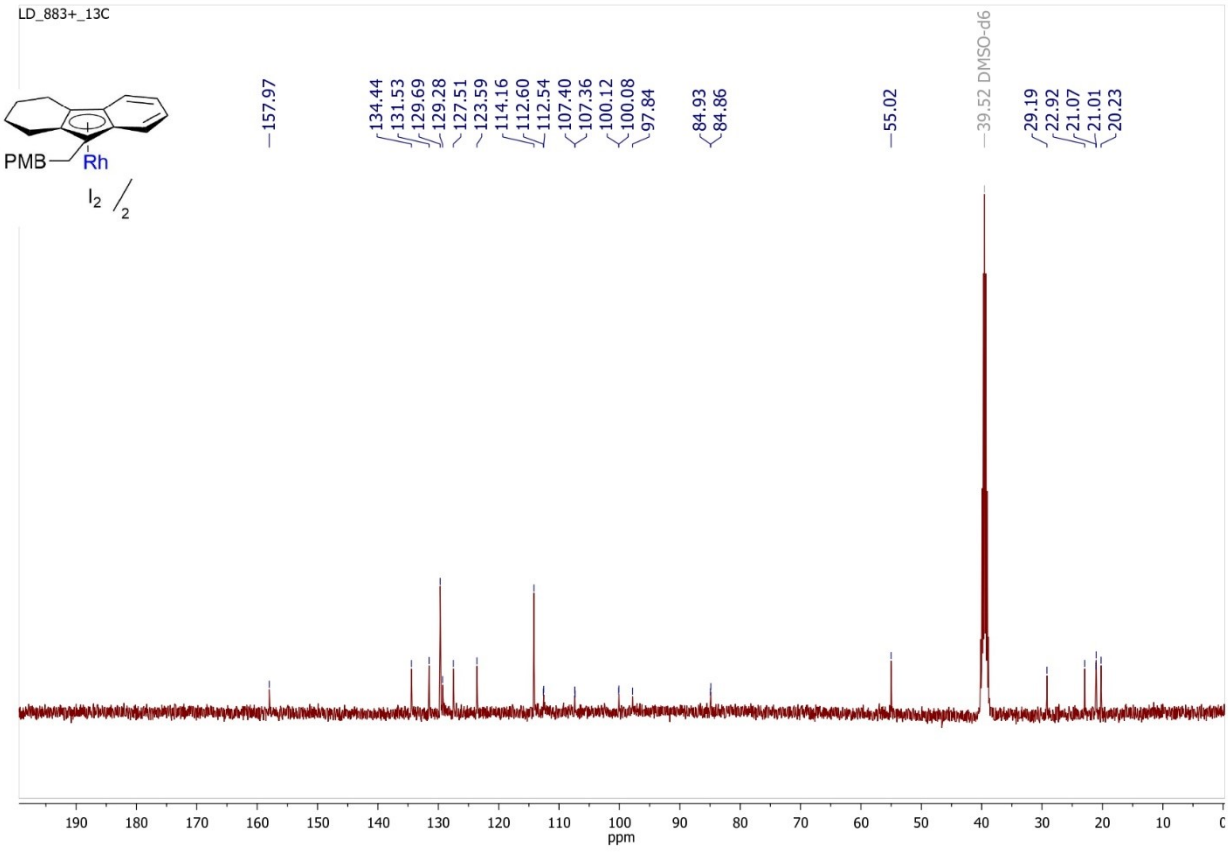

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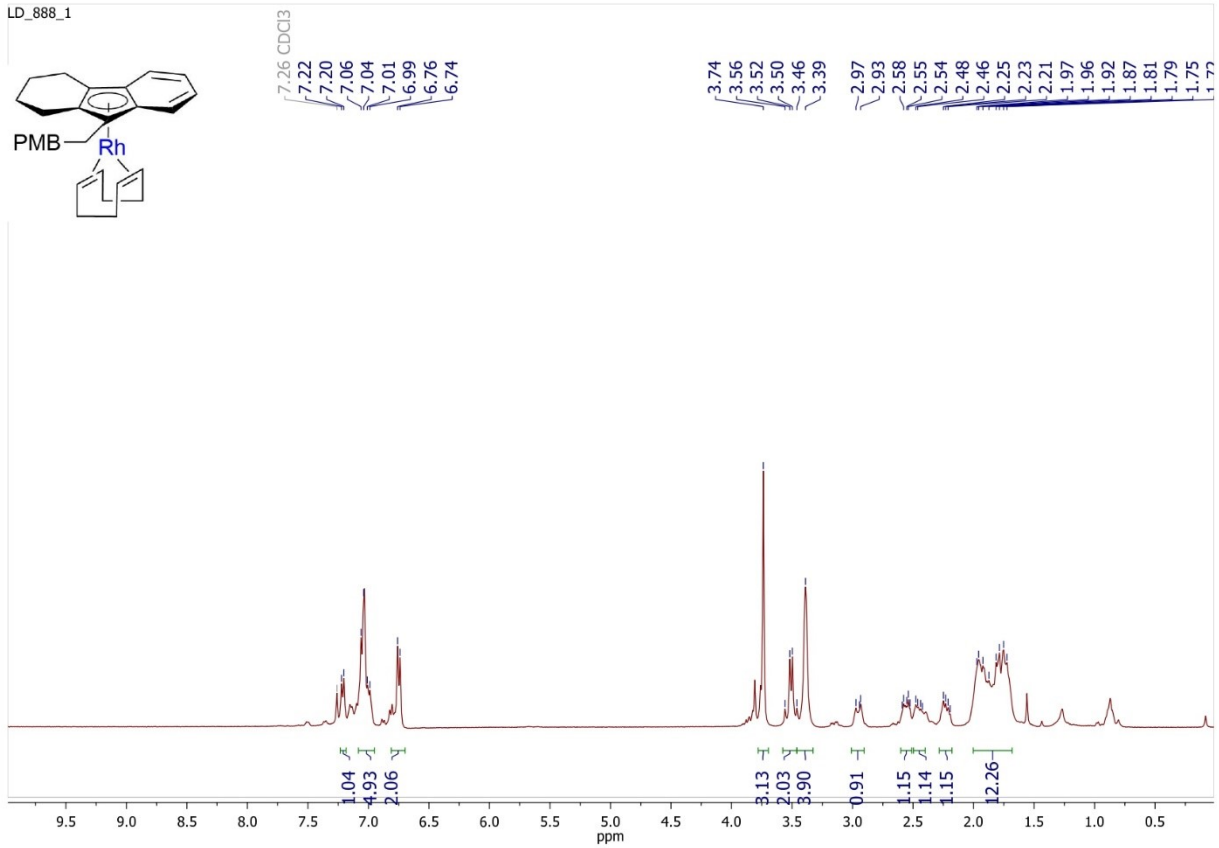

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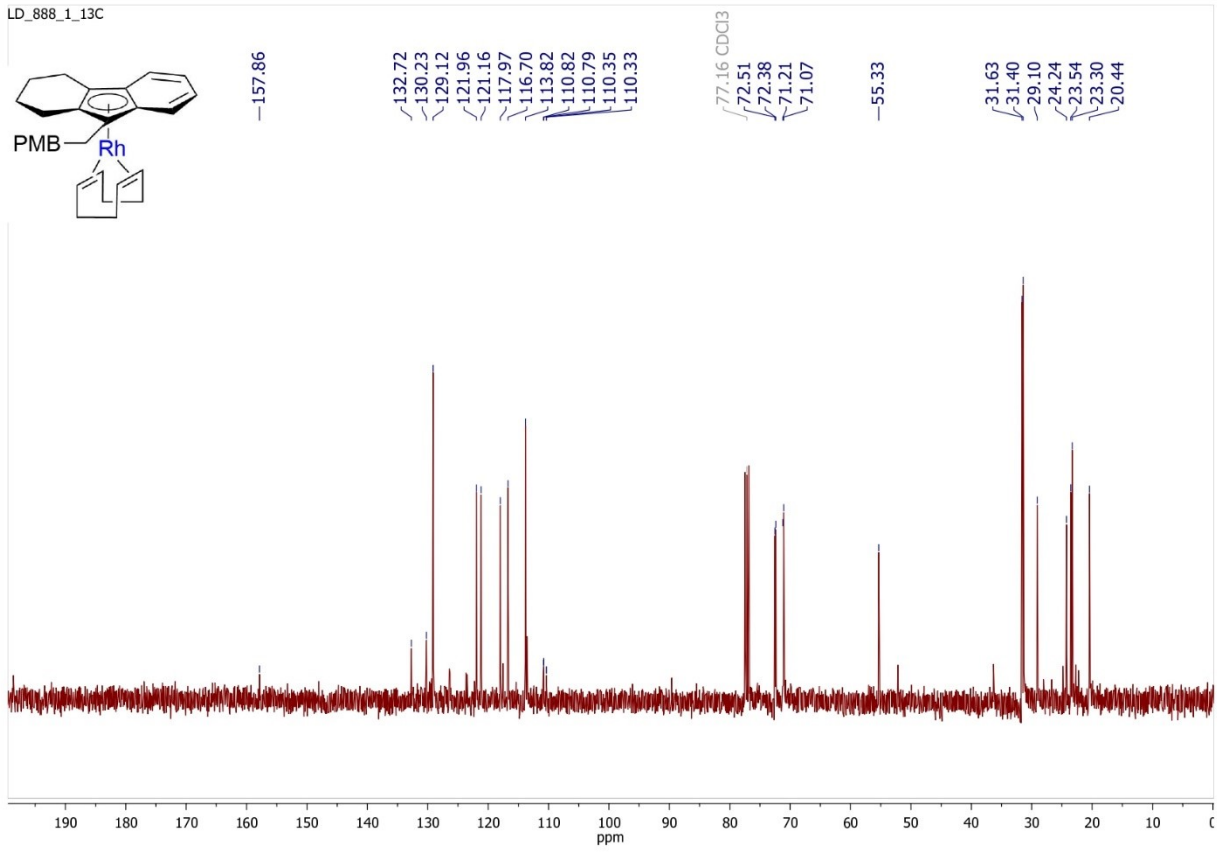
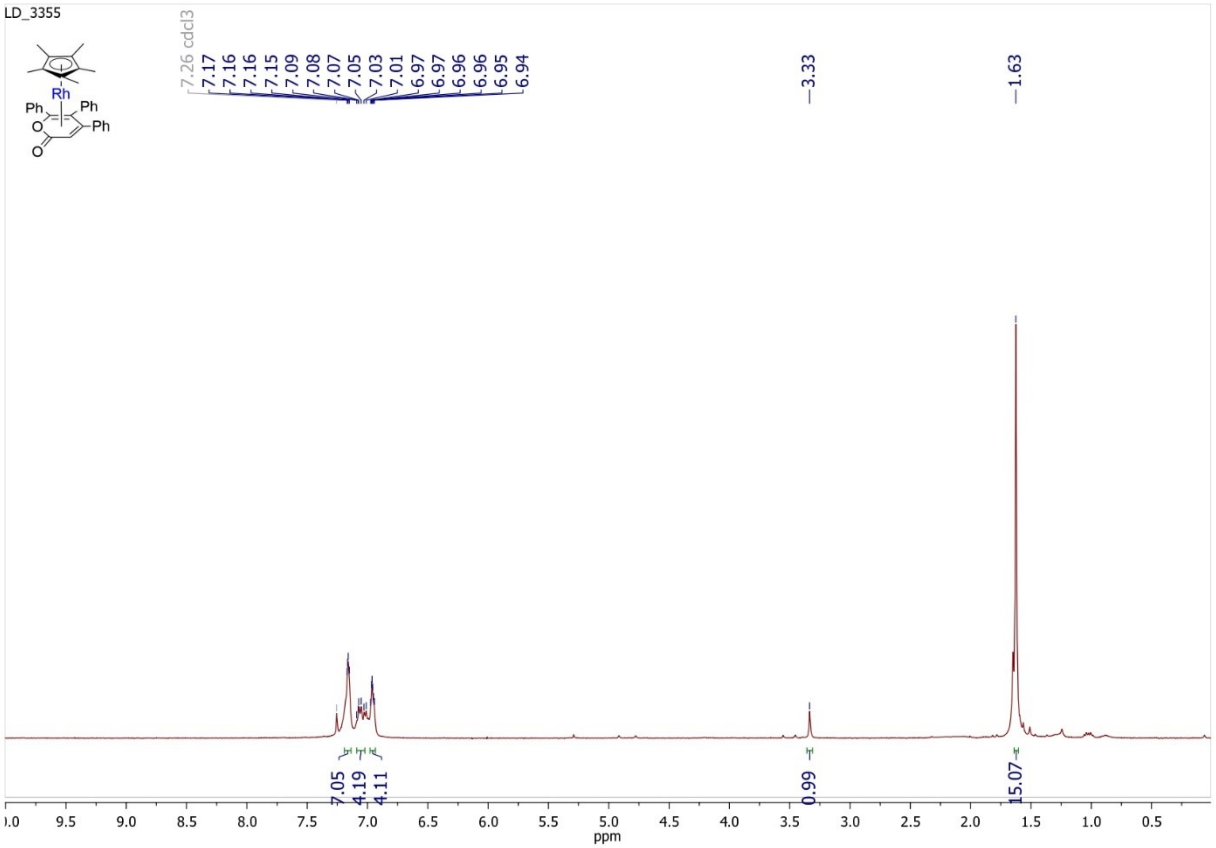
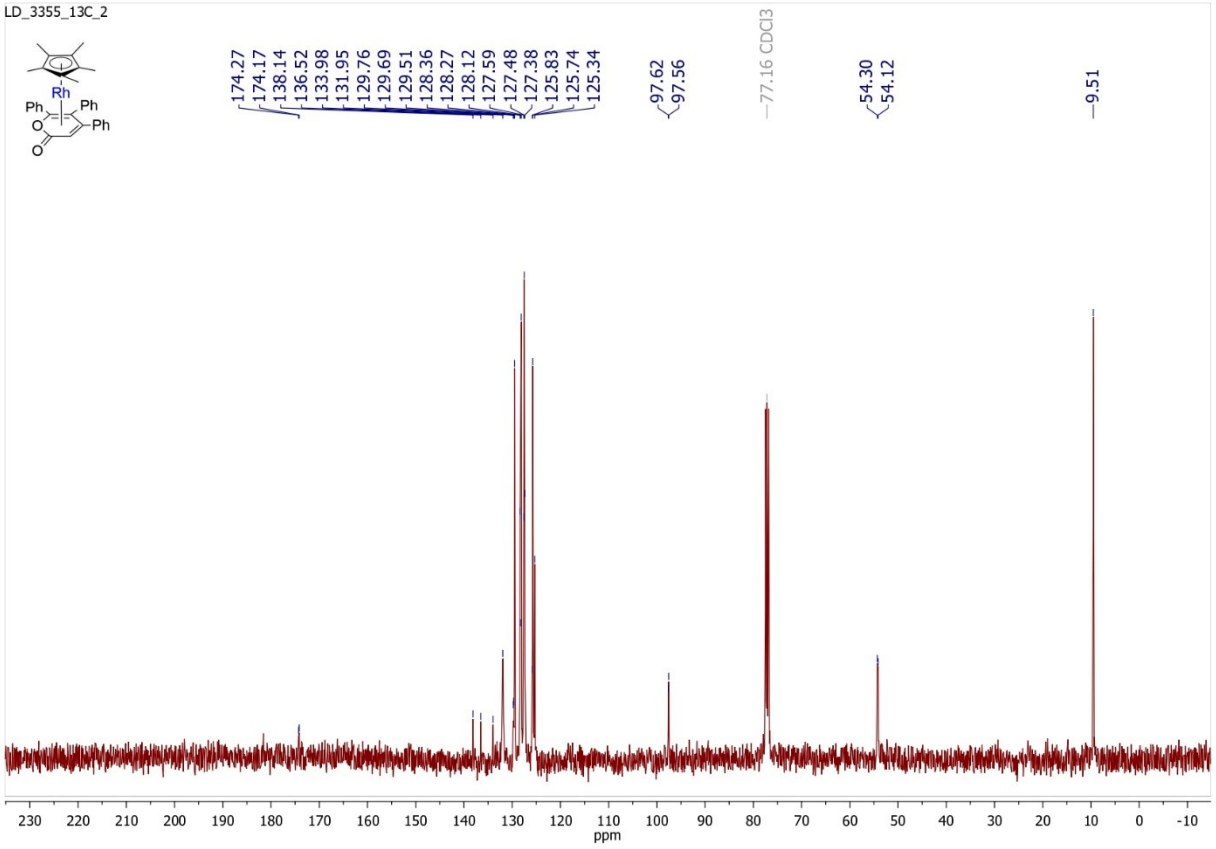


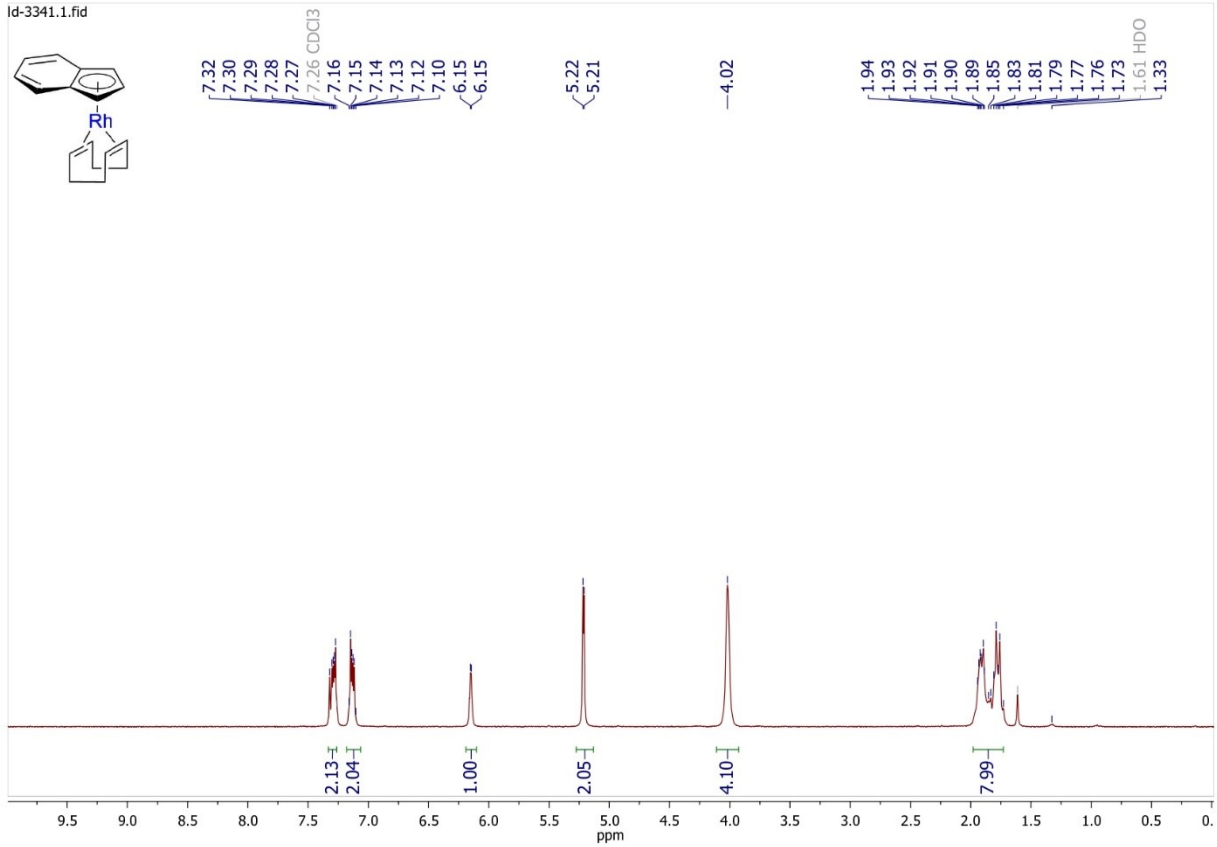
^{1}H NMR (400 MHz) spectrum of ***Rh-I-4*** in $CDCl_3$



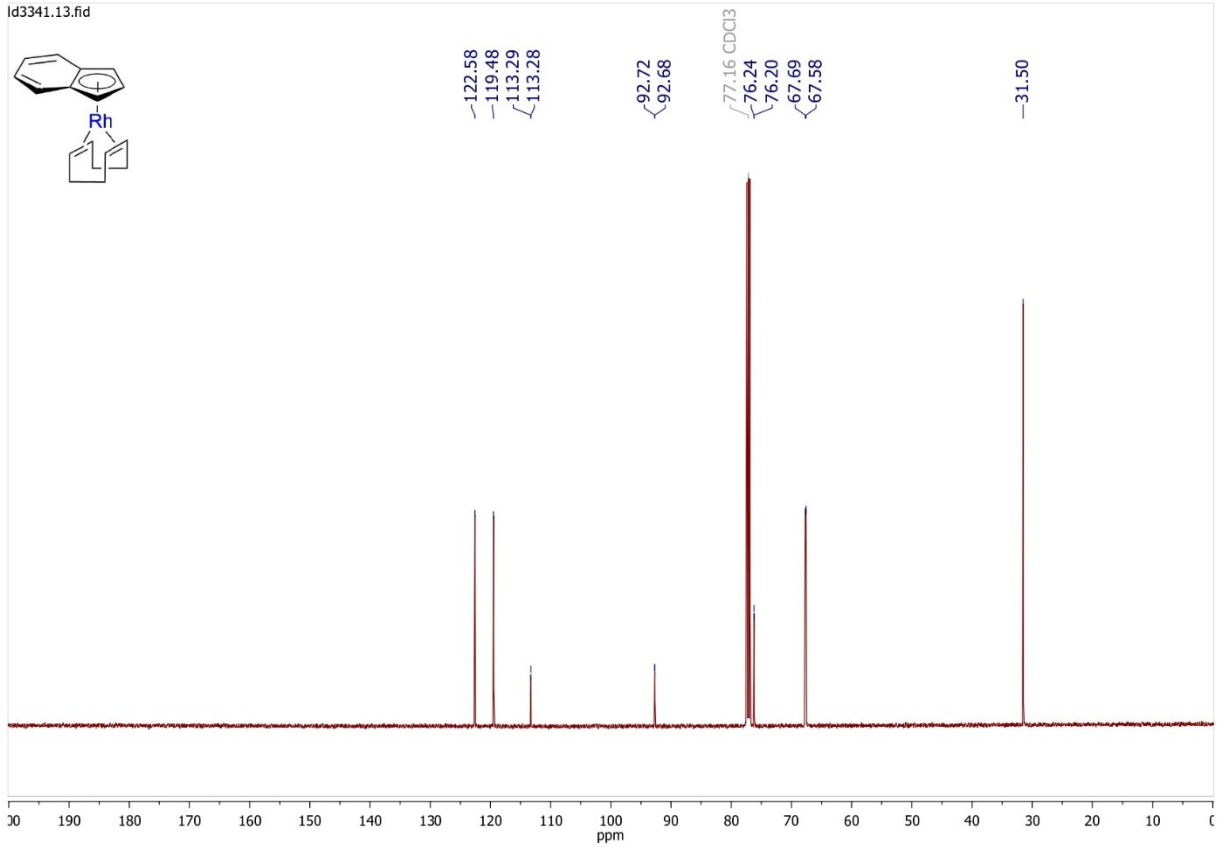
^{13}C{^{1}H} NMR (101 MHz) spectrum of ***Rh-I-4*** in $CDCl_3$



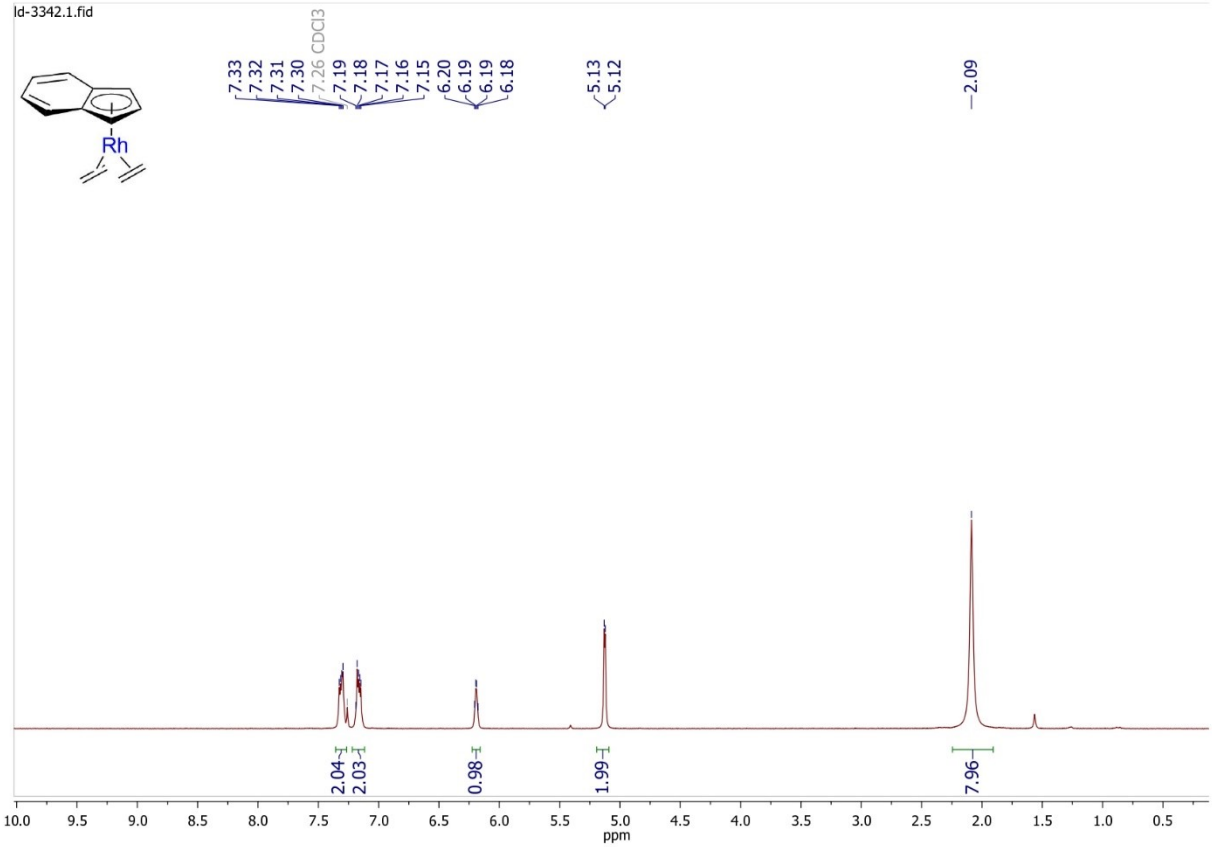
^{1}H NMR (300 MHz) spectrum of ***Rh-I-2*** in $CDCl_3$



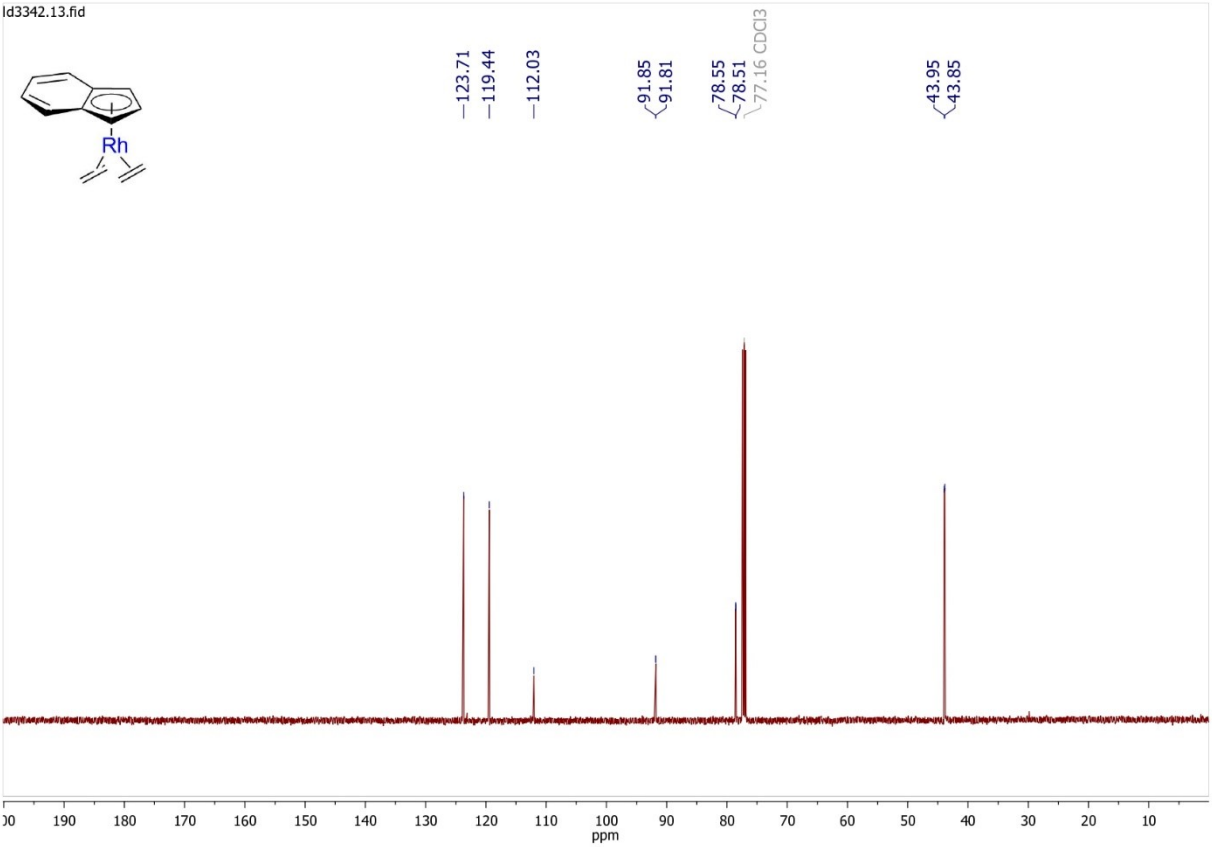
^{13}C{^{1}H} NMR (126 MHz) spectrum of ***Rh-I-2*** in $CDCl_3$



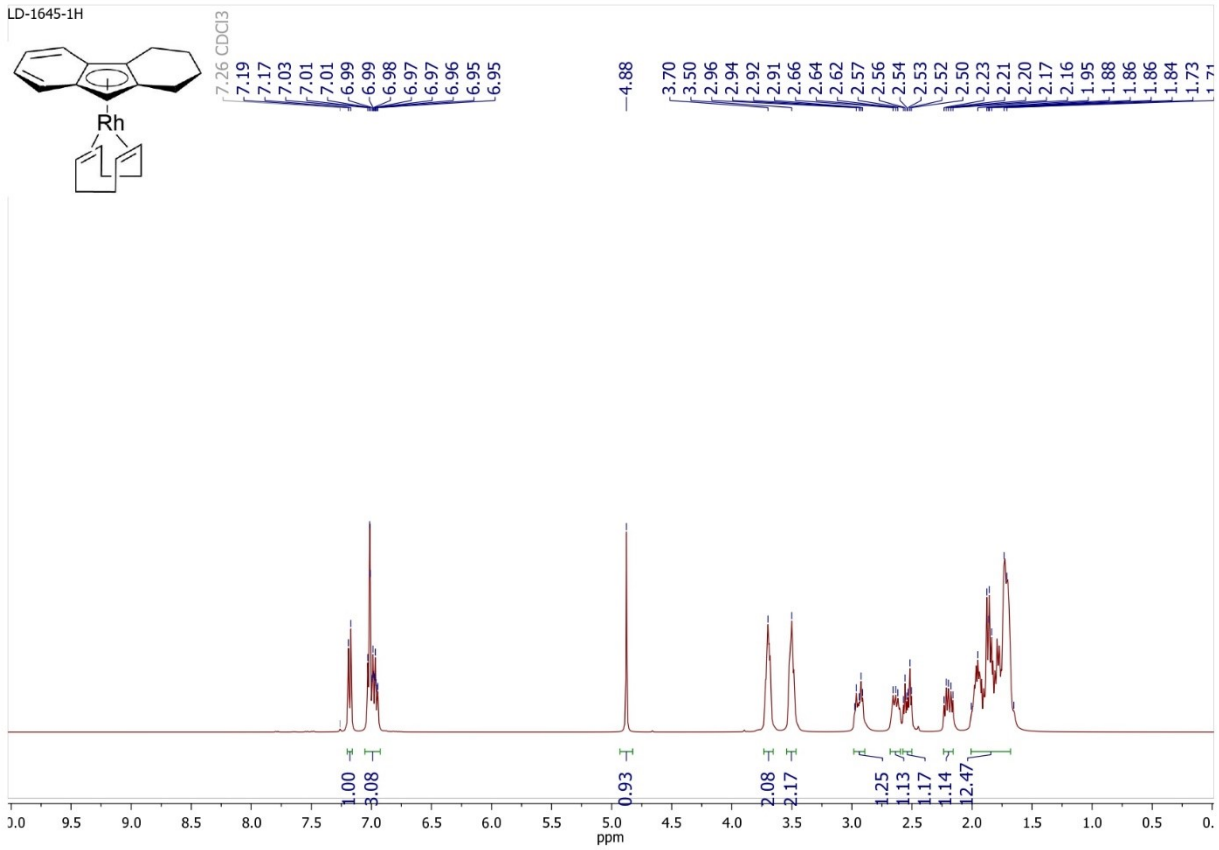
^{1}H NMR (300 MHz) spectrum of ***Rh-I-3*** in $CDCl_3$



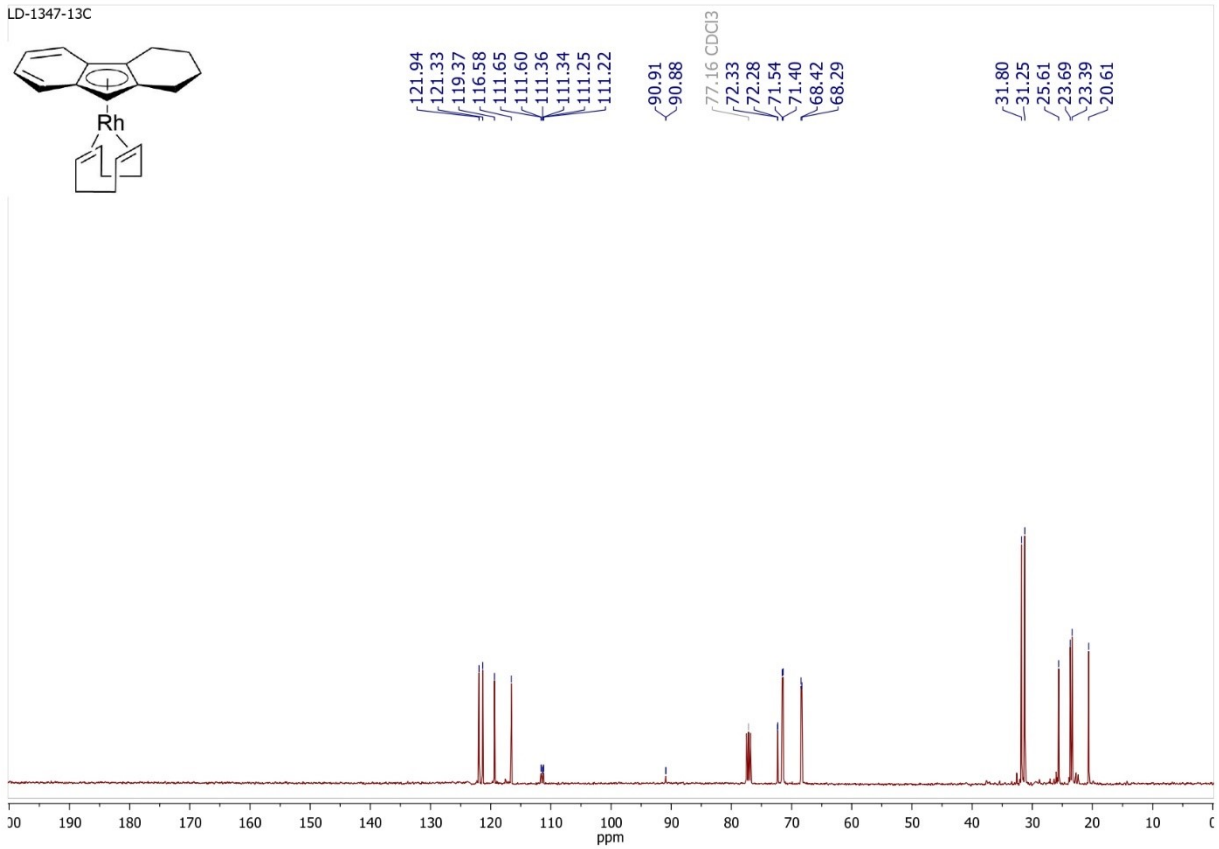
^{13}C{^{1}H} NMR (126 MHz) spectrum of ***Rh-I-3*** in $CDCl_3$



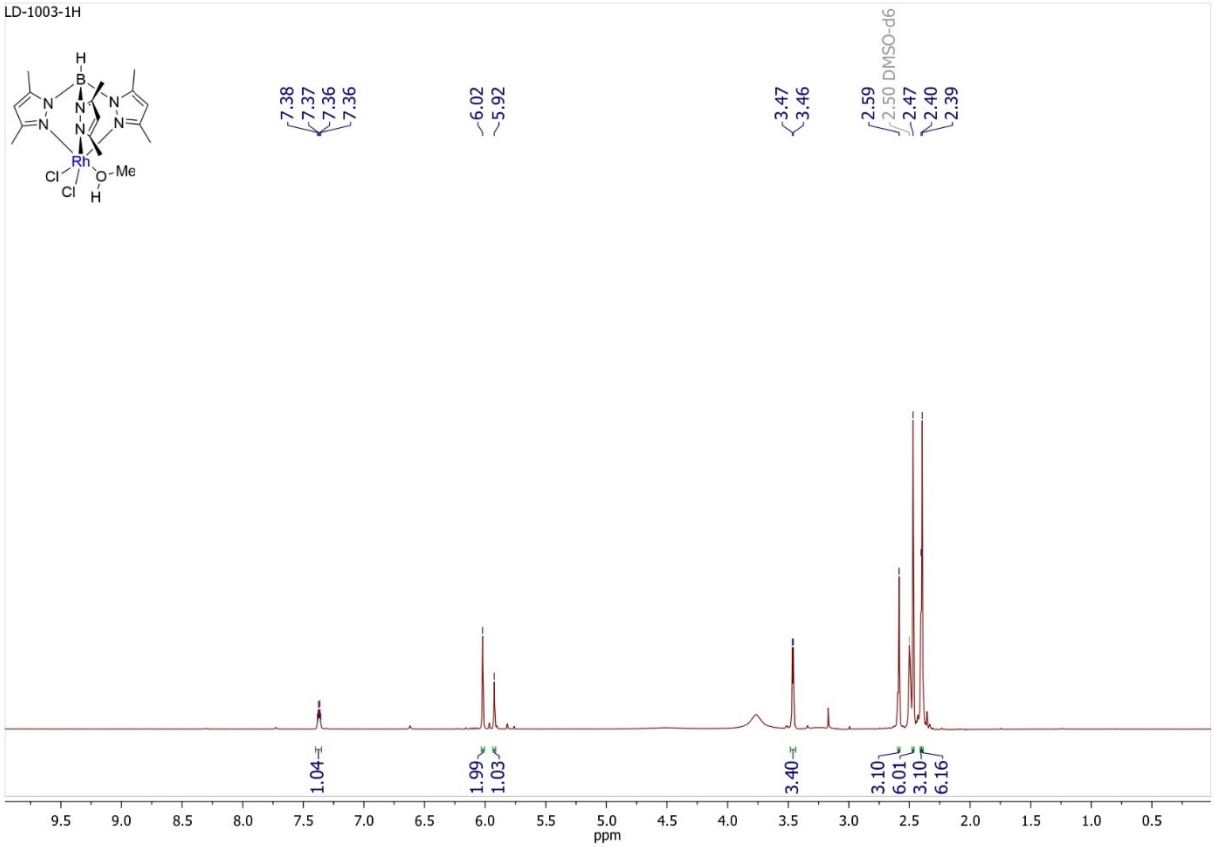
^{1}H NMR (400 MHz) spectrum of ***Rh-I-1*** in $CDCl_3$



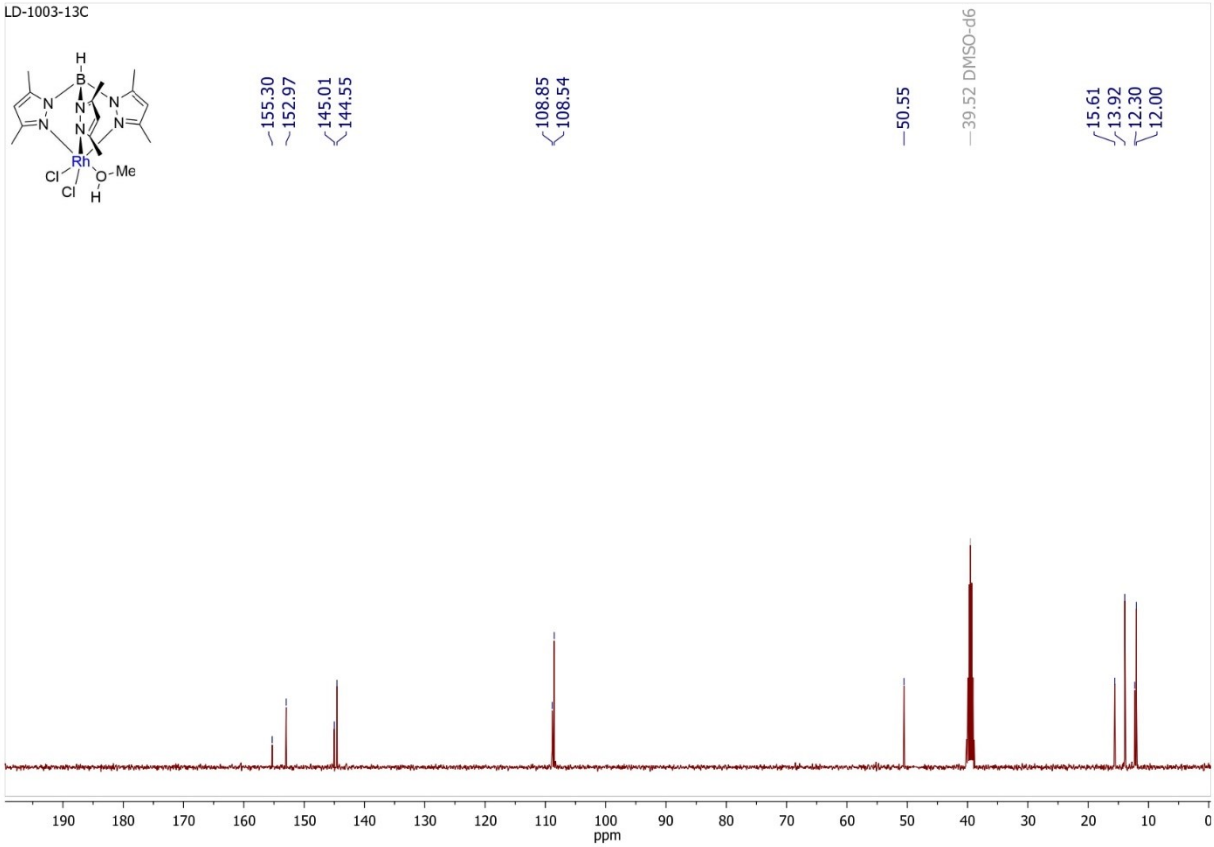
^{13}C{^{1}H} NMR (101 MHz) spectrum of ***Rh-I-1*** in $CDCl_3$



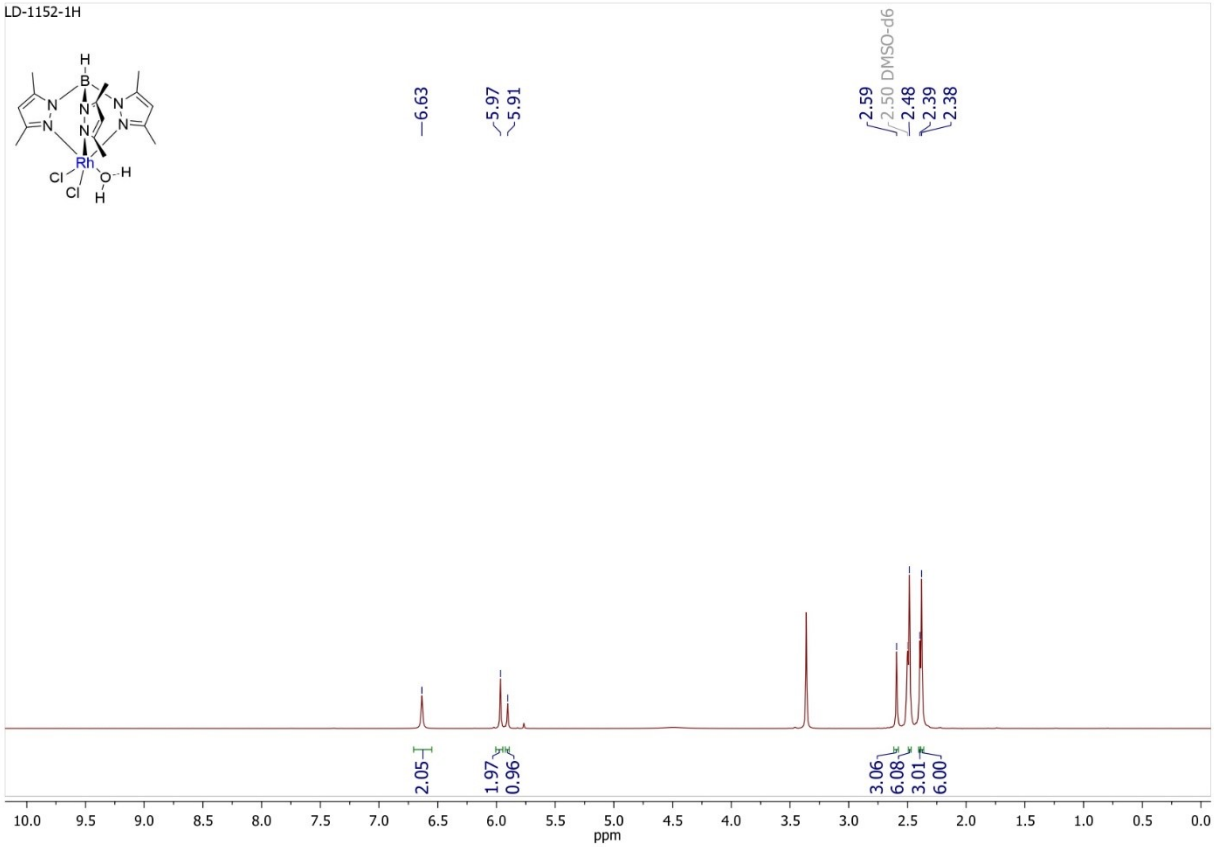
^{1}H NMR (400 MHz) spectrum of ***Rh-III-13*** in DMSO-d_6



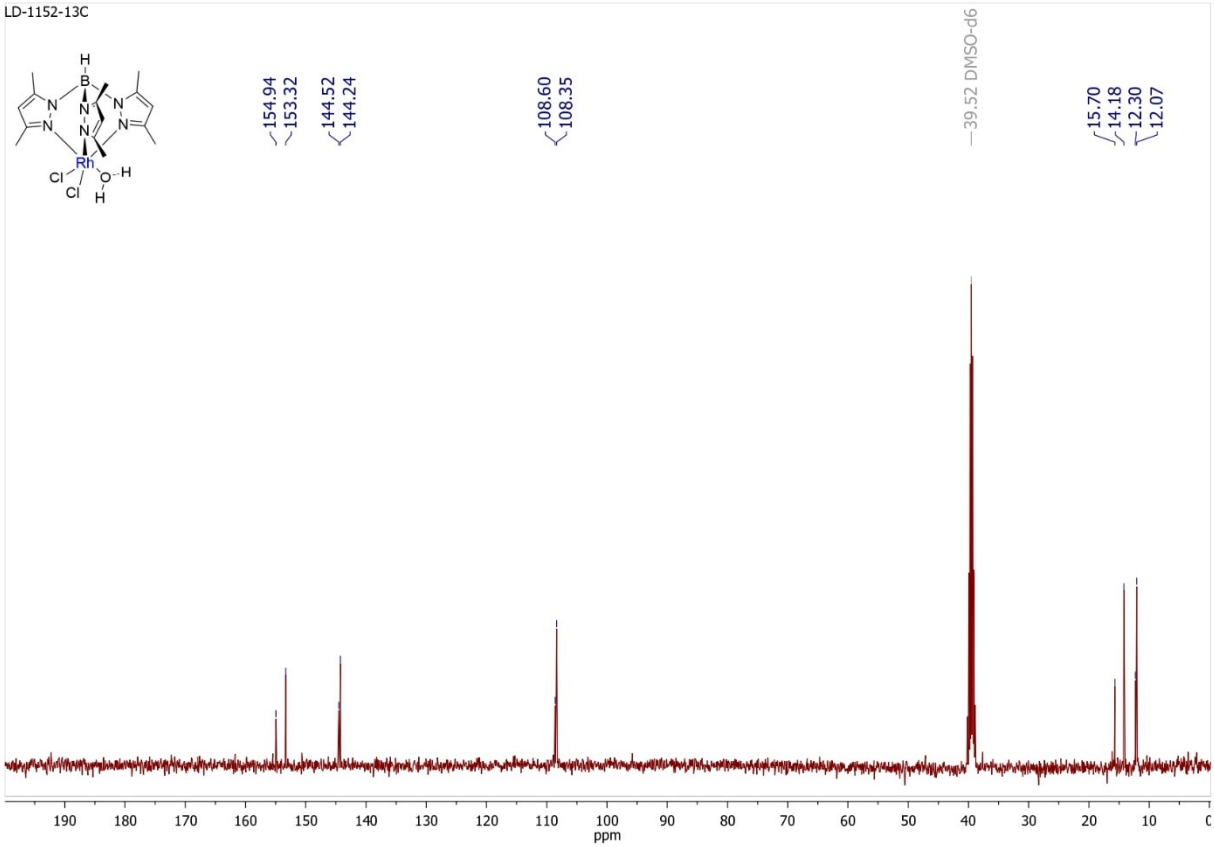
^{13}C{^{1}H} NMR (101 MHz) spectrum of ***Rh-III-14*** in DMSO-d_6



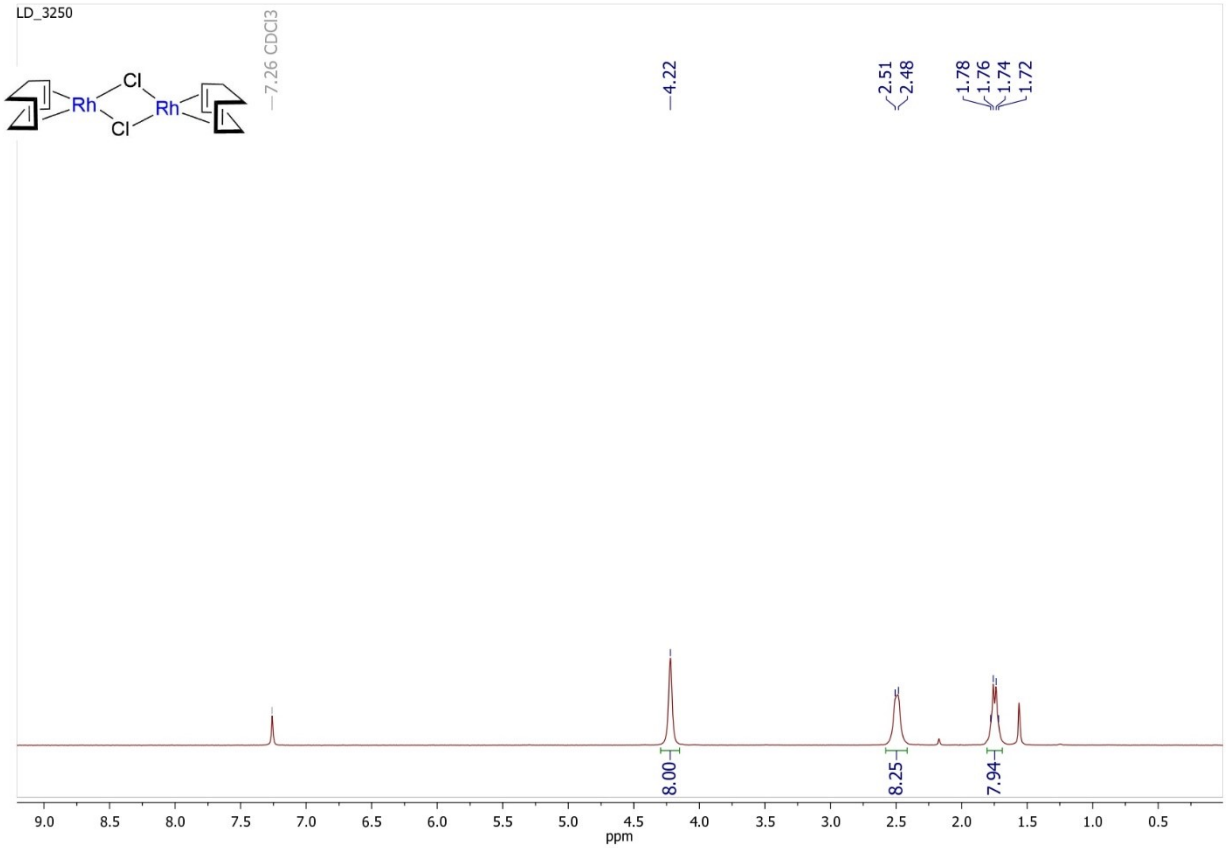
^{1}H NMR (400 MHz) spectrum of ***Rh-III-14*** in DMSO-d_6



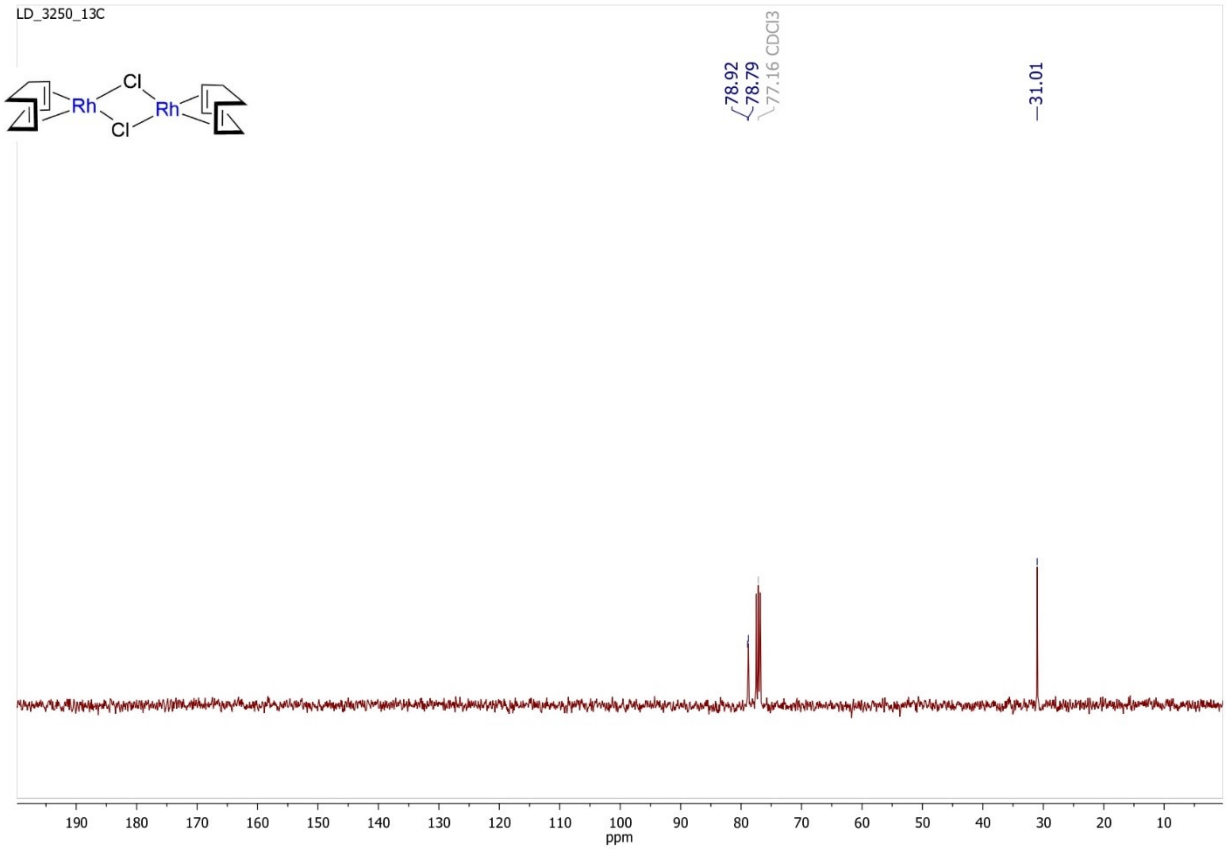
^{13}C{^{1}H} NMR (101 MHz) spectrum of ***Rh-III-14*** in DMSO-d_6



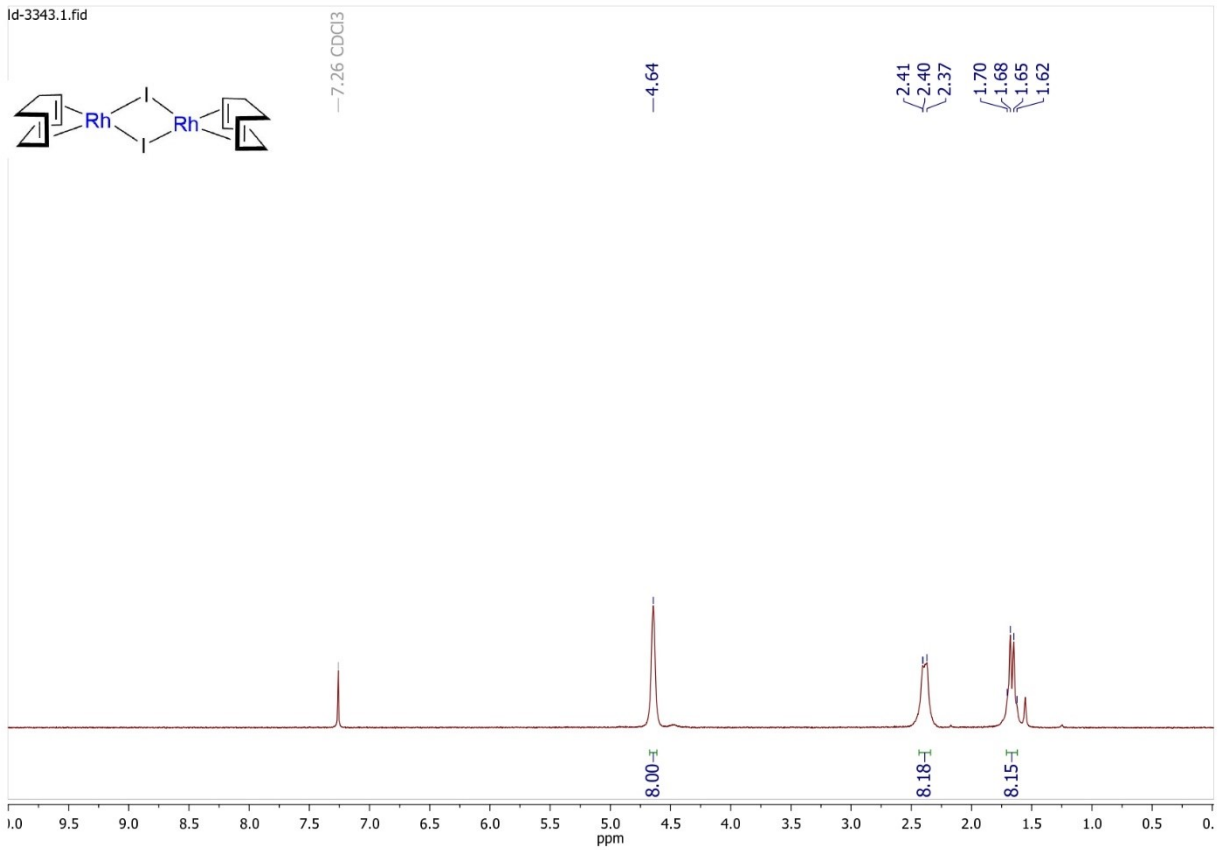
^{1}H NMR (400 MHz) spectrum of ***Rh-I-12*** in $CDCl_3$



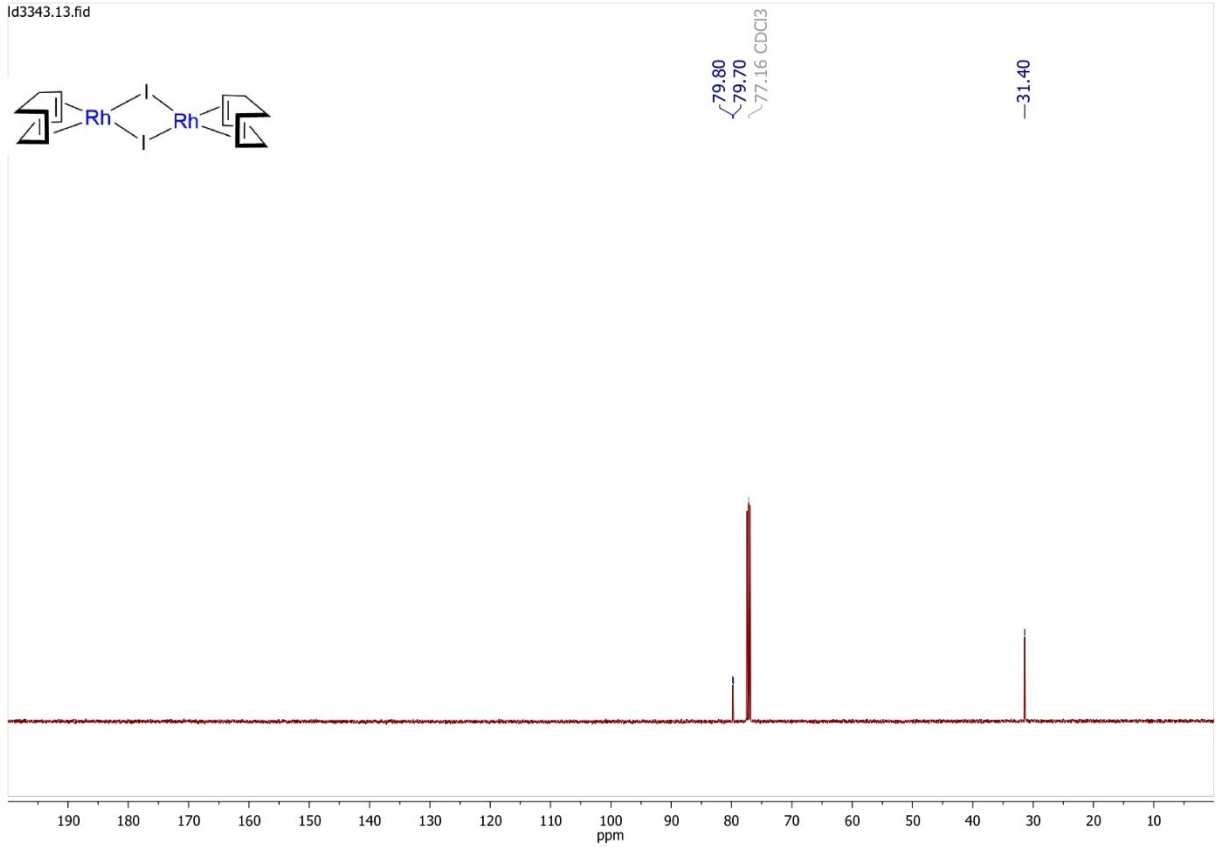
^{13}C{^{1}H} NMR (101 MHz) spectrum of ***Rh-I-12*** in $CDCl_3$



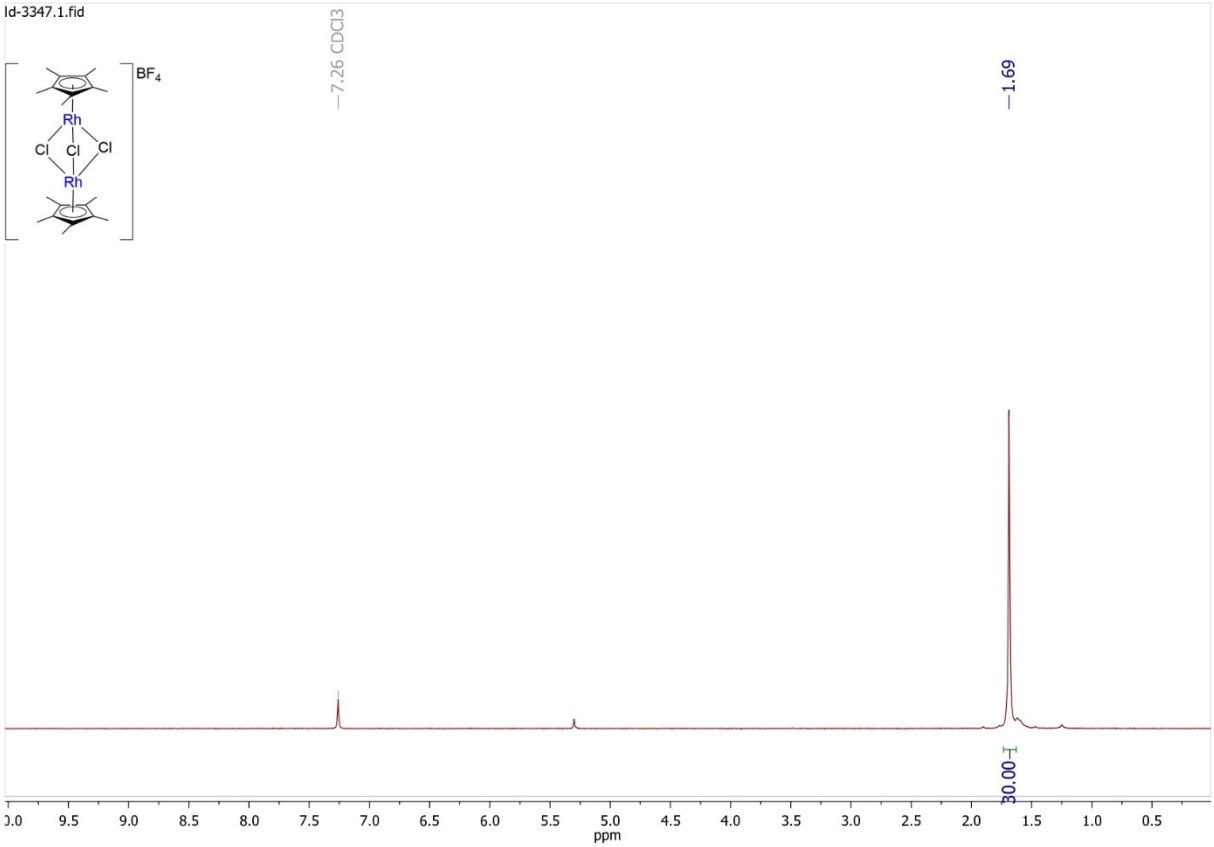
^{1}H NMR (300 MHz) spectrum of ***Rh-I-11*** in $CDCl_3$



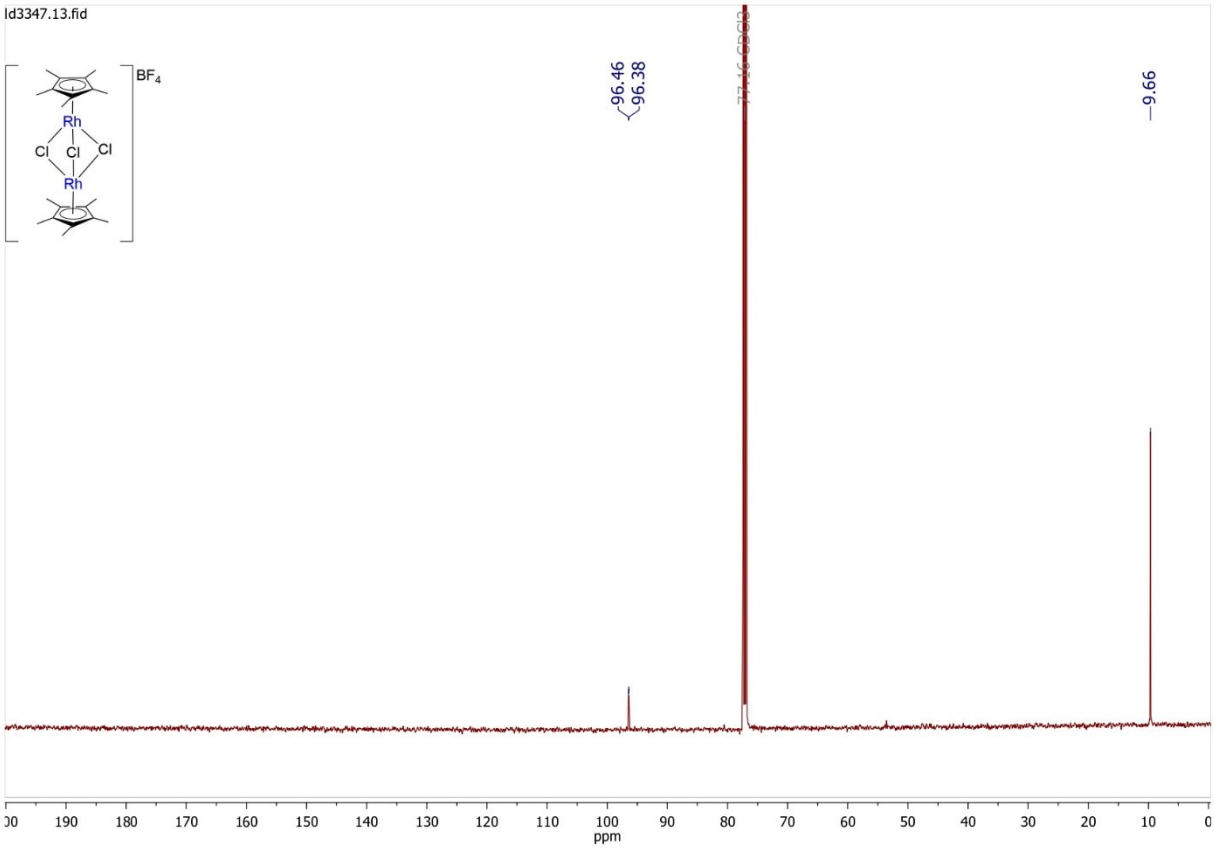
^{13}C{^{1}H} NMR (126 MHz) spectrum of ***Rh-I-11*** in $CDCl_3$



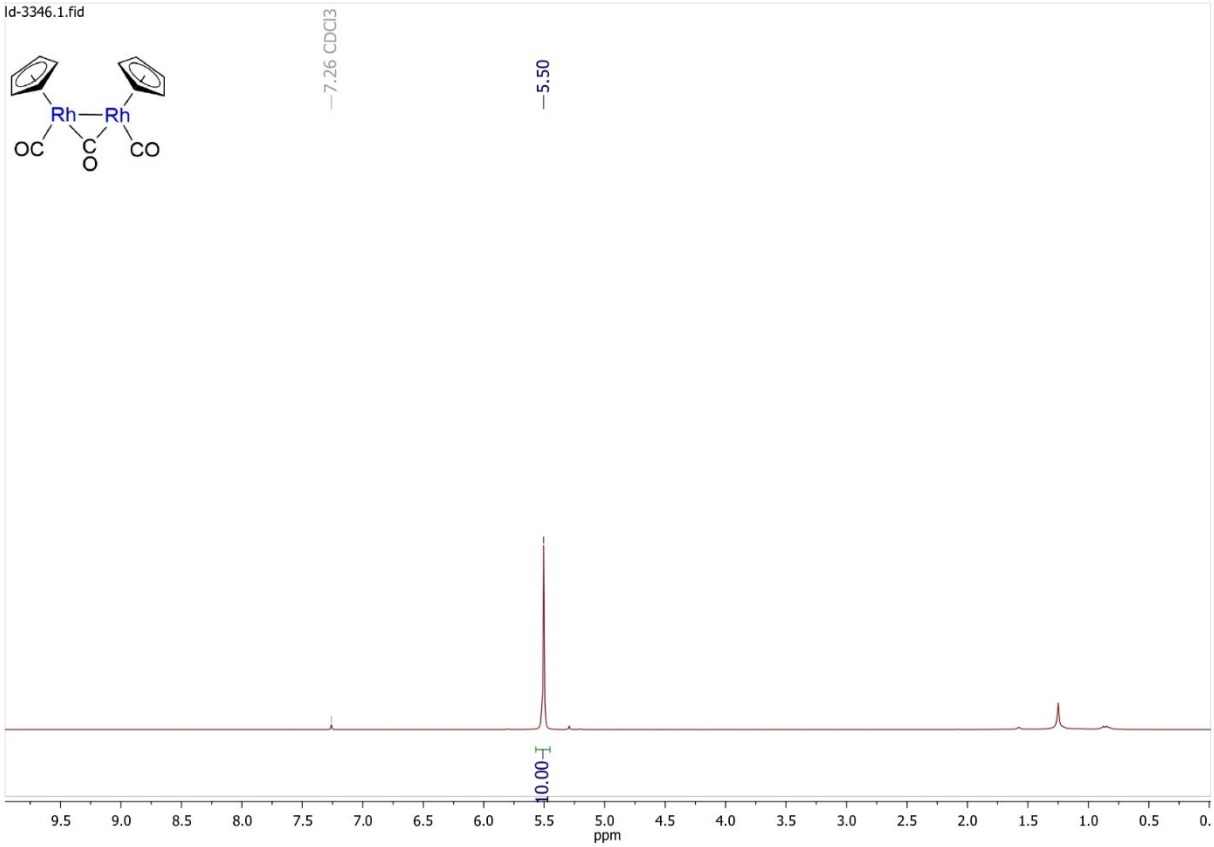
^{1}H NMR (300 MHz) spectrum of ***Rh-III-3*** in $CDCl_3$



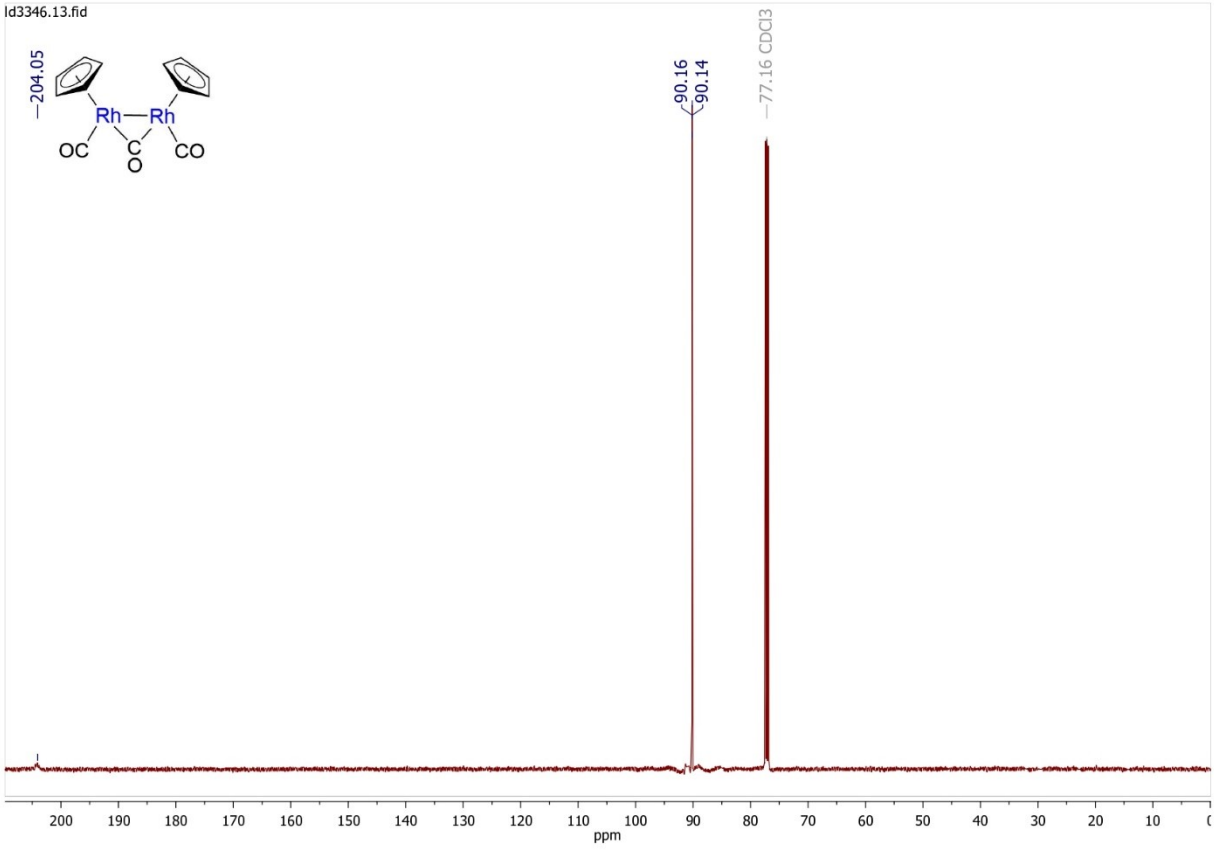
^{13}C{^{1}H} NMR (126 MHz) spectrum of ***Rh-III-3*** in $CDCl_3$



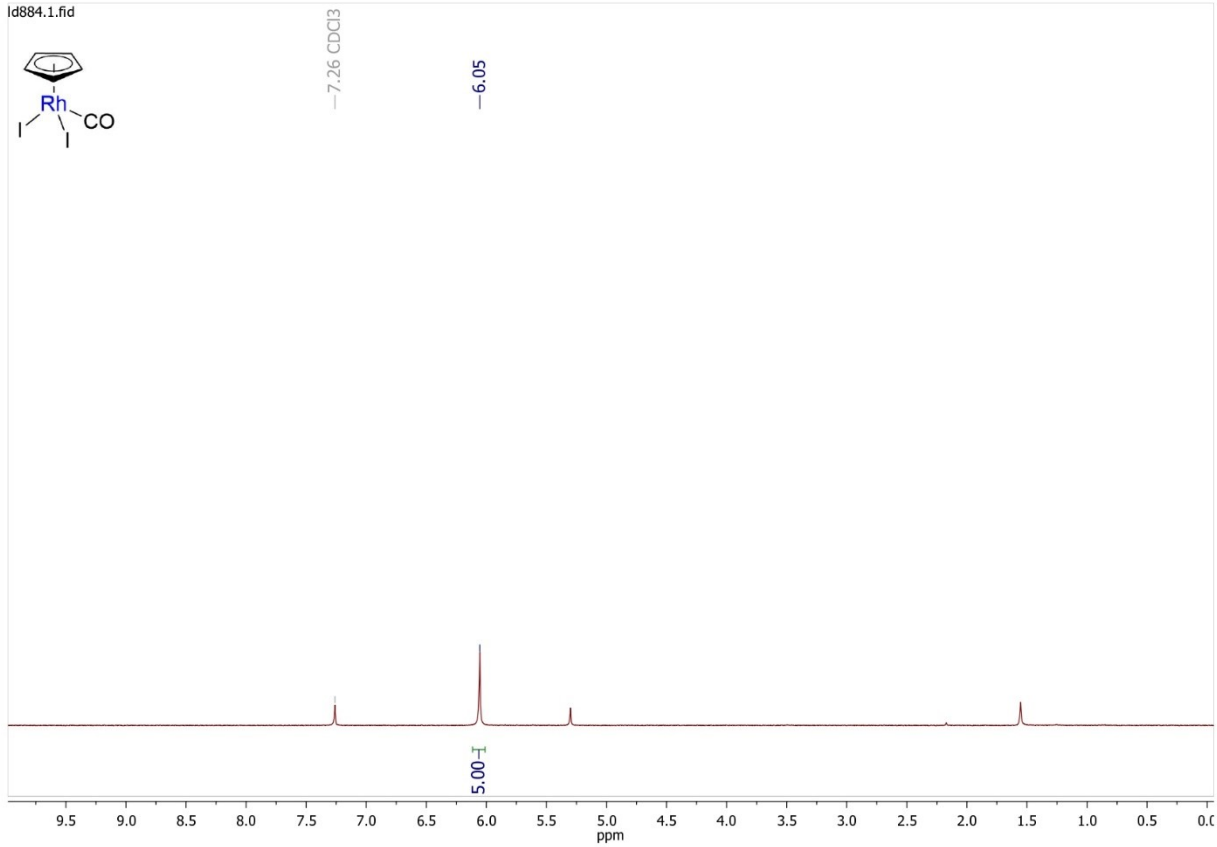
^{1}H NMR (300 MHz) spectrum of ***Rh-I-10*** in $CDCl_3$



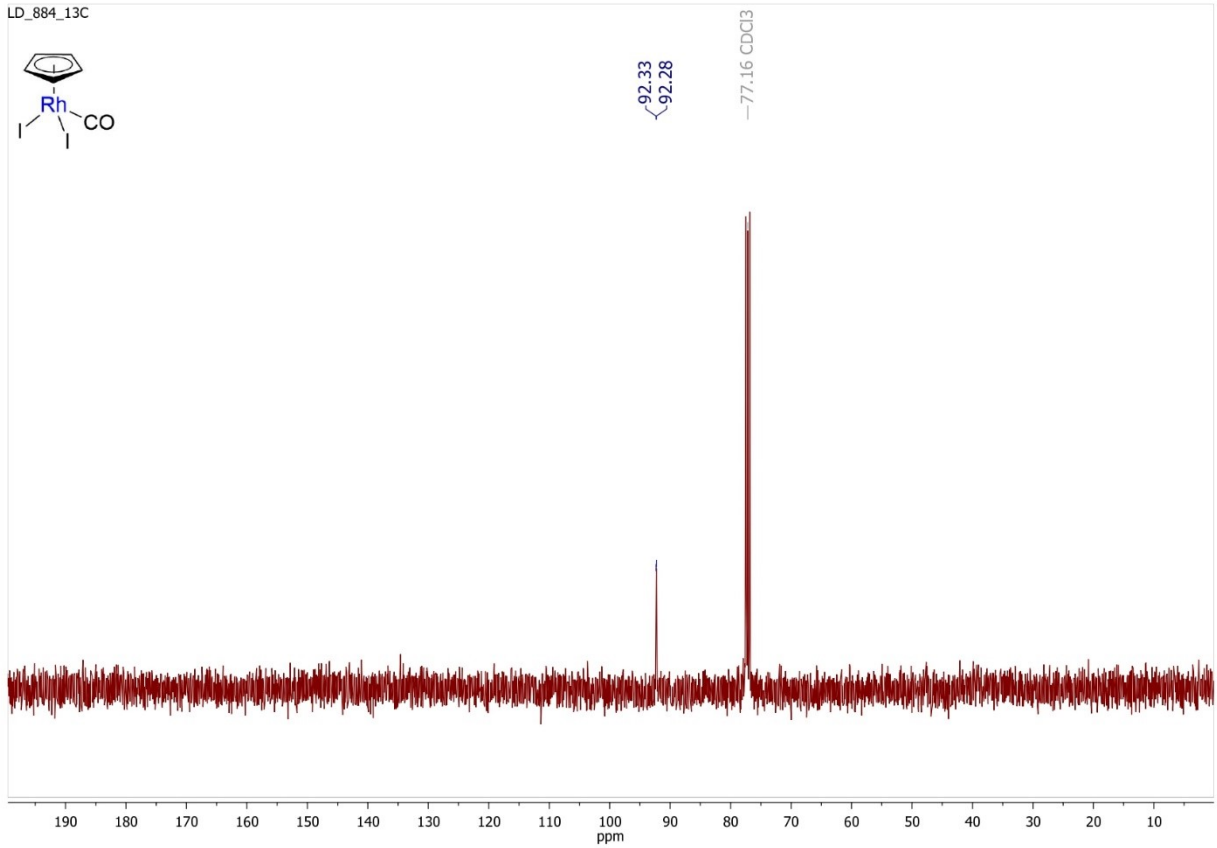
^{13}C{^{1}H} NMR (126 MHz) spectrum of ***Rh-I-10*** in $CDCl_3$



^{1}H NMR (300 MHz) spectrum of ***Rh-III-5*** in $CDCl_3$

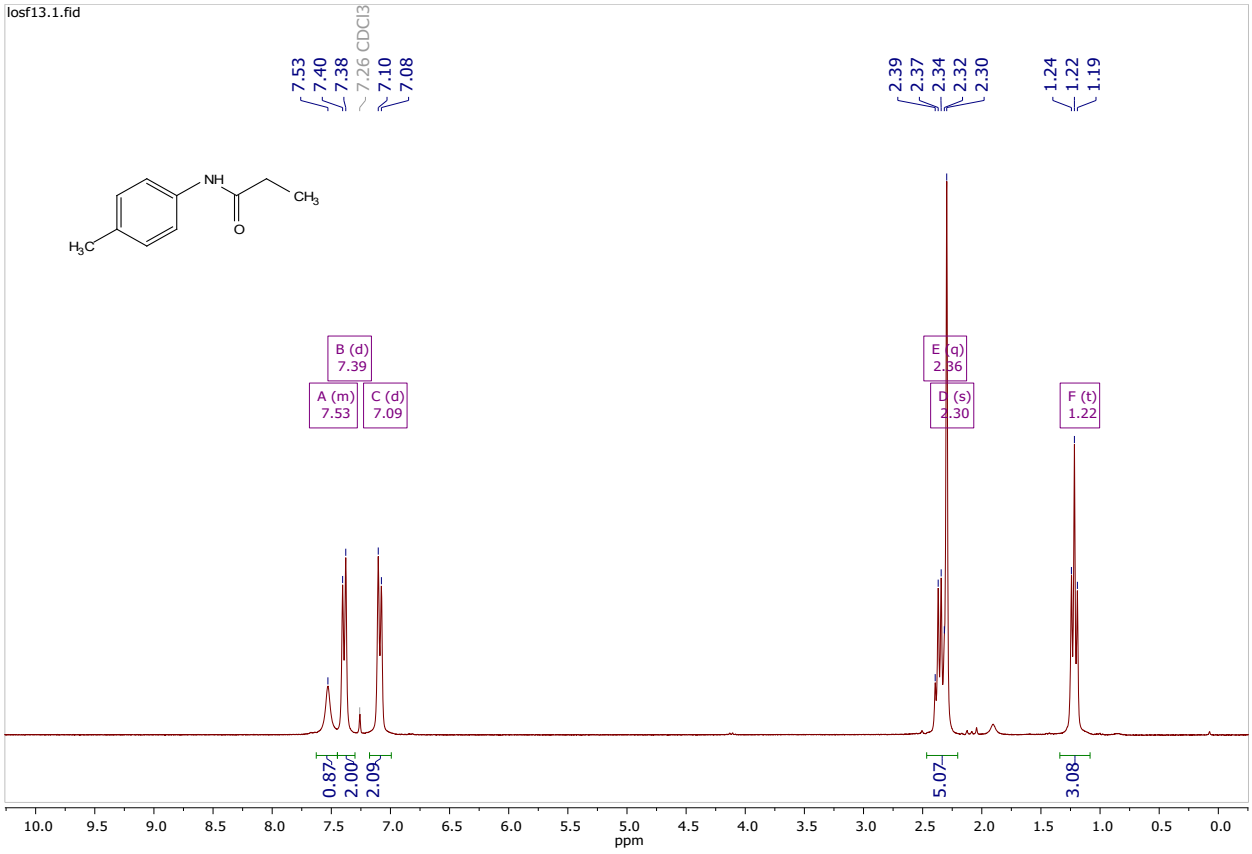


^{13}C{^{1}H} NMR (101 MHz) spectrum of ***Rh-III-5*** in $CDCl_3$

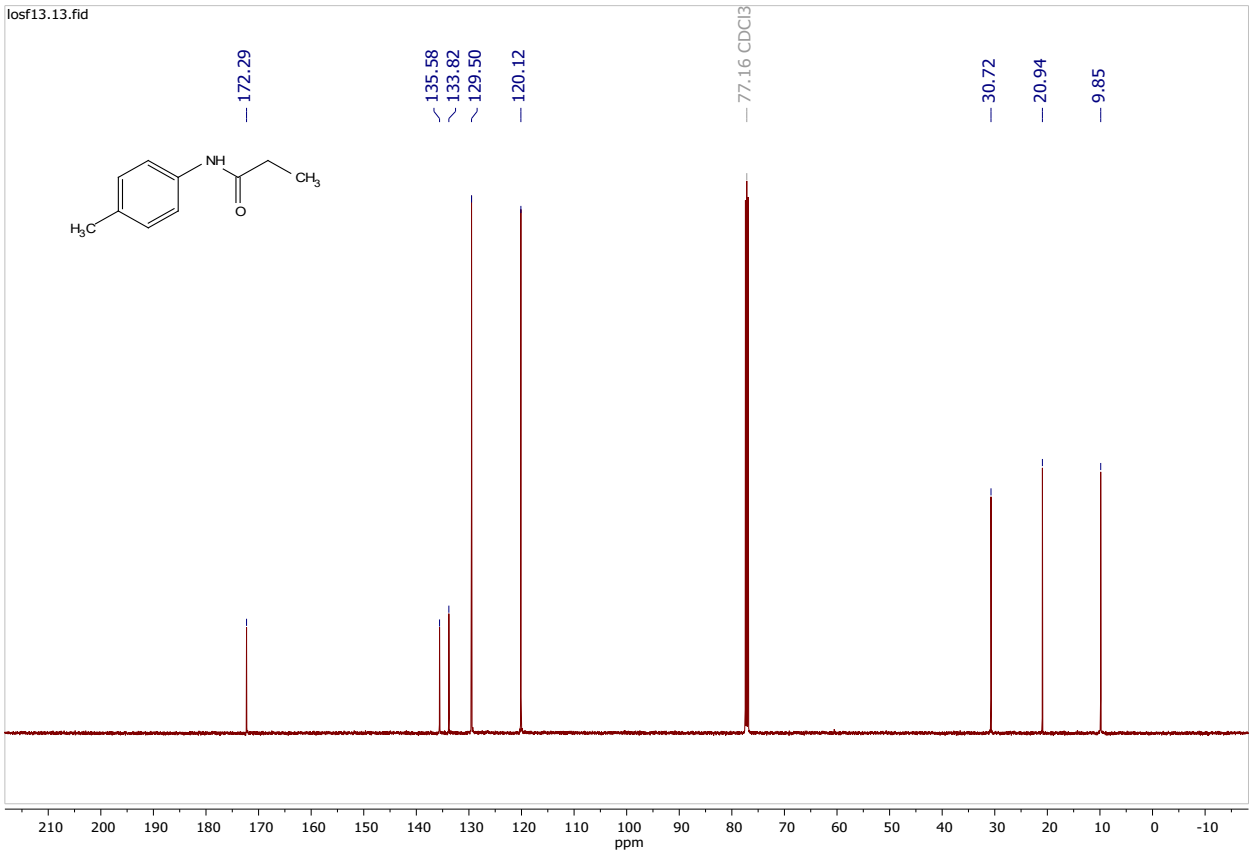


NMR Spectra of Products

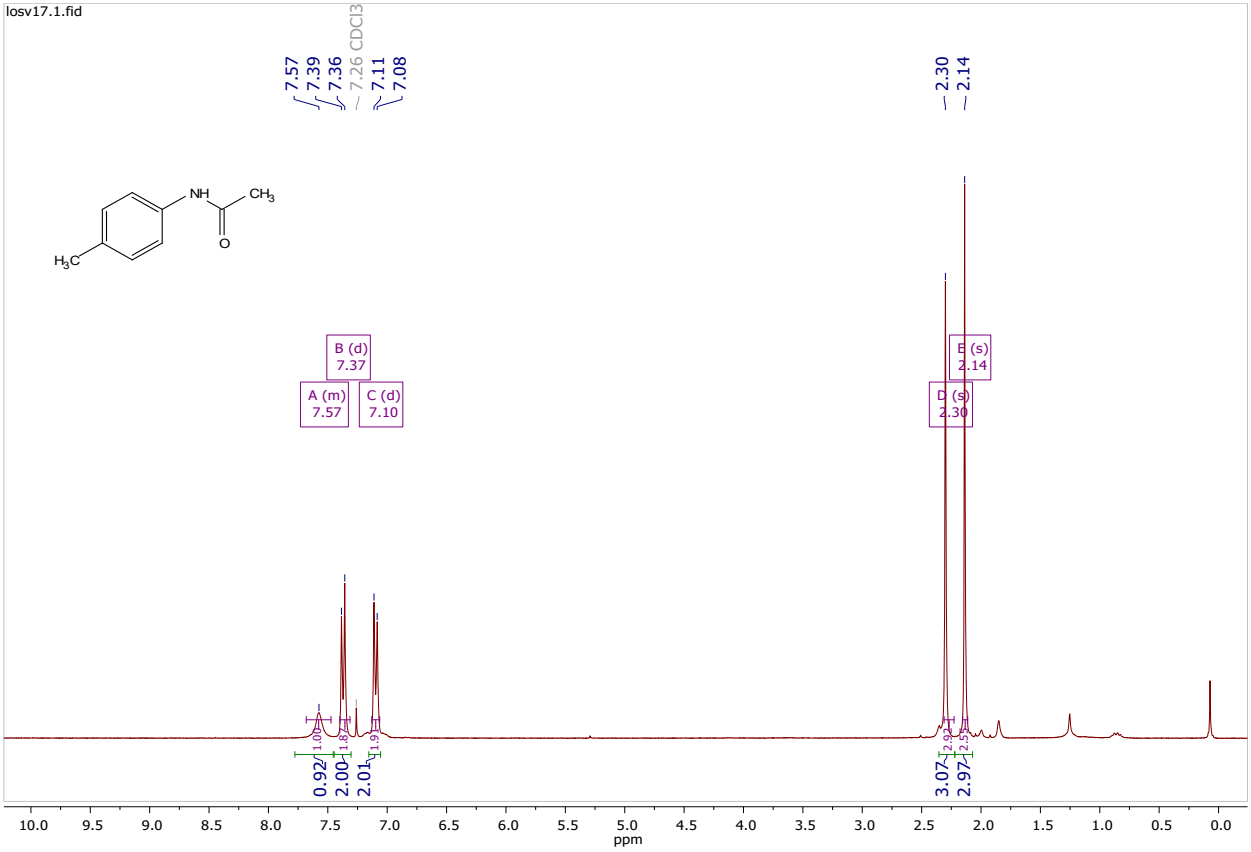
^{1}H NMR (300 MHz) spectrum of *N*-(*p*-tolyl)propionamide **(3a)** in $CDCl_3$.



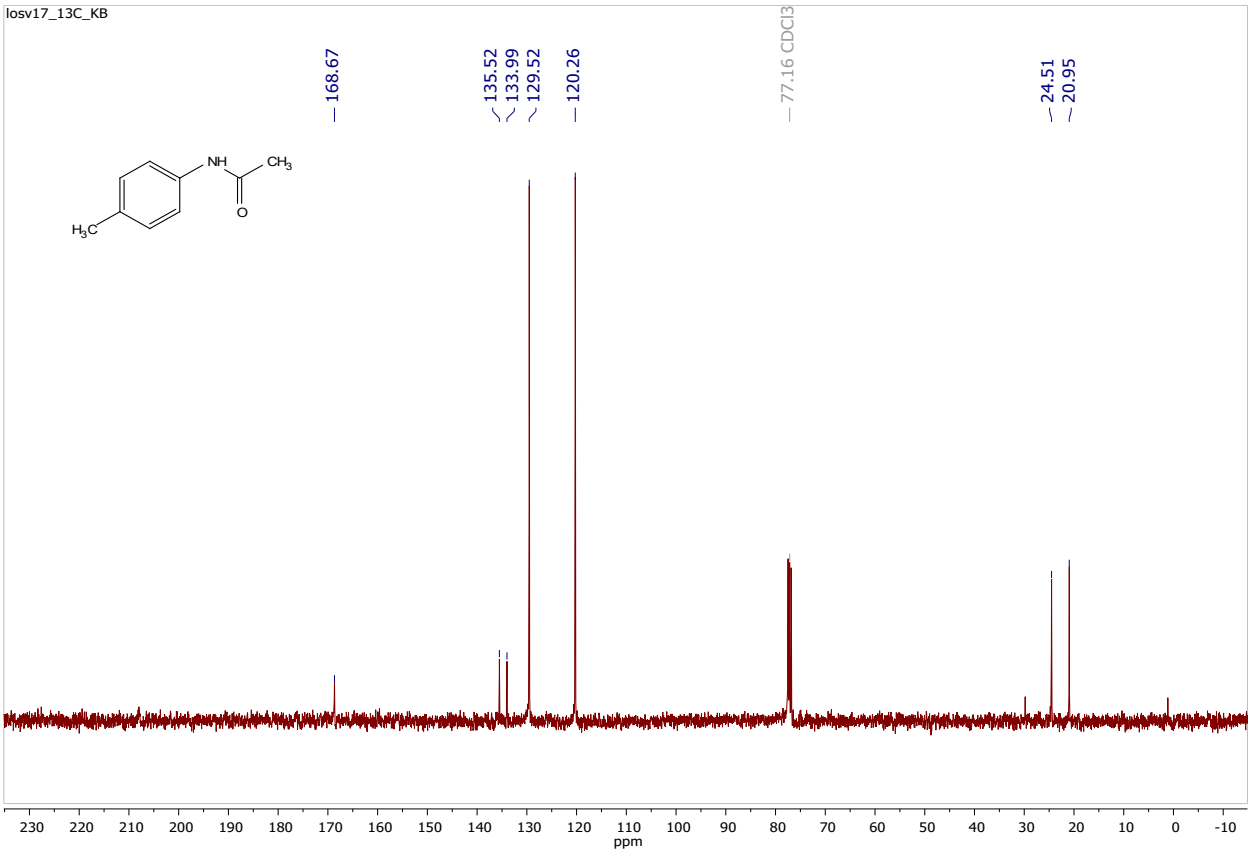
^{13}C{^{1}H} NMR (126 MHz) spectrum of *N*-(*p*-tolyl)propionamide **(3a)** in $CDCl_3$.



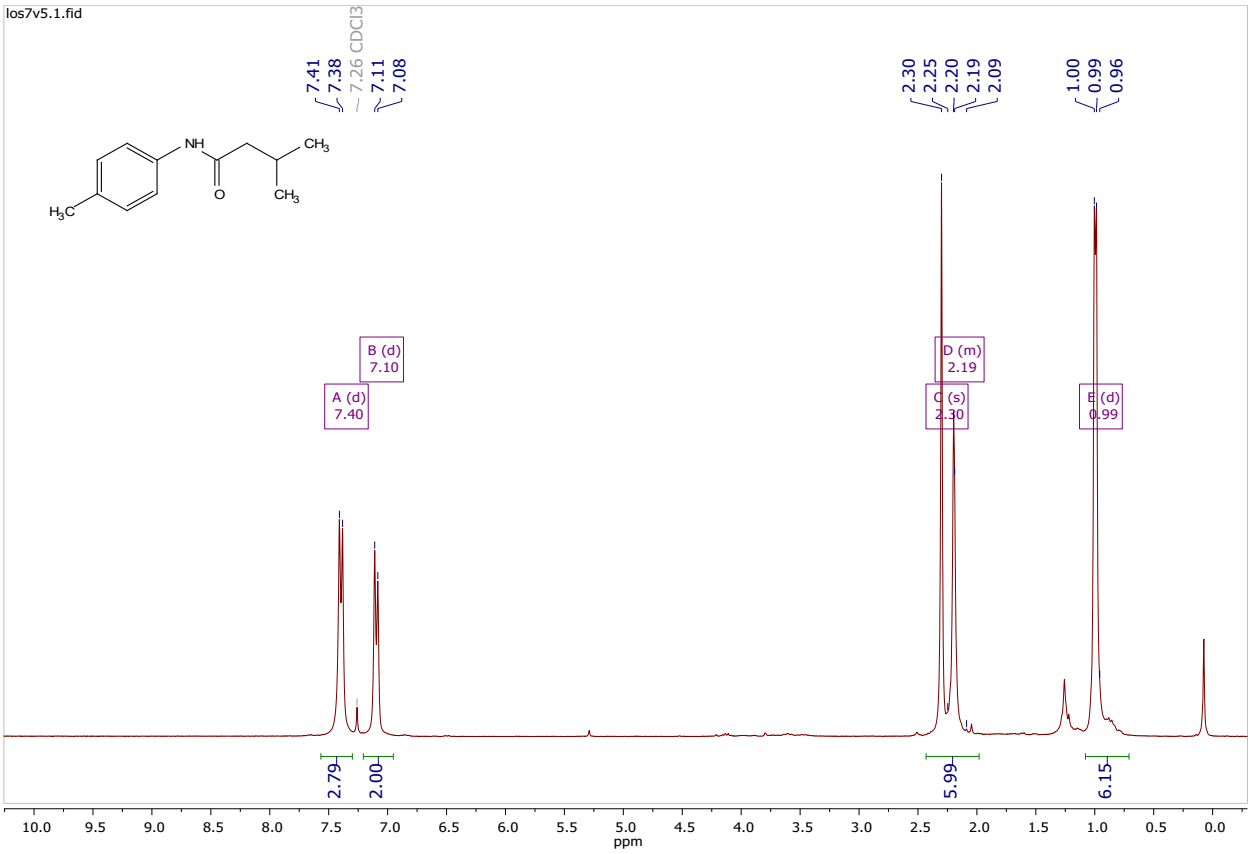
^{1}H NMR (300 MHz) spectrum of *N*-(*p*-tolyl)acetamide **(3b)** in $CDCl_3$.



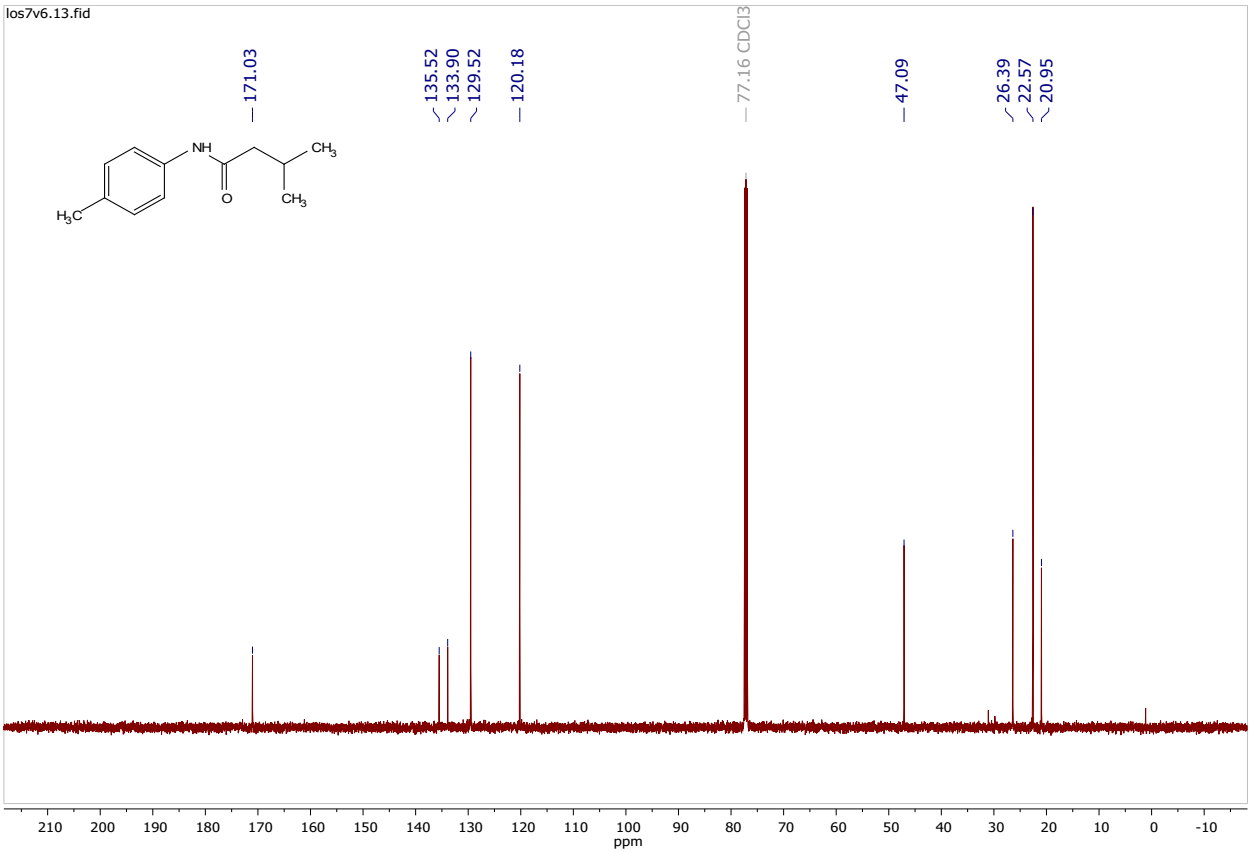
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-(*p*-tolyl)acetamide **(3b)** in $CDCl_3$.



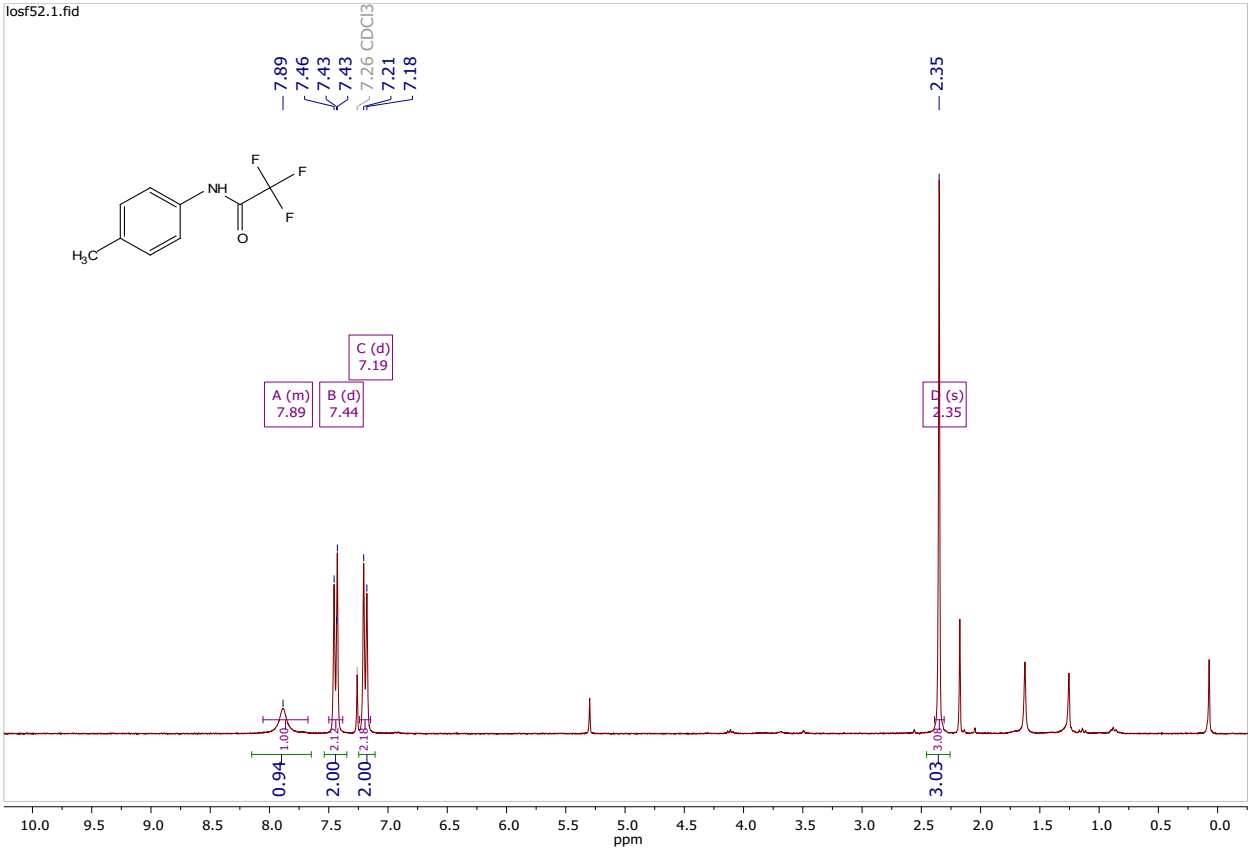
^{1}H NMR (300 MHz) spectrum of 3-methyl-*N*-(*p*-tolyl)butanamide **(3c)** in $CDCl_3$.



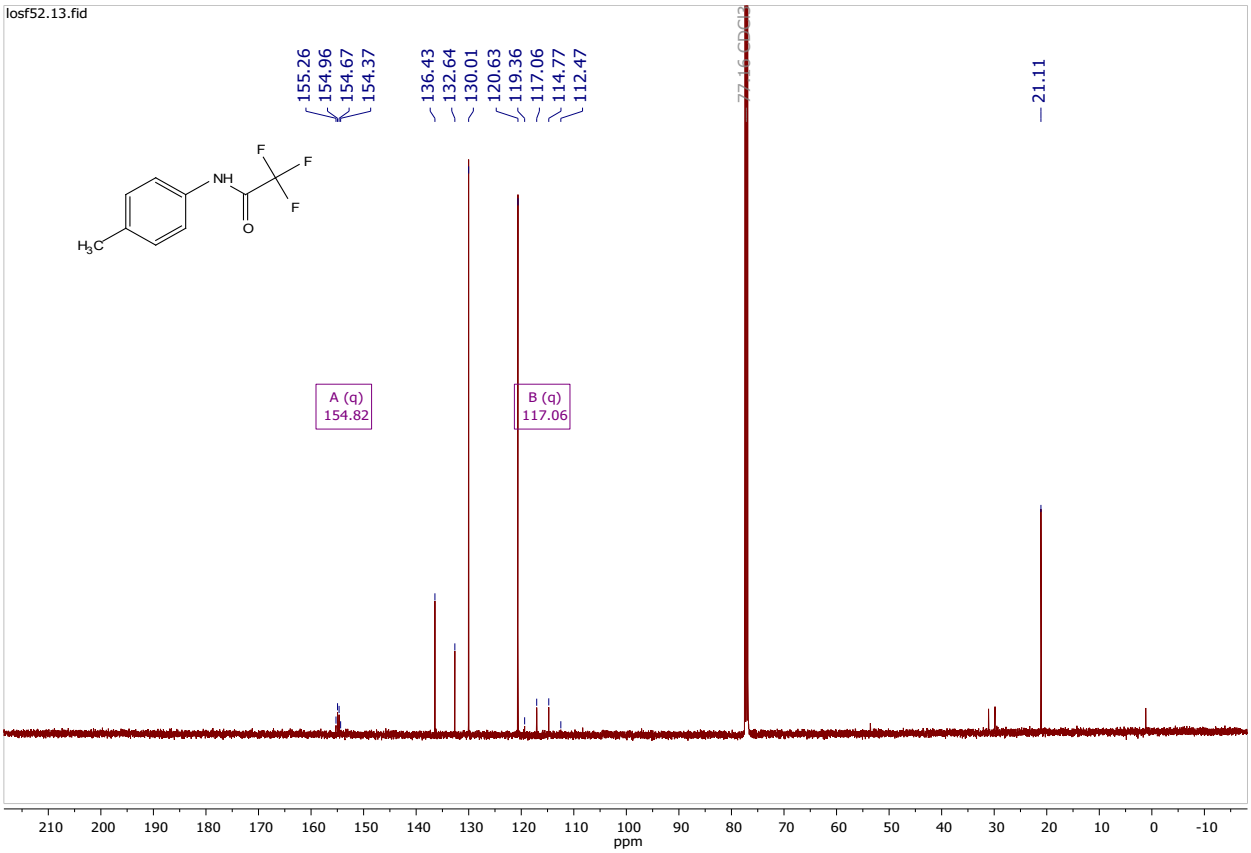
^{13}C{^{1}H} NMR (126 MHz) spectrum of 3-methyl-*N*-(*p*-tolyl)butanamide **(3c)** in $CDCl_3$.



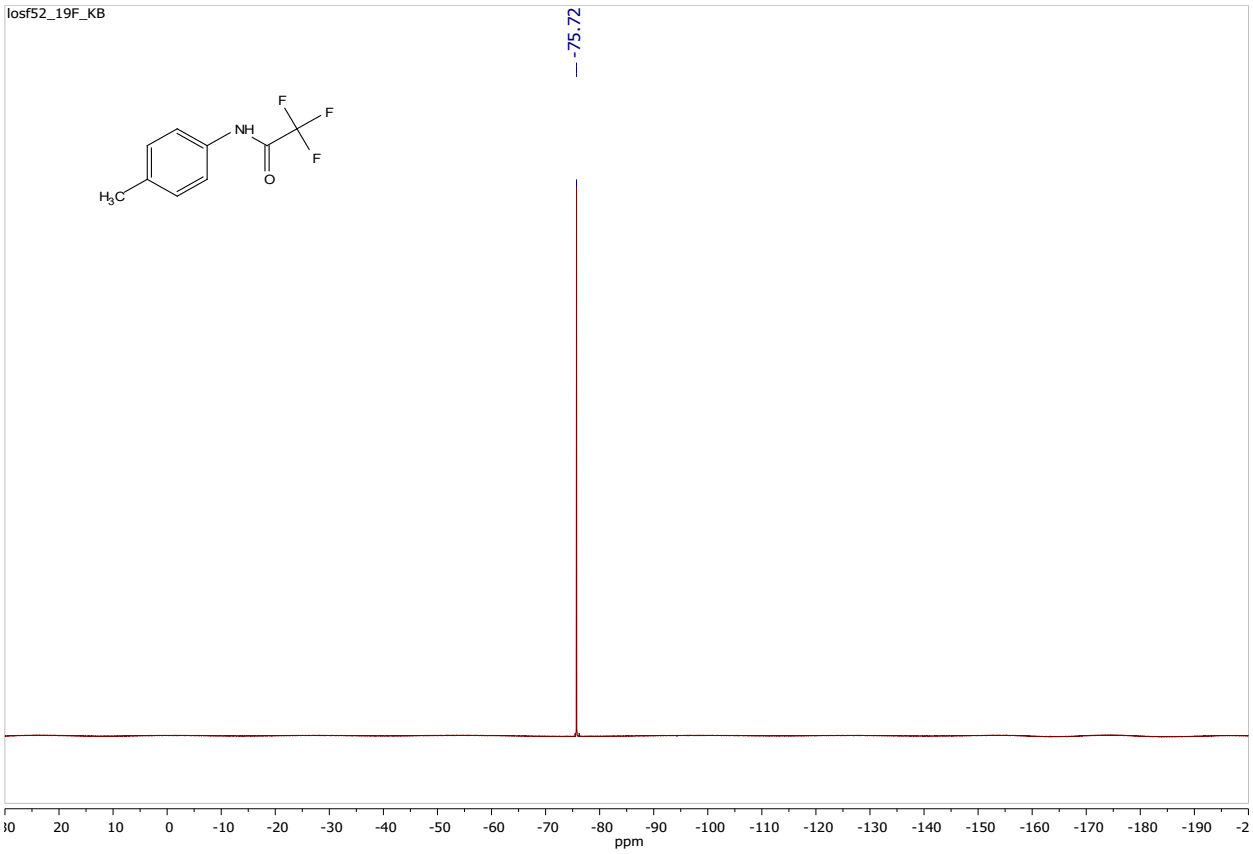
^{1}H NMR (300 MHz) spectrum of 2,2,2-trifluoro-*N*-(*p*-tolyl)acetamide **(3d)** in $CDCl_3$.



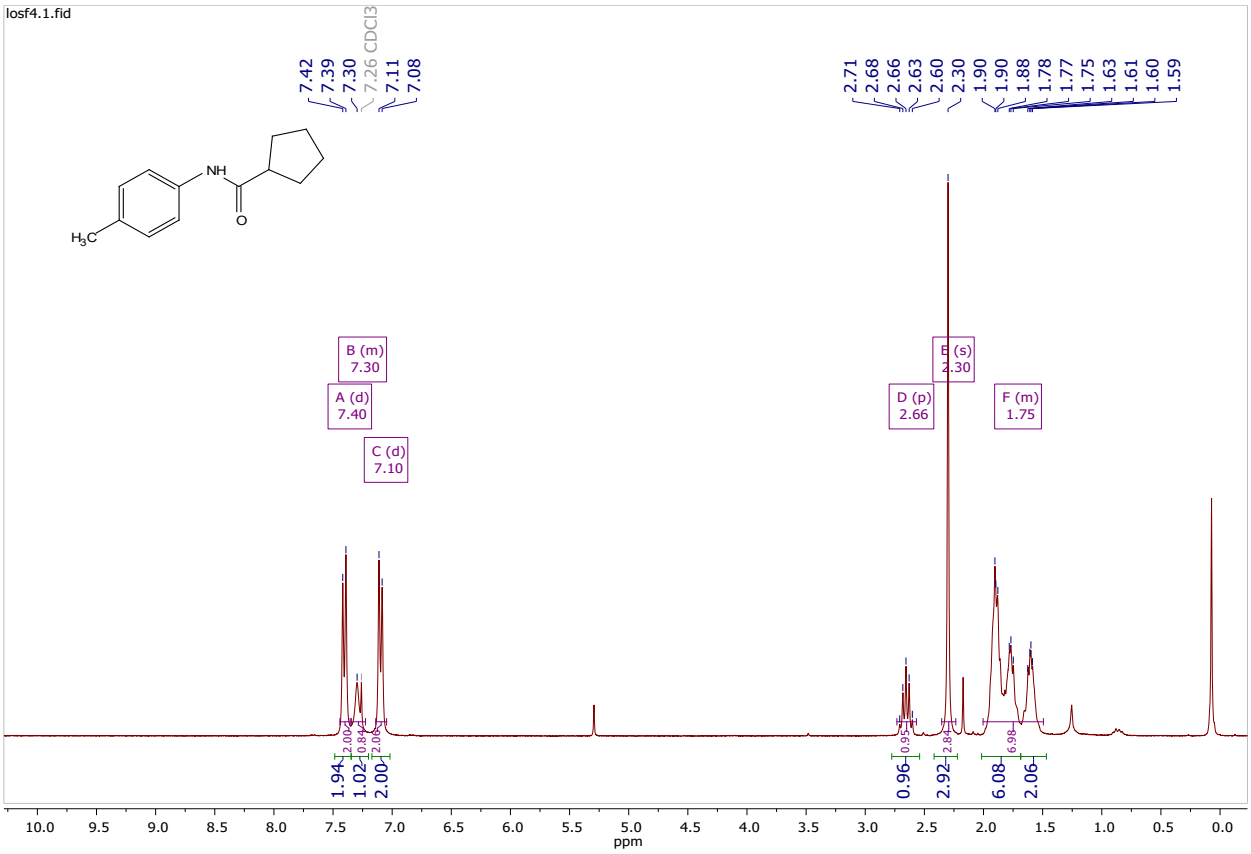
^{13}C{^{1}H} NMR (126 MHz) spectrum of 2,2,2-trifluoro-*N*-(*p*-tolyl)acetamide **(3d)** in $CDCl_3$.



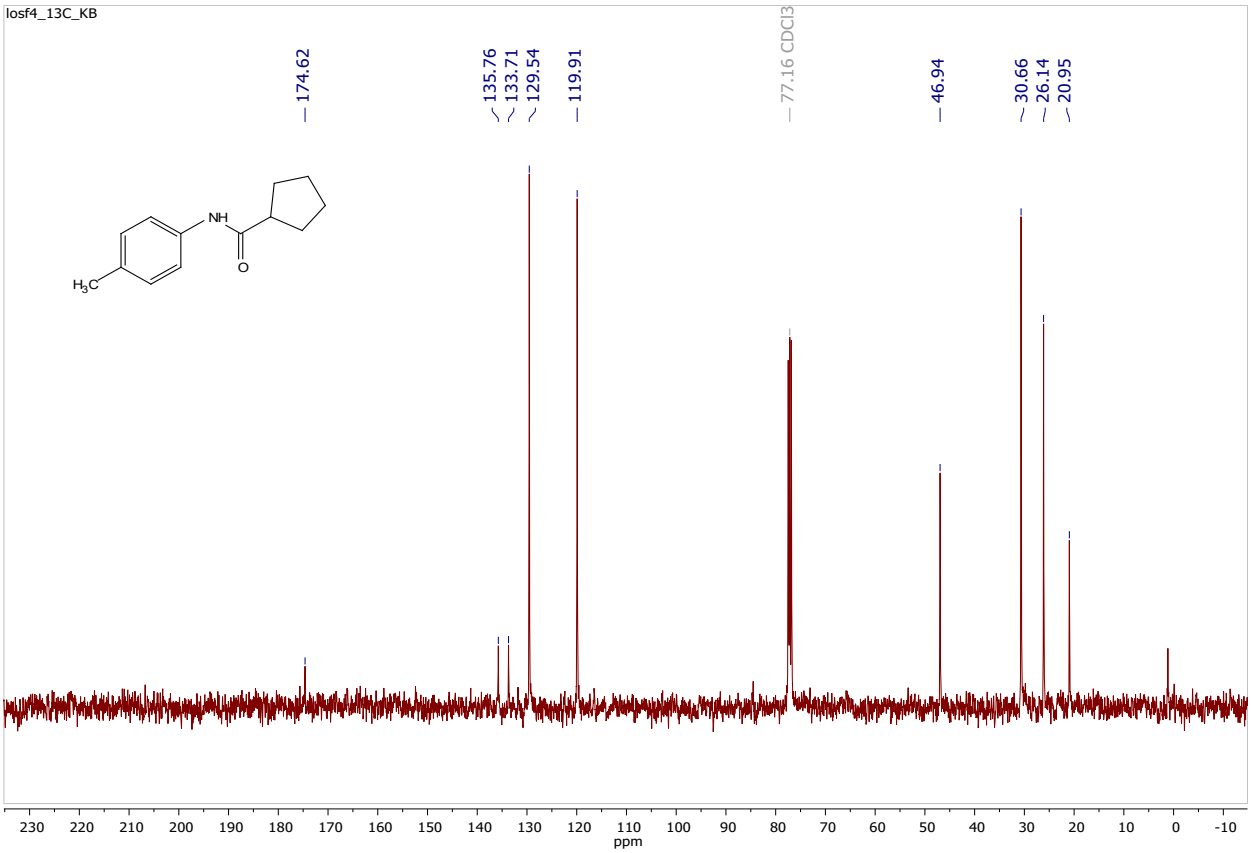
^{19}F NMR (376 MHz) spectrum of 2,2,2-trifluoro-*N*-(*p*-tolyl)acetamide **(3d)** in $CDCl_3$.



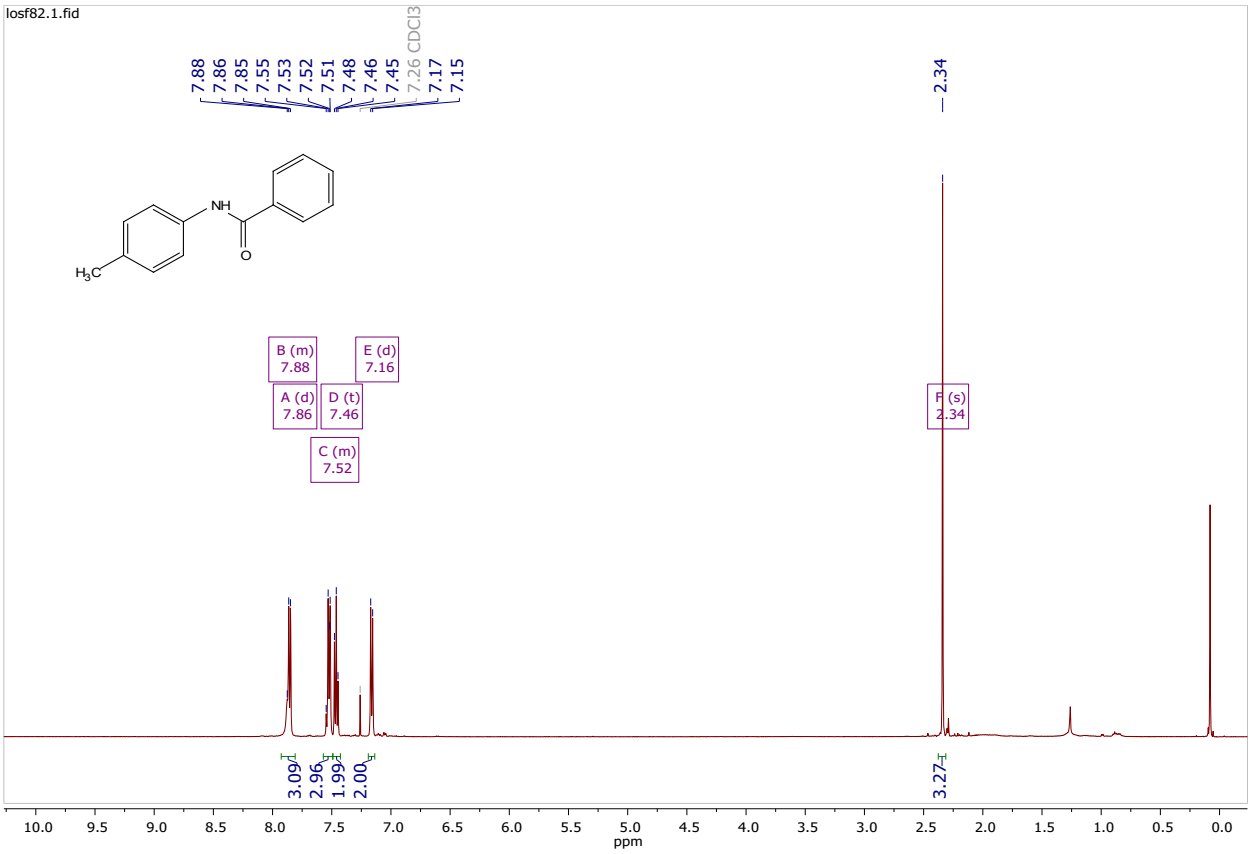
^{1}H NMR (300 MHz) spectrum of *N*-(*p*-tolyl)cyclopentanecarboxamide **(3e)** in $CDCl_3$.



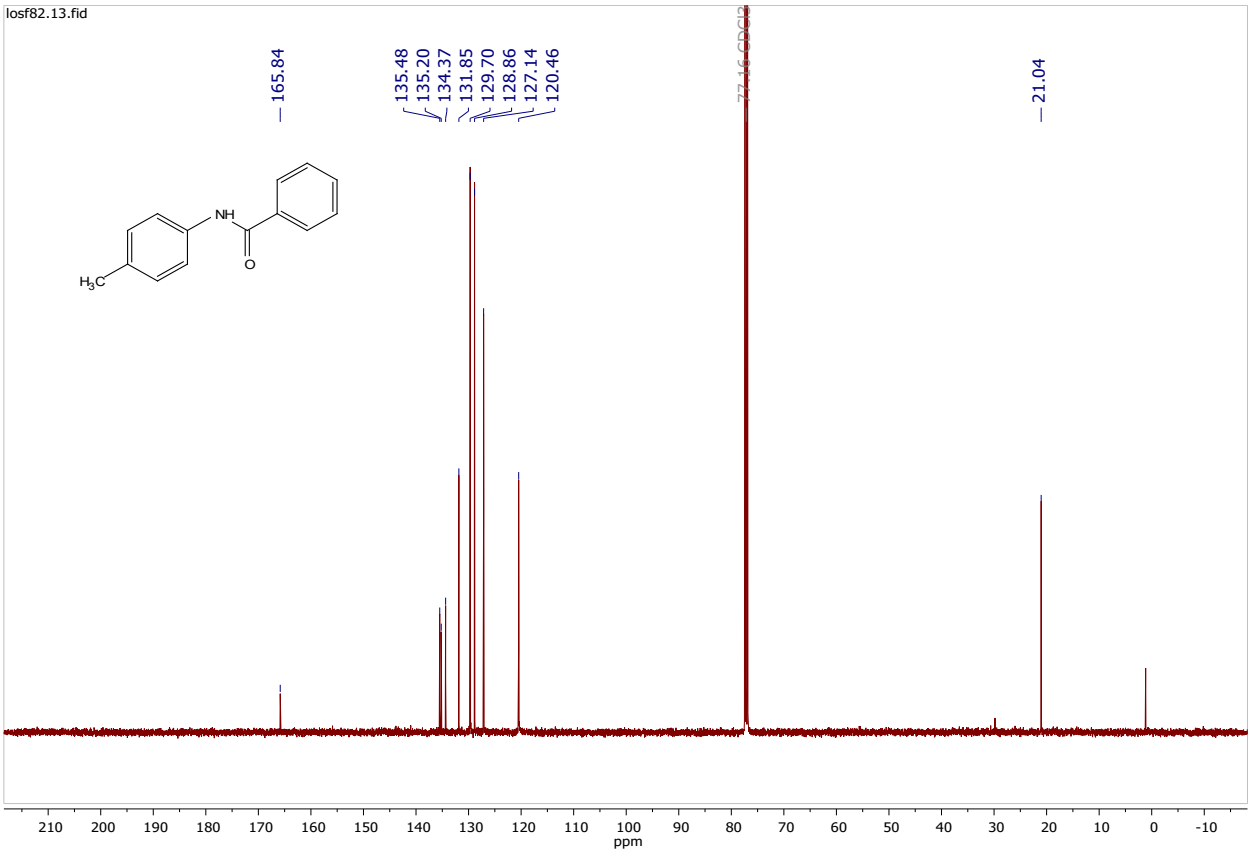
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-(*p*-tolyl)cyclopentanecarboxamide **(3e)** in $CDCl_3$.



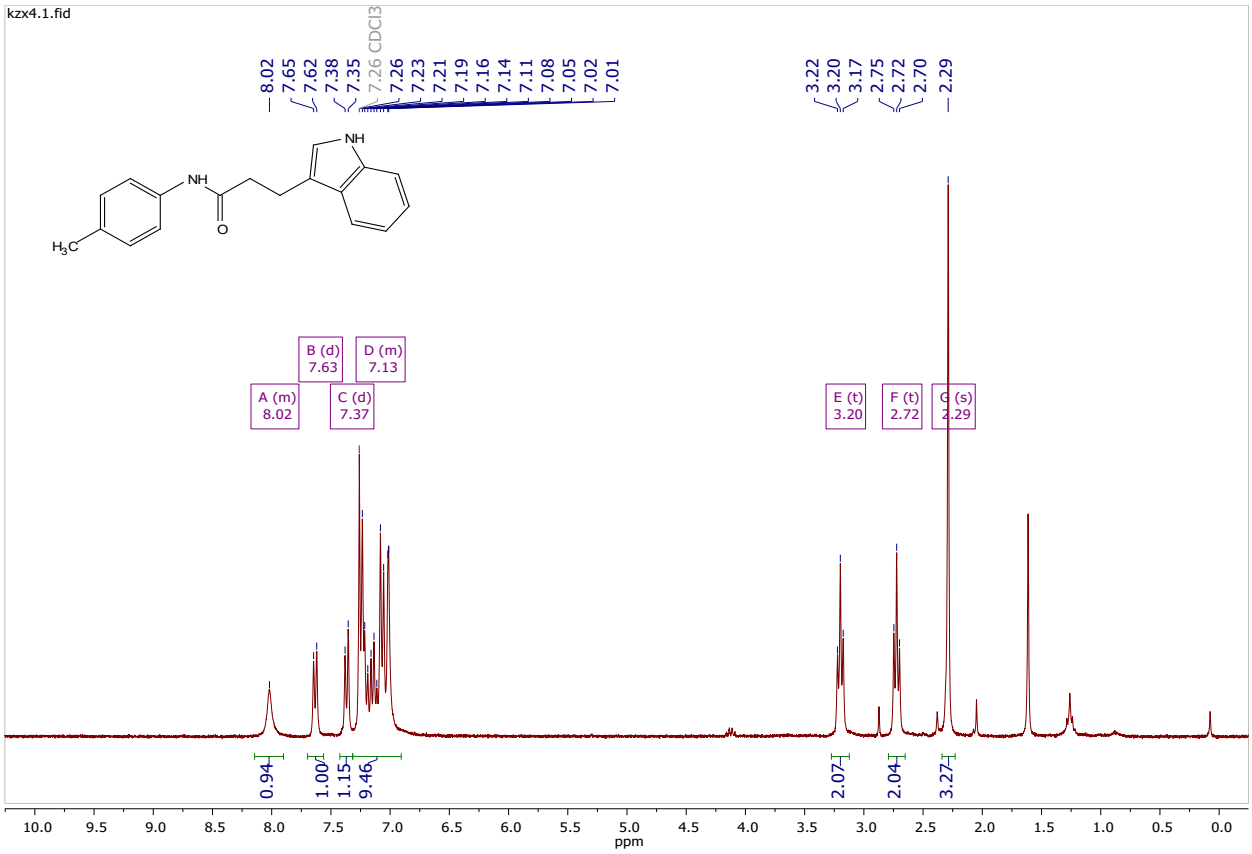
^{1}H NMR (500 MHz) spectrum of *N*-(*p*-tolyl)benzamide **(3f)** in $CDCl_3$.



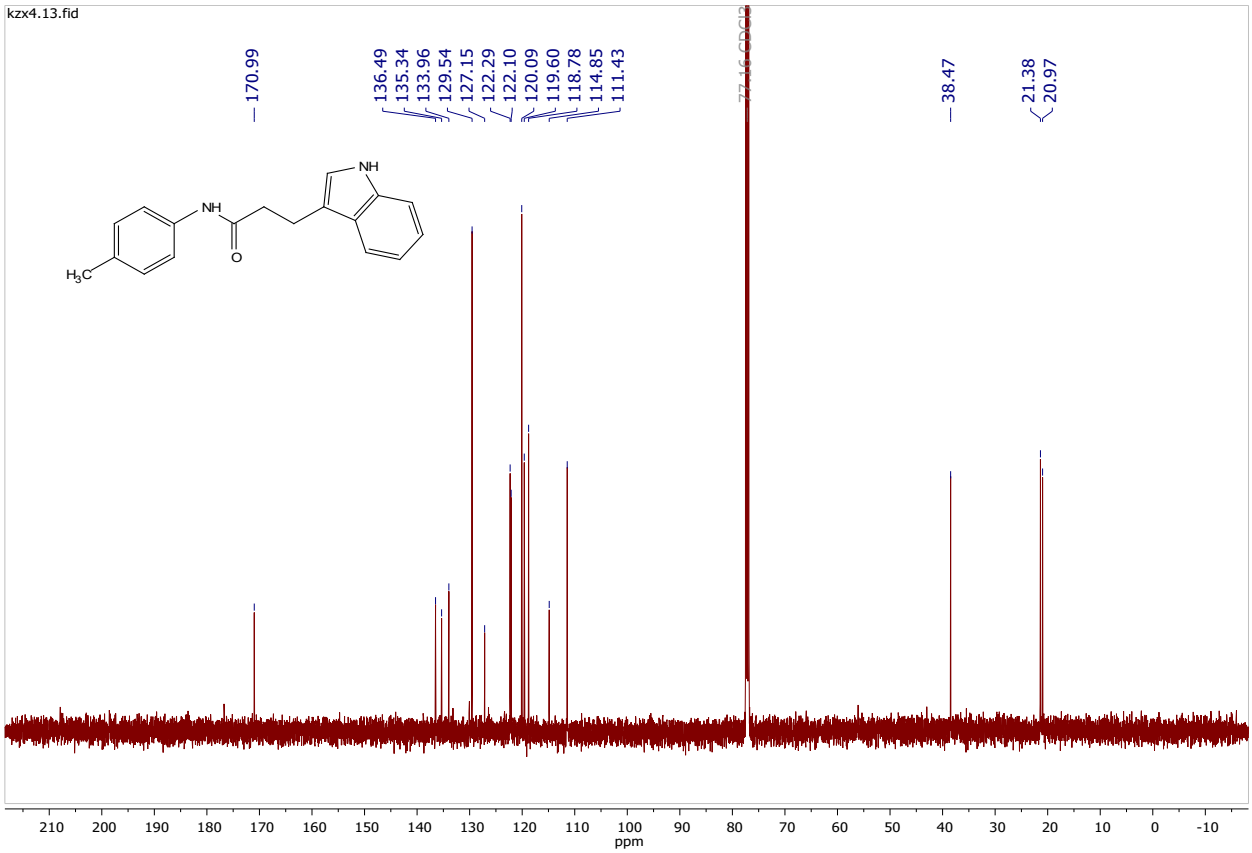
^{13}C{^{1}H} NMR (126 MHz) spectrum of *N*-(*p*-tolyl)benzamide **(3f)** in $CDCl_3$.



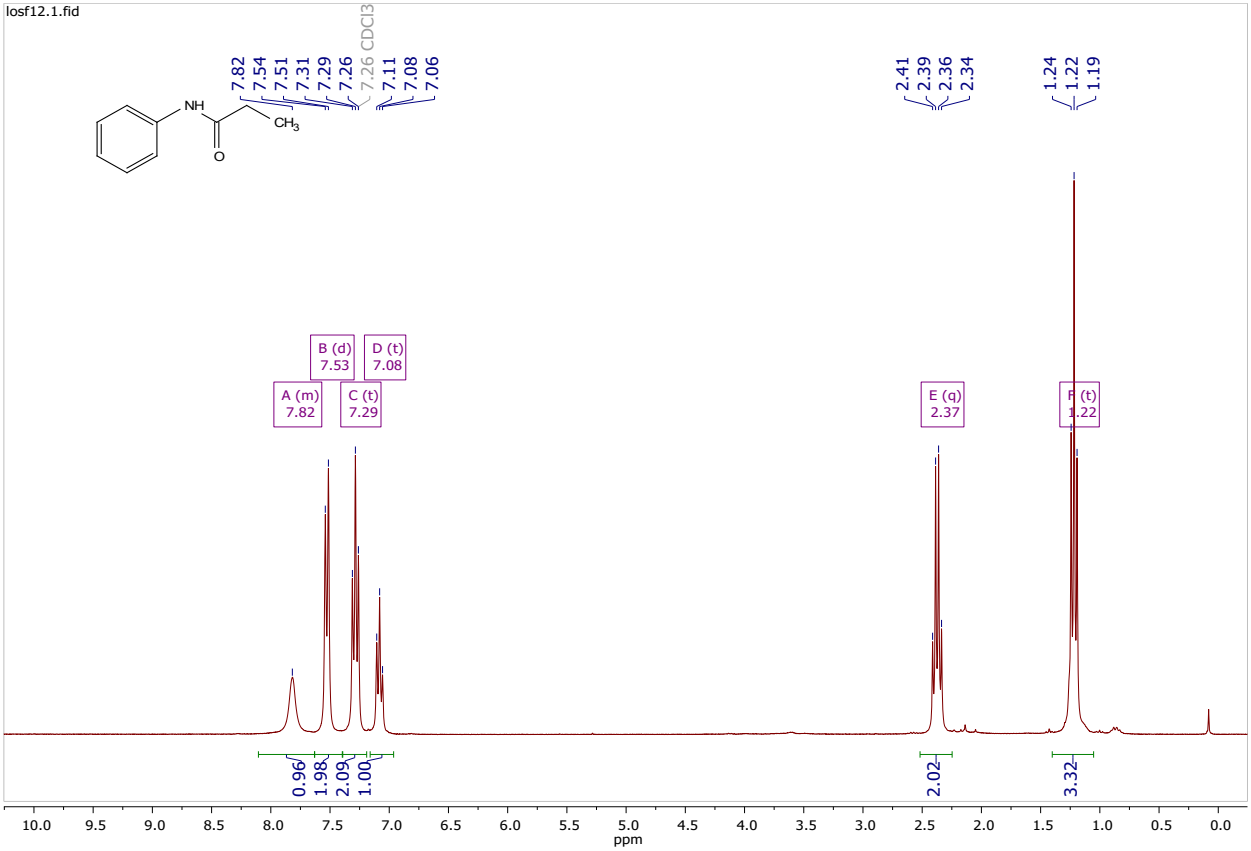
^{1}H NMR (300 MHz) spectrum of 3-(1*H*-indol-3-yl)-*N*-(*p*-tolyl)propanamide **(3g)** in $CDCl_3$.



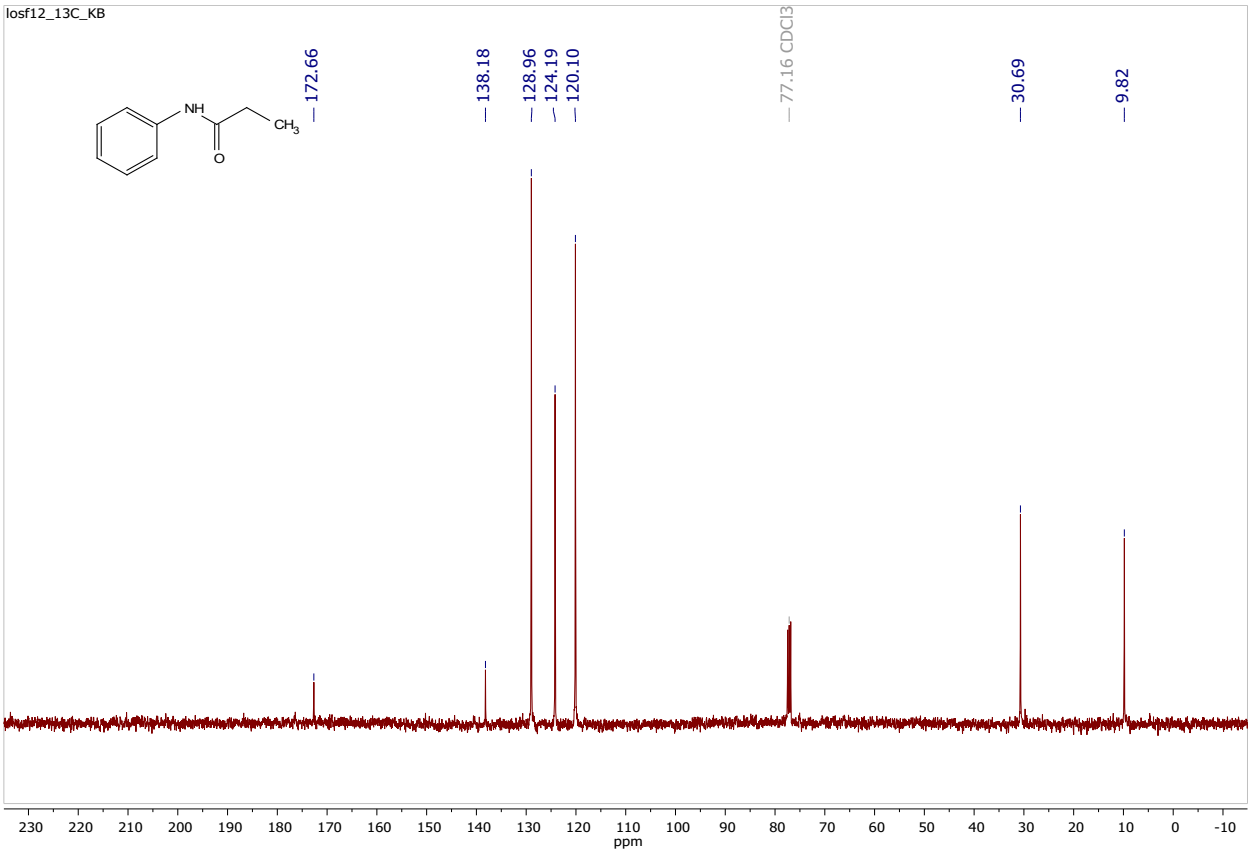
^{13}C{^{1}H} NMR (126 MHz) spectrum of 3-(1*H*-indol-3-yl)-*N*-(*p*-tolyl)propanamide **(3g)** in $CDCl_3$.



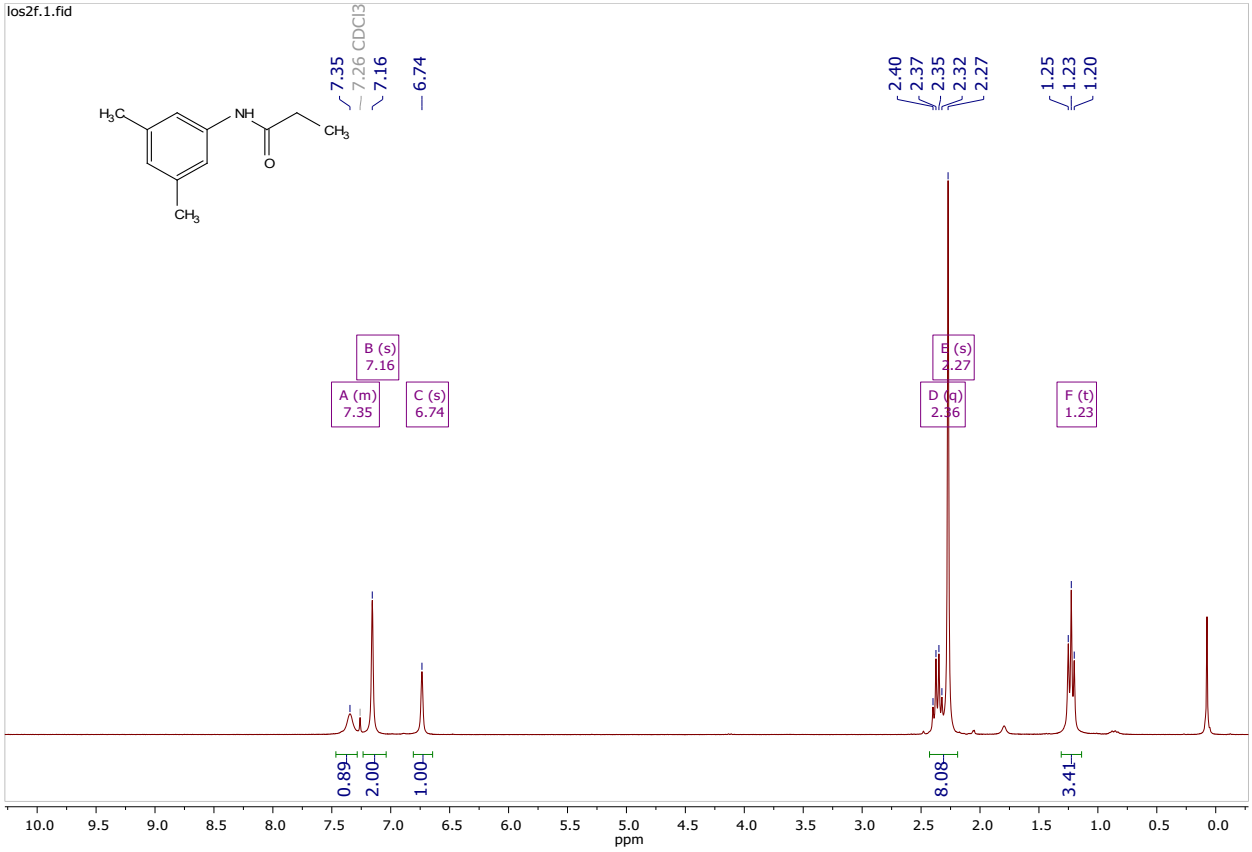
^{1}H NMR (300 MHz) spectrum of *N*-phenylpropionamide **(3h)** in $CDCl_3$.



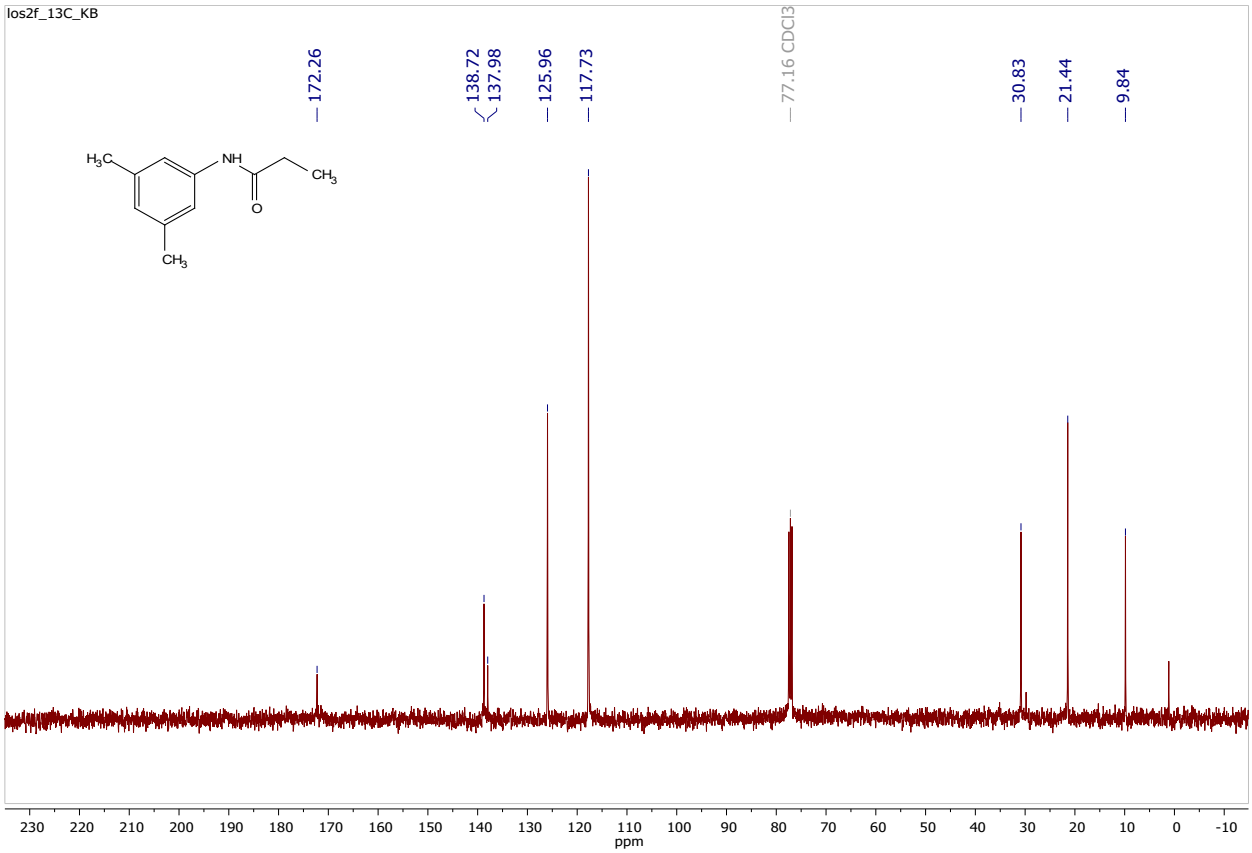
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-phenylpropionamide **(3h)** in $CDCl_3$.



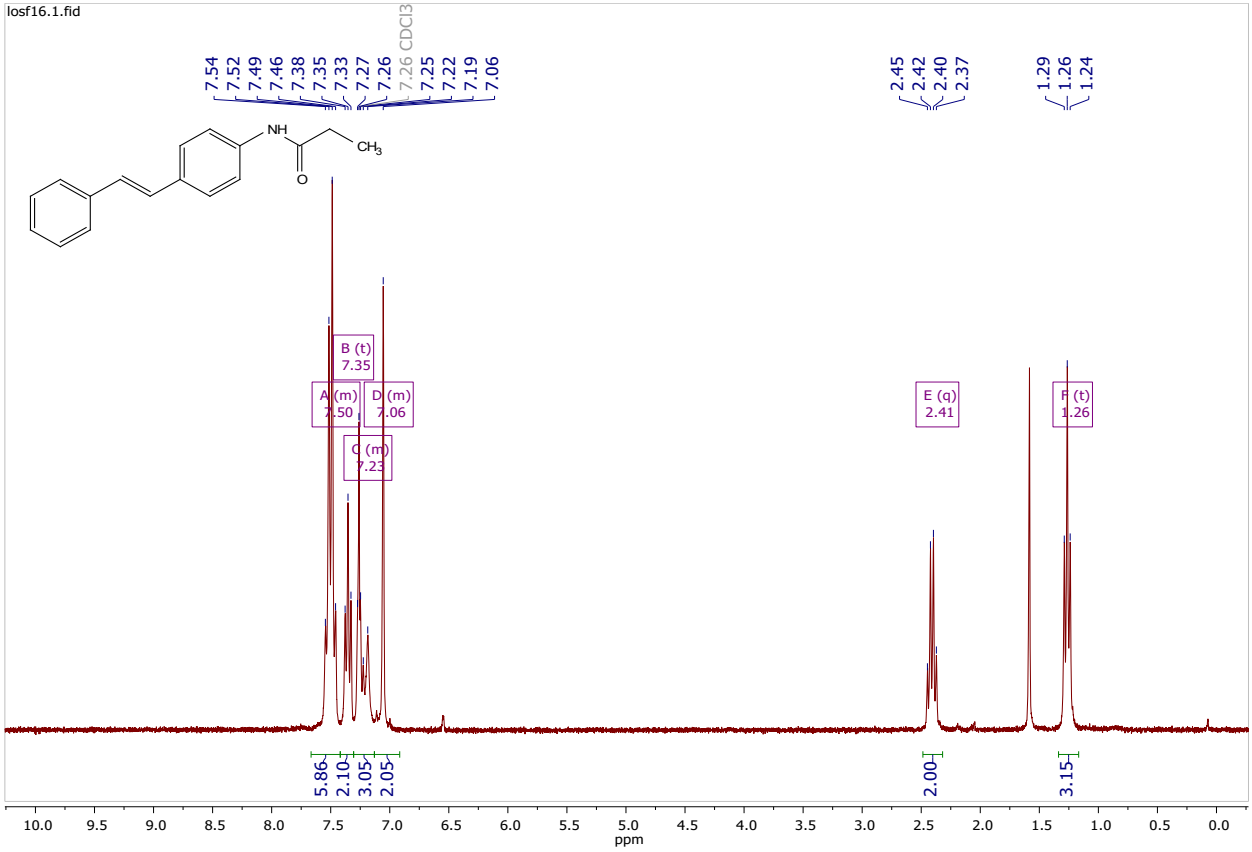
^{1}H NMR (300 MHz) spectrum of *N*-(3,5-dimethylphenyl)propionamide **(3i)** in $CDCl_3$.



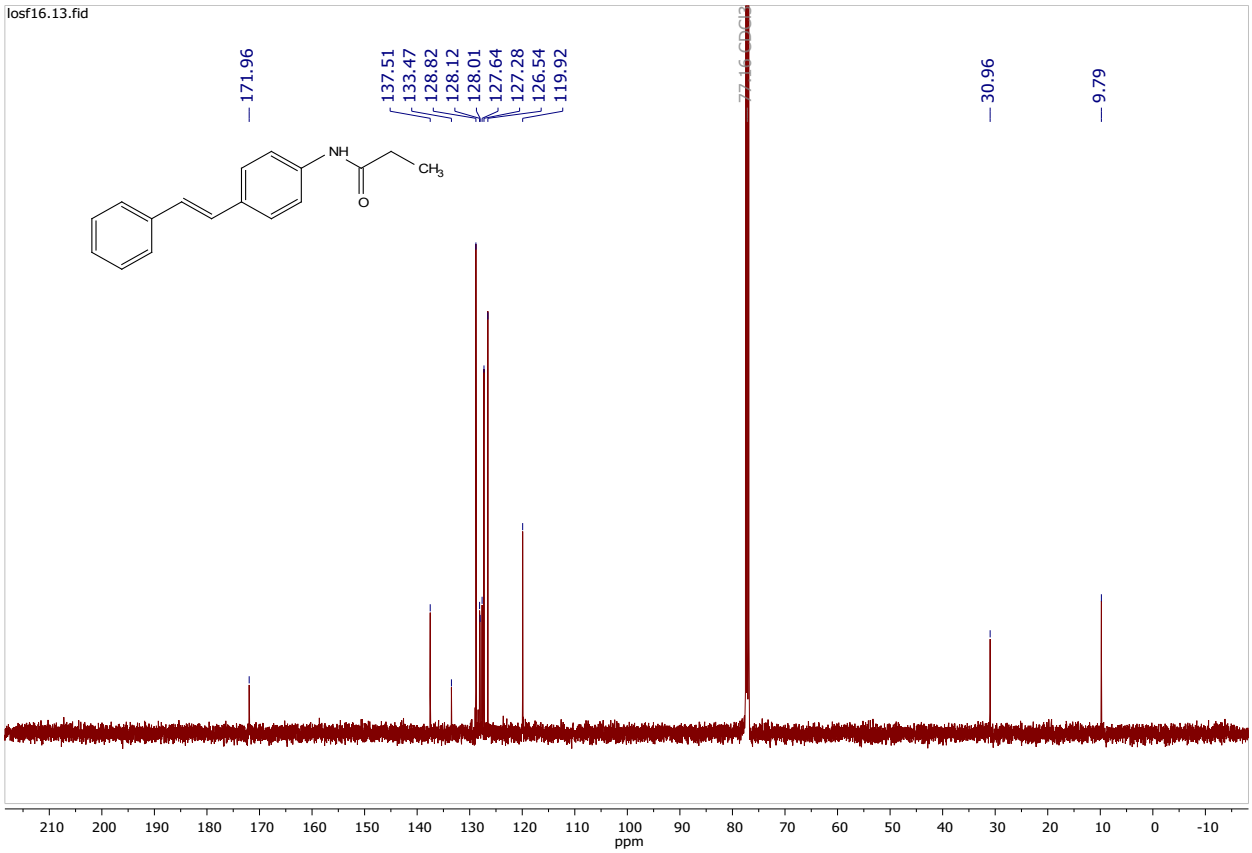
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-(3,5-dimethylphenyl)propionamide **(3i)** in $CDCl_3$.



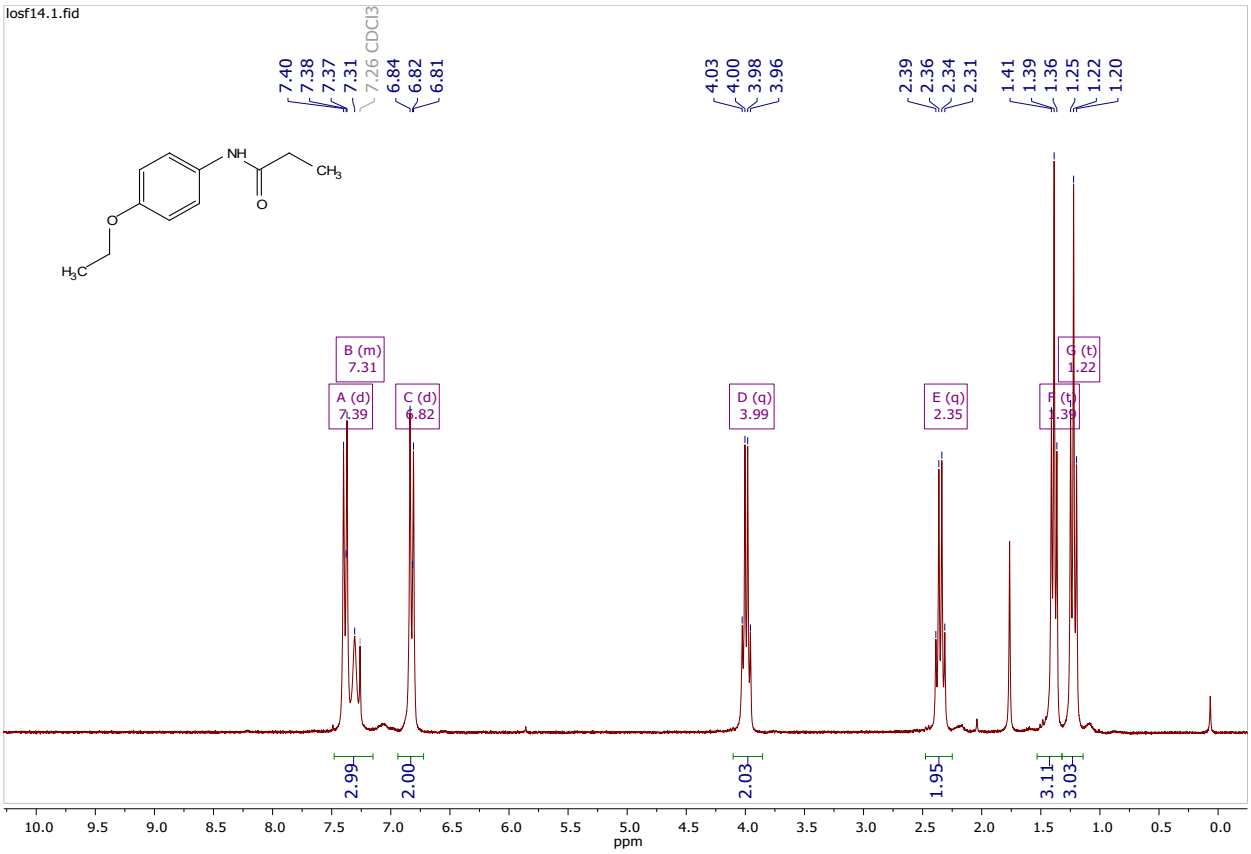
^{1}H NMR (300 MHz) spectrum of *(E)-N-(p*-styrylphenyl)propionamide **(3j)** in $CDCl_3$.



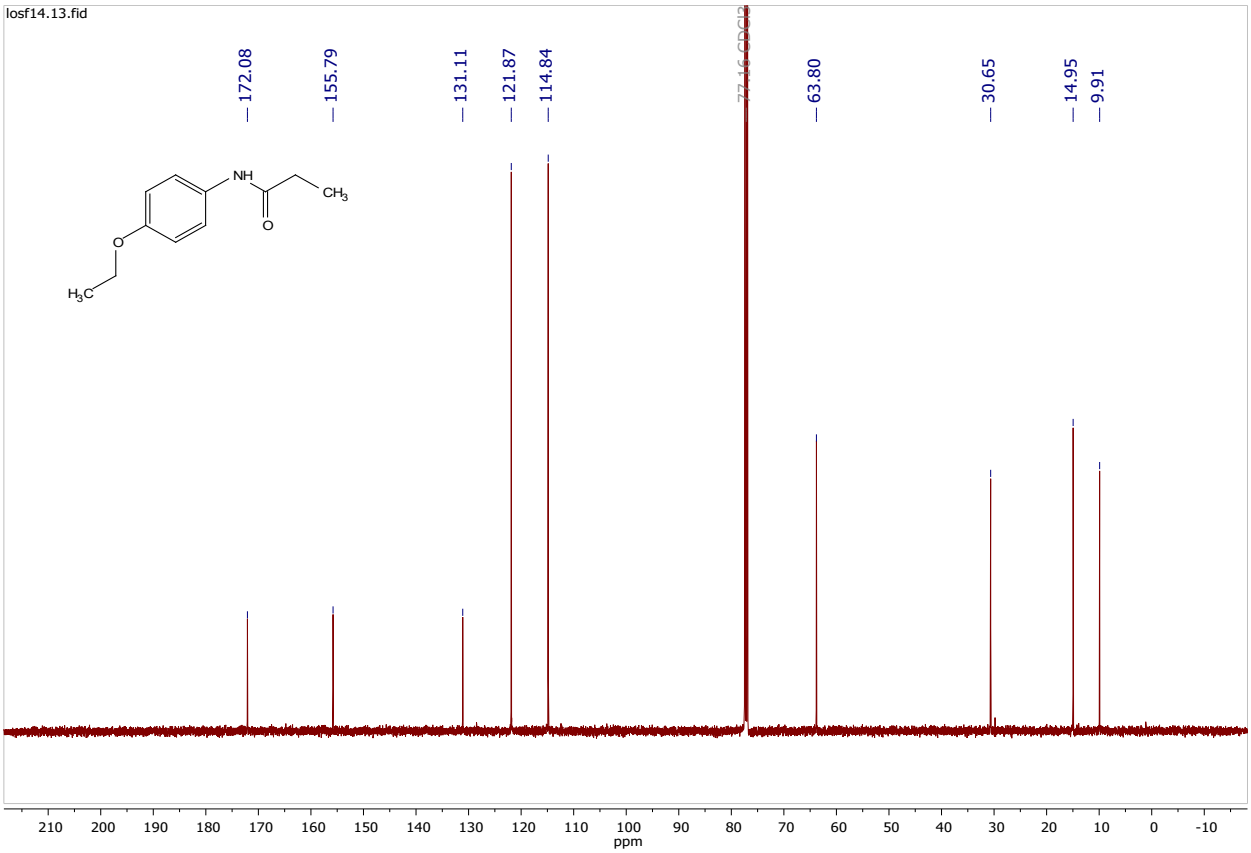
^{13}C{^{1}H} NMR (126 MHz) spectrum of *(E)-N-(p*-styrylphenyl)propionamide **(3j)** in $CDCl_3$.



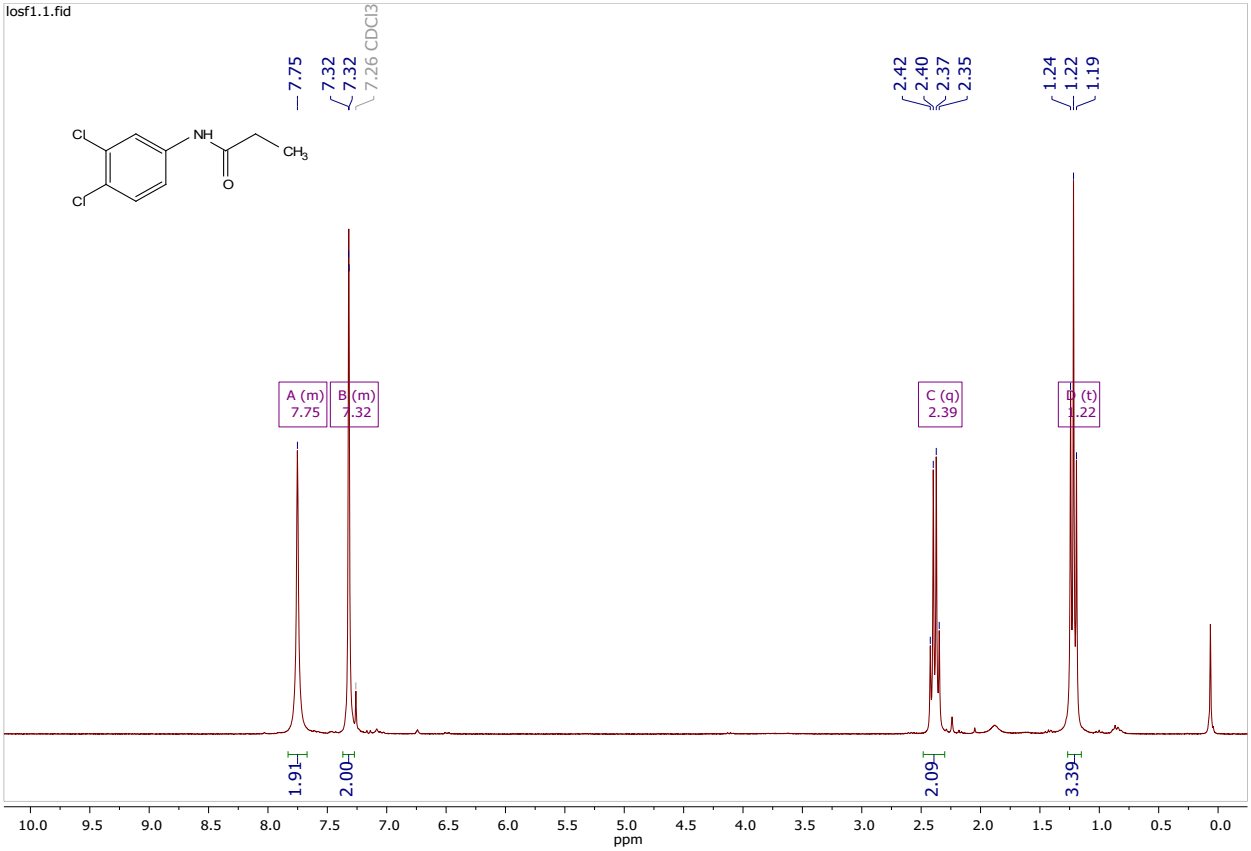
^{1}H NMR (300 MHz) spectrum of *N*-(*p*-ethoxyphenyl)propionamide **(3k)** in $CDCl_3$.



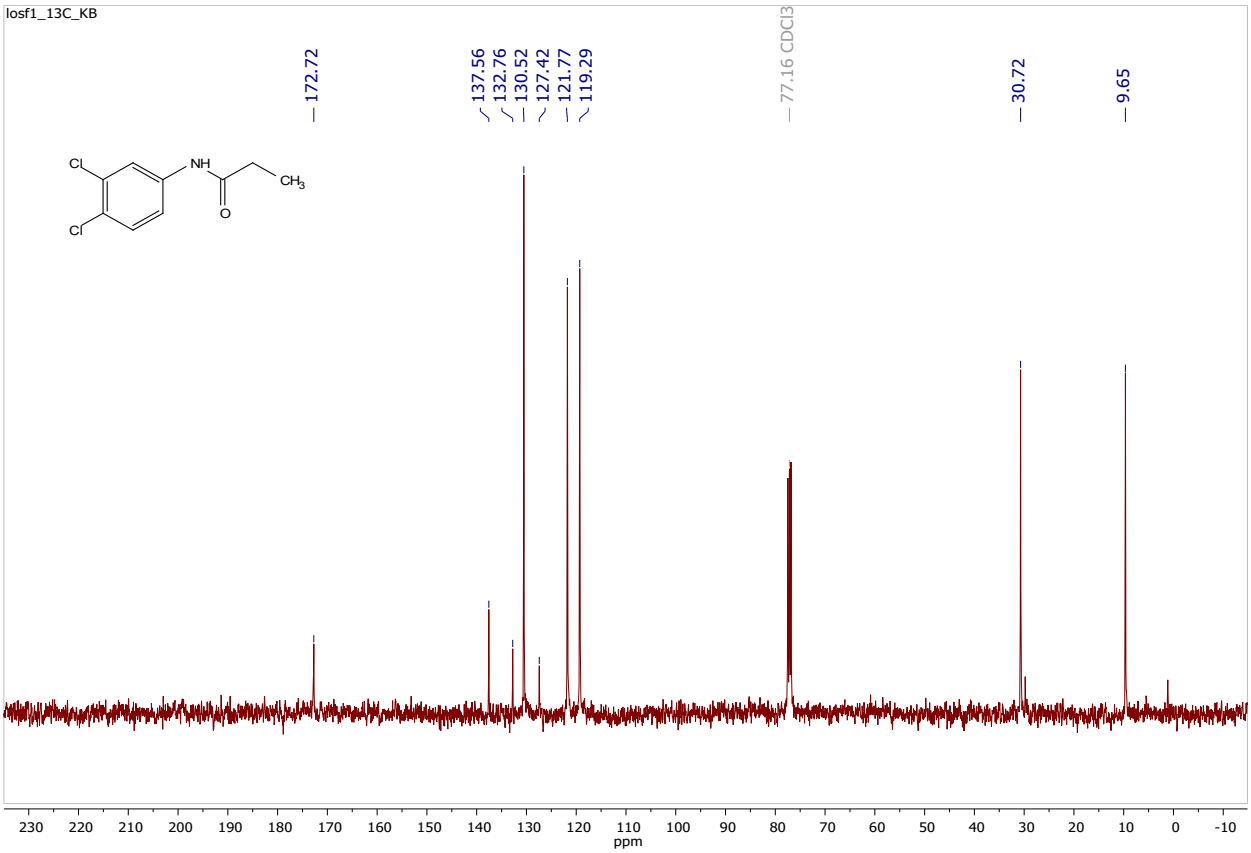
^{13}C{^{1}H} NMR (126 MHz) spectrum of *N*-(*p*-ethoxyphenyl)propionamide **(3k)** in $CDCl_3$.



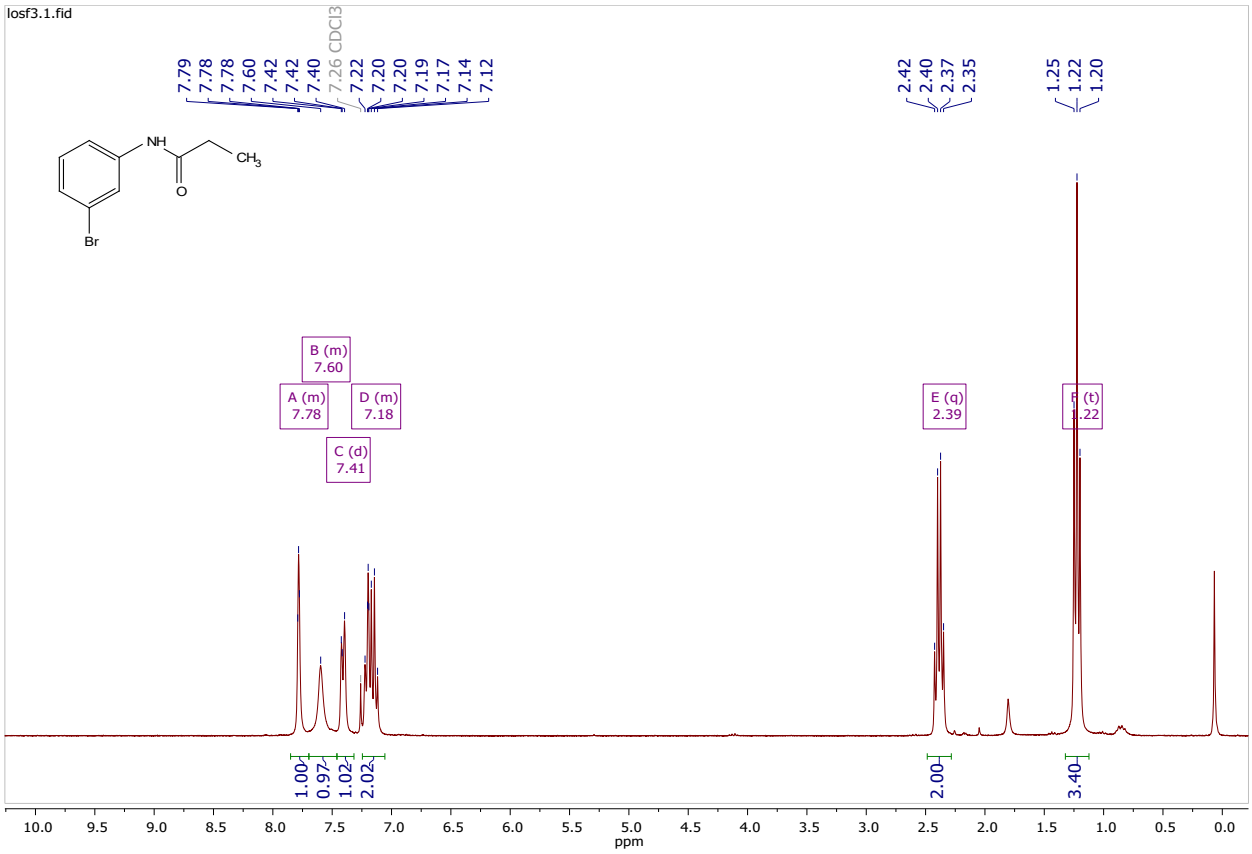
^{1}H NMR (300 MHz) spectrum of *N*-(3,4-dichlorophenyl)propionamide **(3l)** in $CDCl_3$.



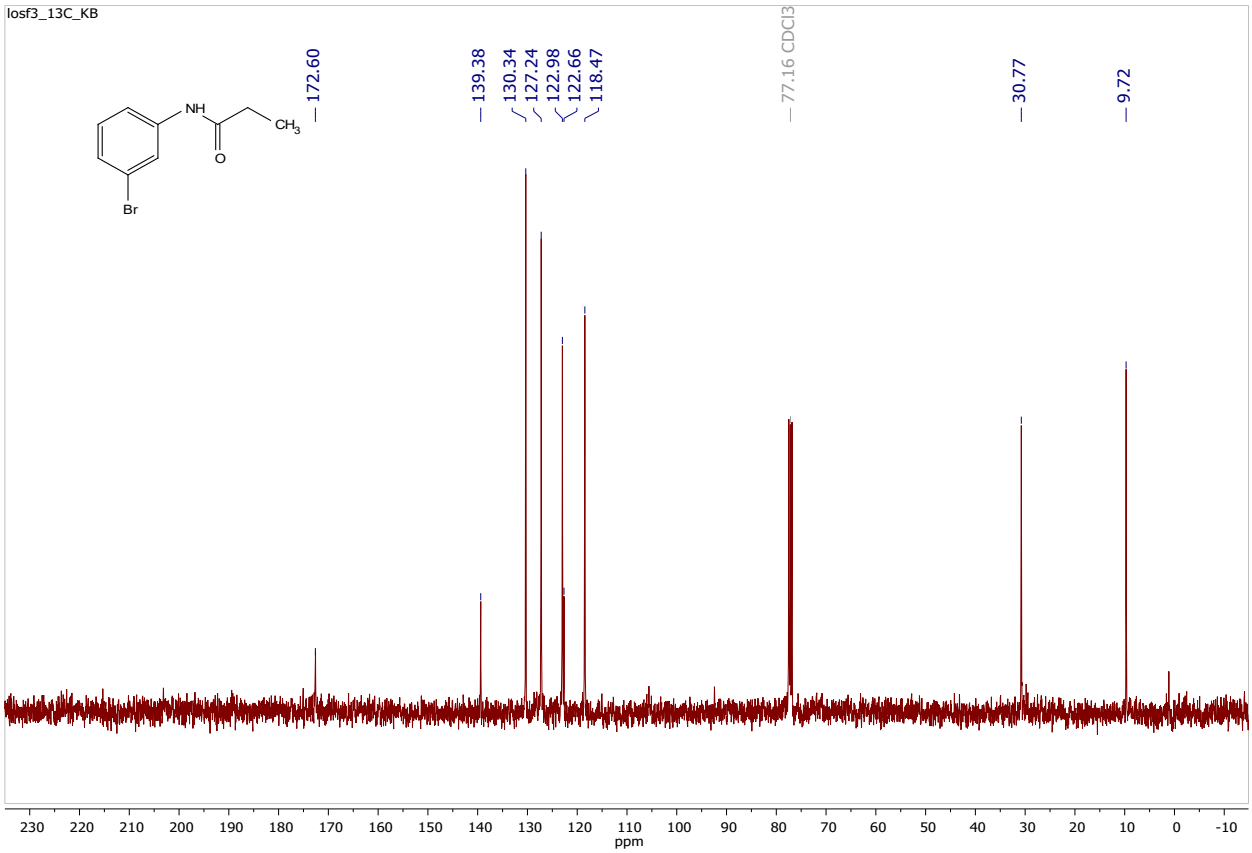
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-(3,4-dichlorophenyl)propionamide **(3l)** in $CDCl_3$.



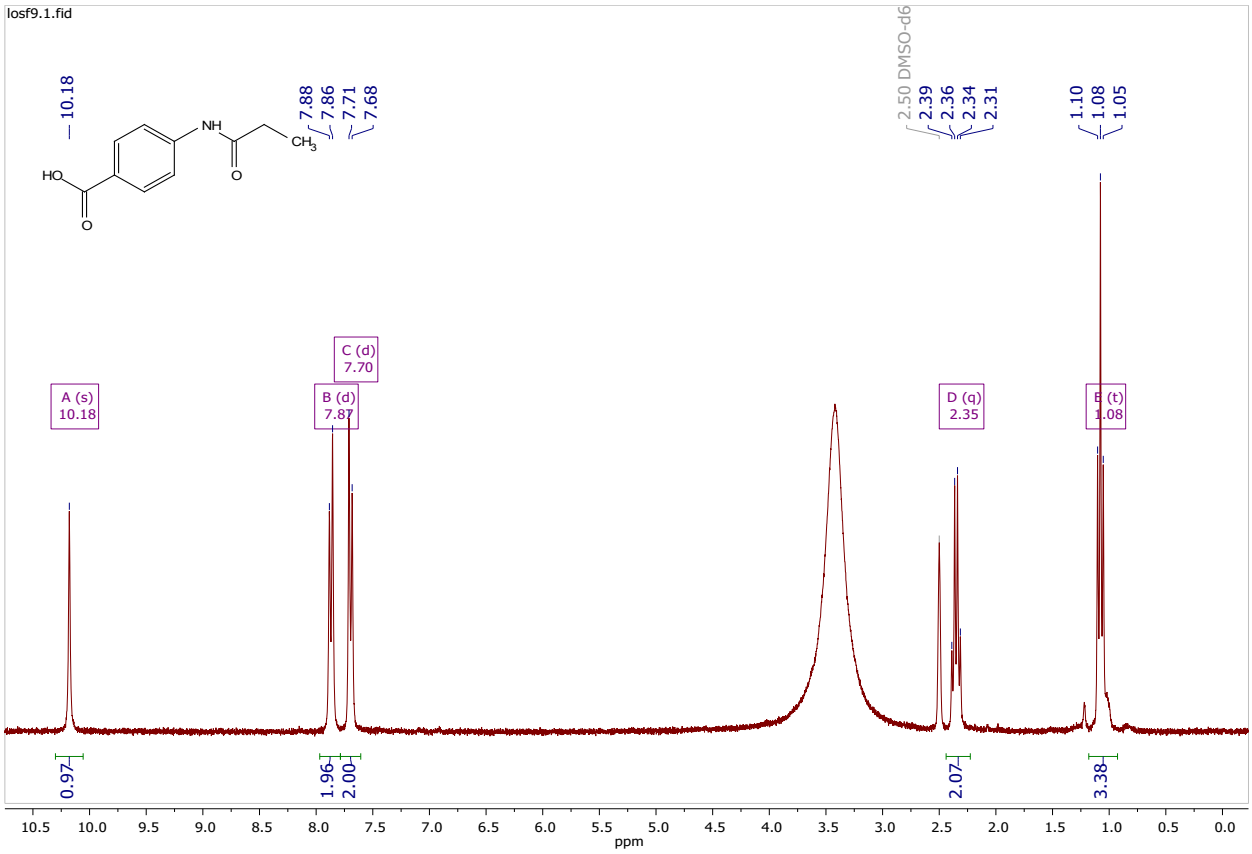
^{1}H NMR (300 MHz) spectrum of *N*-(*m*-bromophenyl)propionamide **(3m)** in $CDCl_3$.



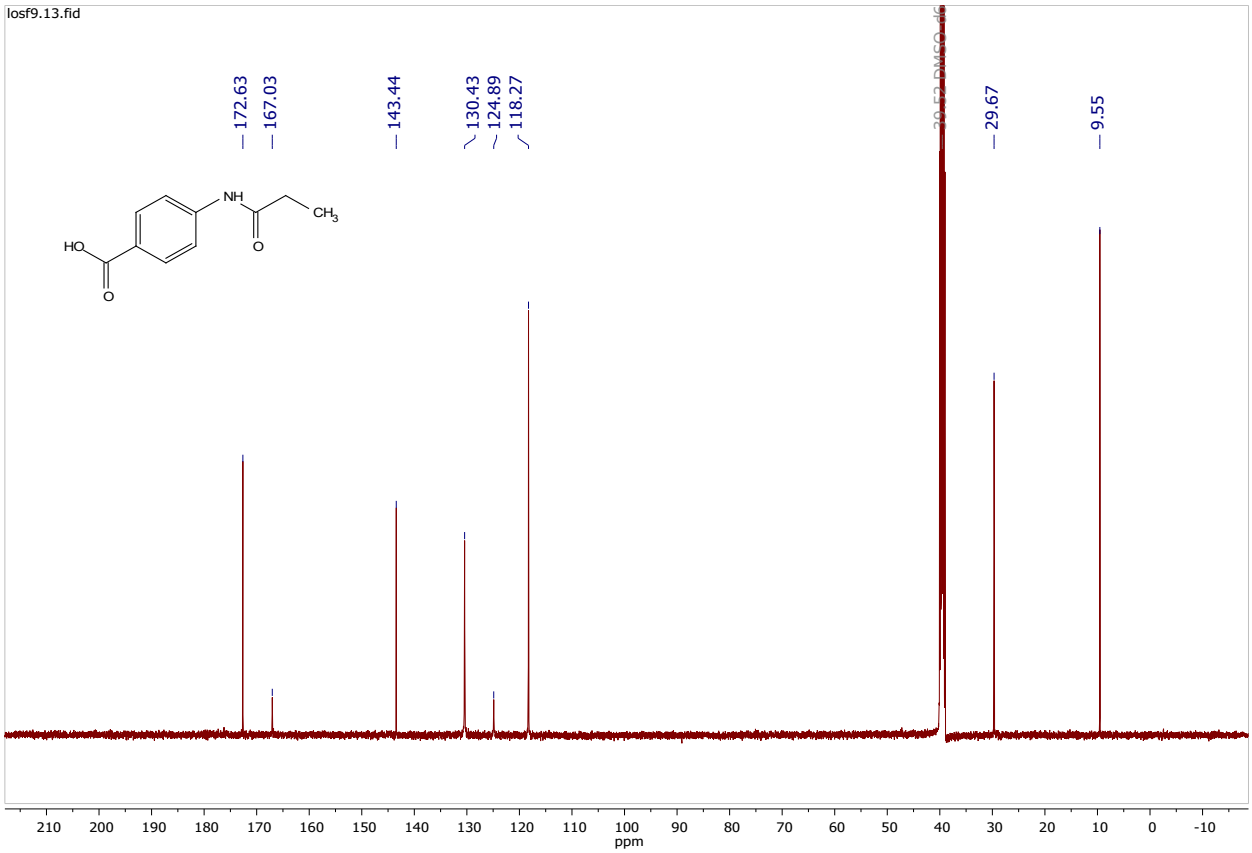
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-(*m*-bromophenyl)propionamide **(3m)** in $CDCl_3$.



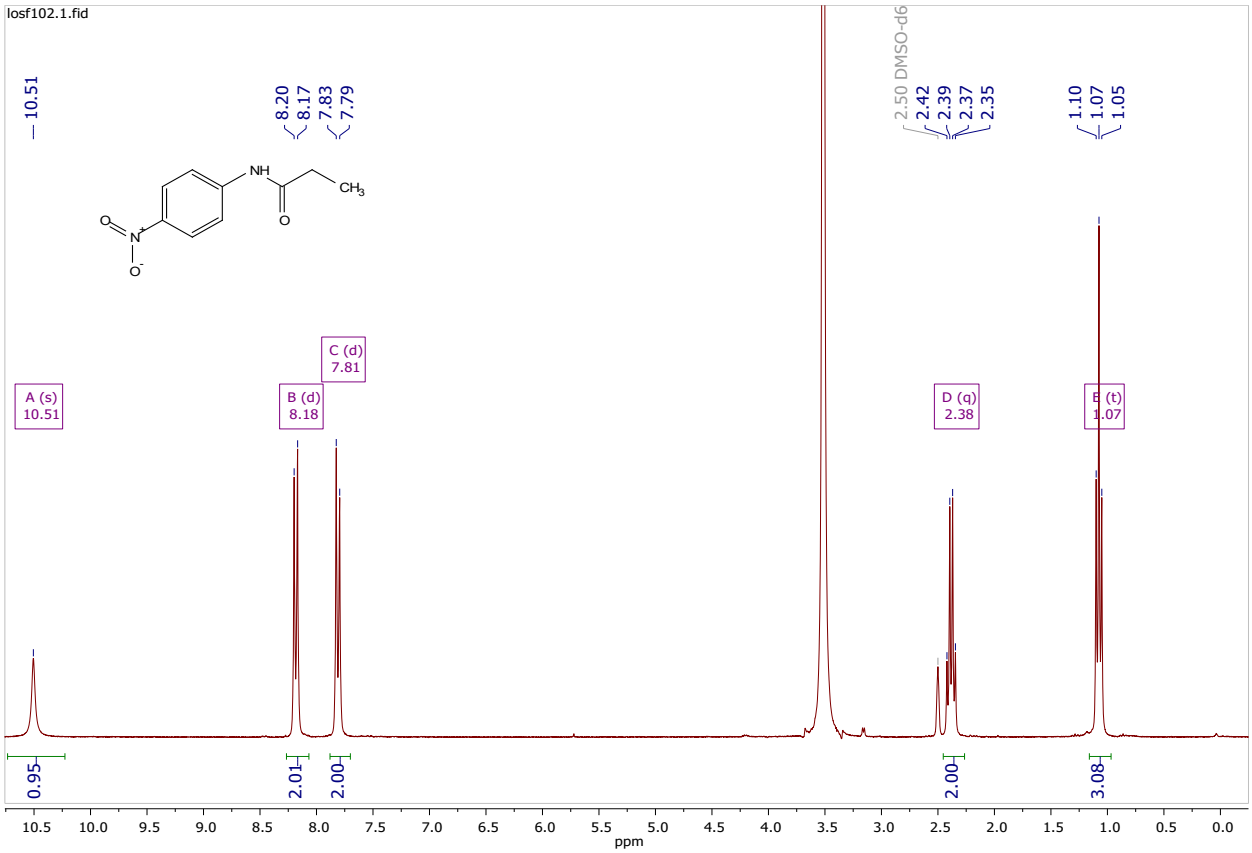
^{1}H NMR (300 MHz) spectrum of *p*-propionamidobenzoic acid **(3n)** in DMSO-d6.



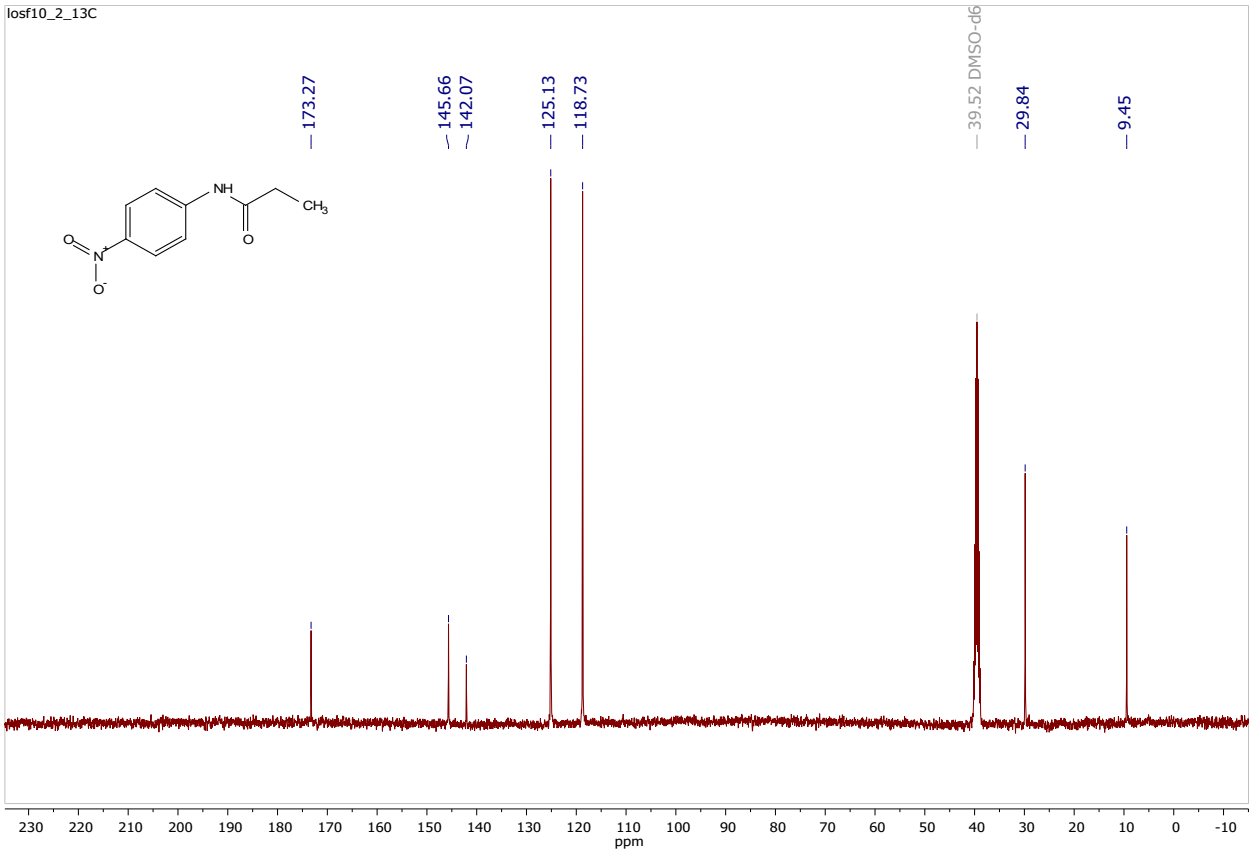
^{13}C{^{1}H} NMR (126 MHz) spectrum of *p*-propionamidobenzoic acid **(3n)** in DMSO-d6.



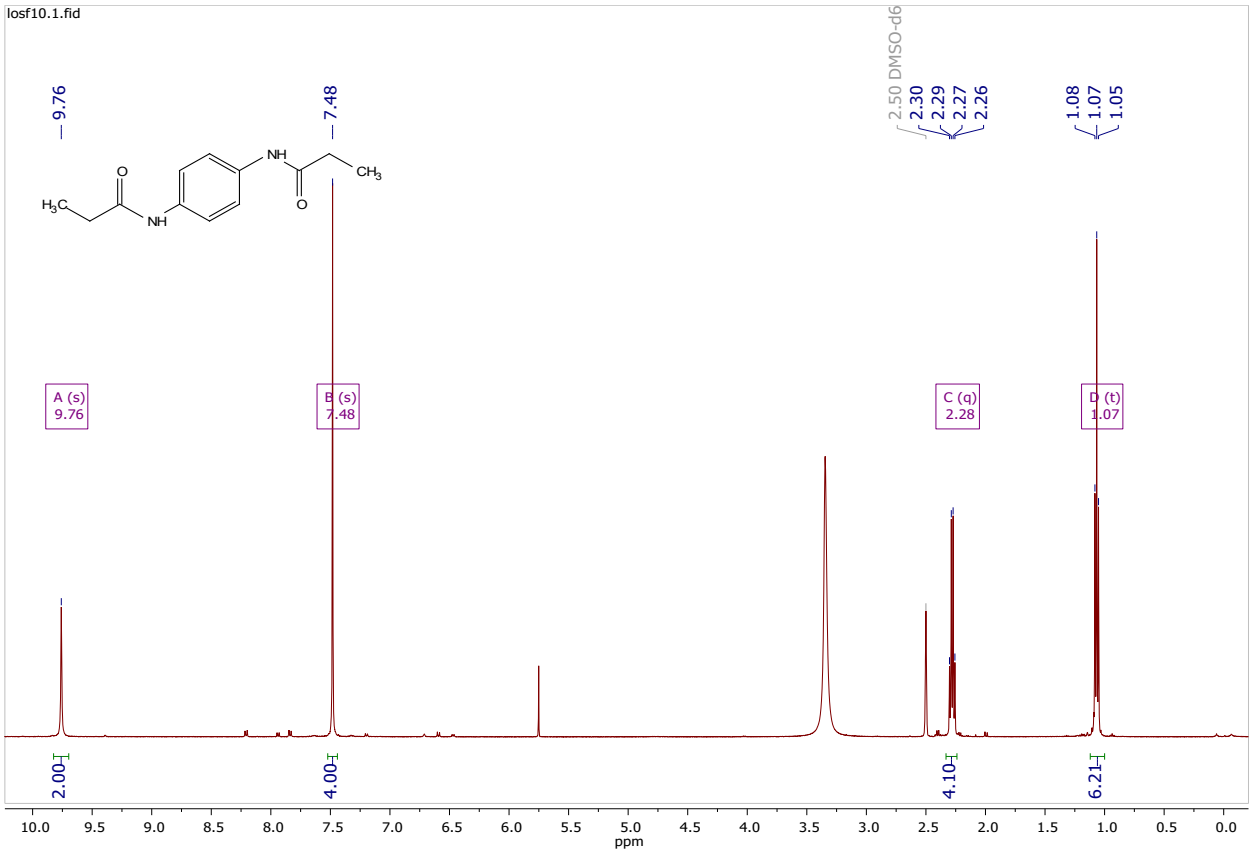
^{1}H NMR (300 MHz) spectrum of *N*-(*p*-nitrophenyl)propionamide **(3o)** in DMSO-d6.



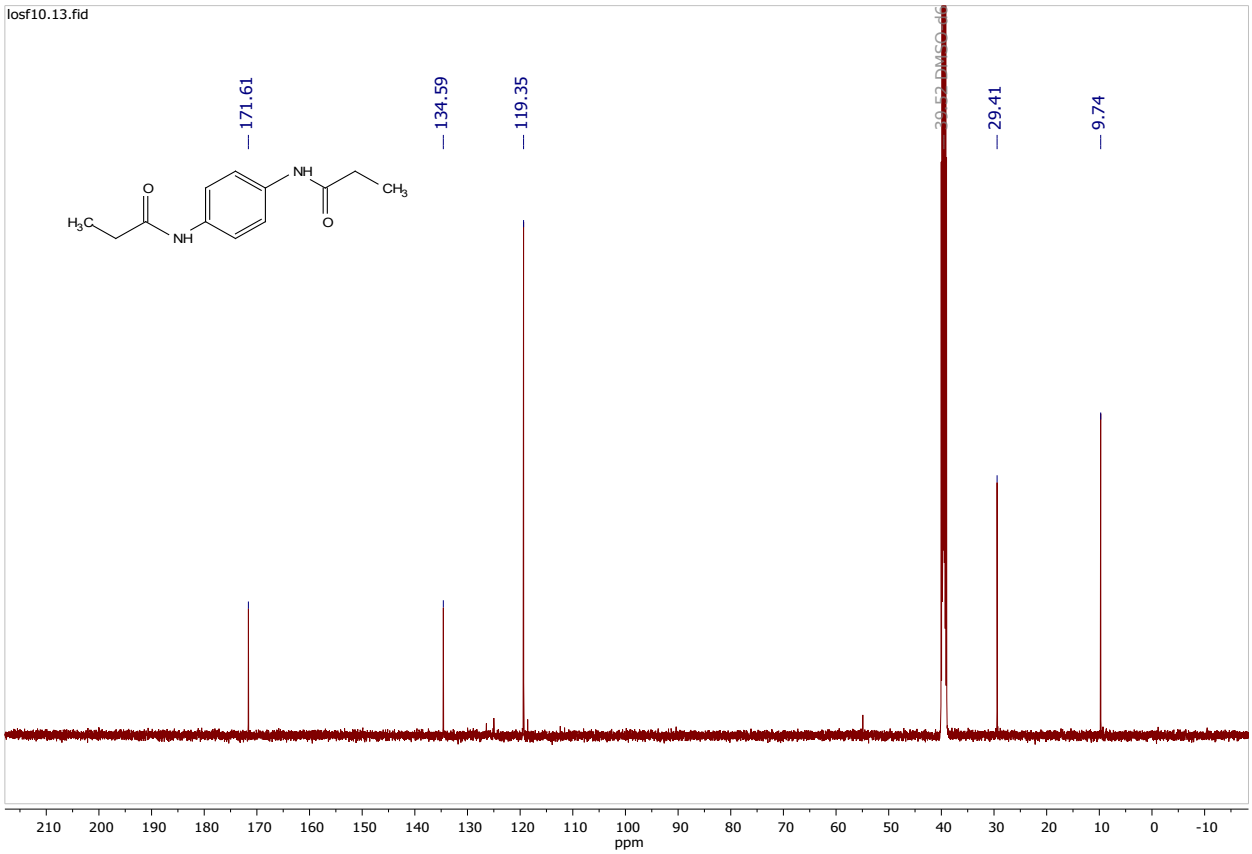
^{13}C{^{1}H} NMR (101 MHz) spectrum of *N*-(*p*-nitrophenyl)propionamide **(3o)** in DMSO-d6.



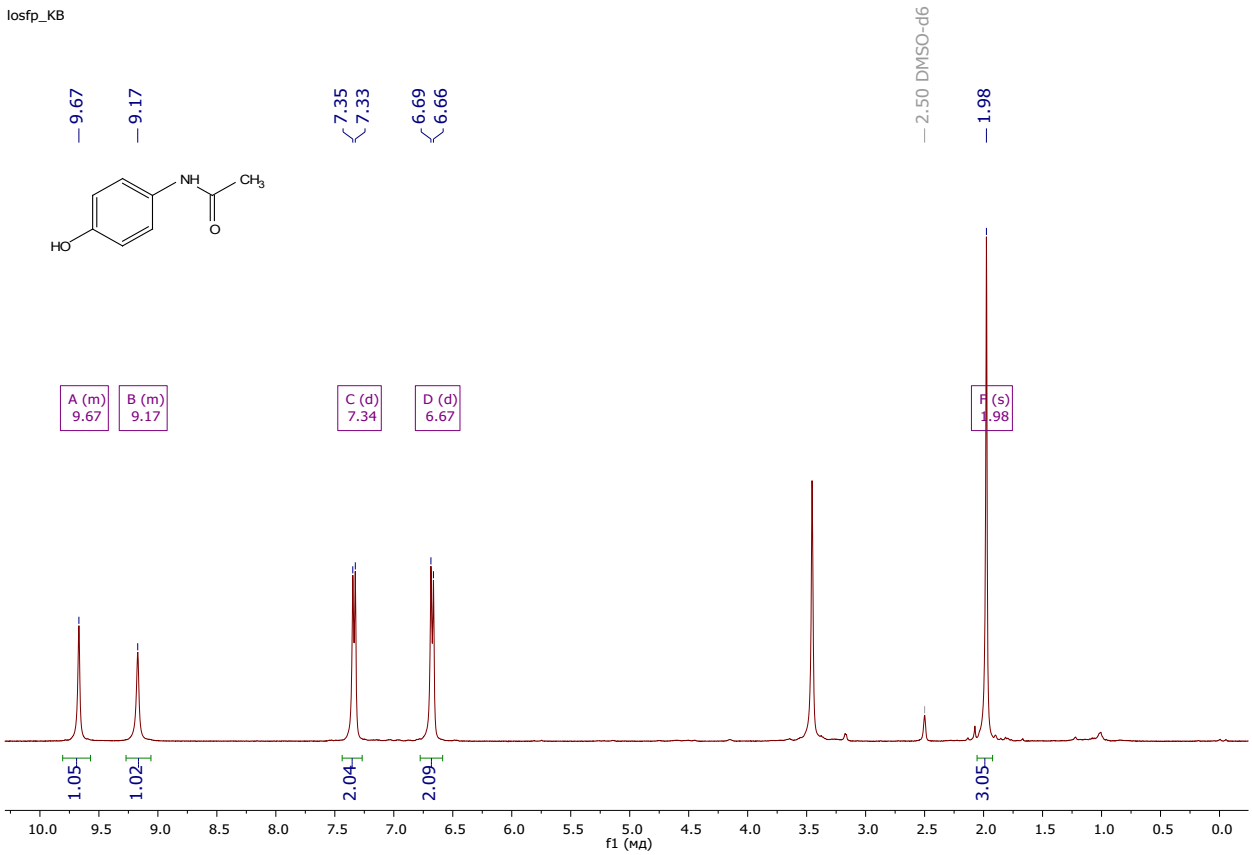
^{1}H NMR (500 MHz) spectrum of *N,N′*-(1,4-phenylene)dipropionamide **(3p)** in DMSO-d6.



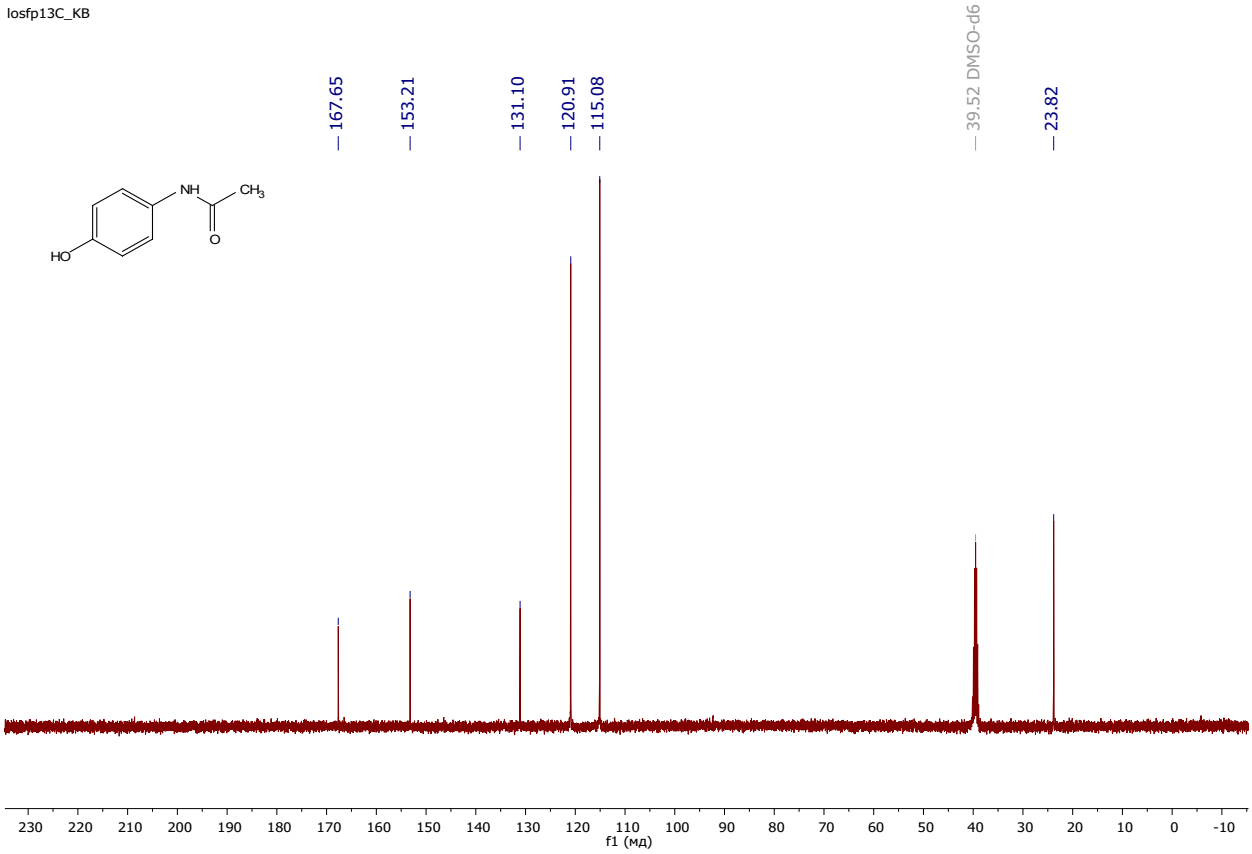
^{13}C{^{1}H} NMR (126 MHz) spectrum of *N,N′*-(1,4-phenylene)dipropionamide **(3p)** in DMSO-d6.



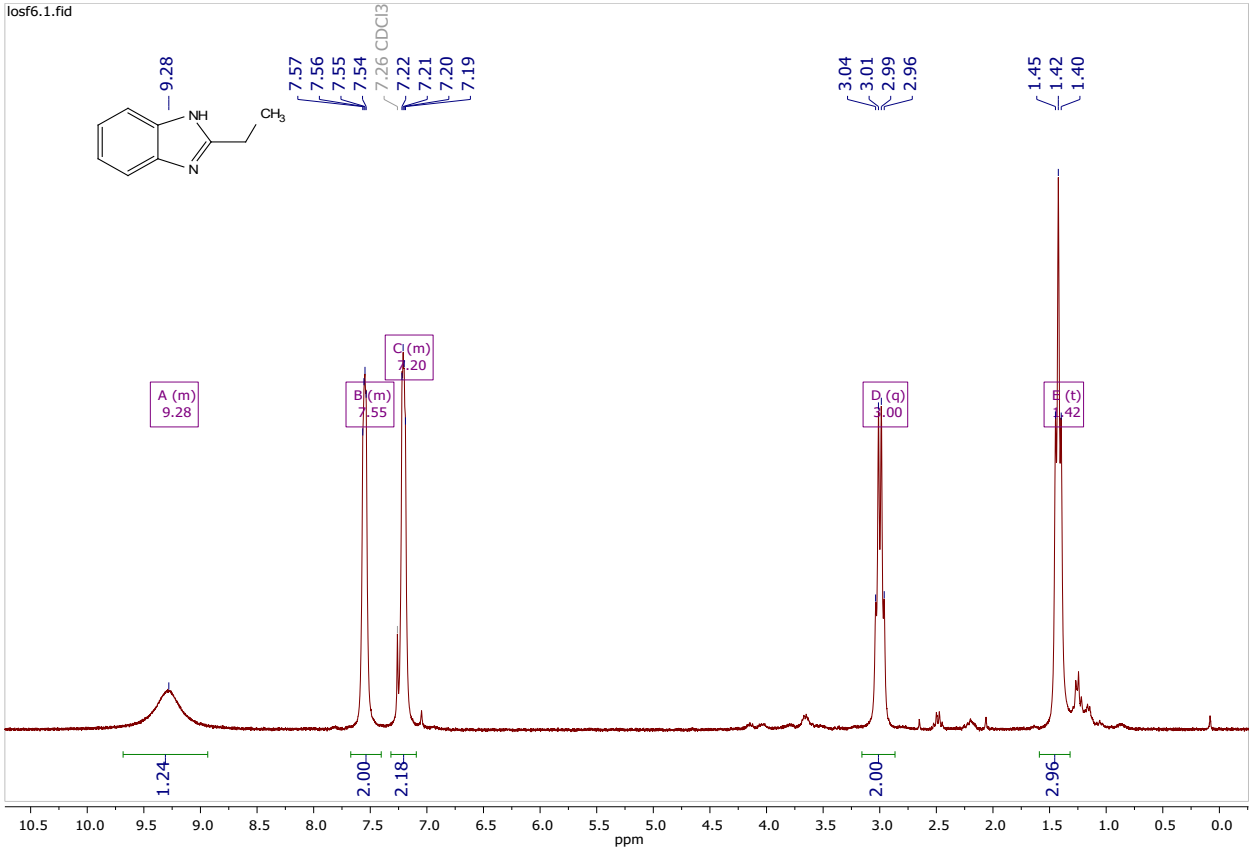
^{1}H NMR (400 MHz) spectrum of *N*-(4-hydroxyphenyl)acetamide **(3q)** in DMSO-d6.



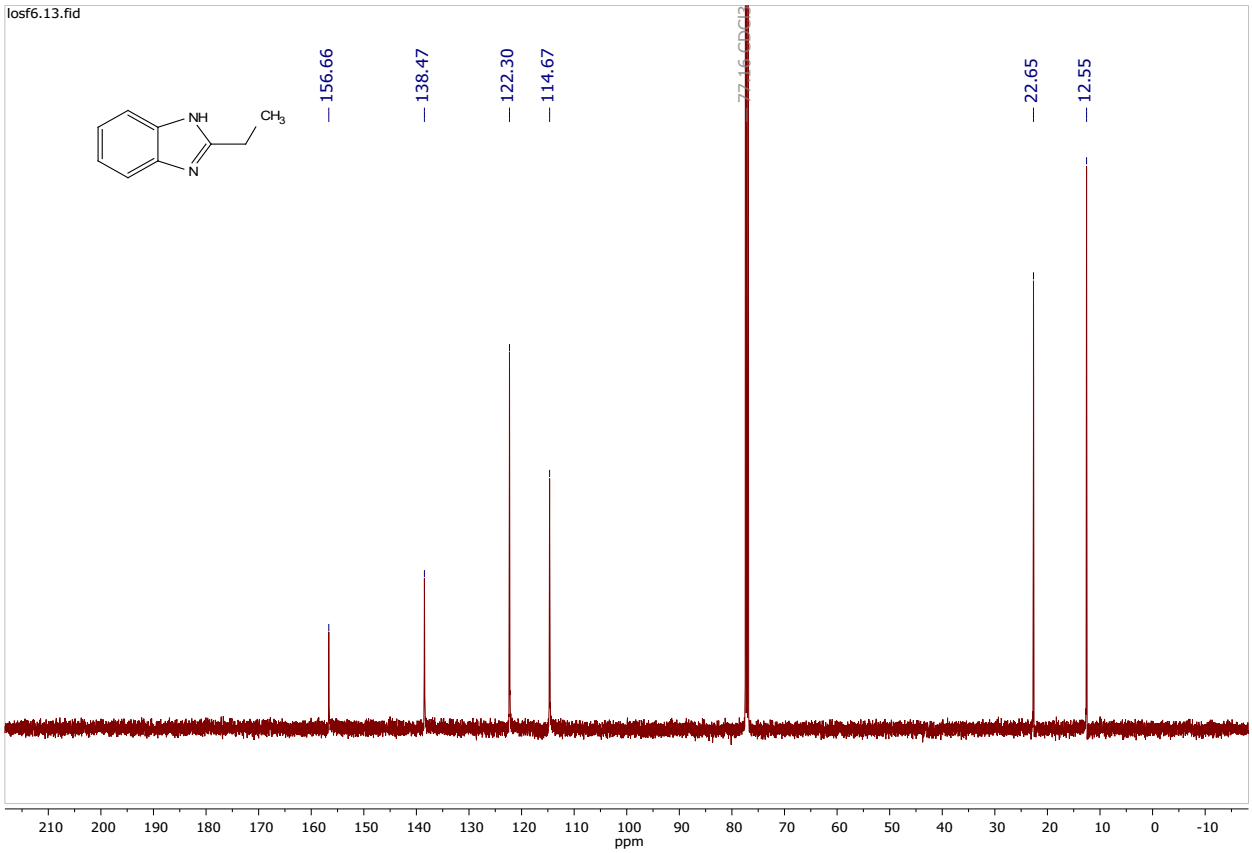
^{13}C{^{1}H} NMR (100 MHz) spectrum of *N*-(4-hydroxyphenyl)acetamide **(3q)** in DMSO-d6.



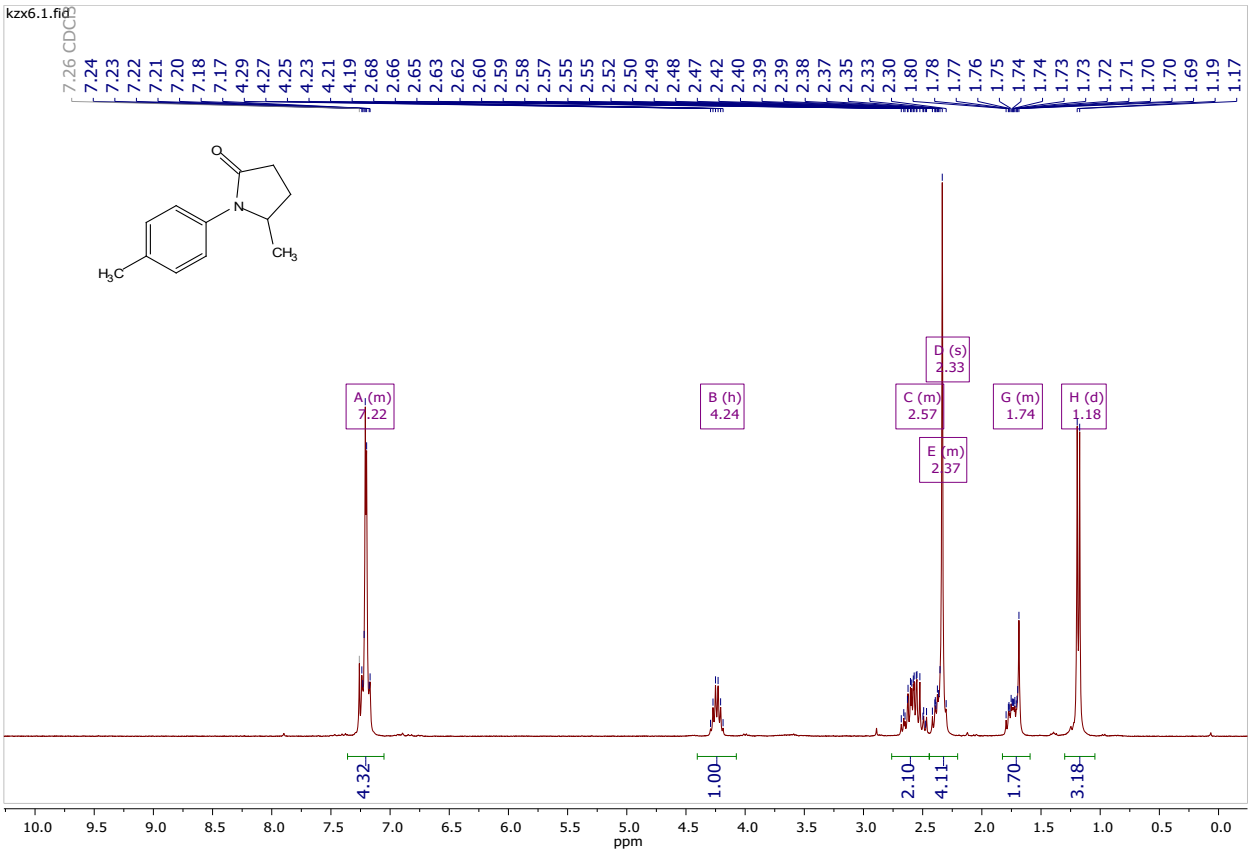
^{1}H NMR (300 MHz) spectrum of 2-ethyl-1*H*-benzo[d]imidazole **(4a)** in $CDCl_3$.



^{13}C{^{1}H} NMR (126 MHz) spectrum of 2-ethyl-1*H*-benzo[d]imidazole **(4a)** in $CDCl_3$.



^{1}H NMR (300 MHz) spectrum of 5-methyl-1-(*p*-tolyl)pyrrolidin-2-one **(4b)** in $CDCl_3$.



^{13}C{^{1}H} NMR (126 MHz) spectrum of 5-methyl-1-(*p*-tolyl)pyrrolidin-2-one **(4b)** in $CDCl_3$.