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Hayashi ligand-based rhodium complex in carbon monoxide and molecular hydrogen-assisted reductive amination

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Contents

1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification, THF was distilled over sodium/benzophenone. DCM was washed with conc H_2SO_4, water, dried over Na_2SO_4 and then distilled from CaH_2 under Ar and stored with MS 3Å for no more than a week.

^{1}H spectra were recorded in $CDCl_3$, DMSO-d_6 and D_2O on Bruker Avance 300, Bruker Avance 400 and Varian Inova-400 spectrometers; ^{13}C spectra were recorded in $CDCl_3$ and DMSO-d_6 on Bruker Avance 400 and Varian Inova-400 spectrometers at 101 MHz or on Bruker Avance 300 at 75 MHz. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively) or DMSO (2.50 and 39.52 ppm for ^{1}H and ^{13}C respectively). Chemical shifts δ are reported in ppm relative to the solvents resonance signal as an internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz).

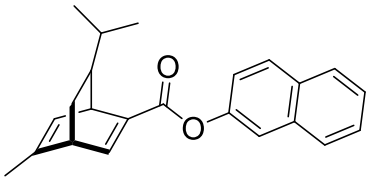
Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 Gas Chromatograph fitted with a flame ionization detector (He was used as carrier gas, 37 mL/min) and MS detector. Injections were made on a Chromatec CR-5 and Chromatec CR-5MS (30 meter) capillary column. The injector temperature was 250 °C, the FID temperature was 250 °C, with a split ratio of 50:1. Column compartment temperature program: 60°C for 4 min, 60°C → 250°C at 30°C/min, 250°C for 10 min. MSD parameters: ion source temperature 200°C, transfer line temperature 230°C. Retention times (t_R) and integrated ratios were obtained using Chromatec Analytic Software.

Chiral HPLC analyses were performed using HPLC equipped with Daicel Chiralpak IA-3 column (4.6 × 150 mm) and diode array detector.

2. Experimental section

Preparation of complexes 4a,b

2-Naphthyl (1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate (1)

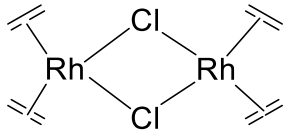


was synthesized according to the literature procedure[S1]

To a solution of (*R*)-α-phellandrene (~65% chemical purity, 2.16 ml, 8.7 mmol) and 2-naphthyl propiolate (1.55 g, 7.9 mmol) in CH_2Cl_2 (30 ml), Me_2AlCl (1.0 M in hexane, 7.92 ml, 7.9 mmol) was added slowly at –78 °C. The resulting orange solution was kept in the cold bath and slowly warmed up to room temperature. After stirring for 18 h, the solution was carefully poured into a vigorously stirred, ice-cooled aqueous solution of 1N HCl (40 ml). The mixture was filtered and the filter cake was washed with dichloromethane (15 ml). The filtrate was then extracted with dichloromethane (3x15 ml). The combined organic extracts were washed with brine (40 ml), dried over $MgSO_4$, filtered, and concentrated under vacuum. NMR yield is 59%. The residue was purified by flash chromatograph InterChim PuriFlash and the following elution was applied: isocratic hexane:EtOAc 98:2 for 10 min., gradient hexane:EtOAc 98:2 → 97:3 for 1 min, isocratic hexane:EtOAc 97:3 for 10 min., gradient hexane:EtOAc 97:3 → 96:4 for 1 min, isocratic hexane:EtOAc 96:4 for 10 min. to give 1.42 g of a mixture of the product **1** and 2-naphthyl (*E*)-3-(5-isopropyl-2-methylidenecyclohex-3-enyl)propenoate in a ratio of 93 to 7. The product was crystallized from a mixture of DCM:hexane = 1:20 in a refrigerator overnight. The crystals were collected by filtration and washed with ice-cooled hexane (5 ml), and then dried under vacuum to give 1.14 g of the product (3.4 mmol, 43% yield) as white needles.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 (m appear as d, J = 9.0 Hz, 2H), 7.80 (d, J = 8.7 Hz, 1H), 7.58 – 7.61 (m, 2H), 7.52 – 7.42 (m, 2H), 7.31 – 7.23 (m, 1H), 5.90 (d, J = 5.6 Hz, 1H), 4.22 (m appear as d, J = 6.1 Hz, 1H), 3.51 – 3.49 (m, 1H), 1.88 (d, J = 1.8 Hz, 3H), 1.70 – 1.65 (m, 1H), 1.36 – 1.24 (m, 1H), 1.10 – 1.20 (m, 1H), 1.14 – 1.00 (m, 4H), 0.87 (d, J = 6.4 Hz, 3H). NMR spectra are in agreement with the literature data.[S1]

Di-μ-chloro-tetrakis(ethene)dirhodium(I)

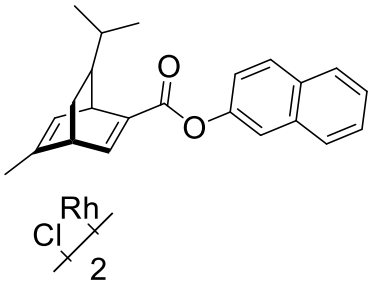


Was synthesized according to the literature procedure.[S2]

"Rhodium trichloride trihydrate" (2.40 g, 9.12 mmol of Rh) is dissolved in water (4 ml) by warming on a steam bath in a round-bottomed flask containing a Teflon-covered magnetic stirring bar, then methanol (50 ml) was added. The flask is freed of oxygen by alternately evacuating (water pump) and repressuring with ethylene to 1 atm. The methanolic solution is stirred at room temperature under ethene at a pressure of about 1.1 atm (balloon). The product begins to precipitate as a finely divided solid after about an hour. It usually has the color of dichromate but occasionally is dark-rust-colored. After about 7 h, it is collected by filtration under vacuum on a sintered-glass funnel. It is best to decant most of the liquid before

transferring the solid to the filter, because the product is sometimes so finely divided that filtration is slow. One should avoid drawing air through the solid. The product is washed with about methanol (ca. 20 ml) and dried on rotary evaporator at room temperature. The yield is 1.45 g (35%). The formed precipitate was introduced as is in the following step.

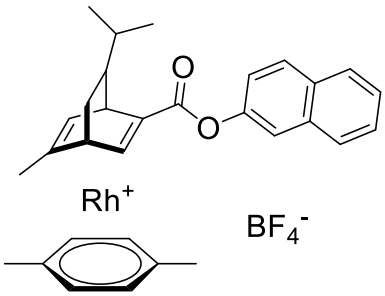
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene]rhodium(I) chloride (3)



Di-μ-Chloro-tetrakis(ethene)dirhodium(I) (410 mg, 0.91 mmol) and 2-naphthyl (1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate **1** (638 mg, 1.92 mmol) were placed in a dry Schlenk tube under argon with a magnetic stirring bar. Then, dry DCM (5 ml) was added, the solution was stirred for an hour. The stopcock of the Schlenk tube was kept open on an argon line to allow the forming ethylene to leave the reaction vessel. In an hour, the transparent solution was slowly dripped to pentane (20 ml), a bright yellow precipitate that formed immediately was centrifuged and washed with pentane (2x5 ml). The solid was dried in vacuum to afford 716 mg (0.76 mmol, 83% yield) of the product as a bright yellow powder.

^{1}H NMR (300 MHz, Chloroform-d) δ 7.77 – 7.54 (m, 4H), 7.41 – 7.25 (m, 2H), 7.27 – 7.20 (m, 1H), 4.77 (d, J = 5.9 Hz, 1H), 4.38 (d, J = 6.1 Hz, 1H), 4.22 – 4.14 (m, 1H), 3.56 (d, J = 5.9 Hz, 1H), 1.61 (br s, 3H), 1.46 – 1.21 (m, 2H), 1.05 – 0.90 (m, 4H), 0.87 – 0.75 (m, 4H).
NMR spectra are in agreement with the literature data.[S1]

[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene]-(*p*-xylene)rhodium(I) tetrafluoroborate (4a)

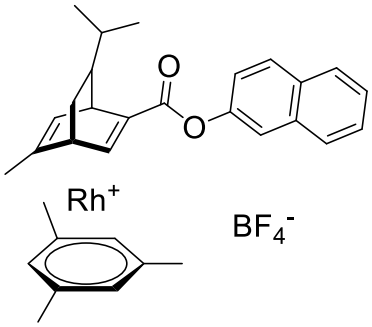


Silver tetrafluoroborate (48.5 mg, 0.25 mmol) and [(1*R*,4*R*,7*R*)-7-isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene]rhodium(I) chloride **3** (117.0 mg, 0.13 mmol) were placed in a dry Schlenk tube under argon with a magnetic stirring bar. Then, dry $MeNO_2$ (2 ml) and dry DCM (1 ml) were added, followed by *p*-xylene (2 ml), the solution was stirred for 3 h, and the formed white powder of silver chloride was centrifuged. The organic fractions were slowly dropped to pentane (10 ml) to form the complex as a yellow precipitate. The precipitate was centrifuged and dried in vacuum to afford 111 mg (0.18 mmol, 71% yield) of the product as a yellow powder. 15 mg of the powder was dissolved in dry $CDCl_3$ under argon and its NMR

spectrum was registered. The compound is sensitive to moisture and even under these conditions it was unstable; some products of its degradation were observed.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 – 7.81 (m, 3H), 7.71 – 7.64 (br s, 1H), 7.50 (m appears as p, J = 6.3 Hz, 2H), 7.29 (dd, J = 8.9, 2.4 Hz, 1H), 6.70 (d, J = 6.4 Hz, 2H), 6.38 (d, J = 6.4 Hz, 2H), 4.46 (d, J = 6.2 Hz, 1H), 4.23 (d, J = 5.9 Hz, 1H), 3.95 (d, J = 5.9 Hz, 1H), 3.78 – 3.71 (m, 1H), 2.32 (s, 6H), 1.72 (s, 3H), 1.48 – 1.41 (m, 1H), 1.35 – 1.20 (m, 1H), 1.06 – 0.99 (m,1H), 0.94 – 0.87 (m, 4H),4 0.81 (d, J = 6.6 Hz, 3H).

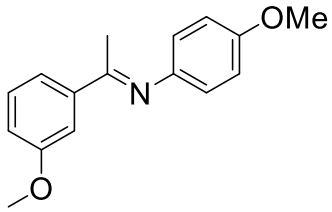
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene]-(mesitylene)rhodium(I) tetrafluoroborate (4b)



Silver tetrafluoroborate (328.6 mg, 1.69 mmol), [(1*R*,4*R*,7*R*)-7-isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene]rhodium(I) chloride **3** (720.0 mg, 0.77 mmol) were placed in a dry Schlenk tube under argon with a magnetic stirring bar. Then, dry DCM (15 ml) was added, followed by mesitylene (321 μl, 2.30 mmol), the solution was stirred for 3 hours, the formed white powder of silver chloride was centrifuged and washed with DCM (2x5 ml). The combined organic fractions were concentrated on a rotary evaporator down to 10 ml and slowly dripped to pentane (40 ml) to form the product as a yellow precipitate. In some cases, the product appeared as yellow oil, and to make it solid, the small drops of oil were triturated in pentane with a spatula until it solidified. The precipitate was centrifuged and dried in vacuum to afford 809 mg (1.26 mmol, 82% yield) of the product.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 – 7.81 (m, 3H), 7.71 (d, J = 2.3 Hz, 1H), 7.51 (m appears as pd, J = 6.9, 1.5 Hz, 2H), 7.30 (dd, J = 8.9, 2.3 Hz, 1H), 6.45 (s, 3H), 4.29 – 4.17 (m, 2H), 4.01 (d, J = 5.9 Hz, 1H), 3.77 (br s, 1H), 2.36 (s, 9H), 1.76 (s, 3H), 1.43 (m appears as ddd, J = 13.7, 10.0, 3.2 Hz, 1H), 1.28 (m appears as dt, J = 14.1, 7.1 Hz, 1H), 1.03 (m appears as q, J = 8.8, 8.1 Hz,1H), 0.93 – 0.87 (m, 4H), 0.81 (d, J = 6.6 Hz, 3H).

1-(3-Methoxyphenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (9)



4-Methoxyaniline (4.040 g, 32.84 mmol), 1-(3-methoxyphenyl)ethan-1-one (4.255 ml, 31.20 mmol, 0.95 equiv.), dry DCM (32 ml), and 4 Å MS (250 mg) of were placed in a round-bottom flask and stirred at room temperature overnight. In 12 hours, the solution was filtered through a layer of silica gel on a fritted glass and evaporated on a rotary evaporator. The obtained residue was dissolved in pentane (40 ml) and cooled in an acetone liquid nitrogen bath, and the formed yellow crystals were dried on a fritted glass to afford 6.780 g (26.6 mmol, yield 81%) of the product.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 (s, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.35 (dd appear as t, J = 7.9 Hz, 1H), 7.01 (dd, J = 8.2, 2.0 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 2.24 (s, 3H).

NMR spectra are in agreement with the literature data.[S3]

Test of the catalytic activity of the 4b in reductive amination

Unless otherwise mentioned all reactions were performed in 10 ml stainless autoclaves.

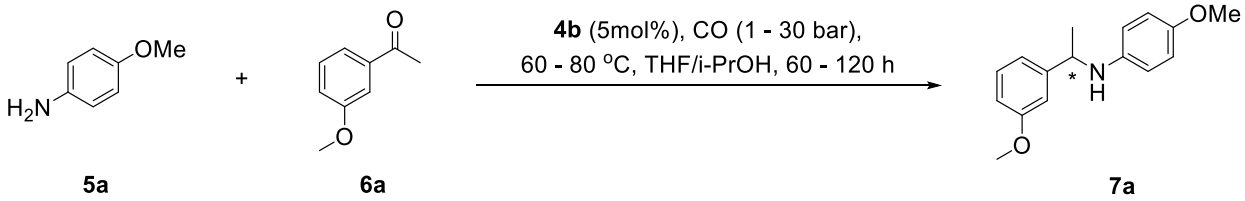
General procedure for a 10 ml autoclave

A glass vial in a 10 ml stainless steel or titanium autoclave was charged with the catalyst **4b** (4 – 5 mol %, 5.0 – 7.8 mg, 0.008 – 0.012 mmol), the corresponding solvent (0.2 ml), amine (4-methoxyaniline **5a** (30.0 mg, 100 mol%, 0.24 mmol) or 2-(piperazin-1-yl)pyrimidine **5b** (29 μl, 100 mol%, 0.20 mmol) or 4-aminobenzoate **5c** (33.0 mg, 100 mol%, 0.20 mmol)) and carbonyl compound [1-(3-methoxyphenyl]ethan-1-one **6a** (133 μl, 400 mol%, 0.98 mmol or 2-phenylpropanal **6b** (108 μl, 400 mol %, 0.80 mmol) or cyclopropyl methyl ketone **6c** (79 μl, 400 mol%, 0.80 mmol)). The autoclave was sealed, flushed three times with 10 atmosphere of converter gas, and then charged with the indicated pressure of converter gas. The reactor was placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. Its content was analyzed using NMR or GC, and the product was isolated using chromatography (preparative TLC, column chromatography on silica gel or using flash chromatograph InterChim PuriFlash).

General procedure for reactions in high-pressure Schlenk tubes

The Schlenk tube was charged a 5 mol % of catalyst **4b** (6.4 mg, 0.010 mmol), 2-(piperazin-1-yl)pyrimidine **5b** (29 μl, 100 mol%, 0.20 mmol), 2-phenylpropanal **6b** (108 μl, 400 mol %, 0.80 mmol), THF (0.2 ml). Then it was cooled with liquid nitrogen, evacuated, and then charged with 1 atm of CO. The Schlenk tube was placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. Its content was analyzed using NMR or GC, and the product was isolated using chromatography (preparative TLC, column chromatography on silica gel or using flash chromatograph InterChim PuriFlash).

Table S1. Catalytic activity of in reductive coupling of amine 5a and ketone 6a

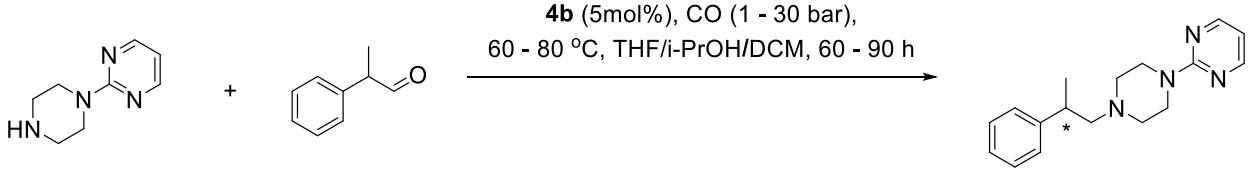


5a **6a** **7a**

Entry	Time (h)	Temperature (°C)	Solvent	Pressure (bar)	NMR yield, %	Isolated yield, %	*ee*
1[a]	60	60	THF	30	9	-	n.d.
3[a,b]	60 + 60	60 => 80	THF	10	84	35	0
4[a,b]	60 + 60	60 => 80	THF	1	6	-	n.d.
5[a,b]	60 + 60	60 => 80	neat	30	83	43	0
6[a,b]	60 + 60	60 => 80	Pr^{i}OH	30	19	19	0

[a] 5 mol % of catalyst **4b** (7.8 mg, 0.012 mmol), 4-methoxyaniline **5a** (30.0 mg, 100 mol%, 0.24 mmol), 1-(3-methoxyphenyl)ethan-1-one **6a** (133 µL, 400 mol %, 0.98 mmol), solvent (0.2 ml). [b] the reaction mixture was heated at 60 °C for 60 hours and then at 80 °C for another 60 hours

Table S2. Catalytic activity of 4b in reductive coupling between amine 5b and aldehyde 6b

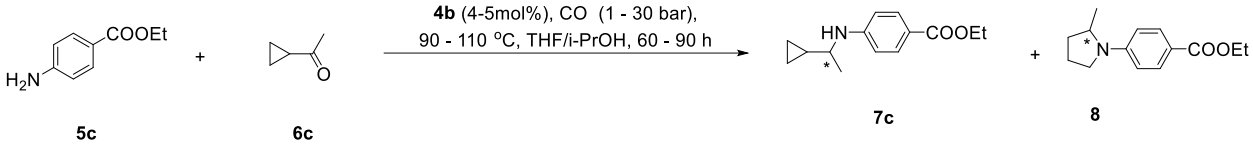


5b **6b** **7b**

Entry	Time (h)	Temperature (°C)	Solvent	Pressure (bar)	GC yield, %	Isolated yield, %	*ee*
1[a]	60	60	THF	30	40	3	0
2[a,b]	60+15	60 => 80	THF	30	90	32	0
3[a,b]	60+15	60 => 80	THF	30	99	20	0
4[a,b]	60+15	60 => 80	THF	1	57	35	0
5[a,b]	60+15	60 => 80	THF	10	91	11	0
6[a,b]	60+15	60 => 80	Pr^{i}OH	30	71	20	0
7[a,b]	60+15	60 => 80	neat	30	52	10	0
8[a,b]	60+15	60 => 80	CH_2Cl_2	30	99	16	0
8[a,b,c]	90	90	THF	1	26	10	0

[a] 5 mol % of catalyst **4b** (6.4 mg, 0.010 mmol), 2-(piperazin-1-yl)pyrimidine **5b** (29 µl, 100 mol%, 0.20 mmol), 2-phenylpropanal **6b** (108 µl, 400 mol %, 0.80 mmol), solvent (0.2 ml), yields were determined by GC
[b] the reaction mixture was heated at 60 °C for 60 hours and then at 80 °C for another 15 hours
[c] the reaction was performed in a high-pressure Schlenk tube

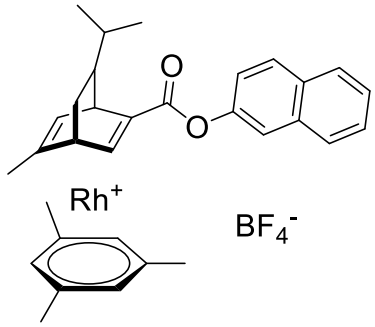
Table S3. Catalytic activity of 4b in reaction between amine 5c and cyclopropyl ketone 6c



Entry	Catalyst loading (mol%)	Time (h)	Temperature (°C)	Solvent	Pressure (bar)	NMR yield **7c**, %	NMR yield **8**, %	Isolated yield **8**, %	*ee*
1	4	60	90	THF	30	0	0	-	-
2	5	90	110	THF	30	0	70	55	0
3	5	90	110	THF	1	0	47	9	0
4	5	90	110	Pr^iOH	30	0	57	57	0

Conditions: 5 mol % of catalyst **4b** (5.0 – 6.4 mg, 0.008 – 0.010 mmol), ethyl 4-aminobenzoate **5c** (33.0 mg, 100 mol%, 0.20 mmol), cyclopropyl methyl ketone **6c** (79 μl, 400 mol %, 0.80 mmol), solvent (0.2 ml).

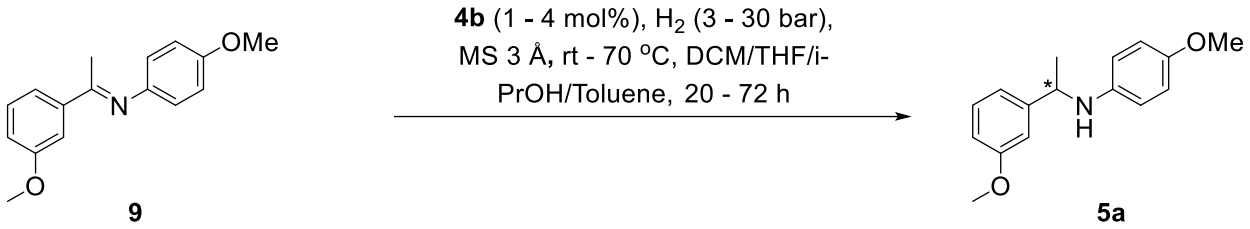
Stability of [(1*R*,4*R*,7*R*)-7-isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)-bicyclo[2.2.2]octa-2,5-diene](mesitylene)rhodium(I) tetrafluoroborate (4b)



Complex **4b** (10.0 mg, 0.016 mmol) was placed in dried Norell valved 5 mm NMR tube for intermediate pressure filled with argon. $CDCl_3$ (0.4 ml) was added and the solution was degassed by freezing the sample with liquid nitrogen and vacuumed (the procedure was repeated three times). Then the NMR tube was filled with 2 atm of CO/H_2, or 1 atm of the air. The tube was placed in preheated oil bath or left at room temperature (see the table). In 20 hours, the tube was cooled down to room temperature and NMR spectrum was registered. The results of the NMR experiments are presented below in the table.

Gas mixture	T (°C)	**4b** (%)	Mesitylene (%)	**1** (%)	Other products
air	90	99	0	0	No
CO	90	0	99	traces	Rhodium black
CO	r.t.	56	30	10	Rhodium black
H_2	90	70	13	0	Rhodium black

Table S4. Catalytic activity of 4b in hydrogenation of Schiff base 9

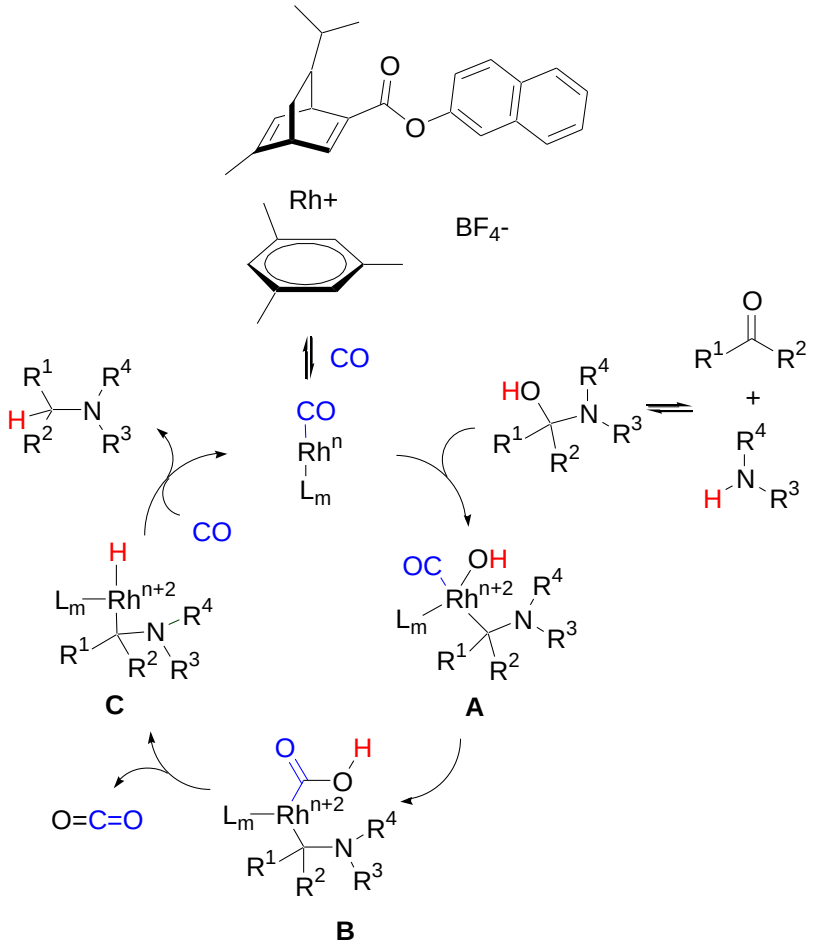


Entry	Time (h)	3 Å MS	Catalyst loading (mol%)	Temperature (°C)	Solvent	Pressure (bar)	NMR yield, %	Isolated yield, %	*ee*
1	65	+	4	90	CH_2Cl_2	5	0	-	n.d.
2	65	+	4	90	THF	5	6	-	n.d.
3	65	+	4	90	Pr^iOH	5	0	-	n.d.
4	65	+	4	90	neat	5	6	-	n.d.
5	65	+	4	90	THF	30	5	-	n.d.
6	65	+	4	110	THF	5	25	10	0
7	65	-	4	90	THF	5	15	5	0
8	20	+	1	70	CH_2Cl_2	3	8,0	-	n.d.
9	20	+	1	70	THF	3	3,0	-	n.d.
10	20	+	1	70	Pr^iOH	3	1,0	-	n.d.
11	20	+	1	70	neat	3	0,0	-	n.d.
12	20	+	1	70	toluene	3	2,0	-	n.d.
13	20	+	1	70	CH_2Cl_2	30	36	-	n.d.
14	20	+	1	70	CH_2Cl_2	60	30	-	n.d.
15	20	+	1	70	CH_2Cl_2	10	43	15	0
16	72	+	1	~ 20	CH_2Cl_2	30	40	10	0

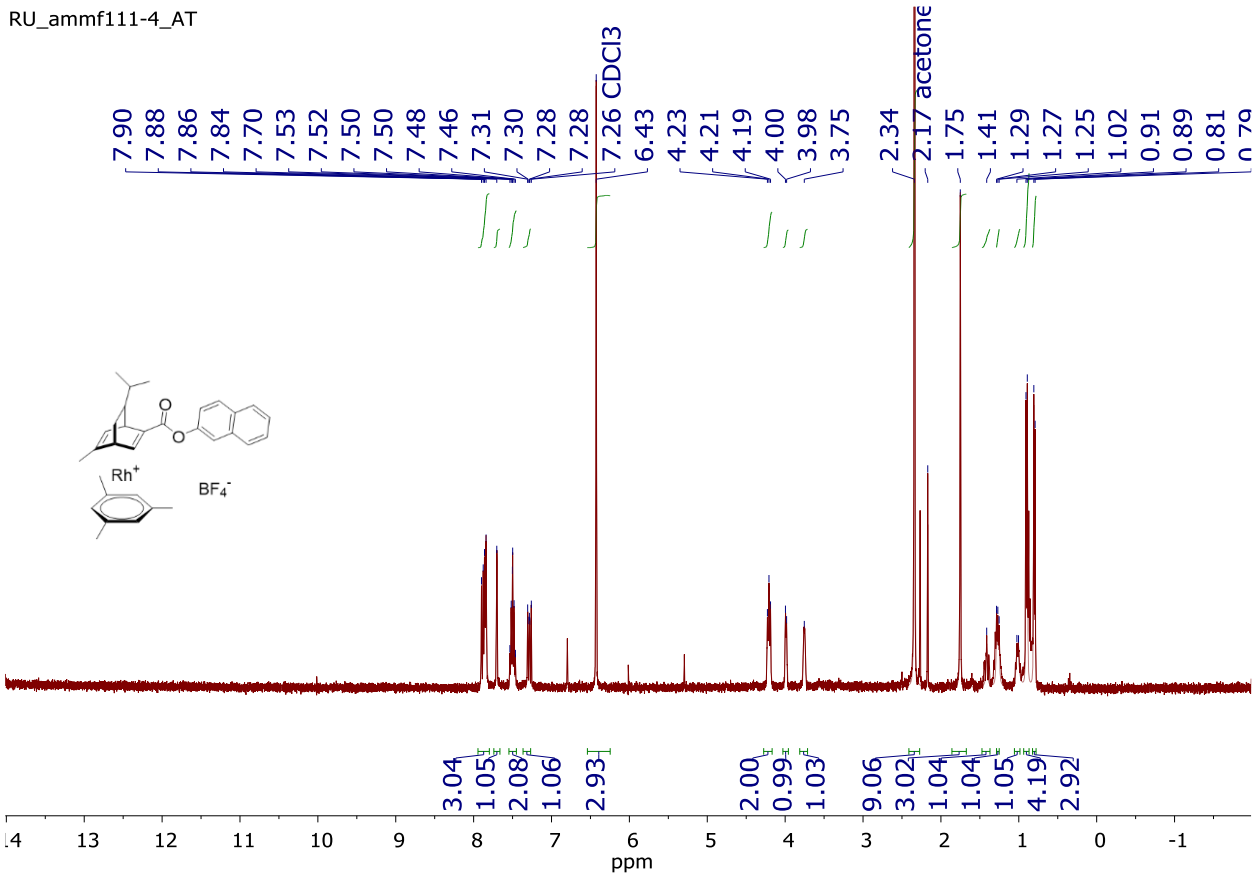
Conditions: 4 mol % of catalyst **4b** (1.3 – 5.0 mg,0,002 – 0.008 mmol), (*E*)-1-(3-methoxyphenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (**9**) (50 mg, 100 mol%, 0.02 mmol), solvent (0.2 ml).

The proposed mechanism of the reaction

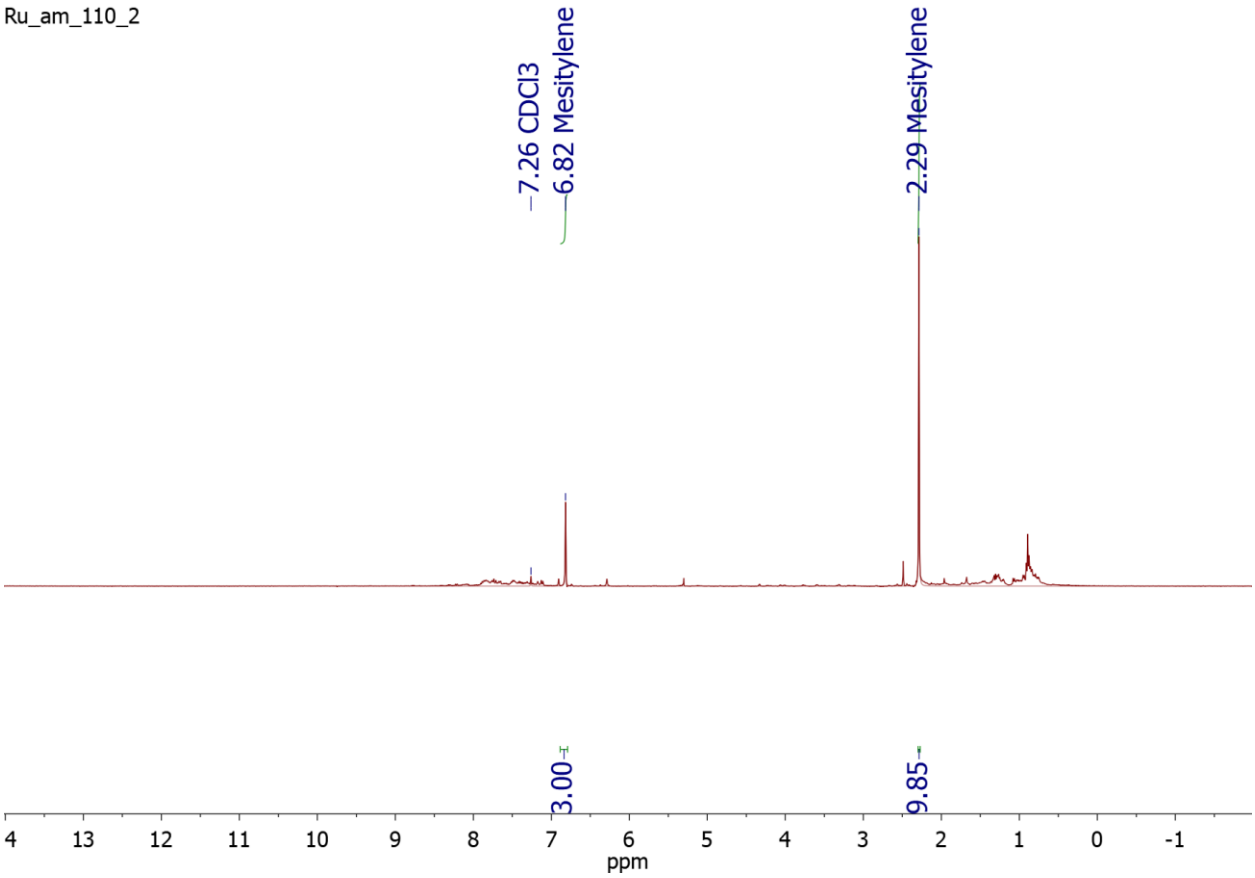
The proposed mechanism of the reaction is similar to the early suggested.[S4] First, oxidative addition of a carbonylated Rh catalyst to the hemiaminal intermediate provides hydroxo complex **A**. An intramolecular hydroxylation of a Rh-bound CO ligand then leads to intermediate **B**. Its decarboxylation gives rhodium hydride species **C**, which upon reductive elimination leads to the amine product and the regenerated catalyst.



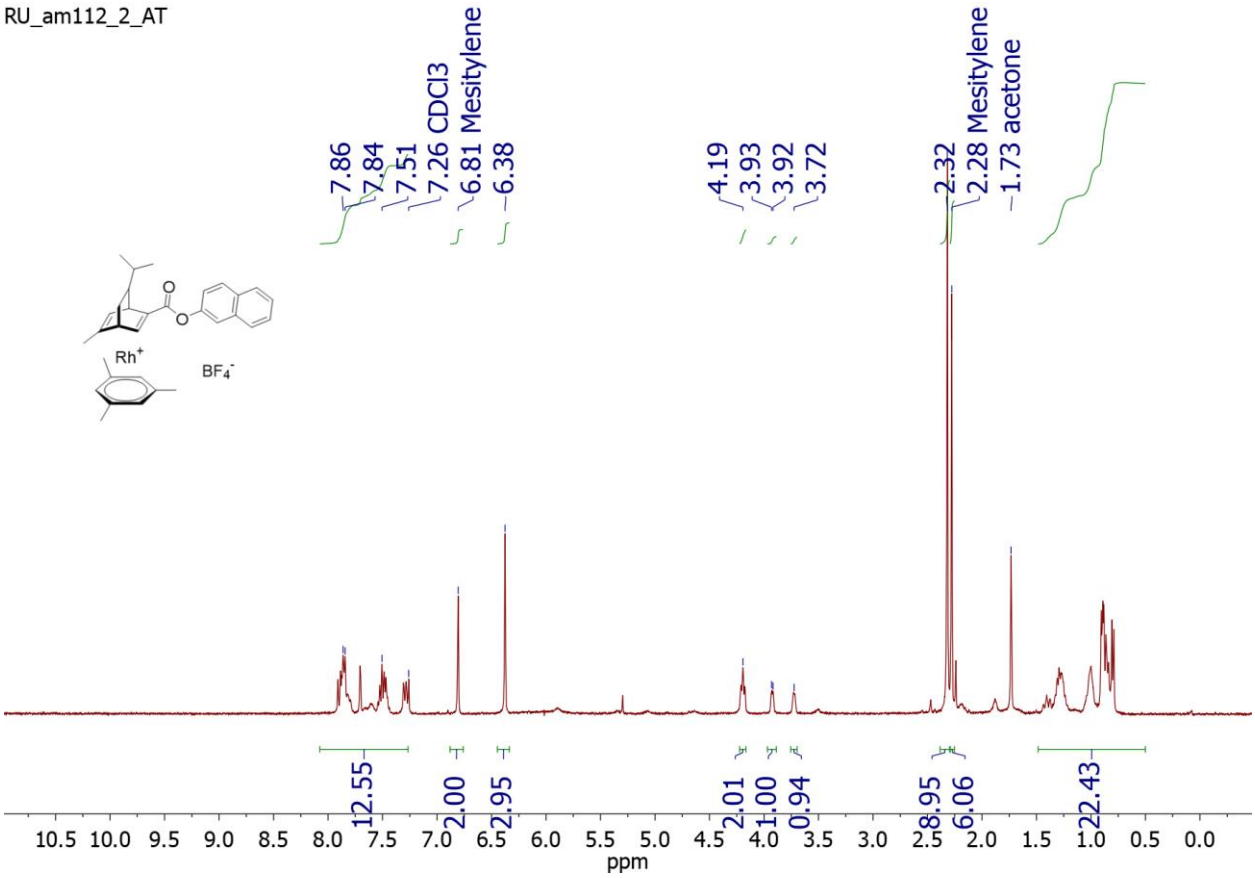
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene](mesitylene)rhodium(I) tetrafluoroborate (4b) in 1 atm air after heating at 90 °C for 20 hours



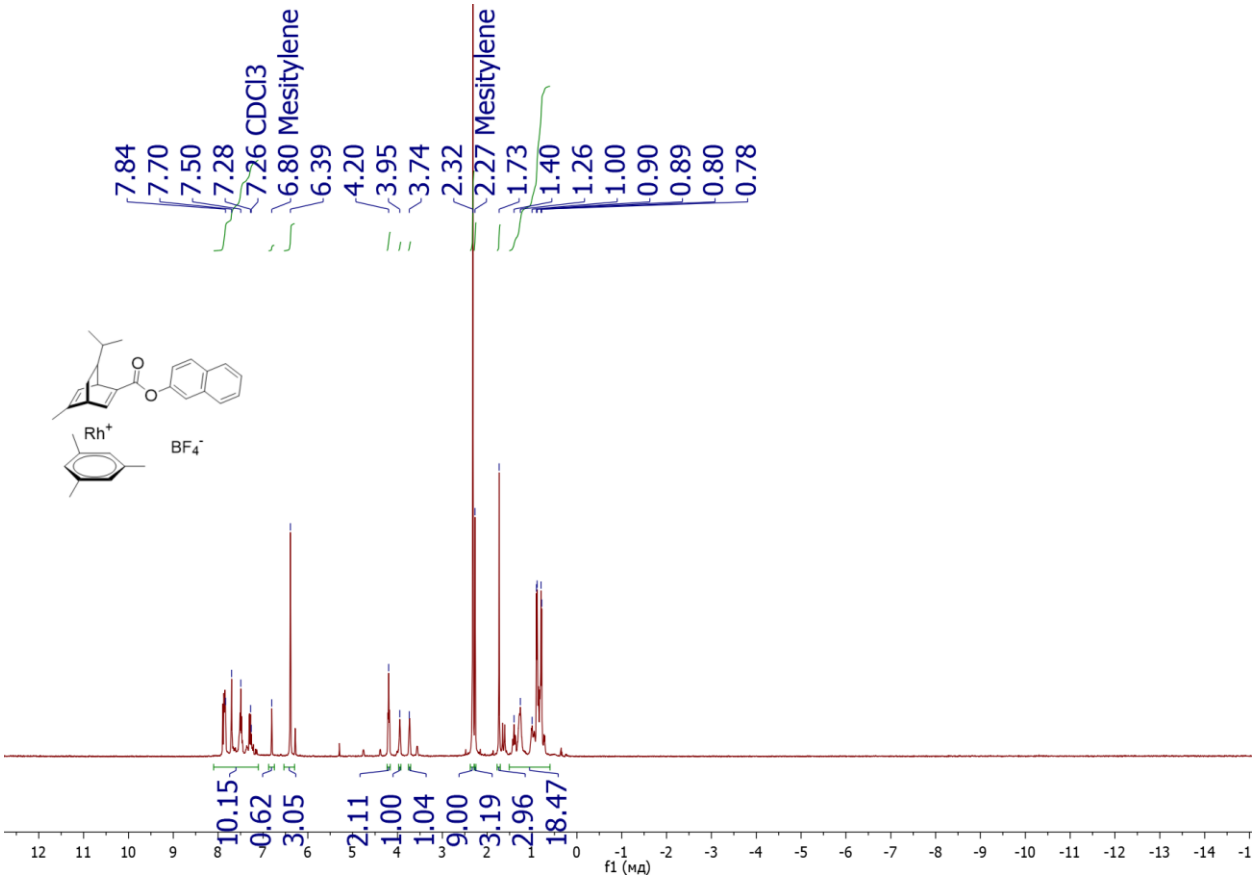
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene] (mesitylene) rhodium(I) tetrafluoroborate (4b) in 2 atm CO after heating at 90 °C for 20 hours



[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene] (mesitylene)rhodium(I) tetrafluoroborate (4b) in 2 atm CO after heating at r.t. for 20 hours

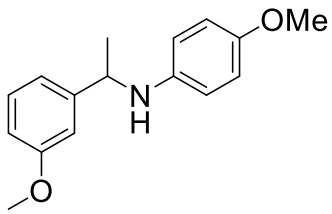


[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene](mesitylene)rhodium(I) tetrafluoroborate (4b) in 2 atm H_2 after heating at 90 °C for 20 hours



Typical procedure for isolation and characterization of the products

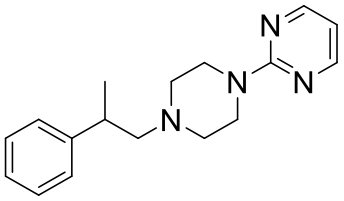
4-Methoxy-*N*-[1-(3-methoxyphenyl)ethyl]aniline (7a)



Catalyst **4b** (6.4 mg, 5 mol %, 0.010 mmol), 4-methoxyaniline (30.0 mg, 100 mol%, 0.24 mmol),1-(3-methoxyphenyl)ethan-1-one (133 µL, 400 mol %, 0.98 mmol) and 0.2 mL of THF were added and the autoclave was sealed, flushed three times with 5 atm of carbon monoxide, and then charged with 10 atm of carbon monoxide. The reactor was placed into an oil bath, preheated to 60° C. After 60 h of heating, the temperature was increased to 80° C. After another 60 h, the reactor was cooled down to room temperature and depressurized. The reaction mixture was transferred into a flask, the autoclave was washed with dichloromethane (2x1mL), and solvents were removed on a rotary evaporator to give 84 % yield by NMR. The residue was purified by flash chromatograph InterChim PuriFlash and the following elution was applied: isocratic DCM for15 min., Rf=0.38 in DCM) to afford 21.9 mg (35%) of the product as a yellowish solid. Enantiomeric ratio was determined by chiral HPLC on Daicel Chiralpak IA-3 column, heptane: isopropanol = 90:10, flow rate: 1 ml/min, tR1 = 4.63, tR2 = 5.06.

^{1}H NMR (300 MHz, Chloroform-d) δ 7.20 (dd appears as t, J = 7.8 Hz, 1H), 6.97 – 6.86 (m, 2H), 6.78 – 6.68 (m, 1H), 6.71 – 6.61 (m, 2H), 6.49 – 6.39 (m, 2H), 4.34 (q, J = 6.7 Hz, 1H), 3.74 (s, 2H), 3.65 (s, 2H), 1.45 (d, J = 6.7 Hz, 3H).
NMR spectra are in agreement with the literature data.[S5]

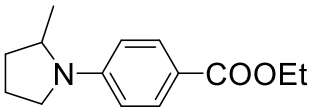
2-[4-(2-Phenylpropyl)piperazin-1-yl]pyrimidine (7b)



Catalyst **4b** (6.4 mg, 5 mol %, 0.010 mmol), 2-(piperazin-1-yl)pyrimidine (29 μL, 100 mol%, 0.20 mmol), 2-phenylpropanal (108 μL, 400 mol %, 0.80 mmol), 0.2 mL of THF were added and the autoclave was sealed, flushed three times with 5 atm of carbon monoxide, and then charged with 30 atm of carbon monoxide. The reactor was placed into an oil bath preheated to 60 °C. After 60 h of heating the temperature was increased to 80 °C. After another 15 h the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), solvents were removed on a rotary evaporator to give 90 % yield by GC. The residue was purified by flash chromatograph InterChim PuriFlash, following elution was applied: isocratic MeOH:DCM 4:96 for 15 min; R_f=0.30 in hexane:EtOAc 95:5 mixture) to afford 18.1 mg (32%) of the product as a yellowish oil. Enantiomeric ratio was determined by chiral HPLC on Daicel Chiralpak IA-3 column, heptane: isopropanol = 99:1, flow rate: 1 ml/min, tR1 = 4.79, tR2 = 5.17.

^{1}H NMR (300 MHz, Chloroform-d) δ 8.29 (d, J = 4.7 Hz, 2H), 7.36 – 7.14 (m, 5H), 6.46 (t, J = 4.7 Hz, 1H), 3.70 – 3.80 (m, 4H), 2.99 (q, J = 7.0 Hz, 1H), 2.60 – 2.31 (m, 6H), 1.31 (d, J = 7.0 Hz, 3H).

Ethyl 4-(2-methylpyrrolidin-1-yl)benzoate (8)



Catalyst **4b** (6.4 mg, 5 mol %, 0.010 mmol), ethyl 4-aminobenzoate (33.0 mg, 100 mol%, 0.20 mmol), cyclopropyl methyl ketone (79 μL, 400 mol %, 0.80 mmol), 0.2 mL of THF were added and the autoclave was sealed, flushed three times with 5 atm of carbon monoxide, and then charged with 30 atm of carbon monoxide. The reactor was placed into an oil bath preheated to 110 °C. After 90 h the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), solvents were removed on a rotary evaporator to give 70 % yield by NMR. The residue was purified by flash chromatograph InterChim PuriFlash, following elution was applied: isocratic hexane:EtOAc 95:5 for 15 min.; R_f=0.32 in hexane:EtOAc 95:5 mixture) to afford 25.6 mg (55%) of the product as colorless oil. Enantiomeric ratio was determined by chiral HPLC on Daicel Chiralpak IA-3 column, heptane: isopropanol = 95:5, flow rate: 1 ml/min, tR1 = 5.55, tR2 = 6.01.

^{1}H NMR (300 MHz, Chloroform-d) δ 7.90 (d, J = 8.9 Hz, 1H), 6.52 (d, J = 8.9 Hz, 1H), 4.31 (q, J = 7.1 Hz, 1H), 4.04 – 3.89 (m, 1H), 3.50 – 3.40 (m, 1H), 3.27 – 3.17 (m, 1H), 2.17 – 1.93 (m, 3H), 1.83 – 1.64 (m, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.18 (d, J = 6.3 Hz, 3H).

NMR spectra are in agreement with the literature data.[S6]

References

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S2 R. Cramer, J. A. McCleverty, J. Bray, *Inorg. Synth.* 1990, **28**, 86.

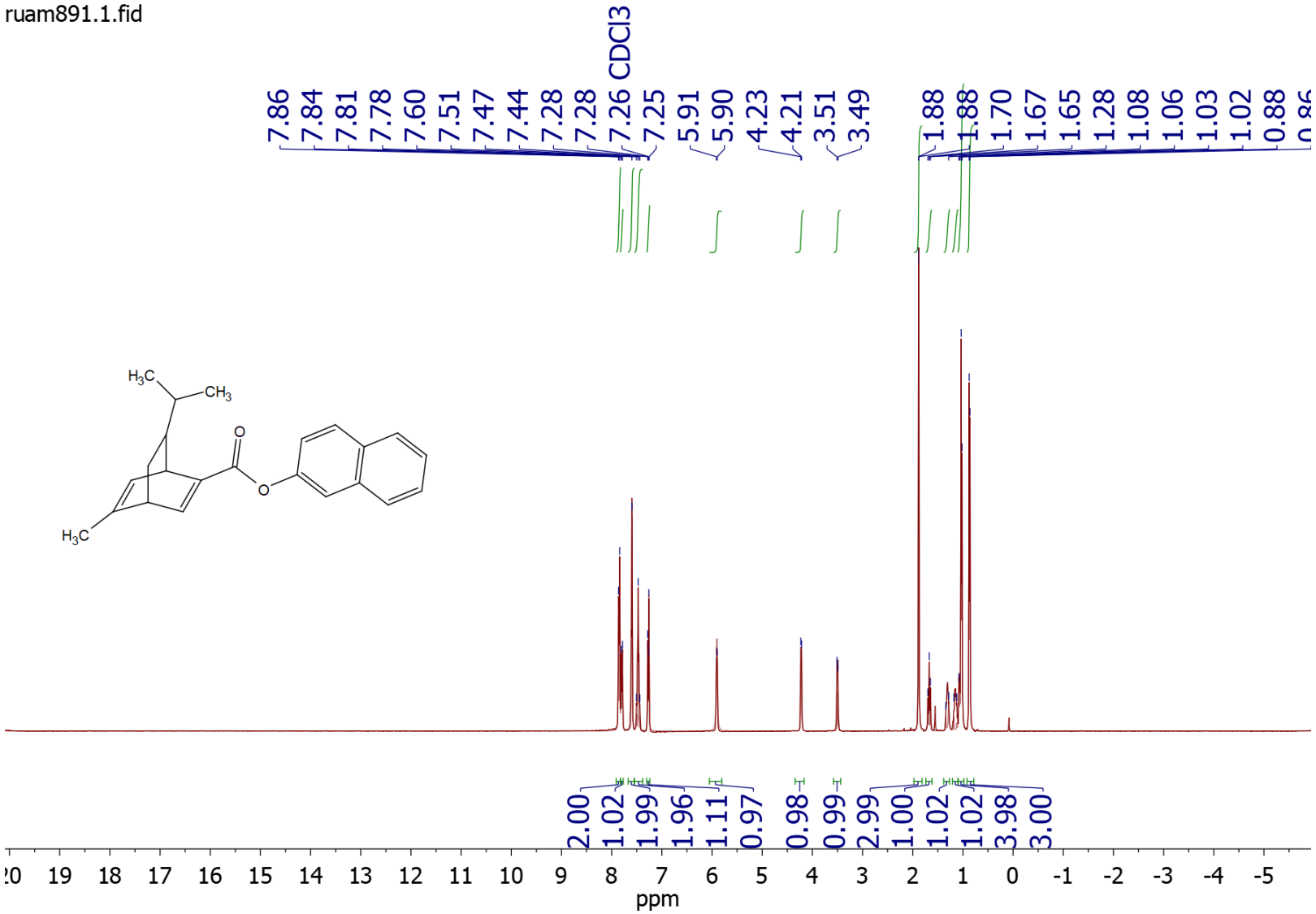
S3 B. A. Suslick, T. D. Tilley, *Org. Lett.* 2021, **23**, 1495.

S4 D. Chusov, B. List, *Angew. Chemie Int. Ed.* 2014, **53**, 5199.

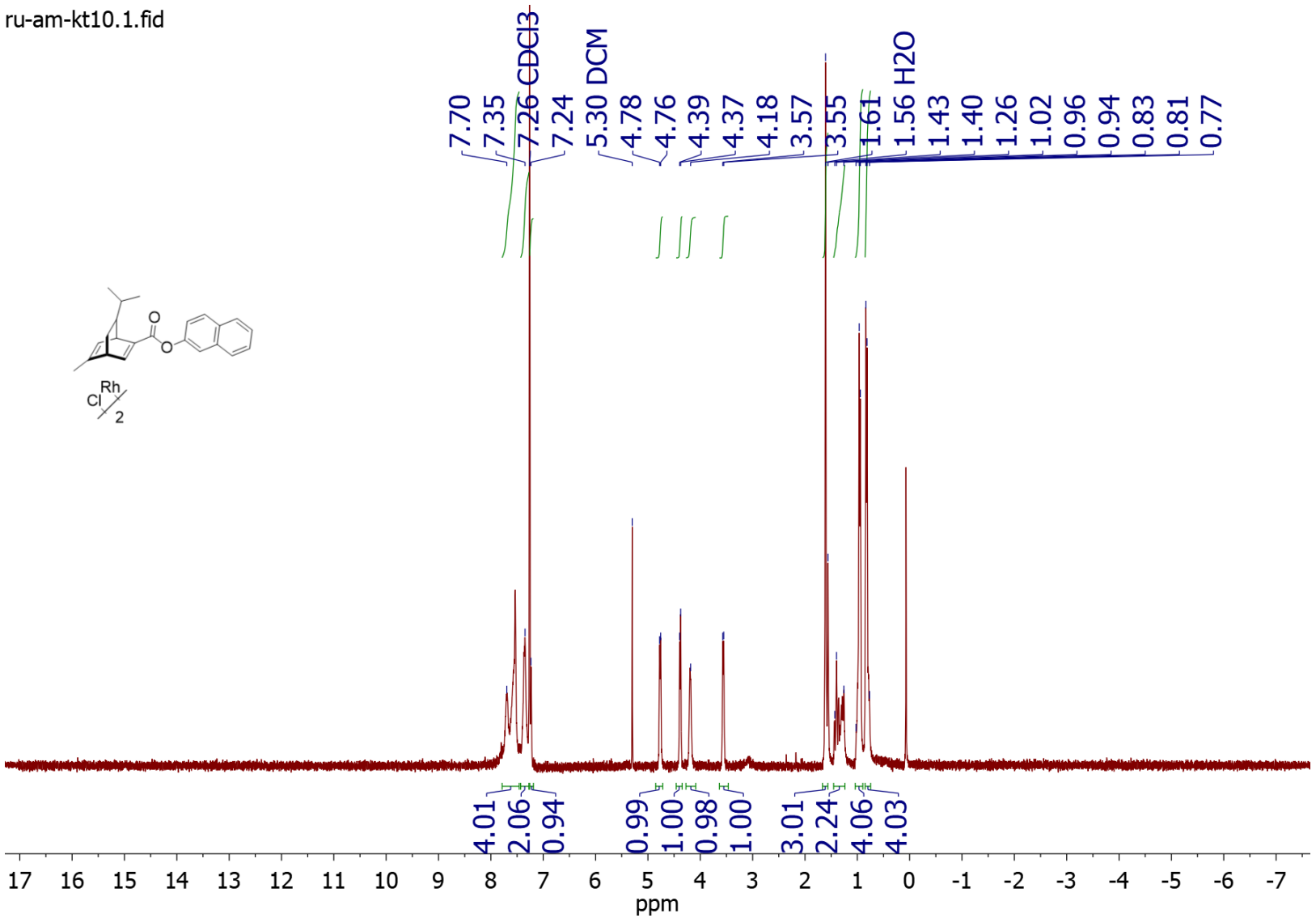
S5 C. Wang, A. Pettman, J. Bacsa, J. Xiao, *Angew. Chemie Int. Ed.* 2010, **49**, 7548.

S6 O. I. Afanasyev, A. A. Tsygankov, D. L. Usanov, D. Chusov, *Org. Lett.* 2016, **18**, 5968.

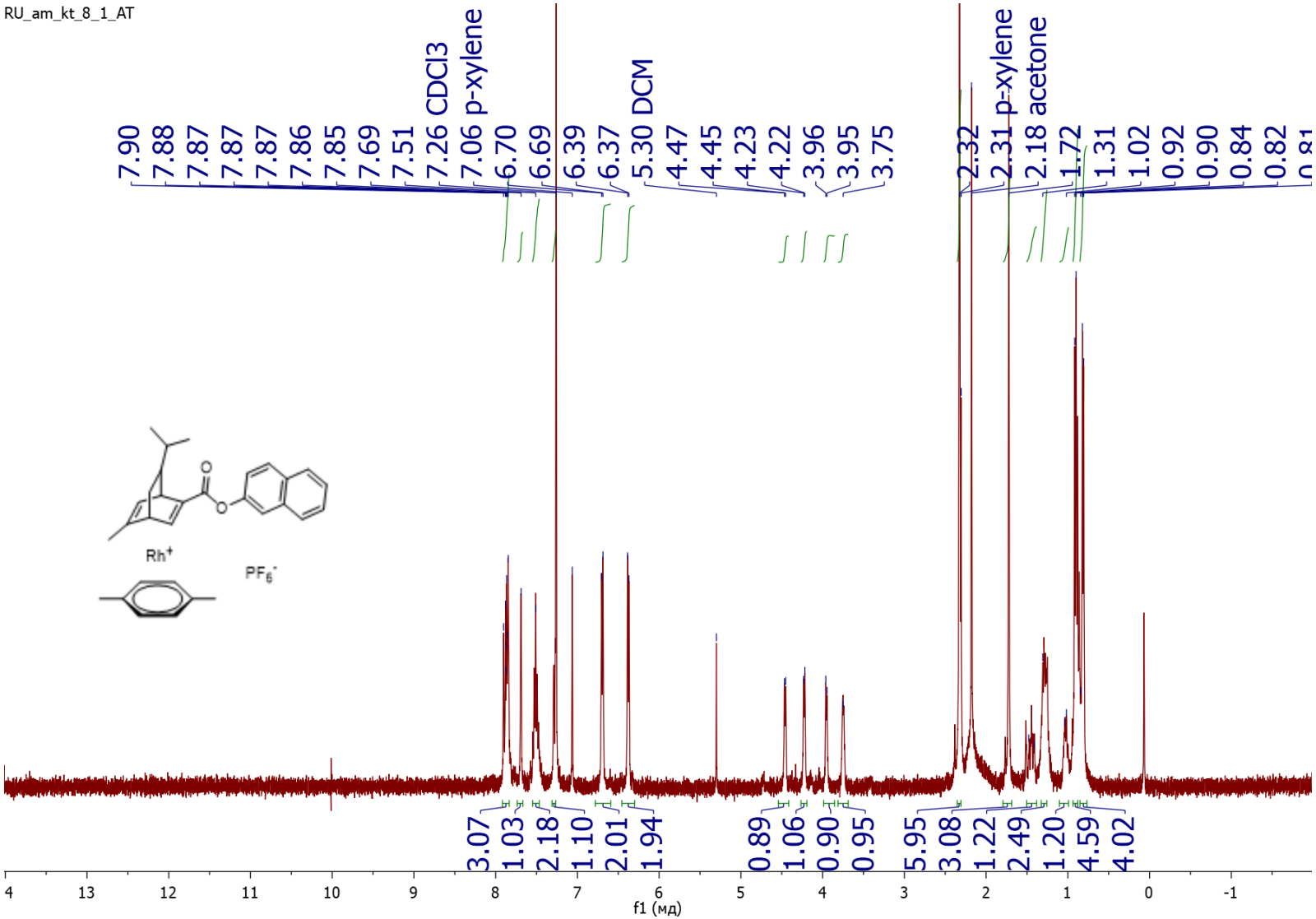
3. ^{1}H NMR of obtained compounds



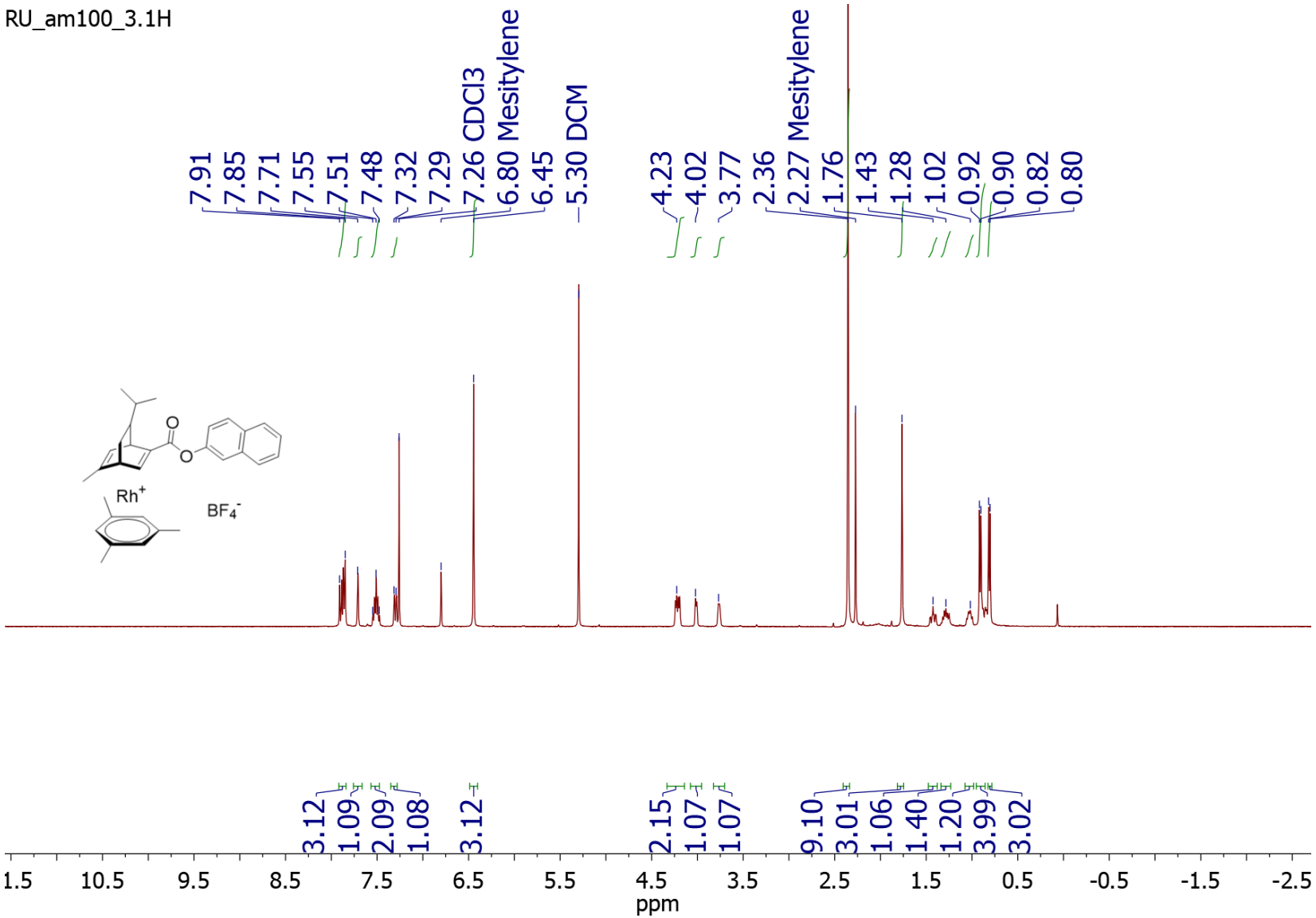
2-Naphthyl (1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate (1) (^{1}H NMR, $CDCl_3$, 400 MHz)



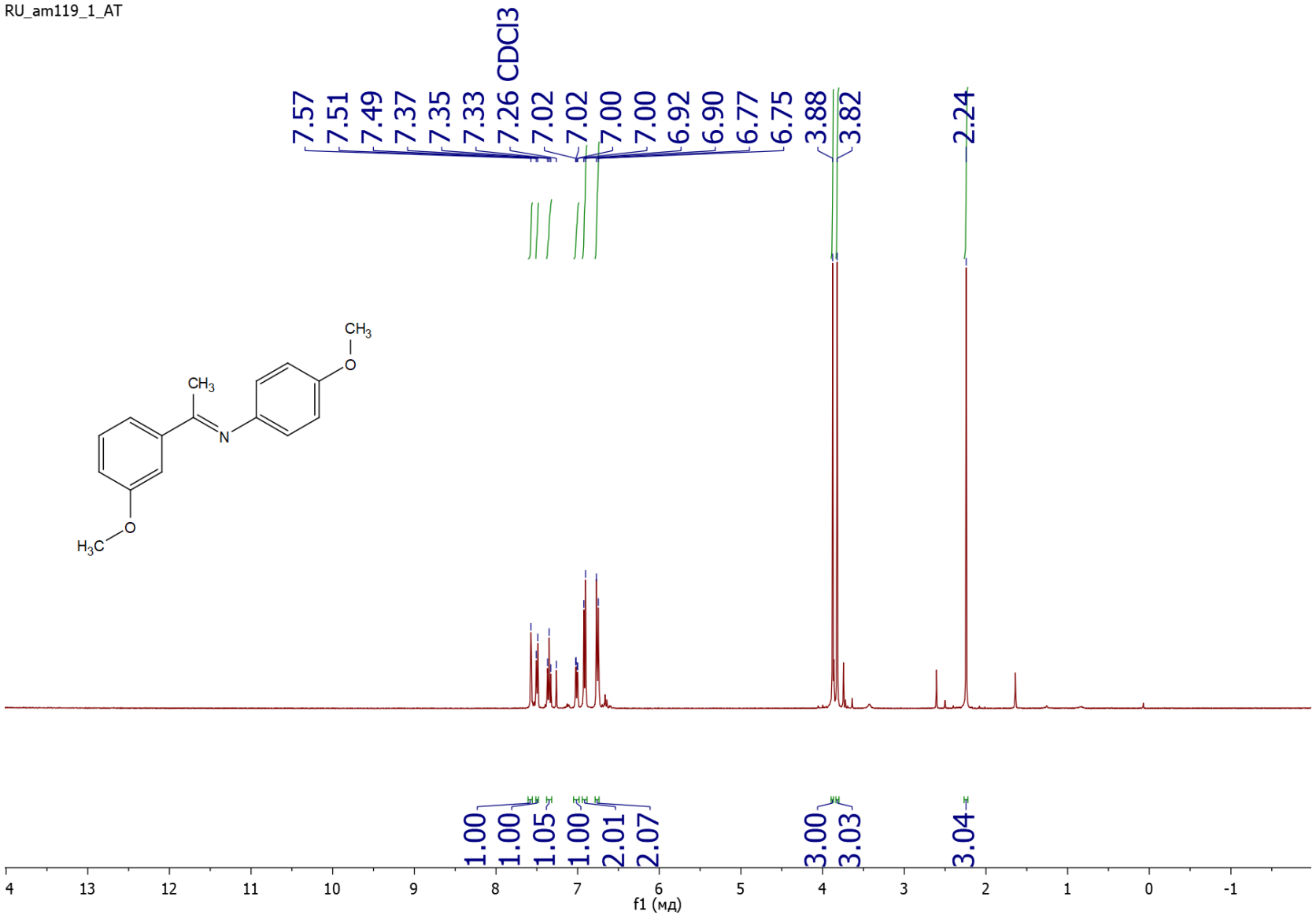
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene]rhodium(I) chloride (3) (^{1}H NMR, $CDCl_3$, 300 MHz)



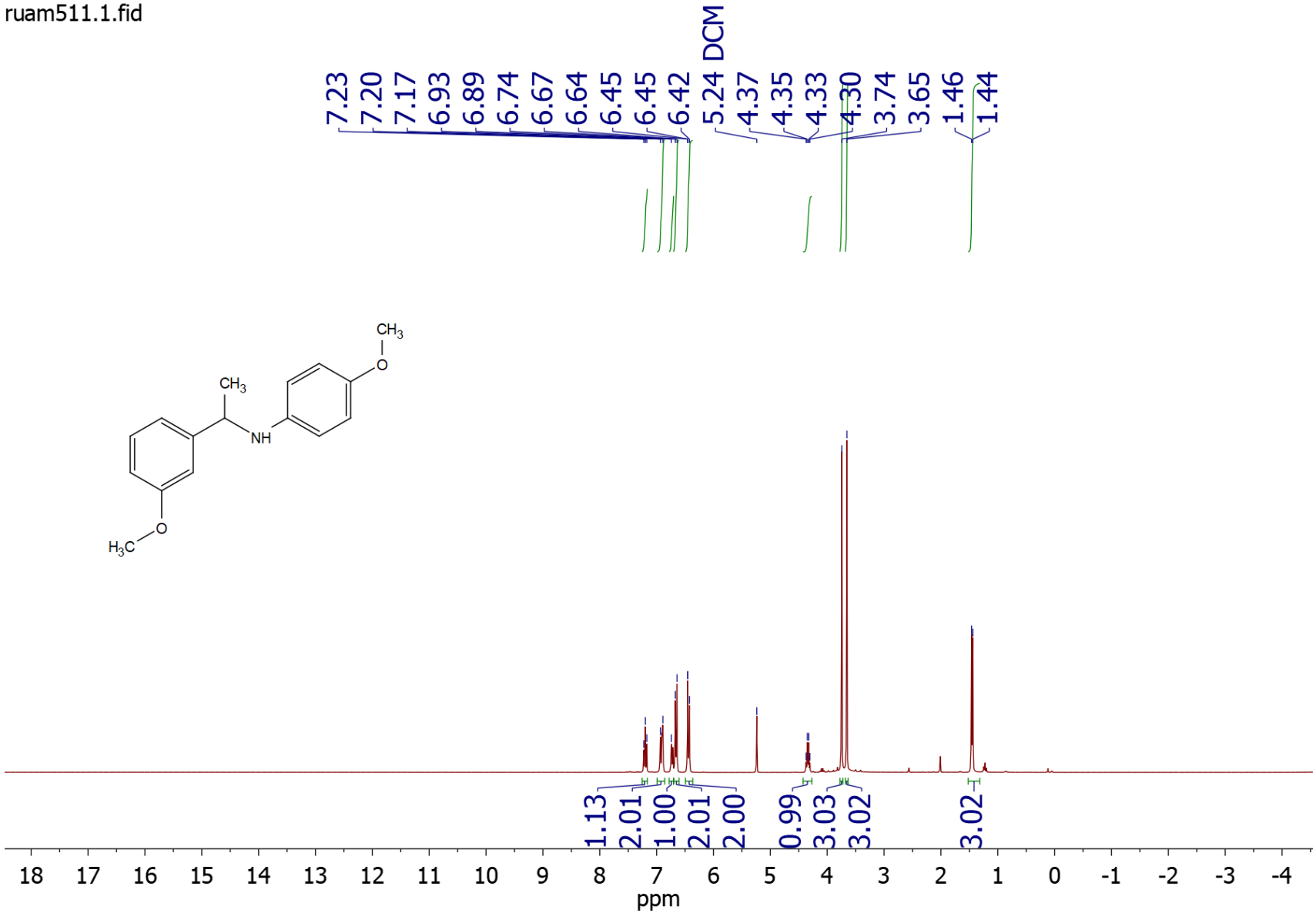
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene](*p*-xylene)rhodium(I) tetrafluoroborate (4a) (^{1}H NMR, $CDCl_3$, 400 MHz)



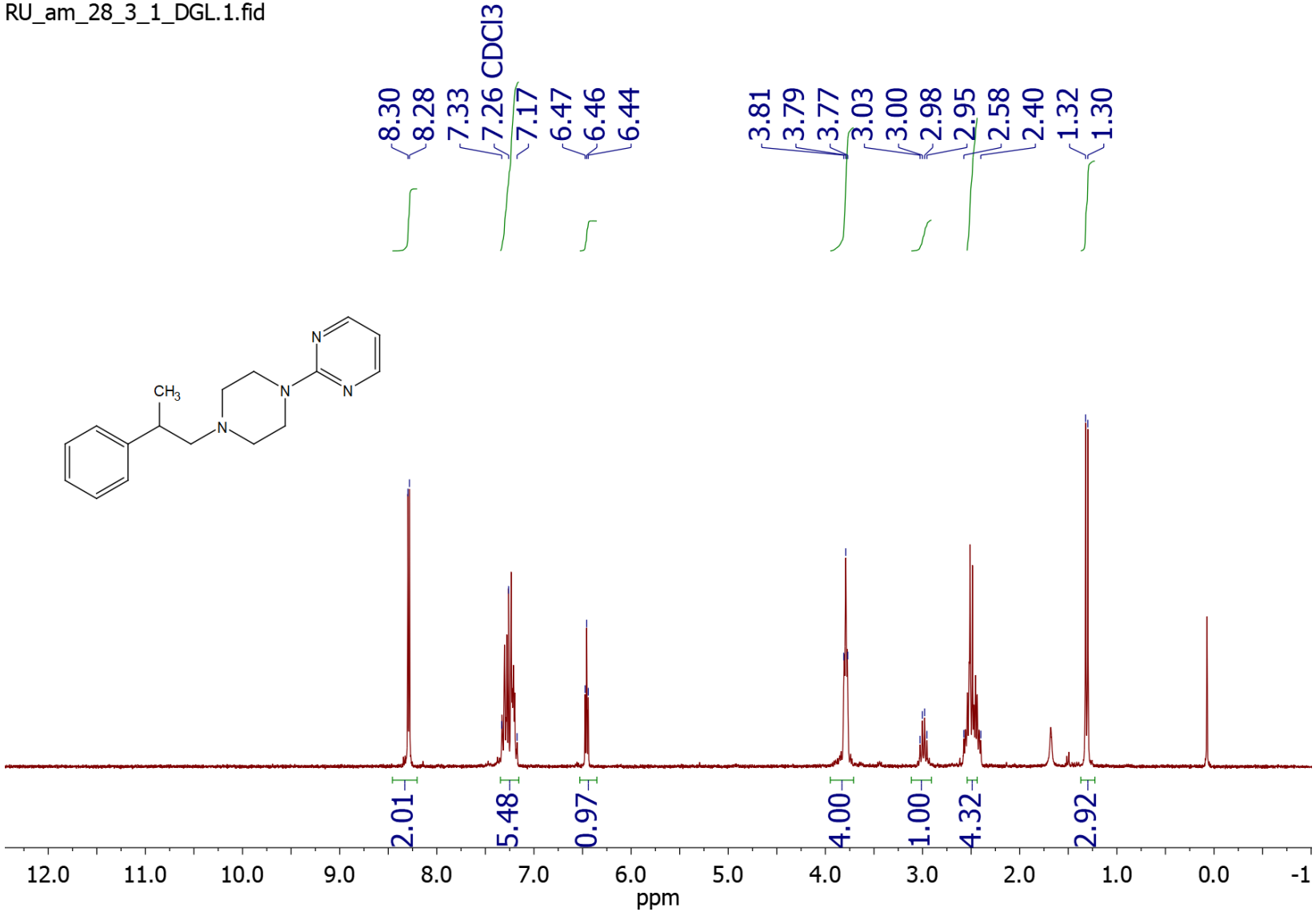
[(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-2-(2-naphthyloxycarbonyl)bicyclo[2.2.2]octa-2,5-diene](mesitylene)rhodium(I) tetrafluoroborate (4b) (^{1}H NMR, $CDCl_3$, 400 MHz)



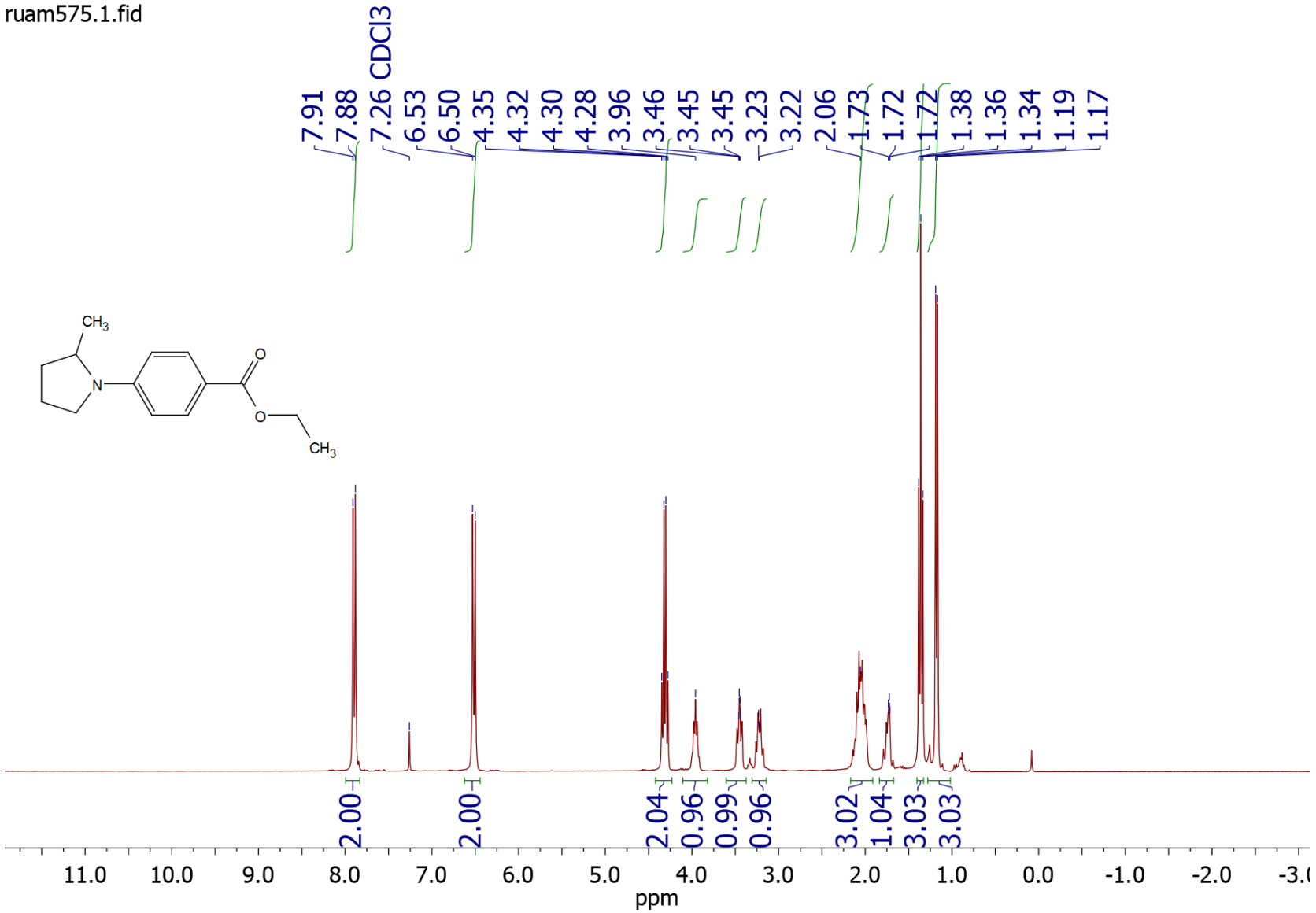
1-(3-Methoxyphenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (9) (^{1}H NMR, $CDCl_3$, 400 MHz)



4-Methoxy-N-(1-(3-methoxyphenyl)ethyl)aniline (7a) (^{1}H NMR, $CDCl_3$, 300 MHz)



2-(4-(2-Phenylpropyl)piperazin-1-yl)pyrimidine (7b) (^{1}H NMR, $CDCl_3$, 300 MHz)



Ethyl 4-(2-methylpyrrolidin-1-yl)benzoate (8) (^{1}H NMR, $CDCl_3$, 300 MHz)