CNN pincer ruthenium complexes for efficient transfer hydrogenation of biomass-derived carbonyl compounds

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Prof. Dr. John Arnold
Chairman of the Editorial Board,
Dalton Transactions
Royal Society of Chemistry,
Berkeley - USA

Dear Professor Arnold,

Please find attached our manuscript entitled "CNN Pincer Ruthenium Complexes for Efficient Transfer Hydrogenation of Biomass-Derived Carbonyl Compounds"
Rosario Figliolia, Paolo Cavigli, Clara Comuzzi, Alessandro Del Zotto, Denise Lovison, Paolo Strazzolini, Sabina Susmel, Daniele Zuccaccia, Maurizio Ballico, Walter Baratta,
which we would like to have considered for the publication as a full paper in *Dalton Transaction.*

The development of new selective, efficient and easily accessible catalysts for organic transformations represents a subject of current industrial and academic interest. This contribution deals with the straightforward synthesis of pincer ruthenium complexes with phosphine and CO ligands and their use in the transfer hydrogenation of lignocellulose biomass ketone and aldehyde compounds. These new complexes have been found extremely active and selective in the reduction of biomass-derived platform furan aldehydes, Cyrene, ethyl levulinate, cinnamaldehyde and vanillin derivatives at S/C up to 100000 and with rate up to 1500000 h^{-1}.
Since this paper reports important new findings for the easy preparation of a class of pincer Ru complexes and their application in the conversion of biomass derivatives, the article should be of interest for the broad readership of *Dalton Transaction.* The article is original, the results are unpublished and not being submitted for publication elsewhere.

Udine, 5 November 2019

Thank you for your kind attention
Yours sincerely,
Walter Baratta

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Dalton Transaction

CNN Pincer Ruthenium Complexes for Efficient Transfer Hydrogenation of Biomass-Derived Carbonyl Compounds

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Abstract

The ligand $HCNN^{OMe}$ (6-(4-methoxyphenyl)-2-aminomethylpyridine) is easily prepared from the commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde by reaction of hydroxylamine and hydrogenation (H_2, 1 atm) with Pd/C. The pincer complexes *cis*-[$RuCl(CNN^{OMe})(PPh_3)_2$] (**1**) and [$RuCl(CNN^{OMe})(PP)$] (PP = dppb, **2**; dppf, **3**) are synthesized from [$RuCl_2(PPh_3)_3$], $HCNN^{OMe}$ and PP (for **2**, **3**) in 2-propanol with NEt_3 at reflux and are isolated in 85-93% yield. Carbonylation of **1** (CO 1 atm) gives [$RuCl(CNN^{OMe})(CO)(PPh_3)$] (**4**) (79% yield) which cleanly reacts with $Na[BAr^f_4]$ and PCy_3, affording the cationic *trans*-[$Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)$][$BAr^f_4$] (**5**) (92% yield). These robust pincer complexes display remarkably high catalytic activity in the transfer hydrogenation (TH) of lignocellulose biomass carbonyl compounds, using 2-propanol at reflux in basic media (NaO*i*Pr, K_2CO_3). Thus, furfural, 5-(hydroxymethyl)furfural and Cyrene are reduced to the corresponding alcohols with **2** and **3**, at S/C in the range of 10000-100000, within minutes or hours (TOF up to 1500000 h^{-1}). The monocarbonyl complex **5** was found extremely active in the TH of cinnamaldehyde, vanillin derivatives and ethyl levulinate at S/C of 10000-50000. Vanillyl alcohol is also obtained by TH of vanillin with **5** (S/C = 500) in 2-propanol in the presence of K_2CO_3.

Introduction

The progress in the development of simple and environmentally friendly processes for the production of valuable chemicals from biosourced compounds is a mandatory issue for a sustainable economy, alleviating the dependence on fossil resources.[1-3] Carbohydrates and lignin are inexpensive and globally accessible biomass feedstock which can be employed for the production of building blocks and biofuels,[1, 4-10] via hydrolysis, pyrolysis, defunctionalization and enzymatic degradation

reactions.[1, 11-14] In addition to the use of lignocellulose biomass for conventional production, an emerging strategy is the preparation of new biomass-based platform chemicals.[3] The advance in the search of clean and efficient processes that involve the use of non-toxic renewable reagents and solvents, without the formation of side-products and waste, represents a prerequisite for reducing the environmental impact, in agreement with the principles of green chemistry.[15, 16] In this context, catalysis will play a leading role for the production of either bulky compounds (biofuels), using heterogeneous catalysts, and biomass-derived platform chemicals through selective transformations with well-defined homogeneous catalysts.[17-19] Hydrogenation (HY)[20-23] and transfer hydrogenation (TH)[24-28] of carbonyl compounds by means of ruthenium complexes[29] are industrially widely accepted processes for the synthesis of alcohols using H_2 or 2-propanol as reducing agents, instead of $NaBH_4$ and $LiAlH_4$.[30] The high control of selectivity imparted by the metal complexes, associated to the high atom economy with respect to the classical methods, make this approach a sustainable pathway for the carbonyl reduction in organic synthesis. A particular successful outcome was the introduction of the Noyori-Ikariya bifunctional amino ruthenium catalysts *trans*-$[RuCl_2(PP)(diamine)]$ (PP = diphosphine) and [RuCl(arene)(NN)] in HY and TH reactions, respectively (Figure 1).[31, 32]

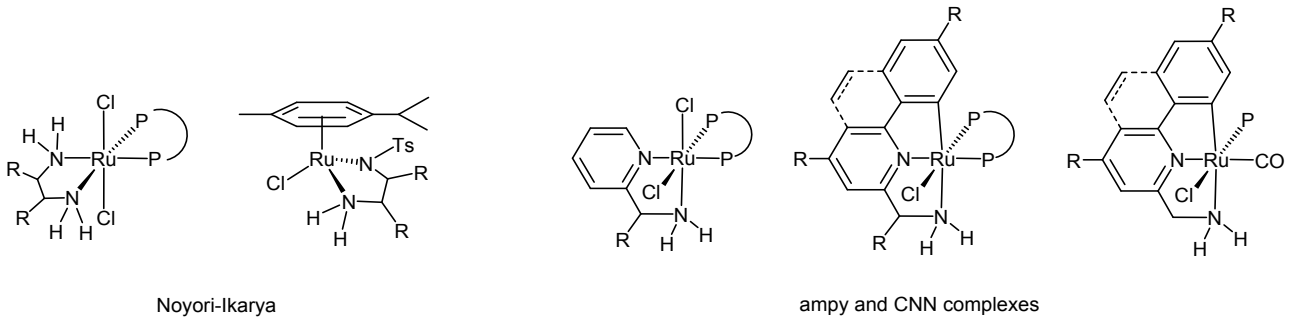


Figure 1. Structure of amino- and ampy-type ruthenium complexes.

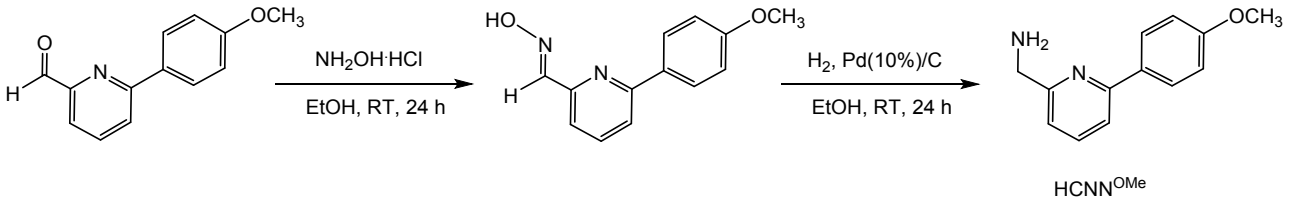
The isolation of *cis*-$[RuCl_2(ampy)(PP)]$[33-36] and the related pincer [RuCl(CNN)(PP)][37-41] and $[RuCl(CNN)(PPh_3)(CO)]$[42] complexes containing the 2-(aminomethyl)pyridine (ampy) motif[43] led to a class of extremely active TH and HY catalysts, which are complementary to the renowned Noyori-Ikariya catalysts[31, 32] (Figure 1). In addition to high selectivity, the pincer complexes display a remarkably high productivity (S/C up to 100000), that is a critical parameter for the application of the catalytic C=O reduction. In particular, the pincer complexes have allowed the clean reduction of commercial-grade ketones and even aldehydes,[37, 44, 45] which can easily undergo aldol condensation,[46] Claisen-Tishchenko,[47-53] Cannizzaro[54] and decarbonylative side-reactions.[55-60] Furthermore, the

pincer CNN Ru complexes have been found active in dehydrogenation,[61] racemization and deuteration of alcohols,[62] as well as imine hydrogenation.[63] It is worth point out that the HCNN ligands have been prepared through rather cumbersome procedures, namely starting from 6-arylpyridines and benzo[*h*]quinolones, via formation of the *N*-oxide and cyano intermediates,[40, 64] entailing chemoenzymatic synthesis[65] and heterocyclization of 1-naphthylamine.[37]

We report herein a straightforward synthesis of several pincer Ru complexes, prepared from the easily accessible 6-(4-methoxyphenyl)-2-aminomethylpyridine ($HCNN^{OMe}$) ligand, in combination with phosphines and carbon monoxide. The robust pincer complexes $[RuCl(CNN^{OMe})(PP)]$ and *trans*-$[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4]$ display high rate and selectivity in the TH of ketones and aldehydes available from lignocellulose biomass to the corresponding alcohols in 2-propanol. High selectivity was attained for 5-HMF, Cyrene, ethyl levulinate, cinnamaldehyde and vanillin derivatives with unprecedented high productivity (S/C up to 100000).

Results and Discussion

Synthesis of the $HCNN^{OMe}$ ligand. The 2,6 functionalized pyridine $HCNN^{OMe}$ ligand is easily synthesized on g-scale by treatment of the commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde with $NH_2OH{\cdot}HCl$, affording the quantitative formation of the corresponding (*E*)-oxime, as inferred from the low field HC=N ^1H NMR signal at δ 8.18 ppm, consistent with the related (*E*)-oxime pyridine derivatives.[66, 67] This intermediate is selectively hydrogenated with H_2 (1 atm) using 10% Pd/C, at room temperature in ethanol (89% yield) (Scheme 1).

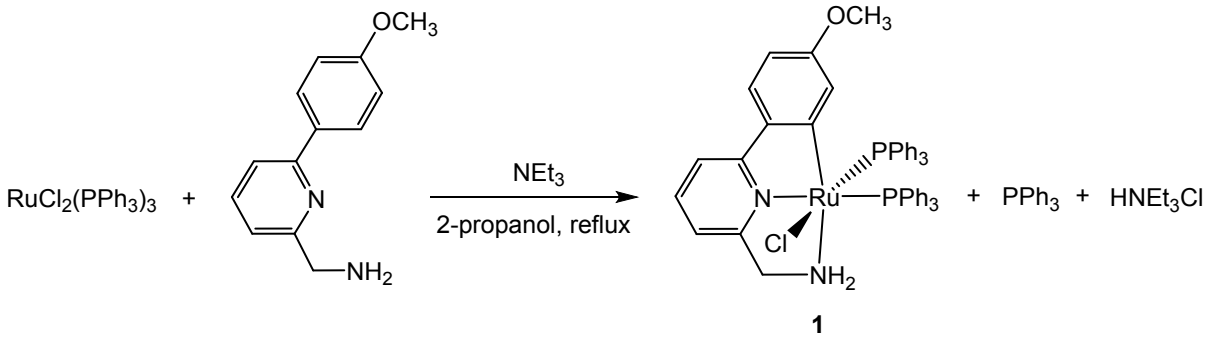


Scheme 1. Synthesis of the ligand $HCNN^{OMe}$.

While the formation of the oxime occurs cleanly, the use of a diluted solution of oxime in ethanol under low hydrogen pressure in presence of palladium catalyst is crucial to avoid both the formation of 6-(4-methoxyphenyl)-2-methylpyridine, via C-N cleavage, and the secondary amine bis((6-(4-methoxyphenyl)pyridin-2-yl)methyl)amine, through the nucleophilic attack of the formed amine towards the intermediate imine. The reported synthesis represents a more straightforward route to

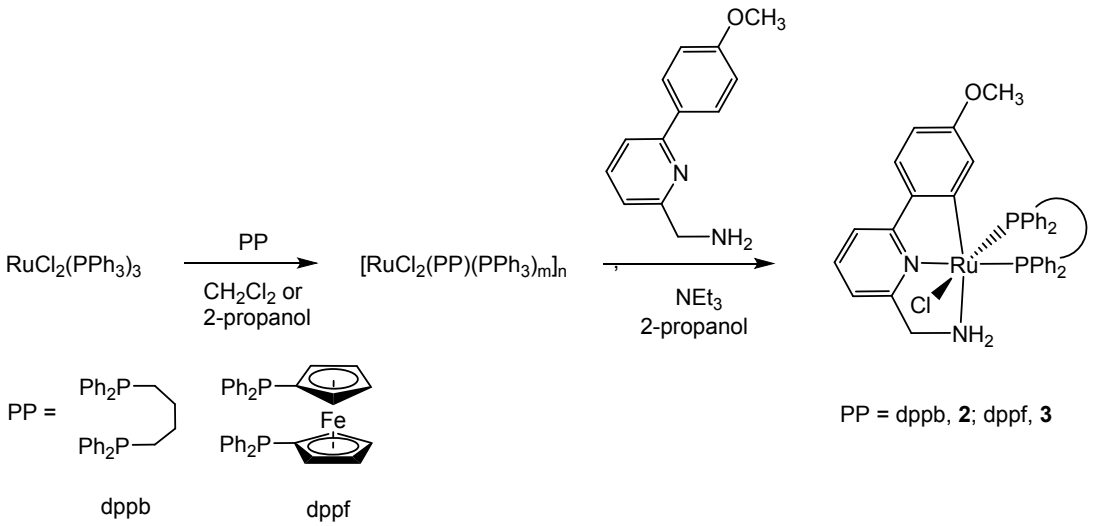
prepare the HCNN pincer ligands on g-scale, with respect to those previously reported, involving the formation of pyridine oxide and the use of Me_3SiCN with dimethylcarbamoyl chloride as cyanation agent in the 2 position, followed by reduction with $LiAlH_4$ or H_2.[40]

Synthesis of the pincer ruthenium complexes. Treatment of $[RuCl_2(PPh_3)_3]$ with 1.2 equiv. of the ligand $HCNN^{OMe}$, in the presence of NEt_3 (10 equiv.) in 2-propanol at reflux (2 h), promptly affords the pincer complex *cis*-$[RuCl(CNN^{OMe})(PPh_3)_2]$ (**1**) in 93% yield, through elimination of one PPh_3 and orthometalation reaction (Scheme 2).



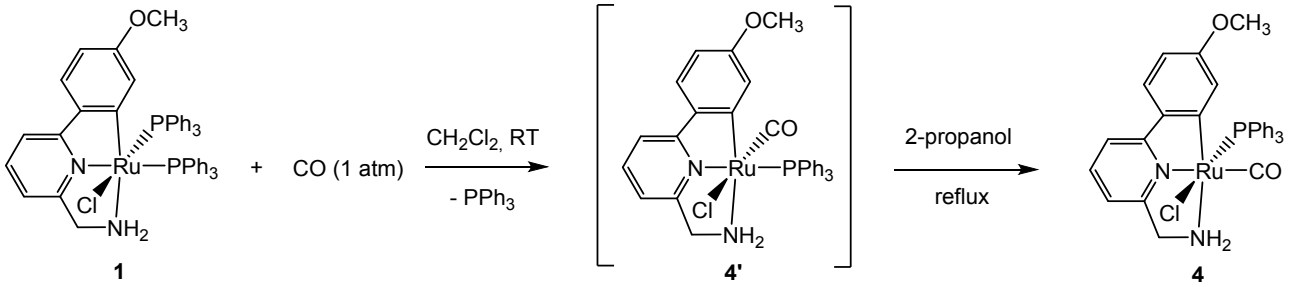
Scheme 2. Synthesis of the complex *cis*-$[RuCl(CNN^{OMe})(PPh_3)_2]$ (**1**).

The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows two doublets at δ 54.6 and 49.4 ppm, with a $^2J_{PP}$ of 32.8 Hz, whereas the cyclometalated carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 183.7 ppm (dd with $^2J_{CP}$ of 13.8 Hz and 8.2 Hz). In addition, the CH_2N proton signals of **1** appear in the ^1H NMR spectrum as a doublet of doublets at δ 4.04 (dd, $^2J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 5.9 Hz) and a multiplet at δ 3.38, whereas the NH_2 signals are found at δ 3.65 and 1.87 ppm. The related diphosphine pincer derivative $[RuCl(CNN^{OMe})(dppb)]$ (**2**) is isolated in 91% yield through a one-pot synthesis starting from $[RuCl_2(PPh_3)_3]$ and 1,4-Bis(diphenylphosphino)butane (dppb) in 2-propanol at reflux (2 h), via the intermediate $[RuCl_2(dppb)(PPh_3)]$, followed by reaction with $HCNN^{OMe}$ and NEt_3 in 2-propanol at reflux (2 h, Scheme 3).



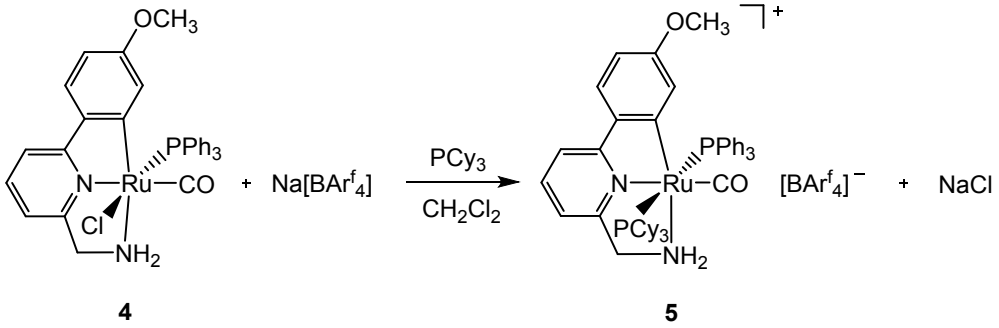
Scheme 3. Synthesis of the diphosphine complexes [RuCl(CNN^{OMe})(PP)] (PP = dppb, **2**; dppf, **3**).

Alternatively, **2** is prepared by reacting [$RuCl_2$(dppb)(PPh_3)][68] with HCNN^{OMe} and NEt_3 in 2-propanol at reflux, and isolated in 88% yield. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets at δ = 56.9 and 41.0 ppm, with a $^2J_{PP}$ = 37.7 Hz, whereas the $^{13}C\{^1H\}$ NMR doublet at δ 52.3 ppm ($^3J_{CP}$ = 2.7 Hz) is for the *C*H_2N group and the doublet of doublets at δ 184.9 ppm ($^2J_{CP}$ = 16.0 and 7.7 Hz) is for the orthometalated carbon atom. The ^1H NMR spectrum of **2** presents a doublet of doublets at δ 4.15 ppm and a triplet of doublets at δ 3.75 ppm for the CH_2N protons, whereas the NH_2 signals are at δ 3.45 and 2.03 ppm, as inferred from the ^1H-^{15}N HSQC 2D NMR spectrum, (see ESI, Fig. S22), according to the related derivative [RuCl(CNN)(dppb)].[40, 41] Similarly, the complex [RuCl(CNN^{OMe})(dppf)] (**3**, 85% yield) has been obtained from [$RuCl_2$(PPh_3)$_3$] and 1,1'-Bis(diphenylphosphino)ferrocene (dppf) in dichloromethane at RT (2 h), followed by reaction with the ligand HCNN^{OMe} in the presence of NEt_3 in 2-propanol at reflux, without isolation of the intermediate [$RuCl_2$(dppf)(PPh_3)$_m$]$_n$ (Scheme 3).[62, 68] The spectroscopic data of **3** resemble those of **2**, with two $^{31}P\{^1H\}$ NMR doublets at δ = 61.5 and 44.1 ppm ($^2J_{PP}$ = 35.6 Hz) and the $^{13}C\{^1H\}$ NMR orthometalated signal at δ 182.5 (dd, $^2J_{CP}$ = 14.9 and 8.2 Hz). The monocarbonyl derivative [RuCl(CNN^{OMe})(PPh_3)(CO)] (**4**) has been isolated in 79% yield by reaction of **1** with CO (1 atm) in CH_2Cl_2 at RT (12 h), followed by a 48 h treatment of the crude product with 2-propanol at reflux (Scheme 4).



Scheme 4. Synthesis of the monocarbonyl complex [RuCl(CNN^{OMe})(CO)(PPh_3)] (**4**).

Control experiments show that during carbonylation of **1** at RT both **4** and its isomer **4′** (δ_P 48.8 ppm, 2:1 ratio) are formed, the latter being completely converted into the thermodynamically most stable complex **4** in 2-propanol at reflux. The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 shows a singlet at δ 56.7 ppm, the ^1H NMR signals for the diastereotopic methylene are at δ 4.23 and 3.41, and the NH_2 protons are at δ 3.87 and 2.79 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the cyclometalated carbon gives a doublet at δ 179.0 ($^2J_{CP}$ = 12.6 Hz), whereas the doublet at δ 207.1 ($^2J_{CP}$ = 17.7 Hz) is for the CO ligand, which displays a IR ν_{CO} absorption band at 1913 cm^{-1}.[42] Treatment of **4** with Na[BAr^f_4] (Ar^f = 3,5-$(CF_3)_2C_6H_3$) in the presence of one equiv. of the bulky phosphine PCy_3 in CH_2Cl_2 at RT, quickly affords the cationic complex *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4] (**5**), isolated in 92% yield, via substitution of Cl with the PCy_3 ligand (Scheme 5).

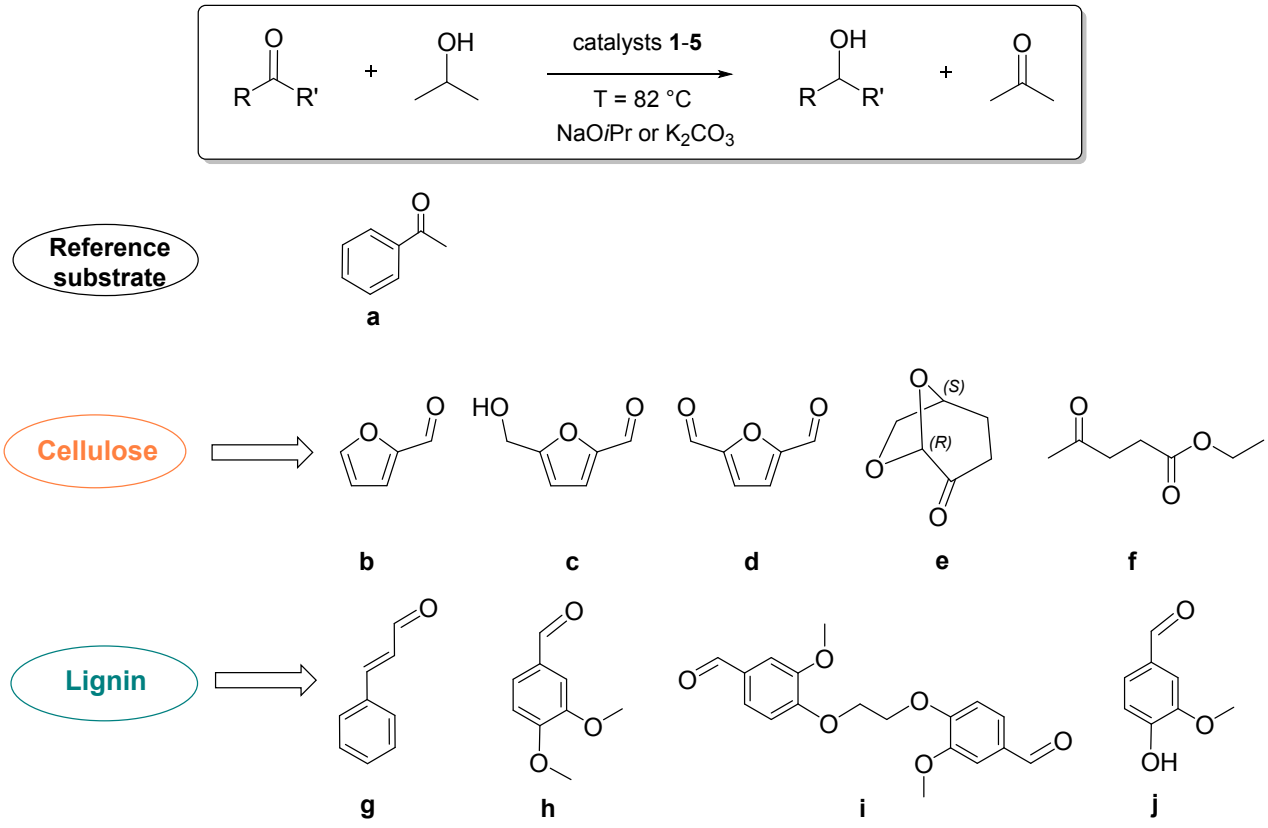


Scheme 5. Synthesis of the cationic carbonyl complex [Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4] (**5**).

The $^{31}P\{^1H\}$ NMR spectrum of **5** in CD_2Cl_2 displays two doublets at δ 34.2 and 22.0 ppm with a $^2J_{PP}$ = 250.9 Hz, in agreement with a *trans* arrangement of the two phosphorus atoms. In the ^1H NMR spectrum of **5** the two diastereotopic CH_2N protons appear as a doublet of doublets at δ 4.28 ppm ($^2J_{HH}$ = 16.3 Hz and $^3J_{HH}$ = 6.5 Hz) and a multiplet in the range δ 3.62-3.46 ppm, partially overlapped with one NH_2 proton, while the other is at δ 2.83. The cyclometalated carbon atom gives

a doublet of doublets at δ 175.3 ppm ($^2J_{CP}$ = 10.9 Hz and 8.9 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, whereas the triplet at δ 206.1 ppm ($^2J_{CP}$ = 15.3 Hz) is for the coordinated CO, which exhibits an IR stretching absorption at 1919 cm^{-1}. All these data are consistent with those found for the related bis PPh_3 complex *trans*-[Ru(CNN)$(PPh_3)_2$(CO)][BAr^f_4].[42] It is worth pointing out that although several homoleptic ruthenium(II) complexes showing the *trans*-Ru(CO)$(P)_2$ core have been described, only few examples containing two phosphines, exerting different *trans* influence, have been reported so far.[69-73]

Reduction of aldehydes and ketones via TH catalyzed by CNN^{OMe} pincer ruthenium complexes. The easily prepared pincer CNN^{OMe} ruthenium complexes **1-5**, have been investigated in the reduction of the model substrate acetophenone **a**, via TH with 2-propanol in the presence of a base. These complexes have been found extremely productive, affording quantitative conversion of **a** at S/C = 10000-100000 (S/C = substrate/catalyst molar ratio) and TOF up to 1000000 h^{-1}. This protocol has been subsequently applied to the TH of carbonyl compounds obtained from lignocellulose biomass (Scheme 6).



Scheme 6. Reduction of carbonyl compounds via TH catalyzed by complexes **1-5**.

Complex **1** at S/C 10000 shows poor activity in the TH of **a**, affording 97% conversion after 8 h with NaO*i*Pr (2 mol%) in 2-propanol at 82 °C (Table 1, entry 1). On the other hand, the diphosphine dppb derivative **2** leads to complete conversion of **a** into 1-phenylethanol at S/C = 20000 and 50000 in 5 and 20 min with TOF values of 1100000 and 450000 h^{-1}, respectively (Table 1, entries 2 and 3), indicating that **2** is a highly productive catalytic TH system with an activity comparable to that observed for related CNN pincer complexes.[41]

Table 1. **Catalytic TH of acetophenone a (0.1 M) with complexes 1-5 (S/C = 10000-100000) and NaO*i*Pr (2 mol%) in 2-propanol at 82 °C**.

Entry	Complex	S/C	Time [min]	Conv.[a] [%]	TOF[b] [h^{-1}]
1	**1**	10000	8 h	97	1200
2	**2**	20000	5	99	1100000
3	**2**	50000	20	99	450000
4	**3**	20000	15	99	260000
5	**3**	50000	60	98	100000
6	**4**	20000	20	99	95000
7	**4**	50000	120	98	60000
8	**5**	10000	20	99	150000
9	**5**	20000	40	99	110000
10	**5**	50000	240	99	92000
11	**5**	100000	8 h	98	42000

[a]Conversions have been determined by GC analyses. [b] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion.

Complex **3**, containing the robust dppf ligand, also allows reduction of **a** at S/C = 20000 and 50000, although with longer reaction times (15 and 60 min) (Table 1, entries 4 and 5), in line with the analogous pincer 2-aminomethylbenzo[*h*]quinoline derivatives [RuCl(CNN^R)(dppf)].[37] Interestingly, the monocarbonyl complex **4**, obtained from **1** by substitution of one PPh_3 with CO, shows a higher activity with respect to **1**, affording quantitative reduction of **a** in 20 and 120 min at S/C = 20000 and 50000, respectively, even if the rate is slower compared to the diphosphine derivatives **2** and **3** (entries 6 and 7). Finally, the cationic complex **5**, formed from **4** by replacement of the chloride ion with PCy_3, shows complete reduction of **a** at S/C = 10000-50000, with higher rate with respect to **4** (TOFs up to 150000 h^{-1}, entries 8-10). It is worth noting that **5**, which unlike complexes **1**-**4**, is highly soluble in alcohols, stable in diluted 2-propanol solution for days and much less oxygen sensitive, allows the TH of **a** even at S/C = 100000, showing that **5** is a practical and productive catalyst for the carbonyl reduction (entry 11). Control experiments, carried out under the

same catalytic conditions and without ruthenium, show a small conversion of **a** (9%) in 12 h, indicating that the base NaO*i*Pr is a poor catalyst.[74] The high performance of the monocarbonyl pincer **5**, containing the PCy_3 phosphine, is in line with our studies on the systems $[RuCl_2(HCNN)(CO)_2]$ / phosphines and the related pincer complex $[Ru(CNN)(PPh_3)_2(CO)][BAr^f_4]$.[42] As a matter of fact, for this class of pincer carbonyl ruthenium complexes the use of the more basic phosphine PCy_3, with respect to PPh_3, resulted in an enhancement of the catalytic activity. Therefore, it is likely that during the TH complex **5** undergoes substitution of PPh_3, generating a robust catalytically active hydride species H-Ru(CNN)(CO)(PCy_3), which is less sensitive towards catalyst deactivation.[75-77]

On the basis of the results obtained with the model substrate **a**, the most promising complexes **2**, **3** and **5** have been investigated in the TH of both aldehydes and ketones available from the cellulose and lignin biomass, using 2-propanol as hydrogen donor, in the presence of NaO*i*Pr or K_2CO_3 (Scheme 6). The reduction of furfural (FAL) **b** to furfuryl alcohol has been achieved with **2** and **3** at S/C = 10000 and 1000 with NaO*i*Pr (2 mol%), affording selective reduction to the corresponding alcohol (94 and 92%) in 30 and 2 min, respectively (Table 2, entries 1 and 2). Conversely, with **5** at S/C = 10000 formation of furfuryl alcohol (90%) is achieved in 10 min, with a small amount of uncharacterized side products (4%) (entry 3). The use of potassium carbonate as weak base under the same catalytic conditions gives poor conversion with the Ru catalysts (47% in 24 h with **2**, see ESI; Table S1, entry 2). The catalytic HY of **b** has been reported for Ru bis(diimine) complexes[78] and Ru(III)-acetylacetonate / dppb at 100-140 °C with H_2 under pressure.[79]

Table 2. **Catalytic TH of lignocellulose biomass carbonyl compounds (0.1 M) to alcohols with 2, 3, 5 (S/C = 500-100000) in 2-propanol at 82 °C.**

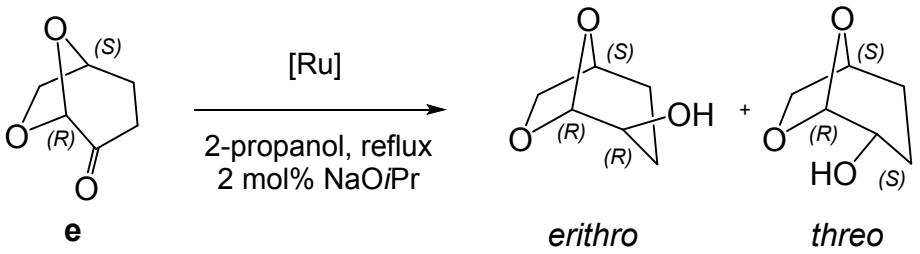
Entry	Substrate	Complex	S/C	Base[a]	Time [min]	Conv.[b] [%]	Alcohol [%]	By-prod. [%]
1	**b**	**2**	10000	NaO*i*Pr	30	94	94	-
2	**b**	**3**	1000	NaO*i*Pr	2	92	92	-
3	**b**	**5**	10000	NaOiPr	10	94	90	4
4	**c**	**2**	10000	NaO*i*Pr	5	99[c]	99	-
5	**c**	**2**	20000	NaO*i*Pr	10	99[c]	96	3
6	**c**	**3**	10000	NaOiPr	10	99[c]	94	5
7	**c**	**3**	50000	NaOiPr	60	99[c]	94	5
8	**c**	**5**	10000	NaO*i*Pr	30	99[c]	98	<1
9	**c**	**5**	50000	NaO*i*Pr	8 h	99[c]	98	1
10	**d**	**5**	1000	K_2CO_3	60	99[c]	95	4
11	**e**	**2**	1000	NaO*i*Pr	1	99	99[d]	-

12	**e**	**2**	10000	NaO*i*Pr	2	99	99[d]	-
13	**e**	**3**	10000	NaO*i*Pr	1	99	99[e]	-
14	**e**	**3**	50000	NaO*i*Pr	5	98	98[e]	-
15	**e**	**5**	50000	NaO*i*Pr	150	98	98[f]	-
16	**e**	**5**	100000	NaO*i*Pr	7 h	99	99[f]	-
17	**f**	**2**	1000	NaO*i*Pr	60	95	92[g]	3[h]
18	**f**	**2**	1000	K_2CO_3	20	99	97[g]	2[h]
19	**f**	**3**	1000	NaO*i*Pr	15	60	58[g]	2[h]
20	**f**	**3**	1000	K_2CO_3	15	99	98[g]	1[h]
21	**f**	**5**	10000	K_2CO_3	30	98	96[g]	2[h]
22	**g**	**2**	10000	K_2CO_3	8 h	98	94	4[i]
23	**g**	**3**	10000	K_2CO_3	8 h	99	92	7[i]
24	**g**	**5**	10000	K_2CO_3	60	99	90	9[i]
25	**g**	**5**	20000	K_2CO_3	120	98	91	7[i]
26	**g**	**5**	50000	K_2CO_3	8 h	99	91	8[i]
27	**h**	**3**	25000	K_2CO_3	3	99[c]	98	1
28	**h**	**5**	25000	K_2CO_3	30	99[c]	99	-
29	**h**	**5**	25000	NaO*i*Pr	15	99[c]	95	4
30	**i**	**3**	25000	NaO*i*Pr	4	99[c]	99	-
31	**j**	**5**	500	K_2CO_3	36 h	96[c]	96	-

[a]Base: NaO*i*Pr (2 mol%) or K_2CO_3 (5 mol%). [b]Conversions have been determined by GC analyses. [c]Conversions have been determined by NMR analyses. [d]*erithro*/*threo* ratio 1:1.2. [e]*erithro*/*threo* ratio 1.4:1. [f]*erithro*/*threo* ratio 1:5.7. [g]% of γ-valerolactone (GVL). [h]isopropyl 4-hydroxypentanoate. [i]3-phenylpropan-1-ol.

The substrate 5-(hydroxymethyl)furfural (5-HMF) **c**, available from cellulose biomass (C6 sugars), can be hydrogenated to 2,5-bis(hydroxymethyl)furan (BHMF) that is a building block for environmental friendly polyurethanes and polyesters,[80, 81] as well for the synthesis of 1,6-hexandiol for adhesives.[82] In spite of the vast literature of heterogeneous catalysis on **c**, only very recently homogeneous TH has emerged as viable and easy to apply route for the reduction of **c** to BHMF.[83] Complex **2** efficiently catalyzes the selective reduction of **c** to BHMF at S/C = 10000 and 20000 in 5 and 10 min, respectively (entries 4 and 5). With **3** and **5** complete conversion is observed at S/C = 10000 and 50000 (10 min - 8 h) (entries 6-9), whereas at S/C = 1000 the reduction occurs with **3** in 1 min (see ESI; Table S1, entry 3), indicating that these pincer complexes are among the most active and productive catalysts for the TH of **c** with 2-propanol.[84] With **2** and **3** in the presence of NaOiPr, incomplete reduction of 2,5-diformylfuran (DFF) **d** to BHMF was observed, whereas with the weak base K_2CO_3 (5 mol%) **3** gives only 4 % conversion to the diol in 3 h (see ESI; Table S1, entry 4). Interestingly, complex **5** at S/C = 1000 with K_2CO_3 afforded the quantitative formation of BHMF in 60 min (entry 10). To the best of our knowledge, no examples of TH of **d** with 2-propanol have been

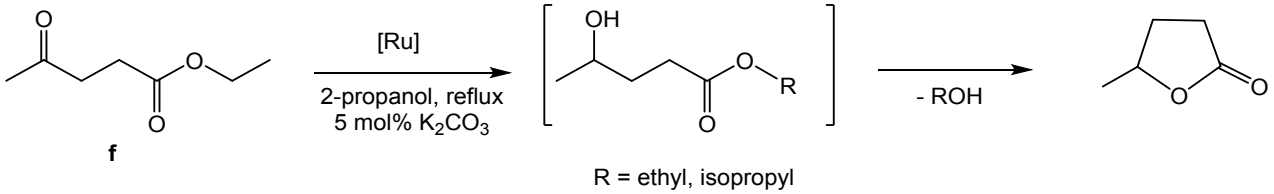
reported in the literature so far. The bicyclic ketone Cyrene (dihydrolevoglucosenone) **e**, obtained by HY of levoglucosenone from cellulosic materials (e.g. Furacell Process),[85] is emerging as a green, non-toxic dipolar aprotic solvents, in place of *N*-methylpyrrolidone, DMF or sulfolane.[86] HY of **e** over supported metal catalysts led to levoglucosanol as a mixture of *erithro* and *threo* diastereoisomers[87, 88] and 1,6-hexanediol through ring opening.[89] Conversely, no examples of homogeneous catalysts for the TH of **e** have been previously reported. Interestingly, we have found that **e** is easily reduced via TH in 2-propanol using complexes **2**, **3** and **5** with NaO*i*Pr (2 mol%) as the base (Scheme 7).



Scheme 7. Reduction of Cyrene **e** to levoglucosanol via TH catalyzed by complexes **2**, **3** and **5**.

With **2** at S/C = 10000 **e** is quantitatively reduced to alcohol in 2 min with an *erithro*/*threo* ratio of 1/1.2. Conversely, **3** affords complete reduction at S/C = 10000 and 50000 in 1 and 5 min, respectively, affording a TOF of 1500000 $h^{-1}$with *erithro*/*threo* = 1.4/1, as confirmed by ^{1}H and $^{13}C\{^{1}H\}$ NMR measurements (entries 11-14).[88, 90] Although **5** shows a lower rate for the TH of **e** with respect to **2** and **3**, complex **5** leads to complete conversion at S/C = 50000 and 100000 in 150 min and 7 h, respectively, with *erithro*/*threo* = 1/5.7 (entries 15 and 16). Notably, the diastereomerically pure *threo* alcohol has been recently isolated by selective reduction of **e** using baker's yeast (*Saccharomyces cerevisiae*).[90, 91] HY of levulinic acid (LA) and levulinate esters,[92-96] that are directly accessible from lignocellulose biomass,[94] is an attractive process for the synthesis of γ-valerolactone (GVL) which shows wide applications as solvent, fuel additive and monomer for polymer synthesis.[97] Most of the processes involve the HY of LA to GVL at high temperatures and H_2 pressure.[96, 98-101] Recently, Ir and Ru complexes based on phosphine and dipyridylamine ligands have been reported to efficiently hydrogenate LA to GVL with formic acid as hydrogen donor and in presence of H_2.[102, 103] In addition, the TH of LA and levulinate derivatives has been described using the Shvo catalyst,[104] $Fe(OTf)_2$/tetraphos[105] with formic acid and the Casey's iron catalyst[94] with 2-propanol at S/C = 100, but no examples of Ru complexes for the TH of levulinate esters with 2-propanol have been reported to date. The pincer complex **2** (S/C =1000) catalyzes efficiently the TH of ethyl levulinate **f** into GVL

(92%) in 60 min with NaO*i*Pr (2 mol%) (entry 17, and Scheme 8). Interestingly, the use of the weak base K_2CO_3 (5 mol%) as co-catalyst, results in higher conversion and selectivity to GVL (97%) in a shorter reaction time (20 min) (entry 18).



Scheme 8. Conversion of ethyl levulinate to GVL via TH catalyzed by complexes **2**, **3** and **5**.

A similar behavior has been observed for the dppf derivative **3**, leading to 99% conversion with K_2CO_3, whereas with NaO*i*Pr only 60% of GVL was attained in 15 min (entries 19 and 20). Unlike **2** and **3**, complex **5** has proven to be active at lower loading, affording complete conversion of **f** at S/C = 10000 in the presence of K_2CO_3 (5% mol) in 30 min, with a TOF of 20000 h^{-1}. To the best of our knowledge, the cationic monocarbonyl PCy_3 pincer complex **5** is one of the most active systems for the TH of **f** (entry 21). Control ^1H NMR experiments show that the reaction proceeds via reduction of **f** to a mixture of ethyl and isopropyl 4-hydroxyvalerate, generated in the 2-propanol basic media, followed by an intramolecular cyclization to GVL and alcohol elimination, in accordance with literature data (Scheme 8 and see ESI, Fig. S40).[103] The HY of *trans*-cinnamaldehyde **g**, which can be obtained from lignin defunctionalization, leads to 3-phenylpropanal, 3-phenylpropan-1-ol and 3-phenyl-2-propenol (cinnamyl alcohol), which can find applications as feedstocks in pharmaceuticals, cosmetics and fine chemicals.[105-107] The chemoselective reduction at the C=O bond is more challenging because the HY of the C=C bond is thermodynamically more favorable than that at the carbonyl group and many efforts have been devoted to improve the selectivity towards cinnamyl alcohol with metal based catalysts.[108] Nevertheless, we have found that **g** can be easily reduced via TH to the corresponding allylic alcohol with complexes **2** and **3** (S/C = 10000) in 94 and 92% conversion, respectively, in the presence of K_2CO_3, with formation of 3-phenylpropan-1-ol as by-product in 4 and 7% yield in 8 h, as the result of the concomitant reduction of the C=C bond (entries 22 and 23). Control experiments with **2** at higher loading (S/ C = 1000) gives cinnamyl alcohol (94%) in 5 min, while after prolonged reaction time (1 h) 3-phenylpropan-1-ol is formed in up to 35% yield (see ESI; Tab. S1, entry 7 and Fig. S41). Complex **5** has proven to catalyze the TH of **g** at higher S/C ratio, namely 10000, 20000 and 50000, with formation of 7-8% of 3-phenylpropan-1-ol (1-8 h, entries 24-26). The functionalized vanillin derivatives 3,4-dimethoxybenzaldehyde (veratraldehyde) **h**, 4,4'-[ethane-1,2-diylbis(oxy)]bis(3-methoxybenzaldehyde) **i** and also vanillin **j** have been reduced to the

corresponding alcohols with the pincer ruthenium complexes. For these bio-derivatives, no examples of TH Ru catalysts have been previously described. Veratraldehyde **h** is promptly converted to veratryl alcohol (3,4-dimethoxybenzyl alcohol) by complex **3** (S/C = 25000) in 3 min (entry 27). By using the cationic complex **5** (S/C = 25000) the quantitative reduction occurs in 30 and 15 min, using K_2CO_3 (5 mol%) and NaO*i*Pr (2 mol%), respectively (entries 28-29). The dialdehyde **i** is rapidly and selectively reduced to the corresponding dibenzyl alcohol in 99% yield with **3** (S/C = 25000) in the presence of NaO*i*Pr in 4 min, with a remarkably high TOF value of 500000 h^{-1} and without observation of the monoalcohol or by-products of the aldol condensation, due to the high reaction rate (entry 30). Interestingly, vanillin **j**, which is an acidic phenolic compound, is selectively reduced to vanillyl alcohol (96%) with **5** (S/C = 500) in the presence of K_2CO_3 (5 mol%) in 36 h at 82 °C, while complex **3** shows no conversion under these catalytic conditions (entry 31). To the best of our knowledge, complex **5** is the first example of catalyst for the selective TH of vanillin to the corresponding alcohol. The use of $[RuCl_2(PPh_3)_3]$ in the HY of **j** (S/C = 30 and 33 atm of H_2) leads to the formation of vanillyl alcohol, 2-methoxy-4-methylphenol and 2-methoxy-phenol, as result of hydrogenation and decarbonylative aldehyde reactions,[109] whereas with the Shvo catalyst (S/C = 200 and 10 atm of H_2) under acidic conditions the alcohol product is formed at 145 °C.[110] Conversely, the TH of **j** with formic acid on palladium results in the exclusive formation of 2-methoxy-4-methylphenol.[111]

Conclusions

In summary, a straightforward synthesis of a series of pincer CNN^{OMe} ruthenium complexes is reported from a $HCNN^{OMe}$ ligand prepared in high yield from the commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde, by reaction with hydroxylamine and subsequent hydrogenation. These pincer complexes are highly productive catalysts for the transfer hydrogenation (TH) of several biomass-derived carbonyl compounds with 2-propanol as hydrogen source, affording an unprecedented activity (S/C ratio up to 100000 and TOF up to 1500000 h^{-1}). Interestingly, the derivatives $[RuCl(CNN^{OMe})(PP)]$ (PP = dppb, dppf) display high catalytic activity in the reduction of furfural, 5-HMF and Cyrene. Conversely, the monocarbonyl *trans*-$[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4]$ shows an unprecedented high productivity in the TH of ethyl levulinate, cinnamaldehyde and vanillin derivatives. These results indicate that since no universal catalyst can be designed for the TH of carbonyl compounds, specific substrates can be efficiently reduced by pincer ruthenium complexes through a suitable tuning of the ancillary ligands.

Further studies on the development of highly active pincer catalysts for C-H bond formation reactions of biomass relevant products, including asymmetric transformations, are underway.

Experimental

General

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The substrate **i** was synthetized following a previous reported method.[112, 113] The ruthenium complexes $[RuCl_2(PPh_3)_3]$[114] and $[RuCl_2(dppb)(PPh_3)]$[68] were prepared according to literature procedures, whereas all other chemicals were purchased from Aldrich and Strem and used without further purification. NMR measurements were recorded on a Bruker Avance III HD NMR 400 spectrometer. Chemical shifts (ppm) are relative to TMS for ^{1}H and $^{13}C\{^{1}H\}$, whereas H_3PO_4 was used for $^{31}P\{^{1}H\}$. Infrared measurements were obtained with a Bruker Vector 22 FTIR spectrometer. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 analyzer, whereas GC analyses were performed with a Varian CP-3380 gas chromatograph equipped with a 25 m length MEGADEX-ETTBDMS-β chiral column with hydrogen (5 psi) as the carrier gas and flame ionization detector (FID). ESI-MS analysis and multi-stage mass spectrometry (MS^n) experiments were performed with a Finnigan LXQ Linear Ion Trap (Thermo Scientific, San Jose, CA, USA) fitted with an ESI source operating in positive mode. The data acquisition was under the control of Xcalibur software (Thermo Scientific).

Synthesis of (*E*)-6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime

Hydroxylamine hydrochloride (0.57 g, 8.2 mmol) was carefully added to a solution of commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde (1.50 g, 7.04 mmol) in a mixture of acetonitrile (47.5 mL), methanol (82.5 mL) and water (3.75 mL), which was heated up and turned yellow. The obtained clear solution was then stirred for 30 min at room temperature. The solvents were evaporated off and the residue was dissolved in 100 mL of ethyl acetate and extracted with 5% aqueous $NaHCO_3$ (2x50 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure to give the oxime as a white solid. Yield 1.53 g (95%). Elemental analysis calcd (%) for $C_{13}H_{12}N_2O_2$: C 68.41, H 5.30, N 12.27; found: C 68.37, H 5.39, N 12.21. MS (*m*/*z*, ESI^+): 251.16 (M + Na), 229.18 (M + H). ^{1}H NMR (400.1 MHz, CD_3OD, 25 °C): δ = 8.18 (s, 1H; HC=N), 7.95 (d, 8.9 Hz, $^{4}J_{HH}$ = 2.9 Hz, $^{5}J_{HH}$ = 2.1 Hz, 2H; aromatic protons), 7.81 (pseudo-t, $^{3}J_{HH}$ =

7.9 Hz, 1H; aromatic proton), 7.75-7.72 (m, 2H; aromatic protons), 7.02 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.9 Hz, $^5J_{HH}$ = 2.1 Hz, 2H; aromatic protons), 3.85 ppm (s, 3H; CH_3O); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3OD, 25 °C): δ = 160.9 (s; C*C*OCH_3), 157.0 (s; N*C*C), 152.1 (s; N*C*CH=N), 149.1 (s; C*C*H=N), 137.4-113.7 (m; aromatic carbon atoms), 54.4 ppm (s; *C*H_3O).

Synthesis of 6-(4-methoxyphenyl)-2-aminomethylpyridine HCNN^{OMe}

A solution of (*E*)-6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime (1.5 g, 6.58 mmol) in absolute ethanol (450 mL) was introduced into a 500 mL three necks round bottomed flask under stirring and inert atmosphere. After the addition of 10% Pd/C (150 mg), the reaction mixture was hydrogenated (1 atm of H_2) at room temperature overnight, affording complete conversion as found by TLC analysis. The catalyst was removed from the reaction mixture by filtering over a Celite pad, which was thoroughly washed with absolute EtOH. The resulting clear solution was concentrated to dryness under reduced pressure, affording 1.45 g of crude product as an off-white solid. The residue was purified by silica gel flash chromatography (eluent: Et_2O/MeOH/NH_4OH (94:5:1), affording the pure compound as a colorless powder. Yield 1.25 g (89%). Elemental analysis calcd (%) for $C_{13}H_{14}N_2O$: C 72.87, H 6.59, N 13.07; found: C 72.85, H 6.63, N 13.01. MS (*m*/*z*, ESI$^+$): 215.20 [M + H]. ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.05 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.0 Hz, $^5J_{HH}$ = 2.0 Hz, 2H; aromatic protons), 7.72 (t, $^3J_{HH}$ = 7.7 Hz, 1H; aromatic proton), 7.59 (d, $^3J_{HH}$ = 7.8 Hz, 1H; aromatic proton), 7.20 (d, $^3J_{HH}$ = 7.6 Hz, 1H; aromatic proton), 7.03 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.0 Hz, $^5J_{HH}$ = 2.1 Hz, 2H; aromatic protons), 4.00 (s, 2H; CH_2N), 3.89 (s, 3H; CH_3O), 1.77 ppm (s, 2H; NH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 162.0 (s; N*C*C), 160.5 (s; C*C*OCH_3), 156.0 (s; N*C*CH_2), 137.1-113.9 (m; aromatic carbon atoms), 55.3 (s; *C*H_3O), 47.9 ppm (s; *C*H_2N).

Synthesis of *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (1)

The ligand HCNN^{OMe} (54 mg, 0.252 mmol, 1.2 equiv.) and NEt_3 (291 µL, 2.09 mmol, 10 equiv.) were added to [$RuCl_2(PPh_3)_3$] (200.0 mg, 0.209 mmol) in 2-propanol (5 mL) and the mixture was stirred at reflux for 2 h. The resulting suspension was filtered and the yellow solid washed with 2-propanol (2x3 mL), methanol (2x3 mL), *n*-heptane (2x5 mL) and dried under reduced pressure. Yield: 170 mg (93%). Elemental analysis calcd (%) for $C_{49}H_{43}ClN_2OP_2Ru$ (874.36): C 67.31, H 4.96, N 3.20; found: C 67.22, H 5.01, N 3.16. ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.02 (dt, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H; aromatic proton), 7.77 (m, 1H; aromatic proton), 7.63 (d, $^3J_{HH}$ = 2.2 Hz, 1H; aromatic proton), 7.53-7.01 (m, 13H; aromatic protons), 6.98-6.79 (m, 18H; aromatic protons), 6.61

(d, $^3J_{HH}$ = 7.5 Hz, 1H; aromatic proton), 6.41 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.6, 1H; aromatic proton), 4.04 (dd, $^2J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 6.0 Hz, 1H; CH_2N), 3.68 (s, 3H; CH_3O), 3.74-3.60 (m, 1H; NH_2), 3.38 (m, 1H; CH_2N), 1.87 ppm (m, 1H; NH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $C_2D_2Cl_4$, 25 °C): δ = 183.7 (dd, $^2J_{CP}$ = 13.2 Hz, $^2J_{CP}$ = 8.9 Hz; CRu), 163.0 (s; N*C*C), 157.2 (s; C*C*OCH$_3$), 156.8 (s; N*C*CH$_2$), 142.2-109.0 (m; aromatic carbon atoms), 55.1 (s; *C*H$_3$O), 50.8 ppm (d, $^2J_{CP}$ = 1.8 Hz; *C*H$_2$N). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 54.6 (d, $^2J_{PP}$ = 32.8 Hz), 49.4 (d, $^2J_{PP}$ = 32.8 Hz).

Synthesis of [RuCl(CNN^{OMe})(dppb)] (2)

Method A: The complex [$RuCl_2(PPh_3)_3$] (200 mg, 0.209 mmol) and dppb (98 mg, 0.230 mmol, 1.10 equiv.) were suspended in 2-propanol (4.0 mL), and the mixture was stirred at reflux for 3 h. The ligand HCNN^{OMe} (54 mg, 0.252 mmol, 1.21 equiv.) and NEt_3 (291 μL, 2.09 mmol, 10 equiv.) were added and the mixture was refluxed for 2 h. The suspension was cooled to room temperature and the yellow precipitate was filtered, washed with 2-propanol (3 mL), MeOH (2x3 mL), *n*-heptane (2x5 mL) and dried under reduced pressure. Yield: 147 mg (91%). Elemental analysis calcd (%) for $C_{41}H_{41}ClN_2OP_2Ru$ (776.26): C 63.39, H 5.32, N 3.61; found: C 63.34, H 5.27, N 3.65. ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.21 (tt, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 1.5 Hz, 2H; aromatic protons), 7.78 (tt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.3 Hz, 2H; aromatic protons), 7.58-7.41 (m, 7H; aromatic protons), 7.41-7.32 (m, 6H; aromatic protons), 7.30 (d, $^3J_{HH}$ = 8.5 Hz, 1H; aromatic proton), 7.19 (t, $^3J_{HH}$ = 7.8 Hz, 1H; aromatic proton), 7.00 (d, $^3J_{HH}$ = 8.1 Hz, 1H; aromatic proton), 6.88 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; aromatic proton), 6.67 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; aromatic proton), 6.64 (d, $^3J_{HH}$ = 7.1 Hz, 1H; aromatic proton), 6.53 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.5 Hz, 1H; aromatic proton), 6.06 (t, $^3J_{HH}$ = 8.1 Hz, 2H; aromatic protons), 4.15 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 4.6 Hz, 1H; CH_2N), 3.75 (td, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 4.7 Hz, 1H; CH_2N), 3.61 (s, 3H; CH_3O), 3.45 (td, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 5.4 Hz, 1H; NH_2), 3.16 (pseudo-q, J_{HH} = 12.3 Hz, 1H; CH_2P), 3.03 (tt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 3.3 Hz, 1H; CH_2P), 2.33 (dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 9.0 Hz, 1H; CH_2P), 2.24 (t, $^2J_{HH}$ = 14.6 Hz, 1H; CH_2P), 2.08-1.85 (m, 3H; C*H*$_2$CH$_2$P and NH_2), 1.79-1.65 (m, 1H; C*H*$_2$CH$_2$P), 1.65-1.56 (m, 1H; C*H*$_2$CH$_2$P), 1.25-1.06 ppm (m, 1H; C*H*$_2$CH$_2$P). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 184.9 (dd, $^2J_{CP}$ = 16.0 Hz, $^2J_{CP}$ = 7.7 Hz; CRu), 162.9 (s; N*C*C), 157.7 (s; C*C*OCH$_3$), 155.9 (s; N*C*CH$_2$), 144.3-107.3 (m; aromatic carbon atoms), 54.6 (s; *C*H$_3$O), 52.2 (d, $^3J_{CP}$ = 2.7 Hz; *C*H$_2$N), 32.7 (dd, $^1J_{CP}$ = 24.7 Hz, $^3J_{CP}$ = 1.5Hz; *C*H$_2$P), 30.7 (d, $^1J_{CP}$ = 31.5 Hz; *C*H$_2$P), 26.5 (d, $^2J_{CP}$ = 1.6 Hz; *C*H$_2$CH$_2$P), 21.8 ppm (d, $^2J_{CP}$ = 1.2 Hz; *C*H$_2$CH$_2$P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C) δ 56.9 (d, $^2J_{PP}$ = 37.7 Hz), 41.0 ppm (d, $^2J_{PP}$ = 37.7 Hz).

Method B: To a suspension of [$RuCl_2(PPh_3)$(dppb)] (100 mg, 0.116 mmol) in 2-propanol (3.0 mL) the ligand $HCNN^{OMe}$ (28 mg, 0.131 mmol, 1.13 equiv.) and triethylamine (162 µL, 1.16 mmol, 10 equiv.) were added. The mixture was stirred under reflux for 2 h and the yellow precipitate was filtered, washed with 2-propanol (2x2 mL), methanol (2x2 mL), *n*-heptane (2x5 mL) and dried under reduced pressure. Yield: 80.1 mg (89%).

Synthesis of [RuCl(CNN^{OMe})(dppf)] (3)

The complex [$RuCl_2(PPh_3)_3$] (200 mg, 0.209 mmol) and dppf (128 mg, 0.230 mmol, 1.10 equiv.) were dissolved in dichloromethane (4.0 mL) and the solution was stirred for 3 h at room temperature. The solvent was evaporated under reduced pressure and the ligand $HCNN^{OMe}$ (54 mg, 0.252 mmol, 1.21 equiv.) dissolved in 2-propanol (4.0 mL) and NEt_3 (291 µL, 2.09 mmol, 10 equiv.) were added. The mixture was refluxed for 3 h obtaining a yellow precipitate, which was filtered, washed with 2-propanol (2x4 mL), methanol (2x4 mL), *n*-heptane (2x5 mL) and dried under reduced pressure. Yield: 161 mg (85%). Elemental analysis calcd (%) for $C_{47}H_{41}ClFeN_2OP_2Ru$ (904.17): C 62.43, H 4.57, N 3.10; found: C 62.36, H 4.50, N 3.02. ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.51 (t, $^3J_{HH}$ = 8.3 Hz, 2H; aromatic protons), 8.06 (t, $^3J_{HH}$ = 7.4 Hz, 2H; aromatic protons), 8.01 (d, $^4J_{HH}$ = 1.6 Hz, 1H; aromatic proton), 7.73 (t, $^3J_{HH}$ = 8.5 Hz, 1H; aromatic proton), 7.54 (d, $^3J_{HH}$ = 7.2 Hz, 1H; aromatic proton), 7.49 (t, $^3J_{HH}$ = 8.3 Hz, 2H; aromatic protons), 7.41 (d, $^3J_{HH}$ = 7.3 Hz, 1H; aromatic proton), 7.37 (t, $^3J_{HH}$ = 7.2 Hz, 2H; aromatic protons), 7.31 (d, $^3J_{HH}$ = 8.5 Hz, 1H; aromatic proton), 7.28-7.15 (m, 4H; aromatic protons), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, 1H; aromatic proton), 6.95 (d, $^3J_{HH}$ = 7.2 Hz, 1H; aromatic proton), 6.75-6.69 (m, 4H; aromatic protons), 6.55 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.2 Hz, 1H; aromatic proton), 6.49 (t, $^3J_{HH}$ = 8.5 Hz, 2H; aromatic protons), 5.37 (s, 1H; C_5H_4), 4.90 (s, 1H; C_5H_4), 4.39 (s, 1H; C_5H_4), 4.27 (s, 1H; C_5H_4), 4.21 (s, 1H; C_5H_4), 4.14 (dd, $^2J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 4.8 Hz, 1H; CH_2N), 4.00 (s, 1H; C_5H_4), 3.90 (s, 1H; C_5H_4), 3.79 (s, 3H; CH_3O), 3.67-3.57 (m, 1H; NH_2), 3.47 (ddd, $^2J_{HH}$ = 16.7 Hz, $^3J_{HH}$ = 11.8 Hz, $^3J_{HH}$ = 5.6 Hz, 1H; CH_2N), 3.21 (s, 1H; C_5H_4), 2.06 ppm (dd, $^2J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 5.3 Hz, 1H; NH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 182.5 (dd, $^2J_{CP}$ = 14.9 Hz, $^2J_{CP}$ = 8.2 Hz; CRu), 163.1 (s; N*C*C), 156.7 (s; C*C*OCH_3), 156.6 (s; N*C*CH_2), 143.6-108.0 (m; aromatic carbon atoms), 87.4 (dd, $^1J_{CP}$ = 38.3 Hz, $^3J_{CP}$ = 4.3 Hz; *ipso*-C_5H_4), 86.3 (d, $^1J_{CP}$ = 49.6 Hz; *ipso*-C_5H_4), 77.4 (d, $^2J_{CP}$ = 13.2 Hz; C_5H_4), 76.4 (d, $^2J_{CP}$ = 7.7 Hz; C_5H_4), 75.5 (d, $^3J_{CP}$ = 2.5 Hz; C_5H_4), 73.4 (d, $^2J_{CP}$ = 6.8 Hz; C_5H_4), 73.1 (d, $^3J_{CP}$ = 4.8 Hz; C_5H_4), 69.2 (d, $^3J_{CP}$ = 1.3 Hz; C_5H_4), 69.1 (br s; C_5H_4), 68.7 (d, $^2J_{CP}$ = 5.0 Hz; C_5H_4), 54.9 (s; *C*H_3O), 51.3 ppm (d, $^3J_{CP}$ = 2.1 Hz; *C*H_2N). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 61.5 (d, $^2J_{PP}$ = 35.6 Hz), 44.1 ppm (d, $^2J_{PP}$ = 35.6 Hz).

Synthesis of [RuCl(CNN^{OMe})(CO)(PPh$_3$)] (4)

The complex *cis*-[RuCl(CNN^{OMe})(PPh$_3$)$_2$] (**1**) (251.9 mg, 0.29 mmol) was suspended in dichloromethane (5 mL) and the mixture was stirred under CO atmosphere (1 atm) overnight at room temperature. The obtained yellow solution was concentrated to about 1 mL by evaporation of the solvent under reduced pressure. Addition of *n*-heptane (10 mL) afforded the precipitation of a light-yellow solid that was washed with diethyl ether (3x5 mL), *n*-heptane (3x10 mL) and dried under reduced pressure. The residue was suspended in 2-propanol (5 mL) and stirred at reflux for 48 h providing the product as a single isomer. Yield: 115 mg (79%). Anal. Calcd (%) for $C_{32}H_{28}ClN_2O_2PRu$ (640.08): C 60.05, H 4.41, N 4.38; found: C 60.09, H 4.36, N 4.42. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25°C): δ = 7.51 (t, $^3J_{HH}$ = 7.8 Hz, 1H; aromatic proton), 7.45-7.37 (m, 3H; aromatic protons), 7.35-7.16 (m, 14H; aromatic protons), 7.04 (d, $^4J_{HH}$ = 1.8 Hz, 1H; aromatic proton), 6.65 (d, $^3J_{HH}$ = 7.5 Hz, 1H; aromatic proton), 6.36 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.4 Hz, 1H; aromatic proton), 4.23 (dd, $^2J_{HH}$ = 16.4 Hz, $^3J_{HH}$ = 6.4 Hz, 1H; CH_2N), 3.87 (dd, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 9.0 Hz, 1H; NH_2), 3.70 (s, 3H; CH_3O), 3.41 (ddd, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 6.1 Hz, 1H; CH_2N), 2.79 ppm (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.8 Hz, 1H; NH_2). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 207.1 (d, $^2J_{CP}$ = 17.7 Hz; CO), 179.0 (d, $^2J_{CP}$ = 12.6 Hz; CRu), 161.6 (s; N*C*C), 159.2 (s; C*C*OCH$_3$), 156.6 (s; N*C*CH$_2$), 138.4-108.6 (m; aromatic carbon atoms), 54.7 (s; *C*H$_3$O), 50.9 (s; CH_2N). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 56.7 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1913 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (5)

Na[BAr$^f_4$] (60.0 mg, 0.0677 mmol) and PCy$_3$ (17.6 mg, 0.0628 mmol) were added to [RuCl(CNN^{OMe})(CO)(PPh$_3$)] (**4**) (40.0 mg, 0.0625 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 30 min at room temperature and filtered to remove NaCl. The obtained solution was concentrated (1 mL) and addition of *n*-heptane (5 mL) afforded a light-yellow precipitate, which was filtered, washed with *n*-heptane (3x5 mL) and dried under reduced pressure. Yield 100.5 mg (92%). Anal. Calcd (%) for $C_{82}H_{73}BF_{24}N_2O_2P_2Ru$ (1748.29): C 56.34, H 4.21, N 1.60; found: C 56.38, H 4.26, N 1.65. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 7.79 (m, 8H; aromatic protons), 7.66 (t, $^3J_{HH}$ = 8.0 Hz, 1H; aromatic proton), 7.62 (br s, 4H; aromatic protons),

7.52 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H; aromatic proton), 7.50 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H; aromatic proton), 7.44-7.39 (m, 3H; aromatic protons), 7.34-7.26 (m, 6H; aromatic protons), 7.25-7.17 (m, 6H; aromatic protons), 6.84 (m, 1H; aromatic proton), 6.77 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H; aromatic proton), 6.51 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HH}$ = 2.5 Hz, 1H; aromatic proton), 4.28 (dd, $^{2}J_{HH}$ = 16.3 Hz, $^{3}J_{HH}$ = 6.5 Hz, 1H; CH_2N), 3.67 (s, 3H; CH_3O), 3.62-3.46 (m, 2H; CH_2N and NH_2), 2.83 (m, 1H; NH_2), 2.15 (m, 3H; PCH), 2.00-1.72 (m, 10H; CH_2 of Cy), 1.71-1.56 (m, 5H; CH_2 of Cy), 1.55-1.27 (m, 4H; CH_2 of Cy), 1.20 (q, J_{HH} = 10.3 Hz, 4H; CH_2 of Cy), 1.05 (q, J_{HH} = 13.1 Hz, 4H; CH_2 of Cy), 0.81-0.64 ppm (m, 3H; CH_2 of Cy). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 206.1 (t, $^{2}J_{CP}$ = 15.3 Hz; CO), 175.3 (dd, $^{2}J_{CP}$ = 10.9 Hz, $^{2}J_{CP}$ = 8.9 Hz; CRu), 162.8 (s; N*C*C), 161.8 (q, $^{1}J_{CB}$ = 50.1 Hz; CB), 160.0 (s; C*C*OCH$_3$), 157.1 (s; N*C*CH$_2$), 137.9-109.2 (aromatic carbon atoms), 124.6 (q, $^{1}J_{CF}$ = 272.3 Hz; *C*F$_3$), 54.7 (s; *C*H$_3$O), 50.4 (s; CH$_2$N), 35.6 (dd, $^{1}J_{CP}$ = 15.7 Hz, $^{3}J_{CP}$ = 1.5 Hz; P*C*H), 30.5 (s; CH_2 of Cy), 28.7 (d, J_{CP} = 2.9 Hz; CH_2 of Cy), 27.5 (d, J_{CP} = 12.3 Hz; CH_2 of Cy), 27.4 (d, J_{CP} = 9.5 Hz CH_2 of Cy), 26.8 (d, J_{CP} = 11.8 Hz; CH_2 of Cy), 26.0 ppm (s; CH_2 of Cy). $^{31}P\{^{1}H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 34.2 (d, $^{2}J_{PP}$ = 250.9 Hz), 22.0 ppm (d, $^{2}J_{PP}$ = 250.9 Hz). IR (Nujol): $\tilde{\nu}$ = 1919 (s) (C≡O) cm^{-1}.

Catalytic TH of of ketones and aldehydes in the presence of NaO*i*Pr

The ruthenium catalyst solution used for TH was prepared by dissolving the ruthenium complexes **1-5** (2.0 μmol) in 2 mL of 2-propanol. A 0.1 M solution of NaO*i*Pr (200 μL, 20 μmol) in 2-propanol and the catalyst solution (1 mL, 1.0 μmol) were added to the ketone or aldehyde solution (1.0 mmol) in 2-propanol (final volume 10 mL) and the resulting mixture was heated under reflux. The reaction was sampled by removing an aliquot of the reaction mixture (0.5 mL), which was quenched by addition of diethyl ether (1:1 v/v), filtered over a short silica pad and submitted to GC analysis. The addition of the base was considered as the start time of the reaction. The S/C molar ratio was 1000/1, whereas the base concentration was 2 mol% respect to the substrate (0.1 M). The same procedure was followed for TH reactions with other S/C (in the range 1000-100000) using the appropriate amount of catalyst. For solid and high-boiling compounds, the solvent was evaporated under vacuum and the crude mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

Catalytic TH of of ketones and aldehydes in the presence of K_2CO_3

When potassium carbonate was used as base in place of NaO*i*Pr, the substrate (1 mmol), K_2CO_3 (6.9 mg, 0.05 mmol) and 2-propanol were introduced into a Schlenk and heated at reflux. The catalyst solution of complexes **2**, **3** and **5** in 2-propanol (1 mL, 1.0 μmol of Ru) was added to the mixture to

reach a final volume of 10 mL. Addition of the Ru complex was considered as the start time of the catalysis. The TH reductions were monitored analogously as described previously, by removal of an aliquot of the reaction mixture (approximately 0.5 mL) followed by the addition of diethyl ether (1:1 v/v). After filtration through a short silica pad, the conversion was determined by GC analysis. The S/C molar ratio was 1000/1, whereas the base concentration was 5 mol% respect to the substrate (0.1 M). The same procedure was followed for TH reactions with other S/C (in the range 500-50000) using the appropriate amount of catalysts.

†Electronic supplementary information (ESI) available: NMR spectra of the isolated complexes and further data about the aldehyde and ketone TH reductions catalyzed by the ruthenium derivatives. For ESI and other electronic format, see DOI: ***

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Conflicts of interest

The authors declare no competing financial interests.

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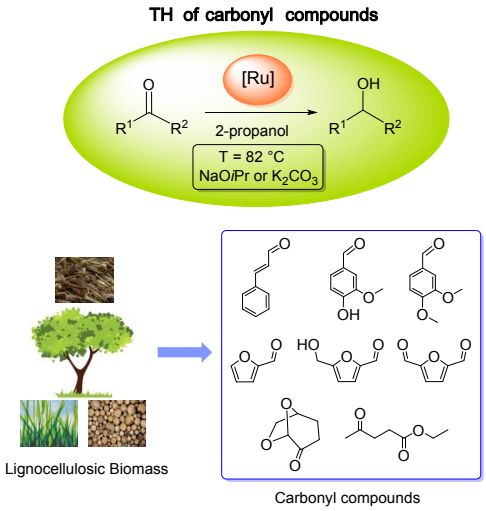
CNN Pincer Ruthenium Complexes for Efficient Transfer Hydrogenation of Biomass-Derived Carbonyl Compounds

Rosario Figliolia,[a] Paolo Cavigli,[a] Clara Comuzzi,[a] Alessandro Del Zotto,[a] Denise Lovison,[a] Paolo Strazzolini,[a] Sabina Susmel,[a] Daniele Zuccaccia,[a] Maurizio Ballico,[a,*] Walter Baratta[a,*]

Robust and easily accessible CNN^{OMe} pincer ruthenium complexes display unprecedented selectivity and productivity in the TH of lignocellulose-derived carbonyl compounds with 2-propanol.



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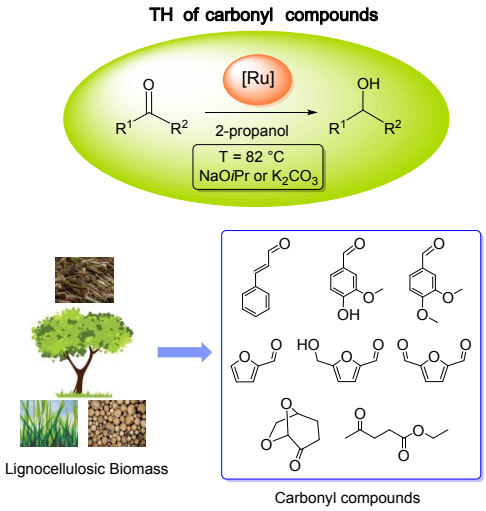

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Supporting Information

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Figure S41. GC-FID chromatograms of the reaction mixture of the TH of cinnamaldehyde **g** in 2-propanol at reflux promoted by complex **2** at S/C 1000 Pag. S38

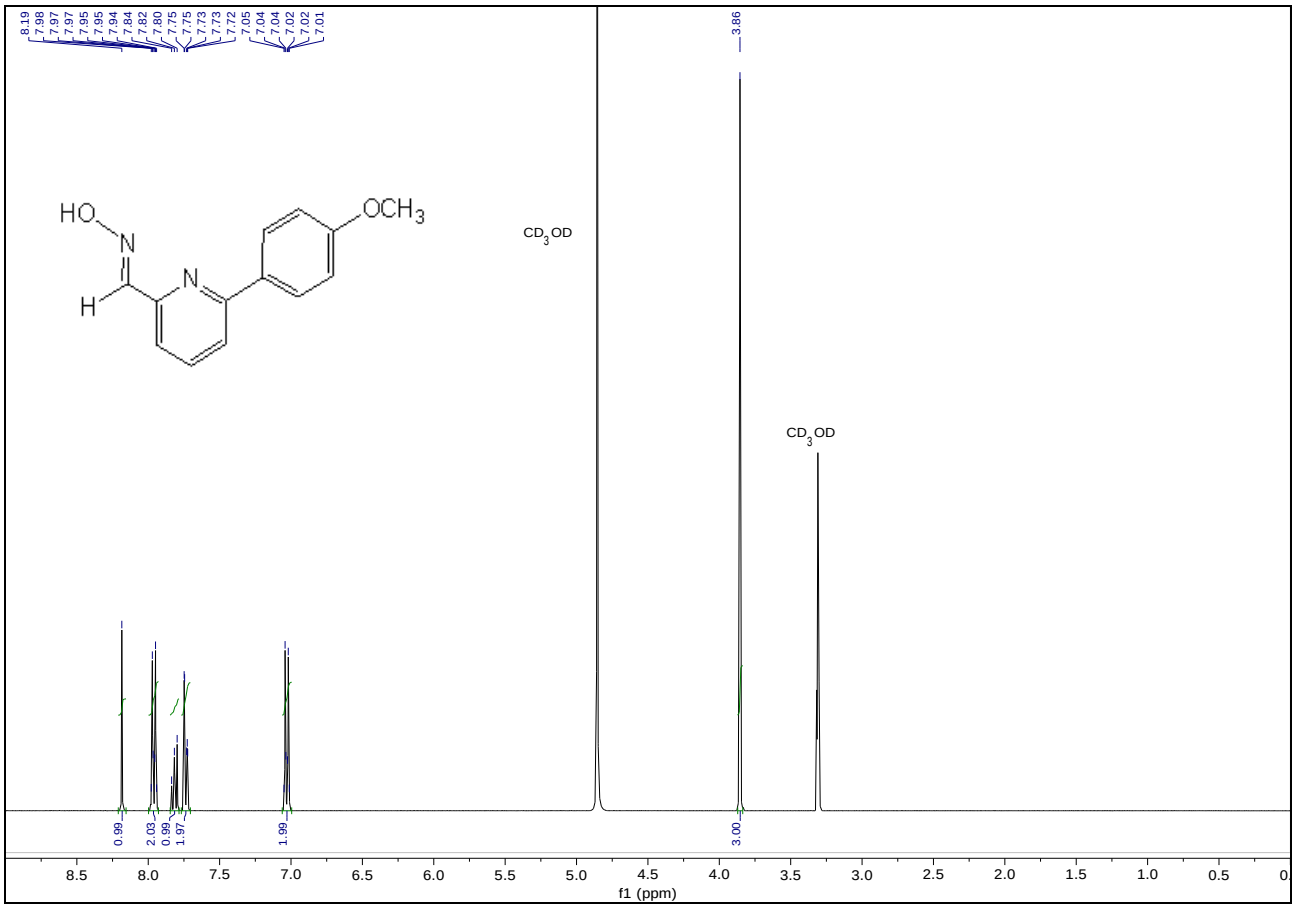

Figure S1. ^{1}H NMR spectrum (400.1 MHz) of 6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime in CD_3OD at 25 °C.

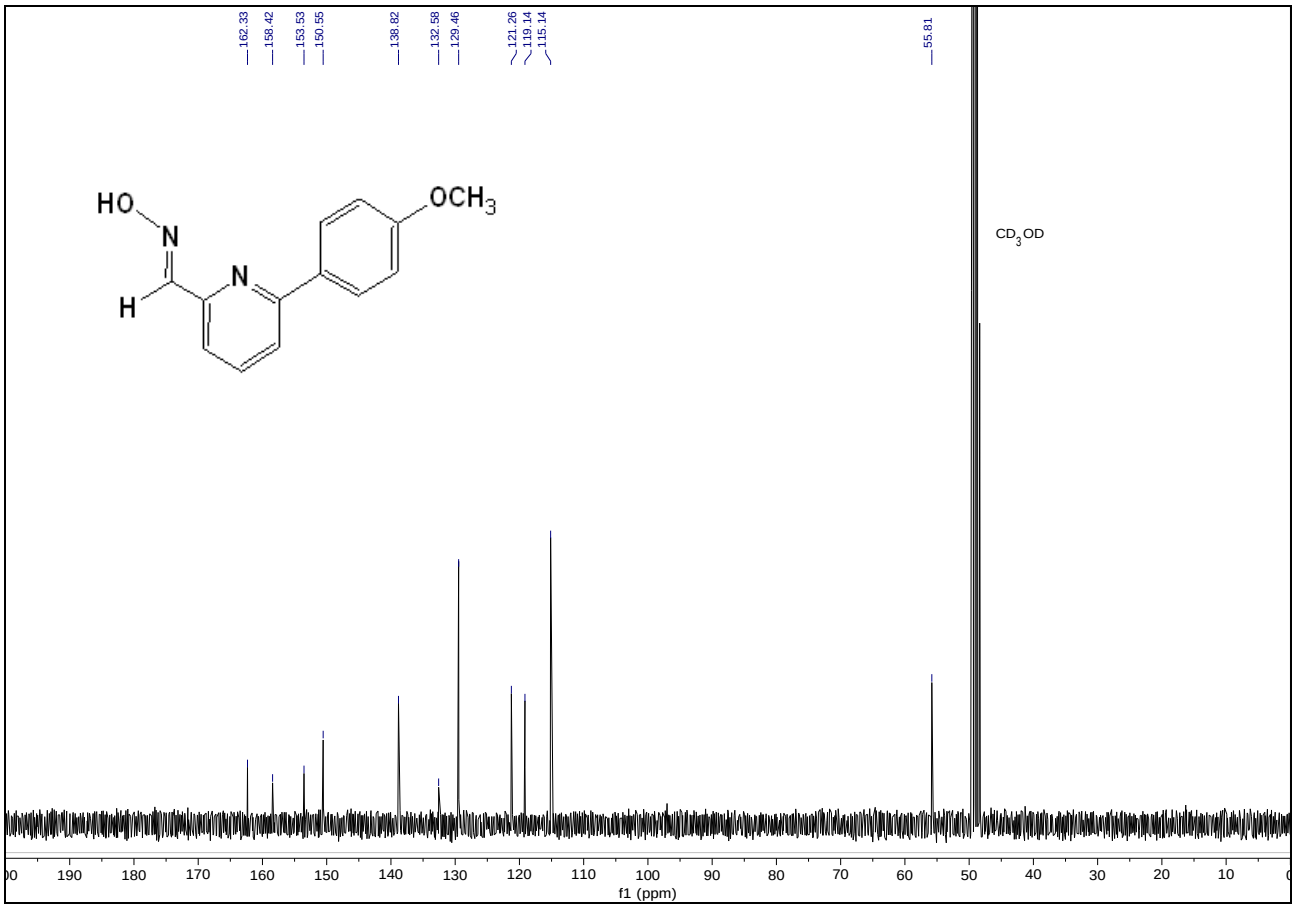

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz) of 6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime in CD_3OD at 25 °C.

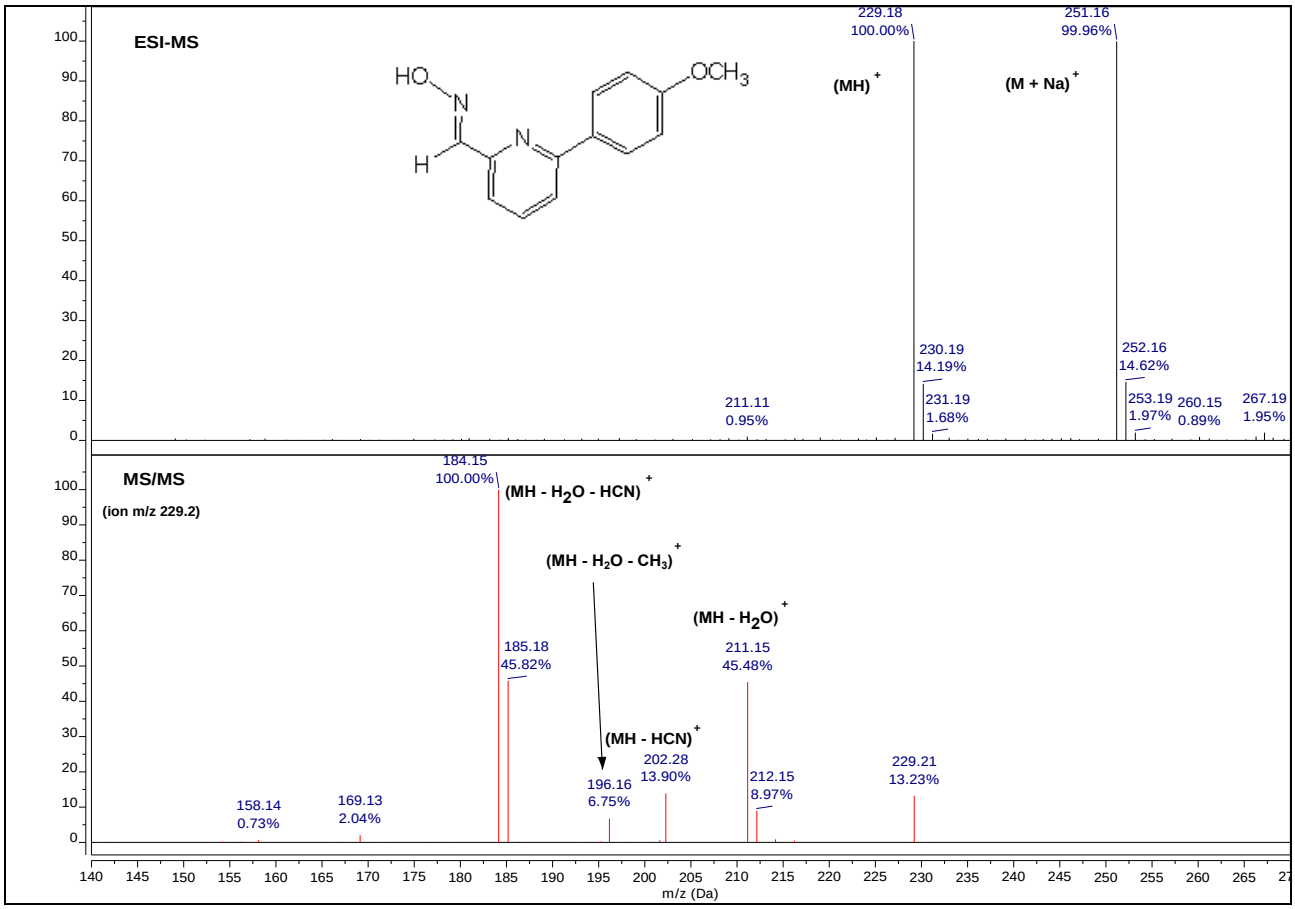

Figure S3. (+)-ESI-MS and MS/MS spectra of 6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime in CH_3OH

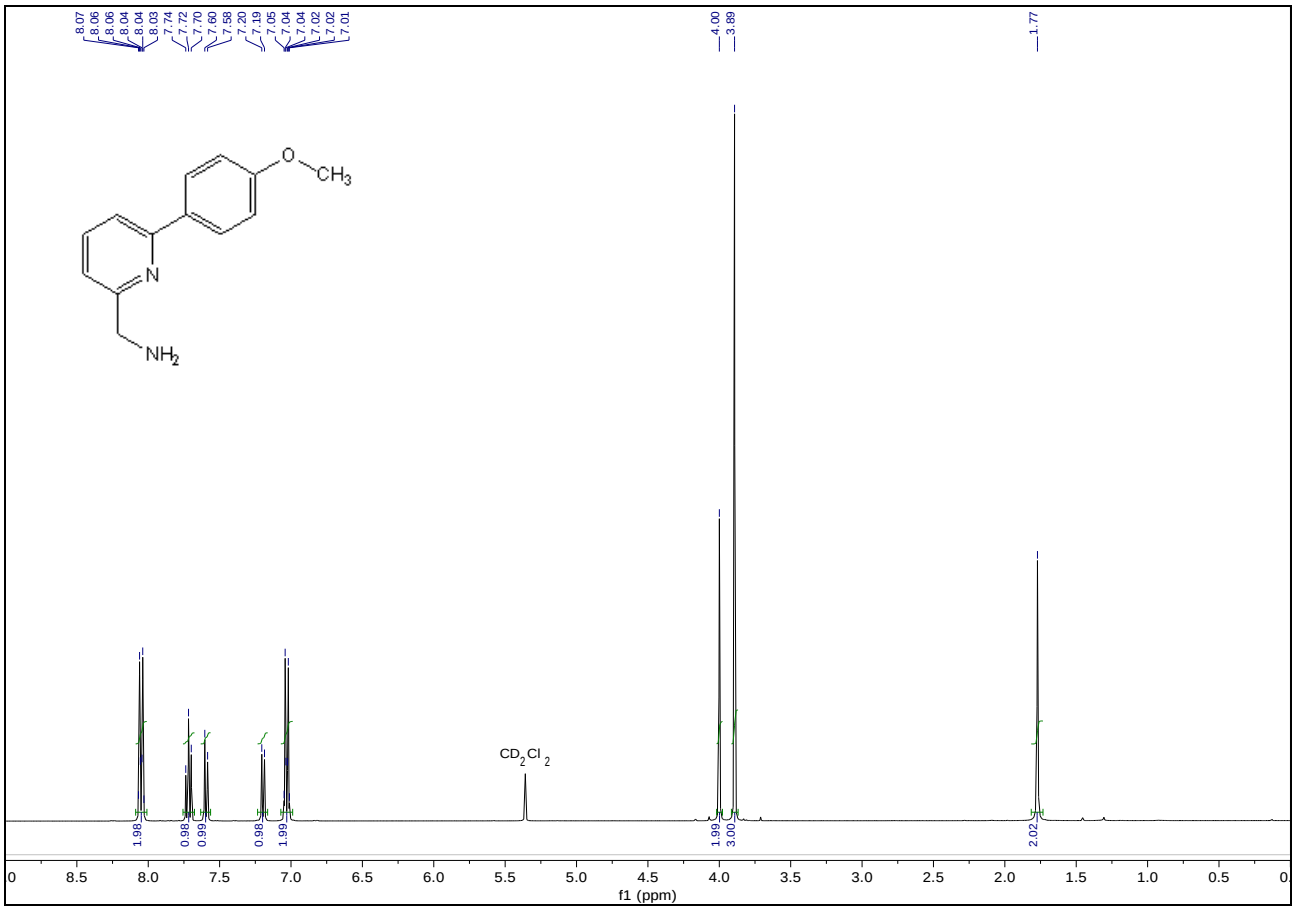

Figure S4. ^{1}H NMR spectrum (400.1 MHz) of (6-(4-methoxyphenyl)pyridin-2-yl)methanamine ($HCNN^{OMe}$) in CD_2Cl_2 at 25 °C.

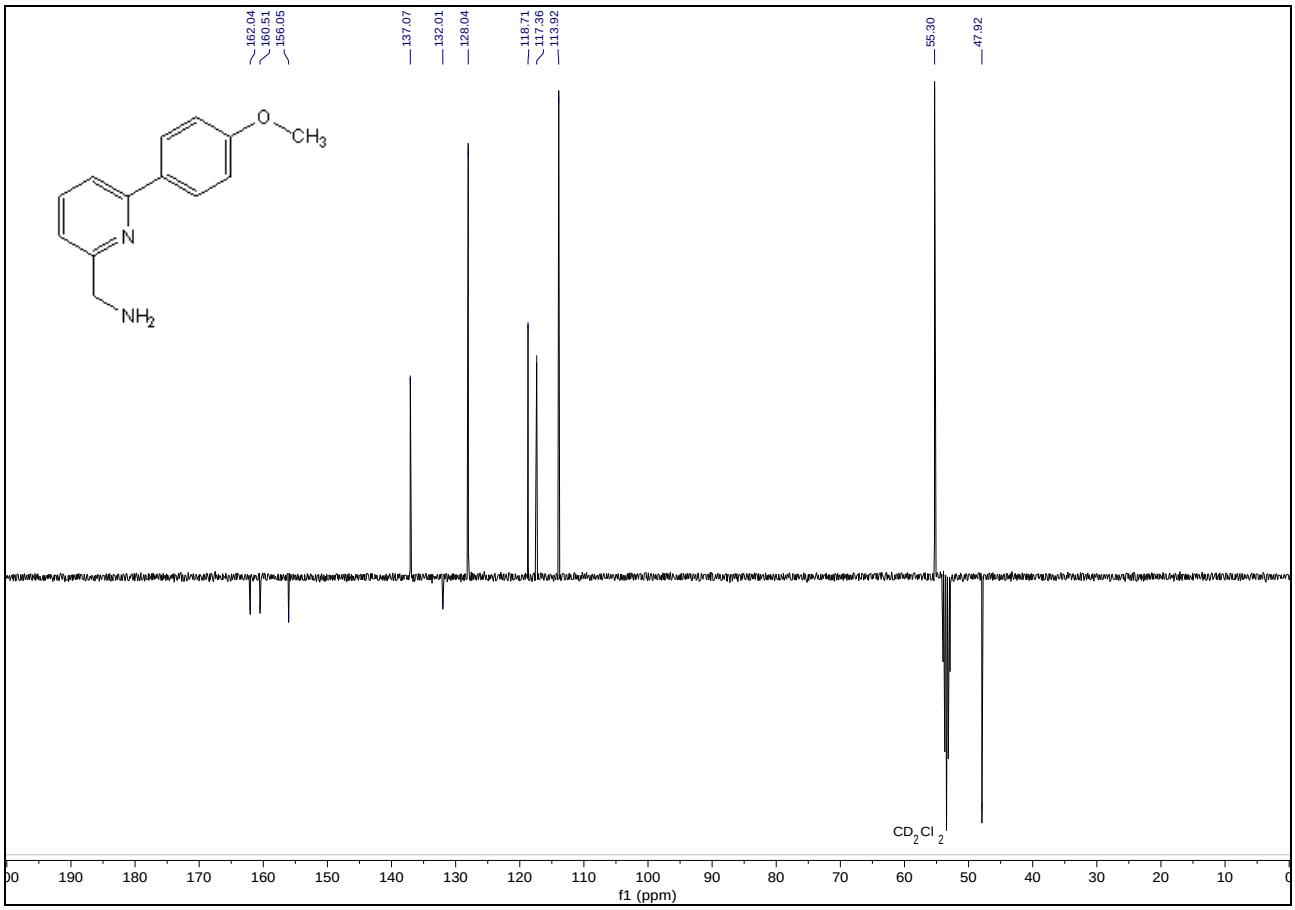

Figure S5. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum (100.6 MHz) of (6-(4-methoxyphenyl)pyridin-2-yl)methanamine ($HCNN^{OMe}$) in CD_2Cl_2 at 25 °C.

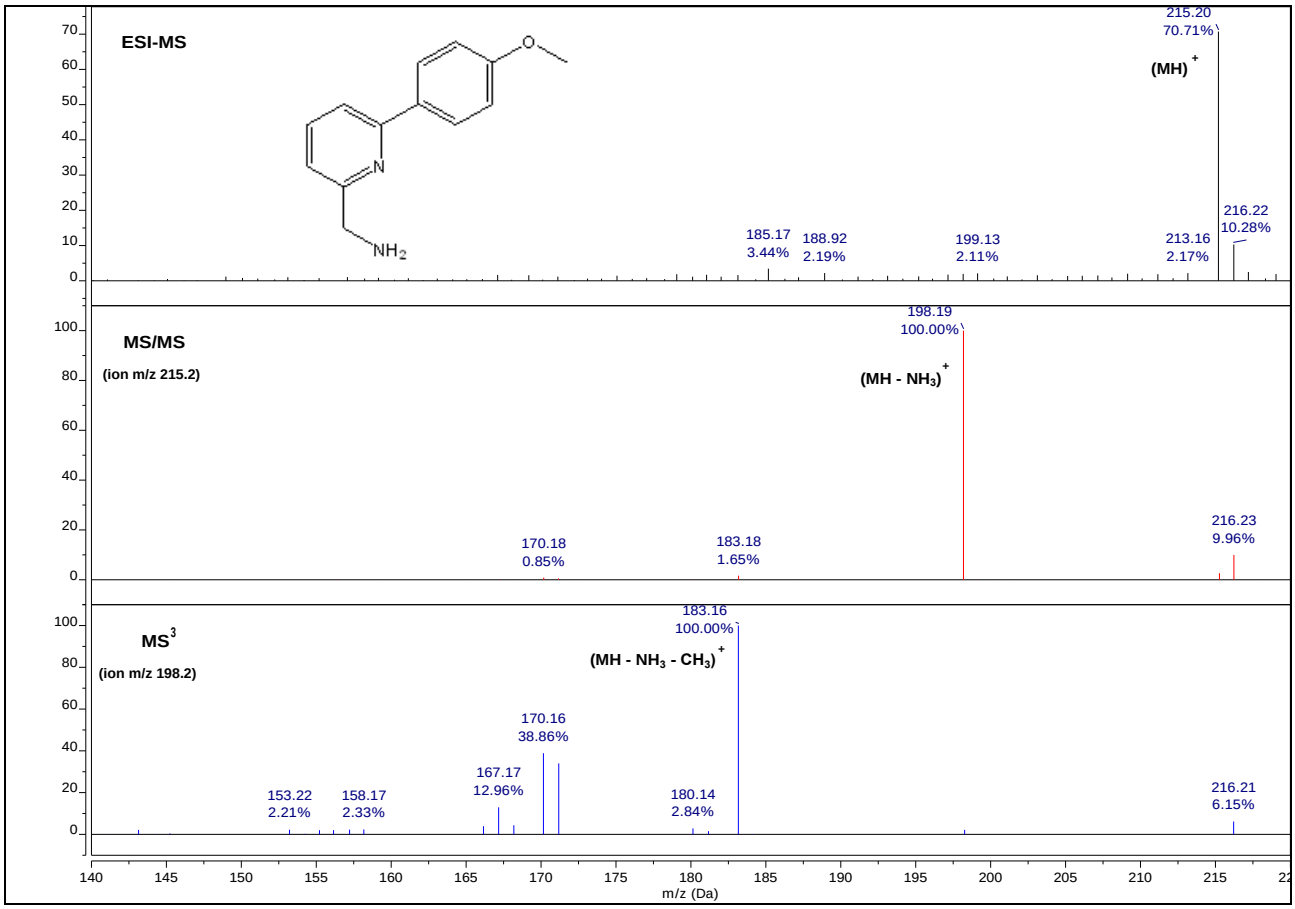

Figure S6. (+)-ESI-MS and MS^n spectra of (6-(4-methoxyphenyl)pyridin-2-yl)methanamine ($HCNN^{OMe}$) in CH_3OH

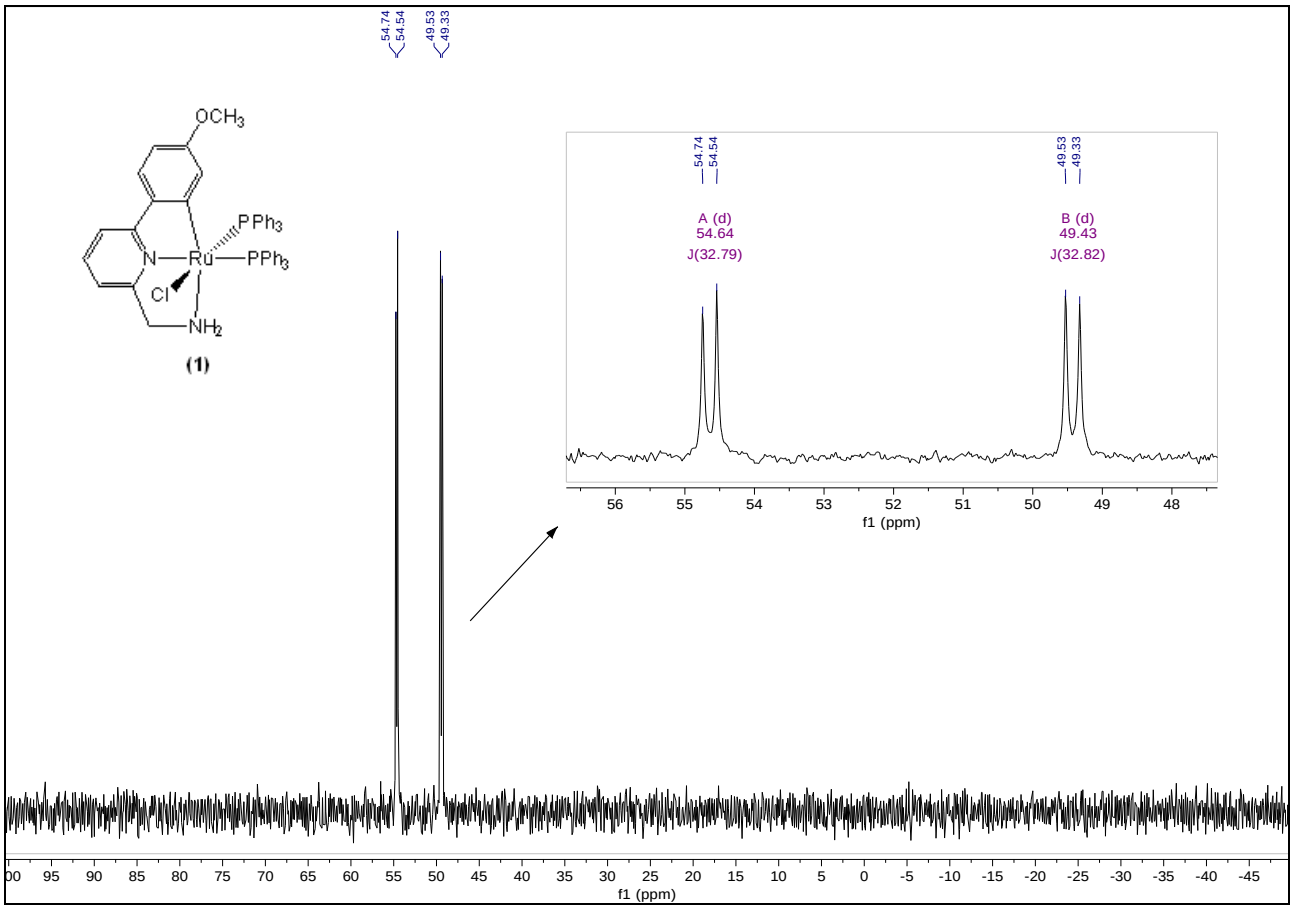

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (**1**) in CD_2Cl_2 at 25 °C.

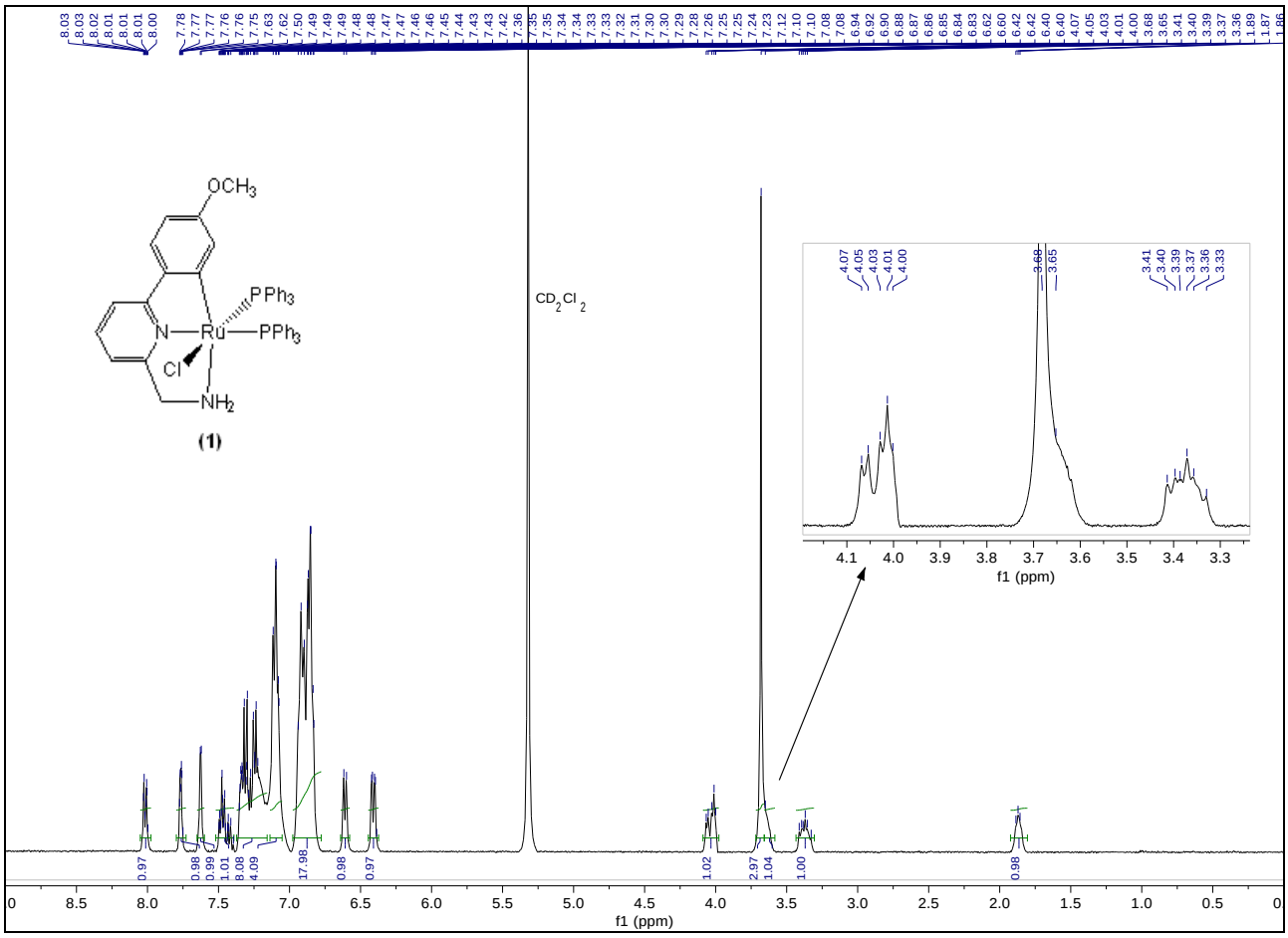

Figure S8. ^{1}H NMR spectrum (400.1 MHz) of *cis*-[RuCl(CNN^{OMe})(PPh$_3$)$_2$] (**1**) in CD_2Cl_2 at 25 °C.

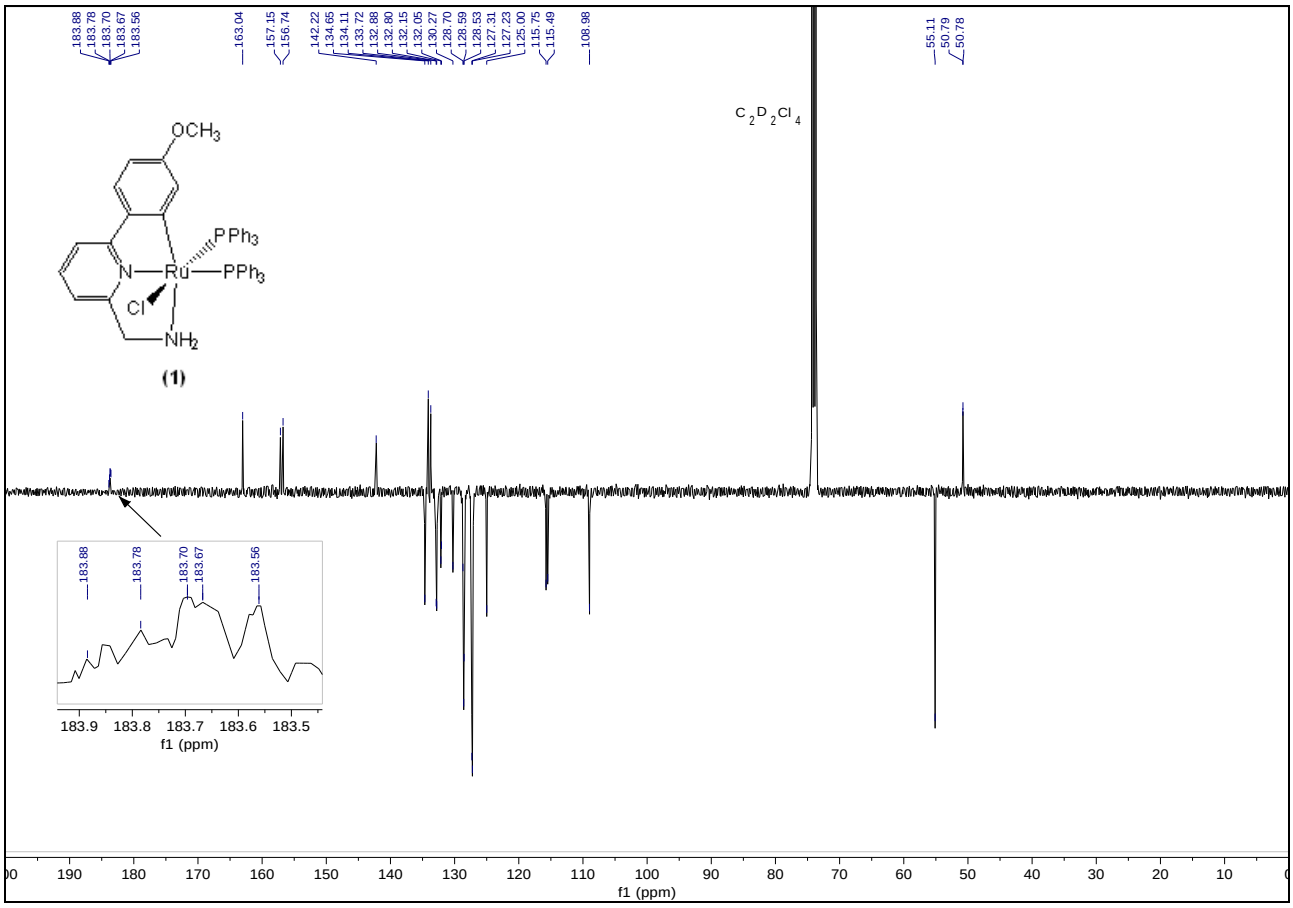

Figure S9. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum (100.6 MHz) of *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (**1**) in $C_2D_2Cl_4$ at 25 °C.

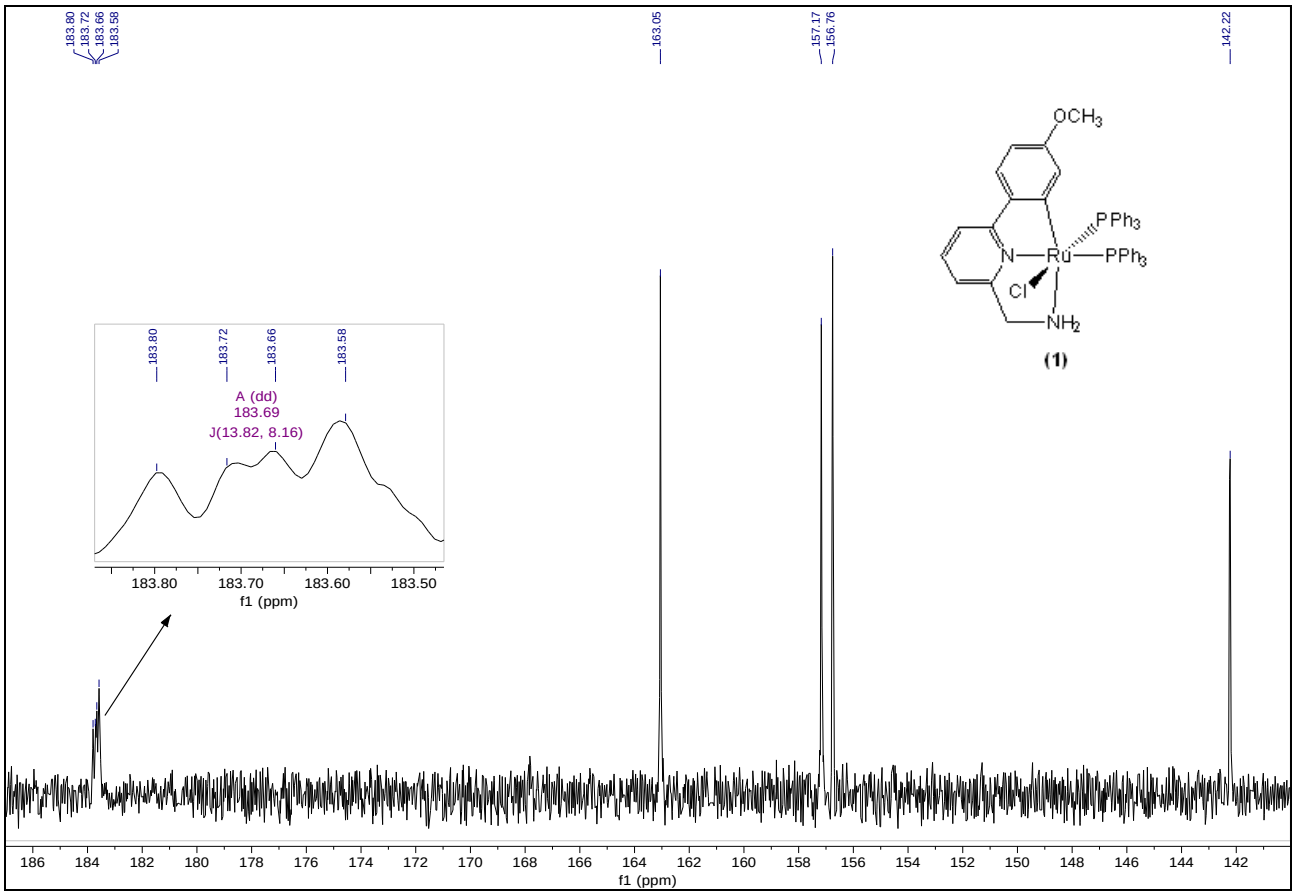

Figure S10. $^{13}C\{^{1}H\}$ QUATD NMR spectrum (100.6 MHz) of *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (**1**) in $C_2D_2Cl_4$ at 25 °C.

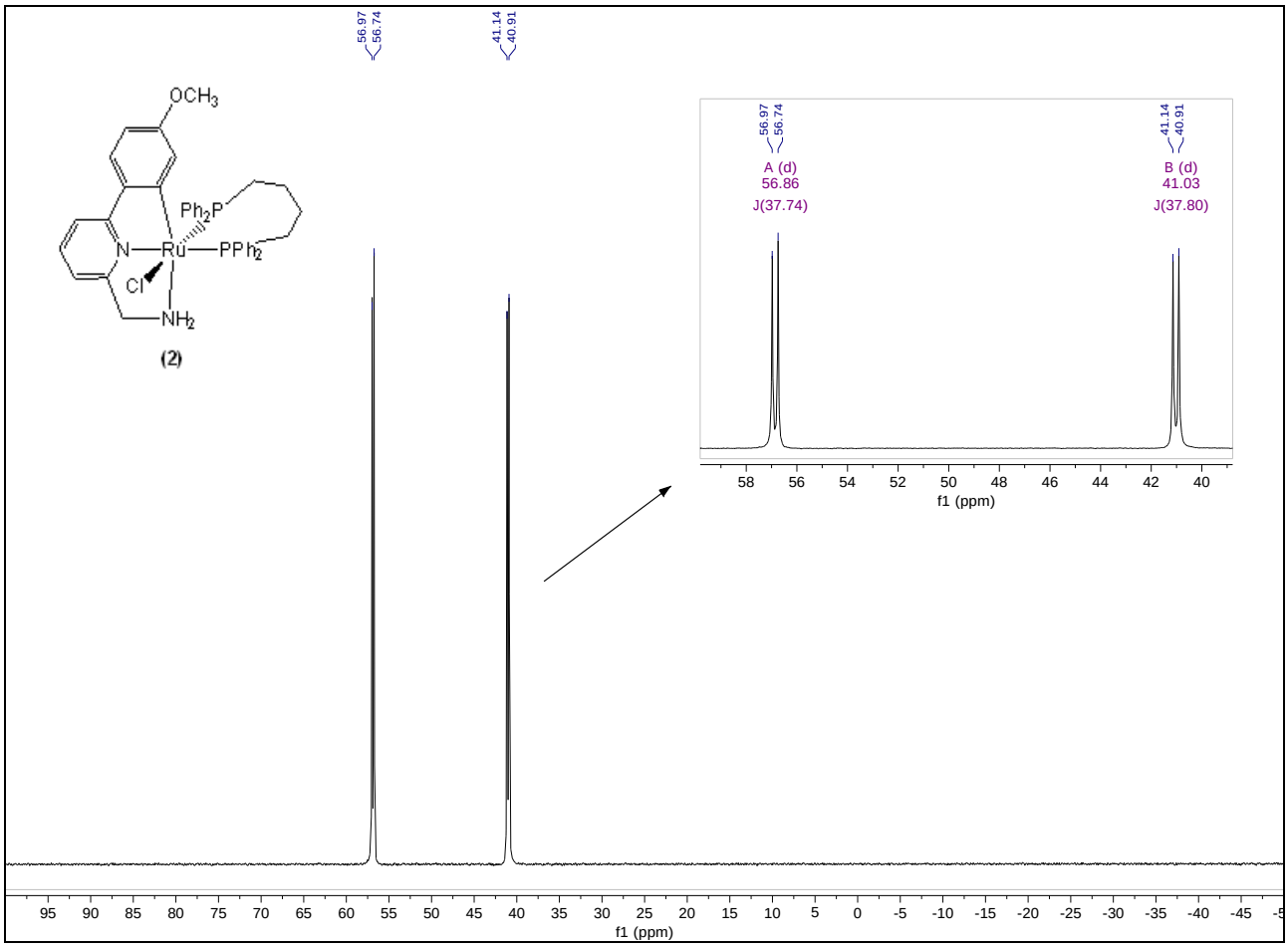

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

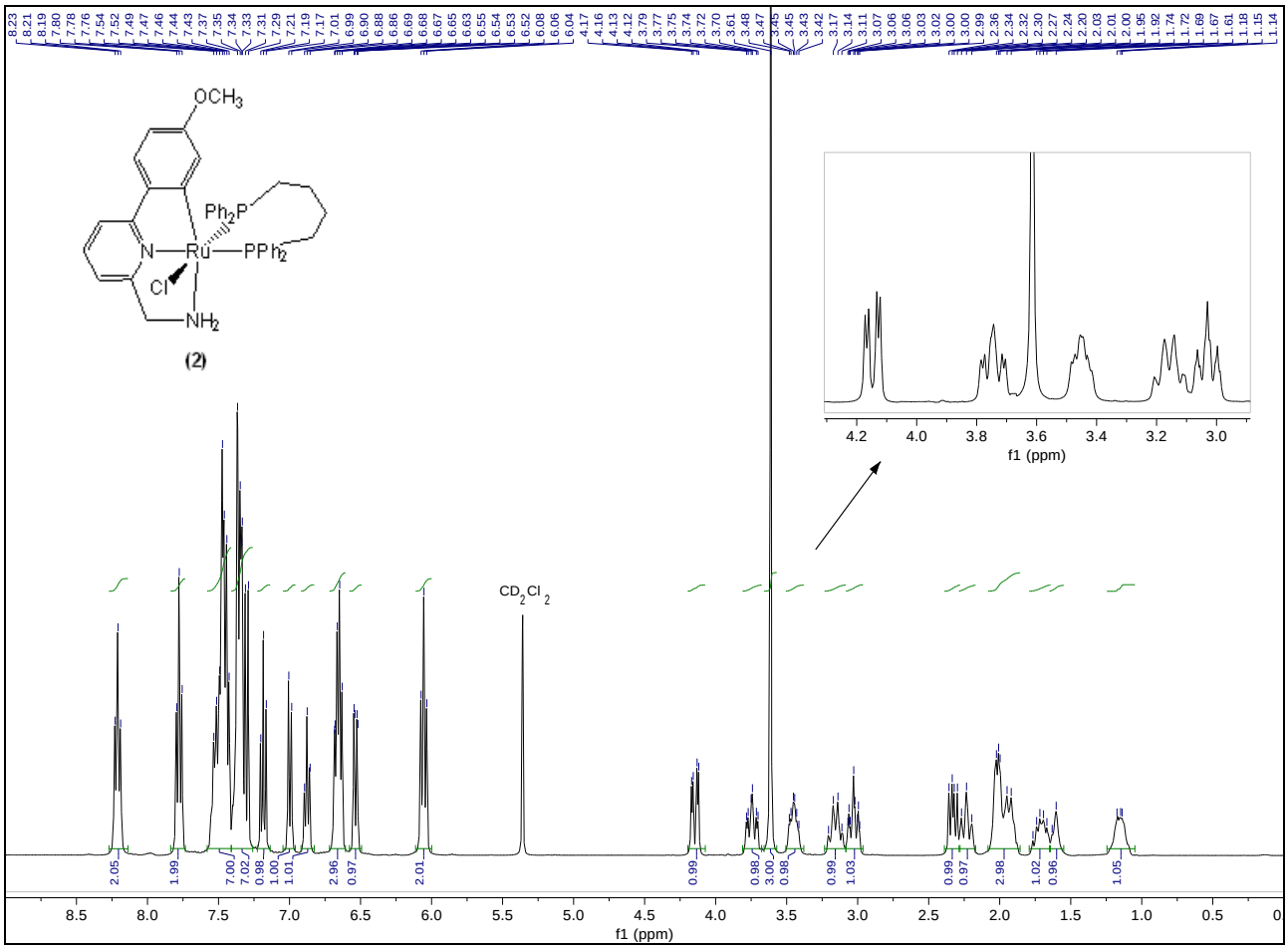

Figure S12. ^{1}H NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

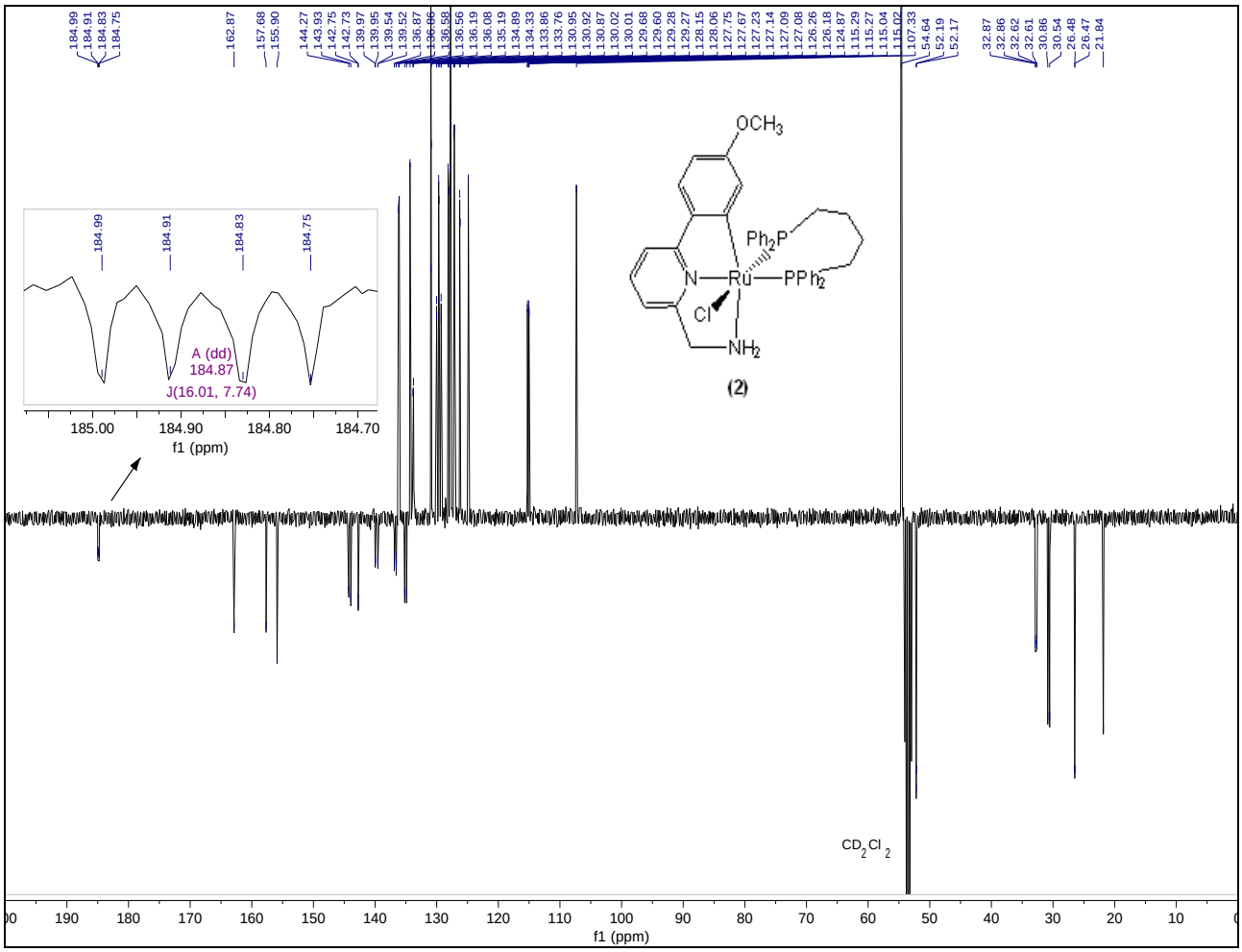

Figure S13. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum (100.6 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

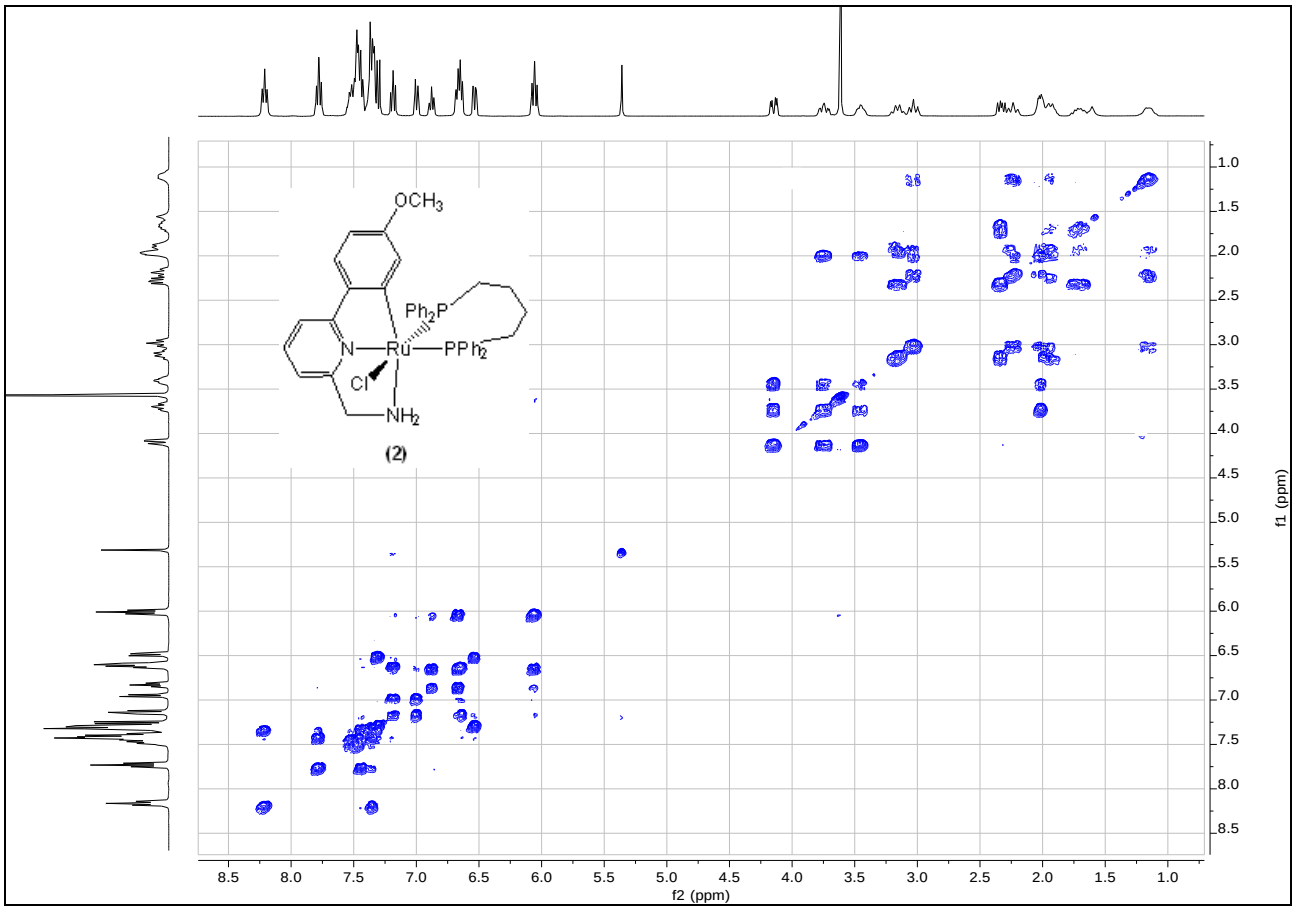

Figure S14. ^{1}H-^{1}H COSY 2D NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

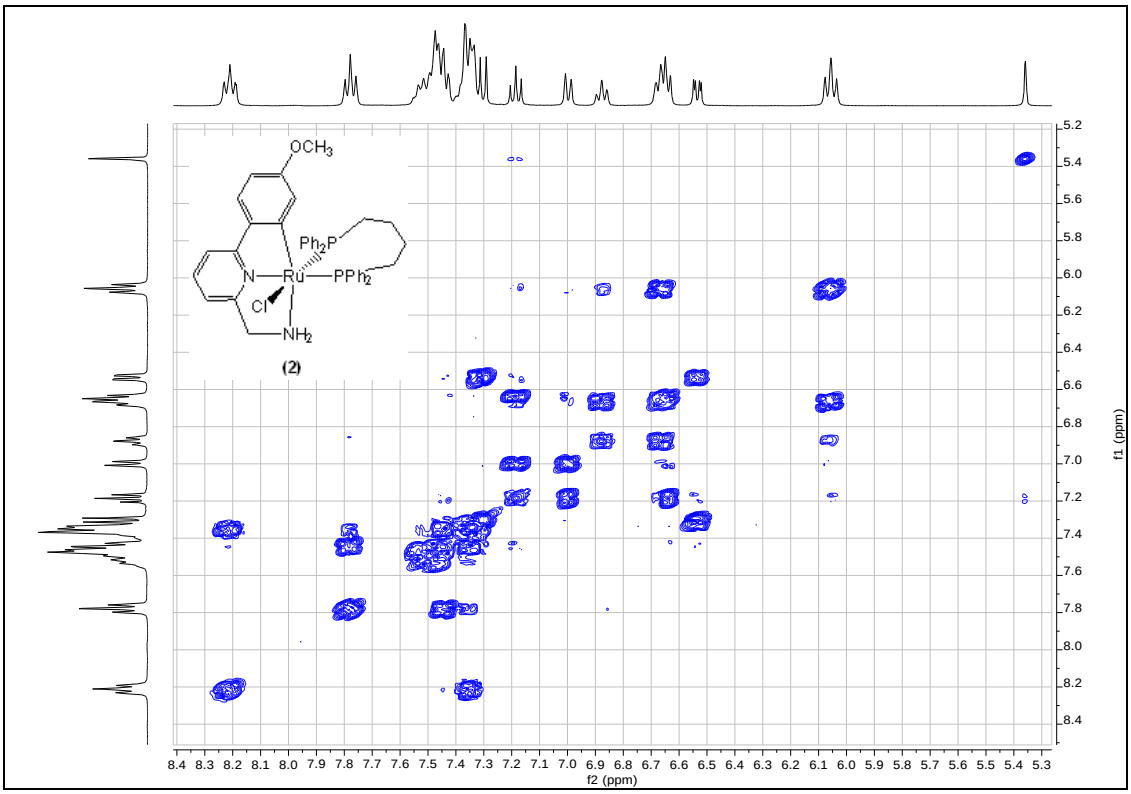

Figure S15. Aromatic region of the ^{1}H-^{1}H COSY 2D NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

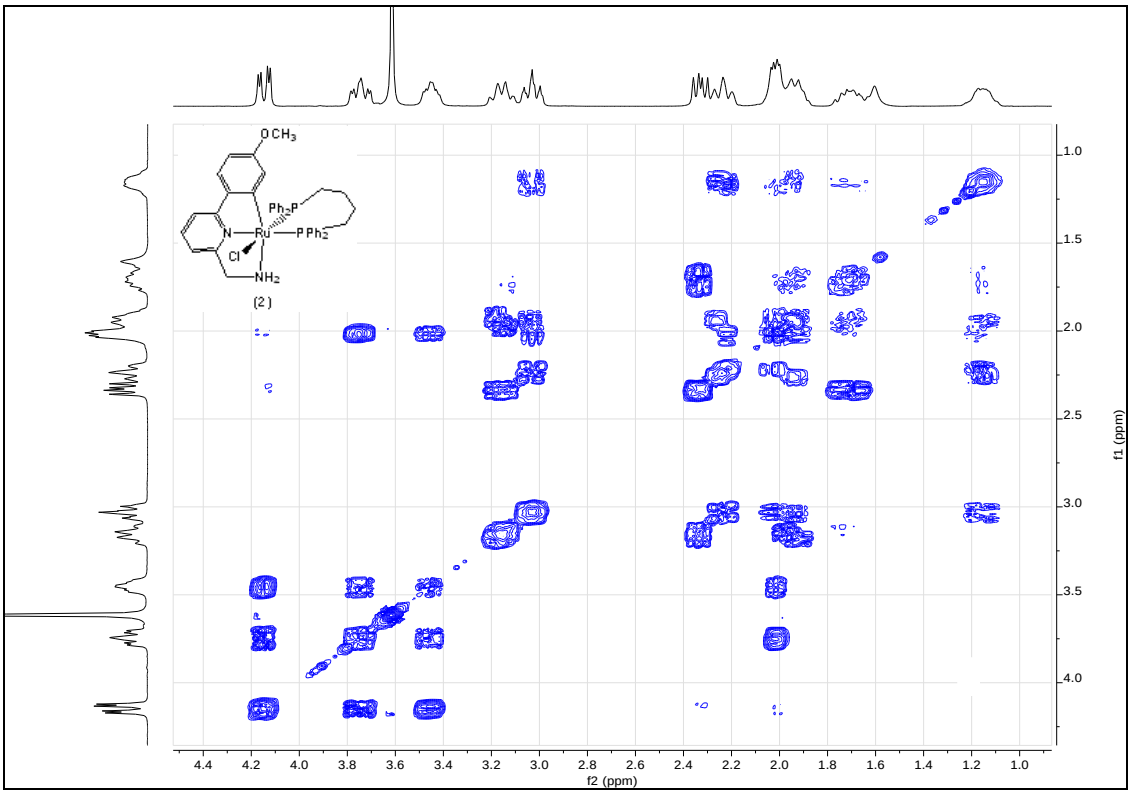

Figure S16. Alkylic region of the ^{1}H-^{1}H COSY 2D NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

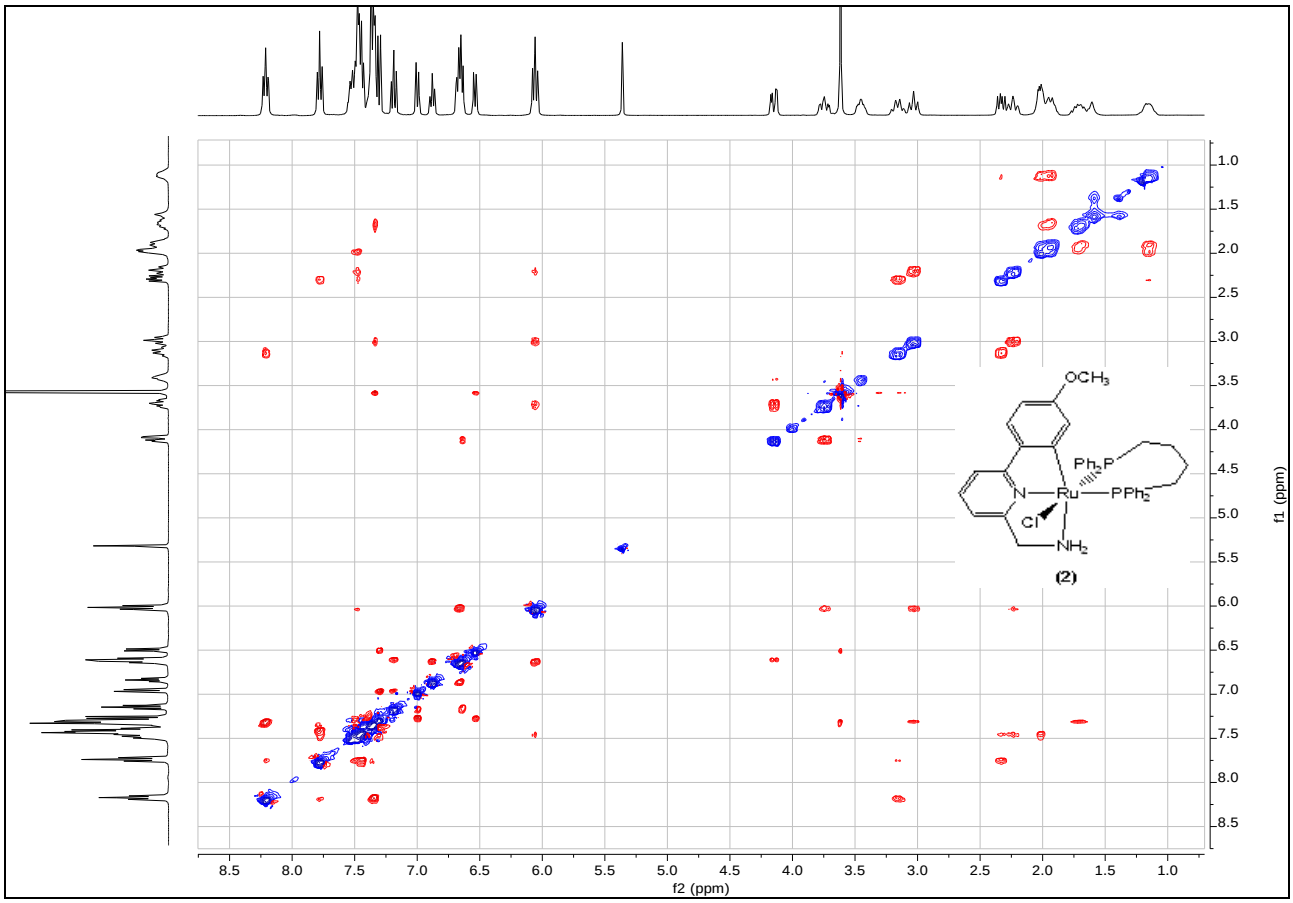

Figure S17. ^{1}H-^{1}H NOESY 2D NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

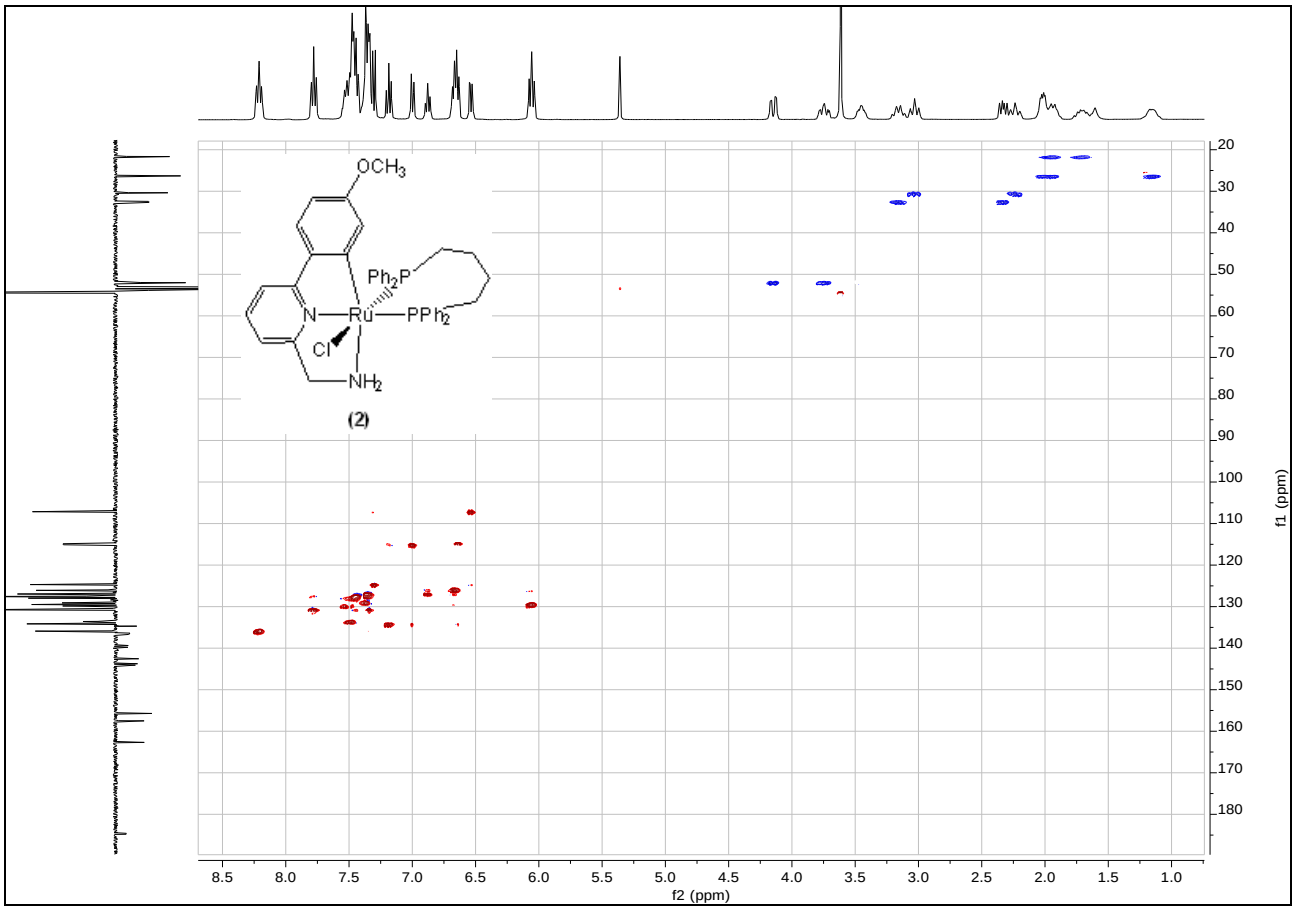

Figure S18. ^{1}H-^{13}C HSQC 2D NMR spectrum of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

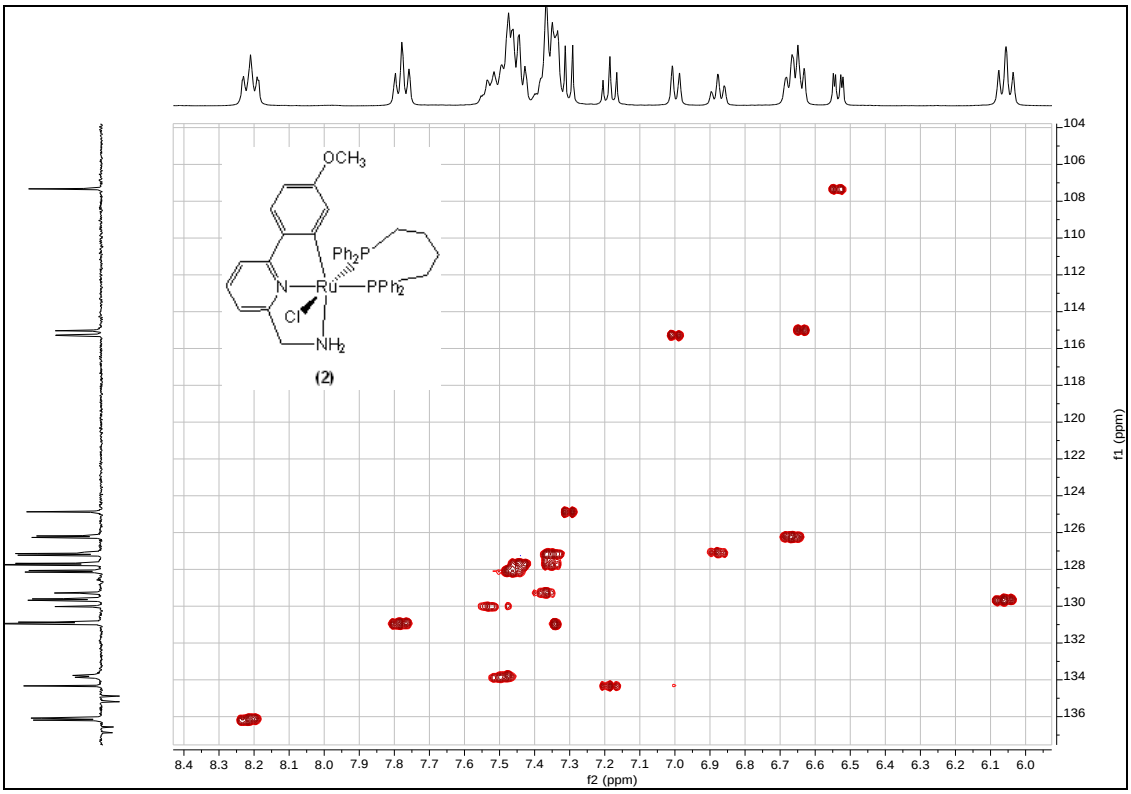

Figure S19. Aromatic region of the ^{1}H-^{13}C HSQC 2D NMR spectrum of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

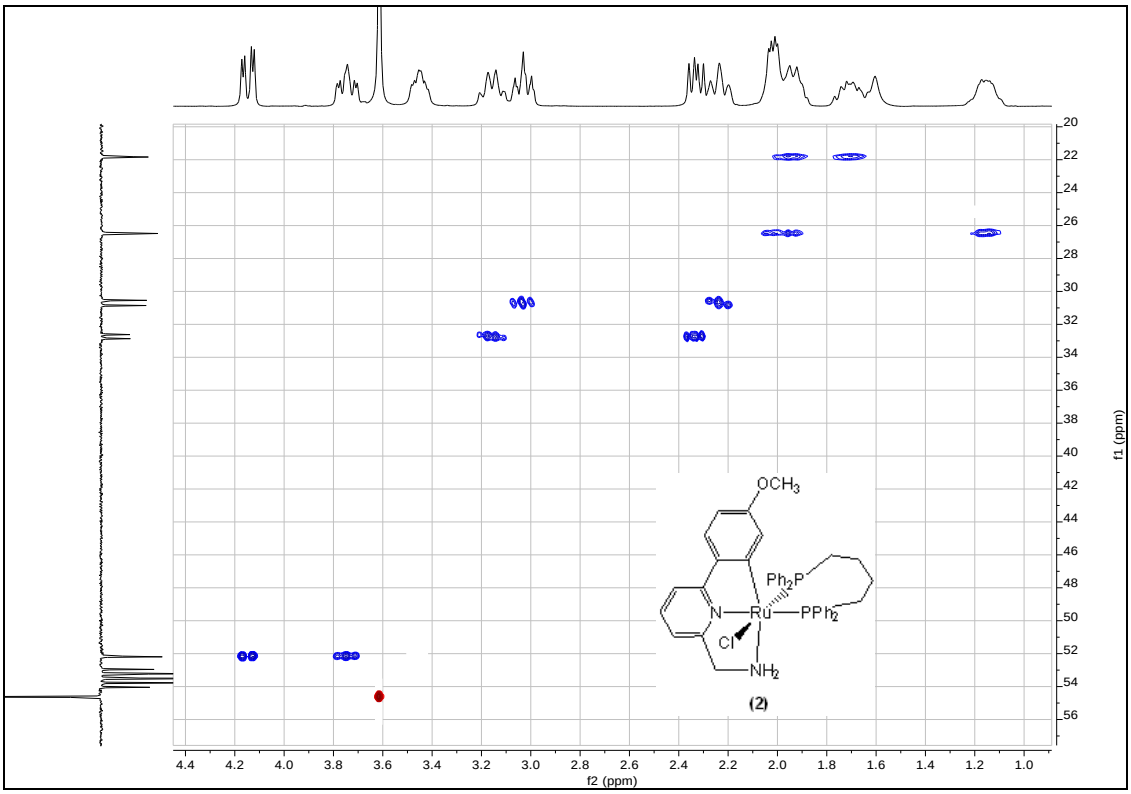

Figure S20. Alkylic region of the ^{1}H-^{13}C HSQC 2D NMR spectrum of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

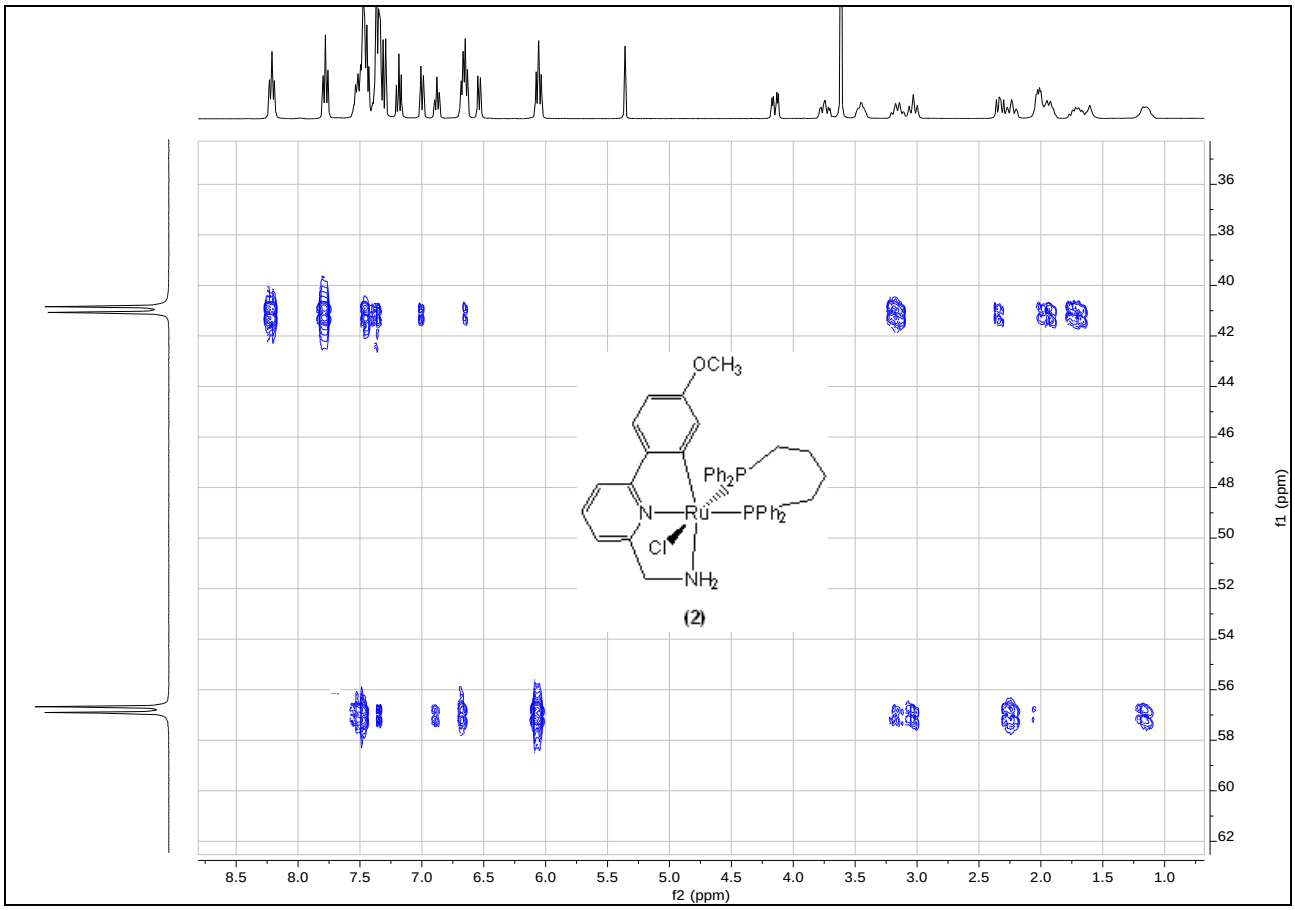

Figure S21. ^{1}H-^{31}P HMBC 2D NMR spectrum of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

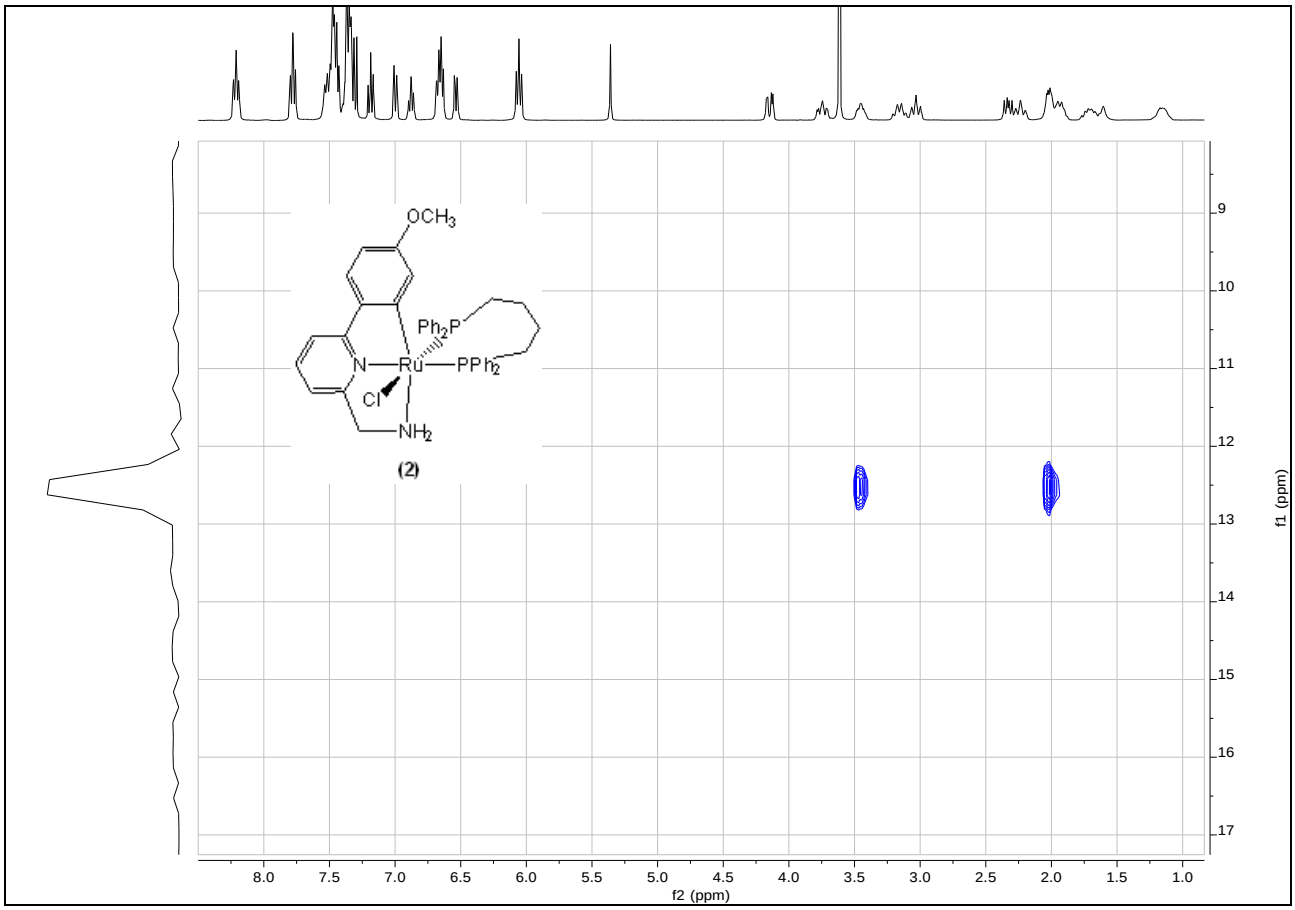

Figure S22. ^{1}H-^{15}N HSQC 2D NMR spectrum of [RuCl(CNN^{OMe})(dppb)] (**2**) in CD_2Cl_2 at 25 °C.

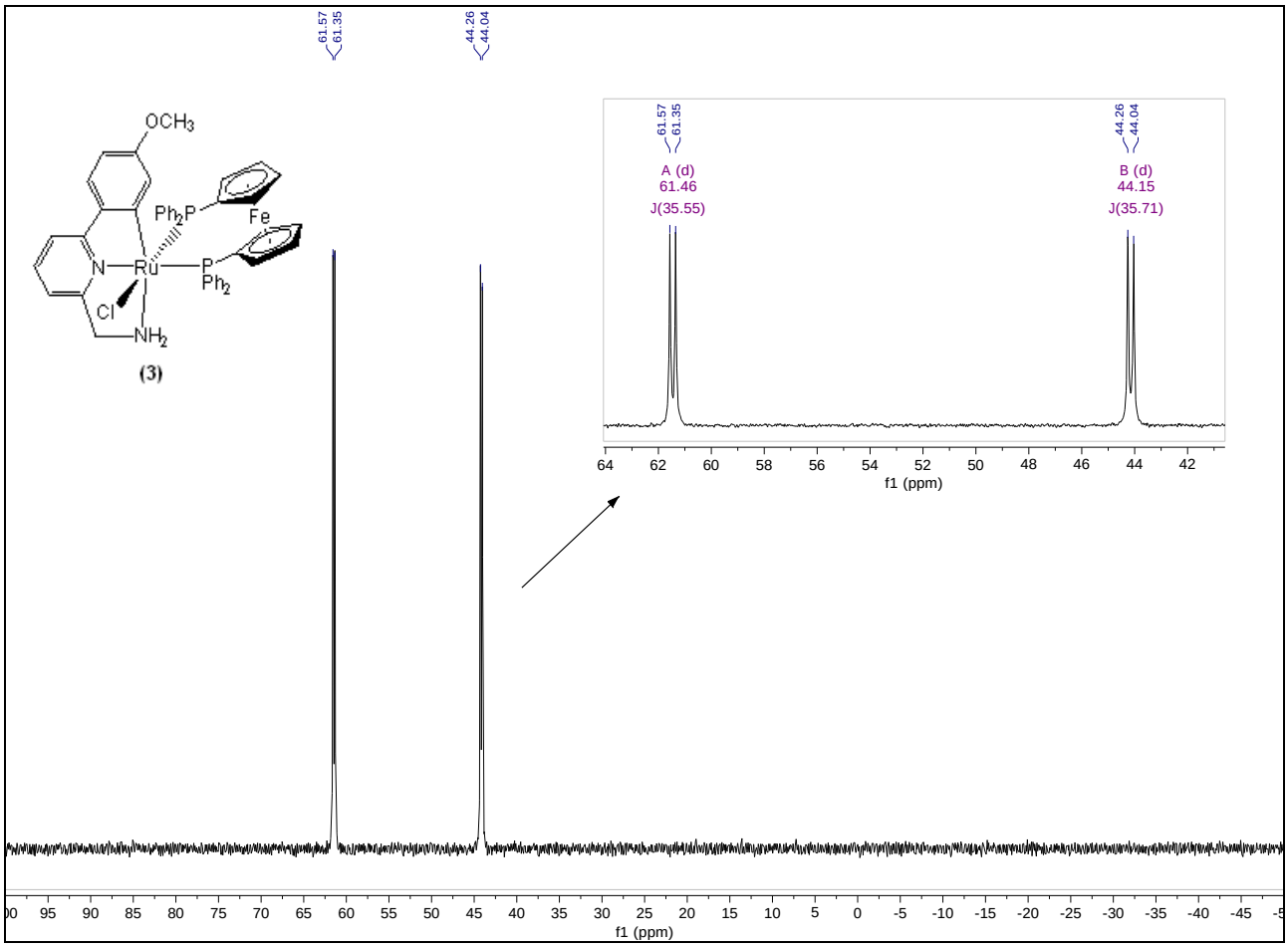

Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of [RuCl(CNN^{OMe})(dppf)] (**3**) in CD_2Cl_2 at 25 °C.

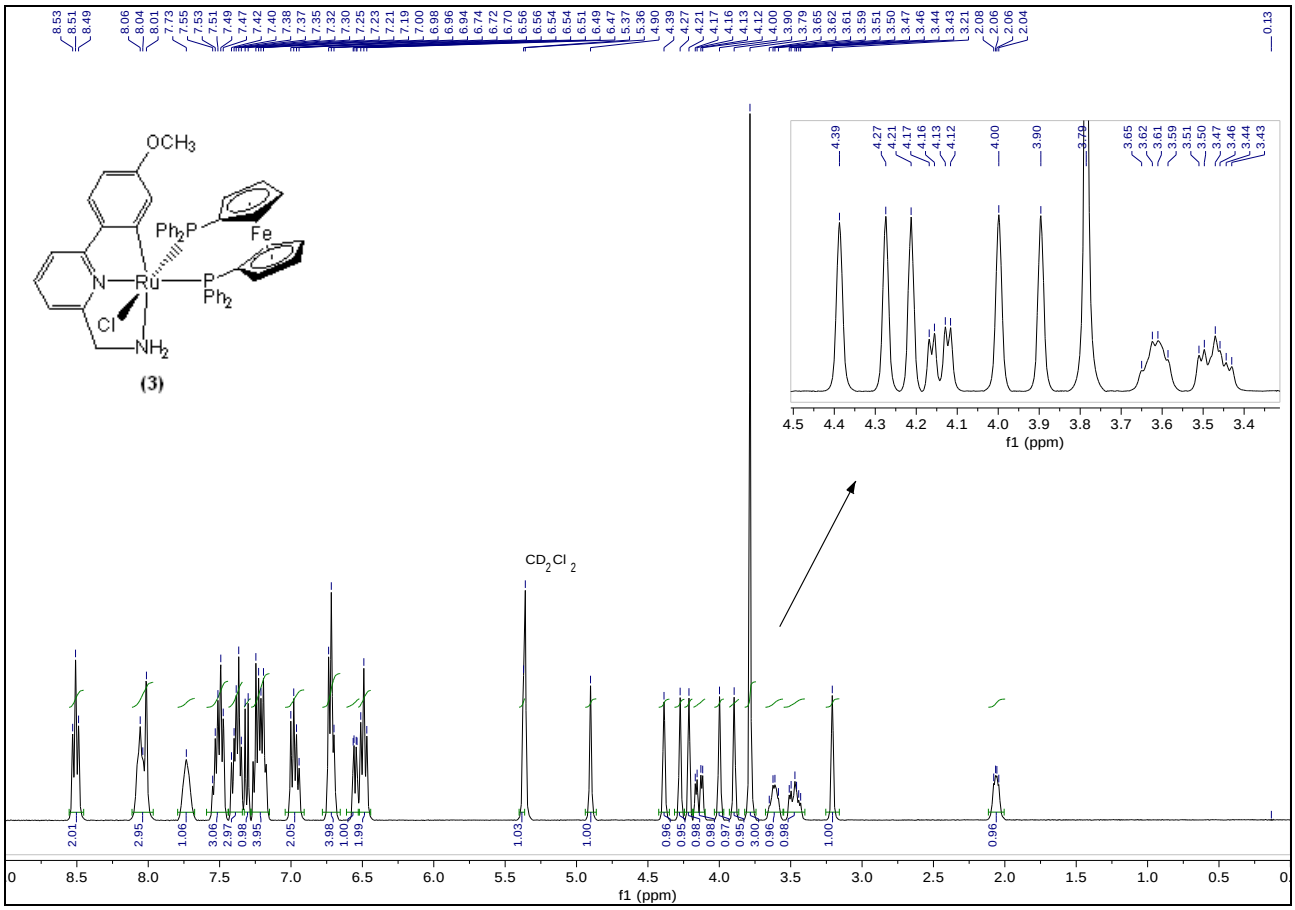

Figure S24. ^{1}H NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(dppf)] (**3**) in CD_2Cl_2 at 25 °C.

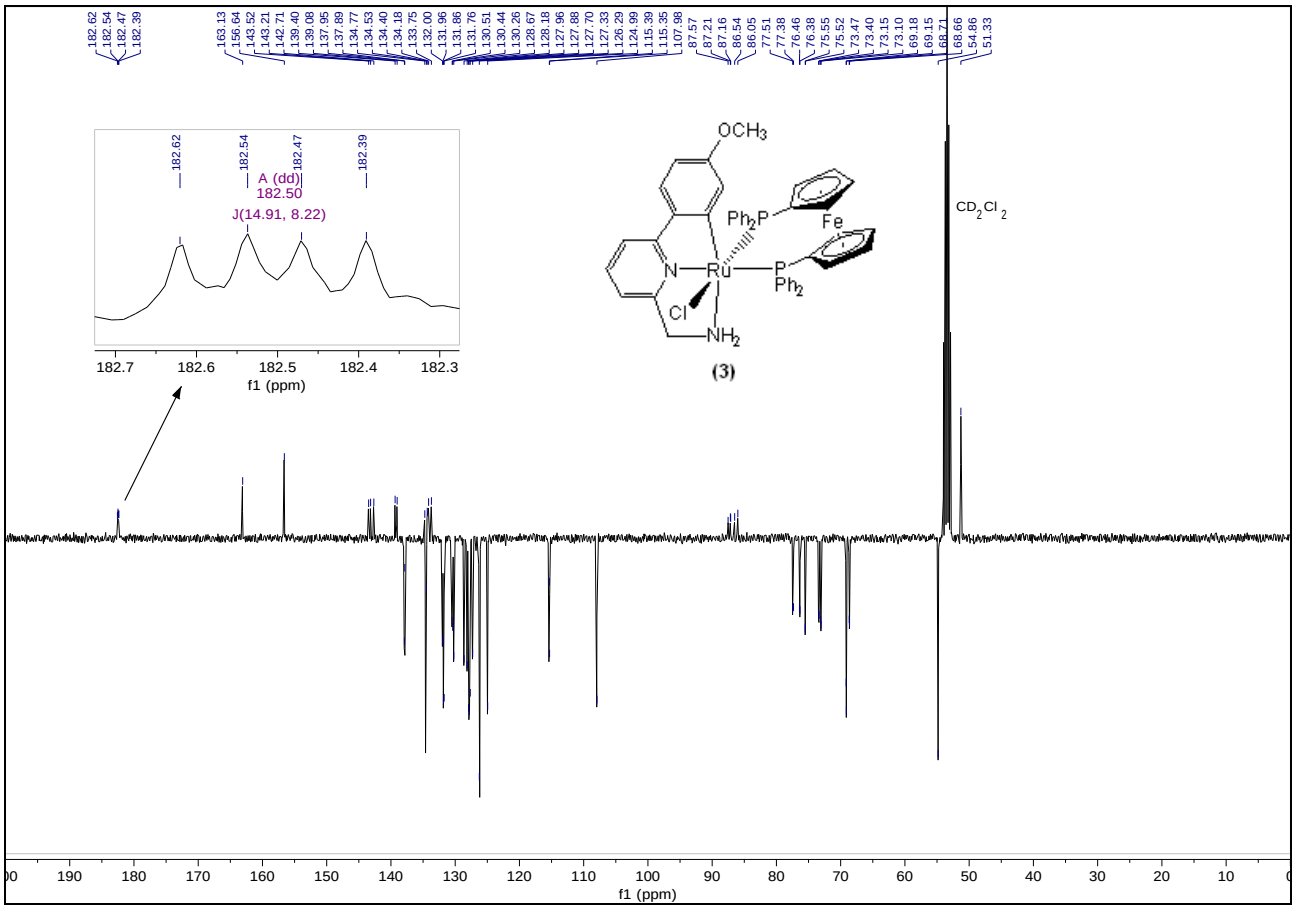

Figure S25. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum (100.6 MHz) of [RuCl(CNN^{OMe})(dppf)] (**3**) in CD_2Cl_2 at 25 °C.

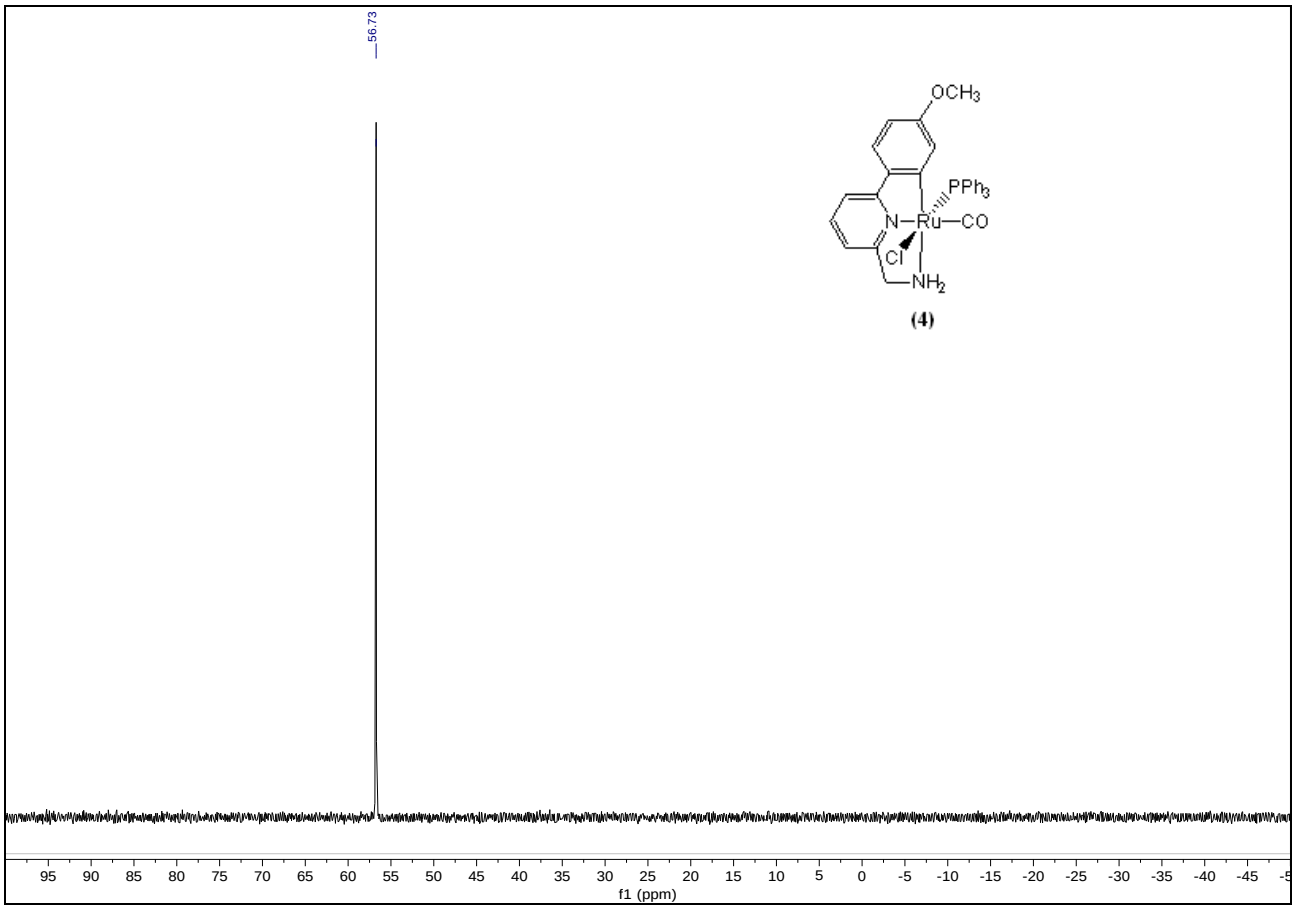

Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of [RuCl(CNN^{OMe})(CO)(PPh_3)] (**4**) in CD_2Cl_2 at 25 °C.

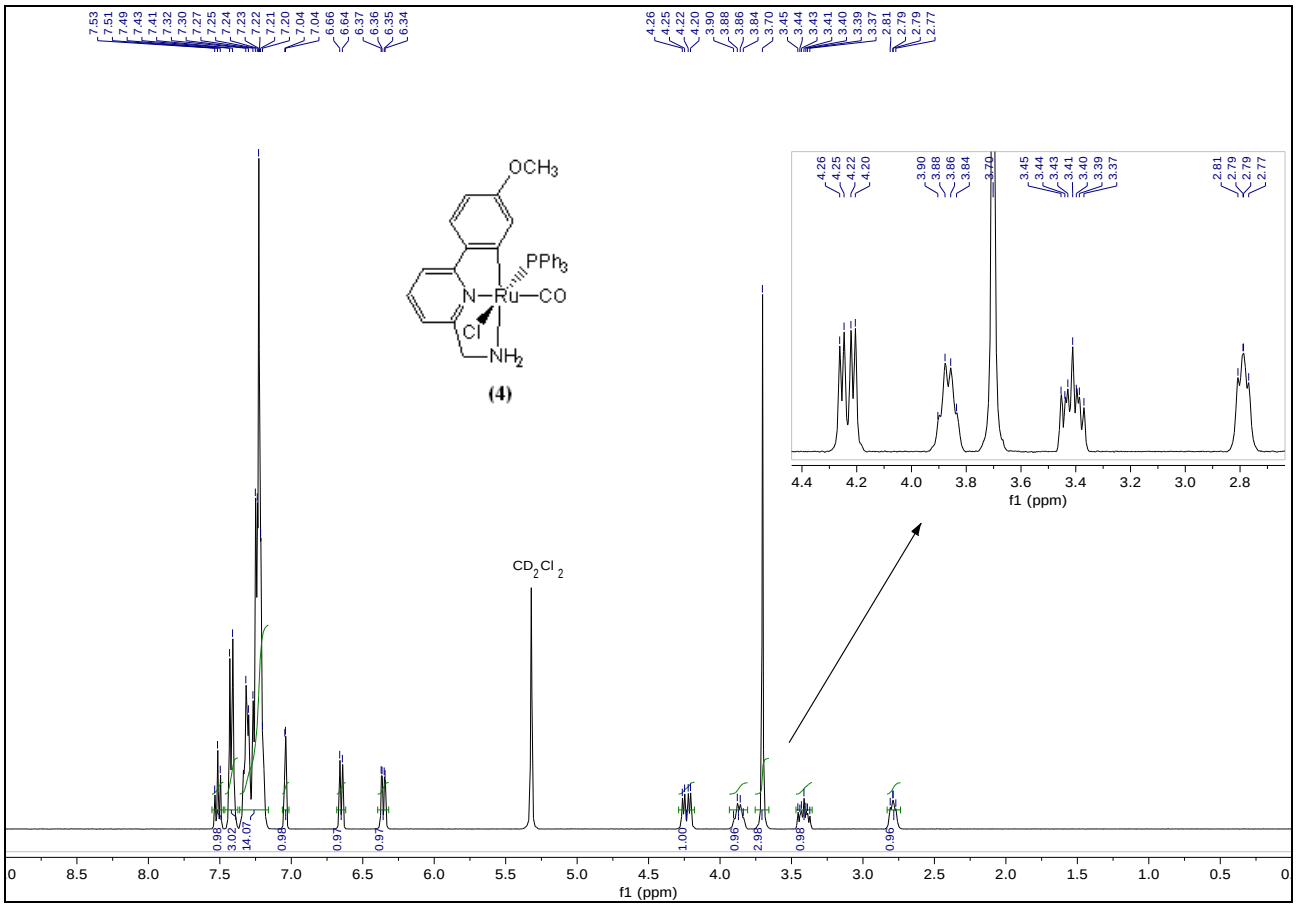

Figure S27. ^{1}H NMR spectrum (400.1 MHz) of [RuCl(CNN^{OMe})(CO)(PPh_3)] (**4**) in CD_2Cl_2 at 25 °C.

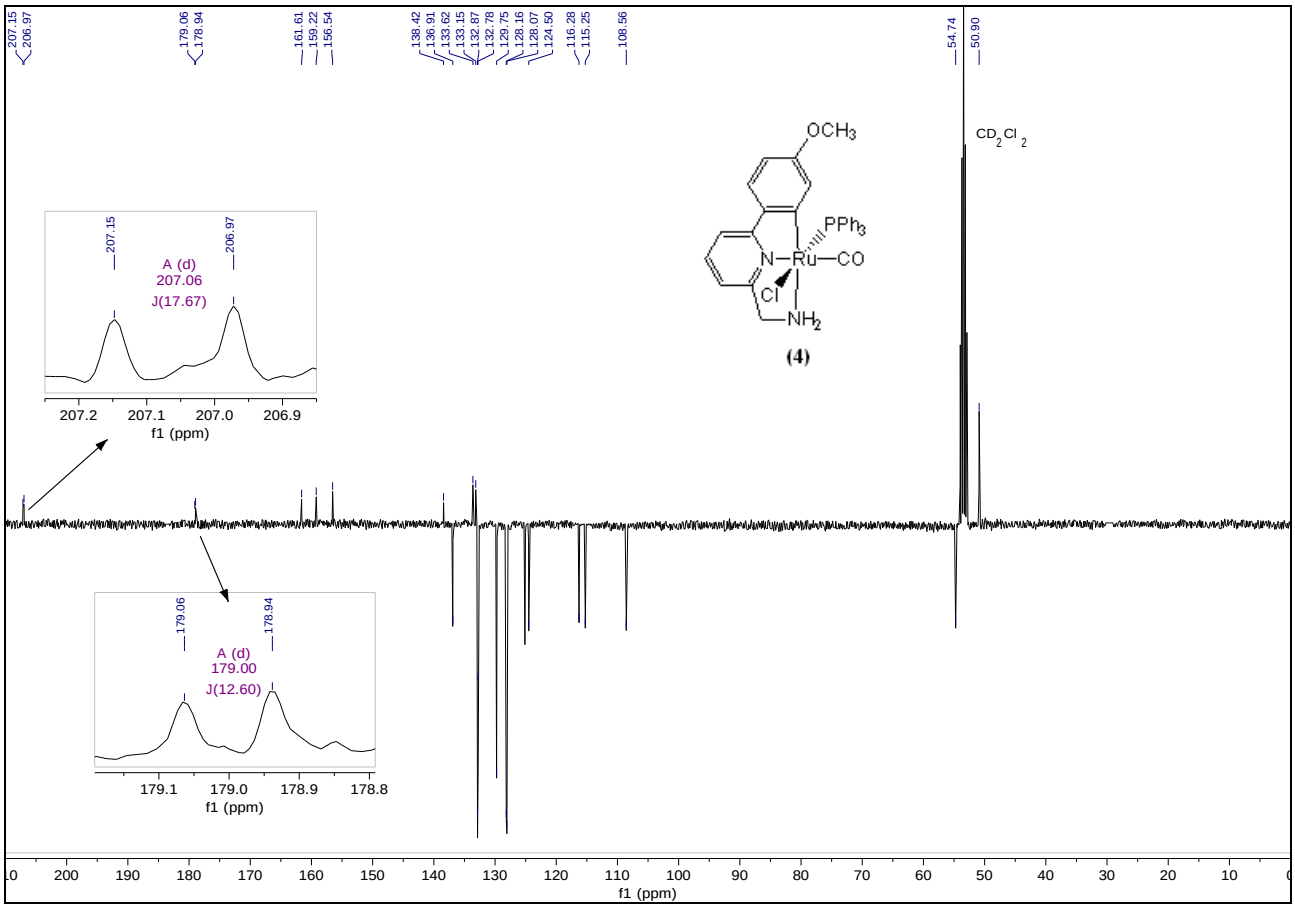

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz) of [RuCl(CNN^{OMe})(CO)(PPh_3)] (**4**) in CD_2Cl_2 at 25 °C.

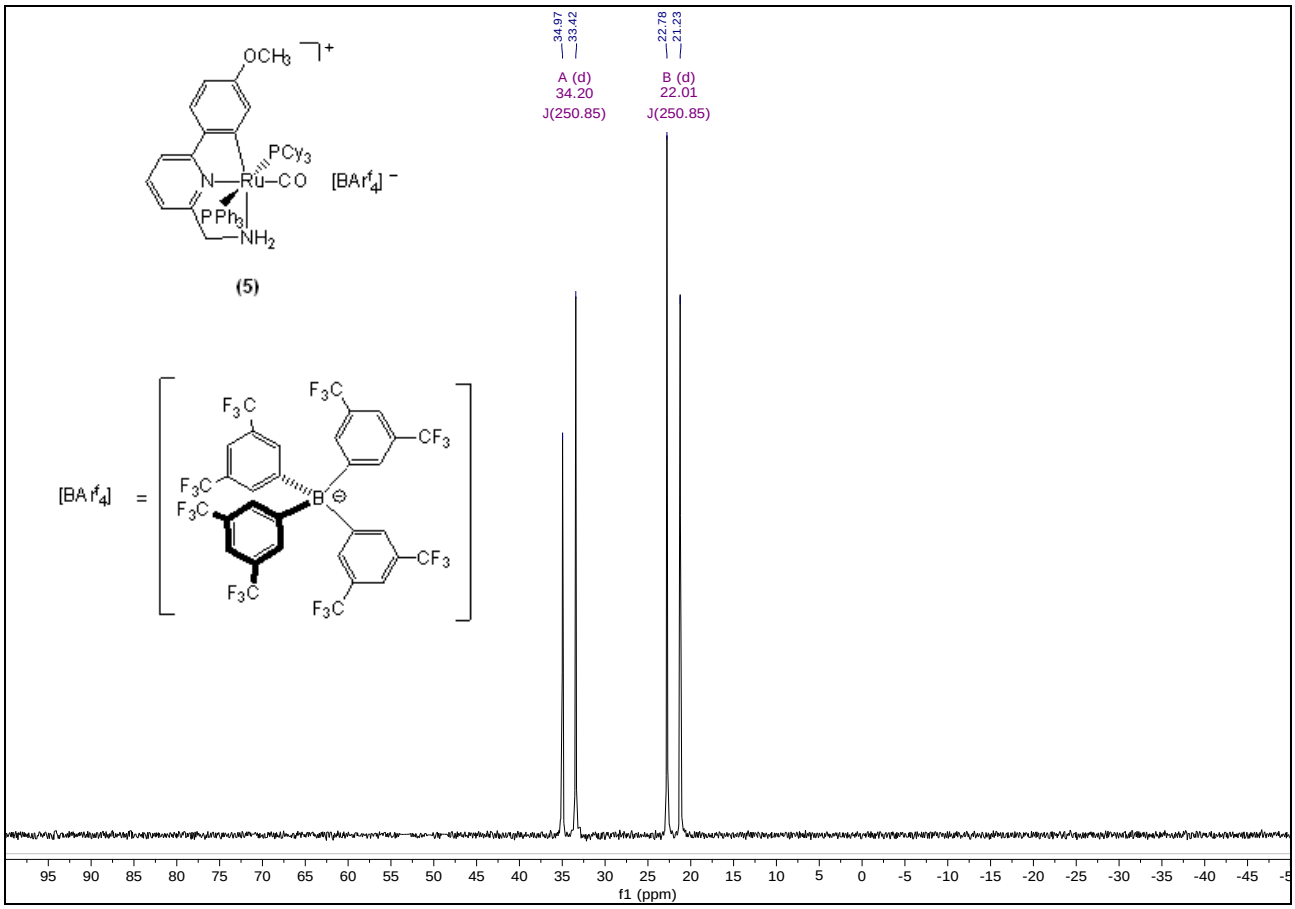

Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][$BAr^f{}_4$] (**5**) in CD_2Cl_2 at 25 °C.

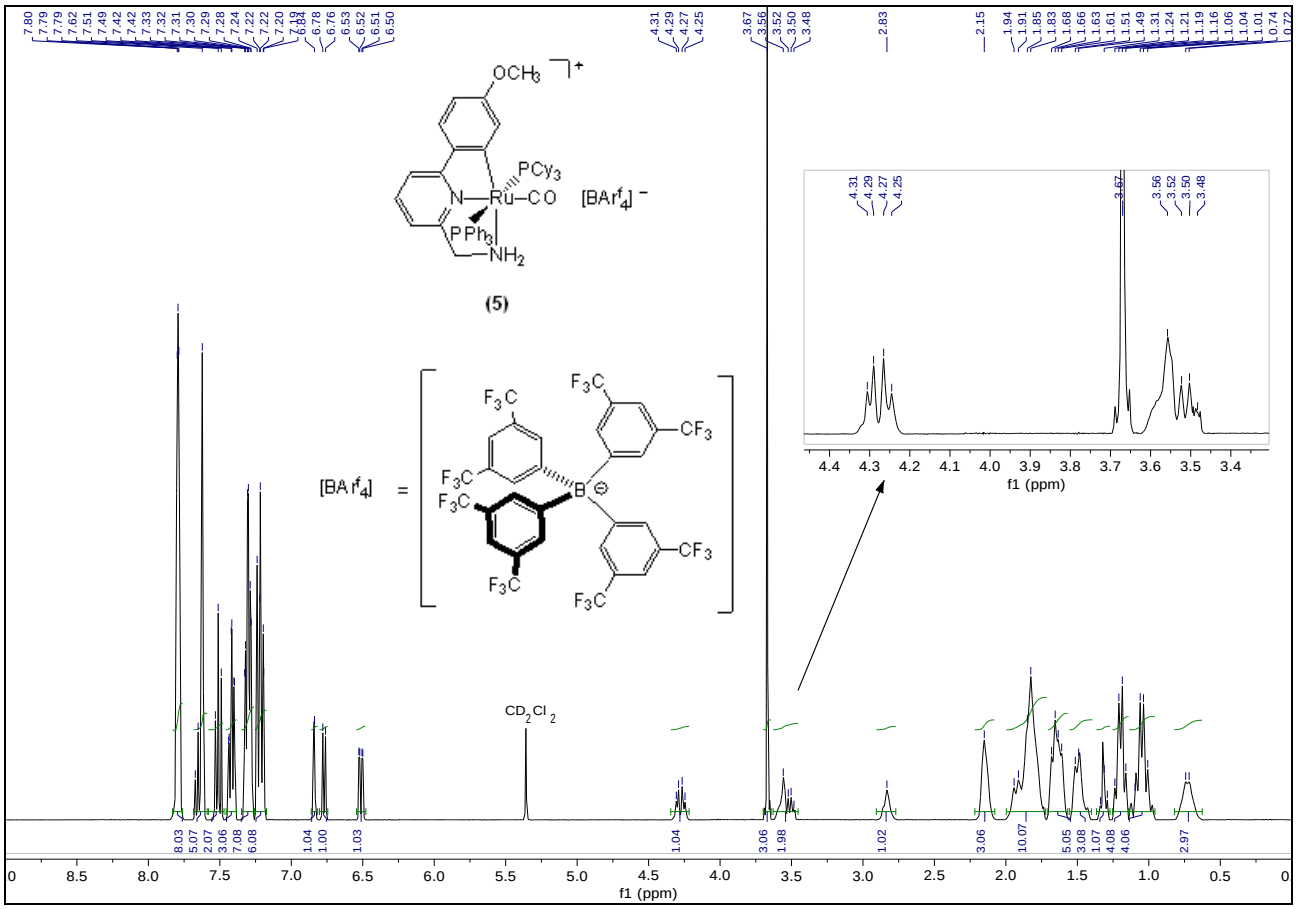

Figure S30. ^{1}H NMR spectrum (400.1 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (**5**) in CD_2Cl_2 at 25 °C.

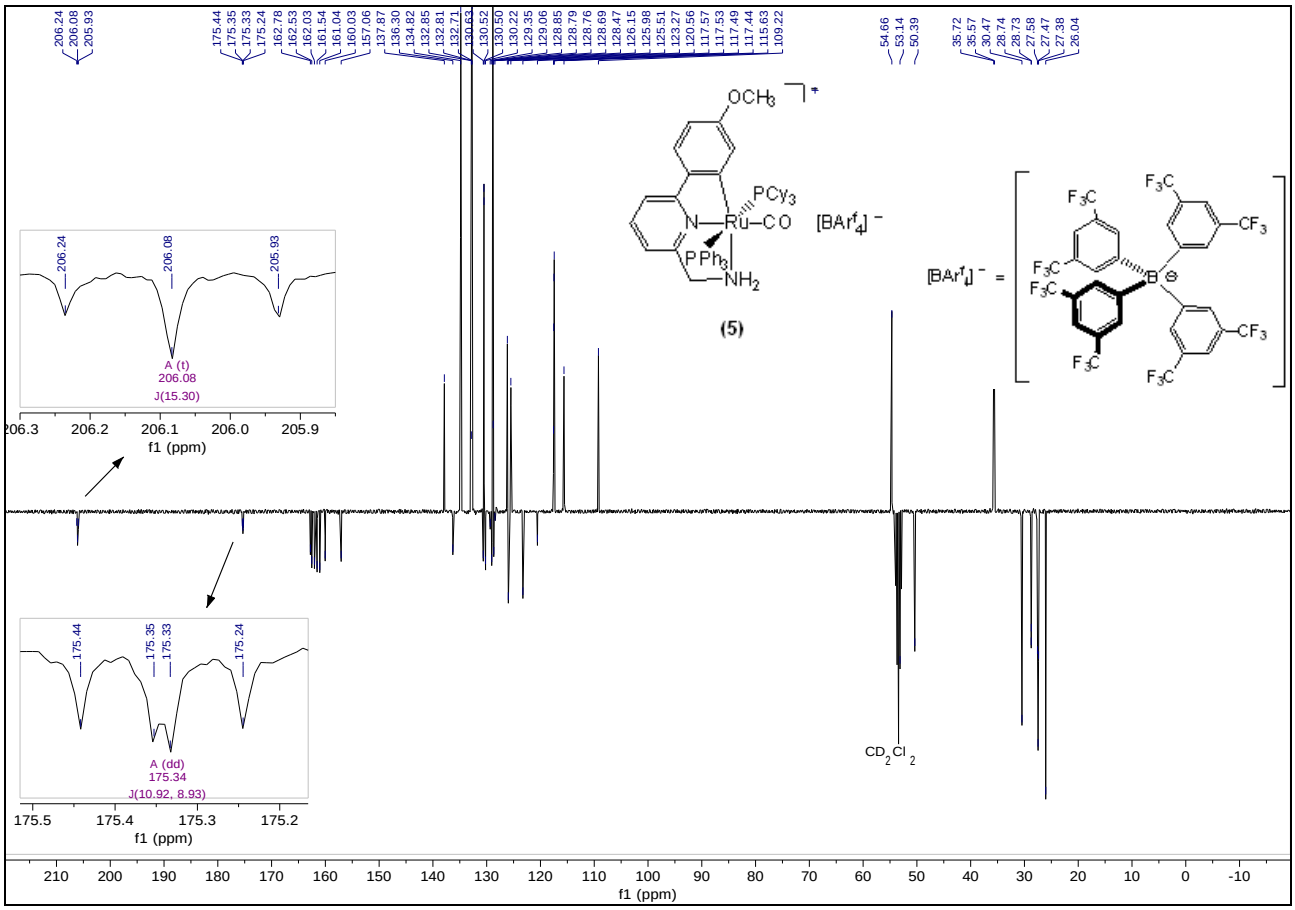

Figure S31. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum (100.6 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (**5**) in CD_2Cl_2 at 25 °C.

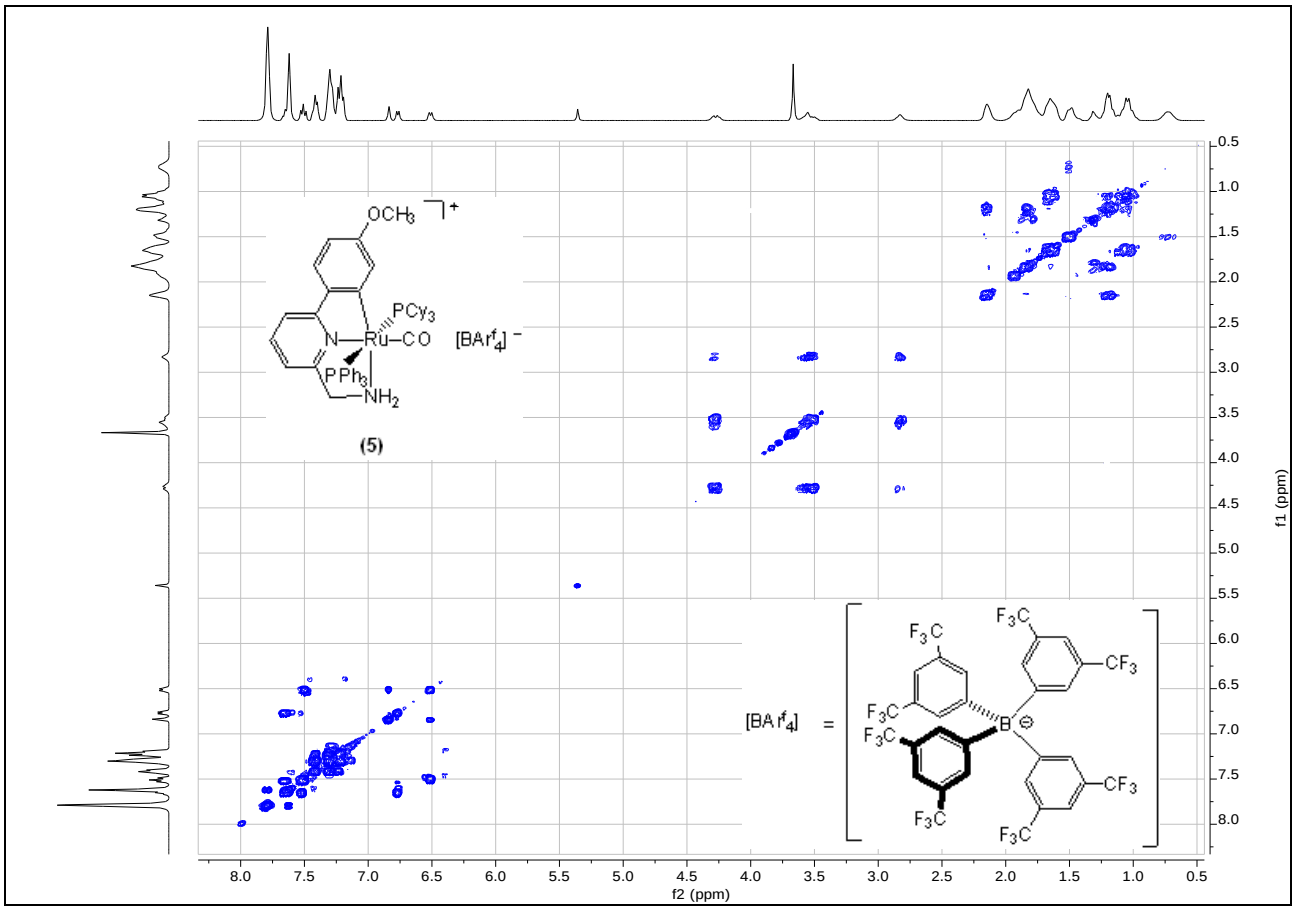

Figure S32. ^{1}H-^{1}H COSY 2D NMR spectrum (400.1 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (**5**) in CD_2Cl_2 at 25 °C.

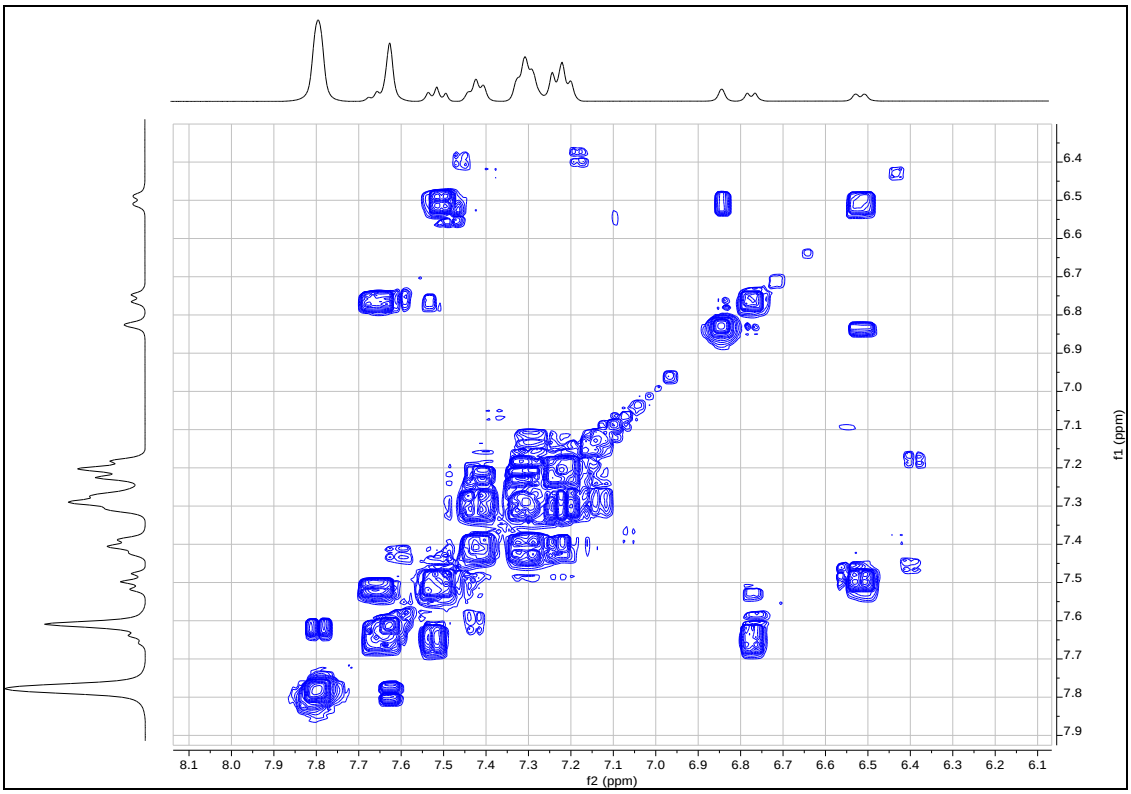

Figure S33. Aromatic region of the ^{1}H-^{1}H COSY 2D NMR spectrum (400.1 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (**5**) in CD_2Cl_2 at 25 °C.

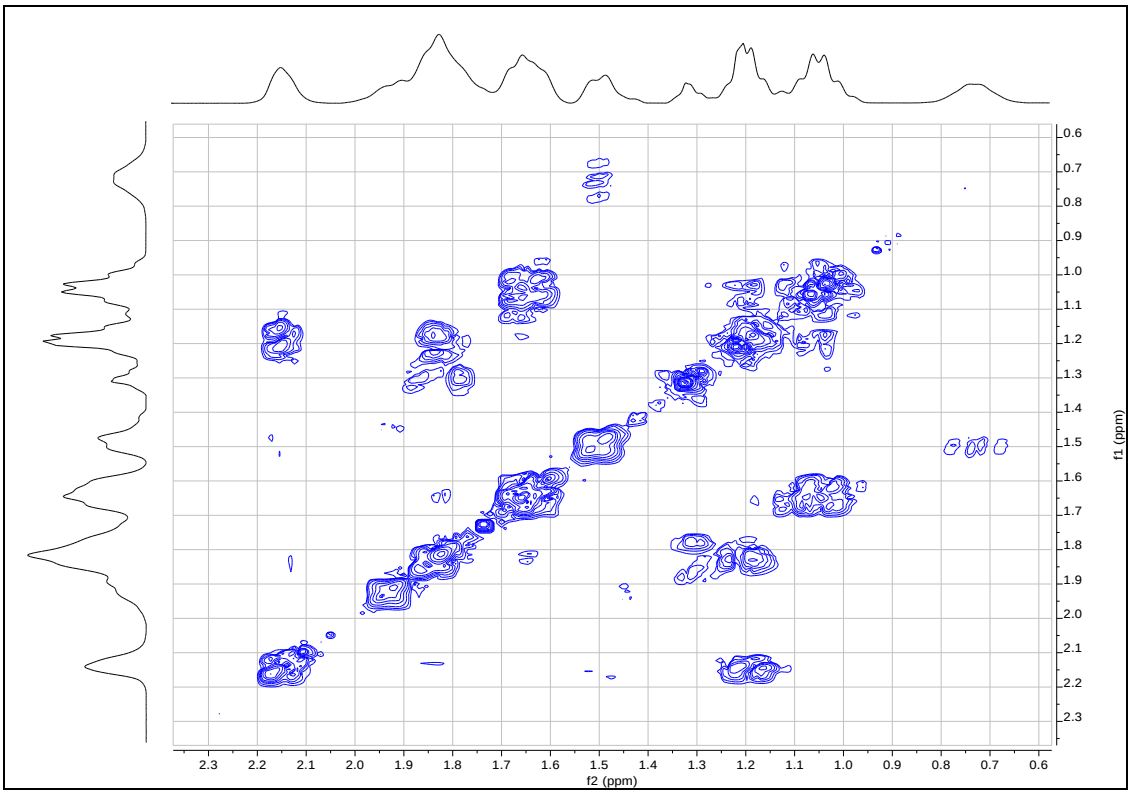

Figure S34. Alkylic region of the ^{1}H-^{1}H COSY 2D NMR spectrum (400.1 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (**5**) in CD_2Cl_2 at 25 °C.

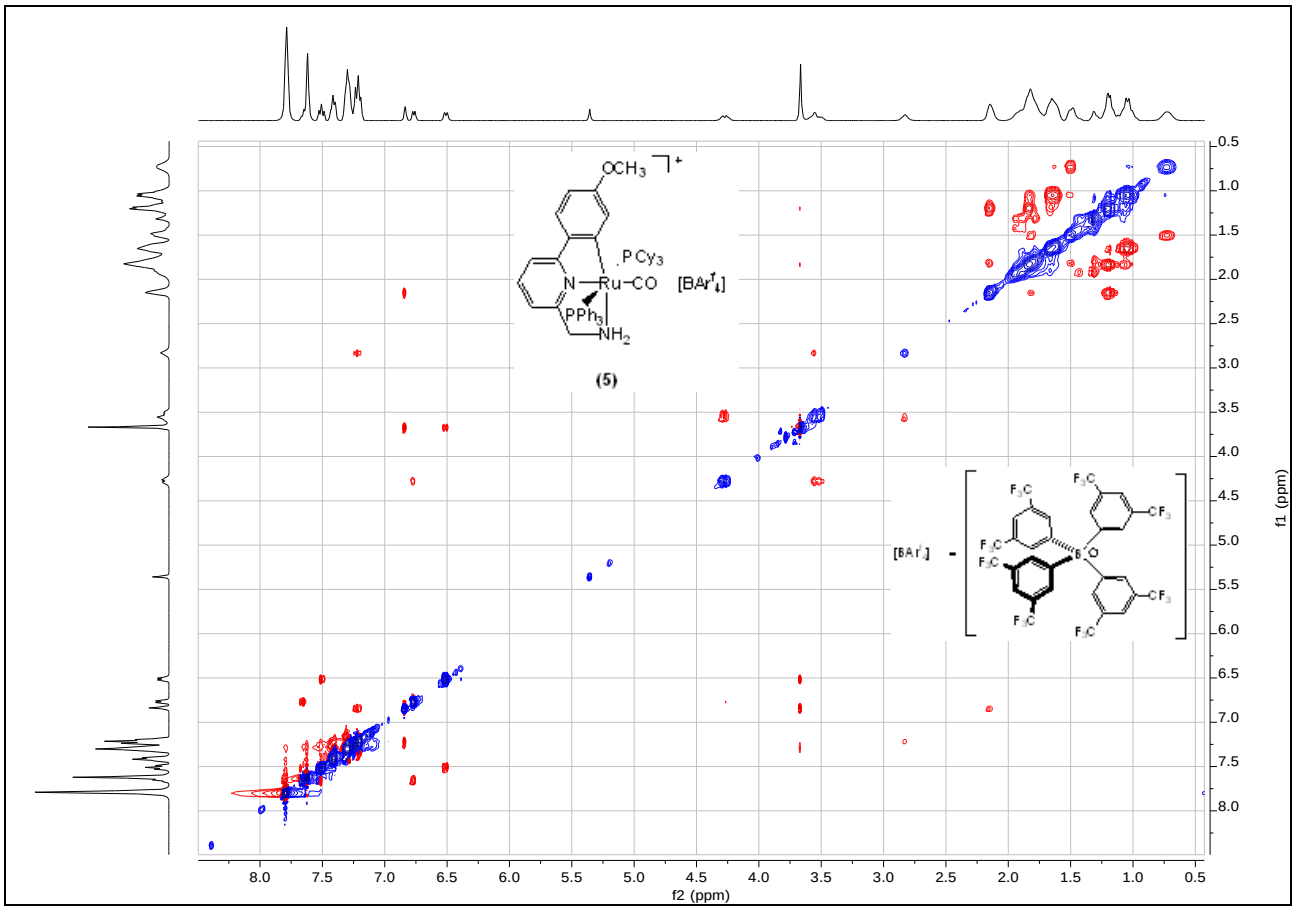

Figure S35. ^{1}H-^{1}H NOESY 2D NMR spectrum (400.1 MHz) of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^f_4$] (**5**) in CD_2Cl_2 at 25 °C.

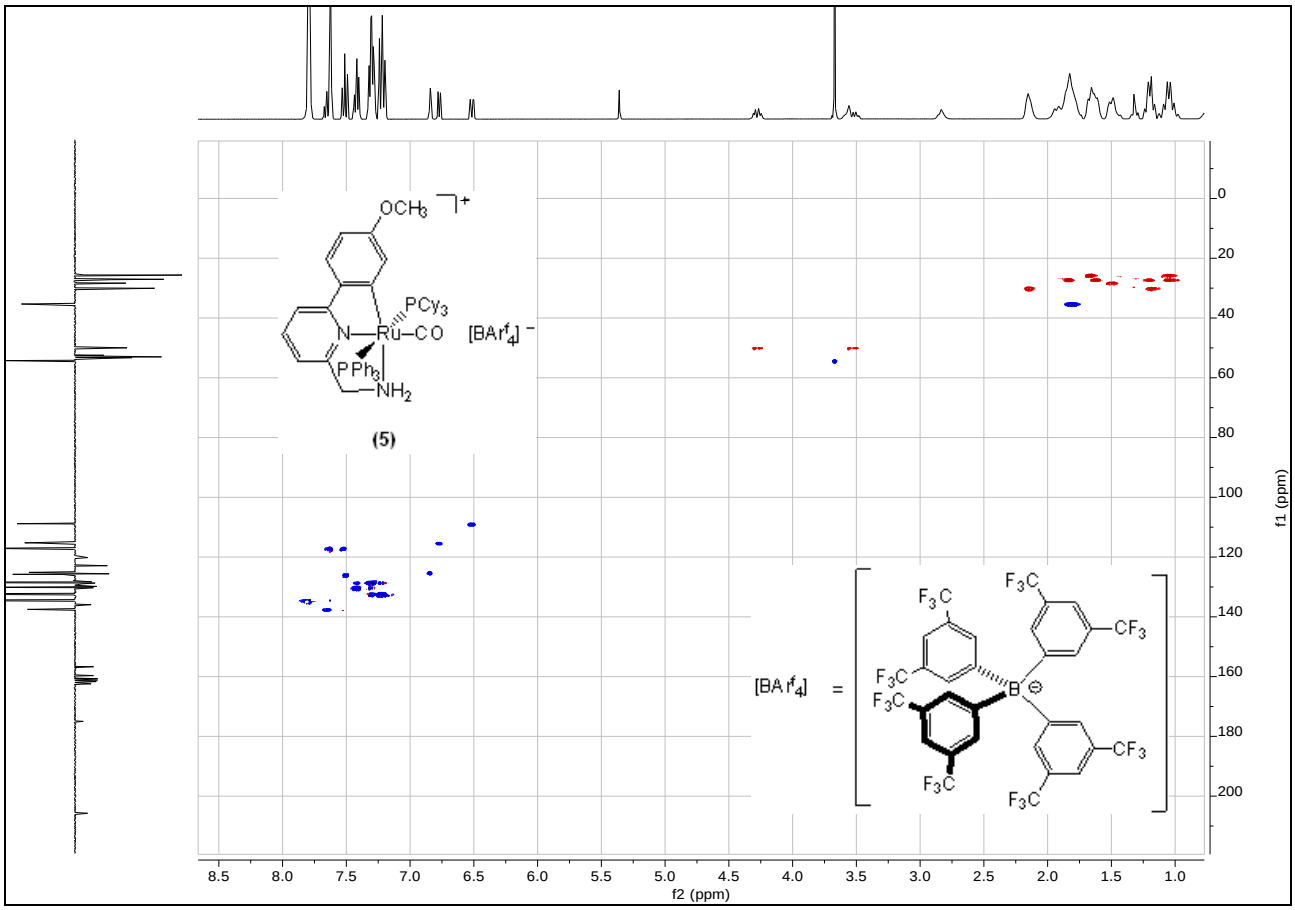

Figure S36. ^{1}H-^{13}C HSQC 2D NMR spectrum of *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][$BAr^f{}_4$] (**5**) in CD_2Cl_2 at 25 °C.

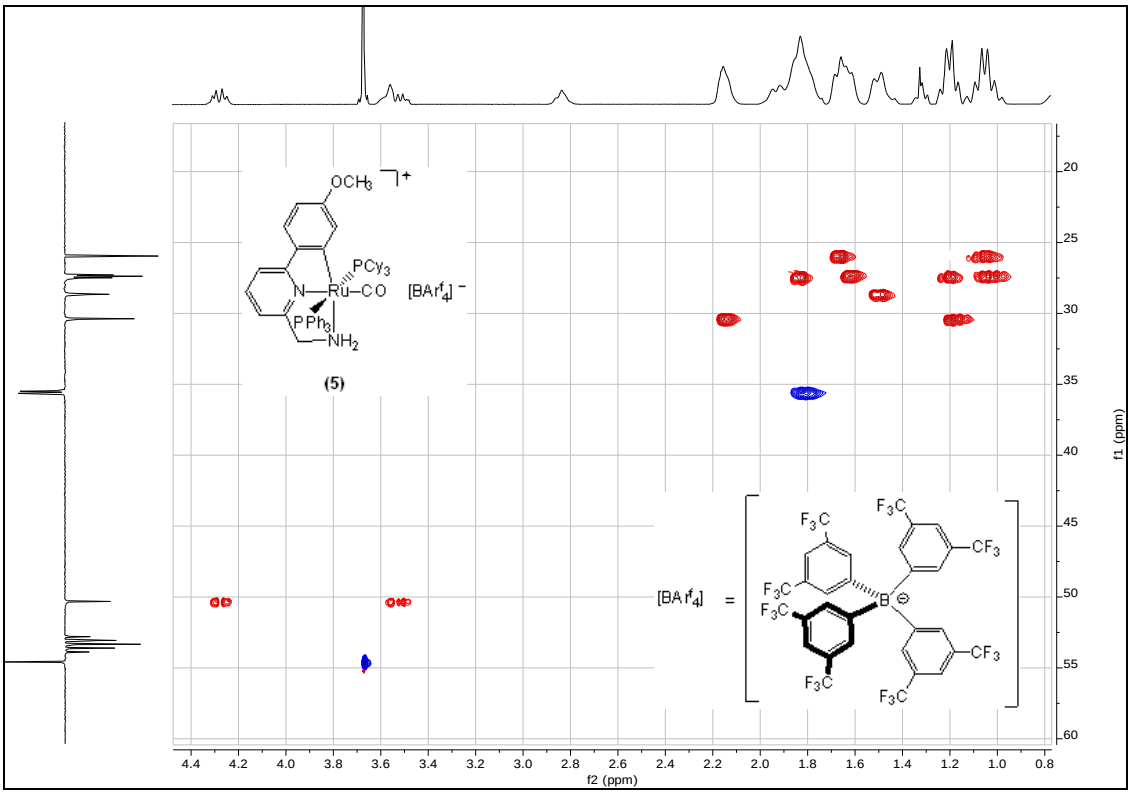

Figure S37. Alkylic region of the ^{1}H-^{13}C HSQC 2D NMR spectrum of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^{f}_4$] (**5**) in CD_2Cl_2 at 25 °C.

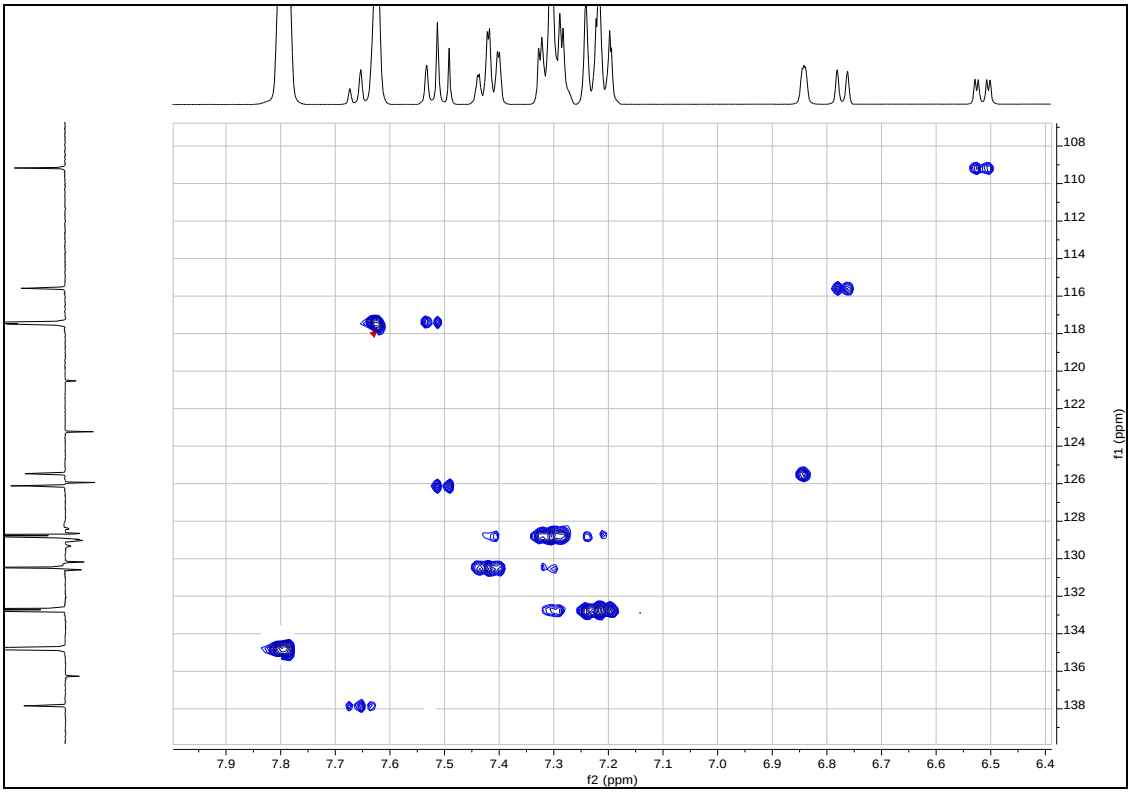

Figure S38. Aromatic region of the ^{1}H-^{13}C HSQC 2D NMR spectrum of *trans*-[Ru(CNN^{OMe})(CO)(PCy$_3$)(PPh$_3$)][BAr$^{f}_4$] (**5**) in CD_2Cl_2 at 25 °C.

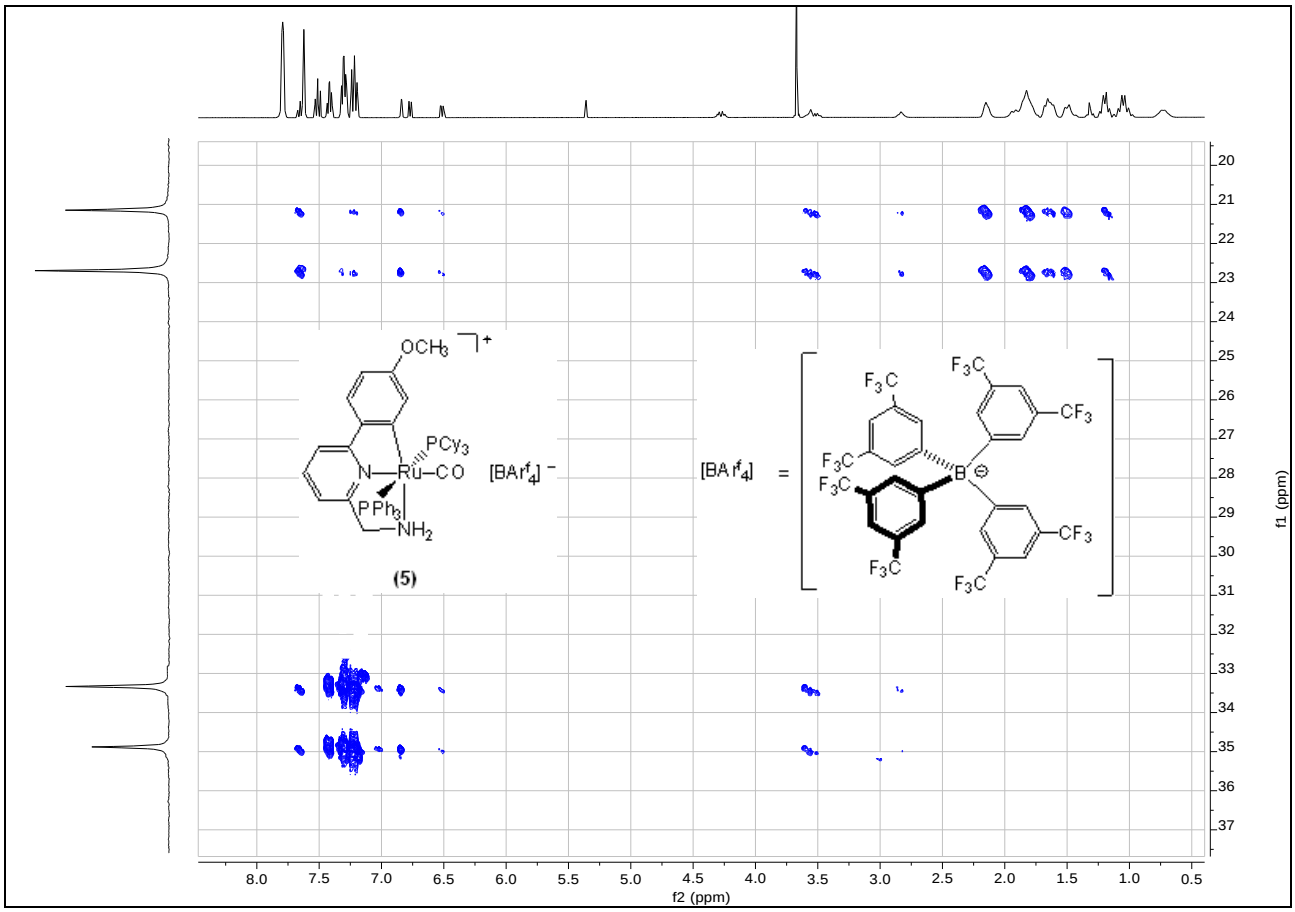

Figure S39. ^{1}H-^{31}P HMBC 2D NMR of *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][$BAr^f{}_4$] (**5**) in CD_2Cl_2 at 25 °C.

Table S1. Further data regarding the catalytic TH of lignocellulose biomass carbonyl compounds (0.1 M) to alcohols with **2**, **3**, **5** (S/C = 1000-10000) in 2-propanol at 82 °C.

Entry	Substrate	Complex	S/C	Base[a]	Time [min]	Conv.[b] [%]	Alcohol [%]	By-prod. [%]
1	**b**	**2**	1000	NaO*i*Pr	5	97	97	-
2	**b**	**2**	10000	K_2CO_3	24 h	47	47	-
3	**c**	**3**	1000	NaOiPr	1	99[c]	98	<1
4	**d**	**3**	1000	K_2CO_3	180	60[c]	4	56[d]
5	**f**	**3**	10000	K_2CO_3	30	64	62[e]	2[f]
6	**g**	**2**	1000	K_2CO_3	5	98	96	2[g]
7	**g**	**2**	1000	K_2CO_3	60	98	63	35[g]
8	**g**	**3**	1000	K_2CO_3	10	98	95	3[g]
9	**g**	**5**	1000	K_2CO_3	15	99	94	5[g]
10	**h**	**5**	1000	K_2CO_3	5	99[c]	98	<1
11	**h**	**5**	10000	K_2CO_3	20	99[c]	90	9[h]
12	**i**	**2**	1000	NaO*i*Pr	60	99[c]	97	2[i]
13	**i**	**3**	1000	NaOiPr	1	99[c]	99	-

[a]Base: NaO*i*Pr (2 mol%) or K_2CO_3 (5 mol%). [b]Conversions have been determined by GC analyses. [c]Conversions have been determined by NMR analyses. [d]5-(hydroxymethyl)furfural (5-HMF). [e]% of γ-valerolactone (GVL). [f]isopropyl 4-hydroxypentanoate. [g]3-phenylpropan-1-ol. [h]4-(isopropoxymethyl)-1,2-dimethoxybenzene. [i]4-(2-(4-(hydroxymethyl)-2-methoxyphenoxy)ethoxy)-3-methoxybenzaldehyde.

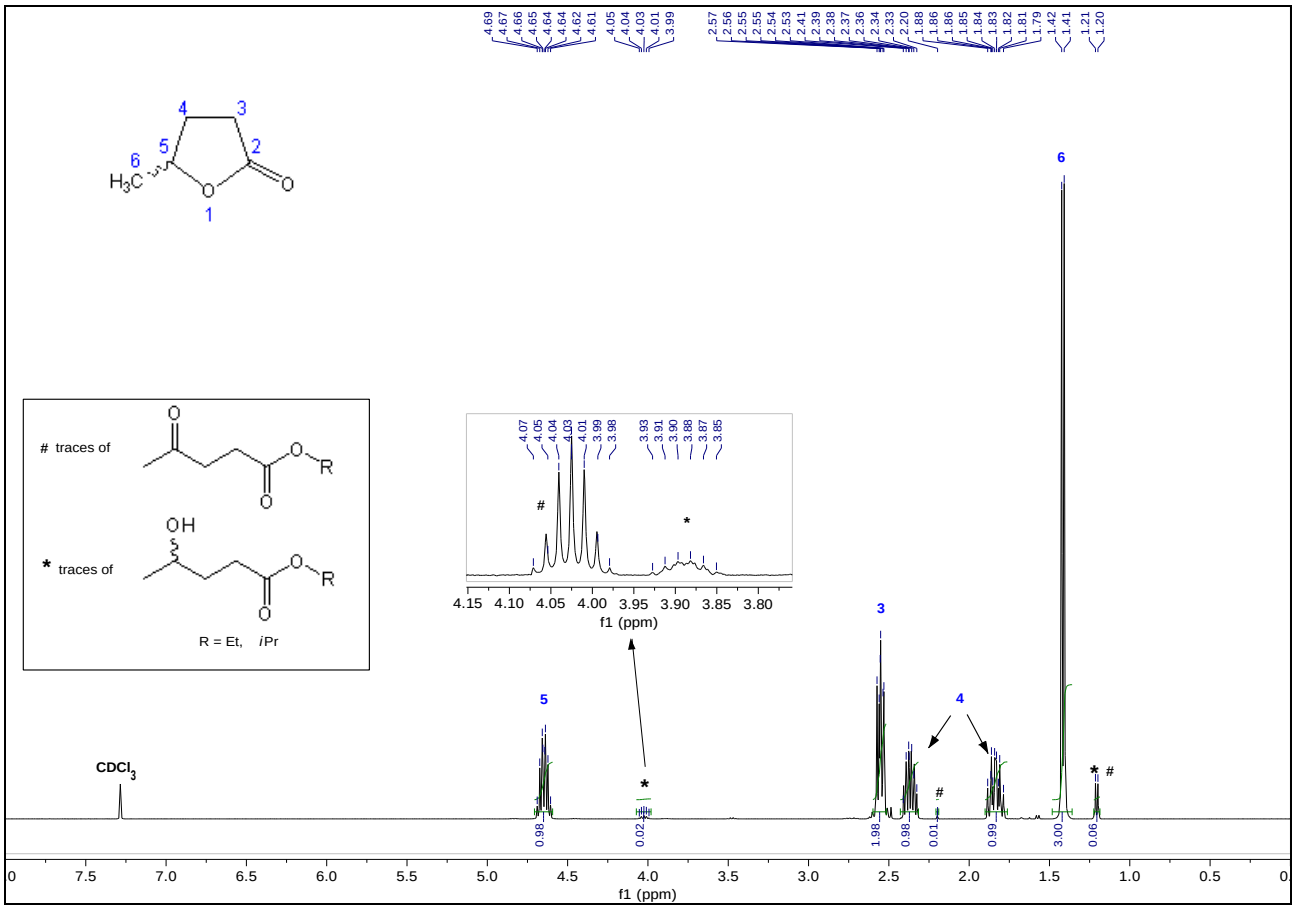

Figure S40. ^{1}H NMR spectrum (400.1 MHz) in $CDCl_3$ at 25 °C of γ-valerolactone (GVL) obtained from TH reduction of ethyl levulinate in 2-propanol catalyzed by ruthenium pincer complexes **2**, **3** and **5**.

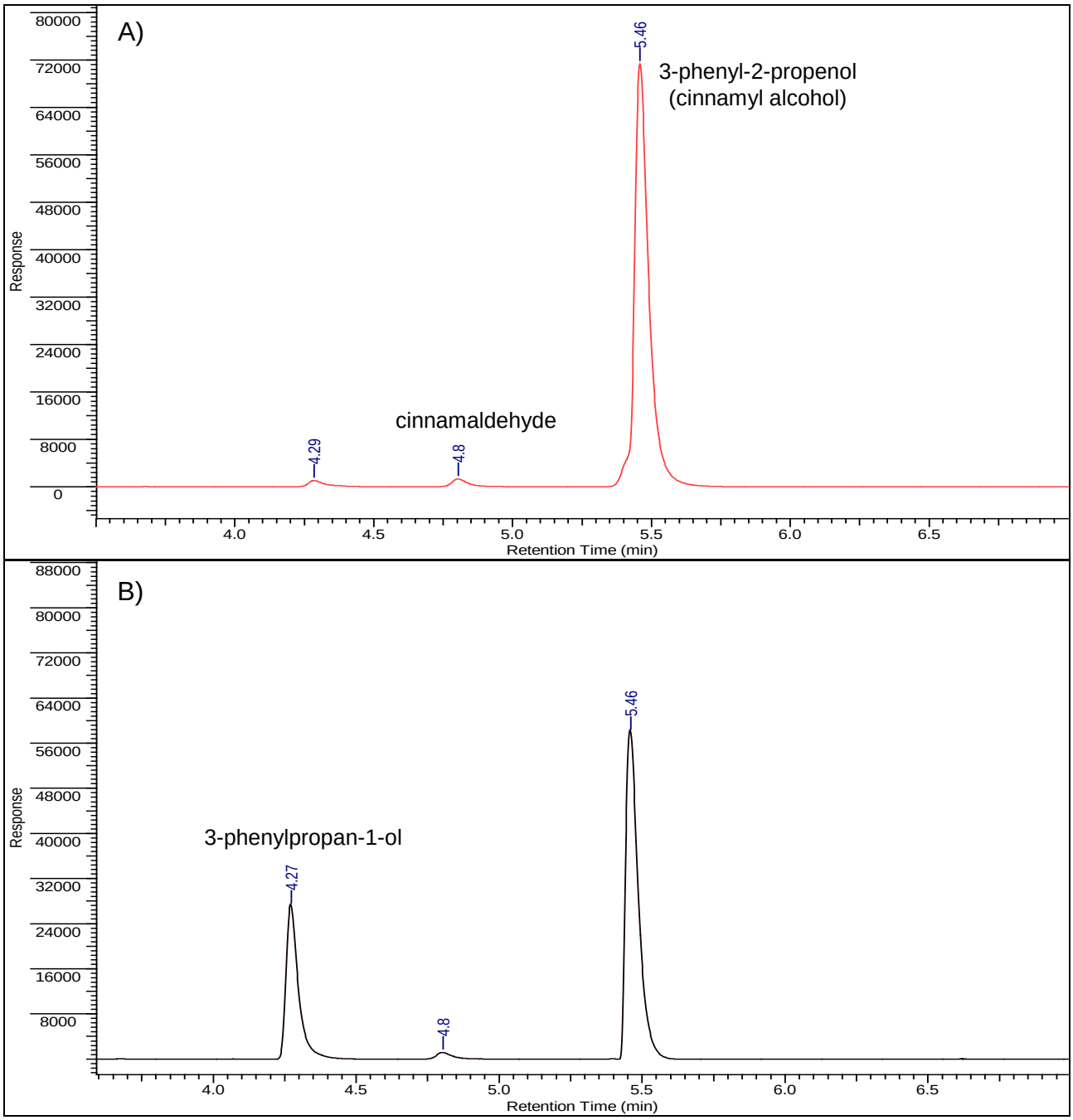

Figure S41. GC-FID chromatograms of the reaction mixture of the TH of cinnamaldehyde **g** in 2-propanol at reflux promoted by complex **2** at S/C 1000 after 5 min (A) and 1 h (B).