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# Amide vs. Amine Ligand Paradigm in the Direct Amination of Alcohols with Ru-PNP Complexes

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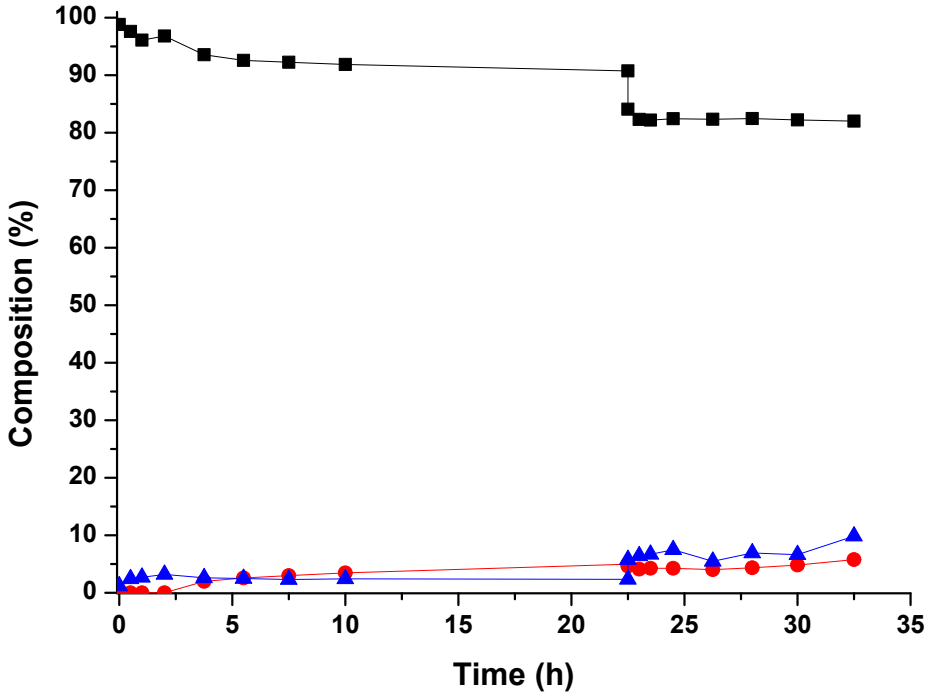
# Supporting Information

## GC-analysis:

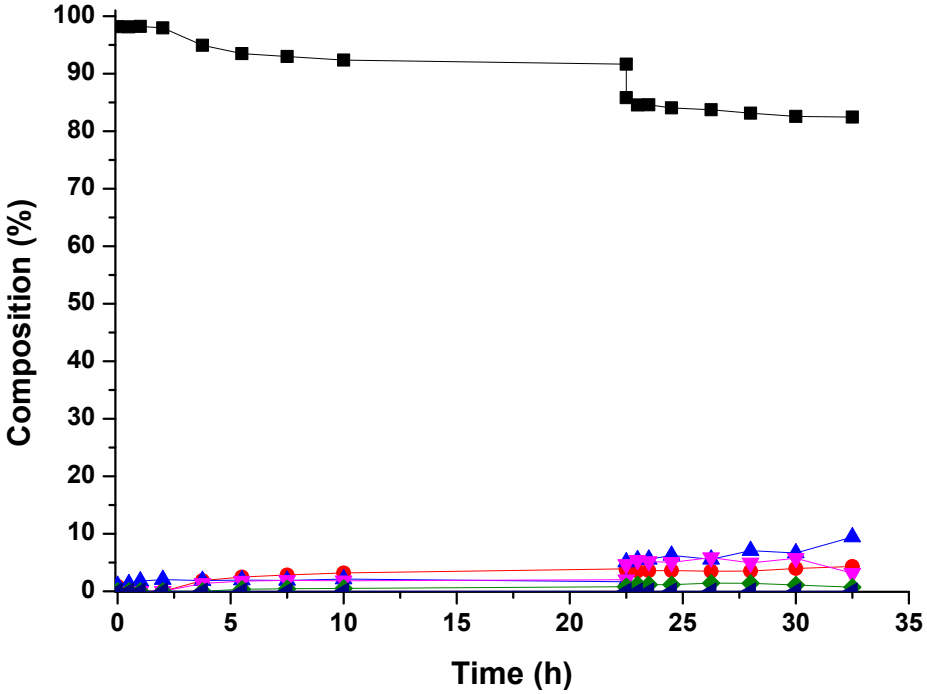
| GC-method details | |
|---|---|
| Injection Mode/ ratio: | Split/ 100 |
| Temperature: | 270°C |
| Carrier Gas: | He |
| Flow Control Mode: | Velocity |
| Pressure: | 121.0 kPa |
| Total Flow: | 73.6 mL/min |
| Column Flow: | 0.70 mL/min |
| Liner Velocity: | 26.1 cm/sec |
| Temperature program: | 80°C → 199°C @ 8°C/min 199°C → 270°C @50°C/min hold 2 min |
| Column type: | Ultra-2 serial nr.: US8649351H |
| Column length: | 25 m, 0.33 µm film thickness, 0.20 mm inner diameter |
| Column Max Temp. | 310°C |

## Catalysis:

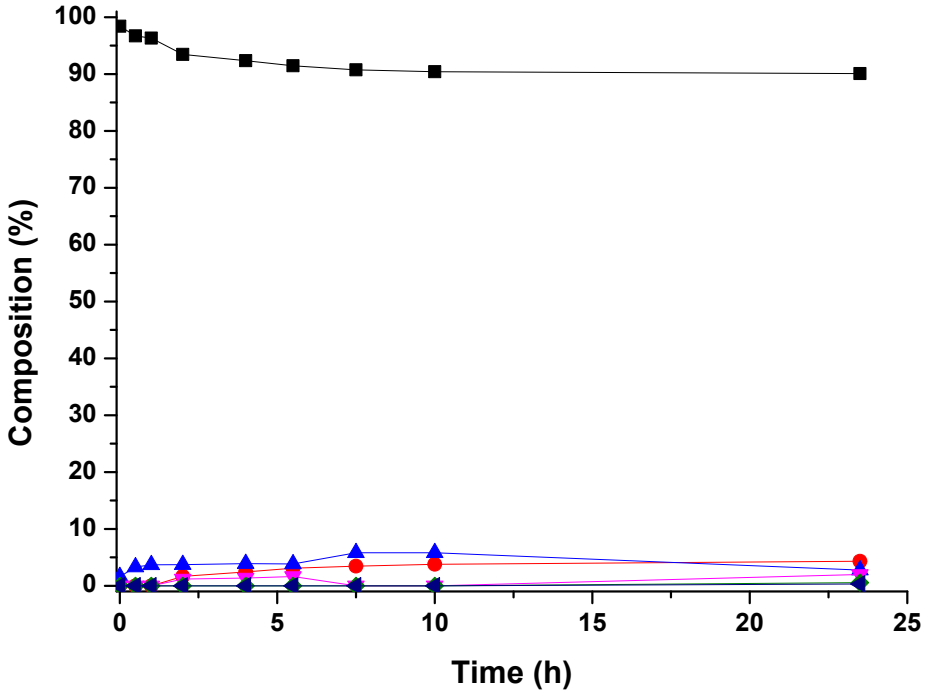
### Complex 13 and 15



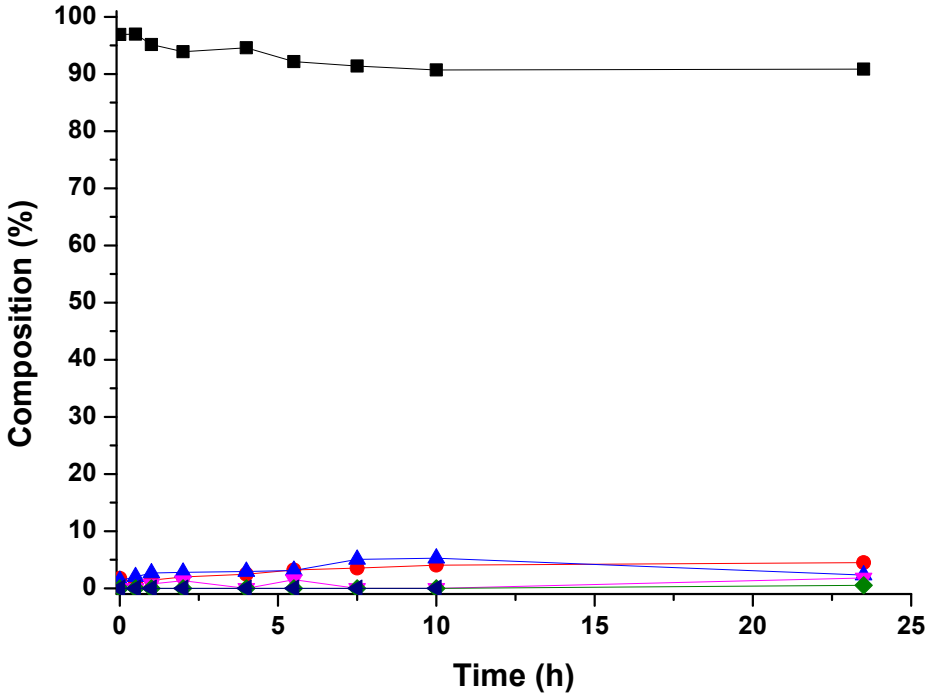

**Graph S1: Amination of cyclohexanol employing complex 13 followed by the addition of cyclohexanone. Conditions: 0.04 mmol complex 13, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone (after 22.5 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 22.5 h then cyclohexanone added and another 10 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone.**



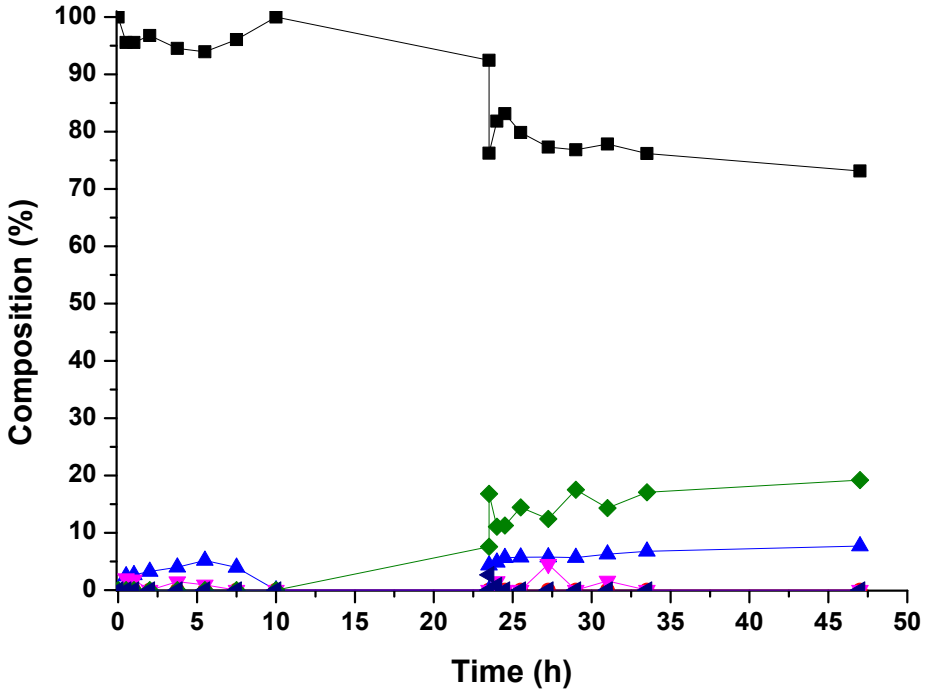

**Graph S2: Amination of cyclohexanol employing complex 15 followed by addition of cyclohexanone. Conditions: 0.04 mmol complex 15, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone (after 22.5 h) 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 22.5 h then cyclohexanone added and another 10 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**



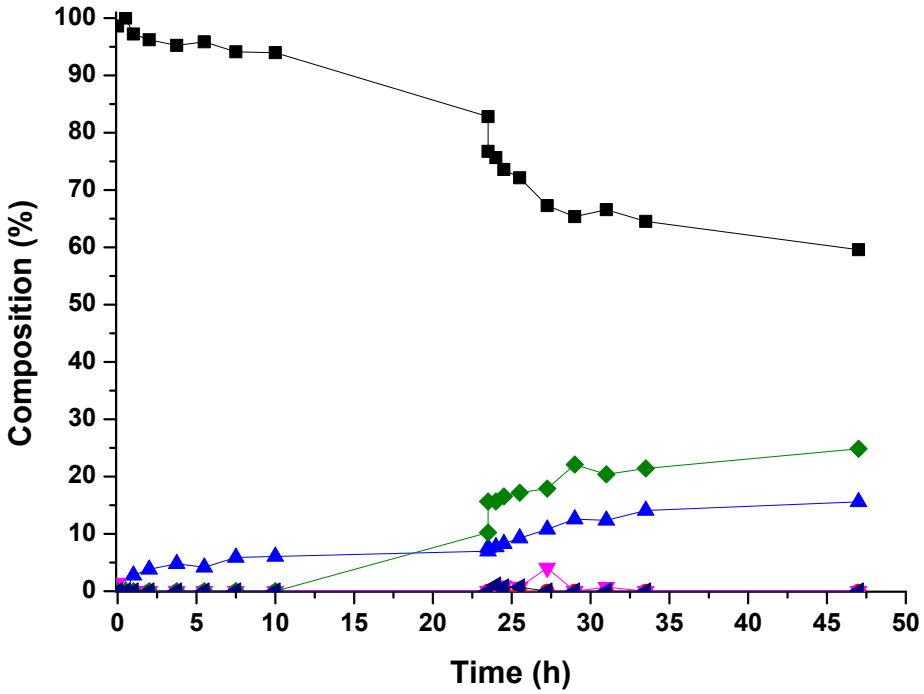

**Graph S3: Amination of cyclohexanol employing complex 13 with additional 1 mol% KO$^t$Bu. Conditions: 0.04 mmol complex 13, 5 mmol cyclohexanol, 0.05 mmol KO$^t$Bu, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**




**Graph S4: Amination of cyclohexanol employing complex 15 with additional 1 mol% KO$^t$Bu. Conditions: 0.04 mmol complex 15, 5 mmol cyclohexanol, 0.05 mmol KO$^t$Bu, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h. ■ = cyclohexanol, ● = cyclohexylamine, ◻ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**



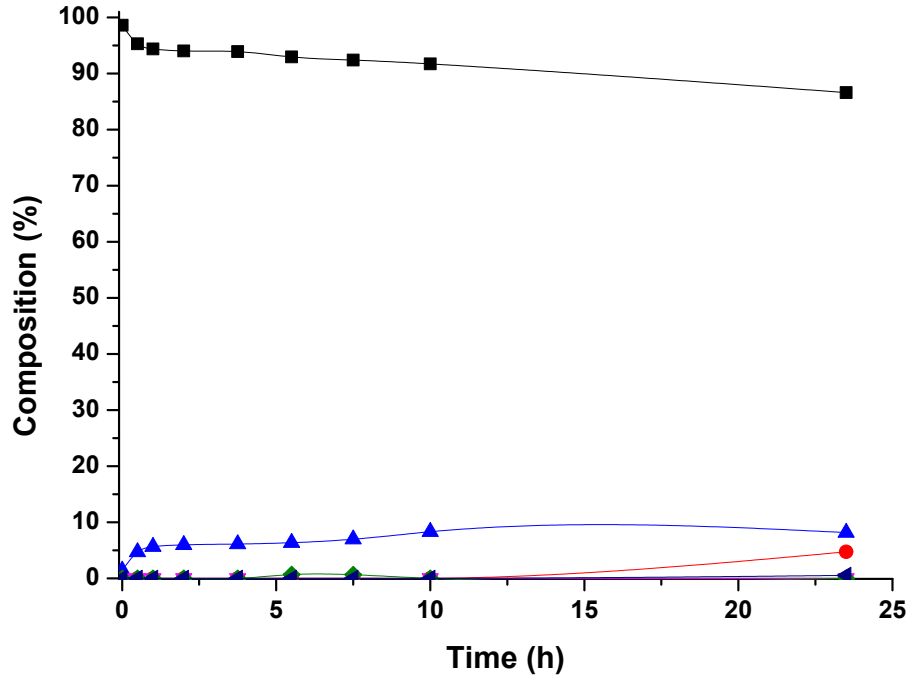

**Graph S5: Amination of benzylalcohol employing complex 13 followed by the addition of benzaldehyde. Conditions: 0.04 mmol complex 13, 5 mmol benzylalcohol, 0.5 mmol benzaldehyde (after 23.5 h) 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h then benzaldehyde was added and another 23.5 h. ■ = benzylalcohol, ● = benzylamine, ◻ = benzaldehyde, ❑ = benzylimine, ◆ = dibenzylimine, ♦ = dibenzylamine.**



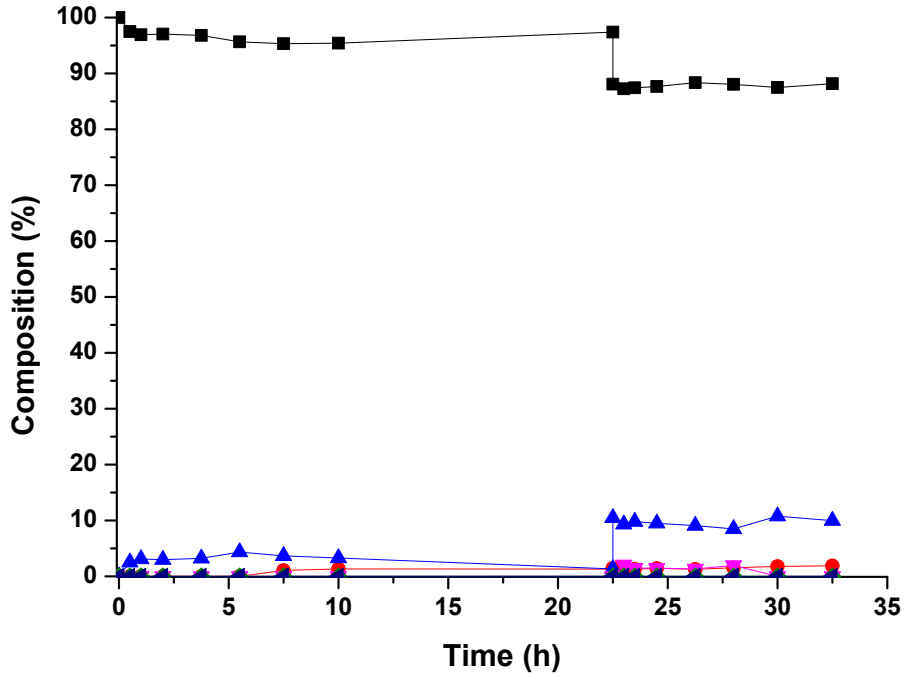

**Graph S6: Amination of benzylalcohol employing complex 15 followed by addition of benzaldehyde. Conditions: 0.04 mmol complex 15, 5 mmol benzylalcohol, 0.5 mmol benzaldehyde (after 23.5 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h then addition of benzaldehyde and another 23.5 h. ■ = benzylalcohol, ● = benzylamine, ◘ = benzaldehyde, ❑ = benzylimine, ◆ = dibenzylimine, ♦ = dibenzylamine.**

For both complex **13** and **15**, no activity could be found employing primary alcohols, even not after the addition of benzaldehyde (Graph S5 and Graph S6).

The reaction was also tested using toluene instead of t-amylalcohol. The results are displayed in Graph S7 and Graph S8.



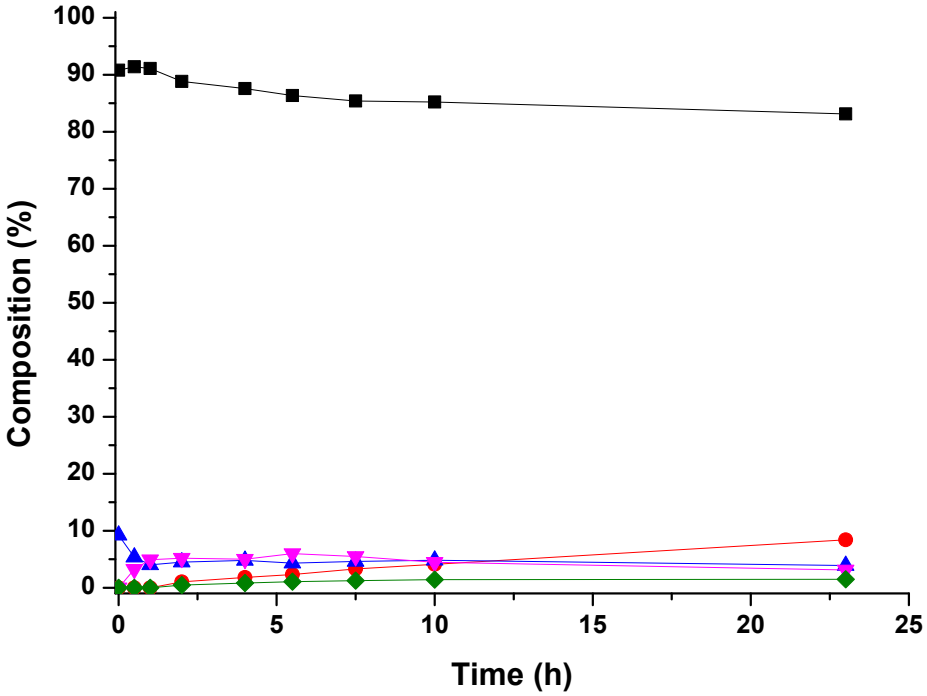

**Graph S7: Amination of cyclohexanol employing complex 13. Conditions: 0.04 mmol complex 13, 5 mmol cyclohexanol, 15 mL toluene, 2.5 mL $NH_3$, 150°C, 23.5 h. ■ = cyclohexanol, ● = cyclohexylamine, ◘ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**




**Graph S8: Amination of cyclohexanol employing complex 15 followed by addition of cyclohexanone. Conditions: 0.04 mmol complex 15, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone (after 22.5 h), 15 mL toluene, 2.5 mL $NH_3$, 150°C, 22.5 h then cyclohexanone was added and another 10 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**

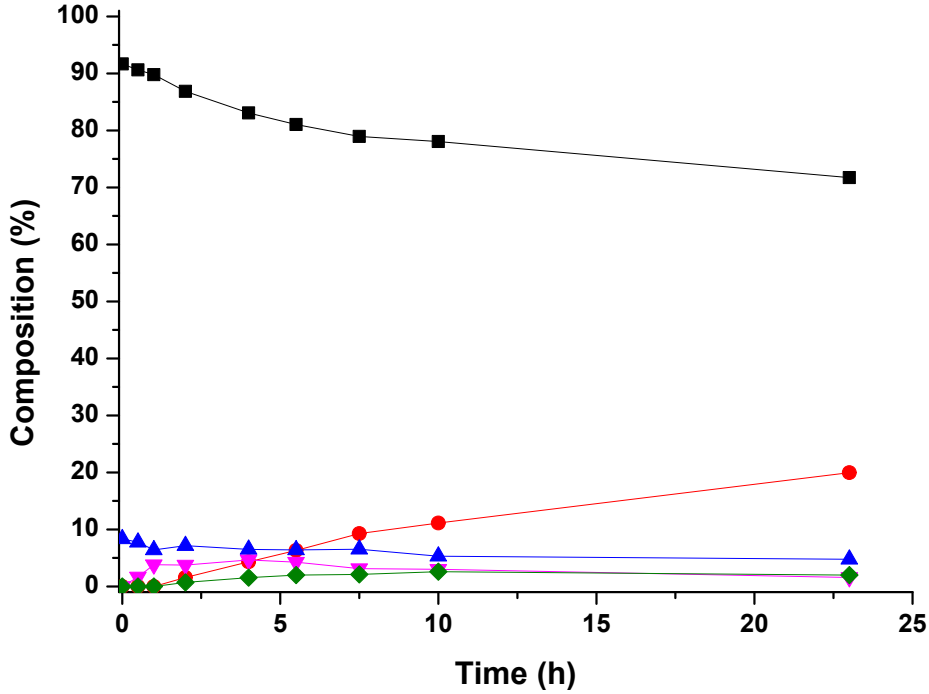
Also changing the solvent did not lead to conversion. It has to be concluded that complex **13** and **15** are inactive in the direct amination of alcohols using ammonia.

### Complex 12 and 14

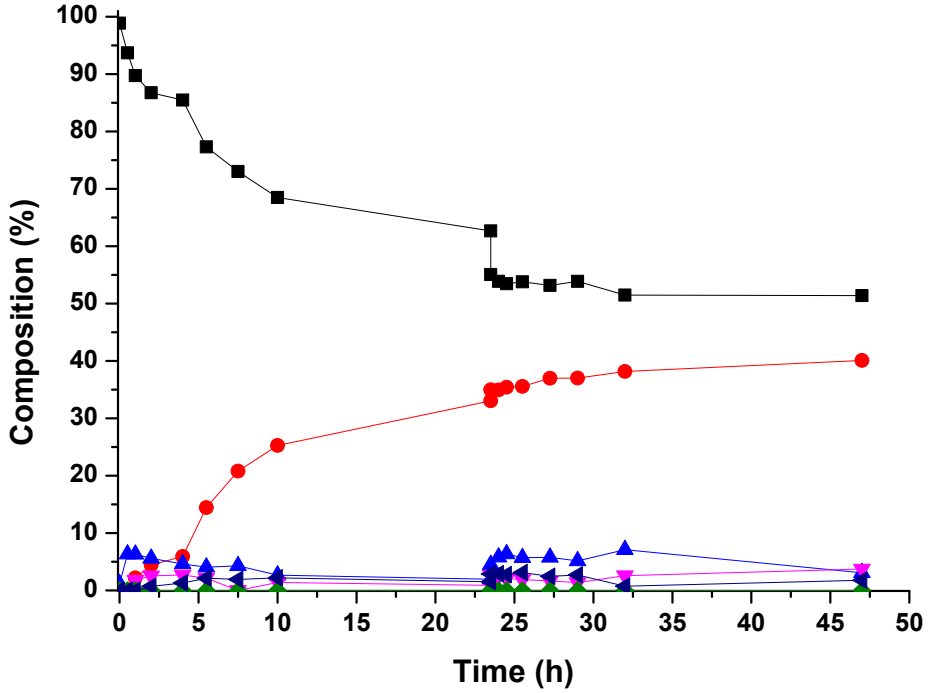



**Graph S9: Amination of cyclohexanol employing complex 12 with 10 mol% cyclohexanone. Conditions: 0.04 mmol complex 12, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h. ■ =**

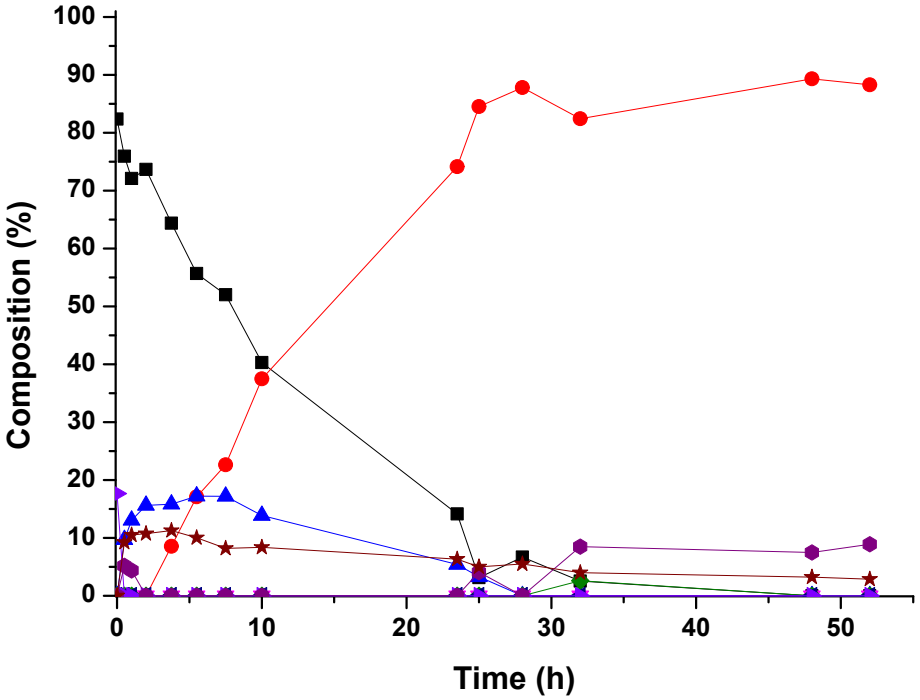
cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.



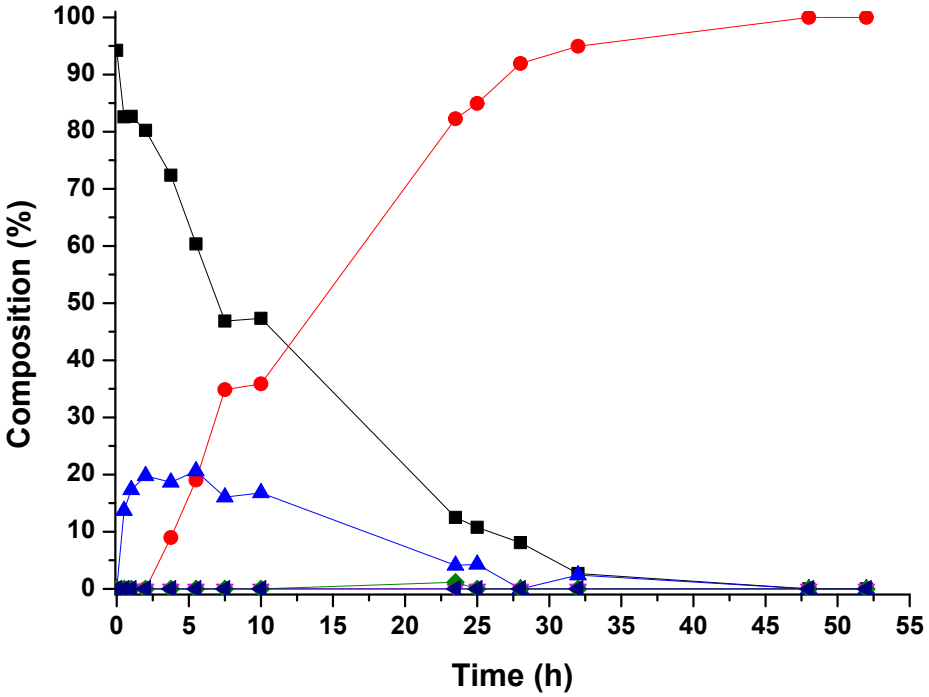

**Graph S10: Amination of cyclohexanol employing complex 14 with 10 mol% cyclohexanone. Conditions: 0.04 mmol complex 14, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**




**Graph S11: Amination of cyclohexanol employing complex 14 followed by addition of cyclohexanone. Conditions: 0.04 mmol complex 14, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone (after 23.5 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h then cyclohexanone added and another 23.5 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**

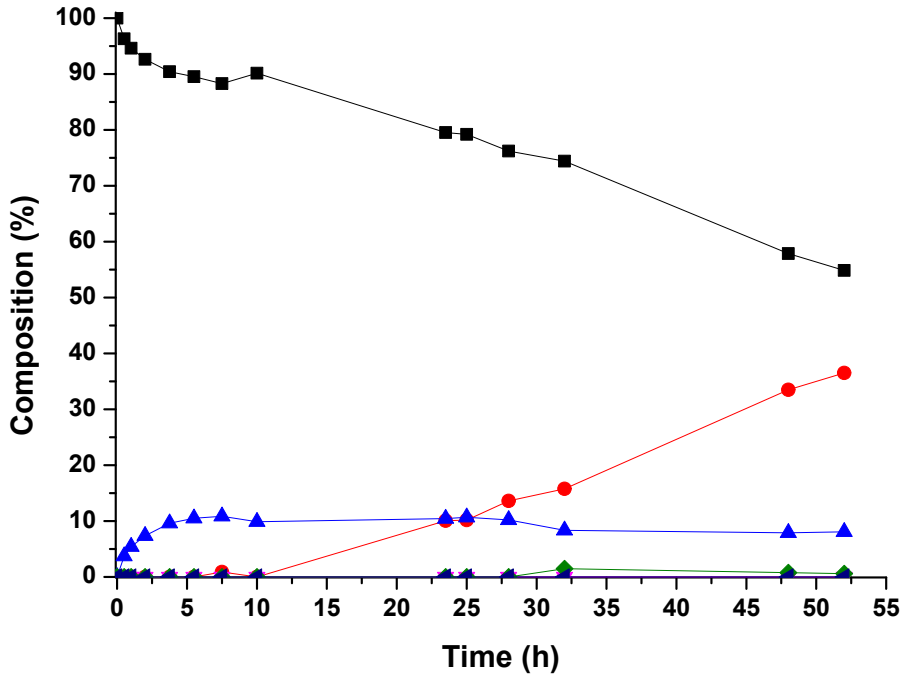



**Graph S12: Amination of cyclohexanol employing complex 12 with 10 mol% benzaldehyde. Conditions: 0.04 mmol complex 12, 5 mmol cyclohexanol, 0.5 mmol benzaldehyde, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 51 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine, ◆ = benzylamine, = benzylalcohol, ★ = benzaldehyde.**

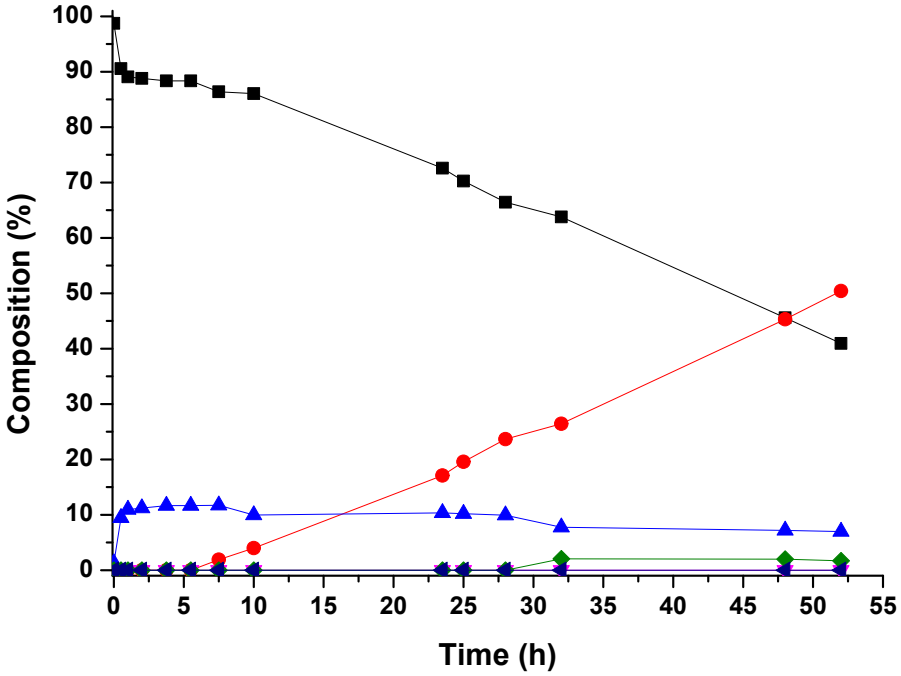



**Graph S13: Amination of cyclohexanol employing complex 14 with 10 mol% benzaldehyde. Conditions: 0.04 mmol complex 14, 5 mmol cyclohexanol, 0.5 mmol benzaldehyde, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 52 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**

The catalytic reactions employing **12** and **14** were also performed in toluene instead of t-amylalcohol.

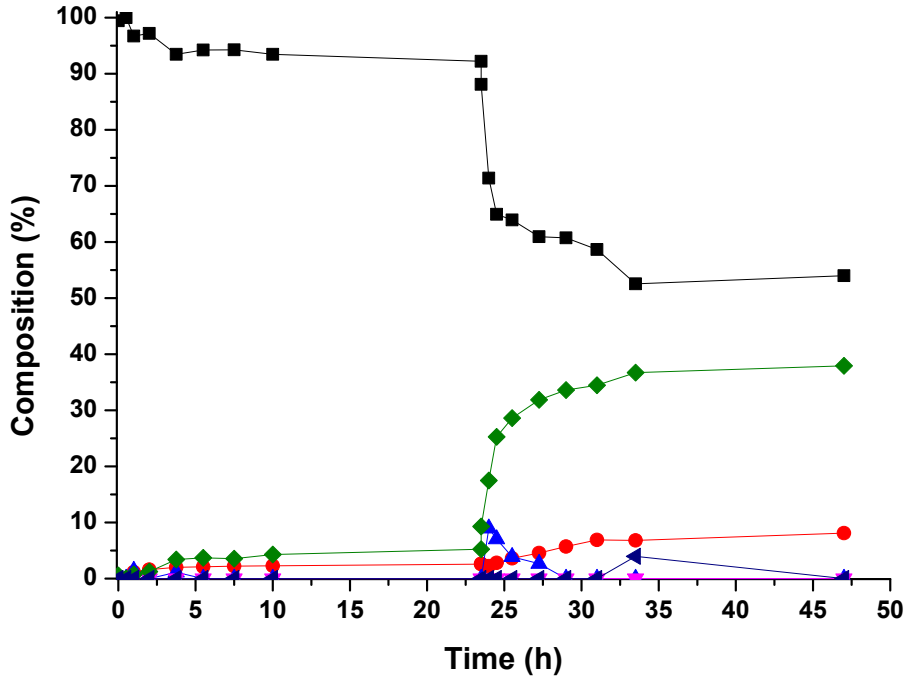



**Graph S14: Amination of cyclohexanol employing complex 12. Conditions: 0.04 mmol complex 12, 5 mmol cyclohexanol, 15 mL toluene, 2.5 mL $NH_3$, 150°C, 52 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**

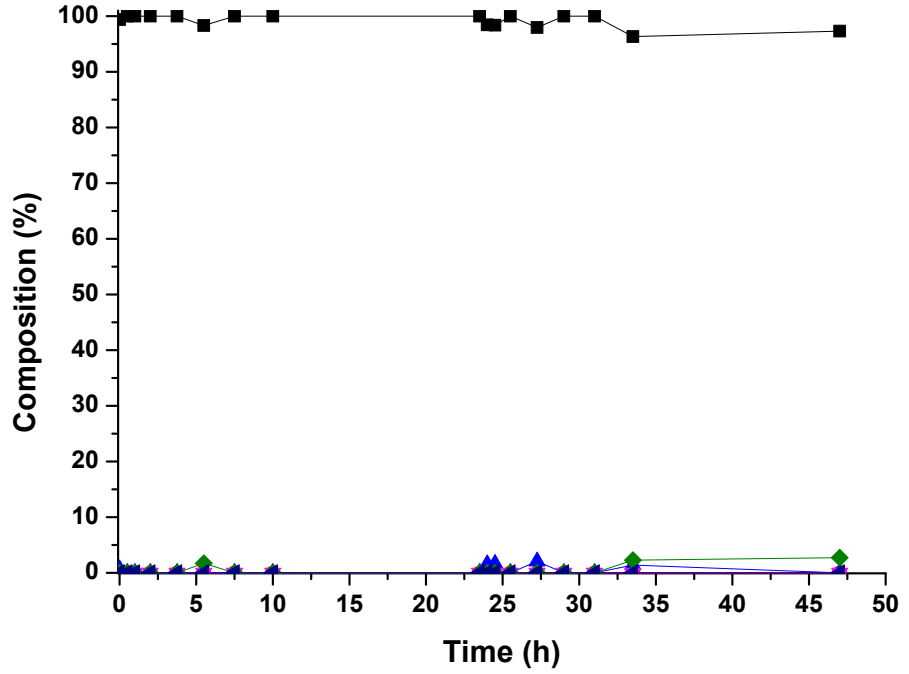



**Graph S15: Amination of cyclohexanol employing complex 14. Conditions: 0.04 mmol complex 14, 5 mmol cyclohexanol, 15 mL toluene, 2.5 mL $NH_3$, 150°C, 52 h. ■ = cyclohexanol, ● = cyclohexylamine, □ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**

In both cases, the activity is lower than in t-amylalcohol (Graph S14 and Graph S15).




**Graph S16: Amination of benzylalcohol employing complex 12 followed by addition of benzaldehyde. Conditions: 0.04 mmol complex 12, 5 mmol benzylalcohol, 0.5 mmol benzaldehyde (after 23.5 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h then addition of benzaldehyde and another 23.5 h. ■ = benzylalcohol, ● = benzylamine, □ = benzaldehyde, ❑ = benzylimine, ◆ = dibenzylimine, ◆ = dibenzylamine.**

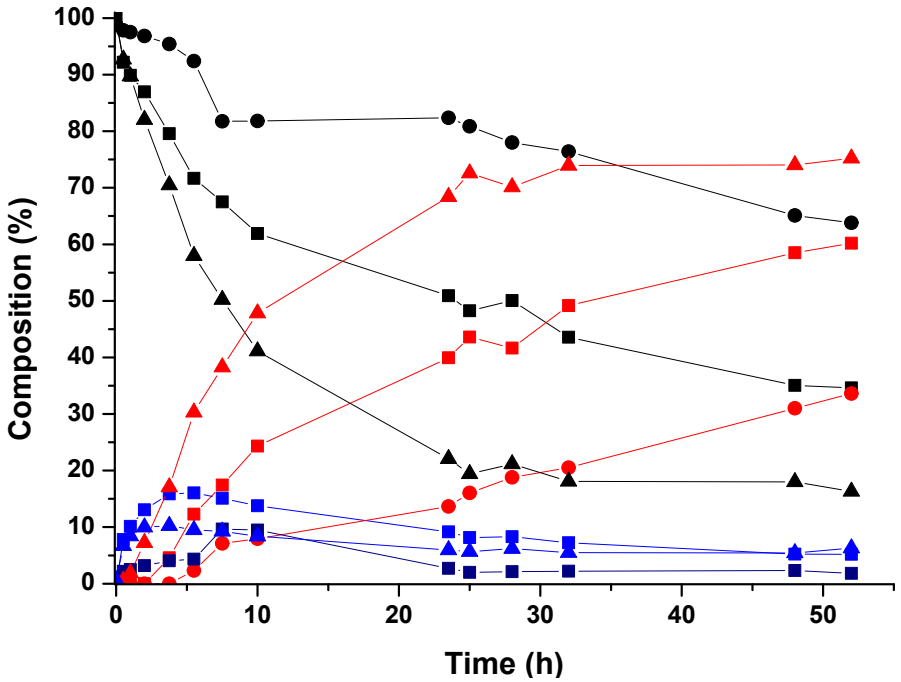



**Graph S17: Amination of benzylalcohol employing complex 14 followed by addition of benzaldehyde. Conditions: 0.04 mmol complex 14, 5 mmol benzylalcohol, 0.5 mmol benzaldehyde (after 23.5 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 23.5 h then addition of benzaldehyde and another 23.5 h. ■ = benzylalcohol, ● = benzylamine, □ = benzaldehyde, ❑ = benzylimine, ◆ = dibenzylimine, ◆ = dibenzylamine.**

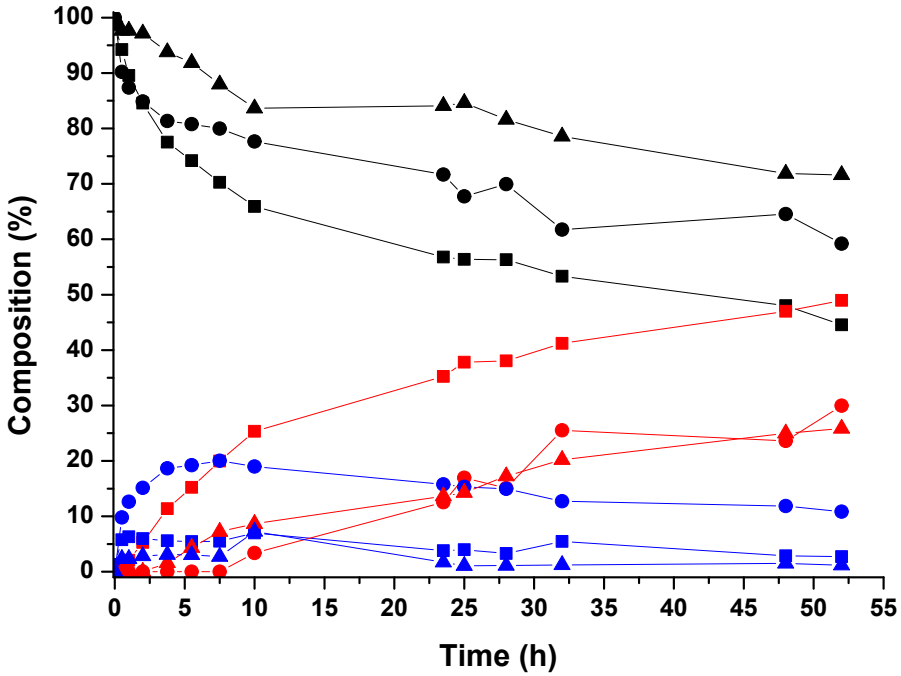
To see if the reaction also works for primary alcohols, benzylalcohol was employed as a substrate under these conditions (Graph S16 and Graph S17).

As the $NH_3$ amount was shown to influence the performance of the catalyst before, reactions were performed in which the amount of $NH_3$ was varied from 2.5 mL to 7.5 mL

(Graph S18 and Graph S19). This was done for both complexes **12** and **14**. This was not done for complexes **13** and **15** as these did not show any conversion under any of the previously tested conditions.

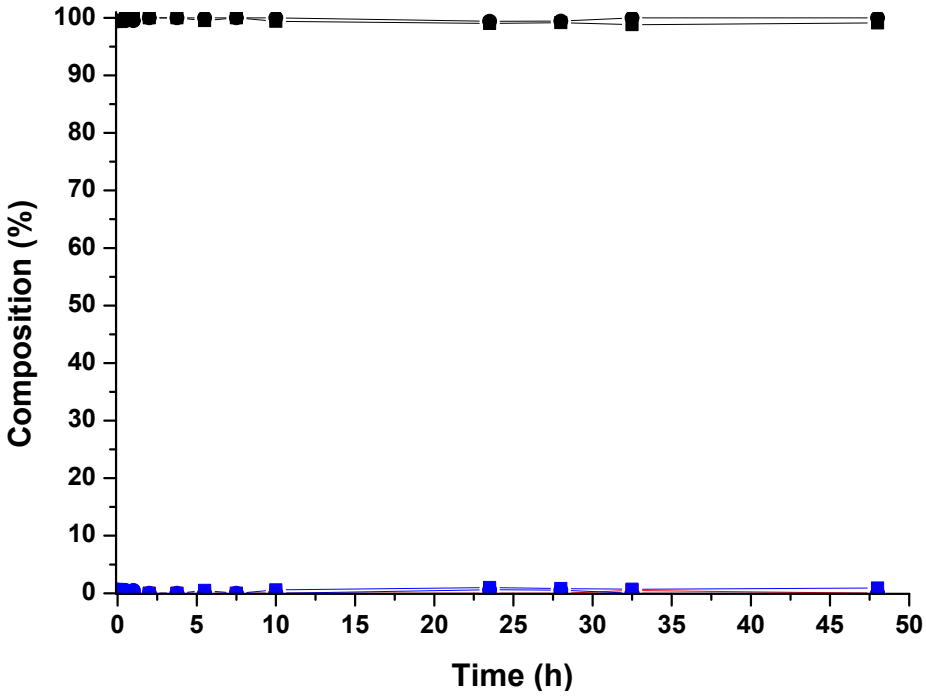



**Graph S18: Amination of cyclohexanol employing complex 12 with different amounts of $NH_3$. Conditions: 0.04 mmol complex 12, 5 mmol cyclohexanol, 15 mL t-amylalcohol, $NH_3$, 150°C, 51 h. □ = 2.5 mL $NH_3$, ■ = 5 mL $NH_3$, ● = 7.5 mL $NH_3$, black = cyclohexanol, red = cyclohexylamine, blue = cyclohexanone.**

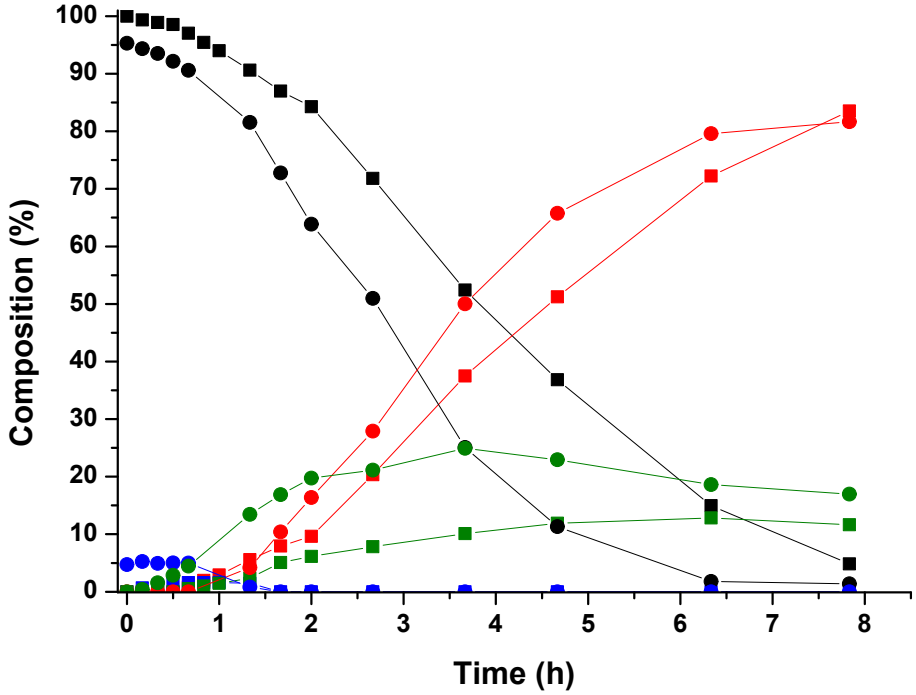



**Graph S19: Amination of cyclohexanol employing complex 14 with different amounts of $NH_3$. Conditions: 0.04 mmol complex 14, 5 mmol cyclohexanol, 15 mL t-amylalcohol, $NH_3$, 150°C, 52 h. □ = 2.5 mL $NH_3$, ■ = 5 mL $NH_3$, ● = 7.5 mL $NH_3$, black = cyclohexanol, red = cyclohexylamine, blue = cyclohexanone.**

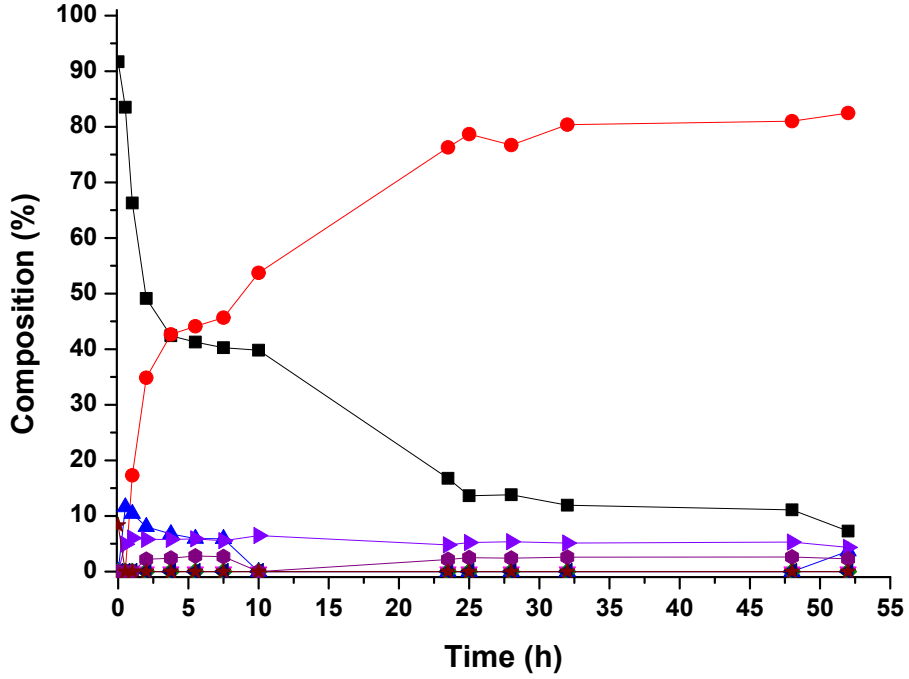
## Other Complexes




**Graph S20: Amination of cyclohexanol using AcridanPhos (10). Conditions: 5 mmol cyclohexanol, 1 mol% $RuHCl(CO)(PPh_3)_3$, 1 mol% Acridanphos (10), 13.3 mL t-amylalcohol, 2.5 mL $NH_3$ (97.5 mmol), 46h, 150°C (■) and 170°C (●), black = cyclohexanol, red = cyclohexylamine, blue = cyclohexanone.**

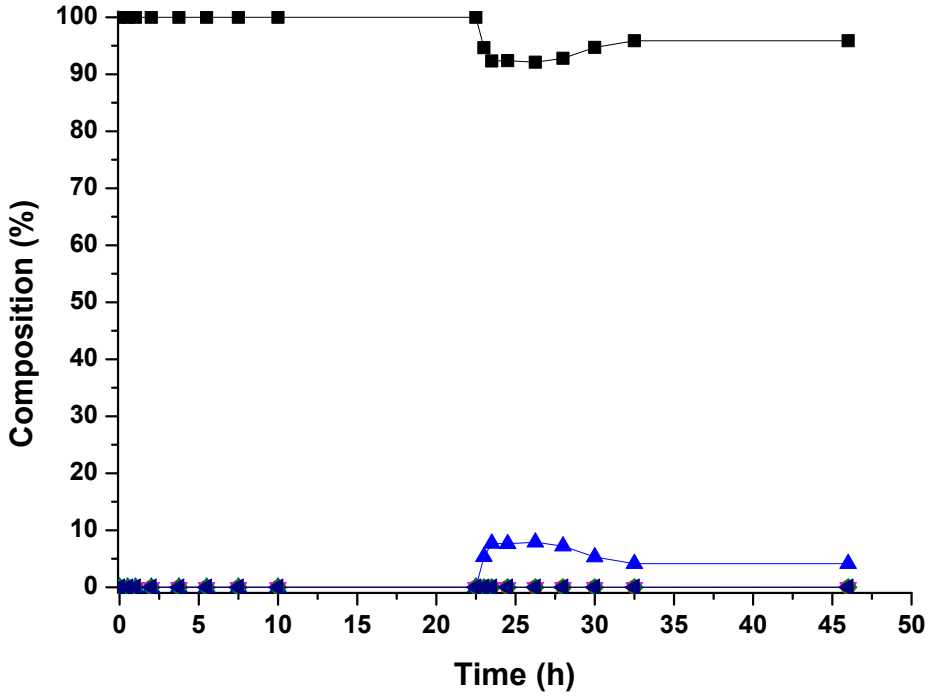



**Graph S21: Amination of benzylalcohol using complex 2 with and without additional 10 mol% benzaldehyde. Conditions: 5 mmol benzylalcohol, 1 mol% complex 2, 15 mL toluene, 2.5 mL NH3, 150°C, 8 h. ■ = no added benzaldehyde, ● = with 10 mol% benzaldehyde, black = benzylalcohol, red = benzylamine, blue = benzaldehyde, green = dibenzylimine.**

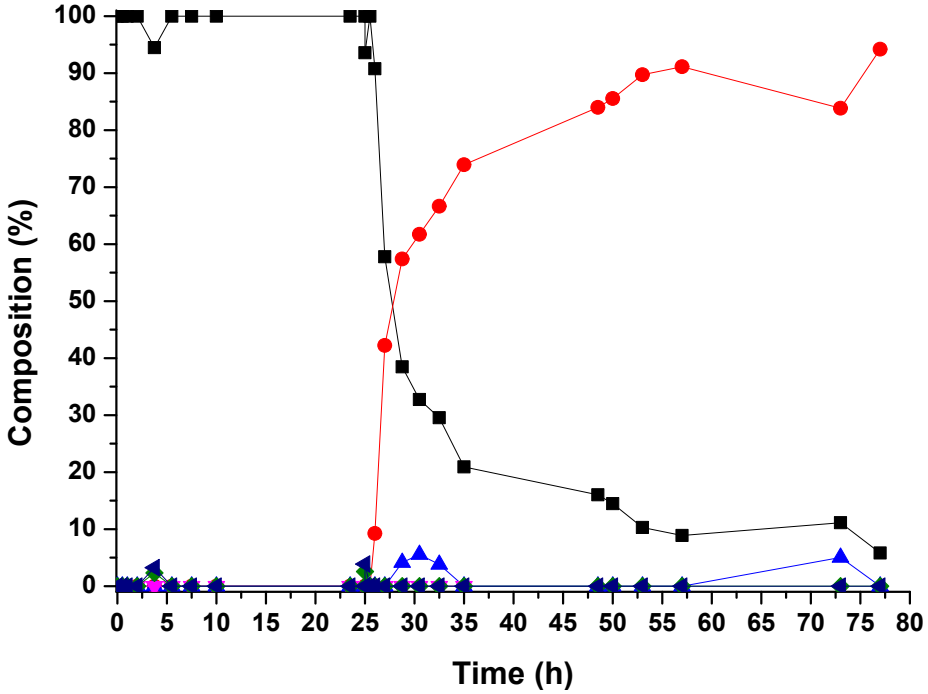



**Graph S22: Amination of cyclohexanol employing complex 18 in the presence of KO$^t$Bu and benzaldehyde. Conditions: 0.04 mmol complex 18, 5 mmol cyclohexanol, 0.5 mmol KO$^t$Bu, 0.5 mmol benzaldehyde, 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 52 h. ■ = cyclohexanol, ● = cyclohexylamine, ◘ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclo hexylamine, ◆ = benzylcyclohexylimine, ⊄ = dibenzylamine.**

The activity is still very good, though slightly less than without benzaldehyde. It can be concluded that in this case, only the base has a positive, activating effect.




**Graph S23: Amination of cyclohexanol employing complex 18 followed by addition of cyclohexanone. Conditions: 0.04 mmol complex 18, 5 mmol cyclohexanol, 0.5 mmol cyclohexanone (after 22.5 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 22.5 h then cyclohexanone added and another 23.5 h. ■ = cyclohexanol, ● = cyclohexylamine, ◘ = cyclohexanone, ❑ = cyclohexylimine, ◆ = dicyclohexylimine, ♦ = dicyclohexylamine.**




**Graph S24: Amination of 1-hexanol employing complex 18 followed by addition of KO$^t$Bu. Conditions: 0.04 mmol complex 18, 5 mmol 1-hexanol, 0.5 mmol KO$^t$Bu (after 25 h), 15 mL t-amylalcohol, 2.5 mL $NH_3$, 150°C, 25 h then KO$^t$Bu added and another 52 h. ■ = 1-hexanol, ● = 1-hexylamine, □ = 1-hexanal, ❑ = 1-hexylimine, ◆ = dihexylimine, ♦ = dihexylamine.**

## Mass Spectrometry

### LIFDI-MS

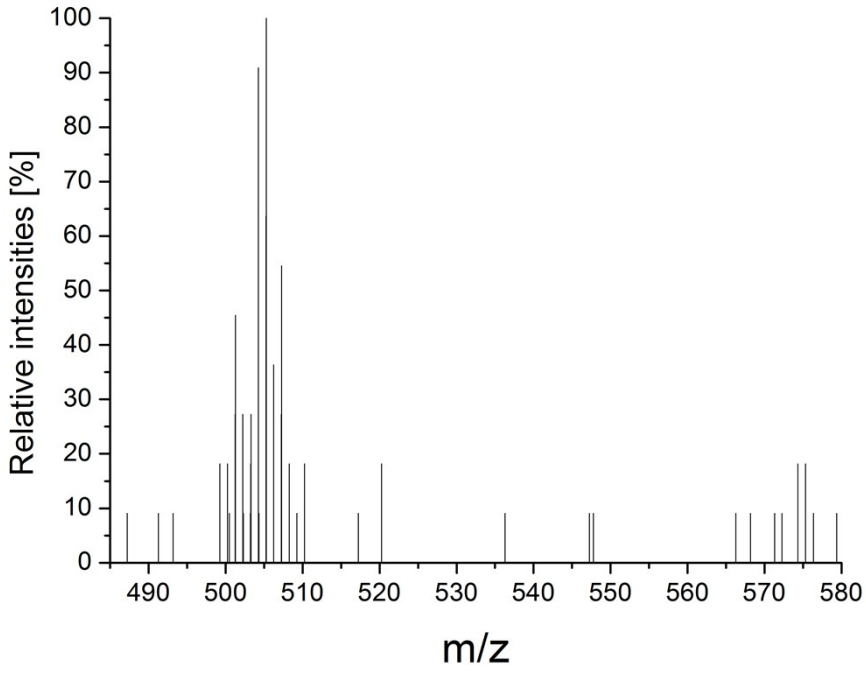



**Figure S1: LIFDI-MS (Argon collided) of complex [RuCO($C_5H_{10}$)(Me-PNP)] 16 in toluene at a retention time of 4.25 min.**

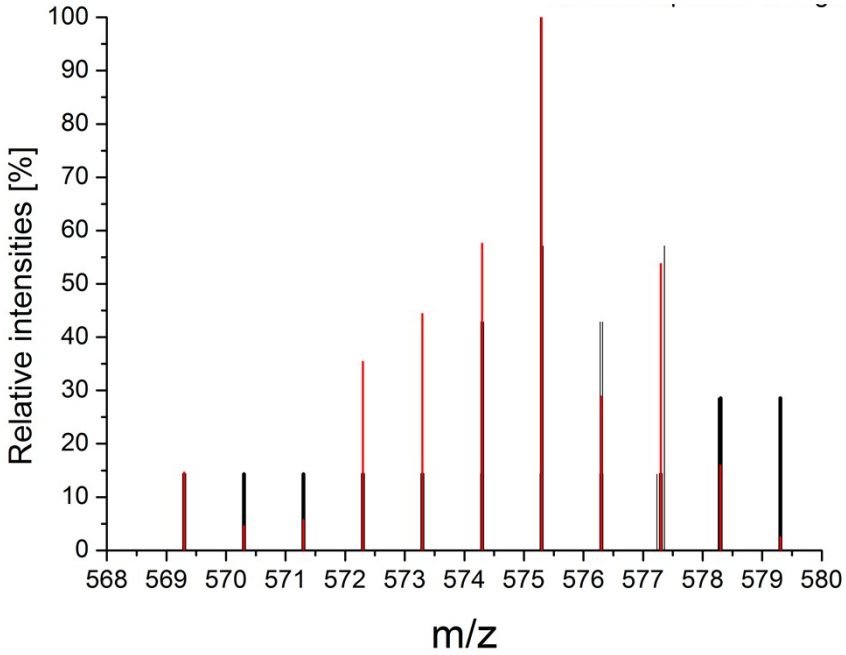



**Figure S2: LIFDI-MS/MS of [RuCO($C_5H_{10}$)(Me-PNP)] (16) at a retention time of 2.90 min (black, 569 – 579) compared to simulated isotope pattern of [RuCO($C_5H_{10}$)(Me-PNP)] 575 (red, 569 – 579).**

## Spectroscopy:

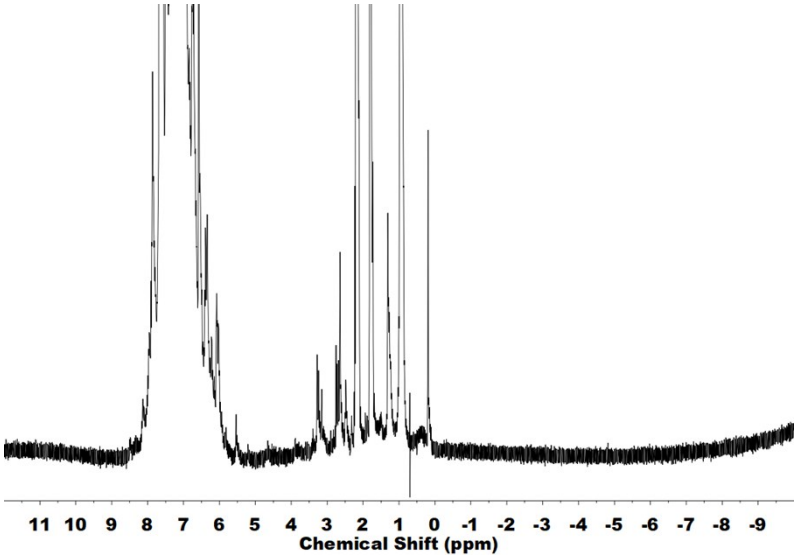



**Figure S3: Reaction of ligand 8 with RuHCl(CO)($PPh_3$)$_3$. $^1$H NMR (400 MHz, 298 K, toluene-d$^8$): Only ligand signylas, but no hydride signals; indication of amide bond formation with elimination of $H_2$ (no signal for this observed).**

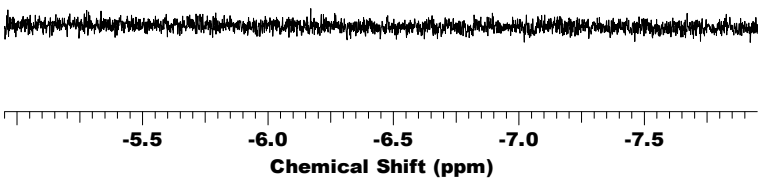



**Figure S4: Reaction of ligand 8 with RuHCl(CO)($PPh_3$)$_3$. $^1$H NMR (400 MHz, 298 K, toluene-d$^8$): no signals; indication of amide bond formation with elimination of $H_2$. Specifically detail of the hydride region.**

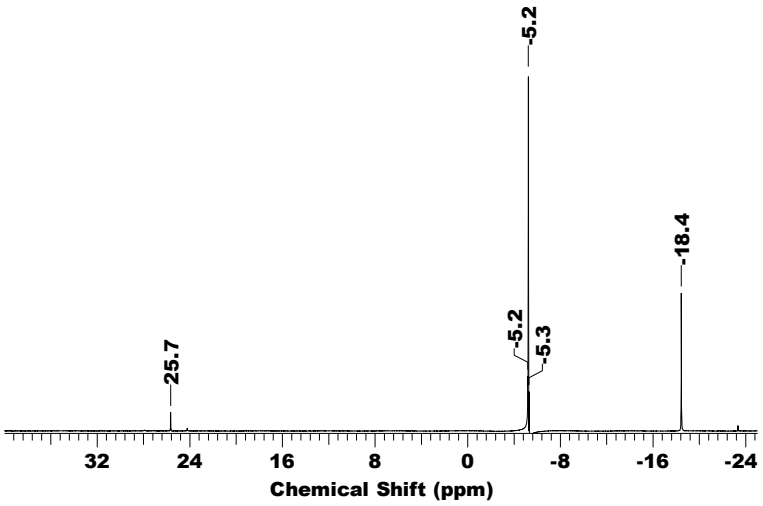
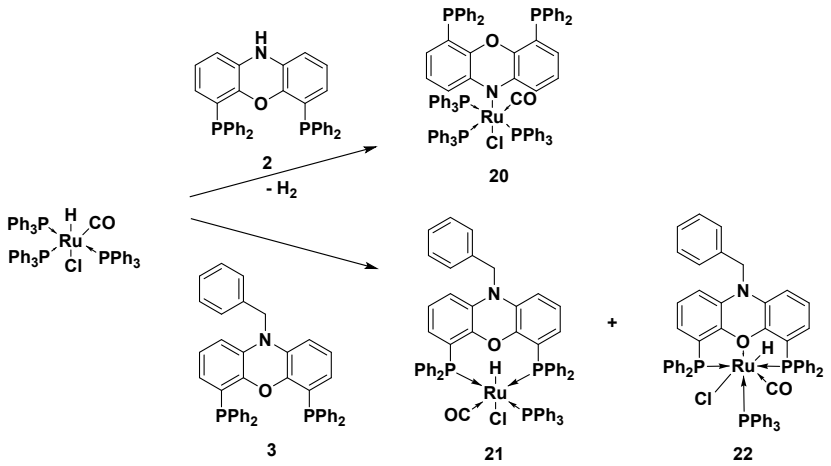



**Figure S5: Reaction of ligand 8 with $RuHCl(CO)(PPh_3)_3$. $^{31}P\{^1H\}$ NMR (162 MHz, 298 K, toluene-$d^8$): 25.7 ($PPh_3$, $RuHCl(CO)(PPh_3)_3$), -5 (free $PPh_3$)$_3$), -18.4 (free Nixantphos).**

The reactions that occur between the ligands **8** and **9** and the precursor are depicted in Scheme S1.




**Scheme S1: Coordination of Nixantphos (8) via N under liberation of $H_2$ and coordination of BnNixantphos (9) to $RuHCl(CO)(PPh_3)_3$.**

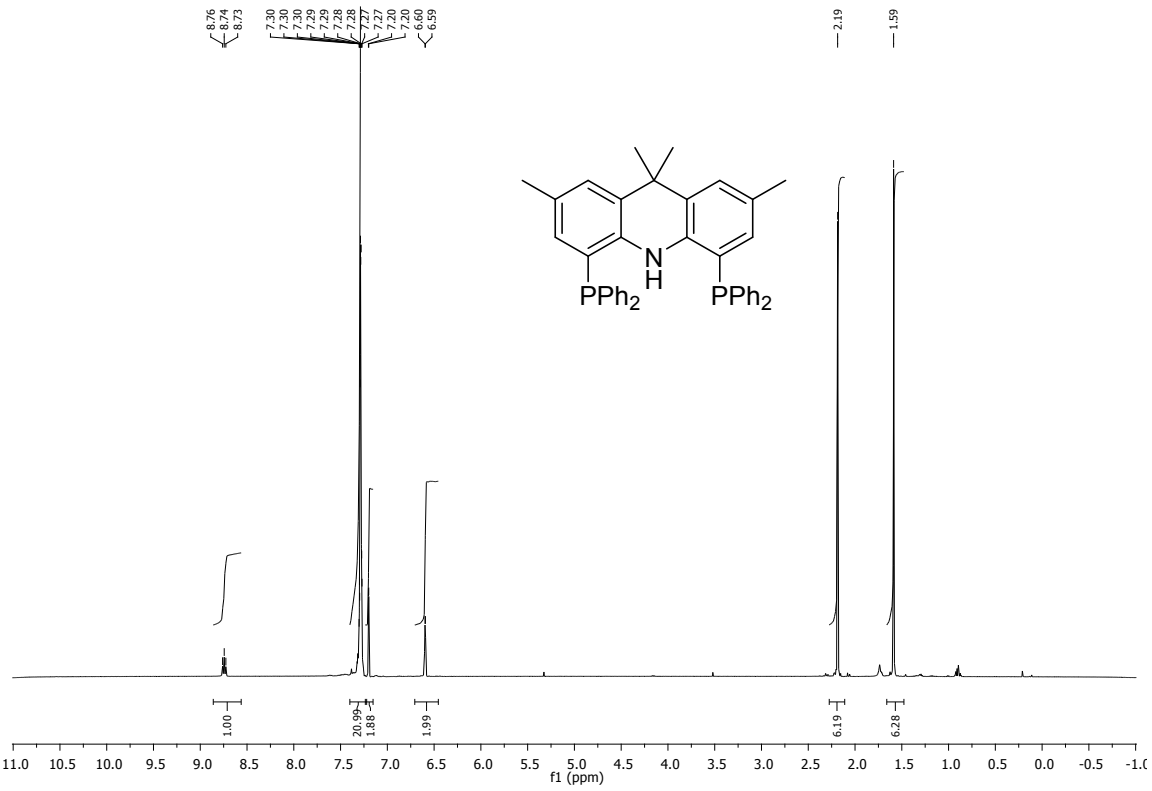



**Figure S6: $^{1}$H NMR (500 MHz, 298K, $CDCl_3$) spectrum of 4,5-Bis(diphenylphosphino)-3,6,9,9-tetramethyl-9,10-dihydroacridine (Acridanphos, 10)**

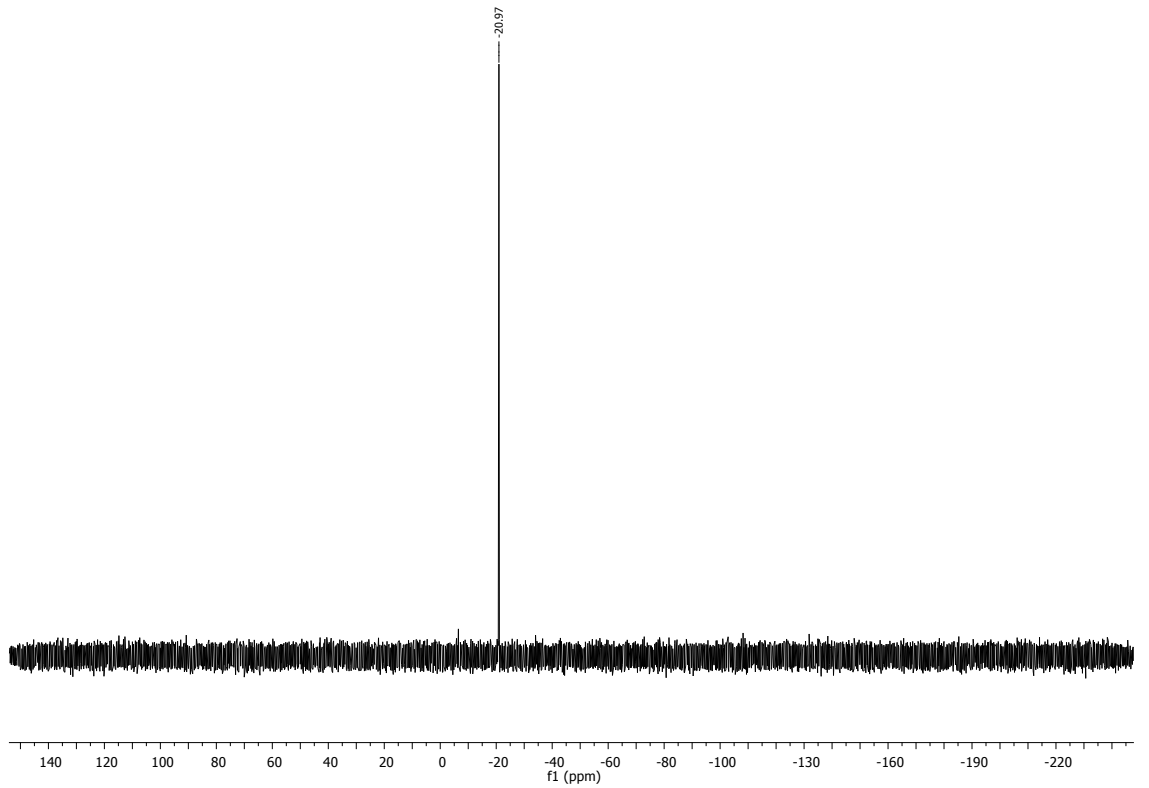



**Figure S7: $^{31}$P{$^{1}$H} NMR (202 MHz, 298K, $CDCl_3$) spectrum of 4,5-Bis(diphenylphosphino)-3,6,9,9-tetramethyl-9,10-dihydroacridine (Acridanphos, 10)**

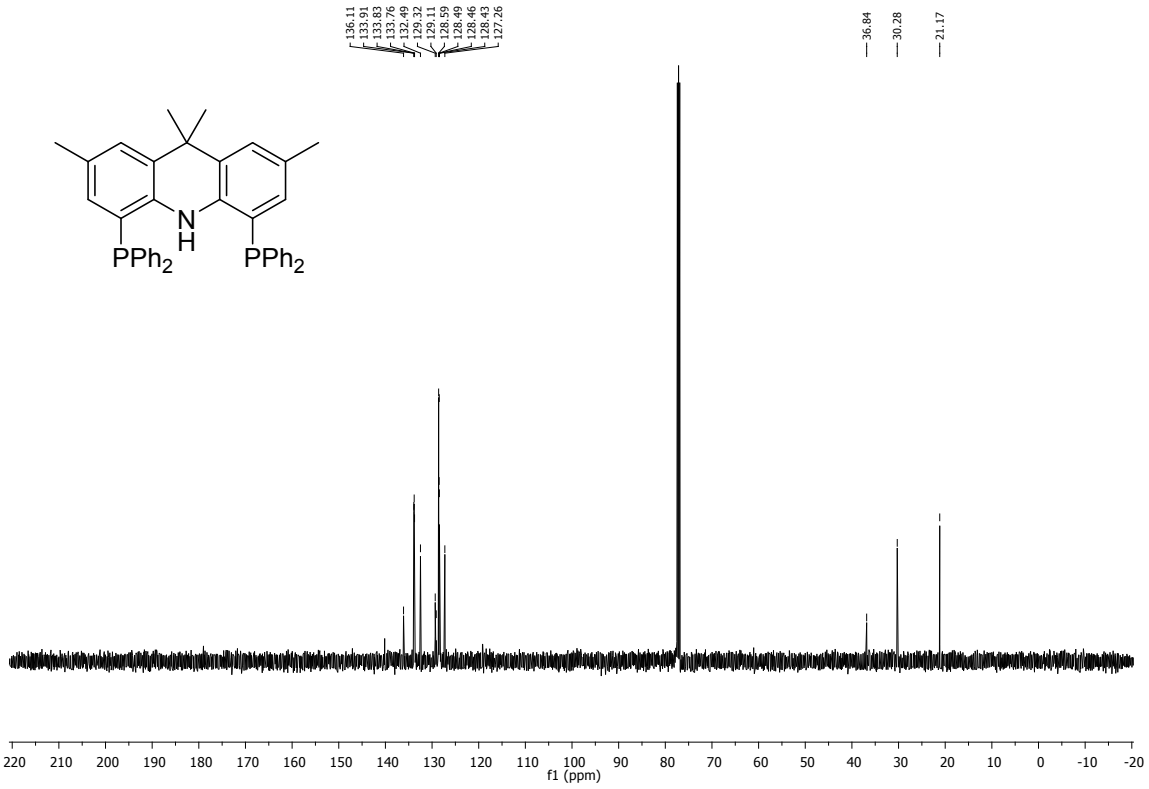



**Figure S8: $^{13}C$ NMR (126 MHz, 298K, $CDCl_3$) spectrum of 4,5-Bis(diphenylphosphino)-3,6,9,9-tetramethyl-9,10-dihydroacridine (Acridanphos, 10).**

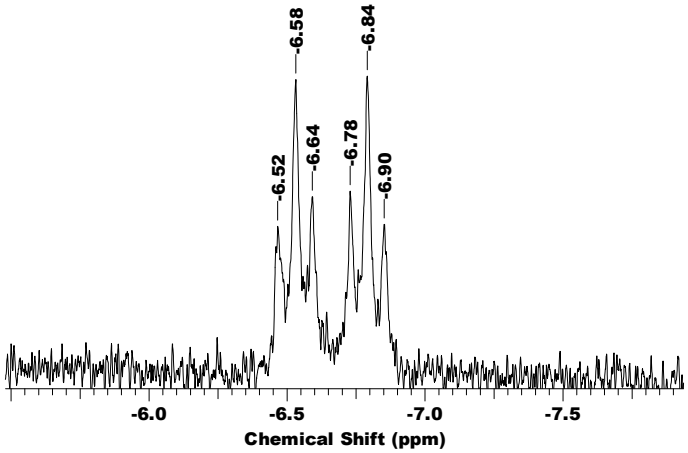



**Figure S9: Hydride region of $RuHCl(CO)(PPh_3)_3$/Acridanphos (10). $^1H$ NMR (400 MHz, 298K, toluene-$d^8$): -6.71 (dt, $^2J_{HP}$ = 103.6, 24.4).**

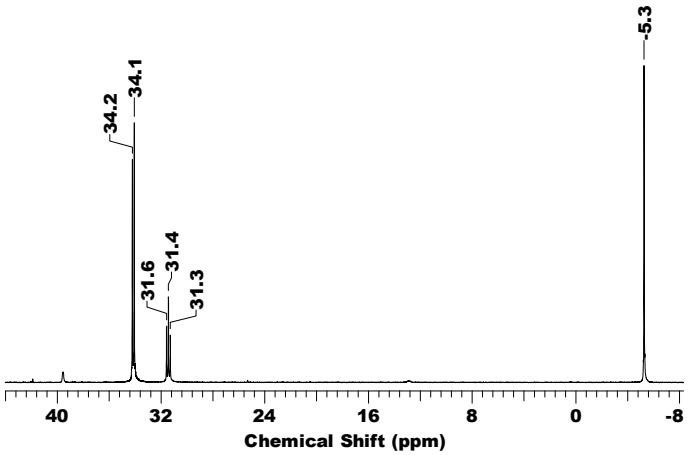



**Figure S10: $^{31}P\{^{1}H\}$ region of $RuHCl(CO)(PPh_3)_3$/Acridanphos (10). $^{31}P$ NMR (162 MHz, 298K, toluene-$d^8$): 34.1 (d, $^{2}J_{PP}$ = 23 Hz), 31.4 (t, $^{2}J_{PP}$ = 23 Hz).**

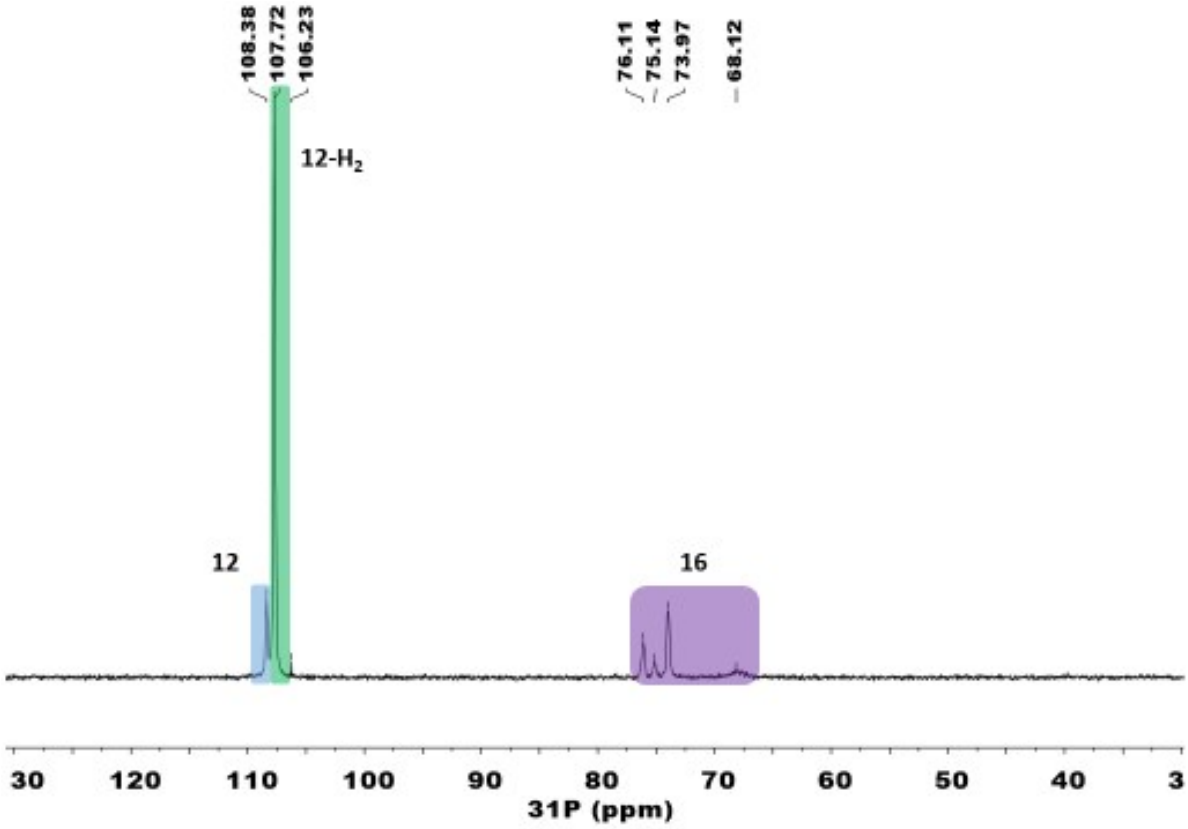



**Figure S11: $^{31}P$ NMR (300 MHz, 298K, toluene-$d^8$) spectrum. Reaction of complex 12 with cyclohexanone at 80°C for 2 hours forming complex 16.**

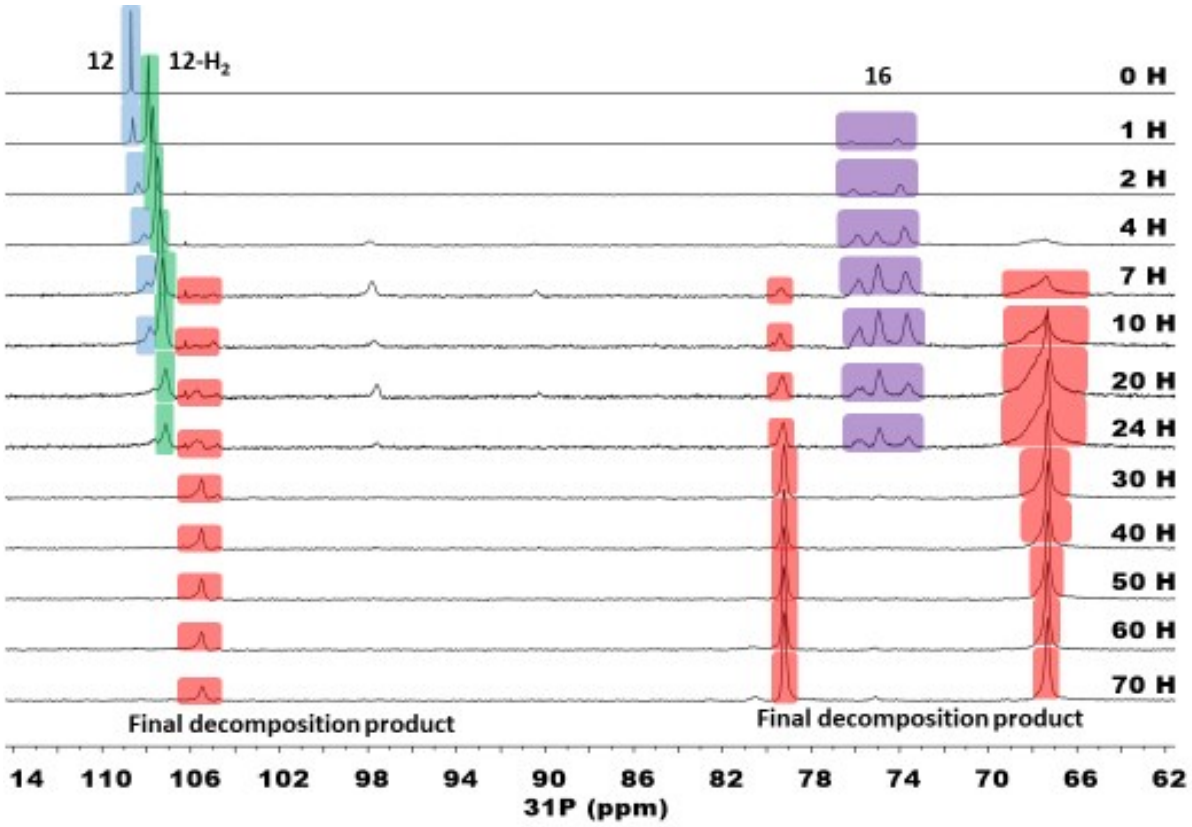



**Figure S12: $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298K, toluene-$d^{8}$) spectrum. Reaction of complex 12 with cyclohexanone at 80°C followed in time. Complex 16 is formed in the first few hours, after which it degrades further.**

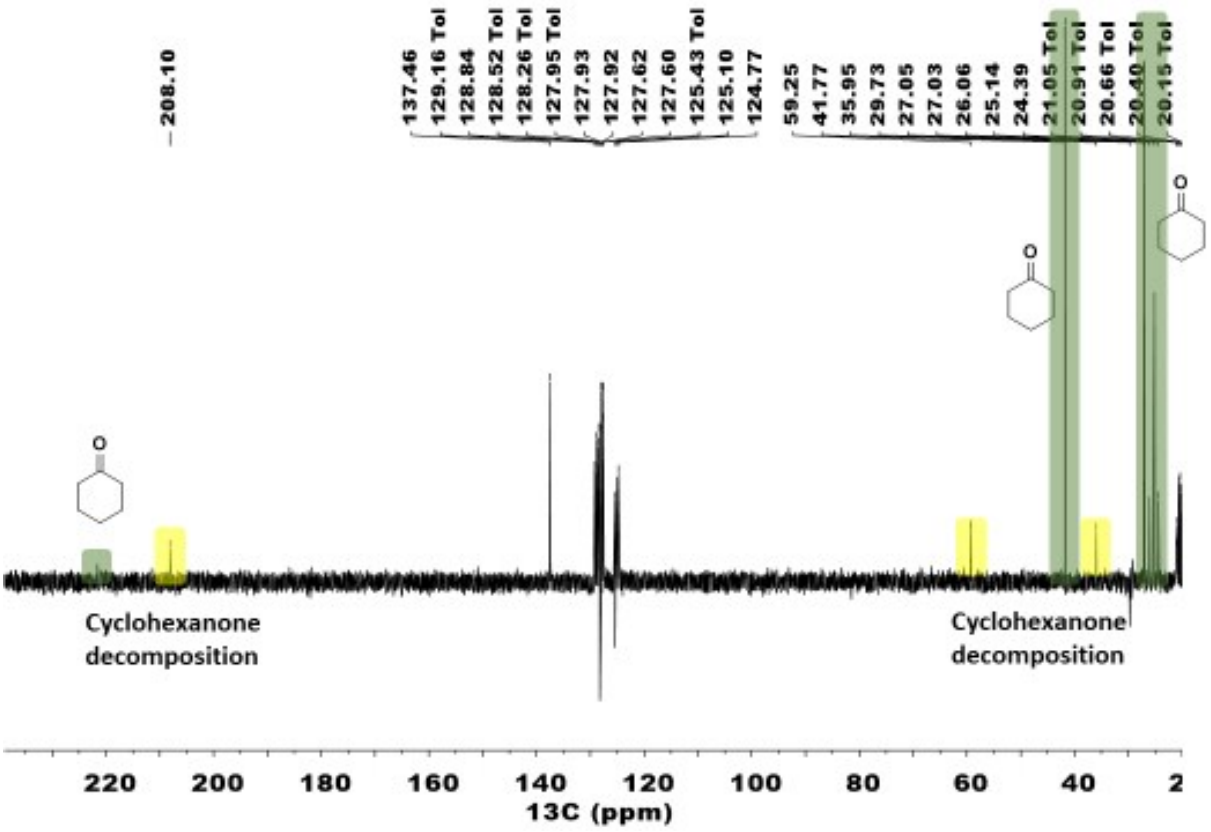



**Figure S13: $^{13}C$ NMR (75 MHz, 298K, toluene-$d^8$) spectrum. Reaction of complex 12 with cyclohexanone at 80°C for 2 hours forming complex 16. The CO signal is observed at 208 ppm, note that the CO of cyclohexanone has a shift of 211.8 ppm.**

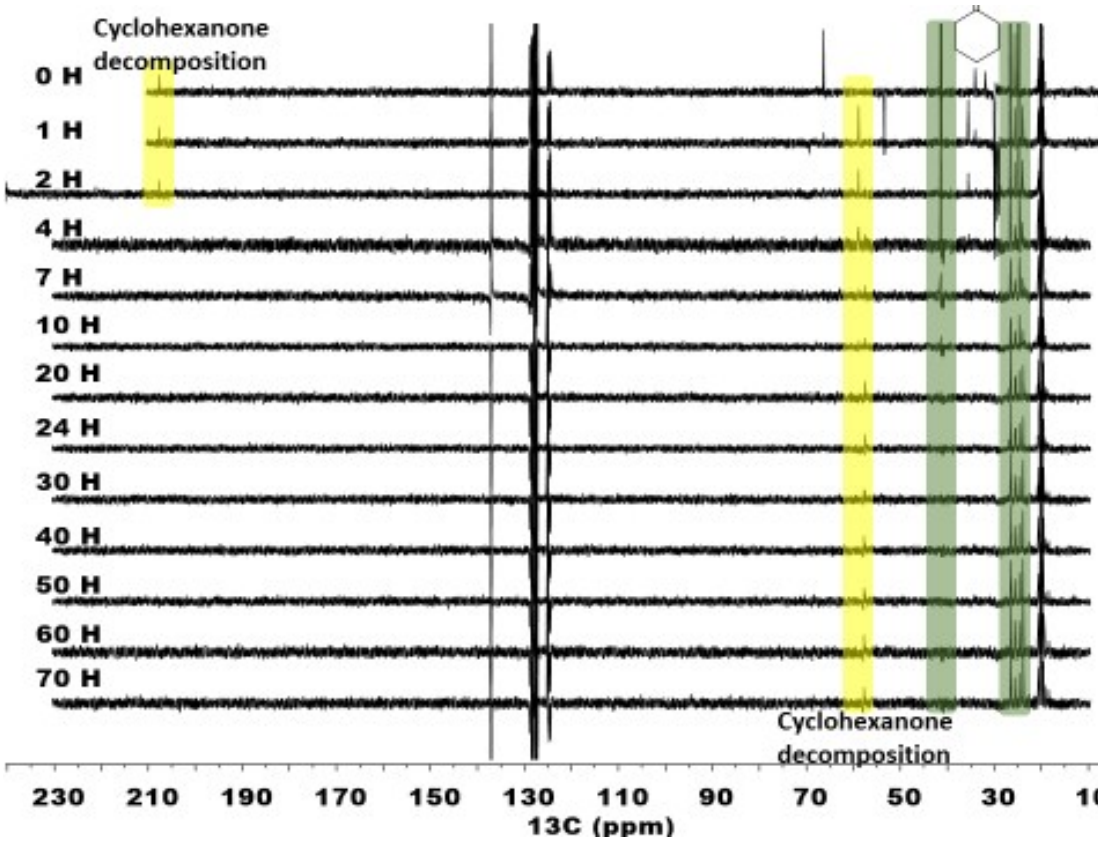



**Figure S14: $^{13}$C NMR (75 MHz, 298K, toluene-d$^8$) spectrum. Reaction of complex 12 with cyclohexanone at 80°C followed in time. Complex 16 is formed in the first few hours, after which it degrades further.**

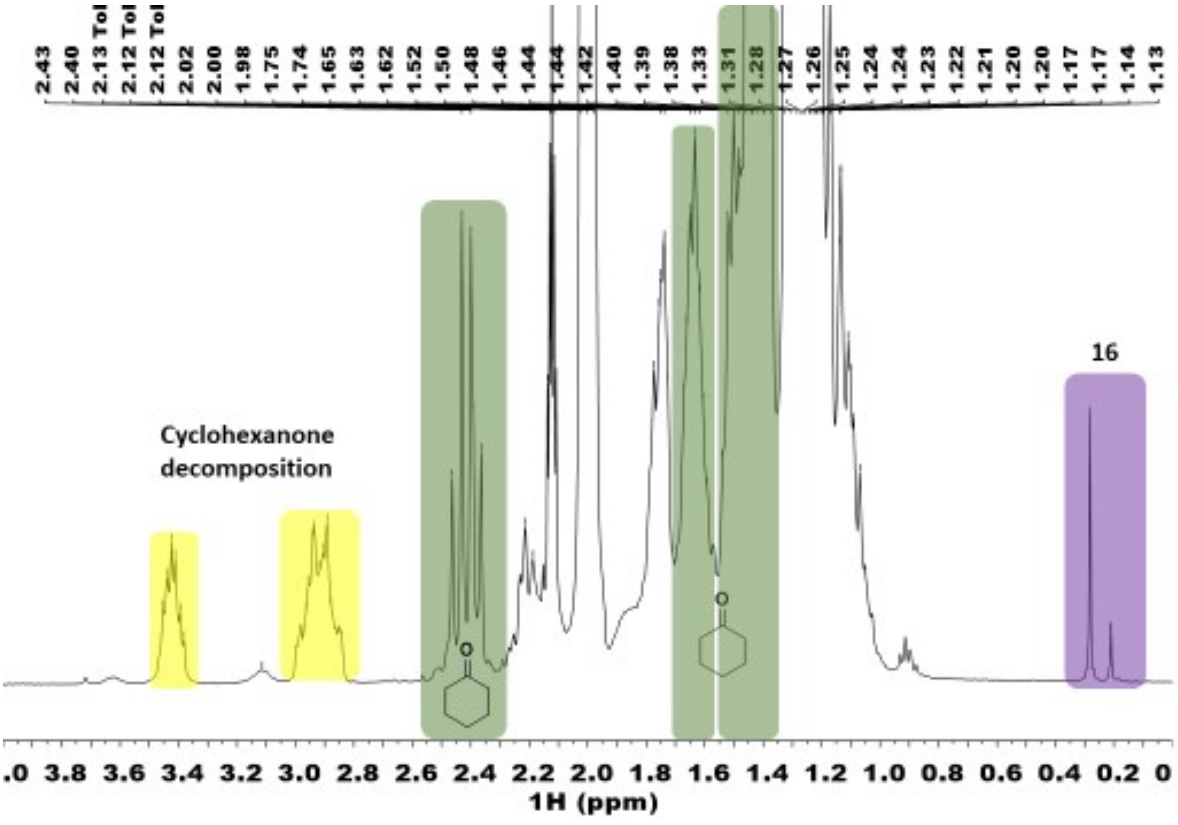



**Figure S15: $^{1}$H NMR (300 MHz, 298K, toluene-d$^8$) spectrum. Reaction of complex 12 with cyclohexanone at 80°C for 2 hours, resulting in the formation of complex 16. The signal around 0.3 ppm might indicate Ru-alkyl species.**

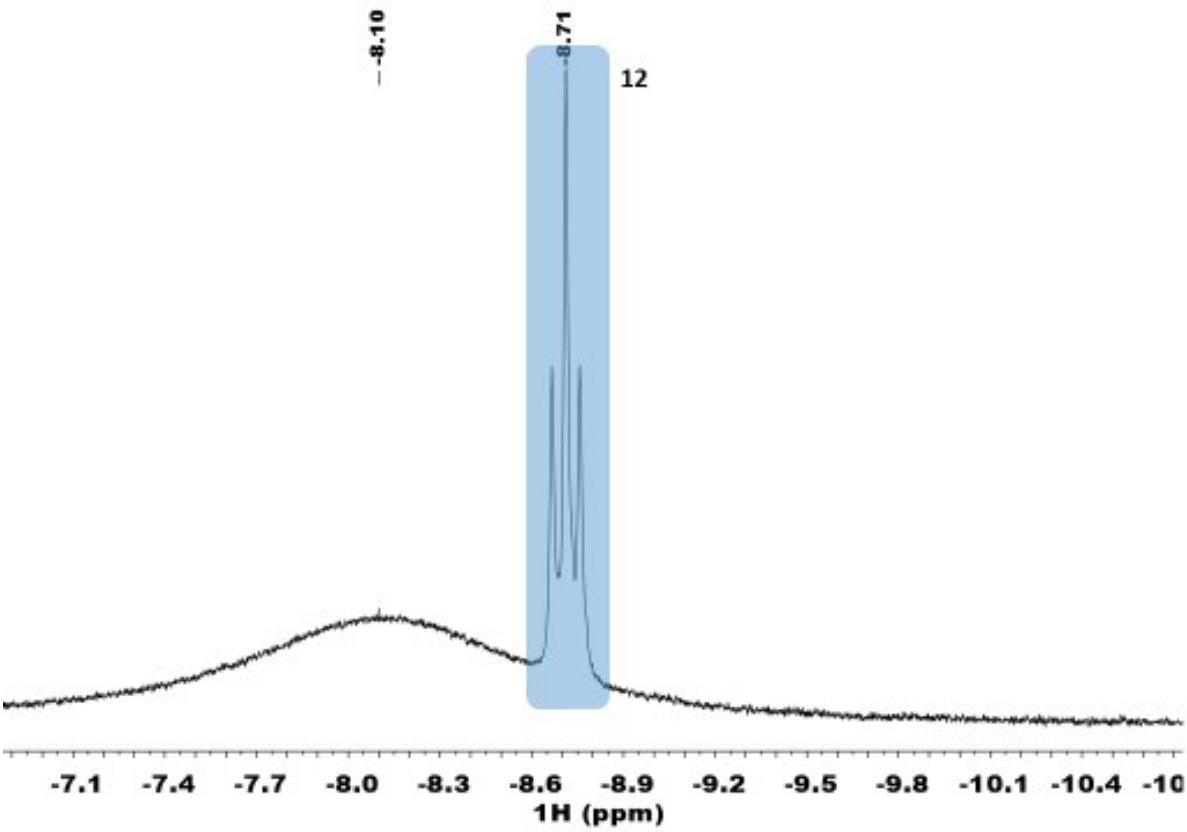



**Figure S16: $^{1}$H NMR (300 MHz, 298K, toluene-d$^{8}$) spectrum, hydride region. Reaction of complex 12 with cyclohexanone at 80°C for 2 hours, resulting in the formation of complex 16.**

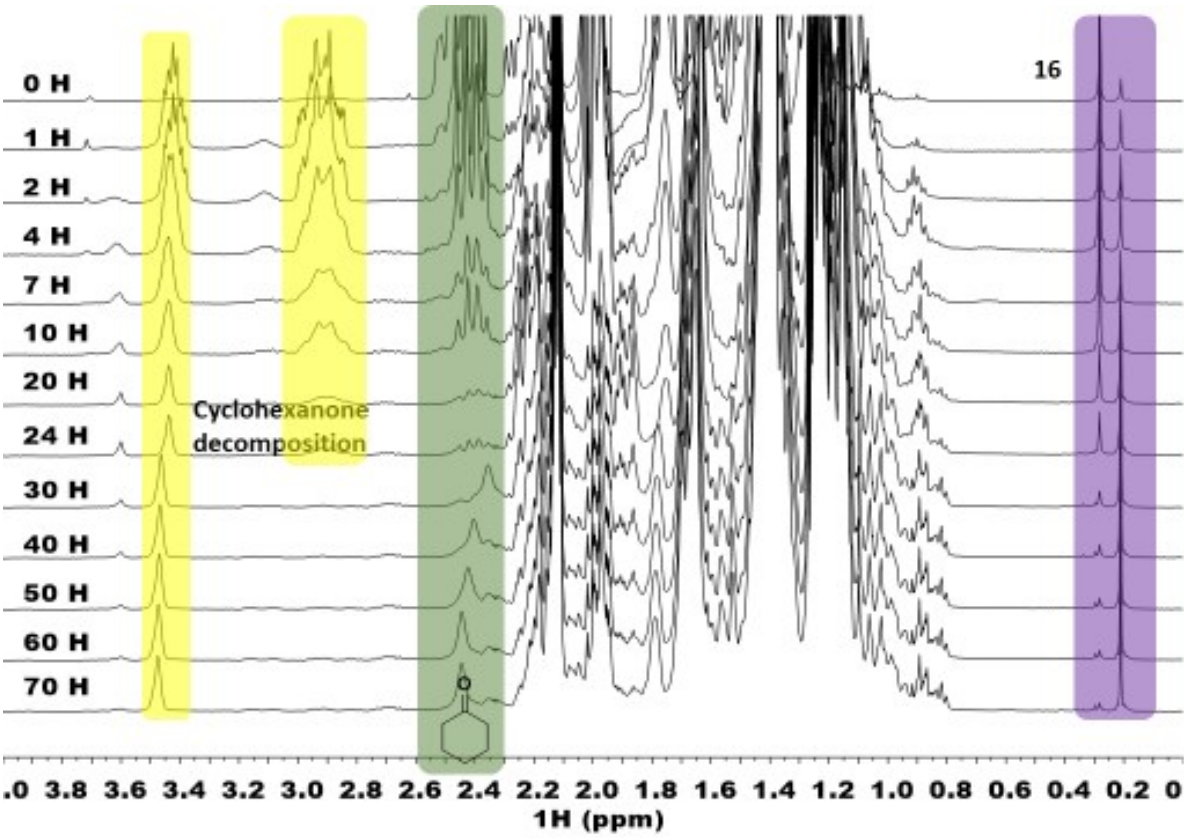



**Figure S17: $^{1}$H NMR (300 MHz, 298K, toluene-d$^{8}$) spectrum. Reaction of complex 12 with cyclohexanone at 80°C followed in time. Complex 16 is formed in the first few hours, after which it degrades further.**

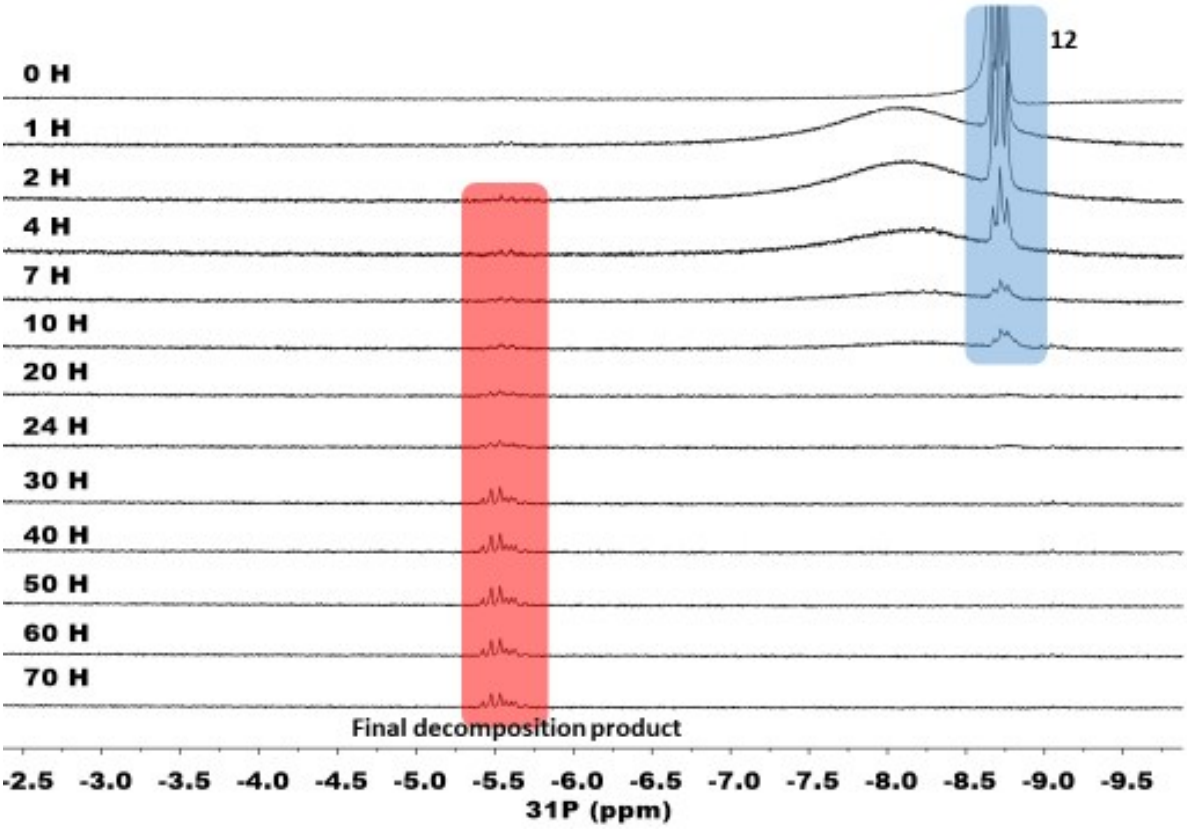



**Figure S18: $^{1}$H NMR (300 MHz, 298K, toluene-d$^{8}$) spectrum of the hydride region. Reaction of complex 12 with cyclohexanone at 80°C followed in time. Complex 16 is formed in the first few hours, after which it degrades further.**

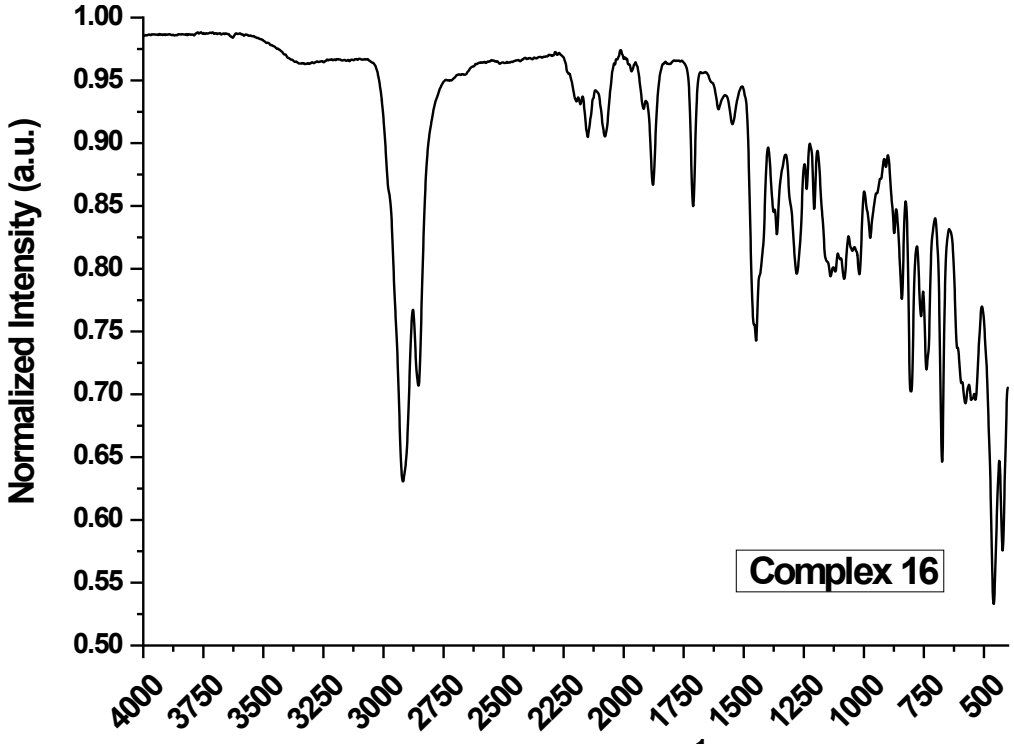



**Figure S19: IR spectrum of compound 16. A strong signal is observed at 1878 $cm^{-1}$. This is a typical region for a CO vibration. The signals between 2000 and 2200 $cm^{-1}$ also indicate a reaction, though it is not clear yet where these vibrations come from exactly. An increase of peaks in the 1000-1200 $cm^{-1}$ region might indicate formation of different M-$CH_n$ bonds. The actual M-C vibrations show up in the 450-600 $cm^{-1}$ region.[1]**

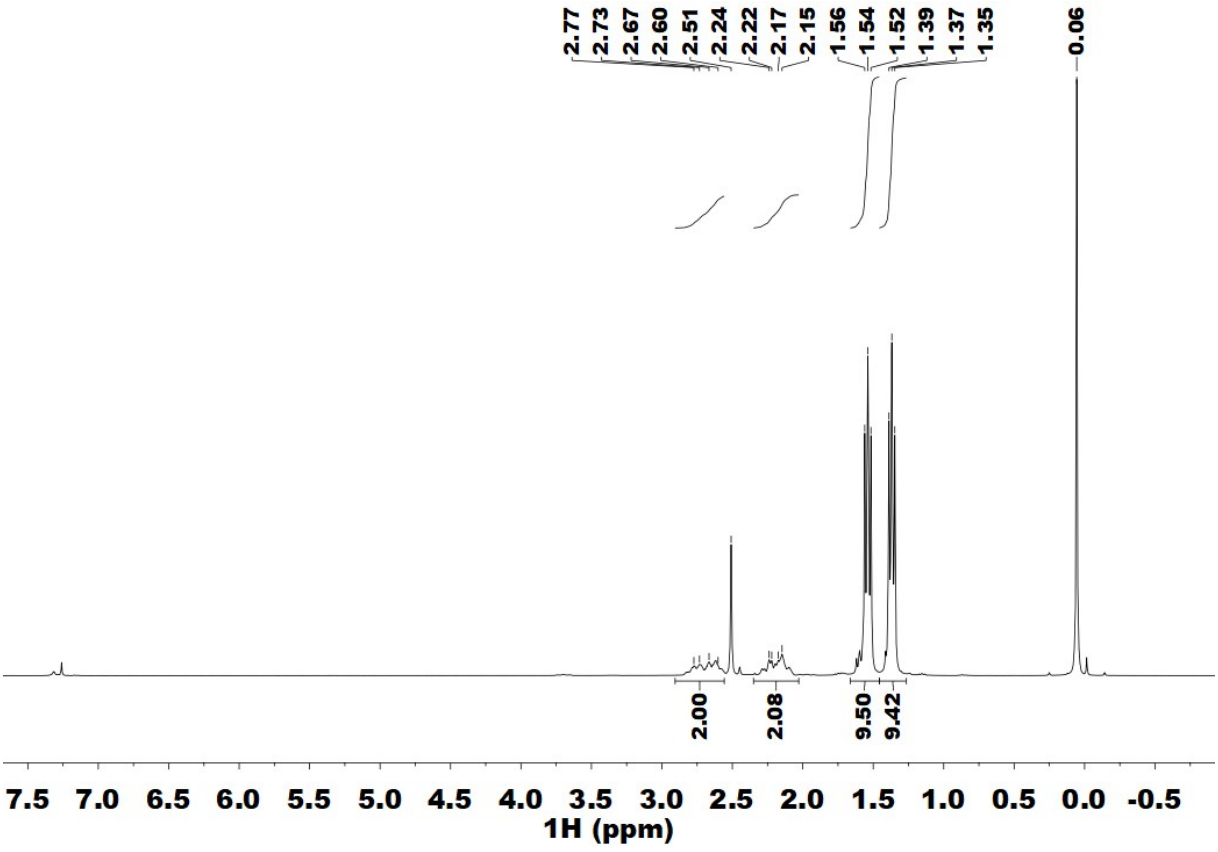



**Figure S20: $^1H$ NMR (300 MHz, 298K, $CDCl_3$) spectrum of complex 18.**

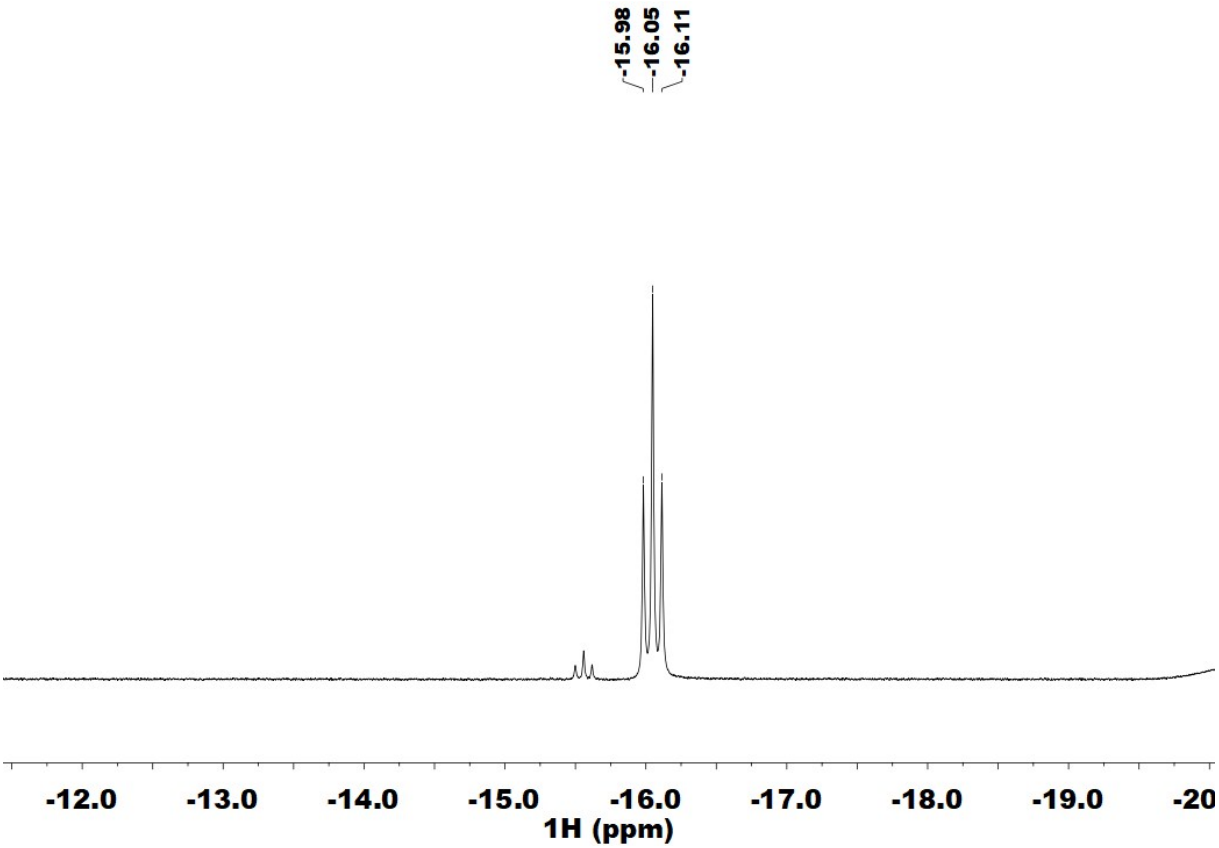



**Figure S21: $^{1}$H NMR (300 MHz, 298K, $CDCl_3$) spectrum of complex 18, hydride region.**

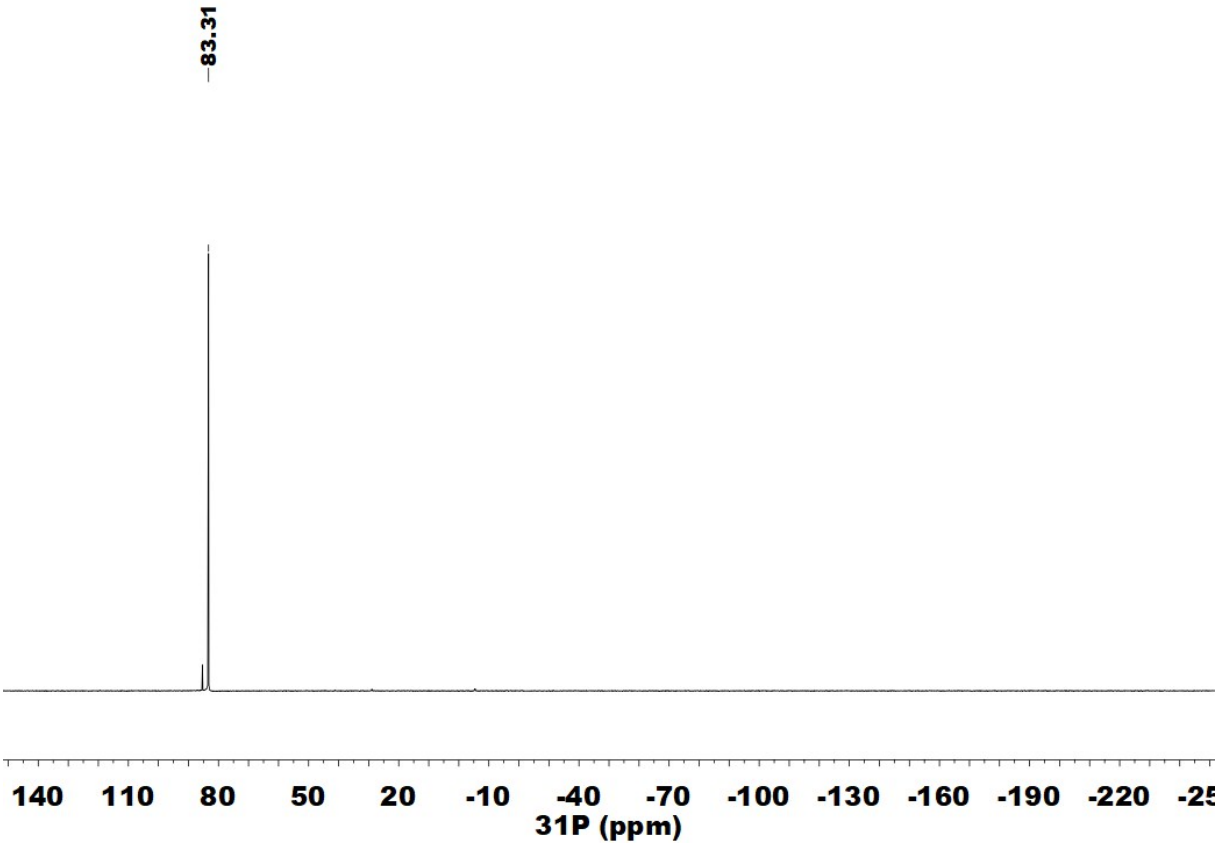



**Figure S22: $^{31}P\{^{1}H\}$ NMR (121 MHz, 298K, $CDCl_3$) spectrum of complex 18.**

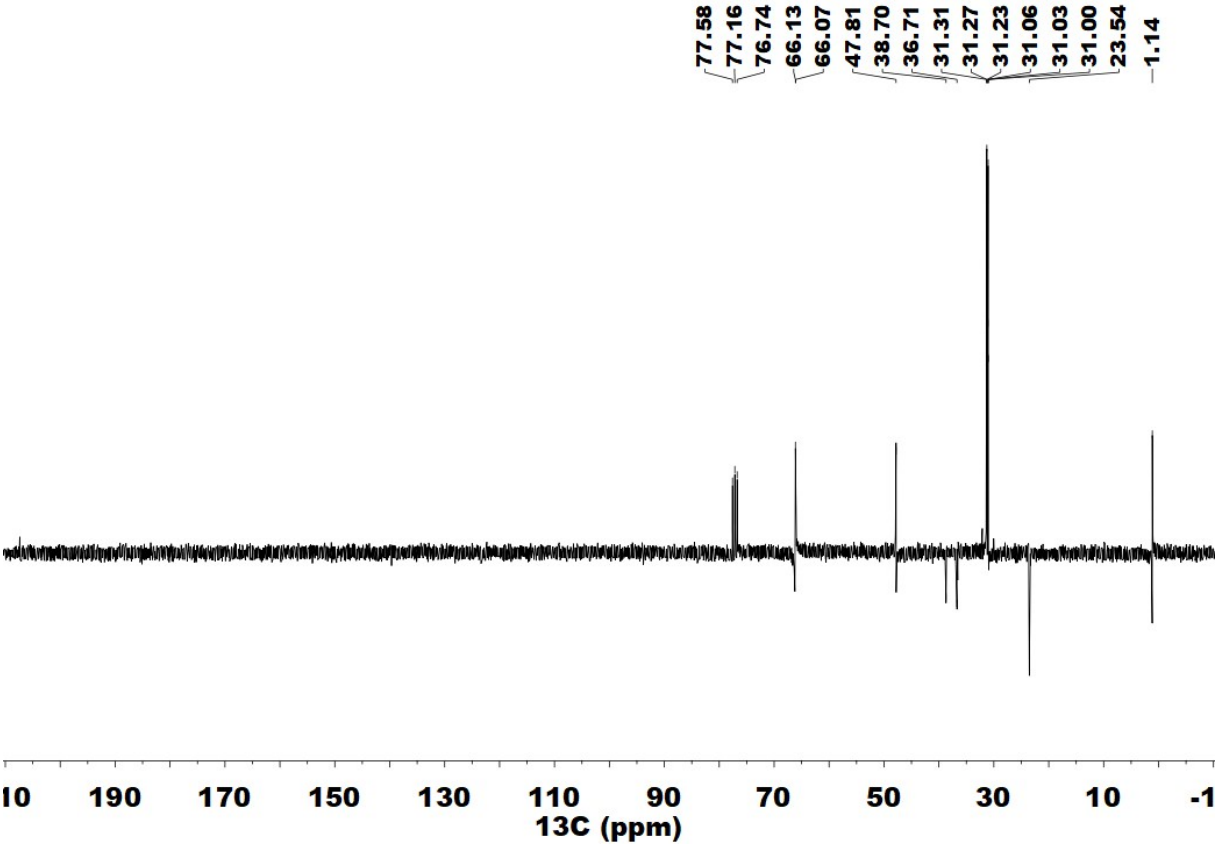



**Figure S23: $^{13}C_{apt}$ NMR (75 MHz, 298K, $CDCl_3$) spectrum of complex 18, CH and $CH_3$ groups are displayed as positive signals, C and $CH_2$ as negative signals.**

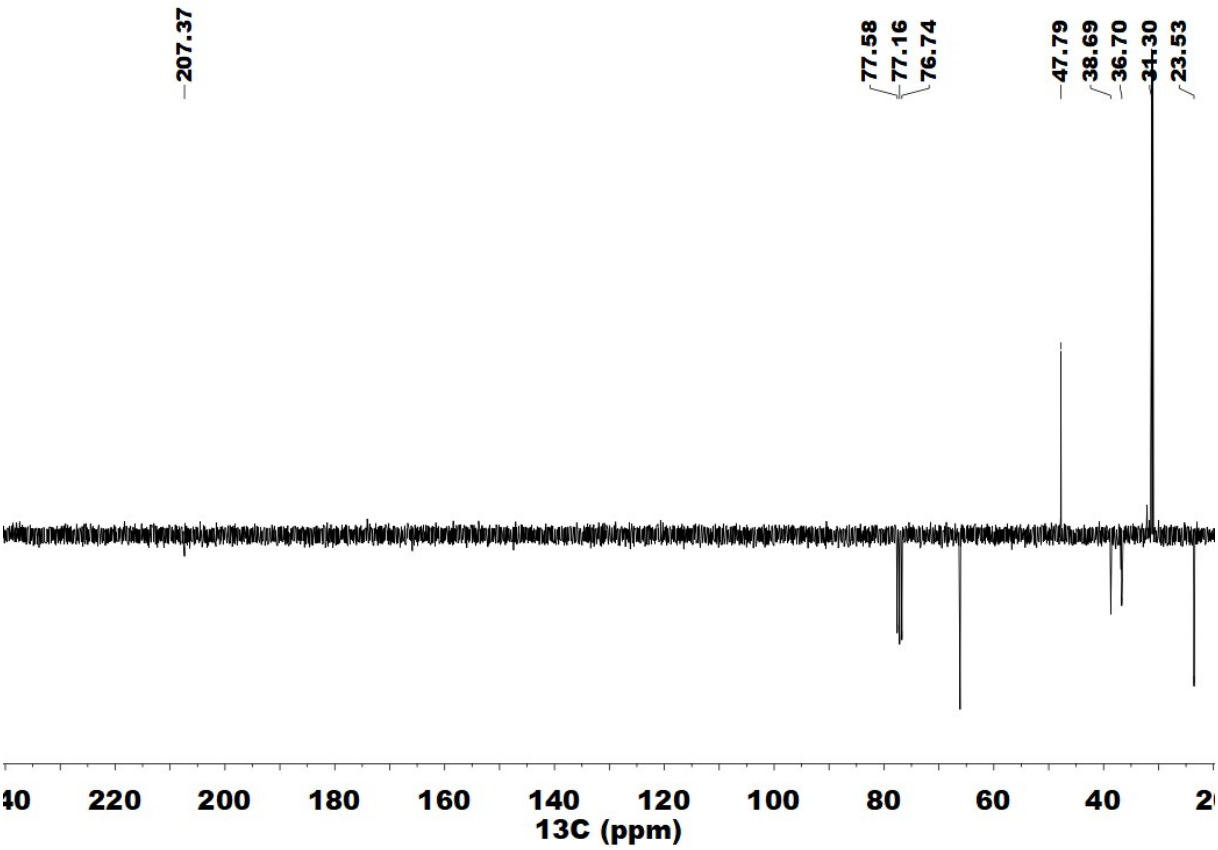



**Figure S24: $^{13}C_{apt}$ NMR (75 MHz, 298K, $CDCl_3$) spectrum of complex 18, range over 240 ppm, CH and $CH_3$ groups are displayed as negative signals, C and $CH_2$ as positive signals.**

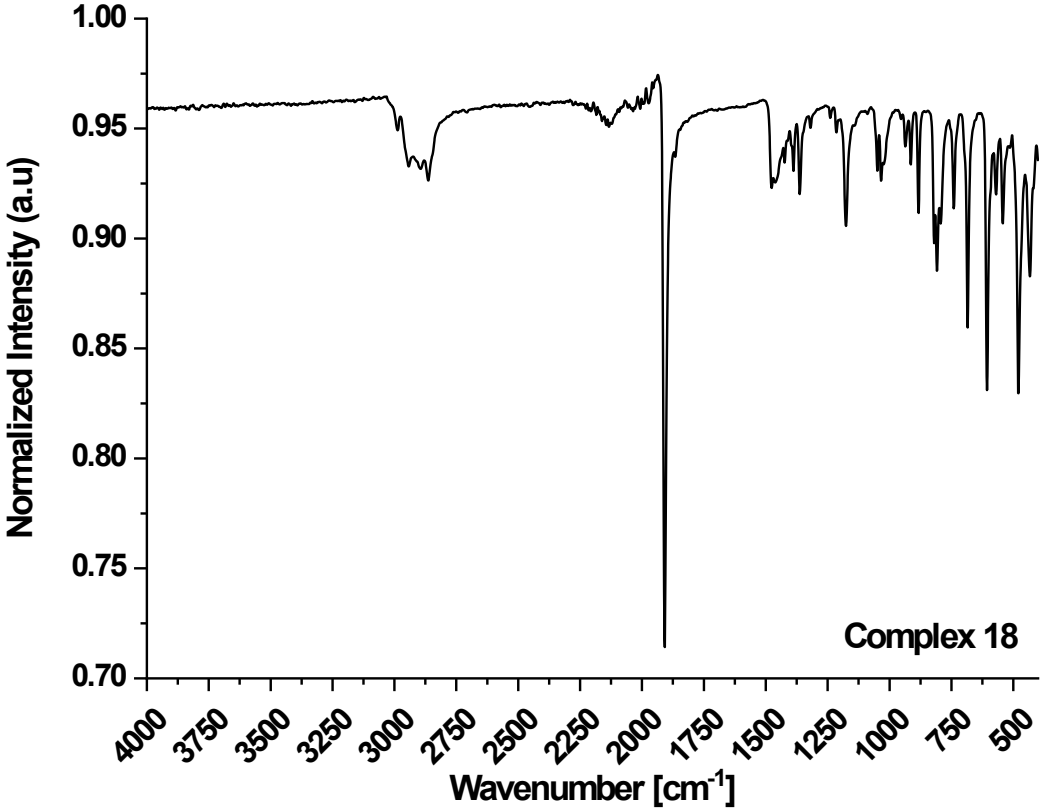



**Figure S25: IR spectrum of complex 18. The carbonyl signal is clearly seen at around 1900 $cm^{-1}$.**

## References

1 J. Chatt, R. G. Hayter, *J. Chem. Soc. (Resumed)* 1963, 6017-6027.