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Synthesis and catalytic activities of bimetallic Ru (II) arene complexes bearing bis-benzimidazoles

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Abstract

In this study, bis-benzimidazole ligands (**1a-d**) were synthesized using linker groups and they were evaluated as catalyst generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$ for transfer hydrogenation (TH) of acetophenone. The bimetallic Ru (II) arene complex (**2b**) synthesized from ligand **1b** which showed the best activity among the ligands in the catalytic TH reaction. The obtained ligands and **2b** complex were characterized by ^{1}H- and ^{13}C-NMR, elemental analysis and IR spectroscopy. The catalytic activities of complexes having different chain lengths and Y (CH_3 or H) groups were compared. The highest conversion (99%) was obtained with **2b**.

Keywords: Bis-benzimidazole; ruthenium; transfer hydrogenation.

1. Introduction

Benzimidazole is a heterocyclic aromatic organic compound consisting of fusion of benzene and imidazole. Transition metal complexes of benzimidazole ligands are frequently used because of their unique properties such as biological activity, high thermal stability and good catalytic performance (1-4).

The benzimidazole can be easily modified due to its pyrrole-type nitrogen. For example, they are alkylated with alkyl halides so as to give 1-alkylbenzimidazoles. Bis-benzimidazoles can also be synthesized when 1,4- and / or 1,6-dialkyl halides are used as linker groups (5-15). Reduction of carbonyl bonds by catalytic transfer hydrogenation using Ru (II) catalyst is of interest due to its simplicity and safety (16-19). Hydrogenation of substrates using a source of H_2 in combination with the catalyst is a highly economical and preferred method.

In this study, primarily a series of bis-benzimidazole ligands were synthesized (**1a-d**) and the catalytic performance of these obtained ligands $[RuCl_2(p\text{-cymene})]_2$ for transfer hydrogenation of acetophenone *in situ* conditions was investigated. The catalytic activity of the Ru (II) (**2b**) complex synthesized from the ligand (**1b**) showing the highest activity was compared with the in situ test results. The structures of the synthesized ligands and complexes were characterized using different spectroscopic techniques.

2. Materials and Methods

Reactions involving air-sensitive components were carried out under argon atmosphere conditions and standard Schlenk techniques of vacuum-line systems were employed during the experiments. For this reason, the glass containers used in the reaction were heated under vacuum, moisture and oxygen were removed and then filled with dry argon gas before the reaction. The solvents and reagents were dried before use and purified in an inert atmosphere.

^{1}H- (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded by Varian AS 400 NMR spectrometer, the chemical shift values (δ) of the compounds in ppm and the coupling constants (J) were given in Hertz. In NMR measurements, $CDCl_3$ and DMSO-d_6 were used as the solvents and TMS was used as the internal standard. ^{1}H NMR signal cleavages were abbreviated as s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet. FTIR measurements were taken in the Perkin Elmer Spectrum 100 spectrophotometer on the ATR unit in the range of 4000-400 cm^{-1}. Elemental analysis was recorded with Perkin Elmer 2400 element analyzer.

2.1. Synthesis and Characterization of Ligands (1a-d, 2a-d)

1a-d were synthesized by N-alkylation using 1,4- and/or 1,6-dialkylhalides in the alkaline solution (Figure 1).

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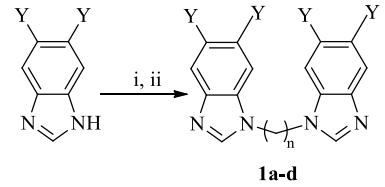
The obtained structures were characterized by elemental analysis, NMR and IR techniques. All spectra are consistent with the proposed structures.



1a: n = 4; Y = H
1b: n = 4; Y = CH_3
1c: n = 6; Y = H
1d: n = 6; Y = CH_3

1a-d

Reaction conditions: i) KOH (1 eq.), Acetone, 56ºC, 1 h.
ii) Alkyl halide (0.5 eq.), 6 h.

Figure 1. Synthesis of bis-benzimidazole ligands (**1a-d**).

2.2. General Procedure for the Synthesis of (1a-d)

Benzimidazole (236 mg; 2 mmol) or 5,6-dimethyl benzimidazole (292 mg; 2 mmol) in a Schlenk was dissolved in acetone in the presence of KOH (112 mg; 2 mmol) with heating under reflux for 1 hour. Subsequently, 1,4-dibromobutane (215 mg; 1 mmol) or 1,6-dichlorohexane (155 mg; 1 mmol) was added and refluxed for 6 hours. Then the solvent was removed in vacum, the residue was dissolved with dichloromethane (5 mL) and filtered. Diethyl ether (10 mL) was added to the solution. The crystals obtained were filtered and dried under vacuum.

2.2.1. 1,1'-butane-1,4-diylbis-1*H*-benzimidazole (1a)

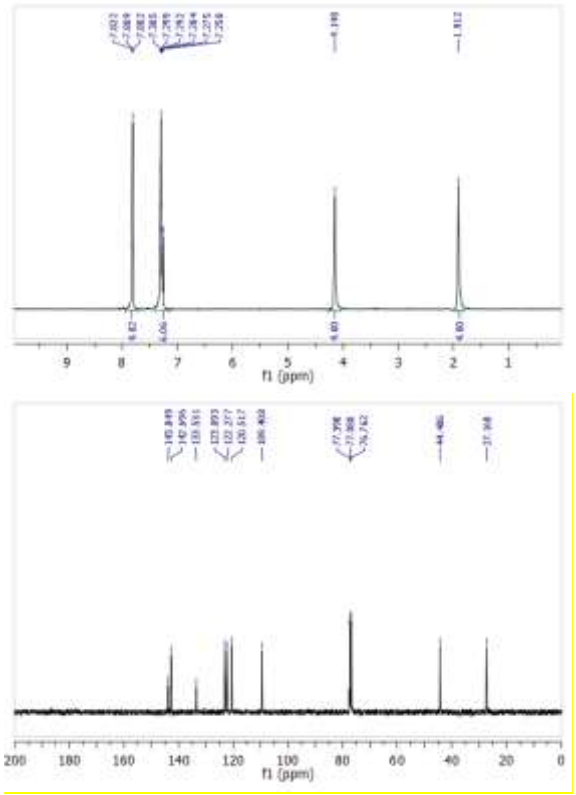


Figure 2. ^{1}H- and ^{13}C-NMR spectra of **1a**.

1a: Yield: 88%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): 1.91 (bs, 4H, NCH_2CH_2), 4.15 (bs, 4H, NCH_2), 7.26-7.31 (m, 2H, NC*H*N, 4H, Benz-*H*) 7.80-7.82 (m, 4H, Benz-*H*). ^{13}C-NMR (100 MHz, $CDCl_3$, TMS, 25 °C, ppm): 27.2, 44.6, 109.4, 120.5, 122.2, 123.0, 133.5, 142.7, 143.8. Elemental analysis: calcd (%) for $C_{18}H_{18}N_4$ (290,36) C 74.46; H 6.25; N 19.30. Found (%): C 74.51; H 6.18; N 19.26. IR (KBr; cm^{-1}): 1493 ($\nu_{C=N}$).

2.2.2. 1,1'-butane-1,4-diylbis(5,6-dimethyl-1H-benzimidazole) (1b)

1b: Yield: 86%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): 1.85 (bs, 4H, NCH_2CH_2), 2.37 (s, 12H, 4xCH_3), 4.08 (bs, 4H, NCH_2), 7.05 (s, 2H, Benz-*H*), 7.55 (s, 2H, NC*H*N), 7.68 (s, 2H, Benz-*H*). ^{13}C-NMR (100 MHz, $CDCl_3$, TMS, 25 °C, ppm): 20.2, 20.5, 27.0, 44.4, 109.6, 120.5, 131.1, 132.0, 132.2, 141.9, 142.5. Elemental analysis: calcd (%) for $C_{22}H_{26}N_4$ (346): C, 76.27; H, 7.56; N, 16.17. Found (%): C, 76.07; H, 7.76; N, 16.09. IR (KBr; cm^{-1}): 1495 ($\nu_{C=N}$).

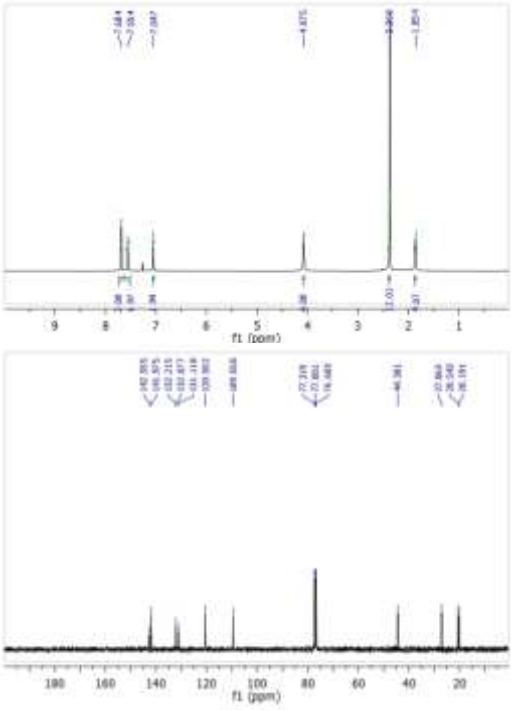


Figure 3. ^{1}H- and ^{13}C-NMR spectra of **1b**.

2.2.3. 1,1'-hexane-1,6-diylbis-1H-benzimidazole (1c)

1c: Yield: 85%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): 1,31-1.34 (m, 4H, $NCH_2CH_2CH_2$), 1.83-1.86 (bs, 4H, NCH_2CH_2), 4.12 (t, 4H, *J*= 7.0 Hz, NCH_2), 7.26-7.35 (m, 2H, NC*H*N, 4H, Benz-*H*), 7.79-7.82 (m, 4H, Benz-*H*). ^{13}C-NMR (100 MHz, $CDCl_3$, TMS, 25 °C, ppm): 26.3, 29.5, 44.8, 109.5, 120.4, 122.0, 122.8, 133.7, 142.8, 143.9. Elemental analysis: calcd (%) for $C_{20}H_{22}N_4$ (318.42): C, 75.44; H, 6.96; N, 17.60. Found (%): C, 75.49; H, 6.92; N, 17.66. IR (KBr; cm^{-1}): 1496 ($\nu_{C=N}$).

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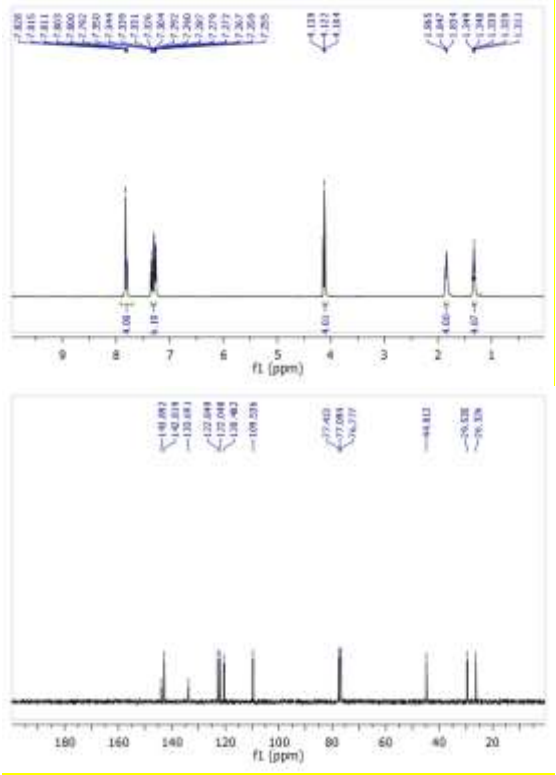

Figure 4. ^{1}H- and ^{13}C-NMR spectra of **1c**.

2.2.4. 1,1'-hexane-1,6-diylbis(5,6-dimethyl-1H-benzimidazole) (1d)

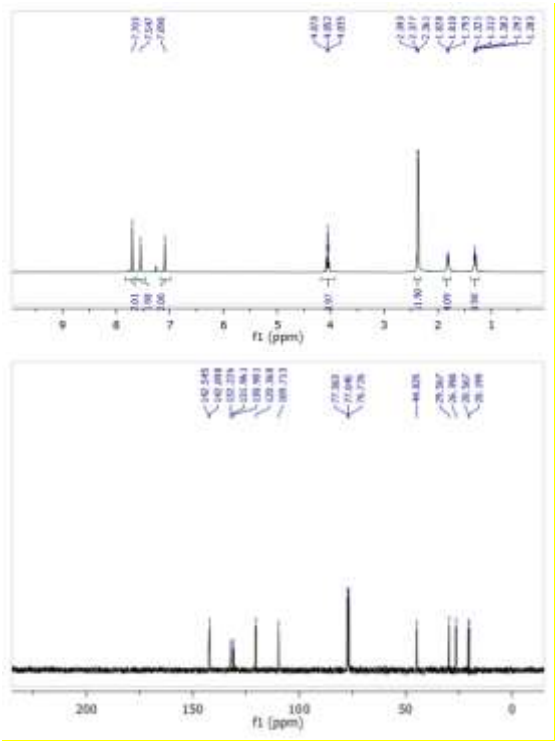

Figure 5. ^{1}H- and ^{13}C-NMR spectra of **1d**.

1d: Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): 1,28-1.32 (m, 4H, $NCH_2CH_2CH_2$), 1.79-1.82 (bs, 4H, NCH_2CH_2), 2.36 (s, 6H, 2xCH_3), 2.39 (s, 6H, 2xCH_3), 4.05 (t, 4H, *J*= 7.0 Hz, NCH_2), 7.09 (s, 2H, Benz-*H*), 7.55 (s, 2H, NC*H*N), 7.70 (s, 2H, Benz-*H*). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C, ppm): 20.2, 20.6, 26.4, 29.6, 44.8, 109.7, 120.4, 130.9, 131.9, 132.2, 142.0, 142.5. Elemental analysis: calcd (%) for $C_{24}H_{30}N_4$ (374.52): C 76.97; H 8.07; N 14.96. Found (%): C 76.91; H 8.13; N 14.91. IR (KBr; cm^{-1}): 1502 ($\nu_{C=N}$).

2.2.5. 1,1'-butane-1,4-diylbis(3-{(dichloro)(p-cymene)ruthenium}-5,6-dimethyl-benzimidazole) (2b)

1b (0.2 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.2 mmol) in dry dichloromethane (5 mL) were stirred at room temperature for 24 hours under Argon in a Schlenk. The solution was reduced in vacuo to a volume of 1 mL and precipitated with diethyl ether to give a solid. The dark yellow precipitate was filtered off and dried in vacuum.

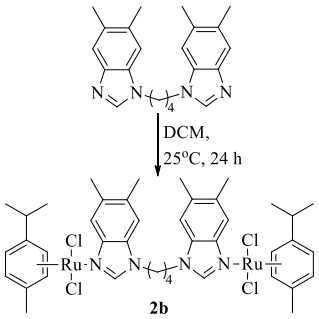

Figure 6. Synthesis of complex **2b.**

As the obtained complex did not have sufficient solubility in chloroform, NMR data of both **2b** complex and **1b** ligand were recorded using DMSO-d_6.

2b: Yield: %78. ^{1}H-NMR (400 MHz, DMSO-d_6, TMS, 25 °C, ppm): TMS, 25 °C, ppm): 1.17 (d, 12H, *J*=6.4 Hz, p-cymene- 4xCH_3), 1.90 (bs, 4H, NCH_2CH_2), 2.07 (s, 6H, p-cymene- 2xCH_3), 2.36 (s, 12H, 4xCH_3), 2.77-2.85 (m, 2H, p-cymene- 2xC*H*), 4.46 (bs, 4H, NCH_2), 5.77 (dd, 8H, J_1=17.2, J_2=6.4 Hz, p-cymene- Ar-*H*), 7.58 (s, 2H, Benz-*H*), 7.72 (s, 2H, Benz-*H*), 9.49 (s, 2H, NC*H*N). ^{13}C-NMR (100 MHz, DMSO-d_6, TMS, 25 °C, ppm): 18.3, 20.3, 20.5, 25.8, 30.4, 46.1, 86.0, 86.8, 100.5, 106.8, 113.0, 115.0, 129.9, 130.4, 135.7, 136.0, 140.8. Elemental analysis: calcd (%) for $C_{42}H_{54}Cl_4N_4Ru_2$ (958.86) Calcd (%): C 52.61; H 5.68; N 5.84. Found (%): C 52.47; H 5.81; N 5.86. IR (KBr; cm^{-1}): 1512 ($\nu_{C=N}$).

1b: ^{1}H-NMR (400 MHz, DMSO-d_6, TMS, 25 °C, ppm): 1.71 (bs, 4H, NCH_2CH_2), 2.26 (s, 12H, 4xCH_3), 4.17 (bs, 4H, NCH_2), 7.27 (s, 2H, Benz-*H*), 7.37 (s, 2H,

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Benz-*H*), 8.02 (s, 2H, NC*H*N). ^{13}C NMR (100 MHz, DMSO-d_6, TMS, 25 °C, ppm): 20.3, 20.5, 27.1, 43.9, 110.7, 119.9, 130.2, 131.3, 132.7, 142.5, 143.5.

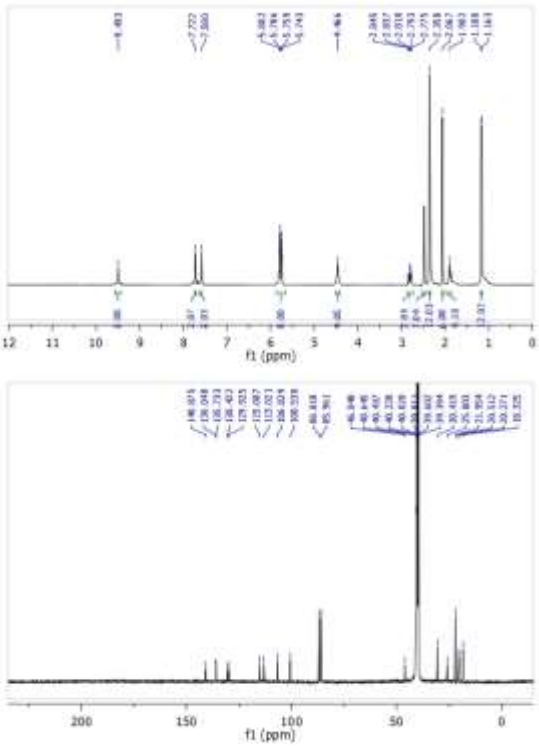

Figure 7. ^{1}H- and ^{13}C-NMR spectra of **2b**.

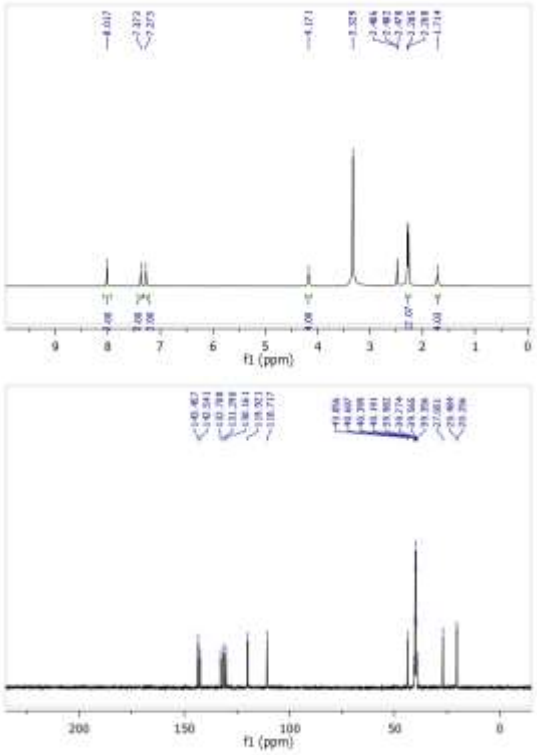

Figure 8. ^{1}H- and ^{13}C-NMR spectra of **1b** in DMSO-d_6.

2.2.6. General Procedure of Transfer Hydrogenation (TH) Reactions

A mixture of acetophenone (1 mmol), catalyst ($5x10^{-3}$ mmol, 1 mol%), propan-2-ol (2 mL) and KOH (0.2 mmol) in a two-necked flask was mixed for 1 hour at 82 °C. at reflux temperature. At the desired reaction times, the fractions were withdrawn from the reaction vessel. Yields were determined by ^{1}H-NMR.

3. Results and Discussion

Bis-benzimidazole ligands (**1a-d**) were obtained in high yields (81-88%) by reacting benzimidazole or 5,6-dimethylbenzimidazole with dialkyl halides in acetone at 56 °C for 6 hours. In the ^{1}H-NMR spectrum of these ligands, characteristic singlet peaks of N=CH-N group were observed in the range of δ = 7.28-7.55 ppm. In IR spectra, C = N vibrations signal in the range of 1493-1502 cm^{-1}. The spectroscopic values of the synthesized ligands were consistent with the proposed structures. Some spectroscopic data of complex **2b** and ligand **1b** are given in Table 1.

Table 1. Spectroscopic data of **1b** and **2b**.

	N=C*H*-N (ppm)	IR ($\nu_{C=N}$) (cm^{-1})
1b	8.02	1495
2b	9.49	1512

The catalytic performances of the catalysts formed by the interaction of the obtained ligands (**1a-d**) in the presence of $[RuCl_2(p\text{-cymene})]_2$ in the transfer hydrogenation reaction of acetophenone were investigated. Since the optimum conditions the reaction temperature as 82 °C and the use of KOH as the base were determined in our previous studies [4], therefore in this study same conditions were employed. The obtained results are summarized in Table 2.

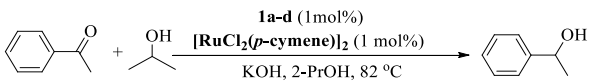

Table 2. Optimization table for TH of acetophenone[a].

Entry	Catalyst	Ligand	Yield (%)
1	$[RuCl_2(p\text{-cymene})]_2$	**1a**	50
2	$[RuCl_2(p\text{-cymene})]_2$	**1b**	**76**
3	$[RuCl_2(p\text{-cymene})]_2$	**1c**	45
4	$[RuCl_2(p\text{-cymene})]_2$	**1d**	59
5	$[RuCl_2(p\text{-cymene})]_2$	-	29
6	-	**1b**	9
7	-	-	7

[a] Reaction conditions: KOH (0.2 mmol), 1h, Ketone (1 mmol), 2-PrOH (2 mL).

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In the study, the best result was obtained with ligand **1b** (Table 2, entry 2). In the case where only [$RuCl_2$(*p*-cymene)]$_2$ was used as catalyst (Table 2, entry 5), a conversion of 29% was achieved, whereas ligand **1b** was used only without [$RuCl_2$(*p*-cymene)]$_2$ (Table 2, entry 6) a conversion of 9% was achieved. The preferred KOH as the base showed a 7% conversion after 1 hour (Table 2, entry 7). In view of these results, Ru (II) arene complex (**2b**) was synthesized in the next step using ligand **1b** and the activity of the aromatic ketones in which the complex of **1b** ligand as in situ **2b** as the catalyst in the same reaction conditions was compared by means of the transfer hydrogenation reaction activities (Table 3).

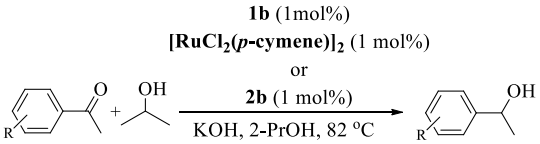

Table 3. Comparison table of TH reaction.

Entry	Ketone	Product	Yield (%)
1	**3a**	**3aa**	**in situ:** 76 **2b**: 93
2	**3b**	**3ba**	**in situ:** 88 **2b**: >99
3	**3c**	**3ca**	**in situ:** 83 **2b**: >99
4	**3d**	**3da**	**in situ:** 67 **2b**: 84
5	**3e**	**3ea**	**in situ:** 60 **2b**: 78

4. Conclusion

In this study, the catalytic properties of the synthesized bis-benzimidazole ligands (**1a-d**) and **2b** complex in the transfer hydrogenation reaction of acetophenone were investigated. In the in situ study, the highest results were obtained when **1b** was used with 76% yield in 1 hour. The bimetallic **2b** complex synthesized using this ligand yielded 93% yield under the same reaction conditions. The results were compared in cases where the **1b** ligand in situ and **2b** complex were used as catalysts in the transfer hydrogenation reaction using different ketones. Catalytic activity varies depending on the groups in the phenyl ring of acetophenone. In the presence of electron attractive groups it exhibited an increment. The best result was obtained using 4-chloro and 4-bromo acetophenone for a 1 hour reaction time, and when **2b** was used as a catalyst, a yield of 99% was achieved.

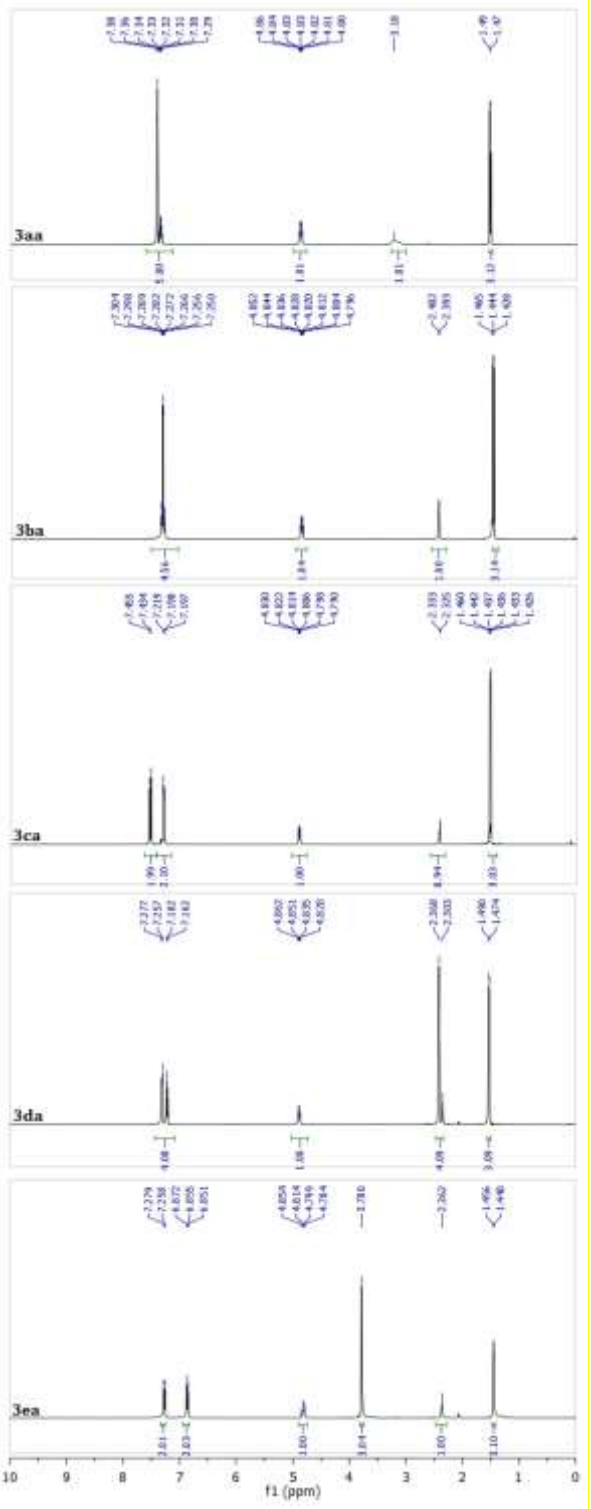

Figure 9. ^{1}H-NMR spectra of the catalytic products

Ethics
There are no ethical issues after the publication of this manuscript.

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