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Research Article

Zinc(II) and Cadmium(II) Salphen Catalyzed Alkylation Reactions to Form *α*-Alkylated Ketones

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Abstract

The catalytic α–alkylation reaction is one of the methods commonly used to form C-C bonds. In this study the zinc (II) and cadmium (II)-salphen catalyzed α-alkylation of ketones with primary alcohols is reported. Various α-alkylated ketones were obtained in good yields through a borrowing hydrogen strategy by using 1 % of catalysts and a catalytic amount of NaOH (10 mol%) as the base under air atmosphere. All synthesized compounds were characteized by ^{1}H and ^{13}C NMR. The highest conversion was obtained using the complex **1a**.

Keywords: Zinc, cadmium, salphen, alkylation, ketone

α-Alkillenmiş Ketonlar Oluşturmak için Çinko(II) ve Kadmiyum(II) Salfen Katalizli Alkilasyon Reaksiyonları

Öz

Katalitik α–alkilasyon reaksiyonu, C-C bağları oluşturmak için yaygın olarak kullanılan yöntemlerden biridir. Bu çalışmada, ketonların birincil alkollerle çinko (II) ve kadmiyum (II)-salfen katalizli α-alkilasyonu rapor edilmiştir. Hava atmosferi altında %1 katalizör ve baz olarak katalitik miktarda (%10 mol) NaOH kullanılarak bir ödünç hidrojen stratejisi yoluyla çeşitli α-alkillenmiş ketonlar iyi verimlerle elde edilmiştir. Sentezlenen tüm bileşikler, ^{1}H ve ^{13}C NMR ile karakterize edilmiştir. En yüksek dönüşüm kompleks **1a** kullanılarak elde edilmiştir.

Anahtar Kelimeler: Çinko, kadmiyum, salfen, alkilasyon, keton

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1. Introduction

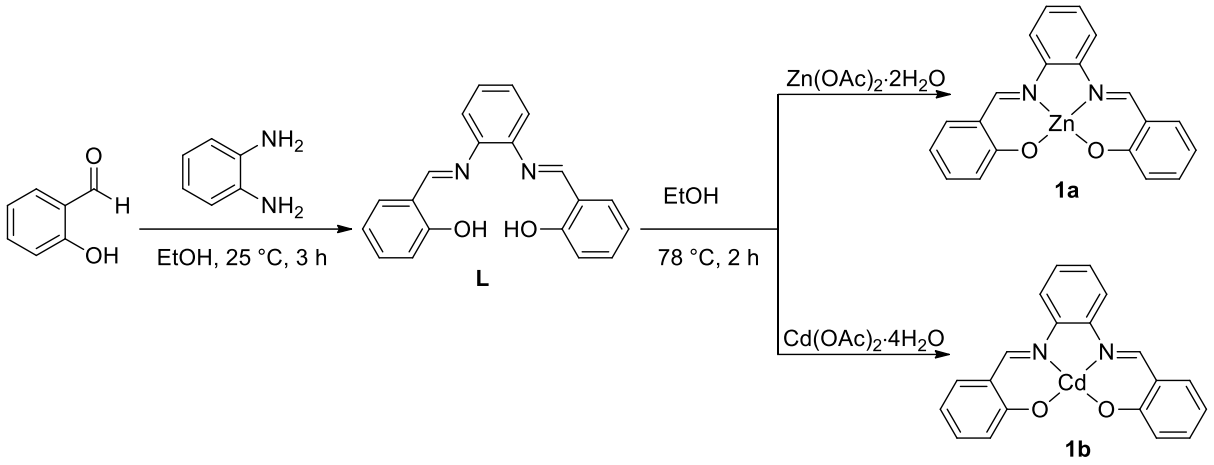
Condensation of salicylaldehyde derivatives with 1,2-diamines leads to the formation of an important class of ligand known as " Salens and Salphens ". Many different salen ligands can be synthesized using of numerous differently substituted salicylic aldehydes or diamine derivatives. The variety of metal-salen complexes can be expressed by numerous references to these complexes available in chemical databases. The most prominent metals examined are cobalt [1], manganese[2], copper[3], nickel[4], iron[5] and chromium[6]. Metal-salen complexes of these elements are extensively used in catalysis. Due to the multifunctionality of the Salen complexes, they have been shown by Jacobsen as "privileged ligands for catalysis".[7]

Catalysts are highly important in the development of sustainable chemical processes. The catalytic α–alkylation reaction is one of the methods commonly used to form C-C bonds. Transition-metal catalysts based on ruthenium[8], rhodium[9], iridium[10] and gold[11] have confirmed to be highly efficient for this reaction. Although used in low catalyst loading, the attention in the use of more sustainable alternatives has increased as these metals bear inherent disadvantages such as limited availability, high price, and toxicity. In this regard, there has been increased interest in the use of earth-abundant first-row transition metals such as iron[12], manganese[13], cobalt[14], or nickel. [15]

The aim of the present work is to design an inexpensive catalyst that can be easily prepared for the α–alkylation reaction of ketones, utilizing the coordination between Schiff base. Herein, the synthesis and structure of Zn(II)- and Cd(II)-Salphen complexes (**1a-b**) incorporating N,N'-Bis(salicylidene)-1,2-phenylenediamine (**L**) ligand have been described. The complexes have been characterized via NMR spectroscopy techniques and screened to examine the catalytic activity for the α–alkylation of ketones. From the promising results, Zn(II)-salphen complex has been found to be potentially useful for this purpose. Zinc is a cheaper and more abundant metal, however, to the best of our knowledge, the activities of salphen ligands with zinc for the α–alkylation of ketones have not been reported in the literature.

2. Material and Methods

Scheme 1 describes the method used for the synthesis of the ligand (**L**) and complexes (**1a-b**). The four-coordinate Zn (II)- and Cd(II)-salphen complexes (**1a-b)** were synthesized by reaction of $M(OAc)_2.xH_2O$ (M = Zn, Cd) with **L** at 78 ºC in ethanol. The Zn (II) and Cd (II) complexes were synthesized according to a modified literature procedure in good yield. All complexes are stable in air, insoluble in H_2O and soluble in DMSO, DMF, moderately soluble in chlorinated solvents, partly soluble in ethanol. Synthesized compounds were characterized by NMR spectra. The physical properties and spectroscopic data of the obtained compounds are in accordance with previous reports. [16]



Scheme 1. Preparation of Zn(II)- and Cd(II)-Salphen Complexes **1a-b**.

Experimental Details. Unless otherwise specified, all reagents were obtained commercially and used without further purification. NMR spectra were recorded on Varian AS 400 Mercury NMR spectrometer and reported in units of parts per million (ppm) relative to tetramethyl silane (δ = 0 ppm), $CDCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C NMR) or DMSO-*d*$_6$ (δ = 2.48 ppm for ^{1}H and δ = 39.97 ppm for ^{13}C NMR).

Synthesis of ligand (L). A solution of salicylaldehyde (4.0 mmol) in ethanol (2 mL) was added dropwise to a solution of *o*-Phenylenediamine (2.0 mmol) in the same solvent (2 mL). The mixture was stirred at room temperature 3h, during which time a precipitate was formed. The product was filtered out, washed with ethanol (2x2 mL) and dried under reduced pressure.

Ligand L. Yield: 83%, yellow solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$,): δ = 12.95 (bs, 2 H, O*H*, [H19, H20]), 8.91 (s, 2 H, N=C*H*, [H5, H6]), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2 H, [H9, H18]), 7.45-7.37 (m, 6H, [H11, H16, H21, H22, H23, H24]), 6.97-6.94 (m, 4H, [H10, H12, H15, H17]). ^{13}C NMR (100.6 MHz, DMSO-*d*$_6$, TMS): δ = 164.5 (*C*=N, [C5, C6]), 160.8 [C13, C14], 142.7 [C1, C2], 133.9 [C11, C16], 132.9 [C9, C18], 128.2 [C22, C23], 120.2 [C21, C24], 119.9 [C7, C8], 119.5 [C10, C17], 117.1 [C12, C15].

General procedures for the synthesis of complexes 1a-b. To hot 5 mL ethanol solution containing 1.0 mmol of the ligand, 5 mL of ethanol solution containing 1.0 mmol of $M(OAc)_2.xH_2O$ (M = Zn, Cd) was added dropwise. After stirring for 2 h at 78ºC the formed red complexes were filtered, collected, and then washed with ethanol. The complexes were dried under reduced pressure.

Complex 1a. Yield: 86%, yellow solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS, 25ºC, ppm): 8.99 (s, 2H, N=C*H*, [H5, H6]), 7.88-7.85 (m, 2H, [H9, H18]), 7.41 (dd, 2H, J_1 = 7.6 Hz, J_2 = 2.0 Hz, [H11, H16]), 7.37-7.33 (m, 2H, [H22, H25]), 7.23 (td, 2H, J_1 = 7.4 Hz, J_2 = 2.0 Hz, [H23, H24], 6.71 (d, 2H, J = 8.4 Hz, [H10, H17]), 6.50 (td, 2H, J_1 = 7.4 Hz, J_2 = 2.0 Hz, [H12, H15]). ^{13}C NMR (100.6 MHz, DMSO-*d*$_6$, TMS): δ = 172.7 (*C*=N, [C5, C6]), 163.3 [C13, C14], 139.8 [C1, C2], 136.7 [C11, C16], 134.8 [C9, C18], 127.7 [C23, C24], 123.5 [C22, C25], 119.9 [C7, C8], 116.9 [C10, C17], 113.5 [C12, C15].

Complex 1b. Yield: 84%, yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, 25ºC, ppm): 8.61 (s, 2H, N=C*H*, [H5, H6]), 7.55-7.53 (m, 2H, [H9, H18]), 7.33-7.28 (m, 4H, [H11, H16, H22, H25]), 7.14-7.10 (m, 2H, [H23, H24]), 6.62 (d, J = 8.4 Hz, 2 H, [H10, H17]), 6.40 (t, J = 7.4 Hz, 2H, [H12, H15]). ^{13}C NMR (100.6 MHz, DMSO-d_6, TMS): δ = 173.5 (*C*=N, [C5, C6]), 165.3 [C13, C14], 141.7 [C1, C2], 137.5 [C11, C16], 133.7 [C9, C18], 127.3 [C23, C24], 124.4 [C22, C25], 121.3 [C7, C8], 118.1 [C10, C17], 112.7 [C12, C15].

In ^{1}H-NMR spectra of the Schiff base, the -OH proton was observed at around δ 12.95 ppm. The proton of -N=CH ligand appear around δ 8.91 ppm. Upon coordination of Zn (II) (**1a**) and Cd (II) (**1b**), the ^{1}H-NMR spectra of complexes showed some differences from the ligand (**L**). The ^{1}H-NMR spectra of the metal complexes display lack of phenolic –OH, confirming involvement of the –OH proton in complexation. In ^{13}C-NMR spectra of the ligands, -N=CH carbons appeared at about 164.5 ppm. This azomethine carbon in the spectra of metal complexes shifted upfield compared to the free ligand. These results agree with the literature data[1-3]. NMR spectral data for free ligand and the complexes (**1a, 1b**) together with their assignments are presented in Table 1.

Table 1. NMR comparison between ligand and complexes.

^{1}H-NMR N=C*H*			^{13}C-NMR *C*=N		
L	**1a**	**1b**	**L**	**1a**	**1b**
8.91	8.99	8.61	164.5	172.7	173.5

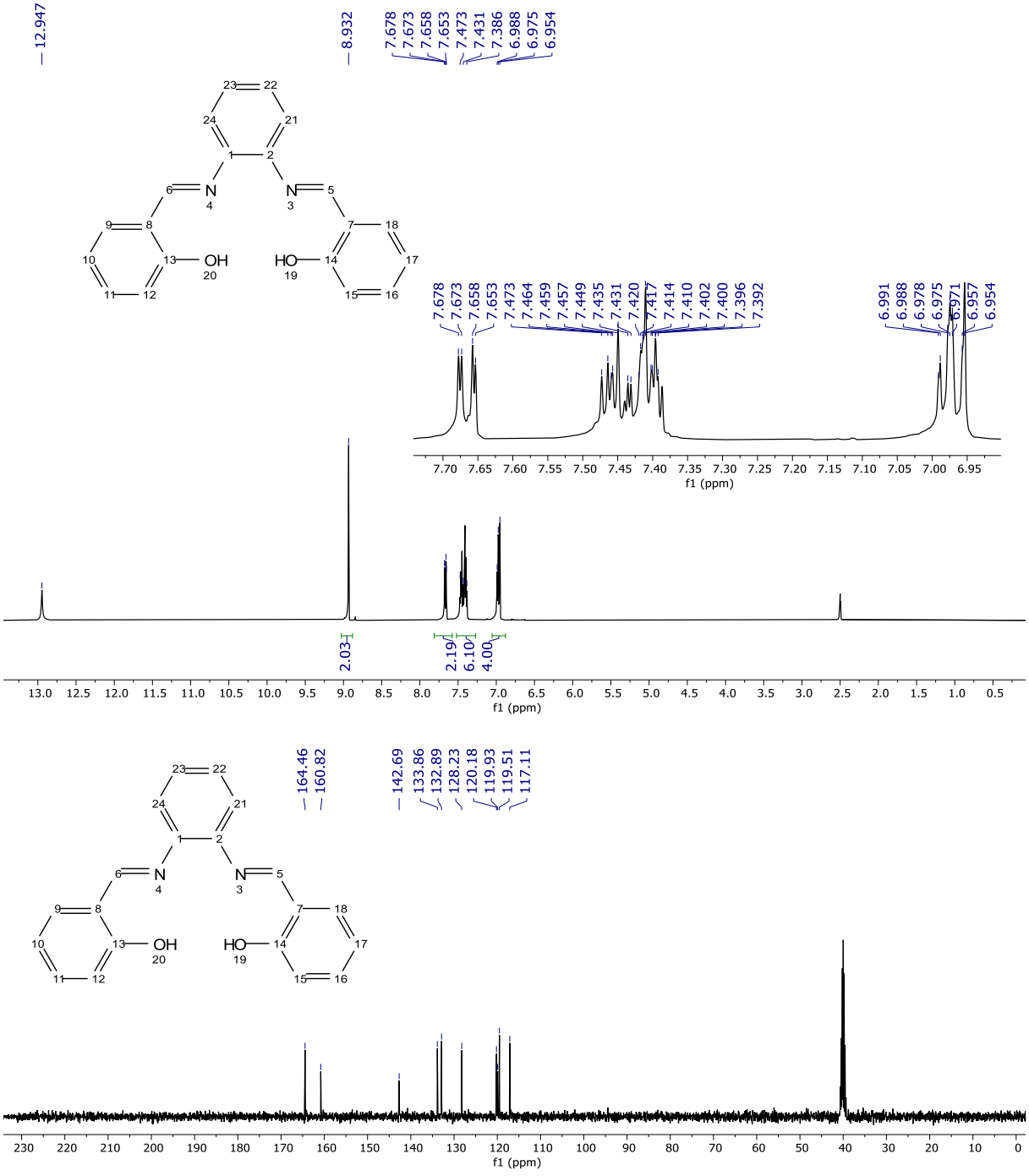


Figure 1. ^{1}H and ^{13}C NMR (DMSO-d_6) of **L**.

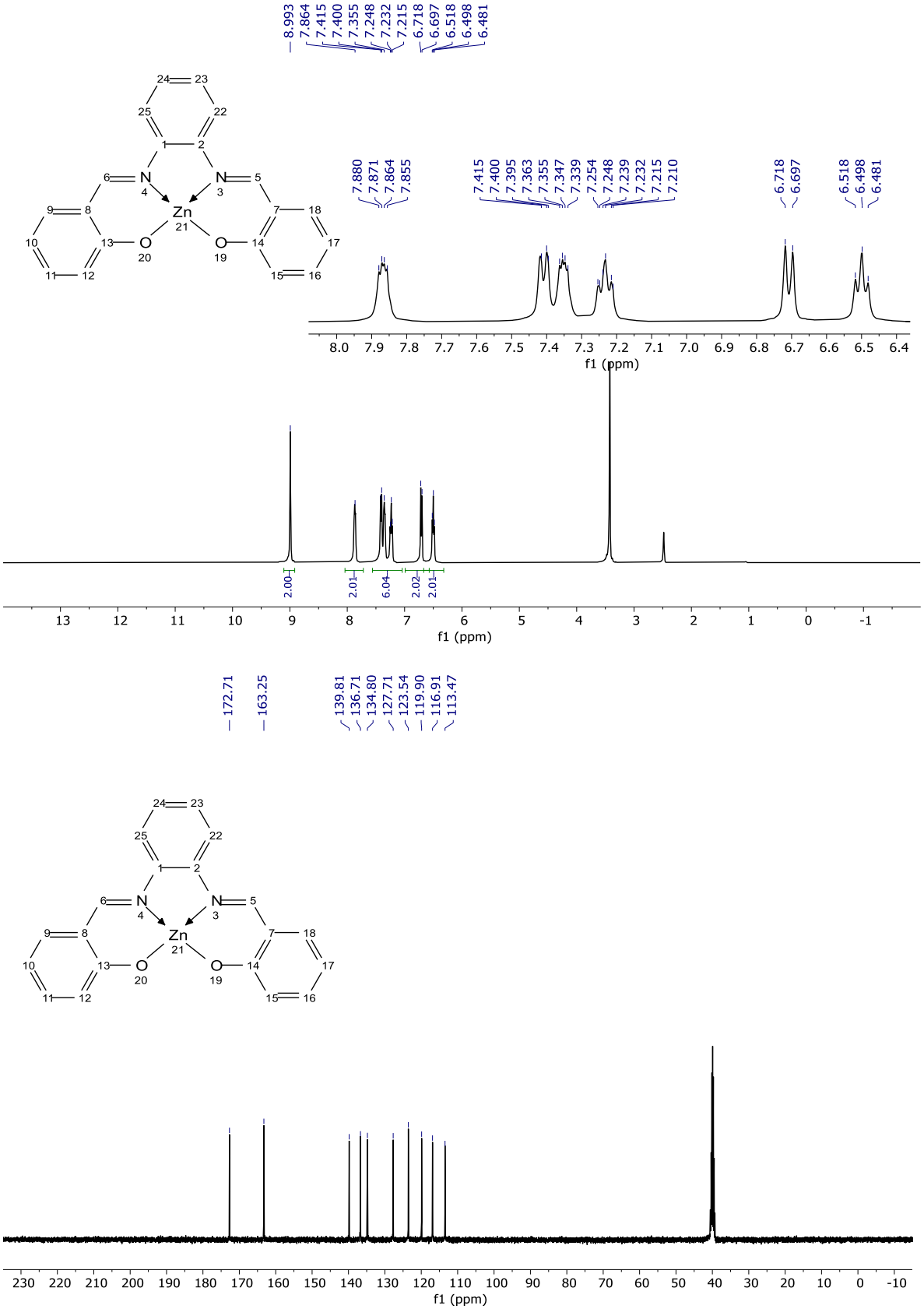


Figure 2. ^{1}H and ^{13}C NMR (DMSO-d_6) of **1a**.

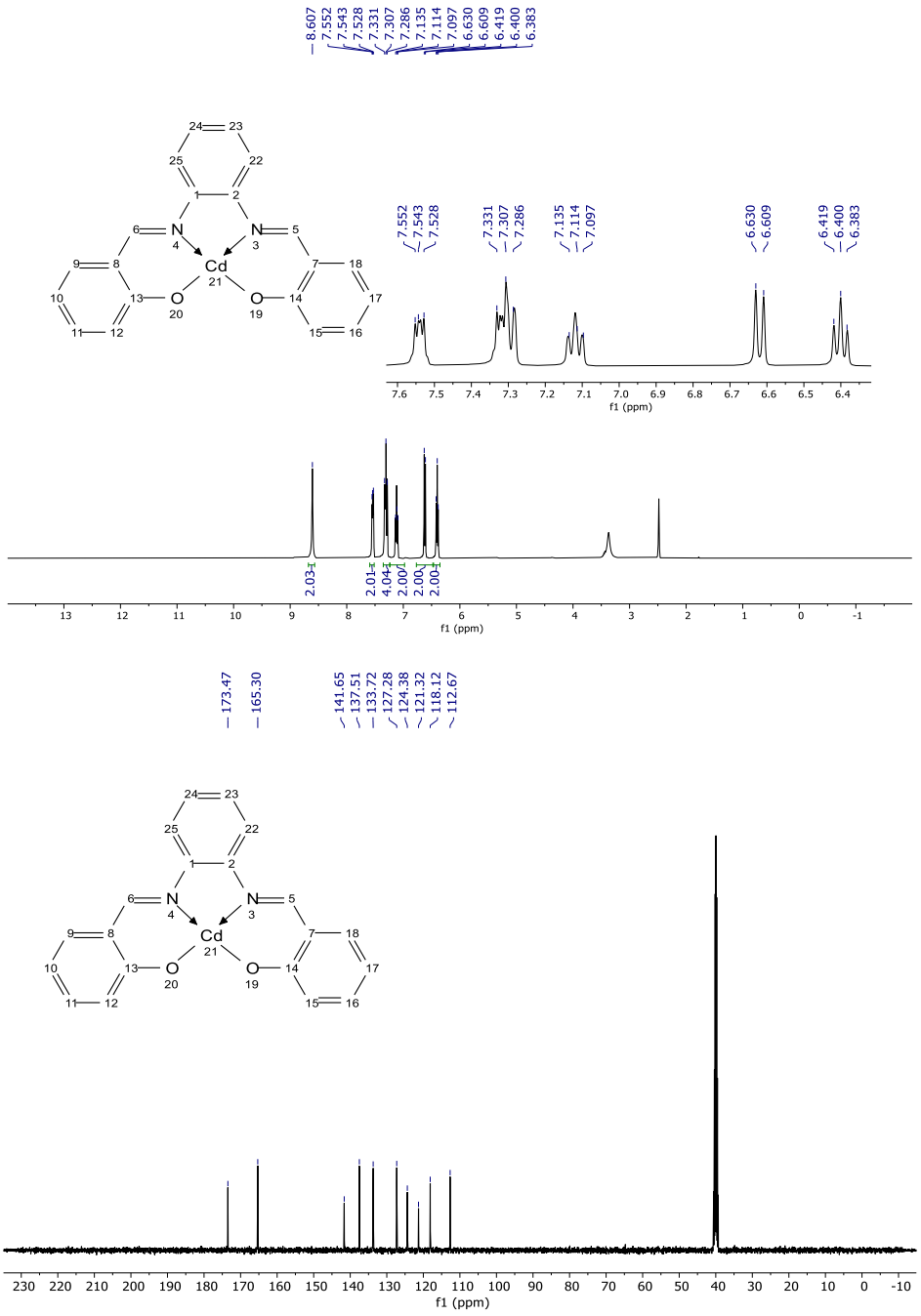
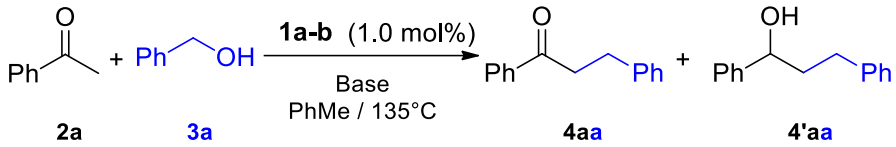


Figure 3. ^{1}H and ^{13}C NMR (DMSO-d_6) of **1b**.

3. Results and Disscussion

To explore the effect of the catalysts on the alpha- alkylation of ketones with alcohols, the reaction of acetophenone (**2a**) with benzyl alcohol (**3a**) was chosen as a model reaction to evaluate the influence of catalysts (**1a-b**). The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and the yields are based on 1,3,5-trimethoxybenzene as the internal standard (Table 2).

Table 2. Optimization of reaction conditions[a]



2a **3a** **4aa** **4'aa**

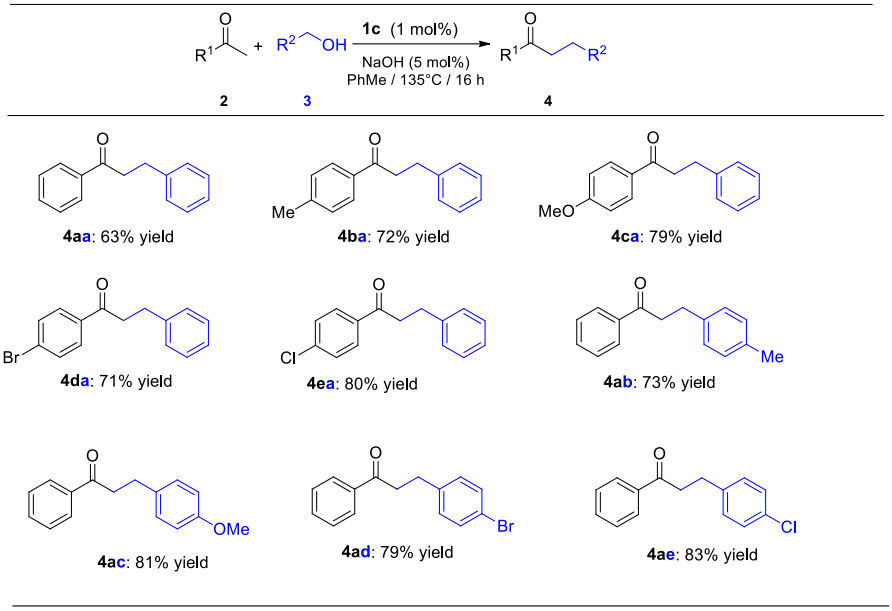
entry	cat.	base	solvent	T (°C)	time (h)	yield of 4aa[b] (%)	yield of 4'aa [b] (%)
1	**1a**	NaOH	Toluene	135	16	63	20
2	**1b**	NaOH	Toluene	135	16	54	16
3	**1a**	KOH	Toluene	135	16	41	18
4	**1a**	KO^{t}Bu	Toluene	135	16	37	16
5	**1a**	NaO^{t}Bu	Toluene	135	16	53	21
6	**1a**	Na_2CO3	Toluene	135	16	-	-
7	**1a**	$NaHCO_3$	Toluene	135	16	-	-
8	**1a**	NaOH	DMSO	135	16	-	-
9	**1a**	NaOH	Toluene	100	16	18	06
10	**1a**	-	Toluene	135	16	-	-
11	-	NaOH	Toluene	135	16	38	12
12	**$Zn(OAc)_2$**	NaOH	Toluene	135	16	-	-
13[c]	**1a**	NaOH	Toluene	135	16	61	21
14[d]	**1a**	NaOH	Toluene	135	16	59	23

[a]Reaction Conditions: **2a** (1.0 mmol), **3a** (1.0 mmol), **1a-c** (1 mol%), base (10 mol%), toluene (2.0 mL), 135 ºC, under air. [b]Yields were determined by ^{1}H NMR analyses. [c]Reaction was performed under an argon atmosphere. [d]Reaction was performed under closed system.

The reaction was performed in the presence of catalysts (**1a-b**) (1 mol %) and NaOH (10 mol %) in toluene (2 ml) at 135 °C (bath temp.) under air atmosphere for 16h (entries 1-2). Among all catalysts tested, the best conversion was obtained with catalyst **1a** (entry 1). Replacing NaOH with KOH decreased the yield of the reaction to 41% (entry 3), Replacing NaOH with KO^{t}Bu and NaO^{t}Bu decreased the yield of the reaction to 37 and 53 % respectively (entry 4 and 5), Na_2CO_3 and $NaHCO_3$ were inactive under same conditions (entries 6 and 7). No conversion

was observed when DMSO was used as the solvent (entry 8). When the temperature was 100 degrees, the yield decreased to 18% (entry 9). Additional experiments were performed without NaOH, no product formation was observed (entry 10). In the experiment with NaOH without catalyst, 38% conversion was observed (entry 11). Moreover, no conversion was observed when Zn-acetate was used in the same reaction conditions instead of Zn (II) –salphen, which indicates the critical role of the salphen ligands (entry 12). Using the closed systems or inert reaction conditions did not improve the yield of the reaction significantly and the rest of the reactions were performed open to air (entries 13 and 14).

To study the scope of the reaction, various ketones and primary alcohols were reacted under optimized conditions (Scheme 2). All reactions resulted in conversion of starting materials affording selective formation of the corresponding ketone **4**.



Scheme 2. Scope of α–Alkylation of Ketones with Primary Alcohols Catalyzed by Complex **1a**[a]

[a]Reaction Conditions: Ketone (1.0 mmol), primary alcohol (1.0 mmol), **1a** (1 mol%), base (10.0 mol%), toluene (2.0 mL), 135 ºC, under air.

Various electron–rich or electron–deficient 1-arylketones (**2a**–**e**) were transformed into the corresponding ketones (**4aa**–**4ea**) in good yields by using **1c** (1 mol%) as the catalyst. The reaction of ketones bearing electron-donating -Me and -OMe substituents and electron-withdrawing –Br and -Cl substituents with benzyl alcohol gave desired products **4aa**−**4ea** with 72−80% isolated yields. Then the scope of the α-alkylation reaction compared to primary alcohols (**3**) were studied. For benzyl alcohol with electron-donating or electron with-drawing groups the reactions produced α-alkylated ketones with good yields. The reactions of acetophenone with 4–Me, 4–OMe, 4–Br, and 4–Cl benzyl alcohols, were afforded the desired ketone products (**4ab-4ae**) in good yields (73-83%).

General procedure for the *α*-alkylation of ketones with primary alcohols to give *α*-alkylated ketones. In a 20 mL reaction tube (1 cm × 20 cm) with a condenser were added NaOH (2.0 mg, 0.05 mmol) ketone (1.0 mmol), primary alcohol (1.0 mmol) and complex **1** (0.01 mmol, 1 mol%) in toluene (2.0 mL) under air atmosphere. The reaction mixture was vigorously stirred (1400 rpm) under reflux in a preheated oil bath at 135 ºC for 3–24 h. Then the reaction mixture was cooled to ambient temperature and a 10 μL solution was syringed out for GC analysis. The solvent was evaporated, and the crude product was submitted for NMR analysis to calculate the conversion. All the crude products were combined after analysis and purified by silica gel column chromatography using hexane and ethyl acetate (9:1) mixture as eluent to afford the desired ketone.

1,3-Diphenylpropan-1-one (4aa). Yield: 66%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.98 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.34-7.21 (m, 5H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.1, 141.3, 136.9, 133.0, 128.6, 128.6, 128.5, 128.0, 126.1, 40.4, 30.2.

3-Phenyl-1-(p-tolyl)propan-1-one (4ba). Yield: 77%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.89 (d, *J* = 8.0 Hz, 2H), 7.34-7.23 (m, 7H), 3.29 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.8, 143.8, 141.4, 134.5, 129.3, 128.5, 128.4, 128.2, 126.1, 40.3, 30.3, 21.6.

1-(4-Methoxyphenyl)-3-phenylpropan-1-one (4ca). Yield: 81% white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 8.8 Hz, 2H), 7.32-7.19 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.25 (t, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.8, 163.4, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.7, 55.4, 40.1, 30.3.

1-(4-Bromophenyl)-3-phenylpropan-1-one (4da). Yield: 74% white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.81 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.32-7.21 (m, 5H), 3.26 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.1, 141.0, 135.6, 131.9, 129.6, 128.6, 128.4, 128.2, 126.2, 40.4, 30.1.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (4ea). Yield: 80%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.89 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.32-7.19 (m, 5H), 3.27 (t, *J* = 7.4 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.9, 141.1, 139.5, 135.2, 129.4, 129.0, 128.9, 128.6, 128.5, 128.4, 126.2, 40.4, 30.1.

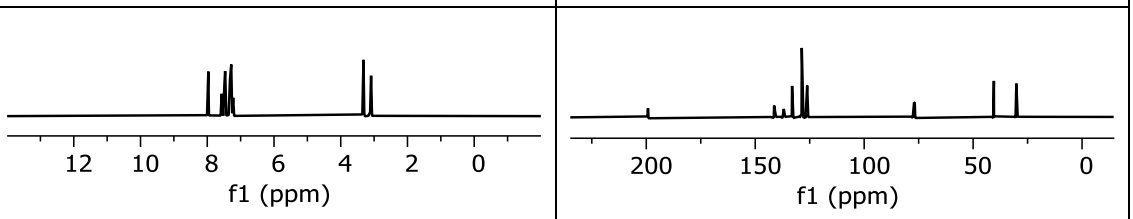
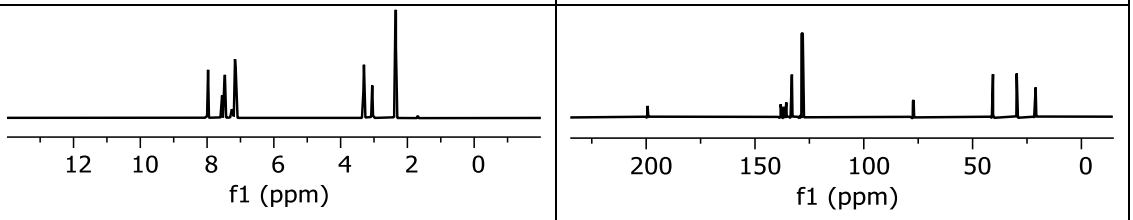
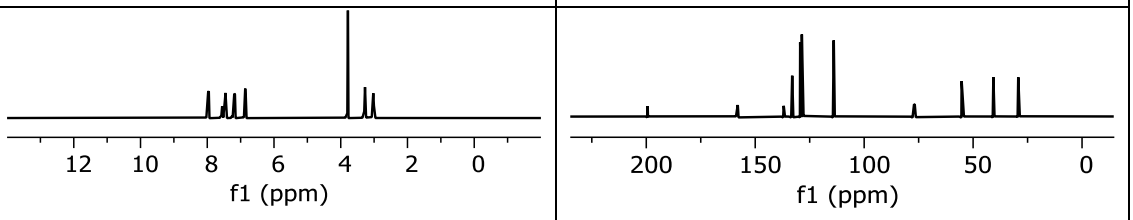
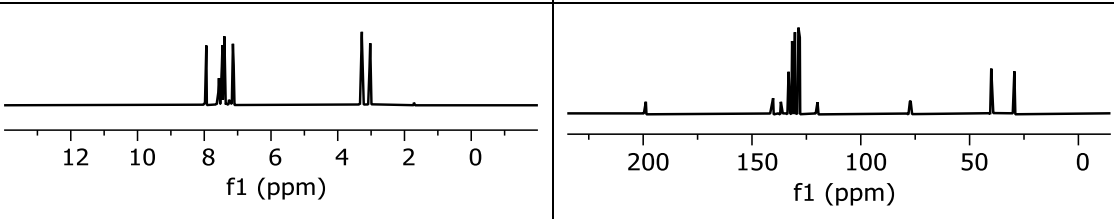
1-Phenyl-3-(p-tolyl)propan-1-one (4ab). Yield: 76%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.99 (d, *J* = 8.0 Hz, 2H), 7.56 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.49-7.45 (m, 2H), 7.19-7.13 (m, 4H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.3, 138.2, 137.0, 135.6, 133.0, 129.2, 128.6, 128.3, 128.1, 40.6, 29.8, 21.0.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (4ac). Yield: 87%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.97 (d, *J* = 8.0 Hz, 2H), 7.56 (tt, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 1H),

7.45 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 9.2 Hz, 2H), 3.79 (s, 3H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.3, 158.0, 136.9, 133.3, 132.9, 129.3, 128.6, 128.0, 113.9, 55.3, 40.7, 29.3.

3-(4-Bromophenyl)-1-phenylpropan-1-one (4ad). Yield: 79%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.28 (t, *J* = 7.4 Hz, 2H), 3.03 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.7, 140.2, 136.7, 133.1, 131.5, 130.2, 128.6, 127.9, 119.8, 40.0, 29.4.

3-(4-Chlorophenyl)-1-phenylpropan-1-one (4ae). Yield: 89%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.7, 139.7, 136.7, 133.1, 131.8, 129.8, 128.6, 128.5, 127.9, 40.1, 29.4.

	^{1}H-NMR ($CDCl_3$, 400 MHz)	^{13}C-NMR ($CDCl_3$, 100 MHz)
4aa		
4ab		
4ac		
4ad		

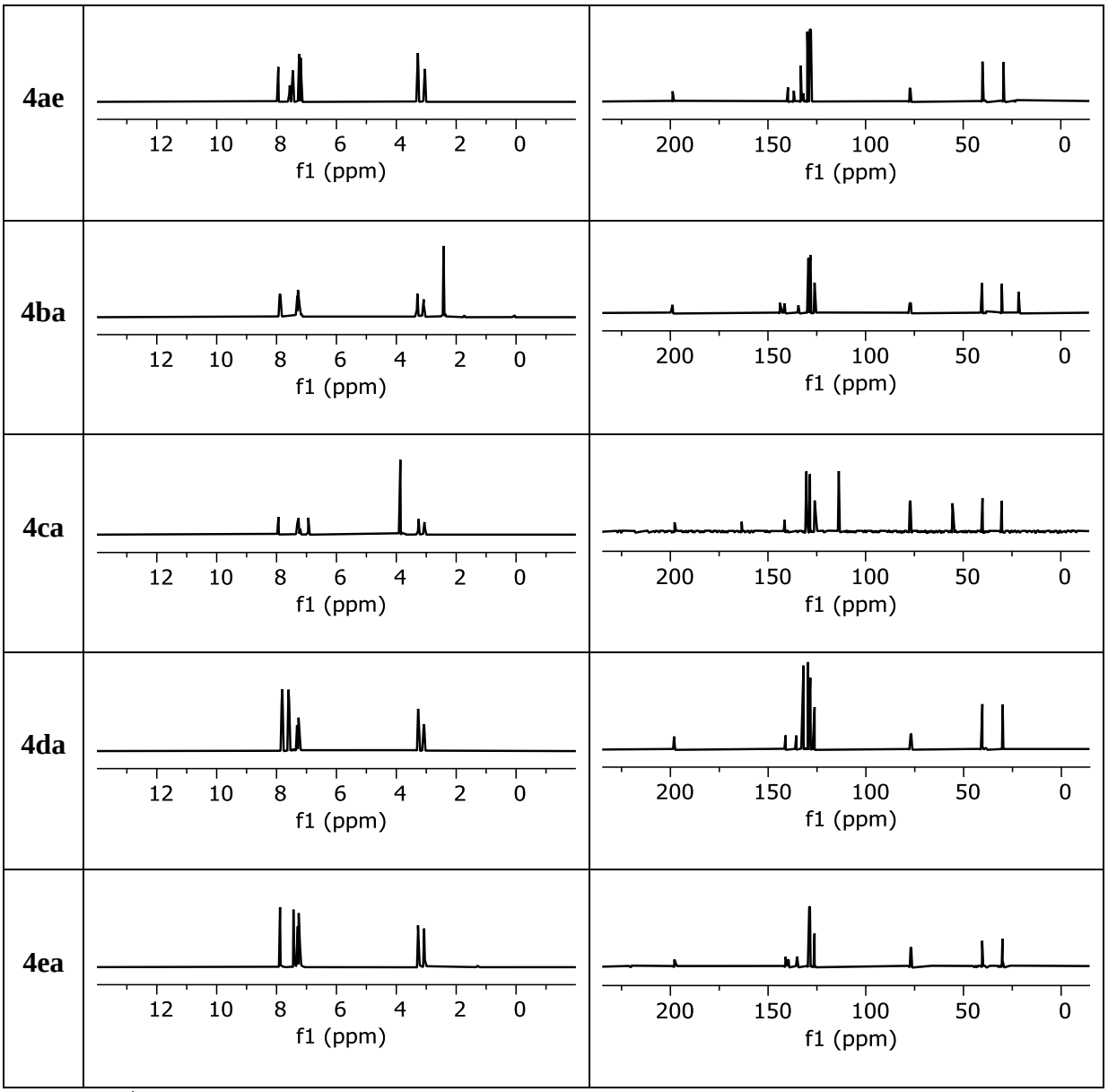


Figure 4. ^{1}H-NMR spectra of the catalytic products.

4. Conclusions

In this study, the preparation and characterization of Zn (II) and Cd (II) complexes (**1a-b**) were reported. Their catalytic activities were investigated for the *α*–alkylation of ketones. The zinc complex demonstrated higher catalytic activity compared to the cadmium complex under air atmosphere. Catalytic activity varies depending on the groups in the phenyl ring of acetophenone and benzyl alcohol. The best result was obtained using 4-chloro acetophenone and 4-chloro benzyl alcohol for 16 hours reaction time, and when **1a** was used as a catalyst, a yield of 83% was achieved. Based on these results, it is thought that the complexes obtained with Zn (II), which are quite cheap and abundant in nature, may be a good alternative to other metals frequently used in the α–alkylation reaction.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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