Supplementary Information

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Dinuclear cobalt complexes supported by biphenol and binaphthol-derived bis (salicylaldimine) ligands: Synthesis, characterization and catalytic application in β-enaminones synthesis from 1,3-dicarbonyl compounds and Aliphatic amines

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Fig. S63  GCMS trace of 14 (m/z 211) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-butyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes. 

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Fig. S65  1H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine. 

Fig. S66  GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine. 

Fig. S67  1H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by Co(OAc)$_2$•4H$_2$O. 

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Fig. S71  1H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by H$_2$L$_2$ (3). 

Fig. S72  1H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes in the presence of Hg. 

Fig. S73  GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes in the presence of Hg.
Table 1S. Solvent variation study for the β-enaminone reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes

\[
\begin{align*}
\text{O} & \quad \text{O} \\
& \quad \text{Me} \text{NH}_2 \\
\longrightarrow & \quad \text{2/4} \\
& \quad \text{solvent, RT, 6 h} \\
\end{align*}
\]

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<td>5</td>
<td>DMF</td>
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(a). Reaction conditions: 1.00 mmol of ketone, 4.0 mmol of amine, 1 mol % of catalyst (2/4), 2.5 mL of solvent at room temperature, stir for 6 h. (b) Isolated yields (%).
Table 2S. Time variation study for the β-enaminone reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.

\[
\begin{align*}
\text{Ketone} + \text{Me-NH}_2 & \xrightarrow{2/4} \text{THF, RT, 6 h} \quad \text{HNMe} \\
\end{align*}
\]

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(a). Reaction conditions: 1.00 mmol of ketone, 4.0 mmol of amine, 1 mol % of catalyst (2/4), 2.5 mL of THF at room temperature, stir for the given time. (b). Isolated yields (%).
Table 3S. Selected results of blank, control and mercury drop experiments for the β-enaminone reaction of acetyl acetone and methylamine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.

![Chemical structure](image)

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\(^a\). Reaction conditions: 1.00 mmol of ketone, 4.0 mmol of amine, 1 mol % of catalyst (2/4) or 2 mol % of Co(OAc)\(_2\)•4H\(_2\)O/H\(_2\)L\(_1\)/H\(_2\)L\(_2\), 2.5 mL of THF at room temperature, stir for 6 h.  
\(^b\). Isolated yields (%).
Fig. S1 1H NMR spectrum of 1 in CDCl3.
Fig. S2 Expanded 1H NMR spectrum of 1 in CDCl$_3$. 
Fig. S3 $^{13}$C{¹H} NMR spectrum of 1 in CDCl₃.
Fig. S4 Infrared spectrum of 1 in KBr.
Fig. S5 High Resolution Mass Spectrometry (HRMS) data of 1.
### Eager 300 Report

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- **Method File:** D:\CHNS2016\PGCP16052016.mth  
- **Chromatogram:** PG-AE-2-27-1  
- **Operator ID:** CHANDNI  
- **Company Name:** C.E. Instruments  
- **Analysed:** 05/16/2016 12:53  
- **Printed:** 05/17/2016 10:26  
- **Sample ID:** PG-AE-2-27-1 (# 13)  
- **Instrument N.:** Instrument #1  
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**Calib. method:** using 'K Factors'

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Fig. S6 Elemental analysis data of 1.
Fig. S7 Infrared spectrum of 2 in KBr.
Table 4S. Important IR bands of 1(H$_2$L$_1$) and 3 (H$_2$L$_2$) dinuclear complexes 2 and 4

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Fig. S8  High Resolution Mass Spectrometry (HRMS) data of 2.
Fig. S9 Elemental analysis data of 2.
Fig. S10  $^1$H NMR spectrum of 3 in CDCl$_3$. 
Fig S11  Expanded $^1$H NMR spectrum of 3 in CDCl$_3$. 
Fig. S12 $^{13}$C{^1}H} NMR spectrum of 3 in CDCl$_3$. 
Fig S13 Expanded $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 3 in CDCl$_3$. 
Fig.S14  Infrared spectrum of 3 in KBr.
Fig. S15  High Resolution Mass Spectrometry (HRMS) data of 3.
**Eager 300 Report**

Page: 1  Sample: PG-AE-1-86-2 (PG-AE-1-86-2)

Method Name : SP-230712  
Method File : D:\CHNS2012\SP-230712.mth  
Chromatogram : PG-AE-1-86-2  
Operator ID : MNRAO  
Analysed : 07/23/2012 15:16  
Sample ID : PG-AE-1-86-2 (# 9)  
Analysis Type : UnkNown (Area)

Calib. method: using 'K Factors'

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**Fig. S16**  Elemental analysis data of 3.
Fig. S17  Infrared spectrum of 4 in KBr.
Fig. S18 High Resolution Mass Spectrometry (HRMS) data of 4.
Eager 300 Report

Page: 1  Sample: PG-CP-14-60-1 (PG-CP-14-60-1)

Method Name : PGCP28082017
Method File : D:\chns2016 -1\PGCP28082017.mth
Chromatogram : PG-CP-14-60-1
Operator ID : CHANDNI
Analysed : 08/28/2017 17:47
Sample ID : PG-CP-14-60-1 (# 7)
Analysis Type : UnKnNow (Area)

Company Name : C.E. Instruments
Printed : 8/28/2017 19:13
Instrument N. : Instrument #1
Sample weight : .856

Calib. method : using 'K Factors'

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Fig.S19  Elemental analysis data of 4.
Fig. S20 $^1$H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$(2) and [CoL$_2$]$_2$(4) complexes.
Fig. S21 Expanded $^1$H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S22 $^{13}$C($^1$H) NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S23  GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL]$_2$ (2) and [CoL']$_2$ (4) complexes.
Fig.S24 Elemental analysis data of 5 formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S25 $^1$H NMR spectrum of 6 in CDCl$_3$ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S26 Expanded $^1$H NMR spectrum of 6 in CDCl$_3$ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes.
Fig. S27 $^{13}$C-$^1$H NMR spectrum of 6 in CDCl$_3$ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
**Fig. S28** GCMS trace of 6 (m/z 127) in EtOAc formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the the dinuclear [CoL\(^1\)]\(_2\) (2) and [CoL\(^2\)]\(_2\) (4) complexes.
Fig. S29 ¹H NMR spectrum of 7 in CDCl₃ formed in the reaction of acetyl acetone and n-propyl amine as catalyzed by the dinuclear [CoL¹]₂ (2) and [CoL²]₂ (4) complexes.
Fig. S30 Expanded $^1$H NMR spectrum of 7 in CDCl$_3$ formed in the reaction of acetyl acetone and $n$-propyl amine as catalyzed by the dinuclear [CoL$^1$]**2**(2) and [CoL$^2$]**2**(4) complexes.
Fig. S31 $^{13}$C\{$^1$H} NMR spectrum of 7 in CDCl$_3$ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$^2$ (2) and [CoL$^2$]$^2$ (4) complexes.
Fig. S32 GCMS trace of 7 (m/z 141) in EtOAc formed in the reaction of acetyl acetone and n-propyl amine as catalyzed by the dinuclear [CoL₁]₂ (2) and [CoL₂]₂ (4) complexes.
Fig. S33 $^1$H NMR spectrum of 8 in CDCl$_3$ formed in the reaction of acetyl acetone and $i$-propyl amine as catalyzed by the dinuclear [CoL$_1^2$]$_2$ (2) and [CoL$_2^2$]$_2$ (4) complexes.
Fig. S34 Expanded $^1$H NMR spectrum of 8 in CDCl$_3$ formed in the reaction of acetyl acetone and $i$-propyl amine as catalyzed by the dinuclear [CoL$_2$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes.
Fig. S35 13C{1H} NMR spectrum of 8 in CDCl3 formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.
Fig. S36 GCMS trace of 8 (m/z 141) in EtOAc formed in the reaction of acetyl acetone and i-propyl amine as catalyzed by the dinuclear [CoL₁]₂ (2) and [CoL₂]₂ (4) complexes.
Fig. S37 $^1$H NMR spectrum of 9 in CDCl$_3$ formed in the reaction of acetyl acetone and $n$-butyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes.
Fig. S38  Expanded 1H NMR spectrum of 9 in CDCl3 formed in the reaction of acetyl acetone and n-butyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.
Fig. S39 \(^{13}\text{C}^{1}\text{H}\) NMR spectrum of 8 in CDCl\(_3\) formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL\(^{-1}\)]\(_2\) (2) and [CoL\(^{2}\)]\(_2\) (4) complexes.
Fig. S40 GCMS trace of 9 (m/z 155) in EtOAc formed in the reaction of acetyl acetone and n-butyl amine as catalyzed by the dinuclear [CoL$_1$]$_2$ (2) and [CoL$_2$]$_2$ (4) complexes.
Fig. S41 ¹H NMR spectrum of 10 in CDCl₃ formed in the reaction of acetyl acetone and 2-picoly amine as catalyzed by the dinuclear [CoL¹]₂ (2) and [CoL²]₂ (4) complexes.
Fig. S42  Expanded $^1$H NMR spectrum of 10 in CDCl$_3$ formed in the reaction of acetyl acetone and 2-picoyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$(2) and [CoL$^2$]$_2$(4) complexes.
Fig. S43 $^{13}$C{[$^1$H]} NMR spectrum of 10 in CDCl$_3$ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig.S44 GCMS trace of 10 (m/z 190) in EtOAc formed in the reaction of acetyl acetone and 2-picolyl amine as catalyzed by the the dinuclear [CoL₁]₂ (2) and [CoL₂]₂ (4) complexes.
Fig. S45 $^1$H NMR spectrum of 11 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S46 Expanded $^1$H NMR spectrum of 11 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear [CoL]$^1)_2$ (2) and [CoL]$^2)_2$ (4) complexes.
Fig. S47 $^{13}$C{\textsuperscript{1}H} NMR spectrum of 11 in CDCl$_3$ formed in the reaction of acetyl acetone and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S48  GCMS trace of 11 (m/z 183) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear [CoL^1]_2 (2) and [CoL^2]_2 (4) complexes.
Fig. S49 Elemental analysis data of 11 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and ethyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S50 $^1$H NMR spectrum of 12 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and $n$-propyl amine as catalyzed by the dinuclear [CoL$_1$]$^2$ (2) and [CoL$_2$]$^2$ (4) complexes.
Fig. S51 Expanded $^1$H NMR spectrum of 12 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and $n$-propyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S52 $^{13}$C-$^1$H NMR spectrum of 12 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentane-1-carboxylate and $n$-propyl amine as catalyzed by the dinuclear [CoL$_1^{12}$]$_2$ (2) and [CoL$_2^{2}$]$_2$ (4) complexes.
**Fig. S53** GCMS trace of 12 (m/z 197) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-propyl amine as catalyzed by the the dinuclear [CoL\textsuperscript{1}]\textsubscript{2} (2) and [CoL\textsuperscript{2}]\textsubscript{2} (4) complexes.
Fig. S54 Elemental analysis data of 12 formed in the reaction of ethyl 2-oxocyclopentane carboxylate and n-propyl amine as catalyzed by the dinuclear [CoL\textsubscript{1}\textsubscript{2}]\textsubscript{(2)} and [CoL\textsubscript{2}\textsubscript{2}]\textsubscript{(4)} complexes.
Fig. S55 $^1$H NMR spectrum of 13 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and $i$-propyl amine as catalyzed by the dinuclear [CoL]$^1$$_2$(2) and [CoL]$^2$$_2$(4) complexes.
Fig. S56 Expanded $^1$H NMR spectrum of 13 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and i-propyl amine as catalyzed by the dinuclear [CoL1]$_2$ (2) and [CoL2]$_2$ (4) complexes.
Fig. S57 $^{13}$C\{1H\} NMR spectrum of 13 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and $i$-propyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$ (2) and [CoL$^2$]$_2$ (4) complexes.
Fig. S58 GCMS trace of 13 (m/z 197) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and i-propyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.
Fig. S59 Elemental analysis data of 13 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and i-propyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.
Fig. S60 1H NMR spectrum of 14 in CDCl3 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-butyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.
Fig. S61  Expanded 1H NMR spectrum of 14 in CDCl₃ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-butyl amine as catalyzed by the dinuclear [CoL₁]₂ (2) and [CoL₂]₂ (4) complexes.
Fig. S62 $^{13}$C{'^{1}H} NMR spectrum of 14 in CDCl$_3$ formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and $n$-butyl amine as catalyzed by the dinuclear [CoL]$^1_2$(2) and [CoL]$^2_2$(4) complexes.
Fig. S63  GCMS trace of 14 (m/z 211) in EtOAc formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-butyl amine as catalyzed by the dinuclear [CoL1]2 (2) and [CoL2]2 (4) complexes.
Fig. S64  Elemental analysis data of 14 formed in the reaction of ethyl 2-oxocyclopentanecarboxylate and n-butyl amine as catalyzed by the dinuclear [CoL$^1$]$_2$(2) and [CoL$^2$]$_2$(4) complexes.
Fig. S65 $^1$H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetylacetone and methyl amine.
Fig. S66 GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine.
Fig. S67  1H NMR spectrum of 5 in CDCl3 formed in the reaction of acetyl acetone and methyl amine as catalyzed by Co(OAc)₂•4H₂O.
Fig. S68  GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by Co(OAc)$_2$•4H$_2$O.
Fig. S69 $^1$H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by H$_2$L$^1$ (1).
Fig. S70 GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by H$_2$L$^1$ (1).
Fig. S71  $^1$H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by H$_2$L$^2$ (3).
Fig. S72  $^1$H NMR spectrum of 5 in CDCl$_3$ formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL1]$_2$ (2) and [CoL2]$_2$ (4) complexes in the presence of Hg.
Fig. S73  GCMS trace of 5 (m/z 113) in EtOAc formed in the reaction of acetyl acetone and methyl amine as catalyzed by the dinuclear [CoL']₂ (2) and [CoL²]₂ (4) complexes in the presence of Hg.