A Heterometallic (Fe6Na8) Cage-like Silsesquioxane: Synthesis, Structure, Spin Glass Behavior and High Catalytic Activity


[a] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str., 28, 119991 Moscow, Russia
[b] People's Friendship University of Russia, Miklukho-Maklay Str., 6, 117198 Moscow, Russia
[c] Pirogov Russian National Research Medical University, Ostrovitianov str., 1, 117997 Moscow, Russia
[d] Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina, dom 4, 119991 Moscow, Russia
[e] Plekhanov Russian University of Economics, Stremyannyi pereulok, dom 36, 117997 Moscow, Russia
[f] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal
[g] Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, CNRS, Université de Montpellier, ENSCM, Site Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5, France
[h] ICGM - UMR5253- Equipe IMNO, Université de Montpellier, Place Eugène Bataillon - CC 1502 34095 Montpellier CEDEX 5, France
[i] National Research Center “Kurchatov Institute”, pl. Akad. Kurchatova, dom 1, 123098 Moscow, Russia

Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2016
## Supporting Information

<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure of compound I</td>
<td>S3</td>
</tr>
<tr>
<td>A study of compound I by EXAFS</td>
<td>S9</td>
</tr>
<tr>
<td>Magnetic properties</td>
<td>S10</td>
</tr>
<tr>
<td>Kinetic analysis of catalytic oxidation by I</td>
<td>S11</td>
</tr>
<tr>
<td>Selectivity parameters for the catalytic oxidation of hydrocarbons</td>
<td>S13</td>
</tr>
<tr>
<td>Experiments on the Alkane Oxidation in the Presence of $^{18}\text{O}<em>2$ and $^2\text{H}</em>{18}\text{O}$</td>
<td>S15</td>
</tr>
<tr>
<td>Catalytic oxidative amidation of alcohols:</td>
<td>S18</td>
</tr>
<tr>
<td>Description of amides</td>
<td>S18</td>
</tr>
<tr>
<td>Spectra NMR of obtained amides</td>
<td>S20</td>
</tr>
<tr>
<td>References</td>
<td>S33</td>
</tr>
</tbody>
</table>
Structure of Compound I.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structural fragment</th>
<th>d…plane</th>
<th>Plane-plane angle</th>
<th>( \angle \text{O–Fe–O} )</th>
<th>( \angle \text{Fe–O–Fe} )</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><img src="image1.png" alt="Image" /></td>
<td>cn 5</td>
<td>cn 6</td>
<td>0.6</td>
<td>14 – 89</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95.4</td>
<td>98.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>121</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td><img src="image2.png" alt="Image" /></td>
<td>1.16</td>
<td></td>
<td>1 - 89</td>
<td>81.3 – 170.7</td>
<td>26a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93.9 – 106.5</td>
<td>95.7 – 110.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na\textsubscript{9}[(Fe(H\textsubscript{2}O))\textsubscript{3}P\textsubscript{2}W\textsubscript{15}O\textsubscript{59}] \cdot 19H\textsubscript{2}O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td><img src="image3.png" alt="Image" /></td>
<td>1.05</td>
<td></td>
<td>1 - 89</td>
<td>90.0 – 169.5</td>
<td>26b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>102.6 – 102.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(enH\textsubscript{2})\textsubscript{6}K[HF\textsubscript{6}(B-\alpha-GeW\textsubscript{9}O\textsubscript{34})\textsubscript{2}(\alpha-GeW\textsubscript{6}O\textsubscript{26})(H\textsubscript{2}O)\textsubscript{2}] \cdot 11H\textsubscript{2}O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Following a procedure described by Kostakis et al.\textsuperscript{s1a} one would see that structures I-VI as well as those of the [Fe\textsuperscript{III}\textsubscript{3}(μ\textsubscript{1}-O)(μ-O\textsubscript{2}CR)\textsubscript{6}L\textsubscript{3}] family contain a similar trinuclear fragment as it can be seen through the use of the ToposPro package.\textsuperscript{s1b} The procedure is visualized in Figure S1; only iron atoms and monodentate ligands were taken into account because they provide the most rigid
skeleton, and Fe–O–Fe bridges also provide a magnetic coupling. A topology classification of the metal-containing skeleton using the $NDk$-$m$ notation, wherein $N$ is a set of coordination numbers of topologically nonequivalent nodes ($N = 2$ for 2-connected nodes), $D$ is dimensionality ($D = M$ for discrete 0D molecular clusters), $k$ is the number of metal atoms in the cluster ($k = 3$), and $m$ is a classification number to distinguish topologically distinct clusters with equal $NDk$ parameters, gives the $2M3$-$I$ notation of $[\text{Fe}^{III}_3(\mu_3-O)(\mu-O_2CR)_6L_3]$, $[\text{Fe}_9\text{O}_{12}]$ and $[\text{Fe}_3\text{O}_{13}]$ clusters, where the coupling can be realized through, respectively, the $\mu_3$-oxo dianion and two bridge oxygen atoms of a silsesquioxane cage and the $\mu_3$-O and three $\mu_2$-O atoms of methoxy anions (V) or polydentate Keggin anions (II, III–VI; Figure S1).

Figure S1. Simplified representation of clusters I (top) and V (bottom). a) Fragments of the crystal structure including the first and the second alkaline-containing coordination spheres, b) Fragments of the crystal structure without terminal ligands and the alkaline metals; c) without bridge bidentate and polydentate ligands. d) The resulting $2M3$-$I$ graph of Fe$_3$ skeleton obtained by transformation of oxo-bridges into graph edges.

Indeed, we found that geometry of the Fe$^{III}_3(\mu_3-O)$ clusters in the structures of these compounds strongly differs from the one in $[\text{Fe}^{III}_3(\mu_3-O)(\mu-O_2CR)_6L_3]$ units. First, the oxygen atom is considerably shifted above the mean plane of three iron(III) atoms, whilst for the latter they are situated in this plane. In the Keggin anions for II–IV, and VI, the Fe–O distances between the iron atom and the $\mu_3$-OMe (V) and $\mu_3$-O (EO$_3$) ($E = \text{Ge}, \text{As}, \text{P}$) are the longest and the opposite bonds are
much shortened. In the Keggin anions, the Fe-(μ₂-O) bonds are longer than the opposite Fe–O bonds, and the trend is inverted in V. At the same time, compound I has two pentagonal bipyramidal iron(III) atoms with the μ₃-oxygen in their equatorial plane and the trans-effect of this oxygen is absent. Consequently these are the Fe-(μ₂-O) bonds that are the longest ones in I. As a result, the equatorial planes of FeO₆ and FeO₅ polyhedra are not coplanar in I–VI in contrast with [Fe₃III(μ₃-O)(μ-O₂CR)L₆]. As concerns II–VI, it is difficult to select equatorial plane of their octahedrons; and for each pair of iron(III) atoms, a coplanar Fe₂O₆ fragment can be distinguished (the angle varies from 1 to 7°). The equatorial plane of the third iron is perpendicular with their common mean plane. In I, none polyhedra are coplanar, the angles between mean planes of FeO₄ and FeO₃ species vary from 14 to 89°.

Recently, some of us discussed known examples of metallasilsesquioxanes’ supramolecular organization and main factors governing such nontrivial process. It was found that the molecular cage units of I are capable to assemble into a supramolecular composition and this process needs to be discussed. Neighboring cages of I are combined into 1D chain structures by means of the coordination contacts of sodium ions and solvating molecules of n-butanol. Average parameters of coordination junction, connecting cages, are as follows: bond length Na-O(C) 2.4 Å, angle Na-O-Na 111.8°. These values almost coincide with the values of corresponding distances and angles inside the cage, so formation of entire supramolecular assembly may be concluded. The chains are linear and are packed in an hexagonal rod packing mode (hxI in terms of RCSR notation, Figure S2). It is worth noting that the [Fe₃O₁₃] clusters are inclined to the direction of 1D chains, and the planes of the closest clusters are, again, not coplanar. The angle θ between the meanplanes passing through the iron atoms of two clusters within the silsesquioxane cage and that between the closest clusters of two connected cages is equal to 19° (the distances between the centers of the clusters d are equal to 5.8 and 14.8 Å). The θ and d values for the closest clusters from neighboring chains are equal to 6, 15, 6° and 16.3, 16.7 and 18.3 Å. Vice versa, among discrete compounds III–VI, the meanplanes of closest clusters are typically coplanar.
Figure S2. Schematic view of chains of I. Side view (a, b) and top view (c, d) are shown. Only bimetallic frameworks (a, c) or [Fe₃O₁₃] clusters (b, d) are depicted.
Figure S3. Encapsulated sodium ion Na1 (shown as its polyhedron) in the metallasilsesquioxane shell of I.
A Study of Compound I by EXAFS

Table S2. Radii of atomic shells obtained from EXAFS fitting and X-ray.

<table>
<thead>
<tr>
<th>Fe–X</th>
<th>R, Å</th>
<th>R, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EXAFS data</td>
<td>X-ray</td>
</tr>
<tr>
<td>Fe–O</td>
<td>1.94</td>
<td>1.89–1.93</td>
</tr>
<tr>
<td>Fe–O</td>
<td>2.09</td>
<td>1.98–2.04</td>
</tr>
<tr>
<td>Fe–O</td>
<td>2.26</td>
<td>2.14–2.19</td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>3.19</td>
<td>3.14–3.17</td>
</tr>
<tr>
<td>Fe–Si</td>
<td>3.44</td>
<td>3.40–3.44</td>
</tr>
<tr>
<td>Fe–Si</td>
<td>3.32</td>
<td>3.13–3.31</td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>3.43</td>
<td>3.39</td>
</tr>
<tr>
<td>Fe–Si</td>
<td>3.65</td>
<td>3.60–3.63</td>
</tr>
<tr>
<td>Fe–Na</td>
<td>3.29</td>
<td>3.12–3.29</td>
</tr>
<tr>
<td>Fe–Na</td>
<td>3.52</td>
<td>3.32–3.54</td>
</tr>
</tbody>
</table>
Magnetic Properties

Figure S4. Hysteresis loop at 1.8 K performed for I.
Kinetic analysis of catalytic oxidation

Data on selectivity of alkane oxidations given above testify that an oxidizing species generated by the system exhibits a low selectivity typical for hydroxyl radicals. The conclusion about the participation of hydroxyl radicals in the reaction under discussion is supported by the results shown in Figure 13. The mode of dependence of initial reaction rate \( W_0 = W_{ROOH} \) on initial concentration of cyclohexane (approaching a plateau at high concentration of cyclohexane) indicates a competitive interaction of the oxidizing species with the alkane and acetonitrile. Assuming that this species is hydroxyl radical we can propose the following kinetic scheme for HO\(^{•}\)-induced oxidation of the alkane, RH:

\[
\begin{align*}
I + \text{H}_2\text{O}_2 &\rightarrow \text{HO}^{•} \quad \text{(i)} \\
\text{HO}^{•} + \text{CH}_3\text{CN} &\rightarrow \text{products (1)} \\
\text{HO}^{•} + \text{RH} &\rightarrow \text{products (2)}
\end{align*}
\]

where (i) is the reaction of HO\(^{•}\) generation in the \( \text{H}_2\text{O}_2 \) decomposition with the effective rate constant \( k_i \) and with rate \( W_i \). Reactions (1) and (2) are the sequences of transformations. Their limiting stages are characterized by constants \( k_1 \) and \( k_2 \), respectively. The analysis of the proposed kinetic scheme in quasi-stationary approximation led to the following equation for the rate of alkyl hydroperoxide, ROOH, formation:

\[
W_{ROOH} = \frac{d[\text{ROOH}]}{dt} = \frac{k_2[\text{RH}]W_i}{k_1[\text{CH}_3\text{CN}] + k_2[\text{RH}]}
\]

(3)

Let us transform this equation into equation (4):

\[
\frac{[\text{RH}]}{W_0} = \frac{1}{W_i} \left\{ \frac{k_1[\text{CH}_3\text{CN}]}{k_2} + [\text{RH}] \right\}
\]

(4)

In accord with eq. (4) the dependence of \([\text{RH}]/W_0\) on \([\text{RH}]\) should be linear, and the slope of this line should be \(1/W_i\), whereas the intercept with the Y-axis should be \((1/W_i)(k_1[\text{CH}_3\text{CN}]/k_2)\). Treating the experimental dependence shown in Figure 13, Graph A using eq. (4) gives a linear dependence of \([\text{RH}]/W_0\) on \([\text{RH}]\) (Figure 13, Graph B). This indicates that the experimental data are in agreement with eq. (4). The following parameters have been calculated: \((1/W_i) = 7 \times 10^3 \text{ M}^{-1} \text{ s}\) and \((1/W_i)(k_1[\text{CH}_3\text{CN}]/k_2) = 10^3 \text{ s}\). The ratio of the intercept to the slope of the line presented in Figure 13, Graph B is equal to \((k_1[\text{CH}_3\text{CN}]/k_2) = 0.14 \text{ M}\). This value is in agreement with an assumption that \(k_1\) and \(k_2\) are rate constants of the interaction between hydroxyl radicals with acetonitrile and cyclohexane, respectively.\(^4\)\(^{1a}\), \(^4\)\(^{1b}\) Thus, we may conclude that the kinetic data support our proposal on the participation of hydroxyl radicals in the alkane oxidation.
The observed dependence of the initial rate on catalyst concentration (Figure 11, Graph A) testifies that the reaction order with respect to catalyst \( I \) is not constant and gradually changes from an order close to the second one to the first when \([I]_0\) changes in the interval from \(0.25 \times 10^4\) to \(5 \times 10^4\) M. It is not probable that the quadratic dependence of \( W_0 \) on the concentration of the introduced into the reaction mixture catalyst \( I \) is due to the catalytic activity of an aggregate formed from two molecules of starting hexanuclear iron complex \( I \). A much more reasonable assumption is that the mechanism includes a stage of monomerization of the starting complex in the presence of the acid. Subsequent dimerization of these particles to form dimeric particles affords species which are responsible for the catalytic activity in hydrogen peroxide decomposition. In the frames of this proposal we can present the mechanism of hydroxyl radical generation by the following equations:

\[
I \rightarrow 6 \text{Fe}^{3+}L \quad (5)
\]

\[
2 \text{Fe}^{3+}L \quad \rightleftharpoons \quad (\text{Fe}^{3+}L)_2 \quad (6)
\]

\[
(\text{Fe}^{3+}L)_2 + \text{H}_2\text{O}_2 \rightarrow 2 \text{Fe}^{2+}L + 2 \text{H}^+ + \text{O}_2 \quad (7)
\]

\[
\text{Fe}^{2+}L + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+}L + \text{HO}^+ + \text{HO}^- \quad (8)
\]

Here \( W_8 = W_i \) where \( W_i \) is from the previous kinetic scheme.

The analysis of kinetic scheme (5)-(8) in quasi-equilibrium approximation relative to the dimeric complex \((\text{Fe}^{3+}L)_2\) and in quasi-stationary approximation relative to concentration of \( \text{Fe}^{2+}L \) allowed us to obtain the following equation for the generation of hydroxyl radicals:

\[
W_8 = W_i = k_8[\text{Fe}^{2+}L][\text{H}_2\text{O}_2] = 2k_7[(\text{Fe}^{3+}L)_2][\text{H}_2\text{O}_2] = 2k_7K_6[\text{Fe}^{3+}L]_2[\text{H}_2\text{O}_2] \quad (9)
\]

Taking into account that reaction (5) is a fast and irreversible process and using the equation of material balance (10)

\[
6[I]_0 = [\text{Fe}^{3+}L] + 2[(\text{Fe}^{3+}L)_2] = [\text{Fe}^{3+}L] + 2K_6[\text{Fe}^{3+}L]^2 \quad (10)
\]

we can easily obtain from equations (9) and (10) the following equation (11) which relates \( W_i \) and \([I]_0\):

\[
6[I]_0 = \sqrt{\frac{W_i}{k_7K_6[\text{H}_2\text{O}_2]}} + 2\frac{W_i}{k_7[\text{H}_2\text{O}_2]} \quad (11)
\]

Taking into account also the ratio (3), namely (3a)
we can transform expression (11) to the equation (12) which contains only experimentally measured values:

\[ 6 [I]_0 = \sqrt{\frac{\Gamma W_0}{k_7 K_6 [H_2O_2]}} + 2 \frac{\Gamma W_0}{k_7 [H_2O_2]} \]

Let us present this equation in a form convenient for the analysis of experimental data:

\[ \frac{[I]_0}{\sqrt{W_0}} = \frac{1}{6} \sqrt{\frac{\Gamma}{k_7 K_6 [H_2O_2]}} + \frac{1}{3} \frac{\Gamma}{k_7 [H_2O_2]} \sqrt{W_0} \]

Figure 12, Graph B shows dependence

\[ \frac{[I]_0}{\sqrt{W_0}} \text{ on } \sqrt{W_0} \]

based on the experimental data (Figure 12, Graph A). A satisfactory agreement between the experiment and eq. (13) can be seen.

The following parameters can be obtained from the experimental data:

\[ \frac{1}{3} \frac{\Gamma}{k_7 [H_2O_2]} = 1.5 \text{ s}, \quad \frac{1}{6} \sqrt{\frac{\Gamma}{k_7 K_6 [H_2O_2]}} = 10^{-2} \text{ M}^{1/2} \text{ s}^{1/2} \]

at \([H_2O_2] = 1.5\text{ M}, [HNO_3] = 0.05 \text{ M}, [RH] = 0.46 \text{ M and 30 °C}.\)

Using the obtained data we can calculate parameters \(k_7 = 0.2 \text{ M}^{-1} \text{ s}^{-1}\) and \(K_6 = 1.2 \times 10^3 \text{ M}^{-1}.\) In Figure 12, Graph A the pink curve “a” reflects the calculated dependence \(W_0\) on \([I]_0\) in accord with the fulfilled kinetic analysis. It is obvious that the calculated parameters are in a satisfactory agreement with the experiment.
Selectivity Parameters for the Catalytic Oxidation of Hydrocarbons

Figure S5. Products obtained in the methylcyclohexane oxidation (top) and the chromatogram of the reaction mixture (bottom). Concentrations (M) of the obtained alcohols after 1 h: P5 (0.02); P6 (0.0082); P8 (0.012); P7 (0.015); P9 (0.0057); P10 (0.016); P11 (0.007); P12 (0.0026).
Experiments on the Alkane Oxidation in the Presence of $^{18}$O$_2$ and H$_2^{18}$O

Figure S6. Electron ionization mass spectra of 2-hydroxycyclohexanone. Top: the spectrum of compound labelled apparently at the hydroxyl group. Bottom: the spectrum of compound labelled apparently at the ketone group (this work).
Figure S7. Electron ionization mass spectra of 3-hydroxycyclohexanone. Top: spectrum of compound labelled apparently at the hydroxyl group. Bottom: spectrum of compound labelled apparently at the ketone group (this work).
Figure S8. Electron ionization mass spectra of 4-hydroxycyclohexanone. Top: the spectrum of compound labelled apparently at the hydroxyl group. Bottom: spectrum of compound labelled apparently at the ketone group (this work).
Catalytic oxidative amidation of alcohols

1. Description of amides

(±)-N-(α-Methylbenzyl)benzamide 4aa

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{CH}_3 & \quad \text{N} \\
\end{align*}
\]

\[^1\text{H NMR (400 MHz, CDCl}_3 \text{)} \delta \ 7.70 \ (dt, J = 8.5, 1.7 \text{ Hz, } 2\text{H}), 7.43 – 7.36 \ (m, 1\text{H}), 7.36 – 7.22 \ (m, 6\text{H}), 7.19 \ (tdd, J = 4.9, 3.1, 1.5 \text{ Hz, } 1\text{H}), 6.59 \ (s, 1\text{H}), 5.25 \ (p, J = 7.0 \text{ Hz, } 1\text{H}), 1.48 \ (d, J = 7.0 \text{ Hz, } 3\text{H}).
\]

\[^{13}\text{C NMR (101 MHz, CDCl}_3 \text{)} \delta 166.7, 143.3, 134.6, 131.5, 128.8, 128.6, 127.4, 127.1, 126.3, 49.3, 21.8.
\]

N-n-Butylbenzamide 4ab

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{C} & \quad \text{H}_3 \\
\end{align*}
\]

\[^1\text{H NMR (400 MHz, CDCl}_3 \text{)} \delta \ 7.80 – 7.71 \ (m, 2\text{H}), 7.49 – 7.41 \ (m, 1\text{H}), 7.37 \ (t, J = 7.6 \text{ Hz, } 2\text{H}), 6.52 \ (s, 1\text{H}), 3.41 \ (dd, J = 13.3, 6.7 \text{ Hz, } 2\text{H}), 1.56 \ (dt, J = 15.0, 7.4 \text{ Hz, } 2\text{H}), 1.44 – 1.31 \ (m, 2\text{H}), 0.92 \ (t, J = 7.3 \text{ Hz, } 3\text{H}).
\]

\[^{13}\text{C NMR (101 MHz, CDCl}_3 \text{)} \delta 167.7, 143.9, 134.9, 131.3, 128.5, 127.0, 39.9, 31.8, 20.2, 13.8.
\]

N-Cyclohexylbenzamide 4ac

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{Cy} & \quad \text{N} \\
\end{align*}
\]

\[^1\text{H NMR (400 MHz, CDCl}_3 \text{)} \delta \ 7.74 \ (dd, J = 5.3, 3.3 \text{ Hz, } 2\text{H}), 7.43 \ (t, J = 7.3 \text{ Hz, } 1\text{H}), 7.36 \ (t, J = 7.4 \text{ Hz, } 2\text{H}), 6.28 \ (s, 1\text{H}), 3.93 \ (tdt, J = 11.6, 8.0, 3.9 \text{ Hz, } 1\text{H}), 1.98 \ (dd, J = 12.2, 3.1 \text{ Hz, } 2\text{H}), 1.79 – 1.67 \ (m, 2\text{H}), 1.67 – 1.52 \ (m, 1\text{H}), 1.48 – 1.29 \ (m, 2\text{H}), 1.29 – 1.03 \ (m, 3\text{H}).
\]

\[^{13}\text{C NMR (101 MHz, CDCl}_3 \text{)} \delta 166.7, 135.1, 131.2, 128.5, 127.0, 48.8, 33.2, 25.6, 25.0.
\]

N-tert-Butylbenzamide 4ad

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} & \quad \text{H} \\
\end{align*}
\]

\[^1\text{H NMR (400 MHz, CDCl}_3 \text{)} \delta \ 7.81 – 7.61 \ (m, 2\text{H}), 7.49 – 7.32 \ (m, 3\text{H}), 5.98 \ (s, 1\text{H}), 1.46 \ (s, 9\text{H}).
\]

\[^{13}\text{C NMR (101 MHz, CDCl}_3 \text{)} \delta 167.0, 136.0, 131.2, 128.6, 126.8, 51.7, 29.0.
\]
**N-Benzoylpiperidine 4ae**

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} & \quad \text{Ph}
\end{align*}
\]

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (s, 5H), 3.68 (s, 2H), 3.33 (s, 2H), 1.83 – 1.32 (m, 6H).

\(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.4, 136.6, 129.4, 128.5, 126.9, 48.8, 43.2, 26.5, 25.8, 24.7.

**N-Benzoylsarcosine methyl ester 4af**

\[
\begin{align*}
\text{Ph} & \quad \text{N} \\
\text{O} & \quad \text{CO}_2\text{Me} \\
\text{CH}_3
\end{align*}
\]

Presence of rotamers 66:34

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.30 (m, 5H), 4.25 (s, 2H, 66%), 3.97 (s, 2H, 34%), 3.75 (s, 3H, 66%), 3.71 (s, 3H, 34%), 3.09 (s, 3H, 34%), 3.01 (s, 3H, 66%).

\(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.1, 169.6, 135.5, 129.9, 128.7, 128.6, 128.4, 127.2, 126.6, 53.2, 52.4, 52.2, 49.1, 38.7, 34.4.

**N,N-Dibenzylbenzamide 4ag**

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} \quad \text{Ph} \\
\text{Ph}
\end{align*}
\]

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 – 7.46 (m, 2H), 7.46 – 7.22 (m, 11H), 7.17 (s, 2H), 4.74 (s, 2H), 4.43 (s, 2H).

\(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.3, 137.0, 136.5, 136.2, 129.7, 128.9, 128.8, 128.6, 128.5, 127.7, 127.6, 127.1, 126.8, 51.6, 46.9.
2. Spectra NMR of obtained amides

$^1$H NMR (400 MHz, CDCl$_3$) of $N$-[(±)-1-phenylethyl]benzamide 4aa

![NMR Spectra](image-url)
$^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}$ of $N$-[(±)-1-phenylethyl]benzamide 4aa
$^1$H NMR (400 MHz, CDCl$_3$) of $N$-n-butyIbenzamide 4ab
$^{13}$C NMR (101 MHz, CDCl$_3$) of $N$-$n$-butylbenzamide 4ab
$^1$H NMR (400 MHz, CDCl$_3$) of N-cyclohexylbenzamide 4ac
$^{13}$C NMR (101 MHz, CDCl$_3$) of $N$-cyclohexylbenzamide 4ac
$^1$H NMR (400 MHz, CDCl$_3$) of $N$-tert-butylbenzamide 4ad
$^{13}$C NMR (101 MHz, CDCl$_3$) of $N$-tert-butylbenzamide 4ad
$^1$H NMR (400 MHz, CDCl$_3$) of N-benzoylpiperidine 4ae
$^{13}$C NMR (101 MHz, CDCl$_3$) of $N$-benzoylpiperidine 4ae
$^1$H NMR (400 MHz, CDCl$_3$) of N-benzyolsarcosine methyl ester 4af
$^{13}$C NMR (101 MHz, CDCl$_3$) of N-benzoylsarcosine methyl ester 4af
$^1$H NMR (400 MHz, CDCl$_3$) of $N,N$-dibenzylbenzamide 4ag
$^{13}$C NMR (101 MHz, CDCl$_3$) of $N,N$-dibenzylbenzamide 4ag

References