Synthesis, Characterization, and Catalytic Behaviors of β-Carbonylenamine-derived [O\textsc{´}NS]TiCl₃ Complexes in Ethylene Homo- and Copolymerization

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Spectrum of new compounds.............................................................................................................. 2

¹³C NMR of copolymers..........................................................................................................................26

X-ray crystallographic data for compounds 4m and 5b......................................................................29
$^1$H NMR of compound 4a (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4a (CDCl$_3$, 100 MHz):
$^1$H NMR of compound 4b (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4b (CDCl$_3$, 75 MHz):
$^1$H NMR of compound 4c (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4c (CDCl$_3$, 75 MHz):
$^1$H NMR of compound 4d (CDCl$_3$, 300 MHz):
$^{13}$C NMR of compound 4d (CDCl$_3$, 75 MHz):

$^1$H NMR of compound 4e (CDCl$_3$, 300 MHz):
$^{13}$C NMR of compound 4e (CDCl$_3$, 75 MHz):

$^1$H NMR of compound 4f (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4f (CDCl$_3$, 75 MHz):
$^{1}\text{H NMR of compound 4h (CDCl}_3, 300\text{ MHz):}$

$^{13}\text{C NMR of compound 4h (CDCl}_3, 75\text{ MHz):}$
$^1$H NMR of compound 4i (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4i (CDCl$_3$, 75 MHz):
$^1$H NMR of compound 4j (CDCl₃, 300 MHz):

$^{13}$C NMR of compound 4j (CDCl₃, 75 MHz):
$^1$H NMR of compound 4k (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4k (CDCl$_3$, 100 MHz):
$^1$H NMR of compound 4ll (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 4ll (CDCl$_3$, 75 MHz):
$^1$H NMR of compound 5b (CDCl₃, 300 MHz):

$^{13}$C NMR of compound 5b (CDCl₃, 100 MHz):

$^1$H NMR of compound 5c (CDCl₃, 300 MHz):
$^{13}$C NMR of compound 5c (CDCl$_3$, 75 MHz):

$^1$H NMR of compound 5d (CDCl$_3$, 300 MHz):
$^{13}$C NMR of compound 5d (CDCl$_3$, 75 MHz):

$^1$H NMR of compound 5e (CDCl$_3$, 400 MHz):
$^{13}$C NMR of compound $5e$ (CDCl$_3$, 100 MHz):
$^1$H NMR of compound 5f (CDCl$_3$, 400 MHz):

$^{13}$C NMR of compound 5f (CDCl$_3$, 100 MHz):
$^1$H NMR of compound 5g (CDCl$_3$, 300 MHz):

$^{13}$C NMR of compound 5g (CDCl$_3$, 100 MHz):
$^{19}$F NMR of compound 5g (CDCl$_3$, 282 MHz):

$^{1}$H NMR of compound 5h (CDCl$_3$, 300 MHz):
\begin{align*}
^{13}\text{C} \text{ NMR of compound } 5h \text{ (CDCl}_3, \text{ 75 MHz)}:
\end{align*}

\begin{align*}
^{1}\text{H} \text{ NMR of compound } 5i \text{ (CDCl}_3, \text{ 300 MHz)}:
\end{align*}
$^{13}$C NMR of compound 5i (CDCl$_3$, 75 MHz):

$^1$H NMR of compound 5j (CDCl$_3$, 400 MHz):
$^{13}$C NMR of compound 5j (CDCl₃, 100 MHz):

$^1$H NMR of compound 5k (CDCl₃, 400 MHz):
$^{13}$C NMR of compound 5k (CDCl$_3$, 100 MHz):

$^1$H NMR of compound 5l (CDCl$_3$, 300 MHz):
$^{13}$C NMR of compound 5l (CDCl$_3$, 75 MHz):
$^{13}$C NMR of copolymers: entry 6, Table 4 (1,2-dichlorobenzene-d$_4$, 100 MHz):

![NMR spectrum image]

$^{13}$C NMR of copolymers: entry 11, Table 4 (1,2-dichlorobenzene-d$_4$, 100 MHz):

![NMR spectrum image]
$^{13}$C NMR of copolymers: entry 12, Table 4 (1,2-dichlorobenzene-$d_4$, 100 MHz):

$^{13}$C NMR of copolymers: entry 13, Table 4 (1,2-dichlorobenzene-$d_4$, 100 MHz):
$^{13}$C NMR of copolymers: entry 3, Table 5 (1,2-dichlorobenzene-$d_4$, 100 MHz):


$^{13}$C NMR of copolymers: entry 12, Table 5 (1,2-dichlorobenzene-$d_4$, 100 MHz):


Crystal data and details of data collection and structure refinements for 4m and 5b.

<table>
<thead>
<tr>
<th>data</th>
<th>4m</th>
<th>5b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{24}$H$</em>{23}$NOS</td>
<td>C$<em>{20}$H$</em>{22}$Cl$_3$NOSTi</td>
</tr>
<tr>
<td>Fw</td>
<td>373.49</td>
<td>478.70</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.369 × 0.278 × 0.125</td>
<td>0.486 x 0.092 x 0.070</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/c</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>a / Å</td>
<td>21.6646(19)</td>
<td>7.0434(10)</td>
</tr>
<tr>
<td>b / Å</td>
<td>8.0100(7)</td>
<td>11.2130(15)</td>
</tr>
<tr>
<td>c / Å</td>
<td>24.360(2)</td>
<td>28.939(4)</td>
</tr>
<tr>
<td>α / deg</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β / deg</td>
<td>106.432(2)</td>
<td>96.423(3)</td>
</tr>
<tr>
<td>γ / deg</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V / Å³</td>
<td>4054.6(6)</td>
<td>2271.2(5)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Dc / Mg/m³</td>
<td>1.224</td>
<td>1.400</td>
</tr>
<tr>
<td>μ / mm$^{-1}$</td>
<td>0.173</td>
<td>0.832</td>
</tr>
<tr>
<td>θ max / deg</td>
<td>27.50</td>
<td>27.00</td>
</tr>
</tbody>
</table>

Reflections collected /unique: 23753 / 9119 [R(int) = 0.1314] 13122 / 4923 [R(int) = 0.0548]

Goodness-of-fit on F$^2$: 0.881 0.921

Final R indices [I>2 (I)]: R1 = 0.0654, wR2 = 0.1749  R1 = 0.0503, wR2 = 0.0842

R indices (all data): R1 = 0.1590, wR2 = 0.1931  R1 = 0.0846, wR2 = 0.0928

Data collections for compounds 4m and 5b were performed at 20 °C on a Bruker SMART diffractometer with graphite- monochromated Mo Kα radiation (λ = 0.71073 Å). The SADABS absorption correction was applied. The structure were solved by direct methods and refined on F$^2$ by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using.
the SHELXS-97 program.