Benzoyl Radicals from (Hetero)aromatic Aldehydes. Decatungstate Photocatalyzed Synthesis of Substituted Aromatic Ketones.

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1) Selected absorption spectra of starting aldehydes, TBADT and reaction mixture.

2) $^1$H-NMR and $^{13}$C-NMR spectra of compounds 3-9, 11-15
1) Selected absorption spectra of starting aldehydes, TBADT and reaction mixture.

Figure S1 Absorption spectra of selected aldehydes (0.1 M) and of TBADT (0.002 M, these are the concentration used in preparative experiments).

As it is apparent from Figure S1, when the competitive absorption of the aldehyde is not overwhelming (as for aldehydes 1a-c) the reaction occurred whereas where the absorption is comparable with TBADT (e.g. for napthaldehyde and 4-aminobenzaldehyde) no acylation took place.
Figure S2 Selected absorption spectra concerning the TBADT photocatalyzed reaction between dimethyl maleate (2a) and anisaldehyde (1a) in MeCN.

Figure S2 ruled out both a possible competitive absorption of the olefin (e.g. dimethyl maleate) used as radical traps and the formation of ground state complexes. In fact the absorption spectra of TBADT is virtually superimposable to that of the overall reaction mixture containing aldehyde 1a and olefin 2a confirming again that the photocatalyst is by far the main absorbing species in solution.
2) $^1$H-NMR and $^{13}$C-NMR spectra of compounds 3-9, 11-15

Compound 3.

$^1$H-NMR
Compound 3.

$\text{MeO}^-$

$\text{COOMe}$

$\text{COOMe}$

${}^{13}\text{C-NMR}$

![C-NMR spectrum image]
Compound 4.

\[
\begin{array}{c}
\text{MeO}^- \\
\end{array}
\]

$^1$H-NMR

![NMR spectrum](image-url)
Compound 4.

\[ \text{MeO} \]

\[ \text{O} \]

\[ \text{O} \]

$^{13}$C-NMR

![13C-NMR spectrum]
Compound 5.

$\text{\textsuperscript{1}H-NMR (CDCl}_3\text{)}$
Compound 5.

$\text{MeO}$

$\text{13C-NMR}$

![13C-NMR spectrum]

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Compound 5.

$^1$H-NMR (C$_6$D$_6$)
Compound 5.

$^1$H-NMR ($C_6D_6$, enlarged portion)
Compound 5.

Long-range COSY
Compound 5.

Long-range COSY (enlarged portion)
Compound 5.

\[
\begin{array}{c}
\text{MeO} \\
\end{array}
\]

NOESY
Compound 5.

![Chemical Structure](image)

NOESY (enlarged portion)
Compound 6.

\[ \text{H-NMR} \]

\[ \text{\textsuperscript{1}H-NMR} \]
Compound 6.

$$\text{COOMe}$$

$^{13}$C-NMR

![NMR Spectroscopy Image]
Compound 7.

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{O}
\end{array}
\]

\(^1\text{H-NMR}\)
Compound 7.

\[
\text{Cl} \quad \text{O} \\
\text{O}
\]

\(^{13}\text{C}-\text{NMR}\)

![C-NMR spectrum image]
Compound 8.

$\text{Cl} \quad \text{O} \quad \text{COOMe}$

$^1\text{H-NMR}$
**Compound 8.**

![Chemical structure of Compound 8.]

**$^{13}$C-NMR**

![$^{13}$C-NMR spectrum of Compound 8.](chart)
Compound 9.

\[ \text{COOMe} \]

$^1$H-NMR
Compound 9.

\[
\text{\begin{tikzpicture}
\draw (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw (0,0) -- (1,2) -- (1,1) -- (0,1) -- cycle;
\draw (0,0) -- (1,2) -- (1,1) -- (0,1) -- cycle;
\draw (0,0) -- (1,2) -- (1,1) -- (0,1) -- cycle;
\draw (0,0) -- (1,2) -- (1,1) -- (0,1) -- cycle;
\draw (0,0) -- (1,2) -- (1,1) -- (0,1) -- cycle;
\end{tikzpicture}}
\]

COOMe

\[^{13}\text{C-NMR}\]
Compound 11.

1H-NMR
Compound 11.

\[
\begin{align*}
\text{O} & & \text{O} \\
\text{t-BuMe}_2\text{SiO} & & \\
\end{align*}
\]

\[\text{\textsuperscript{13}C-NMR}\]

\[
\begin{array}{c}
207.16 & 198.96 & 168.11 \\
139.10 & 129.06 & 119.79 \\
77.47 & 77.80 & 77.47 \\
36.50 & 31.59 & 29.50 \\
22.07 & -10.54 & \\
\end{array}
\]
Compound 12.

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

\[^1\text{H-NMR}\]
Compound 12.

\[
\text{OHC}\begin{array}{c}
\text{O} \\
\text{OHC}
\end{array}\text{O}
\]

\(^{13}\text{C-NMR}\)
Compound 13.

\[
\begin{align*}
\text{S} & \quad \text{O} \\
\text{COOMe}
\end{align*}
\]

\textsuperscript{1}H-NMR
Compound 13.

\[ \text{S} \text{O} \text{COOMe} \]

\[^{13}\text{C}-\text{NMR}\]
Compound 14.

\[
\begin{array}{c}
\text{O} \\
\text{\text{\Large P}} \\
\text{CN}
\end{array}
\]

\(^1\text{H-NMR}\)
Compound 14.

\[
\begin{align*}
\text{O} & \quad \text{CN} \\
& \quad \text{Pyridine}
\end{align*}
\]

\[\begin{array}{c}
13\text{C-NMR}
\end{array}\]
Compound 15.

\[
\begin{array}{c}
\text{Py}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{COOMe}
\end{array}
\]

\(^1\text{H-NMR}\)
Compound 15.

\[
\text{\textbf{13C-NMR}}
\]

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