Supplementary Materials: Increased understanding of enolate additions under mechanochemical conditions

Heather Hopgood, and James Mack*

1. Spectral Data of selected compounds
\(^1\text{H-NMR}\) (400 MHz, Chloroform-\(d\)) \(\delta\) 7.93 (d, \(J = 7.2\) Hz, 2H), 7.55 (d, \(J = 7.4\) Hz, 1H), 7.43 (t, \(J = 7.6\) Hz, 2H), 7.27 (m, 7H), 7.17 (dt, \(J = 8.8, 4.5\) Hz, 3H), 4.83 (t, \(J = 7.3\) Hz, 1H), 3.74 (d, \(J = 7.3\) Hz, 2H). same as reported in Iwai, T.; Tanaka, R.; Sawamura, M., Synthesis, Coordination Properties, and Catalytic Application of Triarylmethane-Monophosphines. *Organometallics* 2016, 35 (23), 3959-3969.
$^{13}$C NMR $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.99, 144.15, 137.06, 133.09, 128.61, 128.06, 127.85, 126.39, 45.93, 44.74. same as reported in Iwai, T.; Tanaka, R.; Sawamura, M., Synthesis, Coordination Properties, and Catalytic Application of Triarylmethane-Monophosphines. *Organometallics* **2016**, *35* (23), 3959-3969.
di-addition ¹H-NMR (400 MHz, Chloroform-d) δ 7.44 (d, J = 7.5 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.22 (d, J = 7.5 Hz, 4H), 7.15 (d, J = 7.5 Hz, 5H), 7.06-7.12 (m, 8H), 7.05 – 7.00 (m, 4H), 5.26 – 5.20 (m, 1H), 4.45 (d, J = 8.9 Hz, 2H). IR (ATR): 3085.8, 3061.1, 3027.4, 2924.3, 2854.9, 1675.4, 1493.8, 728.8, 698.5 cm⁻¹ HRMS (ESI) m/z: [M + Na]+ Calcd for (C₃₄H₂₈O)Na⁺ 475.2032; Found 475.2041. colorless viscous oil
**di-addition** $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.03, 142.43, 141.51, 139.63, 132.03, 129.21, 128.70, 128.15, 128.01, 127.87, 126.43, 126.36, 55.23, 54.53.
\[ ^1\text{H-NMR} \quad ^1\text{H NMR} (400 \text{ MHz, Chloroform-}d) \delta \ 7.83 (d, J = 7.2 \text{ Hz, 2H}), 7.50 (t, J = 7.4 \text{ Hz, 1H}), 7.38 (t, J = 7.7 \text{ Hz, 2H}), 7.29 (d, J = 5.3 \text{ Hz, 3H}), 7.26-7.16 (m, 12H), 4.45 (s, 2H). \]

$^{13}$C NMR (101 MHz, CDCl₃) δ 197.24, 147.33, 147.07, 132.87, 131.31, 130.16, 129.58, 129.41, 128.55, 128.15, 128.01, 127.94, 127.53, 126.21, 49.53, 31.10

$^1$H-NMR (400 MHz, Chloroform-$d$) $\delta$ 7.81 (d, $J = 7.3$ Hz, 2H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.30-7.10 (m, 8H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 2H), 6.87 (t, $J = 7.3$ Hz, 1H), 4.38 - 4.25 (m, 2H), 1.01 (d, $J = 4$ Hz, 3H). Same as reported in Jayamani, M.; Pant, N.; Ananthan, S.; Narayanan, K.; Pillai, C. N., Synthesis of indenes from phenylpropanones using alumina catalyst. Tetrahedron 1986, 42 (15), 4325-4332.
$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 203.37, 143.60, 143.08, 136.75, 133.00, 128.68, 128.66, 128.52, 128.45, 128.13, 127.68, 126.54, 126.18, 54.32, 44.79, 18.07. Same as reported in Jayamani, M.; Pant, N.; Ananthan, S.; Narayanan, K.; Pillai, C. N., Synthesis of indenes from phenylpropanones using alumina catalyst. *Tetrahedron* **1986**, *42* (15), 4325-4332.
\textbf{\textsuperscript{1}H-NMR} (400 MHz, Chloroform-\textit{d}) $\delta$ 7.95 (d, $J = 7.2$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.29 – 7.23 (m, 5H), 7.20 (m, 4H), 7.05 (m, 6H), 4.67 (q, $J = 6.8$ Hz, 1H), 1.52 (d, $J = 6.9$ Hz, 3H). IR (ATR): 3083.9, 3058.3, 3024.9, 2972.9, 2927.9, 2870.2, 2853.2, 1681.3, 1220.25, 698.9, 607.6 cm$^{-1}$.

HRMS (ESI-MS) m/z: [M + H]$^+$ Calcd (C\textsubscript{28}H\textsubscript{24}O)$^+$ 377.1900; Found 377.1905. colorless viscous oil
$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 200.55, 143.89, 142.56, 139.41, 136.60, 132.93, 130.06, 129.54, 128.94, 128.61, 128.42, 127.83, 126.44, 77.16, 56.57, 47.43, 19.64.
Mass Spectrum

MW = 376 g/mol
$^1$H-NMR (400 MHz, Chloroform-d) δ 7.41 (d, $J$ = 8.6 Hz, 2H), 7.35 – 7.19 (m, 3H), 7.12 (m, 3H), 7.00 (d, $J$ = 6.4 Hz, 2H), 2.97 (s, 2H), 1.19 (s, 6H). same as reported in Barluenga, J.; Aguilar, E.; Olano, B.; Fustero, S., Mild and regiospecific reduction of masked 1,3-dicarbonyl derivatives to monocarbonyl compounds and primary and secondary amines. J. Org. Chem. 1988, 53 (8), 1741-4.
$^{13}$C NMR (101 MHz, Chloroform-d) δ 209.44, 139.44, 137.89, 130.66, 130.52, 128.06, 127.49, 126.44, 48.78, 46.25, 26.11. Same as reported in Barluenga, J.; Aguilar, E.; Olano, B.; Fustero, S., Mild and regiospecific reduction of masked 1,3-dicarbonyl derivatives to monocarbonyl compounds and primary and secondary amines. J. Org. Chem. 1988, 53 (8), 1741-4.
\textsuperscript{1}H-NMR  \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.28 (t, \(J = 7.0\) Hz, 1H), 7.22 – 7.14 (m, 12H), 7.10 (t, \(J = 7.0\) Hz, 2H), 4.66 (s, 1H), 1.34 (s, 6H). Same as reported in Chen, W.; Liu, Z.; Tian, J.; Li, J.; Ma, J.; Cheng, X.; Li, G., Building Congested Ketone: Substituted Hantzsch Ester and Nitrile as Alkylation Reagents in Photoredox Catalysis. \textit{J. Am. Chem. Soc.} \textbf{2016}, \textit{138} (38), 12312-12315.
Mass Spectrum

\[
\text{MW} = 314 \text{g/mol}
\]
**$^1$H-NMR** (400 MHz, Chloroform-$d$) $\delta$ 7.49 (d, $J = 7.2$ Hz, 2H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.25 (m, 11H), 7.09 (d, $J = 6.9$ Hz, 6H), 1.58 (s, 6H). IR (ATR): 3083.9, 3058.3, 3054.9, 2961.7, 2927.4, 2854.3, 1674.7, 1264.2, 734.6, 704.1 cm$^{-1}$ HRMS (ESI-MS) m/z: [M + Na]$^+$ Calcd for (C$_{29}$H$_{26}$O)$^+$ 391.2056; Found 391.2062. Colorless viscous oil
(59) $^{13}$C NMR. $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 203.80, 143.88, 143.35, 142.45, 136.35, 131.76, 130.10, 129.88, 129.52, 128.44, 127.99, 126.48, 125.87, 56.47, 51.23, 27.87.
Mass Spectrum

MW = 390 g/mol