# Highly Enantioselective Michael Addition Reactions with New Trimeric Chiral Phase Transfer Catalysts 

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Figure S1. ${ }^{1} \mathrm{H}$ NMR Spectrum of 1, 3, 5-tribromomesitylene (7).


Figure S2. ${ }^{13}$ C NMR Spectrum of 1, 3, 5-tribromomesitylene (7).


Figure S3. $\mathbf{H}^{\mathbf{1}}$ NMR Spectrum of Mesitylene based benzylcinchonine (9a).


Figure S4. $\mathrm{C}^{13}$ NMR Spectrum of Mesitylene based benzylcinchonine (9a).


Figure S5. ESI - Mass Spectrum of Mesitylene based benzylcinchonine (9a).


Figure S6. H $^{\mathbf{1}}$ NMR Spectrum of Mesitylene based allylcinchonine (9b).


Figure S7. $\mathbf{C l}^{13}$ NMR Spectrum of Mesitylene based allylcinchonine (9b).


Figure S8. ESI - Mass Spectrum of Mesitylene based allylcinchonine (9b).


Figure S9. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(3-oxo-3-phenyl-1-p-tolylpropyl) malonate (5a).


Figure S10. ${ }^{13}$ C NMR Spectrum of diethyl 2-(3-oxo-3-phenyl-1-p-tolylpropyl) malonate (5a).


Figure S11. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(1-(4-chlorophenyl)-3-oxo-3phenylpropyl)malonate (5b).

$70 \quad 16$
20

Figure S12. ${ }^{13}$ C NMR Spectrum of diethyl 2-(1-(4-chlorophenyl)-3-oxo-3phenylpropyl)malonate (5b).




Figure S13. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3phenylpropyl)malonate (5c).


Figure S14. ${ }^{13}$ C NMR Spectrum of diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3phenylpropyl)malonate (5c).


Figure S15. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(1-(4-nitrophenyl)-3-oxo-3phenylpropyl)malonate (5d).




200

$$
\begin{array}{lllll}
140 & 130 & 120 & 110 & \begin{array}{ll}
100 \\
\mathrm{f} 1(\mathrm{ppm})
\end{array}
\end{array}
$$

Figure S16. ${ }^{13}$ C NMR Spectrum of diethyl 2-(1-(4-nitrophenyl)-3-oxo-3phenylpropyl)malonate (5d).


Figure S17. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-3-oxo-1-ptolylpropylpropyl)malonate (5e).



Figure S18. ${ }^{13}$ C NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-3-oxo-1-ptolylpropylpropyl)malonate (5e).


Figure S19. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-1-(4-chlorophenyl)-3oxopropyl)malonate (5f).


Figure S20. ${ }^{13}$ C NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-1-(4-chlorophenyl)-3oxopropyl)malonate (5f).


Figure S21. ${ }^{1} \mathrm{H}$ NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-1-(4-methoxyphenyl)-3oxopropyl)malonate (5g).


Figure S22. ${ }^{13}$ C NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-1-(4-methoxyphenyl)-3oxopropyl)malonate (5g).


Figure S23. ${ }^{1}$ H NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-1-(4-nitrophenyl)-3oxopropyl)malonate (5h).


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Figure S24. ${ }^{13}$ C NMR Spectrum of diethyl 2-(3-(4-bromophenyl)-1-(4-nitrophenyl)-3oxopropyl)malonate (5h).


Figure S25. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S26. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S27. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and Toluene/ $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ condition.


Figure S28. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Toluene/ $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ condition.


Figure S29. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and Toluene $/ \mathbf{N a O H}$ condition.


Figure S30. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Toluene $/ \mathbf{N a O H}$ condition.


Figure S31. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and Toluene/KOH condition.


Figure S32. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Toluene/KOH condition.


Figure S33. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and Toluene/K ${ }^{\text {t }} \mathbf{O B u}$ condition.


Figure S34. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Toluene/K ${ }^{\text {t }} \mathbf{O B u}$ condition.


Figure S35. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and Cyclohexane $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S36. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Cyclohexane $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S37. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and THF/K $\mathbf{K O}_{3}$ condition.


Figure S38. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and THF/K2 $\mathrm{CO}_{3}$ condition.


Figure S39. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9a) and $\mathrm{ACN} / \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S40. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and $\mathrm{ACN} / \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S41. HPLC spectrum of Michael Adduct (5b) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


1 PDA Multi $1 / 254 \mathrm{~nm} 4 \mathrm{~nm}$
PDACh1 254 mm 4nm

| PeakTable |  |  |  |  |  |
| ---: | ---: | ---: | ---: | ---: | ---: |
| Peakसे | Ret. Time | Area | Height | Area $\%$ | Height $\%$ |
| 1 | 4.461 | 460833 | 38774 | 0.903 | 7.588 |
| 2 | 23.161 | 51223962 | 472181 | 99.097 | 92.412 |
| Total |  | 51690795 | 510954 | 100.000 | 100.000 |

Figure S42. HPLC spectrum of Michael Adduct (5b) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


1 PDA Multi $1 / 254 \mathrm{~nm} 4 \mathrm{~nm}$
PeakTable
PDACh1 254 nm 4 mm

| Peak | Ret. Tme | Area | Height | Area $\%$ | Height $\%$ |
| ---: | ---: | ---: | ---: | ---: | ---: |
| 1 | 13.169 | 391597 | 4333 | 1.857 | 4.614 |
| 2 | 49.491 | 20696094 | 89569 | 98.143 | 95.386 |
| Total |  | 21087691 | 93902 | 100.000 | 100.000 |

Figure S43. HPLC spectrum of Michael Adduct (5c) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


1 PDA Multi $1 / 254 \mathrm{~nm} 4 \mathrm{~nm}$
PeakTable
PDACh1 254 nm 4 nm

| Peak | Ret. Time | Area | Height | Area $\%$ | Height $\%$ |
| ---: | ---: | ---: | ---: | ---: | ---: |
| 1 | 13.169 | 391597 | 4333 | 1.857 | 4.614 |
| 2 | 49.491 | 20696094 | 89569 | 98.143 | 95.386 |
| Total |  | 21087691 | 93902 | 100.000 | 100.000 |

Figure S44. HPLC spectrum of Michael Adduct (5c) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S45. HPLC spectrum of Michael Adduct (5d) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S46. HPLC spectrum of Michael Adduct (5d) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S47. HPLC spectrum of Michael Adduct (5e) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


1 PDA Multi $1 / 254 \mathrm{~nm} 4 \mathrm{~nm}$
PeakTable
PDACh1 254 nm 4 nm

| Peak\# | Ret. Time | Area | Height | Area $\%$ | Height $\%$ |
| ---: | ---: | ---: | ---: | ---: | ---: |
| 1 | 4.136 | 1051451 | 65677 | 5.956 | 25.412 |
| 2 | 20.411 | 16603042 | 192775 | 94.044 | 74.588 |
| Total |  | 17654493 | 258452 | 100.000 | 100.000 |

Figure S48. HPLC spectrum of Michael Adduct (5e) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


1 PDA Multi $1 / 254 \mathrm{~nm} 4 \mathrm{~nm}$

PeakTable
PDACh1 254 mm 4 mm

| Peak\# | Ret. Time | Area | Height | Area \% | Height \% |
| ---: | ---: | ---: | ---: | ---: | ---: |
| 1 | 4.572 | 654306 | 34050 | 8.476 | 34.542 |
| 2 | 12.924 | 7065168 | 64526 | 91.524 | 65.458 |
| Total. |  | 7719474 | 98575 | 100.000 | 100.000 |

Figure S49. HPLC spectrum of Michael Adduct (5f) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S50. HPLC spectrum of Michael Adduct (5f) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S51. HPLC spectrum of Michael Adduct (5g) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S52. HPLC spectrum of Michael Adduct (5g) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S53. HPLC spectrum of Michael Adduct (5h) in presence of CMPTC (9a) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.


Figure S54. HPLC spectrum of Michael Adduct (5h) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ condition.

1 PDA Multi 1/254nm 4nm
PeakTable
PDA Ch1 254 nm 4 nm

| Peak\# | Ret. Time | Area | Height | Area $\%$ | Height $\%$ |
| ---: | ---: | ---: | ---: | ---: | ---: |
| 1 | 6.351 | 4665702 | 201365 | 70.603 | 86.181 |
| 2 | 23.639 | 1942699 | 32287 | 29.397 | 13.819 |
| Totai |  | 6608401 | 233652 | 100.000 | 100.000 |

Figure S55. HPLC spectrum of Michael Adduct (5a) in presence of CMPTC (9b) and Toluene $/ \mathrm{K}_{2} \mathrm{CO}_{3}$ at room temperature.

