Supplementary Material

Synthesis of C4-substituted coumarins via Pechmann condensation catalyzed by sulfamic acid. Insights into the reaction mechanism by HRMS analysis

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1. HRMS spectral data of the mechanism elucidation

Figure S1. HRMS (ESI+) analysis of an aliquot of the reaction between \(m\)-cresol and ethyl 4-chloroacetooacetate to afford the coumarin 3h.

Scheme S1. Plausible fragmentation of intermediate II into the product ion.
Figure S2. Tandem mass spectrometry (ESI-MS/MS) of the protonated molecule with m/z 271.0740 using N₂ as collision gas at 20 eV.
2. Copies of $^1$H and $^{13}$C NMR Spectra of products 3a-o

**Figure S3.** $^1$H NMR spectrum (300 MHz, acetone-$d_6$) of the product 3a.

**Figure S4.** $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3a.
Figure S5. $^1$H NMR spectrum (300 MHz, acetone-\textit{d}_6) of the product 3b.

Figure S6. $^{13}$C NMR spectrum (75 MHz, DMSO-\textit{d}_6) of the product 3b.
**Figure S7.** $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of product 3c.

**Figure S8.** $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3c.
Figure S9. $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of the product 3d.

Figure S10. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3d.
Figure S11. $^1$H NMR Spectrum (300 MHz, DMSO-$d_6$) of the product 3e.

Figure S12. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3e.
Figure S13. $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of the product 3f.

Figure S14. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3f.
Figure S15. $^1$H NMR spectrum (300 MHz, DMSO-d$_6$) of the product 3g.

Figure S16. $^{13}$C NMR spectrum (75 MHz, DMSO-d$_6$) of the product 3g.
Figure S17. $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of the product 3h.

Figure S18. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3h.
Figure S19. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of the product 3i.

Figure S20. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of the product 3i.
Figure S21. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of the product 3j.

Figure S22. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of the product 3j.
**Figure S23.** $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of the product 3k.

**Figure S24.** $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of the product 3k.
Figure S25. $^1$H NMR spectrum (300 MHz, DMSO-d$_6$) of the product 3l.

Figure S26. $^{13}$C NMR spectrum (75 MHz, DMSO-d$_6$) of the product 3l.
Figure S27. $^1$H NMR spectrum (300 MHz, DMSO-d$_6$) of the product 3m.

Figure S28. $^{13}$C NMR spectrum (75 MHz, DMSO-d$_6$) of the product 3m.
Figure S29. \textsuperscript{1}H NMR spectrum (300 MHz, DMSO-\textit{d}_6) of the product 3n.

Figure S30. \textsuperscript{13}C NMR spectrum (75 MHz, DMSO-\textit{d}_6) of the product 3n.
Figure S31. $^1$H NMR spectrum (300 MHz, DMSO-d$_6$) of the product 3o.

Figure S32. $^{13}$C NMR spectrum (75 MHz, DMSO-d$_6$) of the product 3o.