

One-pot two-step synthesis of γ -keto sulfones in deep eutectic solvent

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General Experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. ^1H NMR spectra were recorded in CDCl_3 at ambient temperature on a 500 MHz NMR spectrometer. **All the products are known compounds and their ^1H NMR and melting points are consistent with the literature and our previous report.**

Experimental Procedure

General procedure for the synthesis of 4

A 10 mL round-bottomed flask equipped with a stir bar was charged with aldehyde **1** (0.2 mmol), alkyne **2** (0.3 mmol) and $\text{CHCl}_3/\text{TfOH}$ (1:1.5, 1.0 mL). The reaction mixture was stirred at room temperature for 3 h. TLC was used to monitor the reaction. After the completion of the reaction, sodium arenesulfinate **3** (0.2 mmol) and H_2O (1 mL) were added, and the mixture was further stirred for 20 mins. Then water was added and the product was precipitated. After isolation of the product **4**, the reaction mixture was extracted with EtOAc (3×5 mL) to remove the residual organic starting materials. After removing the water by rotary evaporation, the DES was recovered and reused for next run.

Reaction process and recover the DES

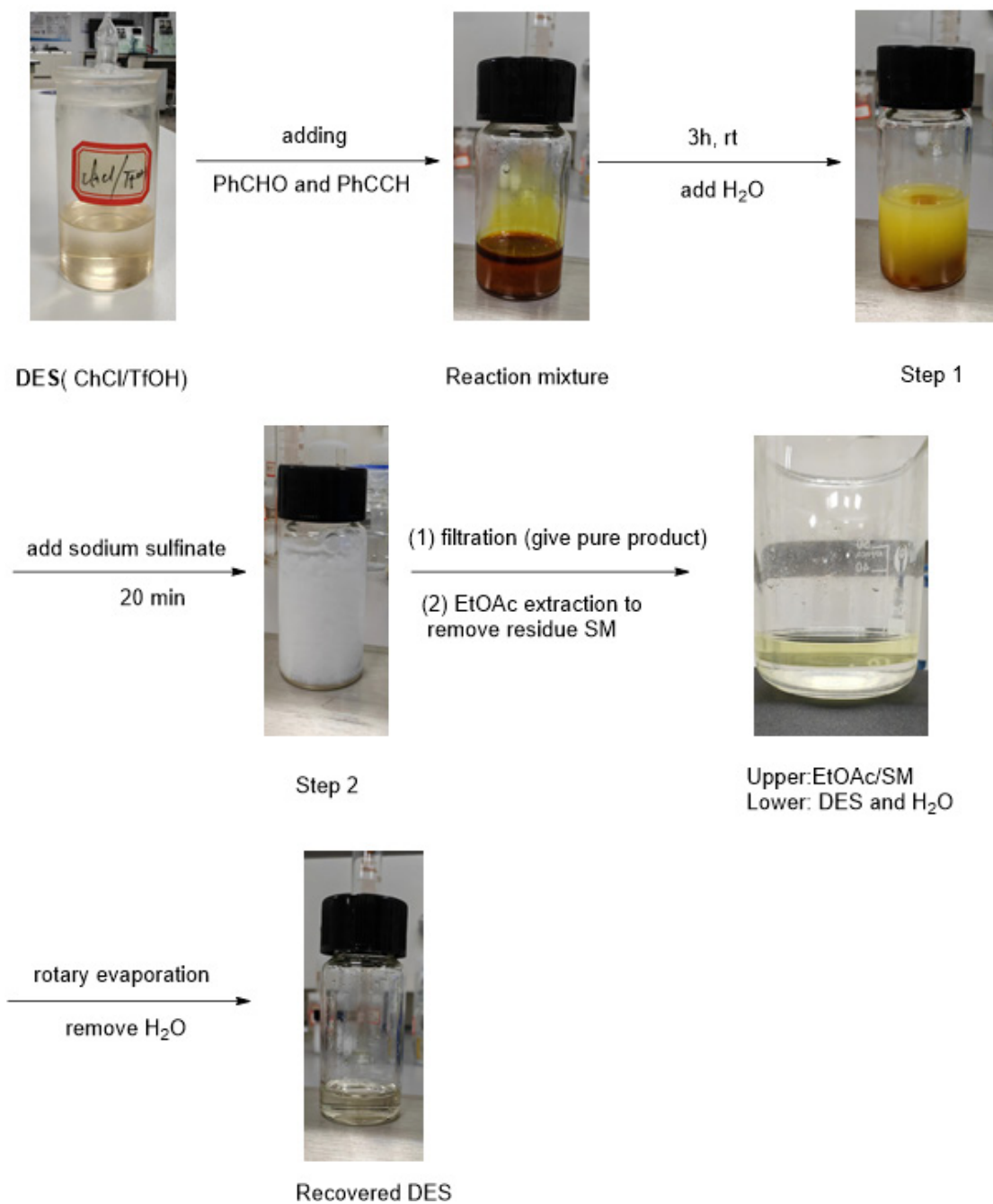
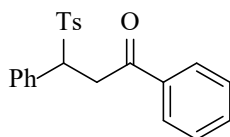
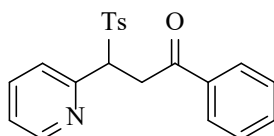


Figure S1

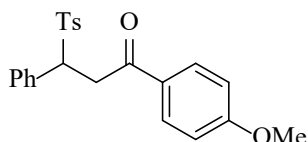
Characterization data



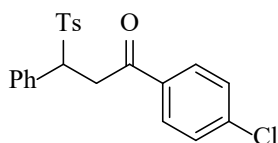
1,3-Diphenyl-3-tosylpropan-1-one (**4a**).^{S1} Yield: 65 mg, 90%. White solid, mp: 175-177 °C (lit. 176-178 °C). ¹H NMR (500 MHz, CDCl₃) δ 2.31 (s, 3H), 3.82-3.88 (dd, *J* = 18.0, 9.5 Hz, 1H), 4.01-4.05 (dd, *J* = 17.5, 3.5 Hz, 1H), 4.82-4.85 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.08-7.18 (m, 7H), 7.34-7.39 (m, 4H), 7.48-7.51 (m, 1H), 7.85 (d, *J* = 8.0 Hz, 2H).



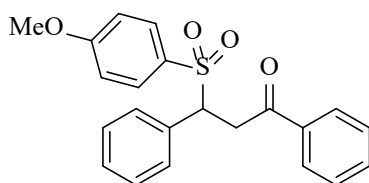
1-Phenyl-3-(pyridin-2-yl)-3-tosylpropan-1-one (**4b**).^{S2} Yield: 53 mg, 72%. White solid, mp: 186-188 °C (lit. 185-187 °C). ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3H), 3.88 (d, *J* = 18.0 Hz, 1H), 4.25-4.31 (m, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.42-7.50 (m, 5H), 7.57-7.61 (m, 2H), 7.88-7.90 (m, 3H), 8.45 (d, *J* = 4.0 Hz, 1H).



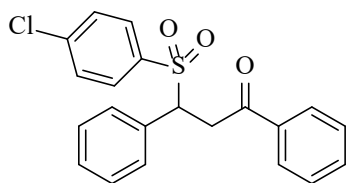
1-(4-Methoxyphenyl)-3-phenyl-3-tosylpropan-1-one (**4c**).^{S3} Yield: 66 mg, 84%. White solid, mp: 193-195 °C (lit. 198 °C). ¹H NMR (500 MHz, CDCl₃) δ 2.38 (s, 3H), 3.86 (s, 3H), 3.87-3.91 (m, 1H), 4.02-4.06 (dd, *J* = 17.5, 3.5 Hz, 1H), 4.89-4.92 (dd, *J* = 10.0, 3.5 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 7.16-7.26 (m, 7H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H).



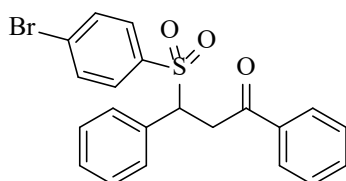
1-(4-Chlorophenyl)-3-phenyl-3-tosylpropan-1-one (**4d**).^{S3} Yield: 64 mg, 81%. White solid, mp: 188-190 °C (lit. 190-191 °C). ¹H NMR (500 MHz, CDCl₃) δ 2.38 (s, 3H), 3.84-3.89 (dd, *J* = 18.0, 9.5 Hz, 1H), 4.07-4.12 (dd, *J* = 17.5, 3.5 Hz, 1H), 4.87-4.90 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.16-7.26 (m, 7H), 7.40-7.43 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 2H).



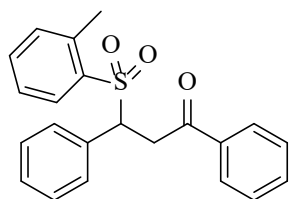
3-(4-Methoxyphenylsulfonyl)-1,3-diphenylpropan-1-one (**4e**).^{S3} Yield: 62 mg, 82%. White solid, mp: 160-162 °C (lit. 162-163 °C). ¹H NMR (500 MHz, CDCl₃) δ 3.83 (s, 3H), 3.90-3.96 (dd, *J* = 17.5, 9.5 Hz, 1H), 4.10-4.15 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.89-4.92 (dd, *J* = 9.5, 3.5 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.21-7.28 (m, 5H), 7.45-7.48 (m, 4H), 7.57-7.60 (m, 1H), 7.93-7.95 (d, *J* = 8.4 Hz, 2H).



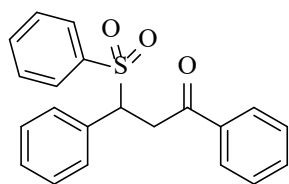
3-(4-Chlorophenylsulfonyl)-1,3-diphenylpropan-1-one (**4f**).^{S4} Yield: 67 mg, 88%. White solid, mp: 173-175 °C (lit. 175-176 °C). ¹H NMR (500 MHz, CDCl₃) δ 3.91-3.96 (dd, *J* = 17.5, 9.5 Hz, 1H), 4.12-4.16 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.93-4.96 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.19-7.27 (m, 5H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.45-7.49 (m, 4H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H).



3-(4-Bromophenylsulfonyl)-1,3-diphenylpropan-1-one (**4g**).^{S2} Yield: 71 mg, 83%. White solid, mp: 180-182 °C (lit. 178-180 °C). ¹H NMR (500 MHz, CDCl₃) δ 3.91-3.96 (dd, *J* = 17.5, 9.5 Hz, 1H), 4.12-4.16 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.93-5.07 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.20-7.29 (m, 5H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 2H).



1,3-Diphenyl-3-(*o*-tolylsulfonyl)propan-1-one (**4h**).^{S2} Yield: 57 mg, 78%. White solid, mp: 150-152 °C (lit. 151-153 °C). ¹H NMR (500 MHz, CDCl₃) δ 2.57 (s, 3H), 3.91-3.96 (dd, *J* = 17.5, 9.5 Hz, 1H), 4.11-4.16 (dd, *J* = 18.0, 3.5 Hz, 1H), 5.05-5.08 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.13-7.16 (m, 1H), 7.19-7.27 (m, 6H), 7.41-7.48 (m, 3H), 7.59-7.61 (m, 2H), 7.96 (d, *J* = 7.5 Hz, 2H).



1,3-Diphenyl-3-(phenylsulfonyl)propan-1-one (**4i**).^{S3} Yield: 58 mg, 83%. White solid, mp: 150-152 °C (lit. 152-153 °C). ¹H NMR (500 MHz, CDCl₃) δ 3.92-3.98 (dd, *J* = 17.5, 9.5 Hz, 1H), 4.12-4.16 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.94-4.96 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.20-7.27 (m, 5H), 7.37-7.41 (m, 2H), 7.45-7.48 (m, 2H), 7.55-7.60 (m, 4H), 7.96 (d, *J* = 8.0 Hz, 2H).

References

- S1. B. Sreedhar, M. A. Reddy and P. S. Reddy, *Synlett*, 2018, 1949.
S2. G. Lu, C. Cai, F. Chen, R. Ye and B. Zhou, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1804.
S3. Z. Jin, J. Xu, S. Yang, B.-A. Song and Y. R. Chi, *Angew. Chem., Int. Ed.*, 2013, **52**, 12354.
S4. H. Gilman and L. F. Cason, *J. Am. Chem. Soc.*, 1950, **72**, 3469.

Copies of ^1H NMR spectrum

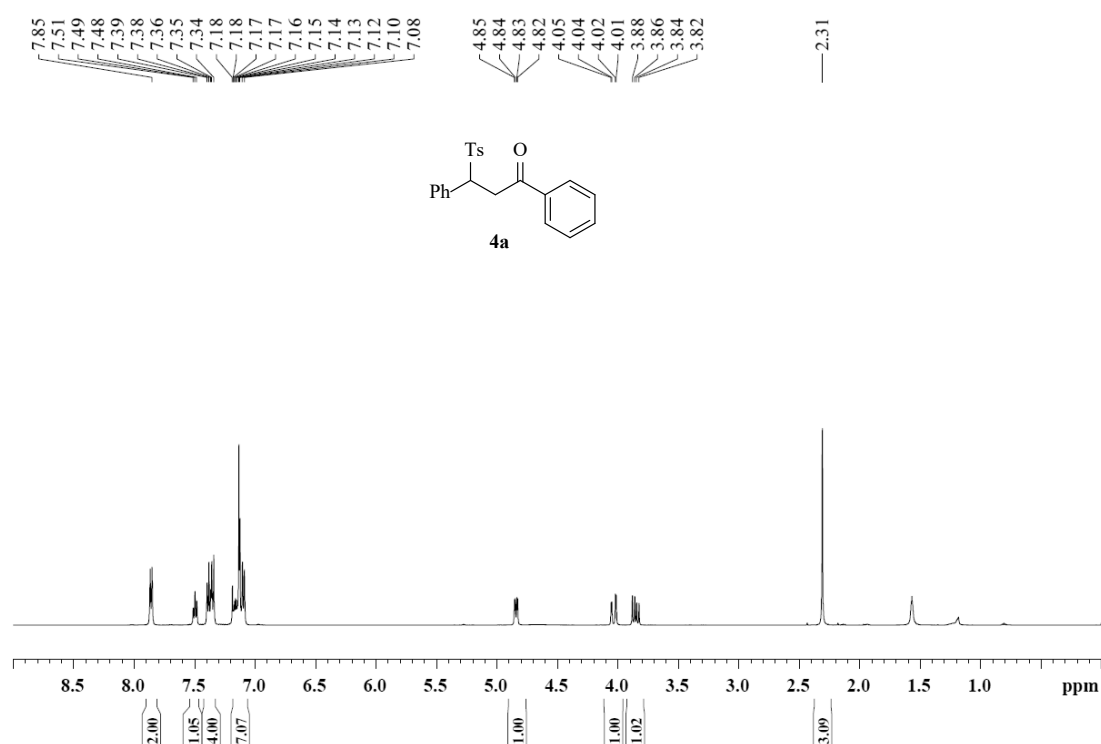


Figure S2. The ^1H NMR for compound **4a**

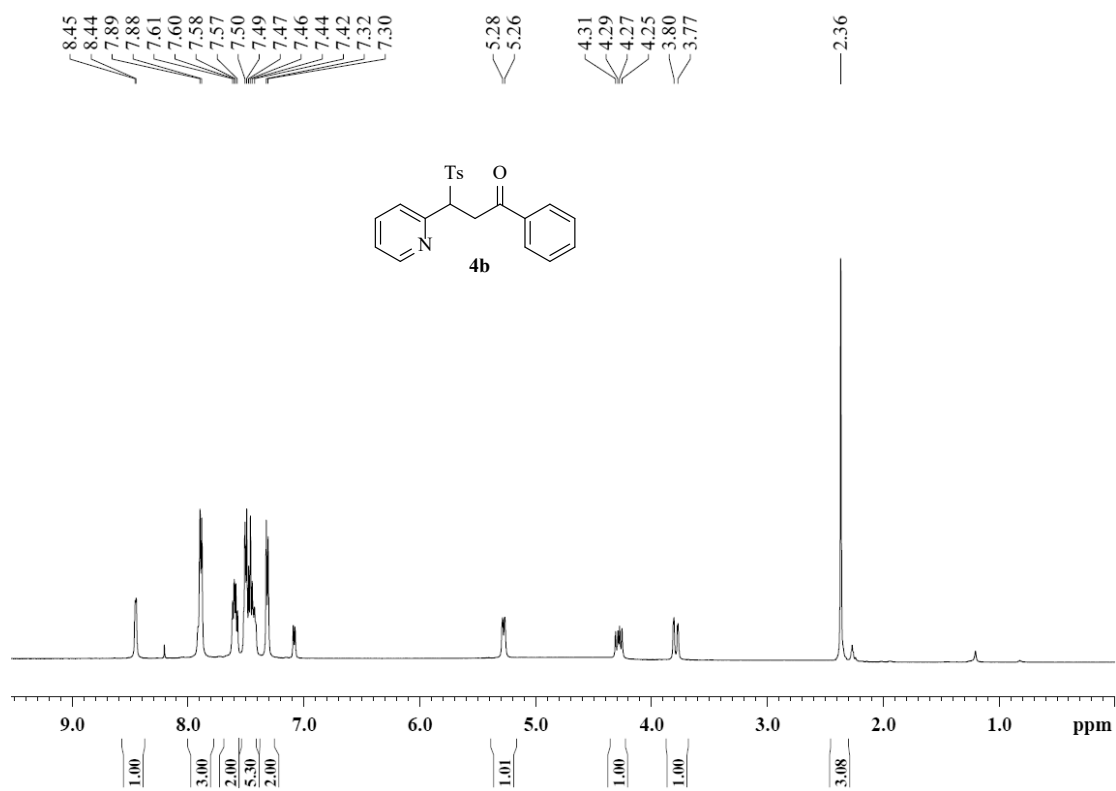


Figure S3. The ¹H NMR for compound **4b**

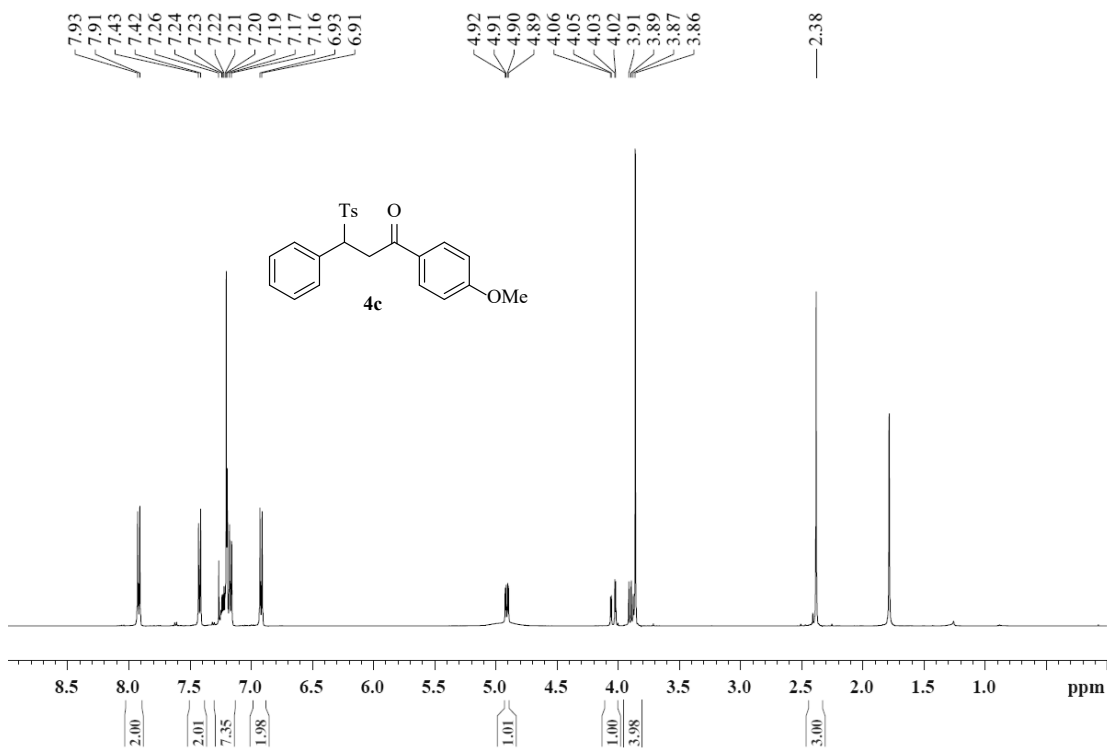


Figure S4. The ¹H NMR for compound **4c**

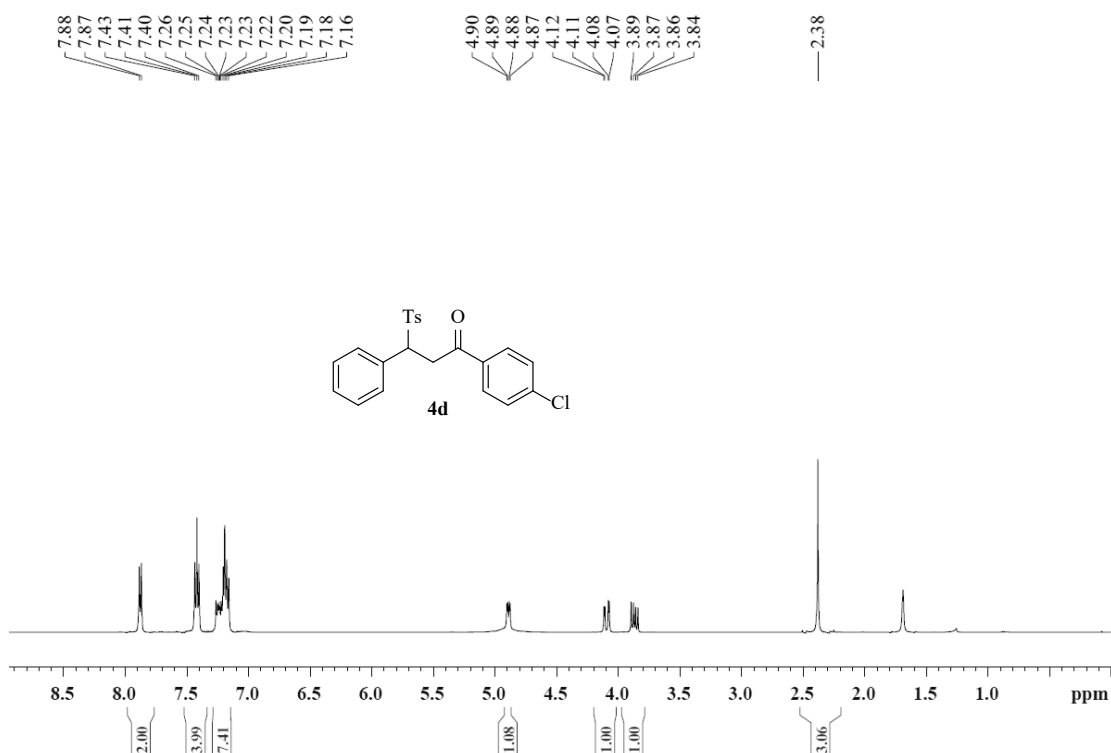


Figure S5. The ¹H NMR for compound **4d**

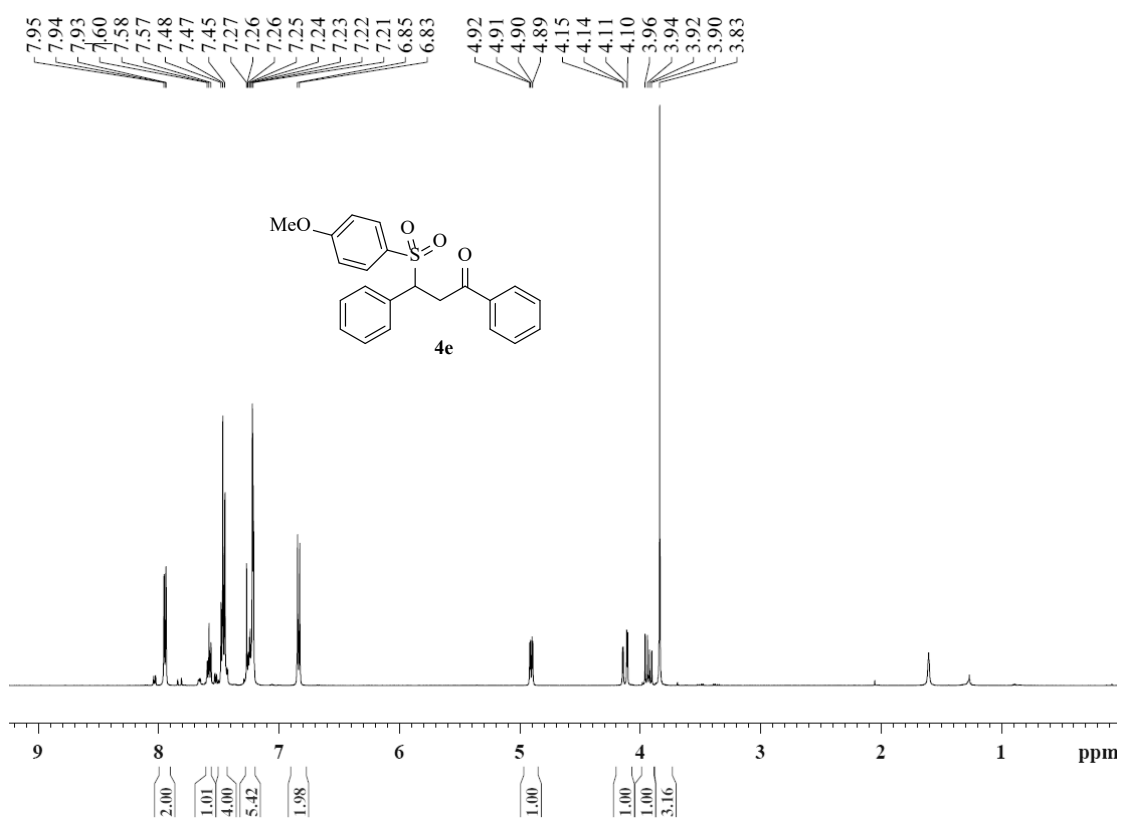


Figure S6. The ¹H NMR for compound **4e**

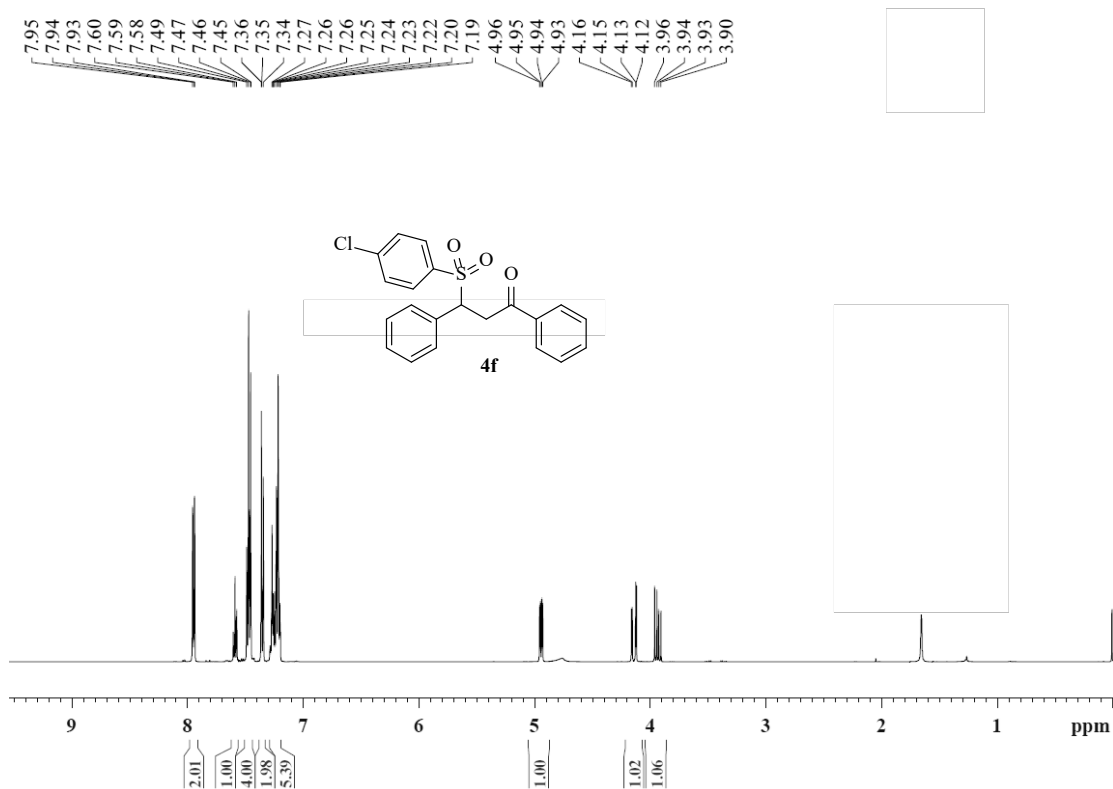


Figure S7. The ¹H NMR for compound **4f**

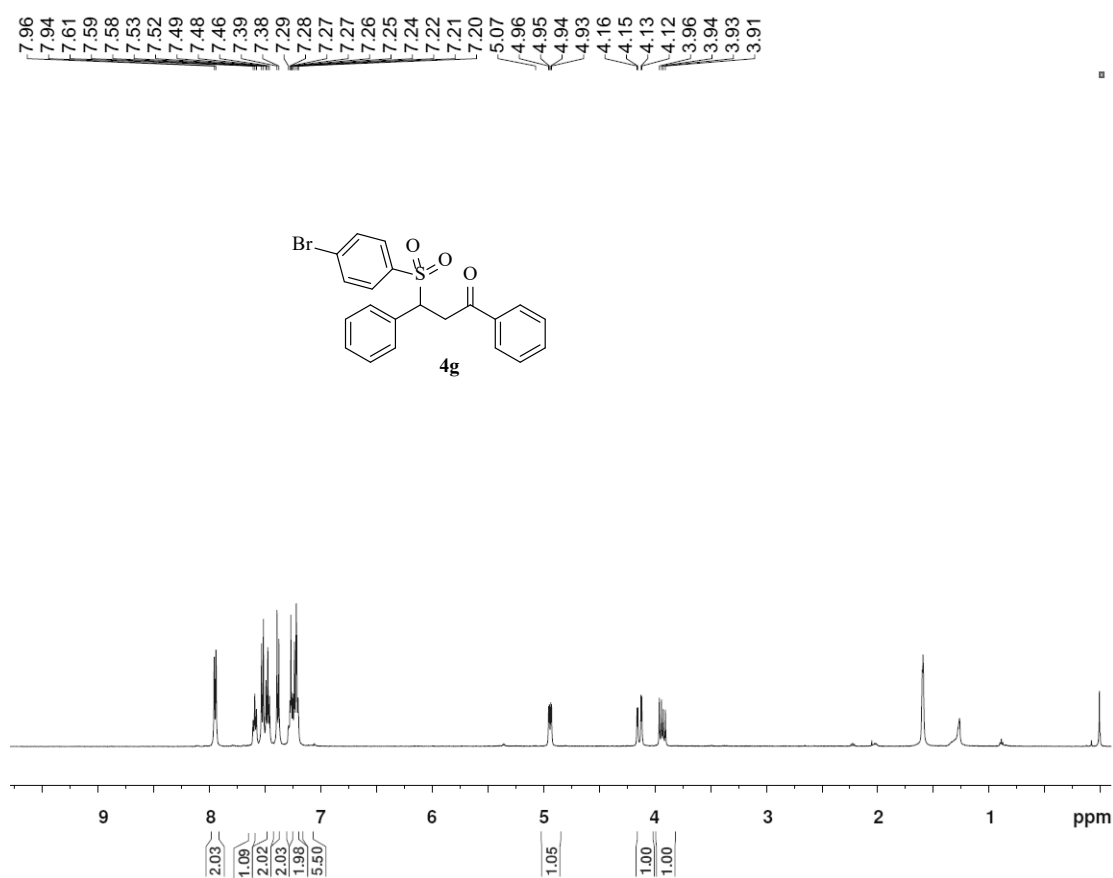


Figure S8. The ¹H NMR for compound **4g**

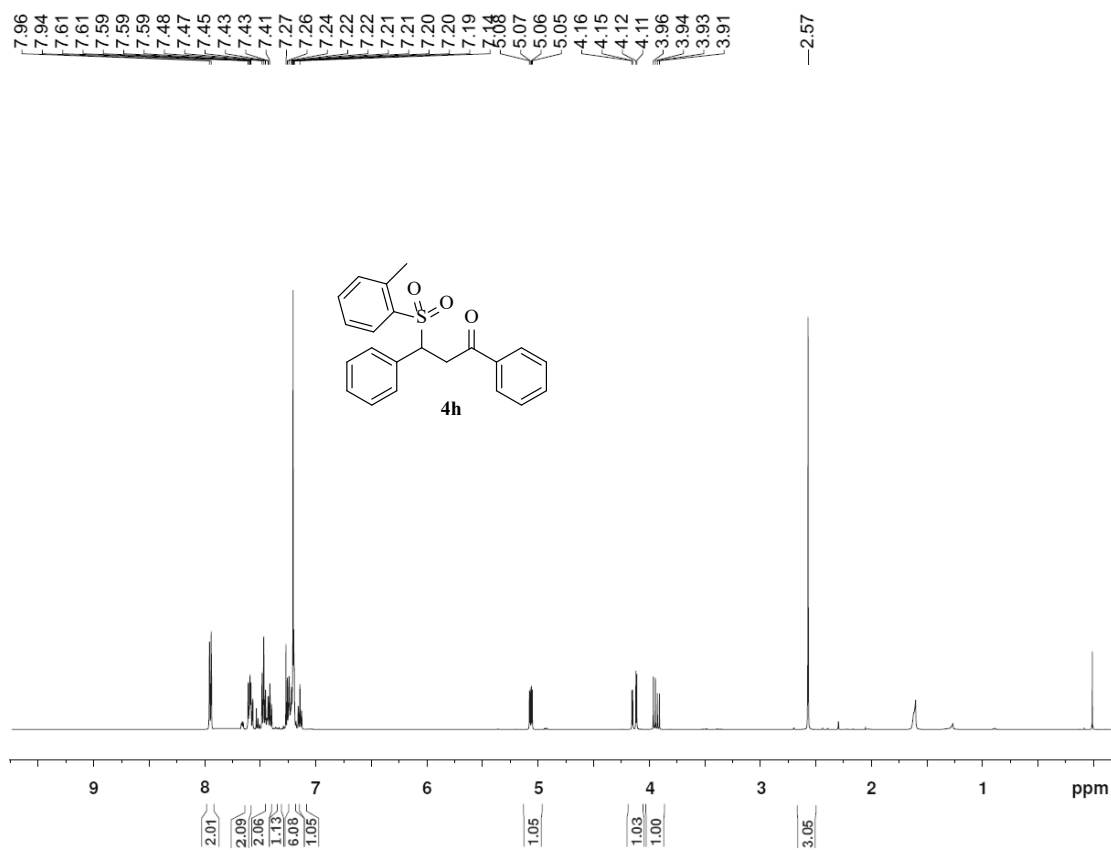


Figure S9. The ¹H NMR for compound **4h**

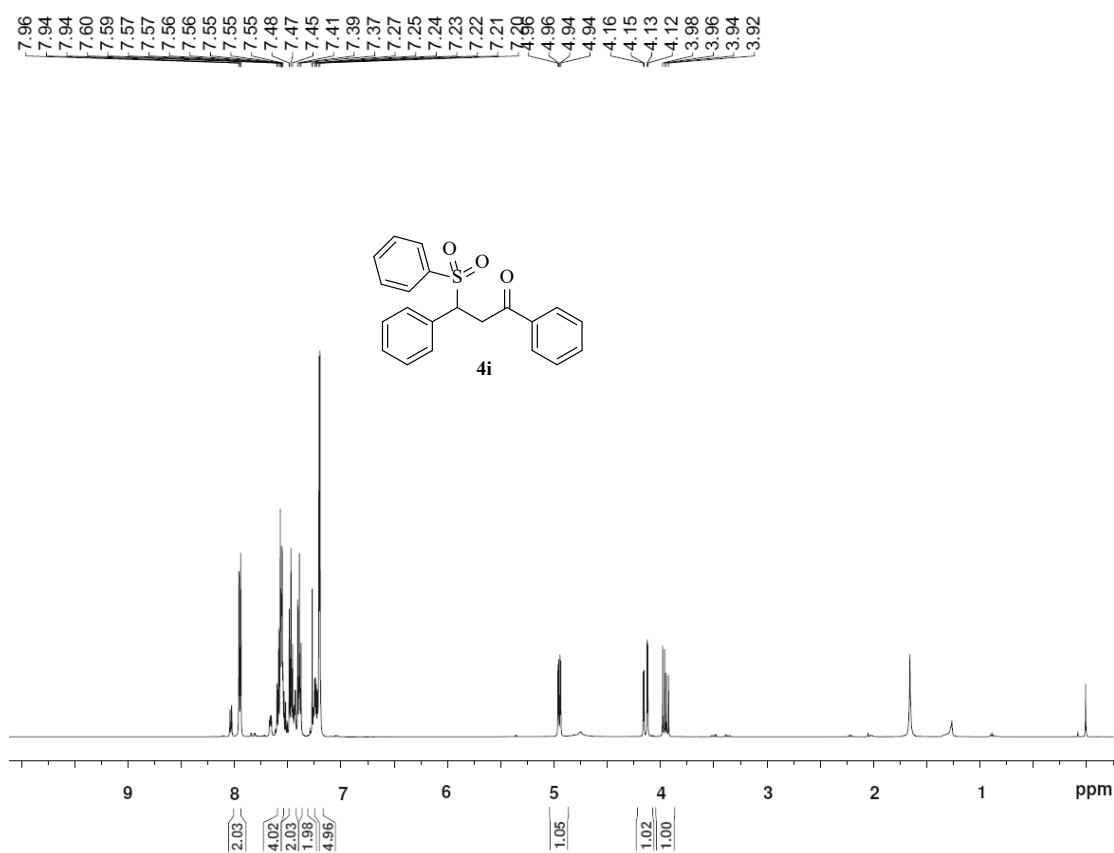


Figure S10. The ¹H NMR for compound **4i**