

Enantiocomplementary bioreduction of 1-(arylsulfanyl)propan-2-ones

Emese Sándor ¹, Pál Csuka ¹, László Poppe ^{1*} and József Nagy ^{1*}

¹ Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1111 Budapest, Műegyetem rkp. 3, Hungary

* Correspondence: LP: poppe.laszlo@vbk.bme.hu; NJ: nagy.jozsef@vbk.bme.hu

Table of contents

S1. Gas chromatography.....	2
S1.1. Temperature programs	2
S1.2. Molar response factors.....	2
S1.3. Gas chromatograms of the starting materials and products	3
S1.4. Gas chromatograms for checking the enantiomeric composition of the products	6
S2. Spectra of the starting materials and products	8

S1. Gas chromatography

S1.1. Temperature programs

Table S1. GC methods and retention times of **2a-e**, (\pm) **1a-e** and (*S*)- and (*R*)-**1d** and (*S*)- and (*R*)-**5a-c,e** to determine conversion and enantiomeric composition.

Substrate	Method	Retention time (min)			
		2	(\pm)-1	(<i>R</i>)-5	(<i>S</i>)-5
2a	160 °C, 5 min; 5 °C min ⁻¹ to 200 °C; 200 °C, 1 min	4.3	5.3		
2a	120 °C, 7 min; 0.8 °C min ⁻¹ to 140 °C			10.4	10.6
2b	160 °C, 5 min; 5 °C min ⁻¹ to 200 °C; 1 min	6.2	7.2		
2b	110 °C, 5 min; 0.8 °C min ⁻¹ to 130 °C			21.4	21.7
2c	170 °C, 3 min; 4 °C min ⁻¹ to 200 °C; 3 min	6.5	7.7		
2c	120 °C, 7 min; 0.8 °C min ⁻¹ to 140 °C			26.4	26.7
2d	170 °C 3 min; 4 °C min ⁻¹ to 200 °C; 3 min	8.9	10.5		
2d	150 °C, 20 min; 0.8 °C min ⁻¹ to 175 °C; 5 °C min ⁻¹ to 190 °C			36.9 ¹	37.4 ¹
2e	160 °C, 5 min; 5 °C min ⁻¹ to 200 °C; 1 min	9.9	10.9		
2e	120 °C, 7 min; 0.8 °C min ⁻¹ to 140 °C			28.3	28.6

¹In the case of (*R*)-**1d** and (*S*)-**1d**, derivatization was not necessary.

S1.2. Molar response factors

To determine molar response factors for FID signals in GC, chromatograms of calibration samples from synthetically prepared (\pm)-**1a-e** and **2a-e** in 1:1 molar ratio were determined. The calculated molar response factors are shown in Table S2.

Table S2. Molar response factors of alcohols **1a-e** to ketones **2a-e**.

Ketone	Response factor
2a	0.9893
2b	1.0250
2c	1.0457
2d	0.7280
2e	0.9122

S1.3. Gas chromatograms of the starting materials and products

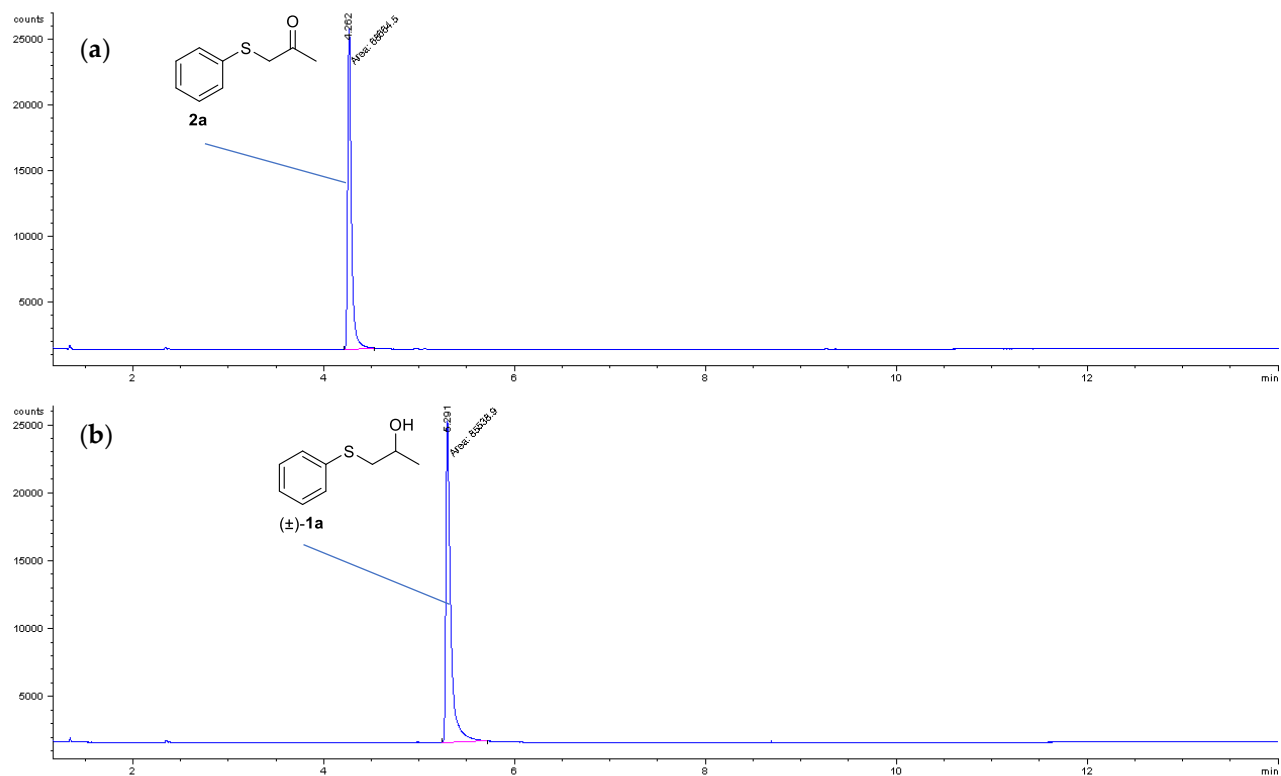


Figure S1. Chromatogram of (a) 1-(phenylsulfanyl)propan-2-one **2a** and (b) 1-(phenylsulfanyl)propan-2-ol (\pm)-**1a**.

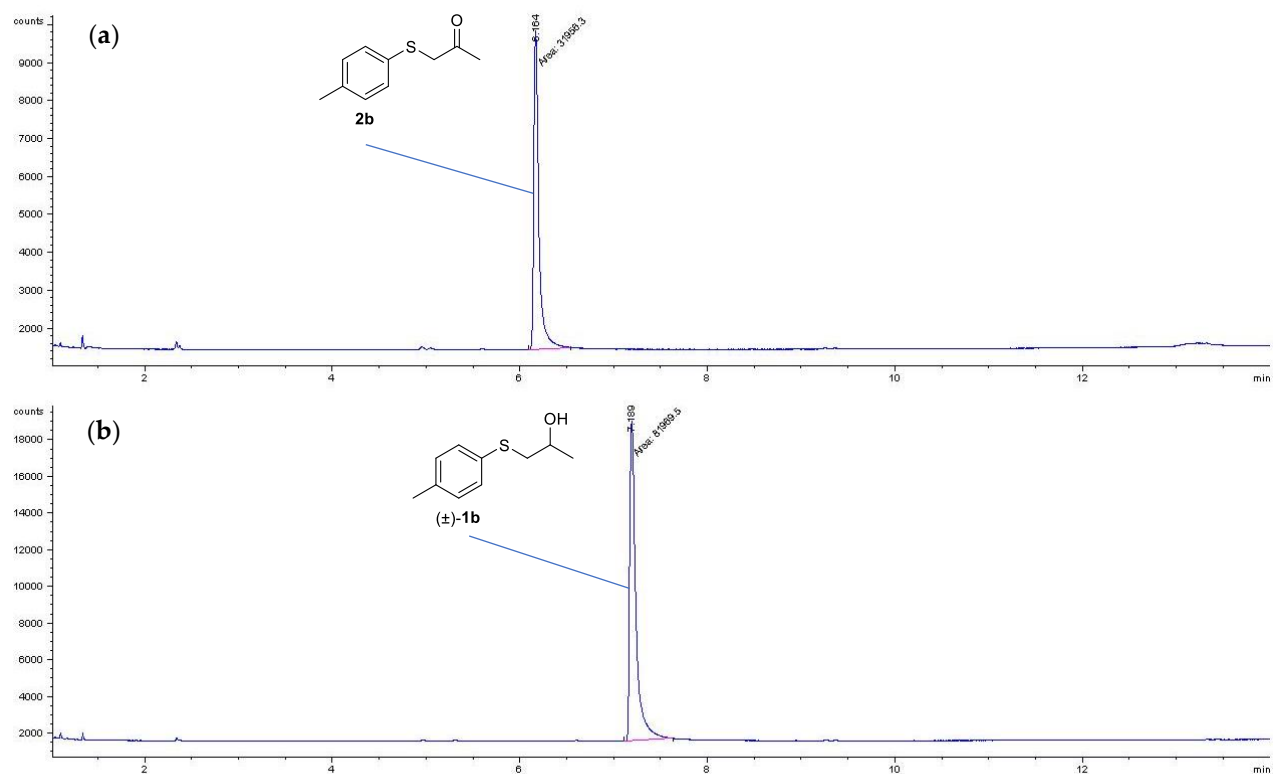


Figure S2. Chromatogram of (a) 1-[(4-methylphenyl)sulfanyl]propan-2-one (**2b**) and (b) 1-[(4-methylphenyl)sulfanyl]propan-2-ol (\pm)-**1b**.

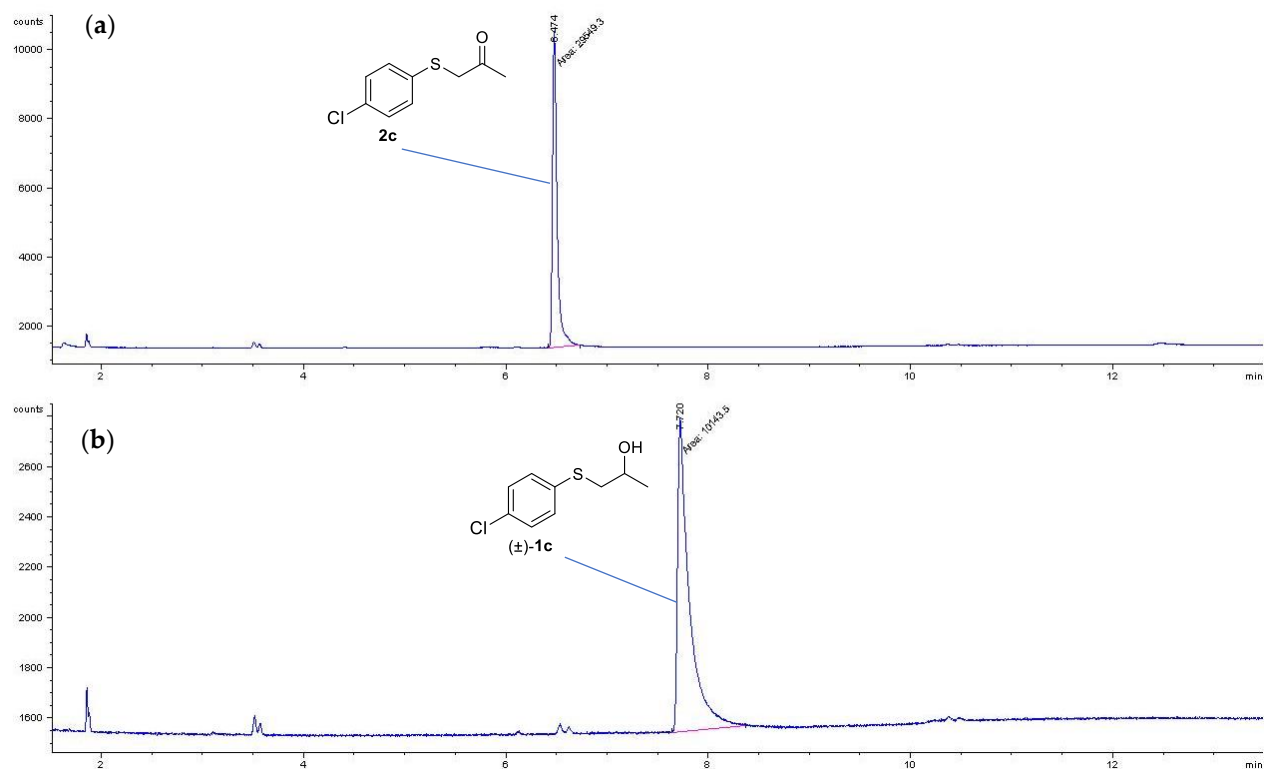


Figure S3. Chromatogram of (a) 1-[(4-chlorophenyl)sulfanyl]propan-2-one (**2c**) and (b) 1-[(4-chlorophenyl)sulfanyl]propan-2-ol (**(±)-1c**).

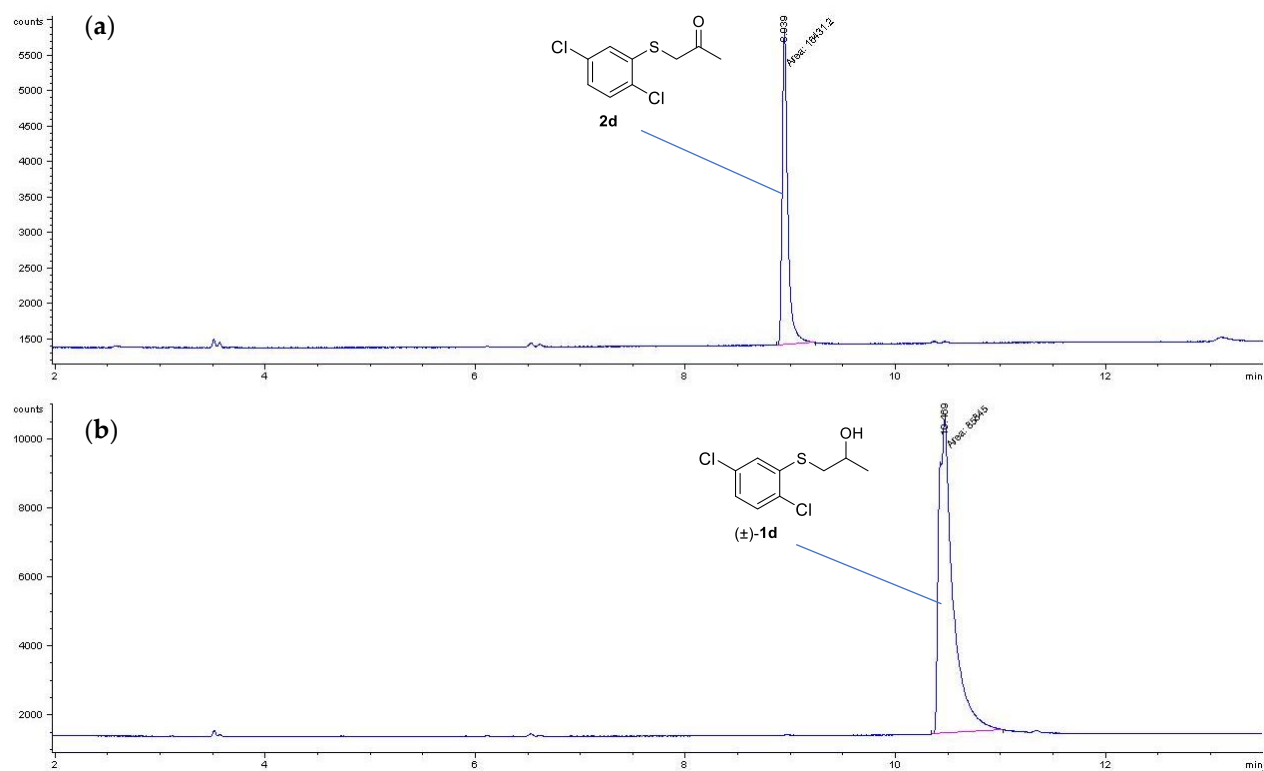


Figure S4. Chromatogram of (a) 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-one **2d** and (b) 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-ol (**(±)-1d**).

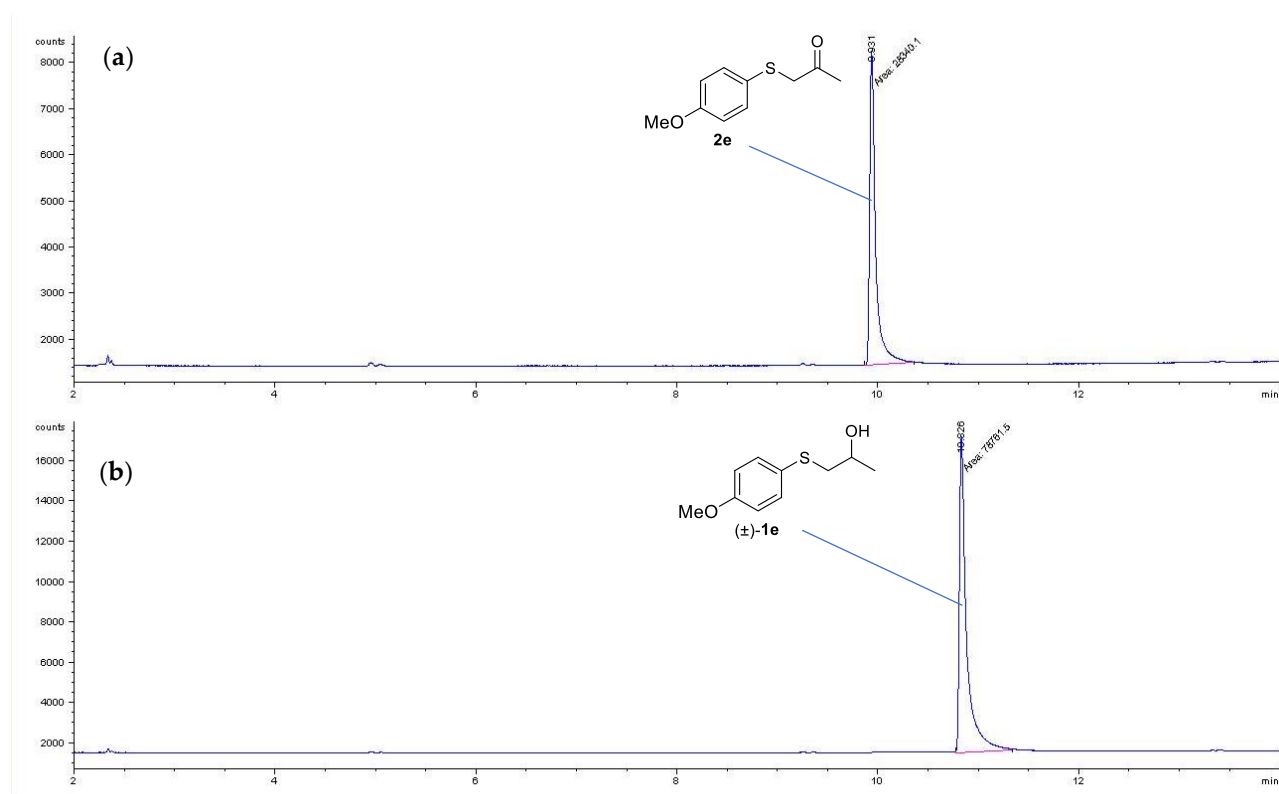


Figure S5. Chromatogram of (a) 1-[(4-methoxyphenyl)sulfanyl]propan-2-one (2e) and (b) 1-[(4-methoxyphenyl)sulfanyl]propan-2-ol (±)-1e.

S1.4. Gas chromatograms for checking the enantiomeric composition of the products

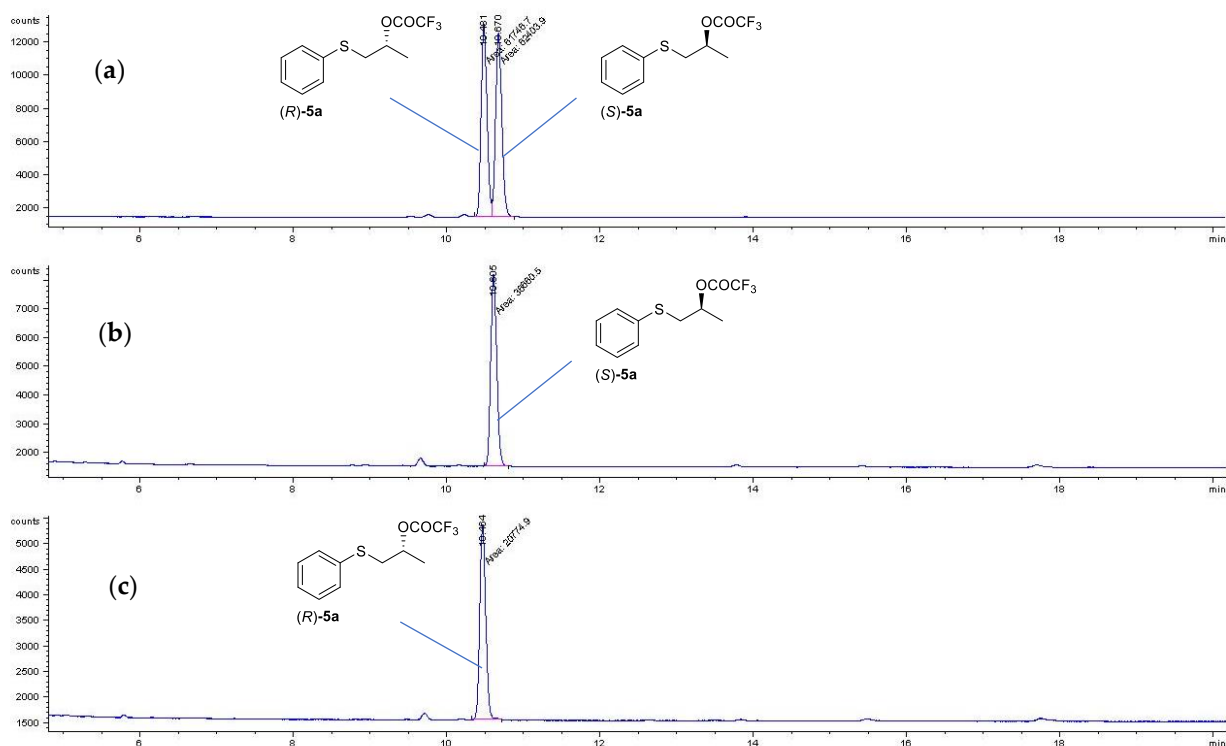


Figure S6. Chromatogram of (a) racemic (\pm)-1-(phenylsulfanyl)propan-2-yl trifluoroacetate [(R)-5a and (S)-5a]; (b) derivatized sample from bioreduction of 1-(phenylsulfanyl)propan-2-one **2a** with WY12 after 24 h and (c) from bioreduction with LkADH after 24 h.

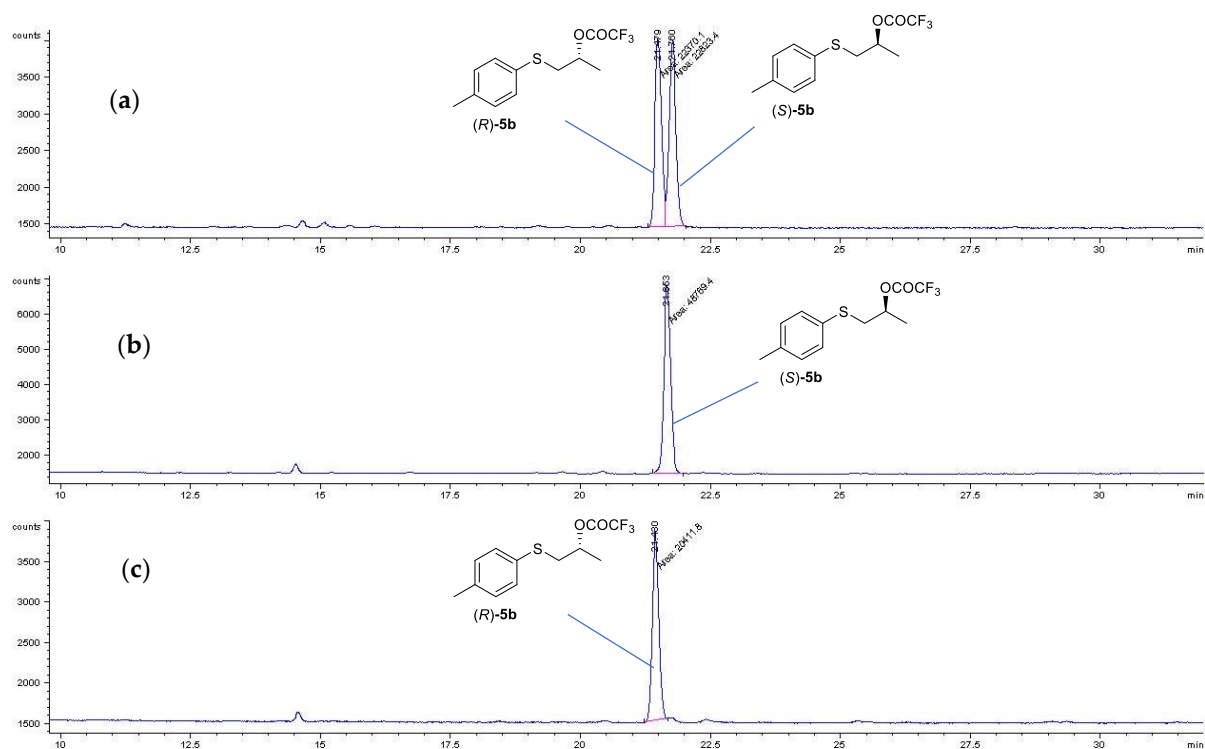


Figure S7. Chromatogram of (a) racemic (\pm)-1-[(4-methylphenyl)sulfanyl]propan-2-yl trifluoroacetate [(R)-5b and (S)-5b]; (b) derivatized sample from bioreduction of 1-[(4-methylphenyl)sulfanyl]propan-2-one **2b** with WY12 after 24 h and (c) from bioreduction with LkADH after 24 h.

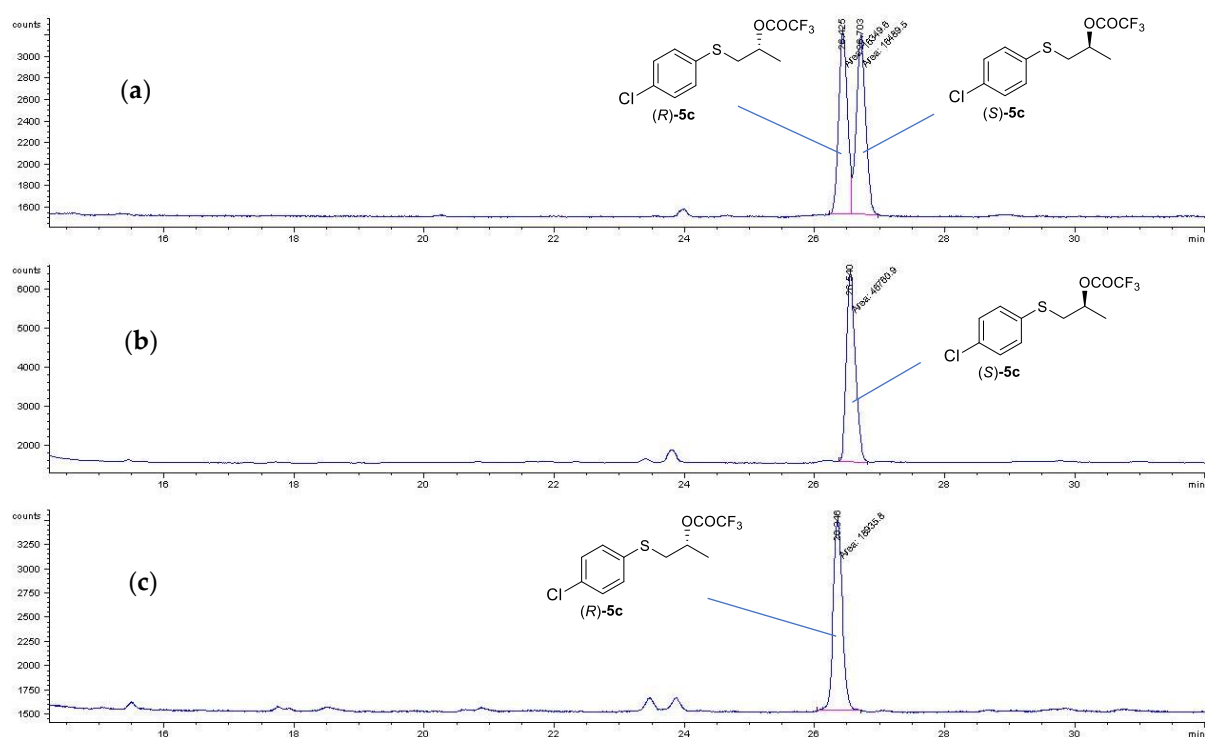


Figure S8. Chromatogram of (a) racemic (\pm)-1-[(4-chlorophenyl)sulfanyl]propan-2-yl trifluoroacetate [(R)-5c and (S)-5c]; (b) derivatized sample from bioreduction of 1-[(4-chlorophenyl)sulfanyl]propan-2-one 2c with WY12 after 24 h and (c) from bioreduction with LkADH after 24 h.

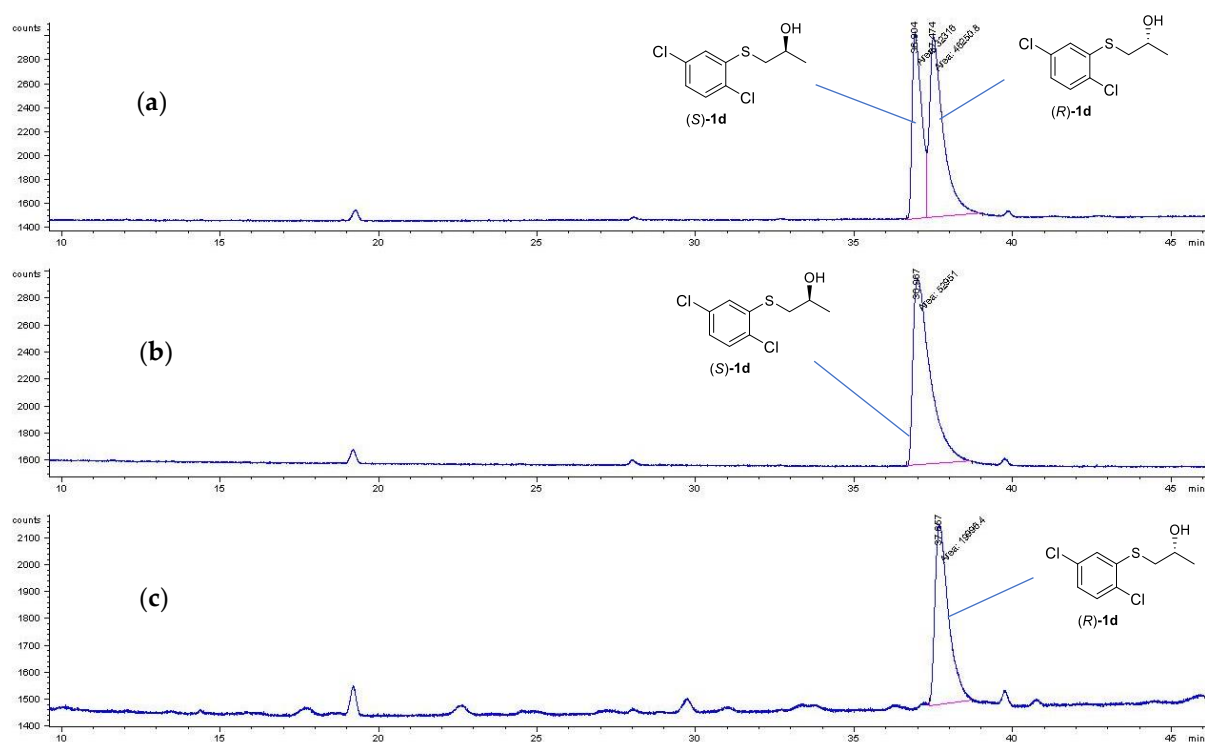


Figure S9. Chromatogram of (a) racemic (\pm)-1-[(2,5-dichlorophenyl)sulfanyl]propan-2-ol [(S)-1d and (R)-1d]; (b) sample from bioreduction of 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-one 2c with WY12 after 24 h and (c) from bioreduction with LkADH after 24 h.

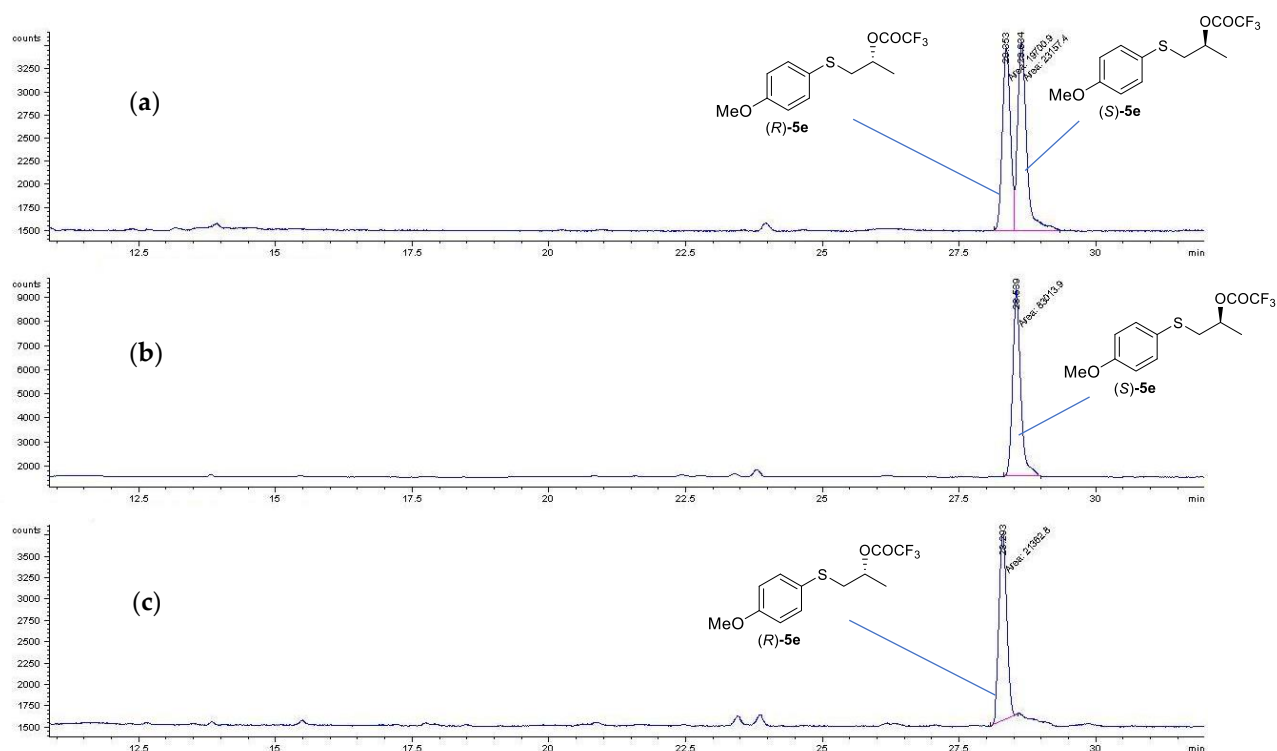


Figure S10. Chromatogram of (a) racemic (\pm)-1-[(4-methoxyphenyl)sulfanyl]propan-2-yl trifluoroacetate [(R)-5e and (S)-5e]; (b) derivatized sample from bioreduction of 1-[(4-methoxyphenyl)sulfanyl]propan-2-one 2e with WY12 after 24 h and (c) from bioreduction with LkADH after 24 h.

S2. Spectra of the starting materials and products

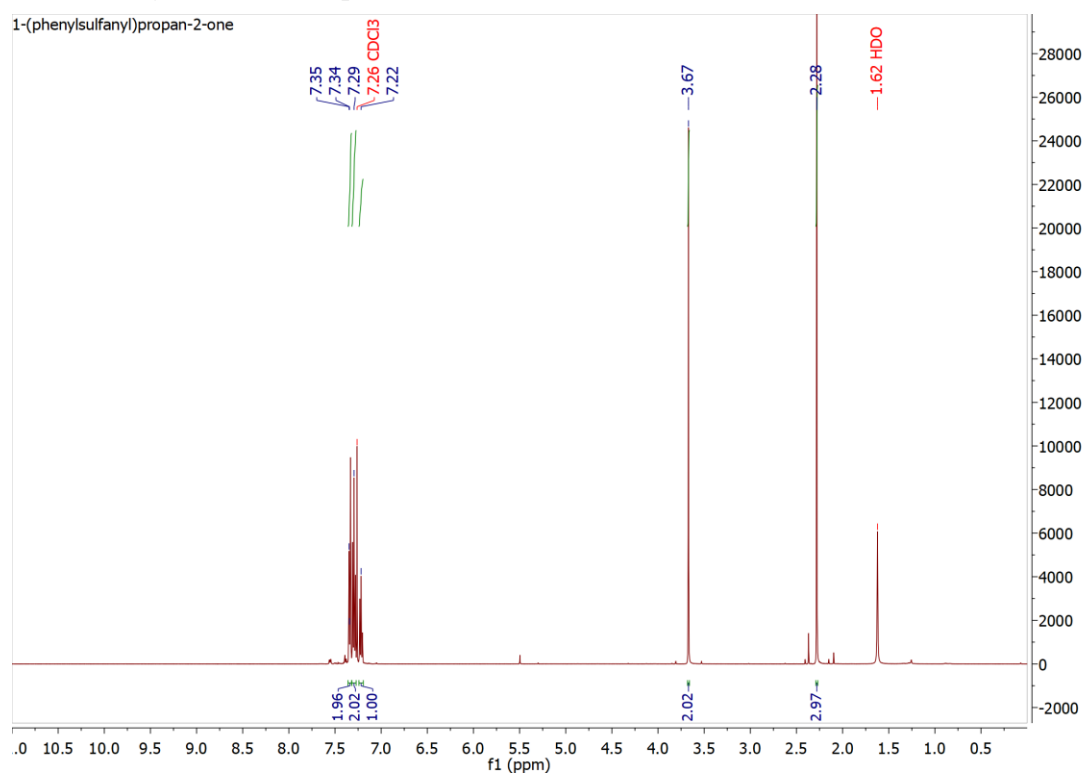


Figure S11. ^1H NMR spectrum of 1-(phenylsulfanyl)propan-2-one 2a.

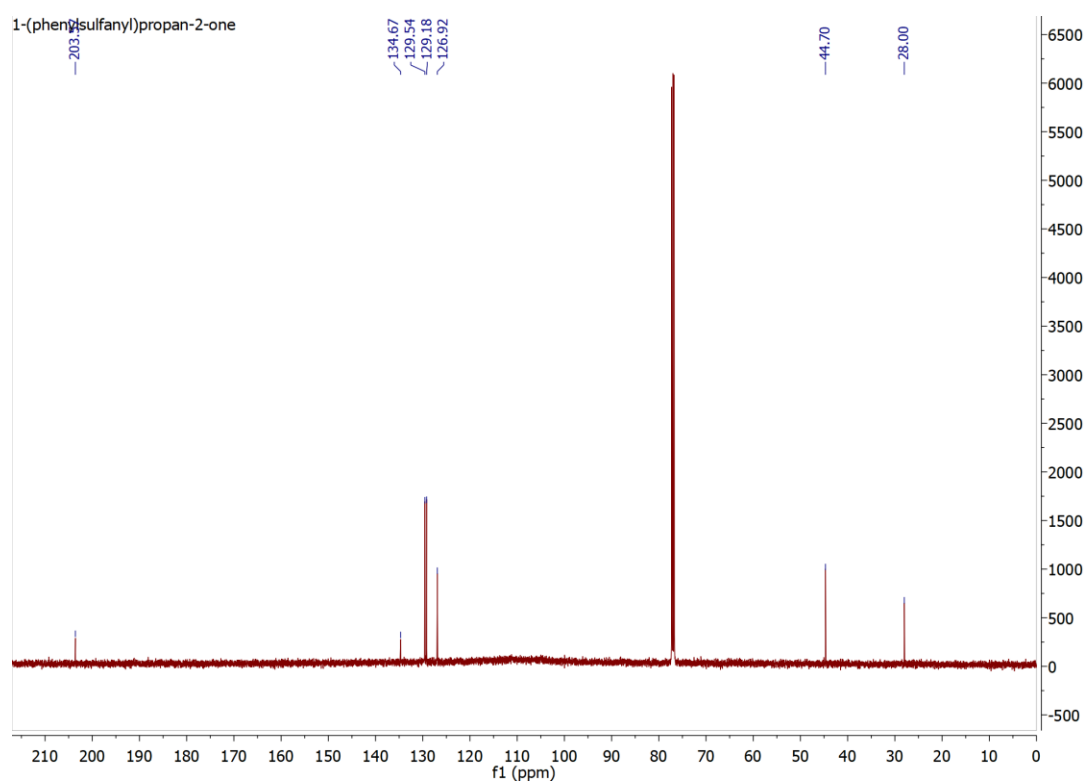


Figure S12. ¹³C NMR spectrum of 1-(phenylsulfonyl)propan-2-one 2a.

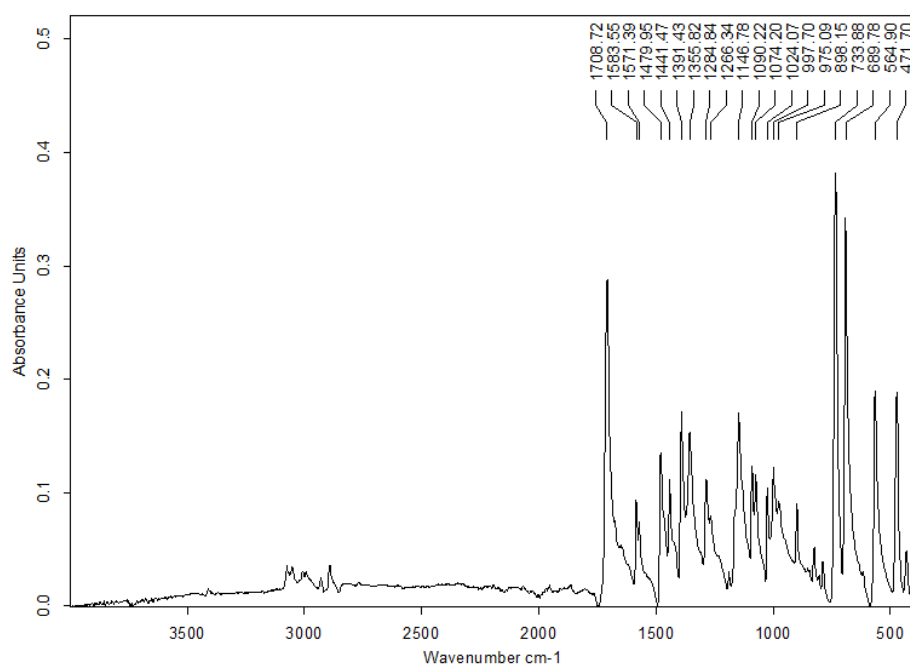


Figure S13. IR spectrum of 1-(phenylsulfonyl)propan-2-one 2a.

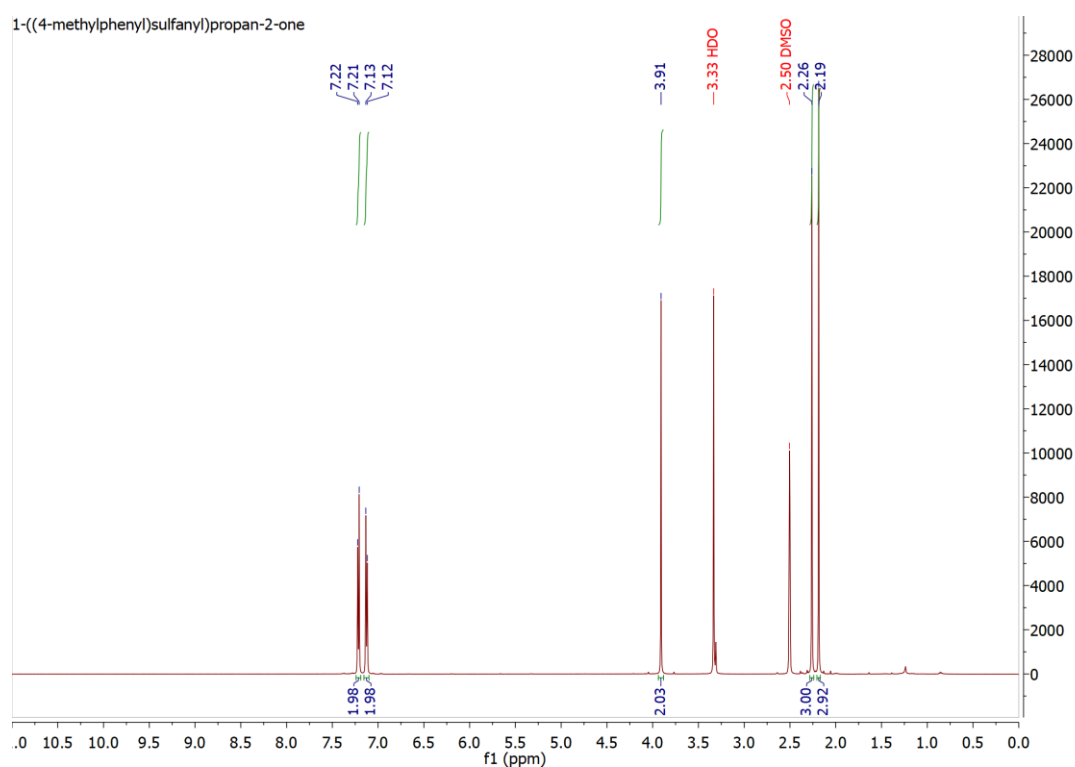


Figure S14. ¹H NMR spectrum of 1-[(4-methylphenyl)sulfonyl]propan-2-one **2b**.

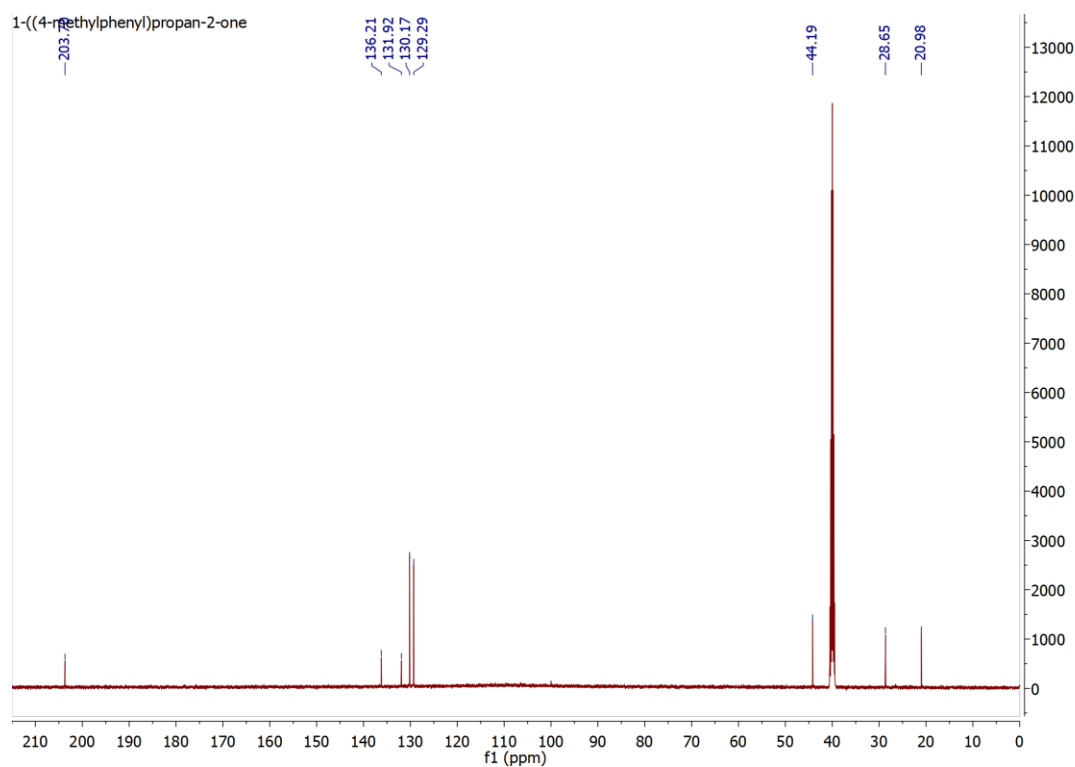


Figure S15. ¹³C NMR spectrum of 1-[(4-methylphenyl)sulfonyl]propan-2-one **2b**.

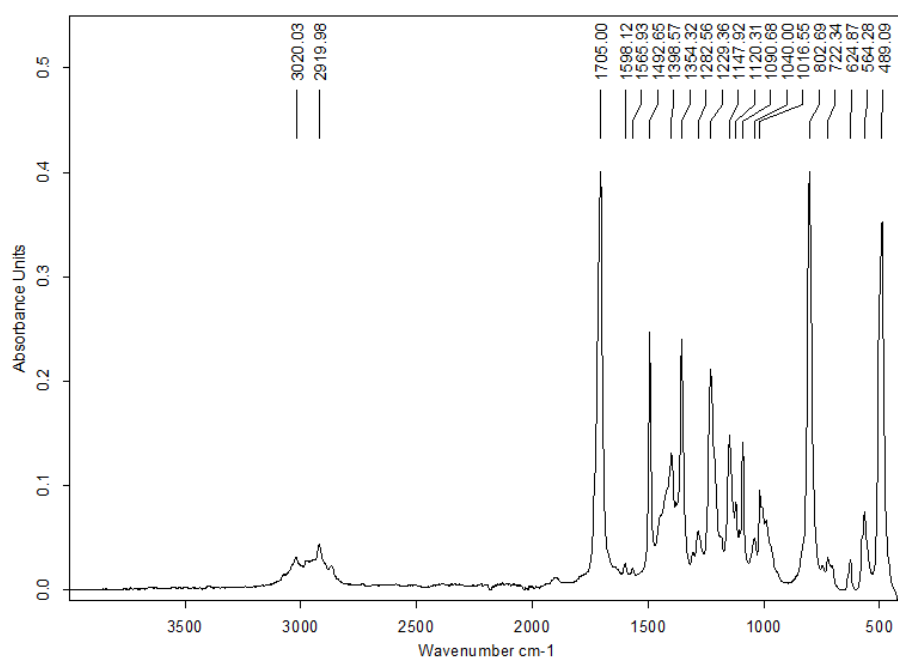


Figure S16. IR spectrum of 1-[(4-methylphenyl)sulfanyl]propan-2-one **2b**.

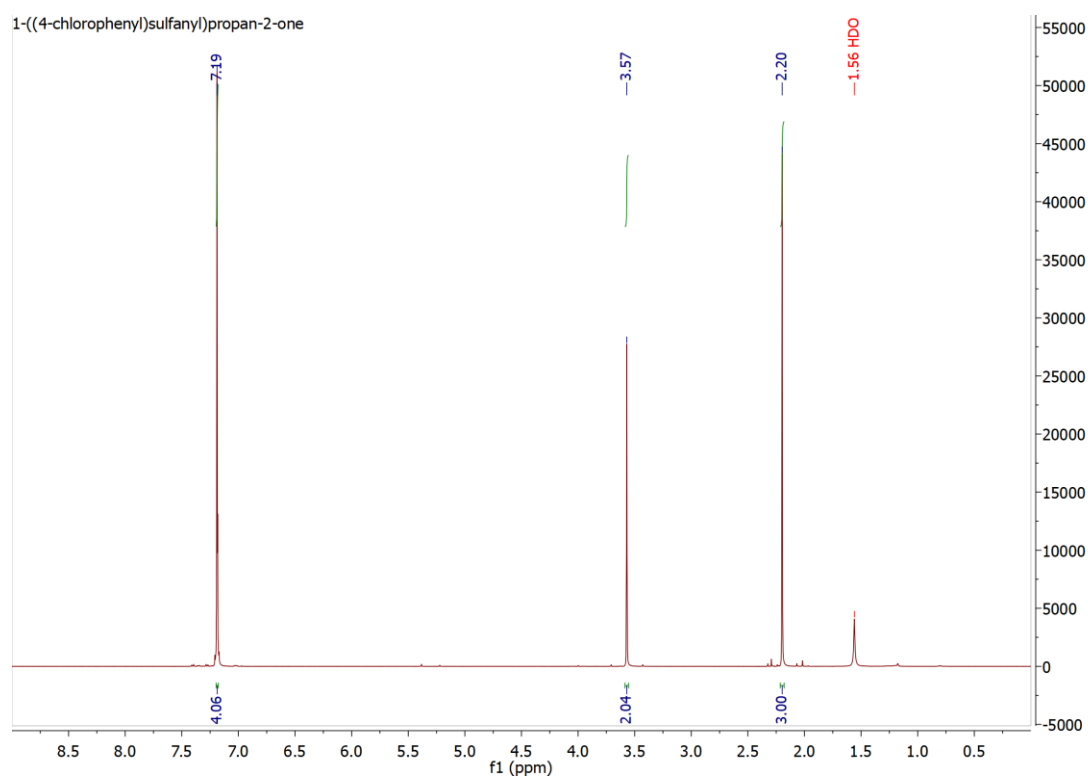


Figure S17. ¹H NMR spectrum of 1-[(4-chlorophenyl)sulfanyl]propan-2-one **2c**.

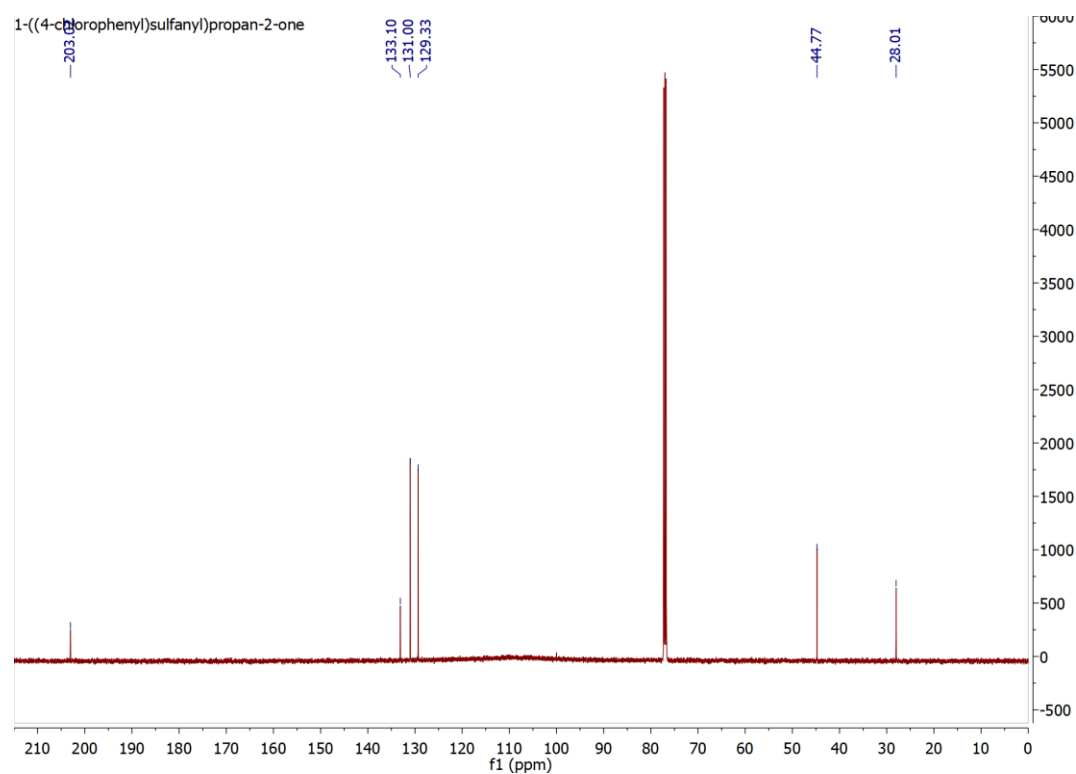


Figure S18. ¹³C NMR spectrum of 1-[(4-chlorophenyl)sulfonyl]propan-2-one 2c.

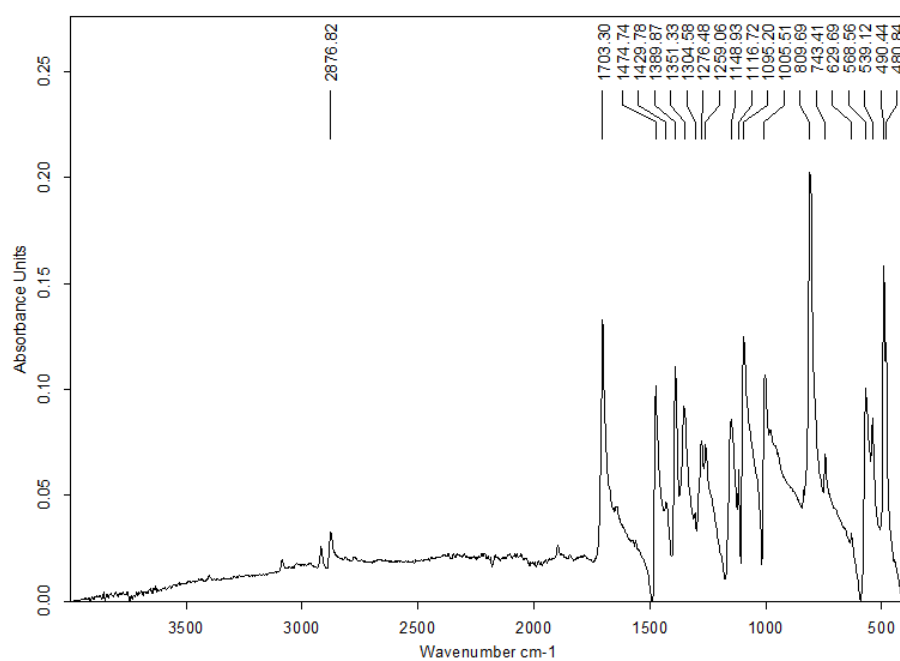


Figure S19. IR spectrum of 1-[(4-chlorophenyl)sulfonyl]propan-2-one 2c.

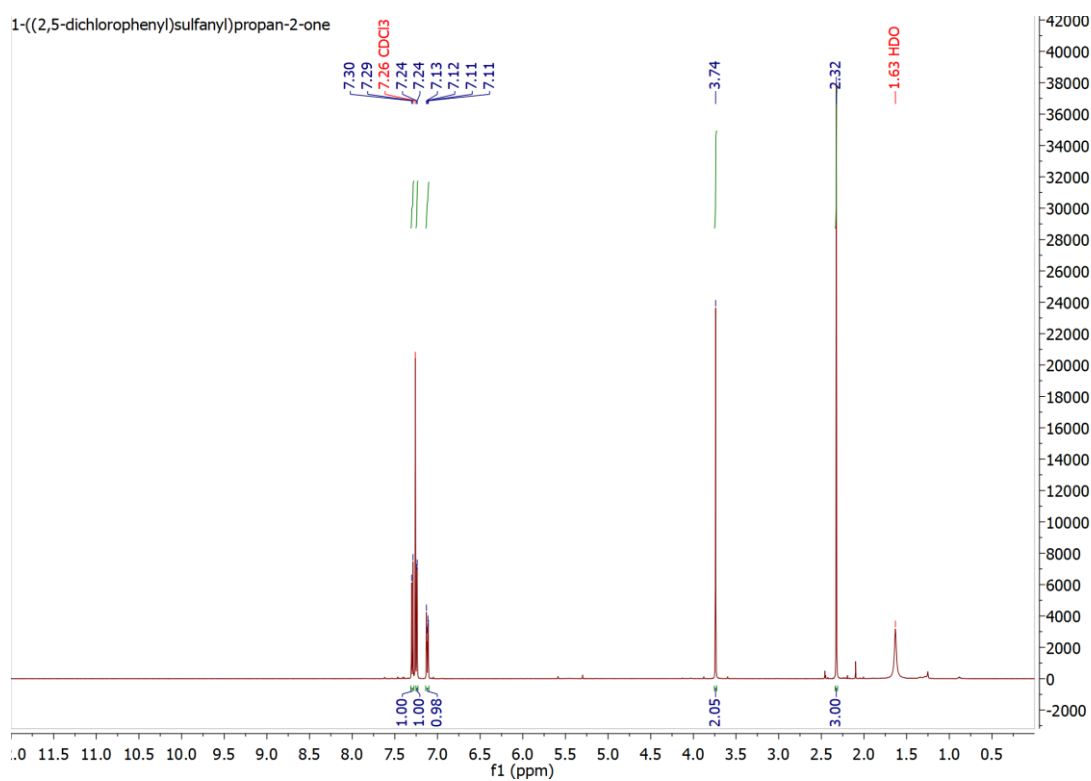


Figure S20. ¹H NMR spectrum of 1-[(2,5-dichlorophenyl)sulfonyl]propan-2-one **2d**.

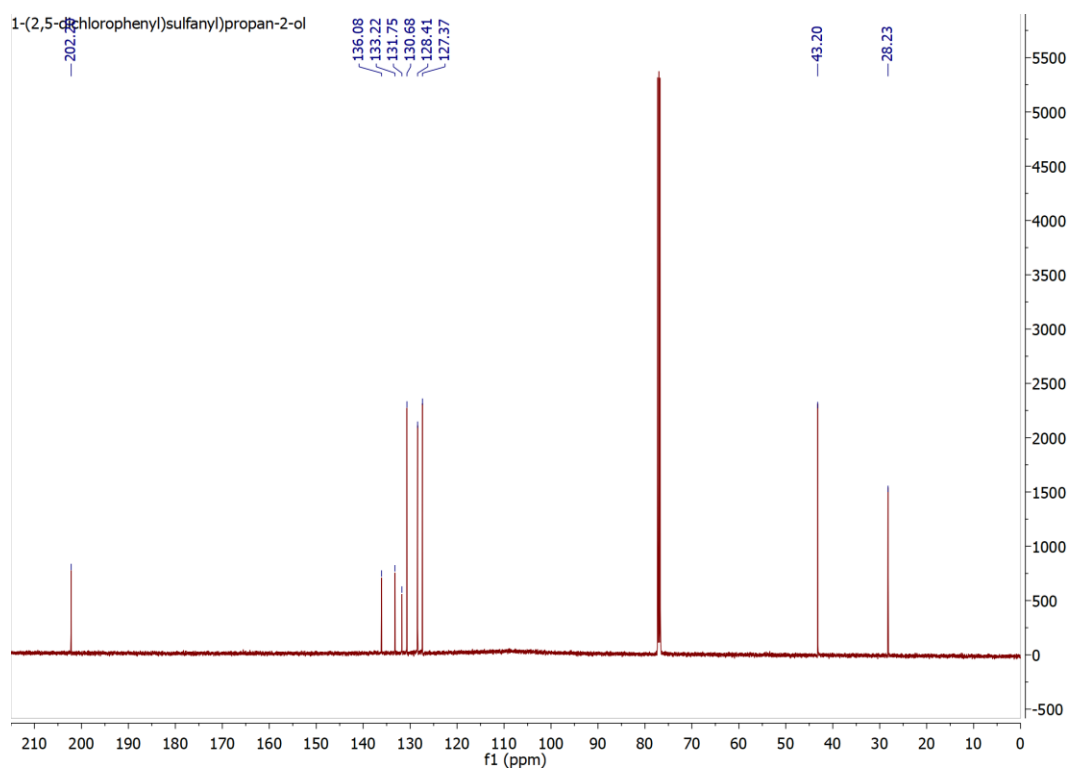


Figure S21. ¹³C NMR spectrum of 1-[(2,5-dichlorophenyl)sulfonyl]propan-2-one **2d**.

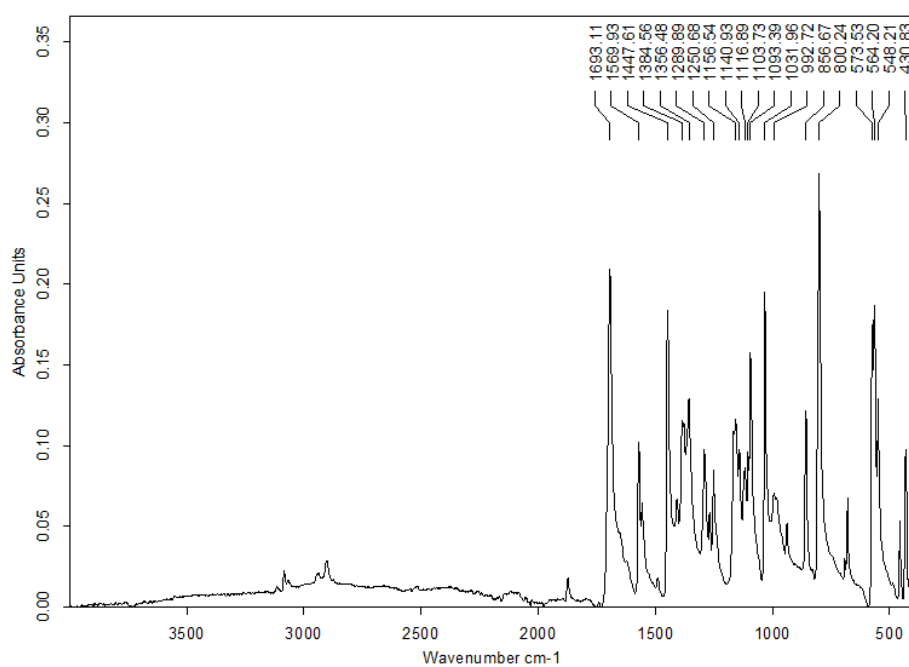


Figure S22. IR spectrum of 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-one **2d**.

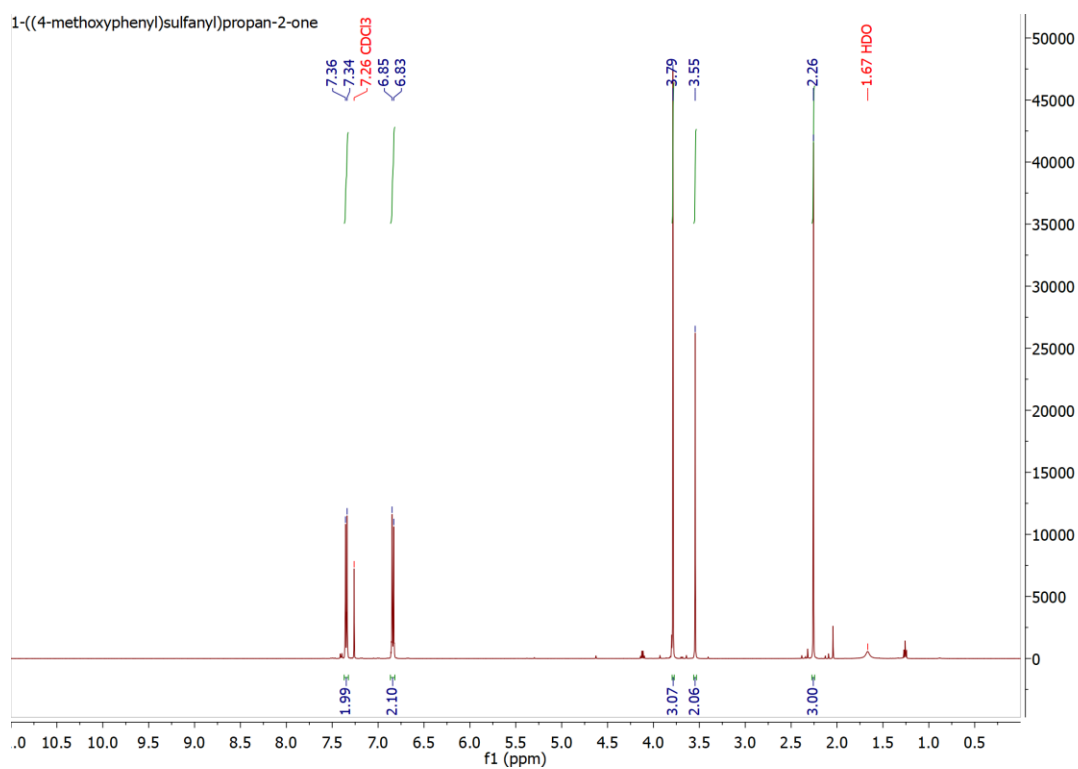


Figure S23. ¹H NMR spectrum of 1-[(4-methoxyphenyl)sulfanyl]propan-2-one **2e**.

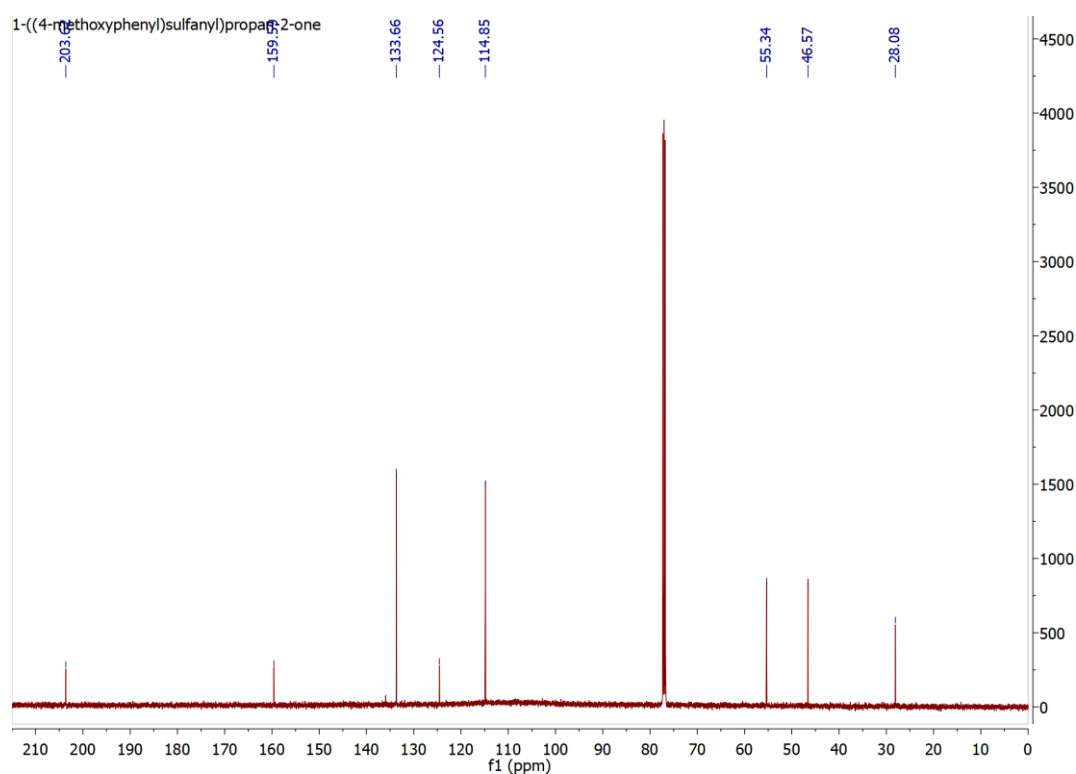


Figure S24. ^{13}C NMR spectrum of 1-[(4-methoxyphenyl)sulfanyl]propan-2-one **2e**.

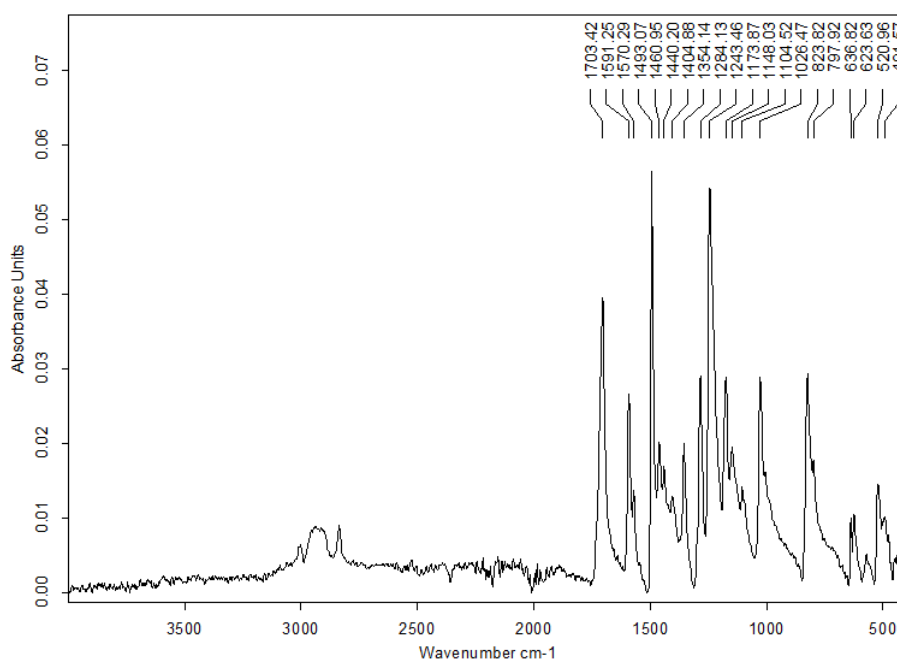


Figure S25. IR spectrum of 1-[(4-methoxyphenyl)sulfanyl]propan-2-one **2e**.

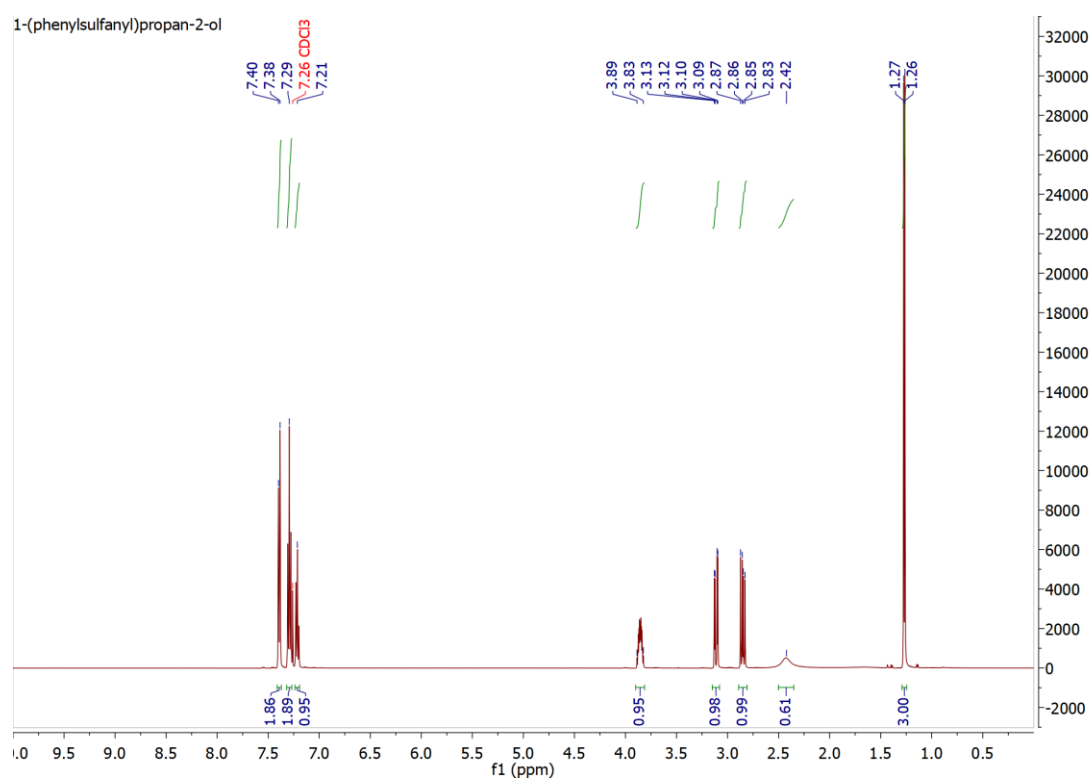


Figure S26. ¹H NMR spectrum of racemic 1-(phenylsulfanyl)propan-2-ol (±)-1a.

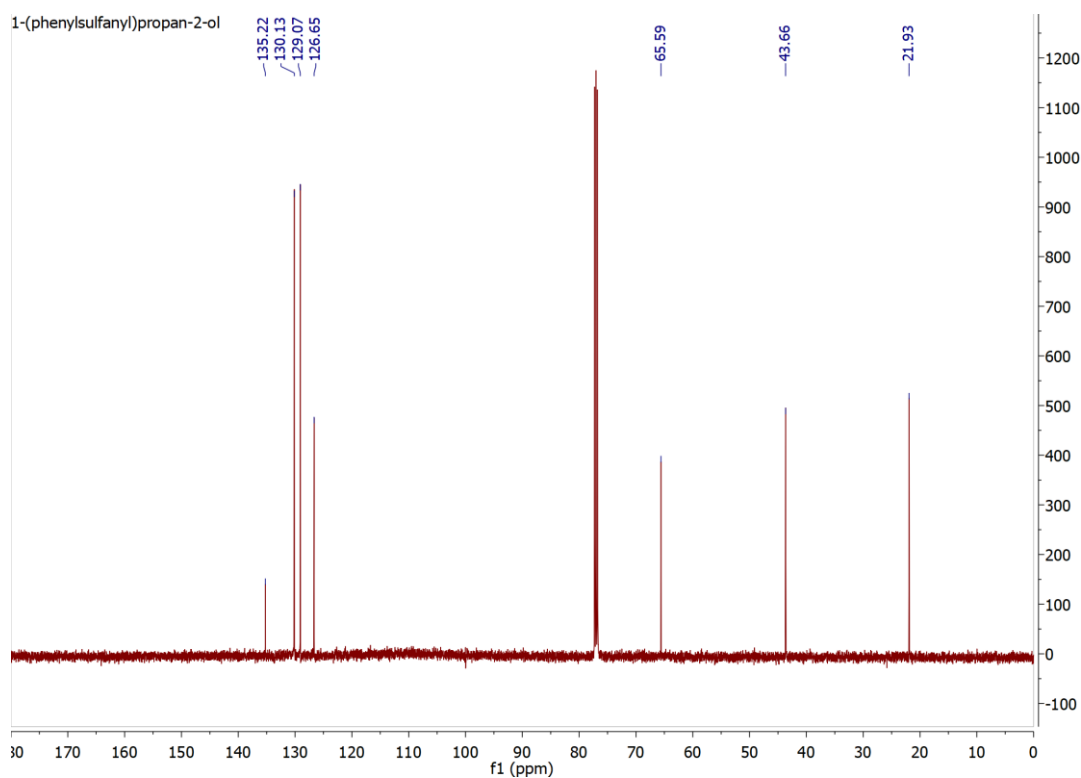


Figure S27. ¹³C NMR spectrum of racemic 1-(phenylsulfanyl)propan-2-ol (±)-1a.

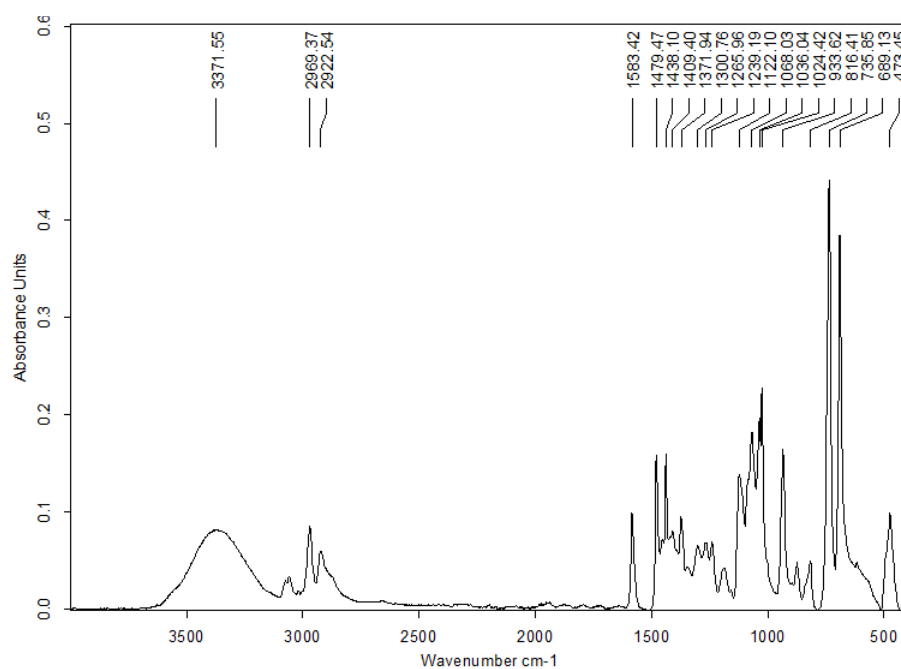


Figure S28. IR spectrum of racemic 1-(phenylsulfanyl)propan-2-ol (±)-1a.

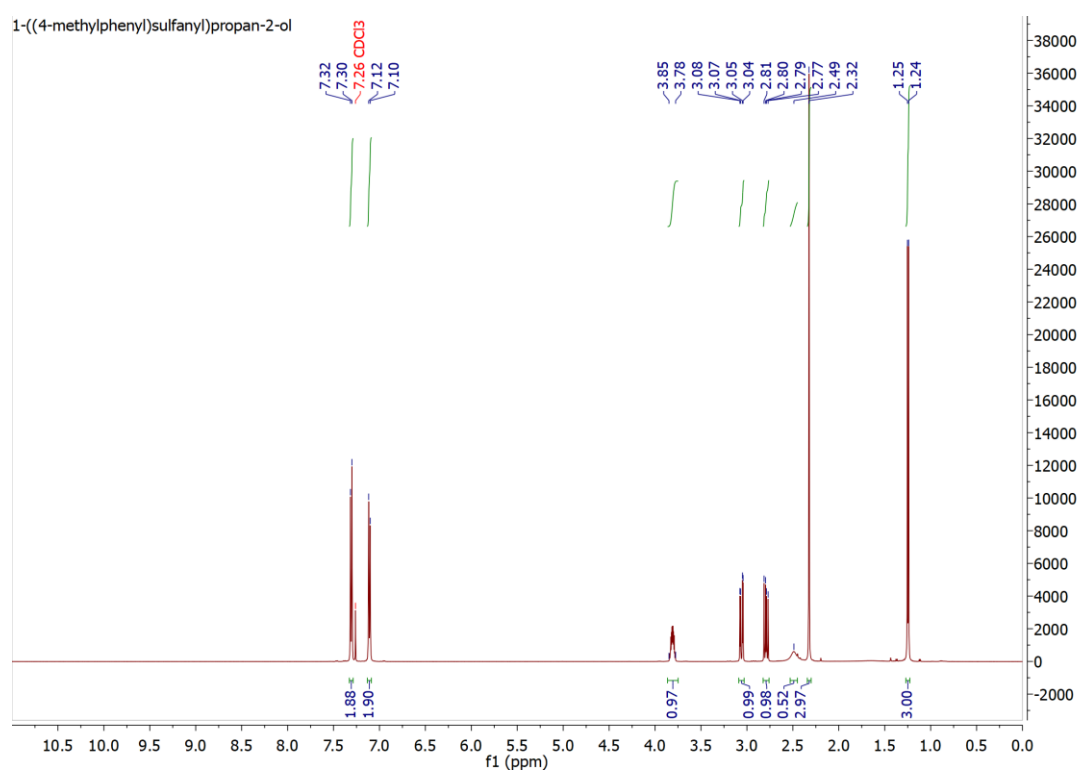


Figure S29. ¹H NMR spectrum of racemic 1-[(4-methylphenyl)sulfanyl]propan-2-ol (±)-1b.

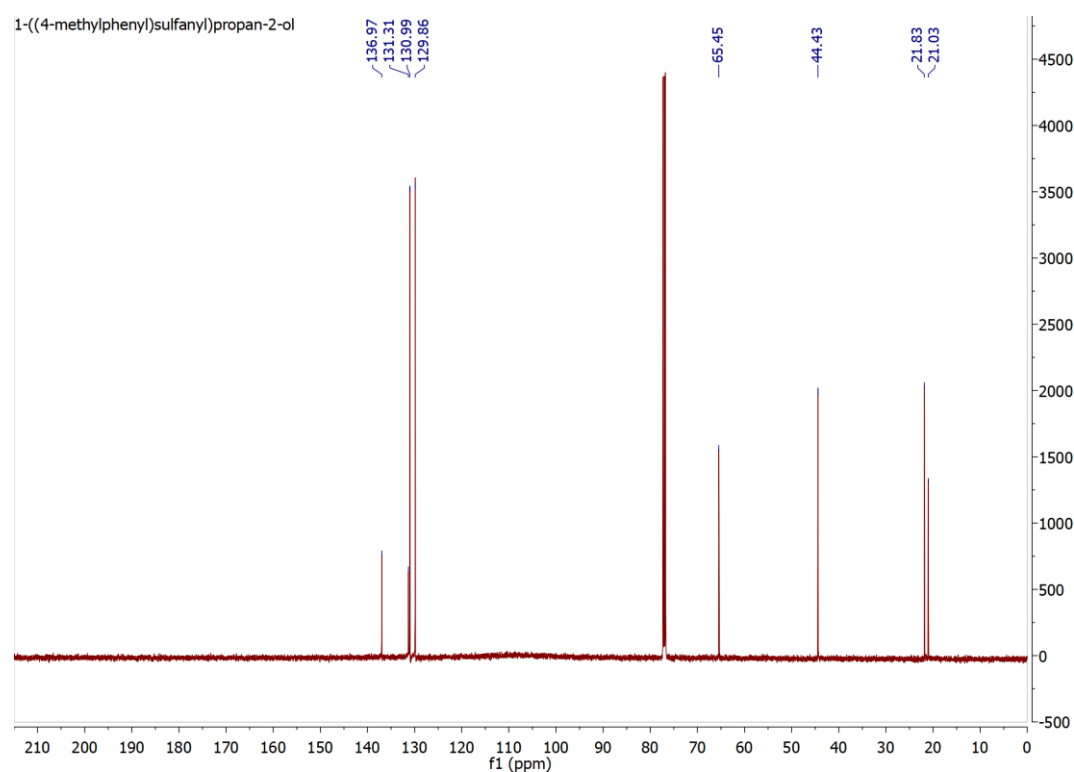


Figure S30. ^{13}C NMR spectrum of racemic 1-[(4-methylphenyl)sulfanyl]propan-2-ol (±)-1b.

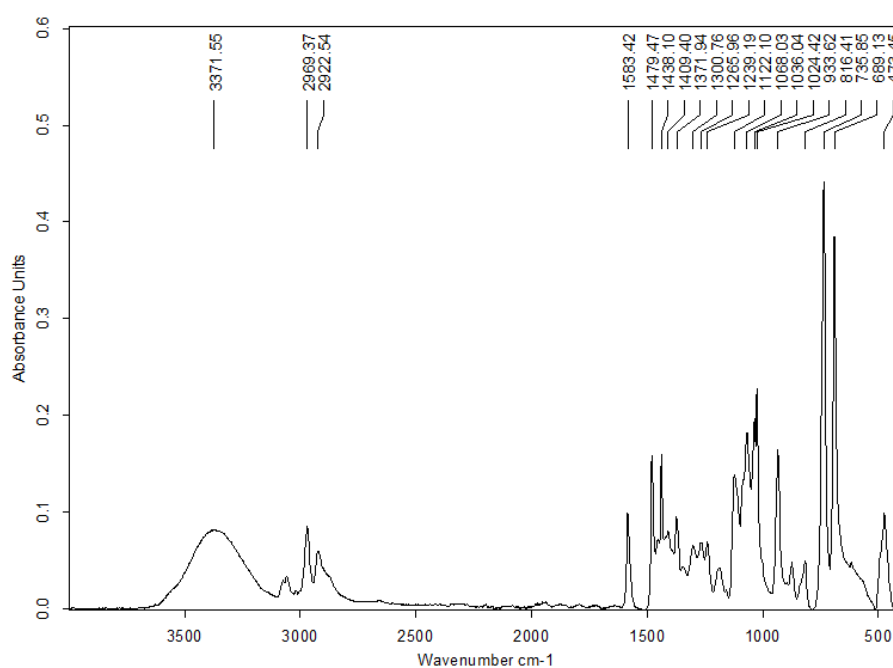


Figure S31. IR spectrum of racemic 1-[(4-methylphenyl)sulfanyl]propan-2-ol (±)-1b.

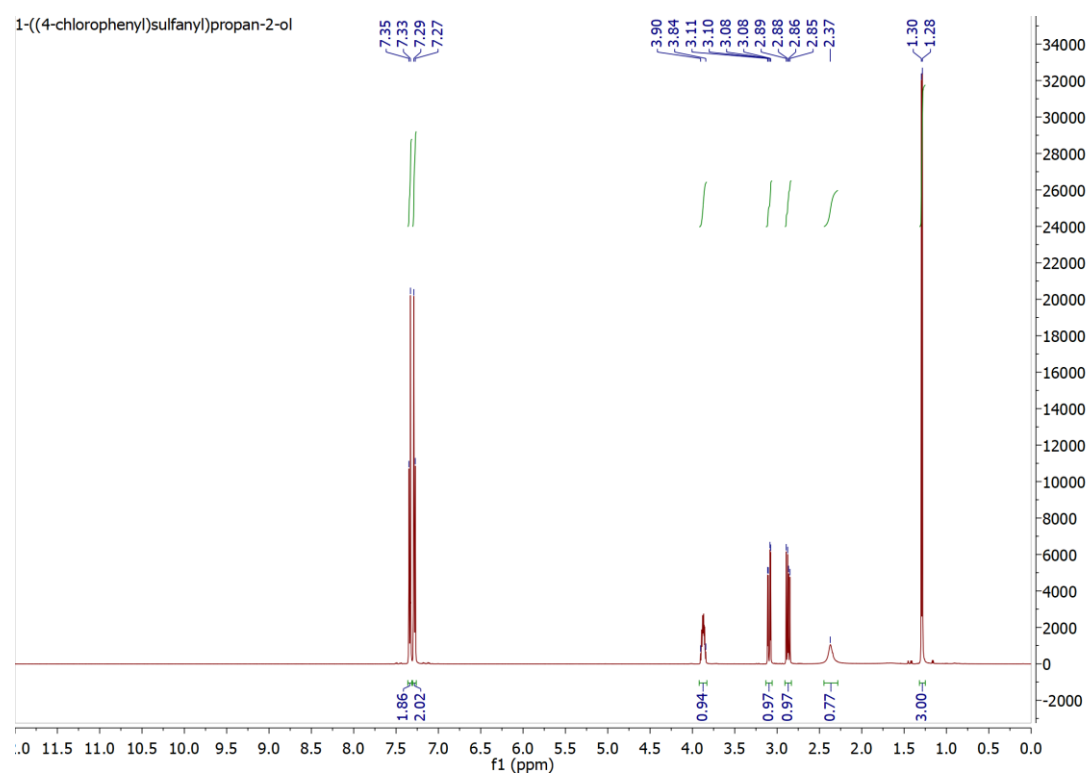


Figure S32. ¹H NMR spectrum of racemic 1-[(4-chlorophenyl)sulfanyl]propan-2-ol (±)-1c.

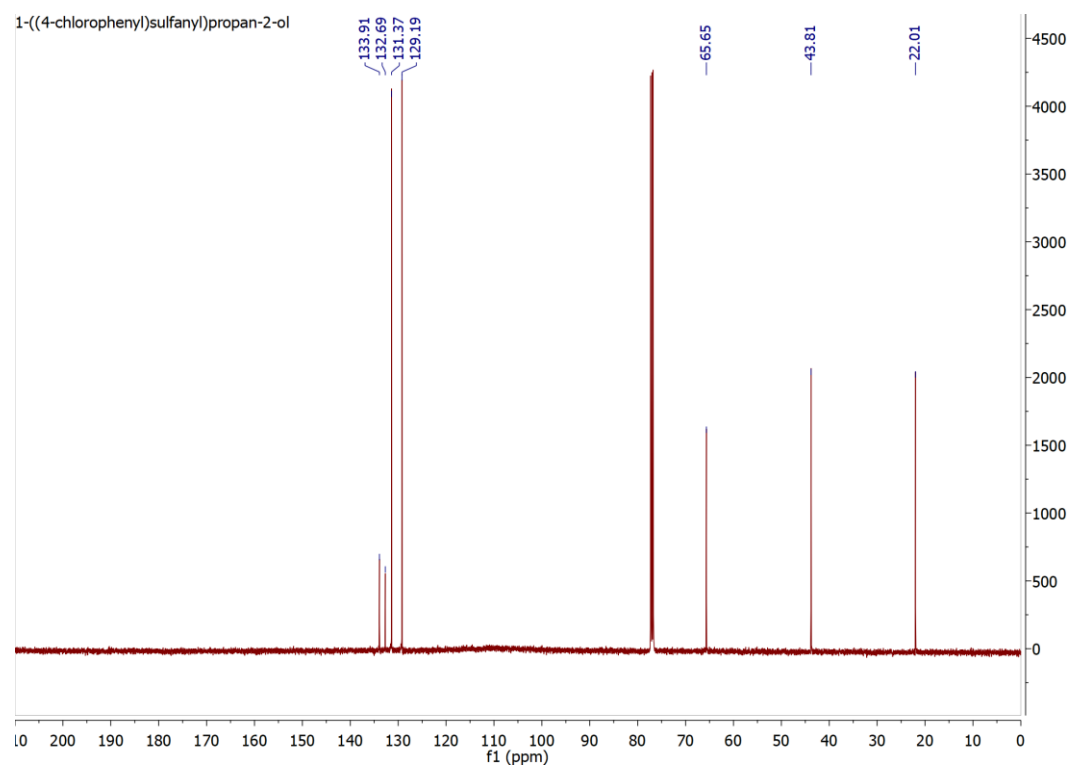


Figure S33. ¹³C NMR spectrum of racemic 1-[(4-chlorophenyl)sulfanyl]propan-2-ol (±)-1c.

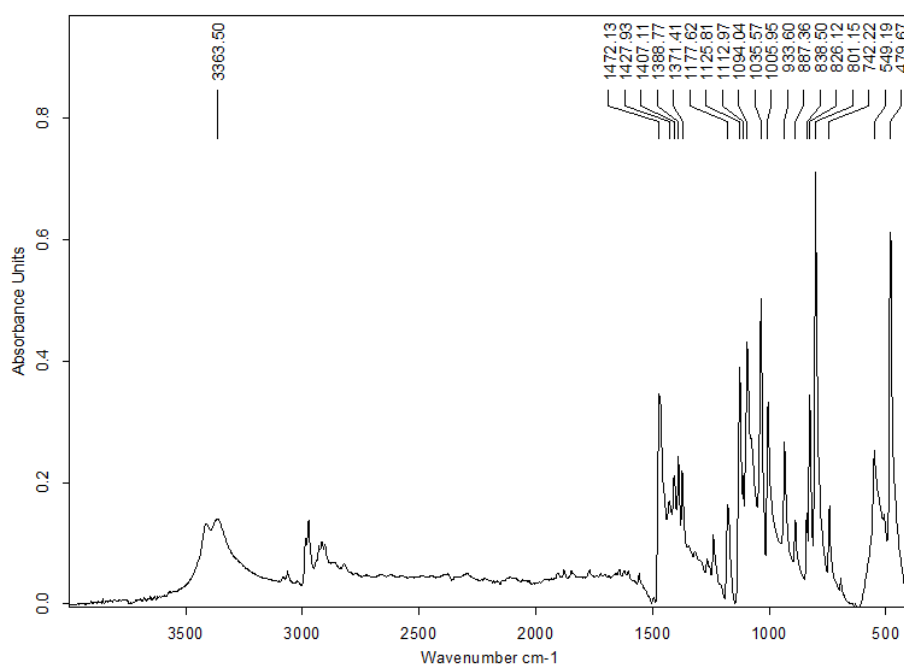


Figure S34. IR spectrum of racemic 1-[(4-chlorophenyl)sulfanyl]propan-2-ol (±)-1c

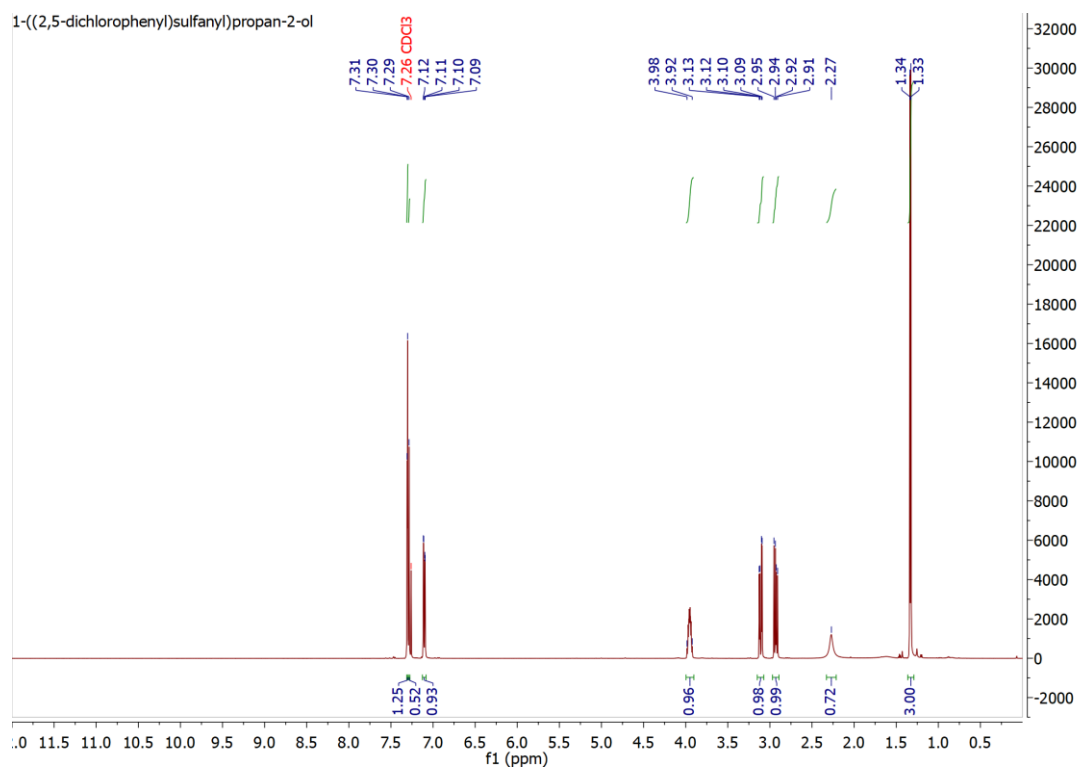


Figure S35. ¹H NMR spectrum of racemic 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-ol (±)-1d.

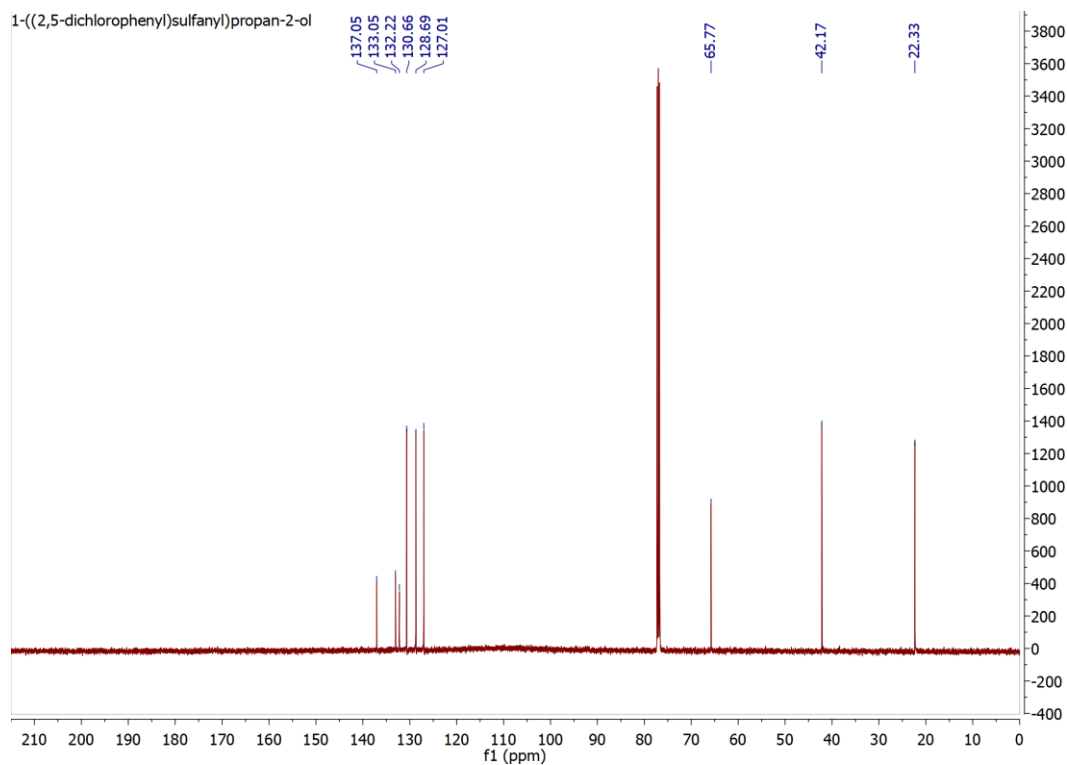


Figure S36. ^{13}C NMR spectrum of racemic 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-ol (±)-1d

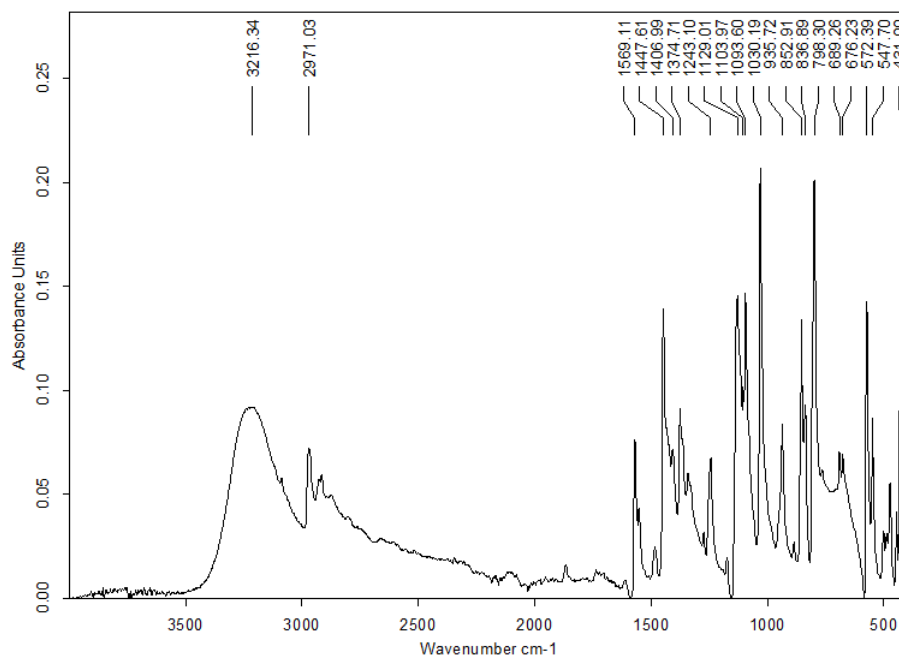


Figure S37. IR spectrum of racemic 1-[(2,5-dichlorophenyl)sulfanyl]propan-2-ol (±)-1d.

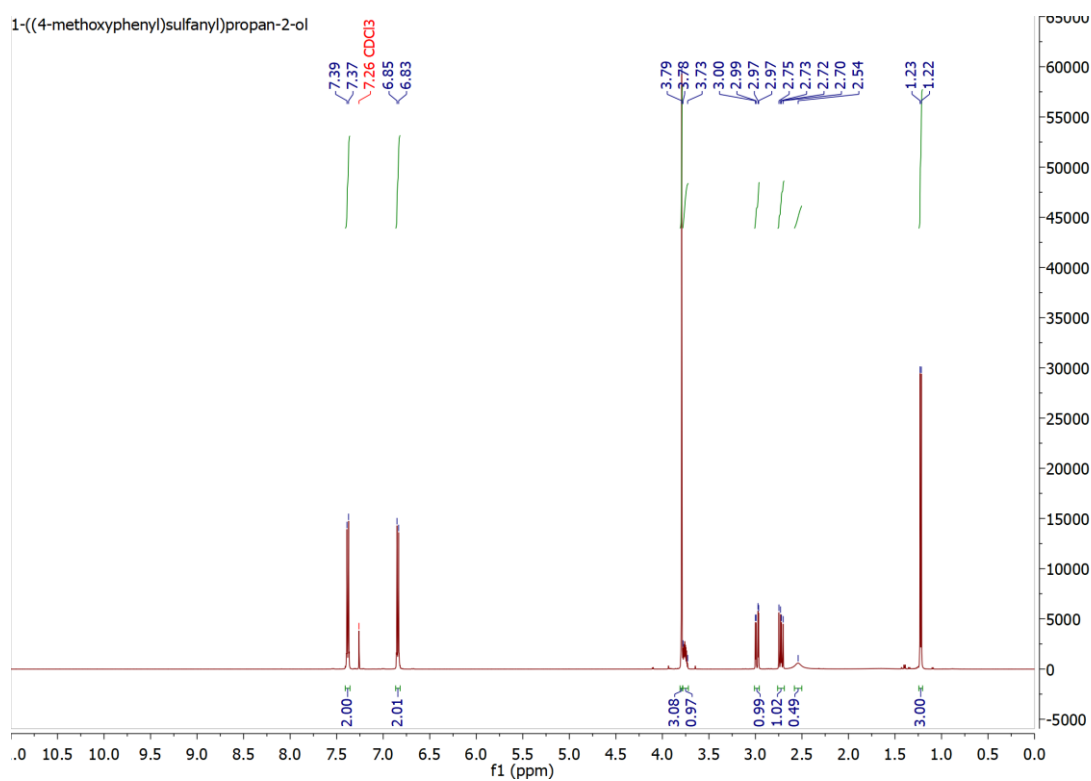


Figure S38. ¹H NMR spectrum of racemic 1-((4-methoxyphenyl)sulfonyl)propan-2-ol (±)-1e.

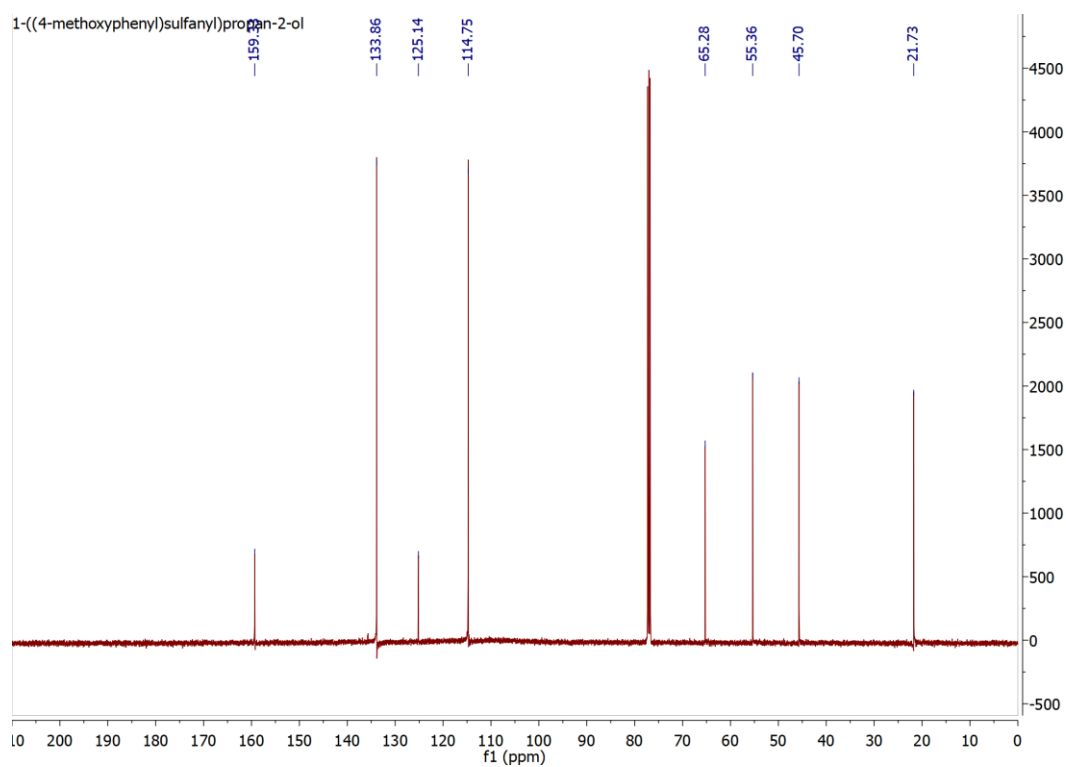


Figure S39. ¹³C NMR spectrum of racemic 1-((4-methoxyphenyl)sulfonyl)propan-2-ol (±)-1e.

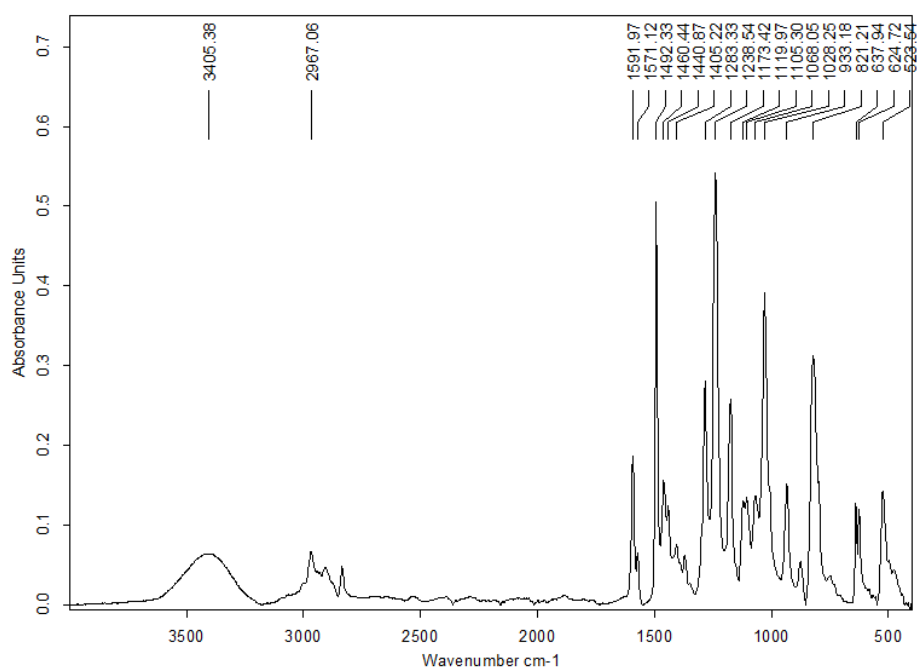


Figure S40. IR spectrum of racemic 1-((4-methoxyphenyl)sulfanyl)propan-2-ol (±)-1e.