Supporting Information

*t*BuOLi Promoted Terminal Alkynes Functionalizations by Aliphatic Thiols and Alcohols

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Content

Table S1. Optimization of base for **4ab**

Entry	Base (mol %)	Yield of 4ab (%)[a]
1	^{t}BuOLi (10.0)	51
2	^{t}BuOLi (15.0)	69
3	^{t}BuOLi (20.0)	62

[a]Isolated yields after column chromatography, Standard reaction conditions: **1a** (60 mg, 0.413 mmol), and ^{t}BuOLi (5 mg, 0.062 mmol) in 1 mL dry EtOH at inert atmosphere for 30 h.

Crystallographic Investigation

The compound **3ad** was recrystallized by the slow evaporation of ethanol and water mixture (ca. 50%). The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Cu-Kα radiation, λ = 1.54184 Å). SAINT+[1] and SADABS[2] were used to integrate the intensities and to correct the absorption respectively The structure was resolved by direct methods and refined on F^2 with SHELXL-97.[3]

Compound (3ad) (CCDC 2044668)

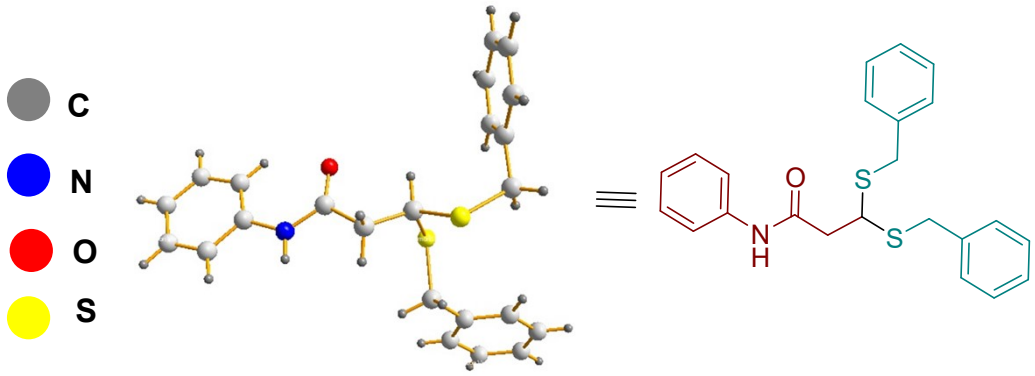


Figure S1. Crystal structure of (**3ad**) (CCDC 2044668).

Crystallographic Data for (3ad)

Empirical formula	$C_{23}H_{23}NOS_2$
Formula weight	393.54
Temperature/K	298.85(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.4011(2)
b/Å	18.3334(4)
c/Å	9.57886(15)
α/°	90
β/°	91.0519(16)
γ/°	90
Volume/Å3	2177.43(7)
Z	4
ρcalcg/cm^3	1.200

μ/mm^{-1}	2.296
F(000)	832.0
Crystal size/mm^3	0.2 × 0.17 × 0.18
Radiation	CuKα (λ = 1.54184)
Reflections collected	33898
Independent reflections	4456 [Rint = 0.0417, Rsigma = 0.0221]
Goodness-of-fit on F2	1.061
Final R indexes [I>=2σ (I)]	R1 = 0.0484, wR2 = 0.1314
Final R indexes [all data]	R1 = 0.0563, wR2 = 0.1371
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.31

References

(1) SAINT+, Bruker AXS Inc., Madison, Wisconsin, USA, 1999 (Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V. 6.02.)

(2) SADABS, Bruker AXS, Madison, Wisconsin, USA, 2004

(3) Sheldrick, G. A Short History of Shelx. *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

NMR SPECTRA

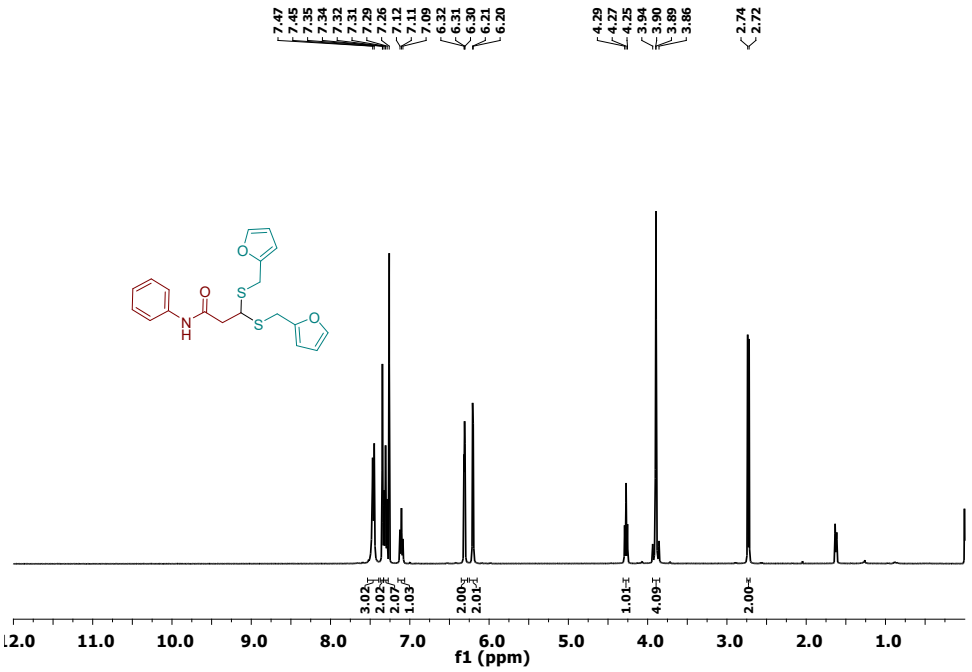


Figure S2. ^{1}H NMR spectrum of 3,3-bis((furan-2-ylmethyl)thio)-N-phenylpropanamide (**3aa**)

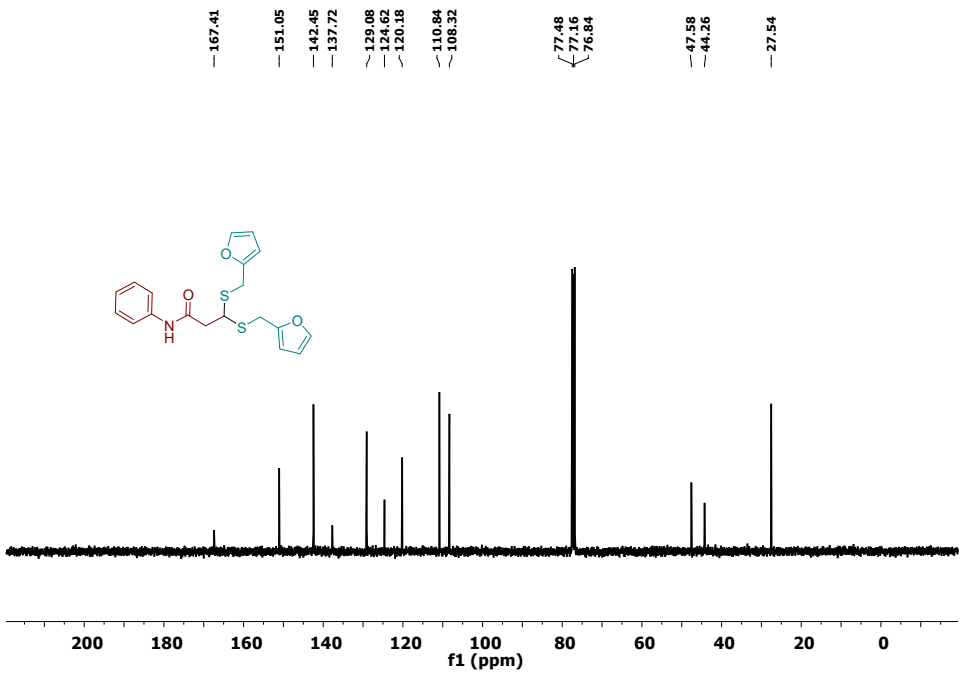


Figure S3. ^{13}C NMR spectrum of 3,3-bis((furan-2-ylmethyl)thio)-N-phenylpropanamide (**3aa**)

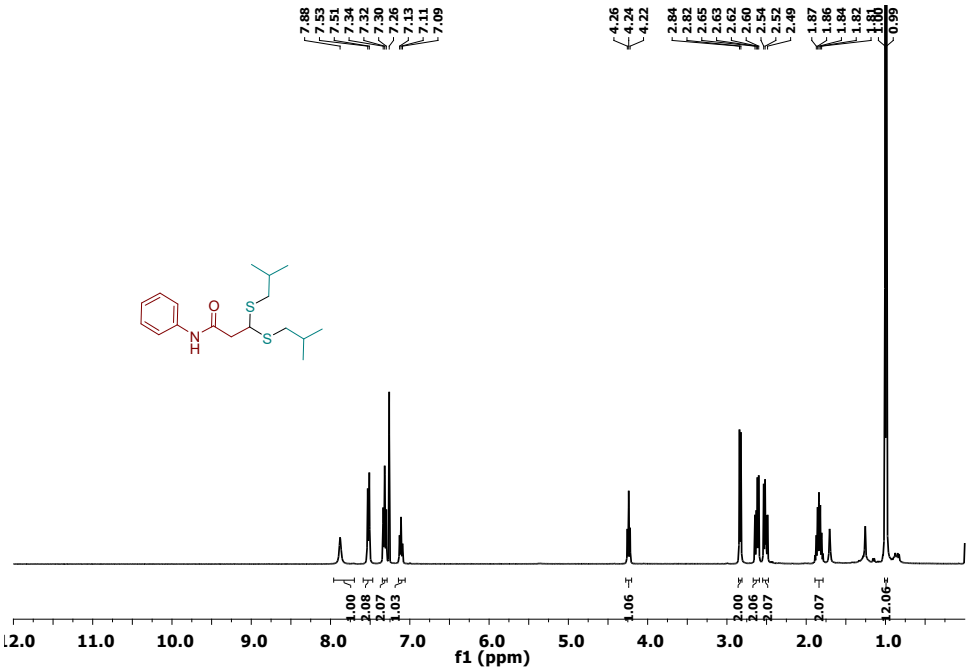


Figure S4. ^{1}H NMR spectrum of 3,3-bis(isobutylthio)-N-phenylpropanamide (**3ab**)

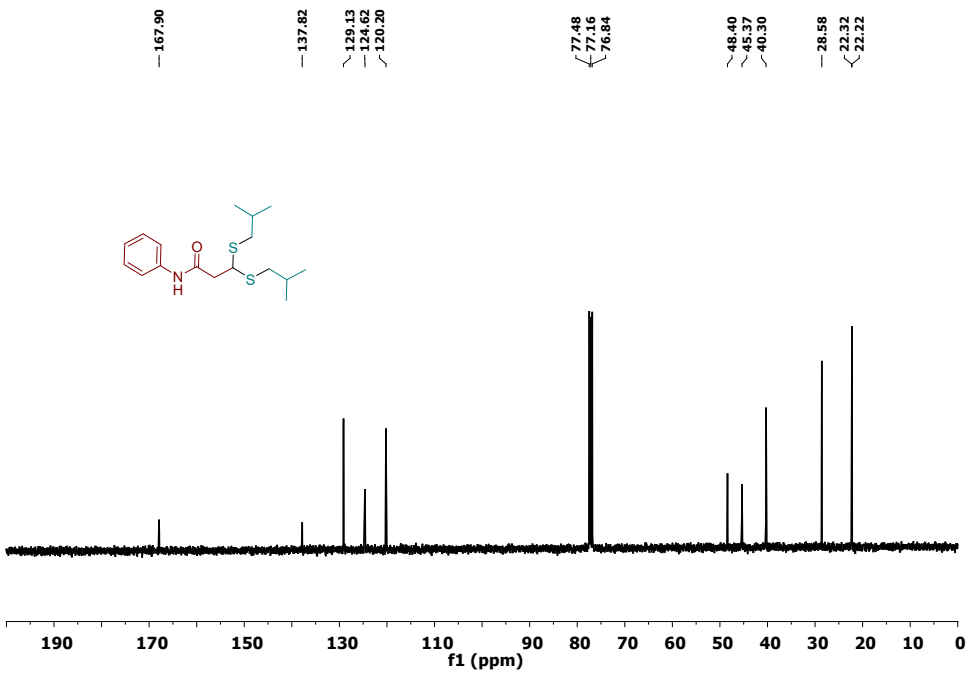


Figure S5. ^{13}C NMR spectrum of 3,3-bis(isobutylthio)-N-phenylpropanamide (**3ab**)

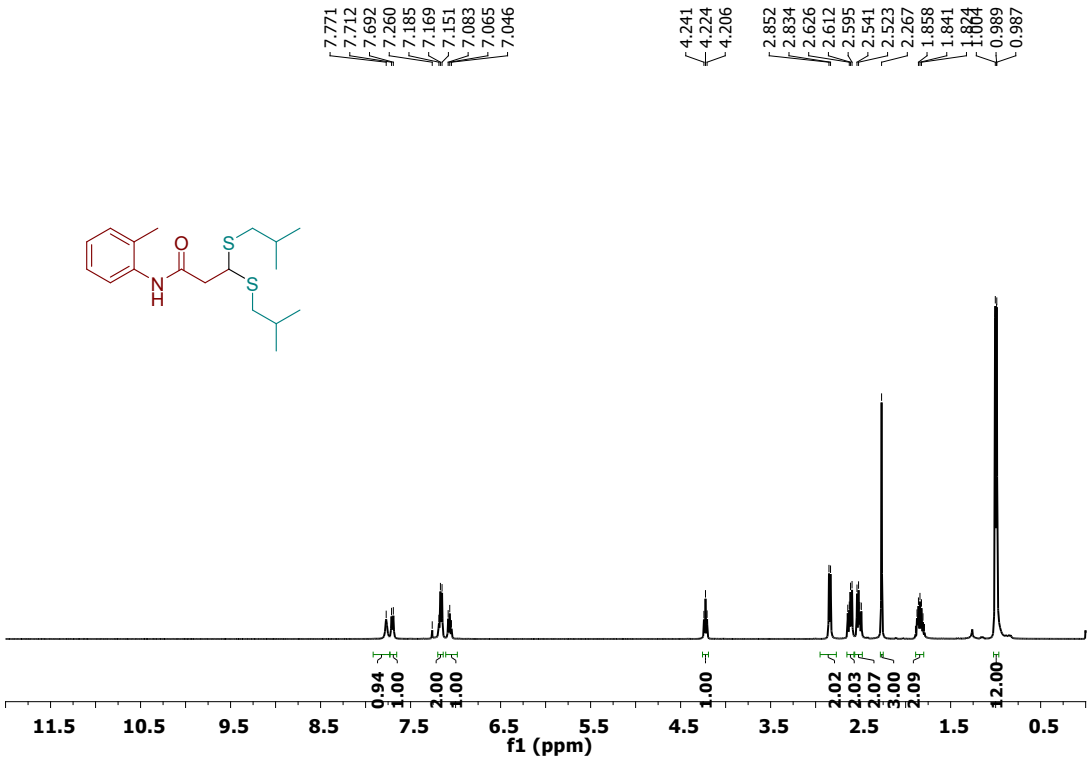


Figure S6. [1]H NMR spectrum of 3,3-bis(isobutylthio)-N-(o-tolyl)propanamide (**3bb)**

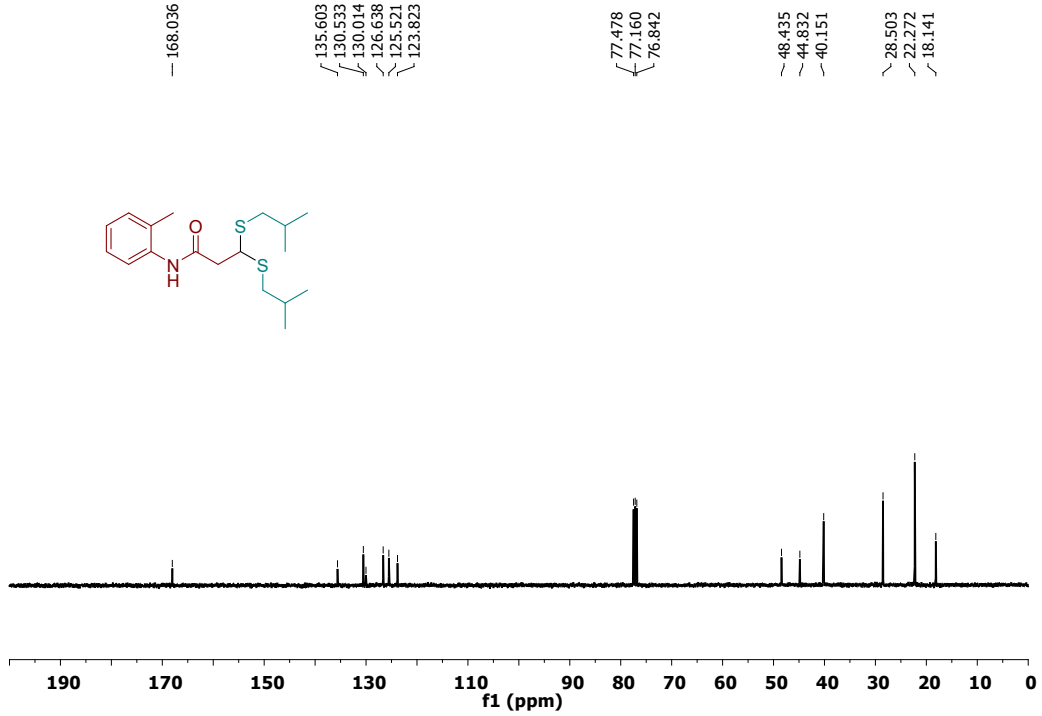


Figure S7. ^{13}C NMR spectrum of 3,3-bis(isobutylthio)-N-phenylpropanamide (**3bb**)

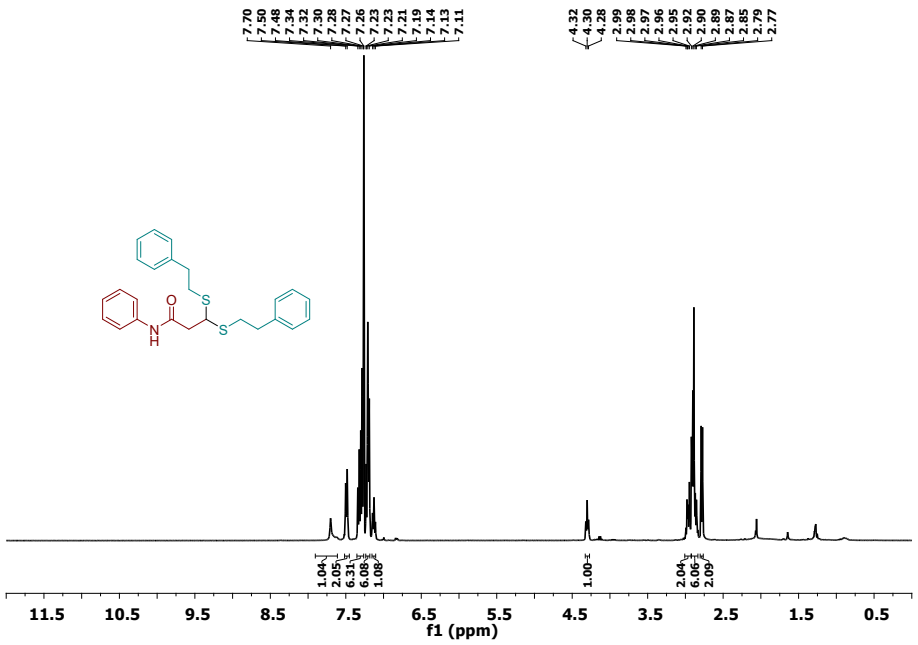


Figure S8. ^{1}H NMR spectrum of 3,3-bis(phenethylthio)-N-phenylpropanamide (**3ac**)

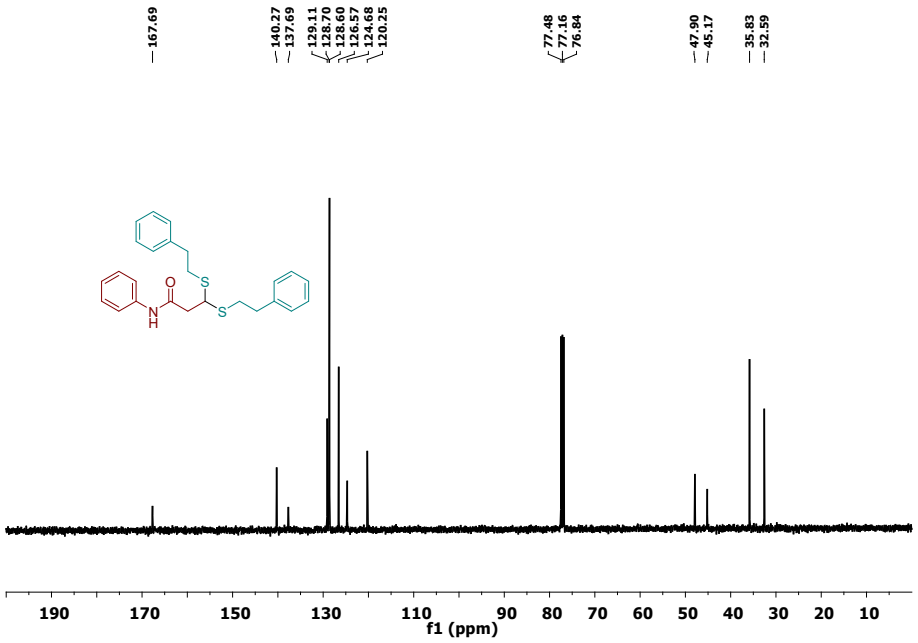


Figure S9. ^{13}C NMR spectrum of 3,3-bis(phenethylthio)-N-phenylpropanamide (**3ac**)

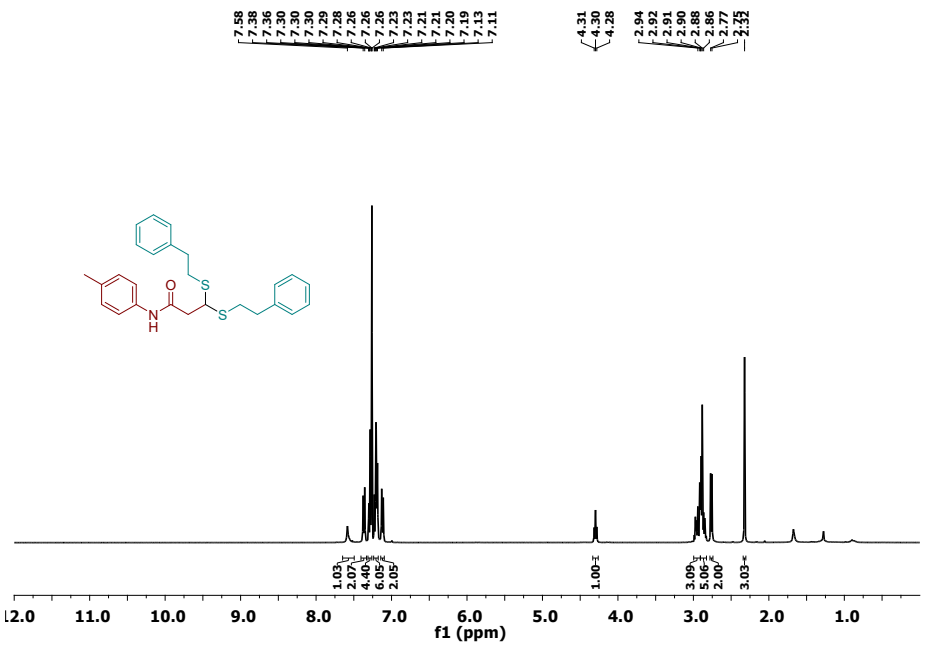


Figure S10. [1]H NMR spectrum of 3,3-bis(phenethylthio)-N-(p-tolyl)propanamide (**3cc**)

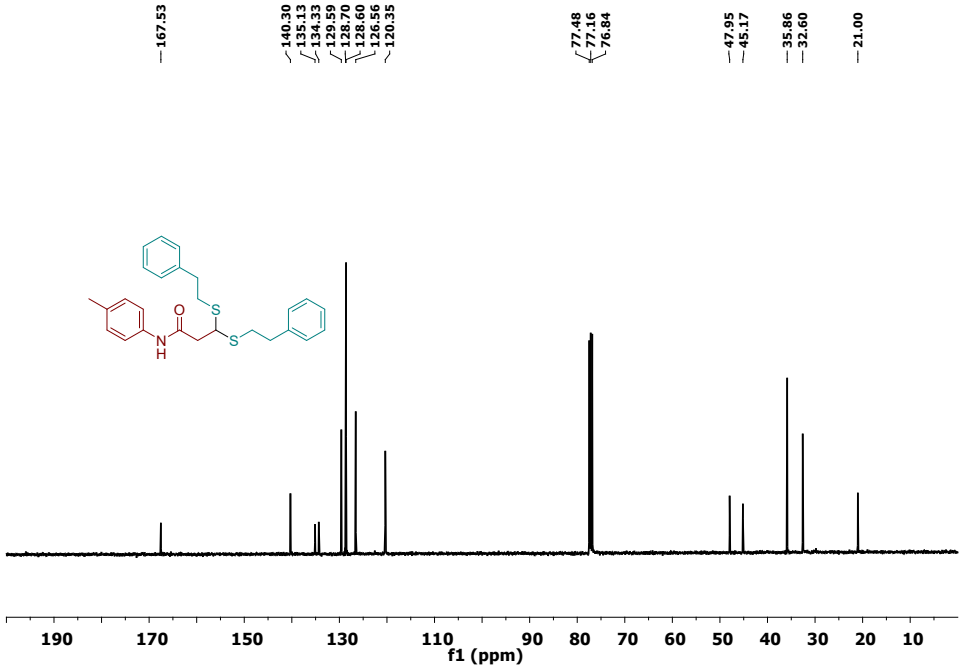


Figure S11. [13]C NMR spectrum of 3,3-bis(phenethylthio)-N-(p-tolyl)propanamide (**3cc**)

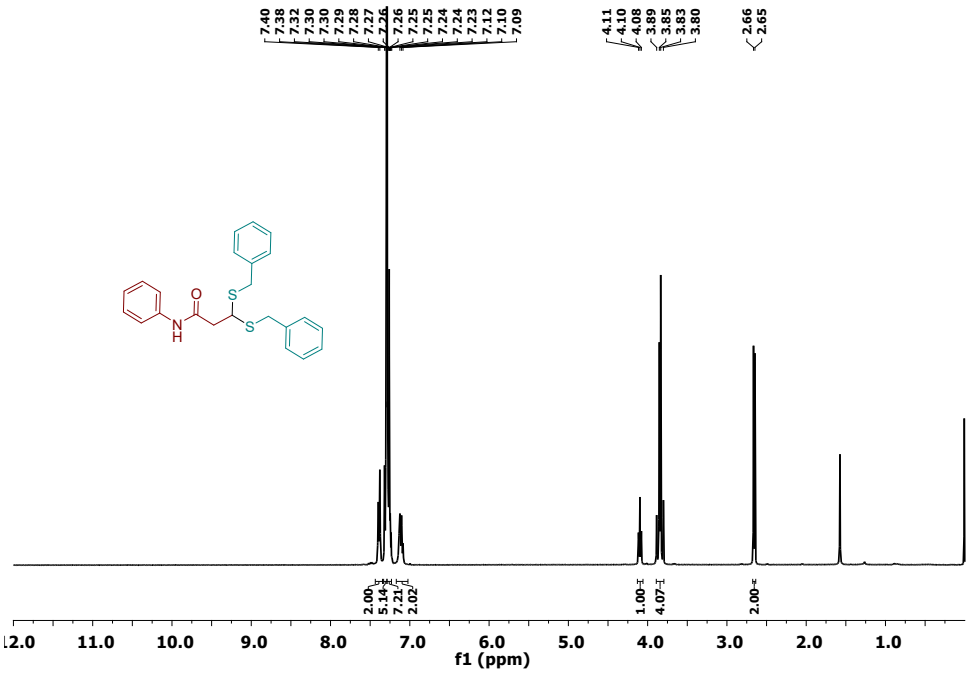


Figure S12. ^{1}H NMR spectrum of 3,3-bis(benzylthio)-N-phenylpropanamide (**3ad**)

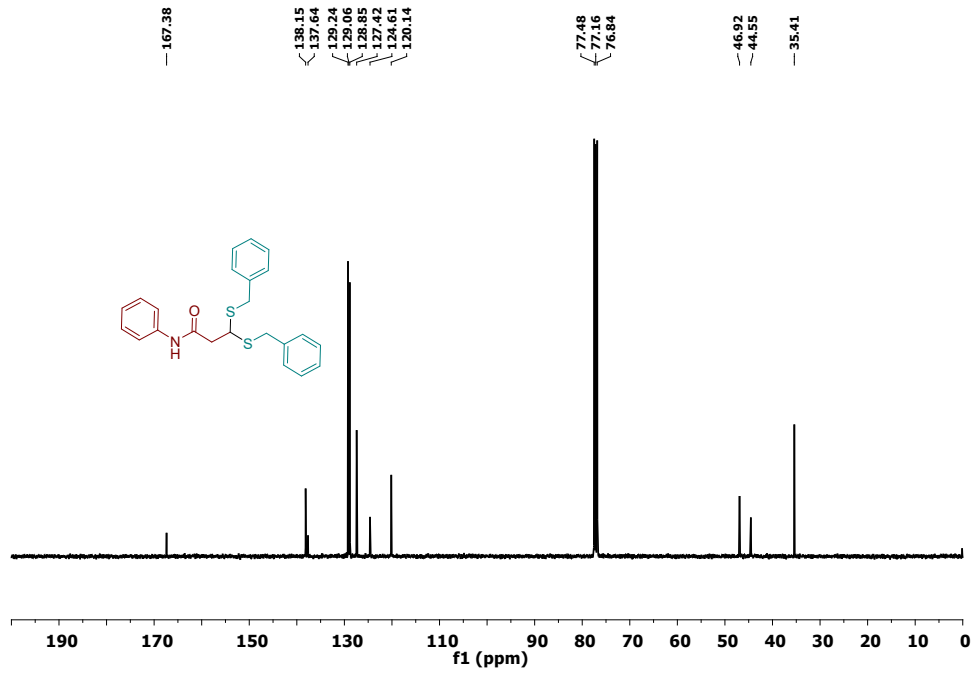


Figure S13. ^{13}C NMR spectrum of 3,3-bis(benzylthio)-N-phenylpropanamide (**3ad**)

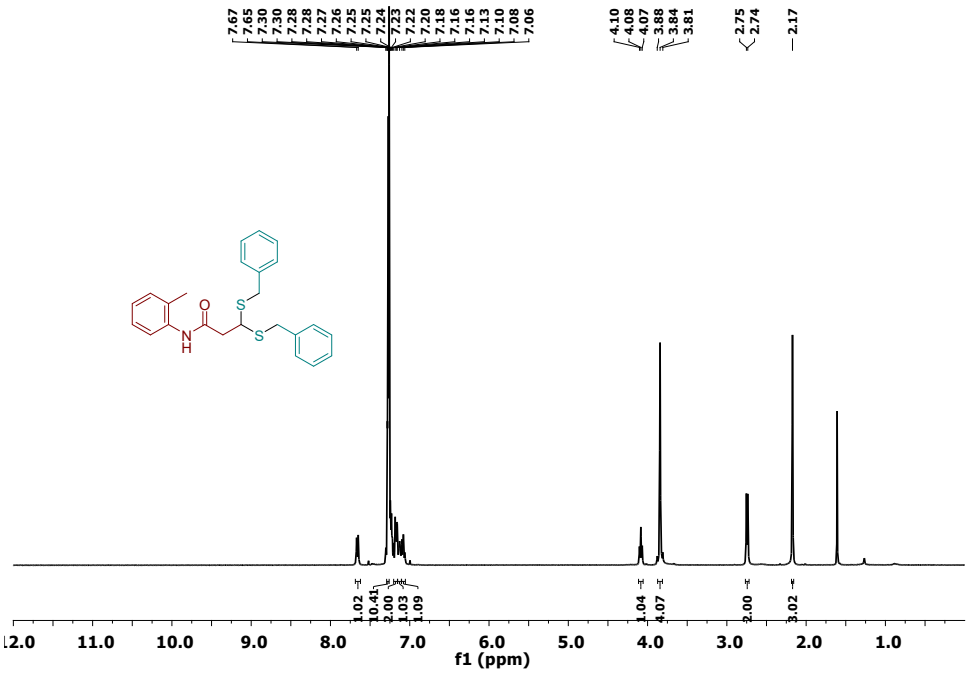


Figure S14. ^{1}H NMR spectrum of 3,3-bis(benzylthio)-N-(o-tolyl)propanamide (**3bd**)

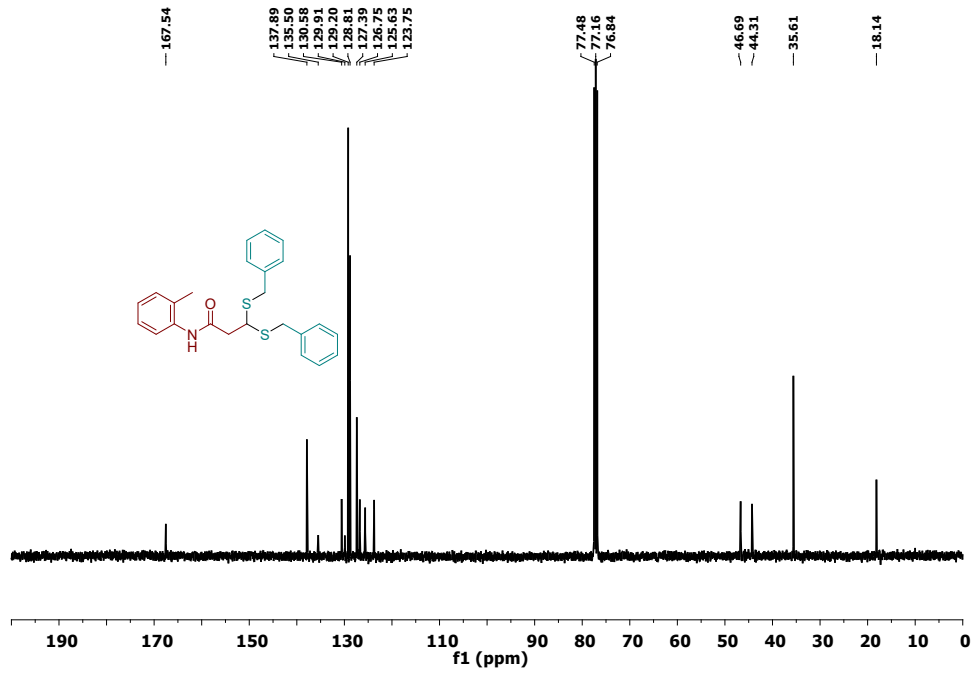


Figure S15. ^{13}C NMR spectrum of 3,3-bis(benzylthio)-N-(o-tolyl)propanamide (**3bd**)

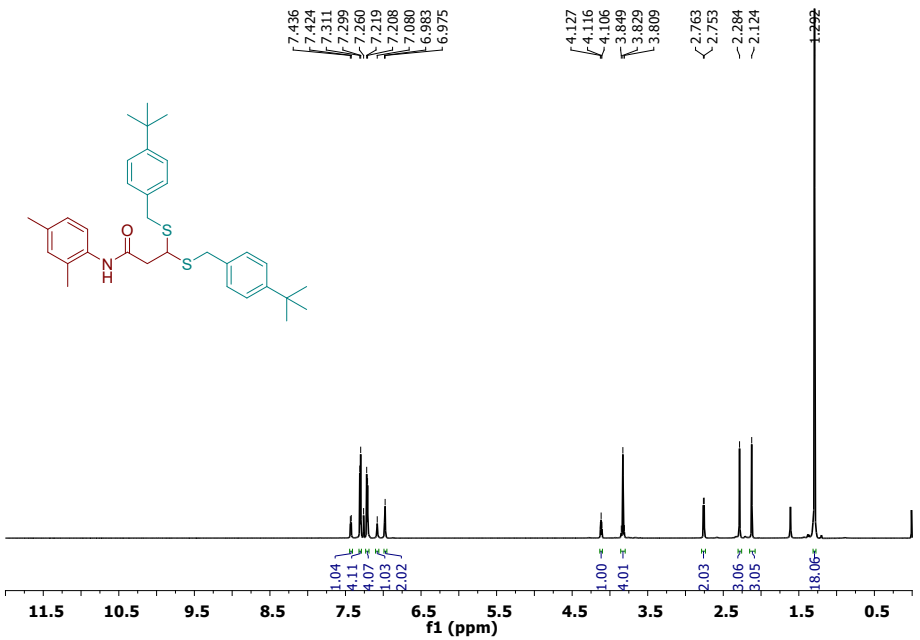


Figure S16. [1]H NMR spectrum of 3,3-bis((4-(tert-butyl)benzyl)thio)-N-(2,4-dimethylphenyl)propanamide (**3de**)

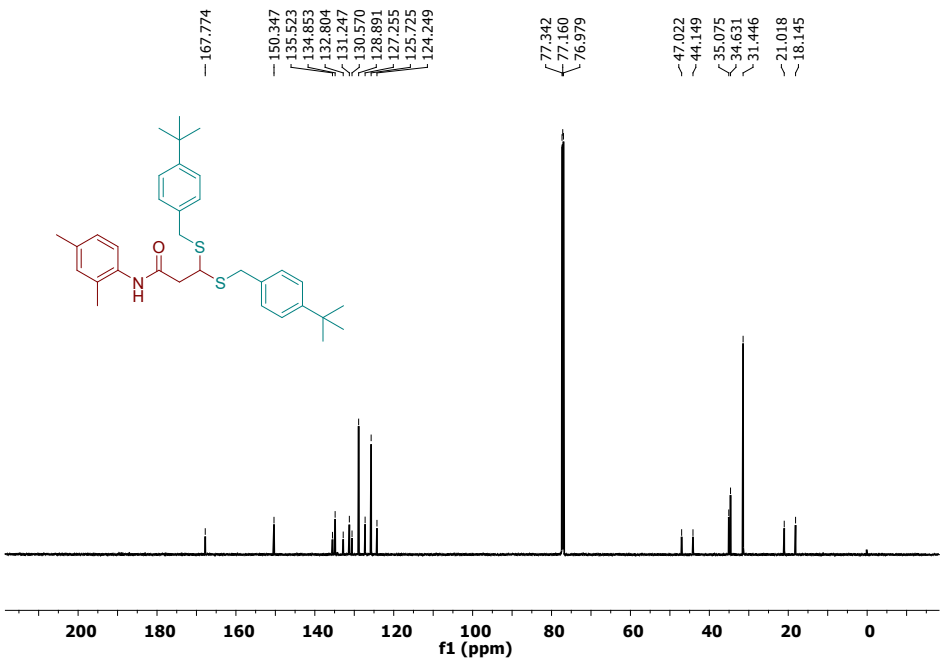


Figure S17. [13]C NMR spectrum of 3,3-bis((4-(tert-butyl)benzyl)thio)-N-(2,4-dimethylphenyl)propanamide (**3de**)

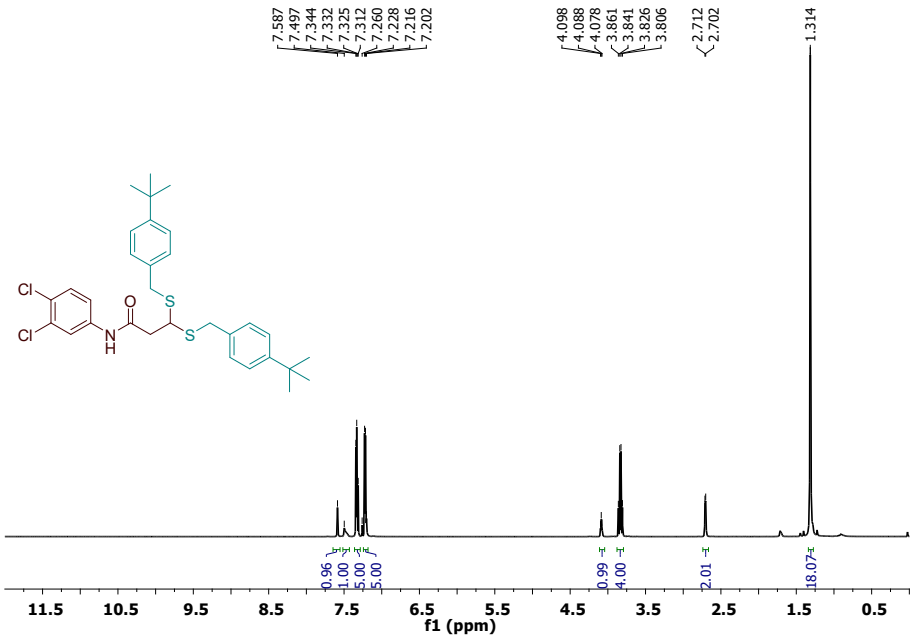


Figure S18. [1]H NMR spectrum of 3,3-bis((4-(tert-butyl)benzyl)thio)-N-(3,4-dichlorophenyl)propanamide (**3ee**)

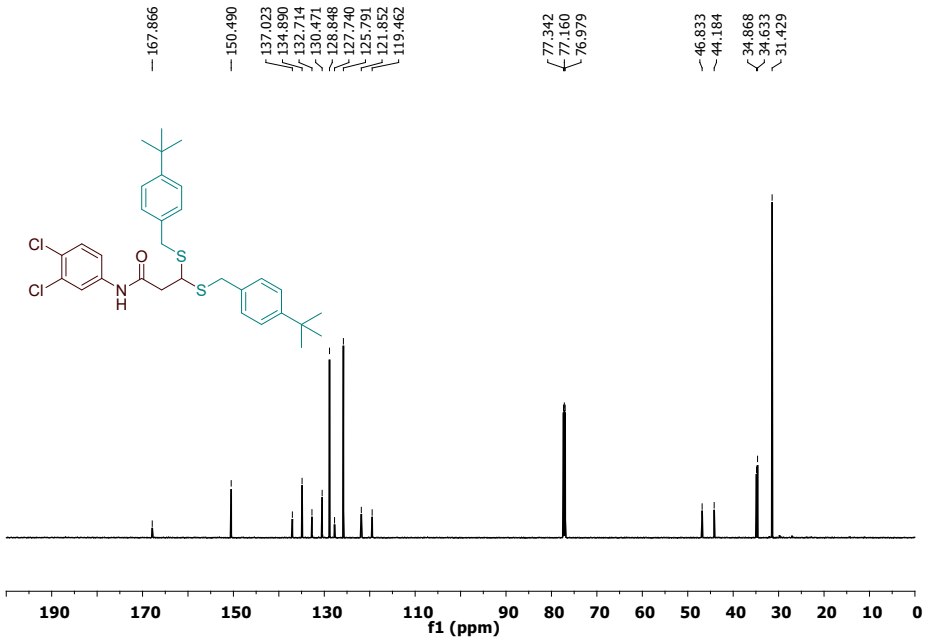


Figure S19. [13]C NMR spectrum of 3,3-bis((4-(tert-butyl)benzyl)thio)-N-(3,4-dichlorophenyl)propanamide (**3ee**)

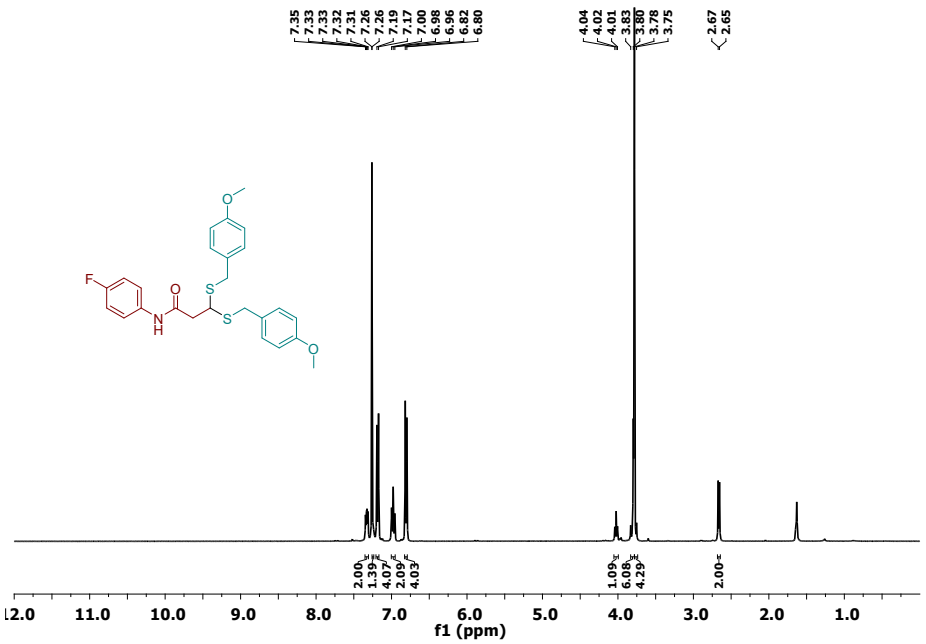


Figure S20. [1]H NMR spectrum of 3,3-bis(benzylthio)-N-(o-tolyl)propanamide (**3ff**)

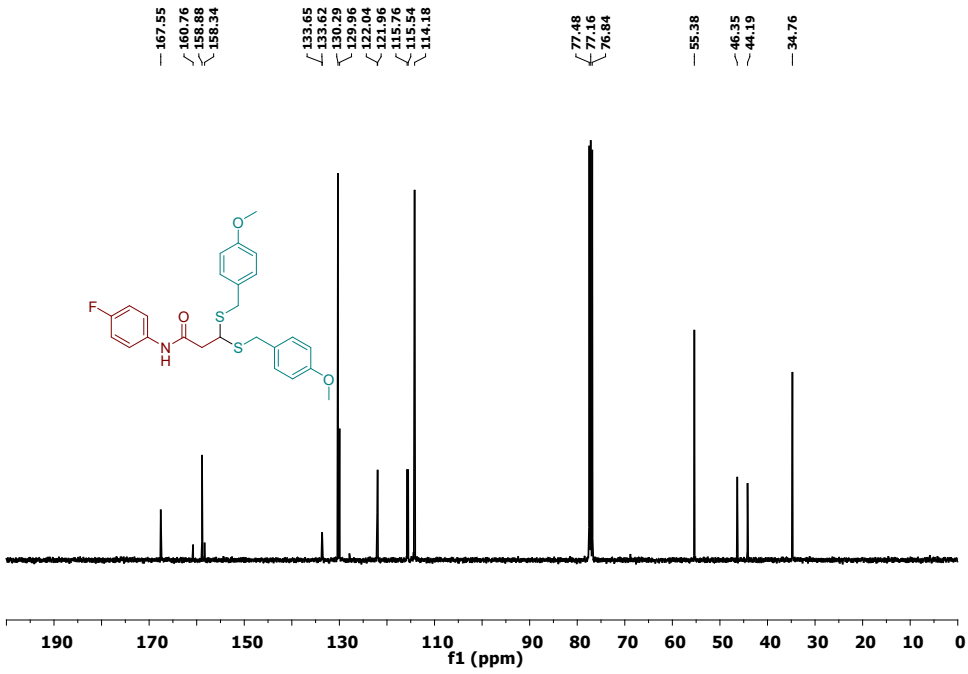


Figure S21. [13]C NMR spectrum of 3,3-bis(benzylthio)-N-(o-tolyl)propanamide (**3ff**)

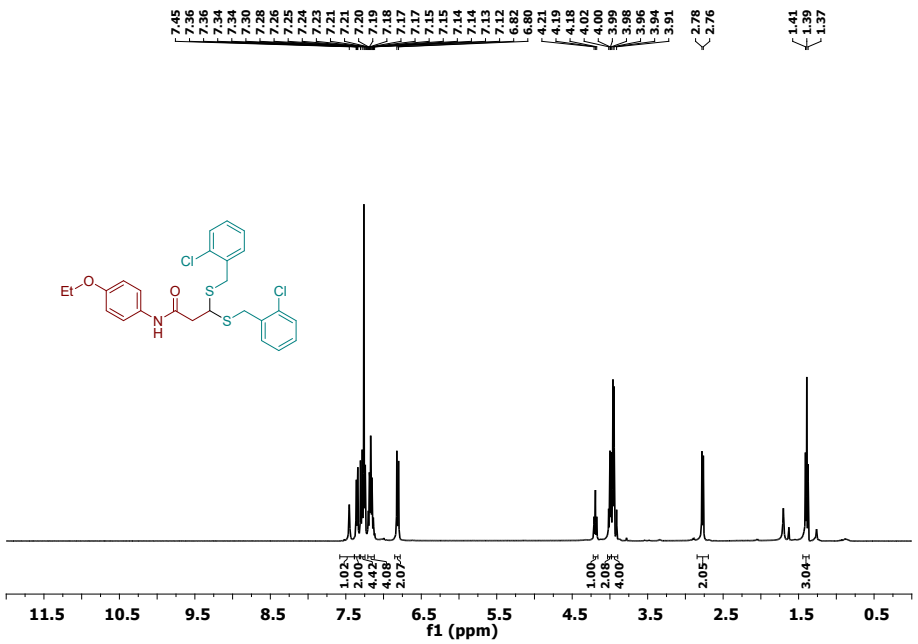


Figure S22. [1]H NMR spectrum of 3,3-bis((2-chlorobenzyl)thio)-N-(4-ethoxyphenyl)propanamide (**3gg**)

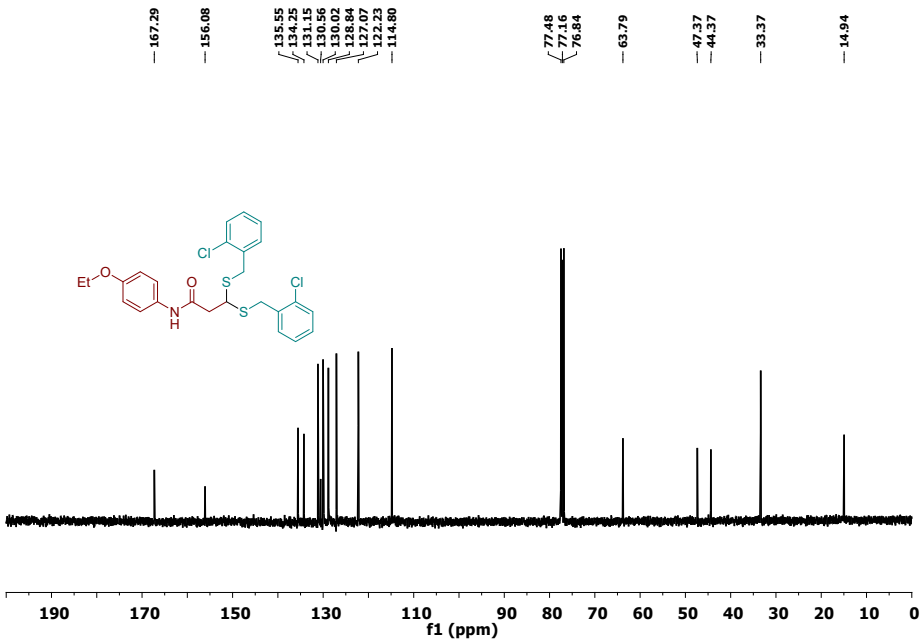


Figure S23. [13]C NMR spectrum of 3,3-bis((2-chlorobenzyl)thio)-N-(4-ethoxyphenyl)propanamide (**3gg**)

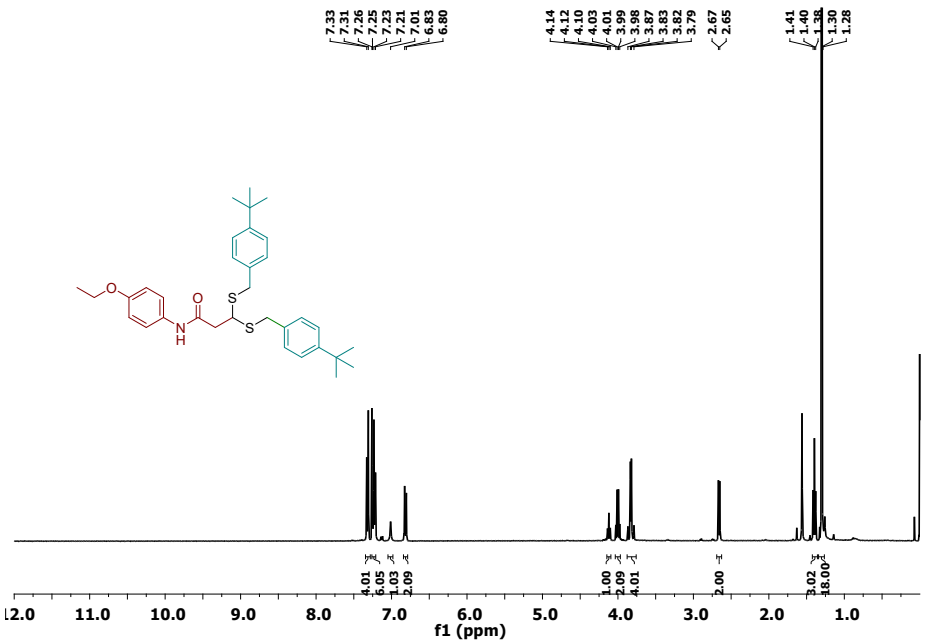


Figure S24. [1]H NMR spectrum of 3,3-bis((4-(tert-butyl)benzyl)thio)-N-(4-ethoxyphenyl)propanamide **(3ge)**

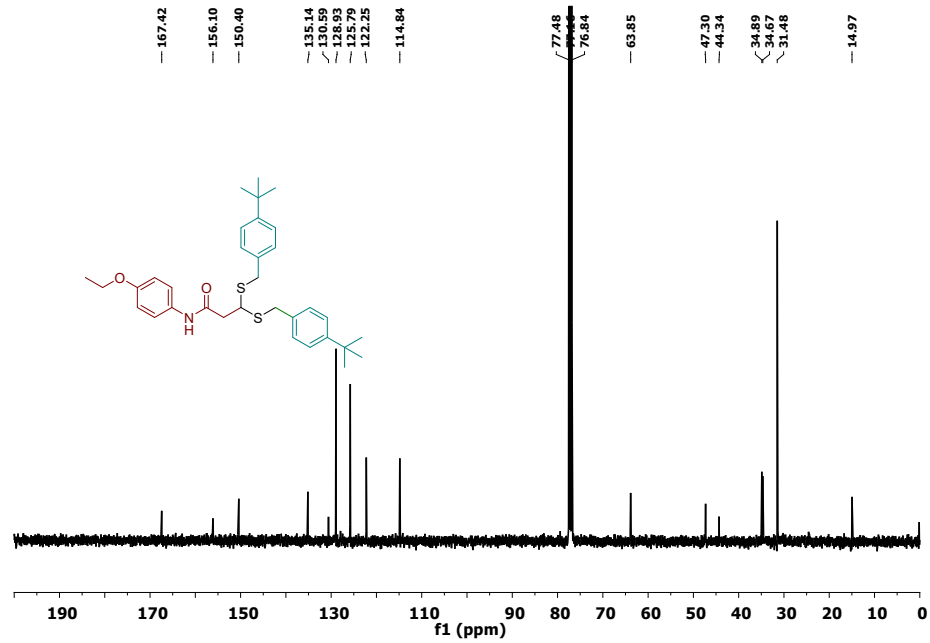


Figure S25. [13]C NMR spectrum of 3,3-bis((4-(tert-butyl)benzyl)thio)-N-(4-ethoxyphenyl)propanamide **(3ge)**

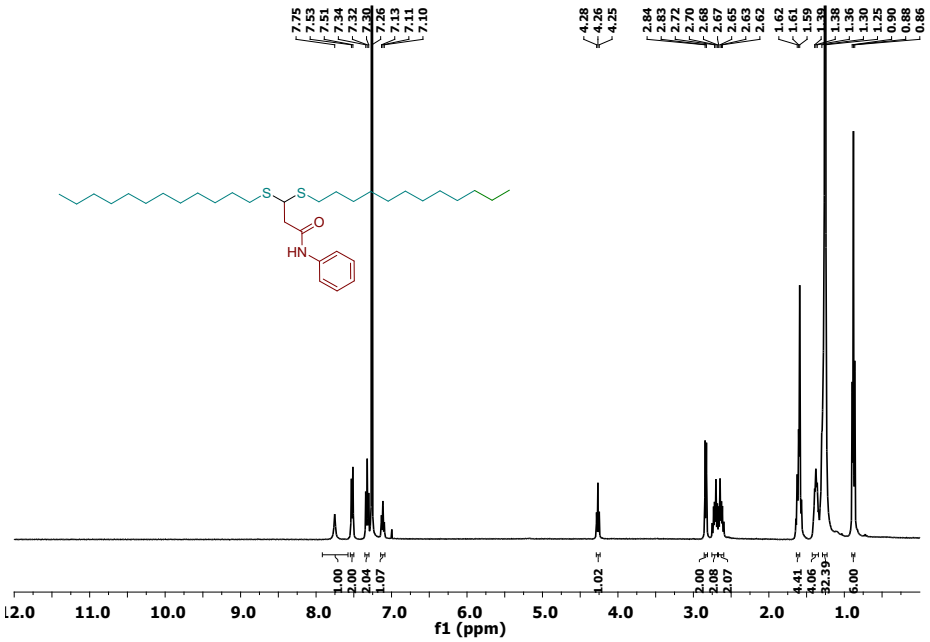


Figure S26. ^{1}H NMR spectrum of 3,3-bis(dodecylthio)-N-phenylpropanamide (**3ai**)

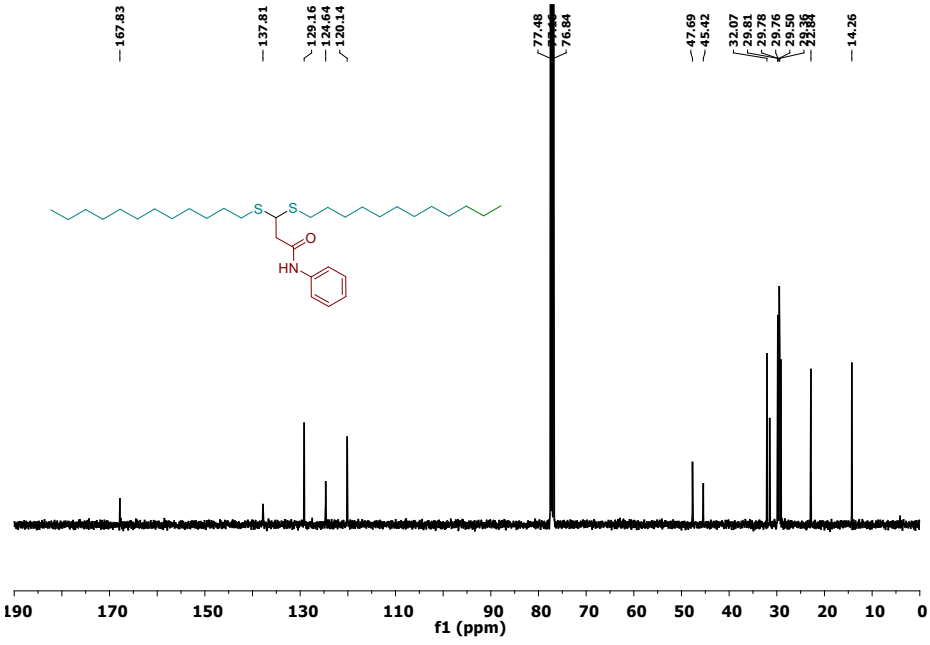


Figure S27. ^{13}C NMR spectrum of 3,3-bis(dodecylthio)-N-phenylpropanamide (**3ai**)

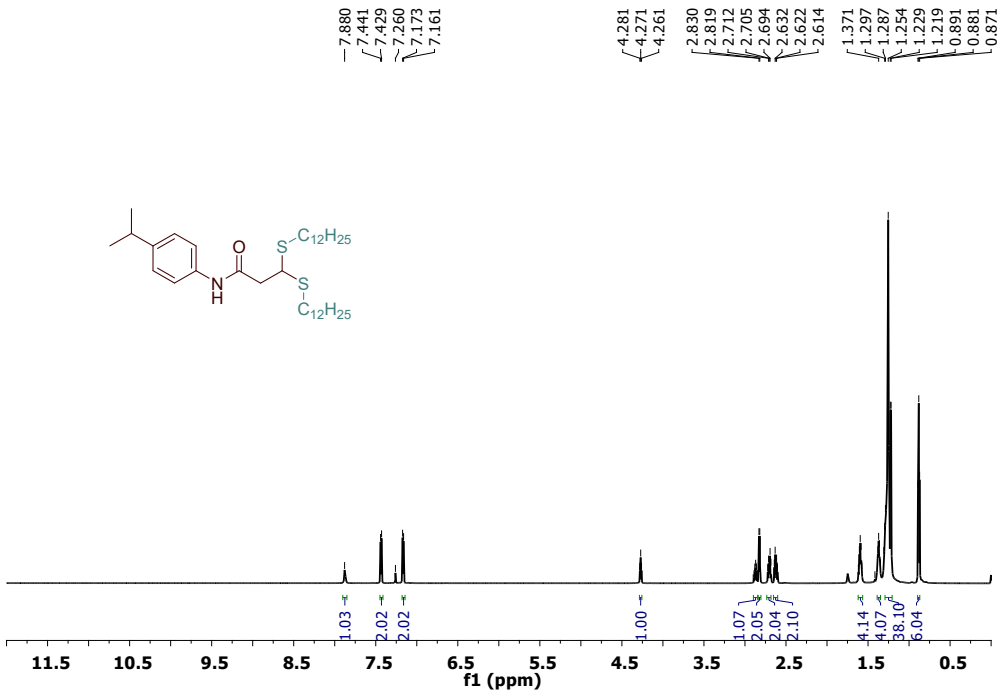


Figure S28. [1]H NMR spectrum of 3,3-bis(dodecylthio)-N-(4-isopropylphenyl)propanamide (**3hi**)

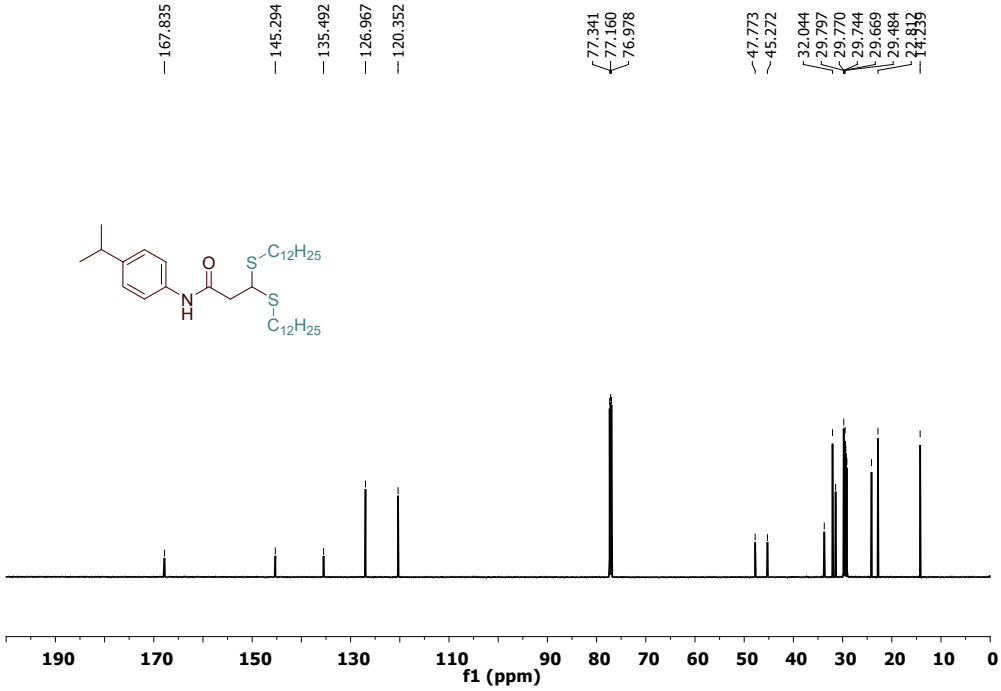


Figure S29. ^{13}C NMR spectrum of 3,3-bis(dodecylthio)-N-(4-isopropylphenyl)propanamide (**3hi**)

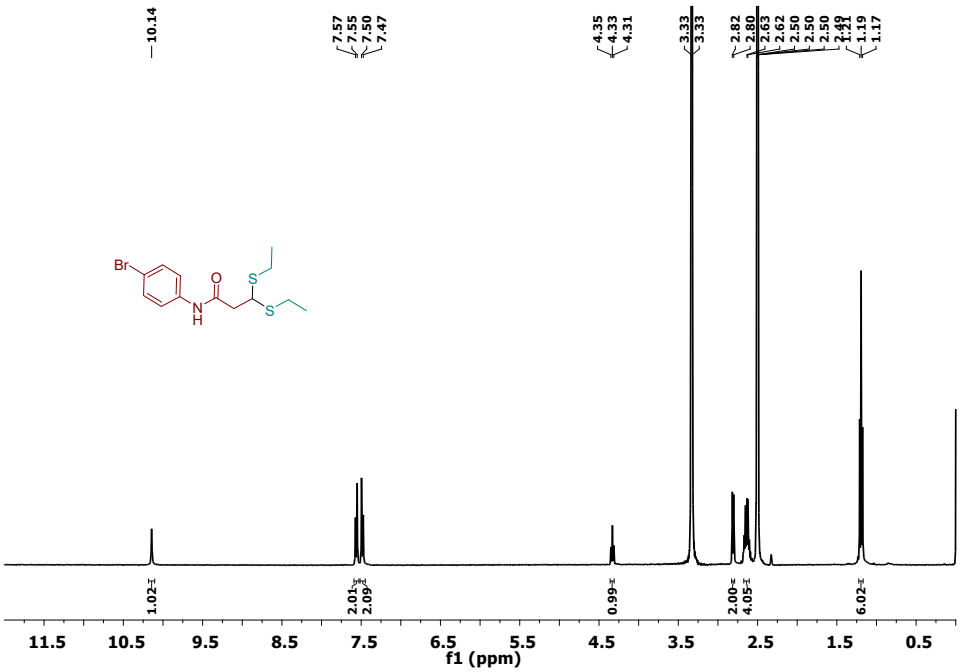


Figure S30. ^{1}H NMR spectrum of N-(4-bromophenyl)-3,3-bis(ethylthio)propanamide (**3ij**)

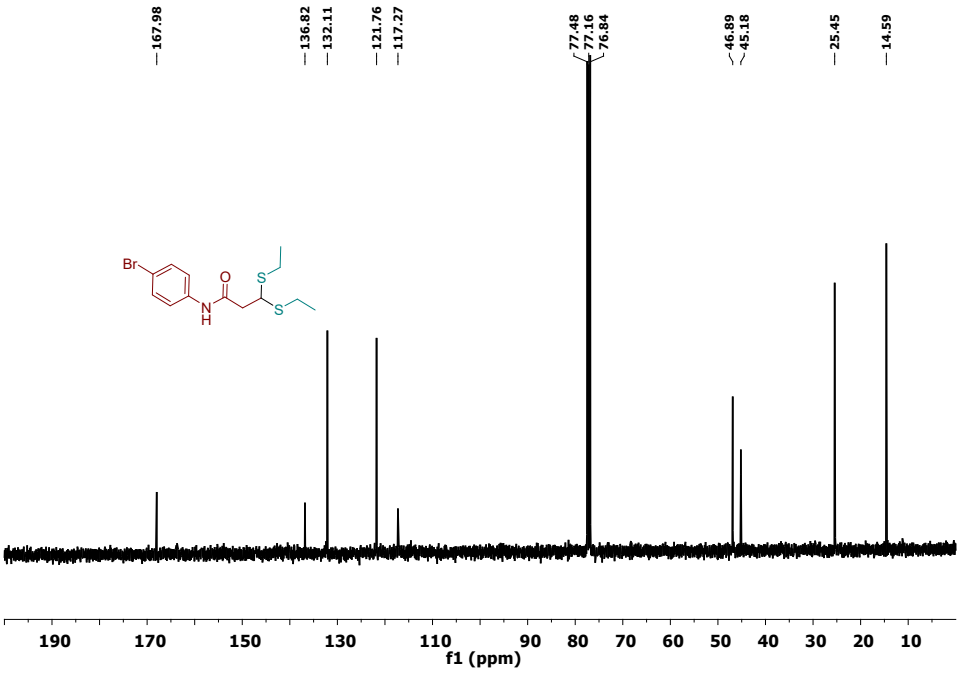


Figure S31. ^{13}C NMR spectrum of N-(4-bromophenyl)-3,3-bis(ethylthio)propanamide (**3ij**)

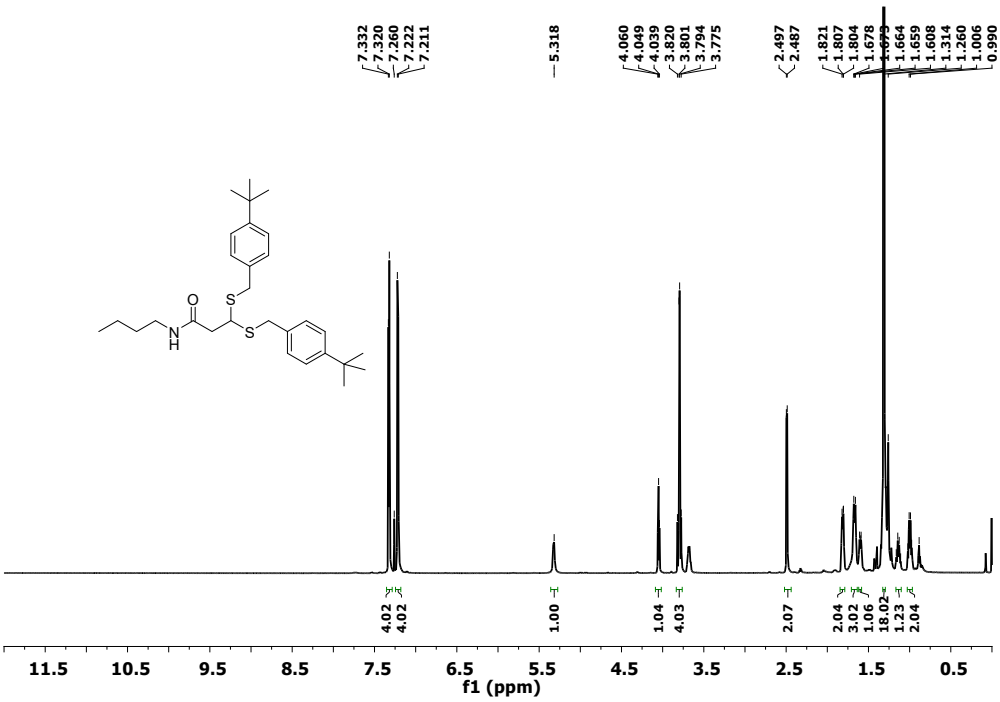


Figure S32. ^{1}H NMR spectrum of N-butyl-3,3-bis((4-(tert-butyl)benzyl)thio)propanamide (**3je**)

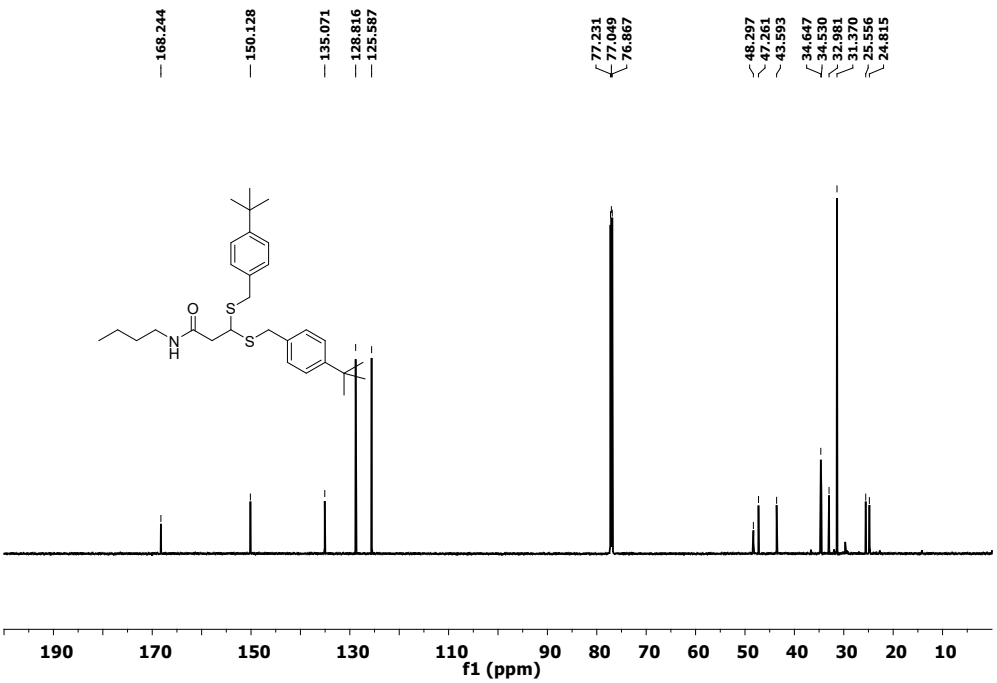


Figure S33. ^{13}C NMR spectrum of N-butyl-3,3-bis((4-(tert-butyl)benzyl)thio)propanamide (**3je**)

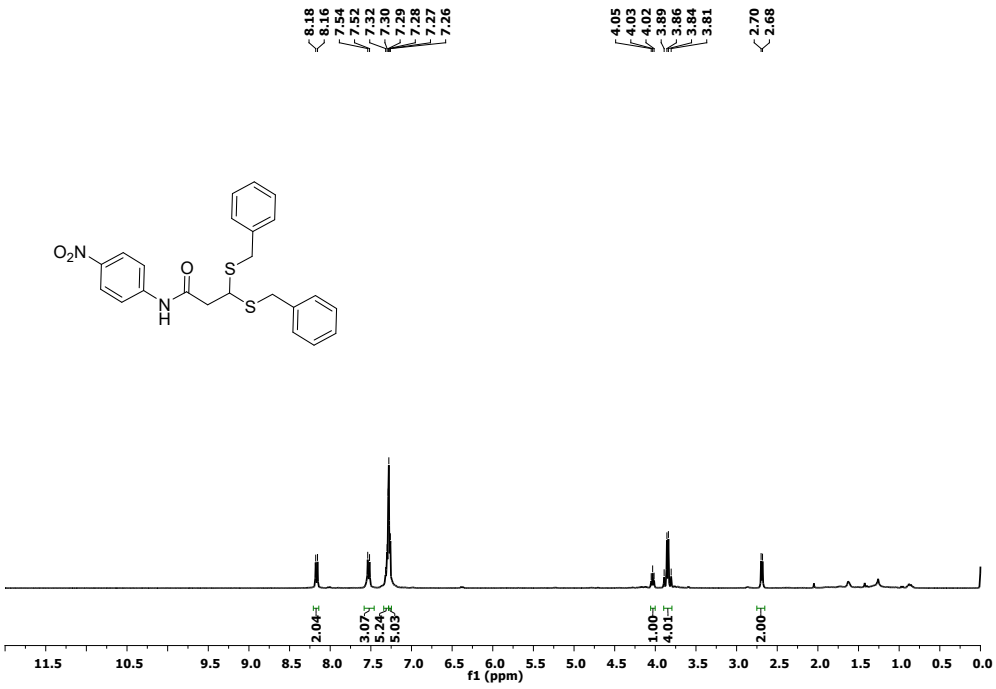


Figure S34. ^{1}H NMR spectrum of 3,3-bis(benzylthio)-N-(4-nitrophenyl)propanamide **(3kd)**

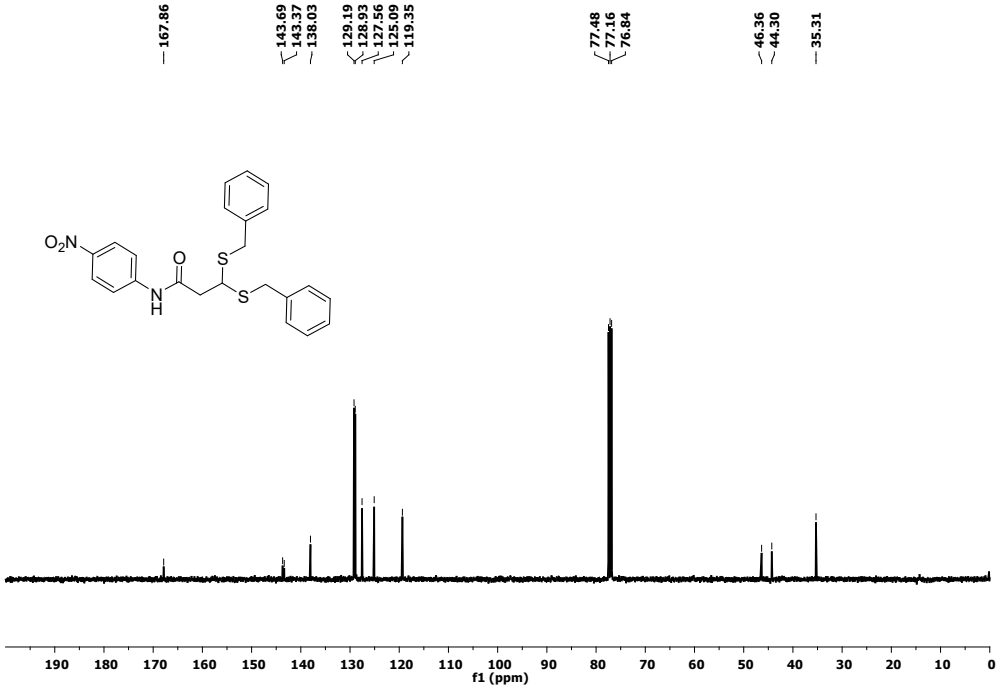


Figure S35. ^{13}C NMR spectrum of 3,3-bis(benzylthio)-N-(4-nitrophenyl)propanamide **(3kd)**

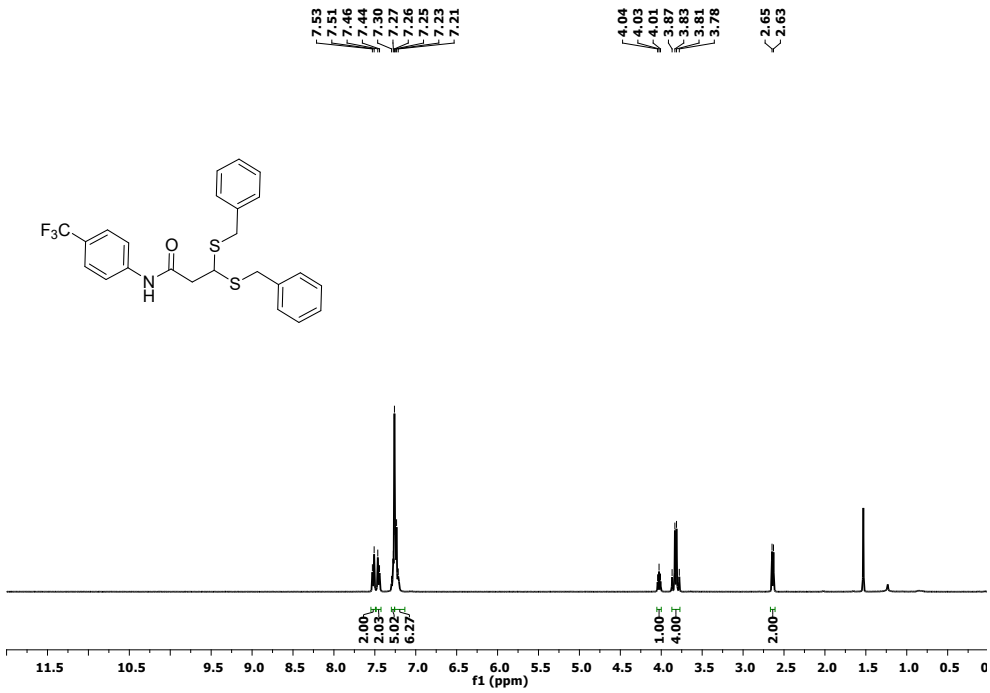


Figure S36. ^{1}H NMR spectrum of 3,3-bis(benzylthio)-N-(4(trifluoromethyl)phenyl)propanamide **(3ld)**

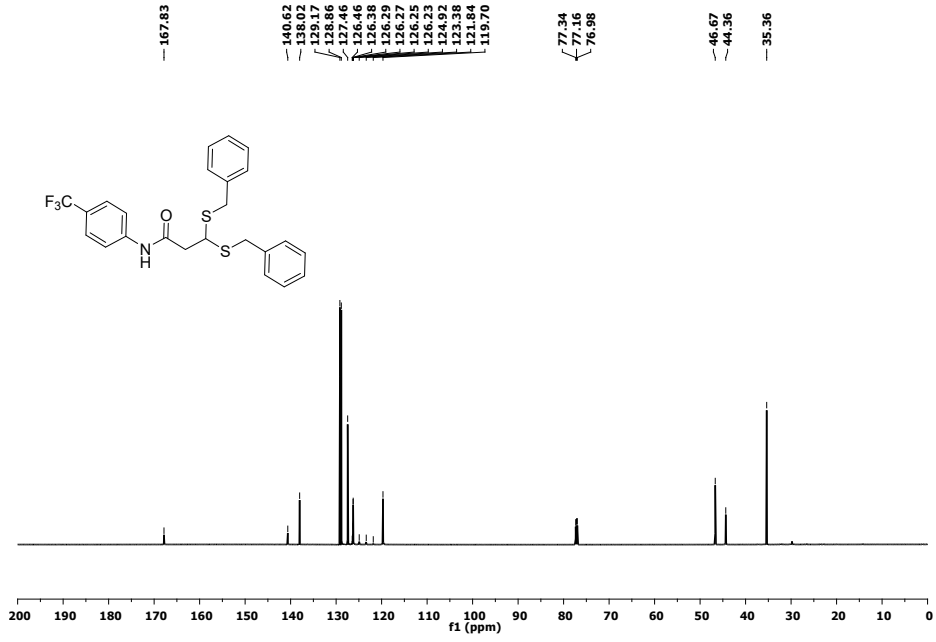


Figure S37. ^{13}C NMR spectrum of spectrum of 3,3-bis(benzylthio)-N-(4(trifluoromethyl)phenyl)propanamide **(3ld)**

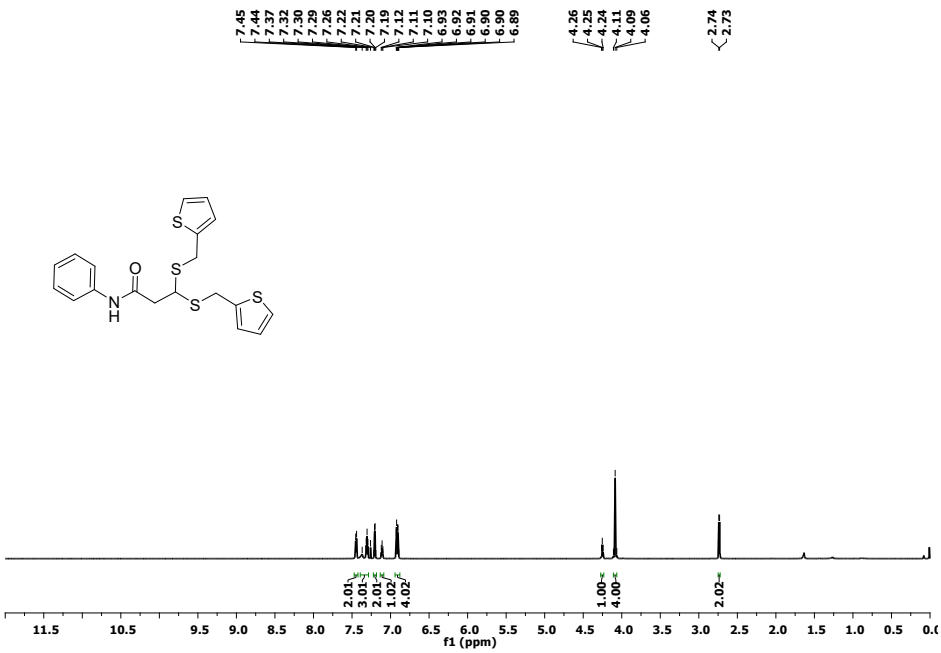


Figure S38. ^{1}H NMR spectrum of N-phenyl-3,3-bis((thiophen-2-ylmethyl)thio)propanamide **(3ak)**

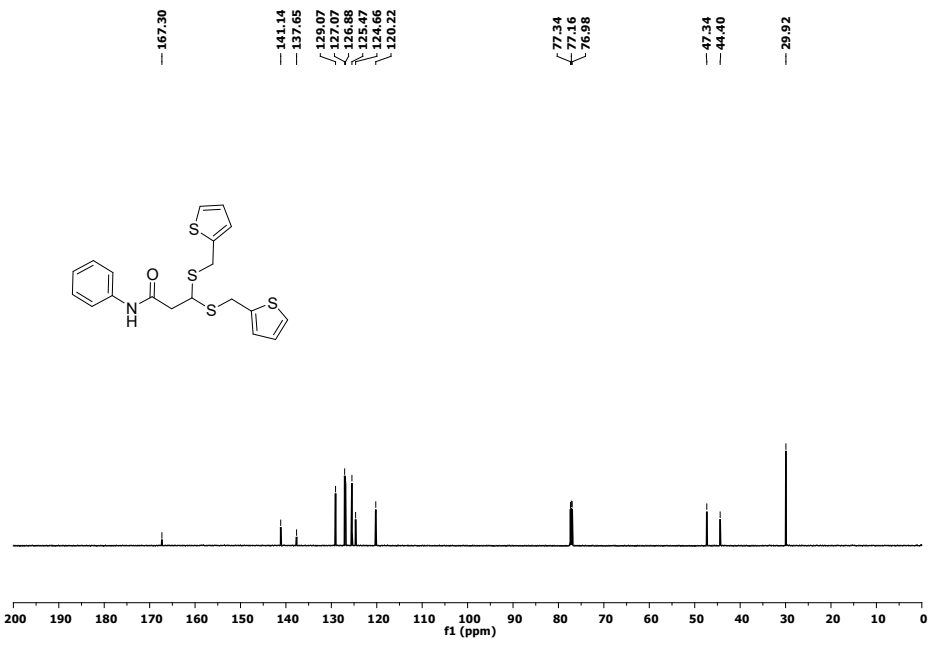


Figure S39. ^{13}C NMR spectrum of N-phenyl-3,3-bis((thiophen-2-ylmethyl)thio)propanamide **(3ak)**

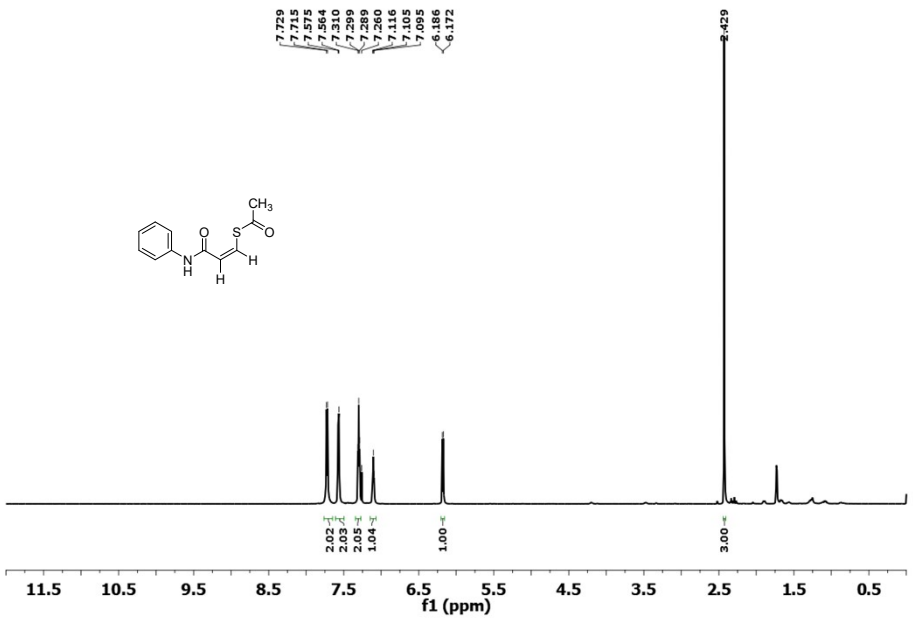


Figure S40. ^{1}H NMR spectrum of (Z)-S-(3-oxo-3-(phenylamino)prop-1-en-1-yl) ethanethioate (**5**)

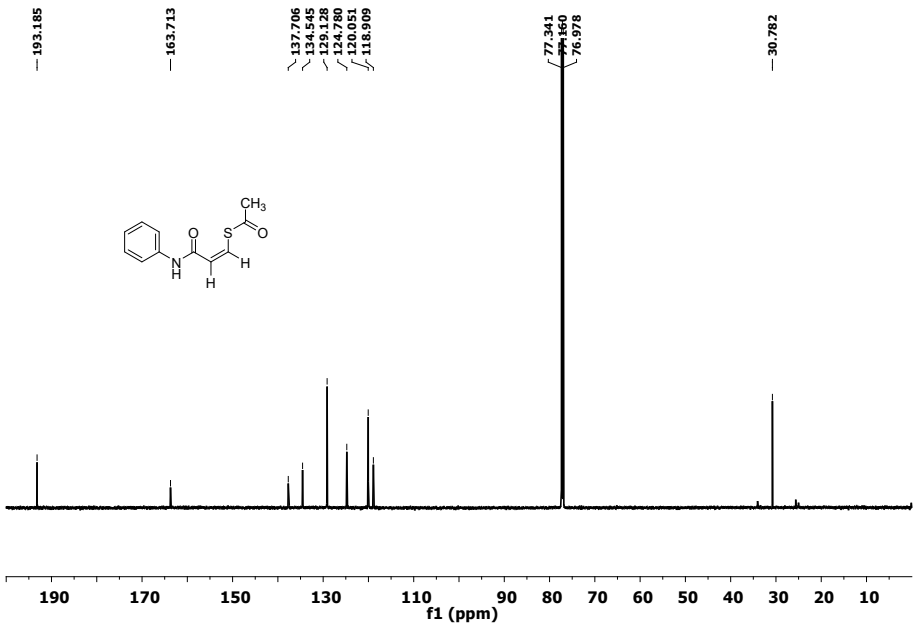


Figure S41. ^{13}C NMR spectrum of (Z)-S-(3-oxo-3-(phenylamino)prop-1-en-1-yl) ethanethioate (**5**)

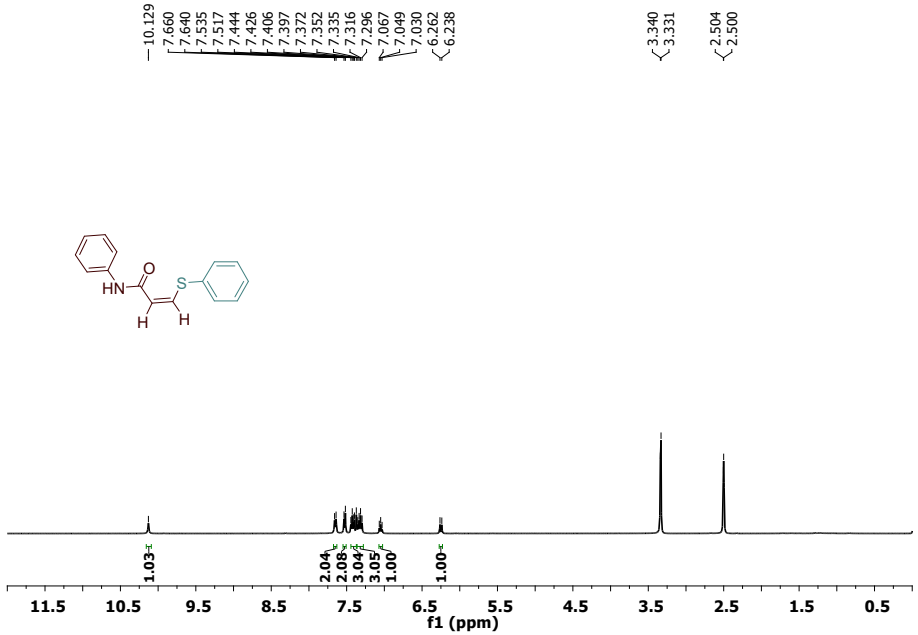


Figure S42. ^{1}H NMR spectrum of (Z)-N-Phenyl-3-(phenylthio)acrylamide (**6**)

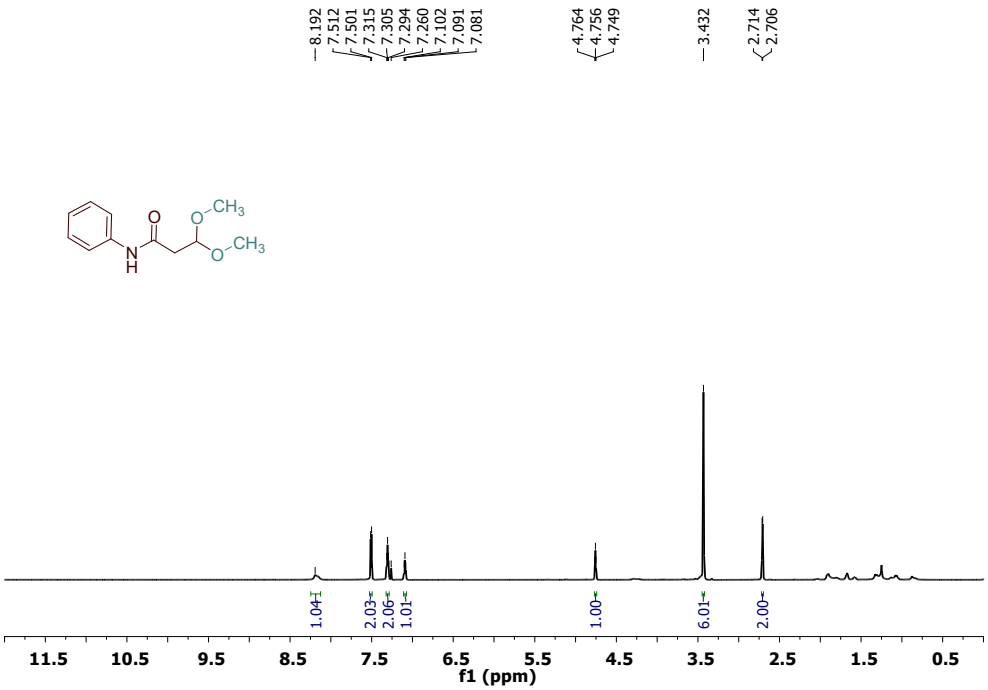


Fig. S43. ^{1}H NMR spectrum of 3,3-dimethoxy-N-phenylpropanamide (**4aa**)

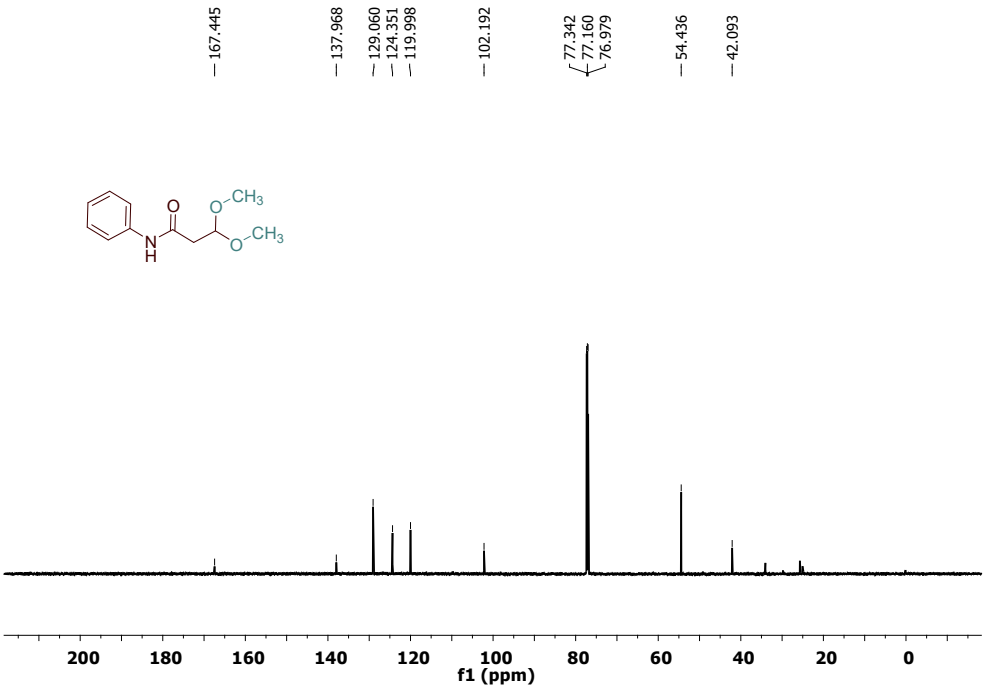


Fig. S44. ^{13}C NMR spectrum of 3,3-dimethoxy-N-phenylpropanamide (**4aa**)

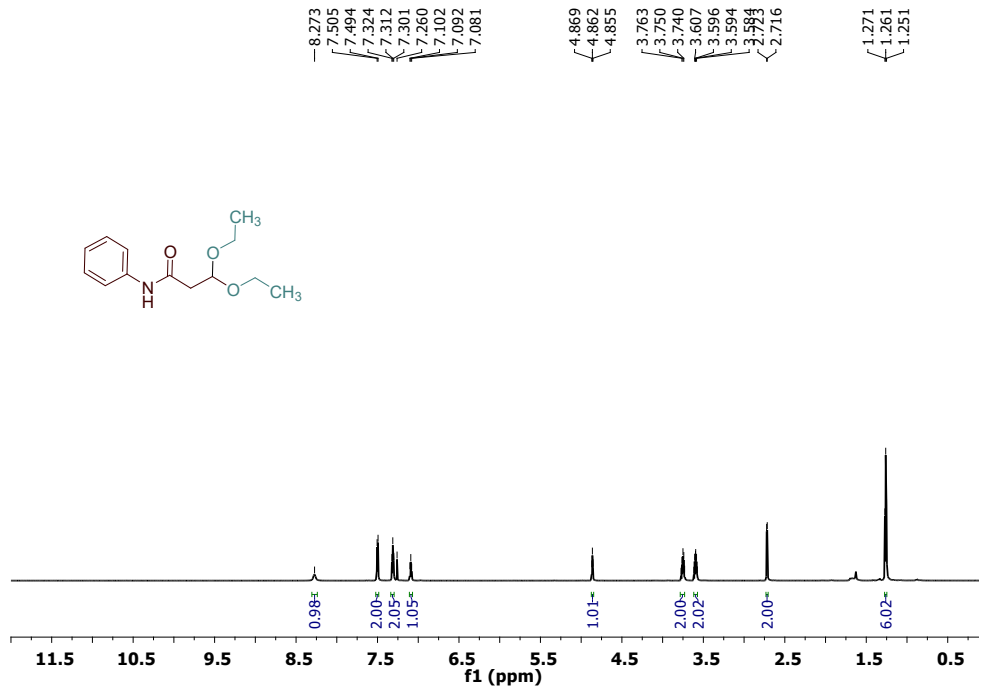


Fig. S45. ^{1}H NMR spectrum of 3,3-diethoxy-N-phenylpropanamide (**4ab**)

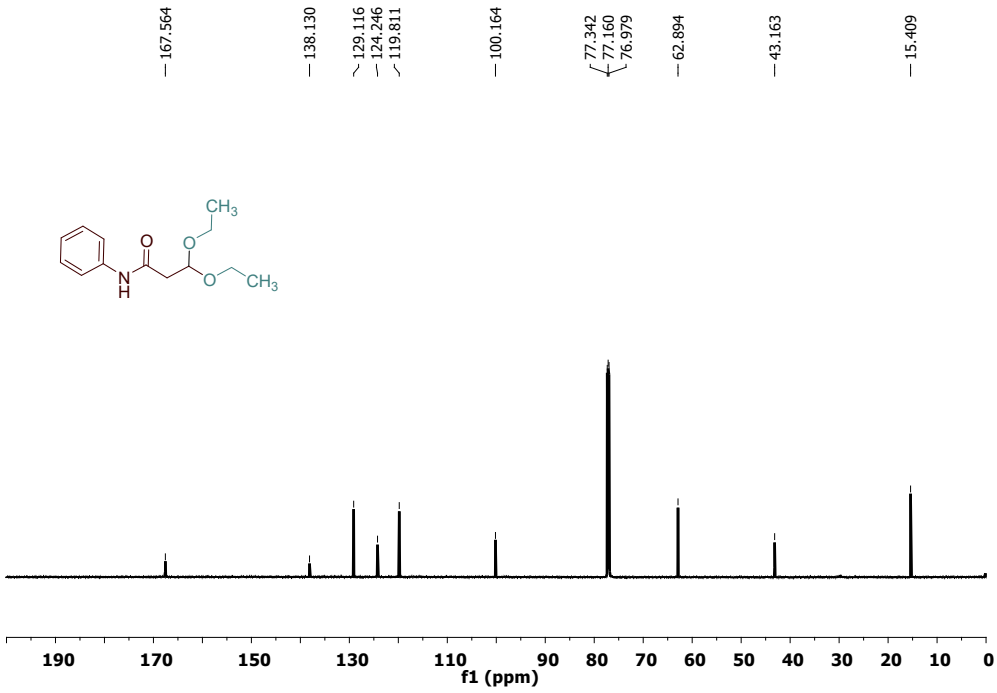


Fig. S46. ^{13}C NMR spectrum of 3,3-diethoxy-N-phenylpropanamide (**4ab**)

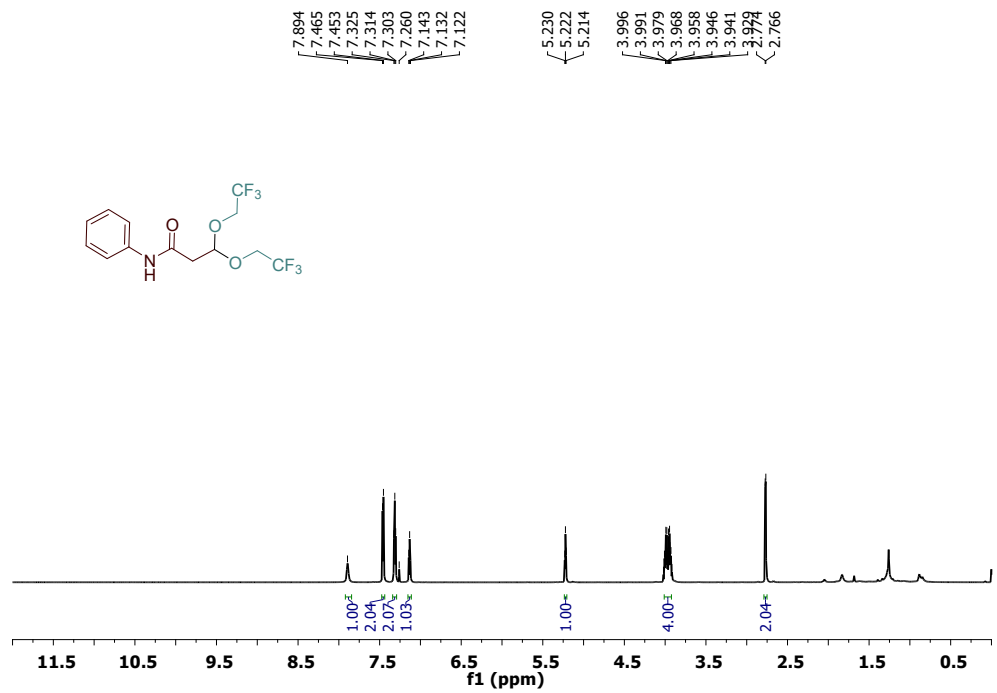


Fig. S47. [1]H NMR spectrum of N-phenyl-3,3-bis(2,2,2-trifluoroethoxy)propanamide (**4ac**)

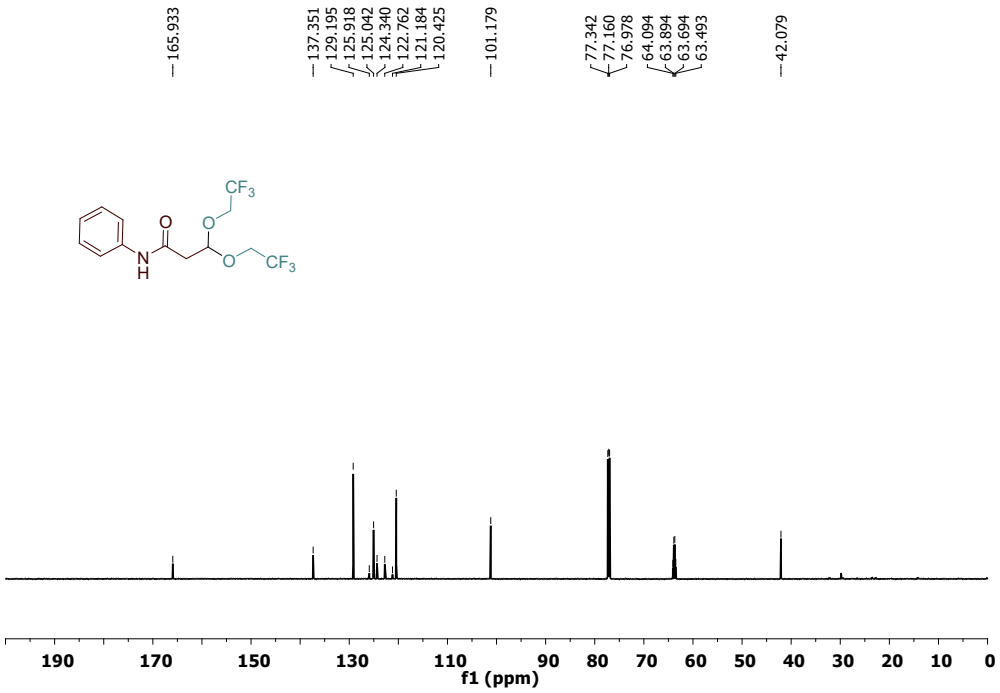


Fig. S48. [13]C NMR spectrum of N-phenyl-3,3-bis(2,2,2-trifluoroethoxy)propanamide (**4ac**)

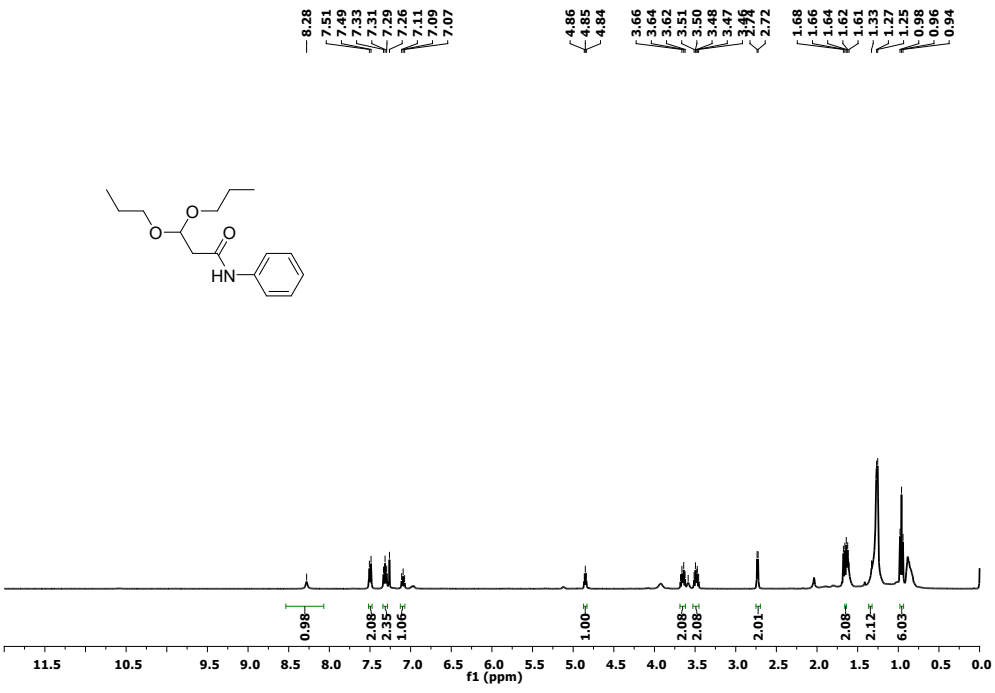


Fig. S49. ^{1}H NMR spectrum of N-phenyl-3,3-dipropoxypropanamide **(4ad)**

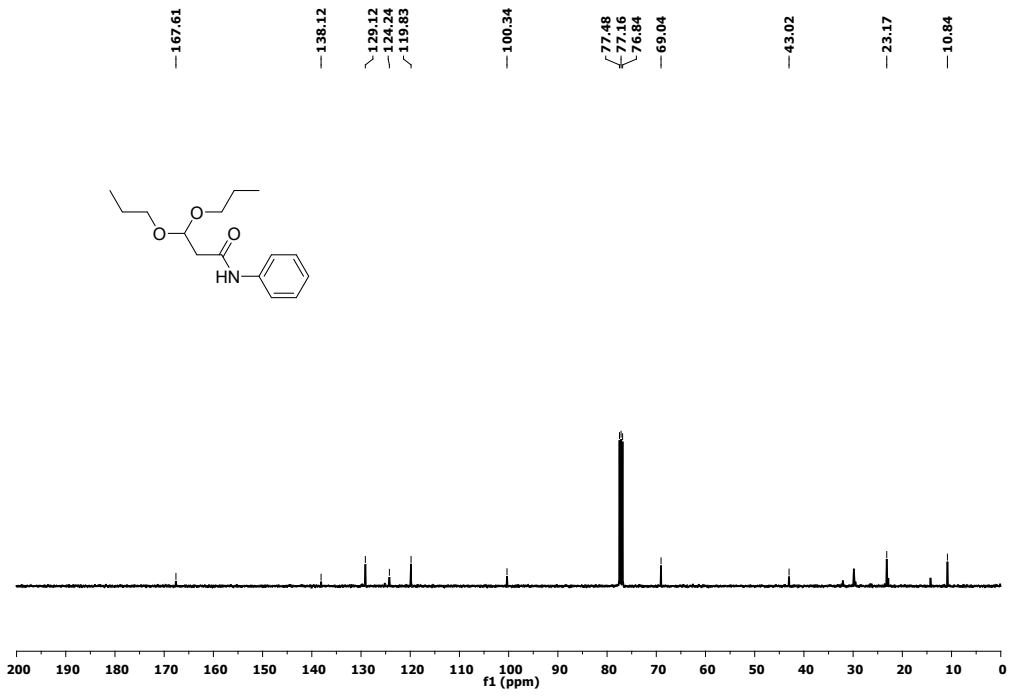


Fig. S50. ^{13}C NMR spectrum of N-phenyl-3,3-dipropoxypropanamide **(4ad)**

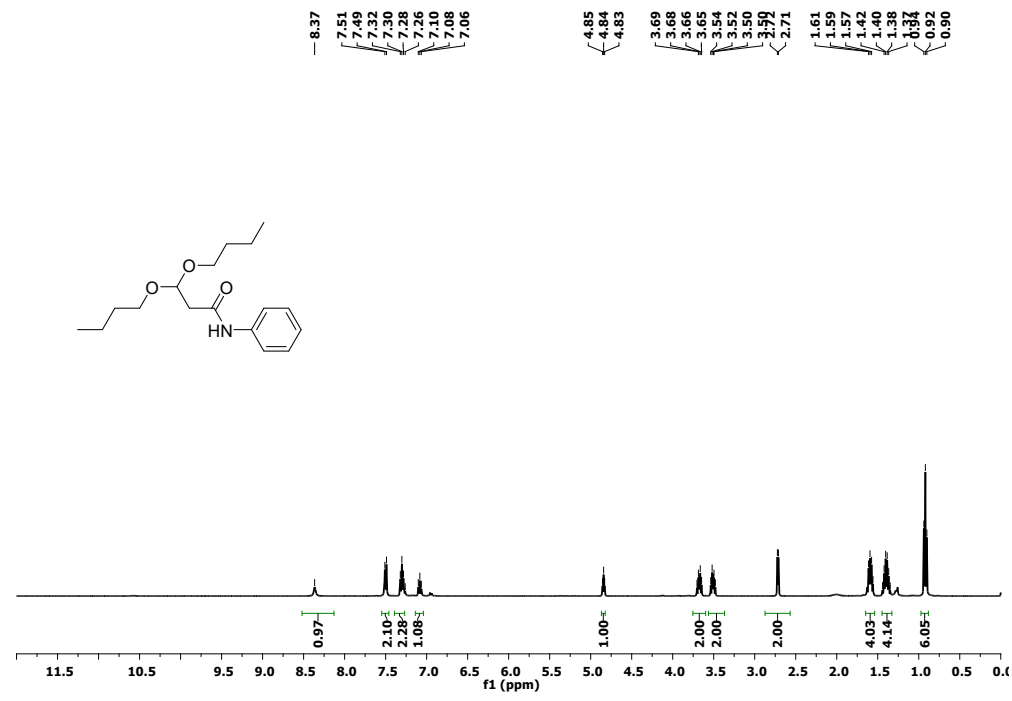


Fig. S51. [1]H NMR spectrum of 3,3-dibutoxy-N-phenylpropanamide **(4ae)**

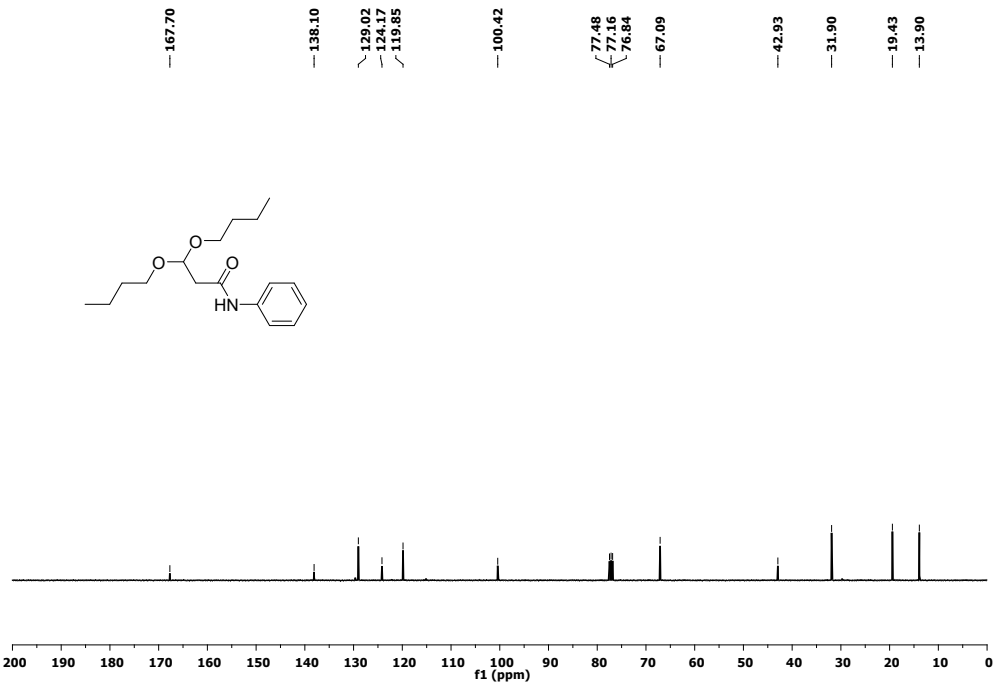


Fig. S52. [13]C NMR spectrum of 3,3-dibutoxy-N-phenylpropanamide **(4ae)**

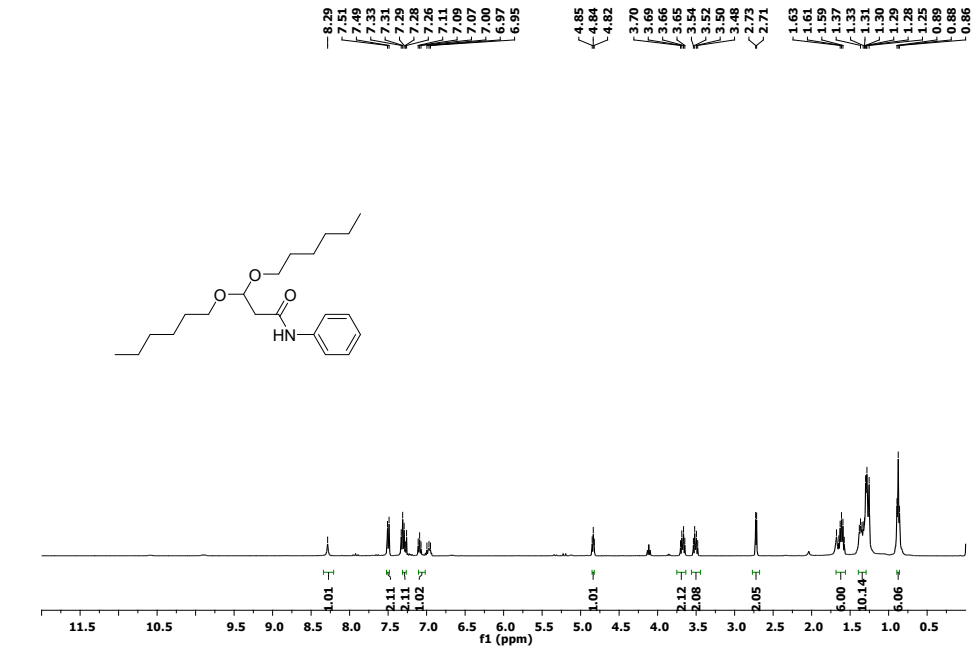


Fig. S53. [1]H NMR spectrum of 3,3-bis(hexyloxy)-N-phenylpropanamide **(4af)**

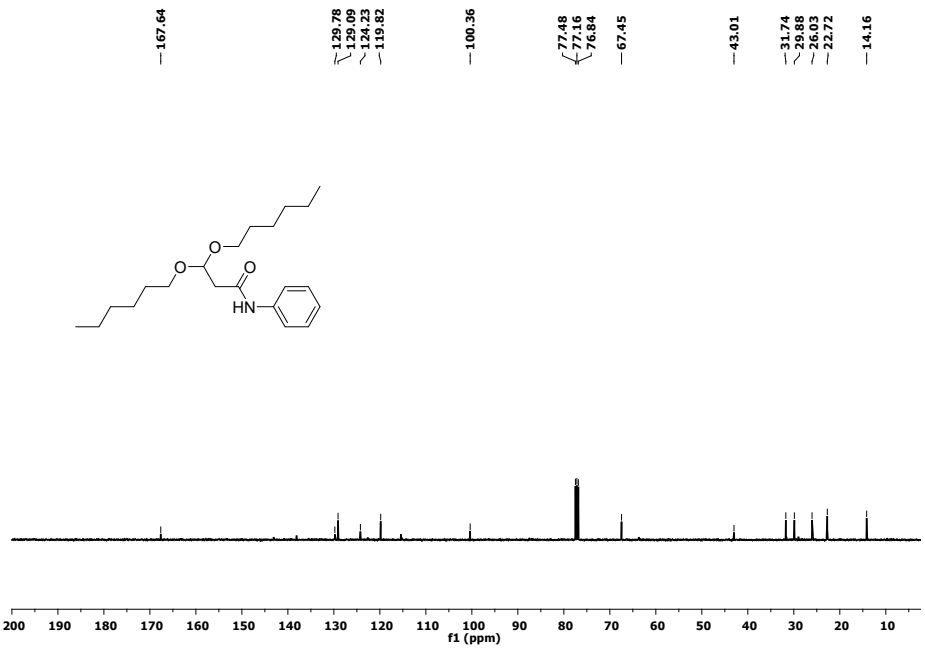


Fig. S54. ^{13}C NMR spectrum of 3,3-bis(hexyloxy)-N-phenylpropanamide **(4af)**

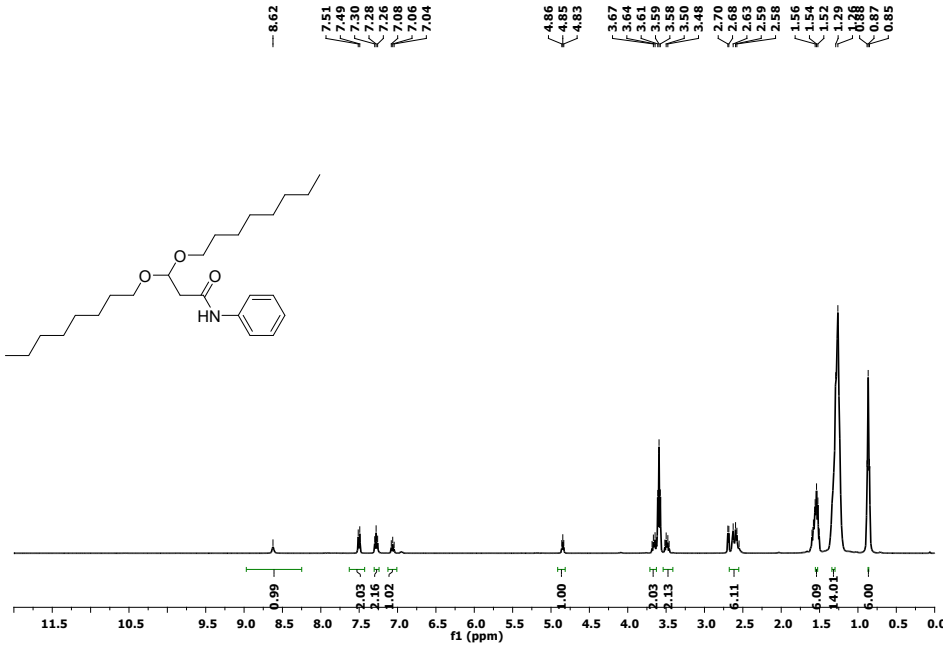


Fig. S55. ^{1}H NMR spectrum of 3,3-bis(octyloxy)-N-phenylpropanamide **(4ag)**

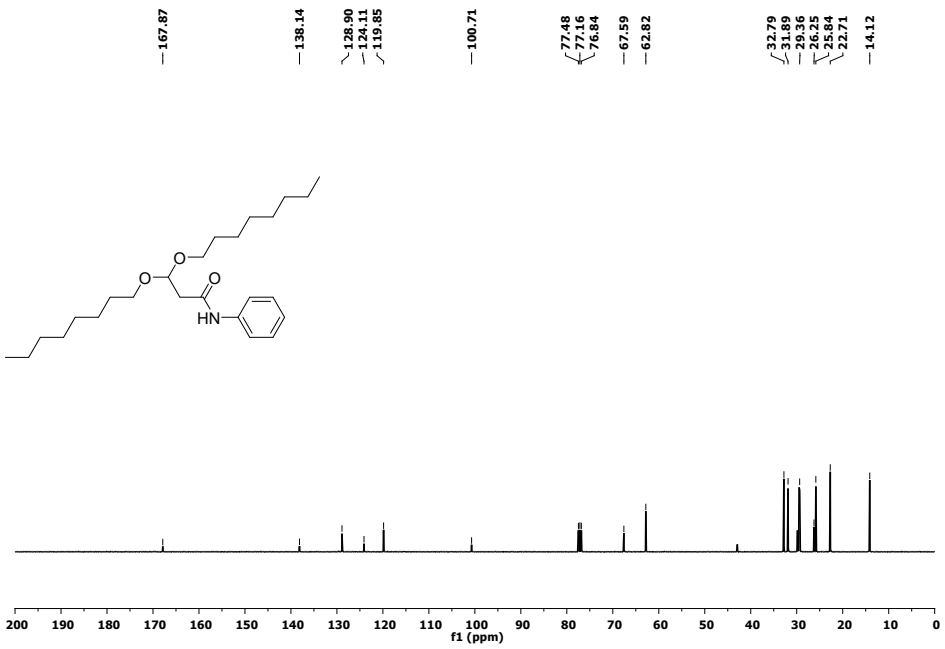


Fig. S56. ^{13}C NMR spectrum of 3,3-bis(octyloxy)-N-phenylpropanamide **(4ag)**

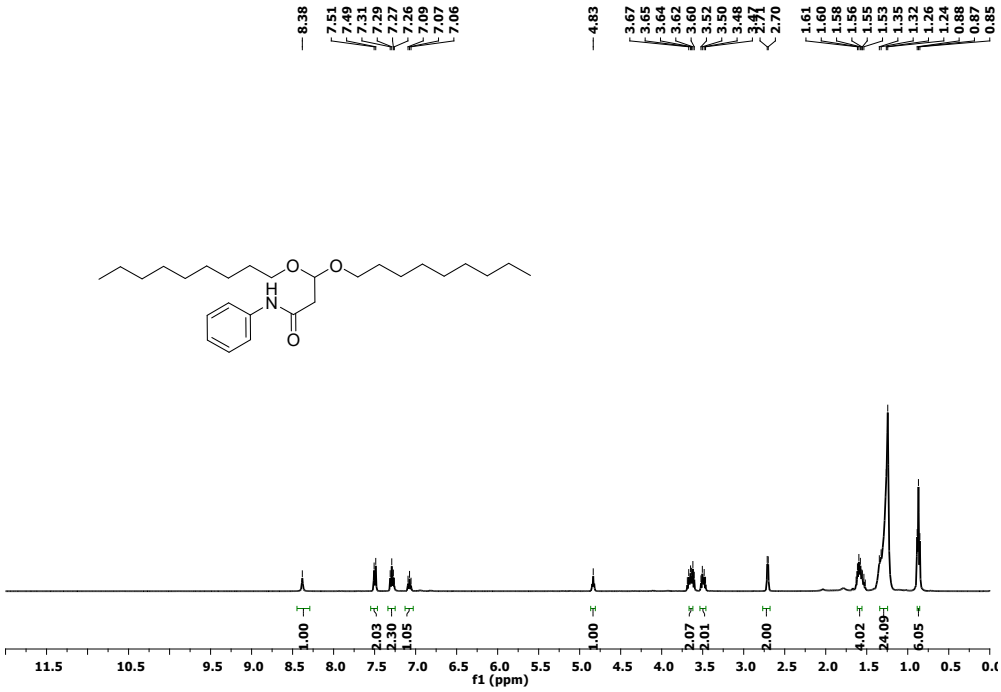


Fig. S57. ^{1}H NMR spectrum of 3,3-bis(nonyloxy)-N-phenylpropanamide **(4ah)**

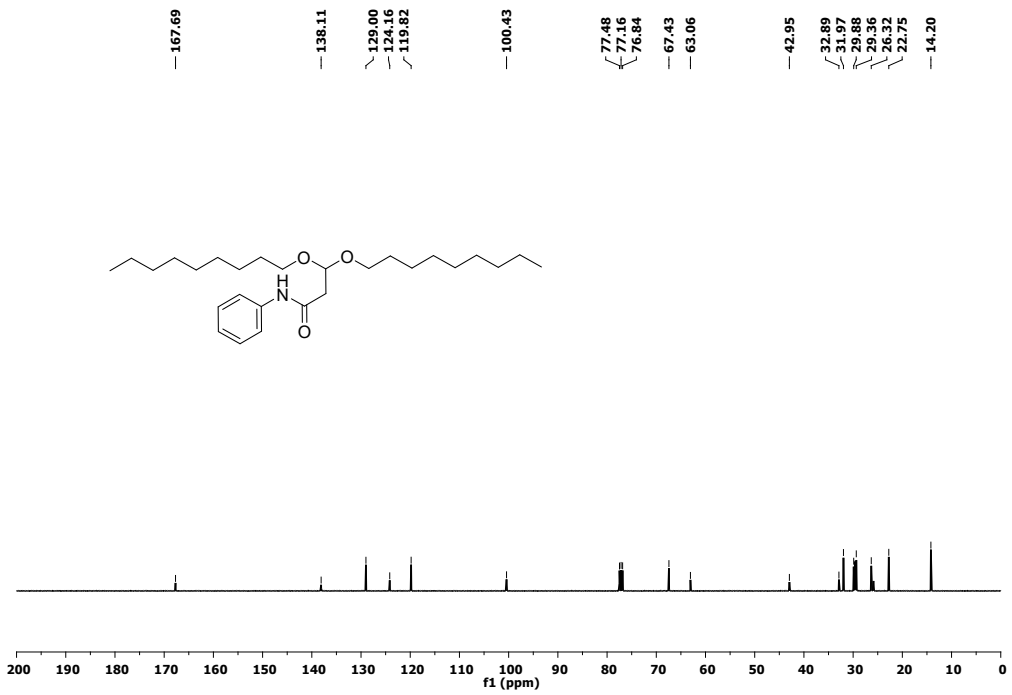


Fig. S58. ^{13}C NMR spectrum of 3,3-bis(nonyloxy)-N-phenylpropanamide **(4ah)**

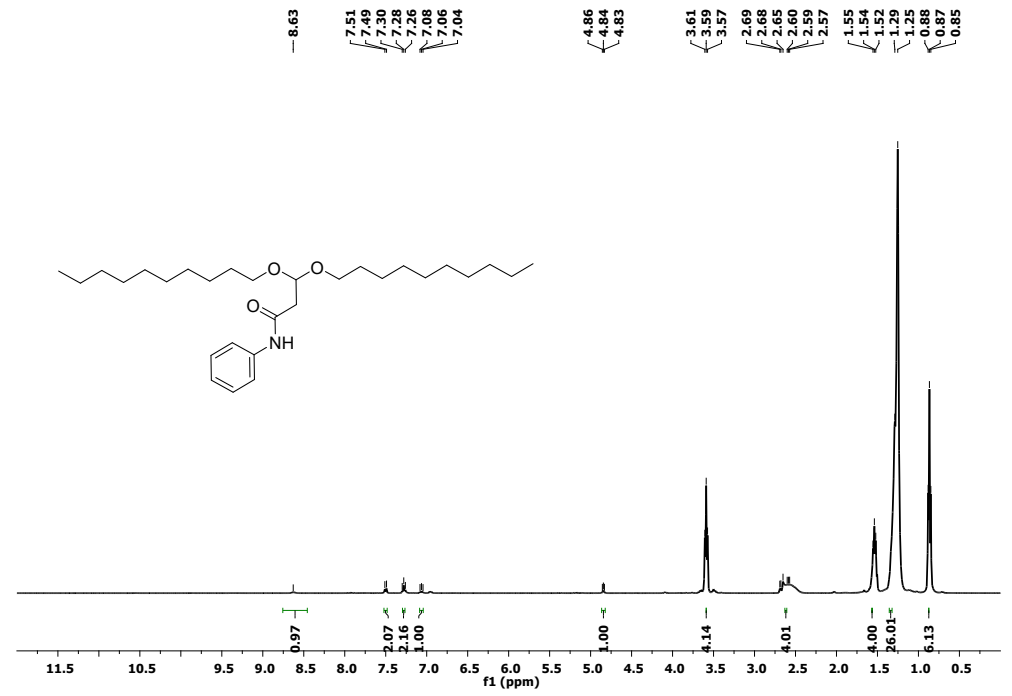


Fig. S59. ^{1}H NMR spectrum of 3,3-bis(decyloxy)-N-phenylpropanamide **(4ai)**

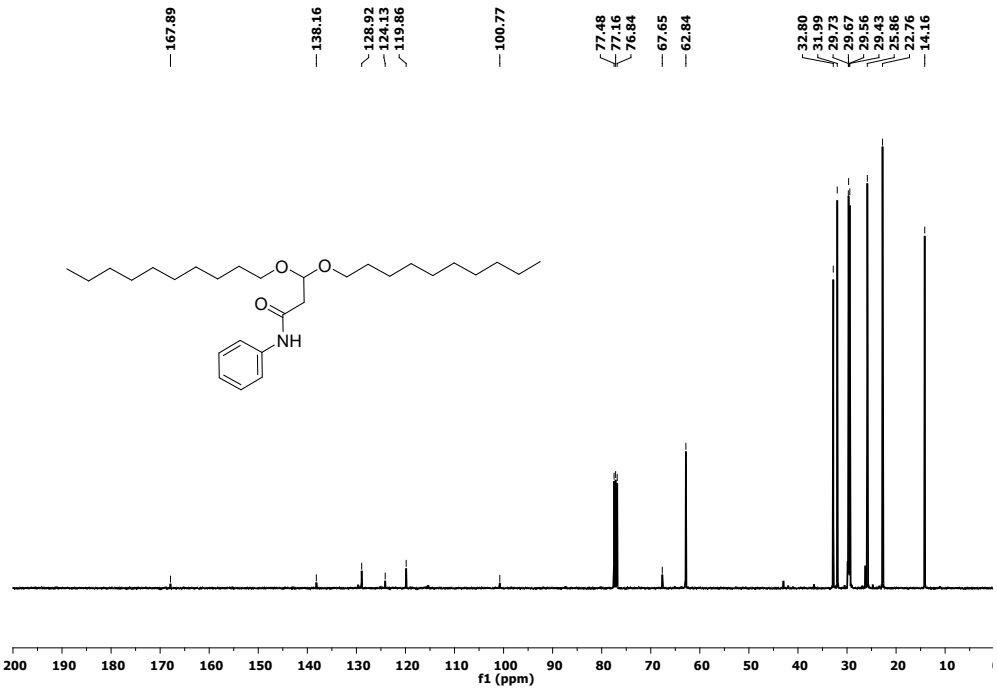


Fig. S60. ^{13}C NMR spectrum of 3,3-bis(decyloxy)-N-phenylpropanamide **(4ai)**

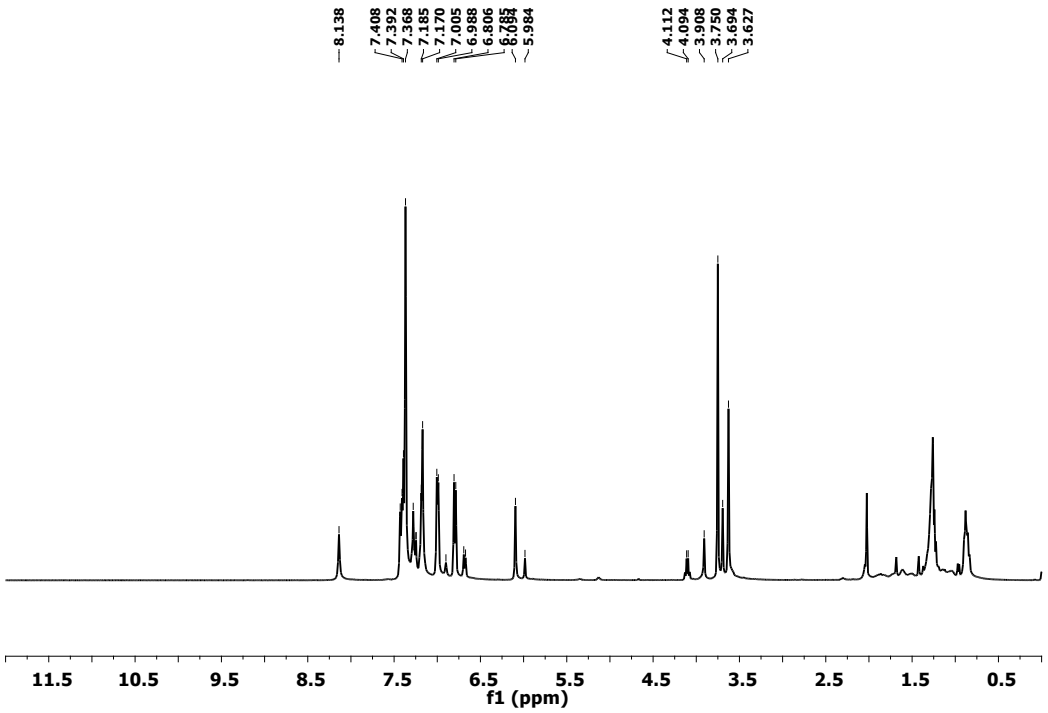


Figure S61. ^{1}H NMR spectrum for the mixture of benzyl (styryl)sulfane and disulfide.

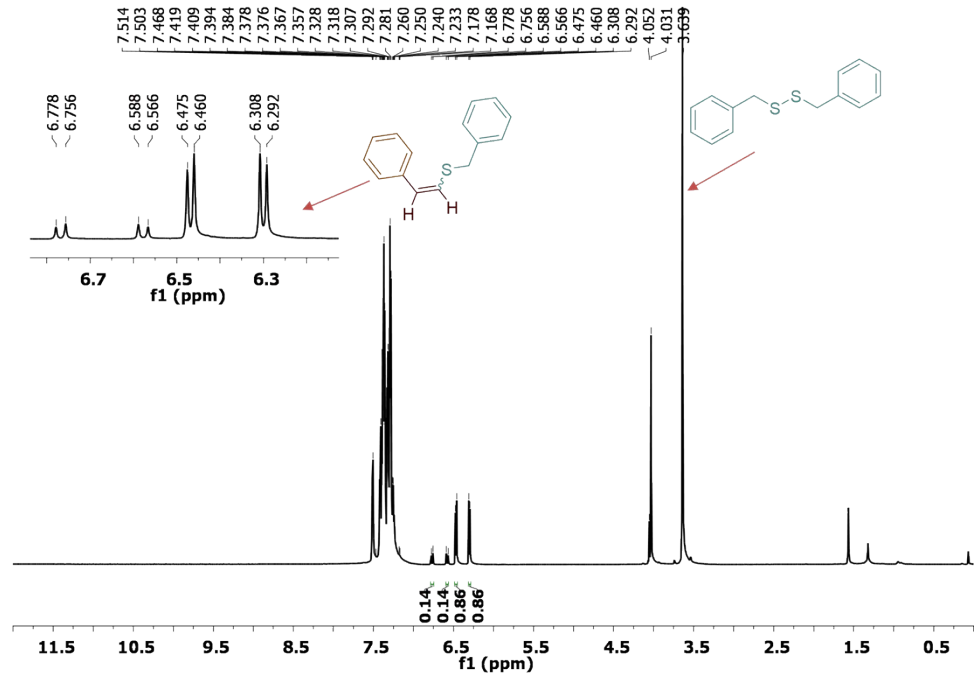
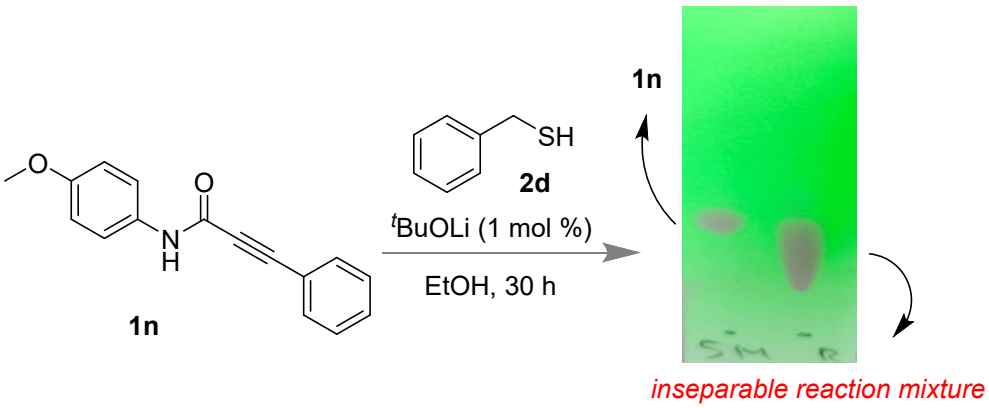


Figure S62. ^{1}H NMR spectrum for the mixture of benzyl (styryl)sulfane and disulfide.



Scheme S1. Reaction of internal alkyne **1n** and benzyl mercaptan 2d shows complex reaction mixture.