

SUPPLEMENTARY MATERIAL

Synthesis and biological screening of a library of macamides as TNF- α inhibitors

Víctor Tena Pérez^a, Luis Apaza Ticona^{a,b,*}, Andreea Madalina Serban^c, Javier Acero Gómez^a, Ángel Rumbero Sánchez^a

Affiliation

^aDepartment of Organic Chemistry, Faculty of Sciences, University Autónoma of Madrid. Cantoblanco, 28049 Madrid, Spain

^bDepartment of Pharmacology, Pharmacognosy and Botany, Faculty of Pharmacy, University Complutense of Madrid. Ciudad Universitaria s/n, 28040 Madrid, Spain

^cMaria Skłodowska Curie University Hospital for Children. Constantin Brâncoveanu Boulevard, 077120 Bucharest, Romania.

*Corresponding author

E-mail addresses: luis.apaza@uam.es; lnapaza@ucm.es (Luis Apaza T.)

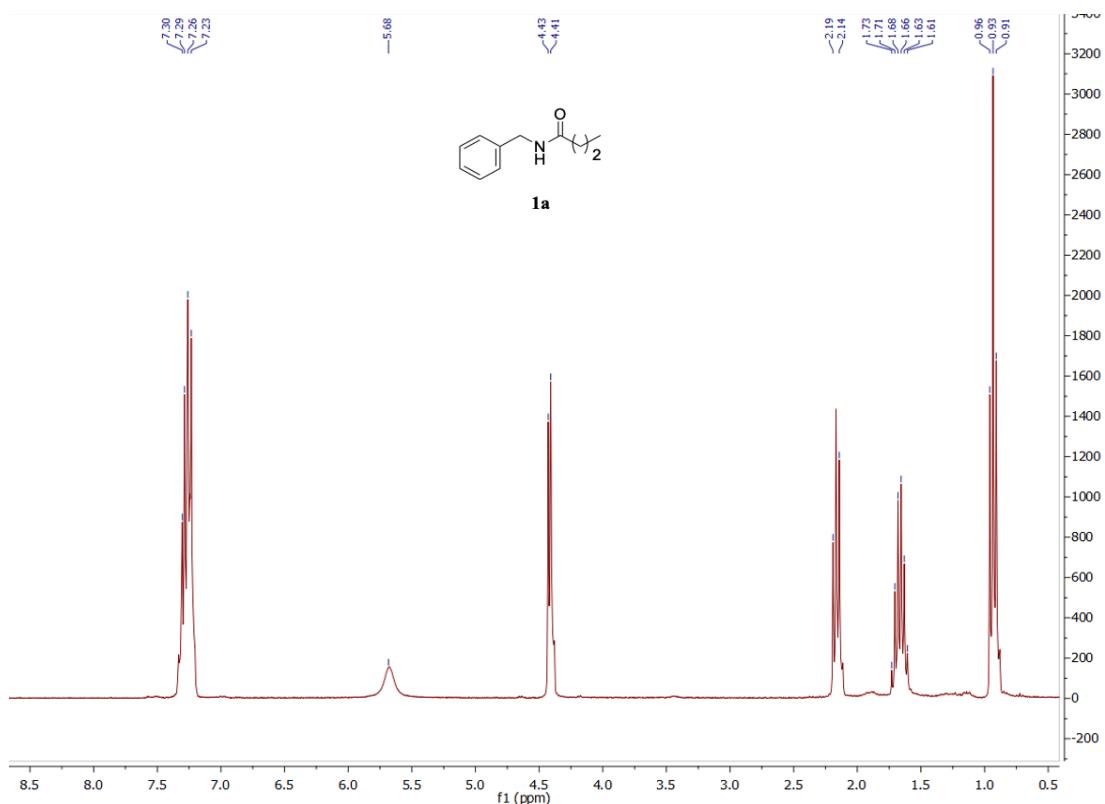
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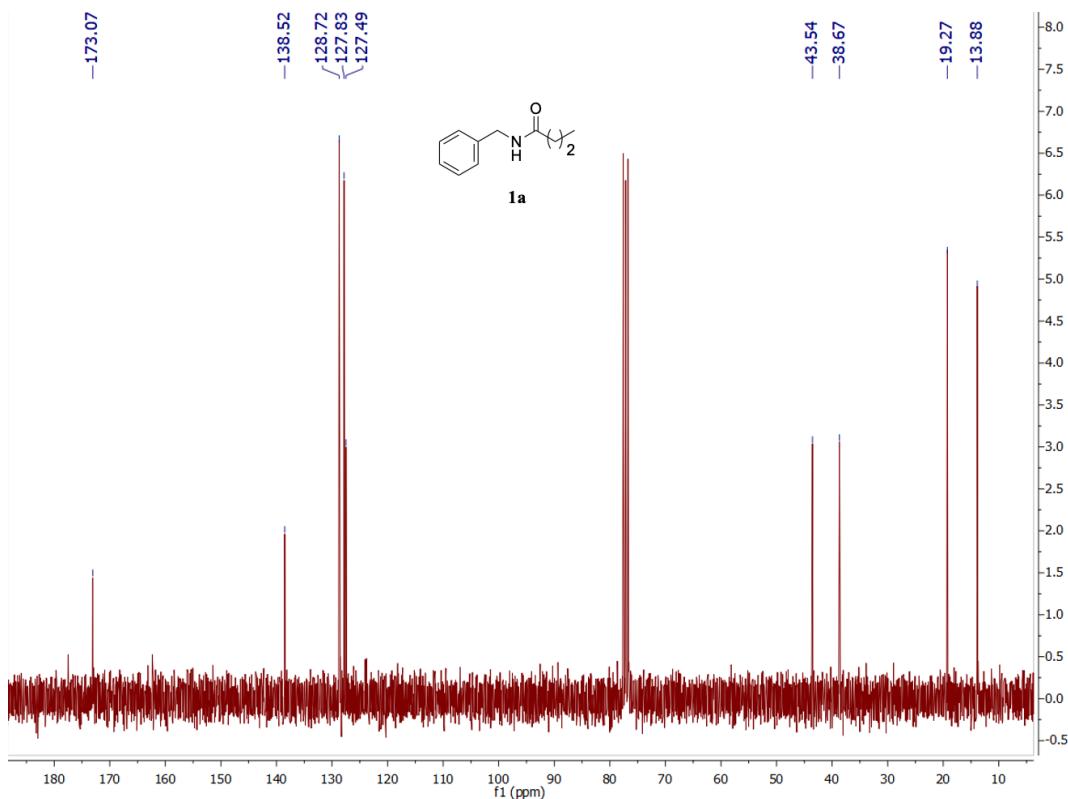
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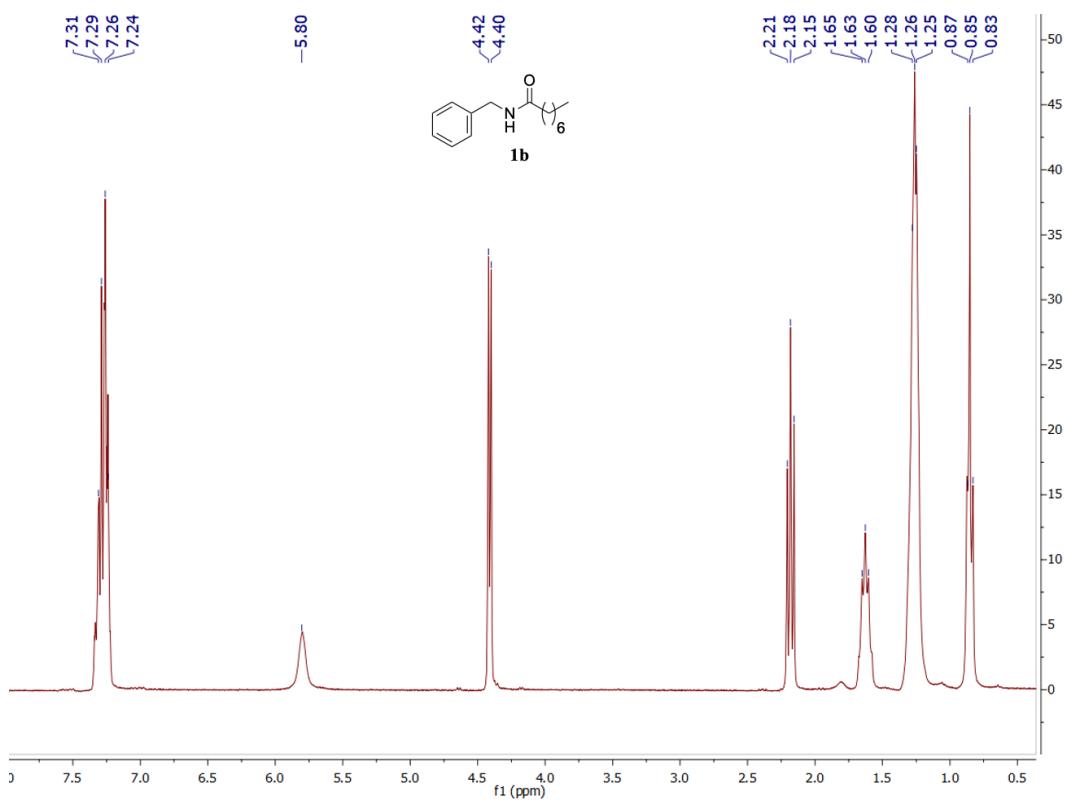
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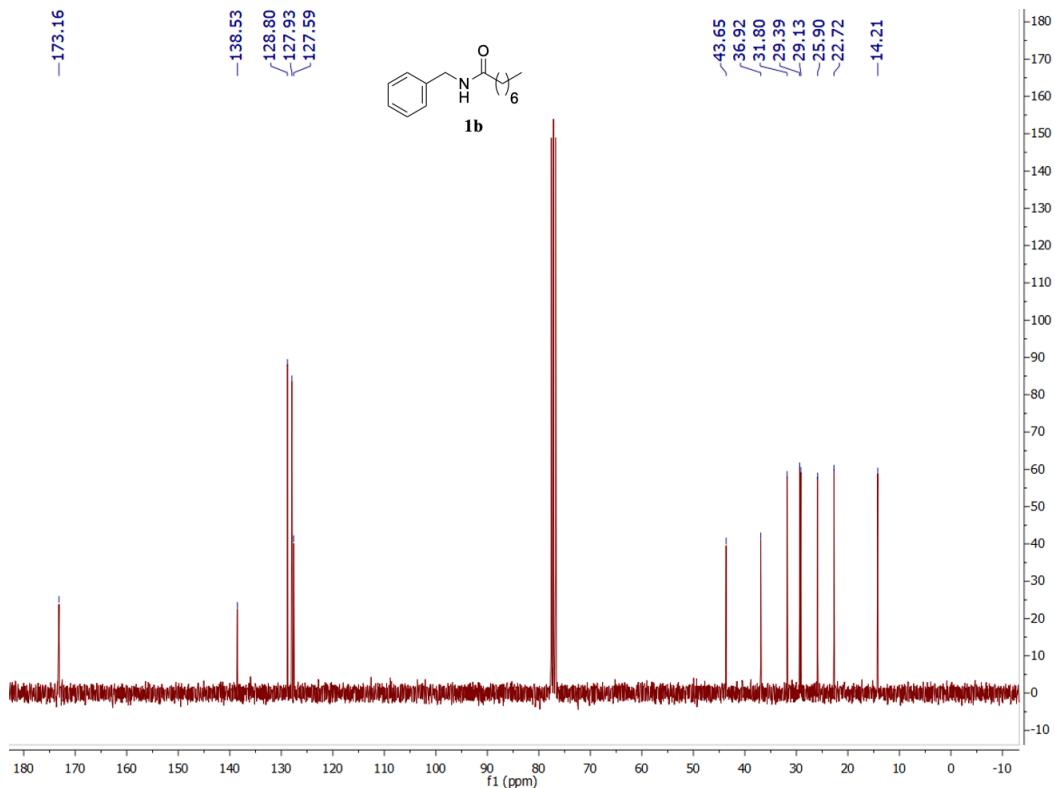
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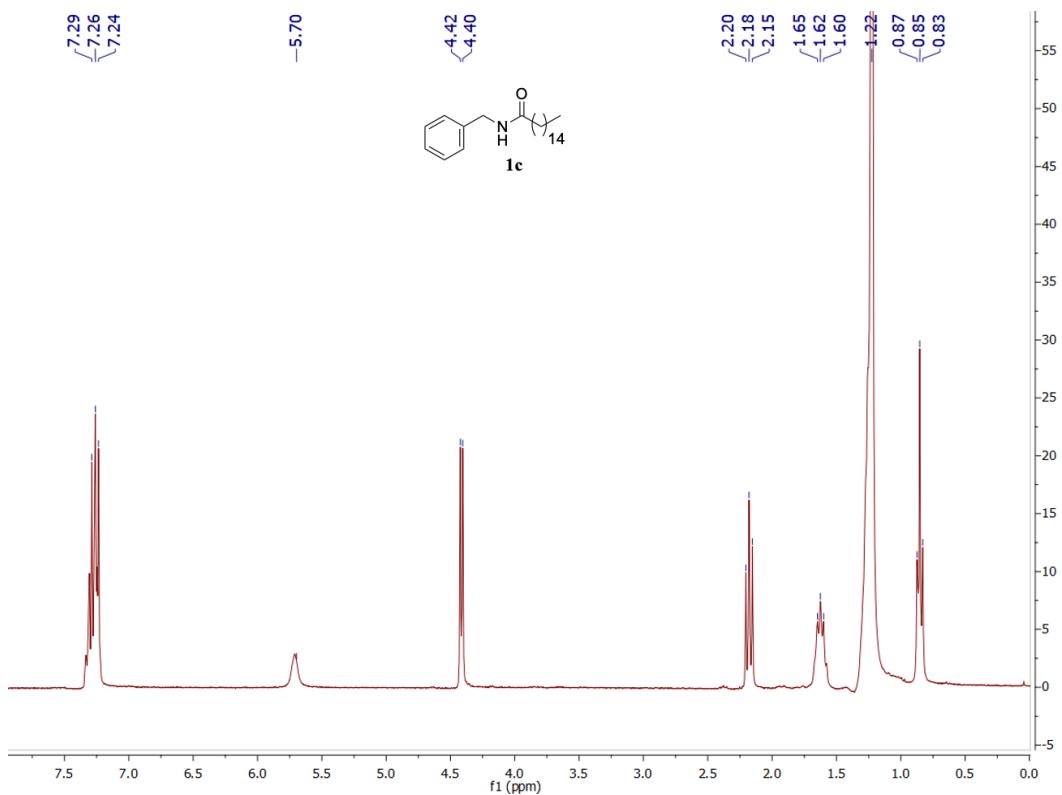
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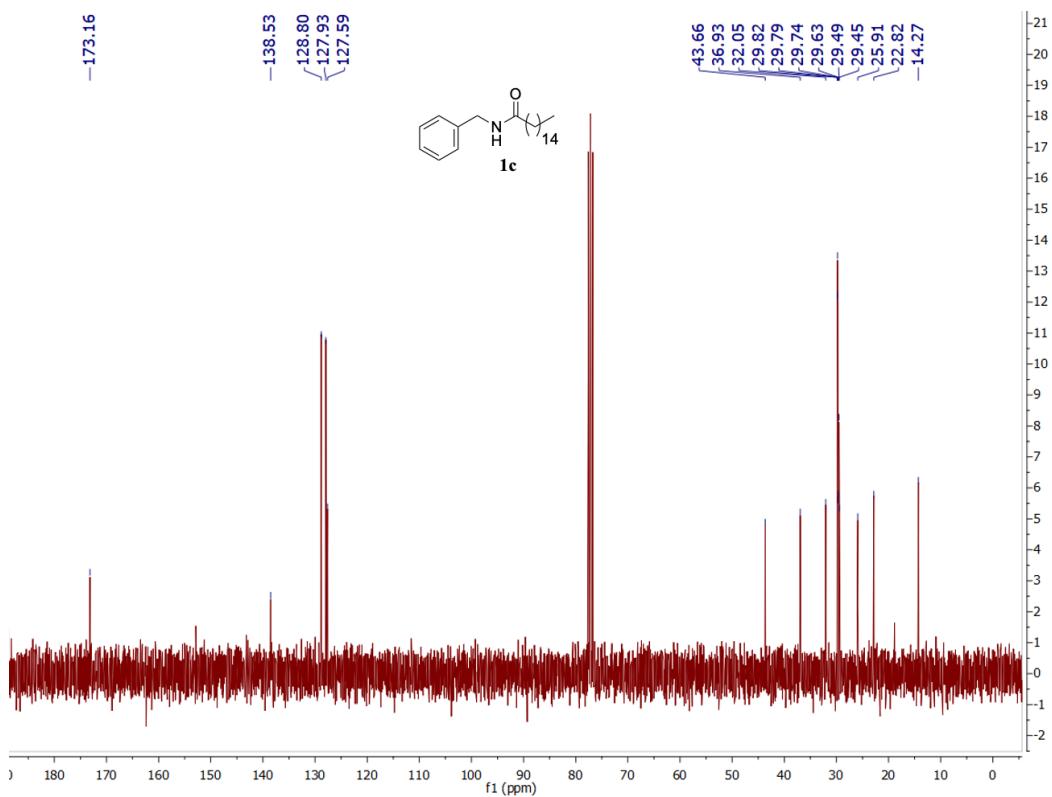
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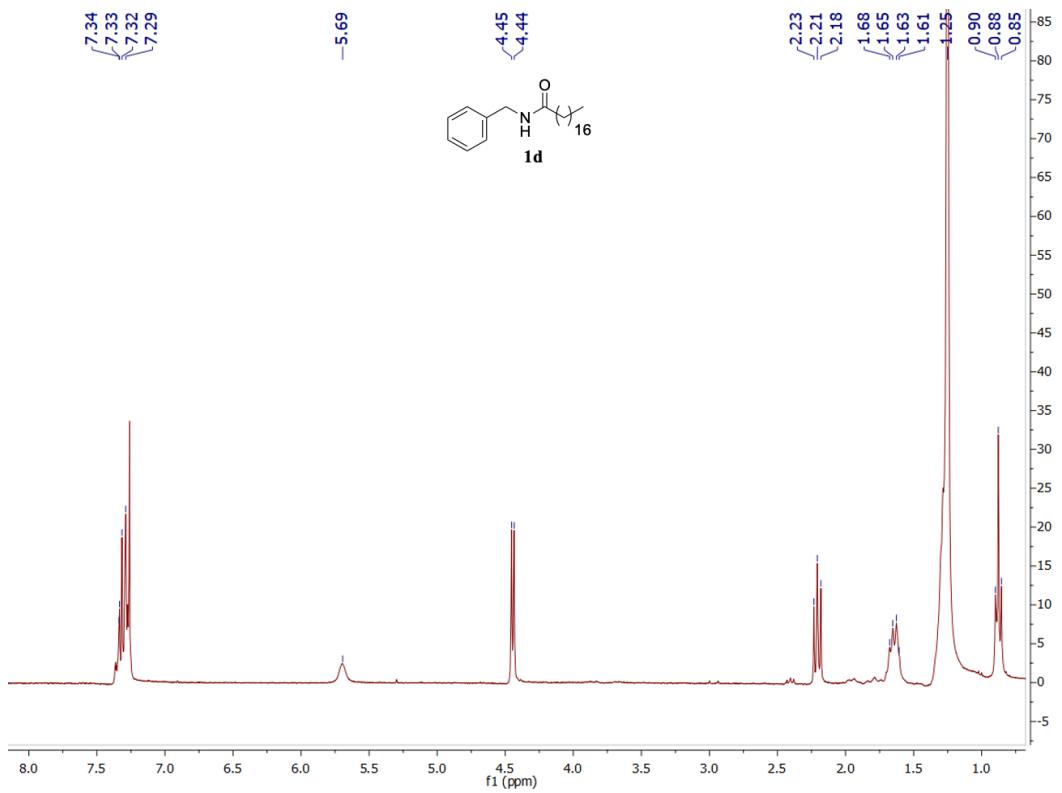
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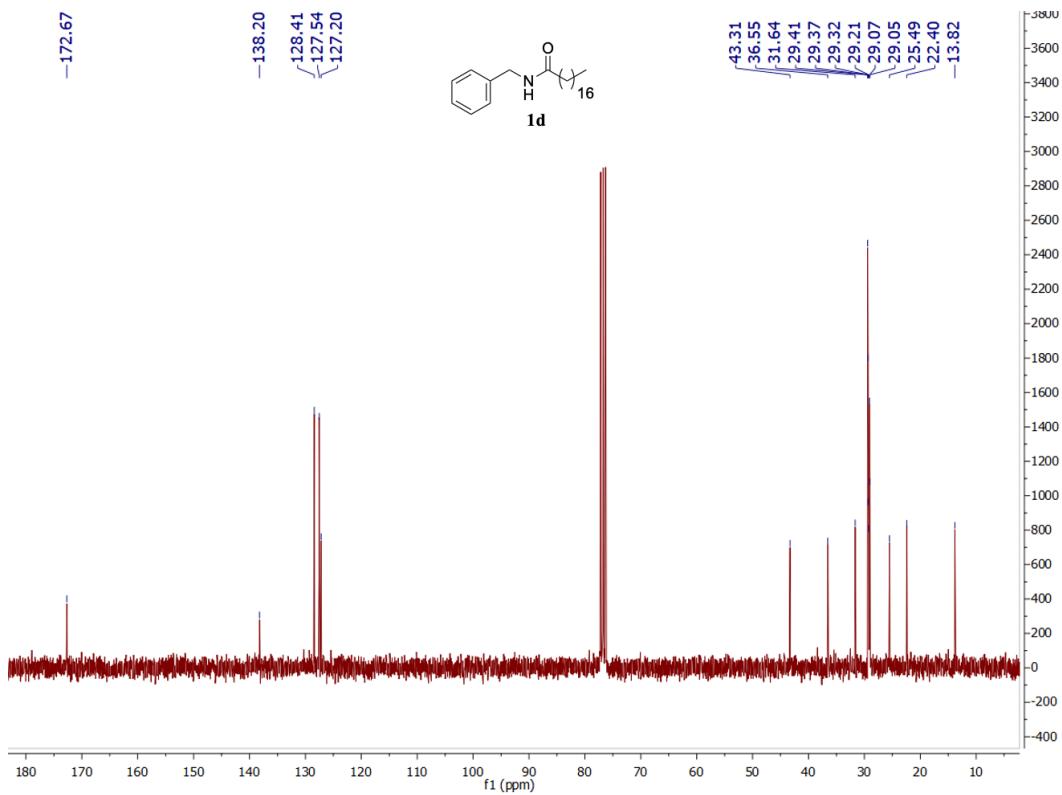
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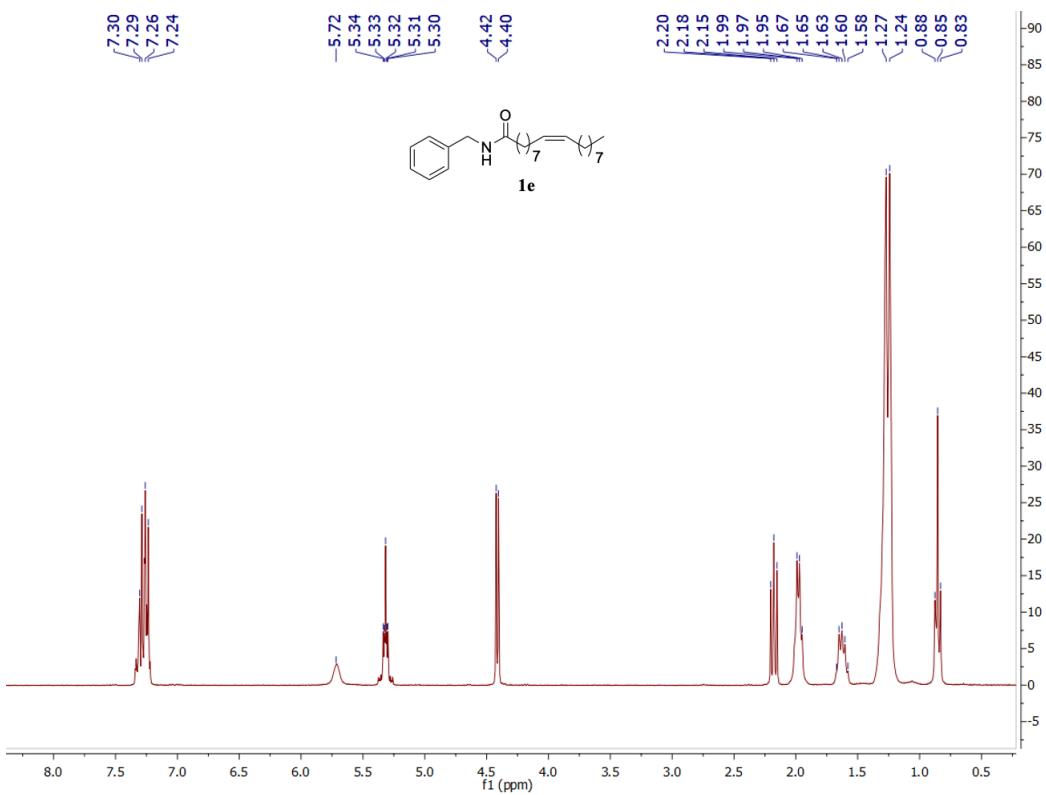
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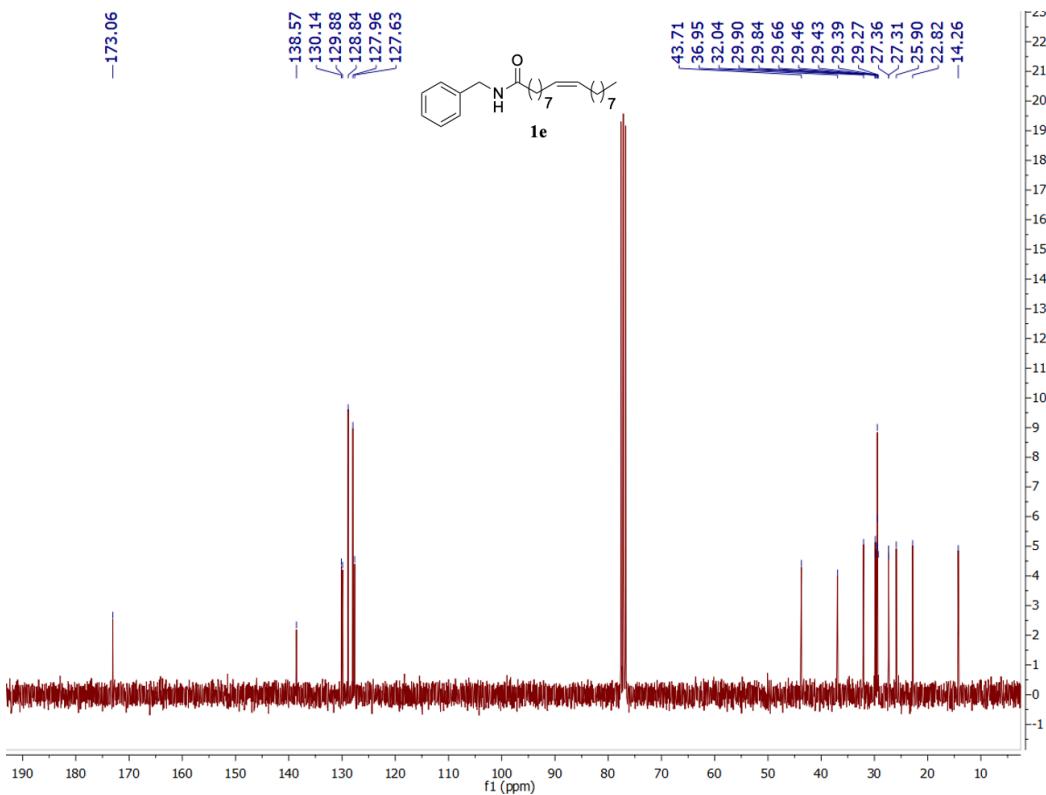
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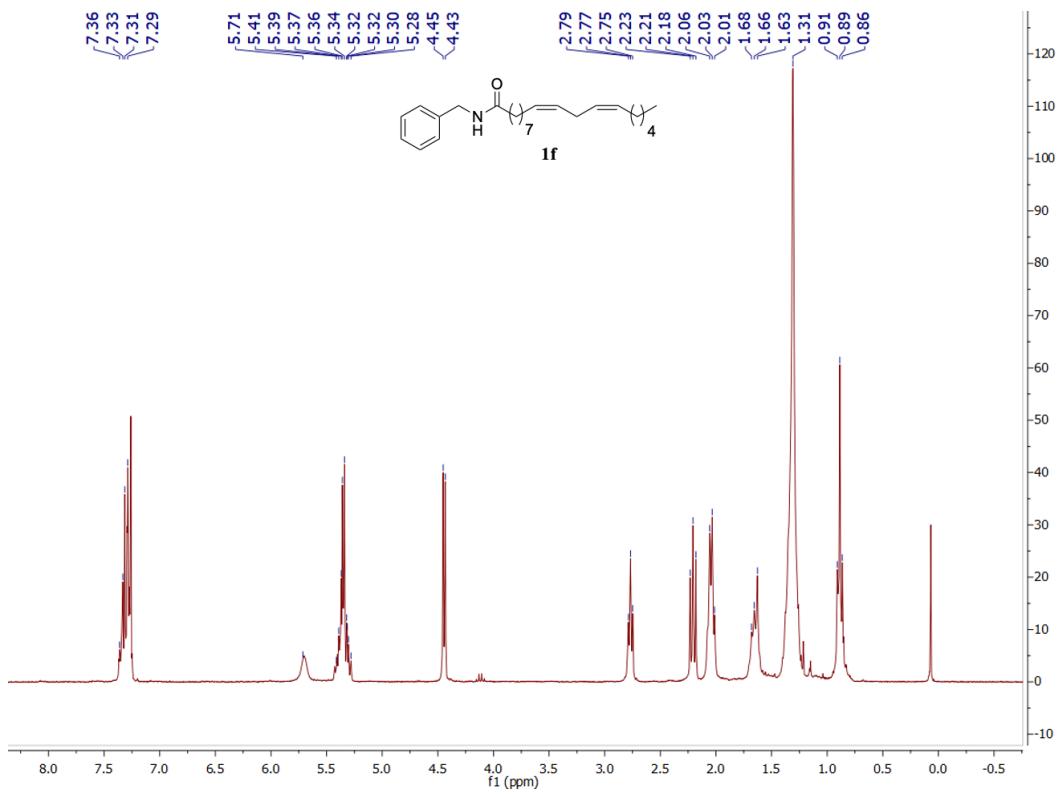
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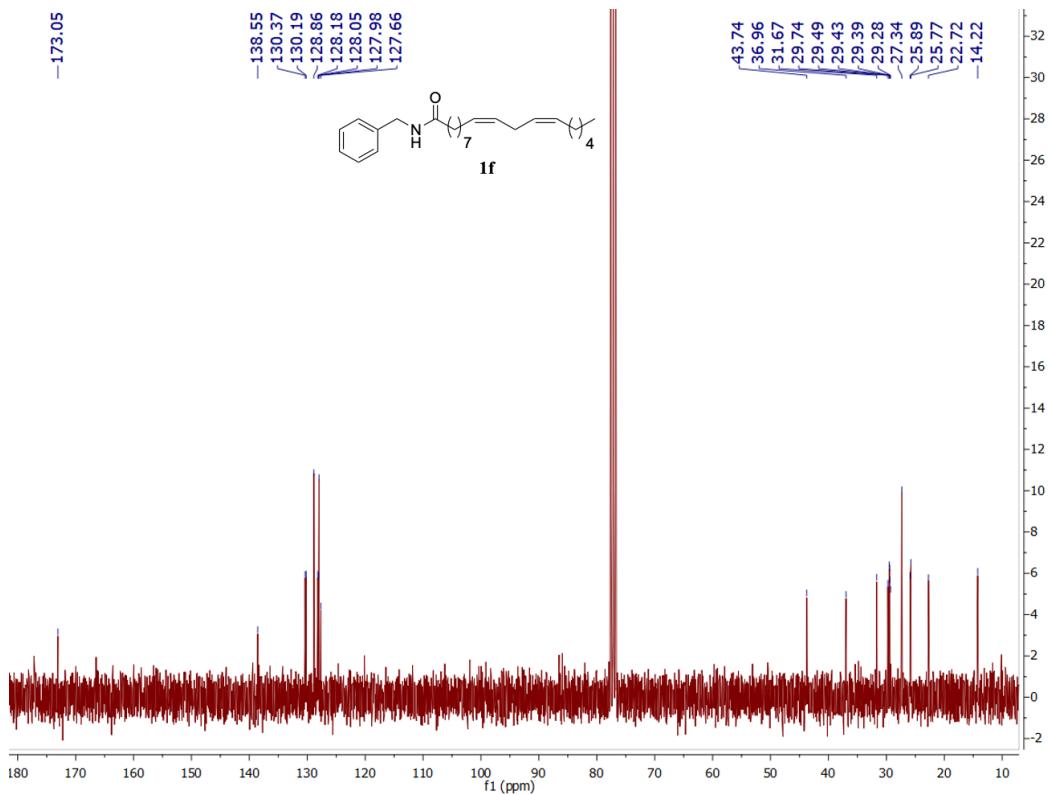
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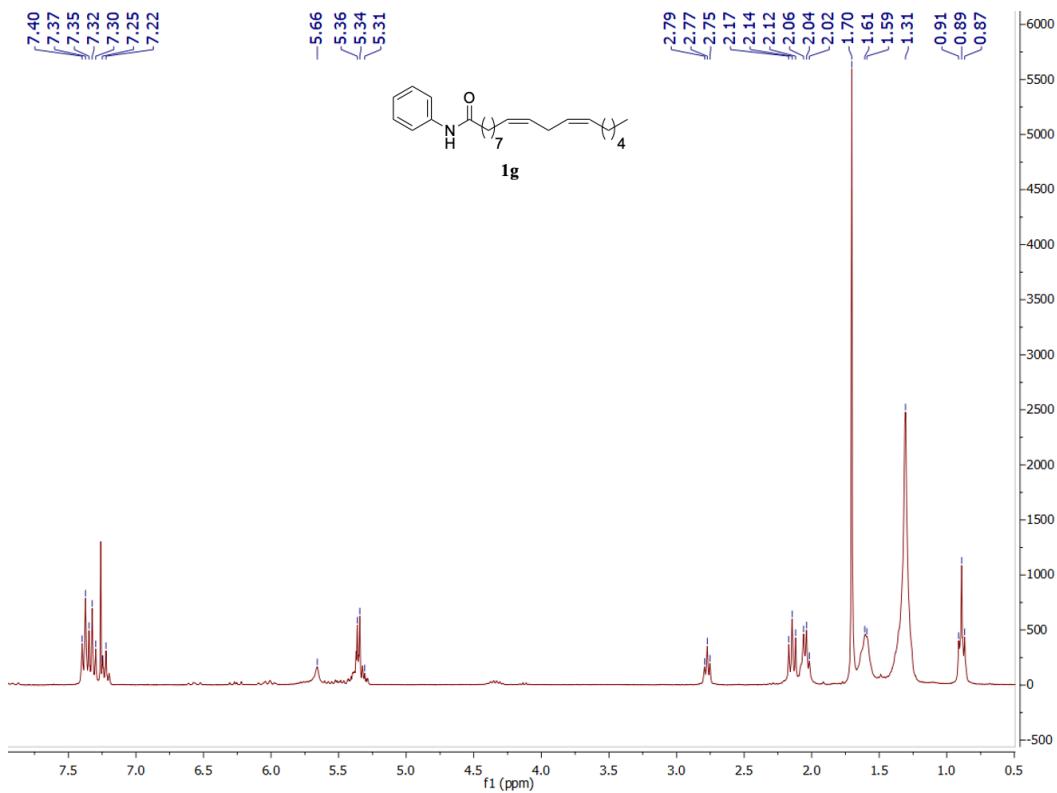
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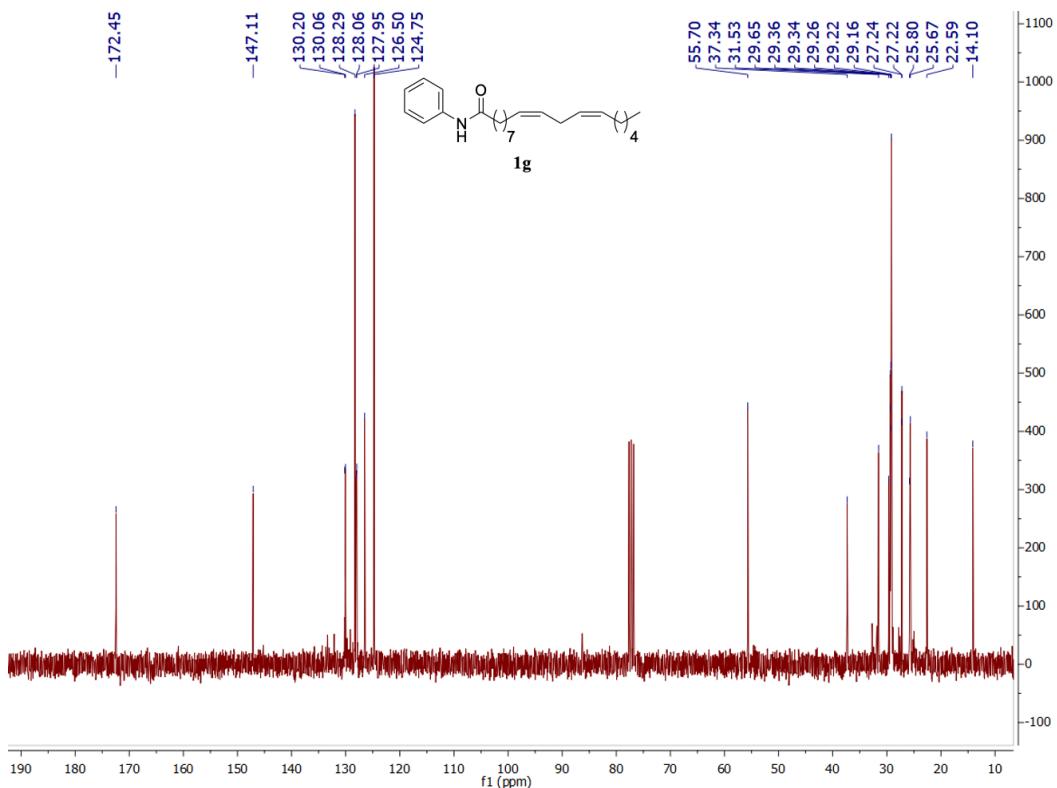
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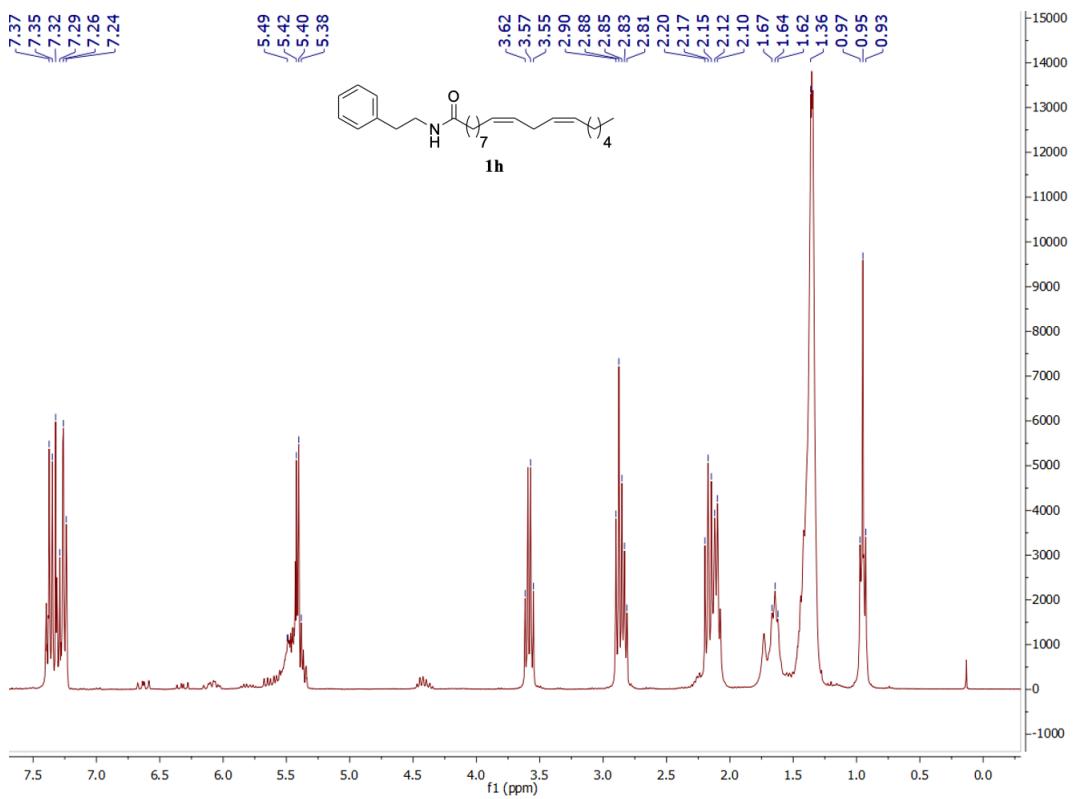
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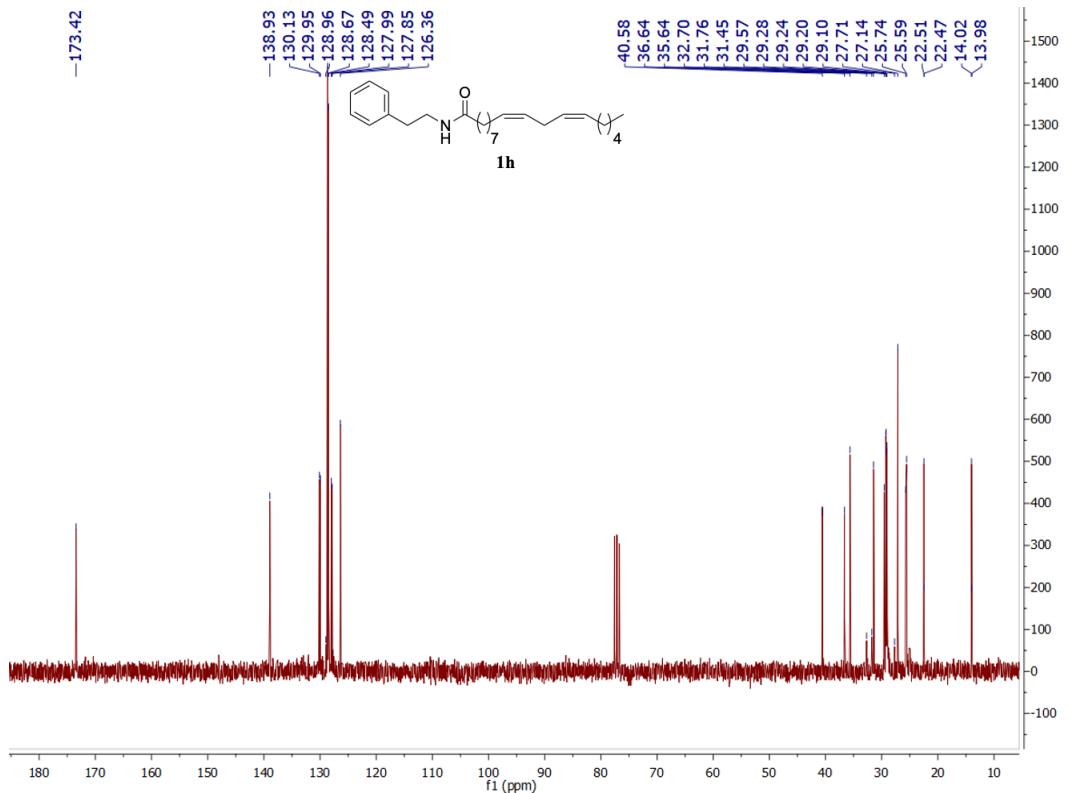
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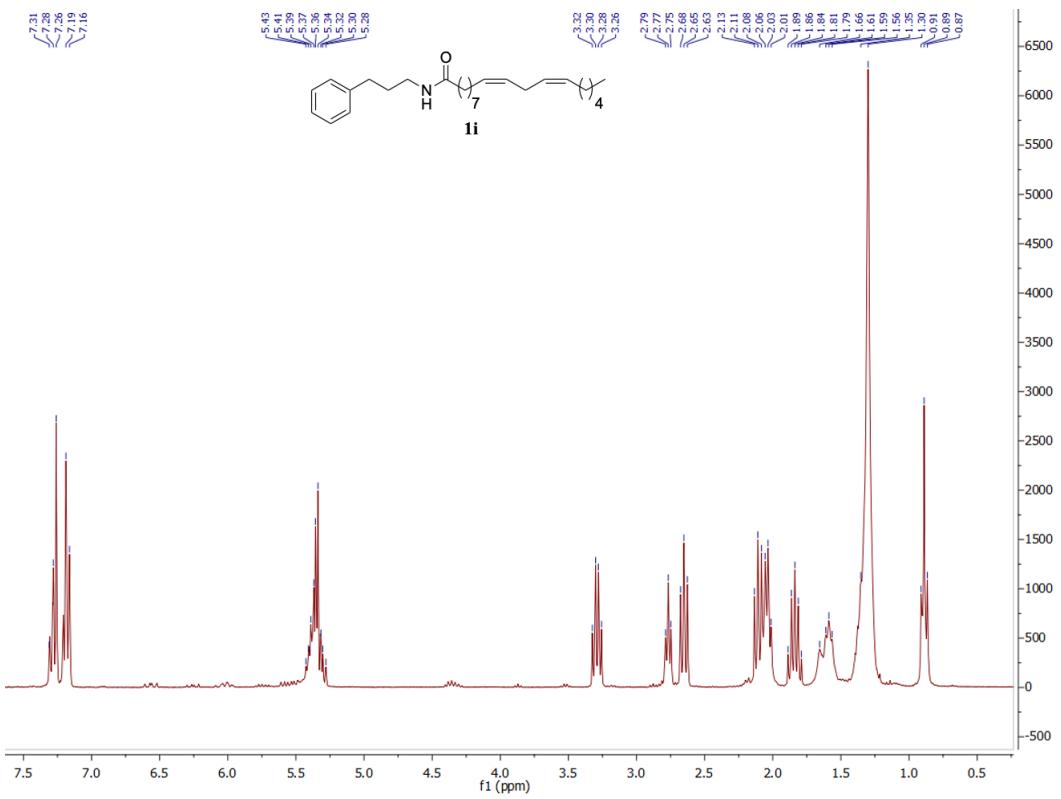
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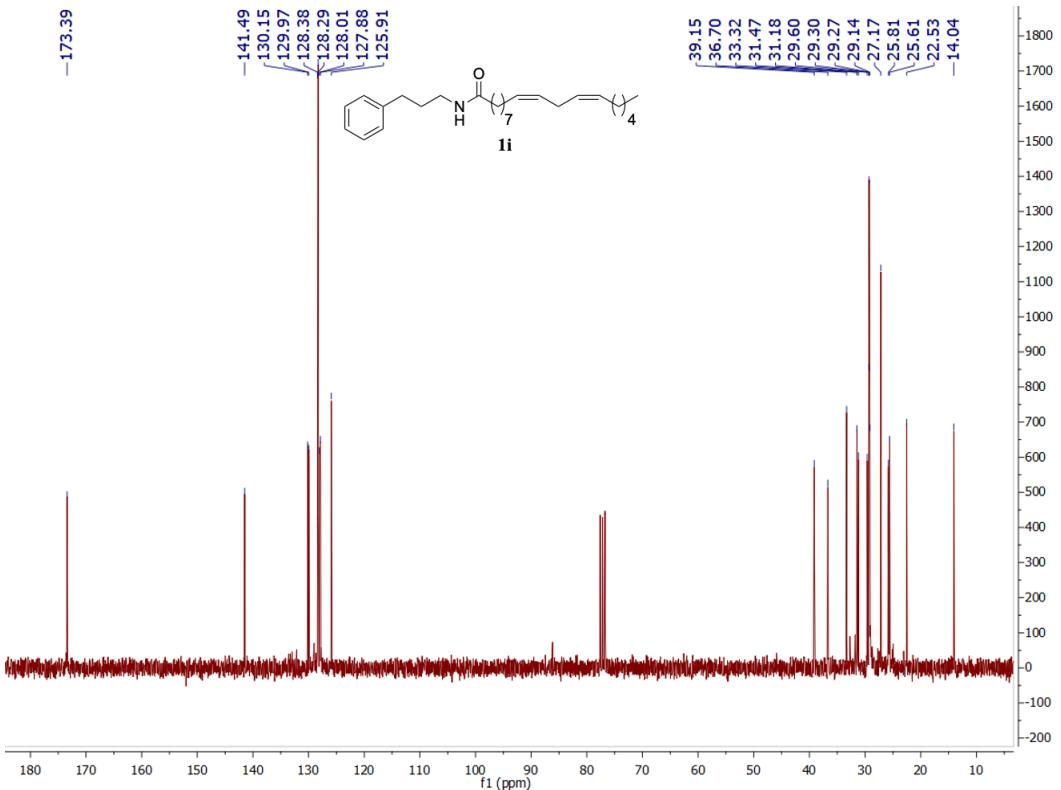
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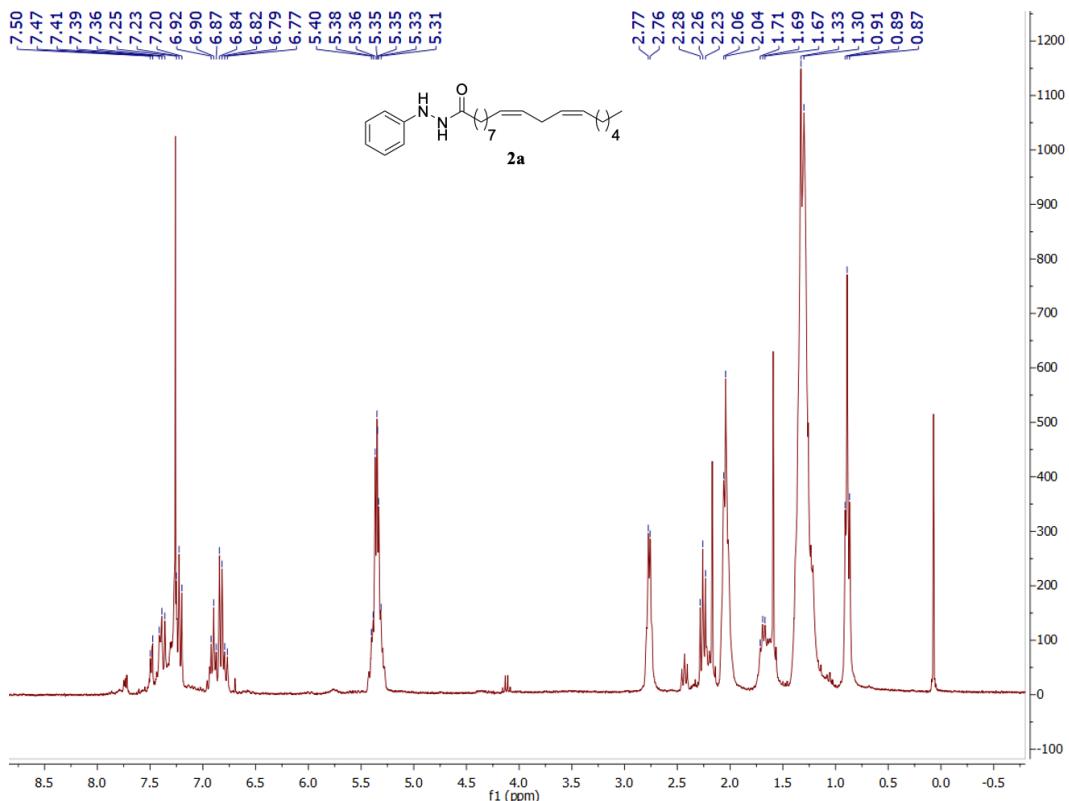
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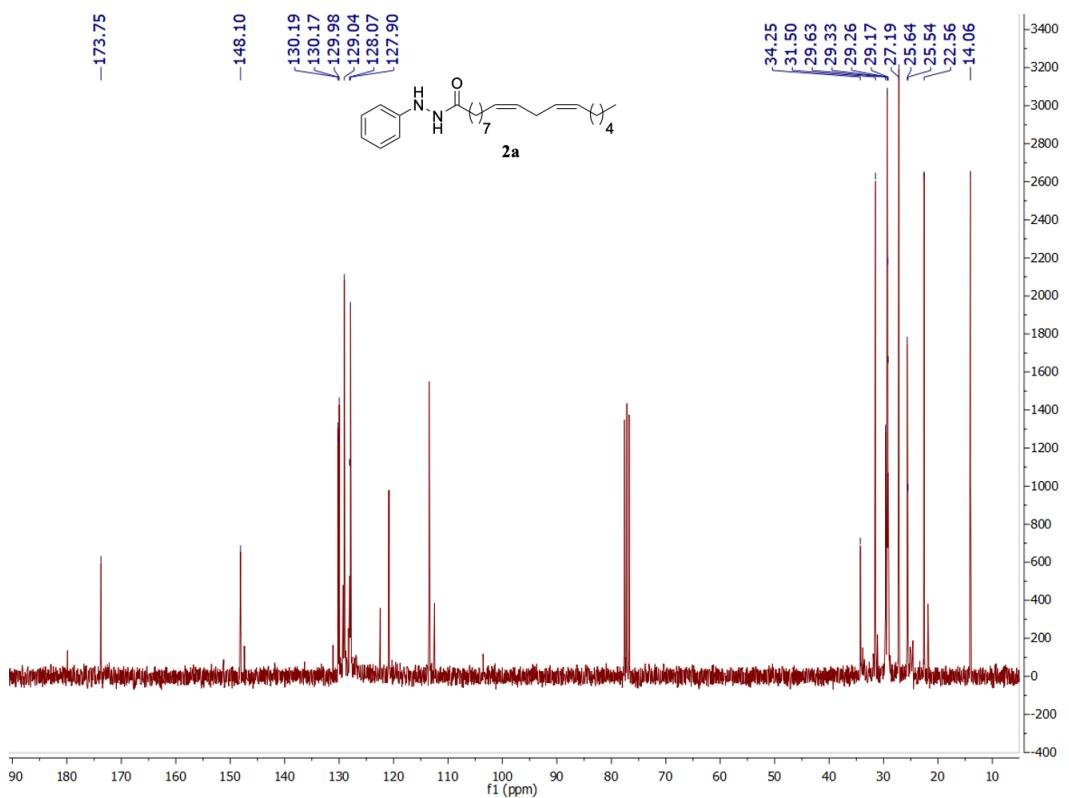
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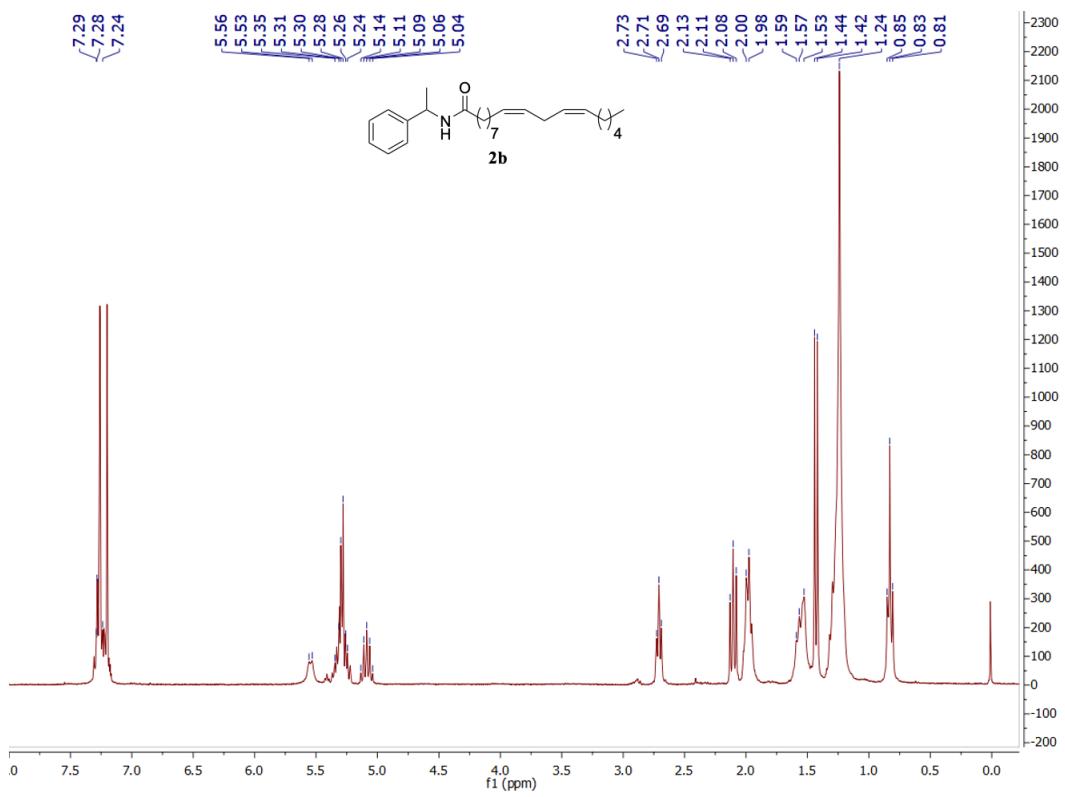
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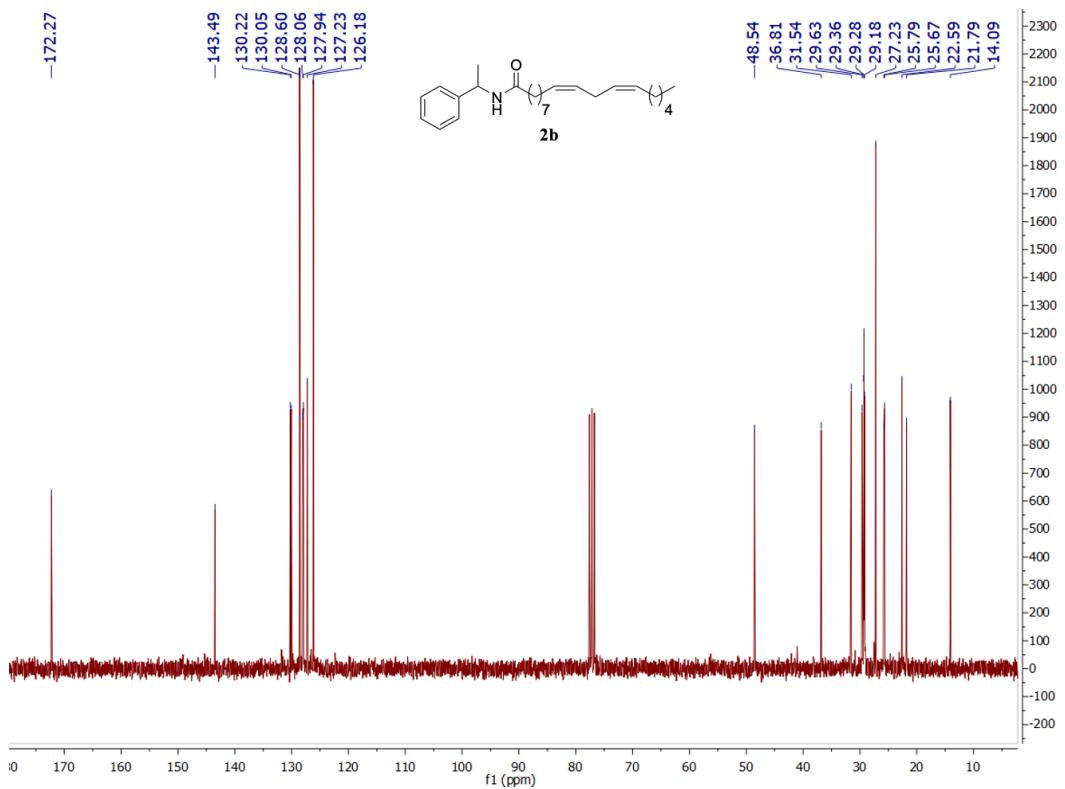
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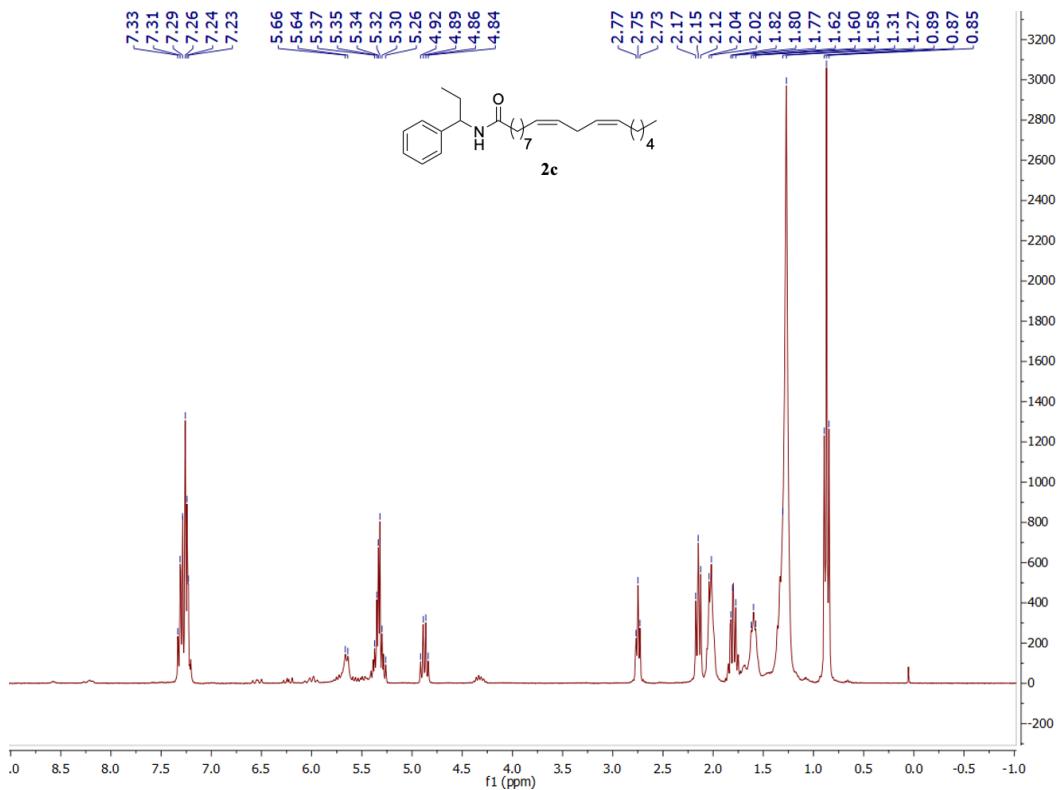
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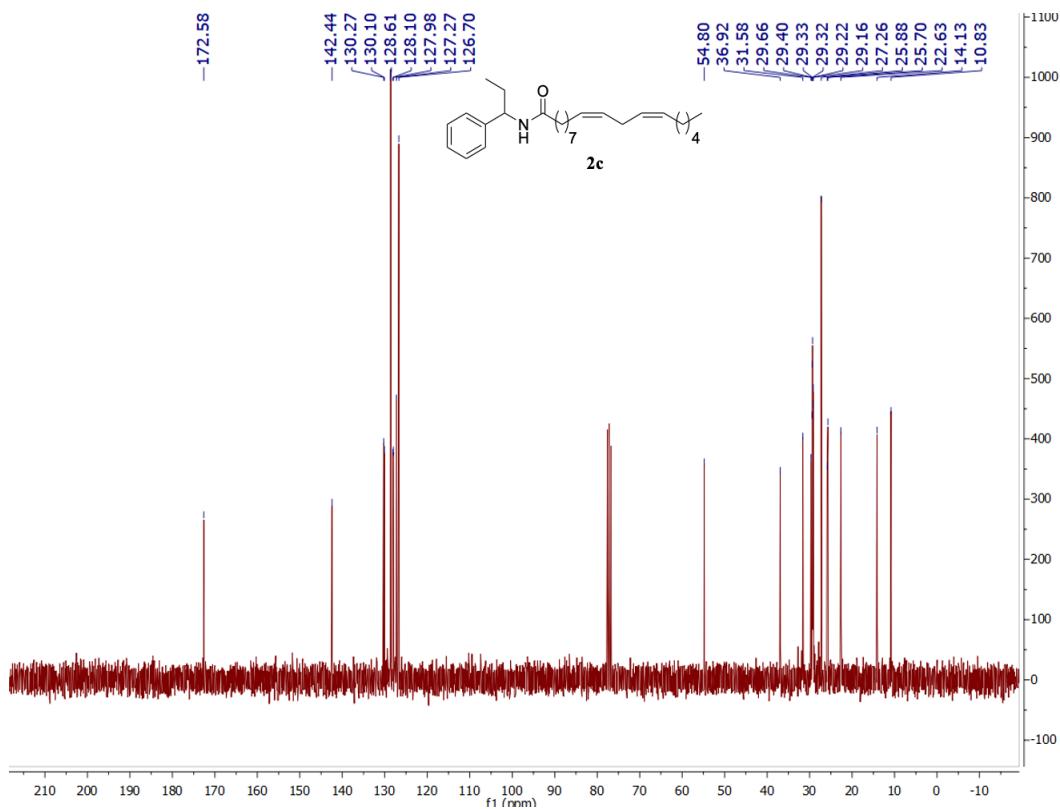
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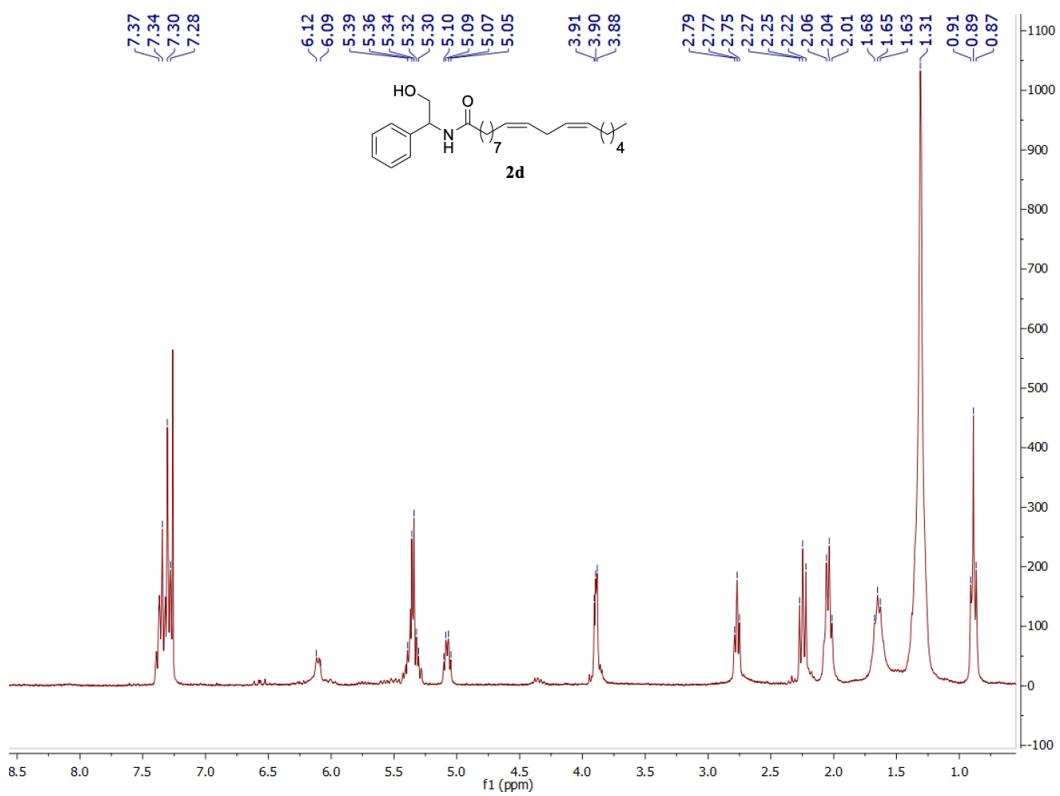
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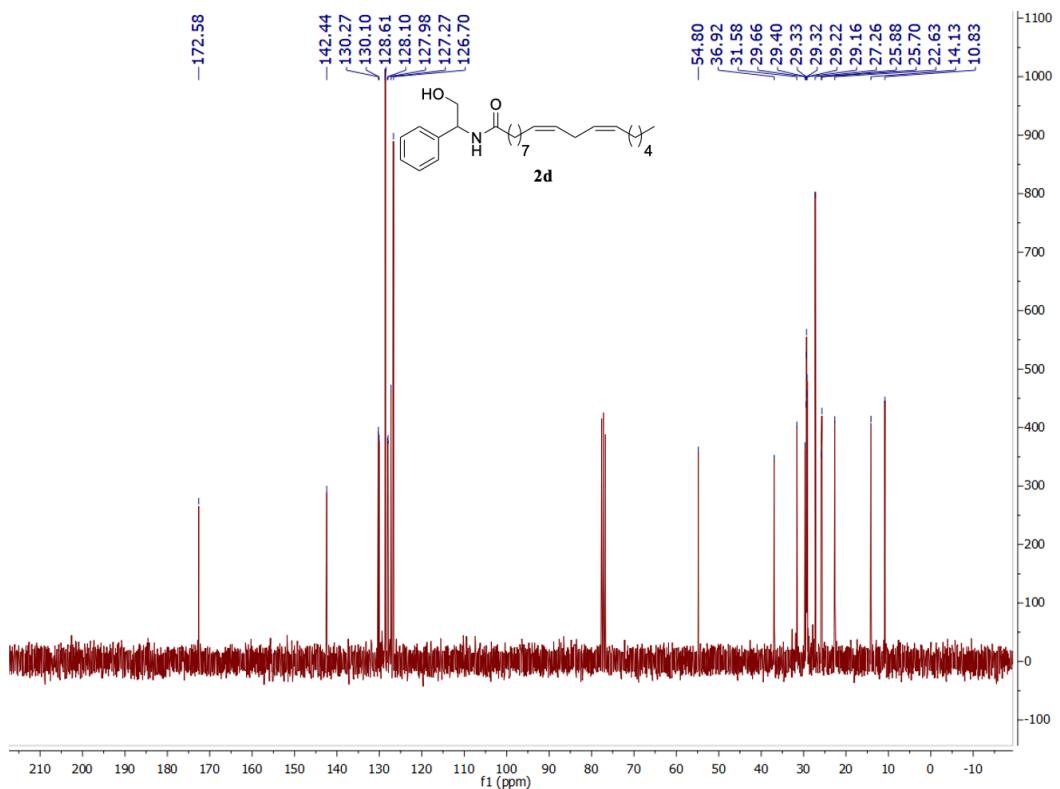
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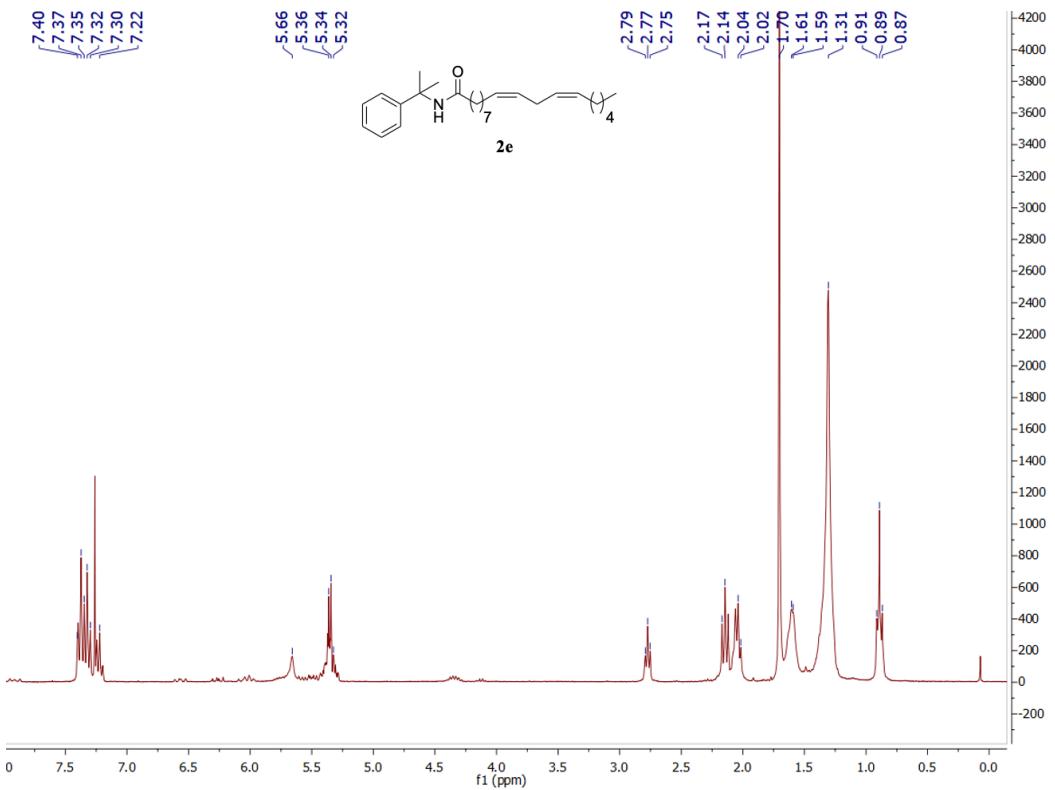
- Figure 24S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of (*9Z,12Z*)-*N*-(1-phenylpropyl)-octadeca-9,12-dienamide (**2c**).



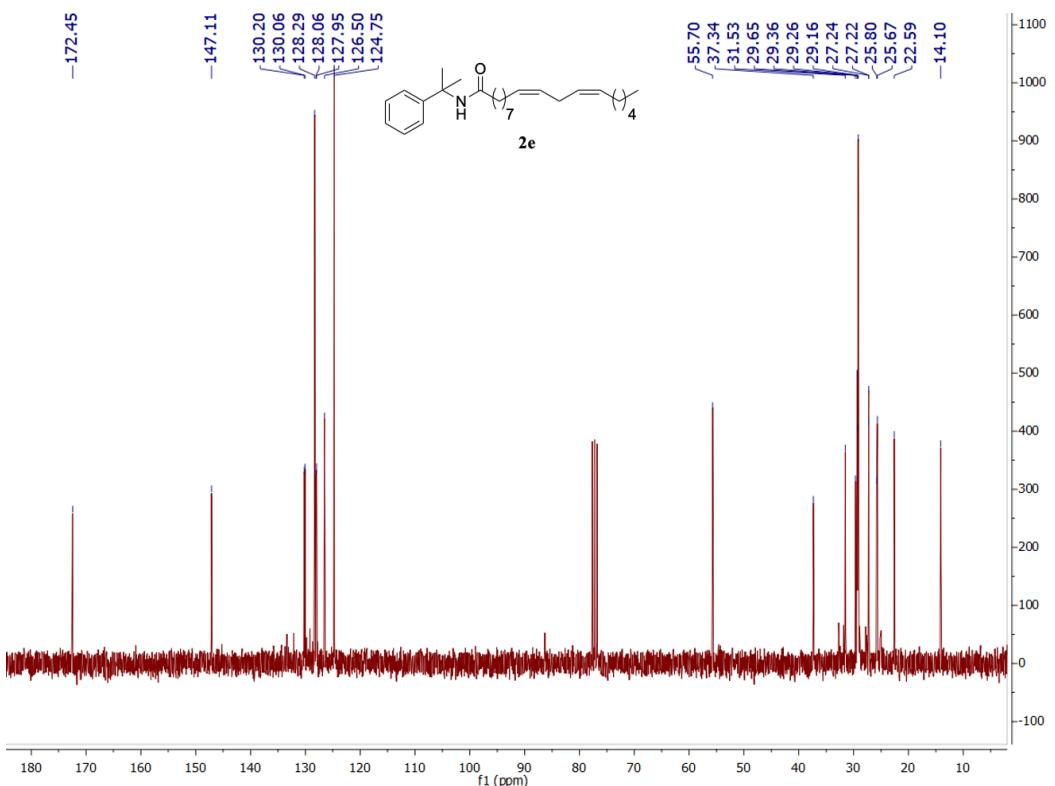
- Figure 25S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of (*9Z,12Z*)-*N*-(2-hydroxy-1-phenylethyl)-octadeca-9,12-dienamide (**2d**).



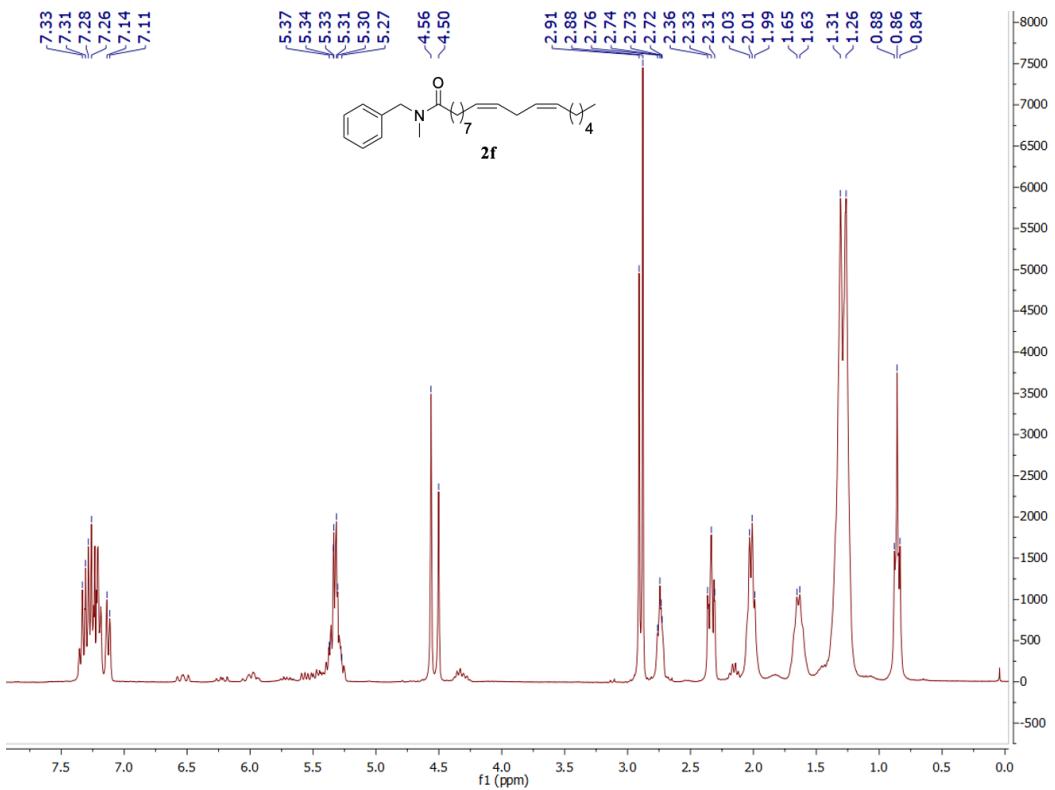
- Figure 26S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of (*9Z,12Z*)-*N*-(2-hydroxy-1-phenylethyl)-octadeca-9,12-dienamide (**2d**).



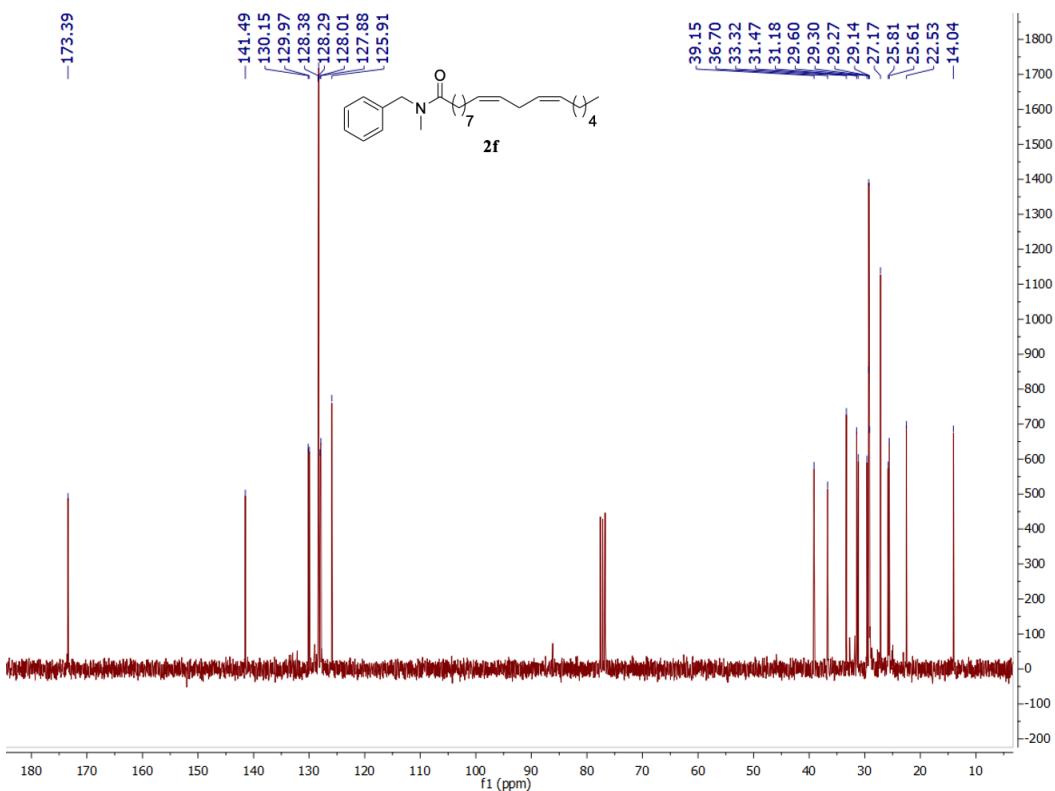
- Figure 27S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of ($9\text{Z},12\text{Z}$)-*N*-(2-phenylpropan-2-yl)-octadeca-9,12-dienamide (**2e**).



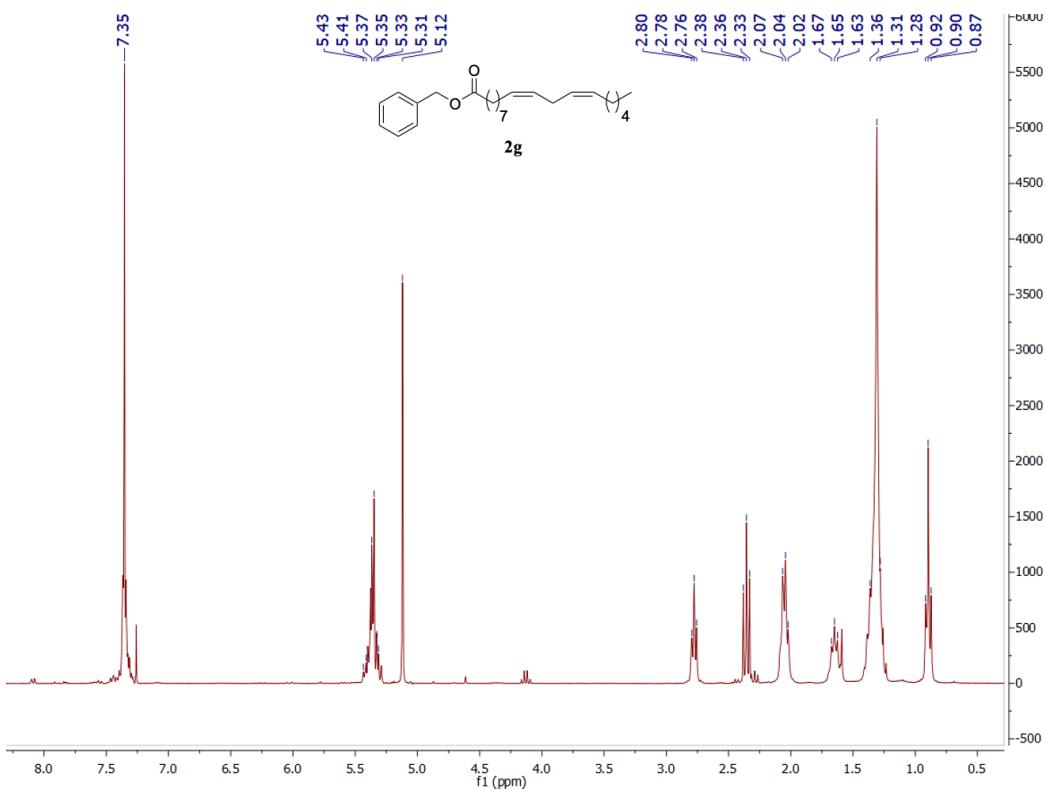
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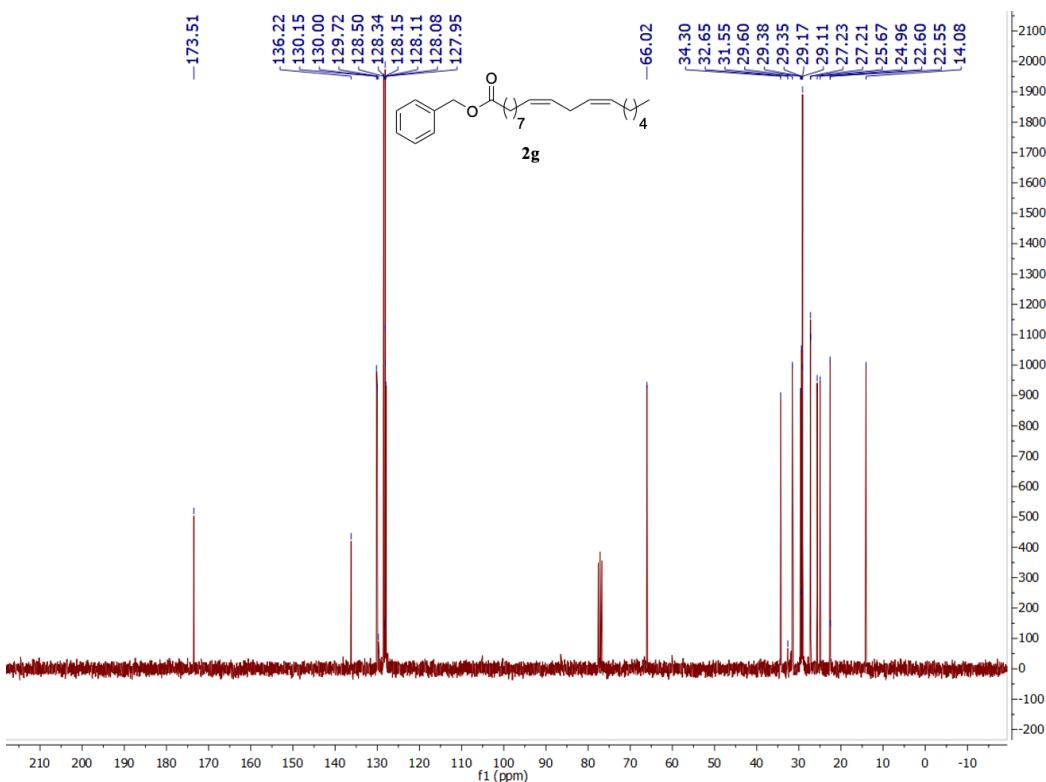
- Figure 29S. ¹H NMR (CDCl₃, 300 MHz) spectrum of (9Z,12Z)-N-benzyl-N-methyloctadeca-9,12-dienamide (**2f**).



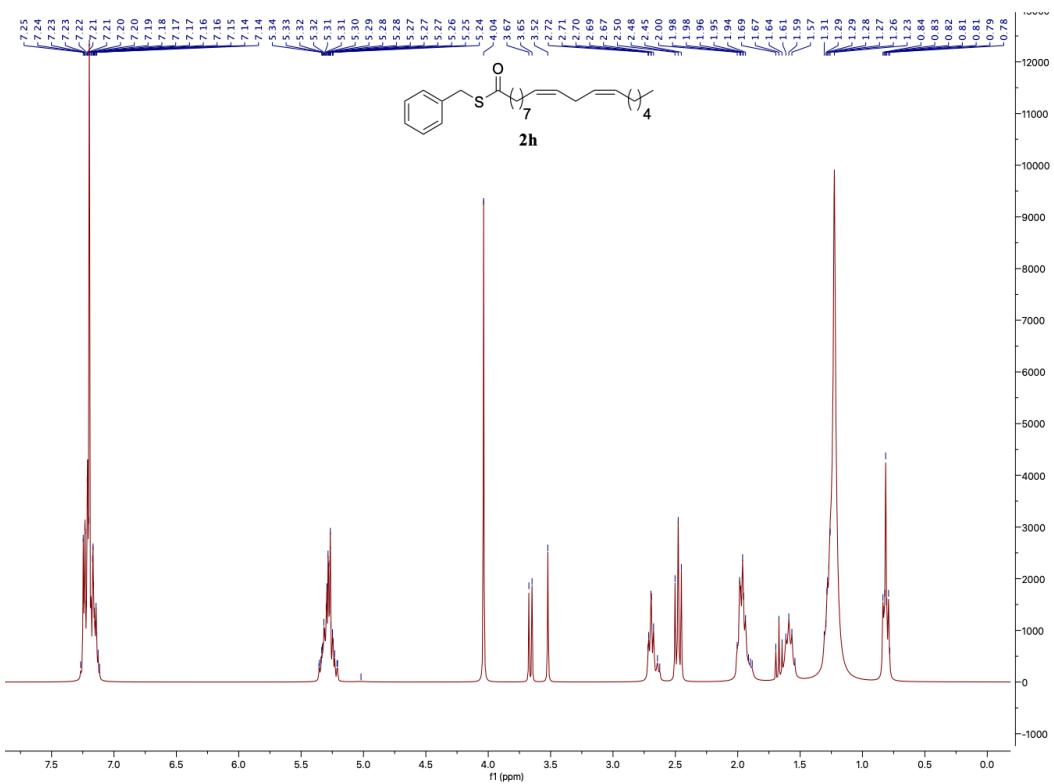
- Figure 30S. ¹³C NMR (CDCl₃, 75 MHz) spectrum of (9Z,12Z)-N-benzyl-N-methyloctadeca-9,12-dienamide (**2f**).



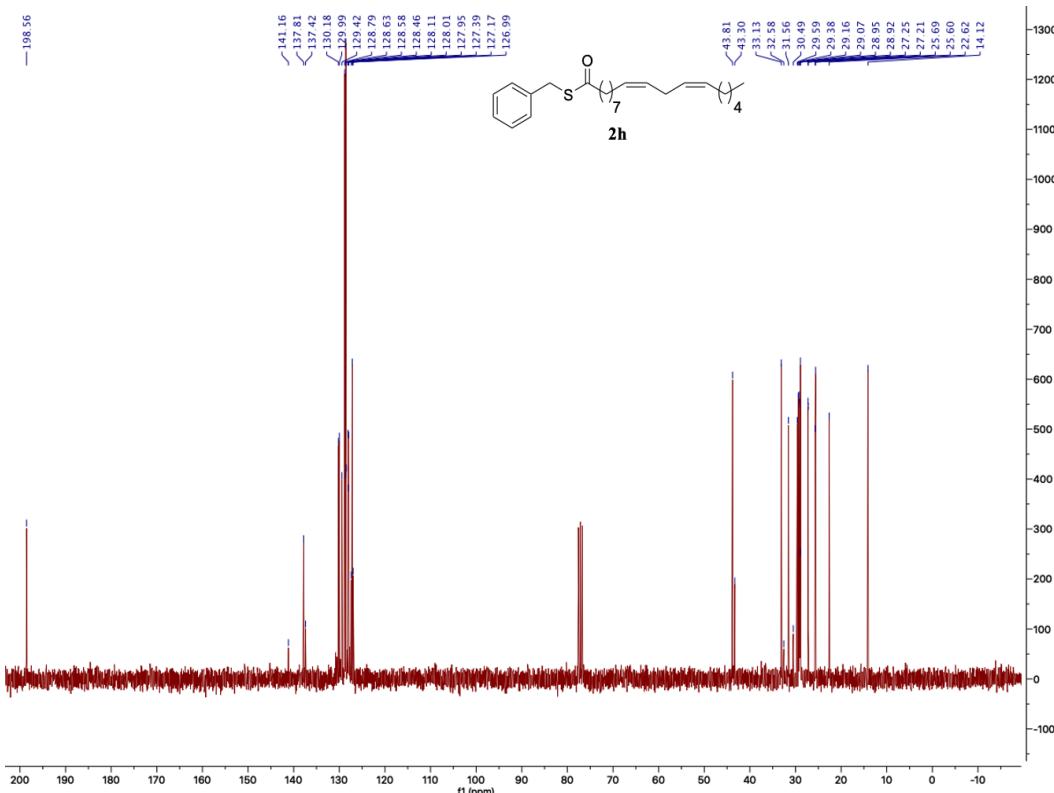
- Figure 31S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-1-(benzyloxy)-octadeca-9,12-dien-1-olate (**2g**).



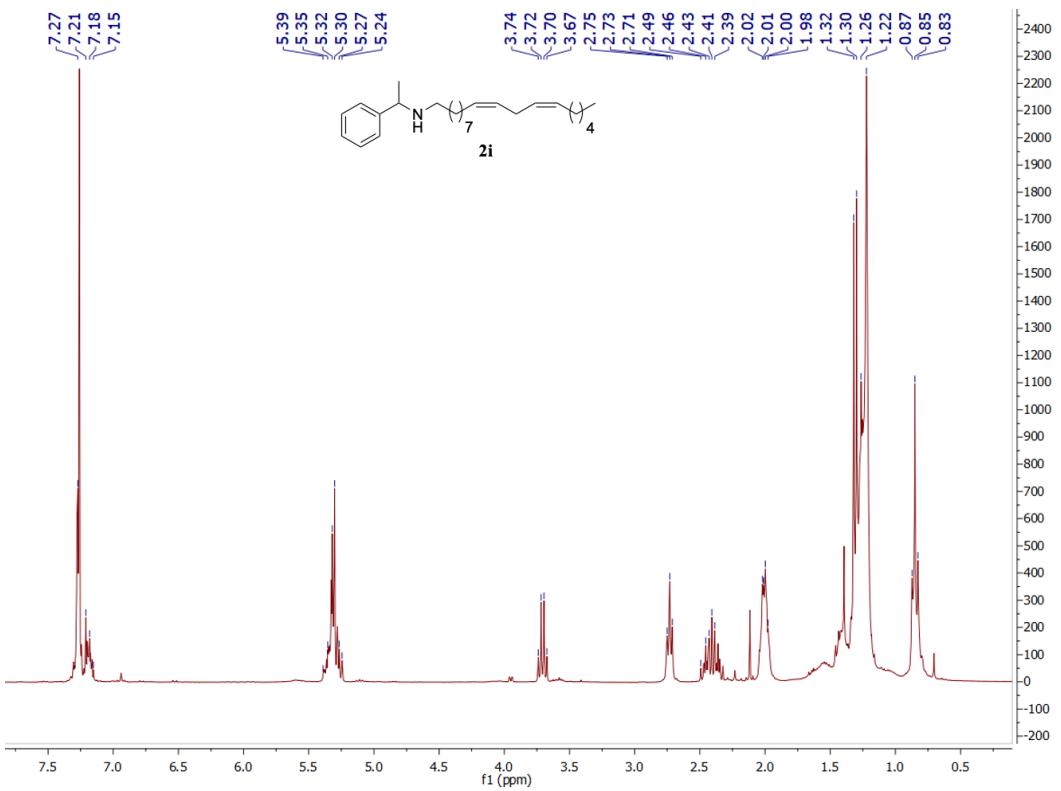
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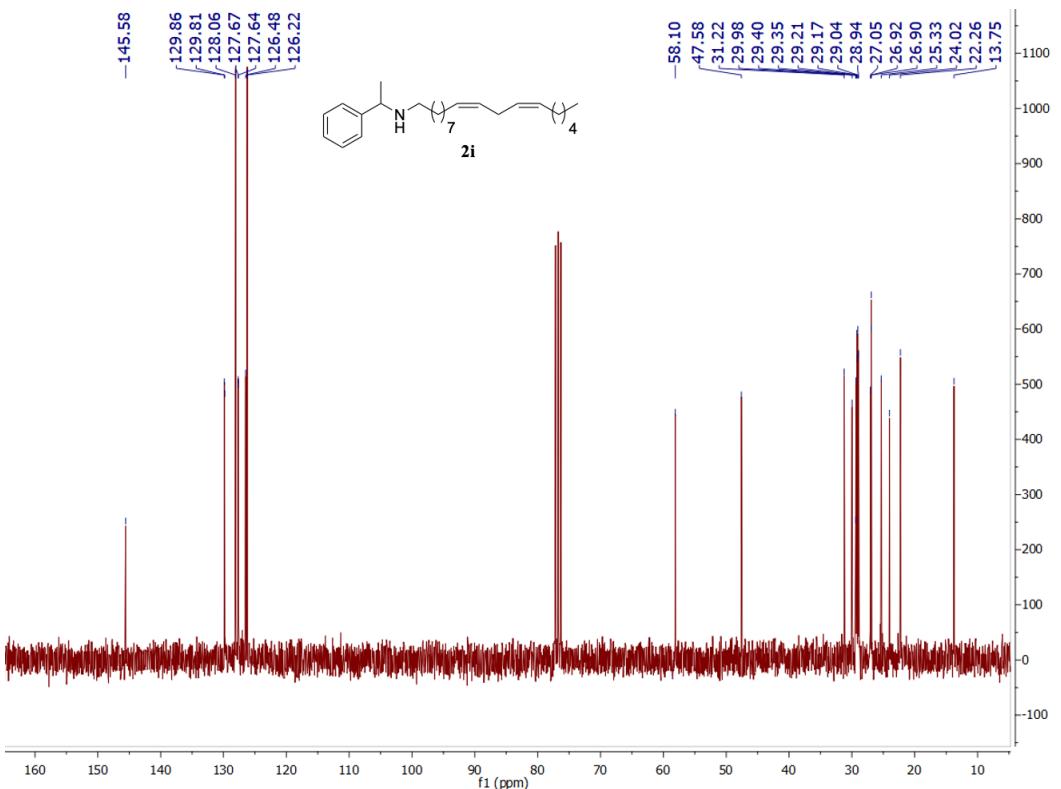
- Figure 33S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-1-(benzylthio)-octadeca-9,12-dien-1-olate (**2h**).



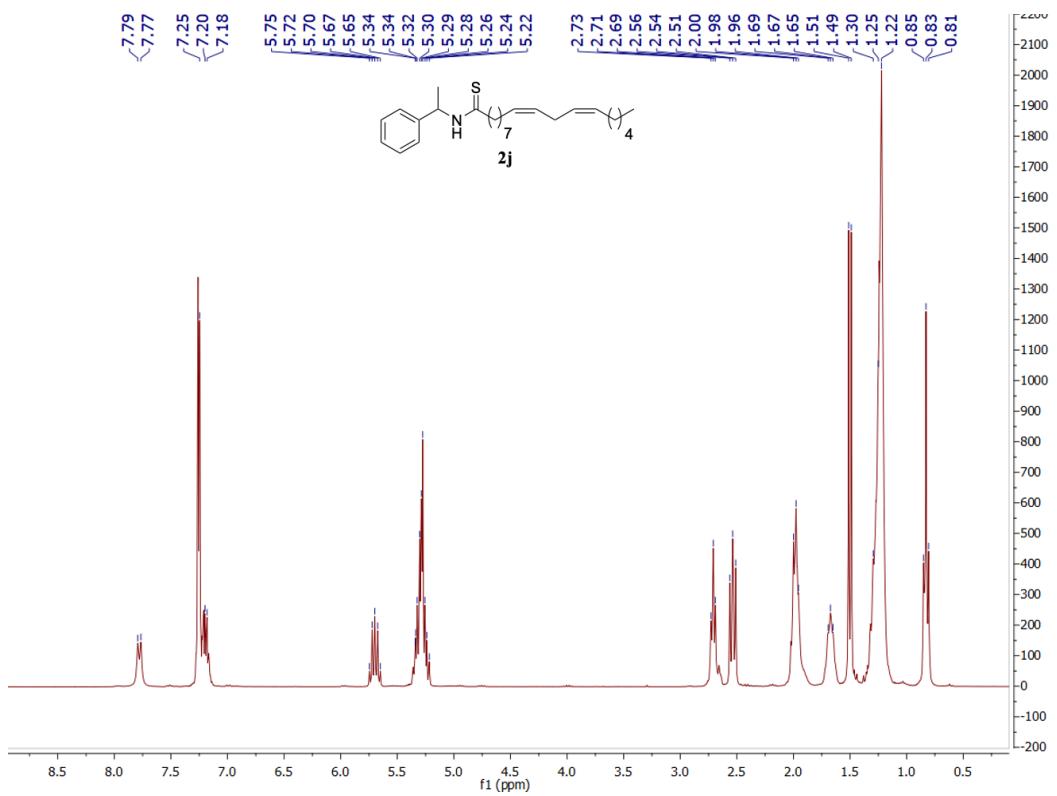
- Figure 34S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-1-(benzylthio)-octadeca-9,12-dien-1-olate (**2h**).



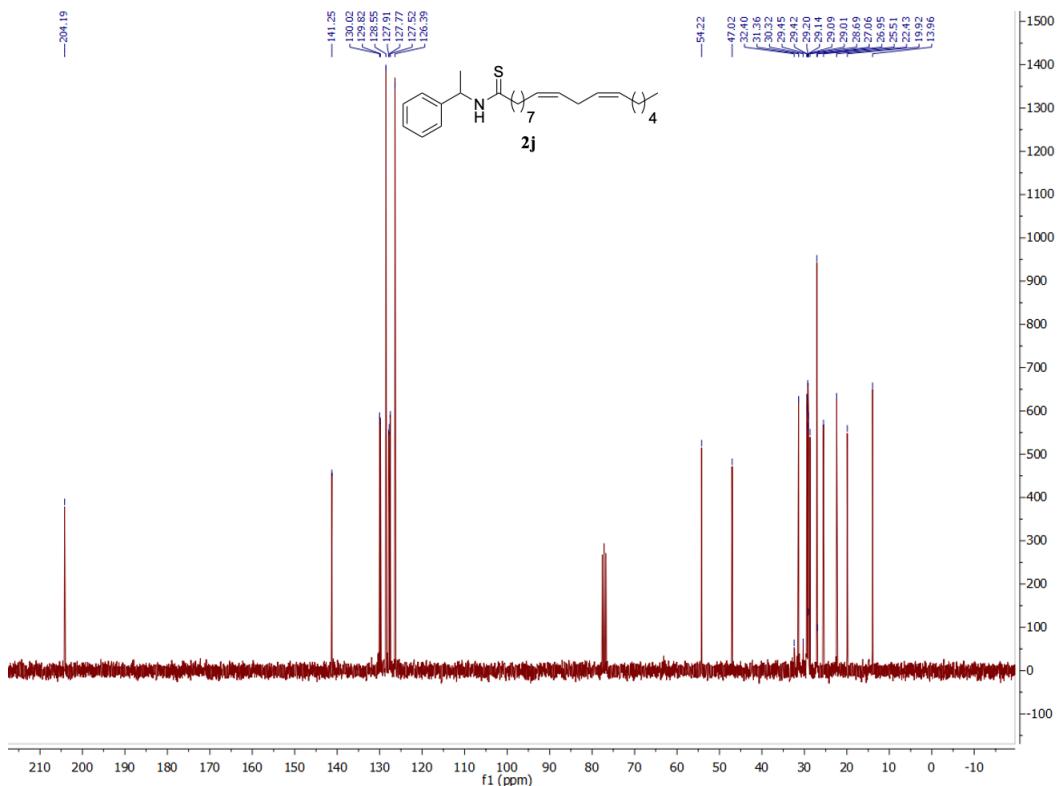
- Figure 35S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (*9Z,12Z*)-*N*-(1-phenylethyl)-octadeca-9,12-dien-1-amine (**2i**).



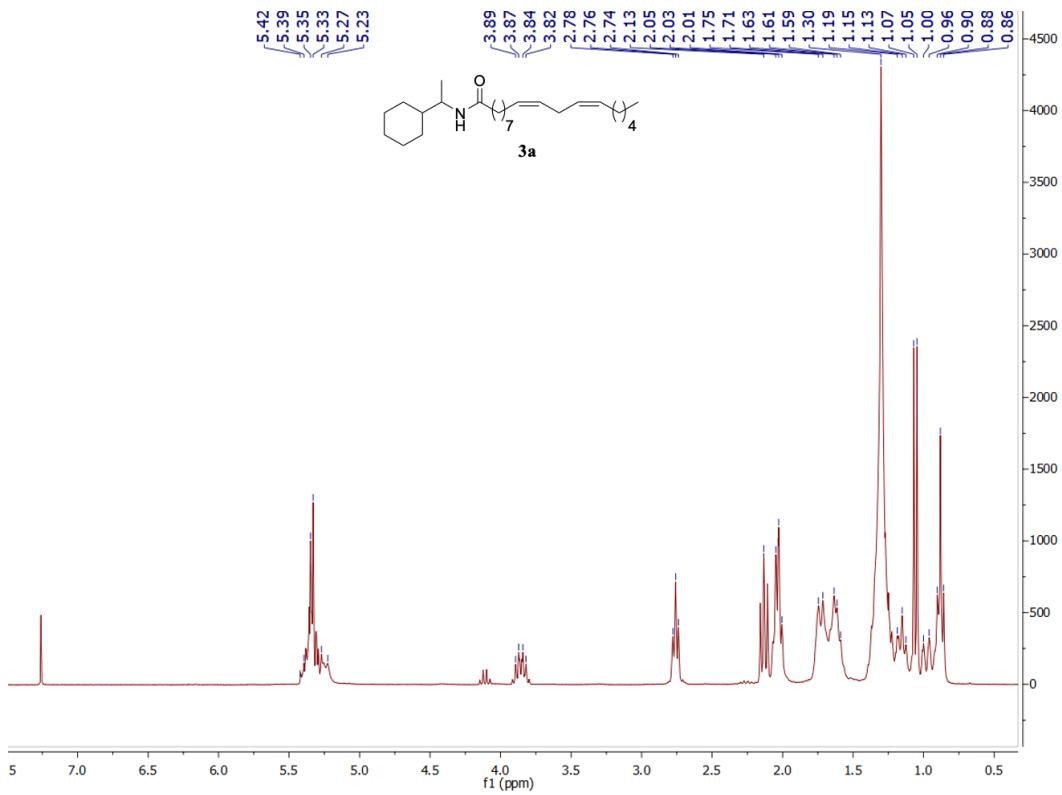
- Figure 36S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-*N*-(1-phenylethyl)-octadeca-9,12-dien-1-amine (**2i**).



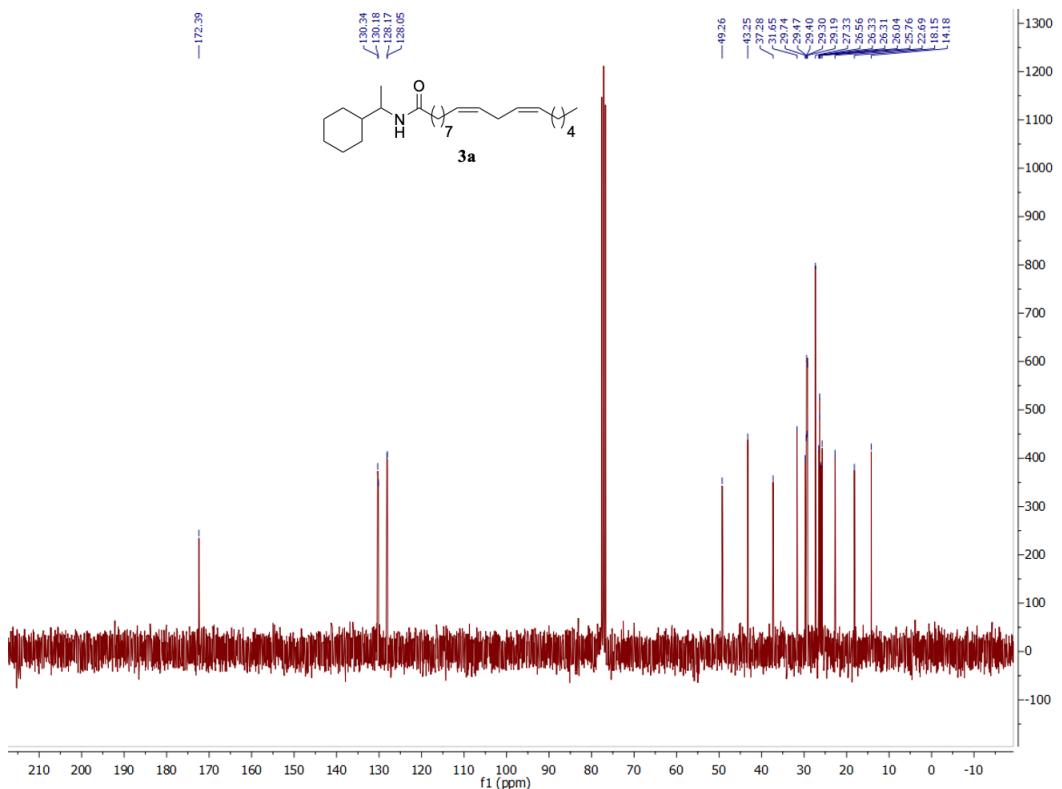
- Figure 37S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-*N*-(1-phenylethyl)-octadeca-9,12-dienothiamide (**2j**).



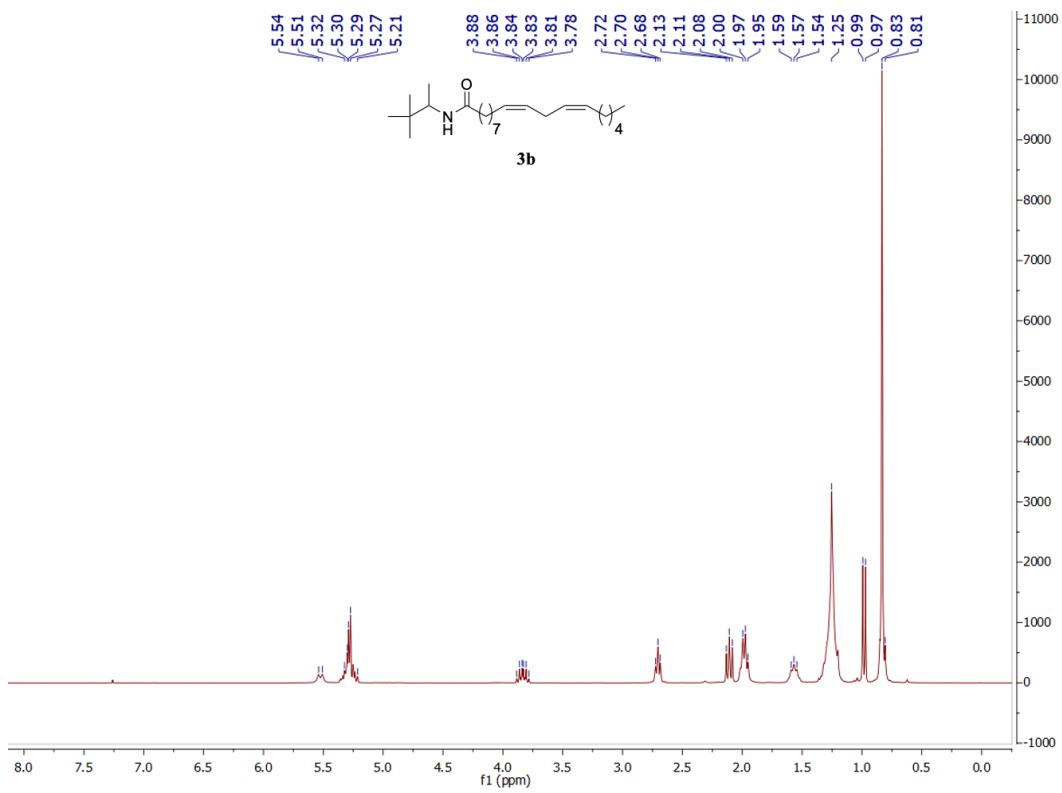
- Figure 38S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-*N*-(1-phenylethyl)-octadeca-9,12-dienothiamide (**2j**).



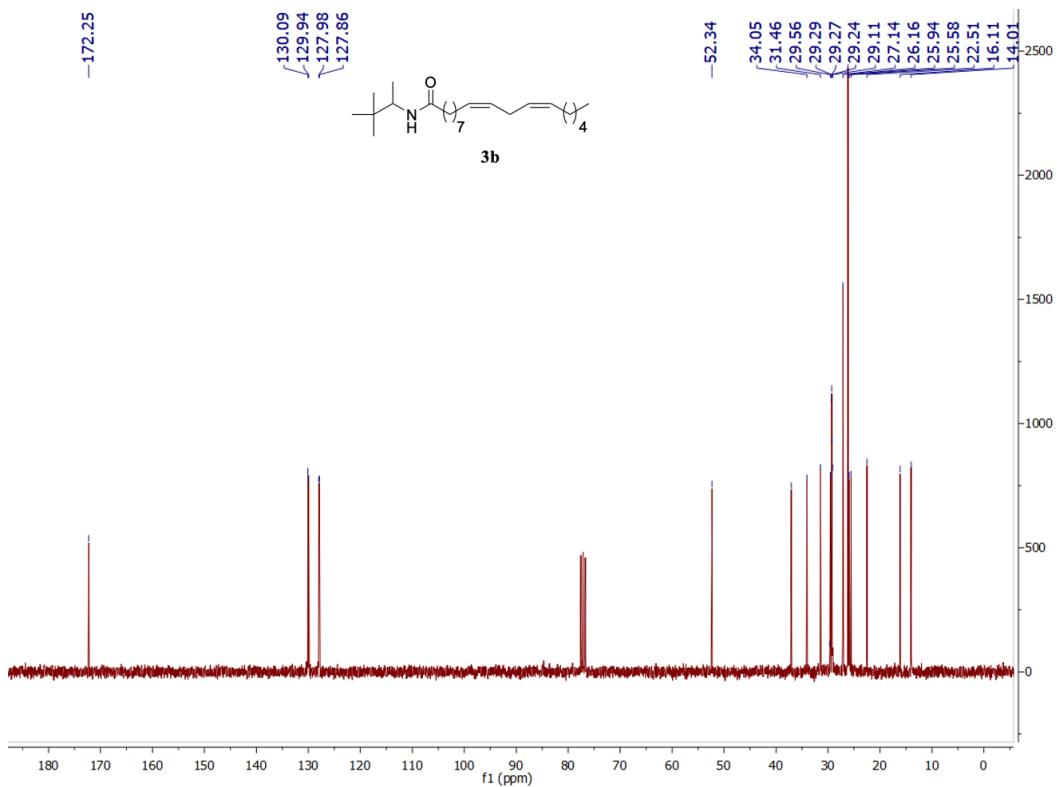
- Figure 39S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of ($9Z,12Z$)-*N*-(1-cyclohexylethyl)-octadeca-9,12-dienamide (**3a**).



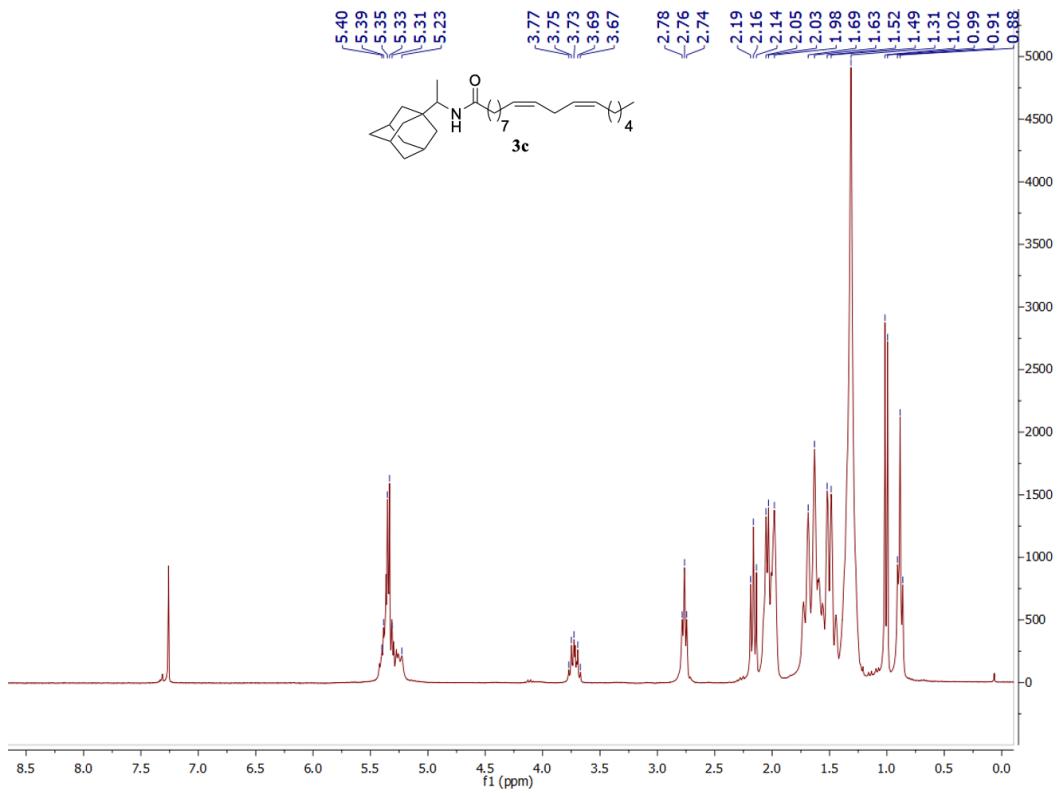
- Figure 40S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of ($9Z,12Z$)-*N*-(1-cyclohexylethyl)-octadeca-9,12-dienamide (**3a**).



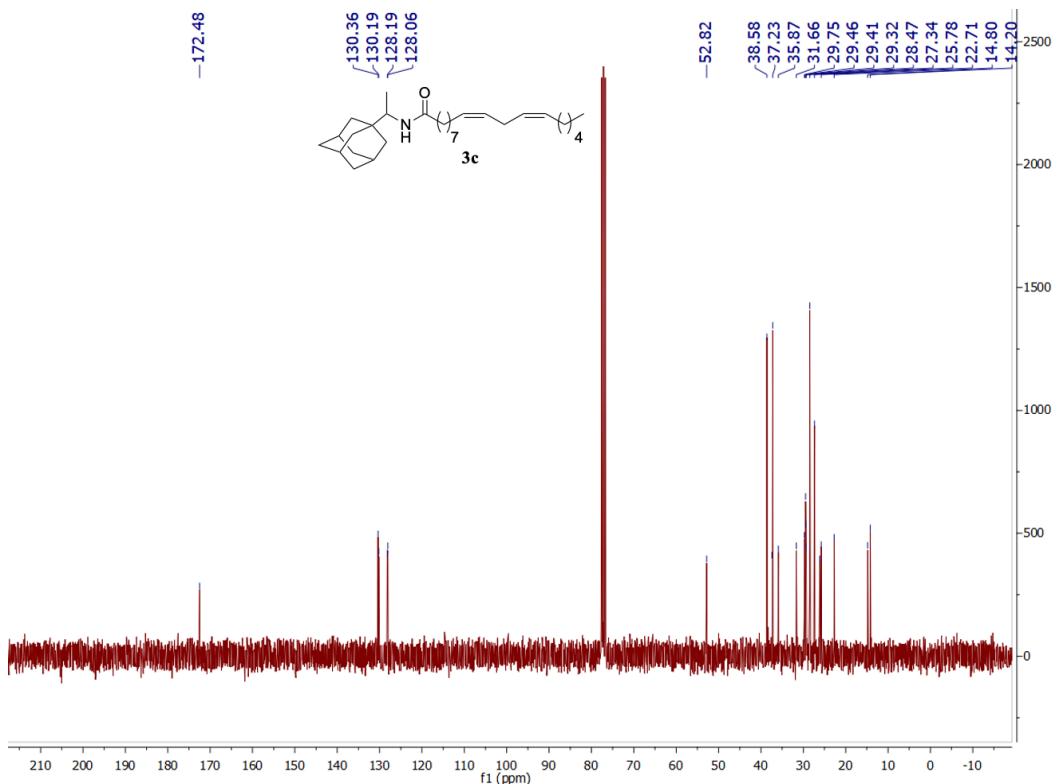
- Figure 41S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of $(9Z,12Z)$ -*N*-(3,3-dimethylbutan-2-yl)-octadeca-9,12-dienamide (**3b**).



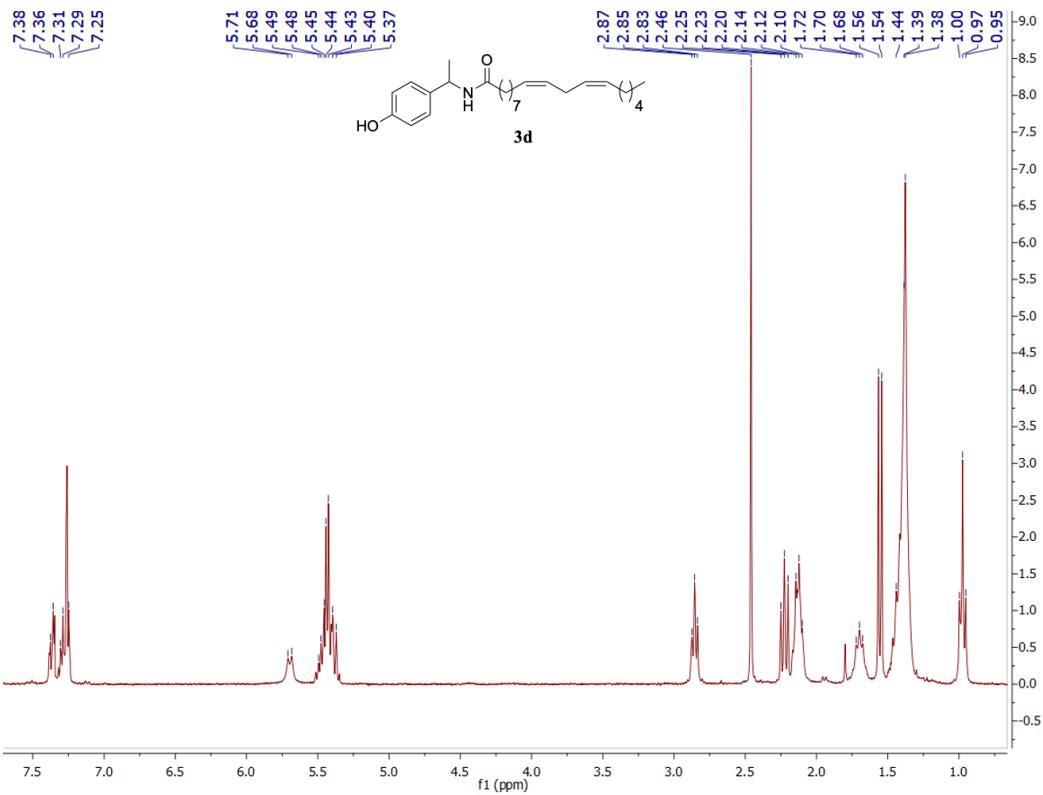
- Figure 42S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of $(9\text{Z},12\text{Z})$ -*N*-(3,3-dimethylbutan-2-yl)-octadeca-9,12-dienamide (**3b**).



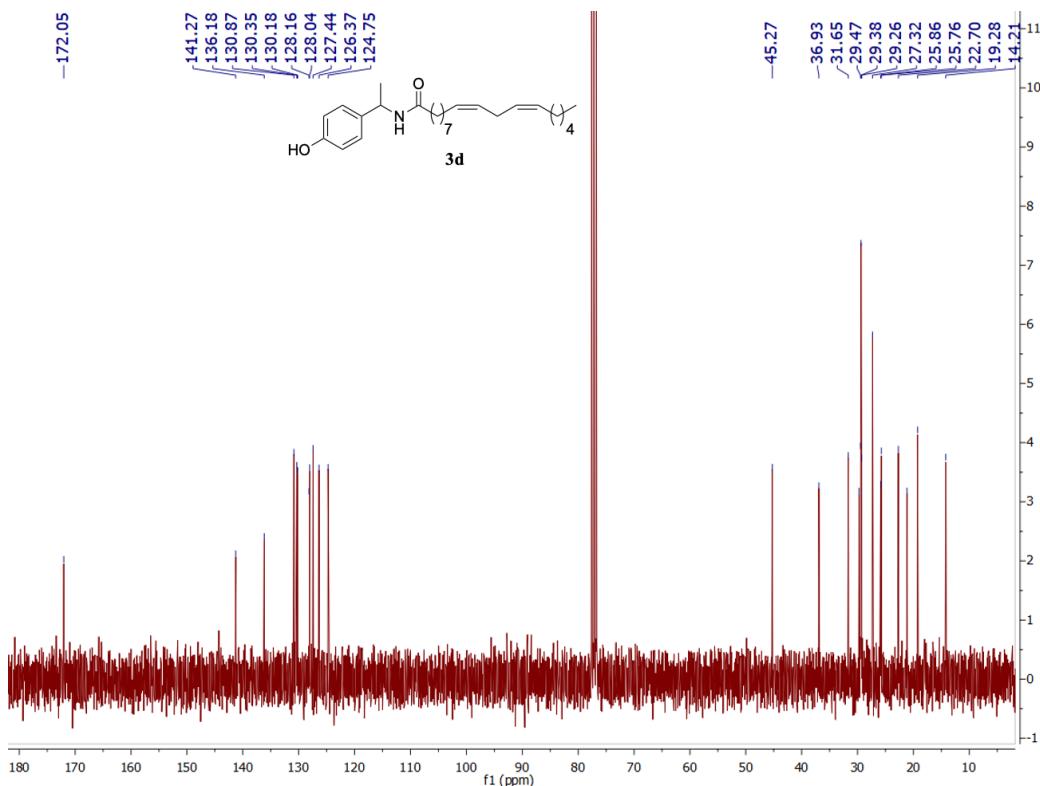
- Figure 43S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-*N*-(1-((3r,5r,7r)-adamantan-1-yl)-ethyl)-octadeca-9,12-dienamide (**3c**).



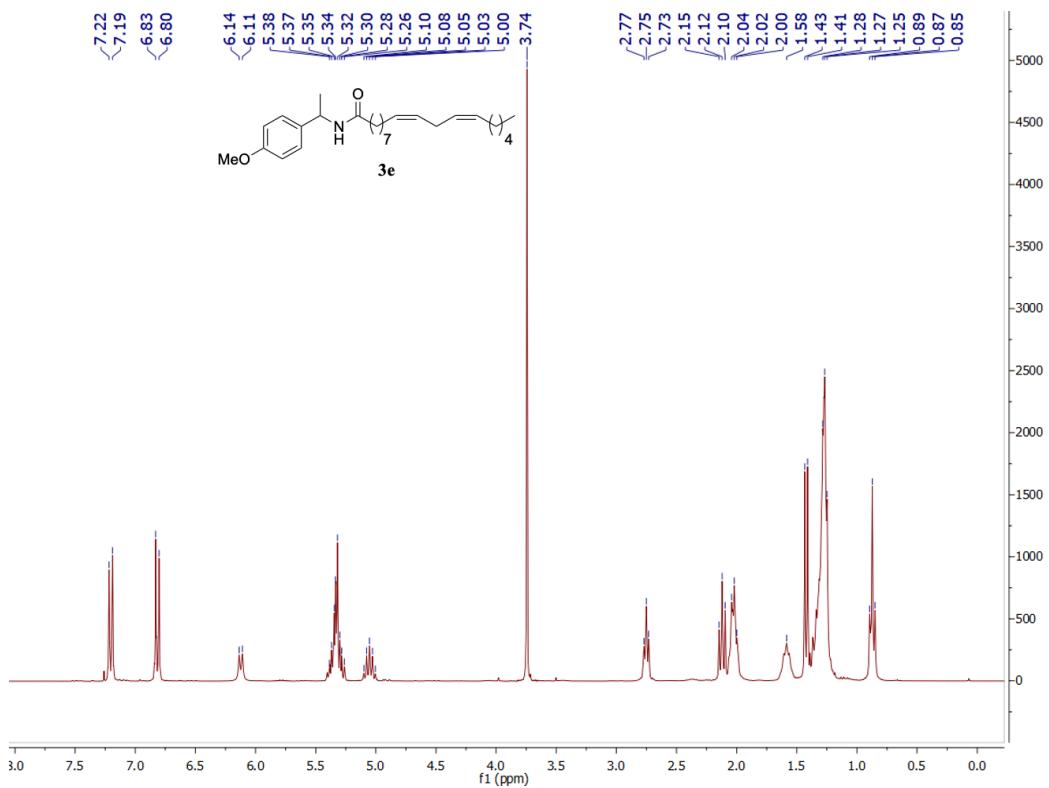
- Figure 44S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-*N*-(1-((3r,5r,7r)-adamantan-1-yl)-ethyl)-octadeca-9,12-dienamide (**3c**).



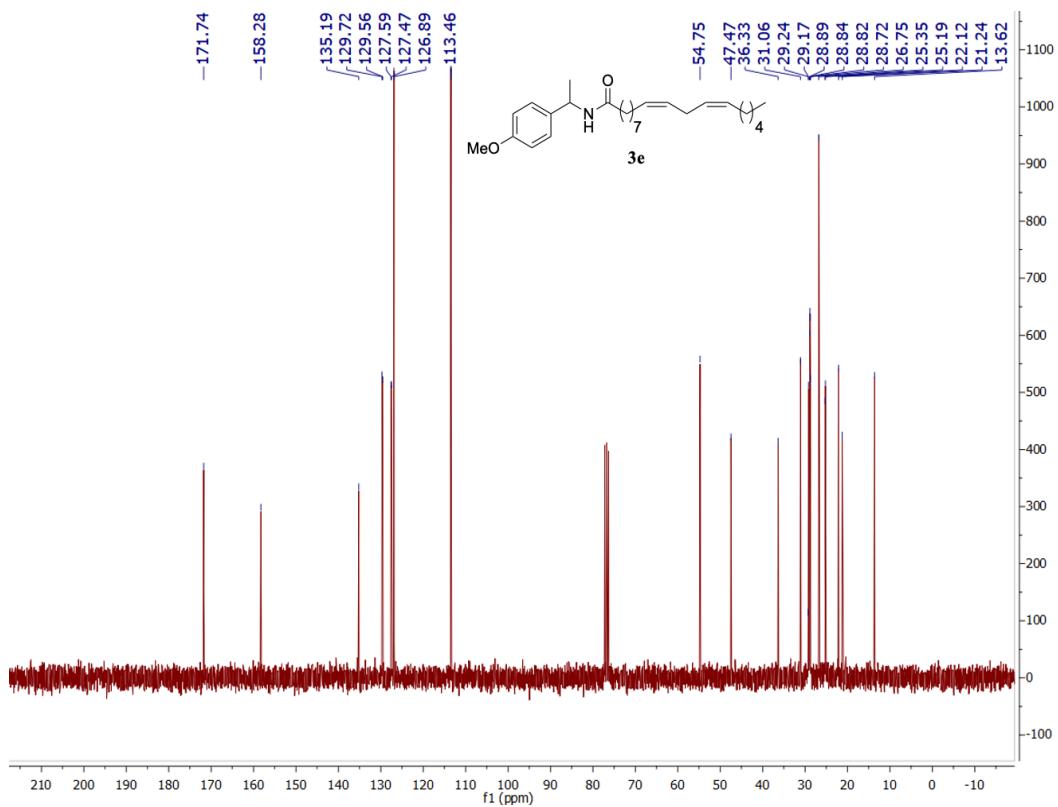
- Figure 45S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-hydroxyphenyl)-ethyl)-octadeca-9,12-dienamide (**3d**).



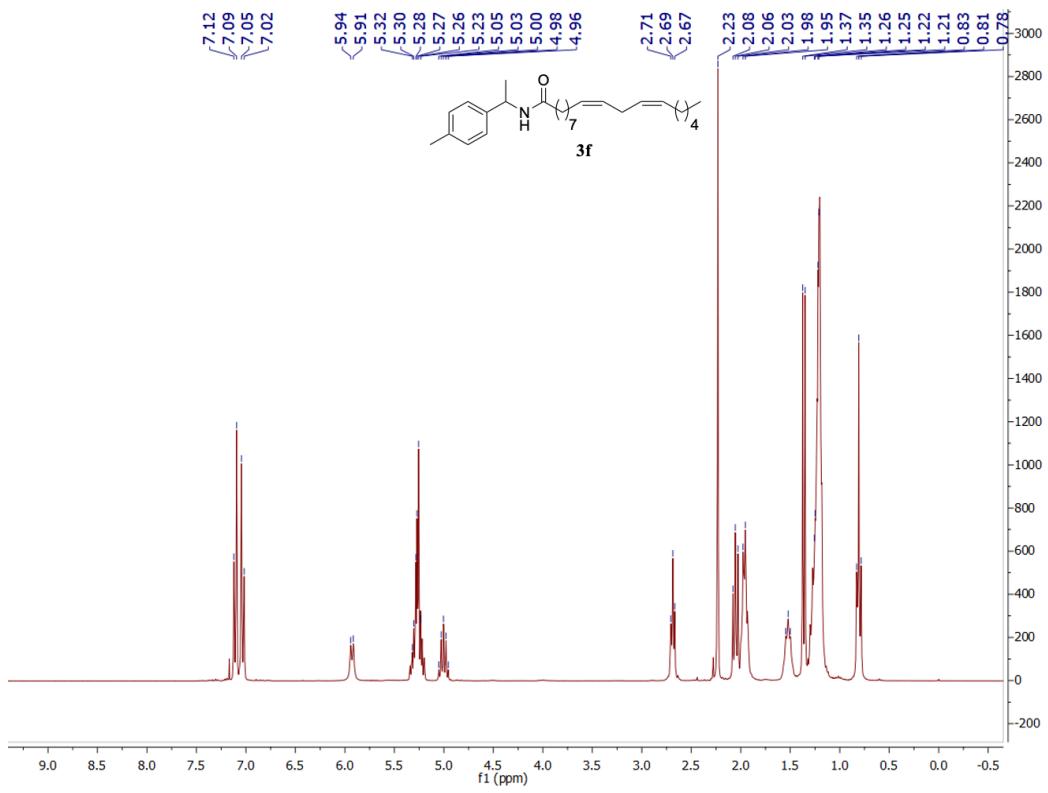
- Figure 46S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-hydroxyphenyl)-ethyl)-octadeca-9,12-dienamide (**3d**).



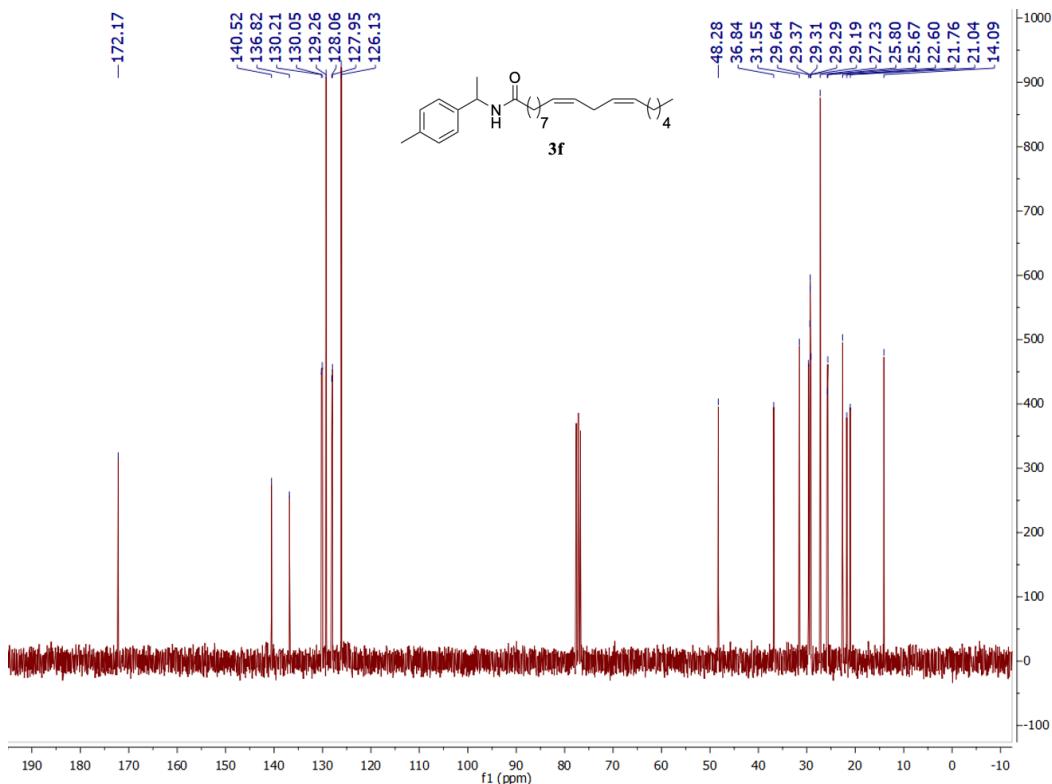
- Figure 47S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-methoxyphenyl)-ethyl)-octadeca-9,12-dienamide (**3e**).



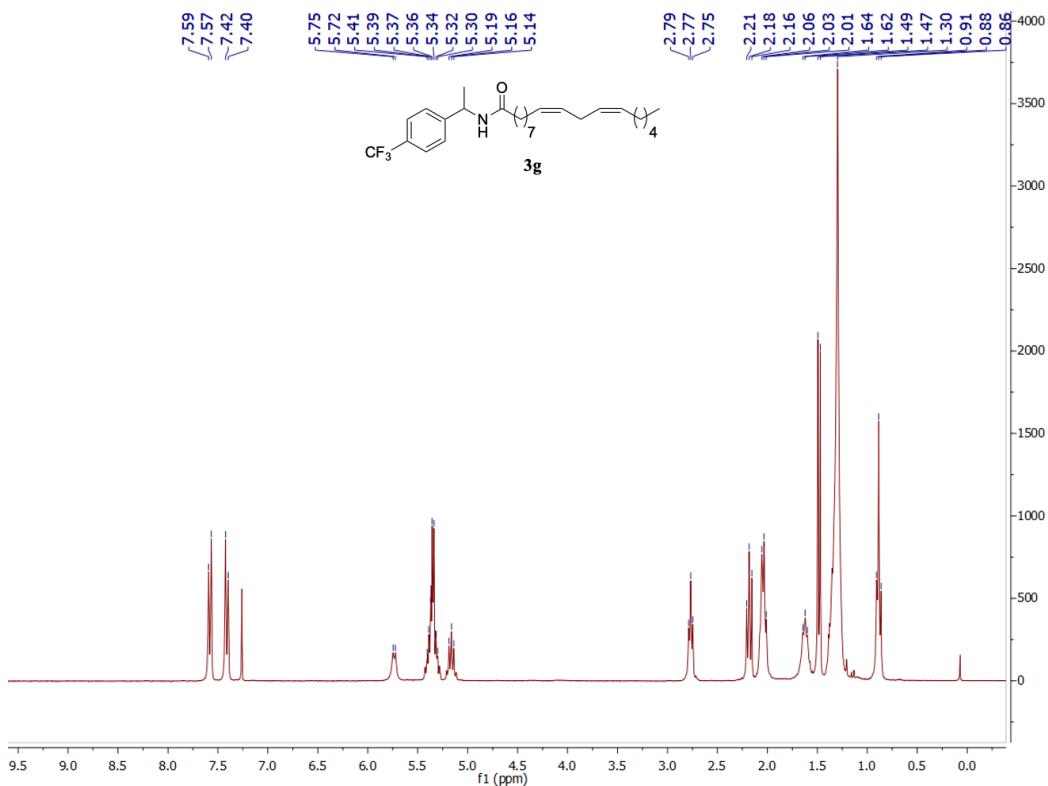
- Figure 48S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-methoxyphenyl)-ethyl)-octadeca-9,12-dienamide (**3e**).



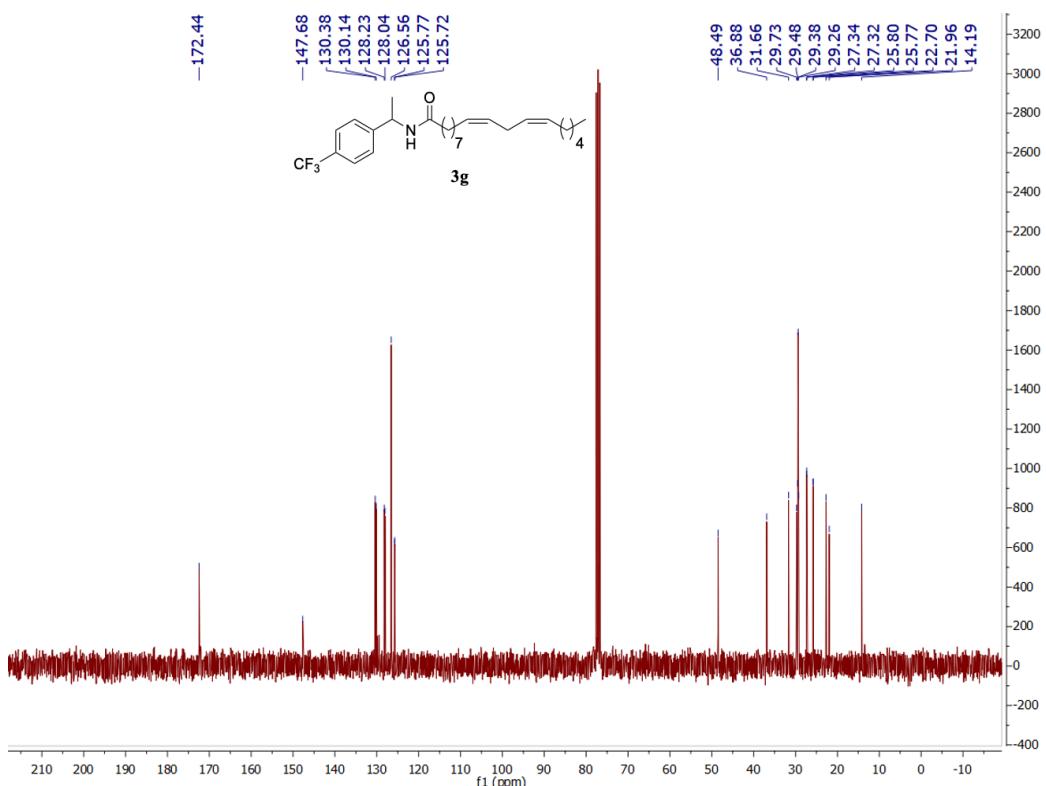
- Figure 49S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-*N*-(1-(*p*-tolyl)-ethyl)-octadeca-9,12-dienamide (**3f**).



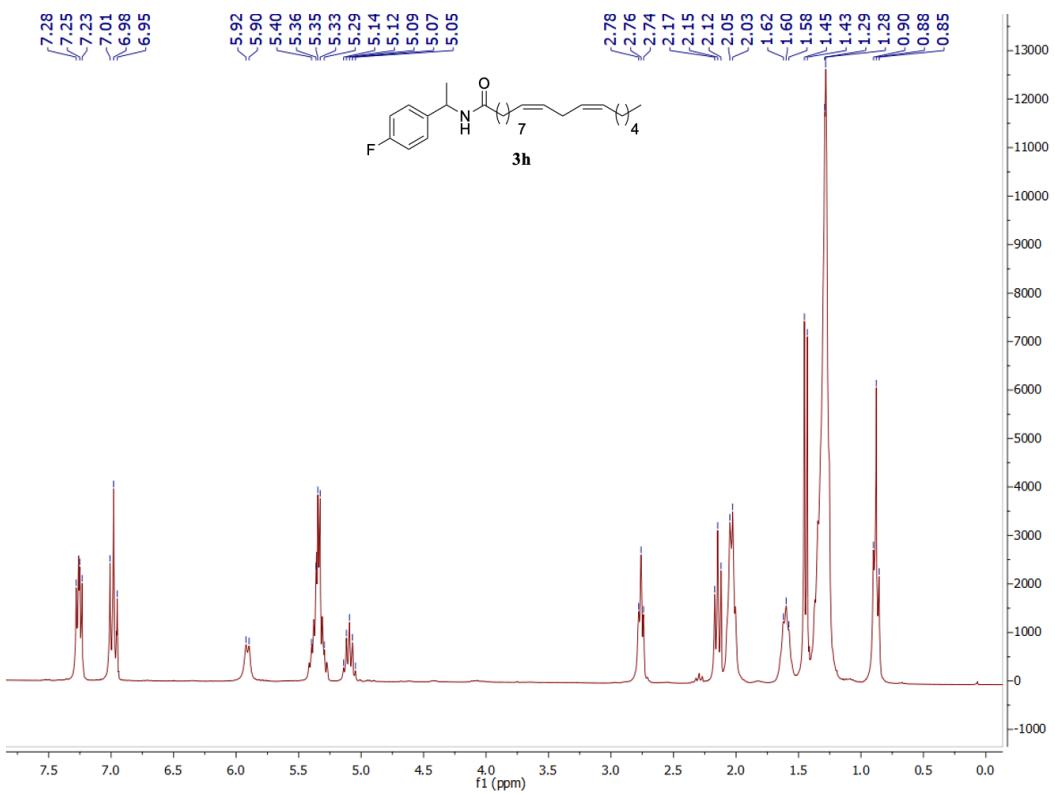
- Figure 50S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-*N*-(1-(*p*-tolyl)-ethyl)-octadeca-9,12-dienamide (**3f**).



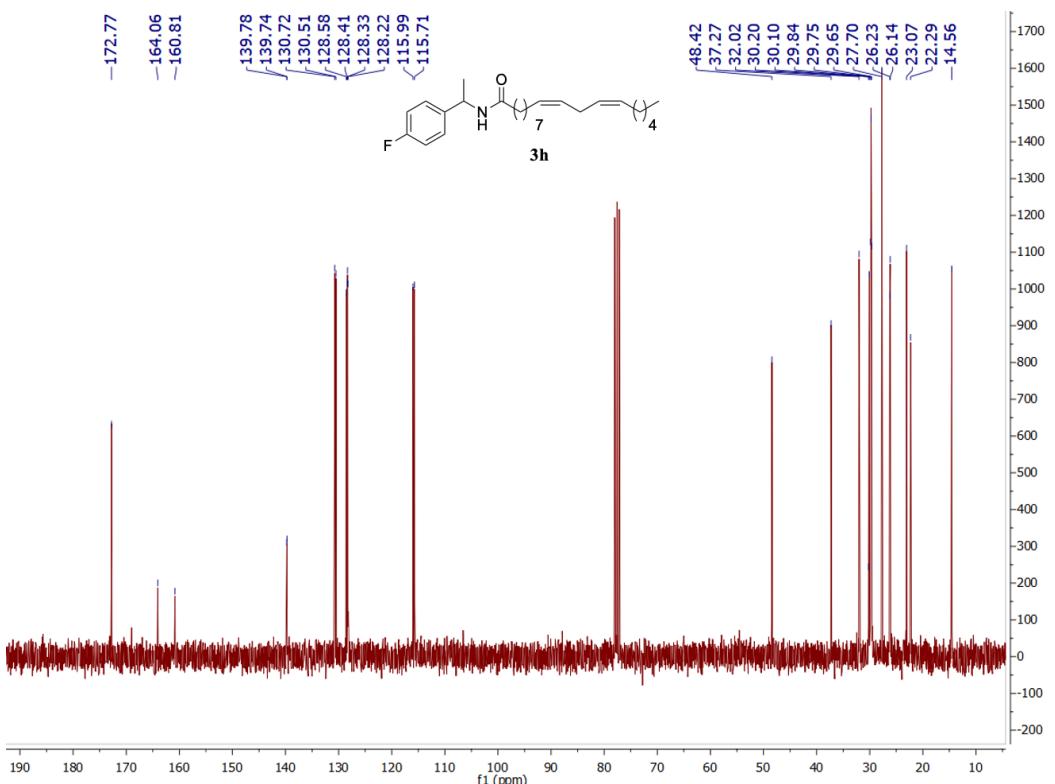
- Figure 51S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-(trifluoromethyl)-phenyl)-ethyl)-octadeca-9,12-dienamide (**3g**).



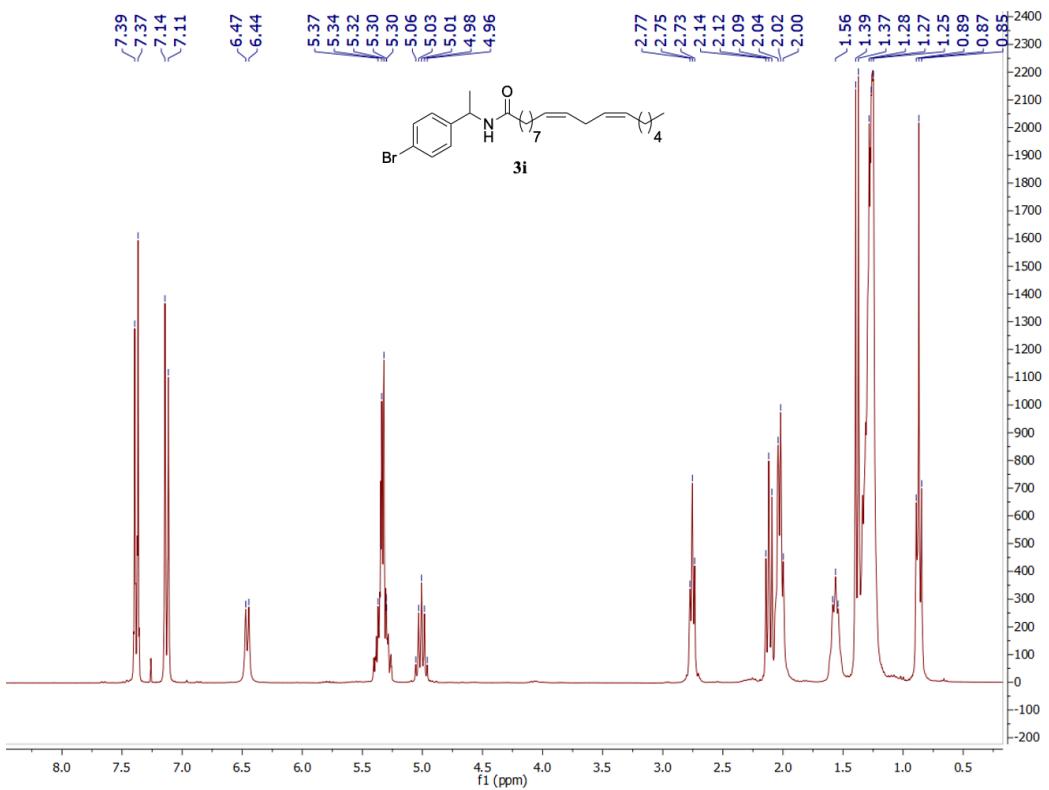
- Figure 52S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-(trifluoromethyl)-phenyl)-ethyl)-octadeca-9,12-dienamide (**3g**).



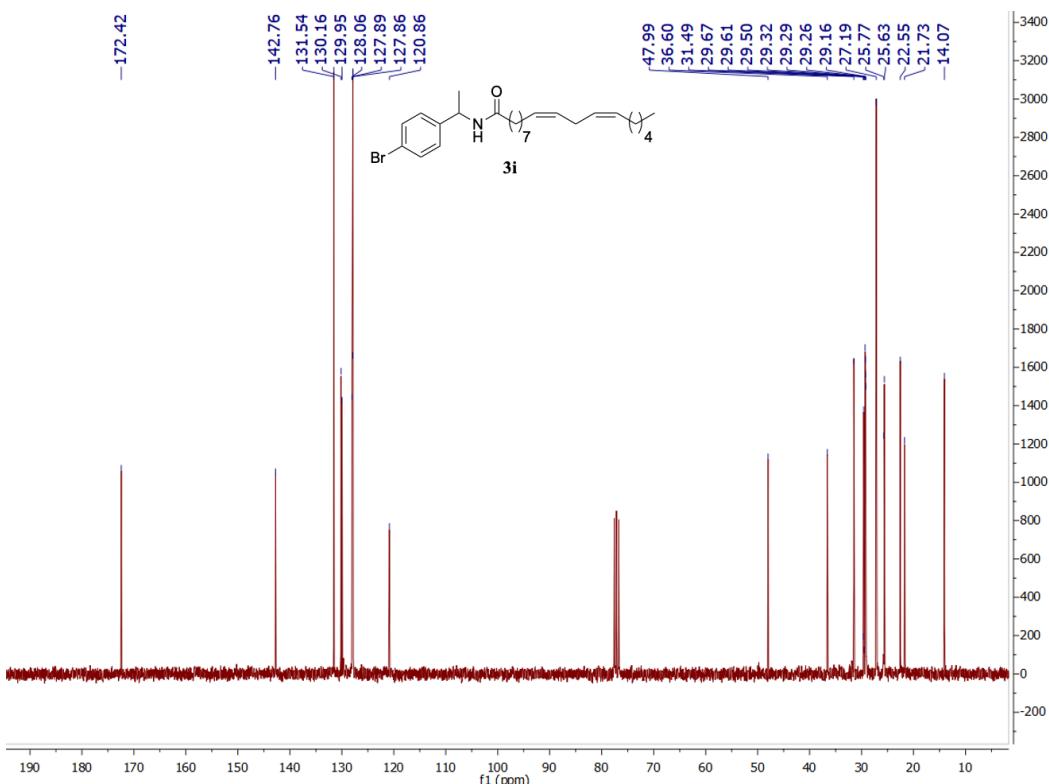
- Figure 53S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of (*9Z,12Z*)-*N*-(1-(4-fluorophenyl)-ethyl)-octadeca-9,12-dienamide (**3h**).



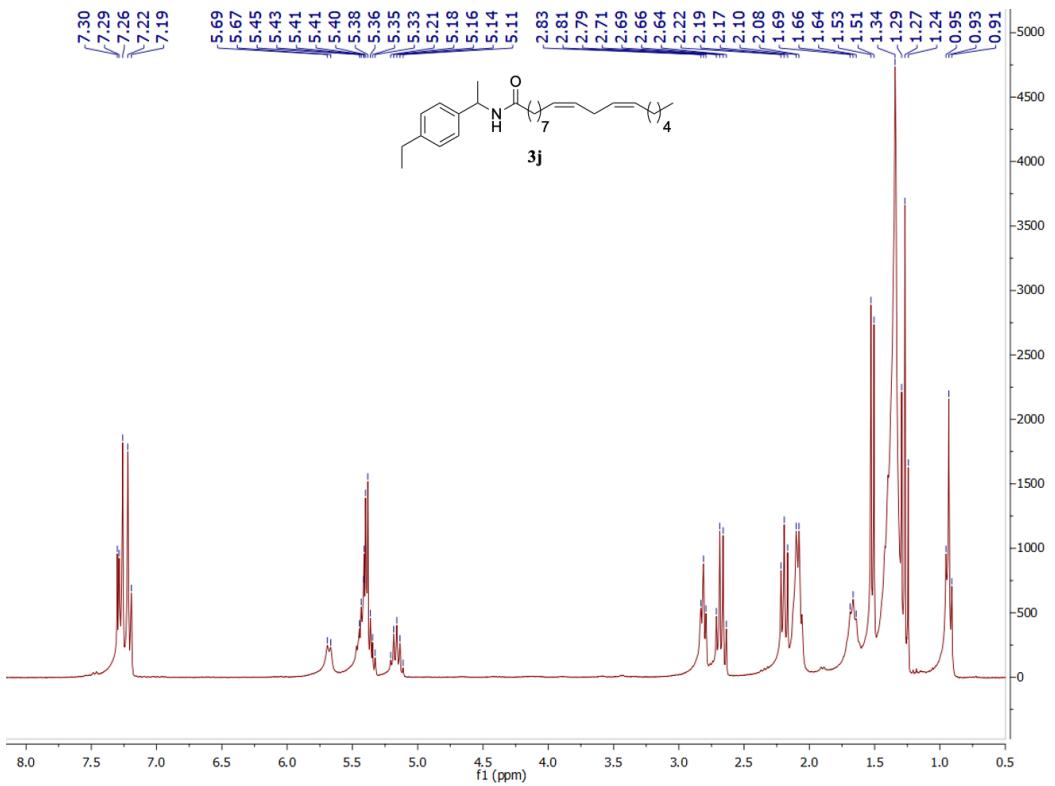
- Figure 54S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of (*9Z,12Z*)-*N*-(1-(4-fluorophenyl)-ethyl)-octadeca-9,12-dienamide (**3h**).



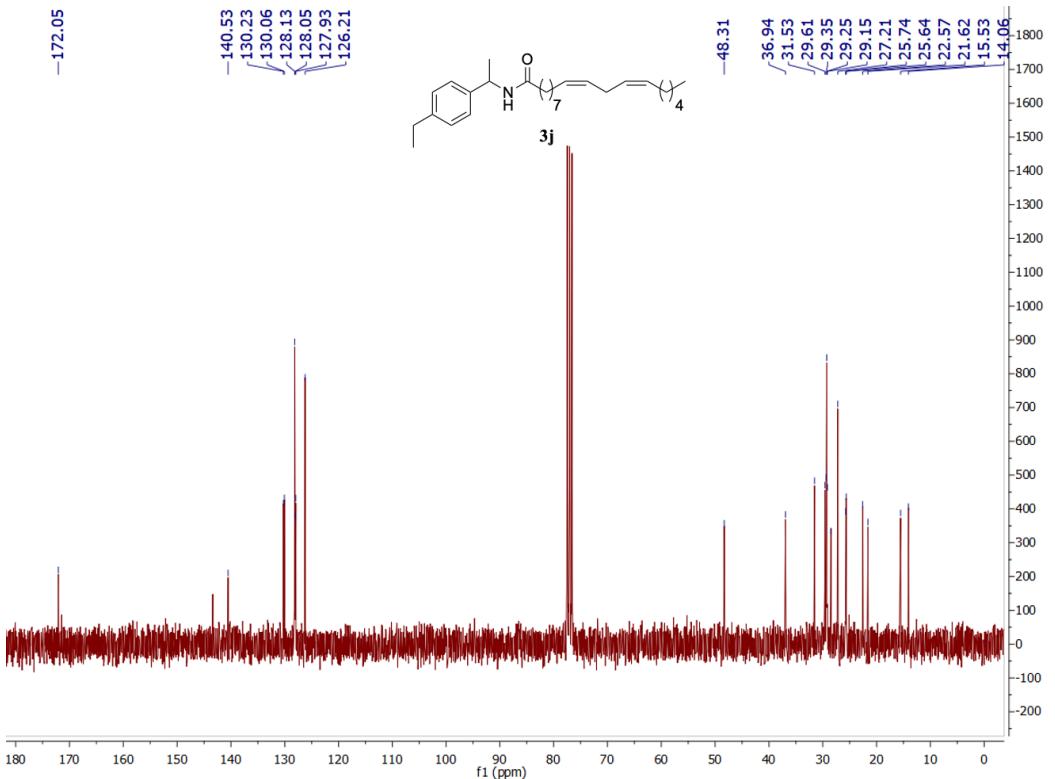
- Figure 55S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-bromophenyl)-ethyl)-octadeca-9,12-dienamide (**3i**).

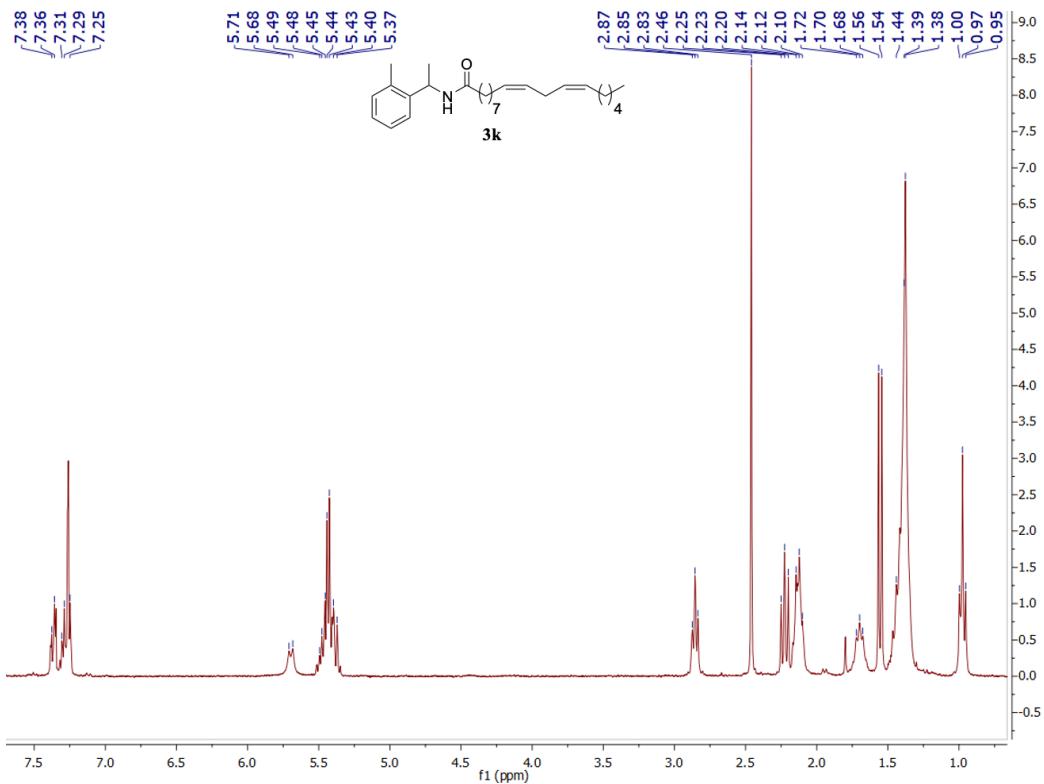


- Figure 56S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(4-bromophenyl)-ethyl)-octadeca-9,12-dienamide (**3i**).

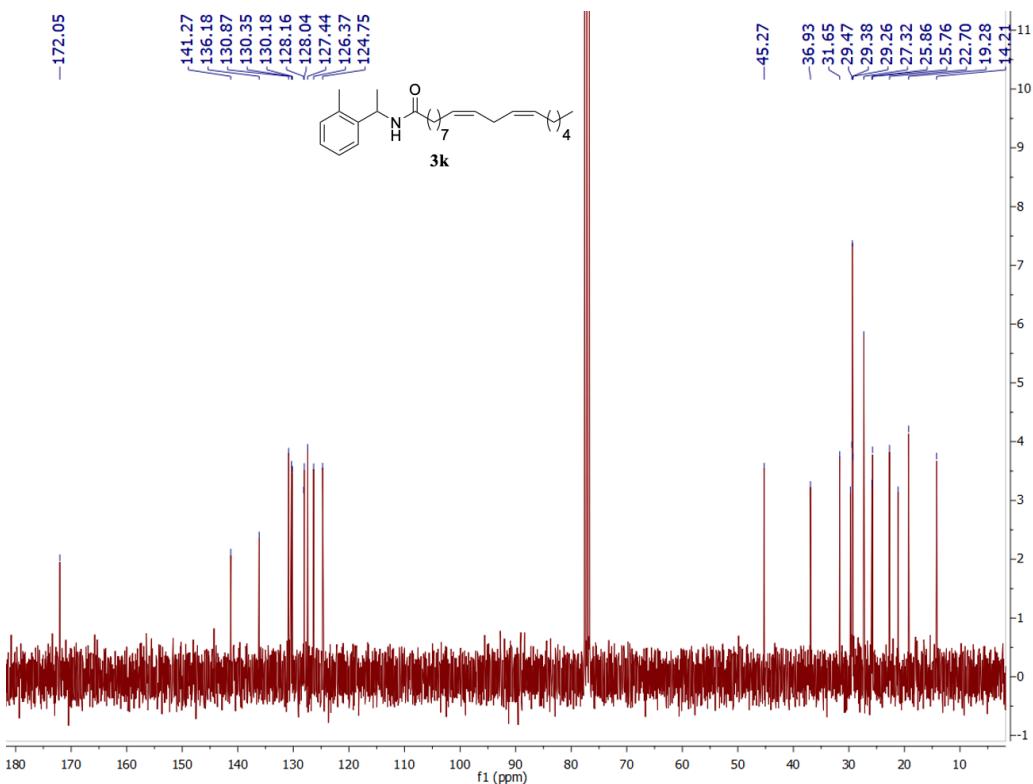


- Figure 57S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-*N*-(1-(4-ethylphenyl)-ethyl)-octadeca-9,12-dienamide (**3j**).

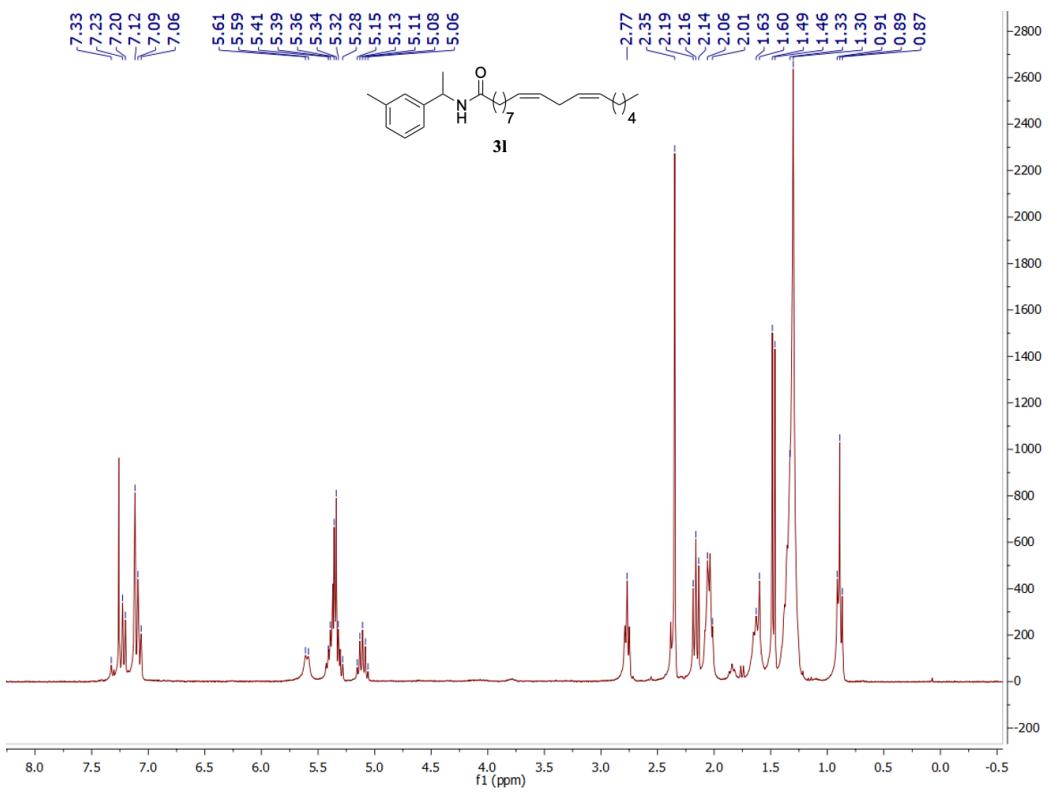




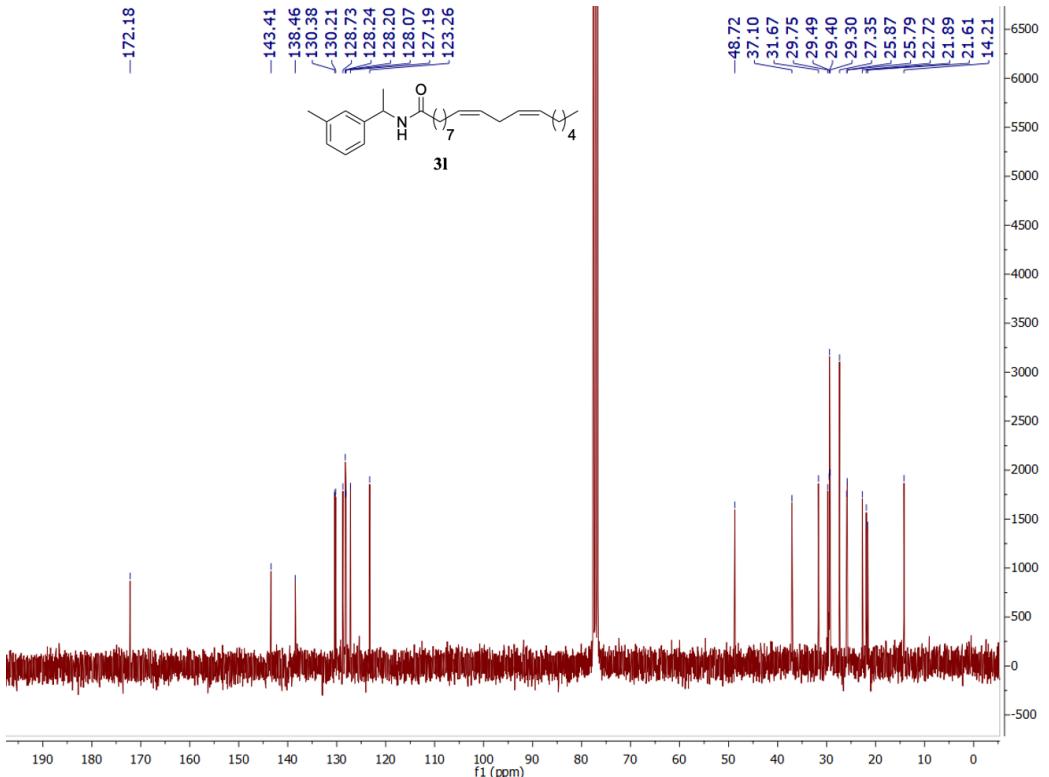
- Figure 59S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-*N*-(1-(*o*-tolyl)-ethyl)-octadeca-9,12-dienamide (**3k**).



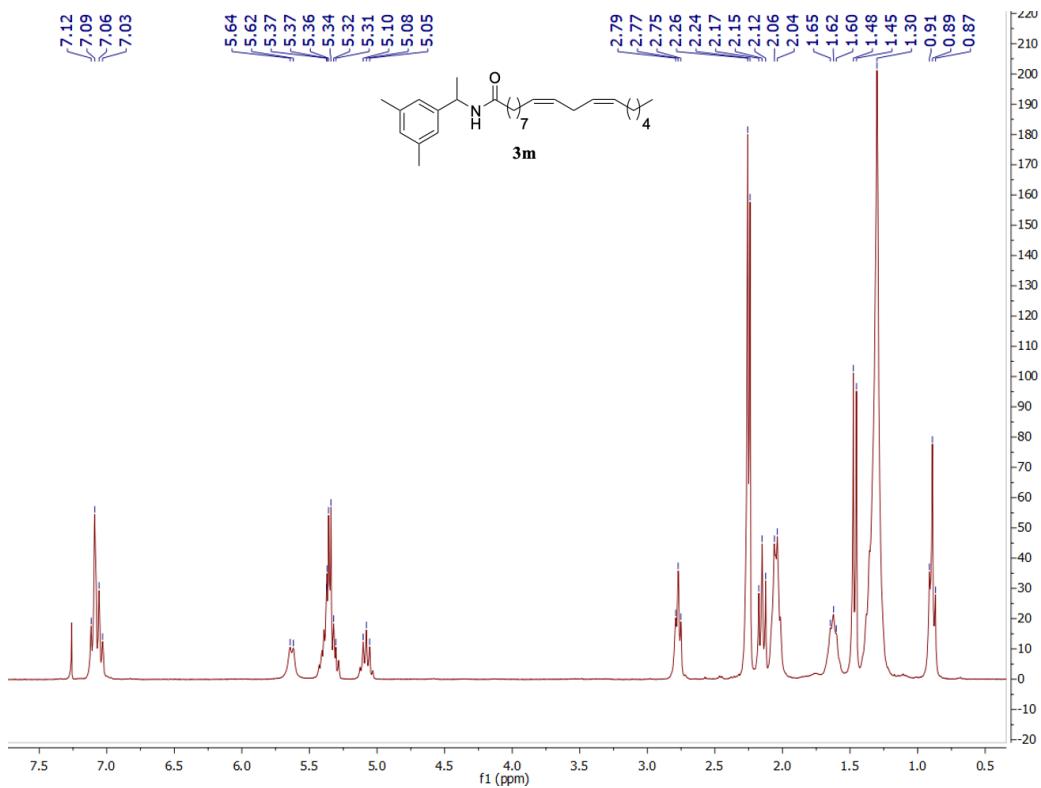
- Figure 60S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-*N*-(1-(*o*-tolyl)-ethyl)-octadeca-9,12-dienamide (**3k**).



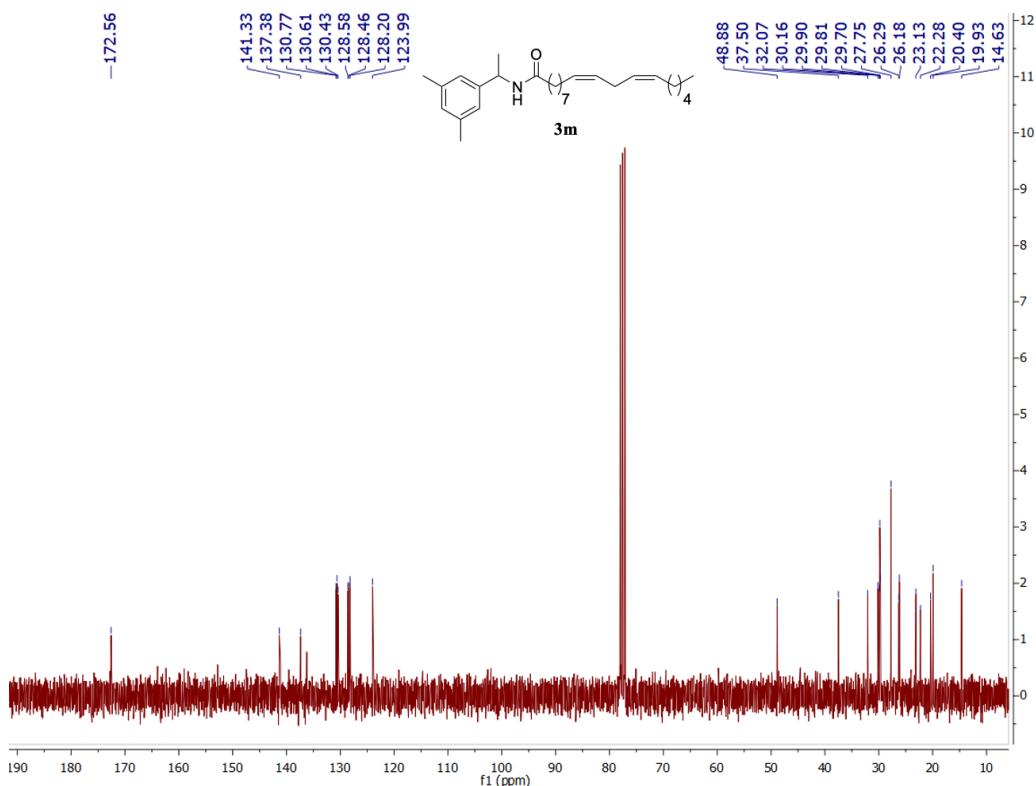
- Figure 61S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(*m*-tolyl)-ethyl)-octadeca-9,12-dienamide (**3l**).



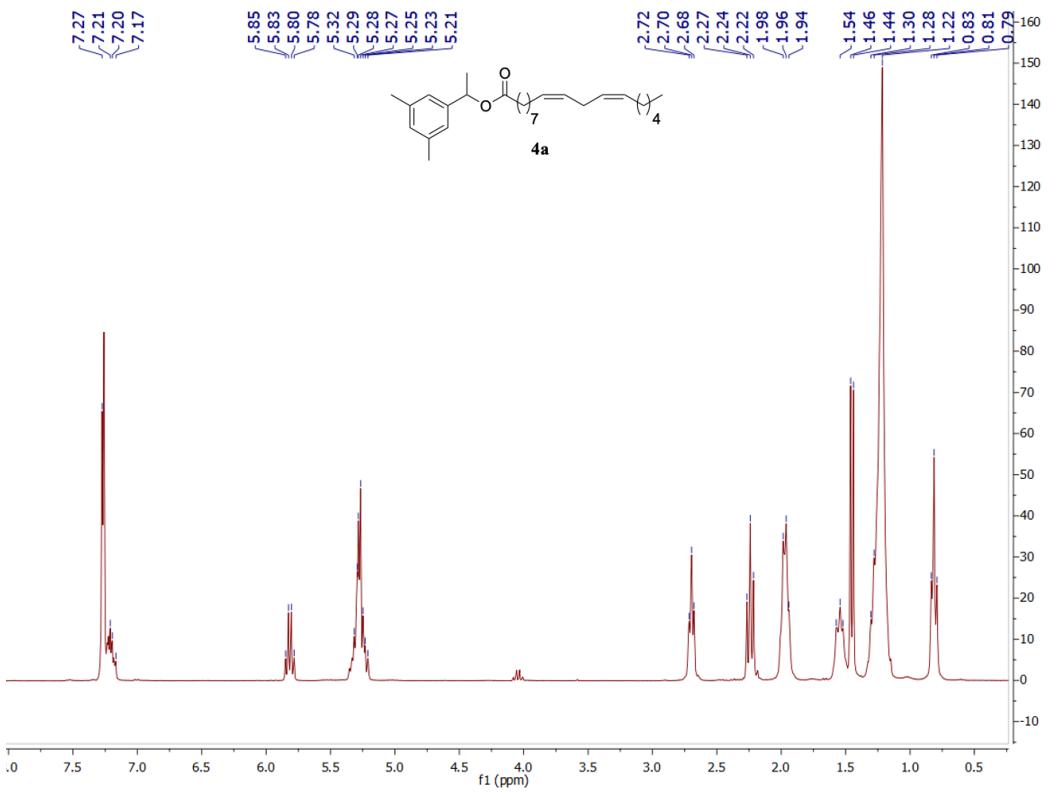
- Figure 62S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of ($9Z,12Z$)-*N*-(1-(*m*-tolyl)-ethyl)-octadeca-9,12-dienamide (**3l**).



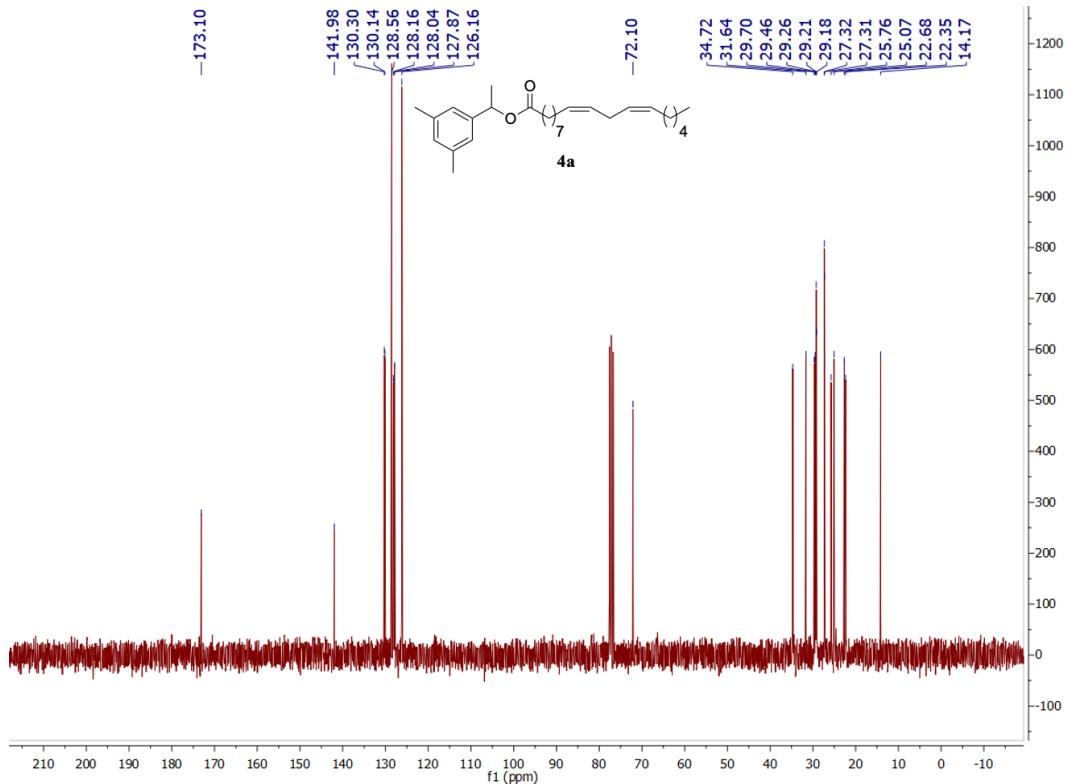
- Figure 63S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of ($9\text{Z},12\text{Z}$)-*N*-(1-(3,5-dimethylphenyl)-ethyl)-octadeca-9,12-dienamide (**3m**).



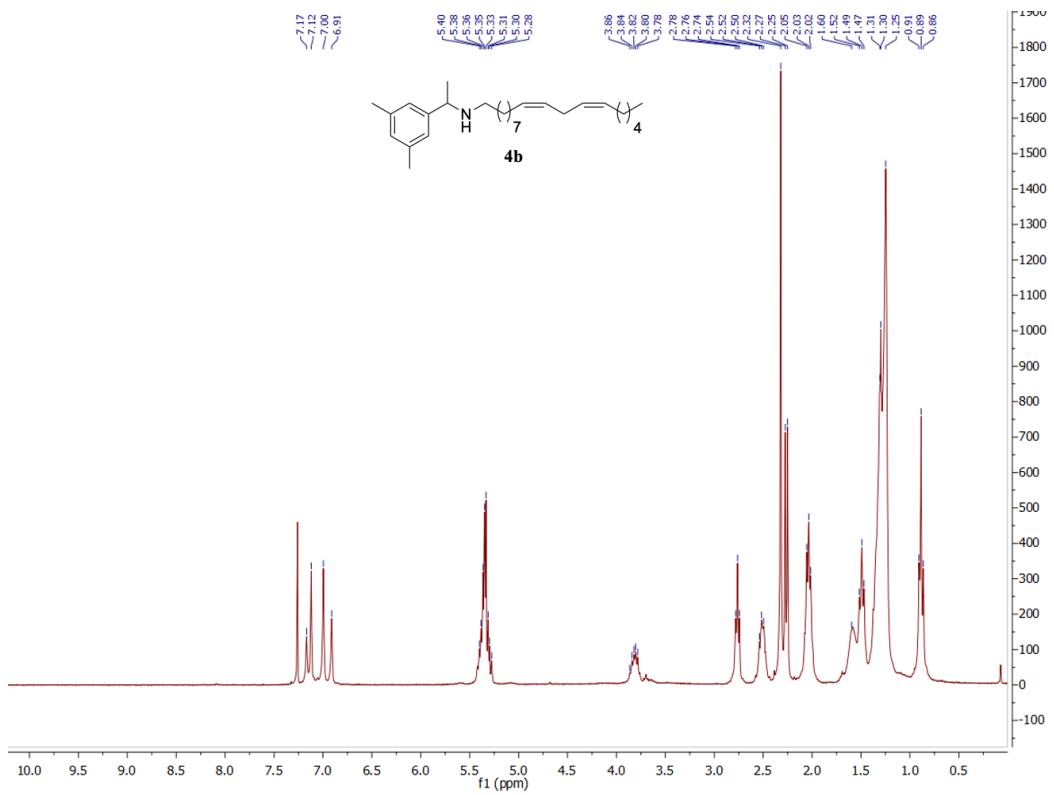
- Figure 64S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of ($9\text{Z},12\text{Z}$)-*N*-(1-(3,5-dimethylphenyl)-ethyl)-octadeca-9,12-dienamide (**3m**).



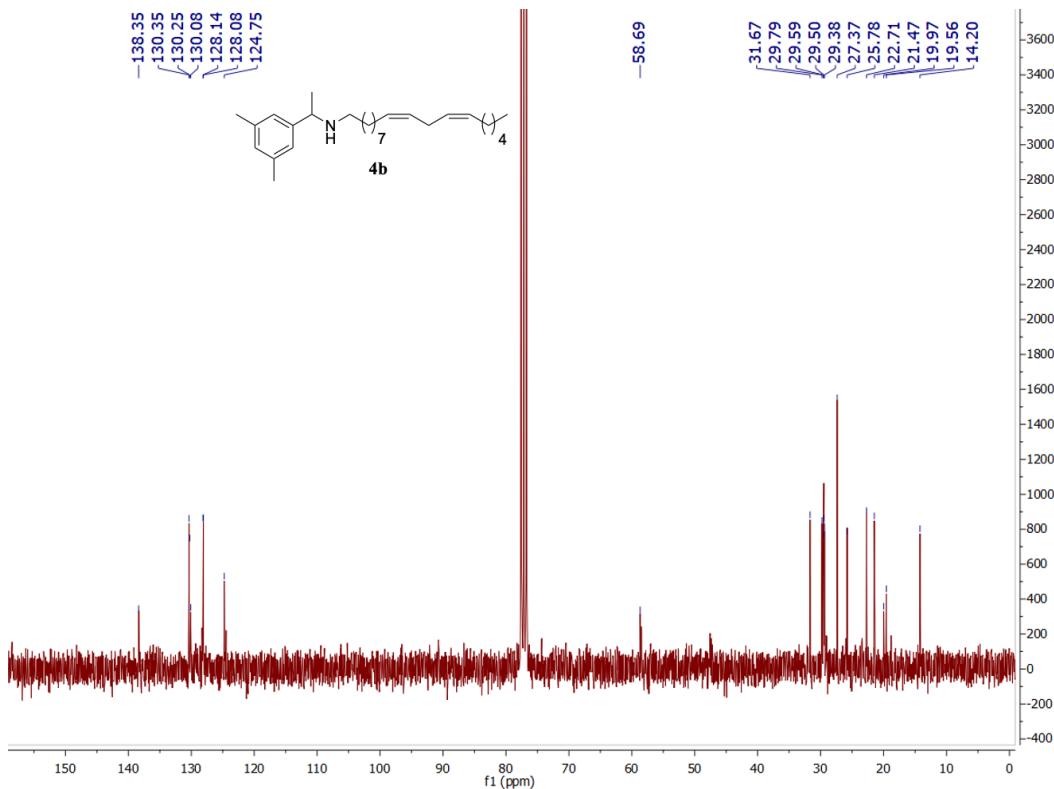
- Figure 65S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-1-(1-(3,5-dimethylphenyl)-ethoxy)-octadeca-9,12-dien-1-olate (**4a**).



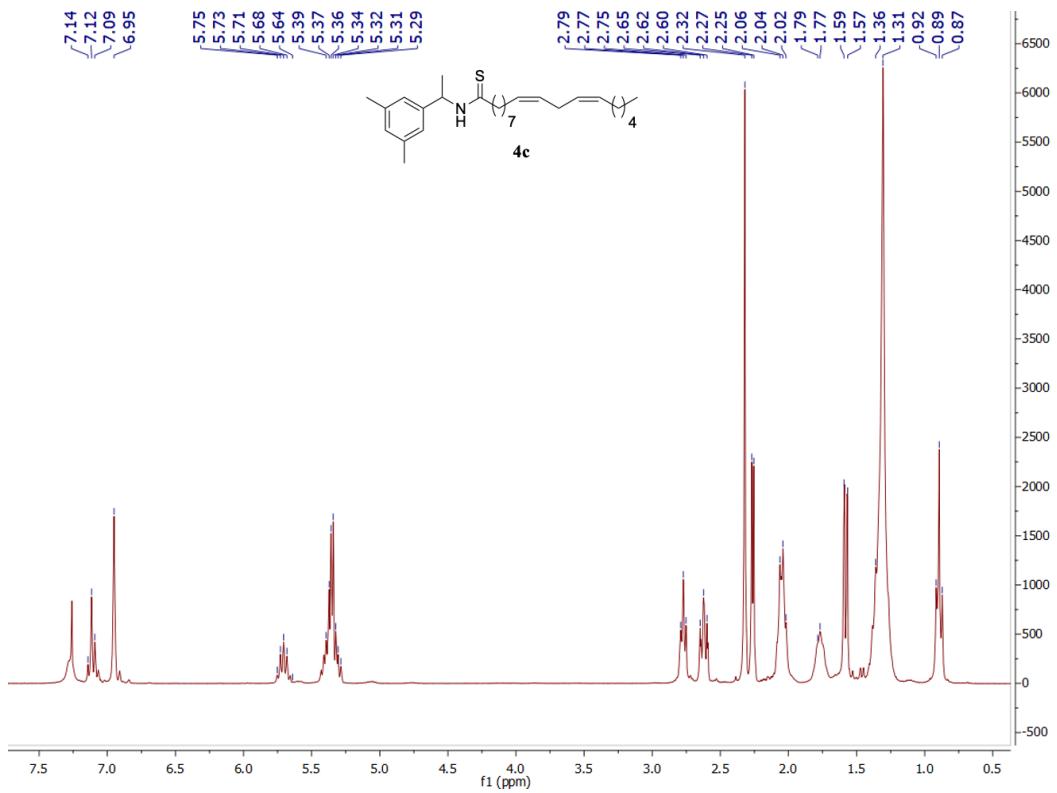
- Figure 66S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-1-(1-(3,5-dimethylphenyl)-ethoxy)-octadeca-9,12-dien-1-olate (**4a**).



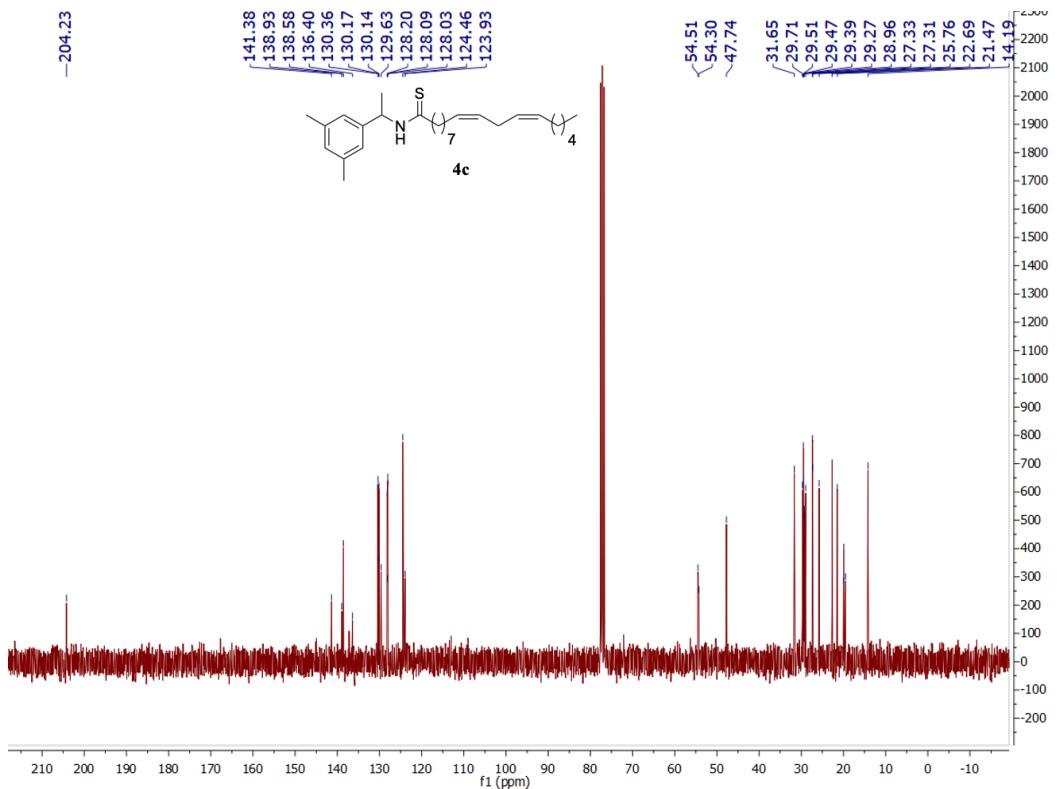
- Figure 67S. ^1H NMR (CDCl_3 , 300 MHz) spectrum of (9Z,12Z)-*N*-(1-(3,5-dimethylphenyl)-ethyl)-octadeca-9,12-dien-1-amine (**4b**).



- Figure 68S. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of (9Z,12Z)-*N*-(1-(3,5-dimethylphenyl)-ethyl)-octadeca-9,12-dien-1-amine (**4b**).



- Figure 69S. ¹H NMR (CDCl_3 , 300 MHz) spectrum of ($9\text{Z},12\text{Z}$)-*N*-(1-(3,5-dimethylphenyl)-ethyl)-octadeca-9,12-dienethioamide (**4c**).



- Figure 70S. ¹³C NMR (CDCl_3 , 75 MHz) spectrum of ($9\text{Z},12\text{Z}$)-*N*-(1-(3,5-dimethylphenyl)-ethyl)-octadeca-9,12-dienethioamide (**4c**).