

Supporting Information

TBAI Assisted Direct C-H Activation of Indoles with β -E-Styrene Sulfonyl Hydrazides: A Stereo selective Access to 3- Styryl Thioindoles.

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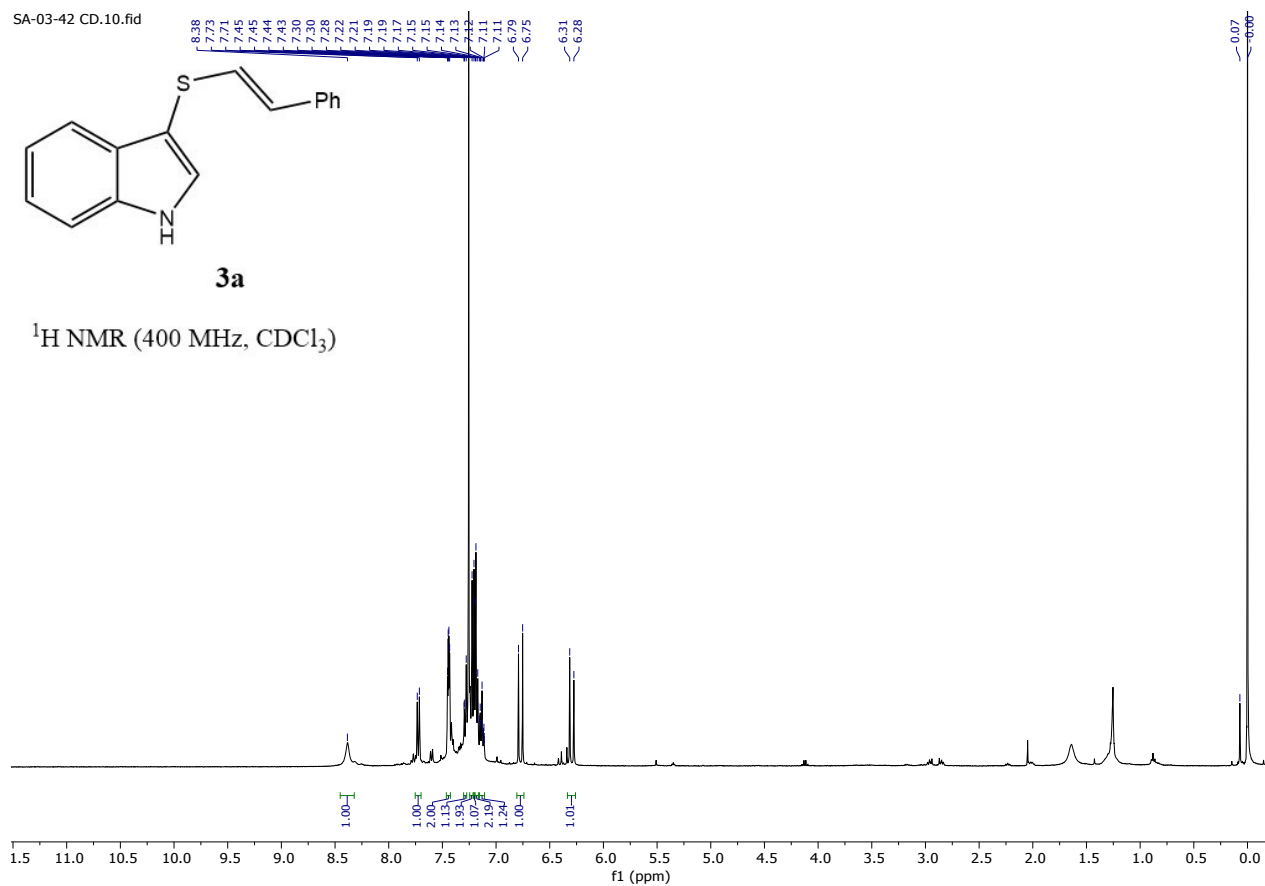


Fig. 1 $^1\text{H NMR}$ Spectrum of (*E*)-3-(Styrylthio)- ^1H -indole **3a**

sa-03-42.2.fid

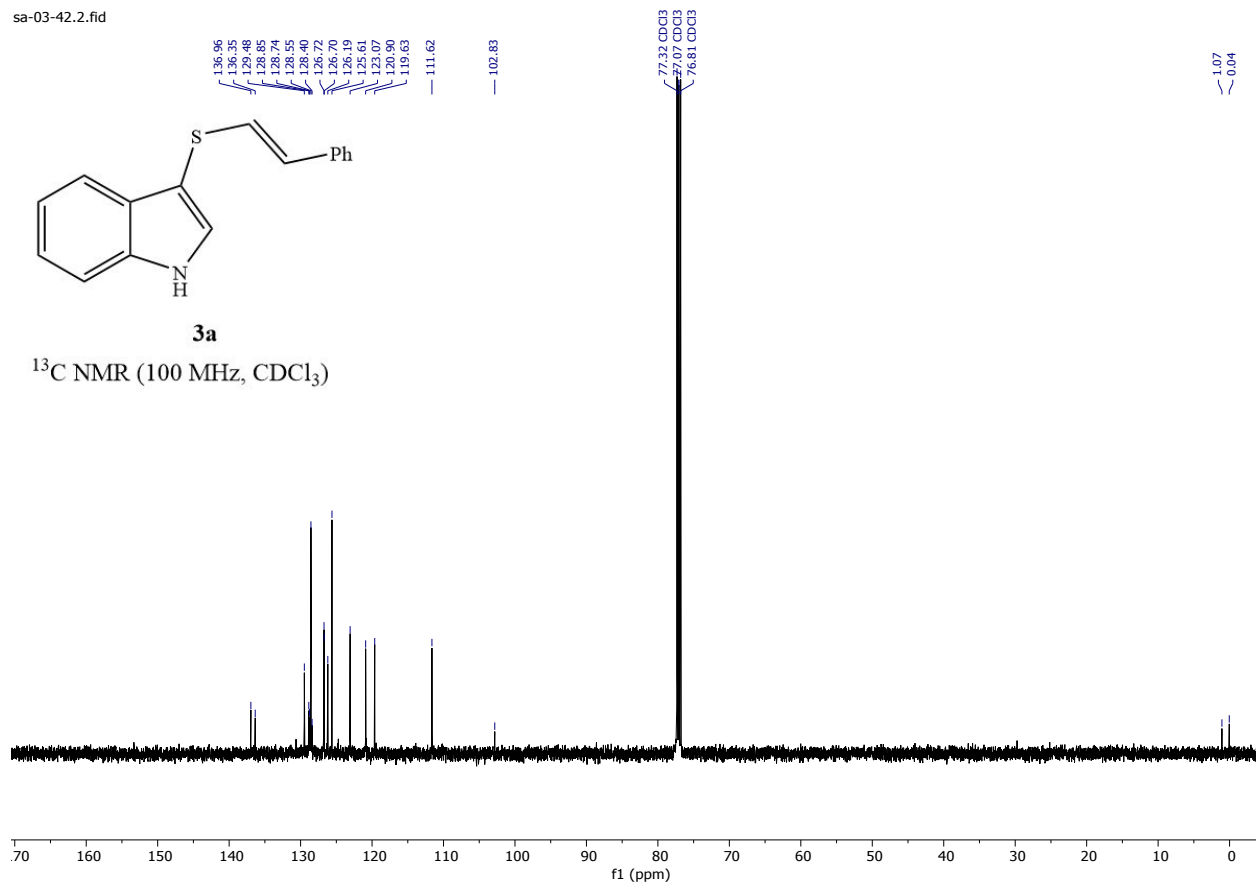


Fig. 2 ^{13}C NMR Spectrum of (*E*)-3-(Styrylthio)- ^1H -indole **3a**

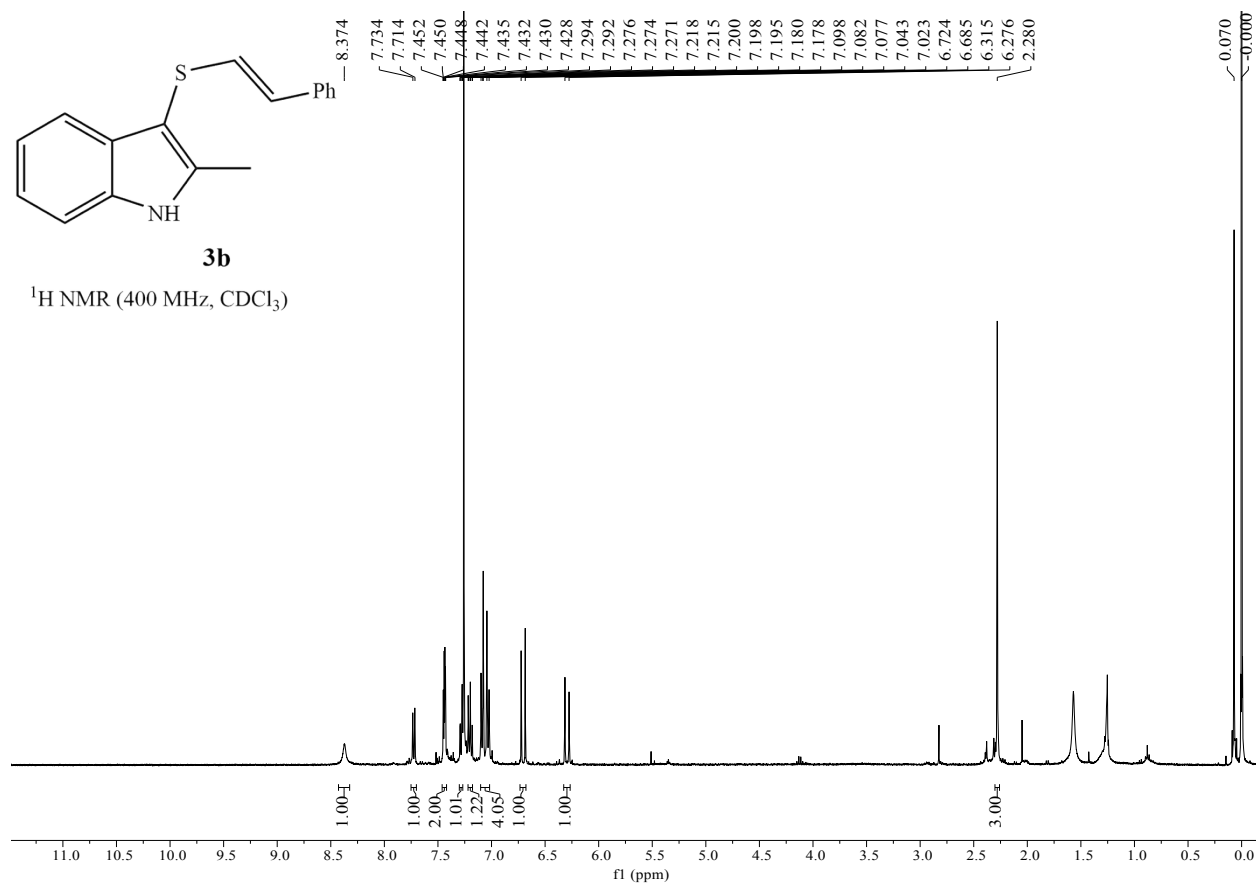


Fig. 3 ¹H NMR Spectrum of (*E*)-2-methyl-3-(styrylthio)-1*H*-indole **3b**

sa03-78.2.fid

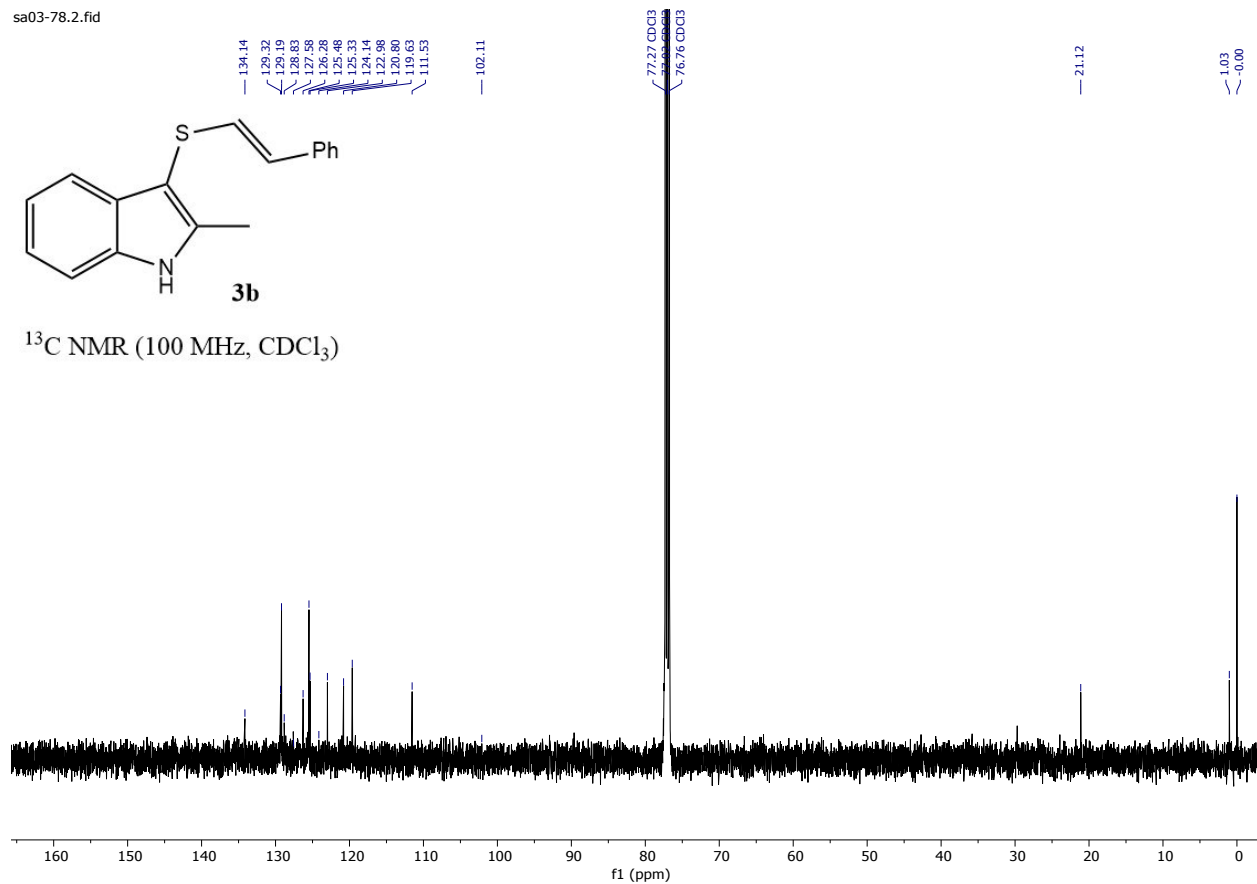


Fig. 4 ^{13}C NMR Spectrum of (*E*)-2-methyl-3-(styrylthio)-1*H*-indole **3b**

SA-03-80

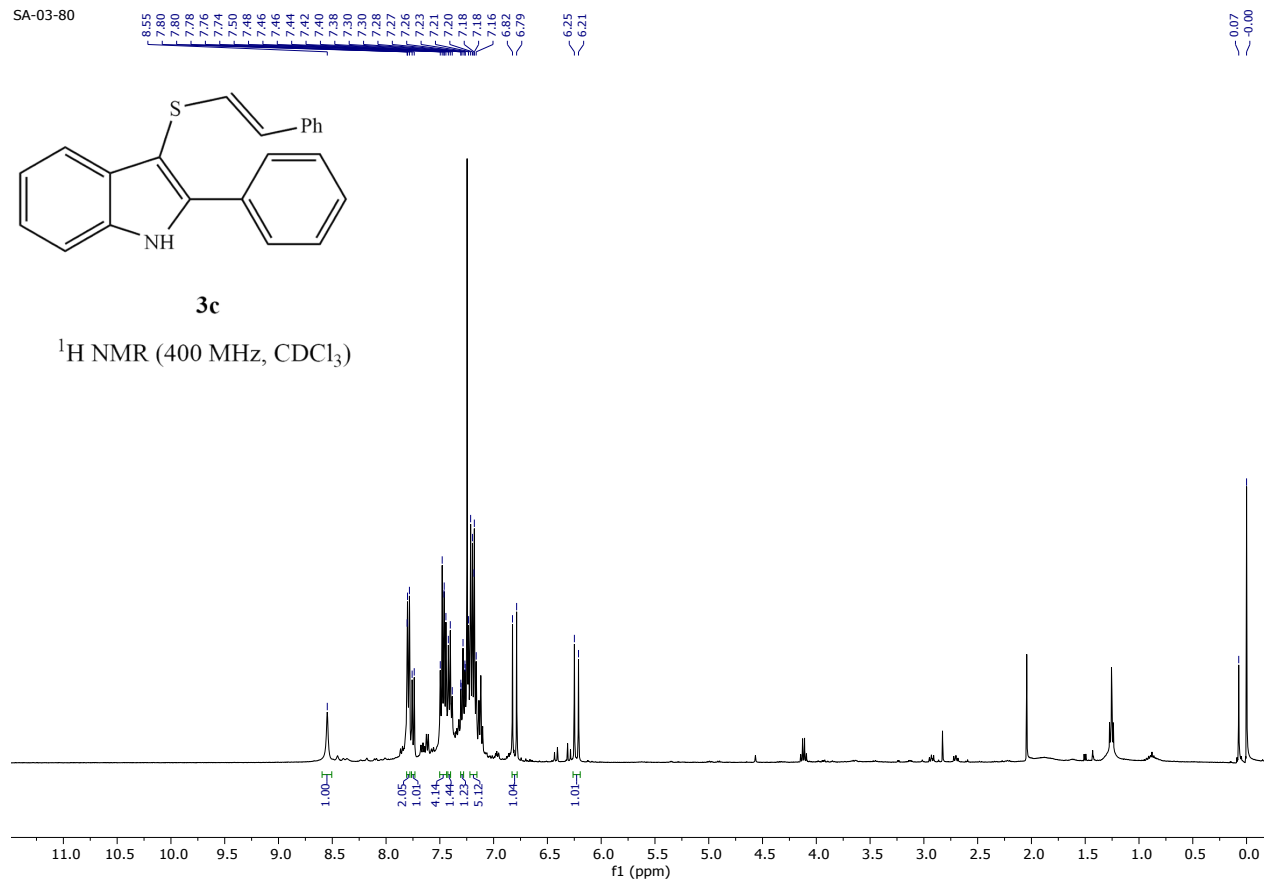


Fig. 5 $^1\text{H NMR}$ Spectrum of (*E*)-2-phenyl-3-(styrylthio)-1*H*-indole **3c**

sa03-80

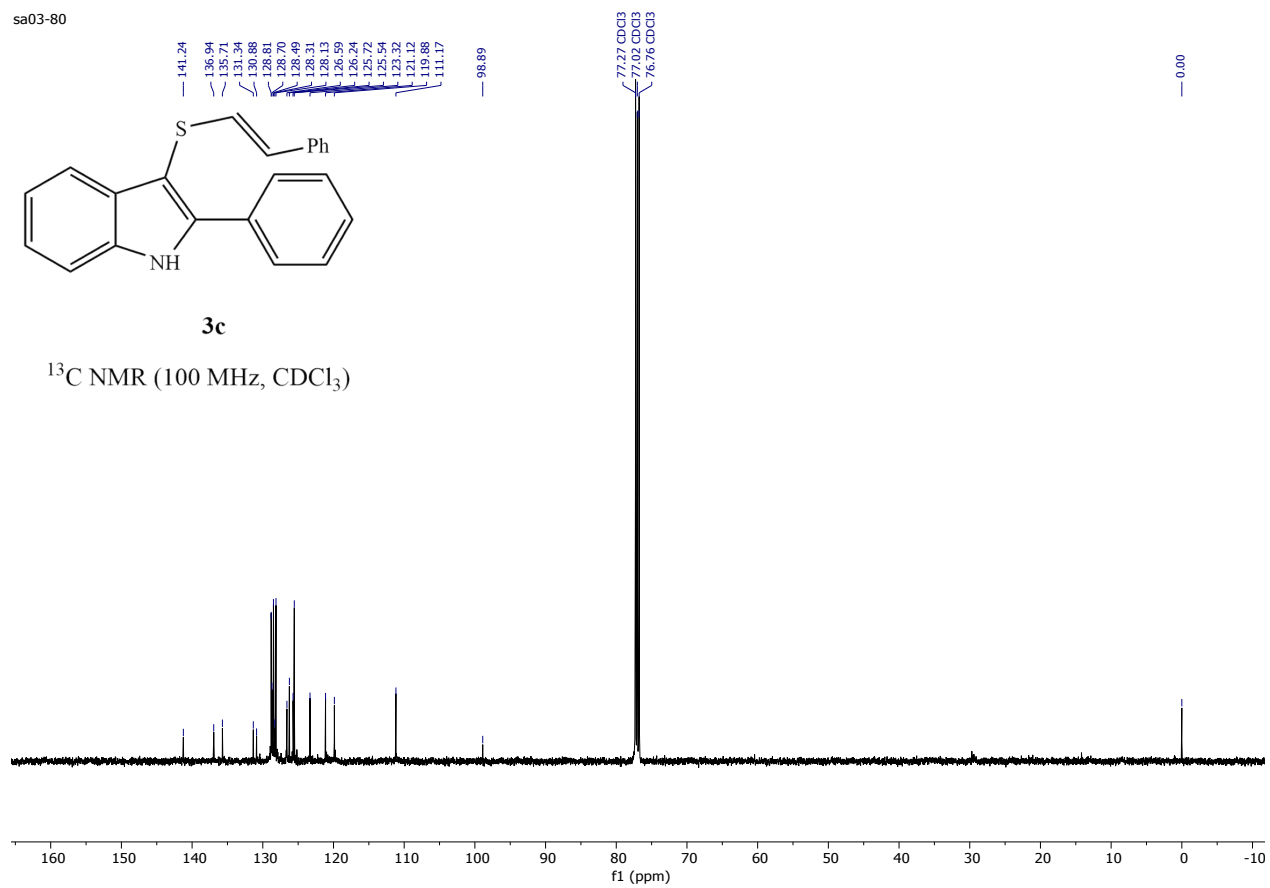


Fig. 6 ^{13}C NMR Spectrum of (*E*)-2-phenyl-3-(styrylthio)-1*H*-indole **3c**

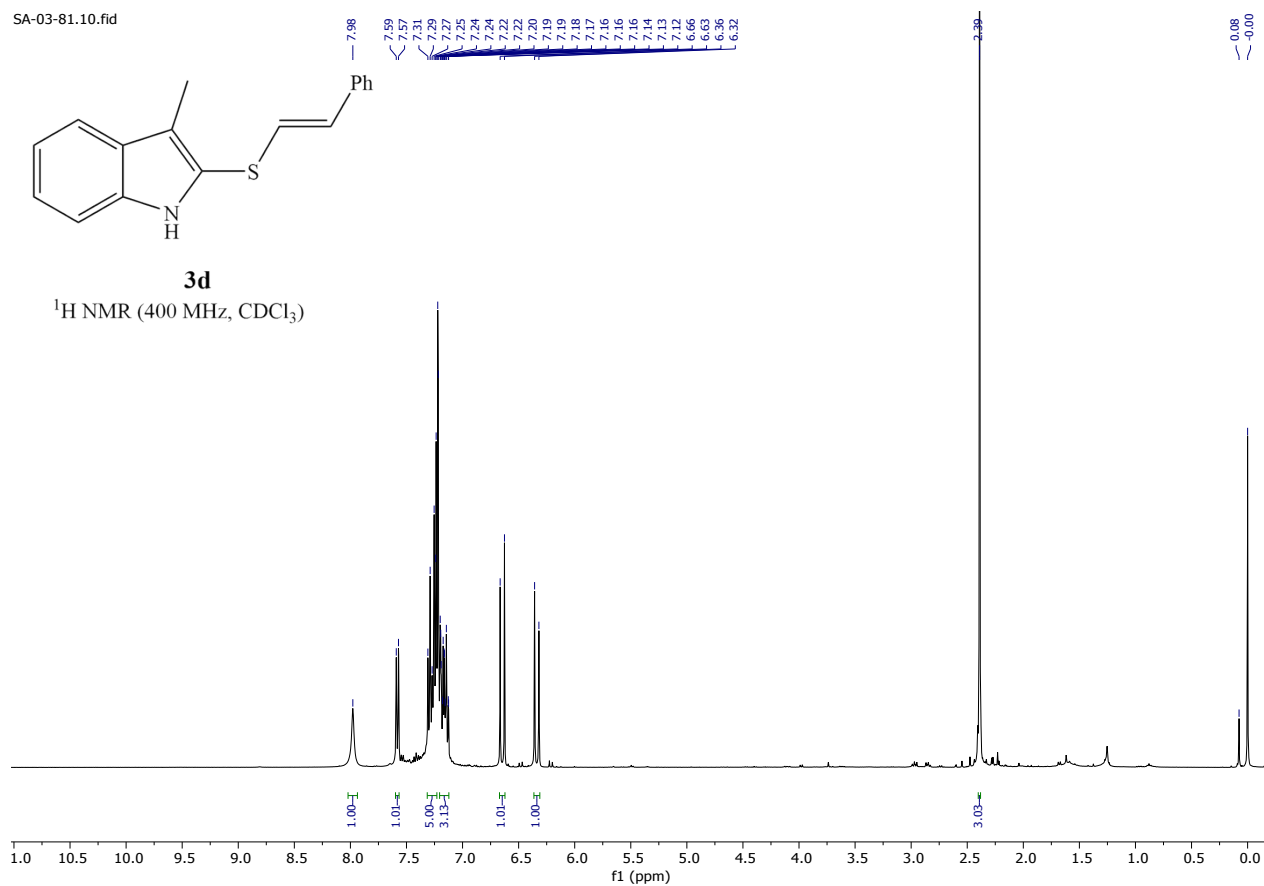
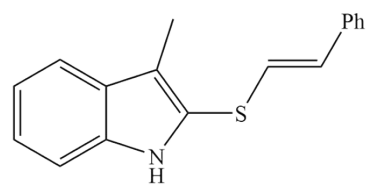


Fig. 7 ¹H NMR Spectrum of (*E*)-3-methyl-2-(styrylthio)-1*H*-indole **3d**

sa-03-81.1.fid



3d

^{13}C NMR (100 MHz, CDCl_3)

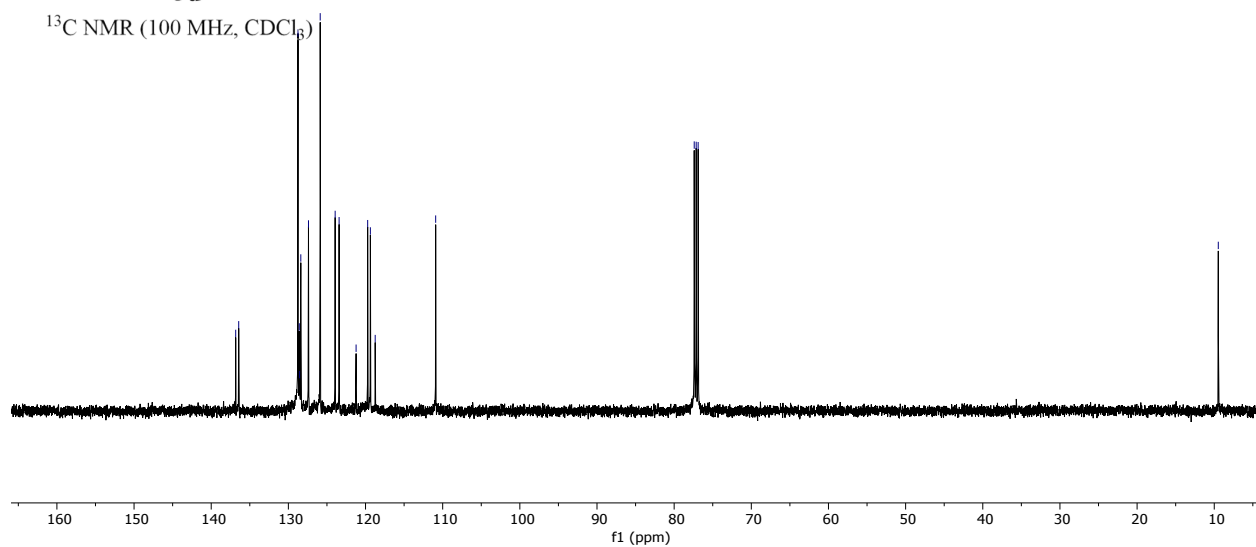


Fig. 8 ^{13}C NMR Spectrum of (*E*)-3-methyl-2-(styrylthio)-1*H*-indole **3d**

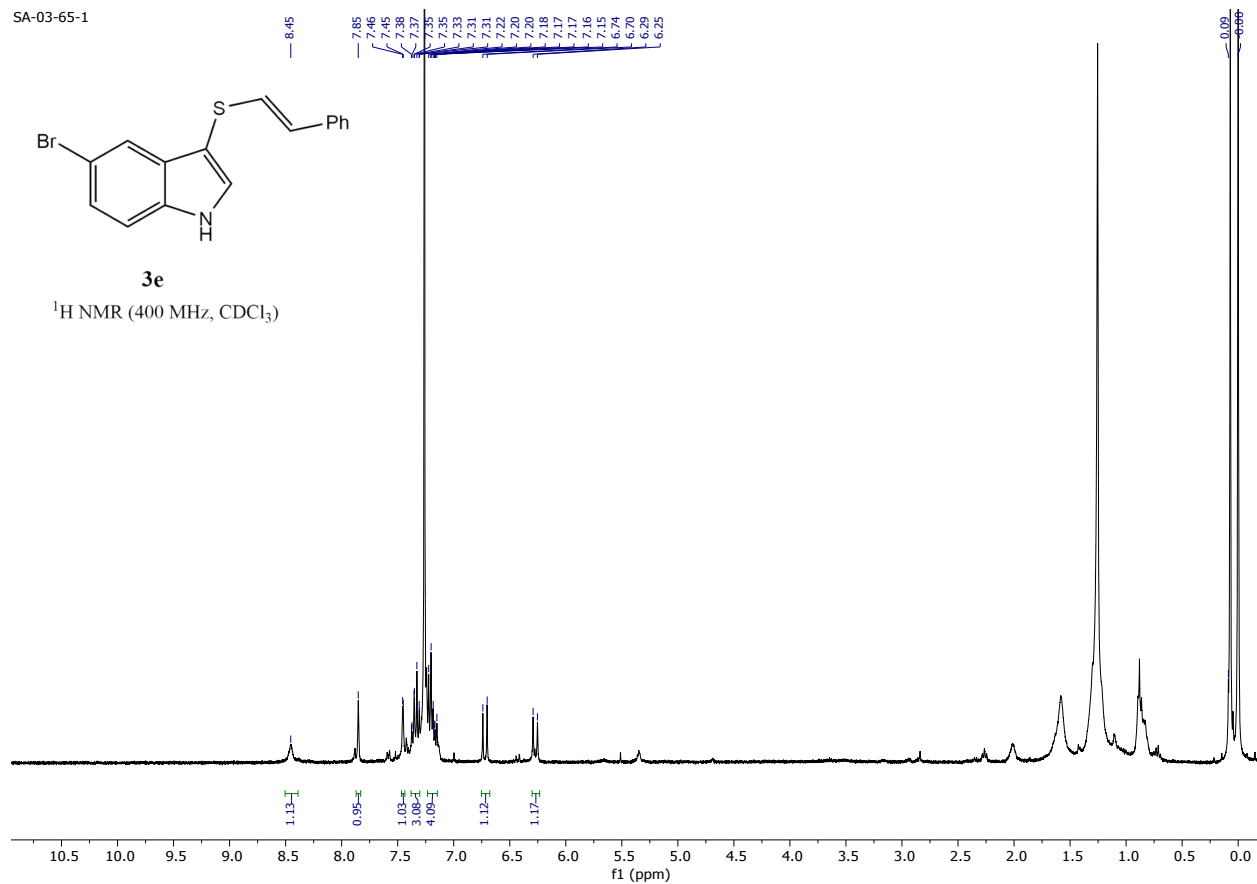


Fig. 9 $^1\text{H NMR}$ Spectrum of (*E*)-5-bromo-3-(styrylthio)-1*H*-indole **3e**

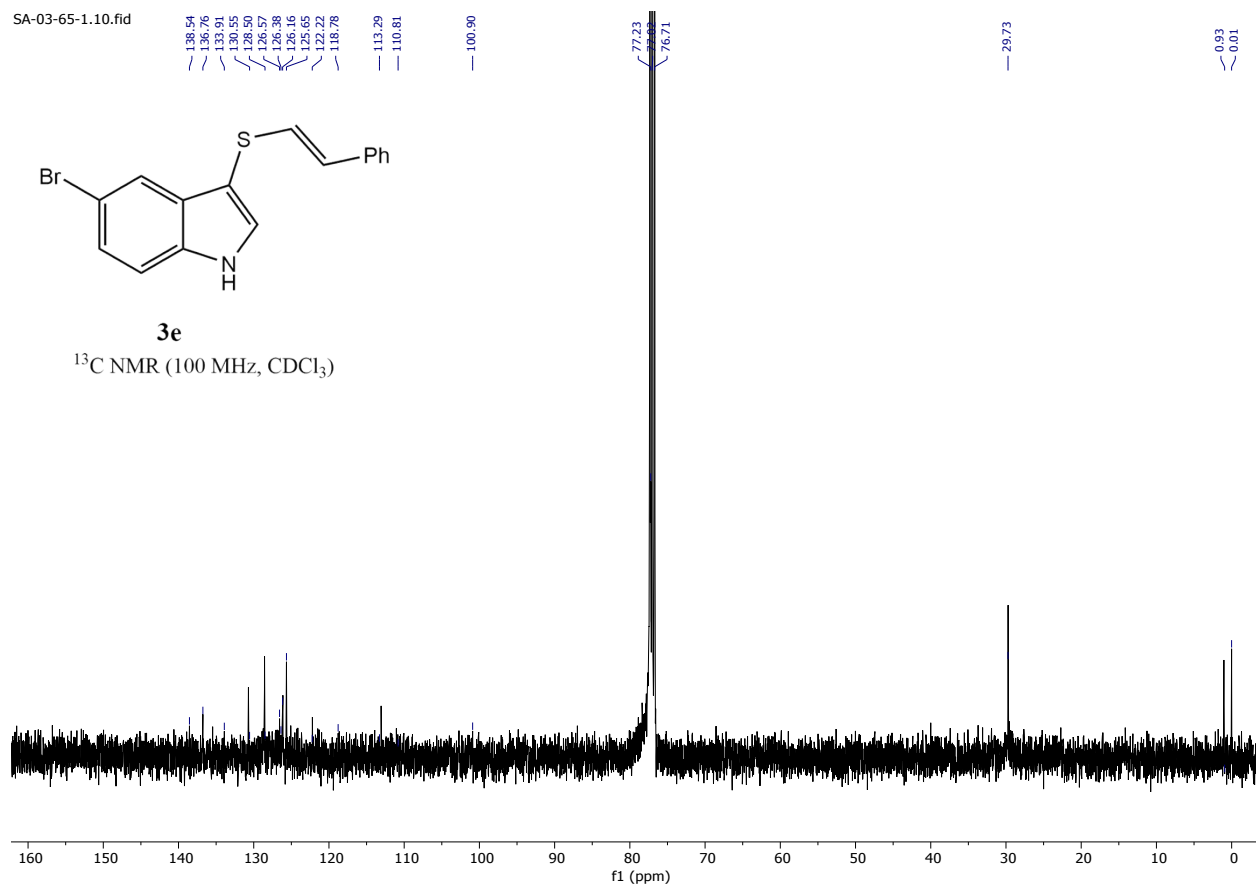


Fig. 10 ^{13}C NMR Spectrum of (*E*)-5-bromo-3-(styrylthio)-1*H*-indole **3e**

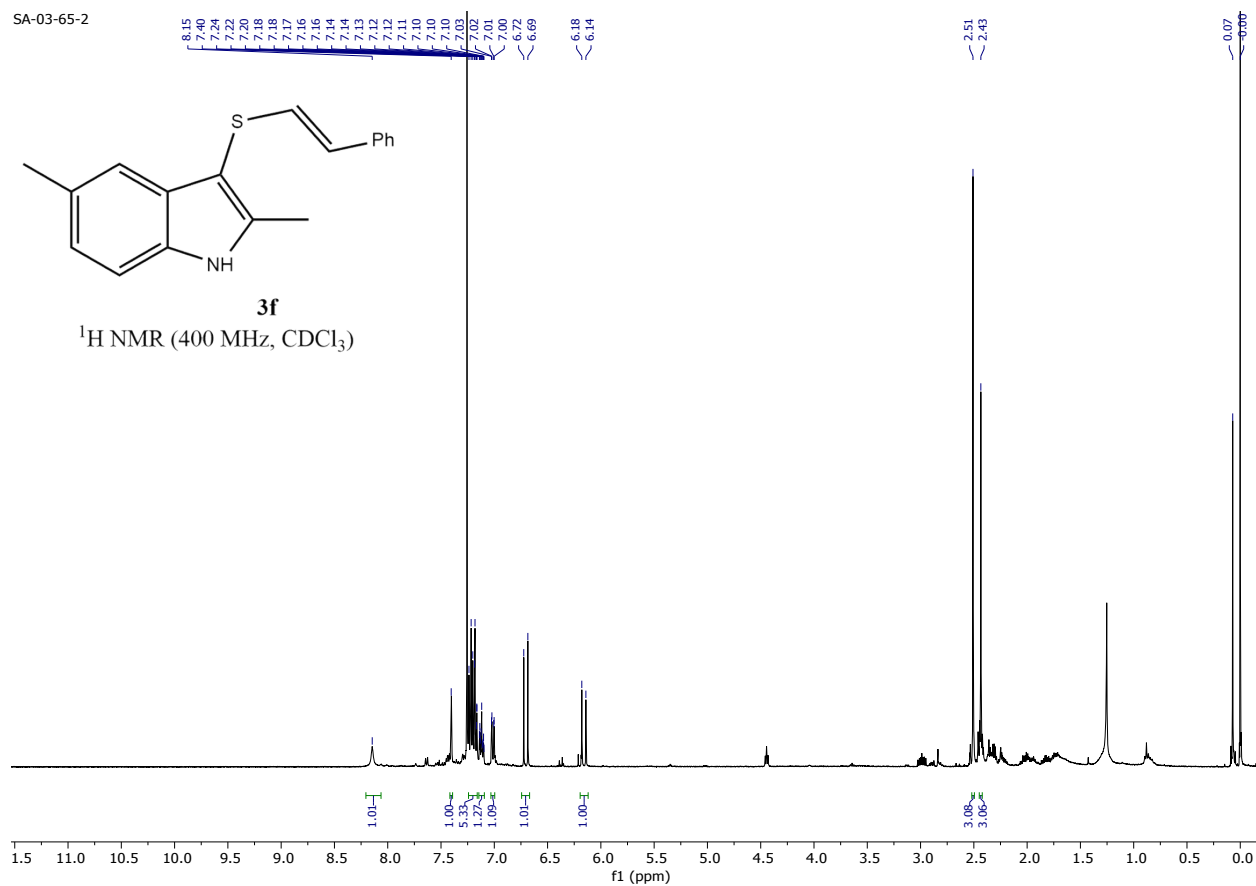


Fig. 11 $^1\text{H NMR}$ Spectrum of (*E*)-2,5-dimethyl-3-(styrylthio)-1*H*-indole **3f**

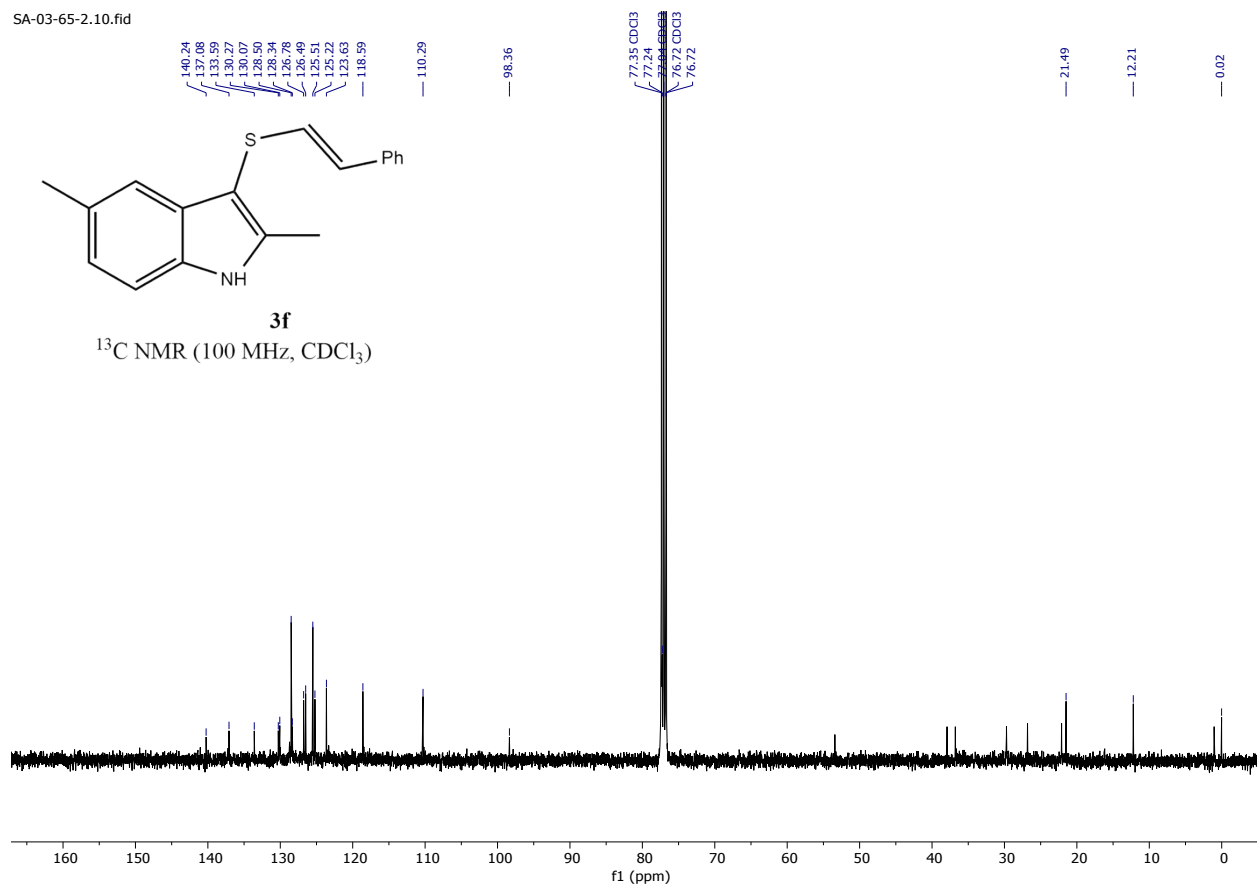


Fig. 12 ^{13}C NMR Spectrum of (*E*)-2,5-dimethyl-3-(styrylthio)-1*H*-indole **3f**

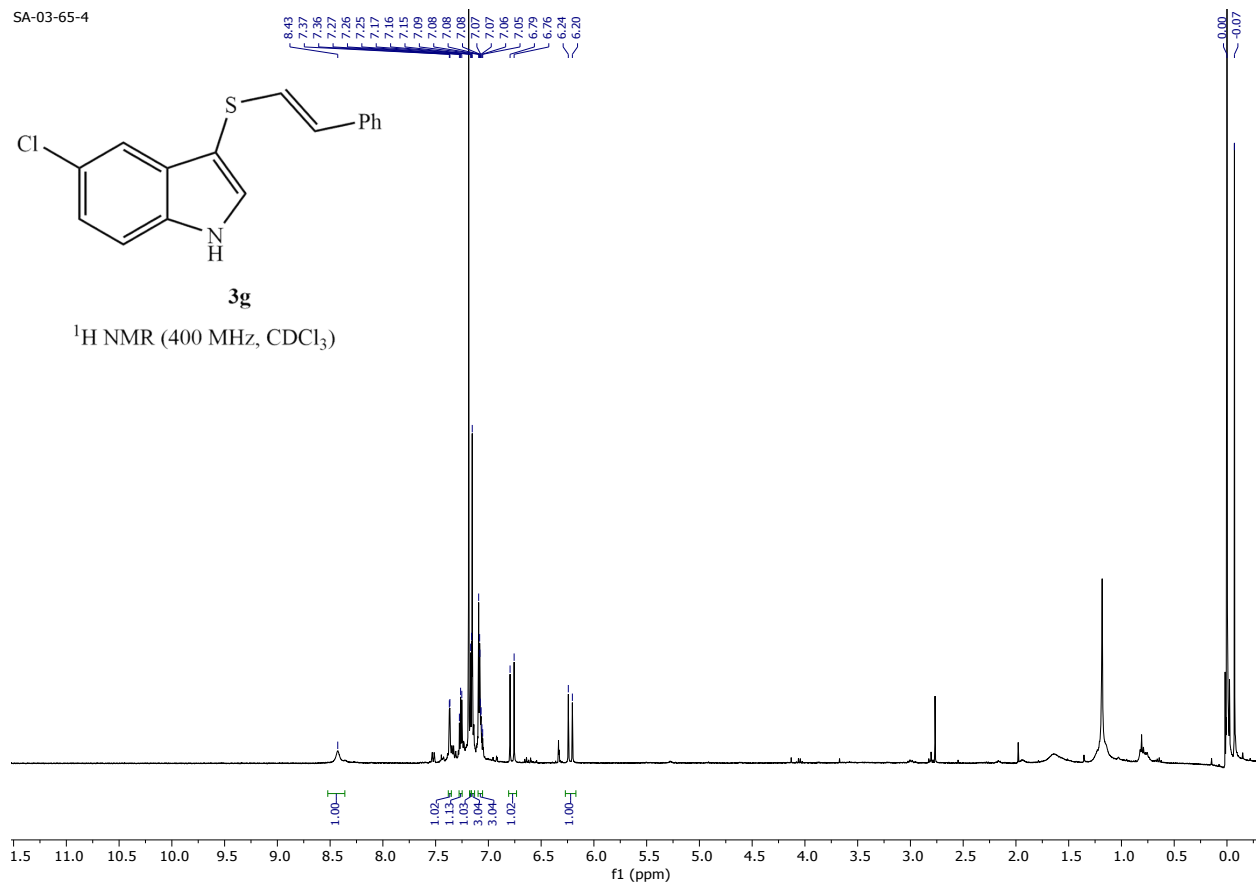


Fig. 13 $^1\text{H NMR}$ Spectrum of (*E*)-5-chloro-3-(styrylthio)-1*H*-indole **3g**

SA-03-65-4.10.fid

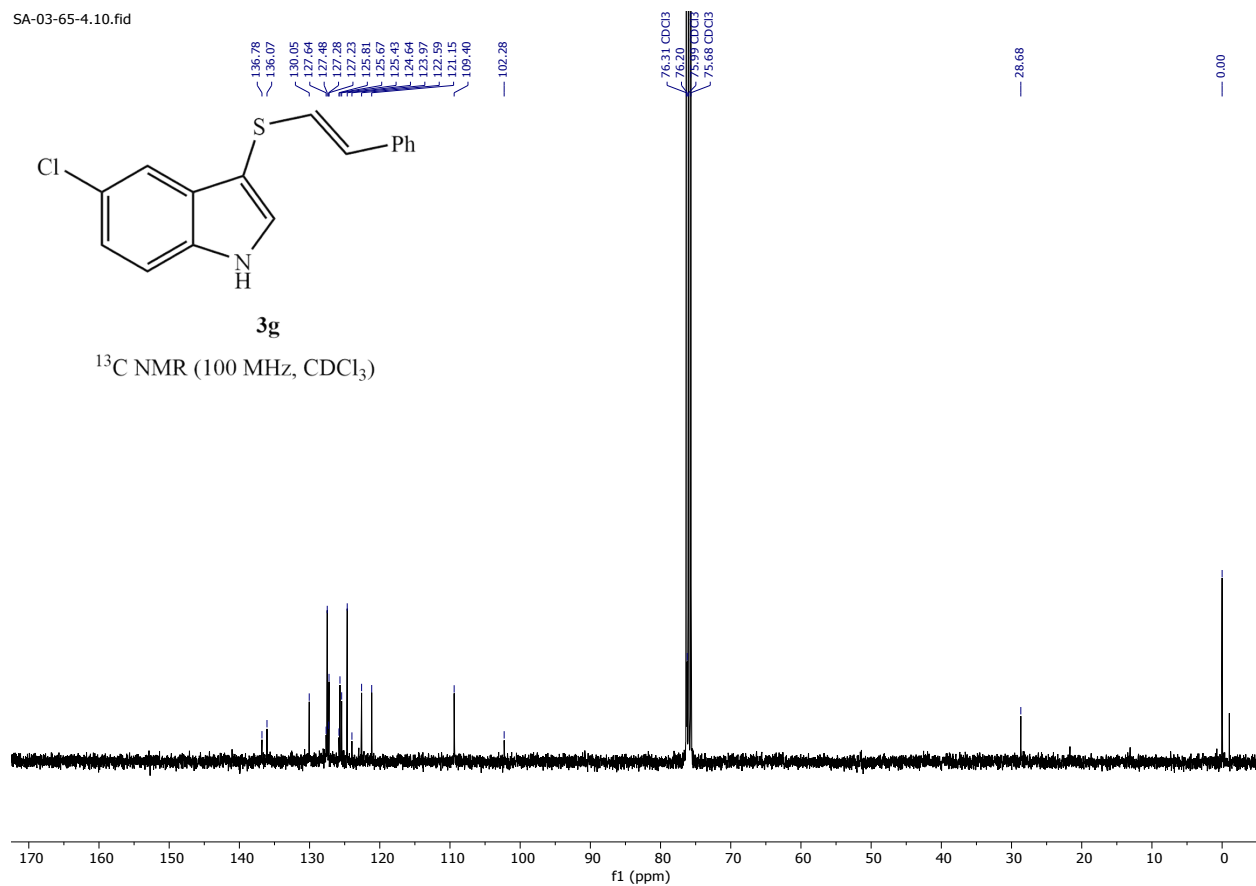


Fig. 14 ^{13}C NMR Spectrum of (*E*)-5-chloro-3-(styrylthio)-1*H*-indole **3g**

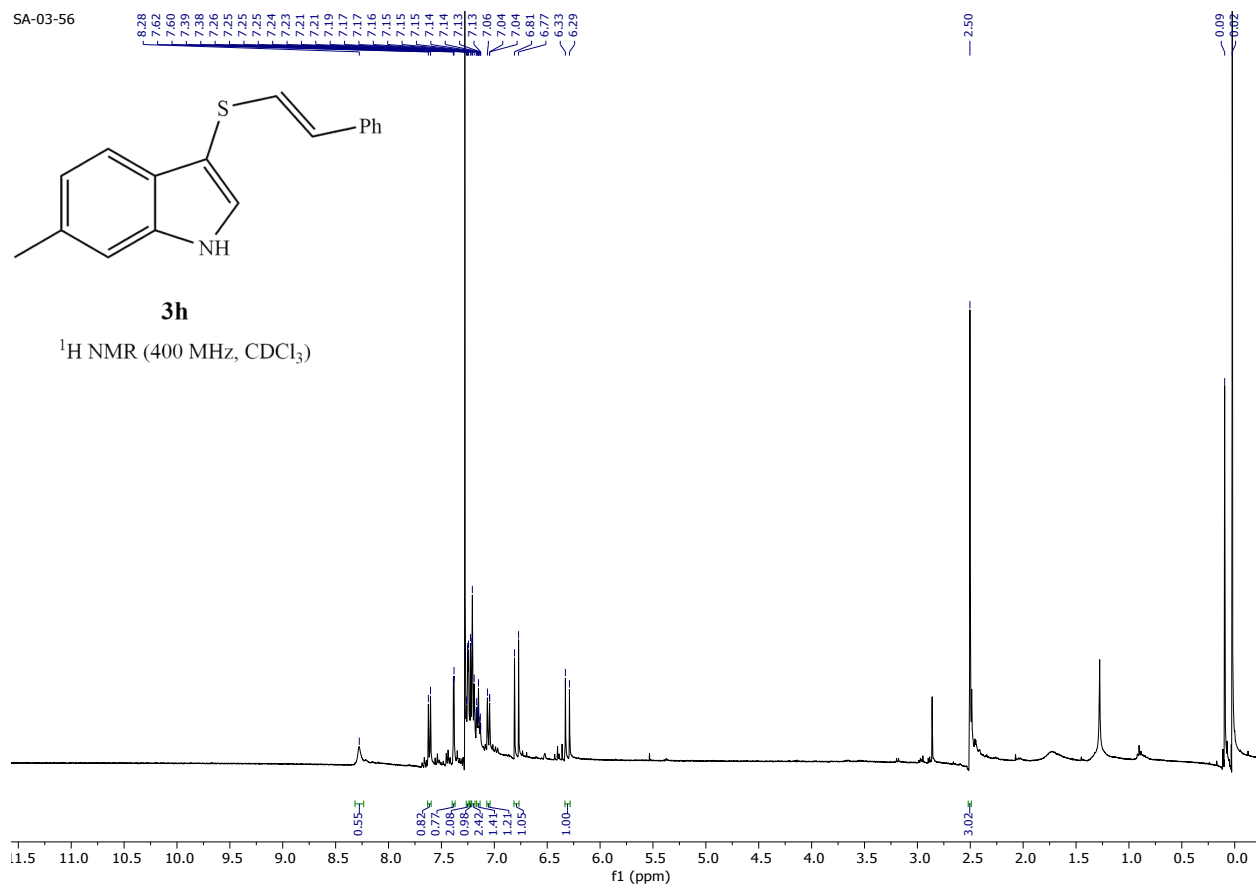


Fig. 15 ¹H NMR Spectrum of (*E*)-6-methyl-3-(styrylthio)-1*H*-indole **3h**

SA-03-56.10.fid

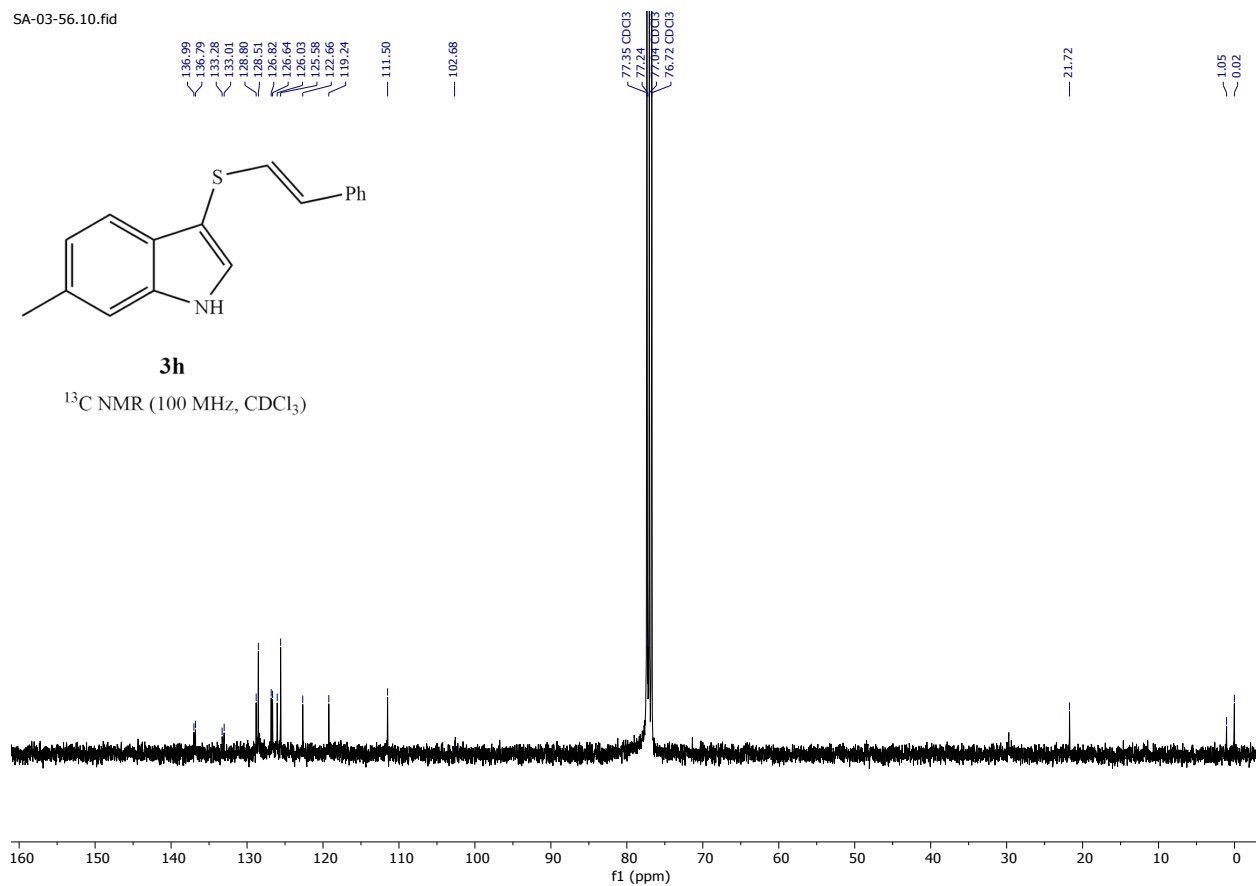


Fig. 16 ¹³C NMR Spectrum of (*E*)-6-methyl-3-(styrylthio)-1*H*-indole **3h**

SA-03-55

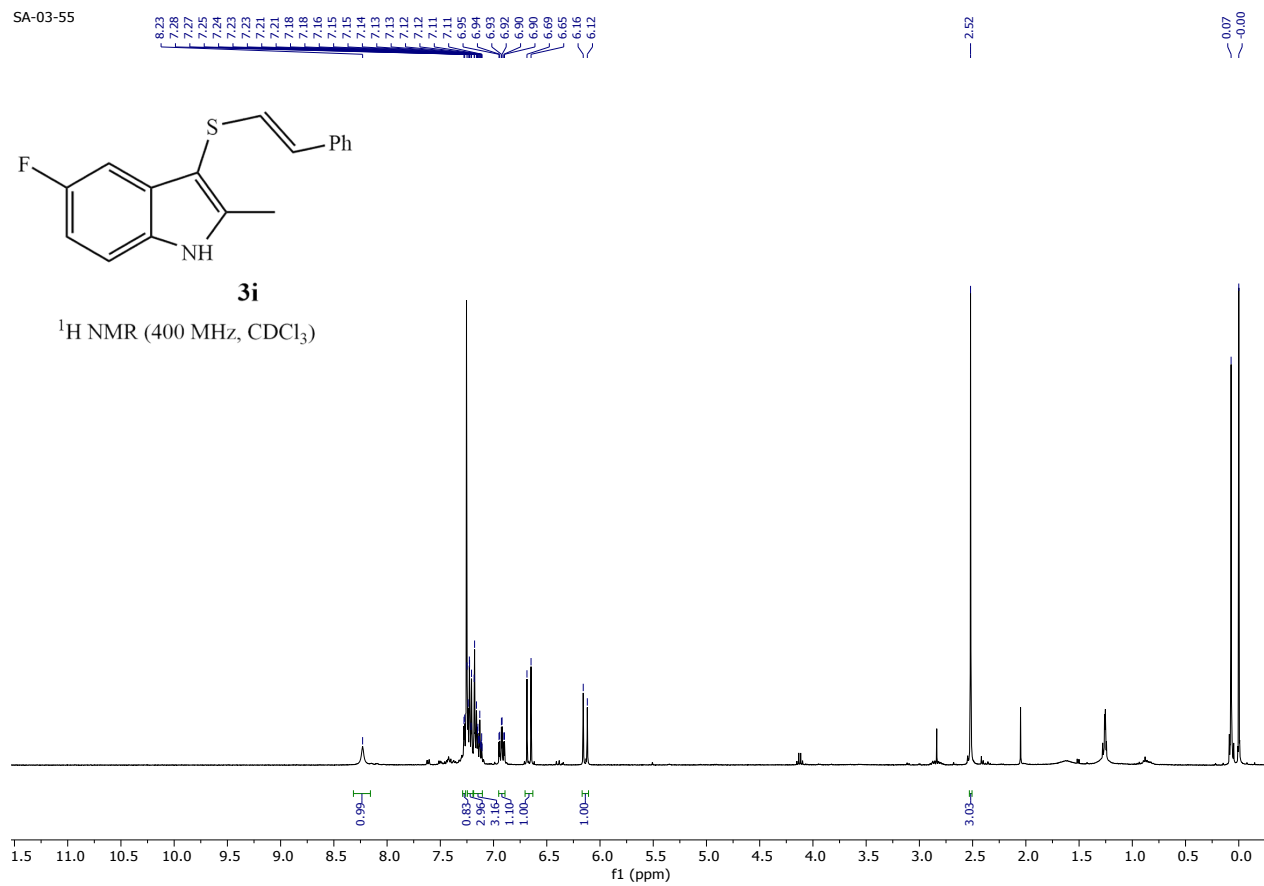


Fig. 17 ¹H NMR Spectrum of (*E*)-5-Fluoro-2-methyl-3-(styrylthio)-1*H*-indole **3i**

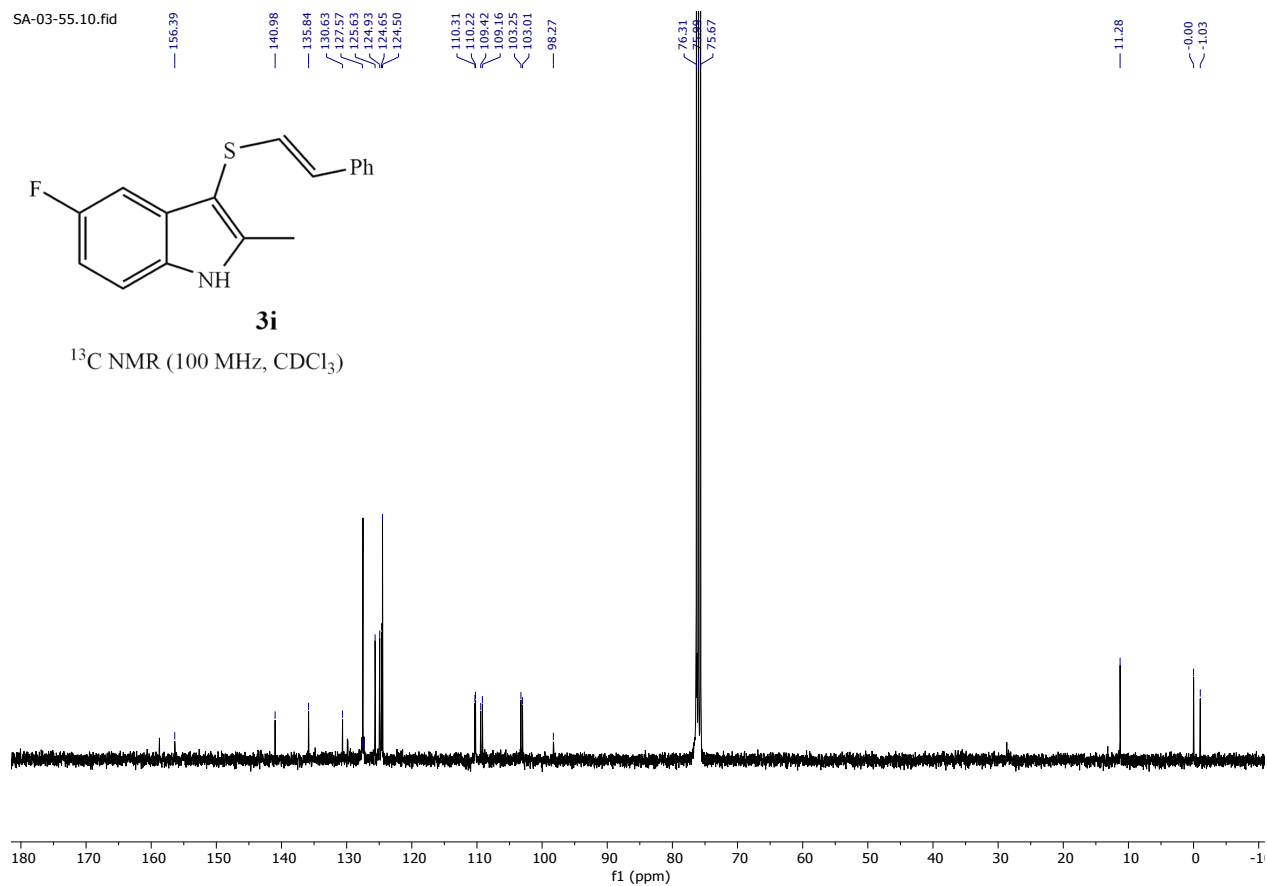


Fig. 18 ^{13}C NMR Spectrum of (*E*)-5-Fluoro-2-methyl-3-(styrylthio)-1*H*-indole **3i**

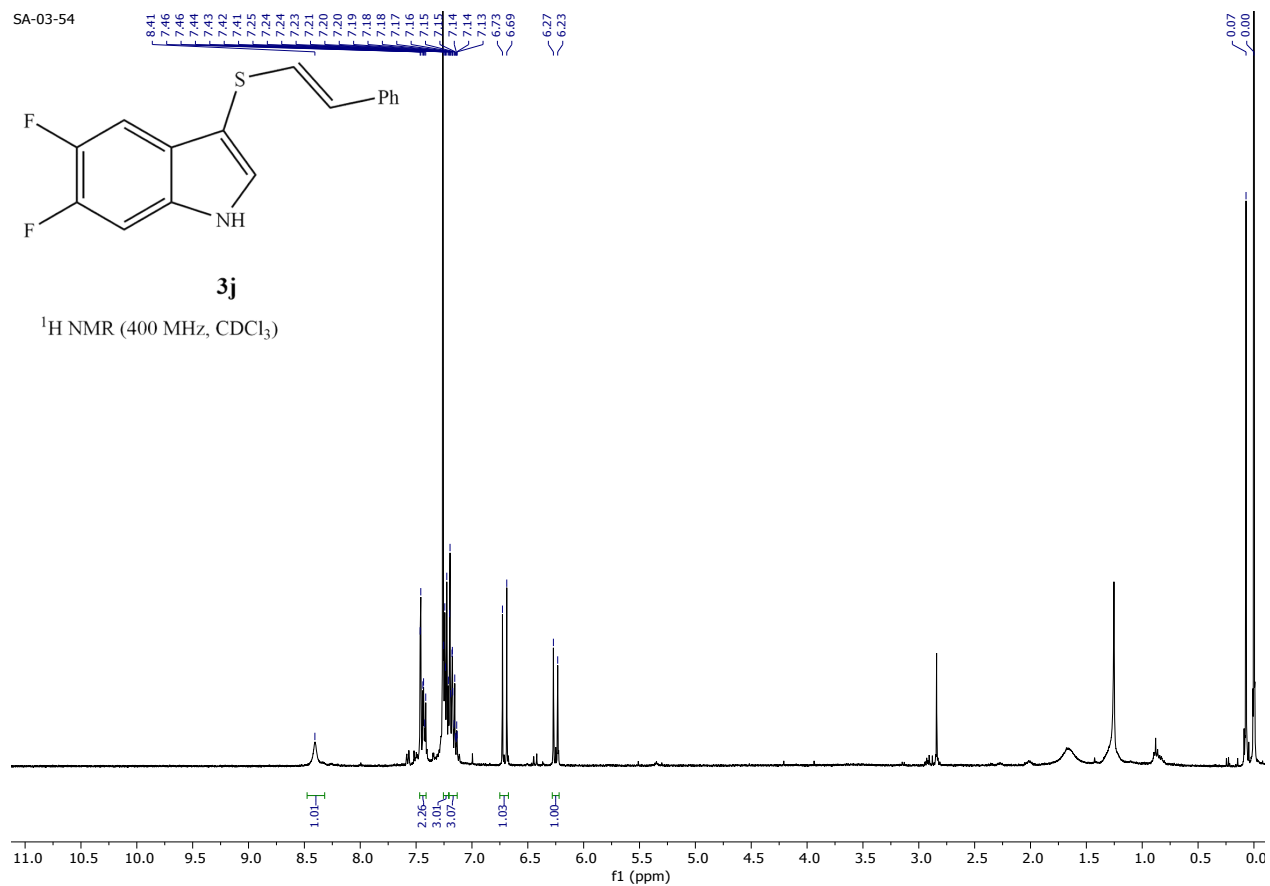


Fig. 1 ¹H NMR Spectrum of (*E*)-5,6-Difluoro-3-(styrylthio)-1*H*-indole **3j**

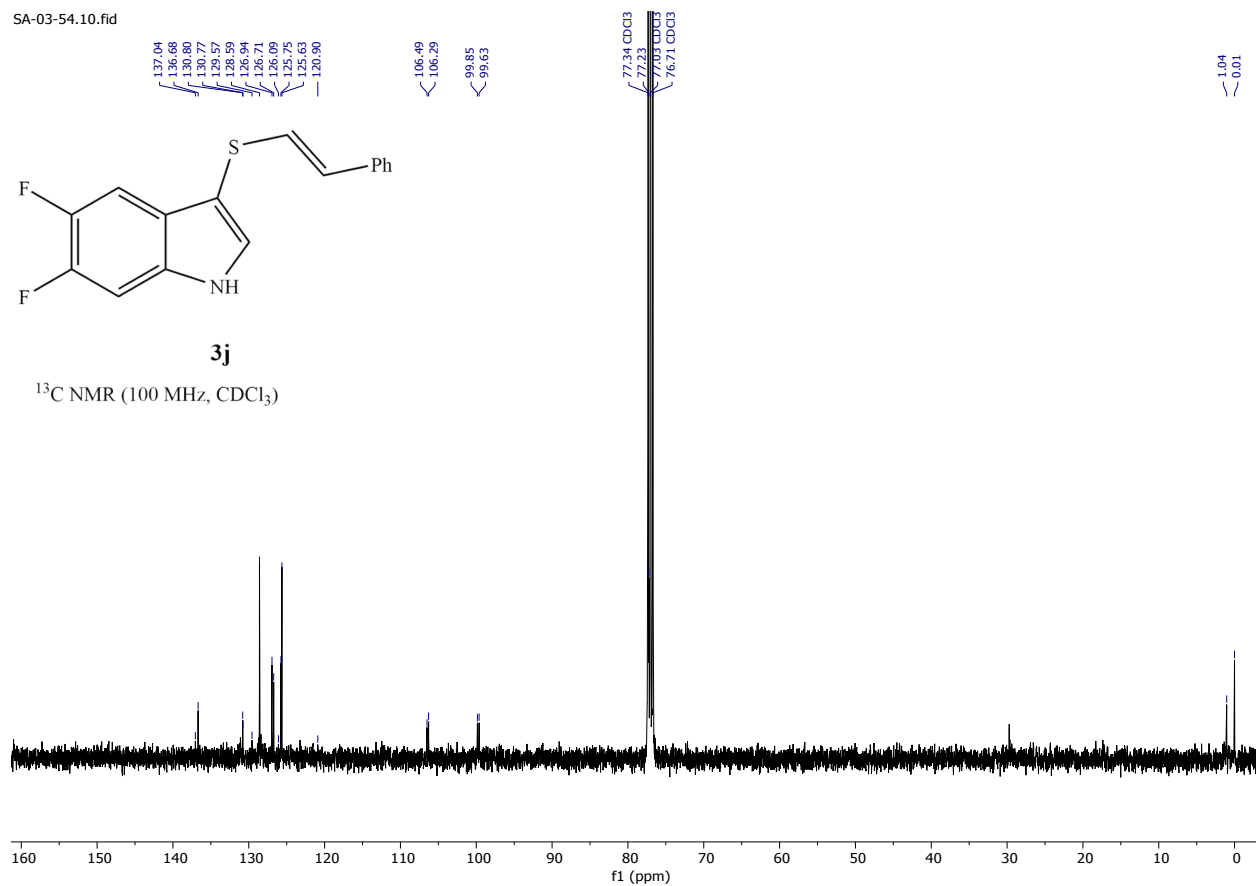


Fig. 20 ^{13}C NMR Spectrum of (*E*)-5,6-Difluoro-3-(styrylthio)-1*H*-indole **3j**

SA-03-65-5

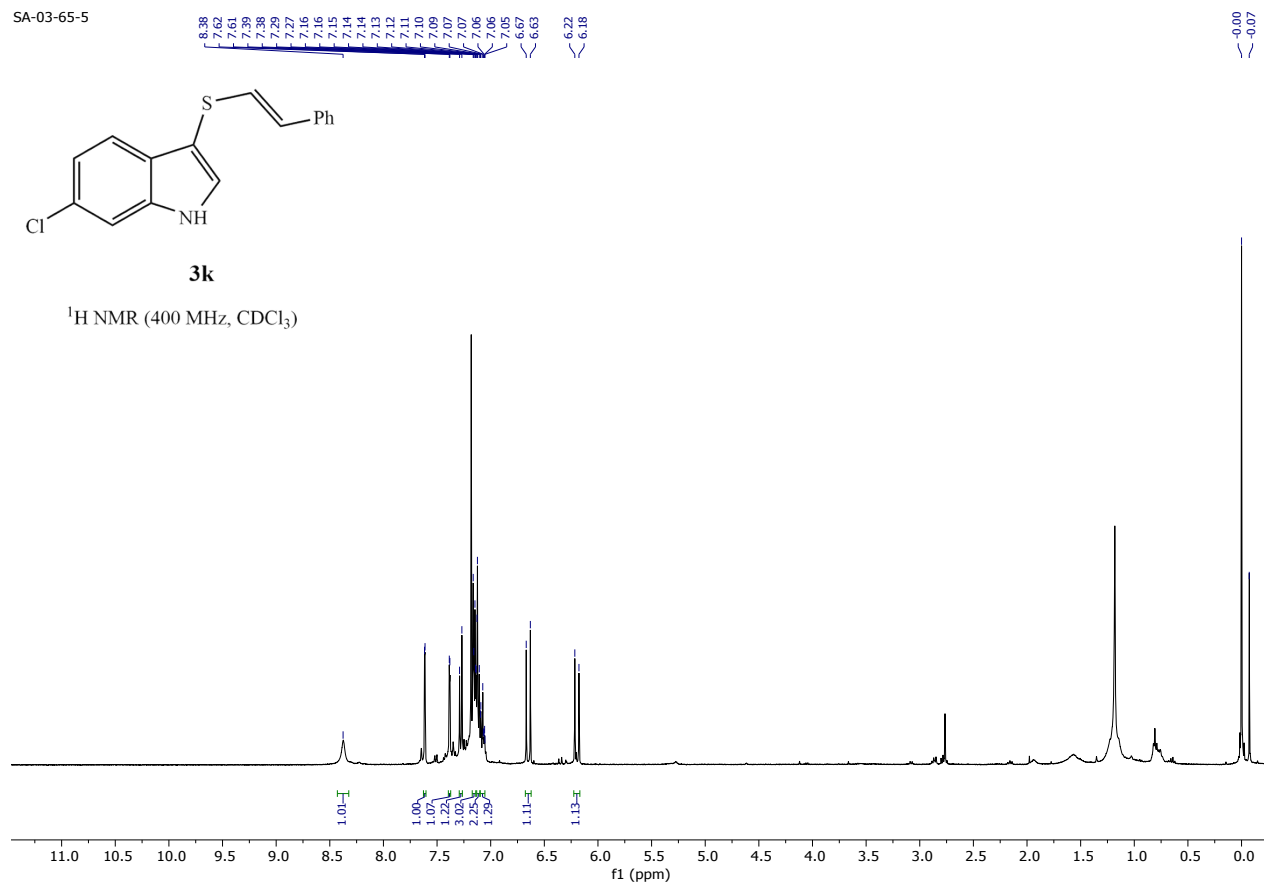


Fig. 21 ¹H NMR Spectrum of (*E*)-6-Chloro-3-(styrylthio)-1*H*-indole **3k**

SA-03-65-5.10.fid

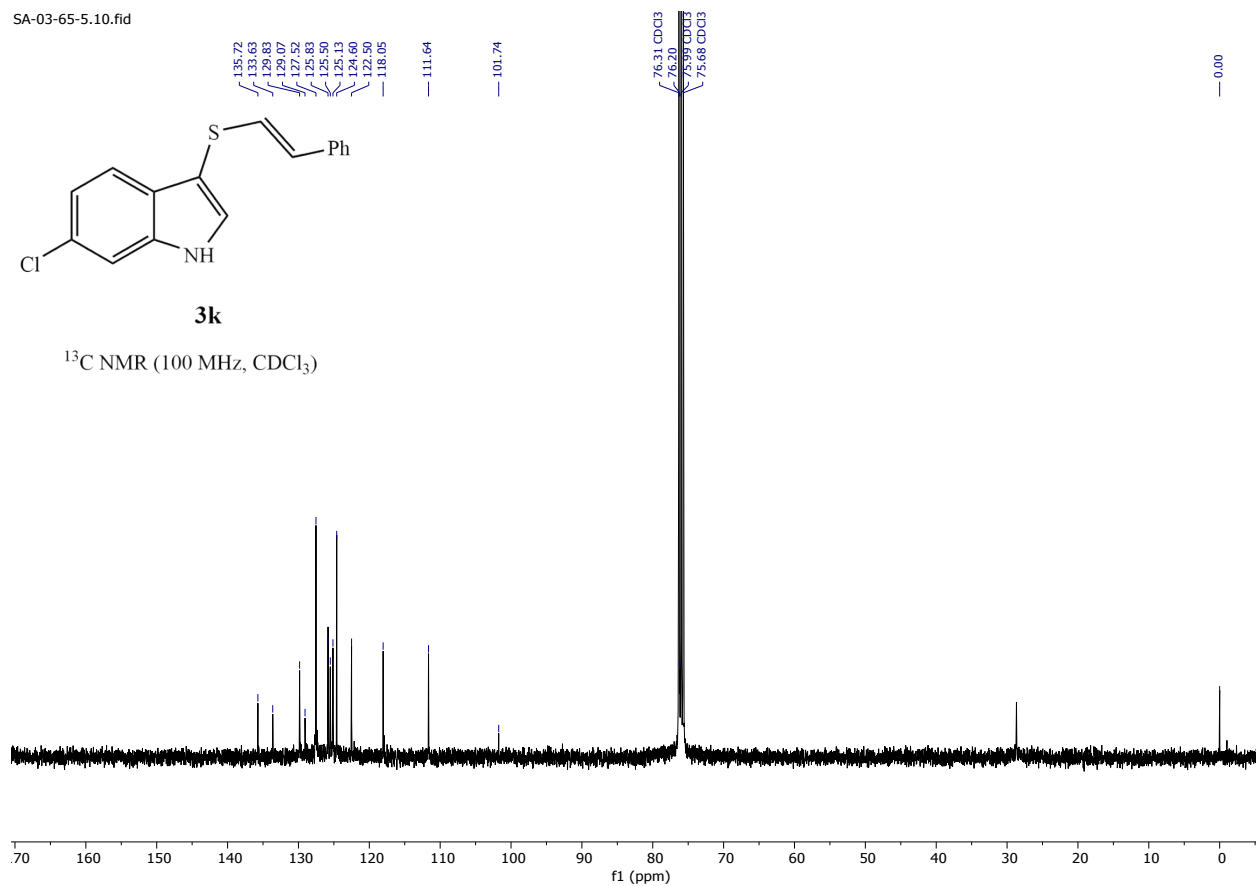


Fig. 22 ^{13}C NMR Spectrum of (*E*)-6-Chloro-3-(styrylthio)-1*H*-indole **3k**

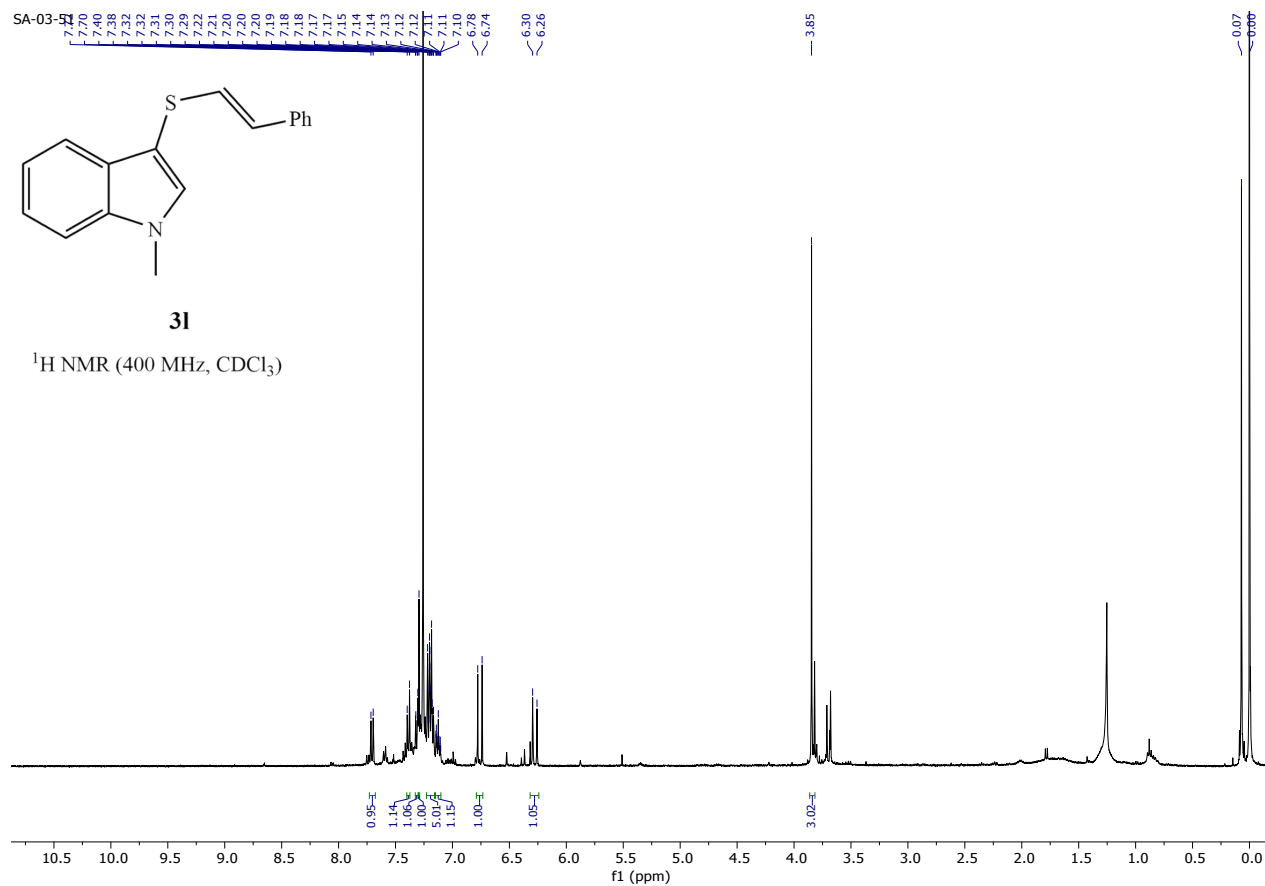


Fig. 23 ¹H NMR Spectrum of (*E*)-1-Methyl-3-(styrylthio)-1*H*-indole **31**

SA-03-51.10.fid

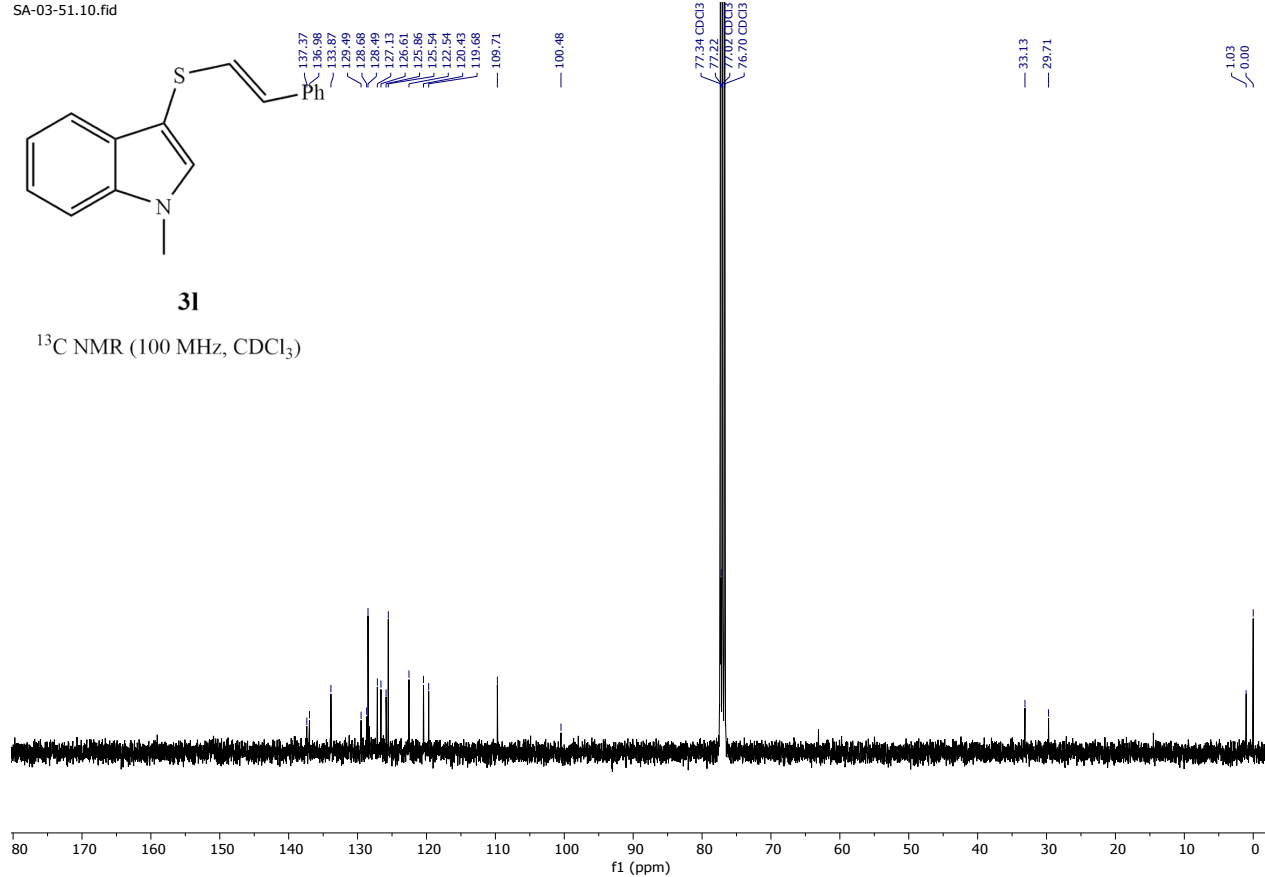


Fig. 24 ^{13}C NMR Spectrum of (*E*)-1-Methyl-3-(styrylthio)-1*H*-indole **31**

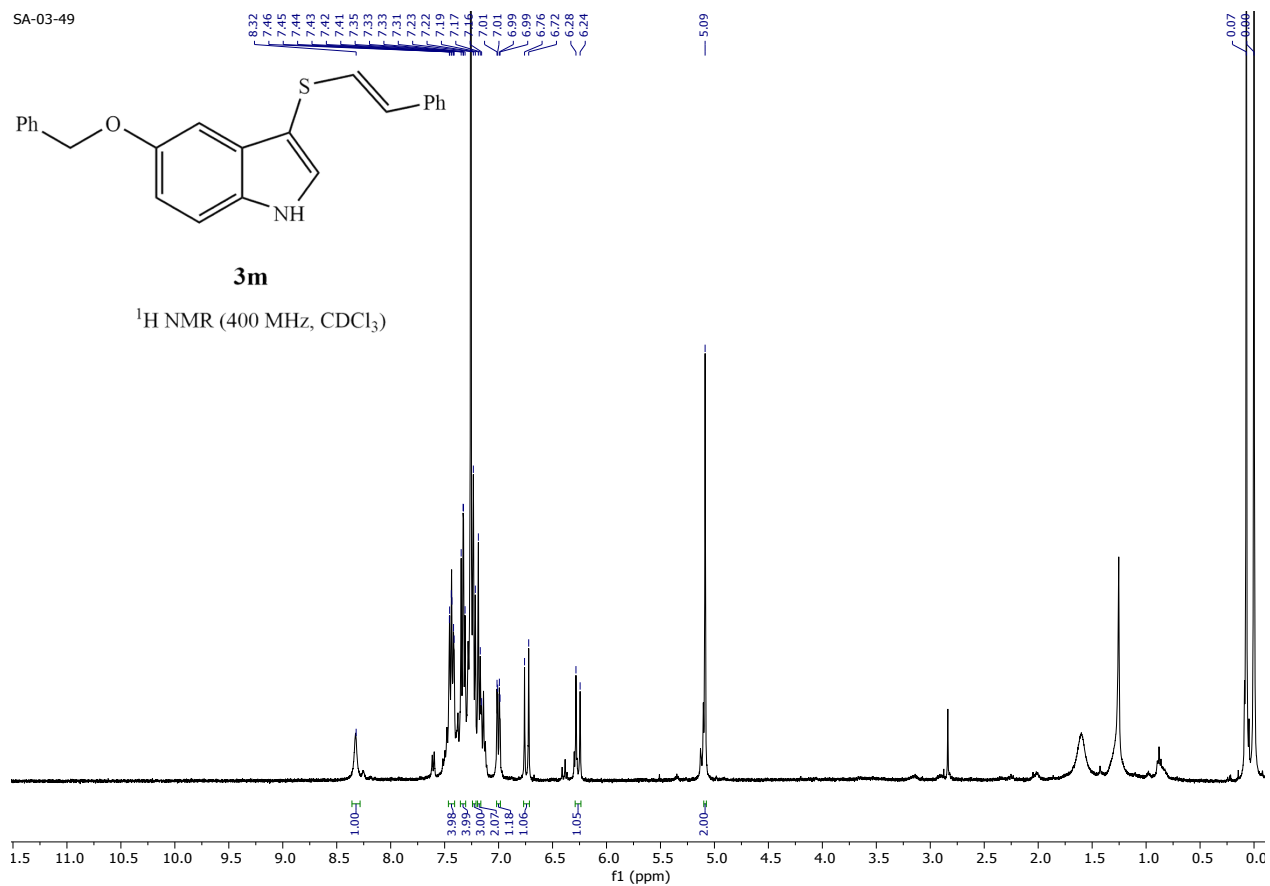


Fig. 25 $^1\text{H NMR}$ Spectrum of (*E*)-5-(Benzyloxy)-3-(styrylthio)-1*H*-indole **3m**

SA-03-49.20.fid

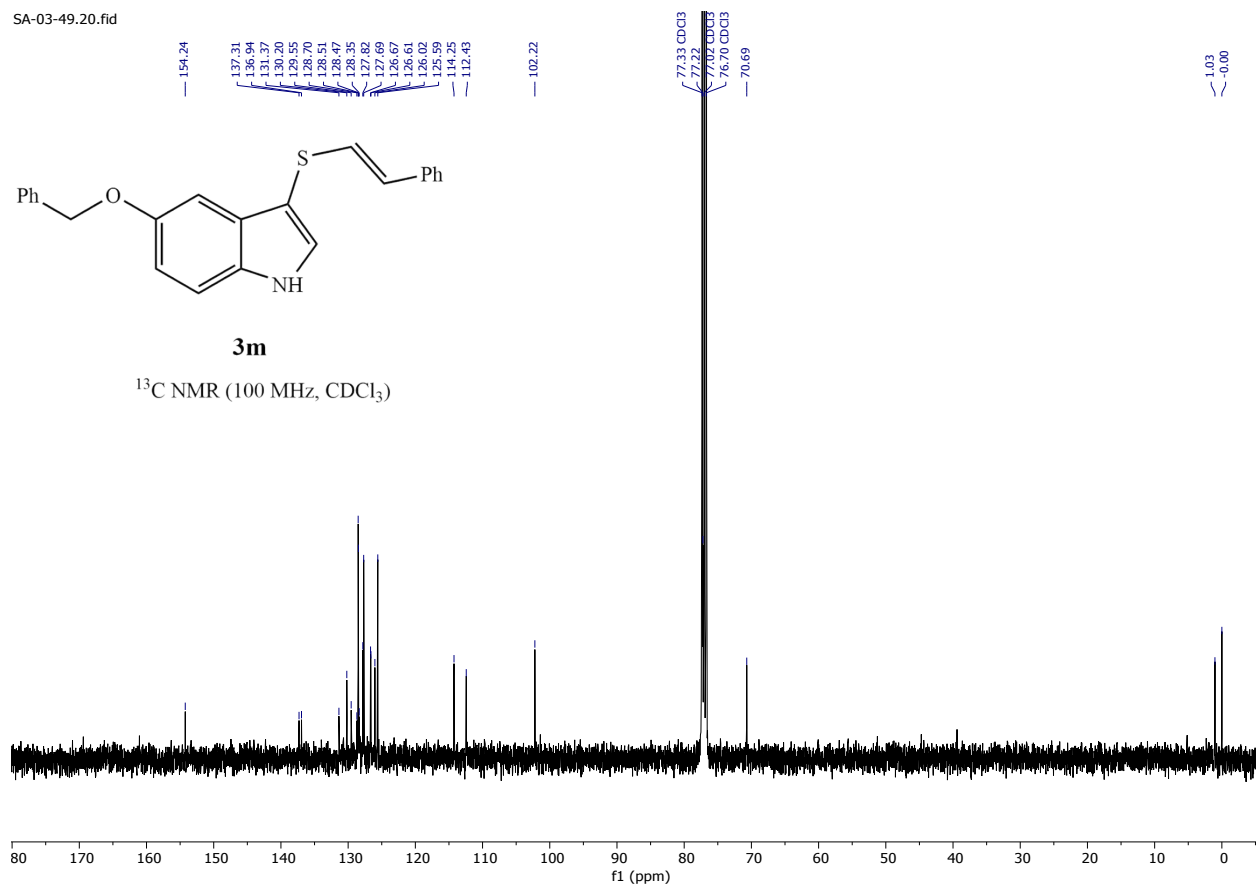


Fig. 26 ^{13}C NMR Spectrum of (*E*)-5-(Benzyloxy)-3-(styrylthio)-1*H*-indole **3m**

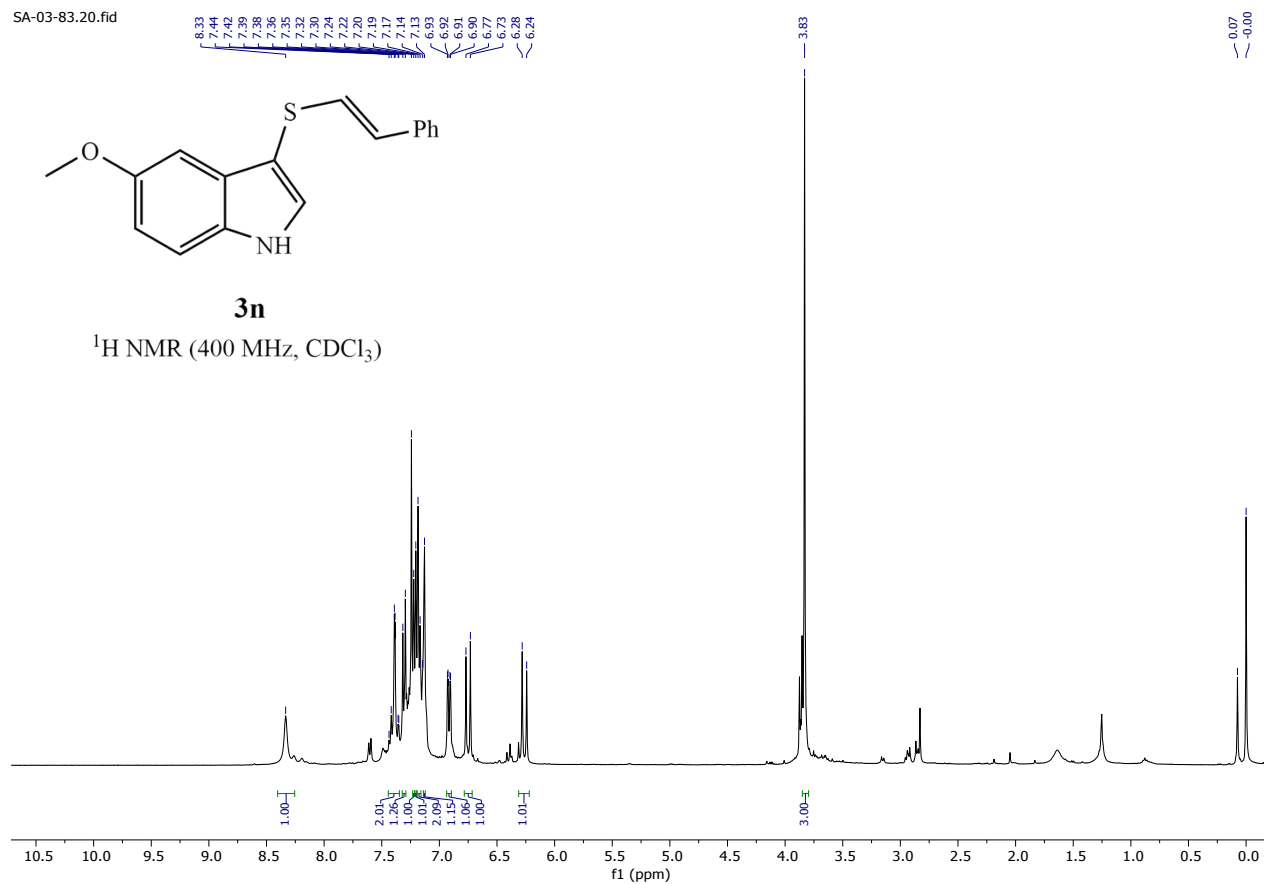


Fig. 27 $^1\text{H NMR}$ Spectrum of (*E*)-5-Methoxy-3-(styrylthio)-1*H*-indole **3n**

sa03-83

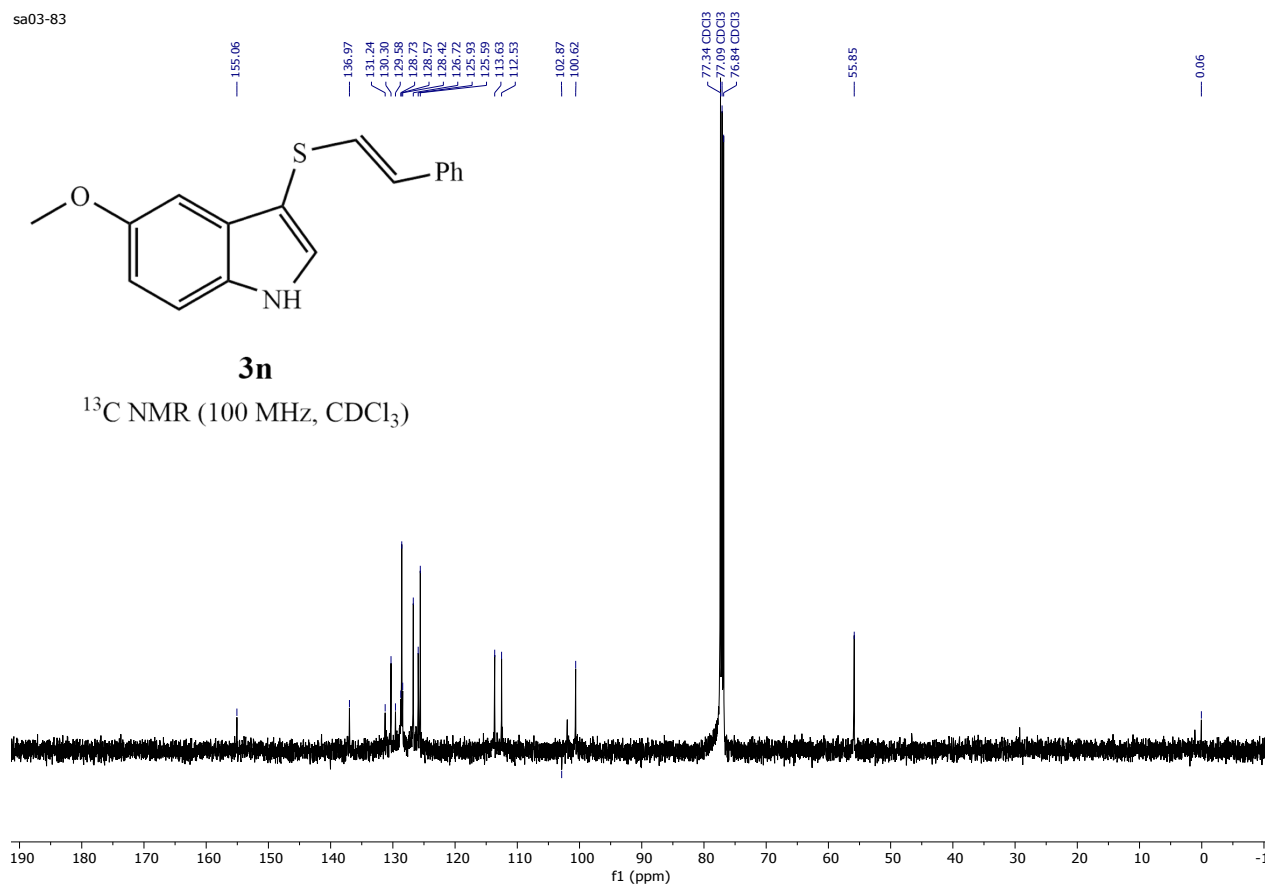


Fig. 28 ¹³C NMR Spectrum of (*E*)-5-Methoxy-3-(styrylthio)-1*H*-indole **3n**

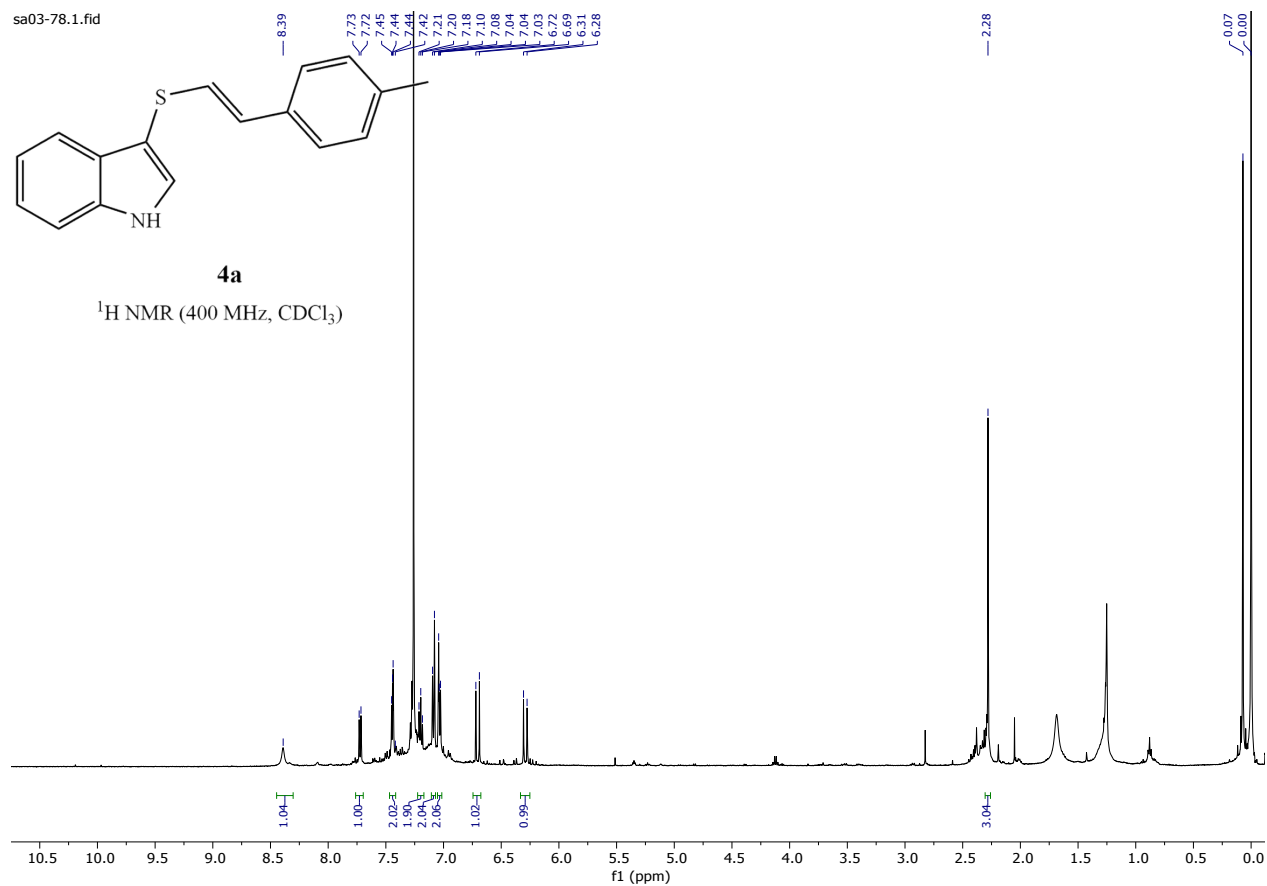


Fig. 29 ¹H NMR Spectrum of (*E*)-3-((4-Methylstyryl)thio)-1*H*-indole **4a**

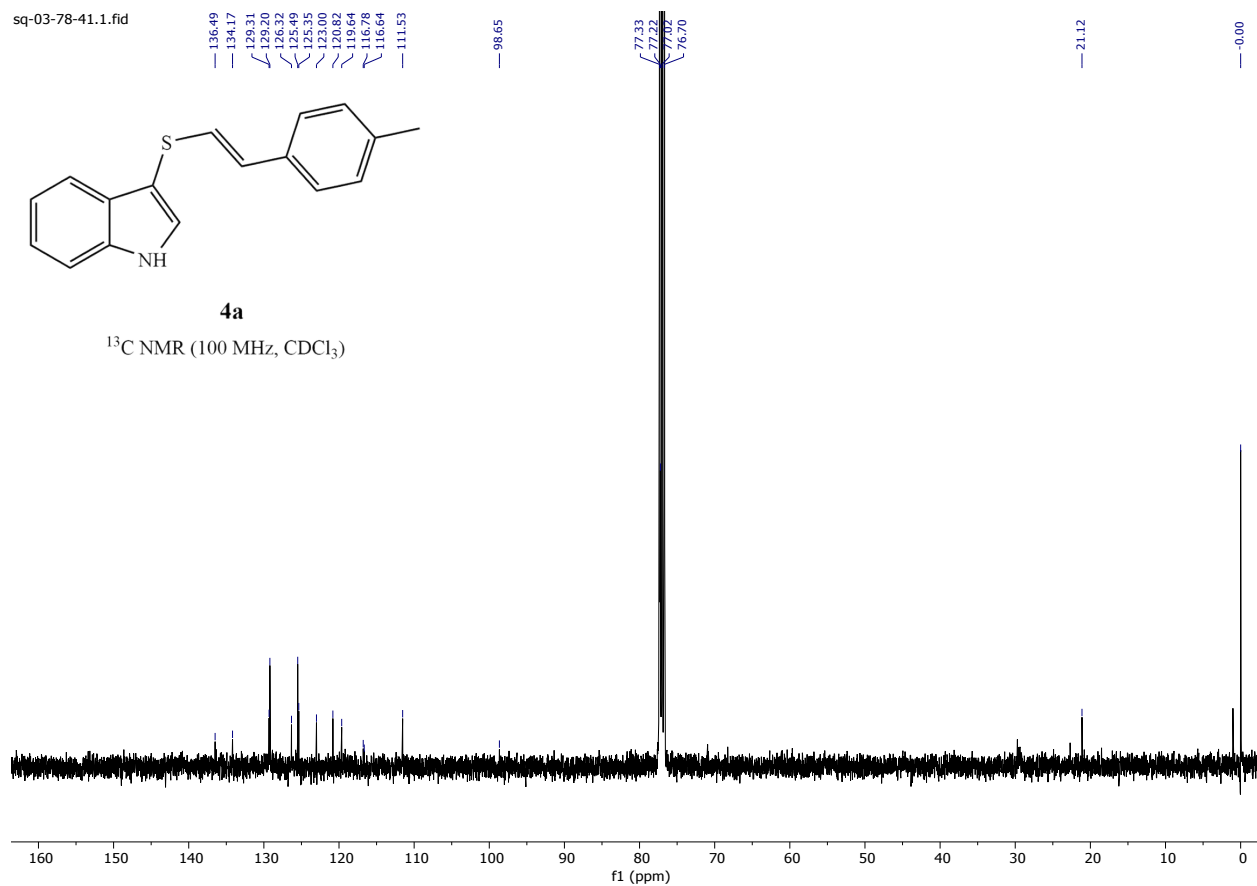


Fig. 30 ¹³C NMR Spectrum of (*E*)-3-((4-Methylstyryl)thio)-1*H*-indole **4a**

sa03-79.1.fid

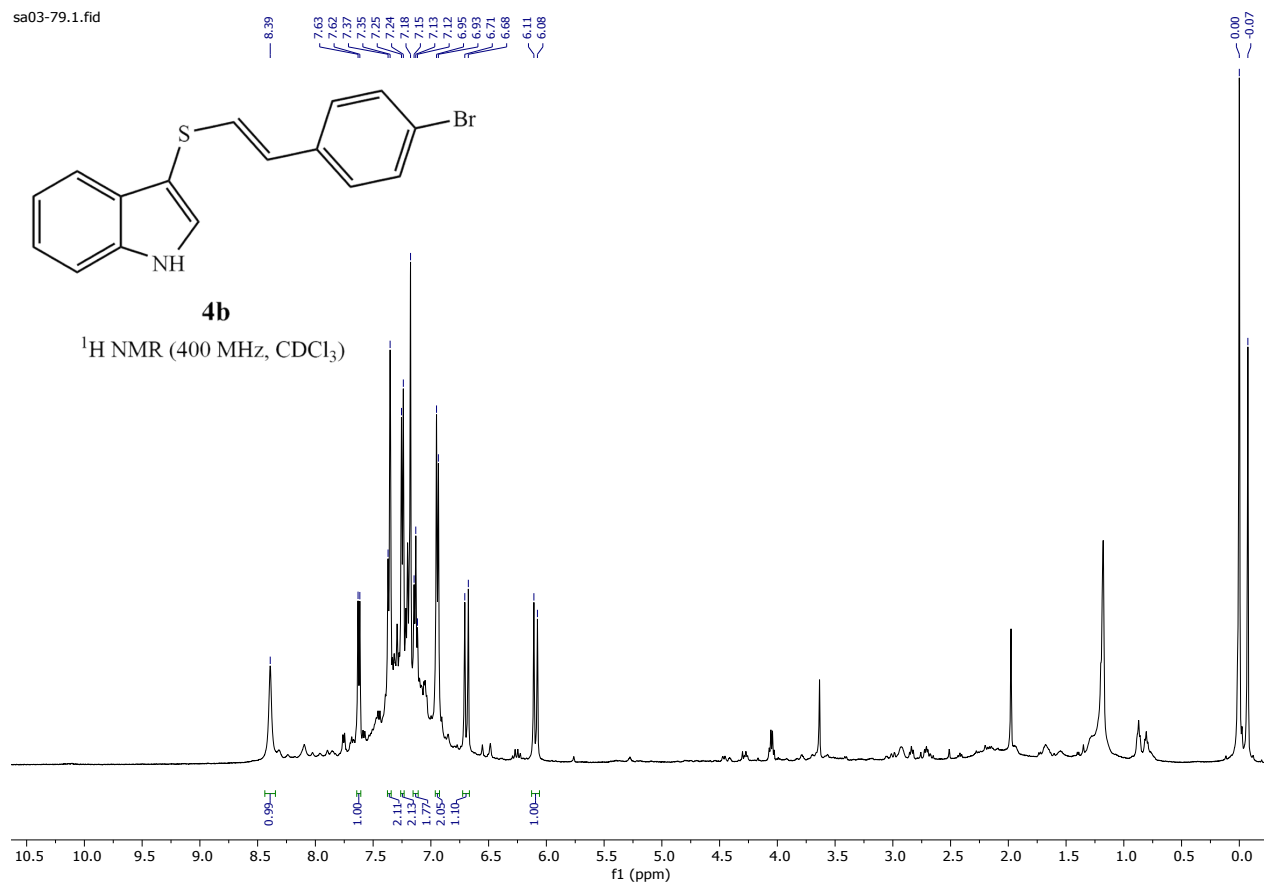


Fig. 31 ¹H NMR Spectrum of (*E*)-3-((4-Bromostyryl)thio)-1*H*-indole **4b**

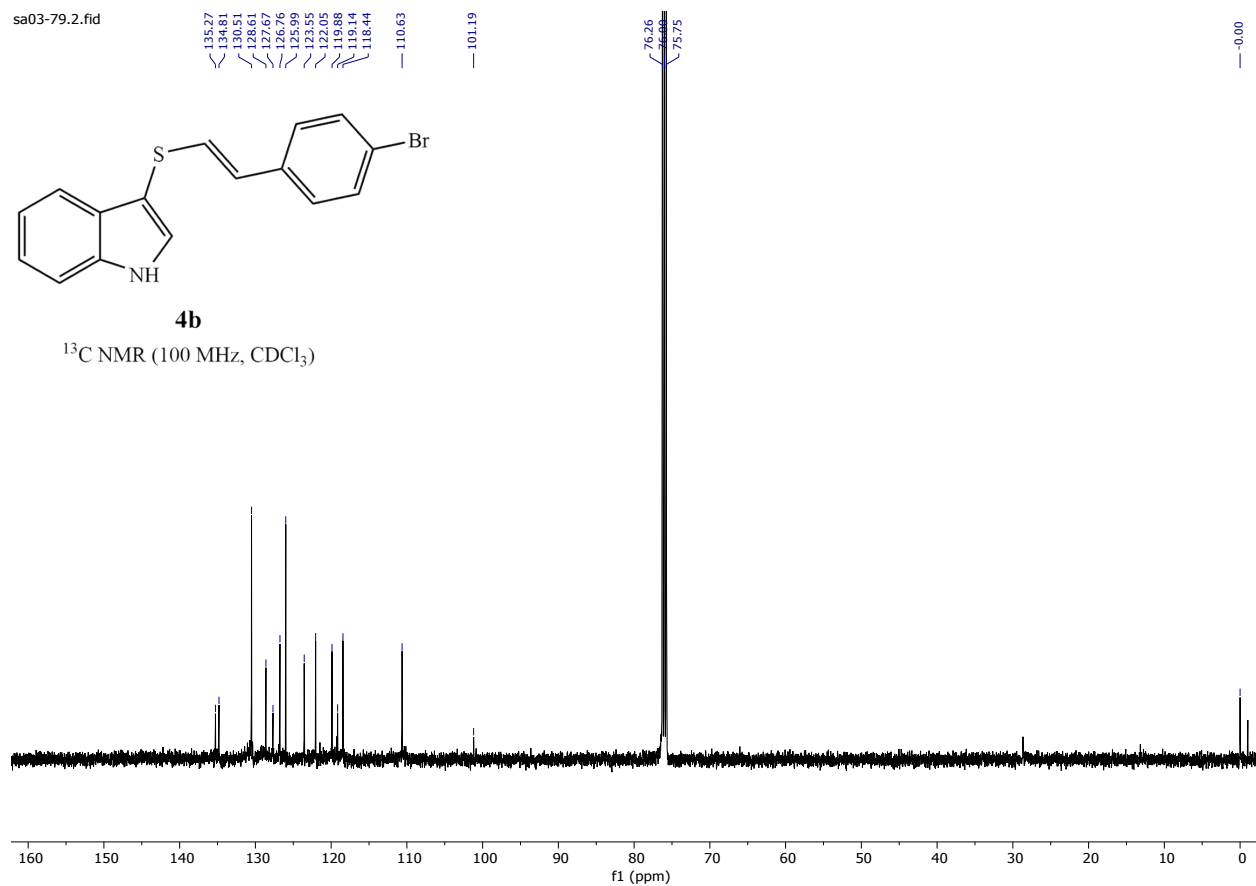


Fig. 32 ^{13}C NMR Spectrum of (*E*)-3-((4-Bromostyryl)thio)-1*H*-indole **4b**

SA-03-98.10.fid

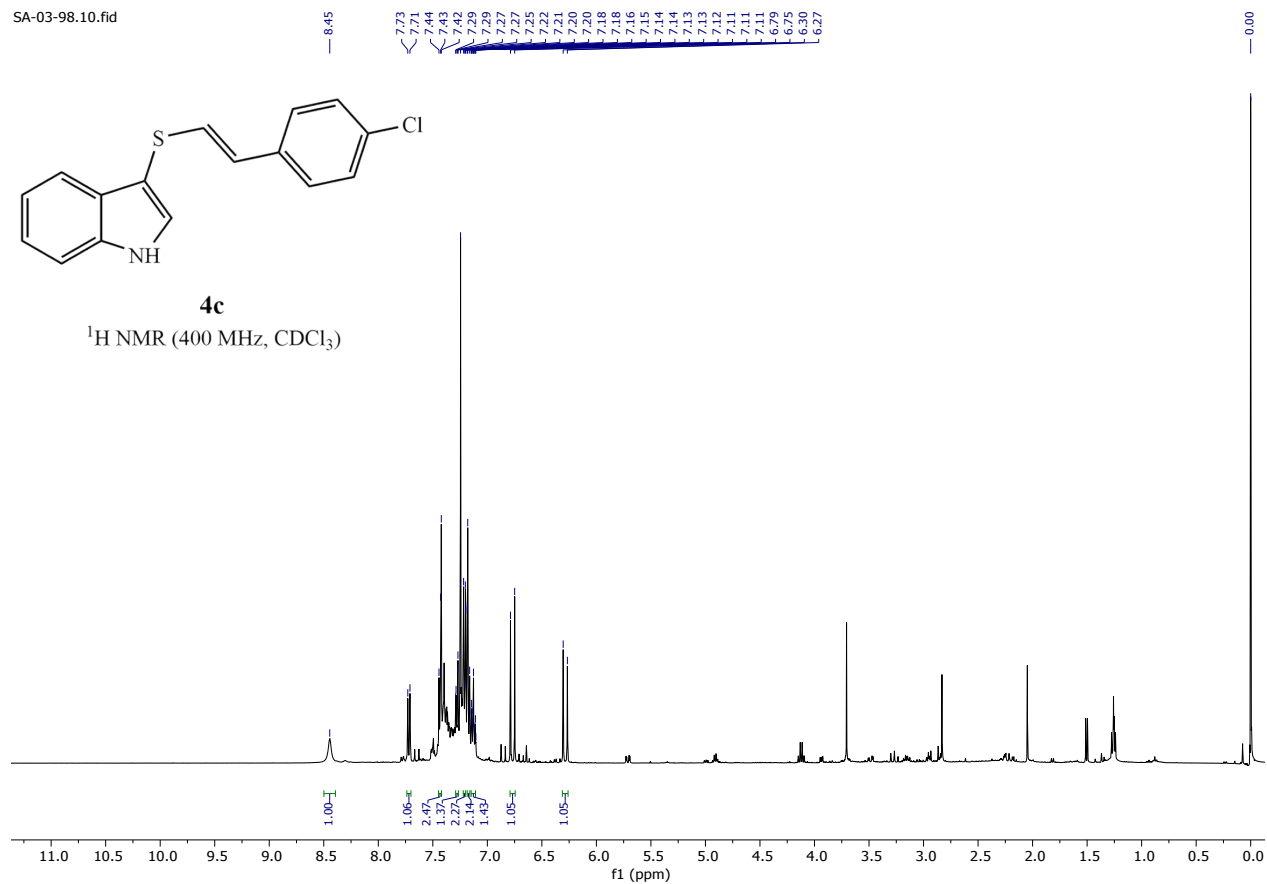


Fig. 33 ¹H NMR Spectrum of (*E*)-3-((4-Chlorostyryl)thio)-1*H*-indole **4c**

SA-03-79.10.fid

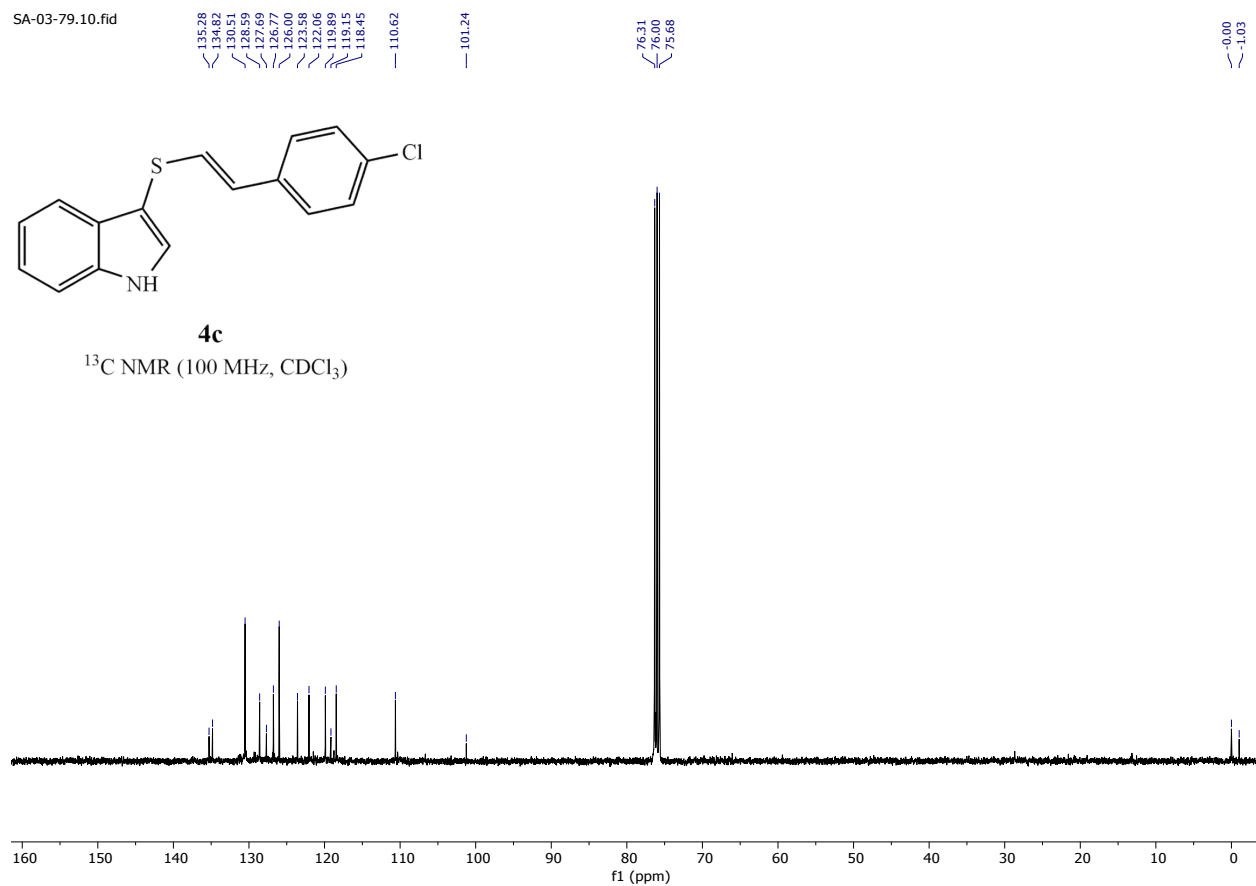


Fig. 34 ¹³C NMR Spectrum of (*E*)-3-((4-Chlorostyryl)thio)-1*H*-indole **4c**

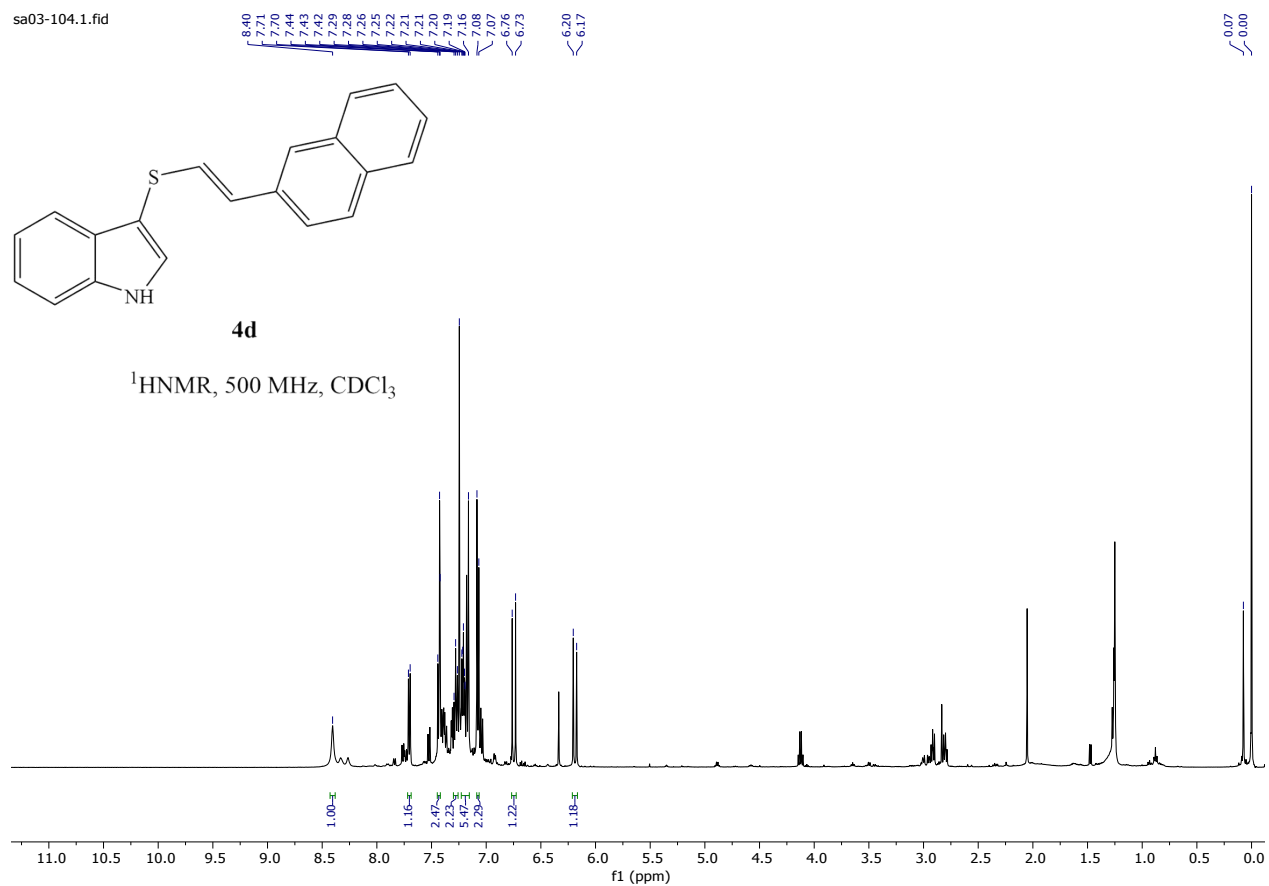


Fig. 35 ¹H NMR Spectrum of (*E*)-3-((2-(Naphthalen-2-yl) vinyl) thio)-1*H*-indole **4d**

20191031EI+sa-03-42_001#303-338 RT: 1.68-1.86 AV: 36 SB: 1 1.28 NL: 9.67E7
 T: FTMS + c EI Full ms [50.0000-600.0000]

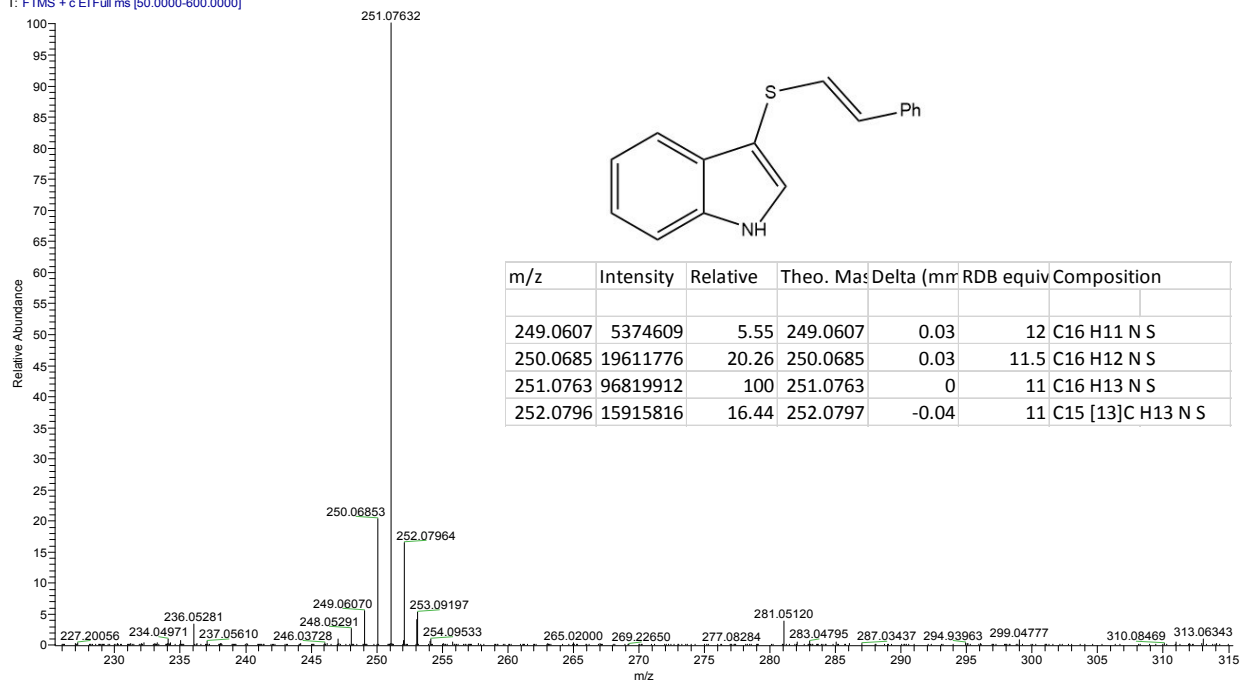
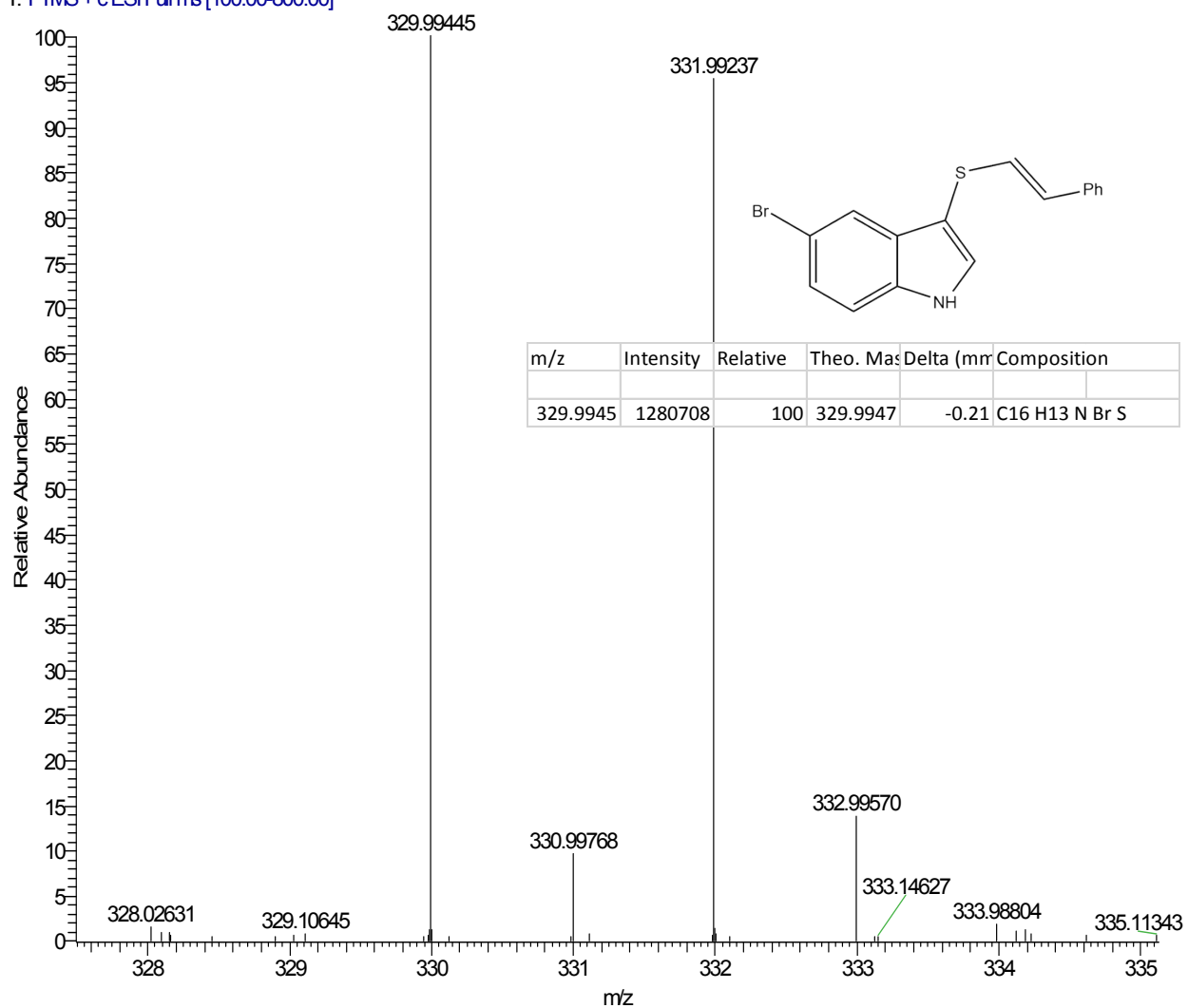


Fig. 36 EIMS of *(E)*-3-(Styrylthio)-1H-indole **3a**

20191120HESI+SA-03-65-1 #15 RT: 0.37 AV: 1 NL: 3.55E6
T: FTMS + c ESI Full ms [100.00-800.00]



m/z	Intensity	Relative	Theo. Mas	Delta (m/z)	Composition
329.9945	1280708	100	329.9947	-0.21	C16 H13 N Br S

Fig. 37 EIMS of (E)-5-bromo-3-(styrylthio)-1H-indole 3e

20191120HESI+SA-03-65-2 #8 RT: 0.18 AV: 1 SB: 1 0.07 NL: 1.63E6
T: FTMS + c ESI Full ms [100.00-800.00]

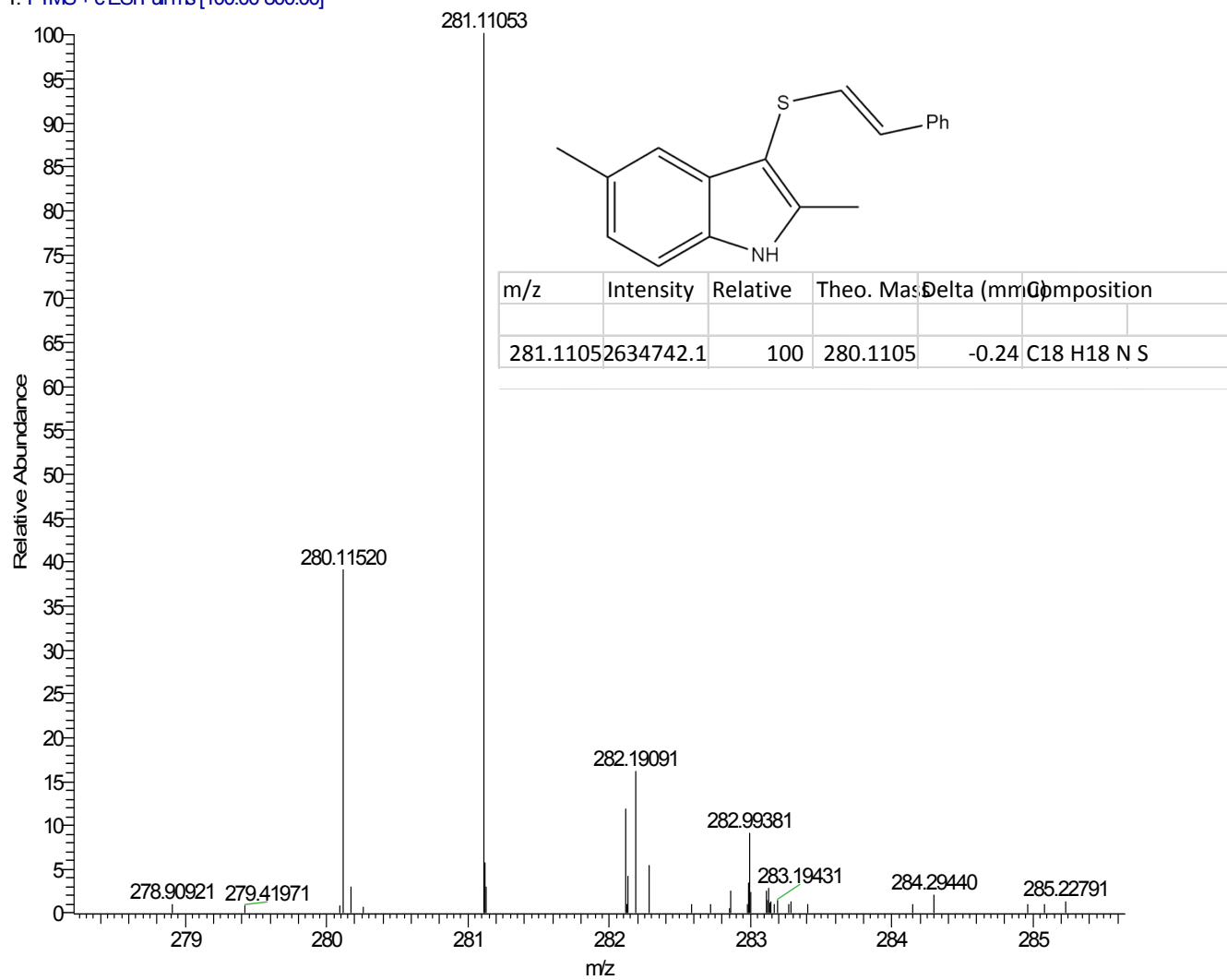


Fig. 38 EIMS of (E)-2,5-dimethyl-3-(styrylthio)-1H-indole 3f

20191120HESI+SA-03-65-4_191128153525#15-18 RT: 0.20-0.25 AV: 4 SB: 1 0.12 NL: 7.06E4
T: FTMS + c ESI Full ms [50.00-500.00]

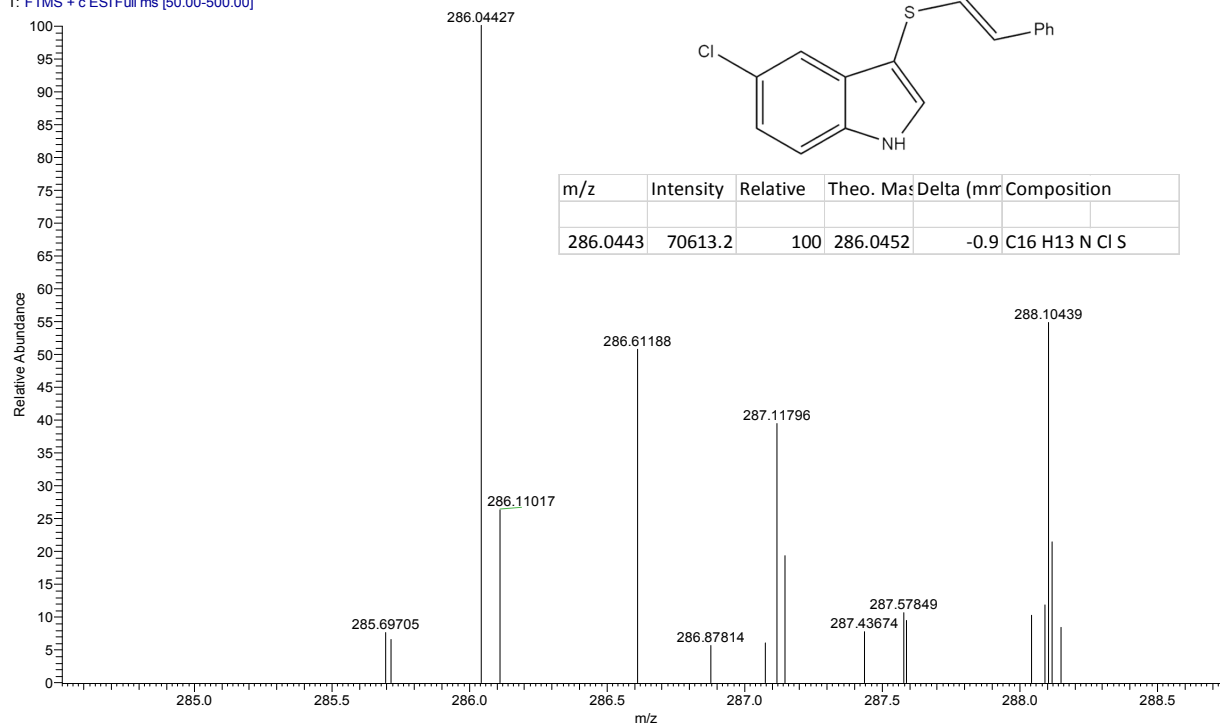


Fig. 39 EIMS of (*E*)-5-chloro-3-(styrylthio)-1*H*-indole **3g**

20191120HESI+SA-03-65-5 #27 RT: 0.70 AV: 1 SB: 1 0.09 NL: 2.15E4
T: FTMS + cESI Full ms [100.00-800.00]

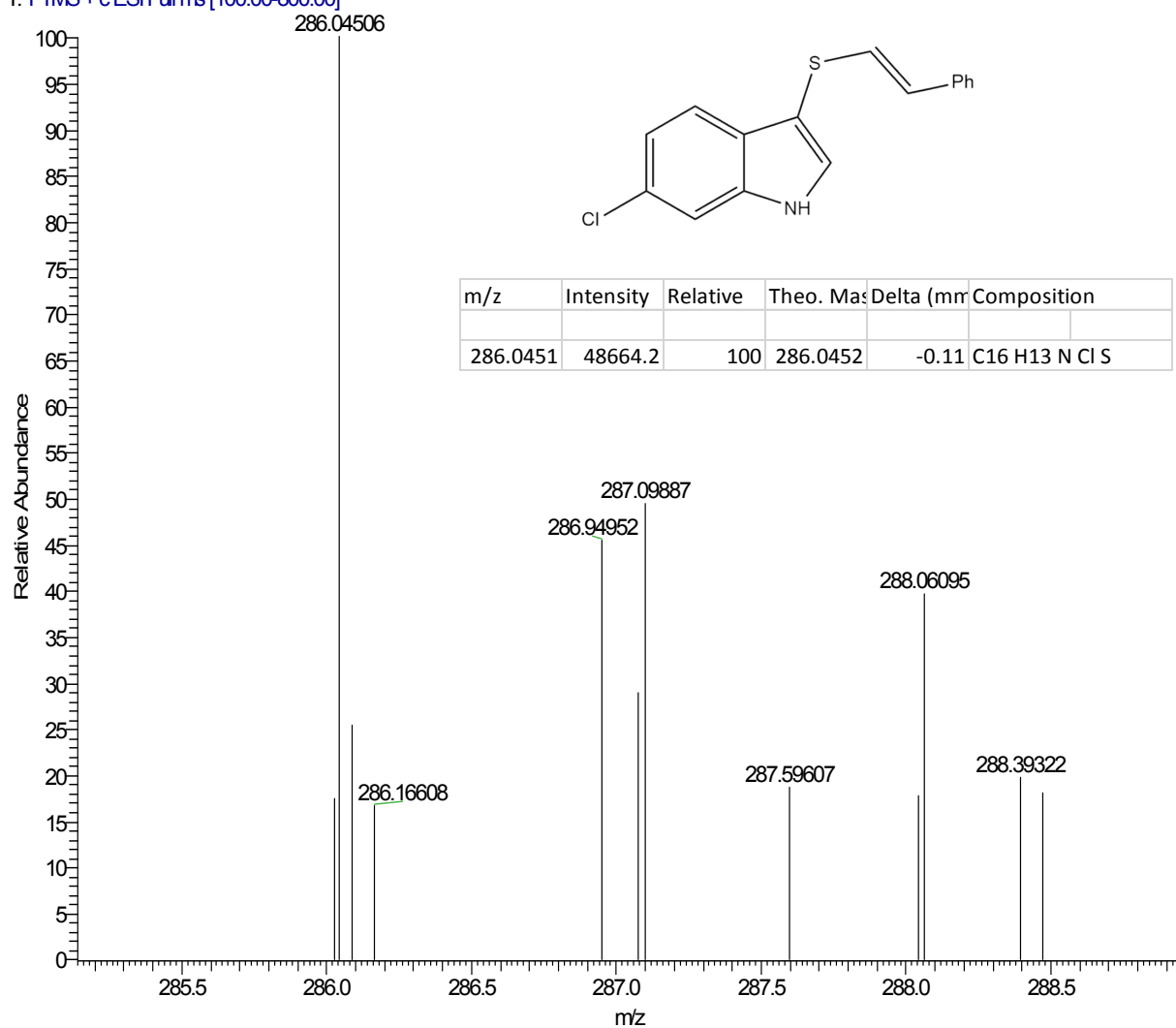


Fig. 40 EIMS of (E)-6-chloro-3-(styrylthio)-1H-indole 3k

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T: FTMS + c ESI Full ms [100.00-800.00]

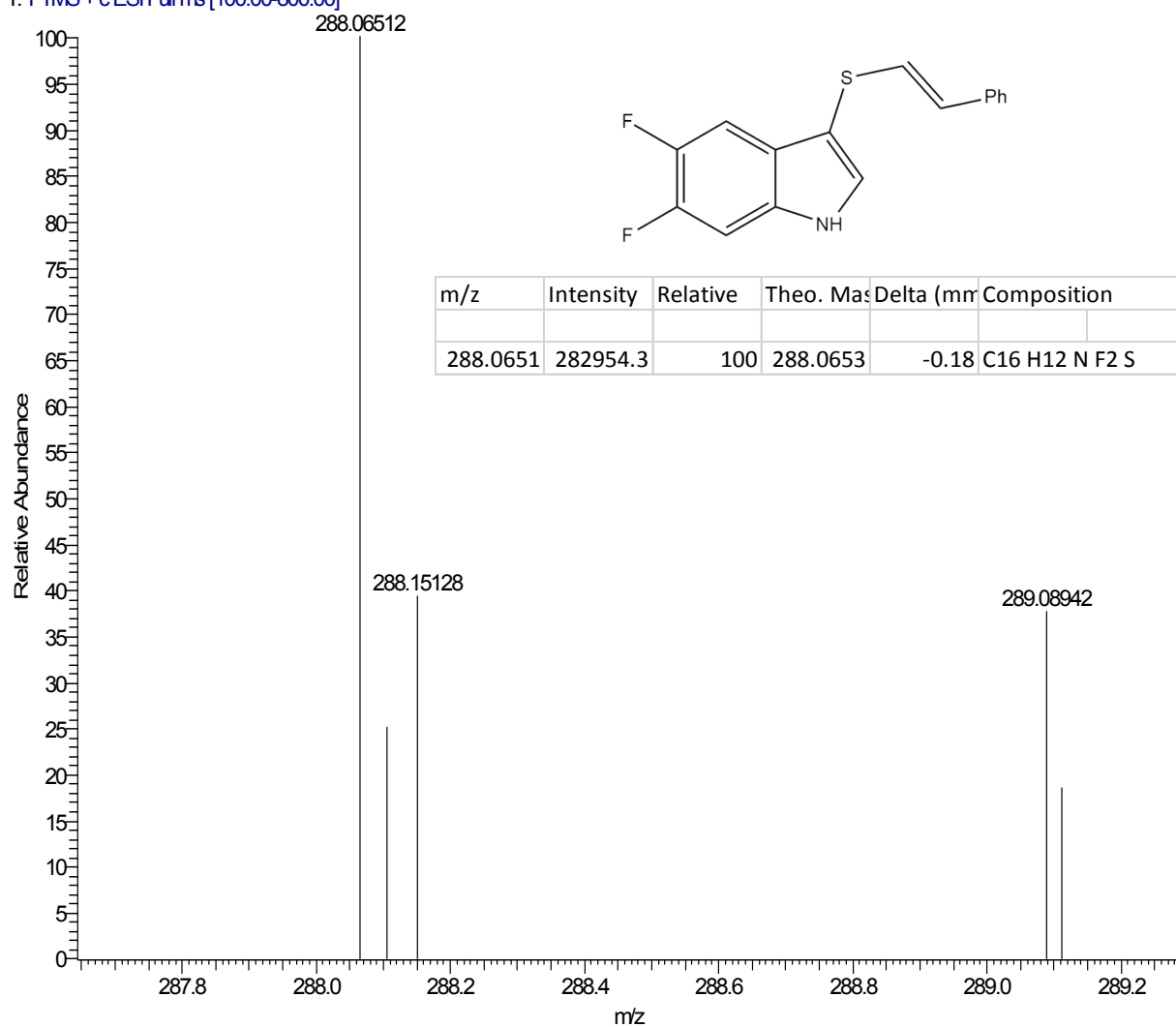


Fig. 41 EIMS of (*E*)-5,6-Difluoro-3-(styrylthio)-1*H*-indole **3j**

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T: FTMS + cESI Full ms [100.00-800.00]

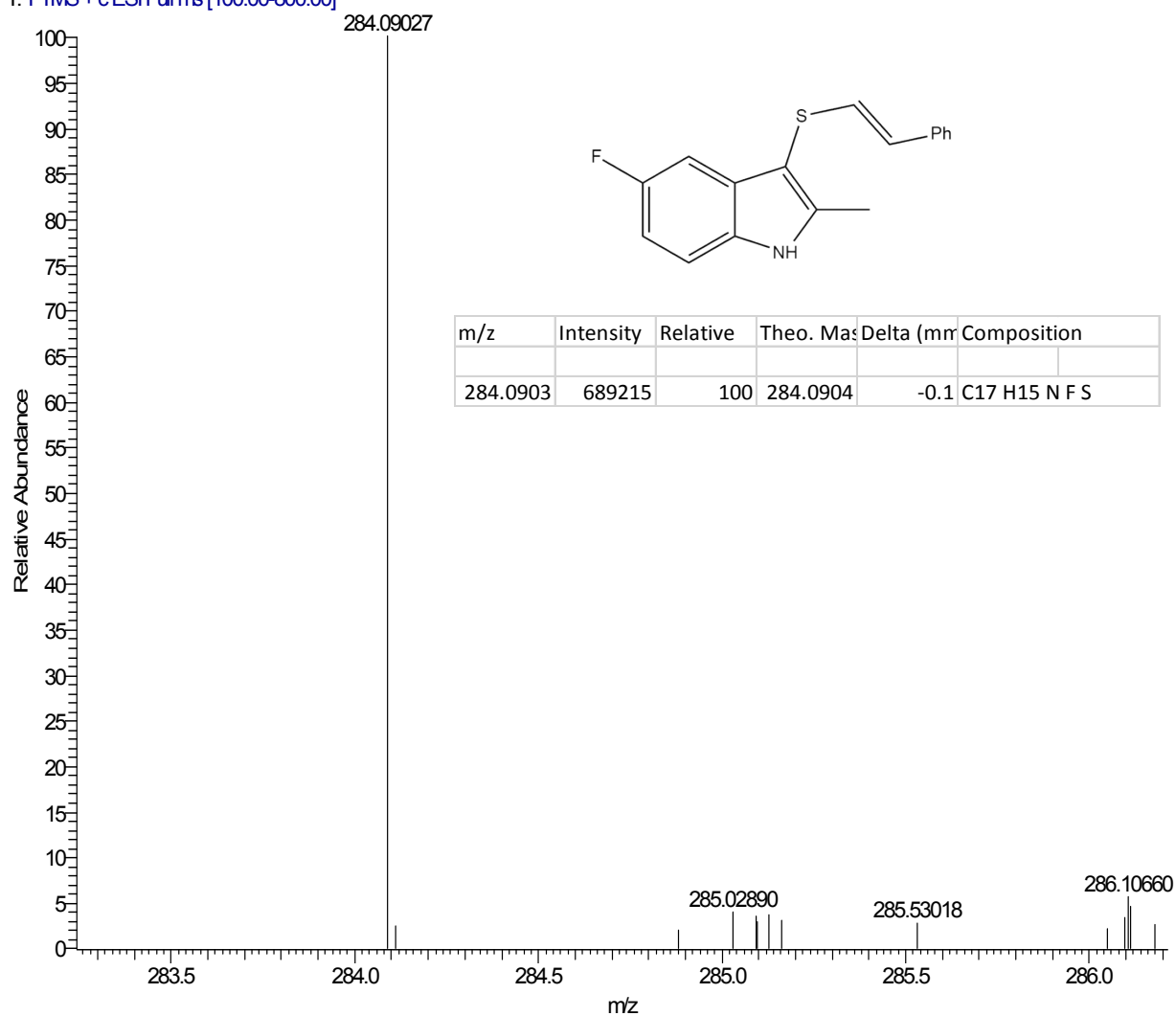
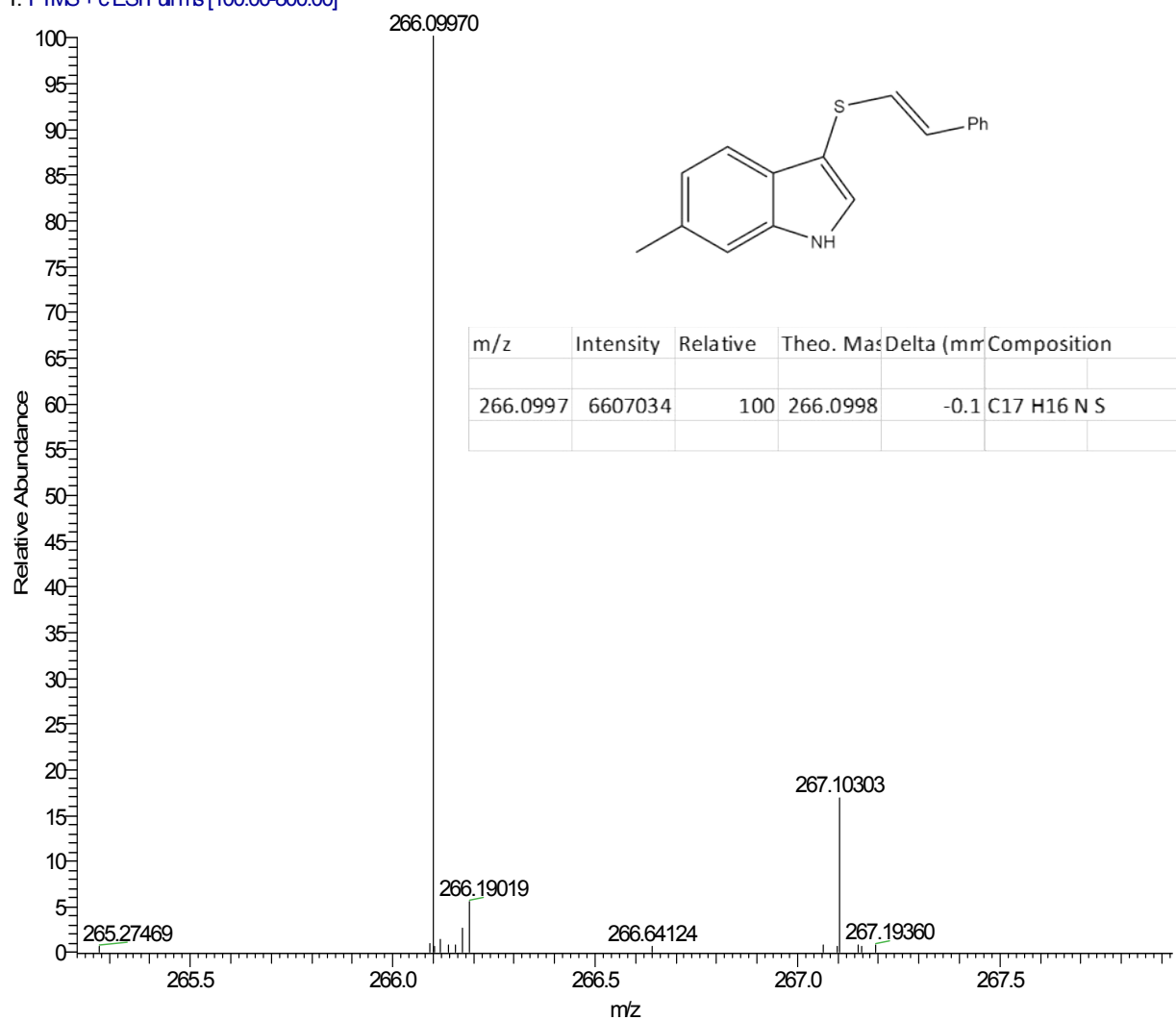


Fig. 42 EIMS of (E)-5-Fluoro-2-methyl-3-(styrylthio)-1H-indole 3i

20191120HESI+SA-03-56 #15 RT: 0.20 AV: 1 NL: 6.61E6
T: FTMS + cESI Full ms [100.00-800.00]



m/z	Intensity	Relative	Theo. Mass	Delta (m/z)	Composition
266.0997	6607034	100	266.0998	-0.1	C17 H16 N S

Fig. 43 EIMS of (E)-6-methyl-3-(styrylthio)-1H-indole 3h

20191120HESI+SA-03-49 #9-14 RT: 0.20-0.34 AV: 6 SB: 1 0.04 NL: 1.67E5
T: FTMS + cESI Full ms [100.00-800.00]

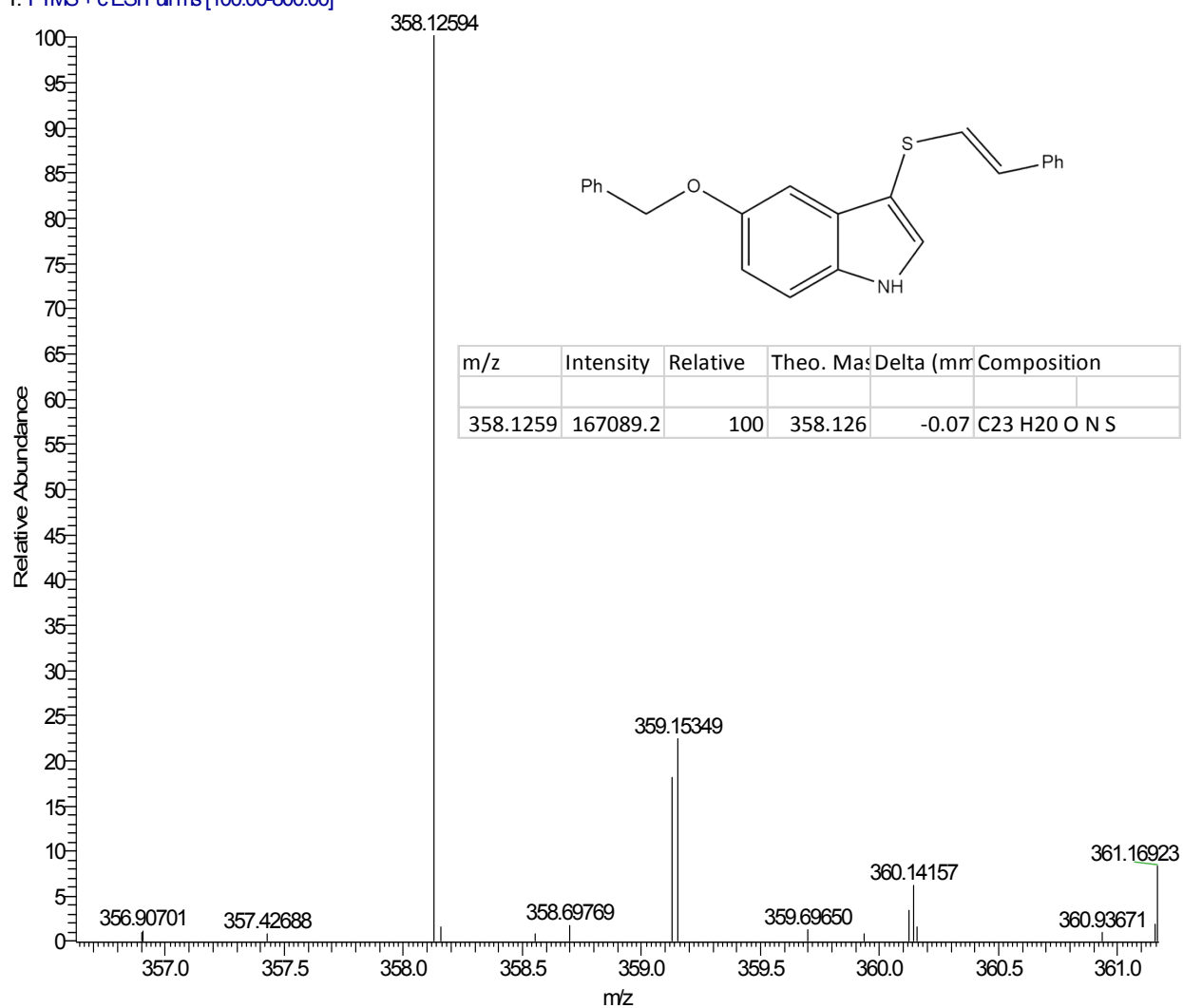


Fig. 44 EIMS of (E)-5-(Benzyloxy)-3-(styrylthio)-1H-indole **3m**

20191120HESI+SA-03-52 #11 RT: 0.26 AV: 1 SB: 1 0.04 NL: 3.07E5
T: FTMS + cESI Full ms [100.00-800.00]

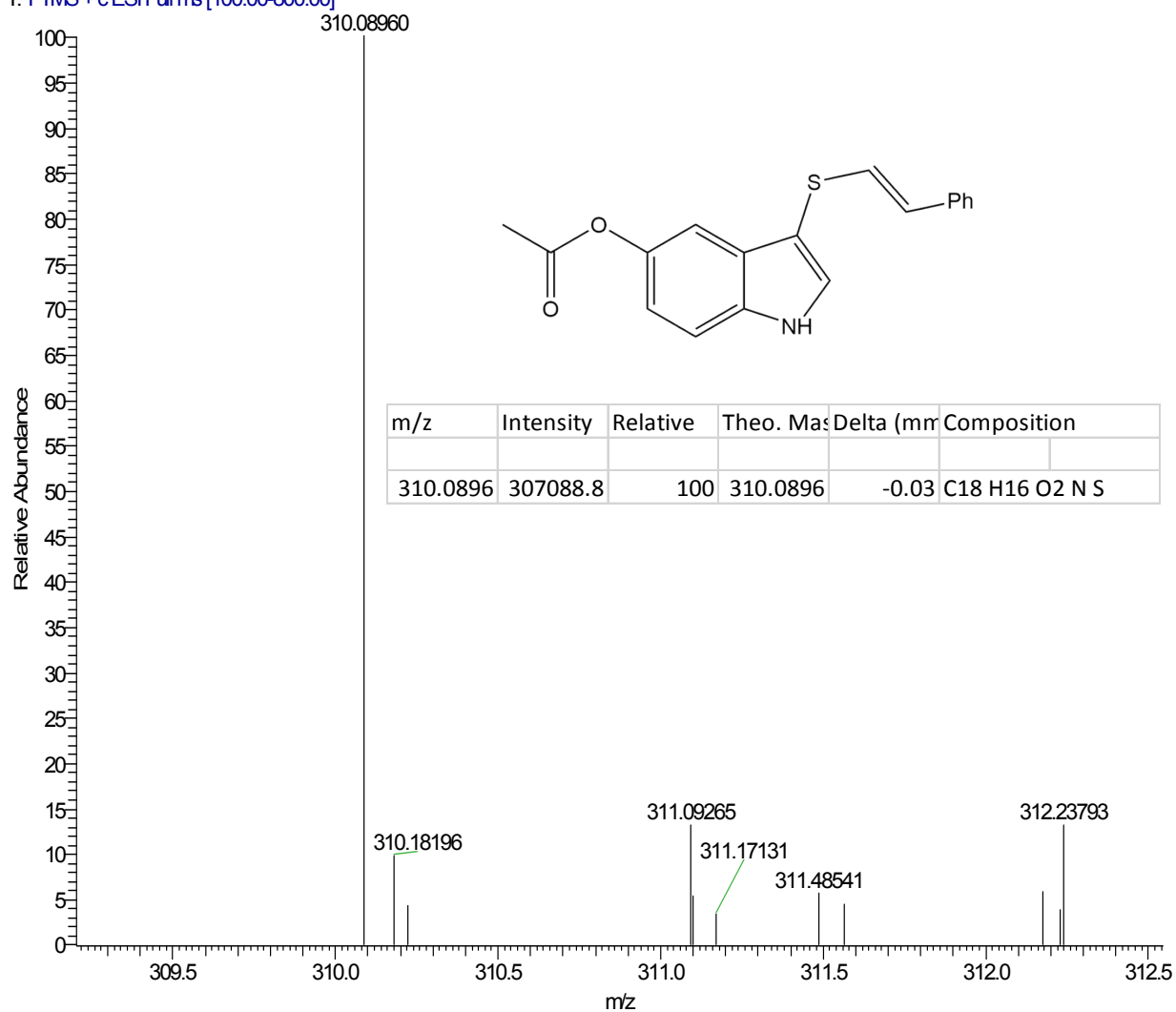


Fig. 45 EIMS of (*E*)-3-(styrylthio)-1H-indol-5-yl acetate

20191120HESI+SA-03-50 #9 RT: 0.20 AV: 1 SB: 1 0.09 NL: 4.04E5
T: FTMS + cESI Full ms [100.00-800.00]

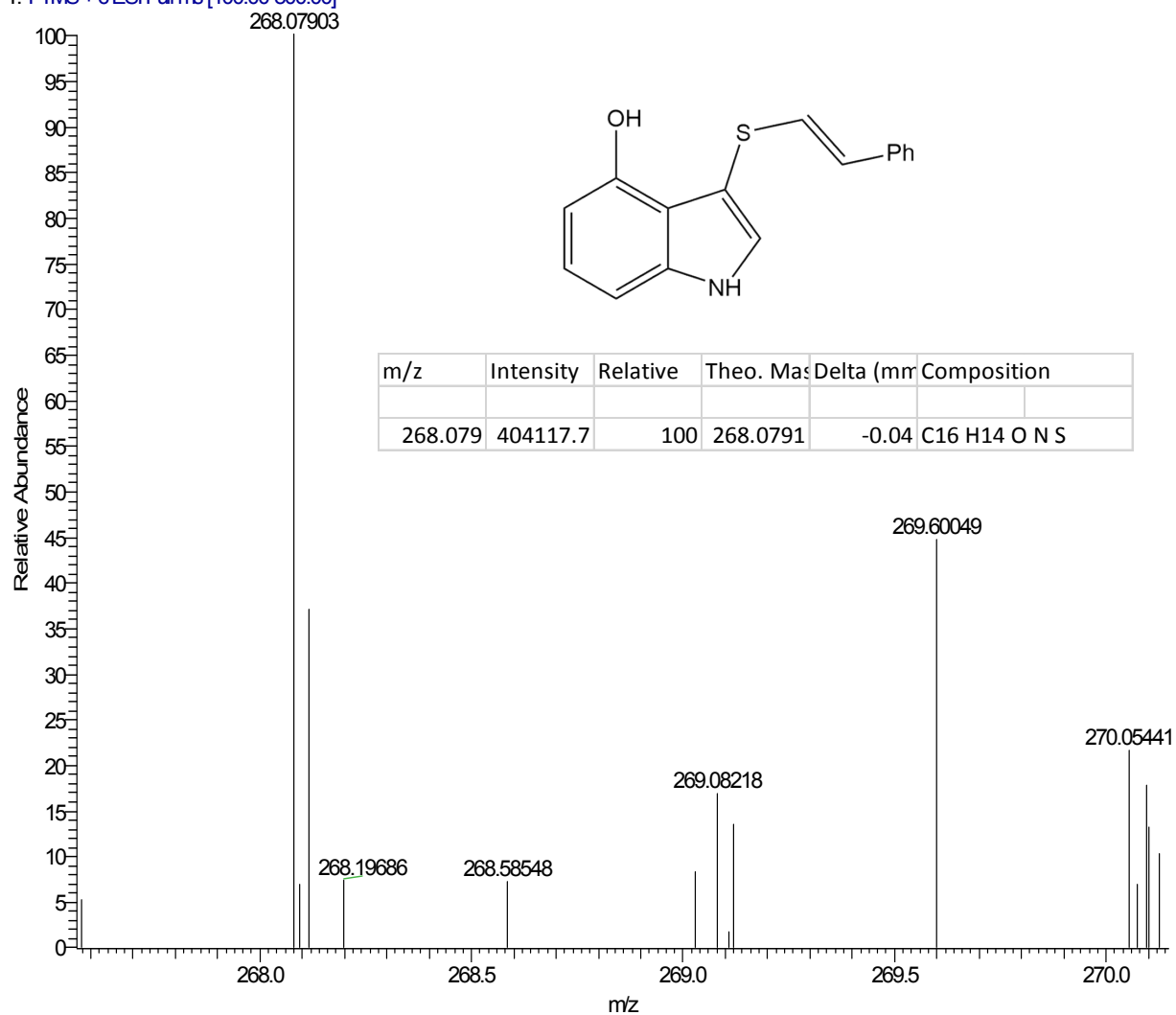


Fig. 46 EIMS of (E)-3-(styrylthio)-1H-indol-4-ol

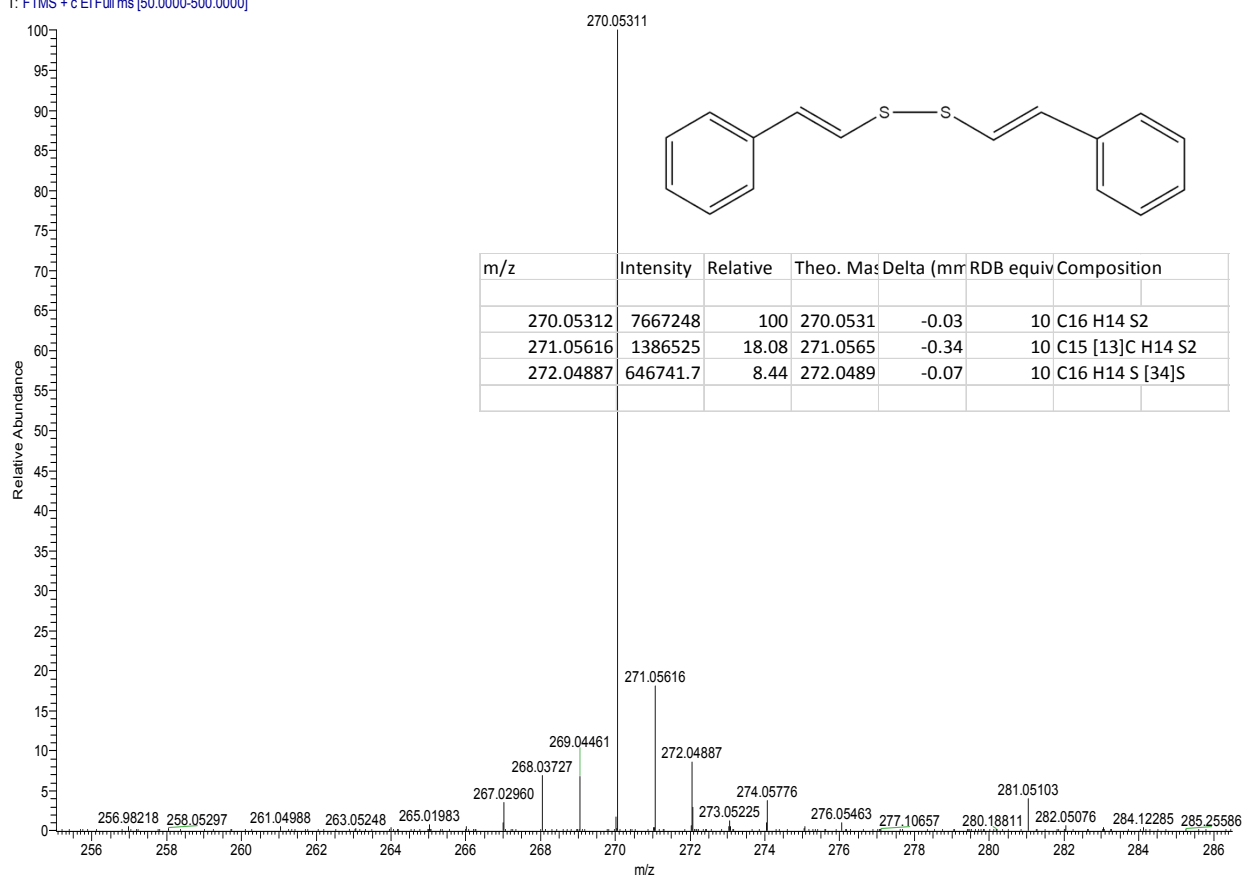


Fig. 47 EIMS of reaction intermediate **3s**

The molecular ion peak M/Z 270.05312 and its isotopic peak of $C_{16}H_{14}S_2$ were detected in E thus confirming the formation of intermediate $Ph-CH=CH-S-S-CH=CH-Ph$. The molecular ion peak of $C_{16}H_{12}S$ was also detected.

20200109E+SA-03-72_002#3483 RT: 17.38 AV: 1 NL: 1.82E9
 T: FTMS + c EI Full ms [50.0000-500.0000]

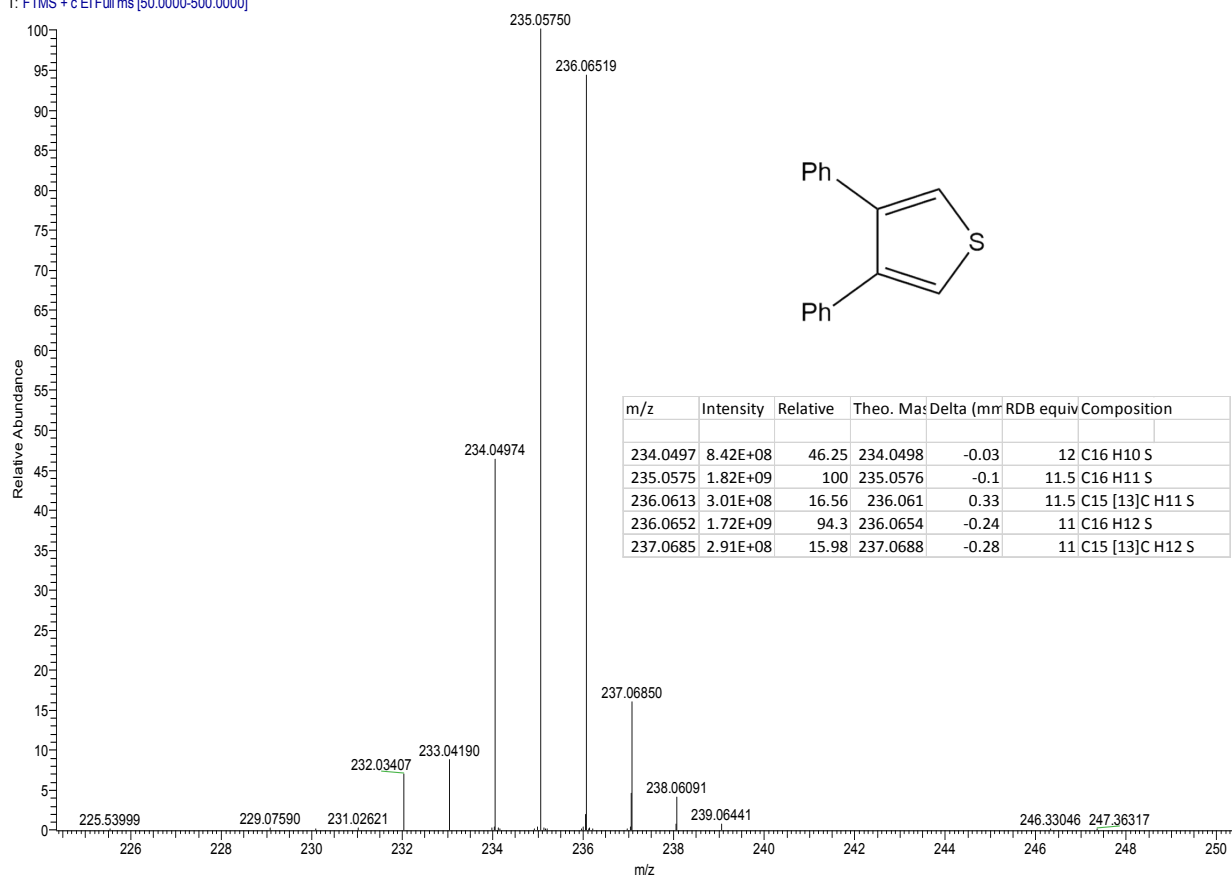


Fig. 48 EIMS of reaction intermediate **3t**