Supporting Information

Regioselective Markovnikov Hydrothiolation of 1-Aryl-1,3-butadienes with Dithiocarbamic Acid to Allyl Dithiocarbamates

Rodney A. Fernandes,* Sanjita Moharana, Priyanka Choudhary and Ravikant S. Ranjan

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India

Email: rfernand@chem.iitb.ac.in

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Experimental Section

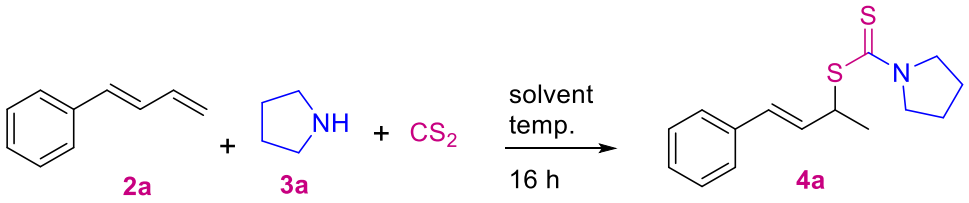
General Information

IR spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer by evaporating compounds dissolved in $CHCl_3$ on CsCl pellet. ^1H NMR and ^{13}C NMR were recorded with the Bruker Avance III HD and Bruker Avance III spectrometers operating at 500 or 400 and 125 or 100 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on $CDCl_3$ peaks at δ = 7.26 ppm for proton NMR and δ = 77.00 ppm (t) for carbon NMR. HRMS (ESI-TOF or Q-TOF) spectra were recorded on Bruker Maxis Impact Sr no. 282001.0008 and Agilent spectrometers using positive electrospray ionization and LCMS quadrupole by the TOF method. Solvents were dried by using standard procedures. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. For all reactions requiring heating, an oil bath was used.

Optimization of reaction conditions

In contemplation of finding suitable reaction conditions for the regioselective hydrothiolation, we examined the reactivity of (*E*)-buta-1,3-dien-1-ylbenzene **2a** as model substrate in the presence of a variety of solvents and temperature conditions (Table S1). The initial attempt with the use of **2a** (1.0 equiv.), amine **3a** (4 equiv.), CS_2 (6 equiv.) without solvent at 90 ^oC for 16 h revealed the formation of desired product **4a** in 59% (79 brsm) isolated yield with unreacted starting material and no side products (Table S1, entry 1). By performing the model reaction in toluene, MeCN, THF, DMF or 1,4-dioxane at 90 ^oC, the same product **4a** was obtained in 26, 37, 29, 17 and 35% isolated yields with similar regioselectivity (entries 2-6), respectively. However, none could improve the yield of **4a** in comparison to neat reaction conditions. DMSO failed to deliver the desired hydrothiolation product (entry 7). Increased time and temperature (90 to 120 ^oC) was not effective for improving the yields of **4a** (entries 8 and 9). A decrease in amine equivalent led to decrease in yield of the product (entry 10). Next, increasing the equivalents of the reagents led to an increase in isolated yields (entries 11-13), while the increase of equivalents of amine to 20 and CS_2 to 25, a complete conversion of diene **2a** occurred with 86% yield of **4a**. We noted that in the work of Halimehjani,[1] the amine was surprisingly considered as limiting substrate in the reaction, though different styrenes were explored. We observed, with 1:15 equivalents of diene and amine, the former remained unreacted until 20 equivalents of the latter were used. We also used 0.5 and 1.0 equiv. of Cs_2CO_3 as additive (entries 15 and 16) for the same reaction time, however the yields of the products were lower than that in entry 14 without additives. A reaction for 8 h (entry 17) with 1.0 equiv. of Cs_2CO_3 could not improve the yields and some diene was recovered. Similar was the case with AcOH (0.5 and 1.0 equiv., entries 18 and 19). Also, with the combination of both Cs_2CO_3 and AcOH (0.5 equiv. each, entry 20), the product yield did not improve. We varied the time to 24 h and 48 h to check whether the product remains, decomposes or yields vary (entries 21 and 22). No significant changes in the product yield were observed. Thus, the reaction conditions as described in entry 14 were chosen as optimal to investigate the substrate scope of this transformation.

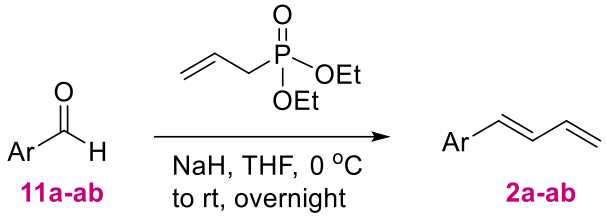
Table S1. Optimization of the reaction conditions[a]



Entry	3a (equiv.)	CS_2 (equiv.)	Solvent	T (°C)	Time (h)	Yield (%)[b]
1	4	6	neat	90	16	59 (79)
2	4	6	Toluene	90	16	26 (44)
3	4	6	MeCN	90	16	37 (76)
4	4	6	THF	90	16	29 (38)[c]
5	4	6	DMF	90	16	17 (37)
6	4	6	1,4-dioxane	90	16	35 (74)
7	4	6	DMSO	90	16	0
8	4	6	neat	90	24	58 (78)
9	4	6	neat	120	16	59 (77)
10	2	4	neat	90	16	49 (72)
11	8	10	neat	90	16	65 (85)
12	10	15	neat	90	16	75 (85)
13	15	20	neat	90	16	84 (90)
14	**20**	**25**	**neat**	**90**	**16**	**86**
15	20	25	neat	90	16	55[d]
16	20	25	neat	90	16	57[e]
17	20	25	neat	90	8	45(89)[e]
18	20	25	neat	90	16	39[f]
19	20	25	neat	90	16	45[g]
20	20	25	neat	90	16	54[h]
21	20	25	neat	90	24	87
22	20	25	neat	90	48	88

[a]Reaction conditions: **2a** (0.4 mmol), amine **3a** (0.8–8 mmol), CS_2 (1.6–10 mmol), 90 to 120 °C, 16 to 24 h. [b]Isolated yields. Values in the parentheses are yields based on recovered starting material **2a**. [c]Equal amount unidentified product. [d]In presence of 0.5 equiv. Cs_2CO_3 additive. [e]In presence of 1.0 equiv. Cs_2CO_3 additive. [f]In presence of 0.5 equiv. AcOH additive. [g]In presence of 1.0 equiv. AcOH additive. [h]In presence of 0.5 equiv. Cs_2CO_3 and 0.5 equiv. AcOH additives together.

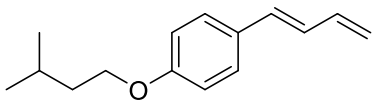
General procedure for synthesis of 1-aryl/alkyl butadienes (2a-ab):



To a stirred solution of diethyl allylphosphonate (534.5 mg, 3.0 mmol, 1.5 equiv.) in dry THF (25 mL) was added NaH (60% dispersion in mineral oil, 120 mg, 3.0 mmol, 1.5 equiv.) portion wise under nitrogen atmosphere at 0 °C. After 15 min, aldehyde **11a-ab** (2.0 mmol) in dry THF (1 mL) was added to the reaction mixture and stirred at 0 °C until the completion (monitored by TLC) of reaction. It was then quenched with saturated aq. NH_4Cl and the solution extracted with EtOAc (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1, common for all compounds unless specified) as eluent to afford the butadienes **2a-ab**.

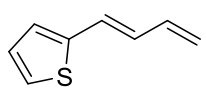
The 1-aryl/alkyl-1,3-butadienes were prepared and fully characterized as reported by us earlier.[2] Additional dienes were prepared by following above procedure and data is presented below.

(*E*)-1-(Buta-1,3-dien-1-yl)-4-(isopentyloxy)benzene (2e):



Following the general procedure, aldehyde **11e** (385 mg, 2.0 mmol) resulted in diene **2e** (302.8 mg, 70%) as a colourless oil. Compound was purified by silica gel column chromatography using petroleum ether/EtOAc (9.5:0.5) as eluent. IR ($CHCl_3$): ν_{max} = 3020, 2898, 1584, 1496, 1417, 1278, 1186, 1146, 1046, 992, 929, 848, 758, 668, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.68 (dd, *J* = 15.3, 10.6 Hz, 1H), 6.54–6.44 (m, 2H), 5.29 (d, *J* = 16.5 Hz, 1H), 5.12 (d, *J* = 9.1 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 2H), 1.91–1.79 (m, 1H), 1.69 (q, *J* = 6.7 Hz, 2H), 0.98 (d, *J* = 6.7 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.9, 137.4, 132.5, 129.7, 127.6, 127.5, 116.3, 114.6, 66.4, 38.0, 25.0, 22.6 ppm; HRMS (Q-TOF): *m/z* $[M + H]^+$ Calcd for $C_{15}H_{21}O$ 217.1587; Found 217.1584.

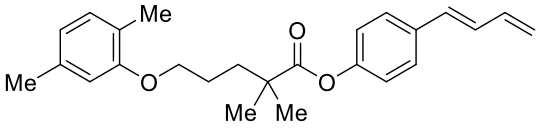
(*E*)-2-(Buta-1,3-dien-1-yl)thiophene (2w):



Following the general procedure, aldehyde **11w** (224.3 mg, 2.0 mmol) resulted in diene **2w** (177.1 mg, 65%) as a pale-yellow oil. Reaction time = 19 h, compound purified by silica gel column chromatography using petroleum ether/EtOAc (9.8:0.2) as eluent. IR ($CHCl_3$): ν_{max} = 2925, 1613, 1431, 1361, 1040, 958, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 5.1 Hz, 1H), 7.05–6.98 (m, 2H), 6.79–6.70 (m, 2H), 6.65–6.46 (m, 1H), 5.40 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H) ppm;

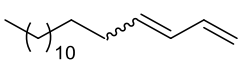
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.4, 136.6, 129.3, 127.5, 126.0, 125.6, 124.4, 117.4 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for C_8H_9S 137.0420; Found: 137.0418.

4-((1*E*,3*E*)-4-Tosylbuta-1,3-dien-1-yl)phenyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (2z):



Following the general procedure, aldehyde **11z** (708.9 mg, 2.0 mmol) resulted in the diene **2z** (340.6 mg, 45%) as a colourless oil. Reaction time = 12 h, compound purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent. IR ($CHCl_3$) ν_{max} = 3019, 2926, 1744, 1613, 1584, 1508, 1474, 1391, 1263, 1129, 1047, 928, 669, 626, 587 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.05–7.36 (m, 3H), 6.90–6.80 (m, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.67–6.64 (m, 1H), 6.58–6.44 (m, 1H), 6.28 (t, *J* = 11.0 Hz, 1H), 5.38 (t, *J* = 17.5 Hz, 1H), 5.23 (dd, *J* = 22.8, 10.2 Hz, 1H), 4.06–3.96 (m, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 1.92–1.89 (m, 4H), 1.41 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 176.3, 156.8, 150.3, 137.0, 136.4, 132.9, 130.3, 129.9, 129.4, 127.2, 123.5, 121.7, 121.3, 120.7, 119.8, 111.8, 67.7, 42.4, 37.1, 25.1, 21.4, 15.8 ppm; HRMS (Q-TOF): *m/z* $[M + H]^+$ Calcd for $C_{25}H_{31}O_3$ 379.2268; Found 379.2240.

(*E*)-Heptadeca-1,3-diene (2ab):

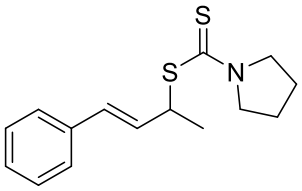


Following the general procedure, tetradecanal **11ab** (425 mg, 2.0 mmol) resulted in diene **2ab** (293.2 mg, 62%) as colorless oil. Purified by silica gel column chromatography using petroleum ether/EtOAc (9.5:0.5) as eluent. IR ($CHCl_3$): ν_{max} = 2954, 2927, 2849, 1650, 1464, 1388, 1005, 896, 765, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ= 6.38–6.25 (m, 1H), 6.10–5.98 (m, 1H), 5.77–5.64 (m, 1H), 5.08 (d, *J* = 16.6 Hz, 1H), 4.95 (d, *J* = 10.1 Hz, 1H), 2.07 (q, *J* = 14.2, 7.7 Hz, 2H), 1.30–1.25 (m, 22H), 0.89 (t, *J* = 6.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ= 137.4, 135.6, 130.8, 114.5, 32.6, 32.0, 29.7, 29.6, 29.5, 29.4, 29.24, 29.2, 22.7, 14.1 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{33}$ 237.2577; Found: 237.2570.

General procedure for hydrothiolation of 1,3-butadienes:

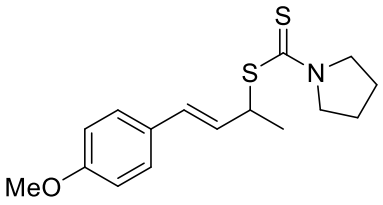
In a flame-dried pressure tube equipped with magnetic stir bar, a substituted 1,3-butadiene **2** (0.4 mmol, 1.0 equiv.) and CS_2 (0.6 mL, 10 mmol, 25 equiv.) were added. The tube was cooled in an ice bath (0-5 ^oC) and the amine **3** (8 mmol, 20 equiv.) was added dropwise. The tube was sealed under open air and the resulting mixture was stirred in an oil bath at 90 ^oC for 16 h. After completion of reaction, the volatiles were evaporated in rotary evaporator and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc as eluent to give corresponding allyl dithiocarbamates **4a-ab** and **4ac-an**.

(*E*)-4-Phenylbut-3-en-2-yl pyrrolidine-1-carbodithioate (4a):



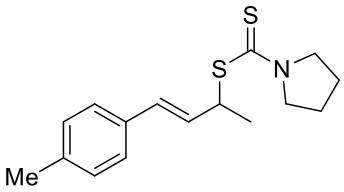
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4a** (95.4 mg, 86%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3020, 2970, 2870, 1430, 1329, 1249, 1219, 1162, 998, 954, 915, 866, 751, 694, 524 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.1 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.39 (dd, *J* = 15.8, 6.9 Hz, 1H), 5.01–4.87 (m, 1H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 2.06 (quint, *J* = 6.4 Hz, 2H), 1.97 (quint, *J* = 6.8 Hz, 2H), 1.64 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.7, 136.8, 130.4, 130.1, 128.5, 127.5, 126.4, 54.8, 50.5, 47.8, 26.0, 24.2, 19.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{20}NS_2$ 278.1032; Found 278.1035.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4b):



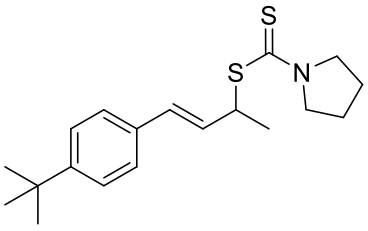
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4b** (109.5 mg, 89%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2966, 2874, 2833, 1607, 1511, 1459, 1431, 1330, 1299, 1219, 1175, 1162, 1035, 998, 954, 916, 851, 818 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 16.2, 6.8 Hz, 1H), 4.95–4.87 (m, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.05 (quint, *J* = 6.9 Hz, 2H), 1.96 (quint, *J* = 6.7 Hz, 2H), 1.62 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.8, 159.1, 129.9, 129.5, 127.7, 127.5, 113.9, 55.2, 54.7, 50.5, 48.0, 26.0, 24.2, 20.0 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NOS_2$ 308.1138; Found 308.1140.

(*E*)-4-(*p*-Tolyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4c):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4c** (95.6 mg, 82%) as a colourless oil; IR ($CHCl_3$) ν_{max} = 2976, 2874, 1512, 1460, 1432, 1330, 1250, 1182, 1162, 1020, 998, 954, 802, 755, 667, 512 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.33 (dd, *J* = 15.8, 6.9 Hz, 1H), 4.94–4.89 (m, 1H), 3.93 (t, *J* = 6.8 Hz, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 2.32 (s, 3H), 2.04 (quint, *J* = 6.8 Hz, 2H), 1.95 (quint, *J* = 6.9 Hz, 2H), 1.63 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.7, 137.3, 133.9, 130.3, 129.1, 128.9, 126.2, 54.7, 50.5, 47.9, 25.9, 24.2, 21.1, 19.9 ppm. HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{16}H_{22}NS_2$ 292.1189; Found 292.1196.

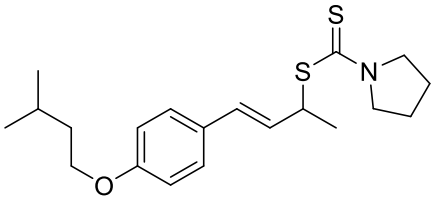
(*E*)-4-(4-(*tert*-Butyl)phenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4d):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4d** (110.7 mg, 83%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2952, 2925, 2854, 1632, 1599, 1513, 1462, 1421, 1377, 1363, 1271, 1110, 1000, 950, 895, 866, 820, 721, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.35–7.31 (m, 4H), 6.64 (d, *J* = 15.7

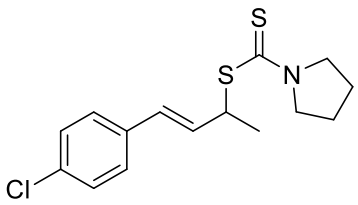
Hz, 1H), 6.35 (dd, *J* = 16.1, 6.8 Hz, 1H), 4.99–4.88 (m, 1H), 3.94 (t, *J* = 7.1 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.05 (quint, *J* = 6.8 Hz, 2H), 1.97 (quint, *J* = 7.0 Hz, 2H), 1.63 (d, *J* = 6.9 Hz, 3H), 1.31 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.8, 150.6, 134.0, 130.2, 129.2, 126.1, 125.4, 54.8, 50.5, 47.9, 34.5, 31.2, 26.0, 24.2, 19.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{28}NS_2$ 334.1658; Found 334.1656.

(*E*)-4-(4-(Isopentyloxy)phenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4e):



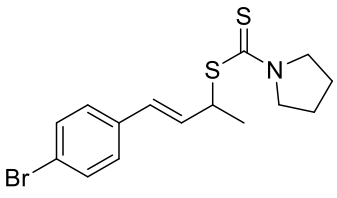
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4e** (122.2 mg, 84%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3031, 2956, 2926, 2870, 1606, 1510, 1461, 1428, 1248, 1174, 1163, 1058, 1021, 999, 954, 817, 733, 697, 525 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.6 Hz, 2H), 6.8 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 16.4, 6.8 Hz, 1H), 4.97–4.86 (m, 1H), 4.01–3.89 (m, 4H), 3.61 (t, *J* = 7.0 Hz, 2H), 2.05 (quint, *J* = 6.9 Hz, 2H), 1.96 (quint, *J* = 6.7 Hz, 2H), 1.89–1.76 (m, 1H), 1.69–1.61 (m, 5H), 0.95 (d, *J* = 6.6 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.8, 158.7, 130.0, 129.3, 127.6, 127.5, 114.5, 66.3, 54.7, 50.5, 48.0, 37.9, 26.0, 25.0, 24.2, 22.5, 20.0 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{30}NOS_2$ 364.1764; Found 364.1765.

(*E*)-4-(4-Chlorophenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4f):



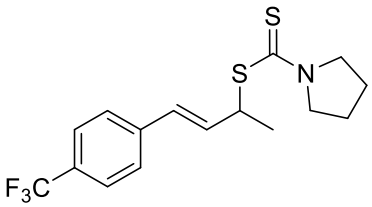
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4f** (101 mg, 81%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2971, 2923, 2870, 1490, 1427, 1329, 1249, 1219, 1181, 1161, 1090, 1011, 998, 954, 857, 808, 772, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 4H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 15.7, 6.7 Hz, 1H), 4.98–4.87 (m, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 2.10–2.02 (m, 2H), 2.03–1.88 (m, 2H), 1.61 (d, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 191.5, 135.3, 133.1, 130.9, 129.1, 128.6, 127.6, 54.8, 50.6, 47.6, 26.0, 24.2, 19.7 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{19}ClNS_2$ 312.0642; Found: 312.0644.

(*E*)-4-(4-Bromophenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4g):



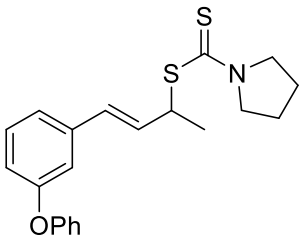
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4g** (107 mg, 75%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3019, 2977, 2873, 1487, 1460, 1432, 1330, 1250, 1183, 1162, 1073, 1009, 953, 806, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 15.8, 6.8 Hz, 1H), 4.96–4.87 (m, 1H), 3.92 (t, *J* = 6.8 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.05 (quint, *J* = 7.1 Hz, 2H), 1.96 (quint, *J* = 7.1 Hz, 2H), 1.61 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.5, 135.8, 131.6, 131.0, 129.1, 127.9, 121.2, 54.9, 50.6, 47.6, 26.0, 24.2, 19.7 ppm; HRMS (Q-TOF): *m/z* [M+H] + calcd for $C_{15}H_{19}NS_2Br$ 358.0116; Found 358.0115.

(*E*)-4-(4-(Trifluoromethyl)phenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4h):



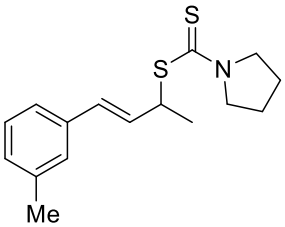
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4h** (105 mg, 76%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2970, 2925, 2873, 1645, 1615, 1461, 1432, 1326, 1163, 1122, 1068, 1016, 999, 954, 916, 864, 819, 761, 697, 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 16.2 Hz, 1H), 6.47 (dd, J = 16.1, 6.9 Hz, 1H), 5.02–4.91 (m, 1H), 3.93 (t, J = 6.9 Hz, 2H), 3.62 (t, J = 6.9 Hz, 2H), 2.06 (quint, J = 6.5 Hz, 2H), 1.97 (quint, J = 6.9 Hz, 2H), 1.63 (d, J = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.3, 140.4, 133.1, 128.9, 126.5, 125.5 (125.47, 125.43, 125.39 and 125.36, q, J_{C-F} = 3.9 Hz), 54.9, 50.6, 47.5, 26.0, 24.2, 19.5 ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ = −62.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{19}F_3NS_2$ 346.0906; Found 346.0909.

(*E*)-4-(3-Phenoxyphenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4j):



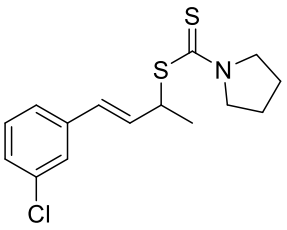
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4j** (122.7 mg, 83%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2970, 2870, 1577, 1487, 1428, 1330, 1246, 1215, 1182, 998, 958, 867, 824, 772, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (t, J = 7.9 Hz, 2H), 7.28 (d, J = 8.9 Hz, 1H), 7.18–7.10 (m, 2H), 7.06 (s, 1H), 7.03 (d, J = 8.3 Hz, 2H), 6.90 (dd, J = 7.9, 2.2 Hz, 1H), 6.63 (d, J = 15.8 Hz, 1H), 6.38 (dd, J = 15.9, 6.9 Hz, 1H), 4.99–4.90 (m, 1H), 3.96 (t, J = 7.1 Hz, 2H), 3.64 (t, J = 6.9 Hz, 2H), 2.13–2.05 (m, 2H), 2.03–1.96 (m, 2H), 1.64 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.6, 157.3, 157.2, 138.8, 131.0, 129.8, 129.76, 129.7, 123.1, 121.6, 118.7, 118.1, 116.8, 54.8, 50.6, 47.7, 26.0, 24.2, 19.8 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{24}NOS_2$ 370.1294; Found: 370.1294.

(*E*)-4-(*m*-Tolyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4k):



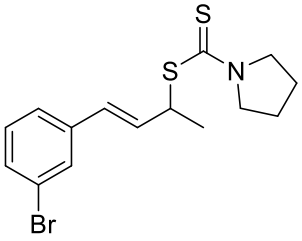
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4k** (89.8 mg, 77%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3023, 2970, 2923, 2871, 1603, 1583, 1459, 1427, 1373, 1337, 1329, 1249, 1219, 1182, 1162, 1020, 998, 954, 916, 866, 826, 778, 695, 511, 461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.23–7.15 (m, 3H), 7.07–7.00 (m, 1H), 6.63 (d, J = 15.9 Hz, 1H), 6.37 (dd, J = 16.0, 6.9 Hz, 1H), 4.98–4.89 (m, 1H), 3.94 (t, J = 6.9 Hz, 2H), 3.62 (t, J = 6.7 Hz, 2H), 2.33 (s, 3H), 2.05 (quint, J = 6.8 Hz, 2H), 1.97 (quint, J = 7.1 Hz, 2H), 1.63 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.8, 138.0, 136.7, 130.5, 129.8, 128.4, 128.3, 127.1, 123.6, 54.8, 50.6, 47.9, 26.0, 24.2, 21.3, 19.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NS_2$ 292.1189; Found 292.1192.

(*E*)-4-(3-Chlorophenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4l):



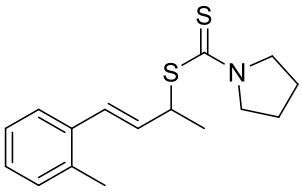
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4l** (83.6 mg, 67%) as a colourless oil; IR ($CHCl_3$) ν_{max} = 2976, 2927, 2875, 1594, 1461, 1433, 1331, 1250, 1183, 1162, 998, 954, 687, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.36 (s, 1H), 7.24–7.20 (m, 2H), 7.18–7.16 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 15.8, 6.8 Hz, 1H), 4.96–4.91 (m, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.06 (quint, *J* = 6.8 Hz, 2H), 1.97 (quint, *J* = 6.8 Hz, 2H), 1.61 (d, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.4, 138.8, 134.4, 131.8, 129.7, 129.0, 127.4, 126.3, 124.7, 54.9, 50.6, 47.6, 26.0, 24.2, 19.6 ppm; HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{15}H_{19}ClNS_2$ 312.0643; Found 312.0642.

(*E*)-4-(3-Bromophenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4m):



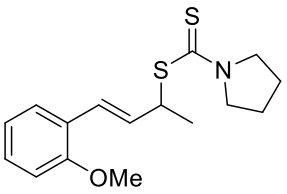
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4m** (102.6 mg, 72%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2970, 2924, 2870, 1590, 1561, 1431, 1372, 1329, 1249, 1219, 1182, 1162, 995, 954, 914, 866, 826, 776, 731, 687, 510, 461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53 (t, *J* = 1.7 Hz, 1H), 7.36–7.26 (m, 2H), 7.19–7.11 (t, *J* = 7.9 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.39 (dd, *J* = 15.9, 6.8 Hz, 1H), 4.99–4.90 (m, 1H), 3.93 (t, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 2.05 (quint, *J* = 6.6 Hz, 2H), 1.96 (quint, *J* = 6.9 Hz, 2H), 1.62 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.1, 138.9, 131.7, 130.1, 129.9, 129.0, 128.7, 125.0, 122.5, 54.7, 50.4, 47.4, 25.9, 24.1, 19.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{19}BrNS_2$ 356.0137; Found 356.0142.

(*E*)-4-(*o*-Tolyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4o):



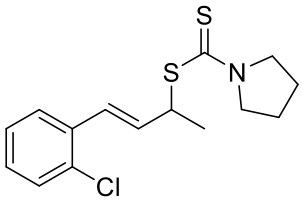
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4o** (84 mg, 72%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2922, 2851, 1460, 1430, 1337, 1249, 1218, 1183, 1162, 1000, 955, 913, 867, 825, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.43 (t, *J* = 2.4 Hz, 1H), 7.17–7.11 (m, 3H), 6.88 (d, *J* = 15.8 Hz, 1H), 6.22 (dd, *J* = 15.7, 7.2 Hz, 1H), 4.97–4.89 (m, 1H), 3.94 (t, *J* = 7.1 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 2.06 (quint, *J* = 6.9 Hz, 2H), 1.97 (quint, *J* = 6.6 Hz, 2H), 1.64 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.7, 135.9, 135.5, 131.3, 130.2, 128.5, 127.4, 126.0, 125.6, 54.8, 50.6, 48.2, 26.0, 24.2, 20.1, 19.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NS_2$ 292.1189; Found 292.1195.

(*E*)-4-(2-Methoxyphenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4p):



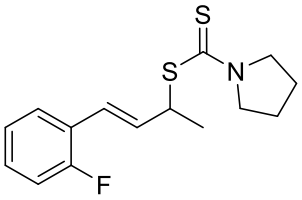
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4p** (101 mg, 82%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3019, 2977, 1598, 1488, 1463, 1434, 1330, 1247, 1183, 1162, 1028, 953, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.42 (dd, J = 7.6, 1.4 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 16.3 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.42 (dd, J = 16.1, 6.8 Hz, 1H), 4.98–4.90 (m, 1H), 3.92 (t, J = 7.0 Hz, 2H), 3.82 (s, 3H), 3.60 (t, J = 7.0 Hz, 2H), 2.02 (quint, J = 6.8 Hz, 2H), 1.94 (quint, J = 6.9 Hz, 2H), 1.65 (d, J = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.7, 156.5, 130.1, 128.5, 126.6, 125.6, 125.1, 120.4, 110.7, 55.3, 54.6, 50.4, 48.2, 25.9, 24.1, 19.8 ppm. HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{16}H_{22}OS_2N$ 308.1137; Found 308.1144.

(*E*)-4-(2-Chlorophenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4q):



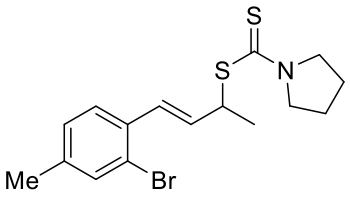
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4q** (99.8 mg, 80%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2923, 2870, 1641, 1590, 1461, 1427, 1372, 1329, 1249, 1219, 1182, 1161, 1047, 1034, 998, 954, 916, 865, 826, 771, 751, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.7, 1.7 Hz, 1H), 7.33 (dd, J = 7.7, 1.4 Hz, 1H), 7.22–7.12 (m, 2H), 7.02 (dd, J = 16.0, 1.0 Hz, 1H), 6.40 (dd, J = 15.9, 6.4 Hz, 1H), 5.01–4.91 (m, 1H), 3.94 (t, J = 7.1 Hz, 2H), 3.63 (t, J = 6.8 Hz, 2H), 2.11–2.02 (m, 2H), 2.01–1.94 (m, 2H), 1.66 (d, J = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.5, 135.0, 133.1, 132.9, 129.6, 128.5, 126.8, 126.7, 126.5, 54.9, 50.6, 47.7, 26.0, 24.2, 19.5 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{19}ClNS_2$ 312.0642; Found: 312.0640.

(*E*)-4-(2-Fluorophenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4r):



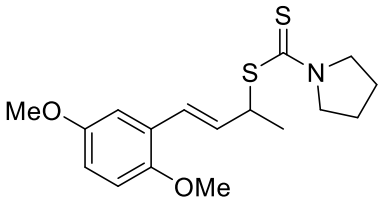
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4r** (76.8 mg, 65%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2969, 2925, 2870, 1487, 1454, 1431, 1330, 1249, 1230, 1182, 1162, 1090, 999, 954, 916, 867, 827, 797, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49–7.40 (m, 1H), 7.23–7.13 (m, 1H), 7.12–6.97 (m, 2H), 6.80 (d, J = 16.2 Hz, 1H), 6.48 (dd, J = 16.4, 6.9 Hz, 1H), 5.02–4.89 (m, 1H), 3.94 (t, J = 6.7 Hz, 2H), 3.62 (t, J = 6.9 Hz, 2H), 2.06 (quint, J = 6.8 Hz, 2H), 1.97 (quint, J = 6.4 Hz, 2H), 1.64 (d, J = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.6, 161.4 and 159.0 (d, $J_{C–F}$ = 248.6 Hz), 132.7 and 132.65 (d, $J_{C–F}$ = 5.0 Hz), 128.8 and 128.7 (d, $J_{C–F}$ = 8.1 Hz), 127.4 and 127.3 (d, $J_{C–F}$ = 3.7 Hz), 124.7 and 124.6 (d, $J_{C–F}$ = 11.5 Hz), 124.0 and 123.98 (d, $J_{C–F}$ = 3.6 Hz), 122.8 and 122.77 (d, $J_{C–F}$ = 3.8 Hz), 115.8 and 115.5 (d, $J_{C–F}$ = 22.4 Hz), 54.8, 50.6, 48.0, 26.0, 24.2, 19.6 ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ = −117.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{19}FNS_2$ 296.0938; Found 296.0944.

(*E*)-4-(2-Bromo-4-methylphenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4s):



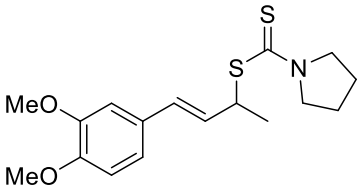
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4s** (115.6 mg, 78%) as a pale yellow oil; IR ($CHCl_3$) ν_{max} = 2969, 2921, 2869, 1602, 1485, 1458, 1430, 1373, 1337, 1329, 1249, 1182, 1162, 1055, 1038, 1020, 998, 954, 868, 811, 696, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.42–7.33 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.00–4.90 (m, 1H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H), 2.06 (quint, *J* = 6.6 Hz, 2H), 1.97 (quint, *J* = 6.7 Hz, 2H), 1.65 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.6, 139.0, 133.7, 133.2, 132.0, 129.0, 128.3, 126.6, 123.5, 54.8, 50.6, 47.7, 26.0, 24.2, 20.7, 19.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{21}BrNS_2$ 370.0294; Found 370.0298.

(*E*)-4-(2,5-Dimethoxyphenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4t):



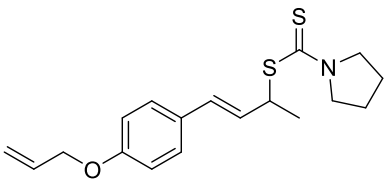
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4t** (110.7 mg, 82%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2952, 2871, 2832, 1605, 1581, 1492, 1431, 1372, 1329, 1284, 1248, 1180, 1162, 1130, 1107, 1046, 1023, 998, 954, 971, 954, 916, 867, 838, 828, 802, 716, 697, 665, 596, 553, 512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.98 (d, *J* = 2.8 Hz, 1H), 6.97–6.92 (m, 1H), 6.80–6.72 (m, 2H), 6.39 (dd, *J* = 16.1, 6.8 Hz, 1H), 4.99–4.89 (m, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.05 (quint, *J* = 6.6 Hz, 2H), 1.95 (quint, *J* = 7.0 Hz, 2H), 1.64 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.8, 153.6, 151.1, 130.6, 126.6, 125.0, 113.6, 112.2, 111.9, 56.2, 55.7, 54.7, 50.5, 48.2, 26.0, 24.2, 19.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{24}NO_2S_2$ 338.1243; Found 338.1244.

(*E*)-4-(3,4-Dimethoxyphenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4u):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4u** (109.3 mg, 81%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 3019, 2977, 1513, 1463, 1433, 1264, 1161, 1141, 1026, 97, 954, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.89–6.85 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.8, 6.9 Hz, 1H), 4.92–4.87 (m, 1H), 3.87 (t, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.60–3.53 (m, 2H), 1.99 (quint, *J* = 4.8 Hz, 2H), 1.90 (quint, *J* = 4.8 Hz, 2H), 1.59 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.4, 148.7, 148.5, 129.9, 129.6, 127.8, 119.4, 110.8, 108.5, 55.7, 55.6, 54.6, 50.3, 47.7, 25.8, 24.0, 19.8 ppm. HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{24}NO_2S_2$ 338.1243; Found 338.1249.

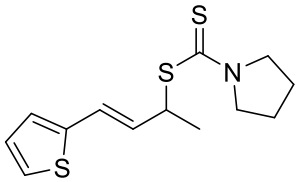
(*E*)-4-(4-(Allyloxy)phenyl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4v):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4v** (97.4 mg, 73%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3032, 2972, 2922, 2870, 1646, 1606, 1575, 1508, 1428, 1371, 1329, 1298, 1247, 1175, 1162, 1107, 1053, 1020, 997,

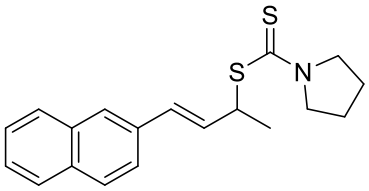
954, 916, 851, 817, 732, 697, 646, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.9 Hz, 1H), 6.08–5.96 (m, 1H), 5.38 (dd, *J* = 5.3, 1.5 Hz, 1H), 5.25 (dd, *J* = 5.2, 1.1 Hz, 1H), 4.95–4.86 (m, 1H), 4.49 (d, *J* = 5.2 Hz, 2H), 3.89 (t, *J* = 6.9 Hz, 2H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.00 (quint, *J* = 6.7 Hz, 2H), 1.92 (quint, *J* = 6.8 Hz, 2H), 1.61 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.4, 157.9, 132.9, 129.7, 129.5, 127.6, 127.3, 117.4, 114.5, 68.5, 54.5, 50.3, 47.7, 25.8, 24.0, 19.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{24}NOS_2$ 334.1295; Found 334.1305.

(*E*)-4-(Thiophen-2-yl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4w):



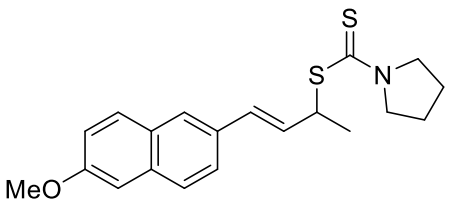
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4w** (81.6 mg, 72%) as a colourless oil; IR ($CHCl_3$) ν_{max} = 2962, 2871, 1433, 1330, 1163, 1041, 998, 954, 851, 699, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.13 (dd, *J* = 6.0, 1.5 Hz, 1H), 6.96–6.91 (m, 2H), 6.78 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 15.7, 7.0 Hz, 1H), 4.95–4.86 (m, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 2.05 (quint, *J* = 6.8 Hz, 2H), 1.96 (quint, *J* = 7.2 Hz, 2H), 1.60 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.6, 142.0, 129.7, 127.3, 125.7, 124.1, 123.8, 54.8, 50.5, 47.8, 26.0, 24.2, 19.8 ppm. HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{13}H_{18}NS_3$ 284.0596; Found 284.0601.

(*E*)-4-(Naphthalen-2-yl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4x):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4x** (104.8 mg, 80%) as a pale yellow oil; IR ($CHCl_3$) ν_{max} = 3042, 2968, 2922, 2870, 1590, 1508, 1459, 1429, 1329, 1281, 1249, 1219, 1182, 1162, 1036, 1012, 998, 954, 916, 865, 825, 796, 776, 697, 557 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.55–7.40 (m, 4H), 6.38 (dd, *J* = 15.7, 7.0 Hz, 1H), 5.11–5.00 (m, 1H), 3.95 (t, *J* = 6.8 Hz, 2H), 3.64 (t, *J* = 6.9 Hz, 2H), 2.06 (quint, *J* = 6.6 Hz, 2H), 1.97 (quint, *J* = 6.7 Hz, 2H), 1.73 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.7, 134.6, 133.5, 133.3, 131.2, 128.4, 127.8, 126.0, 125.7, 125.5, 123.9, 123.8, 54.8, 50.6, 48.2, 26.0, 24.2, 20.0 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{22}NS_2$ 328.1189; Found 328.1183.

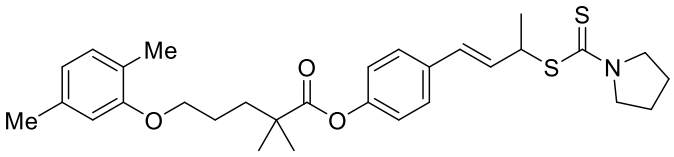
(*E*)-4-(6-Methoxynaphthalen-2-yl)but-3-en-2-yl pyrrolidine-1-carbodithioate (4y):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4y** (121.6 mg, 85%) as a yellow semi-solid; IR ($CHCl_3$): ν_{max} = 2968, 2870, 1657, 1629, 1601, 1546, 1502, 1482, 1460, 1427, 1391, 1338, 1269, 1244, 1218, 1162, 1120, 1030, 998, 953, 855, 810, 772, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.66 (m, 3H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.20–7.08 (m, 2H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.50 (dd, *J* = 15.9, 6.9 Hz, 1H), 5.09–4.96 (m, 1H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 3.67–3.57 (m, 2H), 2.10–1.88 (m, 4H), 1.71 (d, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 191.5, 157.5, 133.9, 132.0, 130.4, 129.3,

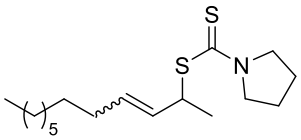
129.2, 128.8, 126.8, 126.0, 123.9, 118.7, 105.6, 55.1, 54.6, 50.4, 47.8, 25.8, 24.0, 19.8 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}NOS_2$ 358.1294; Found: 358.1292.

(*E*)-4-(3-((Pyrrolidine-1-carbonothioyl)thio)but-1-en-1-yl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4z):



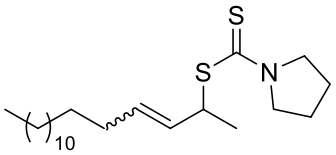
The residue was purified using petroleum ether/EtOAc (85:15) as eluent to give **4z** (176.7 mg, 84%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 2924, 2871, 1750, 1614, 1585, 1507, 1431, 1330, 1264, 1199, 1164, 1113, 1047, 998, 954, 913, 866, 803, 733, 531 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.69–6.61 (m, 3H), 6.33 (dd, *J* = 16.3, 6.8 Hz, 1H), 4.99–4.89 (m, 1H), 4.01–3.97 (m, 2H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 2.06 (quint, *J* = 6.7 Hz, 2H), 1.97 (quint, *J* = 7.0 Hz, 2H), 1.90–1.85 (m, 4H), 1.63 (d, *J* = 6.9 Hz, 3H), 1.36 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.7, 176.3, 156.9, 150.4, 136.4, 134.5, 130.3, 130.28, 129.5, 127.3, 123.6, 121.6, 120.7, 112.0, 67.8, 54.8, 50.6, 47.8, 42.4, 37.1, 26.0, 25.2, 25.1, 24.2, 21.4, 19.8, 15.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{40}NO_3S_2$ 526.2445; Found 526.2440.

(*E*)-Dodec-3-en-2-yl pyrrolidine-1-carbodithioate (4aa):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4aa** (99.1 mg, 79%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 2925, 2854, 1460, 1430, 1338, 1250, 1219, 1183, 1163, 1006, 955, 908, 868, 826, 733, 648 cm^{-1}; (Data for *E*/*Z* = 2:1) ^1H NMR (400 MHz, $CDCl_3$) δ = 5.72–5.55 (m, 2H), 5.48–5.36 (m, 1H), 4.65 (quint, *J* = 6.7 Hz, 1H), 4.57 (q, *J* = 6.5 Hz, 0.5H, minor isomer), 3.89 (t, *J* = 6.9 Hz, 3H), 3.58 (t, *J* = 6.9 Hz, 3H), 2.01 (q, *J* = 7.1 Hz, 4H), 1.94 (q, *J* = 7.1 Hz, 4H), 1.67 (d, *J* = 7.0 Hz, 2H, minor isomer), 1.48 (d, *J* = 6.8 Hz, 3H), 1.39–1.30 (m, 3H), 1.29–1.22 (m, 16H), 0.85 (t, *J* = 7.1 Hz, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 192.1, 192.07, 132.2, 130.3, 129.7, 127.6, 54.6, 54.58, 53.0, 50.4, 47.6, 34.7, 32.3, 31.8, 29.4, 29.3, 29.29, 29.2, 29.1, 29.0, 27.1, 25.9, 24.1, 22.6, 20.1, 17.9, 14.0 ppm; HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{32}NS_2$ 314.1971; Found 314.1978.

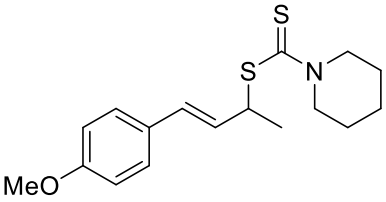
(*E*)-Heptadec-3-en-2-yl pyrrolidine-1-carbodithioate (4ab):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ab** (141.2 mg, 92%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2990, 2940, 2860, 1591, 1489, 1430, 1340, 1280, 1246, 1190, 1185, 1083, 1010, 972, 950, 881, 850 cm^{-1}. (Data for *E*/*Z* = 2:1) ^1H NMR (500 MHz, $CDCl_3$): δ = 5.81–5.67 (m, 1H), 5.59 (dd, *J* = 15.2, 6.8 Hz, 1H), 5.50–5.34 (m, 1H), 4.67 (quint, *J* = 13.8, 6.8 Hz, 1H), 4.58 (q, *J* = 14.9, 8.1 Hz, 0.5H, minor isomer), 3.91 (t, *J* = 6.9 Hz, 3H), 3.59 (t, *J* = 6.6 Hz, 3H), 2.07–1.98 (m, 6H), 1.97–1.91 (m, 4H), 1.68 (d, *J* = 5.2 Hz, 2H, minor isomer), 1.49 (d, *J* = 7.0 Hz, 3H), 1.25–1.22 (m, 30H), 0.86 (t, *J* = 6.7 Hz, 5H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.2, 192.1, 132.2, 130.3, 129.8,

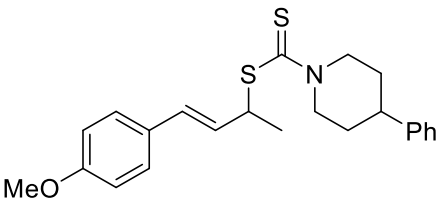
127.6, 54.7, 54.6, 53.0, 50.4, 47.6, 34.7, 32.4, 31.9, 29.6, 29.59, 29.5, 29.48, 29.45, 29.4, 29.3, 29.29, 29.1, 29.08, 27.1, 26.0, 24.2, 22.6, 20.2, 17.9, 14.1 ppm. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{42}NS_2$ 384.2753; Found: 384.2755.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl piperidine-1-carbodithioate (4ac):



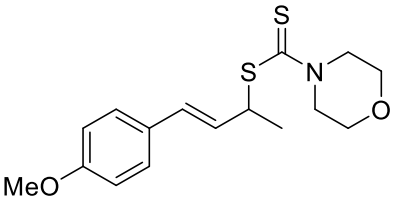
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ac** (78.4 mg, 61%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3031, 2994, 2935, 2857, 2835, 1606, 1576, 1511, 1473, 1455, 1425, 1299, 1244, 1227, 1175, 1132, 1113, 1033, 1017, 973, 892, 852, 816, 763, 665, 603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.33–7.28 (m, 2H), 6.86–6.81 (m, 2H), 6.66–6.56 (m, 1H), 6.25 (dd, *J* = 16.2, 6.9 Hz, 1H), 4.95–4.86 (m, 1H), 4.39–4.16 (m, 2H), 3.96–3.81 (m, 2H), 3.79 (s, 3H), 1.75–1.64 (m, 6H), 1.62 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 194.6, 159.2, 130.0, 129.6, 127.8, 127.6, 113.9, 55.2, 52.6, 51.3, 48.8, 25.9, 25.4, 24.3, 19.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{24}NOS_2$ 322.1295; Found 322.1301.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl 4-phenylpiperidine-1-carbodithioate (4ad):



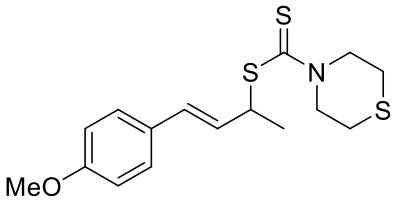
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ad** (98.6 mg, 62%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 3027, 2920, 1606, 1576, 1509, 1493, 1471, 1442, 1421, 1361, 1297, 1248, 1208, 1172, 1102, 1031, 985, 964, 920, 903, 850, 816, 757, 699, 664 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.31 (m, 4H), 7.30–7.20 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.83 (s, 1H), 5.03–4.92 (m, 1H), 4.83 (s, 1H), 3.84 (s, 3H), 3.36–3.06 (m, 2H), 2.97–2.85 (m, 1H), 2.00 (d, *J* = 12.4 Hz, 2H), 1.94–1.76 (m, 2H), 1.71 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 195.1, 159.1, 144.3, 130.0, 129.5, 128.5, 127.5, 126.7, 126.6, 113.9, 55.2, 51.9, 50.5, 49.0, 42.6, 33.2, 32.7, 19.9 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}NOS_2$ 398.1607; Found: 398.1609.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl morpholine-4-carbodithioate (4ae):



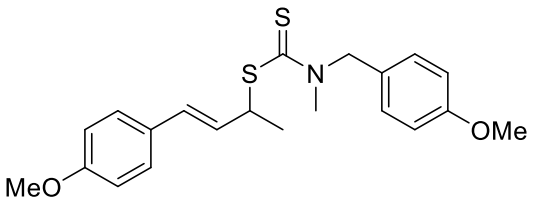
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ae** (75 mg, 58%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 2963, 2924, 2856, 1606, 1576, 1511, 1461, 1418, 1300, 1268, 1249, 1227, 1212, 1175, 1114, 1031, 990, 971, 909, 853, 818, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.36–7.27 (m, 2H), 6.90–6.78 (m, 2H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.22 (dd, *J* = 16.0, 7.0 Hz, 1H), 4.97–4.87 (m, 1H), 4.47–4.15 (m, 2H), 4.15–3.87 (m, 2H), 3.80 (s, 3H), 3.78–3.69 (m, 4H), 1.63 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.6, 159.3, 130.4, 129.4, 127.6, 127.3, 113.9, 66.2 (2C), 55.3, 50.6 (2C), 48.8, 19.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NO_2S_2$ 324.1087; Found 324.1081.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl thiomorpholine-4-carbodithioate (4af):



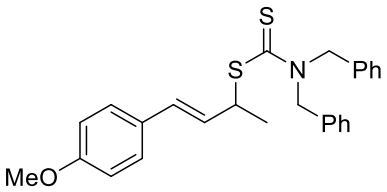
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4af** (89.6 mg, 66%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3030, 2959, 2914, 2833, 1606, 1576, 1510, 1464, 1434, 1411, 1356, 1282, 1247, 1213, 1189, 1175, 1143, 1032, 999, 969, 949, 935, 851, 817, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.4, 6.9 Hz, 1H), 4.96–4.83 (m, 1H), 4.77–4.42 (m, 2H), 4.41–4.06 (m, 2H), 3.79 (s, 3H), 2.84–2.61 (m, 4H), 1.63 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 195.8, 159.2, 130.3, 129.4, 127.5, 127.2, 113.9, 55.2, 53.9, 53.2, 49.0, 27.1 (2C), 19.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NOS_3$ 340.0859; Found 340.0864.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl(4-methoxybenzyl)(methyl) carbamodithioate (4ag):



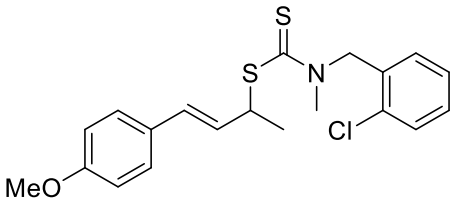
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ag** (116.3 mg, 75%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2928, 2834, 1606, 1509, 1476, 1439, 1381, 1349, 1299, 1242, 1173, 1107, 1030, 967, 845, 809, 751, 665, 638, 606, 558, 529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.2 Hz, 2H), 7.24 (s, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.91–6.80 (m, 4H), 6.63 (d, *J* = 15.8 Hz ,1H), 6.35–6.20 (m, 1H), 5.30 (s, 1H), 4.98–4.86 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.43 (s, 1H), 3.21 (s, 2H), 1.66 (d, *J* = 6.8 Hz , 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 197.4, 196.4, 159.2, 130.5, 130.1, 129.5, 129.2, 128.5, 127.7, 127.6, 126.7, 114.2, 114.0, 113.9, 58.5, 57.1, 55.2, 49.5, 49.4, 42.7, 38.5, 19.8 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{26}NO_2S_2$ 388.1400; Found: 388.1401.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl dibenzylcarbamodithioate (4ah):



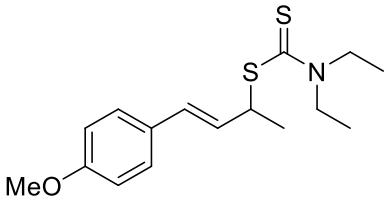
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ah** (119.7 mg, 69%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 3016, 2932, 1664, 1606, 1511, 1495, 1453, 1412, 1358, 1247, 1175, 1149, 1078, 1030, 967, 849, 817, 699, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.37–7.31 (m, 10H), 7.25–7.22 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.36 (s, 2H), 5.05–5.00 (m, 1H), 4.94 (s, 2H), 3.83 (s, 3H), 1.72 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.6, 159.2, 135.5, 134.6, 130.2, 129.4, 128.8, 128.6, 127.8, 127.6, 127.3, 127.0, 113.9, 55.7, 55.2, 53.9, 49.9, 19.8 ppm. HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{26}H_{28}NS_2O$ 434.1607 Found 434.1607.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl(2-chlorobenzyl)(methyl)carbamodithioate (4ai):



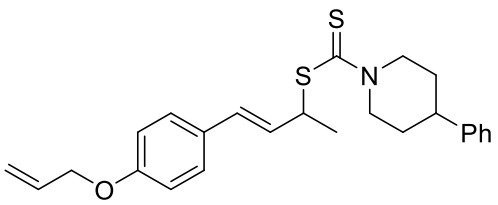
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4ai** (112.9 mg, 72%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2926, 2834, 1691, 1679, 1641, 1606, 1573, 1546, 1510, 1477, 1442, 1380, 1344, 1271, 1248, 1220, 1174, 1104, 1049, 1038, 976, 851, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.00 (m, 6H), 6.94–6.78 (m, 2H), 6.73–6.53 (m, 1H), 6.41–6.12 (m, 1H), 5.48 (s, 1H), 5.09 (s, 1H), 5.00–4.78 (m, 1H), 3.80 (s, 3H), 3.51 (s, 1H), 3.28 (s, 2H), 1.74–1.56 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 198.2, 197.6, 159.2, 133.1, 132.9, 132.6, 132.2, 130.2, 129.6, 129.4, 128.9, 128.7, 128.1, 127.5, 127.3, 127.1, 113.9, 56.5, 55.2, 49.6, 43.4, 39.2, 19.8 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{23}ClNOS_2$ 392.0905; Found: 392.0902.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-yl diethylcarbamodithioate (4aj):



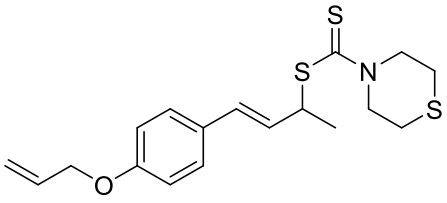
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4aj** (76.8 mg, 62%) as a colorless oil**;** IR ($CHCl_3$) ν_{max} = 3031, 2975, 2932, 2871, 2834, 1607, 1577, 1510, 1485, 1460, 1441, 1416, 1378, 1355, 1300, 1368, 1250, 1208, 1175, 1142, 1068, 1034, 980, 917, 851, 831, 817, 768, 663, 567 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.66–6.55 (m, 1H), 6.26 (dd, *J* = 15.7, 6.8 Hz, 1H), 4.93–4.84 (m, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.71 (q, *J* = 6.9 Hz, 2H), 1.63 (d, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 194.5, 159.1, 129.8, 129.5, 127.6, 127.5, 113.8, 55.1, 49.1, 48.6, 46.6, 19.8, 12.4, 11.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{24}NOS_2$ 310.1294; Found 310.1303.

(*E*)-4-(4-Allyloxyphenyl)but-3-en-2-yl 4-phenylpiperidine-1-carbodithioate (4al):



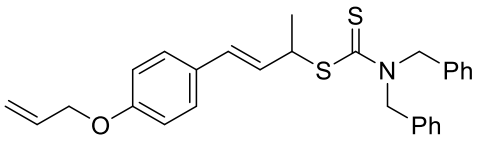
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4al** (144 mg, 85%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2970, 2928, 2872, 1670, 1596, 1492, 1429, 1335, 1276, 1230, 1180, 1160, 1095, 1019, 976, 951, 858, 810, 775, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.29 (m, 4H), 7.28–7.17 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 16.3 Hz, 1H), 6.28 (dd, *J* = 15.9, 7.0 Hz, 1H), 6.12–5.99 (m, 1H), 5.80 (br s, 1H), 5.42 (dd, *J* = 16.3, 1.1 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.94 (q, *J* = 13.8, 6.8 Hz, 1H), 4.80 (br s, 1H), 4.54 (d, *J* = 5.2 Hz, 2H), 3.16 (br s, 2H), 2.94–2.79 (m, 1H), 1.97 (d, *J* = 12.4 Hz, 2H), 1.81 (br s, 2H), 1.66 (d, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 195.1, 158.1, 144.3, 133.1, 130.0, 129.7, 128.6, 127.5, 126.7, 126.6, 117.6, 114.7, 68.7, 51.9, 50.6, 49.0, 42.6, 33.2, 32.7, 19.9 ppm. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NOS_2$ 424.1764; Found: 424.1765.

(*E*)-4-(4-Allyloxyphenyl)but-3-en-2-yl thiomorpholine-4-carbodithioate (4am):



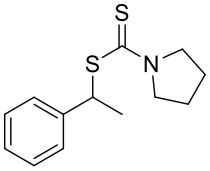
The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4am** (102.4 mg, 70%) as a yellow oil; IR ($CHCl_3$) ν_{max} = 3034, 2964, 2919, 1647, 1606, 1576, 1509, 1465, 1412, 1357, 1284, 1246, 1215, 1190, 1176, 1144, 1029, 997, 949, 935, 909, 850, 818, 734, 649, 599, 529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 7.0 Hz, 1H), 6.11–5.98 (m, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.94–4.82 (m, 1H), 4.75–4.43 (m, 4H), 4.41–4.10 (m, 2H), 2.84–2.61 (m, 4H), 1.62 (d, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.9, 158.2, 133.1, 130.3, 129.5, 127.5, 127.3, 117.7, 114.7, 68.7, 54.0, 53.1, 49.0, 27.2 (2C), 19.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{24}NOS_3$ 366.1015; Found 366.1017.

(*E*)-4-(4-Allyloxyphenyl)but-3-en-2-yl dibenzylcarbamodithioate (4an):



The residue was purified using petroleum ether/EtOAc (9:1) as eluent to give **4an** (145.3 mg, 79%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 3019, 2978, 2924, 1605, 1509, 1495, 1453, 1410, 1354, 1175, 1152, 1079, 1029, 967, 850, 699, 668, 556, 516 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.40–7.34 (m, 10H), 7.27–7.22 (m, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.34 (dd, *J* = 15.9, 7.4 Hz, 1H), 6.15–6.06 (m, 1H), 5.50–5.33 (m, 4H), 5.09–5.03 (m, 1H), 4.96 (s, 2H), 4.59–4.57 (m, 2H), 1.74 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.4, 158.1, 135.4, 134.6, 133.0, 130.1, 129.5, 128.7, 128.6, 127.7, 127.5, 127.3, 127.0, 117.5, 114.6, 68.6, 55.6, 53.8, 49.8, 19.8 ppm; HRMS (Q-TOF): *m/z* $[M+H]^+$ calcd for $C_{28}H_{30}NS_2O$ 460.1764; Found 460.1773.

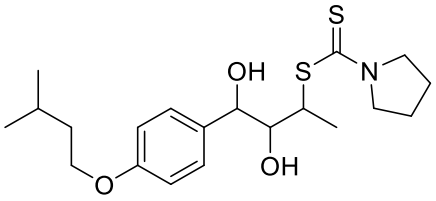
1-Phenylethyl pyrrolidine-1-carbodithioate (6a):



Colorless oil; IR ($CHCl_3$) ν_{max} = 3064, 3027, 2973, 2871, 1601, 1491, 1430, 1369, 1329, 1249, 1219, 1161, 1039, 1008, 953, 914, 867, 826, 765, 731, 699, 583, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 5.32 (q, *J* = 7.1 Hz, 1H), 3.91 (t, *J* = 6.9 Hz, 2H), 3.65–3.48 (m, 2H), 2.00 (quint, *J* = 6.2 Hz, 2H), 1.92 (quint, *J* = 6.7 Hz, 2H), 1.79 (d, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.4, 142.0, 128.3, 127.5, 127.1, 54.6, 50.3, 49.8, 25.8, 24.0, 21.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{18}NS_2$ 252.0876; Found 252.0876.

3,4-Dihydroxy-4-(4-isopentyloxyphenyl)butan-2-yl-pyrrolidine-1 carbodithioate (7):

To a mixture of $K_3[Fe(CN)_6]$ (408 mg, 1.239 mmol, 3.0 equiv.), K_2CO_3 (171.2 mg, 1.239 mmol, 3.0 equiv.), and pyridine (0.3 mL) in *t*-BuOH-H_2O (1:1, 4.0 mL) cooled at 0 °C was added $K_2OsO_4 \cdot 2H_2O$ (0.6 mg, 0.00165 mmol, 0.4 mol%) followed by methane sulfonamide (39.3 mg, 0.413 mmol, 1.0 equiv.). After stirring for 5 min at 0 °C, the olefin **4e** (150 mg, 0.413

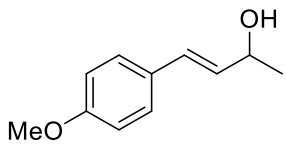


mmol, 1.0 equiv.) was added in one portion. The reaction mixture was stirred at 0 °C for 24 h and then quenched with solid Na_2SO_3 (100 mg). The stirring was continued for an additional 45 min and the solution was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (1:1) as the eluent to give the inseparable diastereomeric mixture of **7** (dr = 1:0.5, 131.4 mg, 80%) as colorless oil; IR ($CHCl_3$) ν_{max} = 3410, 2957, 2928, 2871, 1611, 1584, 1513, 1462, 1430, 1330, 1303, 1248, 1175, 1125, 1058, 1034, 1005, 968, 954, 914, 867, 829, 733, 645, 604, 556 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.30 (overlapped, dd, *J* = 8.9, 2.7 Hz, 4H), 6.88 (overlapped, dd, *J* = 8.9 Hz, 4H), 4.84 (minor, d, *J* = 3.1 Hz, 1H), 4.76 (major, d, *J* = 6.7 Hz, 1H), 4.26–4.11 (overlapped, m, 2H), 3.98 (overlapped, t, *J* = 6.6 Hz, 4H), 3.92 (overlapped, t, *J* = 6.8 Hz, 4H), 3.82–3.73 (overlapped, m, 2H), 3.73–3.64 (overlapped, m, 4H), 2.09 (overlapped, quint, *J* = 6.9 Hz, 4H), 1.99 (overlapped, quint, *J* = 6.7 Hz, 4H), 1.90–1.78 (overlapped, m, 2H), 1.67 (overlapped, q, *J* = 6.6 Hz, 4H), 1.48 (minor, d, *J* = 6.9 Hz, 3H), 1.43 (major, d, *J* = 7.0 Hz, 3H), 0.97 (overlapped, d, *J* = 6.6 Hz, 12H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 192.3, 191.9, 158.9, 158.6, 132.6, 132.5, 128.0, 127.6, 114.4, 114.3, 79.6, 78.4, 74.7, 72.2, 66.3, 55.2, 55.0, 50.9, 50.8, 49.1, 48.7, 37.9, 26.0, 25.9, 25.0, 24.2, 24.17, 22.5, 19.9, 16.4 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{32}NO_3S_2$ 398.1819; Found 398.1818.

General procedure for preparation of 8a and 8b

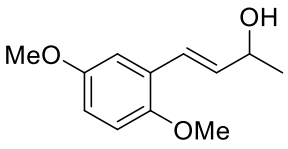
To a stirred solution of **4b** or **4t** (0.097 mmol) in DMF:H_2O (7:1) was added $PdCl_2$ (2 mg, 0.0097 mmol, 10 mol%) and $CuCl_2$ (1.3 mg, 0.0097 mmol, 10 mol%) at room temperature. The reaction mixture was warmed to 60 °C and stirred for 3 h with O_2 bubbling at same temperature. After completion, the mixture was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as eluent to give allyl alcohols **8a** or **8b**, respectively.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-ol (8a):



The residue was purified using petroleum ether/EtOAc (85:15) as eluent to give **8a** (13 mg, 75%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 3407, 3018, 2975, 2839, 1608, 1578, 1512, 1465, 1420, 1372, 1301, 1249, 1175, 1141, 1108, 1034, 968, 946, 807, 668, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 16.2 Hz, 1H), 6.12 (dd, *J* = 15.7, 6.4 Hz, 1H), 4.50–4.42 (m, 1H), 3.80 (s, 3H), 1.71 (s, 1H), 1.35 (d, *J* = 6.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.2, 131.4, 129.4, 129.0, 127.6, 114.0, 69.1, 55.3, 23.4 ppm; HRMS (Q-TOF): *m/z* $[M + H]^+$ $[-H_2O]$ Calcd for $C_{11}H_{13}O$ 161.0961; Found 161.0974.

(*E*)-4-(2,5-Dimethoxyphenyl)but-3-en-2-ol (8b):

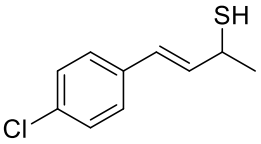


The residue was purified using petroleum ether/EtOAc (85:15) as eluent to give **8b** (14.7 mg, 73%) as a colorless oil; IR ($CHCl_3$) ν_{max} = 3396, 3010, 2970, 2835, 1606, 1583, 1465, 1427, 1367, 1283, 1179, 1162, 1144, 1048, 1027, 974, 939, 868, 841, 798, 716, 668, 605 cm^{-1}; ^1H NMR 500 MHz, $CDCl_3$): δ = 7.00–6.98 (m, 2H), 6.86 (d, *J* = 16.1 Hz, 1H), 6.80–6.76 (m, 2H), 6.25 (dd, *J* = 16.0, 6.6 Hz, 1H), 4.52–4.44 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 1.81 (br s, 1H), 1.36 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 153.6, 151.2, 134.5, 126.4, 124.1, 113.7, 112.2, 112.1, 69.3, 56.1, 55.7. 23.3 ppm; HRMS (Q-TOF): *m/z* $[M + H]^+$ [-H_2O] Calcd for $C_{12}H_{15}O_2$ 191.1067; Found 191.1082.

General procedure for preparation of 9a and 9b

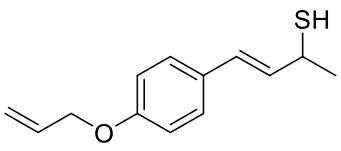
A solution of dithiocarbamate **4f** or **4v** (0.12 mmol) in Et_2O (5.0 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (9.1 mg, 0.24 mmol, 2.0 equiv.) in Et_2O (2.0 mL), and the mixture was refluxed for 2 h. The reaction was carefully quenched with aqueous hydrochloric acid (3 mL) and the solution was extracted with hexane (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether as an eluent to afford thiols **9a** or **9b**, respectively.

(*E*)-4-(4-Chlorophenyl)but-3-ene-2-thiol (9a):



The residue was purified using petroleum ether as eluent to give **9a** (19.3 mg, 81%) as a yellow oil; IR ($CHCl_3$): ν_{max} = 2910, 1606, 1475, 1420, 1297, 1162, 1031, 989, 816 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 4H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, *J* = 15.6, 7.9 Hz, 1H), 3.85–3.73 (m, 1H), 1.78 (d, *J* = 5.5 Hz, 1H), 1.49 (d, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 135.2, 135.1, 133.1, 128.7, 127.5, 126.8, 37.1, 24.3 ppm; HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{12}ClS$ 199.0344; Found: 199.0350.

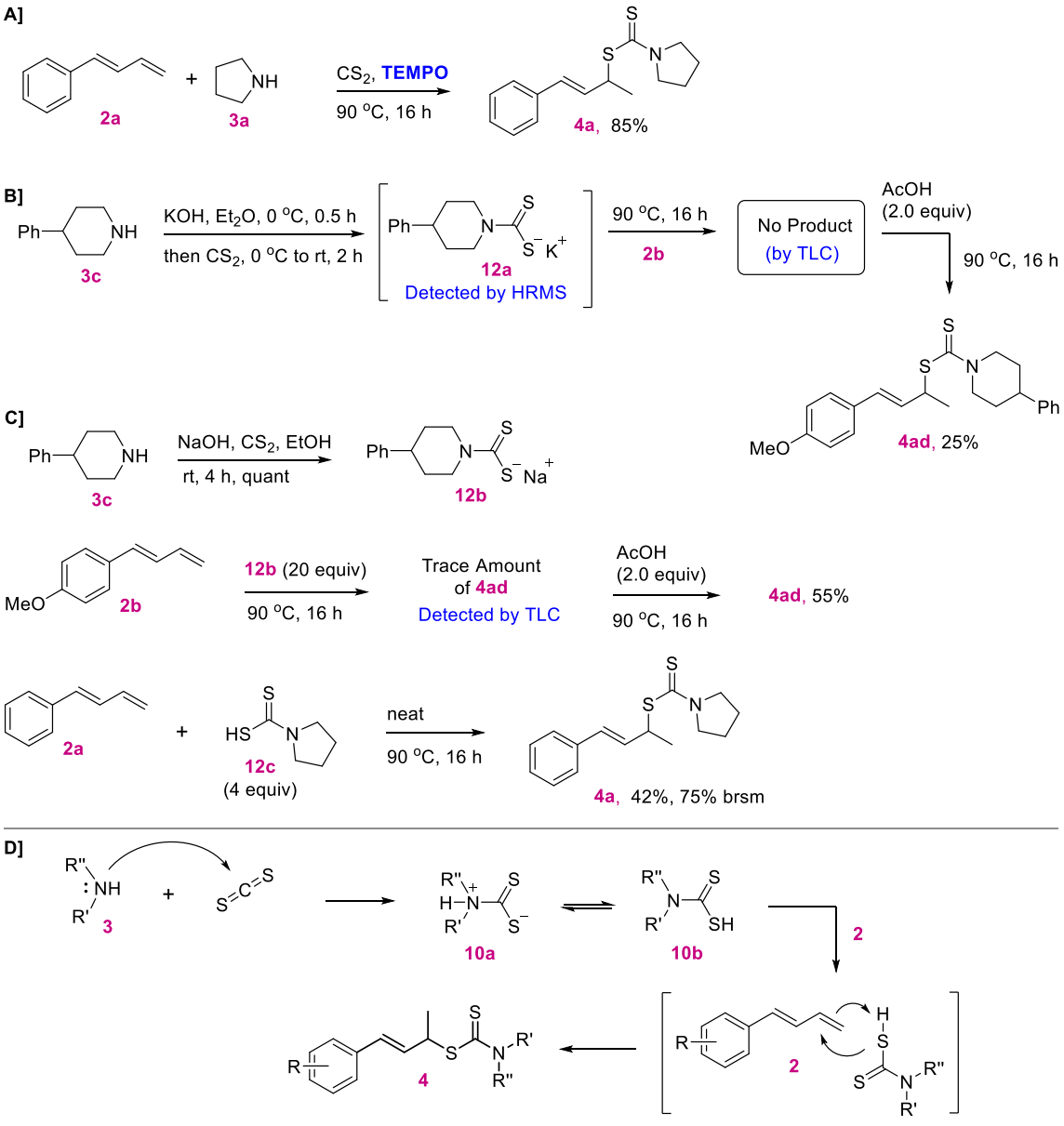
(*E*)-4-(4-Allyloxyphenyl)but-3-ene-2-thiol (9b):



The residue was purified using petroleum ether as eluent to give **9b** (22.5 mg, 85%) as a colourless oil; IR ($CHCl_3$): ν_{max} = 2915, 1610, 1590, 1480, 1410, 1260, 1155, 1030, 1006, 966, 816 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.7 Hz, 2H), 6.86 (dd, *J* = 6.8, 1.9 Hz, 2H), 6.38 (d, *J* = 15.5 Hz, 1H), 6.12 (dd, *J* = 15.7, 8.1 Hz, 1H), 6.08–5.98 (m, 1H), 5.41 (dd, *J* = 16.8, 1.6 Hz, 1H), 5.28 (dd, *J* = 10.6, 1.3 Hz, 1H), 4.53 (dt, *J* = 5.3, 1.3 Hz, 2H), 3.84–3.75 (m, 1H), 1.76 (d, *J* = 5.1 Hz, 1H), 1.49 (d, *J* = 6.7 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 158.2, 133.2, 132.5, 129.5, 127.5, 117.7, 114.8, 68.8, 37.4, 24.5 ppm. HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}OS$ 221.0995; Found: 221.1000.

Experiments for elucidating the probable reaction mechanism.

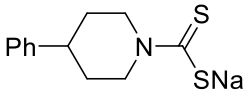
A few controlled experiments were conducted to get insights into the mechanism of the reaction (Scheme S1). Two mechanisms (radical or ionic) are possible in this case.[3] The reactions of **2a** in presence of TEMPO (1.0 equiv.) under standard conditions resulted in **4a** in 85% yields, indicating no radicals being involved (Scheme S1A). Then, to confirm the intermediate formation, the amine **3c** was treated with KOH and then CS_2. An aliquot of this analyzed indicated **12a** by HRMS (Scheme S1B). Further addition of **2b** in this reaction and continuing it for over 16 h at 90 °C, no product **4ad** was observed by TLC. To this reaction mixture, after the addition of AcOH (2.0 equiv.) and continuing for 16 h, the product **4ad** was isolated in 25% yield. This indicated the need for a proton source in the reaction. Furthermore, we prepared the intermediate **12b** quantitatively using NaOH and CS_2 (Scheme S1C).[4] This was reacted with diene **2b** at 90 °C for 16 h, wherein trace of **4ad**



Scheme S1 Control experiments and plausible reaction mechanism.

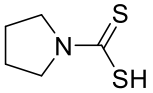
was detected by TLC. Then, the addition of AcOH (2.0 equiv.) and continuing for 16 h, the product **4ad** was isolated in 55% yield. These reactions indicate an ionic or concerted pathway in the reaction. The free aminodithiocarbamic acid **12c** (4 equiv.) reacted with diene **2a** at 90 °C in neat conditions for 16 h to furnish product **4a** in 42% yield (75% brsm). Thus, the reaction proceeds through the intermediate aminodithiocarbamic acid. Considering these observations and literature reports,[1,5] the proposed mechanism is depicted in Scheme 1SD, where amine react with CS_2 to produce the intermediate tautomers **10a** and **10b** of dithiocarbamic acid, which adds to the diene in a Markovnikov fashion *via* possible electrophilic activation of the terminal olefin bond and simultaneous attack on the partial positively charged internal carbon to deliver the final product **4**. No formation of rearranged product supports the simultaneous addition.[6]

Sodium 4-phenylpiperidine-1-carbodithioate (12b):



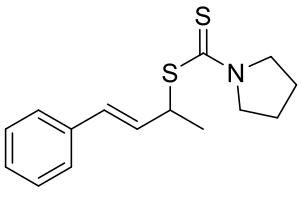
To a solution of 4-phenylpiperidine **3c** (100 mg, 0.62 mmol, 1.0 equiv.) in EtOH (5 mL) were added CS_2 (0.045 mL, 0.744 mmol, 1.2 equiv.) and NaOH (24.8 mg, 0.62 mmol, 1.0 equiv.). After stirring at room temperature for 4 h, the solvent was removed in vacuo at 50 °C to afford **12b** (160.8 mg, quant.) as a pale-yellow solid. ^{1}H NMR (400 MHz, DMSO-d6) δ = 7.28 (t, J = 7.4 Hz, 2H), 7.24–7.13 (m, 3H), 2.83 (t, J = 12.6 Hz, 2H), 2.78–2.68 (m, 1H), 2.52–2.49 (m, 2H), 1.78–1.64 (m, 2H), 1.56–1.39 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 213.3, 146.2, 128.4, 126.7, 126.0, 49.7, 42.3, 33.2 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{12}H_{14}NNa_2S_2$ 282.0358; Found 282.0360.

Pyrrolidine dithiocarbamic acid (12c):[7]



Pyrrolidine (1 mL, 14.06 mmol, 1.0 equiv.) and carbon disulphide (0.8 mL, 14.06 mmol, 1.0 equiv.) were stirred in a round bottom flask in absolute ethanol (10 mL) at 0 °C. After stirring for 2 h, the white precipitate formed was filtered off and washed with Et_2O to afford **12c** (2.0 g, quant.). M.p = 165–166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.82 (t, J = 6.8 Hz, 2H), 3.40 (t, J = 7.3 Hz, 2H), 2.04–1.84 (m, 4H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 205.2, 53.9, 45.1, 26.0, 24.5 ppm; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_5H_{10}NS_2$ 148.0249; Found 148.0247.

(*E*)-4-Phenylbut-3-en-2-yl pyrrolidine-1-carbodithioate (4a) using 12c



The mixture of diene **2a** (52.1 mg, 0.4 mmol) and aminodithiocarbamic acid **12c** (235.6 mg, 1.6 mmol, 4.0 equiv.) was heated neat in a sealed tube closed under open air. After 16 h, the residue was directly purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to give corresponding allyl dithiocarbamate **4a** (46.6 mg, 42%, 75% brsm) as colorless oil. The analytical data is same as before. [Note: we could not load more **12c** due to solubility/mixing issues].

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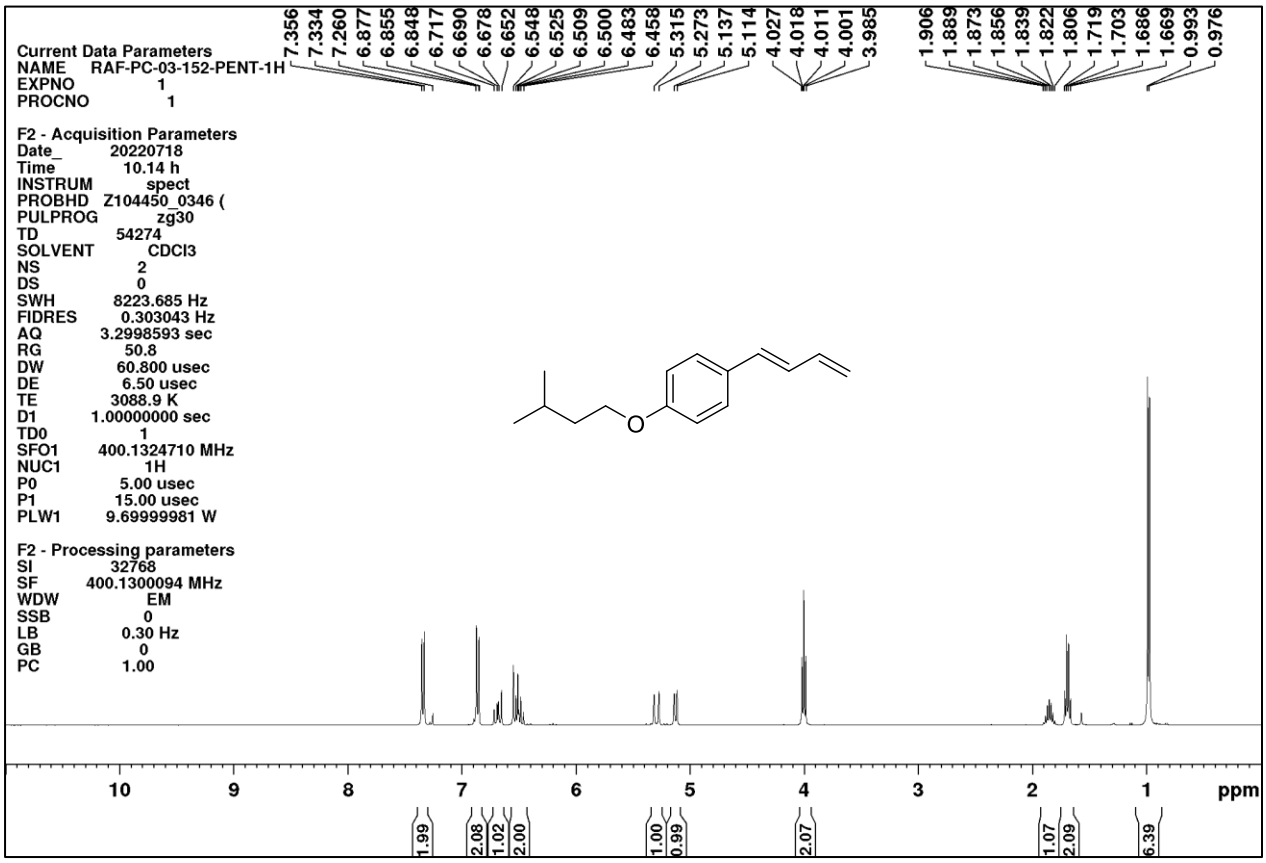
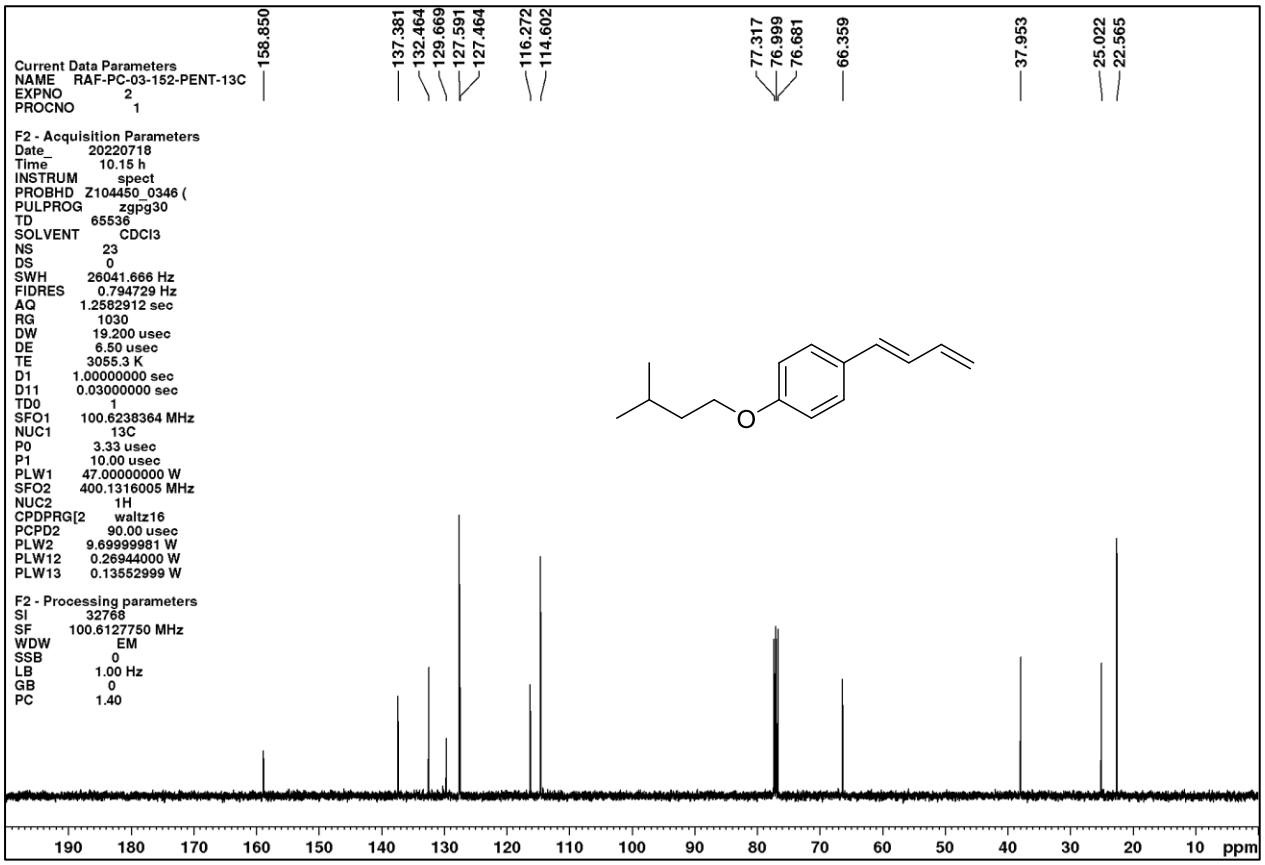
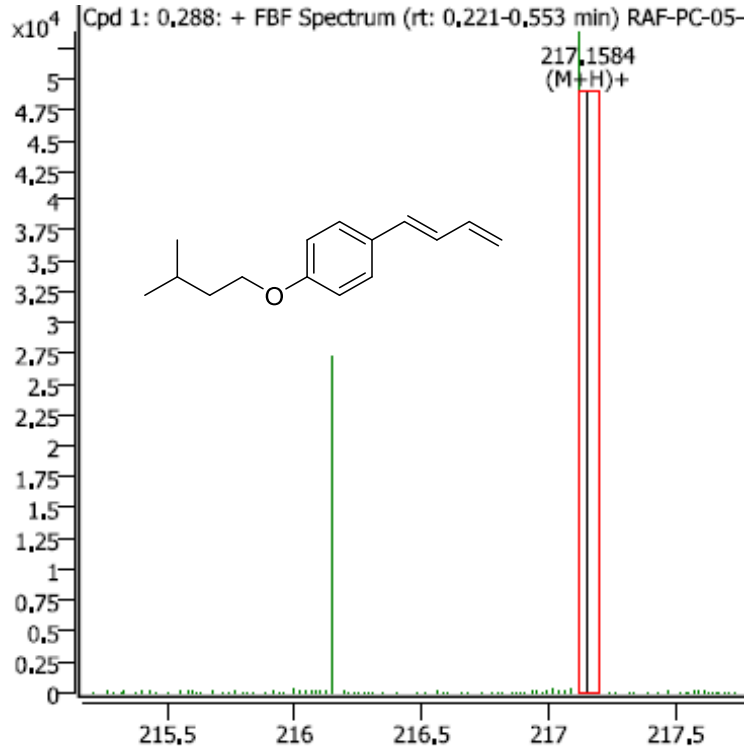
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **2e**

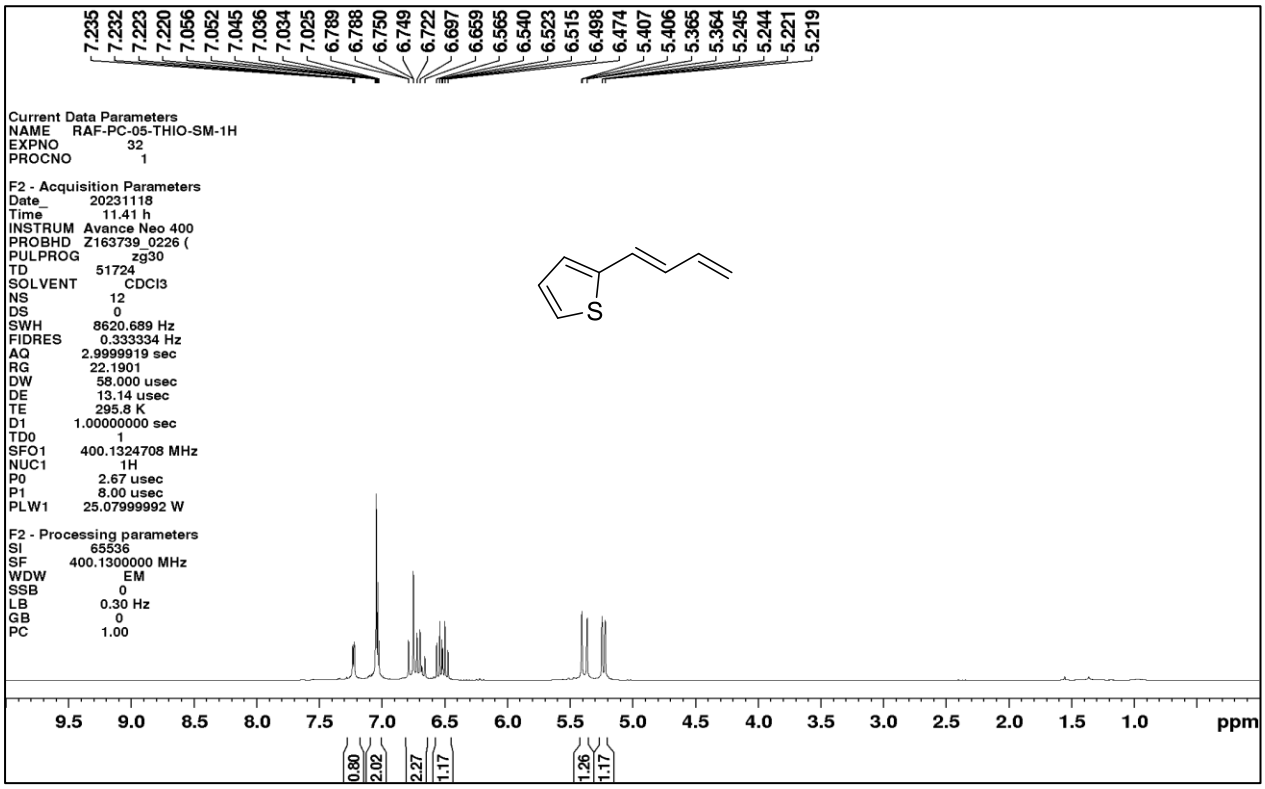


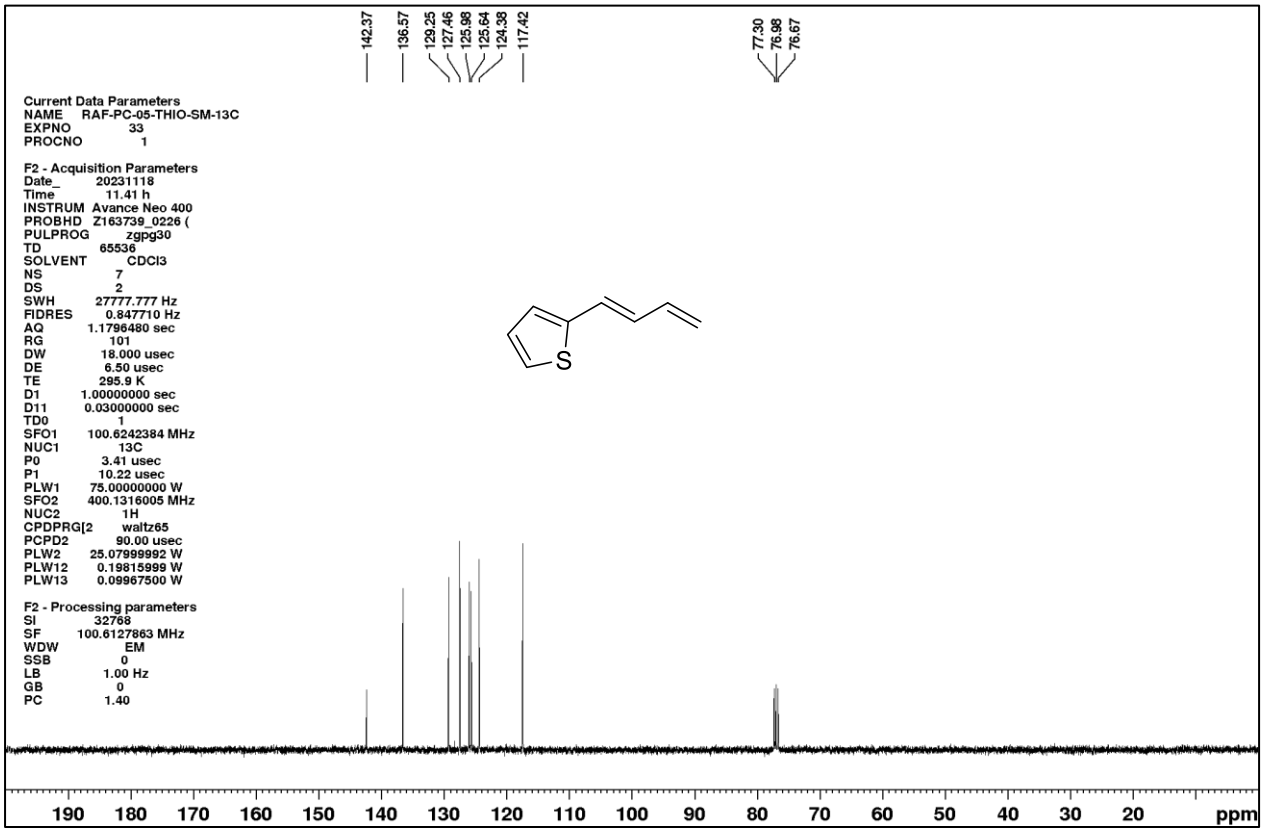


2e: HRMS (Q-TOF): *m/z* [M + H]$^+$ Calcd for $C_{15}H_{21}O$ 217.1587; Found 217.1584.

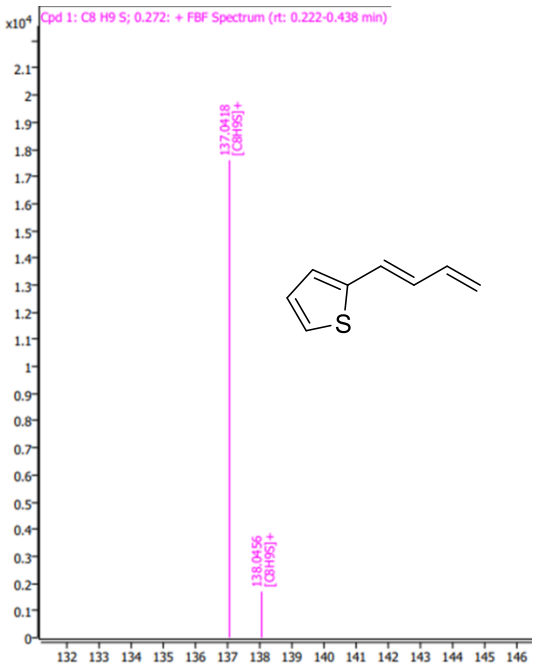


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **2w**

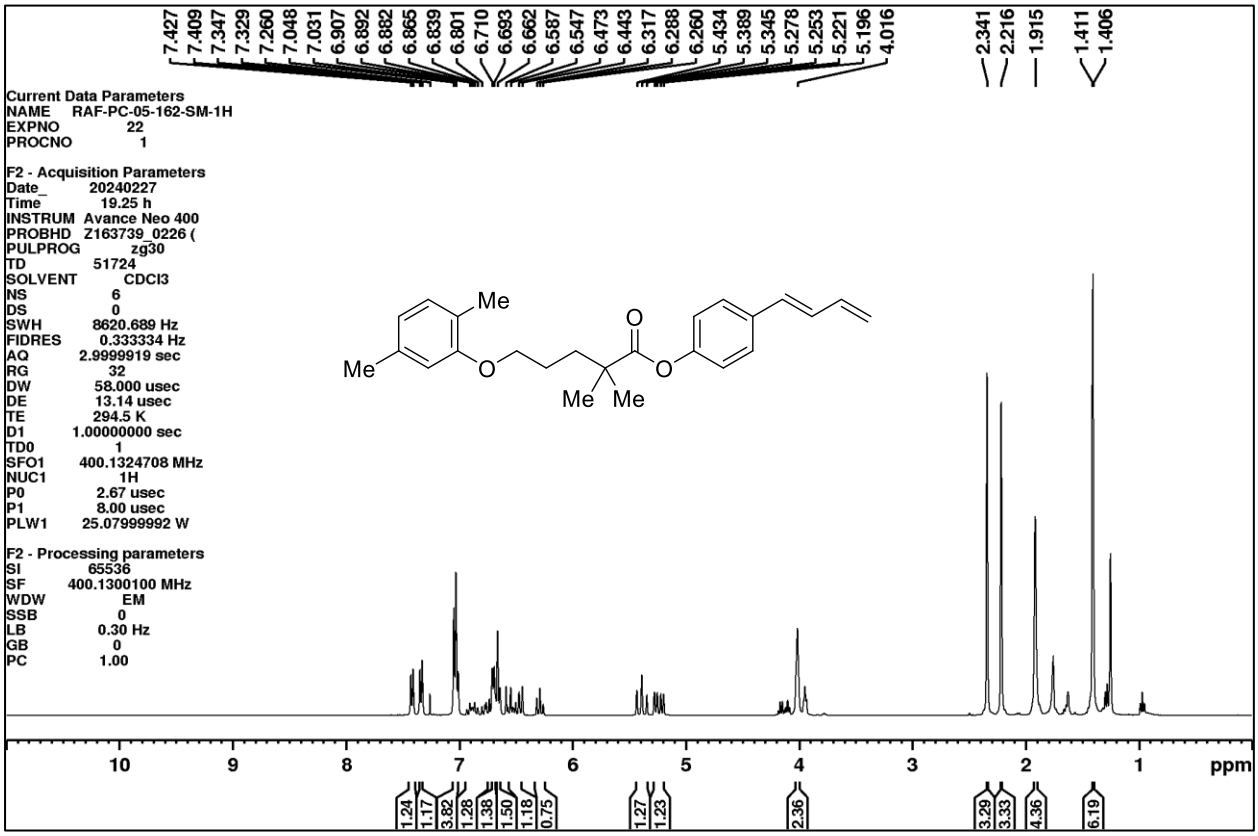


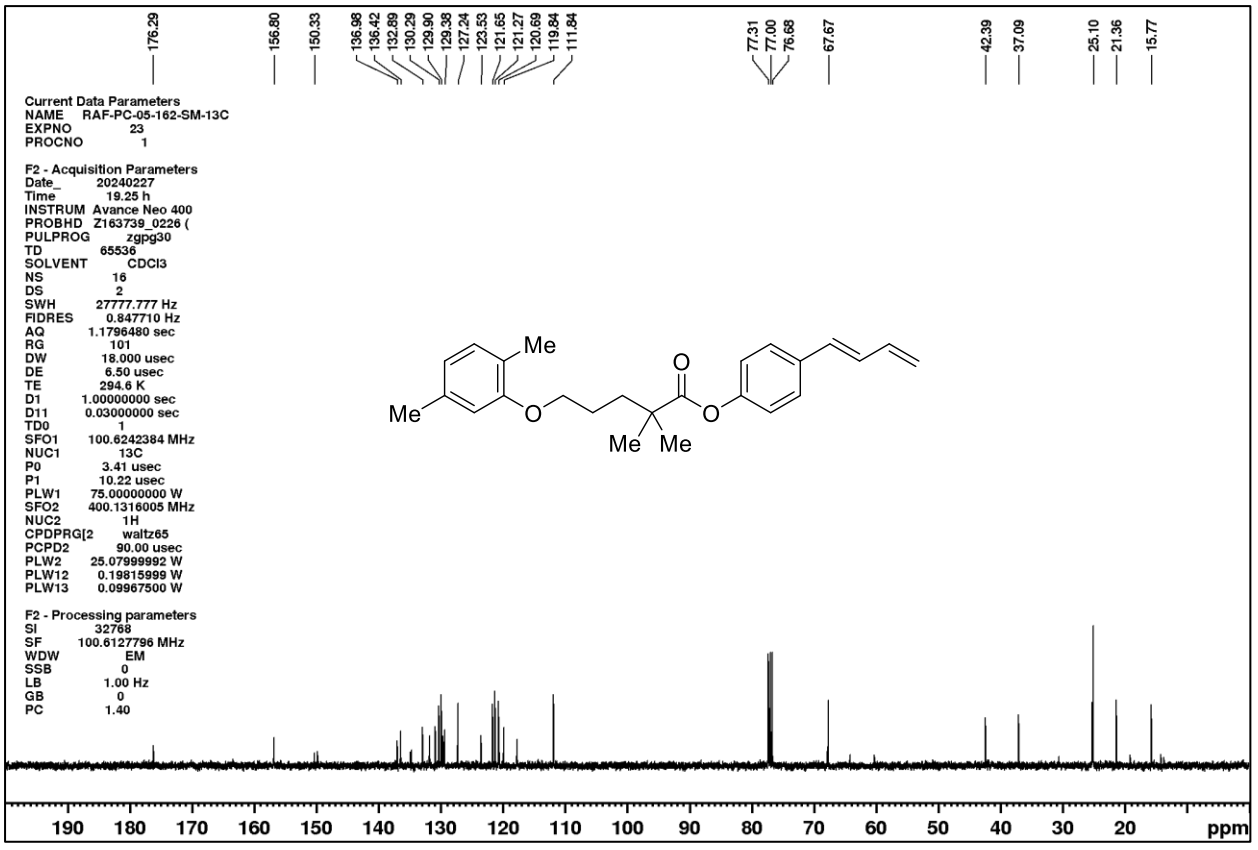


2w: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for C_8H_9S 137.0420; Found: 137.0418.

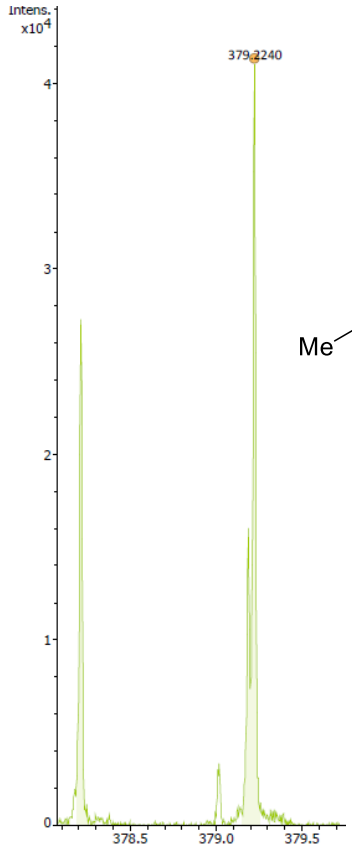


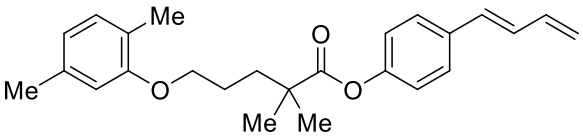
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **2z**



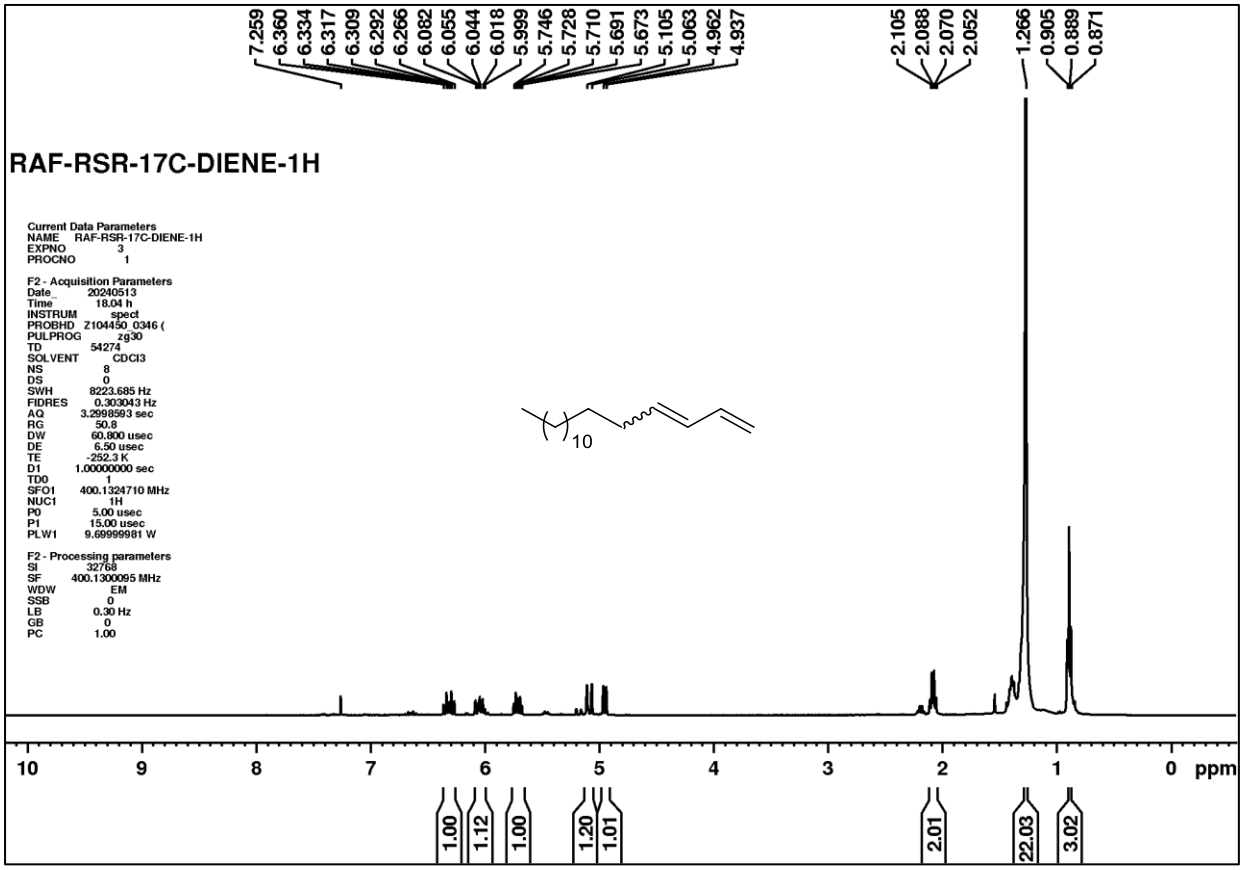


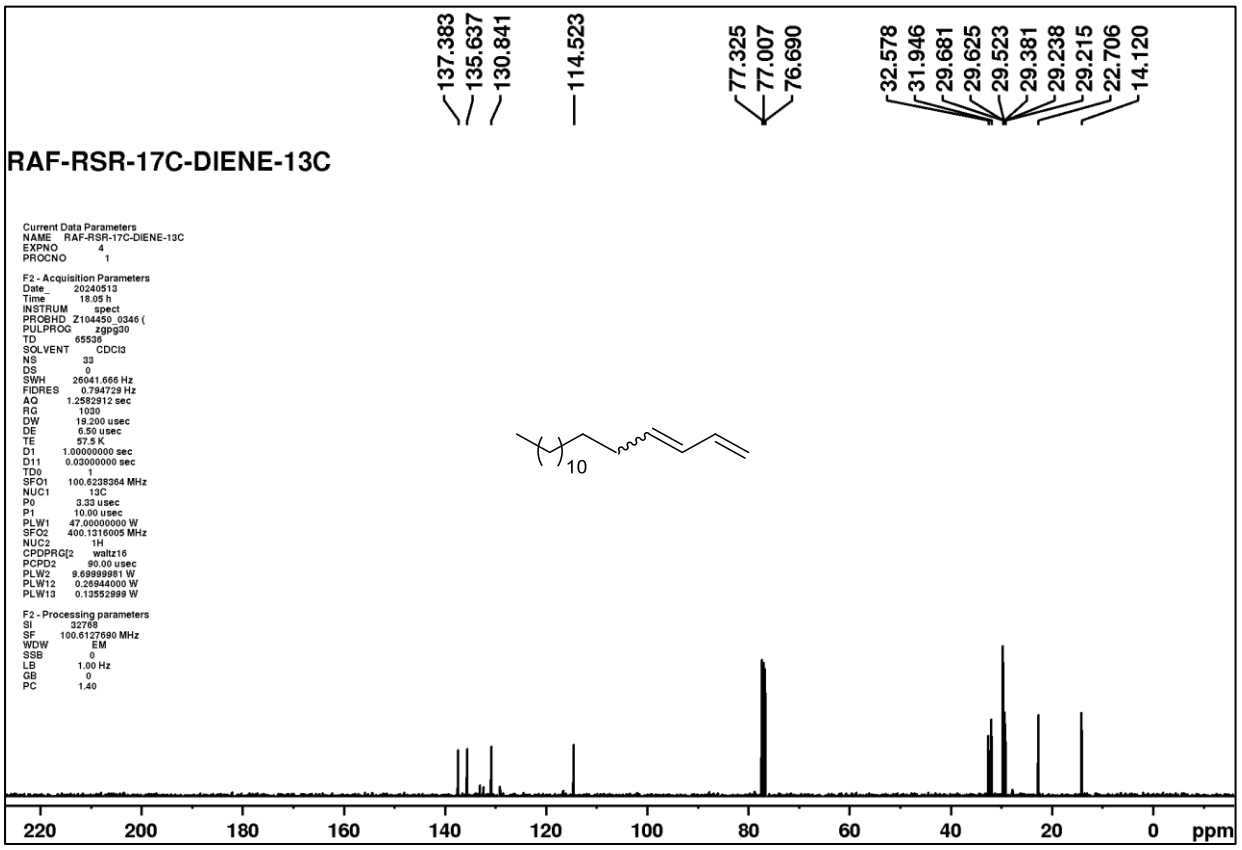
2z: HRMS (Q-TOF): *m/z* [M + H]$^+$ Calcd for $C_{25}H_{31}O_3$ 379.2268; Found 379.2240.



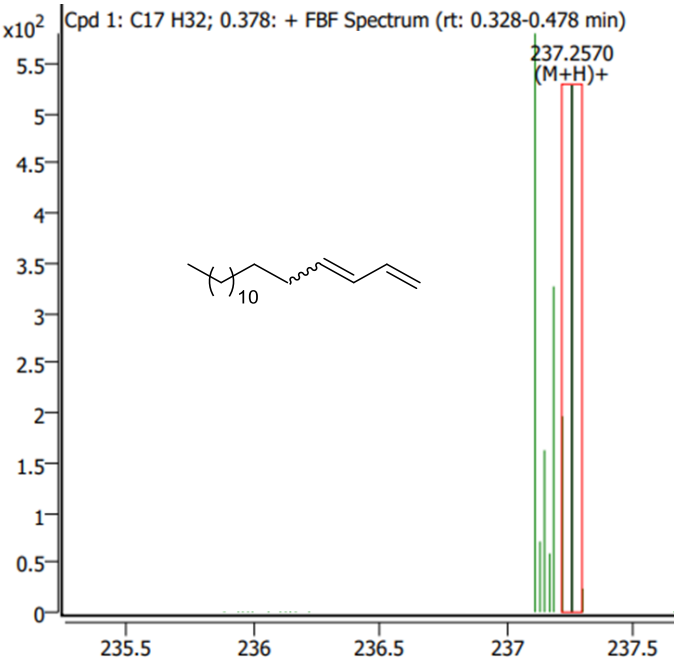


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **2ab**

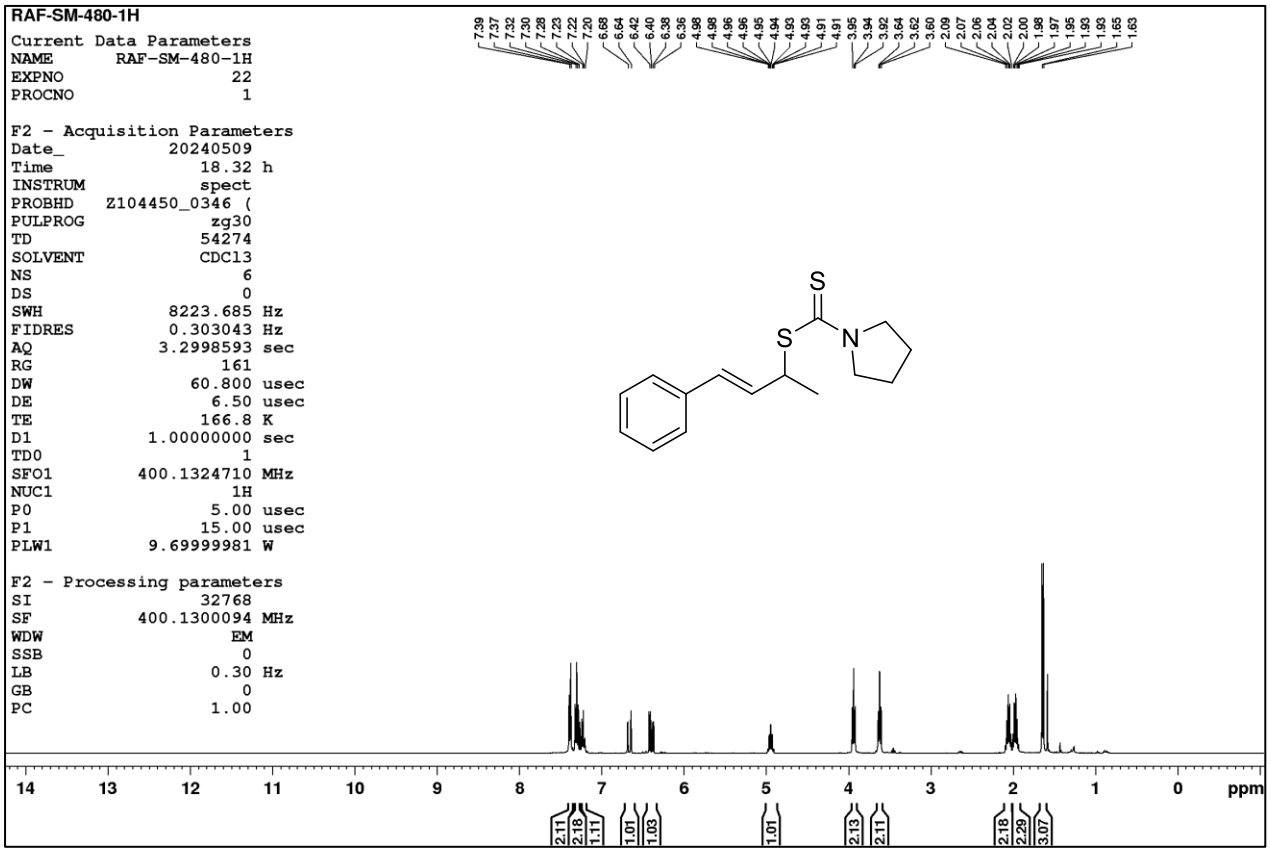


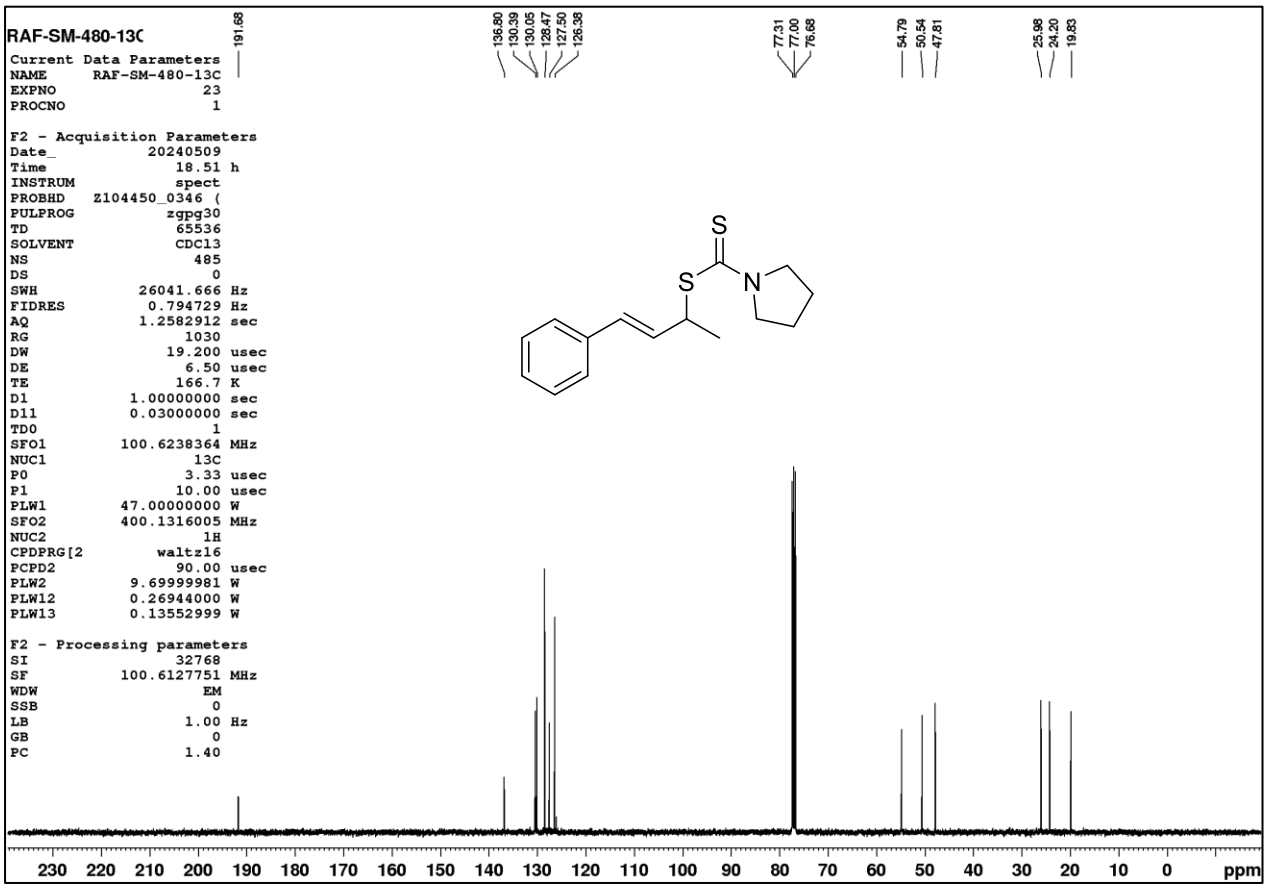


2ab: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{33}$ 237.2577; Found: 237.2570.

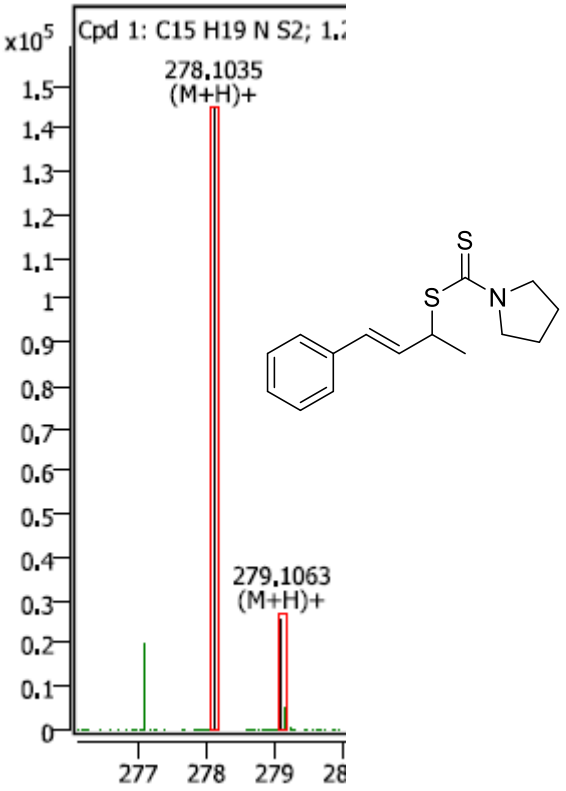


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4a**

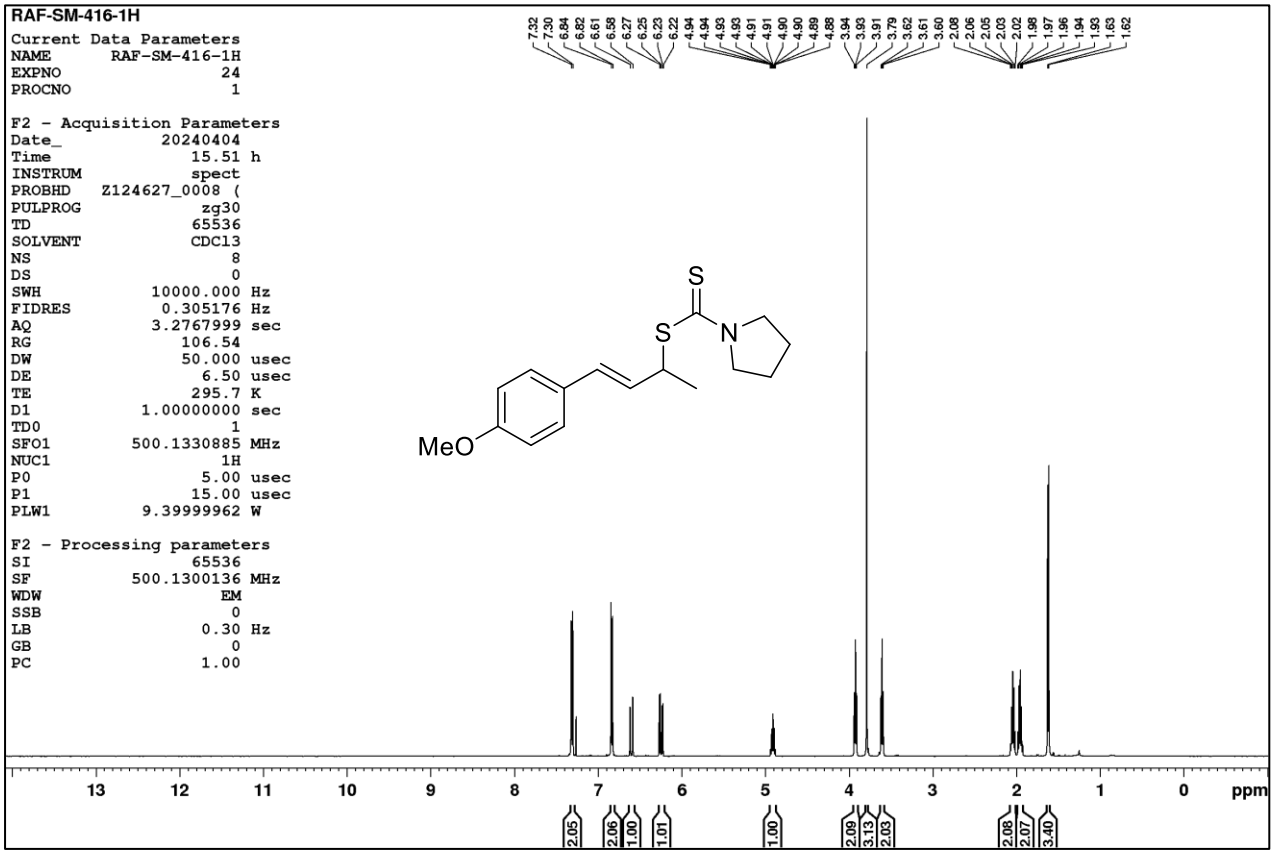


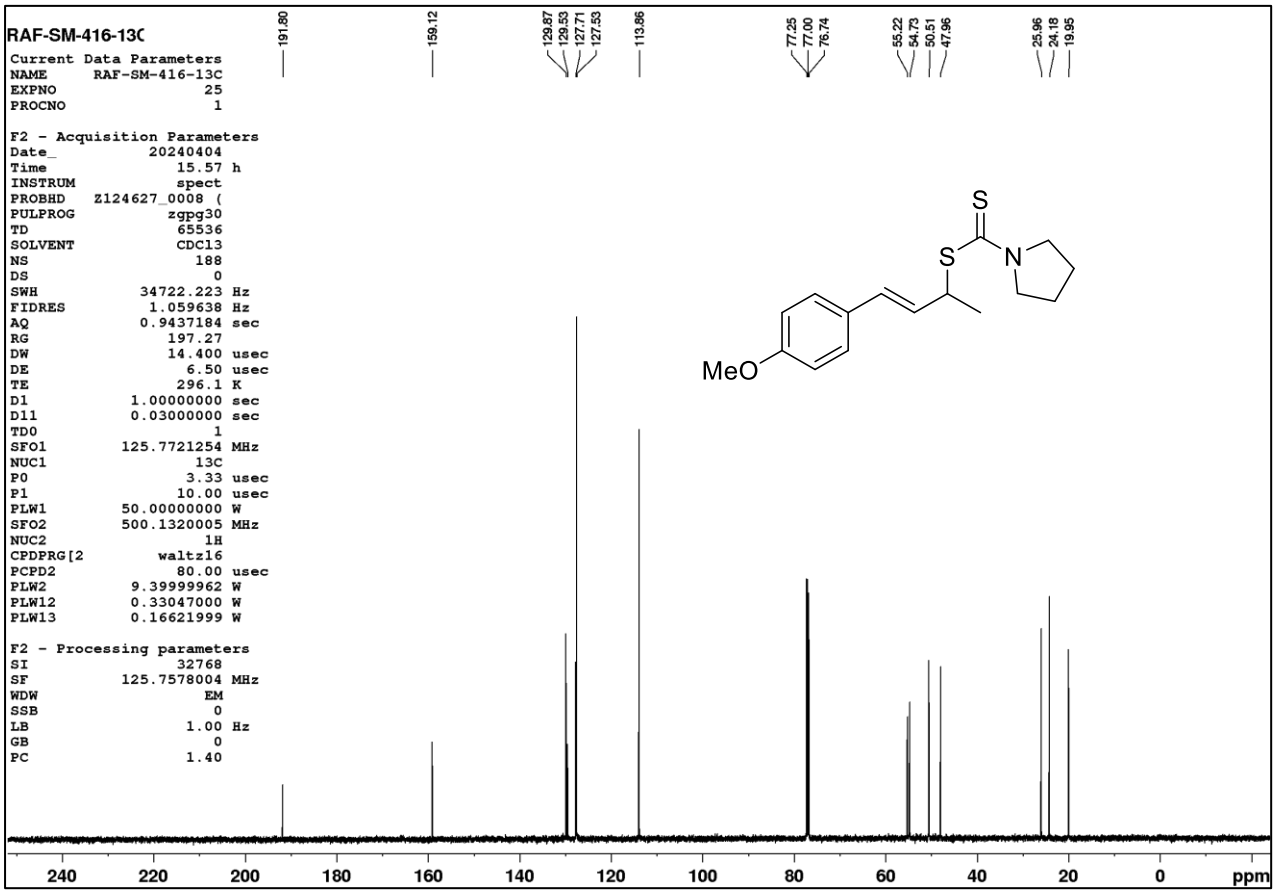


4a: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{20}NS_2$ 278.1032; Found 278.1035.

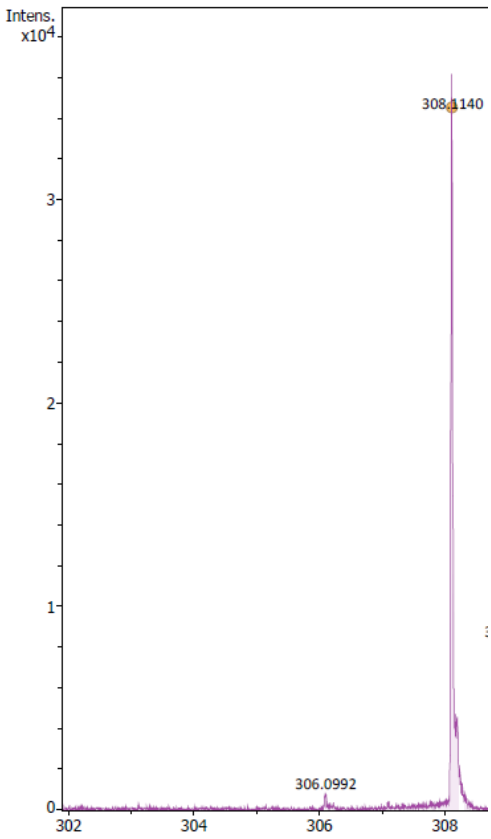


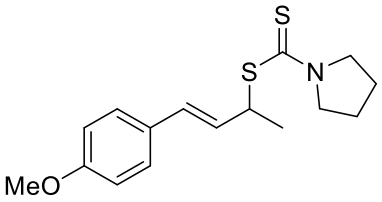
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4b**



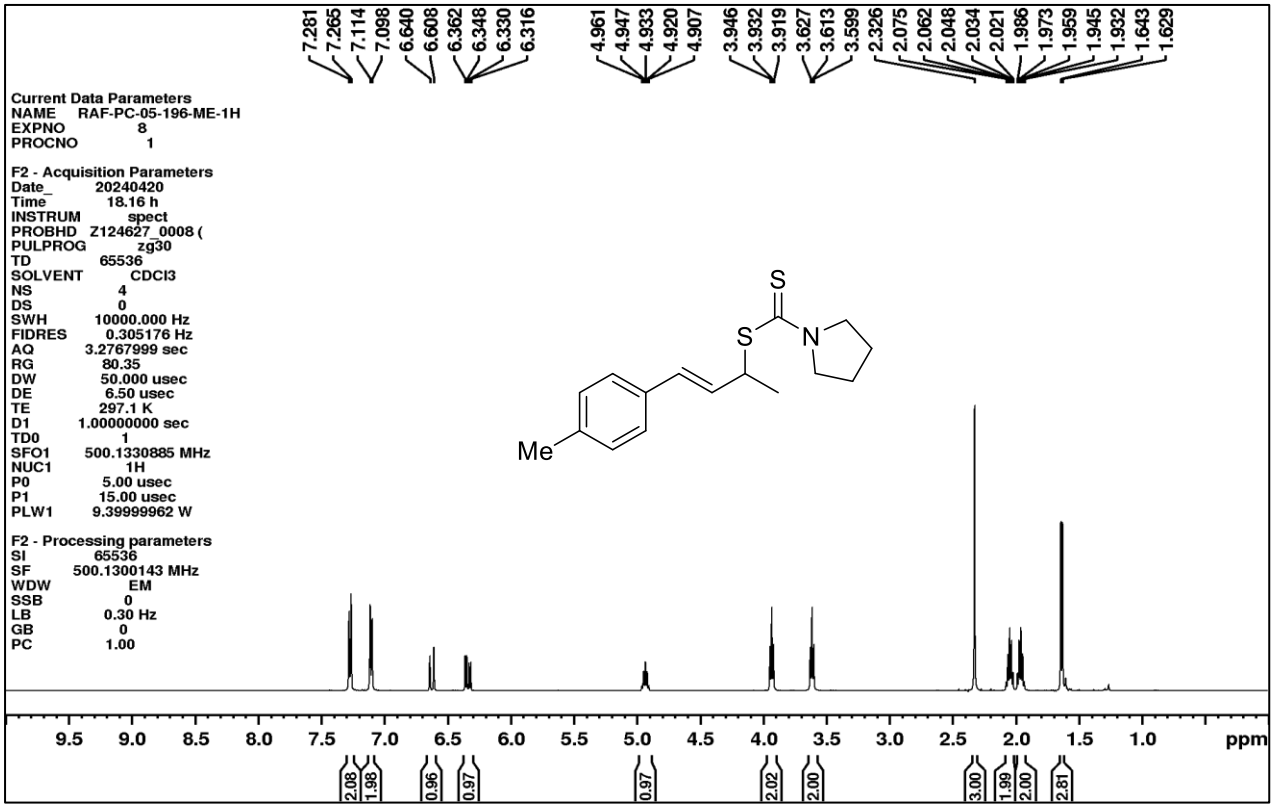


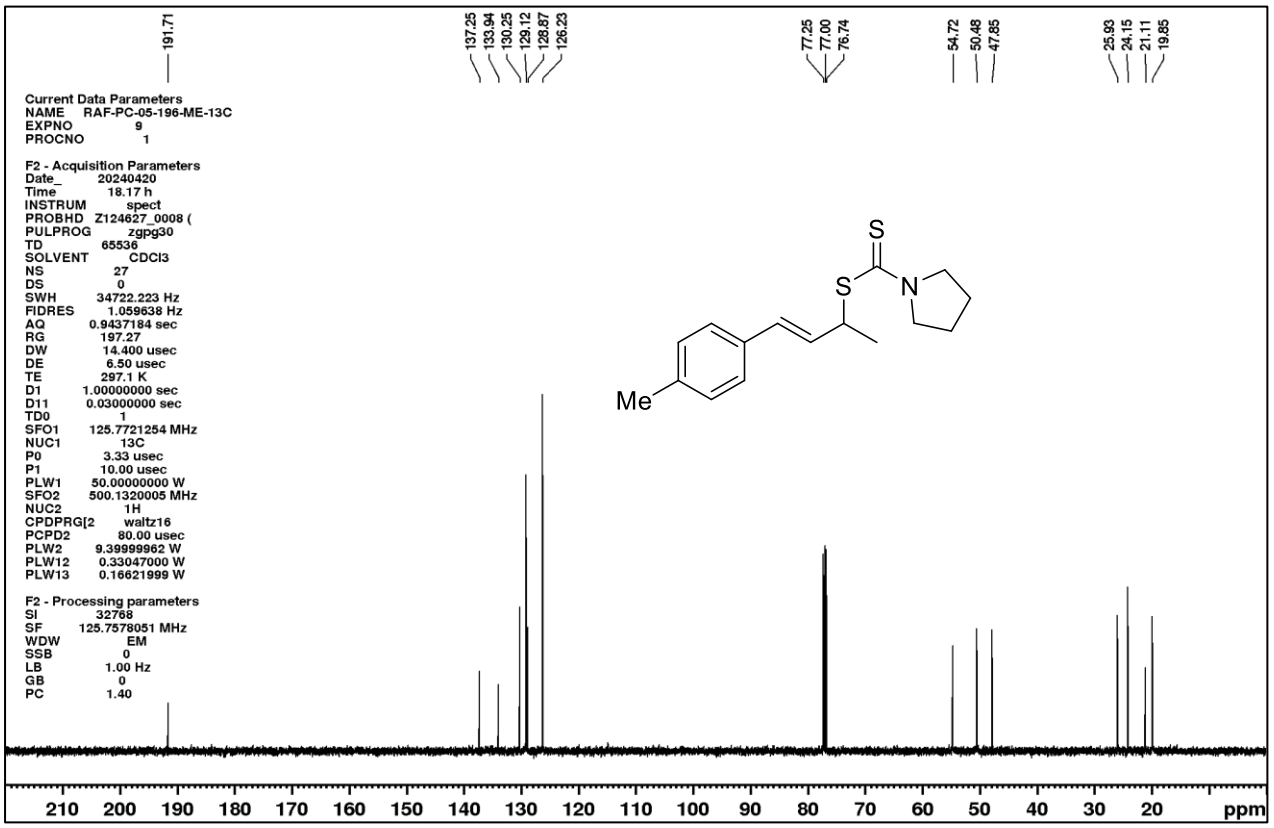
4b: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NOS_2$ 308.1138; Found 308.1140.



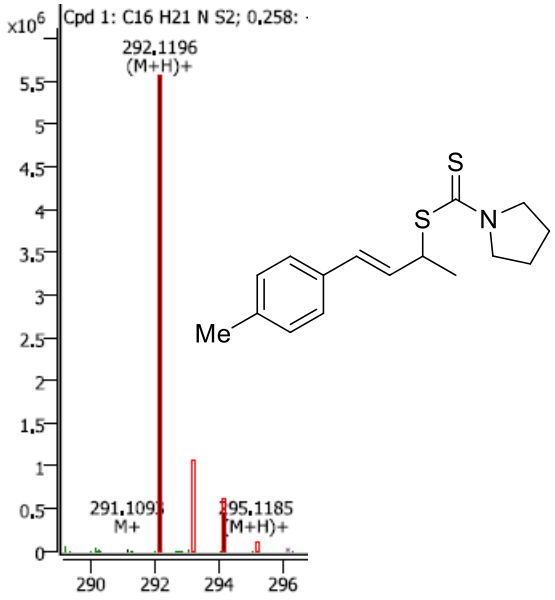


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4c**

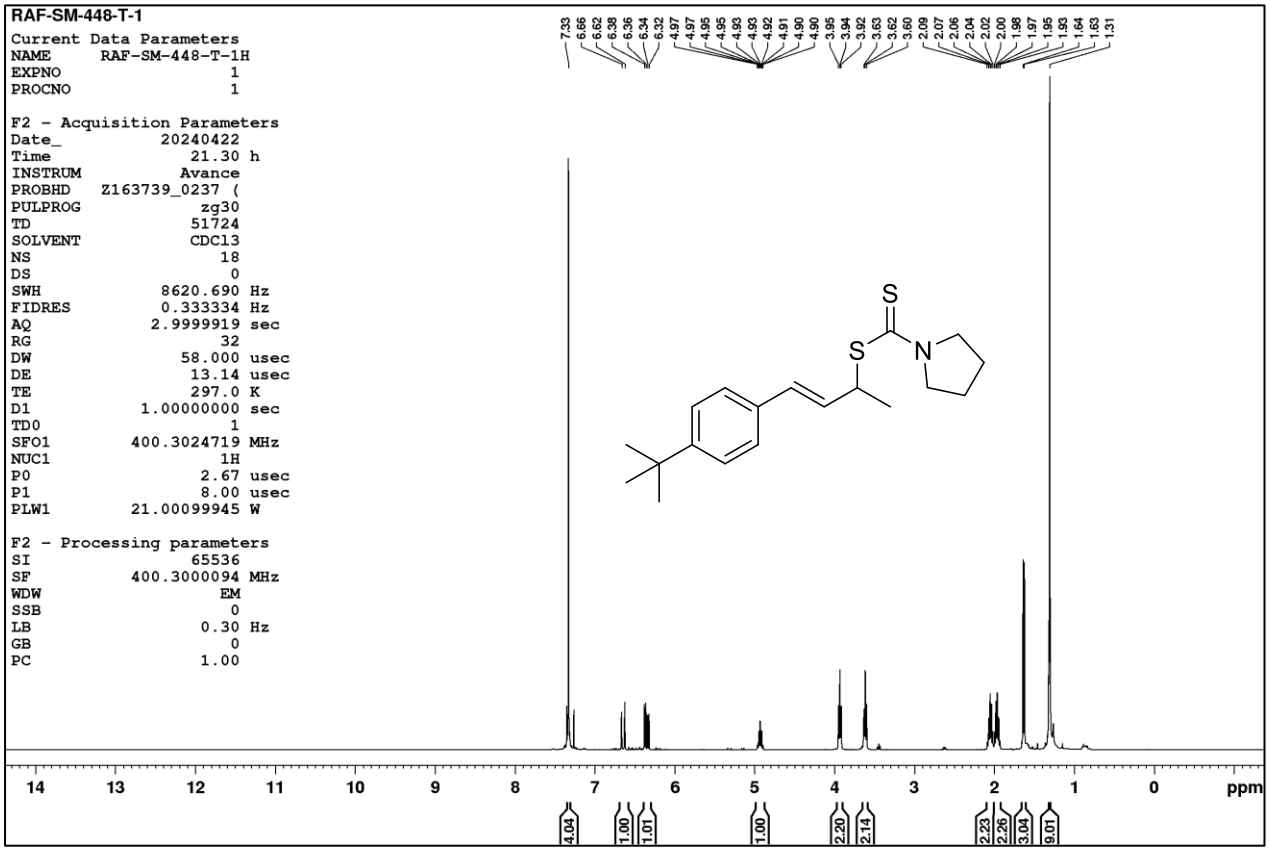


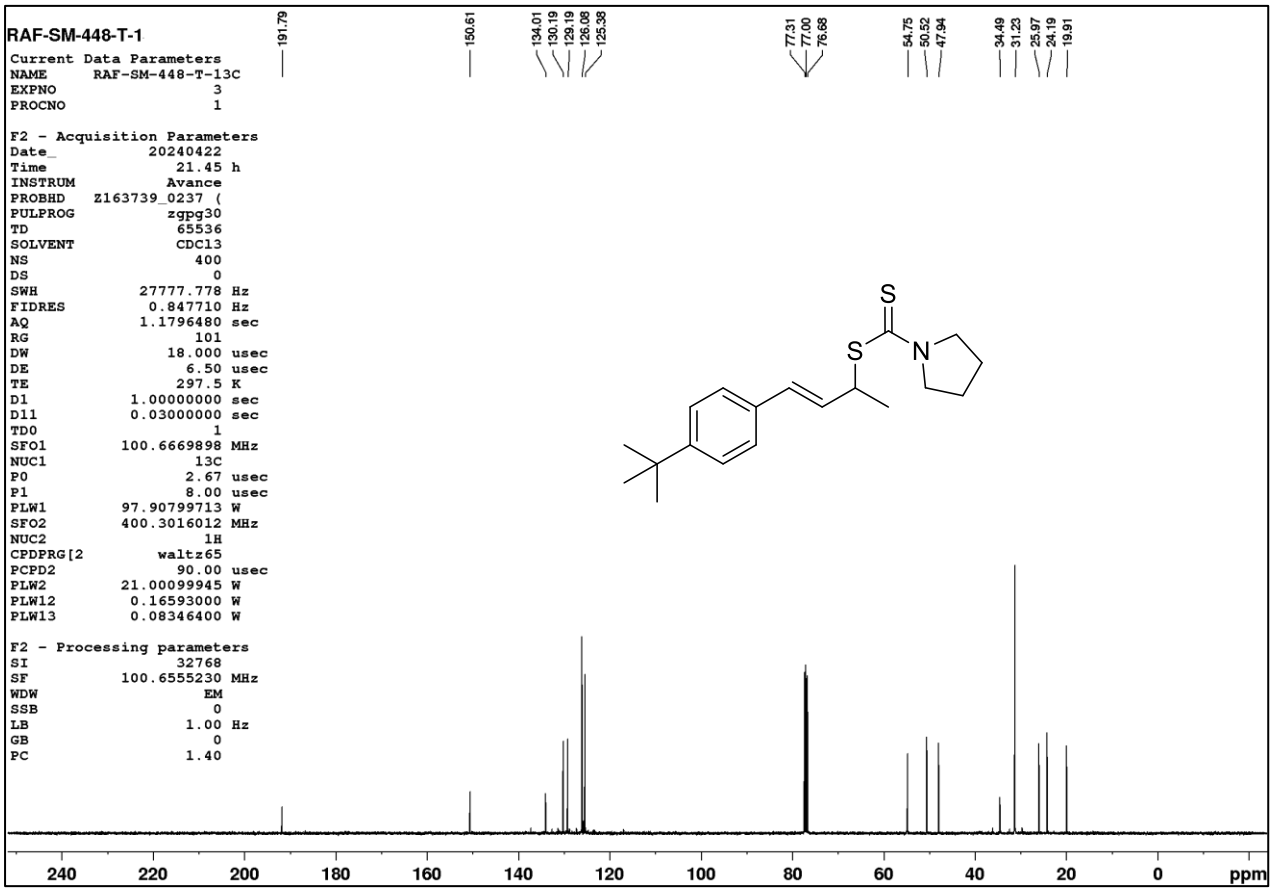


4c: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{16}H_{22}NS_2$ 292.1189 Found 292.1196.

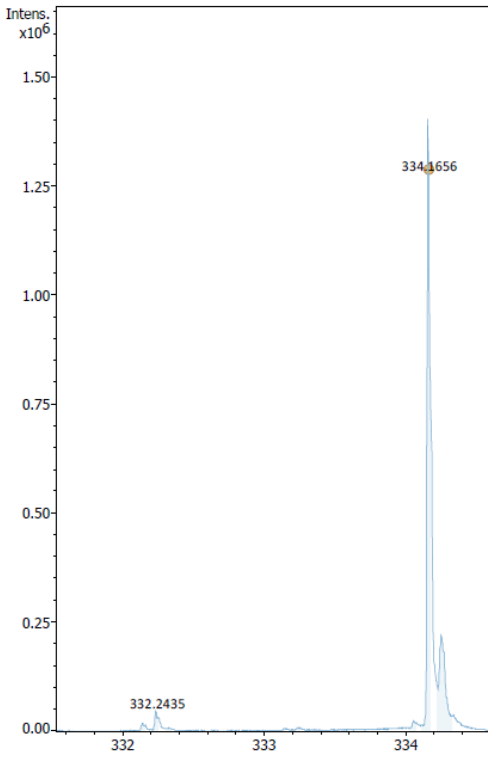


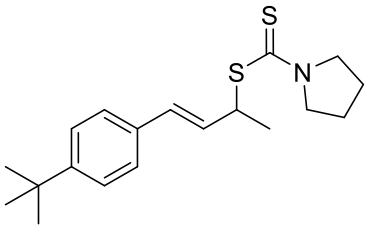
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4d**



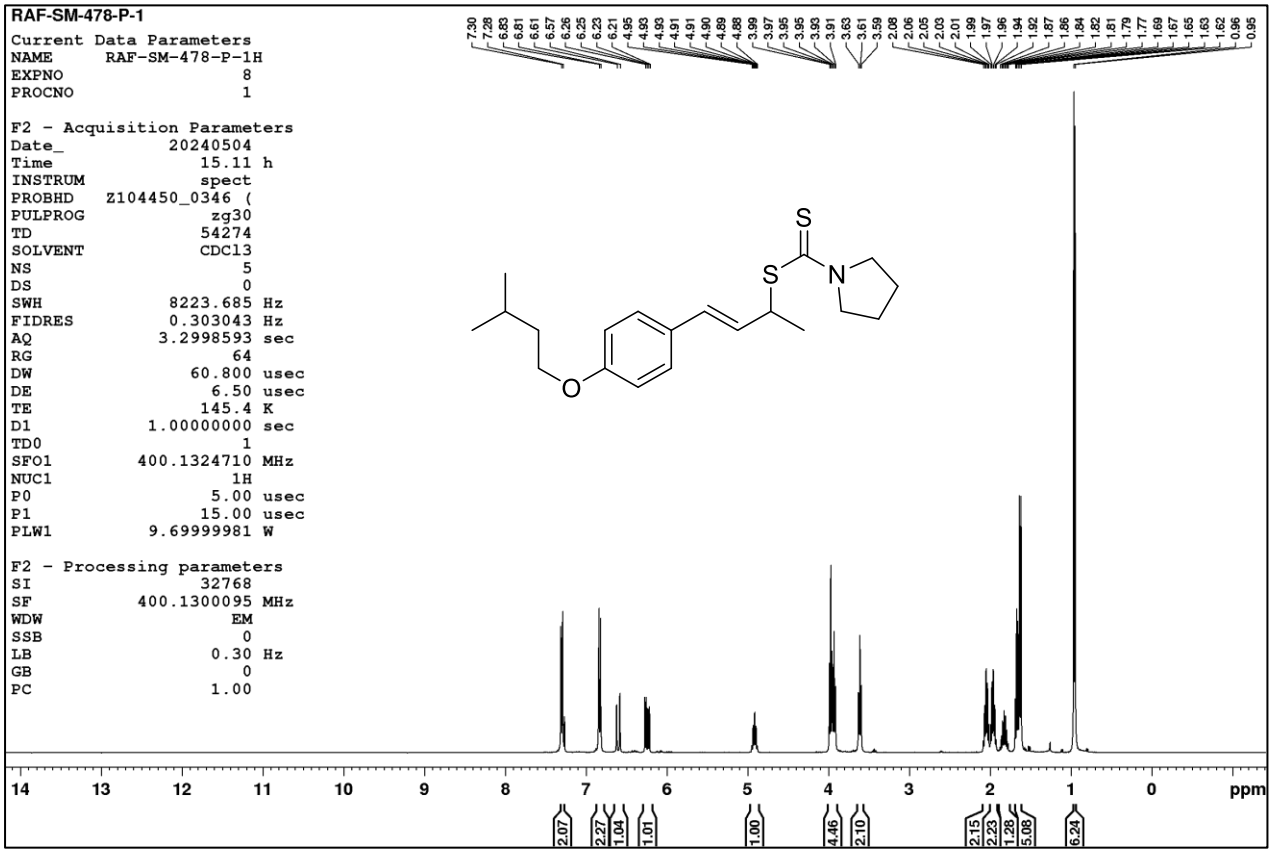


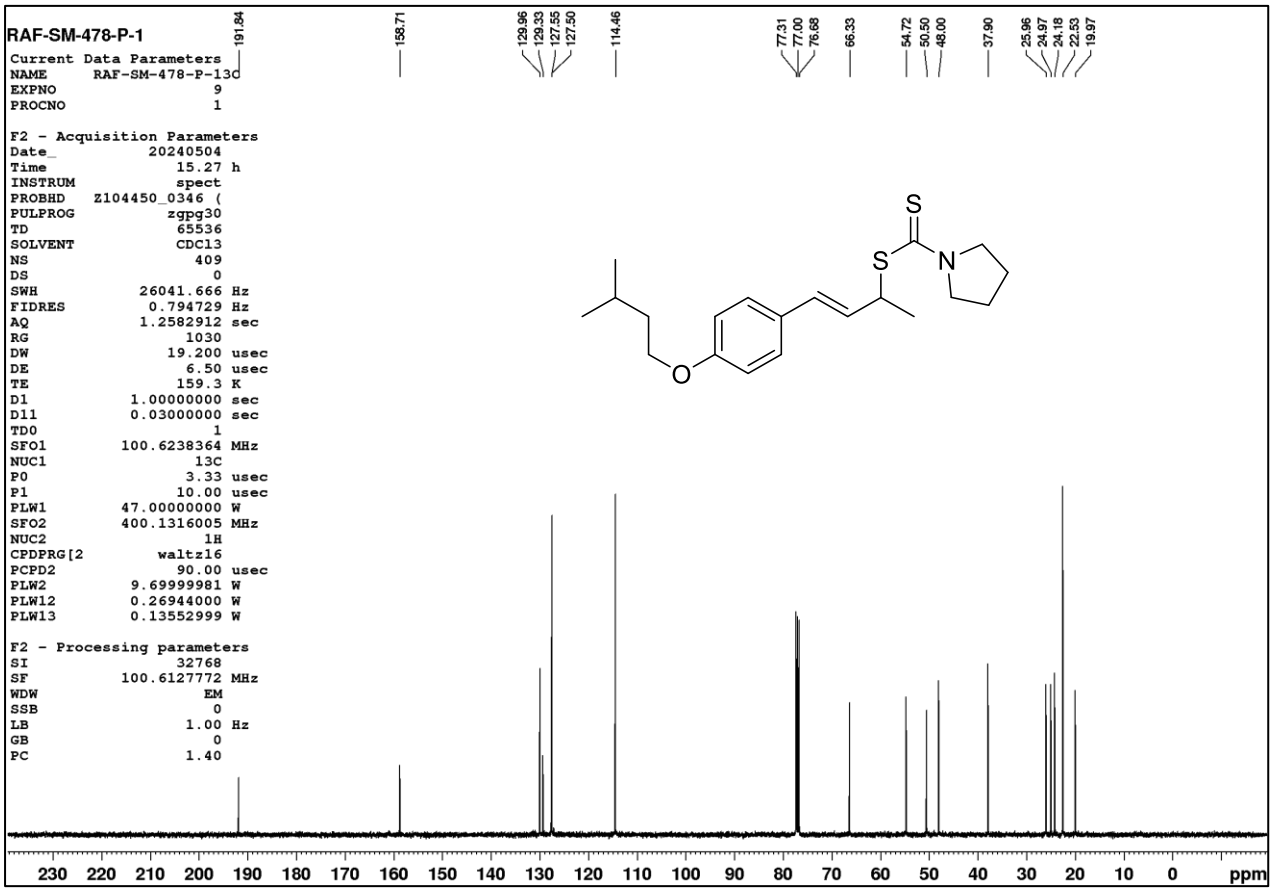
4d: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{19}H_{28}NS_2$ 334.1658; Found 334.1656.



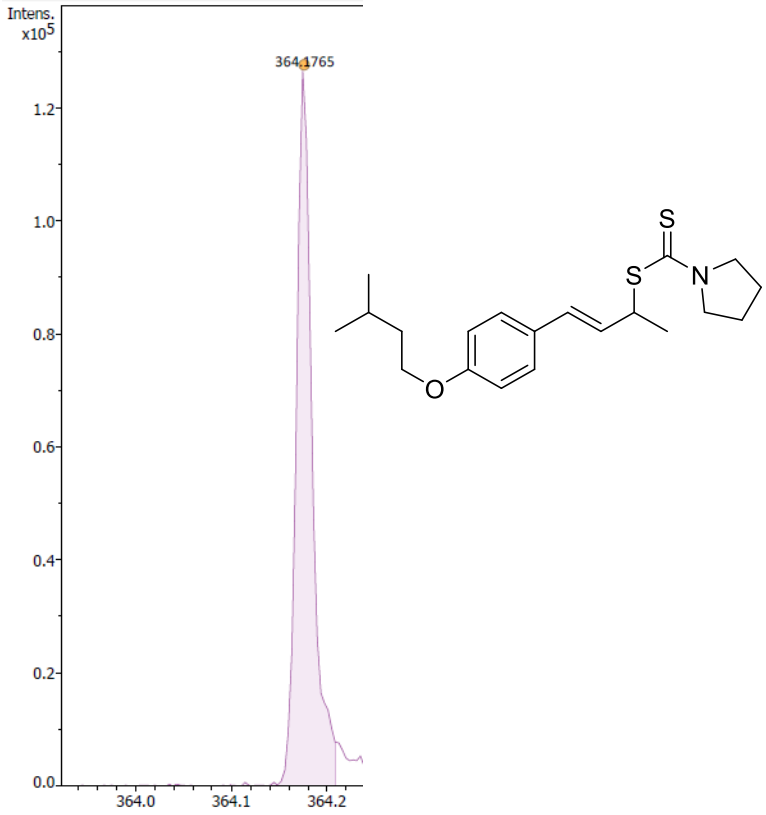


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4e**

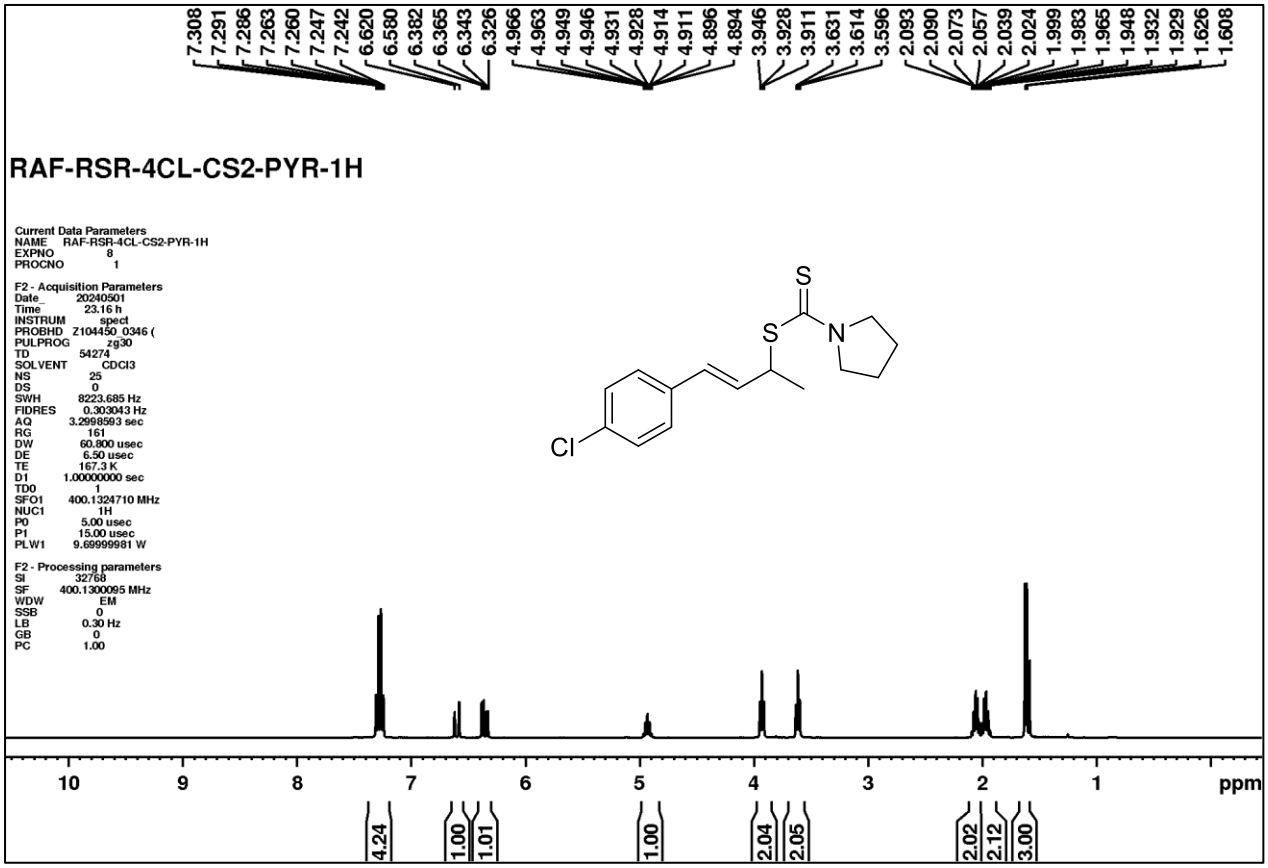


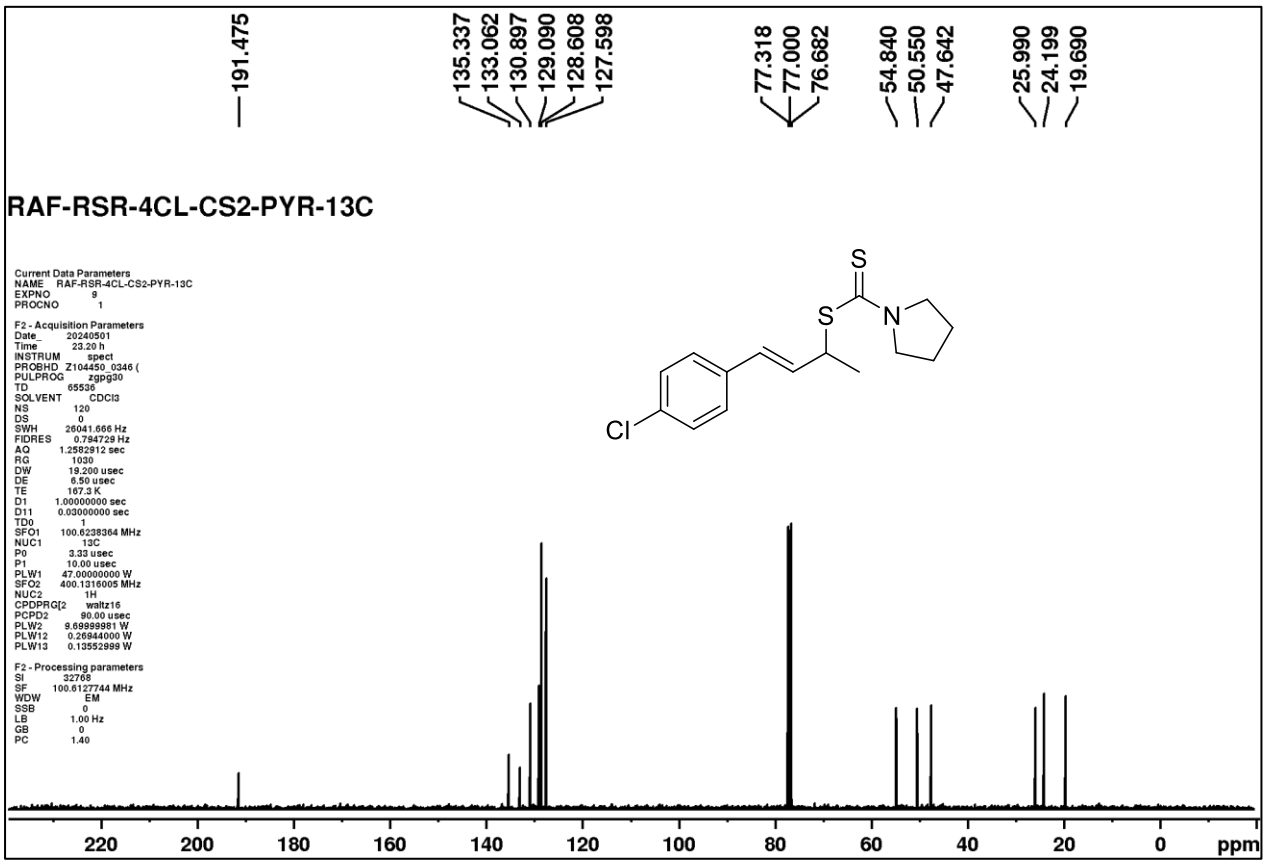


4e: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{30}NOS_2$ 364.1764; Found 364.1765.

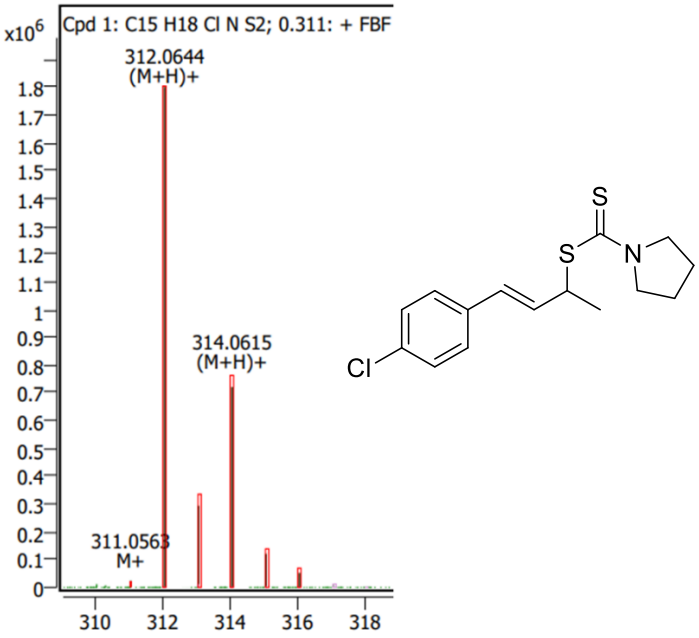


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4f**

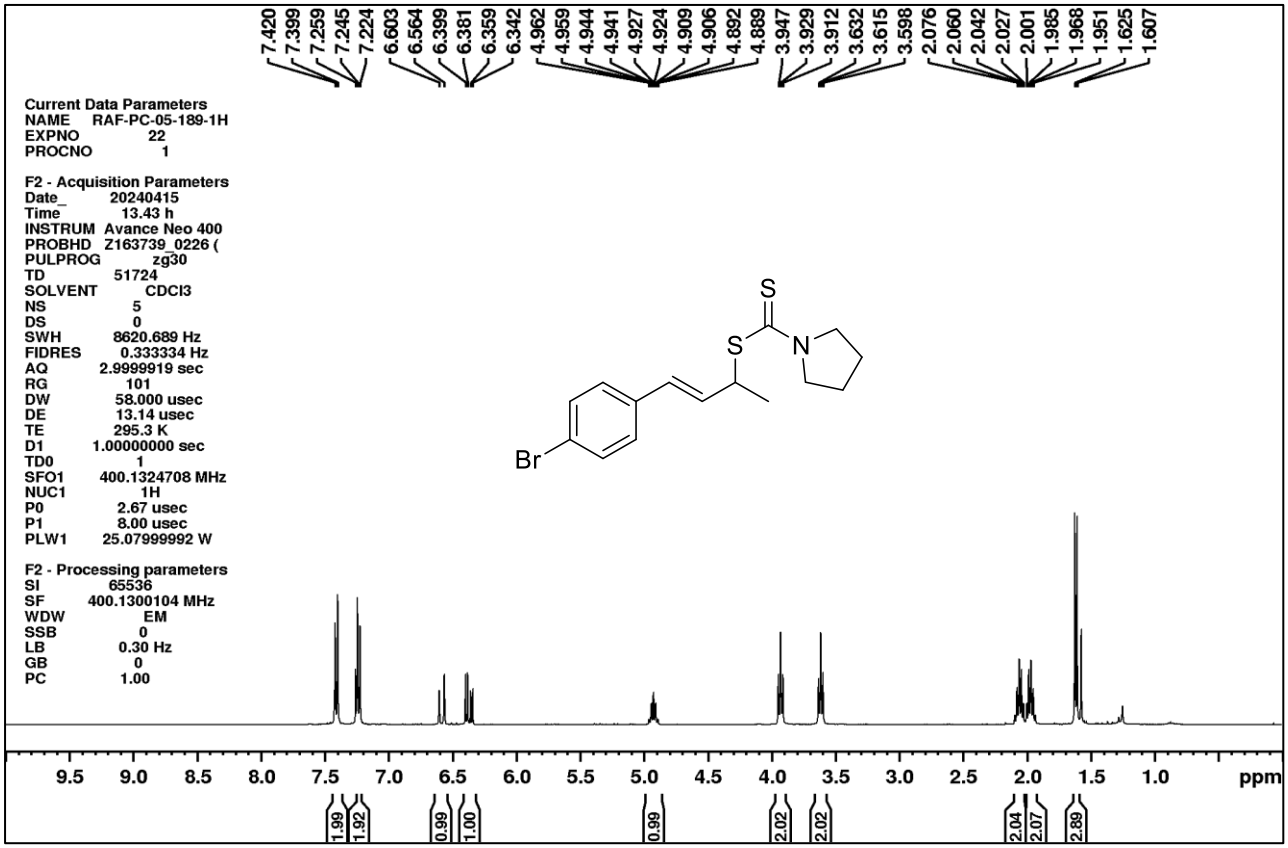


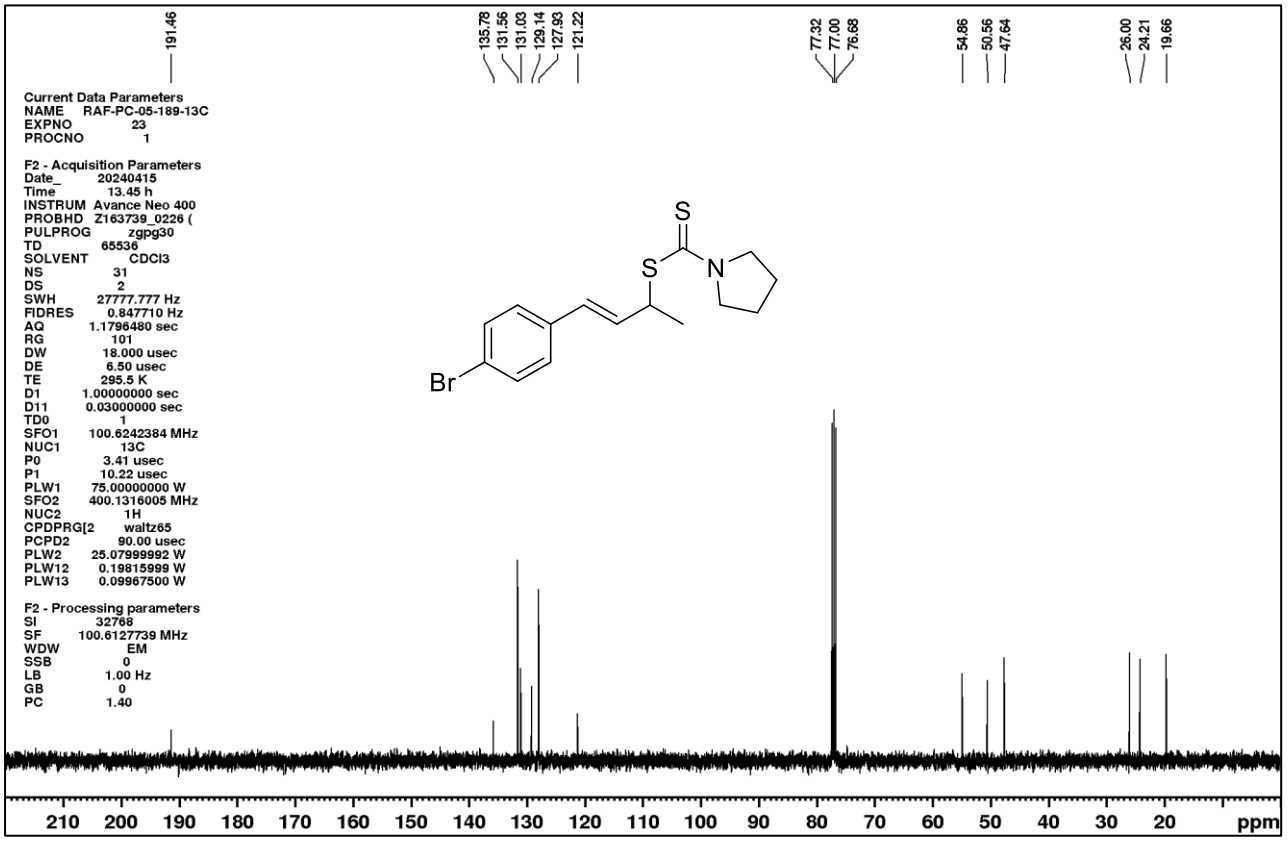


4f: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{19}ClNS_2$ 312.0642; Found: 312.0644.

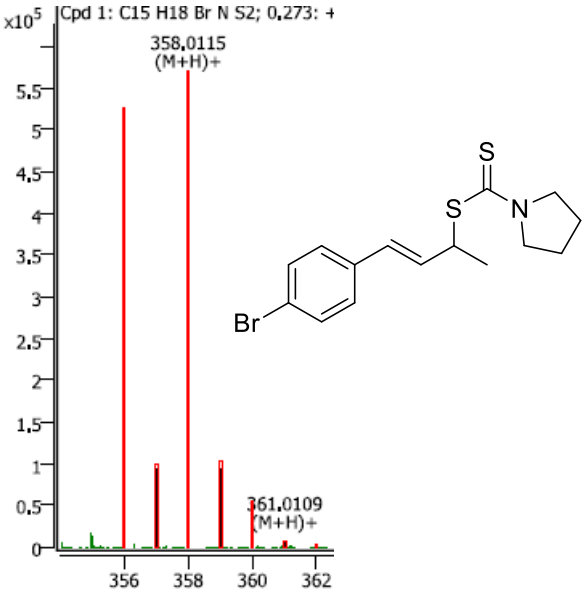


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4g**

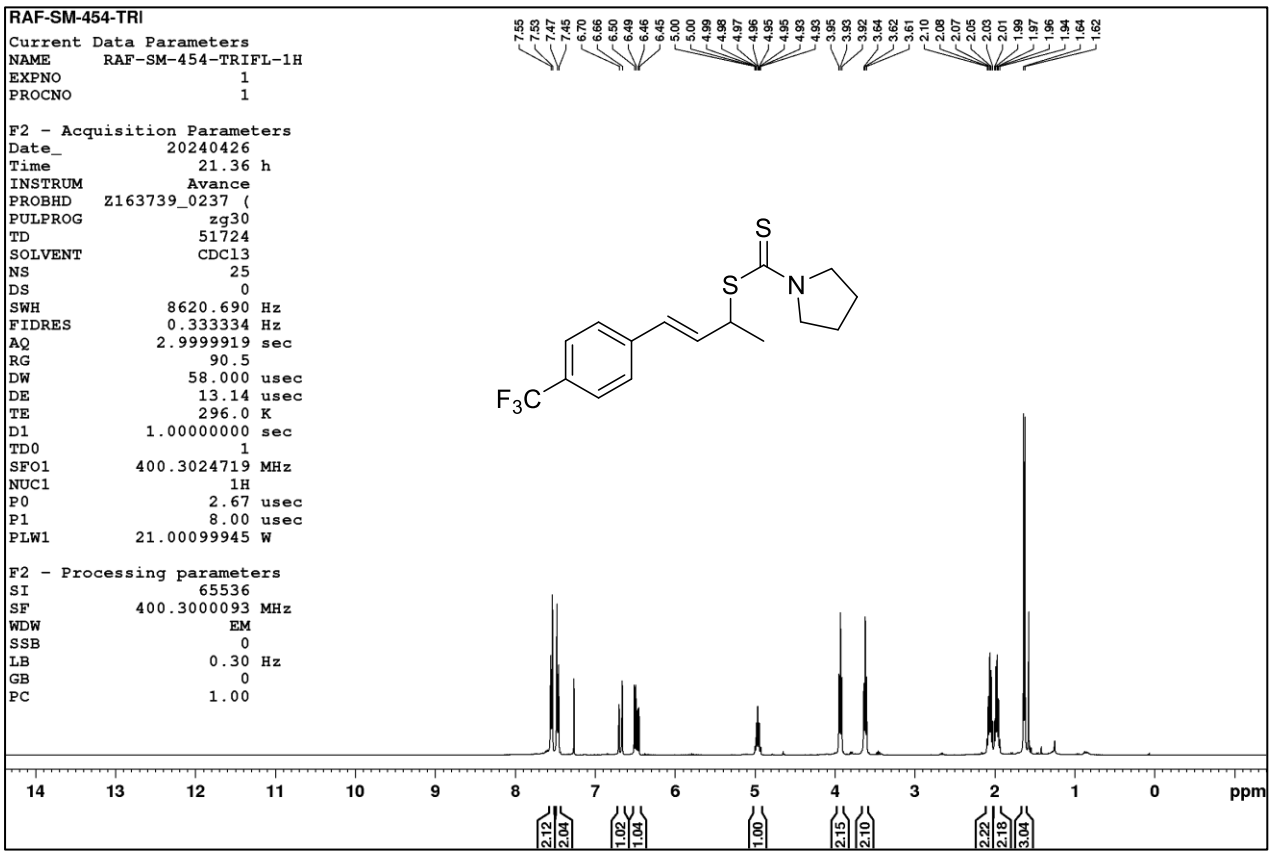


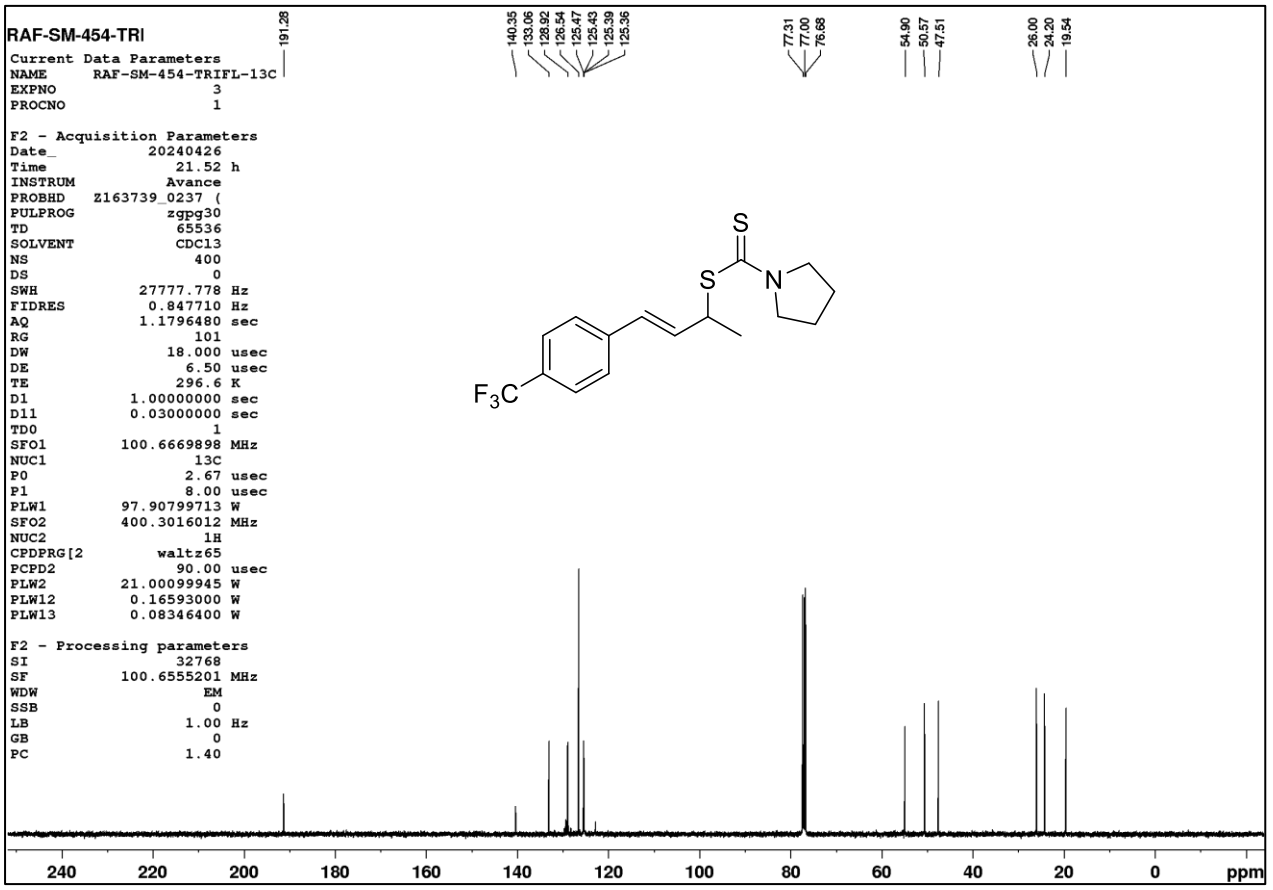


4g: HRMS (Q-TOF): *m/z* [M+H] + calcd for $C_{15}H_{19}NS_2Br$ 358.0116 Found 358.0115.

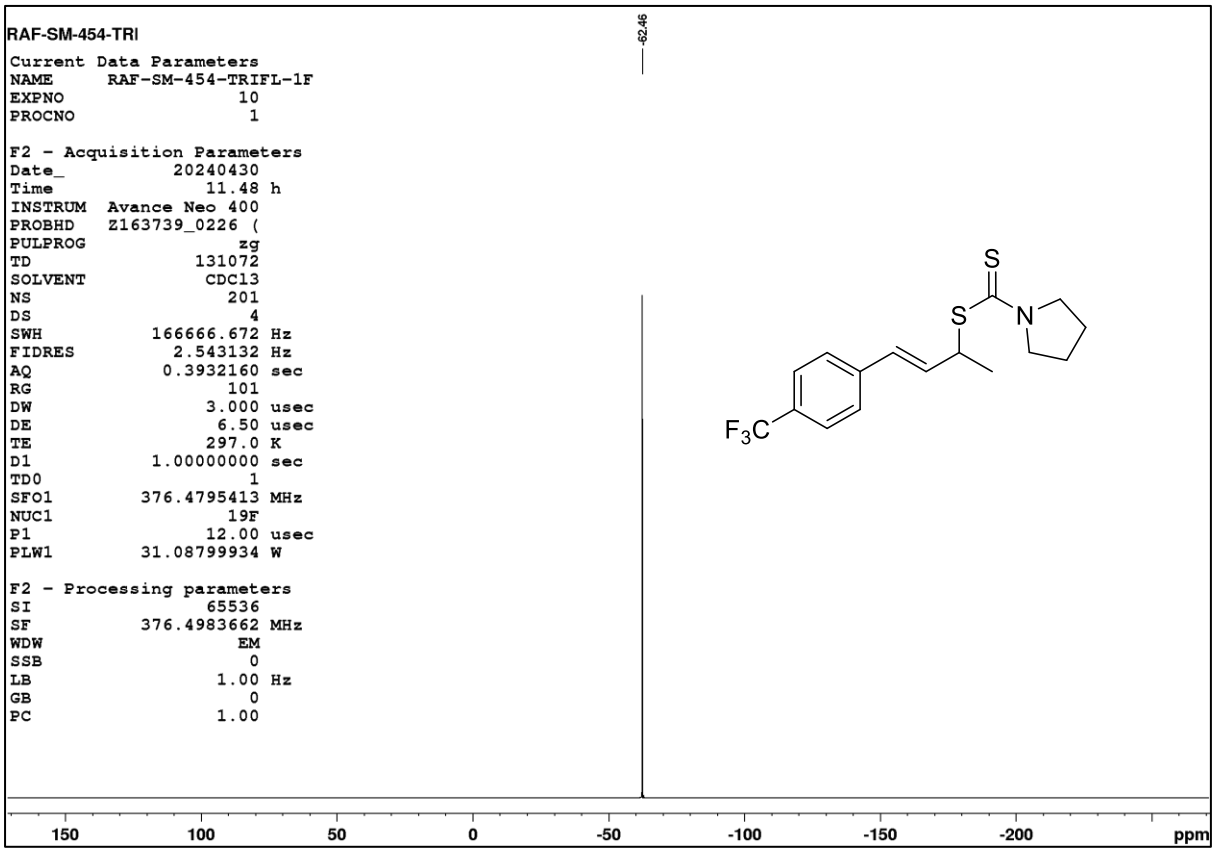


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4h**

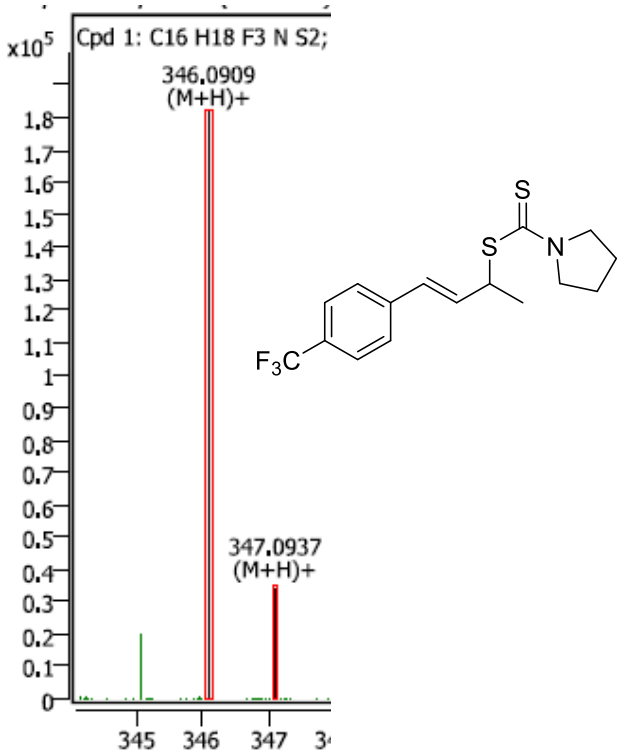




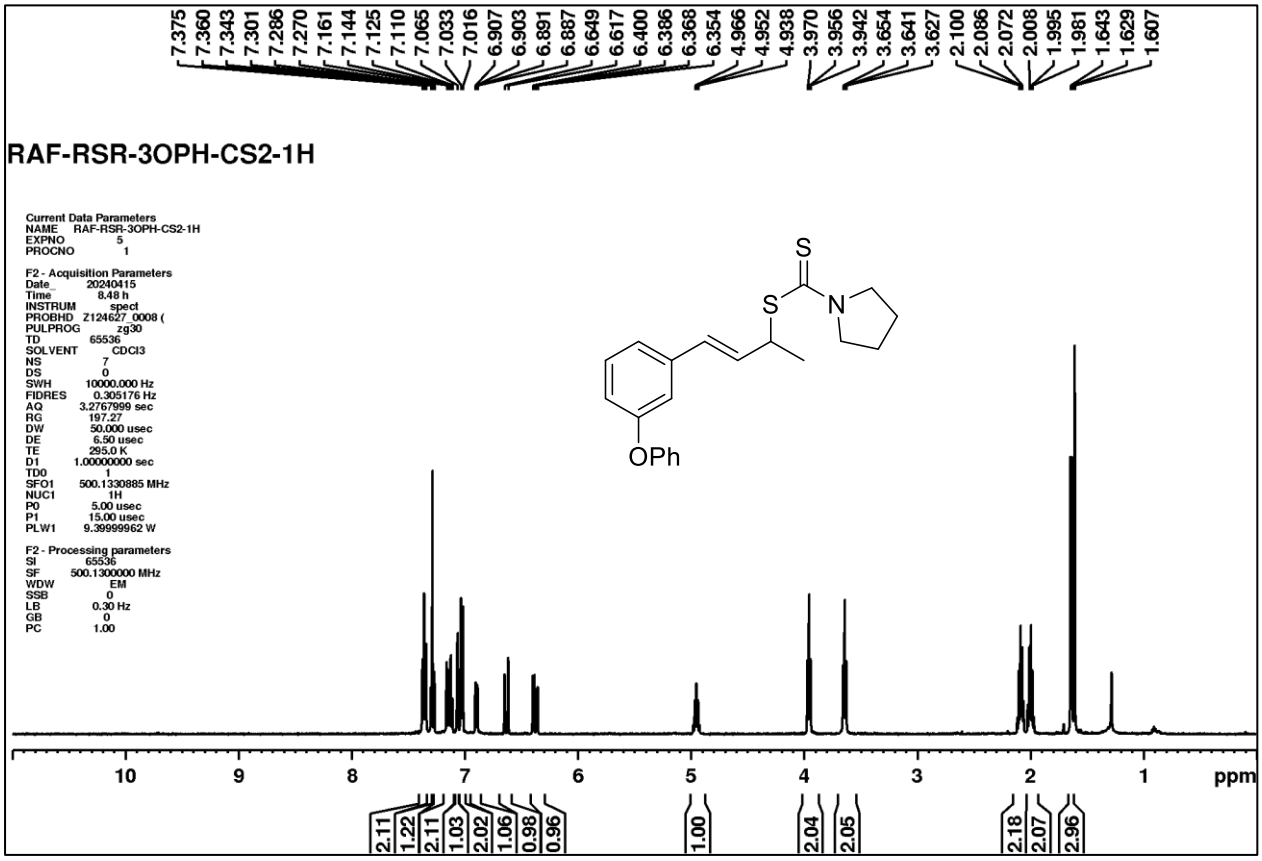
$^{19}F\{H\}$ NMR ($CDCl_3$, 376 MHz) of compound **4h**

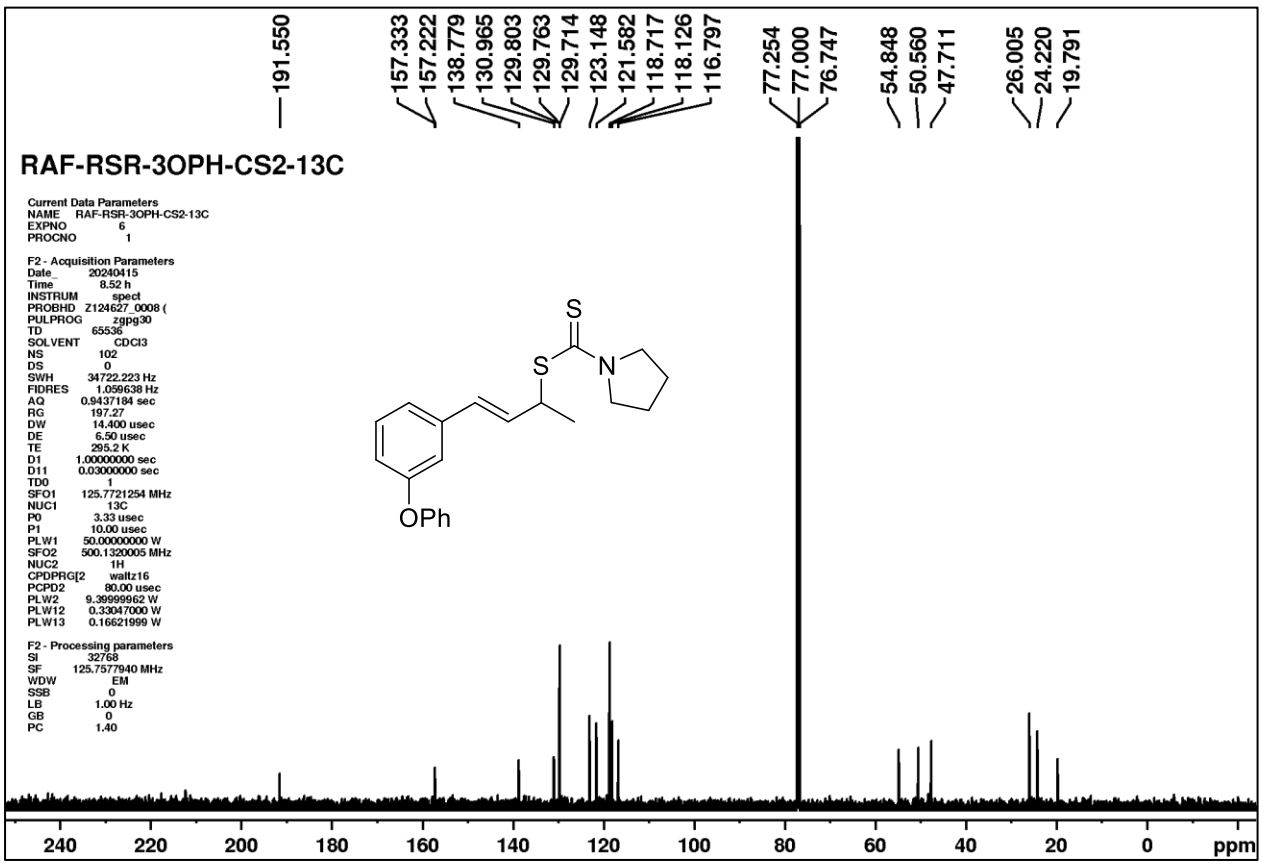


4h: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{19}F_3NS_2$ 346.0906; Found 346.0909.

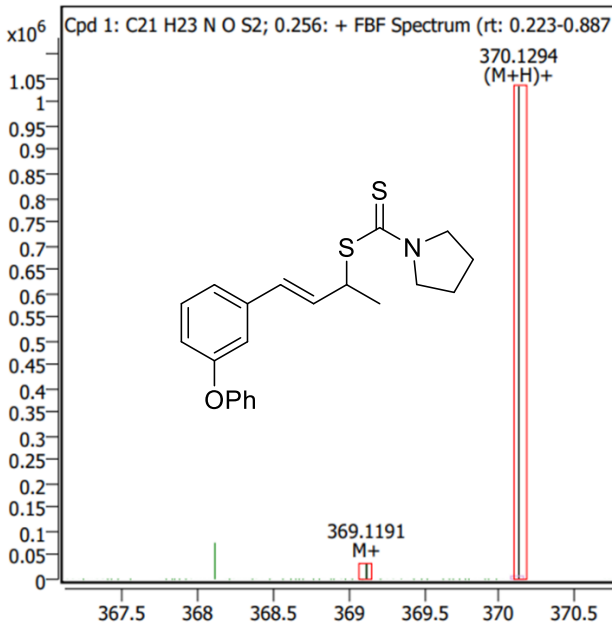


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4j**

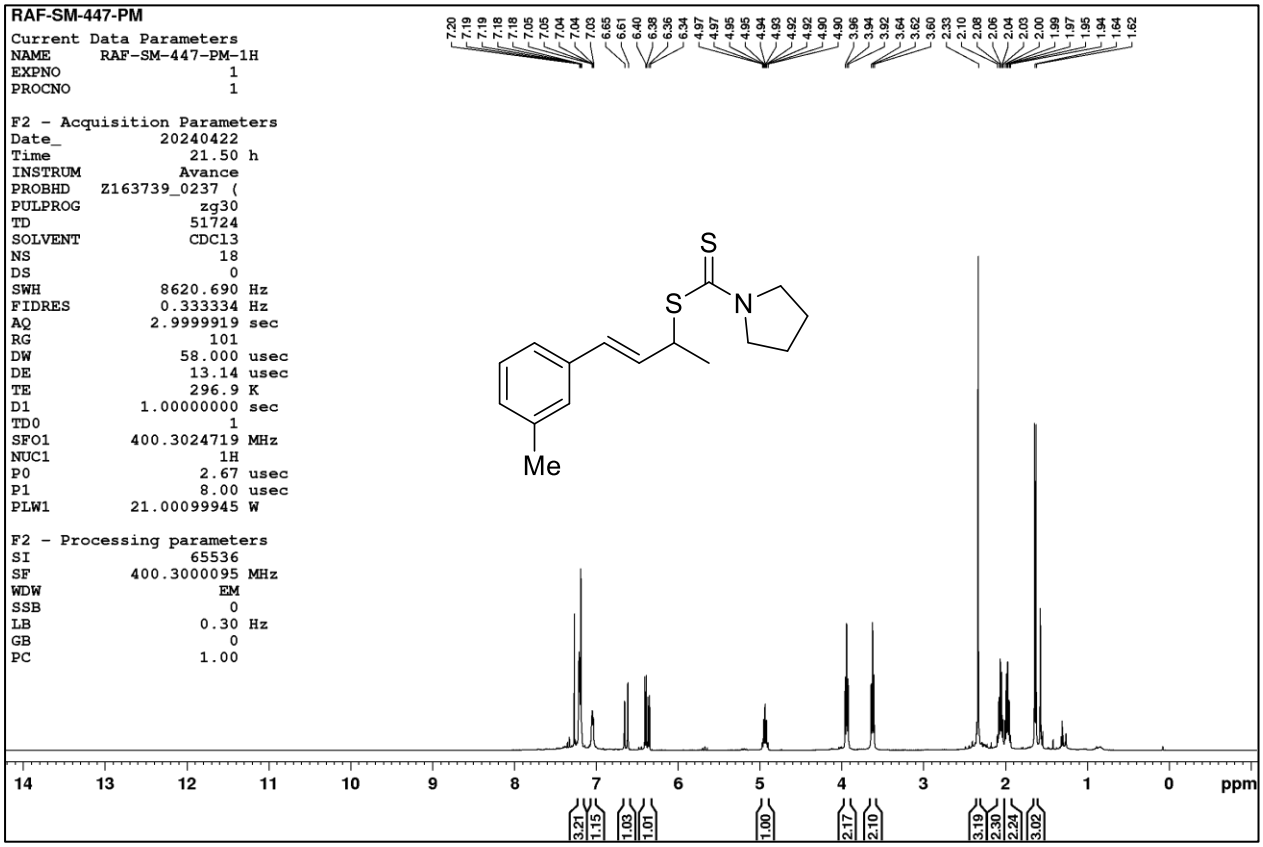


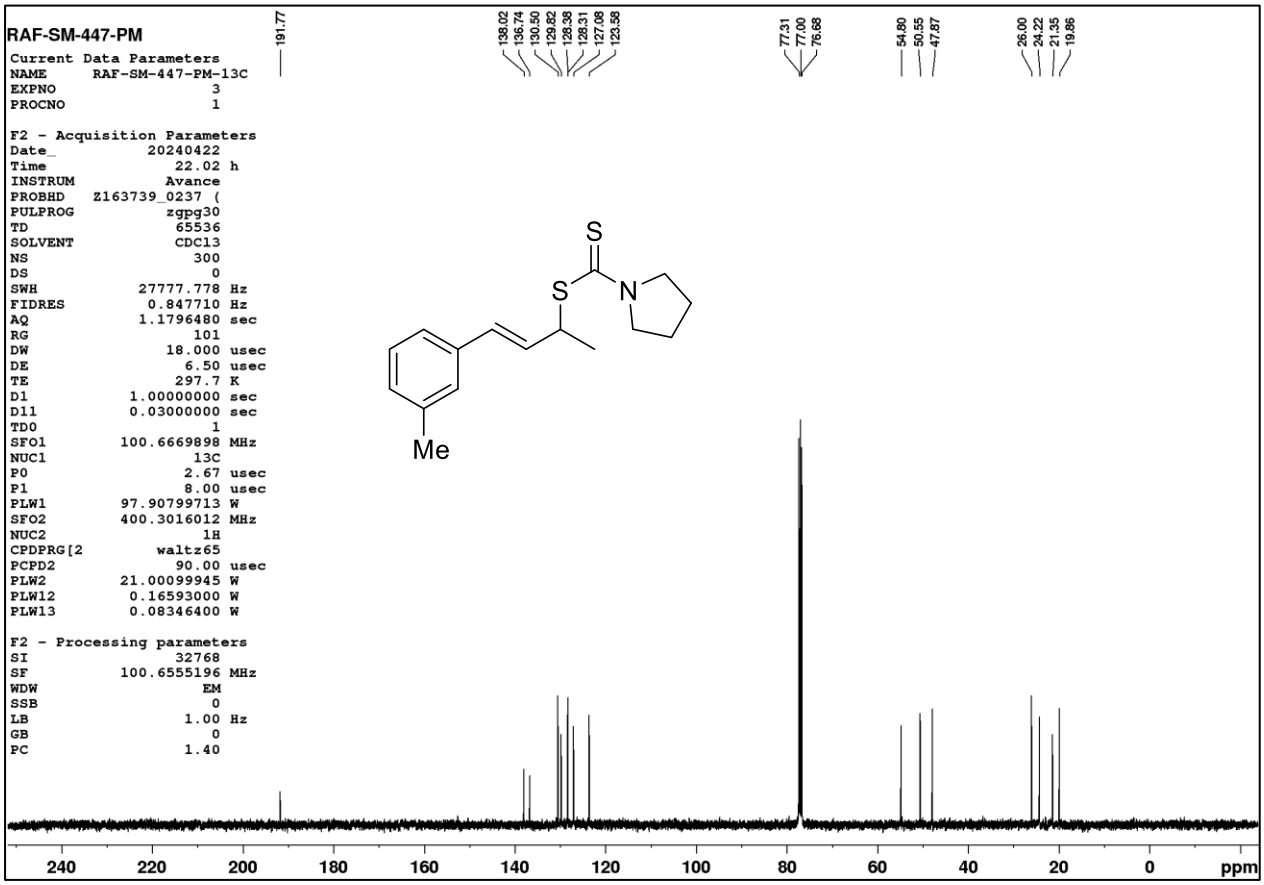


4j: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{24}NOS_2$ 370.1294; Found: 370.1294.

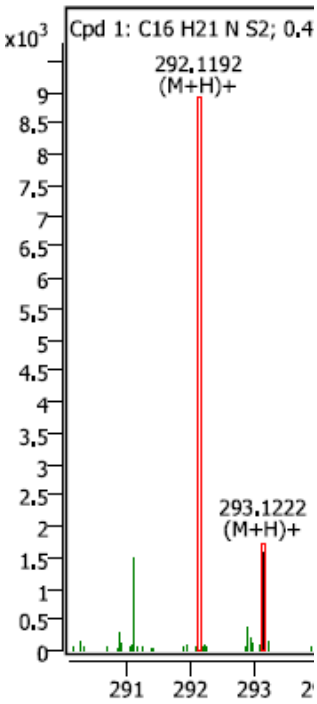


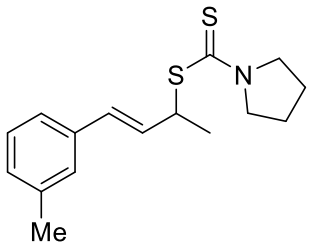
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4k**



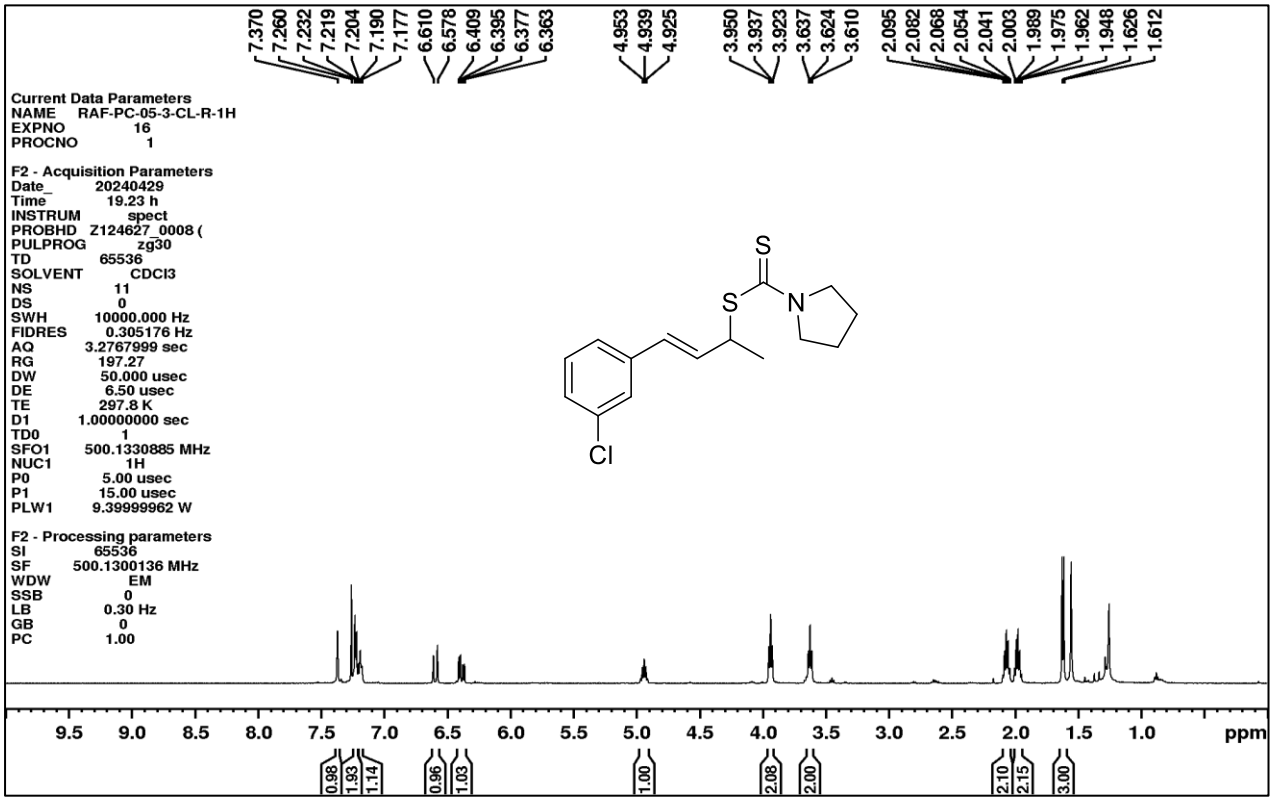


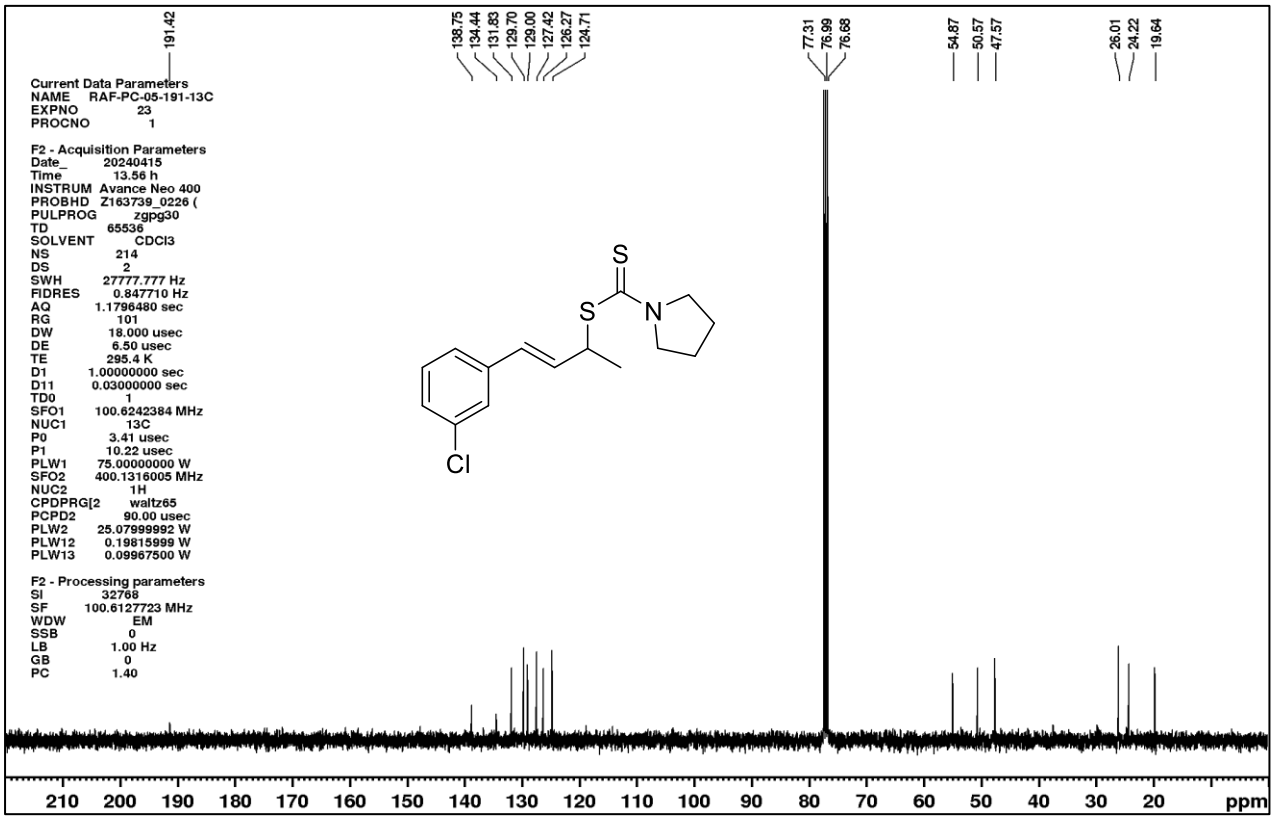
4k: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{22}NS_2$ 292.1189; Found 292.1192.



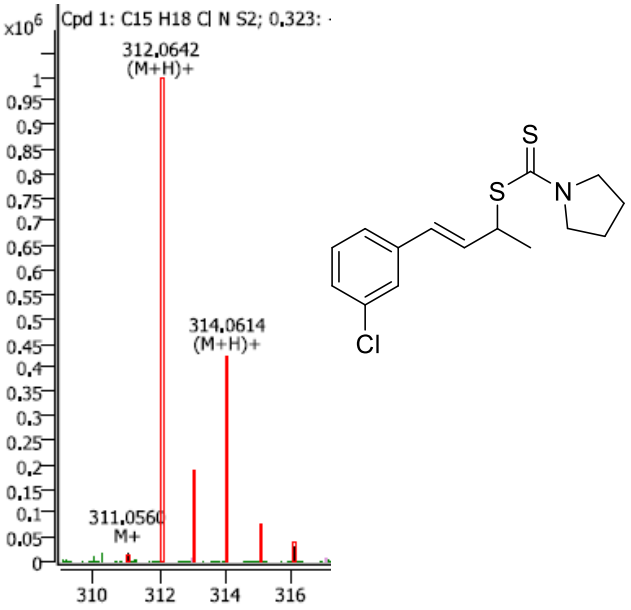


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4l**

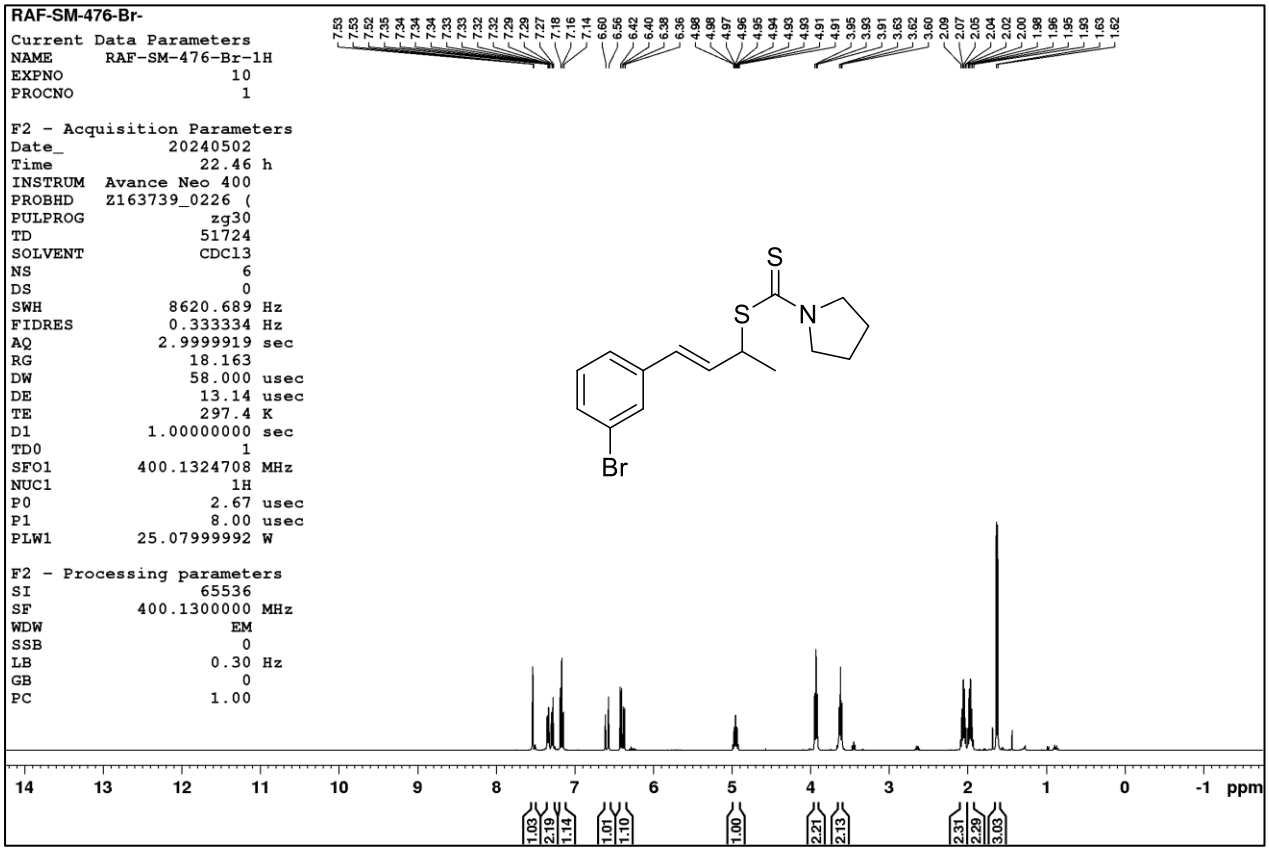


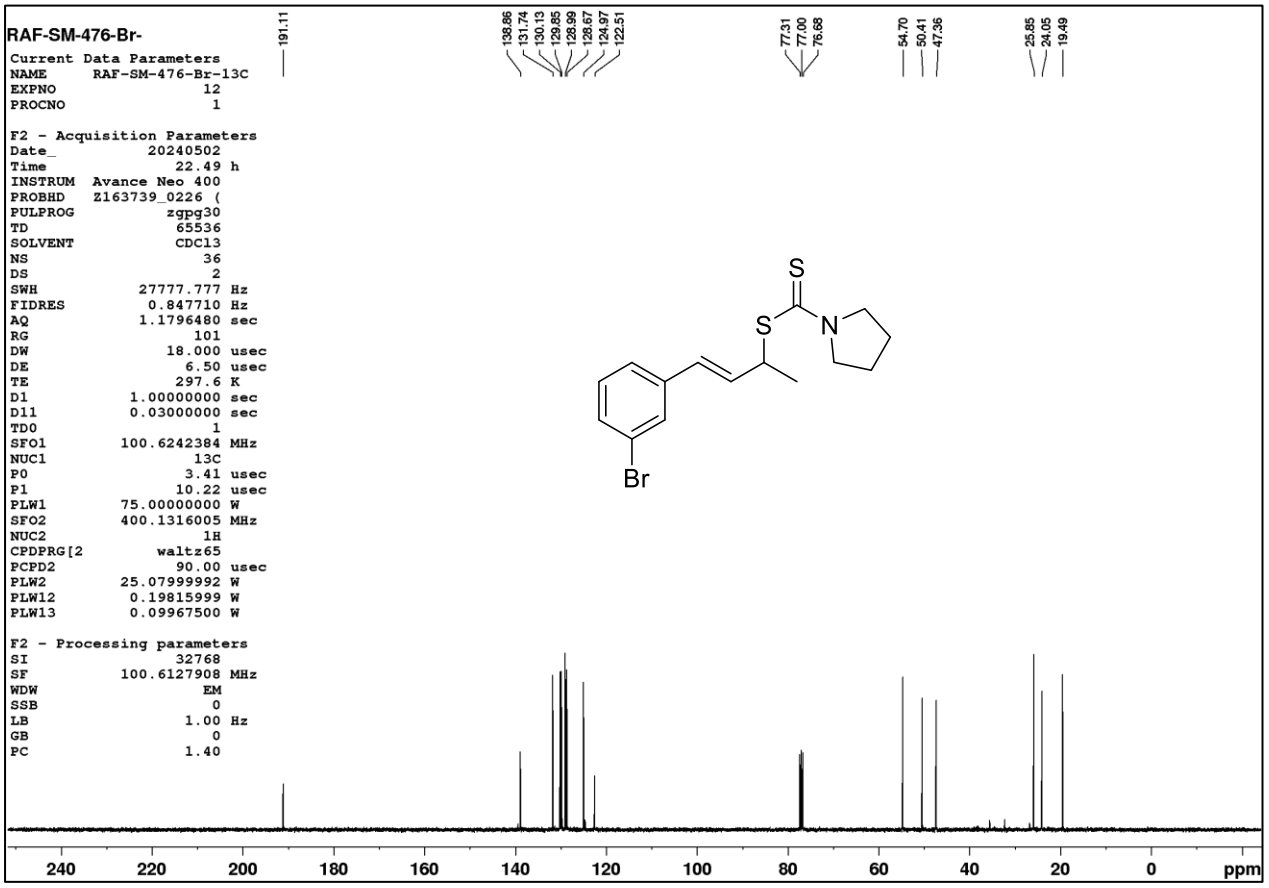


4l: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{15}H_{19}ClNS_2$ 312.0643 Found 312.0642.

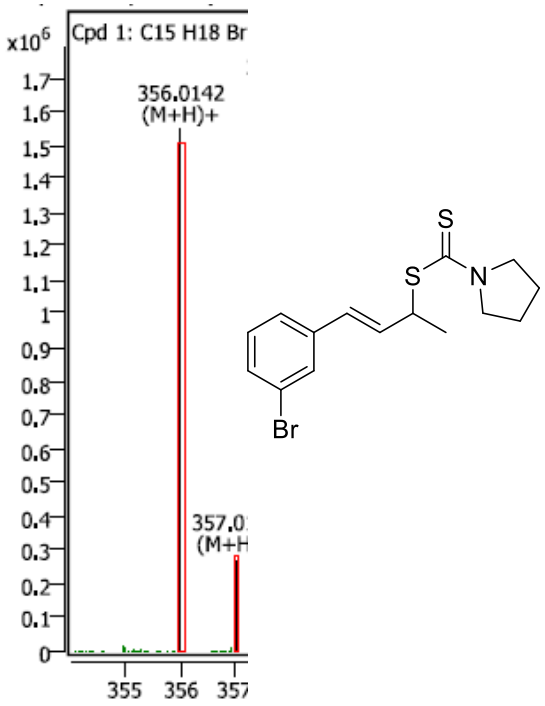


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4m**

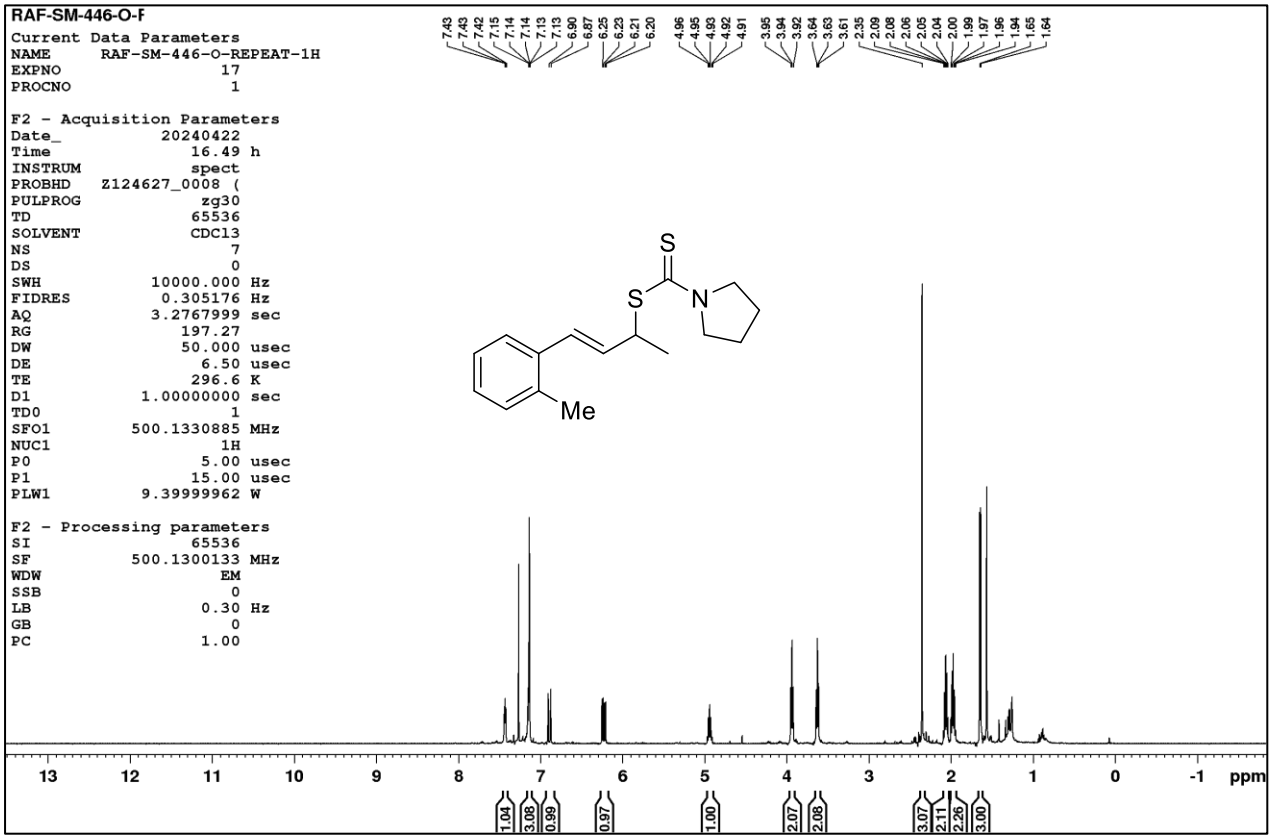


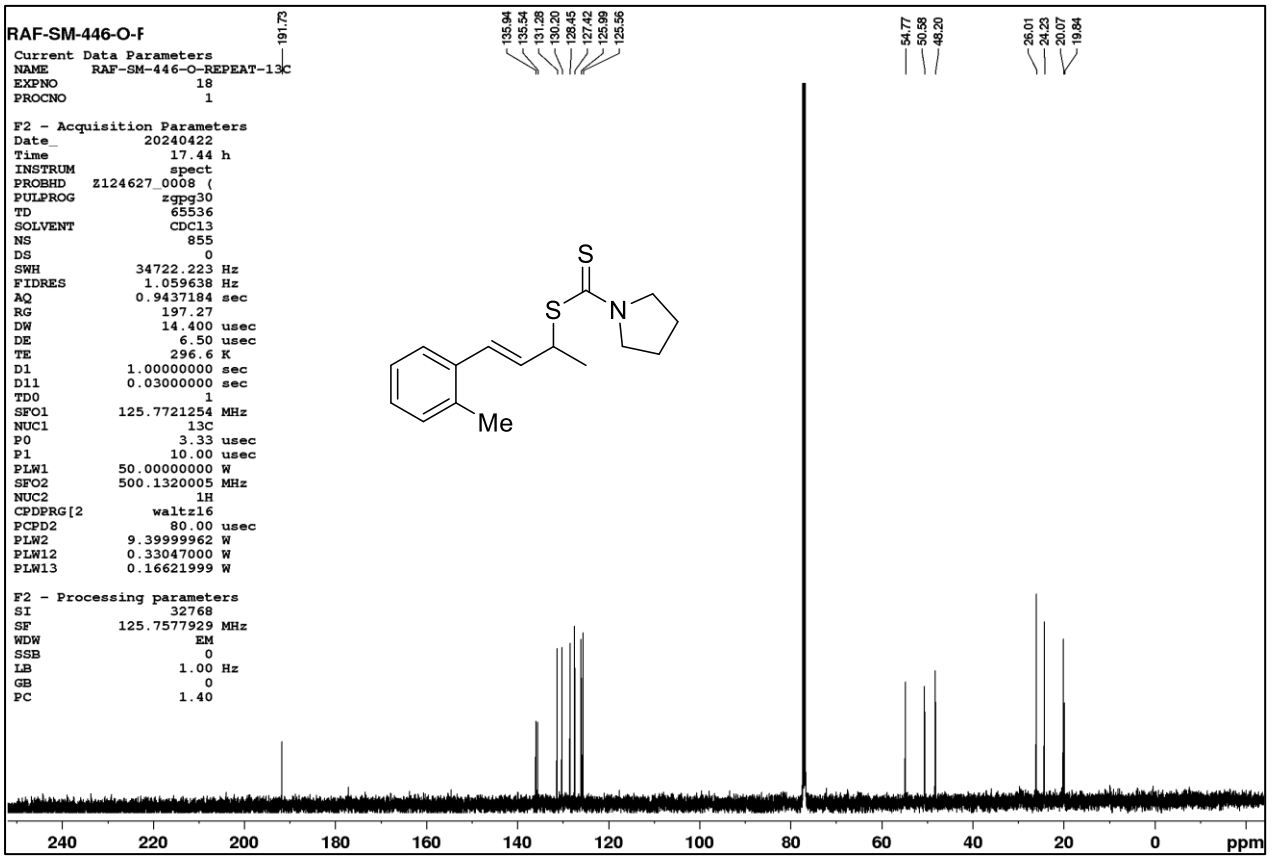


4m: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{15}H_{19}BrNS_2$ 356.0137; Found 356.0142.

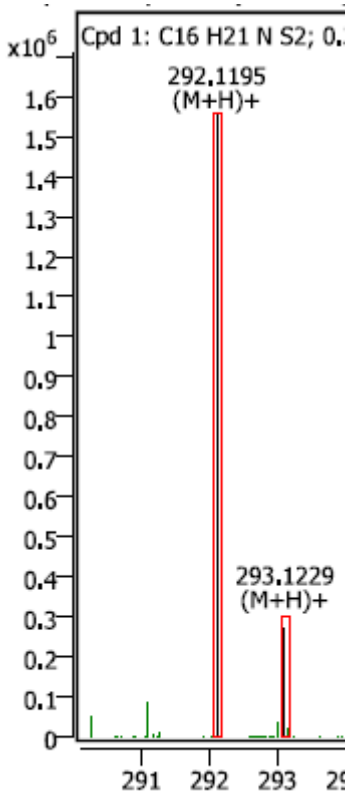


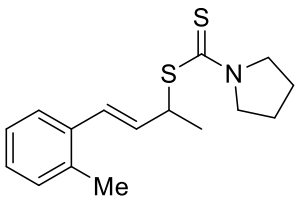
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4o**



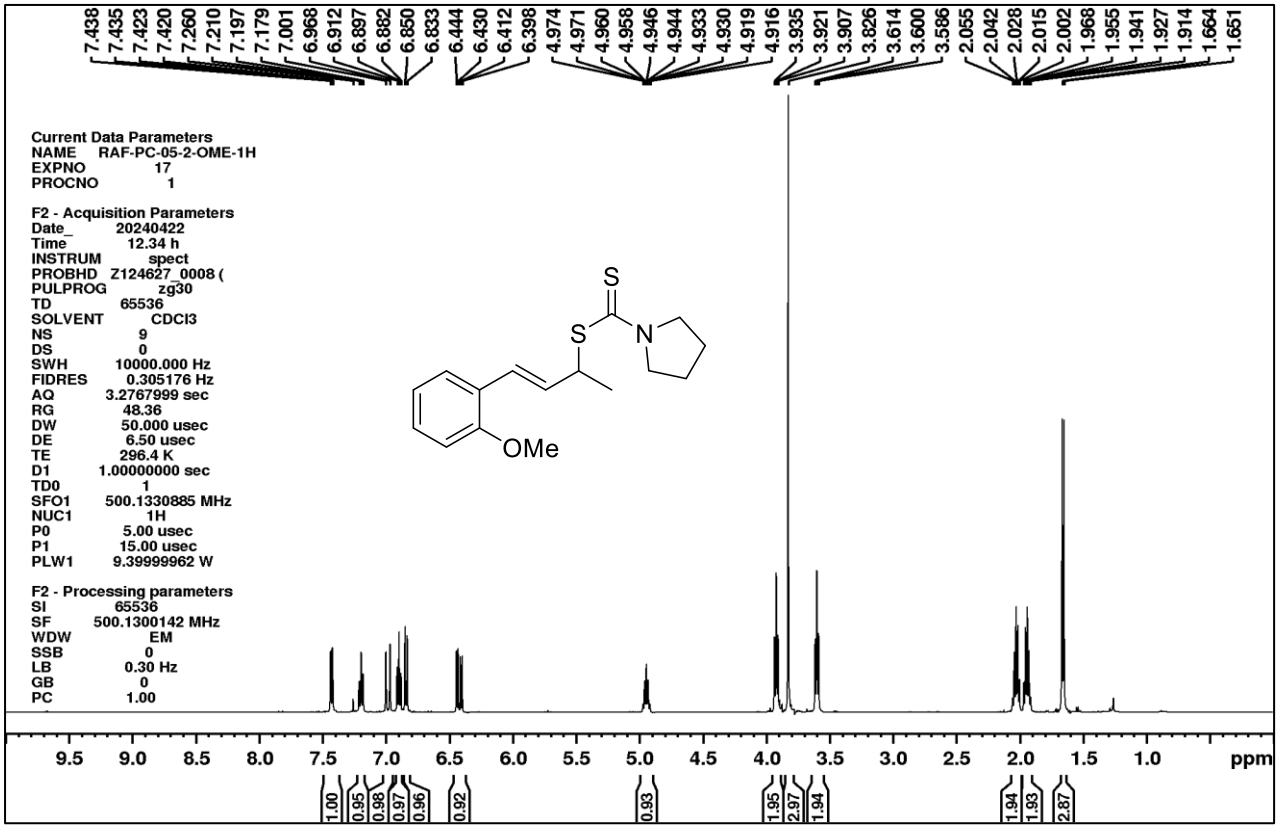


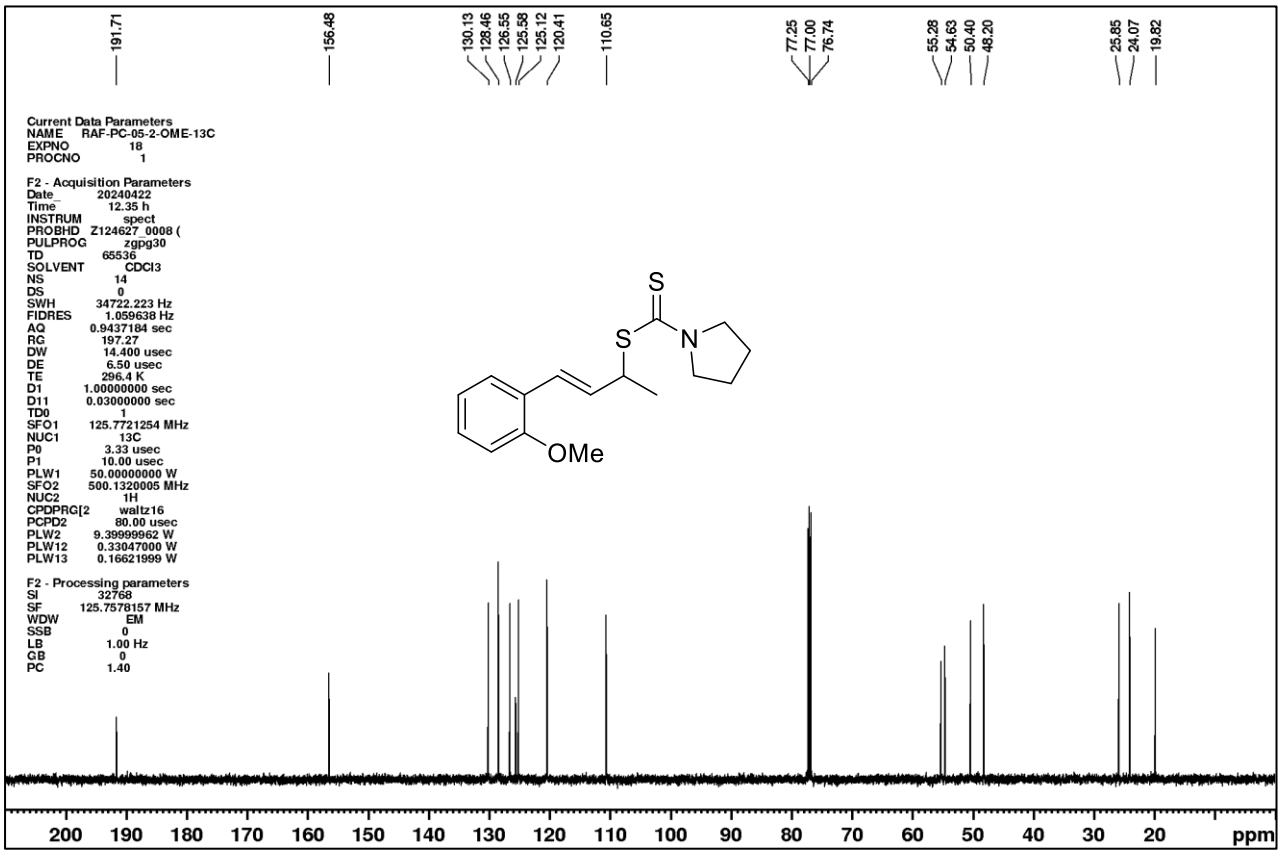
4o: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{16}H_{22}NS_2$ 292.1189; Found 292.1195.



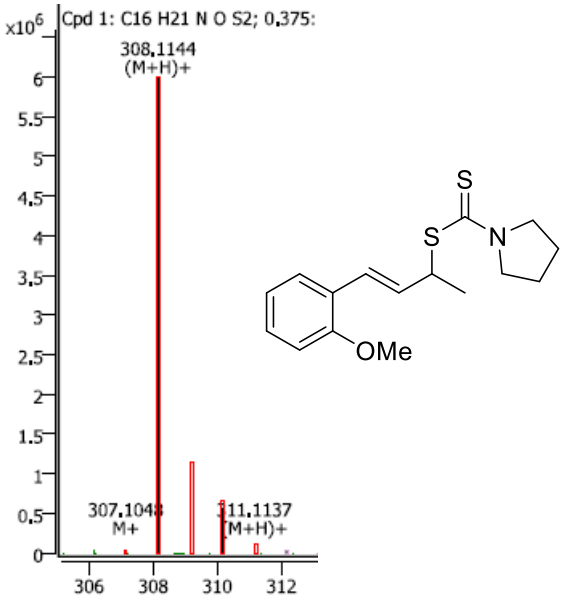


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4p**

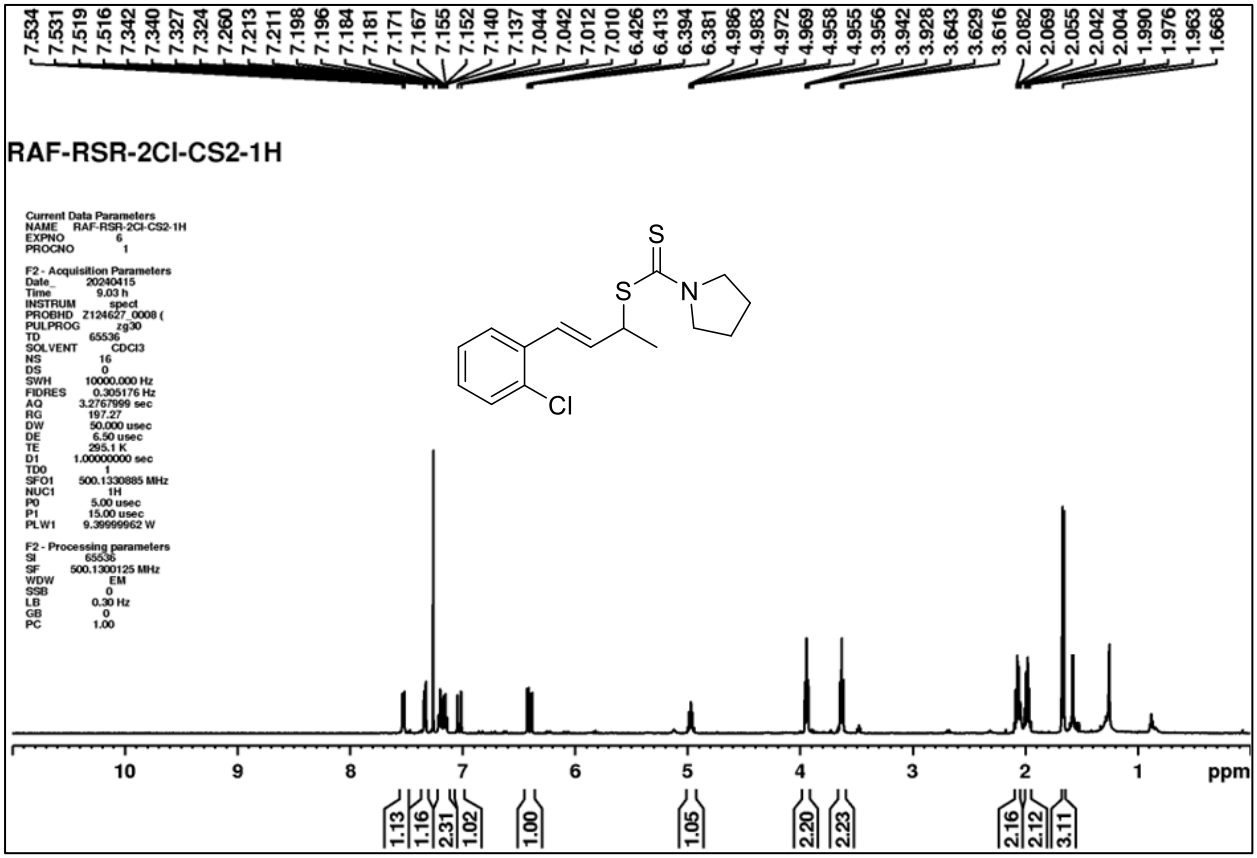


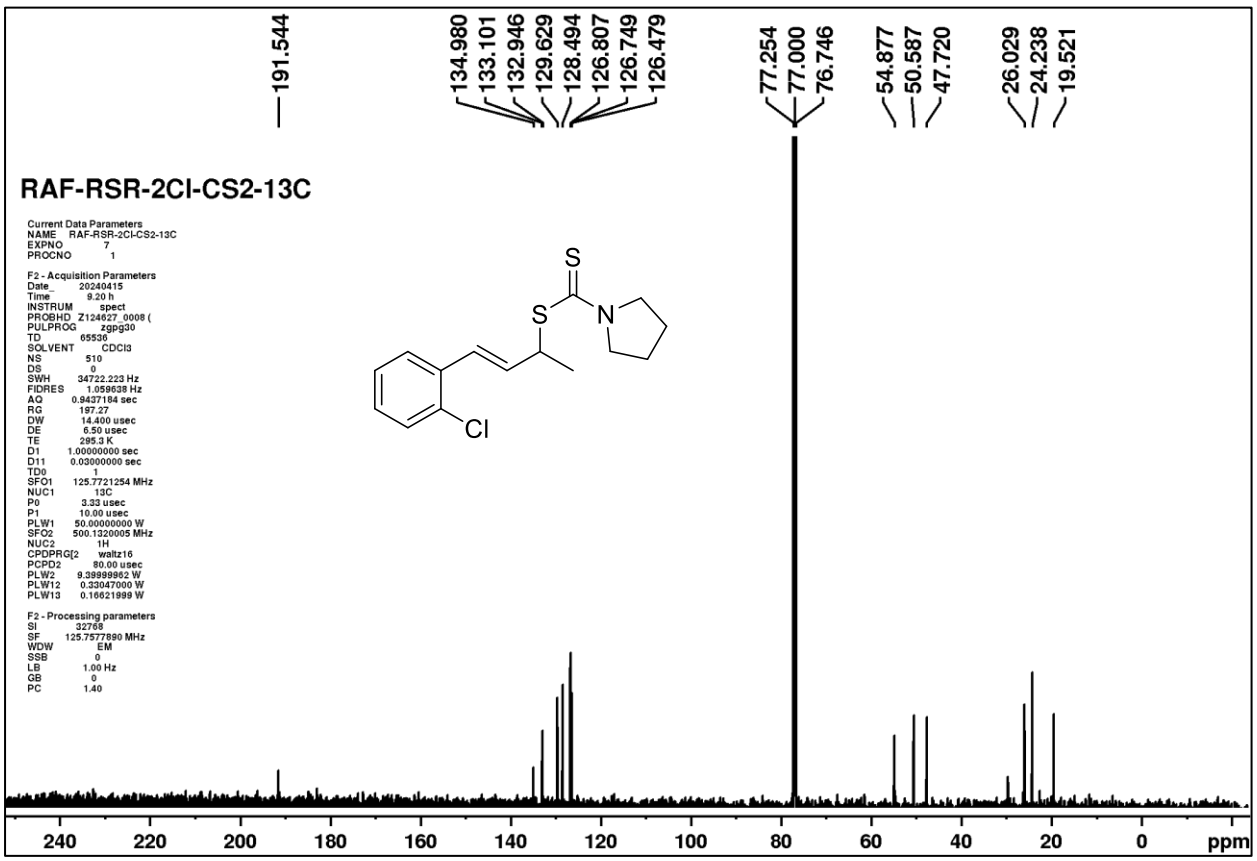


4p: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{16}H_{22}OS_2N$ 308.1137 Found 308.1144.

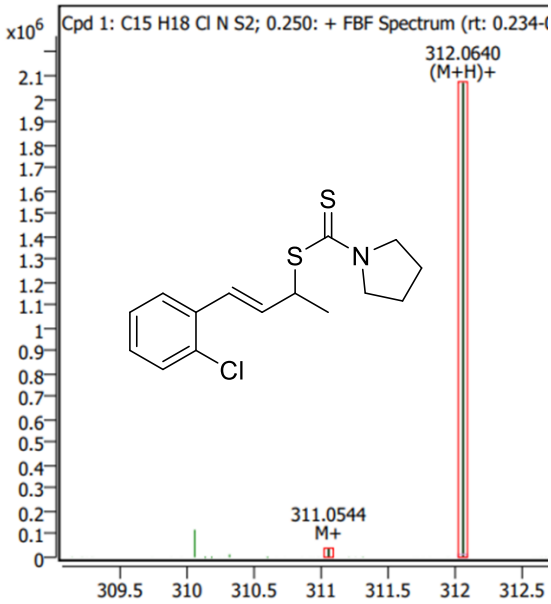


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4q**

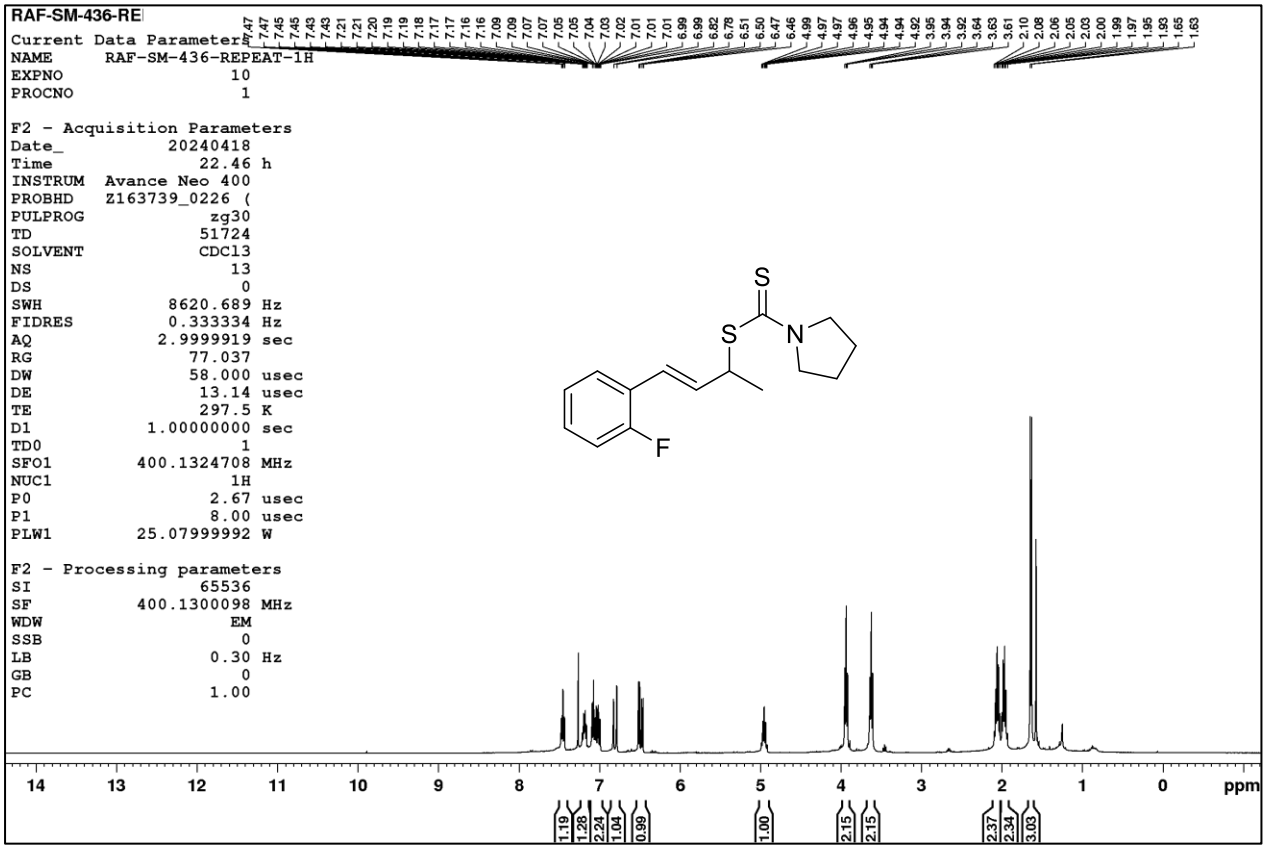


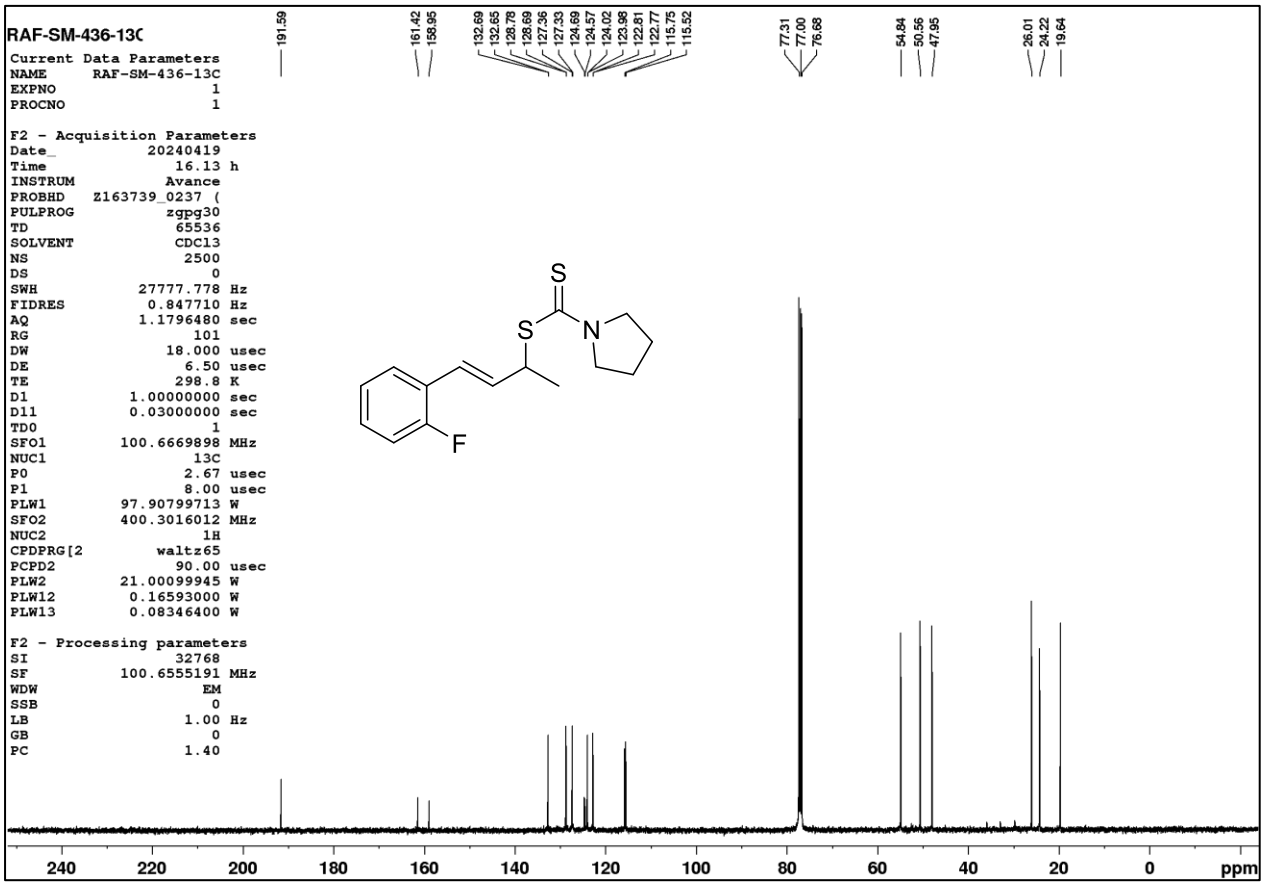


4q: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{19}ClNS_2$ 312.0642; Found: 312.0640.

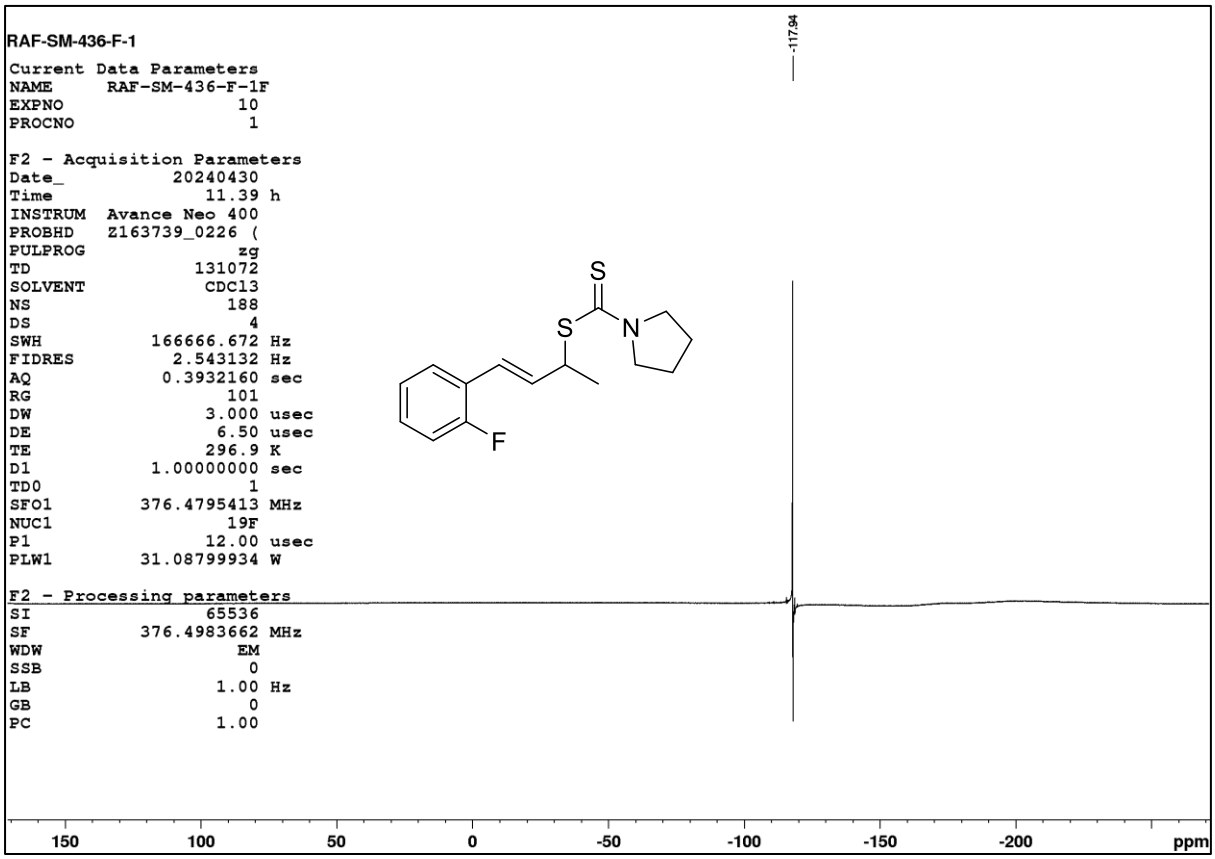


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4r**

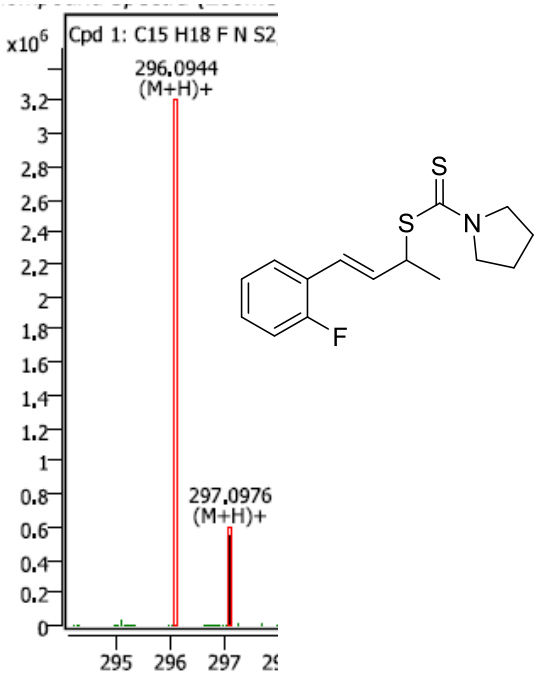




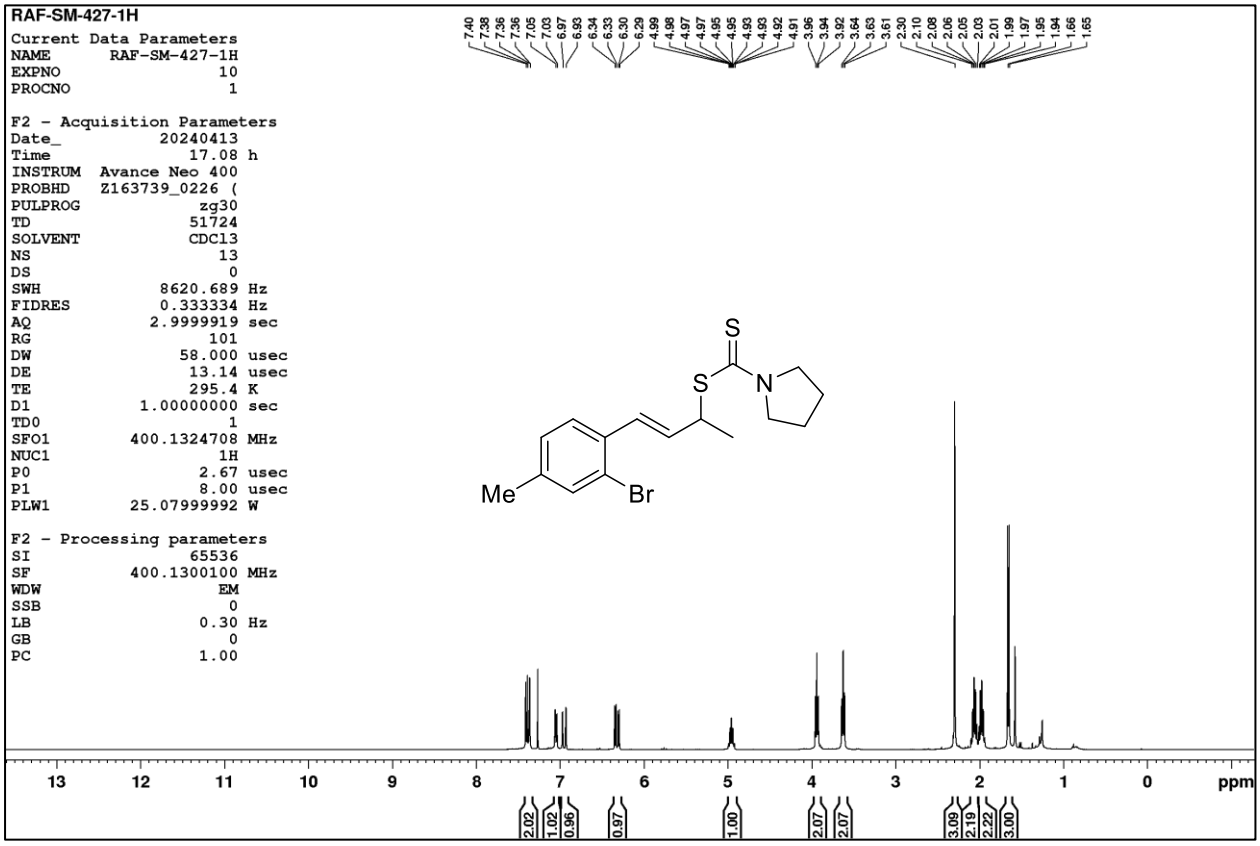
$^{19}F\{H\}$ NMR ($CDCl_3$, 376 MHz) of compound **4r**

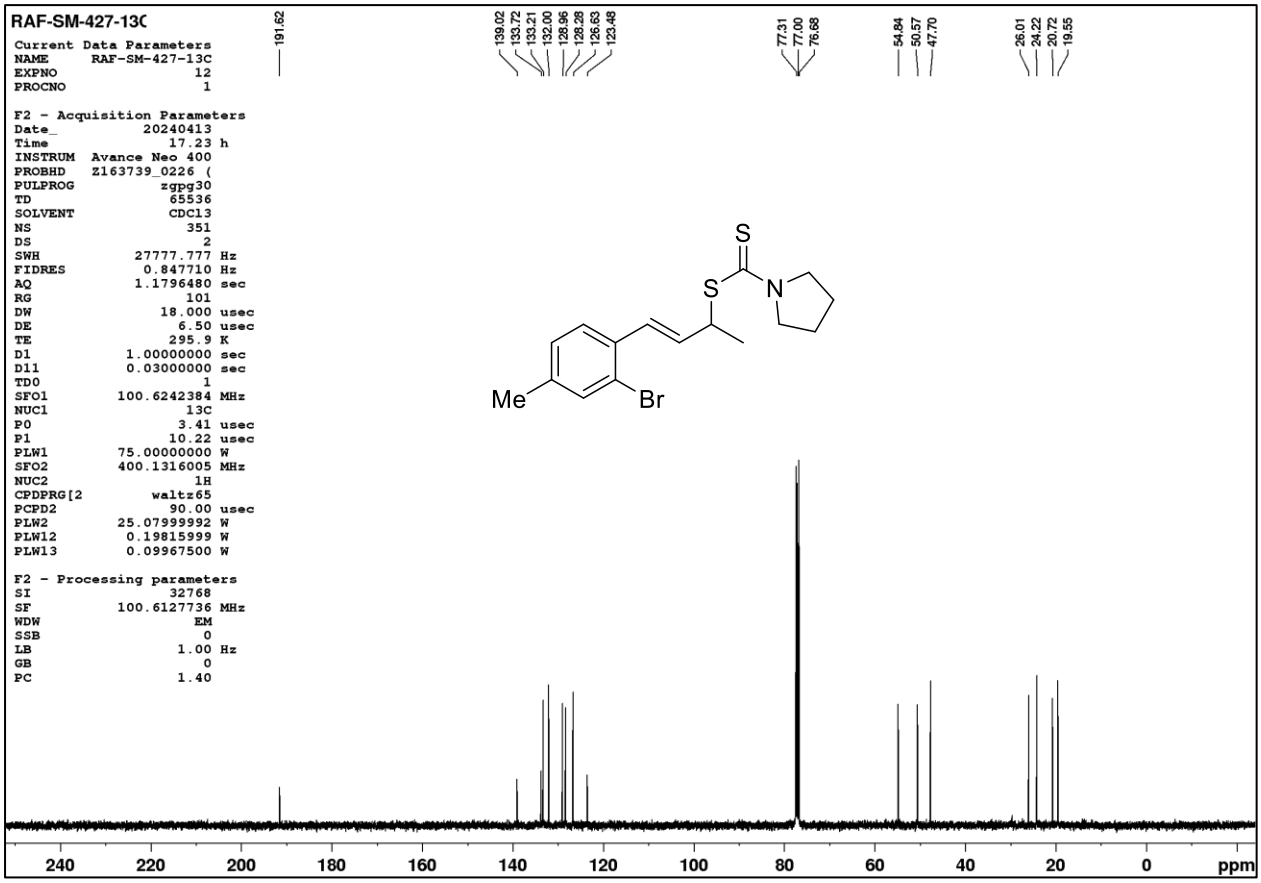


4r: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{19}FNS_2$ 296.0938; Found 296.0944.

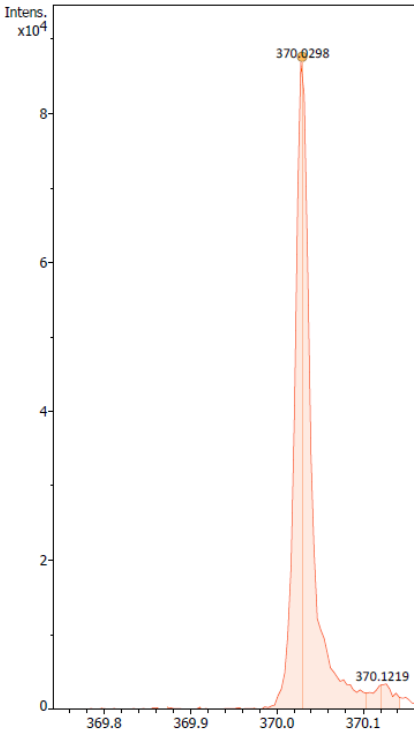


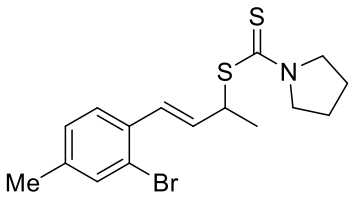
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4s**



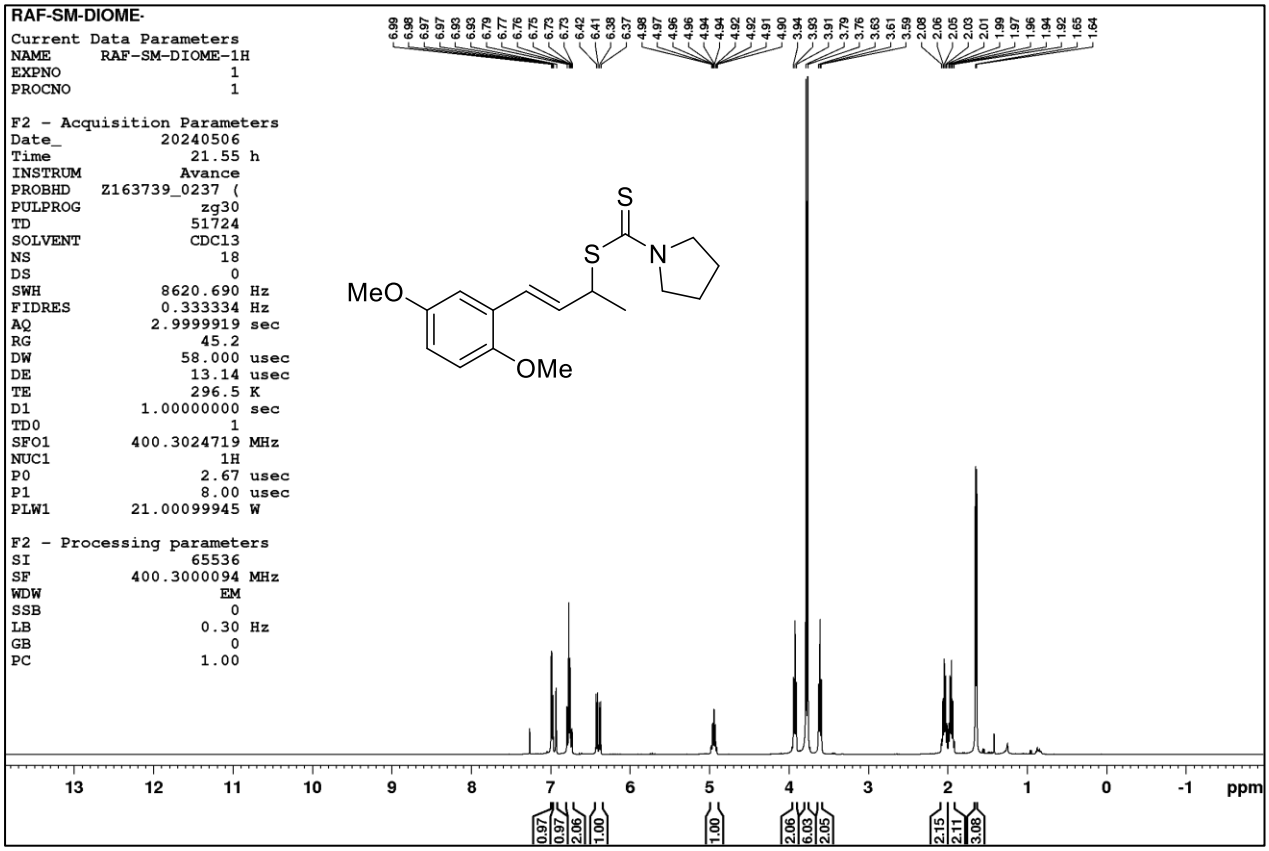


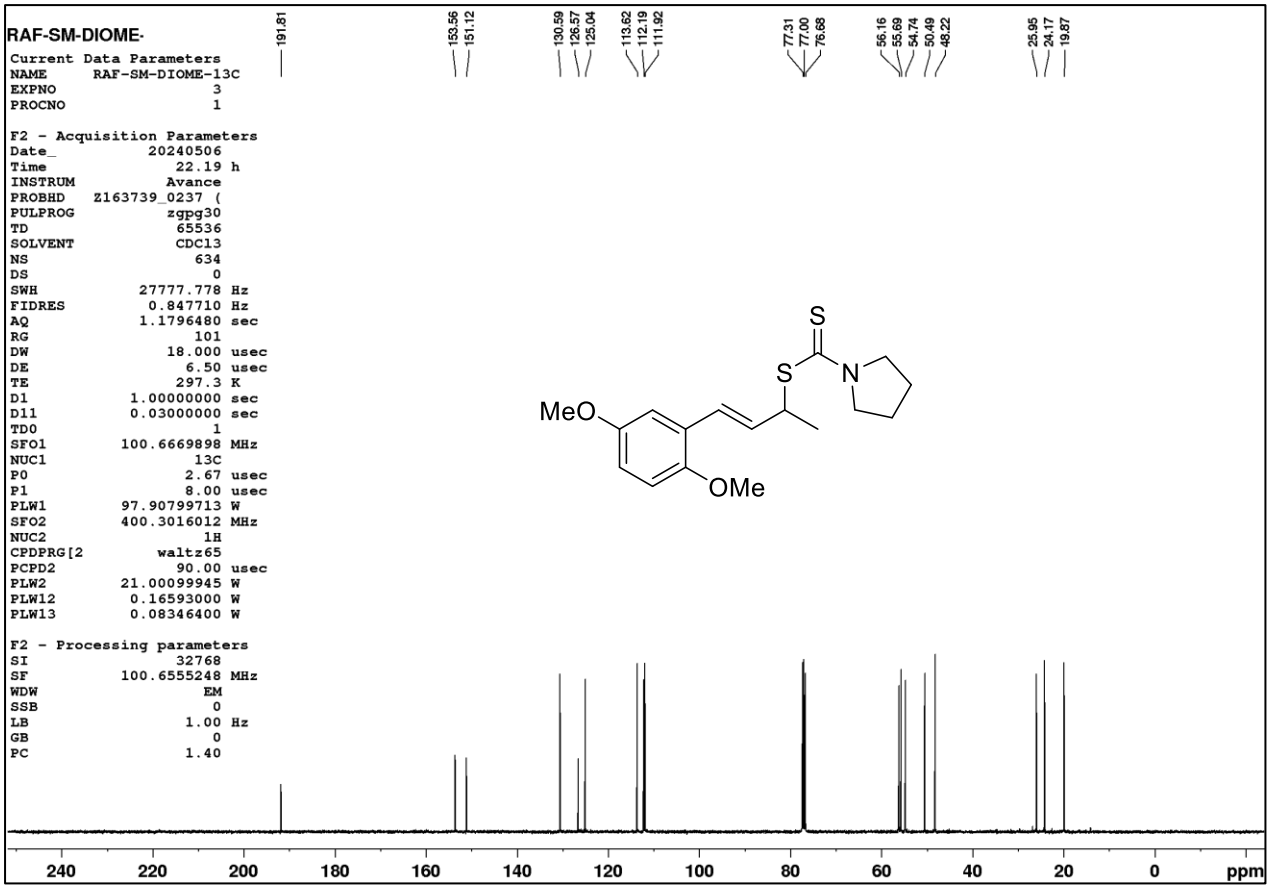
4s: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{21}BrNS_2$ 370.0294; Found 370.0298.



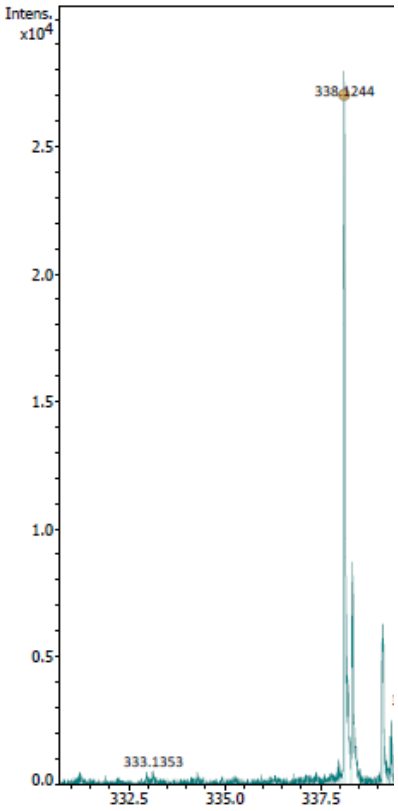


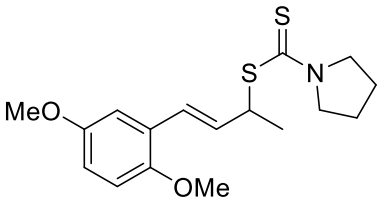
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4t**



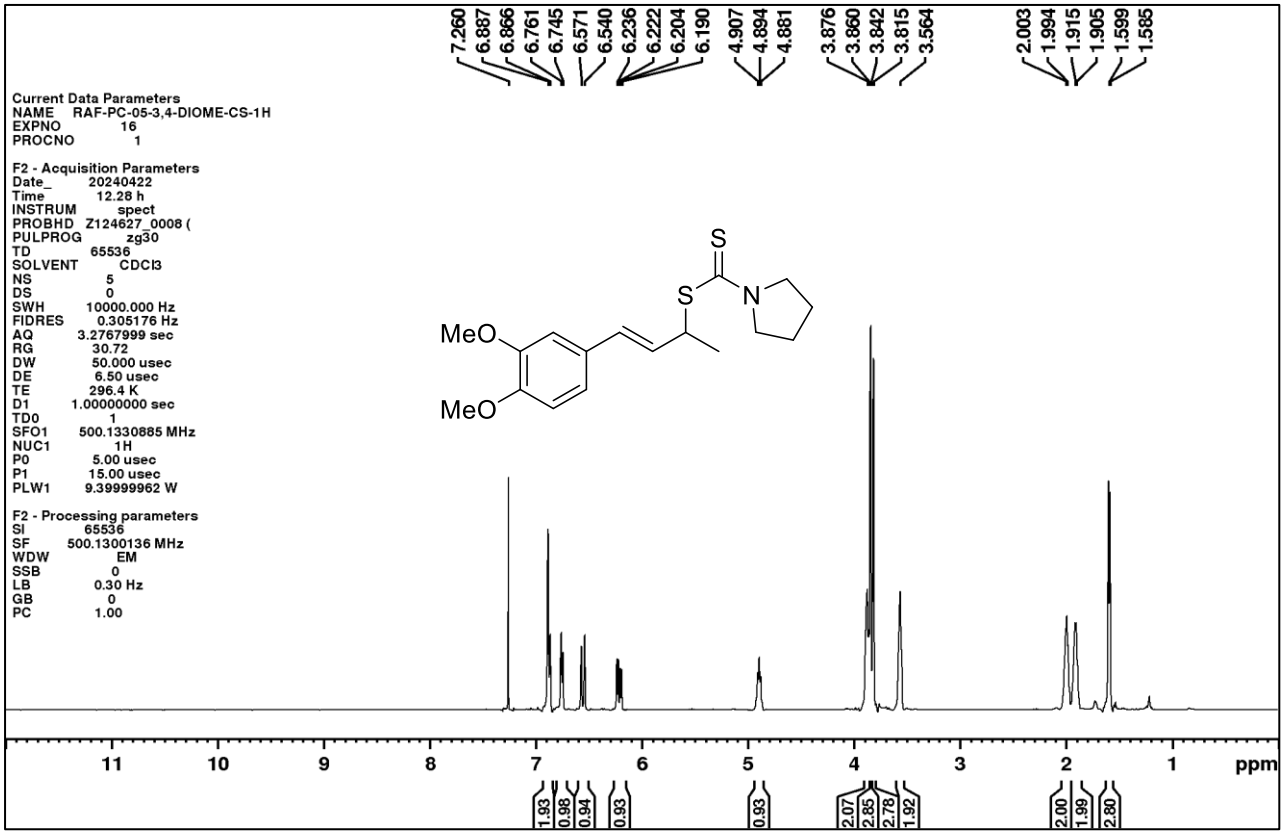


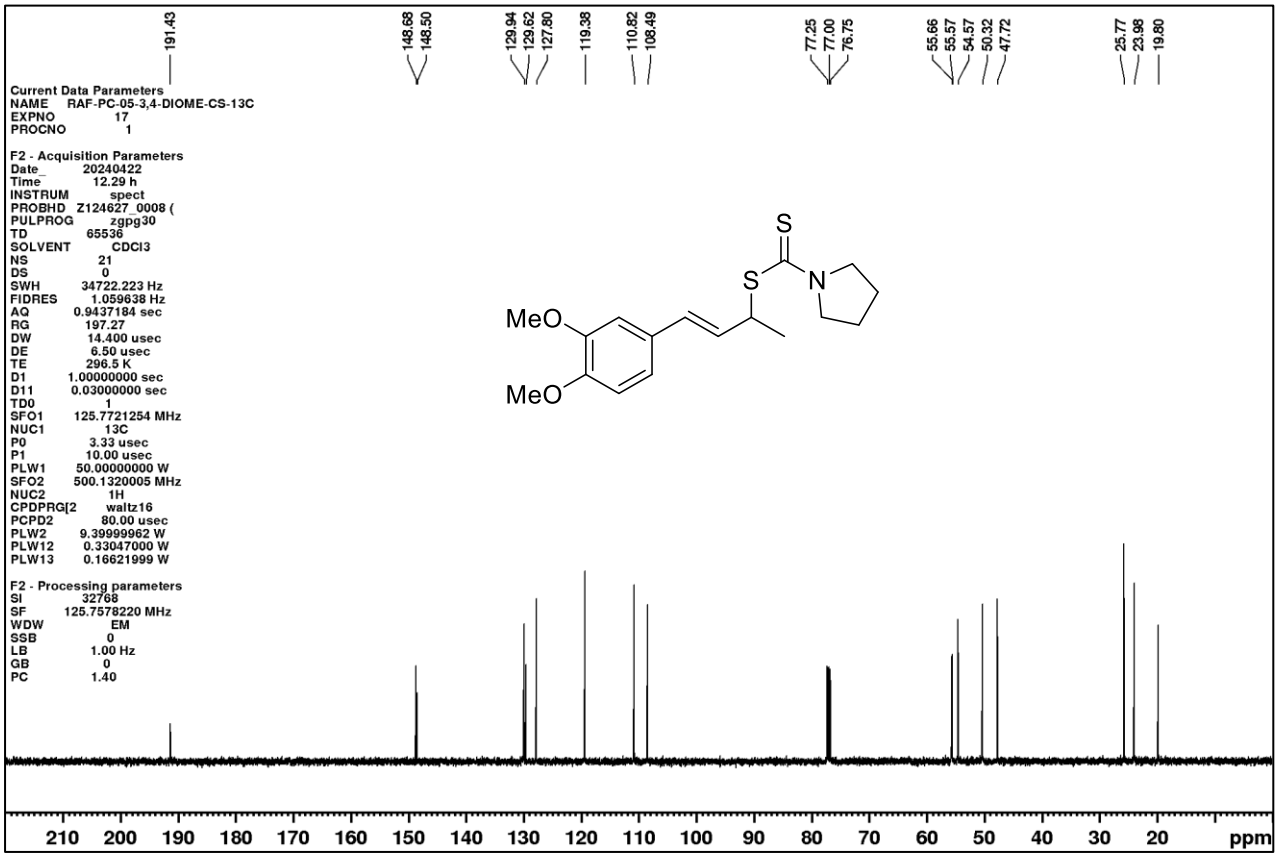
4t: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{24}NO_2S_2$ 338.1243; Found 338.1244.



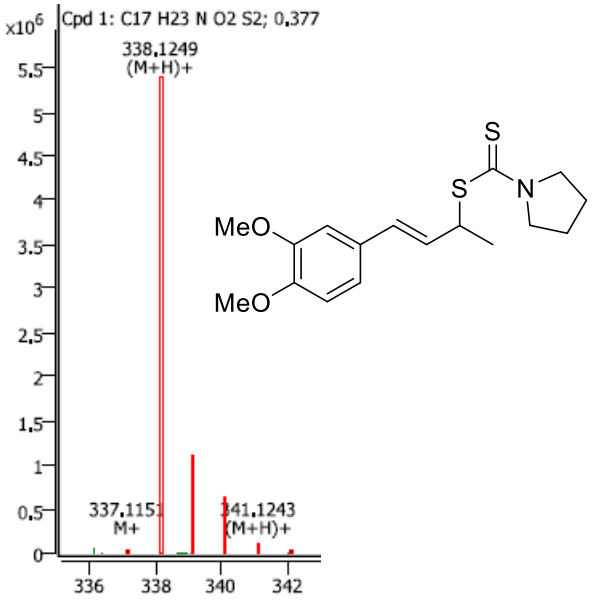


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4u**

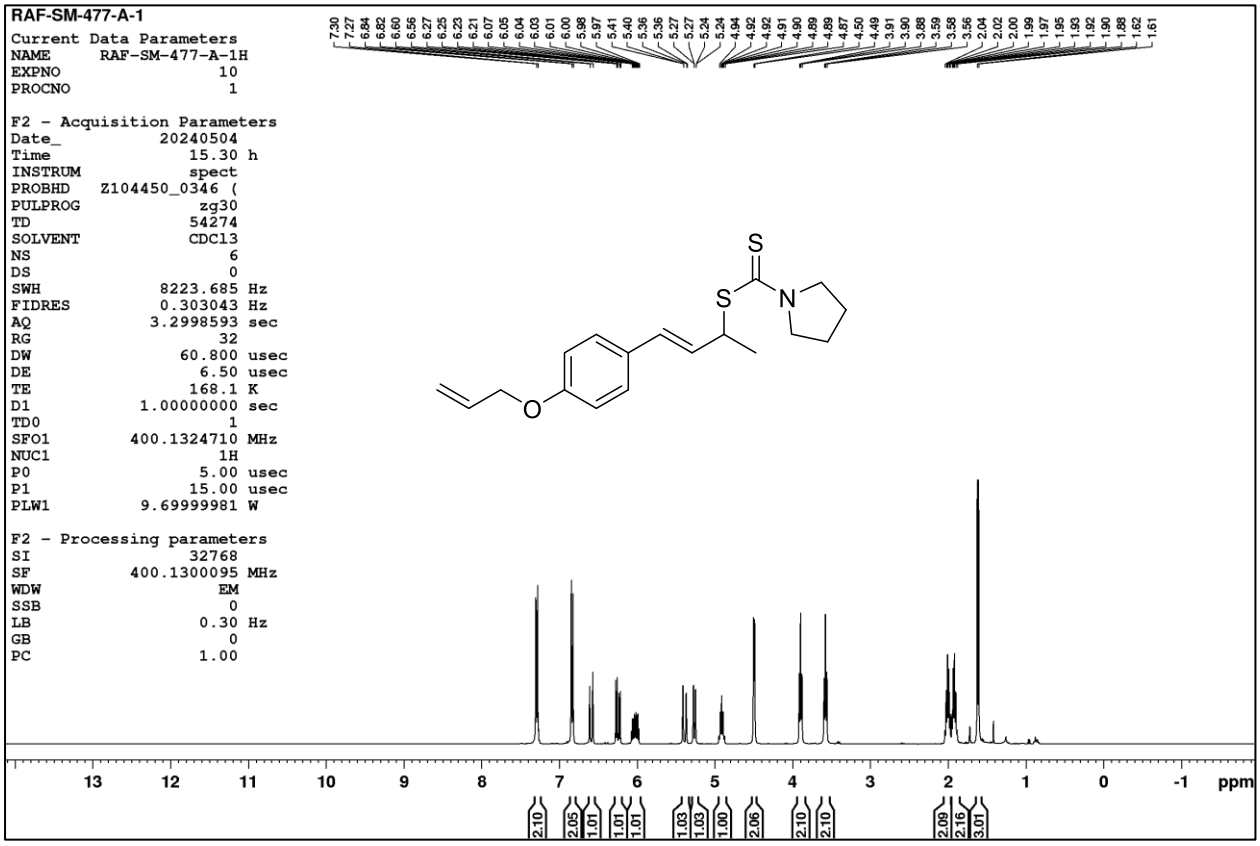


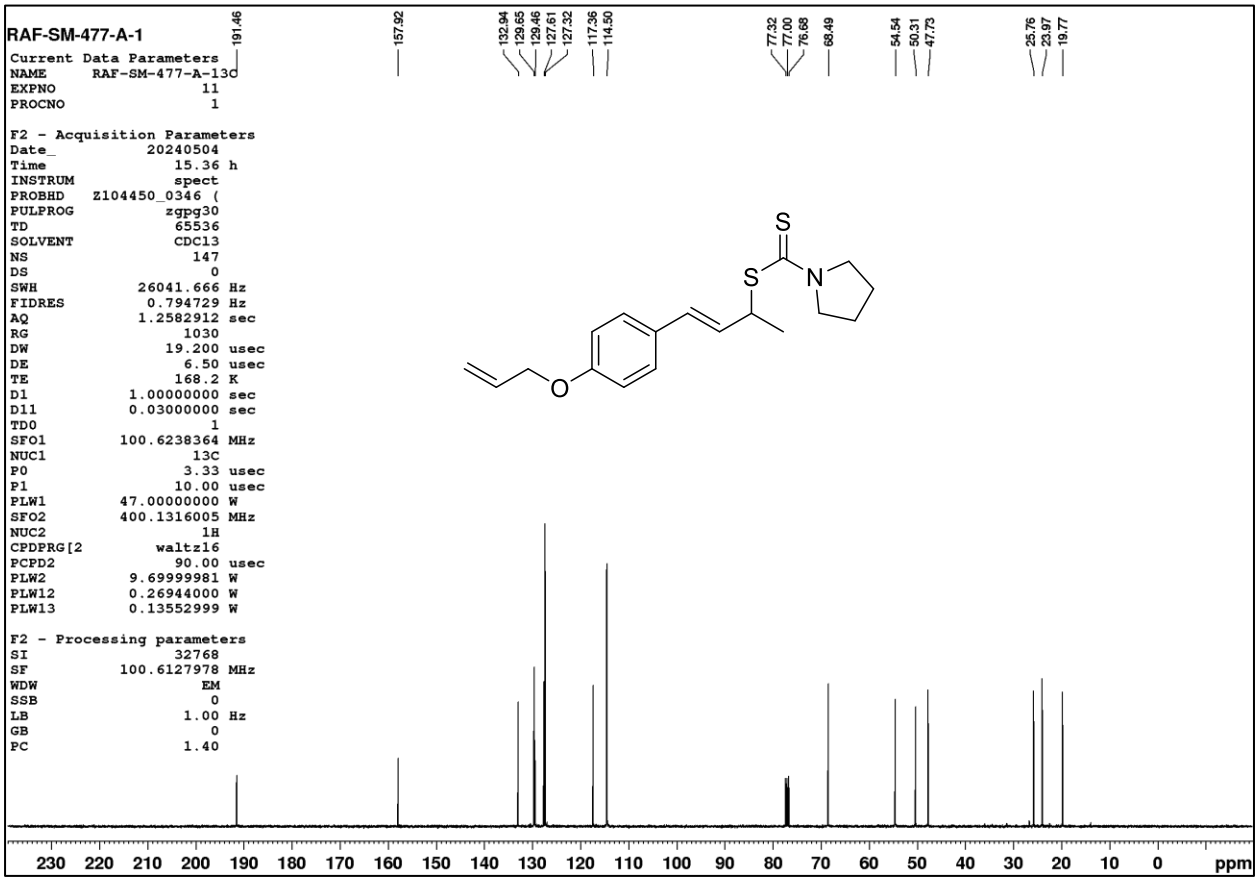


4u: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{17}H_{24}NO_2S_2$ 338.1243 Found 338.1249.

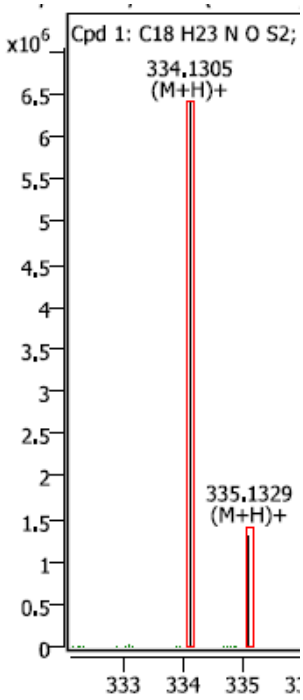


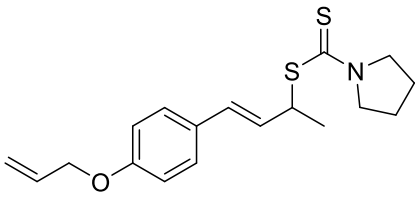
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4v**



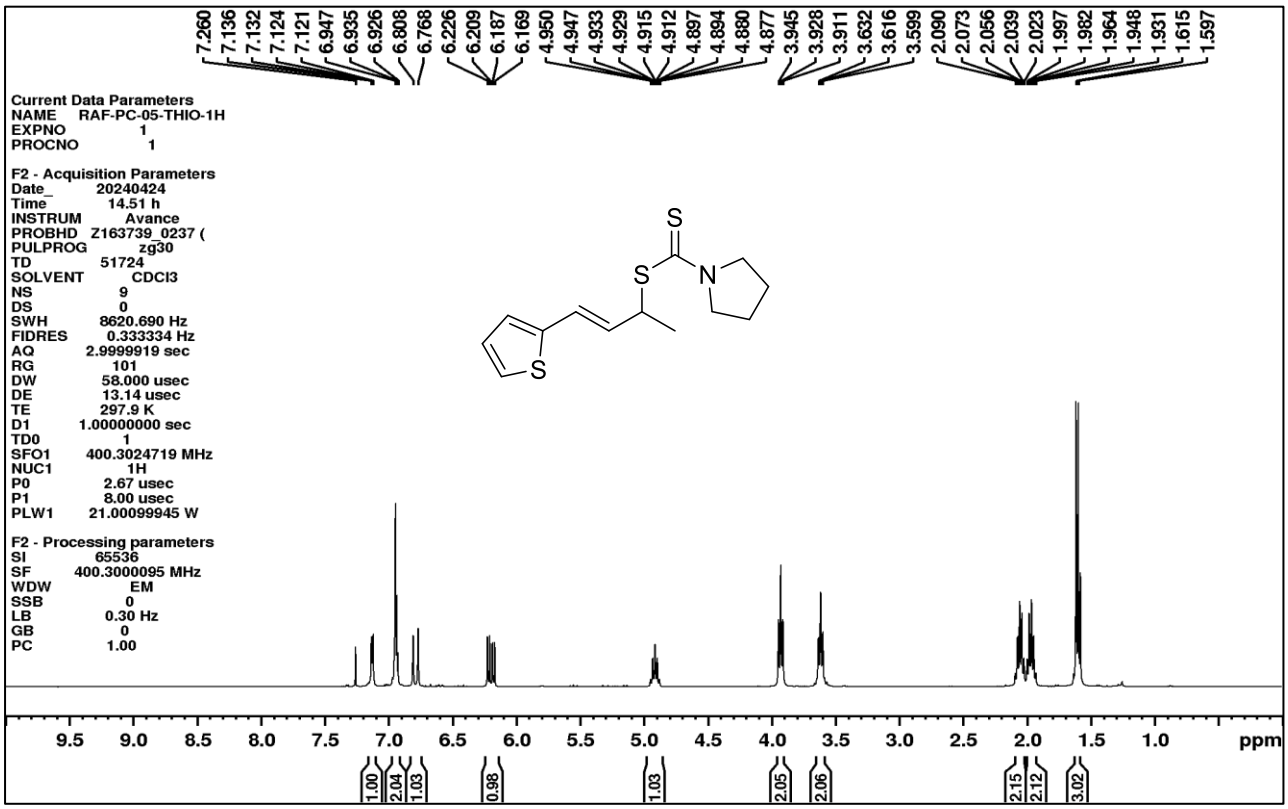


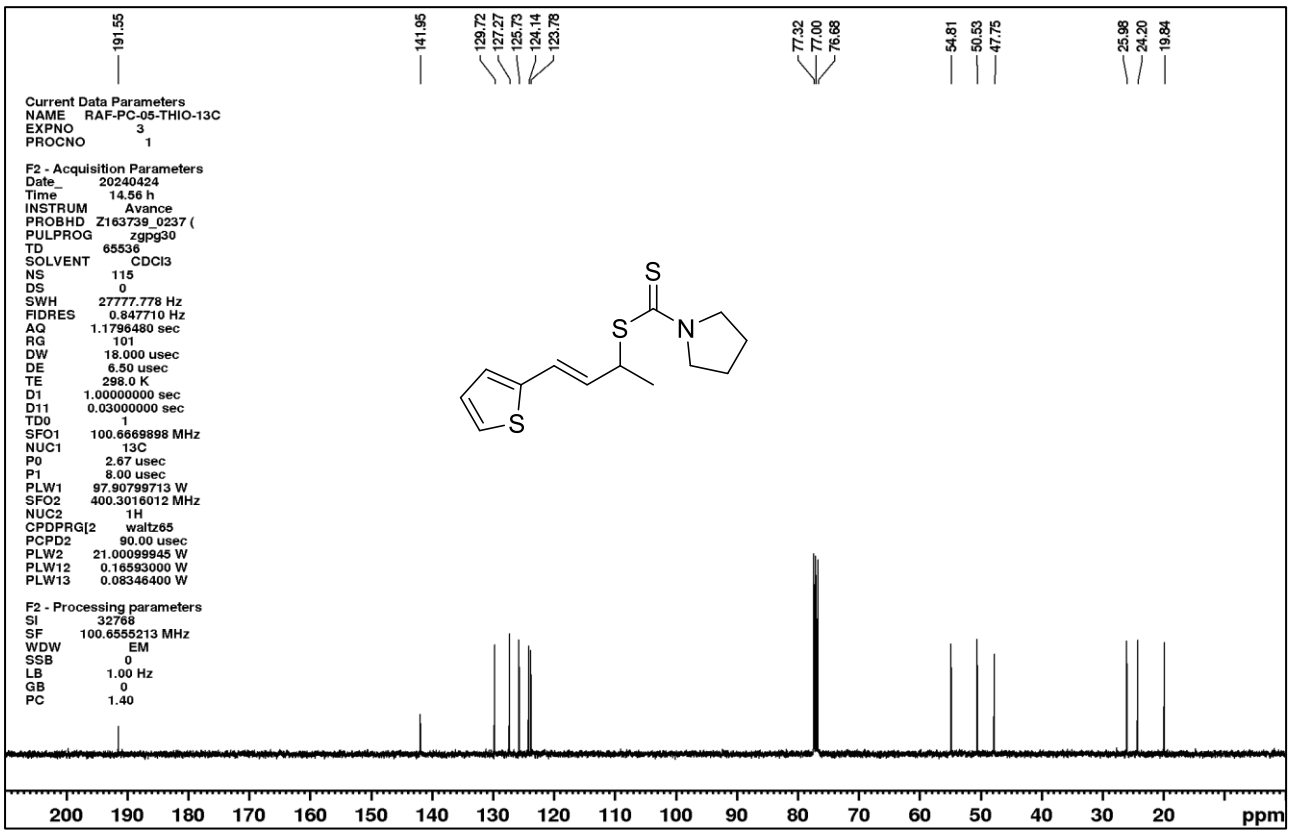
4v: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{24}NOS_2$ 334.1295; Found 334.1305.



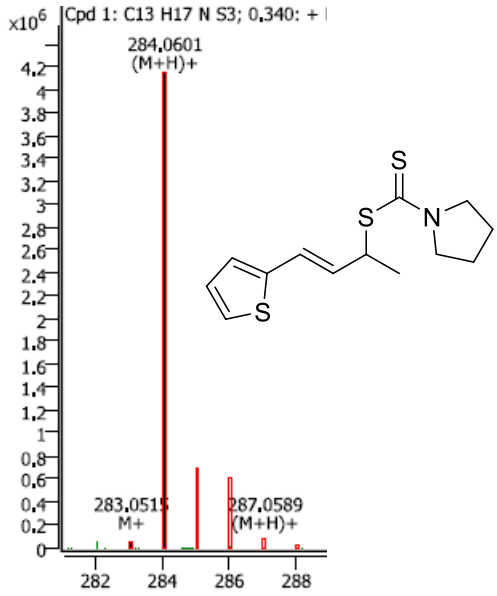


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4w**

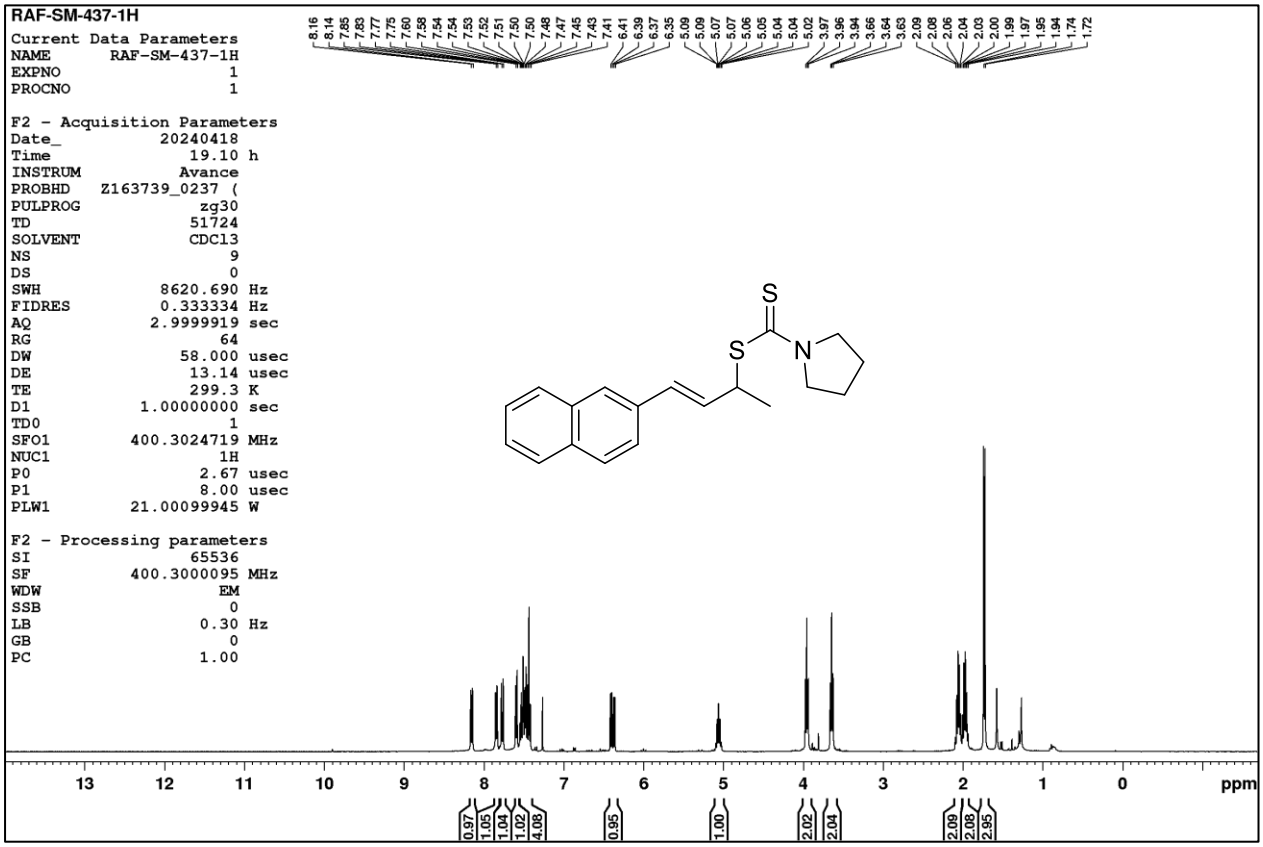


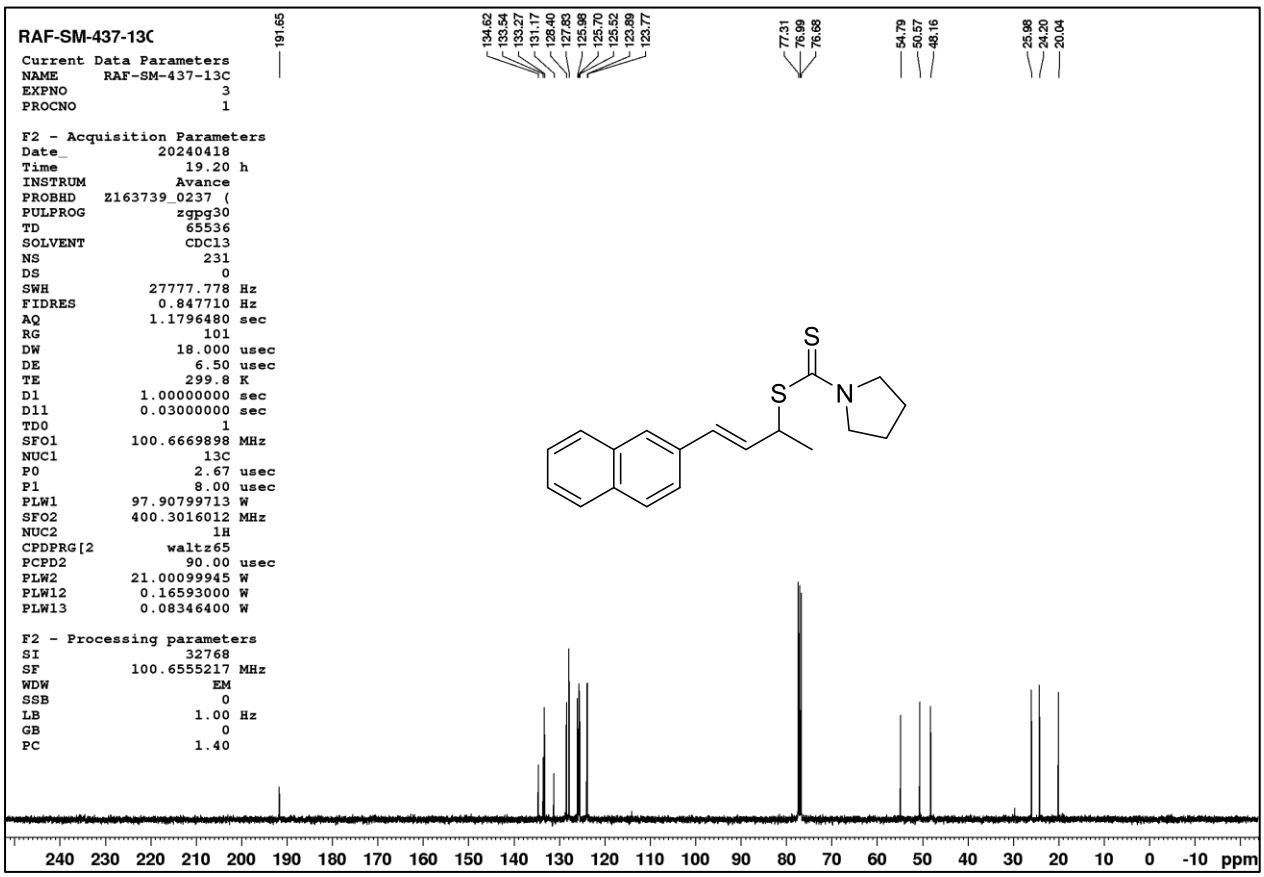


4w: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{13}H_{18}NS_3$ 284.0596 Found 284.0601.

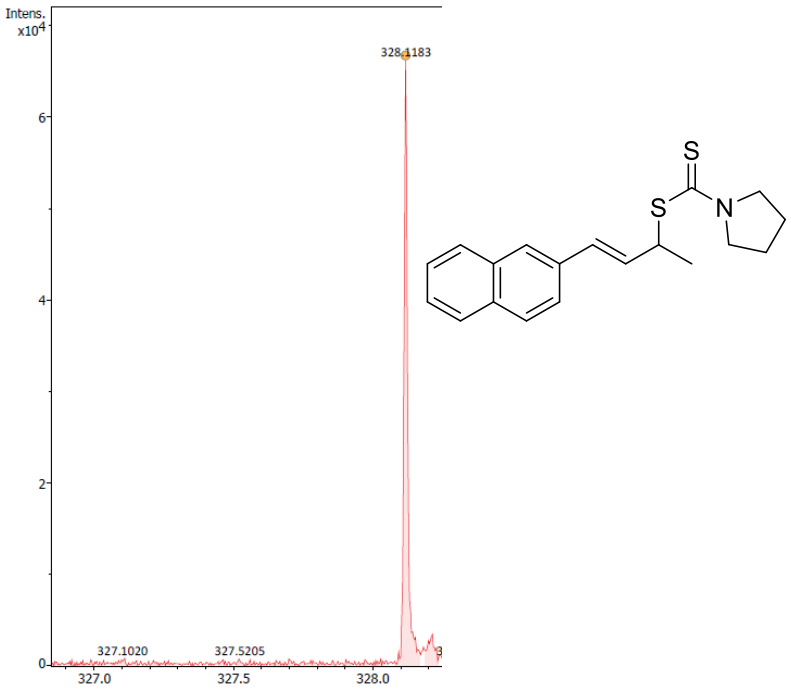


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4x**

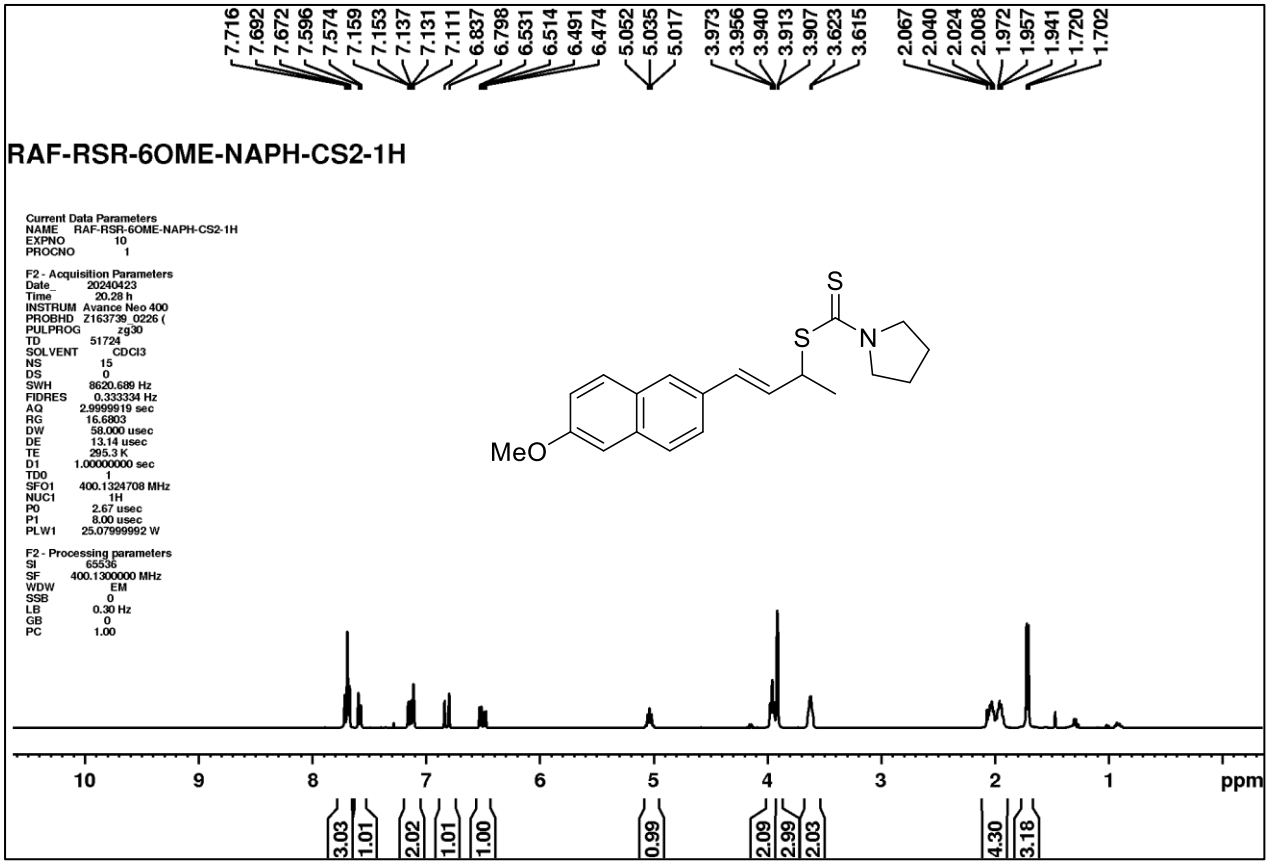


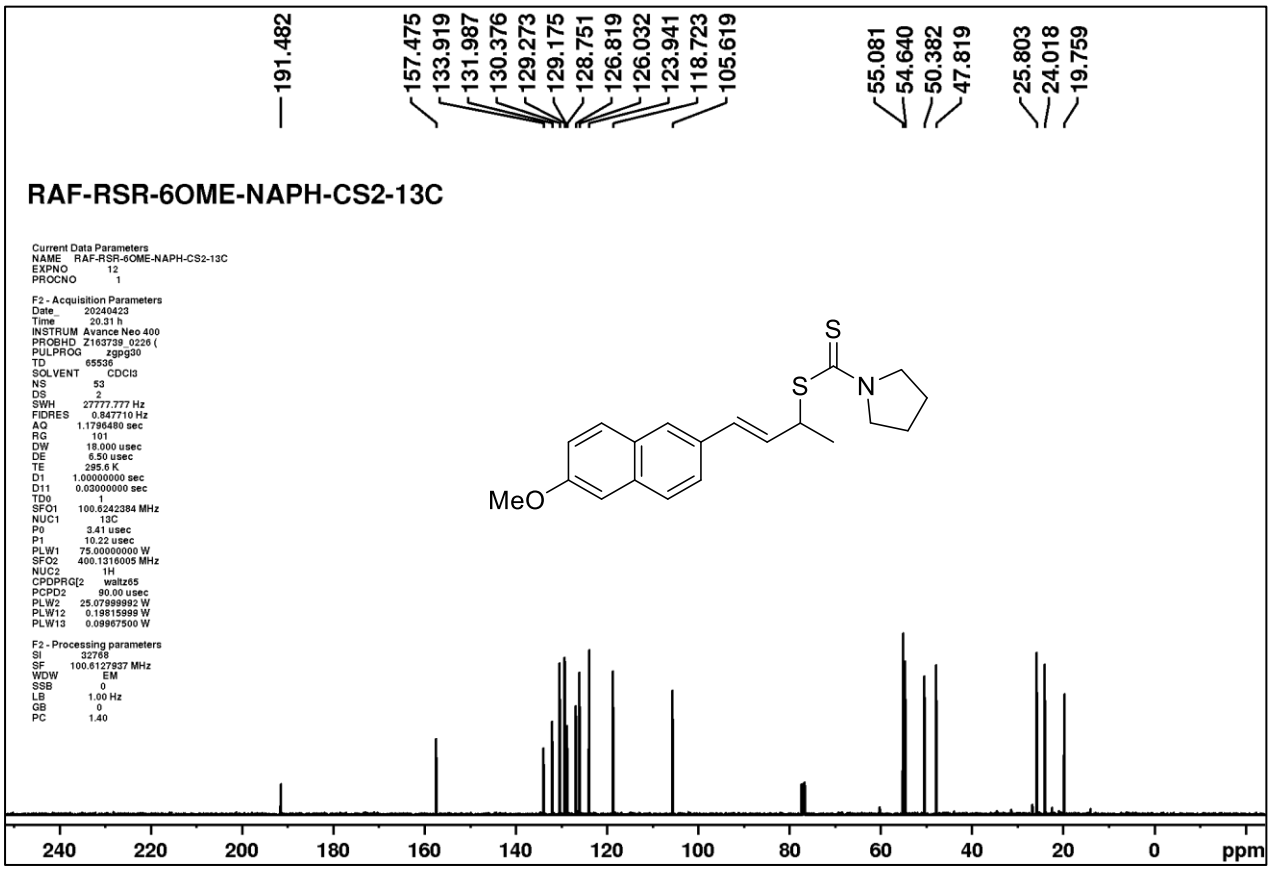


4x: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{19}H_{22}NS_2$ 328.1189; Found 328.1183.

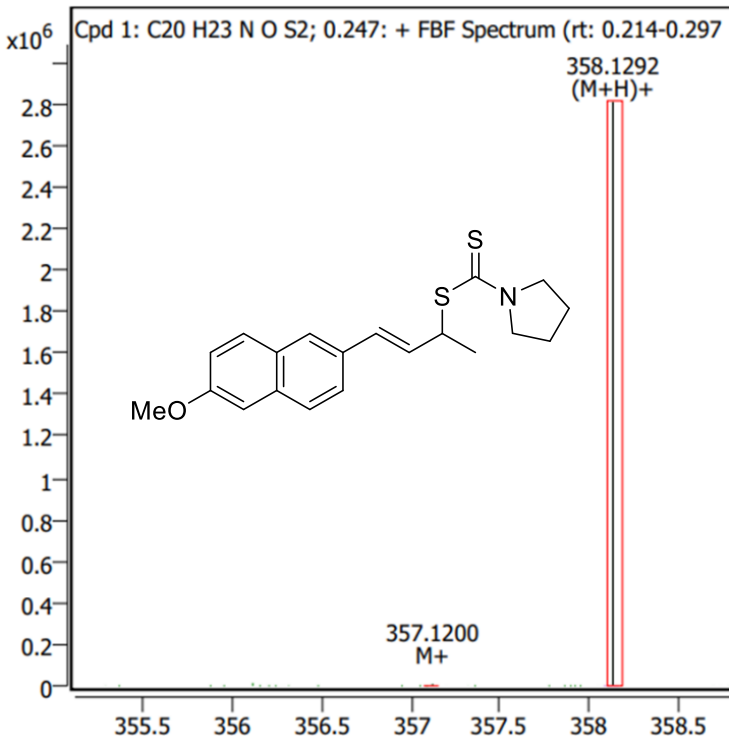


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4y**

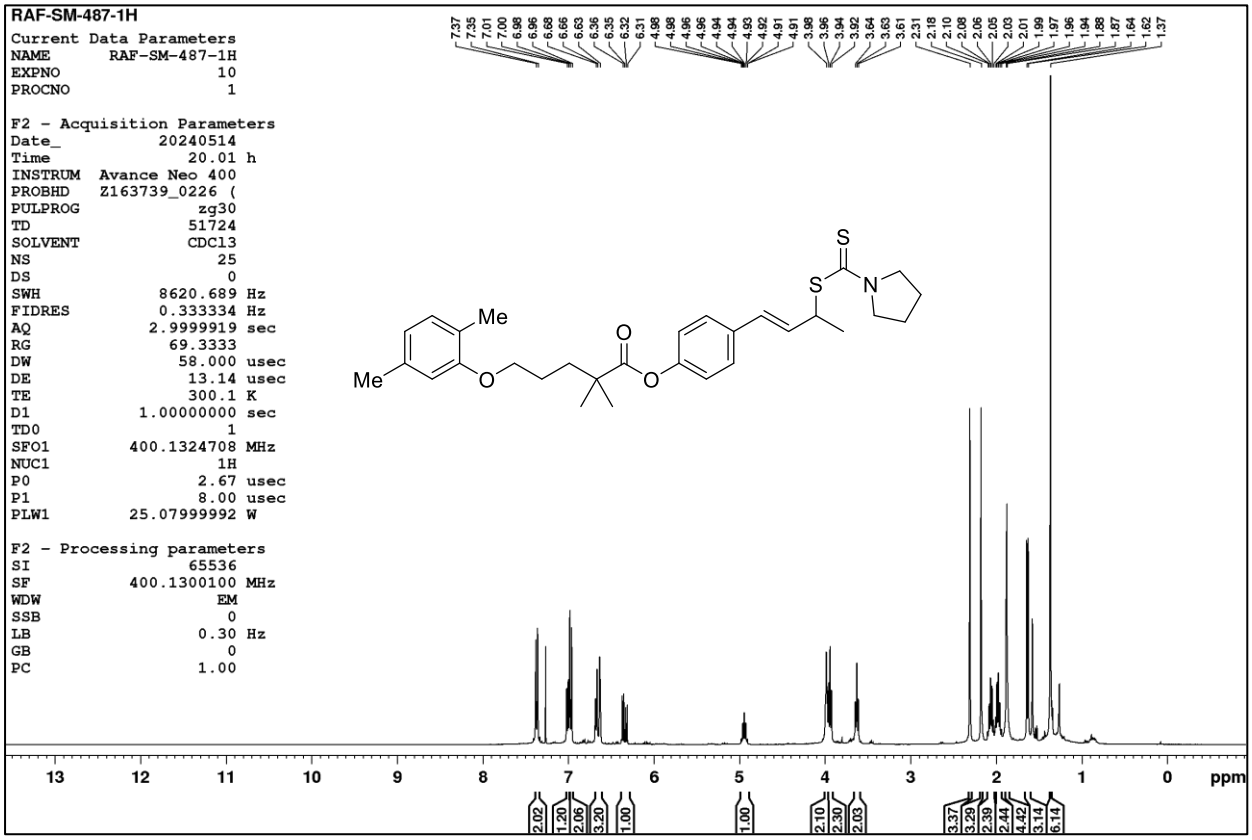


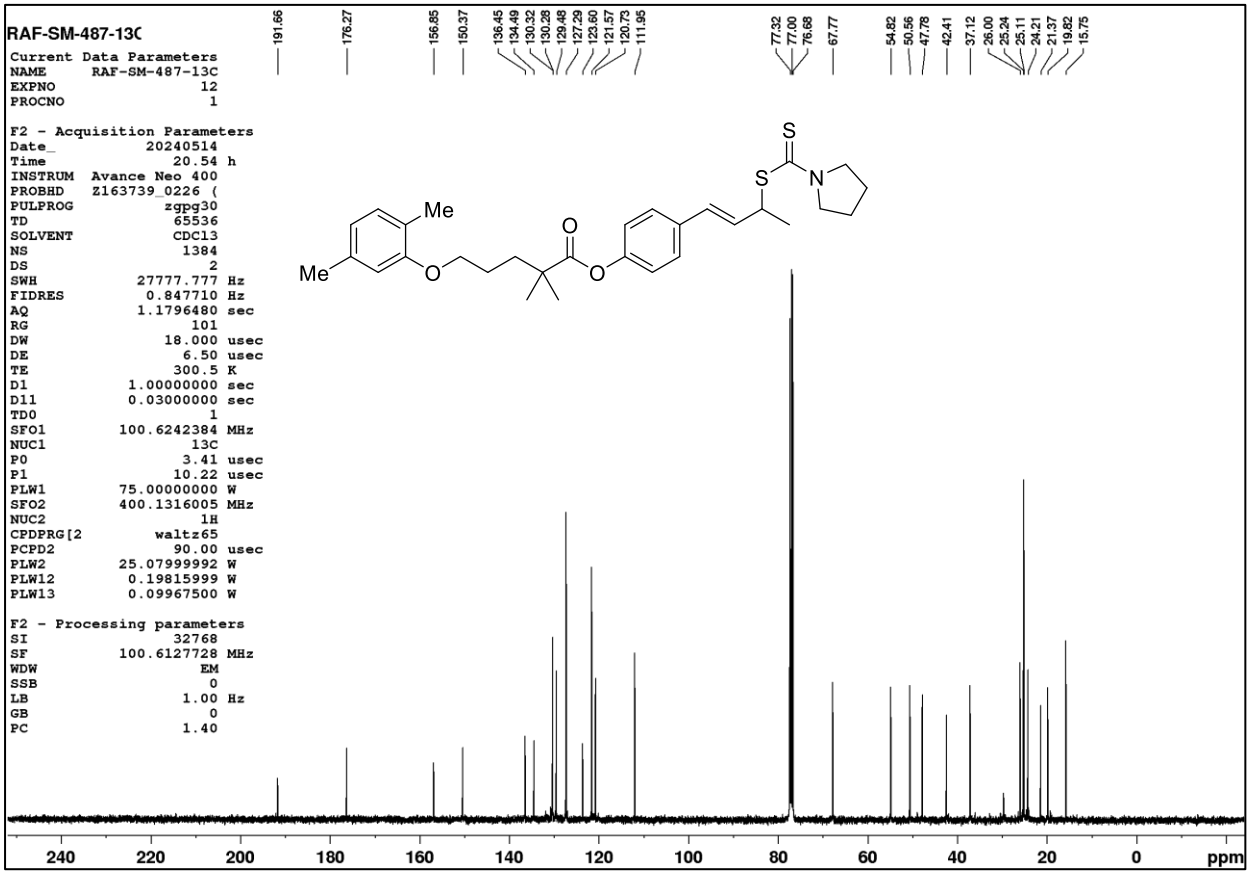


4y: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}NOS_2$ 358.1294; Found: 358.1292.

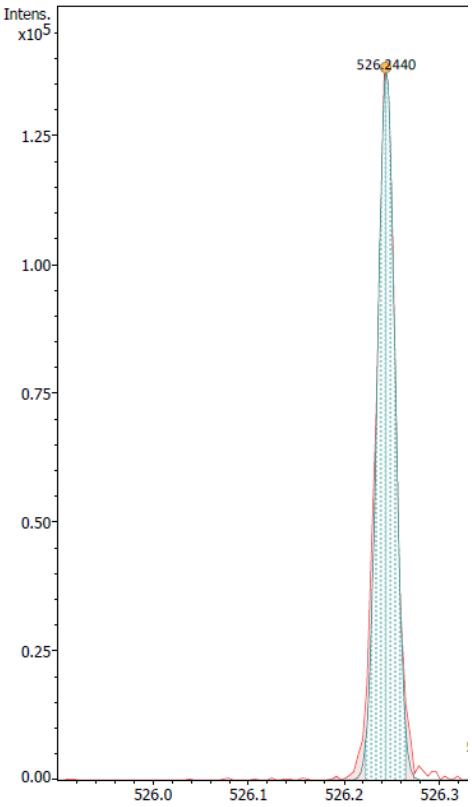


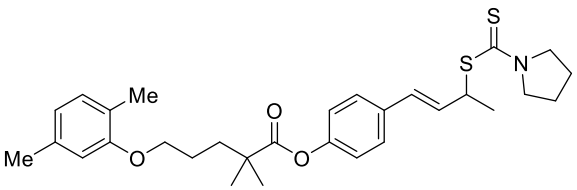
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4z**



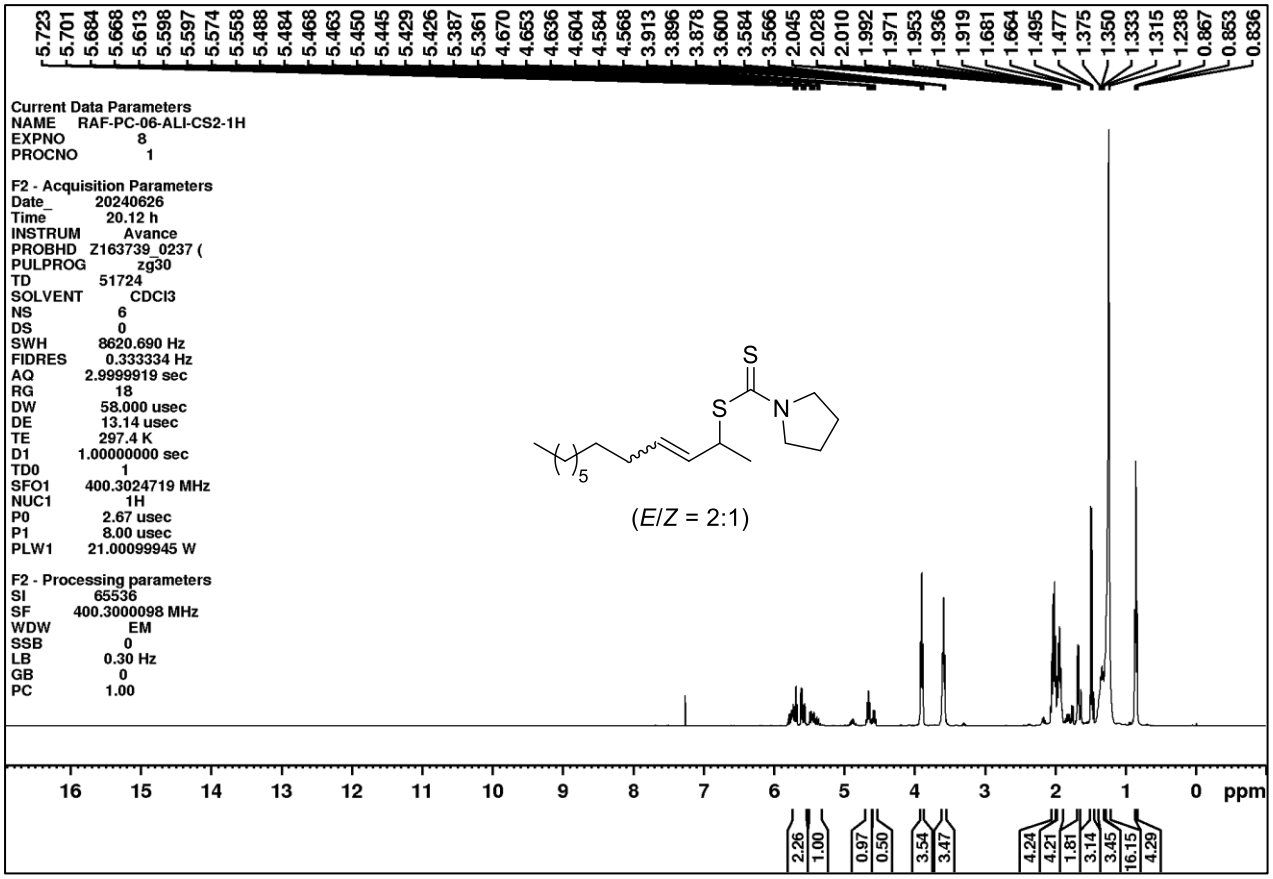


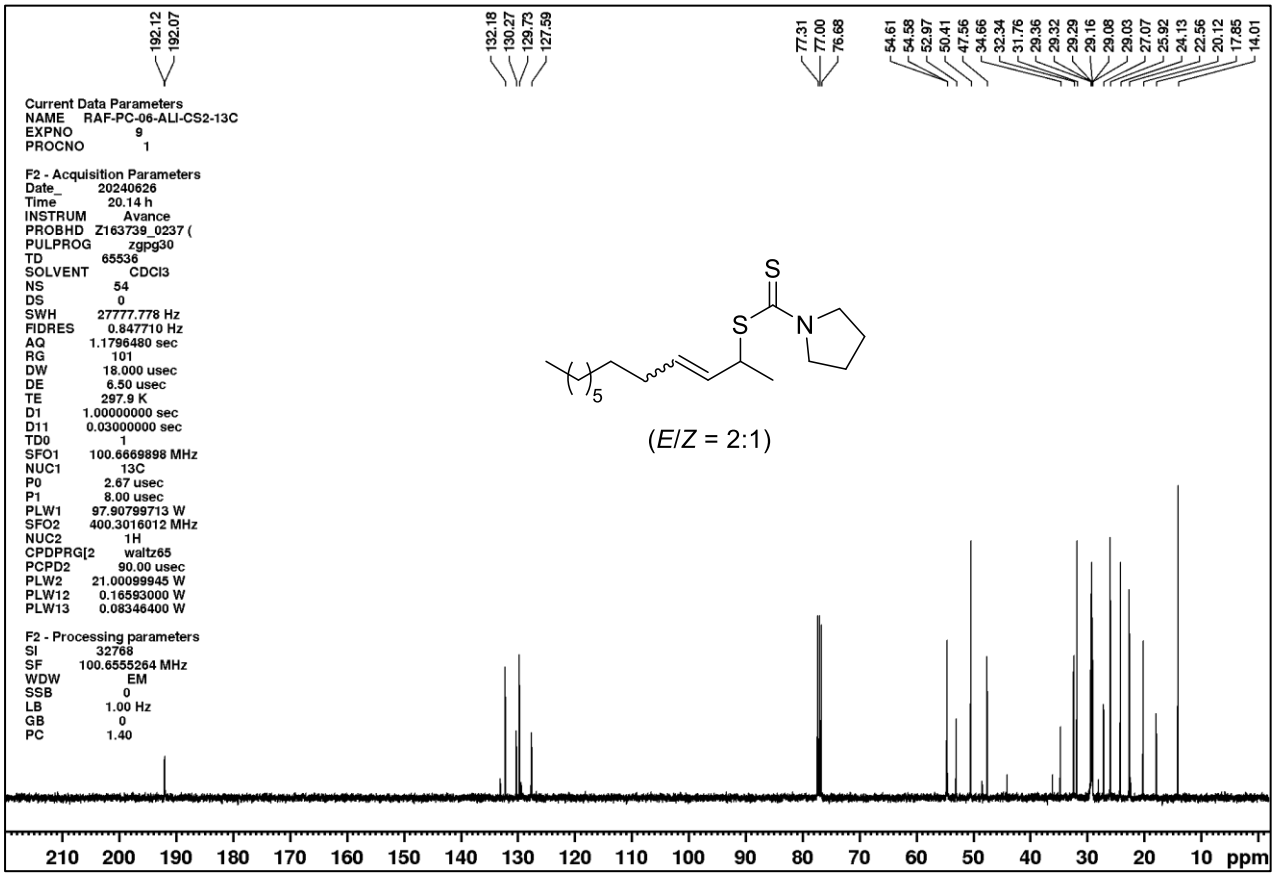
4z: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{40}NO_3S_2$ 526.2445; Found 526.2440.



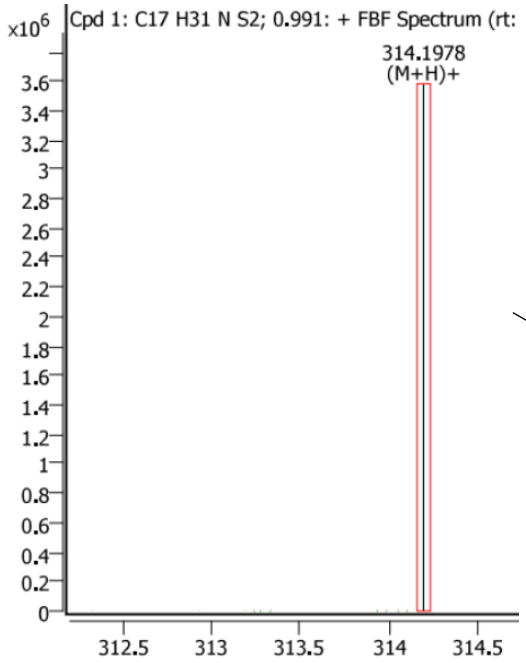


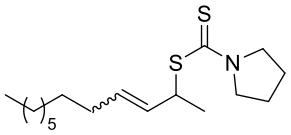
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4aa**



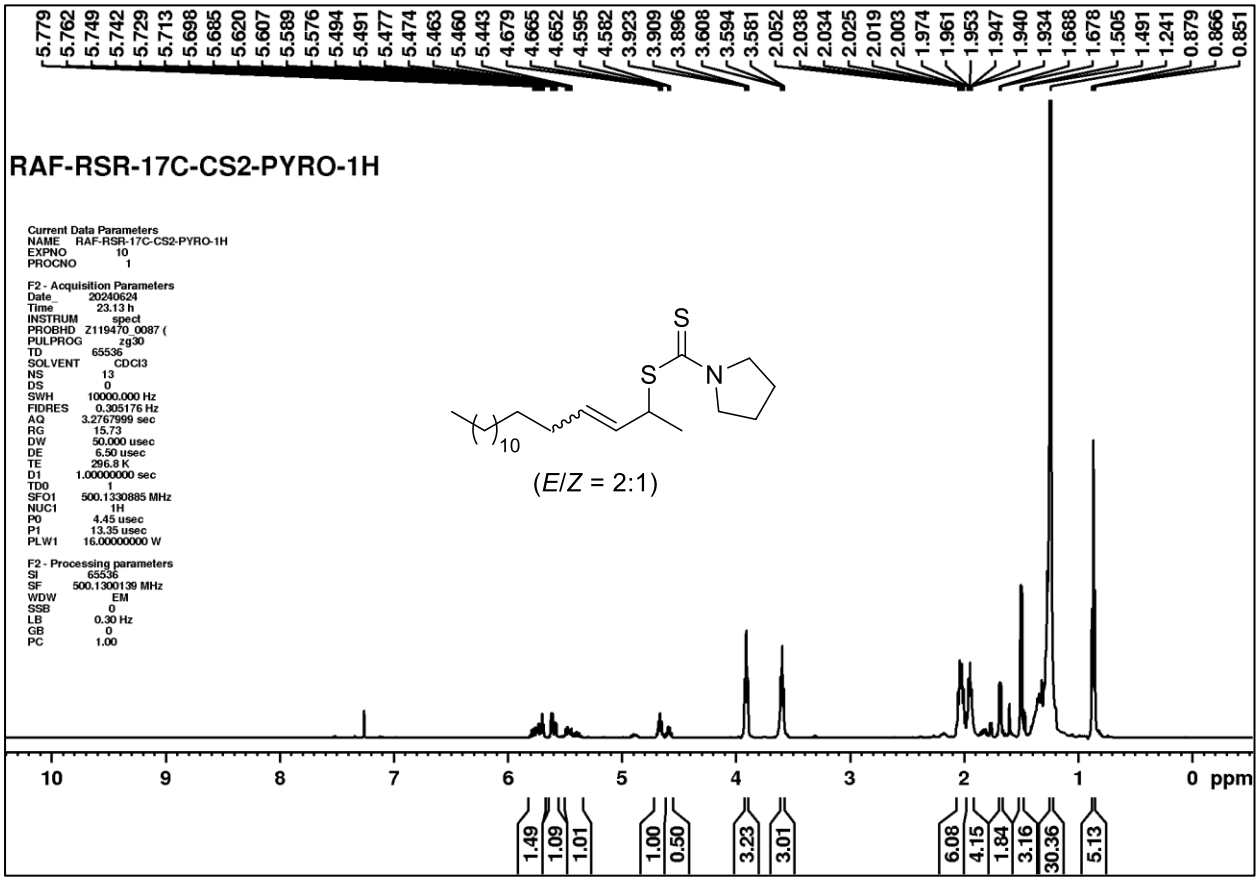


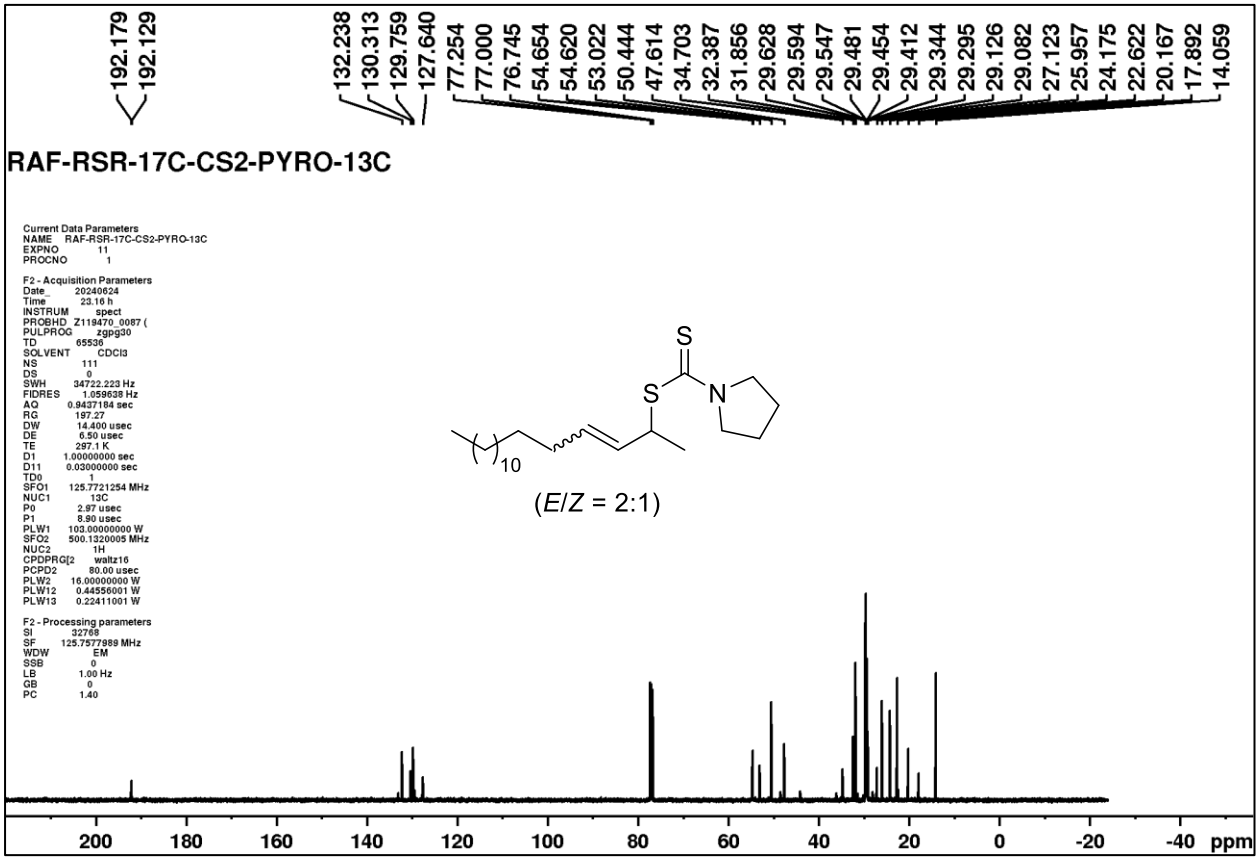
4aa: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{17}H_{32}NS_2$ 314.1971 Found 314.1978.



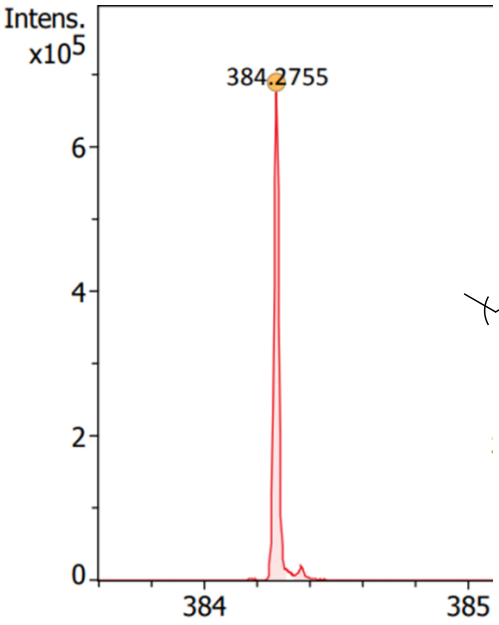


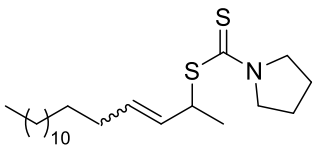
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4ab**



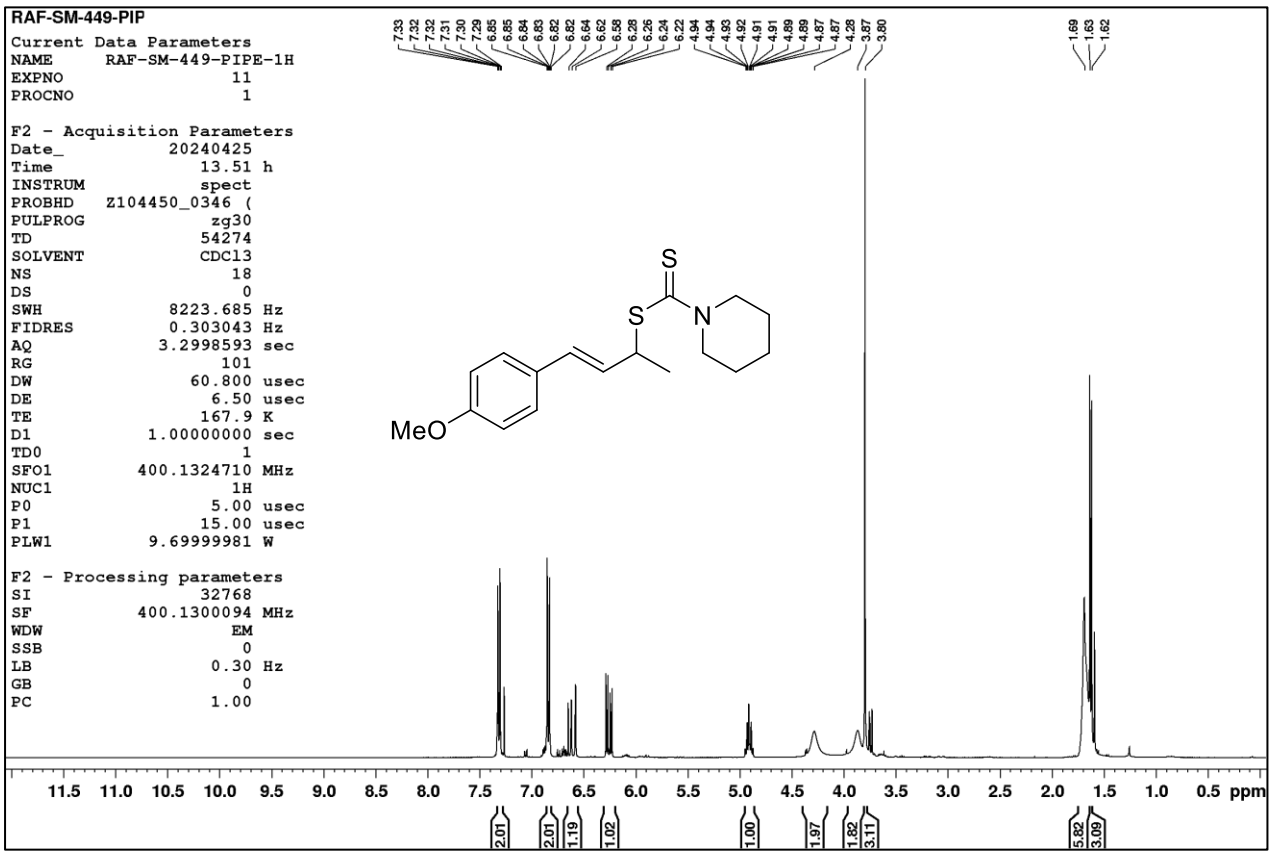


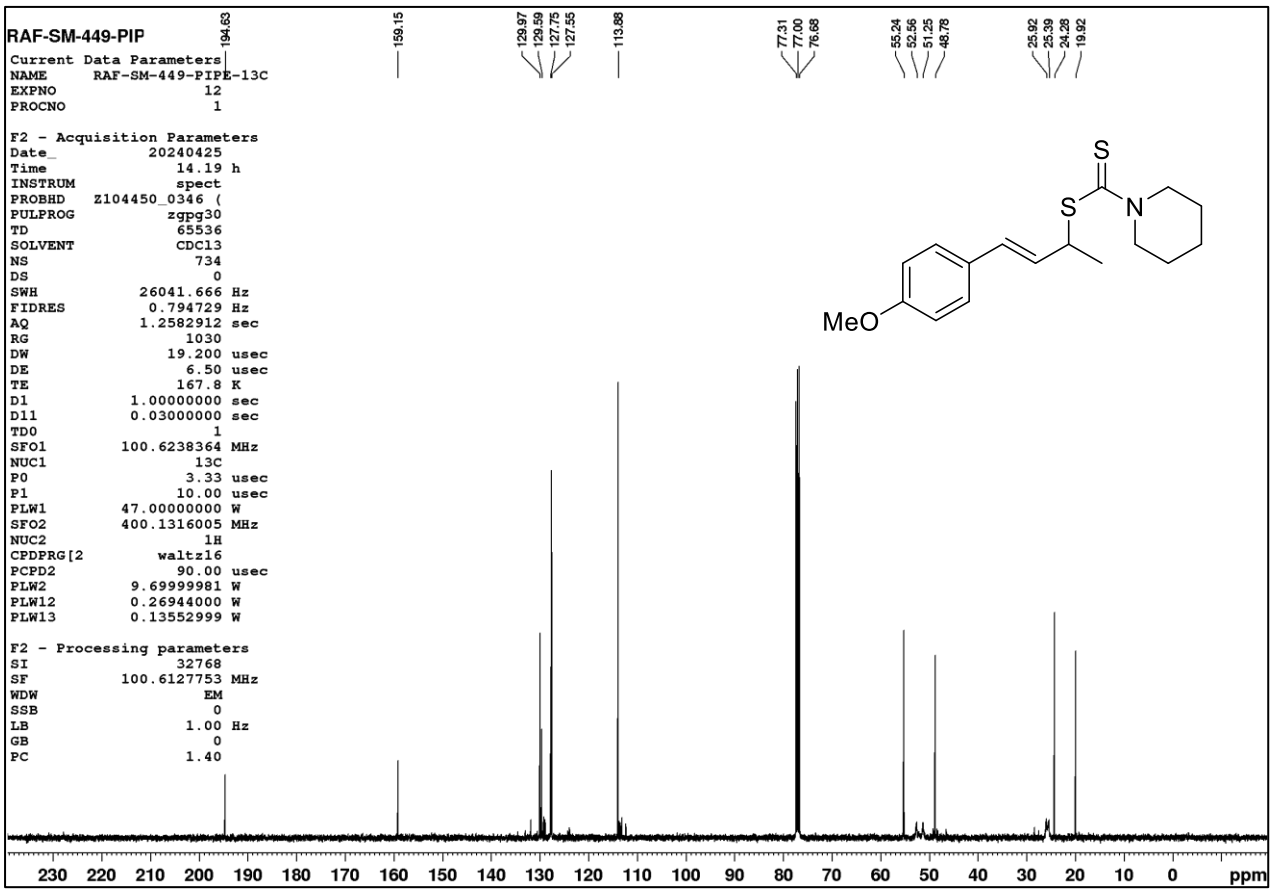
4ab: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{42}NS_2$ 384.2753; Found: 384.2755.



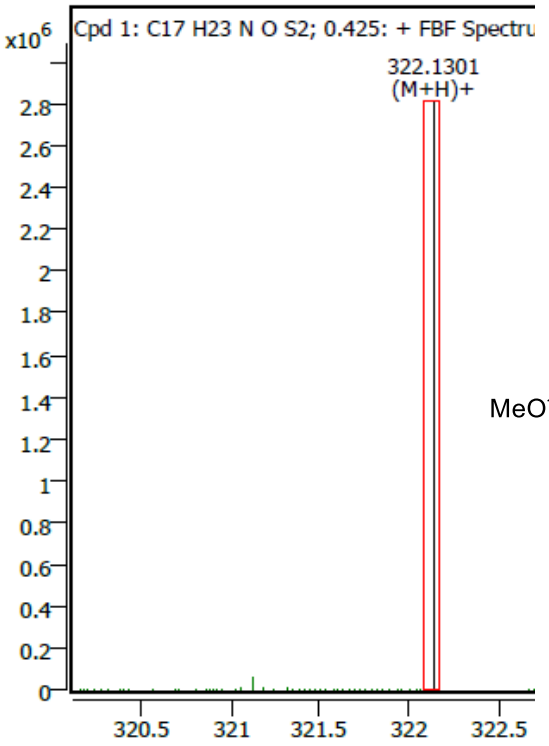


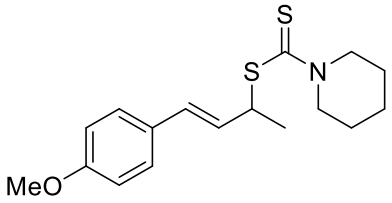
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4ac**



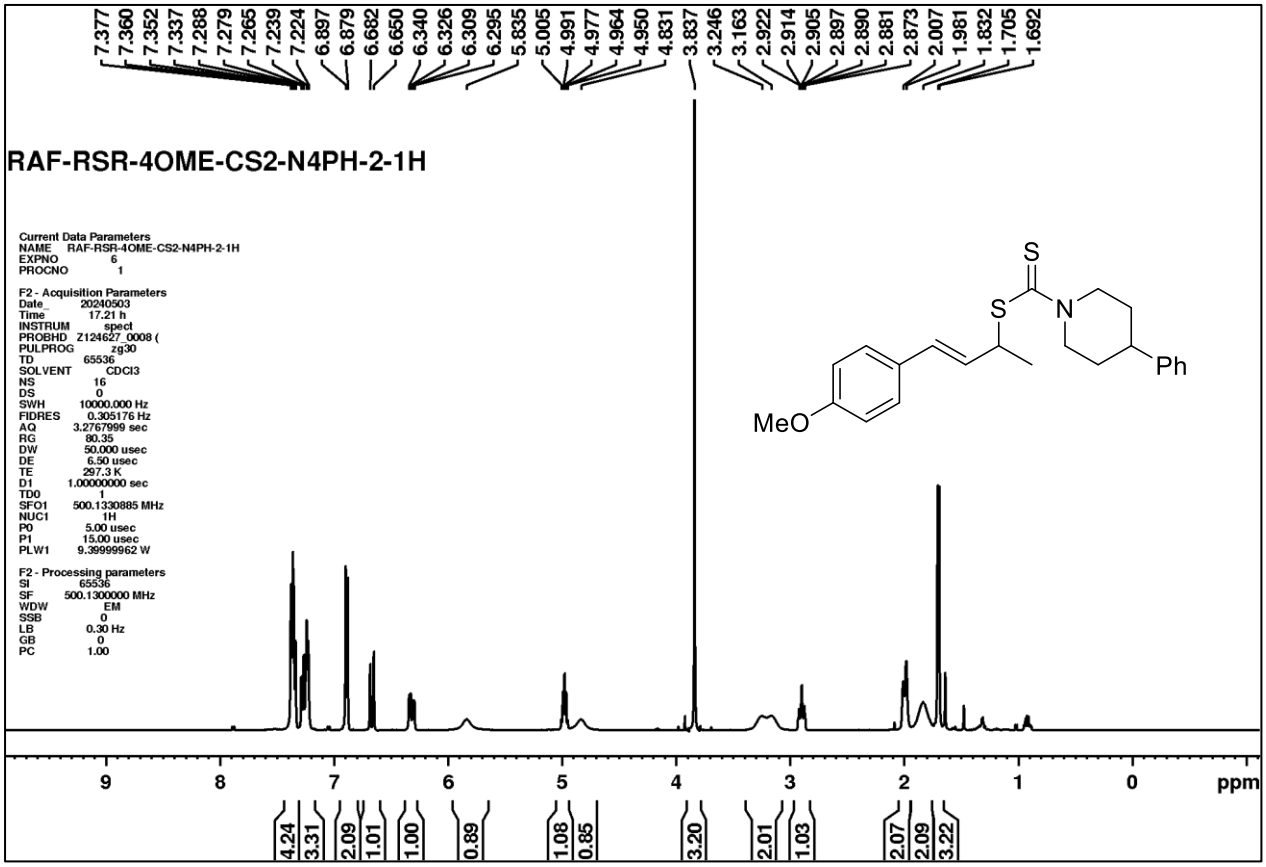


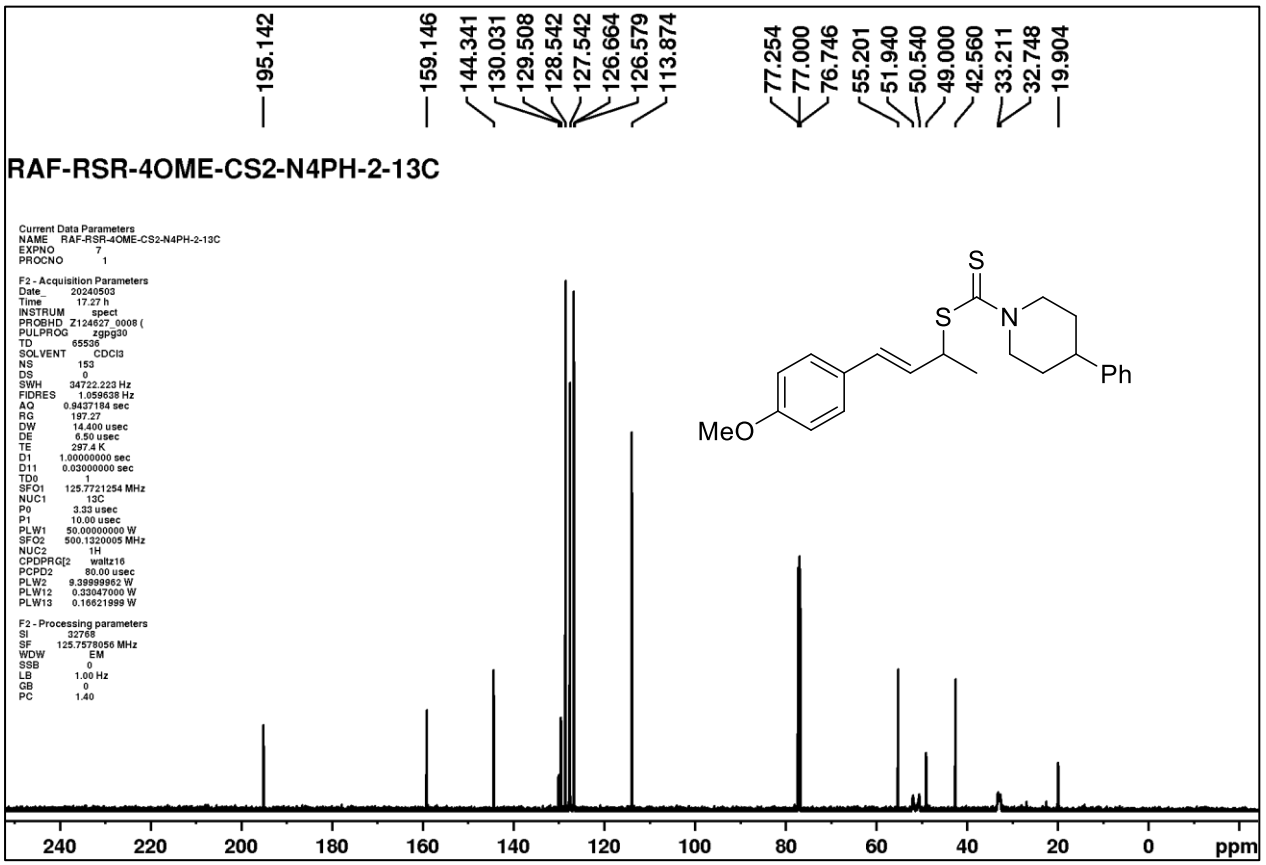
4ac: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{24}NOS_2$ 322.1295; Found 322.1301.



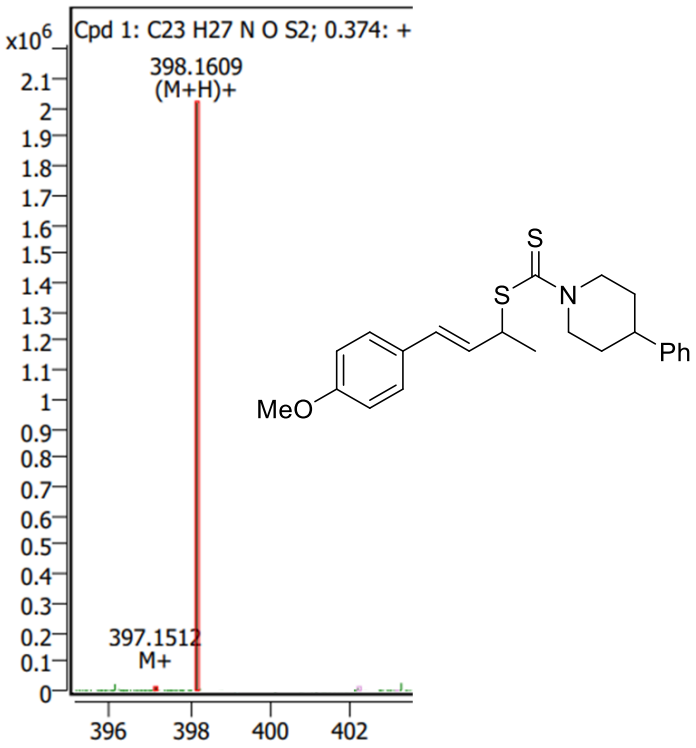


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4ad**

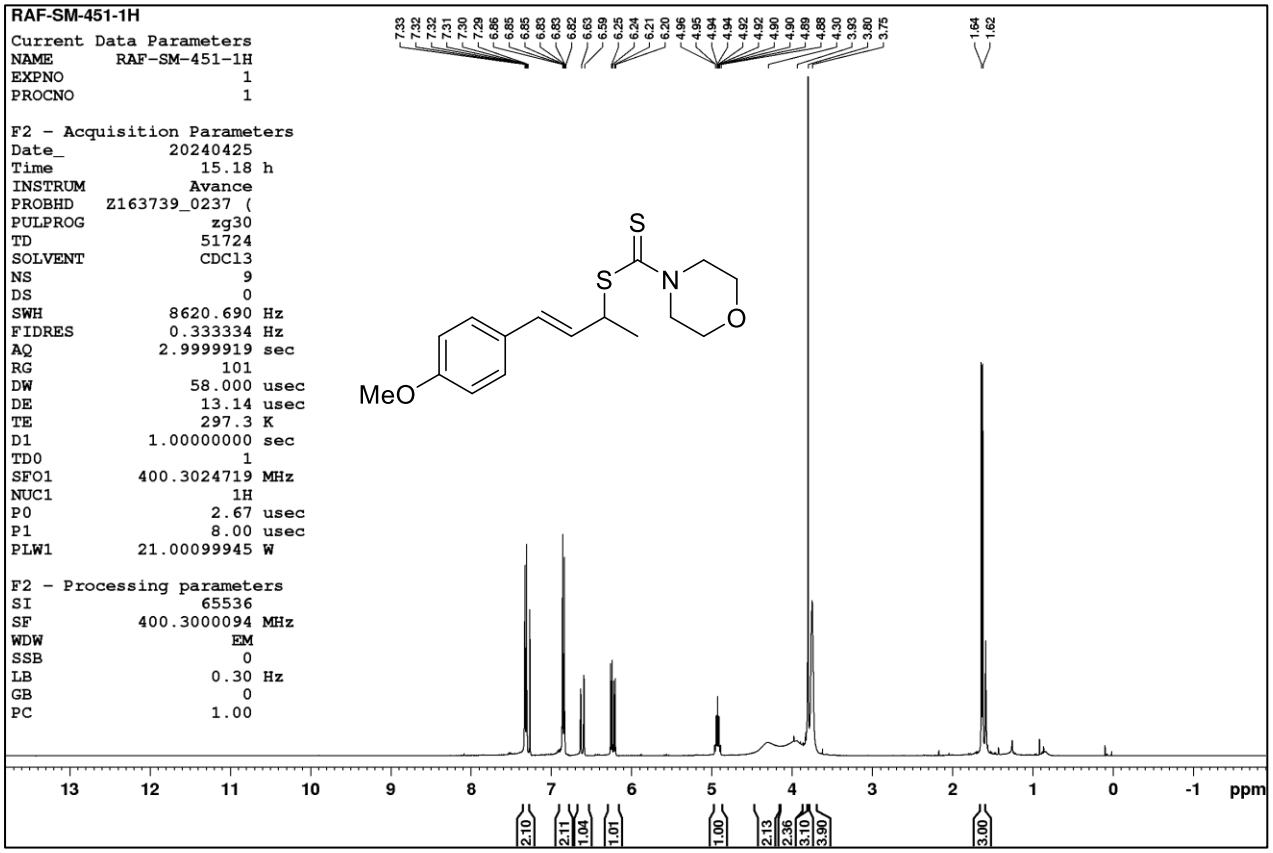


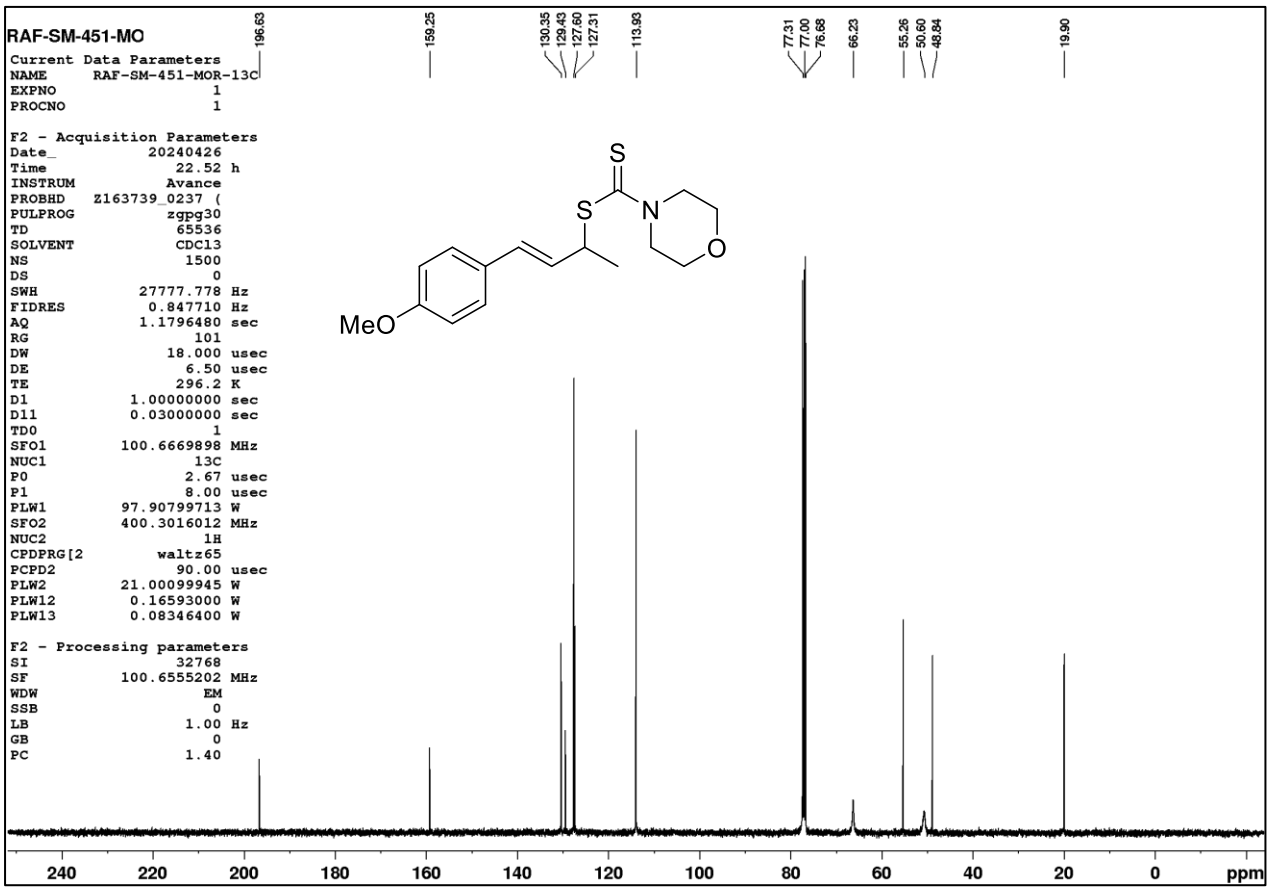


4ad: HRMS (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{23}H_{28}NOS_2$ 398.1607; Found: 398.1609.

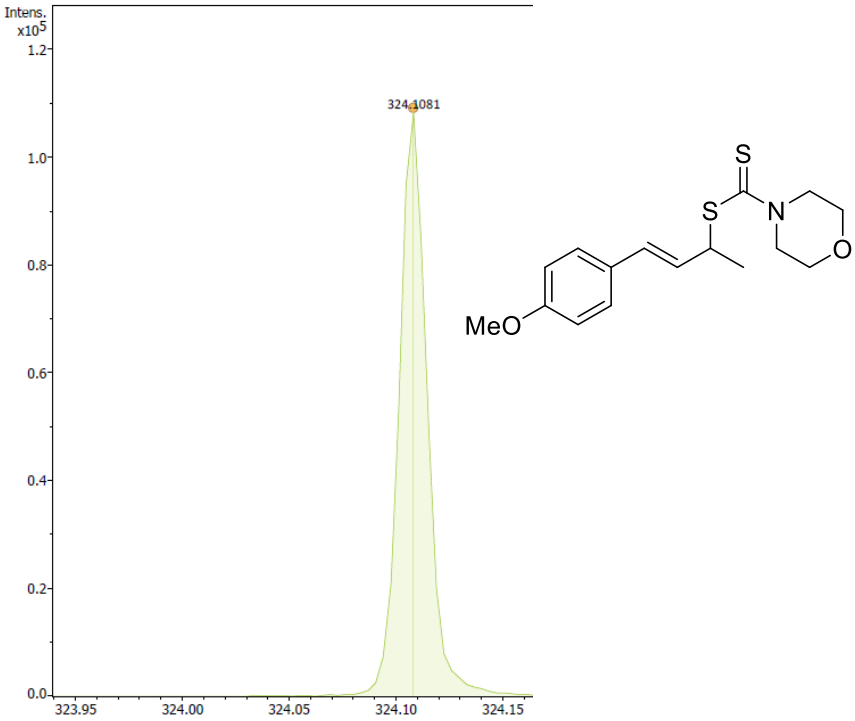


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4ae**

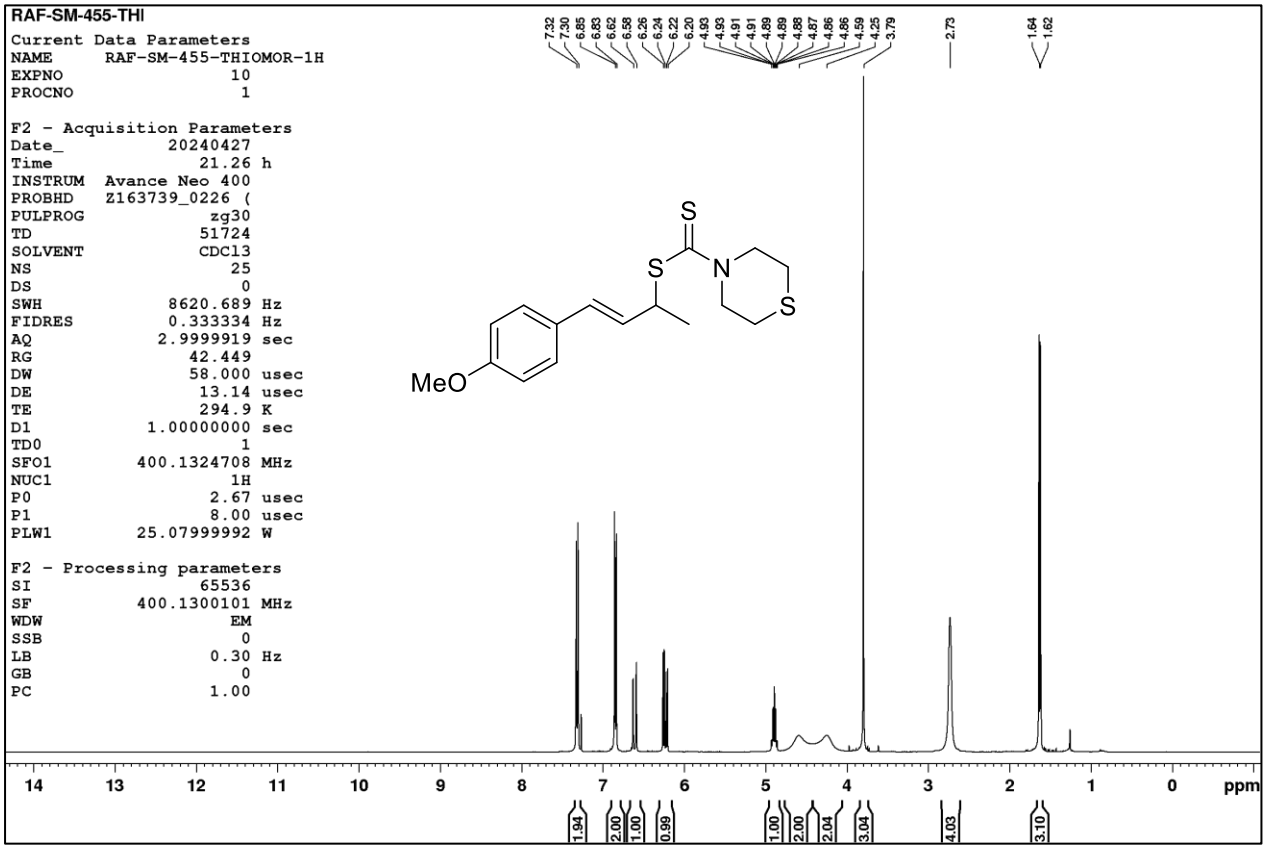


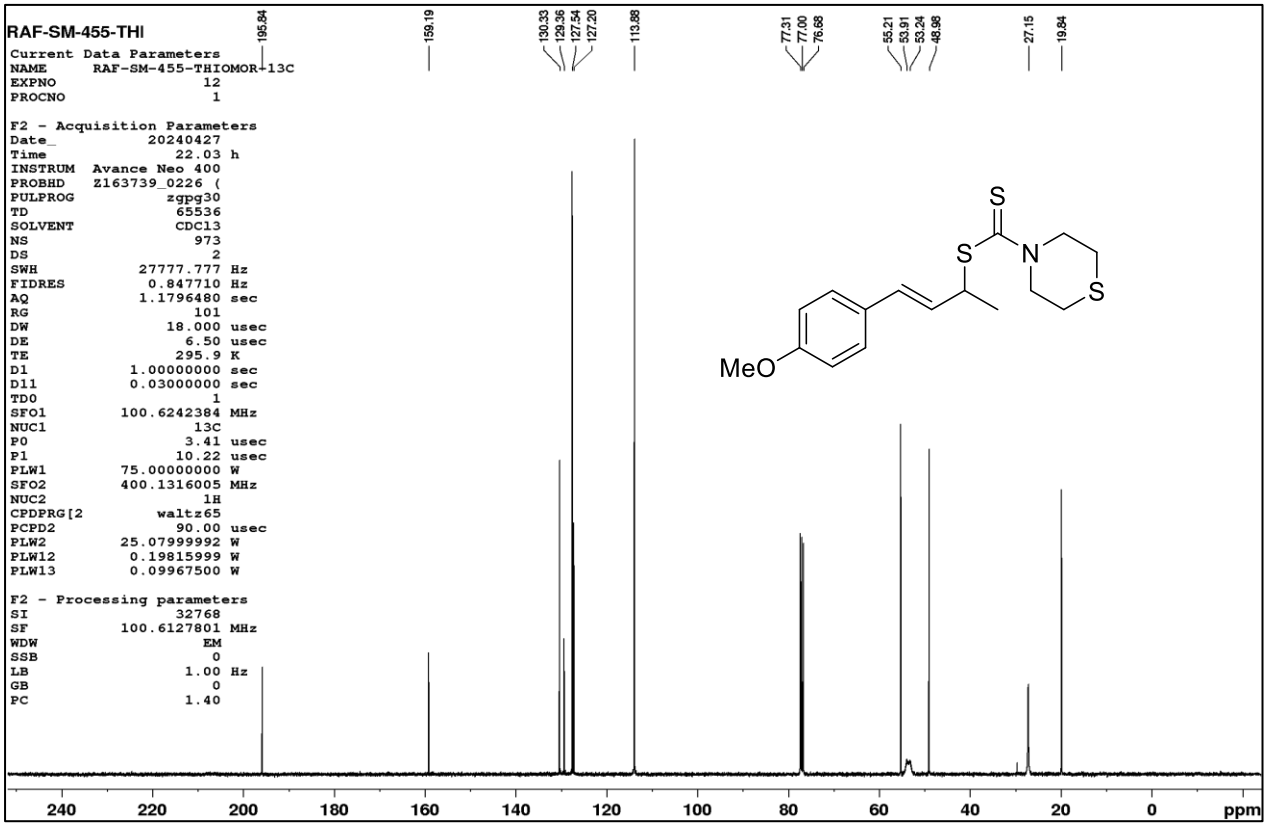


4ae: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{16}H_{22}NO_2S_2$ 324.1087; Found 324.1081.

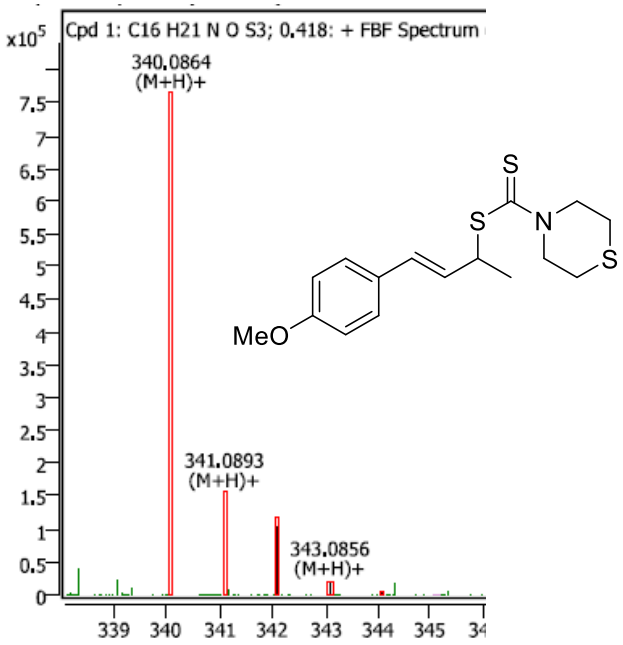


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4af**

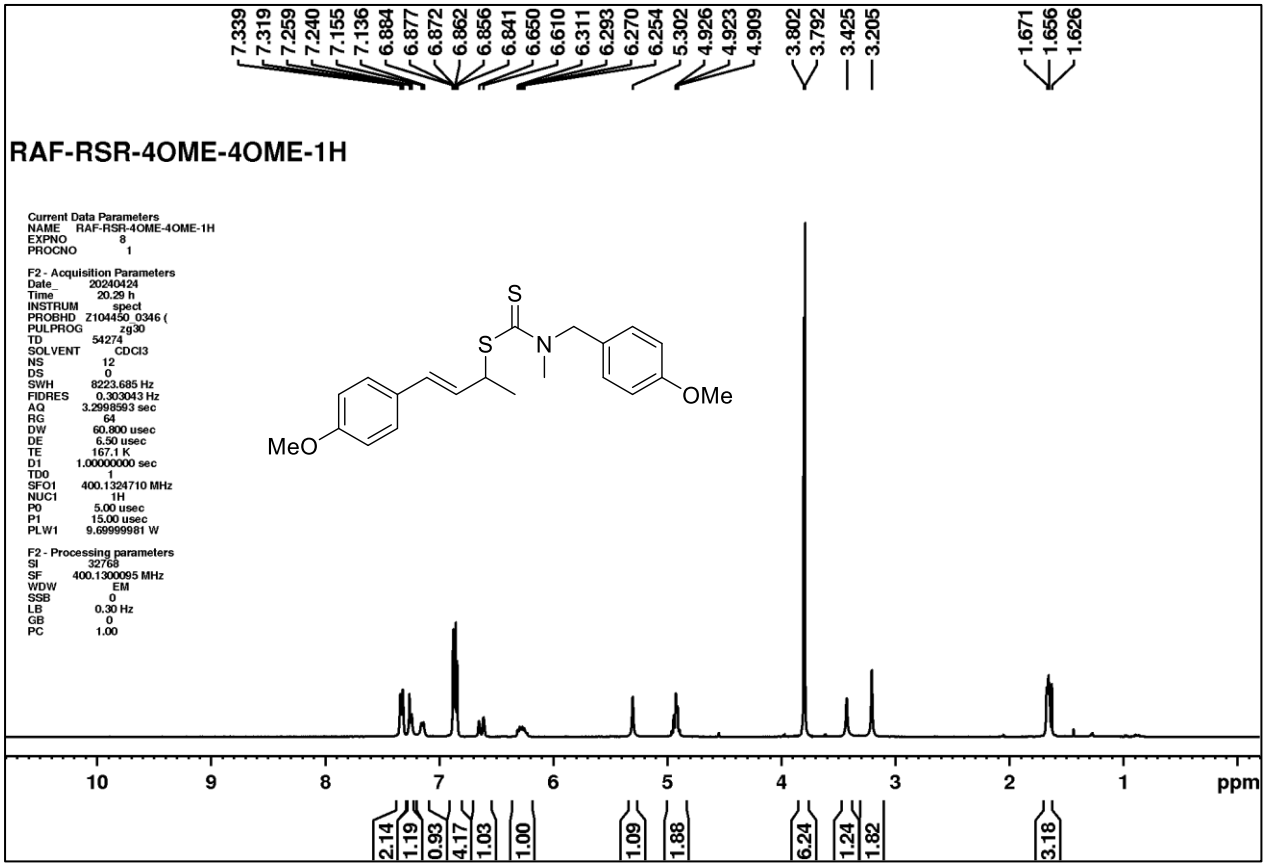


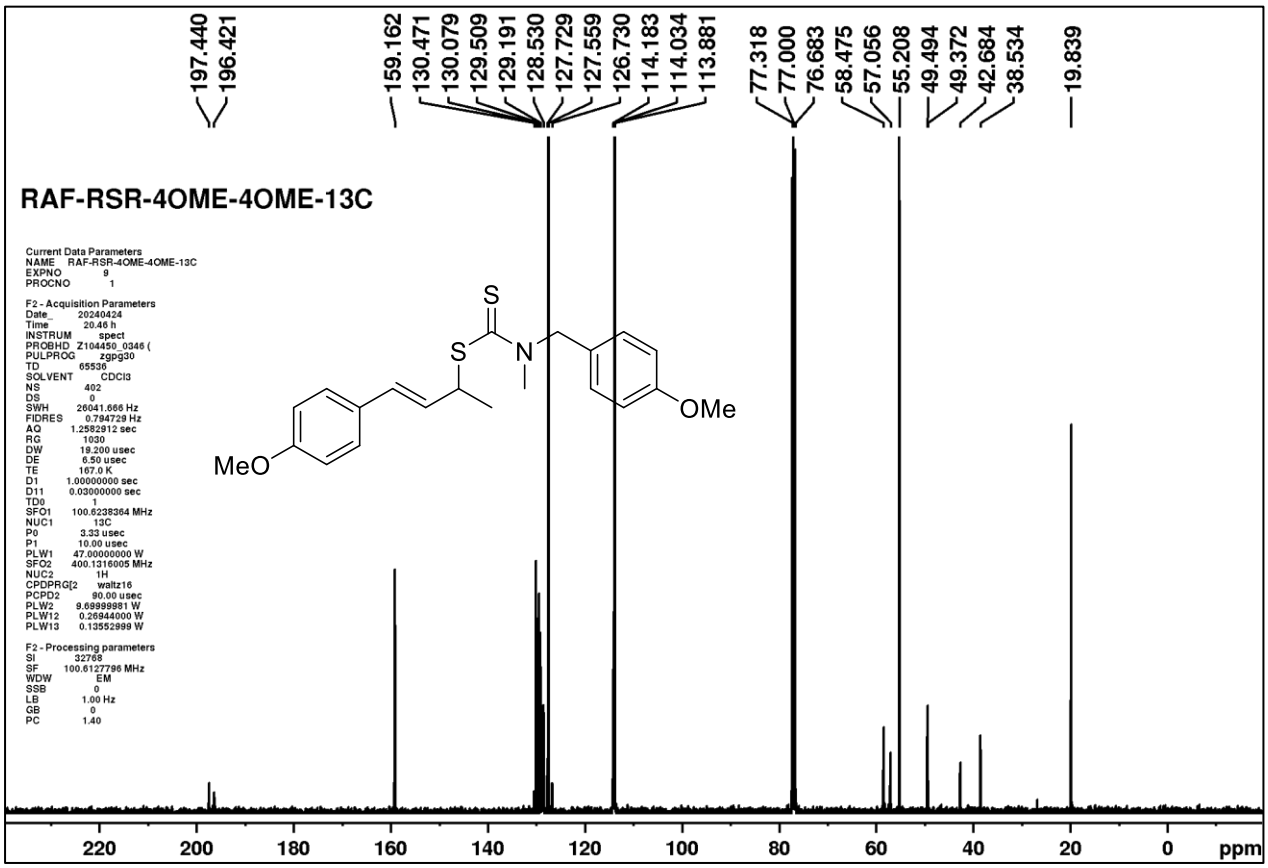


4af: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{16}H_{22}NOS_3$ 340.0859; Found 340.0864.

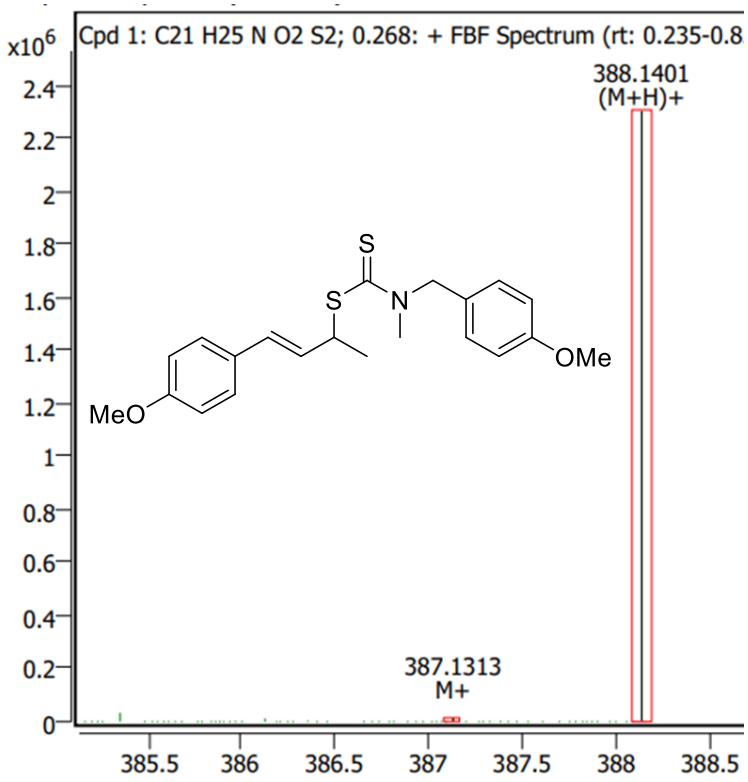


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4ag**

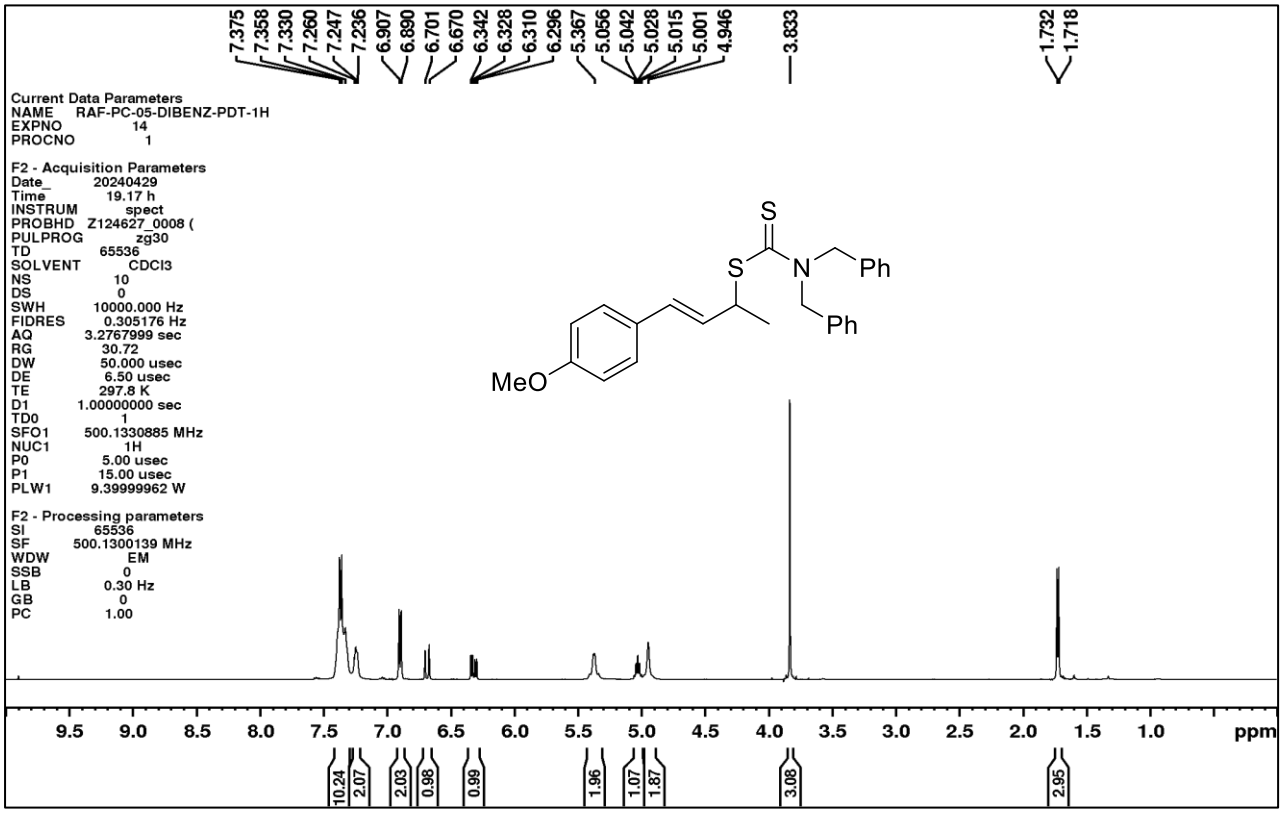


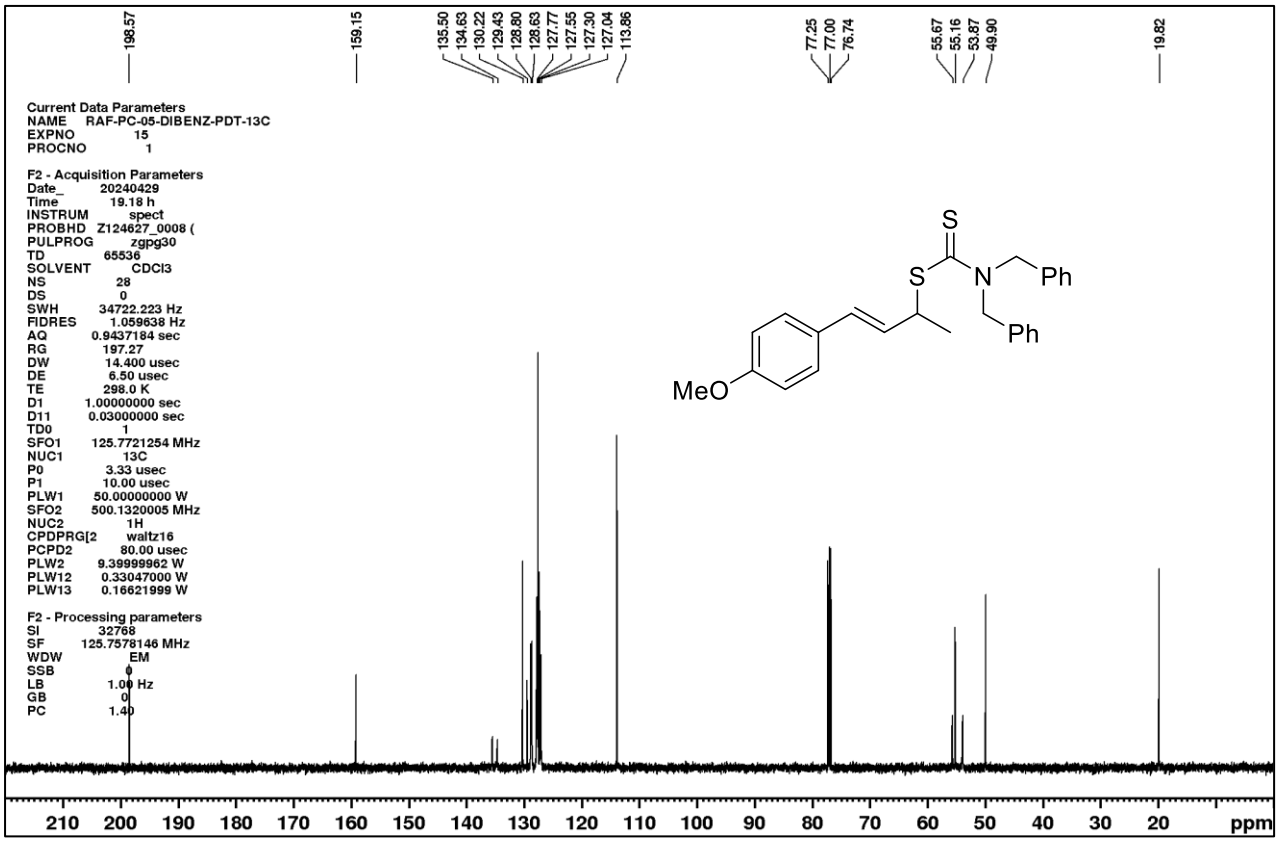


4ag: HRMS (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{21}H_{26}NO_2S_2$ 388.1400; Found: 388.1401.

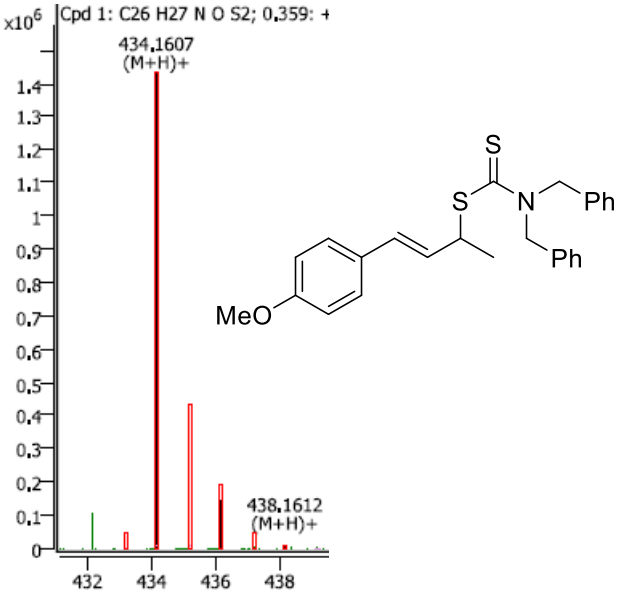


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4ah**

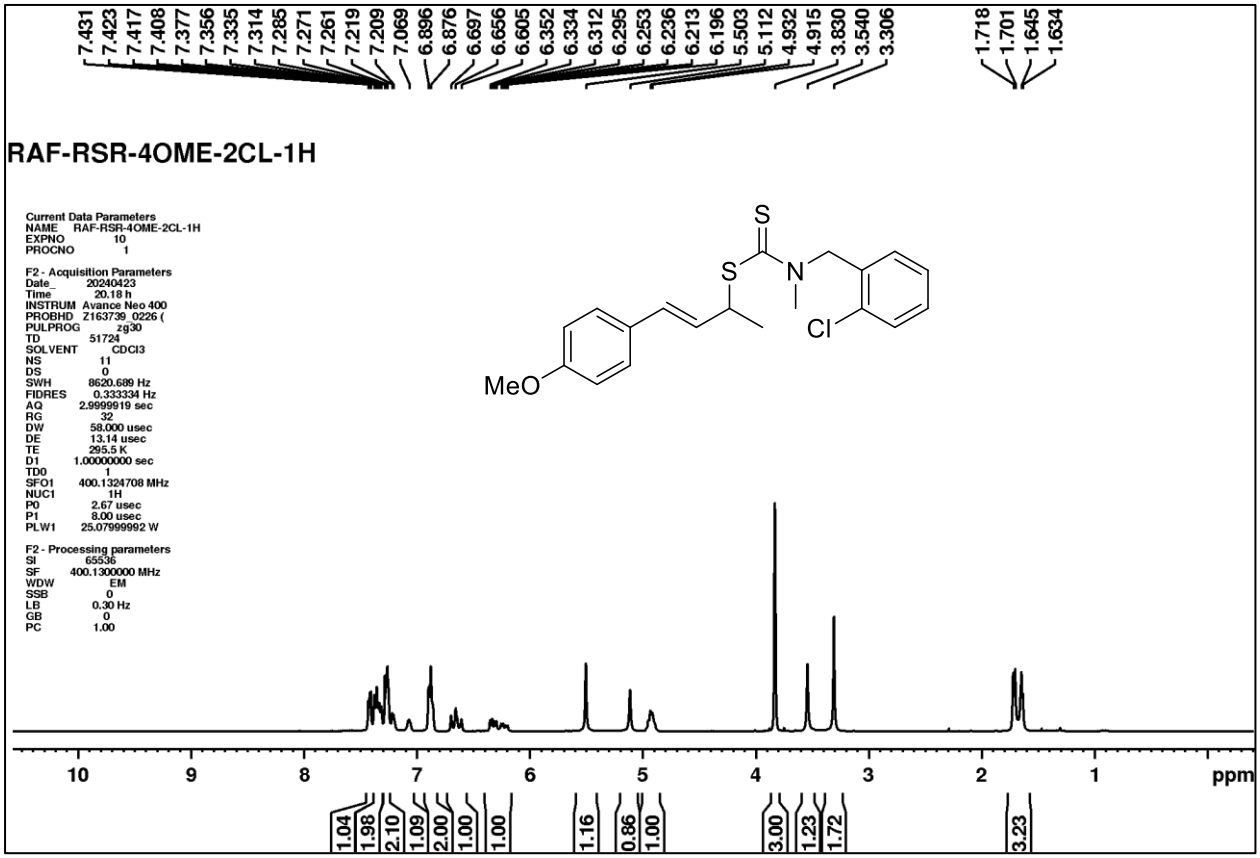


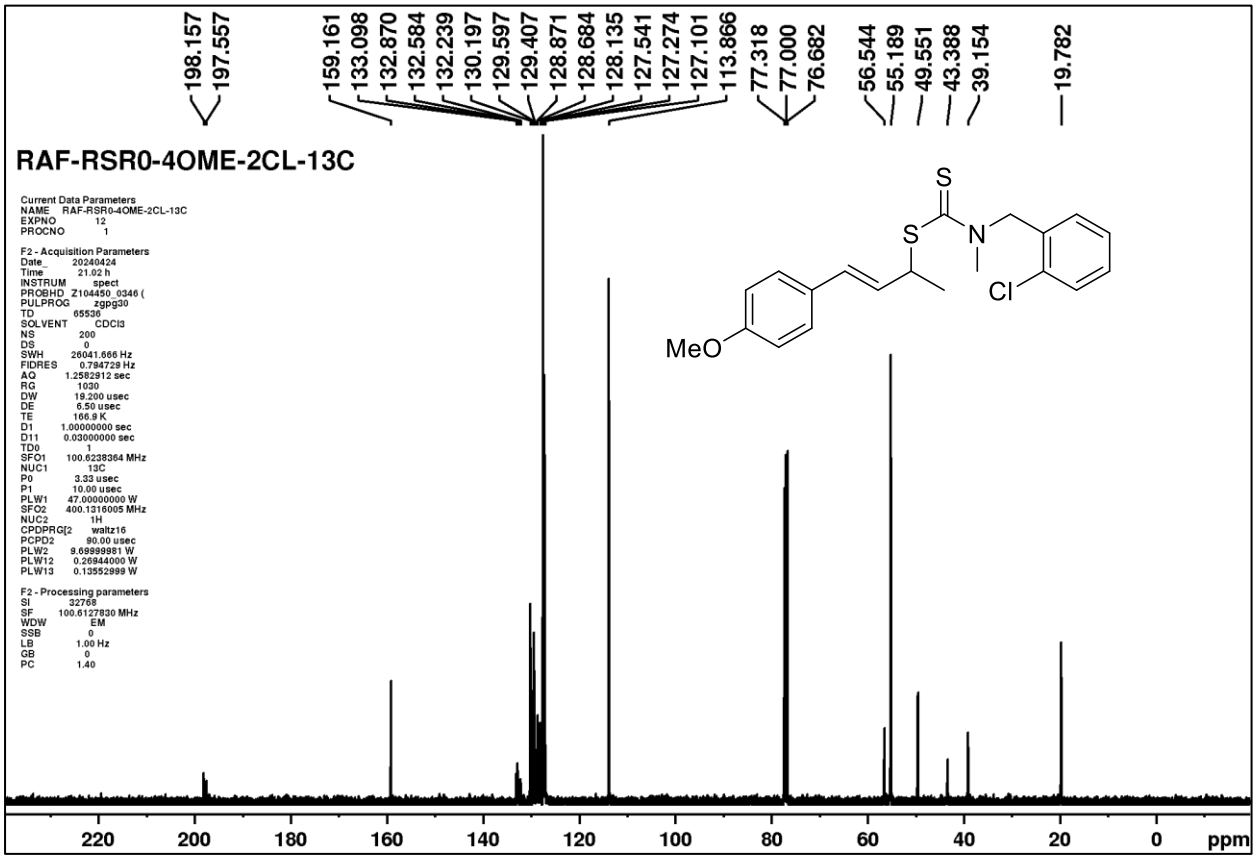


4ah: HRMS (Q-TOF): *m/z* [M+H]$^+$ calcd for $C_{26}H_{28}NS_2O$ 434.1607 Found 434.1607.

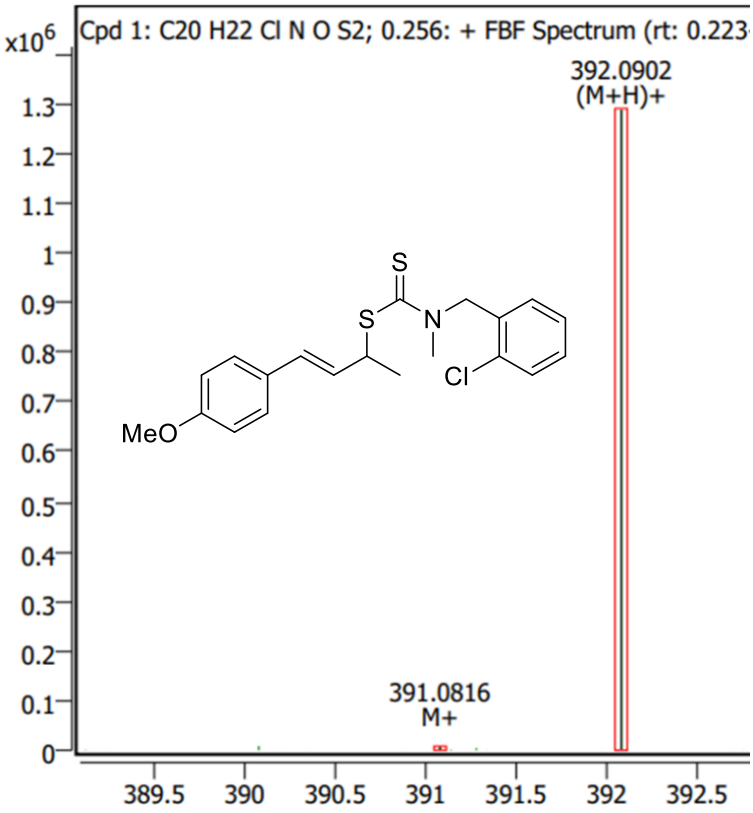


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4ai**

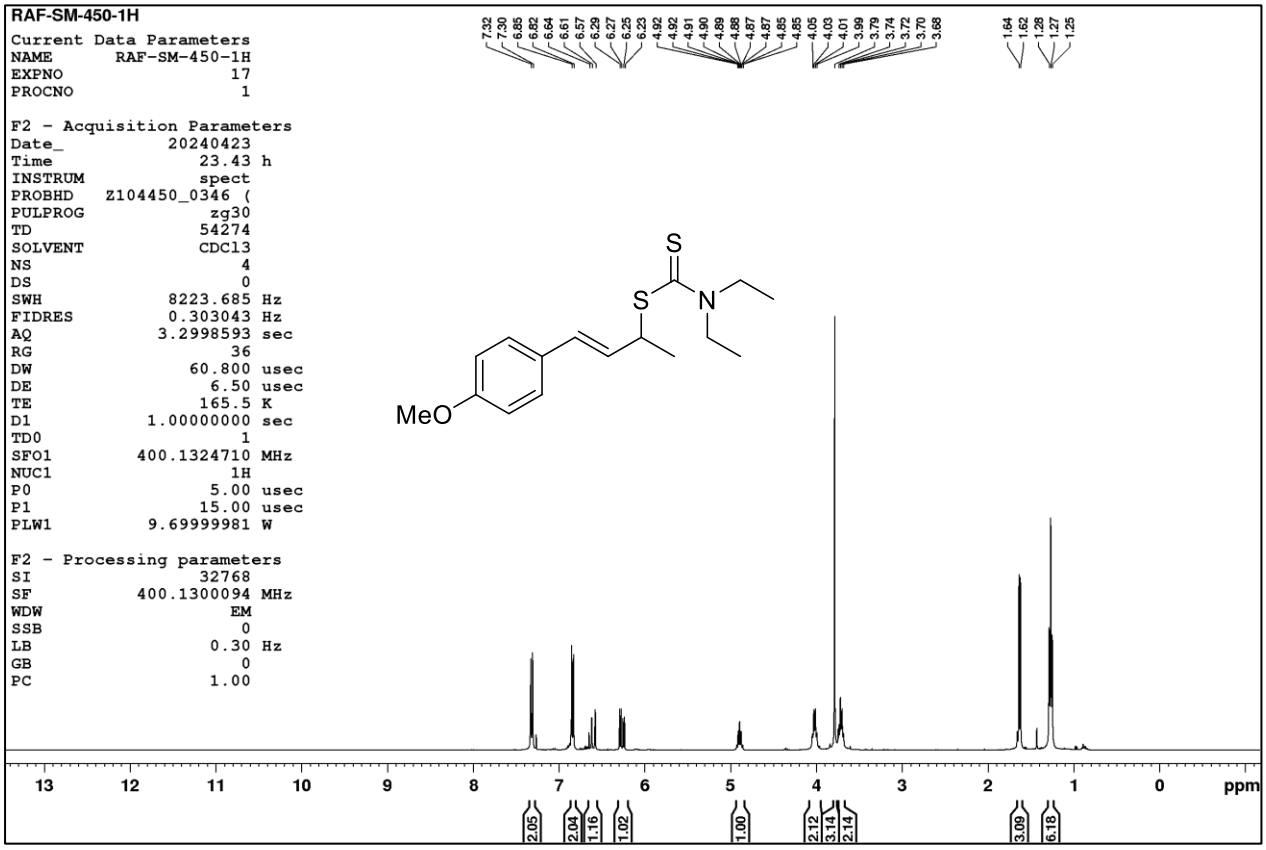


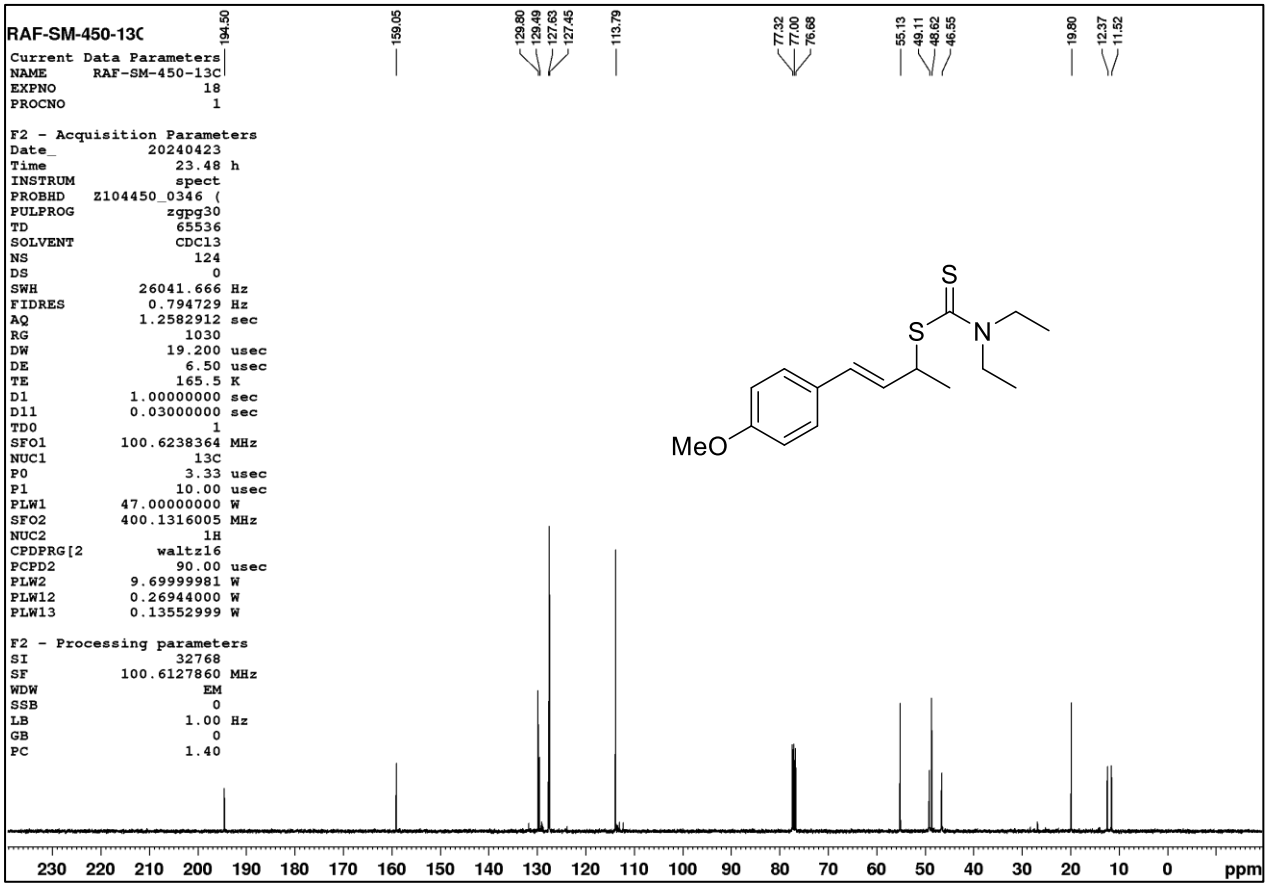


4ai: HRMS (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{23}ClNOS_2$ 392.0905; Found: 392.0902.

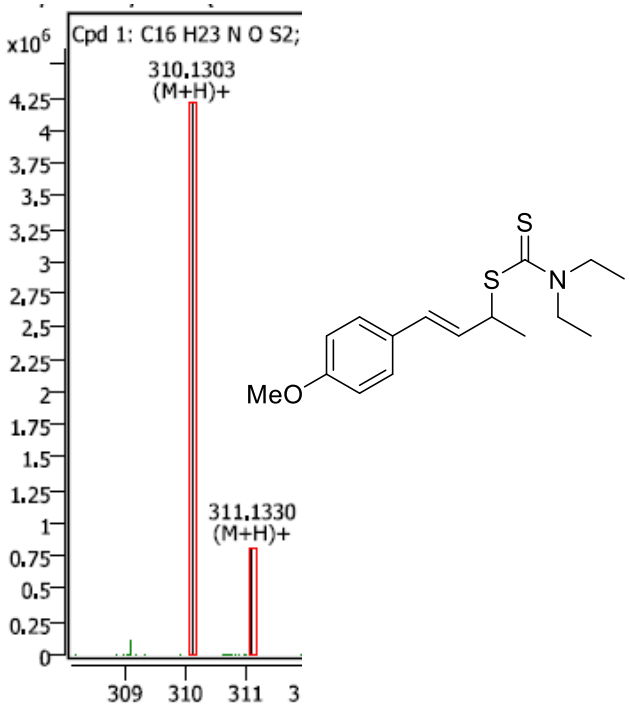


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4aj**

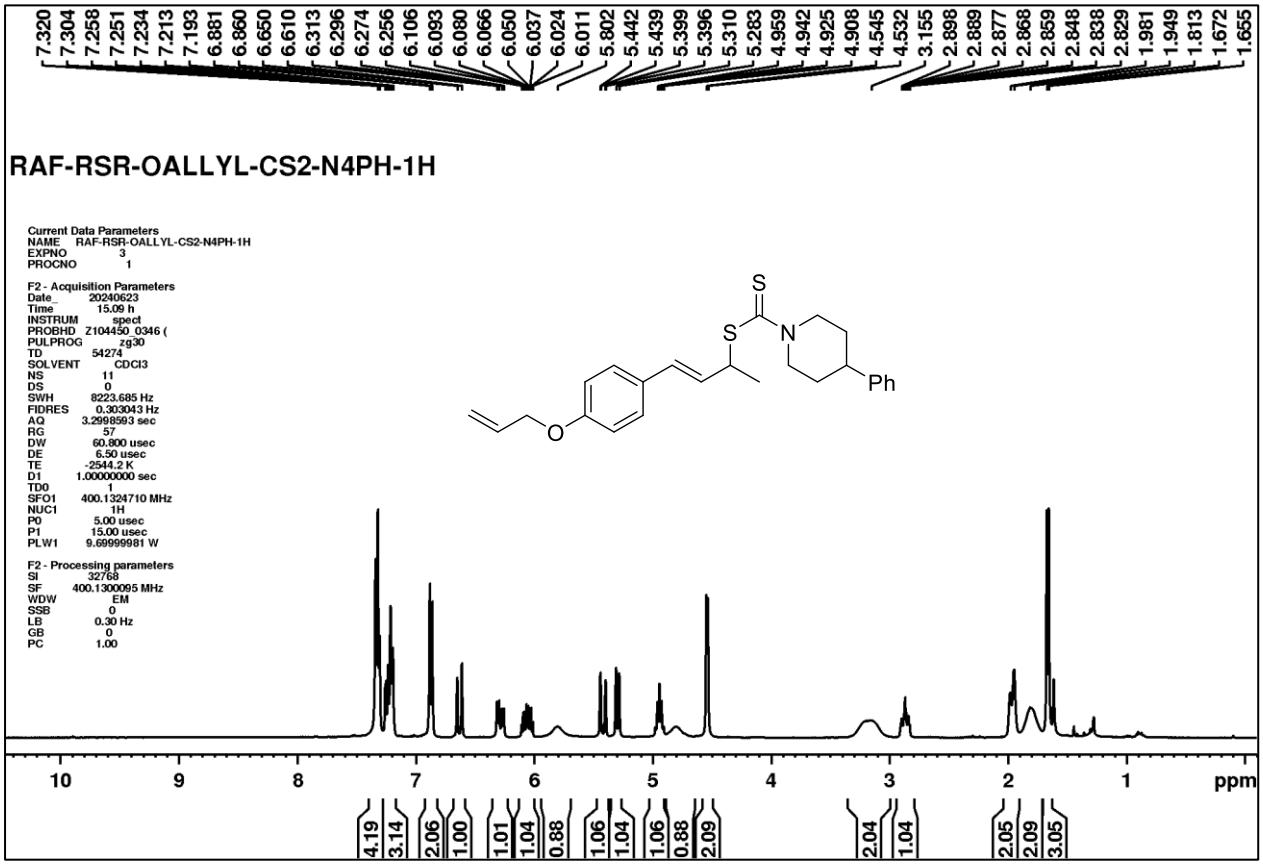


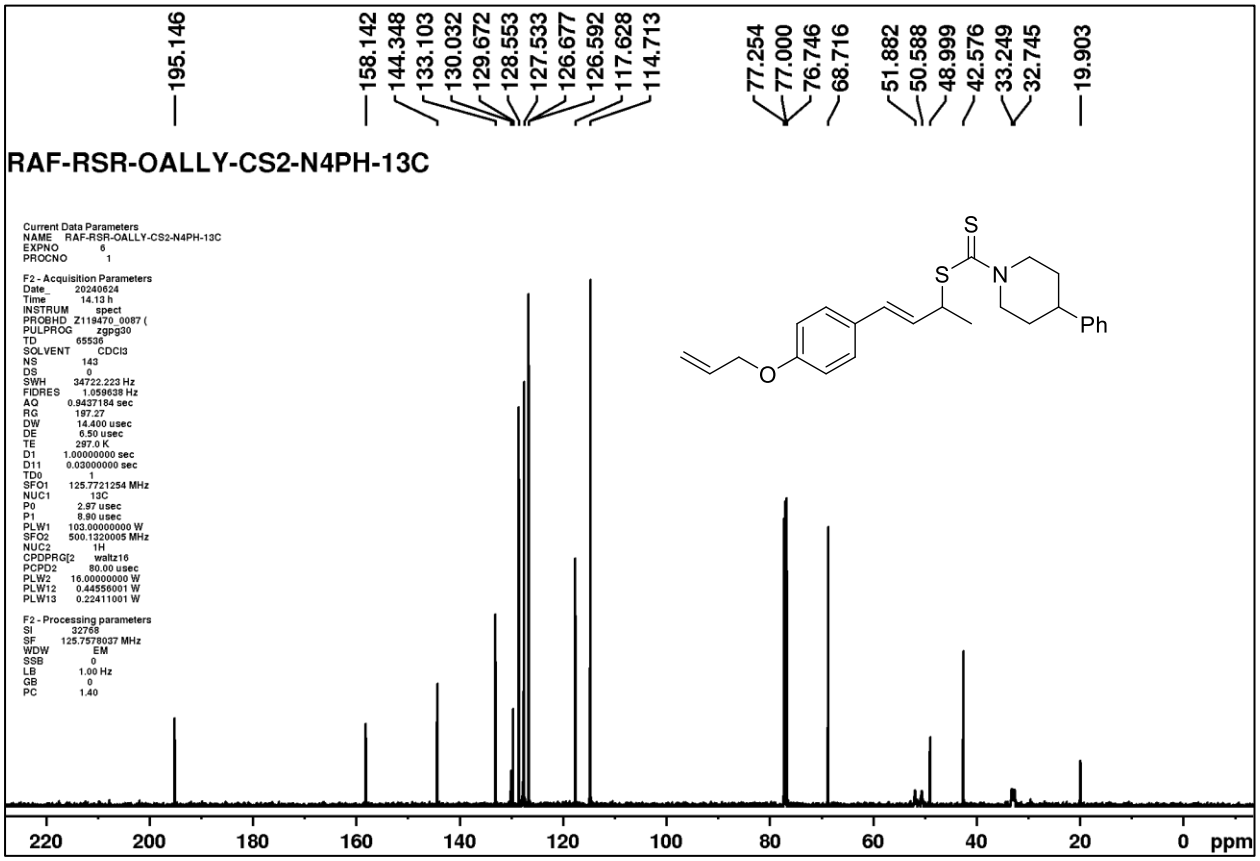


4aj: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{16}H_{24}NOS_2$ 310.1294; Found 310.1303.

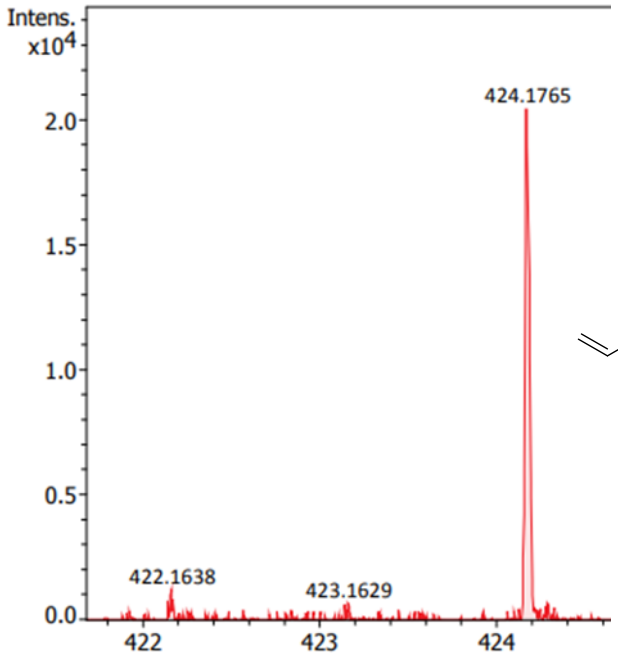


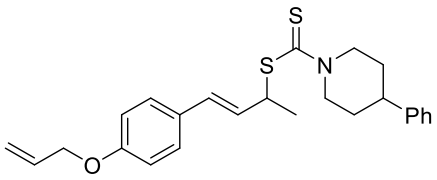
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4al**



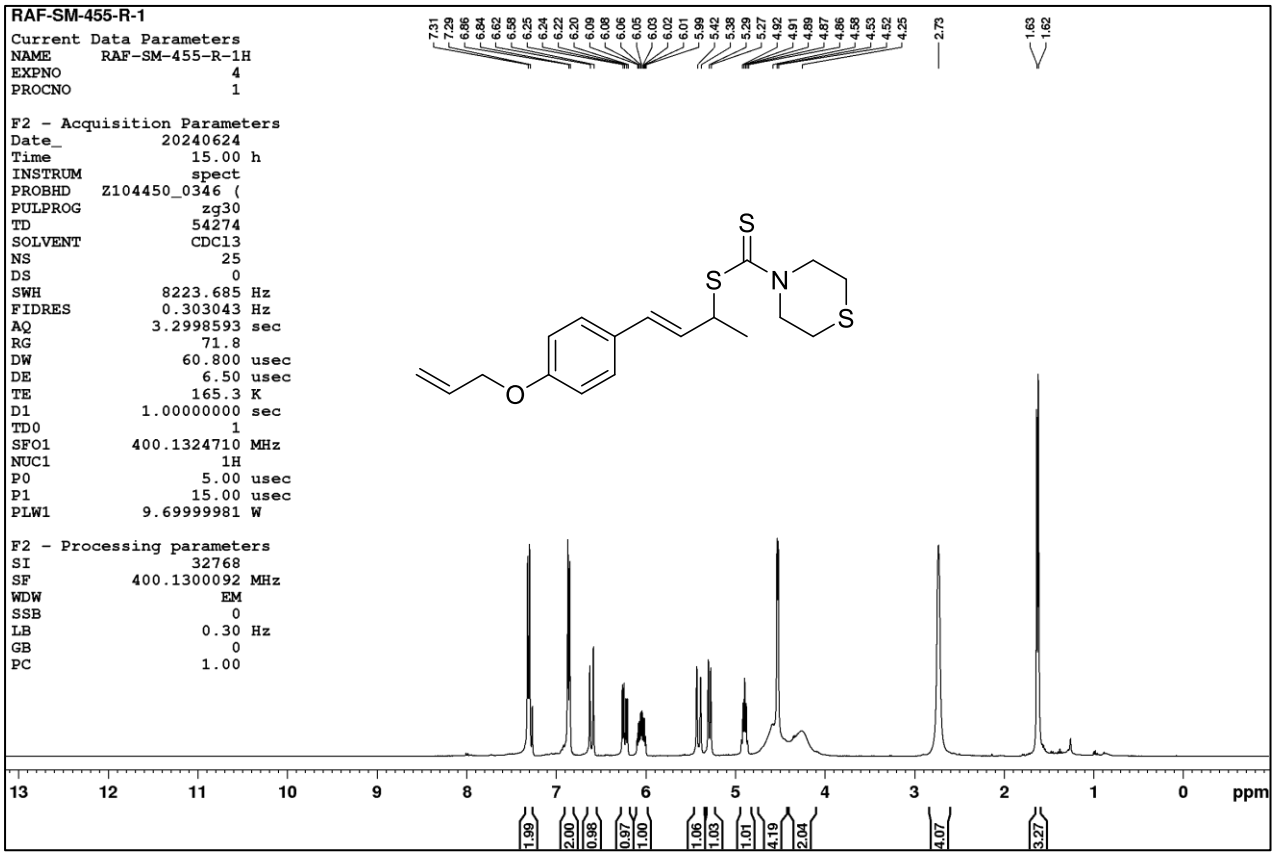


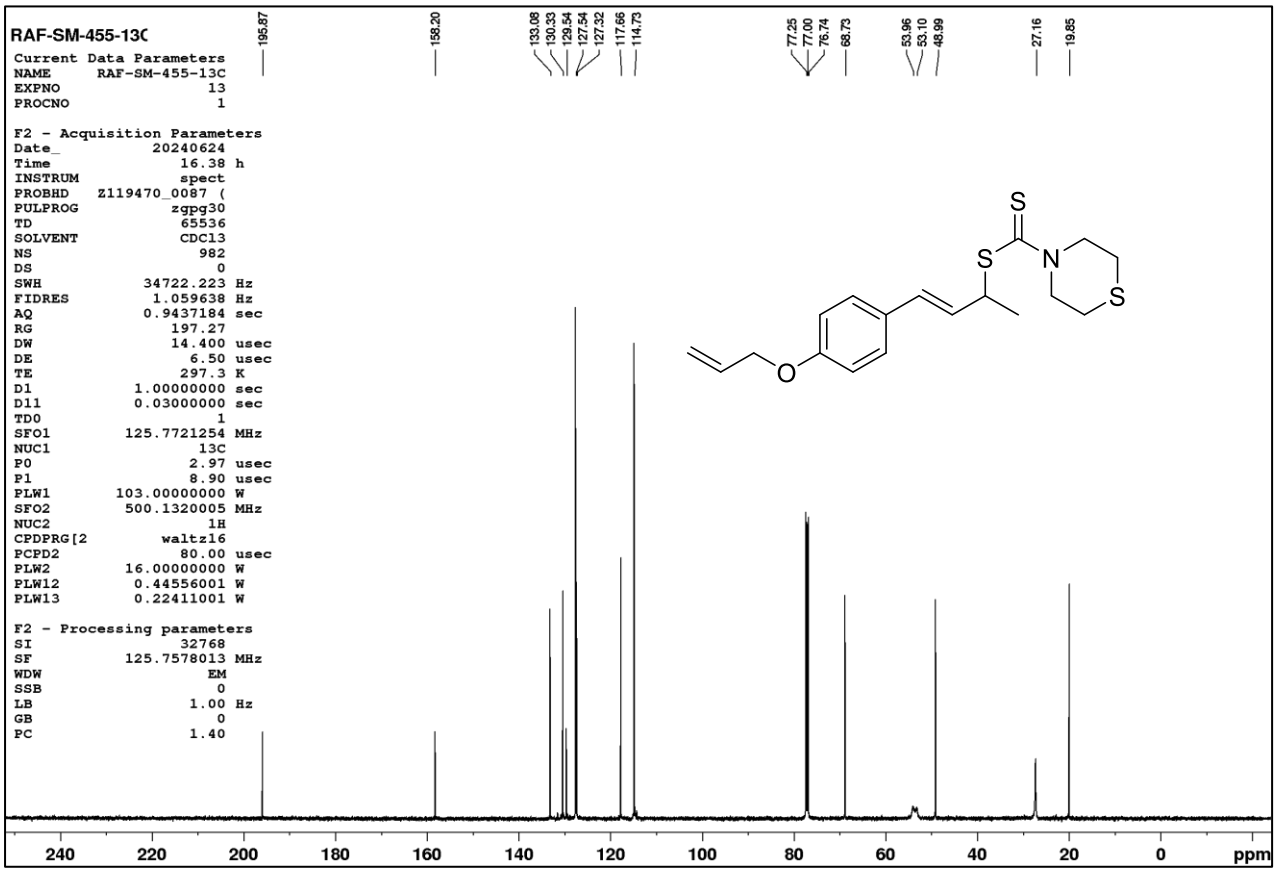
4al: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NOS_2$ 424.1764; Found: 424.1765.



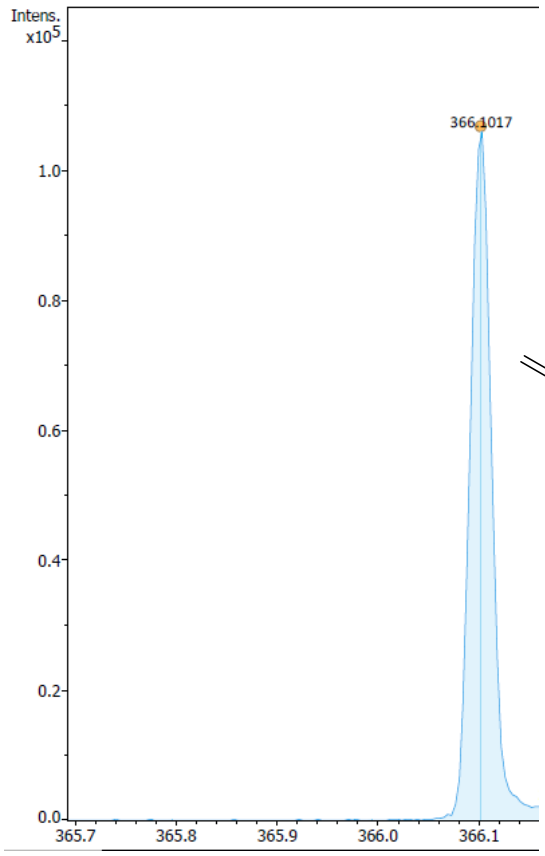


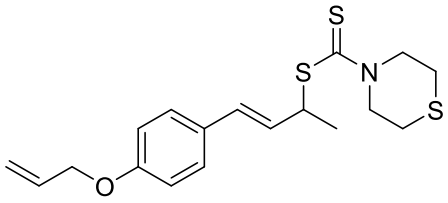
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4am**



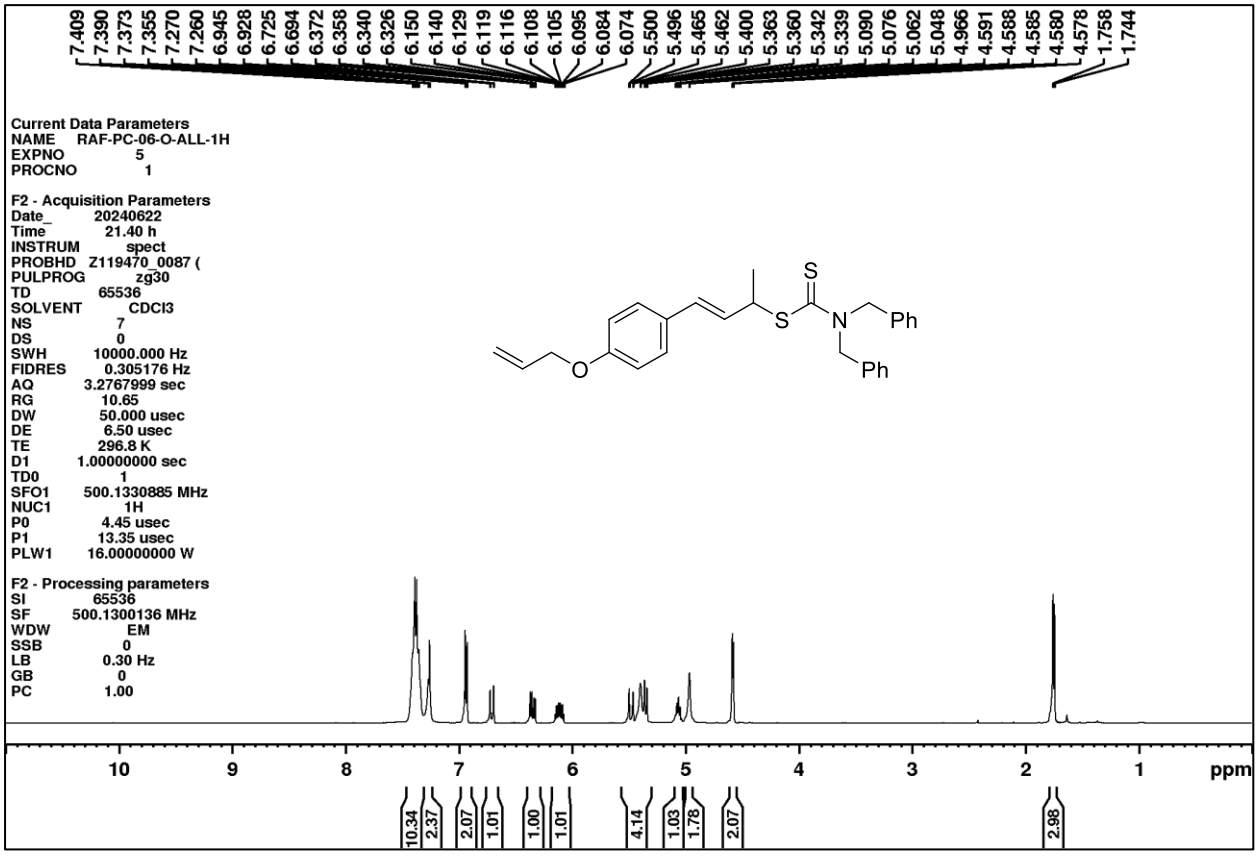


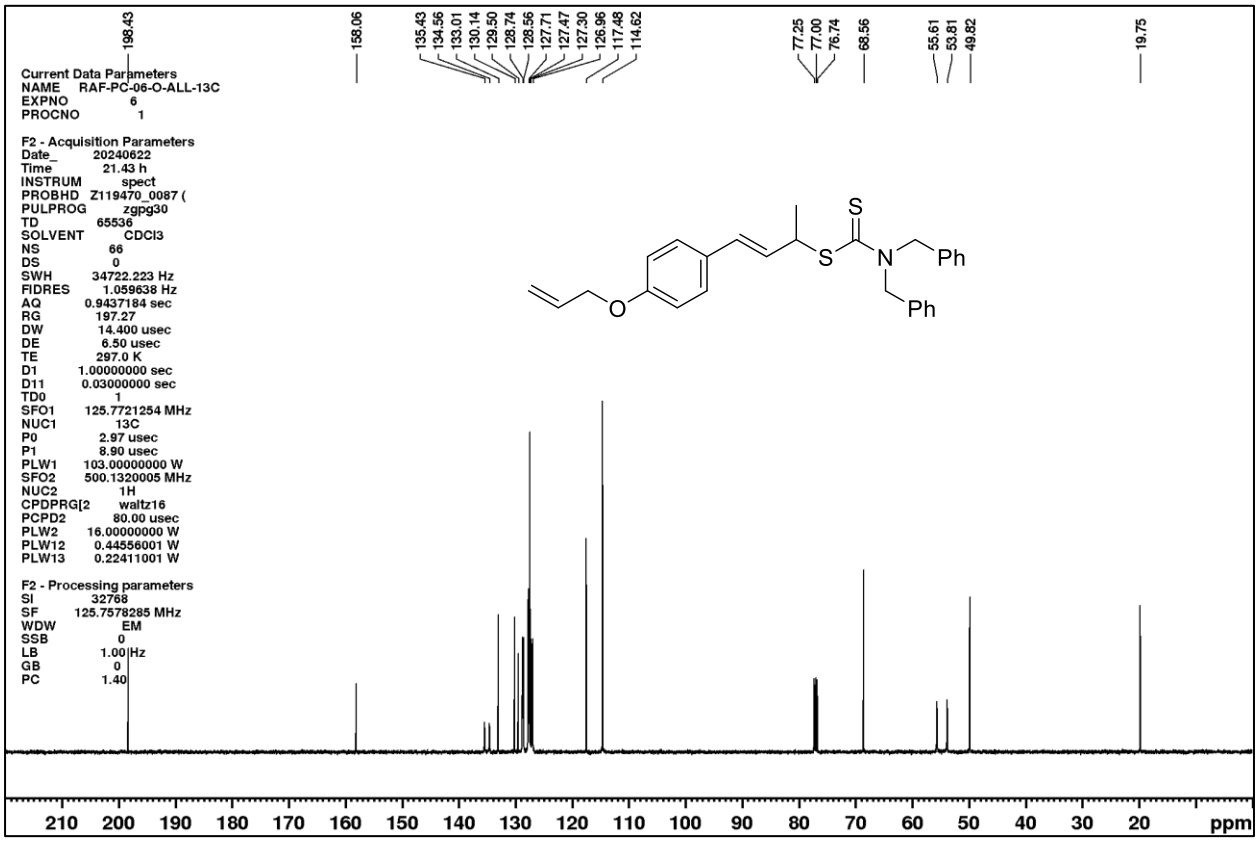
4am: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{24}NOS_3$ 366.1015; Found 366.1017.



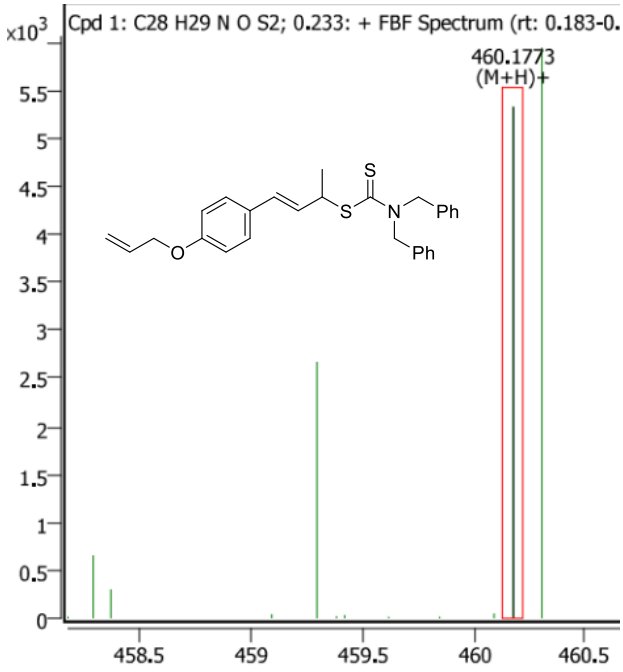


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **4an**

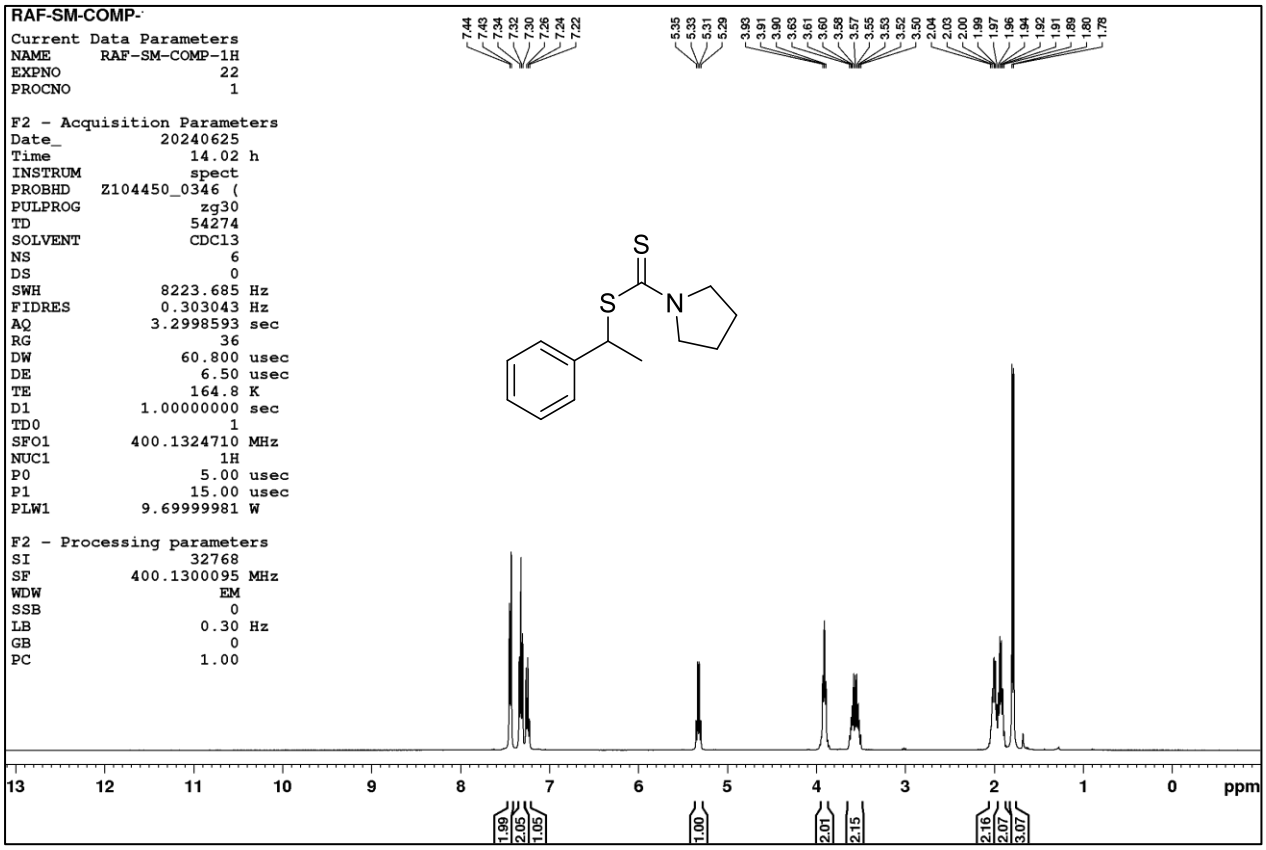


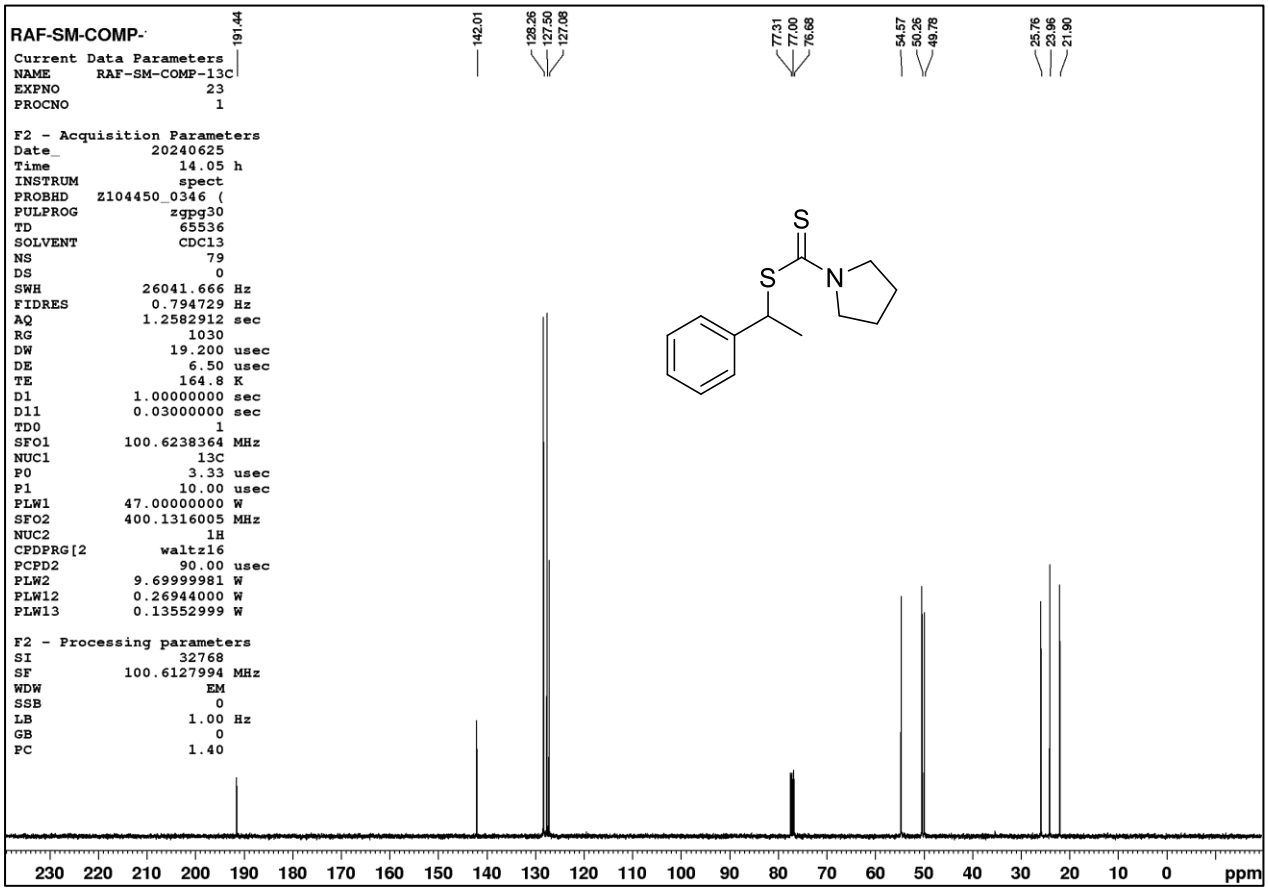


4an: HRMS (Q-TOF): *m/z* [M+H] $^{+}$ calcd for $C_{28}H_{30}NS_2O$ 460.1764 Found 460.1773.

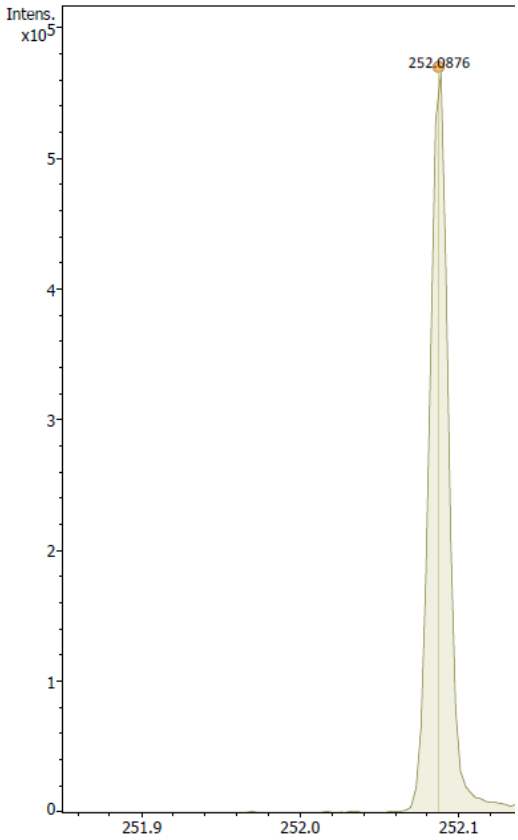


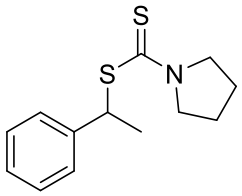
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **6a**



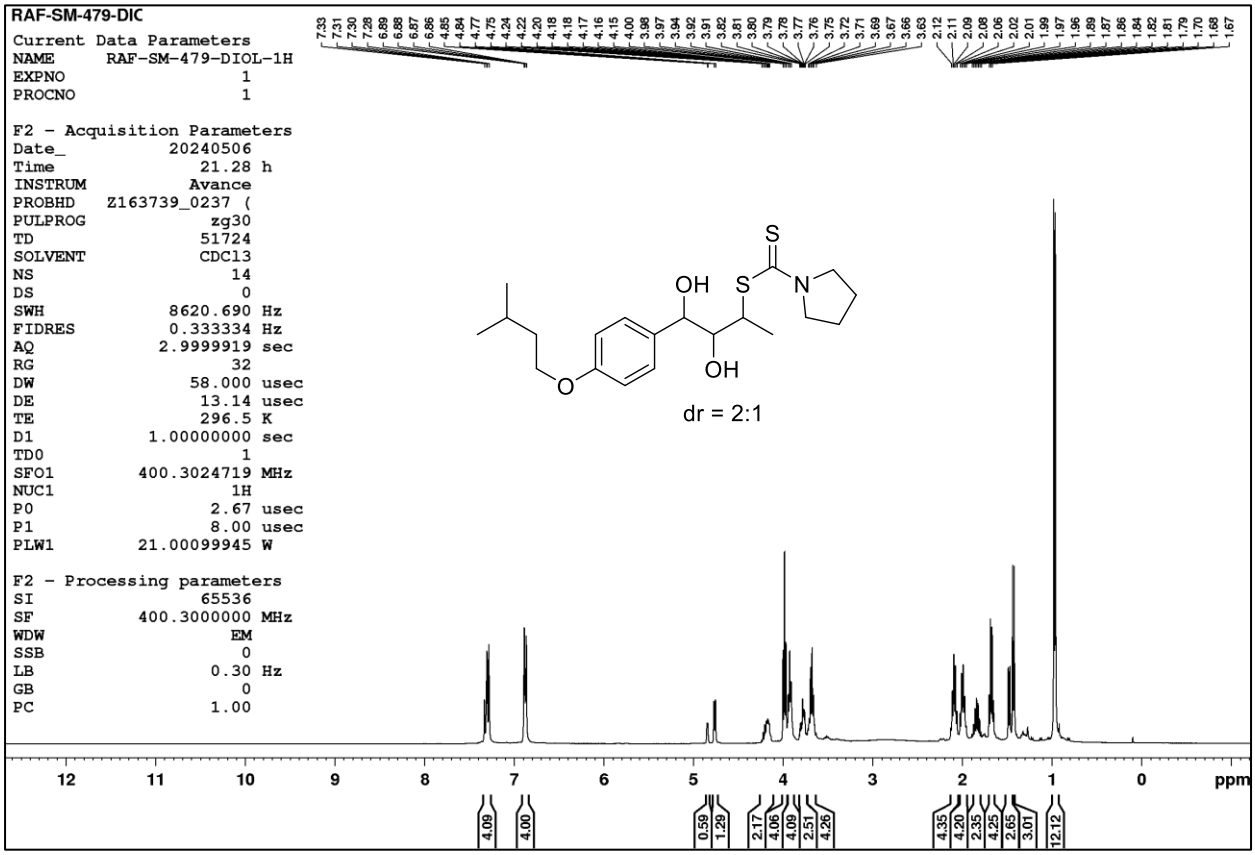


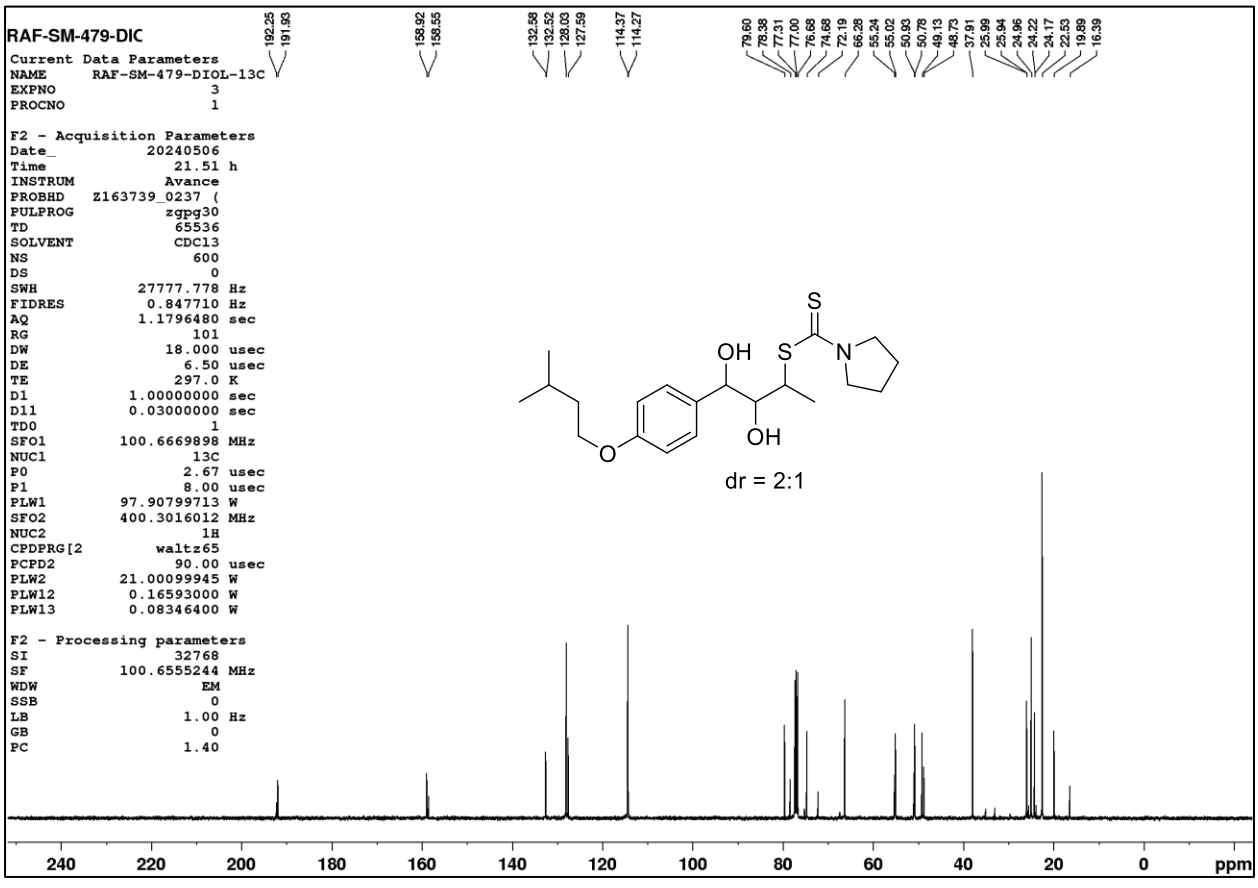
6a: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{18}NS_2$ 252.0876; Found 252.0876.



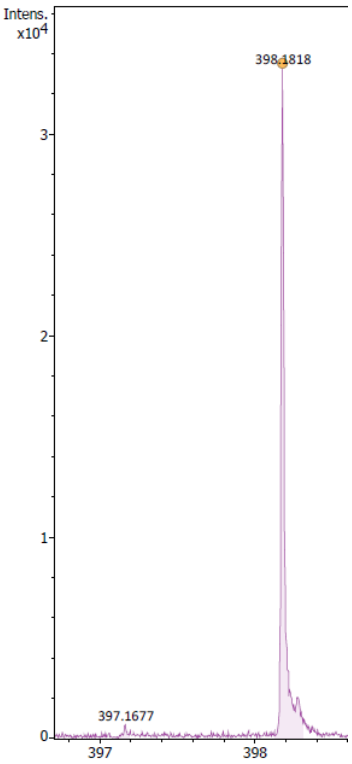


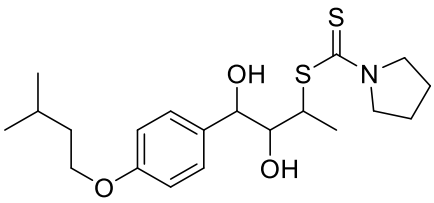
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **7**



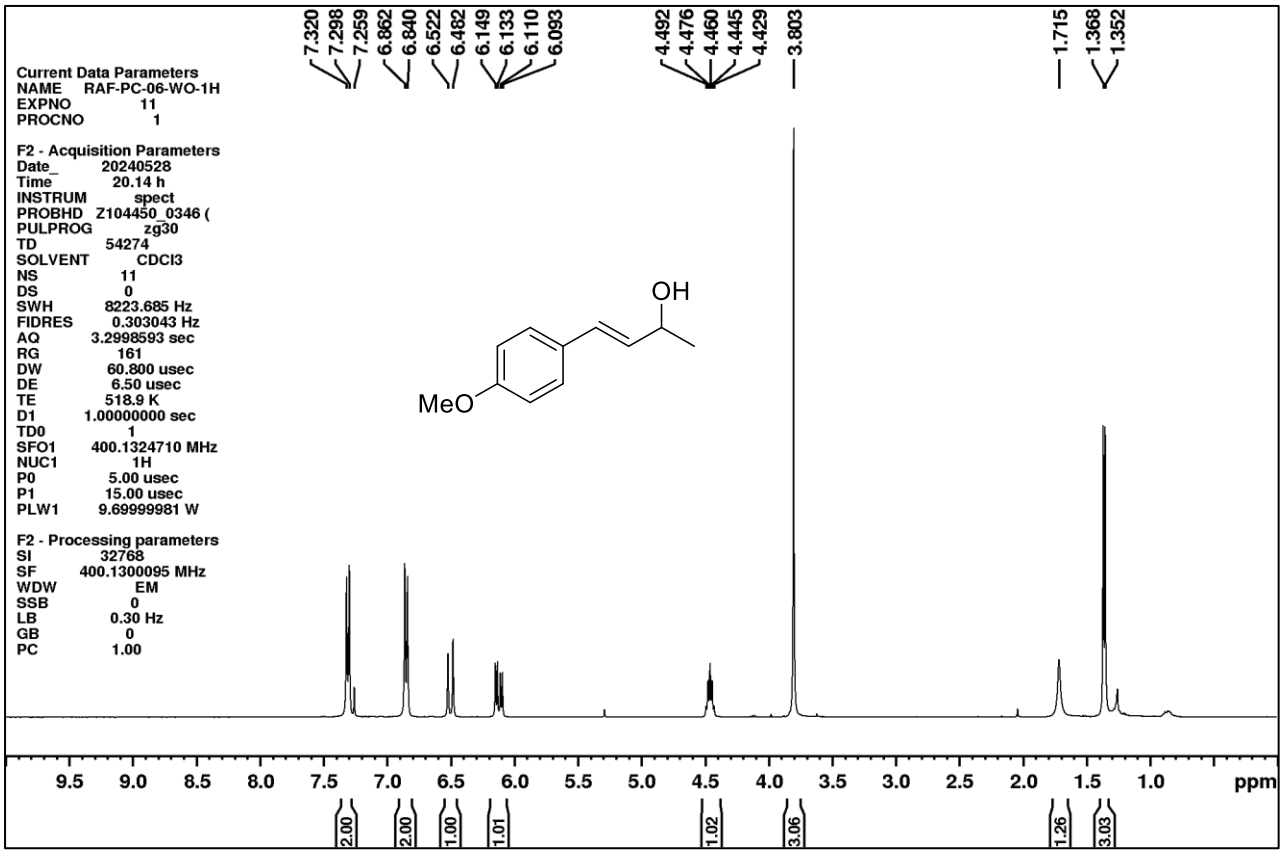


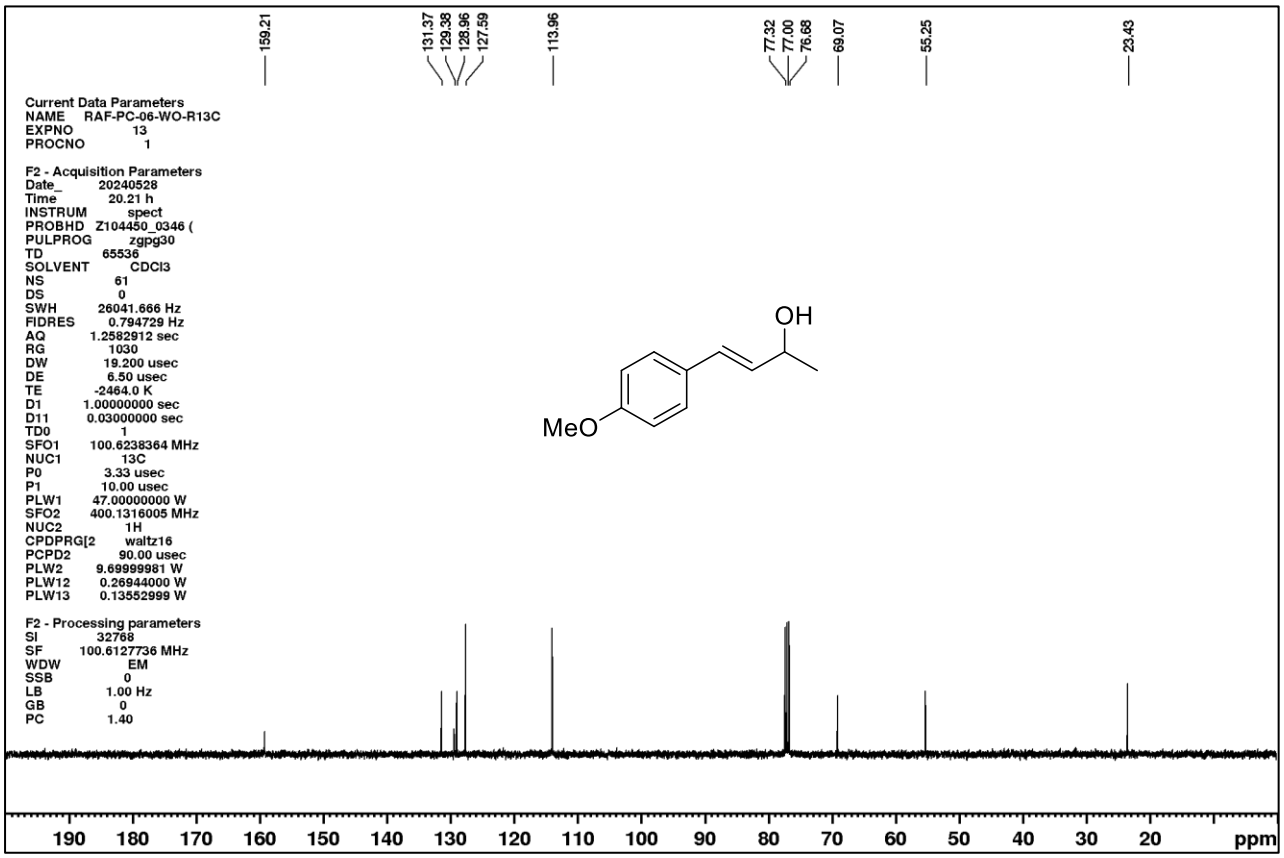
7: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{32}NO_3S_2$ 398.1819; Found 398.1818.



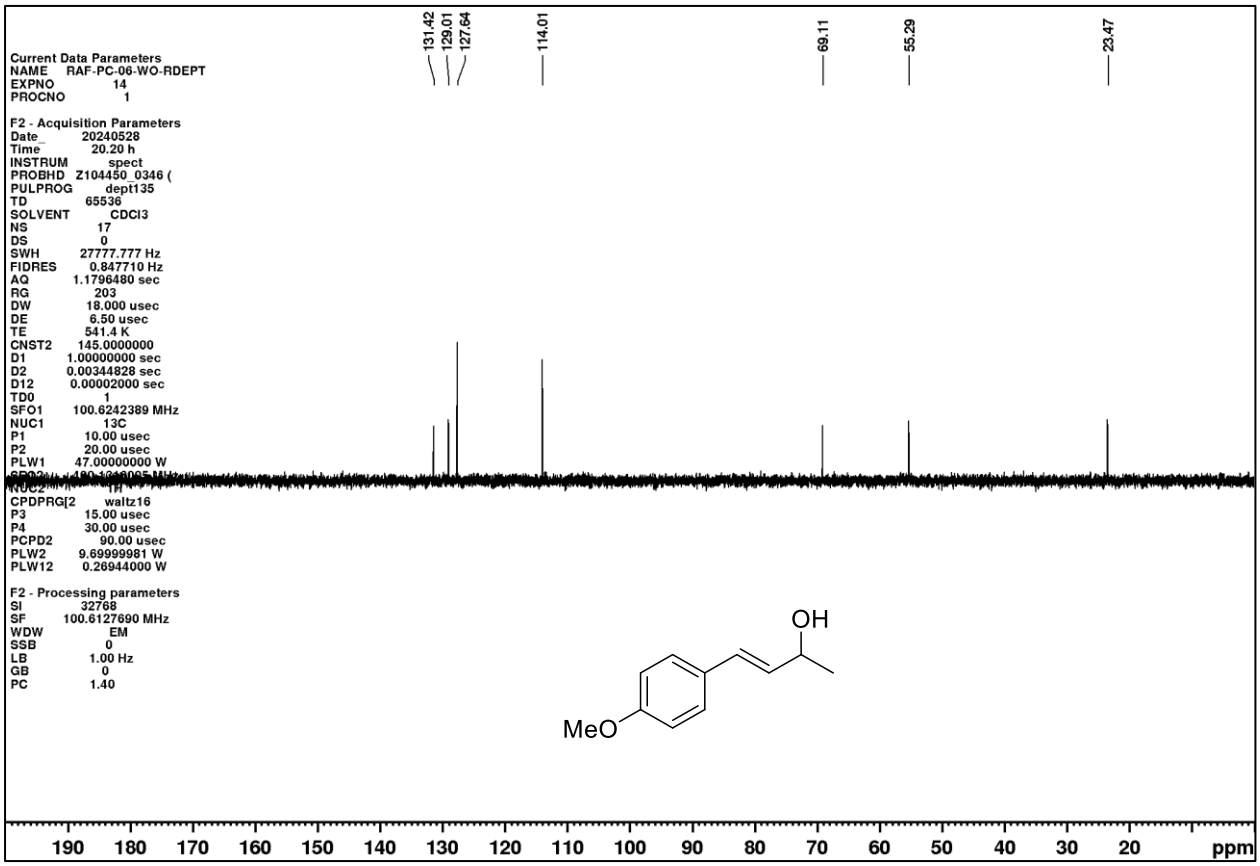


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **8a**

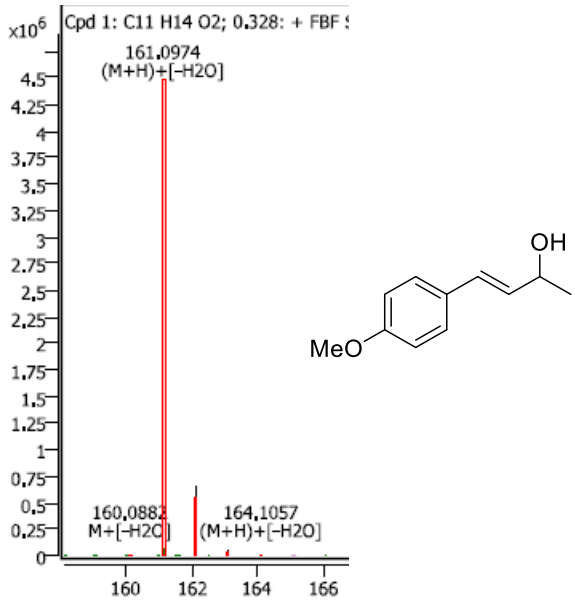




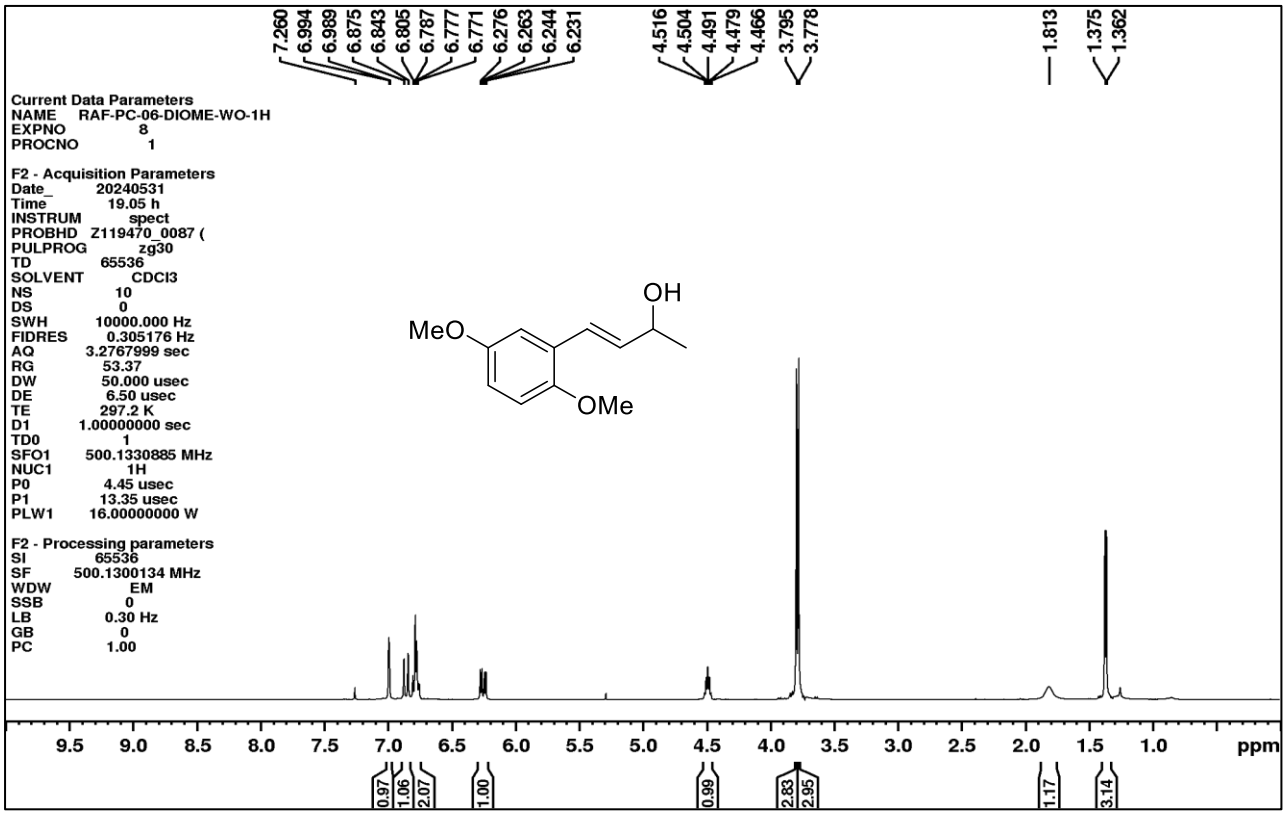
DEPT NMR (100 MHz, $CDCl_3$) of compound **8a**

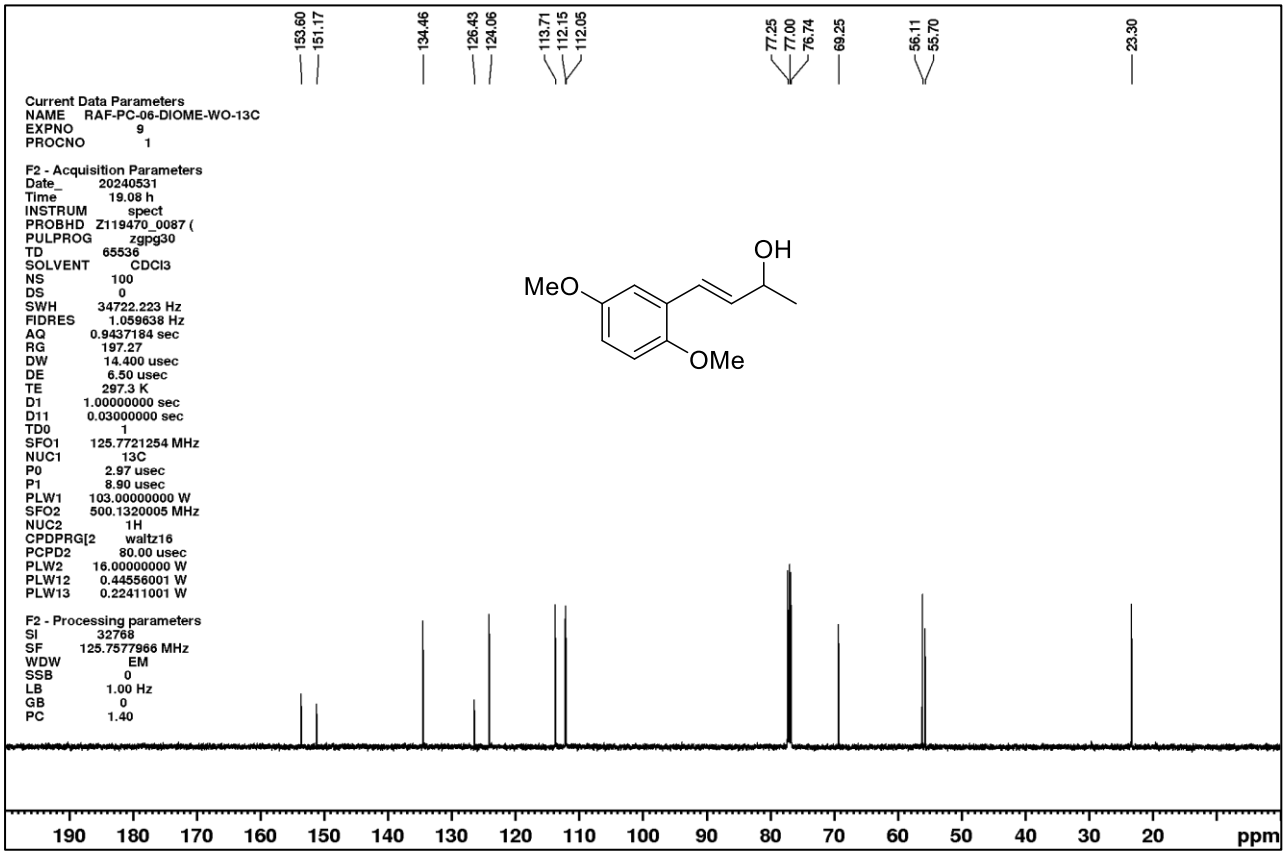


8a: HRMS (Q-TOF): *m/z* $[M + H]^+$ $[-H_2O]$ Calcd for $C_{11}H_{13}O$ 161.0961; Found 161.0974.

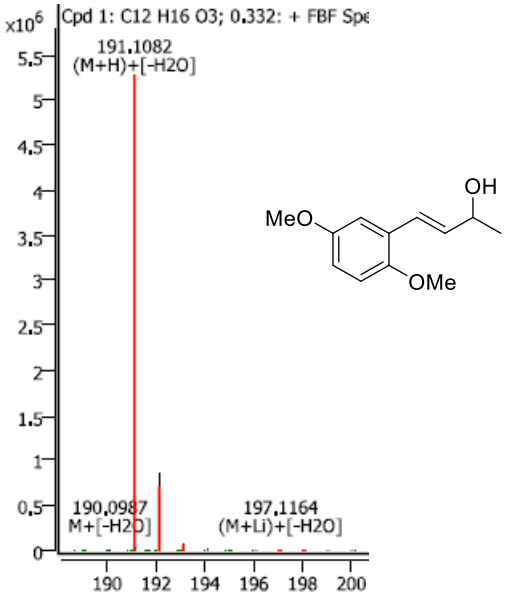


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **8b**

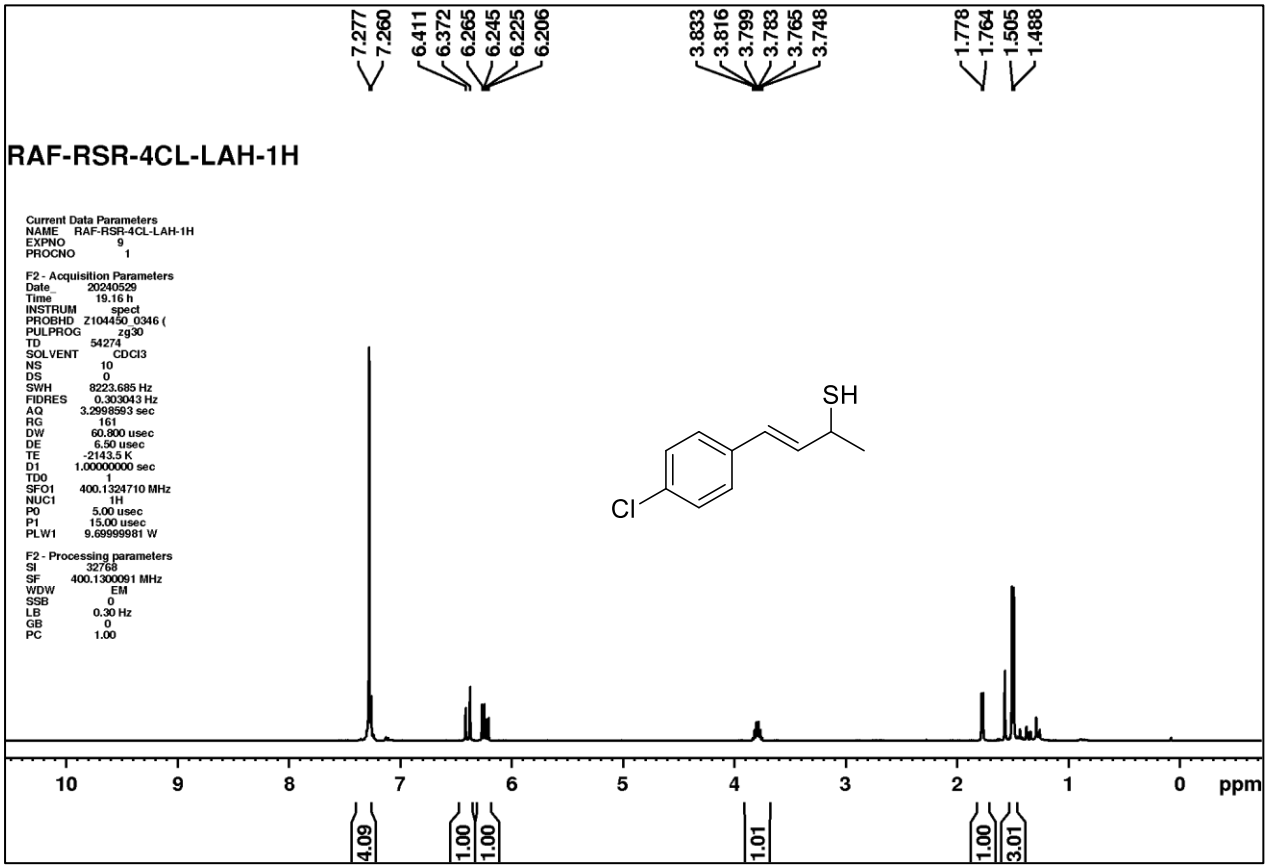


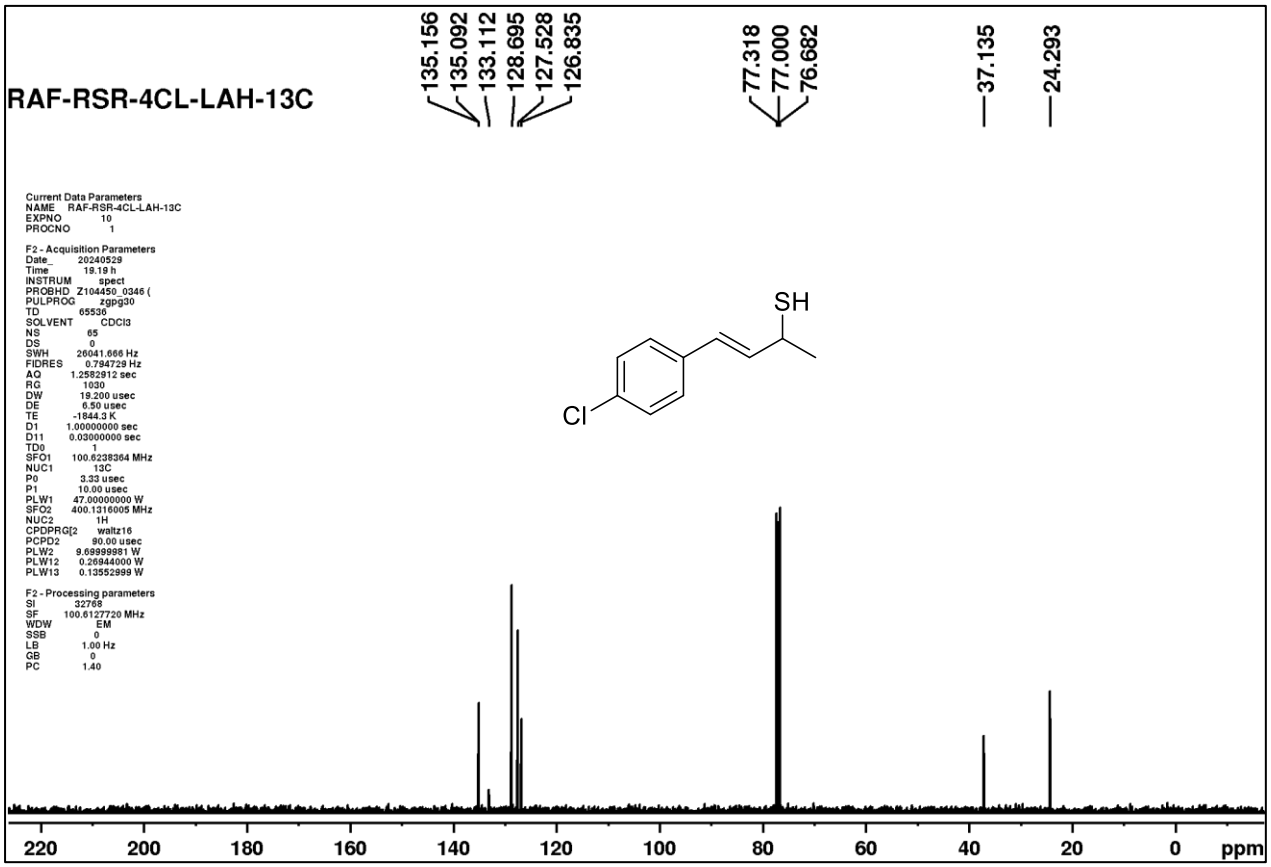


8b: HRMS (Q-TOF): *m/z* [M + H]$^+$ [-H_2O] Calcd for $C_{12}H_{15}O_2$ 191.1067; Found 191.1082.

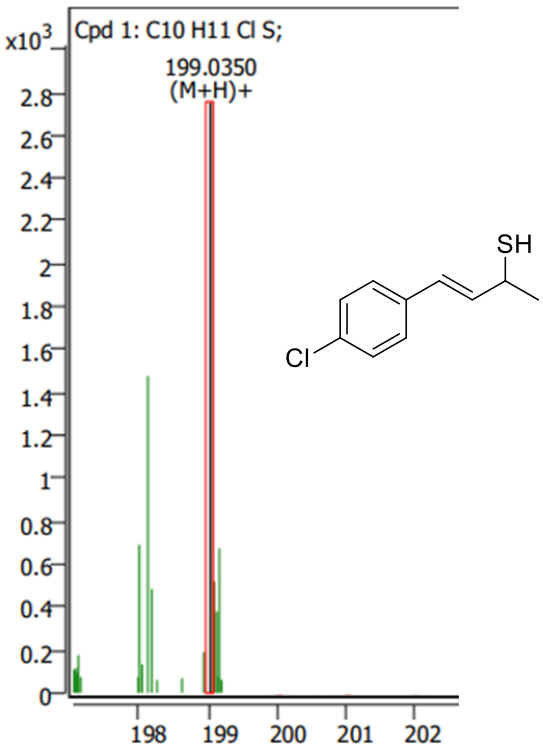


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **9a**

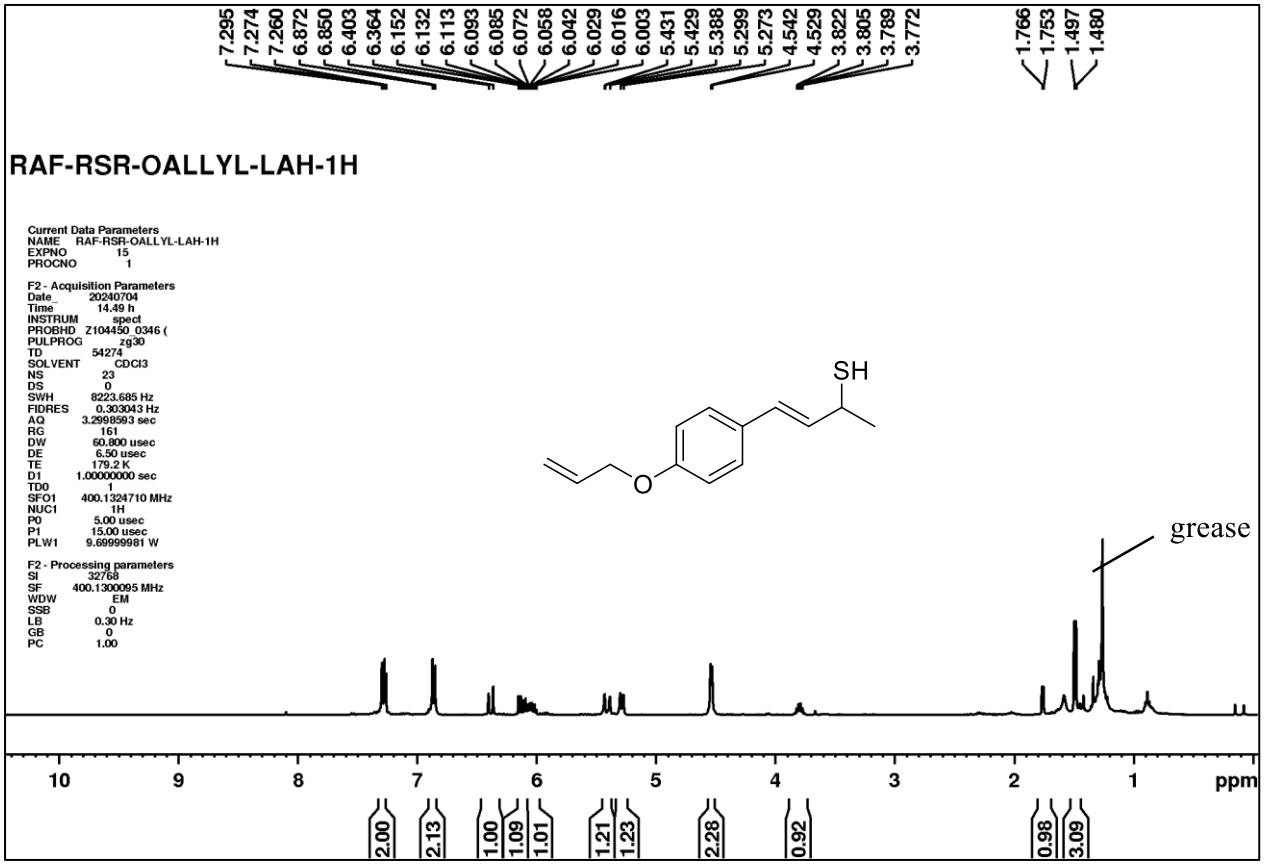


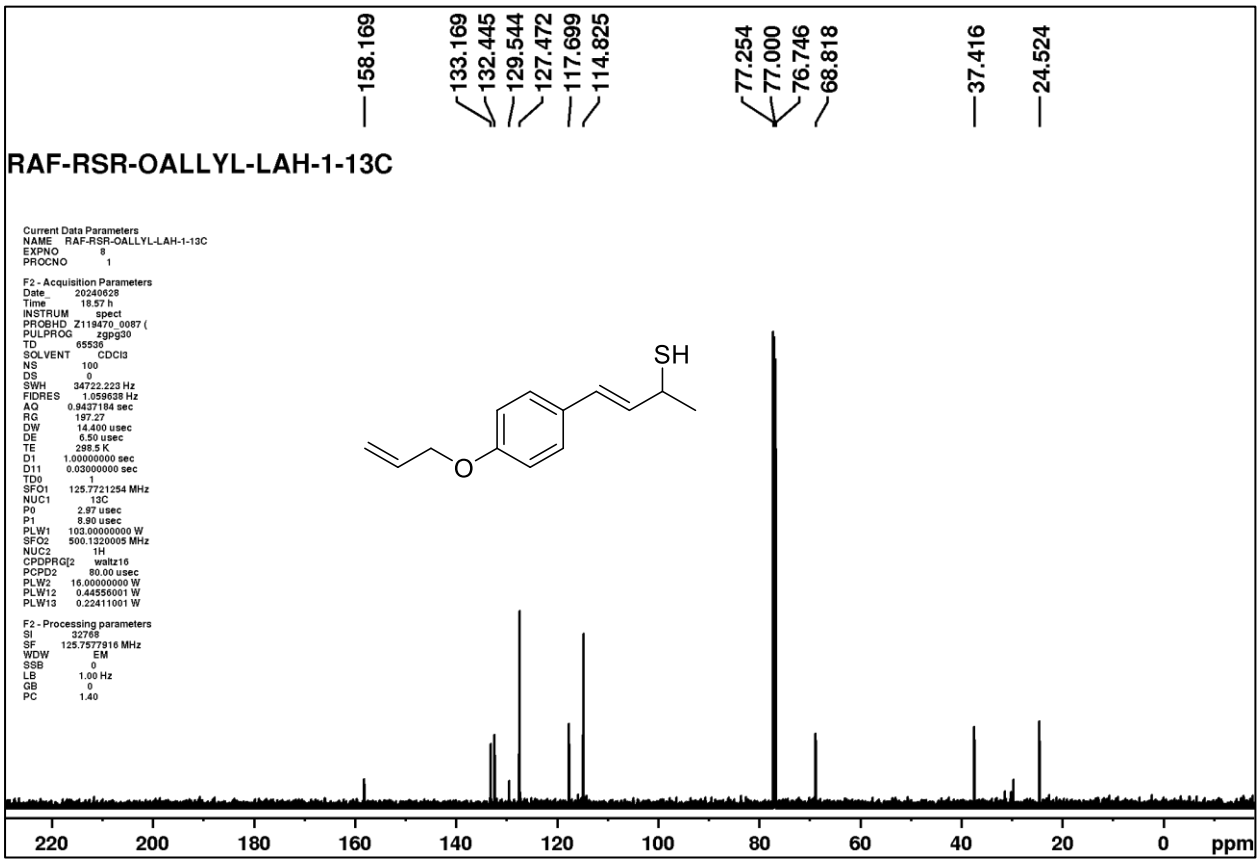


9a: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{12}ClS$ 199.0344; Found: 199.0350.

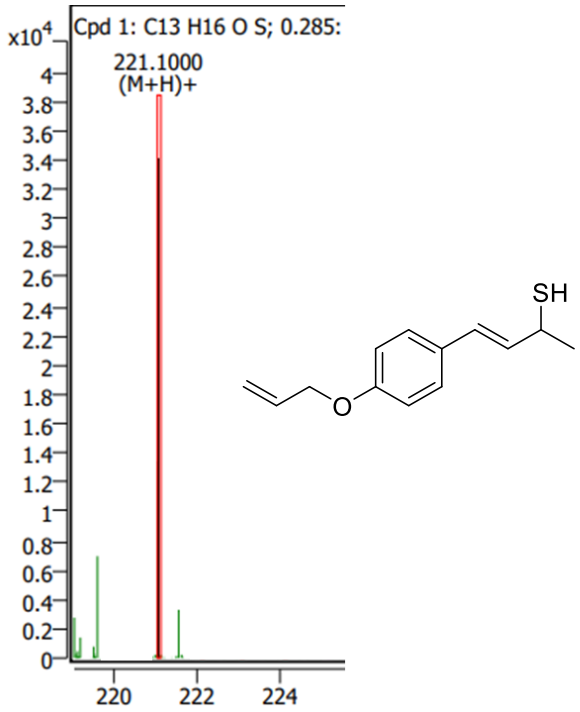


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **9b**

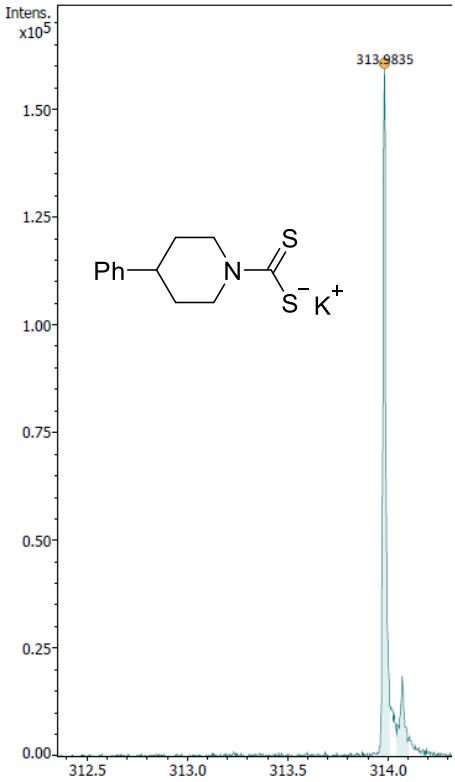




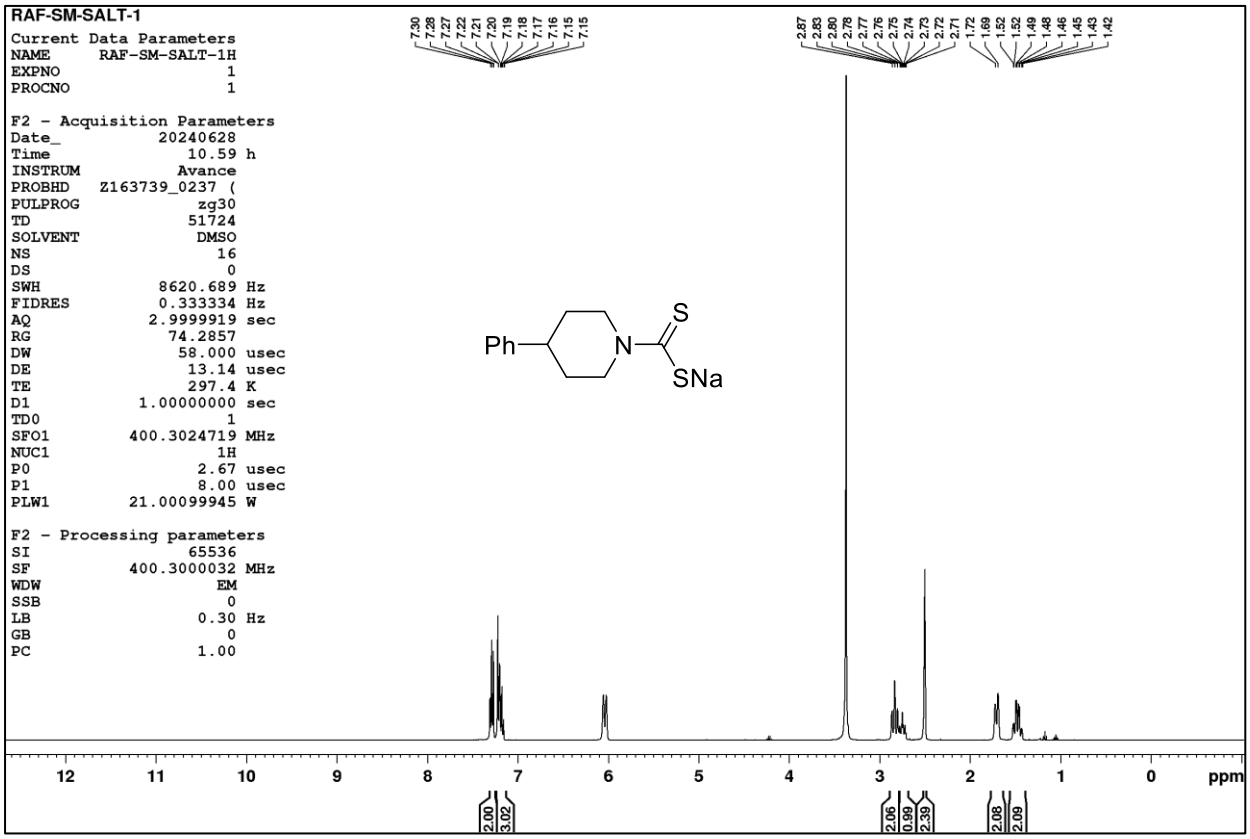
9b: HRMS (Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}OS$ 221.0995; Found: 221.1000.

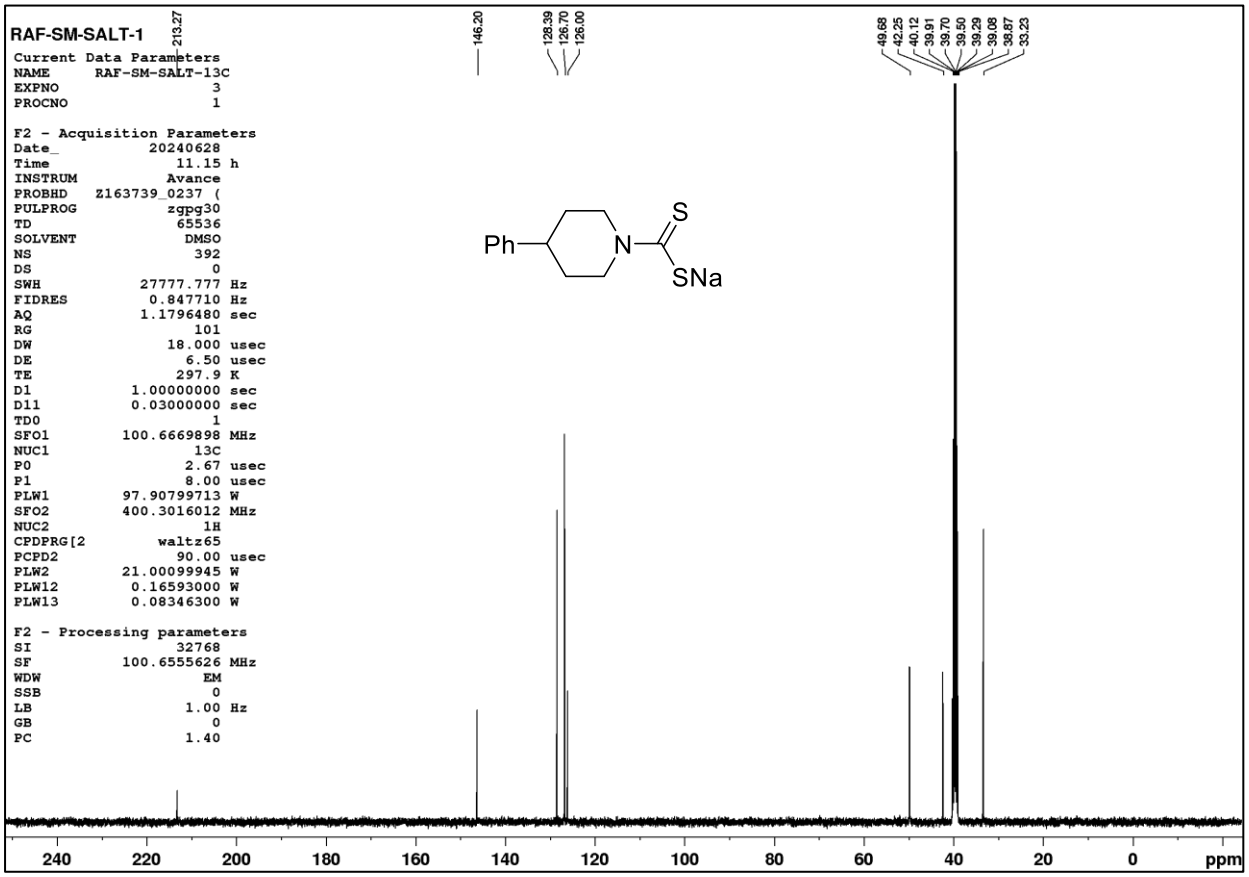


12a: HRMS (Q-TOF): *m/z* $[M + K]^+$ Calcd for $C_{12}H_{14}K_2NS_2$ 313.9837; Found 313.9835.

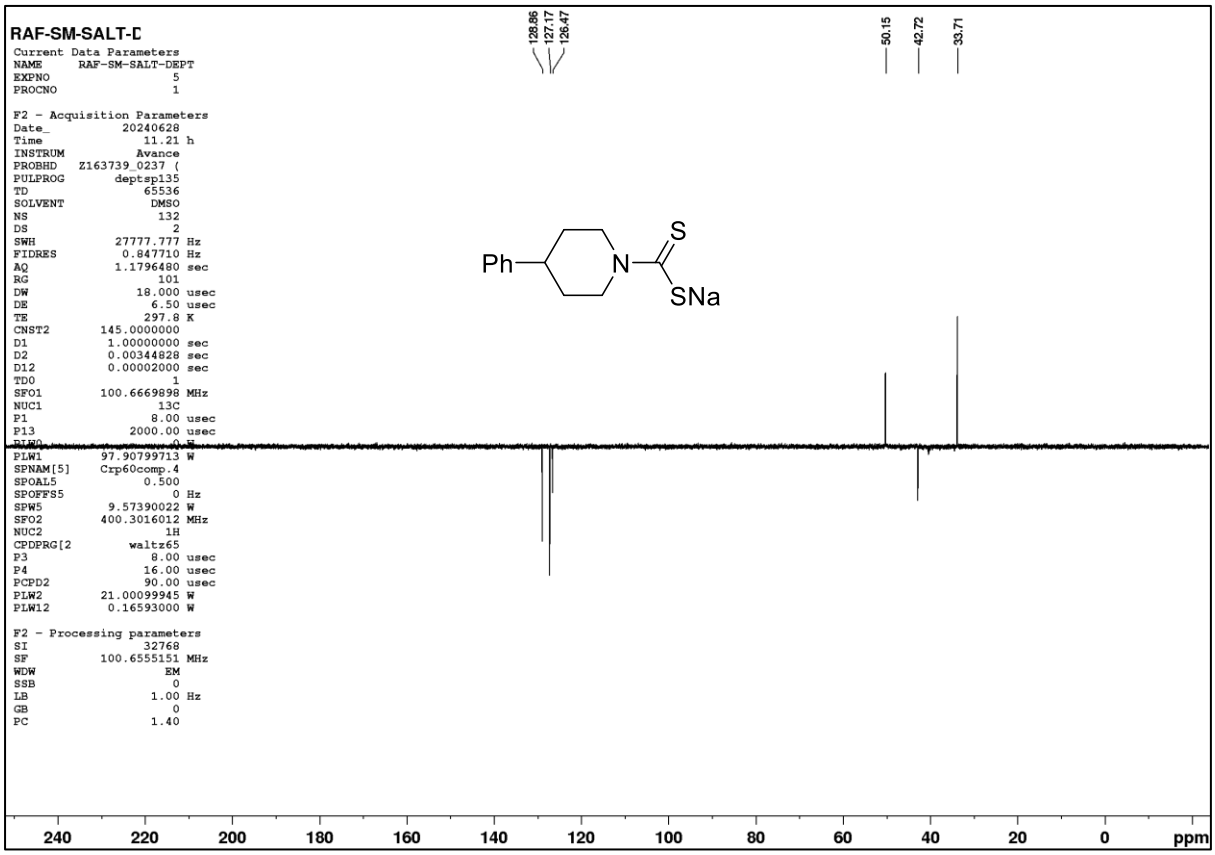


^{1}H NMR (400 MHz, DMSO-d6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6) of compound **12b**

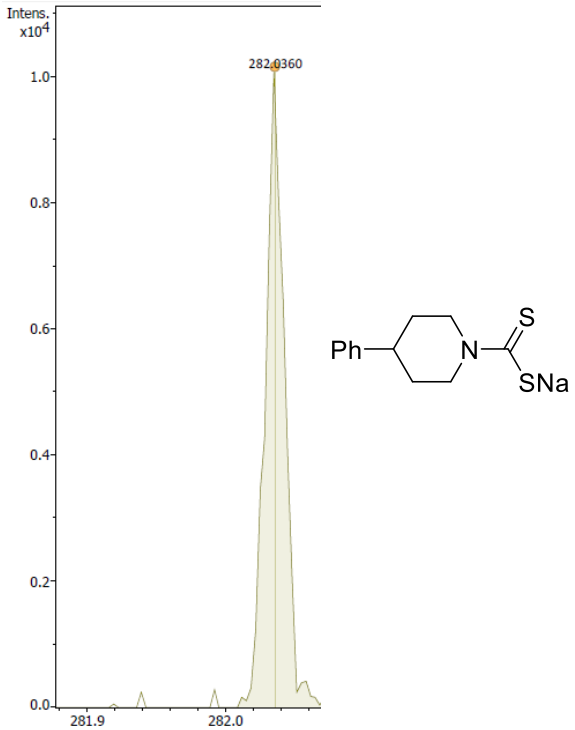




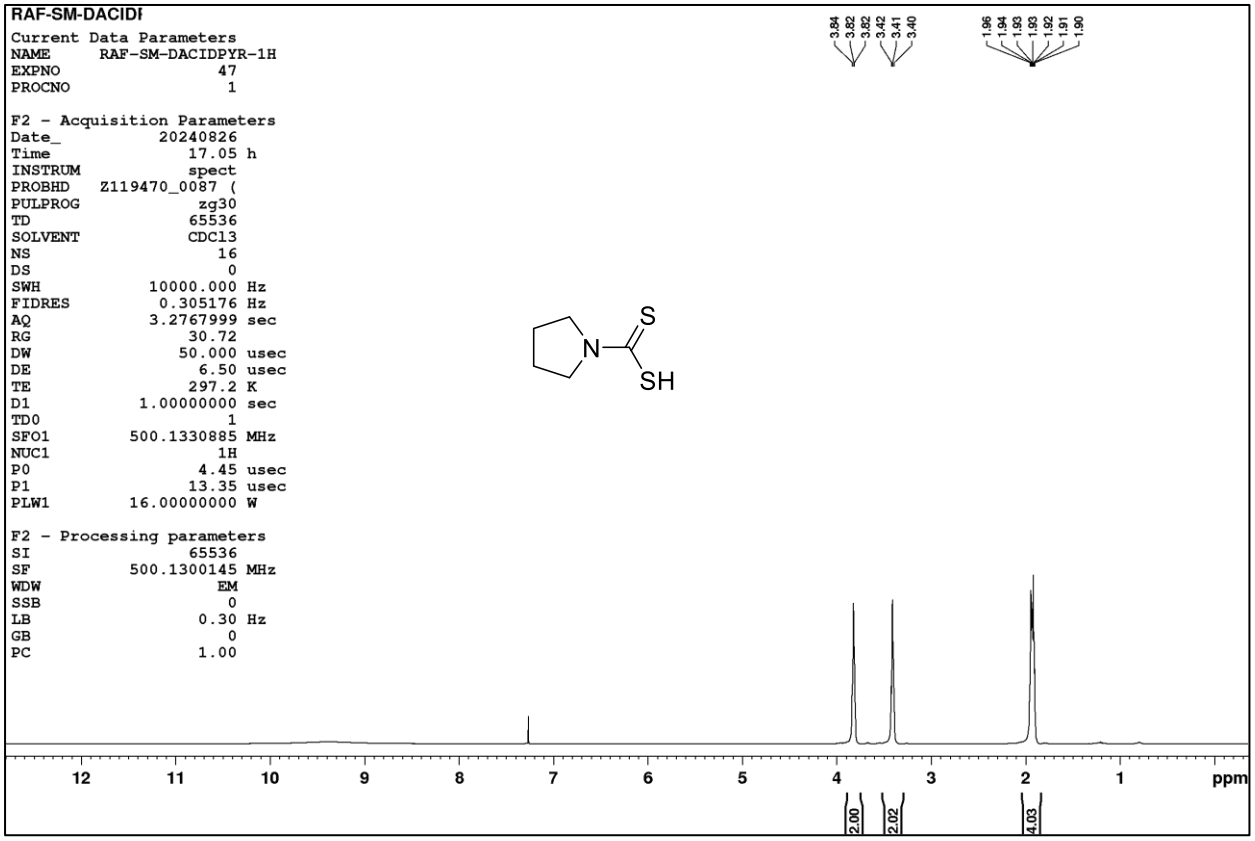
DEPT NMR (100 MHz, DMSO-d6) of compound **12b**

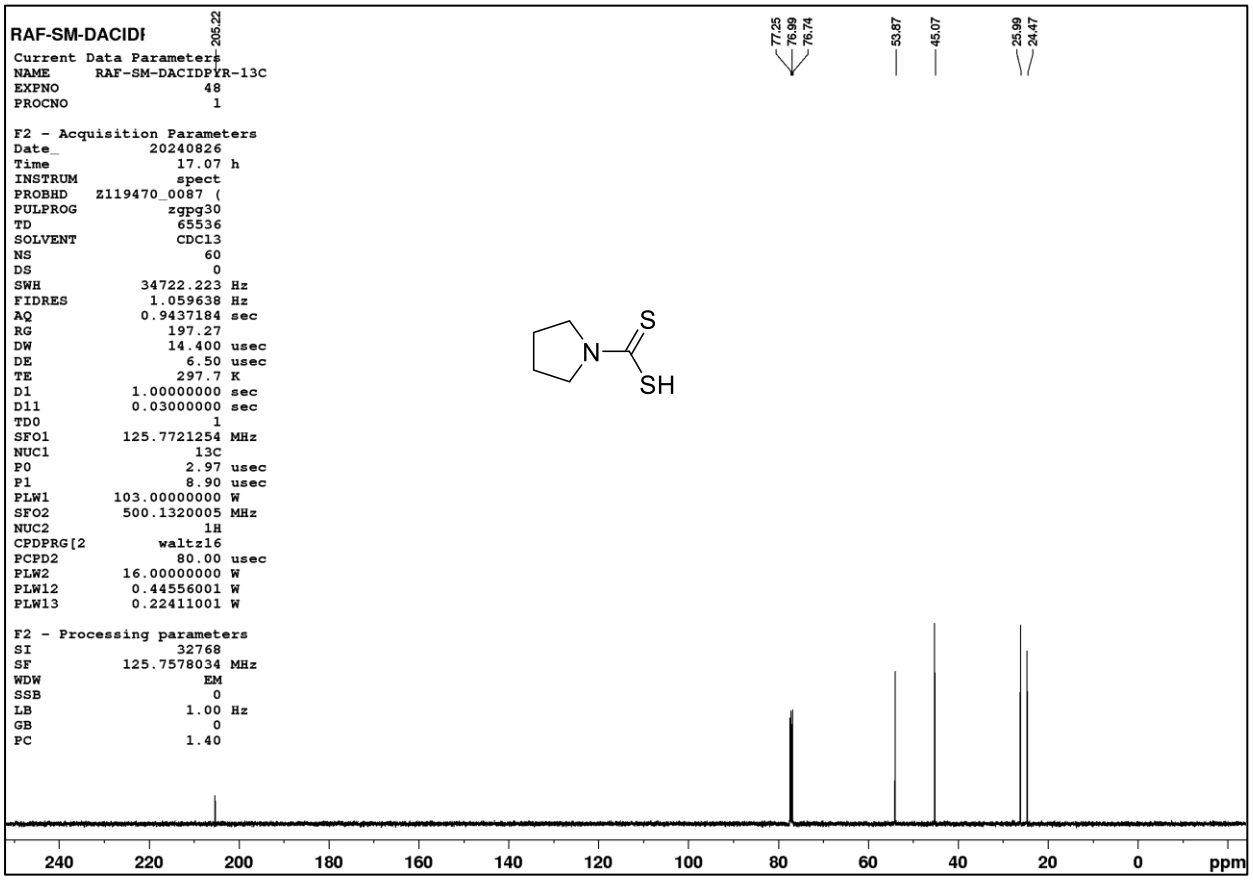


12b: HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{14}NNa_2S_2$ 282.0358; Found 282.0360.



^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **12c**





12c: HRMS (Q-TOF) *m/z*: $[M + H]^+$ calcd for $C_5H_{10}NS_2$ 148.0250; Found 148.0247.