Copper-Mediated Stereospecific C-H Oxidative Sulfenylation of Terminal Alkenes with Disulfides

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Supporting Information

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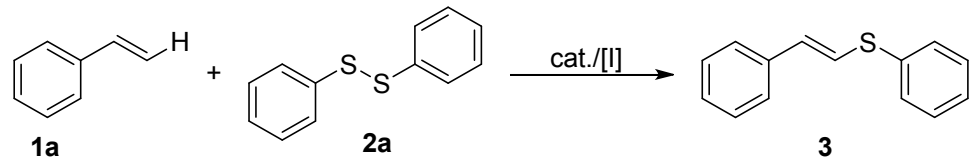
1. General Information.

Chemicals were either purchased or purified by standard techniques. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^{1}H: 500 MHz, ^{13}C: 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometry. All reactions under air atmosphere were conducted using standard Schlenk techniques. Melting points were measured on X4 melting point apparatus and uncorrected. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. Optimization Details.

Table 1. Screening Conditions [a]



1a 2a 3

entry	catalyst	[I] source	base	solvent	yield (%)
1	-	I_2	-	DCE	0
2	-	I_2	-	CH_3CN	0
3	-	I_2	-	DMSO	12
4	$FeCl_3$	I_2	-	DMSO	33
5	$PdCl_2$	I_2	-	DMSO	39
6	CuBr	I_2	-	DMSO	61
7	CuI	I_2	-	DMSO	38
8	CuCl	I_2	-	DMSO	46
9	Cu_2O	I_2	-	DMSO	24
10	CuTc	I_2	-	DMSO	66
11	CuO	I_2	-	DMSO	38

12	CuF_2	I_2	-	DMSO	63
13	$Cu(acac)_2$	I_2	-	DMSO	21
14	$Cu(OAc)_2$	I_2	-	DMSO	60
15	$Cu(TFA)_2$	I_2	-	DMSO	64
16	$Cu(OTf)_2$	I_2	-	DMSO	76
17[b]	$Cu(OTf)_2$	I_2	-	DMSO	58
18	$Cu(OTf)_2$	-	-	DMSO	0
19	$Cu(OTf)_2$	NIS	-	DMSO	52
20	$Cu(OTf)_2$	TBAI	-	DMSO	11
21	$Cu(OTf)_2$	$PhI(OAc)_2$	-	DMSO	0
22[c]	$Cu(OTf)_2$	I_2	-	DMSO	34
23	$Cu(OTf)_2$	I_2	*t*-BuOK	DMSO	Trace
24	$Cu(OTf)_2$	I_2	K_2CO_3	DMSO	16
25	$Cu(OTf)_2$	I_2	NEt_3	DMSO	22
26	$Cu(OTf)_2$	I_2	-	DMF	27
27	$Cu(OTf)_2$	I_2	-	DMAc	18
28	$Cu(OTf)_2$	I_2	-	NMP	0
29	$Cu(OTf)_2$	I_2	-	PhCl	0
30[d]	$Cu(OTf)_2$	I_2	-	DMSO	42
31[e]	$Cu(OTf)_2$	I_2	-	DMSO	73

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.25 mmol), catalyst (10 mol %), [I] source (0.5 mmol) in solvent (2 mL) under air atmosphere at 120 °C for 6 h, isolated yield. [b] 0.5 equiv I_2. [c] 1 mol % $Cu(OTf)_2$. [d] At 100 °C. [e] 2 mmol **1a.**

3. General Procedure for the Synthesis of Vinyl Sulfide 3-24.

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with **1** (0.5 mmol), **2** (0.25 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), I_2 (127mg, 0.5 mmol) in DMSO (2 mL) under air atmosphere. The reaction mixture was stirred at 120 °C until complete consumption of the starting material as detected by TLC or GC-MS analysis. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $Na_2S_2O_3$ (2 x 15 mL) and then brine (1 x 15 mL).

After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired products.

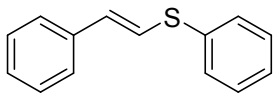
4. Preparation for the Synthesis of Allyl Sulfide 26.

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 1-octene **1m** (1 mmol), 1,2-diphenyldisulfane **2a** (0.25 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), I_2 (127mg, 0.5 mmol) in DMSO (2 mL) under air atmosphere. The reaction mixture was stirred at 120 °C until complete consumption of the starting material as detected by TLC or GC-MS analysis. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $Na_2S_2O_3$ (2 x 15 mL) and then brine (1 x 15 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product **26**.

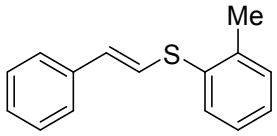
5. Preparation for the Synthesis of Vinyl Sulfone 27.

To a solution containing **3** (1 mmol) in 5 mL of glacial acetic acid was added 30% hydrogen peroxide (0.54 mL) dropwise at room temperature. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 16 h. The mixture was then poured into ice-cold water and stirred for 10 min. The separated solid filtered, and dried to give required compound.

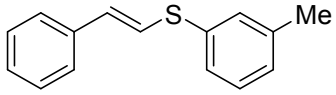
6. Data for All Compouds.



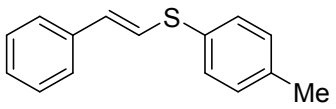
(E)-phenyl(styryl)sulfane (**3**) [1]: Colorless liquid (80.5 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, J = 8.0 Hz, 2H), 7.35-7.31 (m, 6H), 7.27-7.21 (m, 2H), 6.88 (d, J = 15.5 Hz, 1H), 6.73 (d, J = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 136.5, 135.2, 131.8, 129.8, 129.1, 128.7, 127.6, 126.9, 126.0, 123.4; LRMS (EI, 70 eV) m/z (%): 212 (M^+, 100), 178 (39), 167 (32), 121 (35).



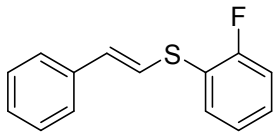
(E)-styryl(o-tolyl)sulfane (**4**) [2]: Yellow liquid (75.7 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42-7.40 (m, 1H), 7.33-7.28 (m, 4H), 7.23-7.19 (m, 4H), 6.82 (d, *J* = 15.5 Hz, 1H), 6.59 (d, *J* = 15.5 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 138.8, 136.7, 133.7, 131.0, 130.9, 130.4, 128.7, 127.45, 127.41, 126.7, 125.9, 123.4, 20.4; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (35), 178 (23), 135 (43).



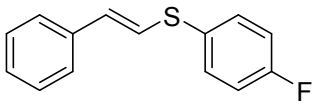
(E)-styryl(m-tolyl)sulfane (**5**) [3]: Yellow liquid (68.9 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35-7.29 (m, 4H), 7.25-7.22 (m, 4H), 7.08-7.06 (m, 1H), 6.88 (d, *J* = 15.5 Hz, 1H), 6.73 (d, *J* = 15.5 Hz, 1H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 139.0, 136.6, 134.9, 131.5, 130.4, 129.0, 128.7, 127.8, 127.5, 126.9, 126.0, 123.7, 21.3; LRMS (EI, 70 eV) m/z (%):226 (M^+, 100), 211 (37), 181 (15), 178 (28).



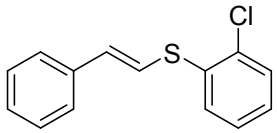
(E)-styryl(p-tolyl)sulfane (**6**) [1]: Yellow liquid (71.2 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.29 (m, 6H), 7.22-7.20 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 15.5 Hz, 1H), 6.64 (d, *J* = 15.5 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 137.3, 136.7, 131.4, 130.6, 130.5, 130.0, 128.6, 127.4, 125.9, 124.5, 21.1; LRMS (EI, 70 eV) m/z (%):226 (M^+, 100), 211 (58), 192 (14), 178 (45), 166 (18).



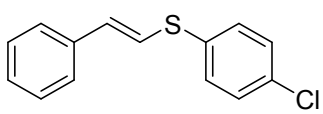
(E)-(2-fluorophenyl)(styryl)sulfane (**7**) [2]: Yellow liquid (87.4 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43-7.40 (m, 1H), 7.34-7.24 (m, 6H), 7.14-7.10 (m, 2H), 6.80 (d, *J* = 15.5 Hz, 1H), 6.73 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 160.8 (d, *J* = 245.3 Hz), 136.3, 132.6, 132.1, 129.0, 128.7, 127.7, 126.1, 124.7, 122.2 (d, *J* = 17.3 Hz), 121.6, 115.9 (d, *J* = 21.9 Hz); LRMS (EI, 70 eV) m/z (%):230 (M^+, 100), 196 (25), 185 (25), 165 (23), 139 (28).



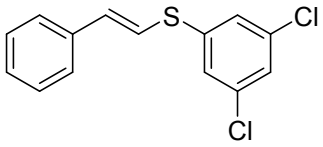
(E)-(4-fluorophenyl)(styryl)sulfane (**8**) [2]: Yellow liquid (70.1 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43-7.39 (m, 2H), 7.33-7.29 (m, 4H), 7.24-7.21 (m, 1H), 7.07-7.03 (m, 2H), 6.81 (d, *J* = 15.5 Hz, 1H), 6.64 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 162.3 (d, *J* = 246.0 Hz), 136.5, 132.6, 131.2, 129.9, 128.7, 127.6, 126.0, 123.9, 116.3 (d, *J* = 21.9 Hz); LRMS (EI, 70 eV) m/z (%):230 (M^+, 100), 196 (24), 185 (31), 165 (19), 139 (22), 121 (21).



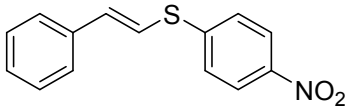
(E)-(2-chlorophenyl)(styryl)sulfane (**9**): Yellow liquid (98.4 mg, 80% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.5 Hz, 3H), 7.36-7.32 (m, 3H), 7.28-7.21 (m, 2H), 7.17-7.14 (m, 1H), 6.89 (d, *J* = 15.5 Hz, 1H), 6.82 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 136.2, 135.4, 135.1, 133.2, 129.8, 129.4, 128.7, 128.1, 127.4, 127.3, 126.3, 120.5; LRMS (EI, 70 eV) m/z (%): 246 (M^+, 100), 211 (56), 178 (72), 155 (27); HRMS (ESI) Calcd for $C_{14}H_{12}ClS^+$ ([M + H]$^+$) 247.0343, Found: 247.0343.



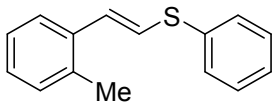
(E)-(4-chlorophenyl)(styryl)sulfane (**10**) [1]: White solid (89.8 mg, 73% yield), m.p. 50-52 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.32 (m, 5H), 7.31-7.29 (m, 3H), 7.26-7.25 (m, 1H), 6.82 (d, *J* = 15.5 Hz, 1H), 6.74 (d, *J* = 15.5 Hz, 1H).; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 136.3, 133.9, 133.0, 132.8, 131.0, 129.3, 128.7, 127.8, 126.1, 122.5; LRMS (EI, 70 eV) m/z (%): 246 (M^+, 100), 211 (40), 178 (52).



(E)-(3,5-dichlorophenyl)(styryl)sulfane (**11**): Yellow liquid (75.8 mg, 54% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39-7.33 (m, 4H), 7.30-7.28 (m, 1H), 7.22-7.18 (m, 3H), 6.89 (d, *J* = 15.5 Hz, 1H), 6.78 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 139.8, 136.0, 135.9, 135.4, 128.8, 128.4, 126.5, 126.4, 126.3, 119.8; LRMS (EI, 70 eV) m/z (%): 280 (M^+, 100), 244 (25), 212 (42), 165 (30), 91 (63), 77 (80); HRMS (ESI) Calcd for $C_{14}H_{11}Cl_2S^+$ ([M + H]$^+$) 280.9953, Found: 280.9963.

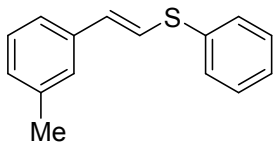


(E)-(4-nitrophenyl)(styryl)sulfane (**12**) [2]: Yellow solid (86.1 mg, 67% yield), m.p. 63-65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.18-8.15 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 4H), 7.39-7.36 (m, 2H), 7.34-7.33 (m, 1H), 7.03 (d, *J* = 15.5 Hz, 1H), 6.87 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 146.5, 138.0, 135.6, 132.1, 128.9, 128.7, 127.1, 126.5, 124.1, 118.2; LRMS (EI, 70 eV) m/z (%): 257 (M^+, 100), 210 (28), 178 (42), 166 (29).

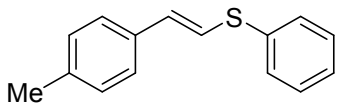


(E)-(2-methylstyryl)(phenyl)sulfane (**13**) [1]: Yellow liquid (85.8 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42-7.40 (m, 3H), 7.34-7.31 (m, 2H), 7.25-7.23 (m, 1H), 7.17-7.14 (m, 3H), 6.97 (d, *J* = 15.0 Hz, 1H), 6.78 (d, *J* = 15.0 Hz, 1H), 2.33 (s, 3H);

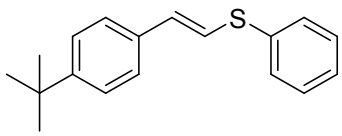
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 135.6, 135.5, 135.1, 130.4, 130.0, 129.6, 129.1, 127.6, 126.8, 126.2, 125.4, 124.3, 19.8; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (43), 178 (34), 115 (80).



(E)-(3-methylstyryl)(phenyl)sulfane (**14**) [1]: Yellow liquid (71.2 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42-7.40 (m, 2H), 7.35-7.32 (m, 2H), 7.26-7.25 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.16-7.14 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 15.5 Hz, 1H), 6.71 (d, *J* = 15.5 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 138.3, 136.5, 135.4, 132.1, 129.8, 129.1, 128.6, 128.4, 126.9, 126.7, 123.2, 123.1, 21.4; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (30), 193 (17), 178 (30).

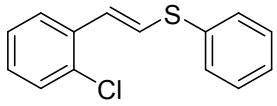


(E)-(4-methylstyryl)(phenyl)sulfane (**15**) [1]: White solid (92.6 mg, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.5 Hz, 2H), 7.33-7.30 (m, 2H), 7.25-7.23 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 15.5 Hz, 1H), 6.73 (d, *J* = 15.5 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 137.5, 135.6, 133.8, 132.4, 129.6, 129.4, 129.1, 126.7, 126.0, 121.9, 21.2; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (64), 178 (40), 115 (25).

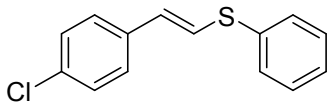


(E)-(4-(tert-butyl)styryl)(phenyl)sulfane (**16**): Colorless liquid (97.7 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40-7.38 (m, 2H), 7.35-7.29 (m, 6H), 7.25-7.21 (m, 1H), 6.83 (d, *J* = 15.5 Hz, 1H), 6.75 (d, *J* = 15.5 Hz, 1H), 1.31 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 150.9, 135.7, 133.8, 132.4, 129.5, 129.1, 126.7, 125.8, 125.6,

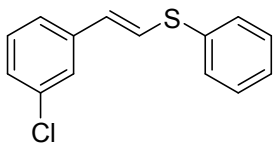
122.1, 34.6, 31.2; LRMS (EI, 70 eV) m/z (%): 268 (M^+, 80), 253 (100), 211 (18); HRMS (ESI) Calcd for $C_{18}H_{21}S^+$ ($[M + H]^+$) 269.1358, Found: 269.1360.



(E)-(2-chlorostyryl)(phenyl)sulfane (**17**): Yellow liquid (56.6 mg, 46% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49-7.44 (m, 3H), 7.37-7.34 (m, 3H), 7.31-7.29 (m, 1H), 7.20-7.15 (m, 2H), 7.06 (d, *J* = 15.5 Hz, 1H), 6.92 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 134.7, 134.6, 132.5, 130.4, 129.9, 129.2, 128.4, 127.34, 127.26, 126.9, 126.7, 126.5; LRMS (EI, 70 eV) m/z (%): 246 (M^+, 26), 211 (100), 178 (48); HRMS (ESI) Calcd for $C_{14}H_{11}ClSNa^+$ ($[M + Na]^+$) 269.0162, Found: 269.0167.

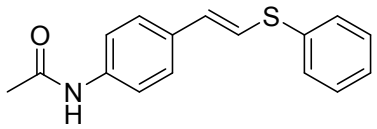


(E)-(4-chlorostyryl)(phenyl)sulfane (**18**) [3]: Yellow solid (87.5 mg, 71% yield), m.p. 48-49 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.5 Hz, 2H), 7.35-7.32 (m, 3H), 7.25-7.24 (m, 4H), 6.86 (d, *J* = 15.5 Hz, 1H), 6.62 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 135.1, 134.7, 133.1, 131.0, 130.2, 129.7, 129.2, 128.8, 127.1, 124.7; LRMS (EI, 70 eV) m/z (%): 246 (M^+, 100), 211 (40), 178 (48).

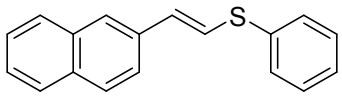


(E)-(3-chlorostyryl)(phenyl)sulfane (**19**): Yellow liquid (62.7 mg, 51% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-7.41 (m, 2H), 7.37-7.33 (m, 3H), 7.31-7.29 (m, 2H), 7.23-7.21 (m, 1H), 7.18-7.16 (m, 1H), 6.91 (d, *J* = 15.5 Hz, 1H), 6.58 (d, *J* = 15.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 138.4, 137.6, 134.7, 134.4, 131.2, 130.5, 129.3, 127.4, 127.3, 126.0, 125.8, 124.1; LRMS (EI, 70 eV) m/z (%): 246 (M^+, 100),

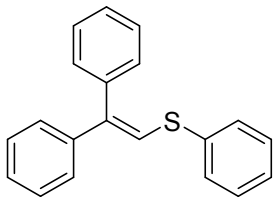
211 (37), 178 (90); HRMS (ESI) Calcd for $C_{14}H_{11}ClSNa^+$ ([M + Na]$^+$) 269.0162, Found: 269.0174.



(E)-N-(4-(2-(phenylthio)vinyl)phenyl)acetamide (**20**): Yellow solid (106.3 mg, 79% yield), m.p. 92-93^{o}C; 1H NMR (500 MHz, $CDCl_3$) δ 7.52 (b, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34-7.31 (m, 2H), 7.29-7.25 (m, 3H), 6.80 (d, *J* = 15.5 Hz, 1H), 6.68 (d, *J* = 15.5 Hz, 1H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 168.3, 137.3, 135.3, 132.7, 131.3, 129.7, 129.1, 126.9, 126.6, 122.4, 112.0, 24.5; LRMS (EI, 70 eV) m/z (%): 269 (M^+, 100), 226 (38), 194 (25), 185 (34), 106 (68); HRMS (ESI) Calcd for $C_{16}H_{16}NOS^+$ ([M + H]$^+$) 270.0947, Found: 270.0949.

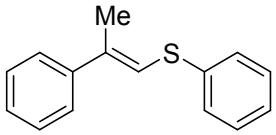


(E)-(2-(naphthalen-2-yl)vinyl)(phenyl)sulfane (**21**): White solid (112.6 mg, 86% yield), m.p. 99-100 ^{o}C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.78-7.75 (m, 3H), 7.66 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.46-7.42 (m, 4H), 7.36-7.33 (m, 2H), 7.28-7.25 (m, 1H), 7.00 (d, *J* = 15.5 Hz, 1H), 6.86 (d, *J* = 15.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 135.1, 134.0, 133.6, 132.9, 131.6, 130.0, 129.2, 128.3, 128.0, 127.7, 127.0, 126.4, 125.9, 125.7, 124.0, 123.2; LRMS (EI, 70 eV) m/z (%): 262 (M^+, 100), 228 (27), 152 (29); HRMS (ESI) Calcd for $C_{18}H_{15}S^+$ ([M + H]$^+$) 263.0889, Found: 263.0888.

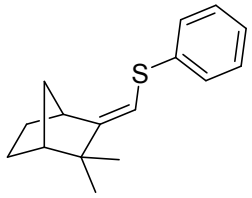


(2,2-diphenylvinyl)(phenyl)sulfane (**22**): Yellow liquid (93.6 mg, 65% yield); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.43-7.39 (m, 4H), 7.36-7.34 (m, 3H), 7.32-7.28 (m, 2H),

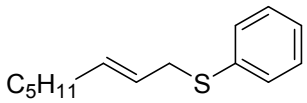
7.26-7.21 (m, 6H), 6.85 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 141.5, 141.1, 139.2, 136.5, 129.7, 129.5, 129.1, 128.4, 128.3, 127.8, 127.3, 127.2, 126.8, 124.1; LRMS (EI, 70 eV) m/z (%): 288 (M^+, 100), 254 (20), 178 (50) ; HRMS (ESI) Calcd for $C_{20}H_{16}SNa^+$ ($[M + Na]^+$) 311.0865, Found: 311.0863.



(E)-phenyl(2-phenylprop-1-en-1-yl)sulfane (**23**): Yellow liquid (38.3 mg, 34% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-7.39 (m, 4H), 7.33-7.28 (m, 4H), 7.24-7.19 (m, 2H), 6.57 (s, 1H), 2.24 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 141.7, 137.2, 136.4, 129.1, 129.0, 128.4, 127.2, 126.4, 125.4, 121.3, 17.7; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (25), 178 (20), 115 (47); HRMS (ESI) Calcd for $C_{15}H_{15}S^+$ ($[M + H]^+$) 227.0889, Found: 227.0889.

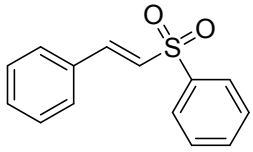


((E)-((1S,4R)-3,3-dimethylbicyclo[2.2.1]heptan-2-ylidene)methyl)(phenyl)sulfane (**24**)[4]: Yellow liquid (68.3 mg, 56% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 4H), 7.13-7.10 (m, 1H), 5.69 (s, 1H), 3.24-3.21 (m, 1H), 2.01-1.97 (s, 1H), 1.75-1.68 (m, 3H), 1.46-1.41 (m, 1H), 1.31-1.26 (m, 2H), 1.12 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 164.9, 138.3, 128.7, 127.2, 125.1, 106.2, 48.3, 43.5, 37.3, 28.9, 27.7, 25.8, 23.7; LRMS (EI, 70 eV) m/z (%): 244 (M^+, 100), 229 (63), 201 (70), 135 (44), 107 (56); HRMS (ESI) Calcd for $C_{16}H_{21}S^+$ ($[M + H]^+$) 245.1358, Found: 245.1360.



(E)-oct-2-en-1-yl(phenyl)sulfane (**26**): Yellow liquid (22.0 mg, 40% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-7.32 (m, 2H), 7.28-7.25 (m, 2H), 7.17 (t, J = 7.0 Hz, 1H),

5.56-5.45 (m, 2H), 3.51 (d, J = 6.0 Hz, 2H), 1.99-1.95 (m, 2H), 1.31-1.24 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 136.2, 134.6, 129.8, 128.7, 126.0, 124.8, 36.5, 32.2, 31.2, 28.8, 22.5, 14.0; LRMS (EI, 70 eV) m/z (%): 220 (M^+, 24), 110 (100), 69 (50), 55 (25); HRMS (ESI) Calcd for $C_{14}H_{20}SNa^+$ ([M + Na]$^+$) 243.1178, Found: 243.1169.



(E)-(2-(phenylsulfonyl)vinyl)benzene (27) [5]: Yellow solid (175.7 mg, 72% yield), m.p. 71-73^{o}C; 1H NMR (500 MHz, $CDCl_3$) δ 7.96-7.95 (m, 2H), 7.69 (d, J = 15.5 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.49-7.48 (m, 2H), 7.41-7.39 (m, 2H), 6.86 (d, J = 15.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 142.5, 140.8, 137.4, 133.3, 131.2, 129.3, 129.1, 128.6, 127.7, 127.4; LRMS (EI, 70 eV) m/z (%): 244 (M^+, 22), 179 (18), 119 (62), 103 (54), 102 (85), 91 (100), 77 (78).

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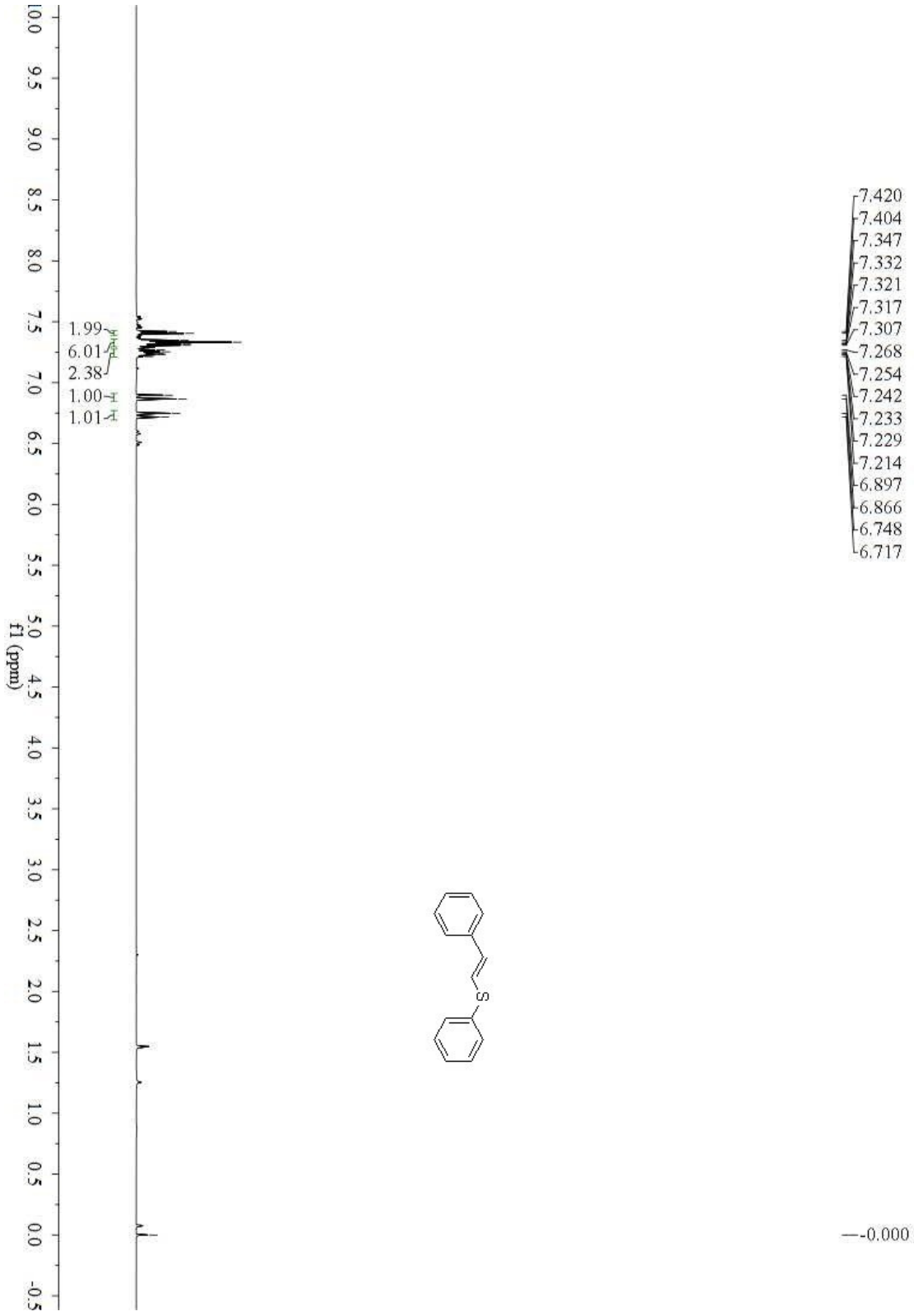
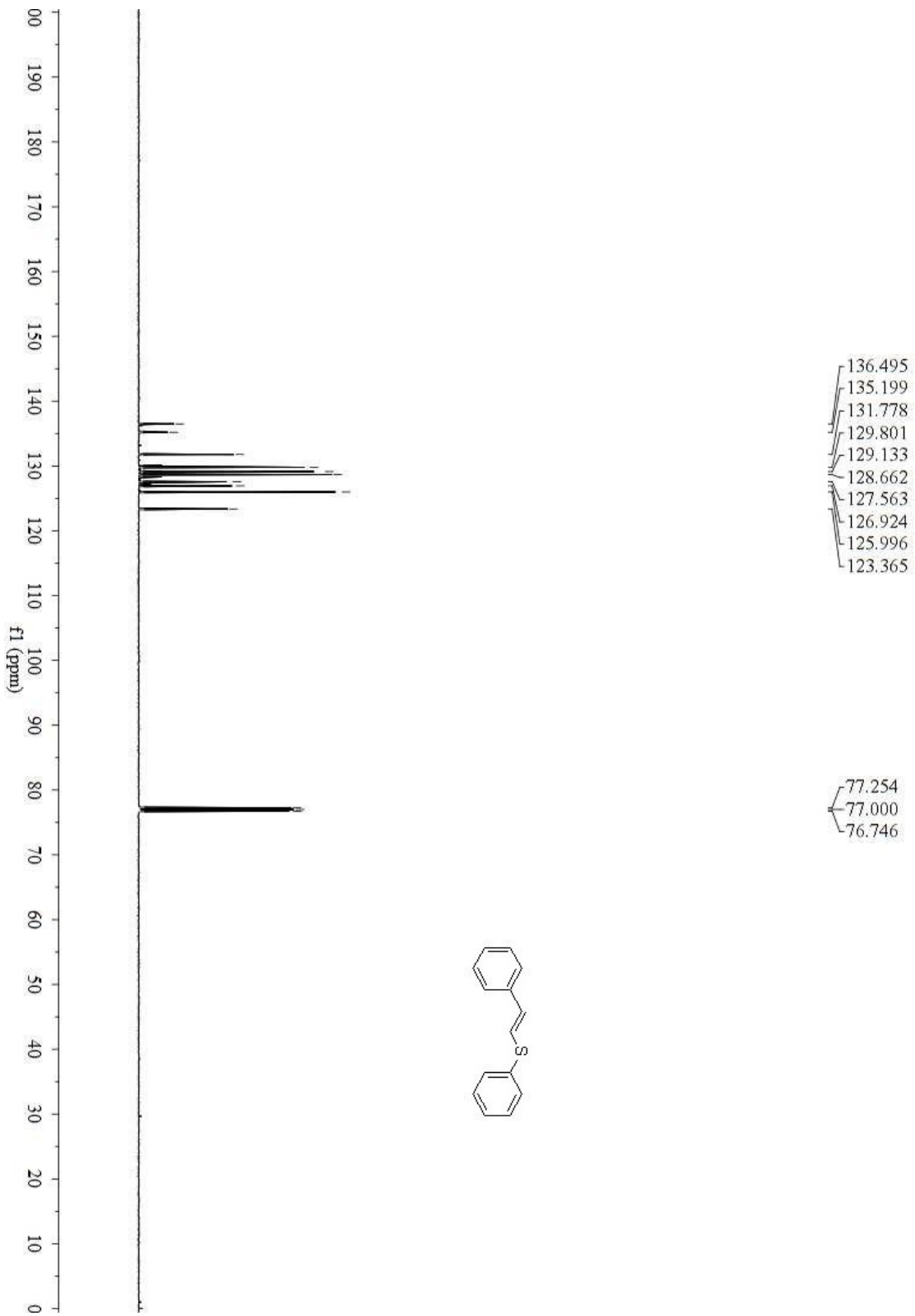
7. NMR Spectra for All Compounds.

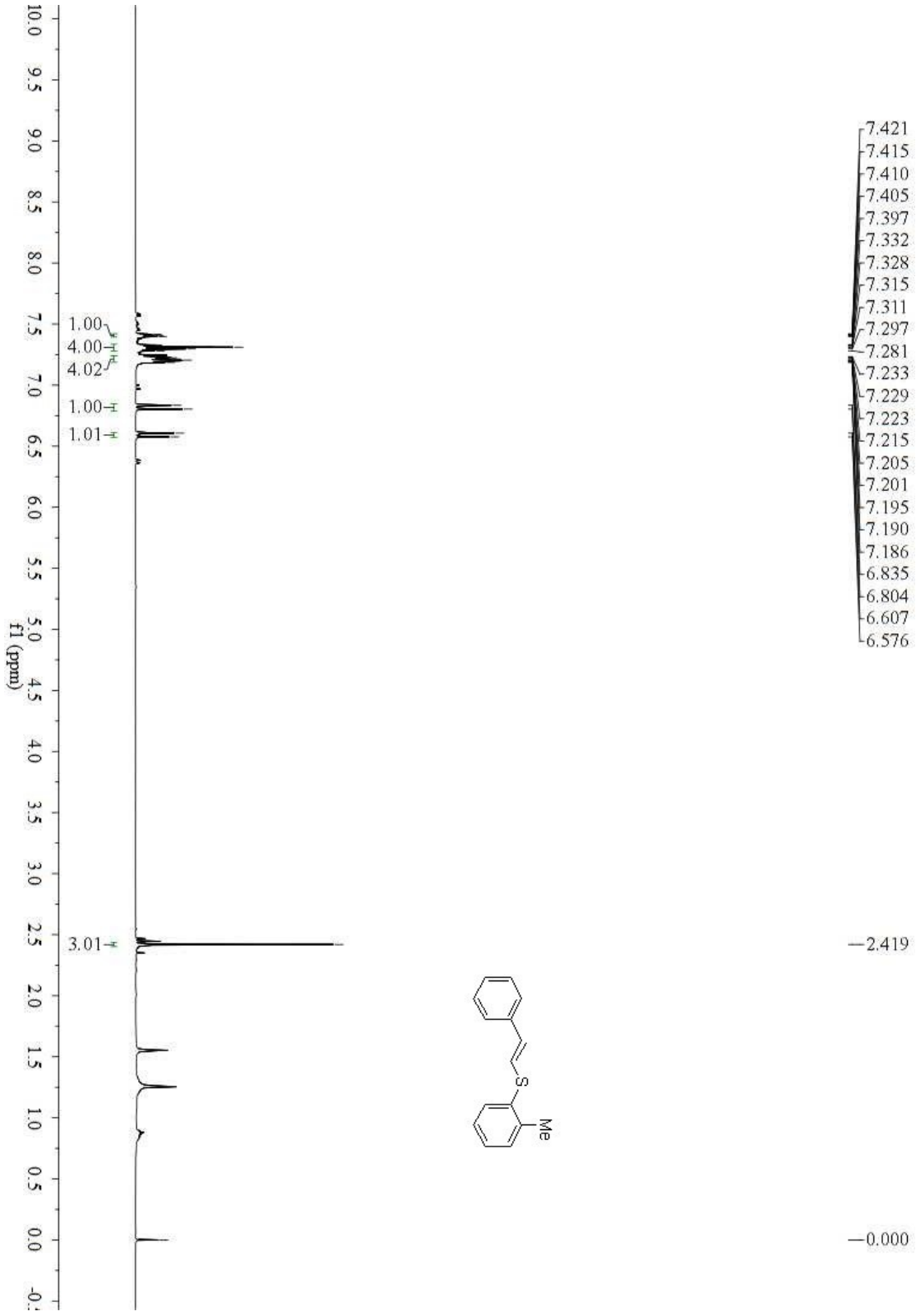
^{1}H NMR: (E)-phenyl(styryl)sulfane (3)



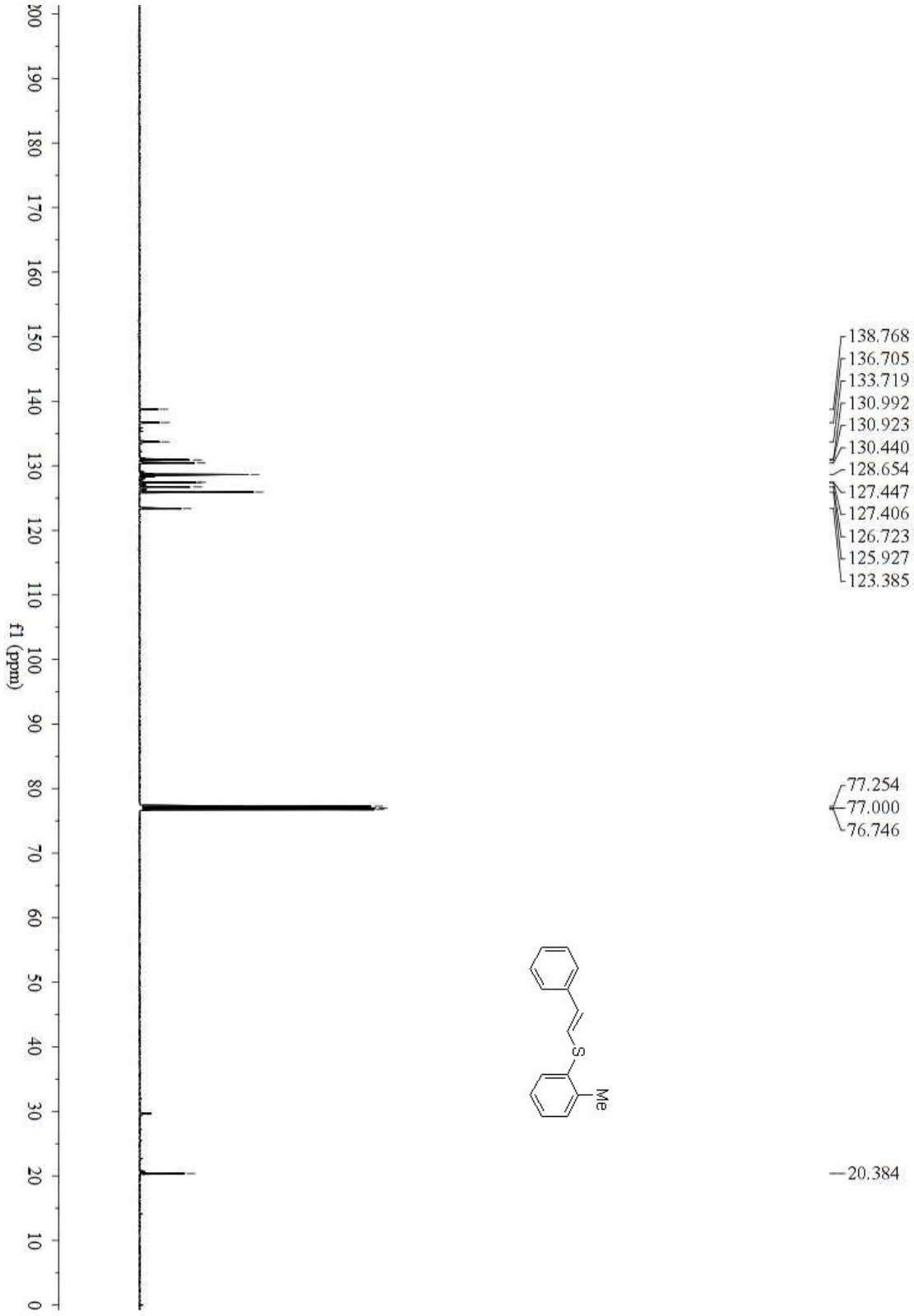
^{13}C NMR: (E)-phenyl(styryl)sulfane (3)



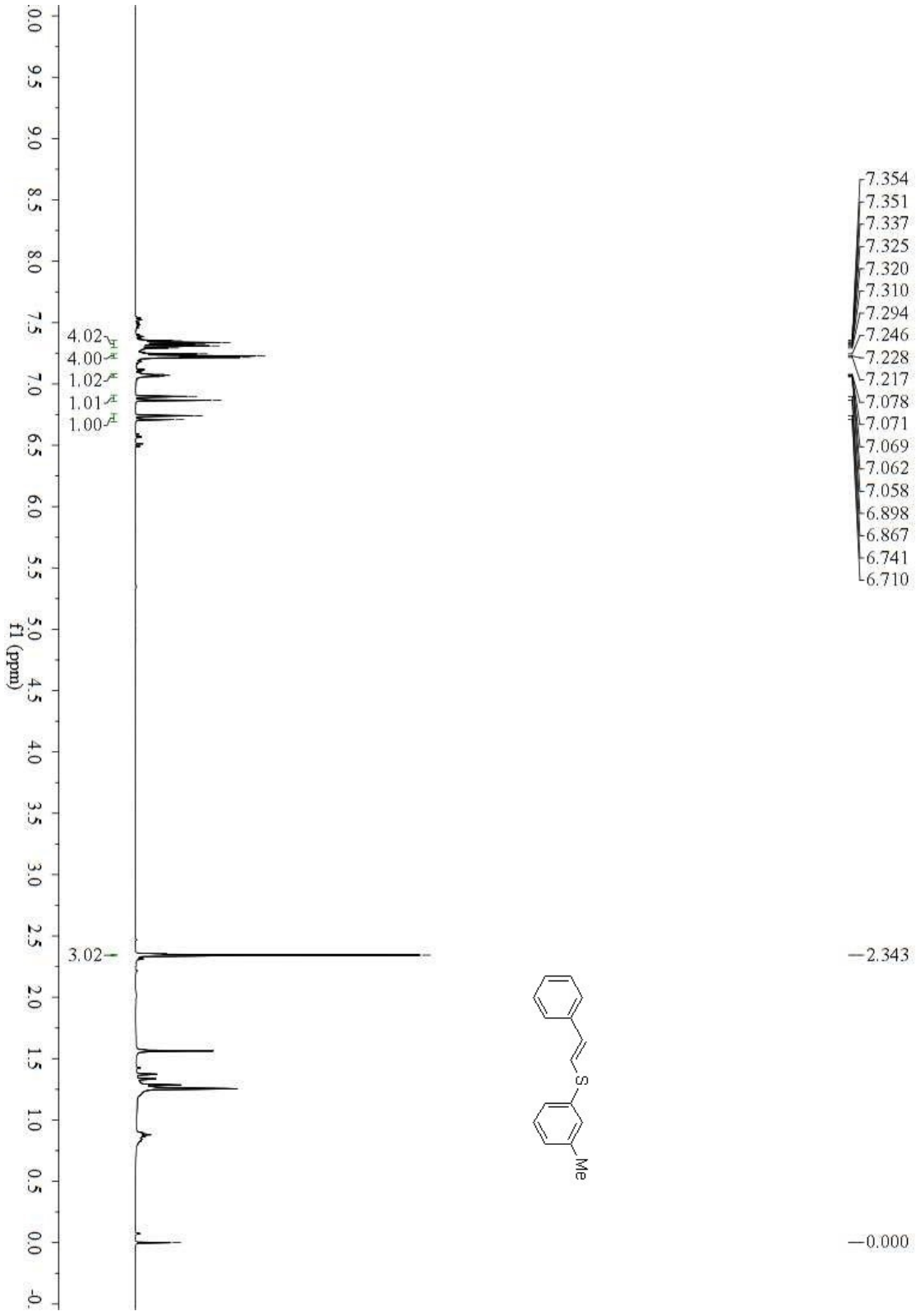
^{1}H NMR: (E)-styryl(o-tolyl)sulfane (4)



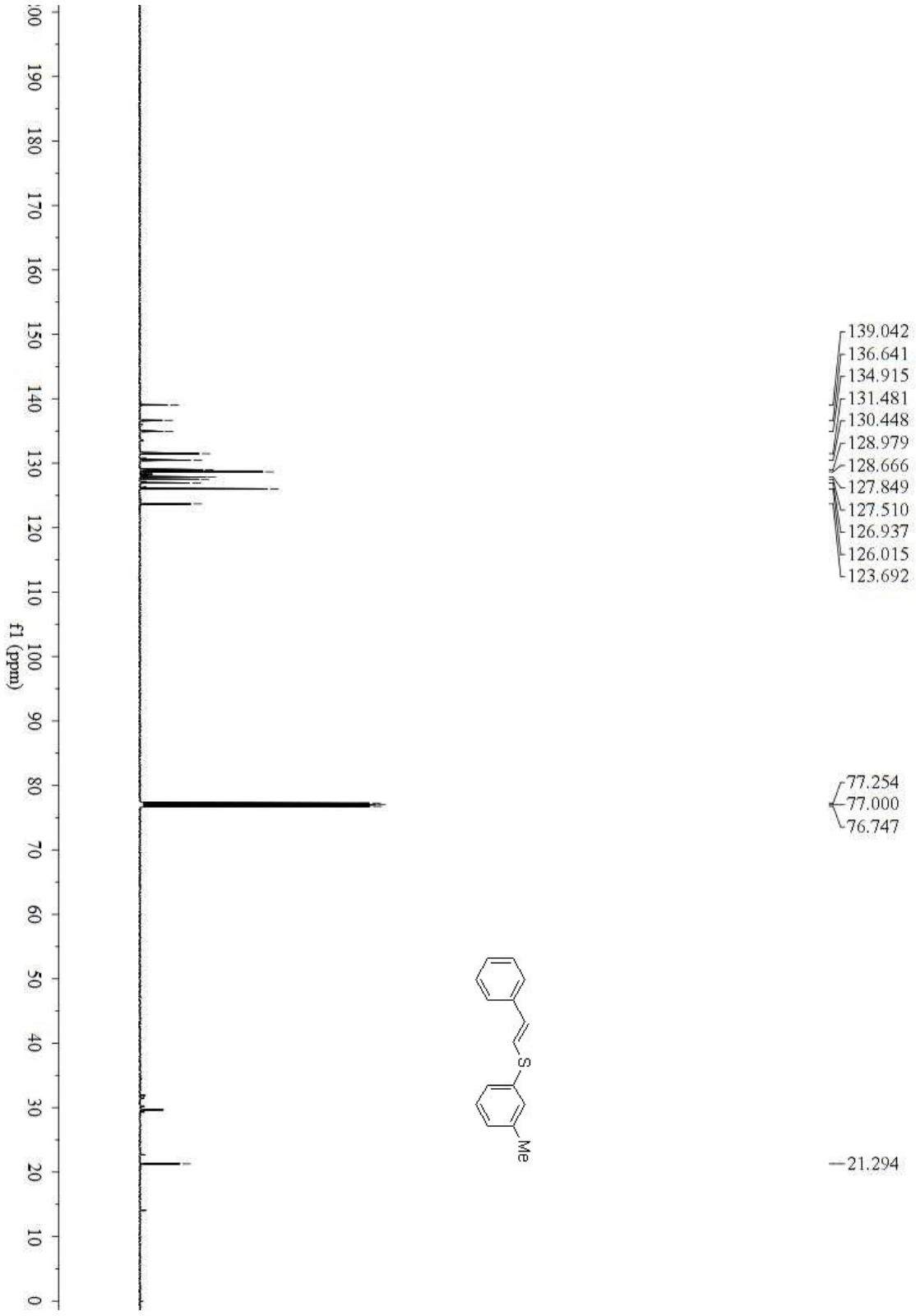
^{13}C NMR: (E)-styryl(o-tolyl)sulfane (4)



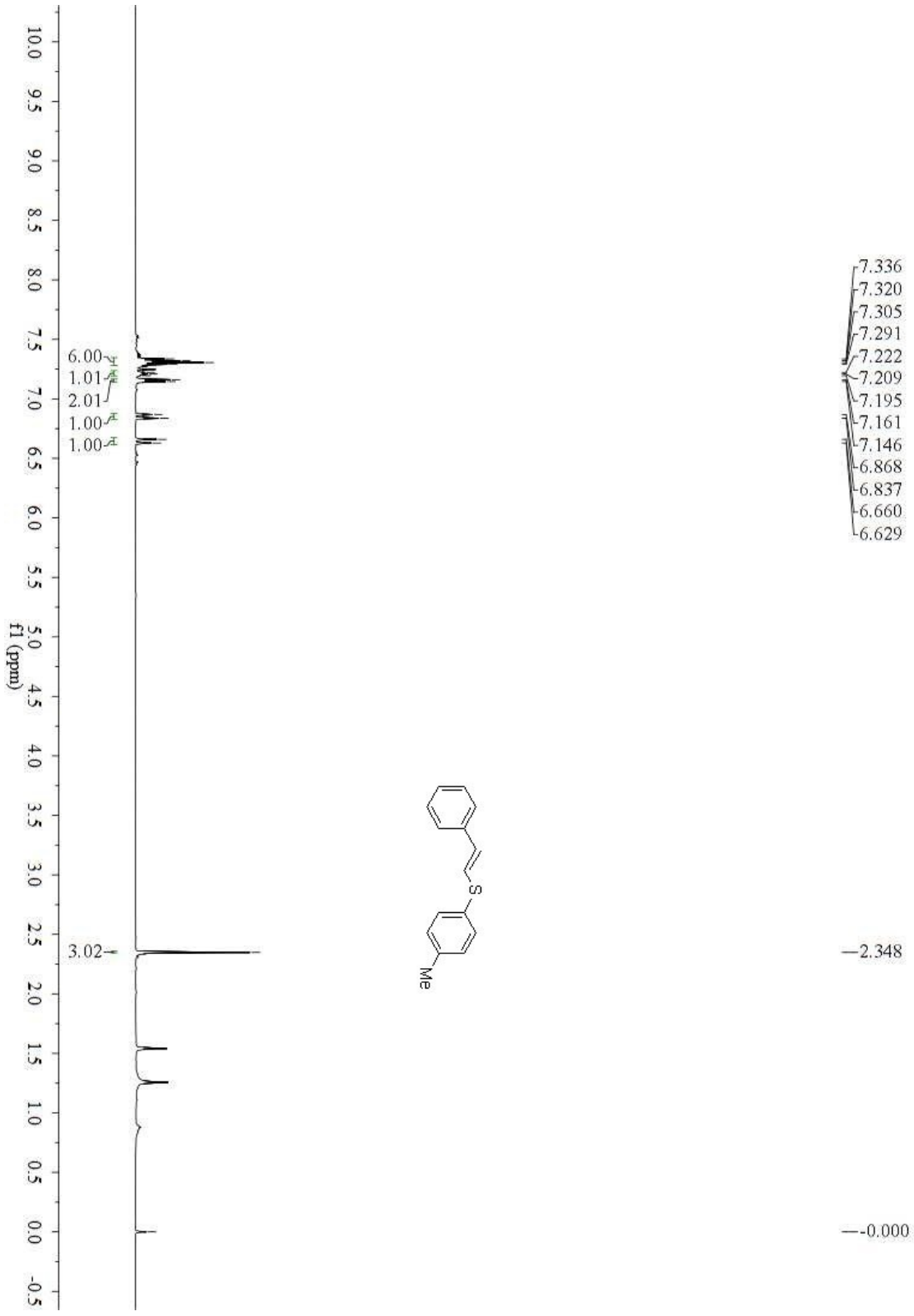
^{1}H NMR: (E)-styryl(m-tolyl)sulfane (5)



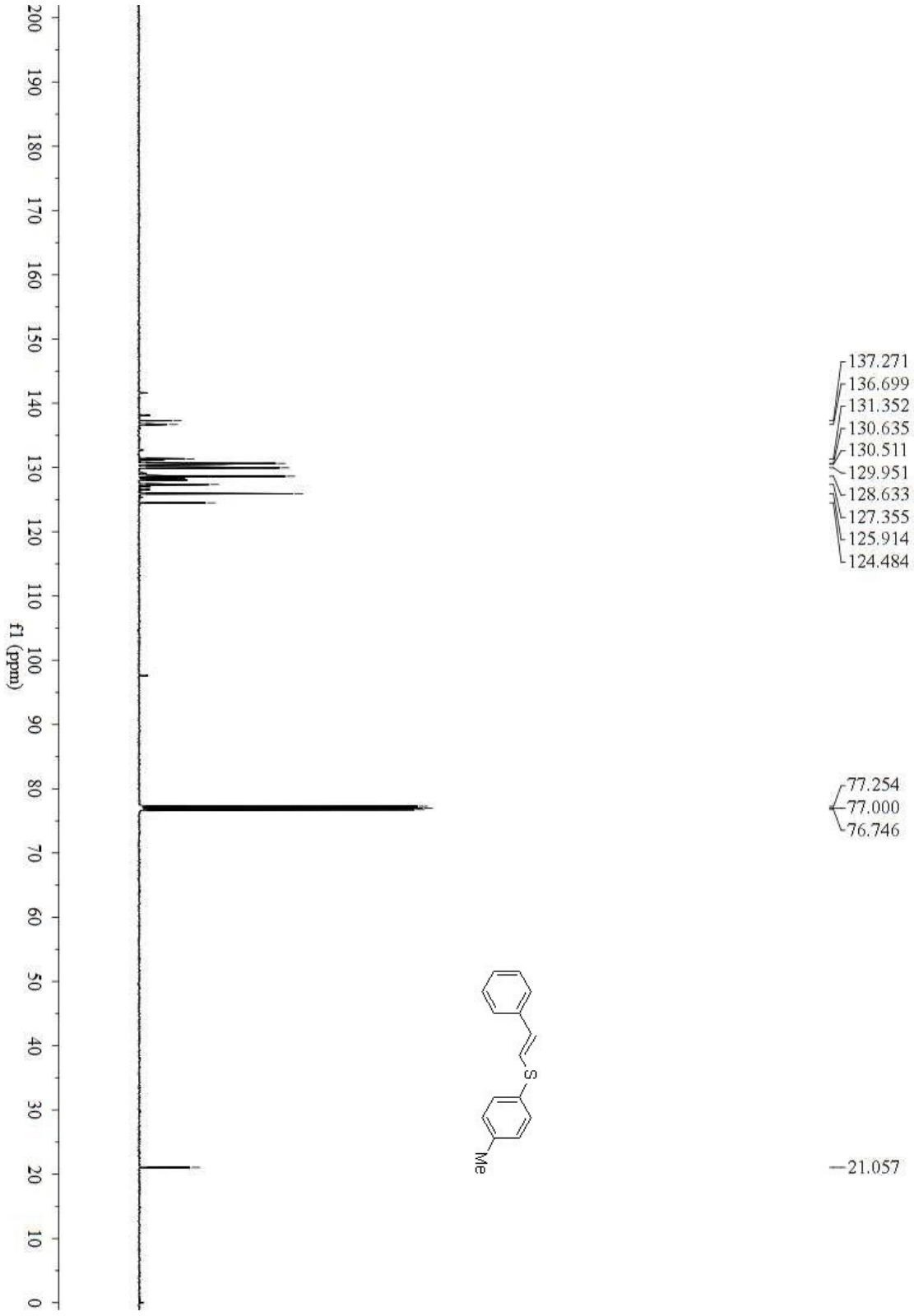
^{13} C NMR: (E)-styryl(m-tolyl)sulfane (5)



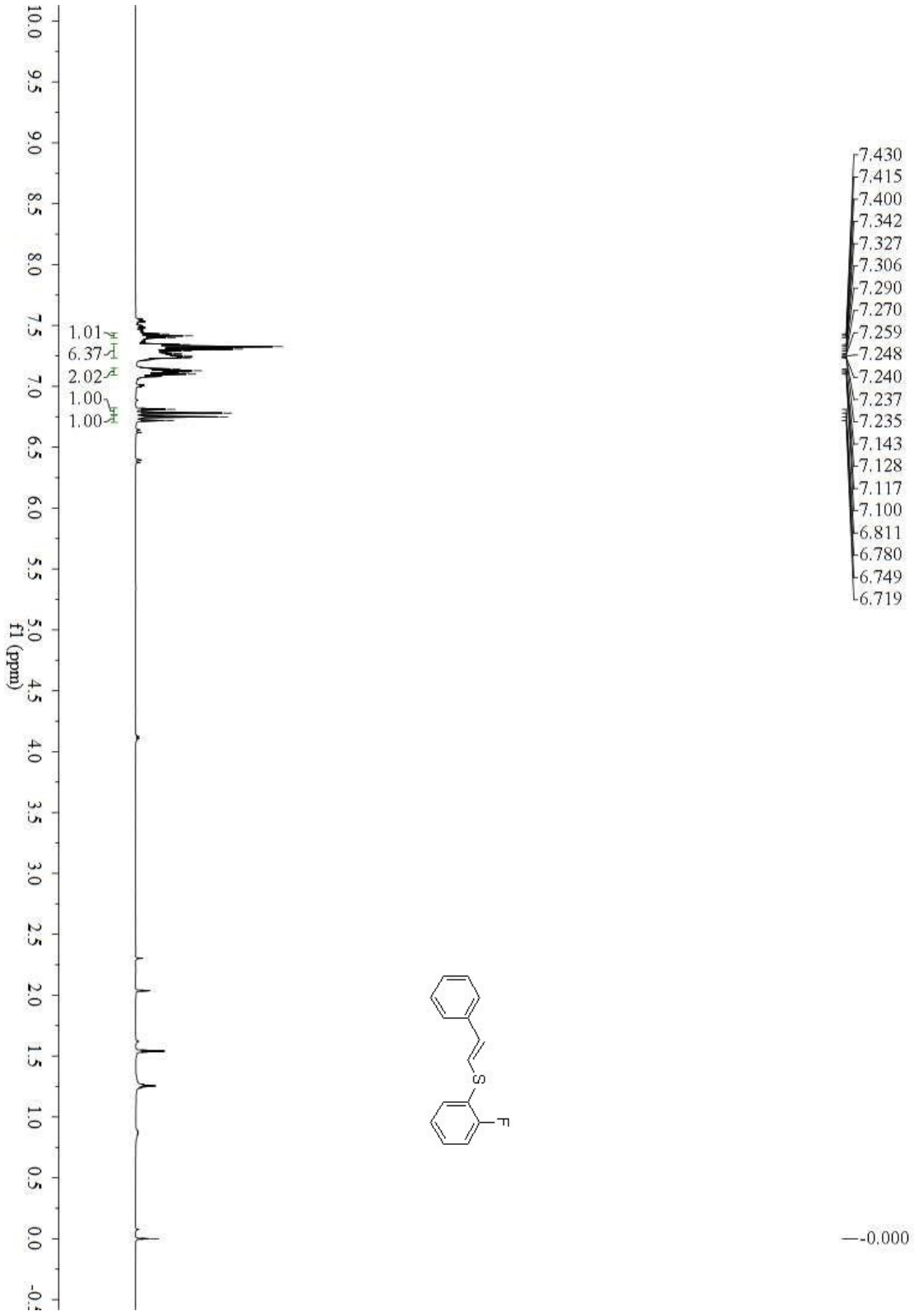
^{1}H NMR: (E)-styryl(p-tolyl)sulfane (6)



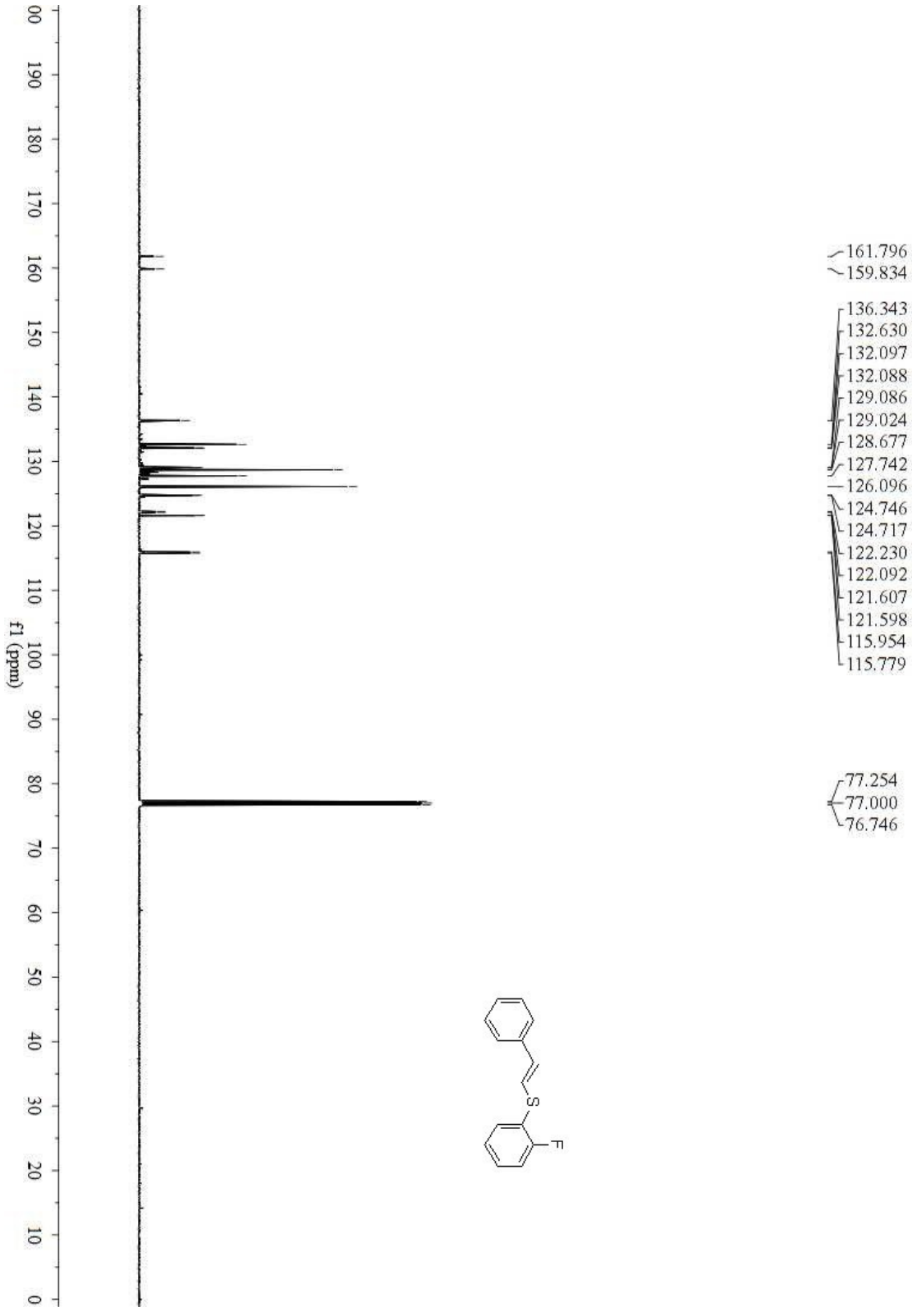
^{13}C NMR: (E)-styryl(p-tolyl)sulfane (6)



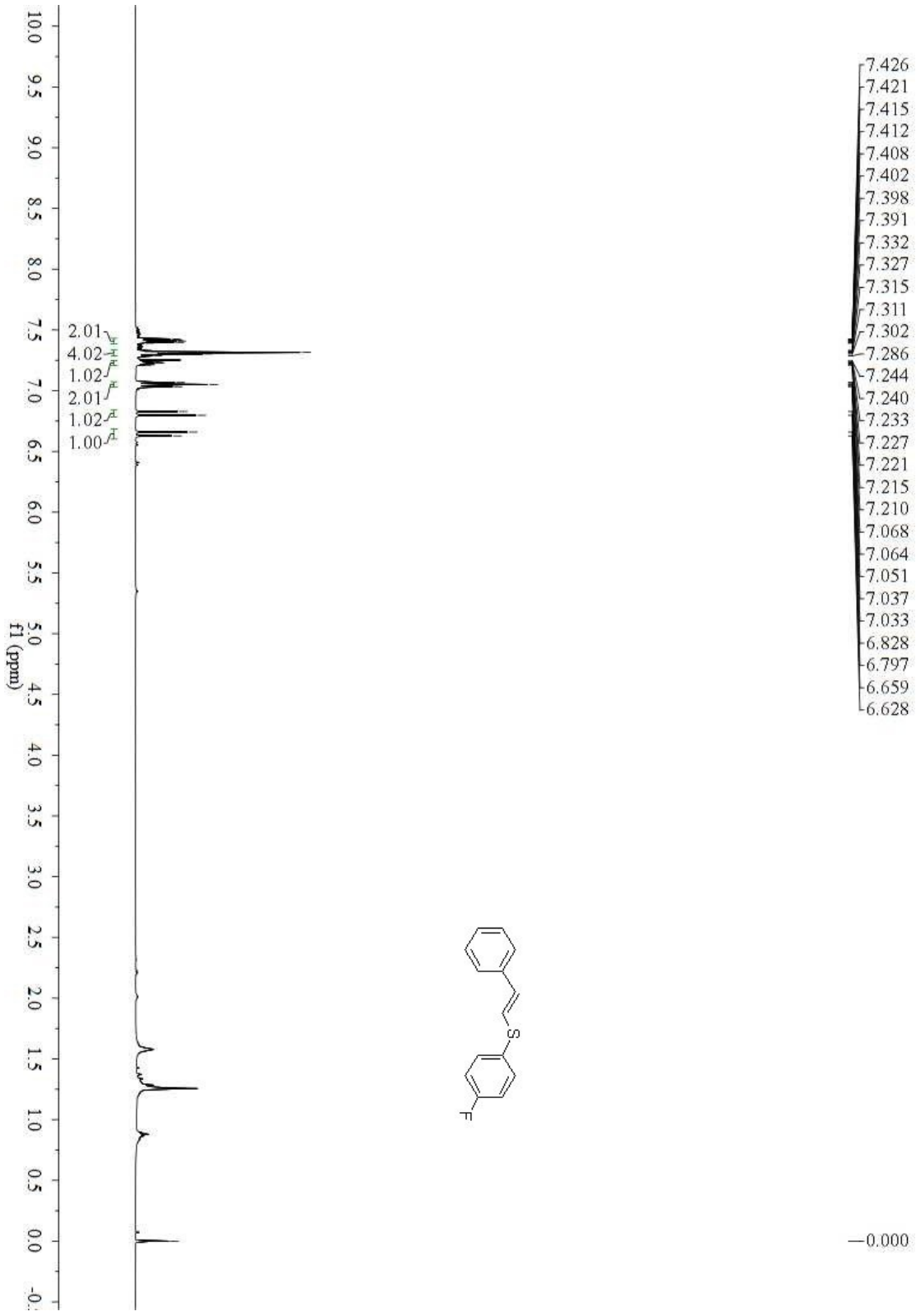
^{1}H NMR: (E)-(2-fluorophenyl)(styryl)sulfane (7)



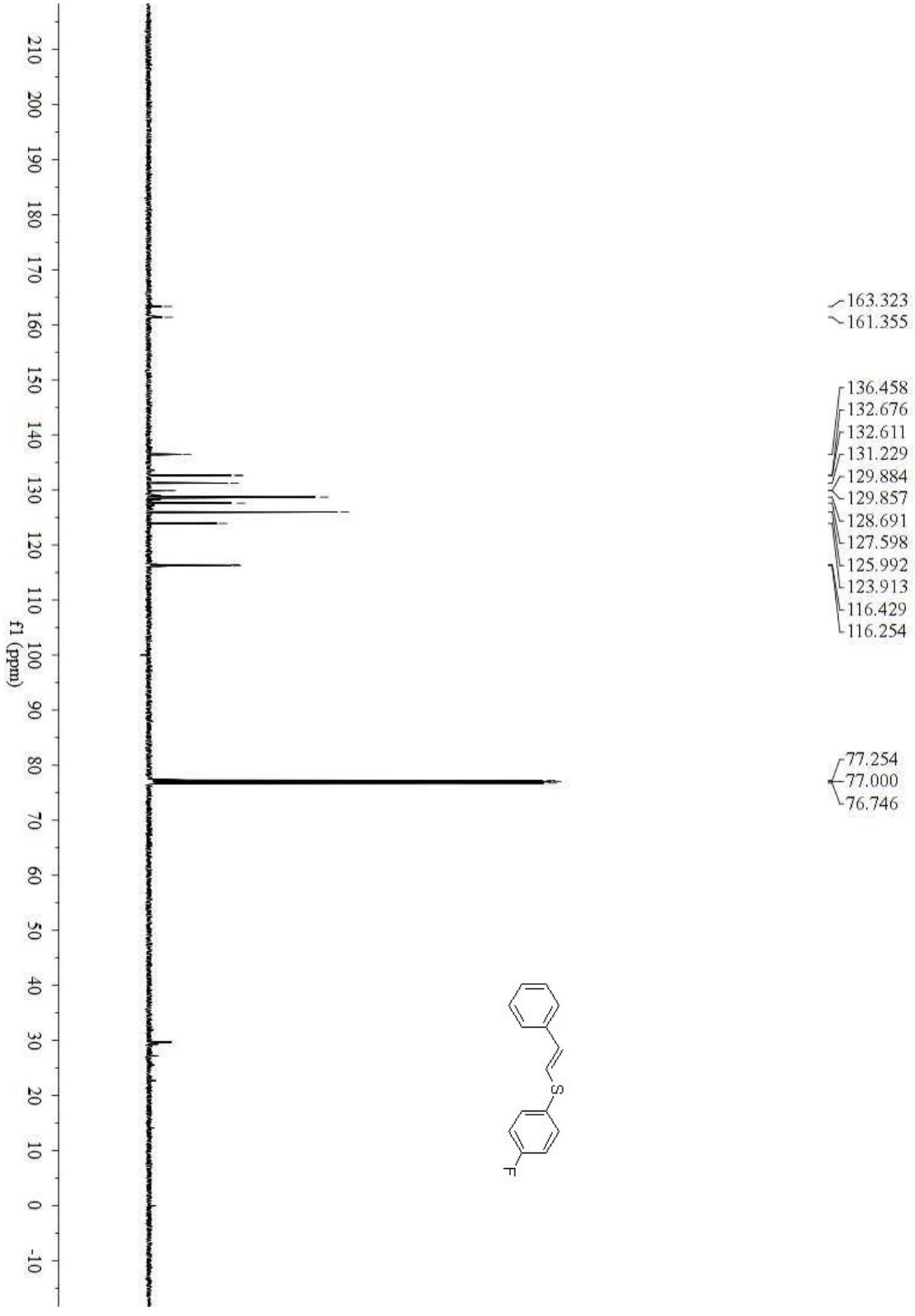
^{13} C NMR: (E)-(2-fluorophenyl)(styryl)sulfane (7)



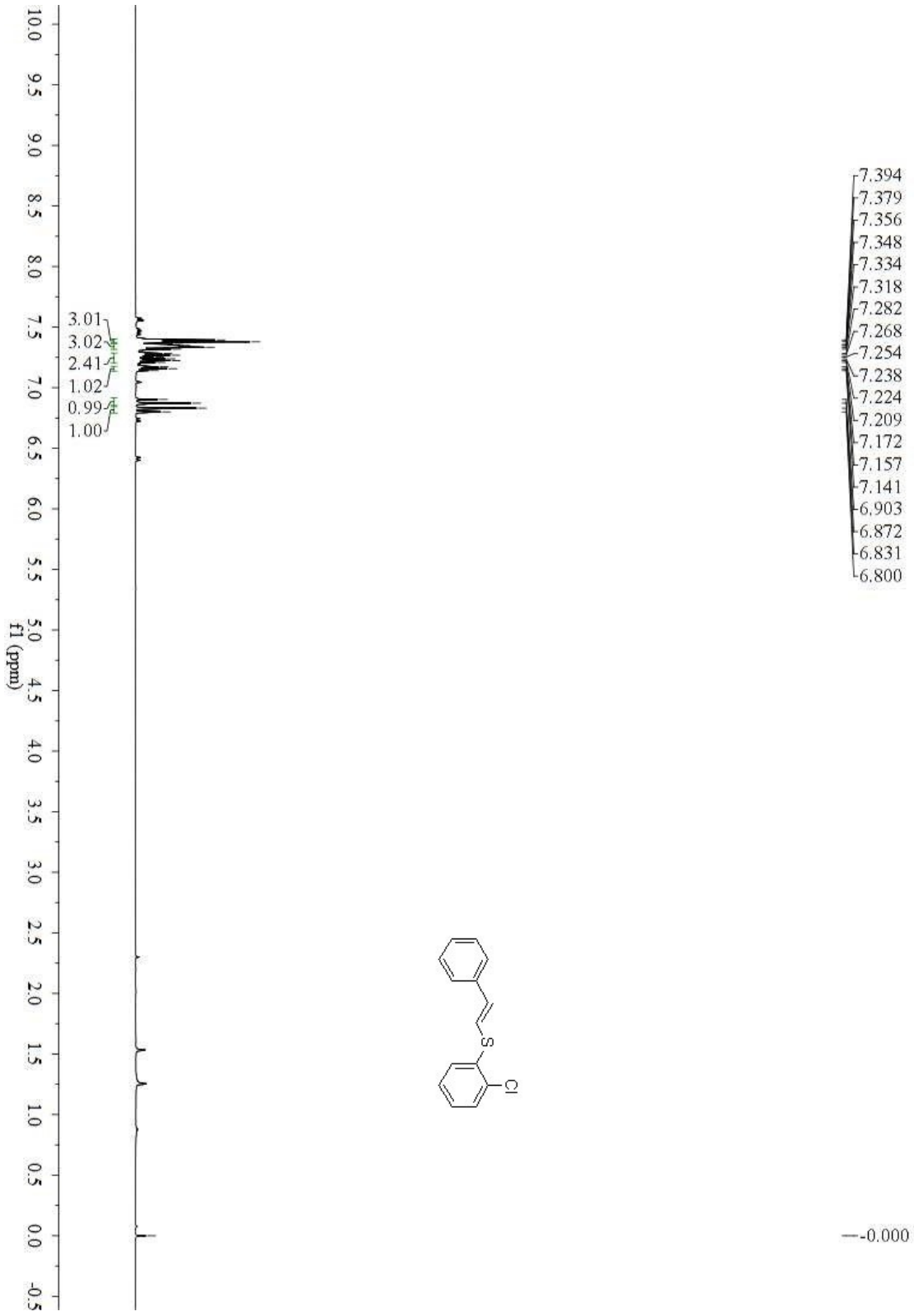
^{1}H NMR: (E)-(4-fluorophenyl)(styryl)sulfane (8)



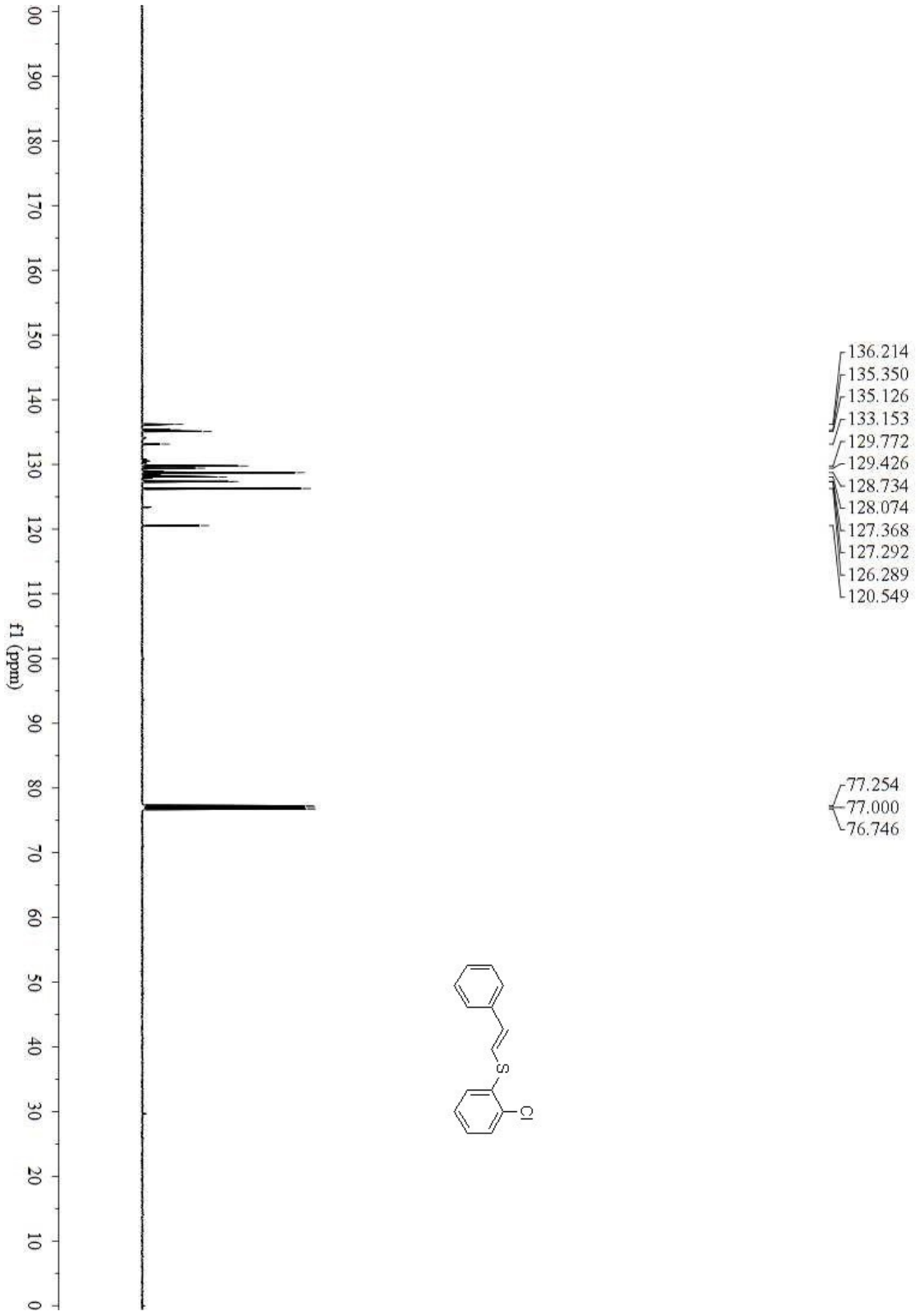
^{13}C NMR: (E)-(4-fluorophenyl)(styryl)sulfane (8)



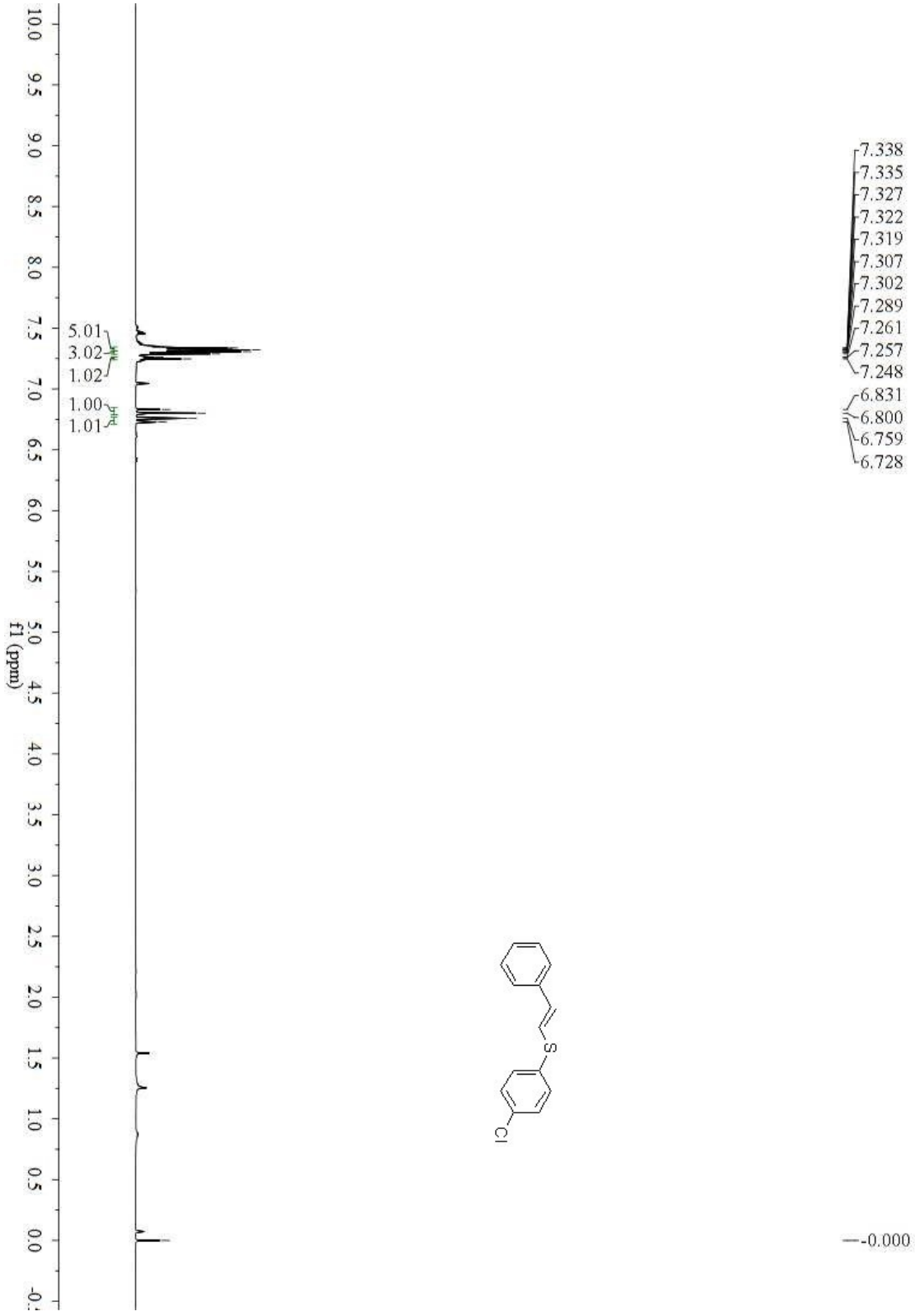
^{1}H NMR: (E)-(2-chlorophenyl)(styryl)sulfane (9)



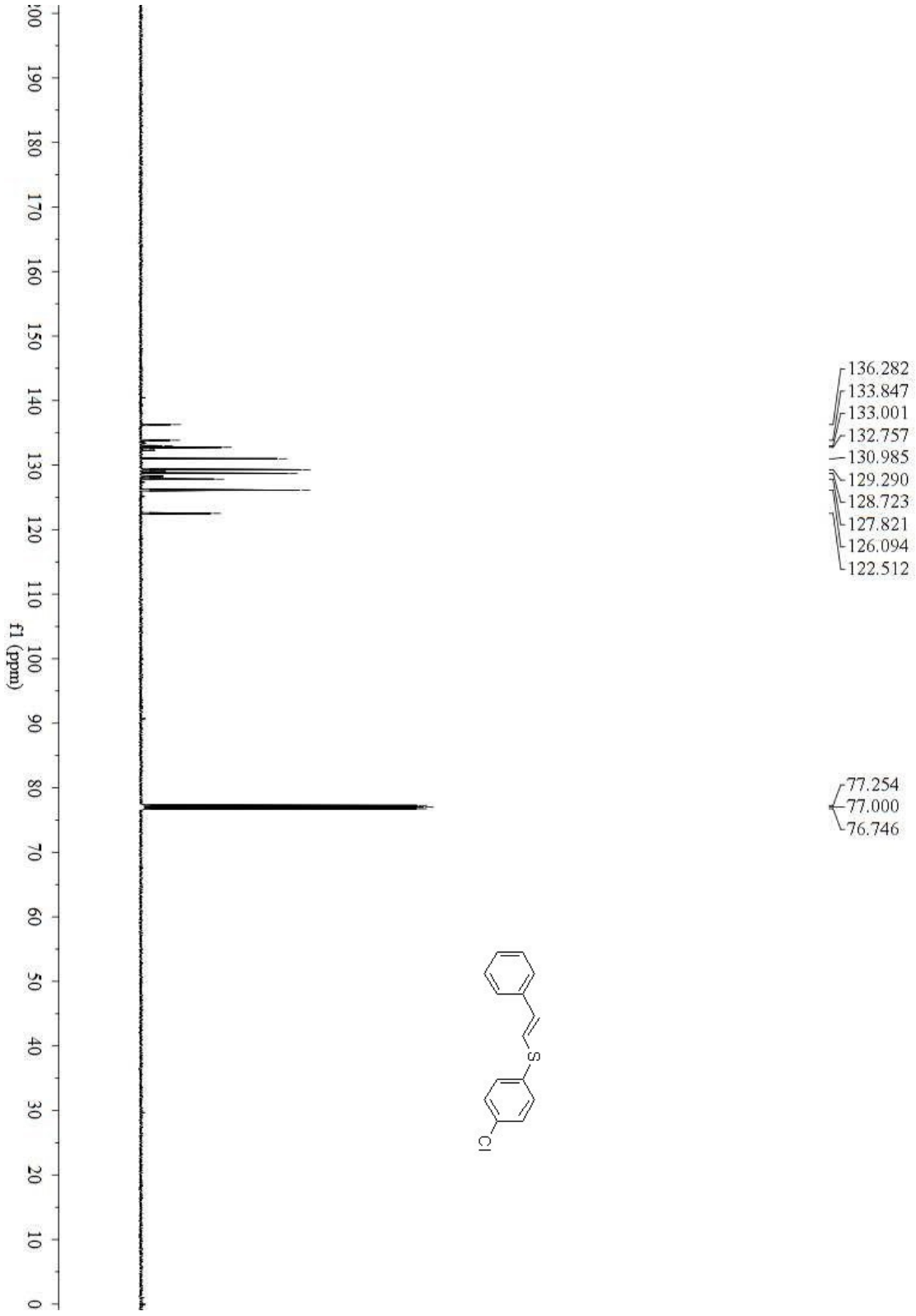
^{13}C NMR: (E)-(2-chlorophenyl)(styryl)sulfane (9)



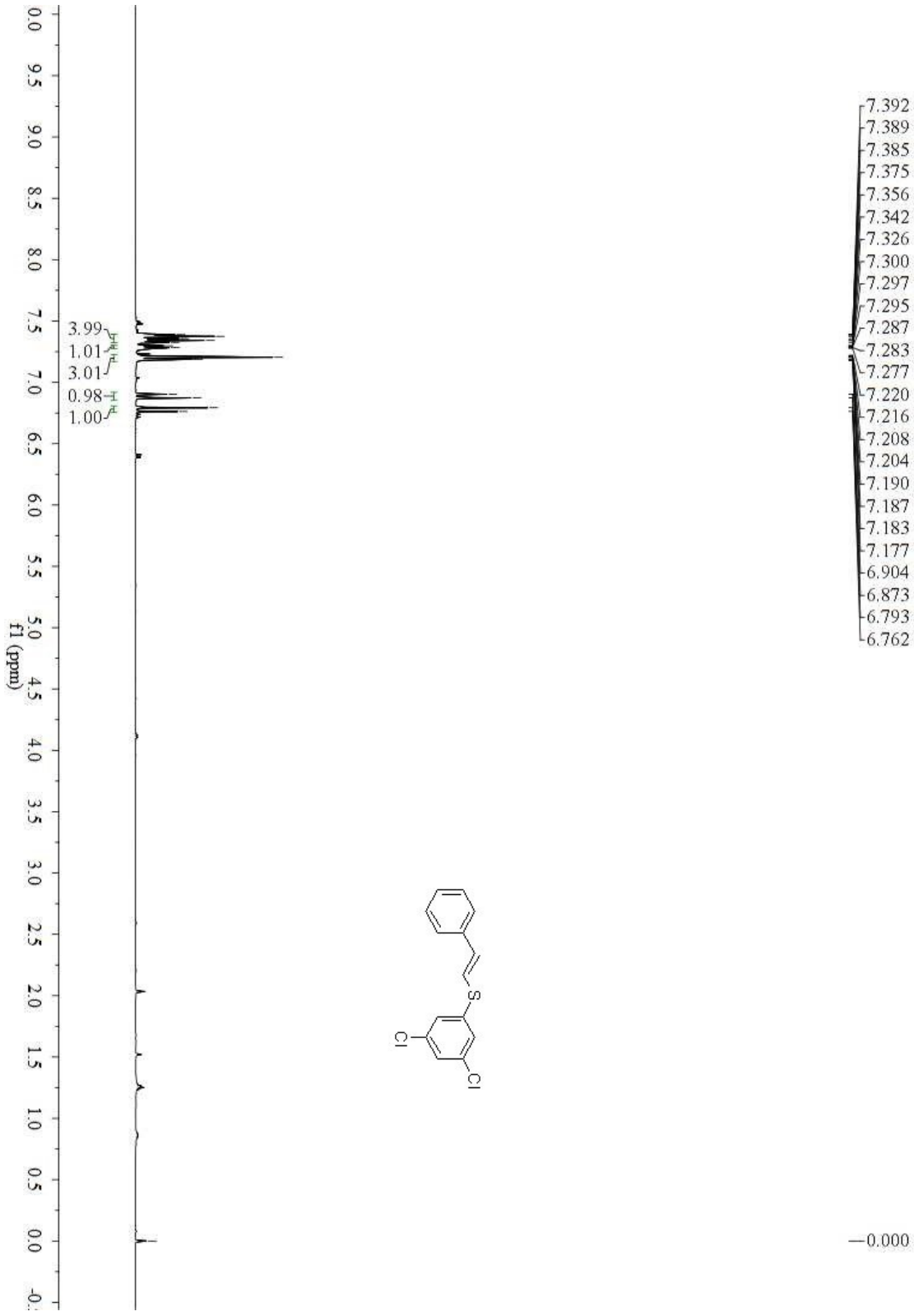
^{1}H NMR: (E)-(4-chlorophenyl)(styryl)sulfane (10)



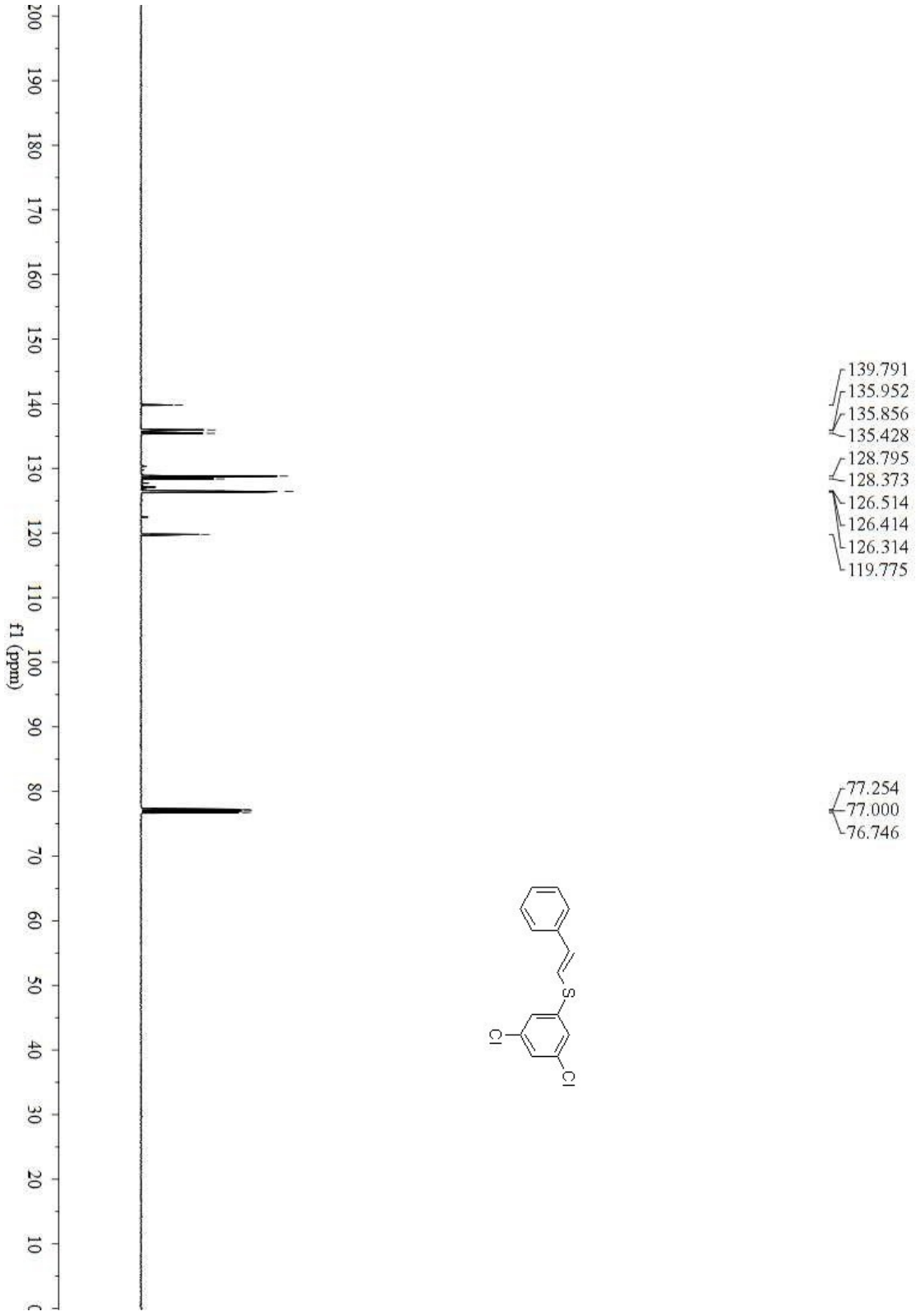
^{13}C NMR: (E)-(4-chlorophenyl)(styryl)sulfane (10)



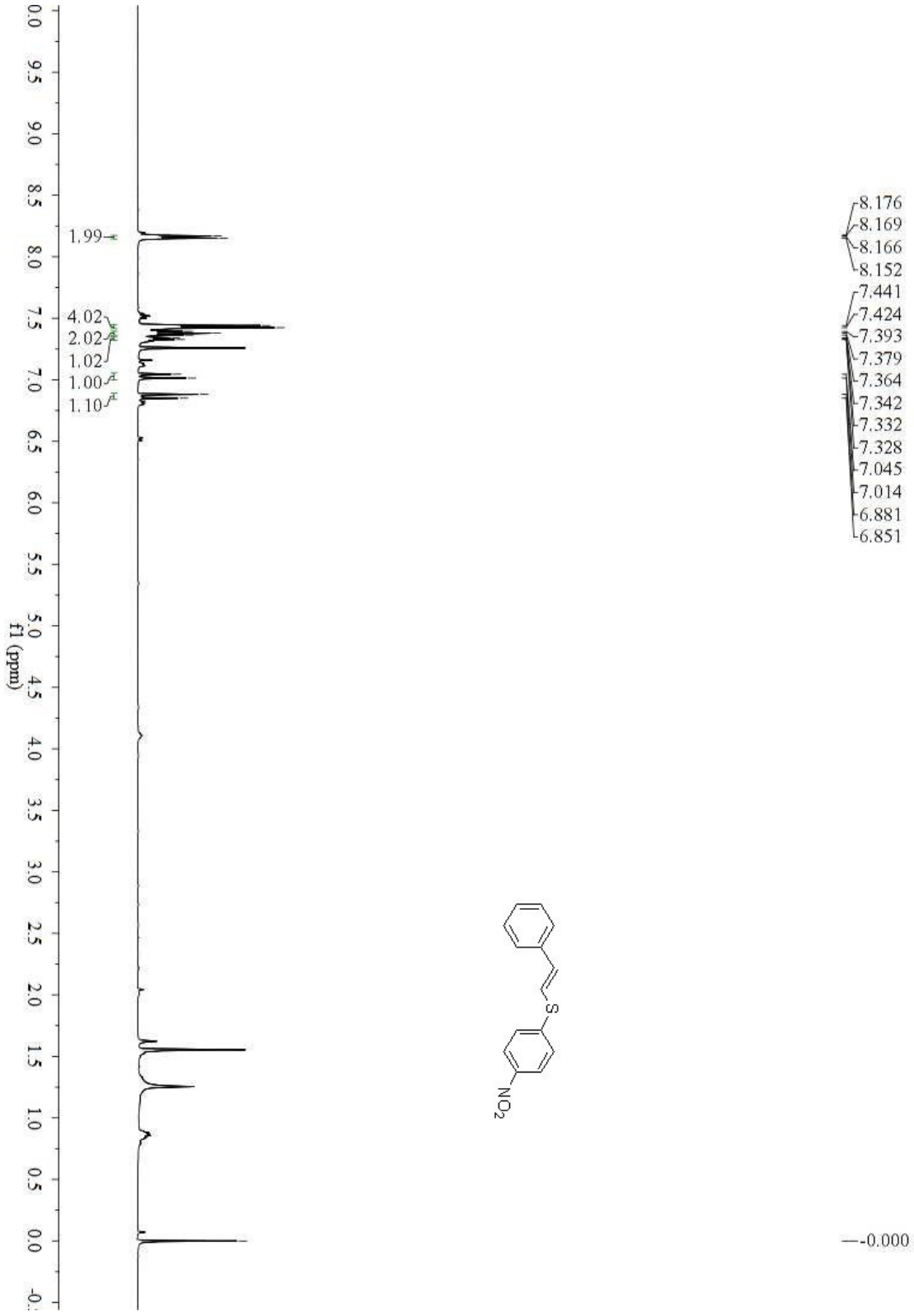
^{1}H NMR: (E)-(3,5-dichlorophenyl)(styryl)sulfane (11)



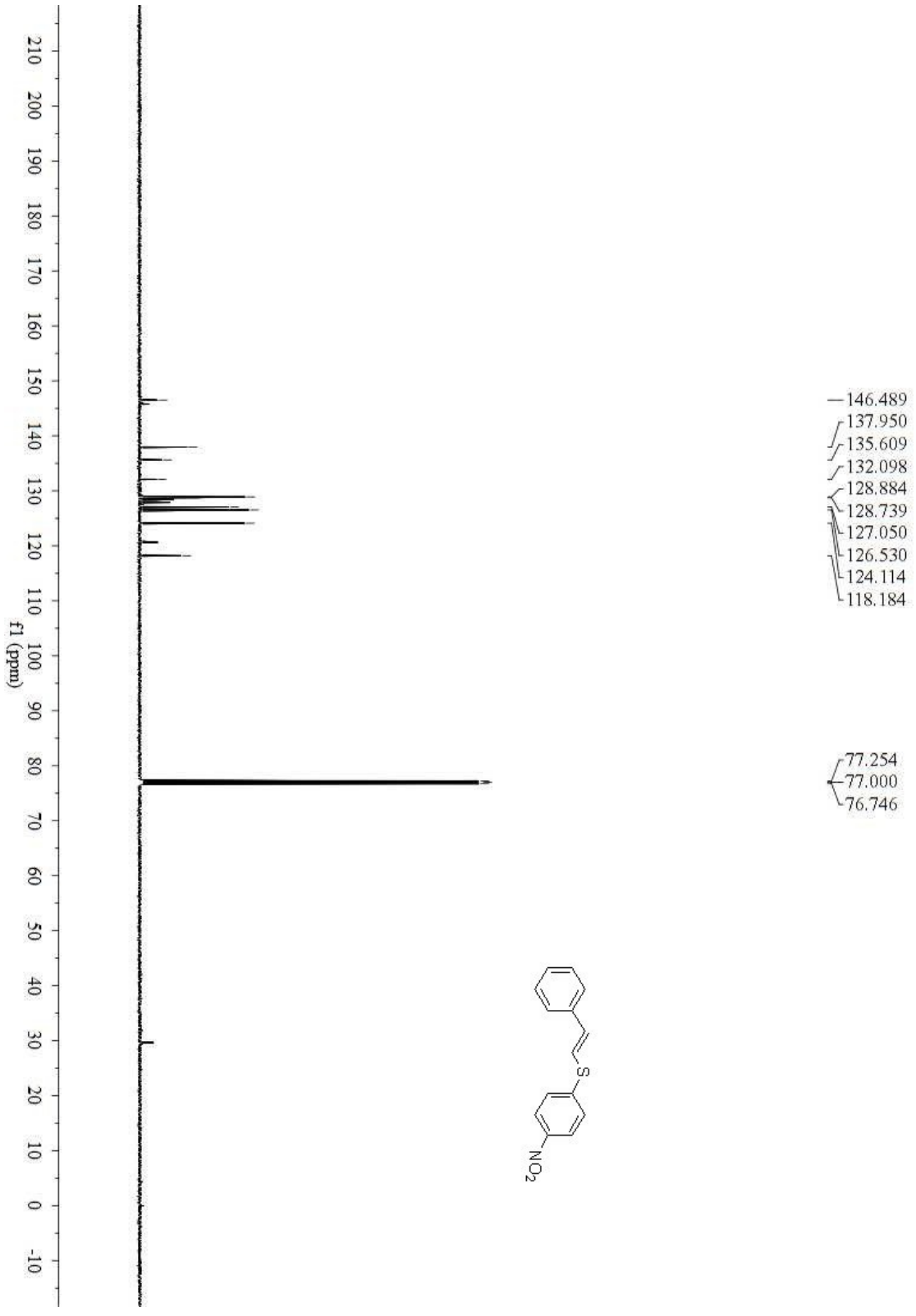
^{13}C NMR: (E)-(3,5-dichlorophenyl)(styryl)sulfane (11)



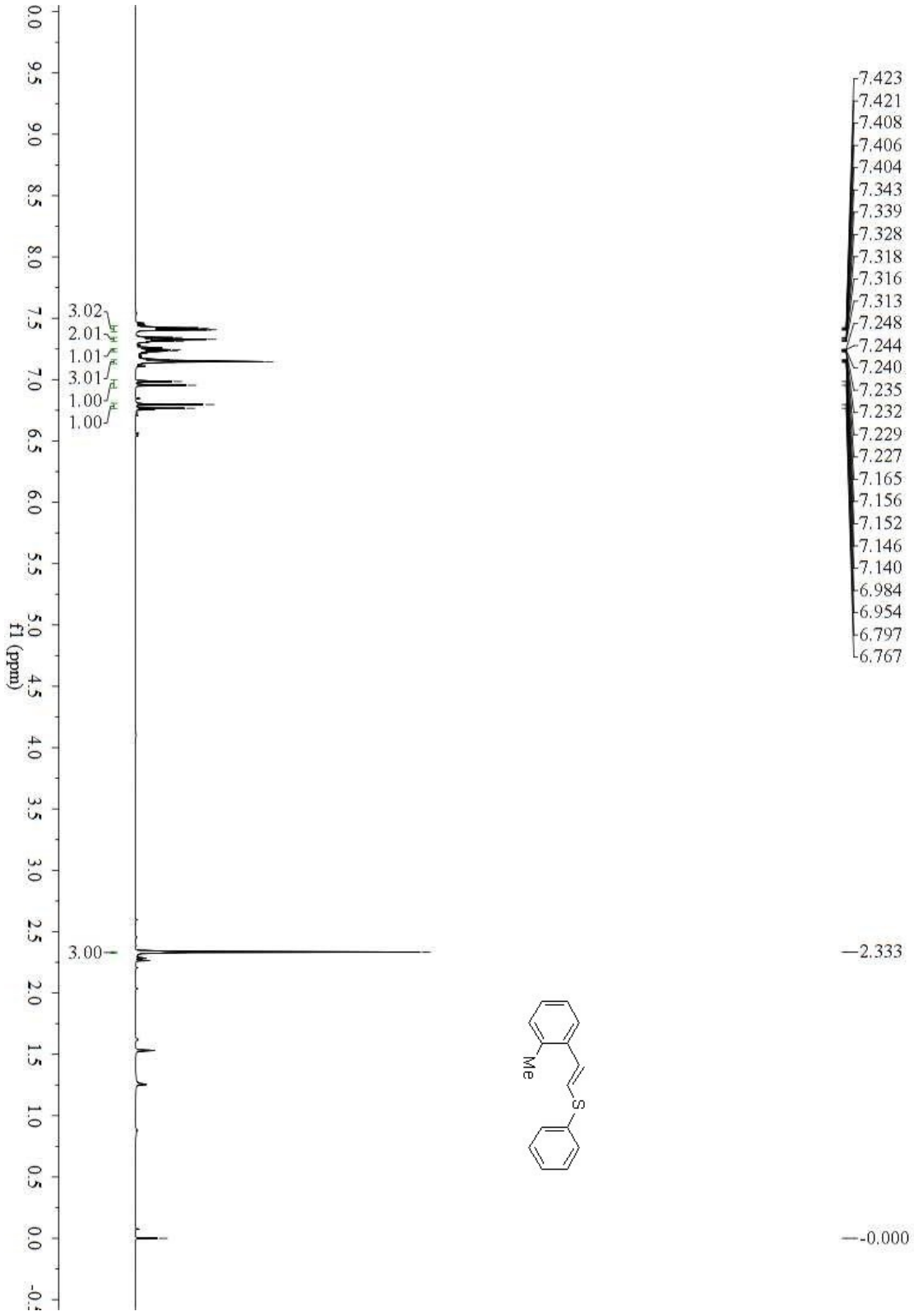
^{1}H NMR: (E)-(4-nitrophenyl)(styryl)sulfane (12)



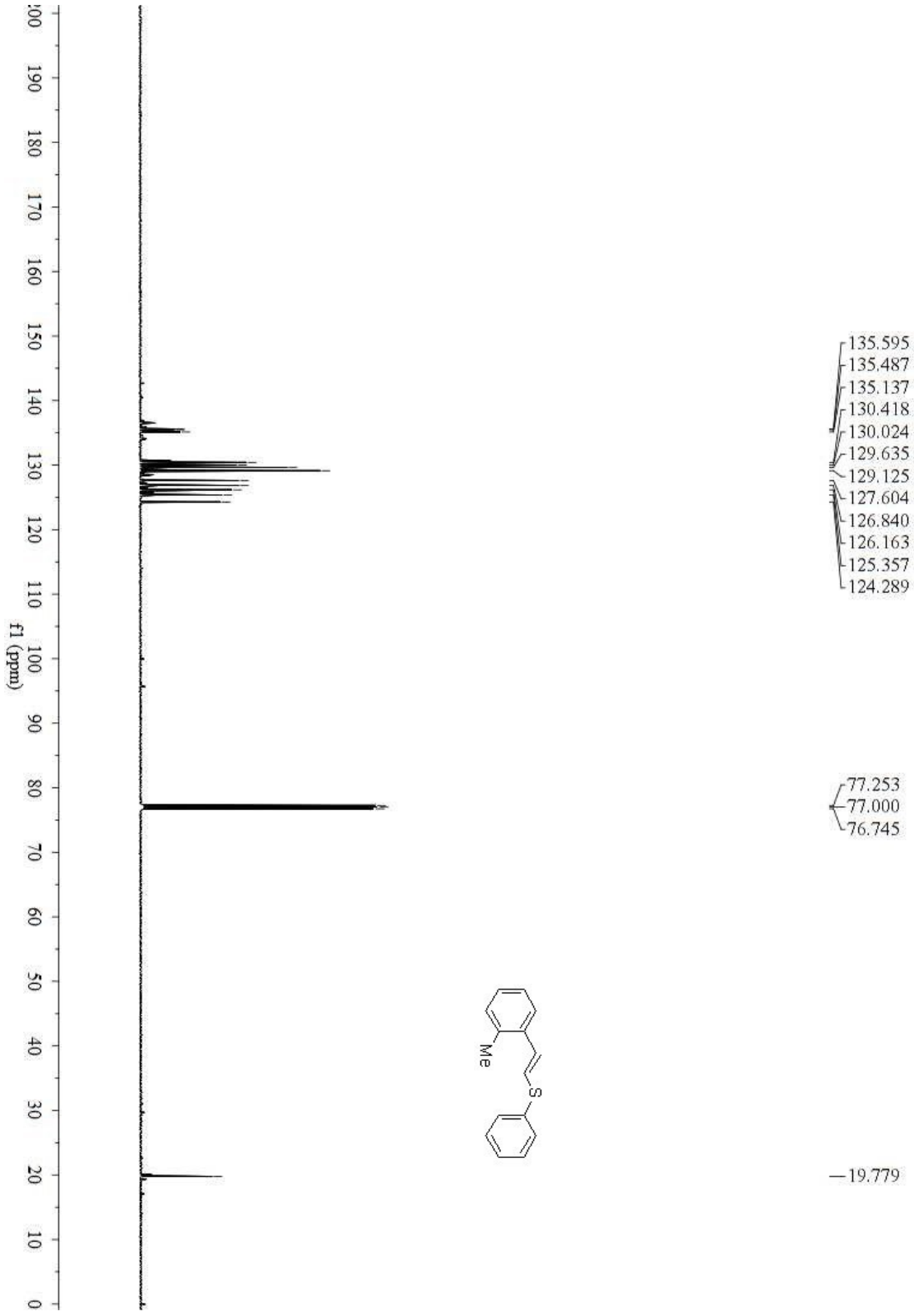
^{13}C NMR: (E)-(4-nitrophenyl)(styryl)sulfane (12)



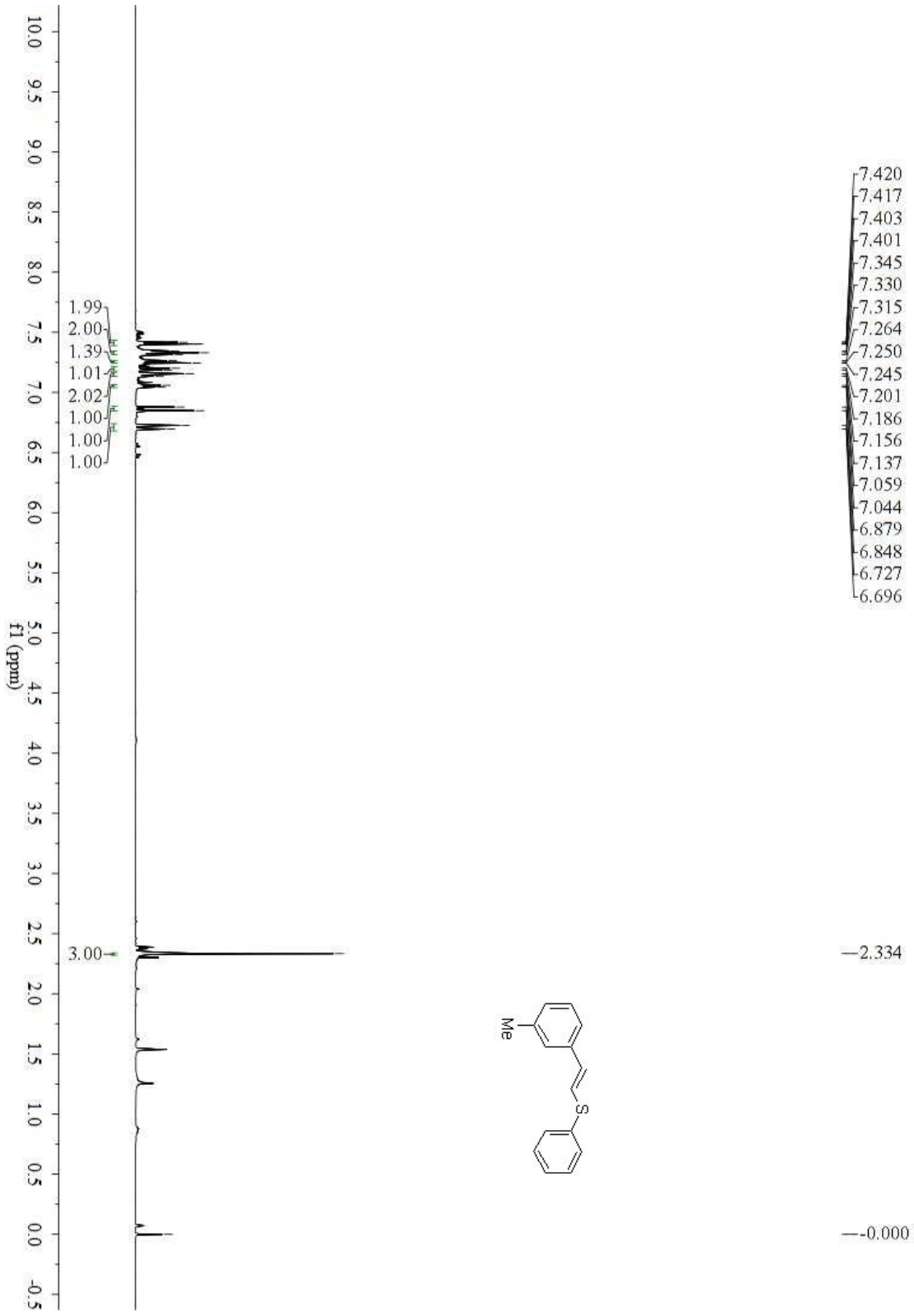
^{1}H NMR: (E)-(2-methylstyryl)(phenyl)sulfane (13)



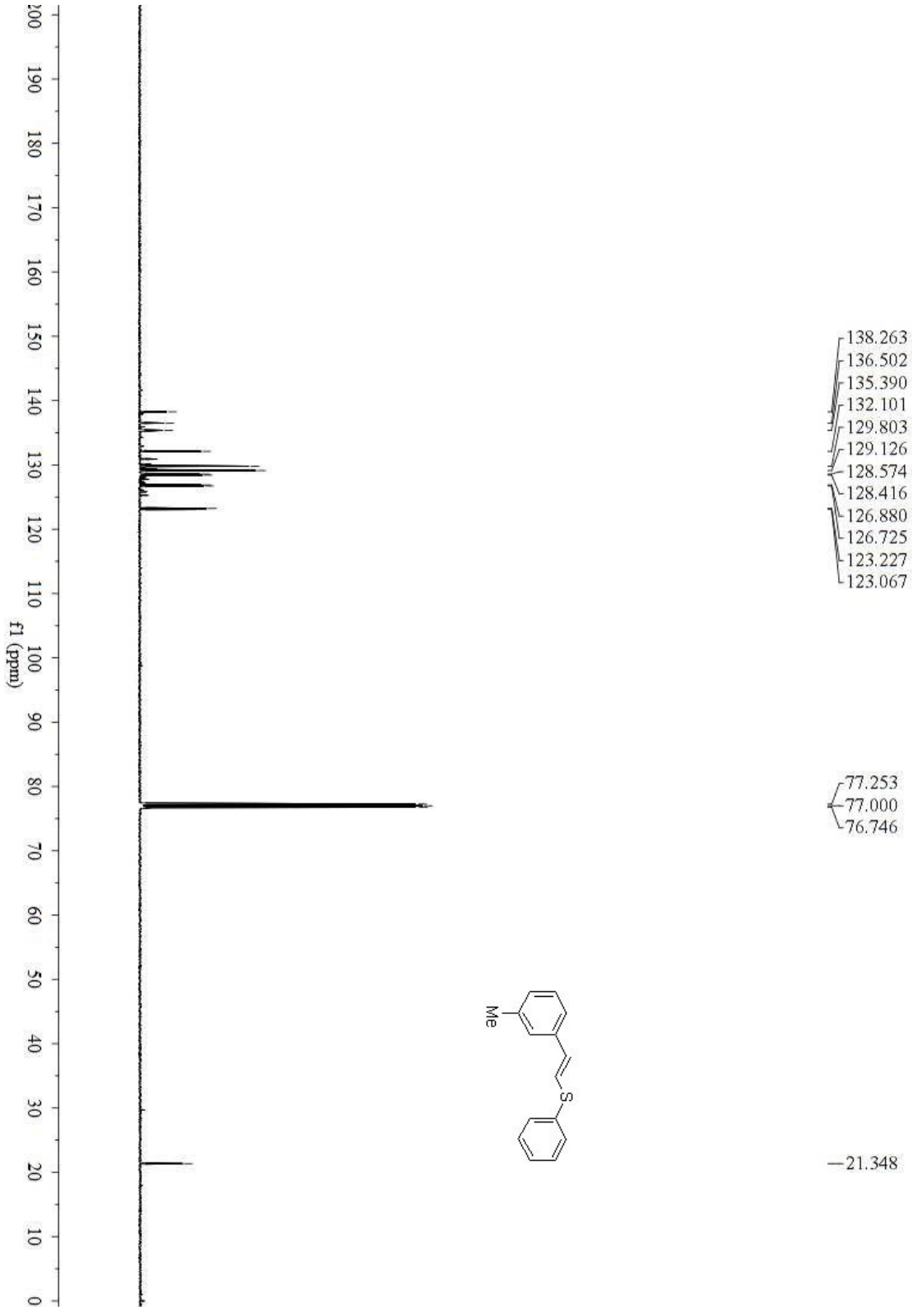
^{13}C NMR: (E)-(2-methylstyryl)(phenyl)sulfane (13)



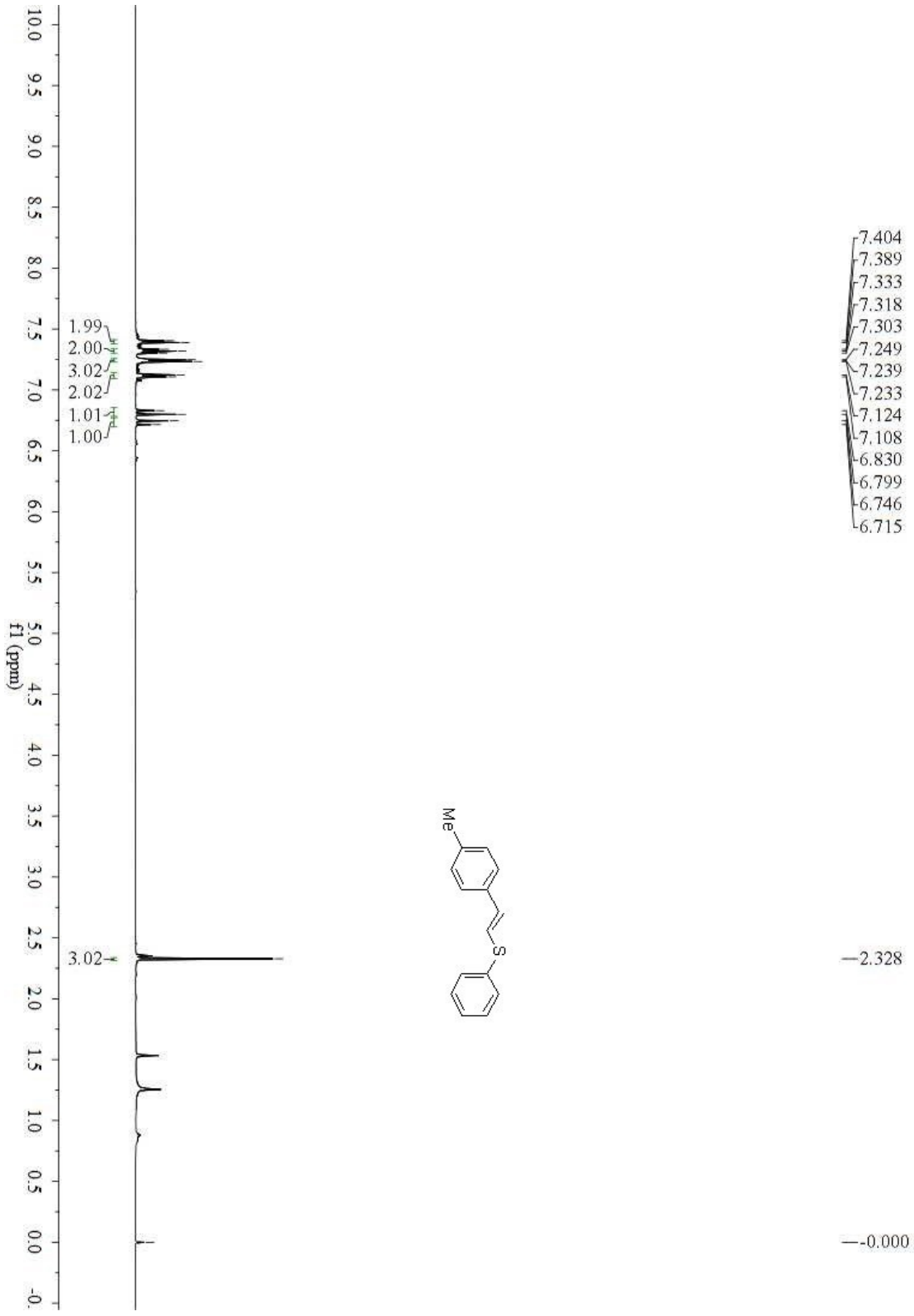
^{1}H NMR: (E)-(3-methylstyryl)(phenyl)sulfane (14)



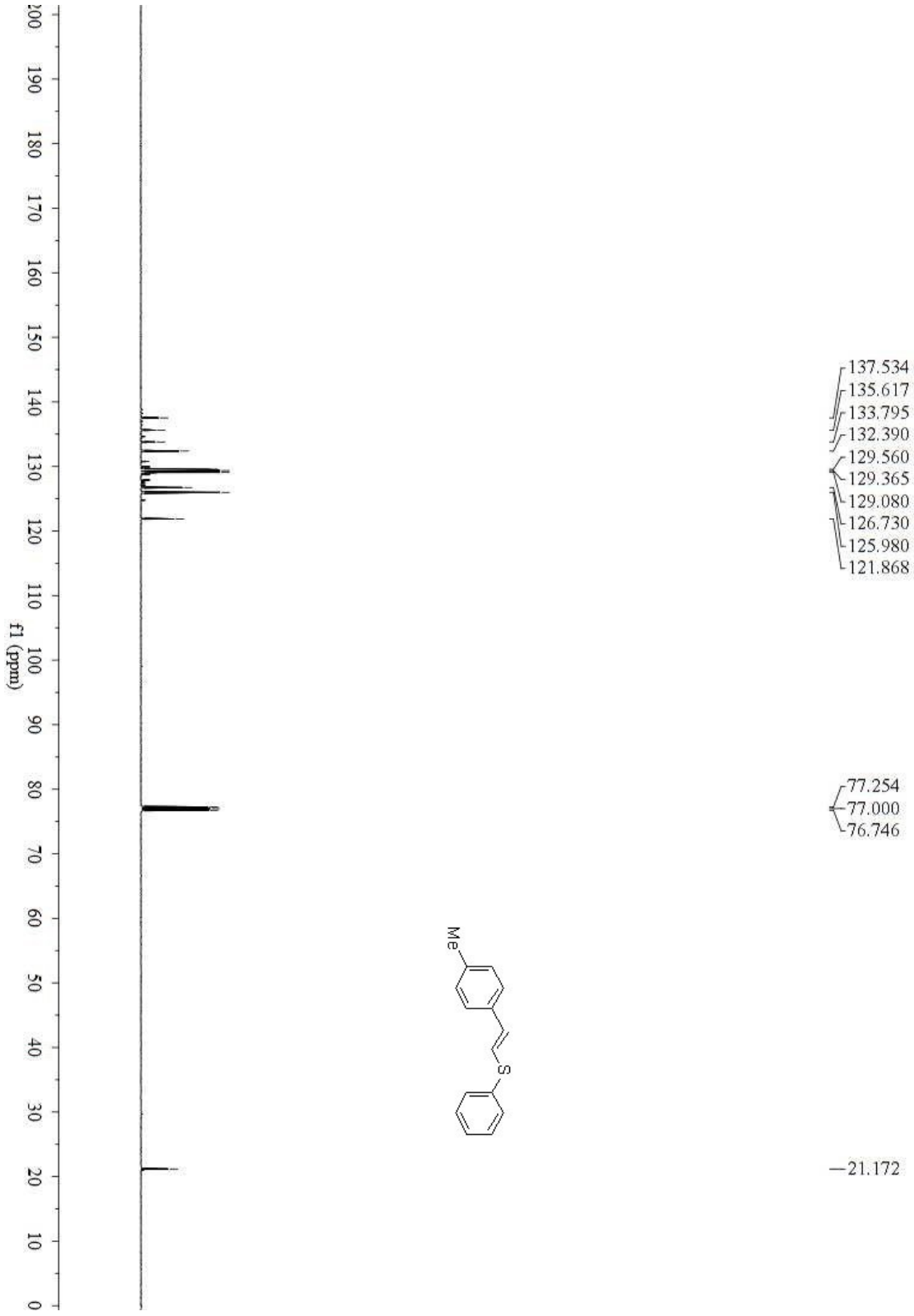
^{13}C NMR: (E)-(3-methylstyryl)(phenyl)sulfane (14)



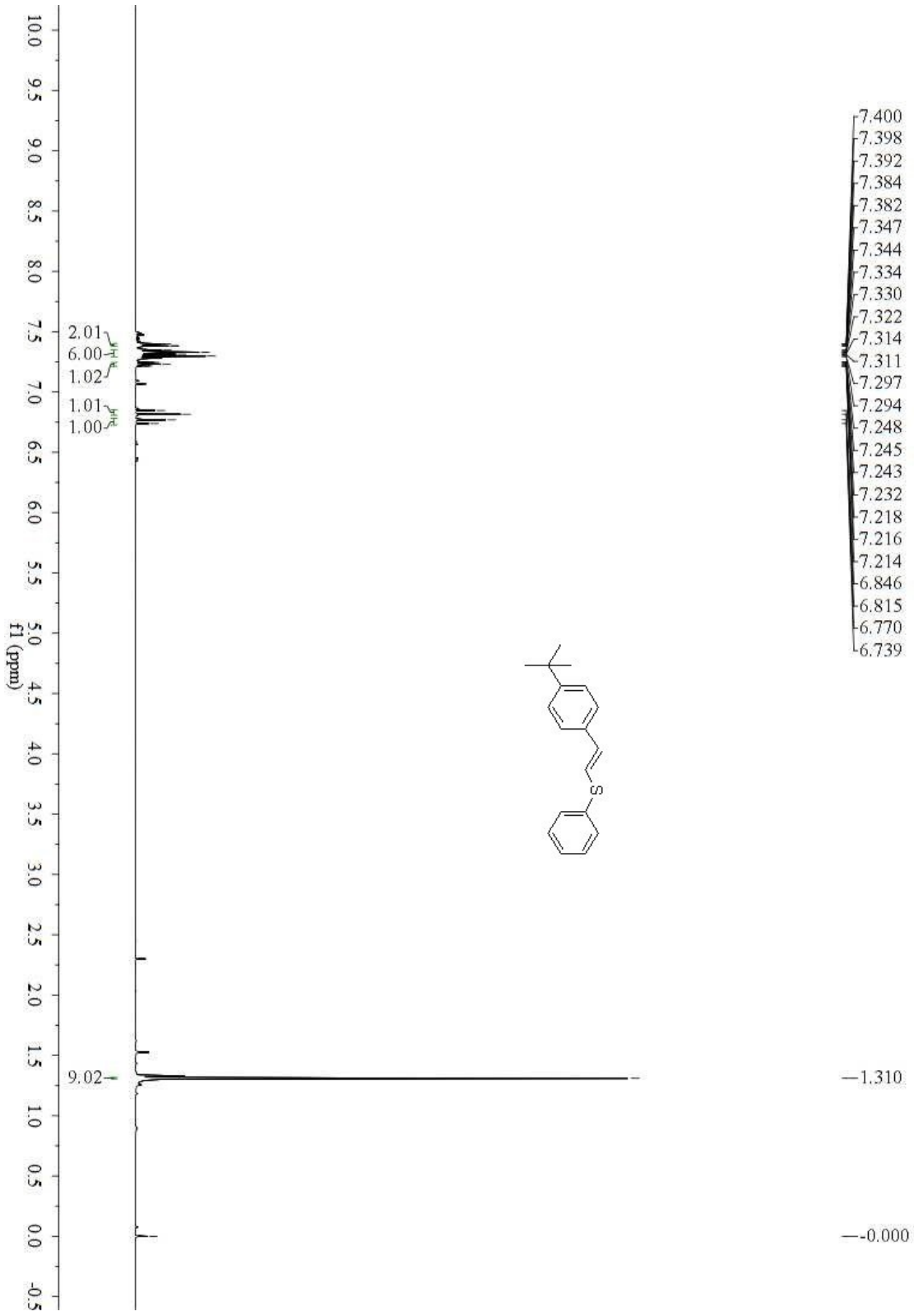
^{1}H NMR: (E)-(4-methylstyryl)(phenyl)sulfane (15)



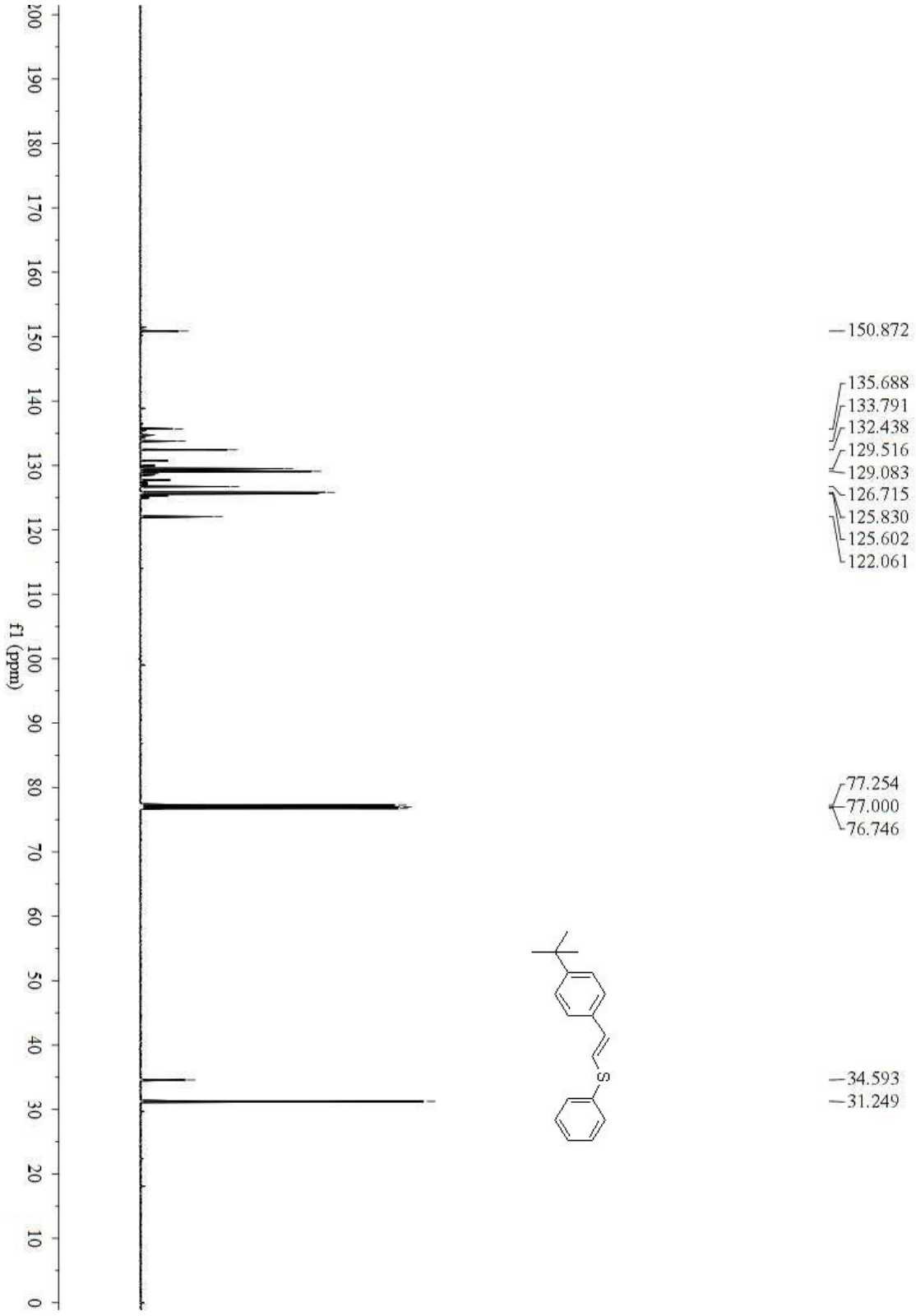
^{13}C NMR: (E)-(4-methylstyryl)(phenyl)sulfane (15)



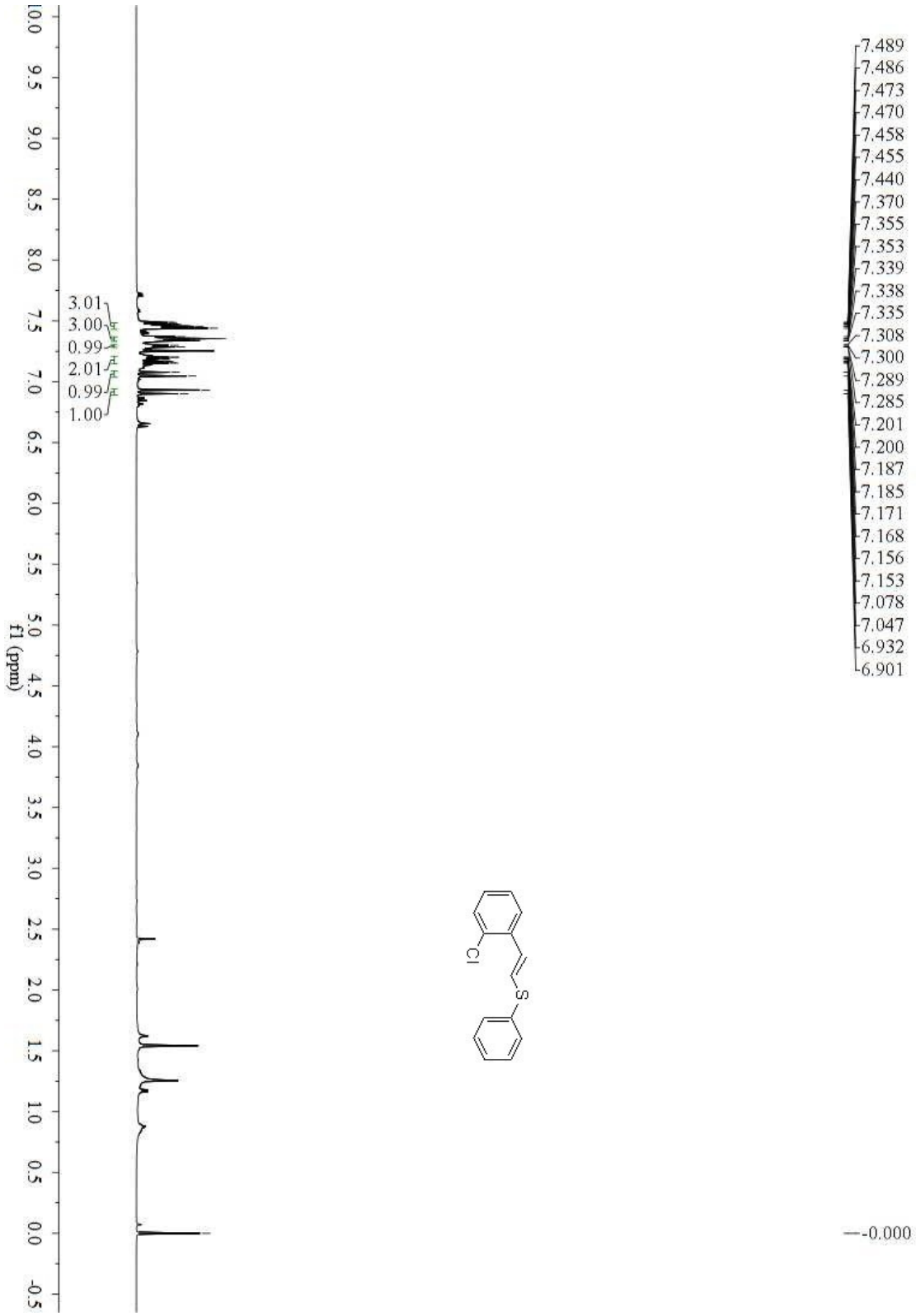
^{1}H NMR: (E)-(4-(tert-butyl)styryl)(phenyl)sulfane (16)



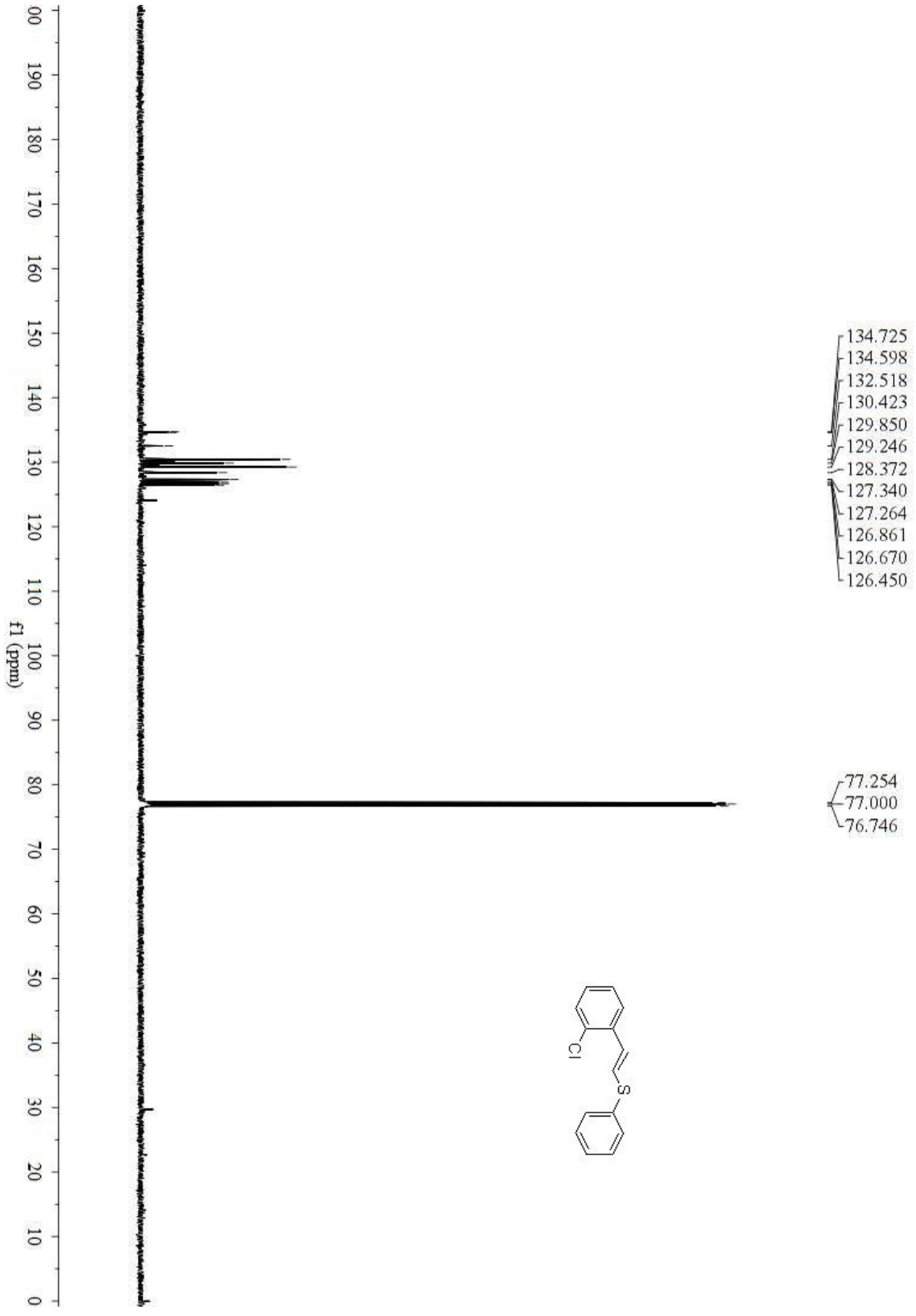
^{13}C NMR: (E)-(4-(tert-butyl)styryl)(phenyl)sulfane (16)



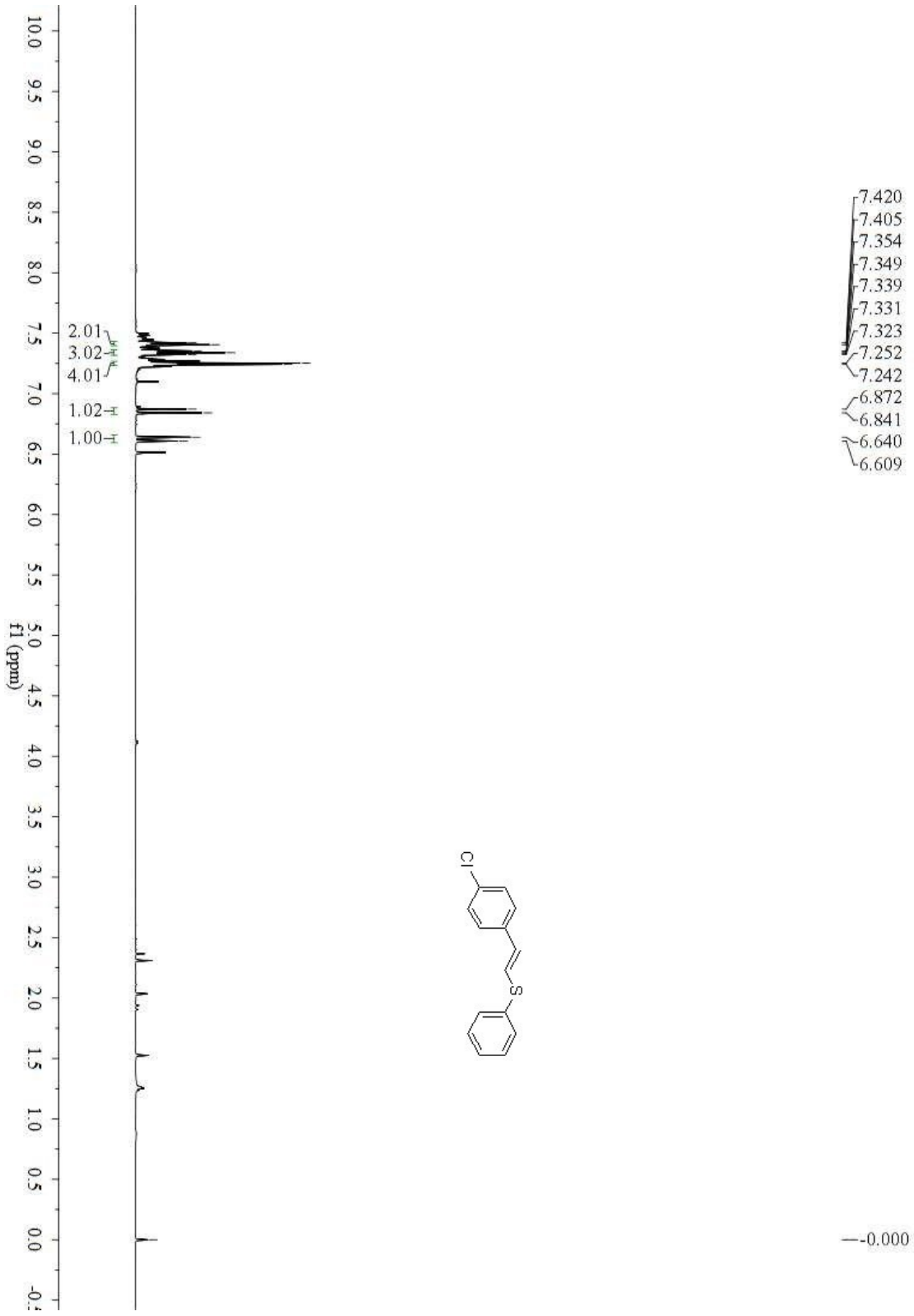
^{1}H NMR: (E)-(2-chlorostyryl)(phenyl)sulfane (17)



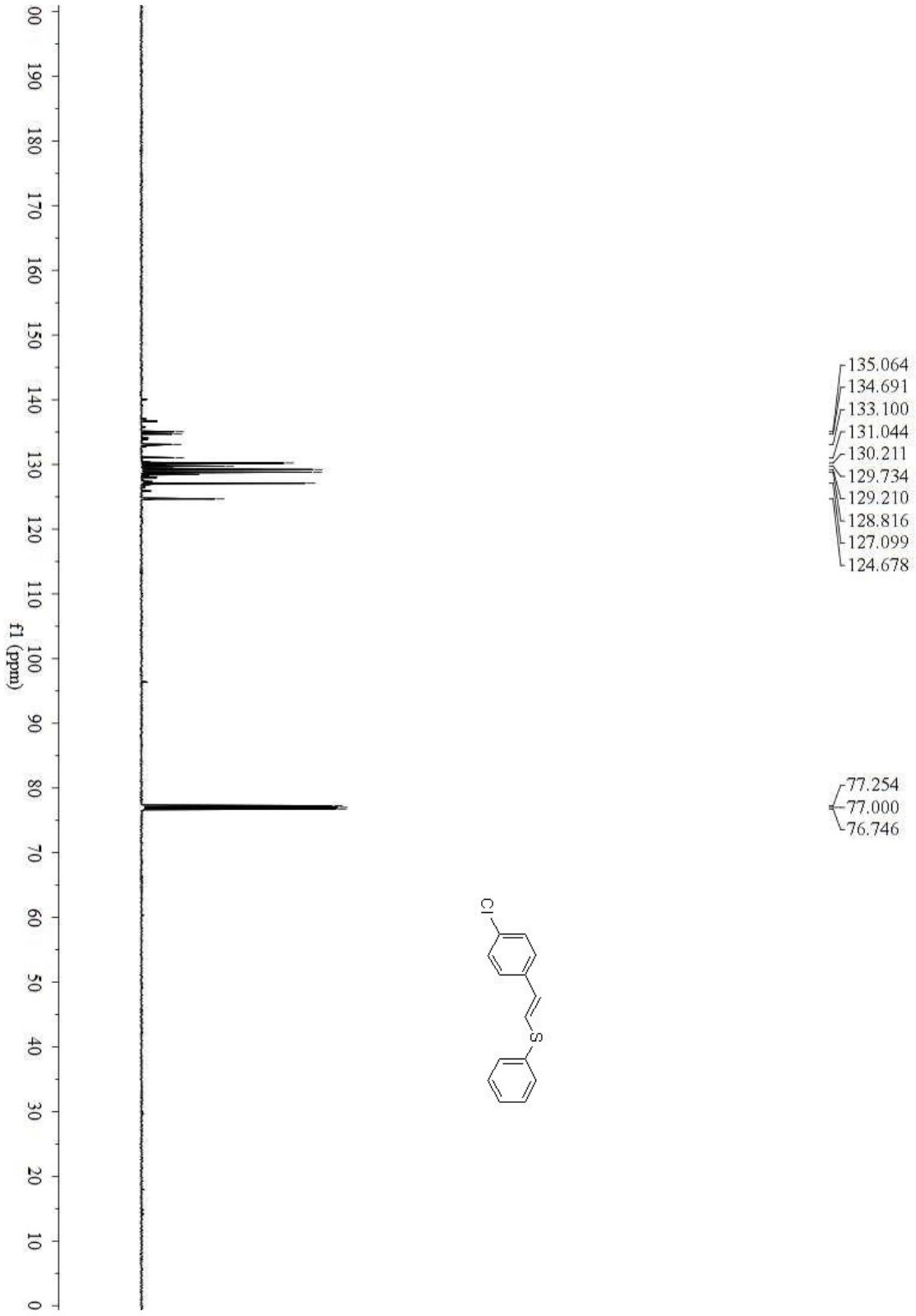
^{13}C NMR: (E)-(2-chlorostyryl)(phenyl)sulfane (17)



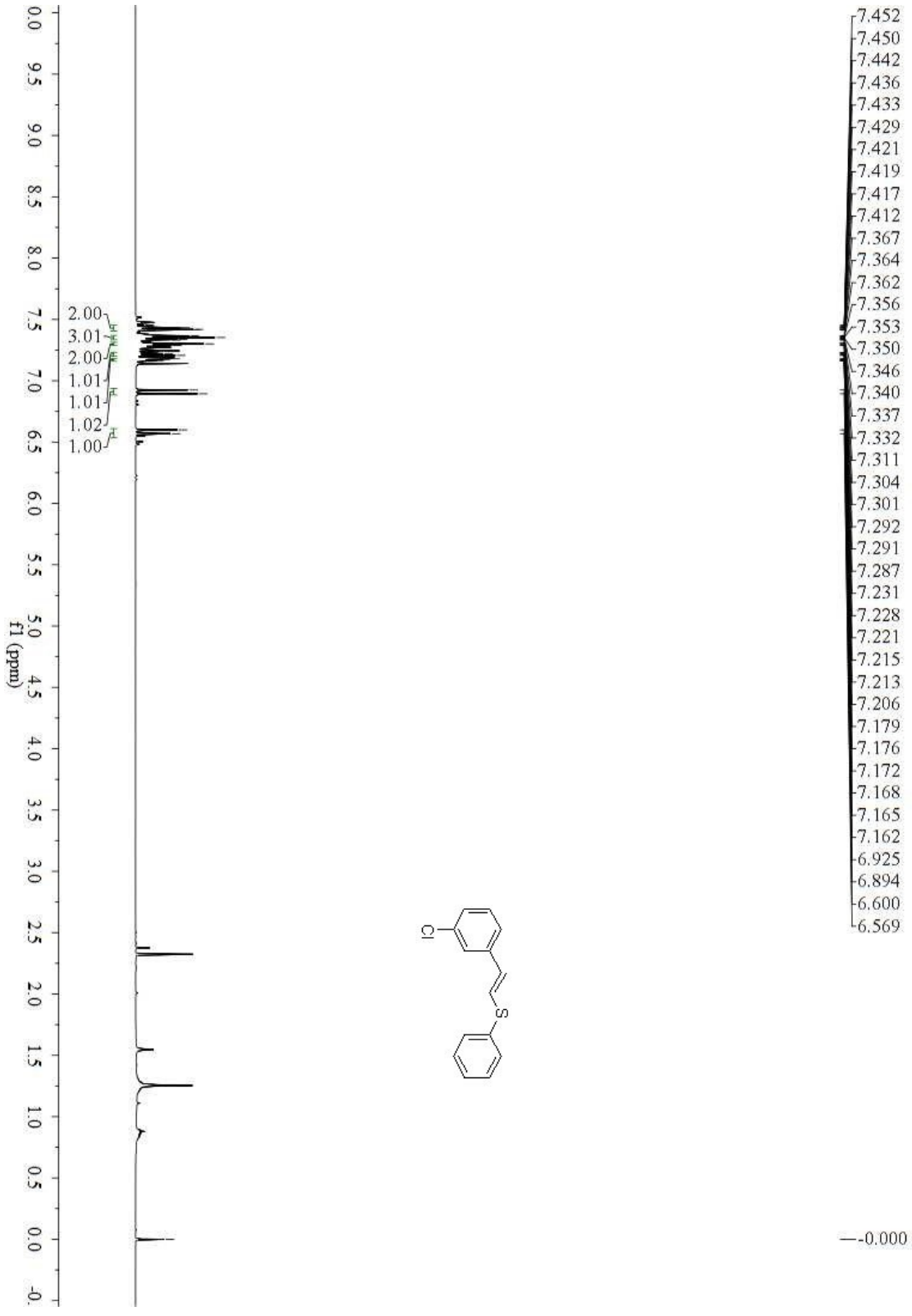
^{1}H NMR: (E)-(4-chlorostyryl)(phenyl)sulfane (18)



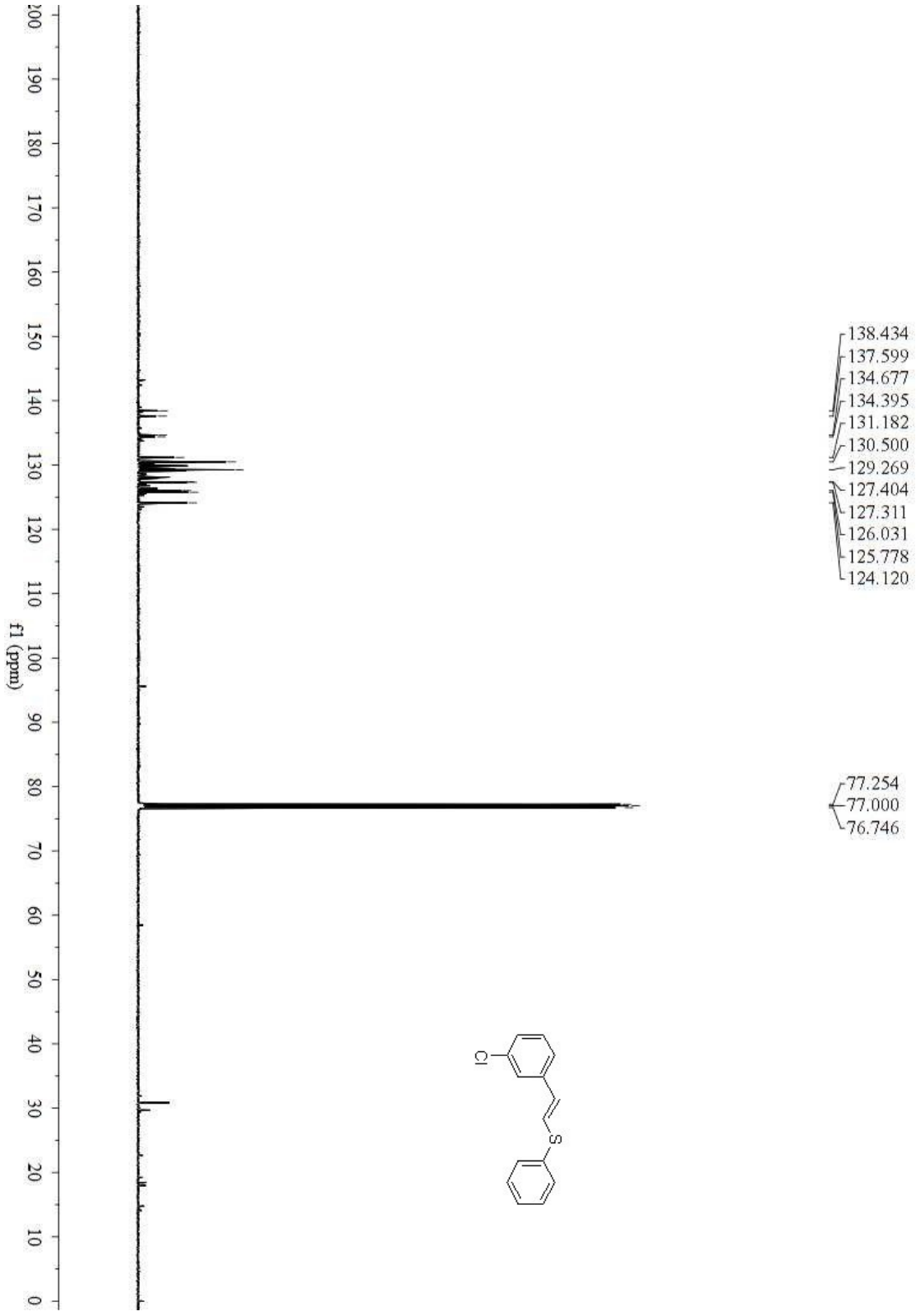
^{13}C NMR: (E)-(4-chlorostyryl)(phenyl)sulfane (18)



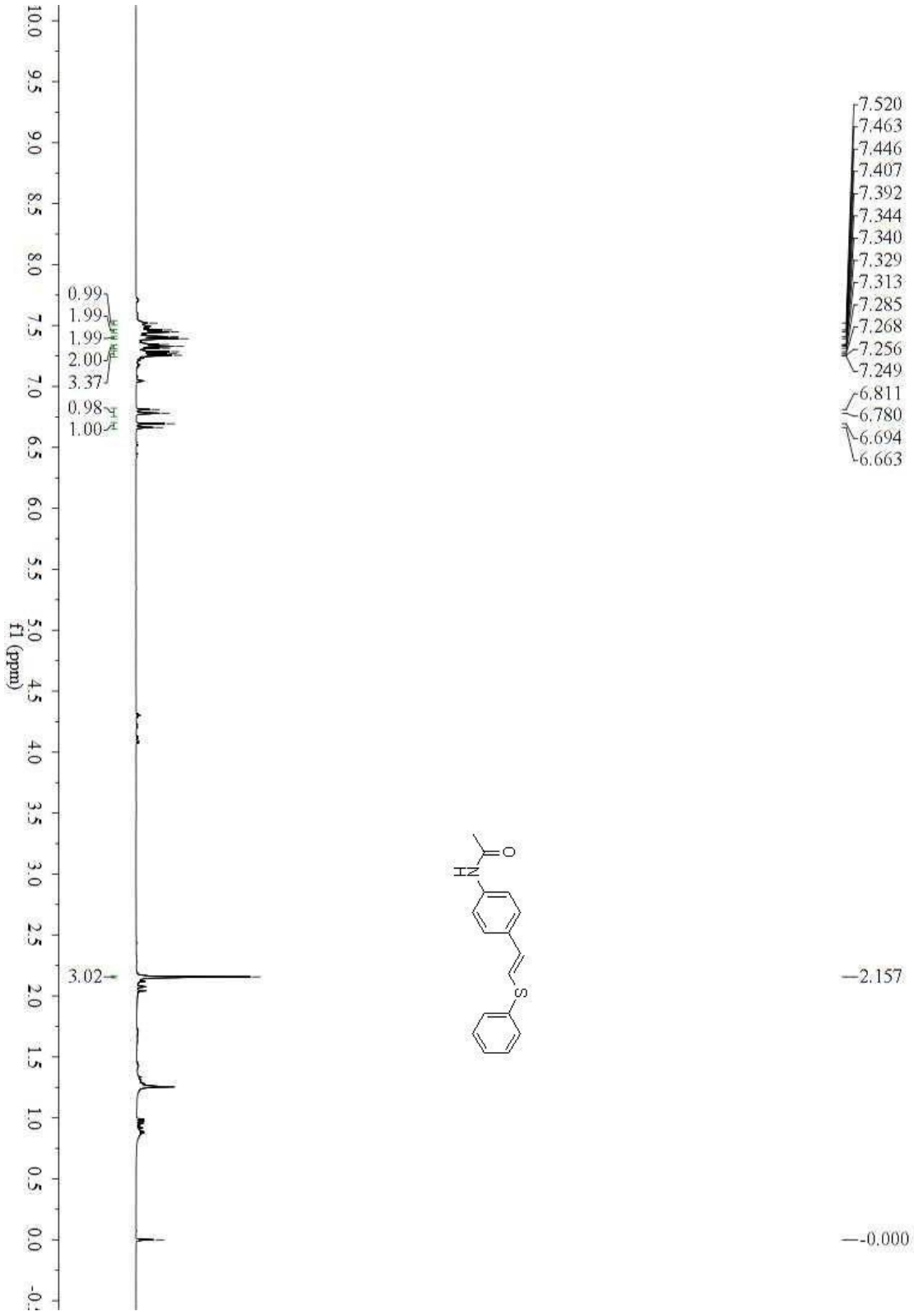
^{1}H NMR: (E)-(3-chlorostyryl)(phenyl)sulfane (19)



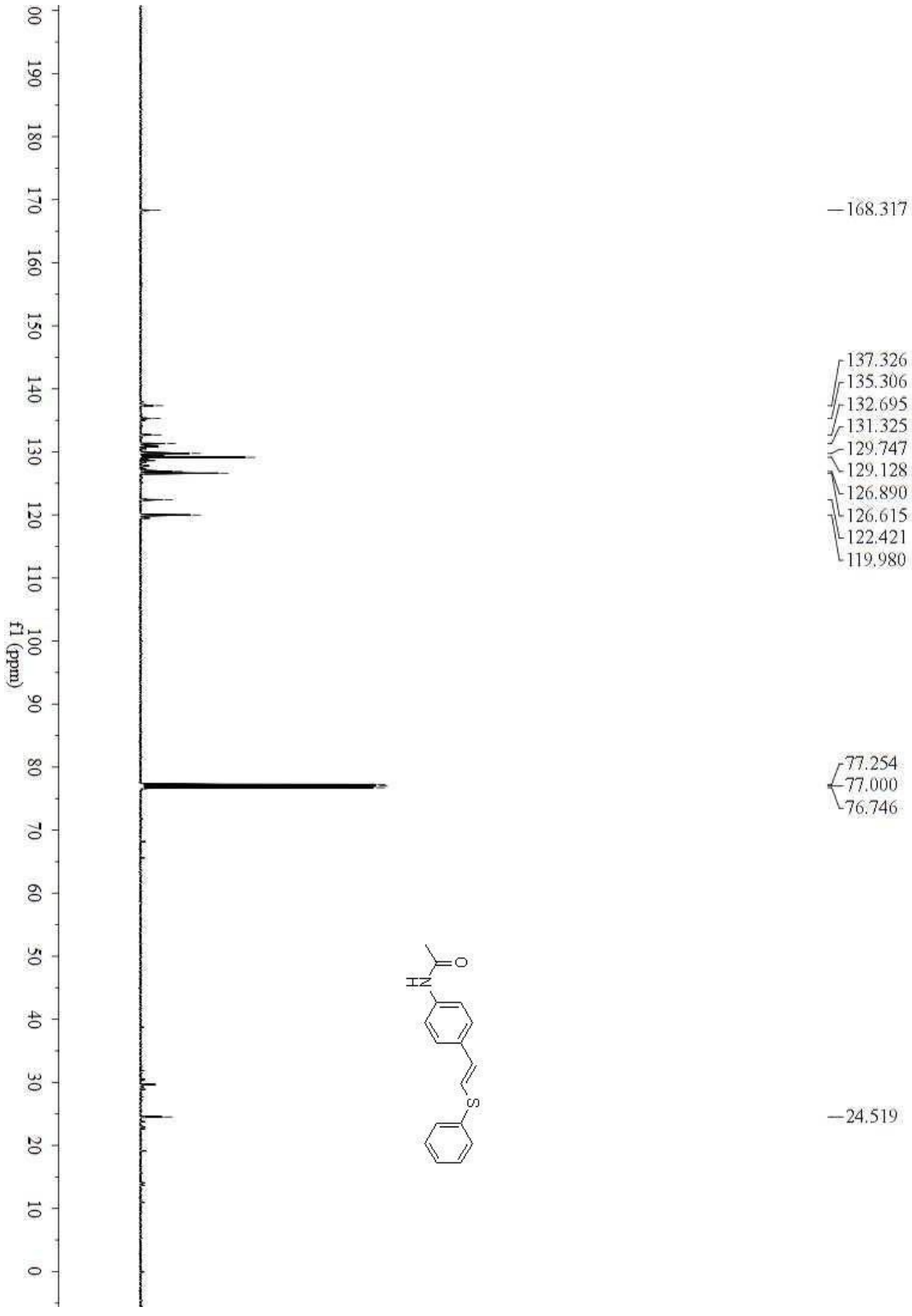
^{13}C NMR: (E)-(3-chlorostyryl)(phenyl)sulfane (19)



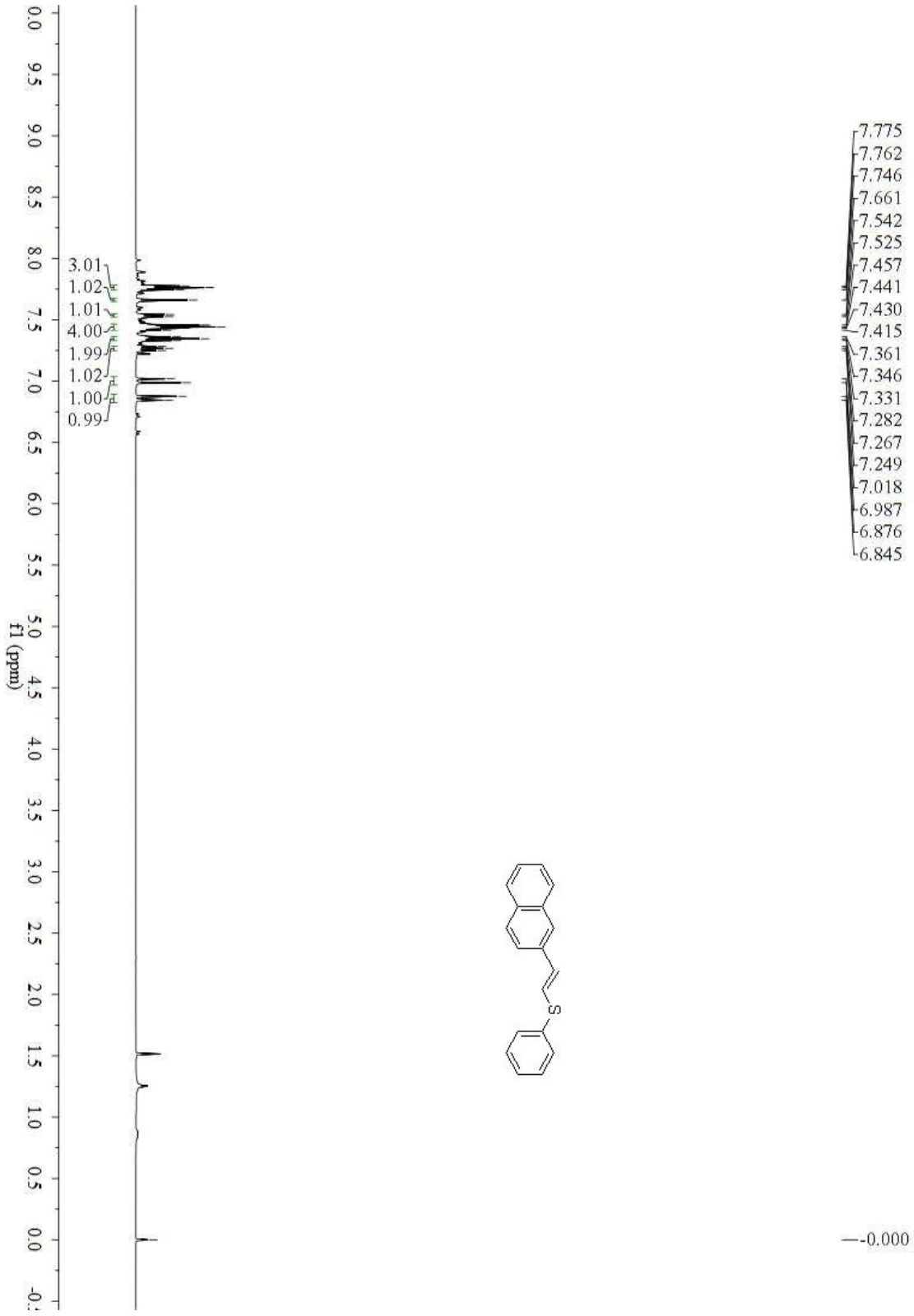
^{1}H NMR: (E)-N-(4-(2-(phenylthio)vinyl)phenyl)acetamide (20)



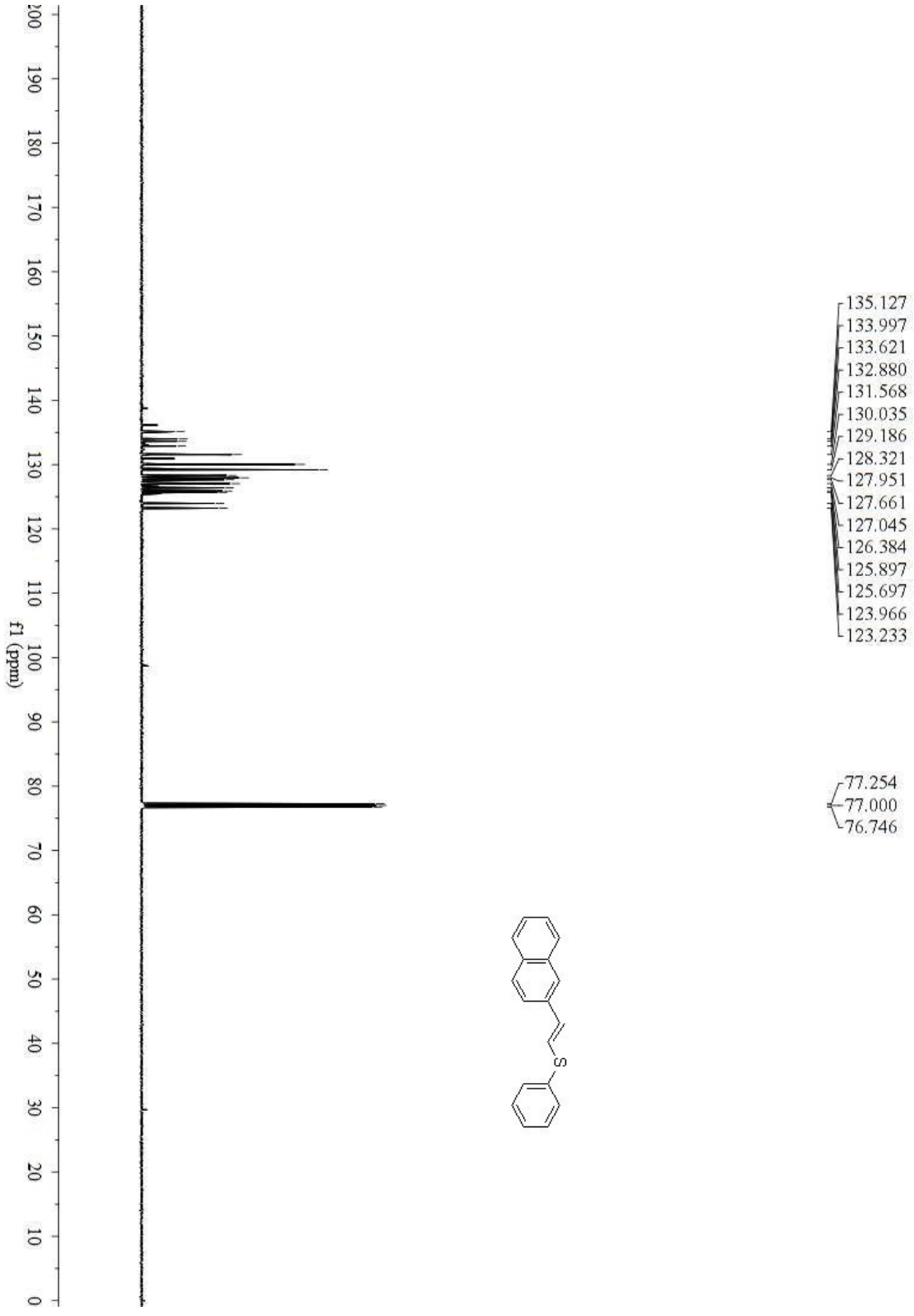
^{13}C NMR: (E)-N-(4-(2-(phenylthio)vinyl)phenyl)acetamide (20)



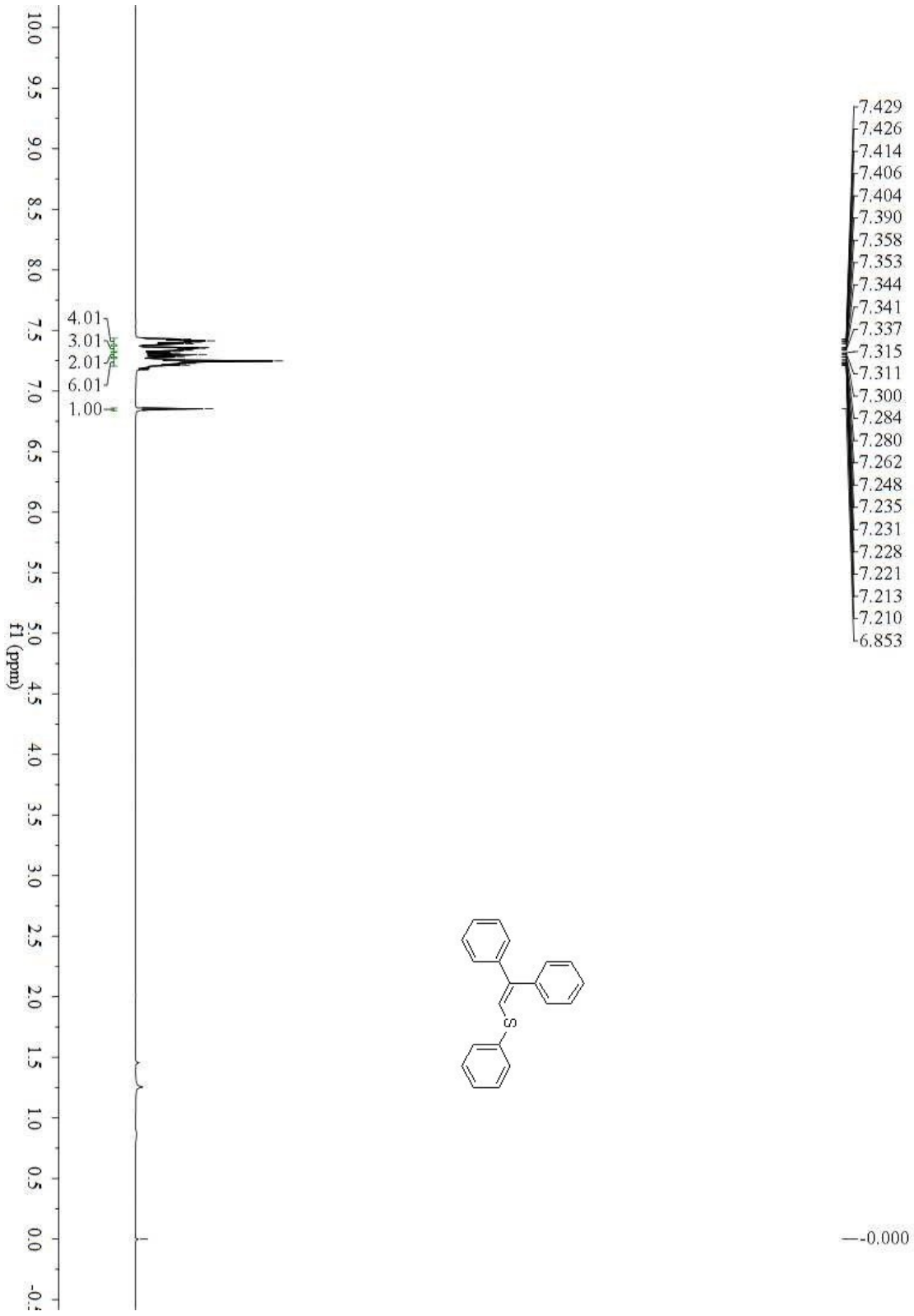
^{1}H NMR: (E)-(2-(naphthalen-2-yl)vinyl)(phenyl)sulfane (21)



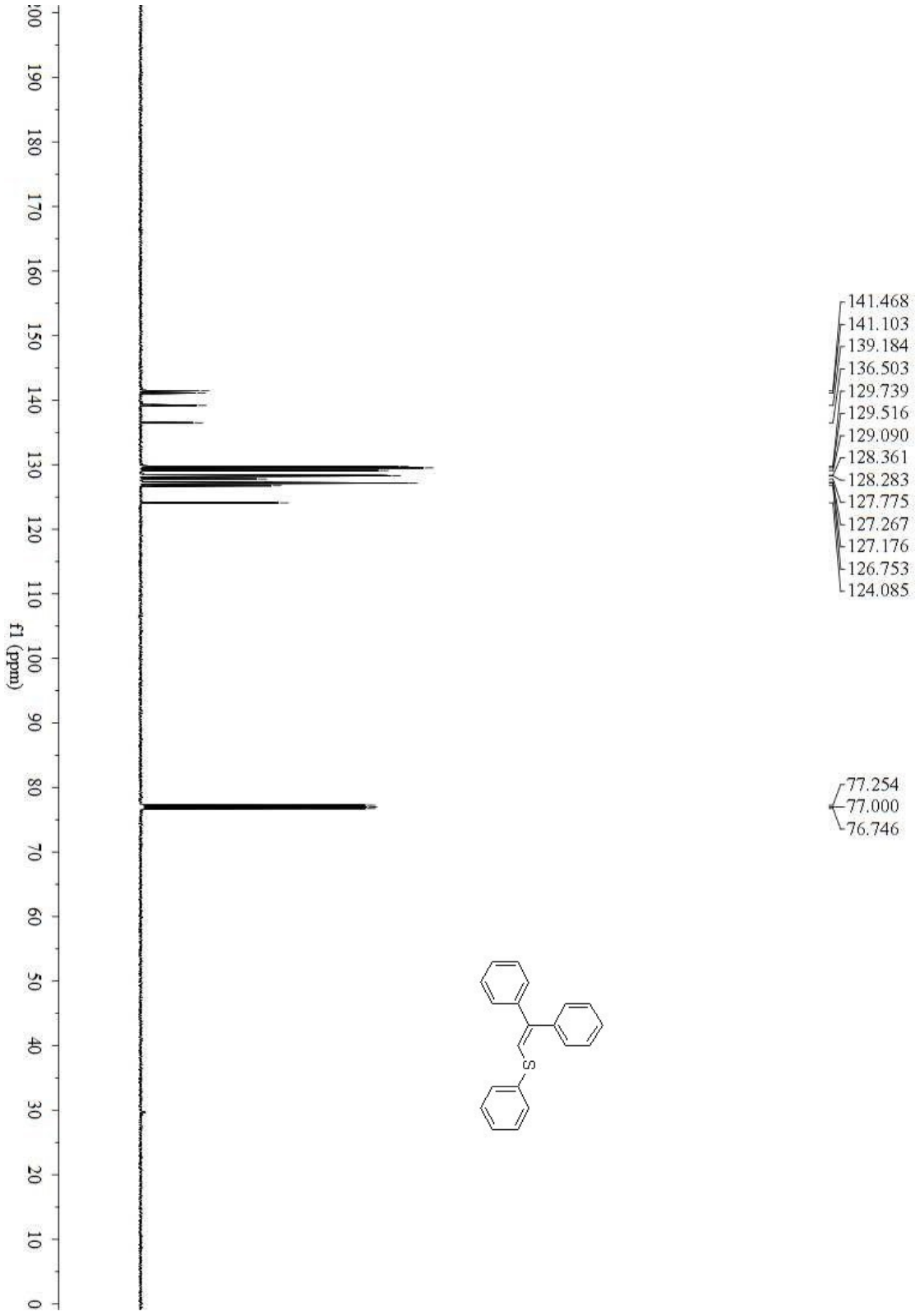
^{13}C NMR: (E)-(2-(naphthalen-2-yl)vinyl)(phenyl)sulfane (21)



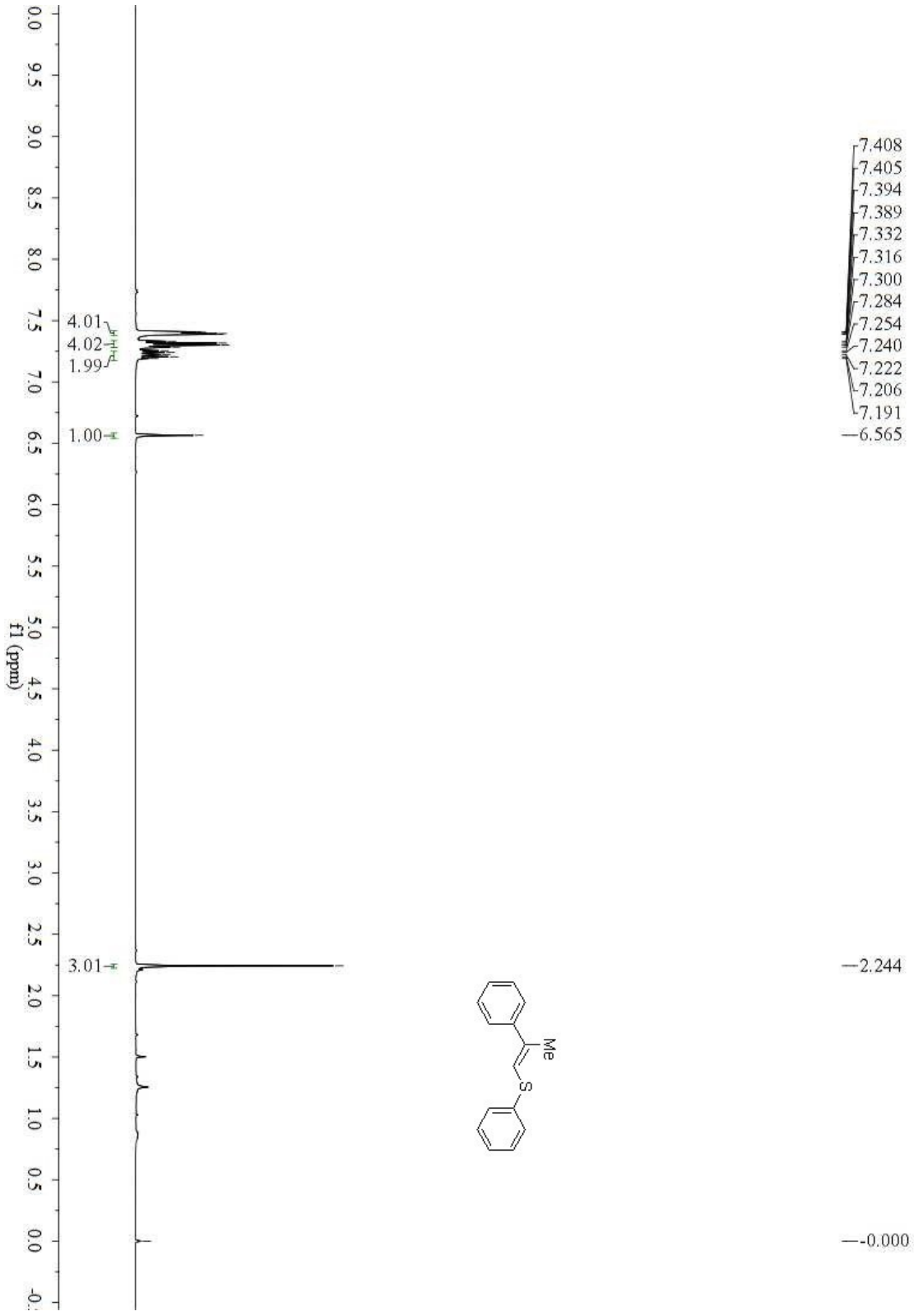
^{1}H NMR: (2,2-diphenylvinyl)(phenyl)sulfane (22)



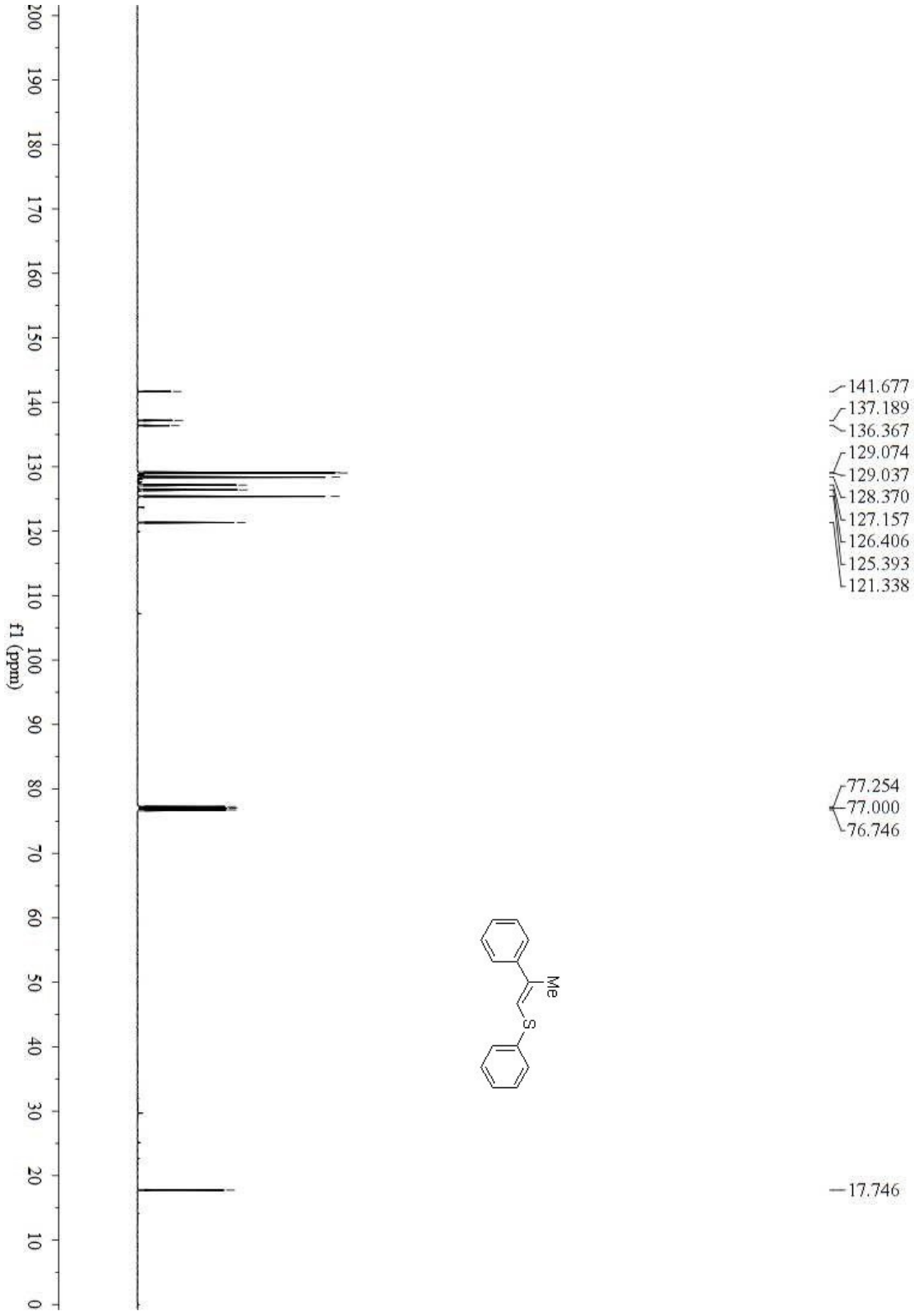
^{13}C NMR: (2,2-diphenylvinyl)(phenyl)sulfane (22)



^{1}H NMR: (E)-phenyl(2-phenylprop-1-en-1-yl)sulfane (23)

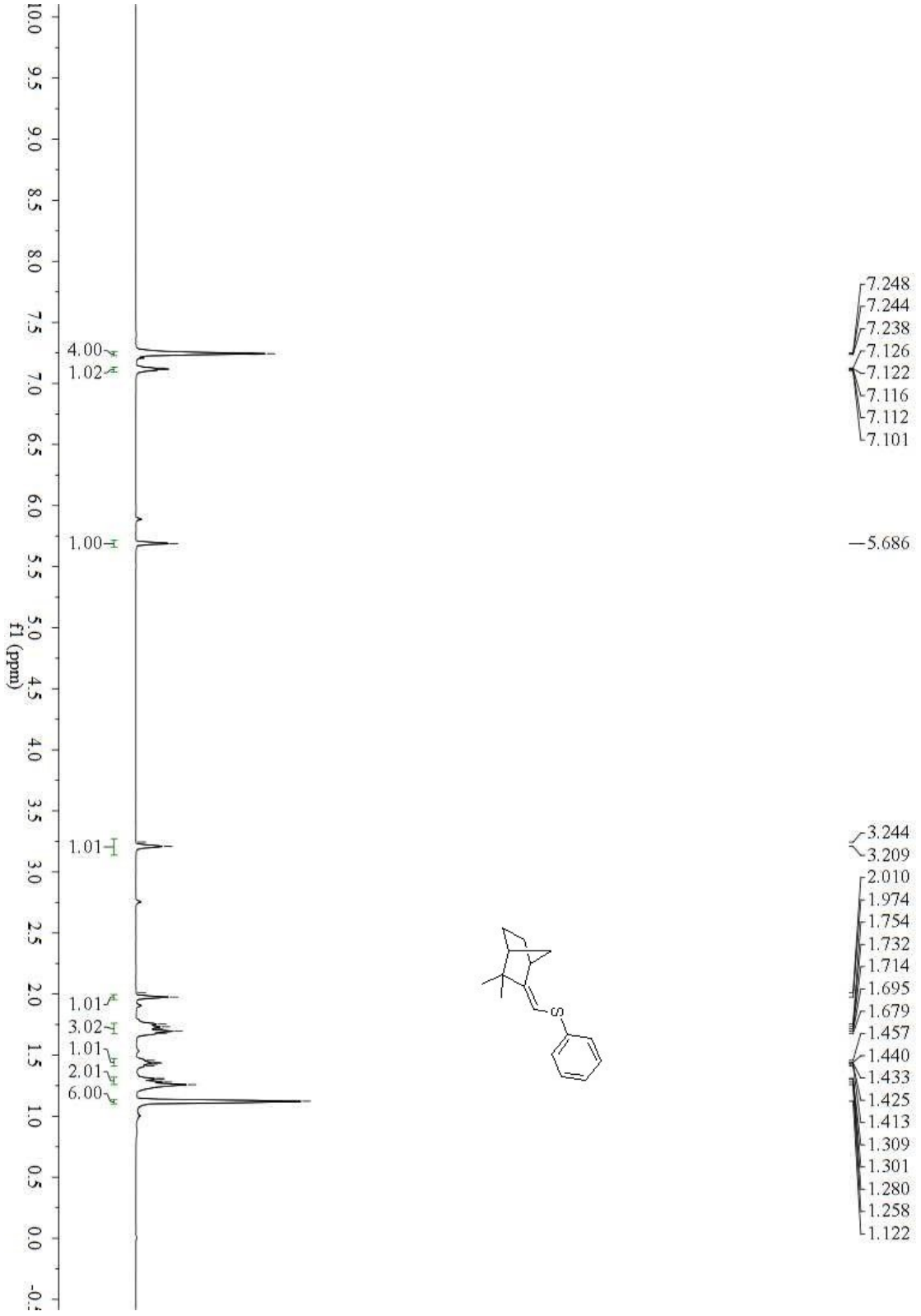


^{13}C NMR: (E)-phenyl(2-phenylprop-1-en-1-yl)sulfane (23)

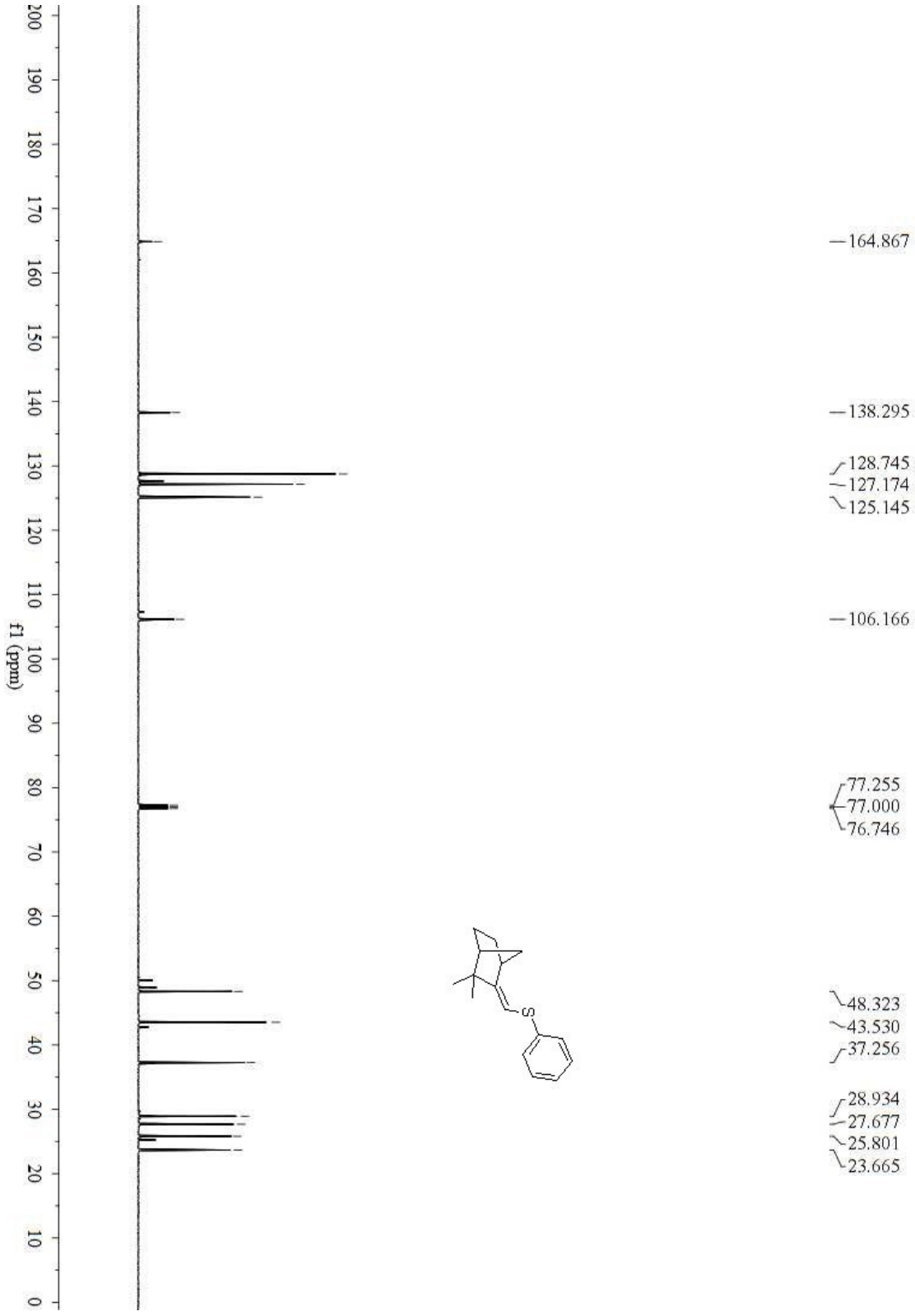


^{1}H NMR: ((E)-((1S,4R)-3,3-dimethylbicyclo[2.2.1]heptan-2-

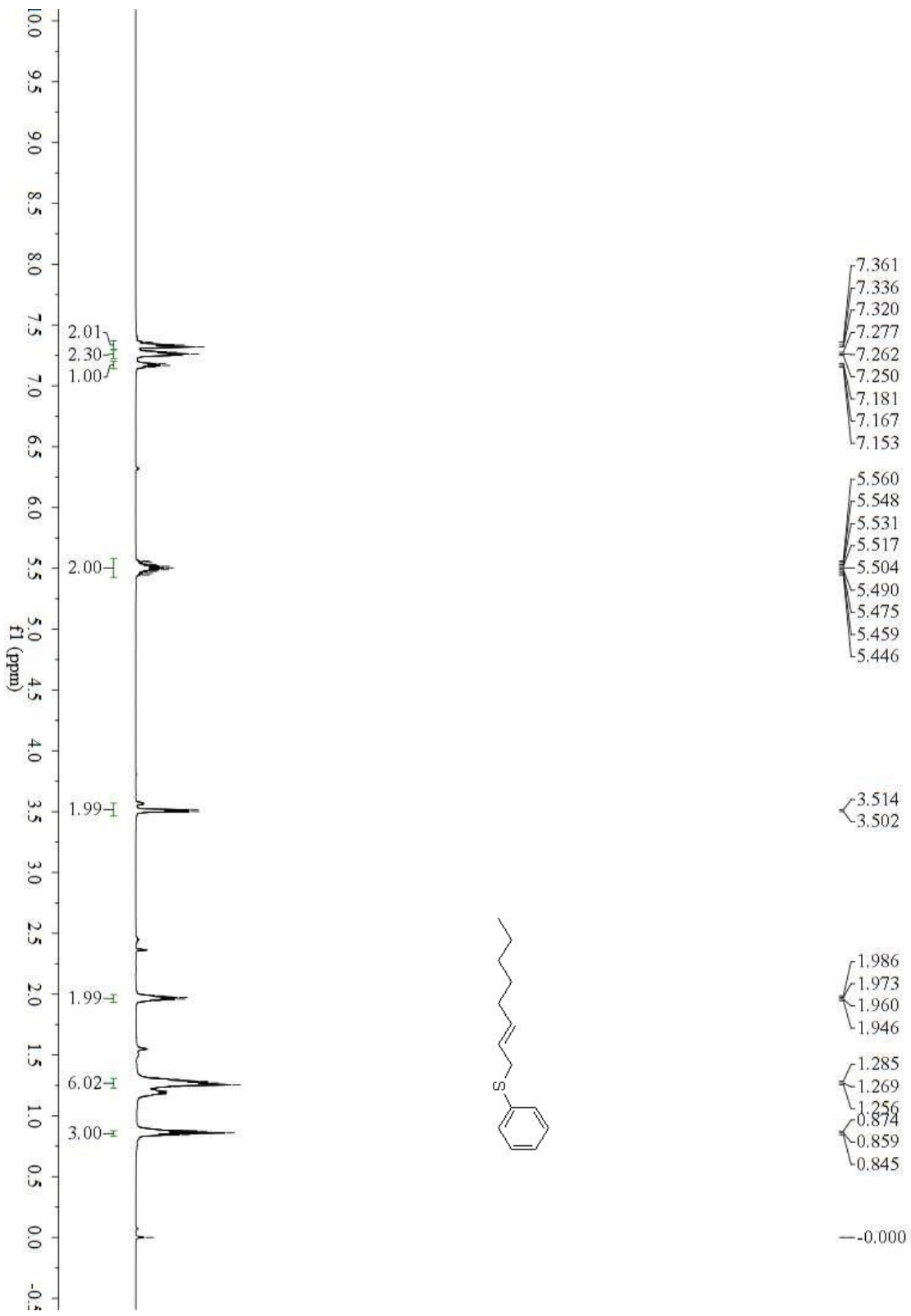
ylidene)methyl)(phenyl)sulfane (24)



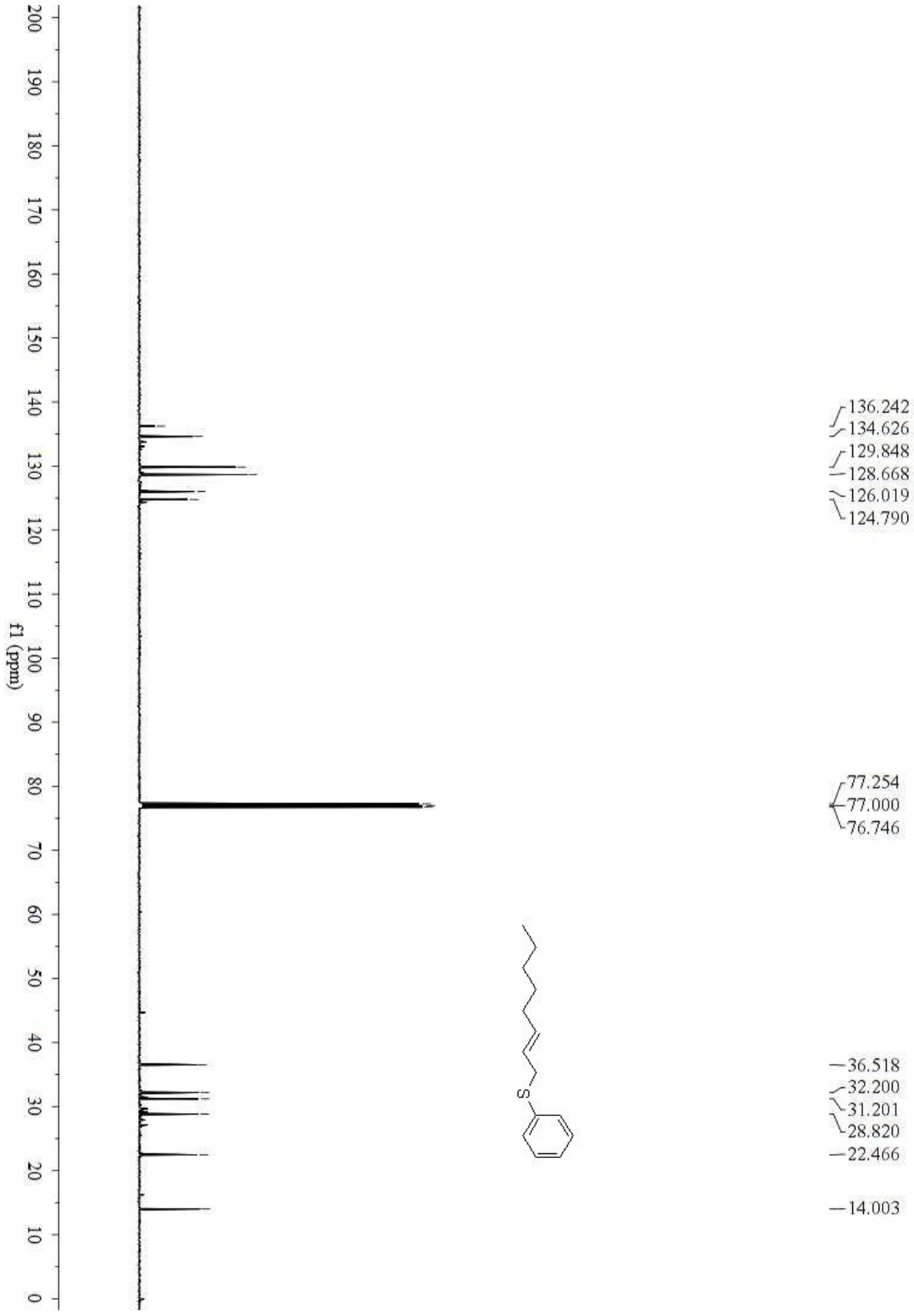
^{13}C NMR: ((E)-((1S,4R)-3,3-dimethylbicyclo[2.2.1]heptan-2-ylidene)methyl)(phenyl)sulfane (24)



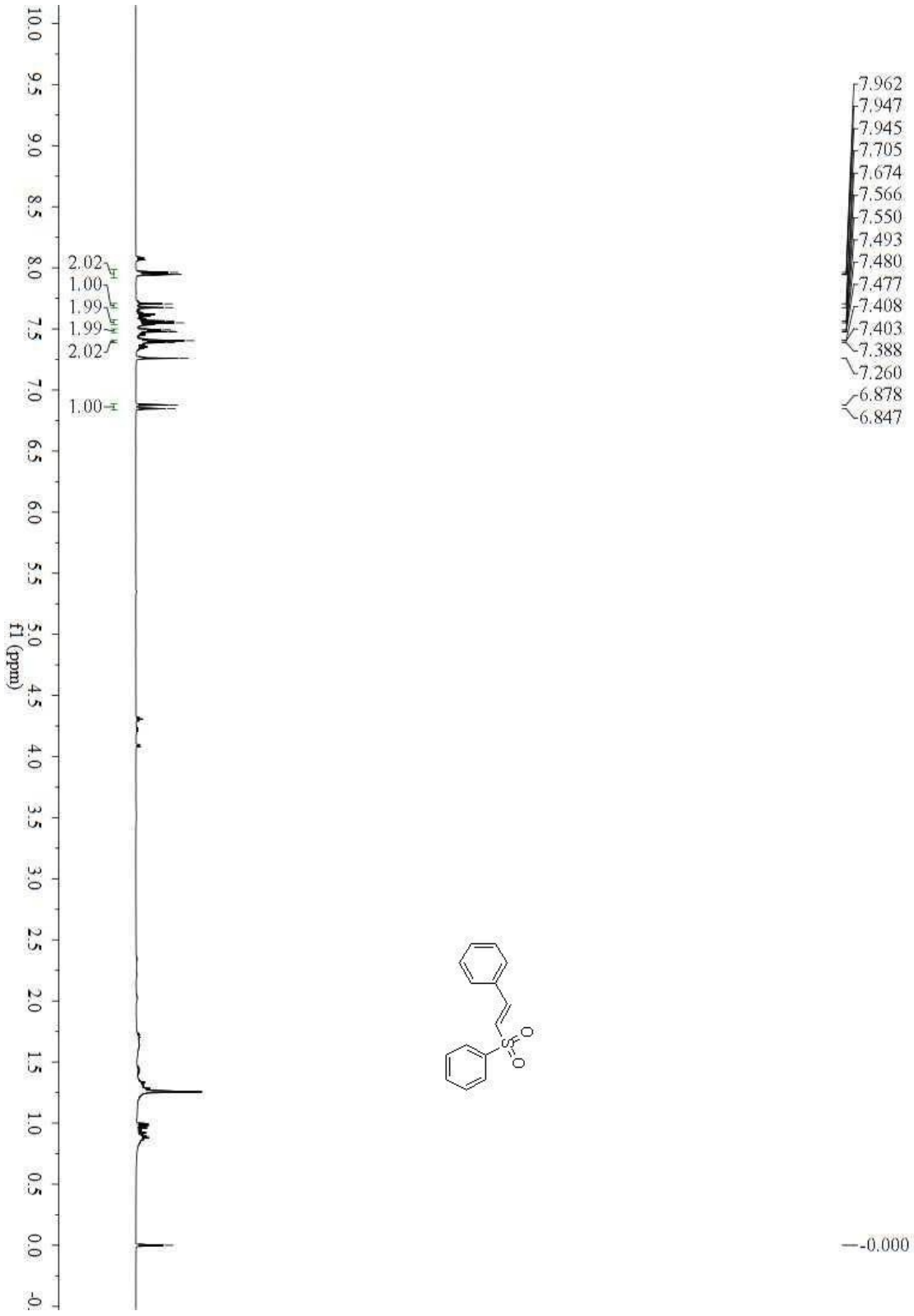
^{1}H NMR: (E)-oct-2-en-1-yl(phenyl)sulfane (26)



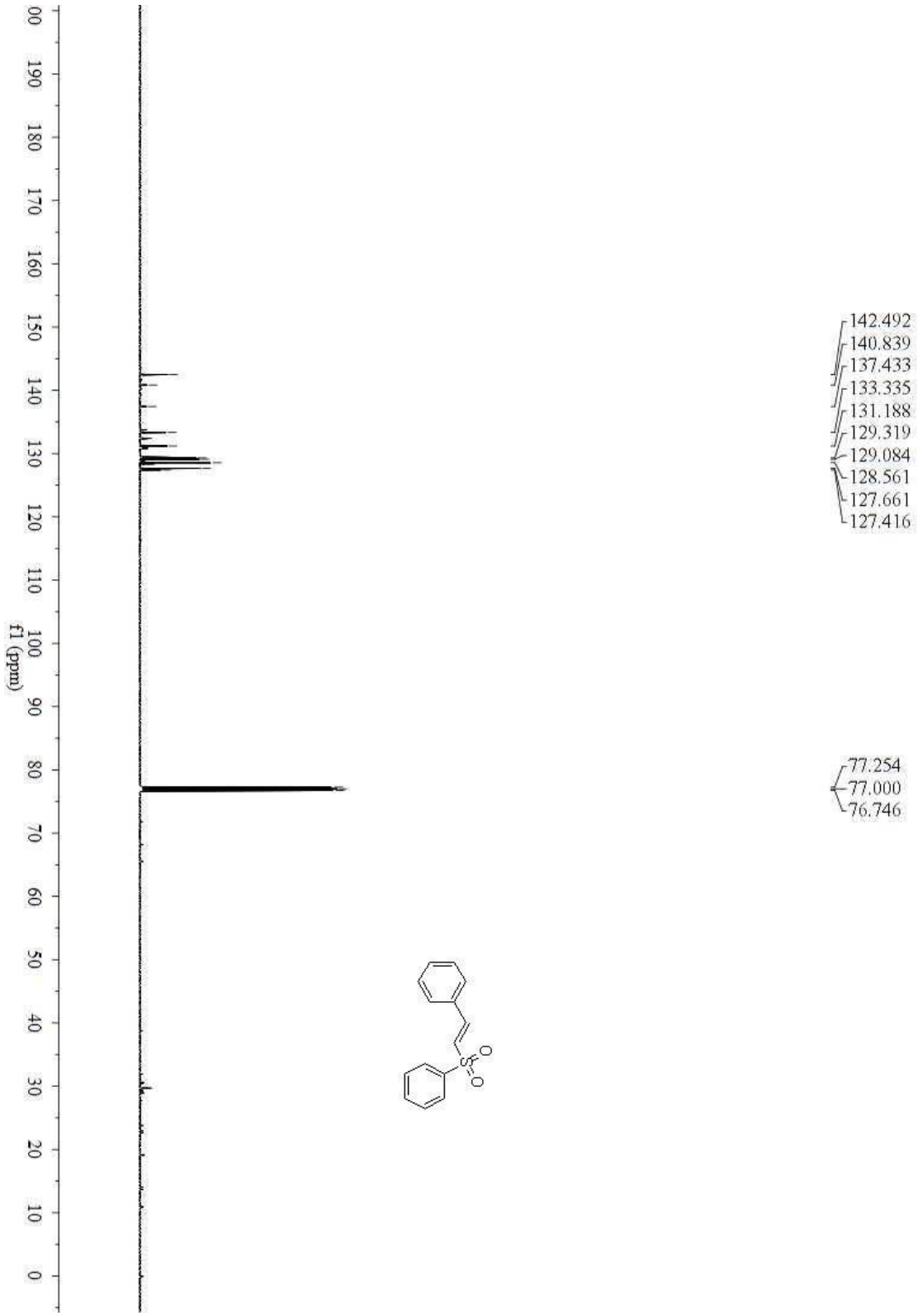
^{13}C NMR: (E)-oct-2-en-1-yl(phenyl)sulfane (26)



^{1}H NMR: (E)-(2-(phenylsulfonyl)vinyl)benzene (27)



^{13}C NMR: (E)-(2-(phenylsulfonyl)vinyl)benzene (27)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f1 (ppm)
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O
O