Supporting Information File

Synthesis of α-Aryl Sulfides by Deaminative Coupling of α-Amino compounds with Thiophenols

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1. General experimental methods.

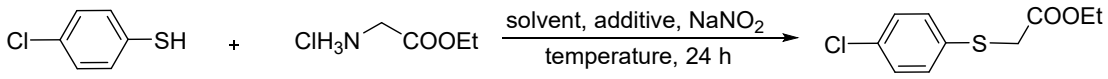
All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. All Solvents were purified following standard literature procedures. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. All NMR experiments were carried out on a Bruker Avance 500 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shift values (δ) are given in parts per million.

2. General procedure of deaminative coupling of α-aminoester salts.

General procedure A: The thiol **1** (0.5 mmol), α-aminoester hydrochloride **2a** (1.0 mmol), $NaNO_2$ (1.25 mmol) and NH_4Cl (2.0 mmol) were added into a reaction tube. Toluene (1.14 ml) and water (114 μl) were added respectively. The mixture was stirred at 100 °C for 24 h. When the reaction was completed, the mixture was crude after the solvent was removed by the vacuum pump. The crude mixture was purified by column chromatography on silica gel to obtain product **3**.

General procedure B: The thiol **1** (0.5 mmol), α-aminoacetonitriles hydrochloride **2b-e** (1.25 mmol), $NaNO_2$ (1.5 mmol) and NH_4Cl (1.0 mmol) were added into a reaction tube. Toluene (1.14 ml) and water (114 μl) were added respectively. The mixture was stirred at 100 °C for 24 h. When the reaction was completed, the mixture was crude after the solvent was removed by the vacuum pump. The crude mixture was purified by column chromatography on silica gel to obtain product **4**.

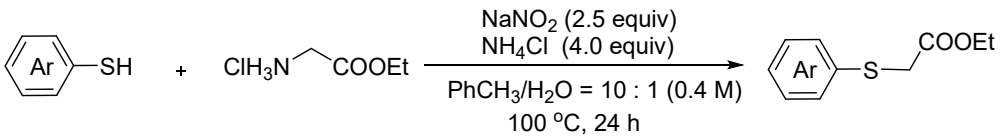
Table S1. Optimization of reaction conditions of α-aminoethlyester salts.

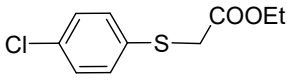


1a **2a** **3a**

entry	**1a**:**2a**	solvent (toluene/H_2O)	$NaNO_2$ (equiv)	additive (equiv)	t (°C)	yield (%)
1	1.0:1.5	20:1	1.8	NH_4Cl (4)	100	70
2	1.0:1.5	20:1[a]	1.8	NH_4Cl (4)	100	68
3	1.0:1.5	20:1[b]	1.8	NH_4Cl (4)	100	0
4	1.0:1.5	20:1[c]	1.8	NH_4Cl (4)	100	0
5	1.0:1.5	20:1	1.8	NH_4F (4)	100	55
6	1.0:1.5	20:1	1.8	$HCOONH_4$ (4)	100	53
7	1.0:1.5	20:1	1.8	HCOONa (4)	100	30
8	1.0:1.5	20:1	1.8	-	100	15
9	1.0:1.5	20:1	2.5	NH_4Cl (4)	100	75
10	1.0:2.0	20:1	2.5	NH_4Cl (4)	100	83
11	1.0:2.0	20:1	2.5	NH_4Cl (4)	80	76
12	**1.0:2.0**	**10:1**	**2.5**	**NH_4Cl (4)**	**100**	**90**
13	1.0:2.0	10:1	2.5	NH_4Cl (2.5)	100	83

[a] Solvent was DCE/H_2O. [b] Solvent was dioxane/H_2O. [c] Solvent was CH_3CN/H_2O.





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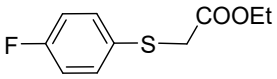

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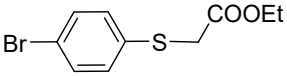

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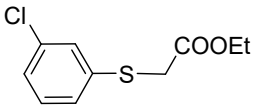

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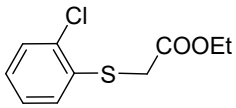

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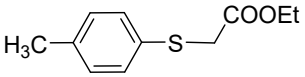

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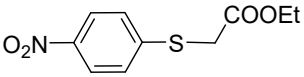

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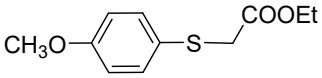

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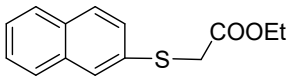

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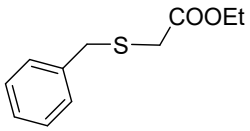

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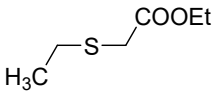
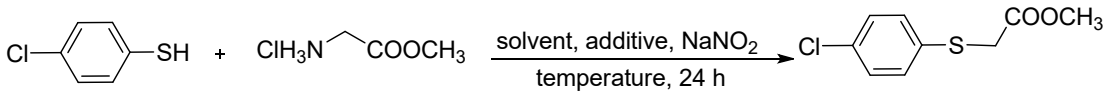


3k,21%

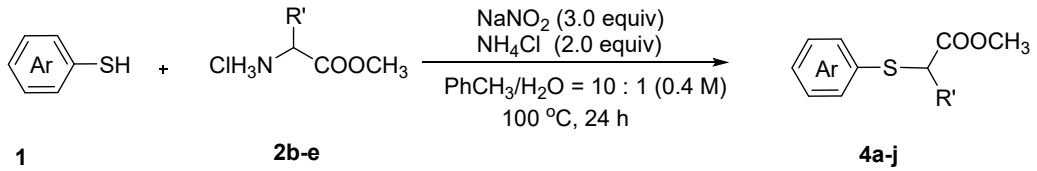
Scheme S1. Deaminative coupling of α-aminoethylester salts.

Table S2. Optimization of reaction conditions of α-aminomethylester salts.

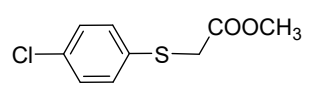


1a **2b** **4a**

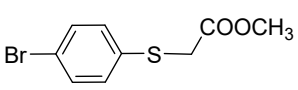
entry	**1a**:**2b**	solvent (toluene/H_2O)	$NaNO_2$ (equiv)	additive (equiv)	t (°C)	yield (%)
1	1.0:2.0	10:1	2.5	NH_4Cl (4)	100	53
2	1.0:2.0	10:1	2.5	HCOOK (4)	100	15
3	1.0:2.0	10:1	3.0	NH_4Cl (4)	100	56
4	1.0:2.5	10:1	3.0	NH_4Cl (4)	100	61
5	1.0:2.5	20:1	3.0	NH_4Cl (4)	100	57
6	1.0:2.5	20:1	3.0	NH_4Cl (4)	80	60
7	**1.0:2.5**	**20:1**	**3.0**	**NH_4Cl (2)**	**100**	**71**
8	1.0:2.5	20:1	3.0	NH_4Cl (1)	100	63



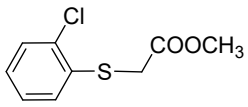
1 **2b-e** **4a-j**



4a,71%



4b,66%



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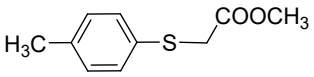
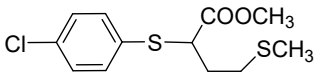


4d,45%



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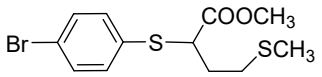

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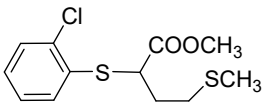

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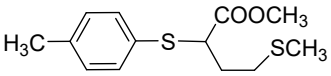
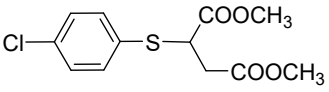
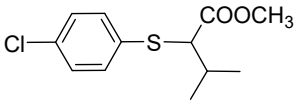


4h,38%



4i,28%



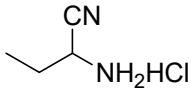
4j,25%

Scheme S2. Deaminative coupling of α-aminomethylester salts.

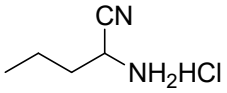
3. General procedure of deaminative coupling of α-aminoacetonitrile salts.

General procedure C: The thiol **1** (0.5 mmol), α-aminoacetonitriles hydrochloride **5a** (1.25 mmol), and $NaNO_2$ (1.75 mmol) were added into a reaction tube. Toluene (1.14 ml) and water (114 μl) were added respectively. The mixture was stirred at 50 °C for 24 h. When the reaction was completed, the mixture was crude after the solvent was removed by the vacuum pump. The crude mixture was purified by column chromatography on silica gel to obtain product **6**.

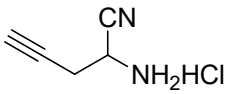
General procedure D: The thiol **1a,c,d,e,f** (0.5 mmol), α-aminoacetonitriles hydrochloride **5b-e** (1.25 mmol), and $NaNO_2$ (1.75 mmol) were added into a reaction tube. Toluene (2.27 ml) and water (227 μl) were added respectively. The mixture was stirred at 25 °C for 24 h. When the reaction was completed, the mixture was crude after the solvent was removed by the vacuum pump. The crude mixture was purified by column chromatography on silica gel to obtain product **7**.



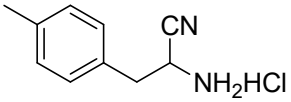
5b



5c



5d



5e

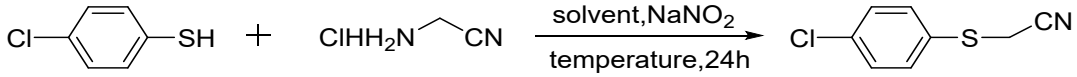
Scheme S3. Synthesis of α-aminoacetonitrile hydrochloride derivatives (5b-e).

The synthesis of 5a and 5b[1]**:** Added ZnI_2 (1.0 mmol) to a mixture of propionaldehyde or butyraldehyde (10 mmol) and TMSCN (12 mmol). Stirring for 20

minutes, then a saturated solution of ammonia of methanol was added and warmed the mixture to 40 °C. After stirring for 3h, the solvent was removed and the residue was extracted with ether, dried by Mg_2SO_4 and filtered, concentrated. Last the concentrate was acidized with MeOH·HCl then collected the powder (yield 40-60%).

The synthesis of 5d and 5e[2]: Added the alkyl halide (11 mmol), saturated sodium hydroxide (100 mmol) and benzyl triethylammonium chloride (1.0 mmol) to a solution of 2-[(diphenyl methylene)amino]acetonitrile (10 mmol) in DCE. The mixture was stirred until the reaction was completed. The diluted mixture with water and extracted with DCM. Combined the organic phase and concentrated it to leave a crude product. Dissolved the crude product with THE, added 1.0 M HCl aqueous (15 ml) and stirred for 3 h. Then poured the reaction mixture into water and washed with ether three times to remove the benzophenone. The aqueous layer was neutralized by 10 M NaOH and extracted with DCM. Combined the organic phase dried with Ma_2SO_4, filtered and concentrated. The residue was dissolved with ether and then acidized with MeOH·HCl. Collected the powder (yield 40-50%).

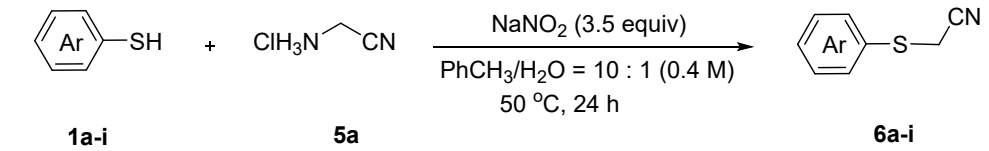
Table S3. Optimization of reaction conditions of α-aminoacetonitriles salts.



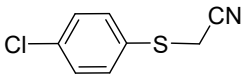
1a **5a** **6a**

entry	**1a**:**5a**	solvent (toluene/H_2O)	$NaNO_2$ (equiv)	t (°C)	yield (%)
1	1.0:2.0	20:1	2.5	50	35
2	1.0:2.0	20:1[a]	2.5	50	30
3	1.0:2.0	20:1[b]	2.5	50	0
4	1.0:2.0	20:1[c]	2.5	50	10
5	1.0:2.0	20:1	3.0	50	44
6	1.0:2.0	20:1	3.5	50	52
7	1.0:2.5	20:1	3.5	50	62
8	**1.0:2.5**	**10:1**	**3.5**	**50**	**72**
9	1.0:2.5	5:1	3.5	50	61
10	1.0:2.5	10:1	3.5	25	63
11	1.0:2.5	10:1	3.5	75	57

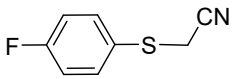
[a] Solvent was DCE/H_2O. [b] Solvent was dioxane/H_2O. [c] Solvent was CH_3CN/H_2O.



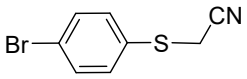
1a-i **5a** **6a-i**



6a,72%



6b,49%



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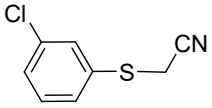
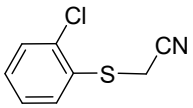
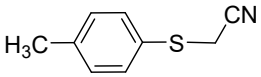


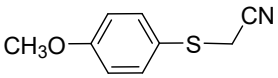
6d,62%



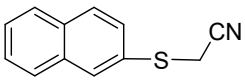
6e,71%



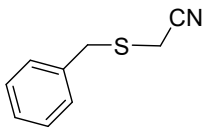
6f,55%



6g,50%



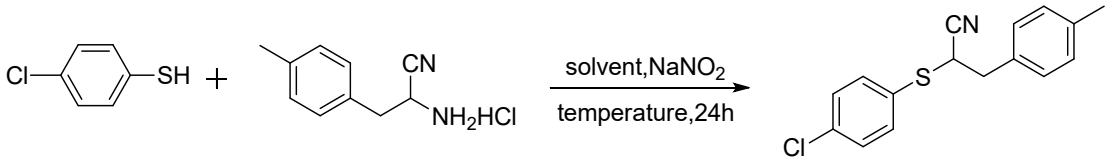
6h,63%



6i,32%

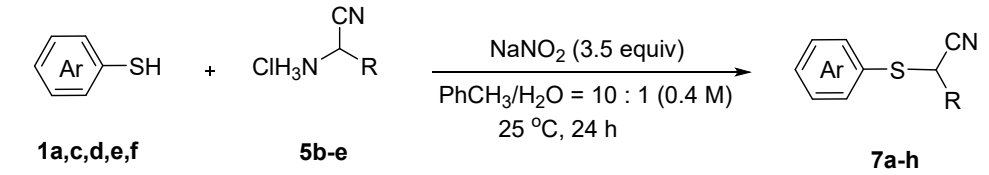
Scheme S4. Deaminative coupling of α-aminoacetonitrile salts.

Table S4. Optimization of reaction conditions of α-benzylaminoacetonitriles salts.

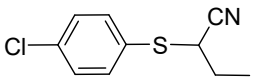


1a **5e** **7g**

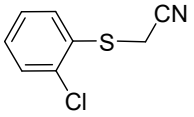
entry	**1a**:**5e**	solvent (toluene/H_2O)	$NaNO_2$ (equiv)	t (°C)	yield (%)
1	1.0:2.5	10:1 (0.4 M)	3.5	50	35
2	1.0:2.5	10:1 (0.4 M)	3.5	25	41
3	1.0:2.5	10:1 (0.2 M)	3.5	25	48
4	1.0:2.5	10:1 (0.1 M)	3.5	25	39



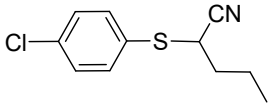
1a,c,d,e,f **5b-e** **7a-h**



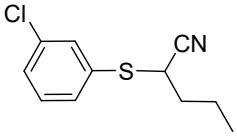
7a,61%



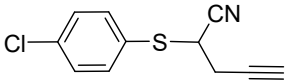
7b,53%



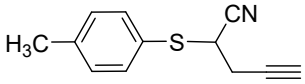
7c,52%



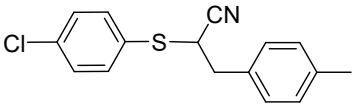
7d,47%



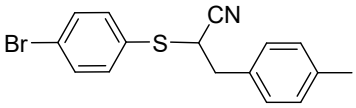
7e,57%



7f,52%

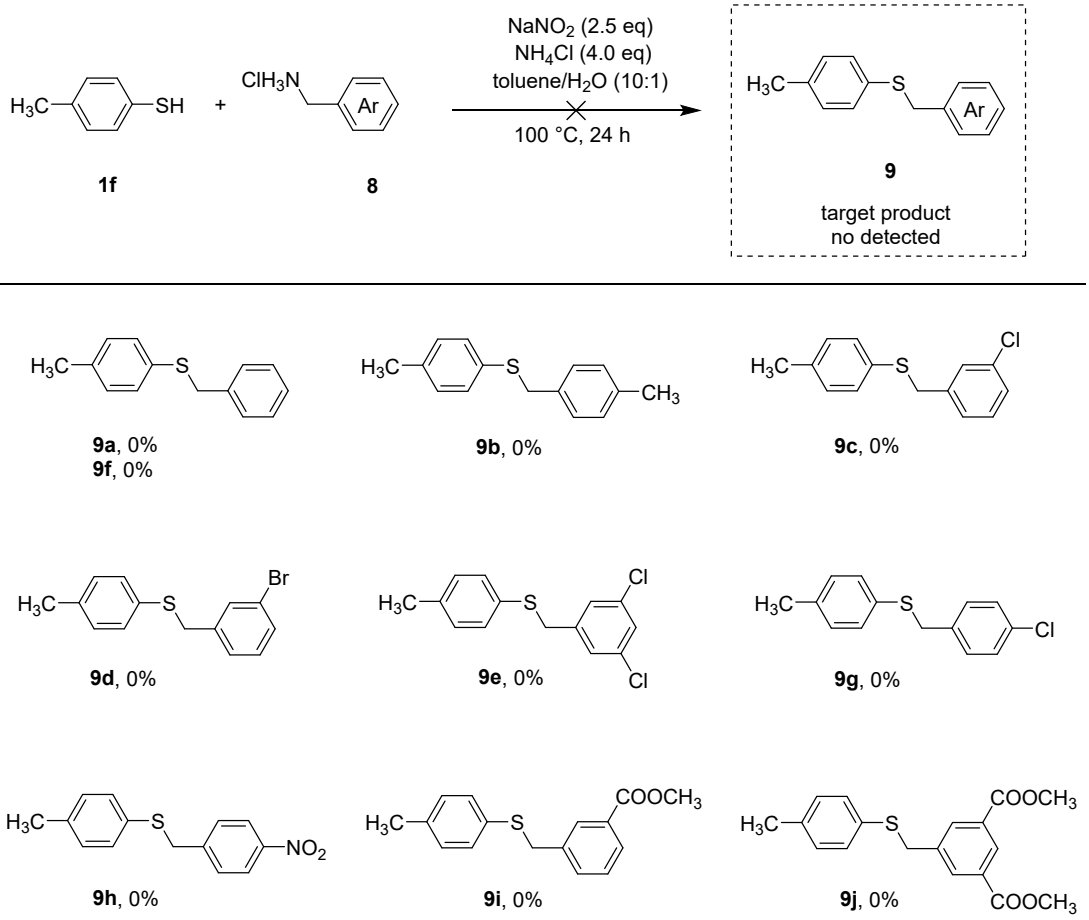


7g,48%



7h,44%

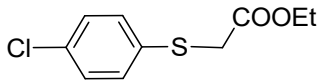
Scheme S5. Deaminative coupling of α-substituted aminoacetonitrile salts.



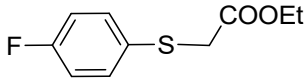
Scheme S6. Extension: deaminative coupling of benzylamines.[a,b,c]

[a] The substrates **8a**-**8e** were benzylamines. [b] The substrates **8f**-**8j** were benzylamine hydrochlorides. [c] Determined by TLC and GC-MS.

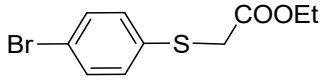
4. Analytical data for all products.



Ethyl 2-[(4-chlorophenyl)thio]acetate (3a): colorless liquid, 103.8 mg (90% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 133.5, 133.1, 131.4, 129.1, 61.6, 36.7, 14.1. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{10}H_{11}ClO_2S$ 260.0168; Found: 260.0168.

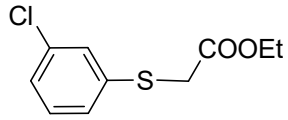


Ethyl 2-[(4-fluorophenyl)thio]acetate (3b)[3]: colorless liquid, 75.0 mg (70% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.32 (m, 2H), 7.00 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.56 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 163.4, 161.4, 133.5, 133.4, 129.8, 129.8, 116.2, 116.1, 61.5, 37.8, 14.1.

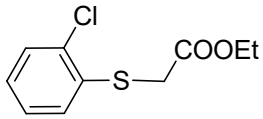


Ethyl 2-[(4-fluorophenyl)thio]acetate (3c)[3]: colorless liquid, 114.2mg (83% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 1.22 (t,

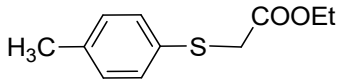
J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 134.2, 132.0, 131.4, 120.9, 61.6, 36.5, 14.1.



Ethyl 2-[(4-fluorophenyl)thio]acetate (3d)[3]: colorless liquid, 91.1 mg (79% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.29 – 7.24 (m, 1H), 7.19 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.64 (s, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 137.2, 134.7, 130.0, 129.1, 127.5, 126.9, 61.7, 36.2, 14.11.

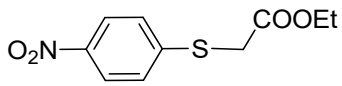


Ethyl 2-[(2-chlorophenyl)thio]acetate (3e)[4]: colorless liquid, 93.4 mg (81% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.22 (m, 1H), 7.16 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 134.2, 134.1, 129.8, 129.7, 127.6, 127.2, 61.6, 35.1, 14.0.

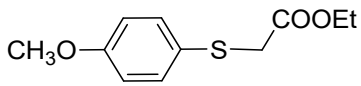


Ethyl 2-[(4-methylphenyl)thio]acetate (3f)[4]: colorless liquid, 84.1 mg (80% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.57 (s, 2H), 2.31 (s,

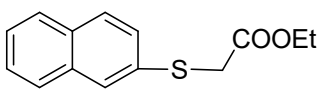
3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 137.2, 131.2, 130.9, 129.7, 61.4, 37.4, 21.0, 14.1.



Ethyl 2-[(4-nitrophenyl)thio]acetate (3g)[4]: yellow oil, 47.0 mg (39% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.77 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 145.7, 145.6, 126.9, 124.1, 62.2, 34.7, 14.2.

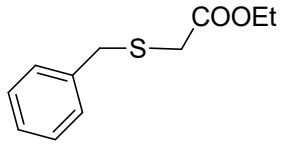


Ethyl 2-[(4-methoxyphenyl)thio]acetate (3h)[4]: colorless liquid, 78.0 mg (69% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.50 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 159.6, 134.1, 124.9, 114.6, 61.3, 55.2, 38.6, 14.1.

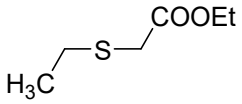


Ethyl 2-(naphthalen-2-ylthio)acetate (3i)[5]: colorless liquid, 103.5 mg (84% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.79 – 7.66 (m, 3H), 7.52 – 7.35 (m, 3H), 4.13 (q, J = 7.1 Hz, 2H), 3.70 (s, 2H),

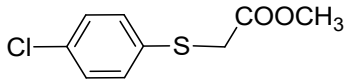
1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 133.6, 132.4, 132.0, 128.5, 128.0, 127.6, 127.4, 127.2, 126.6, 126.0, 61.5, 36.5, 14.0.



Ethyl 2-(benzylthio)acetate (3j)[6]: colorless liquid, 21.0 mg (25% yield); R_f (petroleum ether/ethyl acetate 20:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.83 (s, 2H), 3.06 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 137.3, 129.2, 128.6, 127.3, 61.4, 36.4, 32.3, 14.3.

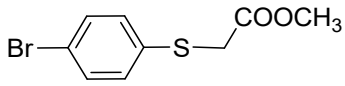


Ethyl 2-(ethylthio)acetate (3k)[7]: colorless liquid, 15.6 mg (21% yield); R_f (petroleum ether/ethyl acetate 20:1) =0.4.^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (q, J = 7.1 Hz, 2H), 3.23 (s, 2H), 2.67 (q, J = 7.4 Hz, 2H), 1.28 (td, J = 7.3, 5.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.60, 170.61, 61.22, 33.27, 33.01, 26.59, 26.53, 14.12, 14.09, 14.03.

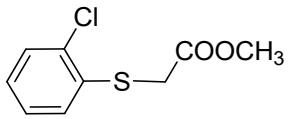


Methyl 2-((4-chlorophenyl)thio)acetate (4a)[8]: colorless liquid, 76.9 mg (71% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J

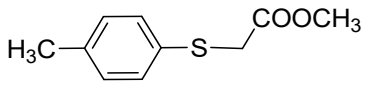
= 8.7 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 3H), 3.62 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 133.4, 133.2, 131.4, 129.2, 52.6, 36.6.



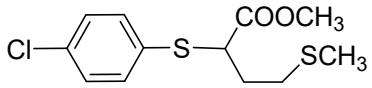
Methyl 2-(4-bromophenylthio)acetate (4b)[8]: colorless liquid, 86.1 mg (66% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 3H), 3.62 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 134.1, 132.1, 131.4, 121.0, 52.6, 36.3.



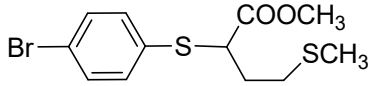
Methyl 2-(2-chlorophenylthio)acetate (4c)[8]: colorless liquid, 69.3 mg (64% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.23 (m, 1H), 7.16 (m, 1H), 3.71 (s, 3H), 3.69 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 134.1, 134.1, 129.8, 129.7, 127.7, 127.4, 52.7, 34.9.



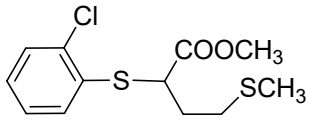
Methyl 2-(*p*-tolylthio)acetate (4d)[8]: colorless liquid, 44.1 mg (45% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 3.70 (s, 3H), 3.60 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 137.4, 131.1, 130.9, 129.9, 52.5, 37.3, 21.1.



Methyl 2-(4-chlorophenylthio)-4-(methylthio)butanoate (4e): colorless liquid, 84.3 mg (58% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 3.83 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.61 (m, 2H), 2.16 m, 1H), 2.07 (s, 3H), 2.00 m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 134.5, 131.2, 129.2, 52.4, 49.2, 31.3, 30.4, 15.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{15}ClO_2S_2$ 290.0202; Found: 290.0204.

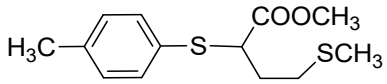


Methyl 2-(4-bromophenylthio)-4-(methylthio)butanoate (4f): colorless liquid, 77.1 mg (46% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 3.83 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.67 – 2.57 (m, 2H), 2.21 – 2.13 (m, 1H), 2.07 (s, 3H), 2.03 – 1.96 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 134.6, 132.1, 132.0, 122.6, 52.4, 49.1, 31.3, 30.4, 15.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{15}BrO_2S_2$ 333.9697; Found: 333.9696.

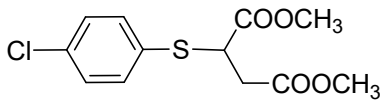


Methyl 2-(2-chlorophenylthio)-4-(methylthio)butanoate (4g): colorless liquid, 64.0 mg (44% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.44 – 7.39 (m, 1H), 7.26 – 7.20 (m, 2H), 3.98 (t, J = 7.3 Hz, 1H), 3.67 (s, 3H), 2.69 – 2.61 (m, 2H), 2.24 (m, 1H), 2.14 – 2.10 (m, 1H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 136.7, 133.8, 132.5, 130.0, 129.1, 127.3, 52.4, 48.0, 31.4, 30.5, 15.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{15}ClO_2S_2$ 290.0202; Found: 290.0205.

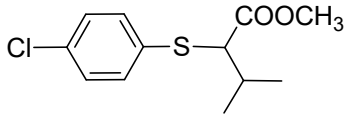


Methyl 4-(methylthio)-2-(*p*-tolylthio)butanoate (4h): colorless liquid, 51.4 mg (38% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 3.77 (t, J = 7.2 Hz, 1H), 3.68 (s, 3H), 2.67 – 2.59 (m, 2H), 2.34 (s, 3H), 2.17 – 2.11 (m, 1H), 2.06 (s, 3H), 2.04 – 1.96 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 138.7, 134.0, 129.8, 128.8, 52.3, 49.5, 31.4, 30.5, 21.2, 15.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{13}H_{18}O_2S_2$ 270.0748; Found: 270.0749.

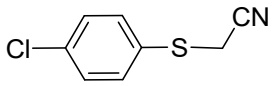


Dimethyl 2-(4-chlorophenylthio)succinate (4i)[9]: colorless liquid, 40.4 mg (28% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 3.98 (dd, J = 9.4, 5.9 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 2.94 (dd, J = 17.0, 9.4 Hz, 1H), 2.73 (dd, J = 17.0, 5.9 Hz, 1H).

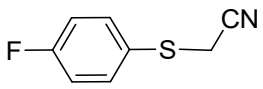
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 170.9, 135.6, 135.3, 130.1, 129.4, 52.6, 52.2, 45.7, 36.3.



Methyl 2-(4-chlorophenylthio)-3-methylbutanoate (4j): colorless liquid, 32.4 mg (25% yield); R_f (petroleum ether/ethyl acetate 10:1) =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 3.65 (s, 3H), 3.39 (d, J = 8.8 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.14 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 134.0, 133.8, 132.8, 129.2, 59.2, 52.1, 30.6, 20.7, 20.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{15}ClO_2S$ 258.0481; Found: 258.0482.

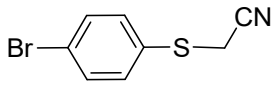


2-[(4-chlorophenyl)thio]acetonitrile (6a)[10]**:** colourless solid, 66.0 mg (72% yield); mp 82-83 °C; R_f (petroleum ether/ethyl acetate 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 3.55 (s, 2H)； ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 134.1, 130.3, 129.9, 116.3, 77.4, 77.1, 76.8, 21.7.

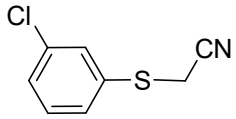


2-[(4-fluorophenyl)thio]acetonitrile (6b)[10]**:** colourless liquid，41.0 mg (49% yield); R_f (petroleum ether/ethyl acetate5:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J

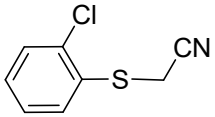
= 8.8, 5.2 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 3.51 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 162.6, 135.9 (d, J = 8.6 Hz), 127.0, 117.0, 116.9, 116.4, 77.4, 77.1, 76.9, 22.4.



2-[(4-bromophenyl)thio]acetonitrile (6c)[10]**:** white solid，72.5 mg (64% yield); mp 87-88 °C; R_f (petroleum ether/ethyl acetate 10:1) =0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.55 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 132.8, 131.1, 123.5, 116.24, 77.4, 77.1, 76.9, 21.3.

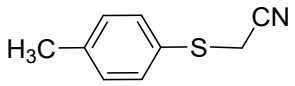


2-[(3-chlorophenyl)thio]acetonitrile (6d)[11]**:** colourless liquid, 56.7 mg (62% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, J = 2.0, 1.6 Hz, 1H), 7.42 (dd, J = 5.3, 3.2 Hz, 1H), 7.33 (dd, J = 5.1, 2.9 Hz, 2H), 3.59 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 133.93, 131.6, 130.7, 130.0, 129.00, 116.10, 77.4, 77.1, 76.9, 21.0.

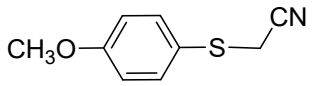


2-[(2-chlorophenyl)thio]acetonitrile (6e)[12]**:** colourless liquid, 65.6 mg (71% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd,

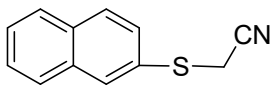
J = 5.8, 3.6 Hz, 1H), 7.46 (dd, *J* = 5.1, 4.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 3.66 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 133.2, 130.8, 130.3, 130.0, 127.9, 115.9, 77.4, 77.1, 76.9, 19.3.



2-[(4-methylphenyl)thio]acetonitrile (6f)[10]**:** colourless liquid, 45.2 mg (55% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 3.51 (s, 2H), 3.51 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 133.2, 130.4, 128.4, 116.7, 77.4, 77.1, 76.9, 22.0, 21.2.

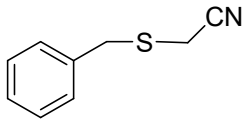


2-[(4-methoxyphenyl)thio]acetonitrile (6g)[10]**:** colourless liquid, 44.8 mg (50% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.45 (s, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 160.9, 136.0, 122.18, 116. 8, 115.2, 77.4, 77.1, 76.9, 55.4, 22. 9.

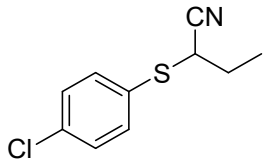


2-(naphthalen-2-ylthio)acetonitrile (6h)[13]**:** colourless solid, 62.8 mg (63%); mp 90-91 °C; R_f (petroleum ether/ethyl acetate 10:1) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ

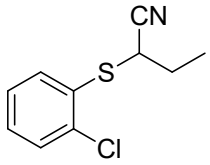
8.05 (d, J = 0.6 Hz, 1H), 7.84 (dd, J = 10.0, 7.0 Hz, 3H), 7.60 – 7.49 (m, 3H), 3.63 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.6, 132.9, 131.7, 129.3 (d, J = 11.8 Hz), 128.7, 127.74 (d, J = 7.7 Hz), 127.0 (d, J = 11.3 Hz), 116.6, 77.36, 77.1, 76.9, 21.2.



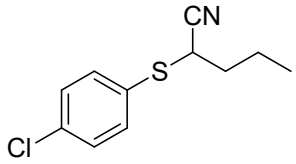
2-(benzylthio)acetonitrile (6i)[14]**:** colourless liquid, 26.1 mg (32%); R_f (petroleum ether/ethyl acetate 10:1) =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 3.92 (s, 2H), 3.07 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 129.1, 128.9, 127.85 (s), 116.3, 77.4, 77.1, 76.9, 36.0, 15.9.



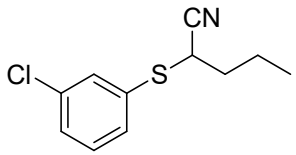
2-[(4-chlorophenyl)thio]butanenitrile (7a)[15]**:** colourless liquid, 61.0 mg (55% yield); R_f (petroleum ether/ethyl acetate 20:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 3.62 (t, J = 7.3 Hz, 1H), 1.87 (dd, J = 14.7, 7.3 Hz, 2H), 1.17 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1 (d, J = 12.7 Hz), 129.8, 129.1, 119.0, 77.36, 77.1, 76.9, 38.9, 26.13, 11.7.



2-[(2-chlorophenyl)thio]butanenitrile (7b)[15]**:** colourless liquid, 58.1 mg (53% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.50 – 7.46 (m, 1H), 7.36 – 7.28 (m, 2H), 3.88 (dd, J = 7.7, 6.3 Hz, 1H), 2.02 – 1.94 (m, 2H), 1.23 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 135.6, 130.68, 130.3, 127.8, 118.8, 77.4, 77.1, 76.9, 37.3, 26.0, 11.7.

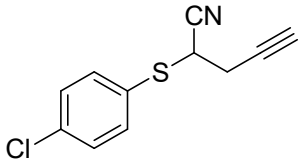


2-[(4-chlorophenyl)thio]pentanenitrile (7c): colourless liquid, 59.1 mg (52% yield); R_f (petroleum ether/ethyl acetate10:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 3.67 (dd, J = 7.9, 7.1 Hz, 1H), 1.85 – 1.77 (m, 2H), 1.64 – 1.56 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1 (d, J = 12.5 Hz), 129.8, 129.2, 119.1, 77.4, 77.1, 76.9, 37.0, 34.4, 20.4, 13.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{11}H_{12}ClNS$ 221.0379; Found: 221.0374.

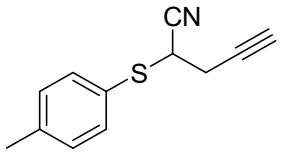


2-[(3-chlorophenyl)thio]pentanenitrile (7d): colourless liquid, 53.3 mg (47% yield); R_f (petroleum ether/ethyl acetate 20:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (t, J = 1.8 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.37 (ddd, J = 8.1, 1.9, 1.3 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 3.73 (dd, J = 8.1, 6.8 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.66 – 1.57 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 133.8, 132.9, 132.2,

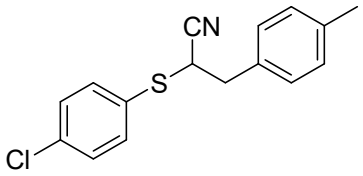
130.6, 129.6), 119.0, 77.4, 77.1), 76.9, 36.8, 34.4, 20.4, 13.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{11}H_{12}ClNS$ 225.0379; Found: 225.0382.



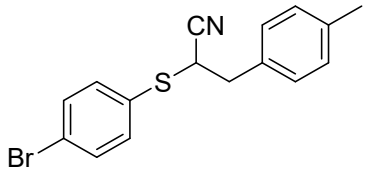
2-[(4-chlorophenyl)thio]pent-4-ynenitrile (7e): colourless liquid, 63.2 mg (57% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 3.83 (t, J = 7.4 Hz, 1H), 2.70 (qdd, J = 17.0, 7.4, 2.6 Hz, 2H), 2.25 (t, J = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9 (d, J = 8.3 Hz), 130.0, 127.5, 117.7, 77.6, 77.4, 77.1, 76.9, 73.1, 36.3, 23.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{11}H_8ClNS$ 221.0066; Found: 221.0067.



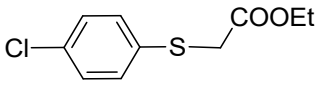
2-[(4-methylphenyl)thio]pent-4-ynenitrile (7f): colourless liquid, 52.3 mg (52% yield); R_f (petroleum ether/ethyl acetate 10:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 3.79 (dd, J = 7.8, 7.1 Hz, 1H), 2.74 – 2.62 (m, 2H), 2.38 (s, 3H), 2.23 (t, J = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 135.8, 130.5, 125.5), 118.00, 78.0, 77.4, 77.1, 76.9, 72.8, 36.4, 23.3, 21.4. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{11}NS$ 201.0612; Found: 201.0611.

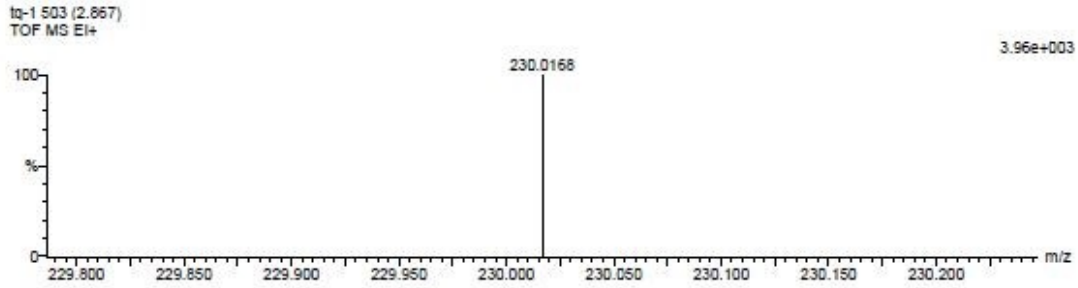


2-[(4-chlorophenyl)thio]-3-(*p*-tolyl)propanenitrile (7g): colourless solid, 68.6 mg (48% yield); mp 102-103 °C; R_f (petroleum ether/ethyl acetate 20:1) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.17 – 7.12 (m, 4H), 3.85 (dd, J = 8.9, 6.2 Hz, 1H), 3.07 (qd, J = 13.9, 7.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 136.2 (d, J = 18.2 Hz), 132.4, 129.9 (d, J = 10.3 Hz), 129.7, 129.0, 127.4, 118.7, 77.4, 77.1, 76.9, 39.1, 38.5, 21.2. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{14}ClNS$ 287.0535; Found: 287.0534.



2-[(4-bromophenyl)thio]-3-(p-tolyl)propanenitrile (7h): colourless solid, 70.4 mg (44% yield); mp 108-109 °C; R_f (petroleum ether/ethyl acetate 20:1) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.18 – 7.12 (m, 4H), 3.85 (dd, J = 8.9, 6.3 Hz, 1H), 3.07 (qd, J = 13.9, 7.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 136.3, 132.8, 132.4, 129.9, 129.7, 129.0, 127.4, 118.7, 77.4, 77.1, 76.9, 39.0, 38.5, 21.2. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{14}BrNS$ 331.0031; Found: 331.0033.





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Maximum:		0.8	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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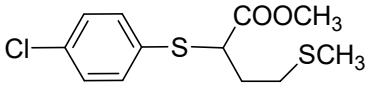
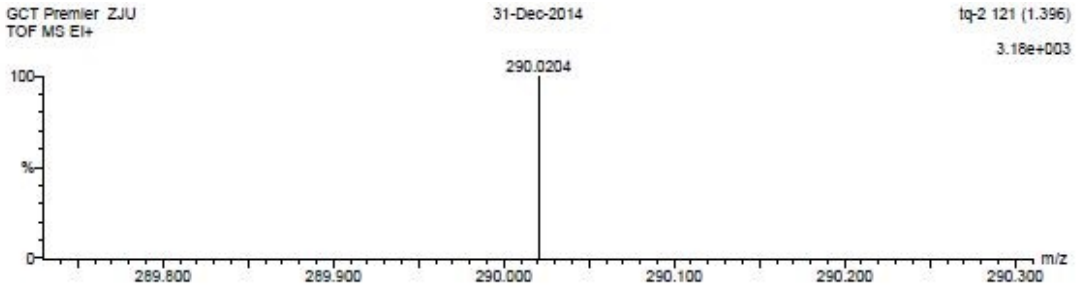
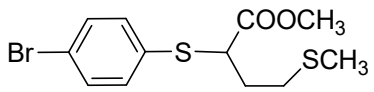
HRMS of Compound **3a**.

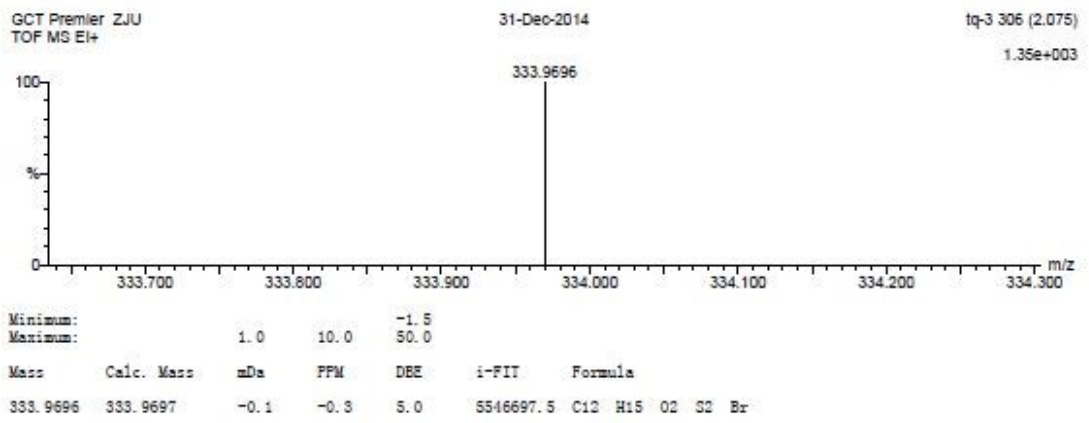




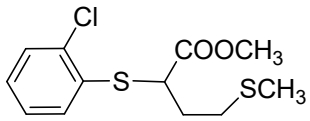
Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
290.0204	290.0202	0.2	0.7	5.0	5547611.5	C12 H15 O2 S2 Cl

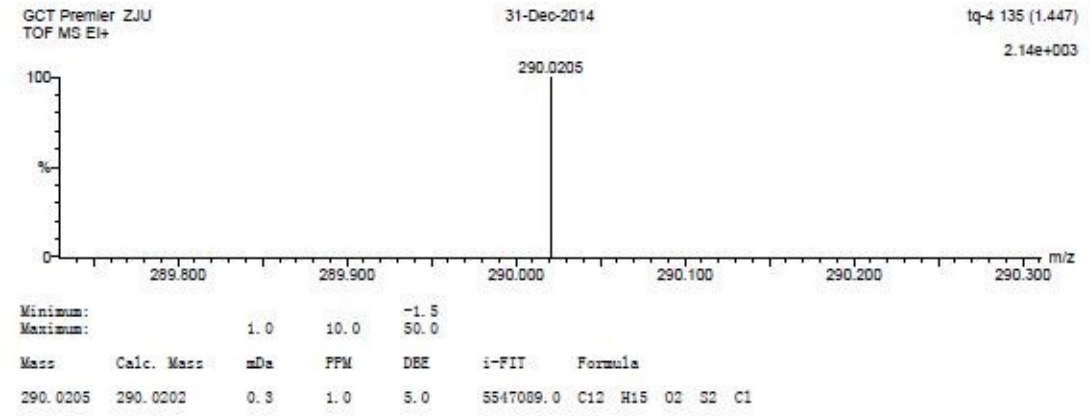
HRMS of Compound **4e**.



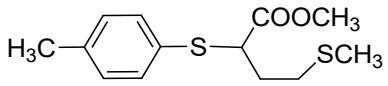


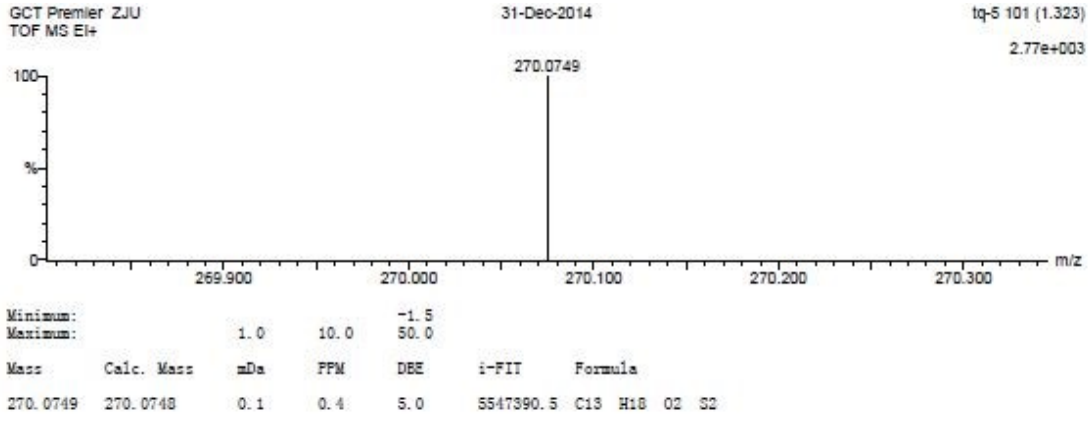
HRMS of Compound **4f**.





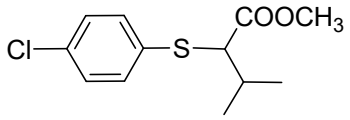
HRMS of Compound **4g**.

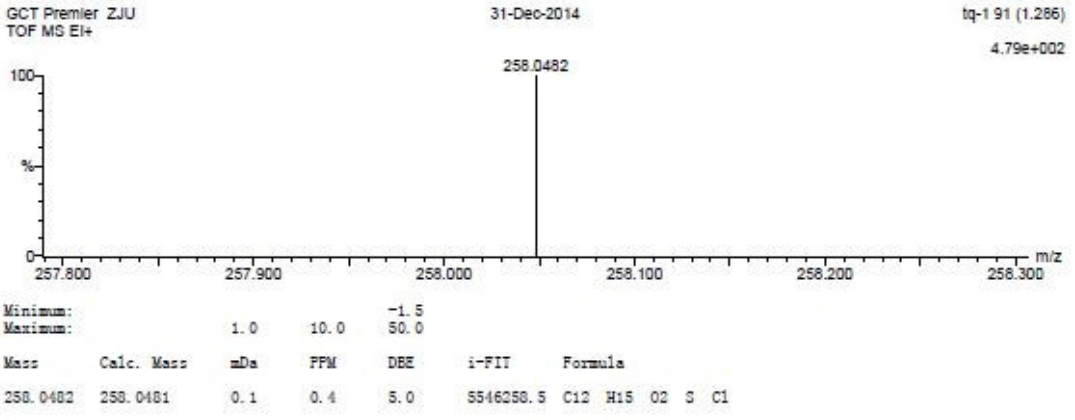




Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
270.0749	270.0748	0.1	0.4	5.0	5547390.5	C13 H18 O2 S2

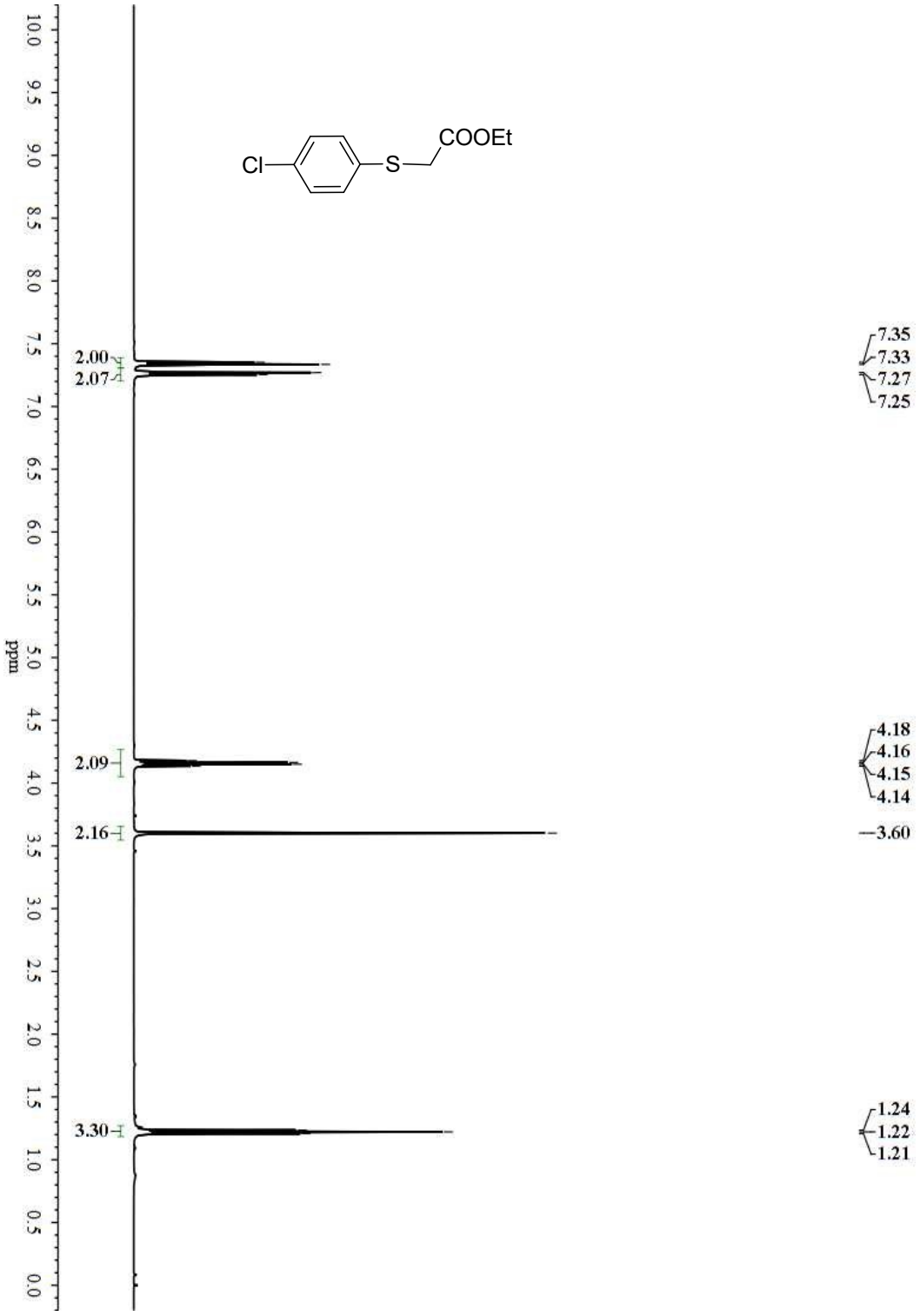
HRMS of Compound **4h**.



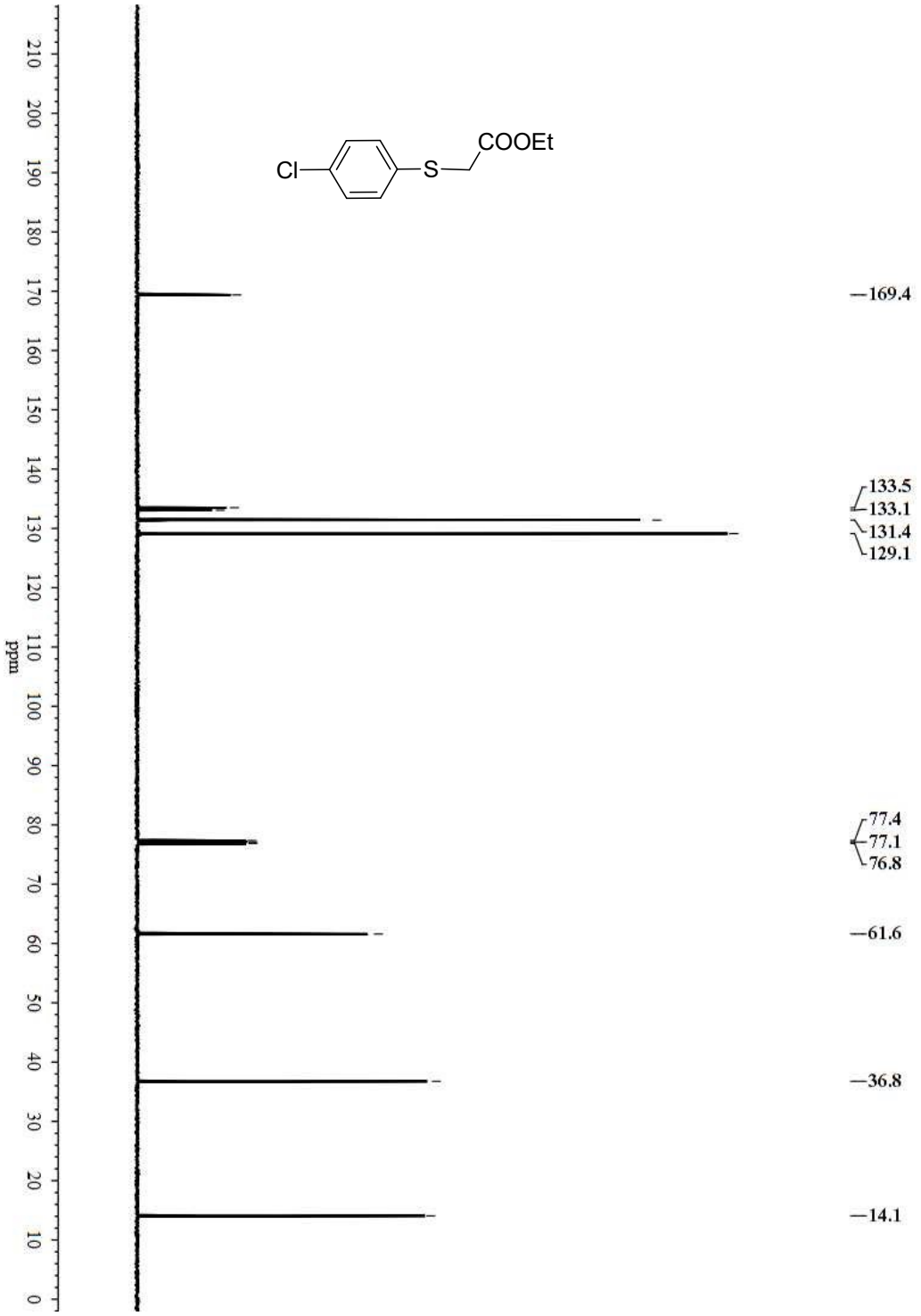


Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
258.0482	258.0481	0.1	0.4	5.0	5546258.5	C12 H15 O2 S Cl

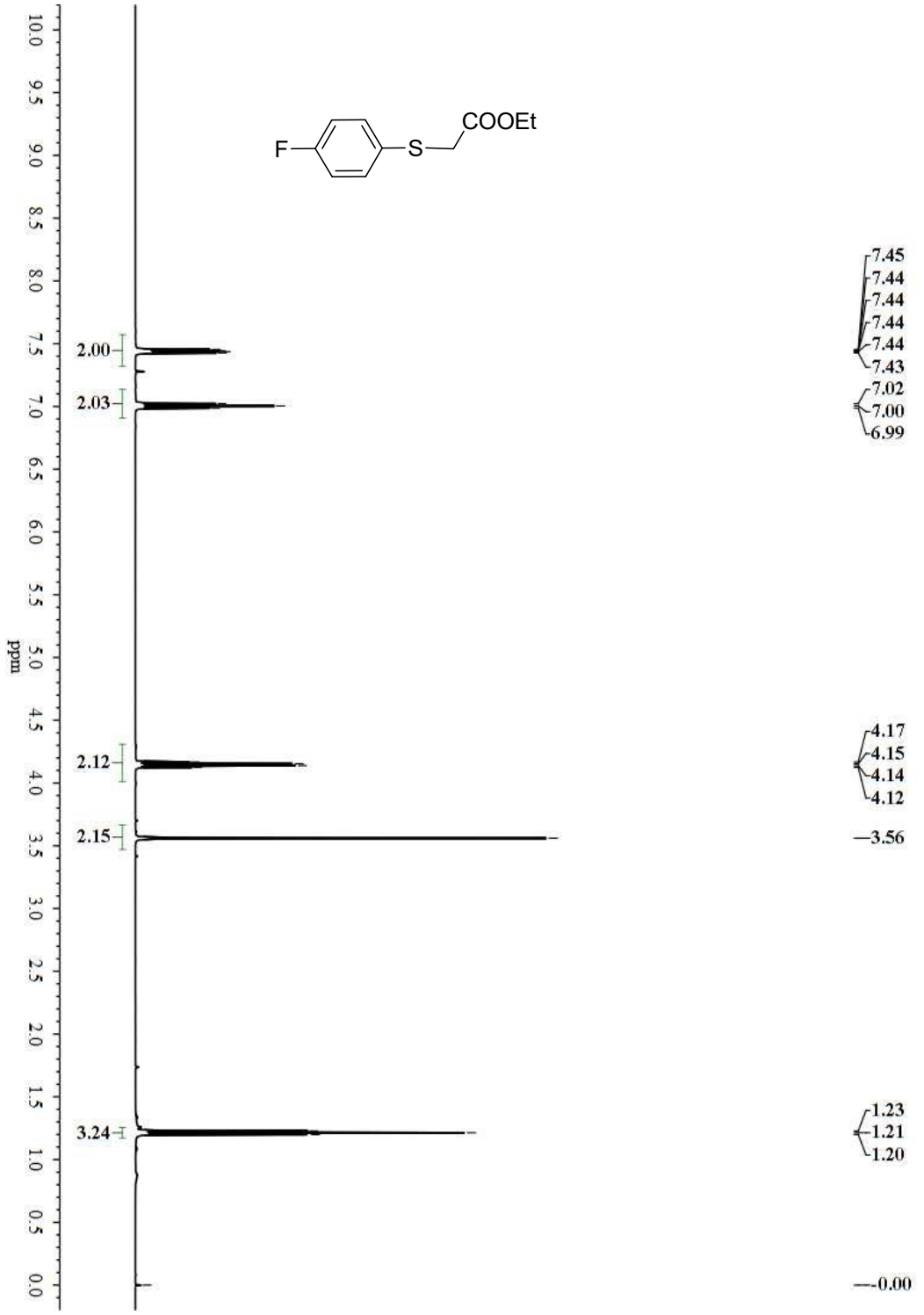
HRMS of Compound **4j**.



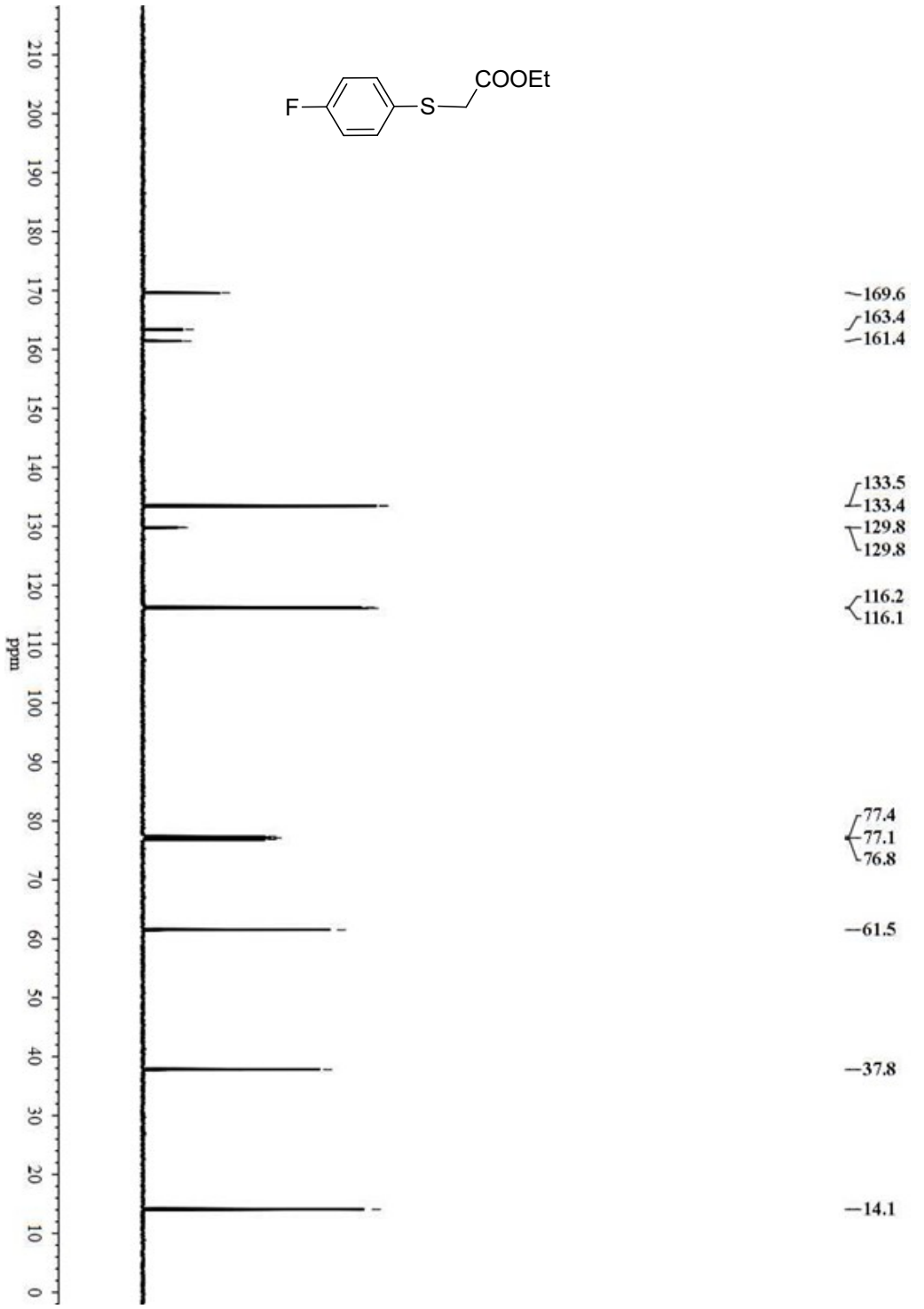
^{1}H NMR Spectra of Compound **3a**.



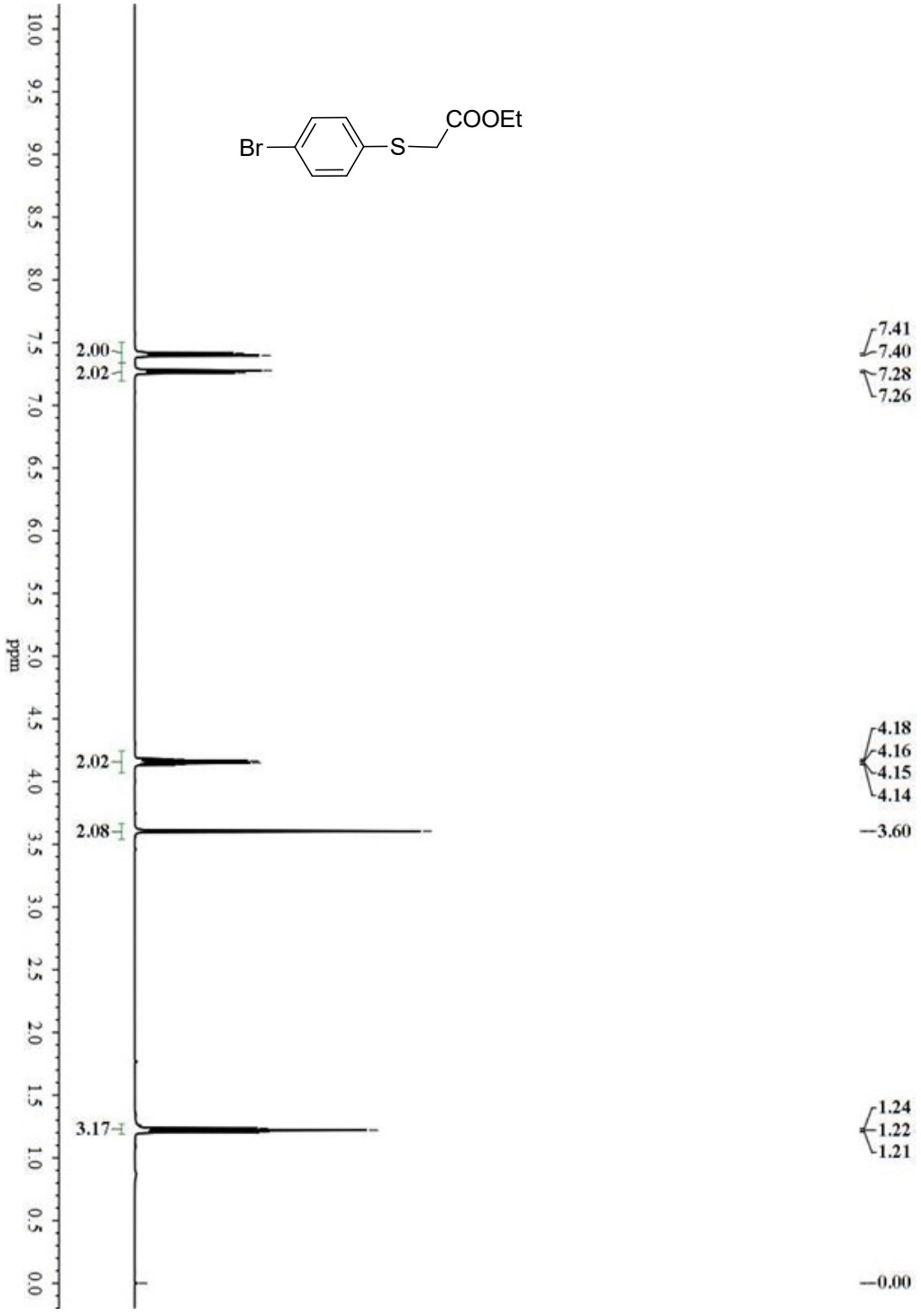
^{13}C NMR Spectra of Compound **3a**.



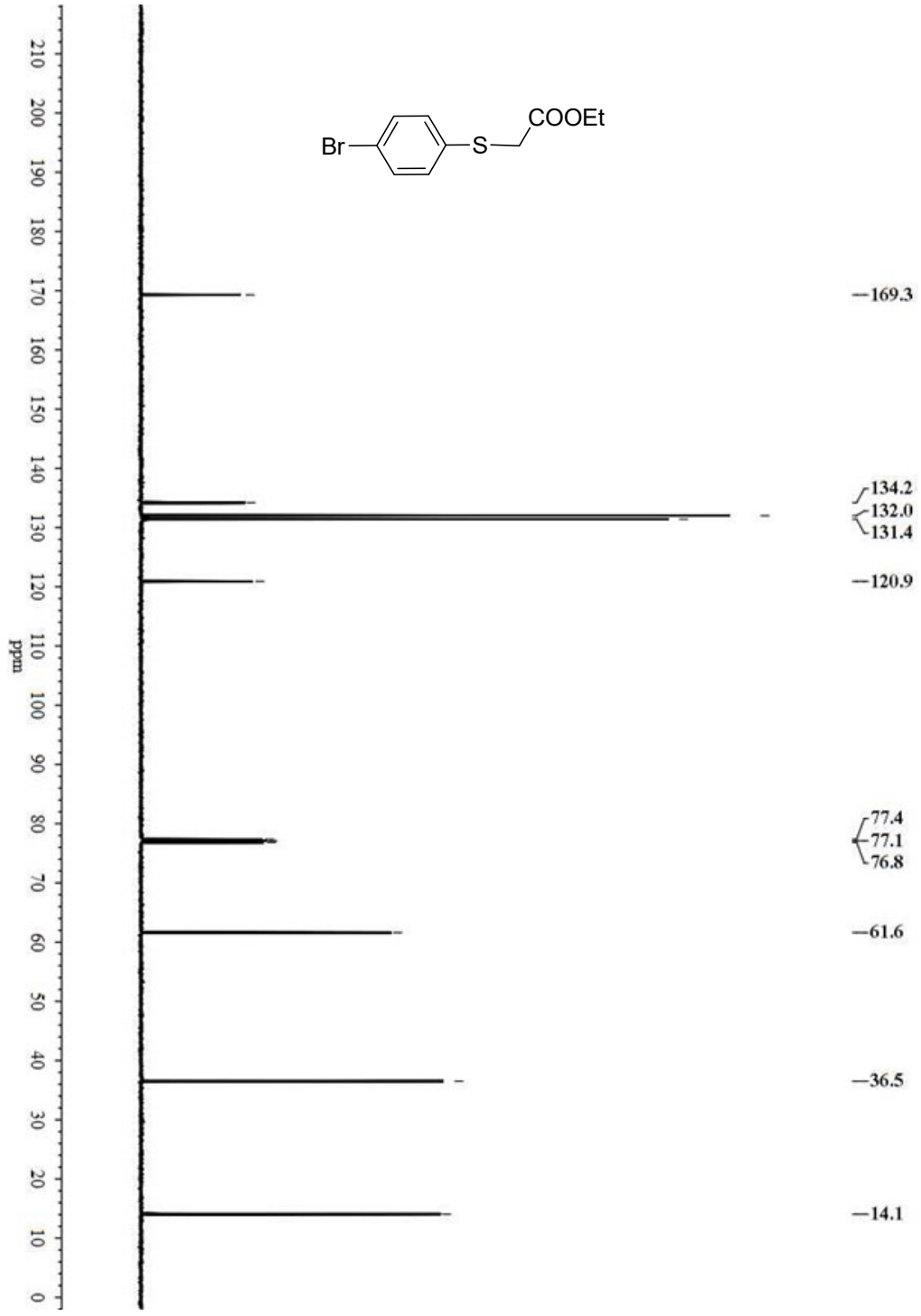
^{1}H NMR Spectra of Compound **3b**.



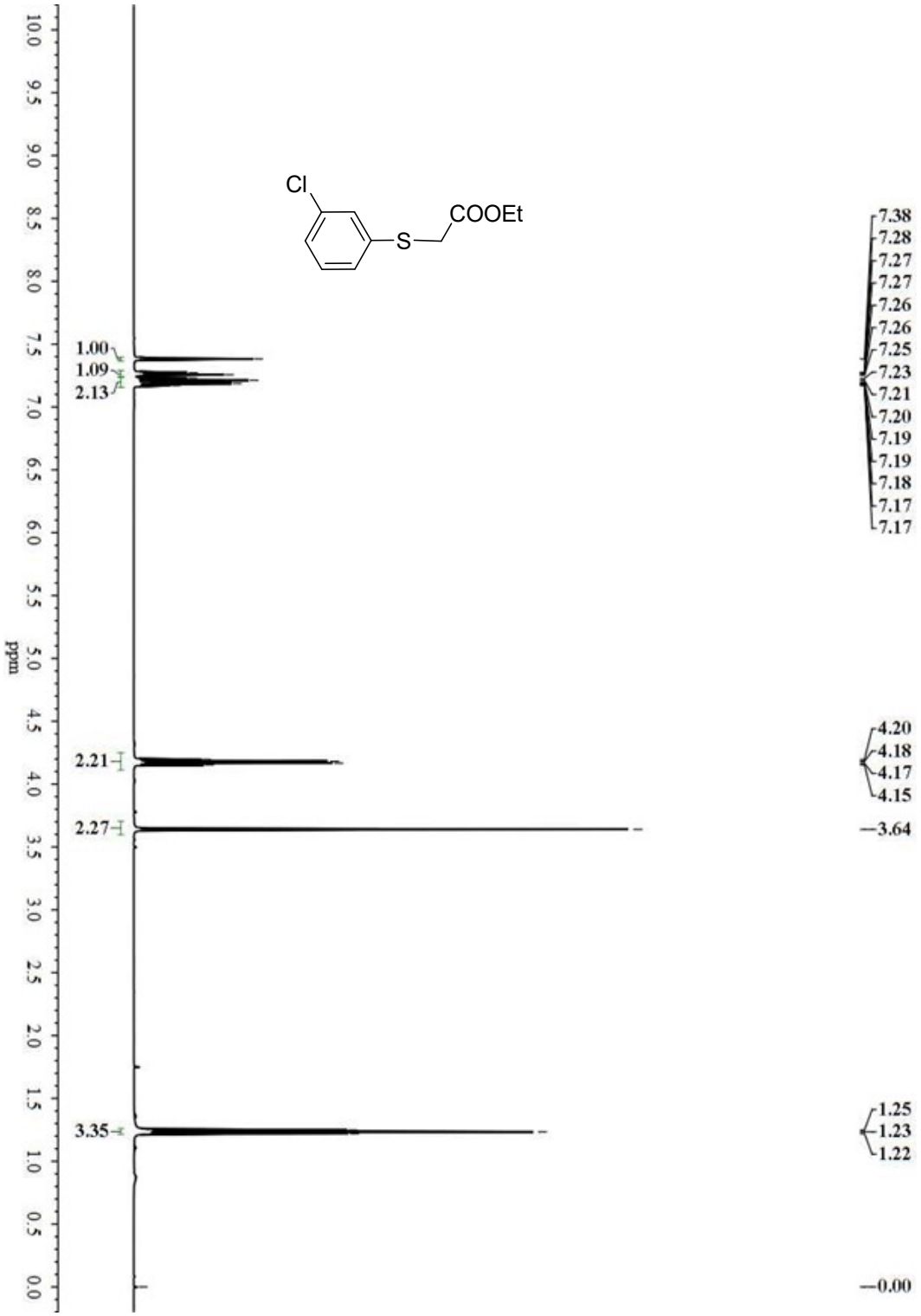
^{13}C NMR Spectra of Compound **3b**.



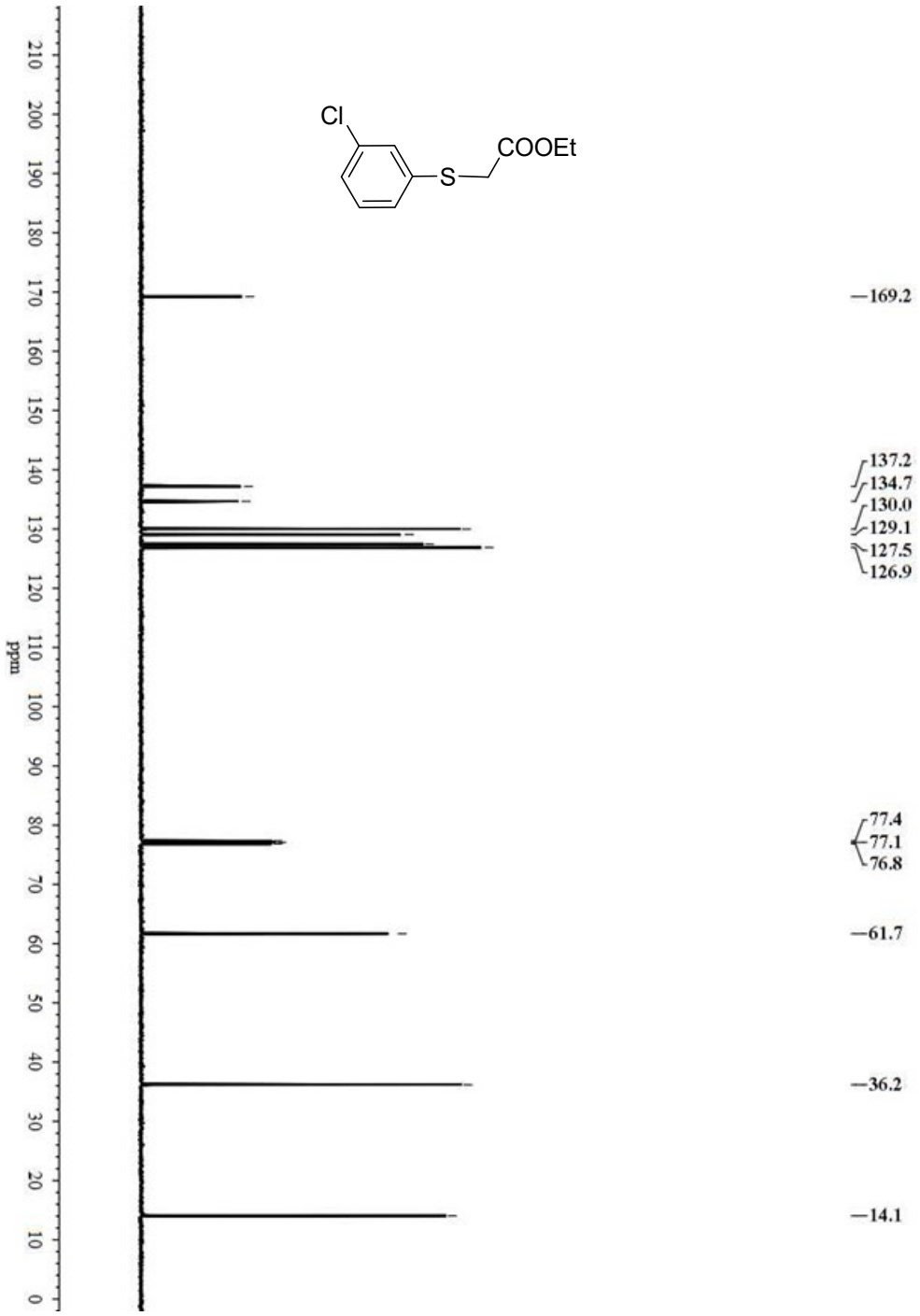
^{1}H NMR Spectra of Compound **3c**.



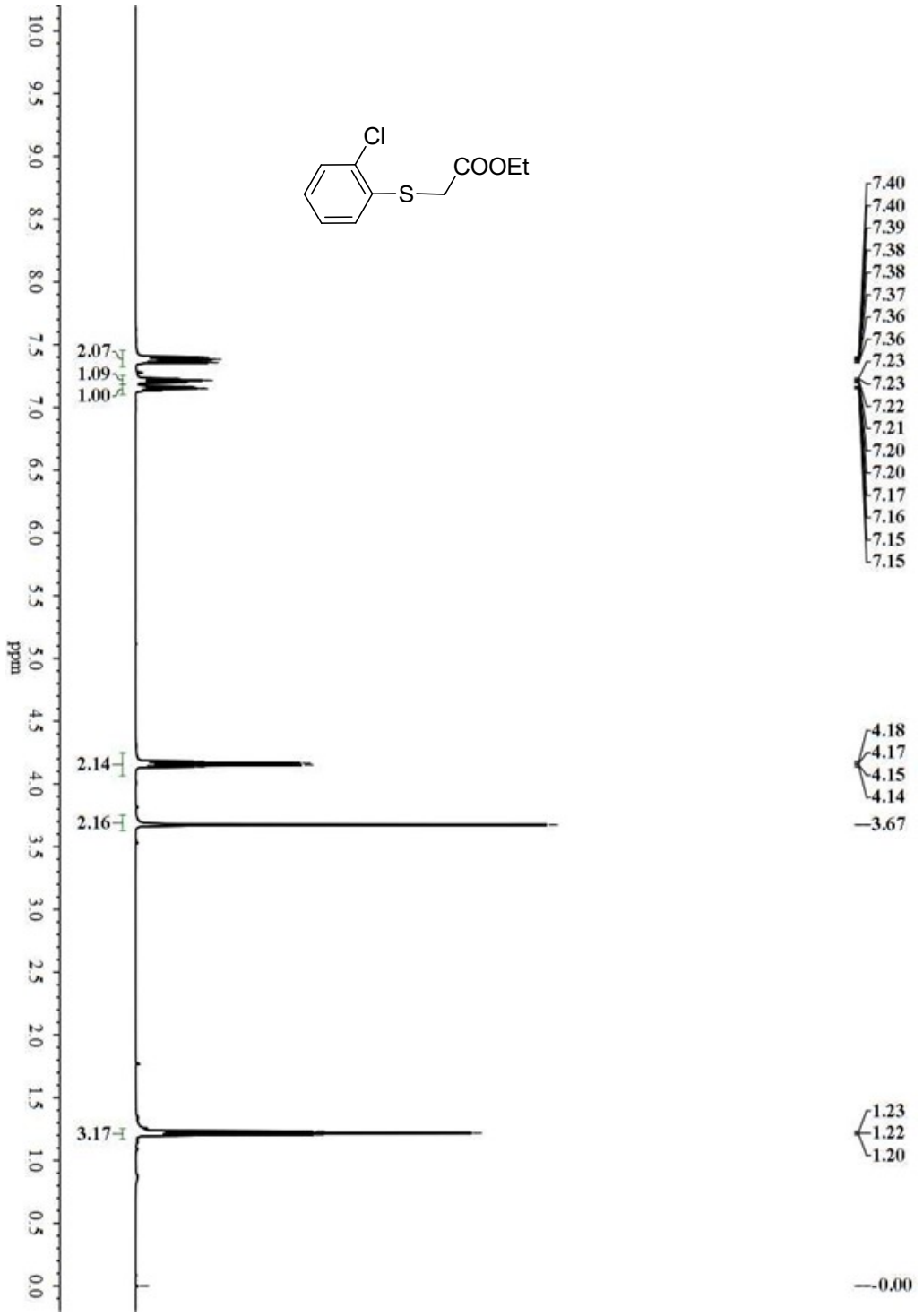
^{13}C NMR Spectra of Compound **3c**.



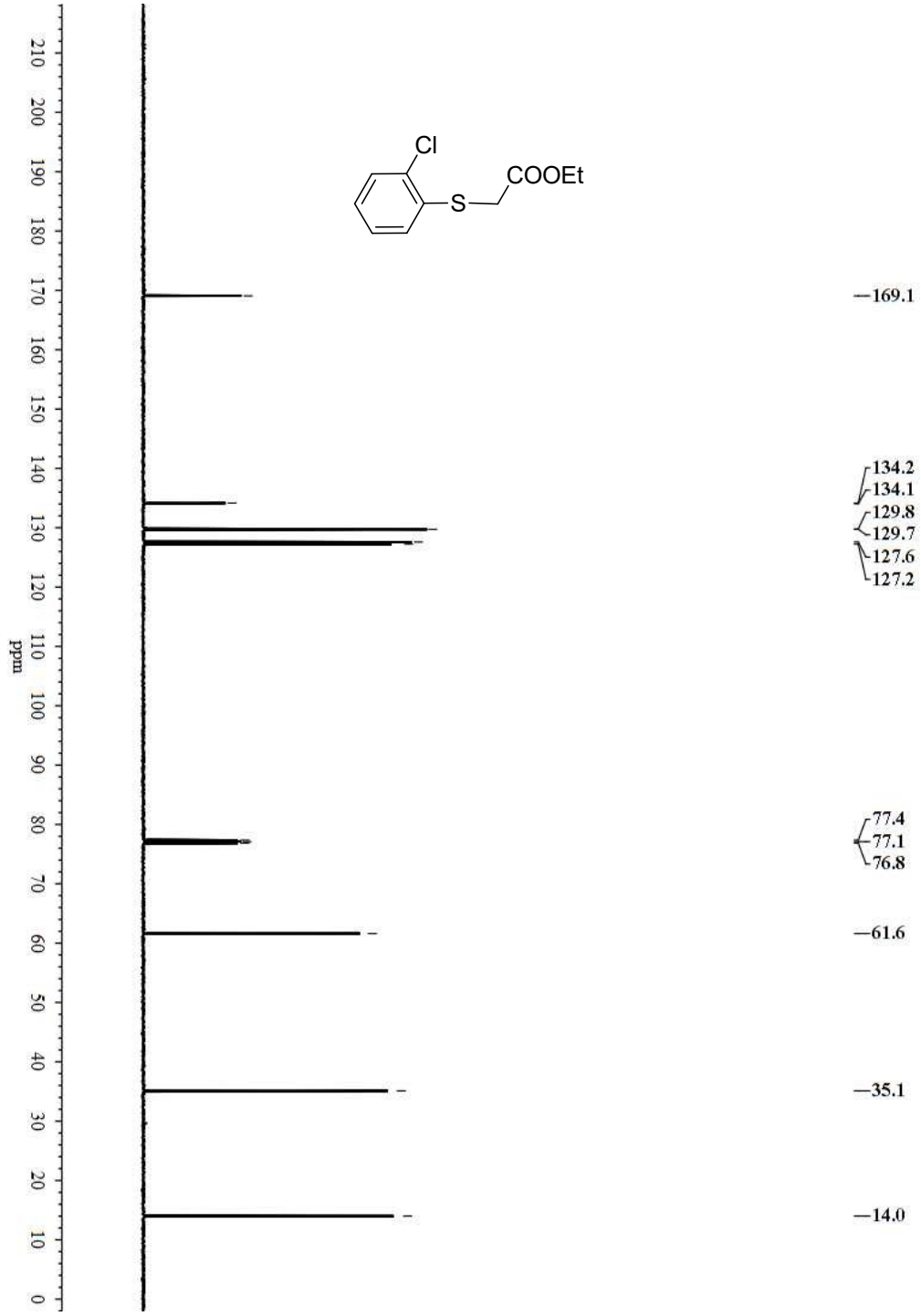
^{1}H NMR Spectra of Compound **3d**.



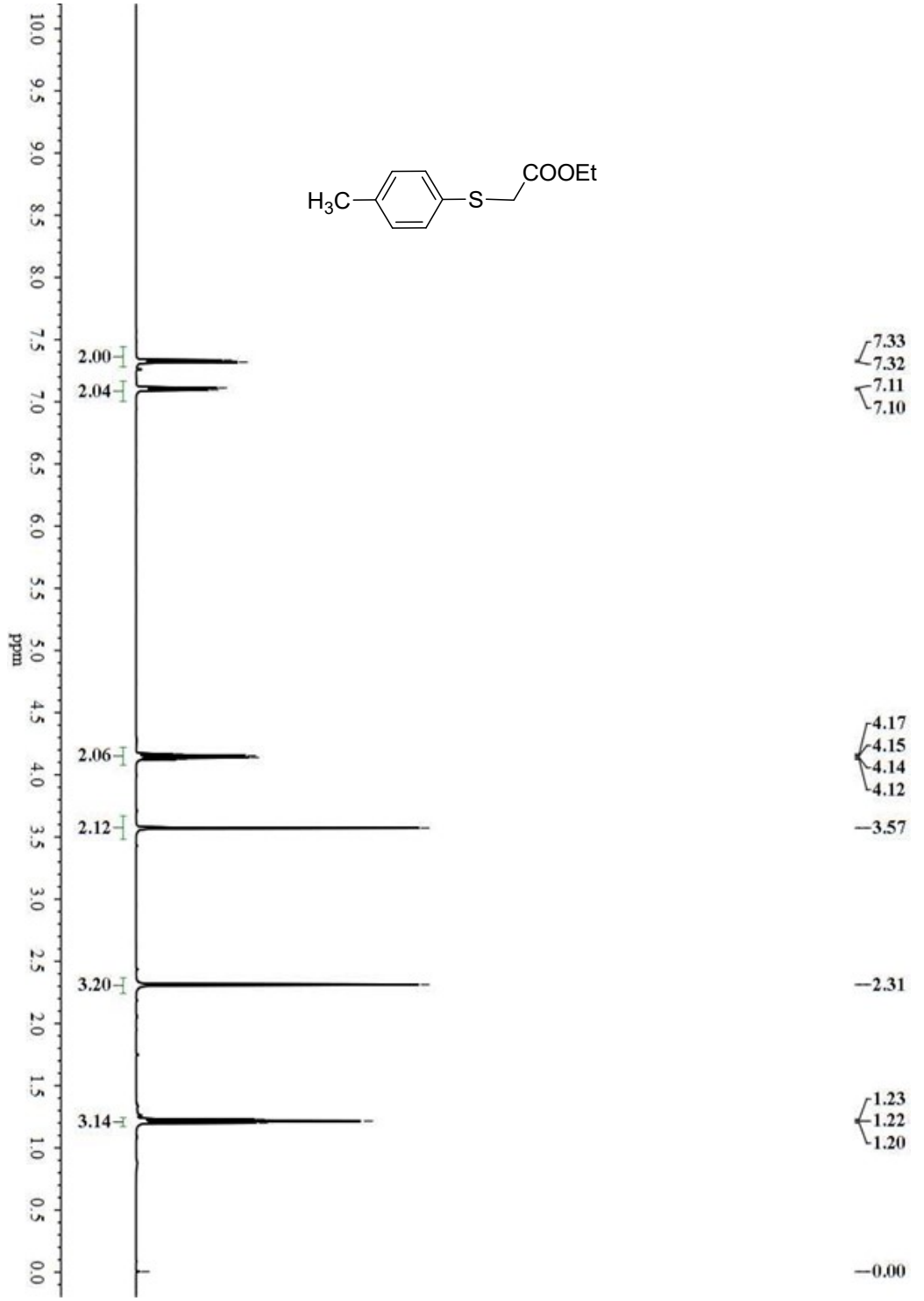
^{13}C NMR Spectra of Compound **3d**.



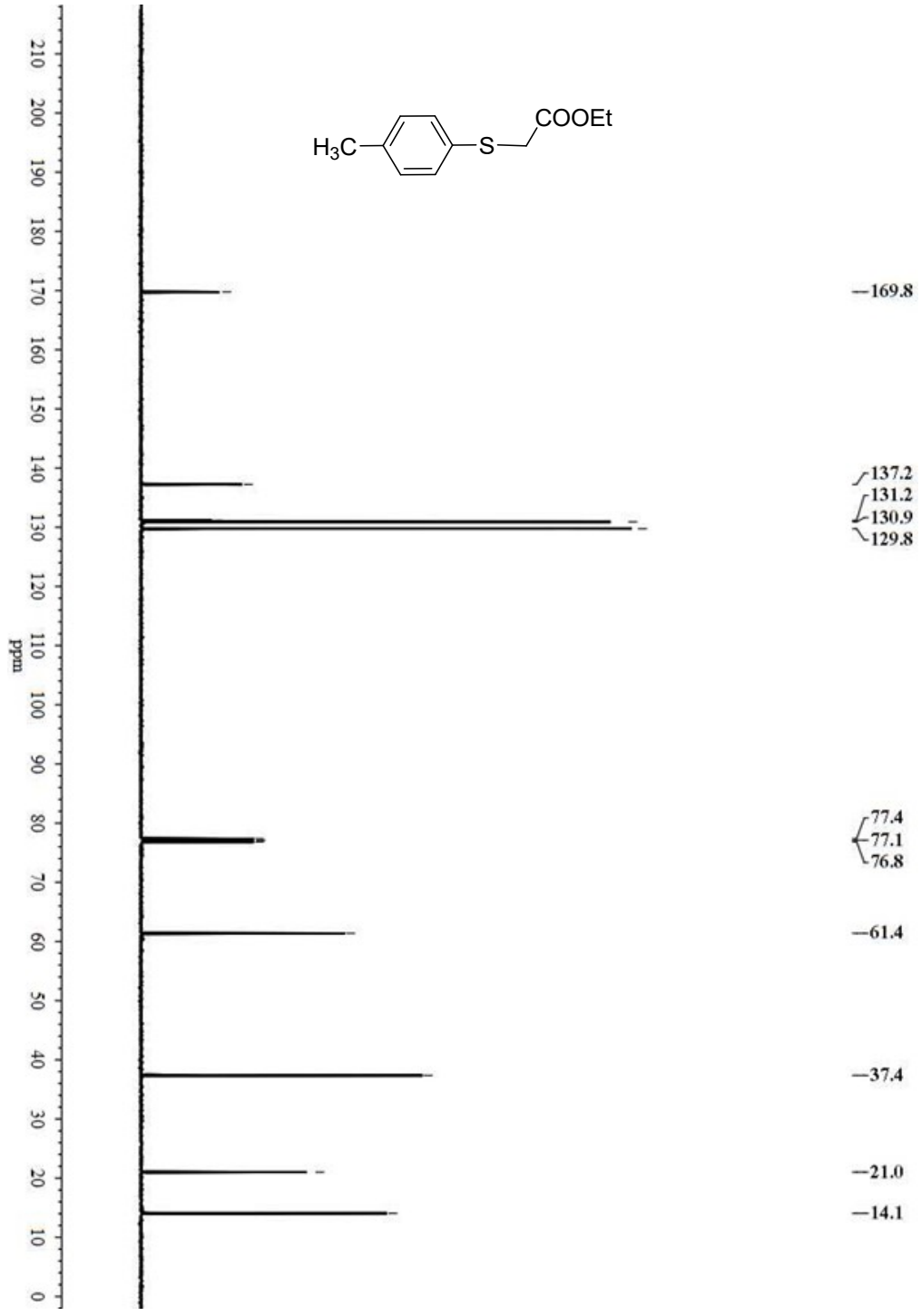
^{1}H NMR Spectra of Compound **3e**.



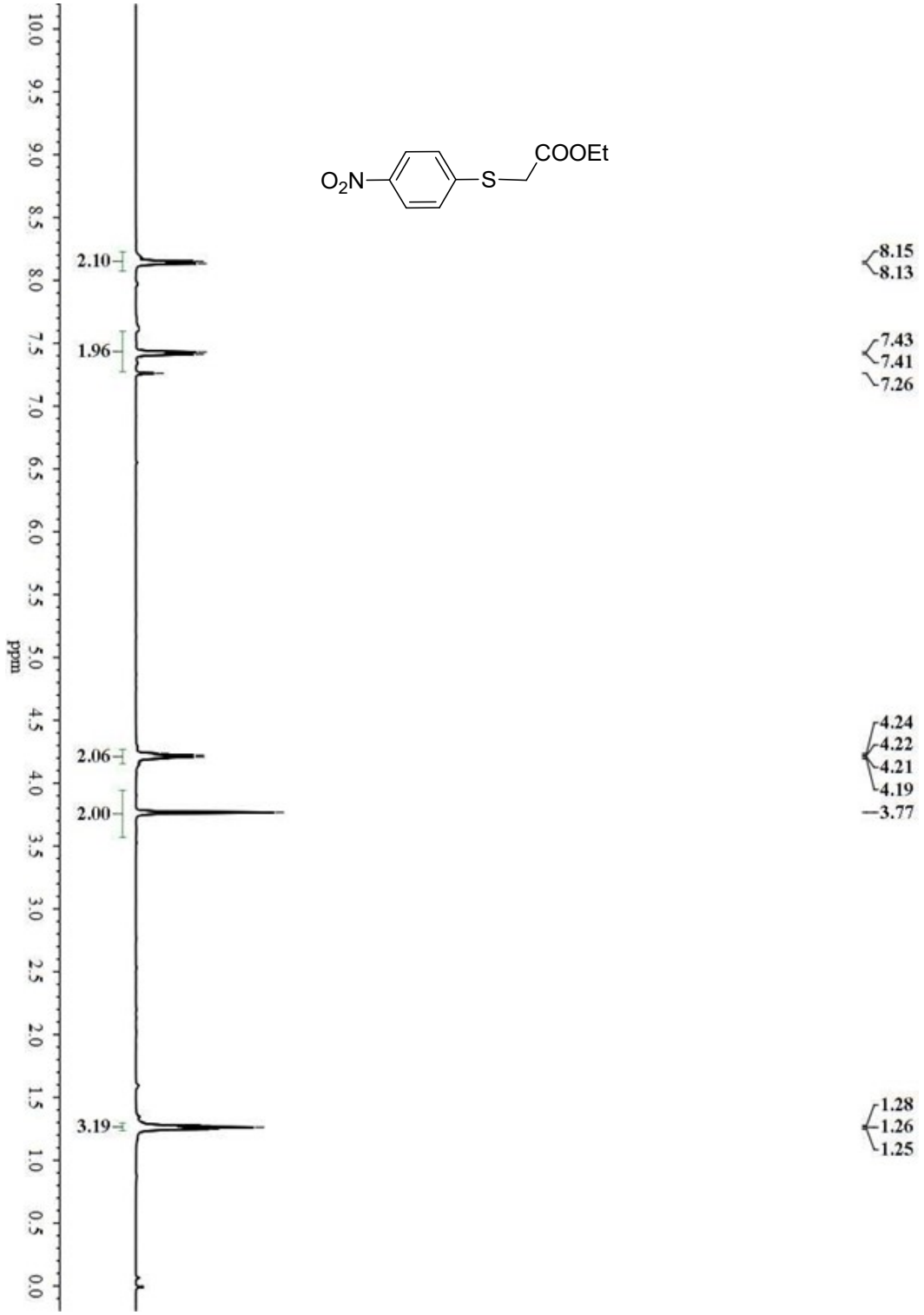
^{13}C NMR Spectra of Compound **3e**.



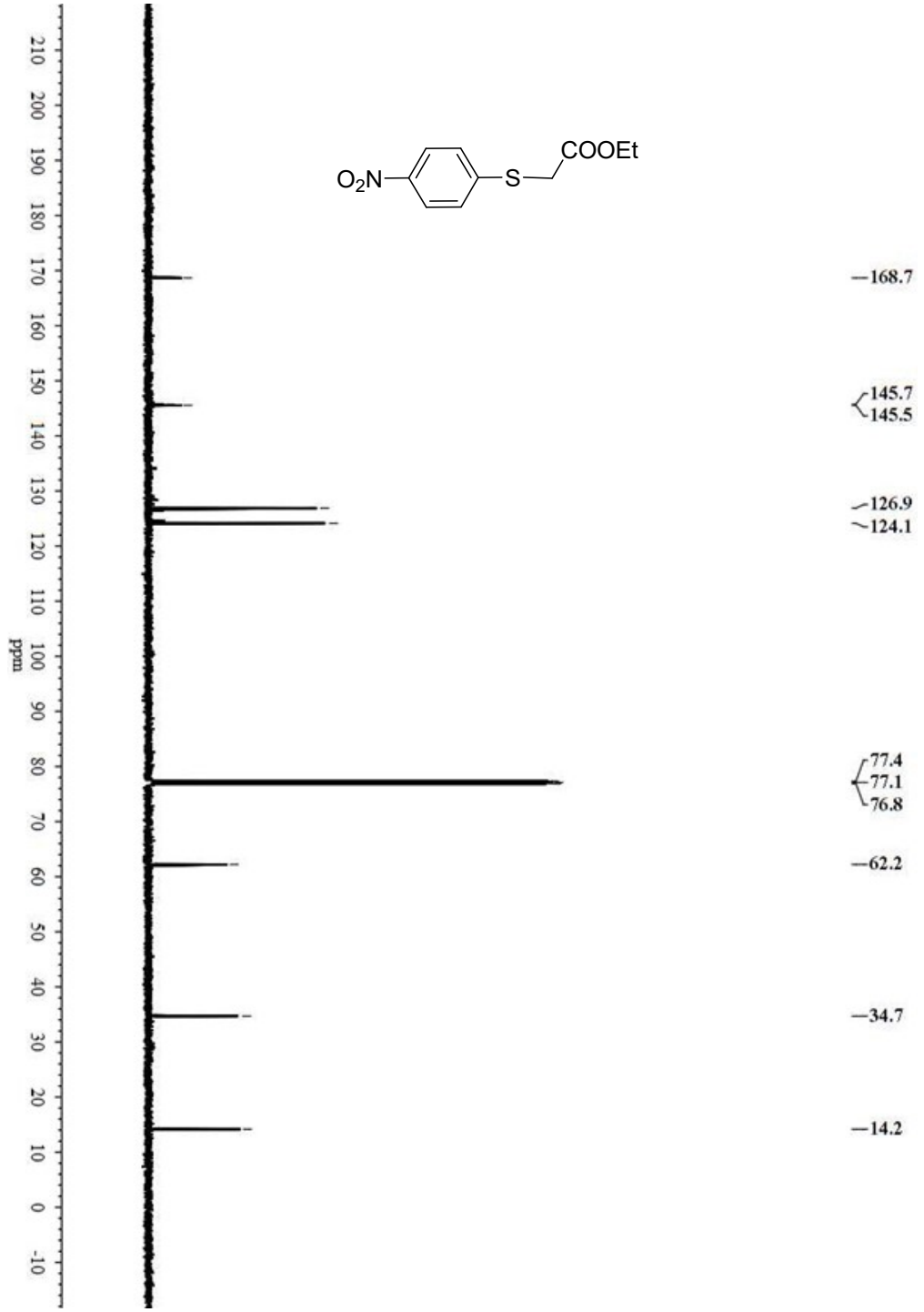
^{1}H NMR Spectra of Compound **3f**.



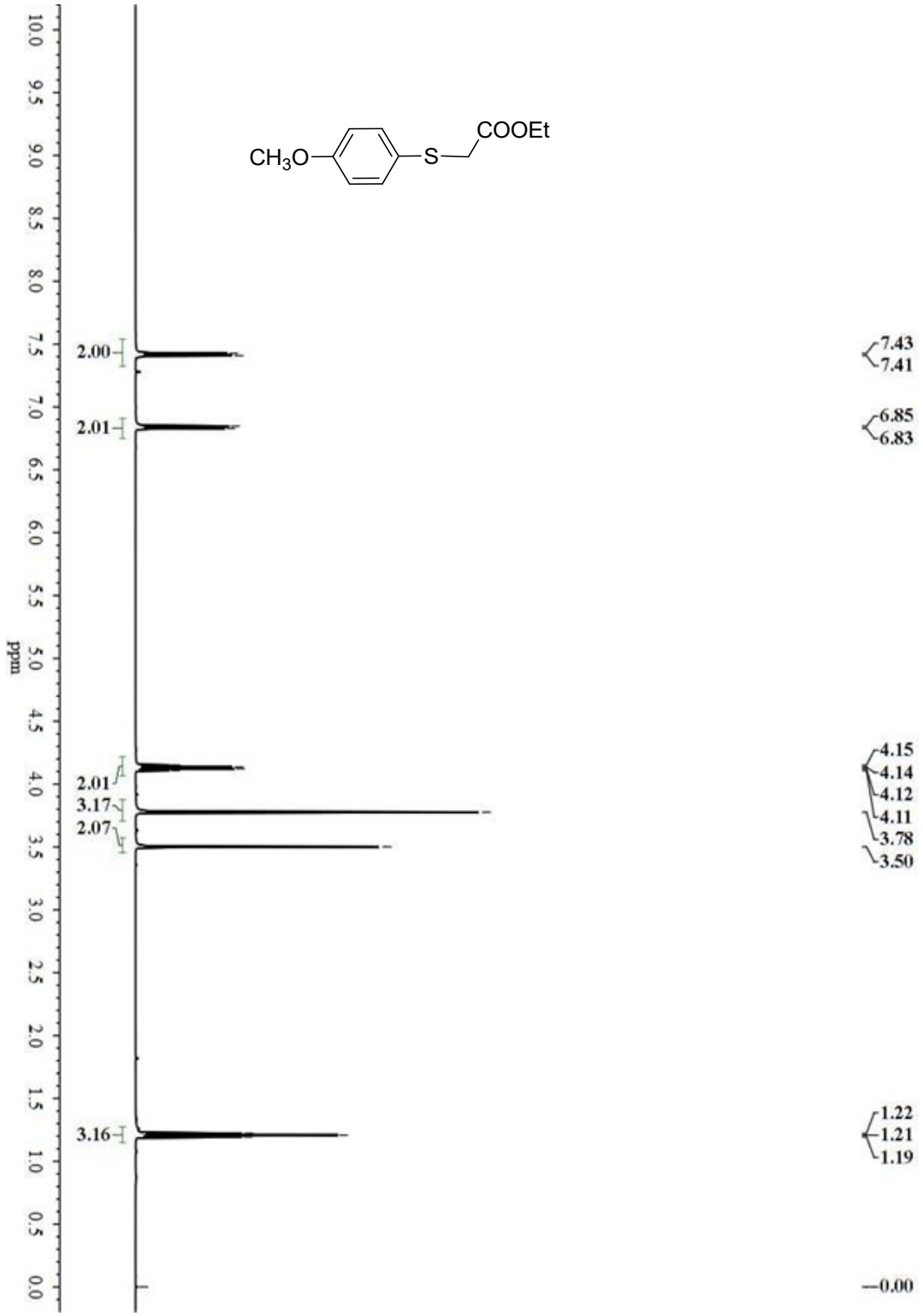
^{13}C NMR Spectra of Compound **3f**.



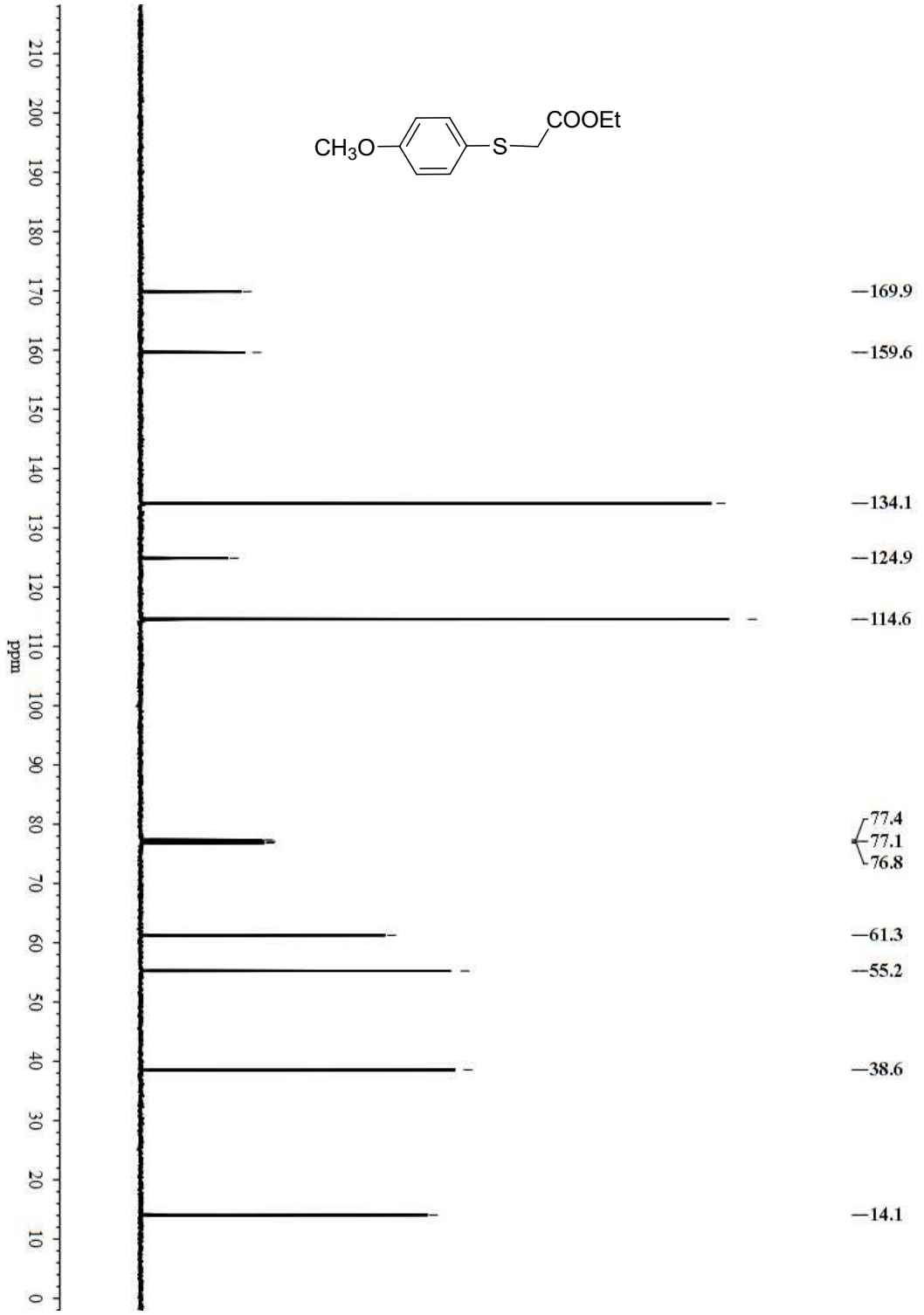
^{1}H NMR Spectra of Compound **3g**.



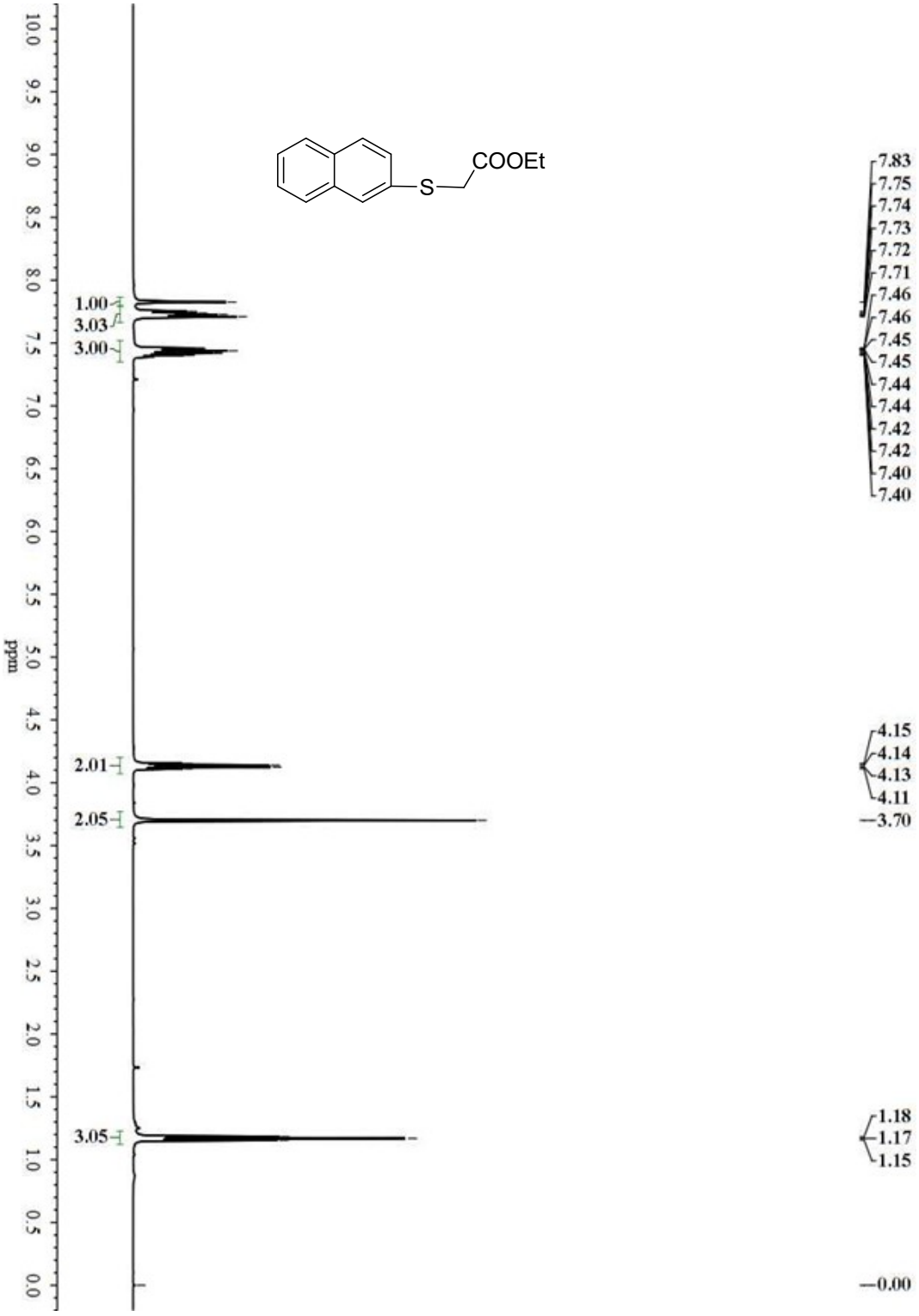
^{13}C NMR Spectra of Compound **3g**.



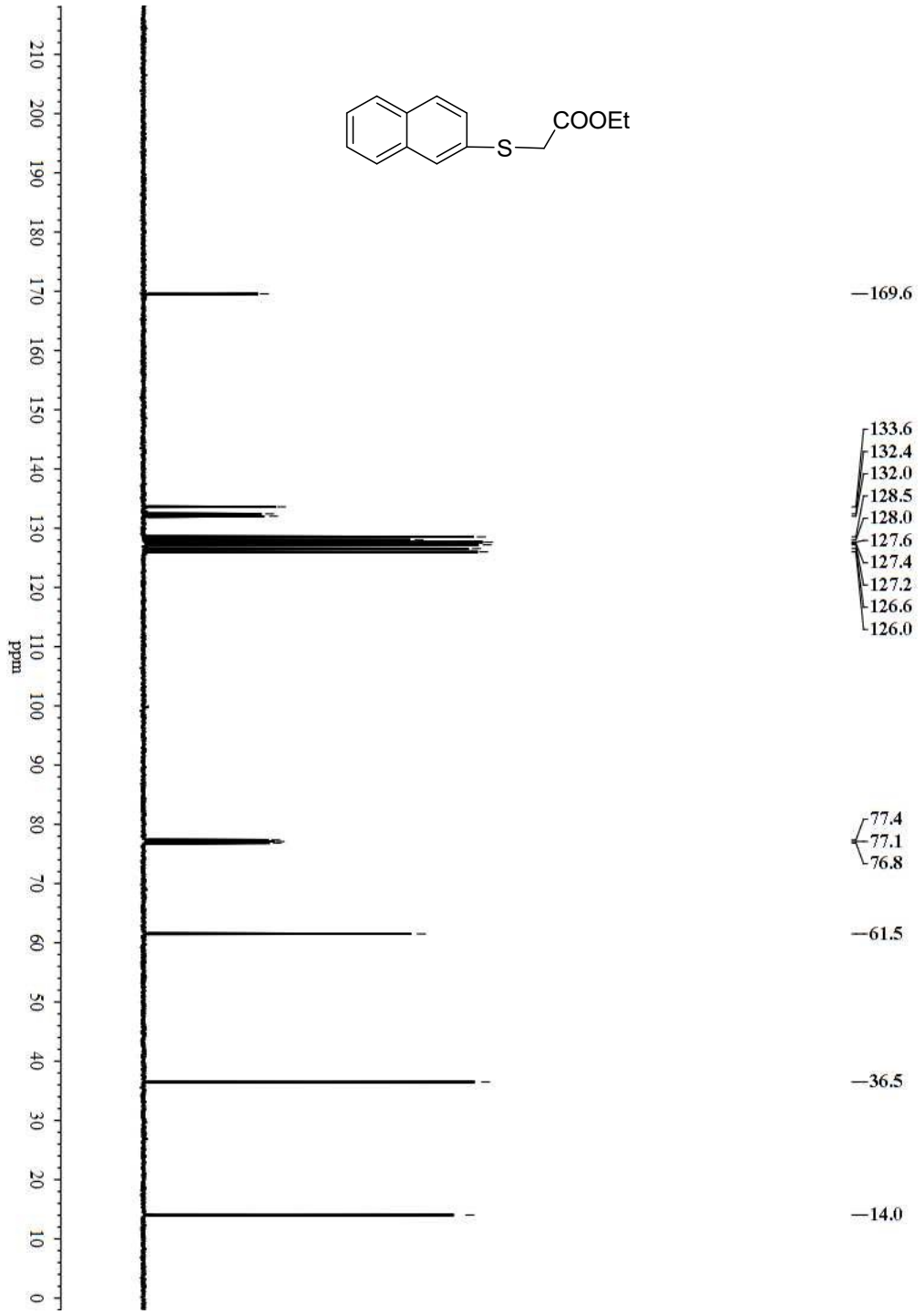
^{1}H NMR Spectra of Compound **3h**.



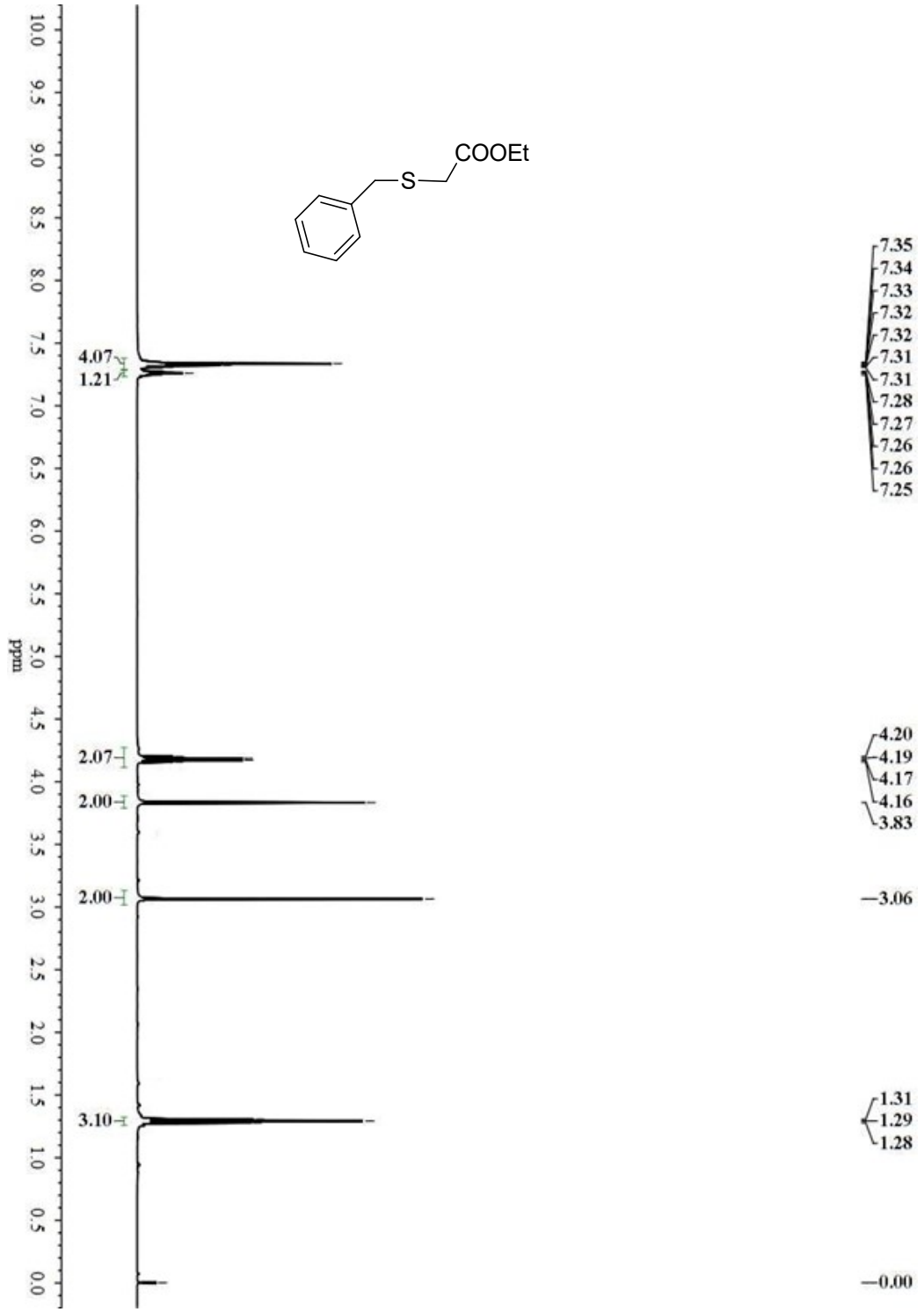
^{13}C NMR Spectra of Compound **3h**.



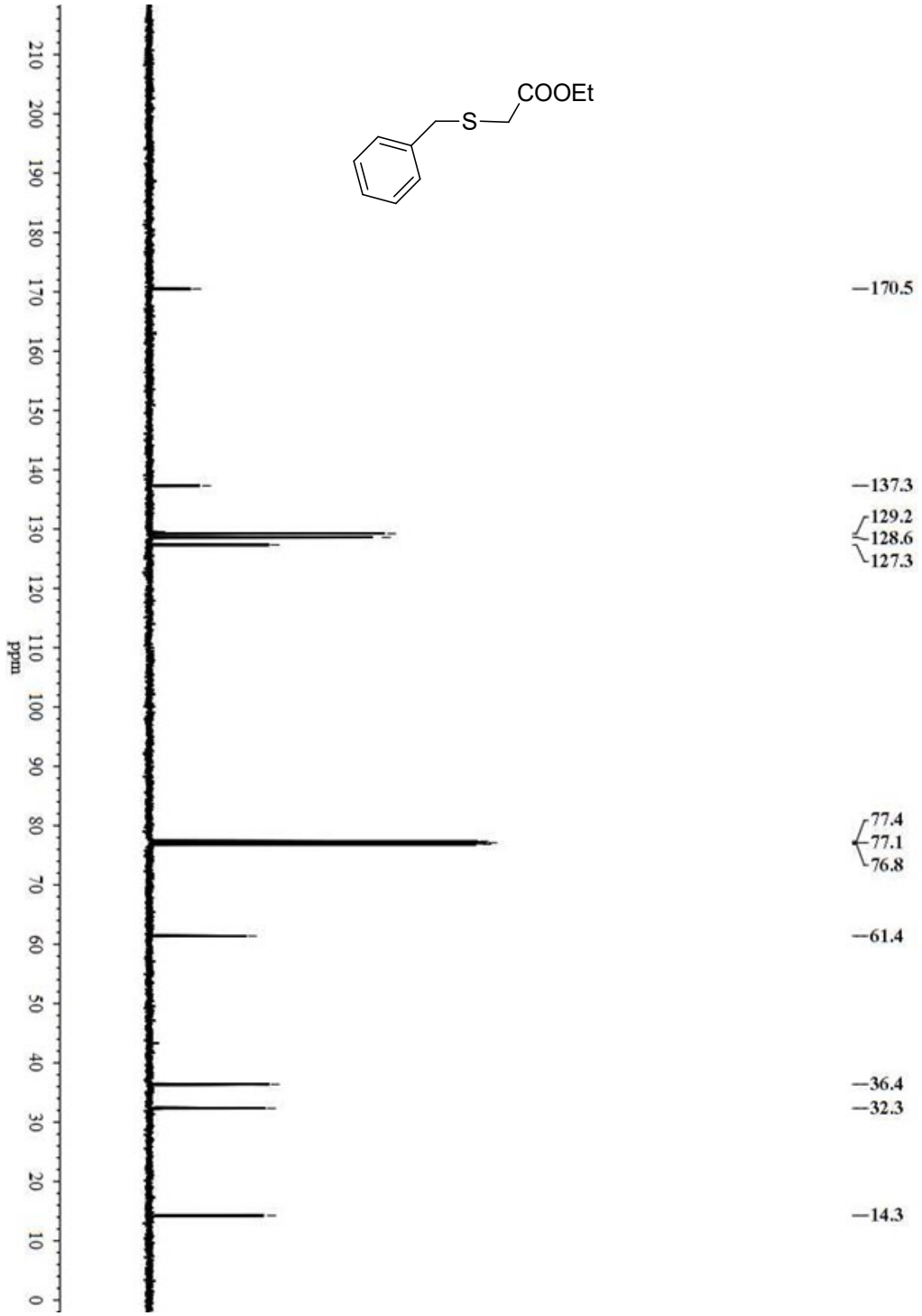
^{1}H NMR Spectra of Compound **3i**.



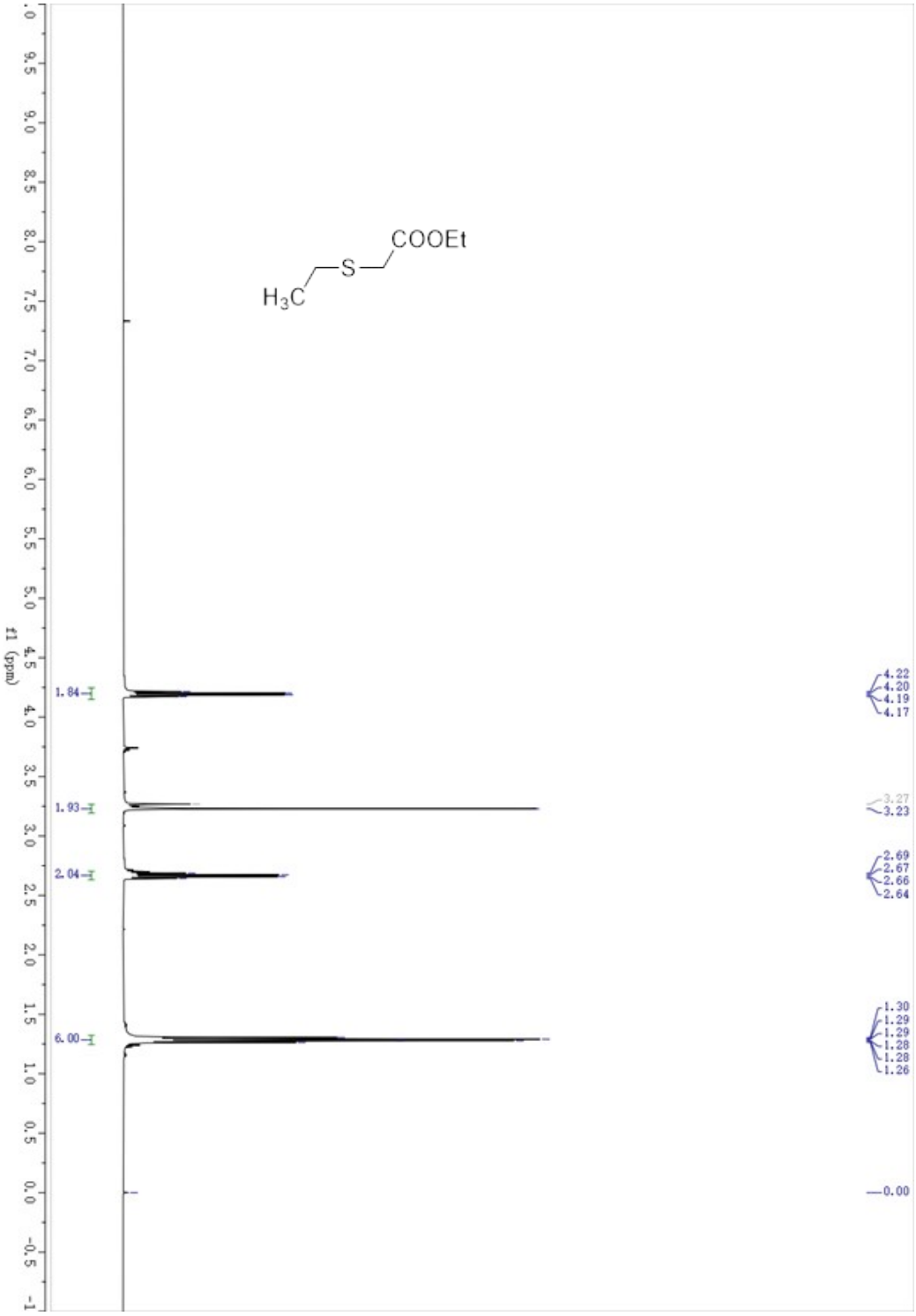
^{13}C NMR Spectra of Compound **3i**.



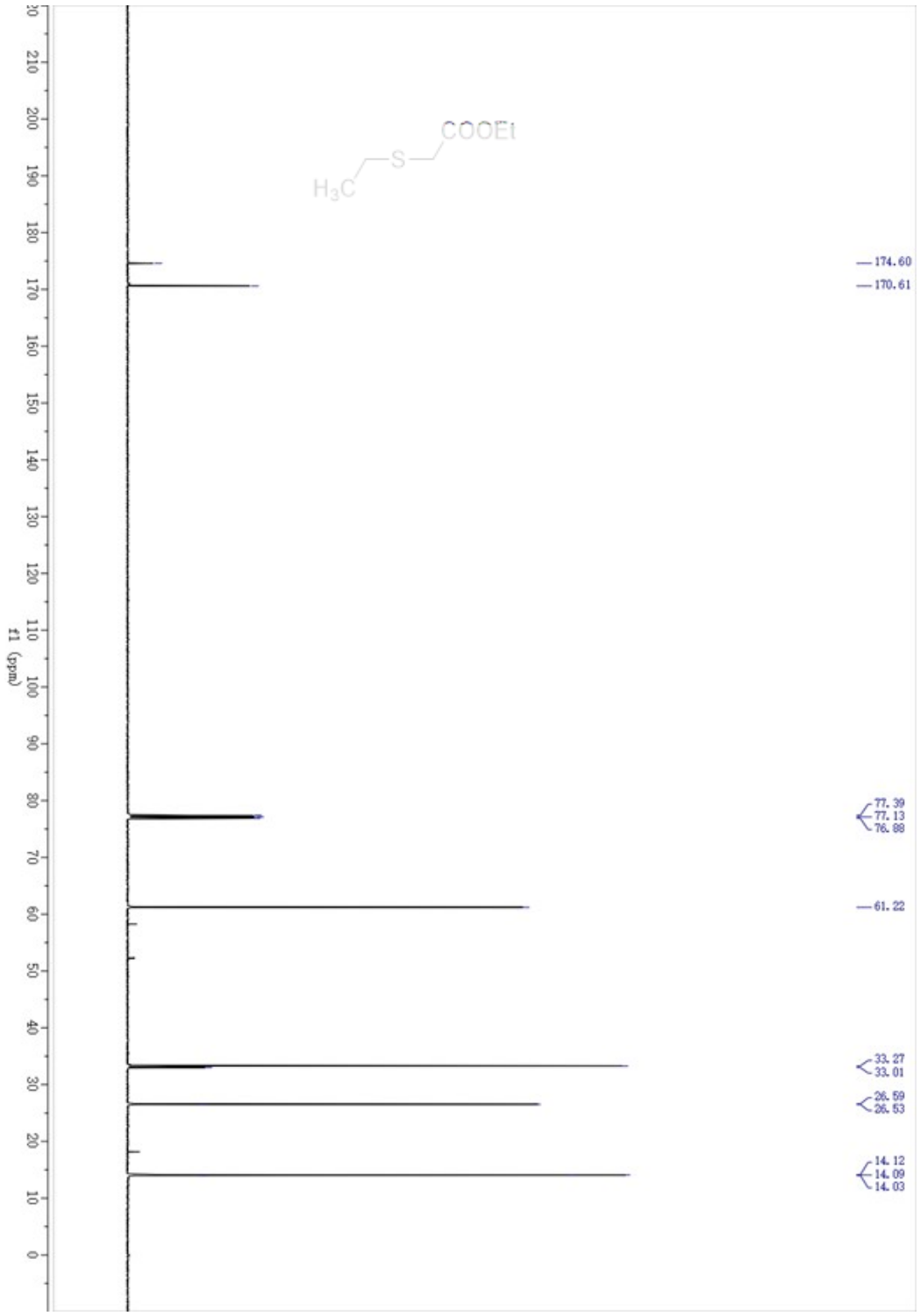
^{1}H NMR Spectra of Compound **3j**.



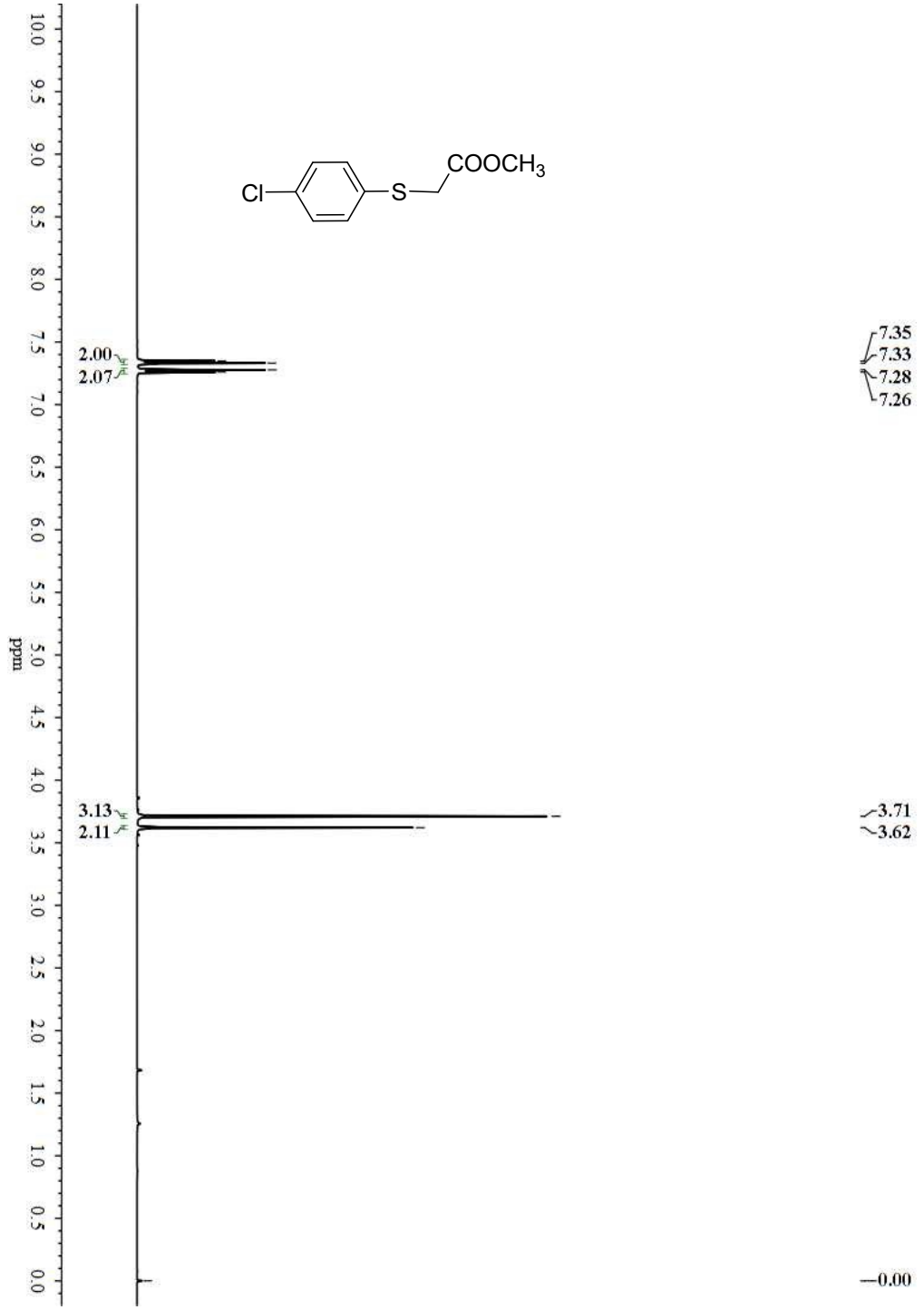
^{13}C NMR Spectra of Compound **3j**.



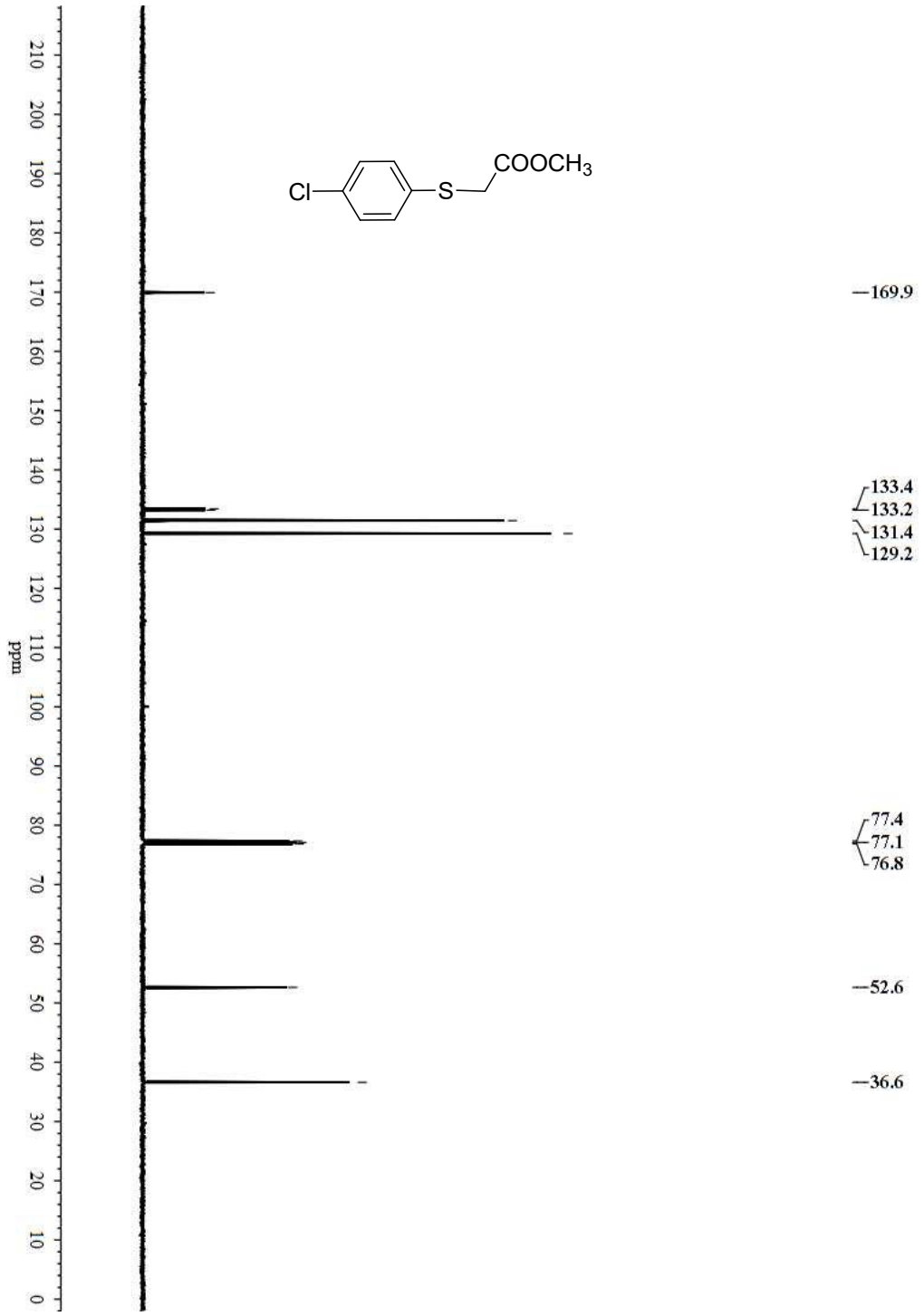
^{1}H NMR Spectra of Compound **3k**.



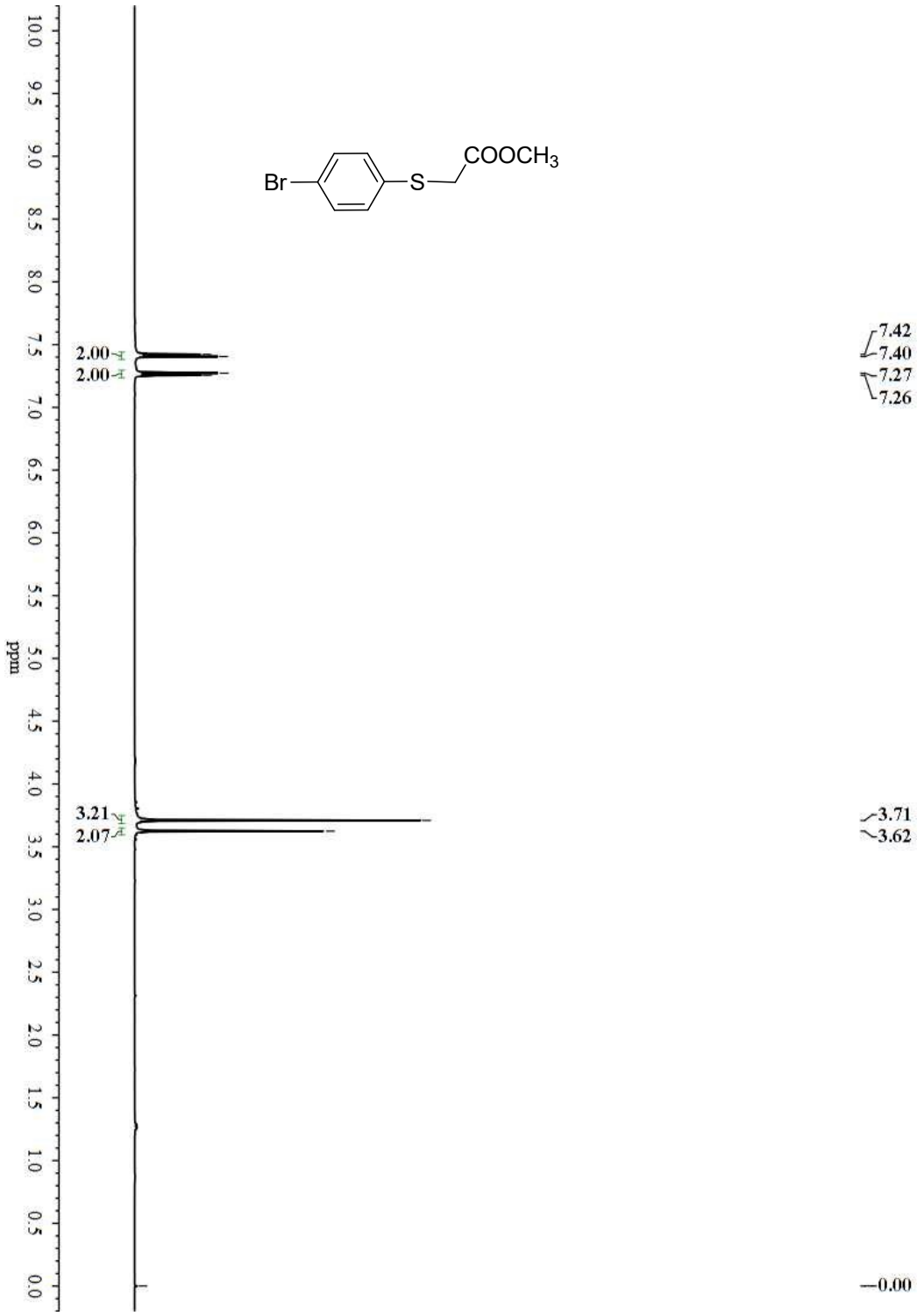
^{13}C NMR Spectra of Compound **3k**.



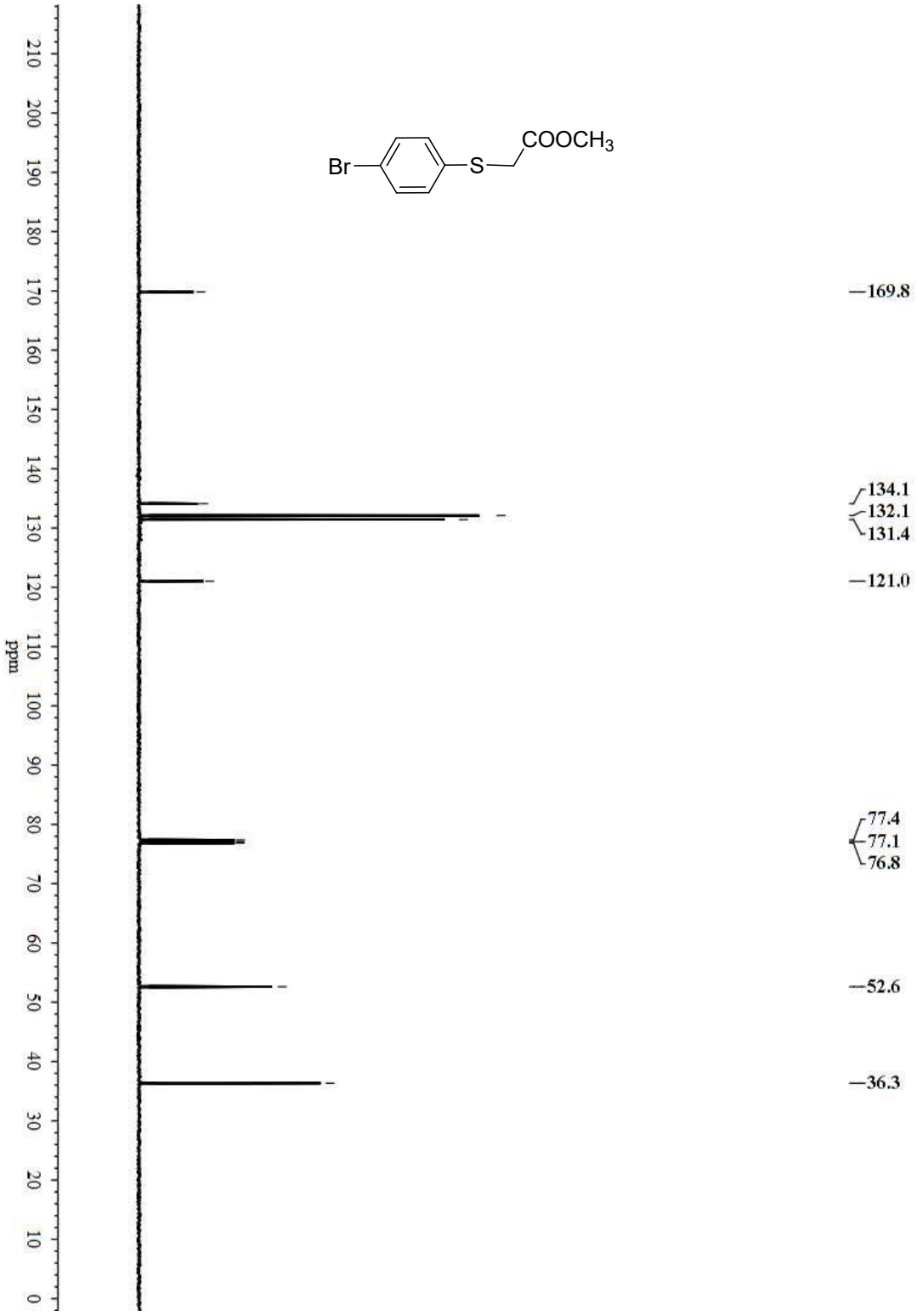
^{1}H NMR Spectra of Compound **4a**.



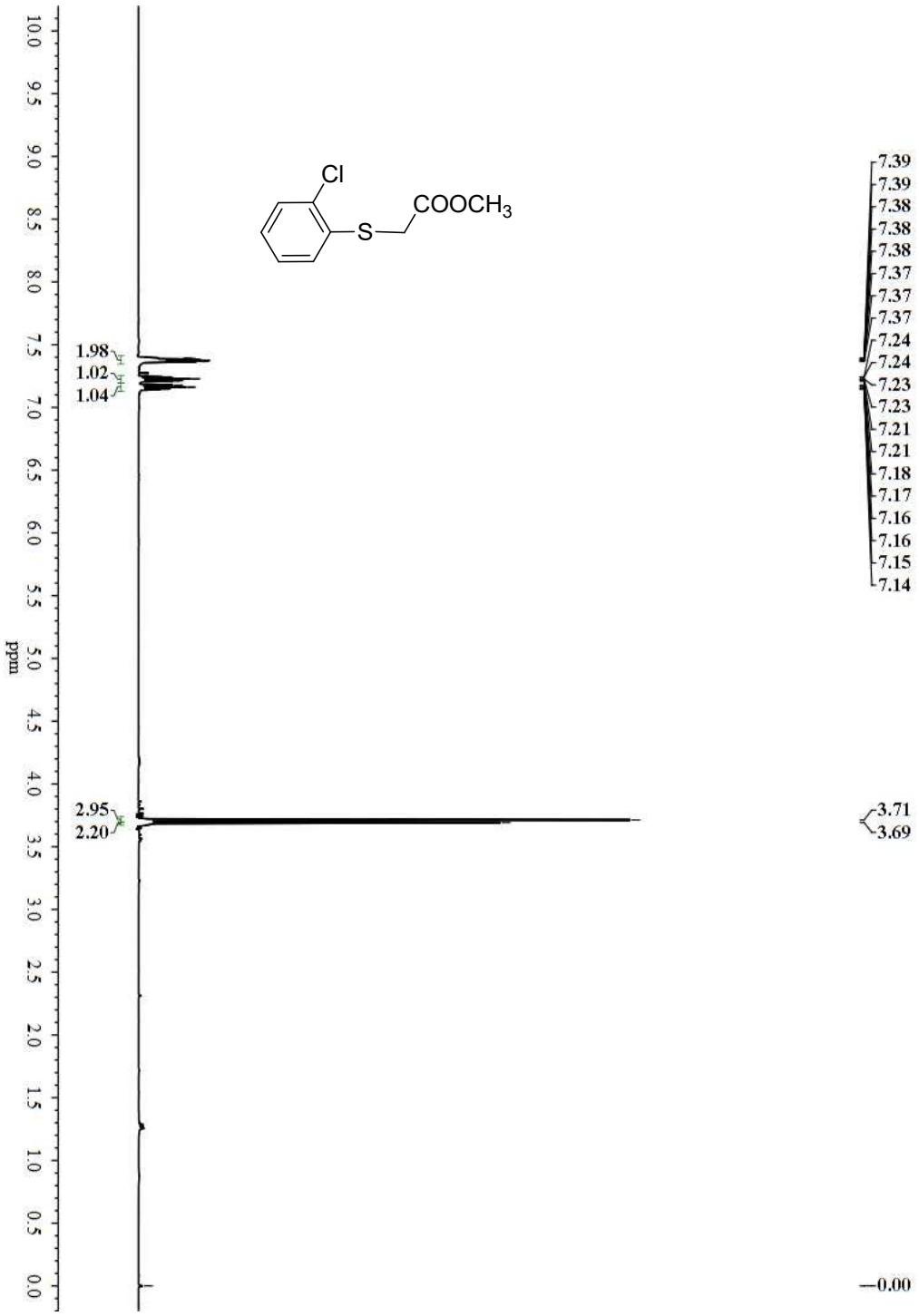
^{13}C NMR Spectra of Compound **4a**.



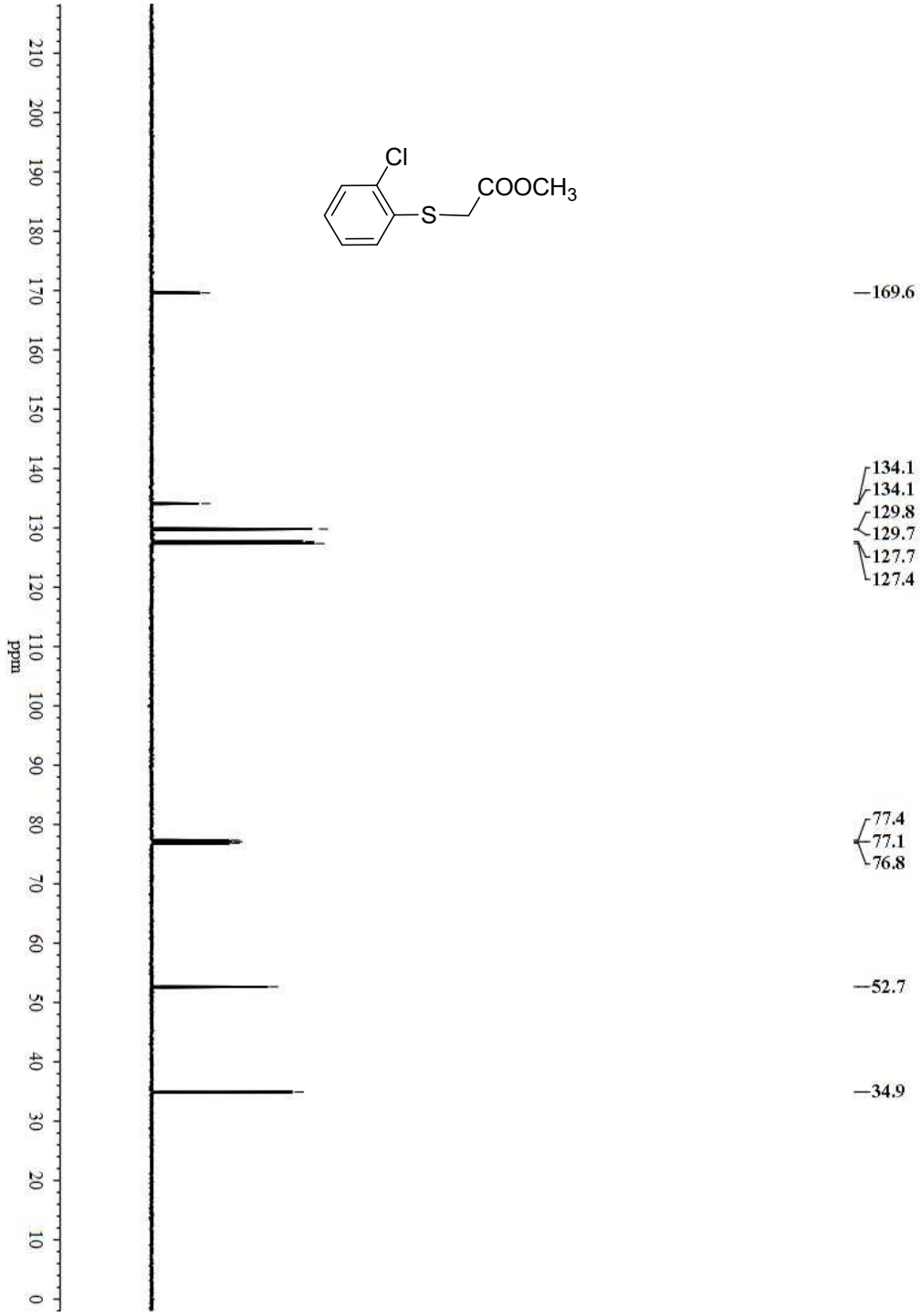
^{1}H NMR Spectra of Compound **4b**.



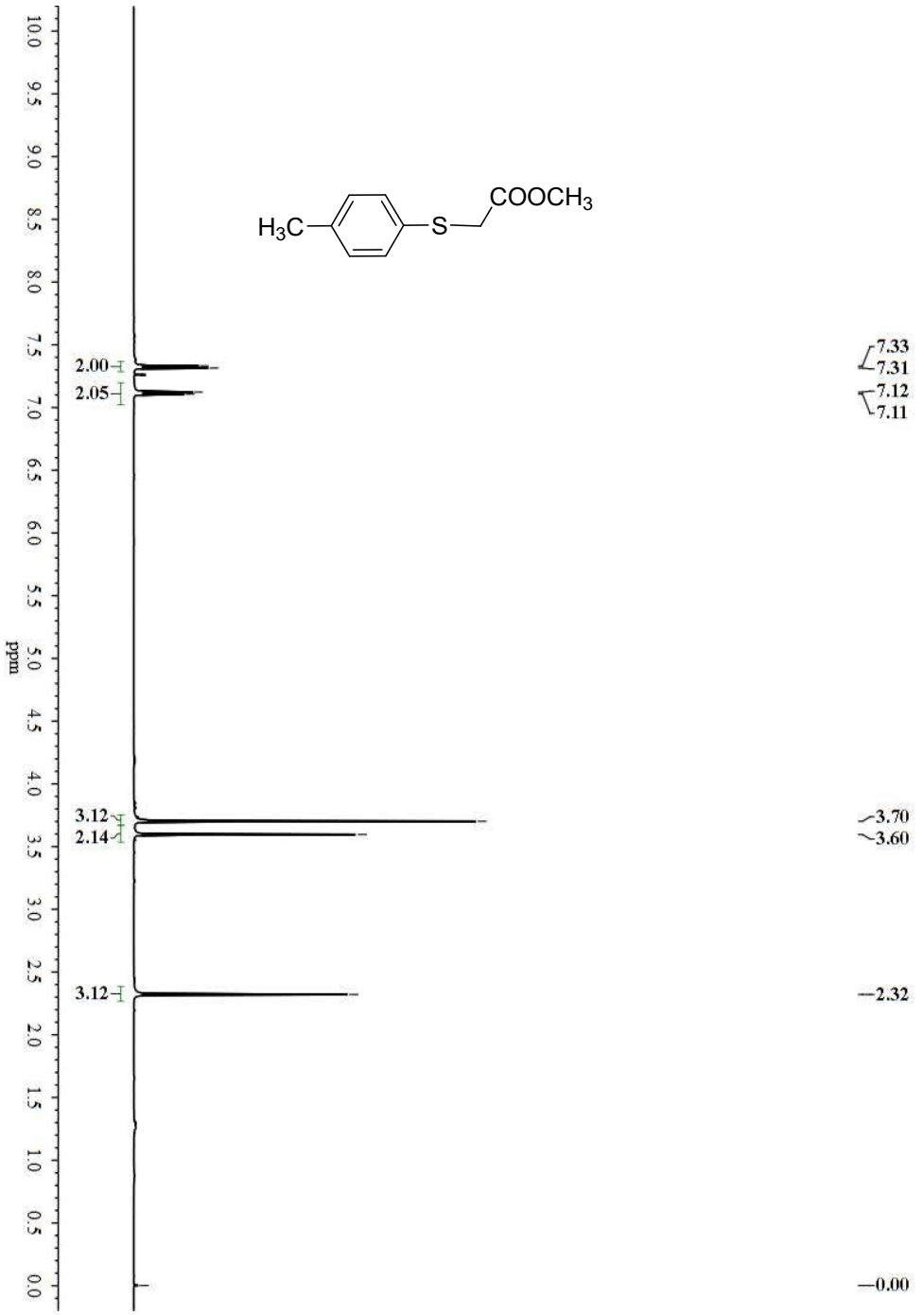
^{13}C NMR Spectra of Compound **4b**.



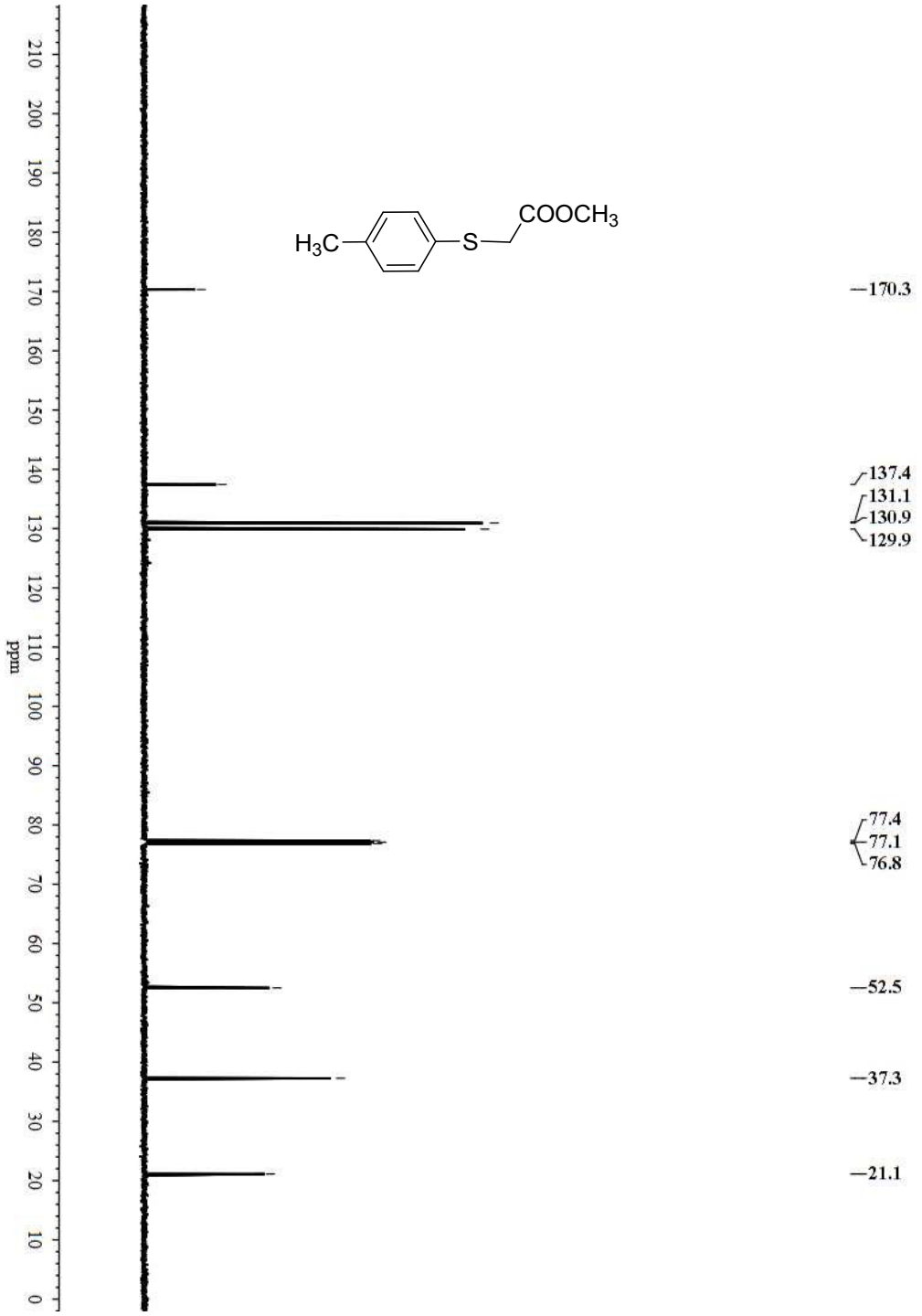
^{1}H NMR Spectra of Compound **4c**.



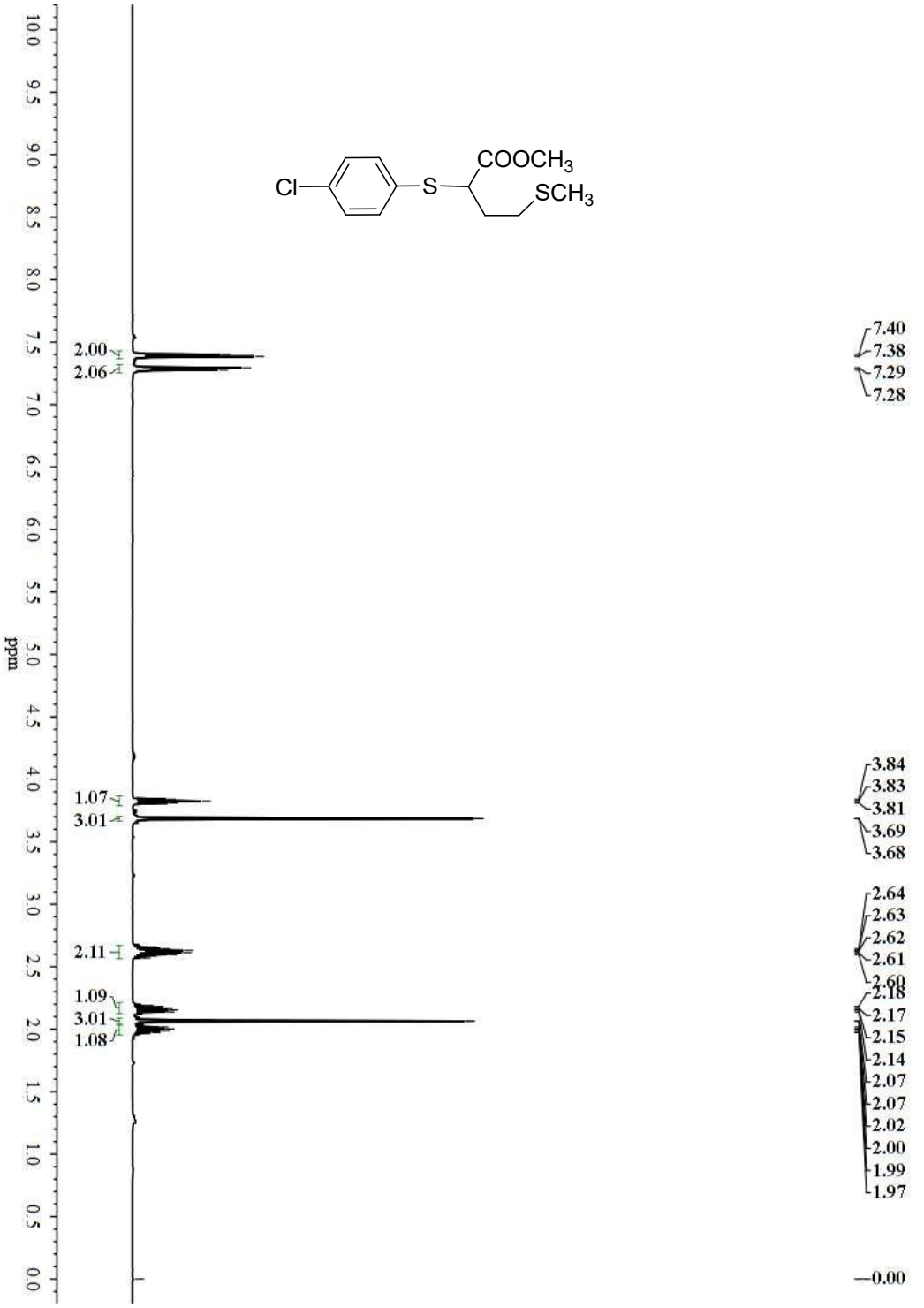
^{13}C NMR Spectra of Compound **4c**.



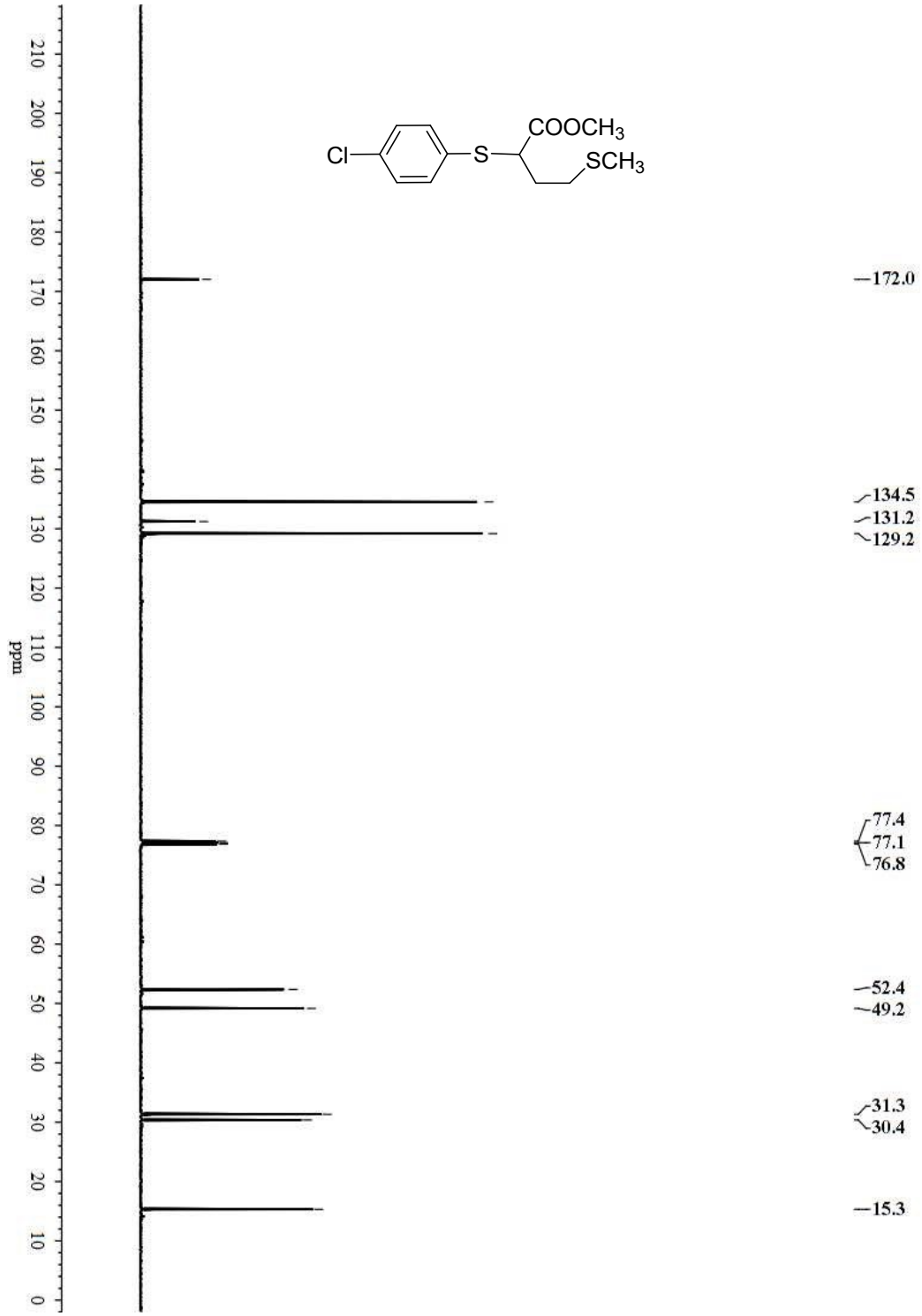
^{1}H NMR Spectra of Compound **4d**.



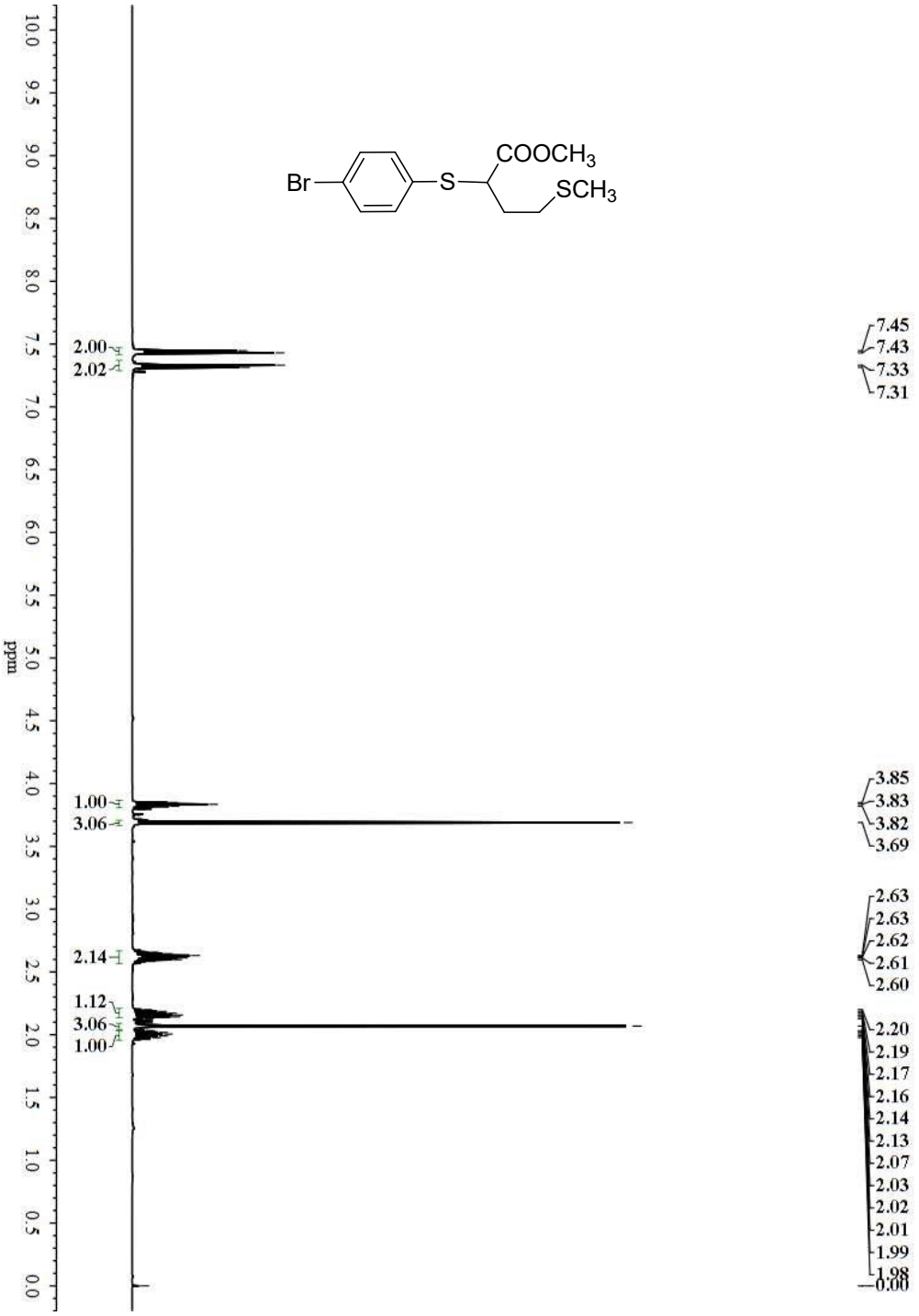
^{13}C NMR Spectra of Compound **4d**.



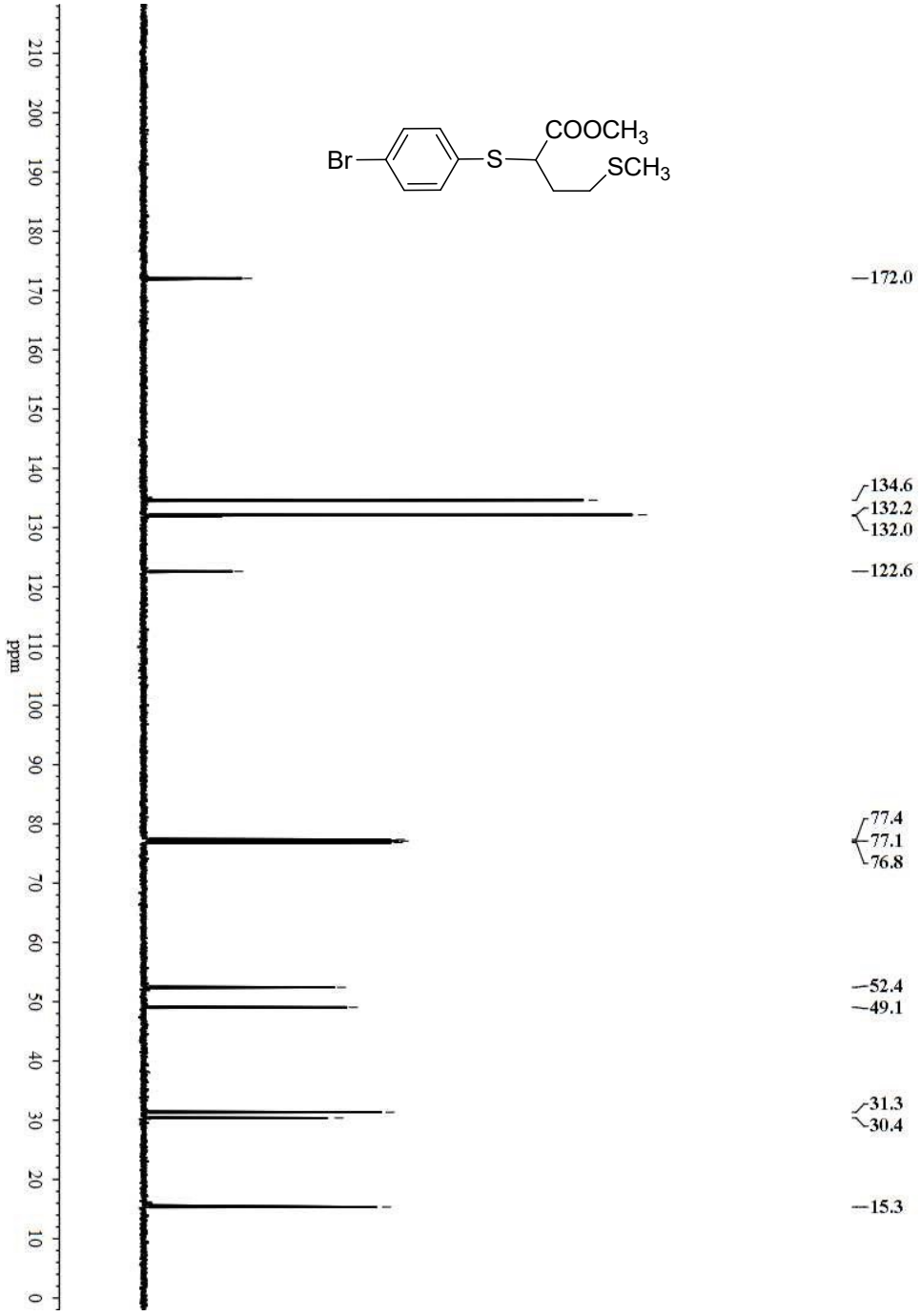
^{1}H NMR Spectra of Compound **4e**.



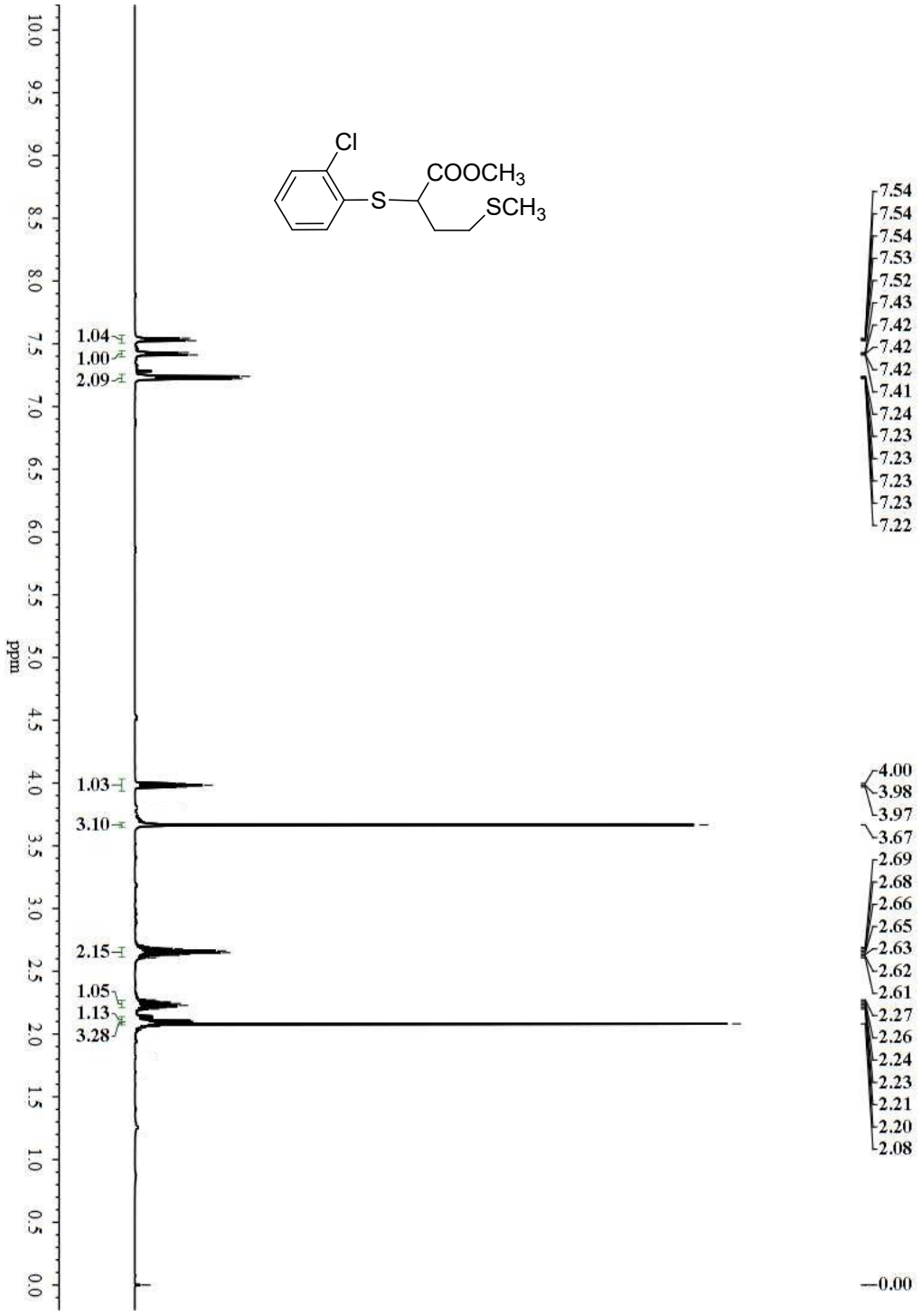
^{13}C NMR Spectra of Compound **4e**.



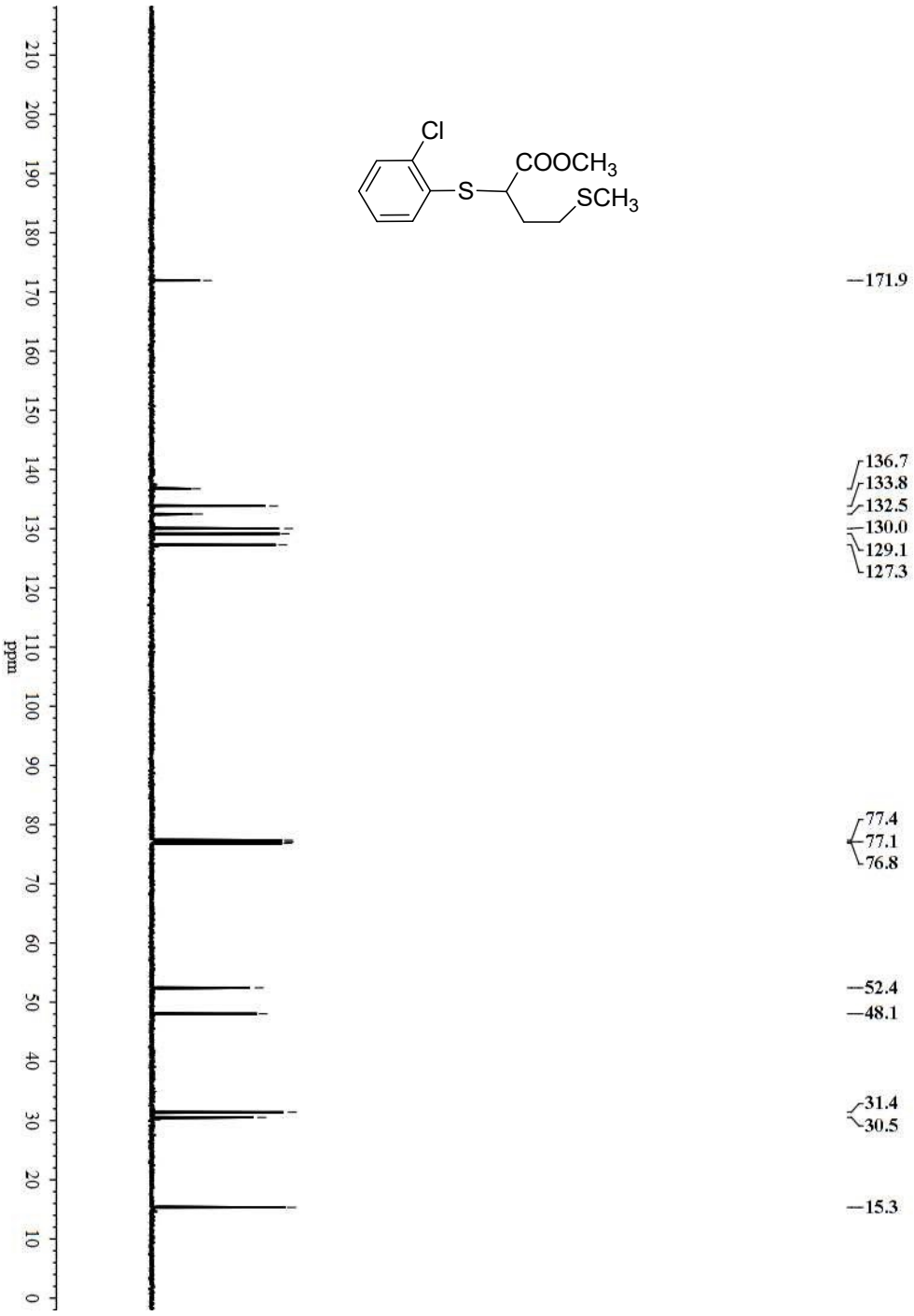
^{1}H NMR Spectra of Compound **4f**.



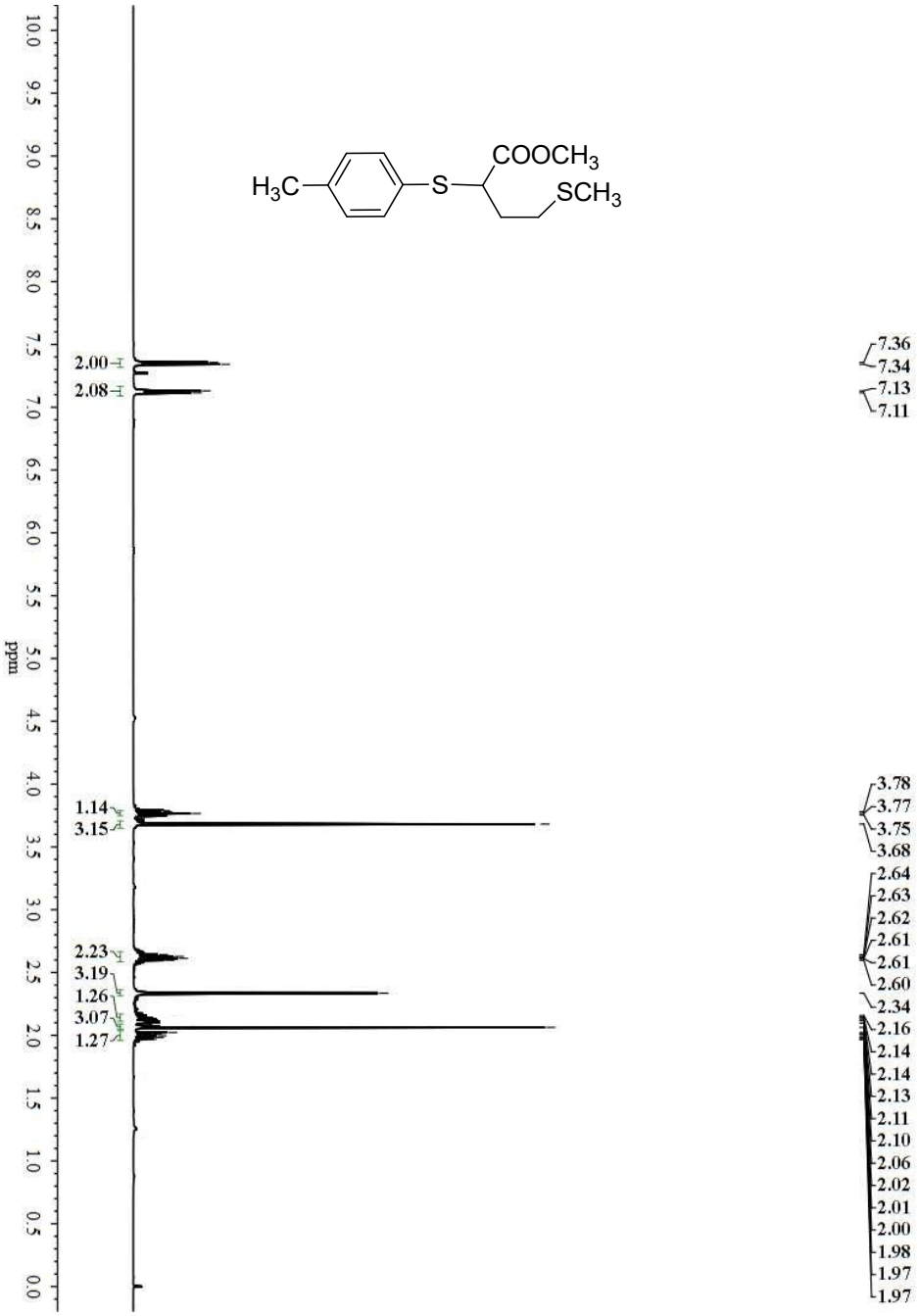
^{13}C NMR Spectra of Compound **4f**.



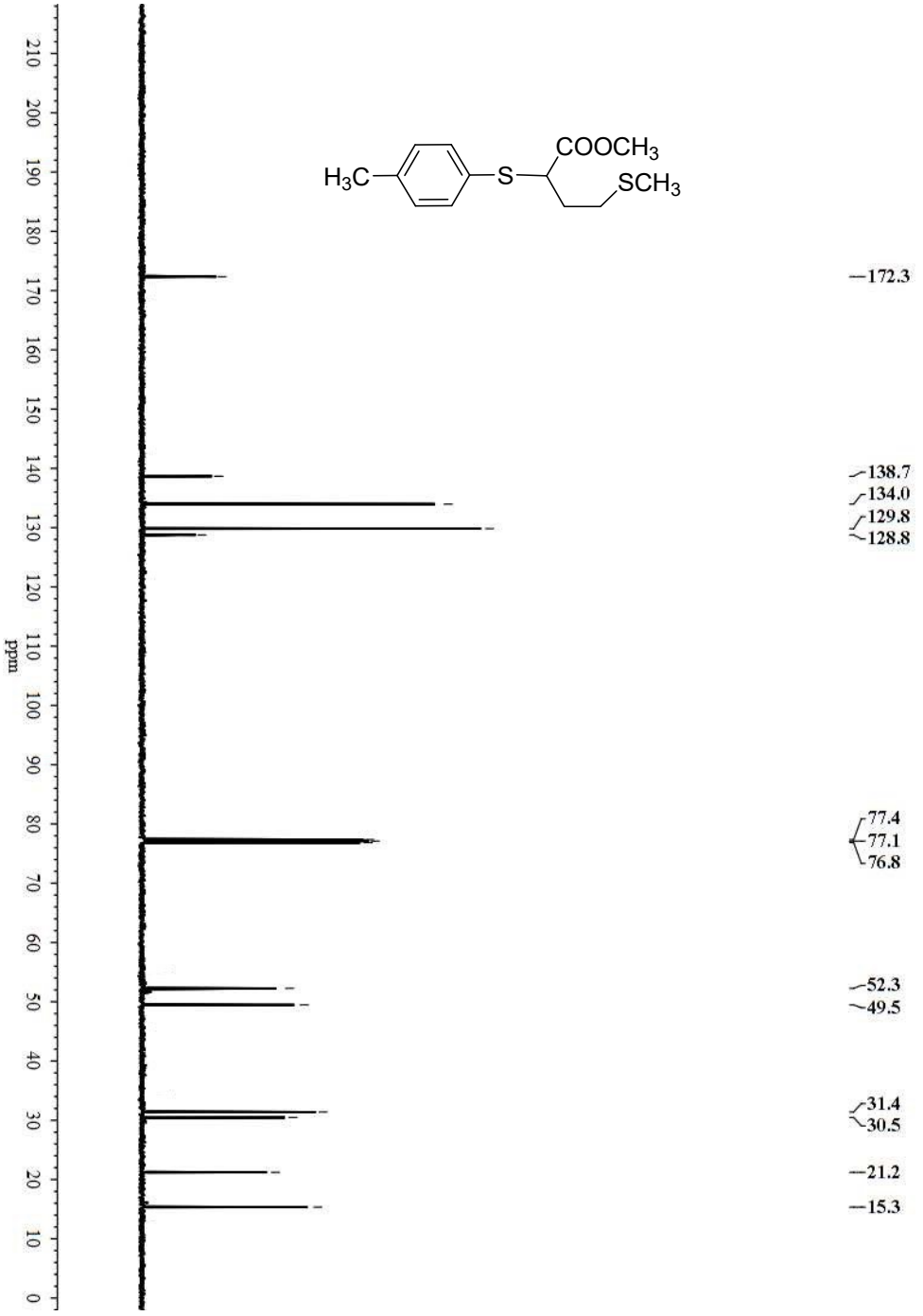
^{1}H NMR Spectra of Compound **4g**.



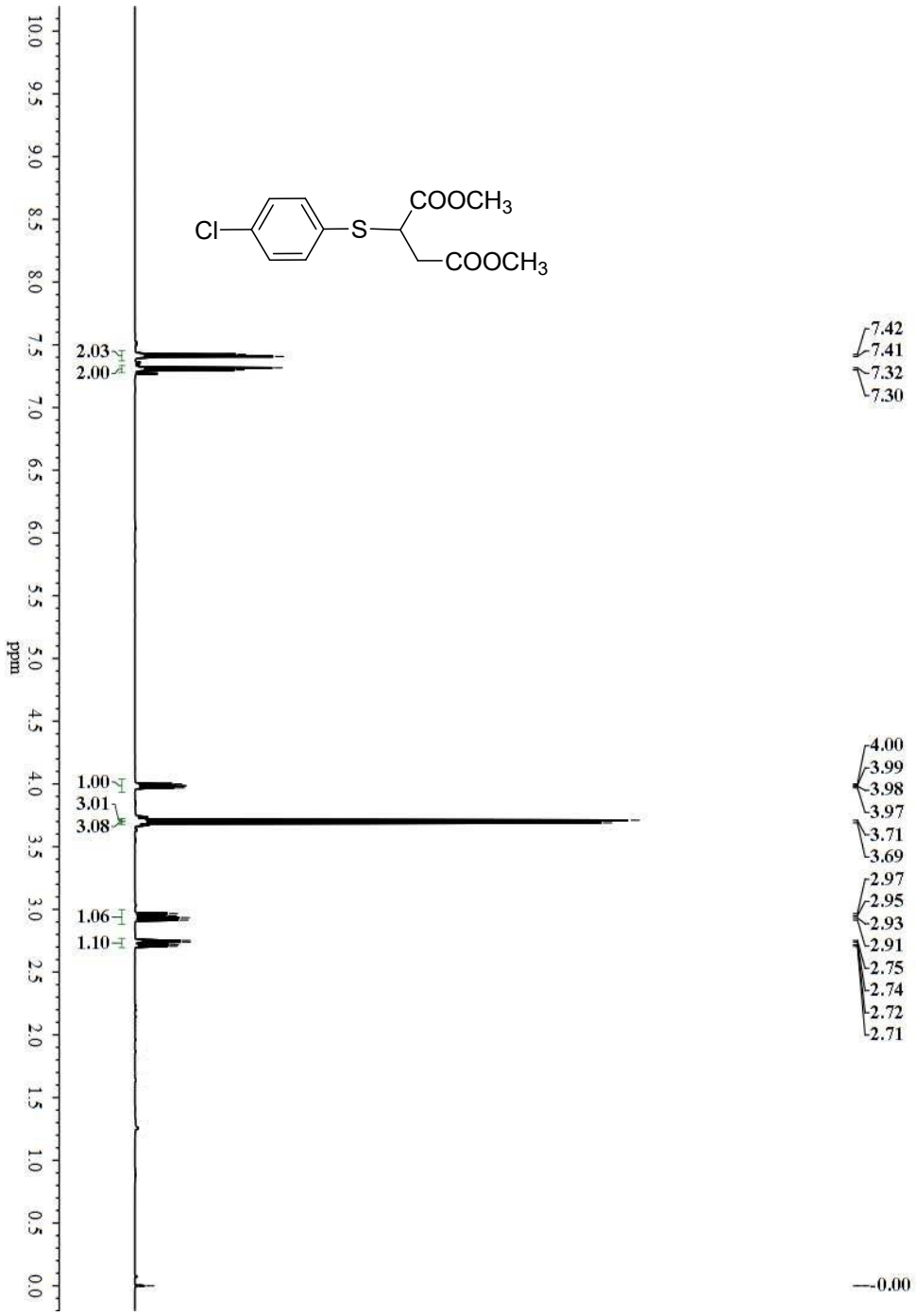
^{13}C NMR Spectra of Compound **4g**.



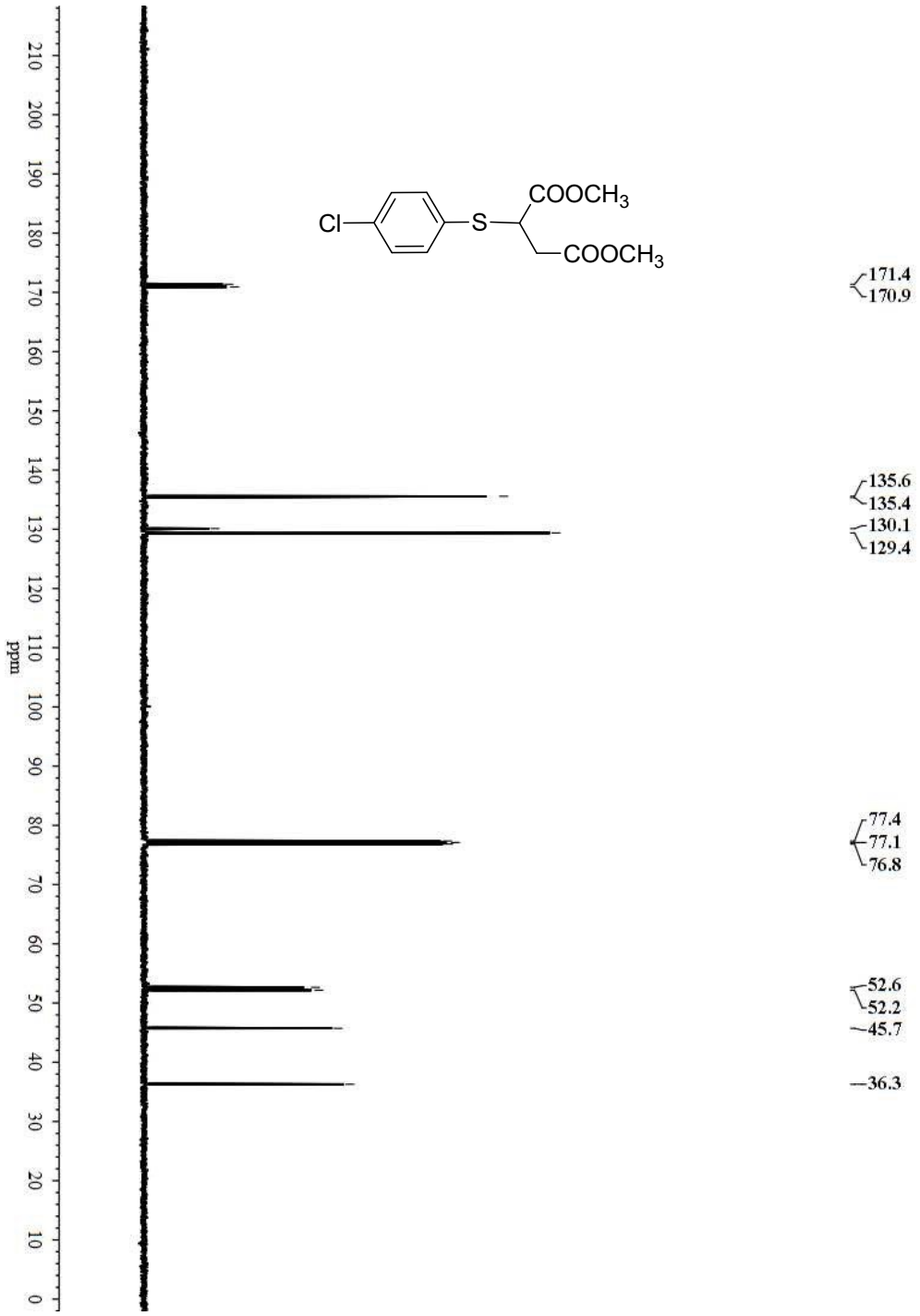
^{1}H NMR Spectra of Compound **4h**.



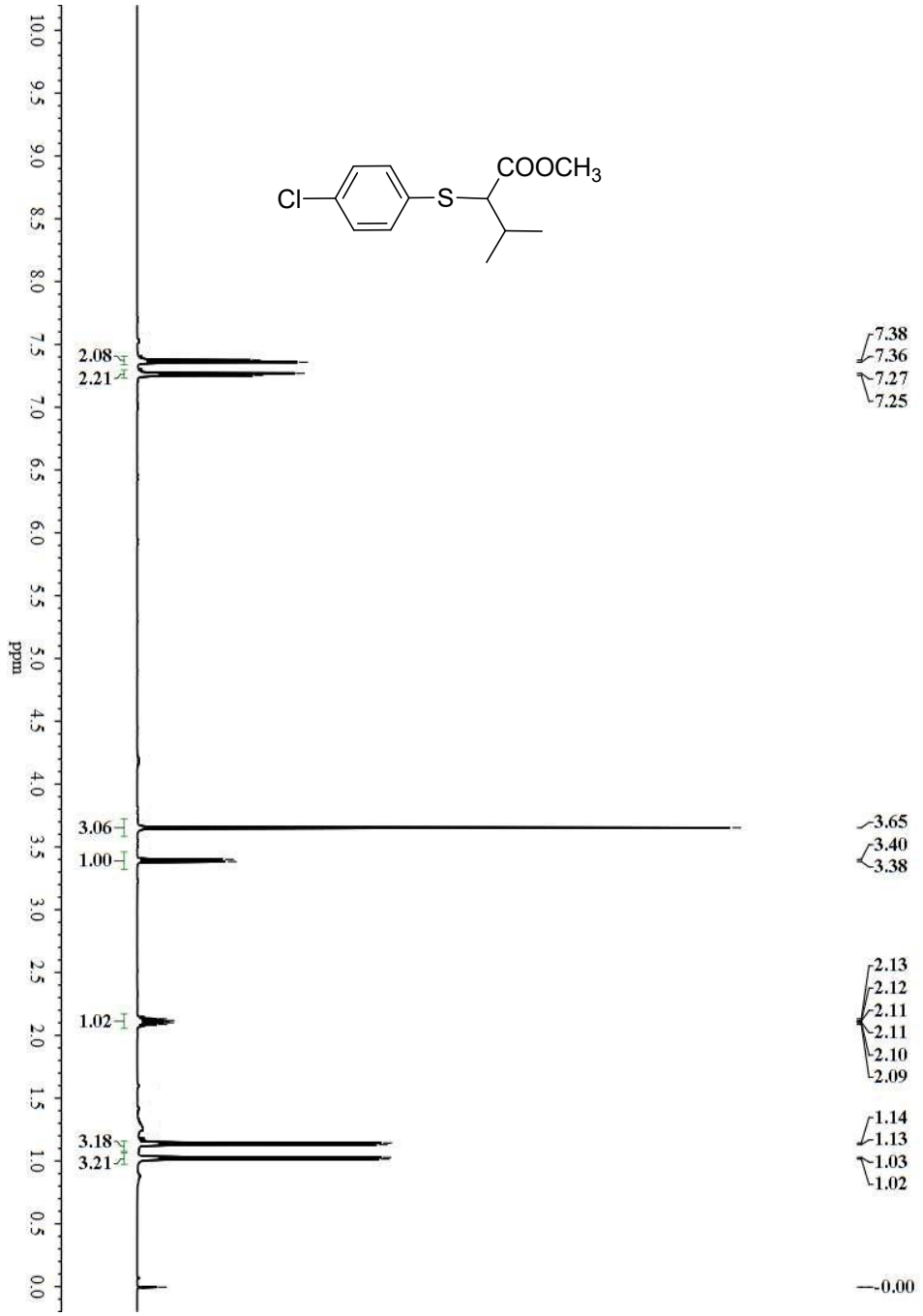
^{13}C NMR Spectra of Compound **4h**.



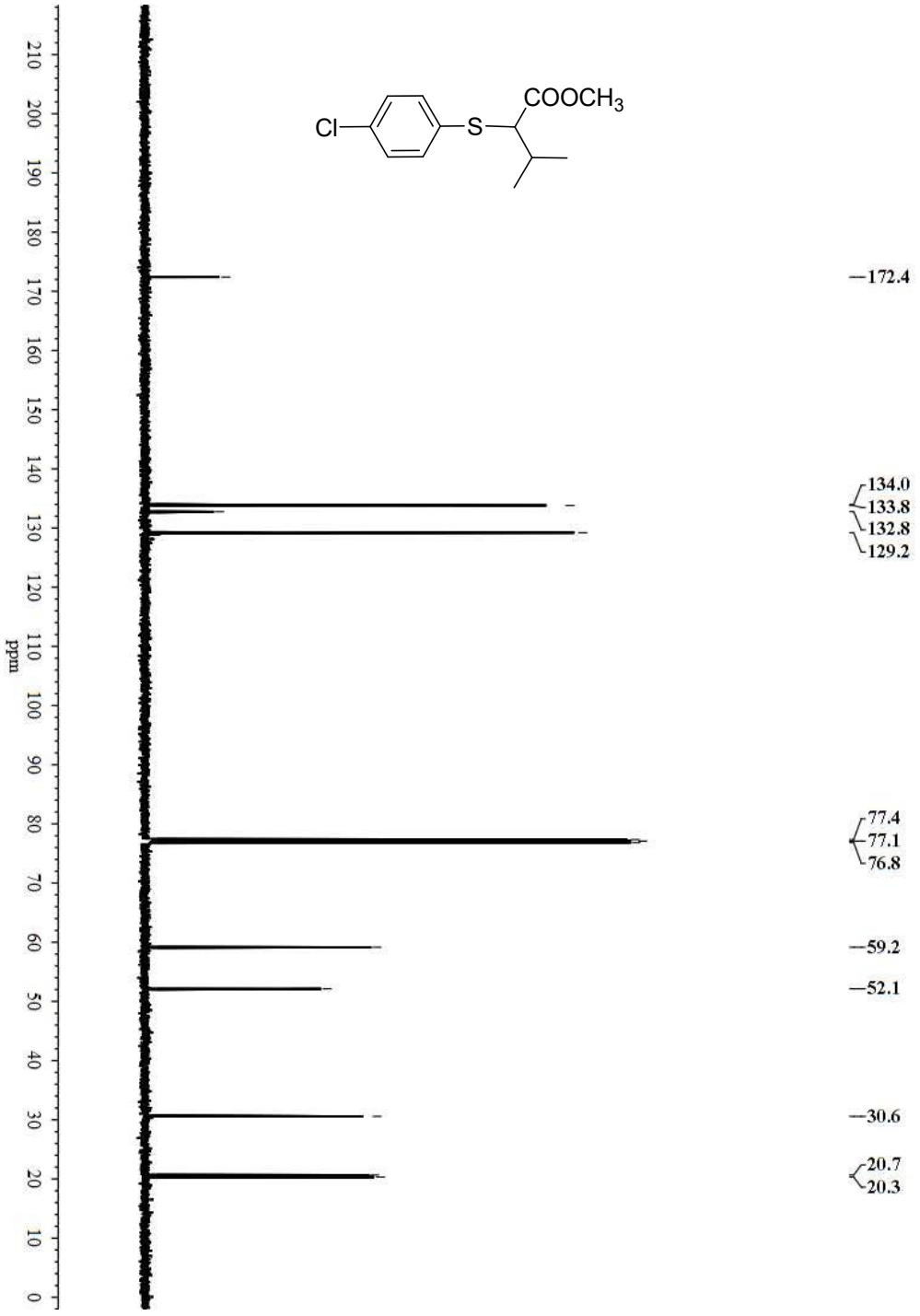
^{1}H NMR Spectra of Compound **4i**.



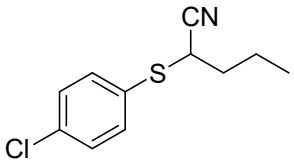
^{13}C NMR Spectra of Compound **4i**.

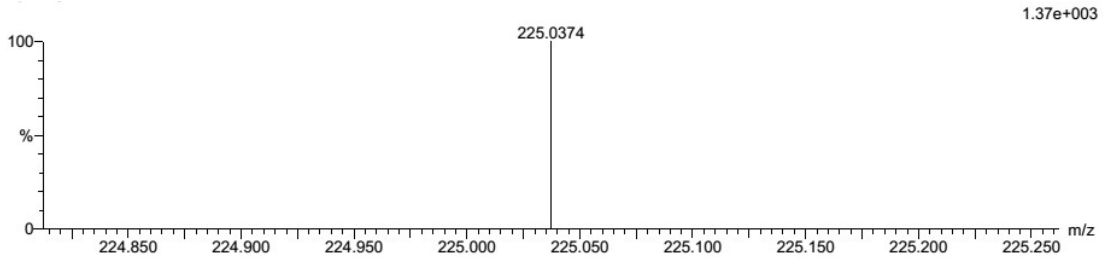


^{1}H NMR Spectra of Compound **4j**.



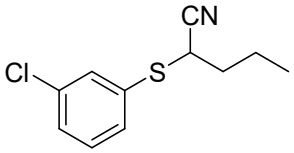
^{13}C NMR Spectra of Compound **4j**.

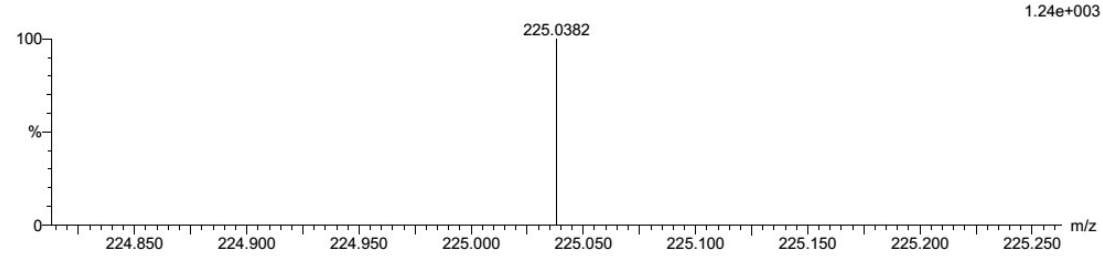




Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
225.0374	225.0379	-0.5	-2.2	6.0	5546704.5	C11 H12 N S Cl

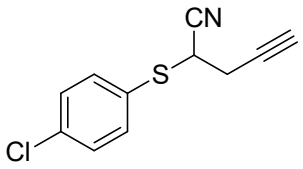
HRMS of Compound **7c**.

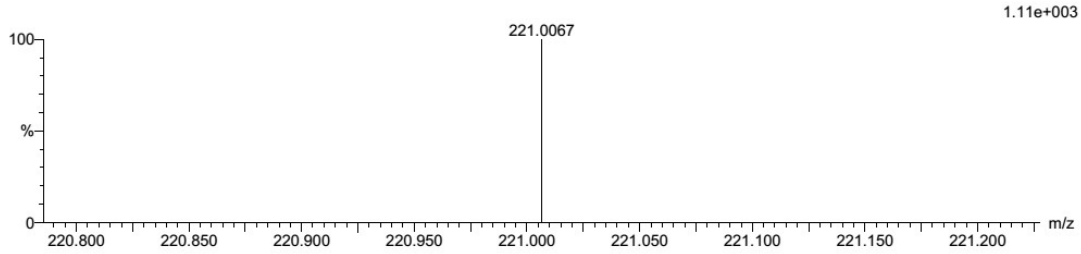




Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
225.0382	225.0379	0.3	1.3	6.0	5546638.0	C11 H12 N S Cl

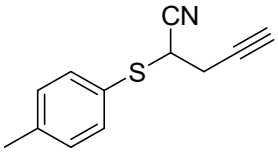
HRMS of Compound **7d**.

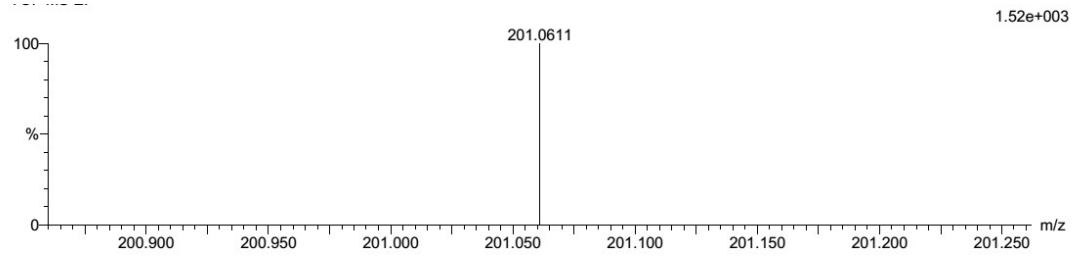




Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
221.0067	221.0066	0.1	0.5	8.0	5546575.5	C11 H8 N S Cl

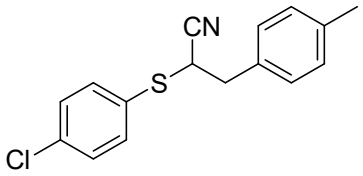
HRMS of Compound **7e**.

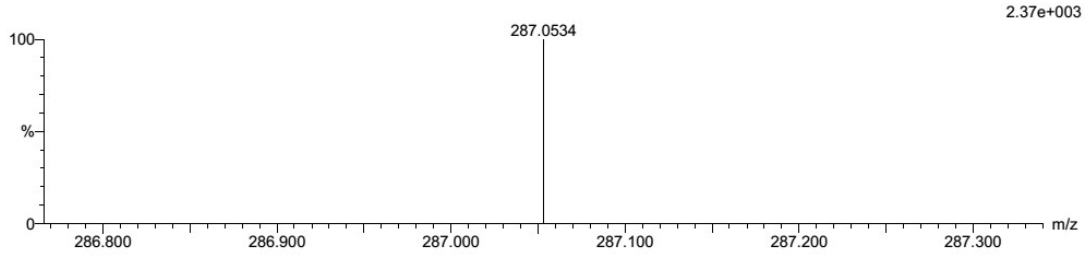




Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
201.0611	201.0612	-0.1	-0.5	8.0	5546757.5	C12 H11 N S

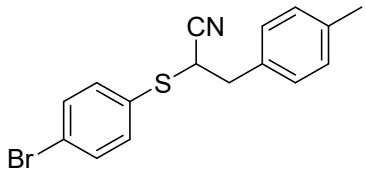
HRMS of Compound **7f**.

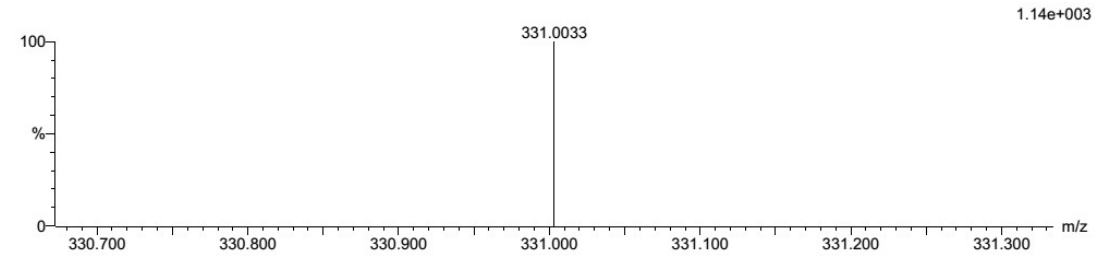




Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
287.0534	287.0535	-0.1	-0.3	10.0	5547204.0	C16 H14 N S Cl

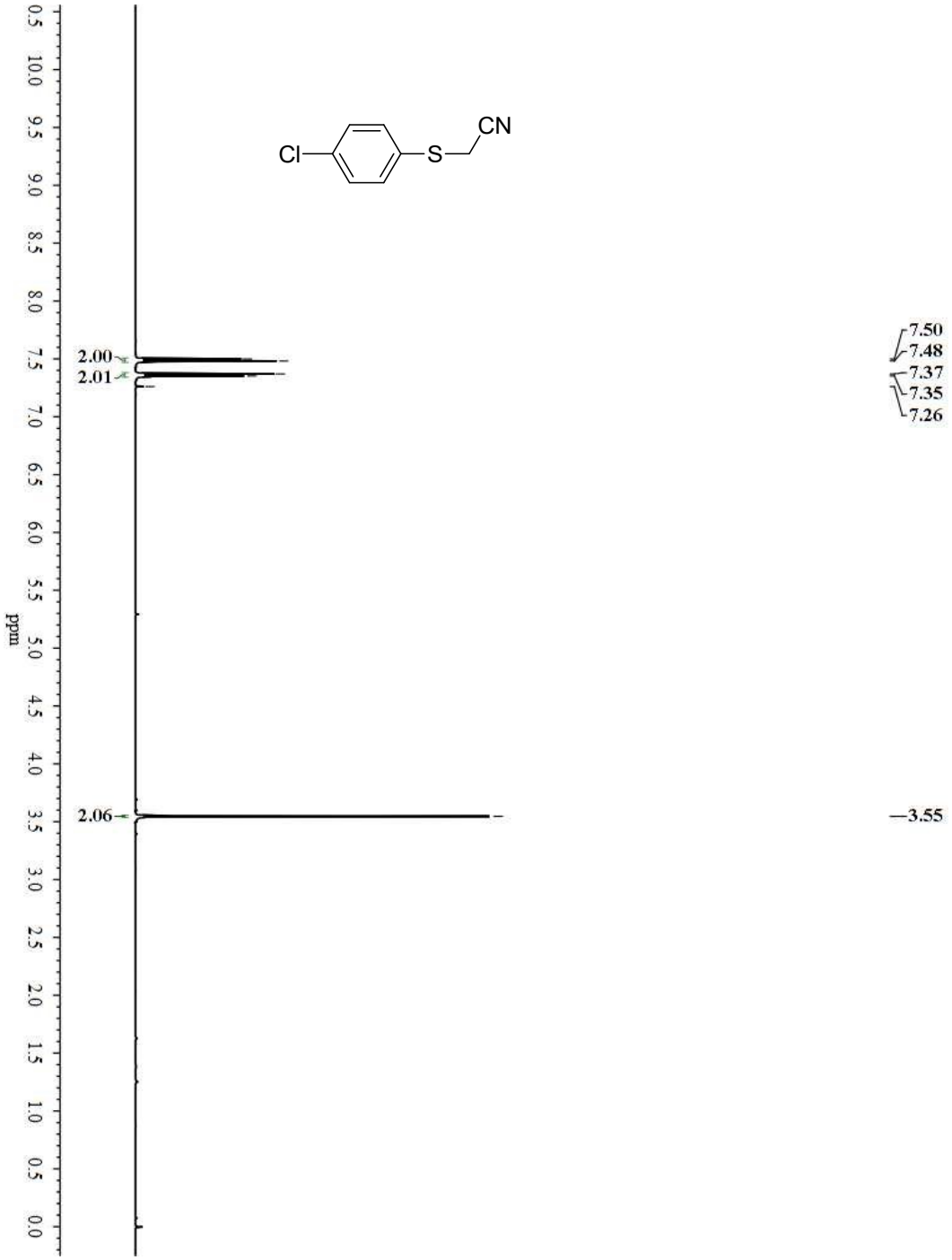
HRMS of Compound **7g**.



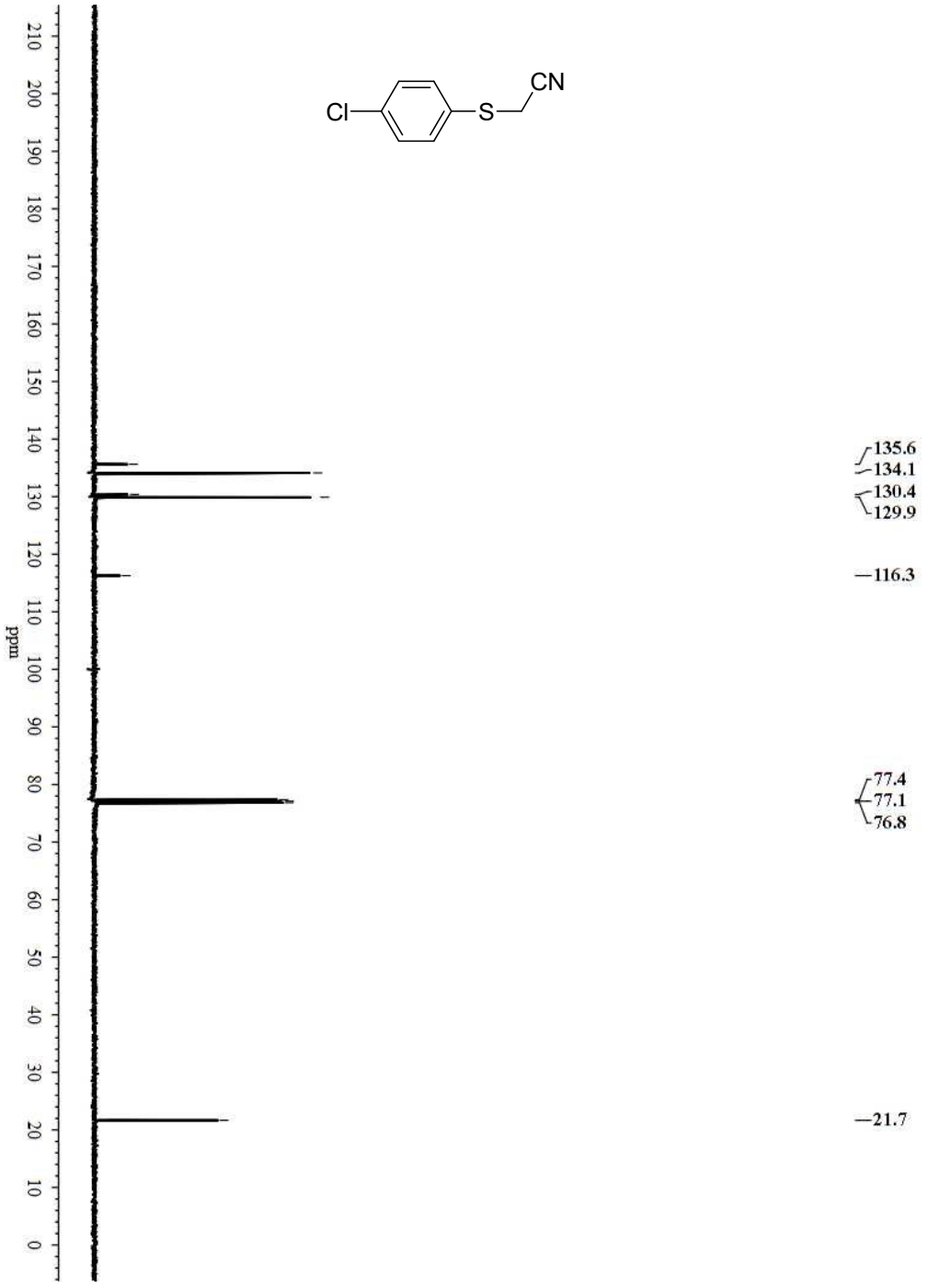


Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
331.0033	331.0030	0.3	0.9	10.0	5546593.5	C16 H14 N S Br

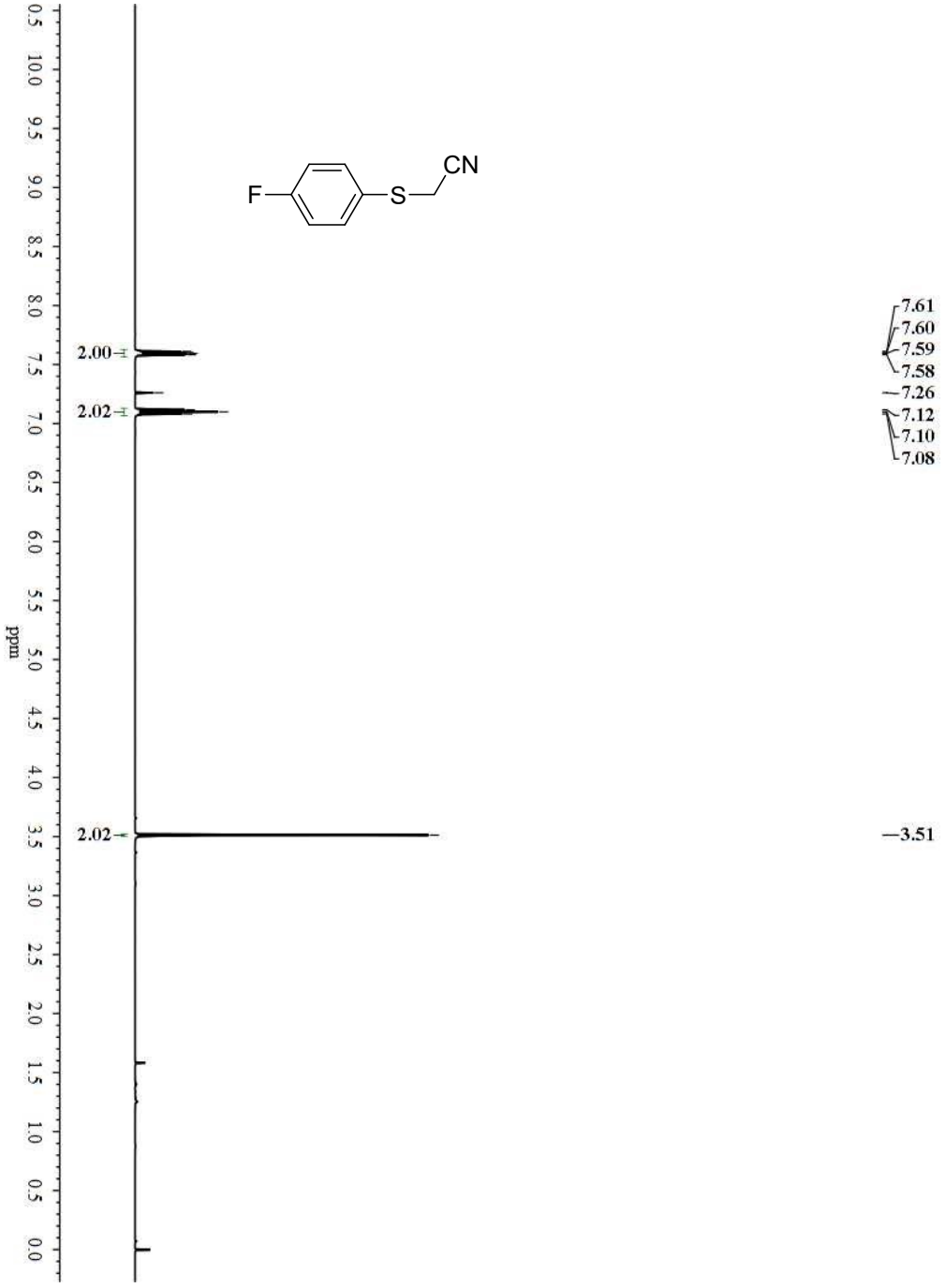
HRMS of Compound **7h**.



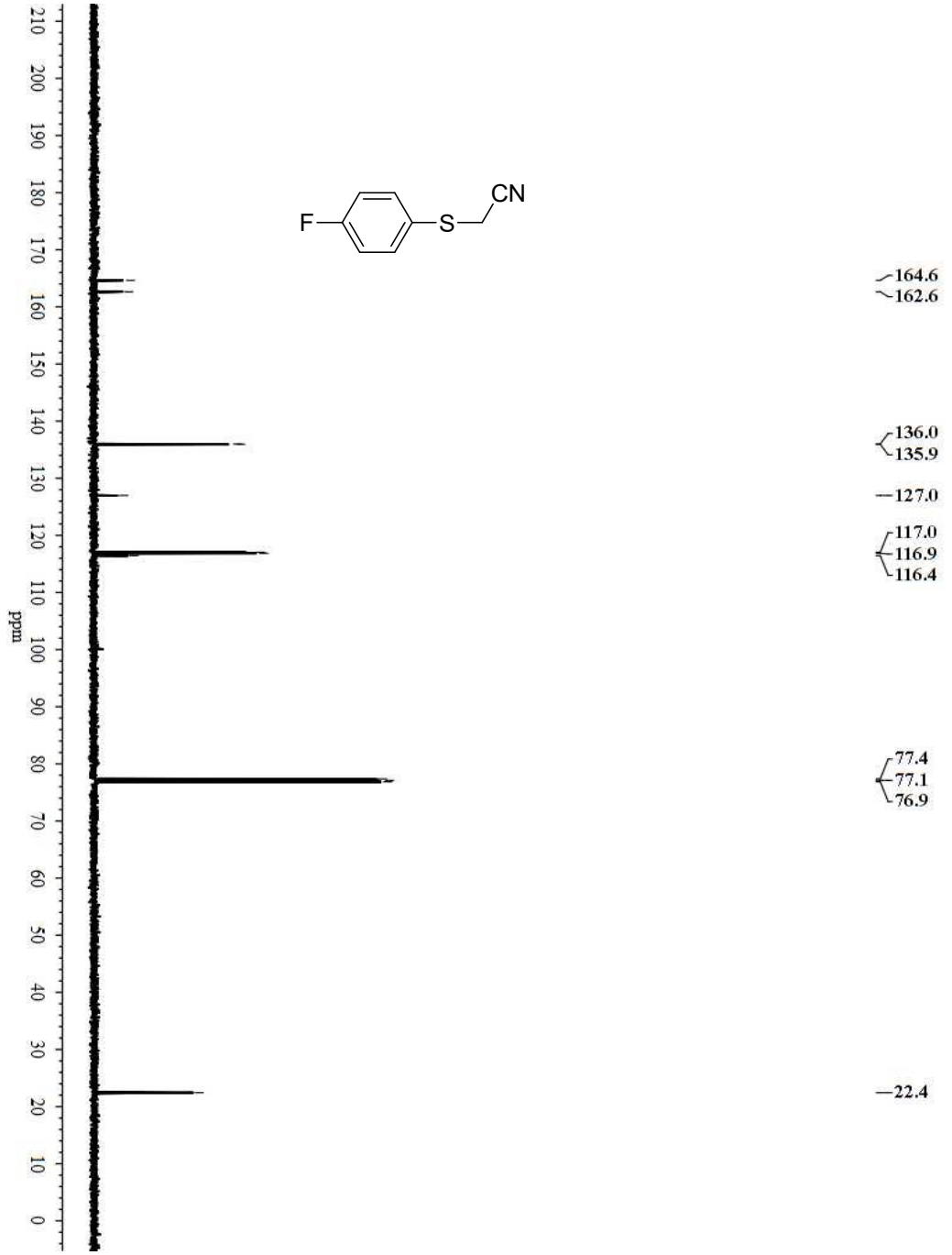
^{1}H NMR Spectra of Compound **6a**.



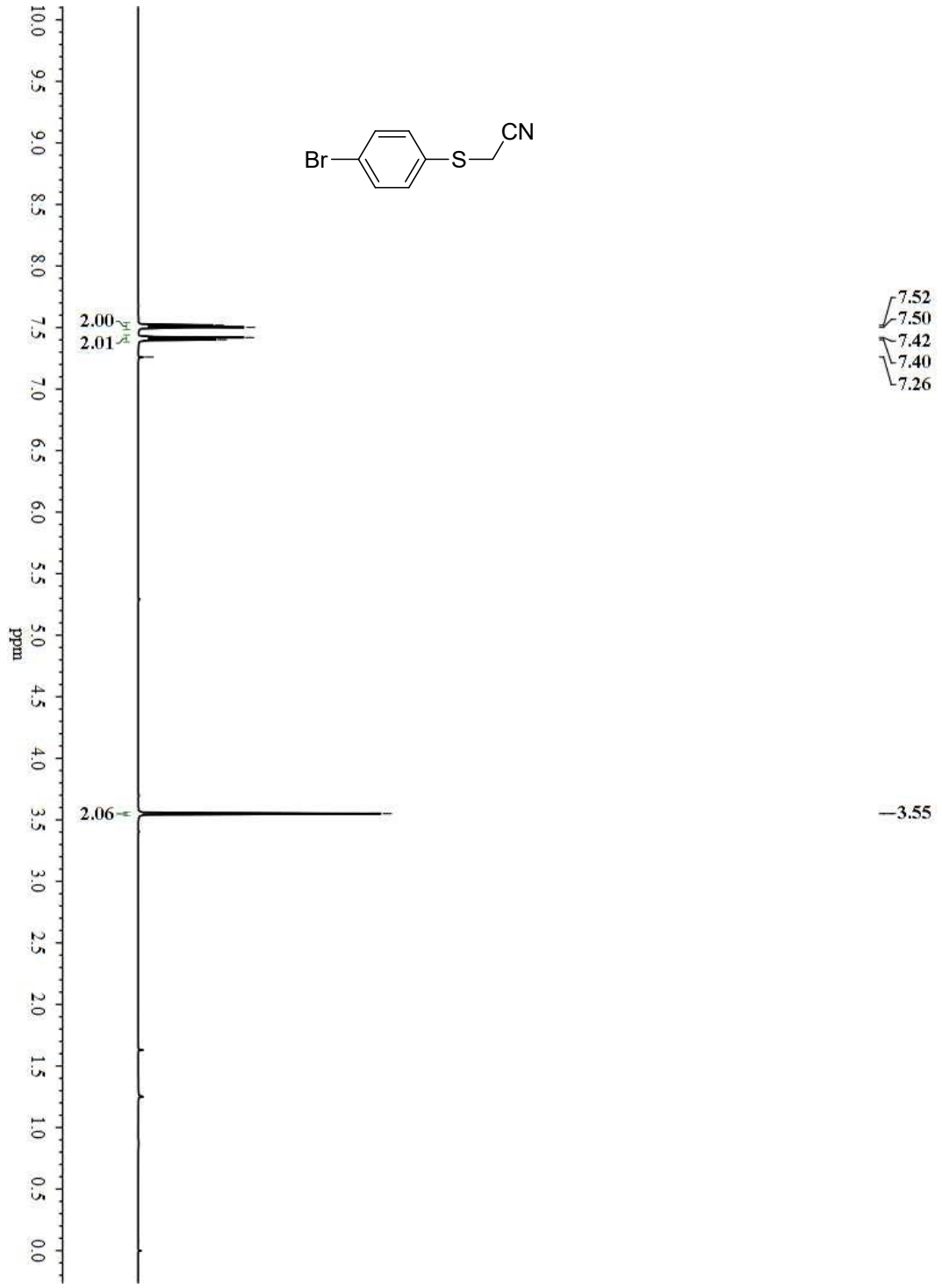
^{13}C NMR Spectra of Compound **6a**.



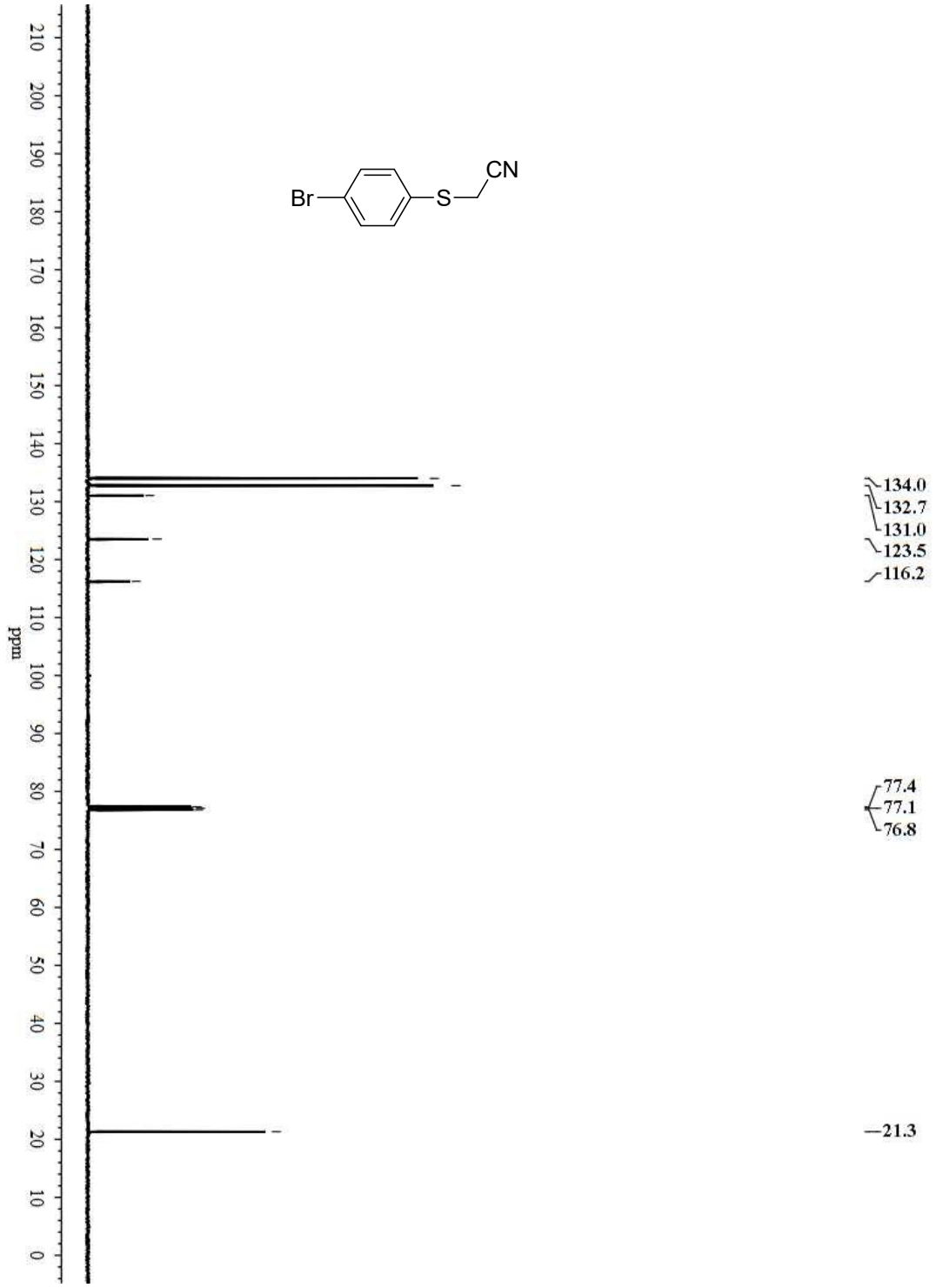
^{1}H NMR Spectra of Compound **6b**.



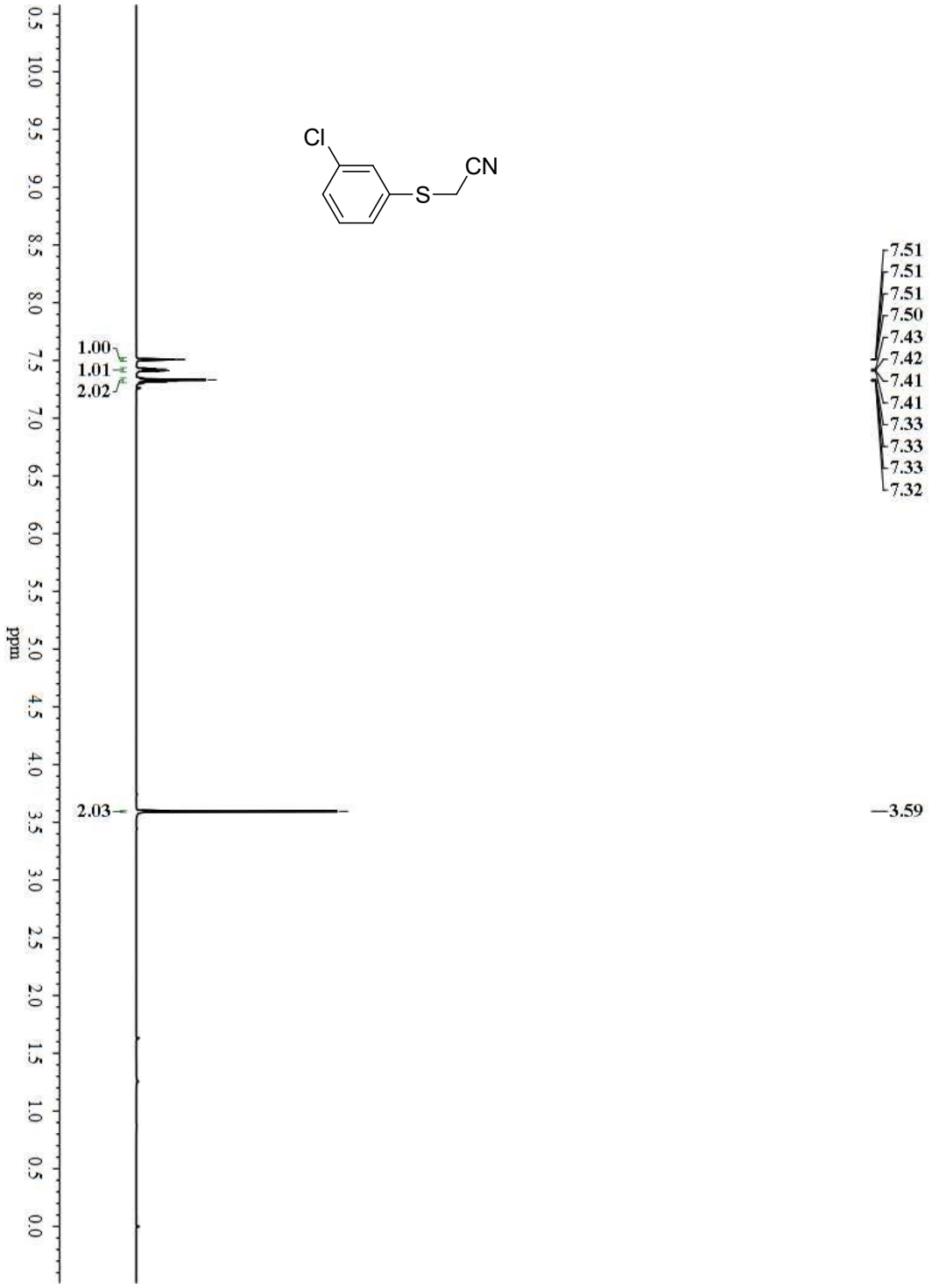
^{13}C NMR Spectra of Compound **6b**.



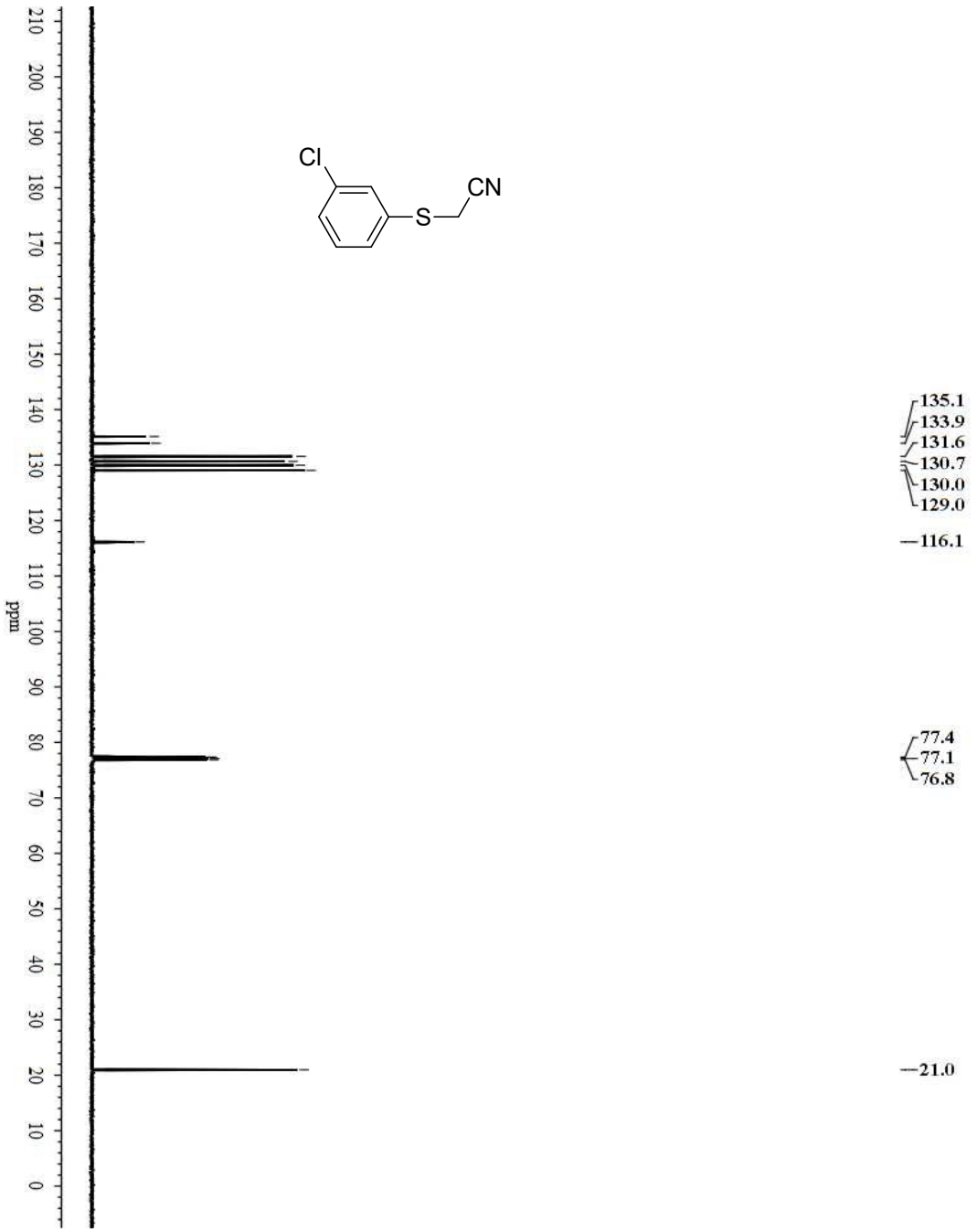
^{1}H NMR Spectra of Compound **6c**.



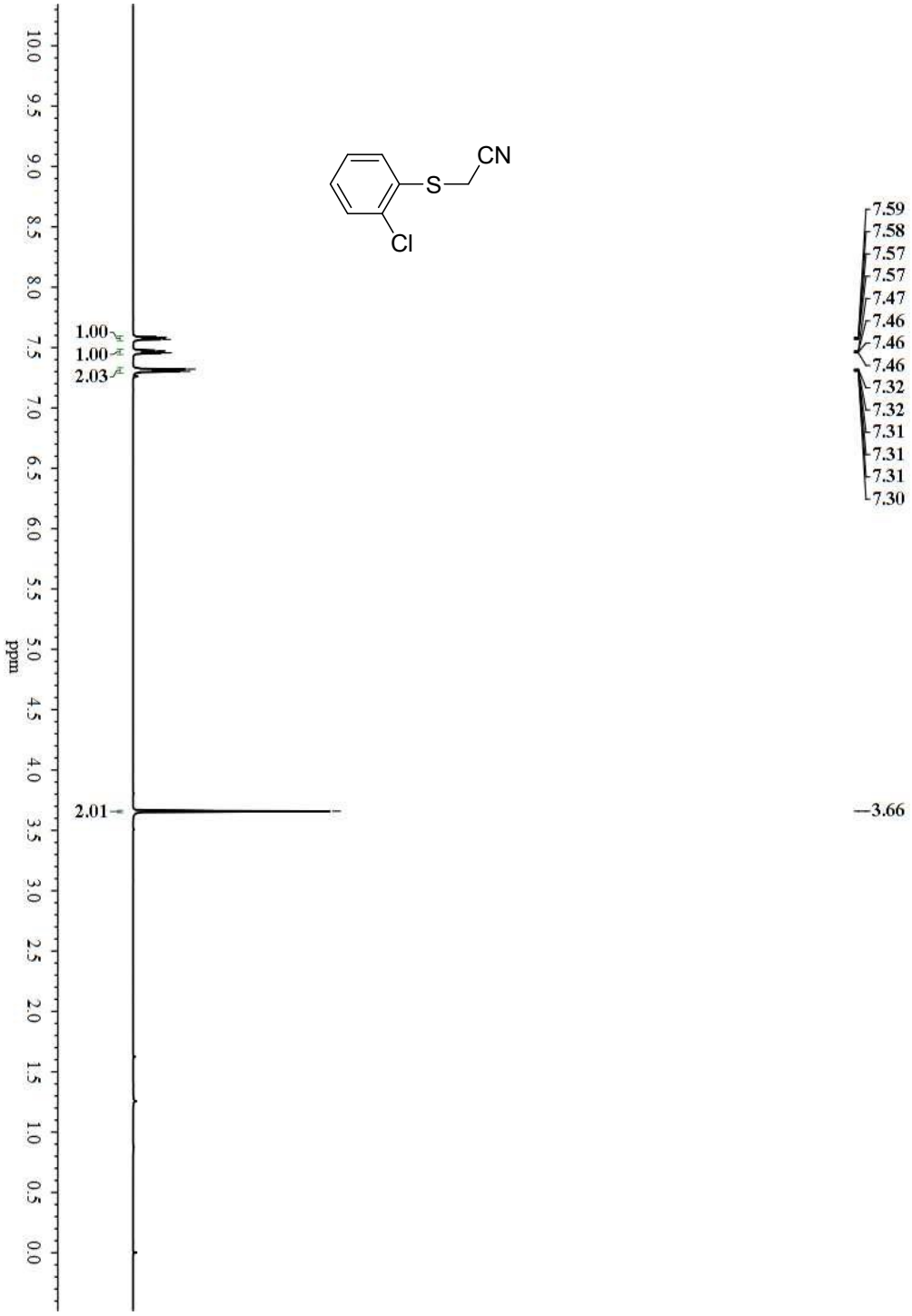
^{13}C NMR Spectra of Compound **6c**.



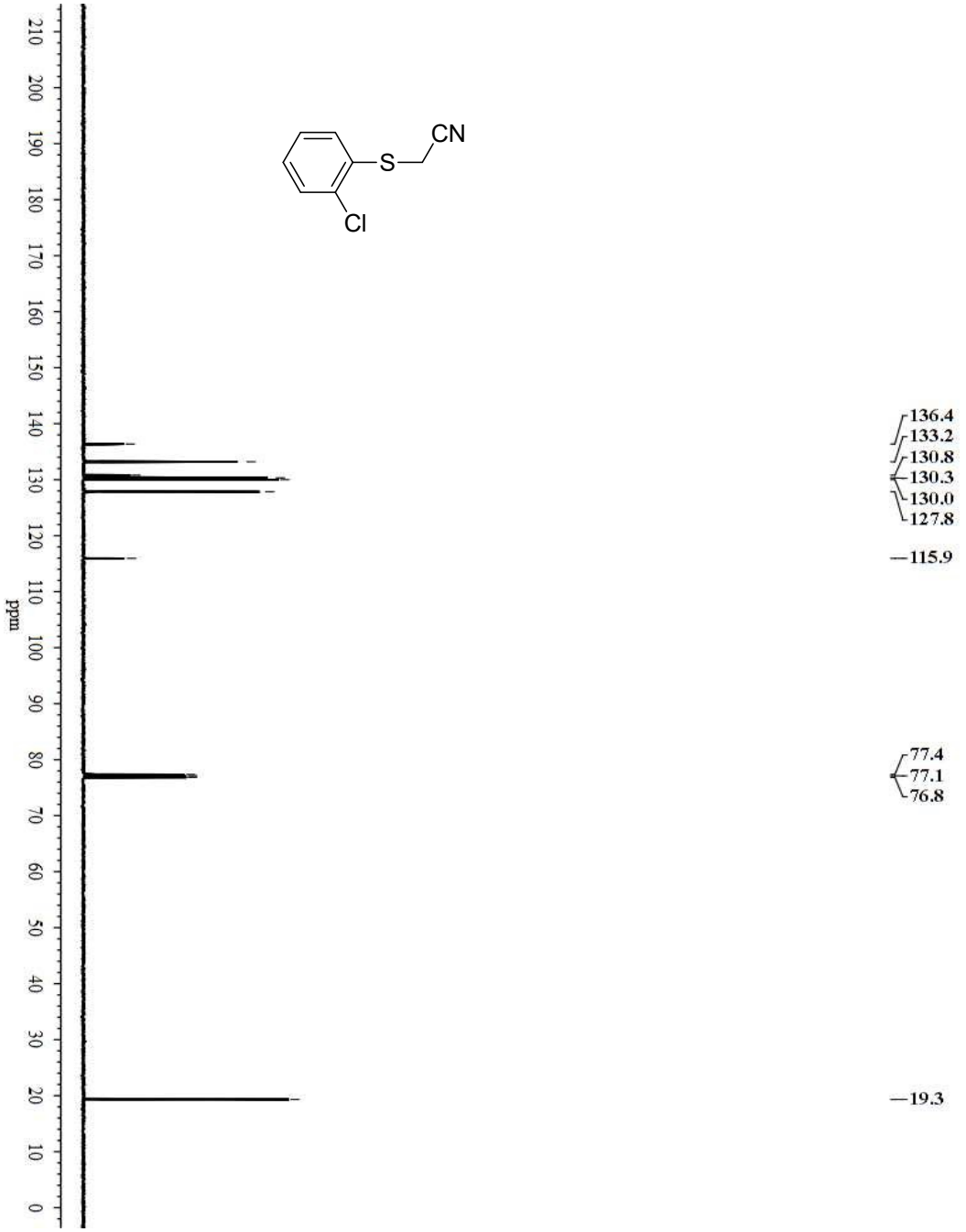
^{1}H NMR Spectra of Compound **6d**.



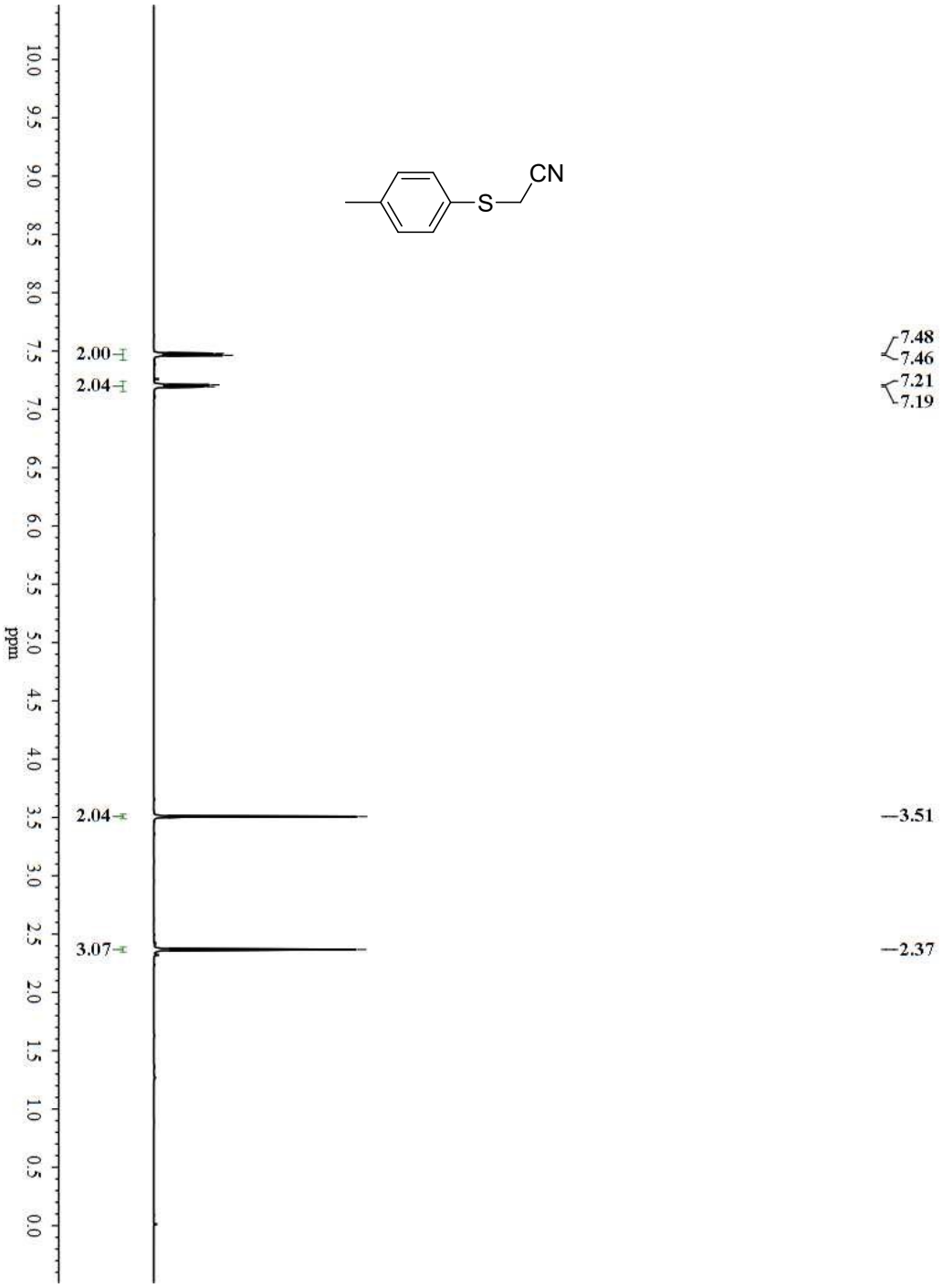
^{13}C NMR Spectra of Compound **6d**.



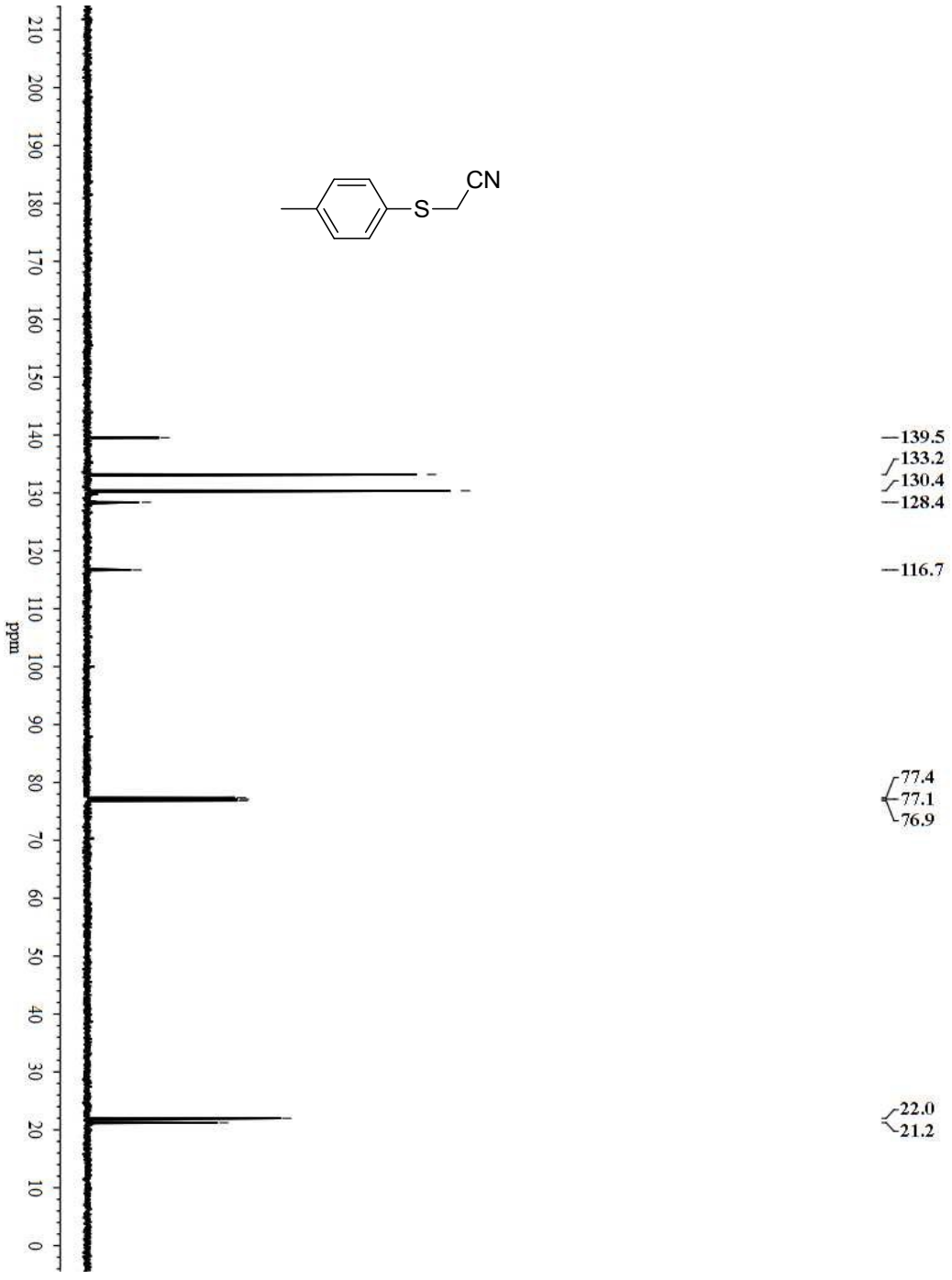
^{1}H NMR Spectra of Compound **6e**.



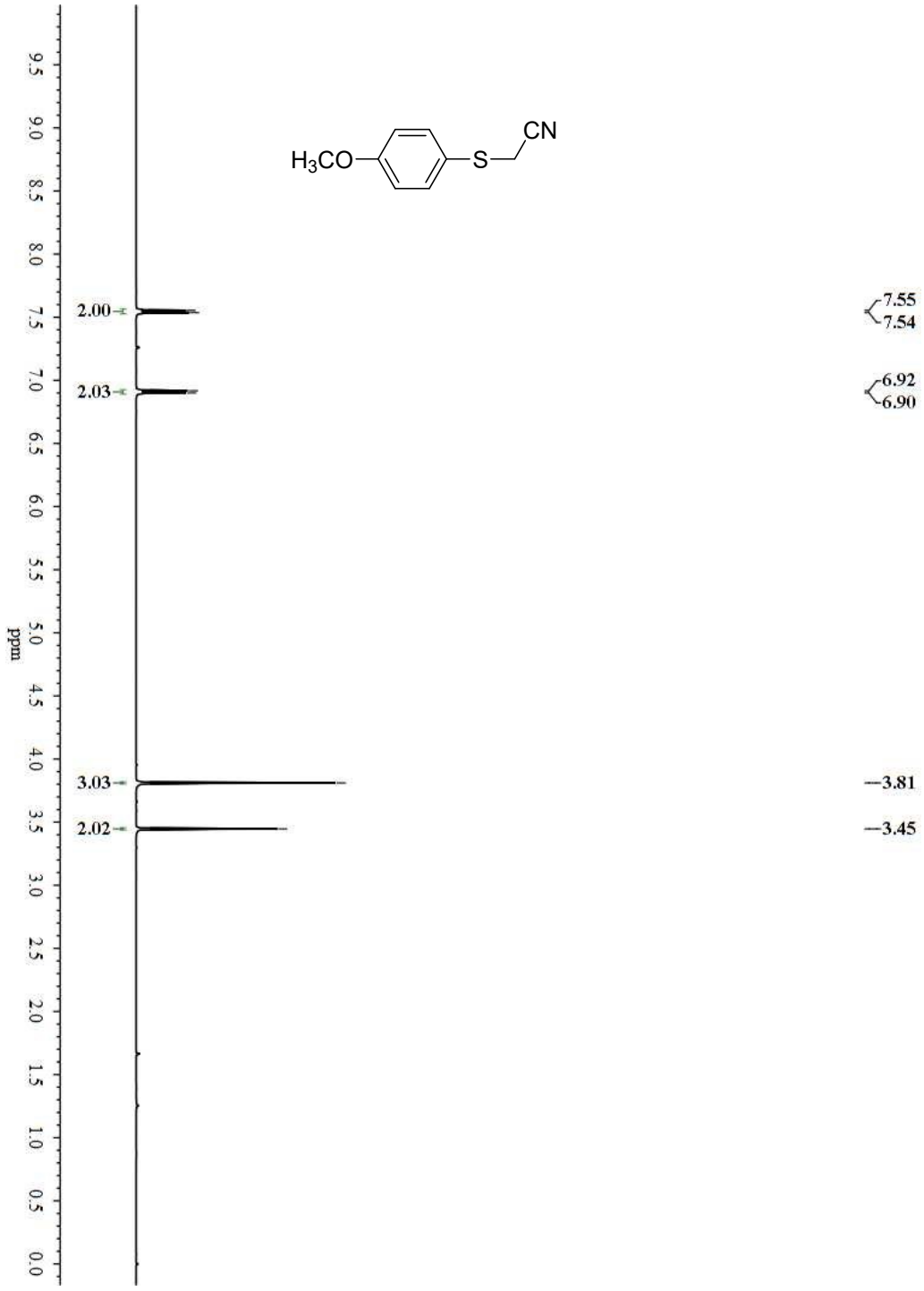
^{13}C NMR Spectra of Compound **6e**.



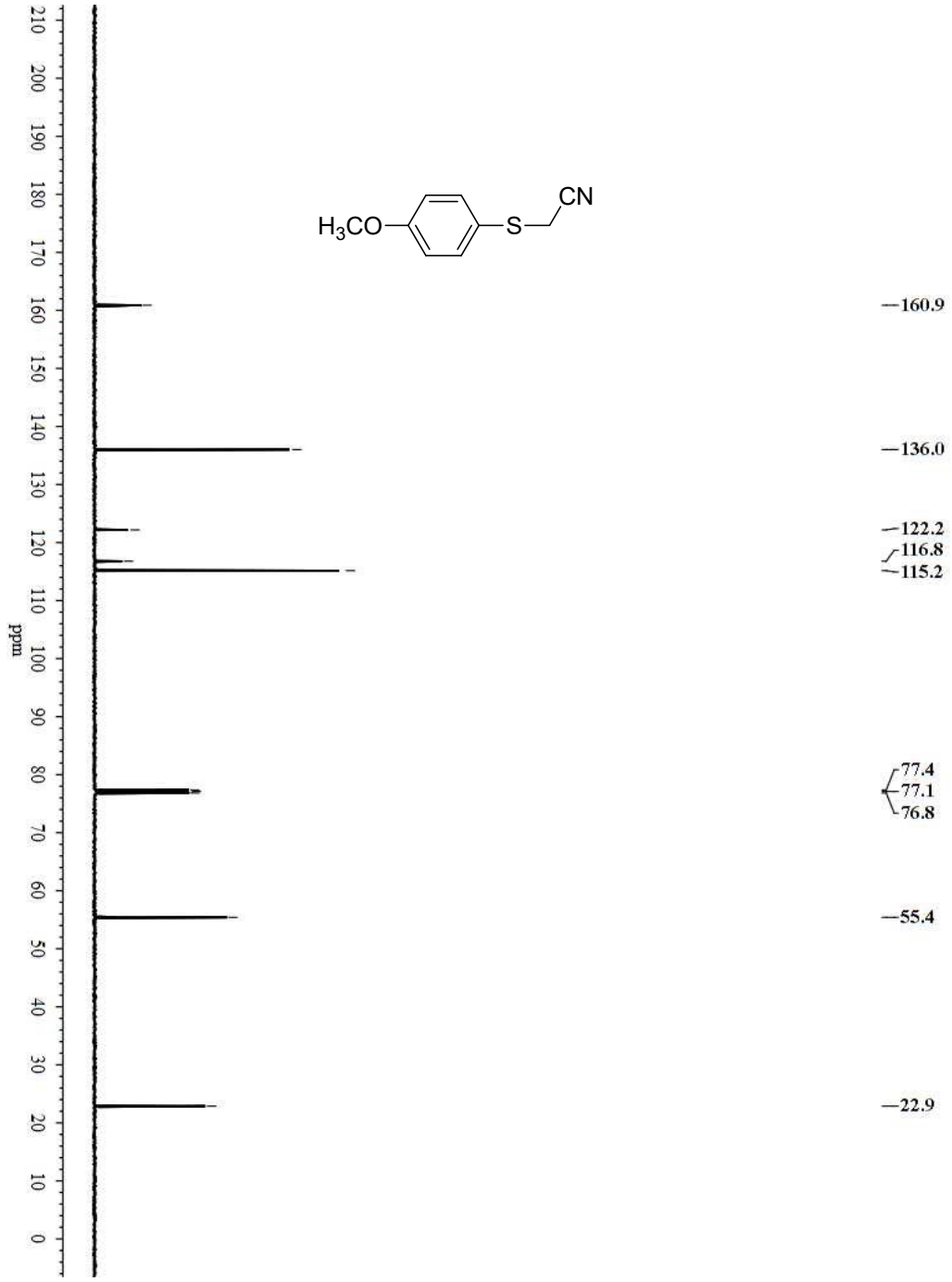
^{13}C NMR Spectra of Compound **6f**.



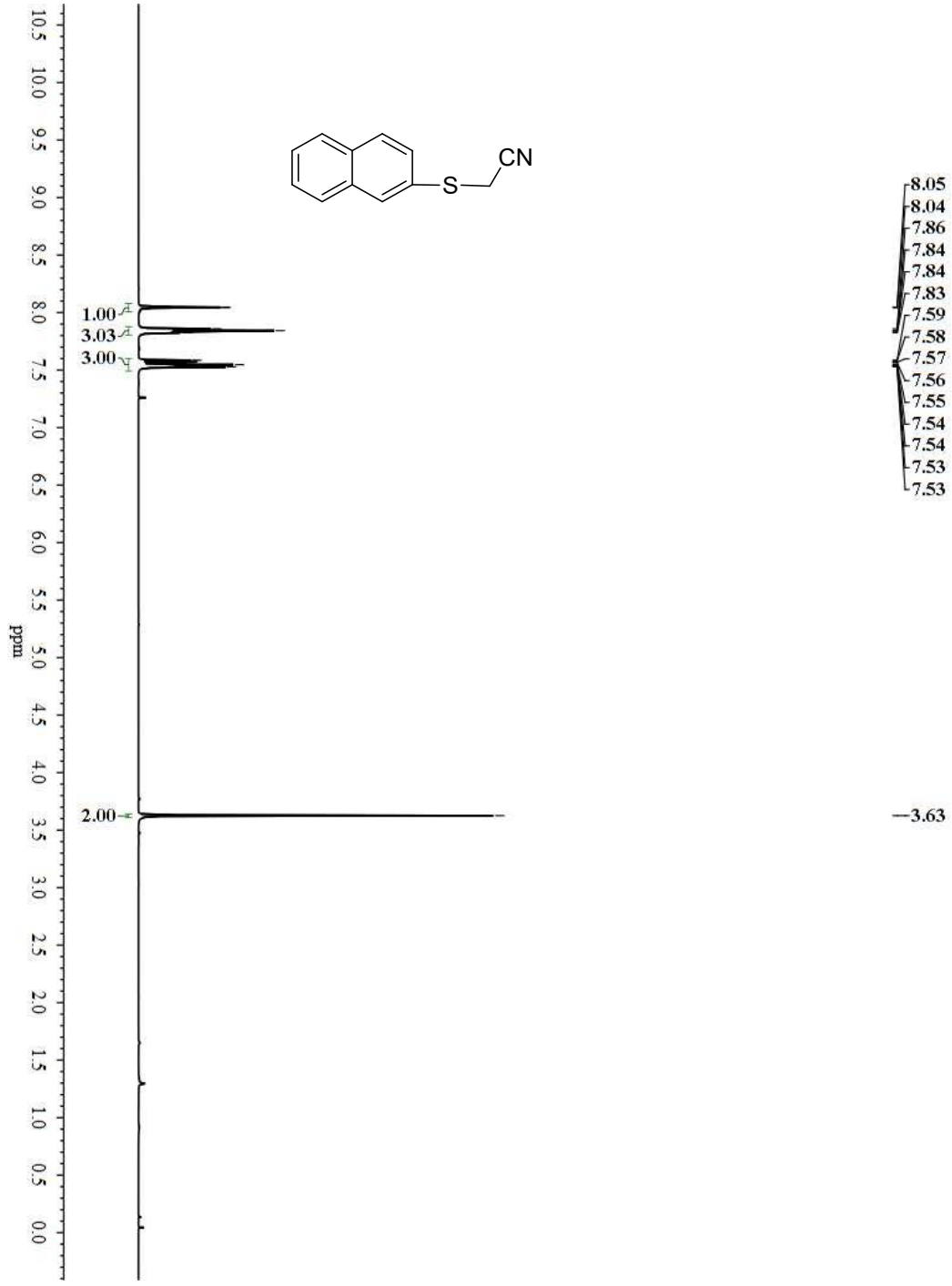
^{13}C NMR Spectra of Compound **6f**.



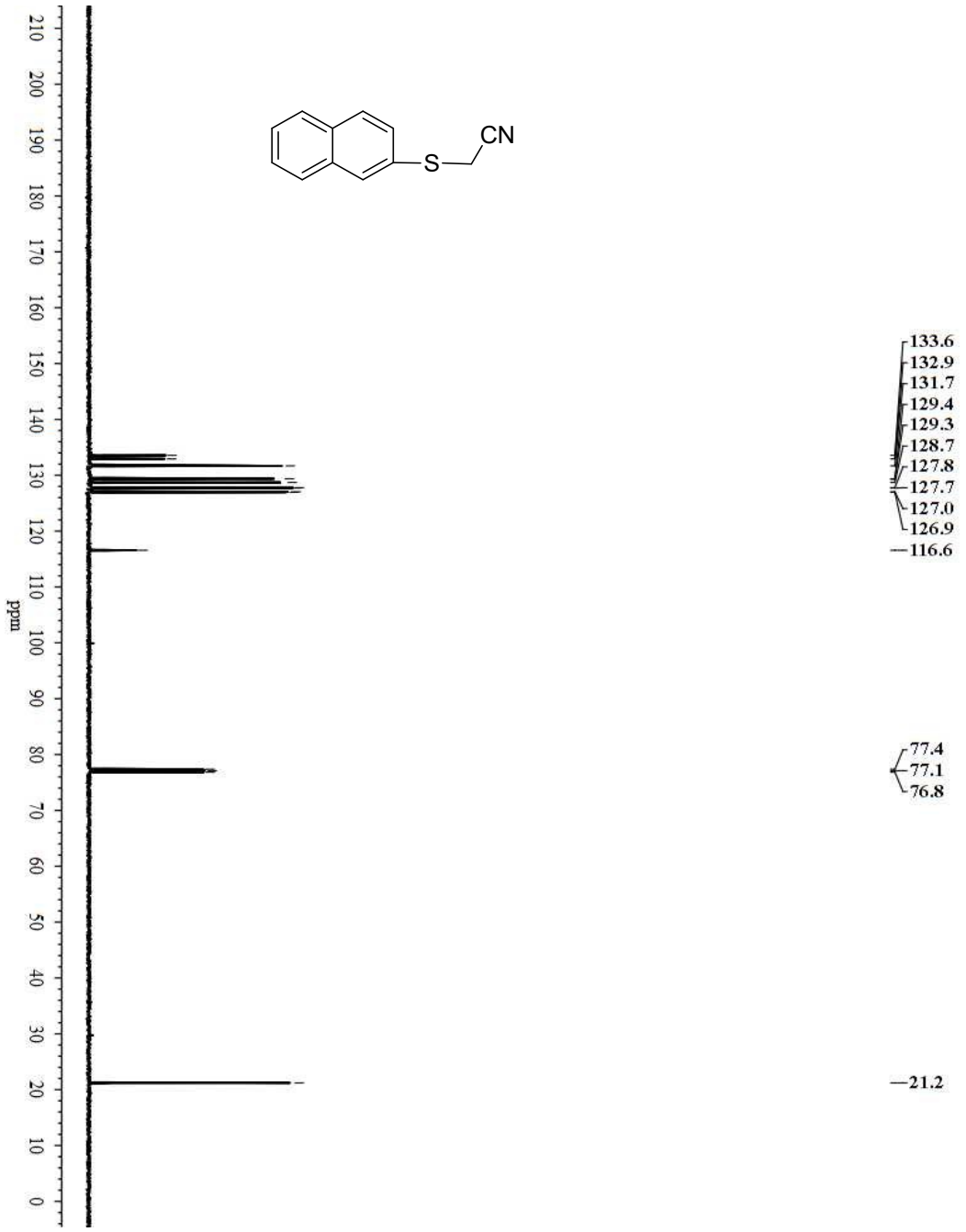
^{1}H NMR Spectra of Compound **6g**.



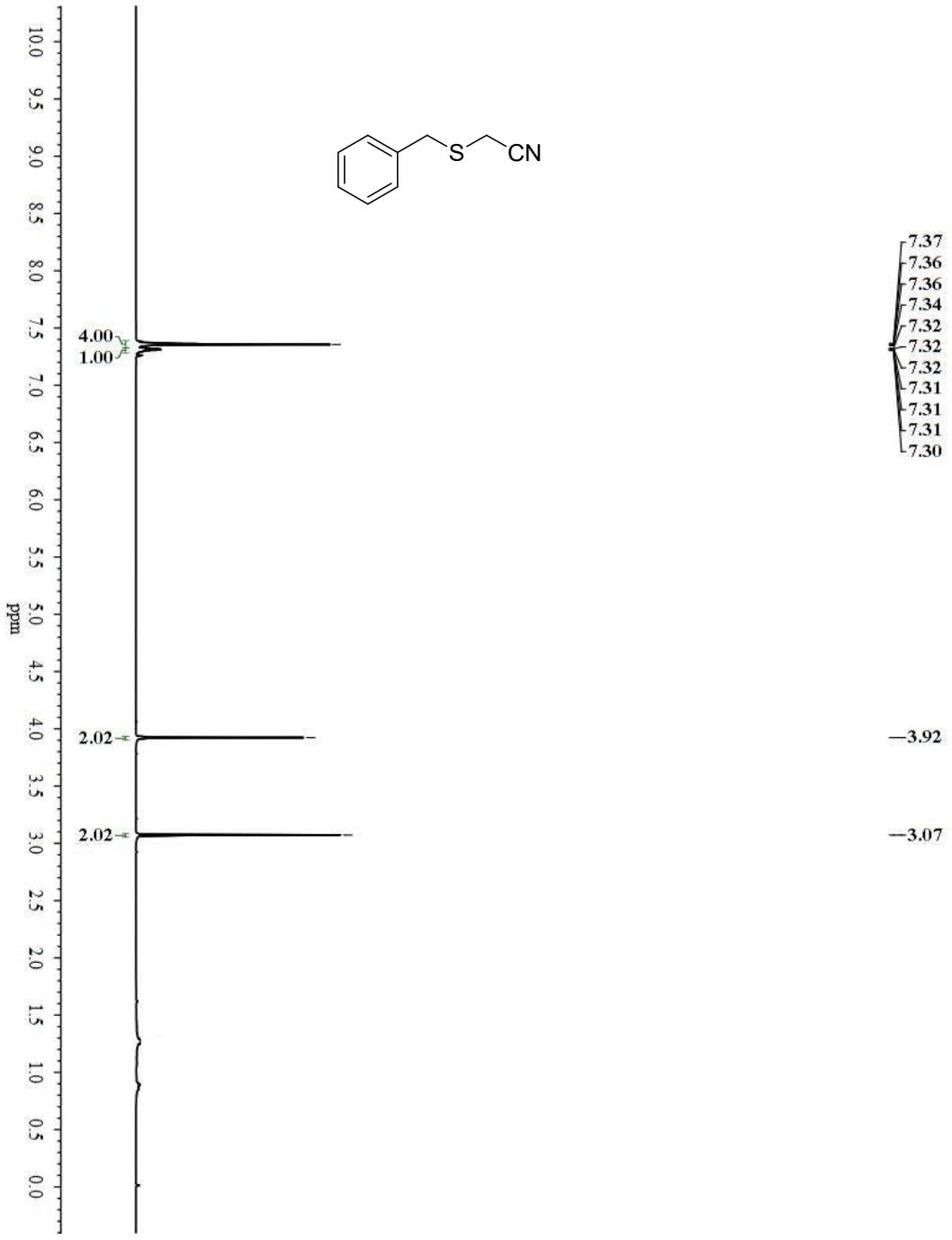
^{13}C NMR Spectra of Compound **6g**.



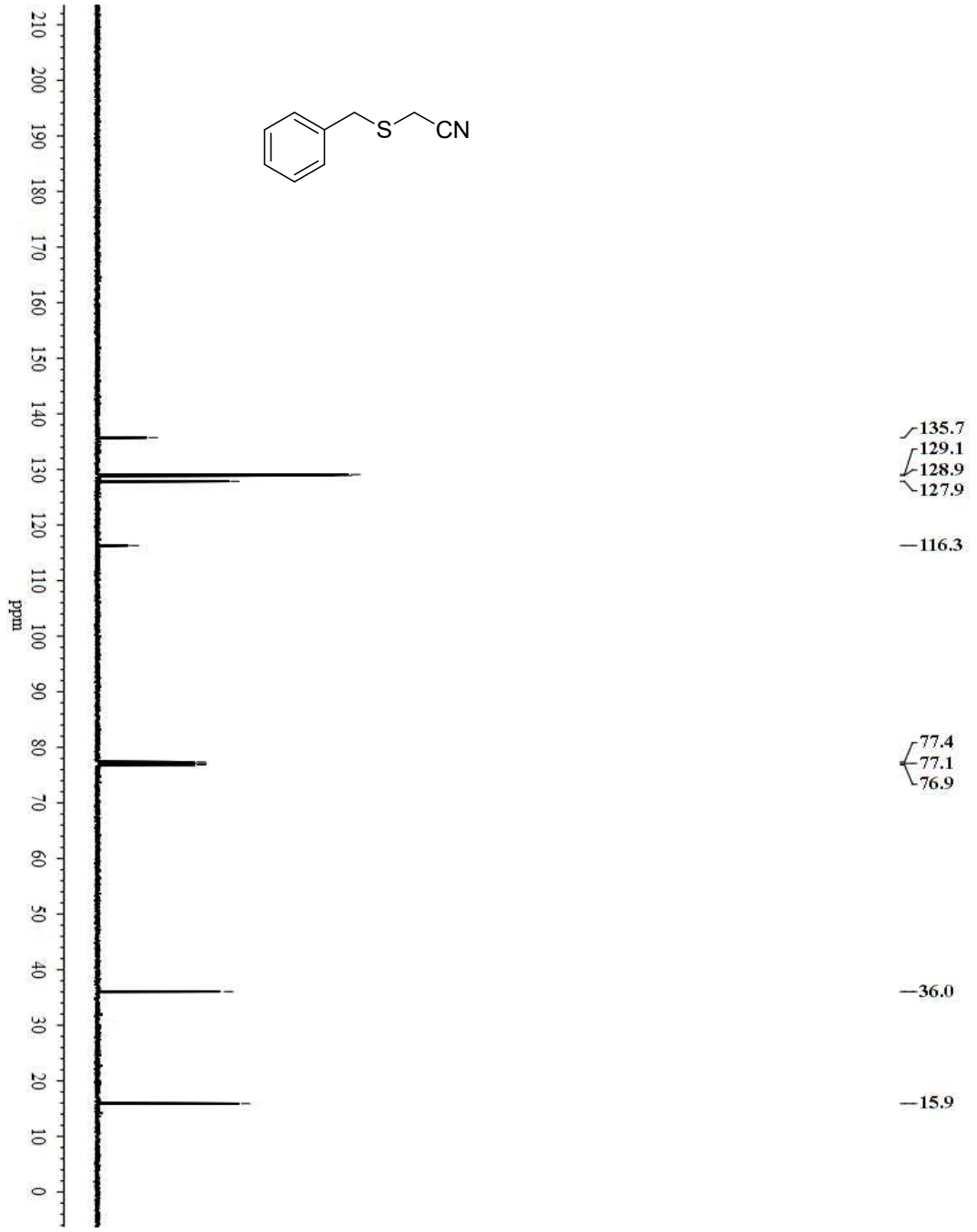
^{1}H NMR Spectra of Compound **6h**.



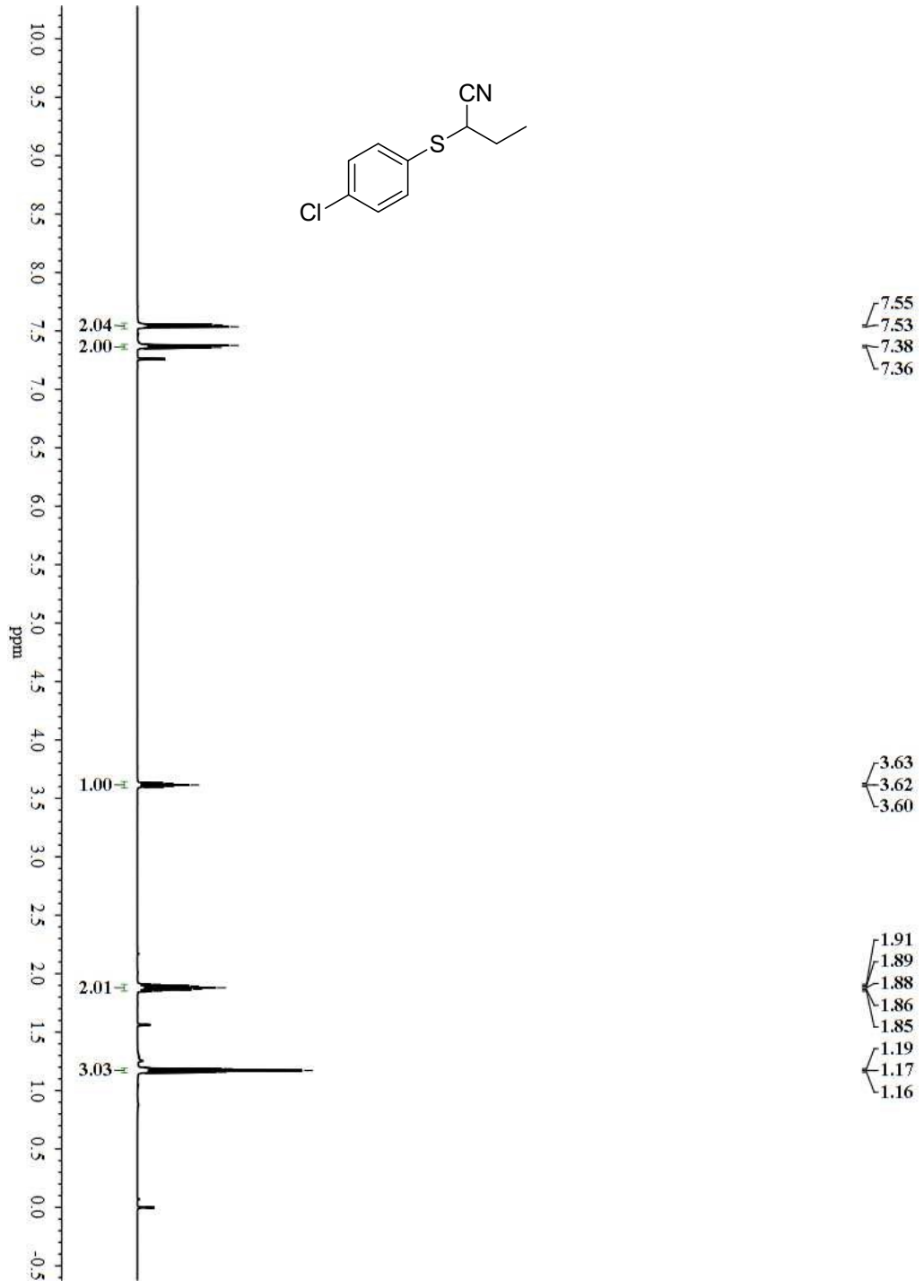
^{13}C NMR Spectra of Compound **6h**.



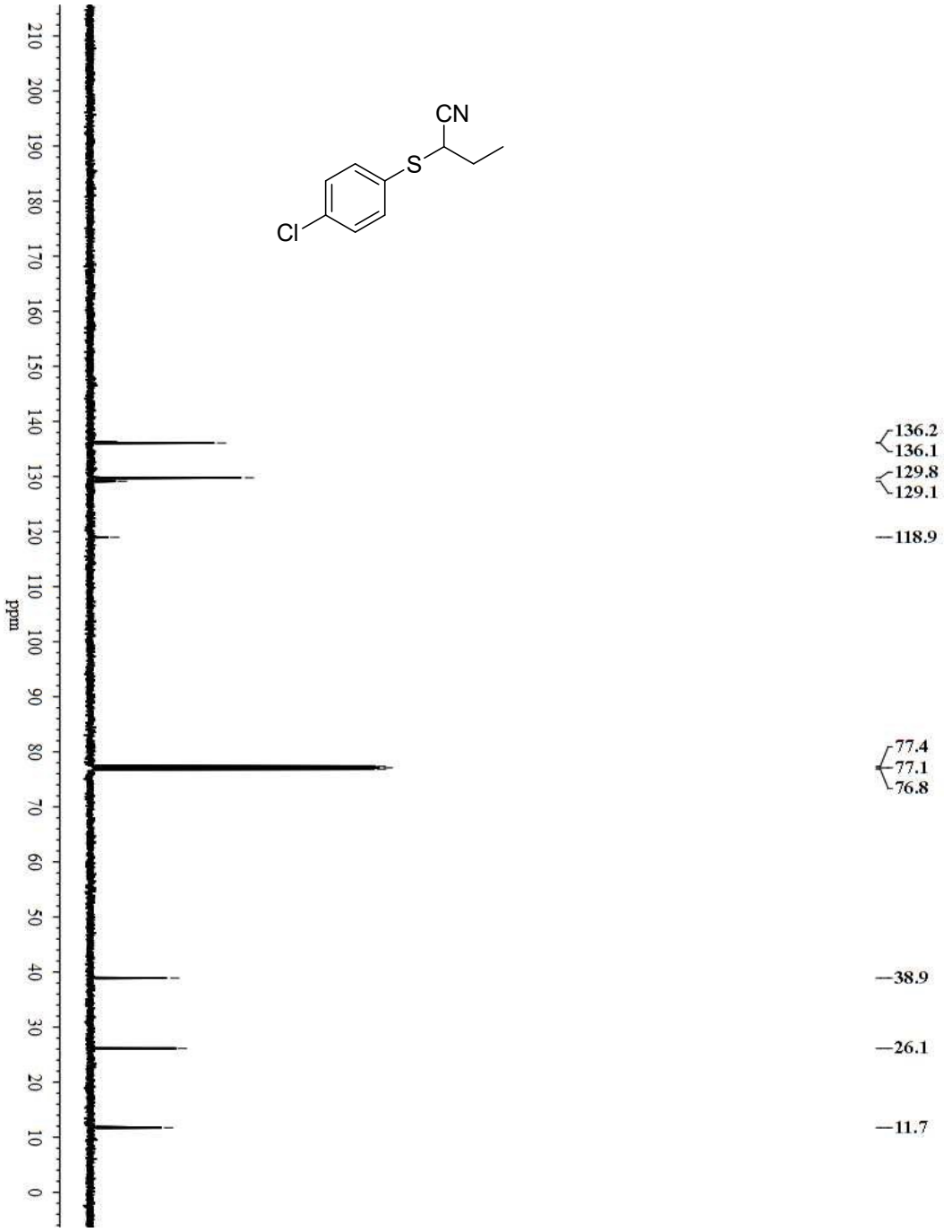
^{1}H NMR Spectra of Compound **6i**.



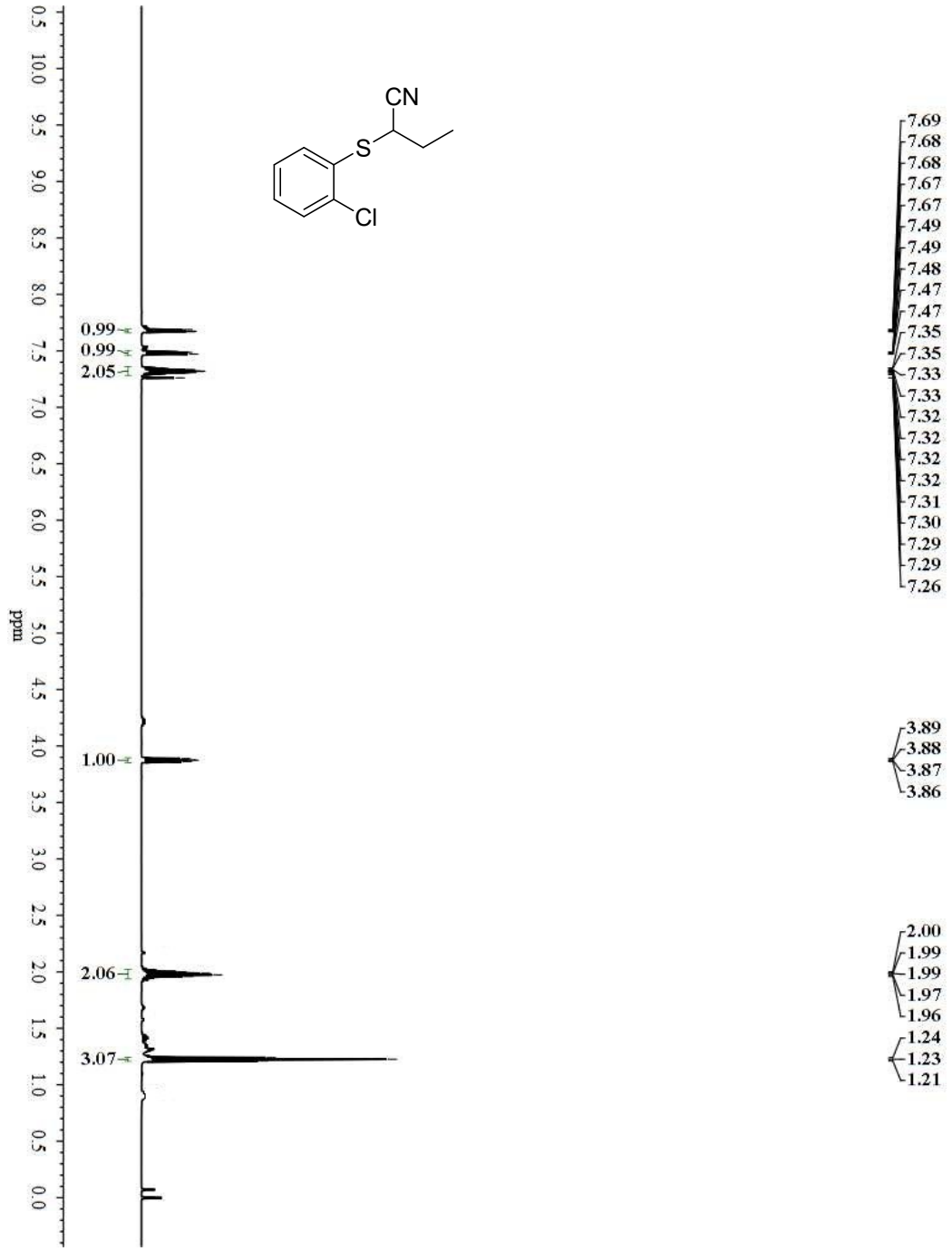
^{13}C NMR Spectra of Compound **6i**.



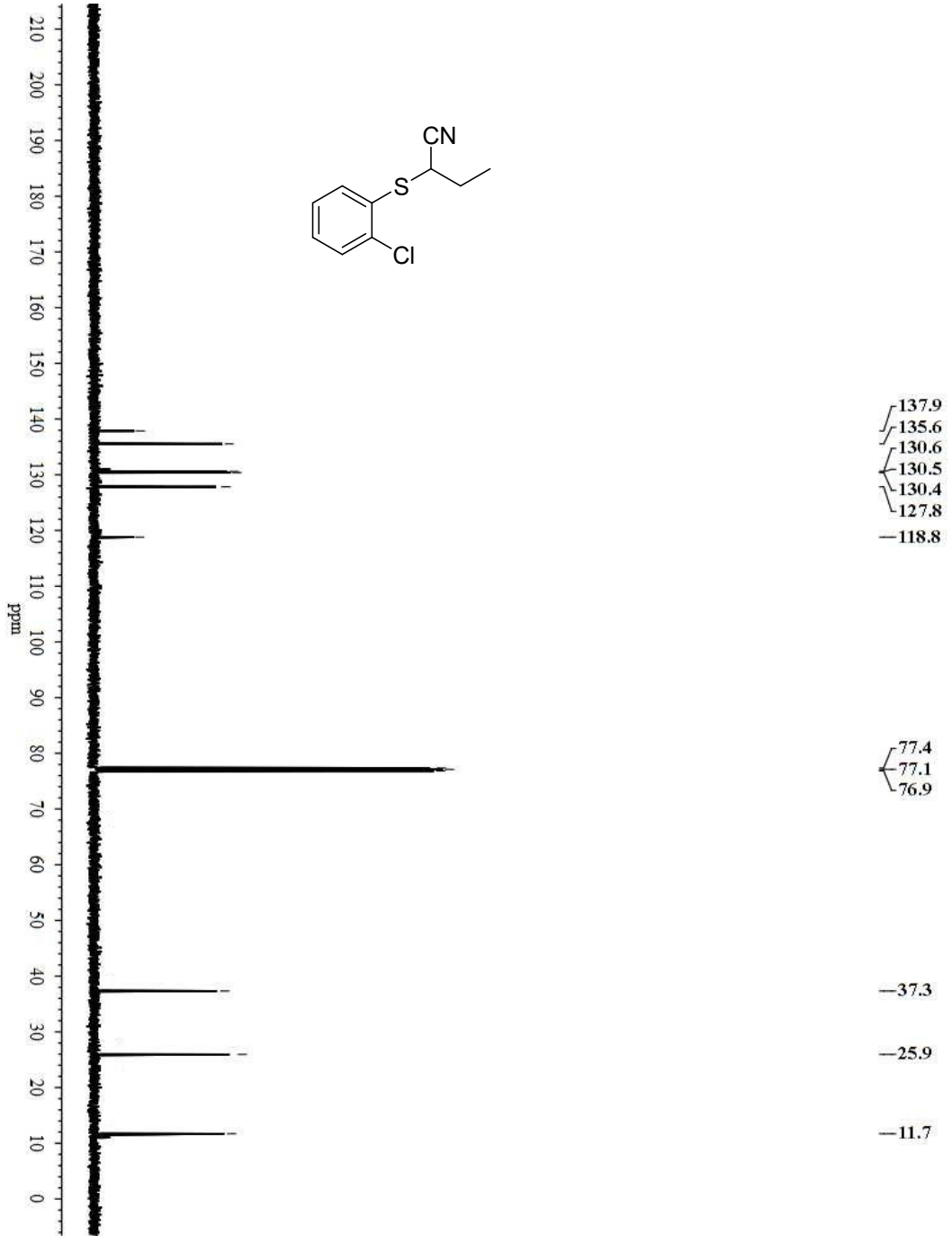
^{1}H NMR Spectra of Compound **7a**.



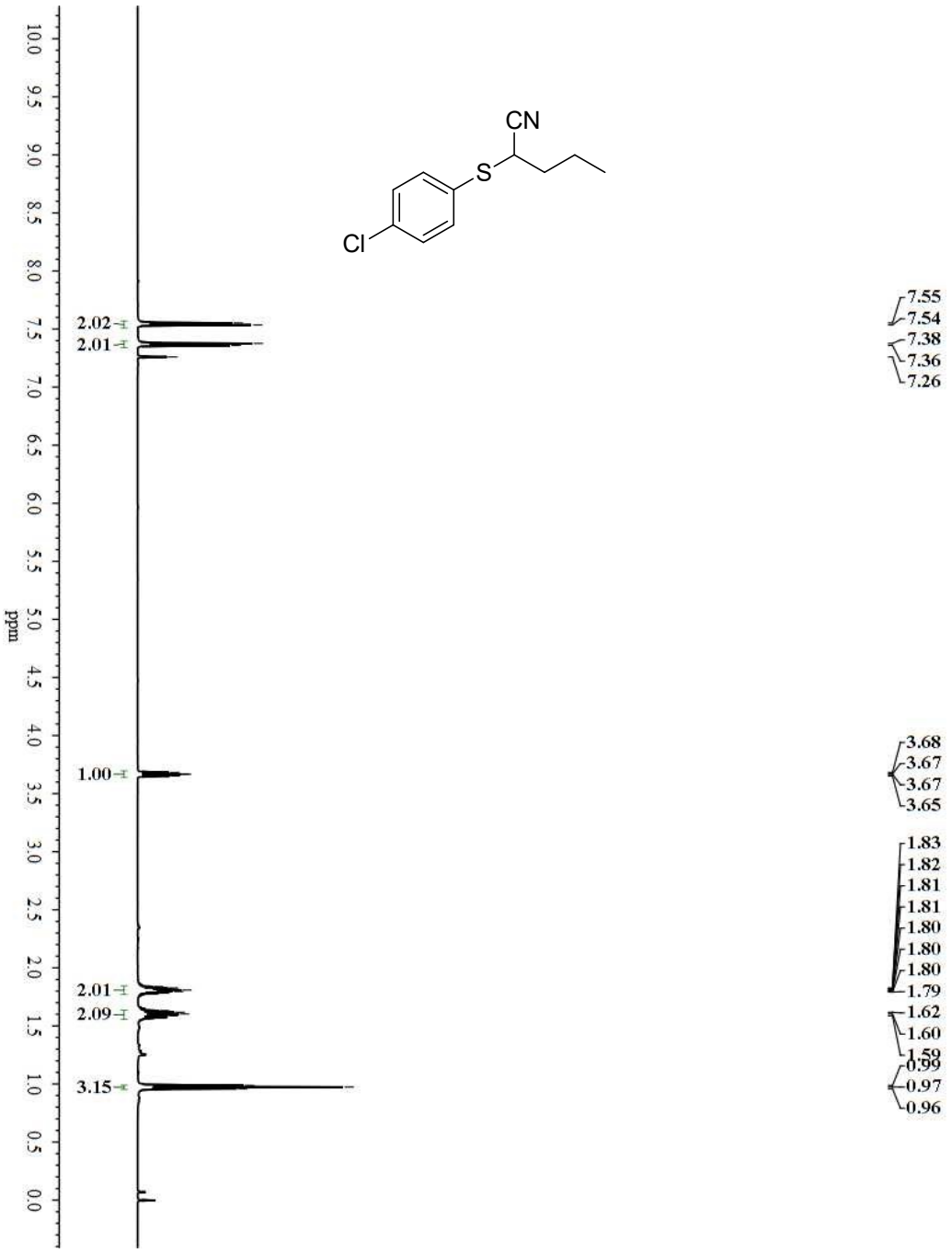
^{13}C NMR Spectra of Compound **7a**.



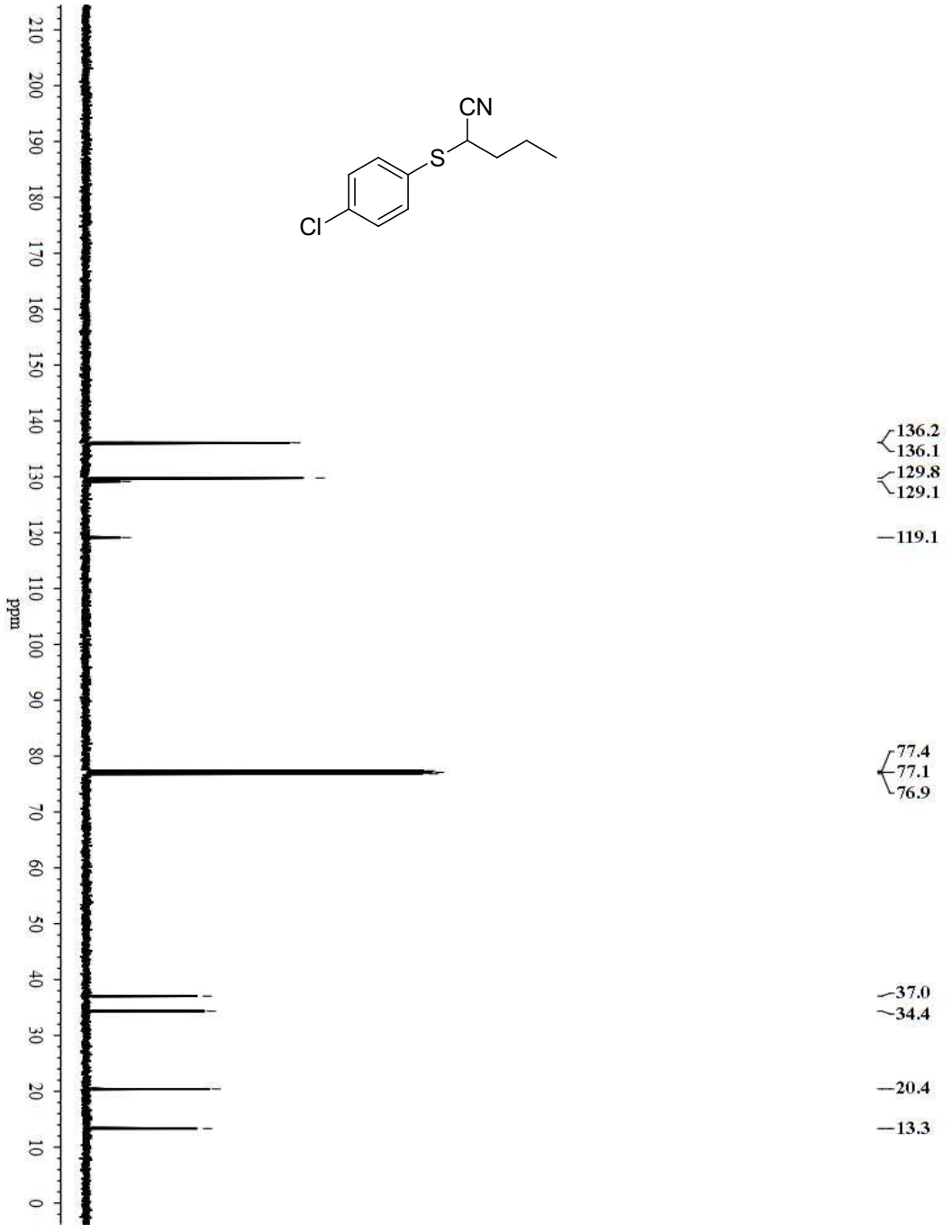
^{1}H NMR Spectra of Compound **7b**.



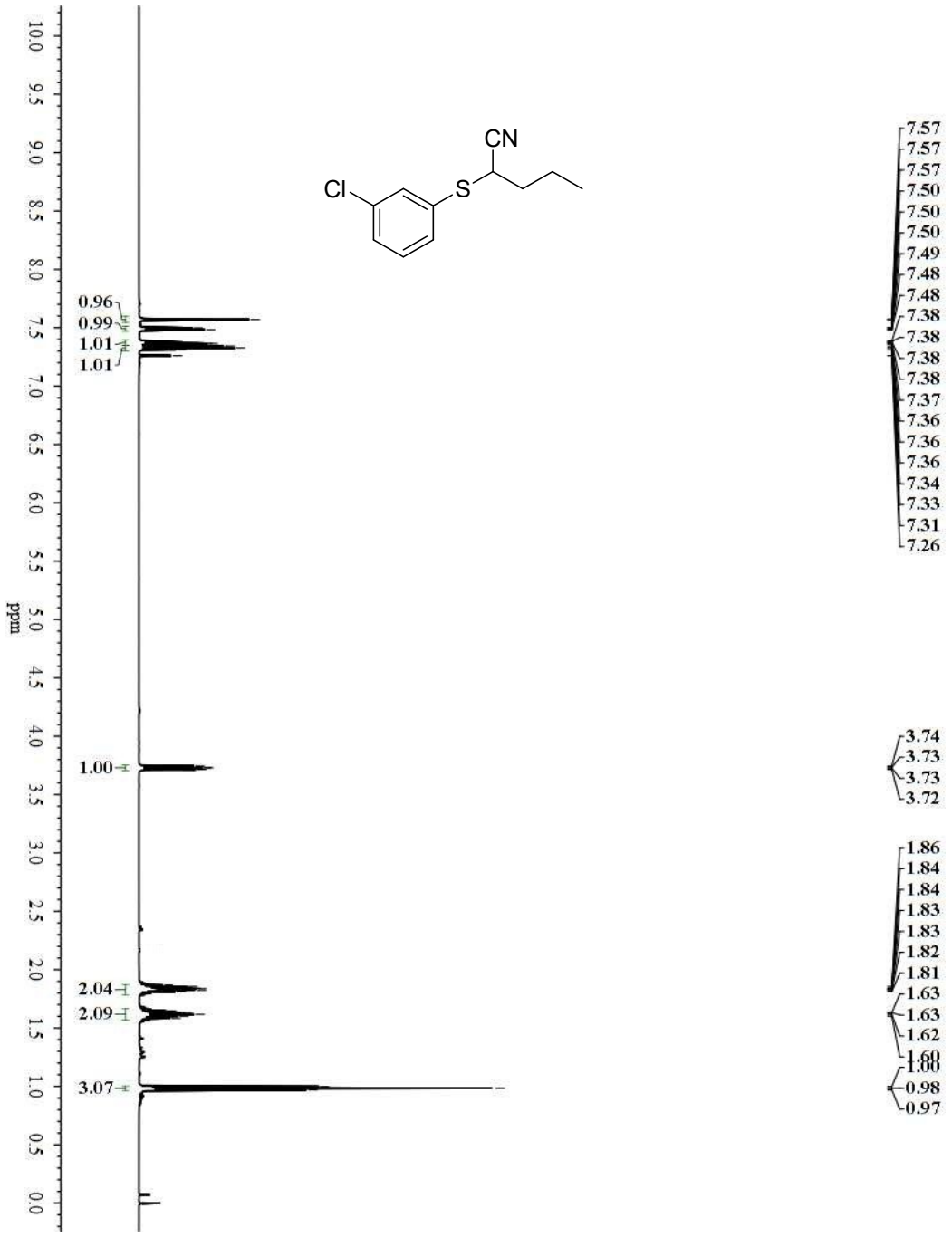
^{13}C NMR Spectra of Compound **7b**.



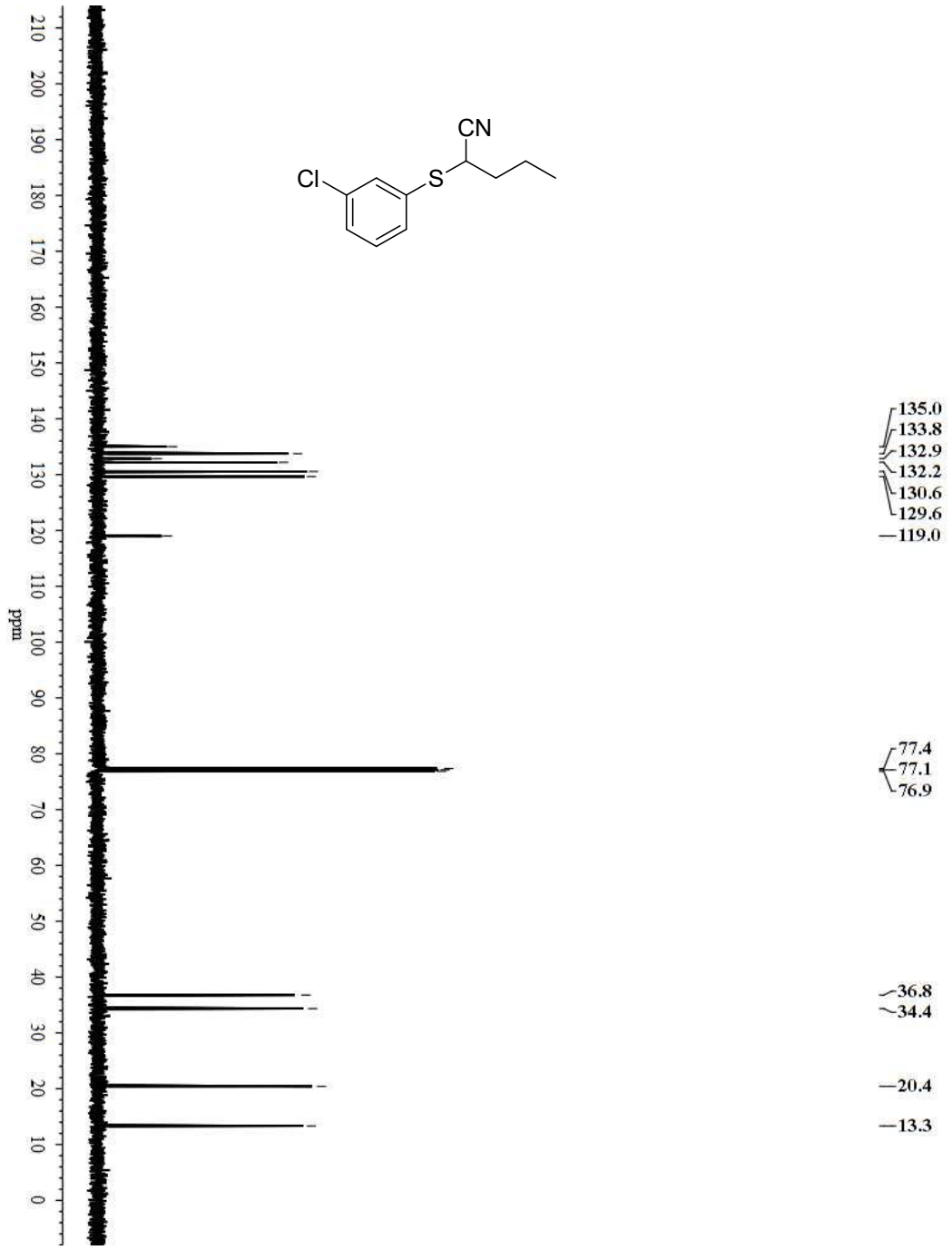
^{1}H NMR Spectra of Compound **7c**.



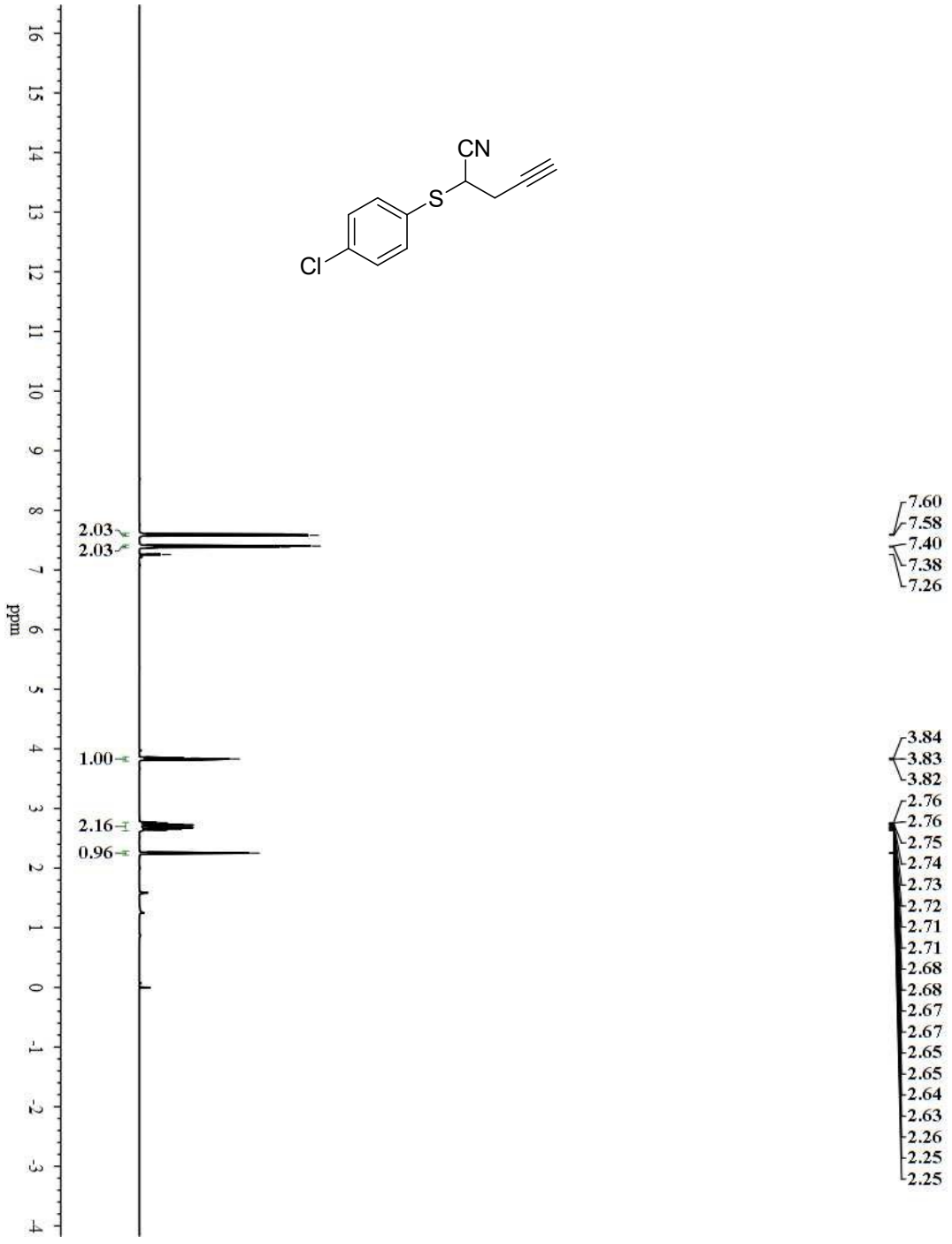
^{13}C NMR Spectra of Compound **7c**.



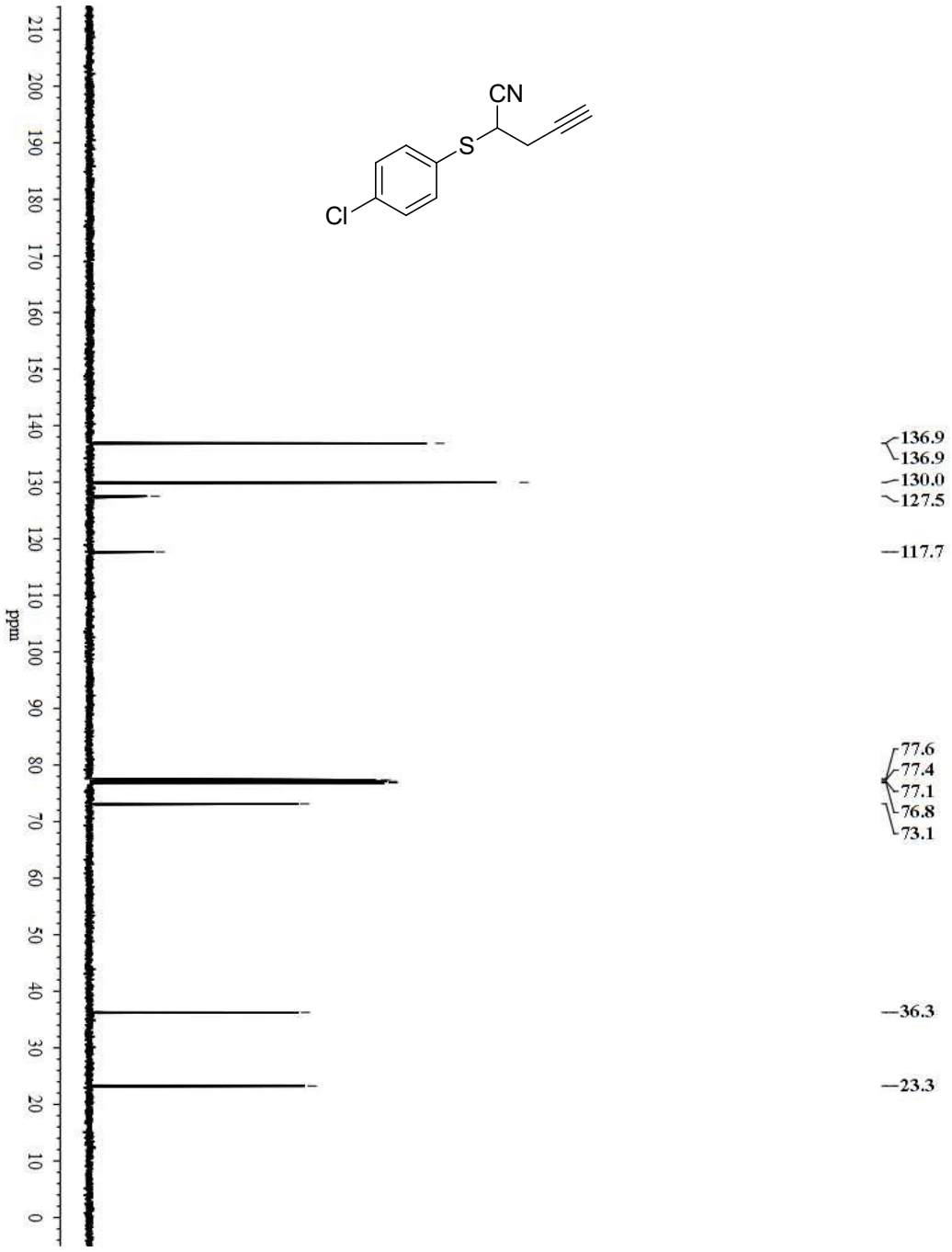
^{1}H NMR Spectra of Compound **7d**.



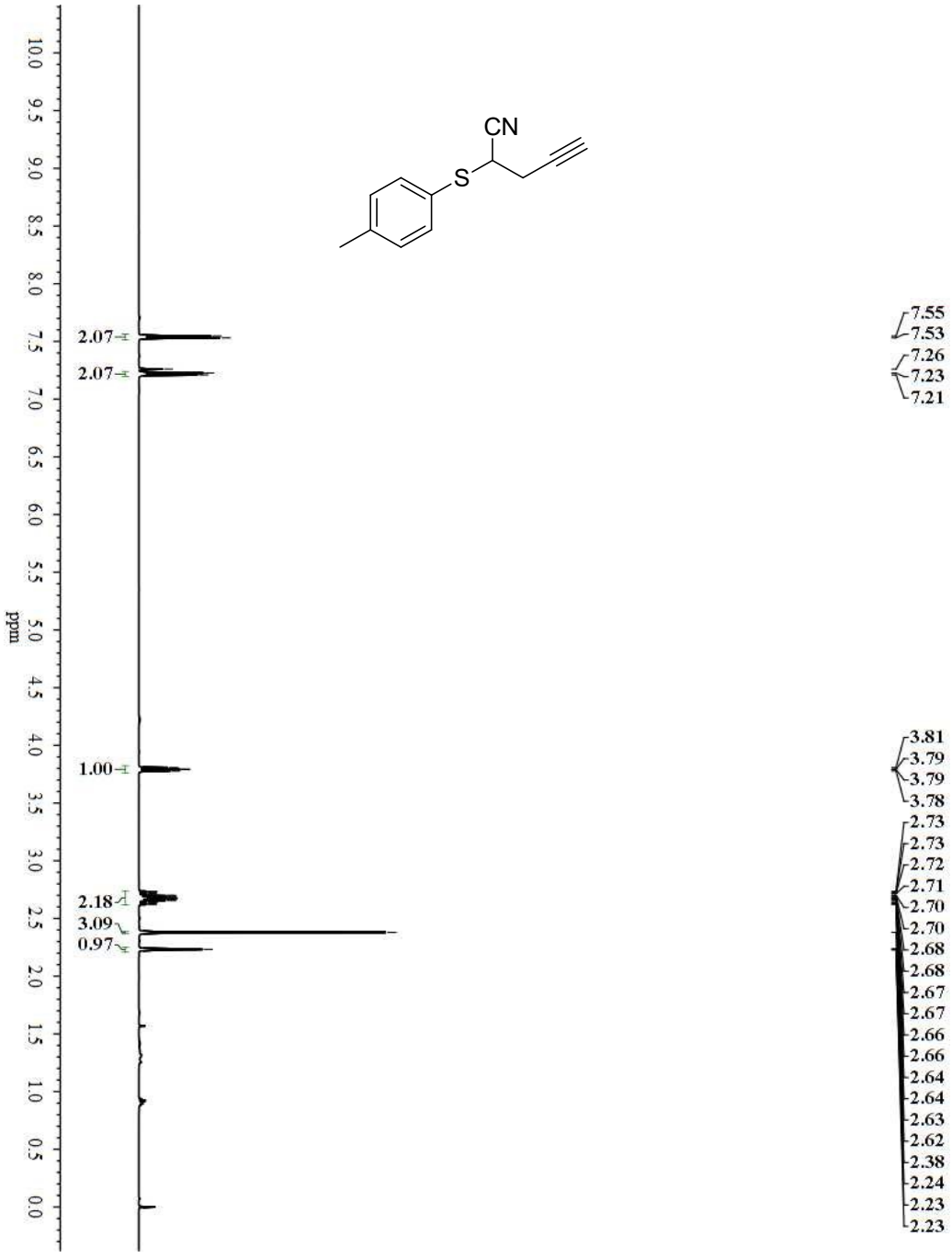
^{13}C NMR Spectra of Compound **7d**.



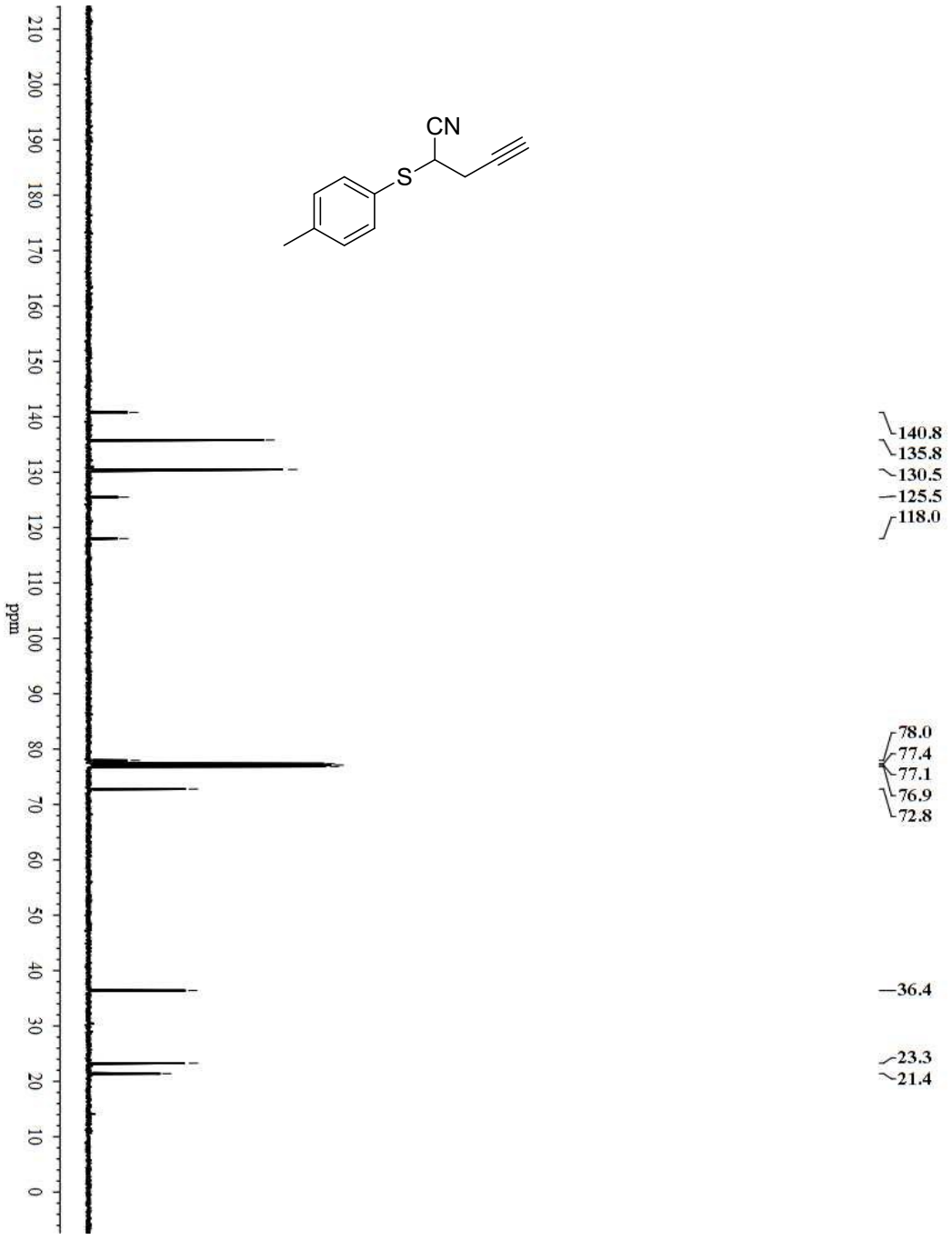
^{1}H NMR Spectra of Compound **7e**.



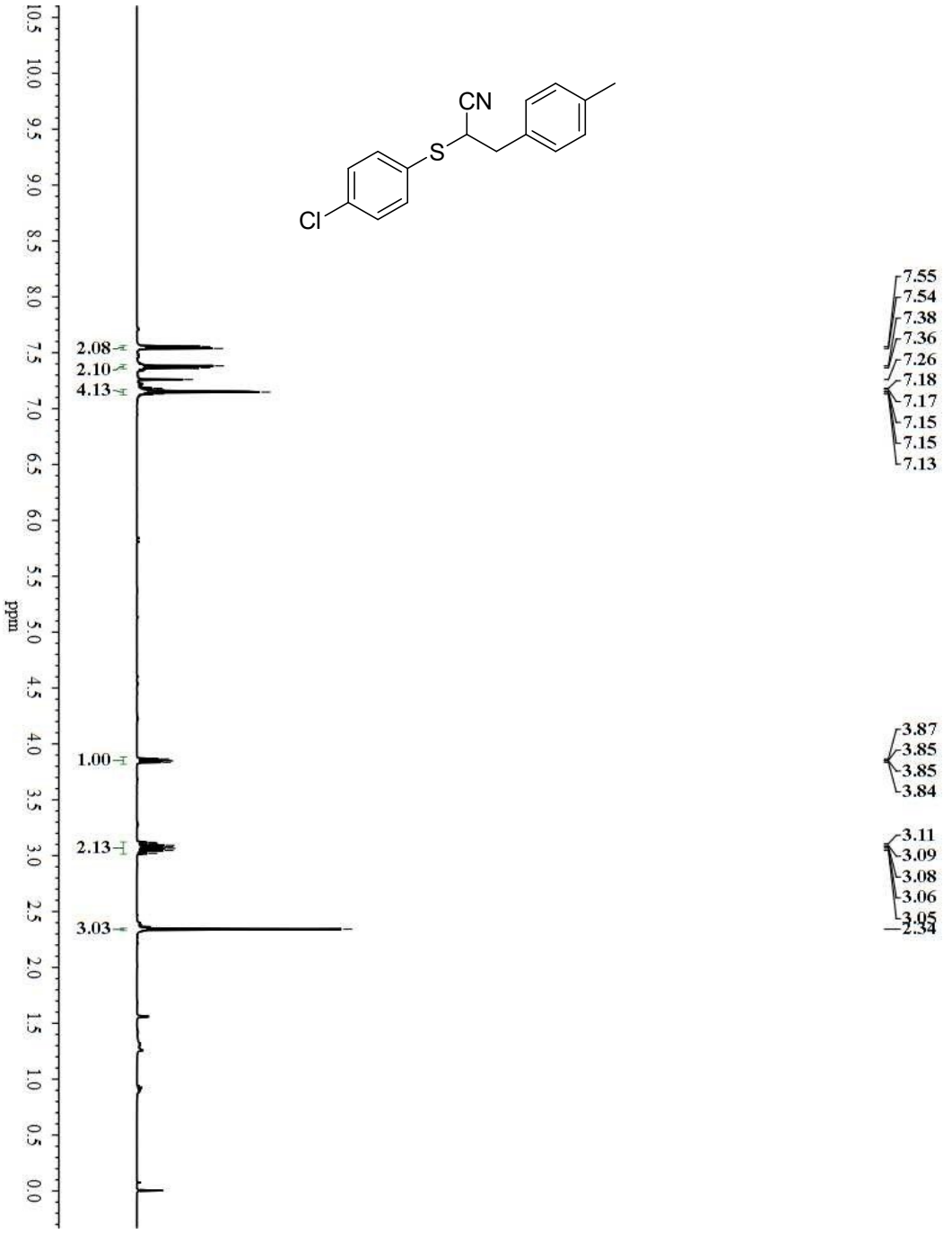
^{13}C NMR Spectra of Compound **7e**.



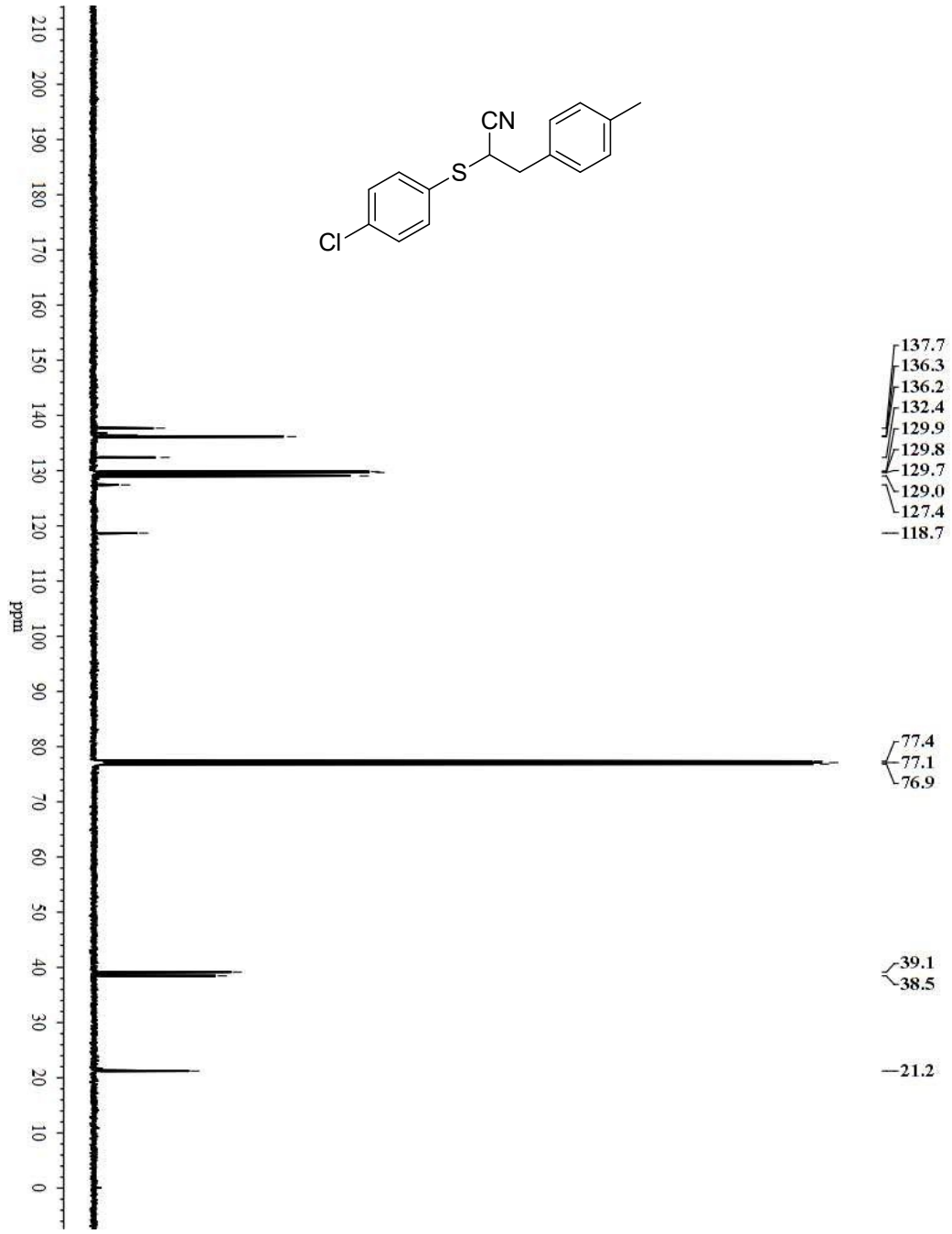
^{1}H NMR Spectra of Compound **7f**.



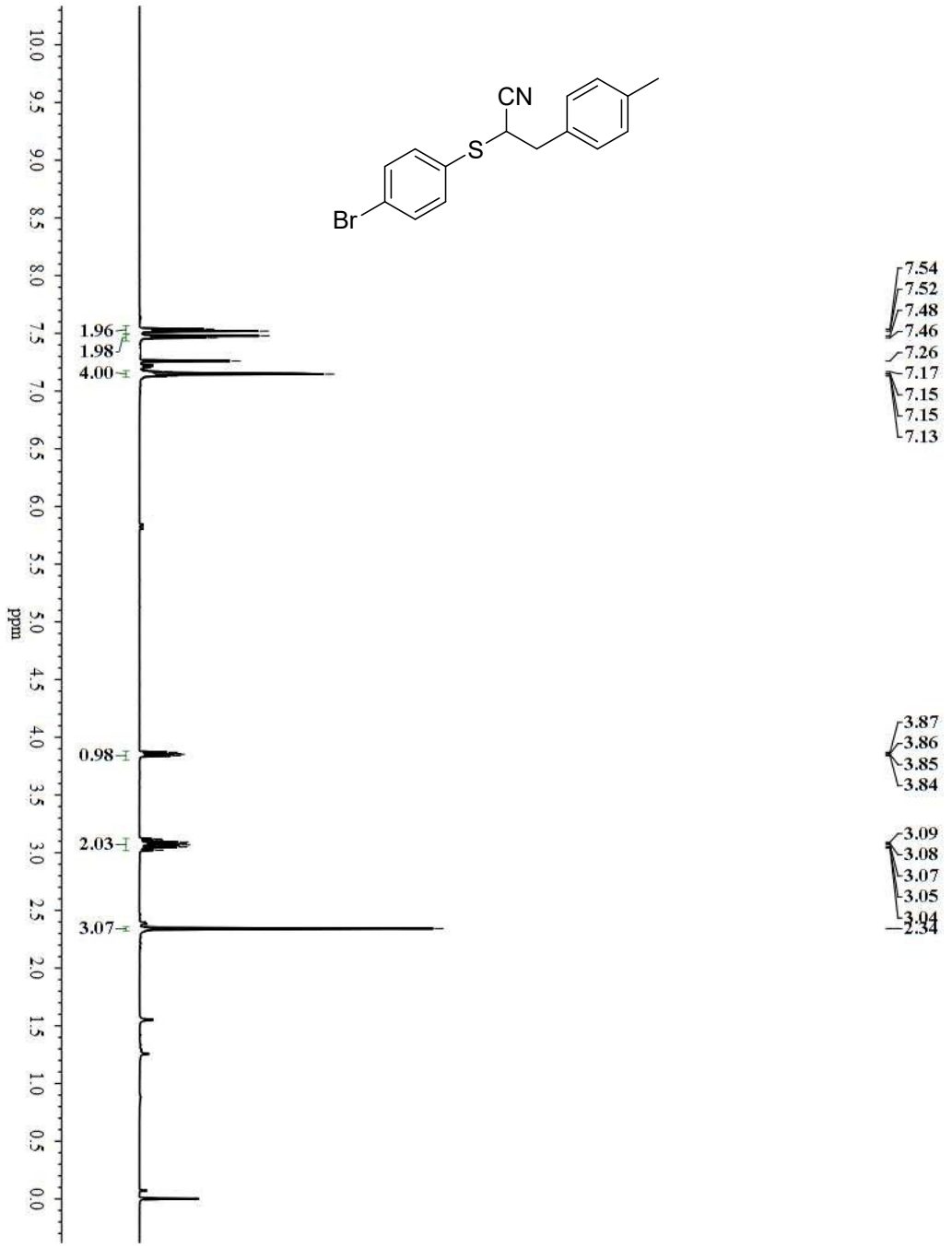
^{13}C NMR Spectra of Compound **7f**.



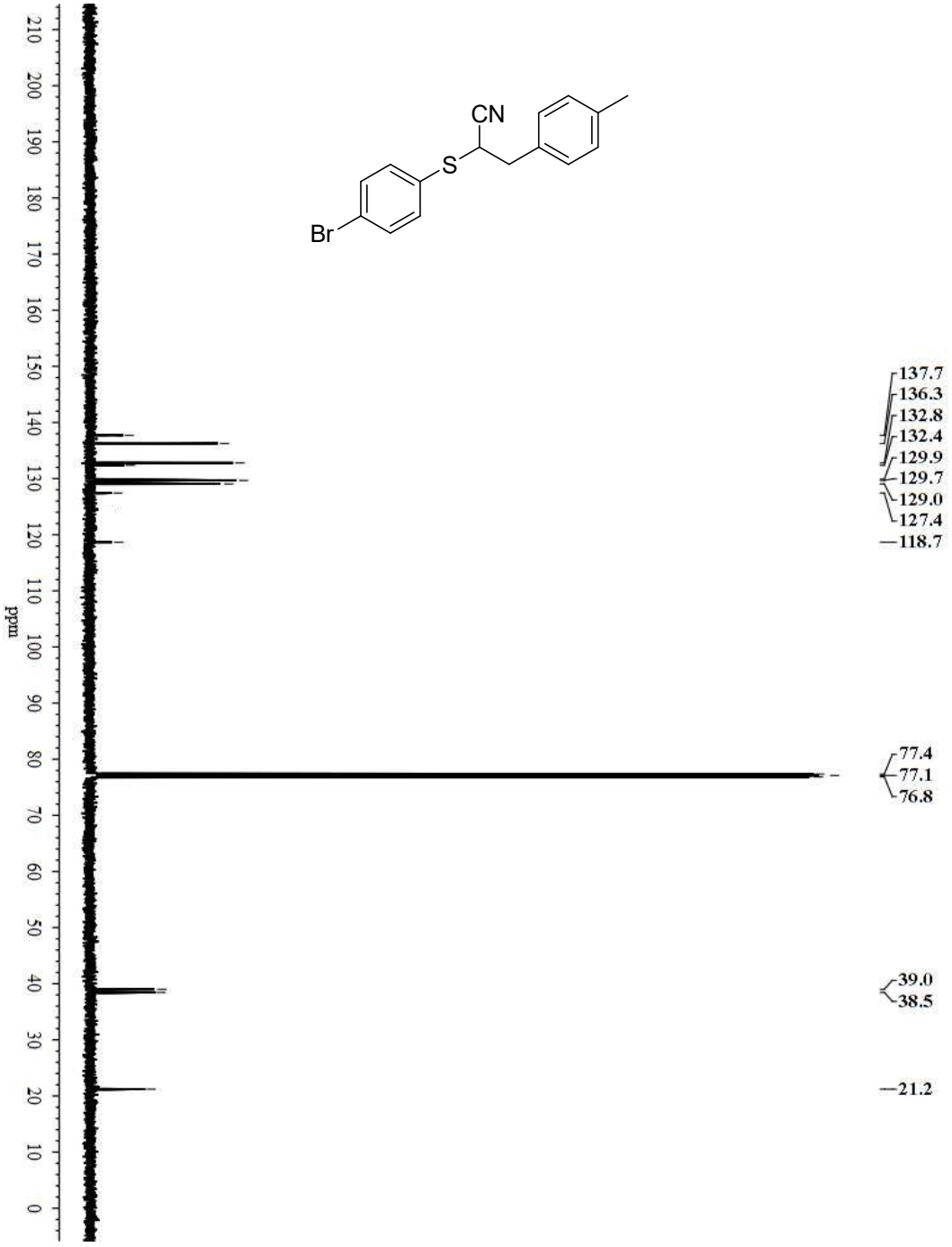
^{1}H NMR Spectra of Compound **7g**.



^{13}C NMR Spectra of Compound **7g**.



^{1}H NMR Spectra of Compound **7h**.



^{13}C NMR Spectra of Compound **7h**.

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