Supporting Information

Palladium-catalyzed *aza*-Wacker cyclization of *O*-homoallyl benzimidates: expeditious access to heteroatom-rich substituted 1, 3-oxazines via alkene trifunctionalization

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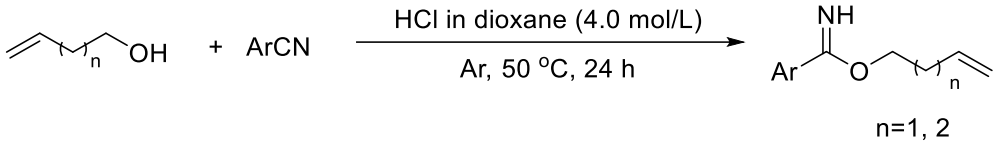
General experimental procedures

Reaction progress was monitored via thin layer chromatography (TLC) performed on GF254 silica gel plates. Column chromatography was carried out with silica gel (200-300 mesh) or aluminum oxide (200-300 mesh). ^{1}H NMR spectra were recorded on 400 MHz or 600 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz or 150 MHz in $CDCl_3$, and ^{19}F NMR spectra were recorded on 564 MHz in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet). The new starting materials **1** and all products **2, 3, 4, 5, 6,** and **7** were further characterized by high-resolution MS (TLQ) (ESI ionization sources); copies of their ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra are provided in the Supporting Information. Commercial grade solvents and reagents were used without further purification.

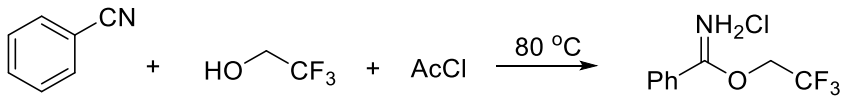
Starting materials

The *O*-homoallyl-benzimidates **1a-s** and **1ee** were synthesized according to literature procedures[1].

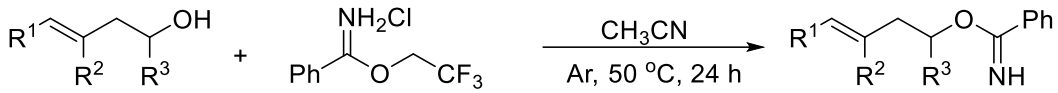


A mixture of aromatic cyanide (10 mmol, 2.0 equiv) in 4 M HCl in dioxane (12.5 mL, 50 mmol, 10.0 equiv) was stirred under argon at room temperature. After 1 h, corresponding but-3-en-1-ol (5 mmol, 1.0 equiv) was added dropwise and stirred for 24 hours at 50 °C. After being cooled again to room temperature, the mixture was concentrated in vacuo. The residue was dissolved in DCM (35 mL) and washed with Sat. $NaHCO_3$ (35 mL). The aqueous layer was extracted with DCM (3 x 35 mL). The combined organic phase was washed with brine (35 mL) and dried over anhydrous Na_2SO_4, concentrated, and purified by silica gel column chromatography in petroleum ethyl acetate (5:1) to afford the desired product.

Preparation of *O*-homoallyl-benzimidates **1t-1z,** and **1aa**[1].



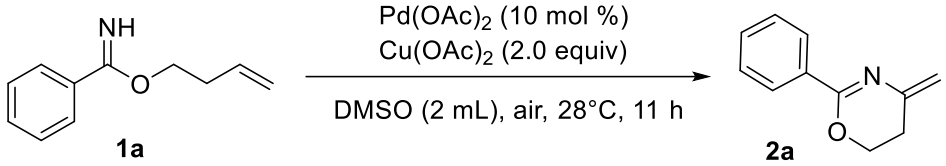
To a pressure tube equipped with a stir bar was added nitrile (1.0 equiv), trifluoroethanol (12.0 equiv), and acetyl chloride (8.0 equiv). The solution was heated to 80 °C and stirred. After 48 h the reaction was cooled to room temperature and carefully vented (Note: HCl gas is formed as a by-product, see below for additional instructions on safe handling), which immediately induced precipitation of the benzimidate hydrochloride salt. The benzimidate salt was collected via filtration with cold hexanes.



A mixture of corresponding alcohol (5 mmol, 1.0 equiv) and 2,2,2-trifluoroethyl benzimidate hydrochloride (8 mmol, 1.6 equiv) in acetonitrile was stirred under argon at 50 °C for 24 hours. The mixture was cooled to room temperature and diluted in dichloromethane, washed with $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (10-40% EtOAc in hexanes) to give the desired product.

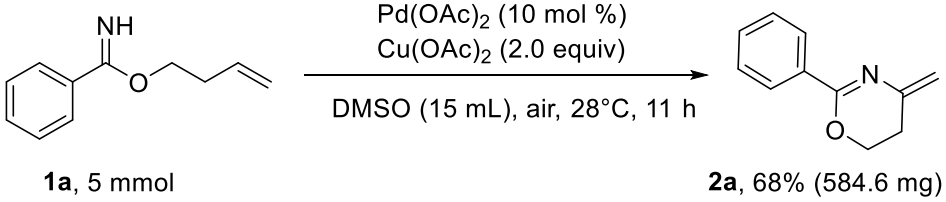
The *O*-homoallyl trichloroacetimidate **1bb**, *N*-(but-3-en-1-yl)-*N*-phenylbenzimidamide **1cc**, and 1-phenylhex-5-en-1-imine **1dd** were synthesized according to literature procedures[1].

The typical procedure for the preparation of product 2a



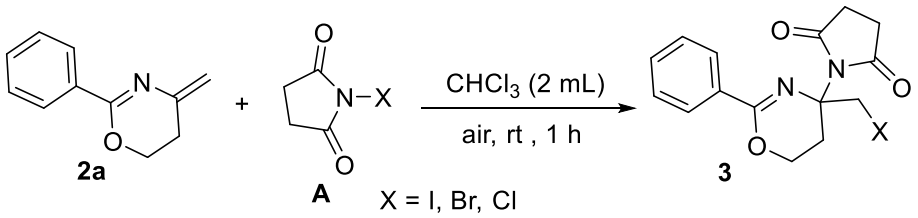
2 mL DMSO was added to 0.3 mmol **1a**, 0.1 equiv $Pd(OAc)_2$ and 2.0 equiv $Cu(OAc)_2$ under air atmosphere. The mixture was stirred for 11 h at 28℃. After the reaction finished as indicated by TLC, the reaction mixture was quenched by water and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with H_2O (1 x 25 mL) and saturated brine (1 x 25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/10, v/v) to give the desired product **2a** (86%).

5 mmol scale reaction for the preparation of product 2a

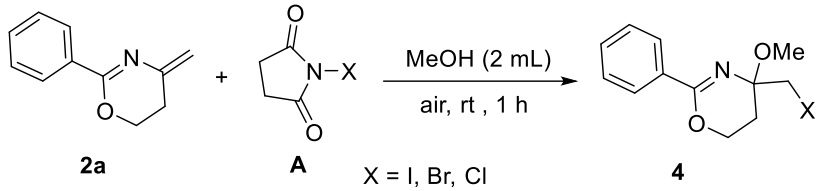


15 mL DMSO was added to 5.0 mmol **1a**, 0.1 equiv $Pd(OAc)_2$ and 2.0 equiv $Cu(OAc)_2$ under air atmosphere. The mixture was stirred for 11 h at 28 ℃. After the reaction finished as indicated by TLC, the reaction mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with H_2O (1 x 25 mL) and saturated brine (1 x 25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/10, v/v) to give the desired product **2a** (68%).

Procedures for the formation of 3[2], 4, 5, 6[2], and 7.

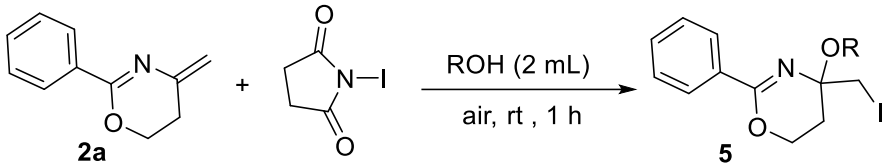


The 4-methylene-1,3-oxazine **2a** (0.2 mmol) and **A** (2.0 equiv) were dissolved in $CHCl_3$ (2 mL) and stirred at room temperature. Upon completion indicated by TLC, the reaction mixture was quenched with water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/10-1/3, v/v) to give the pure product **3**.



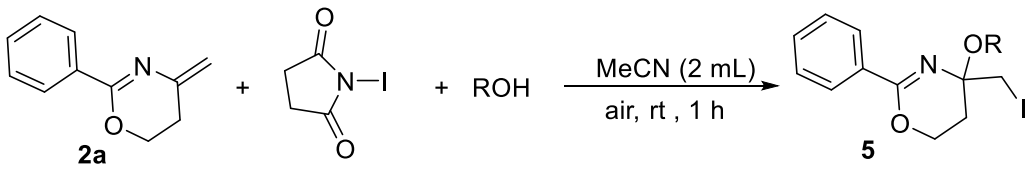
The 4-methylene-1,3-oxazine **2a** (0.2 mmol) and **A** (2.0 equiv) were dissolved in MeOH (2 mL). The mixture was stirred for 1 h at room temperature. Upon completion indicated by TLC, the reaction mixture was quenched with water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/20, v/v) to give the pure product **4**.

Methods A (synthesis of **5a-5b**):



The 4-methylene-1,3-oxazine **2a** (0.2 mmol) and *N*-iodosuccinimide (2.0 equiv) were dissolved in the corresponding alcohol solvent (2 mL). The mixture was stirred for 1 h at room temperature. Upon completion indicated by TLC, the reaction mixture was quenched by water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/20, v/v) to give the pure products **5a-5b**.

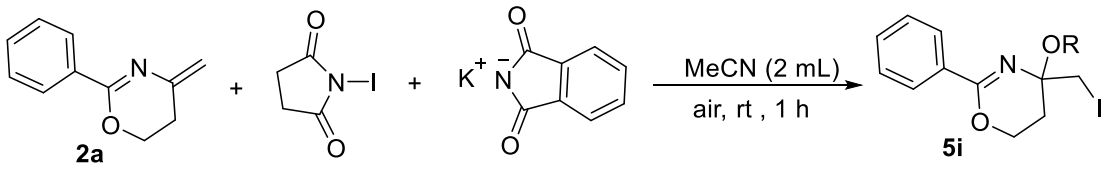
Methods B (synthesis of **5c-5h**):



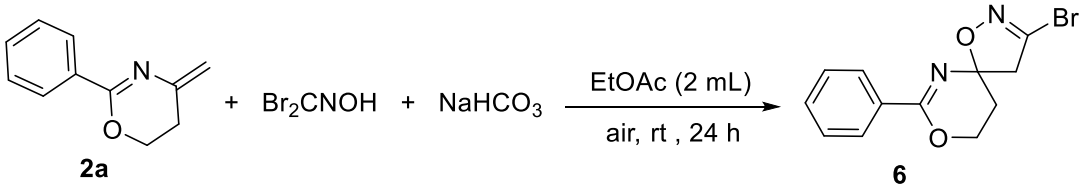
The 4-methylene-1,3-oxazine **2a** (0.2 mmol), *N*-iodosuccinimide (2.0 equiv) and

corresponding alcohol (10.0 equiv) were dissolved in MeCN solvent (2 mL). The mixture was stirred for 1 h at room temperature. Upon completion indicated by TLC, the reaction mixture was quenched by water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on a neutral alumina oxide column (elute: EtOAc/Petroleum ether 1/50-1/20, v/v) to give the pure products **5c-5h**.

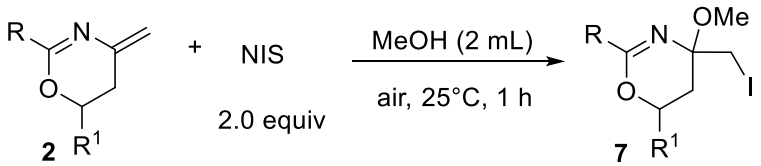
Methods C:



The 4-methylene-1,3-oxazine **2a** (0.2 mmol), *N*-iodosuccinimide (2.0 equiv) and potassium phthalimide (10.0 equiv) were dissolved in MeCN solvent (2 mL). The mixture was stirred for 1 h at room temperature. Upon completion indicated by TLC, the reaction mixture was quenched with water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on a neutral alumina oxide column (elute: EtOAc/Petroleum ether 1/50-1/20, v/v) to give the pure product **5i**.



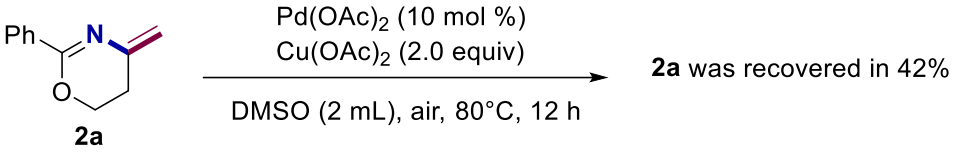
The 4-methylene-1,3-oxazine **2a** (0.2 mmol), Br_2CNOH (1.1 equiv) and $NaHCO_3$ (1.5 equiv) were dissolved in ethyl acetate solvent (2 mL). The mixture was stirred for 24 h at room temperature. Upon completion indicated by TLC, the reaction mixture was quenched with water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/10, v/v) to give the pure product **6**.



The 4-methylene-1,3-oxazines **2** (0.2 mmol) and NIS (2.0 equiv) was dissolved in MeOH (2 mL). The mixture was stirred for 1 h at 25 ℃. Upon completion indicated by TLC, the reaction mixture was quenched with water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with saturated brine (25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/20, v/v) to give

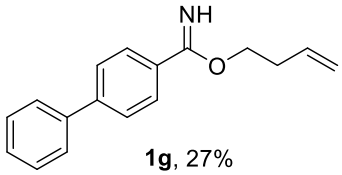
the pure product **7**.

Scheme S1



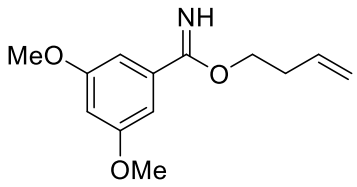
2 mL DMSO was added to 0.3 mmol **2a**, 0.1 equiv $Pd(OAc)_2$ and 2.0 equiv $Cu(OAc)_2$ under air atmosphere. The mixture was stirred for 12 h at 80℃. The reaction mixture was quenched by water and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with H_2O (1 x 25 mL) and saturated brine (1 x 25 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/50-1/10, v/v) to recovered **2a** (42%).

Characterization Data of 1g, 1m-1p, 1s, and 1u-1y



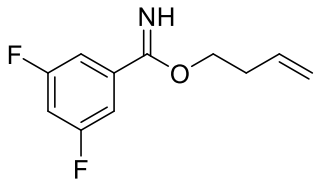
1g, 27%

but-3-en-1-yl [1,1'-biphenyl]-4-carbimidate (**1g**). Colorless oil (0.34 g, 27%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 8.4 Hz, 2H), 7.65-7.60 (m, 4H), 7.46 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 5.99-5.89 (m, 1H), 5.23-5.11 (m, 2H), 4.35 (t, J = 6.8 Hz, 2H), 2.59 (dd, J = 6.4 Hz, J = 6.8 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.5, 143.7, 140.1, 134.7, 131.5, 128.9, 127.9,127.2, 127.2, 127.1, 117.0, 65.2, 33.2. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}NO$, 252.1383; found, 252.1383.



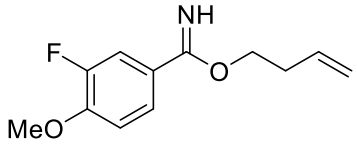
1m, 29%

but-3-en-1-yl 3,5-dimethoxybenzimidate (**1m**). Colorless oil (0.34 g, 29%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.87 (s, 2H), 6.55 (t, J = 2.4 Hz, 1H), 5.97-5.86 (m, 1H), 5.21-5.10 (m, 2H), 4.31 (t, J = 6.4 Hz, 2H), 3.82 (s, 6H), 2.57 (dd, J = 6.4 Hz, J = 6.8 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.8, 135.1, 134.8, 117.1, 105.0, 103.0, 65.3, 55.6, 33.2. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NO_3$, 236.1281; found, 236.1280.



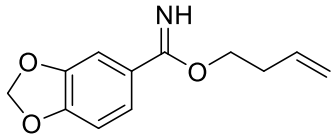
1n, 12%

but-3-en-1-yl 3,5-difluorobenzimidate (**1n**). Colorless oil (0.13 g, 12%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (d, J = 8.0 Hz, 2H), 6.94-6.89 (m, 1H), 5.95-5.85 (m, 1H), 5.22-5.12 (m, 2H), 4.30 (t, J = 6.8 Hz, 2H), 2.57 (dd, J = 6.8 Hz, J = 6.8 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 164.3 (d, J = 12.3 Hz), 161.8 (d, J = 12.3 Hz), 136.3, 134.4, 117.4, 110.2 (dd, J = 7.4 Hz, J = 11.8 Hz), 106.4 (t, J = 25.2 Hz), 65.5, 33.1. ^{19}F NMR ($CDCl_3$, 564 MHz): δ -108.5. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}F_2NO$, 212.0881; found, 212.0881.



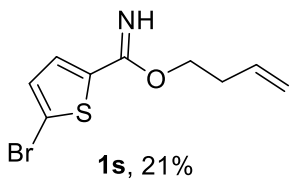
1o, 35%

but-3-en-1-yl 3-fluoro-4-methoxybenzimidate (**1o**). Colorless oil (0.39 g, 35%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 12.0 Hz, 2H), 6.97 (t, J = 8.8 Hz, 1H), 5.96-5.86 (m, 1H), 5.21-5.11 (m, 2H), 4.29 (t, J = 6.4 Hz, 2H), 3.93 (s, 3H), 2.56 (dd, J = 6.4 Hz, J = 6.8 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 166.2, 151.9 (d, J = 245.0 Hz) ,150.0 (d, J = 10.7 Hz), 134.7, 125.7 (d, J = 6.1 Hz), 123.3, 117.2, 114.9 (d, J = 19.9 Hz), 112.7, 65.2, 56.3, 33.2. ^{19}F NMR ($CDCl_3$, 564 MHz): δ -134.4. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}FNO_2$, 224.1081; found, 224.1080.



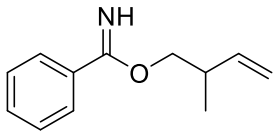
1p, 29%

but-3-en-1-yl benzo[*d*][1,3]dioxole-5-carbimidate (**1p**). Colorless oil (0.33 g, 29%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H), 5.96-5.86 (m, 1H), 5.21-5.10 (m, 2H), 4.28 (t, J = 6.8 Hz, 2H), 2.55 (dd, J = 6.8 Hz, J = 6.4 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 166.9, 149.8, 147.8, 134.7, 127.0, 121.5, 117.0, 108.0, 107.2, 101.7, 65.1, 33.2. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}NO_3$, 220.0968; found, 220.0967.



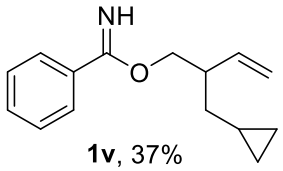
1s, 21%

but-3-en-1-yl 5-bromothiophene-2-carbimidate (**1s**). Yellow oil (0.53 g, 21%), (EtOAc/ Petroleum ether, 1/20-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 5.93-5.82 (m, 1H), 5.20-5.10 (m, 2H), 4.27 (t, J = 5.6 Hz, 2H), 2.52 (dd, J = 6.8 Hz, J = 6.8 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.4, 137.4, 134.3, 130.6, 128.3, 117.4, 116.9, 65.3, 33.1. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_9H_{11}BrNOS$, 259.9739; found, 259.9739.



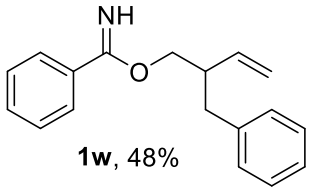
1u, 21%

2-methylbut-3-en-1-yl benzimidate (**1u**). Yellow oil (0.20 g, 21%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.74 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 5.92-5.86 (m, 1H), 5.17-5.07 (m, 2H), 4.20-4.13 (m, 2H), 2.76-2.69 (m, 1H), 1.16 (d, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.9, 140.7, 133.0, 131.0, 128.6, 126.8, 114.8, 70.2, 37.2, 16.8. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NO$, 190.1226; found, 190.1227.



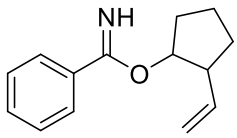
1v, 37%

2-(cyclopropylmethyl)but-3-en-1-yl benzimidate (**1v**). Colorless oil (0.43 g, 37%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 7.2 Hz, 2H), 7.48-7.39 (m, 3H), 5.91-5.82 (m, 1H), 5.21-5.10 (m, 2H), 4.33-4.21 (m, 2H), 2.75-2.66 (m, 1H), 1.53-1.46 (m, 1H), 1.42-1.34 (m, 1H), 0.82-0.72 (m, 1H), 0.50-0.42 (m, 2H), 0.11-0.02 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.9, 139.9, 132.9, 131.0, 128.6, 126.8, 115.8, 68.7, 43.8, 36.8, 8.8, 4.9, 4.8. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{15}H_{20}NO$, 230.1539; found, 230.1540.



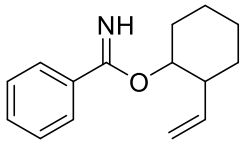
1w, 48%

2-benzylbut-3-en-1-yl benzimidate (**1w**). Colorless oil (0.64 g, 48%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.72 (d, J = 5.4 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.18 (t, J = 7.2 Hz, 3H), 5.87-5.81 (m, 1H), 5.10 (t, J = 9.0 Hz, 2H), 4.23 (s, 2H), 2.95-2.86 (m, 2H), 2.78 (dd, J = 7.2 Hz, J = 6.0 Hz, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 150 MHz): δ 167.9, 139.7, 138.9, 132.9, 131.0, 129.4, 128.6, 128.4, 126.8, 126.2, 116.4, 68.1, 44.6, 38.1. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}NO$, 266.1539; found, 266.1539.



1x, 27%

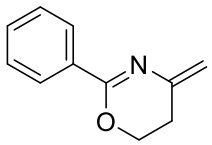
2-vinylcyclopentyl benzimidate (**1x**). Colorless oil (0.29 g, 27%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 6.8 Hz, 2H), 7.47-7.38 (m, 3H), 5.93-5.85 (m, 1H), 5.13 (d, J = 17.2 Hz, 1H), 5.16-5.02 (m, 2H), 2.84-2.77 (m, 1H), 2.23-2.12 (m, 1H), 2.05-1.97 (m, 1H), 1.85-1.72 (m, 3H), 1.58-1.49 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.4, 140.0, 133.3, 130.9, 128.5, 126.9, 114.7, 81.7, 49.6, 31.6, 30.0, 22.8. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}NO$, 216.1383; found, 216.1385.



1y, 43%

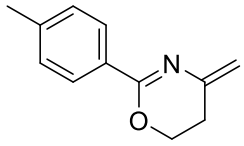
2-vinylcyclohexyl benzimidate (**1y**). Colorless oil (0.49 g, 43%), (EtOAc/ Petroleum ether, 1/10-1/5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, J = 7.2 Hz, 2H), 7.44-7.36 (m, 3H), 5.88-5.79 (m, 1H), 5.11 (d, J = 17.2 Hz, 1H) ,4.99 (d, J = 10.8 Hz, 1H), 4.86 (s, 1H), 2.39-2.28 (m, 2H), 1.87-1.73 (m, 3H), 1.50-1.26 (m, 5H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.4, 140.7, 133.6, 130.7, 128.4, 126.8, 114.8, 76.5, 47.5, 31.3, 31.1, 25.1, 24.5. HRMS (ESI-TLQ) m/z: $[M + H]^+$ calcd for $C_{15}H_{20}NO$, 230.1539; found, 230.1541.

Characterization Data of 2a-2y, 2aa, 3, 4, 5, 6 and 7



2a, 86%

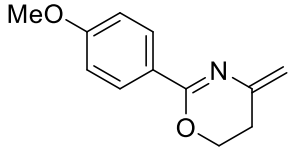
4-methylene-2-(p-tolyl)-5,6-dihydro-4*H*-1,3-oxazine (**2a**)**.** Pale Yellow oil **(**44.7 mg, 86%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 5.10 (s, 1H), 4.61 (s, 1H), 4.41 (t, J = 5.6 Hz, 2H), 2.63 (t, J = 6.0 Hz,, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.1, 143.4, 133.0, 131.1, 128.2, 127.7, 106.4, 65.5, 27.2. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{22}H_{23}N_2O_2$, 347.1754; found, 347.1753.



2b, 82%

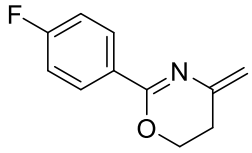
4-methylene-2-(p-tolyl)-5,6-dihydro-4*H*-1,3-oxazine (**2b**). Colorless oil **(**46.1 mg, 82%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89

(d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.07 (s, 1H), 4.58 (s, 1H), 4.39 (t, J = 5.6 Hz,, 2H), 2.61 (t, J = 6.0 Hz, 2H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.3, 143.5, 141.4, 130.2, 129.0, 127.7, 106.0, 65.5, 27.3, 21.6. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{24}H_{27}N_2O_2$, 375.2067; found, 375.2066.



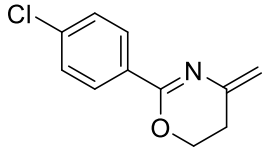
2c, 81%

2-(4-methoxyphenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2c**). Colorless oil (49.5 mg, 81%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.05 (s, 1H), 4.57 (s, 1H), 4.39 (t, J = 6.0 Hz, 2H), 3.84 (s, 3H), 2.62 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.0, 156.1, 143.6, 129.4, 125.4, 113.5, 105.5, 65.4, 55.4, 27.3. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{24}H_{27}N_2O_4$, 407.1965; found, 407.1963.



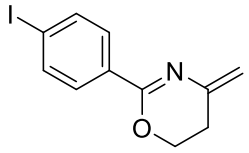
2d, 59%

2-(4-fluorophenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2d**). Yellow oil (36.9 mg, 59%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (dd, J = 5.6 Hz, J = 2.8 Hz, 2H), 7.06 (t, J = 8.4 Hz, 2H), 5.09 (s, 1H), 4.62 (s, 1H), 4.41 (t, J = 5.6 Hz, 2H), 2.64 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 164.8 (d, J = 249.7 Hz), 155.3, 143.2, 129.9 (d, J = 8.7 Hz), 129.2 (d, J = 2.8 Hz), 115.3 (d, J = 21.6 Hz), 106.5, 65.6, 27.2. ^{19}F NMR ($CDCl_3$, 564 MHz): δ -109.4. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{22}H_{21}F_2N_2O_2$, 383.1566; found, 383.1565.



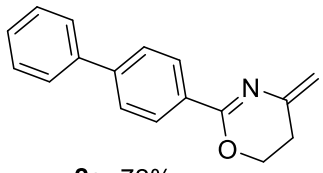
2e, 75%

2-(4-chlorophenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2e**). Yellow solid (46.4 mg, 75%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). mp 79-80 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 5.10 (s, 1H), 4.63 (s, 1H), 4.40 (t, J = 6.0 Hz, 2H), 2.63 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.2, 143.1, 137.3, 131.5, 129.1, 128.5, 106.8, 65.6, 27.2. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{22}H_{21}Cl_2N_2O_2$, 415.0975; found, 415.0973.



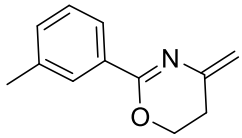
2f, 30%

2-(4-iodophenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2f**). White solid (26.6 mg, 30%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). mp 104-105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (s, 4H), 5.10 (s, 1H), 4.64 (s, 1H), 4.40 (t, J = 5.6 Hz,, 2H), 2.63 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.5, 143.1, 137.4, 132.5, 129.3, 107.0, 98.2, 65.6, 27.1. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{11}INO$, 299.9880; found, 299.9879.



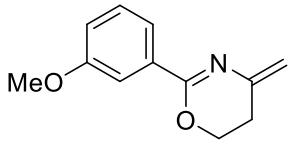
2g, 72%

2-([1,1'-biphenyl]-4-yl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2g**). Yellow solid (53.5 mg, 72%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). mp 104-105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 4H), 7.45 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 5.12 (s, 1H), 4.63 (s, 1H), 4.43 (t, J = 6.0 Hz, 2H), 2.65 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.0, 143.7, 143.5, 140.5, 131.9, 129.0, 128.2, 127.9, 127.3, 126.9, 106.4, 65.6, 27.3. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{16}NO$, 250.1226; found, 250.1226.



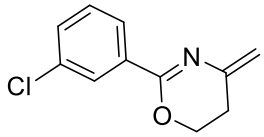
2h, 93%

4-methylene-2-(m-tolyl)-5,6-dihydro-4*H*-1,3-oxazine (**2h**). Yellow oil (54.5 mg, 93%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (s, 1H), 7.79 (d, J = 6.8 Hz, 1H), 7.29-7.23 (m, 2H), 5.10 (s, 1H), 4.60 (s, 1H), 4.41-4.37 (m, 2H), 2.61 (t, J = 6.0 Hz, 2H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.3, 143.4, 137.9, 132.9, 131.9, 128.2, 128.1, 124.8, 106.3, 65.5, 27.3, 21.5. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{24}H_{27}N_2O_2$, 375.2067; found, 375.2066.



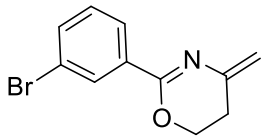
2i, 71%

2-(3-methoxyphenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2i**). Colorless oil (43.1 mg, 71%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 7.29 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 7.00 (dd, J = 2.4 Hz, J = 5.6 Hz, 1H), 5.11 (s, 1H), 4.63 (s, 1H), 4.41 (t, J = 6.0 Hz, 2H), 3.85 (s, 3H), 2.63 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.5, 156.0, 143.3, 134.4, 129.2, 120.2, 117.8, 112.1, 106.5, 65.5, 55.5, 27.2. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{24}H_{27}N_2O_4$, 407.1965; found, 407.1963.



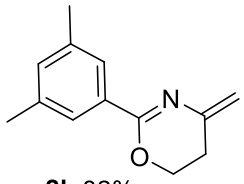
2j, 83%

2-(3-chlorophenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2j**). Colorless oil (51.6 mg, 83%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (s, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 5.12 (s, 1H), 4.65 (s, 1H), 4.41 (t, J = 6.0 Hz, 2H), 2.63 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.8, 143.0, 134.8, 134.4, 131.1, 129.5, 127.8, 125.8, 107.2, 65.7, 27.1. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{22}H_{21}Cl_2N_2O_2$, 415.0975; found, 415.0973.



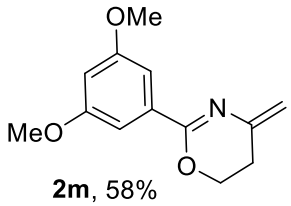
2k, 77%

2-(3-bromophenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2k**). Colorless oil (58.5 mg, 77%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 6.0 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 5.12 (s, 1H), 4.66 (s, 1H), 4.41 (t, J = 6.0 Hz, 2H), 2.64 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.7, 143.0, 135.0, 134.0, 130.7, 129.8, 126.3, 122.4, 107.2, 65.7, 27.1. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{11}BrNO$, 252.0019; found, 252.0017.



2l, 82%

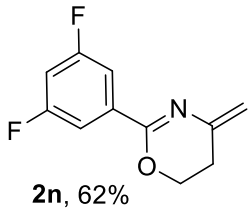
2-(3,5-dimethylphenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2l**). Yellow oil (49.6 mg, 82%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (s, 2H), 7.08 (s, 1H), 5.09 (s, 1H), 4.60 (s, 1H), 4.39 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 6.0 Hz, 2H), 2.33 (s, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.5, 143.4, 137.8, 132.9, 132.8, 125.4, 106.1, 65.5, 27.3, 21.3. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{26}H_{31}N_2O_2$, 403.2380; found, 403.2378.



2m, 58%

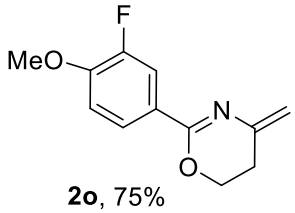
2-(3,5-dimethoxyphenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2m**). Yellow oil (40.2 mg, 58%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400

MHz): δ 7.18 (s, 2H), 6.56 (s, 1H), 5.11 (s, 1H), 4.63 (s, 1H), 4.41 (t, J = 6.0 Hz, 2H), 3.83 (s, 6H), 2.63 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.6, 155.9, 143.3, 135.0, 106.7, 105.4, 104.2, 65.6, 55.6, 27.2. HRMS (ESI-TLQ) *m/z*: $[2M + Na]^+$ calcd for $C_{26}H_{30}N_2NaO_6$, 489.1996; found, 489.1995.



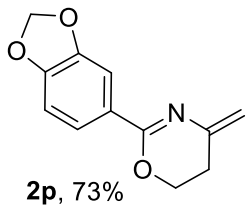
2n, 62%

2-(3,5-difluorophenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2n**). Colorless oil (26.0 mg, 62%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.50 (m, 2H), 6.91-6.85 (m, 1H), 5.13 (s, 1H), 4.68 (s, 1H), 4.41 (t, J = 6.0 Hz, 2H), 2.64 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.8 (dd, J = 12.3 Hz, J = 234.2 Hz), 153.9, 142.8, 136.5 (t, J = 9.7 Hz), 110.7 (dd, J = 7.4 Hz, J = 12.2 Hz), 107.9, 106.3 (t, J = 25.4 Hz), 65.8, 27.0. ^{19}F NMR ($CDCl_3$, 564 MHz): δ -109.8. HRMS (ESI-TLQ) *m/z*: $[2M + Na]^+$ calcd for $C_{22}H_{18}F_4N_2NaO_2$, 441.1196; found, 441.1189.



2o, 75%

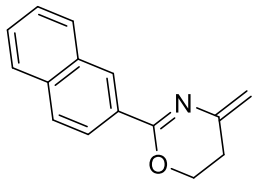
2-(3-fluoro-4-methoxyphenyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2o**). Colorless oil (49.4 mg, 75%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (dd, J = 7.2 Hz, J = 10.4 Hz, 2H), 6.94 (t, J = 8.8 Hz, 1H), 5.07 (s, 1H), 4.60 (s, 1H), 4.39 (t, J = 5.6 Hz, 2H), 3.93 (s, 3H), 2.62 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.0 (d, J = 2.9 Hz), 151.9 (d, J = 243.8 Hz), 150.2 (d, J = 10.7 Hz), 143.3, 126.1 (d, J = 6.8 Hz), 124.2, 115.5 (d, J = 20.2 Hz), 112.4, 106.2, 65.6, 56.3, 27.3. ^{19}F NMR ($CDCl_3$, 564 MHz): δ -135.4. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{13}FNO_2$, 222.0925; found, 222.0926.



2p, 73%

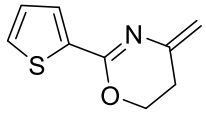
2-(benzo[*d*][1,3]dioxol-5-yl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2p**). Yellow oil (47.7 mg, 73%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (dd, J = 1.6 Hz, J = 6.8 Hz, 1H), 7.49 (s, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.00 (s, 2H), 5.05 (s, 1H), 4.57 (s, 1H), 4.38 (t, J = 5.6 Hz, 2H), 2.61 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.7, 150.2, 147.7, 143.4, 127.2, 122.7, 108.0, 107.9, 105.8, 101.6, 65.5, 27.3. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for

$C_{24}H_{23}N_2O_6$, 435.1551; found, 435.1548.



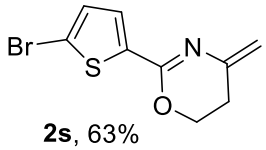
2q, 72%

4-methylene-2-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,3-oxazine (**2q**). White solid (48.5 mg, 72%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). mp 85-86 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.53-7.47 (m, 2H),5.16 (s, 1H), 4.65 (s, 1H), 4.46 (t, J = 5.6 Hz, 2H), 2.67 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.2, 143.5, 134.8, 132.9, 130.4, 129.1, 128.1, 127.9, 127.8, 127.4, 126.4, 124.5, 106.6, 65.6, 27.4. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{14}NO$, 224.1070; found, 224.1070.



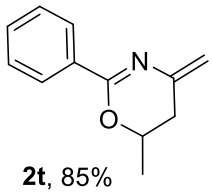
2r, 81%

4-methylene-2-(thiophen-2-yl)-5,6-dihydro-4*H*-1,3-oxazine (**2r**). Colorless oil (43.5 mg, 81%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, J = 3.6 Hz, 1H), 7.41 (d, J = 5.2 Hz, 1H), 7.05 (t, J = 4.4 Hz, 1H), 5.06 (s, 1H), 4.59 (s, 1H), 4.39 (t, J = 6.0 Hz, 2H), 2.63 (t, J = 6.0 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 152.9, 142.9, 137.4, 129.7, 129.2, 127.6, 106.4, 65.7, 27.3. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{19}N_2O_2S_2$, 359.0882; found, 359.0877.



2s, 63%

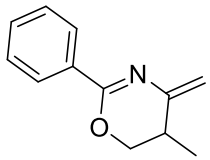
2-(5-bromothiophen-2-yl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (**2s**). Colorless oil (28.5 mg, 63%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 3.6 Hz, 1H), 5.05 (s, 1H), 4.61 (s, 1H), 4.36 (t, J = 5.6 Hz, 2H), 2.62 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.8, 142.6, 138.7, 129.3, 117.2, 106.9, 65.8, 27.3. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{18}H_{17}Br_2N_2O_2S_2$, 514.9092; found, 514.9091.



2t, 85%

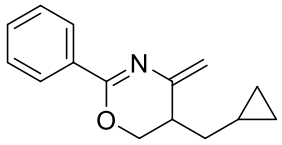
6-methyl-4-methylene-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**2t**). Colorless oil (47.5 mg, 85%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 5.6 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 5.12 (s, 1H), 4.61 (s, 1H), 4.47-4.39 (m, 1H), 2.64 (dd, J = 3.6 Hz, J = 11.2 Hz, 1H), 2.31 (dd, J = 9.6 Hz, J = 4.8 Hz, 1H), 1.43 (d, J = 6.4 Hz, 3H). ^{13}C {^{1}H} NMR

($CDCl_3$, 100 MHz): δ 156.3, 143.8, 133.1, 131.0, 128.2, 127.7, 106.6, 71.9, 34.1, 20.8. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{24}H_{27}N_2O_2$, 375.2067; found, 375.2066.



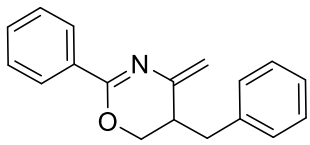
2u, 81%

5-methyl-4-methylene-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**2u**). Yellow oil (45.6 mg, 81%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 6.8 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 5.08 (s, 1H), 4.70 (s, 1H), 4.36 (dd, *J* = 4.4 Hz, *J* = 6.0 Hz, 1H), 3.96 (t, *J* = 8.8 Hz, 1H), 2.70-2.62 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 155.5, 148.9, 132.9, 131.1, 128.2, 127.7, 104.2, 70.4, 30.4, 14.8. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{24}H_{27}N_2O_2$, 375.2067; found, 375.2066.



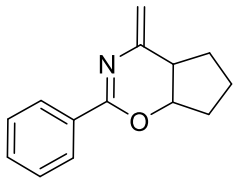
2v, 72%

5-(cyclopropylmethyl)-4-methylene-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**2v**). Yellow oil (48.8 mg, 72%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 5.09 (s, 1H), 4.66 (s, 1H), 4.47 (dd, *J* = 4.0 Hz, *J* = 6.8 Hz, 1H), 4.31 (q, *J* = 5.2 Hz, 1H) 2.70-2.64 (m, 1H), 1.73-1.66 (m, 1H), 1.34-1.26 (m, 1H), 0.84-0.74 (m, 1H), 0.56-0.44 (m, 2H), 0.13-0.05 (m, 2H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 155.4, 147.6, 132.9, 131.1, 128.2, 127.7, 105.4, 68.8, 37.0, 35.2, 8.8, 5.3, 4.3. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{18}NO$, 228.1383; found, 228.1386.



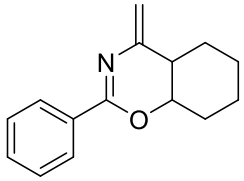
2w, 83%

5-benzyl-4-methylene-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**2w**). Yellow oil (43.8 mg, 83%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.24-7.21 (m, 3H), 5.11 (s, 2H), 4.64 (s, 1H), 4.23 (dd, *J* = 3.2 Hz, *J* = 7.6 Hz, 1H), 4.16 (dd, *J* = 4.4 Hz, *J* = 6.4 Hz, 1H), 3.02 (dd, *J* = 4.8 Hz, *J* = 7.6 Hz, 1H), 2.83-2.71 (m, 2H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 155.6, 147.2, 139.0, 132.8, 131.2, 129.3, 128.7, 128.3, 127.8, 126.6, 106.0, 67.6, 38.3, 36.8. HRMS (ESI-TLQ) *m/z*: $[2M + H]^+$ calcd for $C_{36}H_{35}N_2O_2$, 527.2693; found, 527.2696.



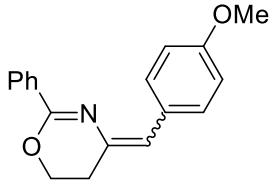
2x, 83%

4-methylene-2-phenyl-4,4a,5,6,7,7a-hexahydrocyclopenta[*e*][1,3]oxazine (**2x**). Coloeless oil (53.4 mg, 83%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, J = 6.8 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 5.06 (s, 1H), 4.57 (s, 1H), 3.93-3.86 (m, 1H), 2.31-2.19 (m, 2H), 2.15-2.08 (m, 1H), 1.98-1.89 (m, 1H), 1.84-1.73 (m, 2H), 1.59-1.49 (m,1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.7, 149.7, 133.0, 131.1, 128.2, 128.1, 102.7, 80.4, 42.5, 28.6, 22.8, 19.0. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{16}NO$, 214.1226; found, 214.1228.



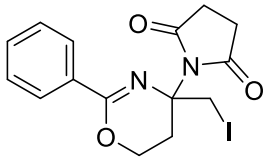
2y, 76%

4-methylene-2-phenyl-4a,5,6,7,8,8a-hexahydro-4H-benzo[*e*][1,3]oxazine (**2y**). Yellow oil (51.6 mg, 76%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 5.06 (s, 1H), 4.62 (s, 1H), 3.89-3.82 (m, 1H), 2.23 (d, J = 13.6 Hz, 2H), 2.15-2.08 (m, 1H), 1.91-1.84 (m, 2H), 1.59-1.49 (m, 1H), 1.45-1.33 (m, 2H), 1.31-1.21 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.6, 148.6, 133.1, 131.0, 128.2, 127.8, 102.8, 78.3, 39.9, 32.0, 26.5, 25.4, 24.0. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{18}NO$, 228.1383; found, 228.1383.



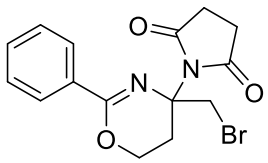
2aa, 8%

4-(4-methoxybenzylidene)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**2aa**). Yellow oil (6.4 mg, 8%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, J = 6.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.46-7.40 (m, 3H), 6.91 (d, J = 8.8 Hz, 2H), 5.76 (s, 1H), 4.51 (t, J = 6.0 Hz, 2H), 3.83 (s, 3H), 2.68 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.3, 155.5, 134.6, 133.4, 131.2, 131.0, 130.0, 128.3, 127.9, 118.9, 113.8, 66.1, 55.4, 28.8. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{18}NO_2$, 280.1332; found, 280.1332.



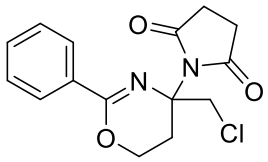
3a, 46%

1-(4-(iodomethyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazin-4-yl)pyrrolidine-2,5-dione (**3a**). Yellow oil (36.7 mg, 46%), (EtOAc/ Petroleum ether, 1/10-1/3, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.42-4.36 (m, 1H), 4.34-4.27 (m, 1H), 4.04 (dd, J = 10.0 Hz, J = 4.4 Hz, 2H), 2.98-2.92 (m, 1H), 2.69 (s, 4H), 2.44-2.36 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 177.0, 157.6, 133.0, 131.4, 128.3, 128.0, 71.5, 62.3, 29.1, 28.6, 15.9. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}IN_2O_3$, 399.0200; found, 399.0201.



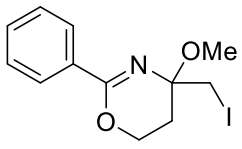
3b, 56%

1-(4-(bromomethyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazin-4-yl)pyrrolidine-2,5-dione (**3b**). Yellow oil (39.2 mg, 56%), (EtOAc/ Petroleum ether, 1/10-1/3, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 4.43-4.30 (m, 3H), 3.93 (d, J = 10.4 Hz, 1H), 3.02-2.96 (m, 1H), 2.69 (s, 4H), 2.46-2.38 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 177.1, 157.6, 133.0, 131.4, 128.2, 128.0, 72.3, 62.2, 38.2, 28.6, 28.4. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}BrN_2O_3$, 351.0339; found, 351.0335.



3c, 57%

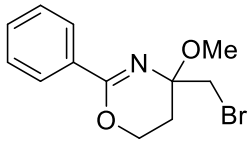
1-(4-(chloromethyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazin-4-yl)pyrrolidine-2,5-dione (**3c**). Colorless oil (35.2 mg, 57%), (EtOAc/ Petroleum ether, 1/10-1/3, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 4.47-4.35 (m, 3H), 3.97 (d, J = 11.6 Hz, 1H), 3.05-2.99 (m, 1H), 2.69 (s, 4H), 2.44-2.37 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 177.1, 157.7, 133.1, 131.4, 128.3, 128.0, 72.9, 62.2, 48.5, 28.6, 27.7. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}ClN_2O_3$, 307.0844; found, 307.0845.



4a, 89%

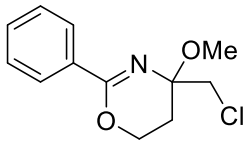
4-(iodomethyl)-4-methoxy-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**4a**). Colorless oil (59.0 mg, 89%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400

MHz): δ 7.98 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 6.8 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H), 4.44-4.38 (m, 1H), 4.30-4.25 (m, 1H), 3.69 (d, J = 11.2 Hz, 1H), 3.42 (s, 3H), 3.25 (d, J = 11.2 Hz, 1H), 2.21-2.09 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.0, 133.2, 131.2, 128.2, 127.8, 80.2, 62.6, 48.8, 31.1, 12.9. HRMS (ESI-TLQ) *m/z*: [M + H]$^+$ calcd for $C_{12}H_{15}INO_2$, 332.0142; found, 332.0144.



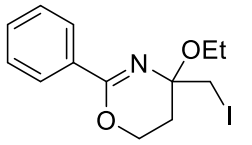
4b, 70%

4-(bromomethyl)-4-methoxy-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**4b**). Yellow oil (39.6 mg, 70%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 4.46-4.40 (m, 1H), 4.35-4.29 (m, 1H), 3.87 (d, J = 11.2 Hz, 1H), 3.44 (s, 3H), 3.33 (d, J = 11.2 Hz, 1H), 2.21-2.08 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.4, 133.2, 131.3, 128.2, 127.8, 80.8, 62.6, 49.0, 36.6, 29.9. HRMS (ESI-TLQ) *m/z*: [M + H]$^+$ calcd for $C_{12}H_{15}BrNO_2$, 284.0281; found, 284.0282.



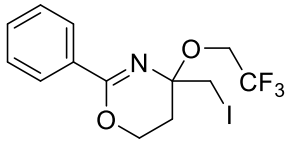
4c, 72%

4-(chloromethyl)-4-methoxy-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**4c**). Colorless oil (34.6 mg, 72%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 4.46-4.40 (m, 1H), 4.36-4.31 (m, 1H), 3.98 (d, J = 12.0 Hz, 1H), 3.44 (s, 3H), 3.41 (d, J = 12.4 Hz, 1H), 2.19-2.04 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.5, 133.2, 131.3, 128.2, 127.8, 81.3, 62.5, 49.1, 47.2, 29.1. HRMS (ESI-TLQ) *m/z*: [M + H]$^+$ calcd for $C_{12}H_{15}ClNO_2$, 240.0786; found, 240.0788.



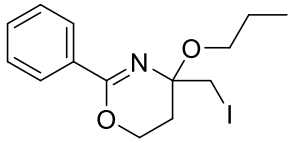
5a, 79%

4-ethoxy-4-(iodomethyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**5a**). Yellow oil (Methods A, 54.7 mg, 79%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 4.45-4.39 (m, 1H), 3.90-3.83 (m, 1H), 3.70 (d, J = 11.2 Hz, 1H), 3.66-3.58 (m, 1H), 3.27 (d, J = 11.2 Hz, 1H), 2.21-2.15 (m, 1H), 2.13-2.06 (m, 1H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.7, 133.2 131.2, 128.2, 127.7, 80.0, 62.6, 56.5, 31.6, 15.8, 14.0. HRMS (ESI-TLQ) *m/z*: [M + H]$^+$ calcd for $C_{13}H_{17}INO_2$, 346.0298; found, 346.0300.



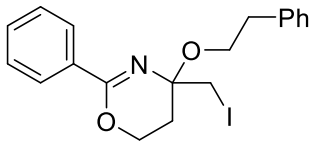
5b, 86%

4-(iodomethyl)-2-phenyl-4-(2,2,2-trifluoroethoxy)-5,6-dihydro-4*H*-1,3-oxazine (**5b**). Yellow oil (Methods A, 68.5 mg, 86%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 4.44-4.38 (m, 1H), 4.34-4.25 (m, 2H), 4.00-3.91 (m, 1H), 3.53 (d, J = 11.2 Hz, 1H) , 3.30 (d, J = 11.2 Hz, 1H), 2.23 (t, J = 5.6 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.2, 132.6, 131.7, 128.3, 127.9, 124.2 (d, J = 276.1 Hz), 81.0, 62.5, 59.3 (q, J = 34.6 Hz), 31.1, 12.2. ^{19}F NMR ($CDCl_3$, 564 MHz): δ -73.9. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{14}F_3INO_2$, 400.0016; found, 400.0018.



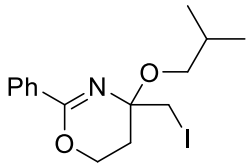
5c, 76%

4-(iodomethyl)-2-phenyl-4-propoxy-5,6-dihydro-4*H*-1,3-oxazine (**5c**). Yellow oil (Methods B, 54.5 mg, 76%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 4.46-4.39 (m, 1H), 4.32-4.26 (m, 1H), 3.78-3.72 (m, 1H), 3.69 (d, J = 10.8 Hz, 1H), 3.55-3.49 (m, 1H), 3.28 (d, J = 10.8 Hz, 1H), 2.22-2.16 (m, 1H), 2.12-2.05 (m, 1H), 1.63-1.54 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.8, 133.3 131.1, 128.2, 127.8, 79.9, 62.7, 31.6, 23.5, 14.0, 11.0. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{19}INO_2$, 360.0455; found, 360.0453.



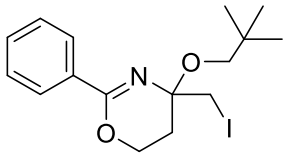
5d, 89%

4-(iodomethyl)-4-phenethoxy-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**5d**). Colorless oil (Methods B, 72.8 mg, 89%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 4.4 Hz, 4H), 7.18-7.12 (m, 1H), 4.33-4.21 (m, 2H), 4.06 (dd, J = 7.6 Hz, J = 8.8 Hz, 1H), 3.78 (dd, J = 7.6 Hz, J = 6.8 Hz, 1H), 3.65 (d, J = 10.8 Hz, 1H), 2.92-2.86 (m, 2H), 2.18-2.13 (m, 1H), 2.10-2.03 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.0, 139.2, 133.2, 131.2, 129.1, 128.3, 128.2, 127.8, 126.2, 80.2, 62.6, 61.9, 36.8, 31.5, 13.9. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{21}INO_2$, 422.0611; found, 422.0608.



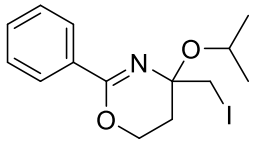
5e, 69%

4-(iodomethyl)-4-isobutoxy-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**5e**). Colorless oil (Methods B, 51.4 mg, 69%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98-7.96 (m, 2H), 7.47-7.42 (m, 1H), 7.39-7.36 (m, 2H), 4.46-4.40 (m, 1H), 4.32-4.27 (m, 1H), 3.67 (d, J = 10.8 Hz, 1H), 3.55 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H) , 3.33 (dd, J = 6.0 Hz, J = 2.4 Hz, 1H), 3.28 (d, J = 10.8 Hz, 1H), 2.23-2.17 (m, 1H), 2.11-2.04 (m, 1H), 1.86-1.76 (m, 1H), 0.92 (d, J = 6.8 Hz, 3H) , 0.88 (d, J = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.8, 133.4 131.1, 128.2, 127.7, 79.7, 67.5, 62.7, 31.7, 28.9, 19.7, 14.1. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{21}INO_2$, 374.0611; found, 374.0610.



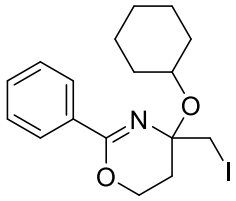
5f, 71%

4-(iodomethyl)-4-(neopentyloxy)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**5f**). Yellow oil (Methods B, 55.1 mg, 71%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.47-4.41 (m, 1H), 4.33-4.28 (m, 1H), 3.66 (d, J = 10.8 Hz, 1H), 3.45 (d, J = 8.4 Hz, 1H), 3.29 (d, J = 10.8 Hz, 1H) ,3.19 (d, J = 8.0 Hz, 1H), 2.24-2.19 (m, 1H), 2.08-2.01 (m, 1H), 0.89 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.8, 133.5 131.1, 128.2, 127.8, 79.4, 70.7, 62.8, 31.9, 31.7, 27.0, 14.2. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{23}INO_2$, 388.0768; found, 388.0765.



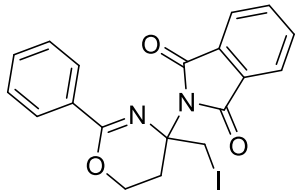
5g, 58%

4-(iodomethyl)-4-isopropoxy-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**5g**). Yellow oil (Methods B, 41.6 mg, 58%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.44-4.34 (m, 2H), 4.32-4.27 (m, 1H), 3.64 (d, J = 10.8 Hz, 1H), 3.33 (d, J = 10.8 Hz, 1H), 2.14-2.09 (m, 2H), 1.28 (d, J = 6.0 Hz, 3H) ,1.07 (d, J = 6.0 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.8, 133.3 131.1, 128.2, 127.7, 80.4, 64.4, 62.6, 32.2, 24.8, 24.7, 15.5. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{19}INO_2$, 360.0455; found, 360.0453.



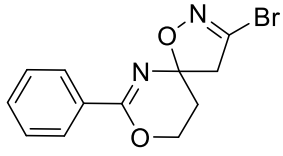
5h, 60%

4-(cyclohexyloxy)-4-(iodomethyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**5h**). Yellow oil (Methods B, 49.9 mg, 60%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, J = 6.8 Hz, 2H), 7.47-7.44 (m, 1H), 7.39 (t, J = 7.6 Hz, 2H), 4.45-4.38 (m, 1H), 4.33-4.27 (m, 1H), 4.05-3.98 (m, 1H), 3.63 (d, J = 10.8 Hz, 1H), 3.35 (d, J = 10.4 Hz, 1H), 2.17-2.08 (m, 2H), 2.02-1.98 (m, 1H), 1.79-1.59 (m, 3H), 1.51 (t, J = 3.6 Hz, 1H), 1.42-1.36 (m, 1H), 1.33-1.28 (m, 1H), 1.27-1.20 (m, 2H), 1.18-1.09 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.8, 133.4 131.1, 128.2, 127.7, 80.3, 70.2, 62.7, 35.0, 34.9, 32.2, 25.7, 24.9, 24.6, 15.8. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{23}INO_2$, 400.0768; found, 400.0766.



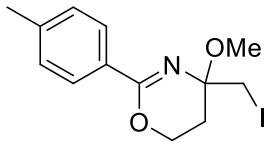
5i, 26%

2-(4-(iodomethyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazin-4-yl)isoindoline-1,3-dione (**5i**). Yellow oil (Methods C, 23.5 mg, 26%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 7.2 Hz, 2H), 7.84-7.80 (m, 2H), 7.74-7.70 (m, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 4.48-4.42 (m, 1H), 4.40-4.34 (m, 1H), 4.21 (d, J = 10.4 Hz, 1H), 4.06 (d, J = 10.4 Hz, 1H), 3.14-3.08 (m, 1H), 2.53-2.46 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 168.3, 157.5, 134.3, 133.1 131.7, 131.4, 128.3, 128.1, 123.3, 71.3, 62.4, 29.6, 16.6. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{16}IN_2O_3$, 447.0200; found, 447.0197.



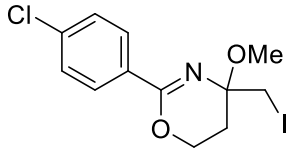
6, 45%

3-bromo-7-phenyl-1,8-dioxa-2,6-diazaspiro[4.5]deca-2,6-diene (**6**). Colorless oil (26.6 mg, 45%), (EtOAc/ Petroleum ether, 1/50-1/10, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 4.58-4.52 (m, 1H), 4.47-4.41 (m, 1H), 3.41 (d, J = 17.6 Hz, 1H), 3.15 (d, J = 17.2 Hz, 1H), 2.40-2.34 (m, 1H), 2.21-2.14 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.5, 136.9, 132.6, 131.7, 128.3, 128.0, 92.7, 62.6, 53.7, 30.8. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{12}BrN_2O_2$, 295.0077; found, 295.0076.



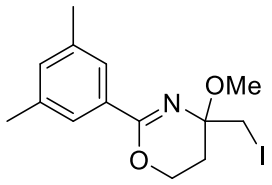
7b, 75%

4-(iodomethyl)-4-methoxy-2-(p-tolyl)-5,6-dihydro-4*H*-1,3-oxazine (**7b**). Yellow oil (51.9 mg, 75%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.42-4.36 (m, 1H), 4.28-4.23 (m, 1H), 3.68 (d, J = 11.2 Hz, 1H), 3.41 (s, 3H), 3.24 (d, J = 11.2 Hz, 1H), 2.38 (s, 3H), 2.20-2.08 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.1, 141.5, 130.4, 128.9, 127.7, 80.2, 62.6, 48.8, 31.1, 21.6, 13.0. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{17}INO_2$, 346.0298; found, 346.0297.



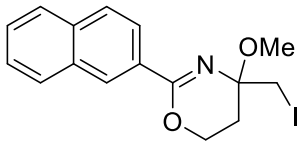
7e, 90%

2-(4-chlorophenyl)-4-(iodomethyl)-4-methoxy-5,6-dihydro-4*H*-1,3-oxazine (**7e**). Yellow oil (65.5 mg, 90%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 4.43-4.37 (m, 1H), 4.29-4.24 (m, 1H), 3.66 (d, J = 10.8 Hz, 1H), 3.40 (s, 3H), 3.24 (d, J = 11.2 Hz, 1H), 2.20-2.08 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.0, 137.4, 131.5, 129.1, 128.4, 80.1, 62.7, 48.8, 31.0, 12.6. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{14}ClINO_2$, 365.9752; found, 365.9752.



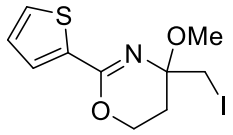
7l, 41%

2-(3,5-dimethylphenyl)-4-(iodomethyl)-4-methoxy-5,6-dihydro-4*H*-1,3-oxazine (**7i**). Yellow oil (29.4 mg, 41%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (s, 2H), 7.09 (s, 1H), 4.43-4.37 (m, 1H), 4.29-4.23 (m, 1H), 3.70 (d, J = 10.8 Hz, 1H), 3.42 (s, 3H), 3.24 (d, J = 11.2 Hz, 1H), 2.34 (s, 6H), 2.20-2.08 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.4, 137.8, 133.1, 133.0, 125.5, 80.2, 62.6, 48.9, 31.1, 21.4, 13.0. HRMS (ESI-TLQ) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{19}INO_2$, 360.0455; found, 360.0453.



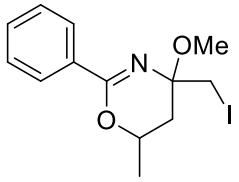
7q, 91%

4-(iodomethyl)-4-methoxy-2-(naphthalen-2-yl)-5,6-dihydro-4*H*-1,3-oxazine (**7q**). Yellow oil (69.6 mg, 91%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H) , 7.84 (t, J = 5.2 Hz, 2H), 7.55-7.48 (m, 2H), 4.50-4.45 (m, 1H), 4.36-4.31 (m, 1H), 3.74 (d, J = 11.2 Hz, 1H), 3.47 (s, 3H), 3.30 (d, J = 11.2 Hz, 1H), 2.26-2.14 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.0, 134.9, 132.8, 130.5, 129.1, 128.2, 127.9, 127.8, 127.5, 126.5, 124.6, 80.4, 62.8, 48.9, 31.2, 12.9. HRMS (ESI-TLQ) *m/z*: [M + H]$^{+}$ calcd for $C_{16}H_{17}INO_2$, 382.0298; found, 382.0297.



7r, 56%

4-(iodomethyl)-4-methoxy-2-(thiophen-2-yl)-5,6-dihydro-4*H*-1,3-oxazine (**7r**). Yellow oil (38.0 mg, 56%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (dd, J = 1.2 Hz, J = 2.4 Hz, 1H), 7.39 (dd, J = 1.2 Hz, J = 4.0 Hz, 1H), 7.03 (dd, J = 3.6 Hz, J = 1.2 Hz, 1H), 4.43-4.37 (m, 1H), 4.28-4.23 (m, 1H), 3.67 (d, J = 11.2 Hz, 1H), 3.40 (s, 3H), 3.23 (d, J = 11.2 Hz, 1H), 2.21-2.07 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 153.7, 137.4, 129.7, 129.3, 127.5, 80.1, 62.9, 48.9, 31.4, 12.7. HRMS (ESI-TLQ) *m/z*: [M + H]$^{+}$ calcd for $C_{10}H_{13}INO_2S$, 337.9706; found, 337.9706.



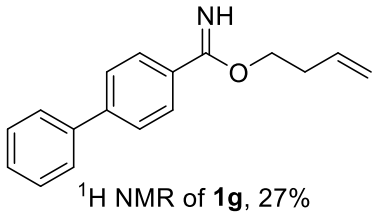
7t, 79%, dr = 5:1

4-(iodomethyl)-4-methoxy-6-methyl-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**7t**). Yellow oil (pure mainly product 23.7 mg, 34%), (EtOAc/ Petroleum ether, 1/50-1/20, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.52-4.44 (m, 1H), 3.71 (d, J = 10.8 Hz, 1H), 3.38 (s, 3H), 3.26 (d, J = 10.8 Hz, 1H), 2.32 (dd, J = 2.4 Hz, J = 11.2 Hz, 1H), 1.55 (t, J = 13.2 Hz, 1H), 1.43 (d, J = 6.4 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.1, 133.3, 131.2, 128.2, 127.9, 81.0, 69.1, 49.4, 39.7, 20.8, 14.0. HRMS (ESI-TLQ) *m/z*: [M + H]$^{+}$ calcd for $C_{13}H_{17}INO_2$, 346.0298; found, 346.0297.

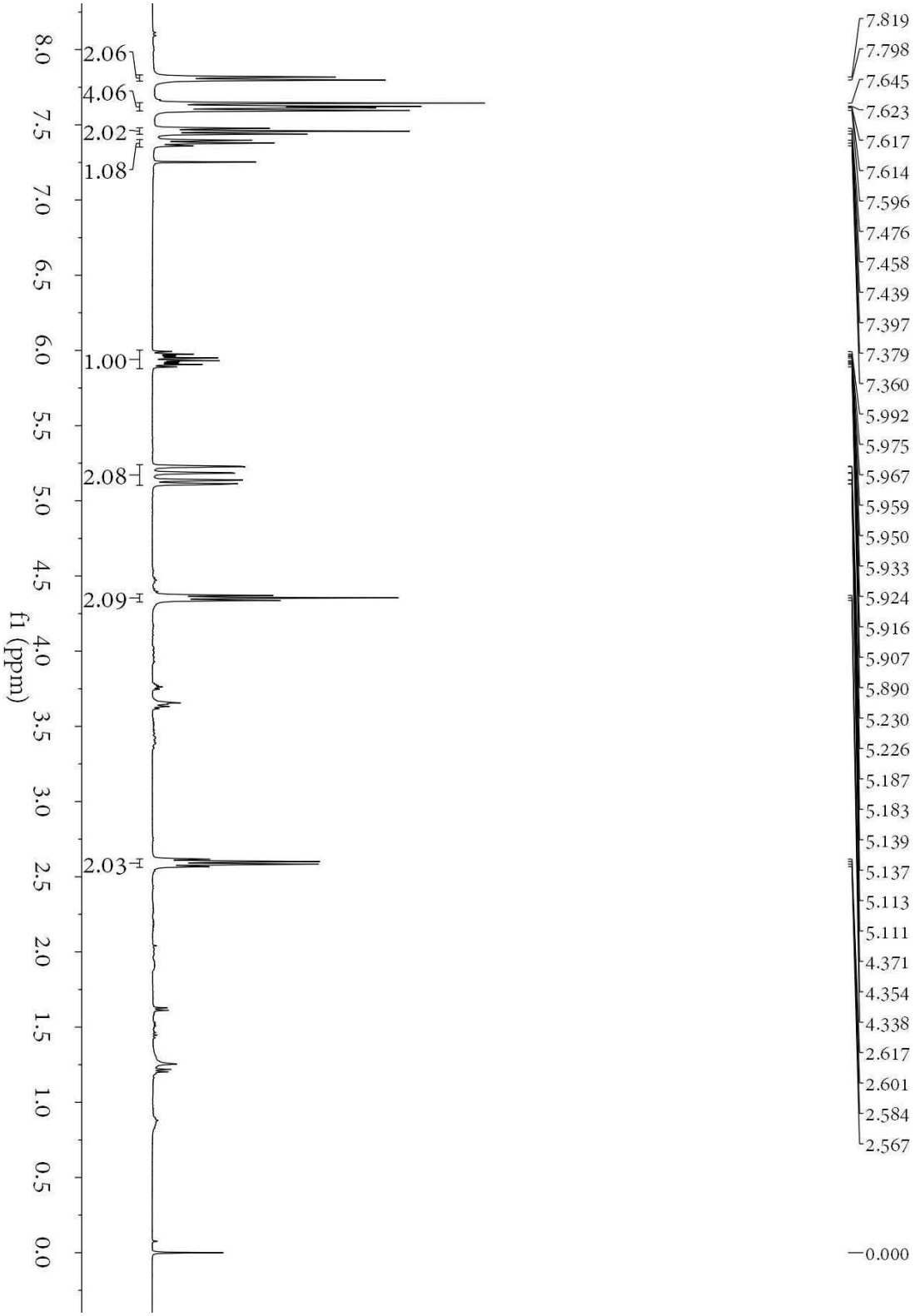
References

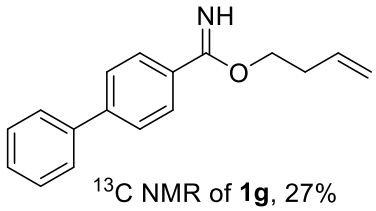
1. (a) Mou, X.-Q.; Rong, F.-M.; Zhang, H.; Chen, G.; He, G. Copper(I)-Catalyzed Enantioselective Intramolecular Aminotrifluoromethylation of *O*-Homoallyl Benzimidates. *Org. Let.*, **2019**, 21, 4657-4661; (b) Dong, W.; Fang, Z.-Y.; Cao, T.-Y.; Cao, J.-H.; Zhao, Z.-Q.; Zhang, L.-L.; Li, W.; Qi, L.; Wang, L.-J. Copper-Catalyzed Aminosulfonylation of *O*-Homoallyl Benzimidates with Sodium Sulfinates to Access Sulfonylated 1,3-Oxazines. *Org. Lett.* **2021**, 23, 15, 5809-5814; (c) Zhang L.-L.; Qi L.; Chen J M.; Dong, W.; Fang, Z.-Y.; Cao, T.-Y.; Li, W.; Wang, L.-J. Preparation of selenyl 1, 3-oxazines via $PhICl_2/Cu_2O$-promoted aminoselenation of *O*-homoallyl benzimidates with diselenides. *Chem. Commun.*, **2021**, 57, 12655-12658; (d) Mou, X. Q.; Ren, L. C.; Zhang, M.; Wang, M.; Jin, Y. F.; Guan, Q. X.; Cai, A.; Zhang, S. M.; Ren, H.; Zhang, Y.; Chen, Y. Z. Complementary Copper-Catalyzed and Electrochemical Aminosulfonylation of O-Homoallyl Benzimidates and N-Alkenyl Amidines with Sodium Sulfinates. *Org. Lett.* **2022**, 24, 1405-1411.

2. Fricke P.-J.; Stasko J.-L.; Robbins D.-T.; Gardner A.-C.; Stash J.; Ferraro M.-J.; Fennie M.-W. Copper-catalyzed hydroamination of propargyl imidates. *Tetrahedron Letters*, **2017**, 58, 4510-4513.

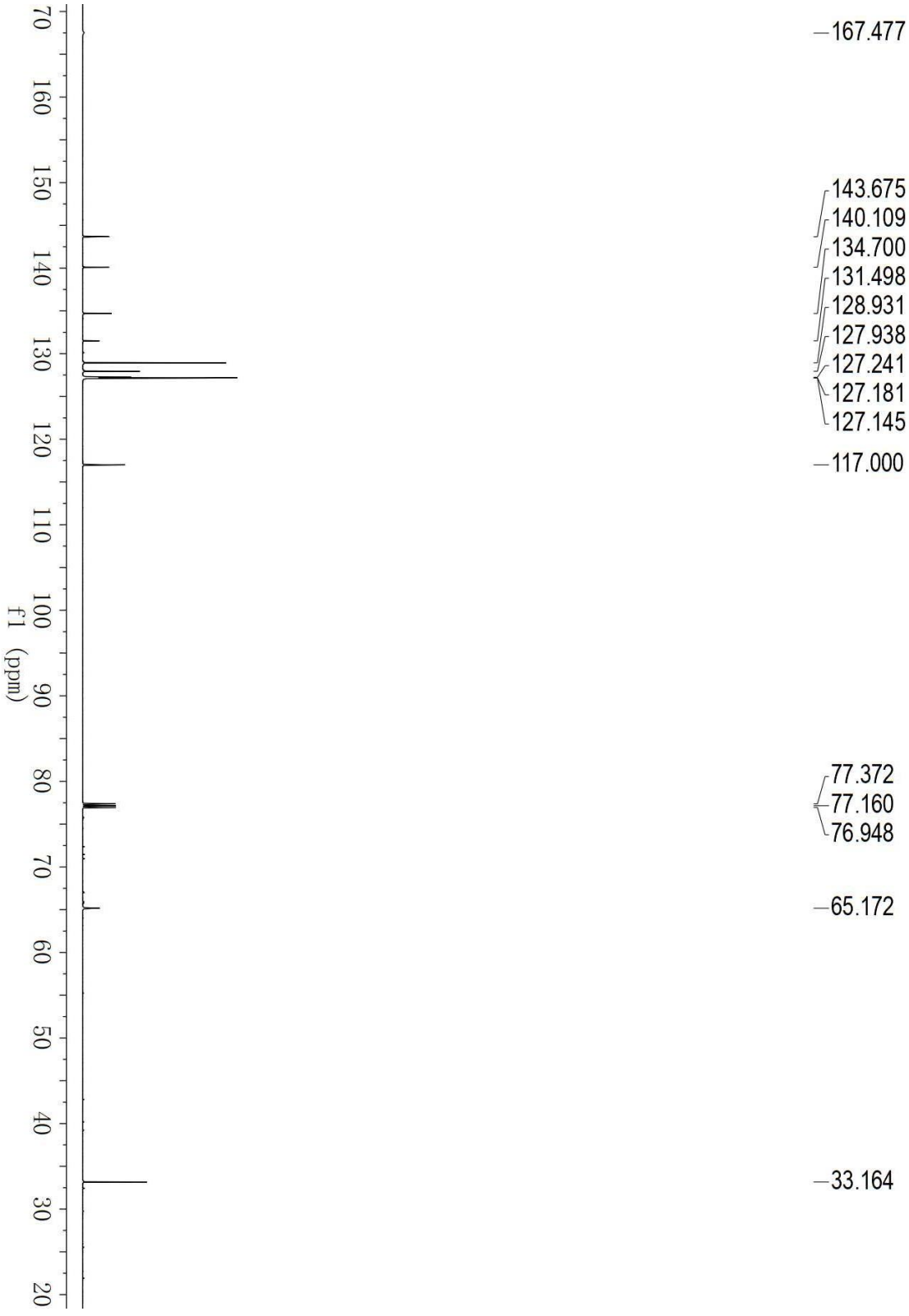


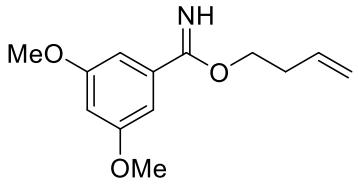
^{1}H NMR of **1g**, 27%
$CDCl_3$, 600 MHz



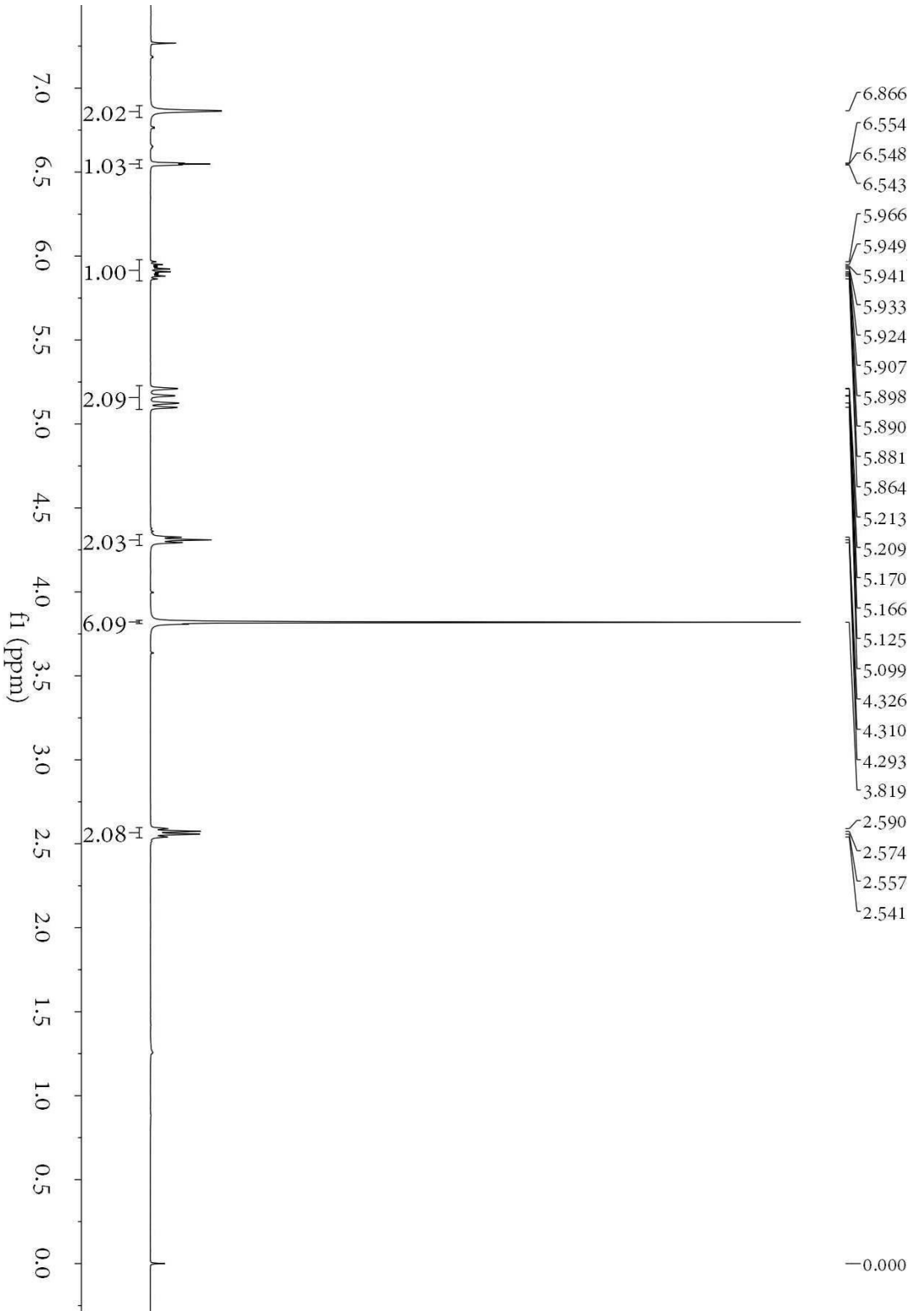


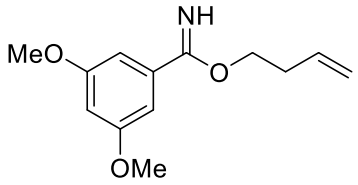
^{13}C NMR of **1g**, 27%
$CDCl_3$, 150 MHz



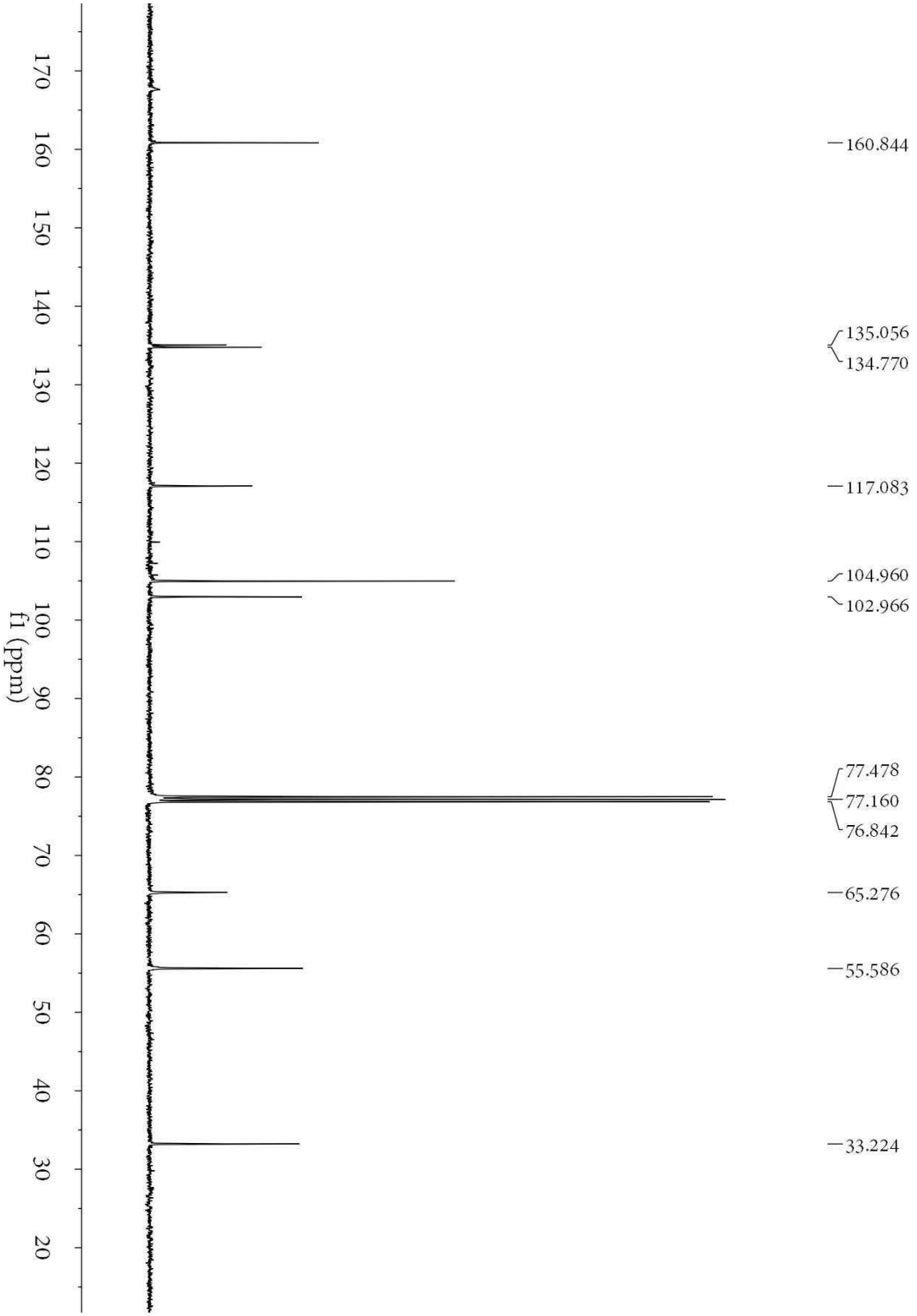


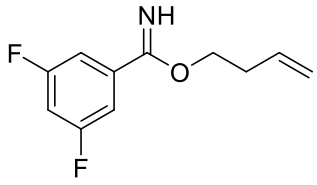
^{1}H NMR of **1m**, 29%
$CDCl_3$, 400 MHz



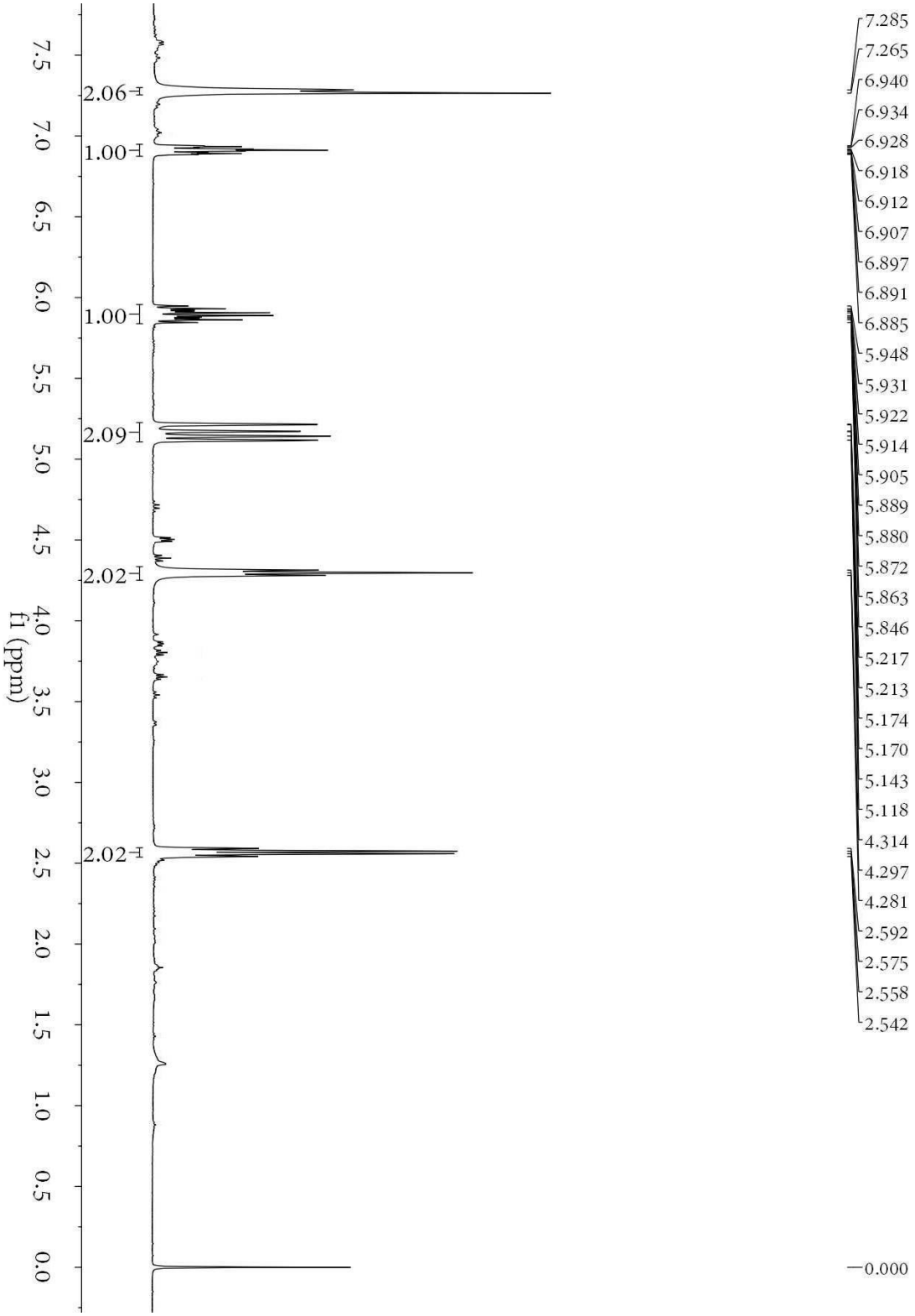


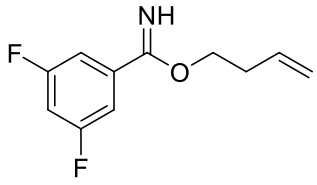
^{13}C NMR of **1m**, 29%
$CDCl_3$, 100 MHz



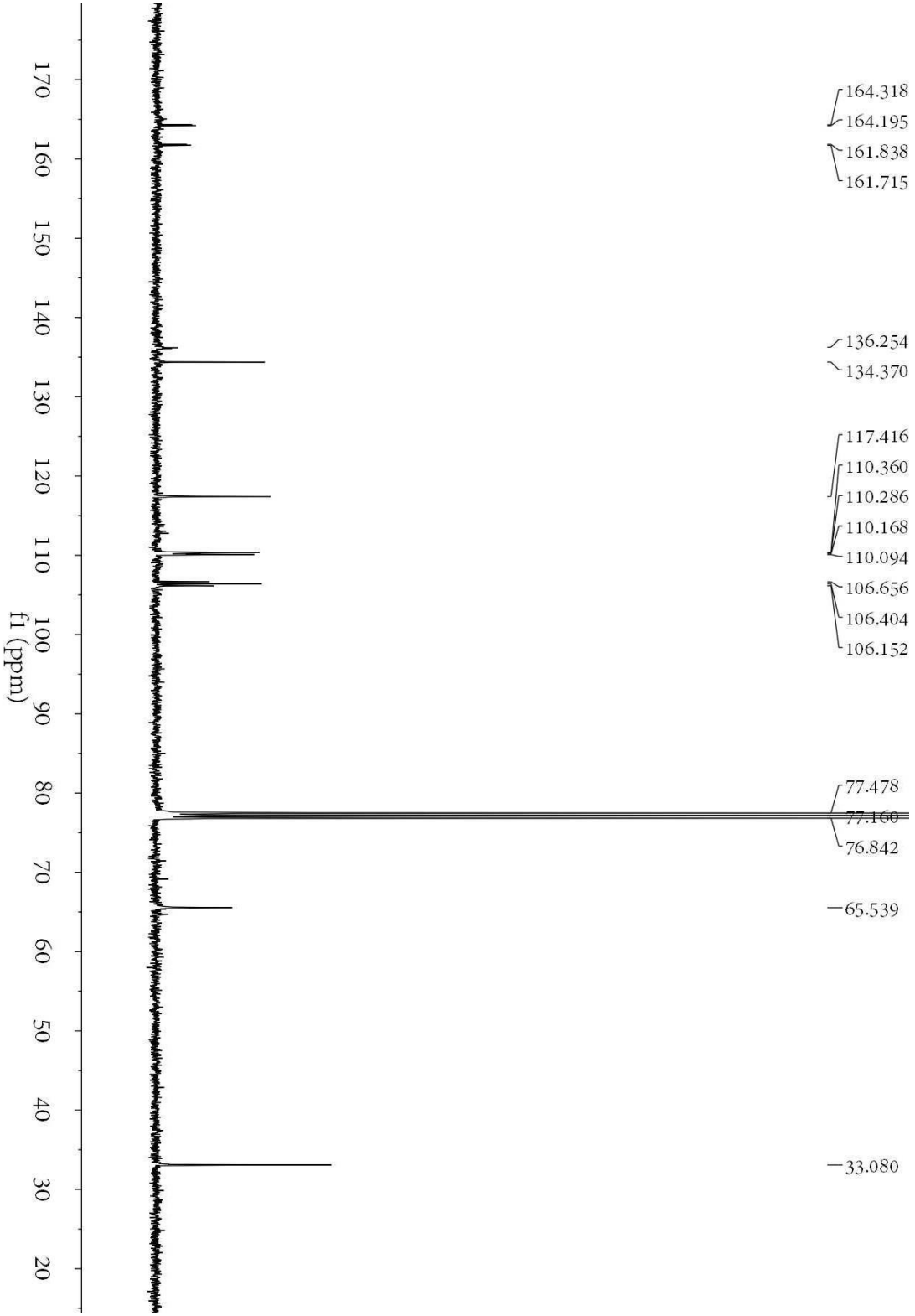


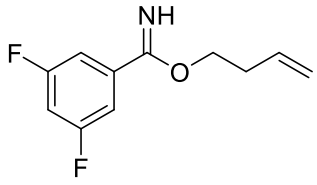
^{1}H NMR of **1n**, 12%
$CDCl_3$, 400 MHz



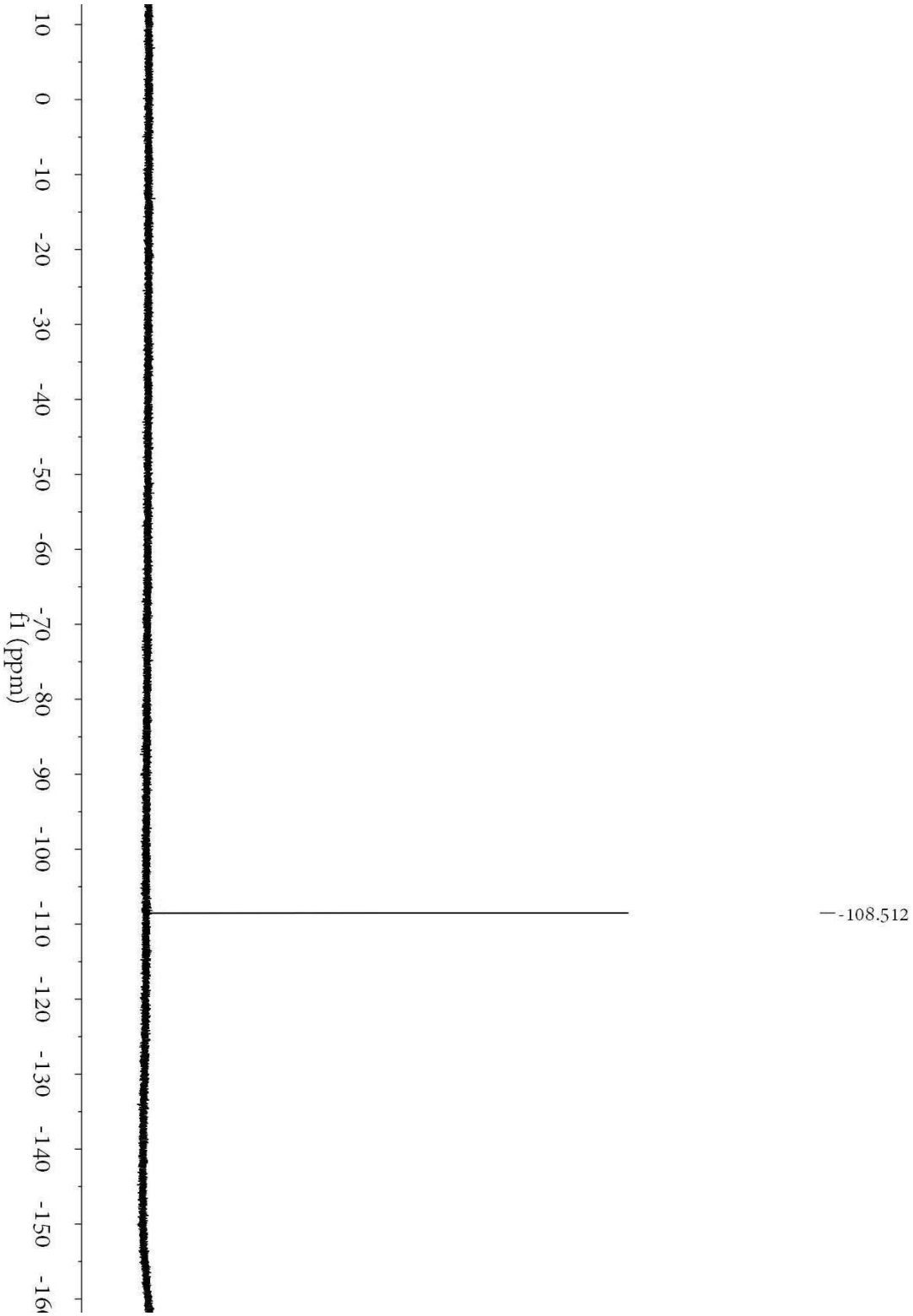


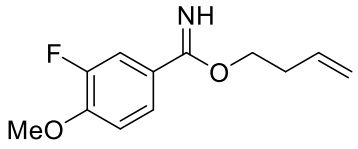
^{13}C NMR of **1n**, 12%
$CDCl_3$, 100 MHz



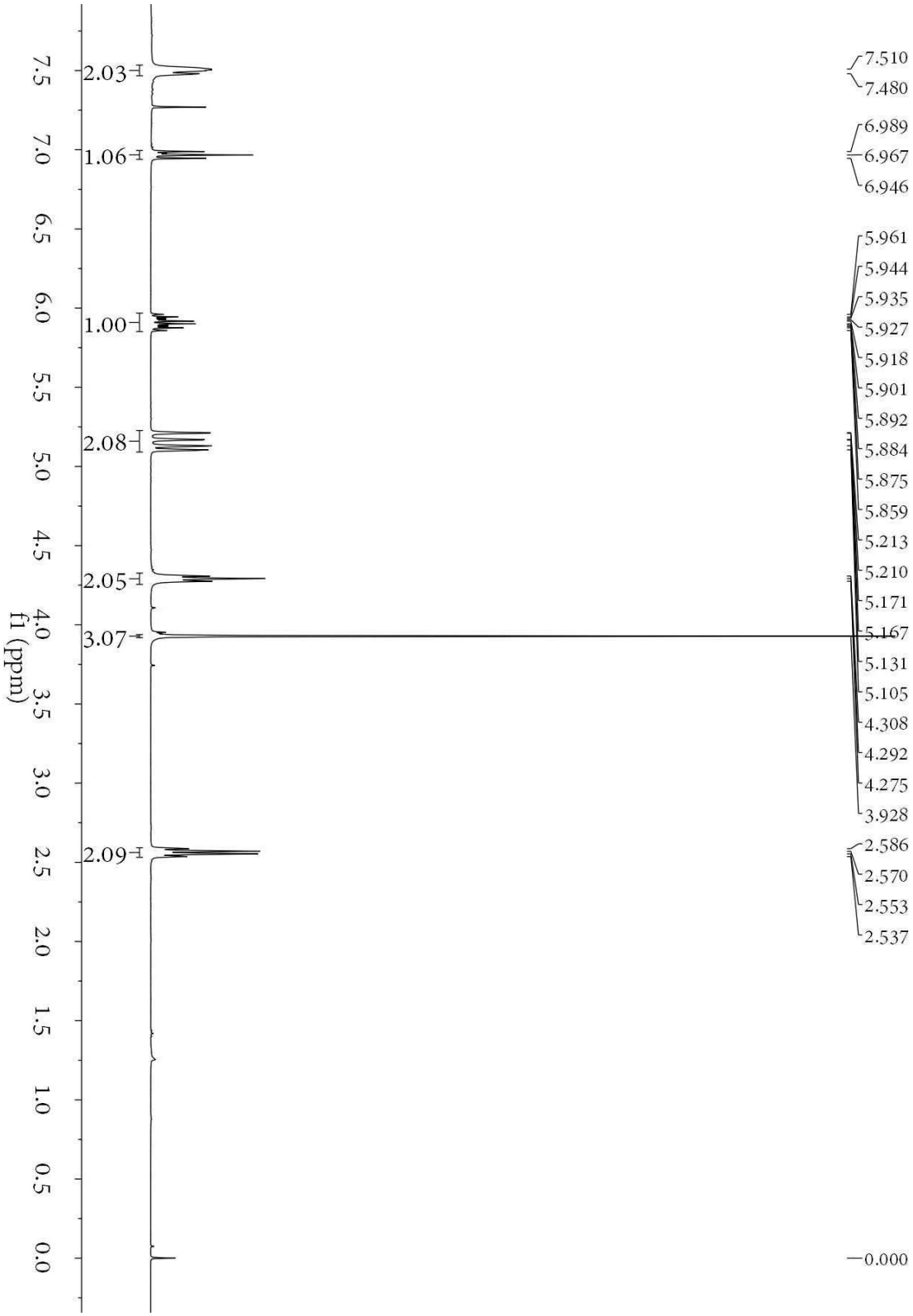


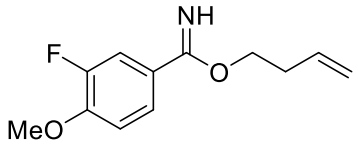
^{19}F NMR of **1n**, 12%
$CDCl_3$, 564 MHz



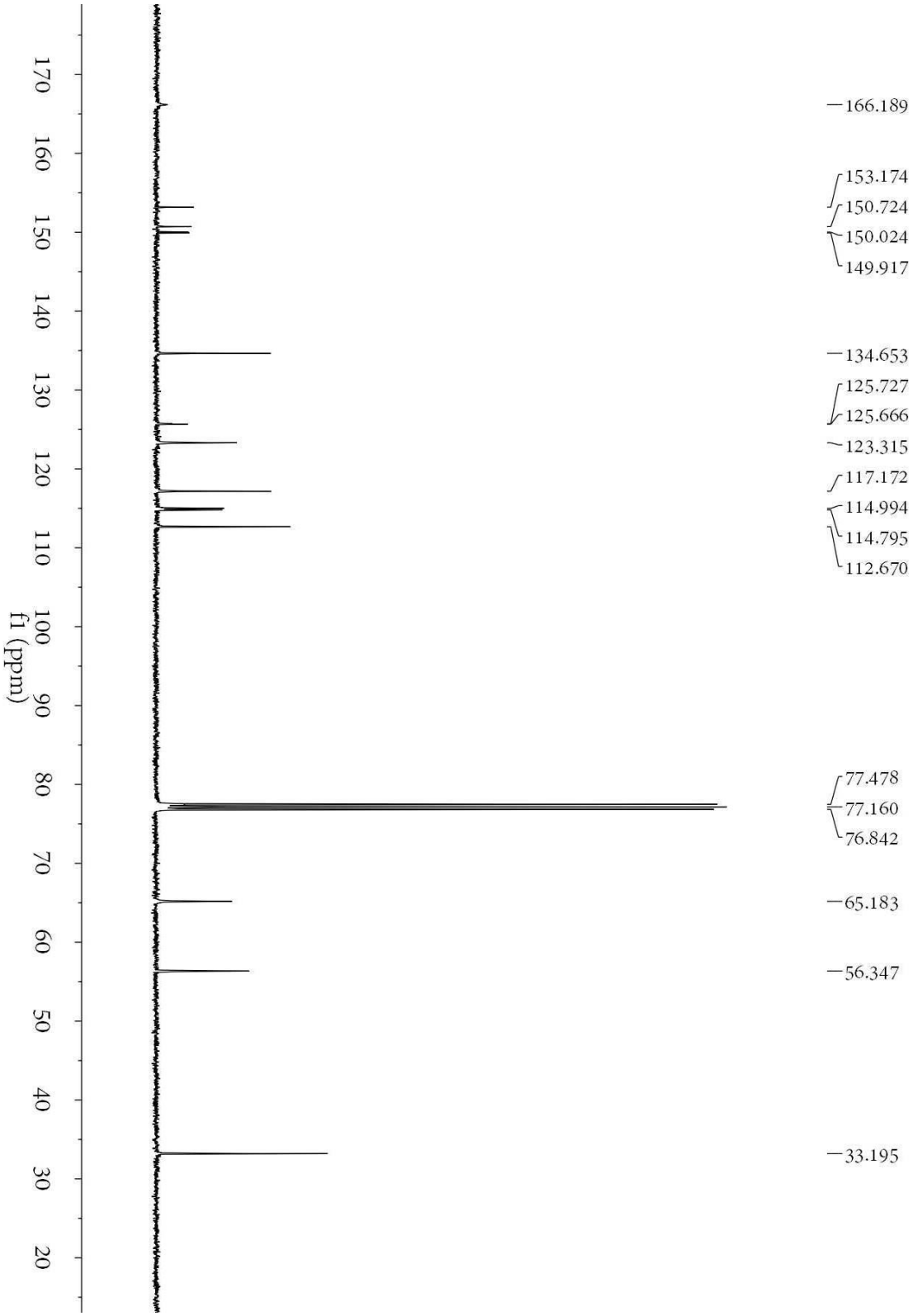


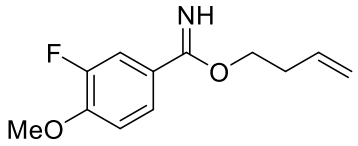
^{1}H NMR of **1o**, 35%
$CDCl_3$, 400 MHz



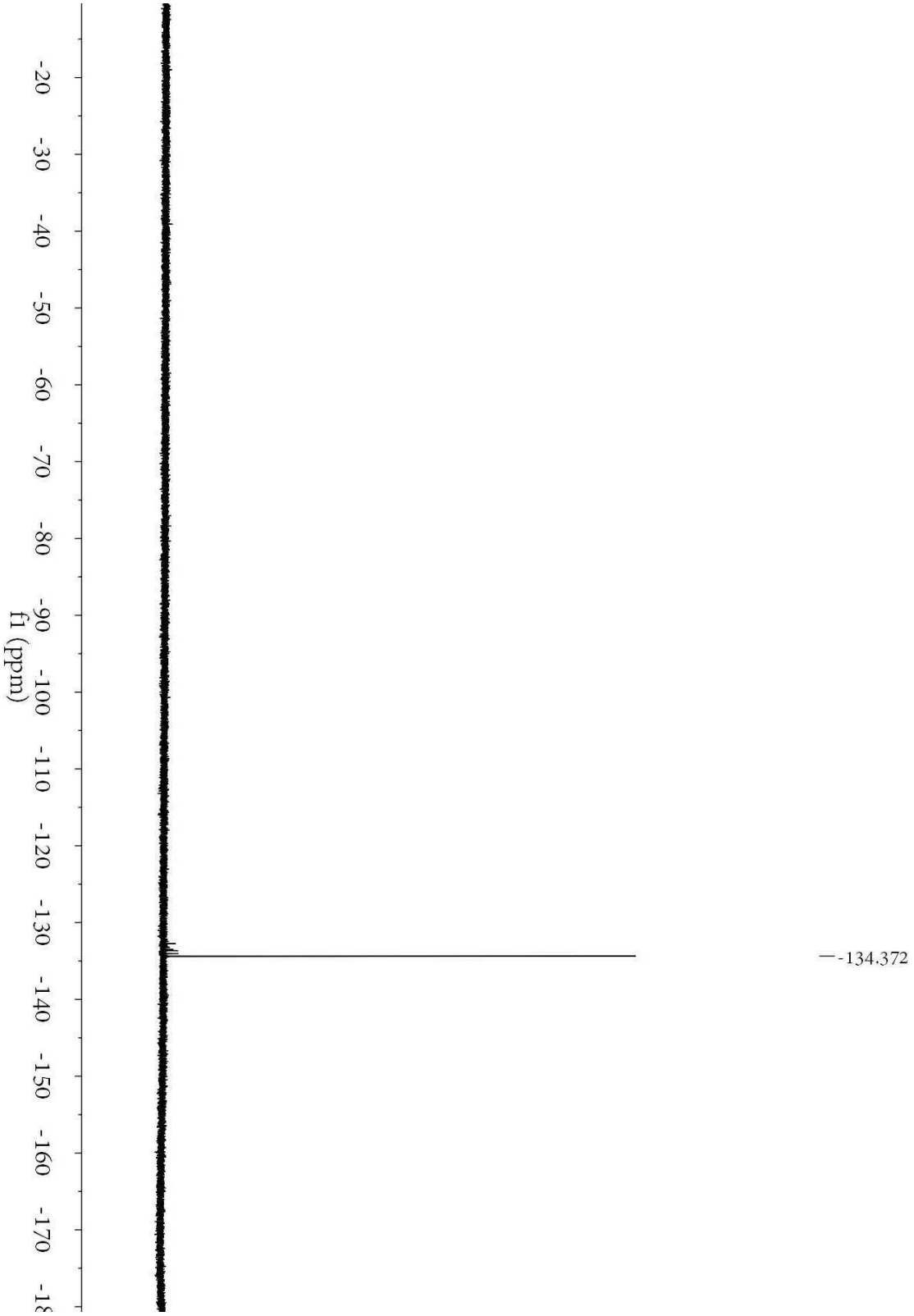


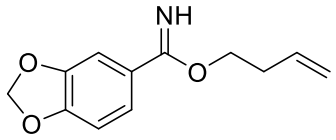
^{13}C NMR of **1o**, 35%
$CDCl_3$, 100 MHz



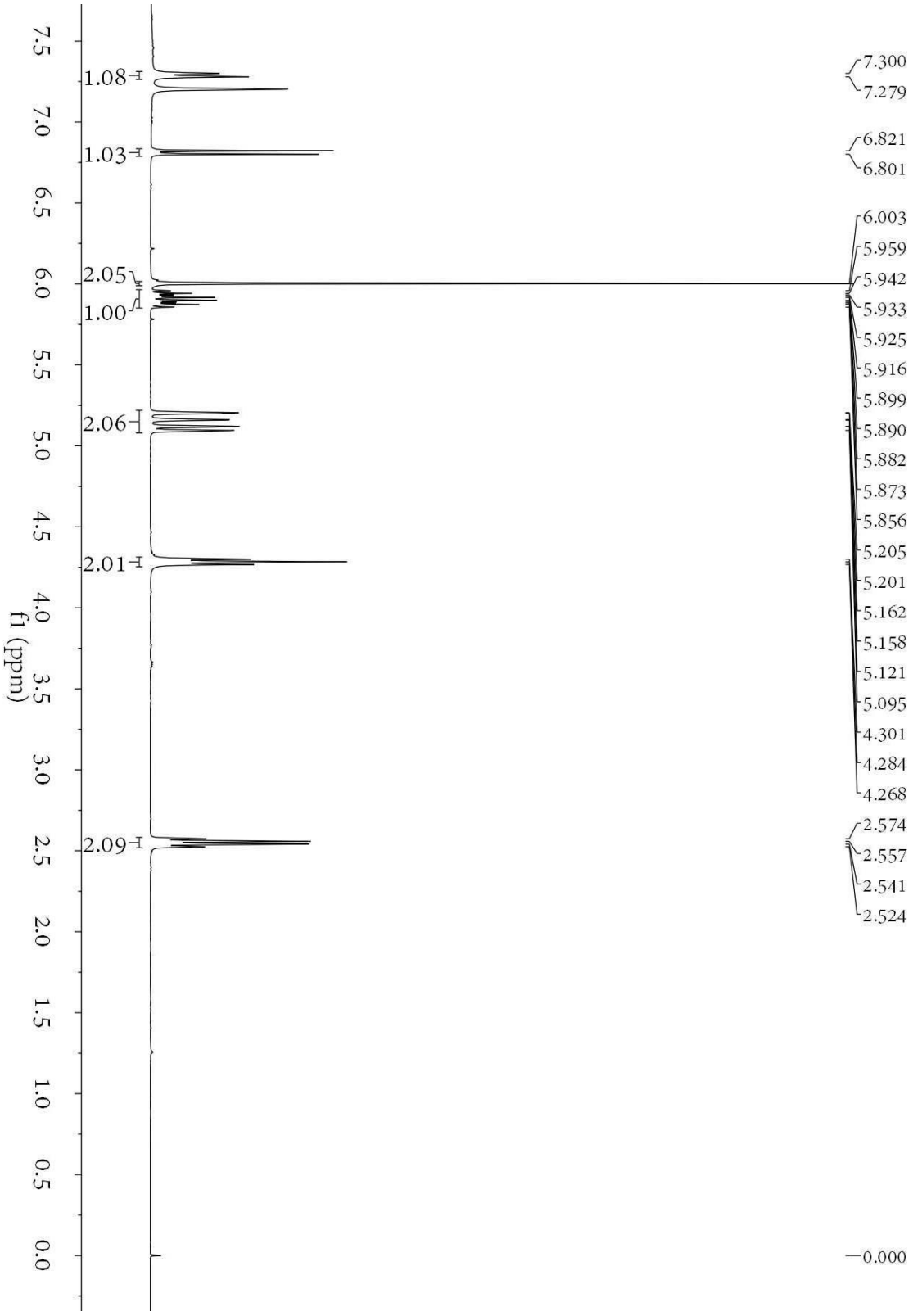


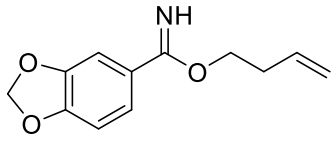
^{19}F NMR of **1o**, 35%
$CDCl_3$, 564 MHz



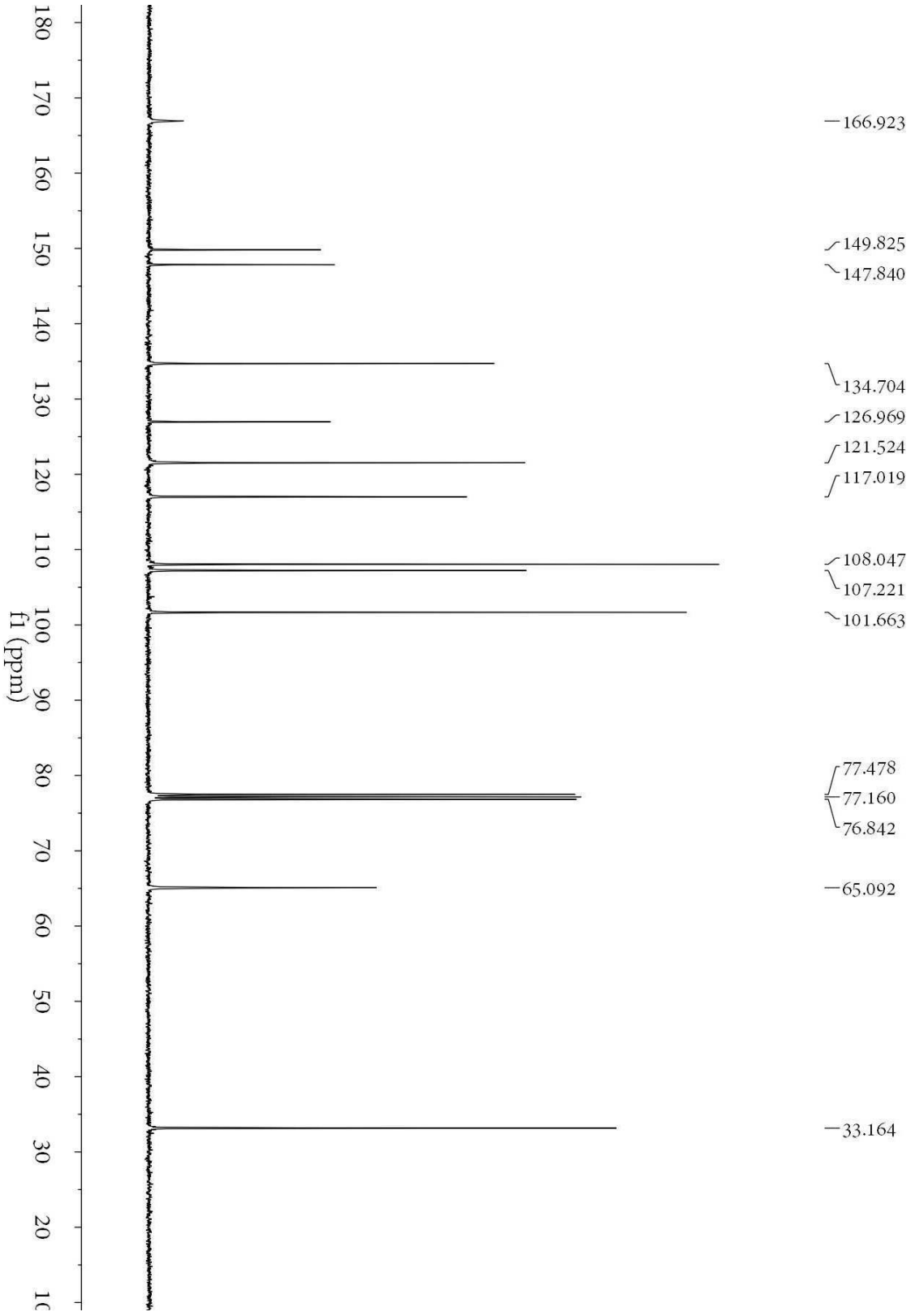


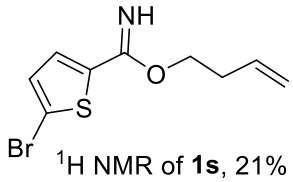
^{1}H NMR of **1p**, 29%
$CDCl_3$, 400 MHz



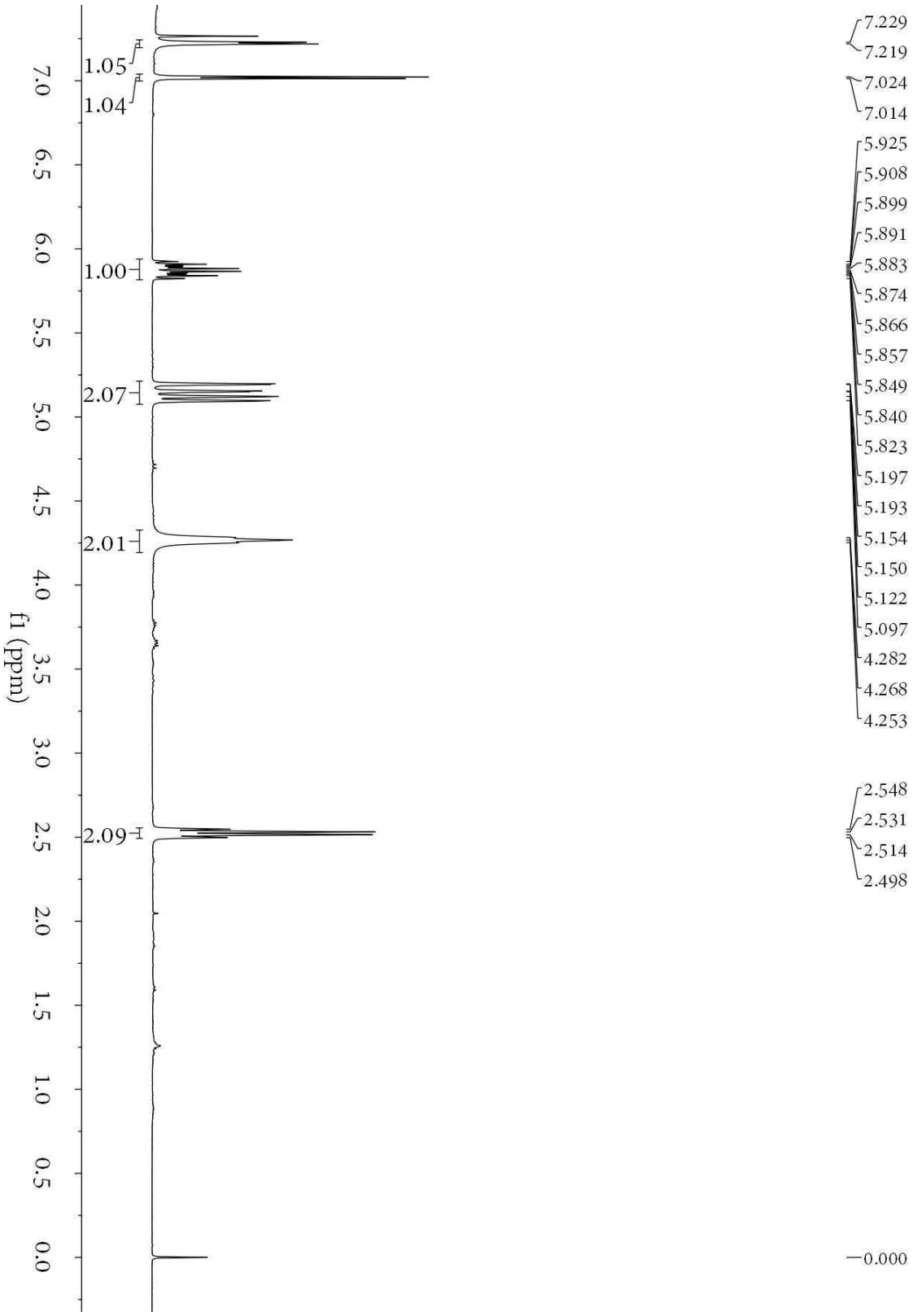


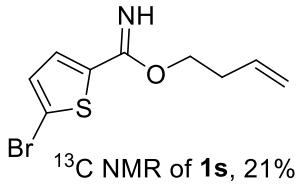
^{13}C NMR of **1p**, 29%
$CDCl_3$, 100 MHz



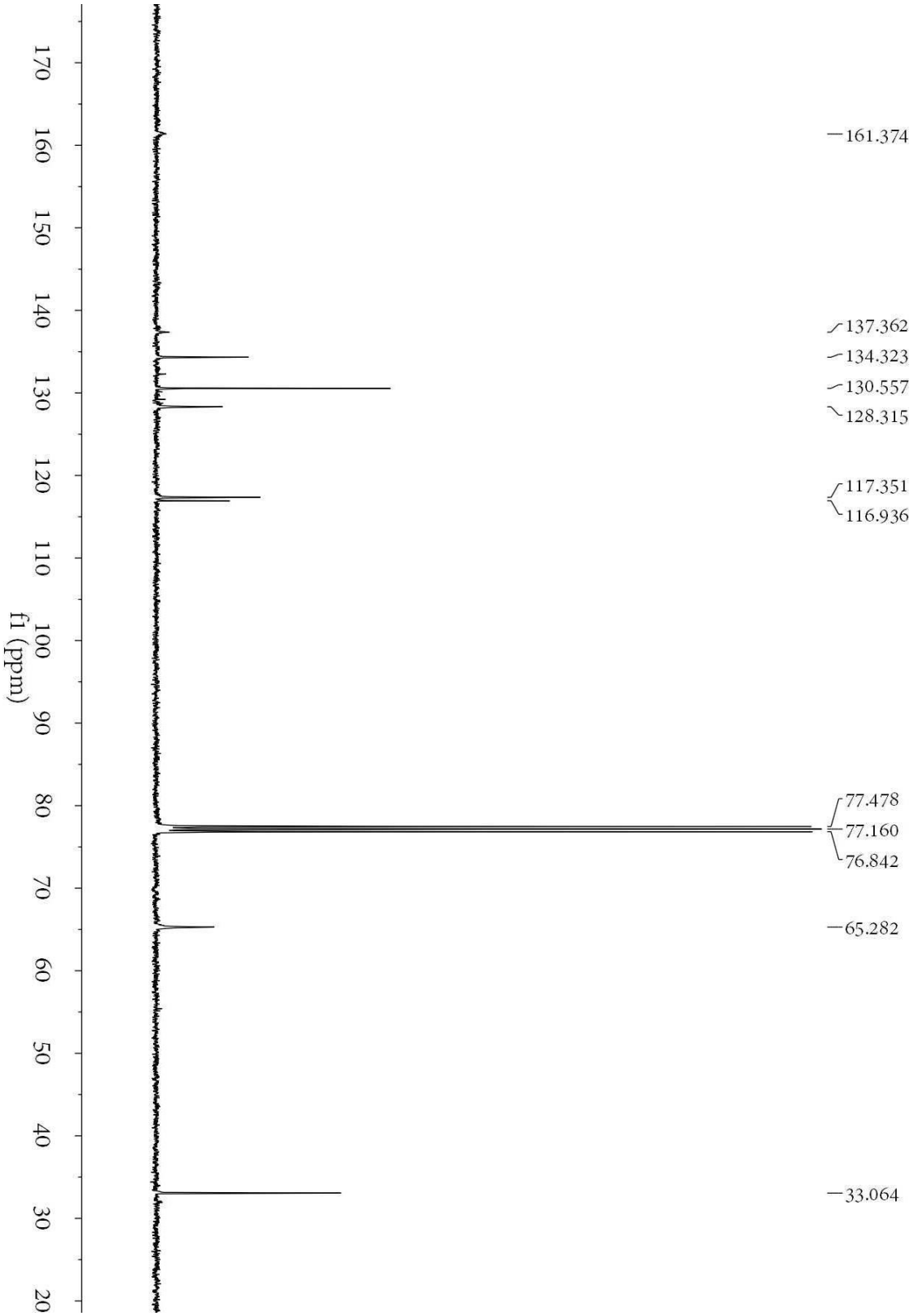


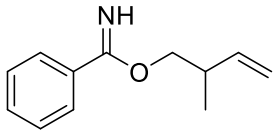
^{1}H NMR of **1s**, 21%
$CDCl_3$, 400 MHz



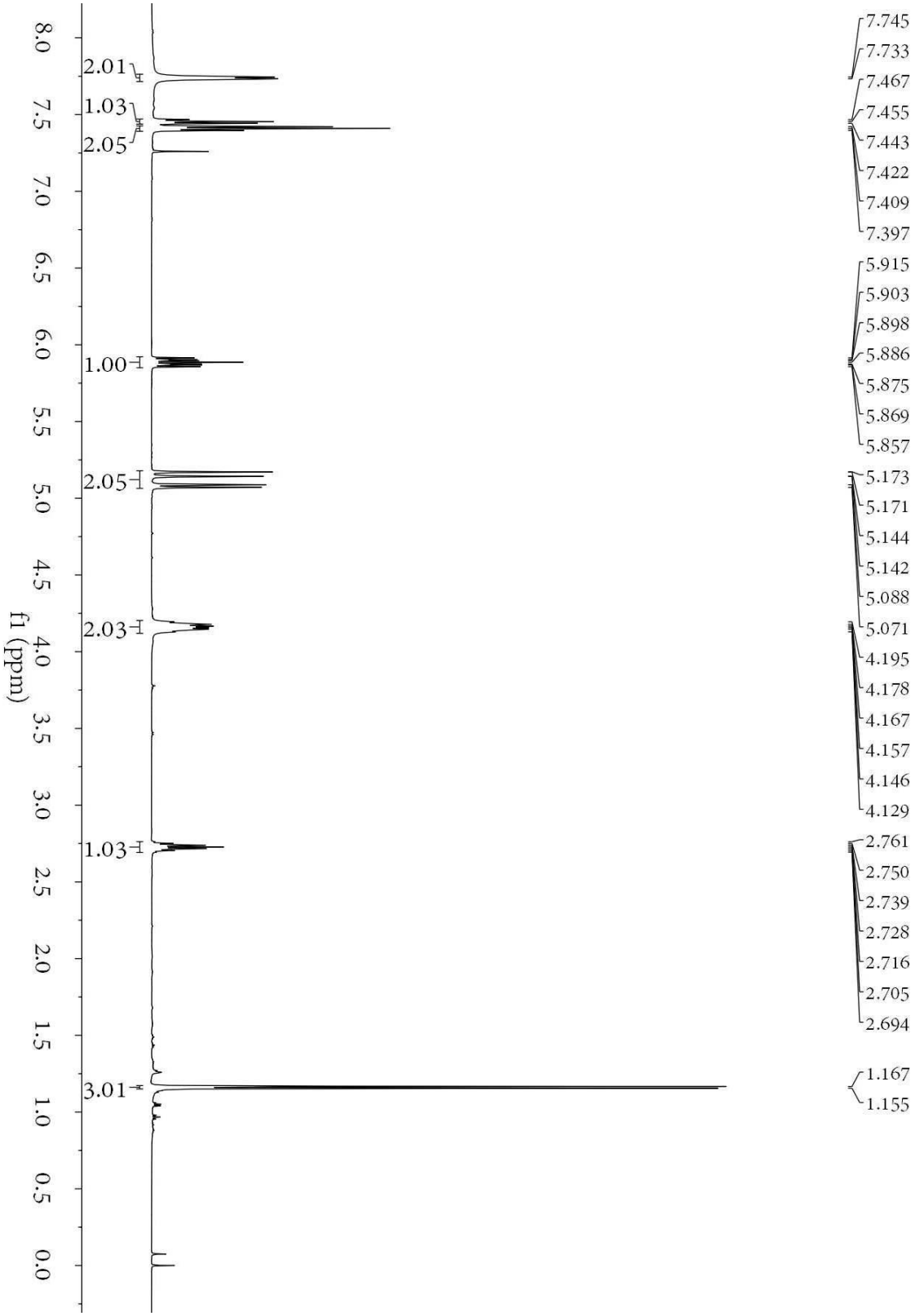


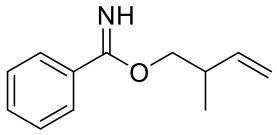
^{13}C NMR of **1s**, 21%
$CDCl_3$, 100 MHz



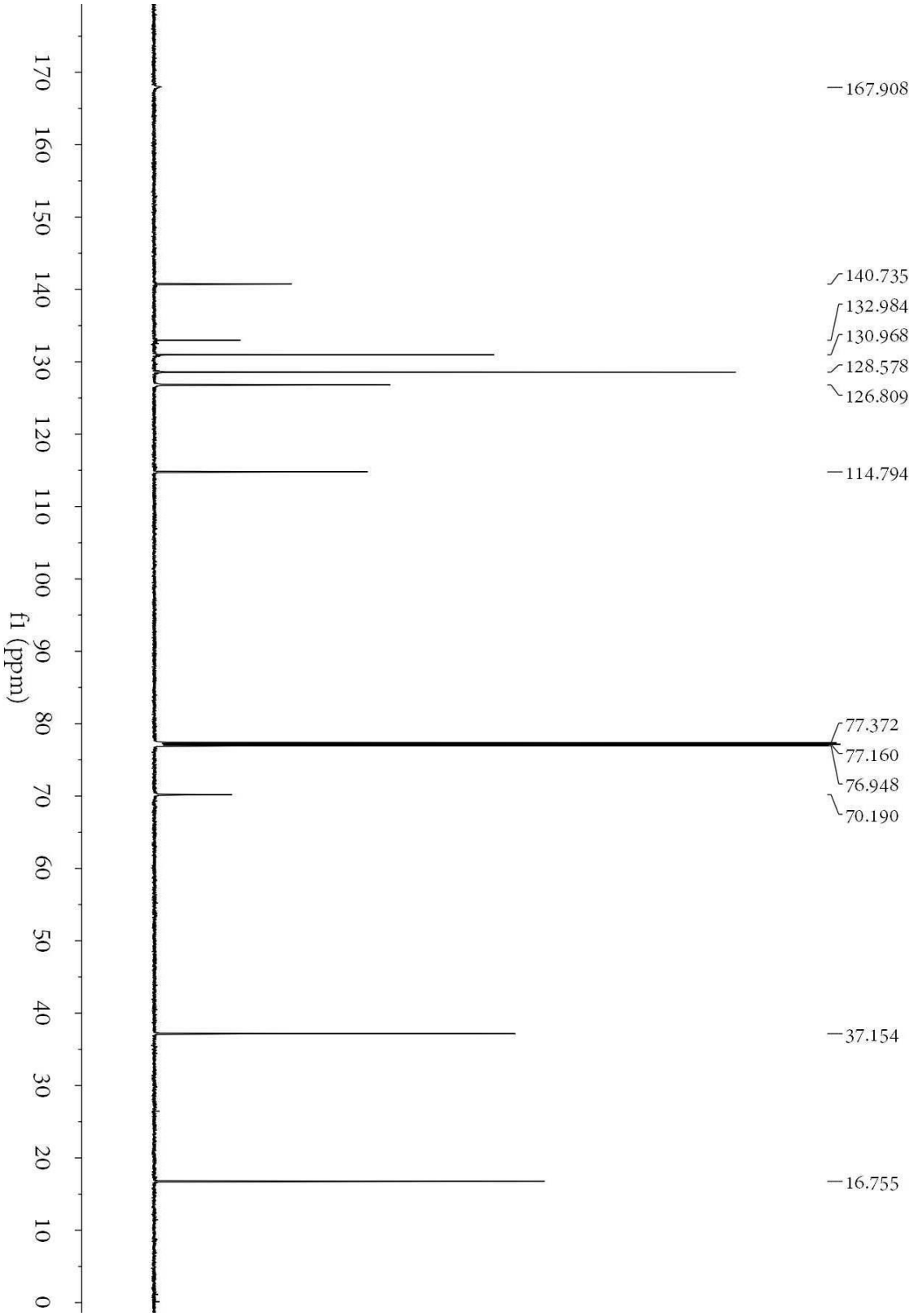


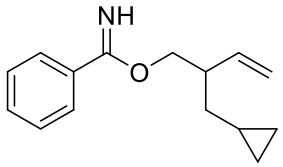
^{1}H NMR of **1u**, 21%
$CDCl_3$, 600 MHz



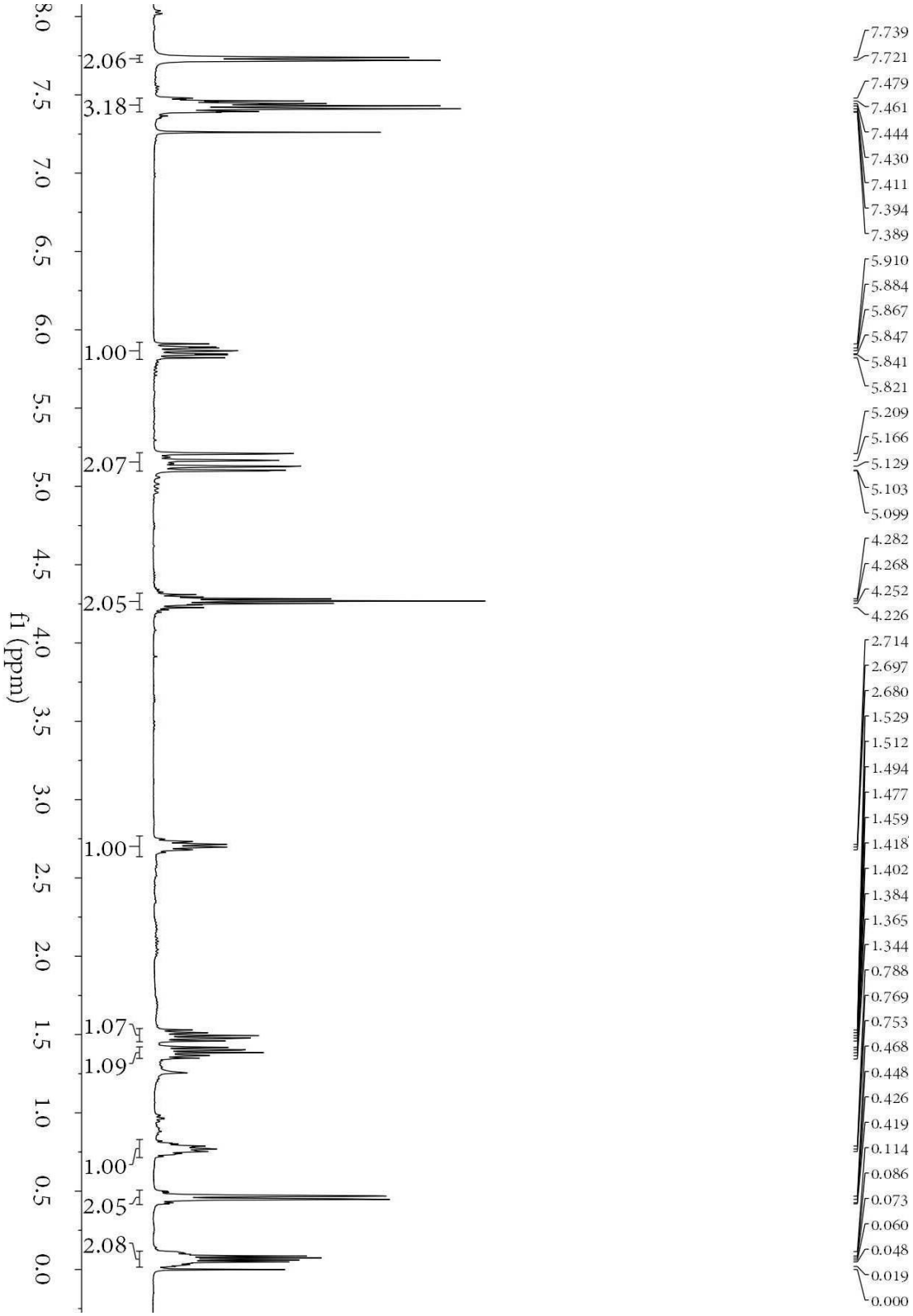


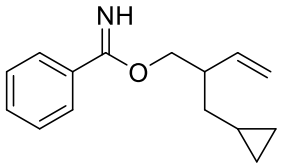
^{13}C NMR of **1u**, 21%
$CDCl_3$, 150 MHz



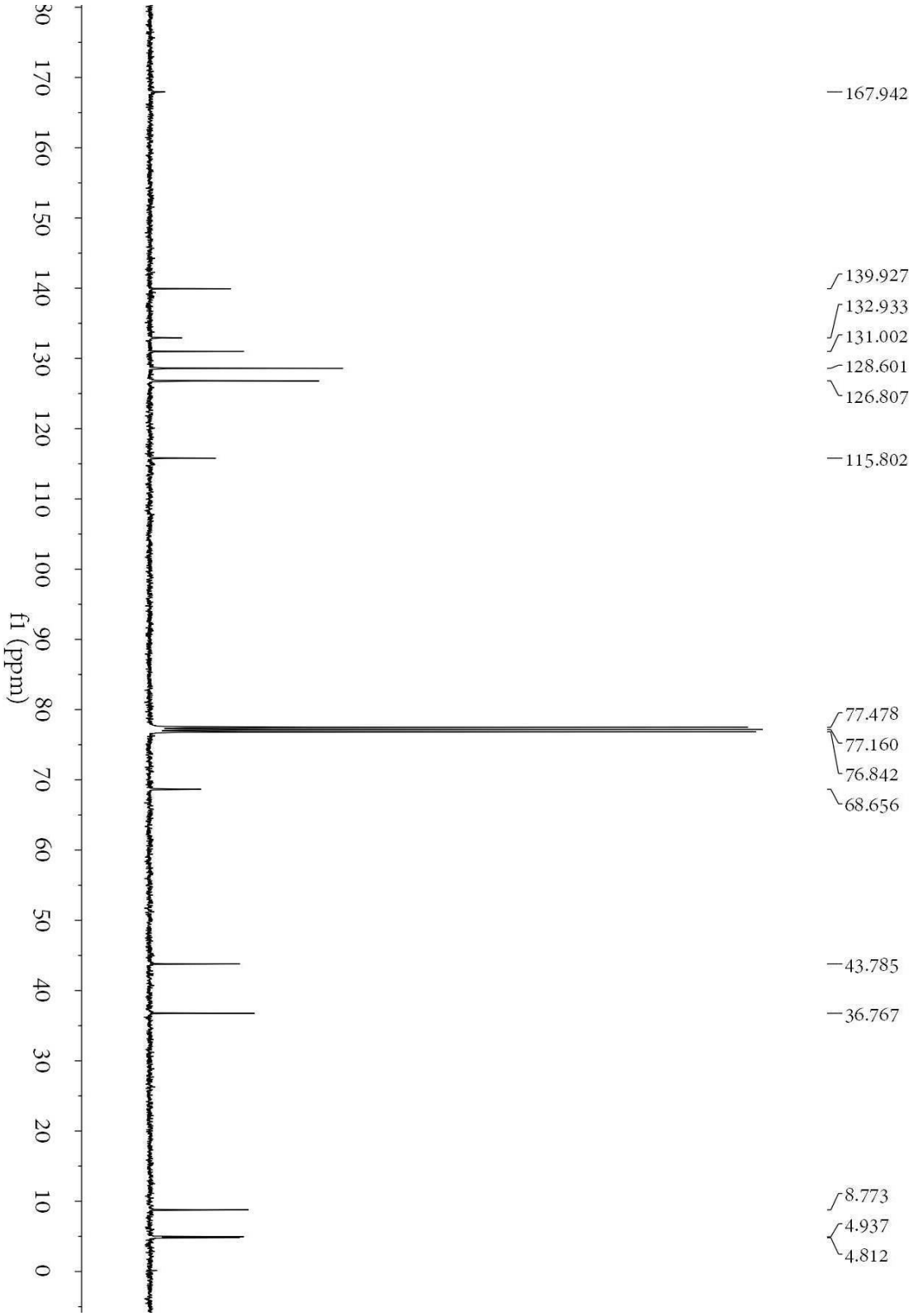


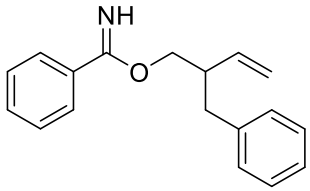
^{1}H NMR of **1v**, 37%
$CDCl_3$, 400 MHz



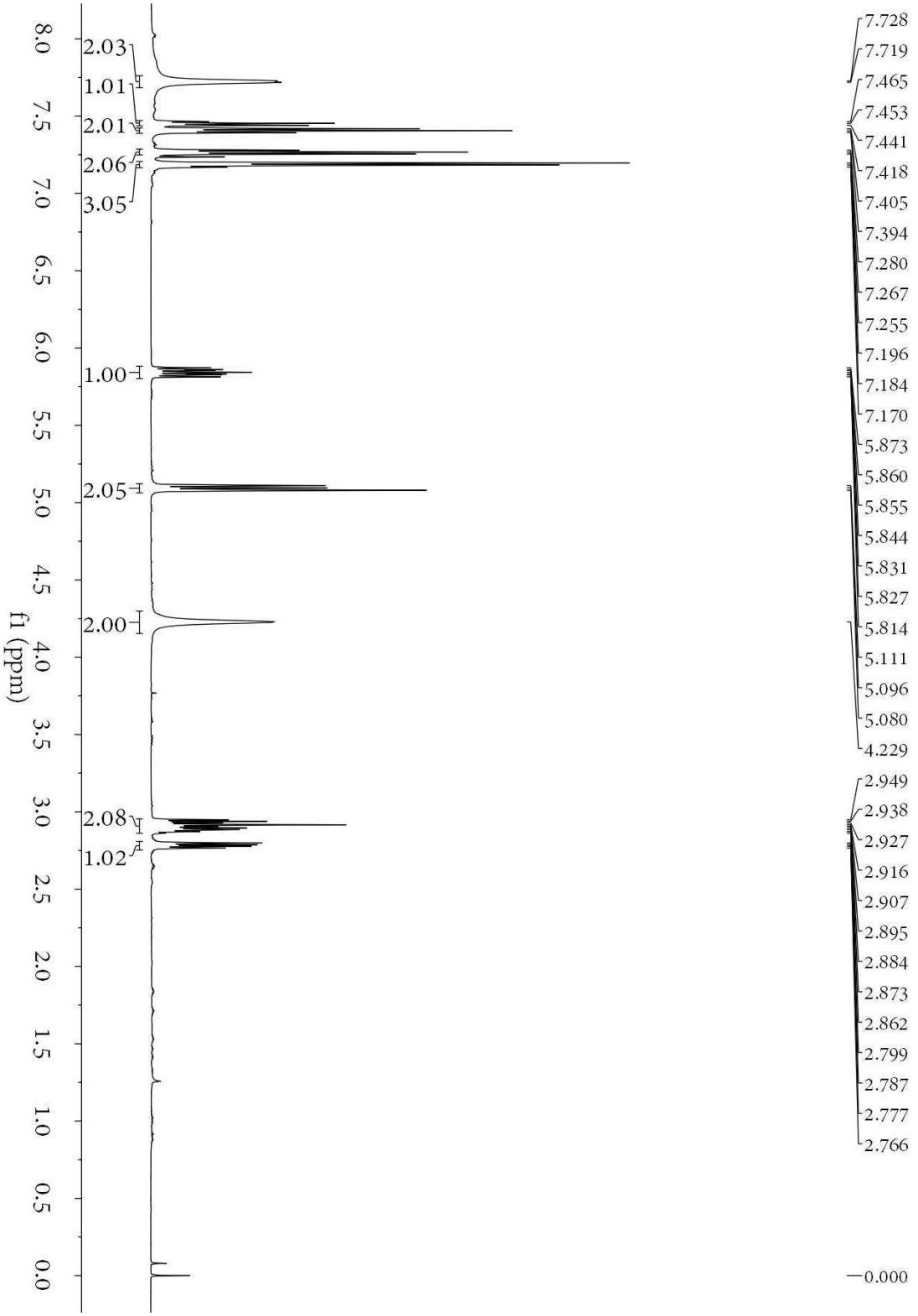


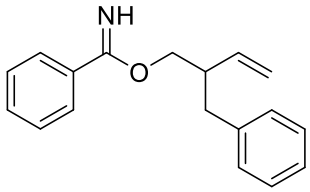
^{13}C NMR of **1v**, 37%
$CDCl_3$, 100 MHz



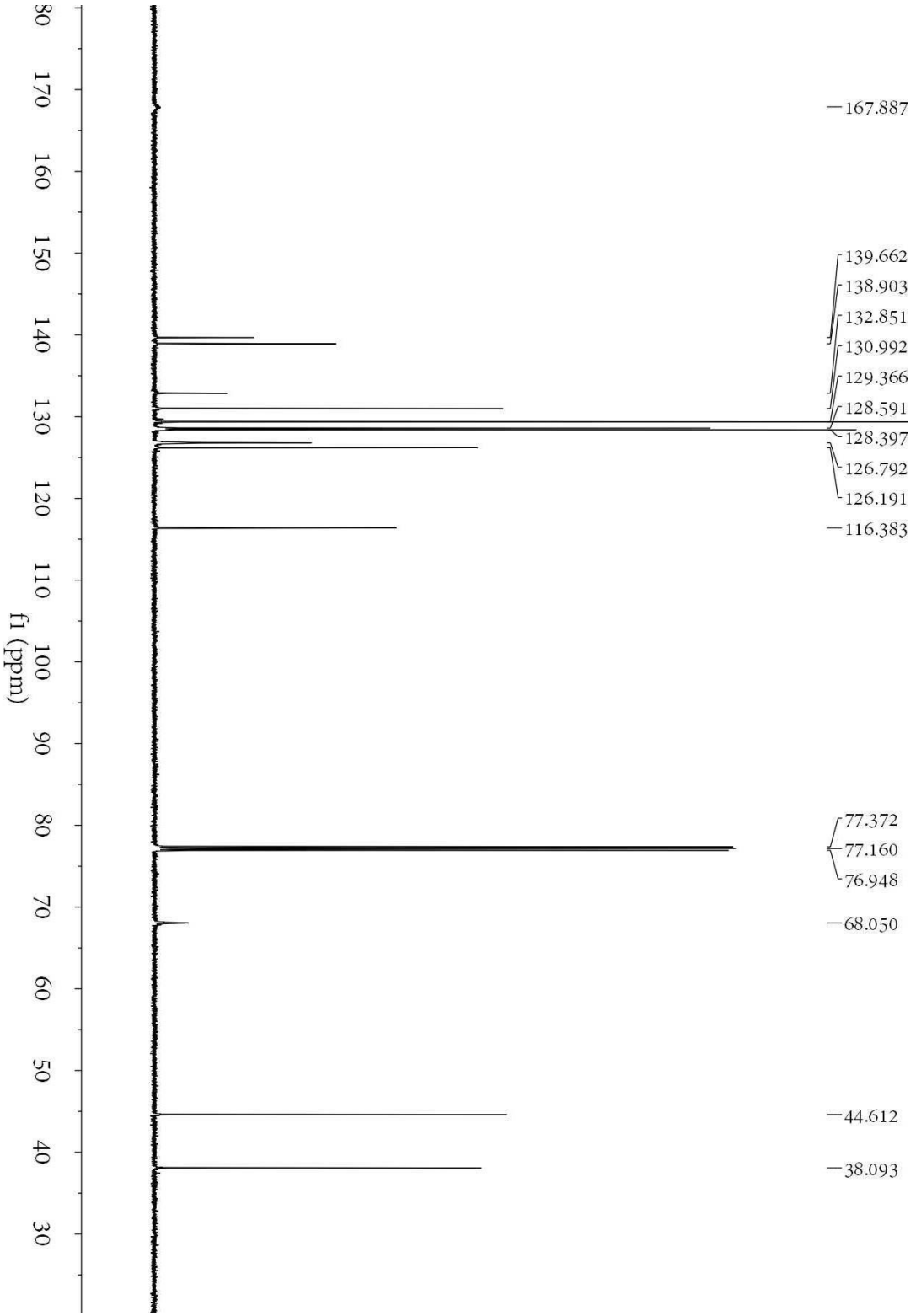


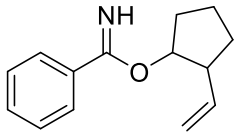
^{1}H NMR of **1w**, 48%
$CDCl_3$, 600 MHz



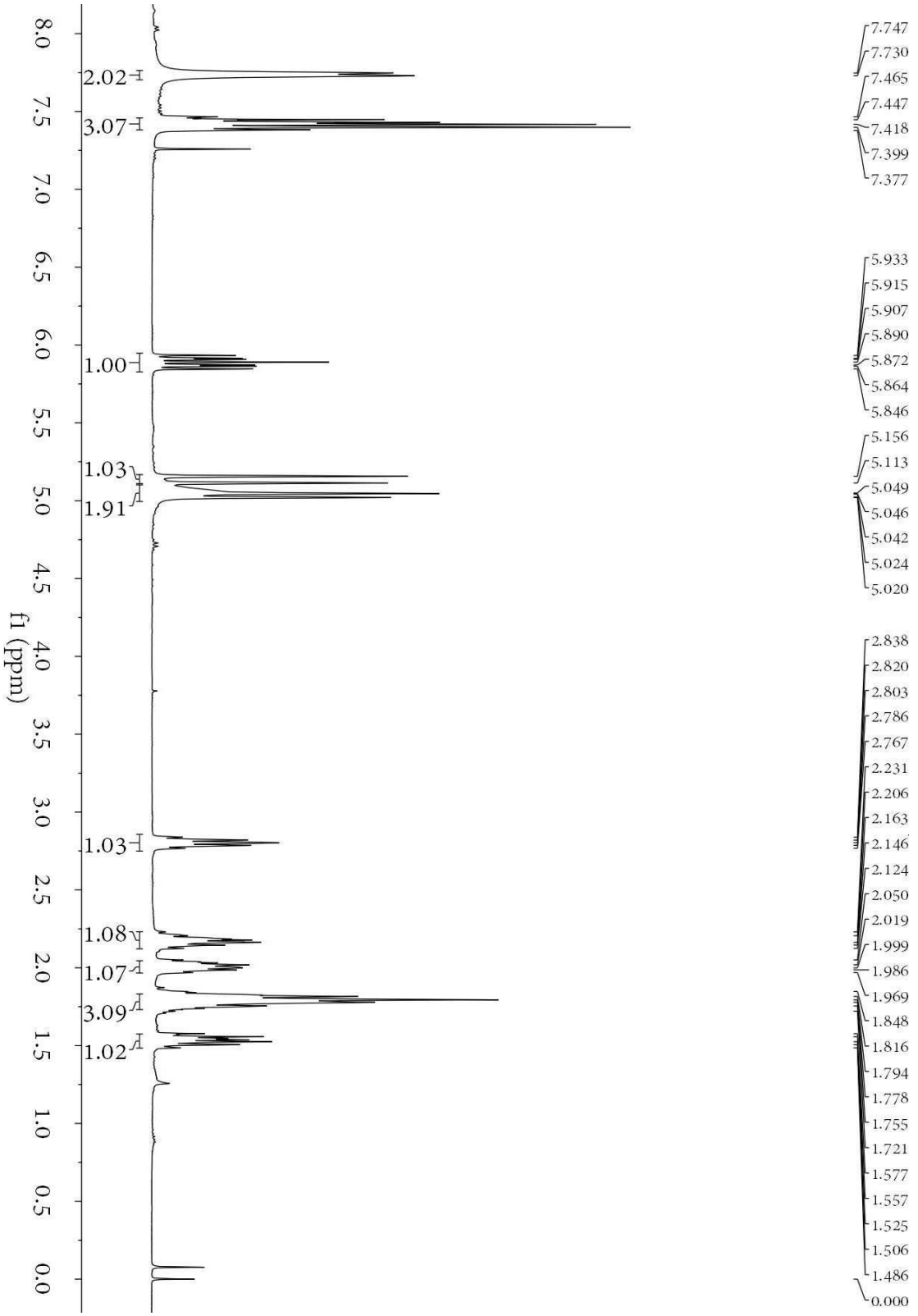


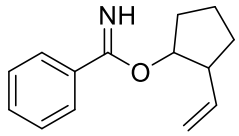
^{13}C NMR of **1w**, 48%
$CDCl_3$, 150 MHz



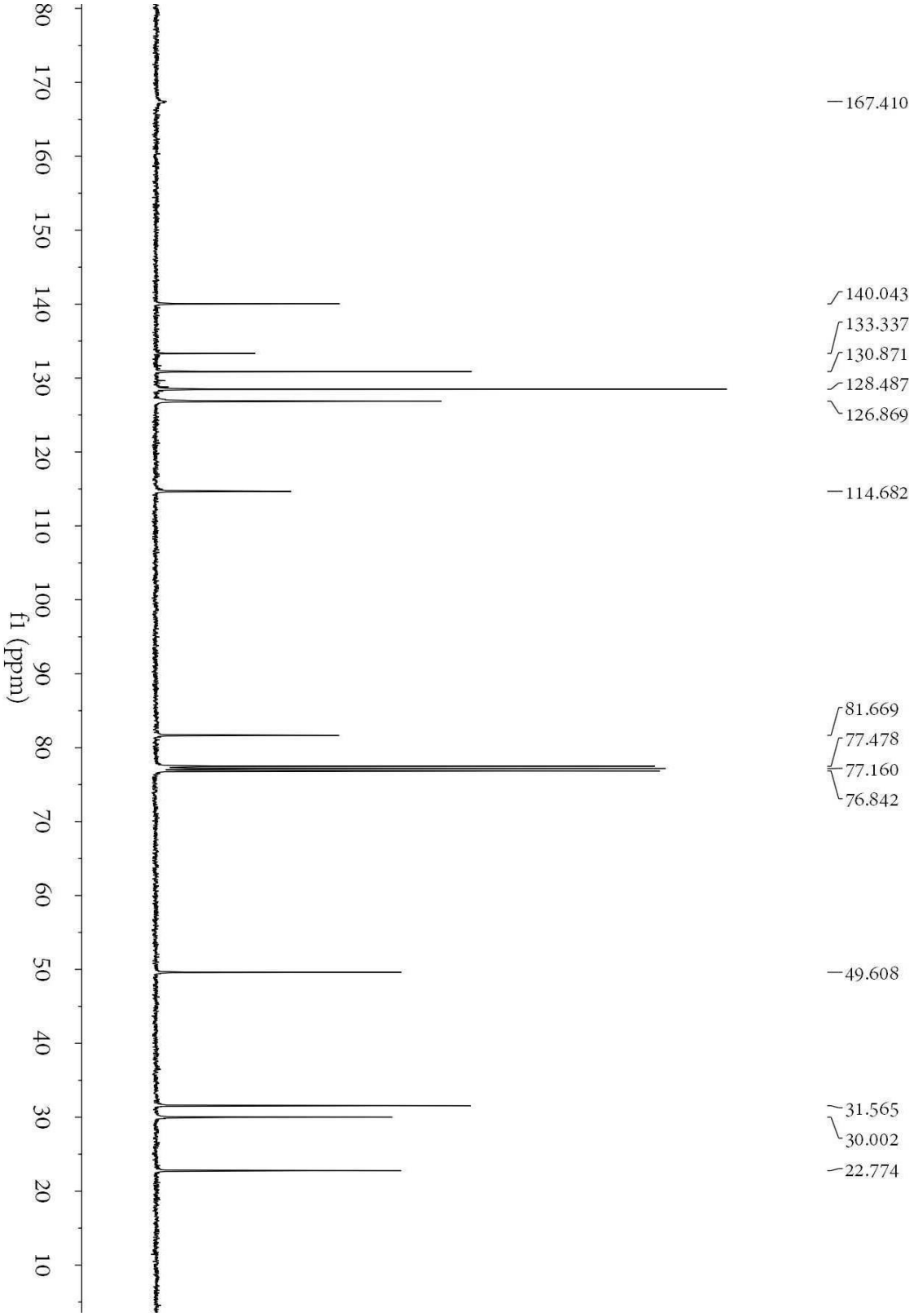


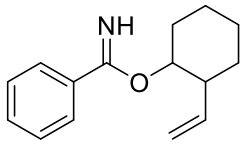
^{1}H NMR of **1x**, 27%
$CDCl_3$, 400 MHz





^{13}C NMR of **1x**, 27%
$CDCl_3$, 100 MHz





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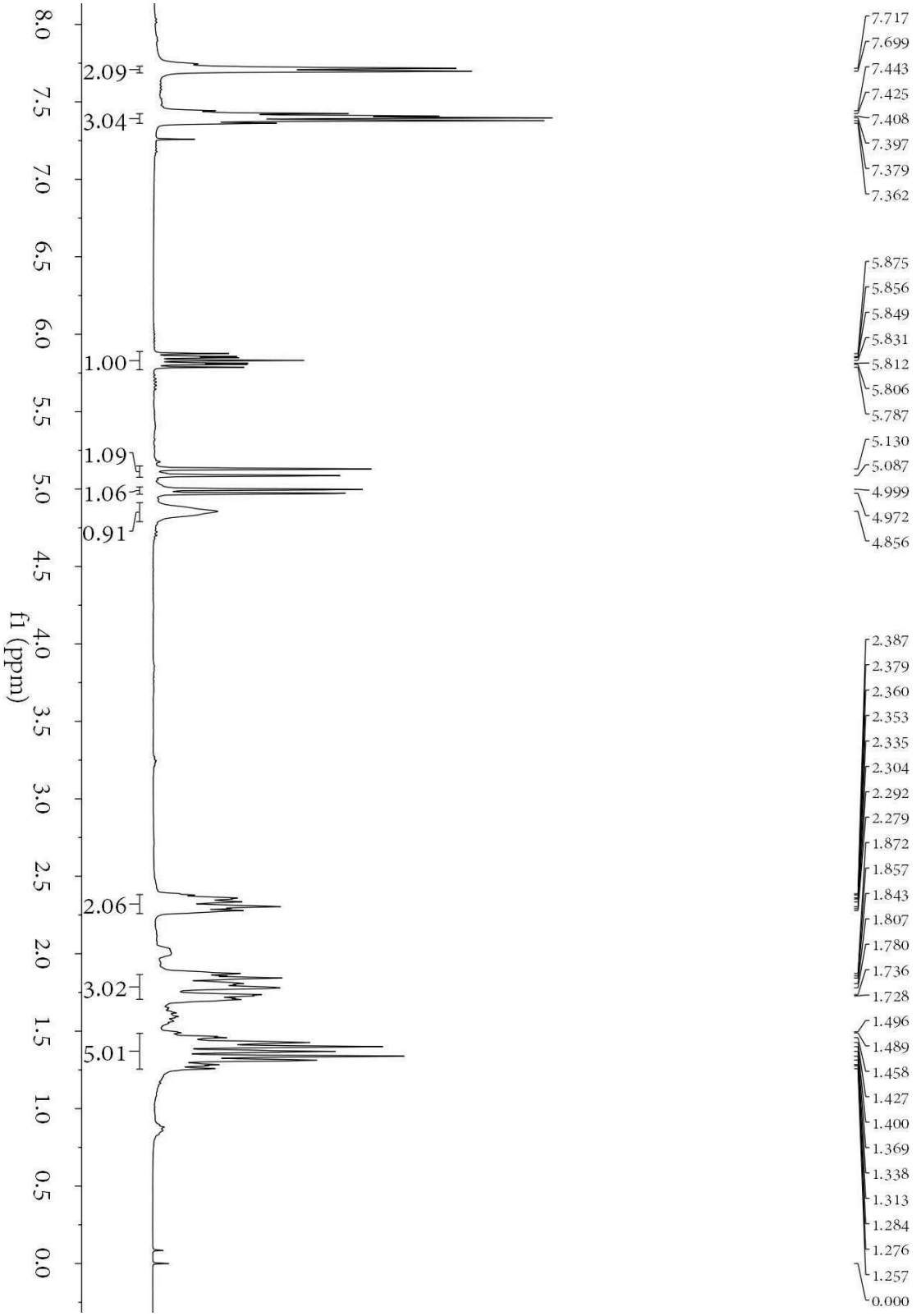
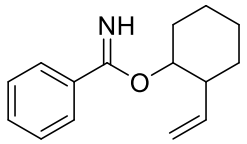
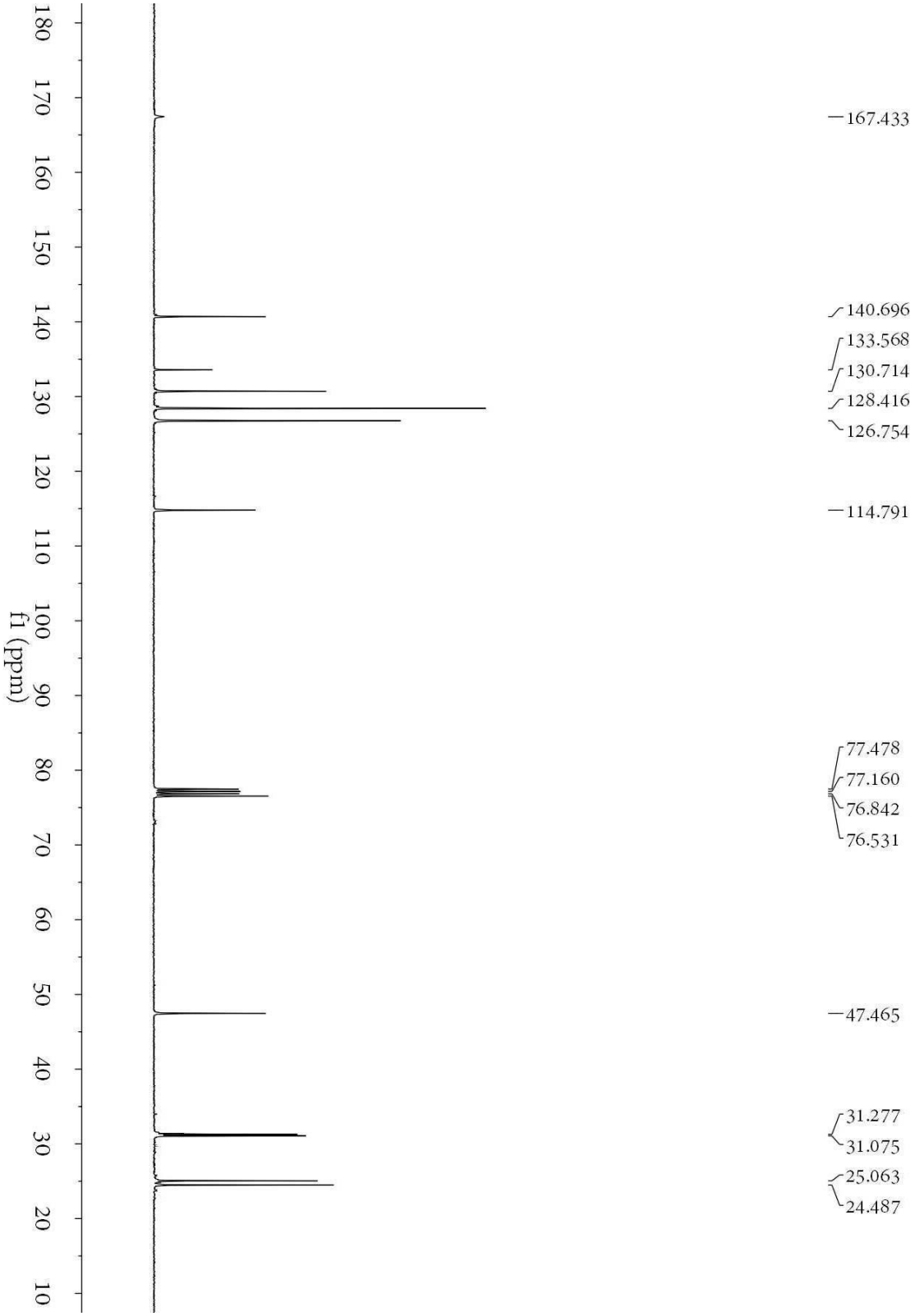
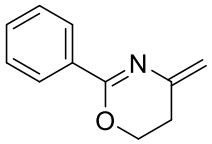




^{13}C NMR of **1y**, 43%
$CDCl_3$, 100 MHz





^{1}H NMR of **2a,** 86%
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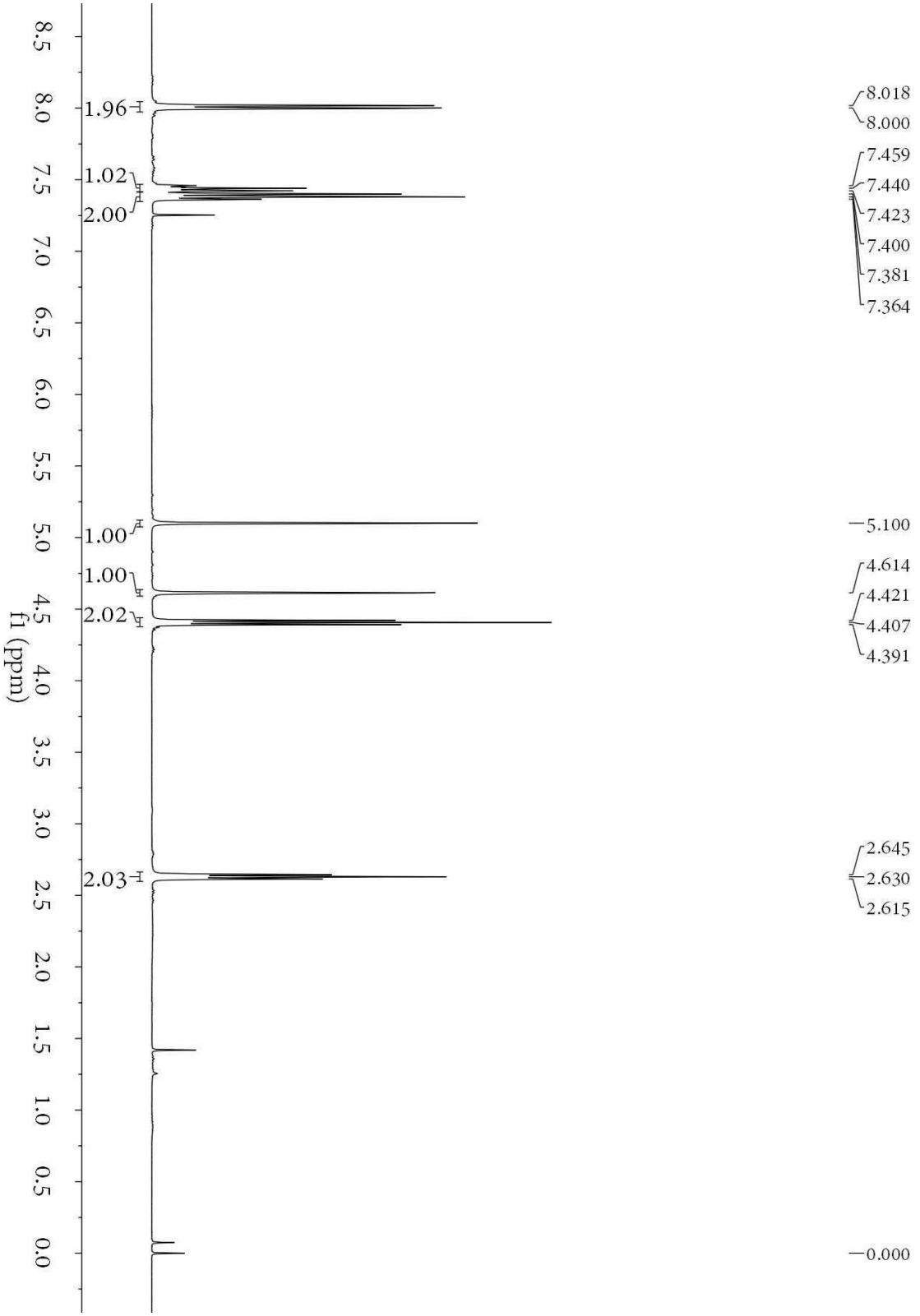
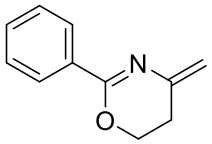
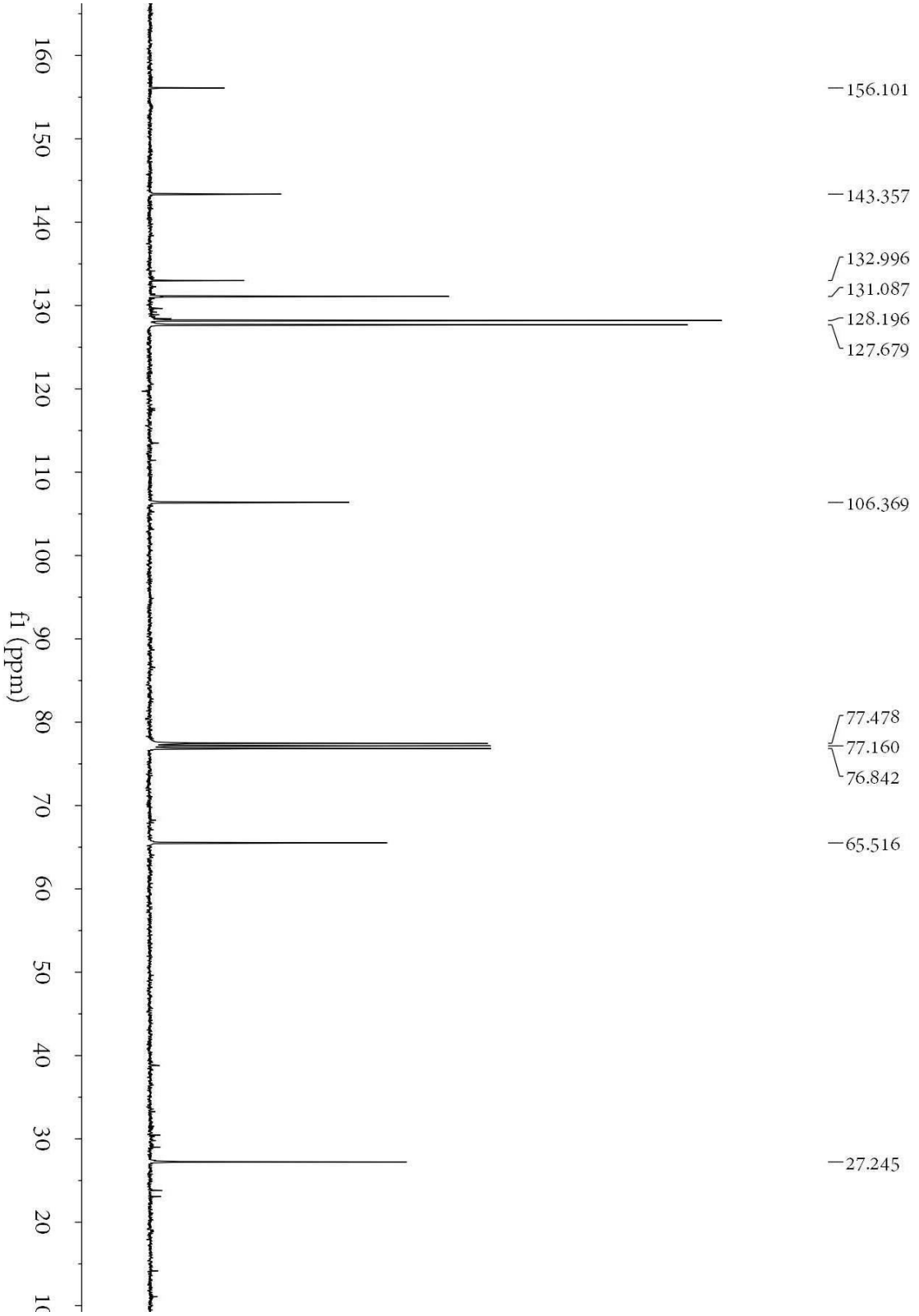
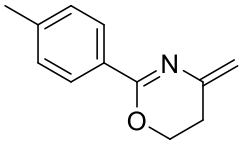


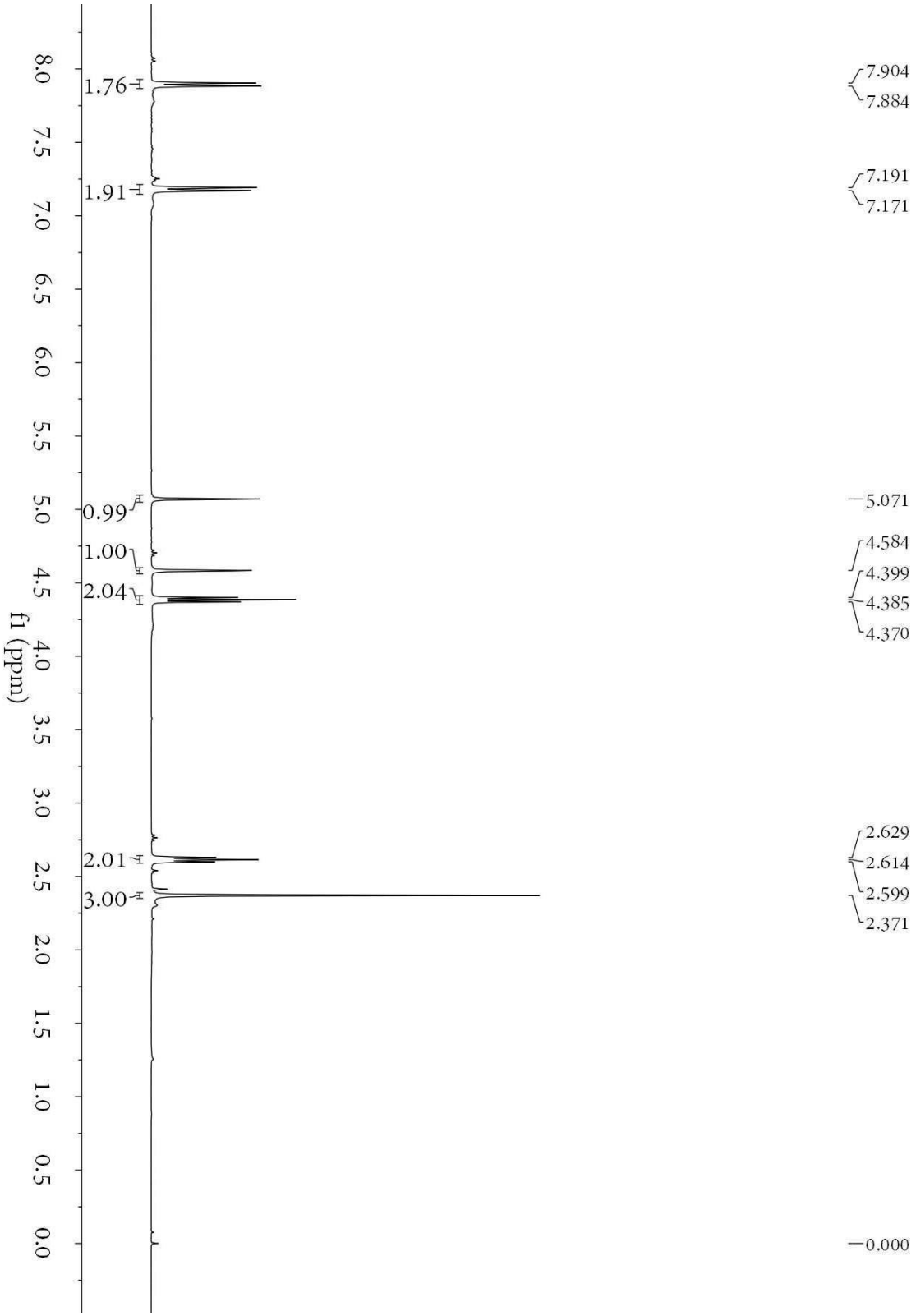


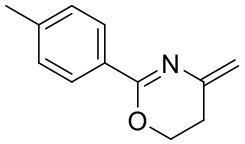
^{13}C NMR of **2a,** 86%
$CDCl_3$, 100 MHz



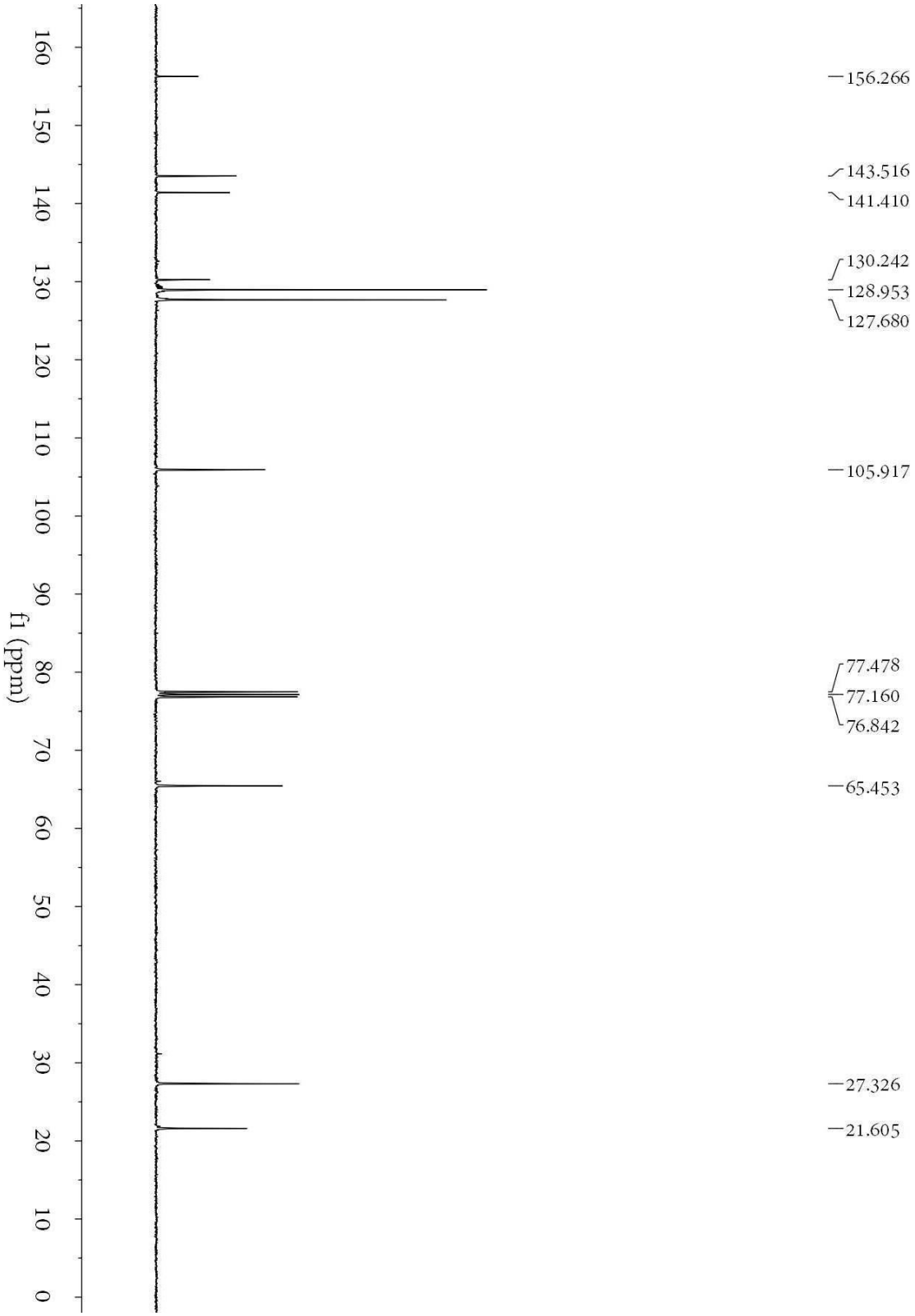


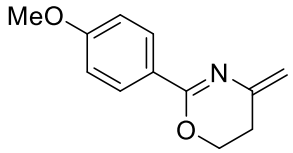
^{1}H NMR of **2b,** 82%
$CDCl_3$, 400 MHz



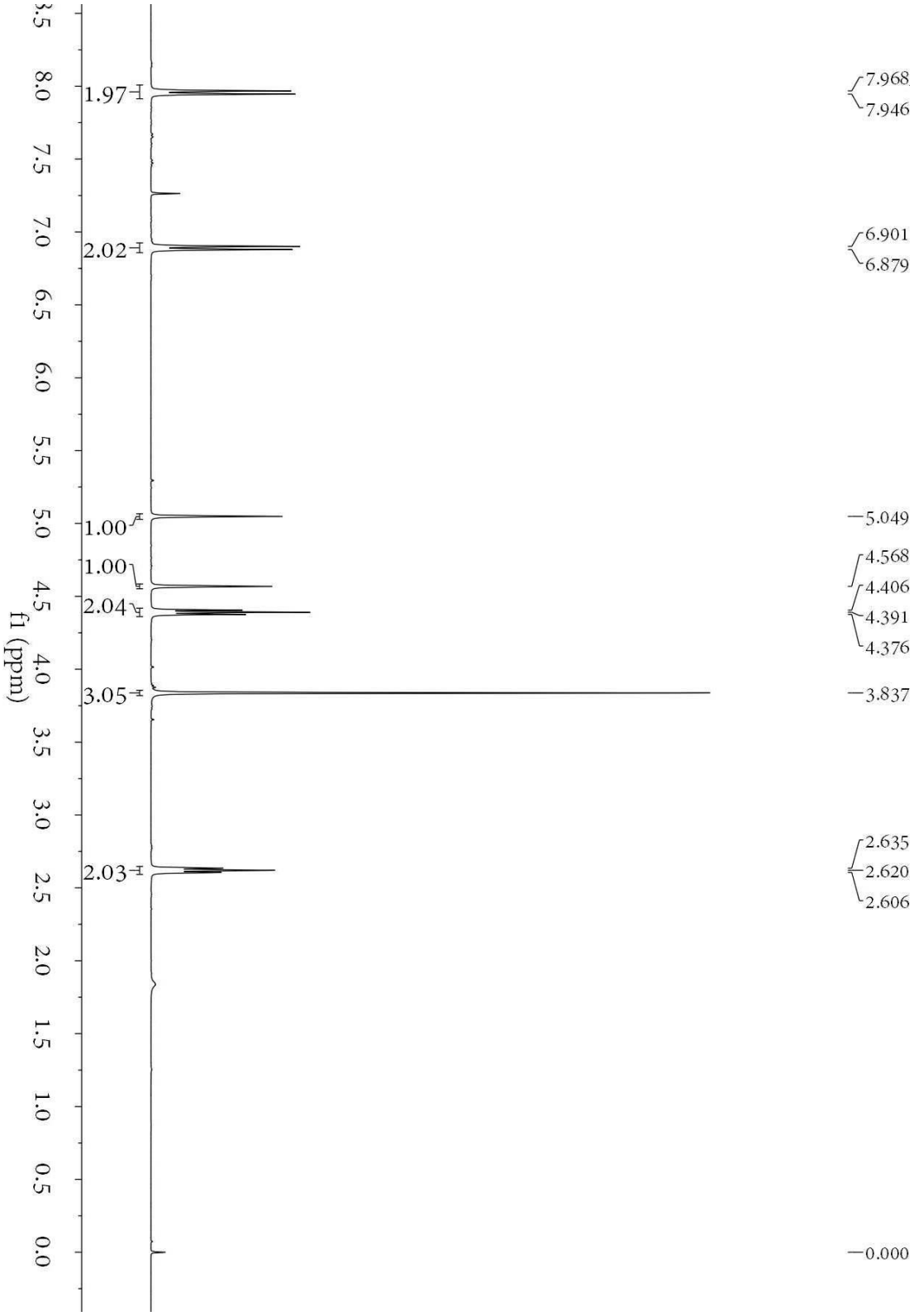


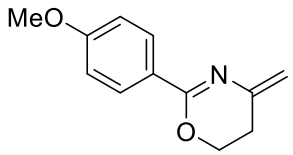
^{13}C NMR of **2b,** 82%
$CDCl_3$, 100 MHz



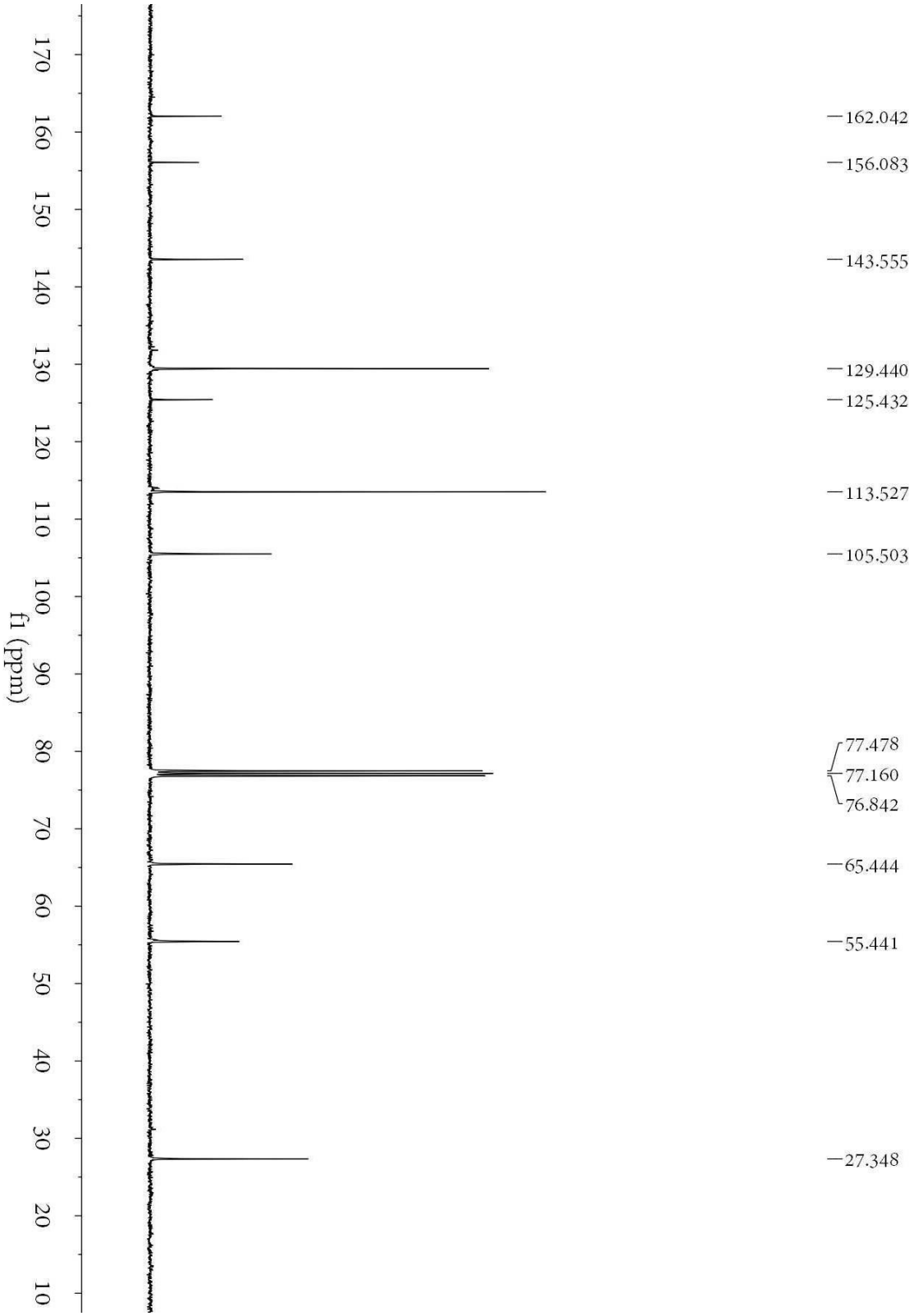


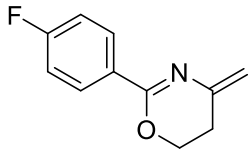
^{1}H NMR of **2c**, 81%
$CDCl_3$, 400 MHz



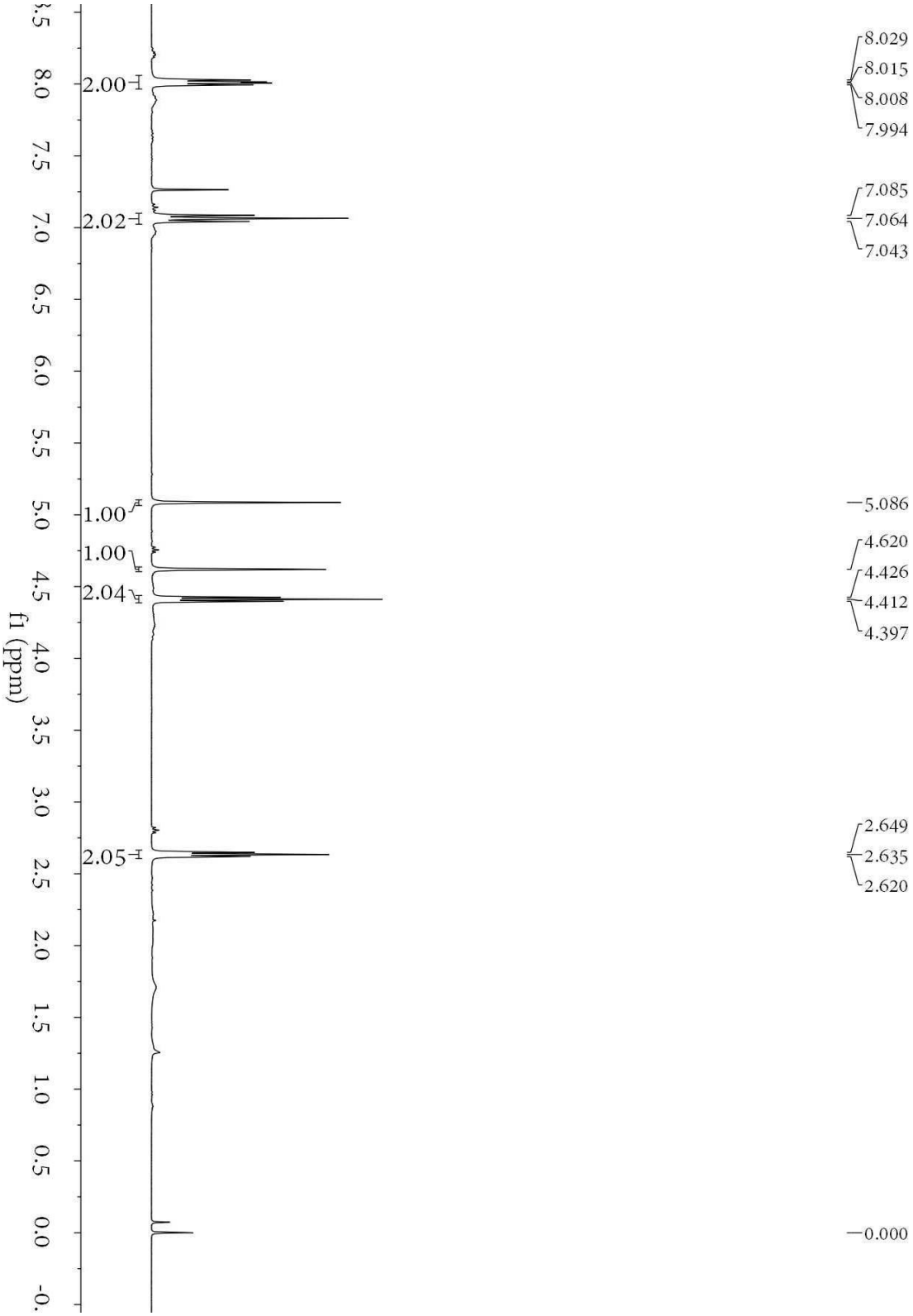


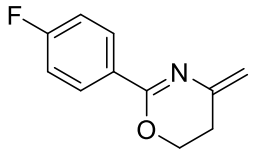
^{13}C NMR of **2c,** 81%
$CDCl_3$, 100 MHz



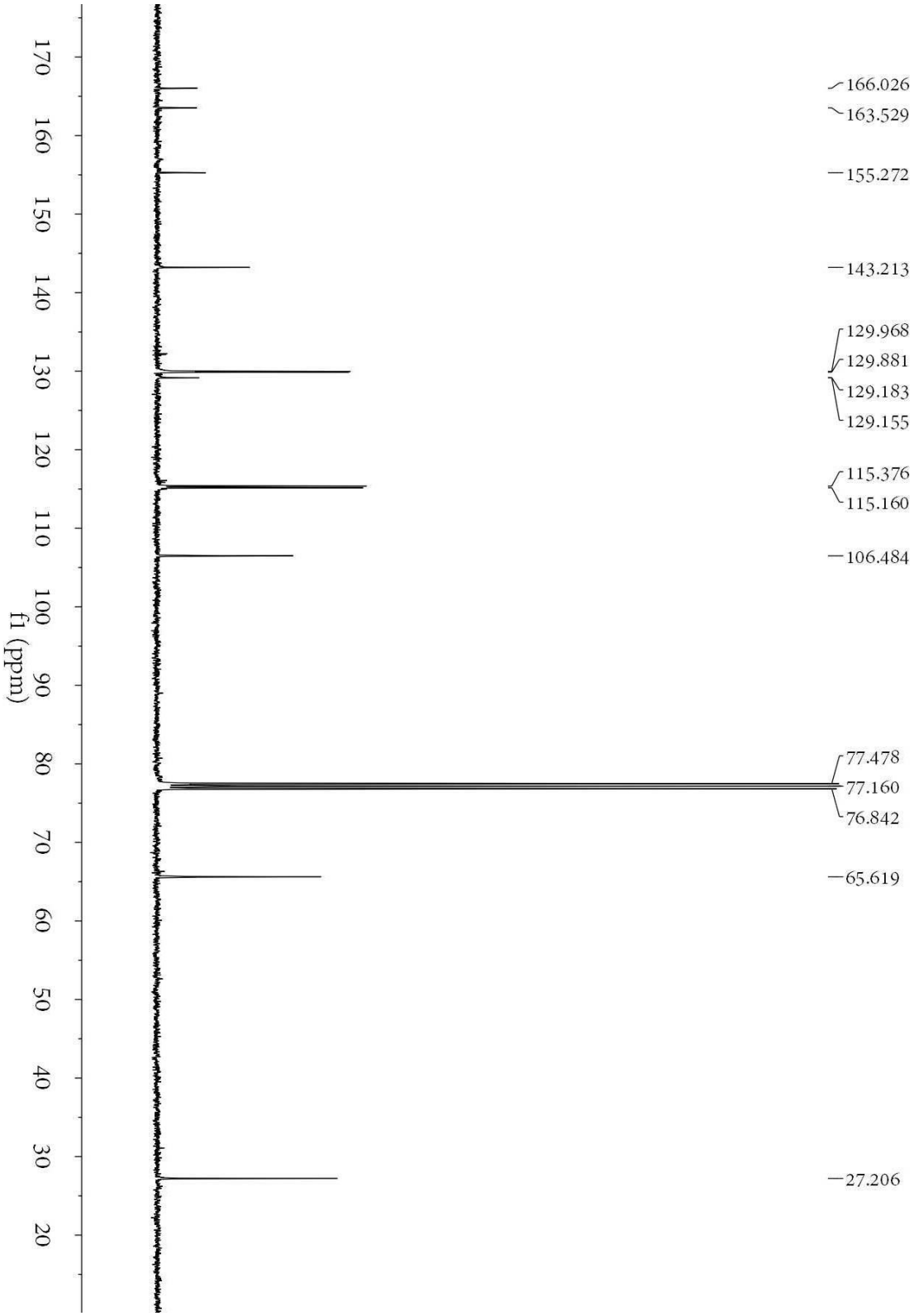


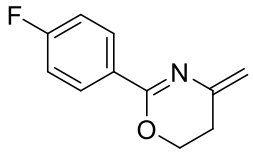
^{1}H NMR of **2d,** 59%
$CDCl_3$, 400 MHz



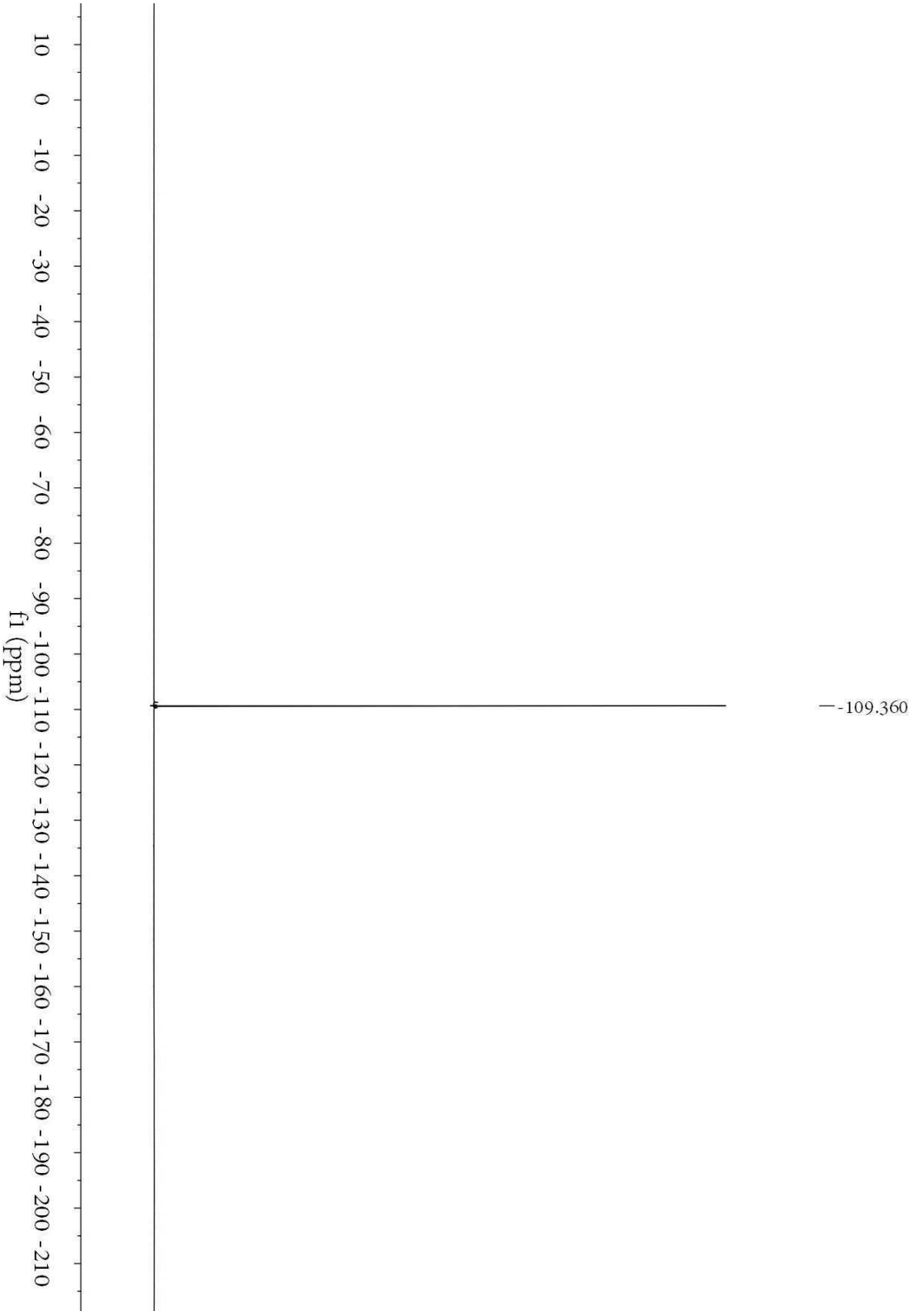


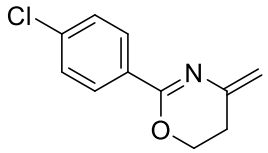
^{13}C NMR of **2d**, 59%
$CDCl_3$, 100 MHz



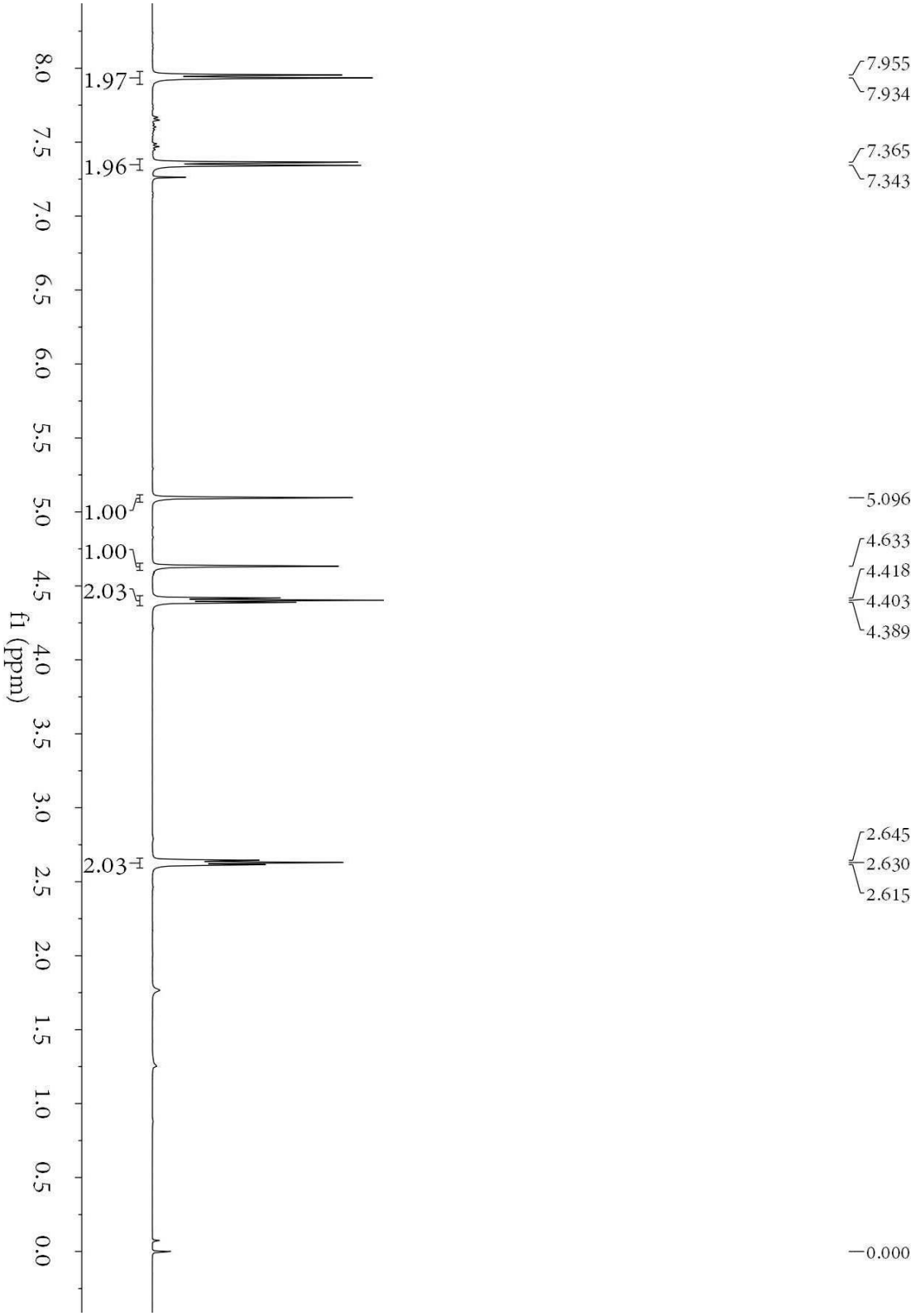


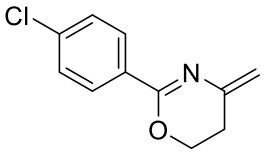
^{19}F NMR of **2d,** 59%
$CDCl_3$, 564 MHz



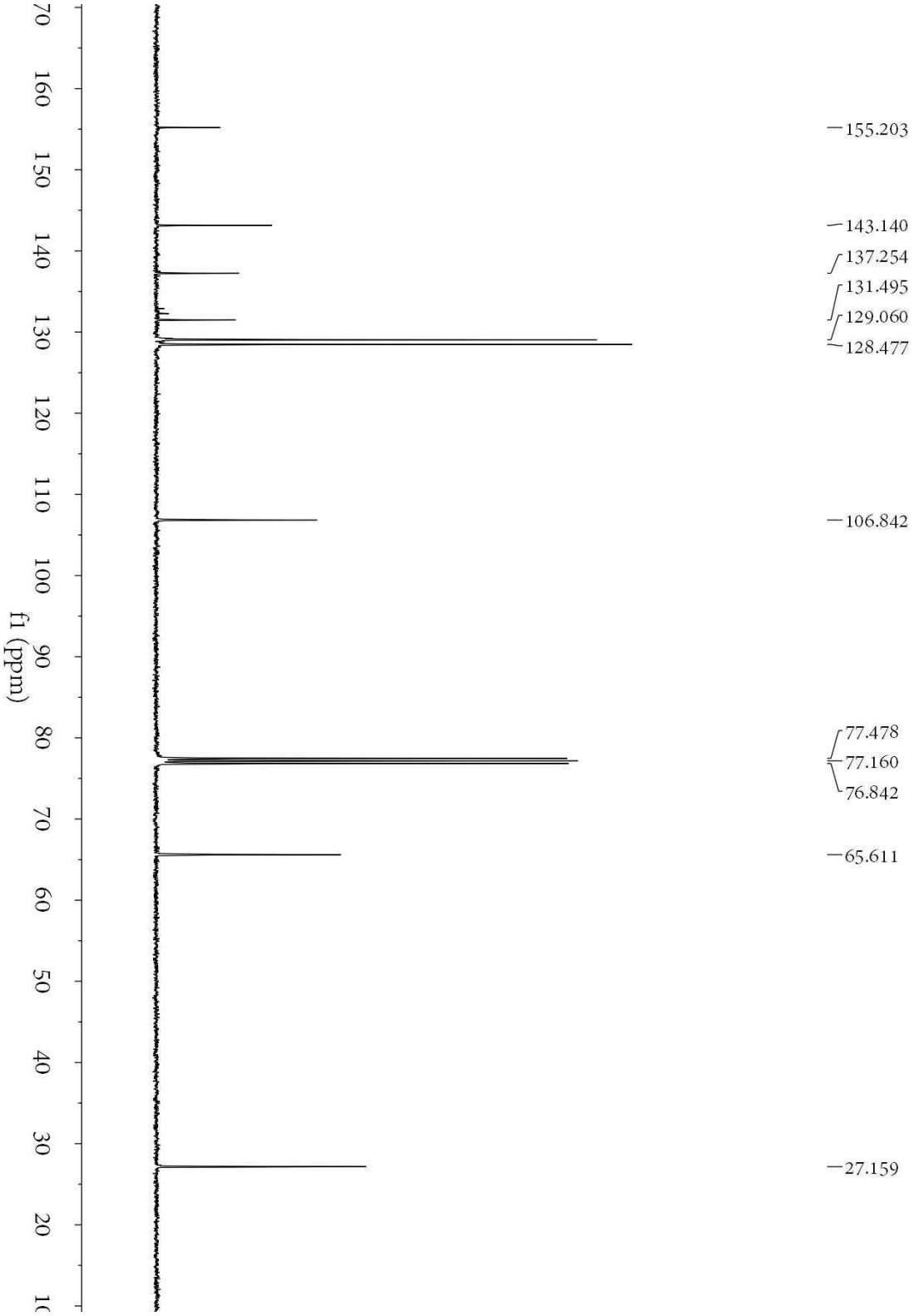


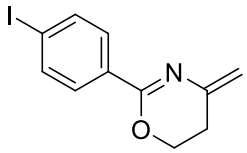
^{1}H NMR of **2e**, 75%
$CDCl_3$, 400 MHz



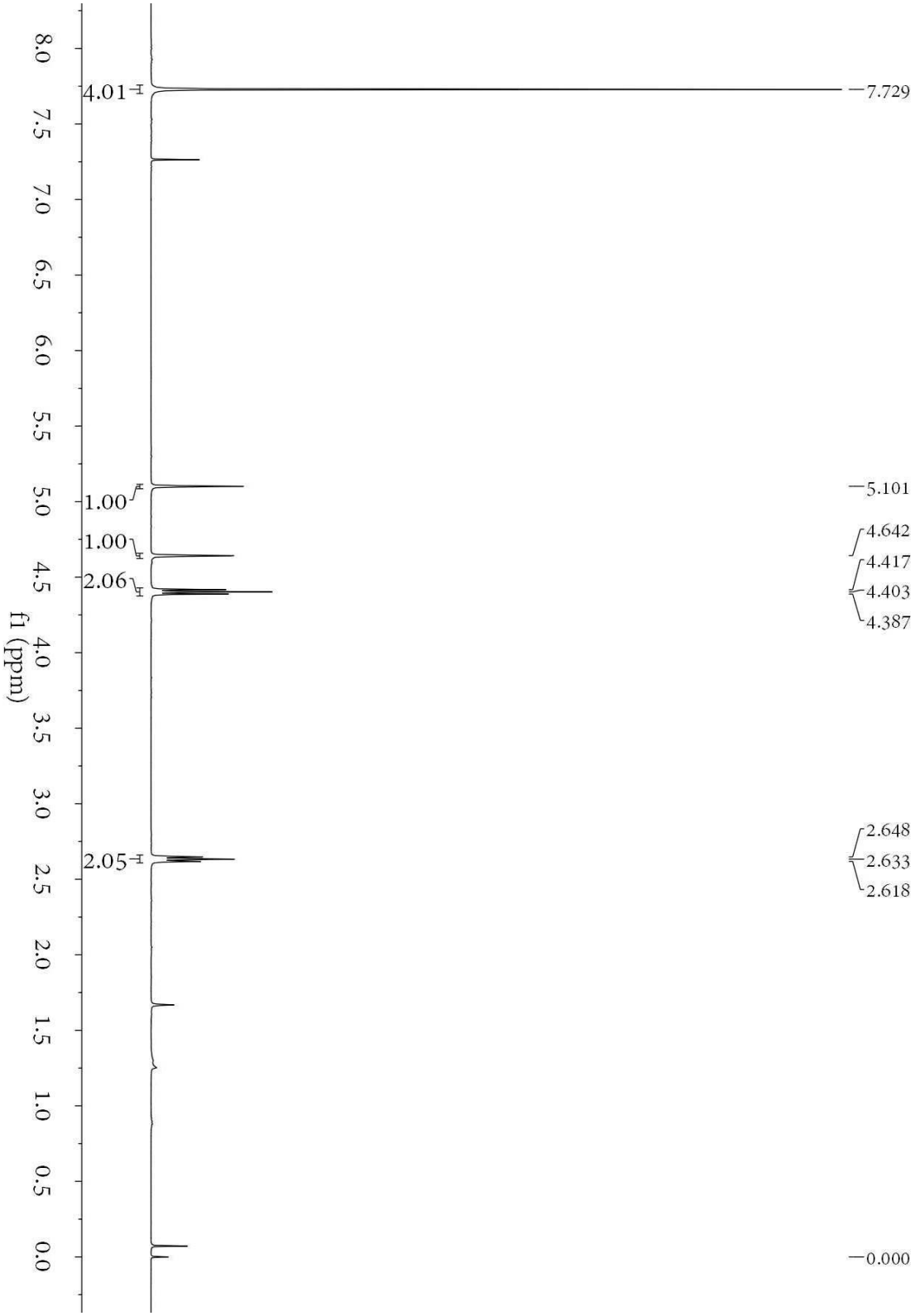


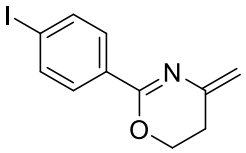
^{13}C NMR of **2e**, 75%
$CDCl_3$, 100 MHz



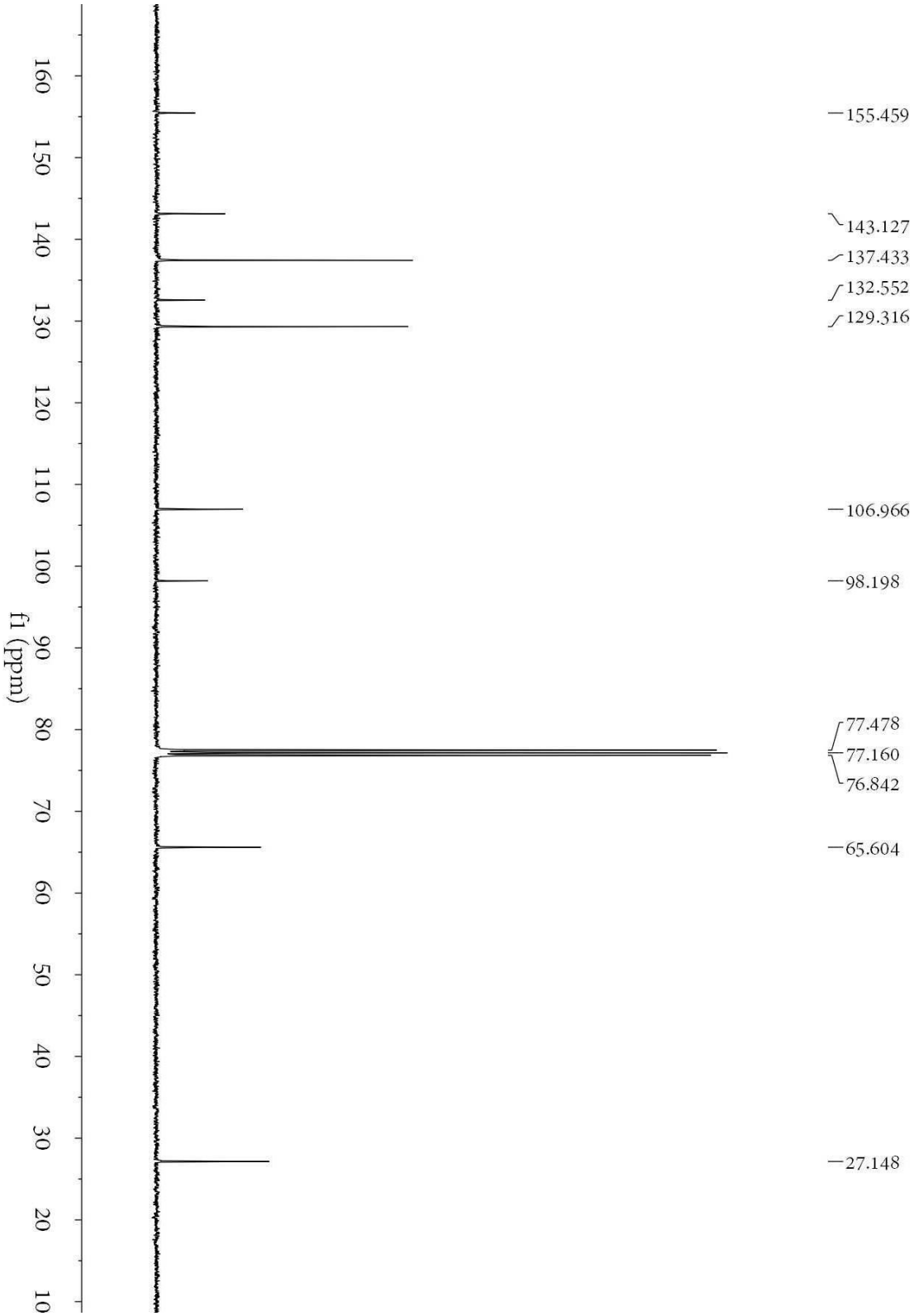


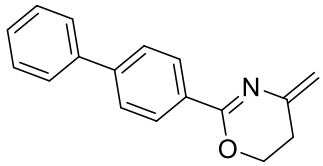
^{1}H NMR of **2f**, 30%
$CDCl_3$, 400 MHz



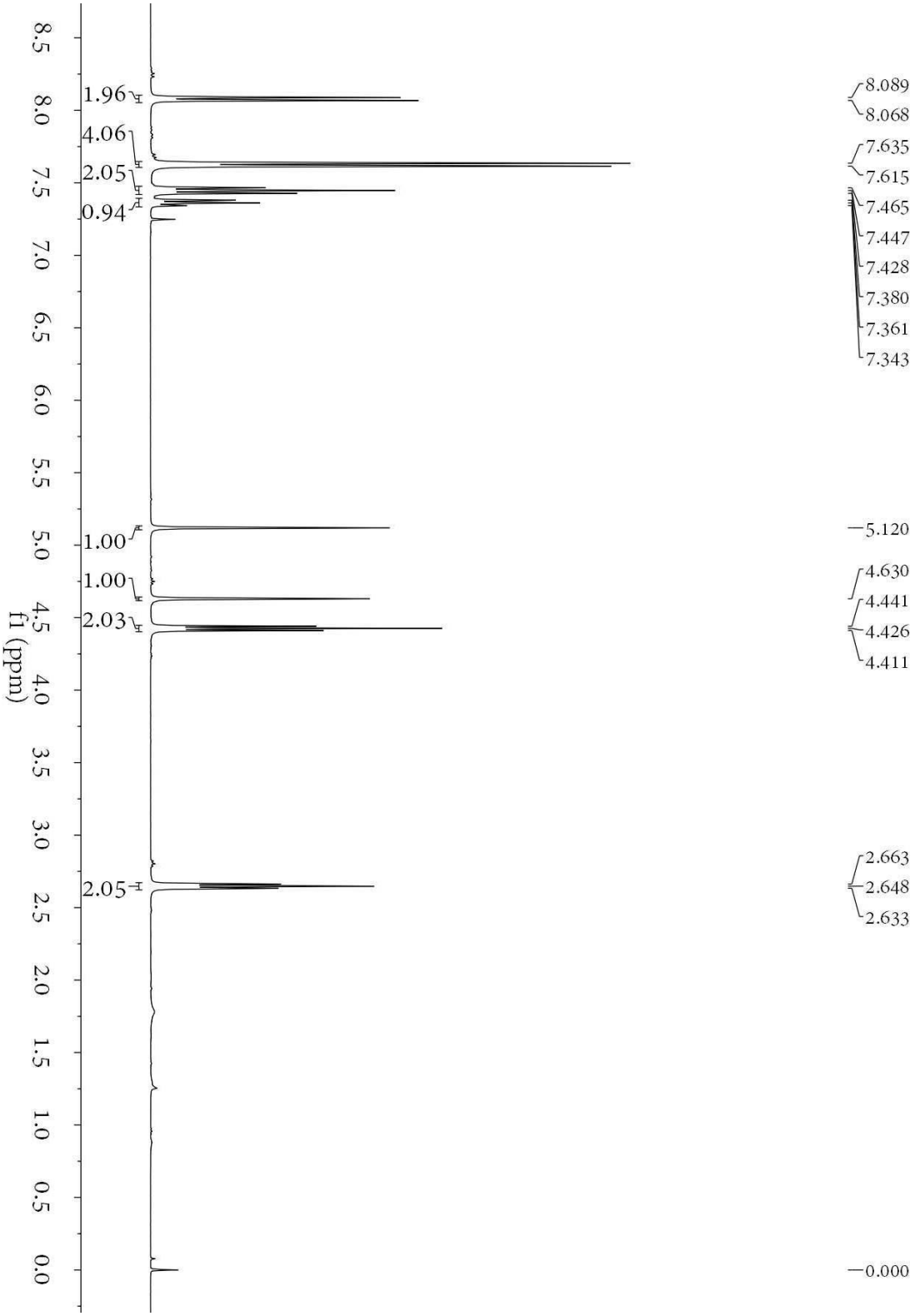


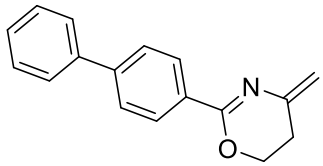
^{13}C NMR of **2f**, 30%
$CDCl_3$, 100 MHz



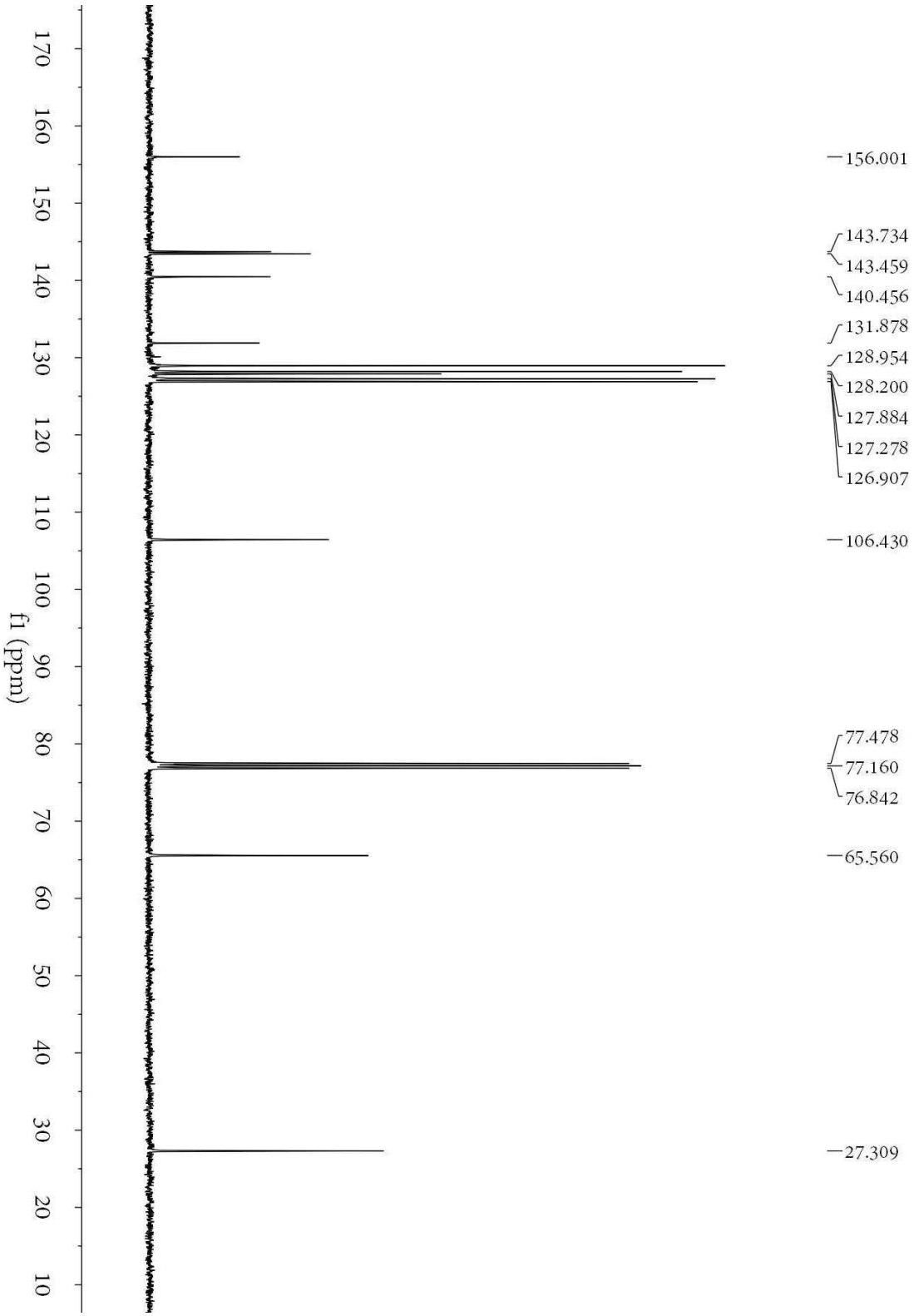


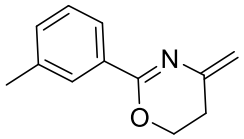
^{1}H NMR of **2g**, 72%
$CDCl_3$, 400 MHz



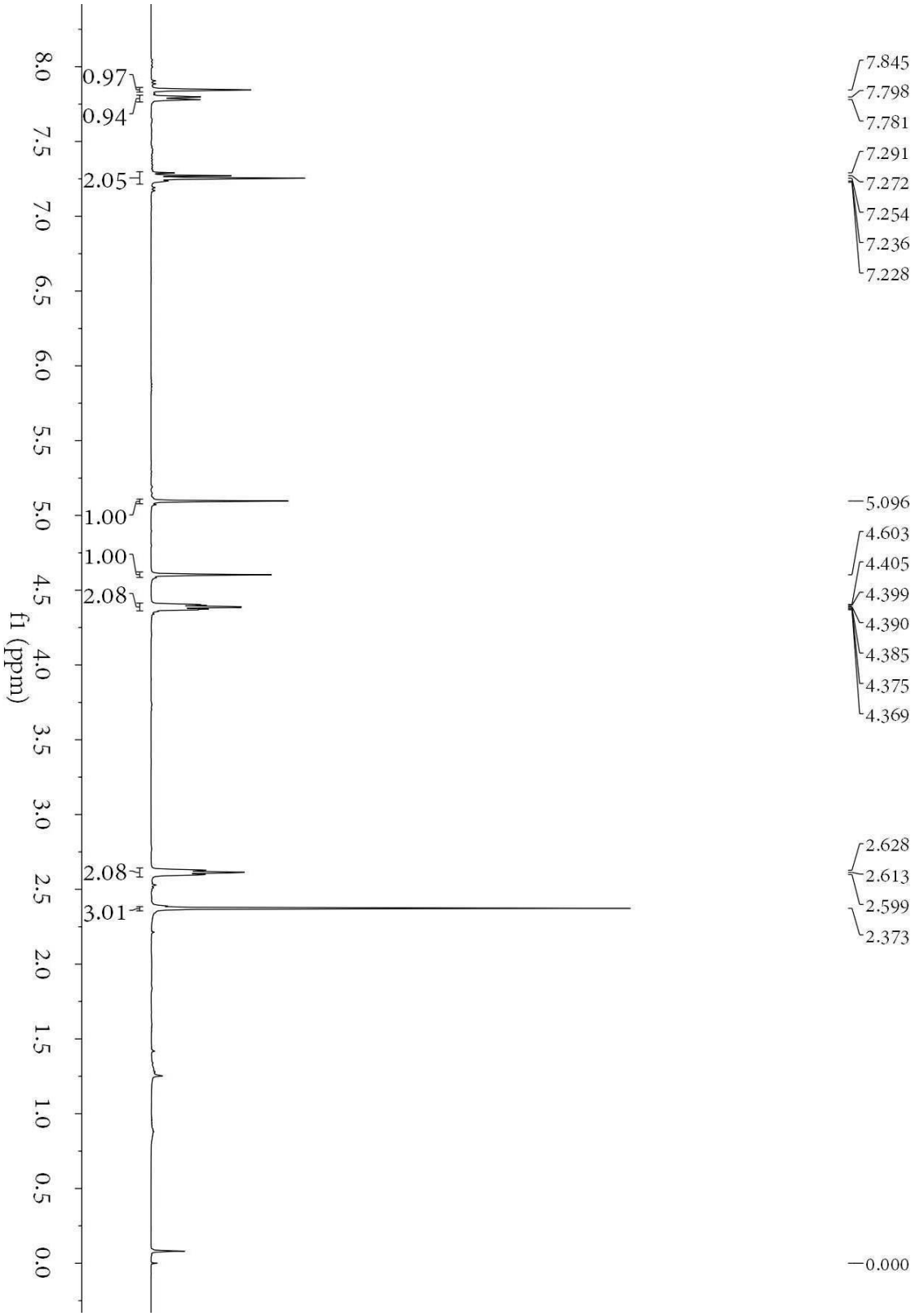


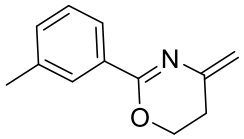
^{13}C NMR of **2g**, 72%
$CDCl_3$, 100 MHz



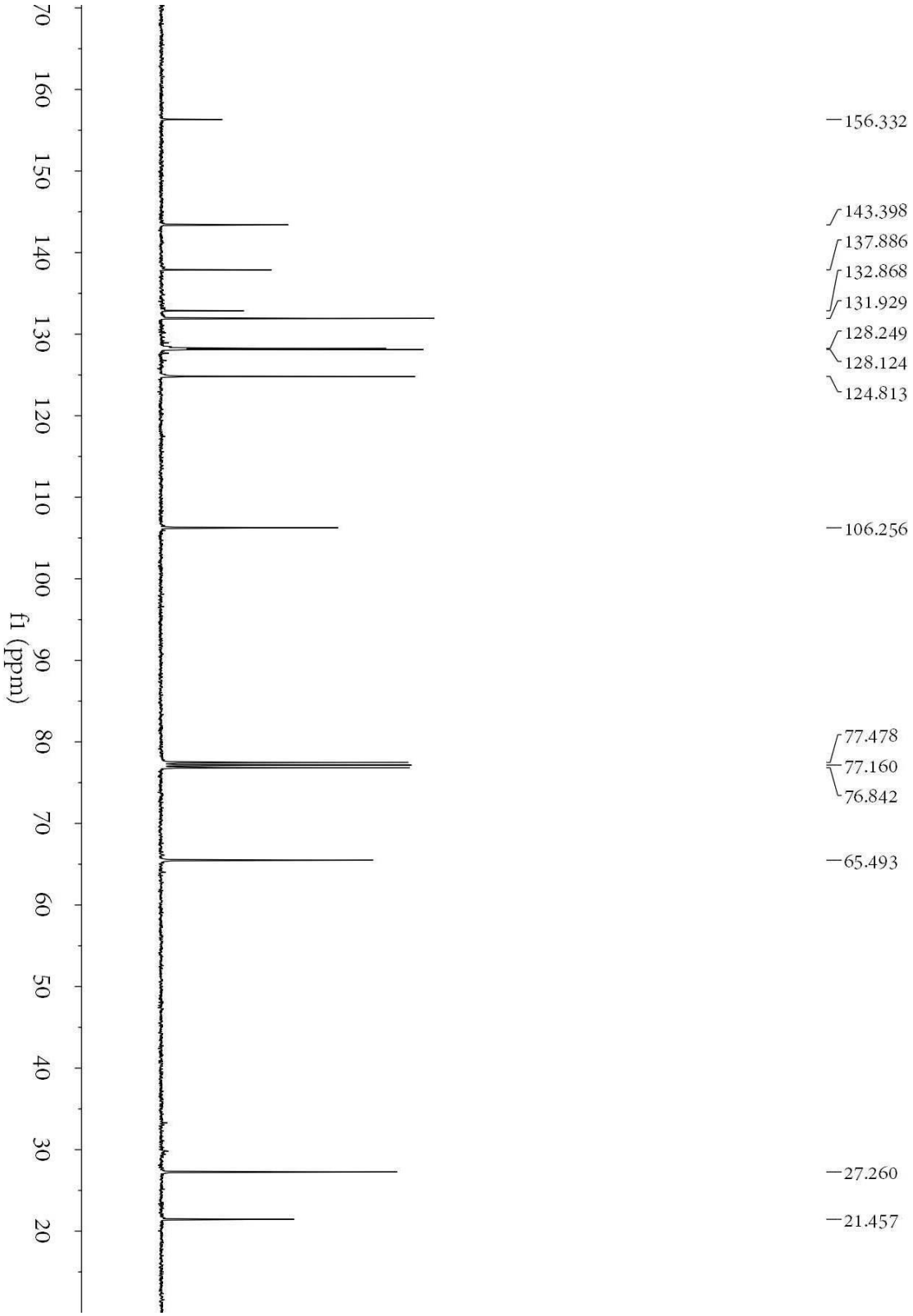


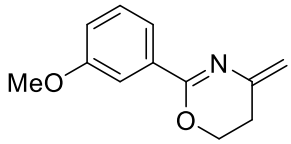
^{1}H NMR of **2h**, 93%
$CDCl_3$, 400 MHz



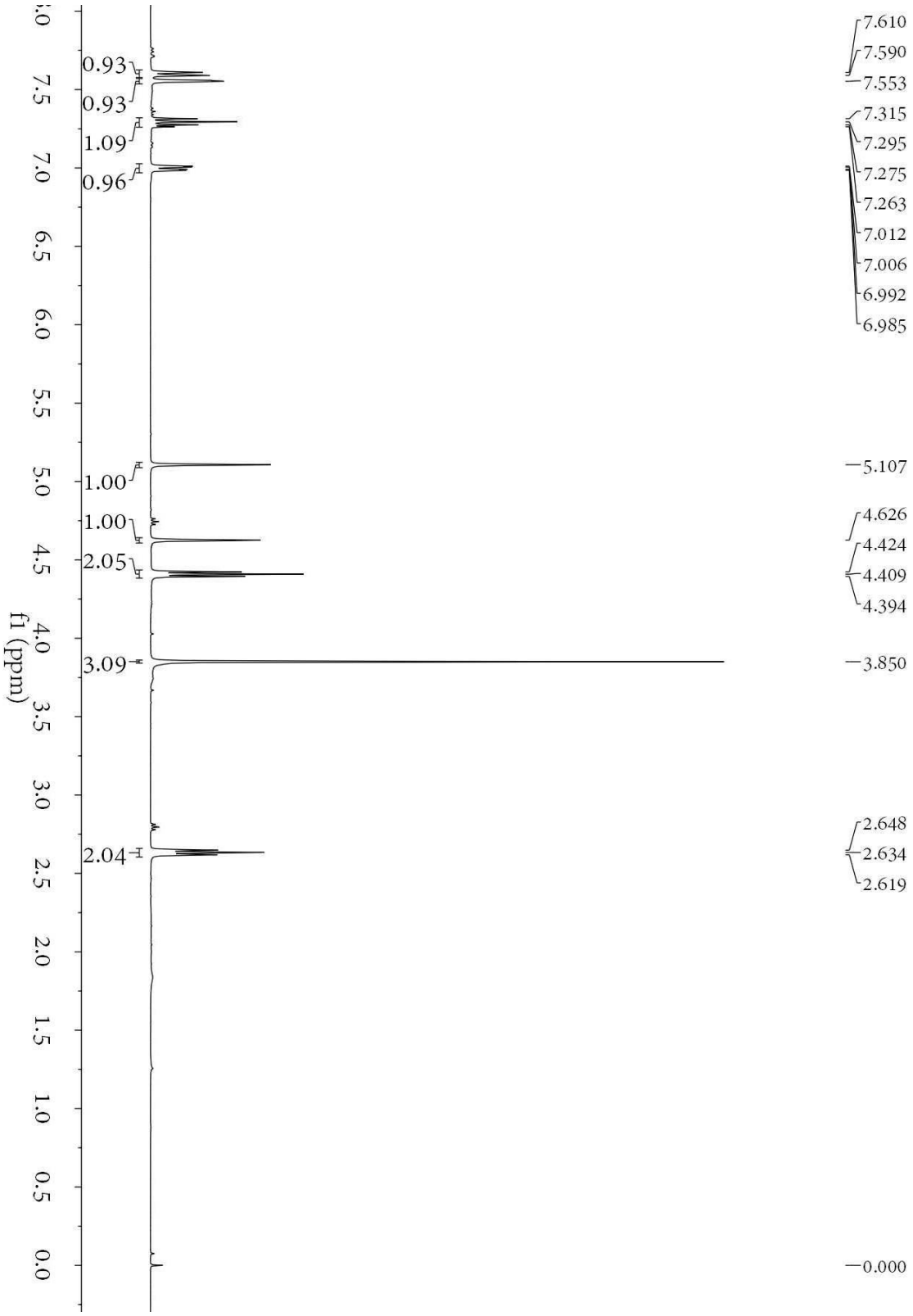


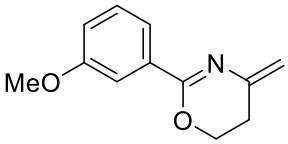
^{13}C NMR of **2h**, 93%
$CDCl_3$, 100 MHz



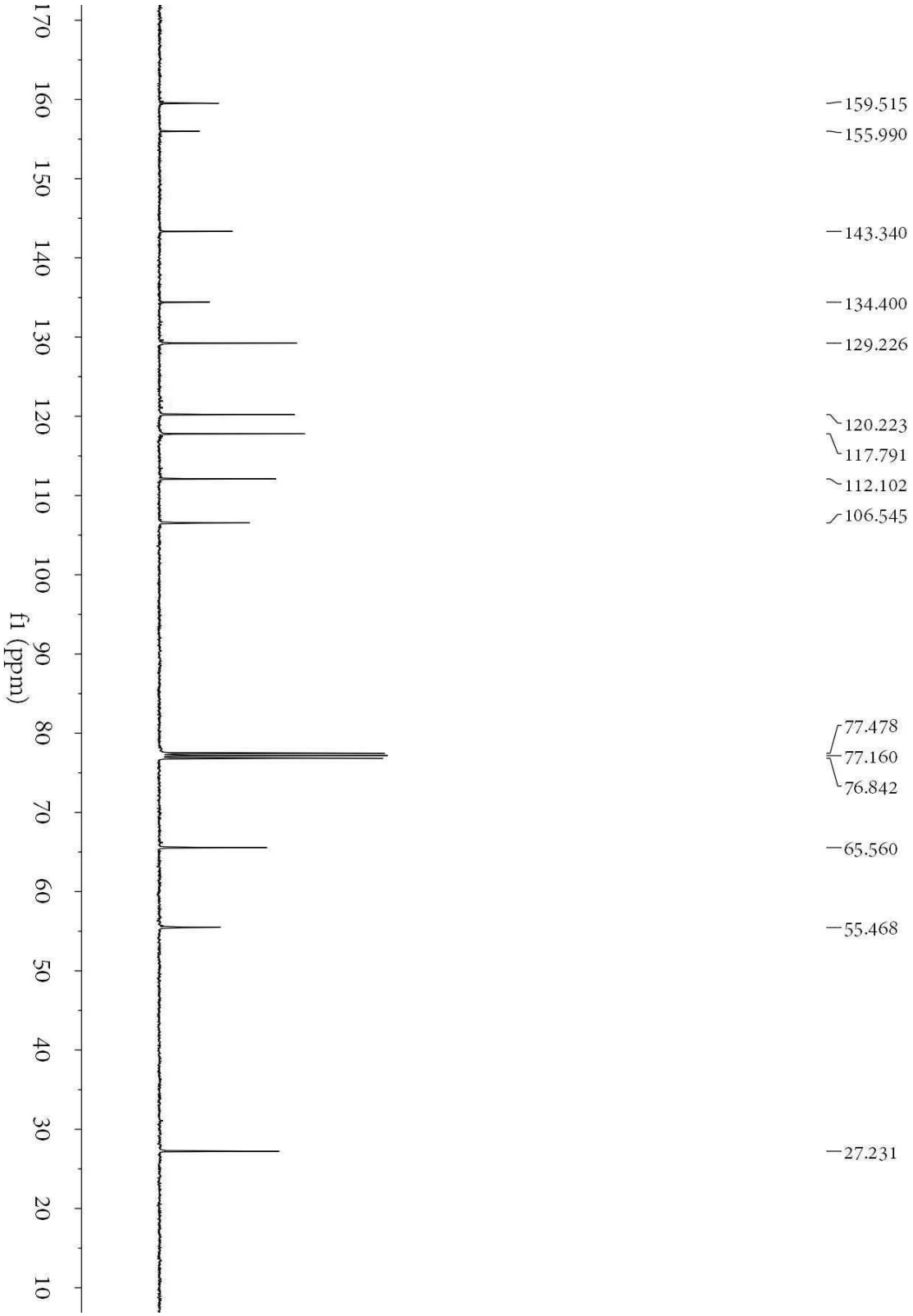


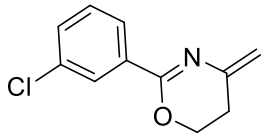
^{1}H NMR of **2i**, 71%
$CDCl_3$, 400 MHz



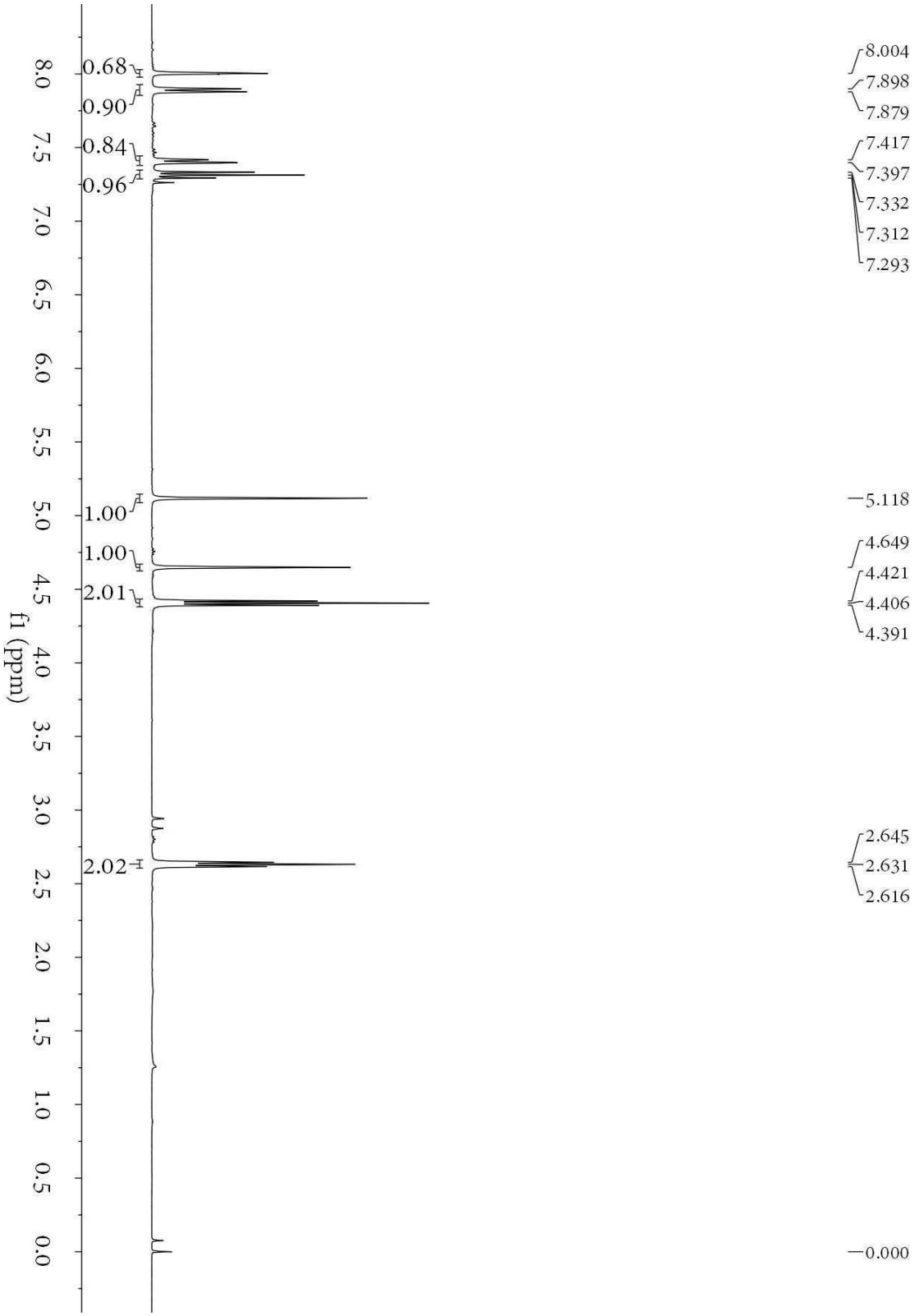


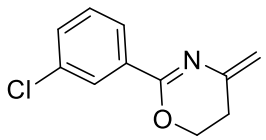
^{13}C NMR of **2i**, 71%
$CDCl_3$, 100 MHz



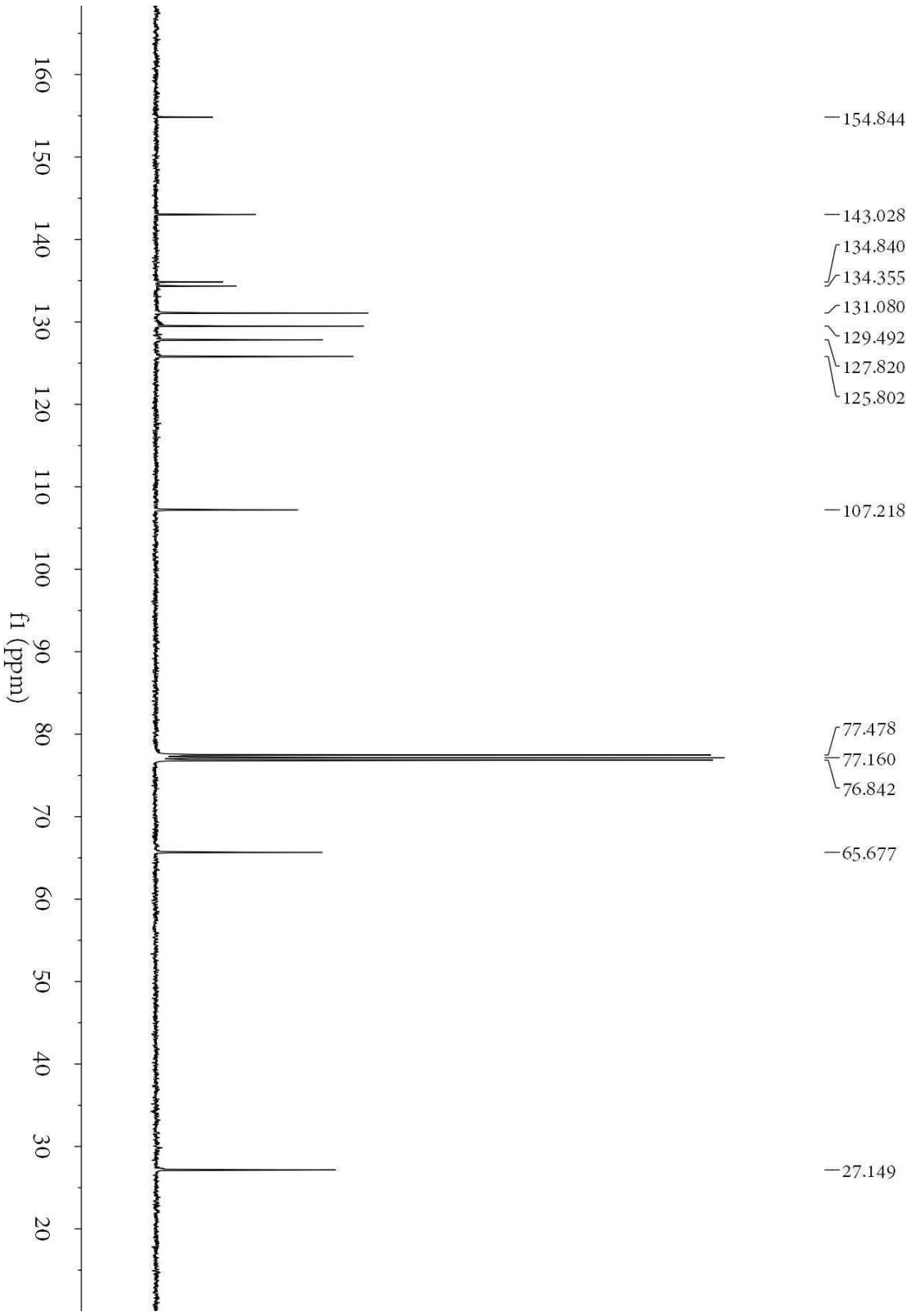


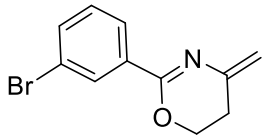
^{1}H NMR of **2j**, 83%
$CDCl_3$, 400 MHz



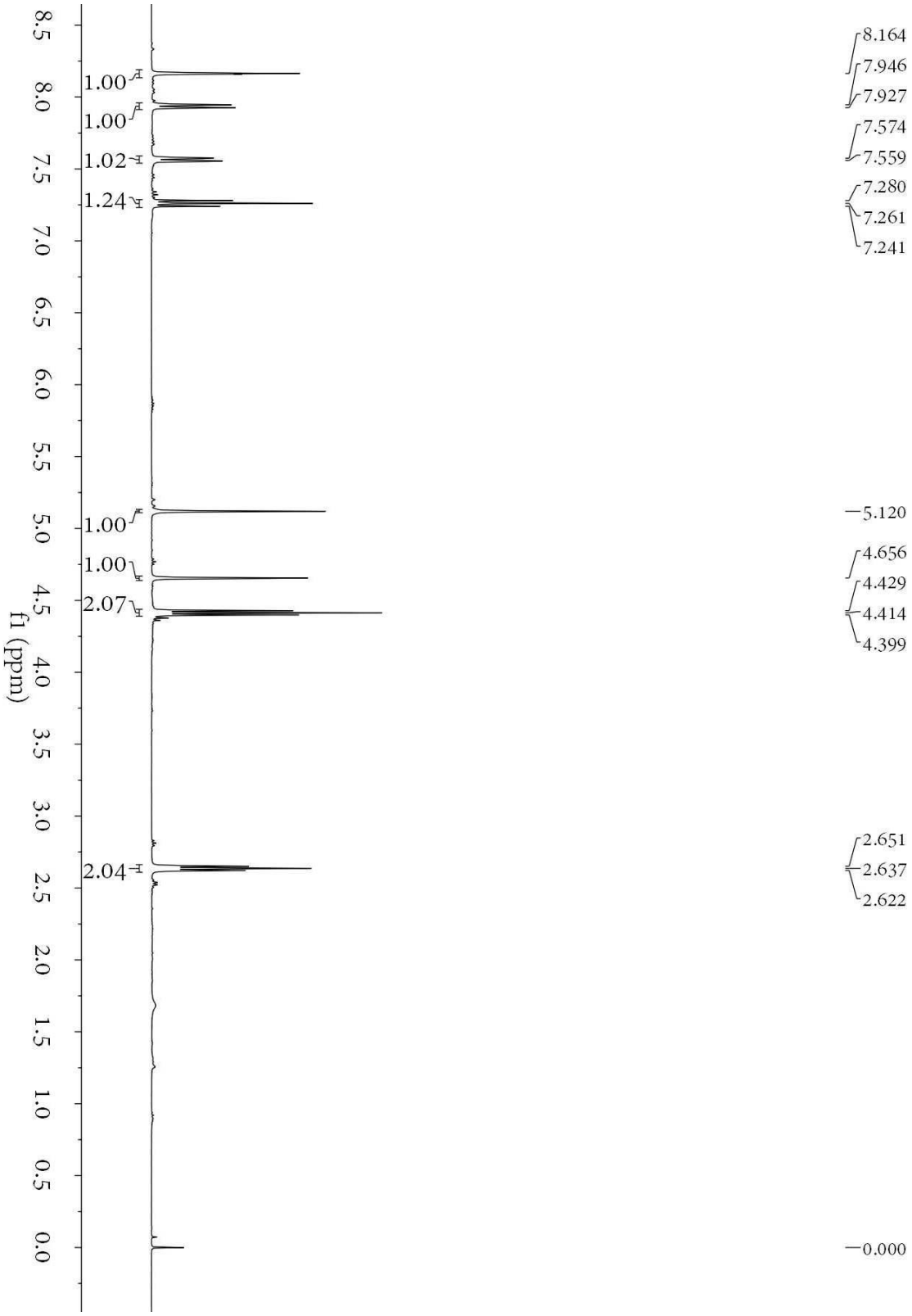


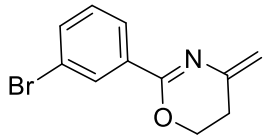
^{13}C NMR of **2j**, 83%
$CDCl_3$, 100 MHz



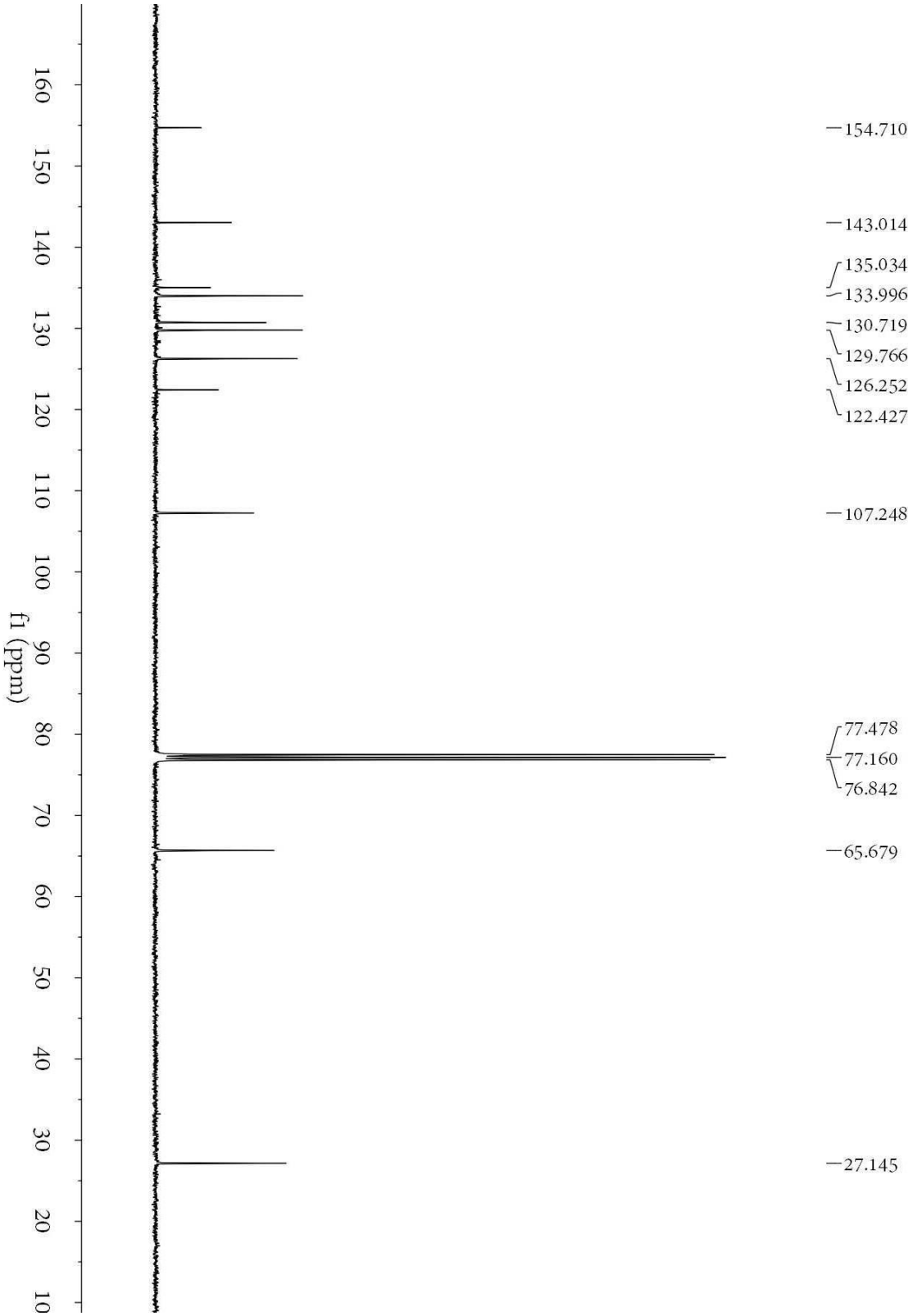


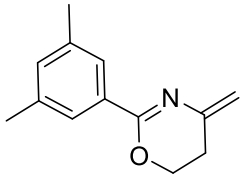
^{1}H NMR of **2k**, 77%
$CDCl_3$, 400 MHz



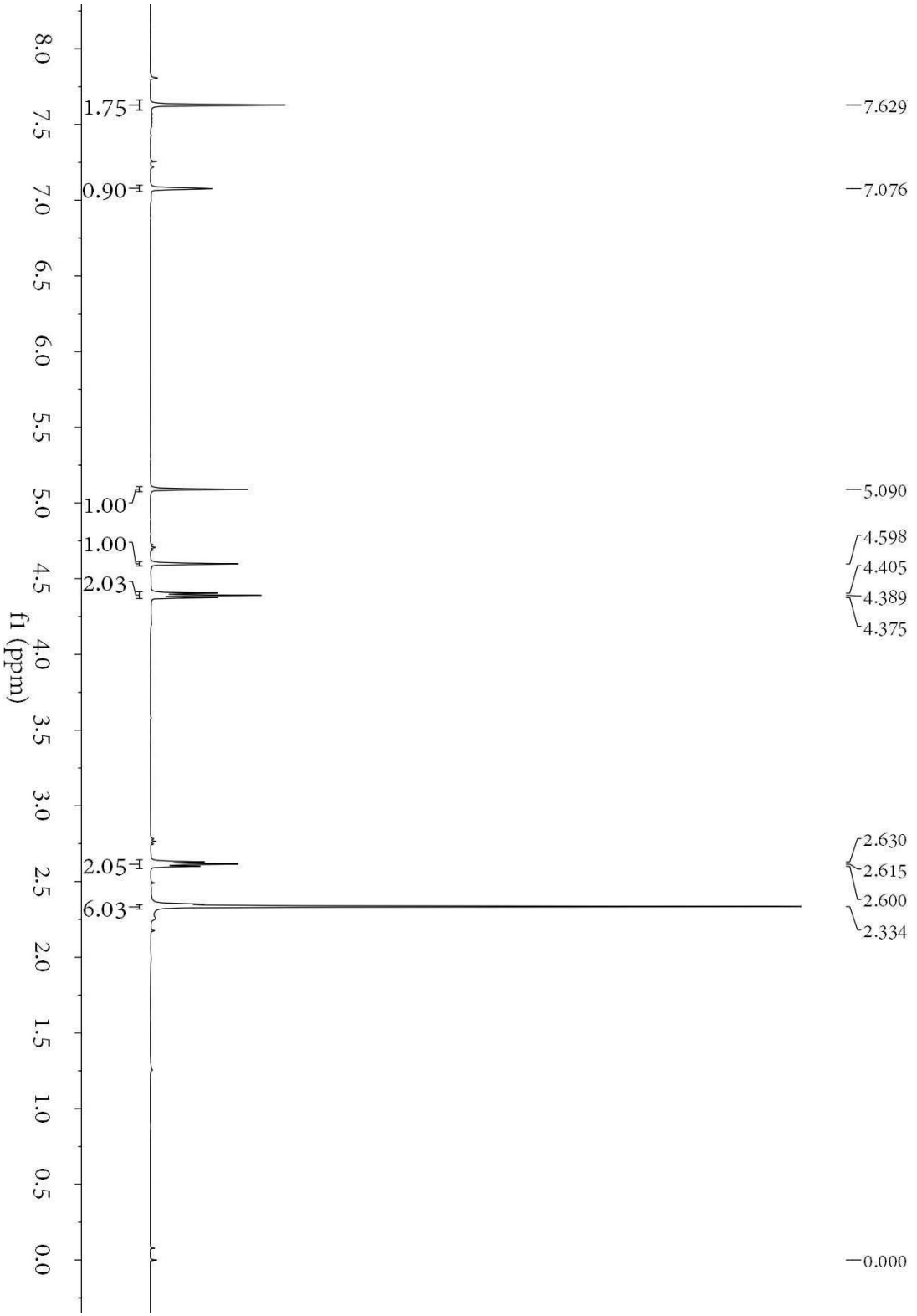


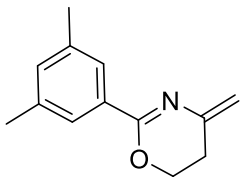
^{13}C NMR of **2k**, 77%
$CDCl_3$, 100 MHz



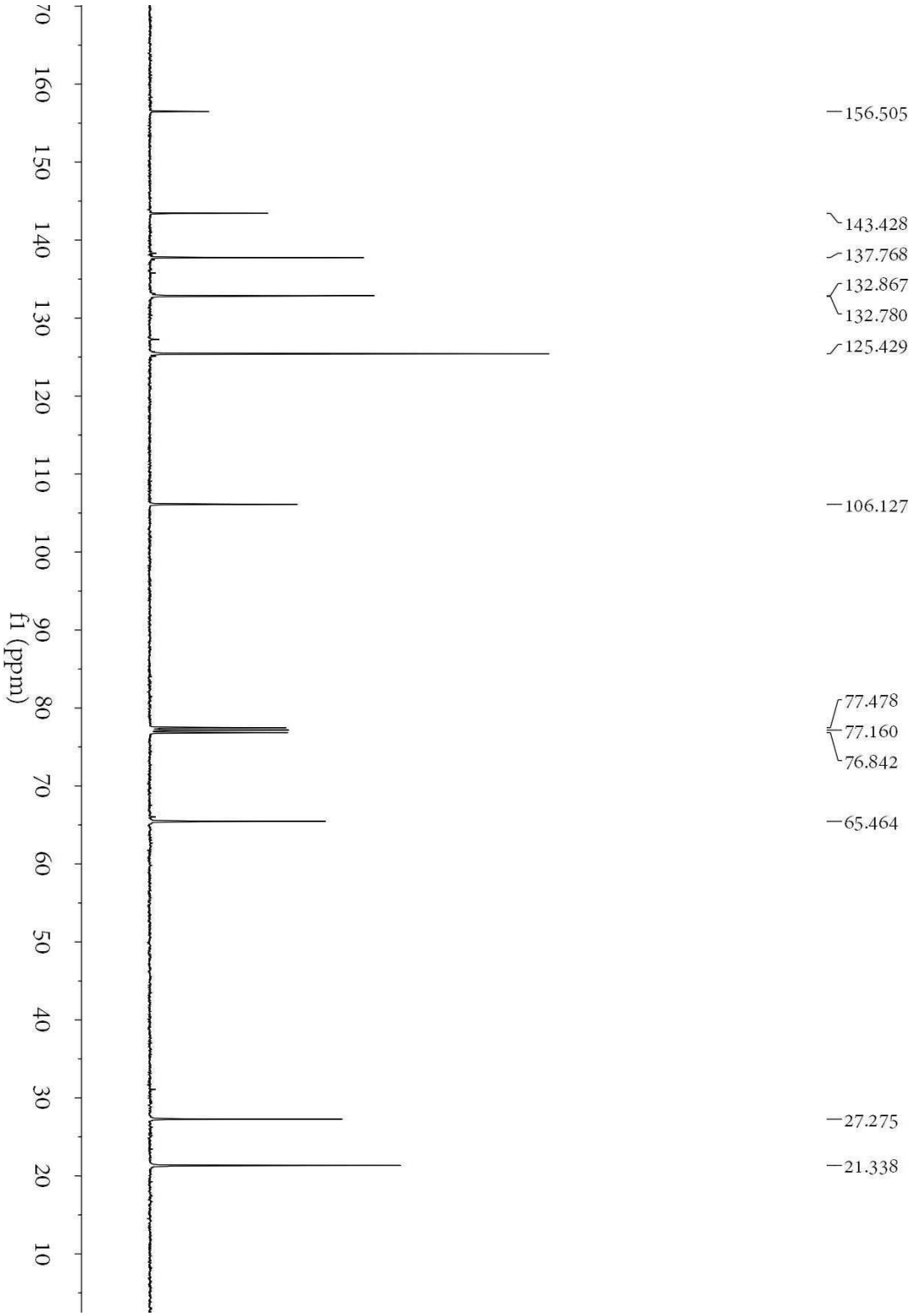


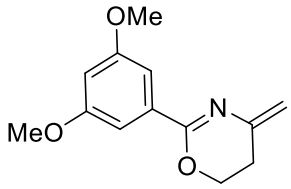
^{1}H NMR of **2l**, 82%
$CDCl_3$, 400 MHz



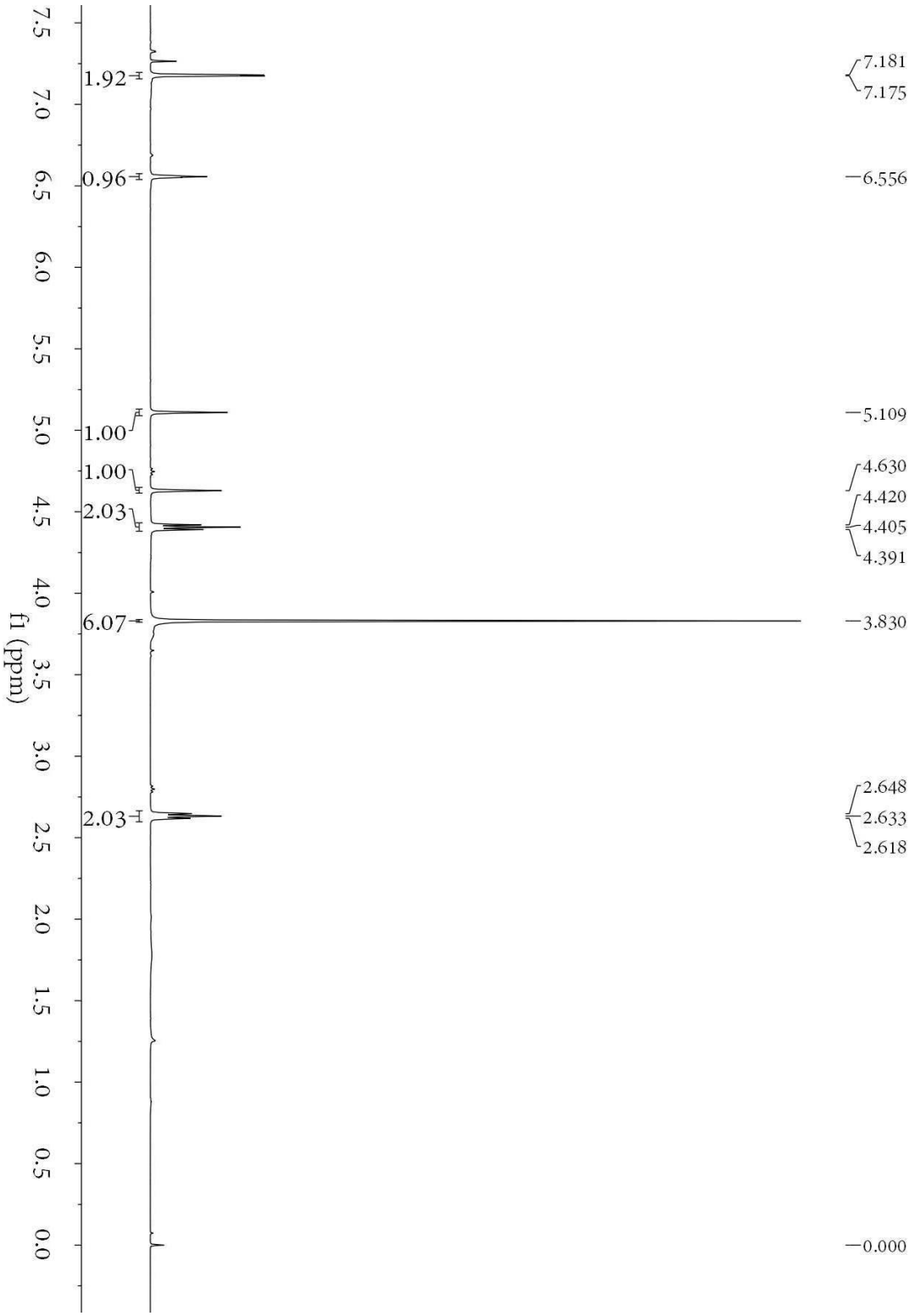


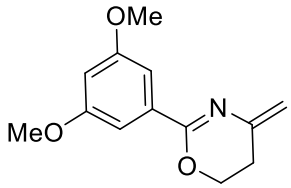
^{13}C NMR of **2l**, 82%
$CDCl_3$, 100 MHz



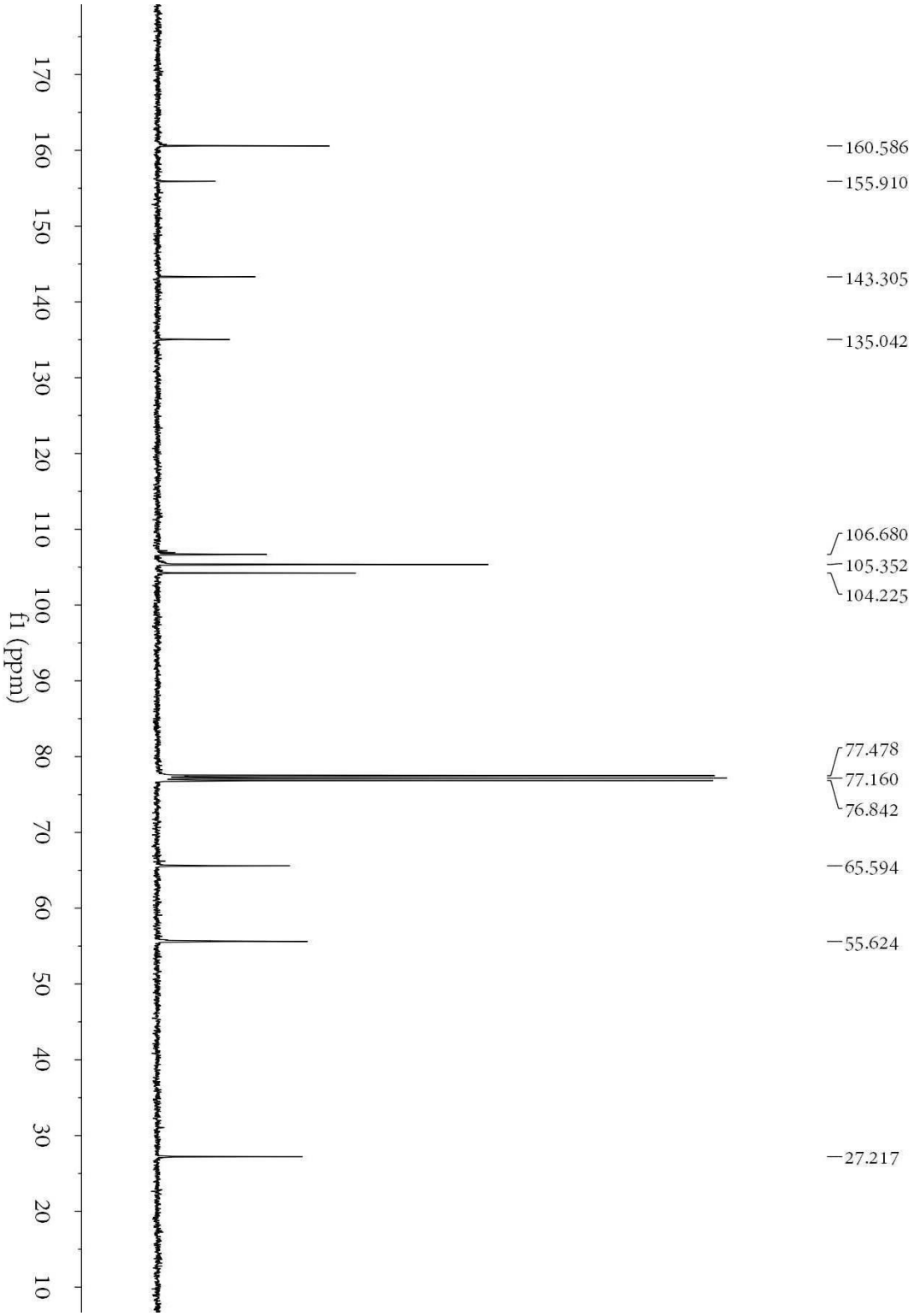


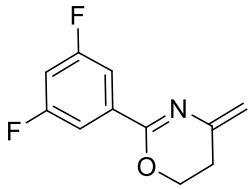
^{1}H NMR of **2m**, 58%
$CDCl_3$, 400 MHz



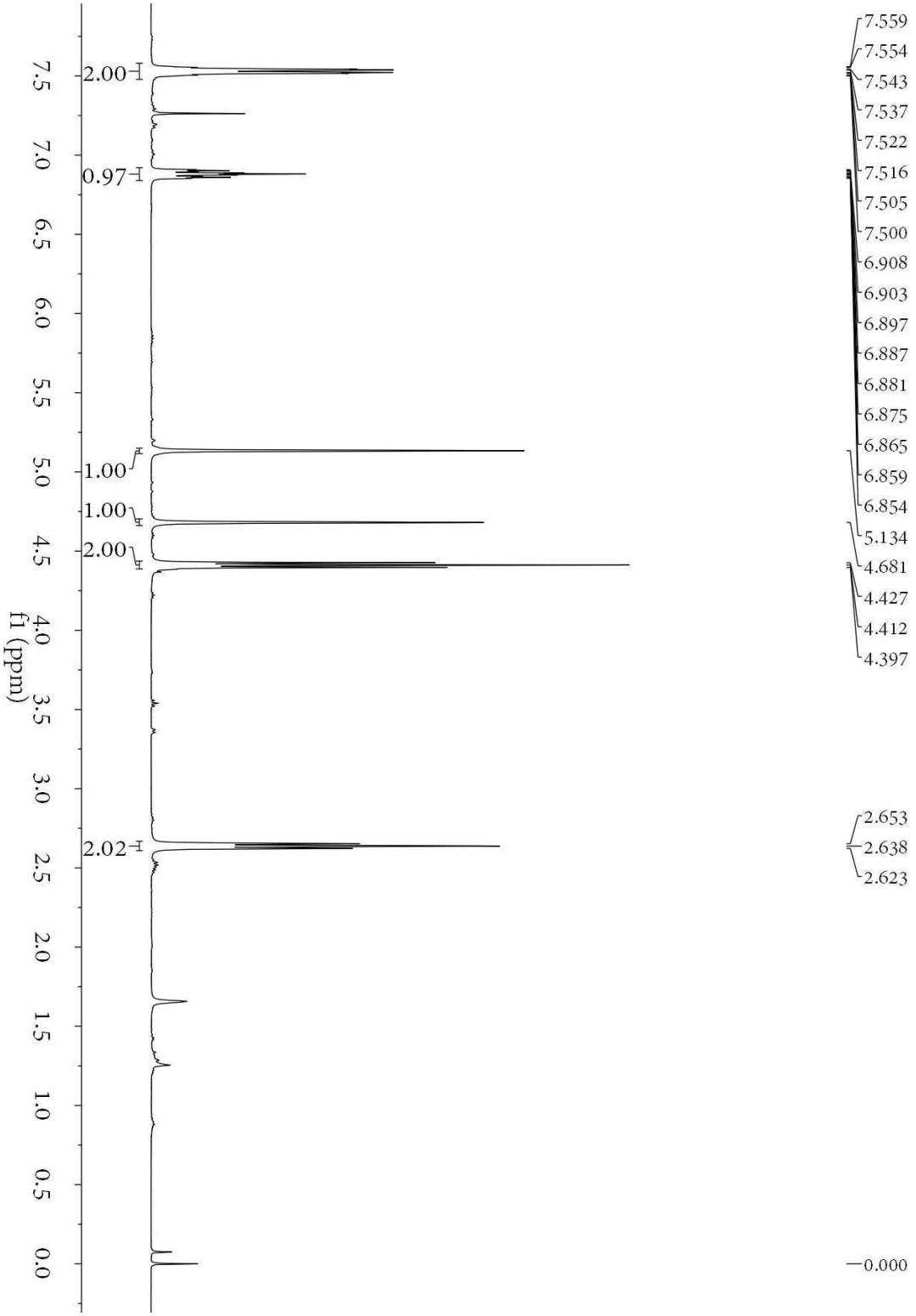


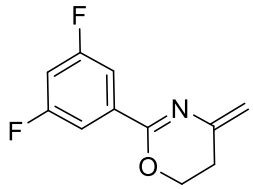
^{13}C NMR of **2m**, 58%
$CDCl_3$, 100 MHz



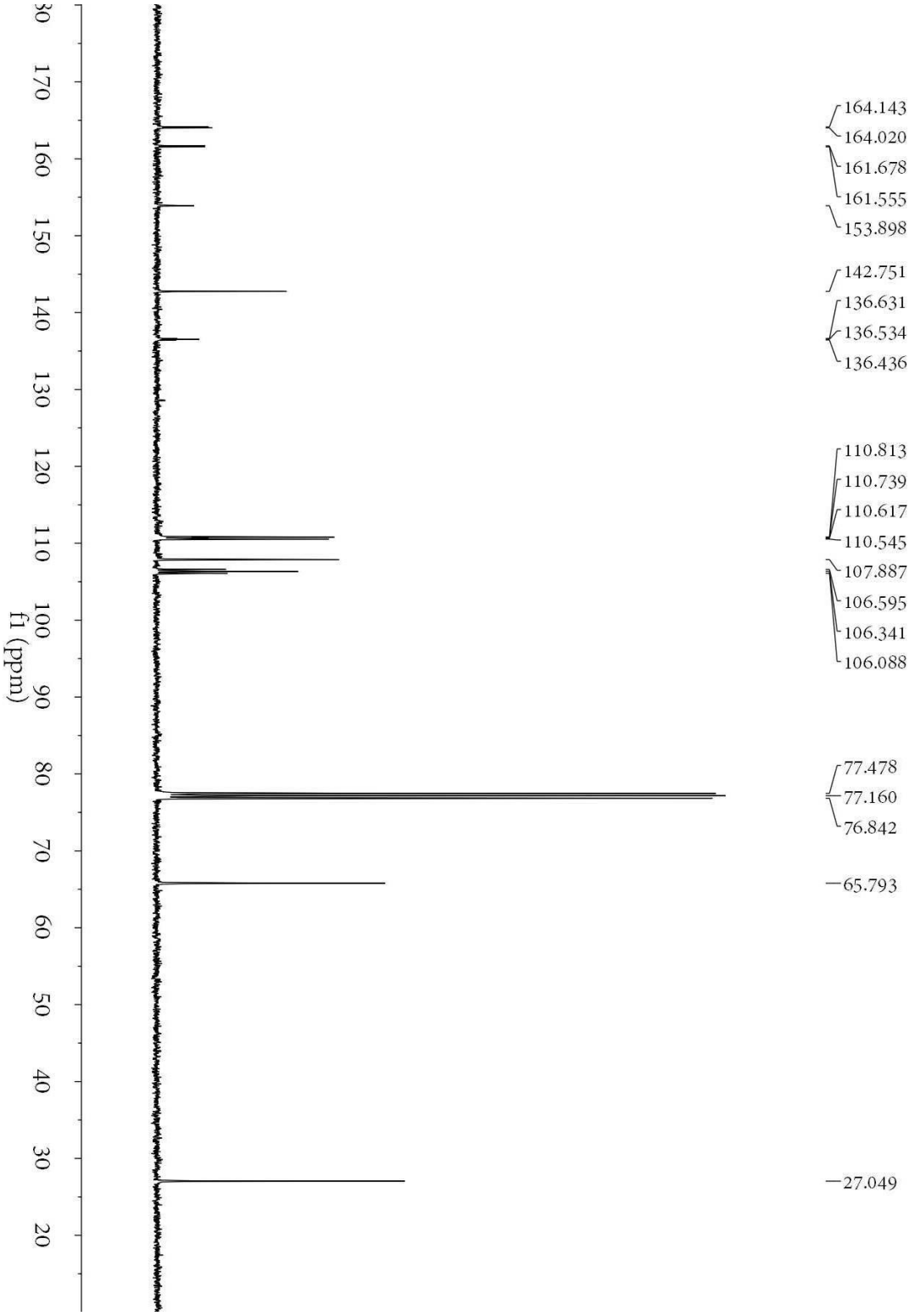


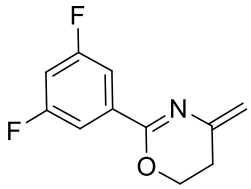
^{1}H NMR of **2n**, 62%
$CDCl_3$, 400 MHz



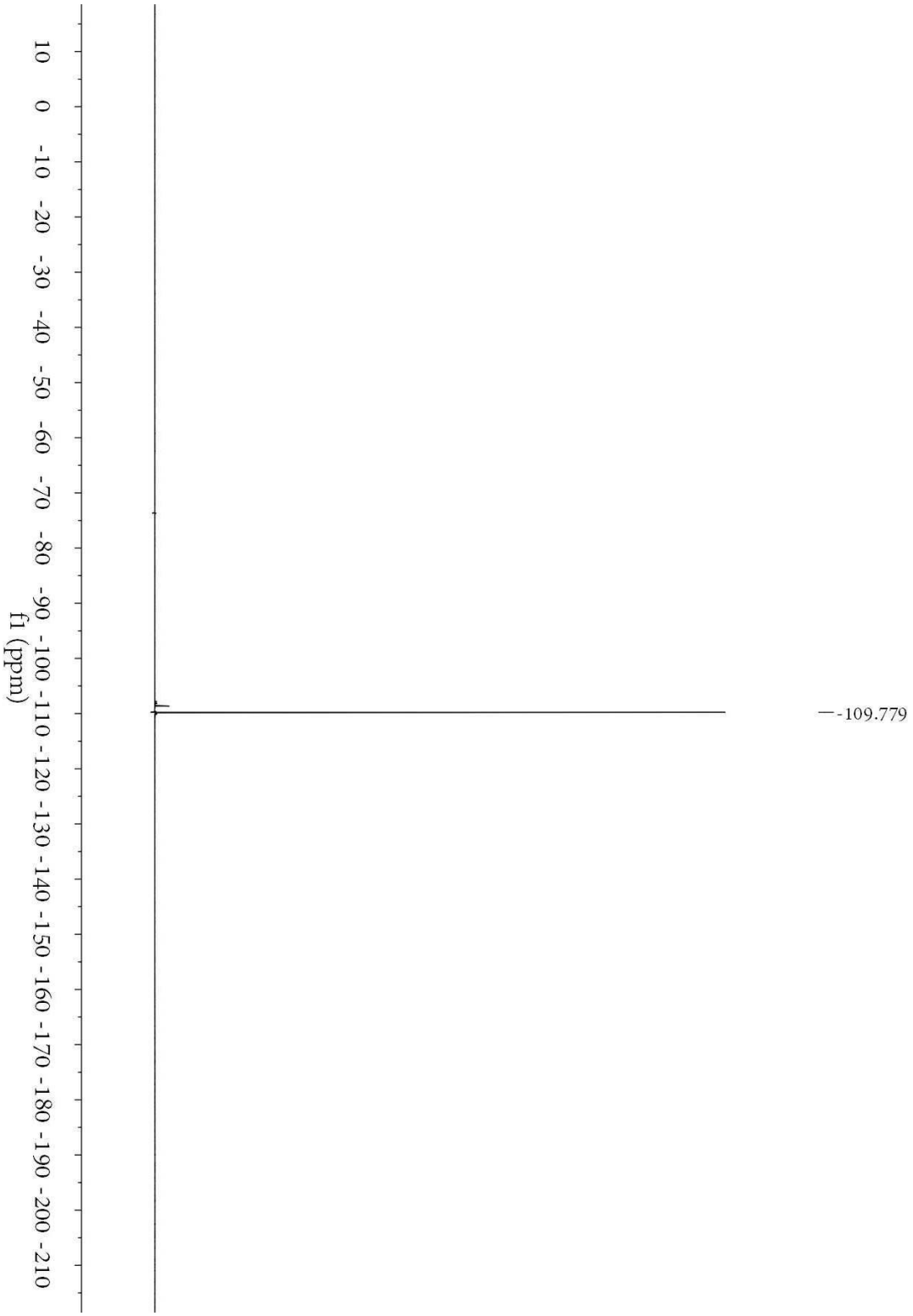


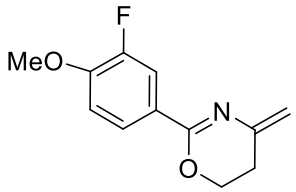
^{13}C NMR of **2n**, 62%
$CDCl_3$, 100 MHz



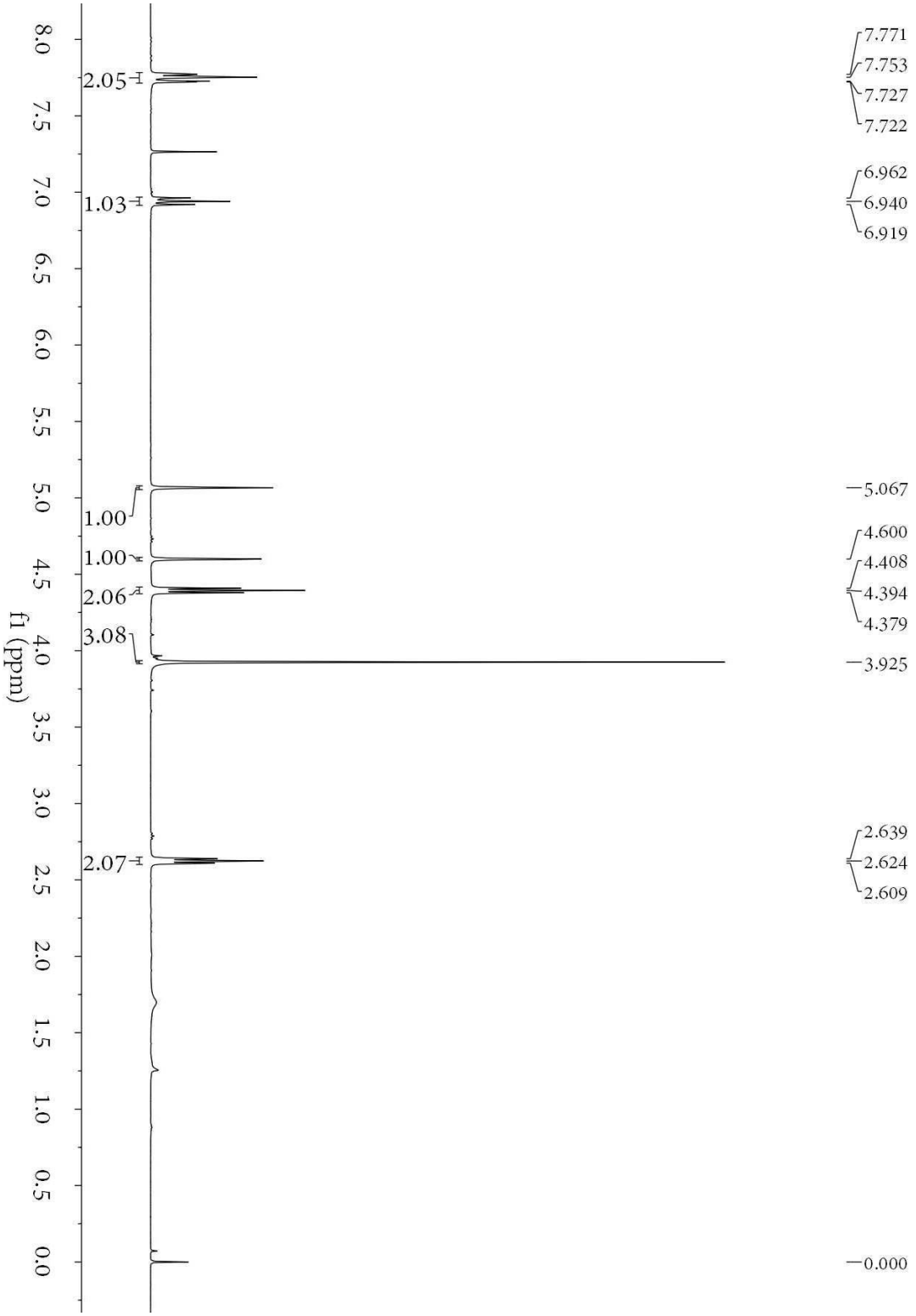


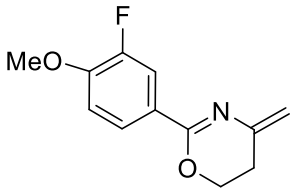
^{19}F NMR of **2n**, 62%
$CDCl_3$, 564 MHz



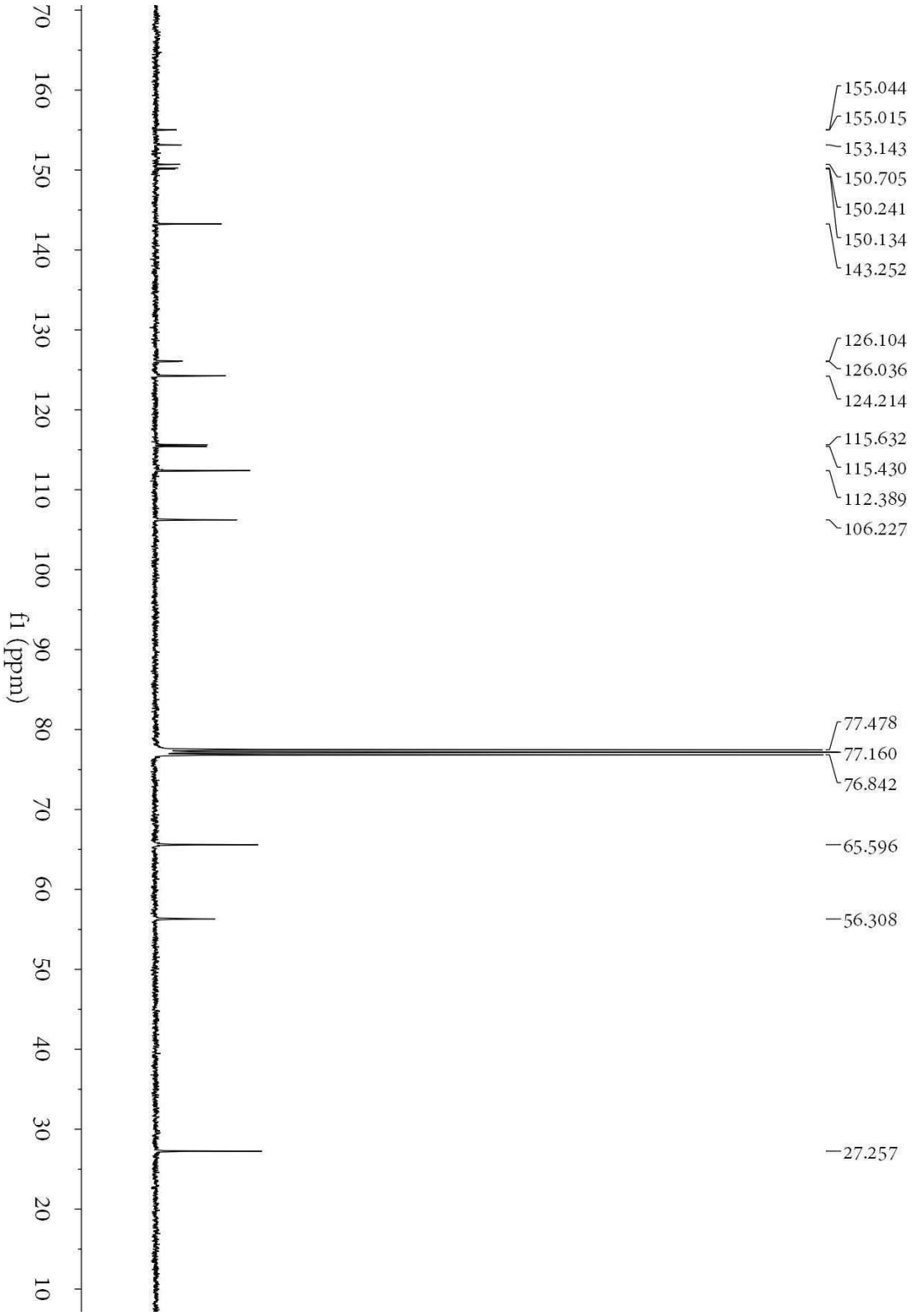


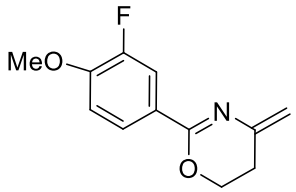
^{1}H NMR of **2o**, 75%
$CDCl_3$, 400 MHz



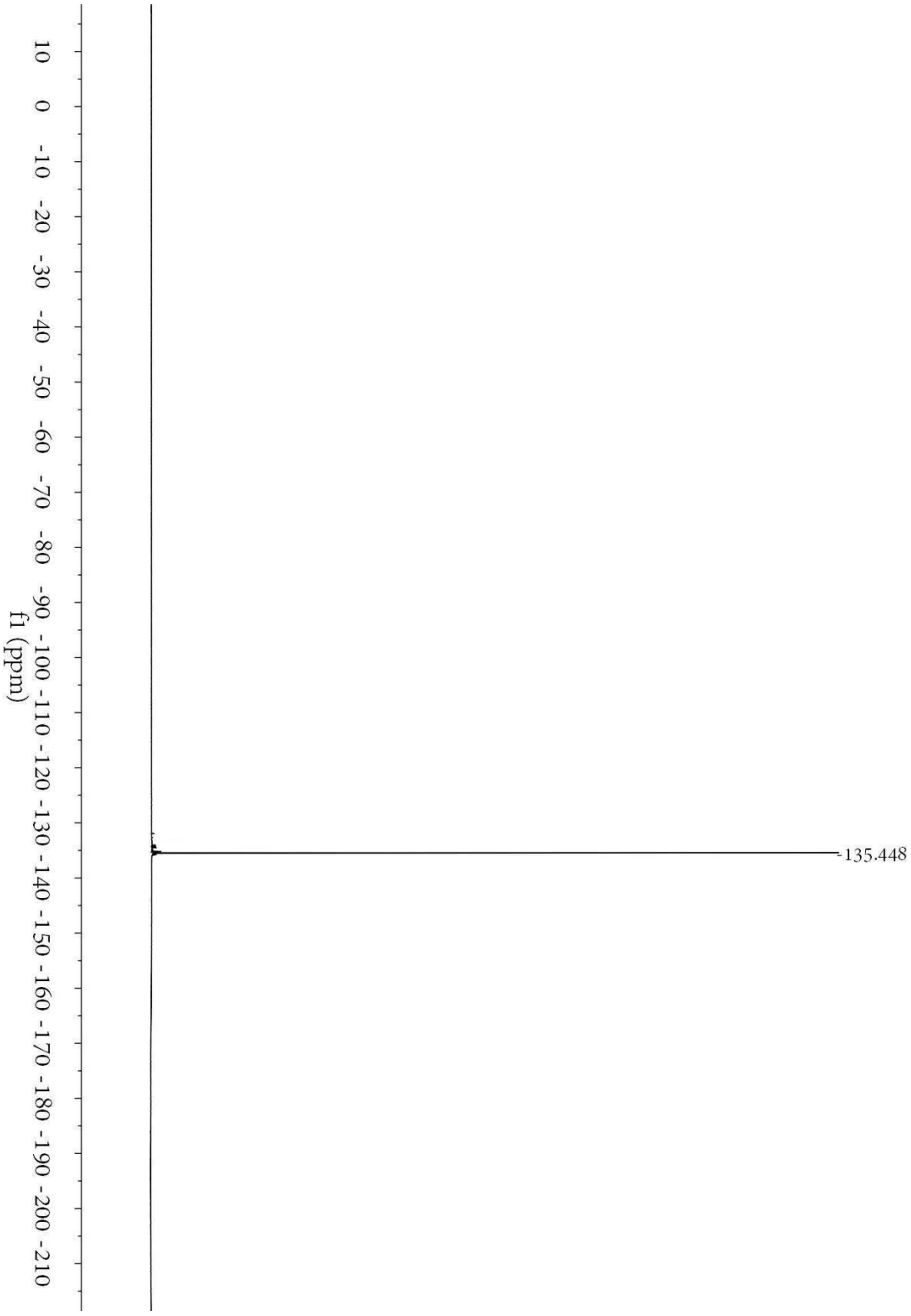


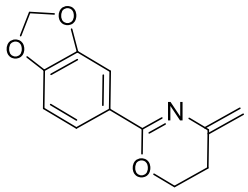
^{13}C NMR of **2o**, 75%
$CDCl_3$, 100 MHz



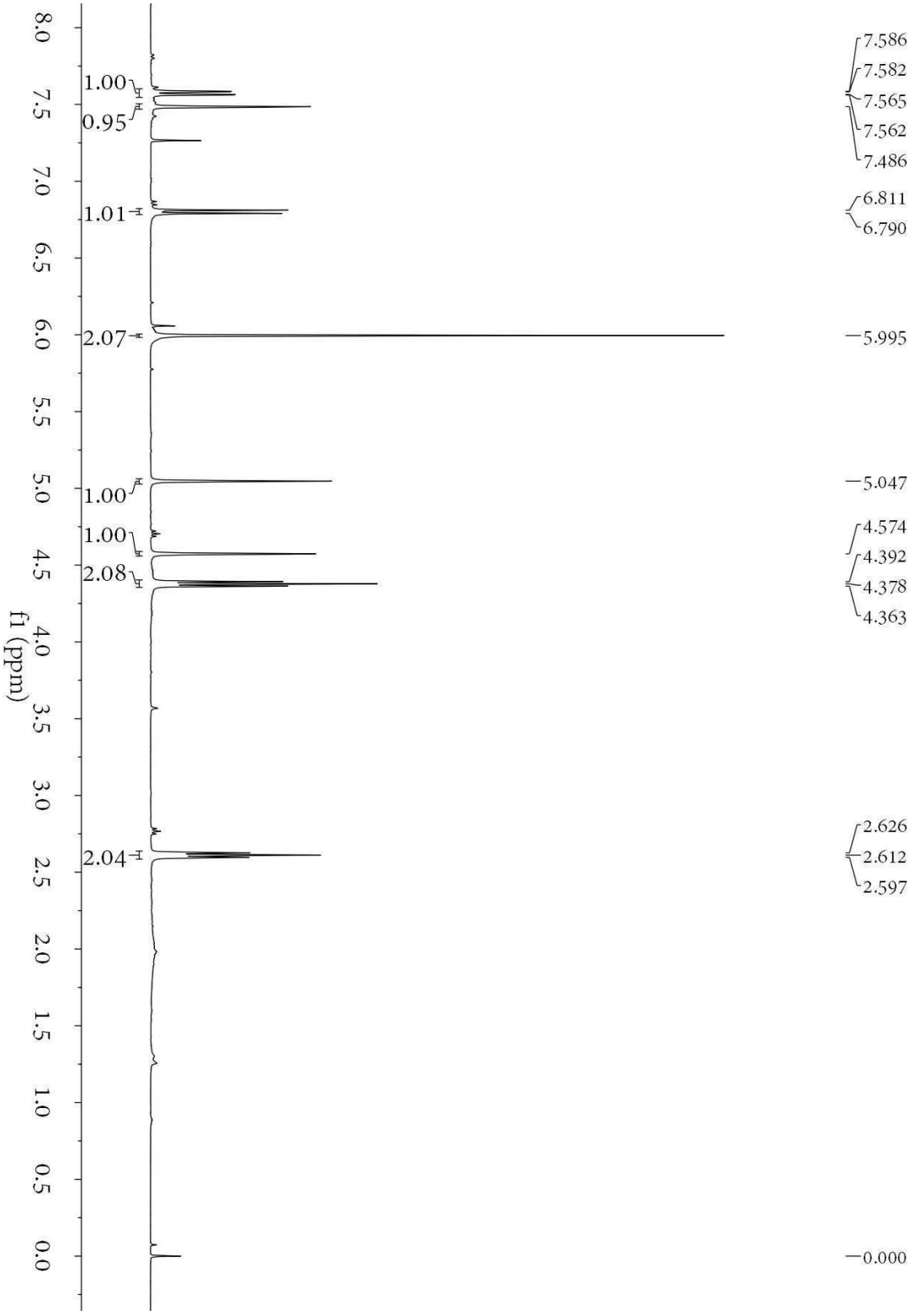


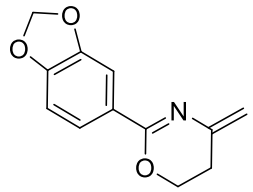
^{19}F NMR of **2o**, 75%
$CDCl_3$, 564 MHz



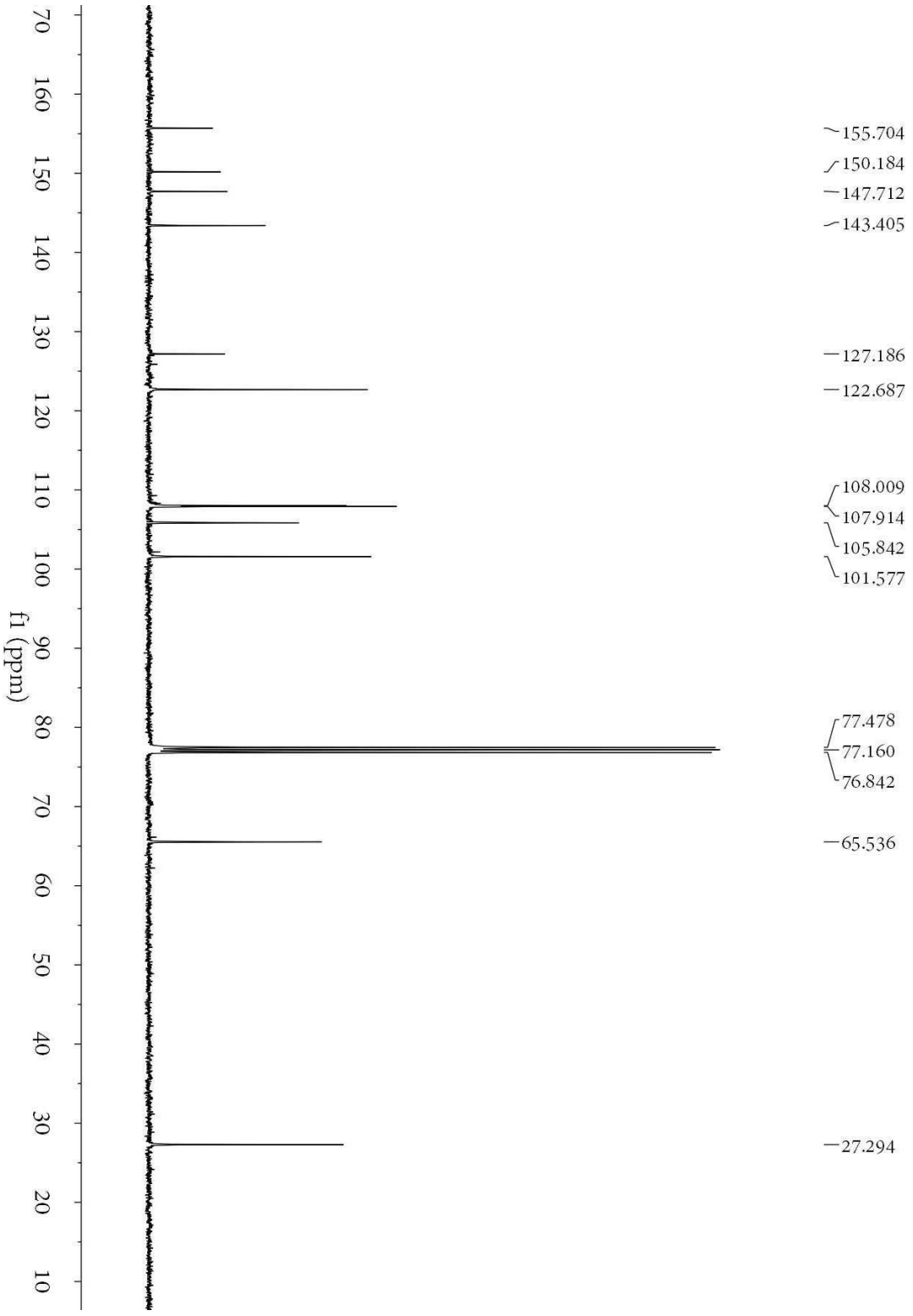


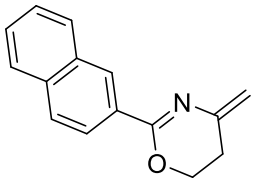
^{1}H NMR of **2p**, 73%
$CDCl_3$, 400 MHz



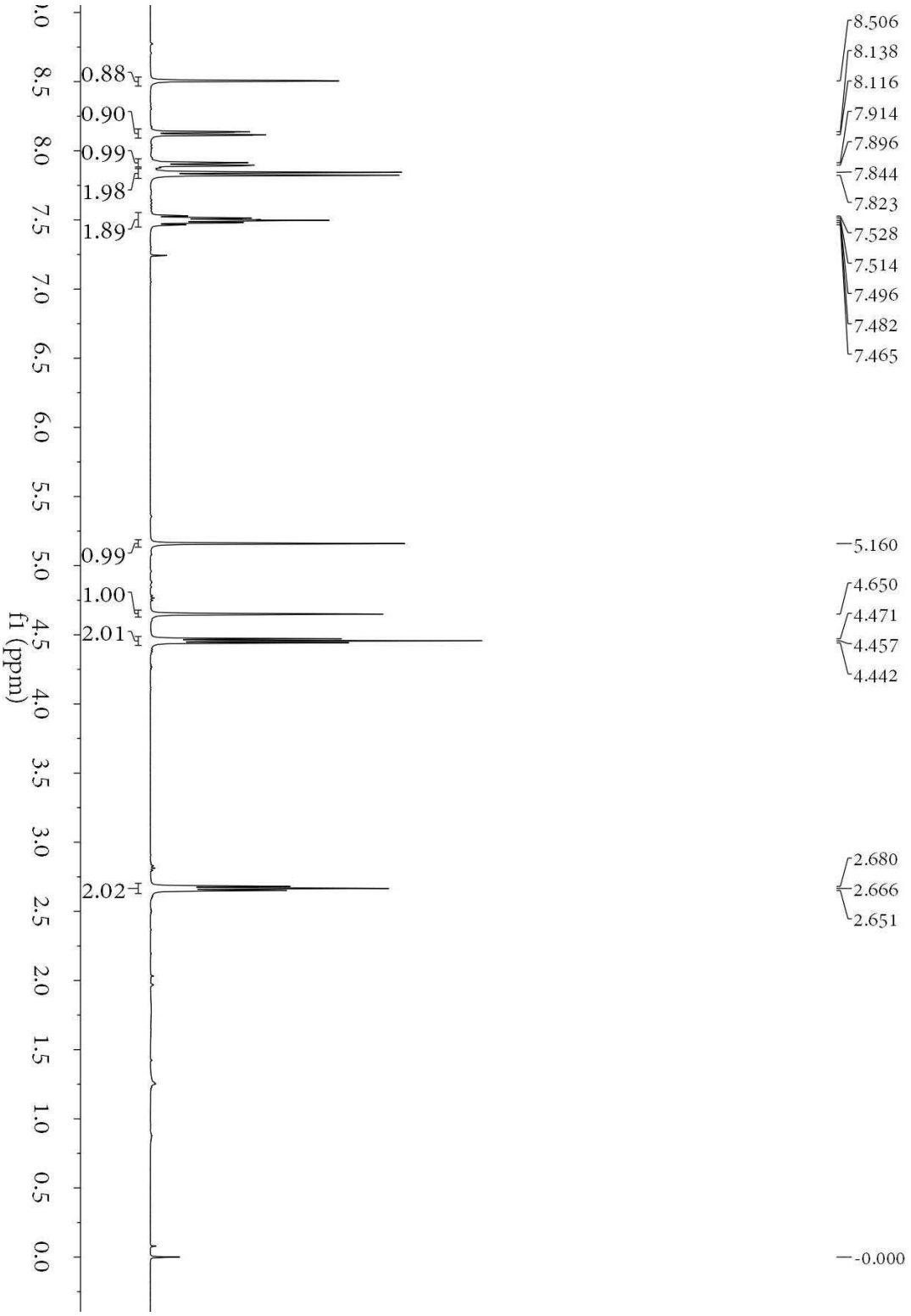


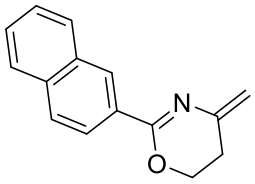
^{13}C NMR of **2p**, 73%
$CDCl_3$, 100 MHz



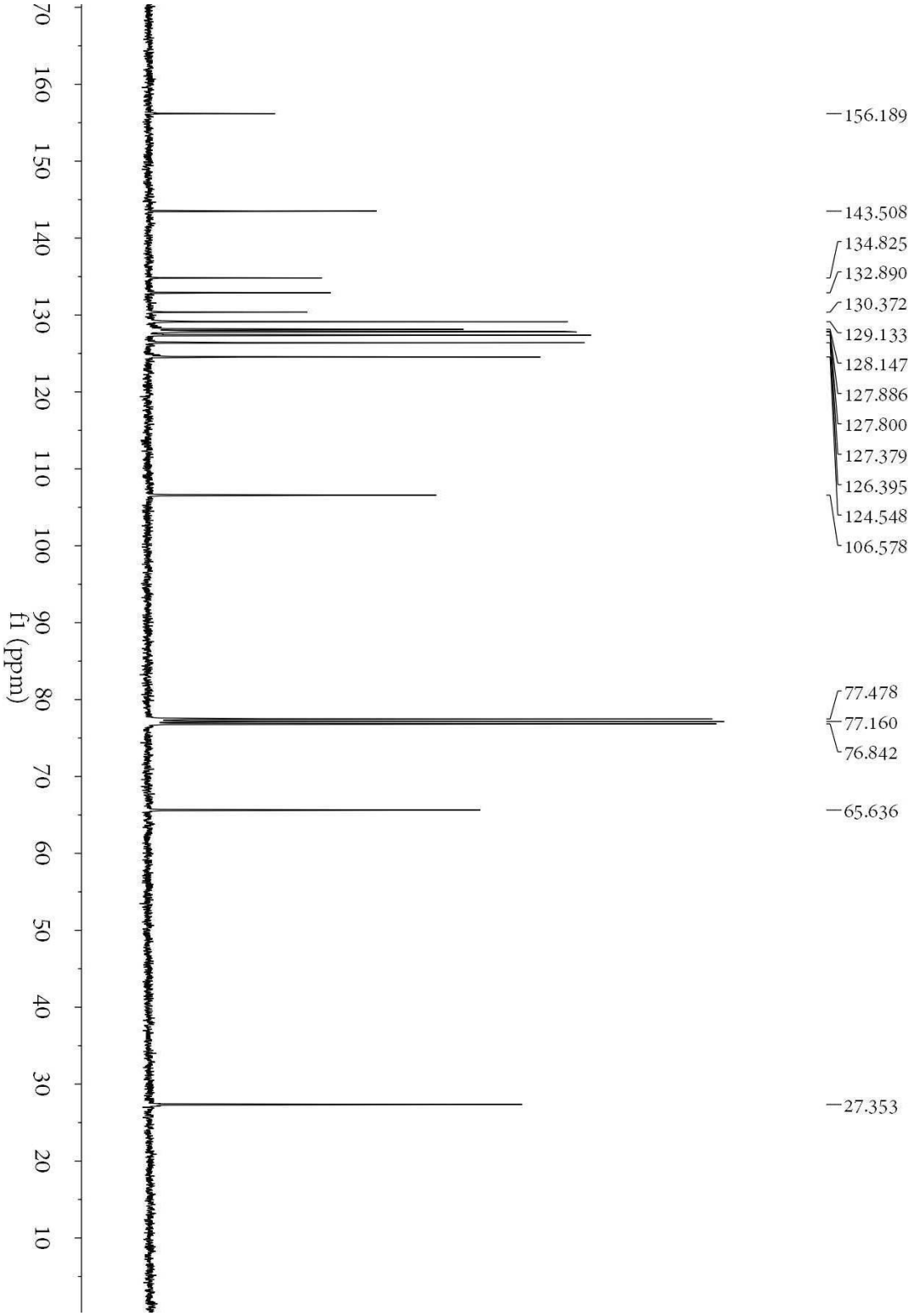


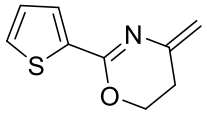
^{1}H NMR of **2q**, 72%
$CDCl_3$, 400 MHz



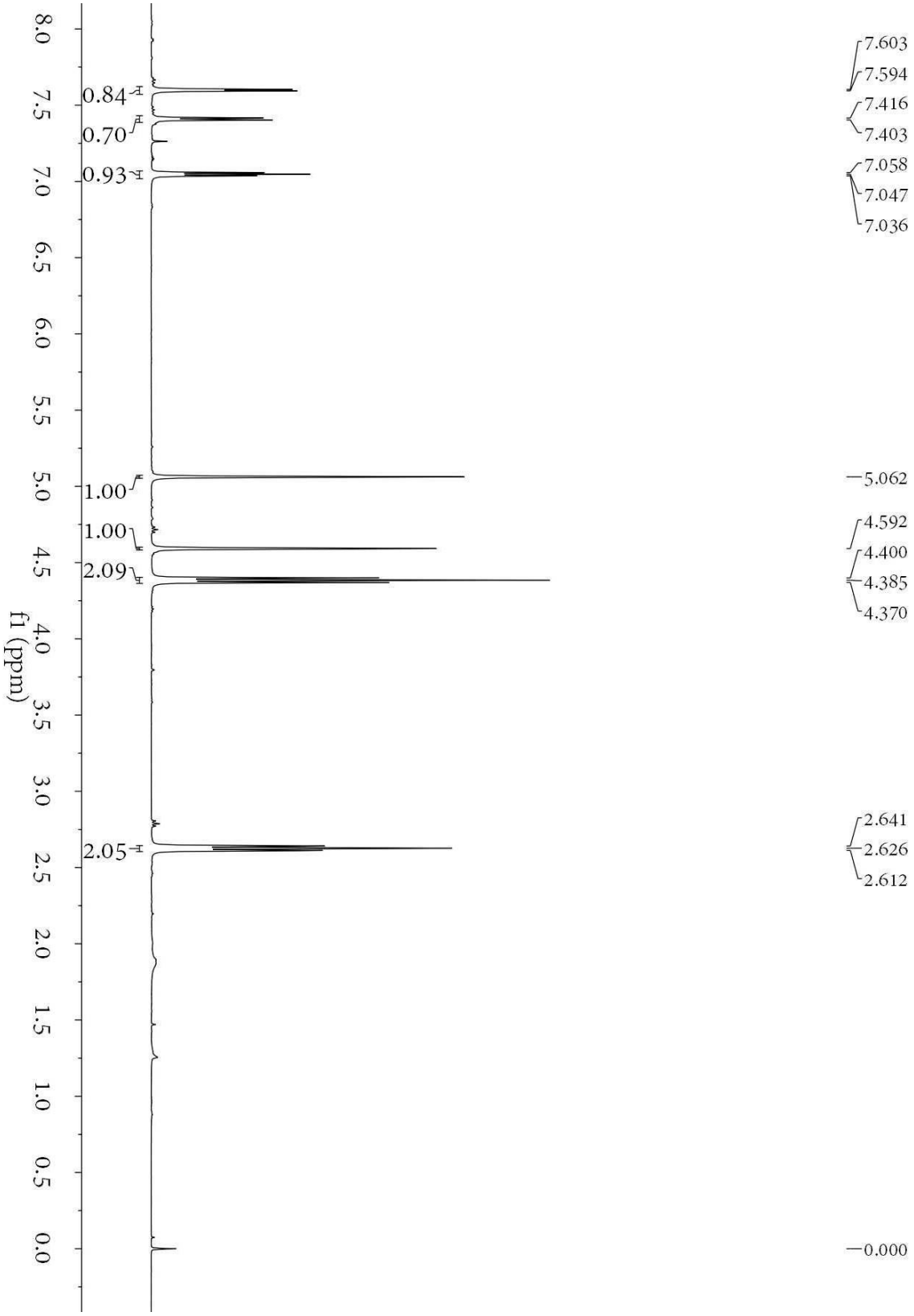


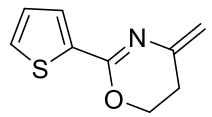
^{13}C NMR of **2q**, 72%
$CDCl_3$, 100 MHz



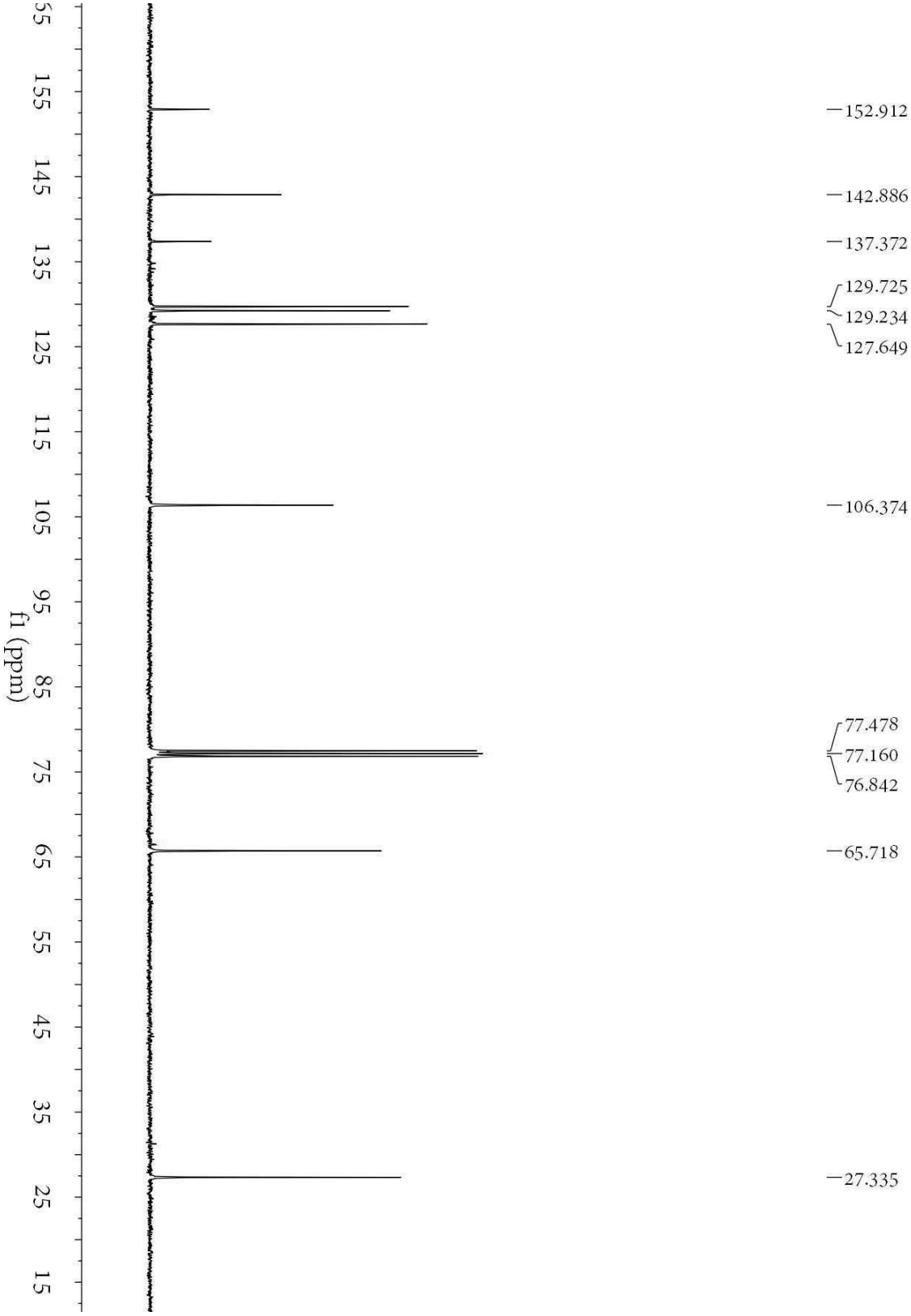


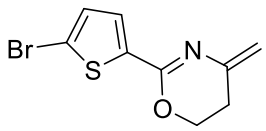
^{1}H NMR of **2r**, 81%
$CDCl_3$, 400 MHz



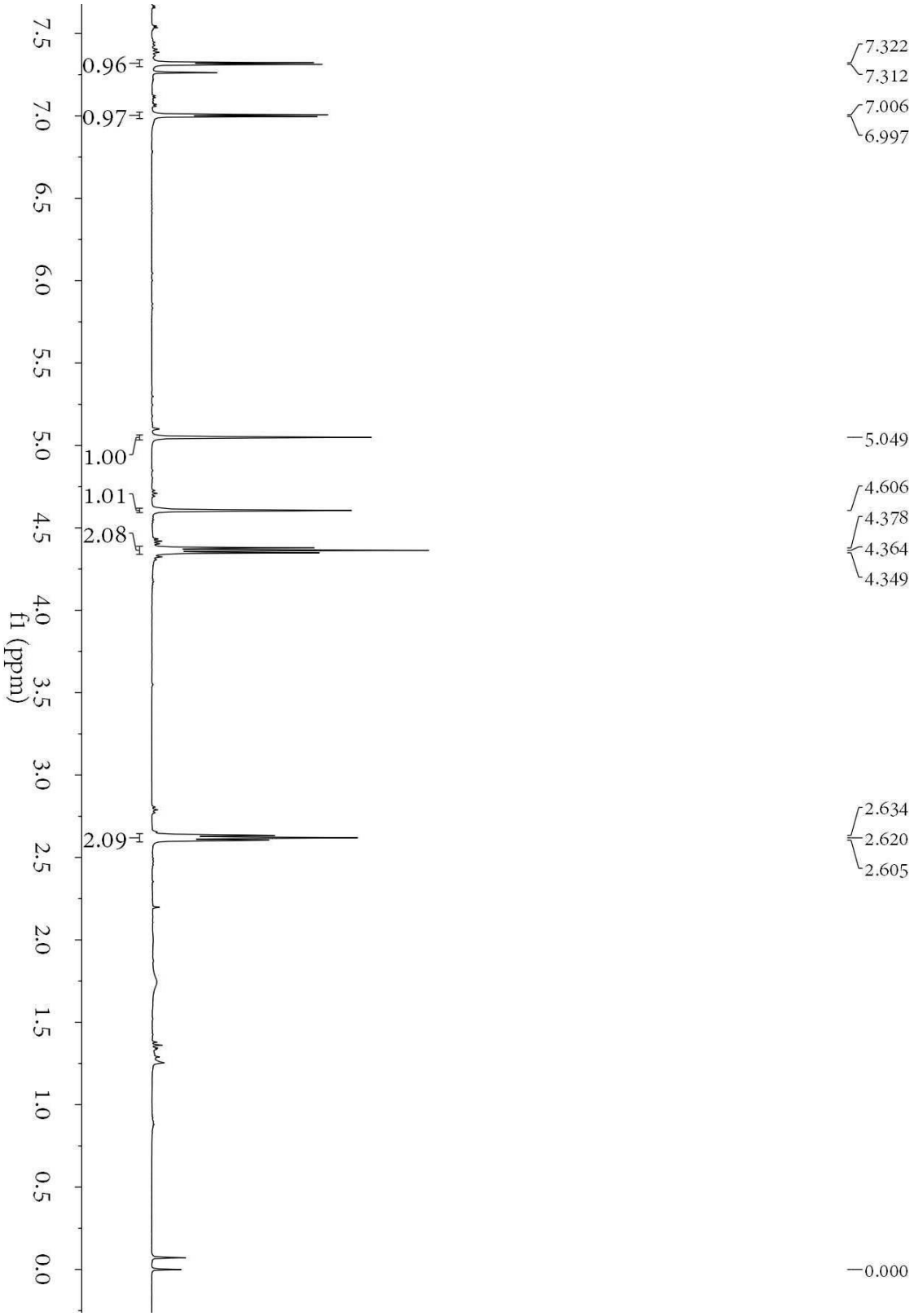


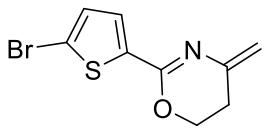
^{13}C NMR of **2r**, 81%
$CDCl_3$, 100 MHz



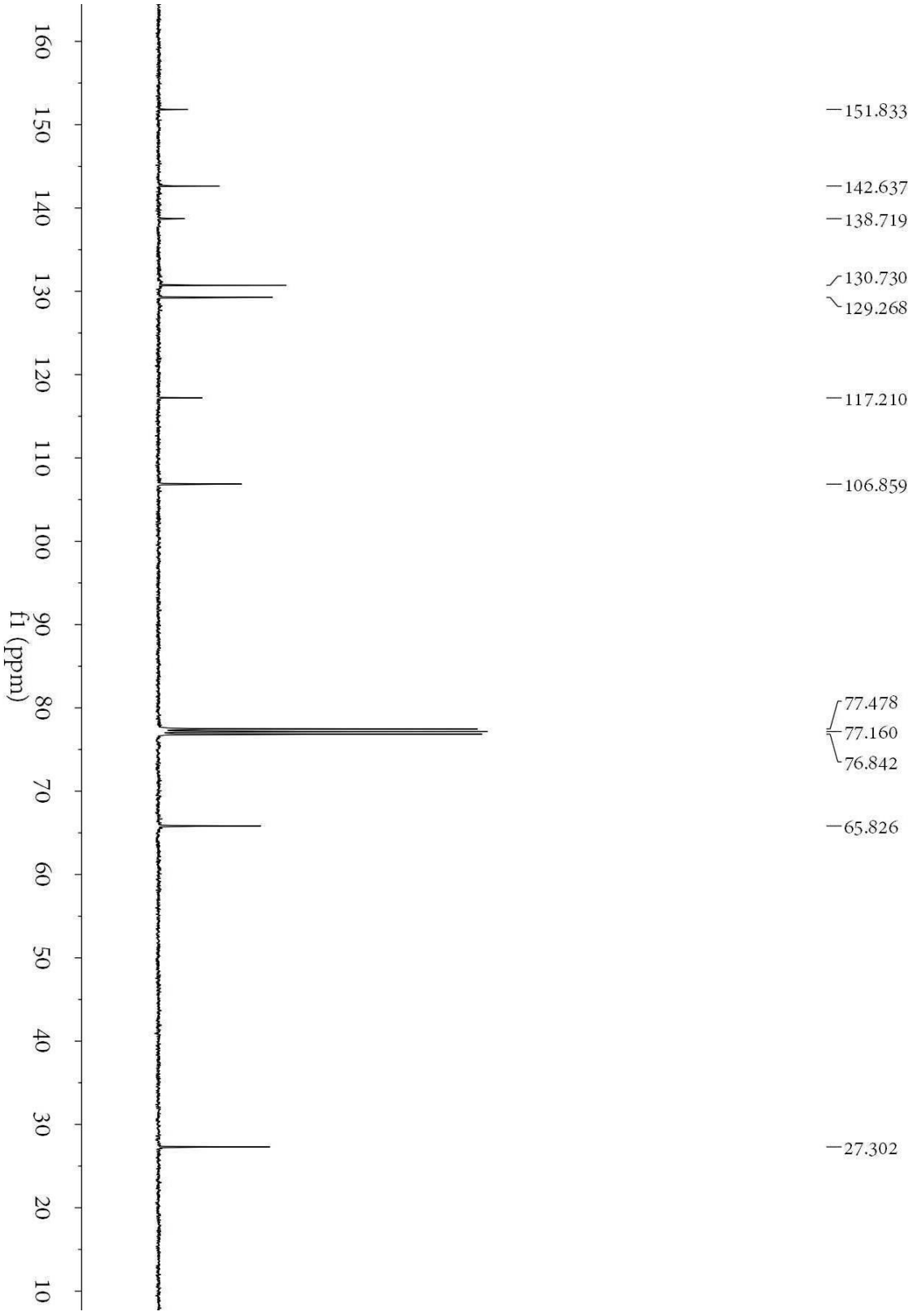


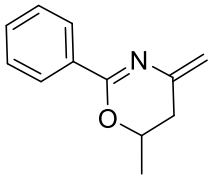
^{1}H NMR of **2s**, 63%
$CDCl_3$, 400 MHz



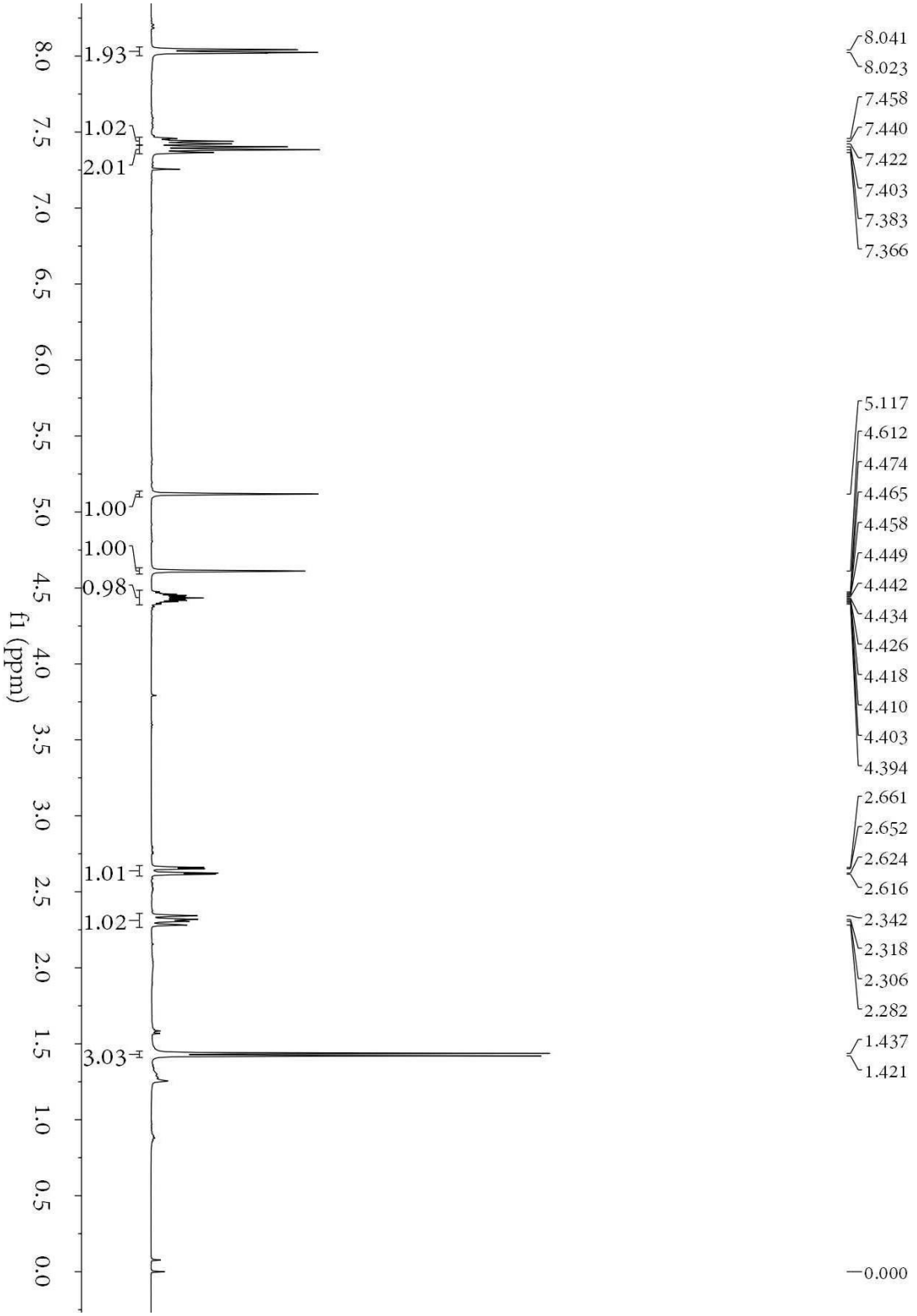


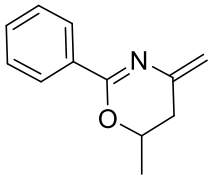
^{13}C NMR of **2s**, 63%
$CDCl_3$, 100 MHz



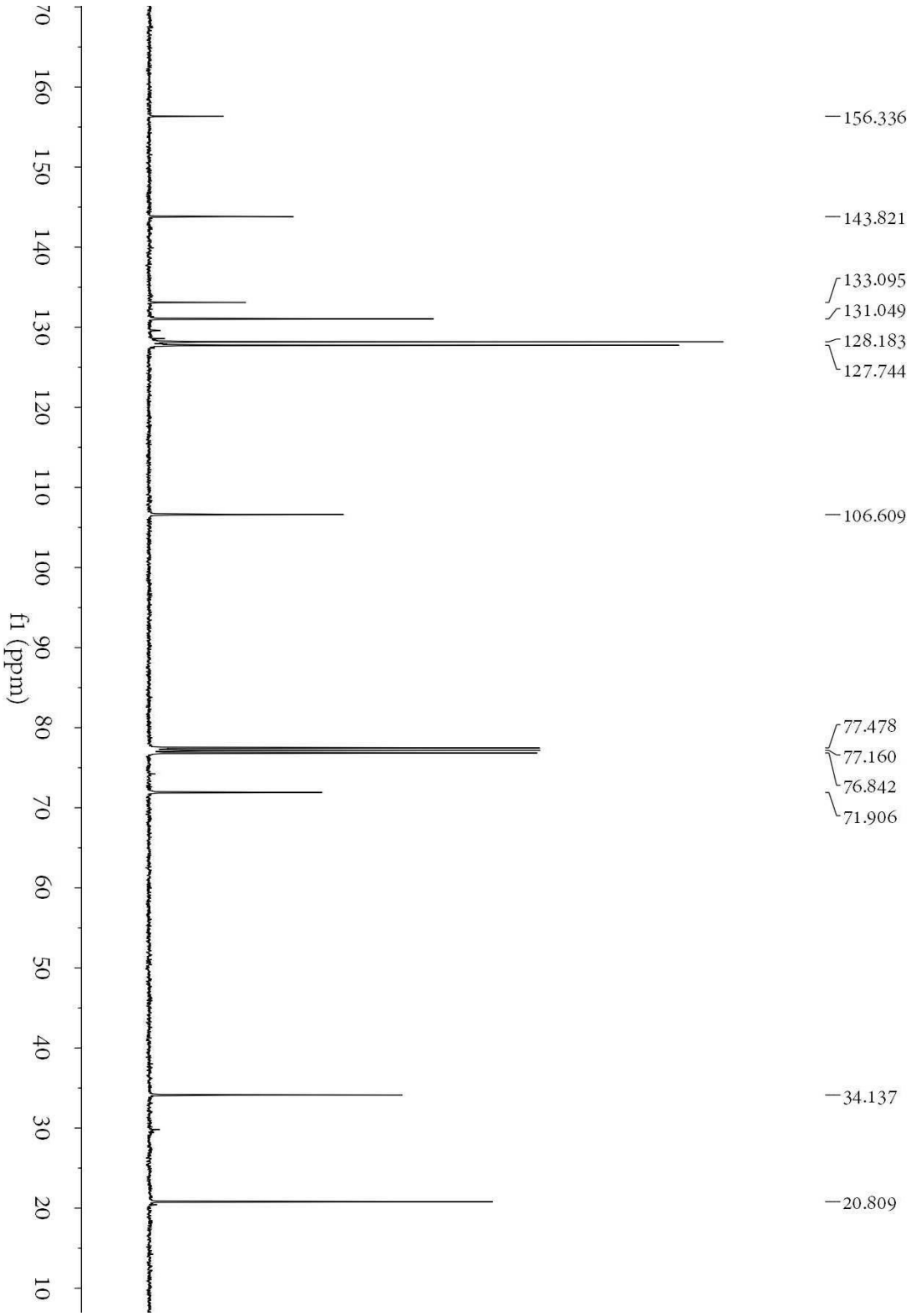


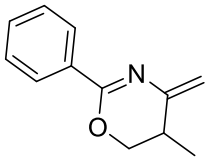
^{1}H NMR of **2t**, 85%
$CDCl_3$, 400 MHz



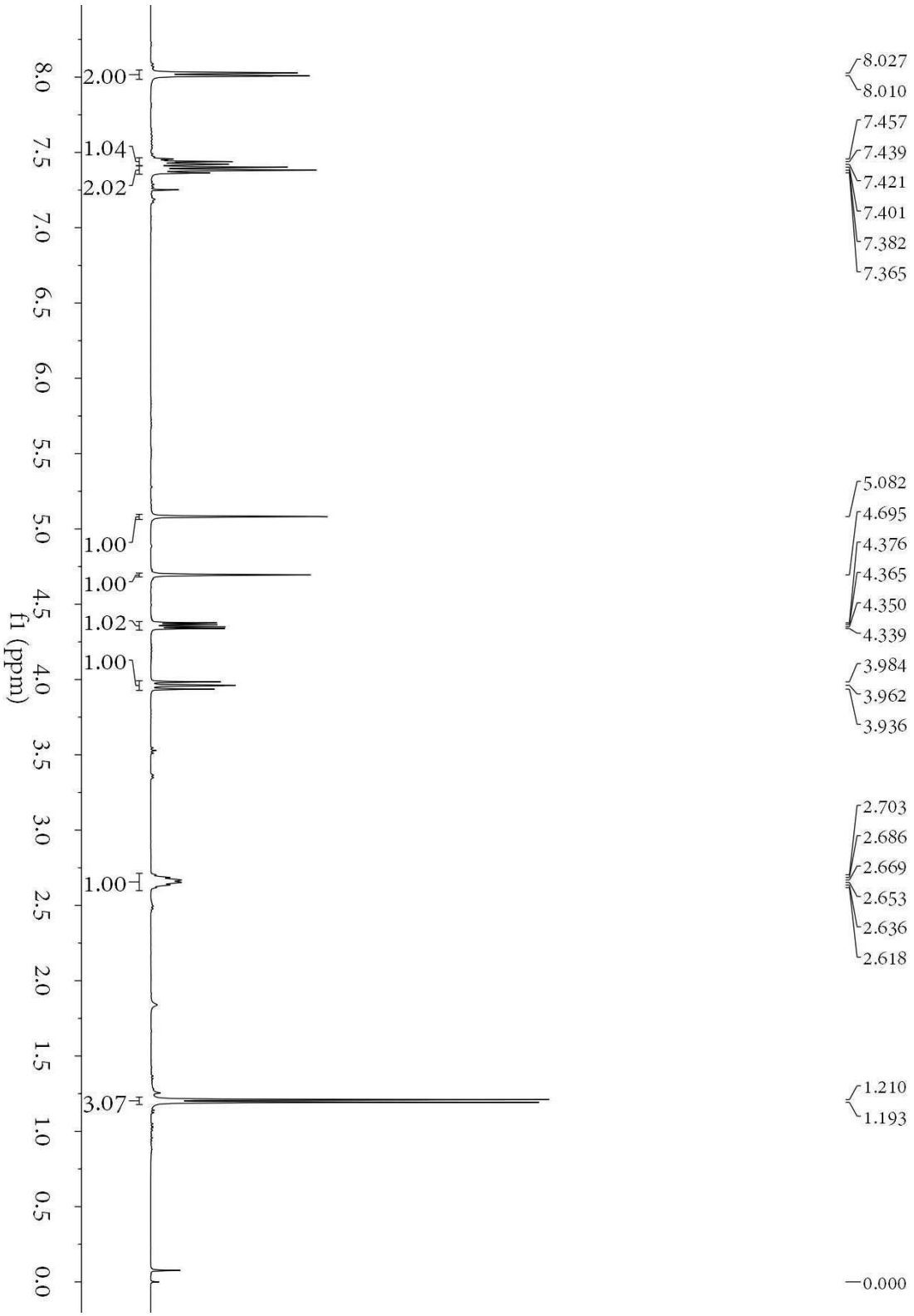


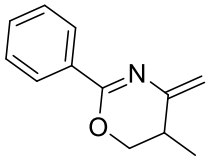
^{13}C NMR of **2t**, 85%
$CDCl_3$, 100 MHz



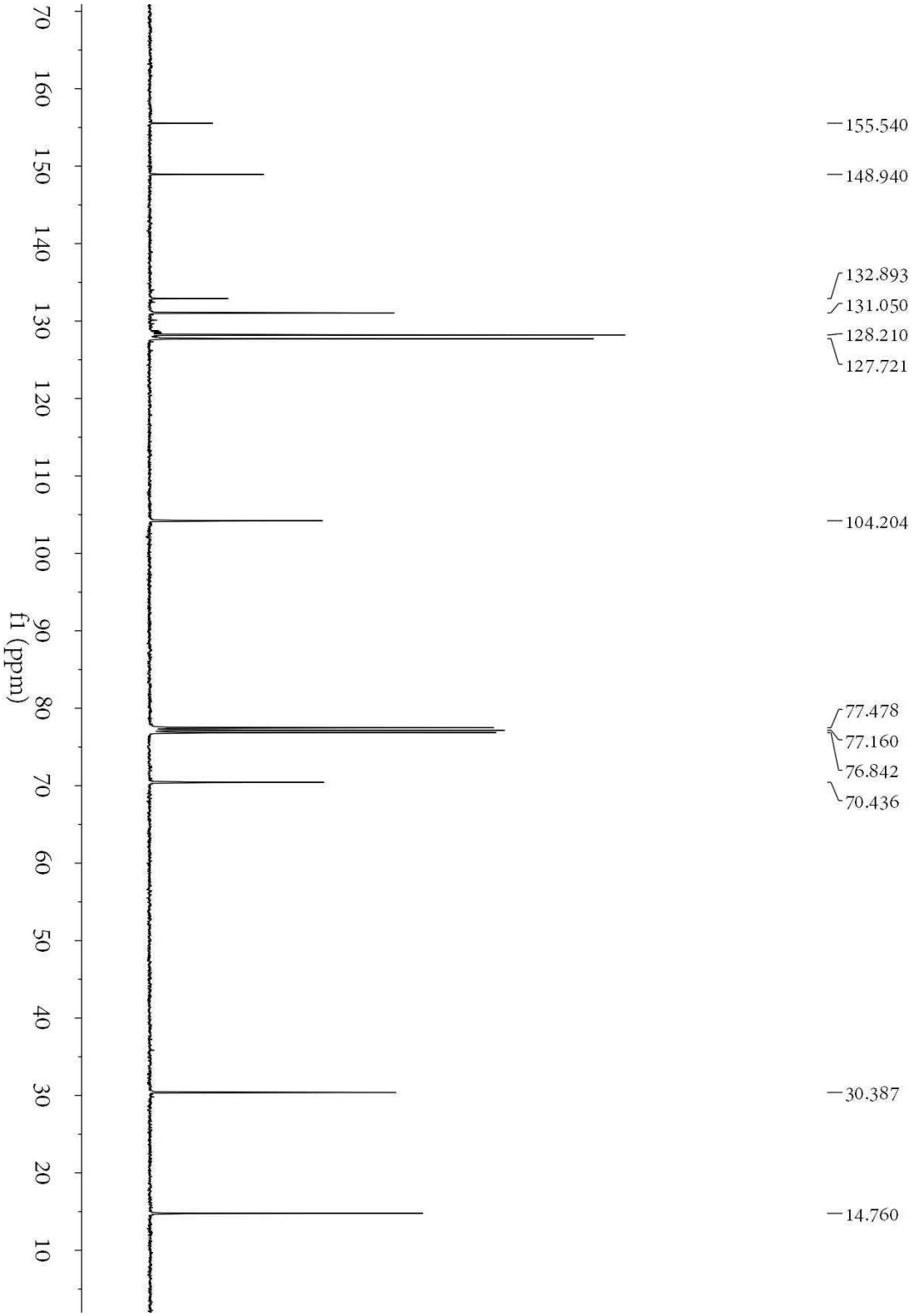


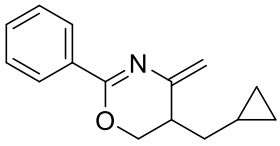
^{1}H NMR of **2u**, 81%
$CDCl_3$, 400 MHz



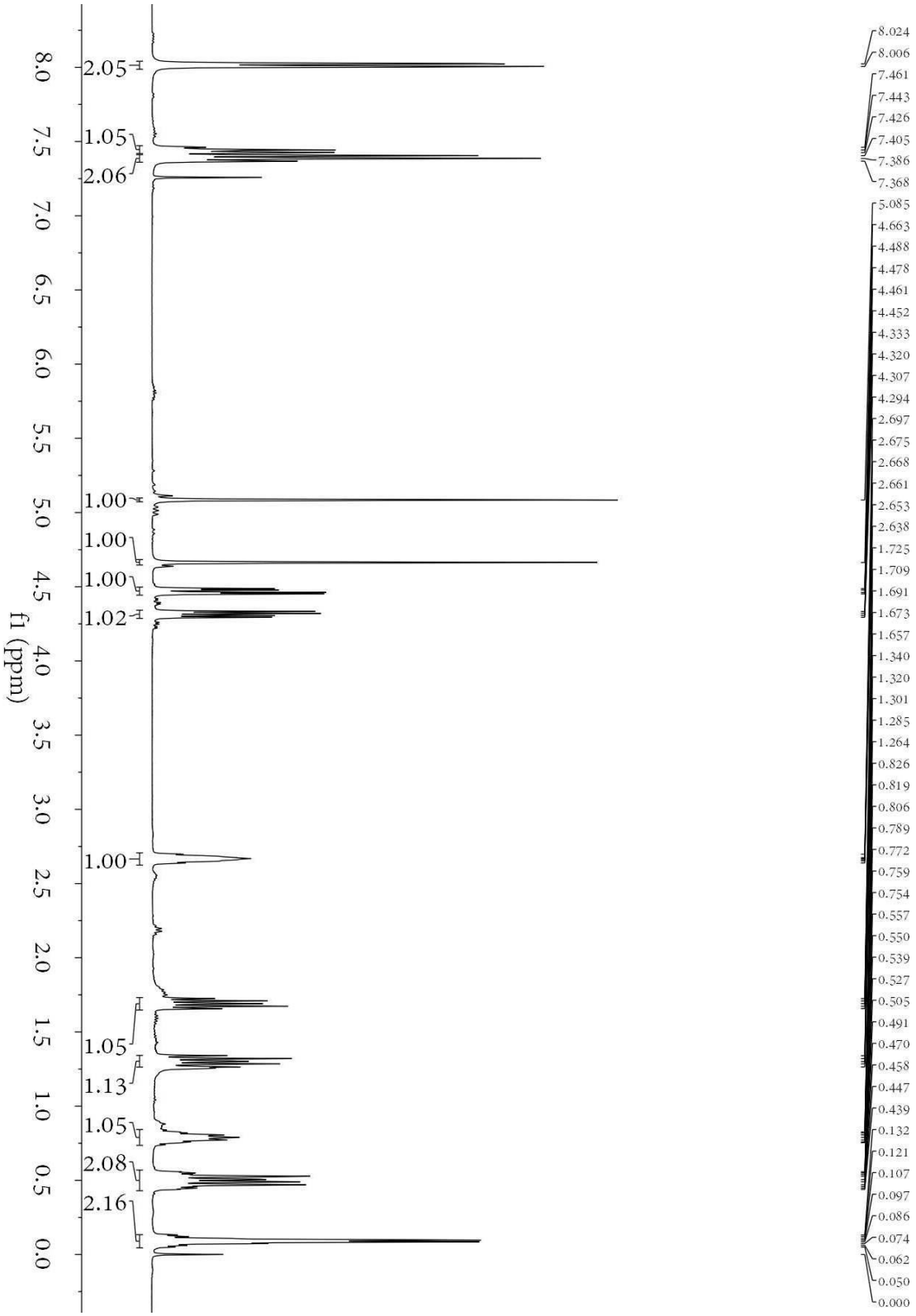


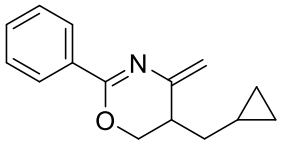
^{13}C NMR of **2u**, 81%
$CDCl_3$, 100 MHz



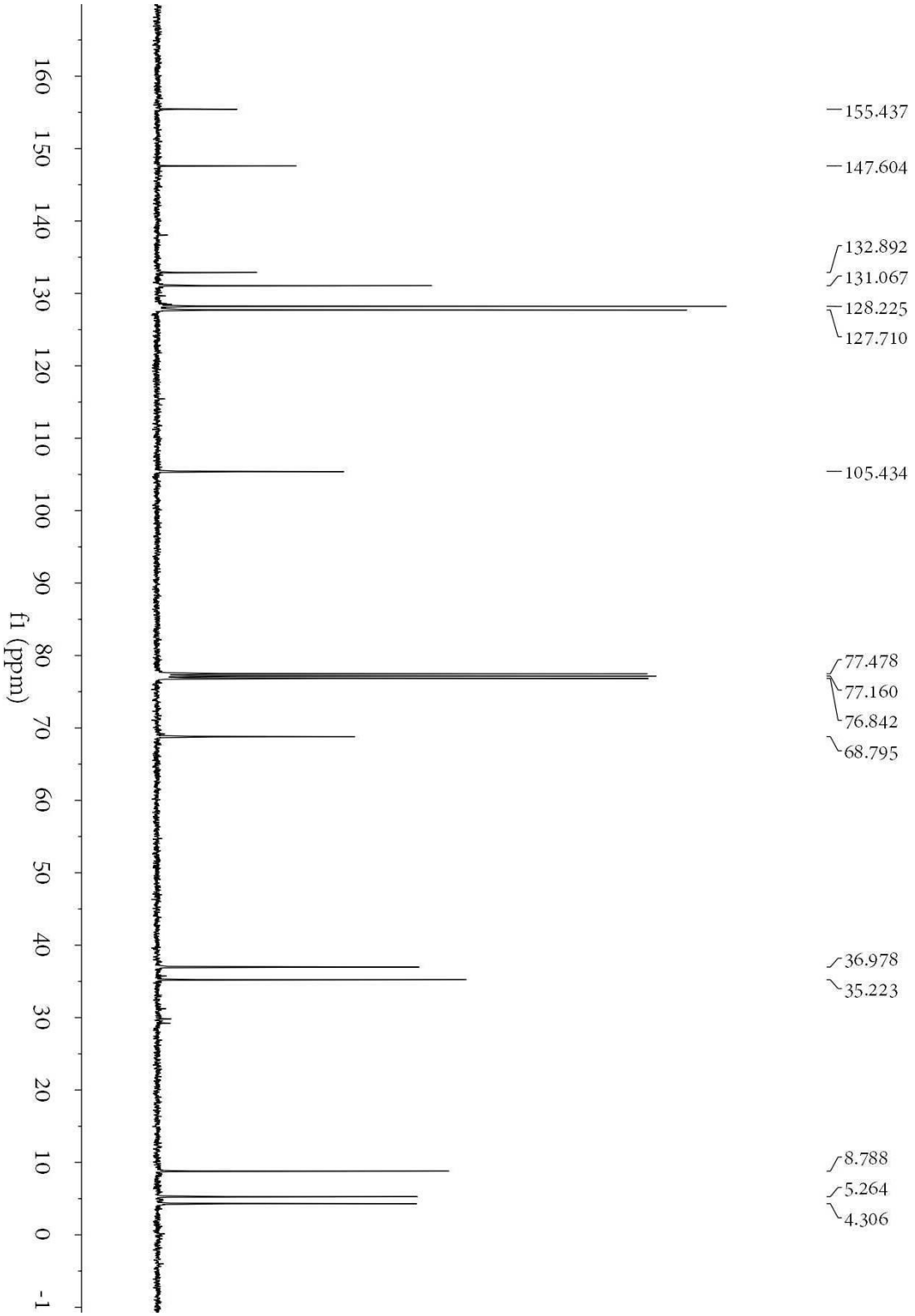


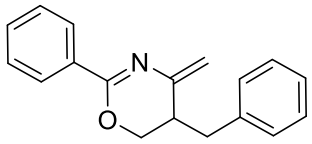
^{1}H NMR of **2v**, 72%
$CDCl_3$, 400 MHz



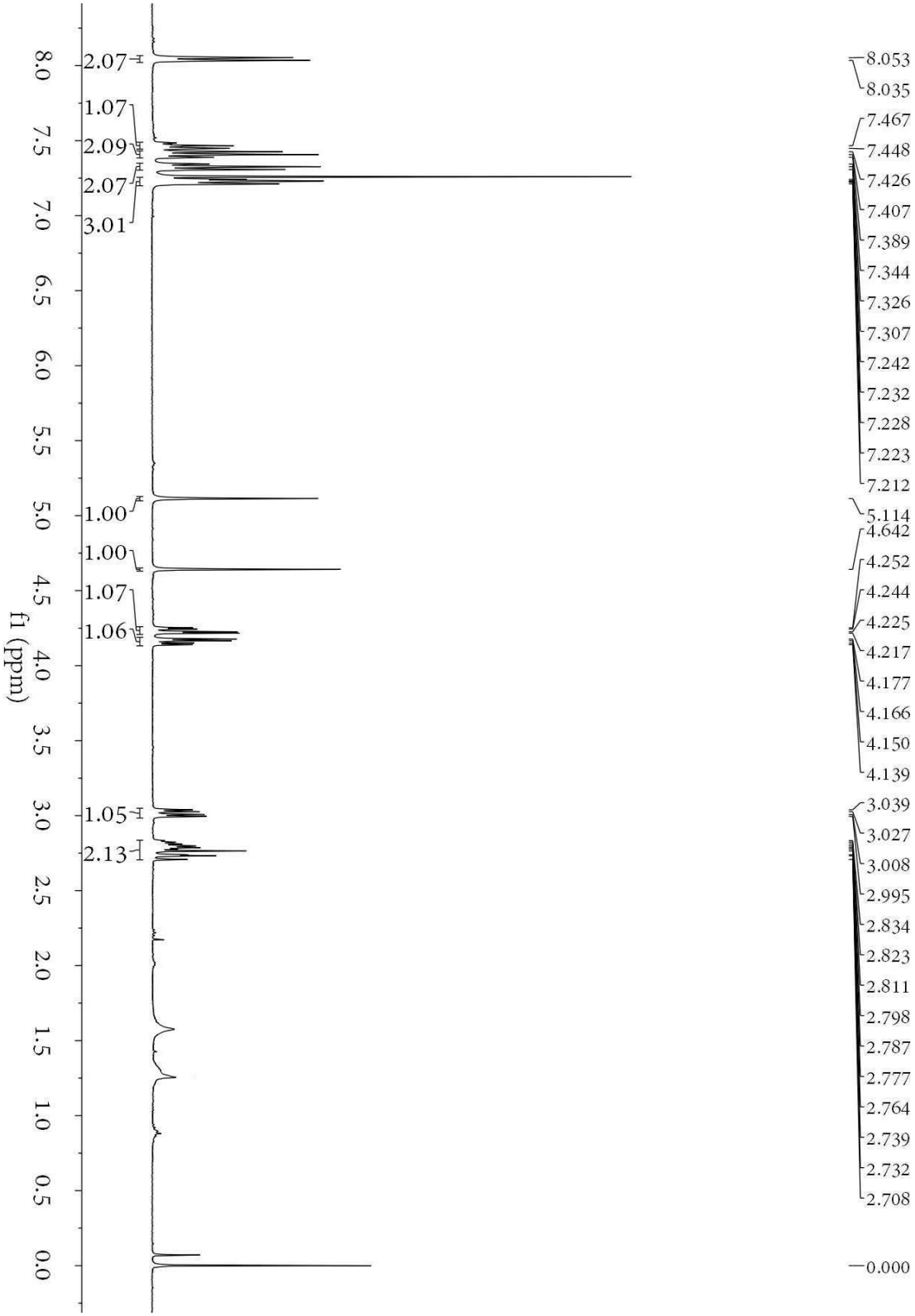


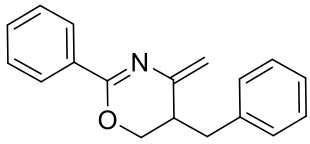
^{13}C NMR of **2v**, 72%
$CDCl_3$, 100 MHz



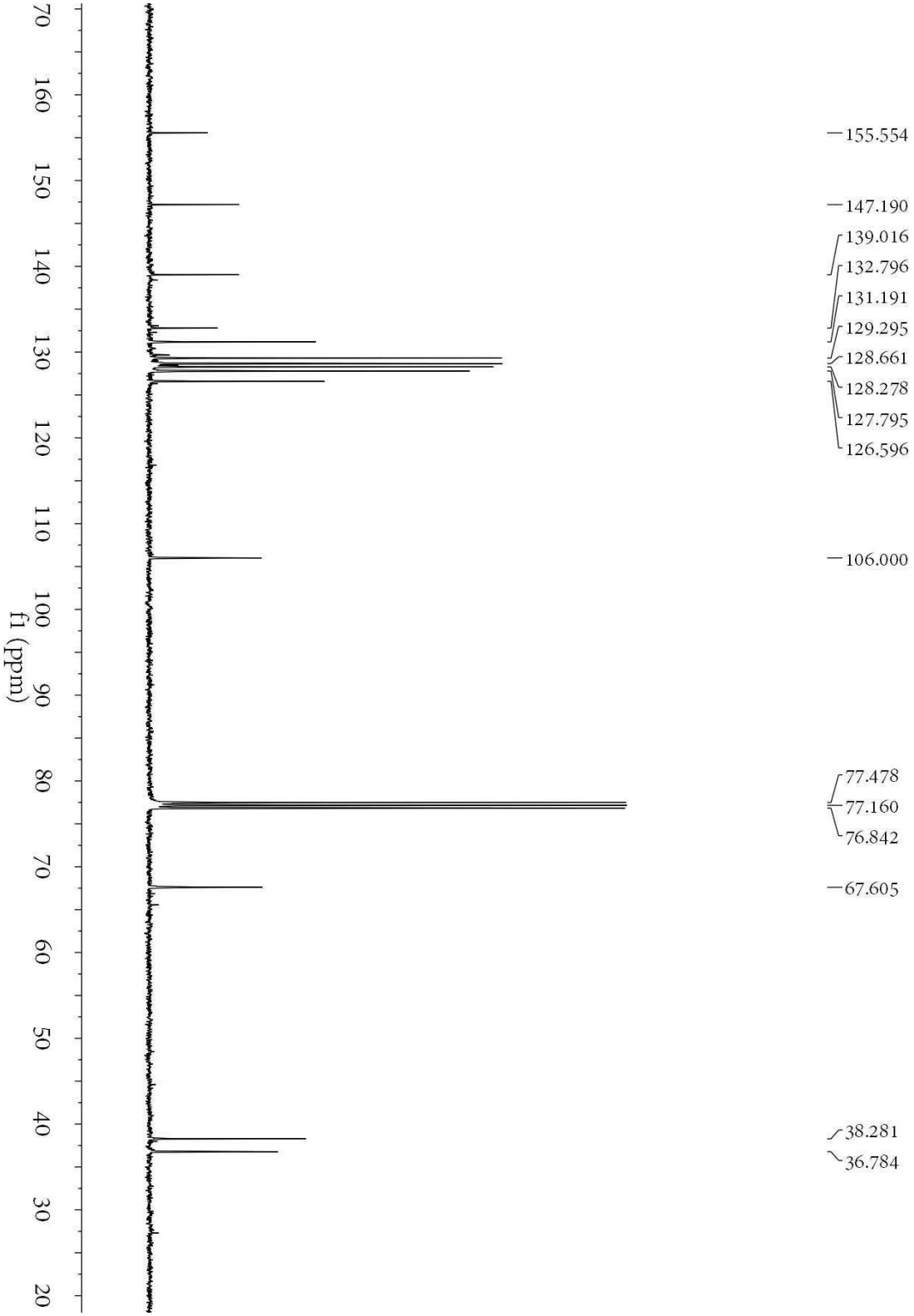


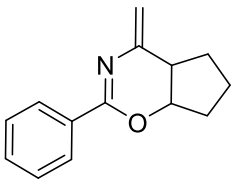
^{1}H NMR of **2w**, 83%
$CDCl_3$, 400 MHz



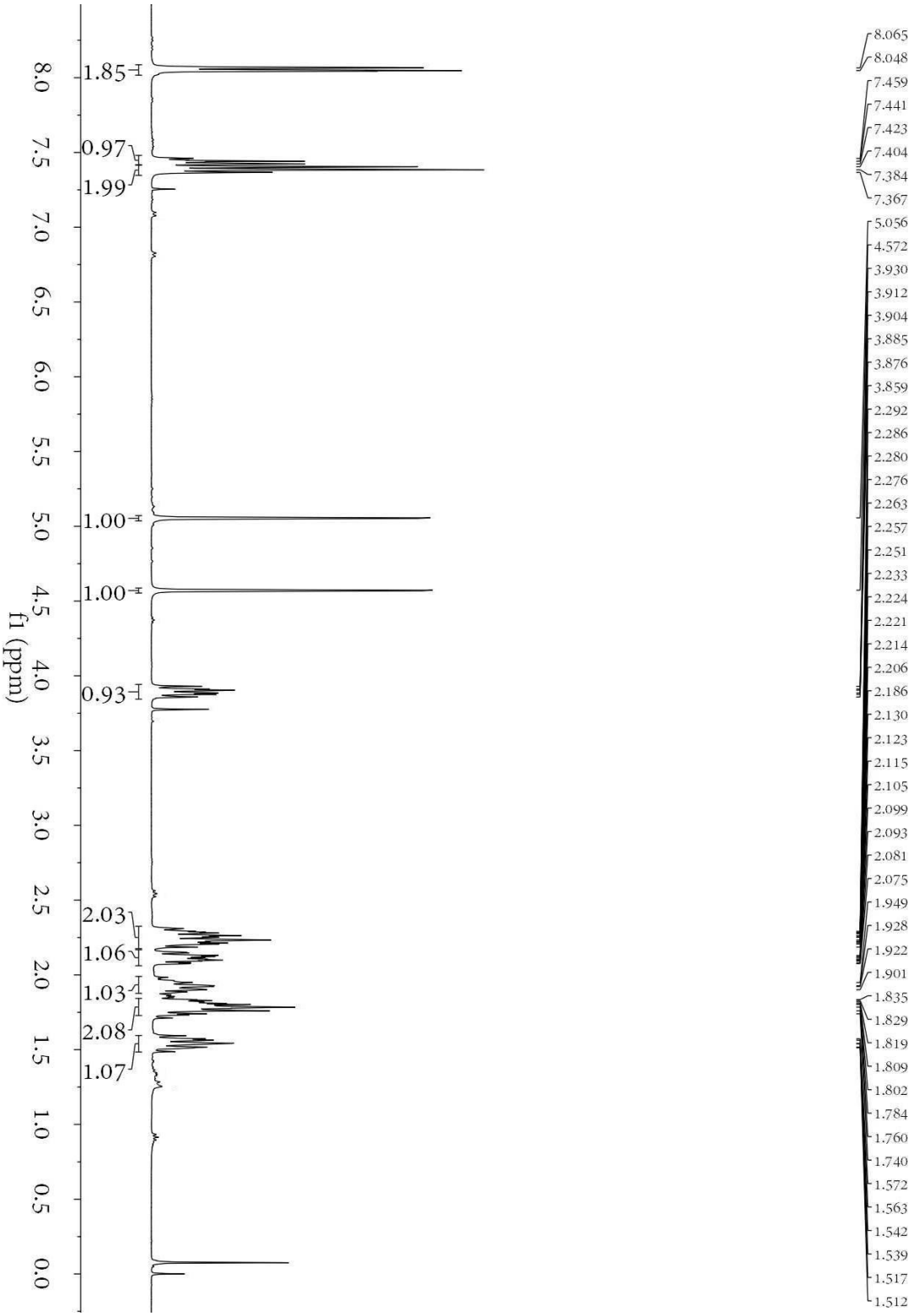


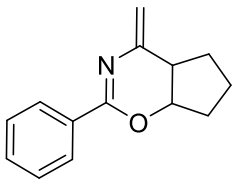
^{13}C NMR of **2w**, 83%
$CDCl_3$, 100 MHz



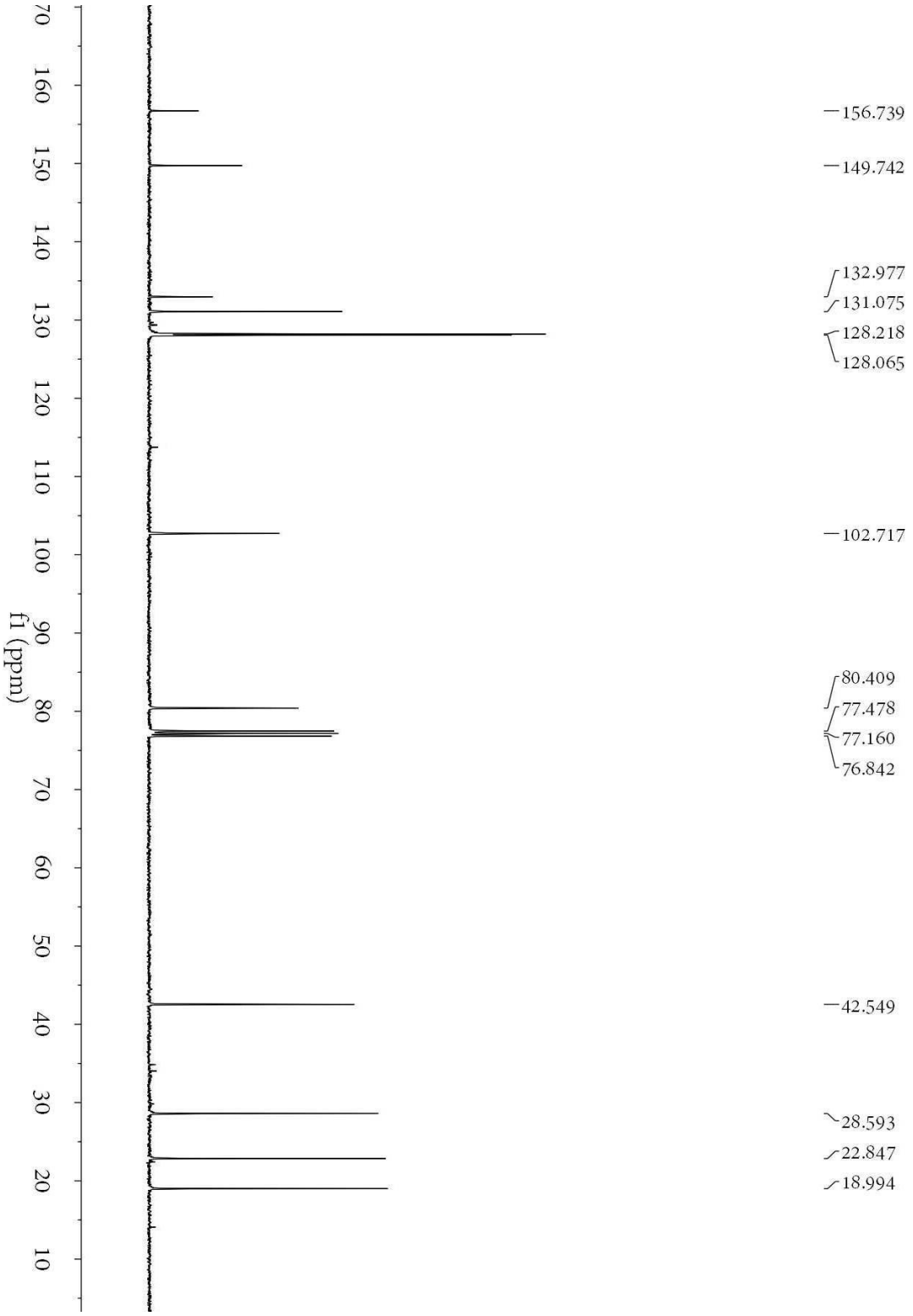


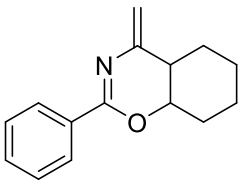
^{1}H NMR of **2x**, 83%
$CDCl_3$, 400 MHz



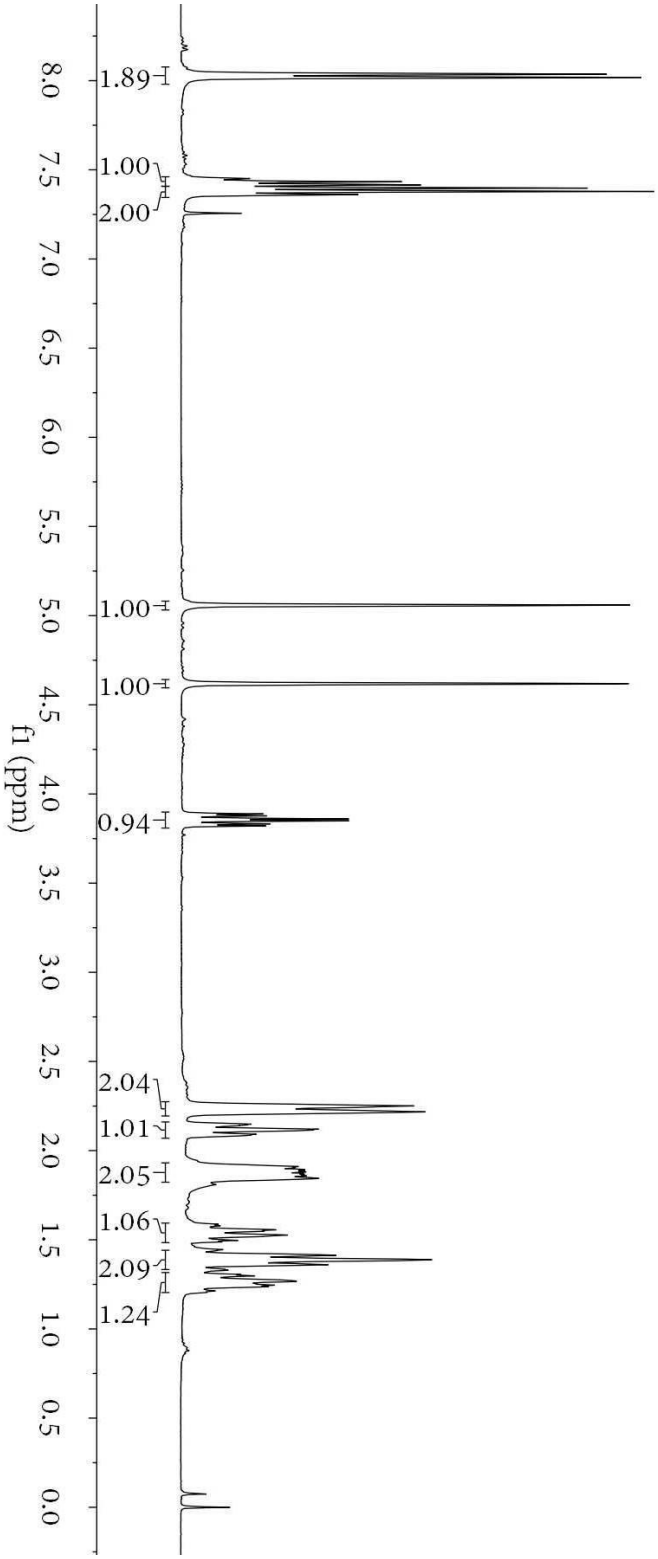


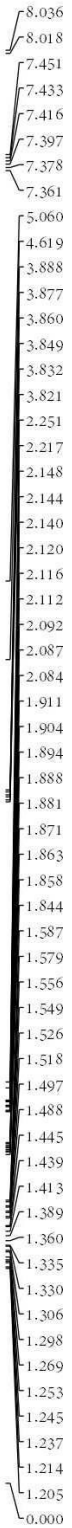
^{13}C NMR of **2x**, 83%
$CDCl_3$, 100 MHz

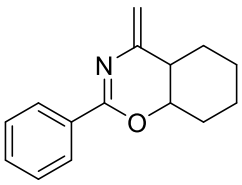




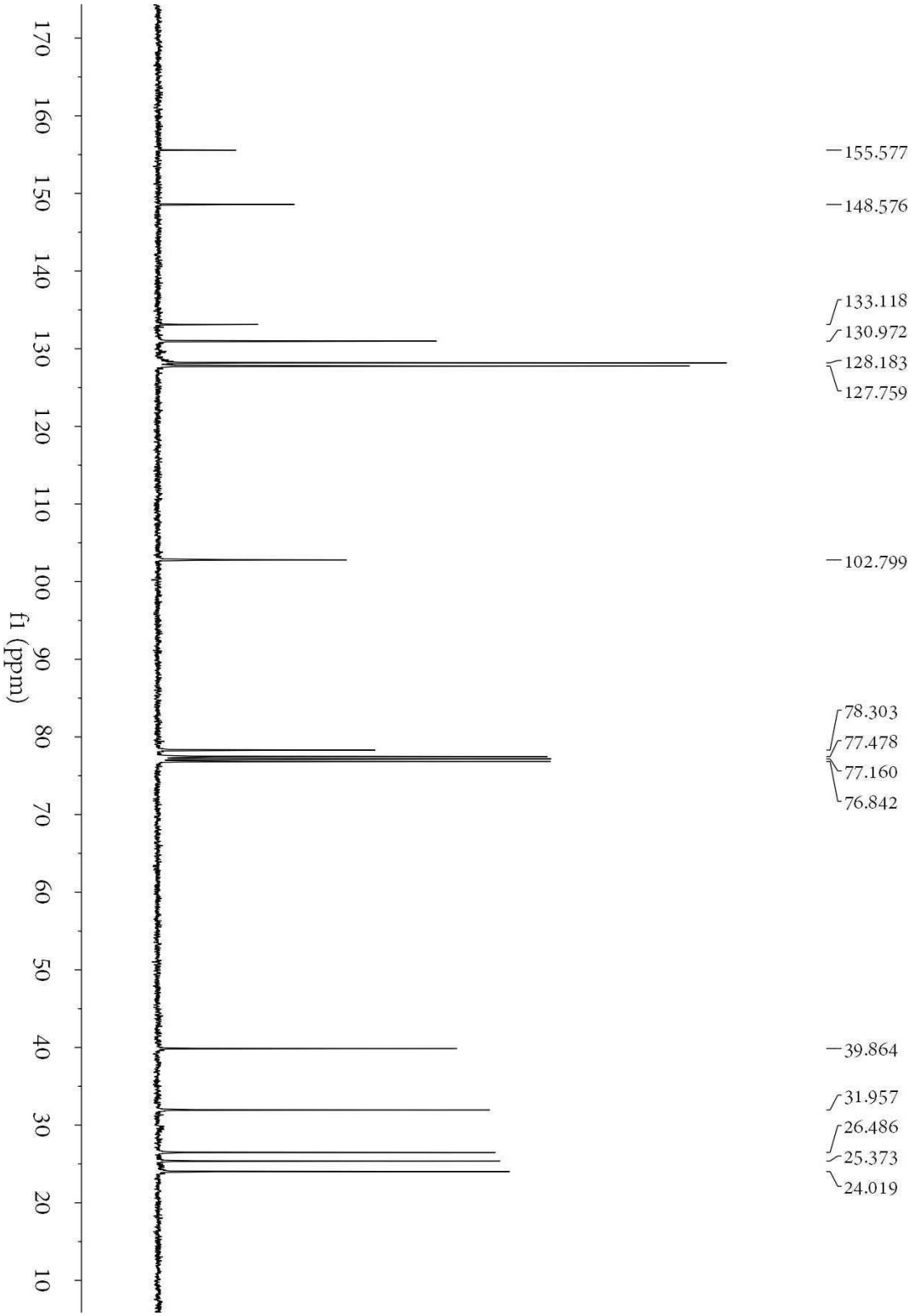
^{1}H NMR of **2y**, 76%
$CDCl_3$, 400 MHz

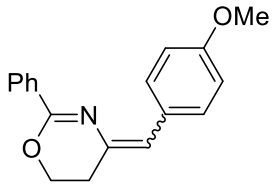




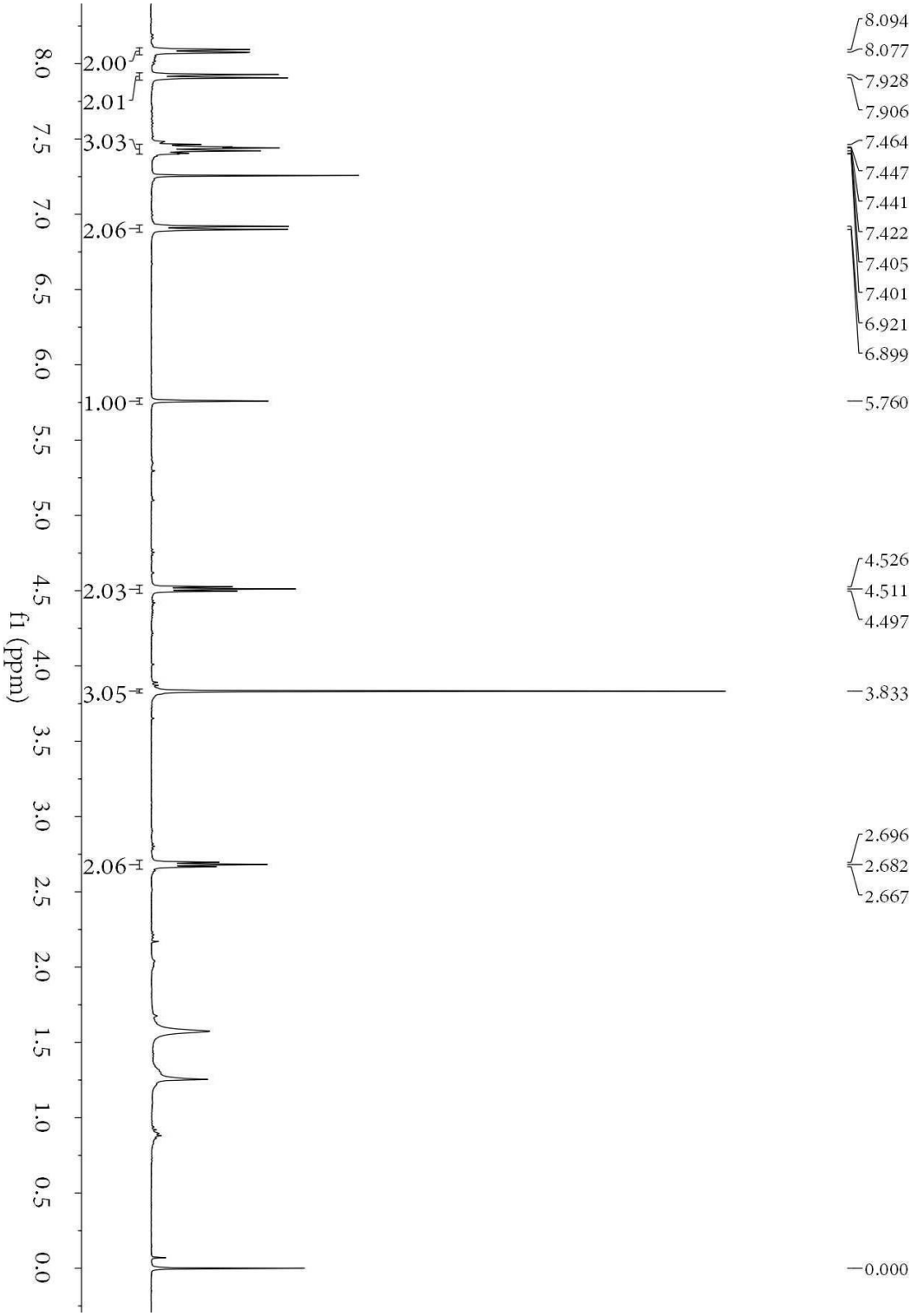


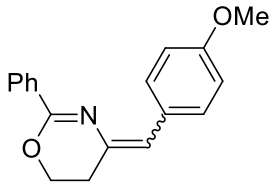
^{13}C NMR of **2y**, 76%
$CDCl_3$, 100 MHz



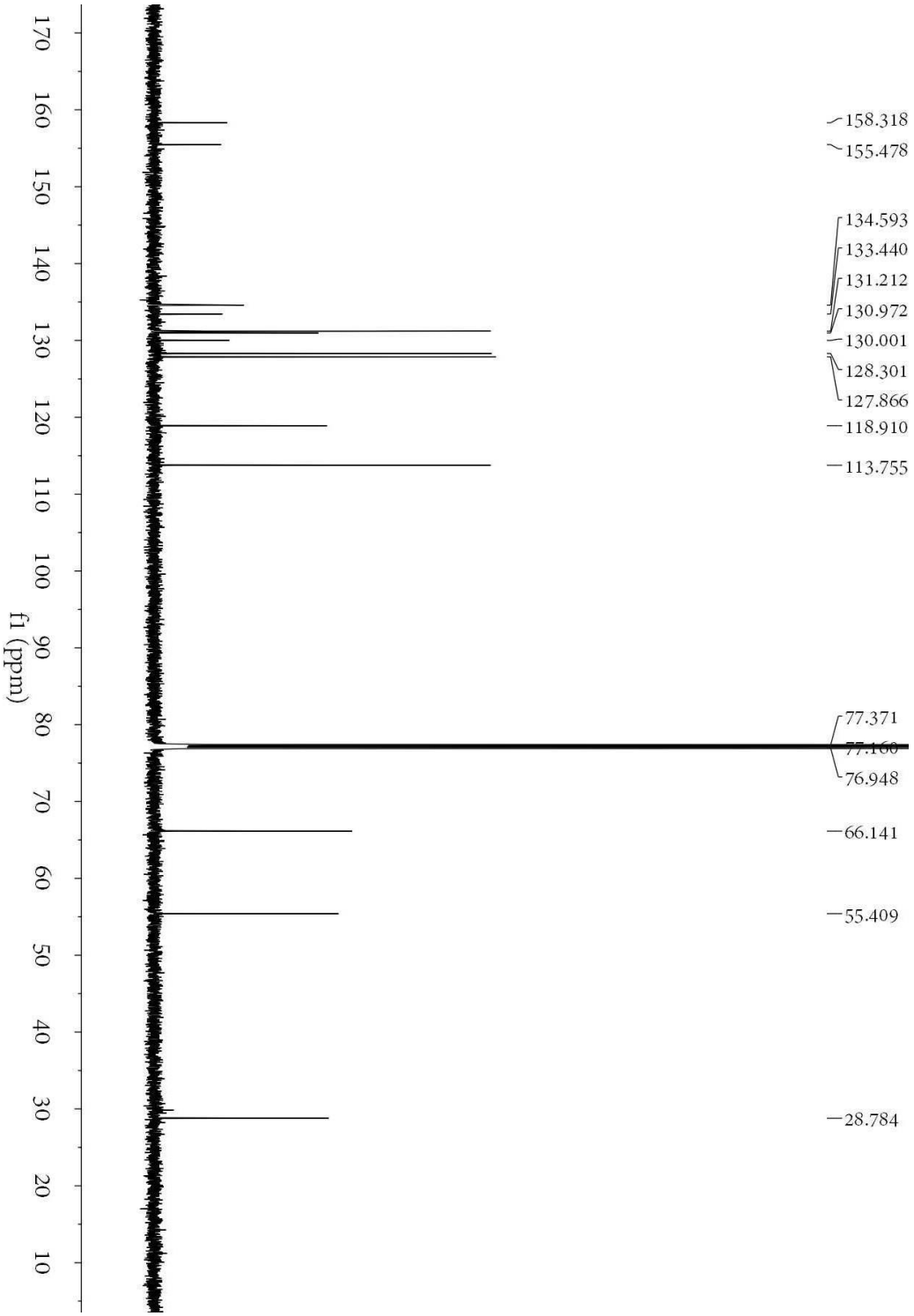


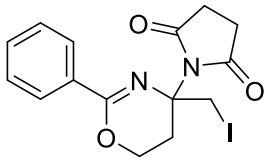
^{1}H NMR of **2aa**, 8%
$CDCl_3$, 400 MHz



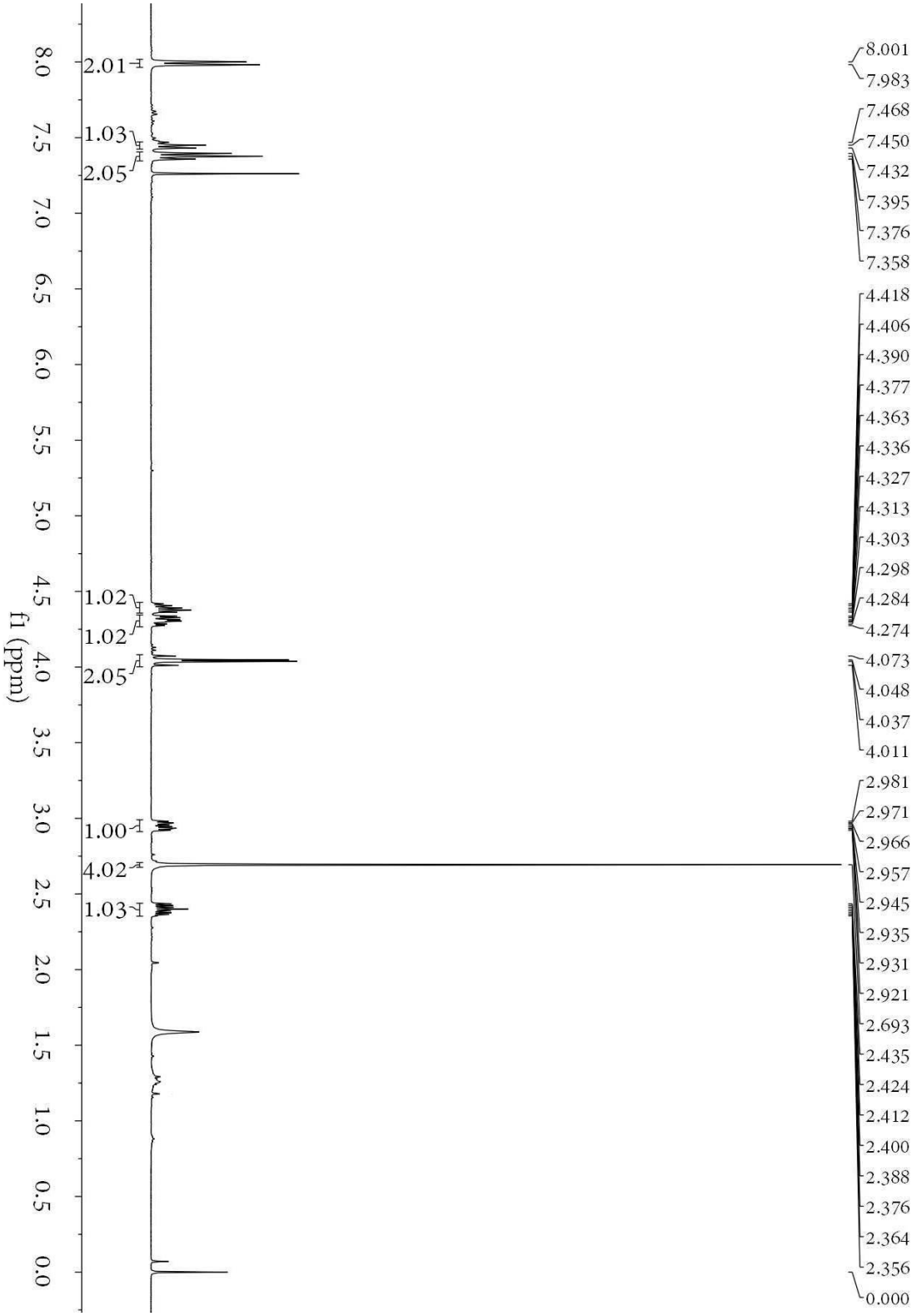


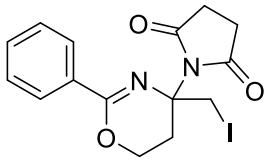
^{13}C NMR of **2aa**, 8%
$CDCl_3$, 100 MHz



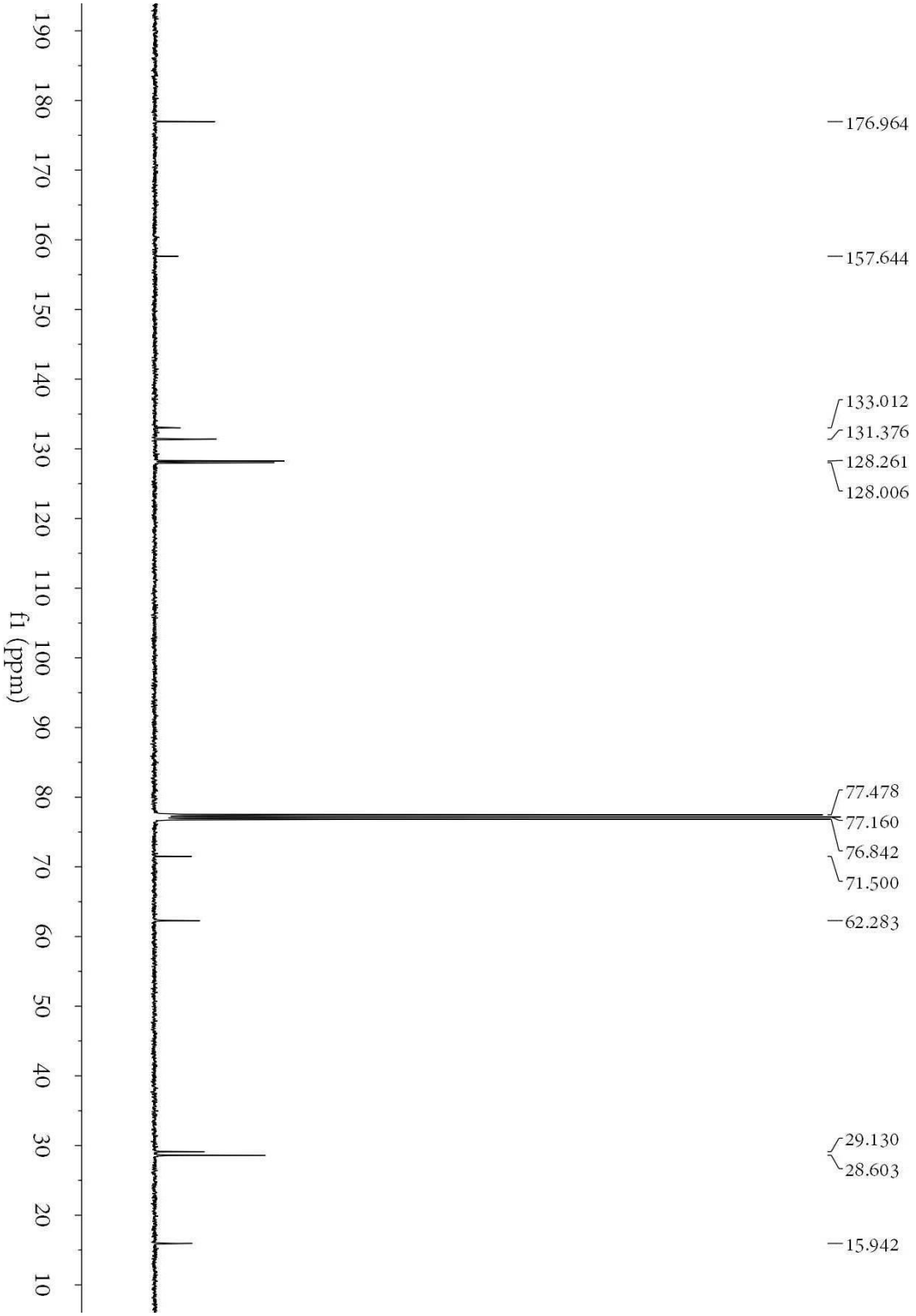


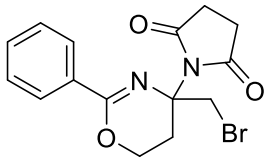
^{1}H NMR of **3a**, 46%
$CDCl_3$, 400 MHz



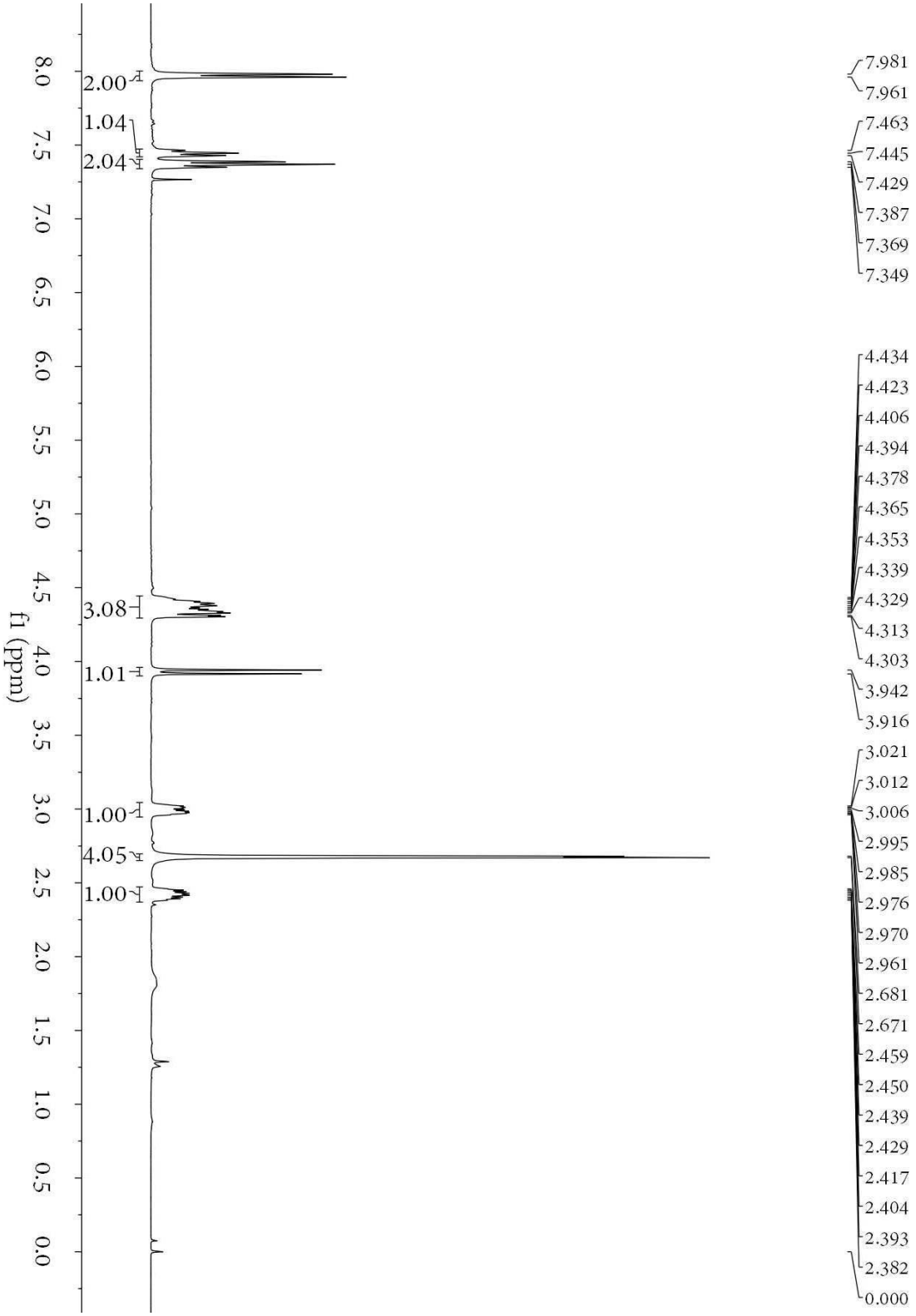


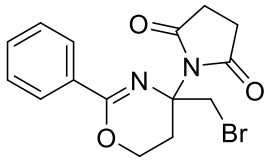
^{13}C NMR of **3a**, 46%
$CDCl_3$, 100 MHz



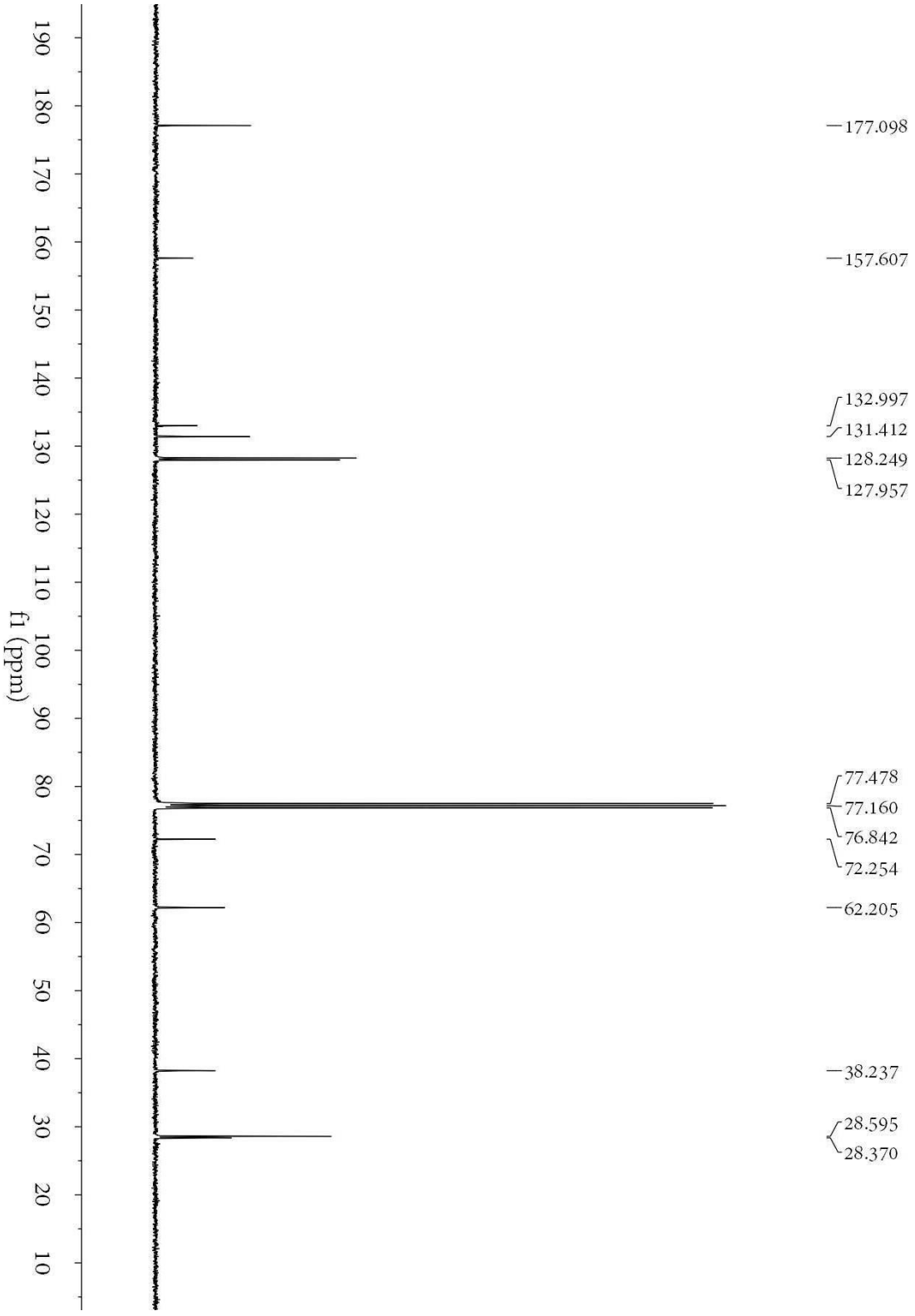


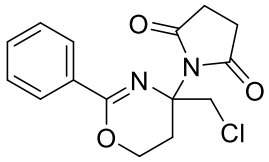
^{1}H NMR of **3b,** 56%
$CDCl_3$, 400 MHz



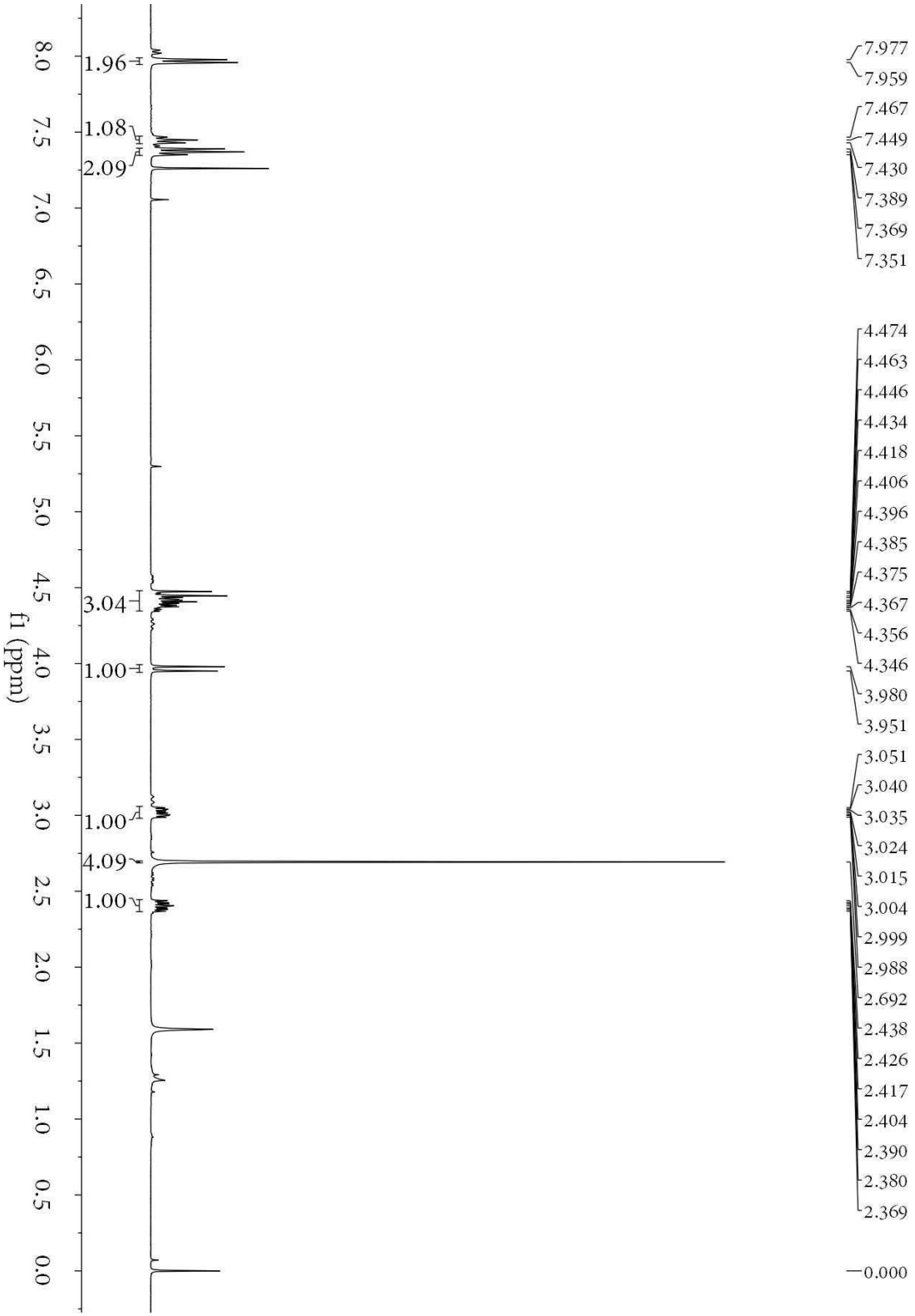


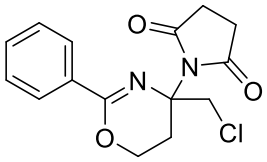
^{13}C NMR of **3b**, 56%
$CDCl_3$, 100 MHz



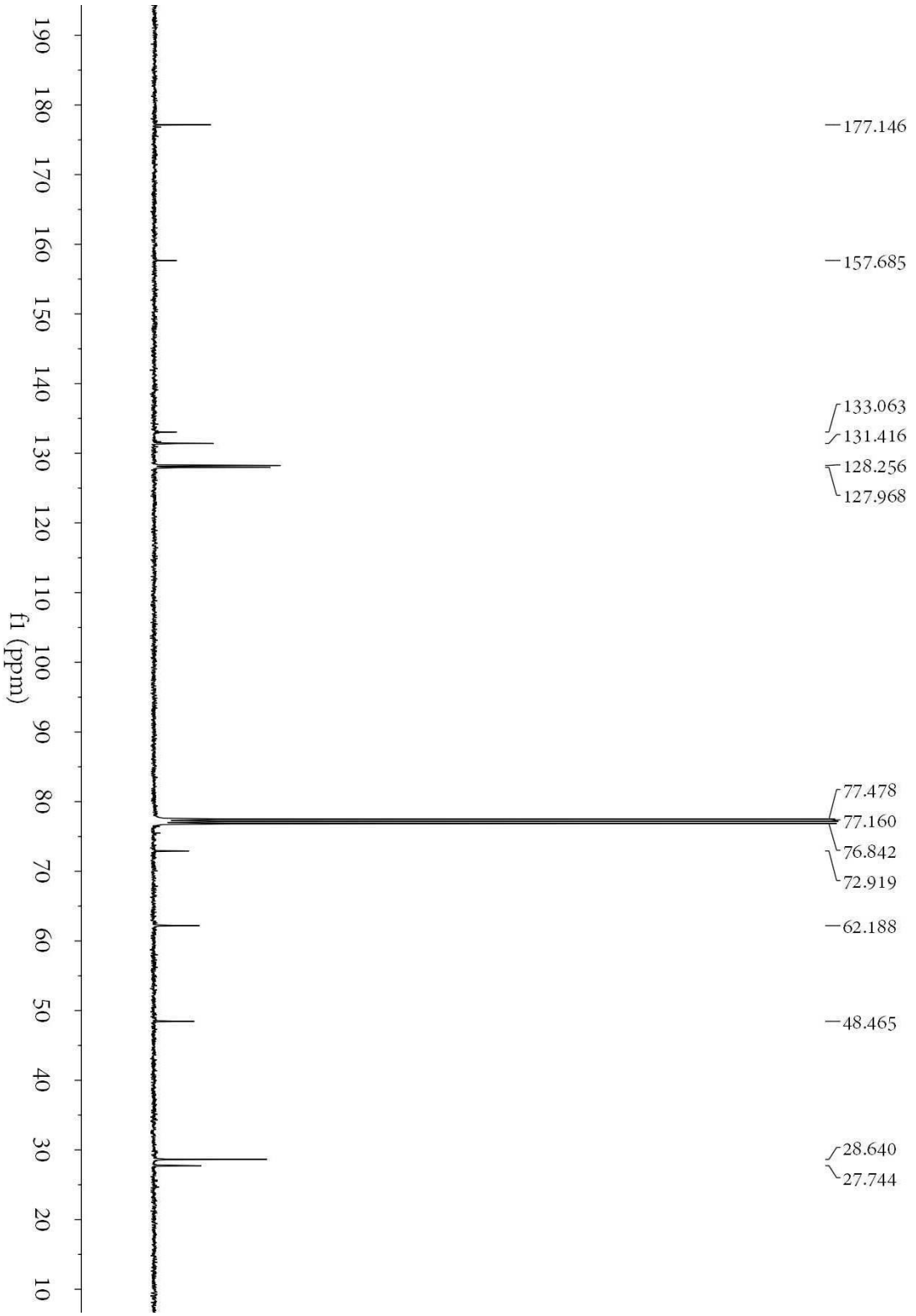


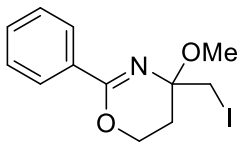
^{1}H NMR of **3c**, 57%
$CDCl_3$, 400 MHz



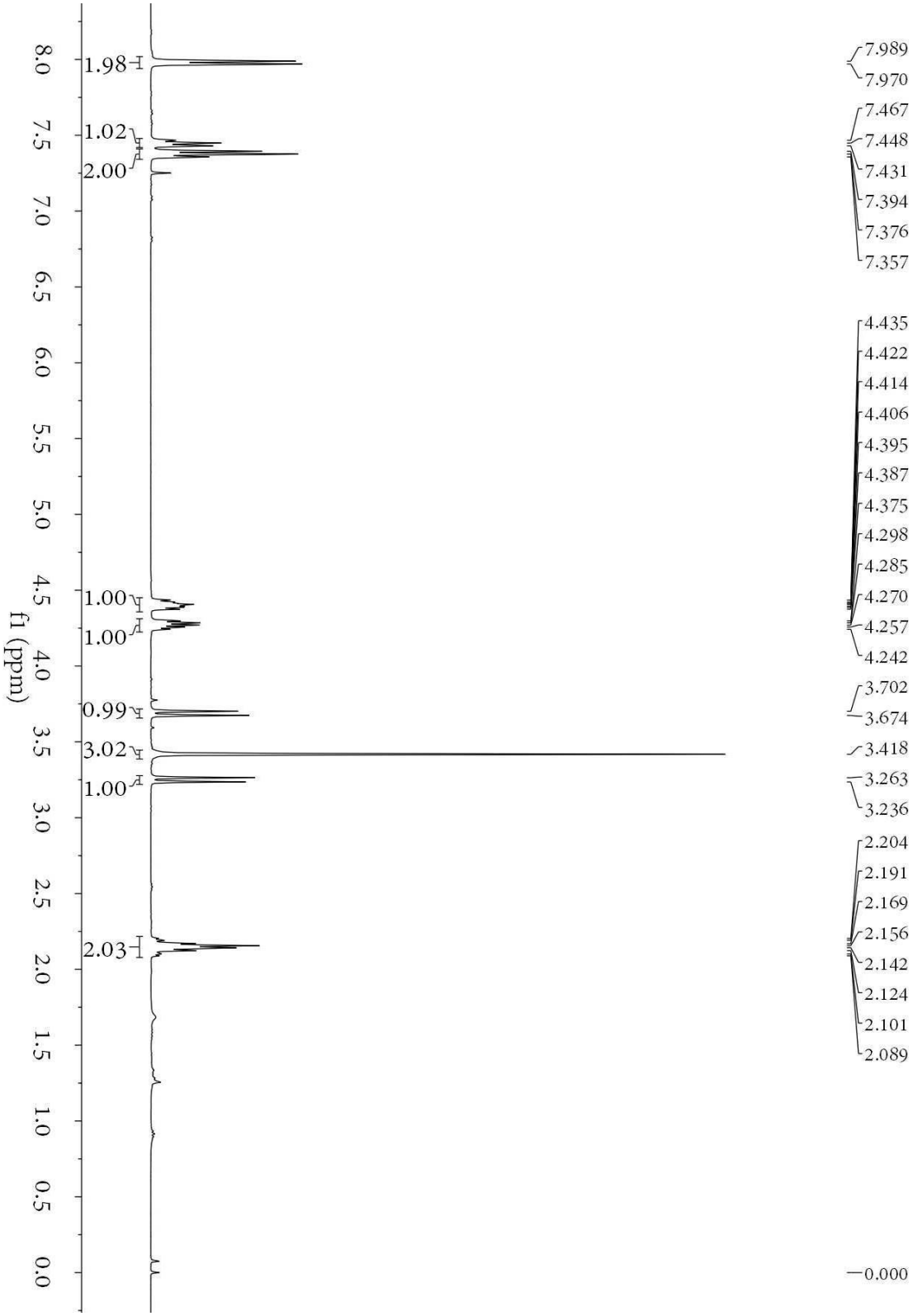


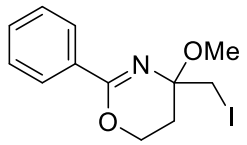
^{13}C NMR of **3c,** 57%
$CDCl_3$, 100 MHz



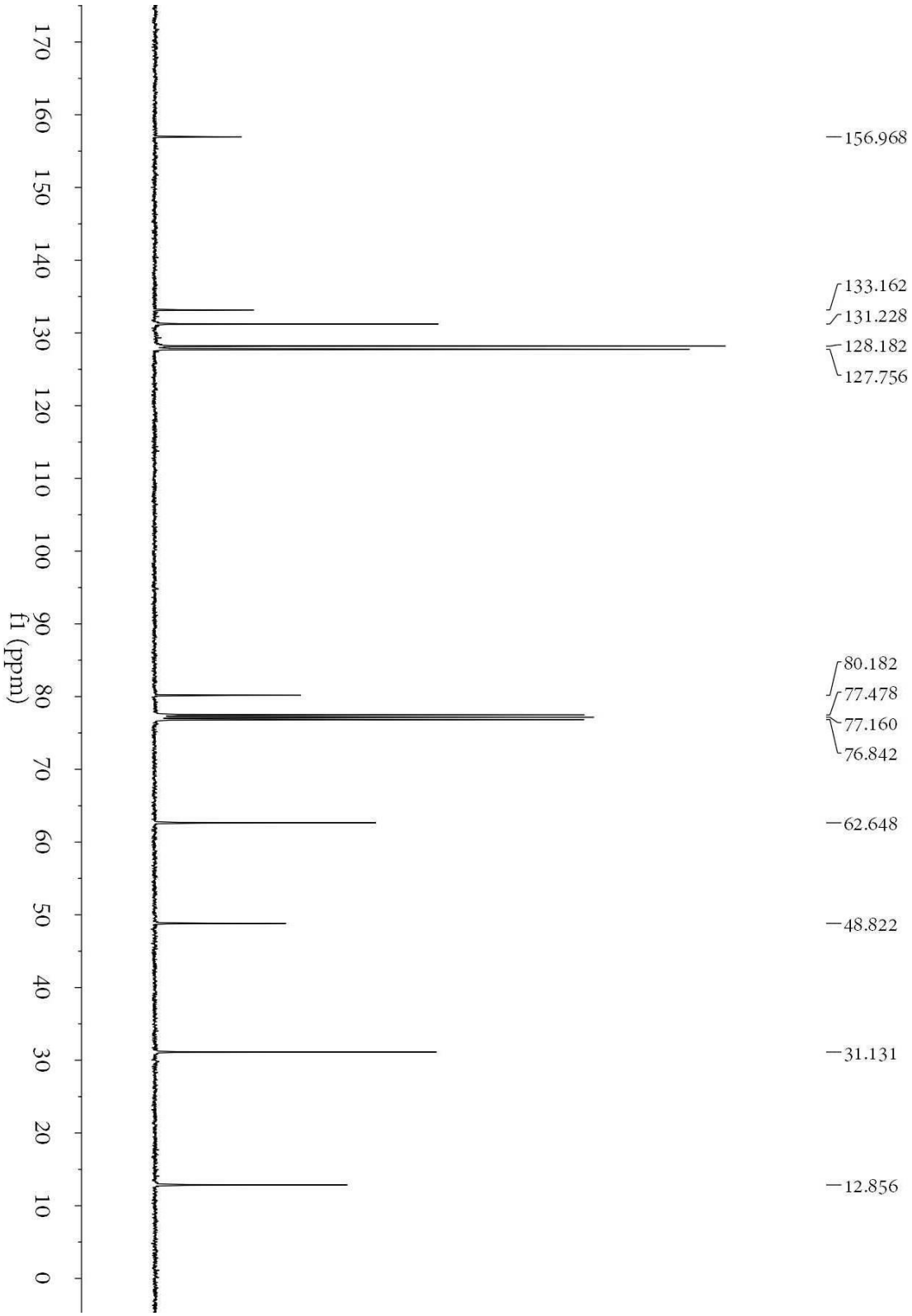


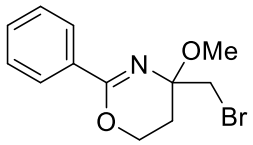
^{1}H NMR of **4a,** 89%
$CDCl_3$, 400 MHz



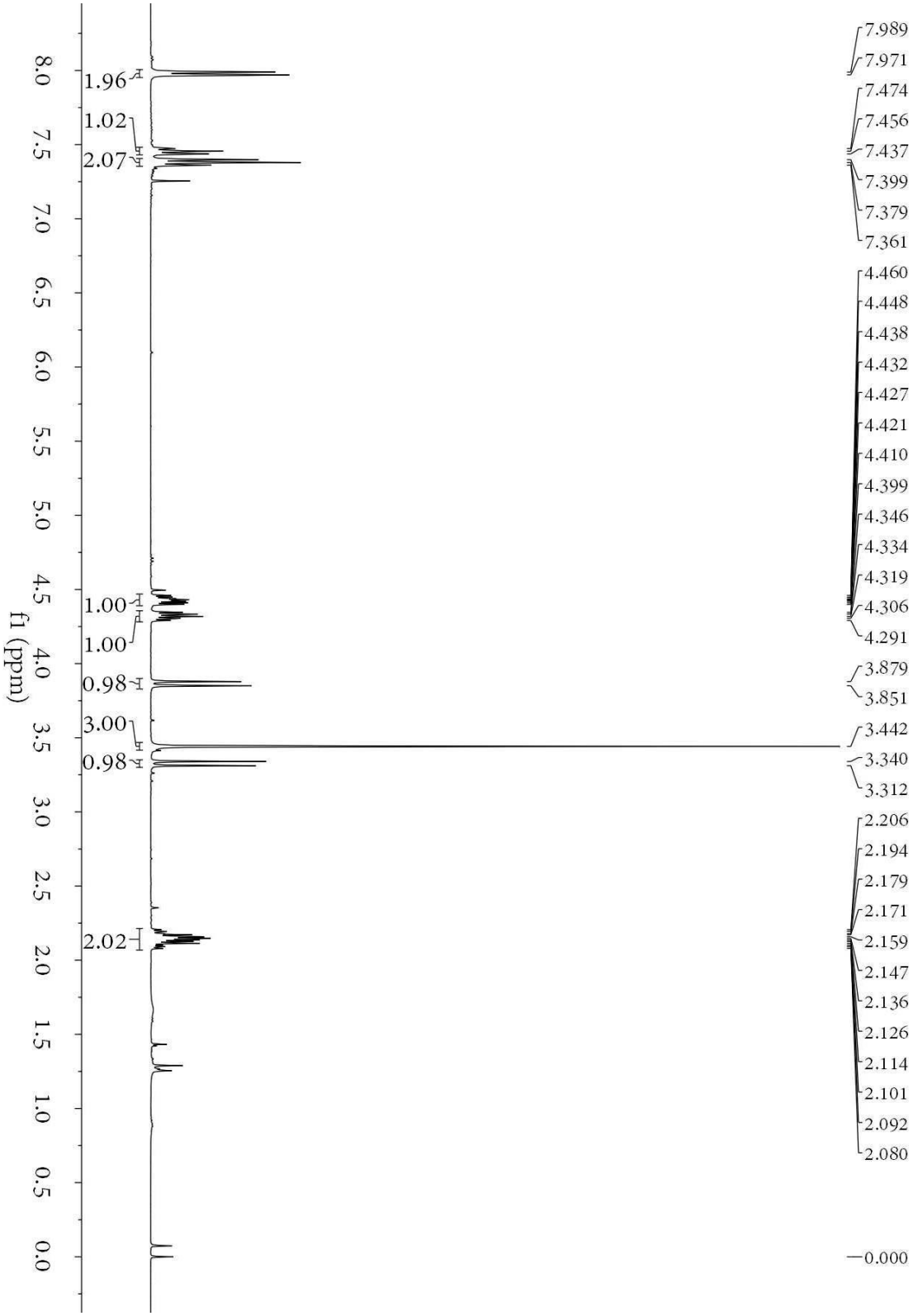


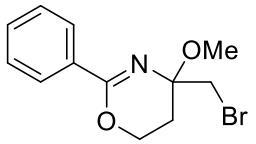
^{13}C NMR of **4a,** 89%
$CDCl_3$, 100 MHz



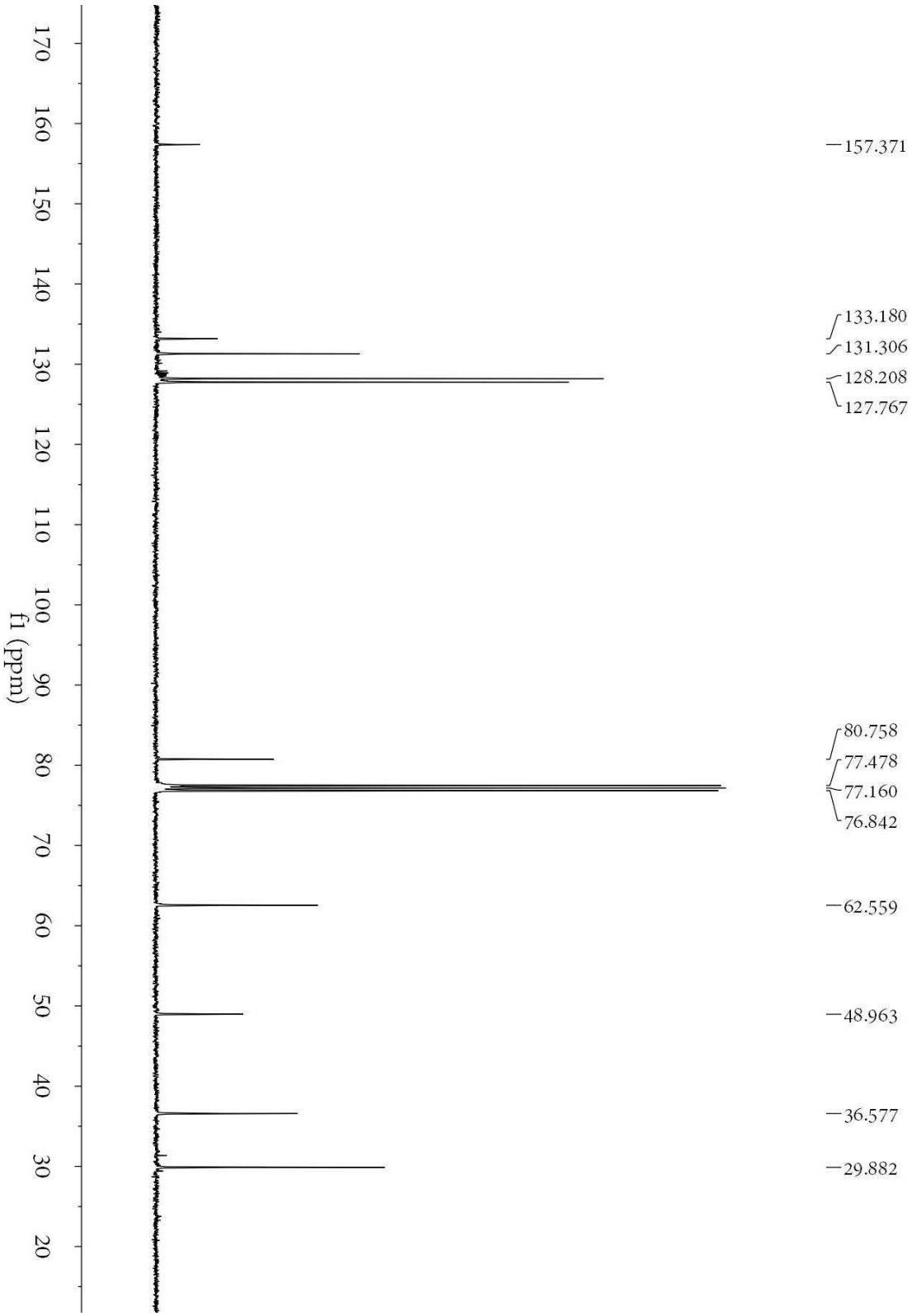


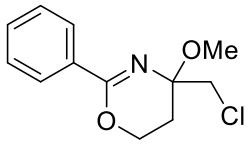
^{1}H NMR of **4b**, 70%
$CDCl_3$, 400 MHz



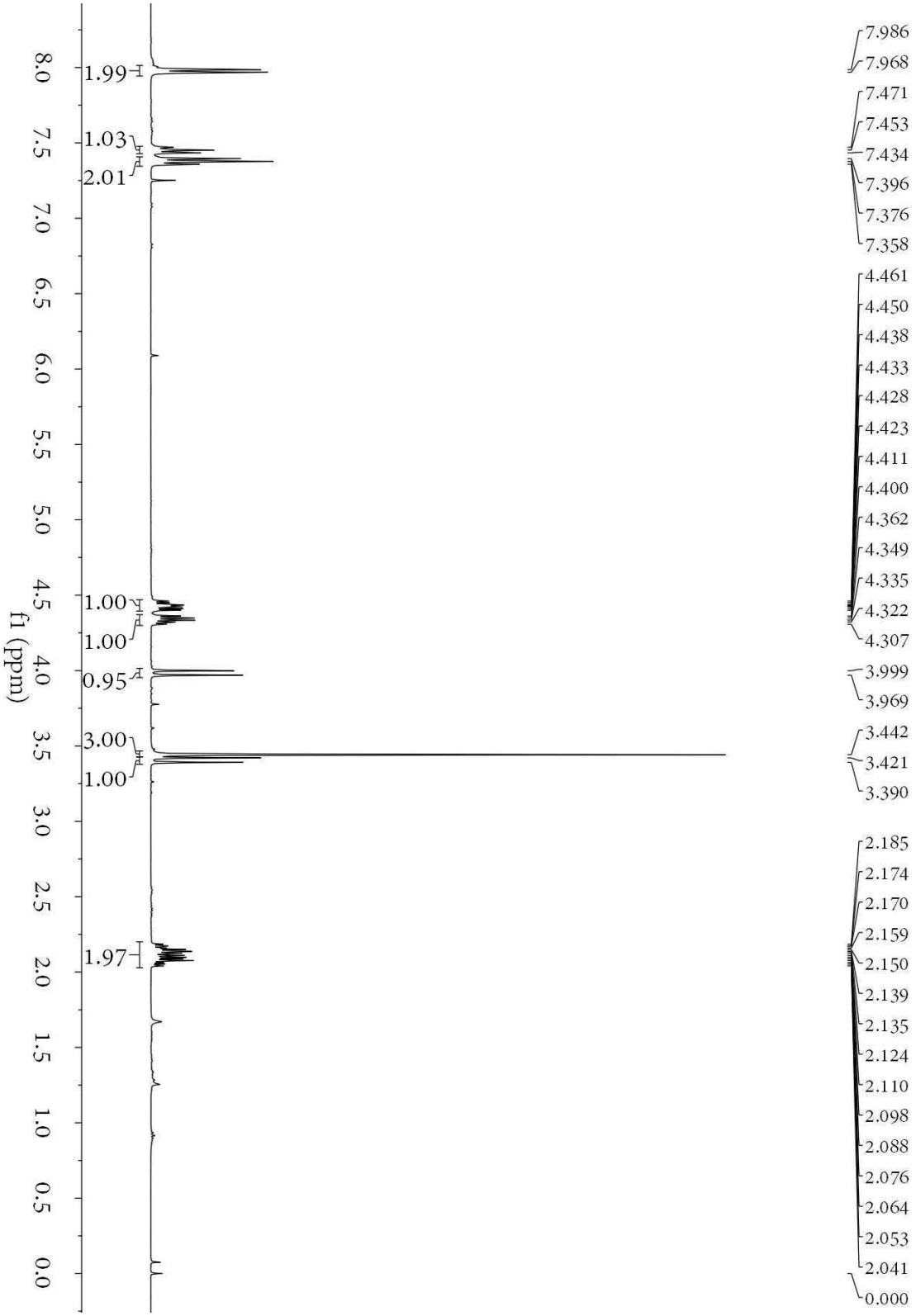


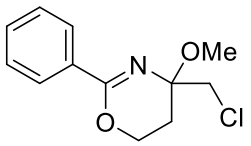
^{13}C NMR of **4b**, 70%
$CDCl_3$, 100 MHz



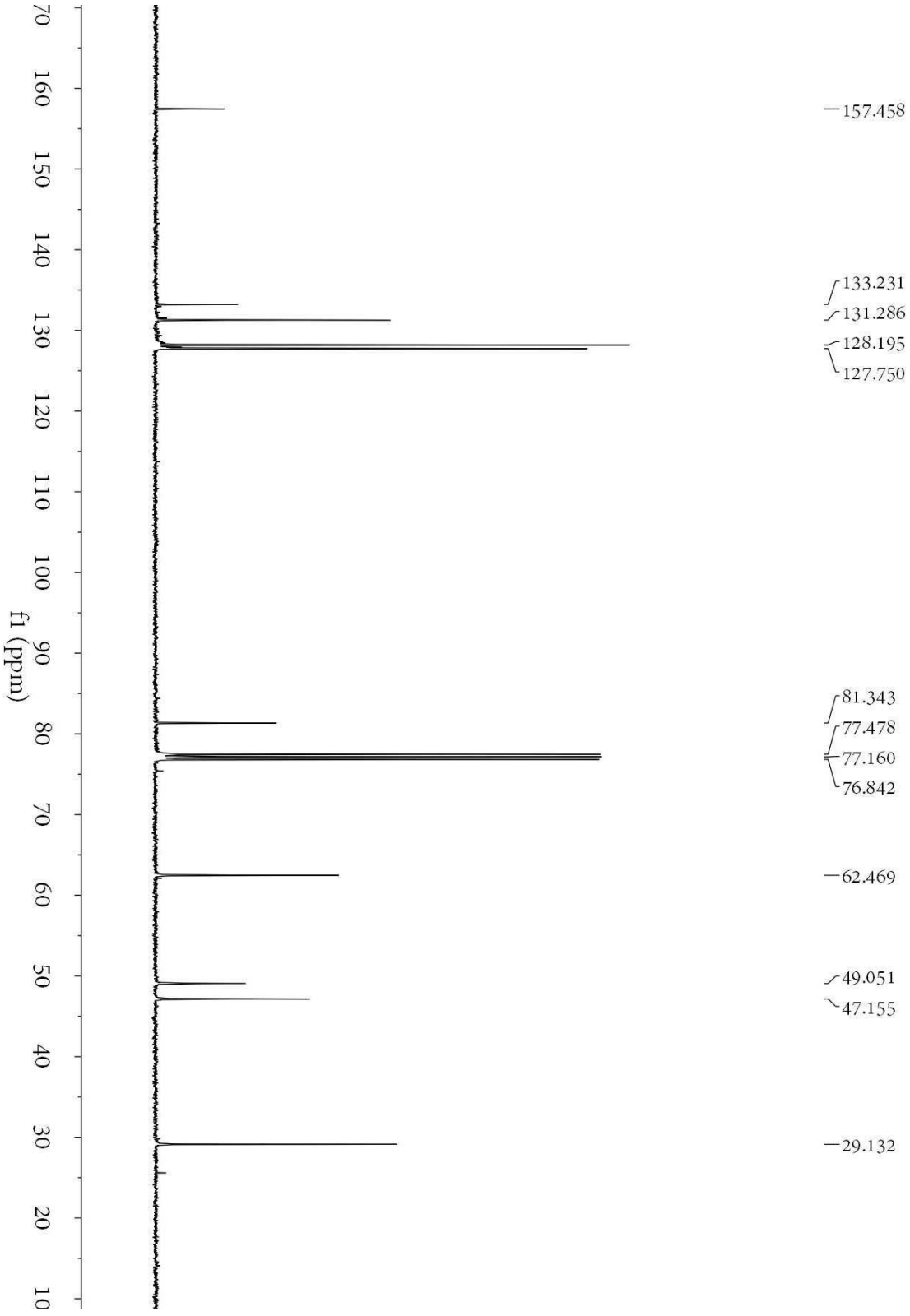


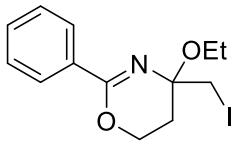
^{1}H NMR of **4c,** 72%
$CDCl_3$, 400 MHz



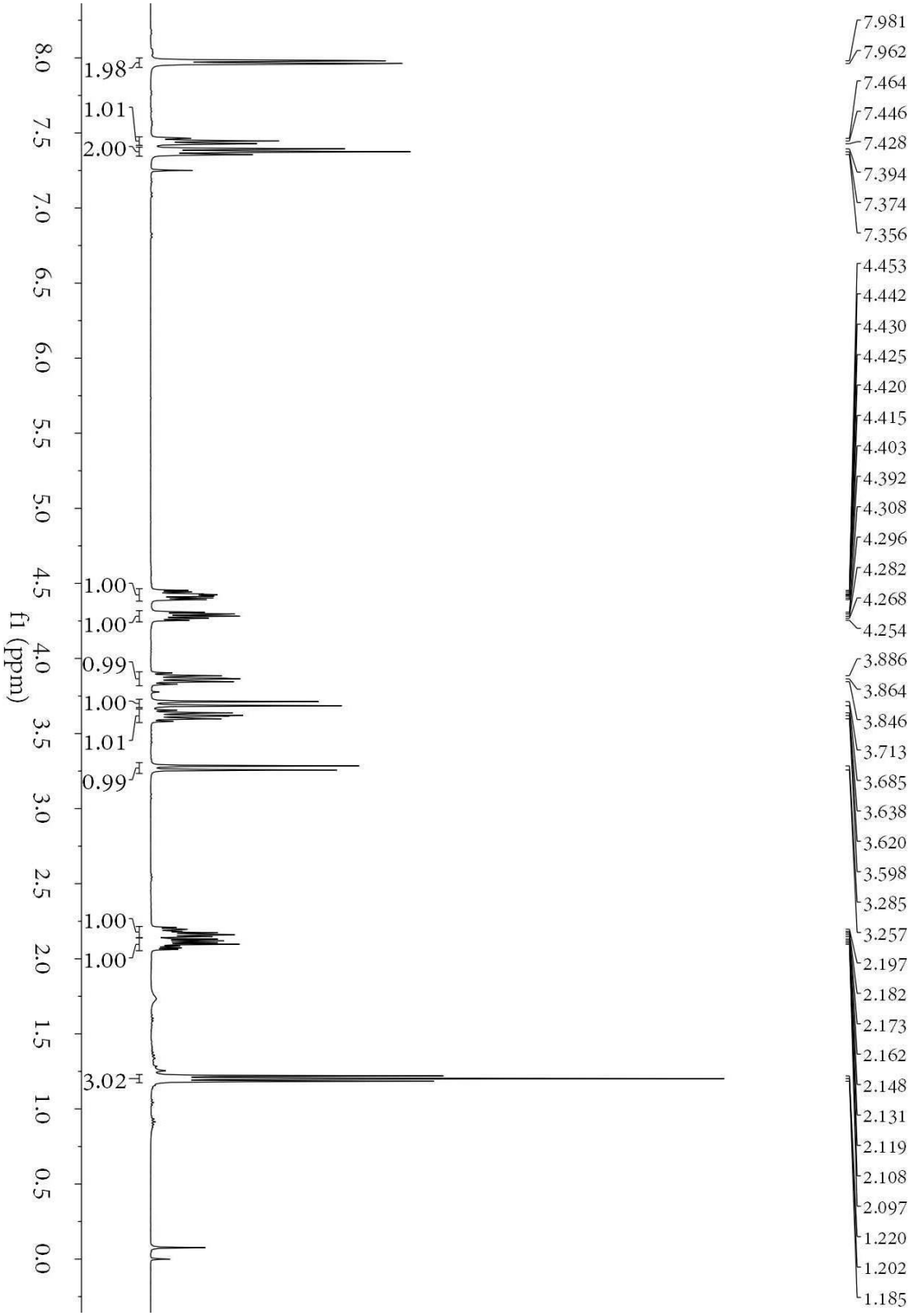


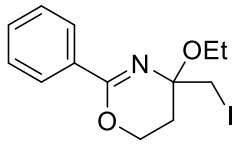
^{13}C NMR of **4c,** 72%
$CDCl_3$, 100 MHz



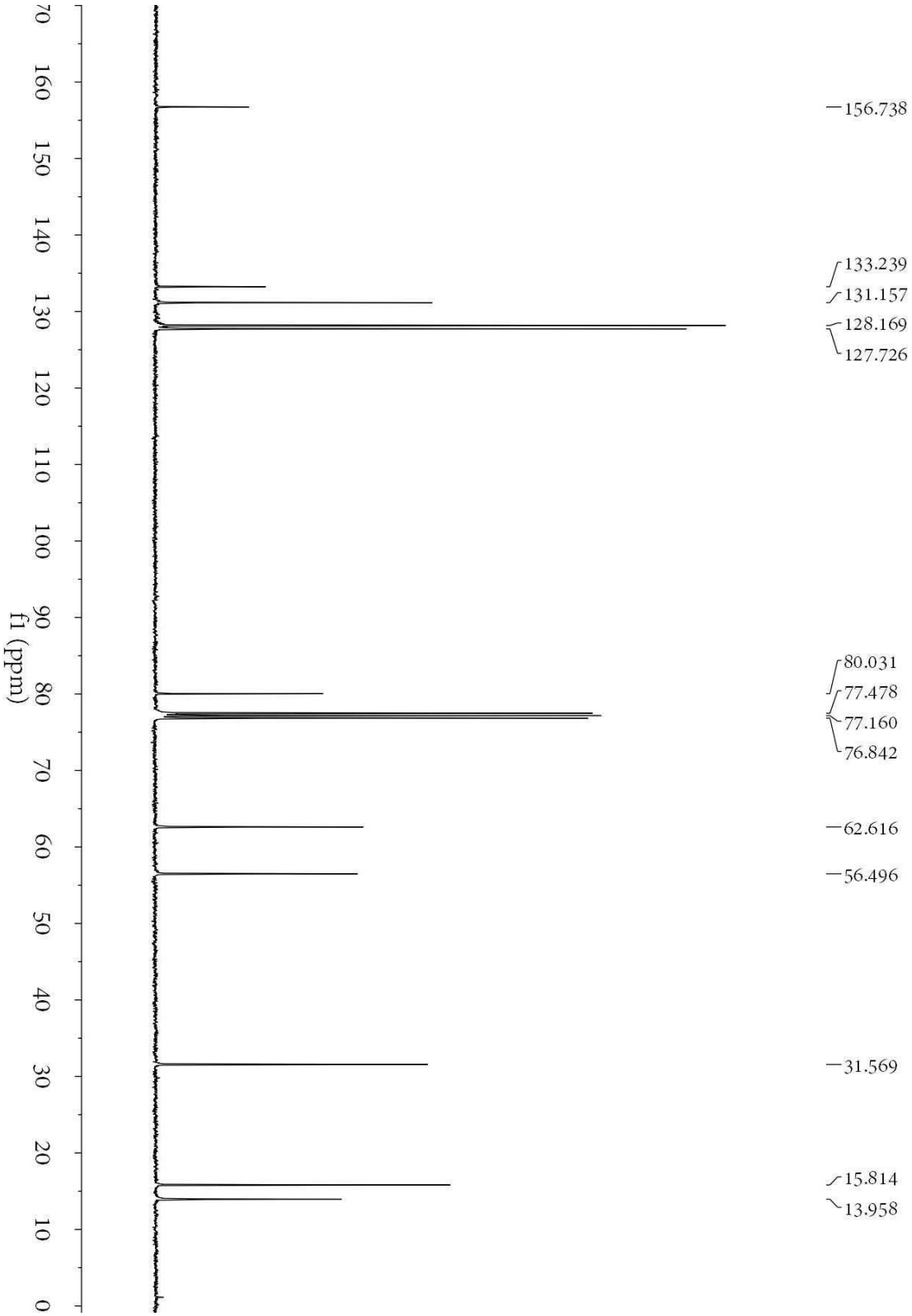


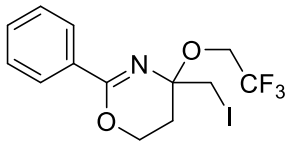
^{1}H NMR of **5a,** 79%
$CDCl_3$, 400 MHz



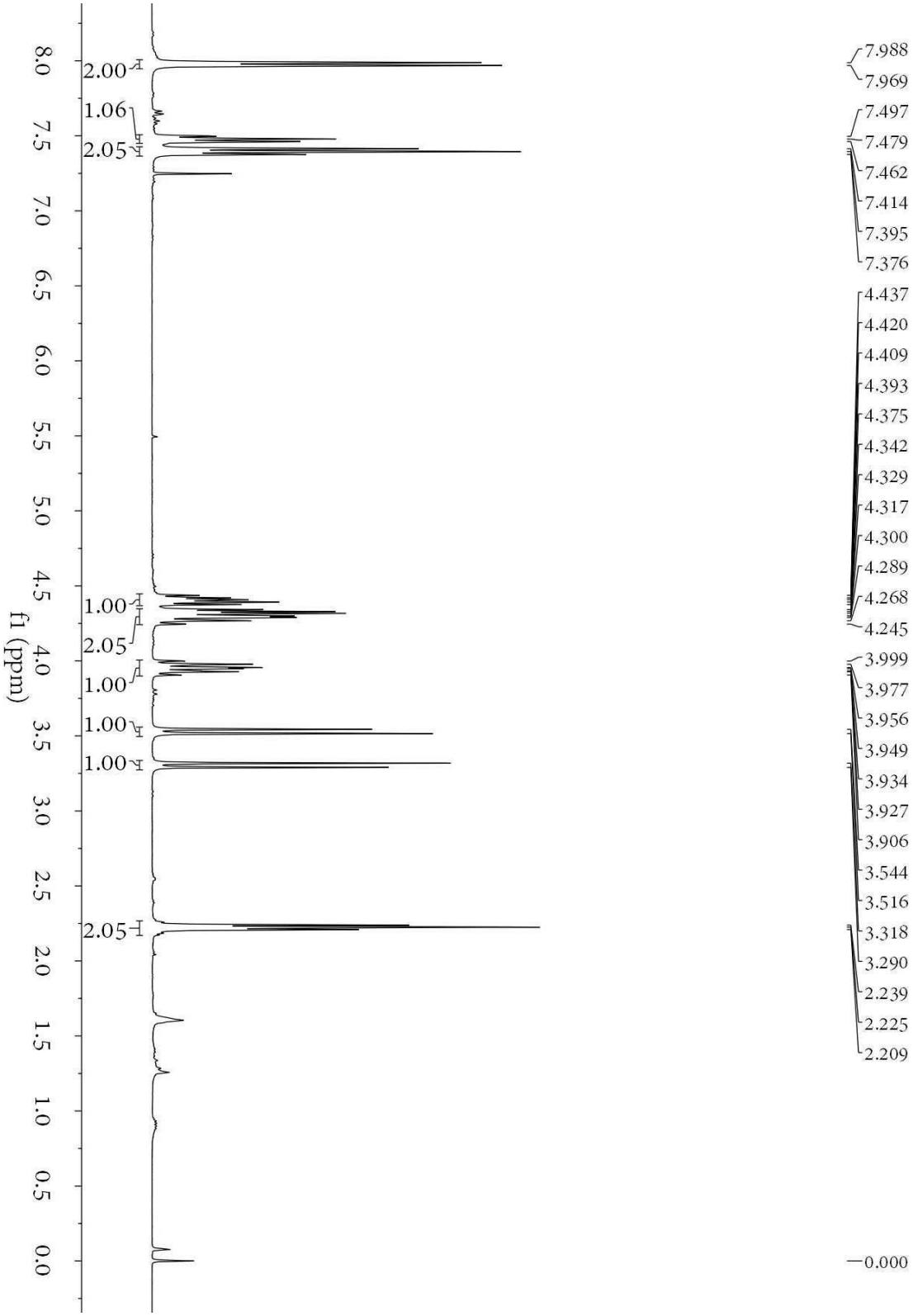


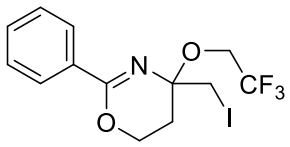
^{13}C NMR of **5a,** 79%
$CDCl_3$, 100 MHz



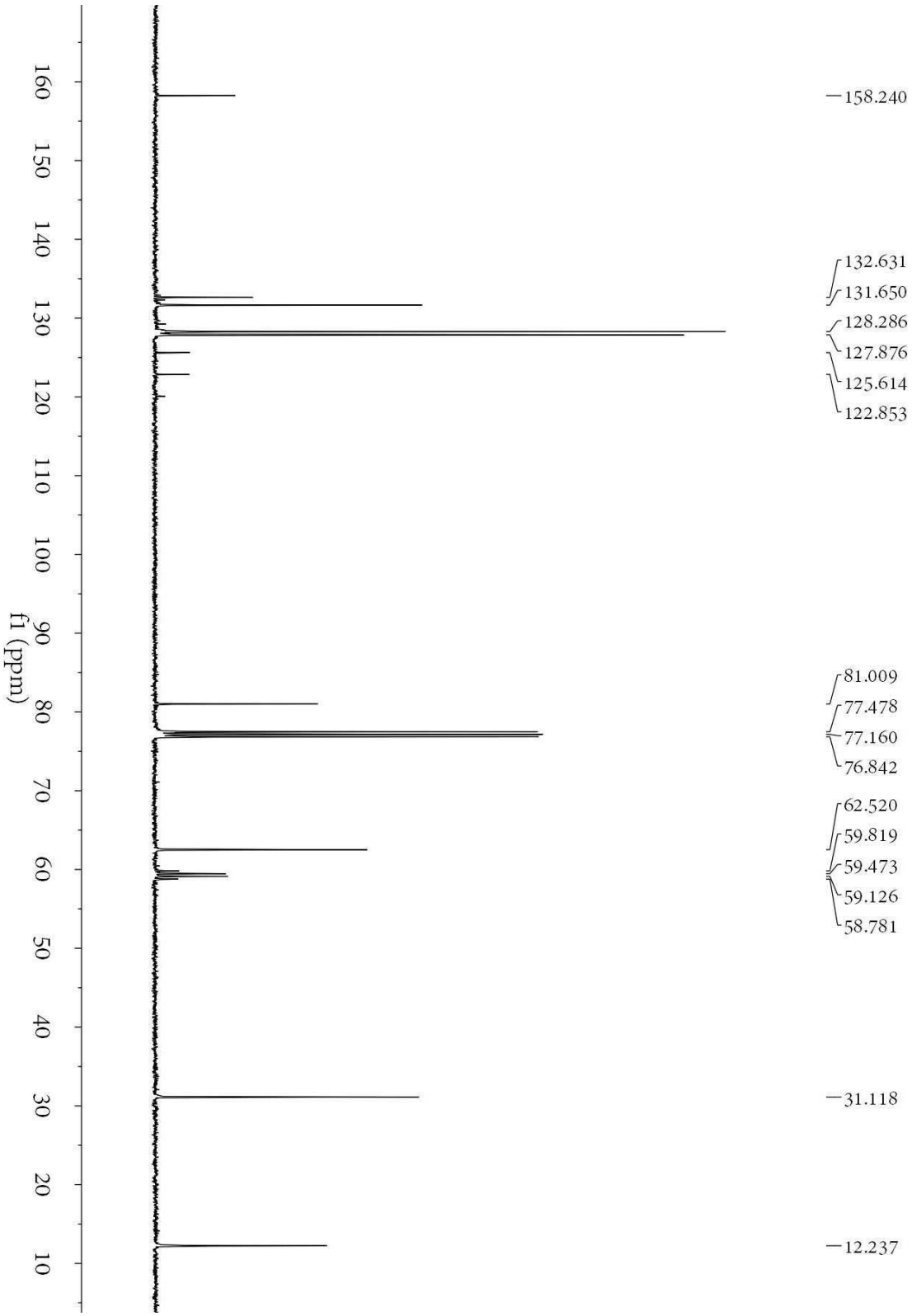


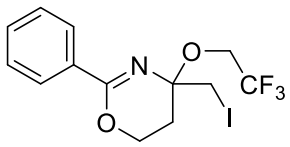
^{1}H NMR of **5b**, 86%
$CDCl_3$, 400 MHz



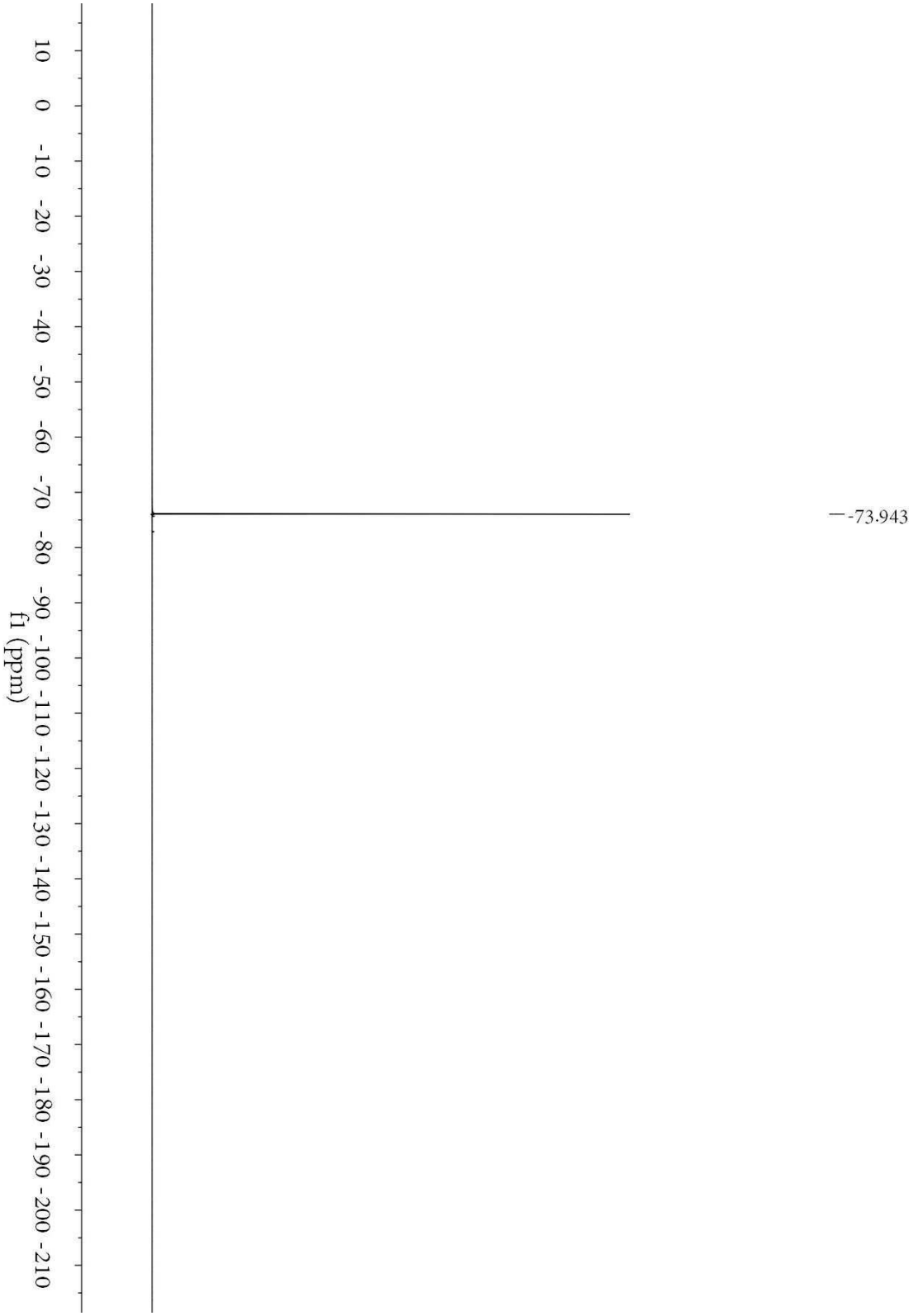


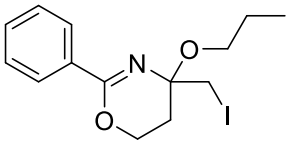
^{13}C NMR of **5b,** 86%
$CDCl_3$, 100 MHz



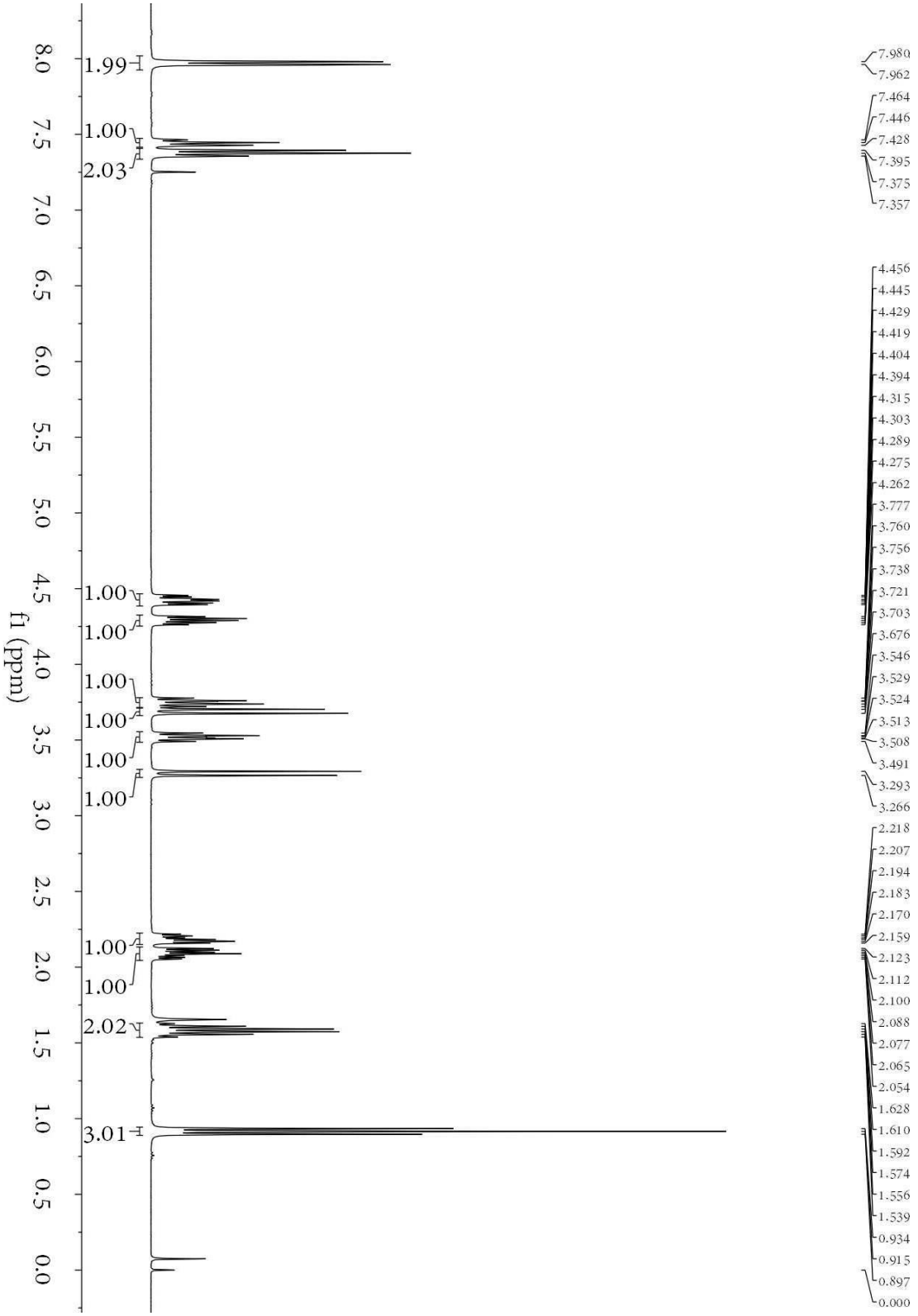


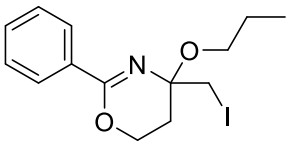
^{19}F NMR of **5b,** 86%
$CDCl_3$, 564 MHz





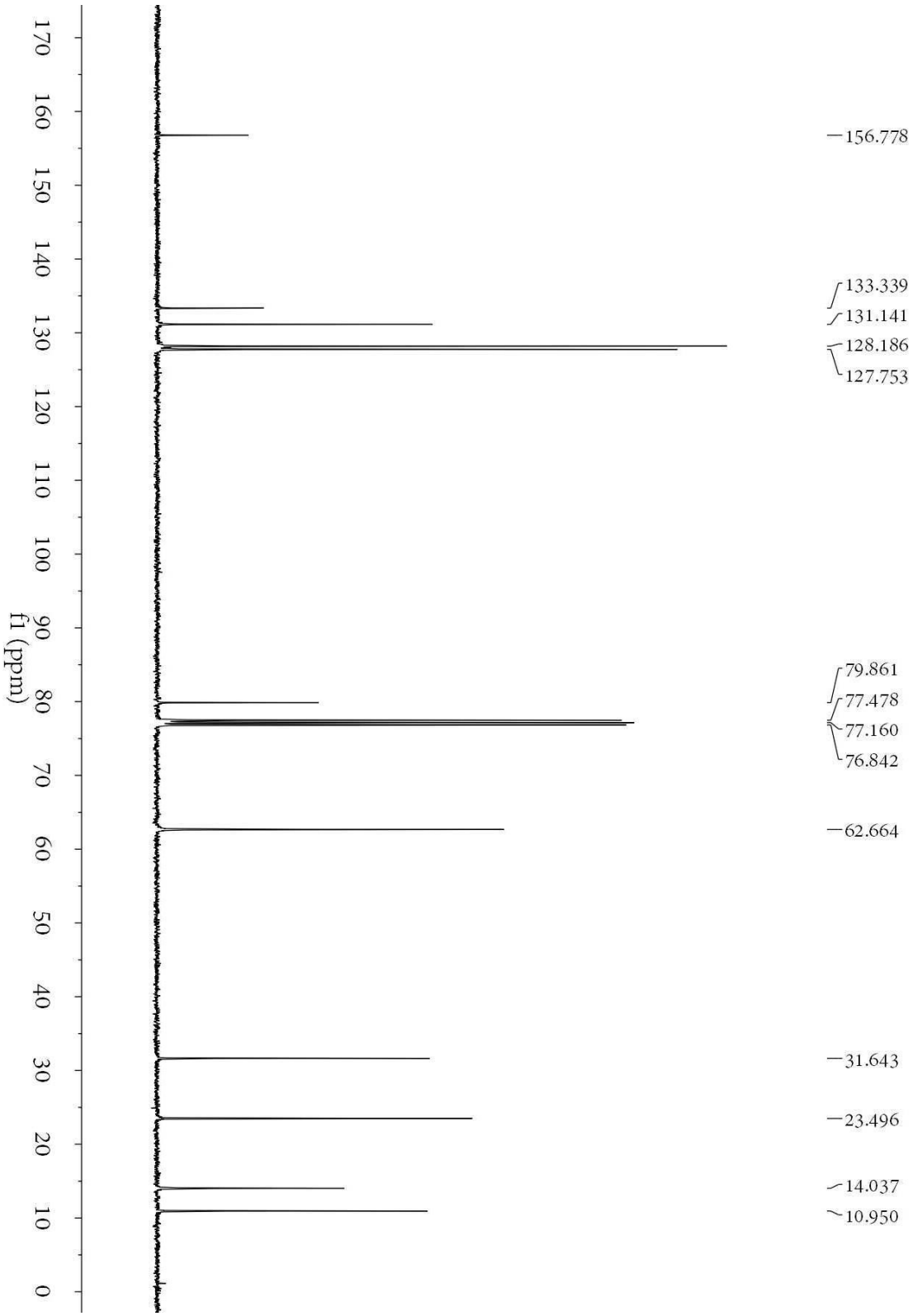
^{1}H NMR of **5c**, 76%
$CDCl_3$, 400 MHz

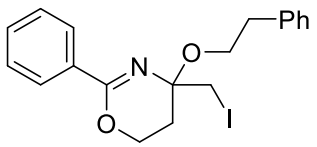




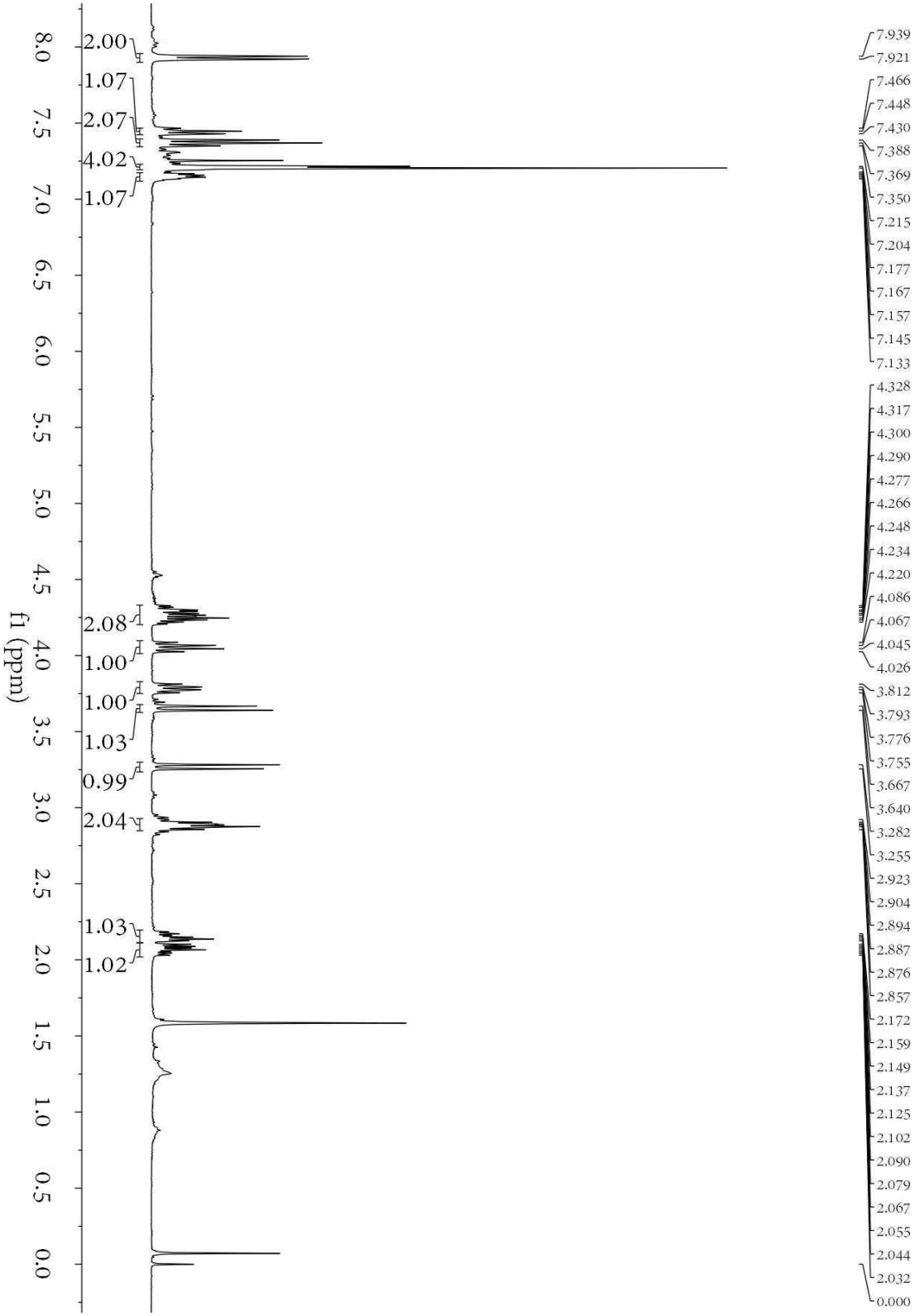
^{13}C NMR of **5c**, 76**%**

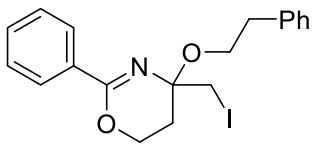
$CDCl_3$, 100 MHz



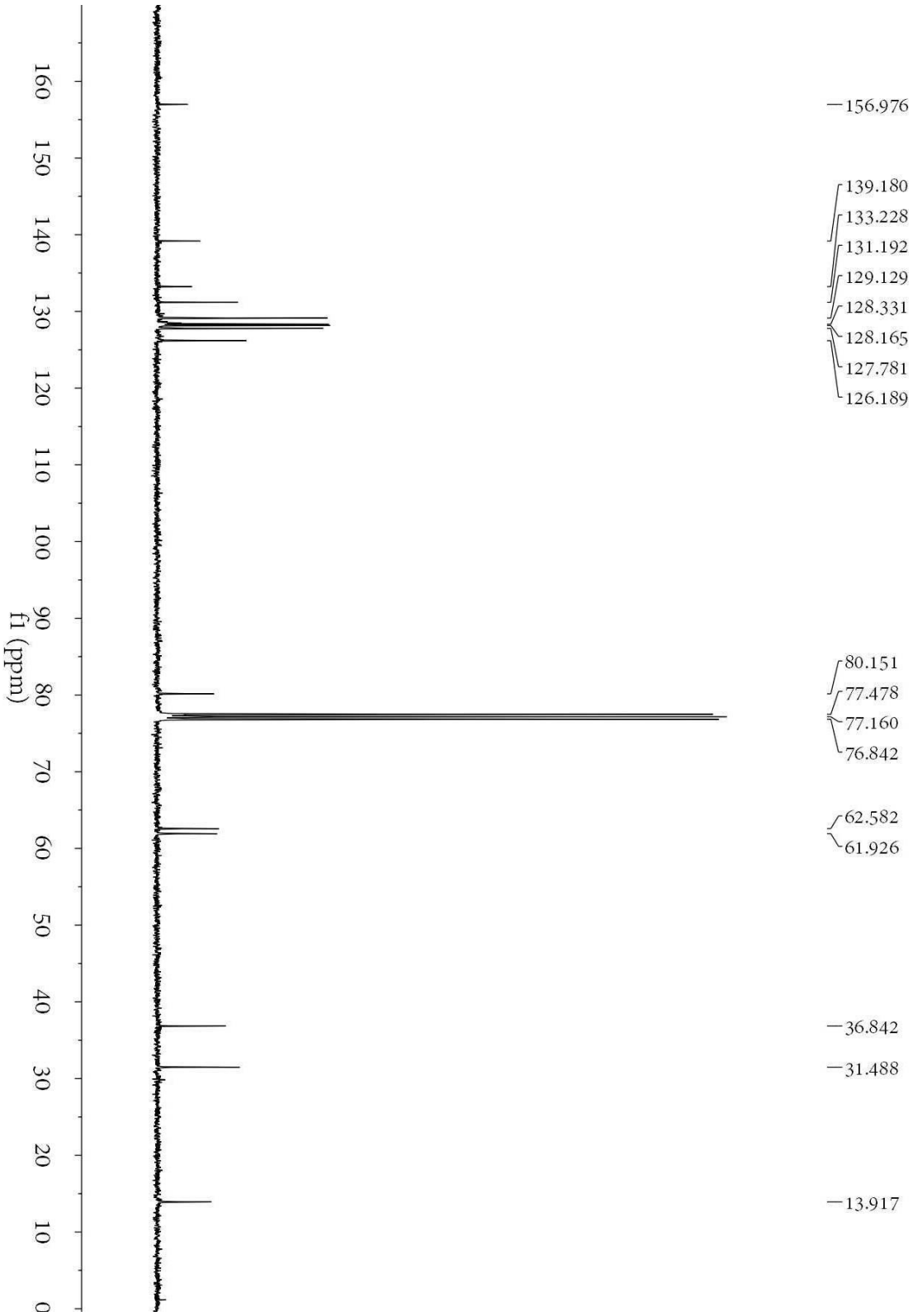


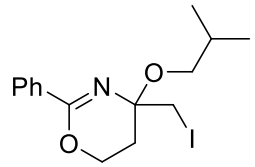
^{1}H NMR of **5d**, 70%
$CDCl_3$, 400 MHz





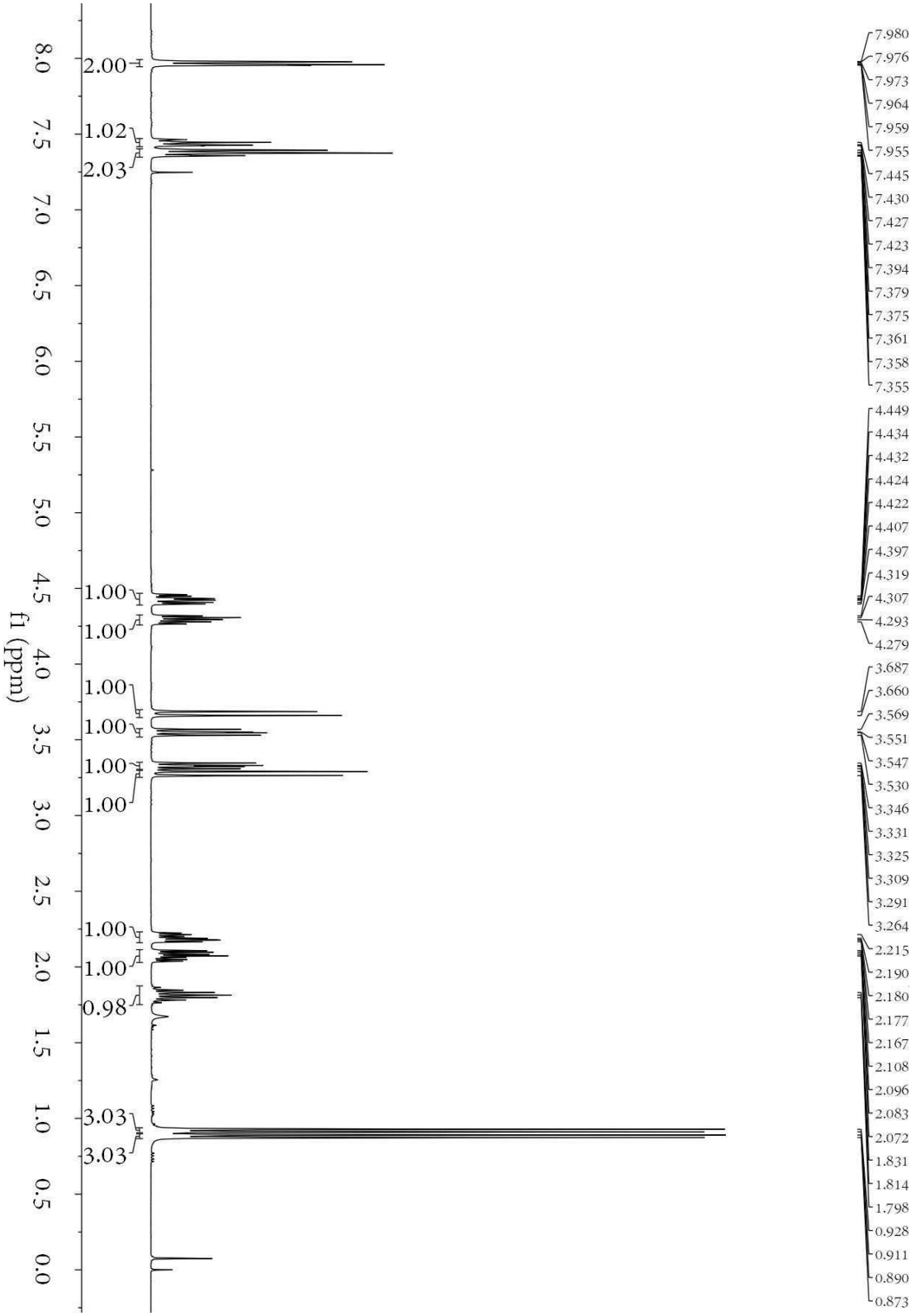
^{13}C NMR of **5d,** 70%
$CDCl_3$, 100 MHz

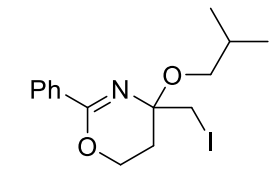




^{1}H NMR of **5e,** 69%

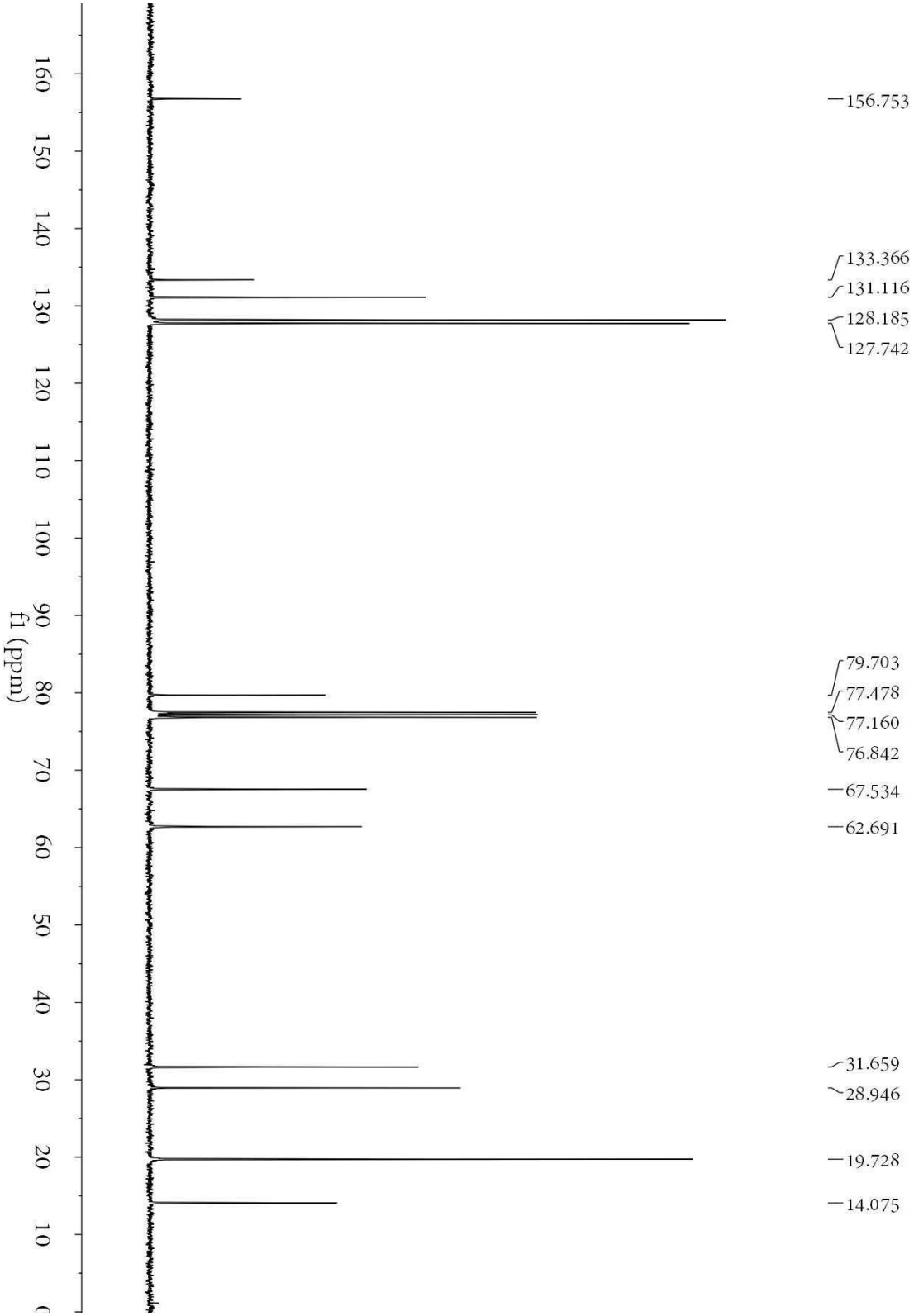
$CDCl_3$, 400 MHz

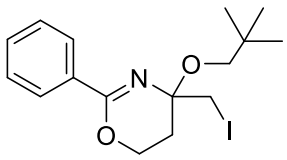




^{13}C NMR of **5e,** 69**%**

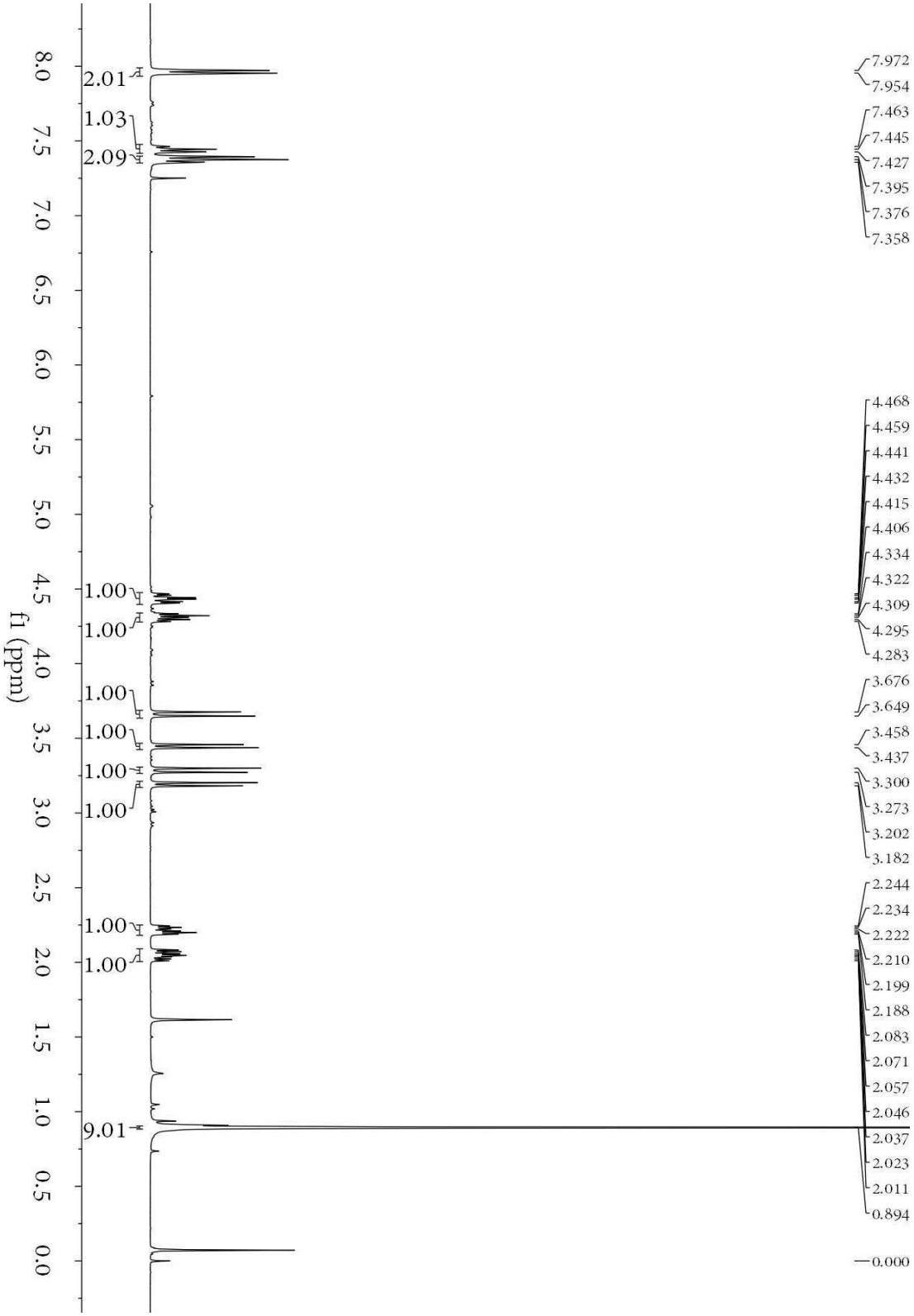
$CDCl_3$, 100 MHz

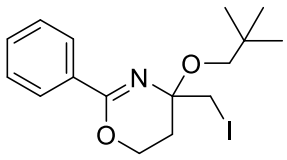




^{1}H NMR of **5f**, 71%

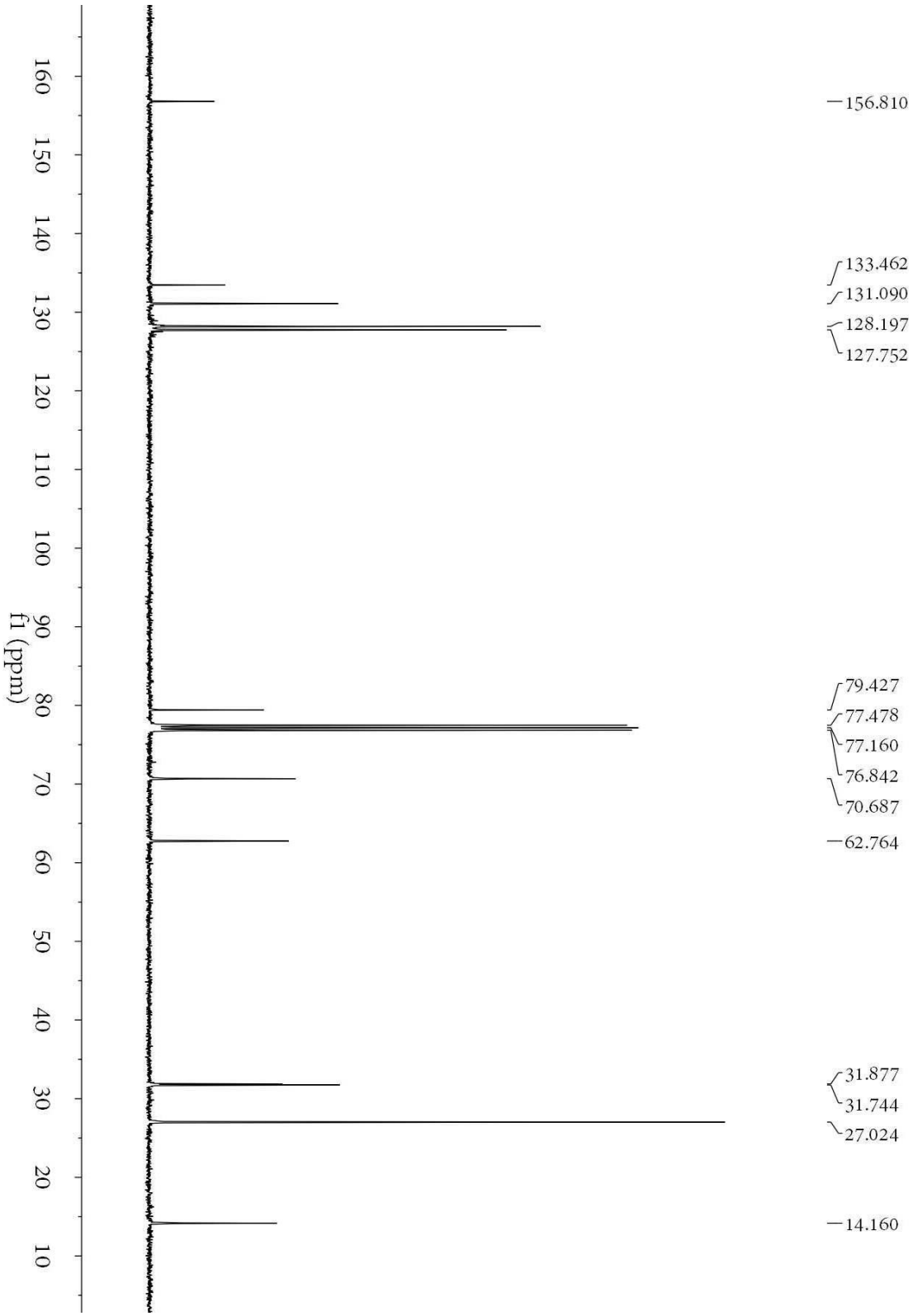
$CDCl_3$, 400 MHz

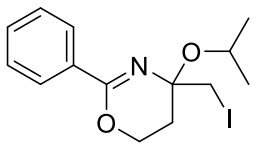




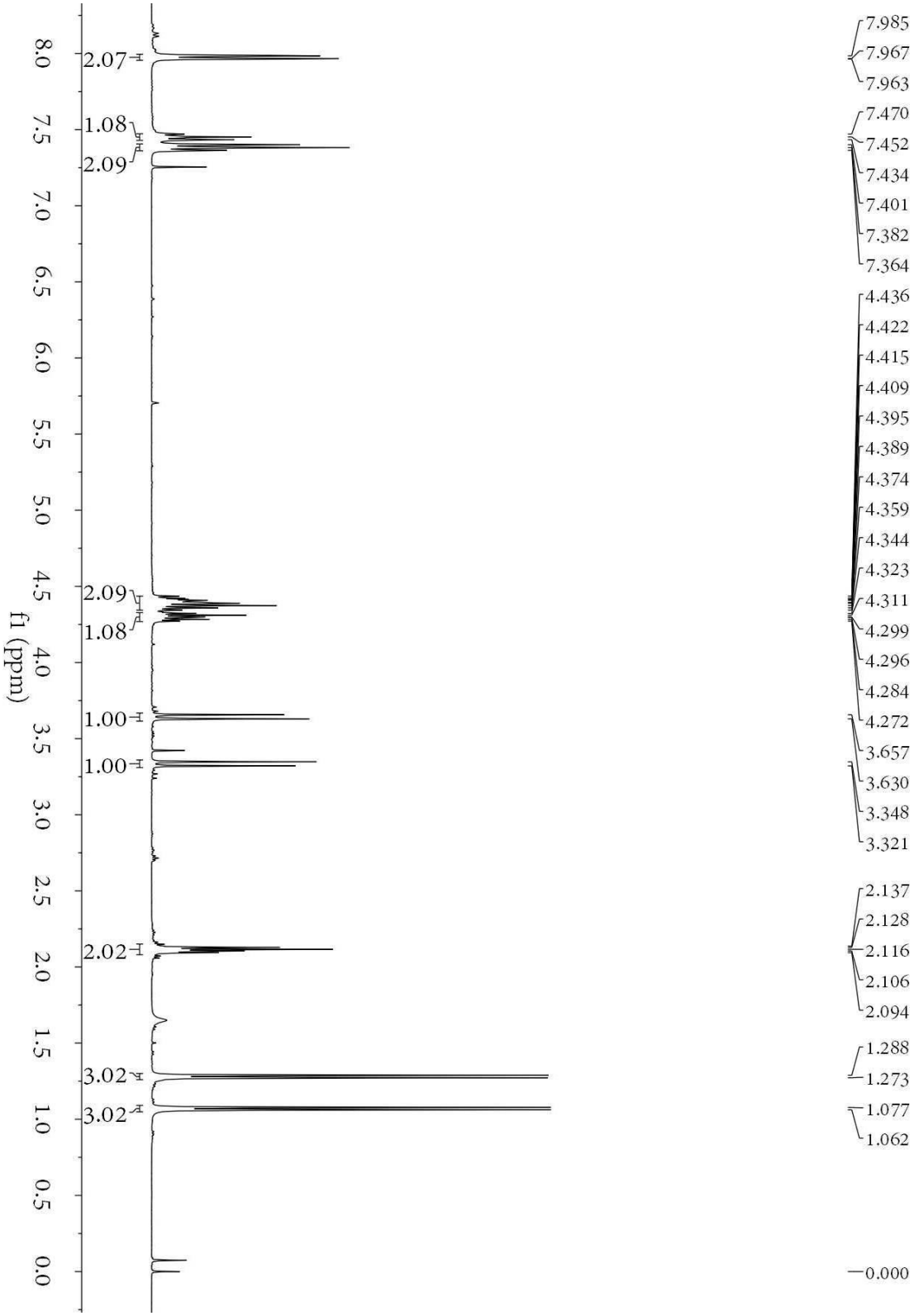
^{13}C NMR of **5f**, 71%

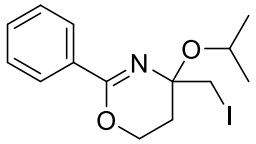
$CDCl_3$, 100 MHz



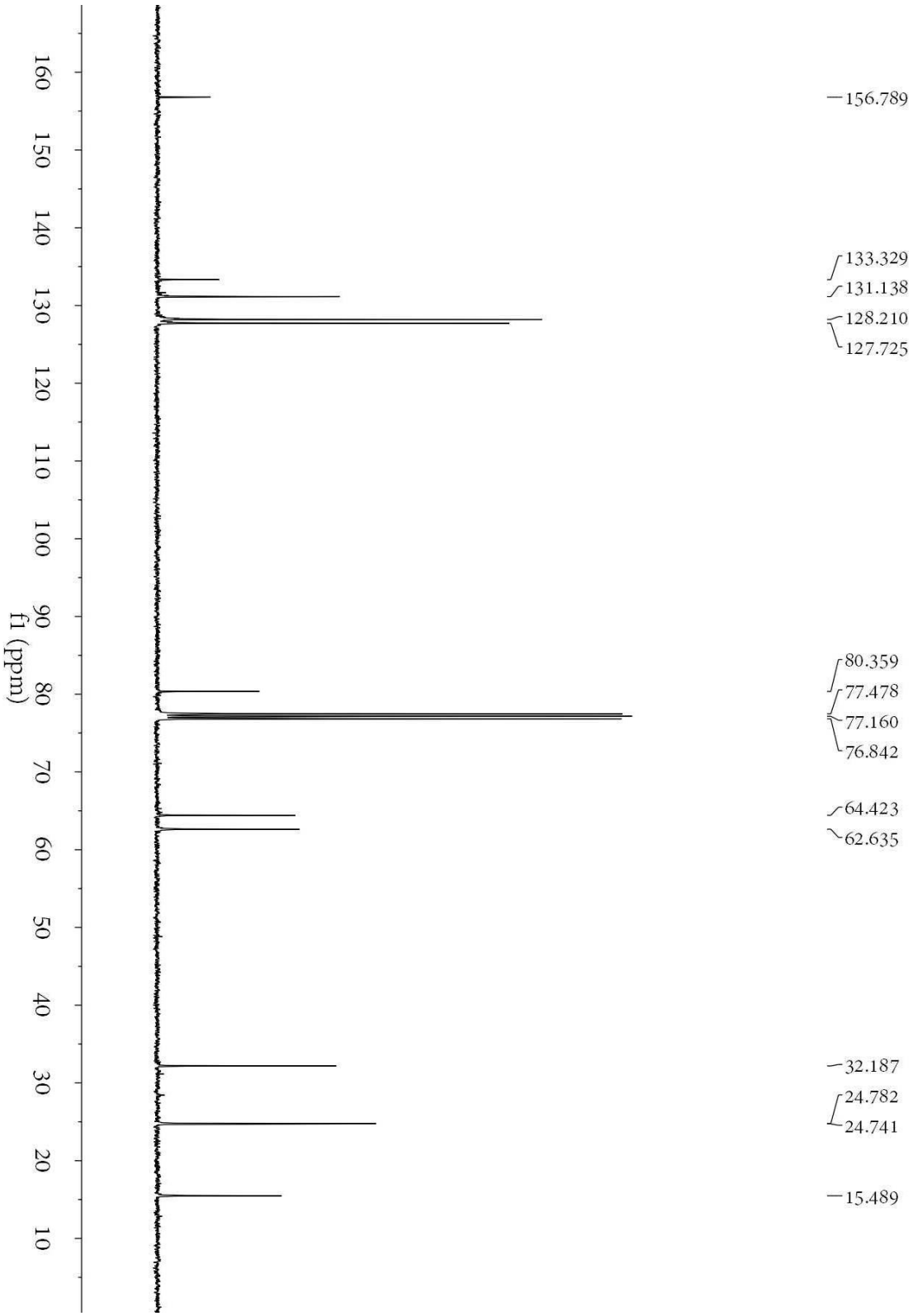


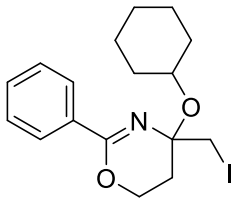
^{1}H NMR of **5g,** 58%
$CDCl_3$, 400 MHz



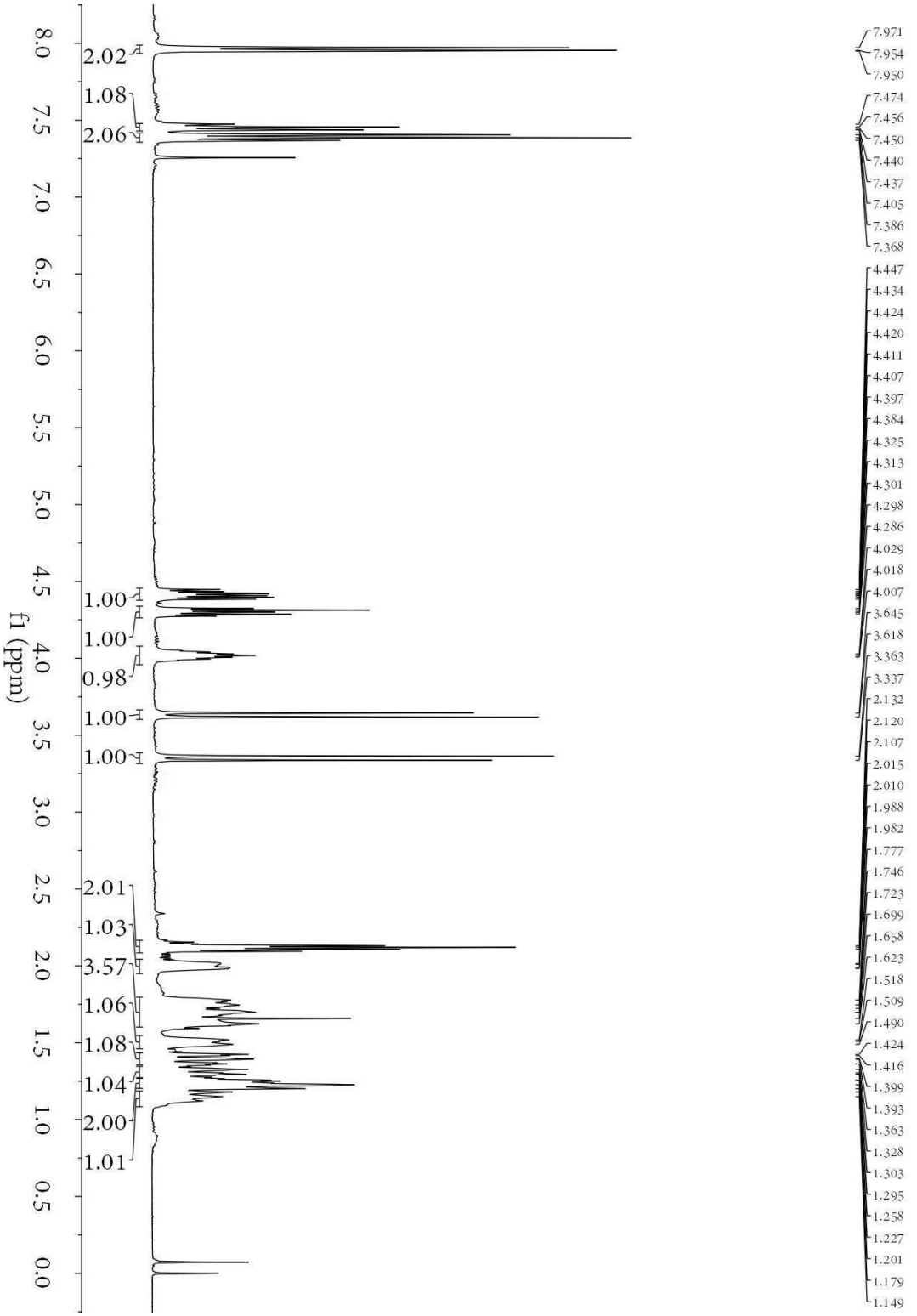


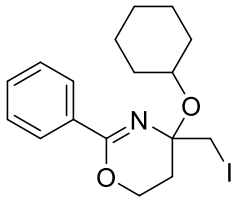
^{13}C NMR of **5g,** 58%
$CDCl_3$, 100 MHz





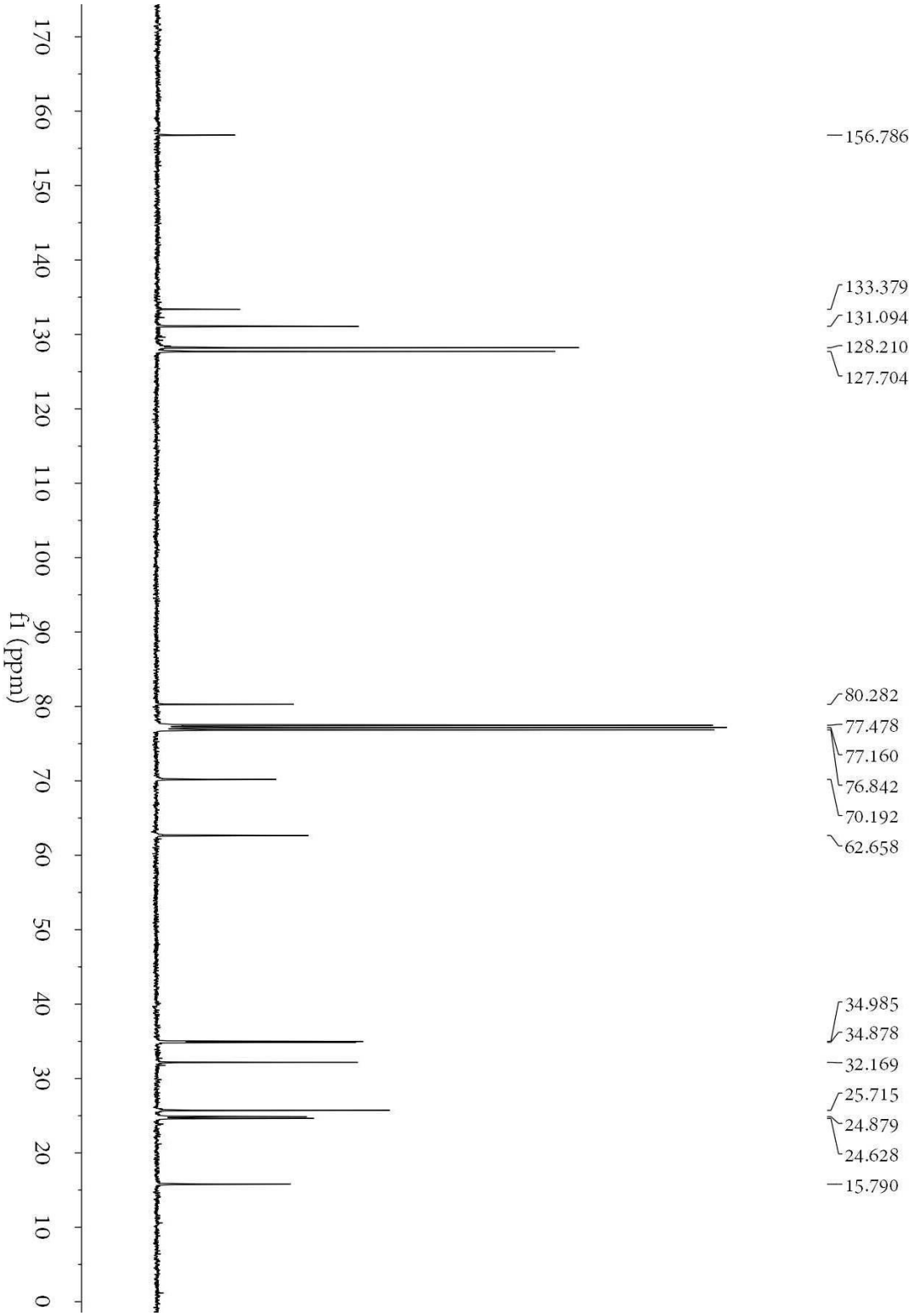
^{1}H NMR of **5h,** 60**%**
$CDCl_3$, 400 MHz

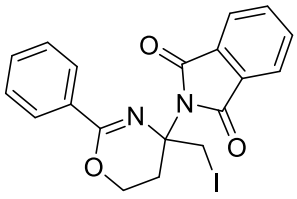




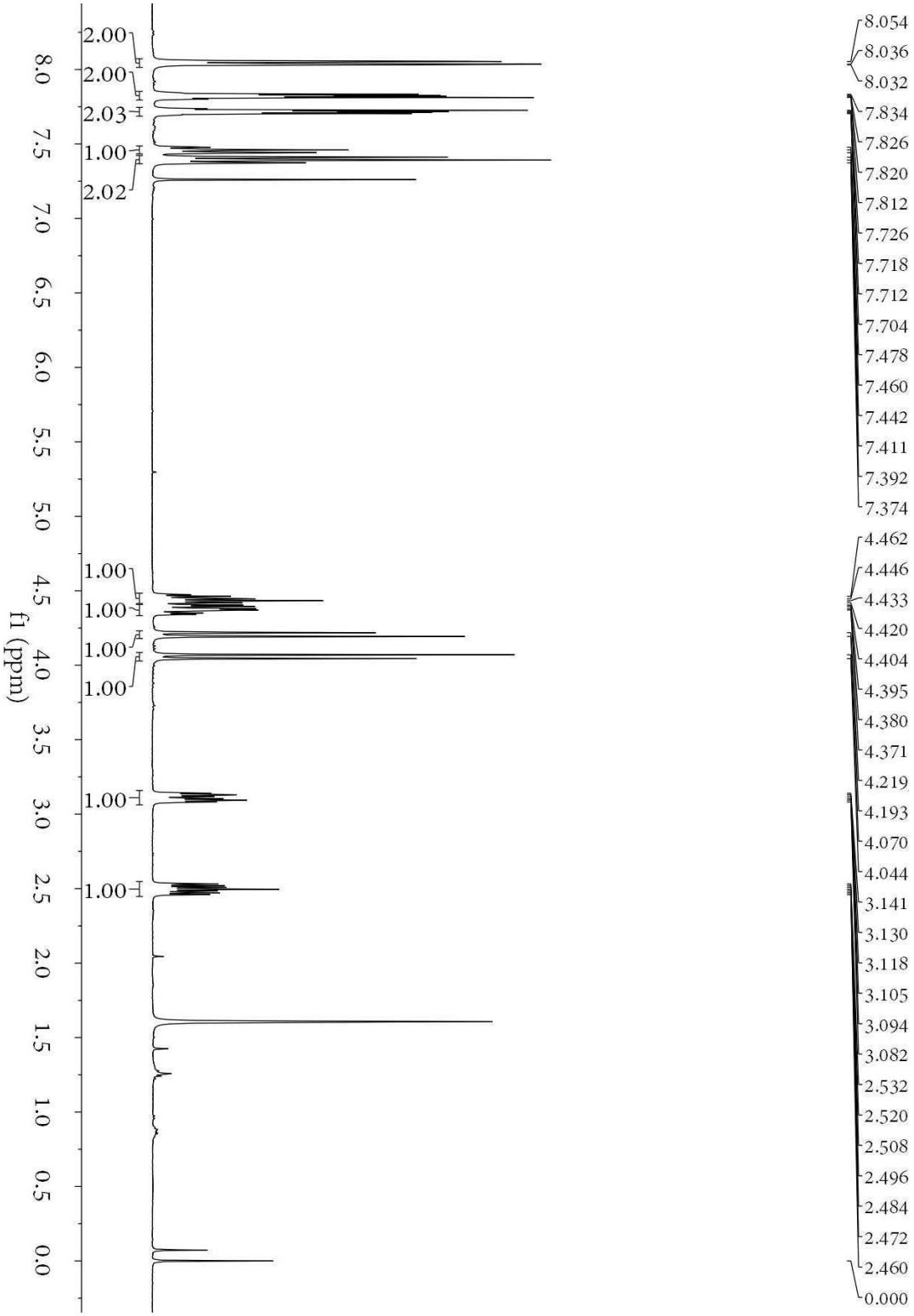
^{13}C NMR of **5h**, 60**%**

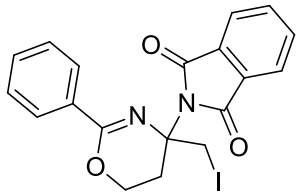
$CDCl_3$, 100 MHz



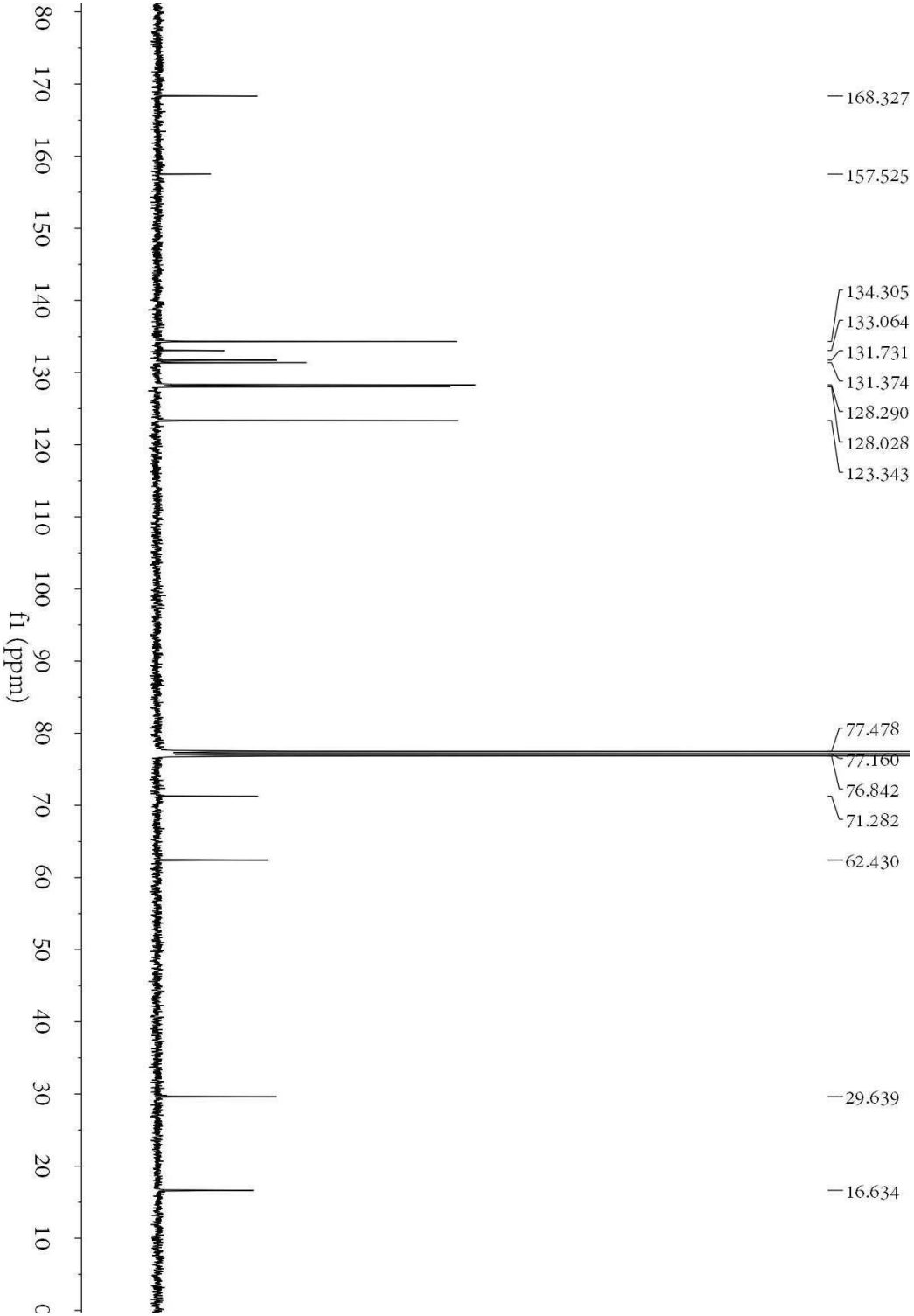


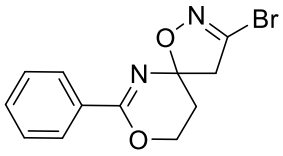
^{1}H NMR of **5i,** 26%
$CDCl_3$, 400 MHz



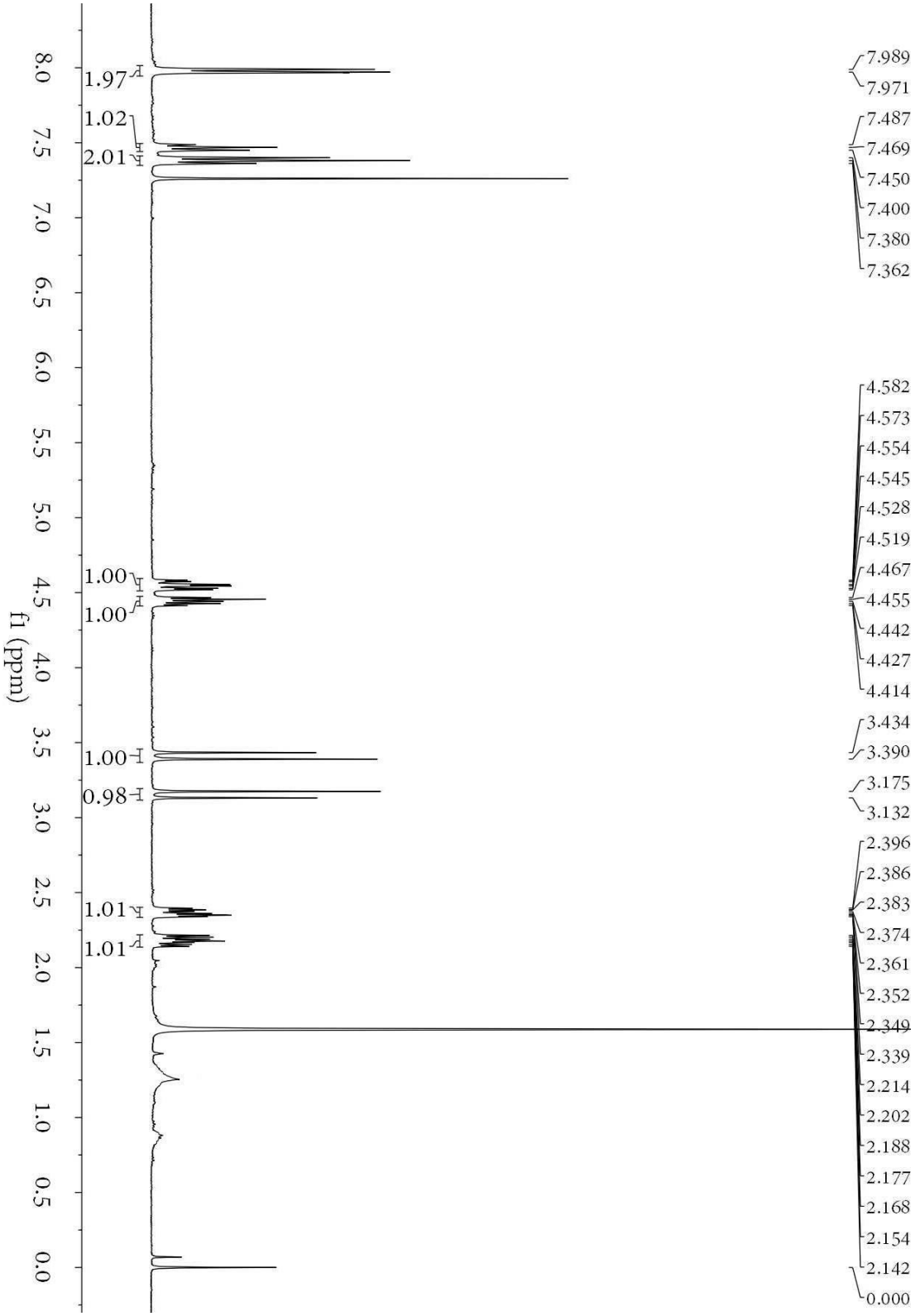


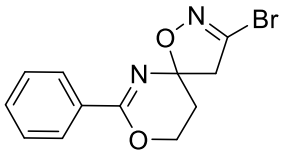
^{13}C NMR of **5i,** 26**%**
$CDCl_3$, 100 MHz



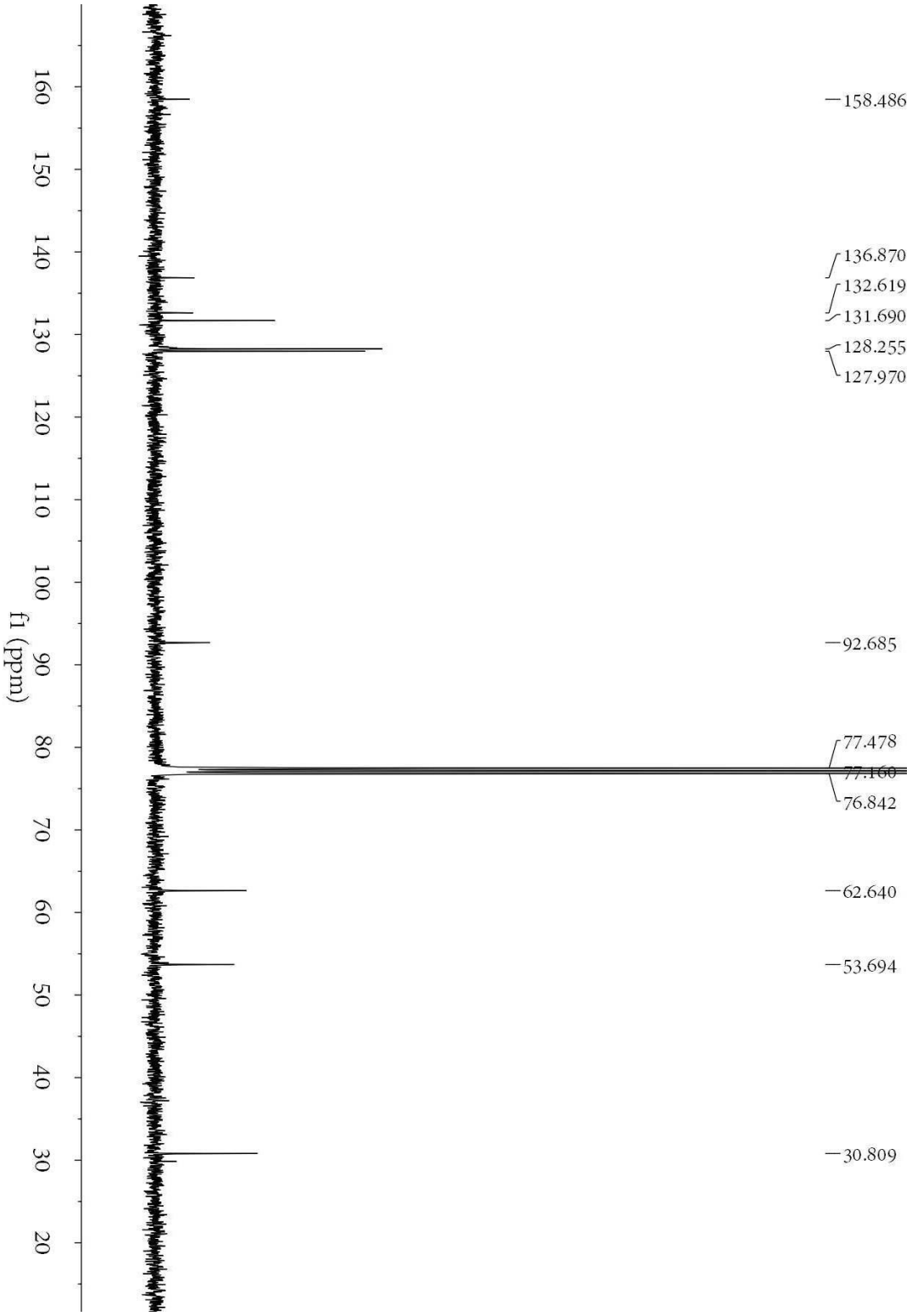


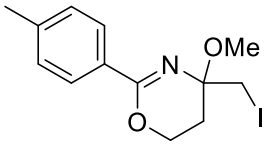
^{1}H NMR of **6**, 45%
$CDCl_3$, 400 MHz



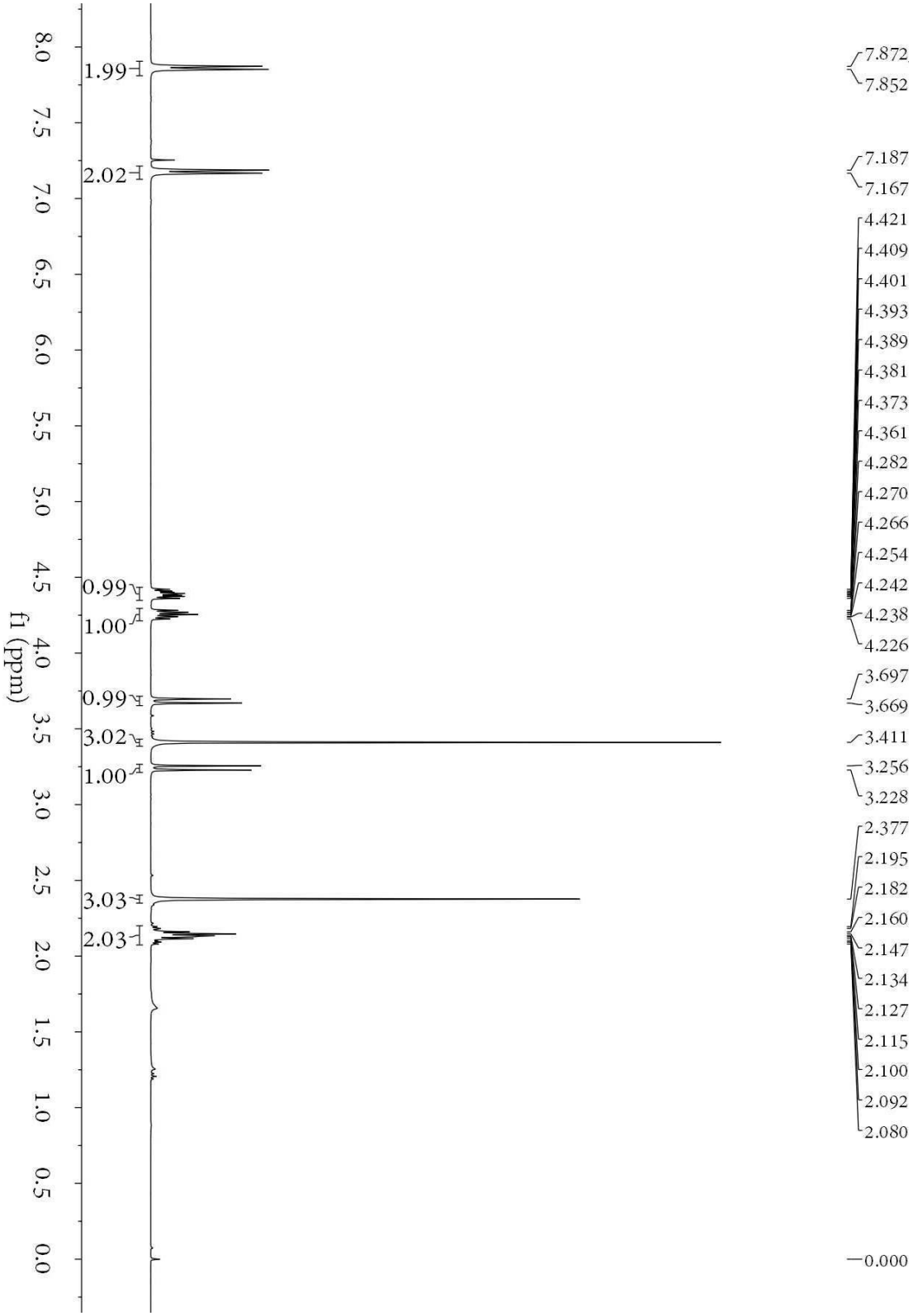


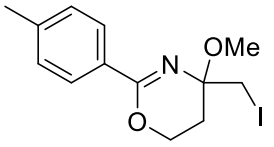
^{13}C NMR of **6,** 45%
$CDCl_3$, 100 MHz



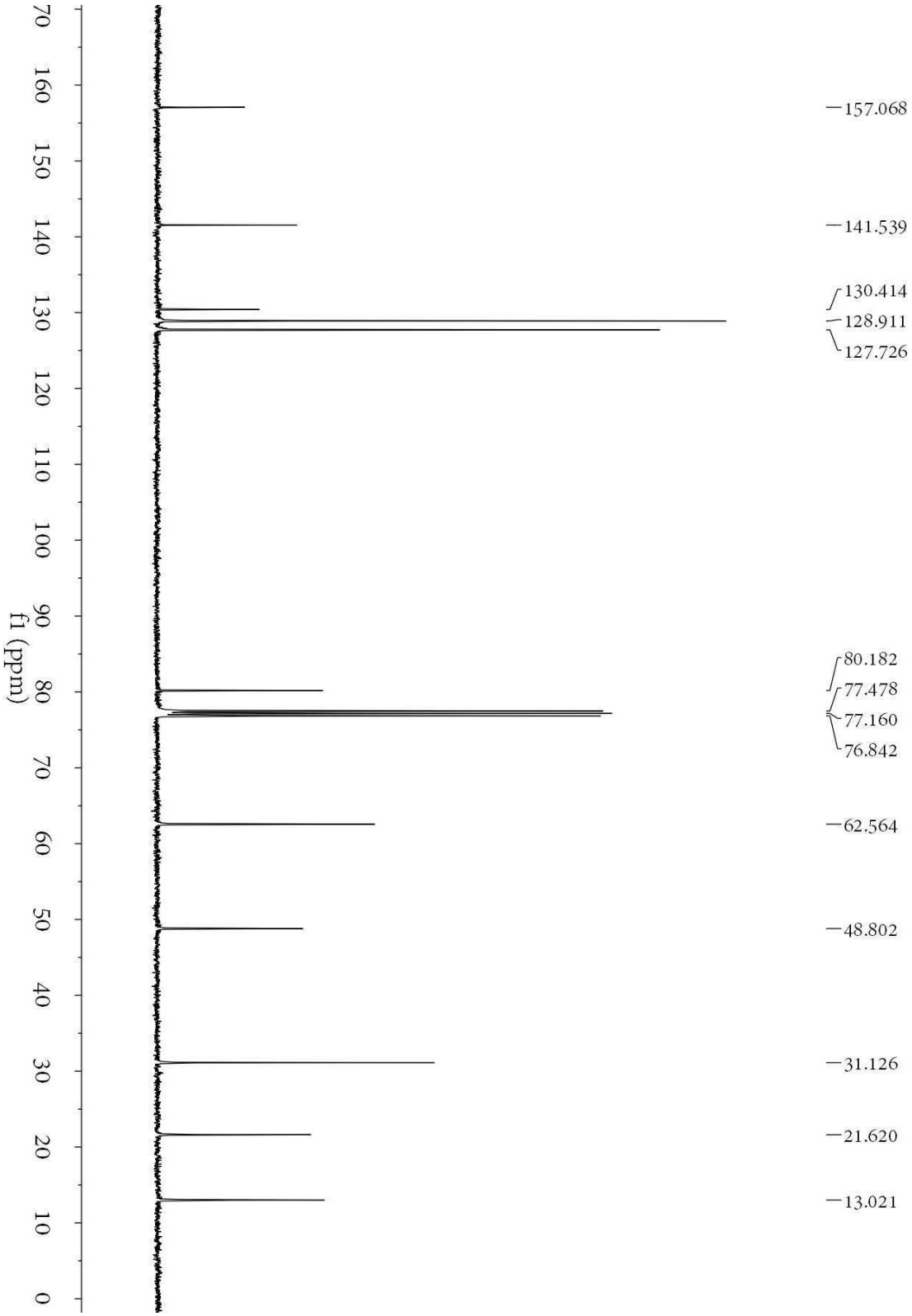


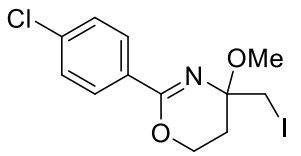
^{1}H NMR of **7b**, 75%
$CDCl_3$, 400 MHz



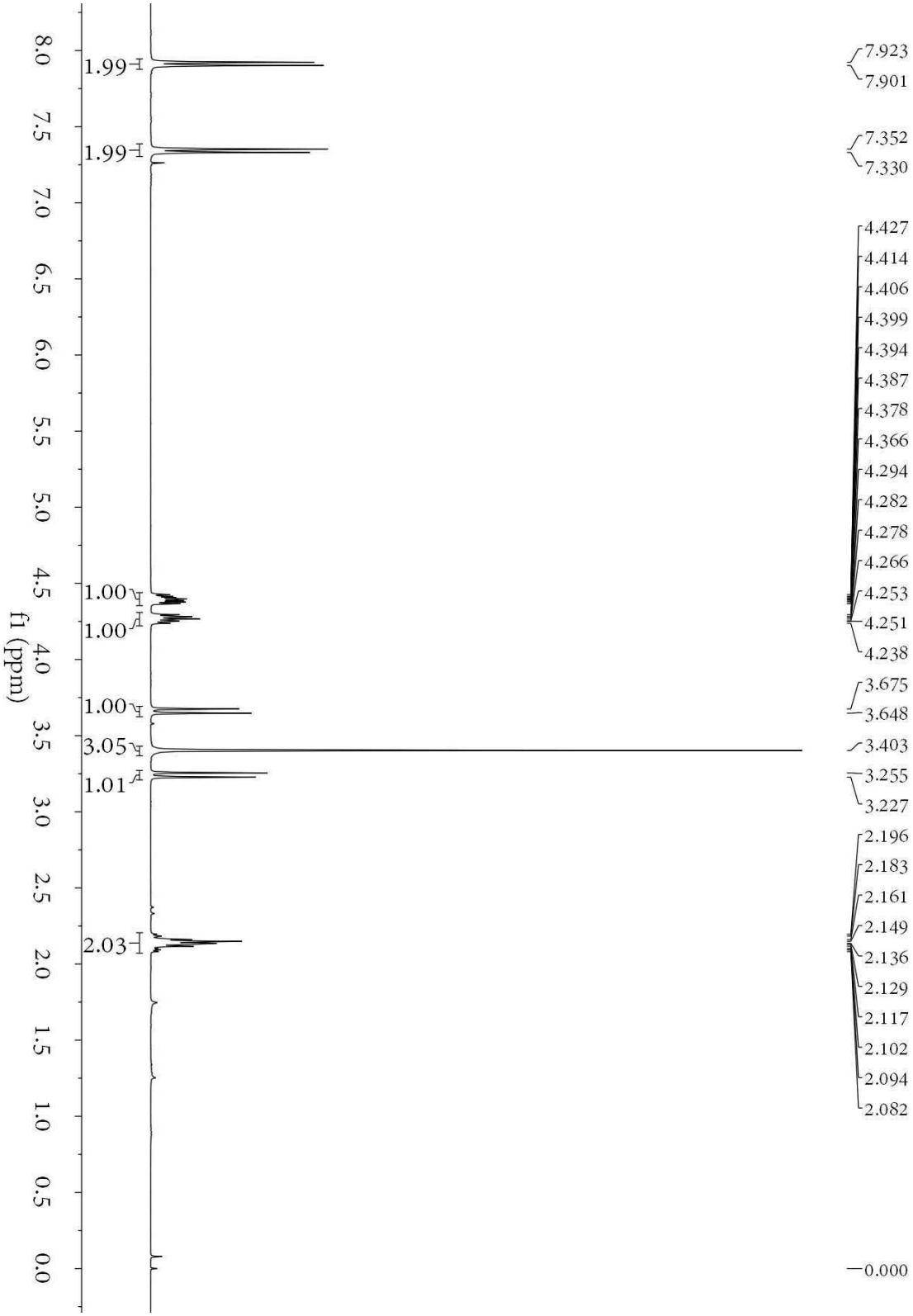


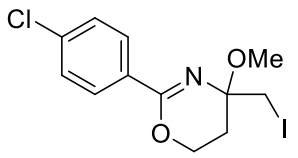
^{13}C NMR of **7b,** 75%
$CDCl_3$, 100 MHz



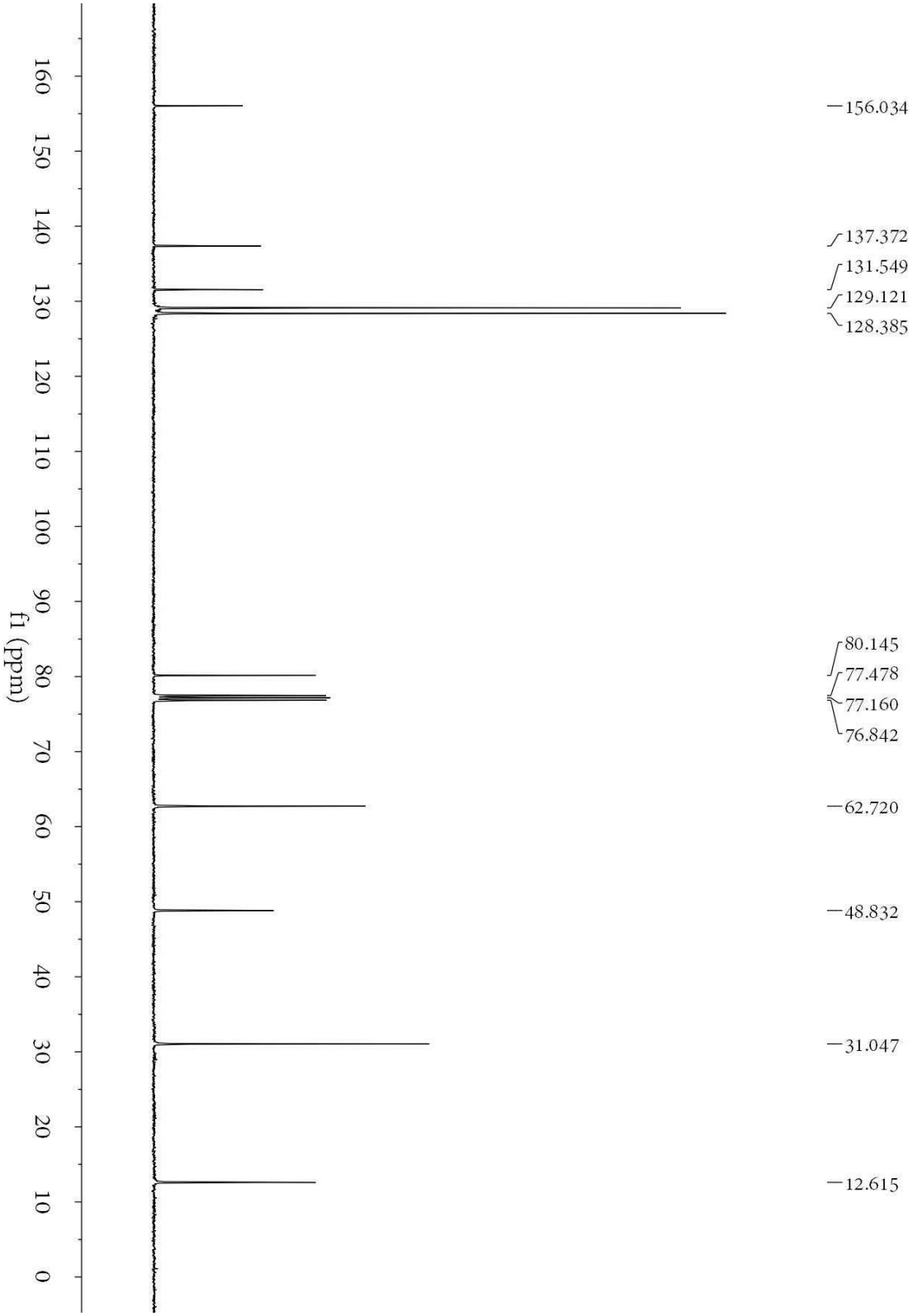


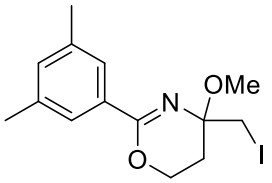
^{1}H NMR of **7e**, 90%
$CDCl_3$, 400 MHz



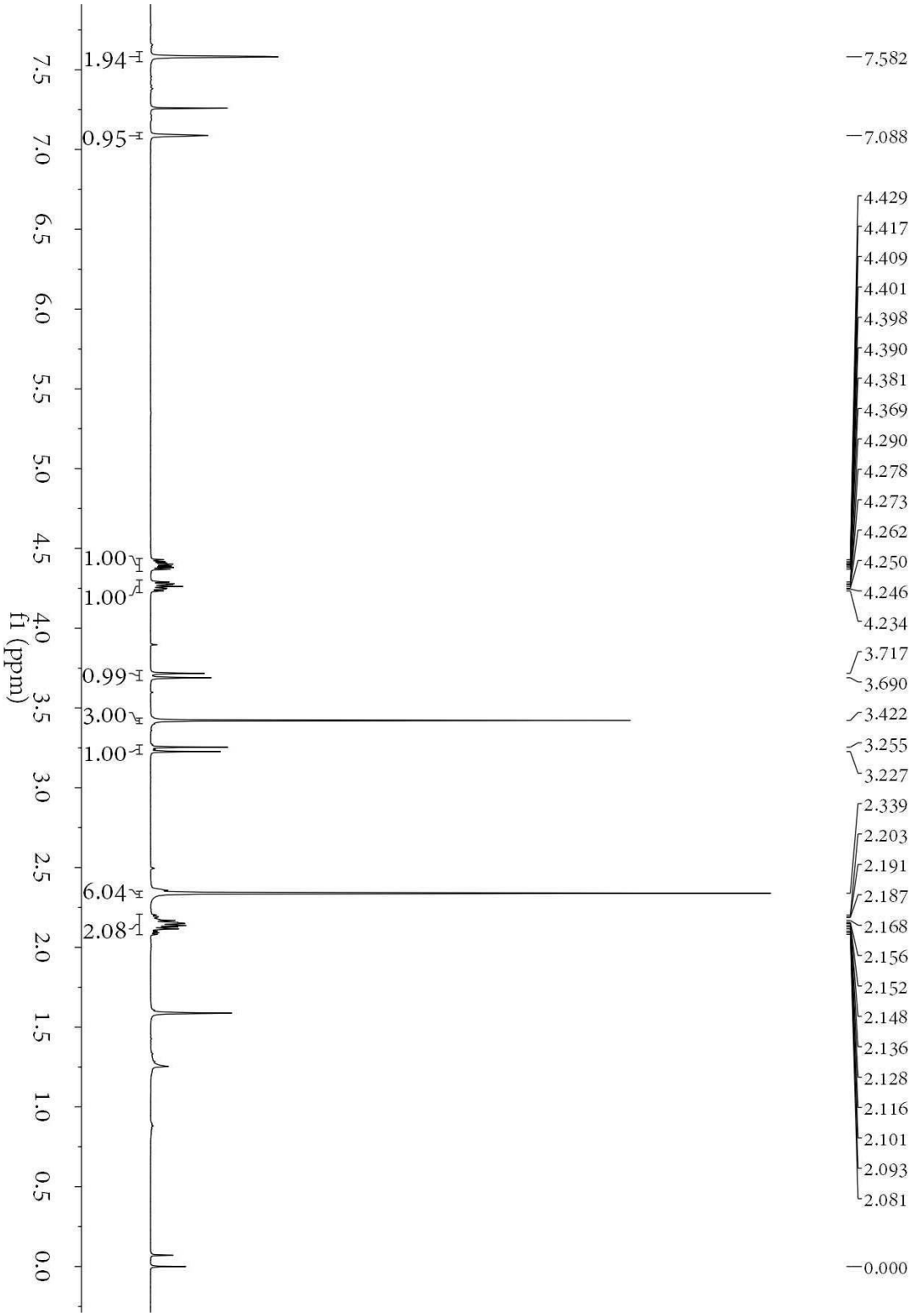


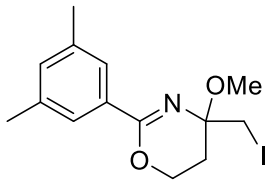
^{13}C NMR of **7e**, 90%
$CDCl_3$, 100 MHz



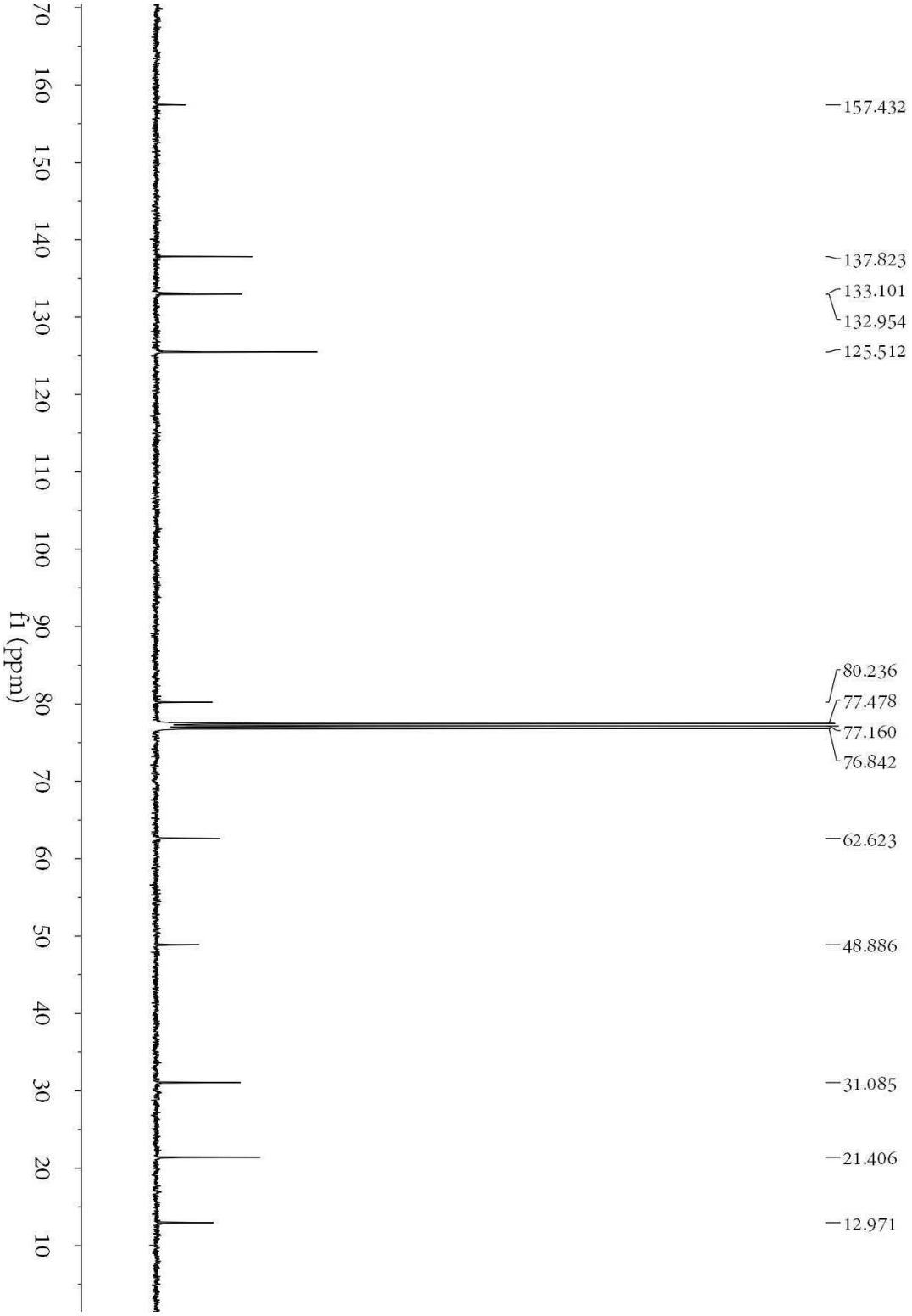


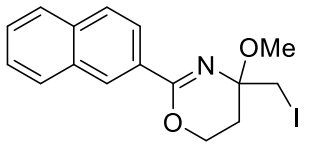
^{1}H NMR of **7l**, 41%
$CDCl_3$, 400 MHz



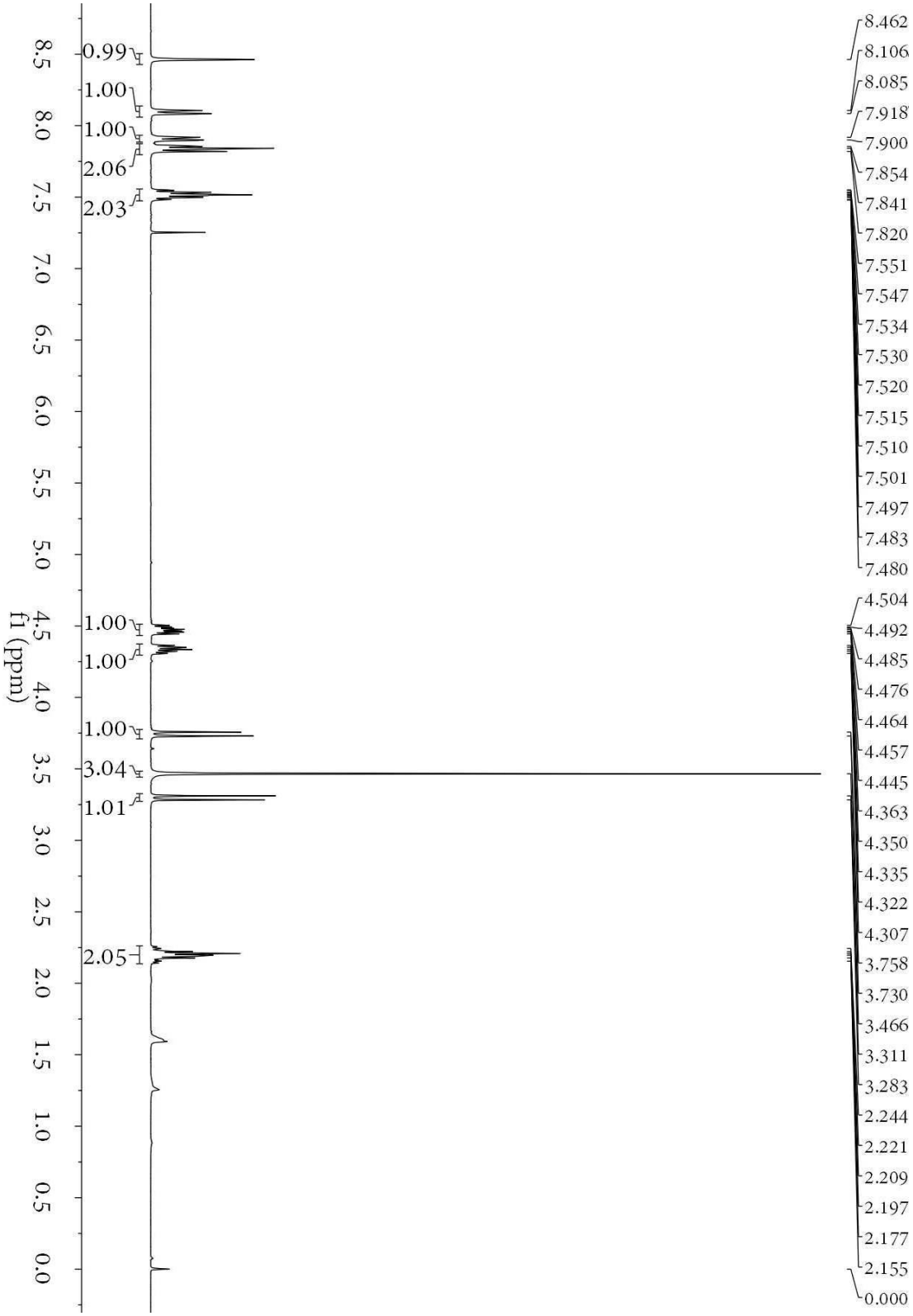


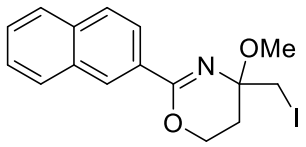
^{13}C NMR of **7l**, 41%
$CDCl_3$, 100 MHz



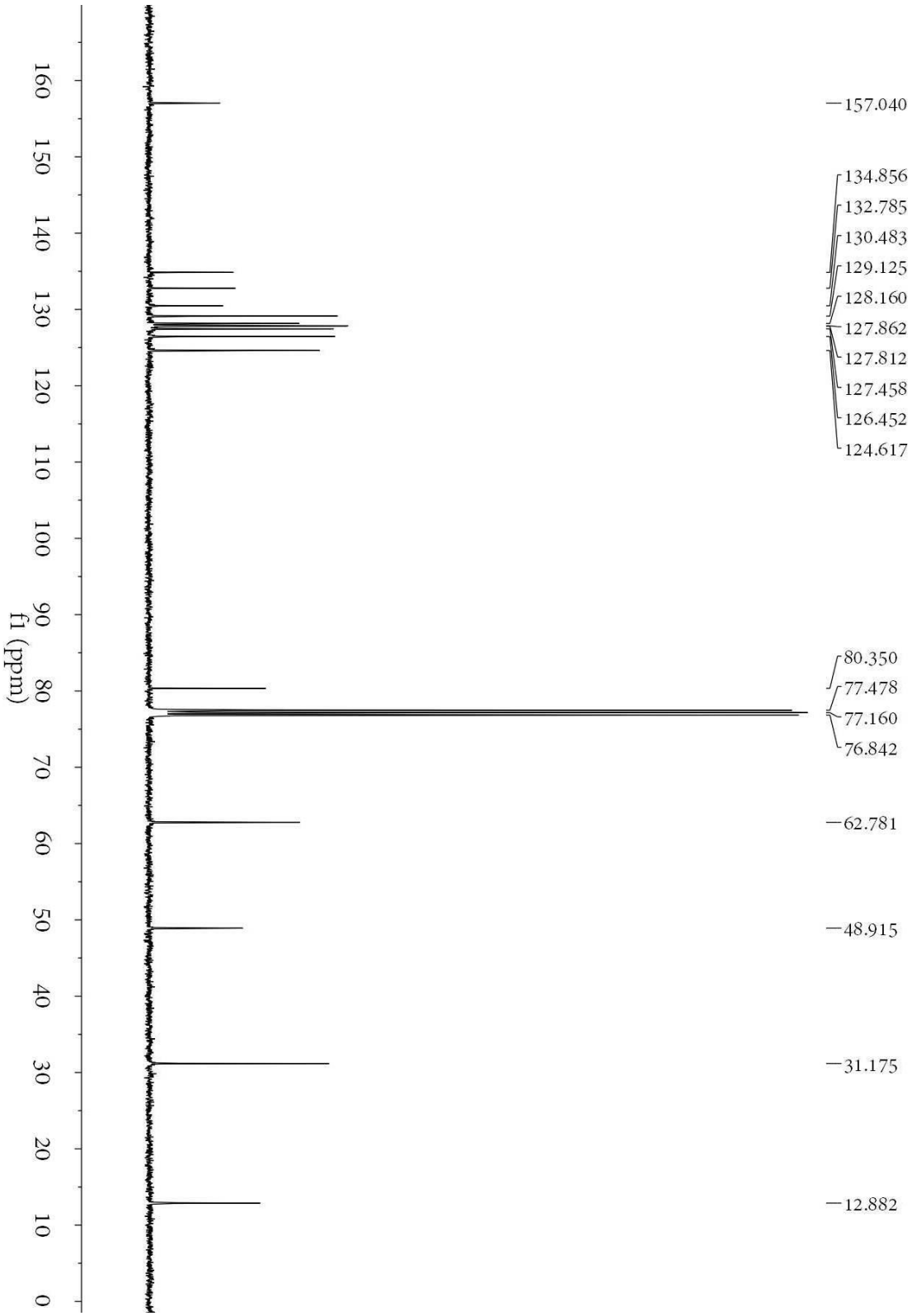


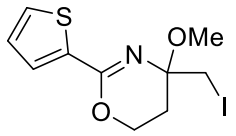
^{1}H NMR of **7q**, 91%
$CDCl_3$, 400 MHz



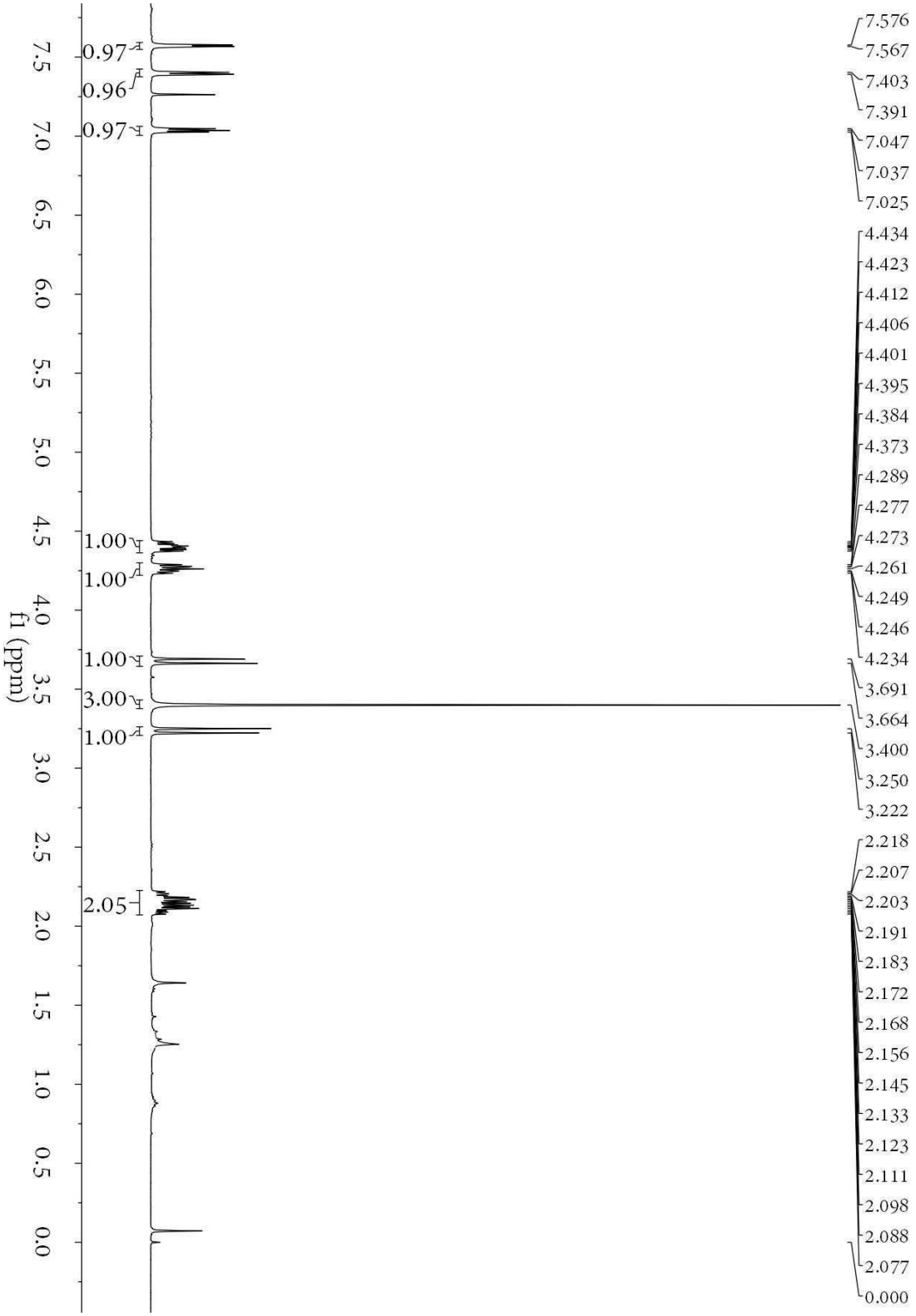


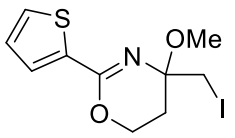
^{13}C NMR of **7q**, 91%
$CDCl_3$, 100 MHz



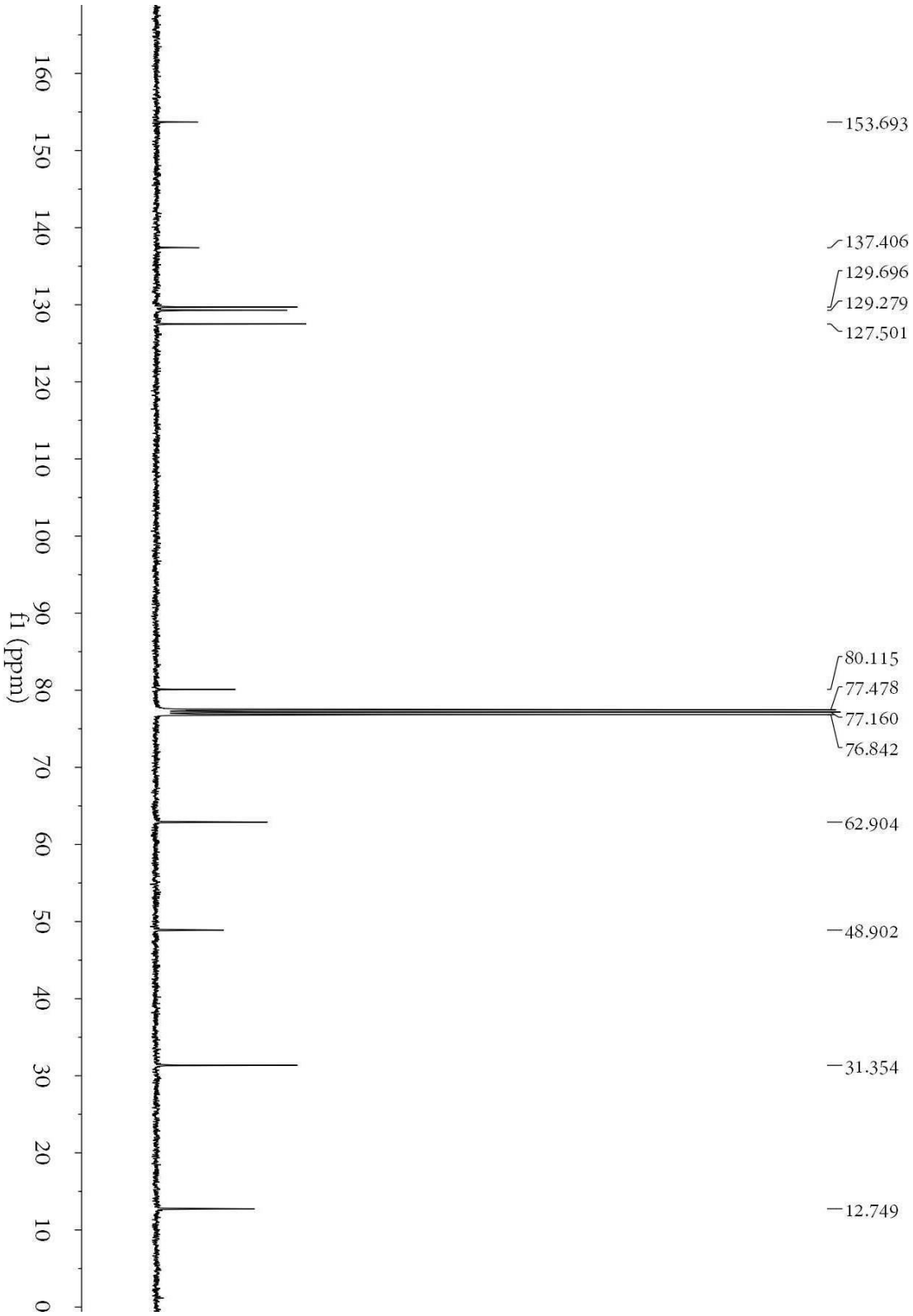


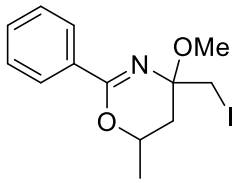
^{1}H NMR of **7r**, 56%
$CDCl_3$, 400 MHz



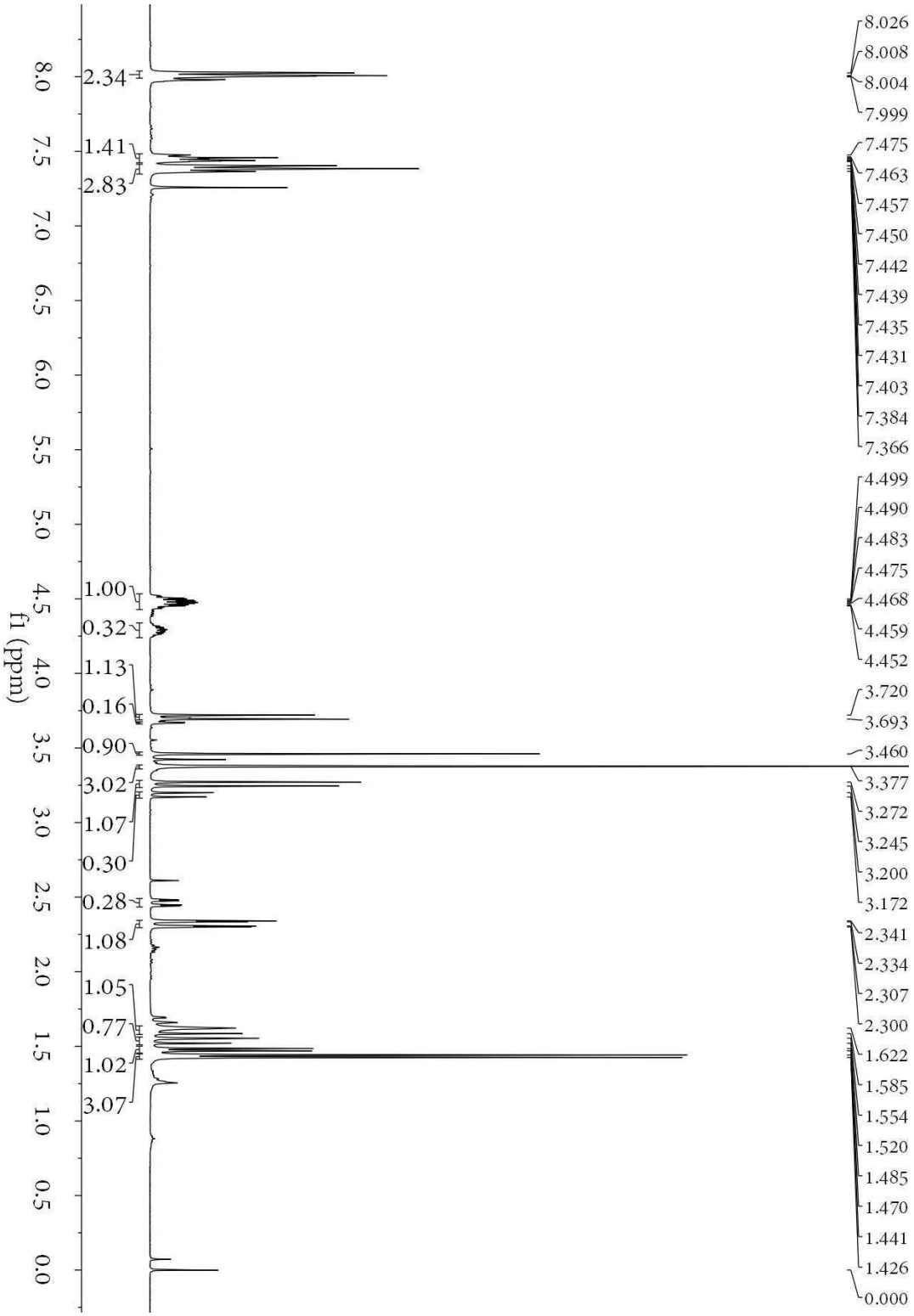


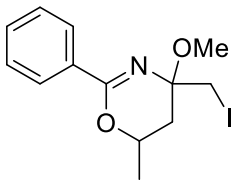
^{13}C NMR of **7r**, 56%
$CDCl_3$, 100 MHz



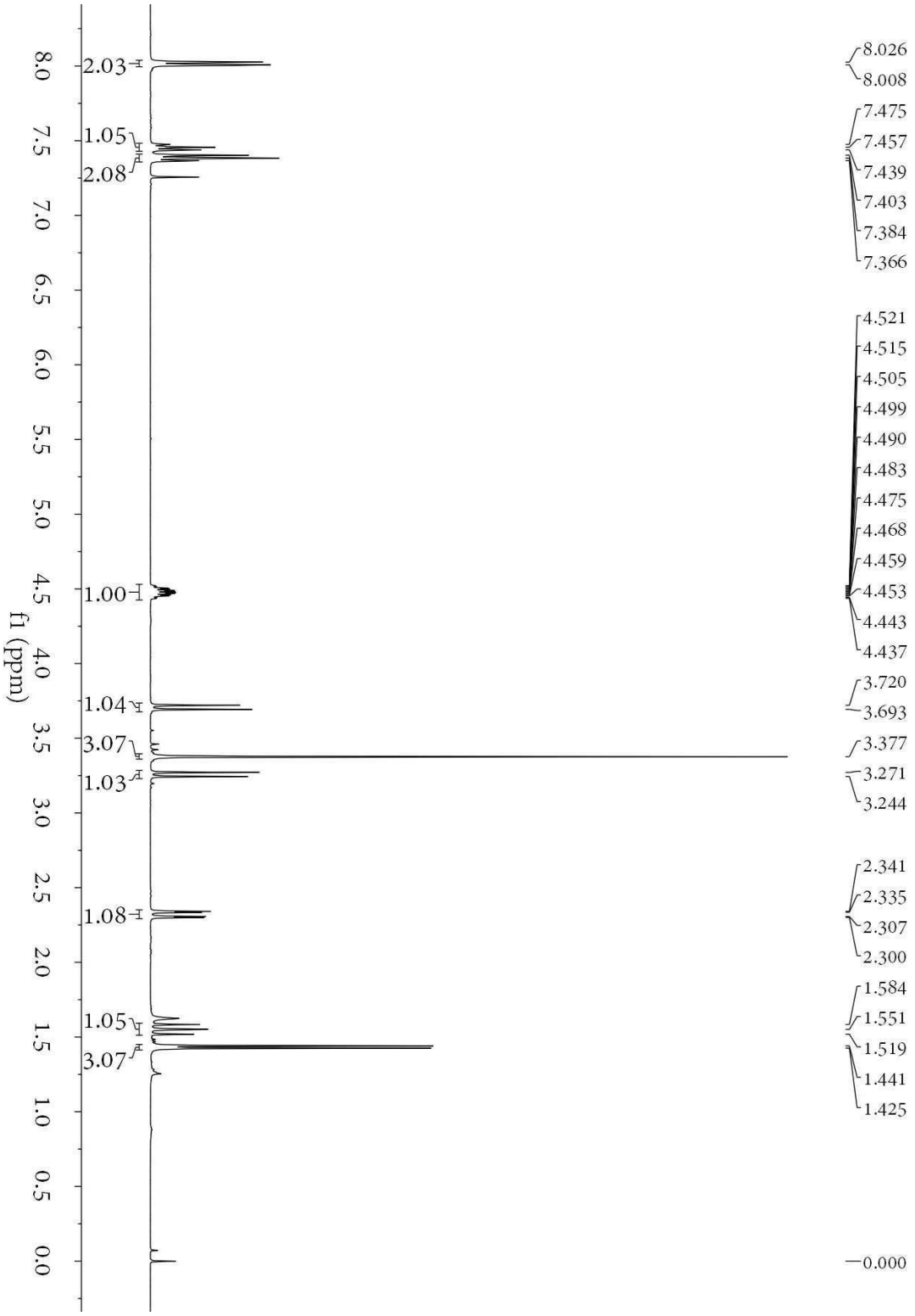


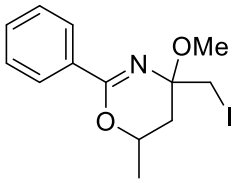
^{1}H NMR of **7t** (mixture), 79%,
dr = 5:1 $CDCl_3$, 400 MHz





^{1}H NMR of **7t** (pure mainly product), 79%,
dr = 5:1 $CDCl_3$, 400 MHz





^{13}C NMR of **7t** (pure mainly product), 79%,
dr = 5:1 $CDCl_3$, 100 MHz