Supporting Information

# Sulfur-directed palladium-catalyzed C($sp^3$)-H $\alpha$-arylation of 3-pyrrolines: easy access to diverse polysubstituted pyrrolidines

Guangwu Sun, Xi Zou, Jinping Wang* and Wen Yang*

*College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China.*

*E-mail: yangwen@hnu.edu.cn; jinpingwang1985@126.com*

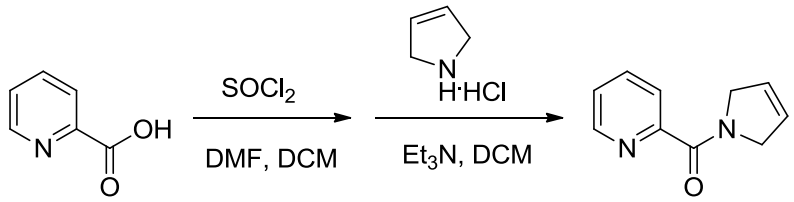
## Table of Contents

## 1 General Information

$^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ or DMSO-*d6* at room temperature on the Varian INOVA-400 spectrometer (400 MHz) or Bruker spectrometer (400 MHz $^{1}H$). The chemical-shifts scale is based on internal TMS. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants (*J*) are reported in Hertz (Hz). Mass spectroscopy data were collected on an HRMS-EI instrument.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $Pd(TFA)_2$ was purchased from Bide Pharmatech Ltd. All solvents were purified and dried according to standard methods prior to use. Products were purified by flash column chromatography on 200-300 mesh silica gel.

## 2 Synthesis of the (Thio)amide Substrates



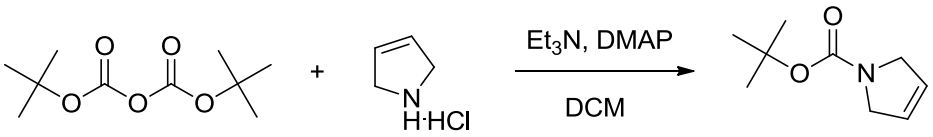

**(2,5-Dihydro-1*H*-pyrrol-1-yl)(pyridin-2-yl)methanone (1a).** To a solution of 2-picolinic acid (86.2 mg, 0.70 mmol) in anhydrous DCM were added thionyl chloride (0.20 mL) and two drops of DMF. The mixture was stirred at 40 °C for 4 h. The excess thionyl chloride was removed under reduced pressure to obtain the crude 2-pyridinecarbonyl chloride.

To a 25 mL round bottom flask charged with a magnetic stir bar were added 3-pyrroline hydrochloride (52.8 mg, 0.50 mmol), anhydrous DCM (3.0 mL), and $Et_3N$ (0.27 mL). The resulting mixture was stirred at 30 °C for 30 minutes, and then cooled to 0 °C. A solution of the 2-pyridinecarbonyl chloride prepared-above in anhydrous DCM (2.0 mL) was added dropwise. After the addition, the reaction was stirred overnight at room temperature. Upon completion, the mixture was diluted with DCM (15 mL), and washed with 1 M HCl and brine successively. The organic phase was separated, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to afford the desired product **1a** as yellow oil (70.1 mg, 80% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.57 (t, $J$ = 4.0 Hz, 1H), 7.90 (dd, $J_1$ = 8.0 Hz, $J_2$ = 2.8 Hz, 1H), 7.80-7.75 (m, 1H), 7.35-7.31 (m, 1H), 5.87-5.84 (m, 1H), 5.80-5.78 (m, 1H), 4.63-4.61 (m, 2H), 4.47-4.45 (m, 2H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 165.9, 153.7, 147.9, 136.8, 126.1, 124.8, 124.7, 124.0, 55.7, 54.3 ppm.

**HRMS** (CI+) calculated for $C_{10}H_{10}N_2NaO$ [M + $Na^+$]: 197.0691, found: 197.0689.



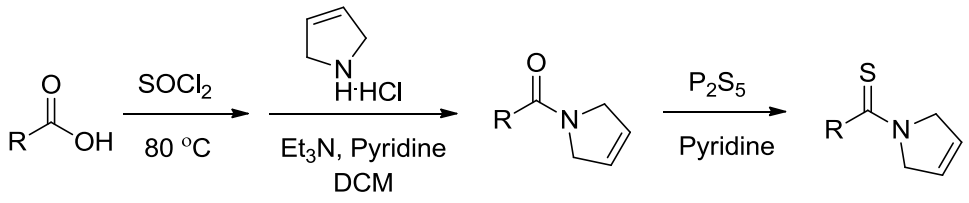

**1b**

***tert*-Butyl 2,5-dihydro-1*H*-pyrrole-1-carboxylate (1b).** To a 50 mL round bottom flask charged with a magnetic stir bar were added 3-pyrroline hydrochloride (317 mg, 3.0 mmol), anhydrous DCM (6.0 mL), $Et_3N$ (0.85 mL), and DMAP (183 mg, 1.5 mmol). The resulting solution was stirred at 30 °C for 30 minutes and then cooled to 0 °C with an ice bath. Afterwards di-*tert*-butyl dicarbonate (786 mg, 3.6 mmol) was added dropwise, and the reaction was stirred overnight at room temperature. Upon completion, the mixture was diluted with DCM (25 mL), and washed with water and brine successively. The organic phase was separated, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford the desired product **1b** as colorless oil (340 mg, 67% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 5.64 (dd, $J_1$ = 19.2 Hz, $J_2$ = 7.6 Hz, 2H), 3.98 (dd, $J_1$ = 16.8 Hz, $J_2$ = 4.8 Hz, 4H), 1.35 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 154.1, 125.8, 125.7, 79.0, 52.9, 52.7, 28.4 ppm.

**HRMS** (CI+) calculated for $C_9H_{15}NNaO$ [M + $Na^+$]: 192.1000, found: 1192.0952.




**1f** R = 1-Ad

**1e** R = 1-Ad

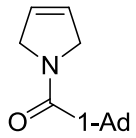
**1c** R = $^t$Bu

To a 125 mL round bottom flask equipped with a magnetic stir bar were added carboxylic acid (2.97 g, 16.5 mmol) and thionyl chloride (4.6 mL). The reaction mixture was refluxed for 2 h. The solvent and excess thionyl chloride were removed under reduced pressure to obtain the crude carbonyl chloride.

To a 125 mL round bottom flask charged with a magnetic stir bar were added 3-pyrroline hydrochloride (1.58 g, 15.0 mmol), anhydrous DCM (20 mL), $Et_3N$ (3.6 mL), and pyridine (3.6 mL) successively. The resulting solution was stirred at 30 °C for 30 minutes, then cooled to 0 °C with an ice bath. A solution of the carbonyl chloride prepared-above in anhydrous DCM (15 mL) was added dropwise. After the addition, the reaction was stirred overnight at room temperature. Upon completion, the mixture was diluted with DCM (40 mL), and washed with 1 M HCl and brine successively. The organic phase was separated, dried over anhydrous $Na_2SO_4$, and concentrated in vacuo. The

residue was used directly for next step or purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6:1) to afford the desired product.

**Adamantan-1-yl(2,5-dihydro-1*H*-pyrrol-1-yl)methanone (1f).**



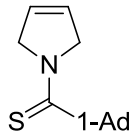

**1f**

White solid (3.35 g, 96% yield). M.p.: 104-105 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 5.73 (s, 2H), 4.40 (br s, 2H), 4.23 (br s, 2H), 1.95-1.92 (m, 9H), 1.64-1.63 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.4, 125.2, 41.7, 38.7, 37.9, 36.5, 28.2 ppm. **HRMS** (CI+) calculated for $C_{15}H_{21}NNaO$ [M + $Na^+$]: 254.1521, found: 254.1470.

To a 100 mL round bottom flask charged with a magnetic stir bar were added the carbonyl amide (1.0 equiv.), $P_2S_5$ (1.25 equiv.), and pyridine (0.4 M). The reaction mixture was heated to 80 °C in an oil bath under $N_2$. After 16 hours, the solution was cooled to room temperature, and acidified with 4 M HCl (pH = 3). The resulting solution was stirred at room temperature for another 2 h, and extracted with DCM. The combined organic layers were washed with 1 M HCl, water, and brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product **1e** and **1c**.

**Adamantan-1-yl (2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (1e).**



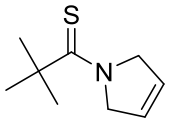

**1e**

White solid (1.89 g, 94%). M.p.: 186-187 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 5.89 (d, $J$ = 4.0 Hz, 2H), 4.73 (s, 4H), 2.16-2.15 (m, 6H), 2.09-2.07 (m, 3H), 1.71-1.70 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 210.2, 125.5, 124.7, 65.6, 57.5, 46.7, 40.5, 36.5, 29.1 ppm.

**HRMS** (CI+) calculated for $C_9H_{21}NNaS$ [M + $Na^+$]: 270.1292, found: 270.1241.

**1-(2,5-Dihydro-1*H*-pyrrol-1-yl)-2,2-dimethylpropane-1-thione (1c).**

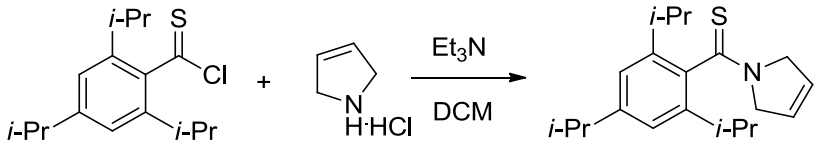



**1c**

Yellow oil (254 mg, 75% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 5.89-5.84 (m, 2H), 4.68-4.66 (m, 2H), 4.58-4.56 (m, 2H), 1.42-1.39 (m, 9H) ppm.

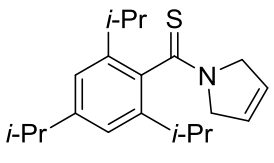
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 209.3, 125.1, 124.8, 64.8, 57.4, 43.7, 43.8, 30.2 ppm.

**HRMS** (CI+) calculated for $C_9H_{15}NNaS$ [M + $Na^+$]: 192.0823, found: 192.0778.




**1d**

**(2,5-Dihydro-1*H*-pyrrol-1-yl)(2,4,6-triisopropylphenyl)methanethione (1d).** The thio-carbonyl chloride was prepared according to the literature procedure.[1] Under $N_2$, to a 50 mL round bottom flask charged with a magnetic stir bar were added 3-pyrroline hydrochloride (52.8 mg, 0.50 mmol), anhydrous DCM (5.0 mL), and $Et_3N$ (0.20 mL). The resulting mixture was stirred at 30 °C for 30 minutes. The prepared thio-carbonyl chloride (170 mg, 0.60 mmol) in anhydrous DCM (3.0 mL) was added dropwise at 0 °C, and the mixture was stirred overnight at room temperature. Upon completion, 1 M HCl (3.0 mL) was added slowly to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with DCM (2 × 10 mL). The organic layers were combined, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the desired product **1d**.



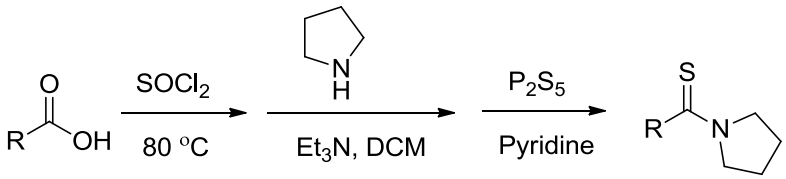

**1d**

White solid (170 mg, 76% yield). M.p.: 135-136 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.99 (s, 2H), 6.00-5.96 (m, 1H), 5.80-5.76 (m, 1H), 4.74-4.72 (m, 2H), 3.96-3.94

(m, 2H), 2.89-2.80 (m, 3H), 1.25-1.19 (m, 18H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 198.4, 148.9, 141.9, 138.2, 126.1, 125.1, 121.7, 58.7, 58.6, 34.3, 30.8, 25.3, 24.1, 23.6 ppm.

**HRMS** (CI+) calculated for $C_{20}H_{29}NNaS$ [M + $Na^+$]: 338.1918, found: 338.1947.




**1g** R = 1-Ad

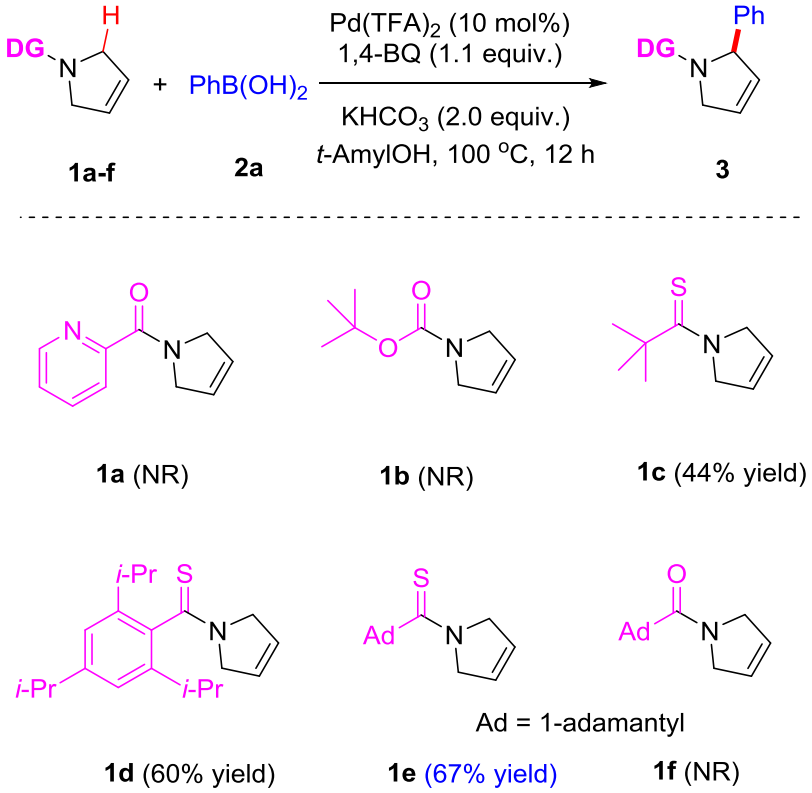
**Adamantan-1-yl(pyrrolidin-1-yl)methanethione (1g)** was prepared according to the same procedure for **1e**.

White solid (2.92 g, 80%yield). M.p.: 152-153 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 3.82 (t, $J$ = 6.8 Hz, 4H), 1.99-1.93 (m, 6H), 1.90-1.88 (m, 2H), 1.78-1.73 (m, 2H), 1.57 (t, $J$ = 3.2 Hz, 6H) ppm.

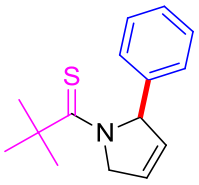
**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 208.5, 58.0, 52.8, 45.8, 40.2, 36.2, 28.6, 27.3, 22.4 ppm.

**HRMS** (CI+) calculated for $C_{15}H_{23}NNaS$ [M + $Na^+$]: 272.1449, found: 272.1391.

## 3 Screening of Different Directing Groups




To a standard 15 mL Schlenk tube charged with a magnetic stir bar were added (thio)amide **1** (0.10 mmol, 1.0 equiv.), phenylboronic acid (24.4 mg, 0.20 mmol, 2.0 equiv.), 1,4-benzoquinone (11.9 mg, 0.11 mmol, 1.1 equiv.), potassium bicarbonate (20.0 mg, 0.20 mmol, 2.0 equiv.), palladium(II) trifluoroacetate (3.32 mg, 10 mol%), and 2-methyl-2-butanol (2.0 mL). The tube was sealed, and the reaction mixture was stirred at 100 °C for 4 h. The mixture was filtered through celite, and washed with ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the desired product.



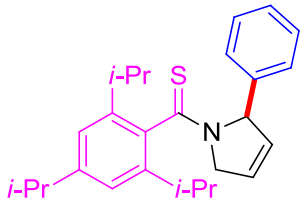

**2,2-Dimethyl-1-(2-phenyl-2,5-dihydro-1*H*-pyrrol-1-yl)propane-1-thione (3ca).**

M.p.: 50-52 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32-7.20 (m, 5H), 6.58 (s, 1H), 5.95-5.91 (m, 1H), 5.88-5.85 (m, 1H), 4.83 (dd, $J_1$ = 53.6 Hz, $J_2$ = 8.0 Hz, 2H), 1.46 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 210.8, 140.2, 131.9, 128.4, 127.2, 126.8, 122.5, 76.5, 58.8, 44.4, 30.7 ppm.

**HRMS** (CI+) calculated for $C_{15}H_{19}NNaS$ [M + $Na^+$]: 268.1136, found: 268.1080.




**(2-Phenyl-2,5-dihydro-1*H*-pyrrol-1-yl)(2,4,6-triisopropylphenyl)methane-thione (3da).** M.p.: 120-121 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) (6:4 mixture of rotamers, peaks corresponding to minor rotamer starred) $\delta$ 7.37 (d, $J$ = 4.4 Hz, 2.3H), 7.33-7.27 (m, 0.7H)*, 7.17-7.05 (m, 2H), 7.01 (d, $J$ = 1.6 Hz, 0.6H)*, 6.95 (d, $J$ = 1.6 Hz, 0.6H), 6.68 (d, $J$ = 1.6 Hz, 0.4H)*, 6.53-6.51 (m, 0.8H), 6.36 (t, $J$ = 2.2 Hz, 0.6H), 6.10-6.07 (m, 0.4H)*, 6.01-5.97 (m, 0.6H), 5.88-5.86 (m, 0.6H), 5.72-5.70 (m, 0.4H)*, 5.34 (t, $J$ = 2.2 Hz, 0.15H)*, 5.29 (t, $J$ = 2.2 Hz, 0.2H)*, 5.25-52.4 (m, 0.4H)*, 4.75-4.73 (m, 0.2H), 4.70-4.68 (m, 0.15H)*, 4.18 (t, $J$ = 2.2 Hz, 1.2H), 3.00-2.93 (m, 0.6H),

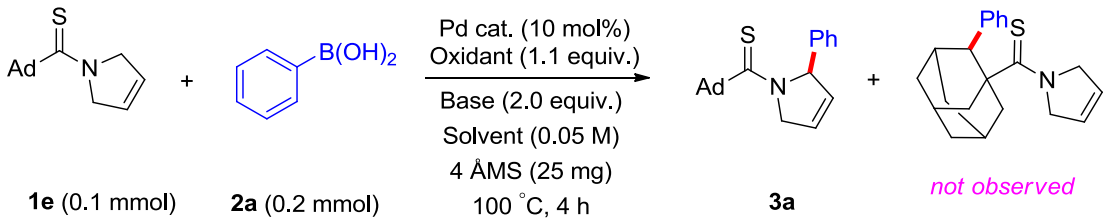
2.91-2.83 (m, 1H), 2.76-2.70 (m, 0.4H)*, 2.69-2.62 (m, 0.6H), 2.34-2.27 (m, 0.4H)*, 1.40 (d, *J* = 7.2 Hz, 1.5H)*, 1.29-1.26 (m, 6.5H), 1.25 (s, 3H), 1.23 (s, 2H), 1.21 (s, 1H), 1.10 (d, *J* = 6.4 Hz, 1.5H)*, 1.02 (d, *J* = 6.8 Hz, 1.5H), 0.09 (d, *J* = 6.8 Hz, 1H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 200.2, 199.0*, 149.2*, 148.8, 144.6, 142.6, 141.6*, 140.7, 139.0*, 138.8, 138.4*, 137.6, 132.3*, 131.2, 128.6, 128.32, 128.28*, 128.0, 127.8, 127.5*, 124.3*, 123.2, 121.7*, 121.3, 120.8, 72.5, 72.2*, 59.8*, 59.7, 34.5, 34.3*, 31.2, 30.89*, 30.88, 29.8, 26.3, 25.9*, 25.3, 24.9, 24.4, 24.1*, 23.8*, 23.4, 22.9, 20.8 ppm.

**HRMS** (CI+) calculated for $C_{26}H_{33}NNaS$ [M + $Na^+$]: 414.2231, found: 414.2222.

## 4 Optimization of Reaction Conditions

**Table S1** Screening results of reaction conditions[a]



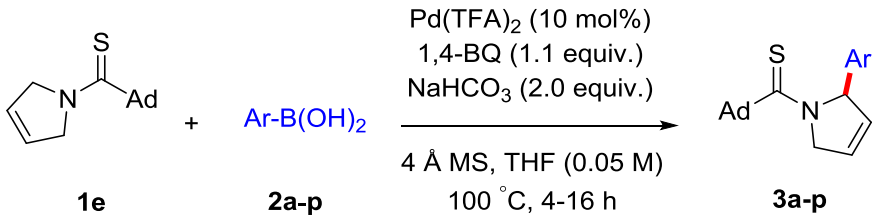

**1e** (0.1 mmol) **2a** (0.2 mmol) **3a**

| Entry | Pd cat. | Solvent | Base | Oxidant | Conv.[b] (%) | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | $Pd(TFA)_2$ | *t*-AmylOH | $KHCO_3$ | 1,4-BQ | 88 | 77 |
| 2 | $Pd(OAc)_2$ | *t*-AmylOH | $KHCO_3$ | 1,4-BQ | 26 | 7 |
| 3 | $Pd_2(dba)_3$ | *t*-AmylOH | $KHCO_3$ | 1,4-BQ | 29 | 8 |
| 4 | $Pd(PPh_3)_2Cl_2$ | *t*-AmylOH | $KHCO_3$ | 1,4-BQ | 39 | 17 |
| 5 | $Pd(PPh_3)_4$ | *t*-AmylOH | $KHCO_3$ | 1,4-BQ | 45 | 6 |
| 6 | $Pd(TFA)_2$ | HFIP | $KHCO_3$ | 1,4-BQ | 50 | 7 |
| 7 | $Pd(TFA)_2$ | $^{i}$PrOH | $KHCO_3$ | 1,4-BQ | - | n. d.[c] |
| 8 | $Pd(TFA)_2$ | Dioxane | $KHCO_3$ | 1,4-BQ | 95 | 73 |
| 9 | $Pd(TFA)_2$ | THF | $KHCO_3$ | 1,4-BQ | 92 | 78 |
| 10 | $Pd(TFA)_2$ | DCE | $KHCO_3$ | 1,4-BQ | 58 | 39 |
| 11 | $Pd(TFA)_2$ | DMF | $KHCO_3$ | 1,4-BQ | 83 | 66 |
| 12 | $Pd(TFA)_2$ | $CH_3CN$ | $KHCO_3$ | 1,4-BQ | 67 | 6 |
| 13 | $Pd(TFA)_2$ | Toulene | $KHCO_3$ | 1,4-BQ | 88 | 42 |
| 14 | $Pd(TFA)_2$ | THF | KO$^{t}$Bu | 1,4-BQ | - | n. d. |
| 15 | $Pd(TFA)_2$ | THF | $K_3PO_4$ | 1,4-BQ | - | n. d. |
| 16 | $Pd(TFA)_2$ | THF | $K_2HPO_4$ | 1,4-BQ | 91 | 73 |
| 17 | $Pd(TFA)_2$ | THF | $KH_2PO_4$ | 1,4-BQ | >95 | 73 |
| 18 | $Pd(TFA)_2$ | THF | $NaH_2PO_4$ | 1,4-BQ | 94 | 73 |
| 19 | $Pd(TFA)_2$ | THF | KOPiv | 1,4-BQ | - | n. d. |
| 20 | $Pd(TFA)_2$ | THF | $Cs_2CO_3$ | 1,4-BQ | - | n. d. |

| | | | | | | |
|---|---|---|---|---|---|---|
| 21 | $Pd(TFA)_2$ | THF | $K_2CO_3$ | 1,4-BQ | - | n. d. |
| 22 | $Pd(TFA)_2$ | THF | $NaHCO_3$ | 1,4-BQ | >95 | 82 |
| 23 | $Pd(TFA)_2$ | THF | KF | 1,4-BQ | 95 | 78 |
| 24 | $Pd(TFA)_2$ | THF | KOPiv | 1,4-BQ | - | n. d. |
| 25 | $Pd(TFA)_2$ | THF | $NaHCO_3$ | TEMPO | - | n. d. |
| 26[d] | $Pd(TFA)_2$ | THF | $NaHCO_3$ | TEMPO | - | n. d. |
| 27 | $Pd(TFA)_2$ | THF | $NaHCO_3$ | $PhI(OAc)_2$ | - | n. d. |
| 28[e] | $Pd(TFA)_2$ | THF | $NaHCO_3$ | 1,4-BQ | 36 | NR |
| 29[f] | $PdCl_2$ | THF | $NaHCO_3$ | 1,4-BQ | 85 | 30 |

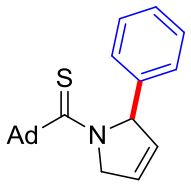
[a] Reactions were conducted on a 0.1 mmol scale. [b] Yield was determined by $^1H$ NMR analysis of the crude products using benzyl benzoate as the internal standard. [c] n. d. = not determined. [d] 4.0 equiv. of TEMPO was used. [e] Reaction was conducted without phenylboronic acid. [h] *p*-Toluenesulfonic acid monohydrate (20 mol%) was added.

## 5 General Procedure for the C(sp³)-H *α*-Arylation of 3-Pyrrolines




**1e** **2a-p** **3a-p**

To a standard 15 mL Schlenk tube charged with a magnetic stir bar were added thioamide **1e** (49.5 mg, 0.20 mmol, 1.0 equiv.), arylboronic acid **2** (0.40 mmol, 2.0 equiv.), 1,4-benzoquinone (23.8 mg, 0.22 mmol, 1.1 equiv., unless otherwise noted), sodium bicarbonate (33.6 mg, 0.40 mmol, 2.0 equiv.), palladium(II) trifluoroacetate (6.65 mg, 10 mol%), anhydrous THF (4.0 mL, 0.05 M), and 4 Å MS (50 mg). The tube was sealed, and the reaction mixture was stirred at 100 ℃ for 4-16 h. Upon completion (monitored by TLC), the mixture was filtered through celite, and washed with ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 200/1 to 100/1, unless otherwise noted) to give the desired product **3**.




**3a**

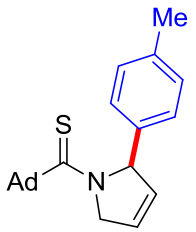
**Adamantan-1-yl(2-phenyl-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3a)** was prepared according to the general procedure for 4 h (pale yellow solid,

45.5 mg, 70% yield). M.p.: 130-131 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32-7.27 (m, 2H), 7.23-7.16 (m, 3H), 6.66 (s, 1H), 5.94-5.92 (m, 1H), 5.87-5.86 (m, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 2.22-2.10 (m, 9H), 1.78-1.55 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.1, 140.2, 131.5, 128.3, 127.0, 126.6, 122.4, 76.8, 58.6, 46.9, 40.5, 36.4, 28.9 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{25}NNaS$ [M + $Na^+$]: 346.1605, Found: 346.1639.



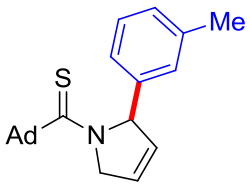

**3b**

**Adamantan-1-yl(2-(*p*-tolyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3b)** was prepared according to the general procedure for 4 h (pale yellow solid, 39.2 mg, 58% yield). M.p.: 168-169 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.12-7.07 (m, 4H), 6.63 (s, 1H), 5.93-5.91 (m, 1H), 5.86-5.84 (m, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 3H), 2.22-2.10 (m, 9H), 1.78-1.58 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.2, 137.3, 136.7, 131.9, 129.2, 126.7, 122.2, 76.7, 58.6, 47.0, 40.6, 36.5, 29.0, 21.2 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{27}NNaS$ [M + $Na^+$]: 360.1762, Found: 360.1771.



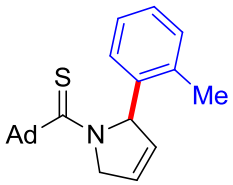

**3c**

**Adamantan-1-yl(2-(m-tolyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3c)** was prepared according to the general procedure for 4 h (pale yellow solid, 39.3 mg, 58% yield). M.p.: 120-121 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.18 (t, $J$ = 7.6 Hz, 1H), 7.03-6.95 (m, 3H), 6.64 (s, 1H), 5.94-5.91 (m, 1H), 5.87-5.84 (m, 1H), 5.04 (d, $J$ = 16.0 Hz, 1H), 4.87 (d, $J$ = 16.0 Hz, 1H), 2.33 (s, 3H), 2.24-2.10 (m, 9H), 1.72-1.57 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.2, 140.2, 138.0, 131.8, 128.4, 127.9, 127.5, 123.5, 122.3, 76.8, 58.7, 47.0, 40.6, 36.5, 29.0, 21.6 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{27}NNaS$ [M + $Na^+$]: 360.1762, Found: 360.1768.



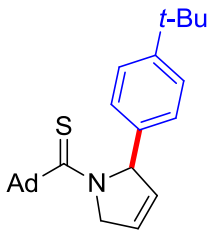

**3d**

**Adamantan-1-yl(2-(o-tolyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3d)** was prepared according to the general procedure for 4 h (pale yellow solid, 28.5 mg, 42% yield). M.p.: 139-140 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.21-7.04 (m, 3H), 6.85 (d, $J$ = 6.0 Hz, 1H), 6.68 (s, 1H), 5.91-5.84 (m, 2H), 5.06 (d, $J$ = 16.0 Hz, 1H), 4.94 (d, $J$ = 16.0 Hz, 1H), 2.47 (s, 3H), 2.24-2.10 (m, 9H), 1.72-1.58 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 210.8, 139.0, 135.3, 130.4, 130.3, 127.0, 126.5, 123.9, 122.3, 74.8, 58.9, 46.9, 40.6, 36.5, 29.1, 19.5 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{27}NNaS$ [M + $Na^+$]: 360.1762, Found: 360.1764.



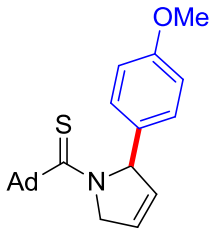

**3e**

**Adamantan-1-yl(2-(4-(tert-butyl)phenyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3e)** was prepared according to the general procedure for 4 h (pale yellow solid, 43.6 mg, 57% yield). M.p.: 172-173 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30 (d, $J$ = 8.0 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 6.69 (s, 1H), 5.95-5.93 (m, 1H), 5.86-5.83 (m, 1H), 5.05 (d, $J$ = 16.0 Hz, 1H), 4.84 (d, $J$ = 15.6 Hz, 1H), 2.24-2.10 (m, 9H), 1.78-1.58 (m, 6H), 1.29 (s, 9H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.2, 149.7, 137.0, 132.0, 126.3, 125.5, 122.2, 76.5, 58.6, 47.1, 40.8, 36.5, 34.5, 31.5, 29.1 ppm.

**HRMS** (CI+) Calcd for $C_{25}H_{33}NNaS$ [M + $Na^+$]: 402.2231, Found: 402.2233.




**3f**

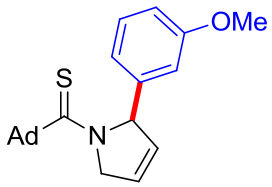
**Adamantan-1-yl(2-(4-methoxyphenyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanet**

**hione (3f)** was prepared according to the general procedure for 4 h (orange solid, 43.2 mg, 61% yield). M.p.: 159-161 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.12 (d, $J$ = 8.4 Hz, 2H), 6.82 (d, $J$ = 8.4 Hz, 2H), 6.62 (s, 1H), 5.92-5.89 (m, 1H), 5.86-5.84 (m, 1H), 5.01 (d, $J$ = 16.0 Hz, 1H), 4.85 (d, $J$ = 15.6 Hz, 1H), 3.77 (s, 3H), 2.20-2.07 (m, 9H), 1.72-1.63 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.2, 158.6, 132.2, 131.9, 128.3, 122.1, 113.7, 76.2, 58.5, 55.2, 47.0, 40.6, 36.5, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{27}NNaOS$ [M + $Na^+$]: 376.1711, Found: 376.1678.



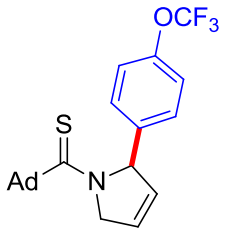

**3g**

**Adamantan-1-yl(2-(3-methoxyphenyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3g)** was prepared according to the general procedure for 4 h (orange solid, 46.1 mg, 65% yield). M.p.: 111-112 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.23-7.11 (m, 1.5H), 6.83-6,70 (m, 2.5H), 6.62 (s, 1H), 5.92-5.84 (m, 2H), 5.02 (dd, $J_1$ = 15.6 Hz, $J_2$ = 4.8 Hz, 1H), 4.86 (d, $J$ = 16.0 Hz, 1H), 3.77 (s, 3H), 2.20-2.07 (m, 9H), 1.77-1.60 (s, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.4, 159.7, 142.0, 131.5, 129.4, 122.6, 118.9, 112.5, 112.0, 76.7, 58.6, 55.1, 47.0, 40.6, 36.4, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{27}NNaOS$ [M + $Na^+$]: 376.1711, Found: 376.1617.



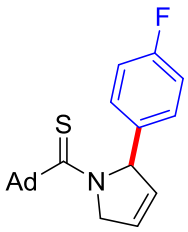

**3h**

**Adamantan-1-yl(2-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1*H*-pyrrol-1-yl) methanethione (3h)** was prepared according to the general procedure for 4 h (pale yellow solid, 49.2 mg, 60% yield). M.p.: 120-121 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.20 (d, $J$ = 8.4 Hz, 2H), 7.12 (d, $J$ = 8.4 Hz, 2H), 6.65 (s, 1H), 5.92-5.88 (m, 2H), 5.04 (d, $J$ = 15.6 Hz, 1H), 4.87 (dd, $J_1$ = 15.6 Hz, $J_2$ = 3.6 Hz, 1H), 2.20-2.08 (m, 9H), 1.78-1.65 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.7, 148.0, 138.9, 131.2, 128.3, 122.9, 120.8, 120.5 (q, $J$ = 255.6 Hz), 76.1, 58.6, 47.1, 40.6, 36.4, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{24}F_3NNaOS$ [M + $Na^+$]: 430.1428, Found: 430.1401.




**3i**

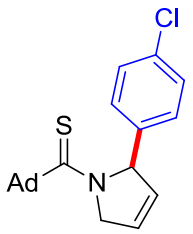
**Adamantan-1-yl(2-(4-fluorophenyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3i)** was conducted with 0.4 mmol **1e** and prepared according to the general procedure for 4 h (white solid, 70.1 mg, 51% yield). M.p.: 155-156 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.17-7.14 (m, 2H), 6.96 (t, $J$ = 8.4 Hz, 2H), 6.62 (s,

1H), 5.91-5.87 (m, 2H), 5.02 (d, $J$ = 16.0 Hz, 1H), 4.87 (dd, $J_1$ = 16.0 Hz, $J_2$ = 3.6 Hz, 1H), 2.19-2.07 (m, 9H), 1.78-1.57 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.5, 161.8 (d, $J$ = 244.1 Hz), 136.0, 131.5, 128.7 (d, $J$ = 7.4 Hz), 122.7, 115.2 (d, $J$ = 21.3 Hz), 76.1, 58.6, 47.1, 40.6, 36.4, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{24}FNNaS$ [M + $Na^+$]: 364.1511, Found: 364.1507.



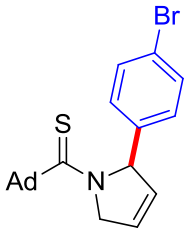

**3j**

**Adamantan-1-yl(2-(4-chlorophenyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3j)** was prepared according to the general procedure for 4 h (pale yellow solid, 37.4 mg, 52% yield). M.p.: 124-126 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28-7.25 (m, 2H), 7.14-7.12 (m, 2H), 6.61 (s, 1H), 5.91-5.90 (m, 2H), 5.06 (dd, $J_1$ = 15.6 Hz, $J_2$ = 4.4 Hz, 1H), 4.87 (dt, $J_1$ = 16.0 Hz, $J_2$ = 4.4 Hz, 1H), 2.21-2.09 (m, 9H), 1.78-1.64 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.7, 138.9, 132.8, 131.3, 128.7, 128.4, 122.9, 76.3, 58.7, 47.2, 40.6, 36.5, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{24}ClNNaS$ [M + $Na^+$]: 380.1216, Found: 380.1180.



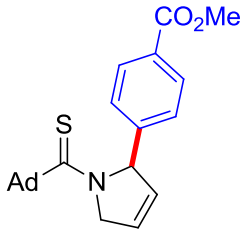

**3k**

**Adamantan-1-yl(2-(4-bromophenyl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3k)** was prepared according to the general procedure for 4 h (pale yellow solid, 53.3 mg, 66% yield). M.p.: 159-160 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 (d, $J$ = 8.0 Hz, 2H), 7.05 (d, $J$ = 8.0 Hz, 2H), 6.58 (s, 1H), 5.90-5.86 (m, 2H), 5.03 (d, $J$ = 16.0 Hz, 1H), 4.87 (dd, $J_1$ = 16.0 Hz, $J_2$ = 3.6 Hz, 1H), 2.19-2.07 (m, 9H), 1.78-1.63 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.7, 139.4, 131.6, 131.2, 128.8, 123.0, 120.9, 76.4, 58.7, 47.1, 40.6, 36.5, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{24}BrNNaS$ [M + $Na^+$]: 424.0711, Found: 424.0687.



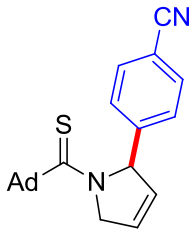

**3l**

**Methyl-4-(1-(adamantane-1-carbonothioyl)-2,5-dihydro-1*H*-pyrrol-2-yl)benzoate (3l)** was prepared according to the general procedure for 4 h (purification by flash silica gel column chromatography: petroleum ether/ethyl acetate = 40:1, pale yellow solid, 45.2 mg, 59% yield). M.p.: 130-131 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.96 (d, $J$ = 7.6 Hz, 2H), 7.22 (d, $J$ = 8.0 Hz, 2H), 6.65 (s, 1H), 5.92-5.88 (m, 2H), 5.05 (d, $J$ = 16.0 Hz, 1H), 4.91 (dd, $J_1$ = 16.0 Hz, $J_2$ = 3.6 Hz, 1H), 3.88 (s, 3H), 2.20-2.08 (m, 9H), 1.80-1.59 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 231.7, 211.8, 166.9, 131.0, 130.0, 128.9, 126.7, 123.3, 76.8, 58.8, 52.1, 47.2, 40.7, 36.5, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{23}H_{27}NNaO_2S$ [M + $Na^+$]: 404.1660, Found: 404.1654.



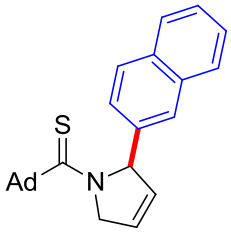

**3m**

**4-(1-(adamantane-1-carbonothioyl)-2,5-dihydro-1*H*-pyrrol-2-yl)benzonitrile (3m)** was prepared according to the general procedure for 4 h (purification by flash silica gel column chromatography: petroleum ether/ethyl acetate = 40:1, white solid, 36.6 mg, 52% yield). M.p.: 172-173 °C.

**$^1$H NMR** (400 MHz, $(CD_3)_2CO$) $\delta$ 7.56 (d, $J$ = 7.6 Hz, 2H), 7.26 (d, $J$ = 8.4 Hz, 2H), 6.62 (s, 1H), 5.95-5.86 (m, 2H), 5.07 (d, $J$ = 15,6 Hz, 1H), 4.91 (d, $J$ = 16.0 Hz, 1H), 2.18-2.07 (m, 9H), 1.79-1.61 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $(CD_3)_2CO$) $\delta$ 212.1, 146.0, 132.4, 130.4, 127.5, 123.9, 118.9, 110.8, 76.6, 58.8, 47.2, 40.7, 36.4, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{24}N_2NaS$ [M + $Na^+$]: 371.1558, Found: 371.1546.



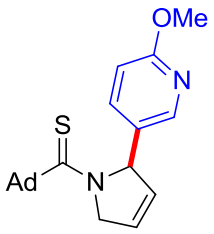

**3n**

**Adamantan-1-yl(2-(naphthalen-2-yl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3n)** was according to the general procedure with 2.0 equiv. 1,4-BQ for 16 h (pale yellow solid, 40.3 mg, 54% yield). M.p.: 162-163 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.84-7.78 (m, 3H), 7.67 (s, 1H), 7.45-7.42 (m, 2H), 7.30-7.26 (m, 1H), 6.82 (s, 1H), 5.98-5.90 (m, 2H), 5.09 (d, $J$ = 16.0 Hz, 1H), 4.98 (d, $J$ = 16.4 Hz, 1H), 2.24-2.03 (m, 9H), 1.79-1.61 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.3, 141.2, 137.8, 133.4, 132.7, 131.5, 128.2, 127.9, 127.7, 126.0, 125.7, 124.9, 122.6, 77.0, 58.8, 47.0, 40.6, 36.4, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{25}H_{27}NNaS$ [M + $Na^+$]: 396.1762, Found: 396.1743.




**3o**

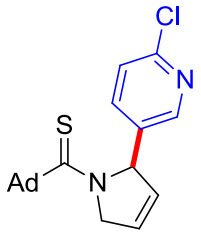
**Adamantan-1-yl(2-(6-methoxypyridin-3-yl)-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione (3o)** was prepared according to the general procedure with 3.0 equiv. 1,4-BQ for 16 h (purification by preparative TLC, petroleum ether/dichloromethane = 4:1, pale yellow semisolid, 32.2 mg, 44% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.03 (s, 1H), 7.44 (d, $J$ = 8.8 Hz, 1H), 6.66 (d, $J$ =

8.4 Hz, 1H), 6.60 (s, 1H), 5.93-5.87 (m, 2H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 3.90 (s, 3H), 2.16-2.04 (m, 9H), 1.74-1.60 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 211.6, 163.2, 146.0, 138.4, 131.1, 128.4, 123.2, 110.5, 73.9, 58.5, 53.6, 47.2, 40.7, 36.5, 29.0 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{26}N_2NaOS$ [M + $Na^+$]: 377.1664, Found: 377.1652.



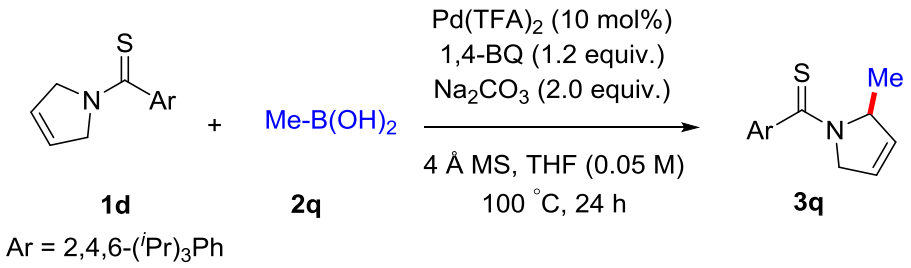

**3p**

**Adamantan-1-yl(2-(6-chloropyridin-3-yl)-2,5-dihydro-1*H*-pyrrol-1-yl)metha nethione (3p)** was prepared according to the general procedure with 3.0 equiv. 1,4-BQ for 16 h (purification by preparative TLC, petroleum ether/dichloromethane = 4:1, pale yellow semisolid, 26.1 mg, 36% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.20 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 5.98-5.95 (m, 1H), 5.87-5.84 (m, 1H), 5.05-5.00 (m, 1H), 4.91-4.85 (m, 1H), 2.14-2.02 (m, 9H), 1.71-1.64 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 212.0, 149.7, 148.9, 138.1, 134.9, 130.1, 124.2, 123.9, 73.9, 58.6, 47.2, 40.5, 36.4, 28.9 ppm.

**HRMS** (CI+) Calcd for $C_{20}H_{23}ClN_2NaS$ [M + $Na^+$]: 381.1168, Found: 381.1184.




**1d** **2q** **3q**

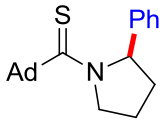
Ar = 2,4,6-($^i$Pr)$_3$Ph

To a standard 15 mL Schlenk tube charged with a magnetic stir bar was added thioamide **1d** (63.1 mg, 0.20 mmol), methylboronic acid **2q** (144 mg, 2.4 mmol), 1,4-benzoquinone (25.9 mg, 0.24 mmol), sodium carbonate (42.4 mg, 0.40 mmol), palladium(II) trifluoroacetate (6.7 mg, 10 mol%), THF (4.0 mL), and 4 Å MS (50 mg). The tube was sealed, and the reaction mixture was stirred at 100 °C for 24 h. The mixture was filtered through celite, and washed with ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by preparative TLC (petroleum ether/dichloromethane = 40:1) to give the desired product **3q** (pale yellow solid, 37.8 mg, 50% yield). M.p.: 84-85 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.98 (dd, $J_1$ = 6.8 Hz, $J_2$ = 1.8 Hz, 2H), 5.98-5.95 (m, 1H), 5.70-5.66 (m, 1H), 5.50-5.44 (m, 1H), 4.01 (t, $J$ = 2.2 Hz, 0.26H), 3.96 (t, $J$ = 2.2 Hz, 0.62H), 3.90 (q, $J$ = 2.6 Hz, 0.62H), 3.85 (q, $J$ = 2.6 Hz, 0.26H), 2.95-2.80 (m, 3H), 1.60 (d, $J$ = 6.4 Hz, 3H), 1.26-1.16 (m, 18H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 198.1, 148.8, 142.1, 141.6, 138.5, 133.0, 122.9, 121.8, 121.7, 64.4, 58.4, 34.3, 30.7, 30.3, 29.8, 25.3, 25.2, 24.1, 23.8, 23.5, 17.3 ppm.

**HRMS** (CI+) calculated for $C_{21}H_{31}NNaS$ [M + $Na^+$]: 352.2075, found: 352.2052



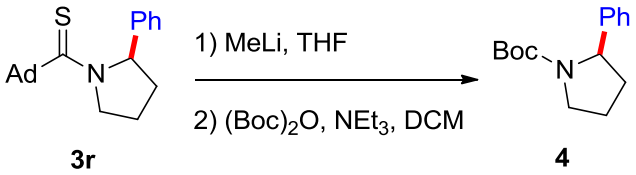

**3r**

**Adamantan-1-yl(2-phenylpyrrolidin-1-yl)methanethione (3r)** was prepared according to the general procedure for 4 h and conducted with 0.80 mmol adamantan-1-yl(pyrrolidin-1-yl)methanethione **1g** (white solid, 167.2 mg, 62% yield). M.p.: 152-153 °C.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) (55:45 mixture of rotamers, peaks corresponding to minor rotamer starred) $\delta$ 7.30-7.11 (m, 3H), 7.02 (t, $J$ = 8.0 Hz, 2H), 6.05 (dd, $J_1$ = 25.2 Hz, $J_2$ = 6.4 Hz, 1H), 4.32-4.06 (m, 2H), 2.32-1.60 (m, 19H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 210.8*, 210.2, 142.3, 141.9*, 128.3*, 128.0, 126.8, 125.9*, 152.1, 124.9*, 69.5, 65.2*, 57.7*, 53.7, 46.4*, 46.3, 41.4*, 40.3, 36.1, 35.1*, 32.5, 28.6, 24.9, 18.7* ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{227}NNaS$ [M + $Na^+$]: 348.1762, found: 348.1720.



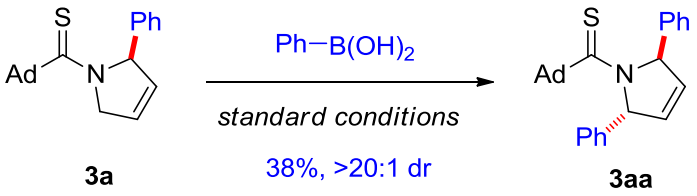

**3r** **4**

***tert*-Butyl 2-phenylpyrrolidine-1-carboxylate (4).**[2] MeLi (0.94 mL of a 1.6 M solution in $Et_2O$, 1.5 mmol, 3.0 equiv.) was added dropwise to a stirred solution of adamantan-1-yl(2-phenylpyrrolidin-1-yl)methanethione (81.5 mg, 0.25 mmol, 1.0 equiv.) in THF (3 mL) at 0 °C under $N_2$. The resulting solution was stirred at 0°C for 2 h. Then 10% HCl solution (0.4 mL) was added

dropwise, and the mixture was stirred for 2 h. After that, the mixture was poured into aq. KOH (1.0 M, 5 mL). The mixture was extracted with DCM (2x10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and carefully concentrated (25 °C, 0.09 MPa). The crude product was dissolved in anhydrous DCM (5 ml), and $NEt_3$ (63.2 mg, 0.625 mmol, 2.5 equiv.) and $Boc_2O$ (81.8 mg, 0.375 mmol, 1.5 equiv.) were added successively at 0 °C. After stirring overnight, the reaction was diluted with 10 mL DCM, washed with 1 M HCl, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography petroleum ether/ethyl acetate = 40:1 to 20:1) to provide the desired product **4** as colorless oil (50.9 mg, 82% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) (70:30 mixture of rotamers, peaks corresponding to minor rotamer starred) $\delta$ 7.37 (t, $J$ = 7.2 Hz, 2H), 7.20-7.14 (m, 3H), 4.94 (d, $J$ = 8.8 Hz, 0.3H), 4.76-4.73 (m, 0.7H), 3.63-3.49 (m, 2H), 2.34-2.22 (m, 1H), 1.92-1.78 (m, 3H), 1.44 (s, 3H), 1.16 (s, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 154.5, 145.1, 128.1, 126.5, 125.5, 79.1, 61.3, 47.1, 36.0, 28.1, 23.2 ppm.




**3a** **3aa**

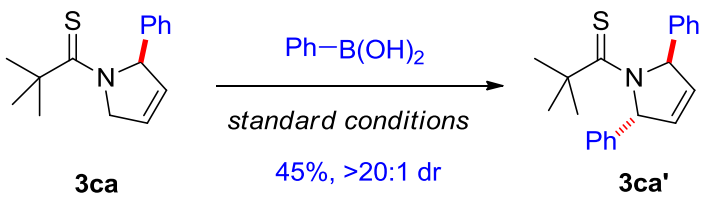
**Adamantan-1-yl(2,5-diphenyl-2,5-dihydro-1*H*-pyrrol-1-yl)methanethione**

**(3aa).** To a standard 15 mL Schlenk tube charged with a magnetic stir bar were added **3a** (65.3 mg, 0.20 mmol), phenylboronic acid (48.4 mg, 0.40 mmol) 1,4-benzoquione (43.2 mg, 0.40 mmol), sodium bicarbonate (33.6 mg, 0.40 mmol), palladium(II) trifluoroacetate (6.6 mg, 10 mol%), THF (4.0 mL), and 4 Å MS (50 mg). The tube was sealed, and the reaction mixture was stirred at 100 °C for 12 h. Upon completion (monitored by TLC), the mixture was filtered through celite, and washed with ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by preparative TLC with the solvent (petroleum ether /dichloromethane = 4:1) to provide the desired product **3aa** as a red-brown semisolid (30.5 mg, 38% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.56-7.28 (m, 10H), 7.27-7.25 (m ,1.2H), 6.95-6.93(m, 0.4H), 6.50-6.48 (m, 0.3H), 6.06 (d, $J$ = 4.0 Hz, 0.4H), 5.82-5.79 (m, 0.3H), 5.77-5.74 (m, 0.3H), 5.67 (s, 0.4H), 3.87 (d, $J$ = 4.0 Hz, 0.4H), 2.16 (s, 1H), 2.07-1.95 (m, 3H), 1.92-1.81 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 219.4, 151.4, 144.3, 143.2, 140.3, 133.5, 129.4, 129.2, 129.13, 129.06, 129.0, 128.8, 128.6, 128.44, 128.40, 128.3, 128.2, 127.8, 127.7, 127.6, 127.53, 127.46, 127.1, 126.5, 125.9, 125.7, 125.1, 119.4, 77.8, 73.3, 60.1, 50.2, 49.4, 43.3, 43.1, 43.0, 36.6, 36.3, 29.0, 28.9, 28.7 ppm.

**HRMS** calculated for $C_{27}H_{29}NS$ [$M^+$]: 399.2021, found: 399.2017.



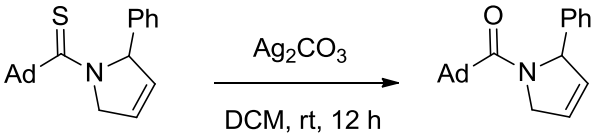
**1-(2,5-Diphenyl-2,5-dihydro-1*H*-pyrrol-1-yl)-2,2-dimethylpropane-1-thione (3ca').** To a standard 15 mL Schlenk tube charged with a magnetic stir bar were added **3ca** (24.5 mg, 0.10 mmol), phenylboronic acid (24.4 mg, 0.20 mmol) 1,4-benzoquione (21.6 mg, 0.20 mmol), sodium bicarbonate (16.8 mg, 0.20 mmol), palladium(II) trifluoroacetate (3.3 mg, 10 mol%), THF (2.0 mL), and 4 Å MS (30 mg). The tube was sealed, and the reaction mixture was stirred at 100 °C for 12 h. Upon completion (monitored by TLC), the mixture was filtered through celite, and washed with ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by preparative TLC with the solvent (petroleum ether/dichloromethane = 4:1) to provide the desired product **3ca'**as a red-brown semisolid (16.4 mg, 45% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.57-7.23 (m, 10H), 6.87-6.85 (m, 1H), 6.38-6.36 (m, 1H), 5.82-5.79 (m, 1H), 5.77-5.74 (m, 1H), 1.24 (s, 2H), 1.15 (s, 7H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 217.7, 143.8, 140.2, 129.3, 129.1, 129.0, 128.6, 128.3, 128.2, 127.8, 127.7, 127.2, 12 5.9, 125.6, 125.1, 77.7, 73.3, 47.4, 32.6, 32.4 ppm.

**HRMS** calculated for $C_{21}H_{23}NS$ [$M^+$]: 321.1551, found: 321.1541.

## 6 Product Derivatizations



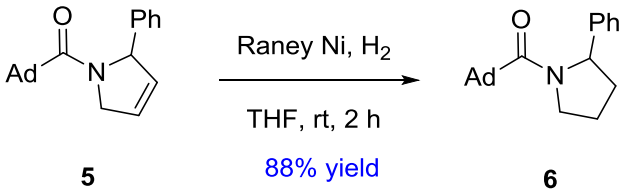

**3a** **5**

**Adamantan-1-yl(2-phenyl-2,5-dihydro-1*H*-pyrrol-1-yl)methanone (5).** To a 100 mL round bottom flask charged with a magnetic stir bar were added **3a** (485 mg, 1.5 mmol) and $Ag_2CO_3$ (647 mg, 3.0 mmol). The flask was evacuated and backfilled with $N_2$, followed by addition of DCM (6.0 mL). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the mixture was filtered through celite, and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give the desired product **5** as a white solid (412 mg, 89% yield). M.p.: 165-166 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30-7.17 (m, 5H), 5.84-5.78 (m, 3H), 4.74-4.63 (m, 2H), 2.06-1.93 (m, 9H), 1.74-1.65 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.4, 142.2, 131.1, 128.4, 127.0, 126.3, 123.8, 70.2, 54.6, 42.1, 38.2, 36.6, 28.3 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{25}NNaO$ [M + $Na^+$]: 330.1834, Found: 330.1806.



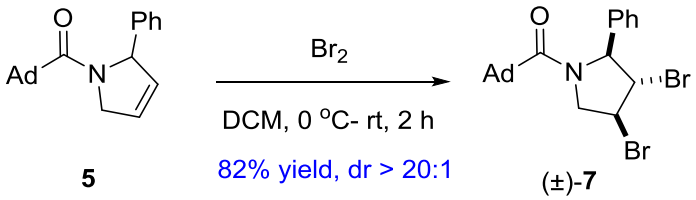

**5** **6**

**Adamantan-1-yl(2-phenylpyrrolidin-1-yl)methanone (6).** To a 25 mL round bottom flask charged with a magnetic stir bar were added **5** (92.2 mg, 0.30 mmol), THF (6.0 mL), and a small amount of Raney nickel. The flask was evacuated quickly, and equipped with a hydrogen balloon. The reaction mixture stirred rapidly at room temperature for 2 h. Upon completion, the mixture was filtered through celite, and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the desired product **6** as a white solid (82.3 mg, 88% yield). M.p.: 111-112 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29-7.10 (m, 5H), 5.27-5.24 (m, 1H), 4.04-3.72 (m, 2H), 2.24-2.15 (m, 2H), 2.13-1.90 (m, 9H), 1.90-1.79 (m, 2H), 1.79-1.56 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.8, 144.3, 128.3, 126.4, 125.2, 62.6, 48.8, 42.0, 38.4, 36.6, 33.1, 28.4, 25.4 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{27}NNaO$ [M + $Na^+$]: 332.1990, Found: 332.1978.




**5** (±)-**7**

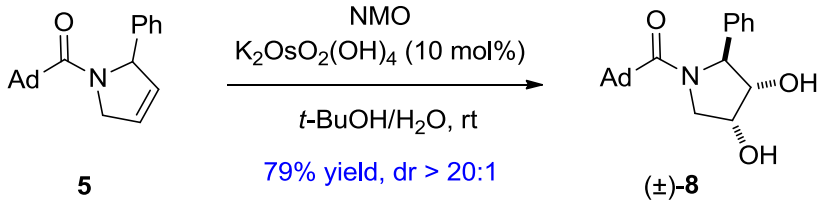
**Adamantan-1-yl(3,4-dibromo-2-phenylpyrrolidin-1-yl)methanethione (7).**

At 0 °C, to a solution of **5** (64.5 mg, 0.21 mmol) in dry DCM (2.0 mL) was added dropwise $Br_2$ (41 μL dissolved in 1.0 mL DCM) over 10 minutes. The mixture was stirred at 0 °C for 30 minutes, then warmed to room temperature for another 2 h. Upon completion, the reaction was quenched with saturated $NaHSO_3$ aqueous solution (5.0 mL), and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to provide the desired product **7** as a white solid (80.2 mg, 82% yield). M.p.: 131-132 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36-7.25 (m, 5H), 5.46 (s, 1H), 4.81-4.77 (m, 1H), 4.44-4.39 (m, 1H), 4.28-4.23 (m, 1H), 4.12-4.07 (m, 1H), 2.05-1.95 (m, 9H), 1.76-1.68 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 175.7, 140.0, 128.8, 127.8, 125.7, 70.5, 57.9, 56.0, 49.0, 42.2, 38.6, 36.5, 28.3 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{25}Br_2NNaO$ [M + $Na^+$]: 490.0180, Found: 490.0172.




**5** (±)-**8**

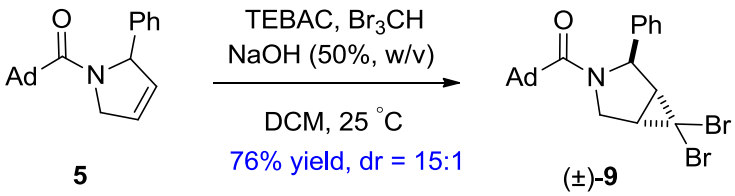
**Adamantan-1-yl(3,4-dihydroxy-2-phenylpyrrolidin-1-yl)methanone (8).** To a solution of **5** (61.5 mg, 0.20 mmol) in *t*-BuOH/$H_2O$ (8.0 mL, *V*/*V* = 3/1) were

added *N*-methylmorpholine *N*-oxide (68.5 mg, 0.60 mmol) and potassiumosmate (VI) dihydrate (7.37 mg, 0.02 mmol). After stirring at room temperature overnight, the reaction was quenched with saturated $NaHSO_3$ aqueous solution, and stirred for another 1 h. The mixture was extracted with EtOAc (2 × 15 mL). The organic layers were combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to the desired product **8** as a white solid (54.2 mg, 79% yield). M.p.: 168-169 °C.

**$^1$H NMR** (400 MHz, DMSO-*d6*) $\delta$ 7.30-7.10 (m, 5H), 5.18 (d, *J* = 5.2 Hz, 0.5H), 5.00 (s, 0.5H), 4.79 (s, 1H), 4.06 (d, *J* = 13.2 Hz, 2H), 3.79 (br s, 1H), 3.66 (br s, 1H), 3.41 (s, 1H), 1.99-1.88 (m, 9H), 1.75-1.62 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, DMSO-*d6*) $\delta$ 174.7, 142.3, 128.1, 126.2, 125.3, 76.6, 69.7, 67.9, 52.5, 41.1, 37.8, 36.2, 27.8 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{27}NNaO_3$ [M + $Na^+$]: 364.1889, Found: 364.1883.




**5** (±)-**9**

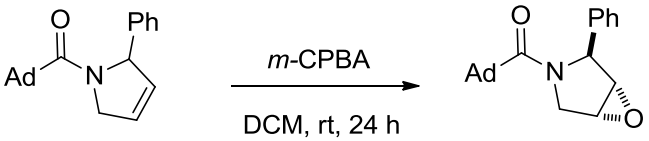
**Adamantan-1-yl(6,6-dibromo-2-phenyl-3-azabicyclo[3.1.0]hexan-3-yl)methanone (9).** To a solution of **5** (61.5 mg, 0.20 mmol) in DCM (1.2 mL) were added a small amount of benzyltriethylammonium chloride and NaOH aqueous

solution (50% wt, 1.2 mL). After that, a solution of bromoform (0.40 mmol) in DCM (0.80 mL) was added dropwise over 20 minutes. After stirring at room temperature overnight, the reaction was quenched with saturated $NaHSO_3$ aqueous solution, and stirred for another 1 h. The mixture was extracted with EtOAc (2 × 15 mL). The organic layers were combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to provide the desired product **9** as a white solid (54.0 mg, 76% yield). M.p.: 180-181 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38-7.16 (m, 5H), 5.35 (s, 1H), 4.33 (d, $J$ = 11.2 Hz, 1H), 4.17 (dd, $J_1$ = 11.2 Hz, $J_2$ = 4.8 Hz, 1H), 2.63-2.60 (m, 1H), 2.32 (d, $J$ = 8.4 Hz, 1H), 2.03-1.66 (m, 15H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 174.9, 141.2, 128.9, 127.5, 126.3, 66.0, 50.6, 42.0, 39.8, 37.9, 36.8, 36.7, 32.2, 28.4 ppm.

**HRMS** (CI+) Calcd for $C_{22}H_{25}Br_2NNaO$ [M + $Na^+$]: 502.0180, Found: 502.0156.




**5** **(±)-10**

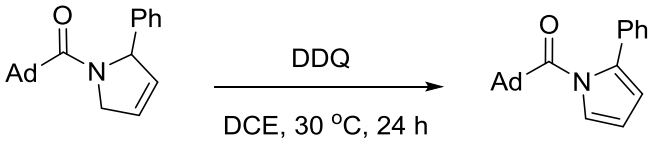
**Adamantan-1-yl(2-phenyl-6-oxa-3-azabicyclo[3.1.0]hexan-3-yl)methanone (10).** To a solution of **5** (0.23 mmol, 71.0 mg) in DCM (3.0 mL) was added 3-chloroperoxybenzoic acid (143 mg, 0.83 mmol). The reaction mixture was

stirred at room temperature for 24 h. Upon completion, the reaction was quenched with saturated $Na_2SO_3$ aqueous solution and stirred for another 1 h. The mixture was extracted with DCM (2 × 15 mL). The organic layers were combined, washed with saturated $NaHCO_3$ aqueous solution and brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 15:1) to provide the desired product **10** as a white solid (44.9 mg, 60% yield). M.p.: 178-179 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34-7.18 (m, 5H), 5.49 (s, 1H), 4.53 (d, $J$ = 12.0 Hz, 1H), 3.87-3.55 (m, 3H), 2.01-1.68 (m, 15H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 176.2, 138.2, 128.8, 127.7, 126.3, 62.5, 57.7, 55.7, 49.3, 41.9, 38.0, 36.5, 28.2 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{25}NNaO_2$ [M + $Na^+$]: 346.1783, Found: 346.1806.




**5** **11**

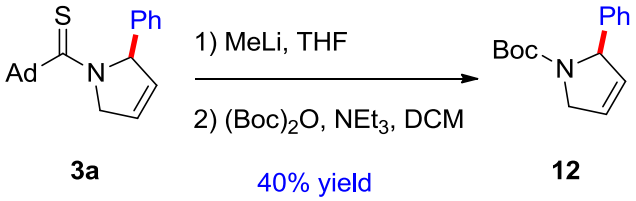
**Adamantan-1-yl(2-phenyl-1*H*-pyrrol-1-yl)methanone (11).** To a solution of **5** (64.6 mg, 0.21 mmol) in DCE (2.0 mL) was added DDQ (90.8 mg, 0.40 mmol). The reaction mixture was stirred at 30 °C for 24 h. Upon completion, the mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column

chromatography (petroleum ether/ethyl acetate = 15:1) to provide the desired product **11** as a yellow solid (30.1 mg, 49% yield). M.p.: 87-88 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.37-7.33 (m, 3H), 7.29-7.24 (m, 3H), 6.30-6.26 (m, 2H), 2.19-2.11 (m, 9H), 1.82-1.74 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 179.3, 136.3, 134.2, 128.2, 127.9, 127.0, 121.6, 113.0, 110.5, 44.8, 40.0, 36.5, 28.3 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{23}NNaO$ [M + $Na^+$]: 328.1677, Found: 328.1702.

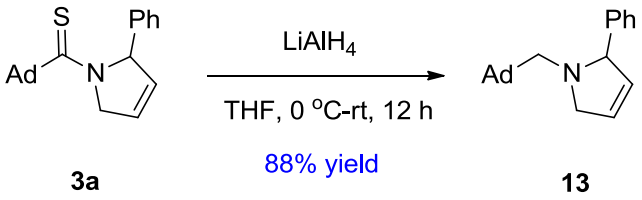



**3a** 40% yield **12**

***tert*-Butyl 2-phenyl-2,5-dihydro-1*H*-pyrrole-1-carboxylate (12).**[3] According to the procedure described above, the reaction was conducted with **3a** (113 mg, 0.35 mmol). The reaction mixture was purified by flash chromatography petroleum ether/ethyl acetate = 100:1) to provide the desired product **12** as pale yellow oil (34.5 mg, 40% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) (70:30 mixture of rotamers, peaks corresponding to minor rotamer starred) $\delta$ 7.33-7.18 (m, 5H), 5.91-5.83 (m, 1H), 5.77-5.70 (m, 1H), 5.53-5.51 (m, 0.3 H), 5.39-5.36 (m, 0.7H), 4.39-4.23 (m, 2H), 1.43 (s, 3H), 1.21 (s, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 154.2, 154.1*, 142.6, 141.9*, 131.4*, 131.3, 128.6*, 128.3, 127.3, 126.8, 126.7*, 124.7, 79.6, 68.3, 68.0*, 54.2*, 53.8, 28.6, 28.3 ppm.




**3a** **13**

**1-(Adamantan-1-ylmethyl)-3-pyrroline (4).** To a 25 mL round bottom flask charged with a magnetic stir bar was added $LiAlH_4$ (404 mg, 10.6 mmol). The flask was evacuated and backfilled with $N_2$, followed by addition of anhydrous THF (8.0 mL). The mixture was cooled to 0 °C, and the solution of **3a** (64.7 mg, 0.20 mmol) in THF (3.0 mL) was added dropwise. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the reaction was quenched at 0 °C with water (0.50 mL, dropwise), NaOH aqueous solution (15%wt, 0.50 mL), and another water (1.5 mL), successively. The mixture was stirred until the precipitate could be conveniently filtered off. The filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to provide the desired product **13** as pale yellow oil (51.9 mg, 88% yield). M.p.: 63-64 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.37-7.23 (m, 5H), 5.87-5.83 (m, 1H), 5.67-5.64 (m, 1H), 4.53-4.50 (m, 1H), 4.16-4.10 (m, 1H), 3.46-3.40 (m, 1H), 2.34 (q, $J$ = 13.2 Hz, 2H), 1.91-1.88 (m, 3H), 1.69-1.56 (m, 6H), 1.45-1.30 (m, 6H) ppm.

**$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 144.4, 132.4, 128.2, 128.1, 127.3, 127.0, 77.8, 69.1, 64.3, 41.4, 37.3, 34.9, 28.7 ppm.

**HRMS** (CI+) Calcd for $C_{21}H_{28}N$ [M + H$^+$]: 294.2222, Found: 294.2240.

## 7 X-ray Structure of Product 3m

The structure of product **3m** was determined by X-ray diffraction. The X-ray data of **3m** have been deposited at the Cambridge Crystallographic Data Center (CCDC 1969285).

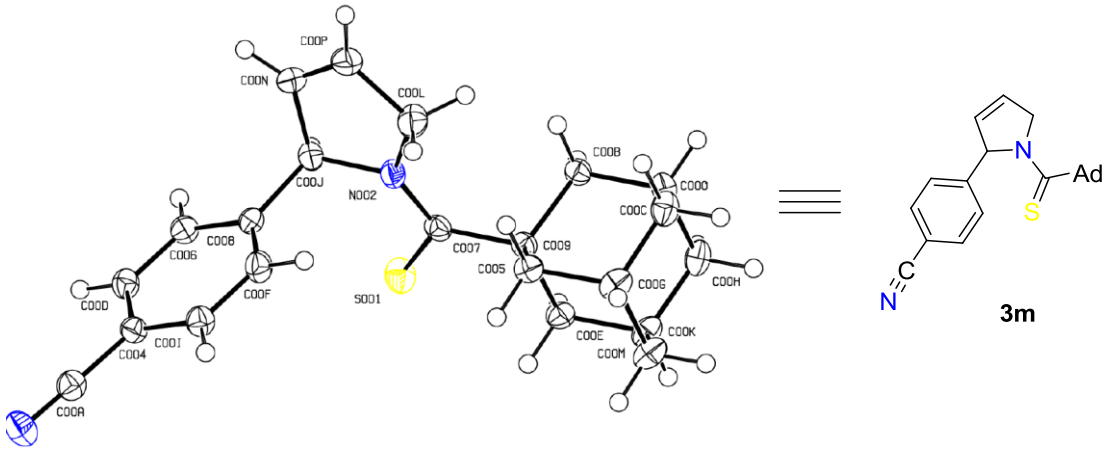



**Figure S1.** X-ray structure of product **3m**

**Table 1 Crystal data and structure refinement for compound 3m.**

| | |
|---|---|
| Identification code | **3m** |
| Empirical formula | $C_{88}H_{96}N_8S_4$ |
| Formula weight | 1393.96 |
| Temperature/K | 150.15 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 48.132(3) |
| b/Å | 6.9037(4) |
| c/Å | 10.8793(6) |
| α/° | 90 |
| β/° | 93.383(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 3608.8(4) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.283 |
| μ/mm$^{-1}$ | 0.186 |

| | |
|---|---|
| F(000) | 1488.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.086 to 56.89 |
| Index ranges | -55 ≤ h ≤ 64, -9 ≤ k ≤ 9, -14 ≤ l ≤ 13 |
| Reflections collected | 18608 |
| Independent reflections | 4544 [$R_{int}$ = 0.0829, $R_{sigma}$ = 0.0708] |
| Data/restraints/parameters | 4544/0/226 |
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0495, $wR_2$ = 0.1067 |
| Final R indexes [all data] | $R_1$ = 0.0863, $wR_2$ = 0.1251 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.35/-0.33 |

**Table 2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for 3m. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| S001 | 3694.4(2) | 1151.1(8) | 3295.1(5) | 29.90(15) |
| N002 | 3661.7(3) | 4246(2) | 4654.9(14) | 22.7(3) |
| N003 | 2429.2(4) | -1773(3) | 6628.6(15) | 32.8(4) |
| C004 | 2795.7(4) | 460(3) | 5707.7(16) | 21.8(4) |
| C005 | 4163.8(4) | 2670(3) | 6210.8(15) | 22.4(4) |
| C006 | 2940.4(4) | 2336(3) | 4010.8(16) | 22.8(4) |
| C007 | 3825.2(4) | 2797(3) | 4295.0(16) | 21.1(4) |
| C008 | 3176.9(4) | 2924(3) | 4705.5(16) | 21.1(4) |
| C009 | 4132.7(4) | 2669(2) | 4784.0(15) | 19.3(4) |
| C00A | 2593.4(4) | -793(3) | 6224.9(17) | 25.5(4) |
| C00B | 4302.4(4) | 4350(3) | 4252.9(15) | 21.1(4) |
| C00C | 4608.4(4) | 4237(3) | 4729.9(16) | 24.3(4) |
| C00D | 2749.6(4) | 1110(3) | 4503.5(16) | 24.0(4) |
| C00E | 4268.3(4) | 777(3) | 4353.8(17) | 23.6(4) |
| C00F | 3221.0(4) | 2275(3) | 5909.0(17) | 26.3(4) |
| C00G | 4473.5(4) | 2565(3) | 6650.8(16) | 25.8(4) |
| C00H | 4736.0(4) | 2353(3) | 4292.8(17) | 26.6(4) |
| C00I | 3031.6(4) | 1046(3) | 6417.4(17) | 25.2(4) |
| C00J | 3368.1(4) | 4388(3) | 4154.2(17) | 24.3(4) |
| C00K | 4576.3(4) | 652(3) | 4798.9(17) | 26.5(4) |
| C00L | 3726.7(4) | 5932(3) | 5475(2) | 33.0(5) |
| C00M | 4602.5(4) | 689(3) | 6207.5(17) | 30.5(5) |

| | | | | |
|---|---|---|---|---|
| C00N | 3289.2(4) | 6411(3) | 4497.4(19) | 30.3(5) |
| C00O | 4626.9(4) | 4309(3) | 6144.9(16) | 27.5(4) |
| C00P | 3483.8(4) | 7243(3) | 5208(2) | 32.6(5) |

**Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S001 | 26.9(3) | 32.7(3) | 30.0(3) | -10.6(2) | -0.13(19) | -3.1(2) |
| N002 | 17.8(8) | 22.3(8) | 28.0(8) | -3.5(7) | 1.1(6) | -1.8(6) |
| N003 | 31.4(10) | 36.5(10) | 30.4(9) | 1.6(8) | 0.2(7) | -9.3(8) |
| C004 | 21.1(9) | 19.7(8) | 25.0(9) | -0.7(8) | 3.6(7) | -0.5(7) |
| C005 | 26.1(10) | 23.9(9) | 17.8(8) | 1.4(7) | 4.6(7) | 1.7(8) |
| C006 | 23.1(10) | 23.9(9) | 21.3(8) | 1.2(8) | 0.1(7) | 0.0(8) |
| C007 | 21.9(9) | 20.8(9) | 21.3(8) | 1.7(7) | 5.5(7) | -2.2(7) |
| C008 | 18.8(9) | 19.3(8) | 25.5(9) | -1.0(8) | 4.7(7) | 2.6(7) |
| C009 | 19.8(9) | 19.2(8) | 19.1(8) | -1.0(7) | 2.1(7) | -1.3(7) |
| C00A | 25.3(10) | 27.0(10) | 23.8(9) | -1.4(8) | -2.0(7) | 0.0(8) |
| C00B | 21.3(9) | 22.5(9) | 19.7(8) | 2.4(7) | 3.0(7) | -0.6(7) |
| C00C | 19.4(9) | 28.2(10) | 25.6(9) | -0.3(8) | 3.2(7) | -3.2(8) |
| C00D | 21.0(9) | 26.5(9) | 24.2(9) | -2.3(8) | -1.4(7) | -0.8(8) |
| C00E | 25.2(10) | 19.9(9) | 25.8(9) | -2.7(8) | 3.6(7) | 1.9(7) |
| C00F | 21.0(10) | 30.6(10) | 26.8(9) | 0.1(8) | -1.8(7) | -1.7(8) |
| C00G | 30.9(11) | 29.3(10) | 17.0(8) | -0.7(8) | 0.1(7) | 6.6(8) |
| C00H | 19.4(9) | 37.3(11) | 23.1(9) | -4.0(9) | 2.4(7) | 3.4(8) |
| C00I | 24.1(10) | 28.5(10) | 22.8(9) | 0.5(8) | 0.1(7) | -0.7(8) |
| C00J | 18.4(9) | 25.7(10) | 28.7(9) | 3.3(8) | 1.0(7) | -1.9(7) |
| C00K | 26.6(10) | 25.9(10) | 26.9(9) | -4.1(8) | 1.9(8) | 8.3(8) |
| C00L | 26.2(11) | 25.7(10) | 47.3(12) | -14.9(9) | 3.7(9) | 1.3(8) |
| C00M | 32.1(11) | 31.5(11) | 27.7(9) | 2.7(9) | 0.9(8) | 10.6(9) |
| C00N | 26.4(11) | 22.2(10) | 42.6(11) | 8.9(9) | 4.3(9) | 3.6(8) |
| C00O | 22.6(10) | 33.3(11) | 26.4(9) | -8.4(9) | -1.4(7) | 0.4(8) |
| C00P | 29.7(11) | 21.4(10) | 47.3(12) | 0.0(9) | 8.4(9) | 1.0(8) |

**Table 4 Bond Lengths for 3m.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S001 | C007 | 1.6702(18) | C009 | C00B | 1.550(2) |
| N002 | C007 | 1.346(2) | C009 | C00E | 1.546(2) |

| | | | | | |
|---|---|---|---|---|---|
| N002 | C00J | 1.487(2) | C00B | C00C | 1.534(2) |
| N002 | C00L | 1.488(2) | C00C | C00H | 1.526(3) |
| N003 | C00A | 1.147(2) | C00C | C00O | 1.538(2) |
| C004 | C00A | 1.441(3) | C00E | C00K | 1.534(3) |
| C004 | C00D | 1.390(2) | C00F | C00I | 1.384(3) |
| C004 | C00I | 1.395(2) | C00G | C00M | 1.527(3) |
| C005 | C009 | 1.551(2) | C00G | C00O | 1.532(3) |
| C005 | C00G | 1.540(3) | C00H | C00K | 1.524(3) |
| C006 | C008 | 1.389(2) | C00J | C00N | 1.500(3) |
| C006 | C00D | 1.380(3) | C00K | C00M | 1.530(3) |
| C007 | C009 | 1.545(2) | C00L | C00P | 1.493(3) |
| C008 | C00F | 1.388(3) | C00N | C00P | 1.311(3) |
| C008 | C00J | 1.514(2) | | | |

**Table 5 Bond Angles for 3m.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C007 | N002 | C00J | 120.12(14) | C00B | C00C | C00O | 109.56(14) |
| C007 | N002 | C00L | 130.53(15) | C00H | C00C | C00B | 109.50(15) |
| C00J | N002 | C00L | 109.26(14) | C00H | C00C | C00O | 109.81(15) |
| C00D | C004 | C00A | 119.19(16) | C006 | C00D | C004 | 119.43(17) |
| C00D | C004 | C00I | 120.47(17) | C00K | C00E | C009 | 111.67(14) |
| C00I | C004 | C00A | 120.32(16) | C00I | C00F | C008 | 120.47(17) |
| C00G | C005 | C009 | 110.21(14) | C00M | C00G | C005 | 110.24(15) |
| C00D | C006 | C008 | 120.69(16) | C00M | C00G | C00O | 109.85(15) |
| N002 | C007 | S001 | 119.39(13) | C00O | C00G | C005 | 109.25(15) |
| N002 | C007 | C009 | 120.45(15) | C00K | C00H | C00C | 108.85(14) |
| C009 | C007 | S001 | 120.16(13) | C00F | C00I | C004 | 119.37(16) |
| C006 | C008 | C00J | 118.49(16) | N002 | C00J | C008 | 113.42(14) |
| C00F | C008 | C006 | 119.57(16) | N002 | C00J | C00N | 102.65(15) |
| C00F | C008 | C00J | 121.76(16) | C00N | C00J | C008 | 110.74(15) |
| C007 | C009 | C005 | 112.23(14) | C00H | C00K | C00E | 109.95(15) |
| C007 | C009 | C00B | 110.14(14) | C00H | C00K | C00M | 109.59(16) |
| C007 | C009 | C00E | 110.90(14) | C00M | C00K | C00E | 109.65(15) |
| C00B | C009 | C005 | 110.56(14) | N002 | C00L | C00P | 102.86(16) |
| C00E | C009 | C005 | 106.61(14) | C00G | C00M | C00K | 108.62(15) |
| C00E | C009 | C00B | 106.18(14) | C00P | C00N | C00J | 111.83(18) |
| N003 | C00A | C004 | 179.0(2) | C00G | C00O | C00C | 109.49(15) |
| C00C | C00B | C009 | 110.63(14) | C00N | C00P | C00L | 111.91(18) |

**Table 6 Torsion Angles for 3m.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| S001 | C007 | C009 | C005 | -126.17(14) | C00B | C009 | C00E | C00K | 58.69(18) |
| S001 | C007 | C009 | C00B | 110.18(15) | C00B | C00C | C00H | C00K | -60.37(18) |
| S001 | C007 | C009 | C00E | -7.06(19) | C00B | C00C | C00O | C00G | 61.50(19) |
| N002 | C007 | C009 | C005 | 54.8(2) | C00C | C00H | C00K | C00E | 58.95(18) |
| N002 | C007 | C009 | C00B | -68.83(19) | C00C | C00H | C00K | C00M | -61.64(19) |
| N002 | C007 | C009 | C00E | 173.94(15) | C00D | C004 | C00I | C00F | -0.4(3) |
| N002 | C00J | C00N | C00P | -7.1(2) | C00D | C006 | C008 | C00F | -0.2(3) |
| N002 | C00L | C00P | C00N | 7.6(2) | C00D | C006 | C008 | C00J | -175.44(16) |
| C005 | C009 | C00B | C00C | 55.51(18) | C00E | C009 | C00B | C00C | -59.75(17) |
| C005 | C009 | C00E | C00K | -59.22(18) | C00E | C00K | C00M | C00G | -59.1(2) |
| C005 | C00G | C00M | C00K | 60.2(2) | C00F | C008 | C00J | N002 | 31.6(2) |
| C005 | C00G | C00O | C00C | -62.02(19) | C00F | C008 | C00J | C00N | -83.2(2) |
| C006 | C008 | C00F | C00I | 0.2(3) | C00G | C005 | C009 | C007 | -179.35(14) |
| C006 | C008 | C00J | N002 | -153.33(16) | C00G | C005 | C009 | C00B | -55.95(19) |
| C006 | C008 | C00J | C00N | 91.9(2) | C00G | C005 | C009 | C00E | 59.04(18) |
| C007 | N002 | C00J | C008 | 75.3(2) | C00H | C00C | C00O | C00G | -58.80(19) |
| C007 | N002 | C00J | C00N | -165.14(15) | C00H | C00K | C00M | C00G | 61.7(2) |
| C007 | N002 | C00L | C00P | 164.53(18) | C00I | C004 | C00D | C006 | 0.4(3) |
| C007 | C009 | C00B | C00C | -179.88(14) | C00J | N002 | C007 | S001 | -0.6(2) |
| C007 | C009 | C00E | C00K | 178.33(14) | C00J | N002 | C007 | C009 | 178.37(15) |
| C008 | C006 | C00D | C004 | -0.1(3) | C00J | N002 | C00L | C00P | -11.9(2) |
| C008 | C00F | C00I | C004 | 0.2(3) | C00J | C008 | C00F | C00I | 175.22(17) |
| C008 | C00J | C00N | C00P | 114.24(19) | C00J | C00N | C00P | C00L | -0.3(3) |
| C009 | C005 | C00G | C00M | -61.59(19) | C00L | N002 | C007 | S001 | -176.80(16) |
| C009 | C005 | C00G | C00O | 59.21(19) | C00L | N002 | C007 | C009 | 2.2(3) |
| C009 | C00B | C00C | C00H | 62.41(18) | C00L | N002 | C00J | C008 | -107.77(17) |
| C009 | C00B | C00C | C00O | -58.08(19) | C00L | N002 | C00J | C00N | 11.76(19) |
| C009 | C00E | C00K | C00H | -59.98(19) | C00M | C00G | C00O | C00C | 59.03(19) |
| C009 | C00E | C00K | C00M | 60.6(2) | C00O | C00C | C00H | C00K | 59.98(19) |
| C00A | C004 | C00D | C006 | 178.92(17) | C00O | C00G | C00M | C00K | -60.3(2) |
| C00A | C004 | C00I | C00F | -178.95(17) | | | | | |

**Table 7 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for 3m.**

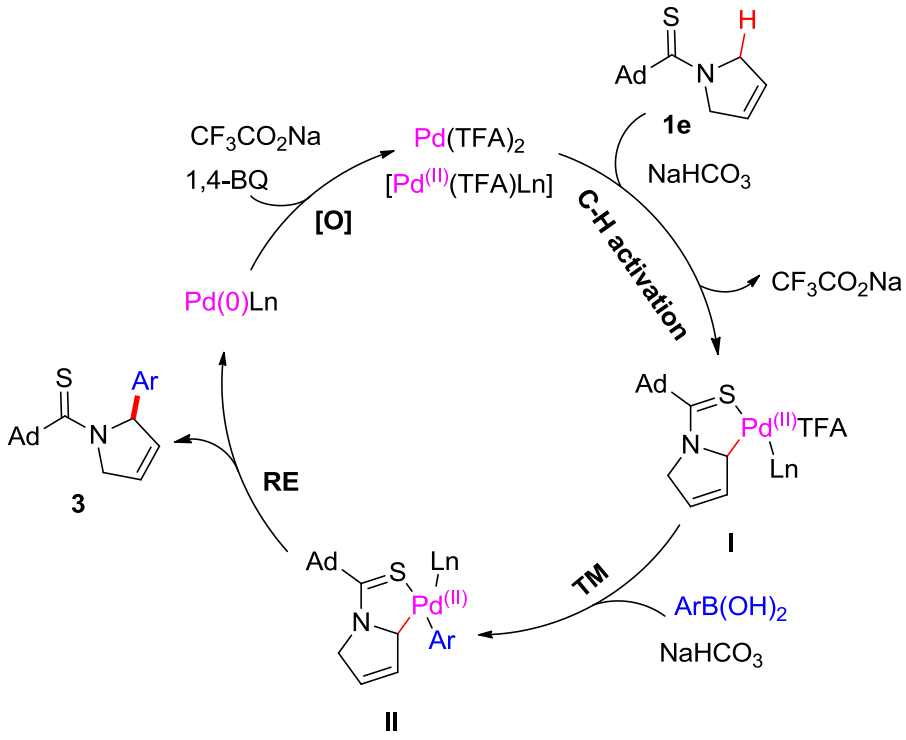
| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| H00A | 4080 | 3864 | 6531 | 27 |
| H00B | 4064 | 1545 | 6534 | 27 |
| H006 | 2910 | 2783 | 3188 | 27 |
| H00C | 4290 | 4277 | 3342 | 25 |
| H00D | 4223 | 5605 | 4496 | 25 |
| H00E | 4712 | 5360 | 4402 | 29 |
| H00F | 2588 | 715 | 4024 | 29 |
| H00G | 4167 | -347 | 4675 | 28 |
| H00H | 4252 | 714 | 3443 | 28 |
| H00I | 3382 | 2677 | 6387 | 32 |
| H00J | 4490 | 2602 | 7571 | 31 |
| H00K | 4725 | 2308 | 3382 | 32 |
| H00L | 4934 | 2280 | 4588 | 32 |
| H00M | 3062 | 606 | 7242 | 30 |
| H00N | 3360 | 4249 | 3238 | 29 |
| H00O | 4656 | -587 | 4500 | 32 |
| H00P | 3903 | 6561 | 5271 | 40 |
| H00Q | 3740 | 5536 | 6352 | 40 |
| H00R | 4505 | -440 | 6542 | 37 |
| H00S | 4801 | 621 | 6499 | 37 |
| H00T | 3119 | 7017 | 4232 | 36 |
| H00U | 4824 | 4285 | 6455 | 33 |
| H00V | 4542 | 5525 | 6428 | 33 |
| H00W | 3472 | 8526 | 5517 | 39 |

**Crystal structure determination of 3m**

**Crystal Data** for $C_{88}H_{96}N_8S_4$ ($M$ =1393.96 g/mol): monoclinic, space group C2/c (no. 15), $a$ = 48.132(3) Å, $b$ = 6.9037(4) Å, $c$ = 10.8793(6) Å, $\beta$ = 93.383(4) °, $V$ = 3608.8(4) Å$^3$, $Z$ = 2, $T$ = 150.15 K, μ(MoKα) = 0.186 mm$^{-1}$, *Dcalc* = 1.283 g/cm$^3$, 18608 reflections measured (5.086° ≤ 2Θ ≤ 56.89°), 4544 unique ($R_{int}$ = 0.0829, $R_{sigma}$ = 0.0708) which were used in all calculations. The final $R_1$ was 0.0495 (I > 2σ(I)) and $wR_2$ was 0.1251 (all data).

## 8 Proposed Catalytic Cycle



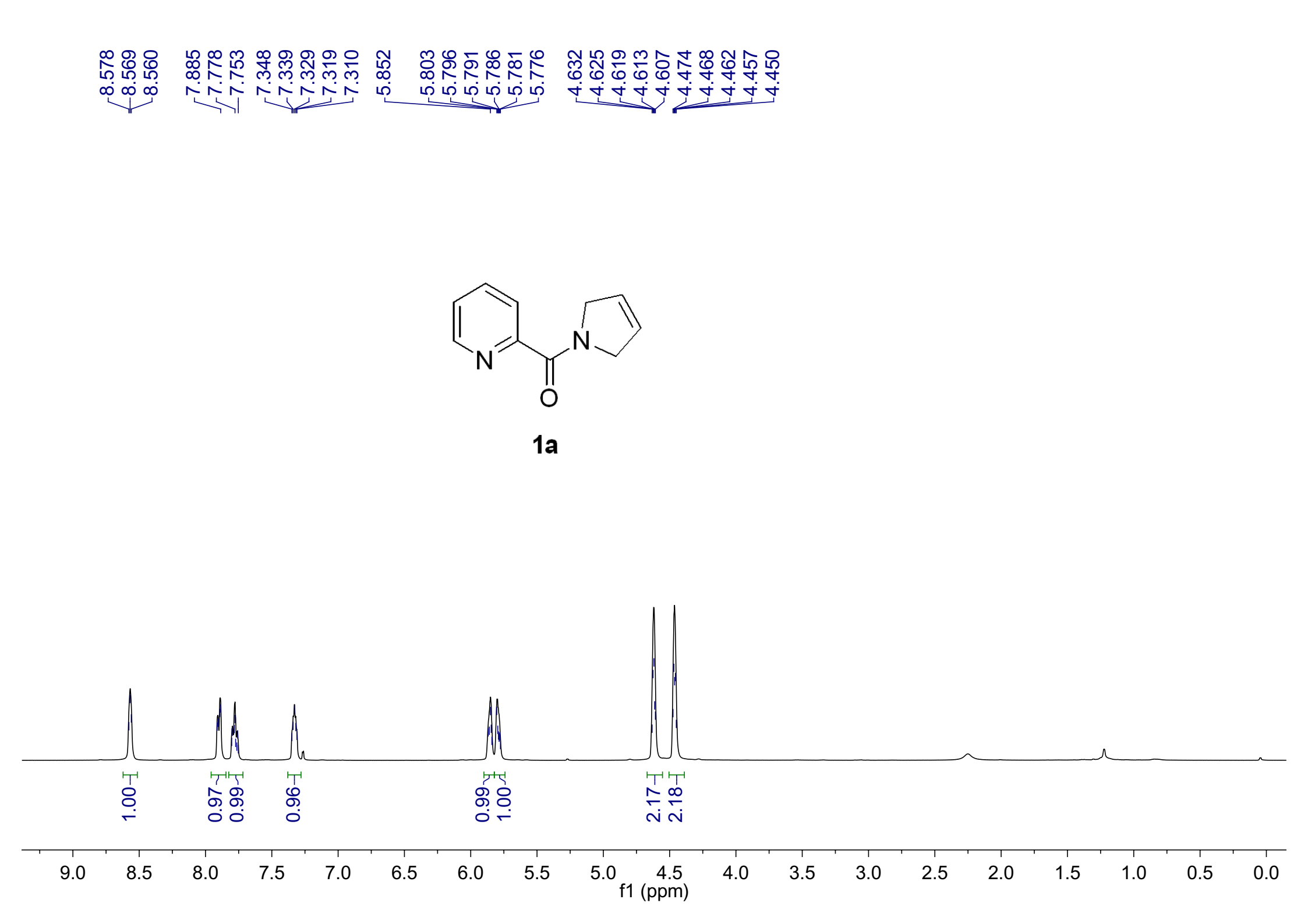

Based on the observed results and previous reports, we proposed a plausible reaction mechanism. The catalytic cycle initiates with $Pd(TFA)_2$ and thioamide **1e** to give the complex **I** *via* the C($sp^3$)–H activation. Subsequently, the intermediate **I** undergoes a transmetalation reaction (TM) with the arylboronic acids to yield the $Pd^{(II)}$–Ar species **II**. Next, a reductive elimination (RE) takes place to afford the *α*-arylated products **3** and a $Pd^{(0)}$-complex. Finally, the $Pd^{(0)}$-complex was oxidized by 1,4-benzoquinone to regenerate the $Pd^{(II)}$-complex that continues the catalytic cycle.

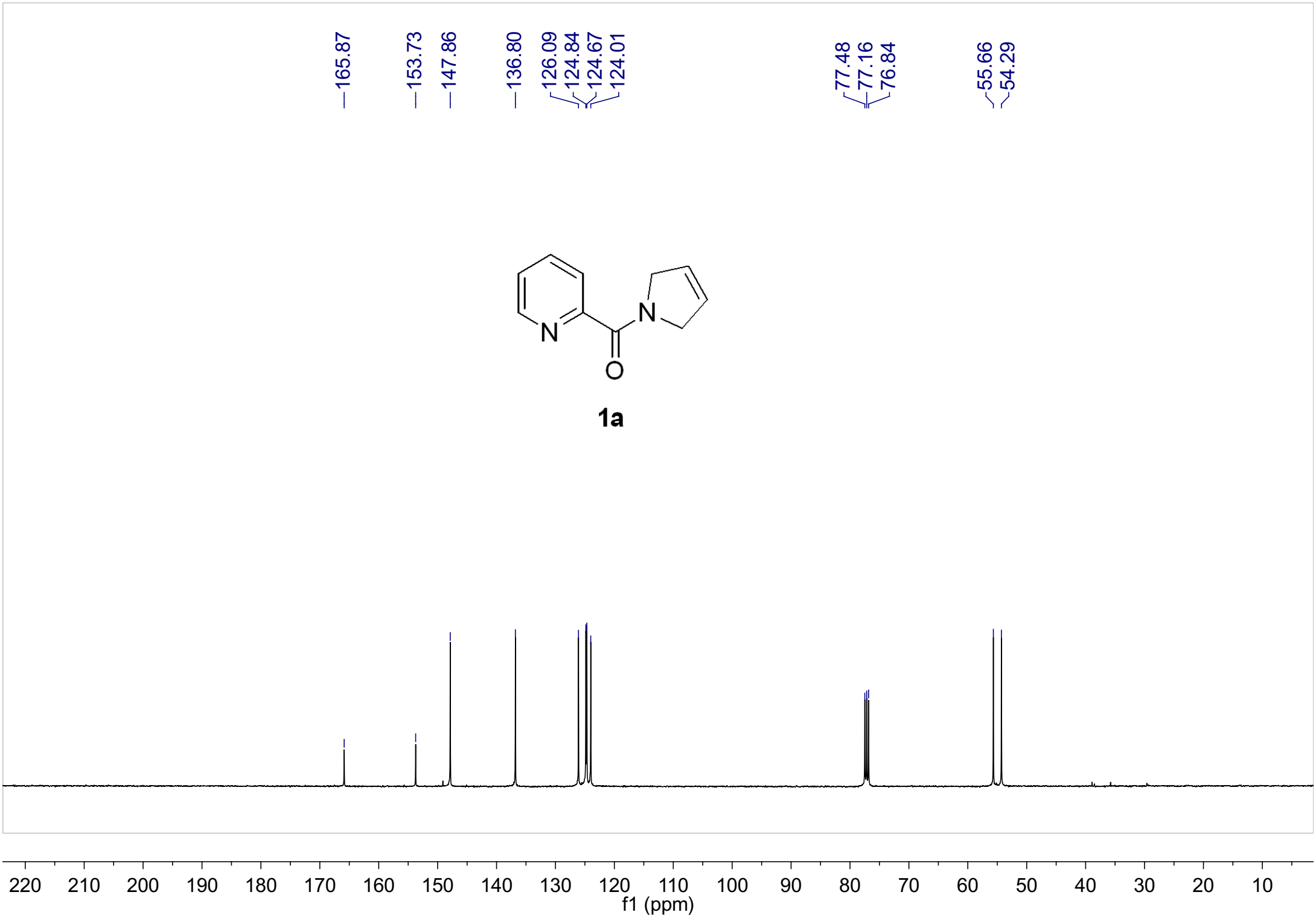
## 9 References

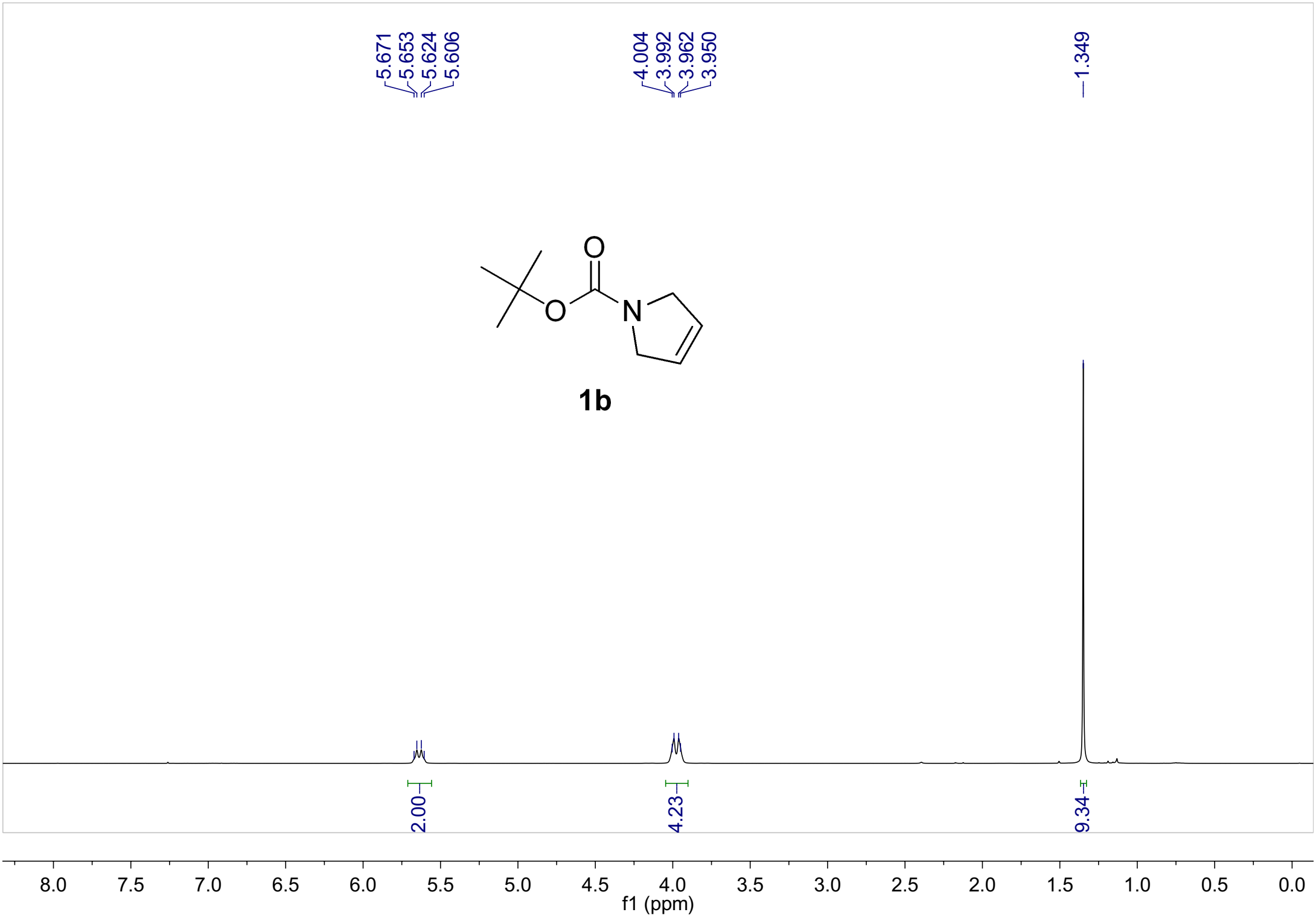
[1] P. Jain, P. Verma, G. Xia and J.-Q. Yu, *Nat. Chem.*, 2016, **9**, 140.

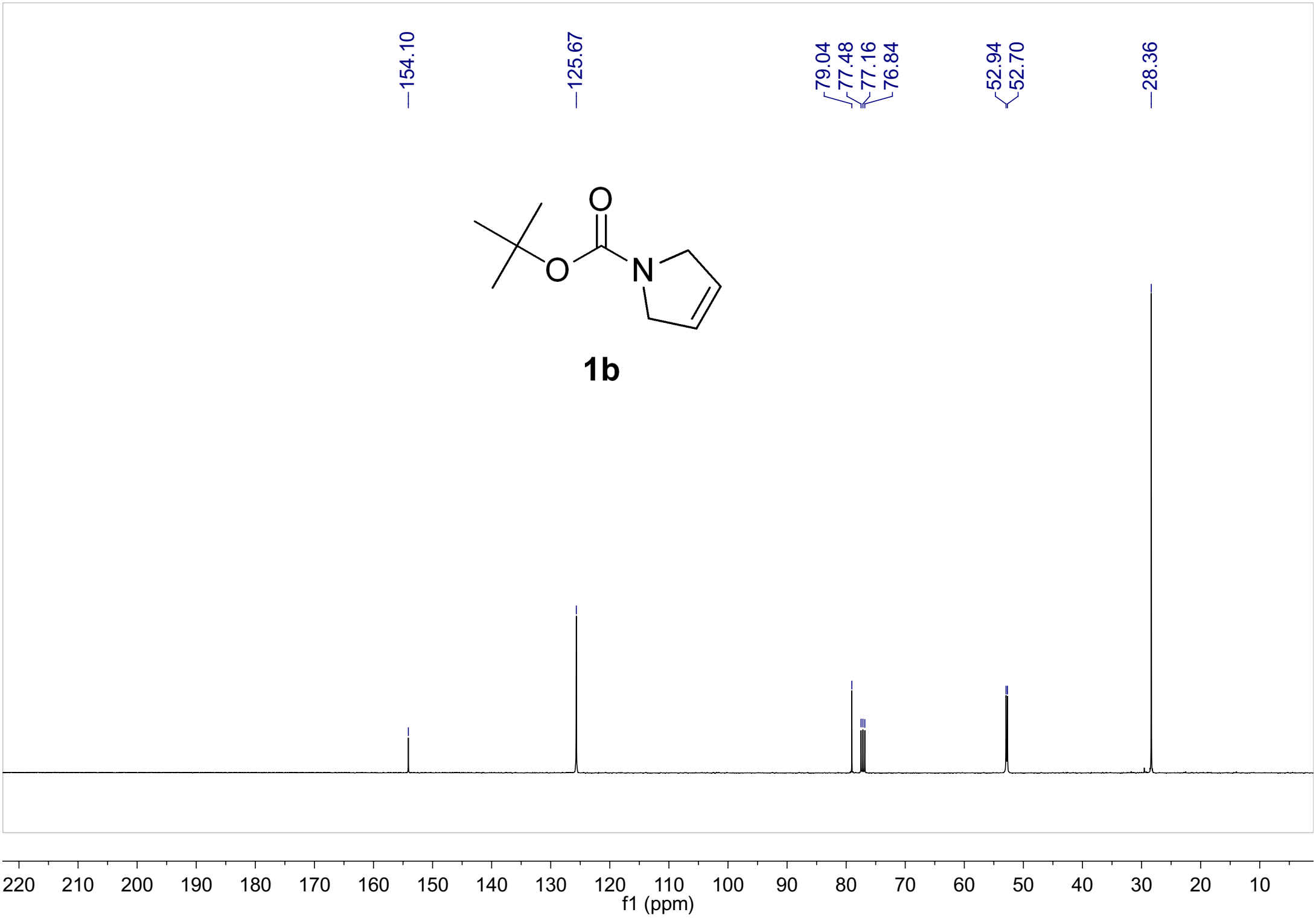
[2] J. E. Spangler, Y. Kobayashi, P. Verma, D.-H. Wang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2015, **137**, 11876.

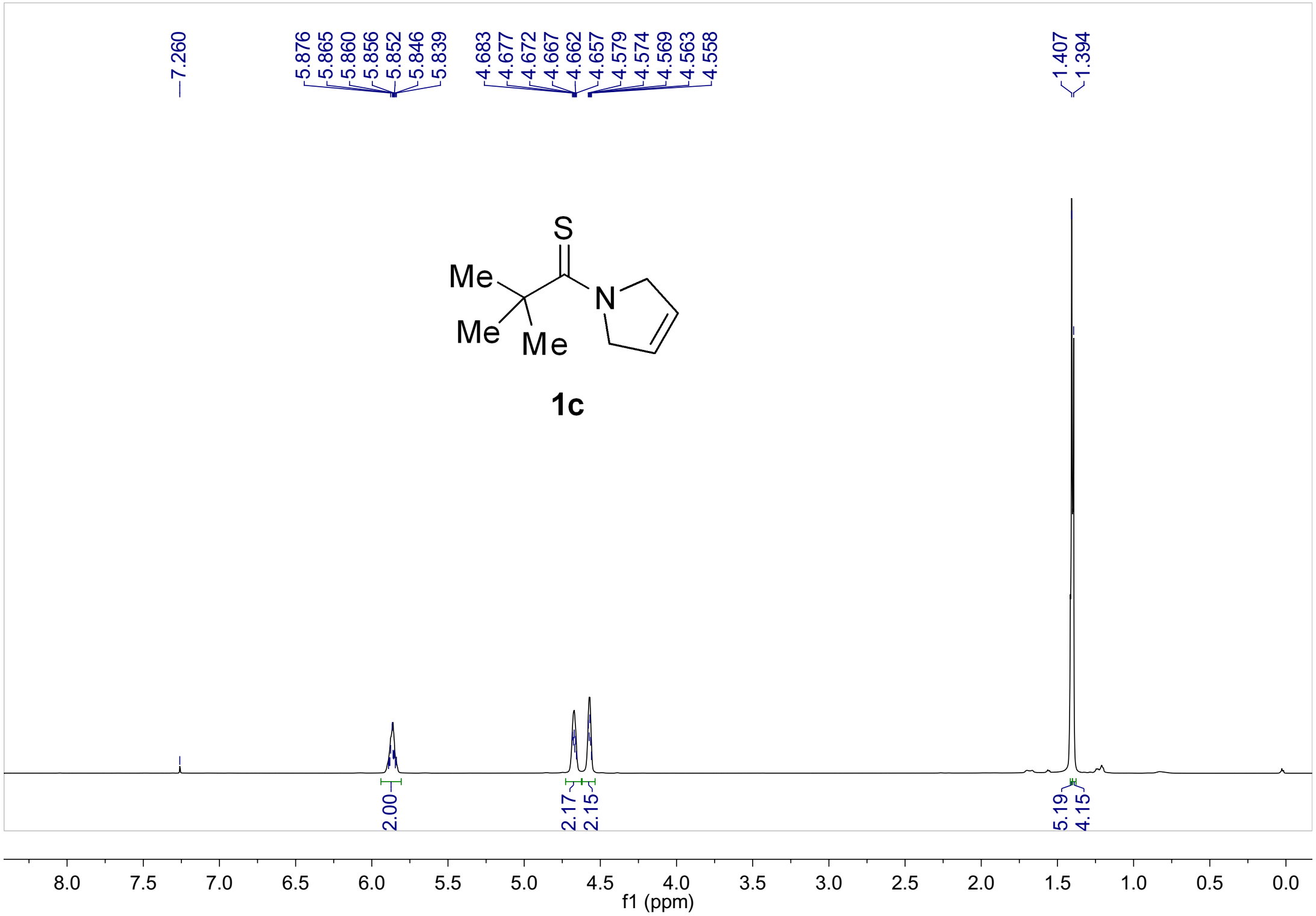
[3] C. Wu and J. Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 650.

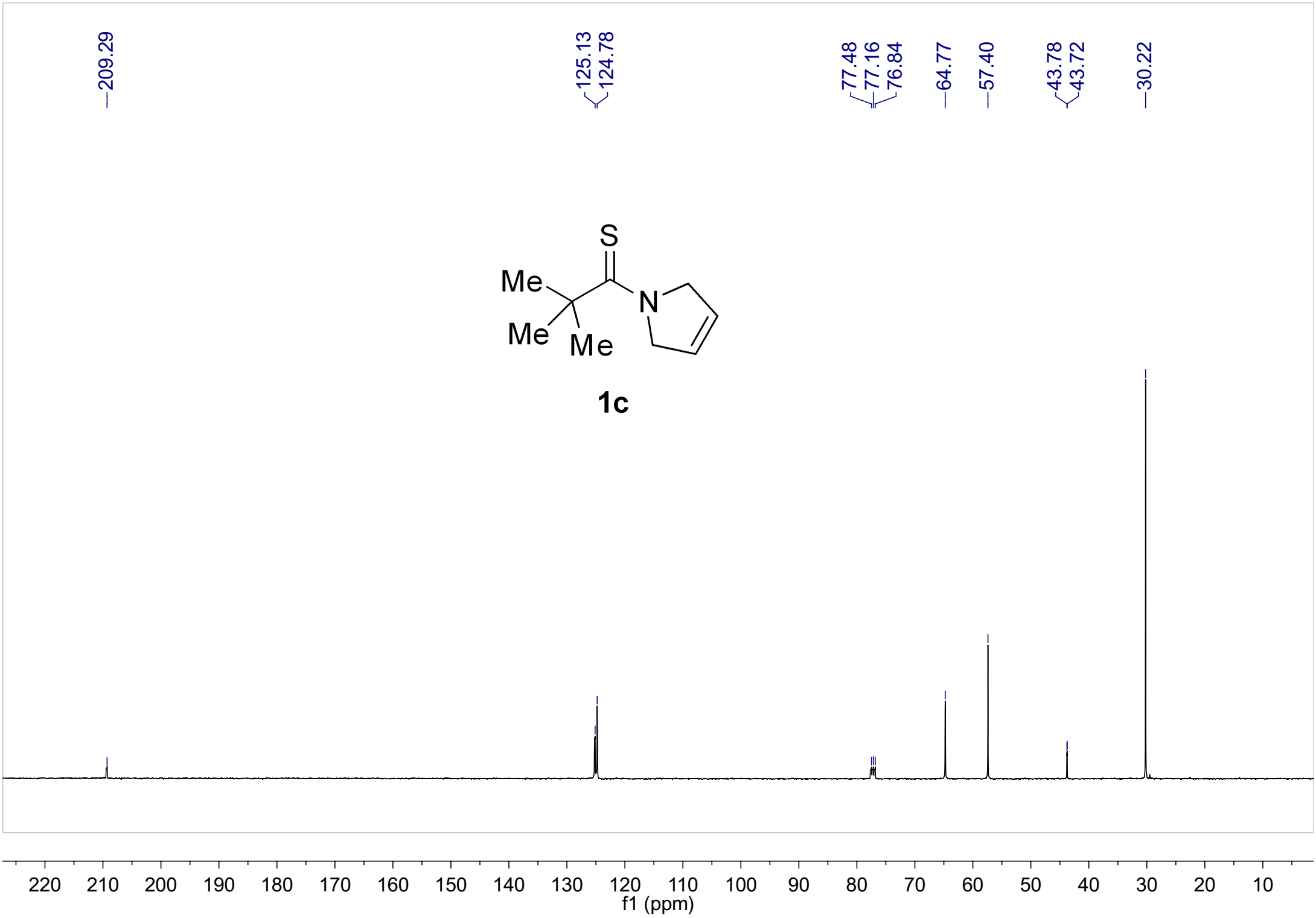

8.578
8.569
8.560
7.885
7.778
7.753
7.348
7.339
7.329
7.319
7.310
5.852
5.803
5.796
5.791
5.786
5.781
5.776
4.632
4.625
4.619
4.613
4.607
4.474
4.468
4.462
4.457
4.450
N
N
O
1a
1.00
0.97
0.99
0.96
0.99
1.00
2.17
2.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

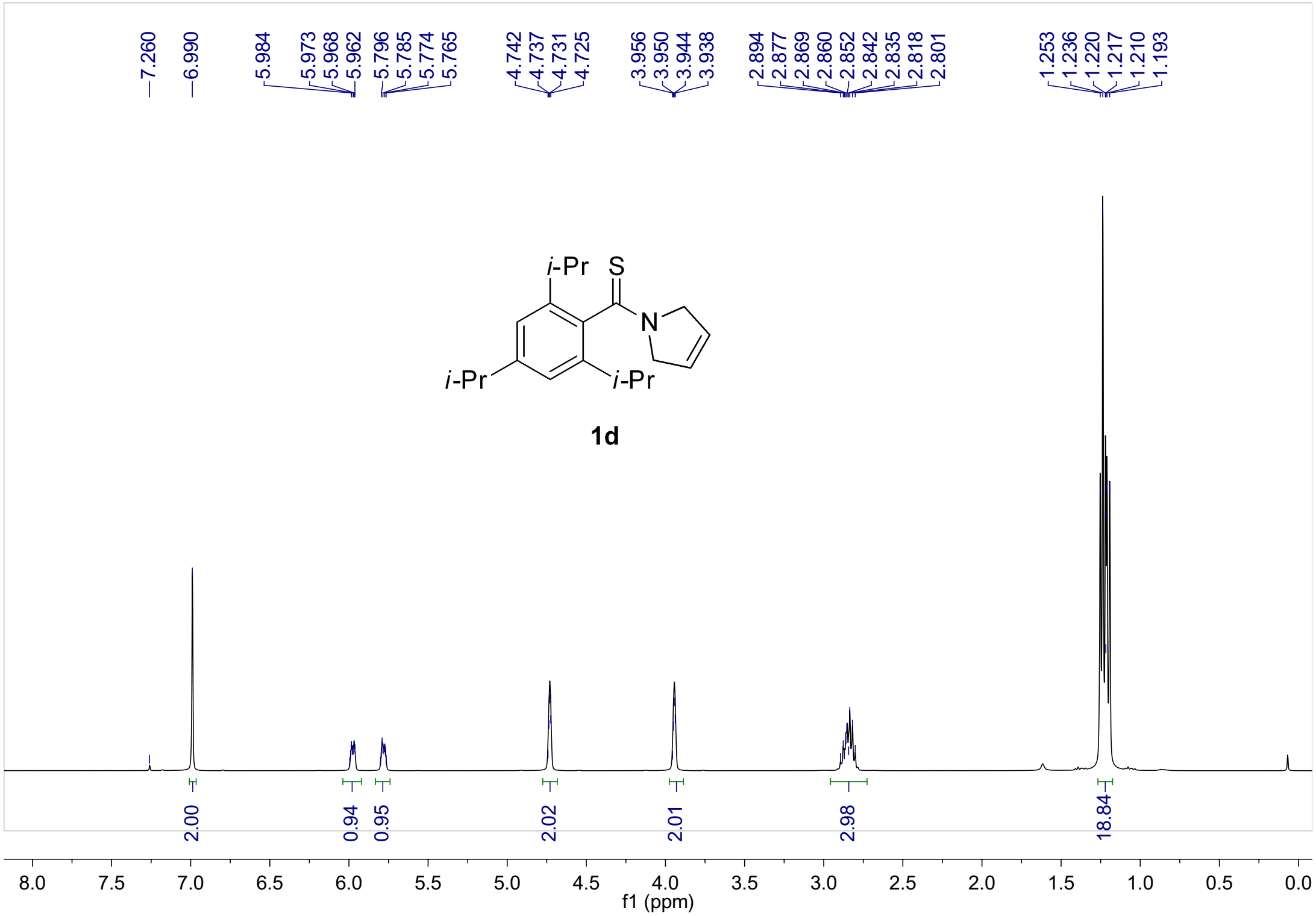

165.87
153.73
147.86
136.80
126.09
124.84
124.67
124.01
77.48
77.16
76.84
55.66
54.29
N
N
O
1a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

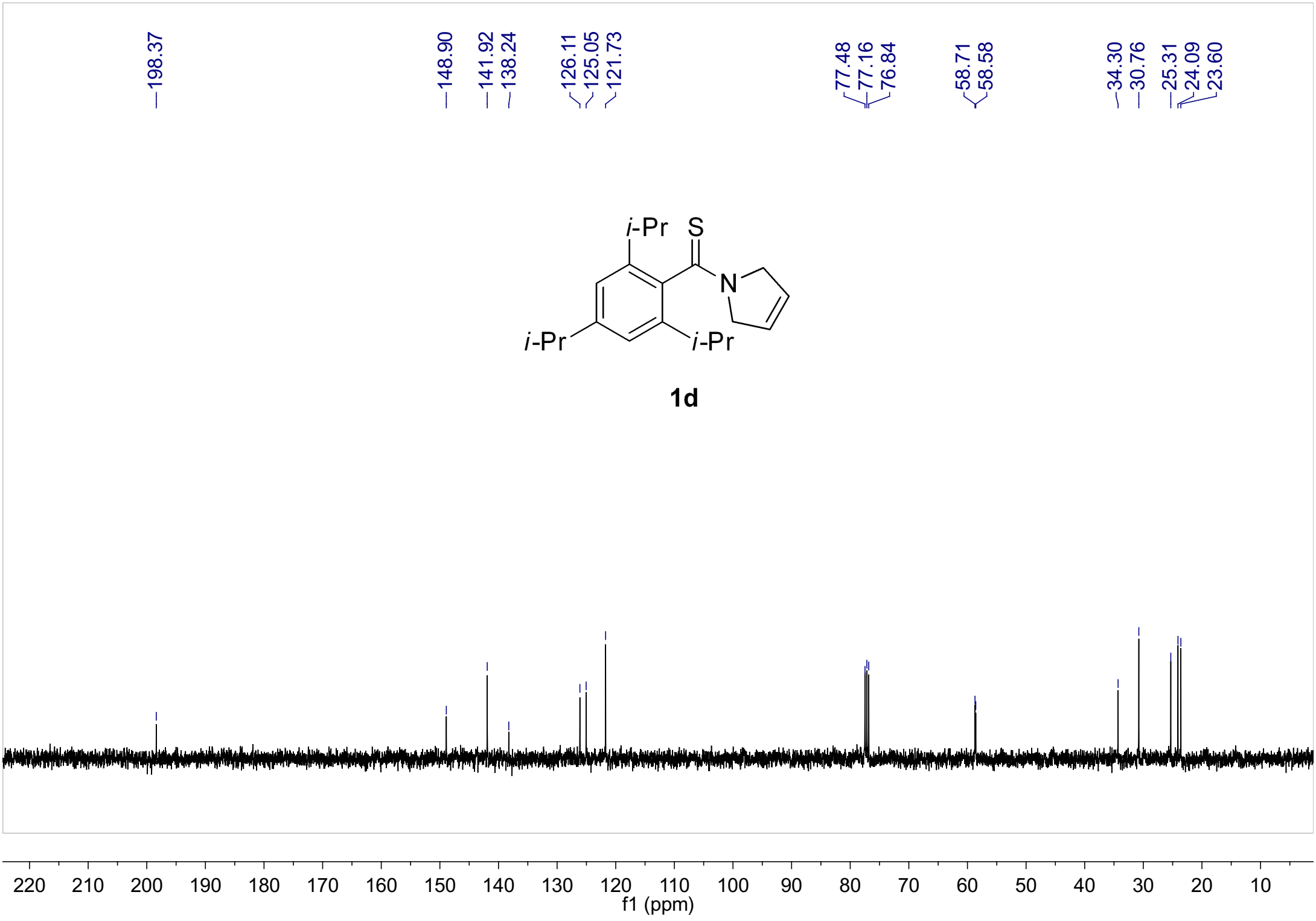

5.671
5.653
5.624
5.606
4.004
3.992
3.962
3.950
1.349
O
O
N
1b
2.00
4.23
9.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

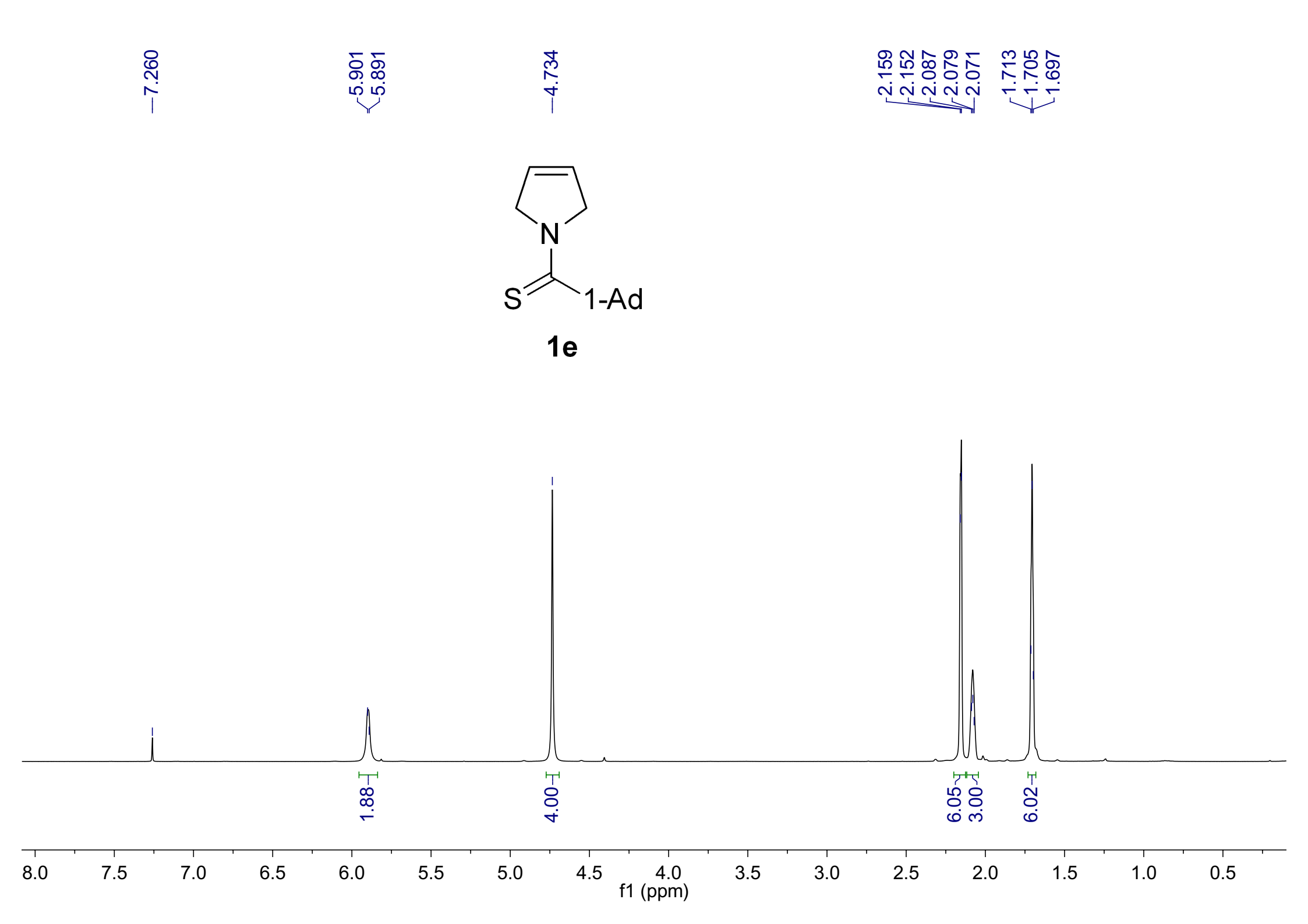

154.10
125.67
79.04
77.48
77.16
76.84
52.94
52.70
28.36
O
O
N
1b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

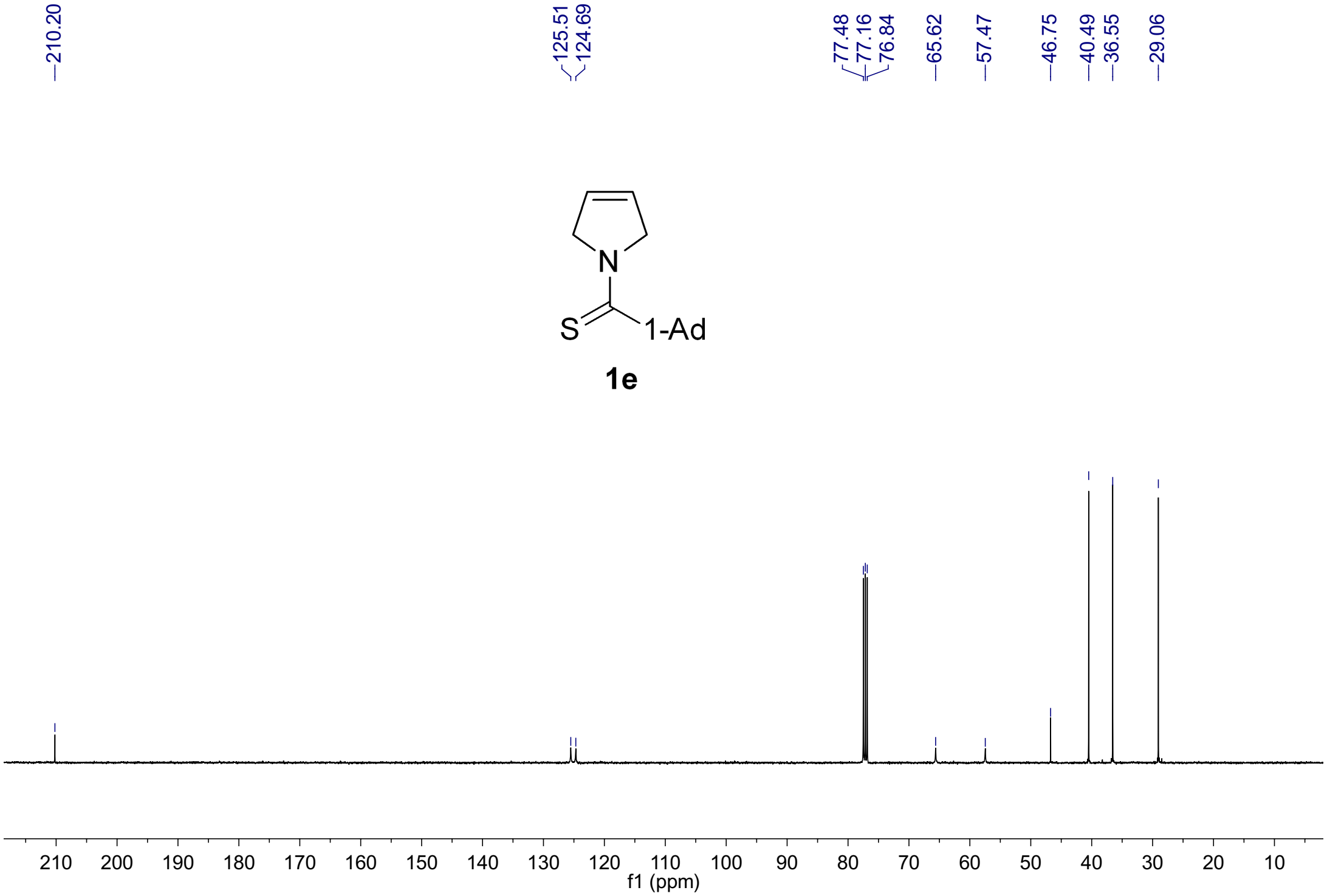

7.260
5.876
5.865
5.860
5.856
5.852
5.846
5.839
4.683
4.677
4.672
4.667
4.662
4.657
4.579
4.574
4.569
4.563
4.558
1.407
1.394
S
Me
Me
Me
N
1c
2.00
2.17
2.15
5.19
4.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

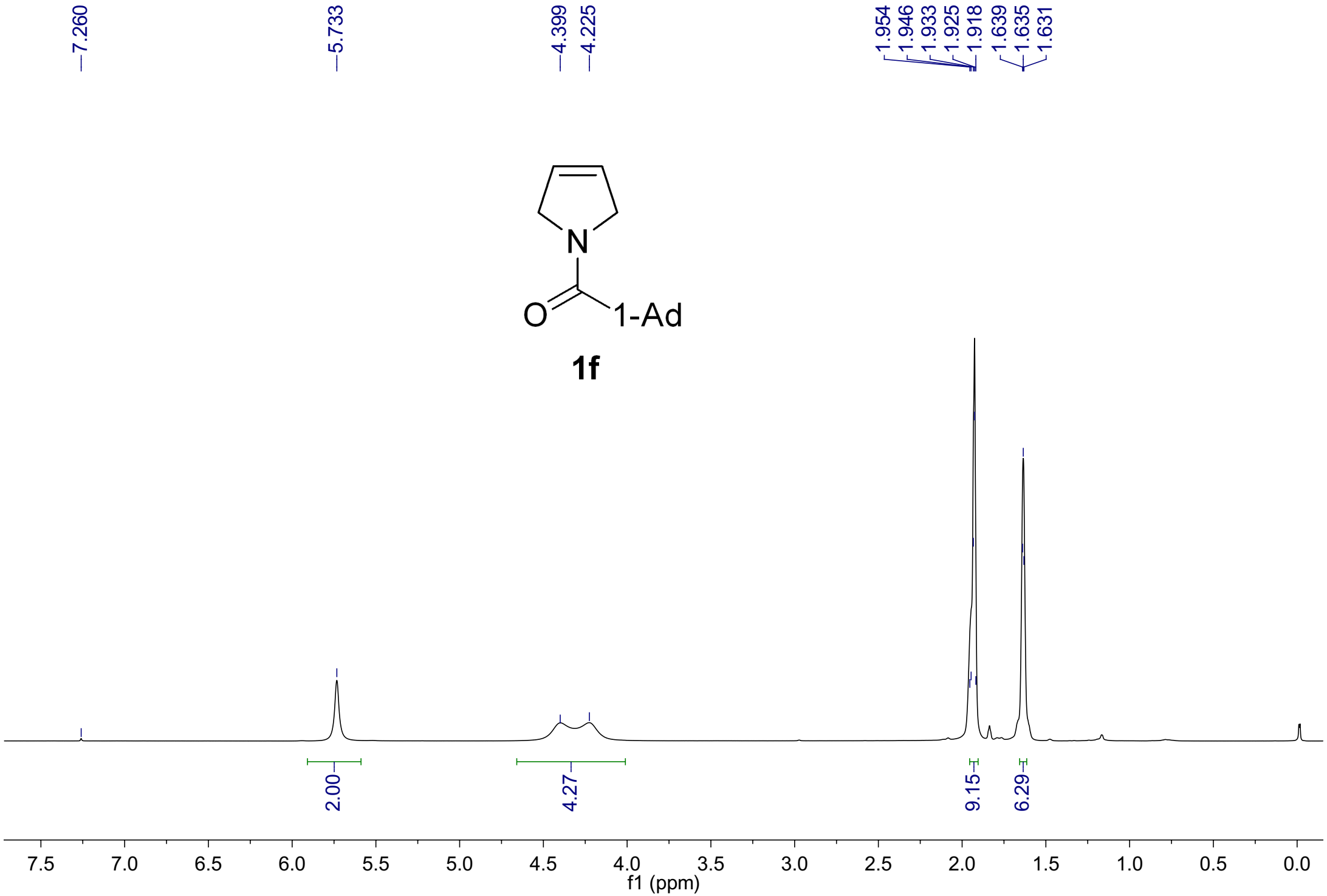

209.29
125.13
124.78
77.48
77.16
76.84
64.77
57.40
43.78
43.72
30.22
S
Me
Me
Me
N
1c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

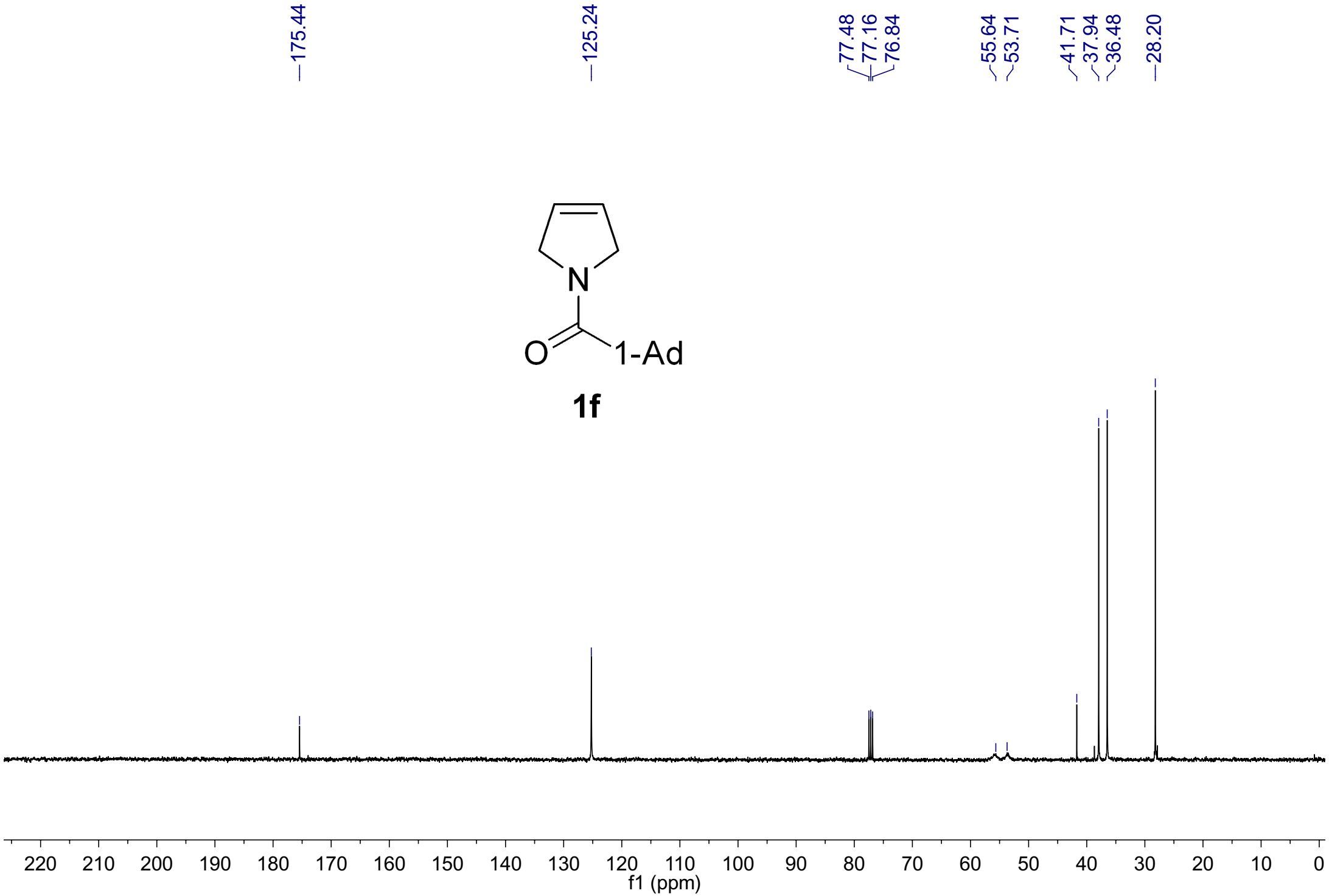

7.260
6.990
5.984
5.973
5.968
5.962
5.796
5.785
5.774
5.765
4.742
4.737
4.731
4.725
3.956
3.950
3.944
3.938
2.894
2.877
2.869
2.860
2.852
2.842
2.835
2.818
2.801
1.253
1.236
1.220
1.217
1.210
1.193
i-Pr
S
N
i-Pr
i-Pr
1d
2.00
0.94
0.95
2.02
2.01
2.98
18.84
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

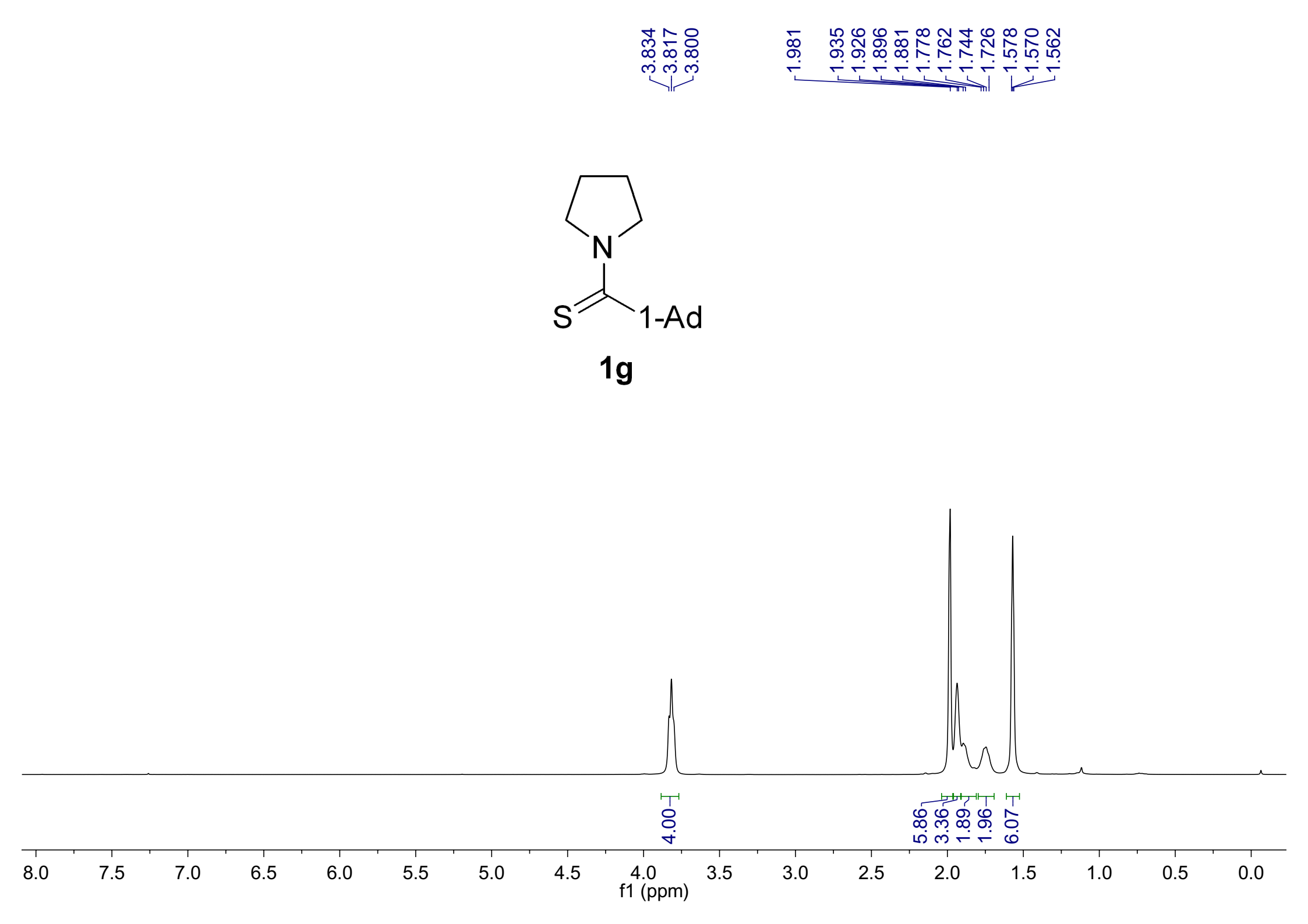

198.37
148.90
141.92
138.24
126.11
125.05
121.73
77.48
77.16
76.84
58.71
58.58
34.30
30.76
25.31
24.09
23.60
i-Pr
S
N
i-Pr
i-Pr
1d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.260
5.901
5.891
4.734
2.159
2.152
2.087
2.079
2.071
1.713
1.705
1.697
N
S
1-Ad
1e
1.88
4.00
6.05
3.00
6.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

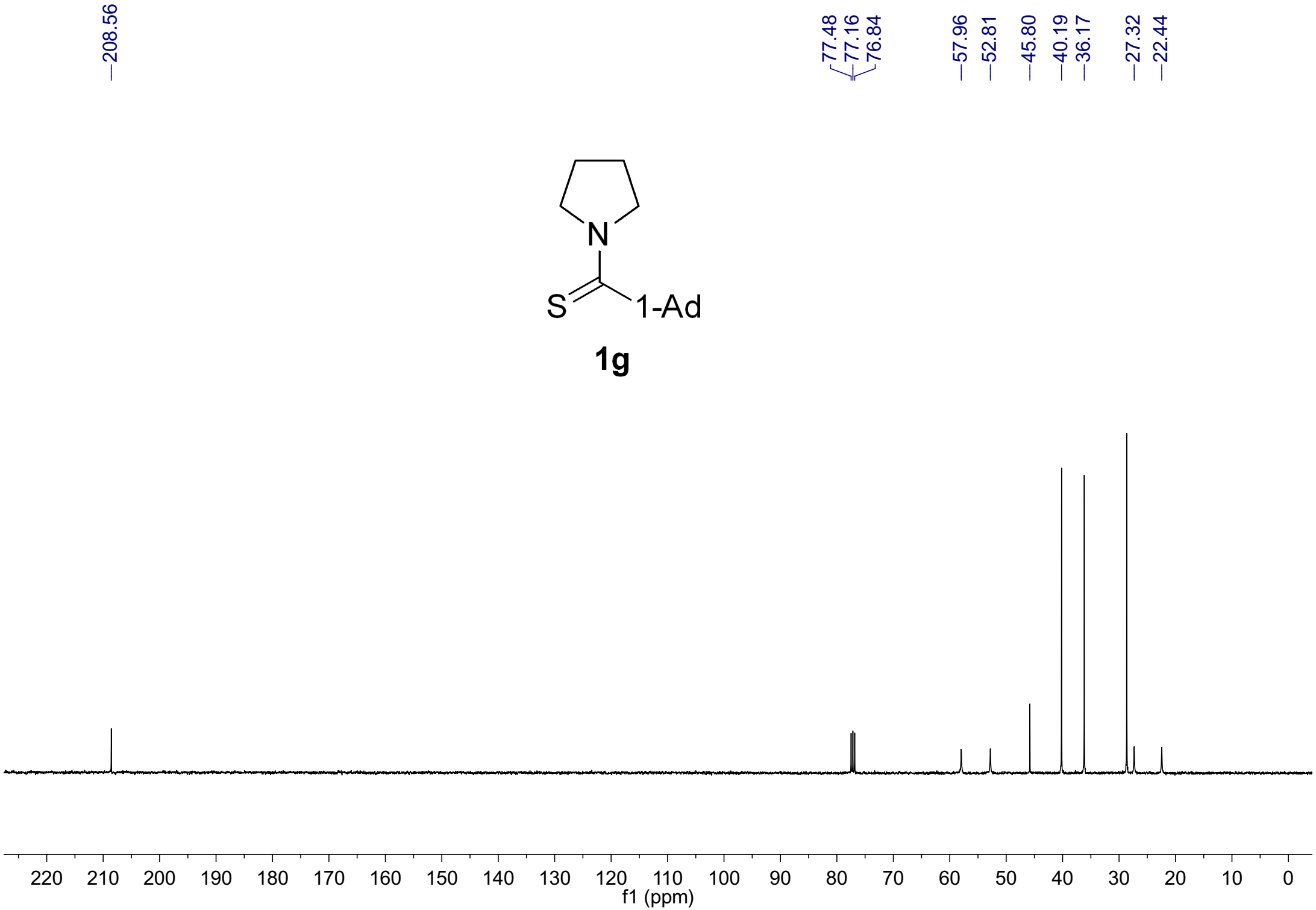

210.20
125.51
124.69
77.48
77.16
76.84
65.62
57.47
46.75
40.49
36.55
29.06
N
S
1-Ad
1e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.260
5.733
4.399
4.225
1.954
1.946
1.933
1.925
1.918
1.639
1.635
1.631
N
O
1-Ad
1f
2.00
4.27
9.15
6.29
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

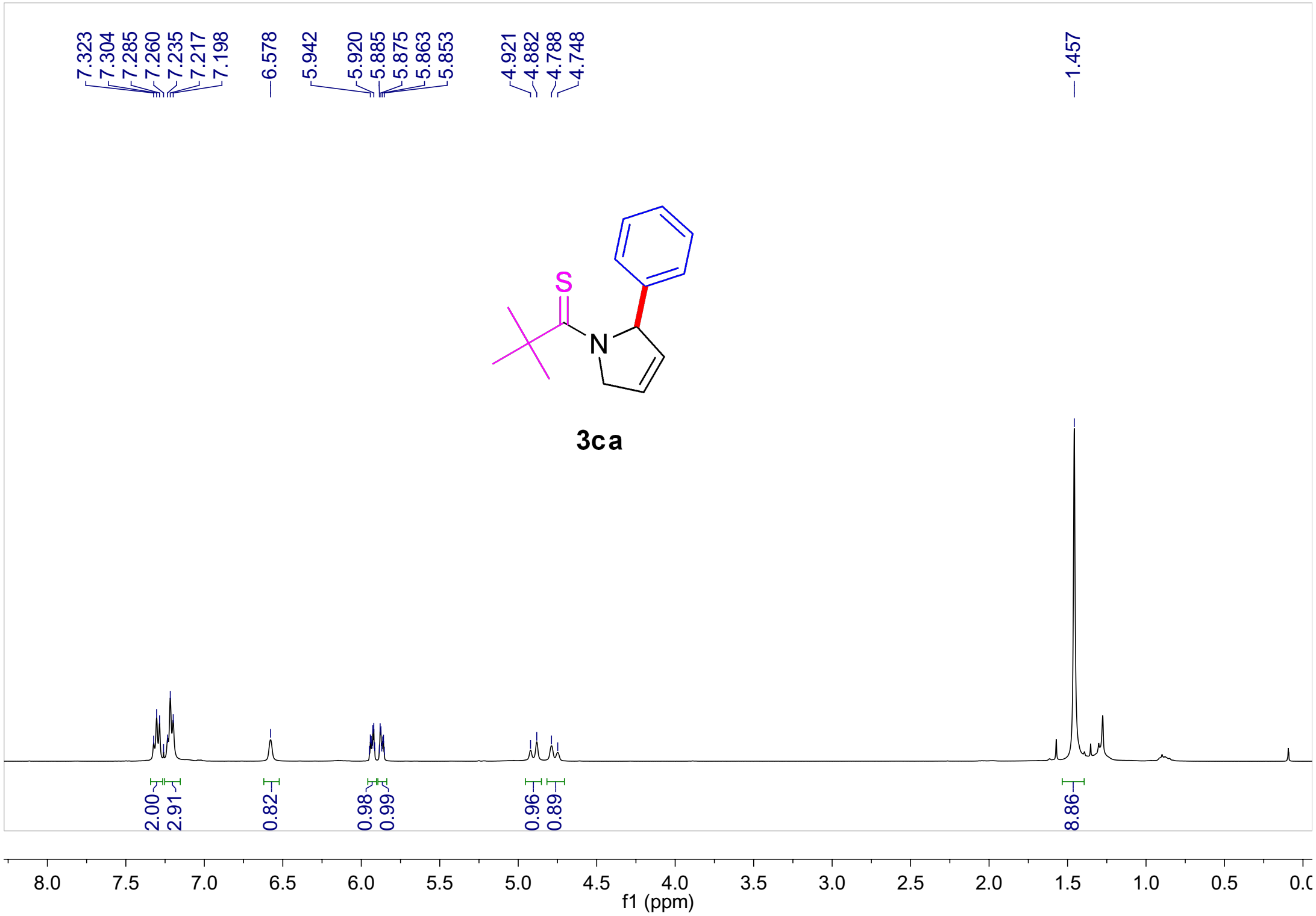

175.44
125.24
77.48
77.16
76.84
55.64
53.71
41.71
37.94
36.48
28.20
N
O
1-Ad
1f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

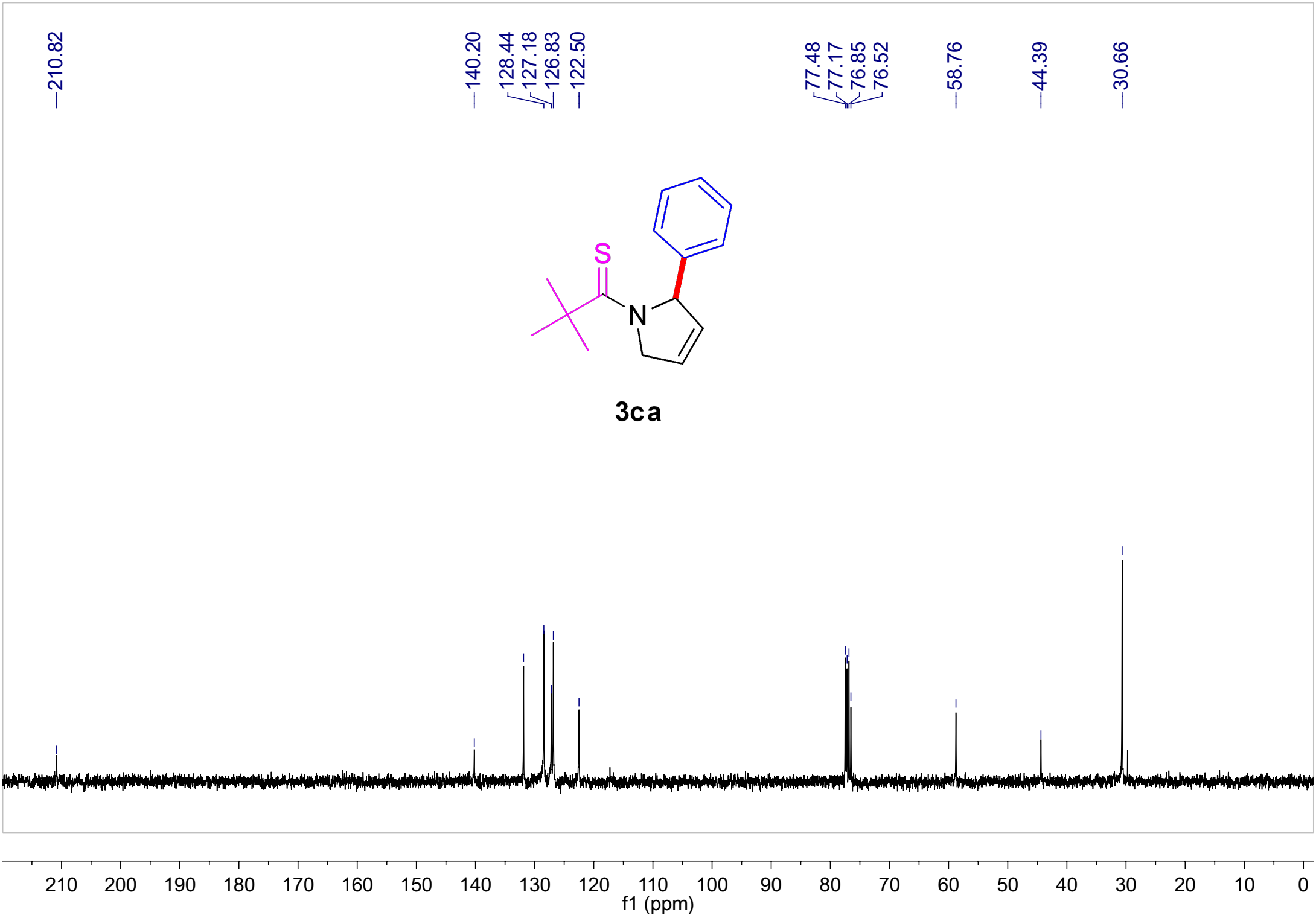

3.834
3.817
3.800
1.981
1.935
1.926
1.896
1.881
1.778
1.762
1.744
1.726
1.578
1.570
1.562
N
S
1-Ad
4.00
5.86
3.36
1.89
1.96
6.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

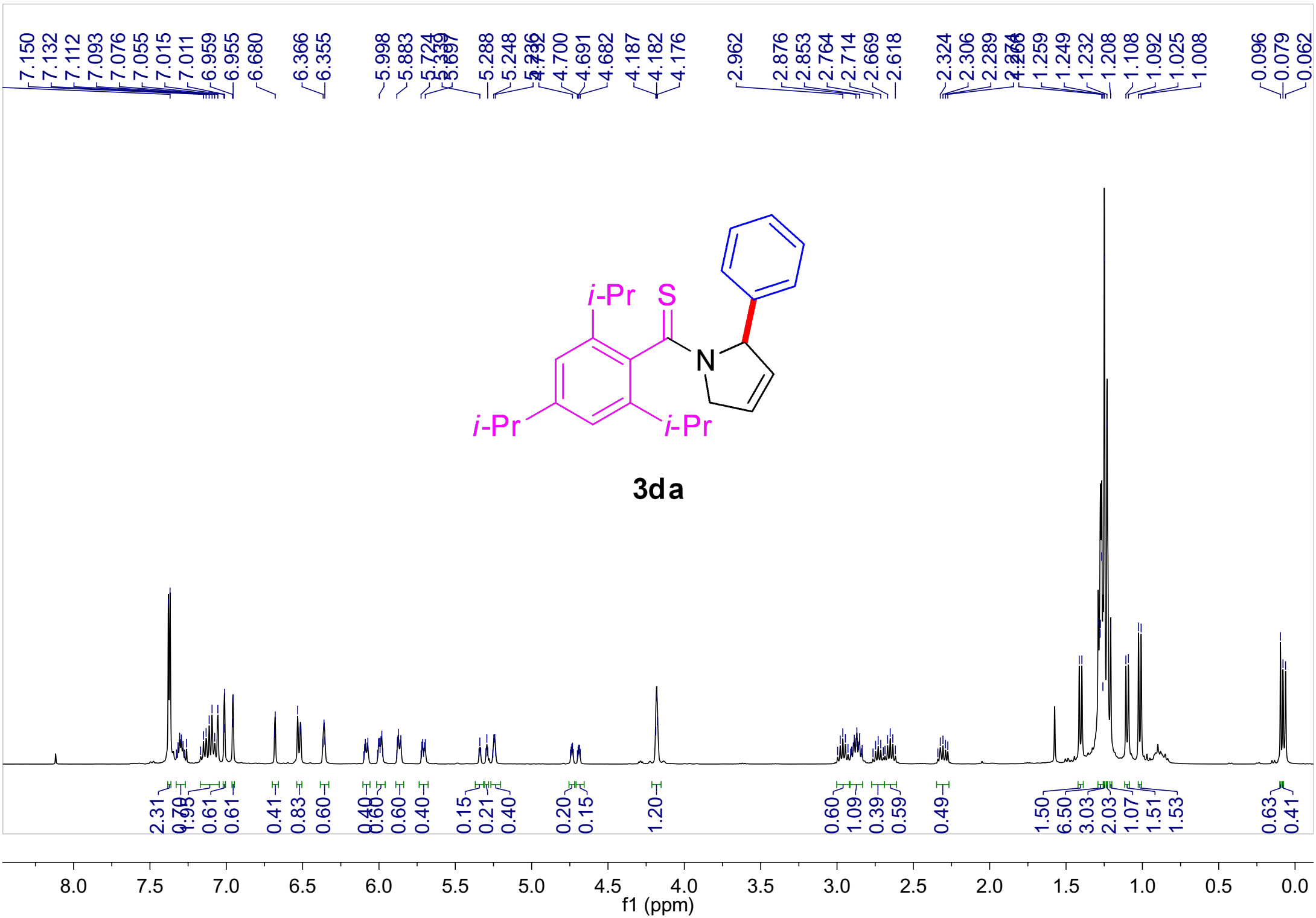
**1g**

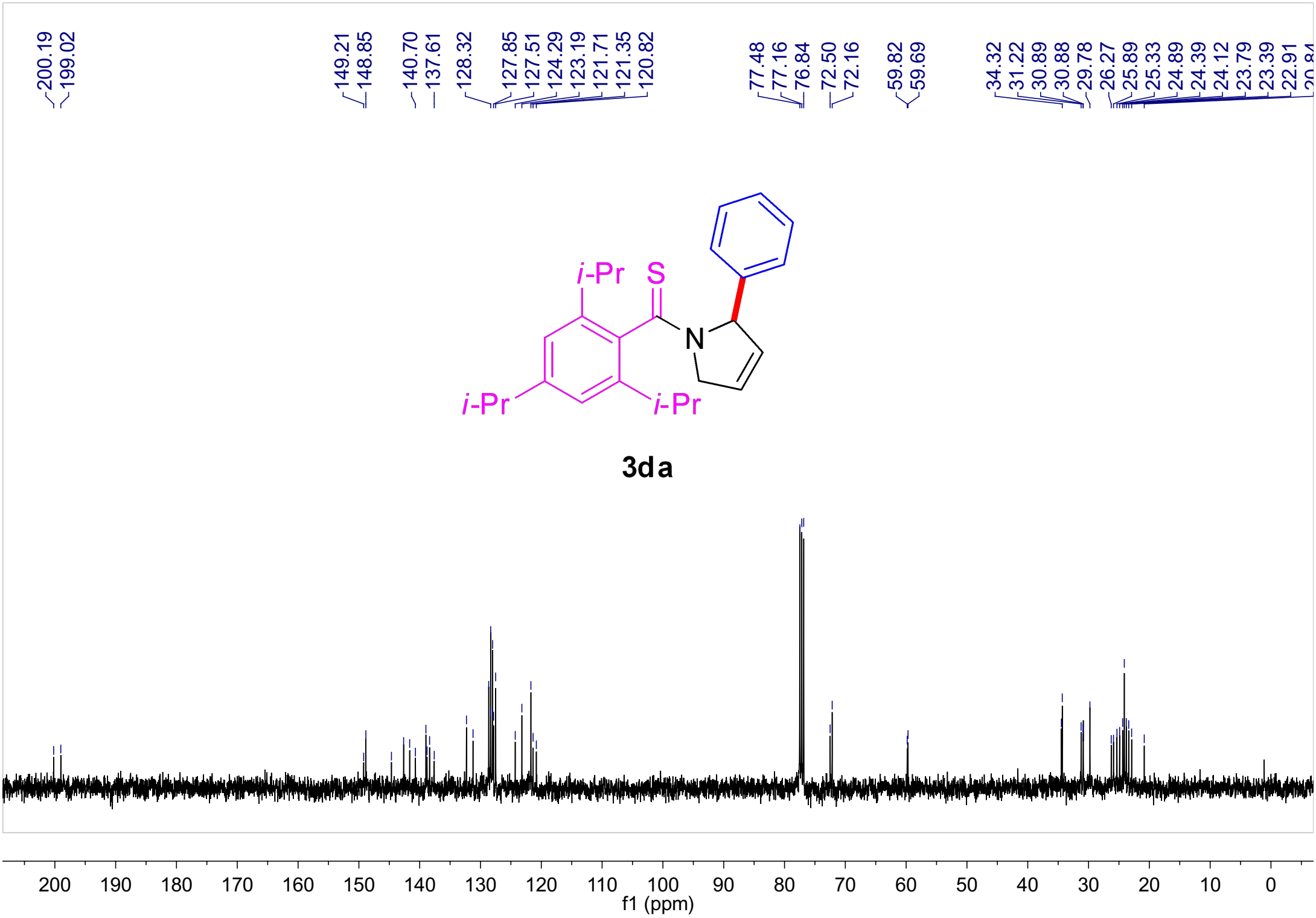

208.56
77.48
77.16
76.84
57.96
52.81
45.80
40.19
36.17
27.32
22.44
N
S
1-Ad
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

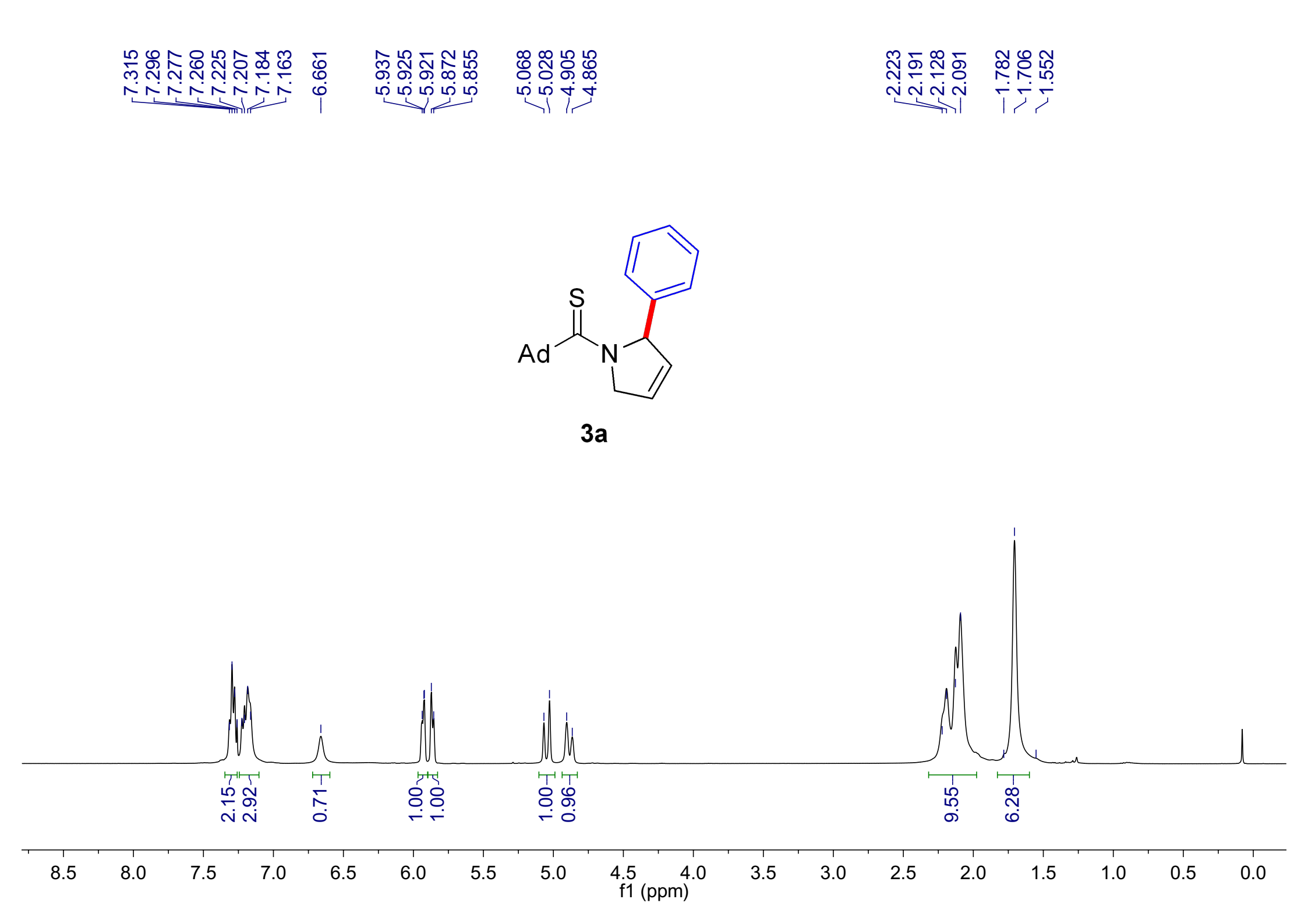
**1g**


7.323
7.304
7.285
7.260
7.235
7.217
7.198
6.578
5.942
5.920
5.885
5.875
5.863
5.853
4.921
4.882
4.788
4.748
1.457
S
N
3ca
2.00
2.91
0.82
0.98
0.99
0.96
0.89
8.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

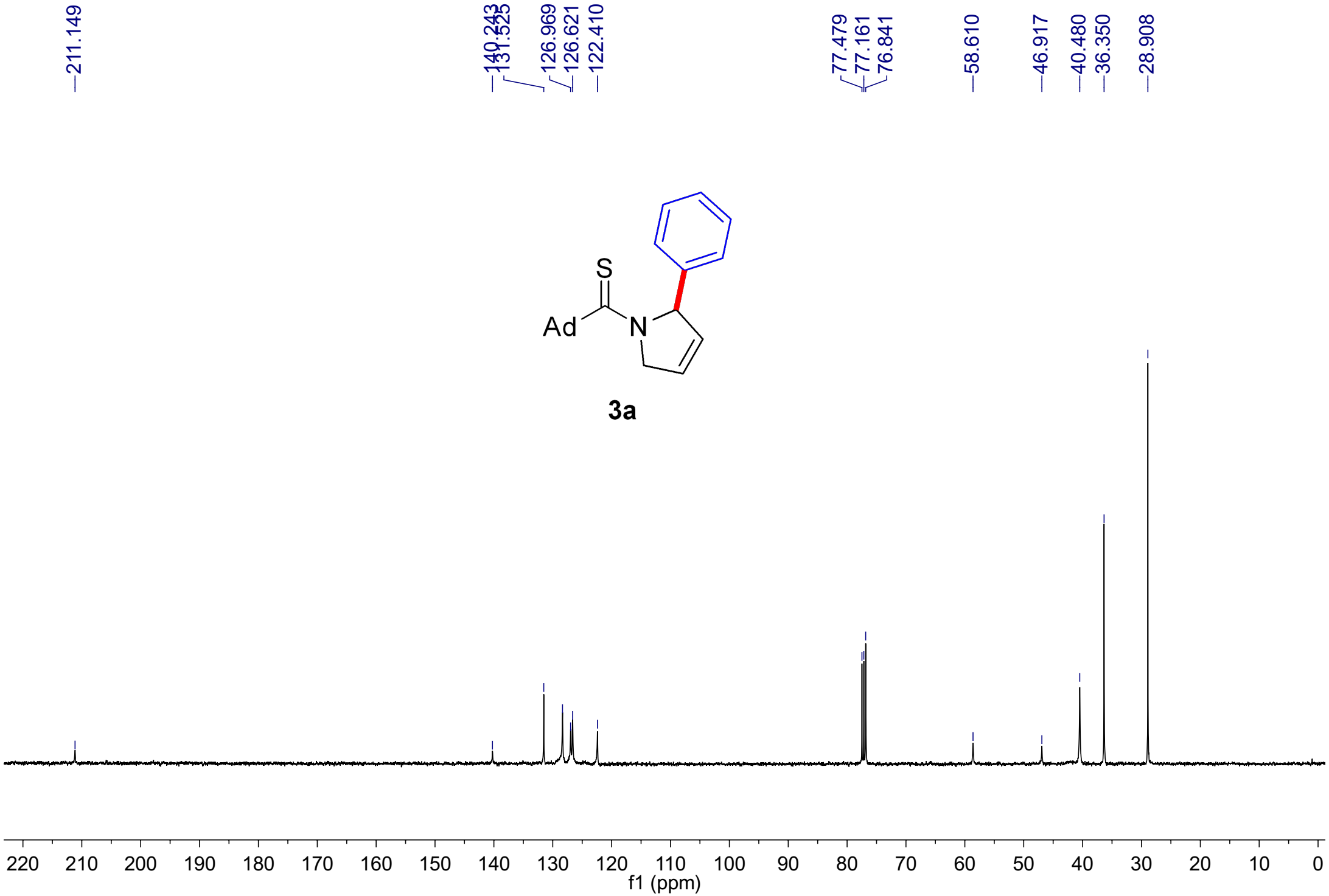

210.82
140.20
128.44
127.18
126.83
122.50
77.48
77.17
76.85
76.52
58.76
44.39
30.66
S
N
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

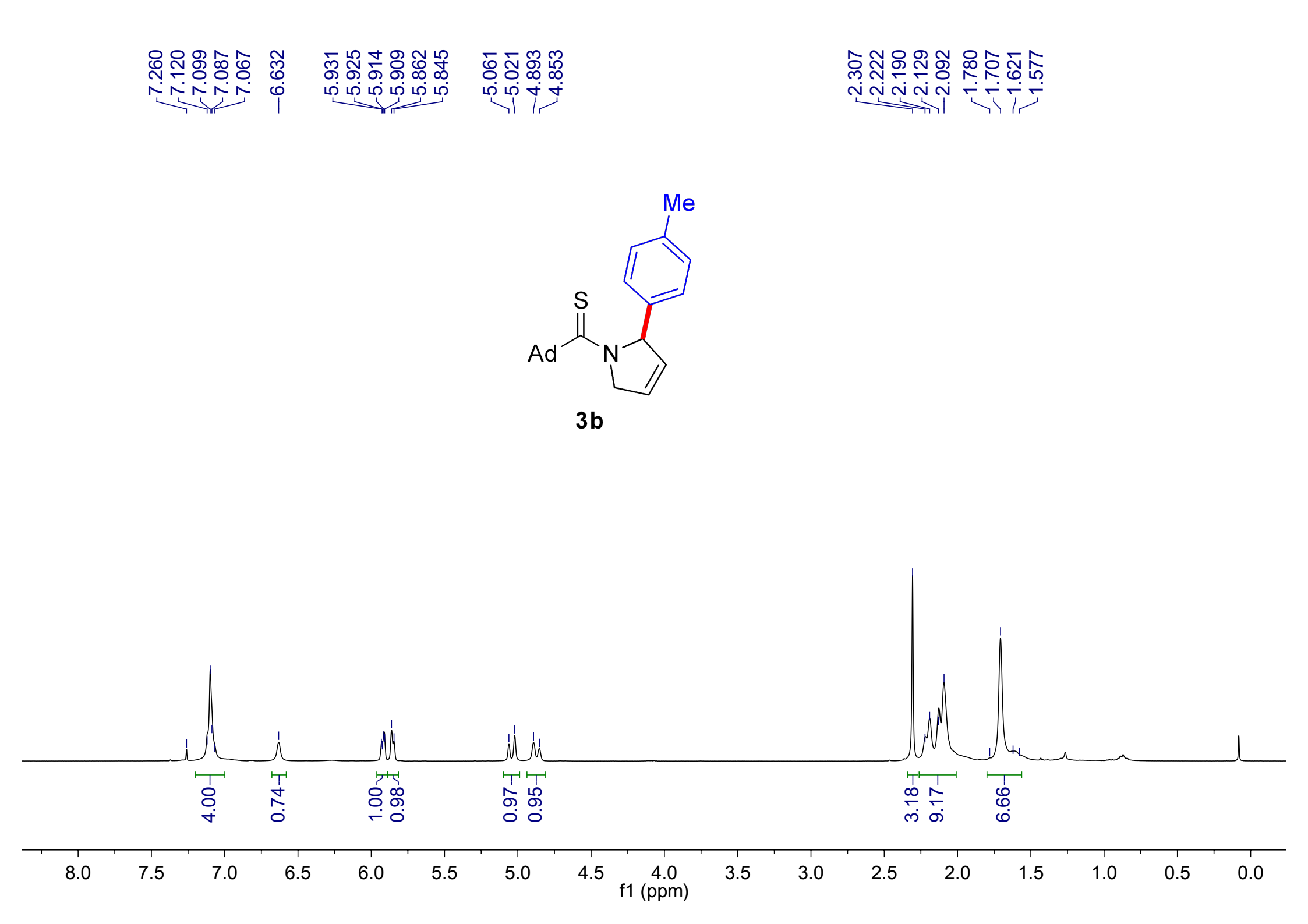

7.150
7.132
7.112
7.093
7.076
7.055
7.015
7.011
6.959
6.955
6.680
6.366
6.355
5.998
5.883
5.724
5.339
5.288
5.248
4.700
4.691
4.682
4.187
4.182
4.176
2.962
2.876
2.853
2.764
2.714
2.669
2.618
2.324
2.306
2.289
1.259
1.249
1.232
1.208
1.108
1.092
1.025
1.008
0.096
0.079
0.062
i-Pr
S
N
i-Pr
i-Pr
3da
2.31
0.70
0.61
0.61
0.41
0.83
0.60
0.40
0.60
0.40
0.15
0.21
0.40
0.20
0.15
1.20
0.60
1.09
0.39
0.59
0.49
1.50
6.50
3.03
2.03
1.07
1.51
1.53
0.63
0.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

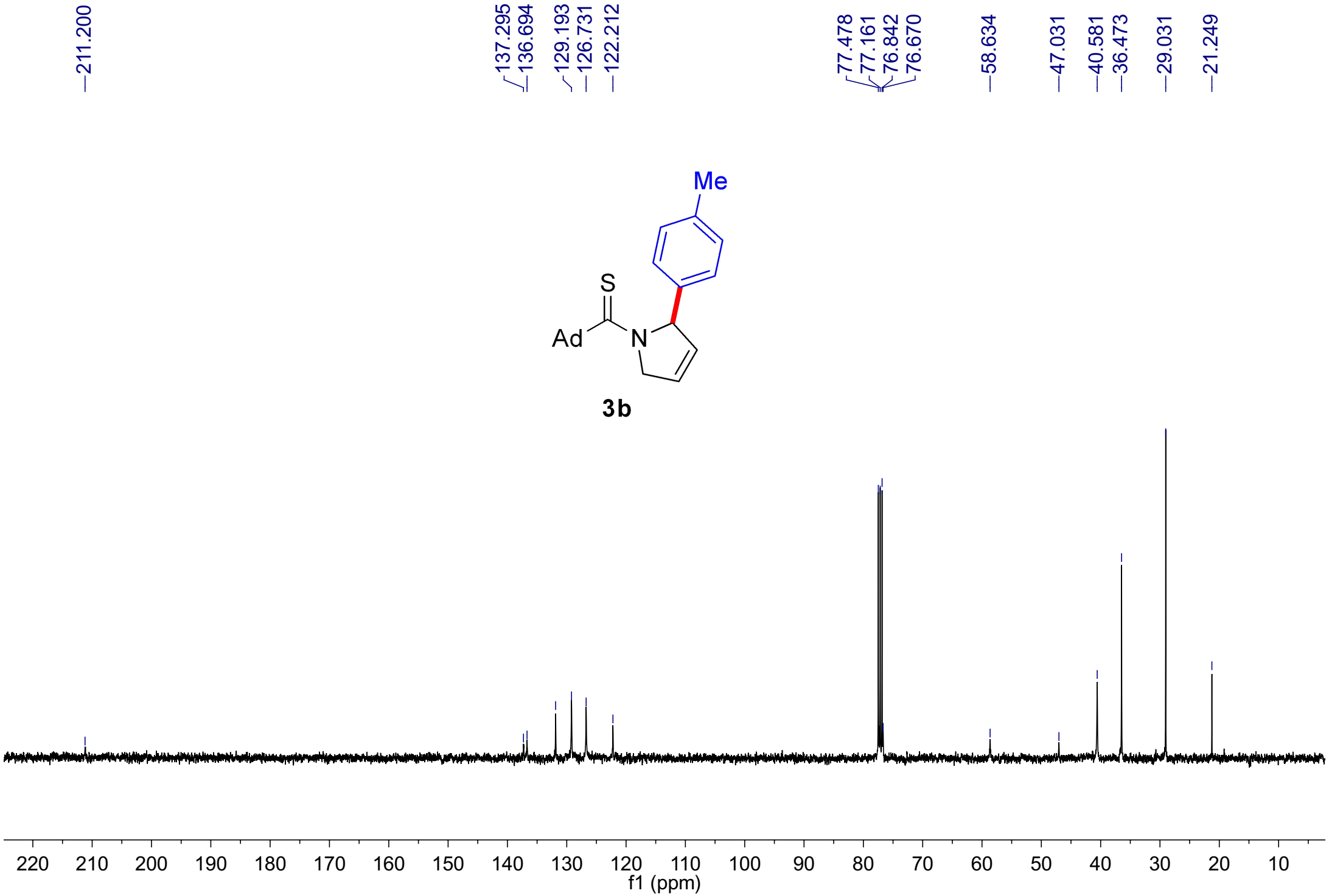

200.19
199.02
149.21
148.85
140.70
137.61
128.32
127.85
127.51
124.29
123.19
121.71
121.35
120.82
77.48
77.16
76.84
72.50
72.16
59.82
59.69
34.32
31.22
30.89
30.88
29.78
26.27
25.89
25.33
24.89
24.39
24.12
23.79
23.39
22.91
i-Pr
S
N
i-Pr
i-Pr
3da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

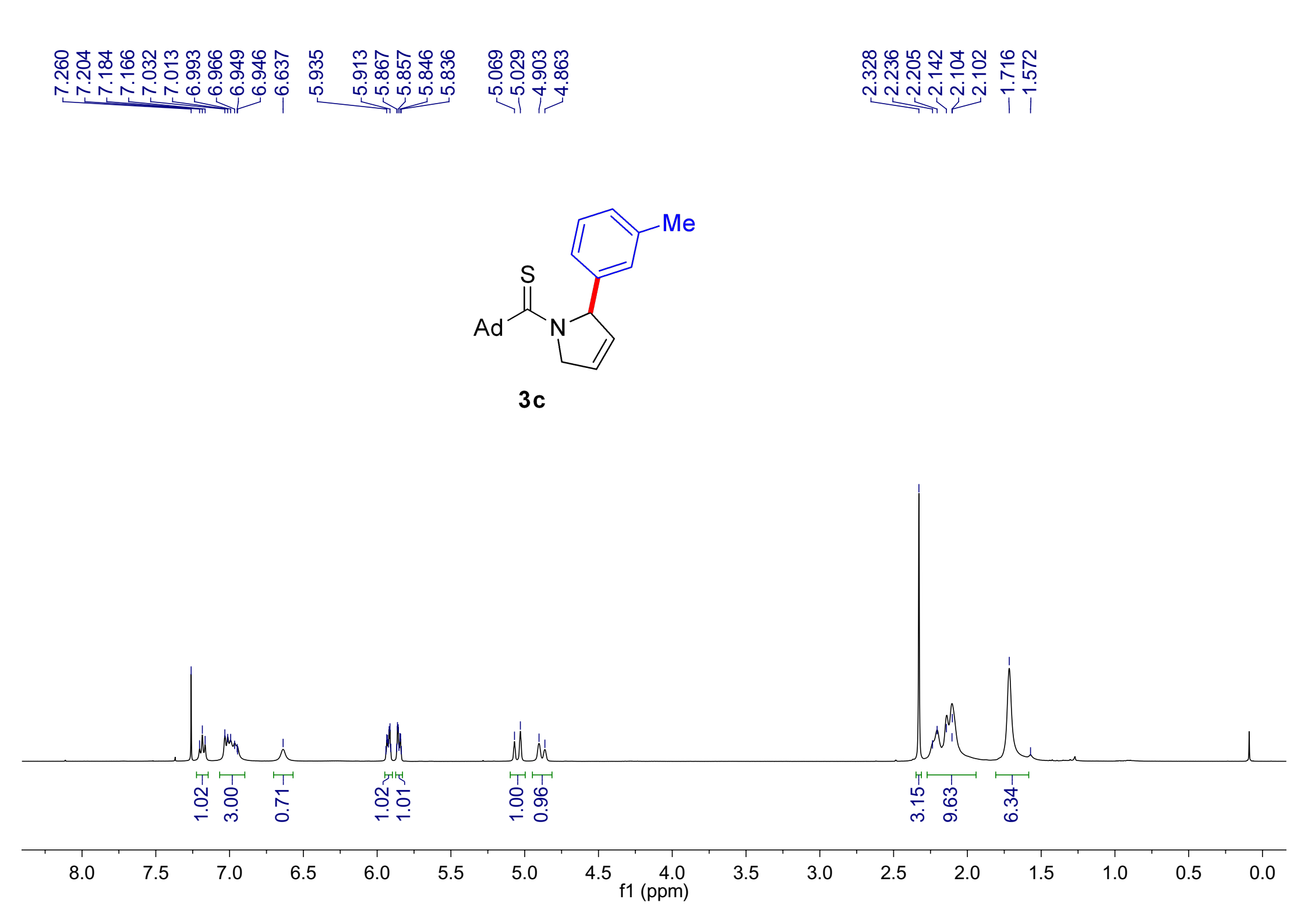

7.315
7.296
7.277
7.260
7.225
7.207
7.184
7.163
6.661
5.937
5.925
5.921
5.872
5.855
5.068
5.028
4.905
4.865
2.223
2.191
2.128
2.091
1.782
1.706
1.552
S
Ad
N
2.15
2.92
0.71
1.00
1.00
1.00
0.96
9.55
6.28
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

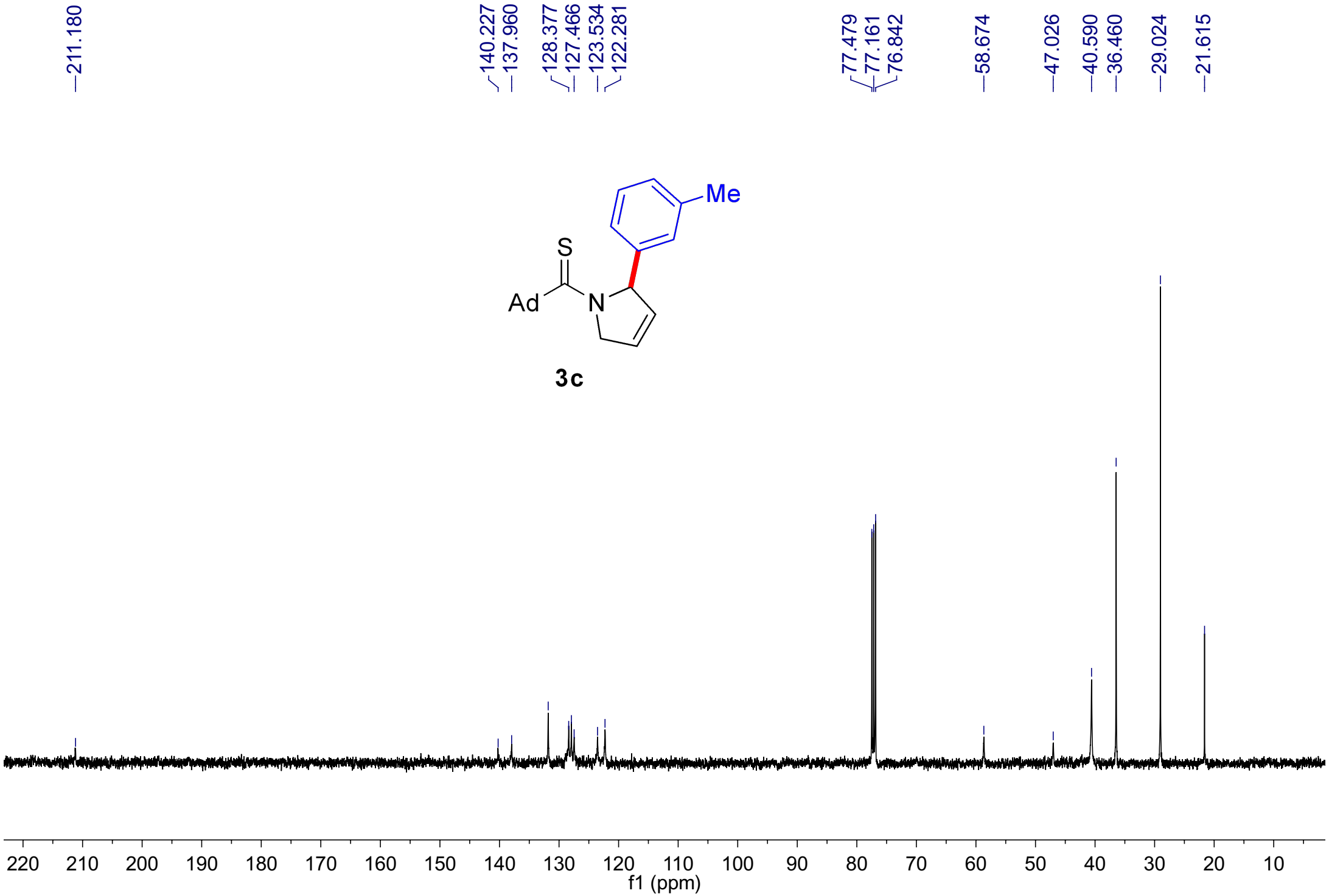
**3a**

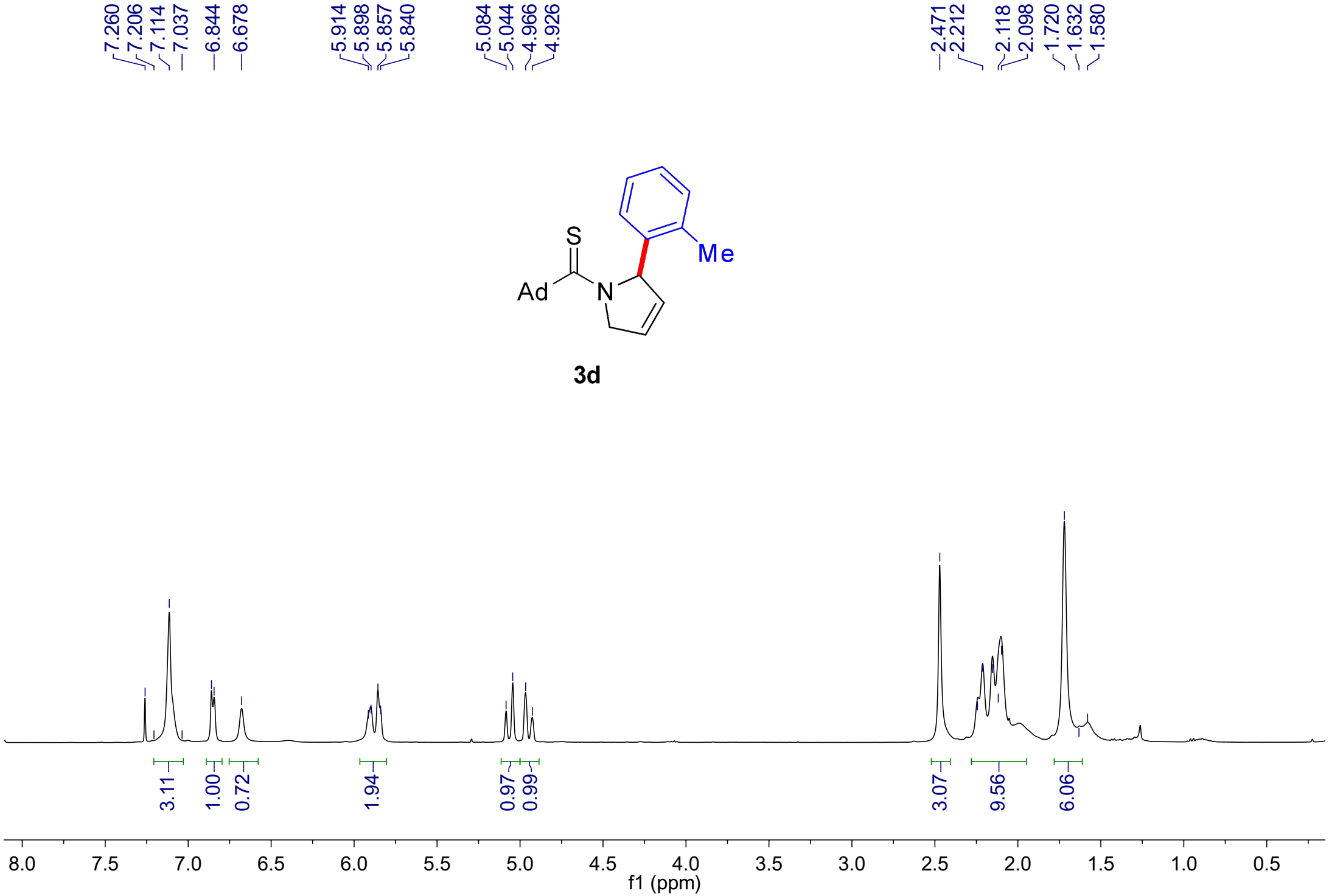

211.149
140.243
131.525
126.969
126.621
122.410
77.479
77.161
76.841
58.610
46.917
40.480
36.350
28.908
S
Ad
N
3a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

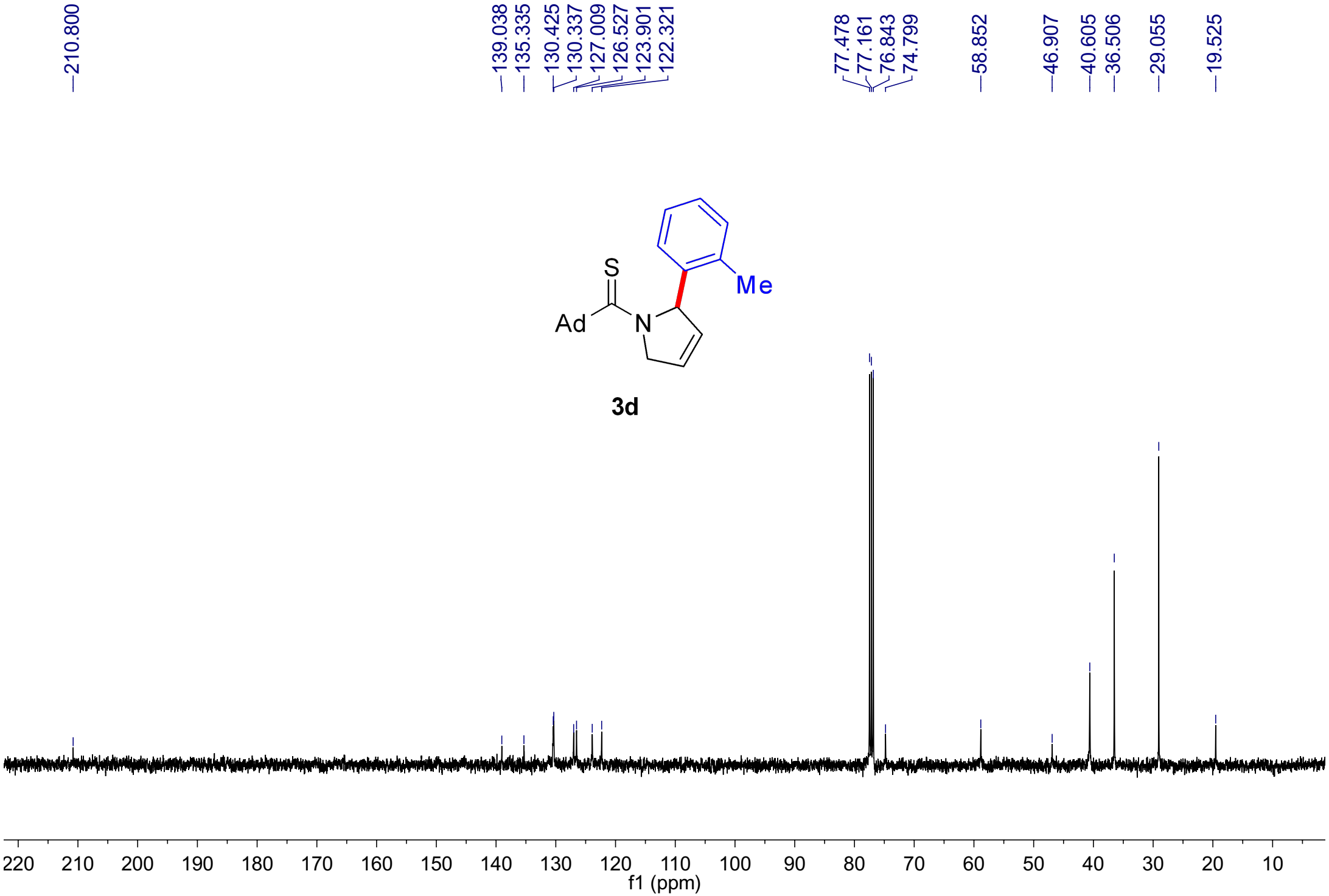

7.260
7.120
7.099
7.087
7.067
6.632
5.931
5.925
5.914
5.909
5.862
5.845
5.061
5.021
4.893
4.853
2.307
2.222
2.190
2.129
2.092
1.780
1.707
1.621
1.577
Me
S
Ad
N
3b
4.00
0.74
1.00
0.98
0.97
0.95
3.18
9.17
6.66
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

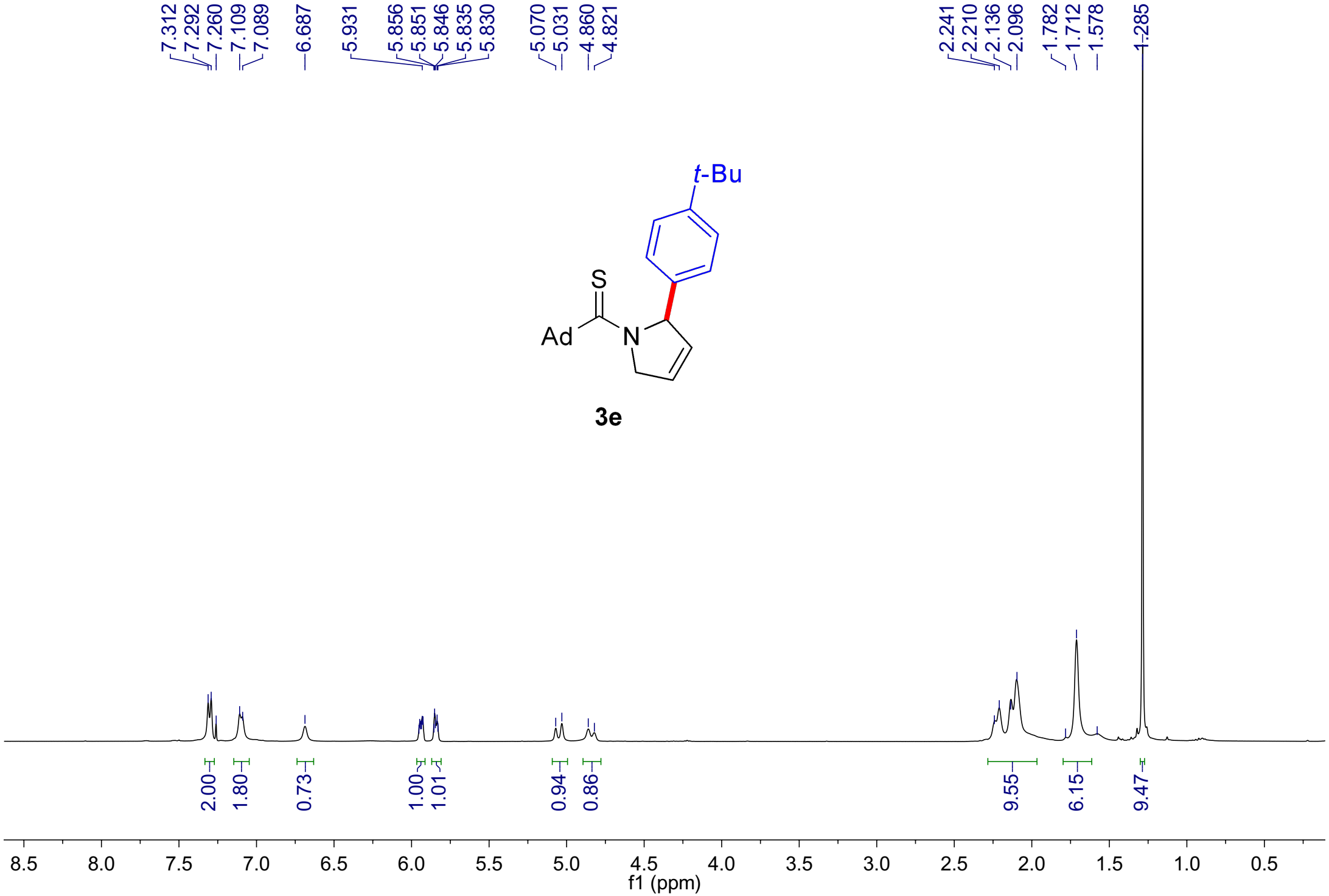

211.200
137.295
136.694
129.193
126.731
122.212
77.478
77.161
76.842
76.670
58.634
47.031
40.581
36.473
29.031
21.249
Me
S
Ad
N
3b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

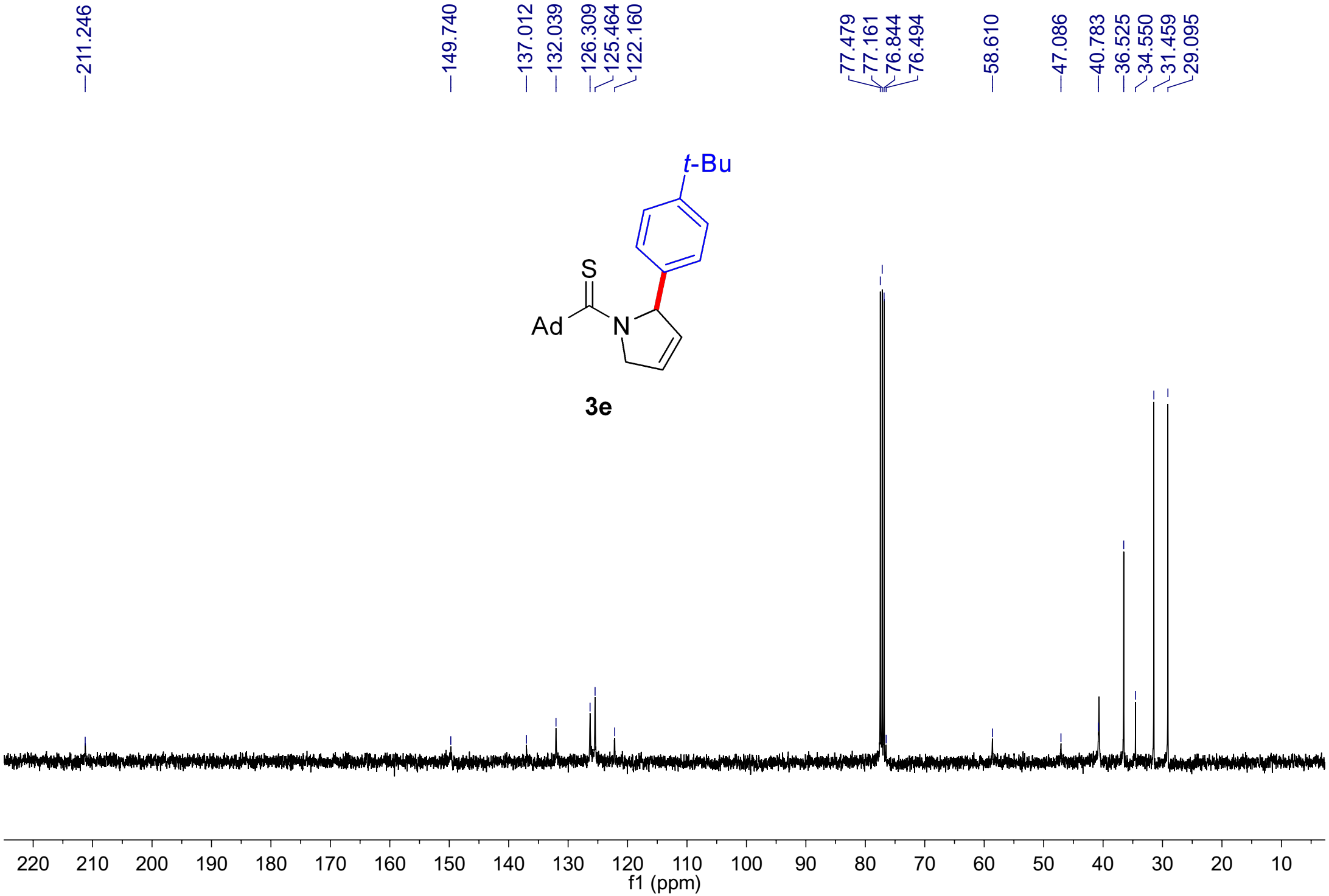

7.260
7.204
7.184
7.166
7.032
7.013
6.993
6.966
6.949
6.946
6.637
5.935
5.913
5.867
5.857
5.846
5.836
5.069
5.029
4.903
4.863
2.328
2.236
2.205
2.142
2.104
2.102
1.716
1.572
Me
S
Ad
N
3c
1.02
3.00
0.71
1.02
1.01
1.00
0.96
3.15
9.63
6.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

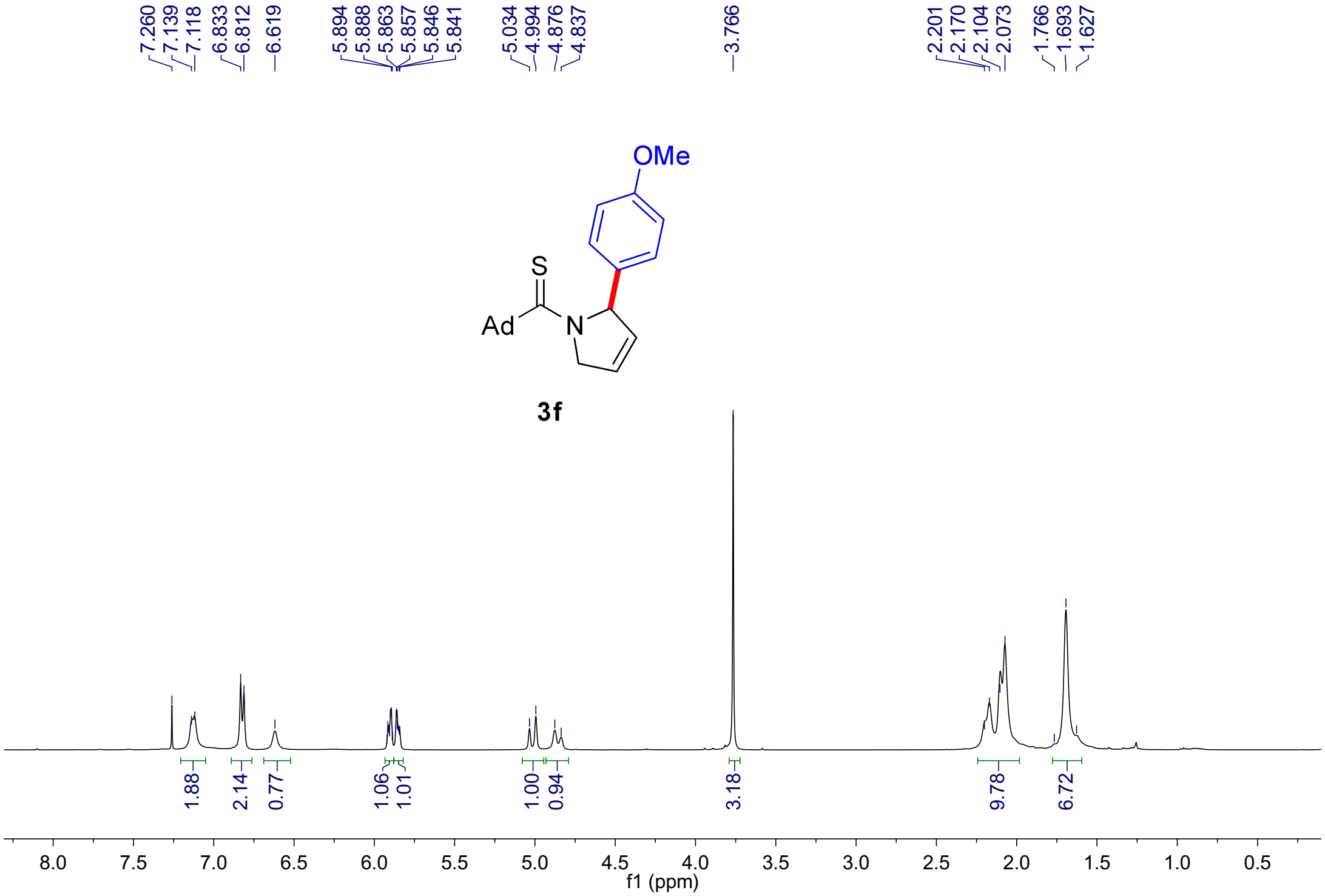

211.180
140.227
137.960
128.377
127.466
123.534
122.281
77.479
77.161
76.842
58.674
47.026
40.590
36.460
29.024
21.615
Me
S
Ad
N
3c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.260
7.206
7.114
7.037
6.844
6.678
5.914
5.898
5.857
5.840
5.084
5.044
4.966
4.926
2.471
2.212
2.118
2.098
1.720
1.632
1.580
S
Ad
N
Me
3d
3.11
1.00
0.72
1.94
0.97
0.99
3.07
9.56
6.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

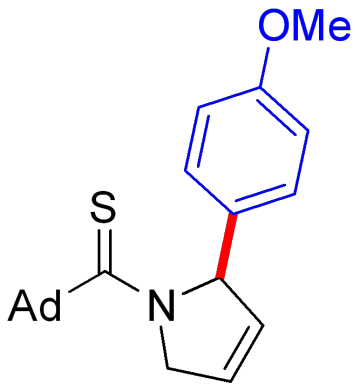

210.800
139.038
135.335
130.425
130.337
127.009
126.527
123.901
122.321
77.478
77.161
76.843
74.799
58.852
46.907
40.605
36.506
29.055
19.525
S
Ad
N
Me
3d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.312
7.292
7.260
7.109
7.089
6.687
5.931
5.856
5.851
5.846
5.835
5.830
5.070
5.031
4.860
4.821
2.241
2.210
2.136
2.096
1.782
1.712
1.578
1.285
t-Bu
S
Ad
N
3e
2.00
1.80
0.73
1.00
1.01
0.94
0.86
9.55
6.15
9.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

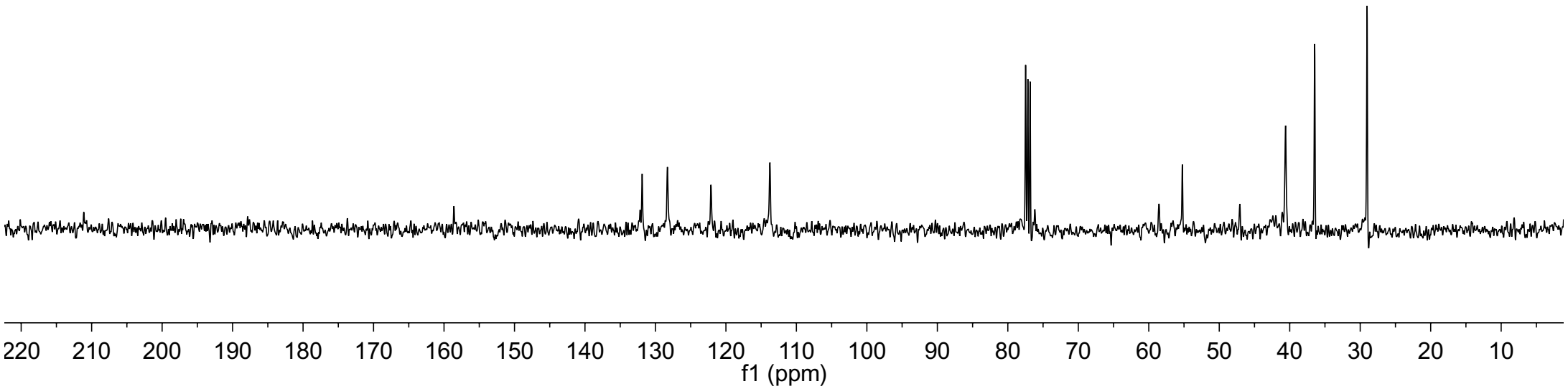

211.246
149.740
137.012
132.039
126.309
125.464
122.160
77.479
77.161
76.844
76.494
58.610
47.086
40.783
36.525
34.550
31.459
29.095
t-Bu
S
Ad
N
3e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

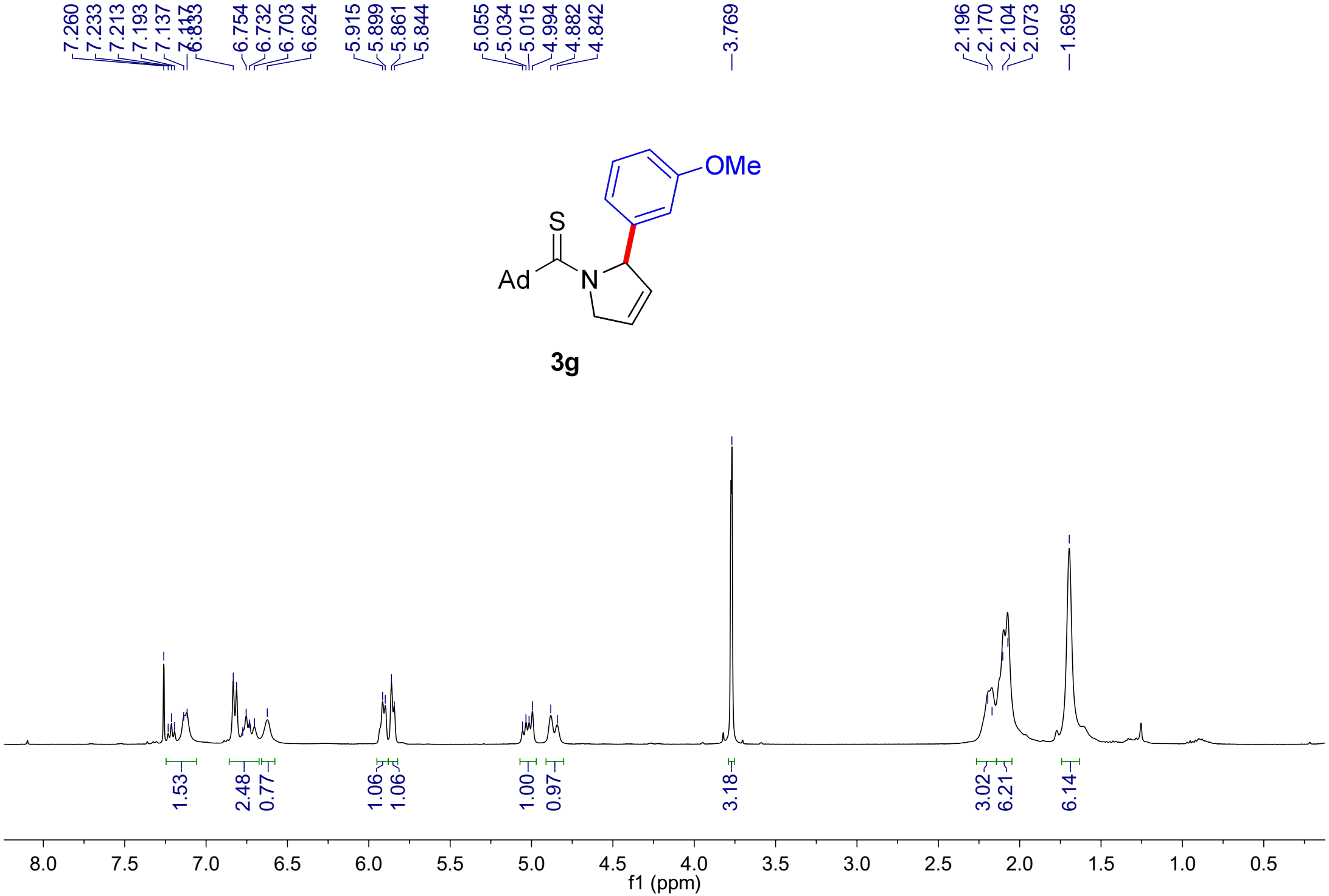

7.260
7.139
7.118
6.833
6.812
6.619
5.894
5.888
5.863
5.857
5.846
5.841
5.034
4.994
4.876
4.837
3.766
2.201
2.170
2.104
2.073
1.766
1.693
1.627
OMe
S
Ad
N
3f
1.88
2.14
0.77
1.06
1.01
1.00
0.94
3.18
9.78
6.72
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

211.110
158.577
132.181
131.885
128.300
122.125
113.747
77.477
77.160
76.843
76.160
58.489
55.235
47.029
40.590
36.457
29.019

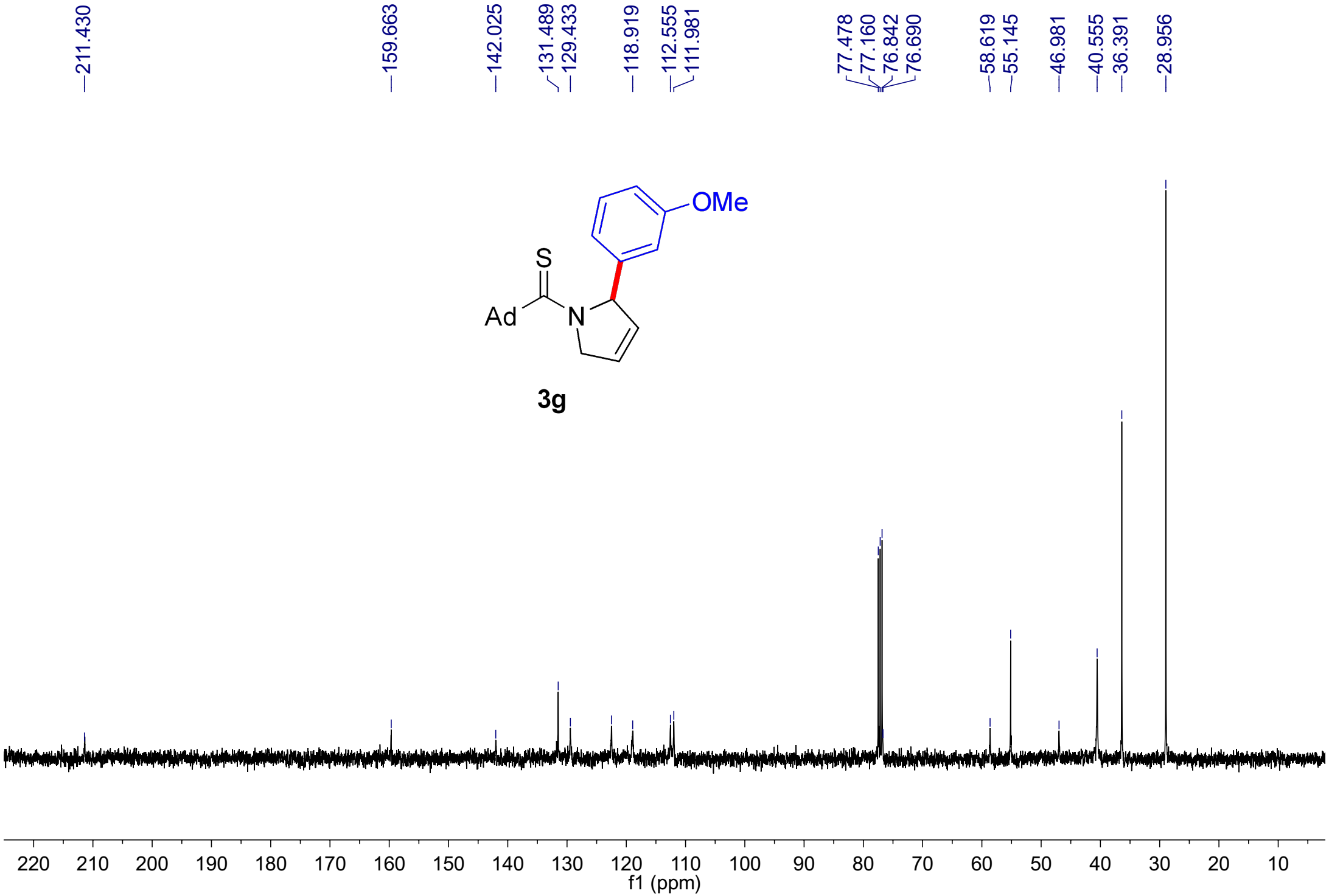


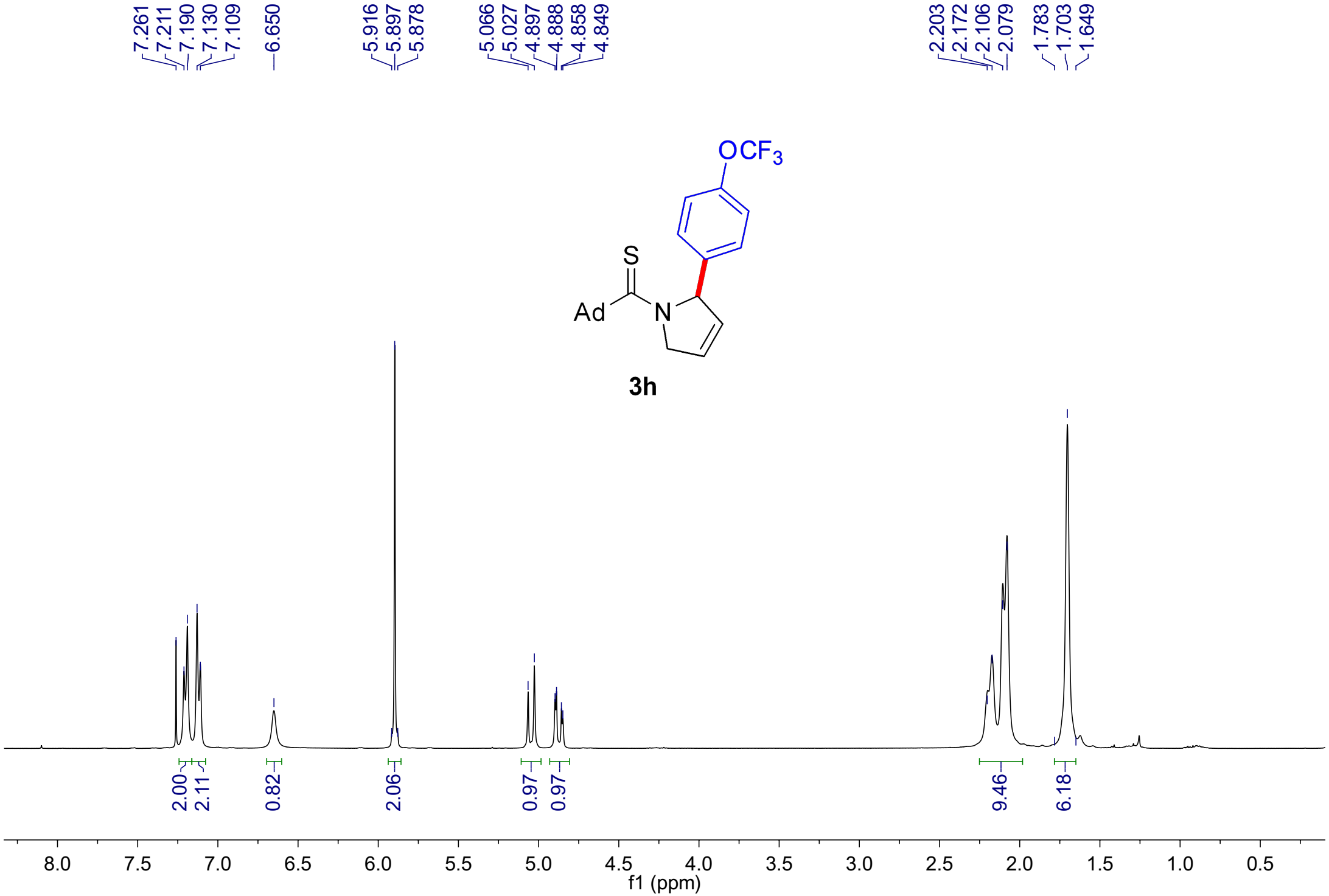

**3f**

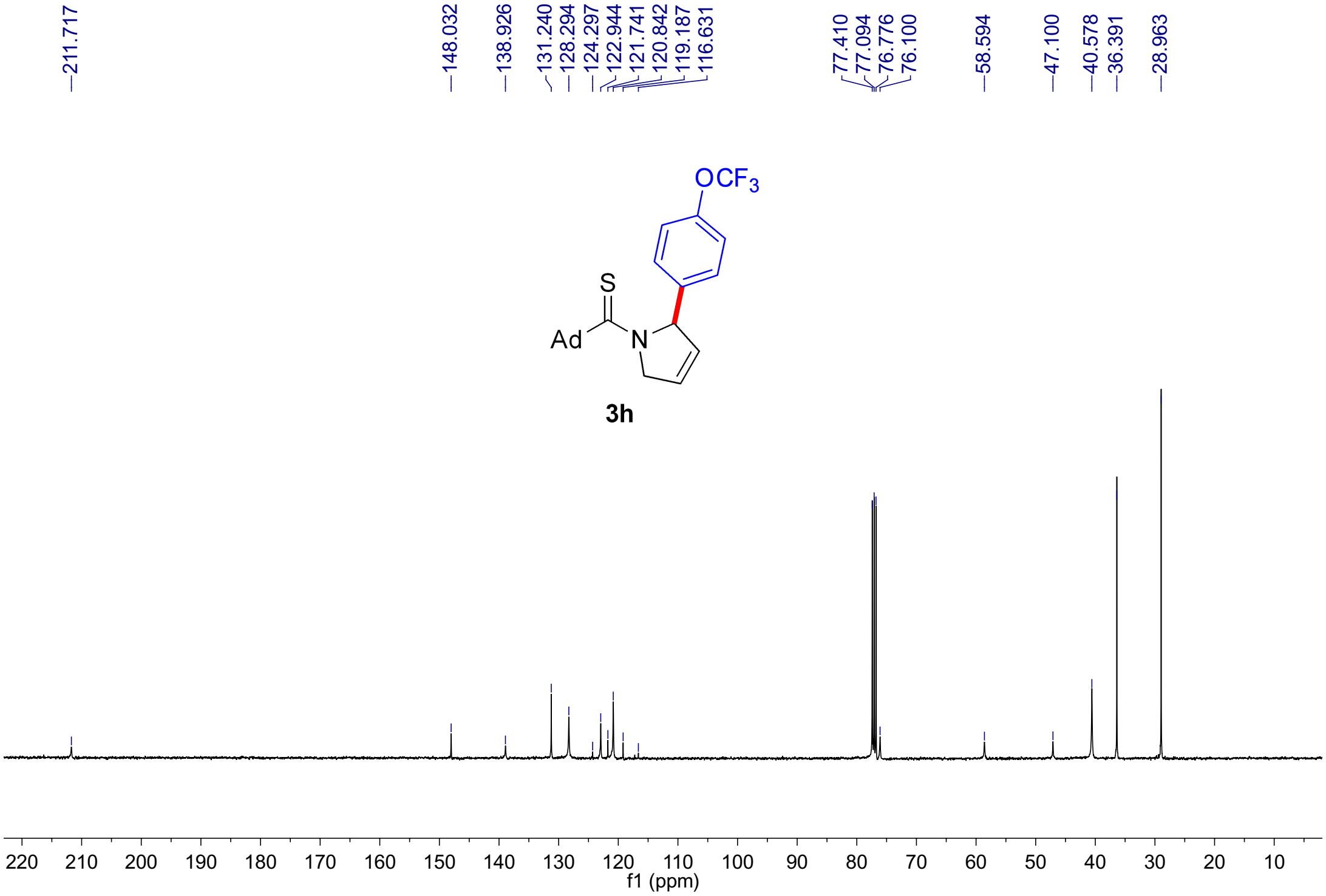


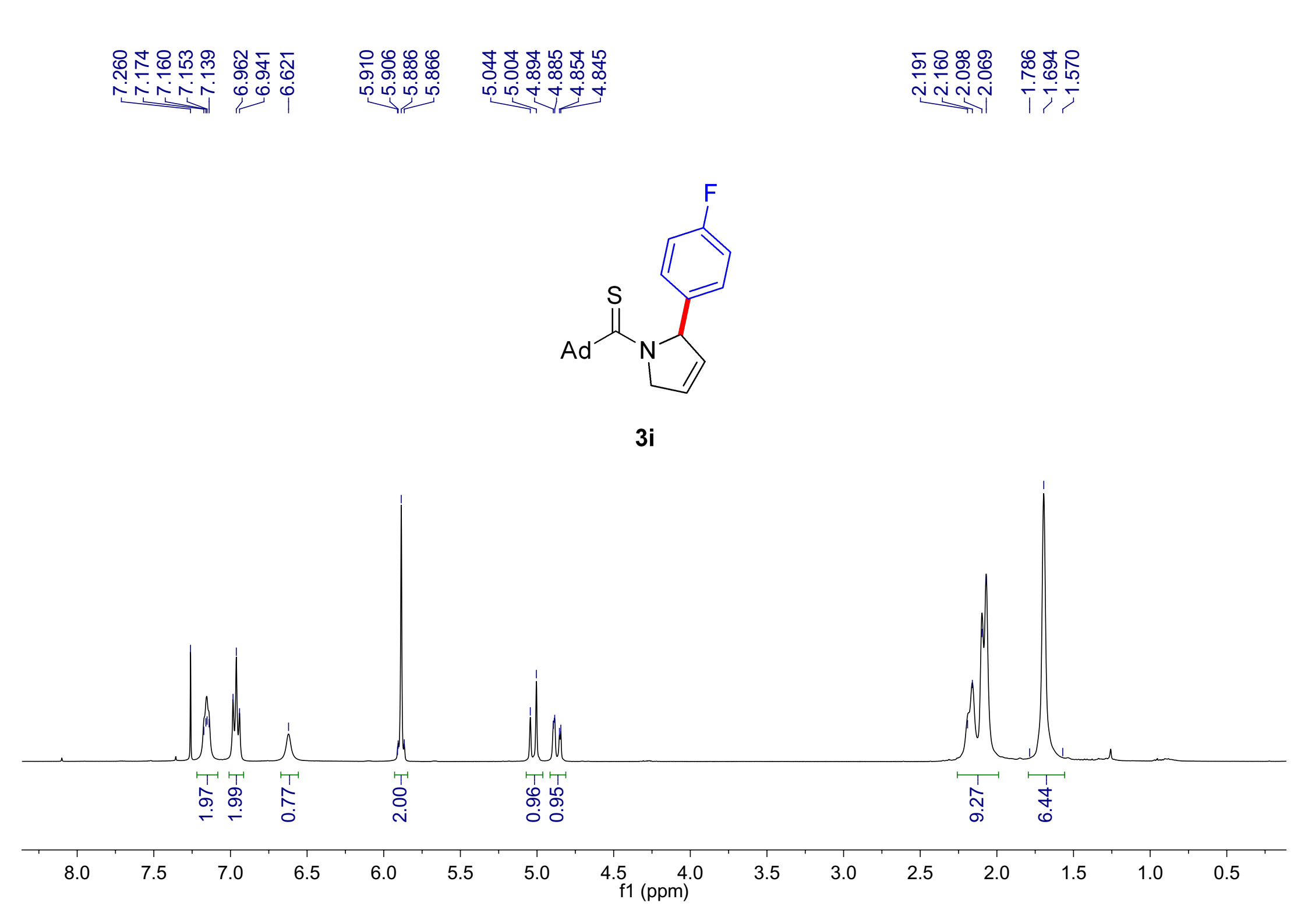

7.260
7.233
7.213
7.193
7.137
7.117
6.833
6.754
6.732
6.703
6.624
5.915
5.899
5.861
5.844
5.055
5.034
5.015
4.994
4.882
4.842
3.769
2.196
2.170
2.104
2.073
1.695
OMe
S
Ad
N
1.53
2.48
0.77
1.06
1.06
1.00
0.97
3.18
3.02
6.21
6.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

**3g**

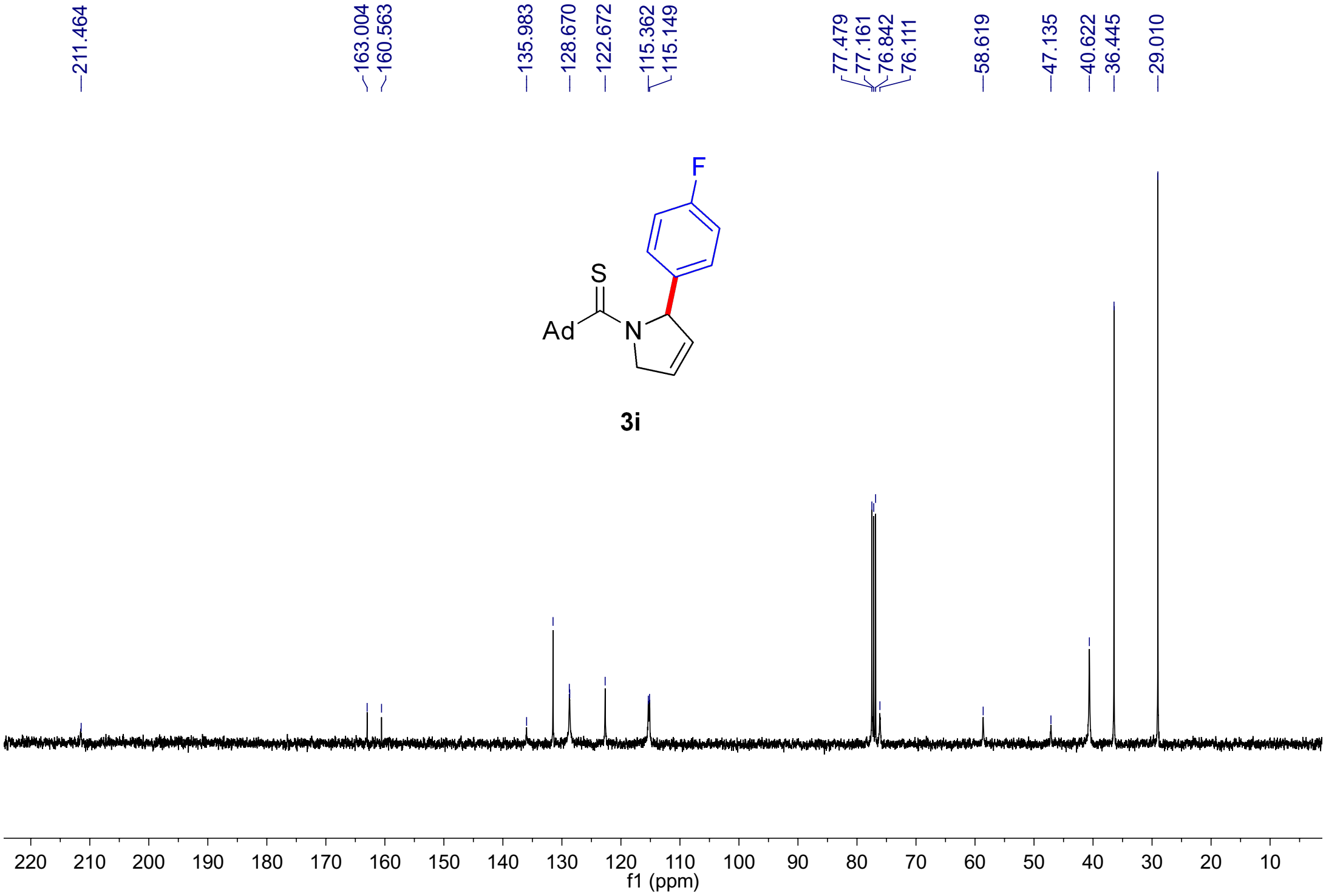

211.430
159.663
142.025
131.489
129.433
118.919
112.555
111.981
77.478
77.160
76.842
76.690
58.619
55.145
46.981
40.555
36.391
28.956
OMe
S
Ad
N
3g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

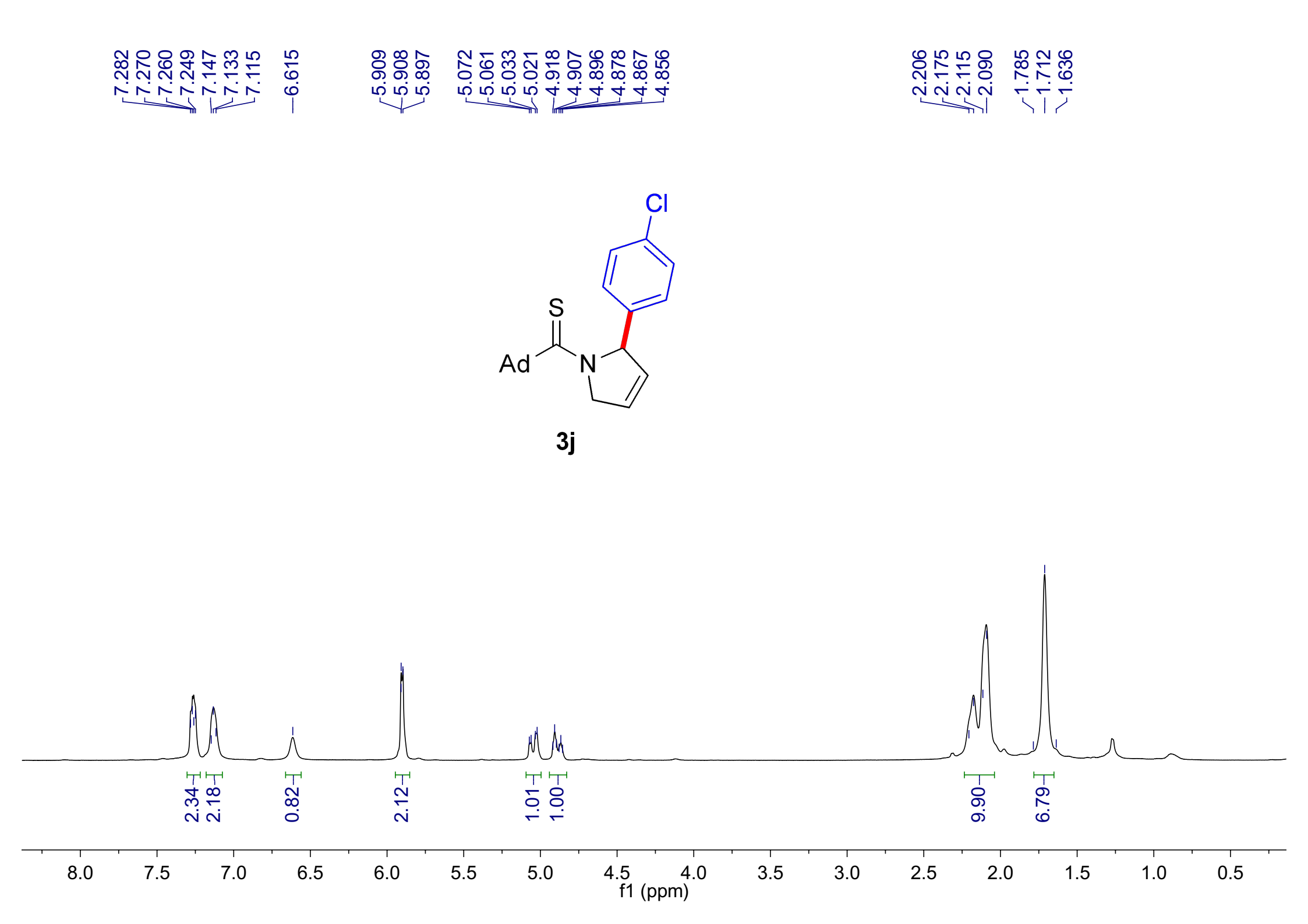

7.261
7.211
7.190
7.130
7.109
6.650
5.916
5.897
5.878
5.066
5.027
4.897
4.888
4.858
4.849
2.203
2.172
2.106
2.079
1.783
1.703
1.649
OCF3
S
Ad
N
3h
2.00
2.11
0.82
2.06
0.97
0.97
9.46
6.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


211.717
148.032
138.926
131.240
128.294
124.297
122.944
121.741
120.842
119.187
116.631
77.410
77.094
76.776
76.100
58.594
47.100
40.578
36.391
28.963
OCF3
S
Ad
N
3h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

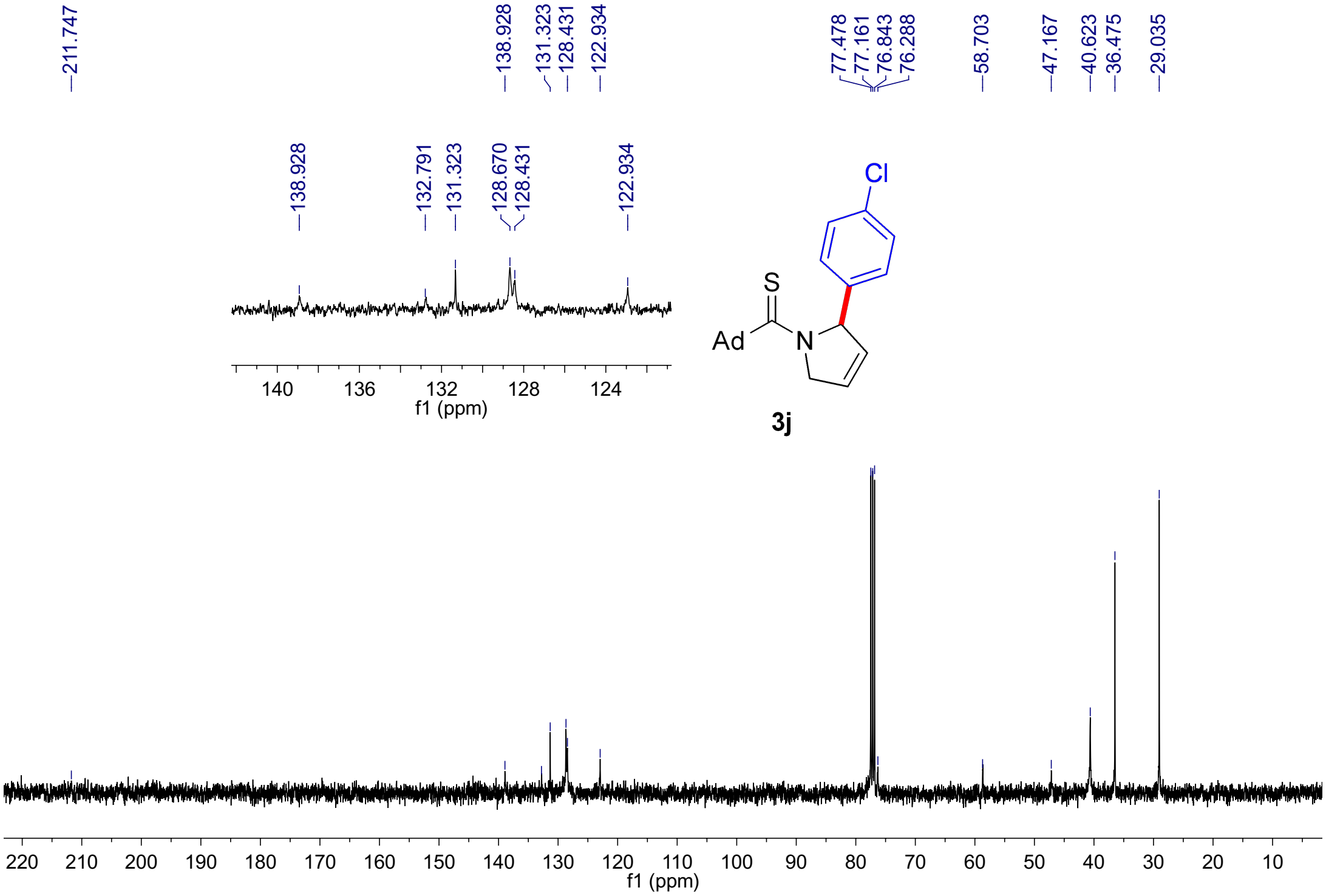

7.260
7.174
7.160
7.153
7.139
6.962
6.941
6.621
5.910
5.906
5.886
5.866
5.044
5.004
4.894
4.885
4.854
4.845
2.191
2.160
2.098
2.069
1.786
1.694
1.570
F
S
Ad
N
1.97
1.99
0.77
2.00
0.96
0.95
9.27
6.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

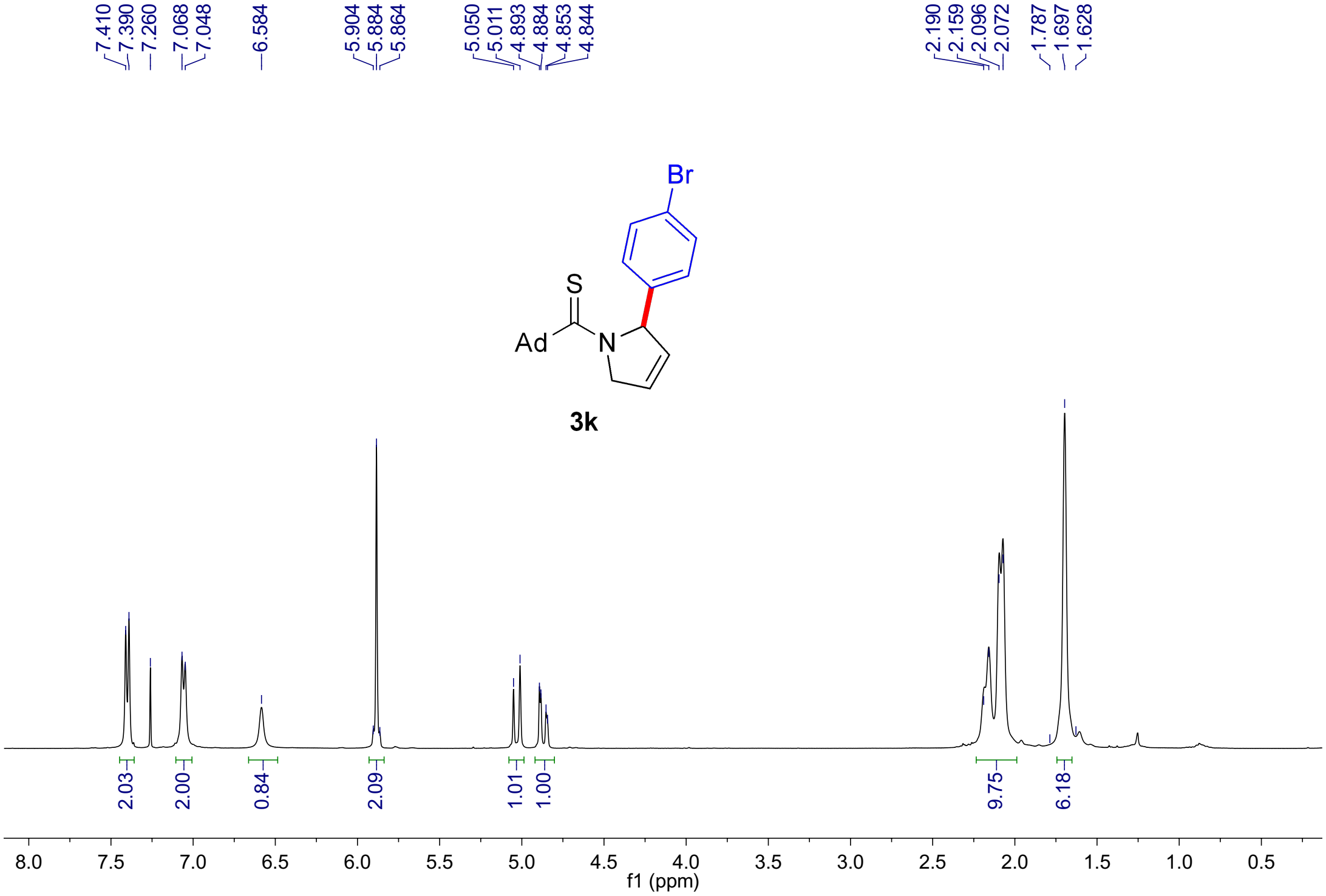
**3i**

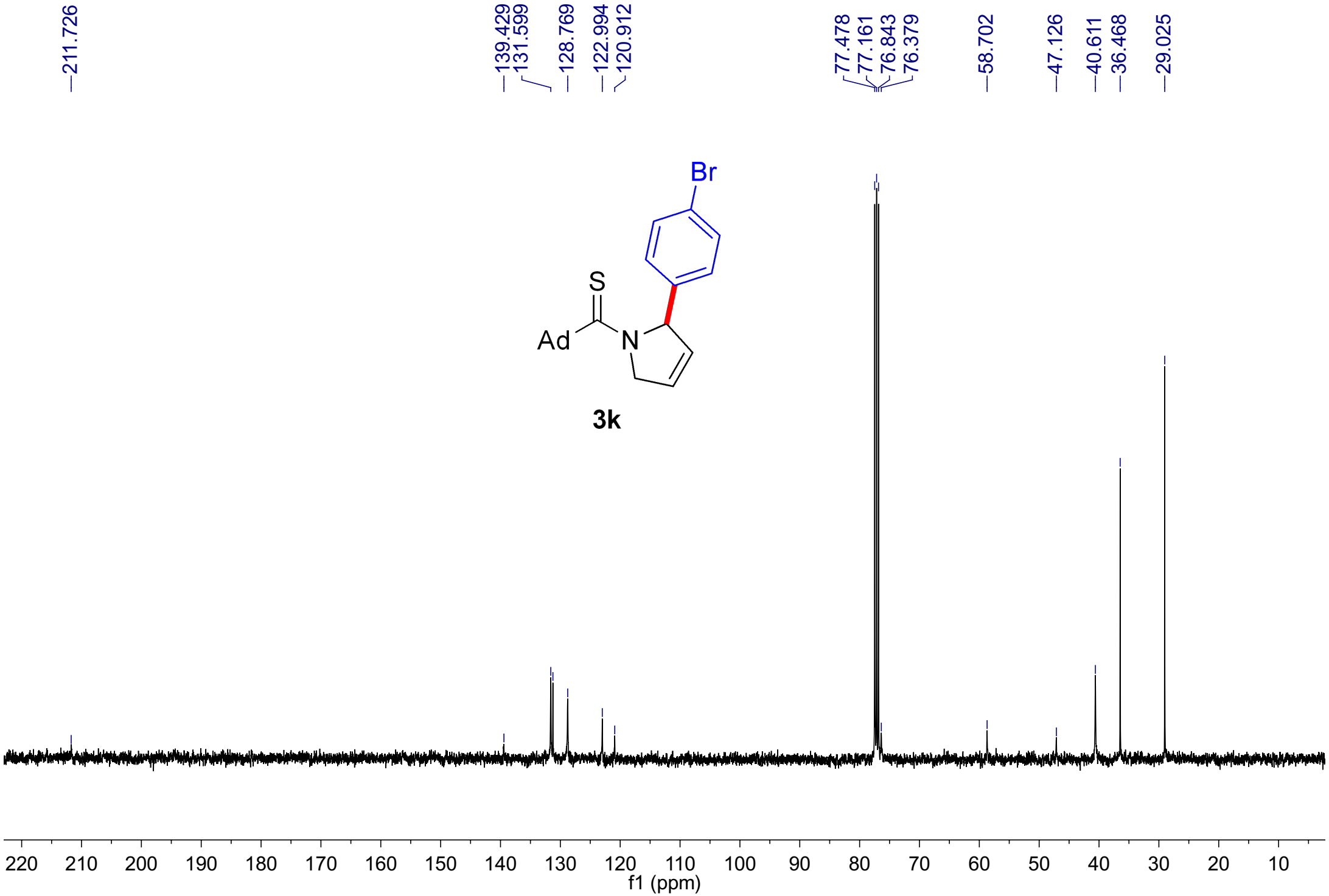

211.464
163.004
160.563
135.983
128.670
122.672
115.362
115.149
77.479
77.161
76.842
76.111
58.619
47.135
40.622
36.445
29.010
F
S
Ad
N
3i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

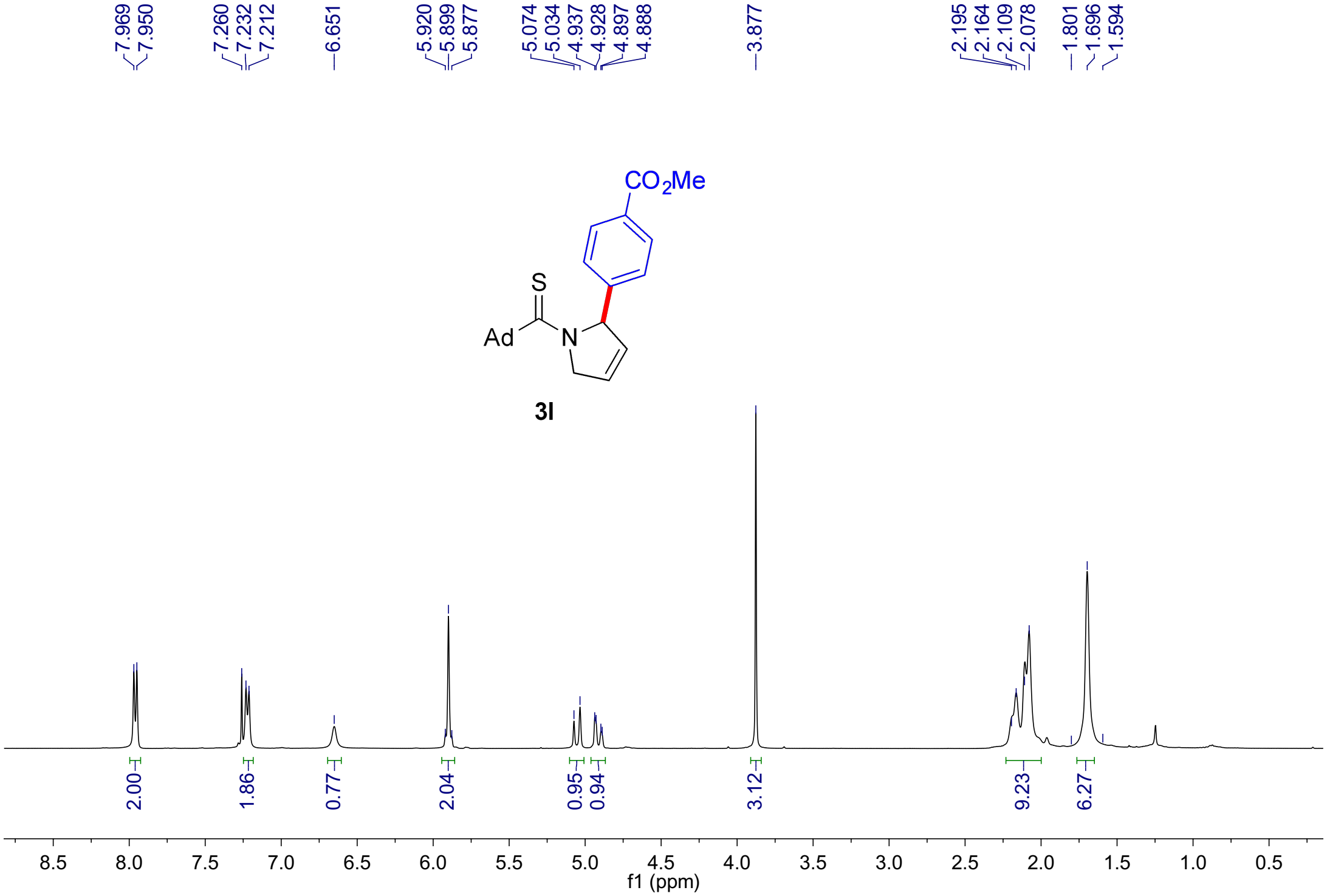

7.282
7.270
7.260
7.249
7.147
7.133
7.115
6.615
5.909
5.908
5.897
5.072
5.061
5.033
5.021
4.918
4.907
4.896
4.878
4.867
4.856
2.206
2.175
2.115
2.090
1.785
1.712
1.636
Cl
S
Ad
N
2.34
2.18
0.82
2.12
1.01
1.00
9.90
6.79
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

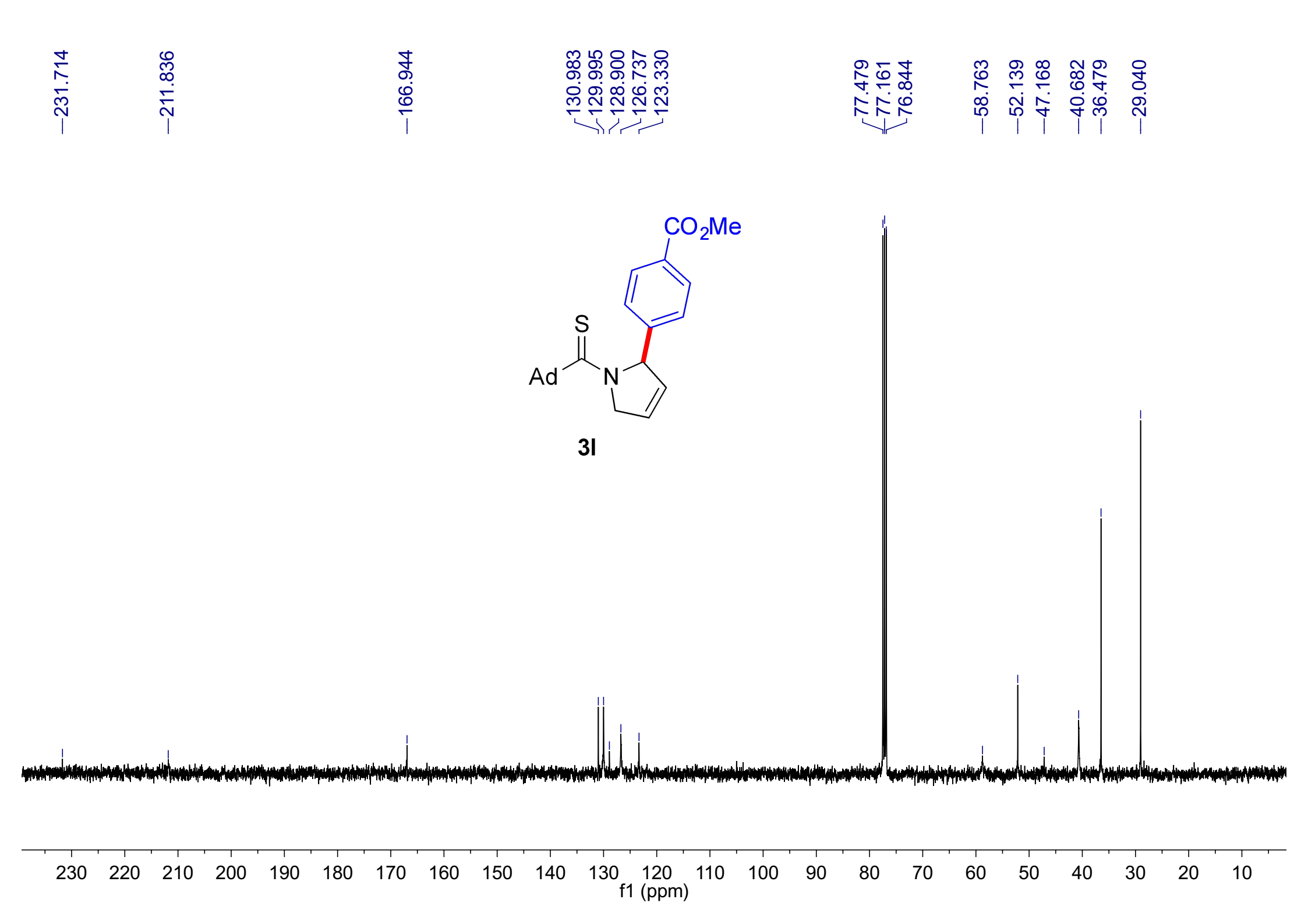
**3j**

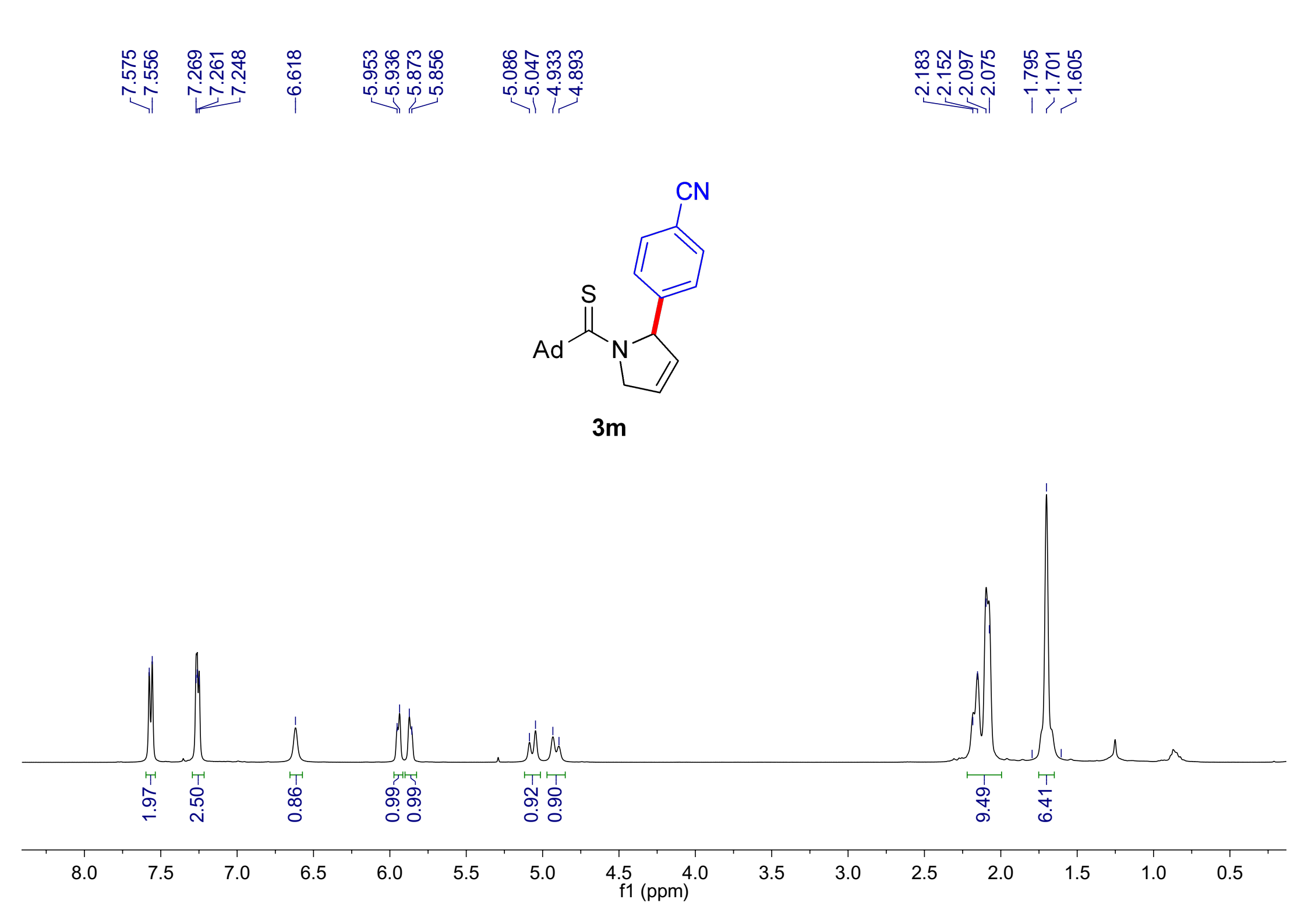

211.747
138.928
131.323
128.431
122.934
77.478
77.161
76.843
76.288
58.703
47.167
40.623
36.475
29.035
138.928
132.791
131.323
128.670
128.431
122.934
140
136
132
128
124
f1 (ppm)
Cl
S
Ad
N
3j
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

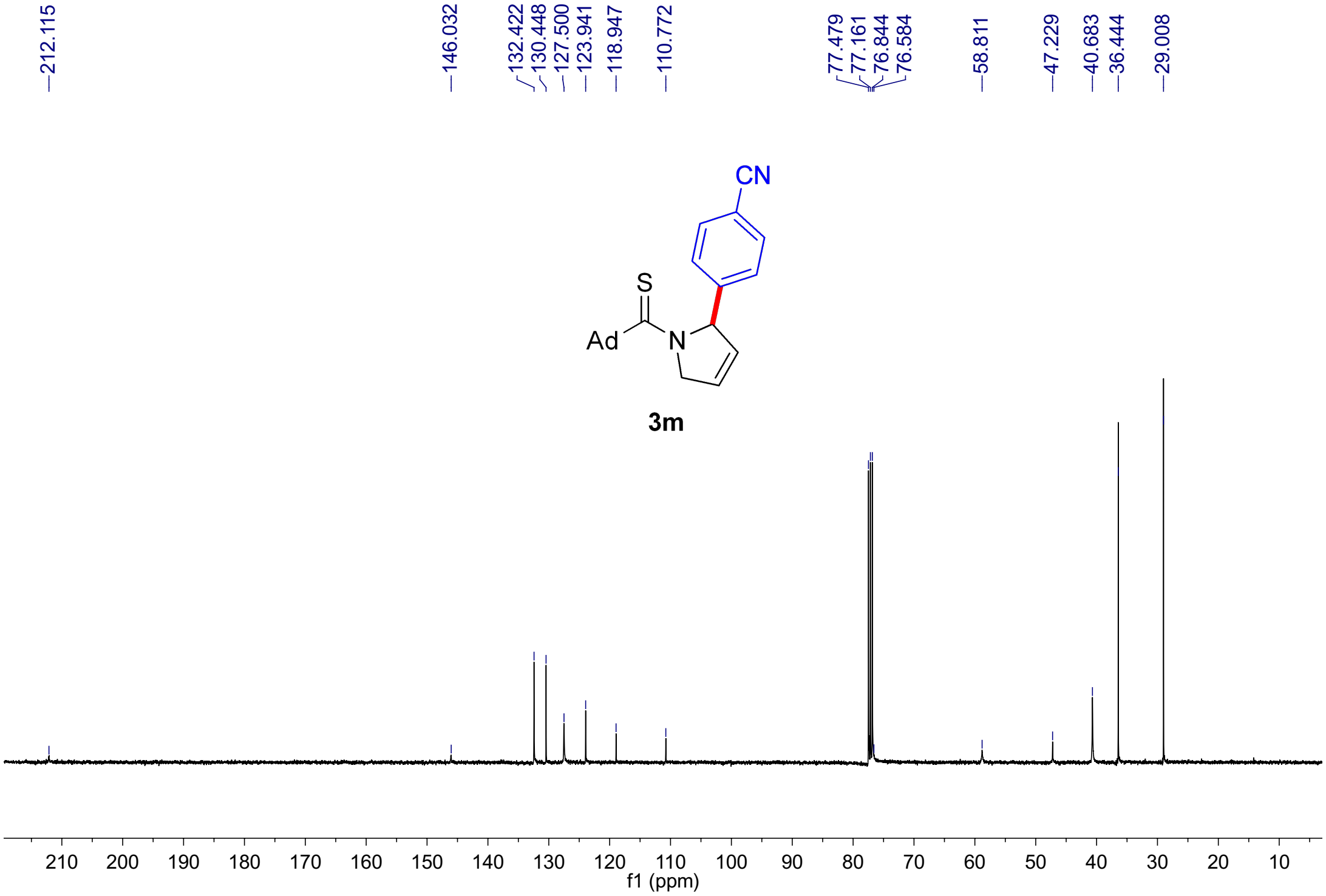

7.410
7.390
7.260
7.068
7.048
6.584
5.904
5.884
5.864
5.050
5.011
4.893
4.884
4.853
4.844
2.190
2.159
2.096
2.072
1.787
1.697
1.628
Br
S
Ad
N
3k
2.03
2.00
0.84
2.09
1.01
1.00
9.75
6.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

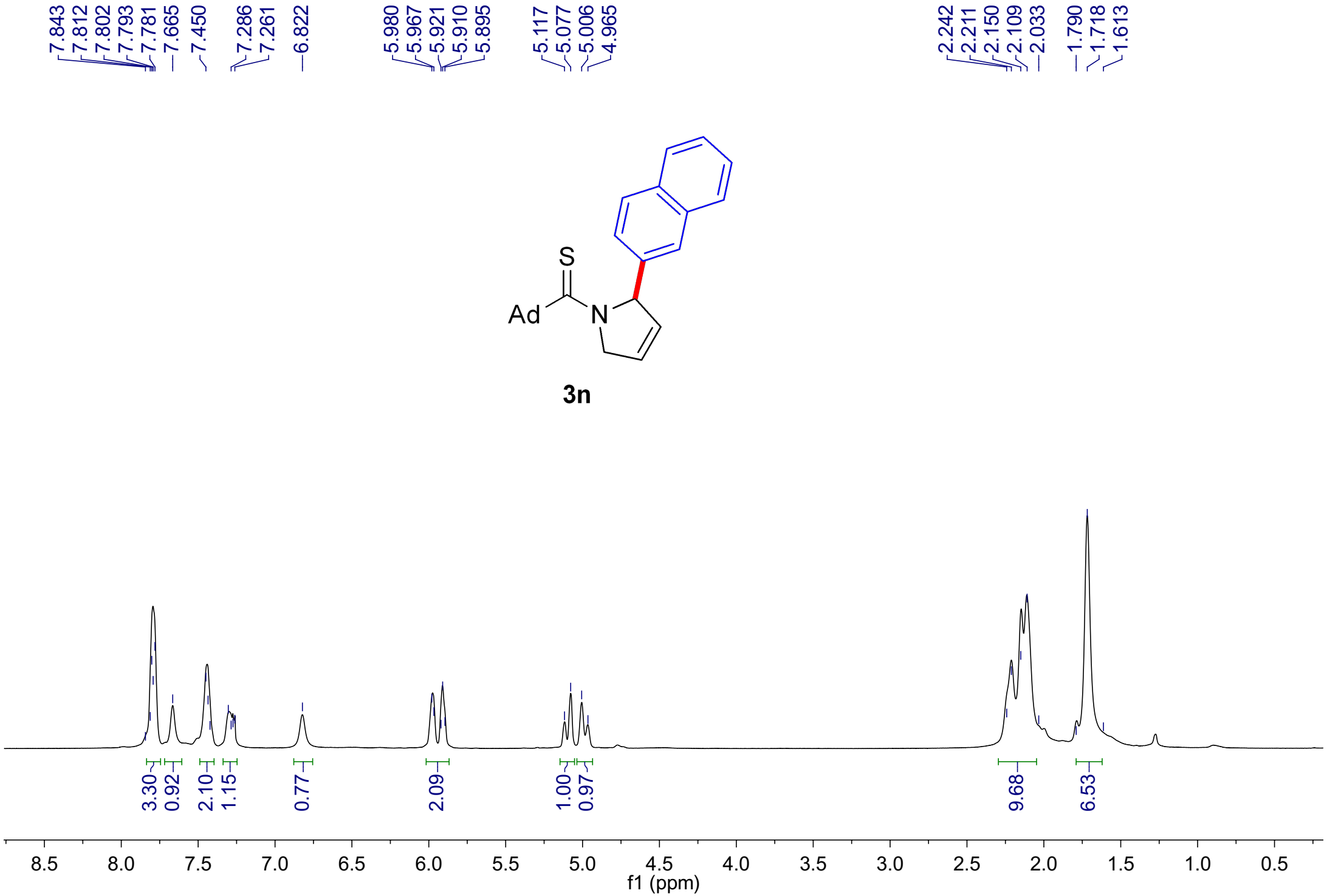

211.726
139.429
131.599
128.769
122.994
120.912
77.478
77.161
76.843
76.379
58.702
47.126
40.611
36.468
29.025
Br
S
Ad
N
3k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.969
7.950
7.260
7.232
7.212
6.651
5.920
5.899
5.877
5.074
5.034
4.937
4.928
4.897
4.888
3.877
2.195
2.164
2.109
2.078
1.801
1.696
1.594
CO2Me
S
Ad
N
3l
2.00
1.86
0.77
2.04
0.95
0.94
3.12
9.23
6.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

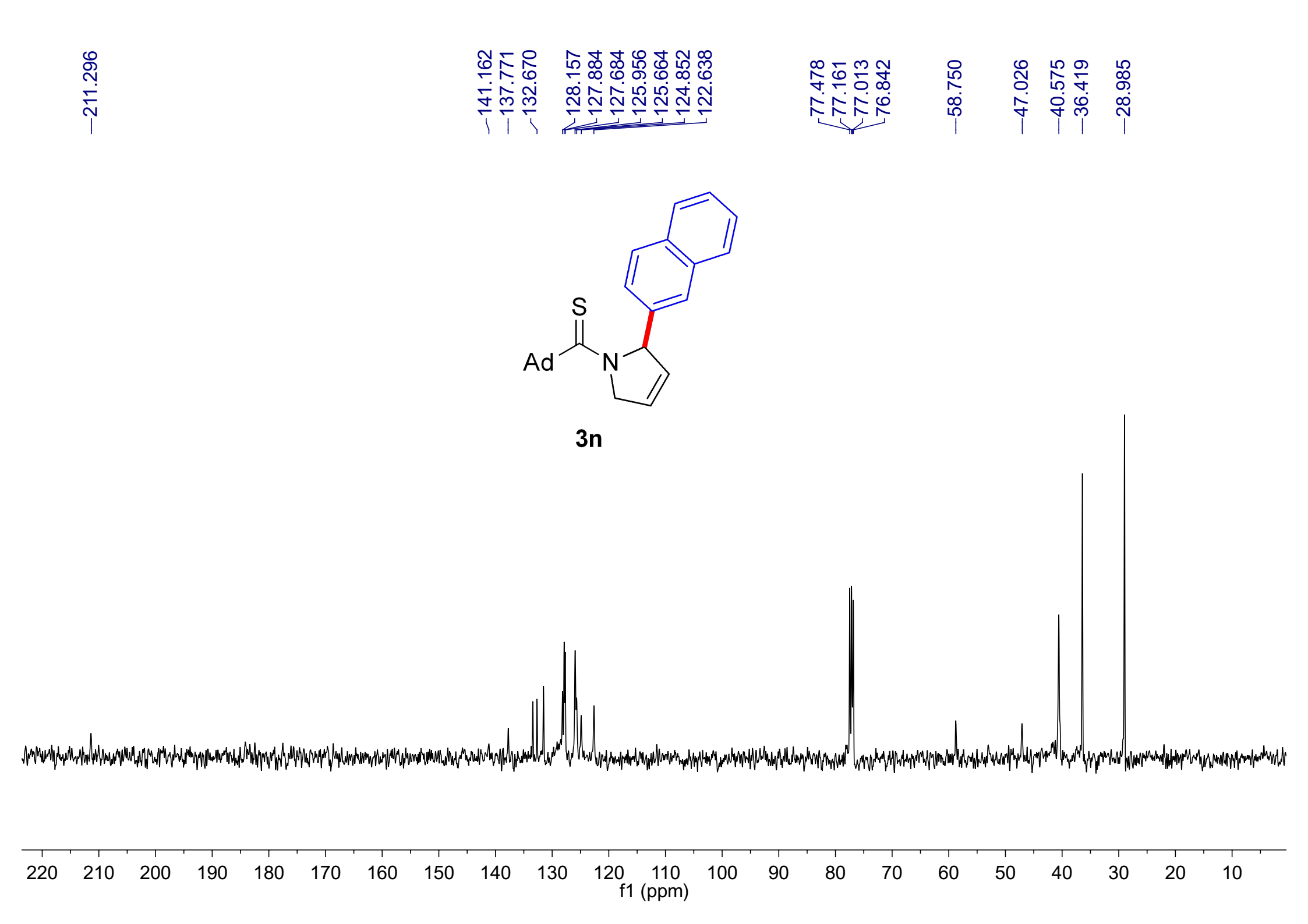

231.714
211.836
166.944
130.983
129.995
128.900
126.737
123.330
77.479
77.161
76.844
58.763
52.139
47.168
40.682
36.479
29.040
CO2Me
S
Ad
N
3l
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

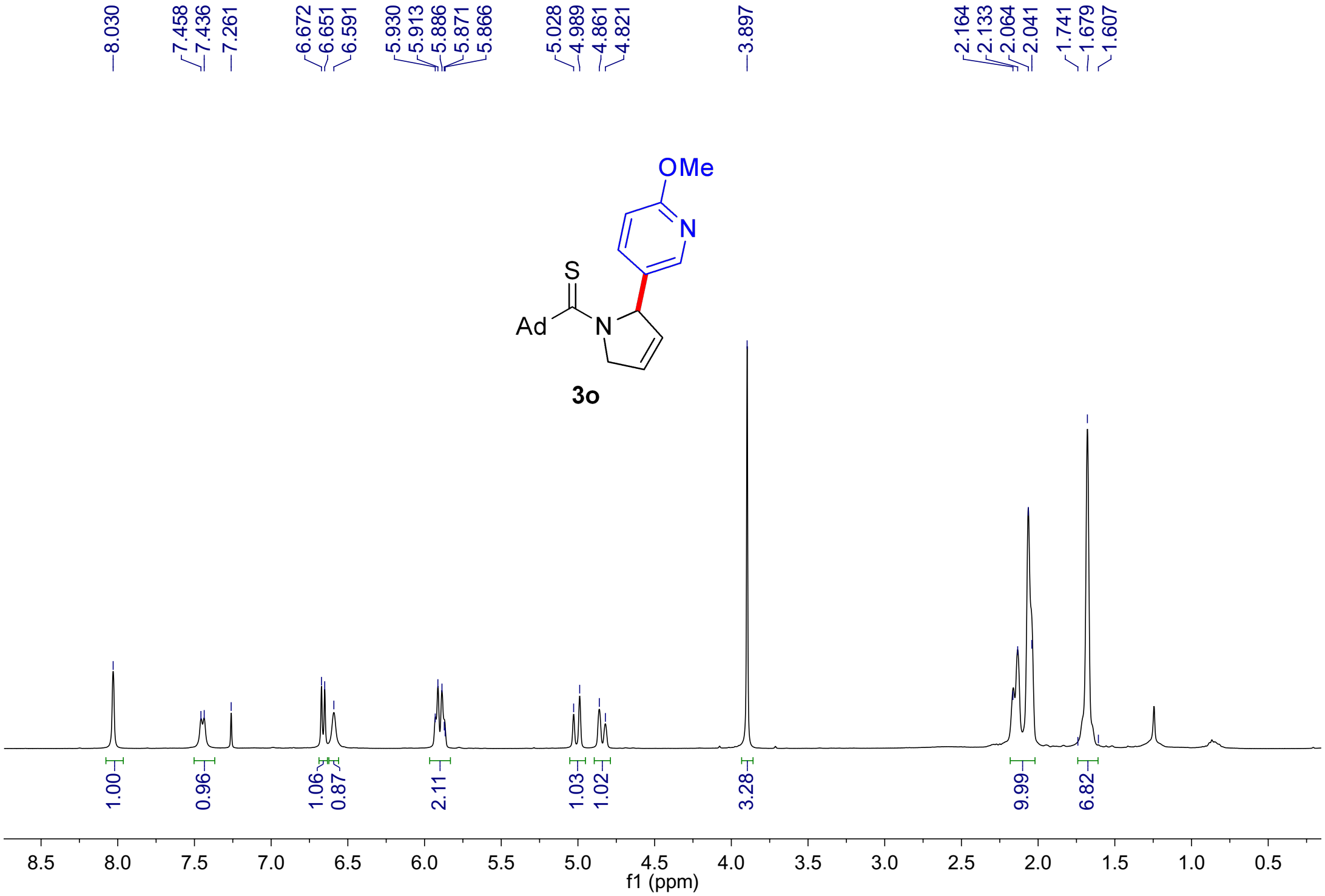

7.575
7.556
7.269
7.261
7.248
6.618
5.953
5.936
5.873
5.856
5.086
5.047
4.933
4.893
2.183
2.152
2.097
2.075
1.795
1.701
1.605
CN
S
Ad
N
3m
1.97
2.50
0.86
0.99
0.99
0.92
0.90
9.49
6.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

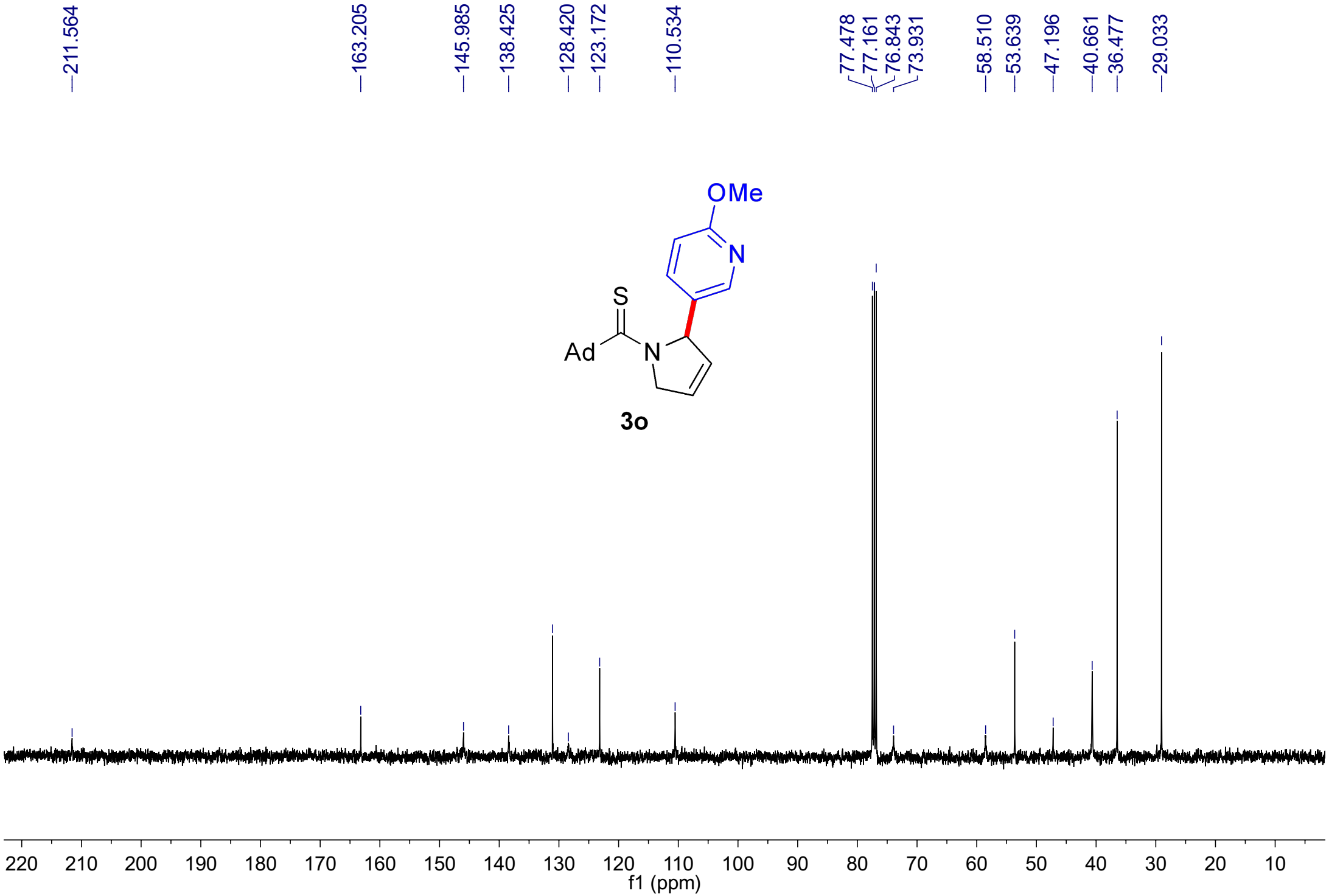

212.115
146.032
132.422
130.448
127.500
123.941
118.947
110.772
77.479
77.161
76.844
76.584
58.811
47.229
40.683
36.444
29.008
CN
S
Ad
N
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

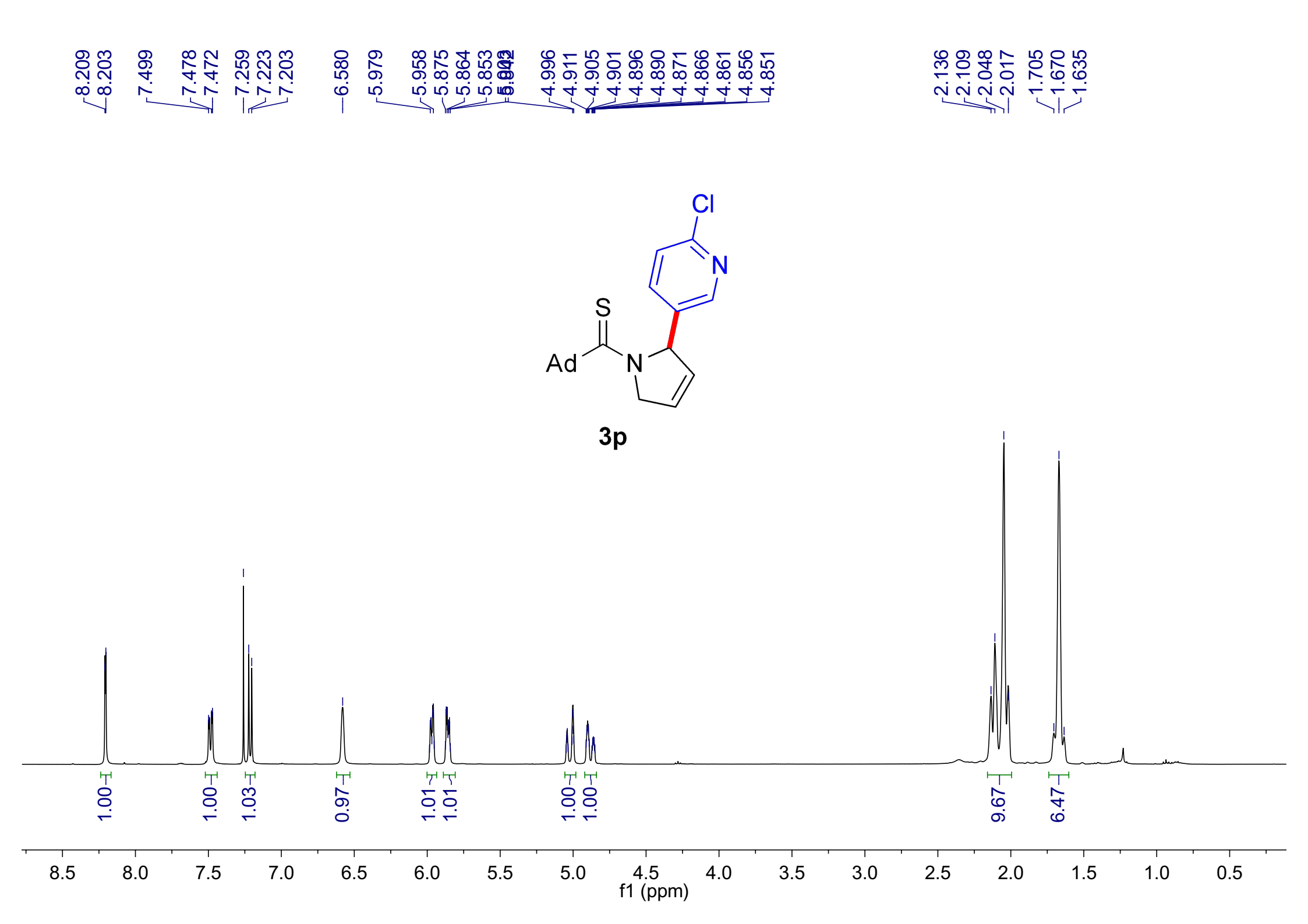

7.843
7.812
7.802
7.793
7.781
7.665
7.450
7.286
7.261
6.822
5.980
5.967
5.921
5.910
5.895
5.117
5.077
5.006
4.965
2.242
2.211
2.150
2.109
2.033
1.790
1.718
1.613
S
Ad
N
3.30
0.92
2.10
1.15
0.77
2.09
1.00
0.97
9.68
6.53
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

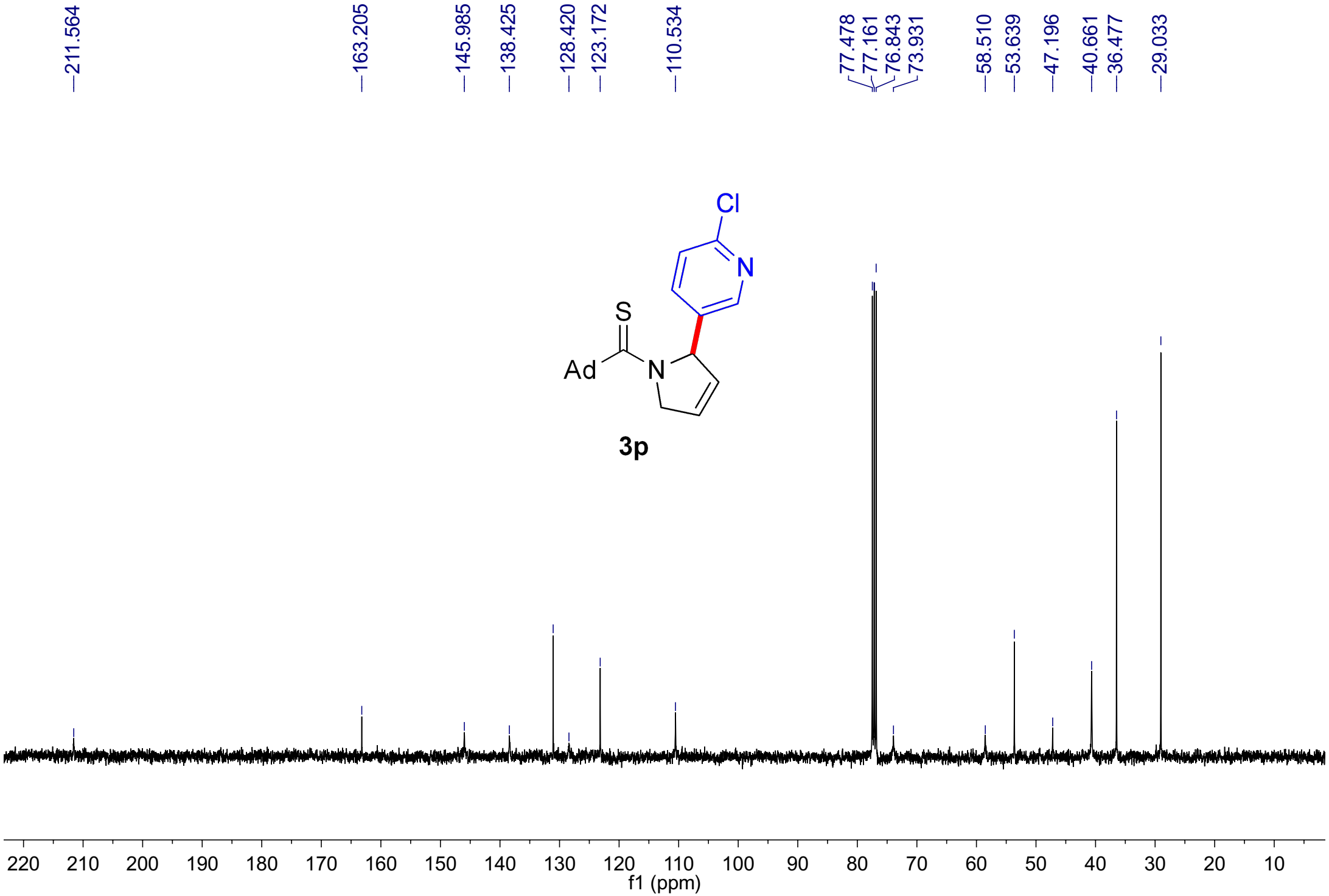
**3n**

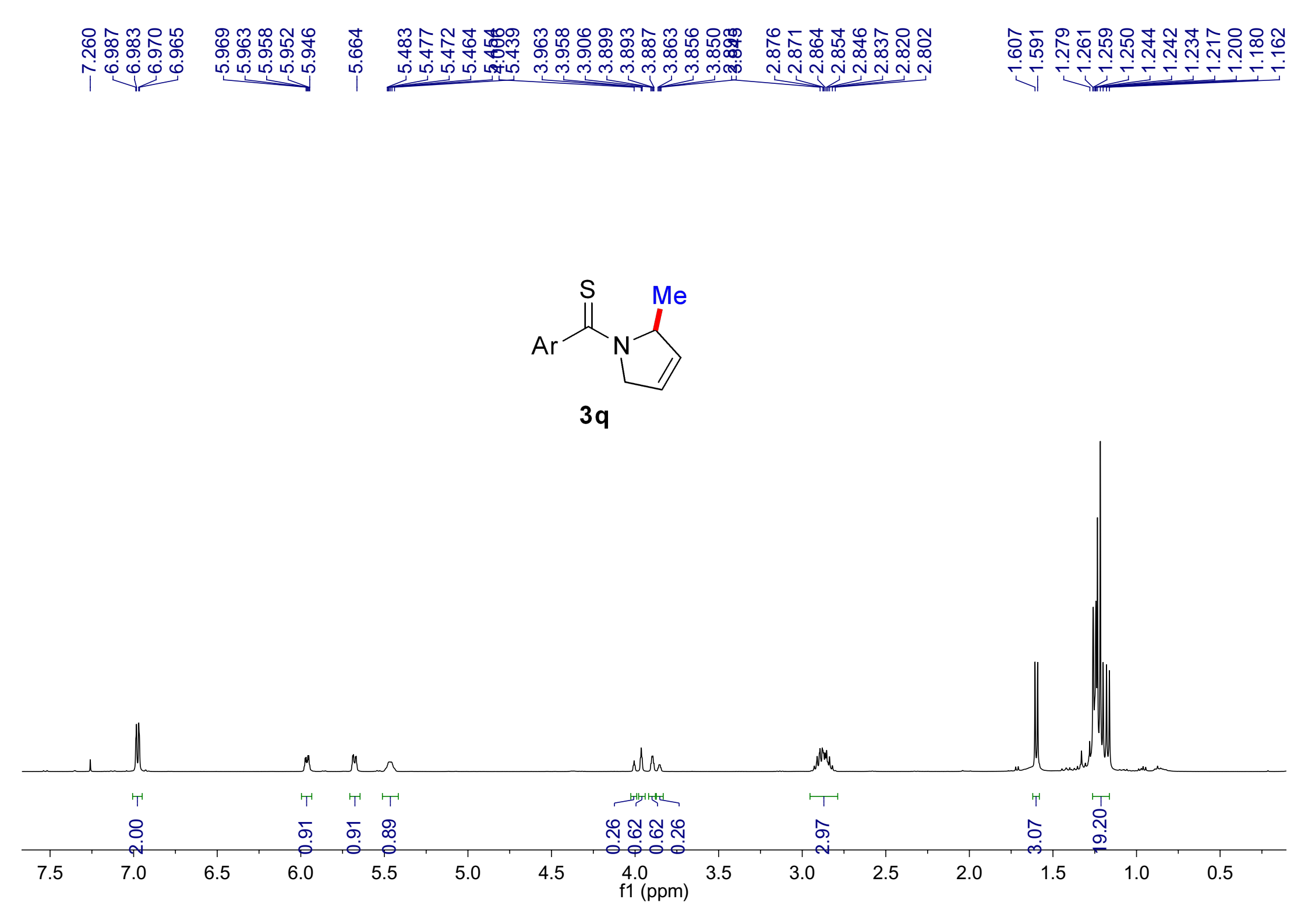

211.296
141.162
137.771
132.670
128.157
127.884
127.684
125.956
125.664
124.852
122.638
77.478
77.161
77.013
76.842
58.750
47.026
40.575
36.419
28.985
S
Ad
N
3n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

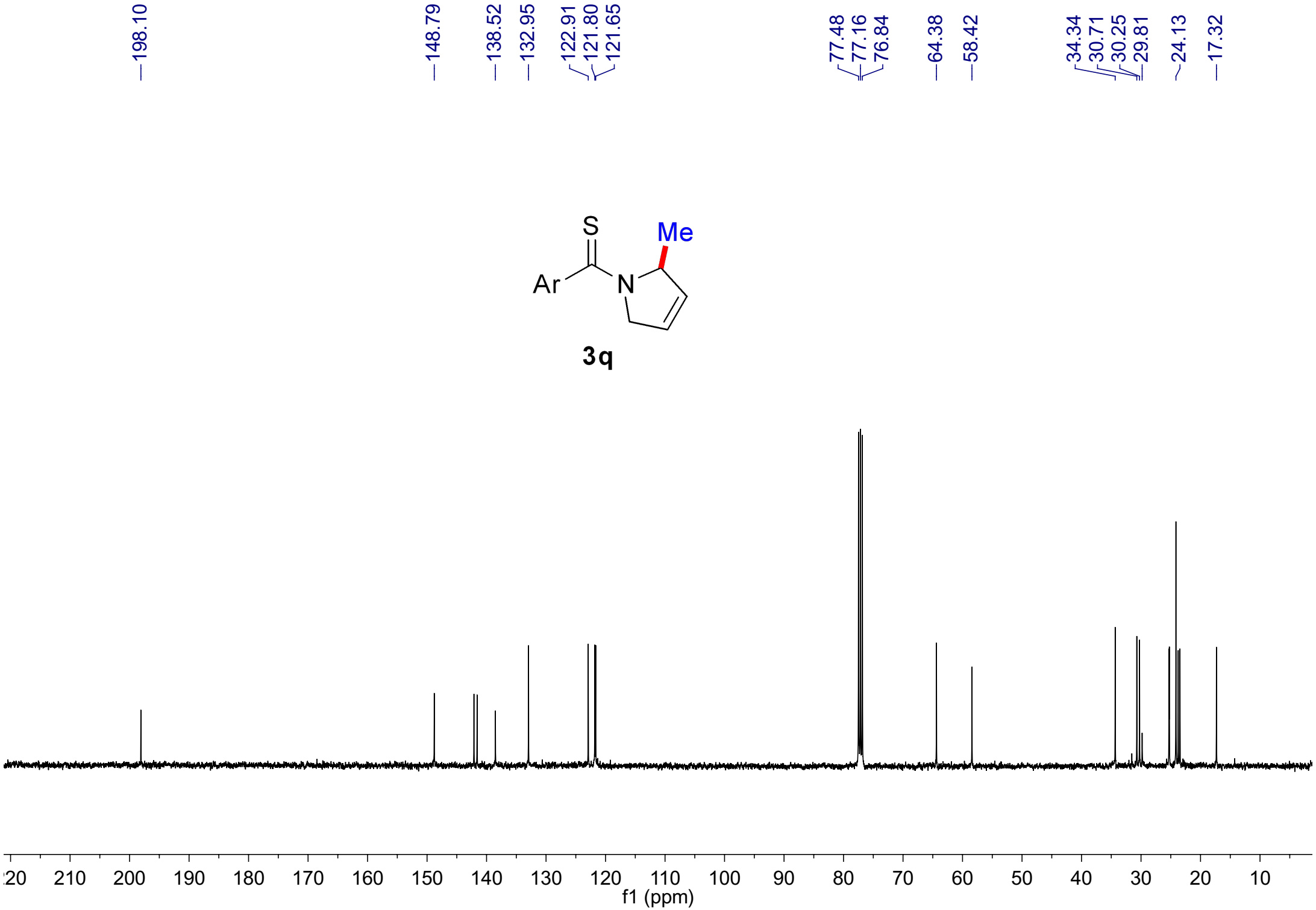

8.030
7.458
7.436
7.261
6.672
6.651
6.591
5.930
5.913
5.886
5.871
5.866
5.028
4.989
4.861
4.821
3.897
2.164
2.133
2.064
2.041
1.741
1.679
1.607
OMe
N
S
Ad
N
3o
1.00
0.96
1.06
0.87
2.11
1.03
1.02
3.28
9.99
6.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

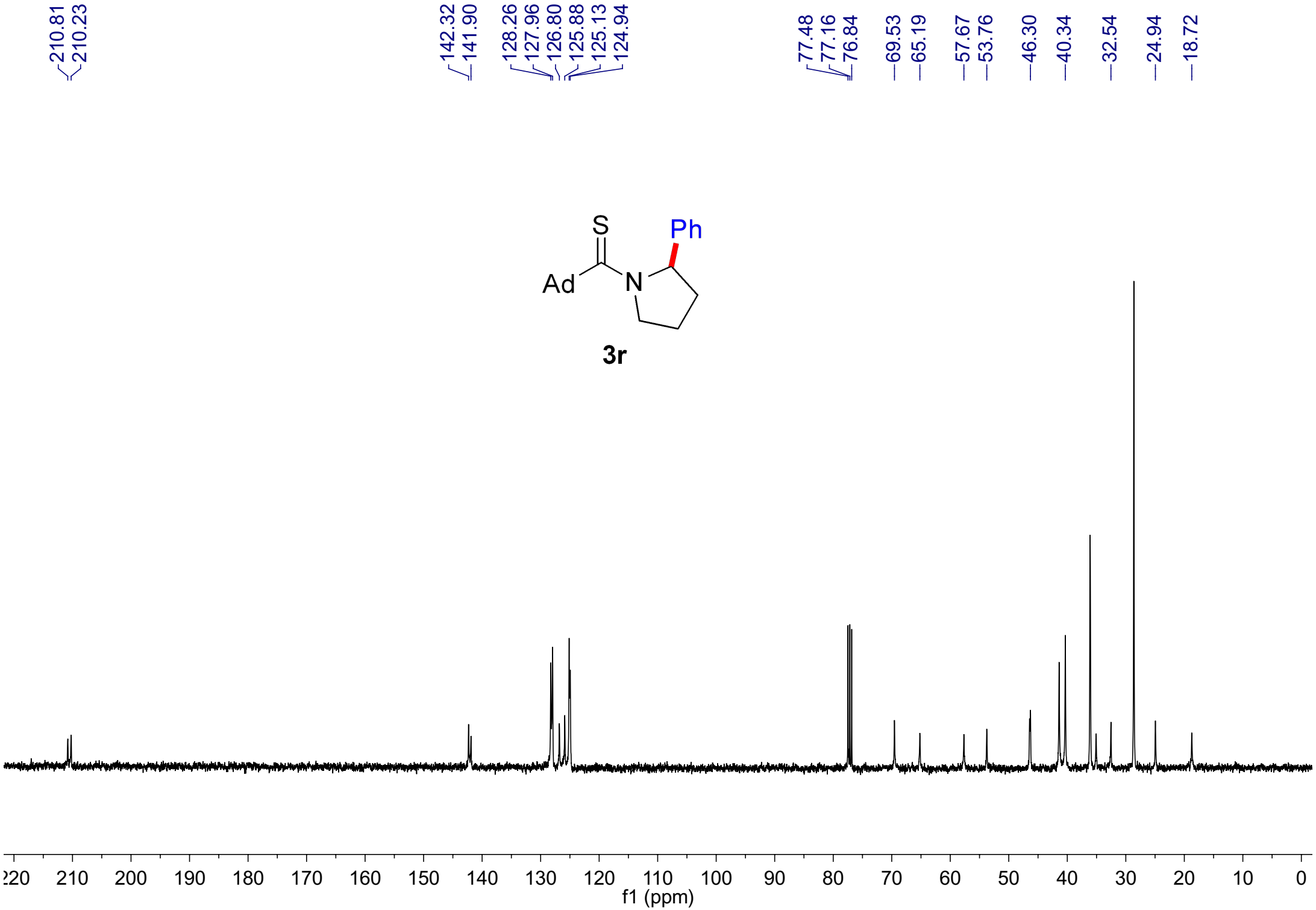

211.564
163.205
145.985
138.425
128.420
123.172
110.534
77.478
77.161
76.843
73.931
58.510
53.639
47.196
40.661
36.477
29.033
OMe
N
S
Ad
N
3o
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

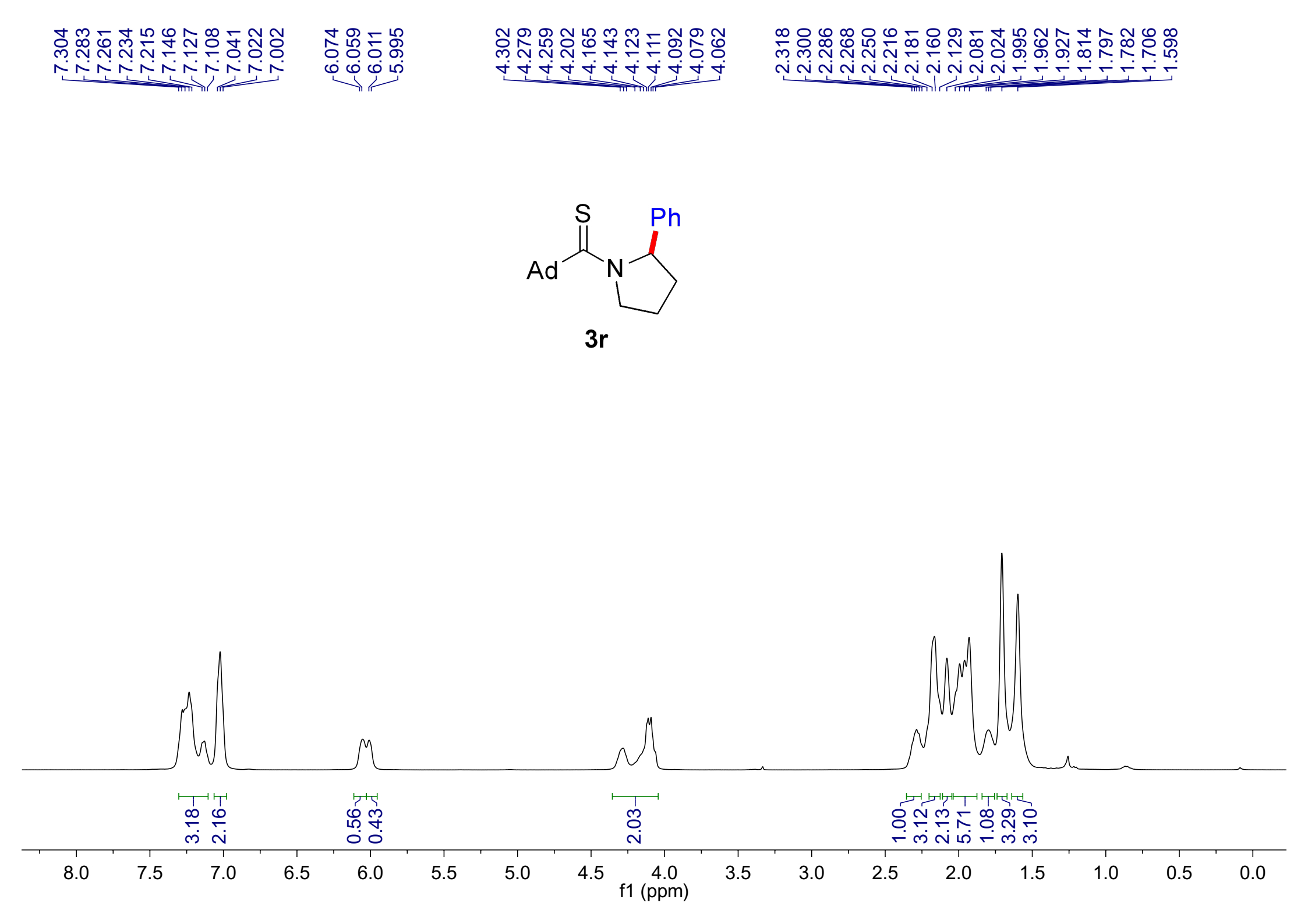

8.209
8.203
7.499
7.478
7.472
7.259
7.223
7.203
6.580
5.979
5.958
5.875
5.864
5.853
4.996
4.911
4.905
4.901
4.896
4.890
4.871
4.866
4.861
4.856
4.851
2.136
2.109
2.048
2.017
1.705
1.670
1.635
Cl
N
S
Ad
N
3p
1.00
1.00
1.03
0.97
1.01
1.01
1.00
1.00
9.67
6.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

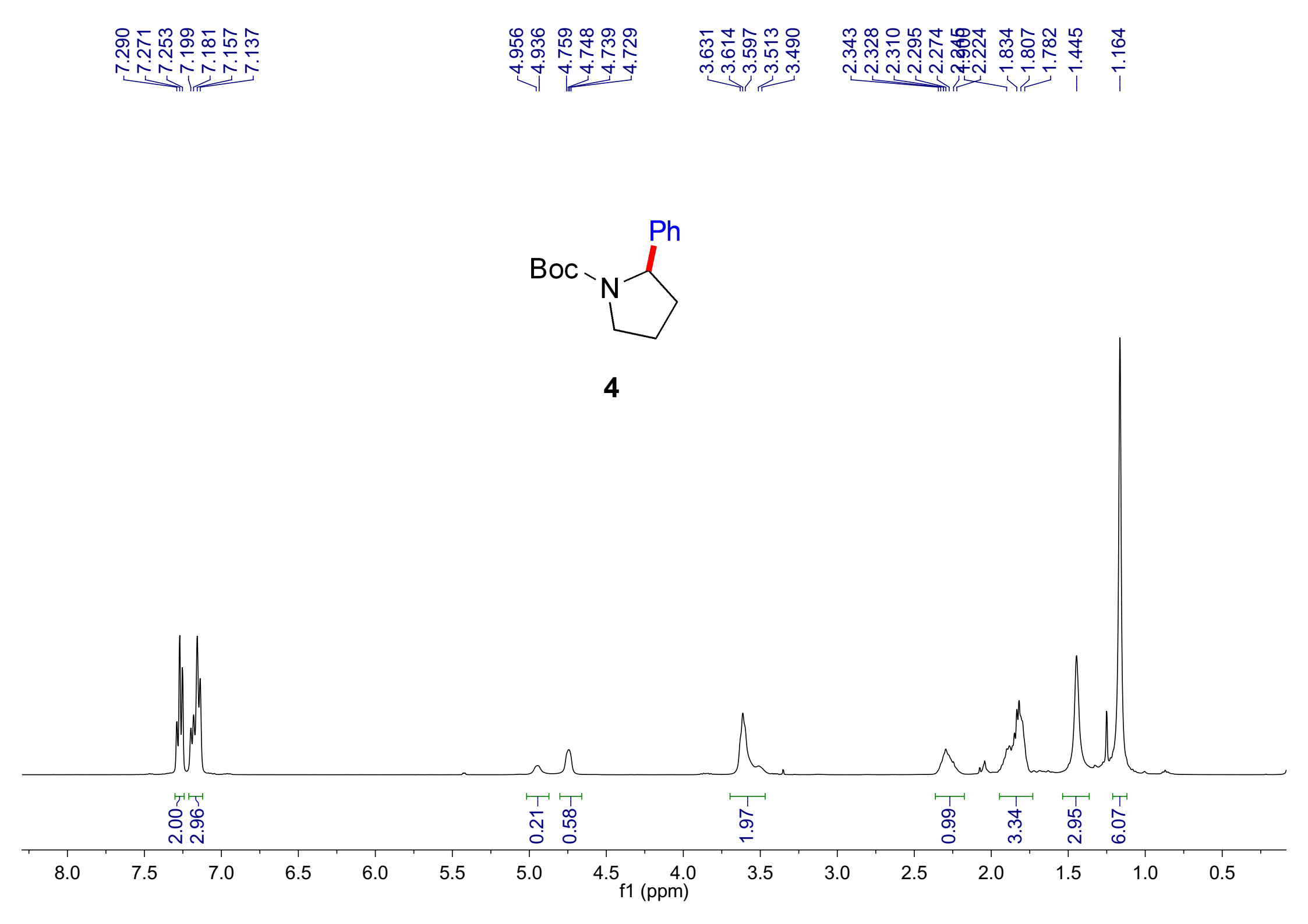

211.564
163.205
145.985
138.425
128.420
123.172
110.534
77.478
77.161
76.843
73.931
58.510
53.639
47.196
40.661
36.477
29.033
Cl
N
S
Ad
N
3p
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

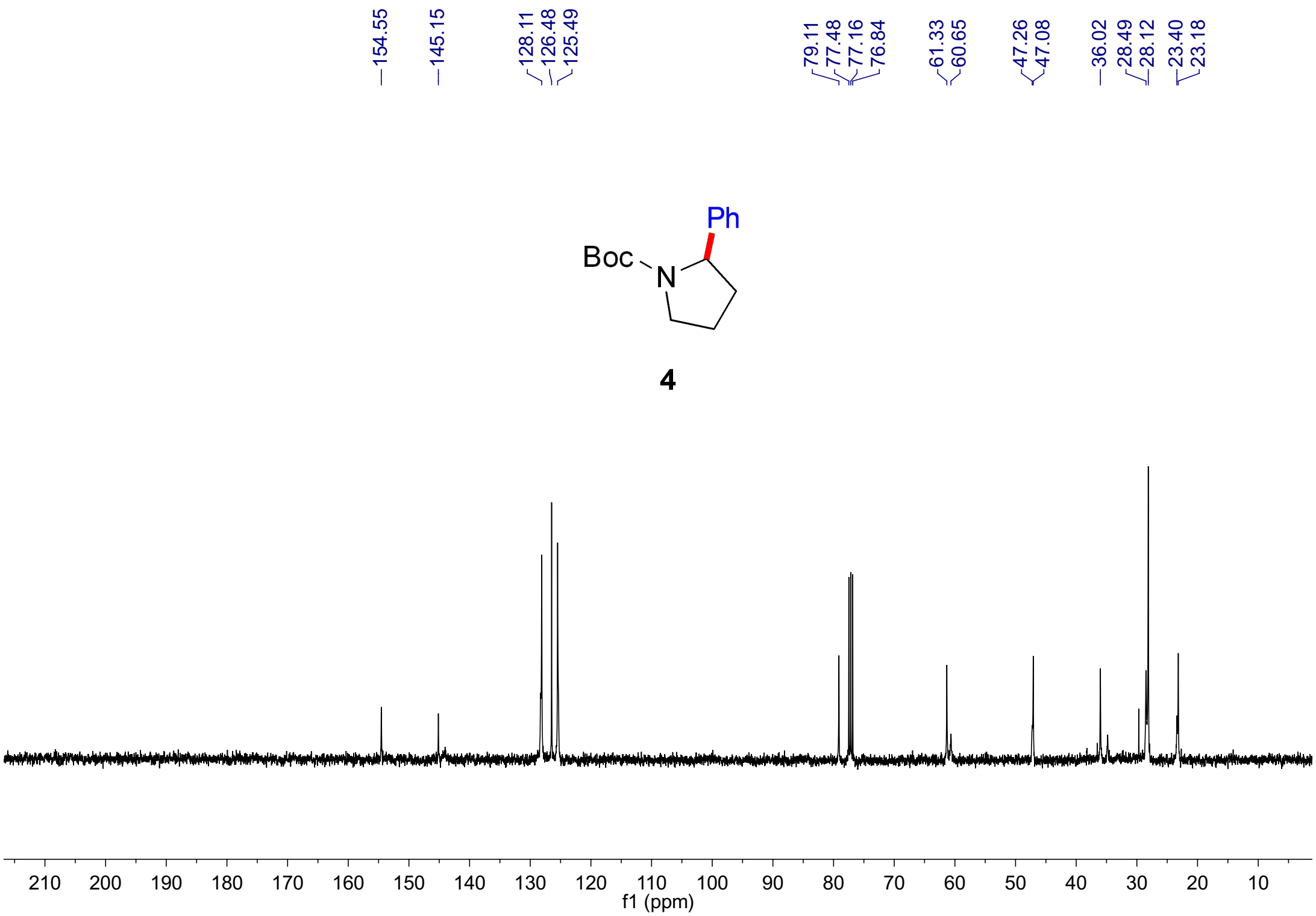

7.260
6.987
6.983
6.970
6.965
5.969
5.963
5.958
5.952
5.946
5.664
5.483
5.477
5.472
5.464
5.439
3.963
3.958
3.906
3.899
3.893
3.887
3.863
3.856
3.850
2.876
2.871
2.864
2.854
2.846
2.837
2.820
2.802
1.607
1.591
1.279
1.261
1.259
1.250
1.244
1.242
1.234
1.217
1.200
1.180
1.162
S
Me
Ar
N
3q
2.00
0.91
0.91
0.89
0.26
0.62
0.62
0.26
2.97
3.07
19.20
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

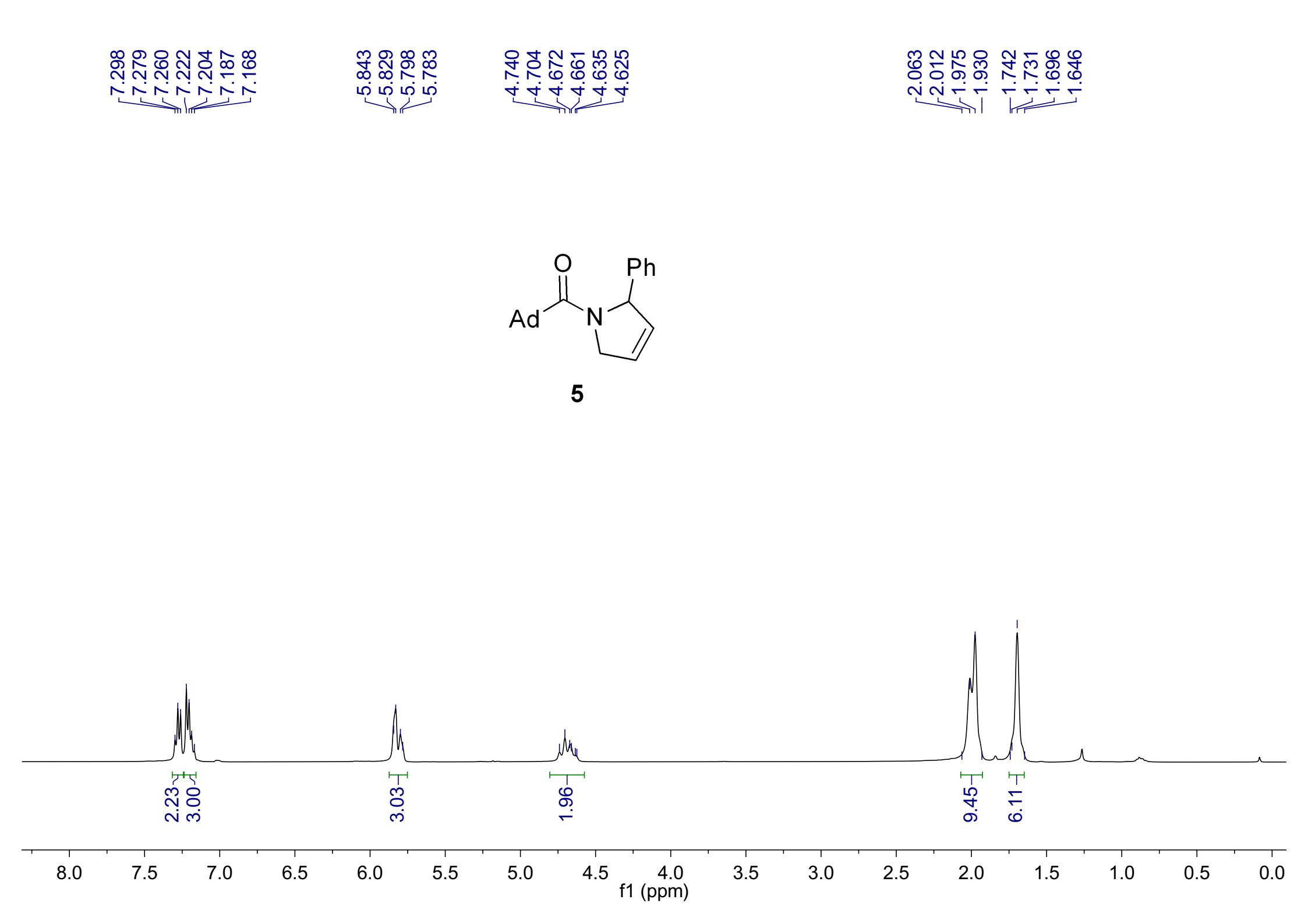

198.10
148.79
138.52
132.95
122.91
121.80
121.65
77.48
77.16
76.84
64.38
58.42
34.34
30.71
30.25
29.81
24.13
17.32
S
Me
Ar
N
3q
f1 (ppm)


210.81
210.23
142.32
141.90
128.26
127.96
126.80
125.88
125.13
124.94
77.48
77.16
76.84
69.53
65.19
57.67
53.76
46.30
40.34
32.54
24.94
18.72
S
Ph
Ad
N
3r
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

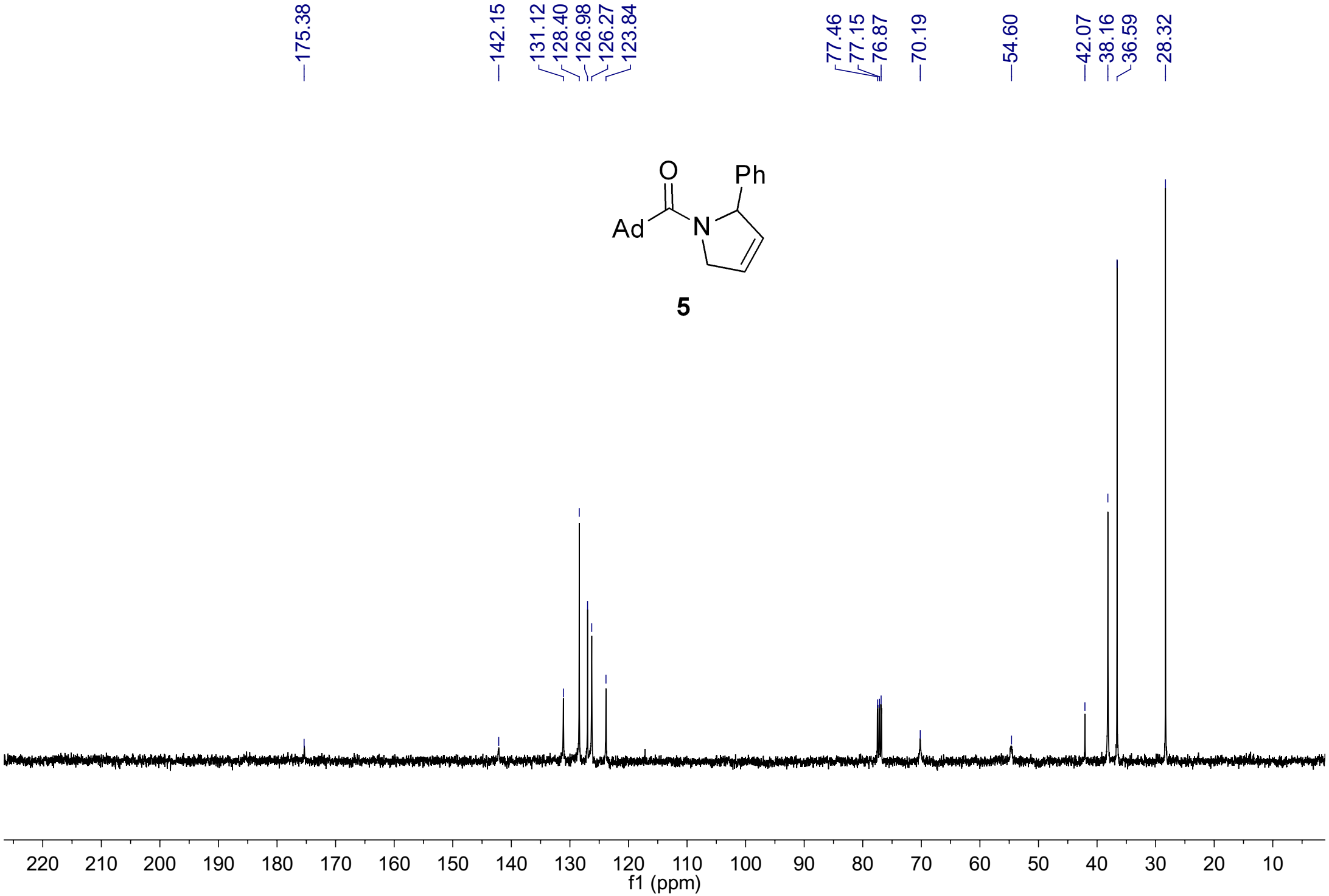

7.304
7.283
7.261
7.234
7.215
7.146
7.127
7.108
7.041
7.022
7.002
6.074
6.059
6.011
5.995
4.302
4.279
4.259
4.202
4.165
4.143
4.123
4.111
4.092
4.079
4.062
2.318
2.300
2.286
2.268
2.250
2.216
2.181
2.160
2.129
2.081
2.024
1.995
1.962
1.927
1.814
1.797
1.782
1.706
1.598
S
Ph
Ad
N
3r
3.18
2.16
0.56
0.43
2.03
1.00
3.12
2.13
5.71
1.08
3.29
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

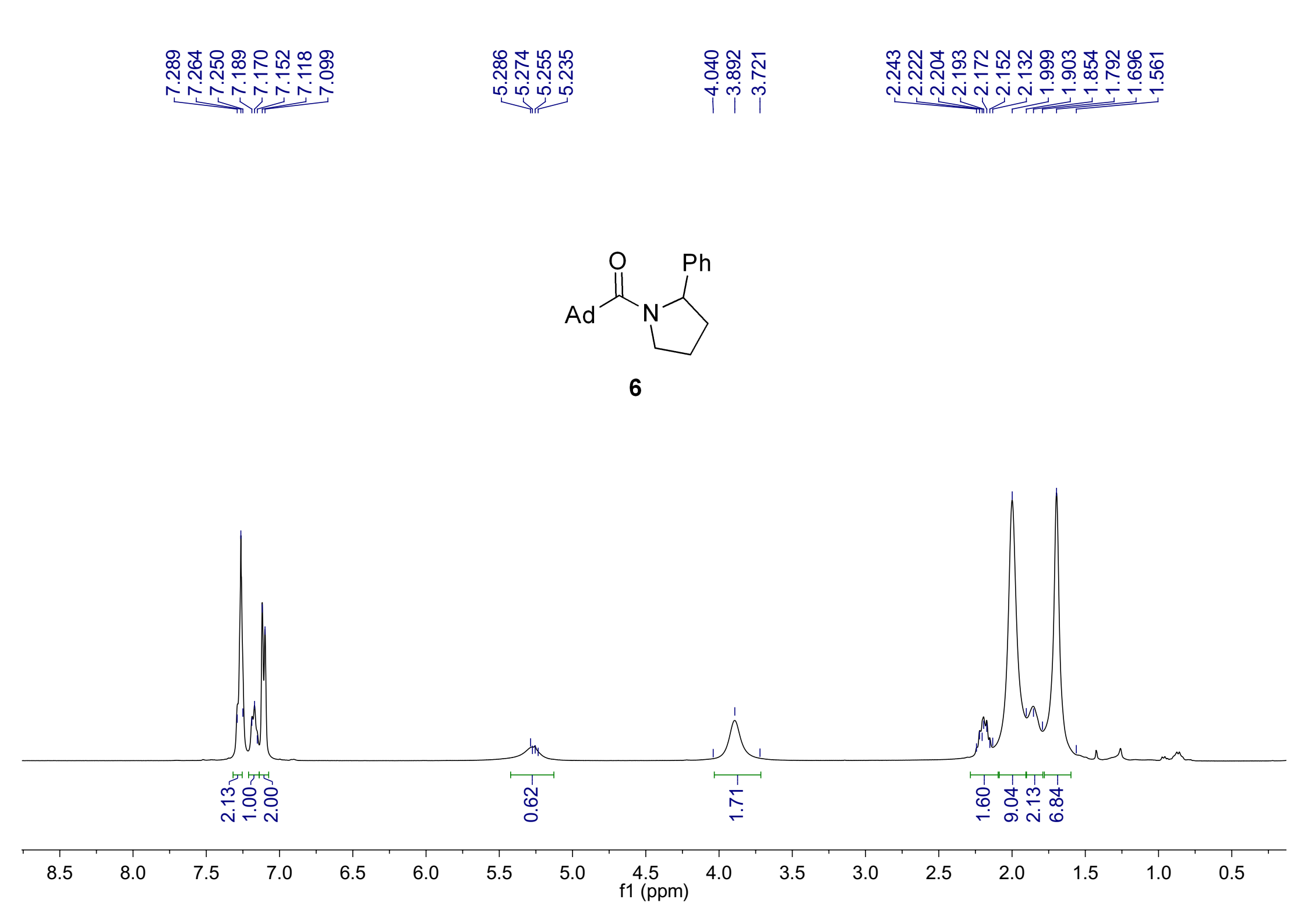

7.290
7.271
7.253
7.199
7.181
7.157
7.137
4.956
4.936
4.759
4.748
4.739
4.729
3.631
3.614
3.597
3.513
3.490
2.343
2.328
2.310
2.295
2.274
2.245
2.224
1.834
1.807
1.782
1.445
1.164
Ph
Boc
N
4
2.00
2.96
0.21
0.58
1.97
0.99
3.34
2.95
6.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


154.55
145.15
128.11
126.48
125.49
79.11
77.48
77.16
76.84
61.33
60.65
47.26
47.08
36.02
28.49
28.12
23.40
23.18
Ph
Boc
N
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

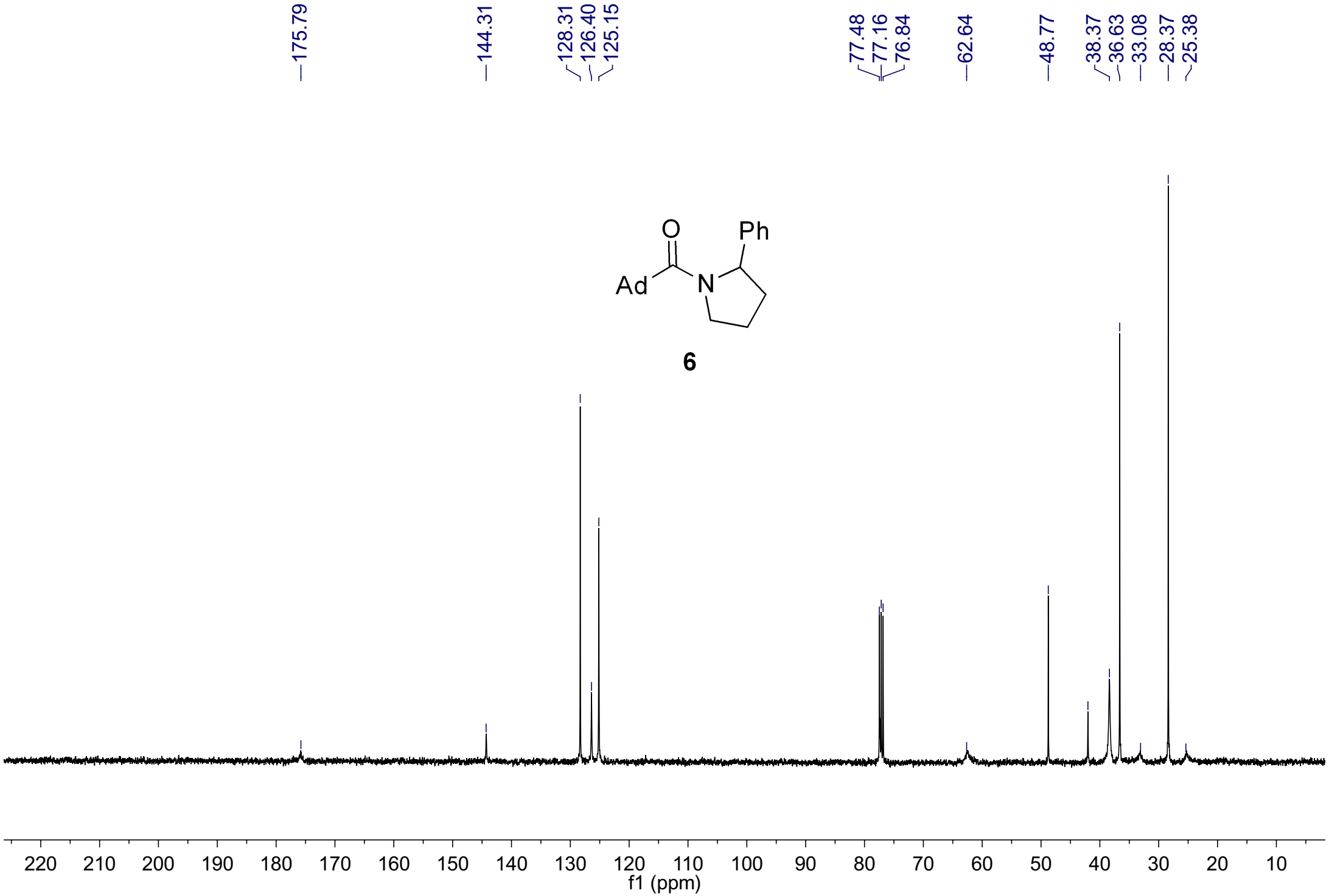

7.298
7.279
7.260
7.222
7.204
7.187
7.168
5.843
5.829
5.798
5.783
4.740
4.704
4.672
4.661
4.635
4.625
2.063
2.012
1.975
1.930
1.742
1.731
1.696
1.646
O
Ph
Ad
N
2.23
3.00
3.03
1.96
9.45
6.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

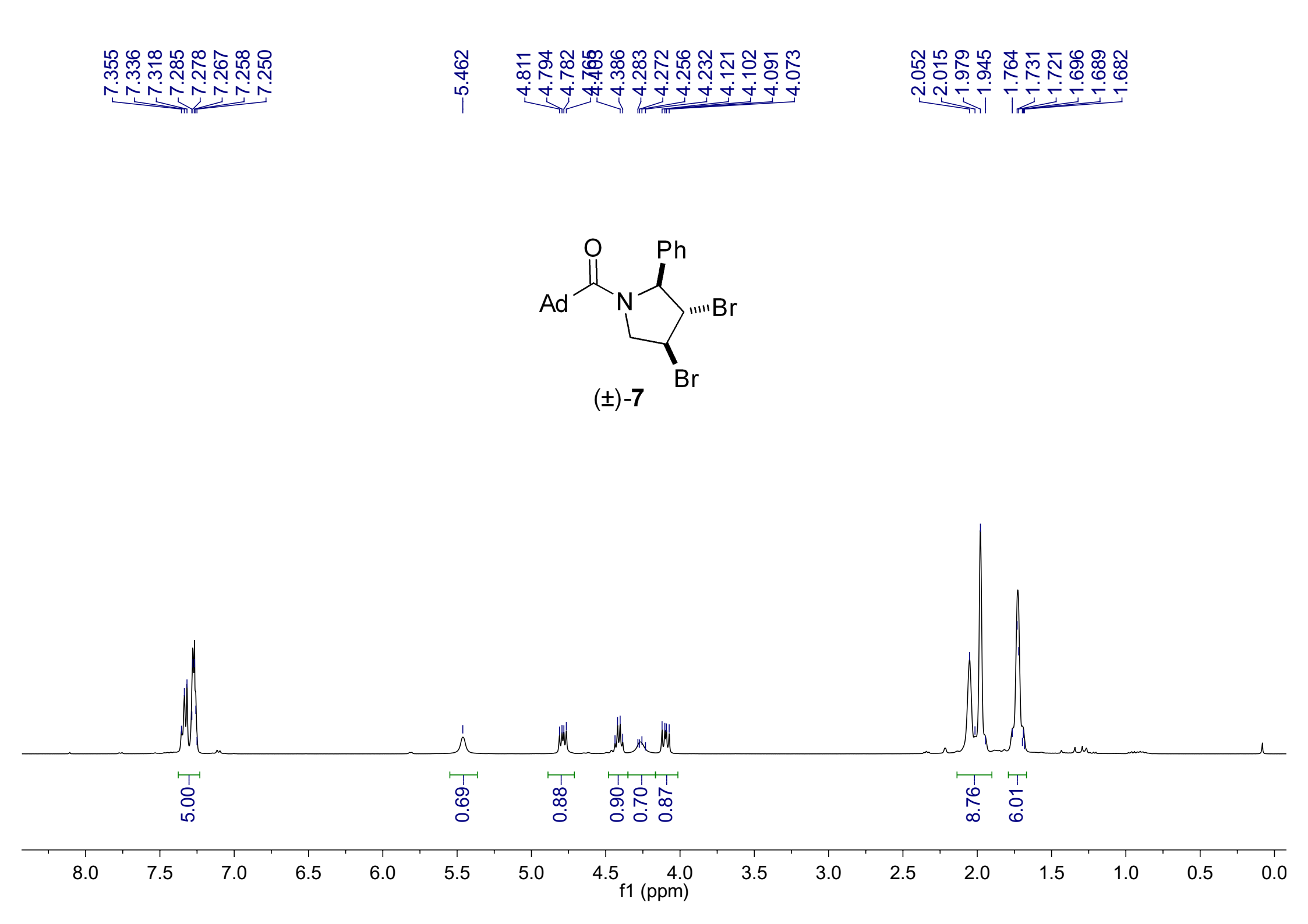
**5**

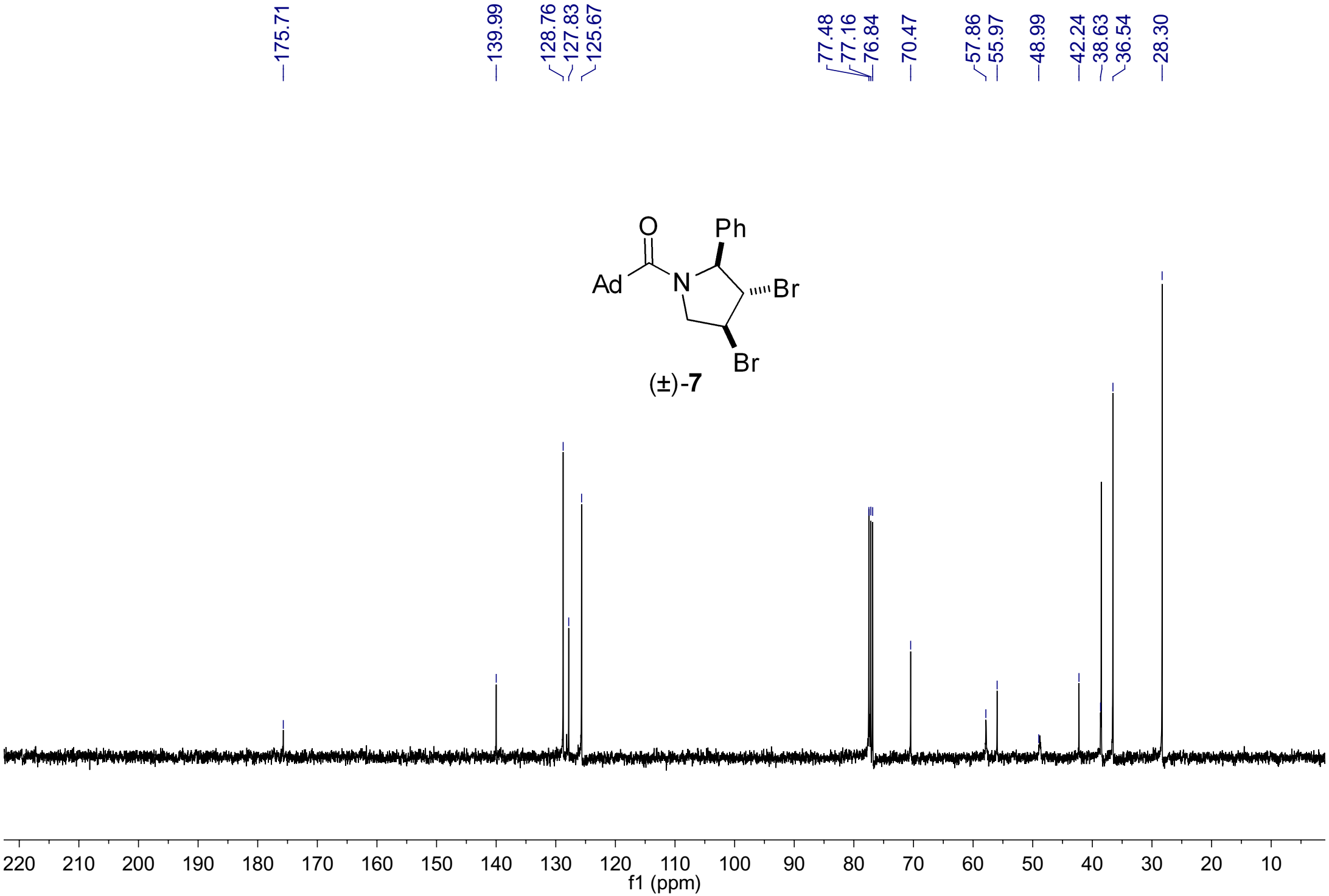

175.38
142.15
131.12
128.40
126.98
126.27
123.84
77.46
77.15
76.87
70.19
54.60
42.07
38.16
36.59
28.32
O
Ph
Ad
N
5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

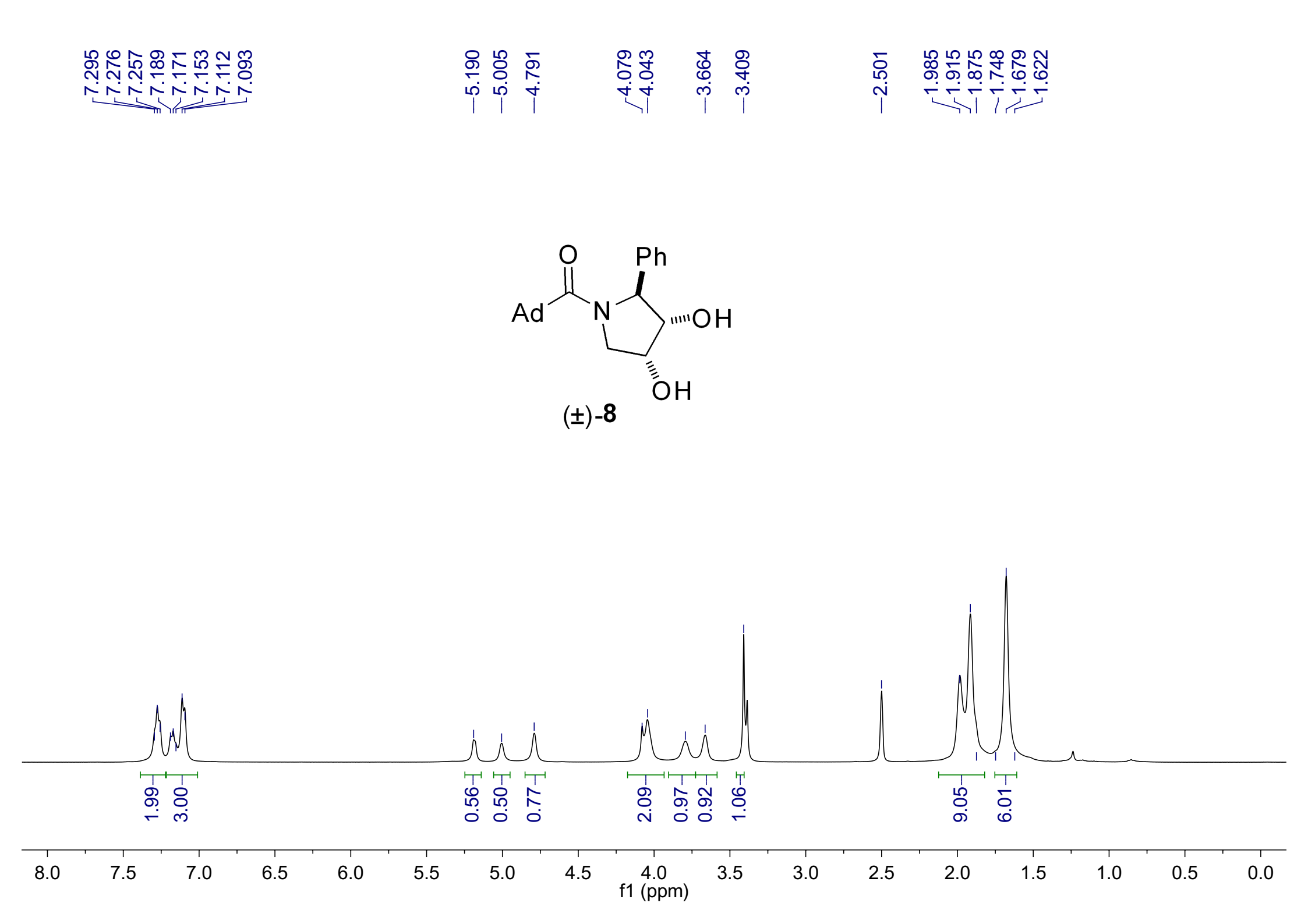

7.289
7.264
7.250
7.189
7.170
7.152
7.118
7.099
5.286
5.274
5.255
5.235
4.040
3.892
3.721
2.243
2.222
2.204
2.193
2.172
2.152
2.132
1.999
1.903
1.854
1.792
1.696
1.561
O
Ph
Ad
N
2.13
1.00
2.00
0.62
1.71
1.60
9.04
2.13
6.84
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

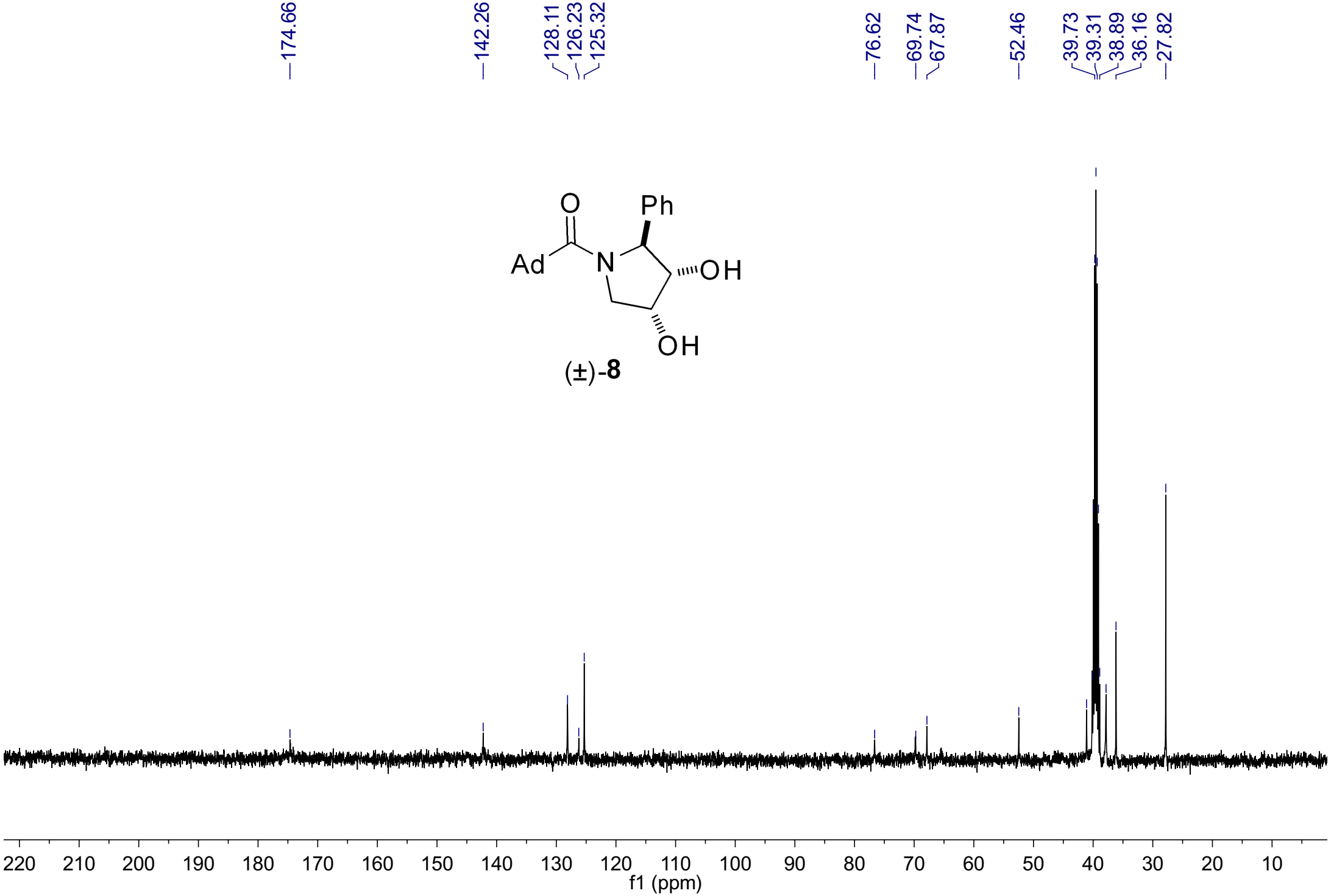
**6**

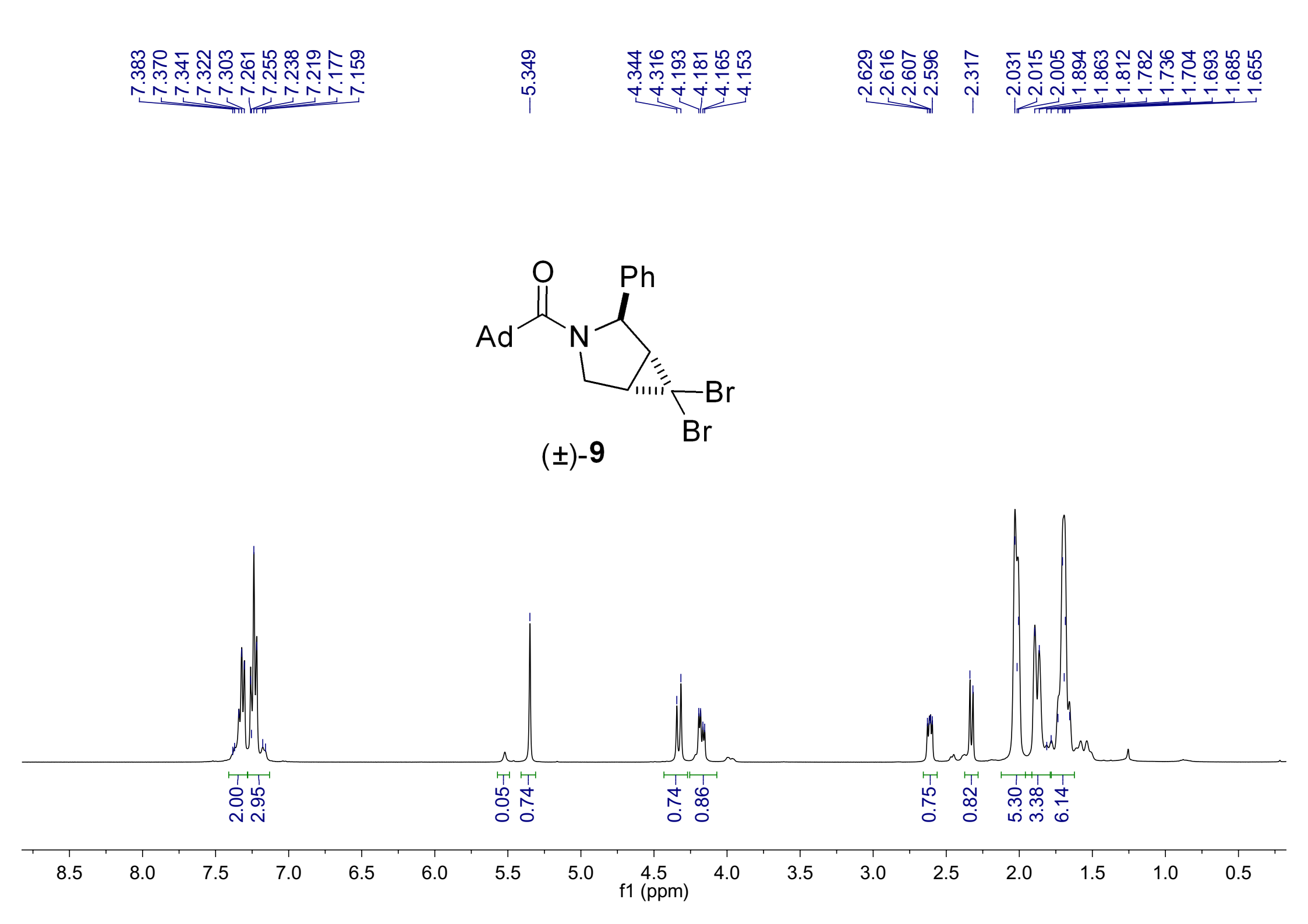

175.79
144.31
128.31
126.40
125.15
77.48
77.16
76.84
62.64
48.77
38.37
36.63
33.08
28.37
25.38
O
Ph
Ad
N
6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

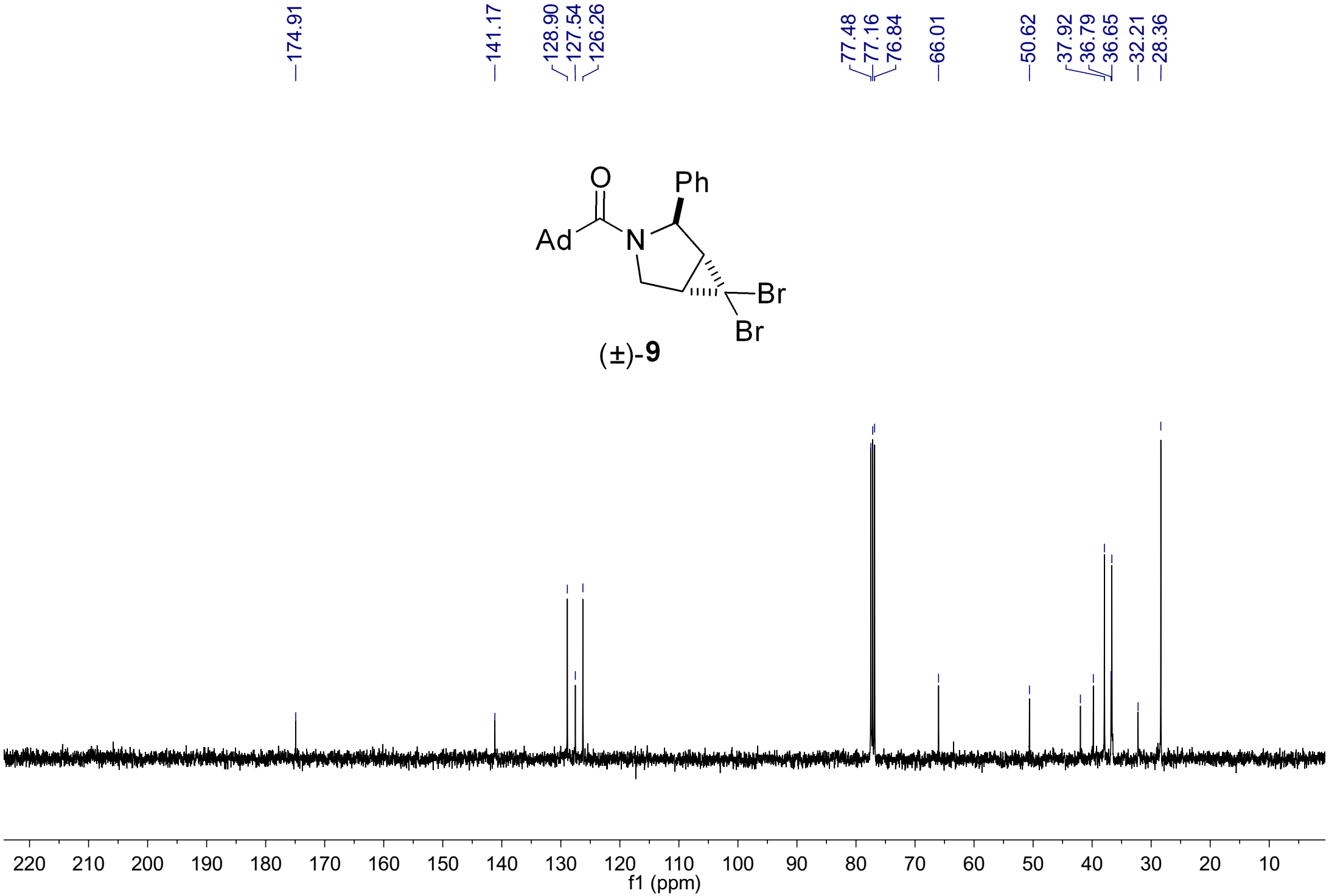

7.355
7.336
7.318
7.285
7.278
7.267
7.258
7.250
5.462
4.811
4.794
4.782
4.765
4.403
4.386
4.283
4.272
4.256
4.232
4.121
4.102
4.091
4.073
2.052
2.015
1.979
1.945
1.764
1.731
1.721
1.696
1.689
1.682
O
Ph
Ad
N
Br
Br
(±)-7
5.00
0.69
0.88
0.90
0.70
0.87
8.76
6.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

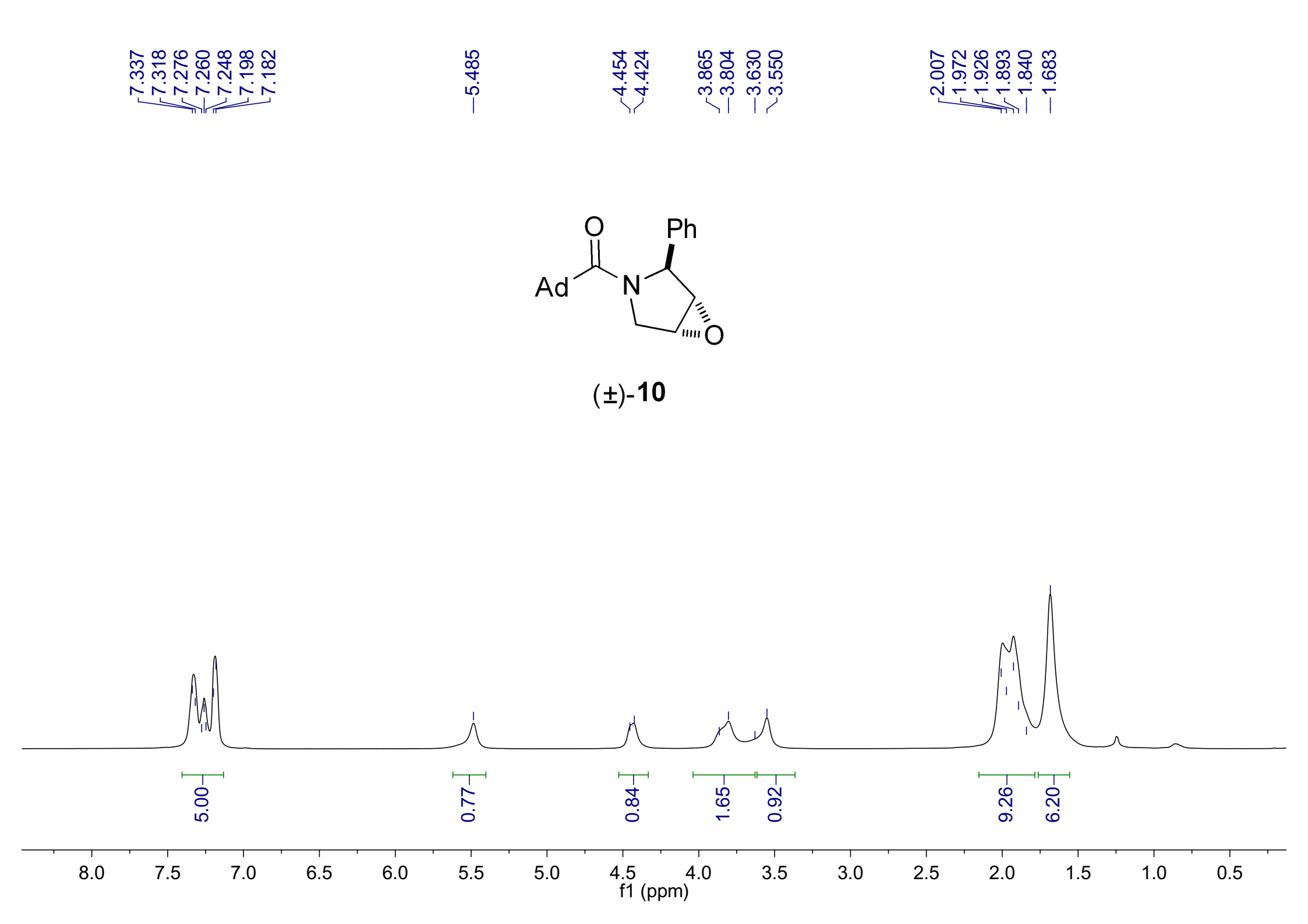

175.71
139.99
128.76
127.83
125.67
77.48
77.16
76.84
70.47
57.86
55.97
48.99
42.24
38.63
36.54
28.30
O
Ph
Ad
N
Br
Br
(±)-7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.295
7.276
7.257
7.189
7.171
7.153
7.112
7.093
5.190
5.005
4.791
4.079
4.043
3.664
3.409
2.501
1.985
1.915
1.875
1.748
1.679
1.622
O
Ph
Ad
N
OH
OH
(±)-8
1.99
3.00
0.56
0.50
0.77
2.09
0.97
0.92
1.06
9.05
6.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

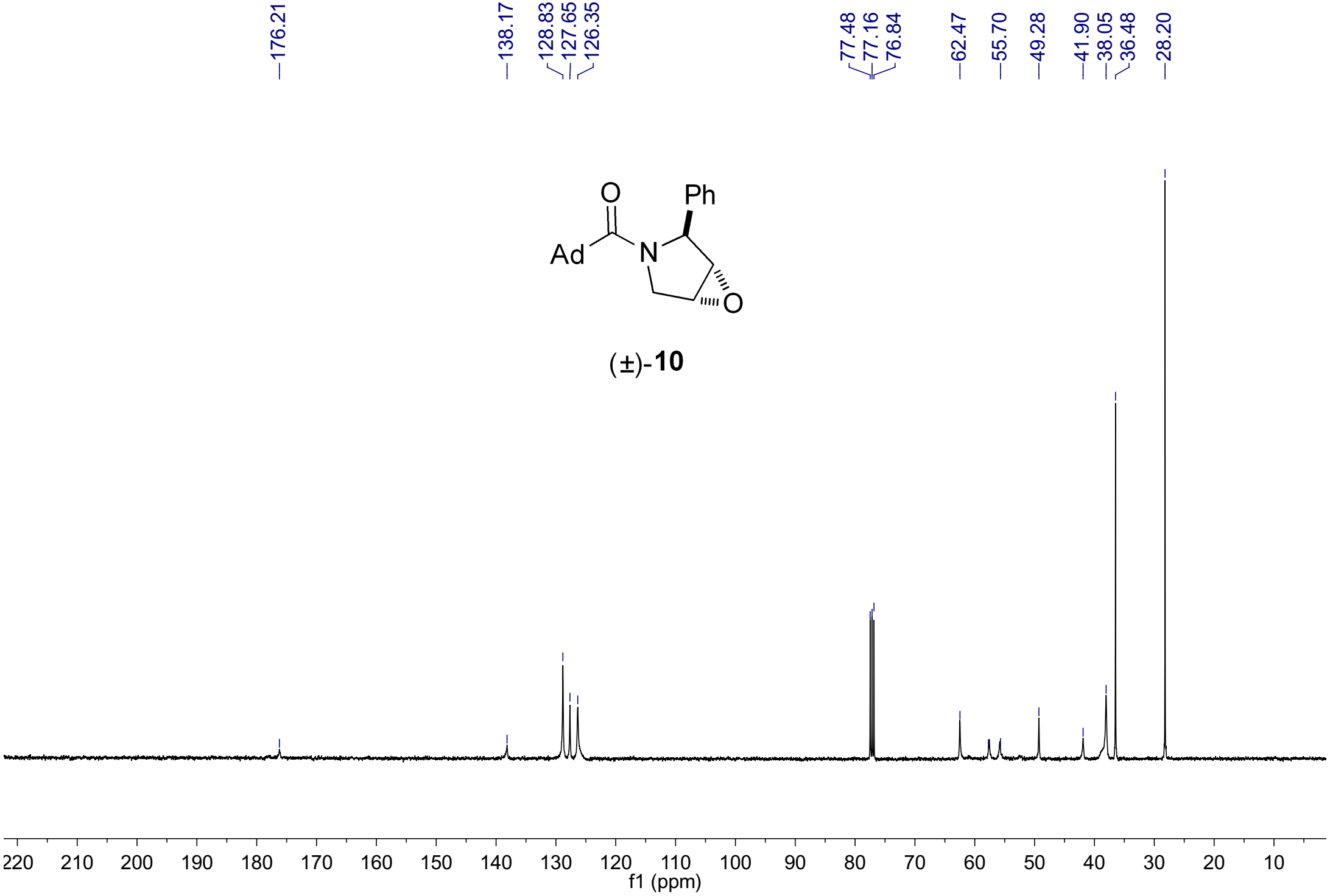

174.66
142.26
128.11
126.23
125.32
76.62
69.74
67.87
52.46
39.73
39.31
38.89
36.16
27.82
O
Ph
Ad
N
OH
OH
(±)-8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

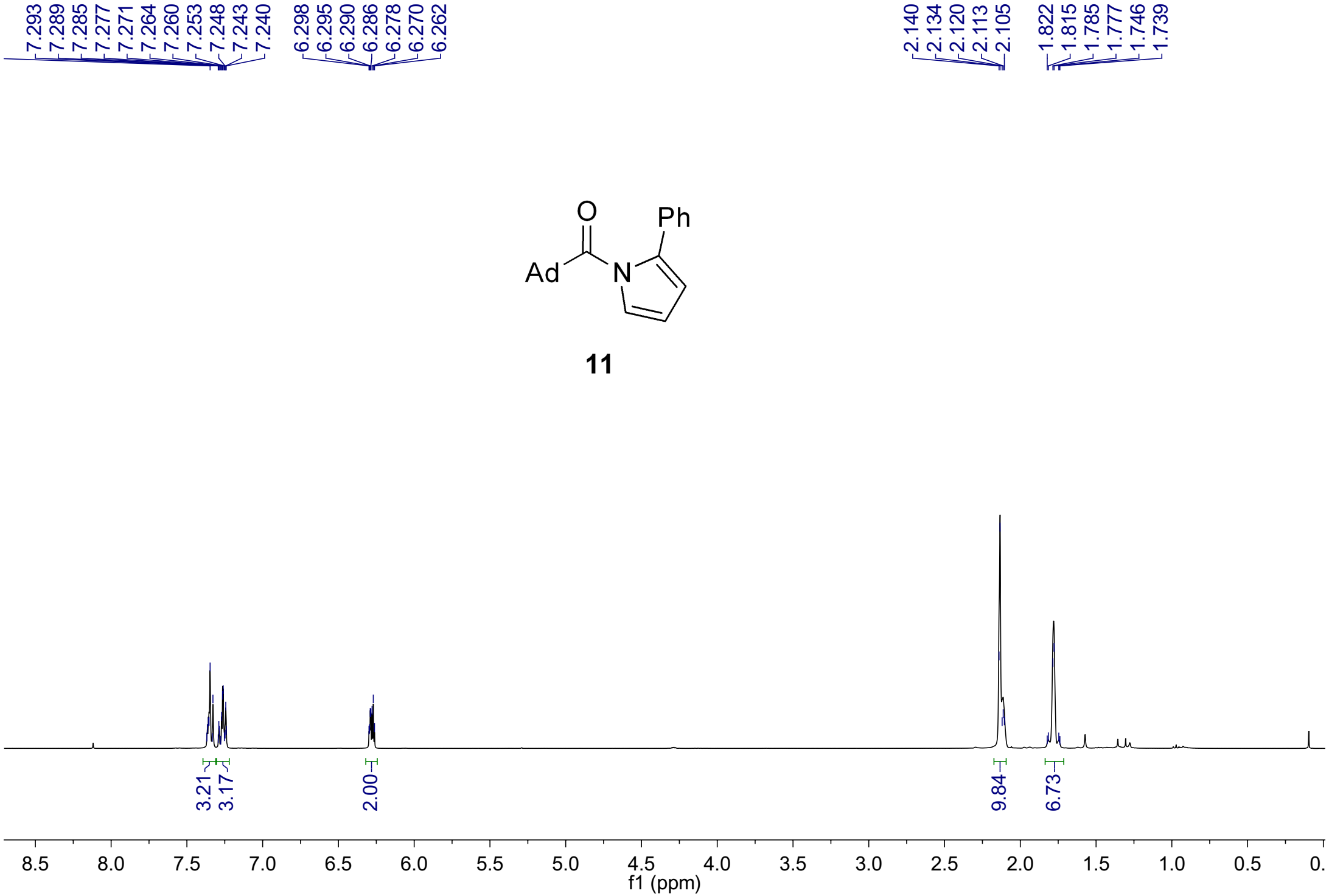

7.383
7.370
7.341
7.322
7.303
7.261
7.255
7.238
7.219
7.177
7.159
5.349
4.344
4.316
4.193
4.181
4.165
4.153
2.629
2.616
2.607
2.596
2.317
2.031
2.015
2.005
1.894
1.863
1.812
1.782
1.736
1.704
1.693
1.685
1.655
O
Ph
Ad
N
Br
Br
(±)-9
2.00
2.95
0.05
0.74
0.74
0.86
0.75
0.82
5.30
3.38
6.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

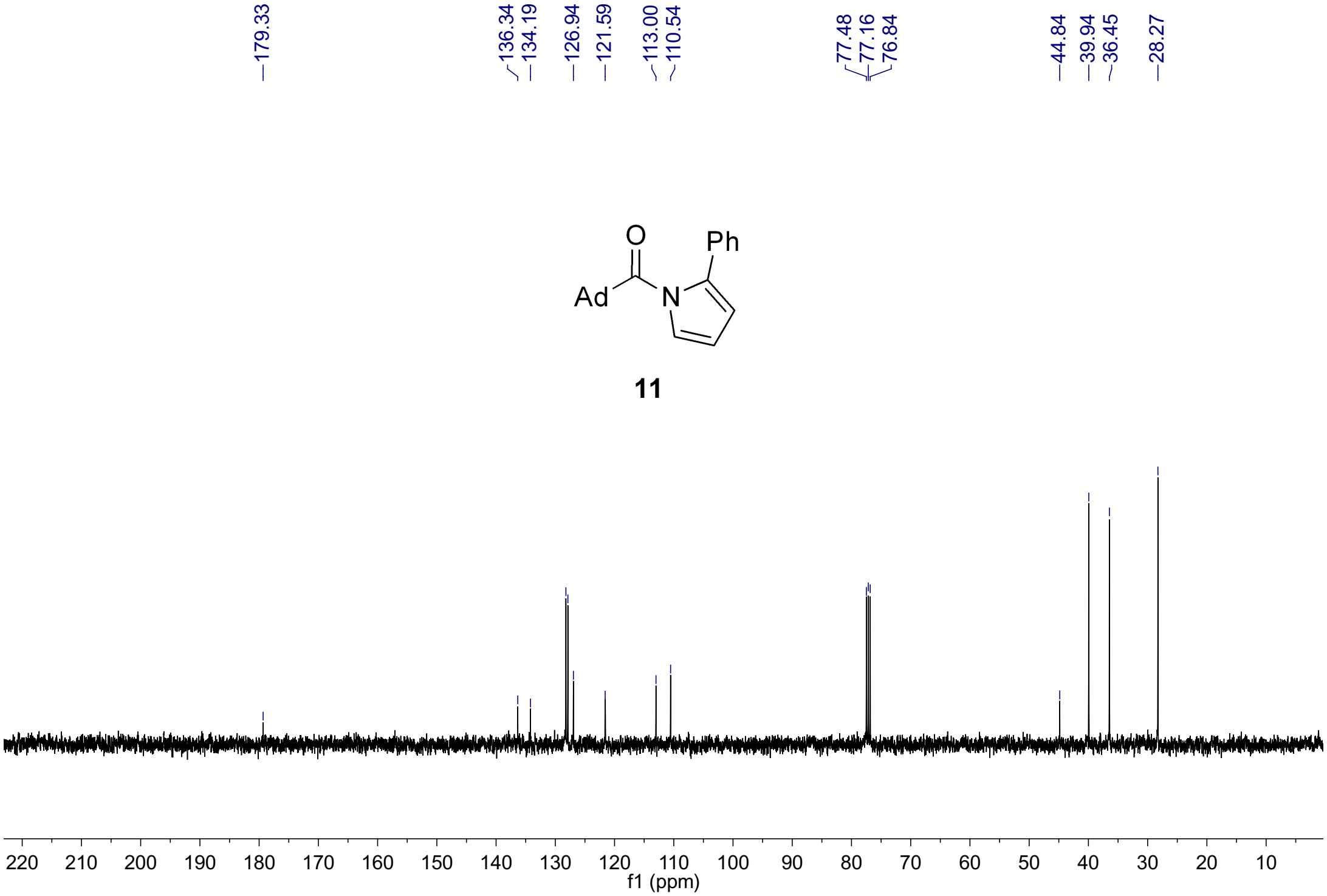

174.91
141.17
128.90
127.54
126.26
77.48
77.16
76.84
66.01
50.62
37.92
36.79
36.65
32.21
28.36
O
Ph
Ad
N
Br
Br
(±)-9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.337
7.318
7.276
7.260
7.248
7.198
7.182
5.485
4.454
4.424
3.865
3.804
3.630
3.550
2.007
1.972
1.926
1.893
1.840
1.683
O
Ph
Ad
N
O
5.00
0.77
0.84
1.65
0.92
9.26
6.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

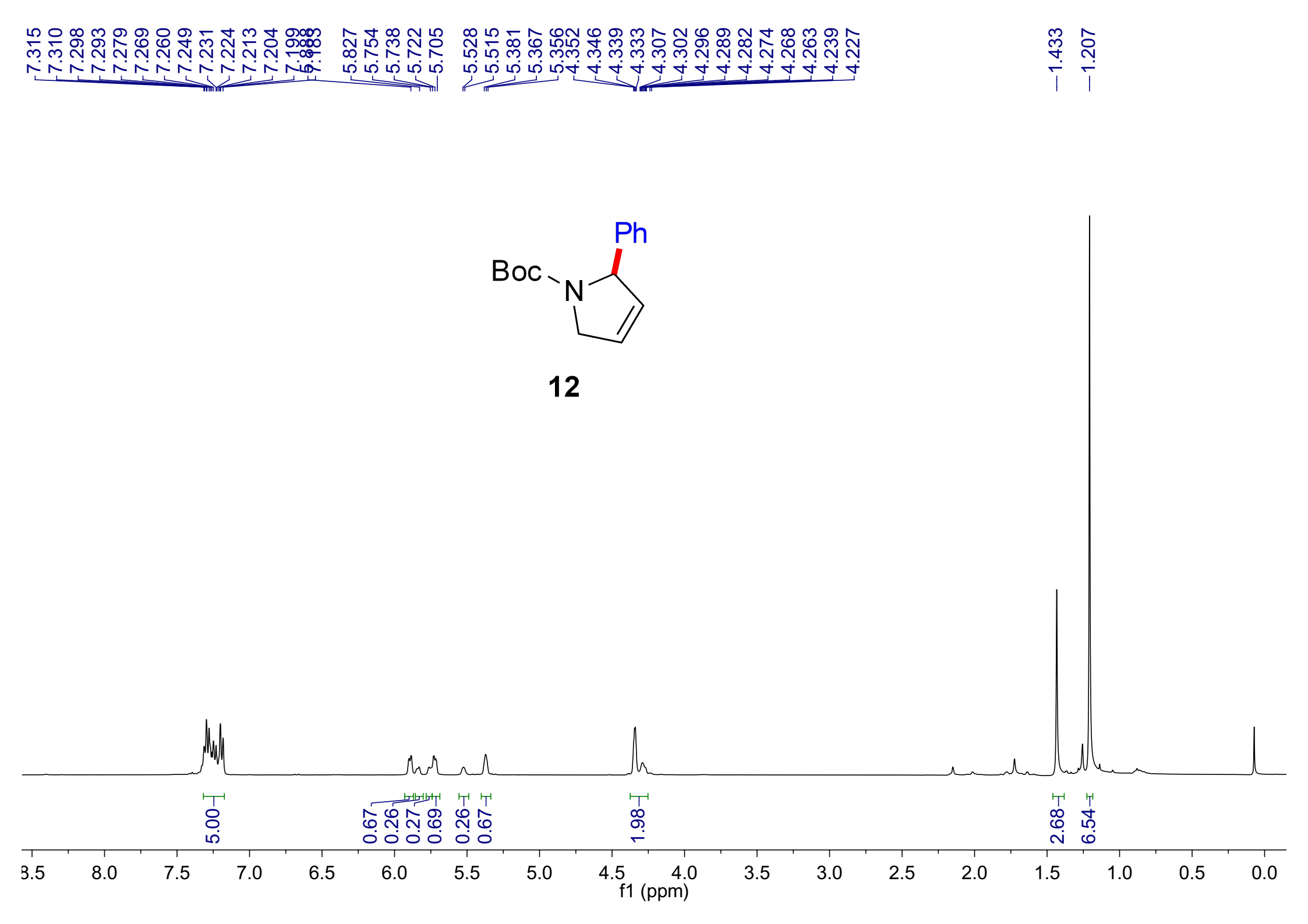
(±)-**10**

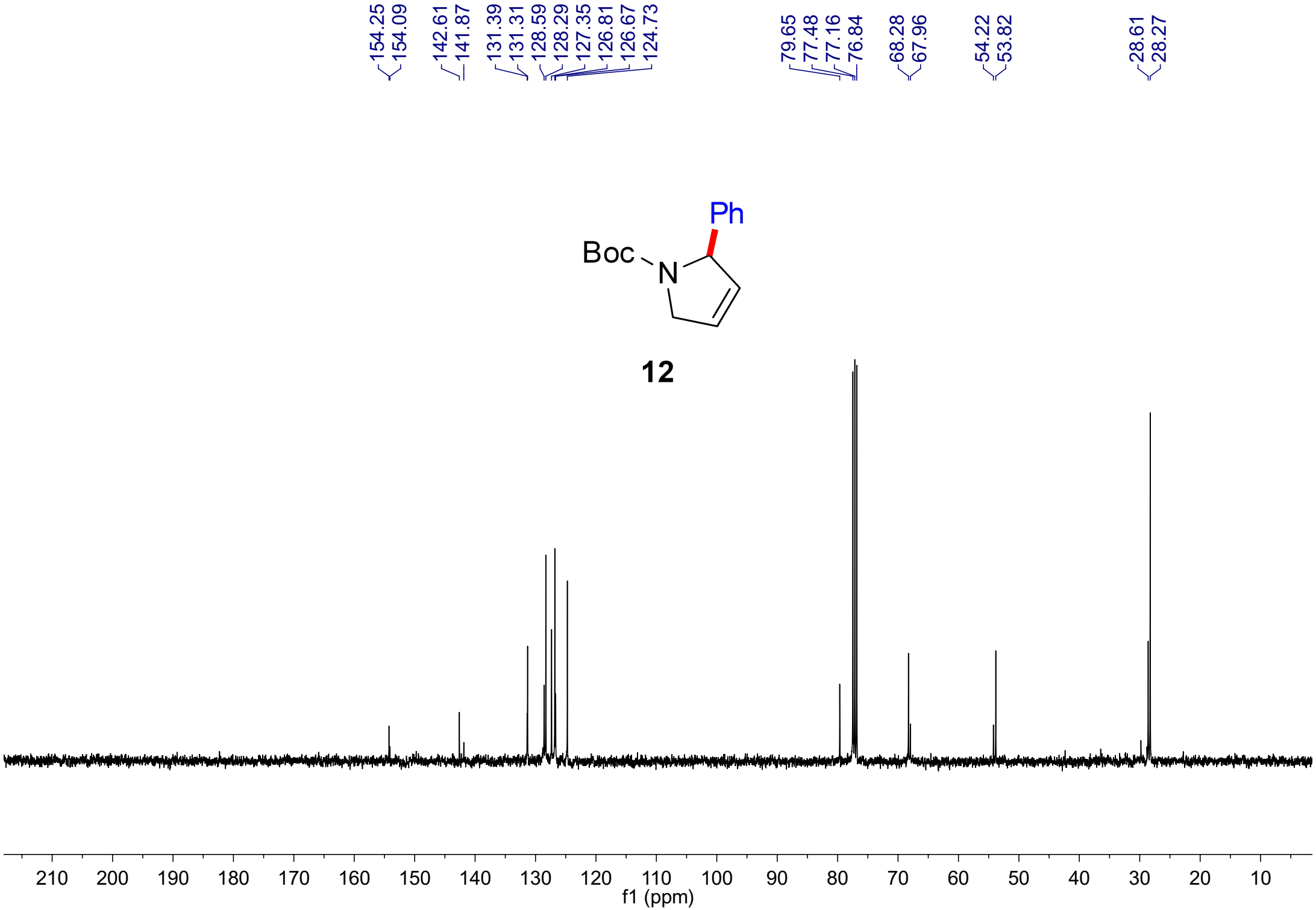

176.21
138.17
128.83
127.65
126.35
77.48
77.16
76.84
62.47
55.70
49.28
41.90
38.05
36.48
28.20
O
Ph
Ad
N
O
(±)-10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

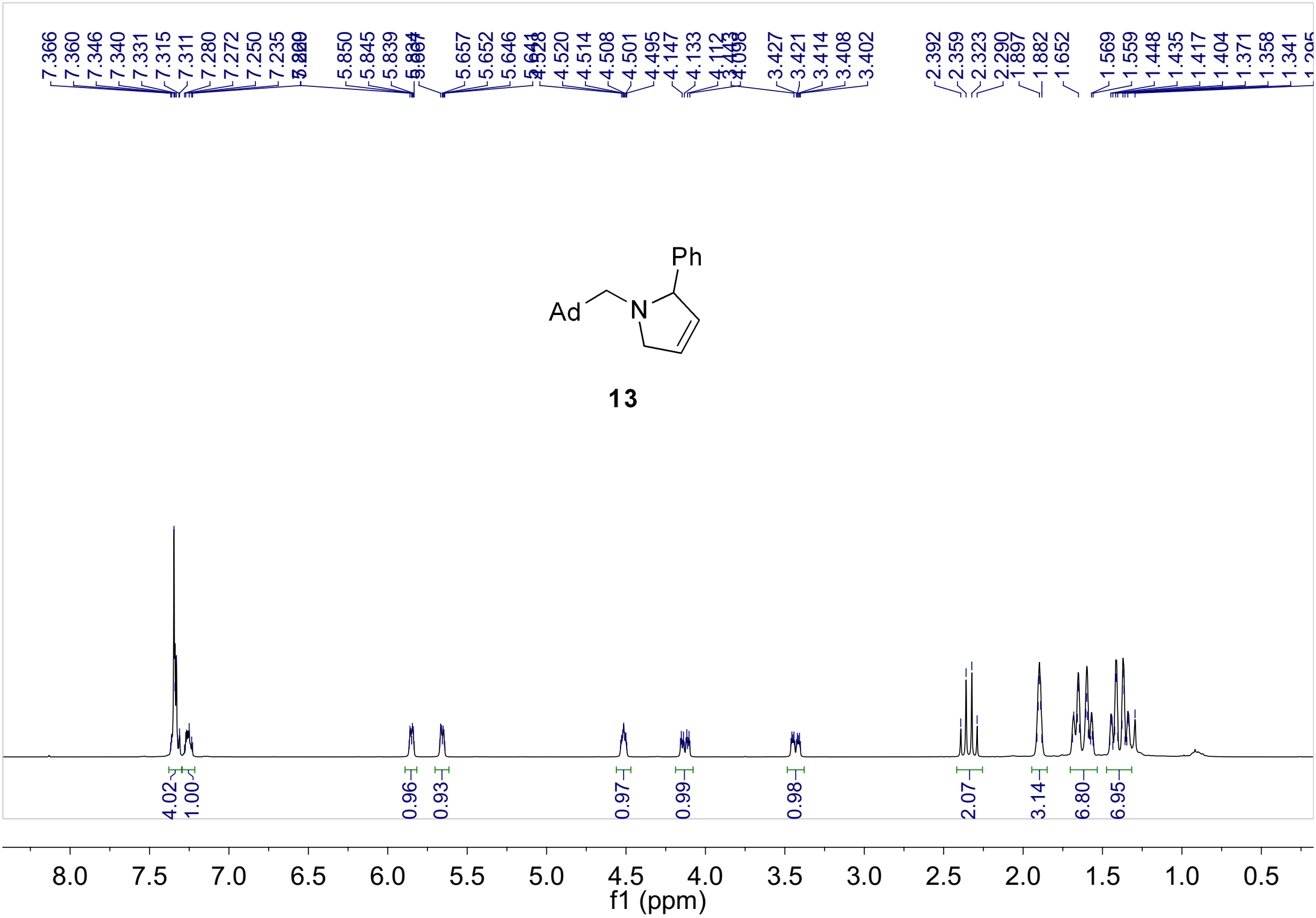

7.293
7.289
7.285
7.277
7.271
7.264
7.260
7.253
7.248
7.243
7.240
6.298
6.295
6.290
6.286
6.278
6.270
6.262
2.140
2.134
2.120
2.113
2.105
1.822
1.815
1.785
1.777
1.746
1.739
O
Ph
Ad
N
11
3.21
3.17
2.00
9.84
6.73
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

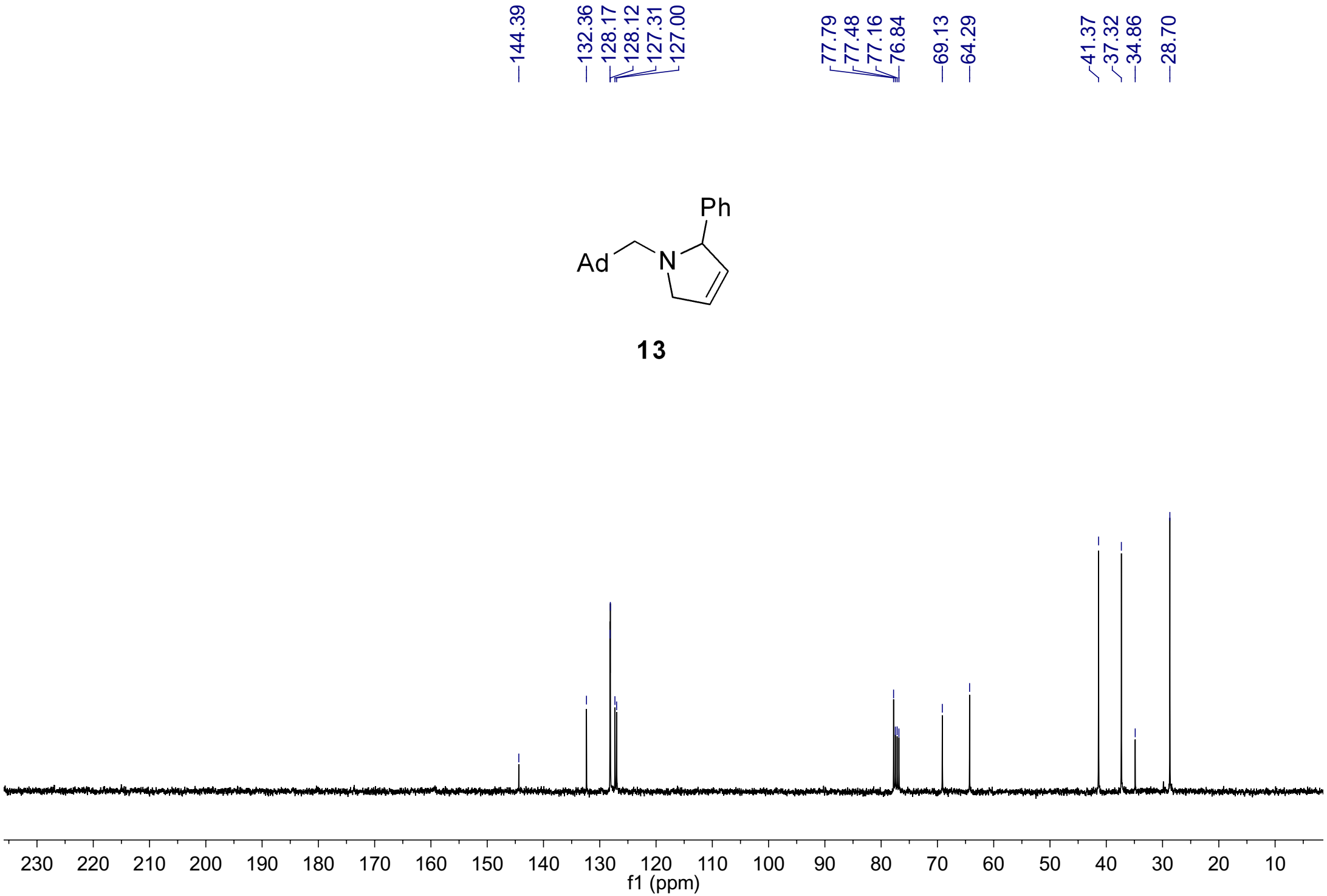

179.33
136.34
134.19
126.94
121.59
113.00
110.54
77.48
77.16
76.84
44.84
39.94
36.45
28.27
O
Ph
Ad
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

**11**

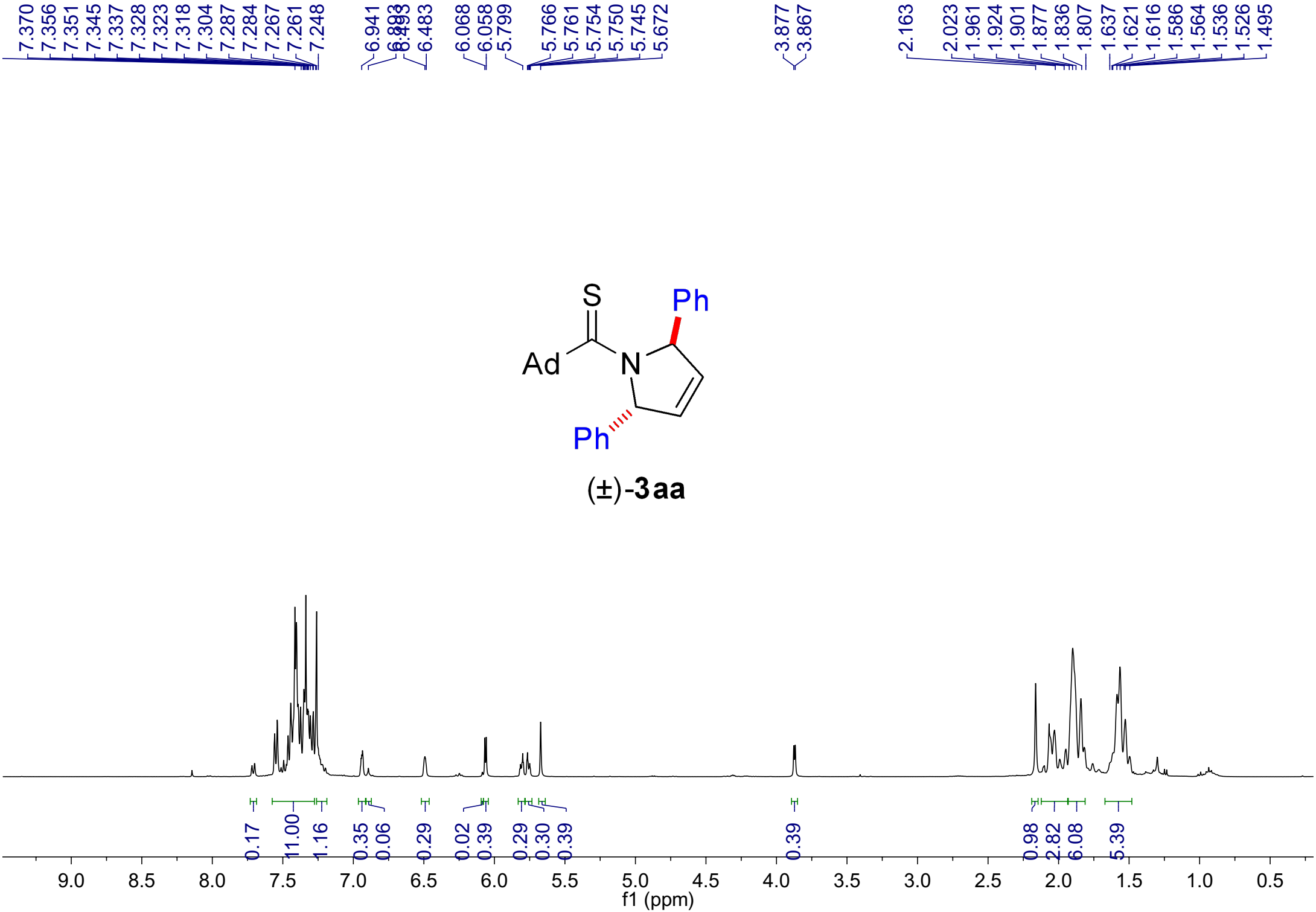

7.315
7.310
7.298
7.293
7.279
7.269
7.260
7.249
7.231
7.224
7.213
7.204
7.199
6.888
6.883
5.827
5.754
5.738
5.722
5.705
5.528
5.515
5.381
5.367
5.356
4.352
4.346
4.339
4.333
4.307
4.302
4.296
4.289
4.282
4.274
4.268
4.263
4.239
4.227
1.433
1.207
Ph
Boc
N
12
5.00
0.67
0.26
0.27
0.69
0.26
0.67
1.98
2.68
6.54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

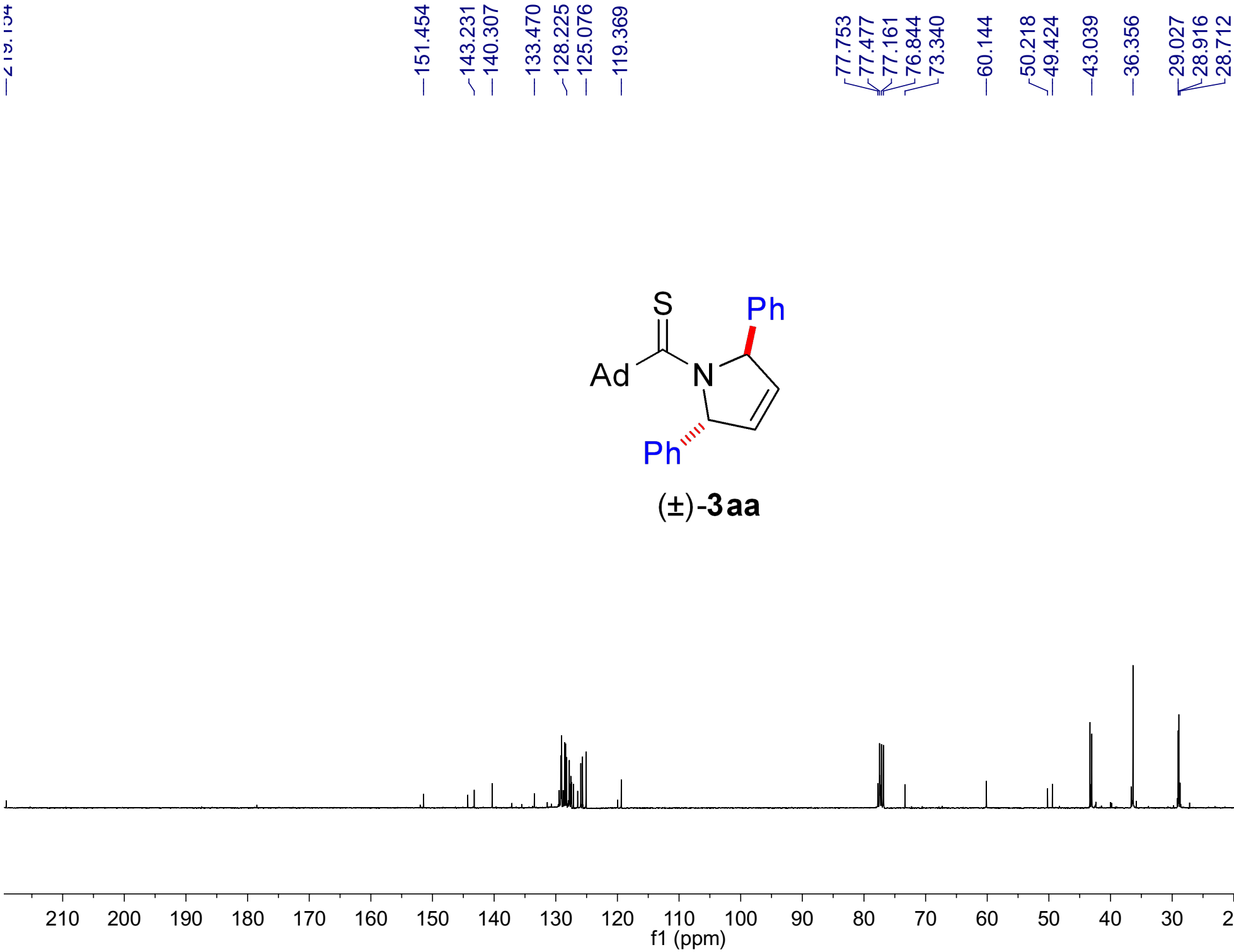

154.25
154.09
142.61
141.87
131.39
131.31
128.59
128.29
127.35
126.81
126.67
124.73
79.65
77.48
77.16
76.84
68.28
67.96
54.22
53.82
28.61
28.27
Ph
Boc
N
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

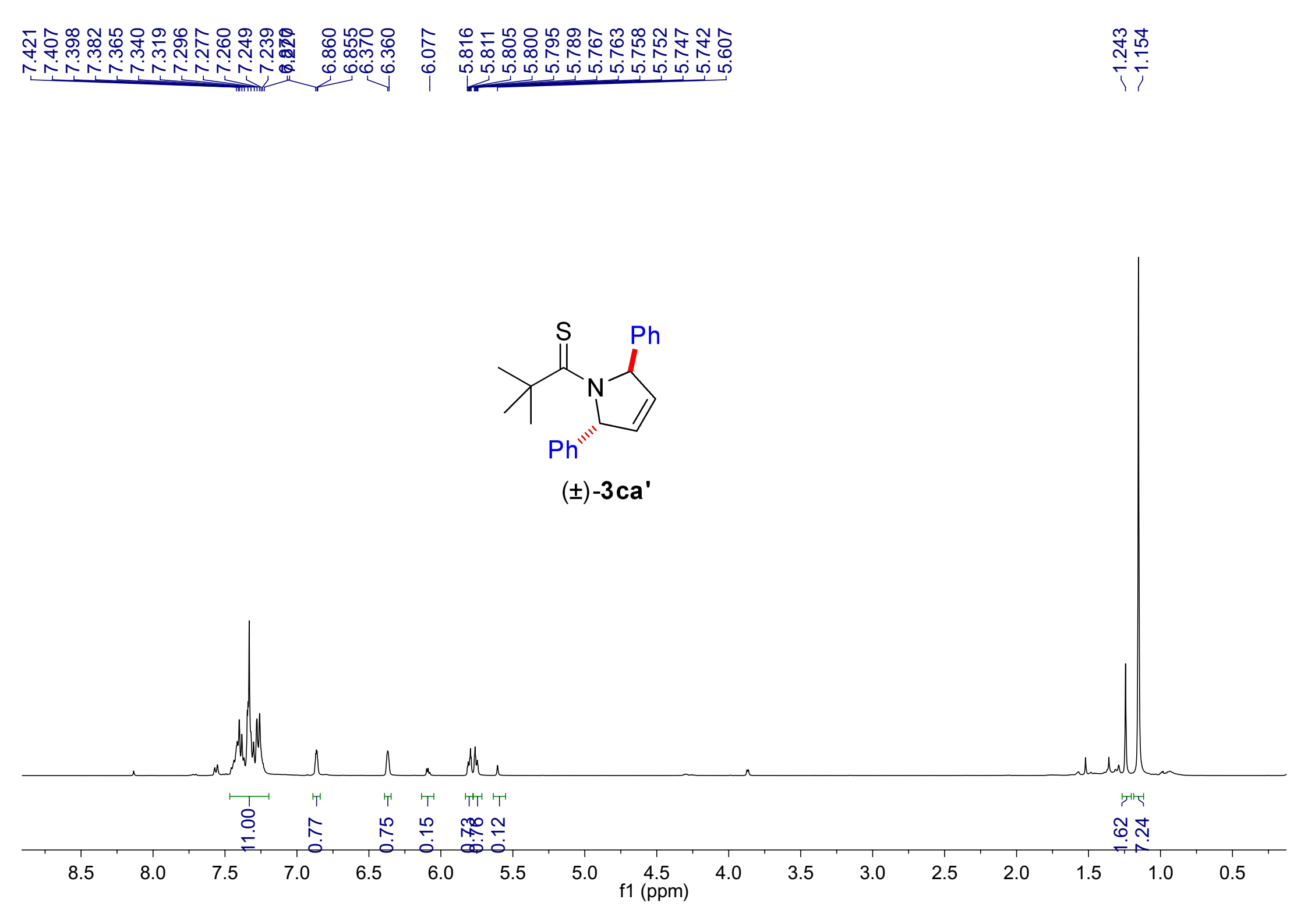

7.366
7.360
7.346
7.340
7.331
7.315
7.311
7.280
7.272
7.250
7.235
5.850
5.845
5.839
5.657
5.652
5.646
4.520
4.514
4.508
4.501
4.495
4.147
4.133
3.427
3.421
3.414
3.408
3.402
2.392
2.359
2.323
2.290
1.897
1.882
1.652
1.569
1.559
1.448
1.435
1.417
1.404
1.371
1.358
1.341
Ph
Ad
N
13
4.02
1.00
0.96
0.93
0.97
0.99
0.98
2.07
3.14
6.80
6.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

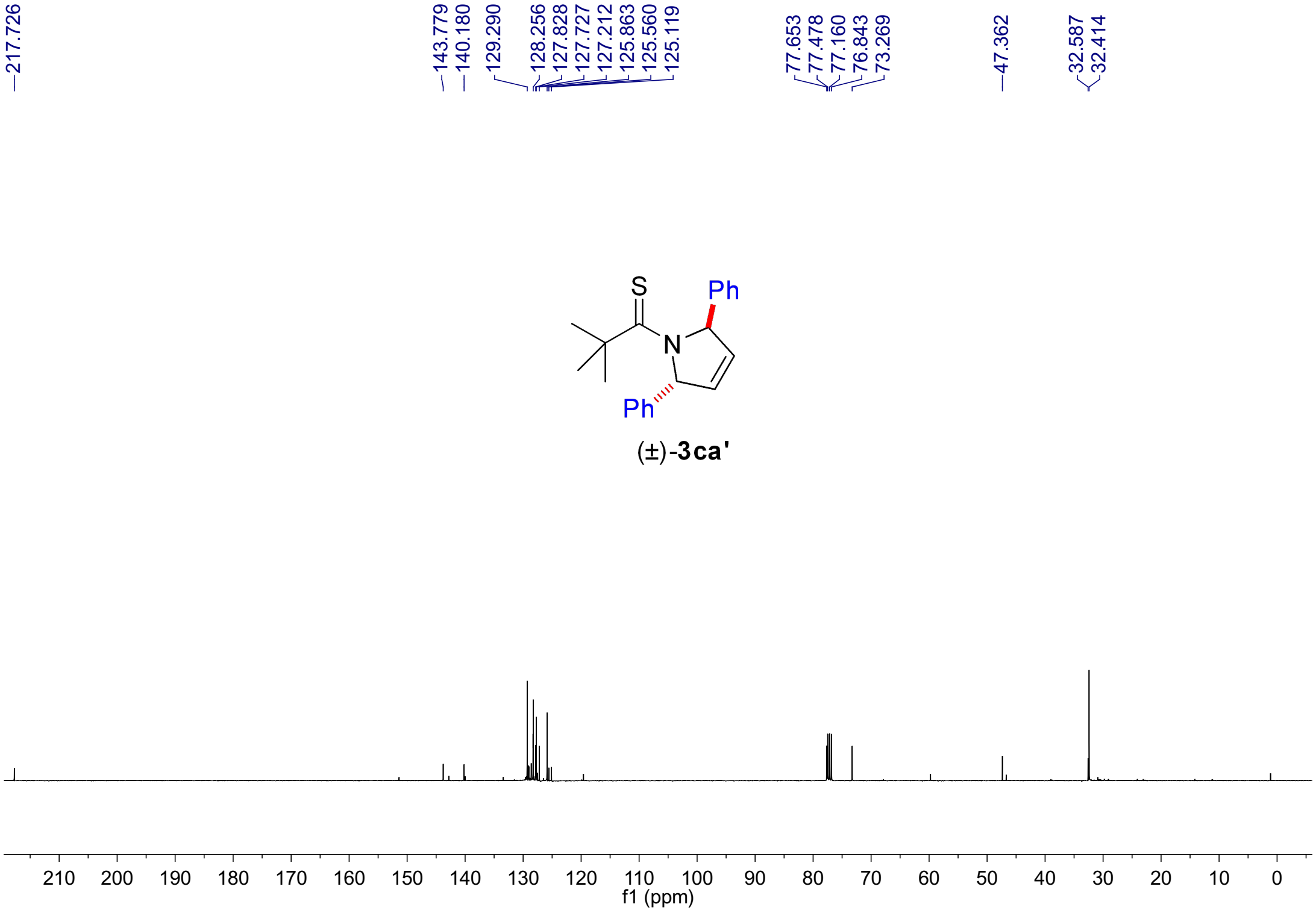

144.39
132.36
128.17
128.12
127.31
127.00
77.79
77.48
77.16
76.84
69.13
64.29
41.37
37.32
34.86
28.70
Ph
Ad
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

**13**


7.370
7.356
7.351
7.345
7.337
7.328
7.323
7.318
7.304
7.287
7.284
7.267
7.261
7.248
6.941
6.483
6.068
6.058
5.799
5.766
5.761
5.754
5.750
5.745
5.672
3.877
3.867
2.163
2.023
1.961
1.924
1.901
1.877
1.836
1.807
1.637
1.621
1.616
1.586
1.564
1.536
1.526
1.495
S
Ph
Ad
N
Ph
(±)-3aa
0.17
11.00
1.16
0.35
0.06
0.29
0.02
0.39
0.29
0.30
0.39
0.39
0.98
2.82
6.08
5.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


219.134
151.454
143.231
140.307
133.470
128.225
125.076
119.369
77.753
77.477
77.161
76.844
73.340
60.144
50.218
49.424
43.039
36.356
29.027
28.916
28.712
S
Ph
Ad
N
Ph
(±)-3aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.421
7.407
7.398
7.382
7.365
7.340
7.319
7.296
7.277
7.260
7.249
7.239
6.860
6.855
6.370
6.360
6.077
5.816
5.811
5.805
5.800
5.795
5.789
5.767
5.763
5.758
5.752
5.747
5.742
5.607
1.243
1.154
S
Ph
N
Ph
(±)-3ca'
11.00
0.77
0.75
0.15
0.73
0.78
0.12
1.62
7.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


217.726
143.779
140.180
129.290
128.256
127.828
127.727
127.212
125.863
125.560
125.119
77.653
77.478
77.160
76.843
73.269
47.362
32.587
32.414
S
Ph
N
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(±)-**3ca'**