Supporting Information

Palladium-Catalyzed Trifluoroacetate-Promoted Mono-Arylation of β Methyl Group of Alanine at Room Temperature: Synthesis of β-Arylated α-Amino Acids through Sequential C-H Functionalization

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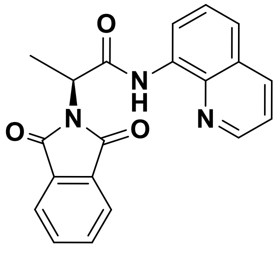
1. **Reagents**: All commercial materials were used as received unless otherwise noted. The toluene for reaction was obtained from a JC Meyer solvent dispensing system and used without further purification. Flash chromatography was performed using 230-400 mesh SiliaFlash 60® silica gel (Silicycle Inc.). $PhI(OAc)_2$ (98%, Aldrich), $Pd(OAc)_2$ (98%, Aldrich), silver trifluoroacetate (98%, Alfa Aesar), 1,1,2,2-tetrachloroethane (98.5%, Acros) and potassium bicarbonate (99.7%-100.5%, Alfa Aesar) were used in the Pd-catalyzed reactions. 8-aminoquinoline (AQ) (98%, Aldrich) were purchased from Aldrich and used without further purification.

2. **Instruments**: NMR spectra were recorded on Bruker CDPX-300 or AV-360 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, q = quartet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument.

3. Preparation of alanine substrate 10



10

Step 1: A mixture of L-alanine (10 g, 112 mmol, 1.0 equiv), phthalic anhydride (18.3 g, 123 mmol, 1.1 equiv), triethylamine (10.5 mL, 123 mmol, 1.1 equiv) in toluene (200 mL) was refluxed in a round bottom flask equipped with a Dean-Stark trap overnight. The reaction mixture was concentrated *in vacuo* to give the crude product. The *N*-Phth protected acid was used in the next step without further purification.

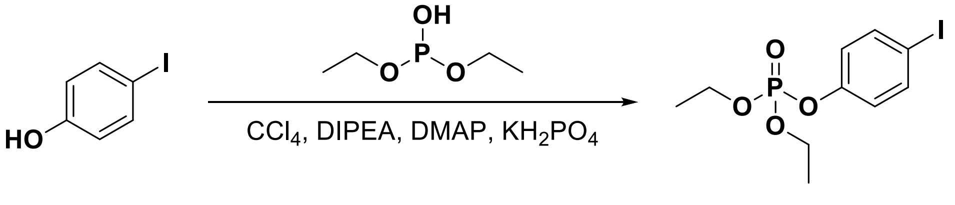
Step 2: A mixture of *N*-Phth protected acid, $SOCl_2$ (10.6 mL, 146 mmol, 1.3 equiv) in anhydrous dichloromethane (200 mL) was stirred at room temperature overnight. The reaction mixture was then concentrated *in vacuo* to give the crude acyl chloride which was used for the next step without further purification.

Step 3: A mixture of acyl chloride, 8-aminoquinoline (19.5 g, 112 mmol, 1 equiv), and triethylamine (23 mL, 168 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (200 mL) was stirred at room temperature overnight. The reaction mixture was then washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography (ethyl acetate : dichloromethane = 1:99) to give compound **10**[1,2] as a yellow solid in about 70% yield over 3 steps.

4. Preparation of aryl iodide for C-H arylation

Aryl iodides for the synthesis of compounds **15**, **18**, **21**, **22**, **23**, **24**, **25**, **26** are commercially available. Aryl iodides for the synthesis of compound **16**, **17**, **19**, **20** are prepared as follows.

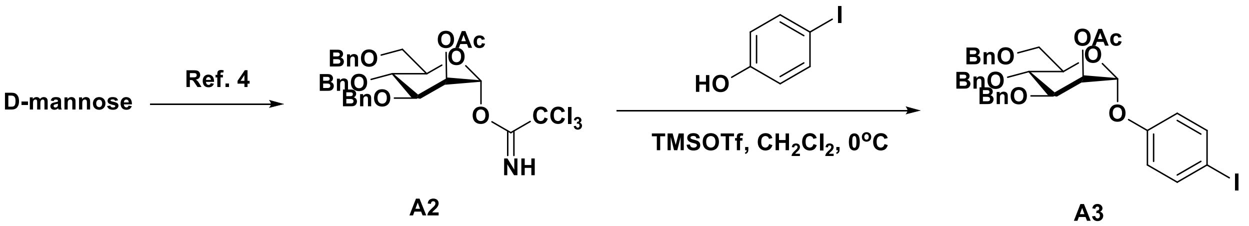
4.1 Preparation of aryl iodide A1 for the synthesis of compound 16



A1

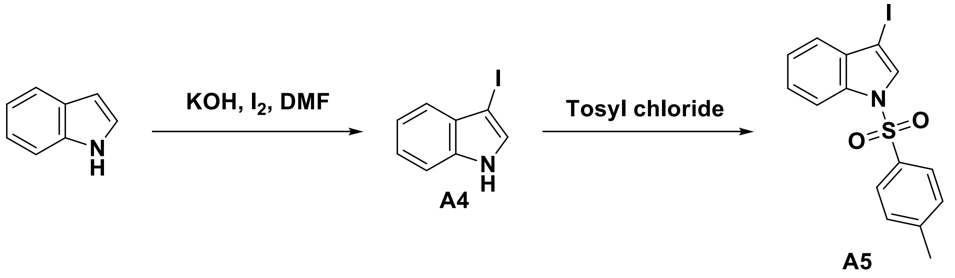
A1 was prepared following modified procedure reported by Silverberg.[3] A multi-necked round-bottom flask containing a stir bar was oven-dried, fitted with septa, a thermometer, and N_2 inlet. The flask was charged with 4-iodophenol (1.1 g, 5 mmol, 1 equiv) and anhydrous acetonitrile (10 mL). The mixture was stirred to dissolve 4-iodophenol and then cooled to -10 ^{o}C. CCl_4 (2.4 mL, 25 mmol, 5 equiv) was added and the solution stirred. N,N-diisopropylethylamine (1.83 mL, 10.5 mmol, 2.1 equiv) followed by N,N-dimethylaminopyridine (61 mg, 0.5 mmol, 0.1 equiv) were added. One minute later, diethyl phosphite (966 µL, 7.5 mmol, 1.5 equiv) was added dropwise, and the internal temperature at was kept at or below -10 ^{o}C. When the reaction was complete as determined by TLC, 0.5 M aqueous KH_2PO_4 (3.2 mL) was added and the mixture was allowed to warm to room temperature. The mixture was extracted three times with ethyl acetate. The combined organic phase was washed successively with water and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Flash silica gel chromatography (hexanes : ethyl acetate = 5:1) gave compound **A1** as a yellowish oil in 84% yield. **^{1}H NMR** ($CDCl_3$, 300 MHz, ppm): δ 1.27-1.32 (m, 6H), 4.10-4.20 (m, 4H), 6.93-6.96 (d, *J* = 8.7 Hz, 2H), 7.56-7.59 (d, *J* = 9.0Hz, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz, ppm) δ 16.55, 16.64, 65.19, 65.27, 89.08, 122.66, 122.73, 139.15, 151.11, 151.20; **HRMS**: calculated for $C_{10}H_{15}IO_4P$ [M+H$^+$]: 356.9753; found: 356.9749.

4.2 Preparation of aryl iodide A3 for the synthesis of compound 17



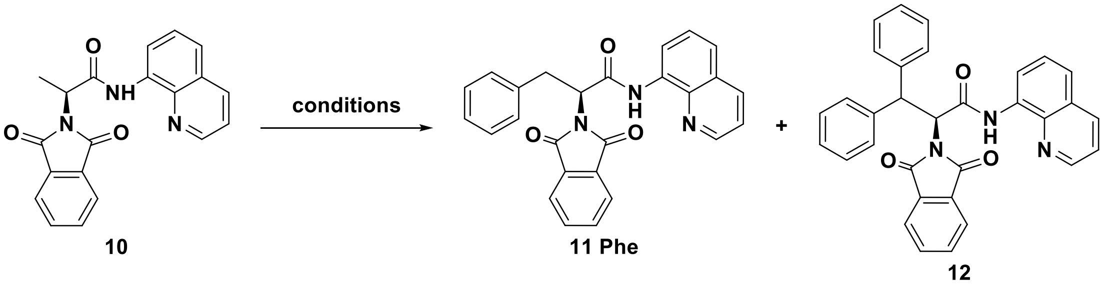
Glycosyl imidate **A2** was prepared from D-mannose following the procedure reported by Barry.[4] To a ice-water cooled solution of **A2** (1.5 g, 2.35 mmol, 1 equiv) and 4-iodophenol (517 mg, 2.35 mmol, 1 equiv) in dichloromethane (10 mL) was added TMSOTf (22 μL, 0.118 mmol, 0.05 equiv). After 30 minutes, the reaction was quenched by adding triethylamine (30 μL). The residue after concentration *in vacuo* was purified by flash silica gel chromatography (hexanes : ethyl acetate = 10:1), giving 1.15 g of product as colorless syrup in 67% yield. **^{1}H NMR** ($CDCl_3$, 300 MHz, ppm): δ 2.31 (s, 3H), 3.76-3.79 (d, *J* = 10.5 Hz, 1H), 3.93-4.02 (m, 2H), 4.15-4.21 (t, *J* = 9.3, 9.6 Hz, 1H), 4.31-4.34 (d, *J* = 9.3 Hz, 1H), 4.54-4.58 (d, *J* = 11.7Hz, 1H), 4.63-4.67 (d, *J* = 10.5Hz, 1H), 4.73-4.80 (t, *J* = 10.8, 12.0 Hz, 1H), 4.89-4.93 (d, *J* = 11.1 Hz, 1H), 5.02-5.06 (d, *J* = 10.8 Hz, 1H), 5.70 (s, 2H), 6.95-6.98 (d, *J* = 8.4 Hz, 2H), 7.30-7.49 (m, 15H), 7.65-7.68 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz, ppm) δ 21.49, 68.73, 68.83, 72.40, 72.47, 73.73, 74.30, 75.66, 78.27, 85.76, 96.34, 119.14, 128.07, 128.11, 128.22, 128.26, 128.50, 128.74, 128.87, 138.18, 138.36, 138.62, 138.80; **HRMS**: calculated for $C_{35}H_{36}IO_7$ [M+H$^+$]: 695.1506; found: 695.1502.

4.3 Preparation of aryl iodide A4 and A5 for the synthesis of compounds 19 and 20



Intermediates **A4** and **A5** were prepared following the procedure reported by Müller[5] starting from commercially available indole.

5. General procedure for screening conditions in Table 1



Reactions in **Table 1** were performed in 4 mL capped vials according to the conditions listed in **Table1** at a 0.1 mmol scale. After completion, the reactions were diluted with dichloromethane (5 mL), then filtrated through a pad of Celite. After concentration *in vacuo*, the crude residue was dissolved in 1000 μL of deuterated chloroform for ^{1}H-NMR analysis. Yields of mono- and di-arylated product were determined as follows:

$$\text{yield}_{\text{mono-}} = \frac{\frac{A1}{2}}{\frac{A1}{2}+\frac{A3}{3}+A2} \times 100\%$$

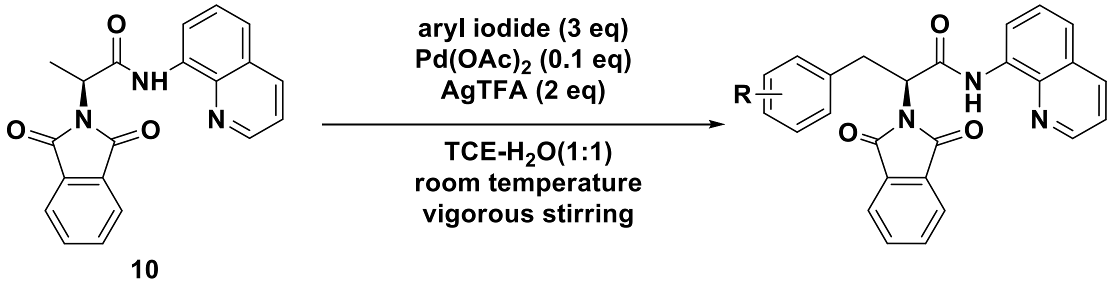
$$\text{yield}_{\text{di-}} = \frac{A2}{\frac{A1}{2}+\frac{A3}{3}+A2} \times 100\%$$

A1 = integration of multiplet (δ 3.83~3.86) which is methylene of compound **11**

A2 = integration of doublet (δ 5.65~5.68) which is *α*-H of compound **12**

A3 = integration of doublet (δ 2.00~2.02) which is methyl of compound **10**

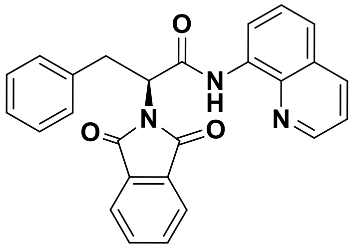
6. General procedure for AQ-directed Pd-catalyzed C-H mono-arylation



Arylation reactions at a 0.2 mmol scale: Alanine substrate **10** (69 mg, 0.2 mmol, 1 equiv), aryl iodide (3 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), silver trifluoroacetate (88.4 mg, 0.4 mmol, 2 equiv) were suspended into 1,1,2,2-tetrachloroethane (TCE) (1 mL) and water (1 mL). The resulting solution was stirred **vigorously** (important) at room temperature. After 2 days, 1 M aq. NaOH solution (2 mL) and dichloromethane (2 mL) were added. Organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 mL) twice. Combined organic layer was concentrated *in vacuo*, and the resulting residue was purified by flash silica gel chromatography.

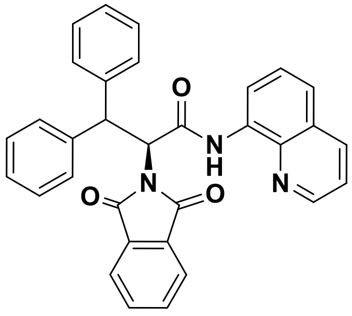
Arylation reactions at a 3 mmol scale: Alanine substrate **10** (1035 mg, 3 mmol, 1 equiv), aryl iodide (3 equiv), $Pd(OAc)_2$ (67.2 mg, 0.3 mmol, 0.1 equiv), silver trifluoroacetate (1.33 g, 6 mmol, 2 equiv) was suspended into TCE (15 mL) and water (15 mL). The resulting reaction mixture was stirred **vigorously** (important) at room temperature. After 2 days, 1M aq. NaOH solution (30 mL) and dichloromethane (30 mL) were added. Organic layer was separated, and the aqueous layer was extracted with dichloromethane (30 mL) twice. Combined organic layer was concentrated *in vacuo*, and the resulting residue was purified by flash silica gel chromatography.

Arylation reactions at a 1 mmol scale at 45 ^{o}C: Alanine substrate **10** (345 mg, 1 mmol, 1 equiv), aryl iodide **A5** (1.2 g, 3 mmol, 3 equiv), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol, 0.1 equiv), silver trifluoroacetate (442 mg, 2 mmol, 2 equiv) was suspended into TCE (5 mL) and water (5 mL). The resulting reaction mixture was stirred **vigorously** (important) at 45 ^{o}C. After 24 hours, 1M aq. NaOH solution (10 mL) and dichloromethane (10 mL) were added. Organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL) twice. Combined organic layer was concentrated *in vacuo*,, and the resulting residue was purified by flash silica gel chromatography.



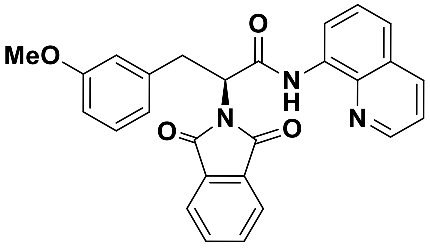
11

Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 75 mg of product as a white solid in 89% yield at a 0.2 mmol scale; 1.26 g product in 88% yield at a 3 mmol scale. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 3.83-3.86 (m, 2H), 5.47-5.51 (t, *J* = 6.8, 9.4 Hz, 1H), 7.20-7.33 (m, 5H), 7.40-7.44 (q, 1H), 7.54-7.55 (m, 2H), 7.72-7.75 (m, 2H), 7.84-7.86 (m, 2H), 8.14-8.16 (d, *J* = 8.3 Hz, 1H), 8.64-8.65 (d, *J* = 4.0 Hz, 1H), 8.76-8.79 (dd, *J* = 2.5, 3.2 Hz, 1H), 10.37 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 34.76, 56.24, 116.77, 121.67, 122.04, 123.59, 127.00, 127.32, 127.85, 128.73, 129.04, 131.62, 133.85, 134.22, 136.28, 136.72, 138.47, 148.33, 166.44, 167.93; **HRMS**: calculated for $C_{26}H_{20}N_3O_3$ [M+H$^+$]: 422.1505; found: 422.1505.



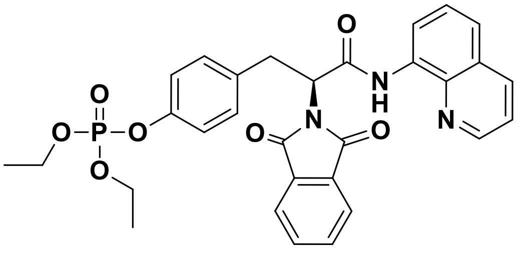
12

Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99). **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 5.60-5.64 (d, *J* = 12.2 Hz, 1H), 5.98-5.62 (d, *J* = 12.2 Hz, 1H), 7.01-7.05 (t, *J*7.2, 7.6 Hz, 1H), 7.13-7.19 (m, 3H), 7.28-7.43 (m, 7H), 7.60-7.64 (m, 4H), 7.73-7.75 (m, 2H), 8.05-8.08 (dd, *J* = 1.4, 6.8 Hz, 1H), 8.62-8.67 (m, 2H), 10.16 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 50.90, 59.11, 117.42, 122.04, 122.45, 124.00, 127.44, 127.68, 127.87, 128.23, 128.36, 128.69, 129.18, 129.78, 131.93, 134.57, 136.54, 139.00, 141.08, 141.37, 148.61, 166.16, 168.43; **HRMS**: calculated for $C_{32}H_{24}N_3O_3$ [M+H$^+$]: 498.1818; found: 498.1815.



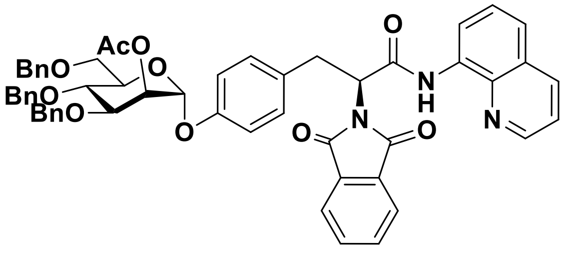
15

Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 75 mg of product as a white foam in 83% yield at a 0.2 mmol scale; 1.15 g of product in 85% yield at a 3 mmol scale. **^{1}H NMR** (CDCl$_3$, 300 MHz, ppm): δ 3.54 (s, 3H), 3.66-3.70 (m, 2H), 5.33-5.39 (q, 1H), 6.57-6.60 (d, *J* = 8.1 Hz, 1H), 6.72-6.78 (m, 2H), 6.99-7.04 (t, *J* = 7.8, 7.8 Hz, 1H), 7.20-7.24 (q, 1H), 7.34-7.36 (m, 2H), 7.54-7.55 (m, 2H), 7.66-7.69 (m, 2H), 7.93-7.96 (d, *J* = 8.1 Hz, 1H), 8.45-8.46 (d, *J* = 3.3 Hz, 1H), 8.60-8.63 (dd, *J* = 2.1, 4.2 Hz, 1H), 10.20 (s, 1H); **^{13}C NMR** (CDCl$_3$, 75 MHz, ppm) δ 35.30, 55.57, 56.63, 113.42, 114.72, 117.17, 121.79, 122.12, 122.51, 123.99, 127.69, 128.27, 130.21, 132.10, 134.31, 134.69, 136.70, 138.76, 138.88, 148.77, 160.25, 166.88, 168.38; **HRMS**: calculated for $C_{27}H_{22}N_3O_4$ [M+H$^+$]: 452.1610; found: 452.1610.



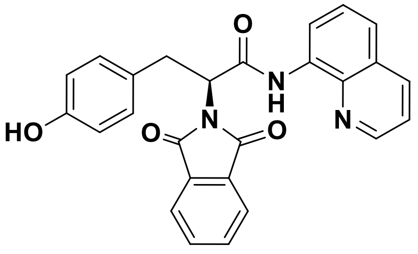
16

Flash silica gel chromatography (ethyl acetate : dichloromethane = 15:85) gave 82 mg of product as a yellowish solid in 72% yield. **^{1}H NMR** (CDCl$_3$, 300 MHz, ppm): δ 1.22-1.26 (m, 6H), 3.77-3.80 (d, *J* = 8.1 Hz, 2H), 4.10-4.14 (m, 4H), 5.40-5.45 (t, *J* = 8.4, 8.1 Hz, 1H), 7.07-7.10 (d, *J* = 8.1 Hz, 2H), 7.25-7.35 (m, 4H), 7.45-7.46 (m, 2H), 7.67-7.68 (m, 2H), 7.77-7.78 (m, 2H), 8.04-8.07 (d, *J* = 8.1 Hz, 1H), 8.56-8.57 (m, 1H), 8.68-8.70 (m, 1H), 10.30 (s, 1H); **^{13}C NMR** (CDCl$_3$, 75 MHz, ppm) δ 16.42, 16.50, 34.39, 56.48, 64.94, 65.02, 117.08, 120.59, 120.66, 122.10, 122.50, 123.97, 127.60, 128.21, 130.72, 131.92, 133.90, 134.15, 134.71, 136.66, 138.78, 148.76, 150.06, 150.15, 166.63, 168.26; **^{31}P NMR** (CDCl$_3$, 145 MHz, ppm) δ -6.44; **HRMS**: calculated for $C_{30}H_{29}N_3O_7P$ [M+H$^+$]: 574.1743; found: 574.1744.



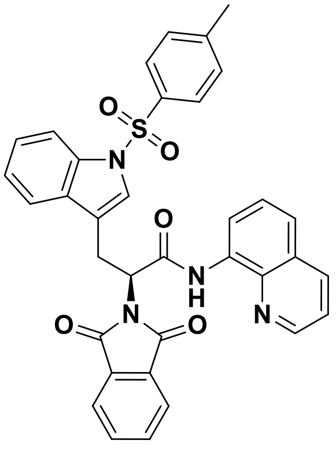
17

Flash silica gel chromatography (ethyl acetate : dichloromethane = 5:95) gave 154 mg of product as a white foam in 85% yield. **^{1}H NMR** ($CDCl_3$, 300 MHz, ppm): δ 2.19-2.20 (d, *J* = 1.8 Hz, 3H), 3.56-3.64 (t, *J*11.1, 12.9 Hz, 1H), 3.78-3.87 (m, 4H), 4.02-4.09 (m, 1H), 4.16-4.20 (dd, *J* = 2.7, 6.9 Hz, 1H), 4.41-4.46 (dd, *J* = 4.5, 7.5 Hz, 1H), 4.51-4.55 (d, *J* = 10.8 Hz, 1H), 4.61-4.70 (m, 2H), 4.76-4.80 (d, *J* = 11.1 Hz, 1H), 4.89-4.93 (d, *J* = 10.5 Hz, 1H), 5.41-5.47 (t, *J* = 7.5, 8.7 Hz, 1H), 5.51-5.53 (m, 2H), 6.94-6.97 (d, *J* = 8.4 Hz, 2H), 7.18-7.37 (m, 20H), 7.50-7.52 (m, 2H), 7.66-7.70 (m, 2H), 7.81-7.84 (m, 2H), 8.08-8.11 (d, *J* = 8.1 Hz, 1H), 8.61-8.62 (m, 1H), 8.75-8.78 (dd, *J* = 2.4, 4.2 Hz, 1H), 10.34 (s, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz, ppm) δ 21.58, 34.43, 56.71, 68.88, 68.99, 72.39, 72.45, 73.81, 74.46, 75.69, 78.41, 96.44, 117.18, 122.11, 122.47, 124.02, 127.73, 128.12, 128.29, 128.57, 128.80, 128.93, 130.63, 131.21, 132.04, 134.30, 134.65, 136.69, 138.31, 138.55, 138.80, 138.89, 148.74, 155.28, 155.34, 166.85, 168.34, 170.87; **HRMS**: calculated for $C_{55}H_{50}N_3O_{10}$ [M+H$^+$]: 912.3496; found: 912.3493.



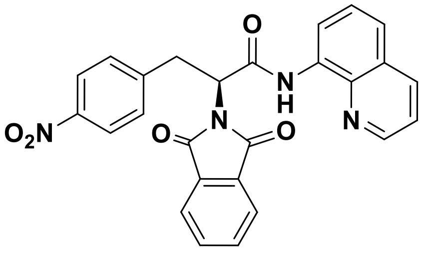
18

Flash silica gel chromatography (ethyl acetate : dichloromethane = 5:95) gave 78 mg of product as a white foam in 90% yield. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 3.70-3.73 (m, 2H), 5.14 (s, 1H), 5.36-5.41 (q, 1H), 6.66-6.68 (d, *J* = 6.9 Hz, 2H), 7.12-7.14 (d, *J* = 6.9 Hz, 2H), 7.38-7.41 (q, 1H), 7.50-7.52 (m, 2H), 7.69-7.72 (m, 2H), 7.81-7.83 (m, 2H), 8.11-8.14 (d, *J* = 6.9 Hz, 1H), 8.62-8.64 (m, 1H), 8.71-8.74 (m, 1H), 10.33 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 34.49, 56.94, 116.16, 117.35, 122.20, 122.60, 124.16, 127.86, 128.39, 129.12, 130.76, 132.12, 134.36, 134.78, 136.82, 139.01, 148.87, 155.12, 167.06, 168.57; **HRMS**: calculated for $C_{26}H_{20}N_3O_4$ [M+H$^+$]: 438.1454; found: 438.1453.



20

Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 78 mg of product as a white foam in 62% yield; 520 mg product in 83% yield at a 1 mmol scale at 45 °C. **^{1}H NMR** (CDCl$_3$, 300 MHz, ppm): δ 2.16 (s, 3H), 3.78-3.86 (m, 1H), 3.94-4.01 (m, 1H), 5.52-5.57 (t, *J* = 7.2, 8.4 Hz, 1H), 6.88-6.91 (d, *J* = 8.1 Hz, 2H), 7.21-7.35 (m, 4H), 7.47-7.72 (m, 8H), 7.80-7.84 (m, 2H), 7.93-7.96 (d, *J* = 8.1 Hz, 1H), 8.05-8.08 (d, *J* = 8.1 Hz, 1H), 8.51-8.52 (m, 1H), 8.69-8.72 (m, 1H), 10.31 (s, 1H); **^{13}C NMR** (CDCl$_3$, 75 MHz, ppm) δ 21.96, 25.55, 54.69, 114.25, 117.18, 118.46, 119.94, 122.21, 122.63, 123.95, 124.16, 125.24, 125.54, 127.08, 127.68, 128.27, 130.15, 130.82, 132.15, 134.25, 134.83, 135.44, 135.77, 136.67, 138.82, 145.14, 148.94, 166.54, 168.30; **HRMS**: calculated for $C_{35}H_{27}N_4O_5S$ [M+H$^+$]: 615.1702; found: 615.1704.



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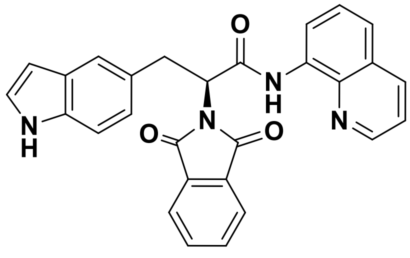
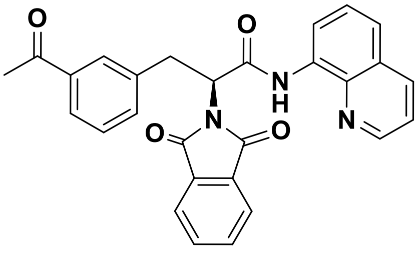
Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 63 mg of product as a yellow solid in 68% yield at a 0.2 mmol scale; 0.95 g product in 68% yield at a 3 mmol scale. **^{1}H NMR** (CDCl$_3$, 300 MHz, ppm): δ 3.89-3.92 (m, 2H), 5.44-5.50 (q, 1H), 7.35-7.39 (q, 1H), 7.44-7.52 (m, 4H), 7.71-7.76 (m, 2H), 7.82-7.85 (m, 2H), 8.06-8.13 (m, 3H), 8.53-8.55 (dd, *J* = 1.5, 2.7 Hz, 1H), 8.68-8.71 (m, 1H), 10.28 (s, 1H); **^{13}C NMR** (CDCl$_3$, 75 MHz, ppm) δ 35.12, 56.03, 117.38, 122.31, 122.84, 124.39, 124.51, 127.86, 128.43, 130.59, 131.94, 134.14, 135.14, 136.93, 138.97, 145.31, 147.66, 148.93, 166.17, 168.33; **HRMS**: calculated for $C_{26}H_{19}N_4O_5$ [M+H$^+$]: 467.1355; found: 467.1356.



22

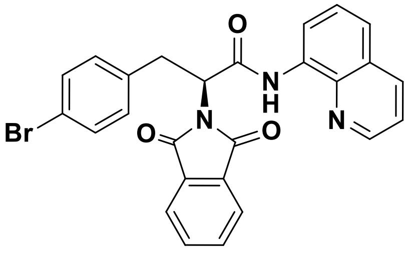
Flash silica gel chromatography (ethyl acetate : dichloromethane = 15:85) gave 73 mg of product as a white solid in 79% yield. **^{1}H NMR** (DMSO-*d6*, 360 MHz, ppm): δ 3.66-3.82 (m, 2H), 5.61-5.66 (dd, *J* = 5.4, 5.8 Hz, 1H), 6.28 (s, 1H), 7.05-7.08 (d, *J* = 8.6 Hz, 1H), 7.22-7.24 (m, 2H), 7.45 (s, 1H), 7.59-7.63 (m, 2H), 7.70-7.72 (d, *J* = 8.3 Hz, 1H), 7.82-7.83 (m, 4H), 8.40-8.43 (d, *J* = 8.3 Hz, 1H), 8.53-8.55 (d, *J* = 7.6 Hz, 1H), 8.81-8.82 (m, 1H), 10.58 (s, 1H), 10.96 (s, 1H); **^{13}C NMR** (DMSO-*d6*, 90 MHz, ppm) δ 34.27, 56.30, 100.82, 111.31, 117.24, 120.19, 121.97, 122.30, 122.60, 123.36, 125.46, 126.98, 127.05, 127.73, 127.90, 130.94, 133.98, 134.81, 134.90, 136.71, 138.37, 149.16, 167.08, 167.70; **HRMS**: calculated for $C_{28}H_{21}N_4O_3$ [M+H$^+$]: 461.1614; found: 461.1612.



23

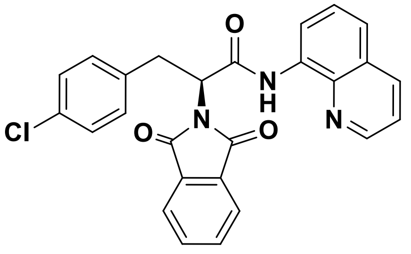
Flash silica gel chromatography (ethyl acetate : dichloromethane = 2:98) gave 73 mg of product as a white foam in 79% yield. **^{1}H NMR** (CDCl$_3$, 360 MHz, ppm): δ 2.47 (s, 3H), 3.84-3.88 (m, 2H), 5.43-5.48 (q, 1H), 7.31-7.33 (d, *J* = 7.6 Hz, 1H), 7.35-7.39 (q, 1H), 7.50-7.51 (m, 3H), 7.69-

7.85 (m, 6H), 8.09-8.12 (dd, *J* = 1.4, 6.8 Hz, 1H), 8.57-8.59 (dd, *J* = 1.4, 2.9 Hz, 1H), 8.71-8.73 (dd, *J* = 3.2, 2.5 Hz, 1H), 10.31 (s, 1H); **^{13}C NMR** (CDCl$_3$, 90 MHz, ppm) δ 27.14, 35.05, 56.49, 117.27, 122.20, 122.64, 124.16, 127.45, 127.78, 128.33, 129.57, 131.98, 134.19, 134.32, 134.88, 136.80, 137.88, 137.93, 138.91, 148.86, 166.56, 168.35, 198.44; **HRMS**: calculated for $C_{28}H_{22}N_3O_4$ [M+H$^+$]: 464.1610; found: 464.1608.



24

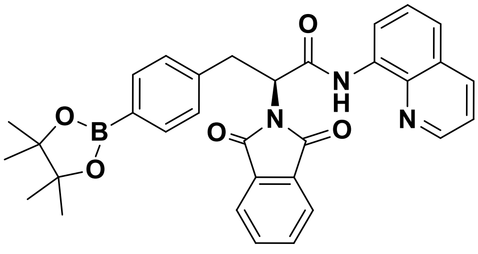
Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 85 mg of product as a white foam in 85% yield. **^{1}H NMR** (CDCl$_3$, 360 MHz, ppm): δ 3.75-3.78 (d, *J* = 8.3 Hz, 2H), 5.40-5.45 (t, *J* = 7.9, 9.0 Hz, 1H), 7.15-7.17 (d, *J* = 7.9 Hz, 2H), 7.31-7.33 (m, 3H), 7.45-7.47 (m, 2H), 7.66-7.68 (m, 2H), 7.78-7.81 (m, 2H), 8.05-8.07 (d, *J* = 8.3 Hz, 1H), 8.55-8.56 (d, *J* = 3.2 Hz, 1H), 8.69-8.71 (dd, *J* = 2.2, 4.0 Hz, 1H), 10.27 (s, 1H); **^{13}C NMR** (CDCl$_3$, 90 MHz, ppm) δ 34.59, 56.27, 117.12, 121.36, 122.09, 122.53, 124.05, 127.63, 128.19, 131.19, 131.86, 132.23, 134.09, 134.75, 136.21, 136.66, 138.73, 148.73, 166.49, 168.29; **HRMS**: calculated for $C_{26}H_{19}BrN_3O_3$ [M+H$^+$]: 500.0610; found: 500.0607.



25

Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 78 mg of product as a white foam in 86% yield at a 0.2 mmol scale; 1.3 g product in 89% yield at a 3 mmol scale. **^{1}H NMR** (CDCl$_3$, 300 MHz, ppm): δ 3.77-3.80 (m, 2H), 5.40-5.46 (q, 1H), 7.15-7.26 (m, 4H), 7.31-7.35 (q, 1H), 7.43-7.50 (m, 2H), 7.66-7.70 (m, 2H), 7.77-7.81 (m, 2H), 8.04-8.08 (dd, *J* = 1.5, 6.69 Hz, 1H), 8.55-8.57 (dd, *J* = 1.5, 2.7 Hz, 1H), 8.69-8.72 (dd, *J* = 2.7, 3.6 Hz, 1H), 10.27

(s, 1H); ^{13}**C NMR** ($CDCl_3$, 75 MHz, ppm) δ 34.61, 56.44, 117.20, 122.17, 122.60, 124.11, 127.71, 128.28, 129.37, 130.90, 131.97, 133.29, 134.20, 134.82, 135.79, 136.74, 138.84, 148.80, 166.59, 168.36; **HRMS**: calculated for $C_{26}H_{19}ClN_3O_3$ [M+H$^+$]: 456.1115; found: 456.1114.

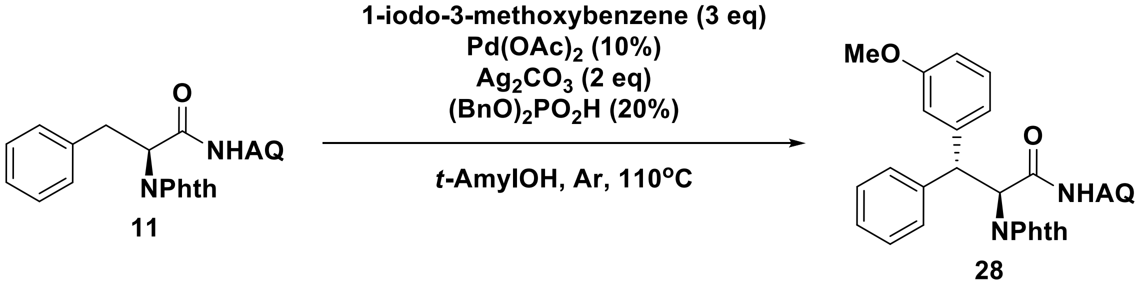


26

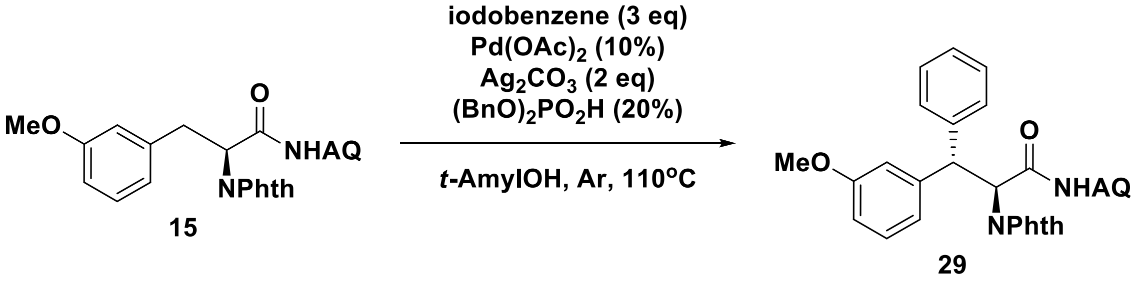
Flash silica gel chromatography (ethyl acetate : dichloromethane = 5:95) gave 84 mg of product as a white solid in 77% yield. ^{1}**H NMR** ($CDCl_3$, 300 MHz, ppm): δ 1.30 (s, 12H), 3.82-3.85 (m, 2H), 5.43-5.49 (q, 1H), 7.29-7.32 (d, *J* = 7.8 Hz, 2H), 7.35-7.40 (q, 1H), 7.49-7.51 (m, 2H), 7.66-7.71 (m, 4H), 7.80-7.83 (m, 2H), 8.09-8.13 (dd, *J* = 1.5, 6.9 Hz, 1H), 8.59-8.61 (dd, *J* = 1.5, 2.4 Hz, 1H), 8.71-8.74 (dd, *J* = 3.0, 2.7 Hz, 1H), 10.31 (s, 1H); ^{13}**C NMR** ($CDCl_3$, 75 MHz, ppm) δ 25.41, 25.55, 35.46, 56.68, 84.36, 117.37, 122.22, 122.61, 124.21, 127.89, 128.44, 129.02, 132.23, 134.45, 134.79, 135.80, 136.84, 139.09, 140.58, 148.90, 166.94, 168.49; **HRMS**: calculated for $C_{32}H_{31}BN_3O_5$ [M+H$^+$]: 548.2357; found: 548.2356.

7. Synthesis of compounds 28 and 29

General conditions C for secondary C-H arylation:[6] Compound **11** or **15** (0.1 mmol), corresponding aryl iodide (0.3 mmol, 3 equiv), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol, 0.1 equiv), silver carbonate (55 mg, 0.2 mmol, 2 equiv) and dibenzyl phosphate (5.6 mg, 0.02 mmol, 0.2 equiv) were suspended in *t*-AmylOH (1 mL). The mixture was heated at 110 °C under argon atmosphere. After 12 hours, reaction mixture was diluted with dichloromethane (5 mL) after cooled to room temperature. The residue after concentration was directly purified on flash silica gel chromatography.

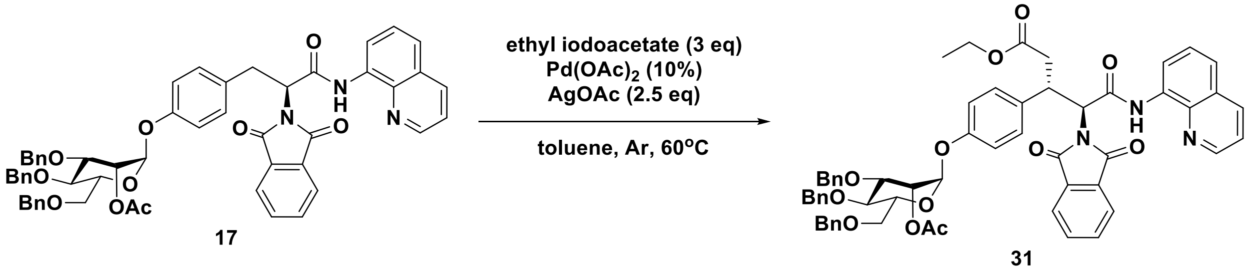


^{1}H-NMR of crude product showed no other diastereomer formed. Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 49 mg of product as a white solid in 93% yield. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 3.74 (s, 3H), 5.62-5.65 (d, *J* = 12.2 Hz, 1H), 6.02-6.05 (d, *J* = 12.2 Hz, 1H), 6.73-6.75 (d, *J* = 7.6 Hz, 1H), 7.05-7.09 (t, *J* = 7.2, 6.8 Hz, 1H), 7.17-7.29 (m, 5H), 7.38-7.45 (m, 5H), 7.62-7.63 (m, 2H), 7.76-7.77 (m, 2H), 8.07-8.09 (d, *J* = 8.3 Hz, 1H), 8.68-8.69 (m, 2H), 10.17 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 50.94, 55.64, 58.99, 113.48, 114.38, 117.34, 120.68, 122.03, 122.42, 123.92, 127.45, 127.60, 128.16, 128.27, 129.14, 130.79, 131.87, 134.52, 136.49, 138.94, 141.23, 142.55, 148.55, 160.65, 166.10, 168.40; **HRMS**: calculated for $C_{33}H_{26}N_3O_4$ [M+H$^+$]: 528.1923; found: 528.1923.

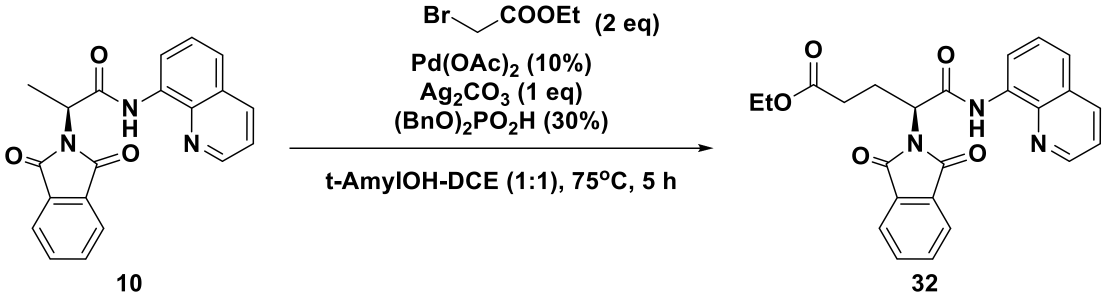


^{1}H-NMR of crude product showed no other diastereomer formed. Flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99) gave 50 mg of product as a white solid in 95% yield. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 3.68 (s, 3H), 5.60-5.64 (d, *J* = 12.2 Hz, 1H), 5.98-6.02 (d, *J* = 12.2 Hz, 1H), 6.56-6.59 (dd, *J* = 1.4, 6.5 Hz, 1H), 6.93 (s, 1H), 6.97-6.99 (d, *J* = 7.9 Hz, 1H), 7.05-7.10 (t, *J* = 7.9, 7.9 Hz, 1H), 7.15-7.19 (t, *J* = 7.6, 7.2 Hz, 1H), 7.28-7.41 (m, 5H), 7.58-7.65 (m, 4H), 7.73-7.75 (m, 2H), 8.03-8.05 (dd, *J* = 1.4, 6.8 Hz, 1H), 8.62-8.67 (m, 2H), 10.18 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 50.79, 55.62, 59.02, 113.31, 113.60, 117.35, 120.59, 122.00, 122.42, 123.95, 127.60, 127.86, 128.16, 128.63, 129.71, 130.13, 131.91, 134.51, 134.55, 136.49, 138.93, 140.92, 142.83, 148.58, 160.01, 166.05, 168.39; **HRMS**: calculated for $C_{33}H_{26}N_3O_4$ [M+H$^+$]: 528.1923; found: 528.1923.

8. Synthesis of compounds 31 and 33

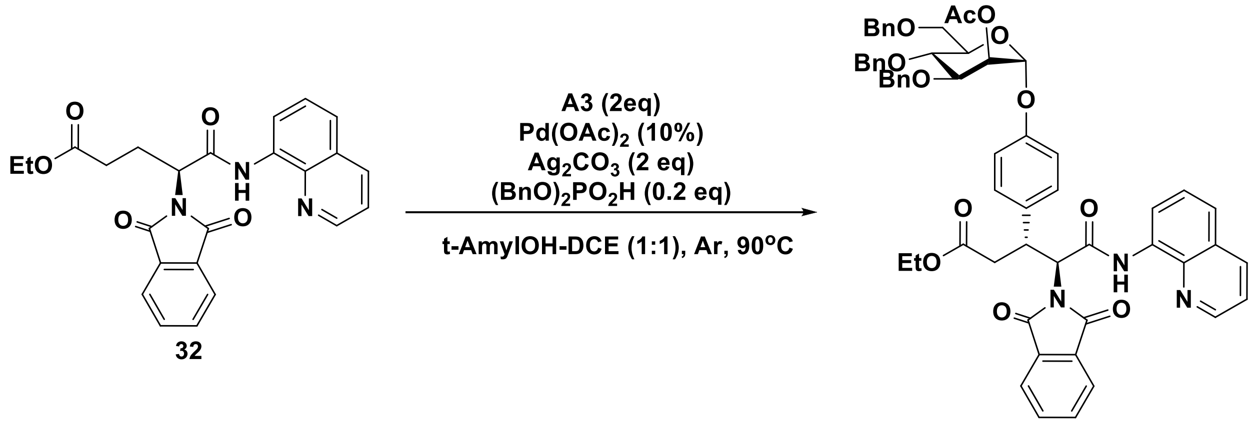


Conditions D for C-H alkylation:[2] Compound **17** (50 mg, 0.055 mmol, 1 equiv), ethyl iodoacetate (35 mg, 0.164 mmol, 3 equiv), $Pd(OAc)_2$ (1.23 mg, 0.0055 mmol, 0.1 equiv) and silver acetate (23 mg, 0.1375 mmol, 2.5 equiv) were suspended in toluene (600 μL). The mixture was heated at 60 °C under argon atmosphere. After 36 hours, reactions were diluted with dichloromethane (5 mL) after cooled to room temperature. ^{1}H-NMR of crude product showed no other diastereomer formed. The residue after evaporation was purified on flash silica gel chromatography (hexanes : ethyl acetate = 3 : 1), giving 45 mg of product as a white foam in 82% yield. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 1.07-1.12 (m, 3H), 2.20 (s, 3H), 2.82-2.90 (m, 1H), 3.17-3.21 (d, *J* = 14.8 Hz, 1H), 3.45-3.55 (dd, *J* = 9.7, 17.6 Hz, 1H), 3.70-3.78 (m, 2H), 3.99-4.08 (m, 3H), 4.11-4.14 (dd, *J* = 2.2, 6.8 Hz, 1H), 4.42-4.52 (m, 2H), 4.59-4.79 (m, 4H), 4.88-4.91 (d, *J* = 10.8 Hz, 1H), 5.38-5.45 (m, 3H), 6.86-6.89 (d, *J* = 7.9 Hz, 2H), 7.17-7.18 (m, 2H), 7.23-7.25 (d, *J* = 8.3 Hz, 2H), 7.29-7.36 (m, 14H), 7.43-7.47 (q, 1H), 7.54-7.63 (m, 4H), 7.73-7.74 (m, 2H), 8.14-8.17 (d, *J* = 8.3 Hz, 1H), 8.82 (s, 2H), 10.67-10.69 (d, *J* = 6.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 14.61, 21.68, 39.97, 40.07, 40.61, 59.69, 59.79, 61.05, 68.77, 68.99, 72.36, 72.40, 72.52, 73.92, 73.96, 74.39, 75.78, 78.40, 96.41, 116.88, 116.93, 117.68, 122.25, 122.81, 124.05, 127.74, 128.24, 128.26, 128.38, 128.42, 128.67, 128.90, 128.94, 129.02, 129.93, 131.67, 133.53, 134.66, 134.73, 134.79, 136.74, 138.34, 138.59, 138.86, 139.18, 149.13, 155.46, 166.69, 166.71, 168.11, 168.14, 171.05, 171.47, 171.49; **HRMS**: calculated for $C_{59}H_{56}N_3O_{12}$ [M+H$^+$]: 998.3864; found: 998.3864.



10 **32**

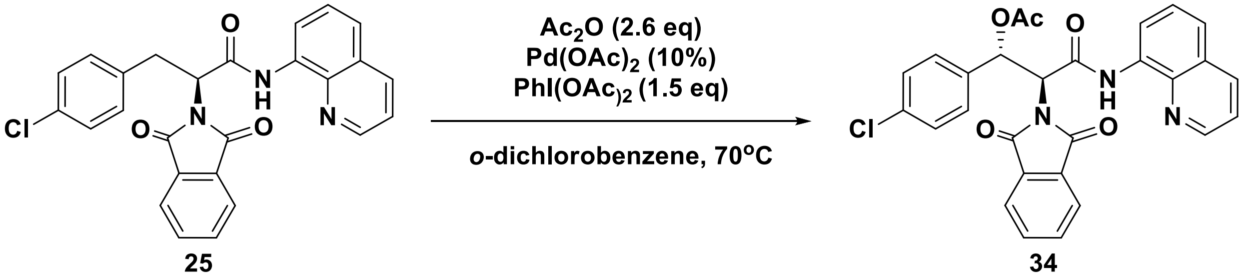
Compound **32**:[7] The mixture of compound **10** (345 mg, 1 mmol, 1 equiv), ethyl α-bromoacetate (334 mg, 2 mmol, 2 equiv), Pd(OAc)$_2$ (22.4 mg, 0.1 mmol, 0.1 equiv), silver carbonate (276 mg, 1 mmol, 1 equiv) and dibenzyl phosphate (84 mg, 0.3 mmol, 0.3 equiv) in dichloroethane and *t*-BuOH (5 mL : 5 mL) was heated at 75 °C for 5 hours. The reaction mixture was filtrated and concentrated *in vacuo*. The resulting residue was purified on flash silica gel chromatography (ethyl acetate : dichloromethane = 1 : 99), giving 280 mg of product as a colorless syrup in 65% yield. ^{1}H-NMR (CDCl$_3$, 300 MHz, ppm): δ 1.16-1.21 (m, 3H), 2.45-2.50 (m, 2H), 2.77-2.85 (q, 2H), 4.04-4.11 (q, 2H), 5.17-5.23 (q, 1H), 7.29-7.33 (dd, *J* = 3.9, 4.2 Hz, 1H), 7.40-7.44 (m, 2H), 7.66-7.71 (m, 2H), 7.79-7.84 (m, 2H), 8.01-8.04 (dd, *J* = 1.5, 6.6 Hz, 1H), 8.56-8.58 (dd, *J* = 1.5, 2.7 Hz, 1H), 8.61-8.66 (m, 1H), 10.26 (s, 1H); **^{13}C NMR** (CDCl$_3$, 75 MHz, ppm) δ 14.59, 24.54, 31.57, 54.56, 61.17, 117.02, 122.09, 122.45, 124.02, 127.55, 128.18, 132.10, 134.15, 134.78, 136.65, 138.74, 148.76, 166.74, 168.38, 172.64; **HRMS**: calculated for $C_{24}H_{22}N_3O_5$ [M+H$^+$]: 432.1559; found: 432.1558.



32 **33**

Compound 33: Compound **32** (43.1 mg, 0.1 mmol, 1 equiv), aryl iodide **A3** (139 mg, 0.2 mmol, 2 equiv), Pd(OAc)$_2$ (2.24 mg, 0.01 mmol, 0.1 equiv), silver carbonate (55 mg, 0.2 mmol, 2 equiv) and dibenzyl phosphate (5.6 mg, 0.02 mmol, 0.2 equiv) were suspended in the mixture of *t*-AmylOH (600 μL) and dichloroethane (600 μL). The mixture was heated at 90 °C under argon atmosphere. After 12 hours, reactions were diluted with dichloromethane (5 mL) after cooled to room temperature. The crude NMR showed conversion is more than 95% with diastereomer ratio of 4:1. The residue after concentration was directly purified on flash silica gel chromatography (hexanes : ethyl acetate = 3 : 1), giving 60 mg of product **33** as a white foam in 60% yield. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 1.01-1.06 (q, 3H), 2.20 (s, 3H), 2.67-2.80 (m, 2H), 3.41-3.44 (d, *J* = 10.8 Hz, 1H), 3.56-3.93 (m, 5H), 4.02-4.07 (t, *J* = 9.4, 9.0 Hz, 1H), 4.13-4.18 (m, 1H), 4.37-4.44 (t, *J* = 11.9, 11.2 Hz, 1H), 4.48-4.51 (d, *J* = 10.8 Hz, 1H), 4.62-4.81 (m, 4H), 4.88-4.91 (d, *J* = 10.8 1H), 5.38-5.41 (d, *J* = 11.2 Hz, 1H), 5.49-5.50 (m, 1H), 7.00-7.02 (d, *J* = 8.3 Hz, 2H), 7.17-7.18 (m, 2H), 7.29-7.49 (m, 20H), 7.78-7.80 (m, 2H), 7.94-7.96 (m, 2H), 8.01-8.10 (dd, *J* = 7.9, 14.4 Hz, 1H), 8.58-8.59 (m, 1H), 8.68-8.69 (m, 1H), 9.94-10.01 (d, *J* = 23.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 14.48, 21.64, 39.62, 40.71, 60.39, 60.50, 61.03, 68.64, 68.77, 68.97, 72.32, 72.40, 72.47, 72.54, 73.87, 74.33, 74.38, 75.70, 78.36, 78.43, 96.52, 96.58, 117.25, 117.31, 117.37, 122.17, 122.39, 122.44, 124.30, 127.60, 127.64, 128.17, 128.32, 128.35, 128.37, 128.64, 128.83, 128.97, 130.18, 132.17, 133.80, 134.35, 134.91, 136.52, 138.33, 138.52, 138.83, 138.88, 148.56, 155.97, 156.02, 165.65, 165.70, 168.55, 168.57, 170.88, 170.94, 171.32; **HRMS**: calculated for $C_{59}H_{56}N_3O_{12}$ [M+H$^+$]: 998.3864; found: 998.3864.

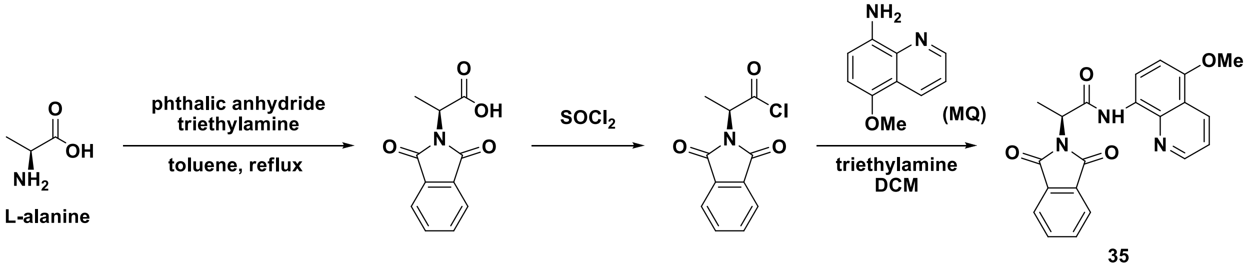
9. Synthesis of compound 34



Compound **34** was synthesized following a reported procedure reported:[2] To a vial was added compound **25** (91.2 mg, 0.2 mmol, 1 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), iodobenzene diacetate (97 mg, 0.3 mmol, 1.5 equiv), acetic anhydride (53 mg, 0.52 mmol, 2.6 equiv) and o-dichlorobenzene (600 μL). The mixture was stirred at 70 °C for 12 hours. After completion, the reaction mixture was concentrated under vacuum. Crude product NMR showed

15:1 diastereomer ratio. The residue after evaporation were purified on flash silica gel chromatography (hexanes : ethyl acetate = 3 : 1), giving 66 mg of product as a white foam in 65% yield. **^{1}H NMR** (CDCl$_3$, 360 MHz, ppm): δ 2.30 (s, 3H), 5.60-5.63 (d, *J* = 10.4 Hz, 1H), 6.86-6.88 (d, *J* = 10.4 Hz, 1H), 7.20-7.22 (m, 2H), 7.41-7.53 (m, 5H), 7.64-7.66 (m, 2H), 7.74-7.77 (m, 2H), 8.15-8.17 (dd, *J* = 1.4, 6.8 Hz, 1H), 8.72-8.77 (m, 2H), 10.69 (s, 1H); **^{13}C NMR** (CDCl$_3$, 90 MHz, ppm) δ 21.87, 57.02, 73.68, 117.83, 122.29, 122.86, 124.21, 127.90, 128.52, 129.33, 129.64, 131.91, 134.51, 134.82, 135.30, 135.83, 137.07, 139.04, 148.67, 164.55, 167.94, 169.64; **HRMS**: calculated for $C_{28}H_{21}ClN_3O_5$ [M+H$^+$]: 514.1170; found: 514.1166.

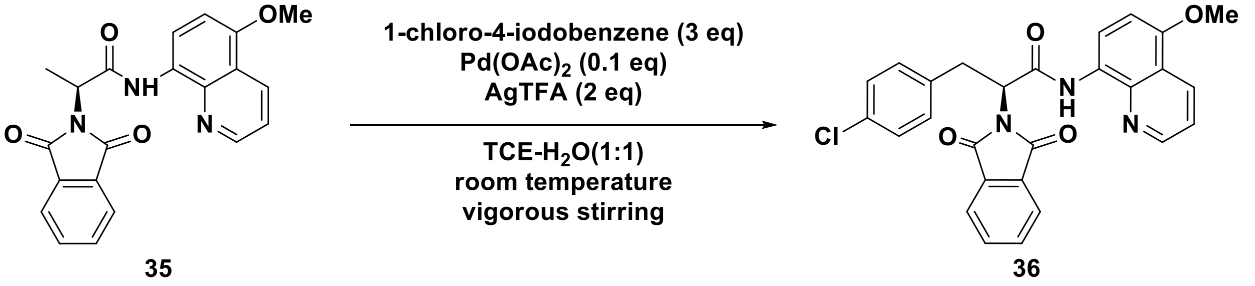
10. Synthesis of compound 37 via intramolecular C-H amidation



A mixture of L-alanine (1 g, 11.2 mmol, 1.0 equiv), phthalic anhydride (1.83 g, 12.3 mmol, 1.1 equiv), triethylamine (1.05 mL, 12.3 mmol, 1.1 equiv) in toluene (20 mL) was refluxed in a round bottom flask equipped with a Dean-Stark trap overnight. The reaction mixture was concentrated *in vacuo* to give the crude product. The *N*-Phth protected acid was used in the next step without further purification.

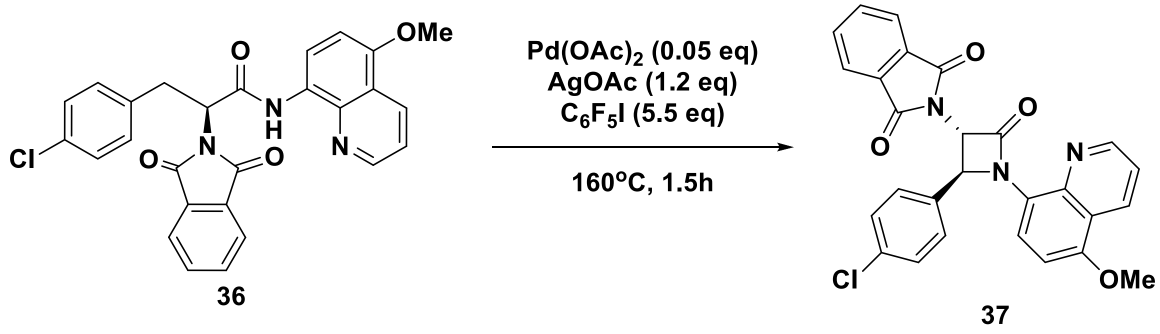
A mixture of *N*-Phth protected acid, SOCl$_2$ (1.06 mL, 14.6 mmol, 1.3 equiv) in anhydrous dichloromethane (20 mL) was stirred at room temperature overnight. The reaction mixture was then concentrated *in vacuo* to give the crude acyl chloride, which was used for the next step without further purification.

A mixture of acyl chloride, 5-methoxyl-8-aminoquinoline MQ[8] (1.95 g, 11.2 mmol, 1 equiv), and triethylamine (2.3 mL, 16.8 mmol, 1.5 equiv) in anhydrous CH$_2$Cl$_2$ (20 mL) was stirred at room temperature overnight. The reaction mixture was then washed with water and brine, dried over anhydrous Na$_2$SO$_4$ and concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography to give compound **35** as a yellow solid in 77% yield over 3 steps. **^{1}H NMR** (CDCl$_3$, 360 MHz, ppm): δ 1.95-1.97 (d, *J* = 7.2 Hz, 3H), 3.93 (s, 3H), 5.21-5.27 (q, 1H), 6.76-6.78 (d, *J* = 8.3 Hz, 1H), 7.35-7.38 (dd, *J* = 4.3, 4.3 Hz, 1H), 7.71-7.72 (d, 2H), 7.85-7.86 (d, 2H), 8.48-8.51 (dd, *J* = 1.1, 7.2 Hz, 1H), 8.60-8.62 (d, *J* = 8.6 Hz, 1H), 8.66-8.67 (d, *J* = 2.9 Hz, 1H), 10.05 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 15.92, 50.49, 56.21, 104.63, 117.21, 120.79, 121.21, 124.00, 127.75, 131.67, 132.45, 134.64, 139.60, 149.24, 151.00, 167.23, 168.37; **HRMS**: calculated for $C_{21}H_{18}N_3O_4$ [M+H$^+$]: 376.1297; found: 376.1298.



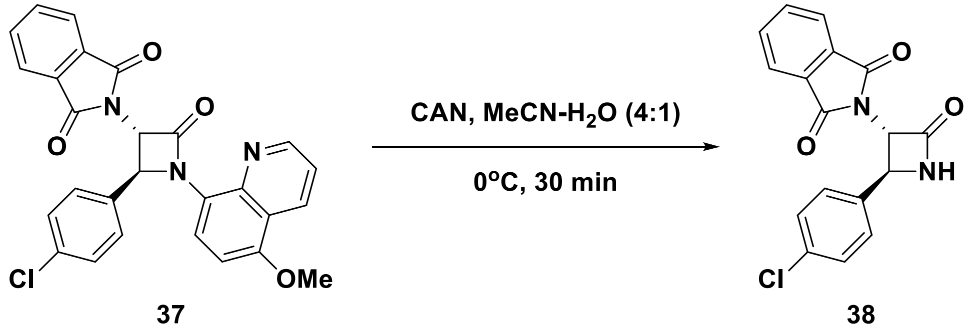
35 **36**

Alanine-MQ substrate **35** (1 g, 2.67 mmol, 1 equiv), 1-chloro-4-iodobenzene (1.9 g, 8.0 mmol, 3 equiv), $Pd(OAc)_2$ (60 mg, 0.267 mmol, 0.1 equiv), silver trifluoroacetate (1.2 g, 5.3 mmol, 2 equiv) was suspended into TCE (10 mL) and water (10 mL). The resulting solution was stirred **vigorously** (important) at room temperature. After 2 days, 1 M aq. NaOH solution (20 mL) and dichloromethane (20 mL) were added. Organic layer was separated, and the aqueous layer was extracted with dichloromethane (20 mL) twice. Combined organic layer was concentrated, and the resulting residue was purified on flash silica gel chromatography (ethyl acetate : dichloromethane = 1:99), giving 1.2 g of product as a yellowish solid in 93% yield. **^{1}H NMR** ($CDCl_3$, 360 MHz, ppm): δ 3.76-3.78 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 3H), 5.38-5.42 (t, *J* = 8.3, 8.6 Hz, 1H), 6.76-6.78 (d, *J* = 8.6 Hz, 1H), 7.16-7.23 (m, 4H), 7.31-7.35 (dd, *J* = 4.3, 4.0 Hz, 1H), 7.66-7.69 (m, 2H), 7.79-7.81 (m, 2H), 8.46-8.49 (d, *J* = 8.3 Hz, 1H), 8.57-8.63 (m, 2H), 10.02 (s, 1H); **^{13}C NMR** ($CDCl_3$, 90 MHz, ppm) δ 34.63. 56.21. 56.41. 104.61. 117.39, 120.78, 121.19, 124.06, 127.62, 129.31, 130.86, 131.63, 132.01, 133.22, 134.73, 135.88, 139.57, 149.19, 141.13, 166.08, 168.36; **HRMS**: calculated for $C_{27}H_{21}ClN_3O_4$ [M+H$^+$]: 486.1221; found: 486.1219.



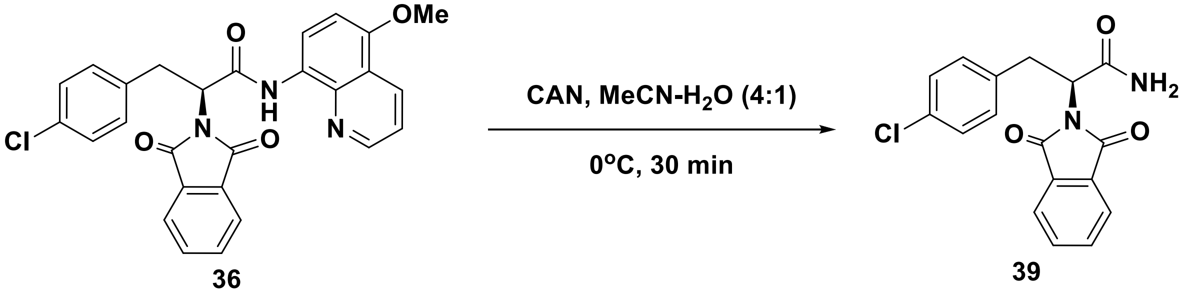
Lactam **37** was synthesized using a modified procedure reported by Wu[9] In a 10 mL of glass tube was placed compound **36** (97 mg, 0.2 mmol, 1 equiv), Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), AgOAc (40 mg, 0.24 mmol, 1.2 equiv) and iodoperfluorobenzene (323 mg, 1.1 mmol, 5.5 equiv). After the reaction mixture was mixed well with stirring at room temperature for about 5 min, the glass tube was placed into 60 °C oil bath for 2 minutes. Increased the temperature gradually to 160 °C within 10 minutes. The temperature was kept for 1.5 hours. After cooled to room temperature, the reaction was concentrated and directly purified on flash silica gel chromatography (ethyl acetate : dichloromethane = 5:95), giving 18 mg of product as a yellow solid in 18% yield. About 43 mg of compound **36** was recovered from the reaction in 45% yield. **^{1}H NMR** (CDCl$_3$, 360 MHz, ppm): δ 3.96 (s, 3H), 5.37-5.38 (d, *J* = 2.5 Hz, 1H), 6.43-6.44 (d, *J* = 2.2 Hz, 1H), 6.82-6.84 (d, *J* = 8.3 Hz, 1H), 7.17-7.19 (m, 2H), 7.27-7.31 (dd, *J* = 4.3, 4.3 Hz, 1H), 7.34-7.36 (m, 2H), 7.73-7.75 (m, 2H), 7.86-7.88 (m, 2H), 8.11-8.14 (d, *J* = 8.3 Hz, 1H), 8.44-8.46 (d, *J* = 8.6 Hz, 1H), 8.74-8.75 (m, 1H); **^{13}C NMR** (CDCl$_3$, 90 MHz, ppm) δ 56.41, 63.35, 65.13, 104.40, 121.15, 141.46, 123.51, 124.30, 125.69, 128.34, 129.47, 131.06, 132.31, 134.54, 135.02, 137.20, 142.63, 150.21, 163.61, 163.43, 167.45; **HRMS**: calculated for $C_{27}H_{19}ClN_3O_4$ [M+H$^+$]: 484.1064; found: 484.1066.

10. Removal of MQ auxiliary



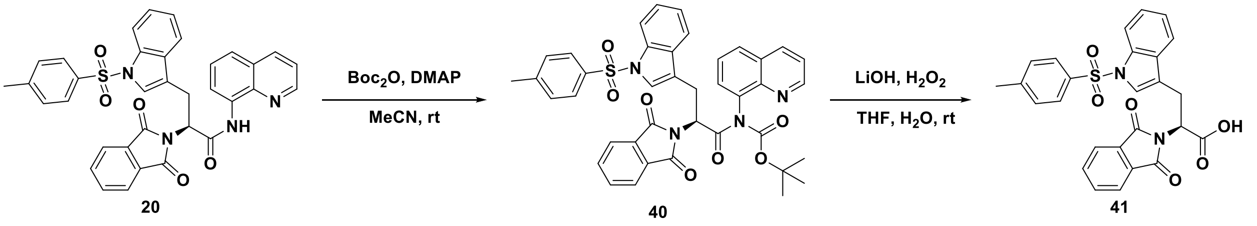
To an ice-water cooled solution of MQ substrate in acetonitrile and water (1600 μL: 400 μL for 0.1 mmol MQ substrate) was added ceric ammonium nitrate (3 equiv) in one portion. The reaction was kept in ice-water bath for 30 minutes. After completion, the reaction was diluted with ethyl acetate, washed with saturated sodium thiosulfate and brine, dried over anhydrous Na_2SO_4, concentrated and purified on flash silica gel chromatography.

Compound **38**: Flash silica gel chromatography (ethyl acetate : dichloromethane = 5:95) gave 8.6 mg of product **38** from compound **37** (18 mg, 0.037 mmol) as a white solid in 70% yield. **^{1}H NMR** ($CDCl_3$, 300 MHz, ppm): δ 5.11-5.12 (d, *J* = 2.7 Hz, 1H), 5.16-5.17 (d, *J* = 2.7 Hz, 1H), 6.58 (s, 1H), 7.30-7.39 (m, 4H), 7.75-7.78 (m, 2H), 7.87-7.90 (m, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz, ppm) δ 57.44, 64.07, 124.51, 127.86, 129.95, 132.23, 135.28, 135.36, 136.73, 165.69, 167.48; **HRMS**: calculated for $C_{17}H_{12}ClN_2O_3$ [M+H$^+$]: 327.0536; found: 327.0536.



Compound **39**: Flash silica gel chromatography (ethyl acetate : dichloromethane = 35:65) gave 46 mg product from compound **39** (97 mg, 0.2 mmol) as a white solid in 70% yield. **^{1}H NMR** (DMSO-*d6*, 300 MHz, ppm): δ 3.25-3.30 (m, 1H), 3.46-3.52 (dd, *J* = 4.5, 9.6 Hz, 1H), 4.88-4.93 (dd, *J* = 4.5, 7.5 Hz, 1H), 7.11-7.14 (d, *J* = 8.7 Hz, 2H), 7.19-7.22 (d, *J* = 8.7 Hz, 2H), 7.32 (s, 1H), 7.70 (s, 1H), 7.80 (s, 4H); **^{13}C NMR** (DMSO-*d6*, 75 MHz, ppm) δ 33.24, 54.07, 123.17, 128.28, 130.62, 131.07, 131.26, 134.60, 136.98, 167.49, 169.52; **HRMS**: calculated for $C_{17}H_{14}ClN_2O_3$ [M+H$^+$]: 329.0693; found: 329.0692.

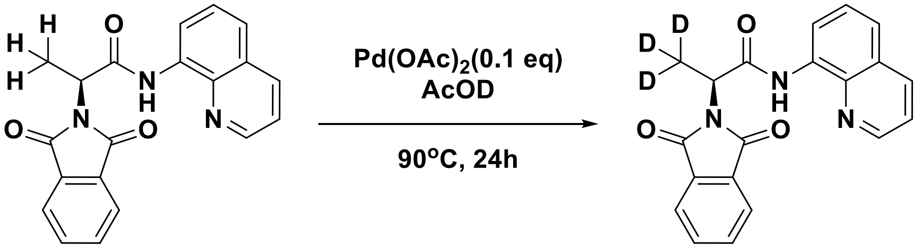
11. Removal of AQ auxiliary



Step 1: To a solution of compound **20** (123 mg, 0.2 mmol, 1 equiv) in dry acetonitrile (3 mL) was added 4-(dimethylamino)pyridine (26 mg, 0.22 mmol, 1.08 equiv) and Boc anhydride (70 mg, 0.32 mmol, 1.6 equiv). The mixture was stirred at room temperature for 24 hours then concentrated under reduced pressure. Purification of the crude mixture by flash silica gel chromatography (dichloromethane : acetone =40:1) gave 136 mg of compound **40** as a yellowish solid in 95% yield. **^{1}H NMR** (CDCl$_3$, 300 MHz, ppm): δ 1.15 (s, 9H), 2.20 (s, 3H), 3.80-3.86 (dd, *J* = 4.8, 9.9 Hz, 1H), 3.96-4.05 (t, *J* = 10.8, 13.8 Hz, 1H), 6.51-6.56 (m, 1H), 6.88-6.91 (m, 2H), 7.23-7.27 (m, 2H), 7.36-7.40 (dd, *J* = 4.2, 3.9 Hz, 1H), 7.48-7.90 (m, 12H), 8.13-8.16 (dd, *J* = 1.5, 6.9 Hz, 1H), 8.82-8.84 (dd, *J* = 1.5, 2.7 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 75 MHz, ppm) δ 21.88, 25.61, 27.87, 55.51, 83.80, 113.99, 118.91, 120.35, 122.07, 123.71, 123.83, 125.17, 125.54, 126.62, 126.93, 128.77, 129.23, 130.03, 131.19, 132.09, 134.48, 135.32, 135.53, 136.40, 136.70, 144.37, 144.92, 150.87, 153.07, 168.11, 172.60; **HRMS**: calculated for $C_{40}H_{35}N_4O_7S$ [M+H$^+$]: 715.2226; found: 715.2222.

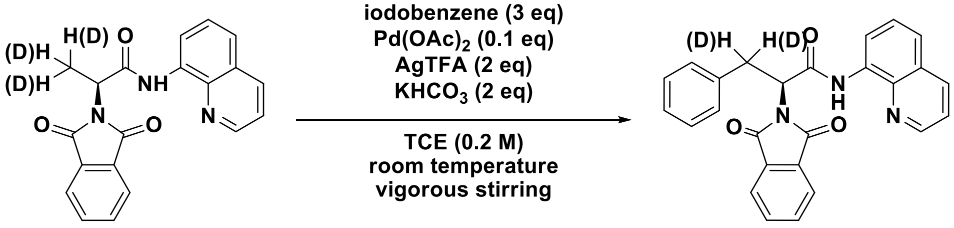
Step 2: A solution of compound **40** (128.5 mg, 0.18 mmol, 1 equiv) in THF and water (1.5 mL : 0.5 mL) was cooled to 0^{o}C then 30% hydrogen peroxide (180 μL, 1.58 mmol, 8.8 equiv) and lithium hydroxide monohydrate (8.1 mg, 0.20 mmol, 1.1 equiv) were added and stirred at 0 ^{o}C for 2.5 hours. The reaction was quenched at 0^{o}C with 1.5 M aqueous sodium thiosulfate (1.3 mL) and the solvent was concentrated under reduced pressure. The residue was washed with dichloromethane (10 mL) twice then the aqueous phase was acidified to pH 2 with 10% aqueous hydrochloric acid and extracted with ethyl acetate (10 mL) twice. The organic extracts were dried with sodium sulfate and concentrated under reduced pressure and purified on flash silica gel chromatography (dichloromethane : methanol = 10:1), giving 75 mg product as a white solid in 85% yield. **^{1}H NMR** (DMSO-*d6*, 300 MHz, ppm): δ 2.19 (s, 3H), 3.54-3.57 (m, 2H), 5.09-5.14 (q, 1H), 7.03-7.05 (m, 2H), 7.17-7.30 (m, 2H), 7.45 (s, 1H), 7.52-7.60 (m, 3H), 7.79-7.85 (m, 5H); **^{13}C NMR** (DMSO-*d6*, 75 MHz, ppm) δ 20.96, 23.99, 52.14, 113.24, 119.29, 119.65, 123.37, 124.05, 124.93, 126.25, 129.95, 130.37, 130.99, 133.83, 134.34, 134.86, 134.99, 145.10, 167.48; **HRMS**: calculated for $C_{26}H_{21}N_2O_6S$ [M+H$^+$]: 489.1120; found: 489.1120.

12. Kinetic isotope effect

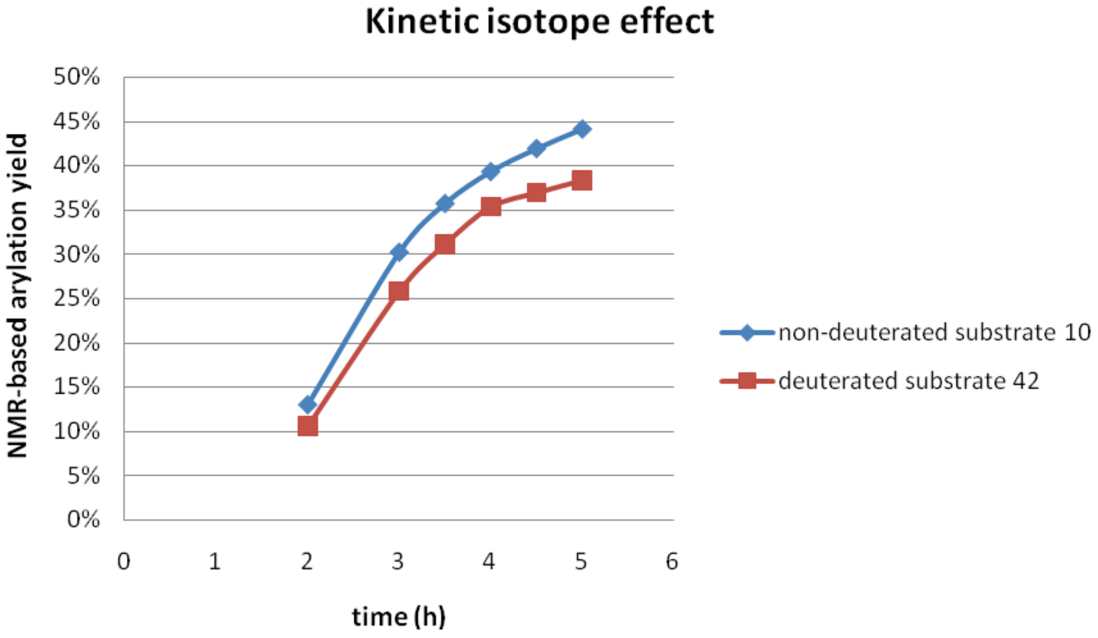


10 42

Preparation of deuterated alanine substrate 42: The solution of alanine substrate **10** (1.38 g, 4 mmol, 1 equiv) and Pd(OAc)$_2$ (90 mg, 0.4 mmol, 0.1 equiv) in deuterated acetic acid (10 mL) was heated at 90 °C for 24 hours. After completion the reaction was filtrated and concentrated. This procedure was repeated twice, and the product was purified on flash silica gel chromatography (ethyl acetate : dichloromethane=1:99), giving 1.0 g of deuterated alanine substrate **42** in 72% yield. **^{1}H NMR** (CDCl$_3$, 360 MHz, ppm): δ 5.25 (s, 1H), 7.38-7.42 (m, 1H), 7.49-7.53 (m, 2H), 7.73-7.75 (m, 2H), 7.88-7.90 (m, 2H), 8.11-8.14 (d, *J* = 8.3Hz, 1H), 8.67-8.72 (m, 2H), 10.31 (s, 1H); **HRMS**: calculated for $C_{20}H_{13}D_3N_3O_3$ [M+H$^+$]: 349.1380; found: 349.1380.



10 vs 42



Arylation yields were determined as follows:

$$\text{yield} = \frac{\text{integration of doublet with } \delta\ 8.64\sim 8.65}{\text{integration of triplet with } \delta\ 8.15\sim 8.19} \times 100\%$$

Deuterated substrate **42** (139.2 mg, 0.4 mmol, 1 equiv) or non-deuterated substrate **10** (138.0 mg, 0.4 mmol, 1 equiv), iodobenzene (245 mg, 1.2 mmol, 3 equiv), $Pd(OAc)_2$ (9 mg, 0.04 mmol, 0.1 equiv), silver trifluoroacetate (176.8 mg, 0.8 mmol, 2 equiv) and potassium bicarbonate (80 mg, 0.8 mmol, 2 equiv) were suspended into TCE (2 mL) in a 4 mL capped vial. The resulting reaction mixture was stirred vigorously for 1-5 h at room temperature. Data was collected at 2, 3, 3.5, 4, 4.5 and 5 hours. (Data taken with 2 hours gave significant error). Data collecting method: at specified reaction time, the reaction vial was centrifuged at 4000 rpm for 2 minutes, and 100 μL of supernatant was taken and mixed with 400 μL of deuterated chloroform for ^{1}H-NMR measurement. Average data of three repeating experiments were used. $k_{H/D}$ (~1.2) was estimated based on the ratio of arylation yield.

13. Reference

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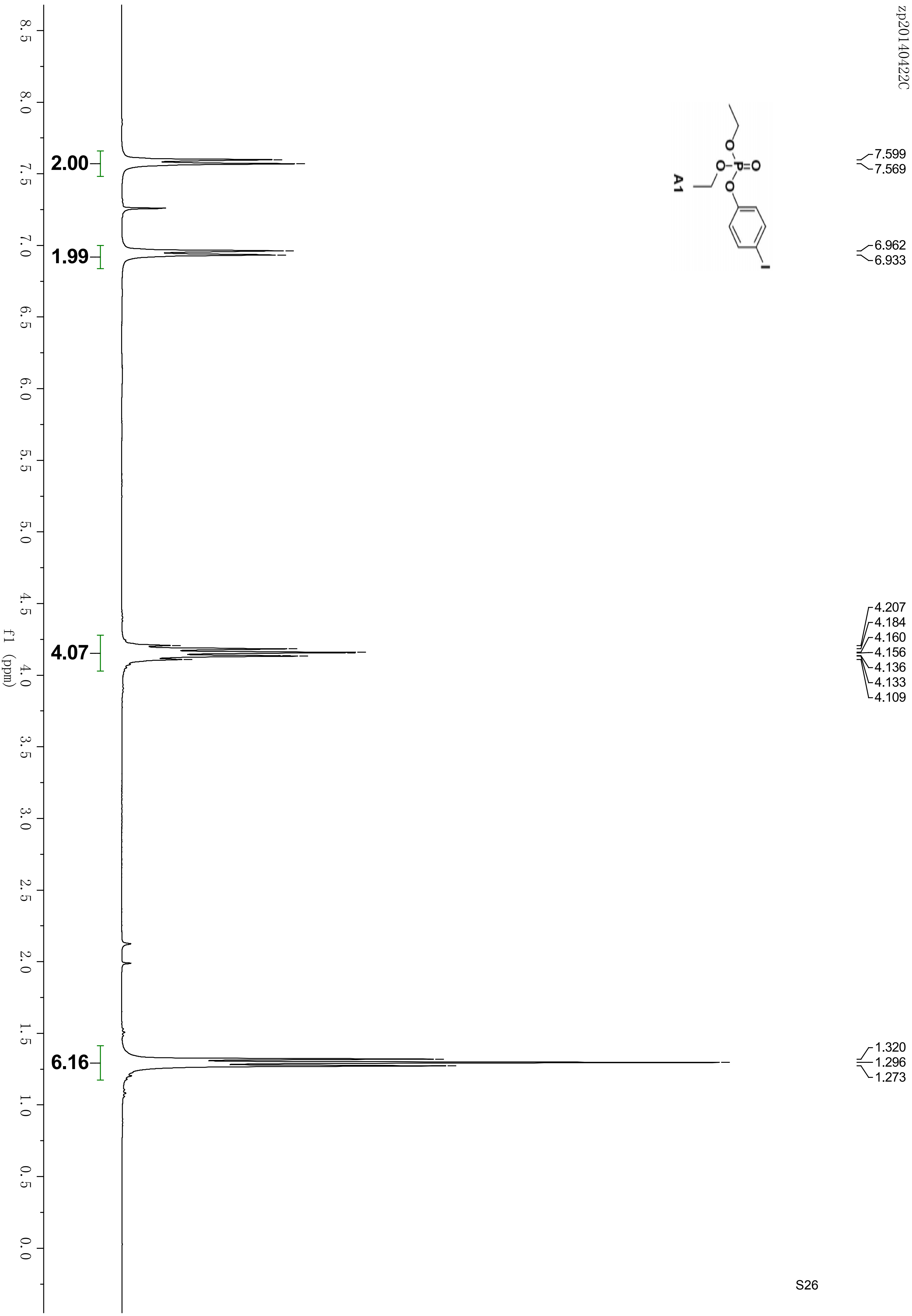
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1.273
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1.99
4.07
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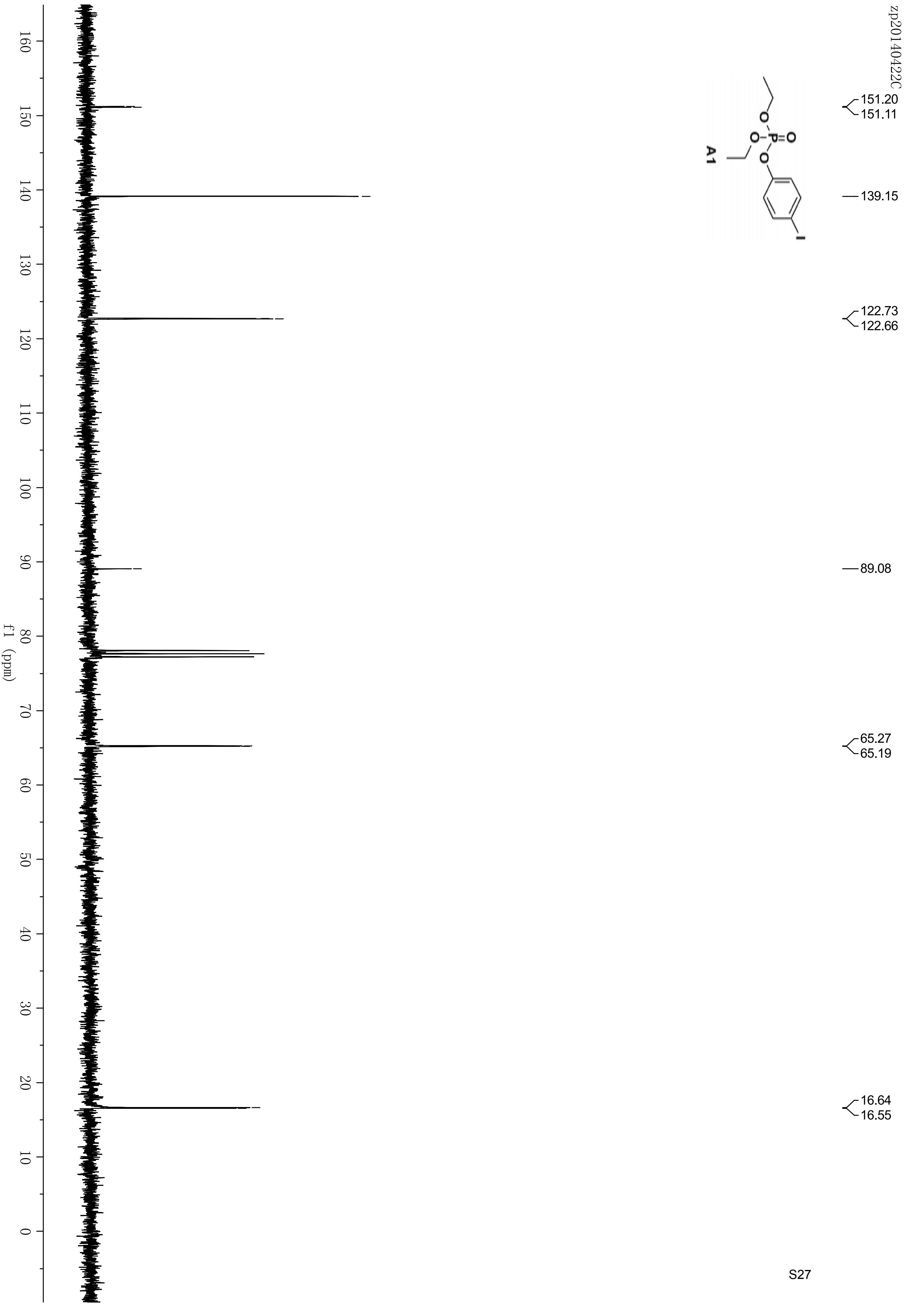
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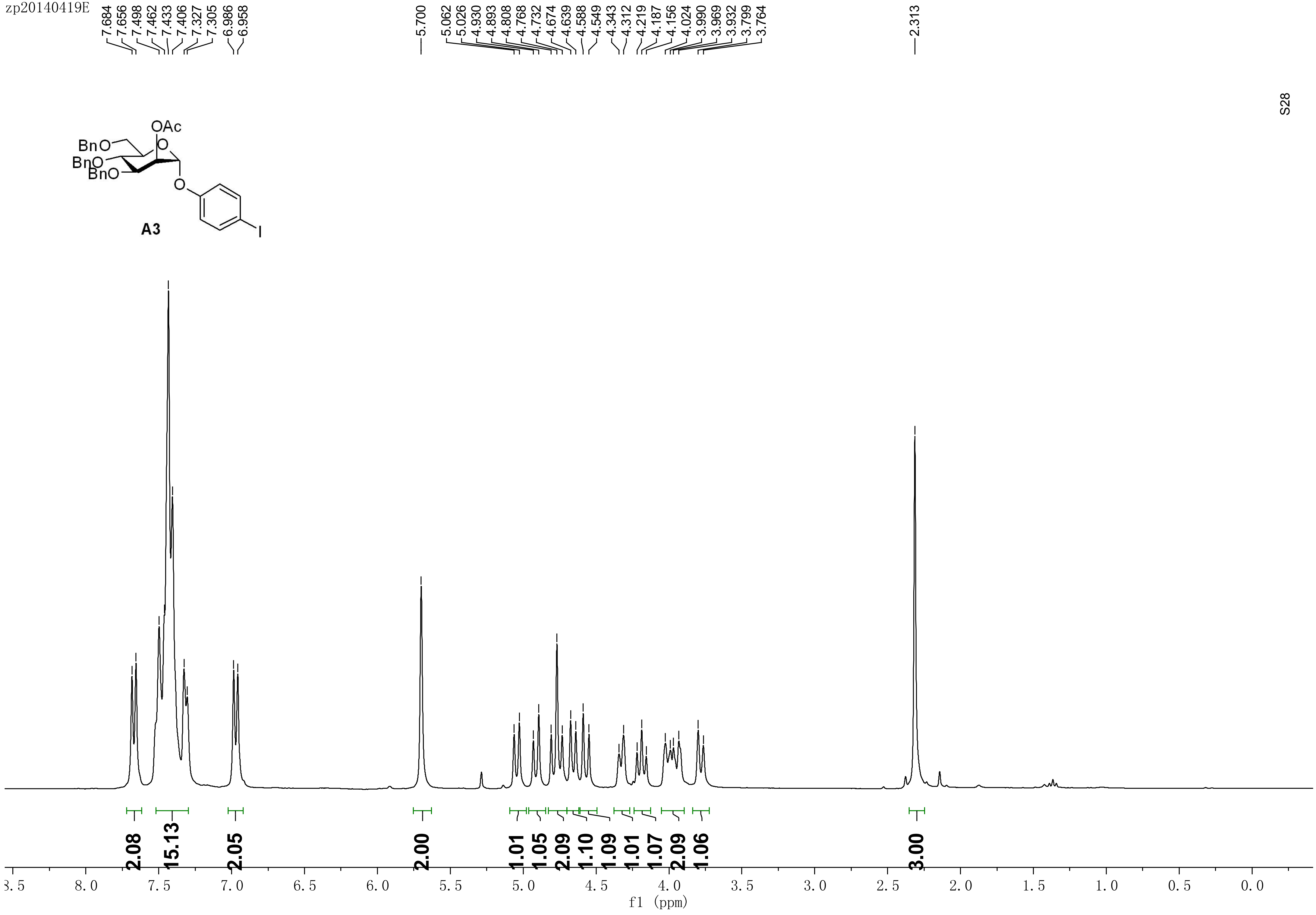
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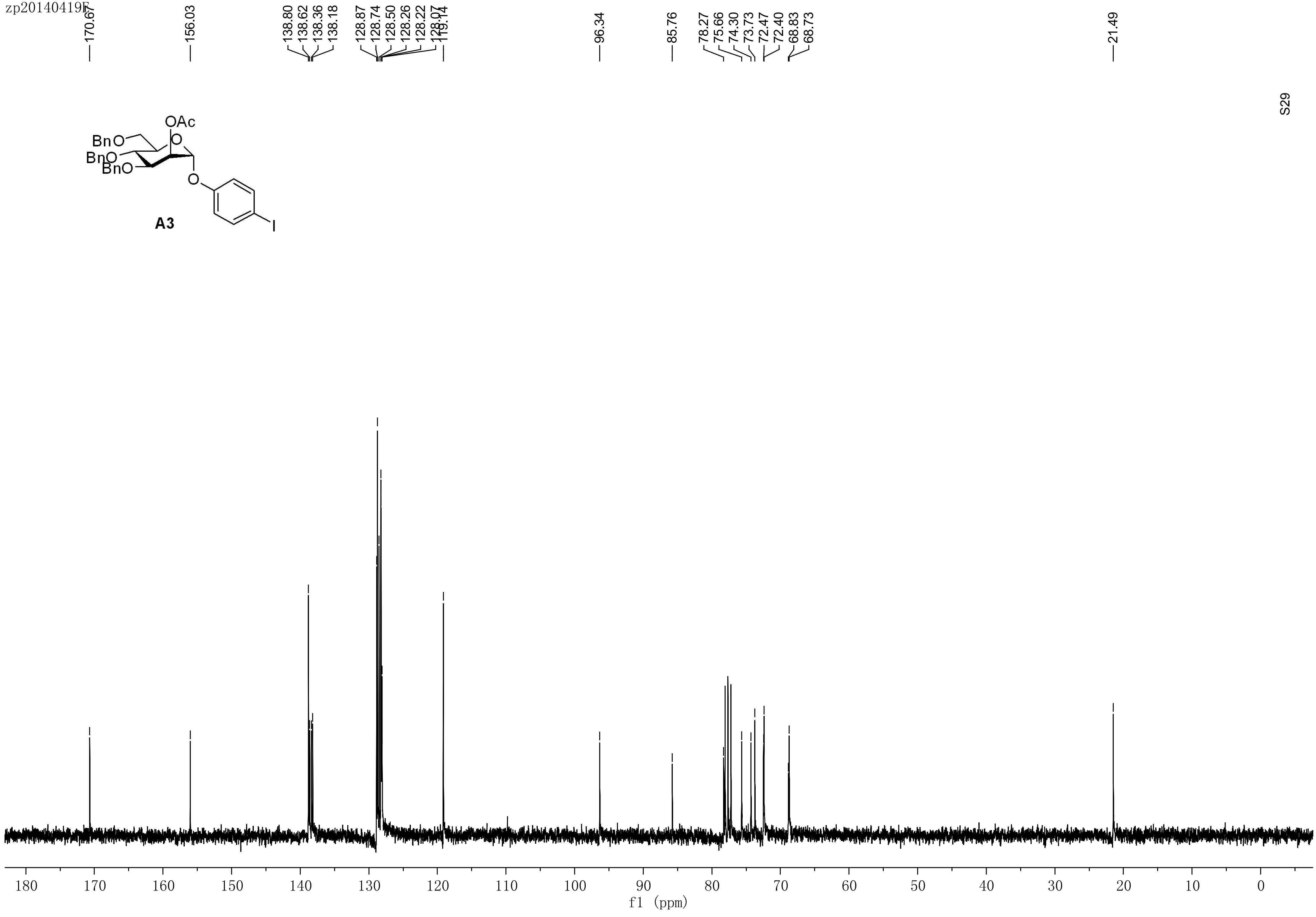
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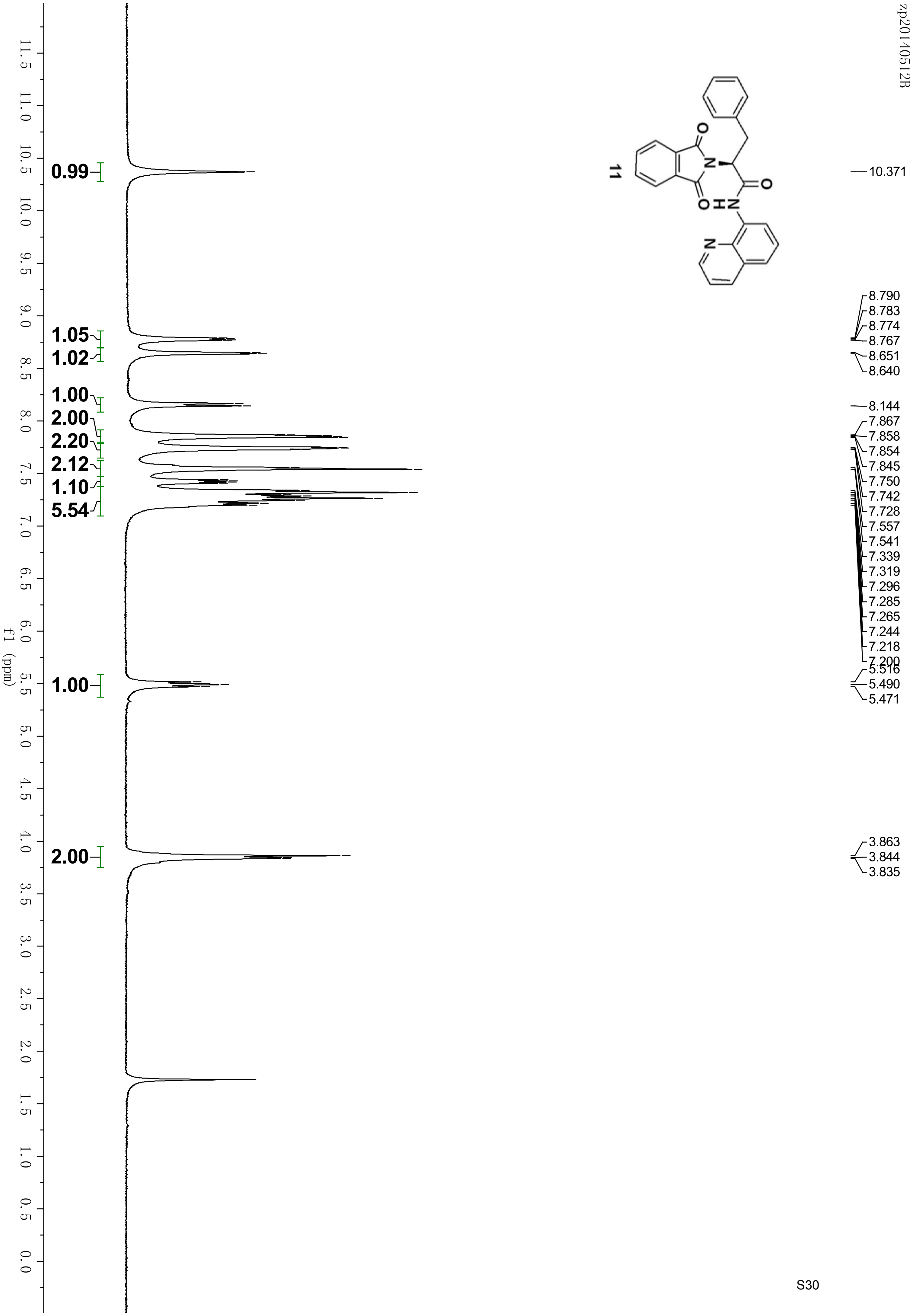
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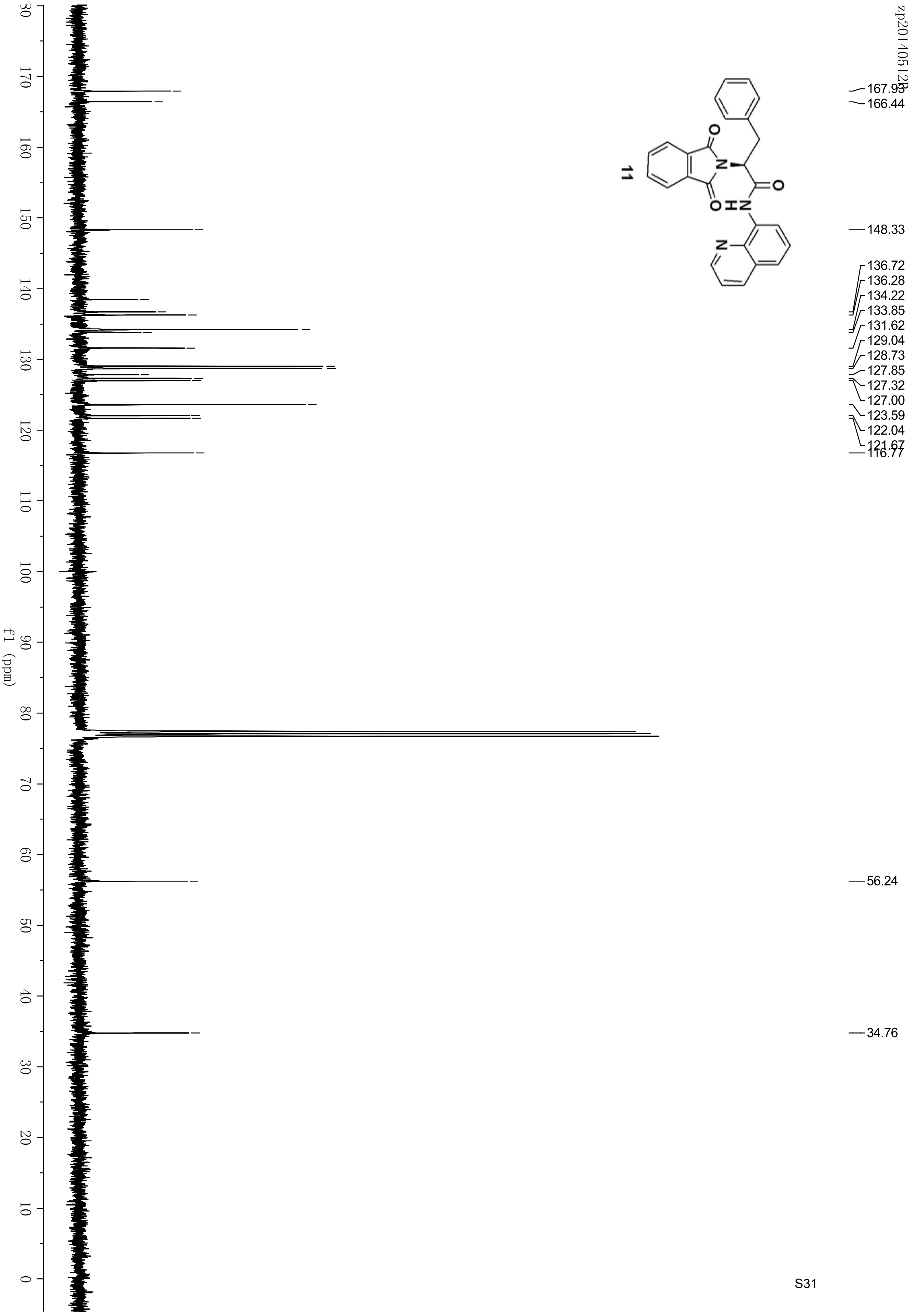
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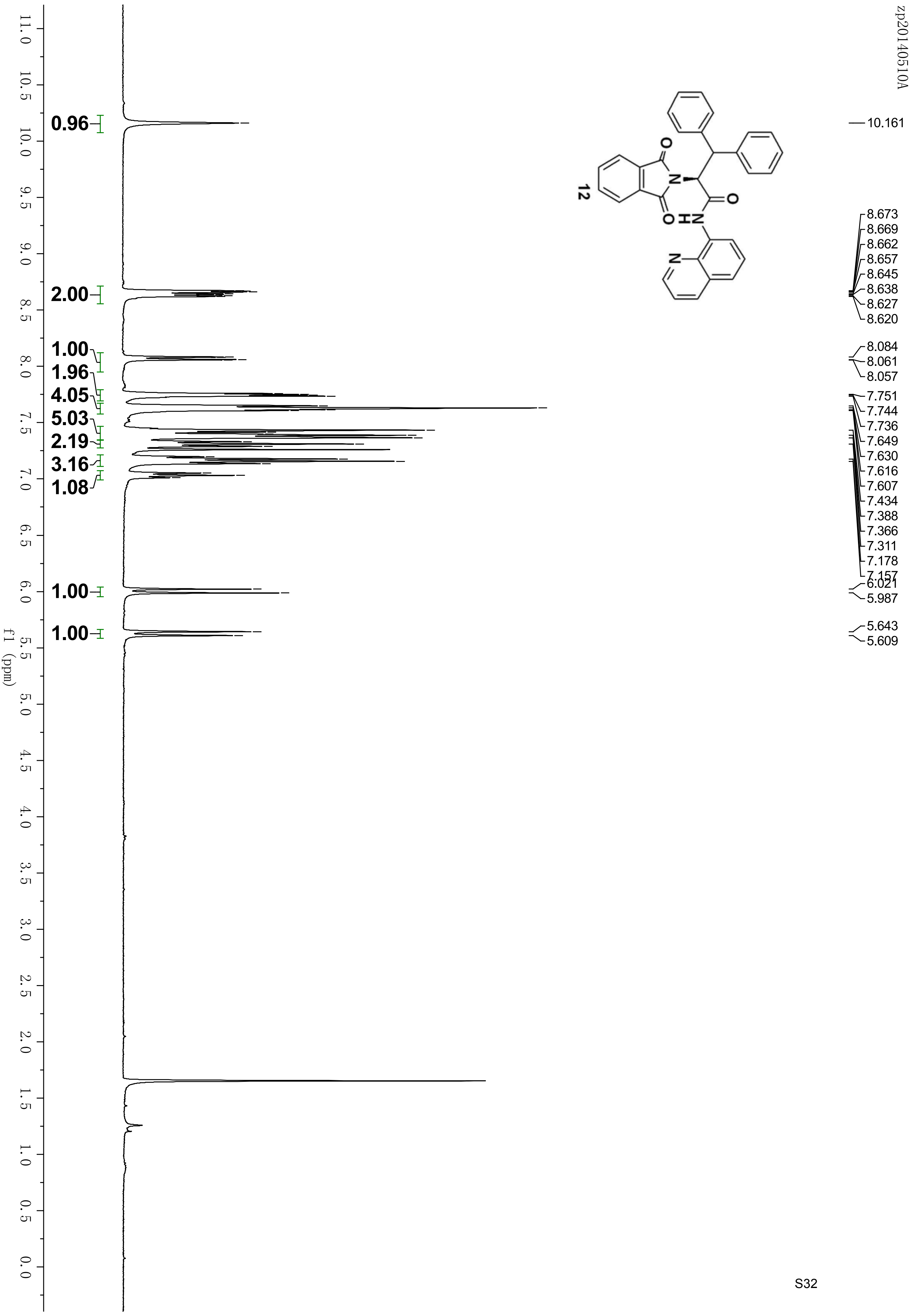
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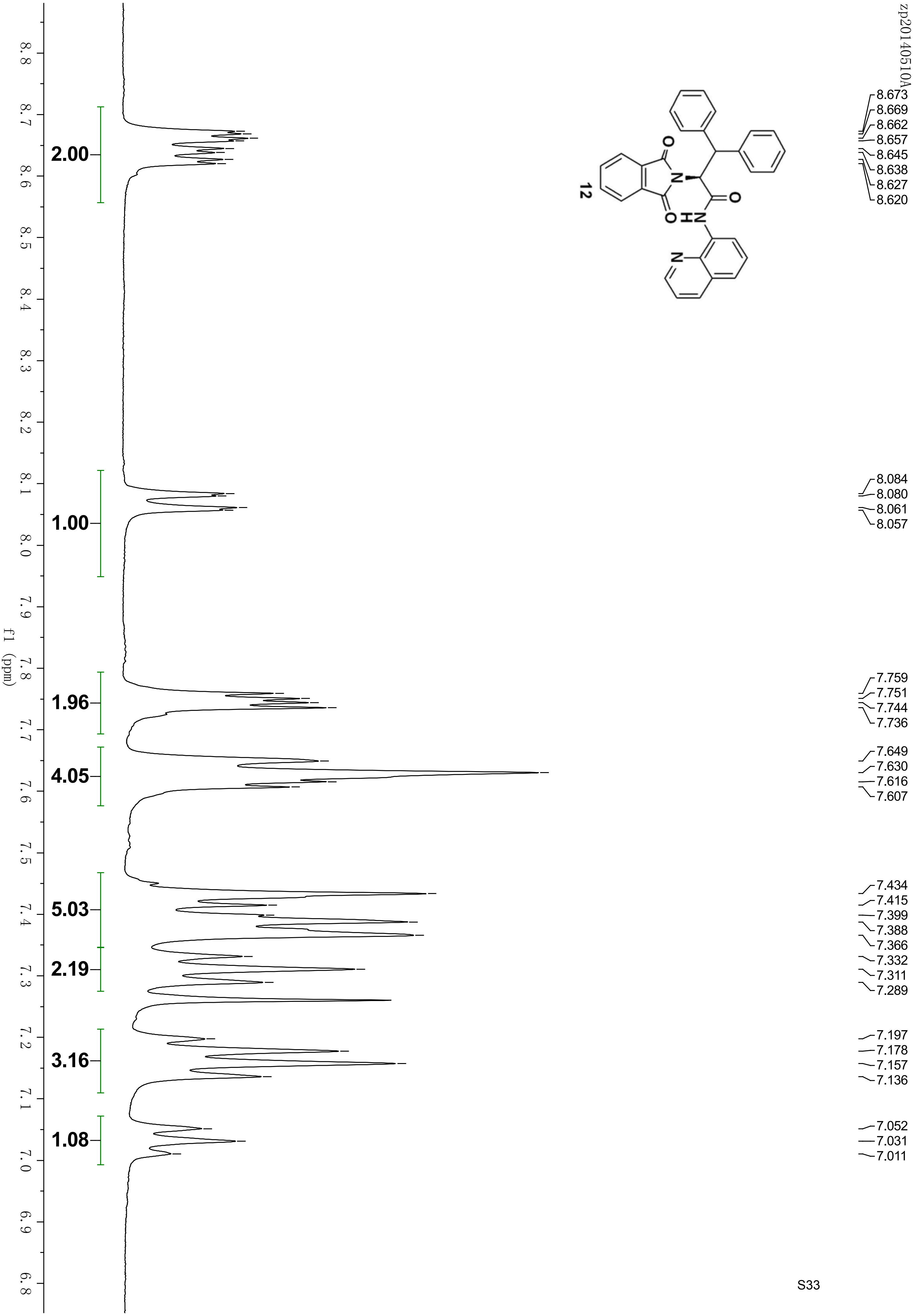
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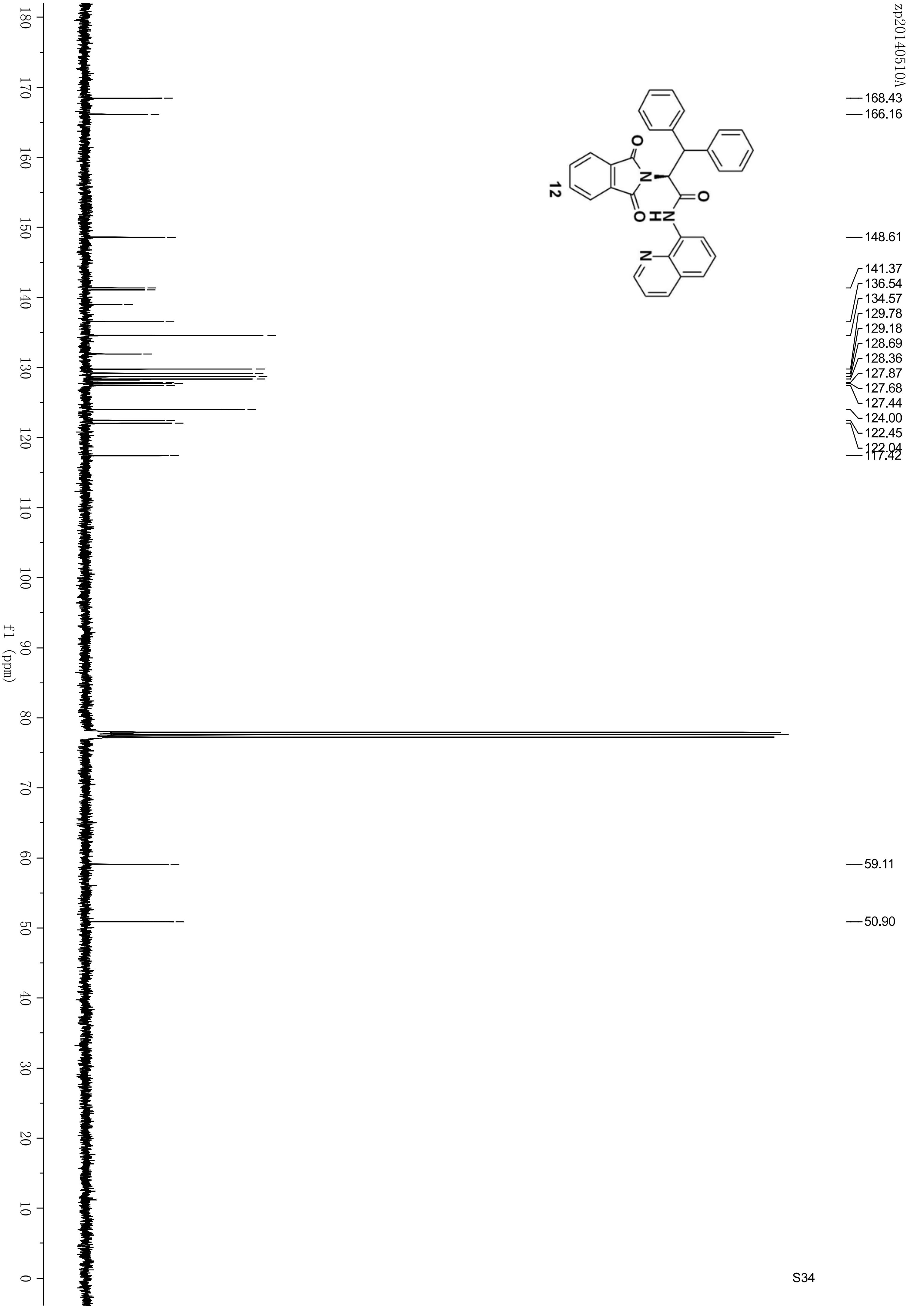
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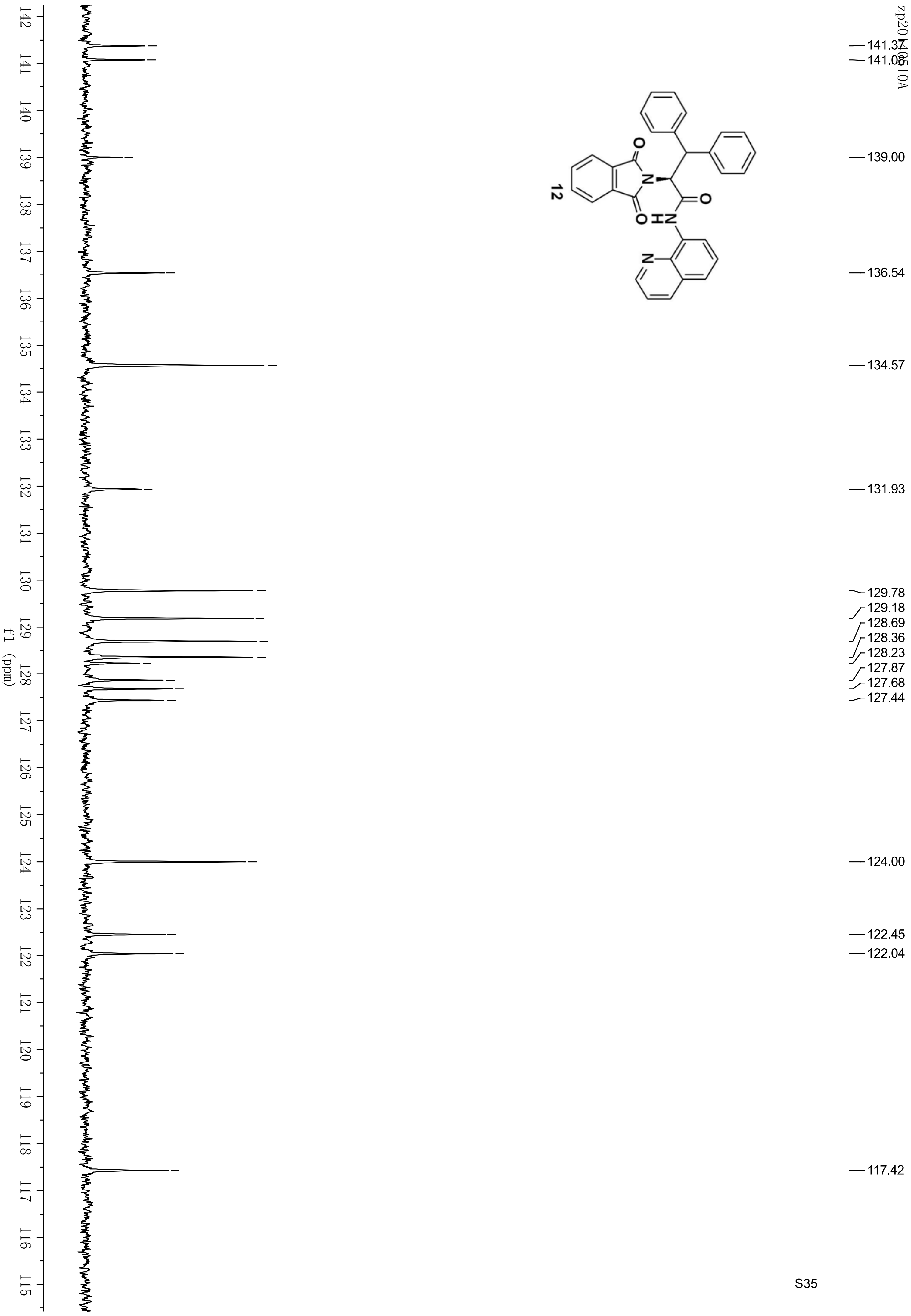
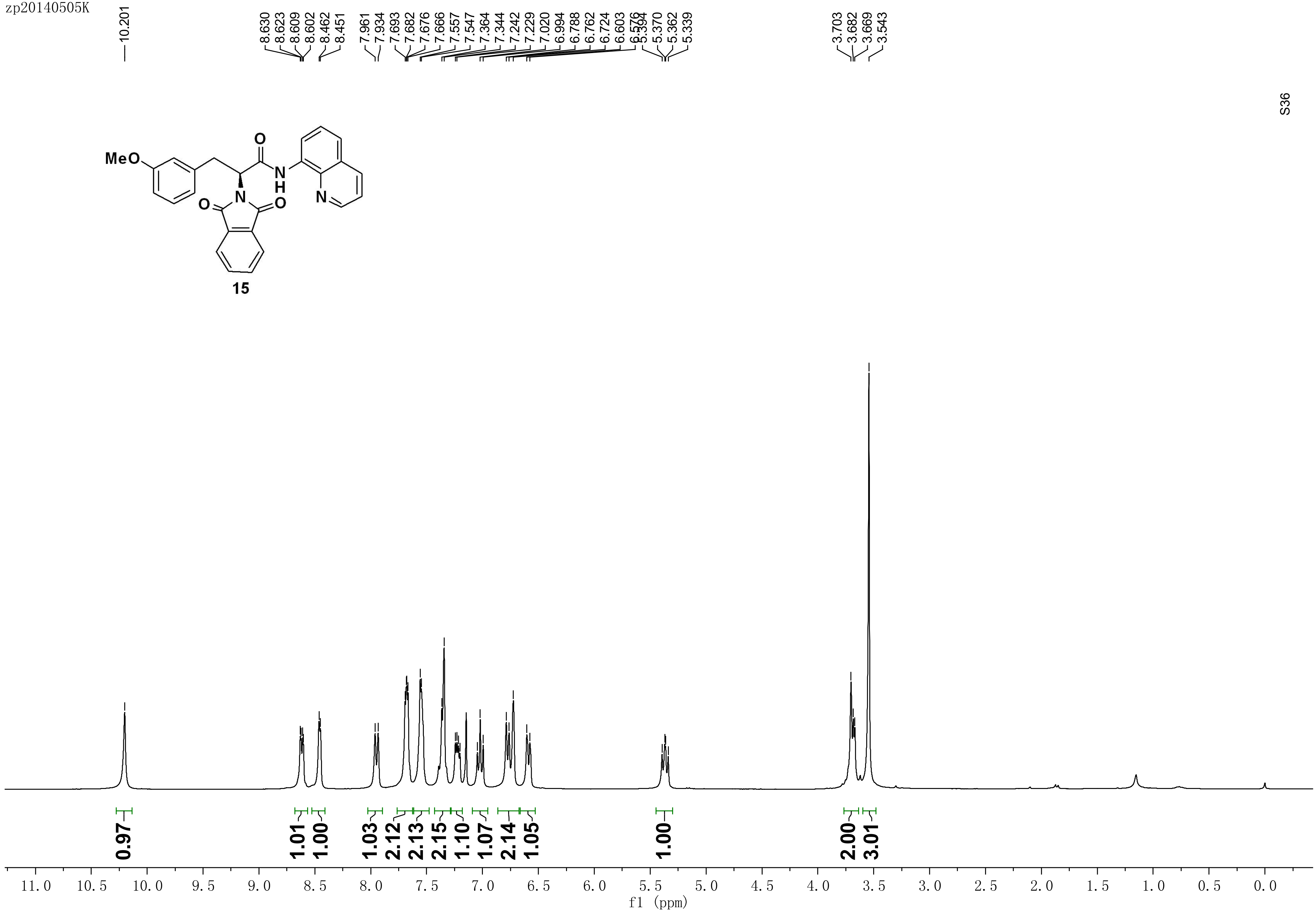
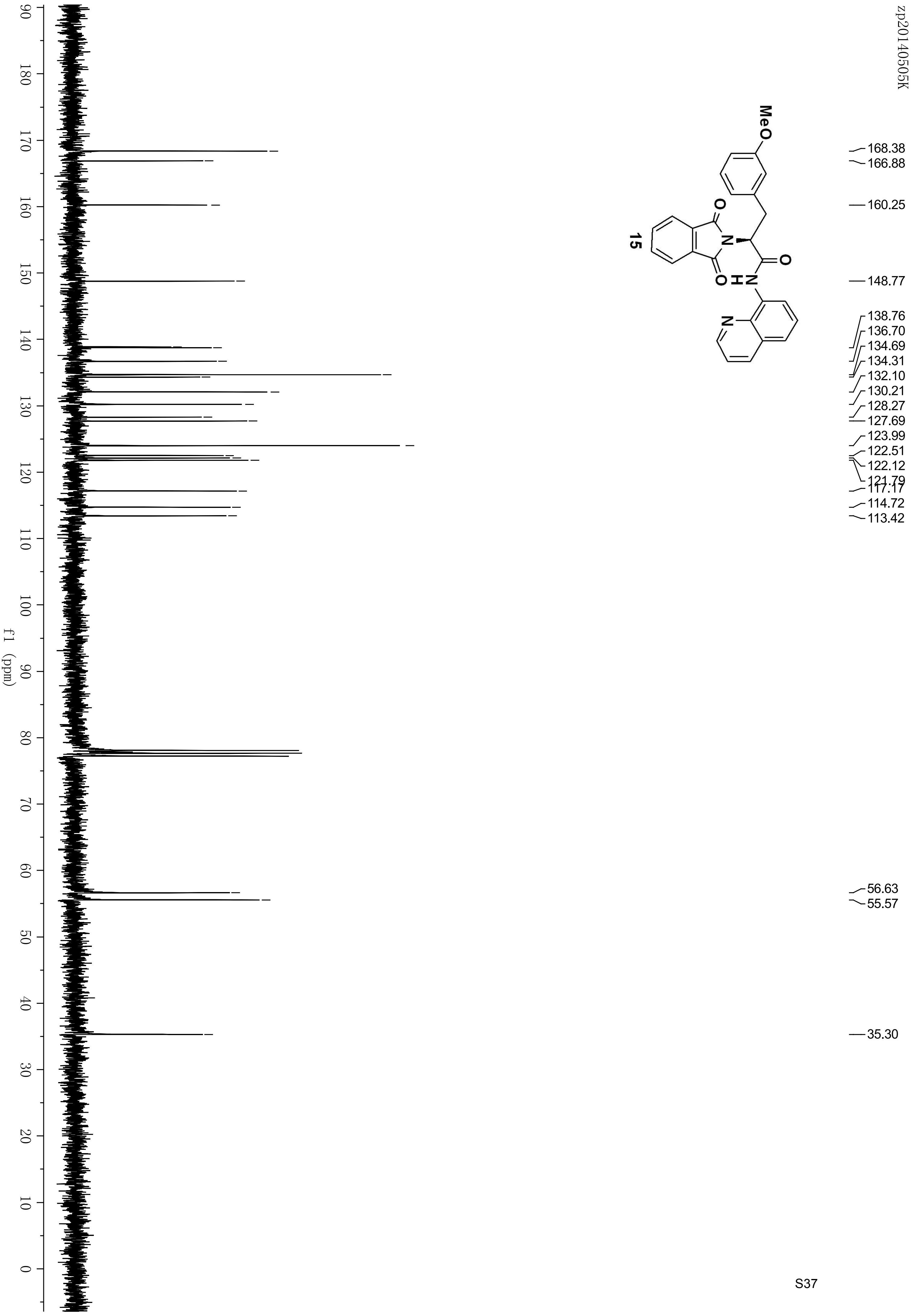
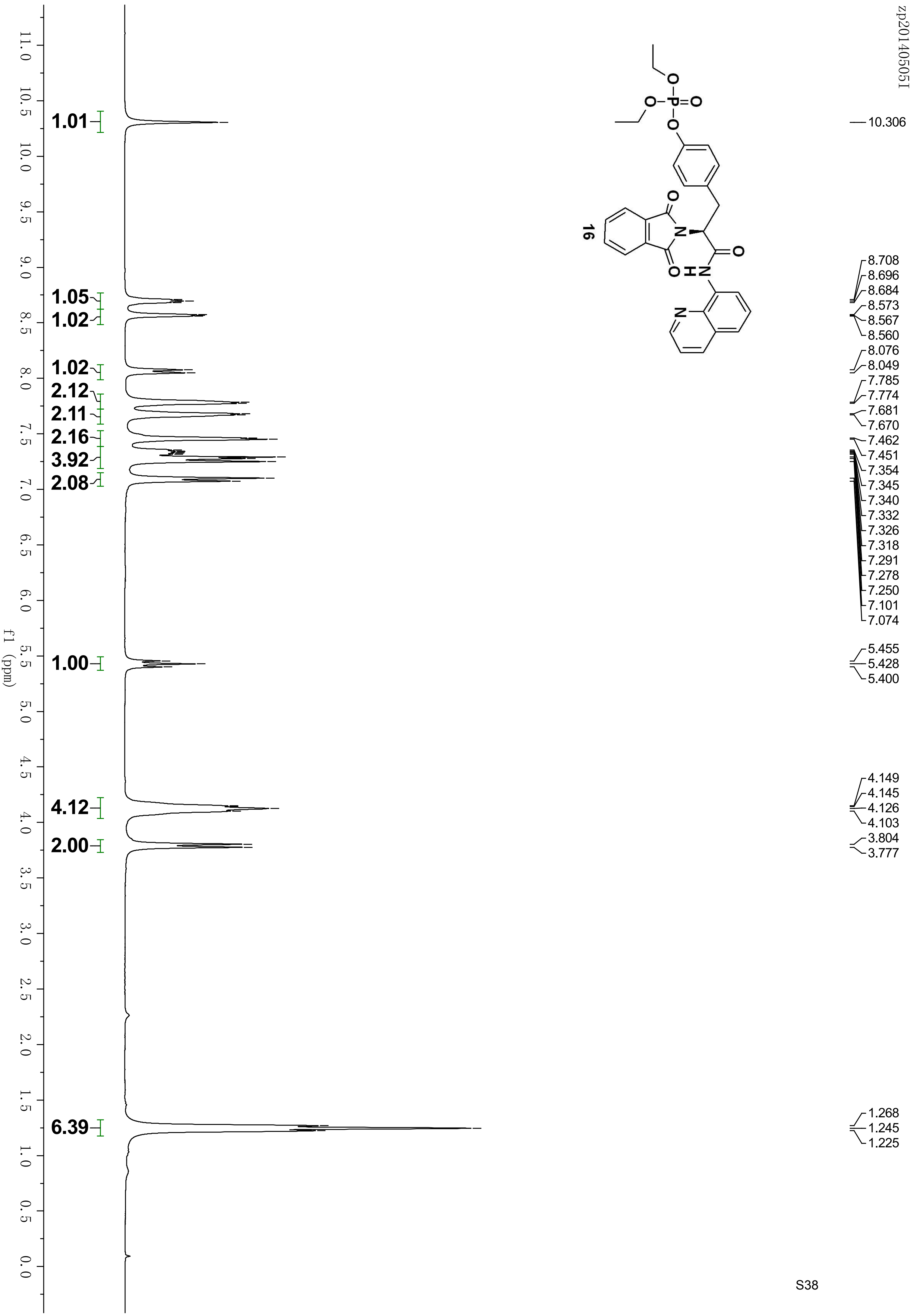
0
f1 (ppm)

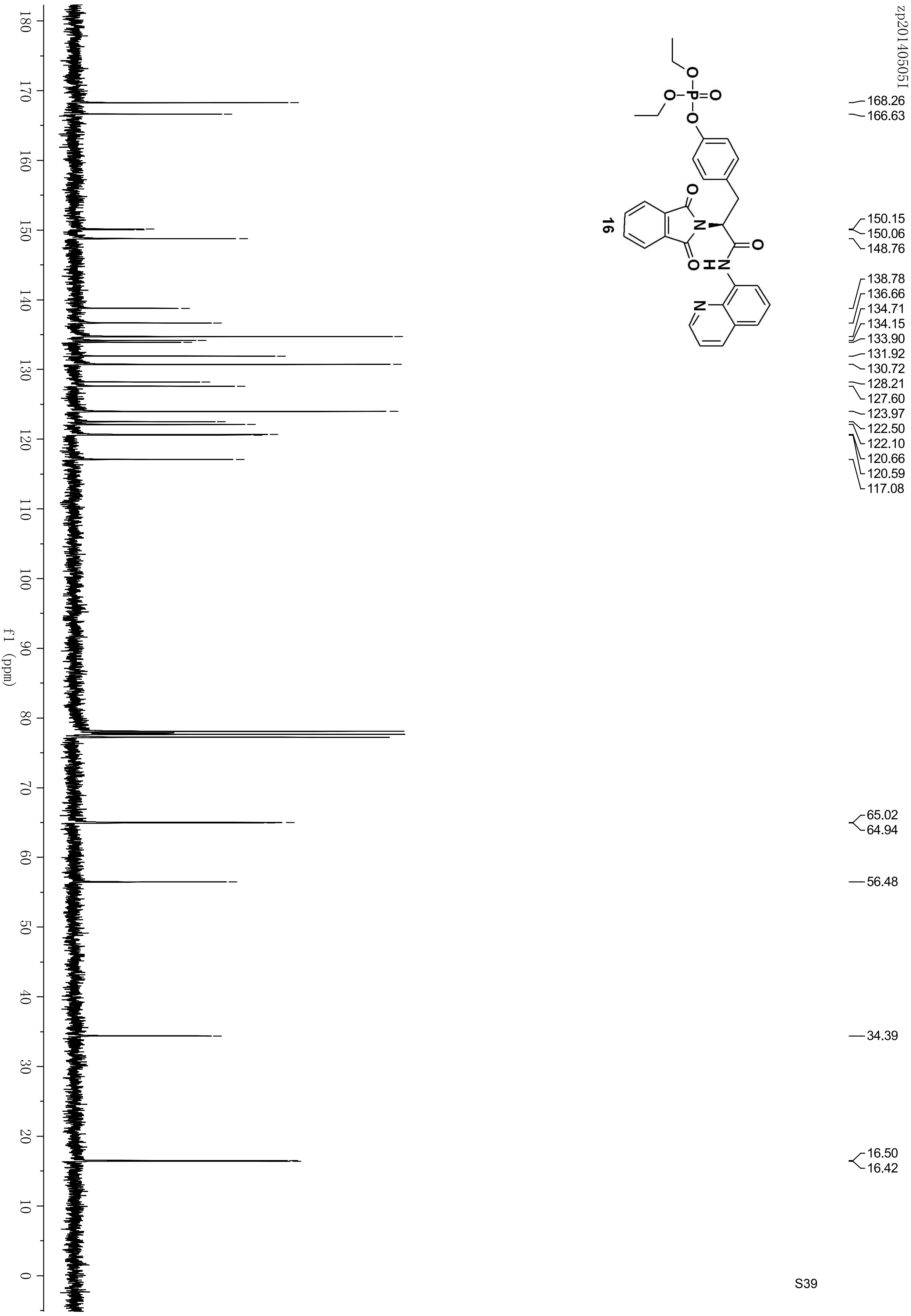

zp20140510A
141.37
141.08
139.00
136.54
134.57
131.93
129.78
129.18
128.69
128.36
128.23
127.87
127.68
127.44
124.00
122.45
122.04
117.42
12
O
N
O
NH
N
142
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115
f1 (ppm)


15

zp20140505K
10.201
8.630
8.623
8.609
8.602
8.462
8.451
7.961
7.934
7.693
7.682
7.676
7.666
7.557
7.547
7.364
7.344
7.242
7.229
7.020
6.994
6.788
6.762
6.724
6.603
6.576
5.394
5.370
5.362
5.339
3.703
3.682
3.669
3.543
MeO
O
N
H
N
O
O
0.97
1.01
1.00
1.03
2.12
2.13
2.15
1.10
1.07
2.14
1.05
1.00
2.00
3.01
11.0
10.5
10.0
9.5
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)

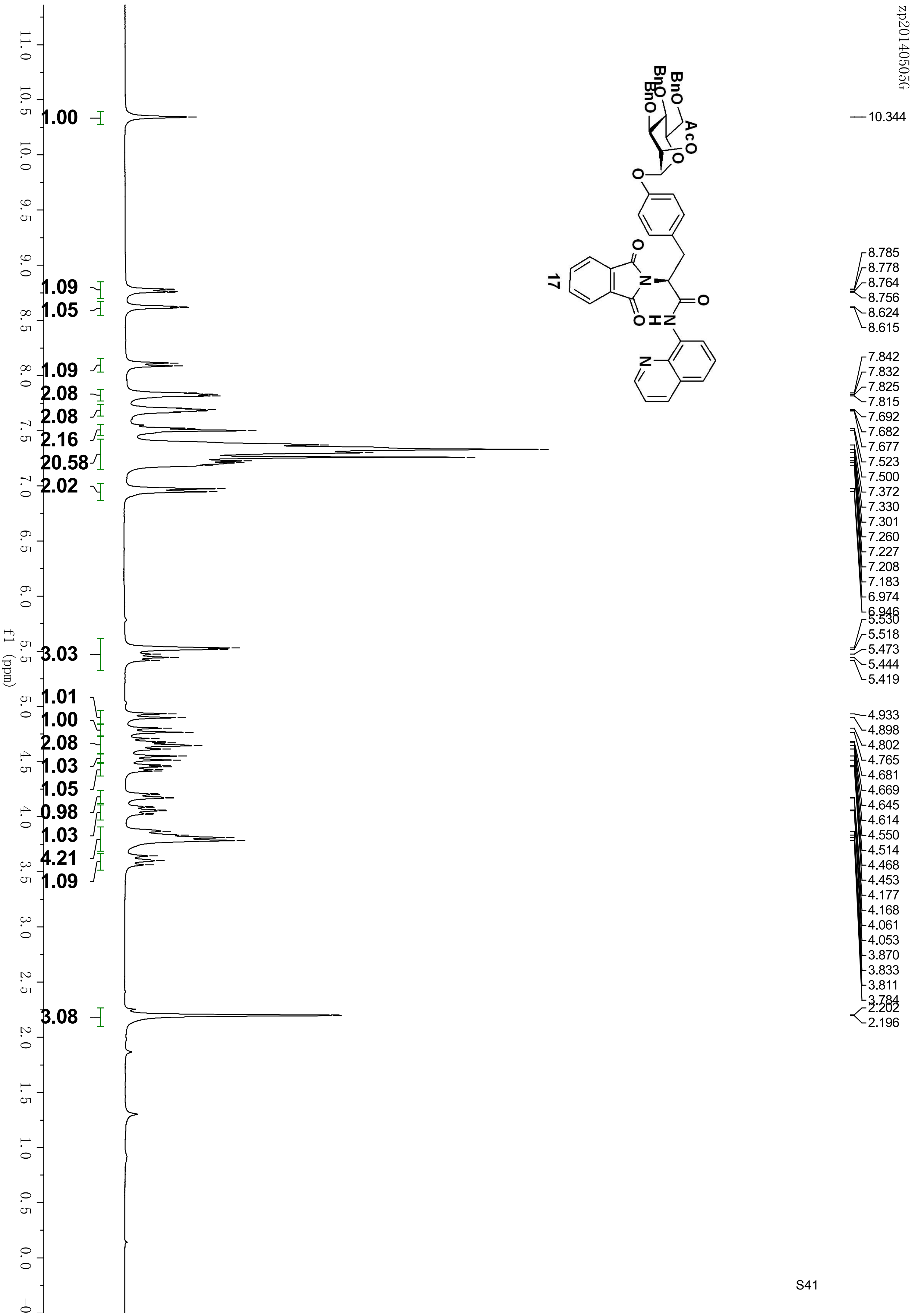

15
zp20140505K
MeO
O
N
O
O
N
H
N
168.38
166.88
160.25
148.77
138.76
136.70
134.69
134.31
132.10
130.21
128.27
127.69
123.99
122.51
122.12
121.79
117.17
114.72
113.42
56.63
55.57
35.30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


zp201405051
16
10.306
8.708
8.696
8.684
8.573
8.567
8.560
8.076
8.049
7.785
7.774
7.681
7.670
7.462
7.451
7.354
7.345
7.340
7.332
7.326
7.318
7.291
7.278
7.250
7.101
7.074
5.455
5.428
5.400
4.149
4.145
4.126
4.103
3.804
3.777
1.268
1.245
1.225
1.01
1.05
1.02
1.02
2.12
2.11
2.16
3.92
2.08
1.00
4.12
2.00
6.39
11.0
10.5
10.0
9.5
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)

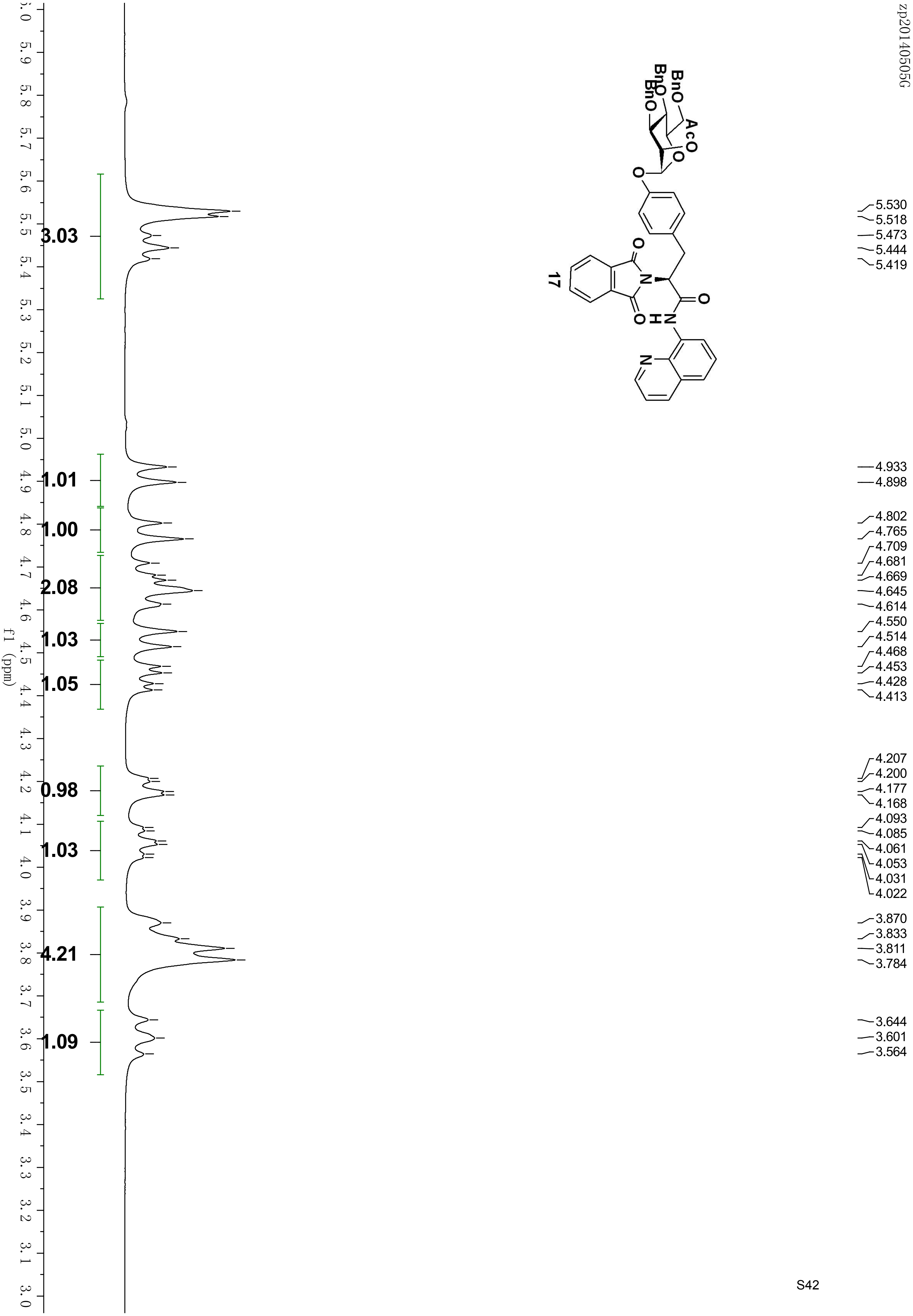

zp201405051
16
168.26
166.63
150.15
150.06
148.76
138.78
136.66
134.71
134.15
133.90
131.92
130.72
128.21
127.60
123.97
122.50
122.10
120.66
120.59
117.08
65.02
64.94
56.48
34.39
16.50
16.42
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
P
N
H

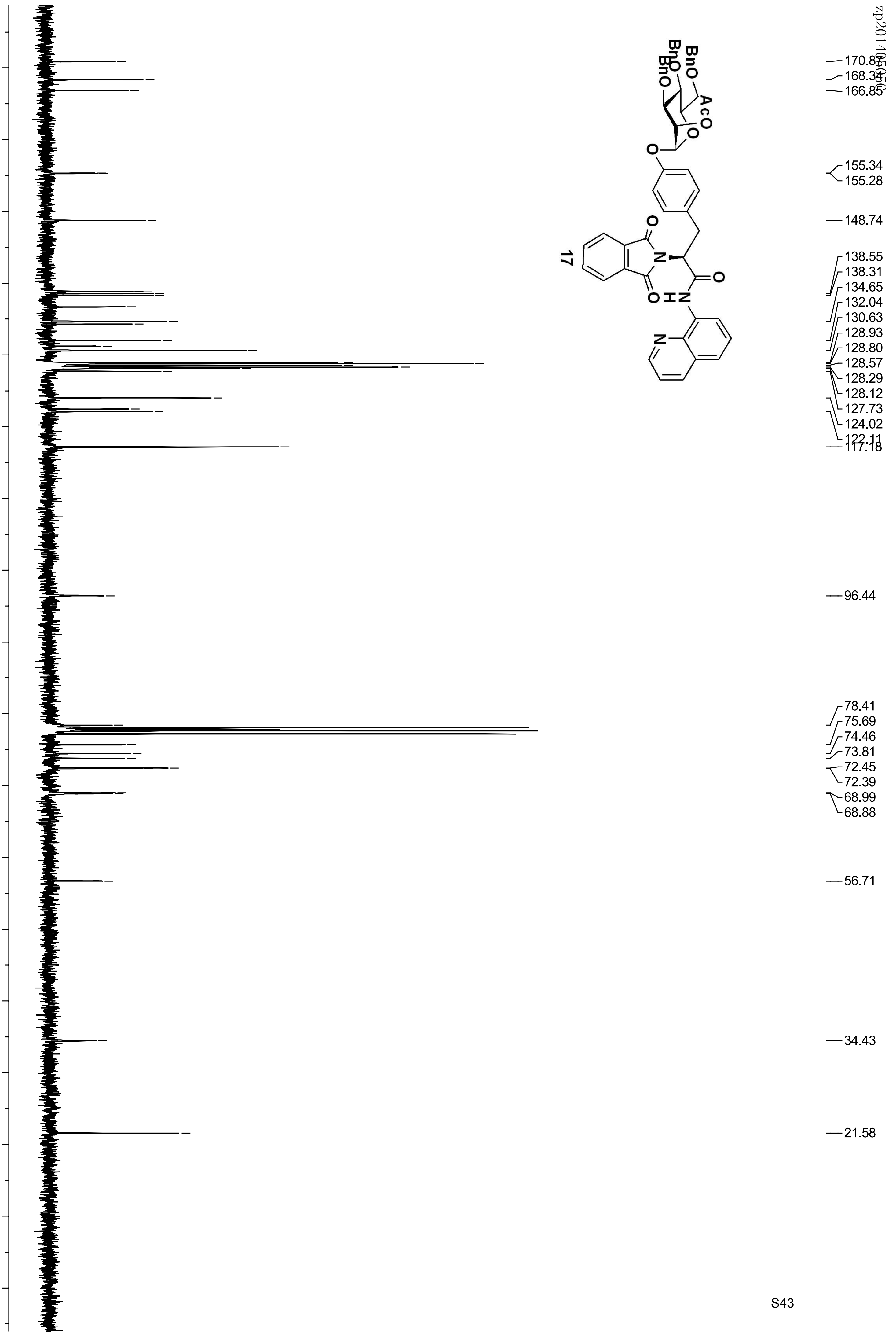
16

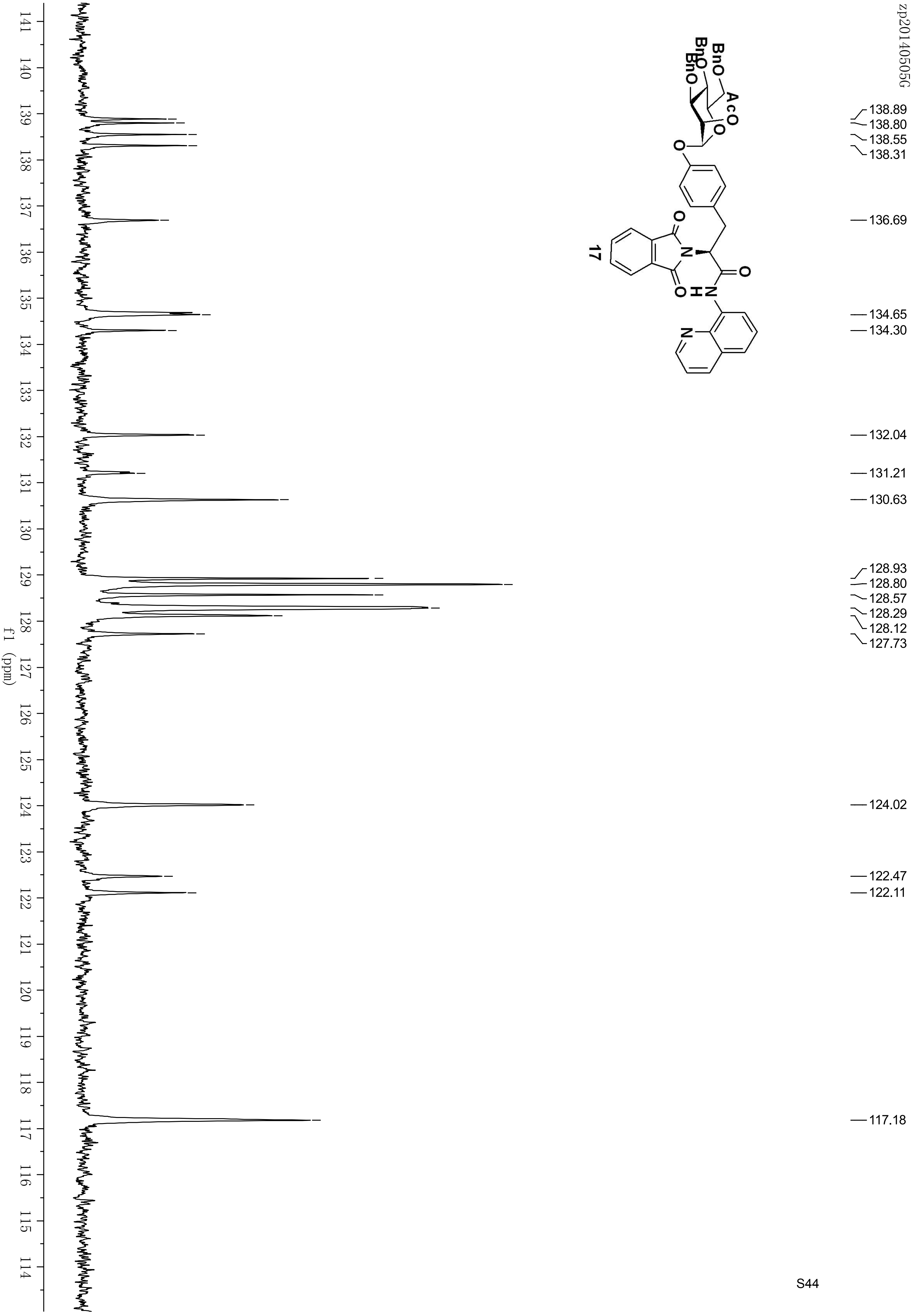
zp20140505H
-6.44
130
110
90
80
70
60
50
40
30
20
10
0
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
f1 (ppm)

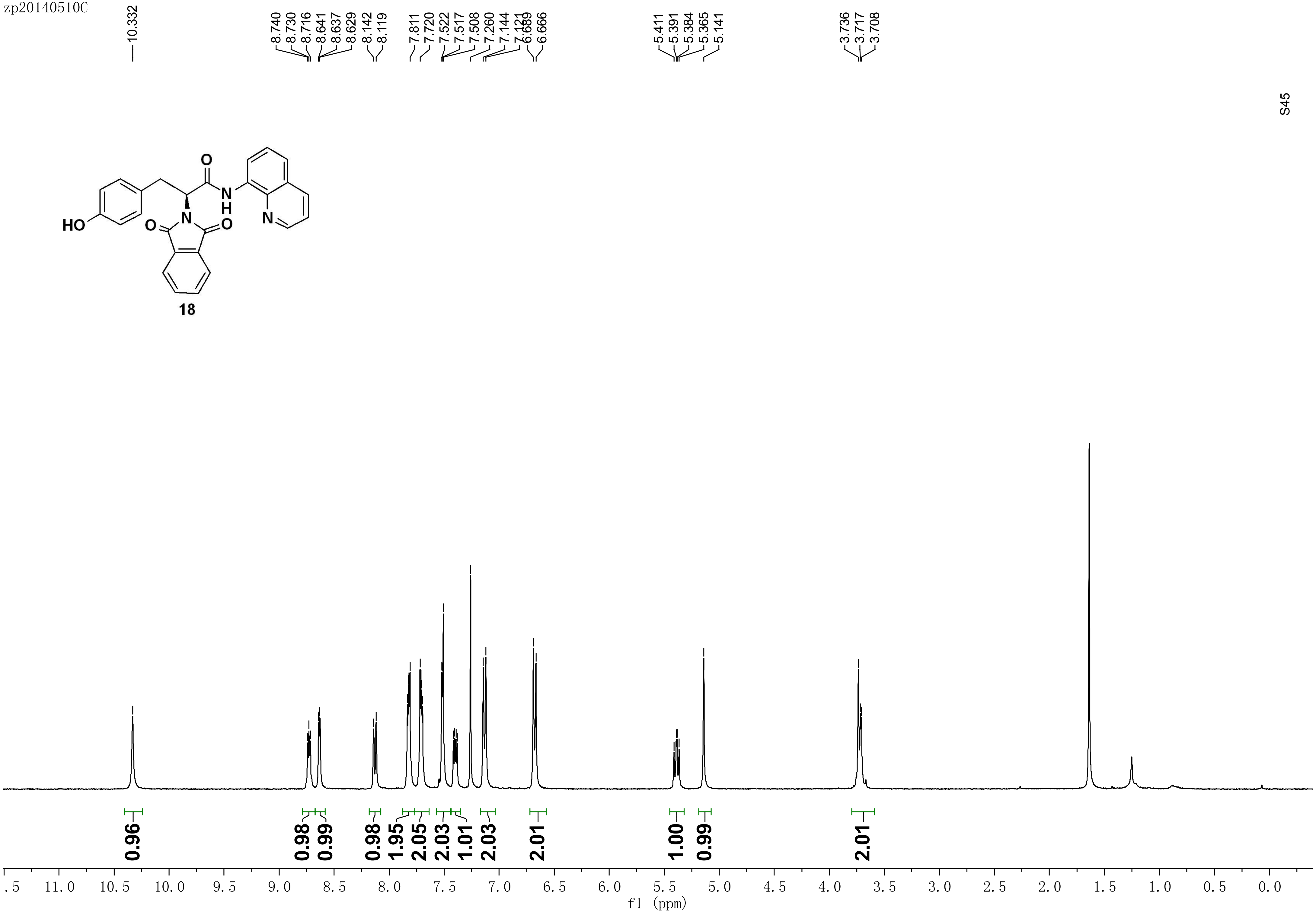

zp20140505G
10.344
8.785
8.778
8.764
8.756
8.624
8.615
7.842
7.832
7.825
7.815
7.692
7.682
7.677
7.523
7.500
7.372
7.330
7.301
7.260
7.227
7.208
7.183
6.974
6.946
5.530
5.518
5.473
5.444
5.419
4.933
4.898
4.802
4.765
4.681
4.669
4.645
4.614
4.550
4.514
4.468
4.453
4.177
4.168
4.061
4.053
3.870
3.833
3.811
3.784
2.202
2.196
1.00
1.09
1.05
1.09
2.08
2.08
2.16
20.58
2.02
3.03
1.01
1.00
2.08
1.03
1.05
0.98
1.03
4.21
1.09
3.08
11.0
10.5
10.0
9.5
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
−0
f1 (ppm)
BnO
BnO
BnO
AcO
O
O
O
N
O
N
H
O
N

17

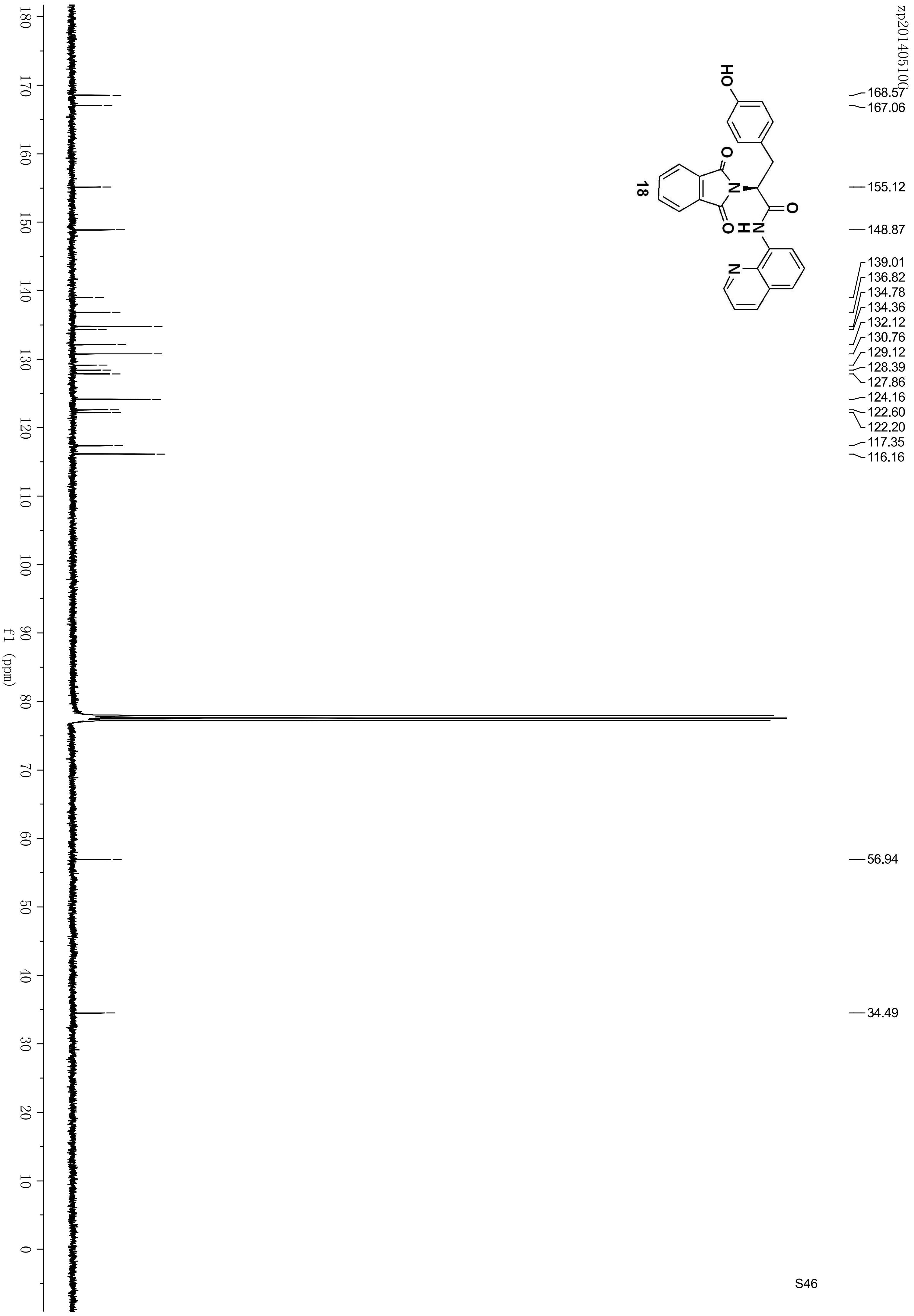

zp20140505G
BnO
BnO
BnO
AcO
O
O
O
O
O
N
H
N
N
17
5.530
5.518
5.473
5.444
5.419
4.933
4.898
4.802
4.765
4.709
4.681
4.669
4.645
4.614
4.550
4.514
4.468
4.453
4.428
4.413
4.207
4.200
4.177
4.168
4.093
4.085
4.061
4.053
4.031
4.022
3.870
3.833
3.811
3.784
3.644
3.601
3.564
3.03
1.01
1.00
2.08
1.03
1.05
0.98
1.03
4.21
1.09
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
f1 (ppm)


zp20140505c
BnO
BnO
BnO
AcO
O
O
O
N
H
N
O
N
O
O
17
170.87
168.34
166.85
155.34
155.28
148.74
138.55
138.31
134.65
132.04
130.63
128.93
128.80
128.57
128.29
128.12
127.73
124.02
122.11
117.18
96.44
78.41
75.69
74.46
73.81
72.45
72.39
68.99
68.88
56.71
34.43
21.58
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

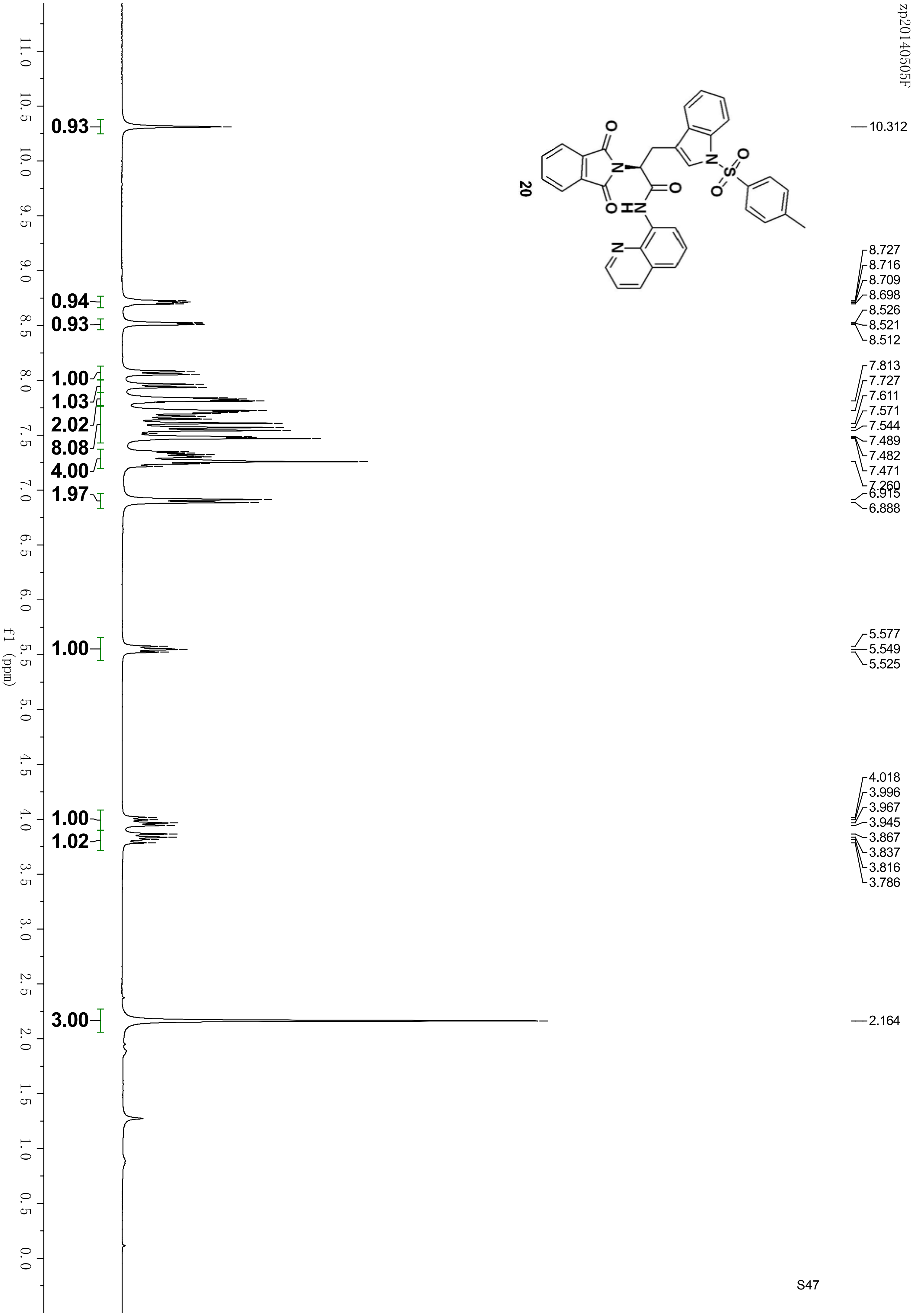

zp20140505G
BnO
BnO
BnO
AcO
O
N
H
17
138.89
138.80
138.55
138.31
136.69
134.65
134.30
132.04
131.21
130.63
128.93
128.80
128.57
128.29
128.12
127.73
124.02
122.47
122.11
117.18
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115
114
f1 (ppm)

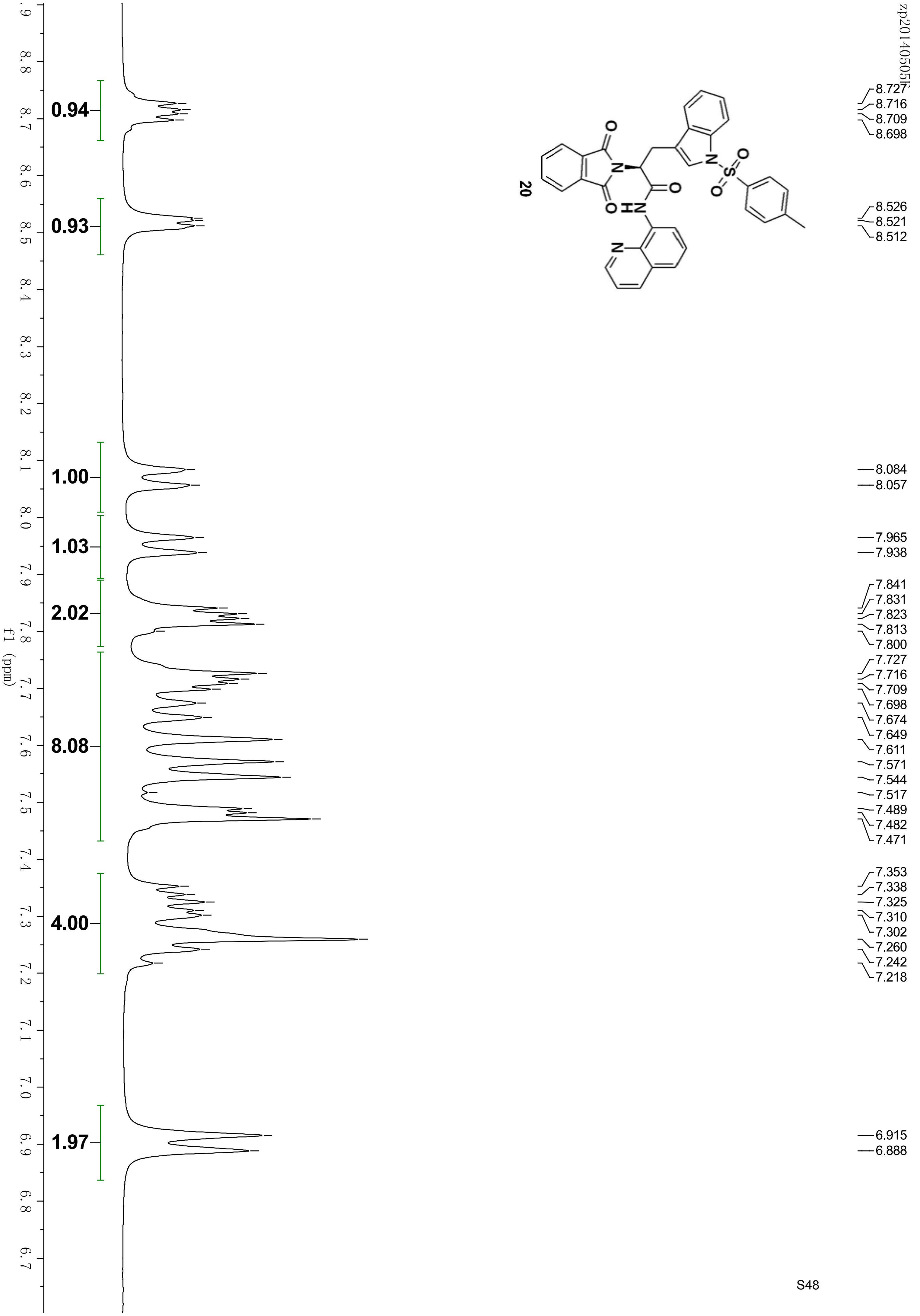

zp20140510C
10.332
8.740
8.730
8.716
8.641
8.637
8.629
8.142
8.119
7.811
7.720
7.522
7.517
7.508
7.260
7.144
7.121
6.689
6.666
5.411
5.391
5.384
5.365
5.141
3.736
3.717
3.708
HO
O
N
H
N
O
O
0.96
0.98
0.99
0.98
1.95
2.05
2.03
1.01
2.03
2.01
1.00
0.99
2.01
.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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)

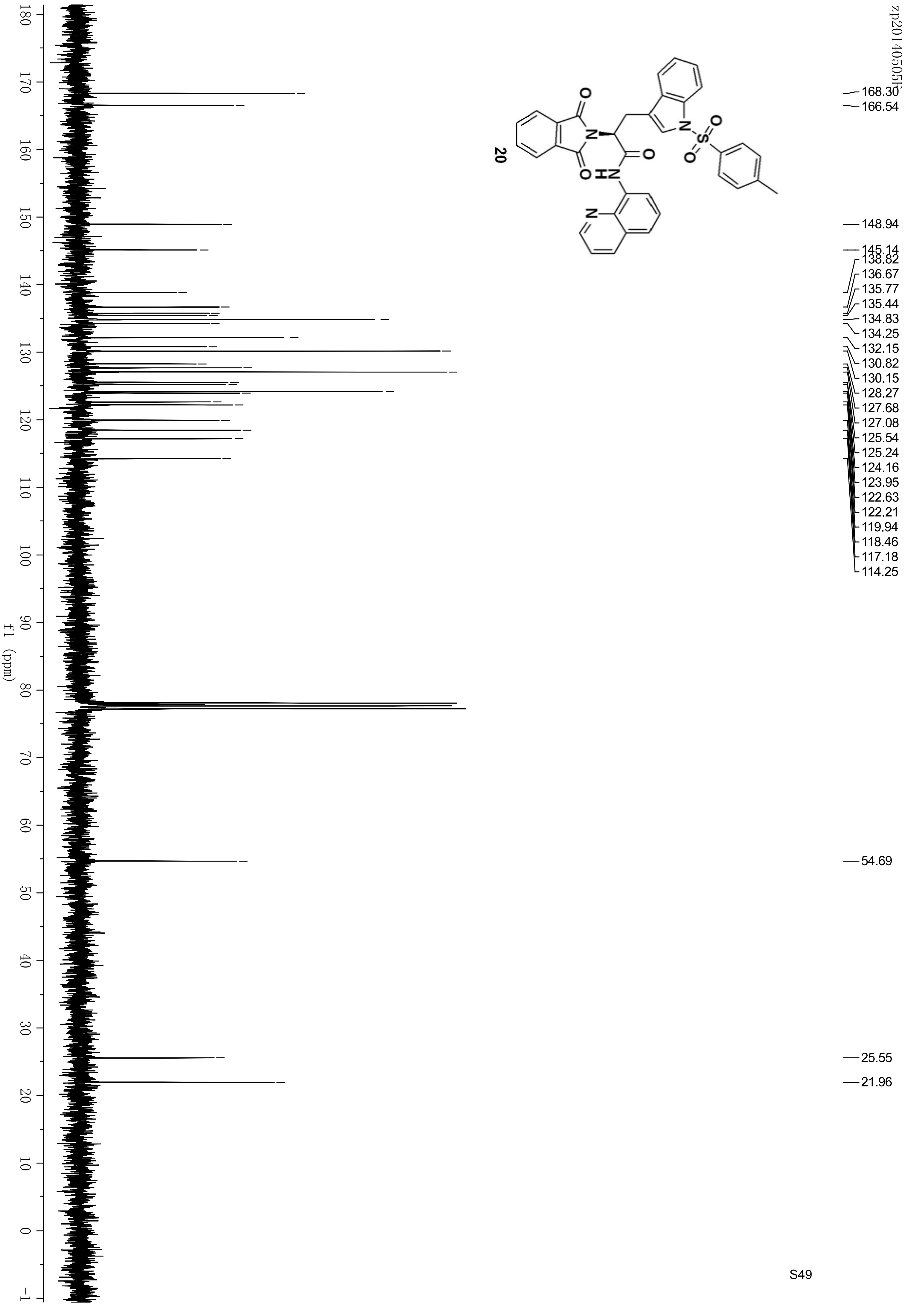
18

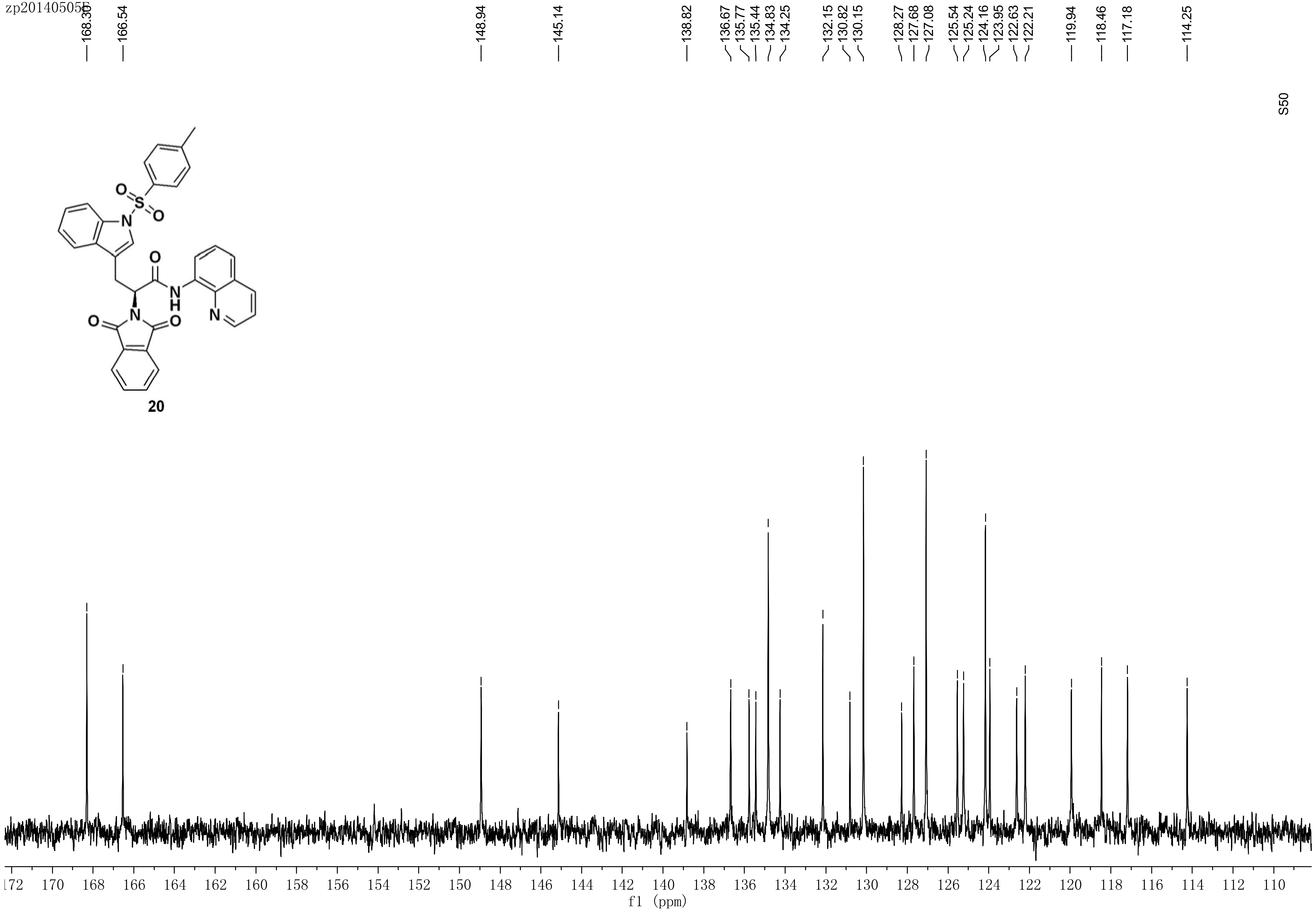

zp20140510C
168.57
167.06
155.12
148.87
139.01
136.82
134.78
134.36
132.12
130.76
129.12
128.39
127.86
124.16
122.60
122.20
117.35
116.16
56.94
34.49
HO
O
N
NH
O
N
O
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

18


zp20140505F
20
O
N
O
O
NH
N
N
S
O
O
O
10.312
8.727
8.716
8.709
8.698
8.526
8.521
8.512
7.813
7.727
7.611
7.571
7.544
7.489
7.482
7.471
7.260
6.915
6.888
5.577
5.549
5.525
4.018
3.996
3.967
3.945
3.867
3.837
3.816
3.786
2.164
0.93
0.94
0.93
1.00
1.03
2.02
8.08
4.00
1.97
1.00
1.00
1.02
3.00
11.0
10.5
10.0
9.5
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)

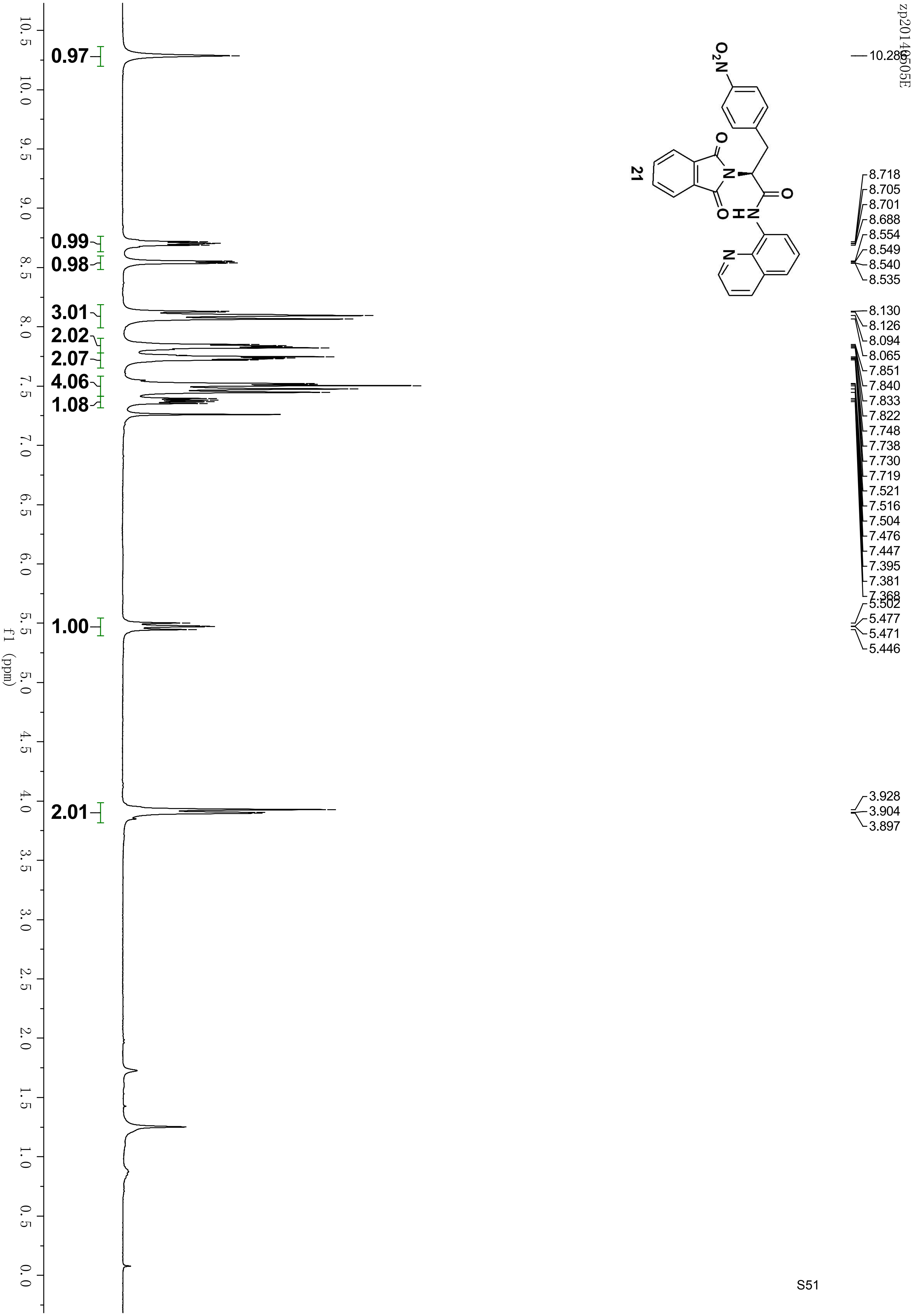

zp20140505F
20
8.727
8.716
8.709
8.698
8.526
8.521
8.512
8.084
8.057
7.965
7.938
7.841
7.831
7.823
7.813
7.800
7.727
7.716
7.709
7.698
7.674
7.649
7.611
7.571
7.544
7.517
7.489
7.482
7.471
7.353
7.338
7.325
7.310
7.302
7.260
7.242
7.218
6.915
6.888
0.94
0.93
1.00
1.03
2.02
8.08
4.00
1.97
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)

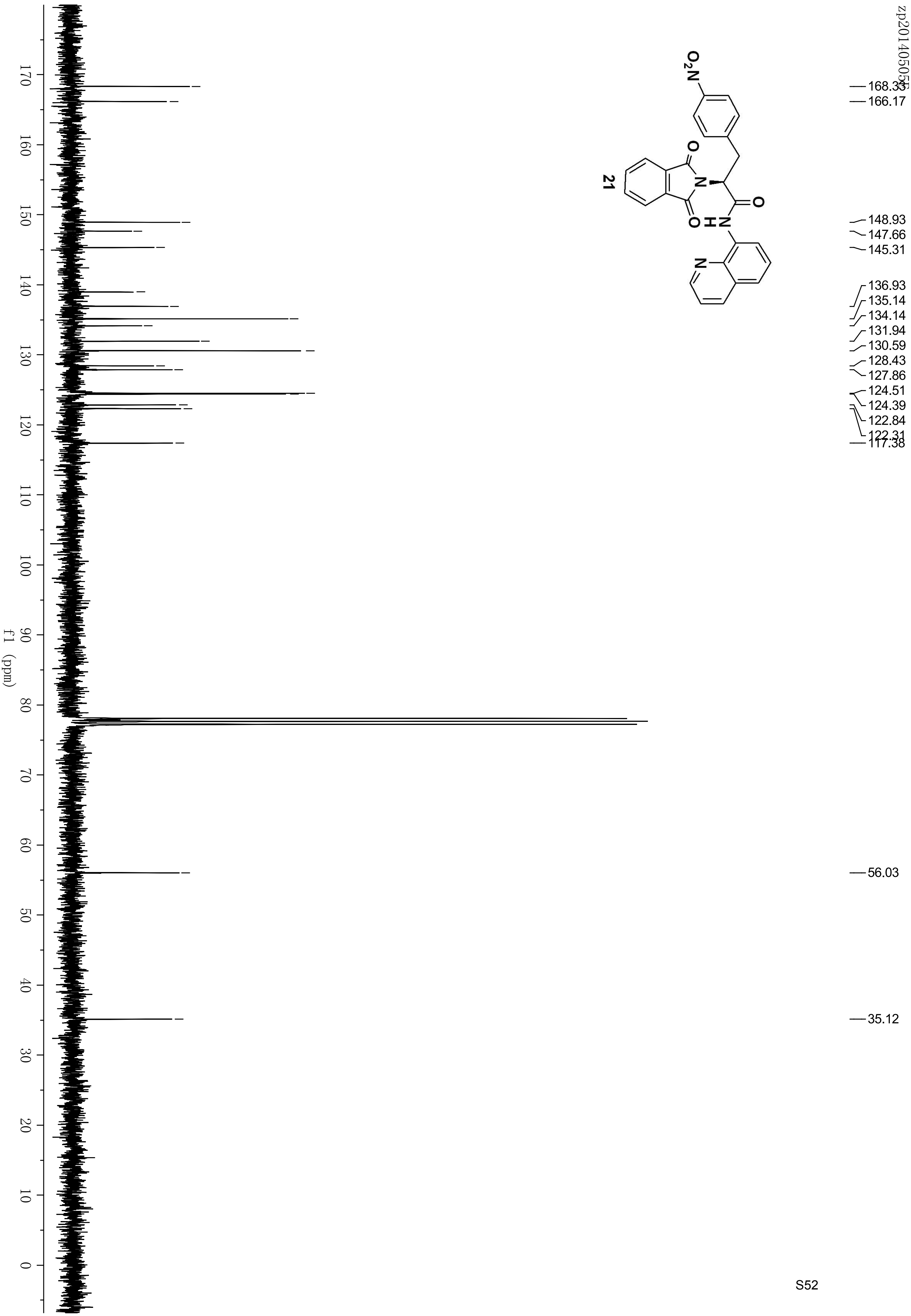

zp20140505F
20
168.30
166.54
148.94
145.14
138.82
136.67
135.77
135.44
134.83
134.25
132.15
130.82
130.15
128.27
127.68
127.08
125.54
125.24
124.16
123.95
122.63
122.21
119.94
118.46
117.18
114.25
54.69
25.55
21.96
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

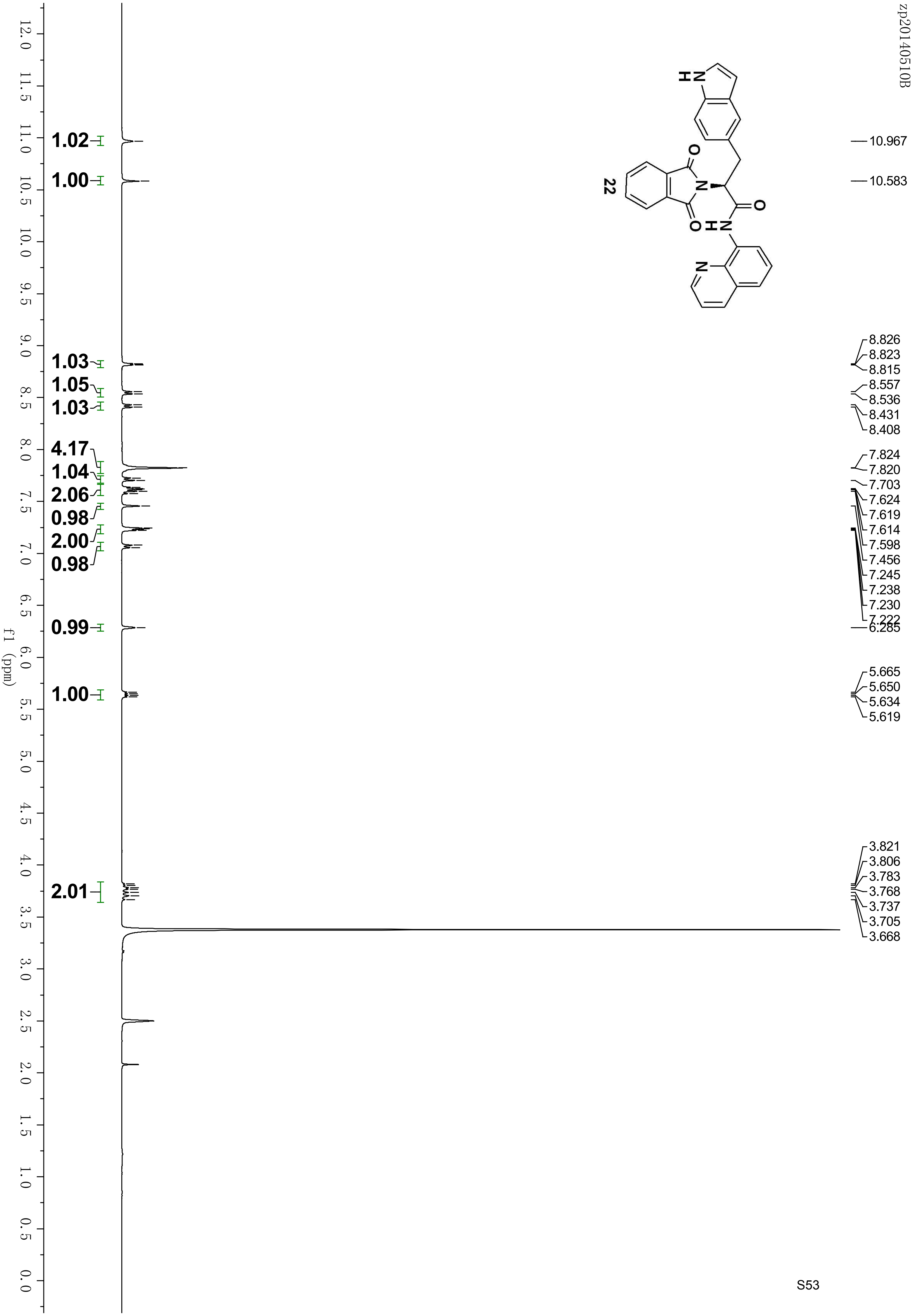


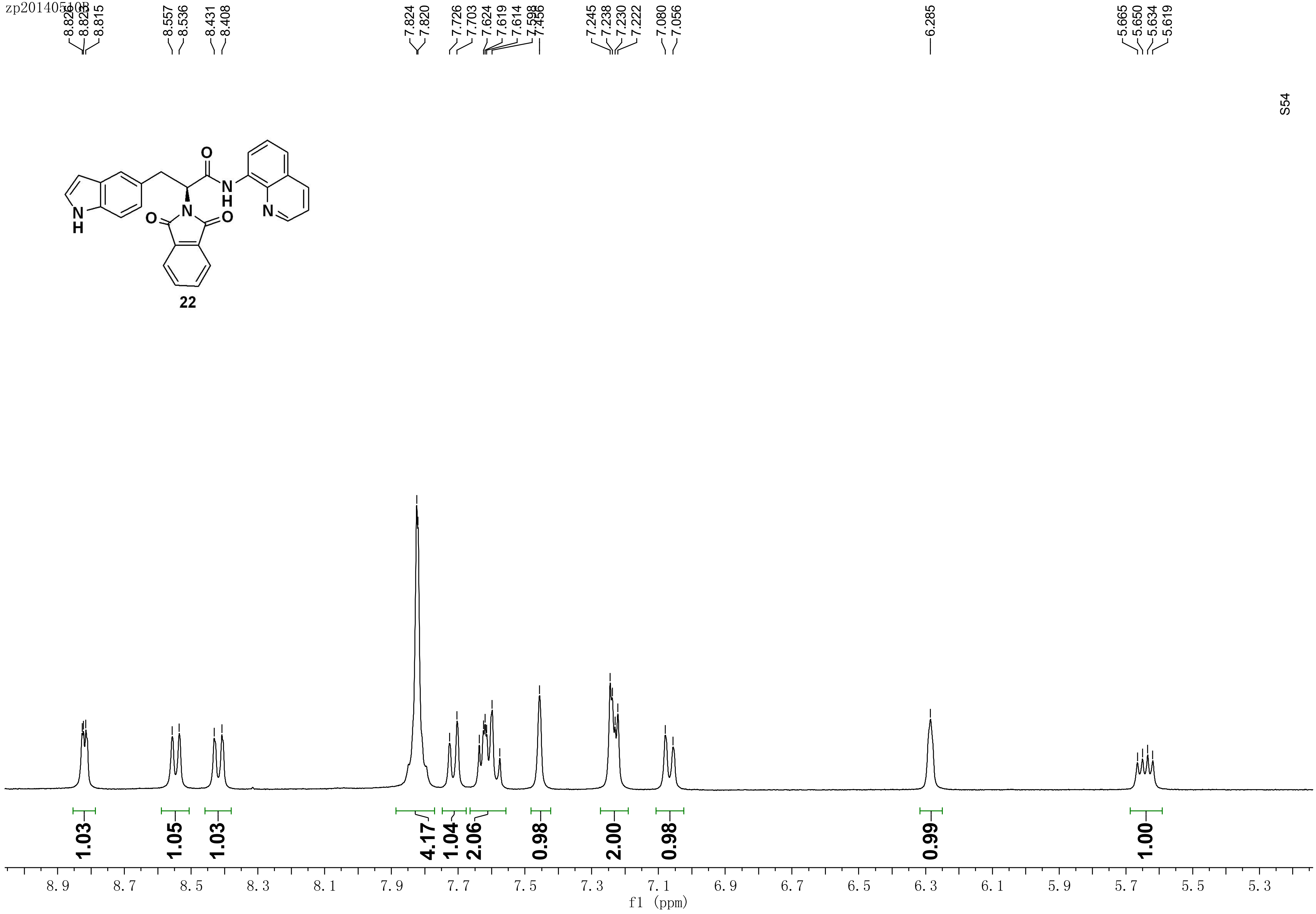
20

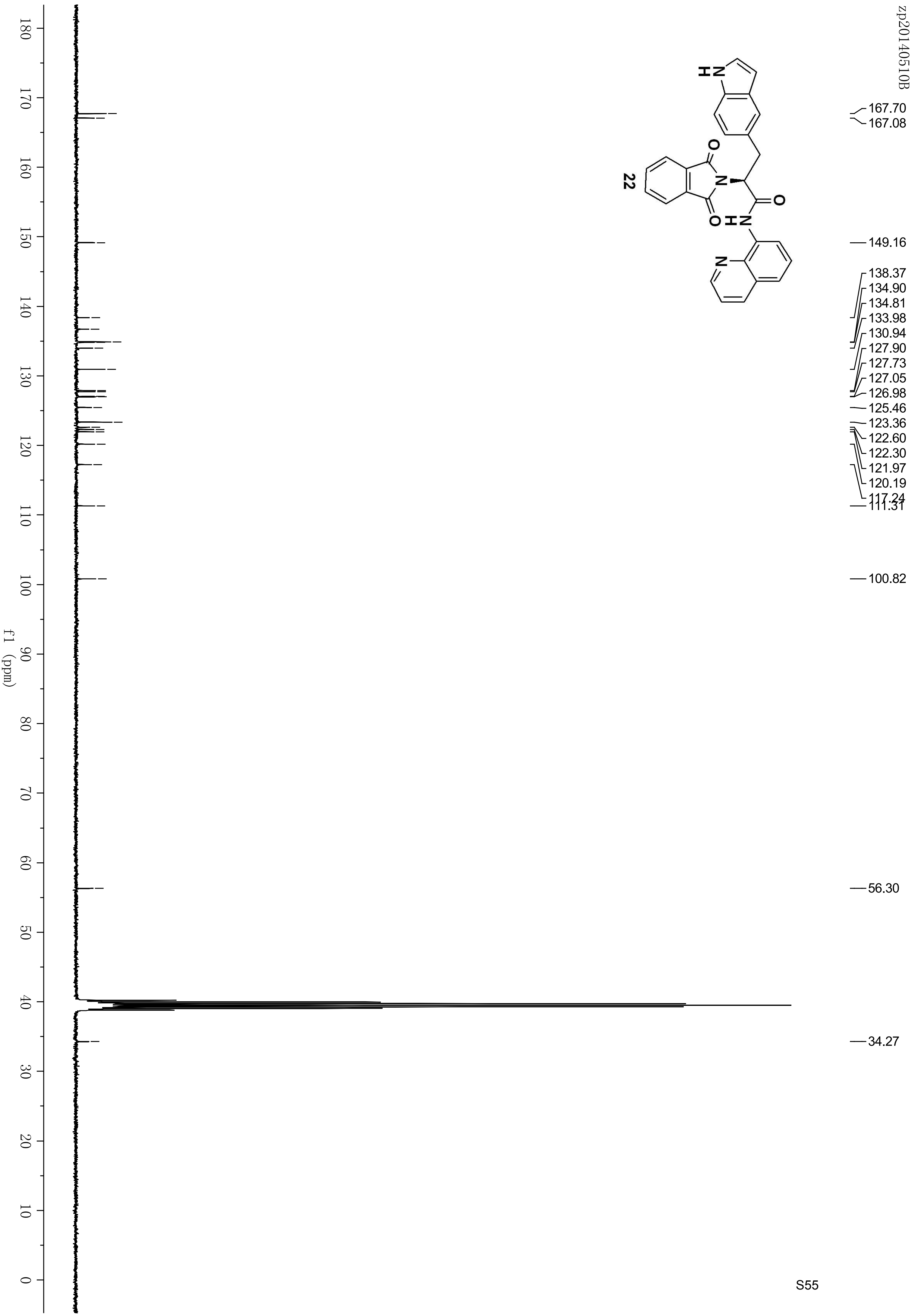
zp20140505E
168.30
166.54
148.94
145.14
138.82
136.67
135.77
135.44
134.83
134.25
132.15
130.82
130.15
128.27
127.68
127.08
125.54
125.24
124.16
123.95
122.63
122.21
119.94
118.46
117.18
114.25
O
S
O
N
O
N
H
N
O
N
O
172 170 168 166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110
f1 (ppm)

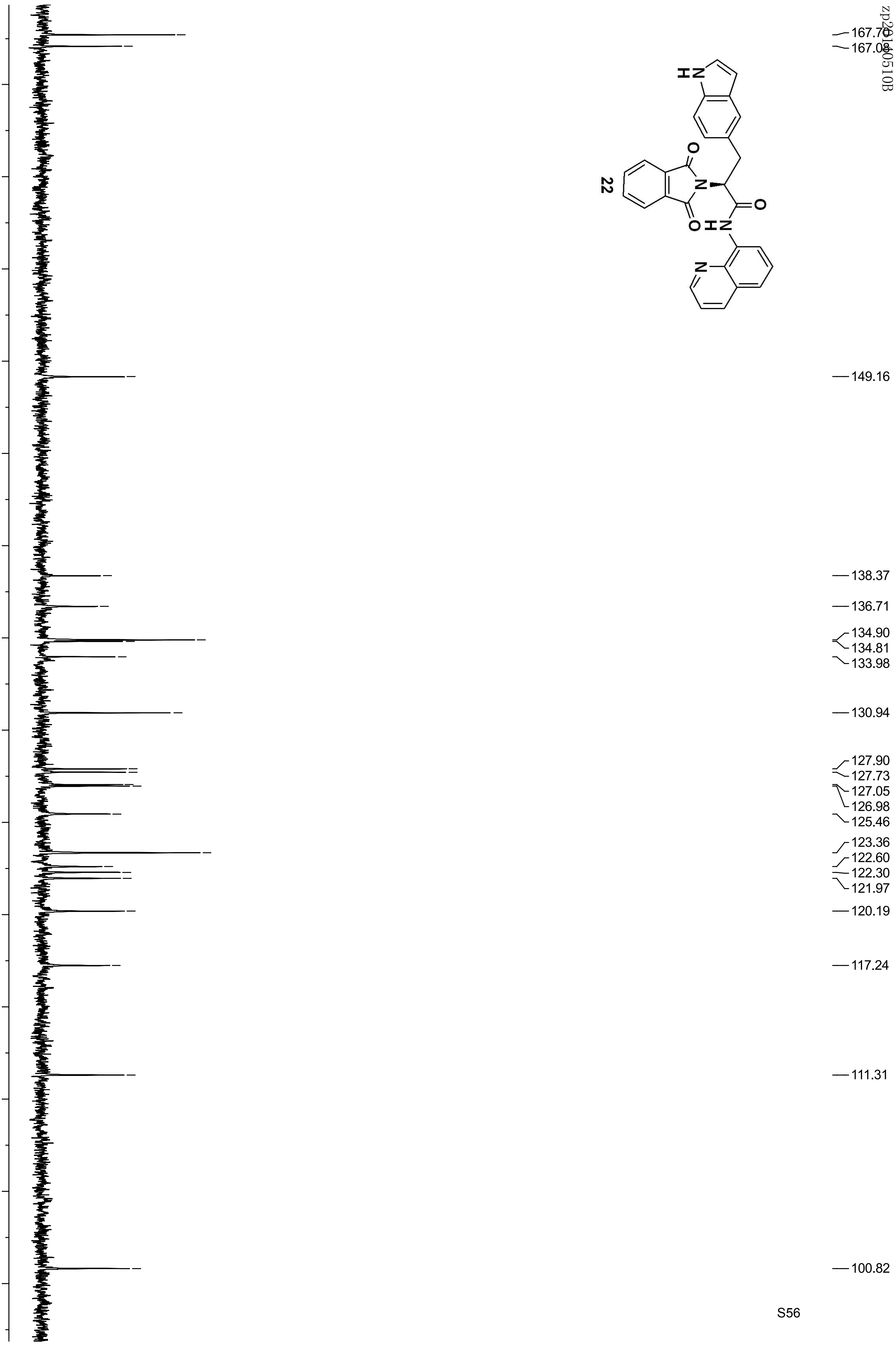

zp20140505E
21
O_2N
O
N
O
H
N
O
N
10.286
8.718
8.705
8.701
8.688
8.554
8.549
8.540
8.535
8.130
8.126
8.094
8.065
7.851
7.840
7.833
7.822
7.748
7.738
7.730
7.719
7.521
7.516
7.504
7.476
7.447
7.395
7.381
7.368
5.502
5.477
5.471
5.446
3.928
3.904
3.897
0.97
0.99
0.98
3.01
2.02
2.07
4.06
1.08
1.00
2.01
10.5
10.0
9.5
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)


zp20140505
168.33
166.17
148.93
147.66
145.31
136.93
135.14
134.14
131.94
130.59
128.43
127.86
124.51
124.39
122.84
122.31
117.38
56.03
35.12
O2N
O
N
O
H
N
O
N
21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


zp20140510B
22
10.967
10.583
8.826
8.823
8.815
8.557
8.536
8.431
8.408
7.824
7.820
7.703
7.624
7.619
7.614
7.598
7.456
7.245
7.238
7.230
7.222
6.285
5.665
5.650
5.634
5.619
3.821
3.806
3.783
3.768
3.737
3.705
3.668
1.02
1.00
1.03
1.05
1.03
4.17
1.04
2.06
0.98
2.00
0.98
0.99
1.00
2.01
12.0
11.5
11.0
10.5
10.0
9.5
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)


zp20140510B
8.826
8.823
8.815
8.557
8.536
8.431
8.408
7.824
7.820
7.726
7.703
7.624
7.619
7.614
7.598
7.456
7.245
7.238
7.230
7.222
7.080
7.056
6.285
5.665
5.650
5.634
5.619
N
H
O
N
O
O
N
H
N
22
1.03
1.05
1.03
4.17
1.04
2.06
0.98
2.00
0.98
0.99
1.00
8.9
8.7
8.5
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
f1 (ppm)


zp20140510B
22
O
N
O
H
N
O
N
N
H
167.70
167.08
149.16
138.37
134.90
134.81
133.98
130.94
127.90
127.73
127.05
126.98
125.46
123.36
122.60
122.30
121.97
120.19
117.24
111.31
100.82
56.30
34.27
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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167.08
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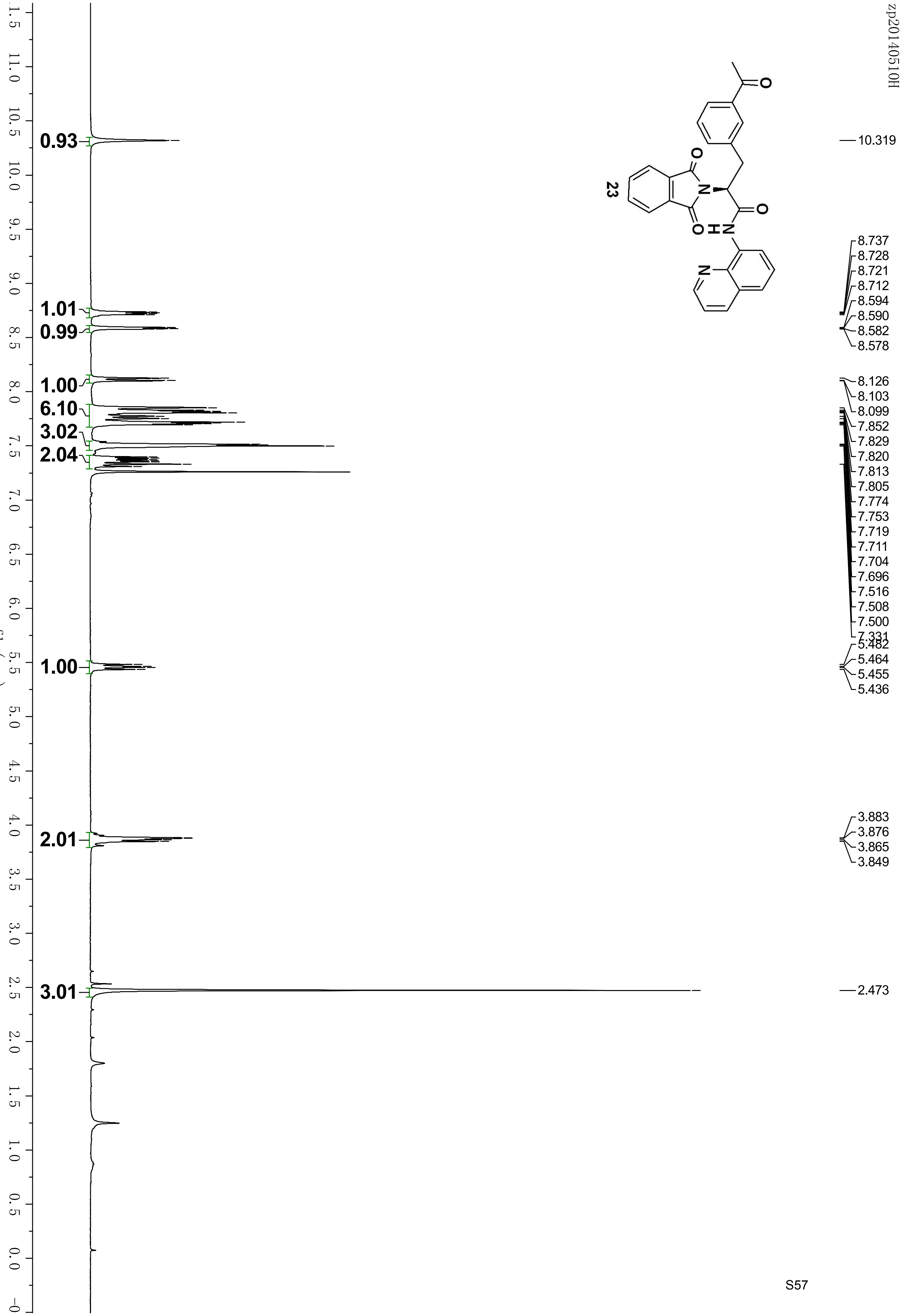
138.37
136.71
134.90
134.81
133.98
130.94
127.90
127.73
127.05
126.98
125.46
123.36
122.60
122.30
121.97
120.19
117.24
111.31
100.82
165
160
155
150
145
140
135
130
125
120
115
110
105
100
f1 (ppm)
NH
O
N
O
O
NH
N

22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8.737
8.728
8.721
8.712
8.594
8.590
8.582
8.578
8.126
8.103
8.099
7.852
7.829
7.820
7.813
7.805
7.774
7.753
7.719
7.711
7.704
7.696
7.516
7.508
7.500
7.331
5.482
5.464
5.455
5.436
3.883
3.876
3.865
3.849
2.473
0.93
1.01
0.99
1.00
6.10
3.02
2.04
1.00
2.01
3.01
f1 (ppm)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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2.5
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1.5
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0.0
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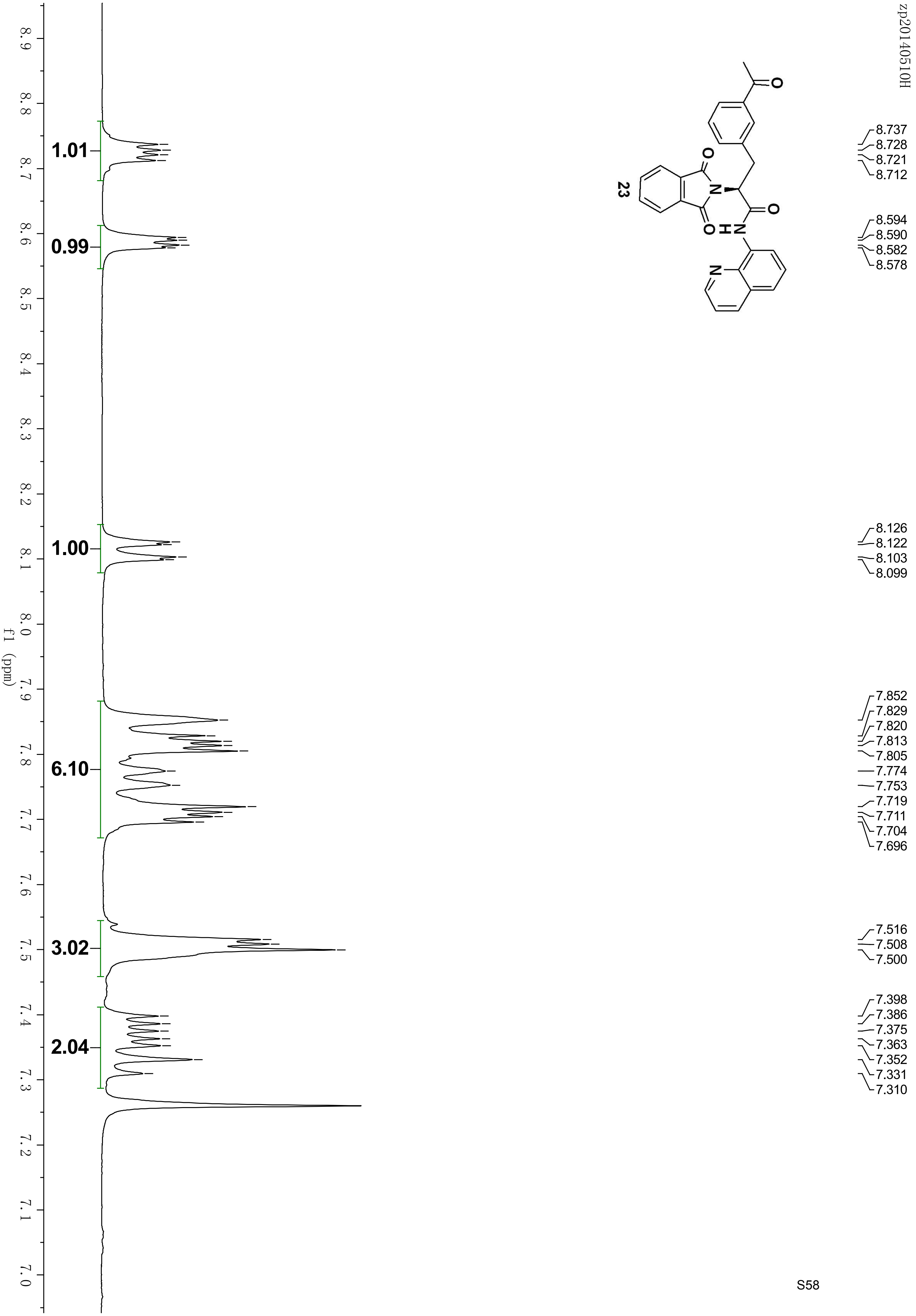
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H
O
O
N
O
8.737
8.728
8.721
8.712
8.594
8.590
8.582
8.578
8.126
8.122
8.103
8.099
7.852
7.829
7.820
7.813
7.805
7.774
7.753
7.719
7.711
7.704
7.696
7.516
7.508
7.500
7.398
7.386
7.375
7.363
7.352
7.331
7.310
1.01
0.99
1.00
6.10
3.02
2.04
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
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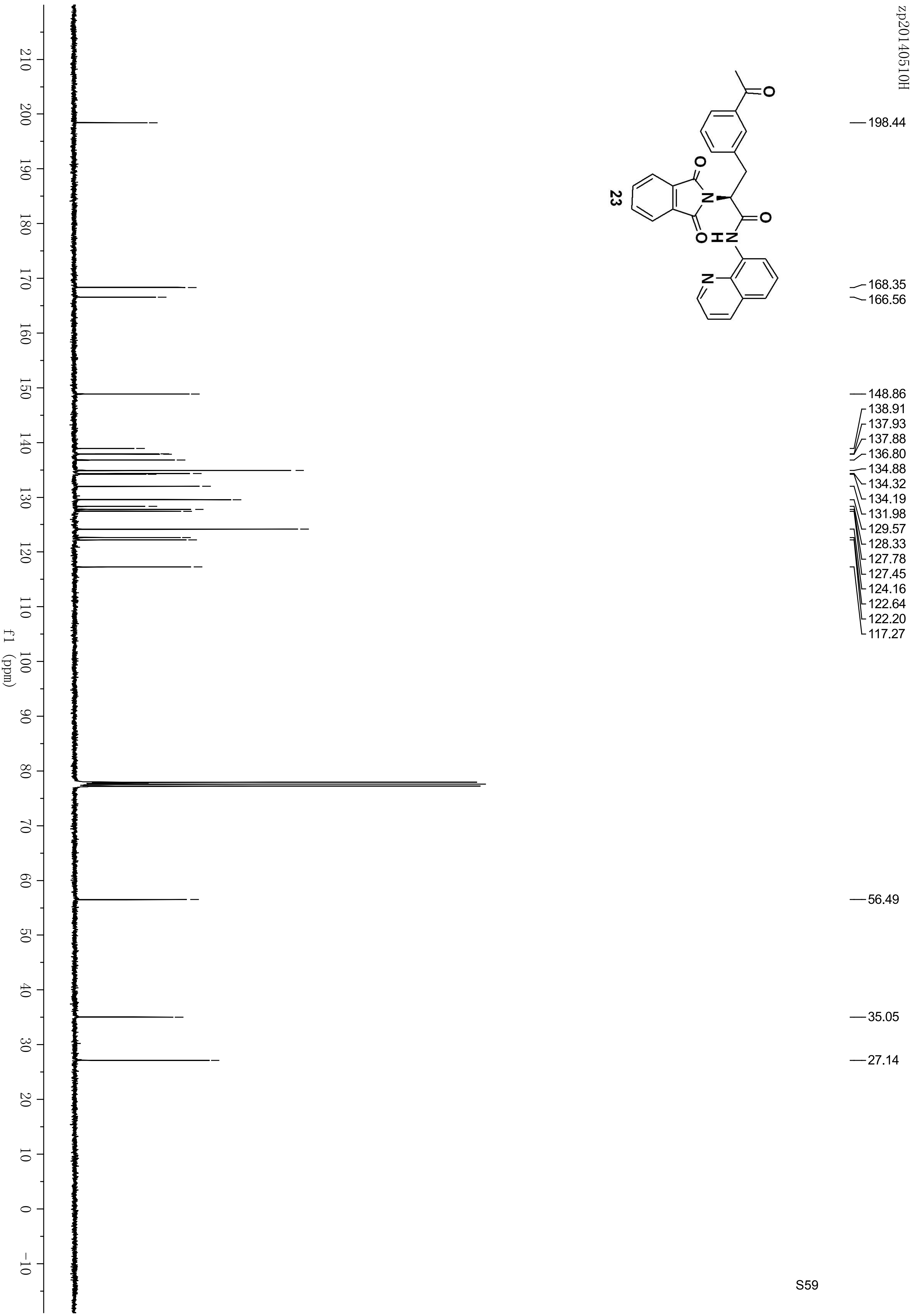
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)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198.44
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137.93
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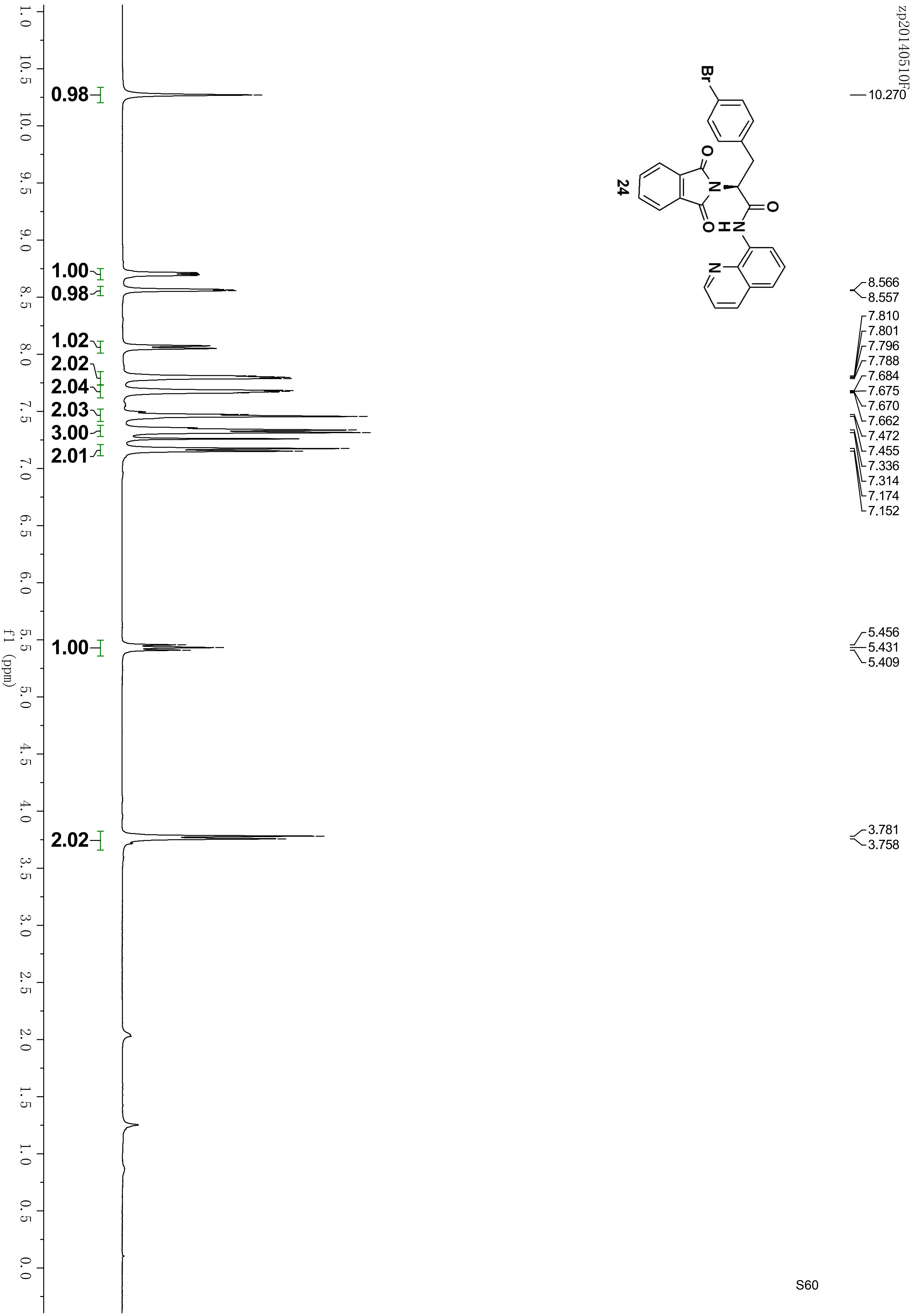
136.80
134.88
134.32
134.19
131.98
129.57
128.33
127.78
127.45
124.16
122.64
122.20
117.27
56.49
35.05
27.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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24
Br
O
N
H
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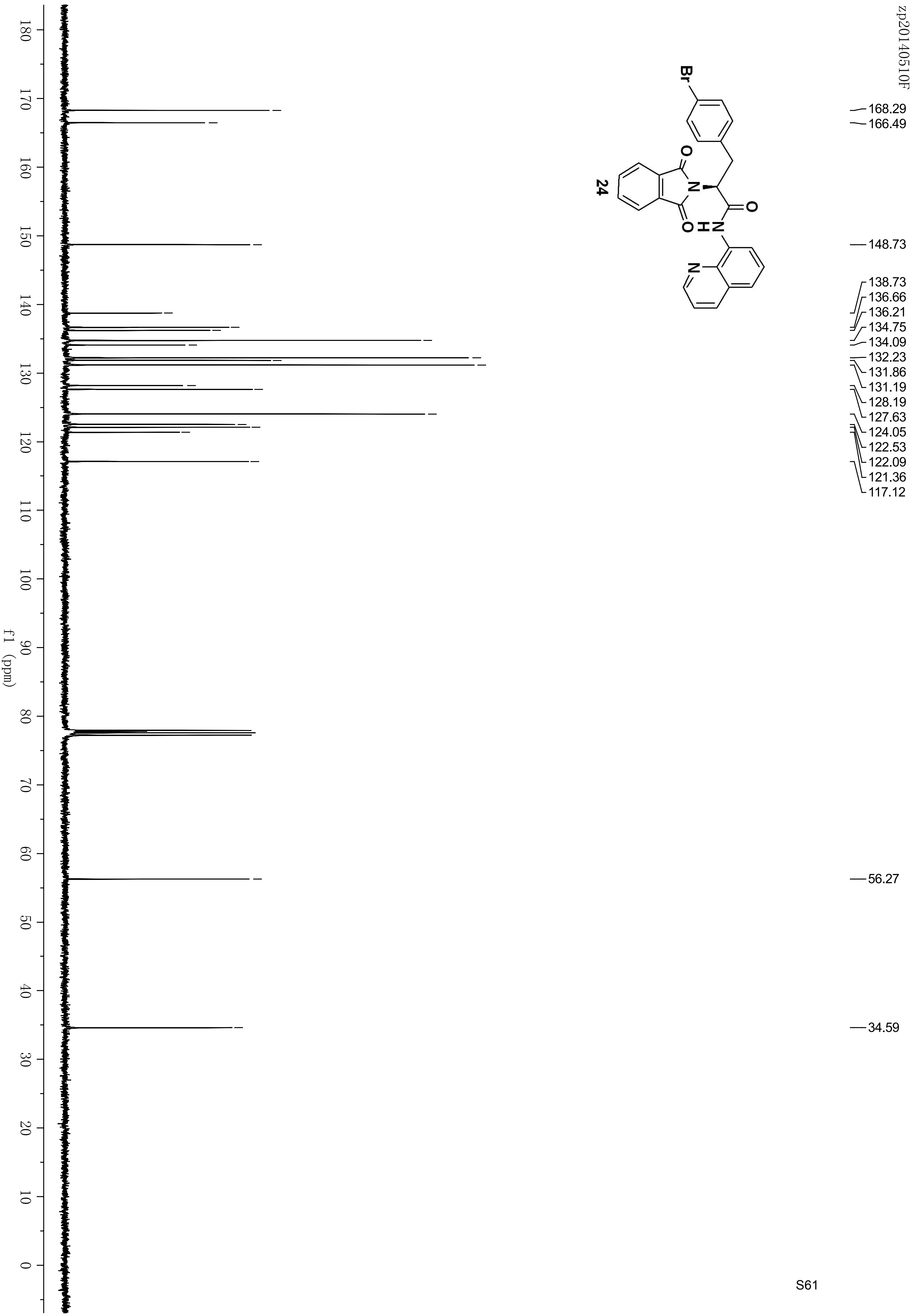
8.566
8.557
7.810
7.801
7.796
7.788
7.684
7.675
7.670
7.662
7.472
7.455
7.336
7.314
7.174
7.152
5.456
5.431
5.409
3.781
3.758
0.98
1.00
0.98
1.02
2.02
2.04
2.03
3.00
2.01
1.00
2.02
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


zp20140510F
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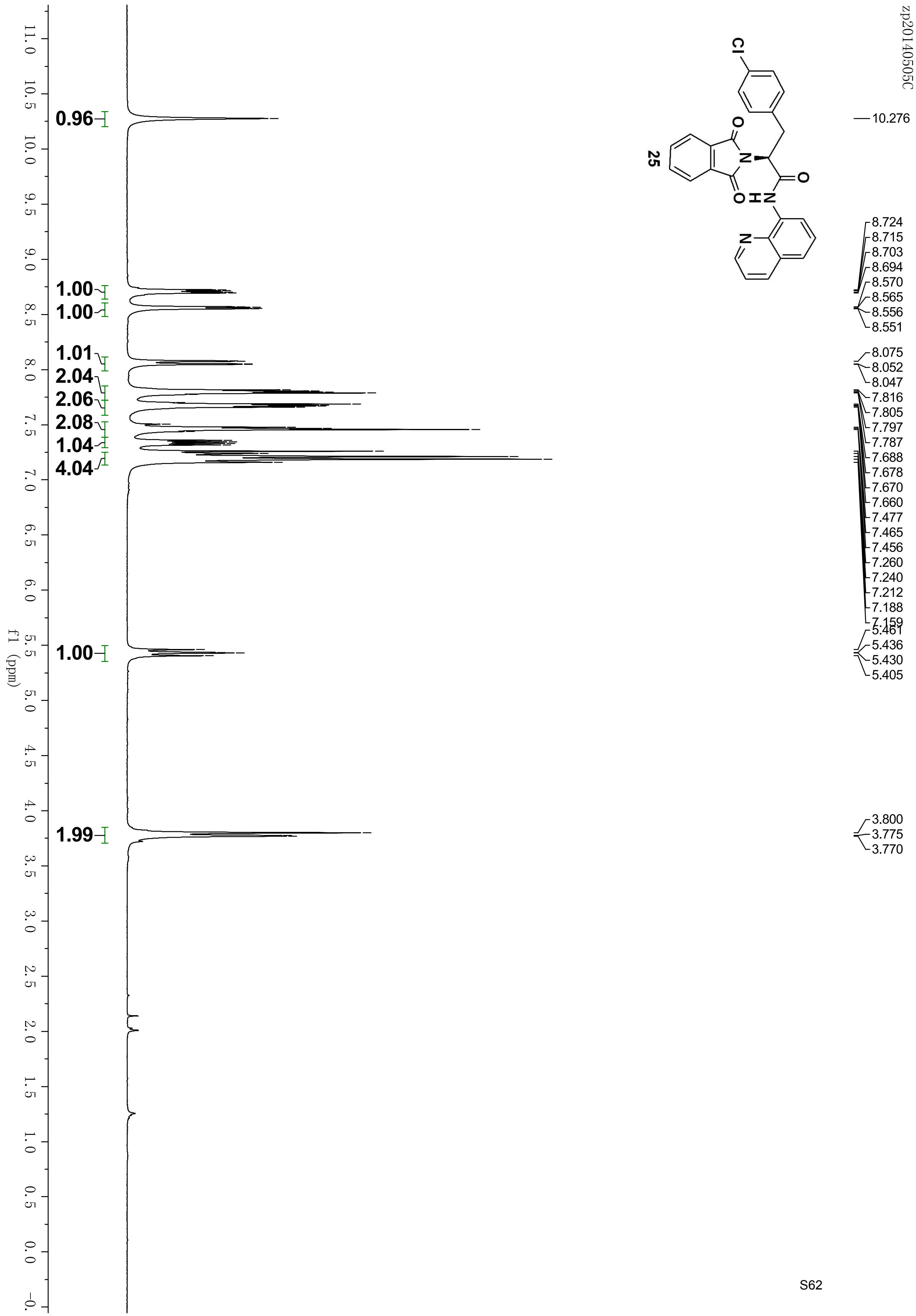
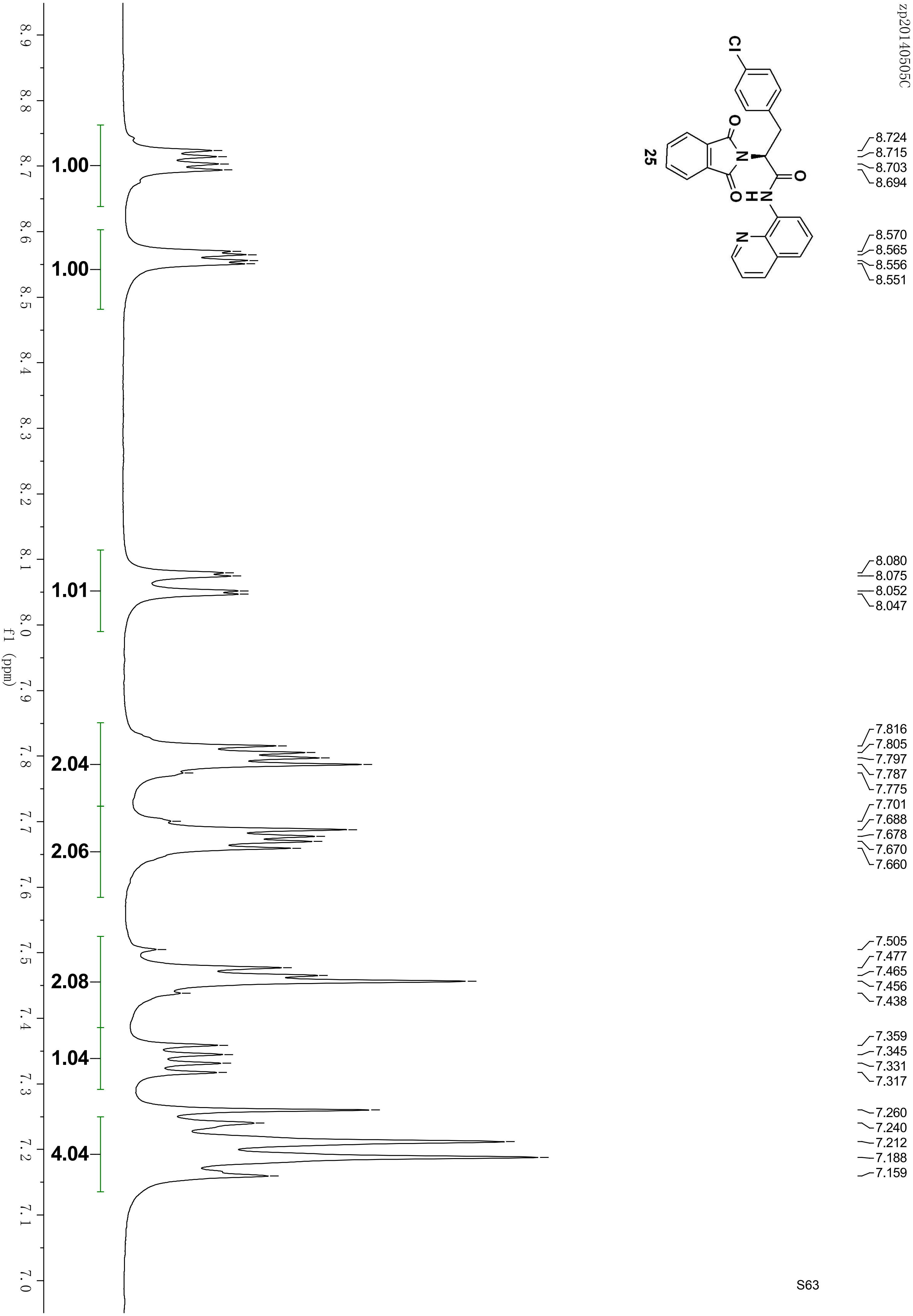
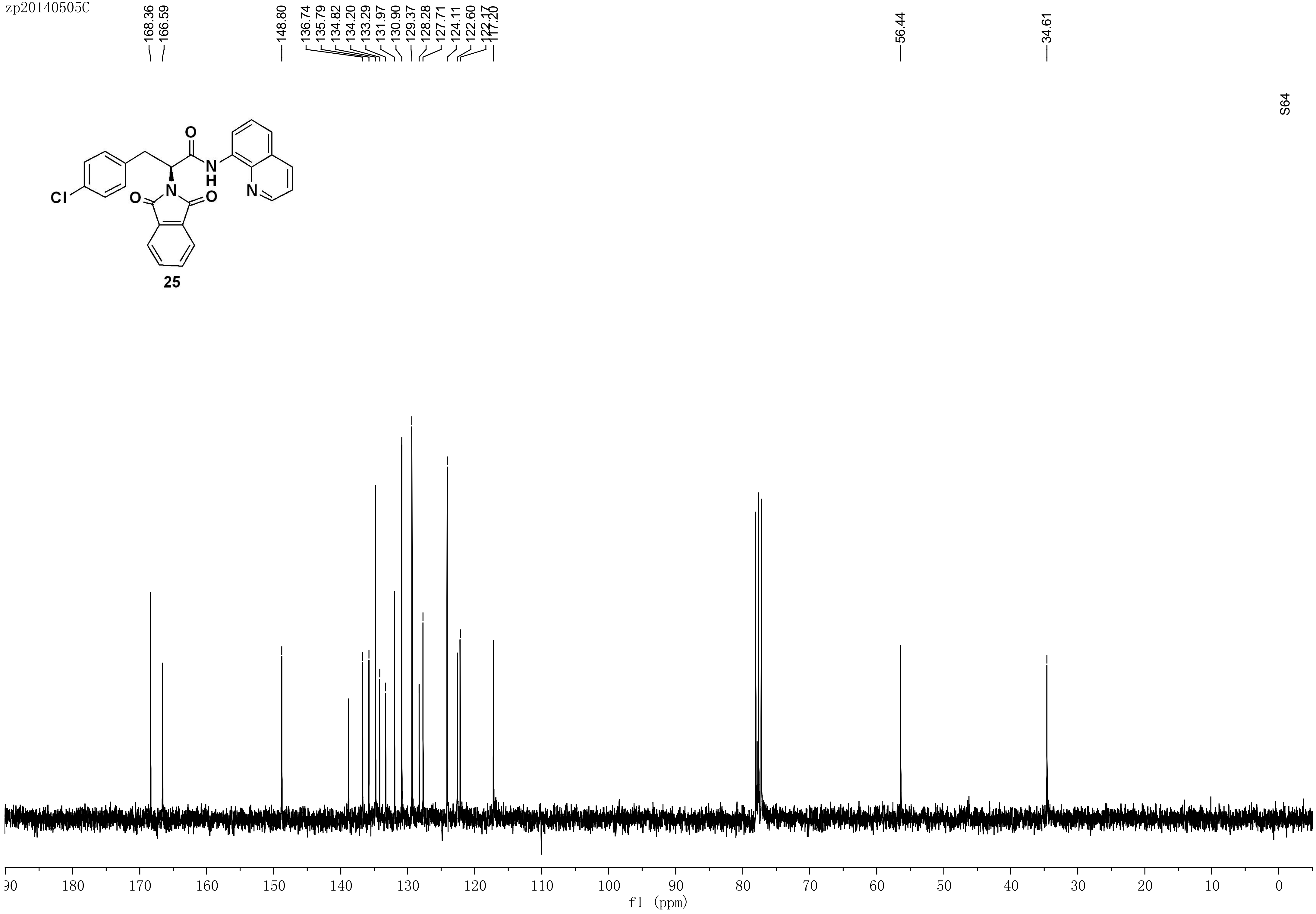
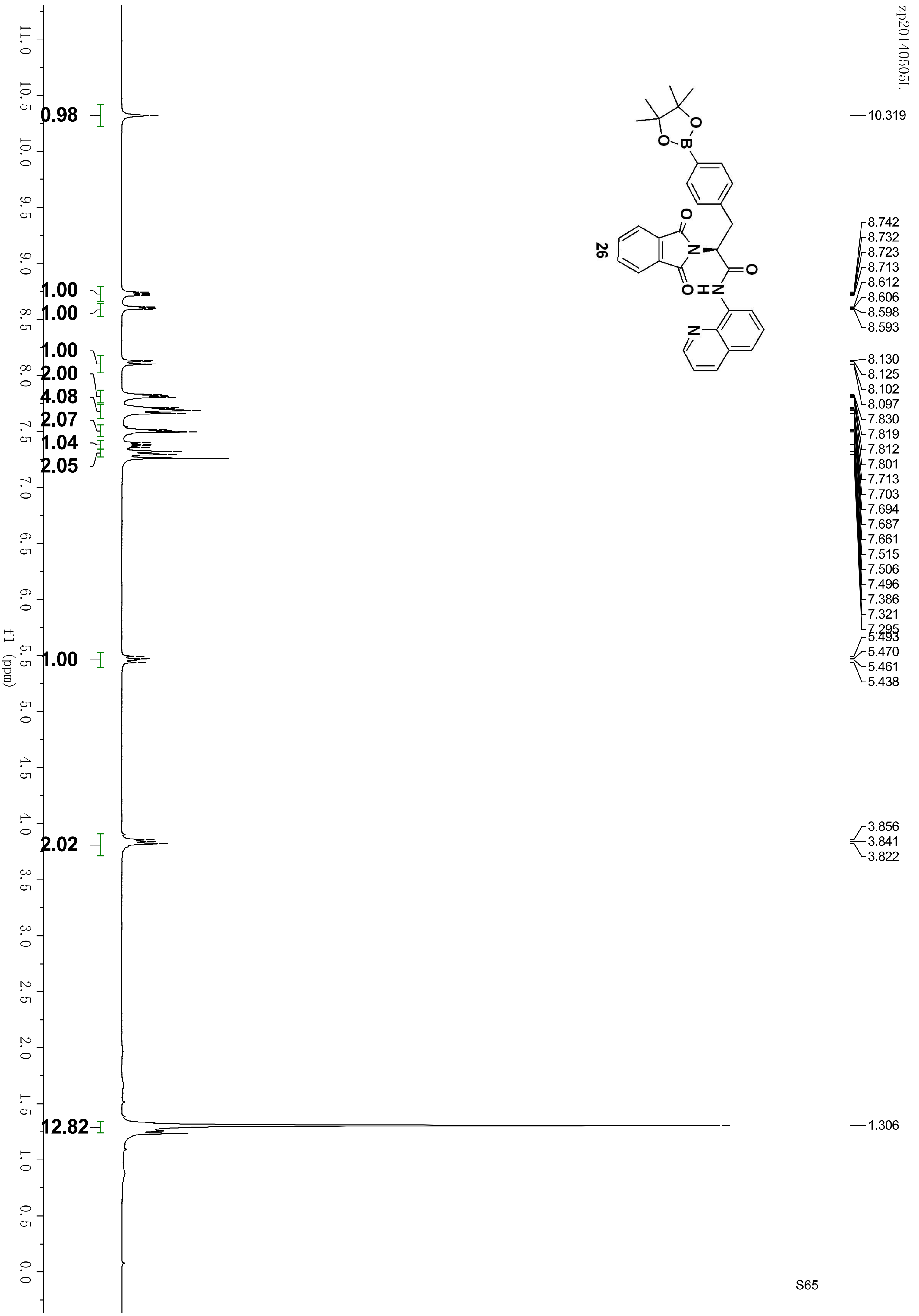
Br
O
N
H
N
O
O
N
168.29
166.49
148.73
138.73
136.66
136.21
134.75
134.09
132.23
131.86
131.19
128.19
127.63
124.05
122.53
122.09
121.36
117.12
56.27
34.59
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


zp20140505C
25
Cl
O
N
O
H
N
O
N
10.276
8.724
8.715
8.703
8.694
8.570
8.565
8.556
8.551
8.075
8.052
8.047
7.816
7.805
7.797
7.787
7.688
7.678
7.670
7.660
7.477
7.465
7.456
7.260
7.240
7.212
7.188
7.159
5.461
5.436
5.430
5.405
3.800
3.775
3.770
0.96
1.00
1.00
1.01
2.04
2.06
2.08
1.04
4.04
1.00
1.99
11.0
10.5
10.0
9.5
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
-0.
f1 (ppm)


zp20140505C
8.724
8.715
8.703
8.694
8.570
8.565
8.556
8.551
8.080
8.075
8.052
8.047
7.816
7.805
7.797
7.787
7.775
7.701
7.688
7.678
7.670
7.660
7.505
7.477
7.465
7.456
7.438
7.359
7.345
7.331
7.317
7.260
7.240
7.212
7.188
7.159
1.00
1.00
1.01
2.04
2.06
2.08
1.04
4.04
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
Cl
O
N
O
H
N
O
N

25


zp20140505C
168.36
166.59
148.80
136.74
135.79
134.82
134.20
133.29
131.97
130.90
129.37
128.28
127.71
124.11
122.60
122.17
117.20
56.44
34.61
Cl
O
N
H
N
25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


zp20140505L
26
0.98
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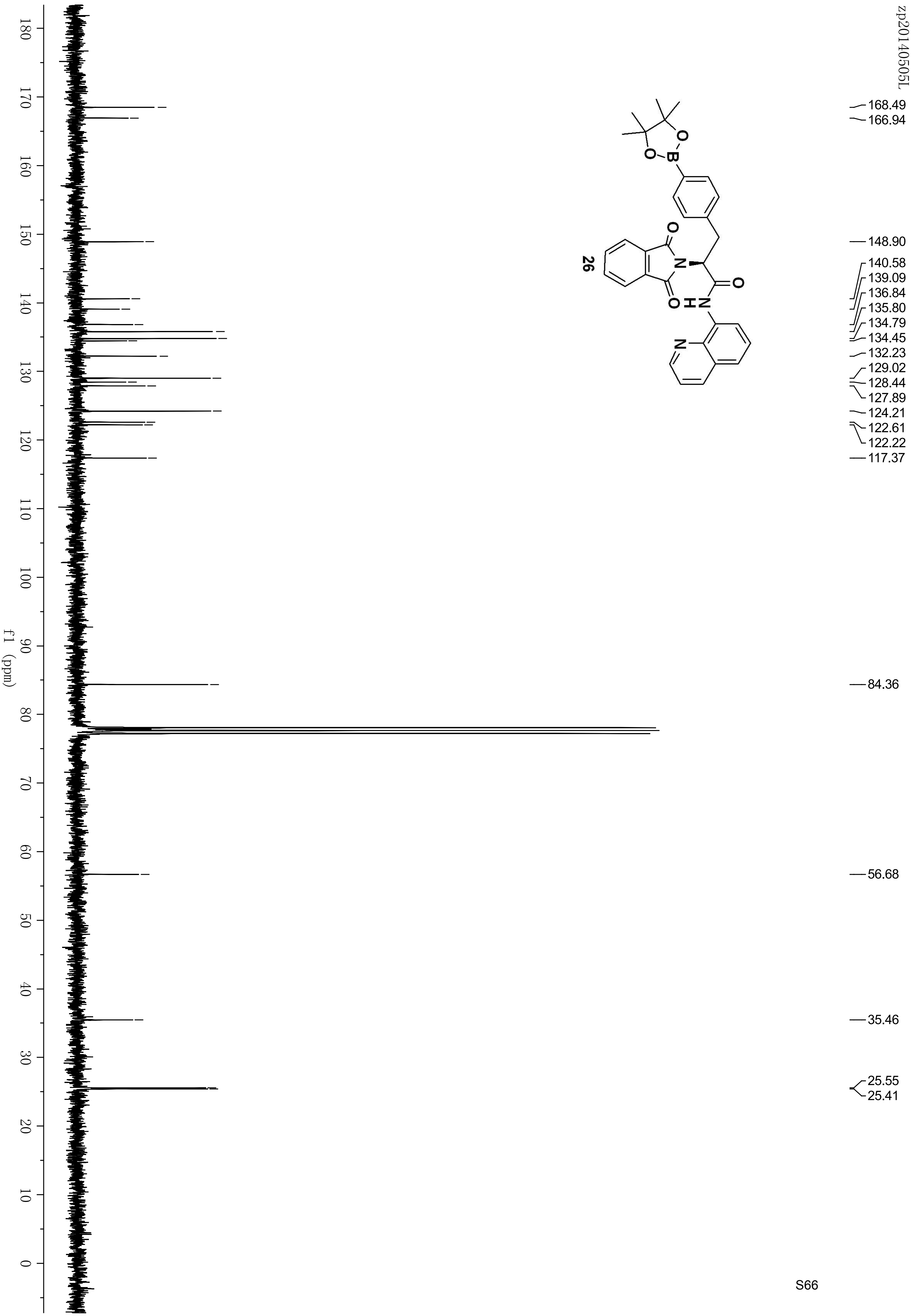
1.00
1.00
2.00
4.08
2.07
1.04
2.05
1.00
2.02
12.82
10.319
8.742
8.732
8.723
8.713
8.612
8.606
8.598
8.593
8.130
8.125
8.102
8.097
7.830
7.819
7.812
7.801
7.713
7.703
7.694
7.687
7.661
7.515
7.506
7.496
7.386
7.321
7.295
5.493
5.470
5.461
5.438
3.856
3.841
3.822
1.306
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
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


zp20140505L
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166.94
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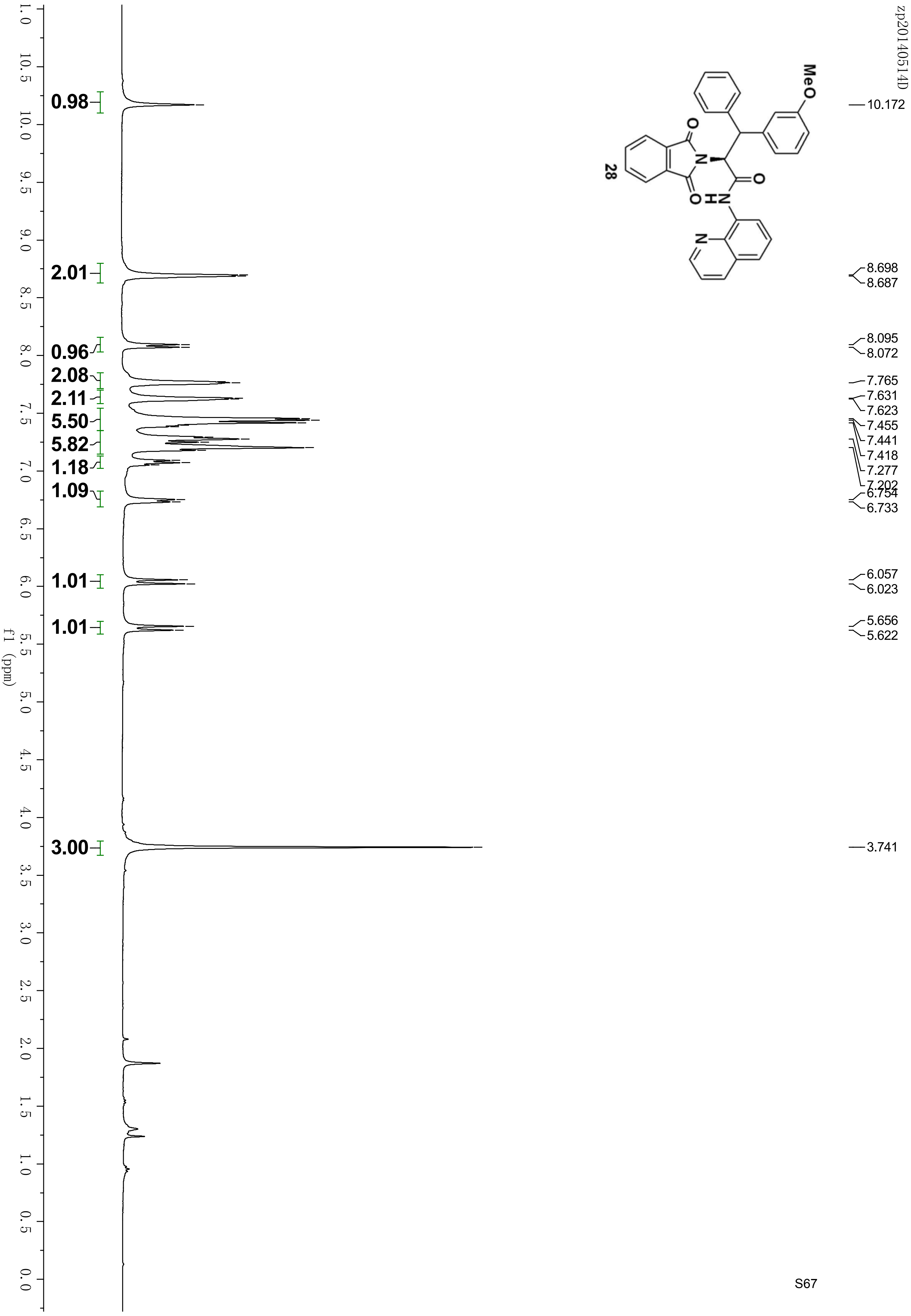
139.09
136.84
135.80
134.79
134.45
132.23
129.02
128.44
127.89
124.21
122.61
122.22
117.37
84.36
56.68
35.46
25.55
25.41
26
O
B
N
H
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


zp20140514D
28
MeO
O
N
H
N
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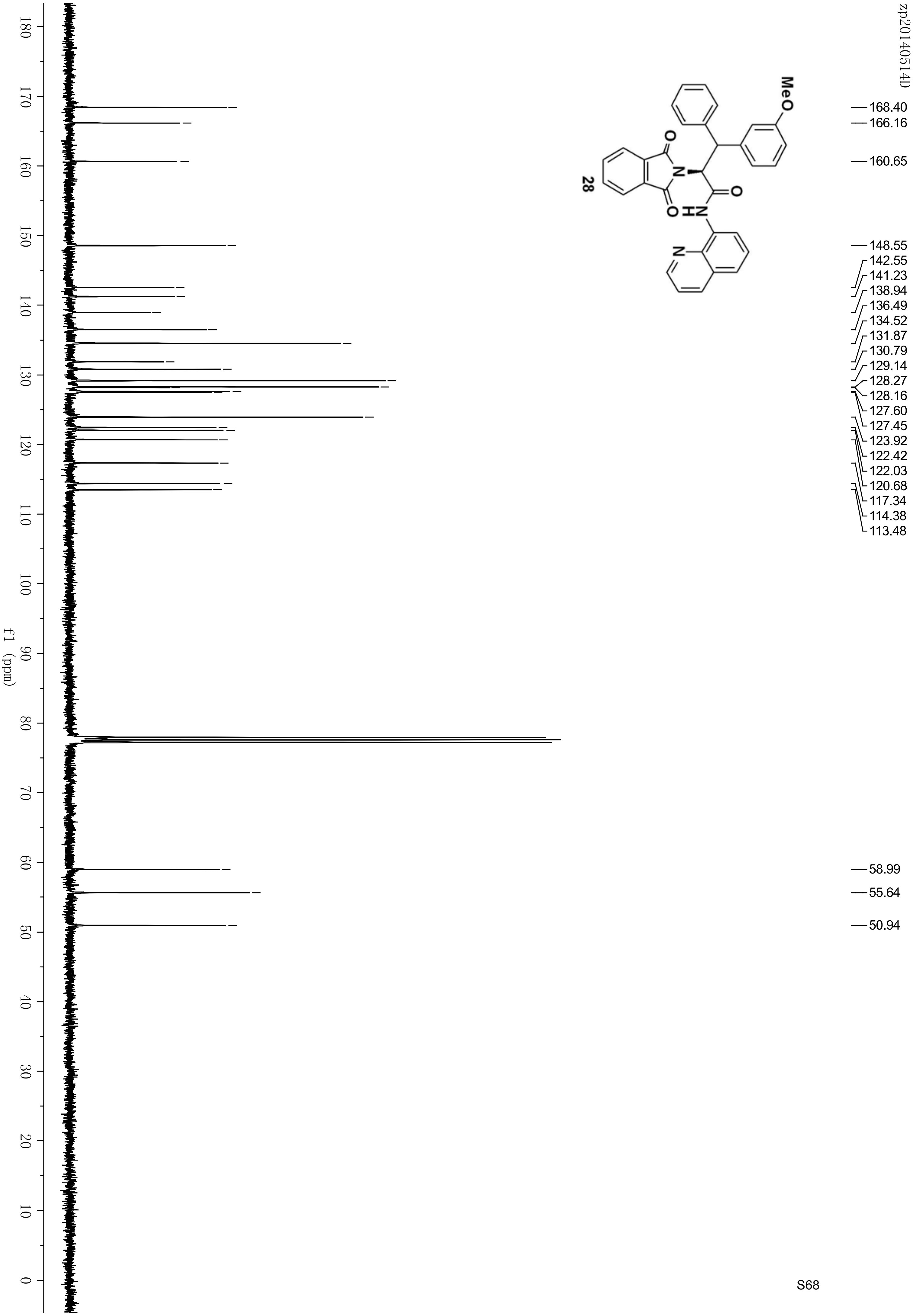
8.687
8.095
8.072
7.765
7.631
7.623
7.455
7.441
7.418
7.277
7.202
6.754
6.733
6.057
6.023
5.656
5.622
3.741
0.98
2.01
0.96
2.08
2.11
5.50
5.82
1.18
1.09
1.01
1.01
3.00
f1 (ppm)
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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28
MeO
O
N
O
O
N
H
N
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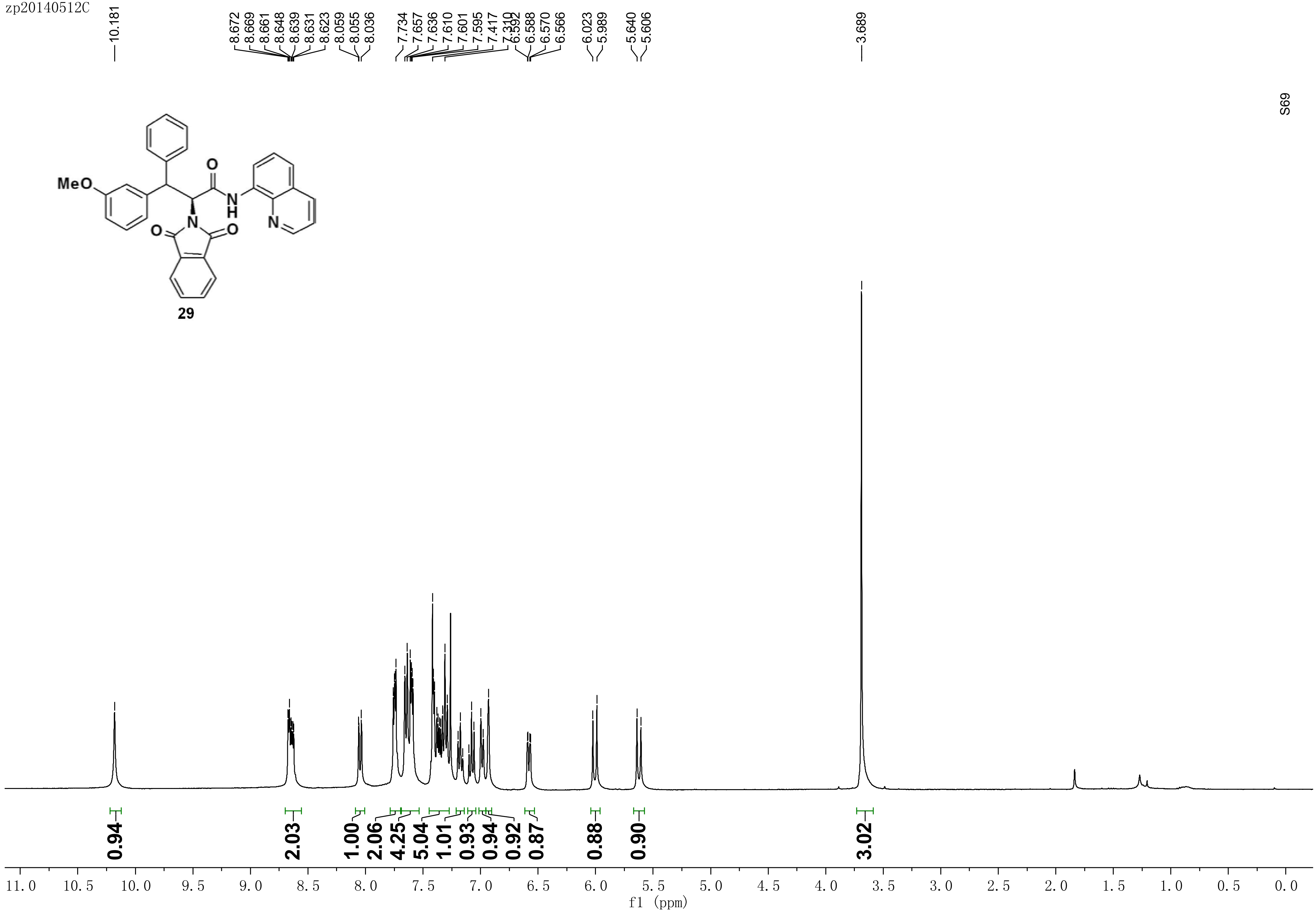
160.65
148.55
142.55
141.23
138.94
136.49
134.52
131.87
130.79
129.14
128.27
128.16
127.60
127.45
123.92
122.42
122.03
120.68
117.34
114.38
113.48
58.99
55.64
50.94
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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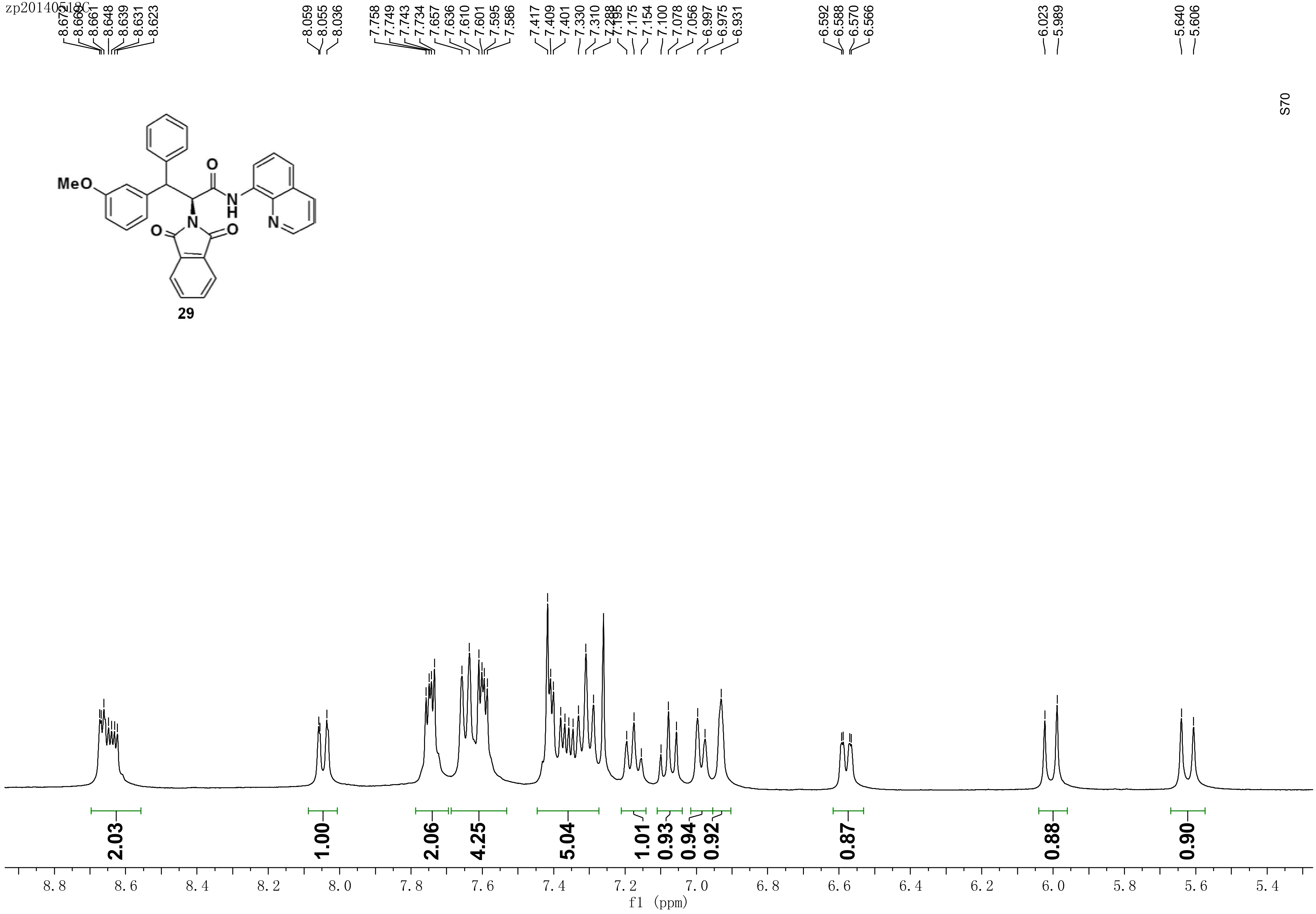
8.661
8.648
8.639
8.631
8.623
8.059
8.055
8.036
7.734
7.657
7.636
7.610
7.601
7.595
7.417
7.310
6.592
6.588
6.570
6.566
6.023
5.989
5.640
5.606
3.689
MeO
O
N
H
N
O
O
29
0.94
2.03
1.00
2.06
4.25
5.04
1.01
0.93
0.94
0.92
0.87
0.88
0.90
3.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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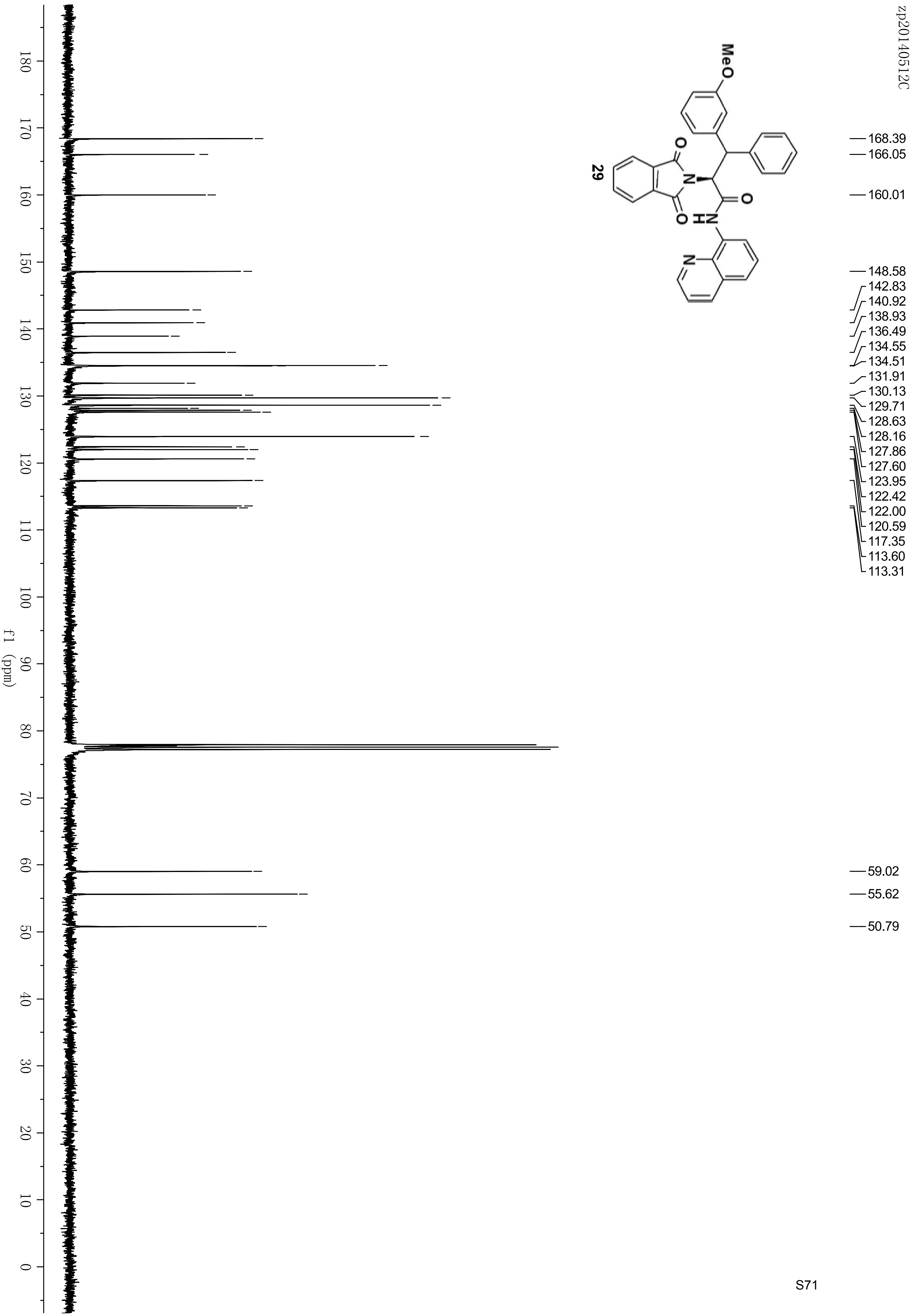
8.623
8.059
8.055
8.036
7.758
7.749
7.743
7.734
7.657
7.636
7.610
7.601
7.595
7.586
7.417
7.409
7.401
7.330
7.310
7.288
7.195
7.175
7.154
7.100
7.078
7.056
6.997
6.975
6.931
6.592
6.588
6.570
6.566
6.023
5.989
5.640
5.606
MeO
O
N
H
N
O
O
29
2.03
1.00
2.06
4.25
5.04
1.01
0.93
0.94
0.92
0.87
0.88
0.90
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
f1 (ppm)


zp20140512C
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MeO
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H
N
O
O
N
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160.01
148.58
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140.92
138.93
136.49
134.55
134.51
131.91
130.13
129.71
128.63
128.16
127.86
127.60
123.95
122.42
122.00
120.59
117.35
113.60
113.31
59.02
55.62
50.79
180
170
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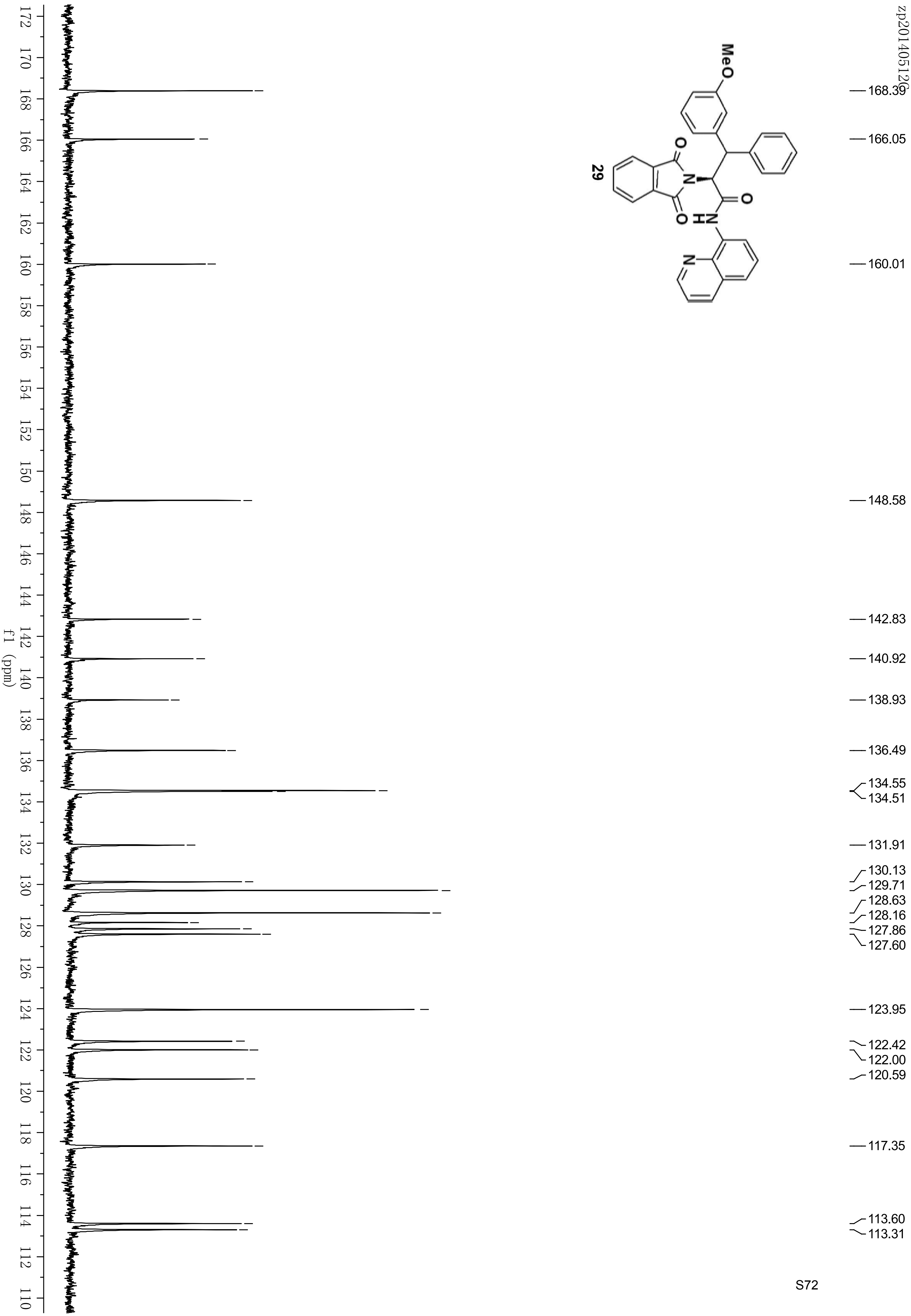
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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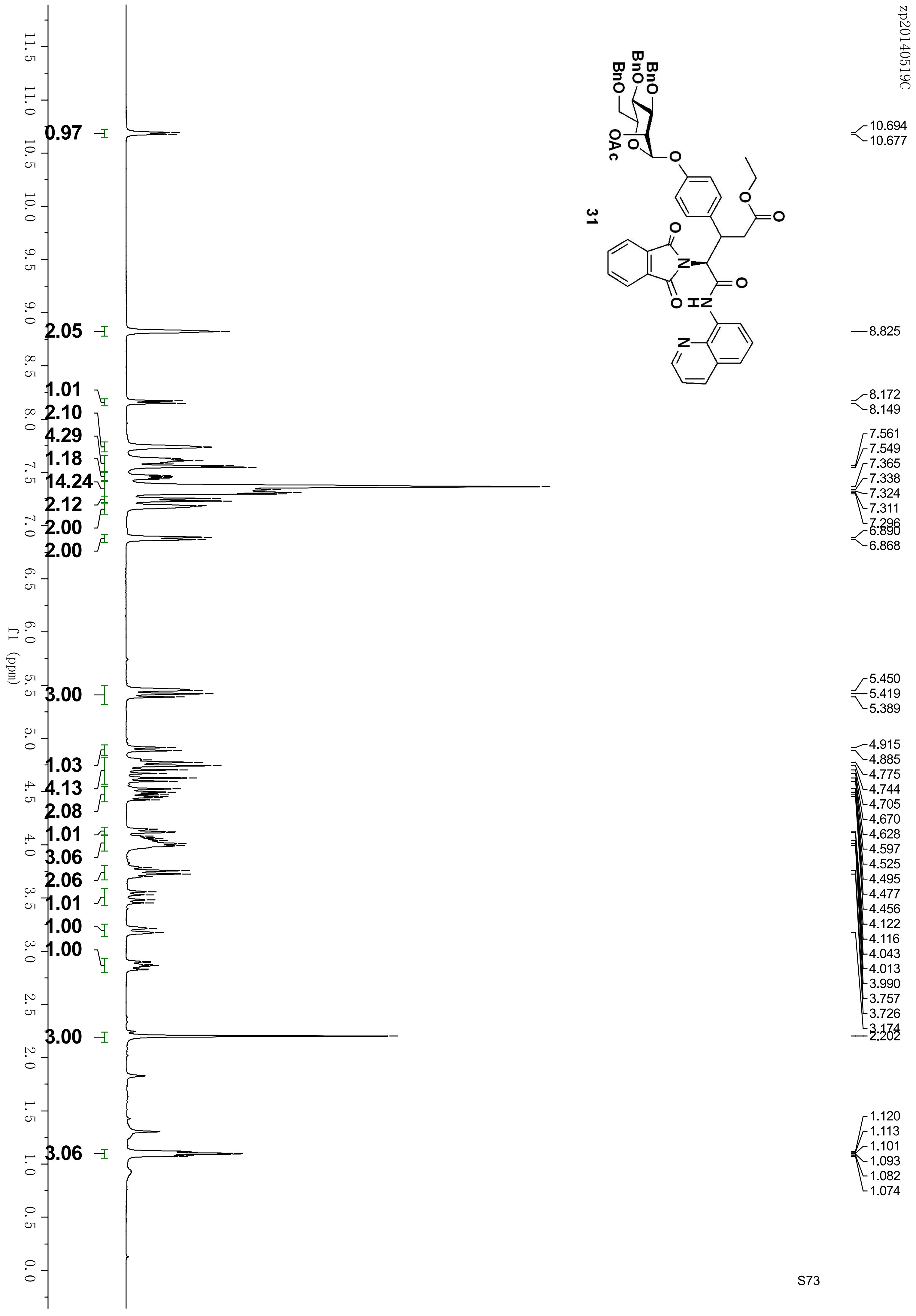
142.83
140.92
138.93
136.49
134.55
134.51
131.91
130.13
129.71
128.63
128.16
127.86
127.60
123.95
122.42
122.00
120.59
117.35
113.60
113.31
172
170
168
166
164
162
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
f1 (ppm)


zp20140519C
BnO
BnO
BnO
O
OAc
O
O
O
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N
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N
H
N
O
10.694
10.677
8.825
8.172
8.149
7.561
7.549
7.365
7.338
7.324
7.311
7.296
6.890
6.868
5.450
5.419
5.389
4.915
4.885
4.775
4.744
4.705
4.670
4.628
4.597
4.525
4.495
4.477
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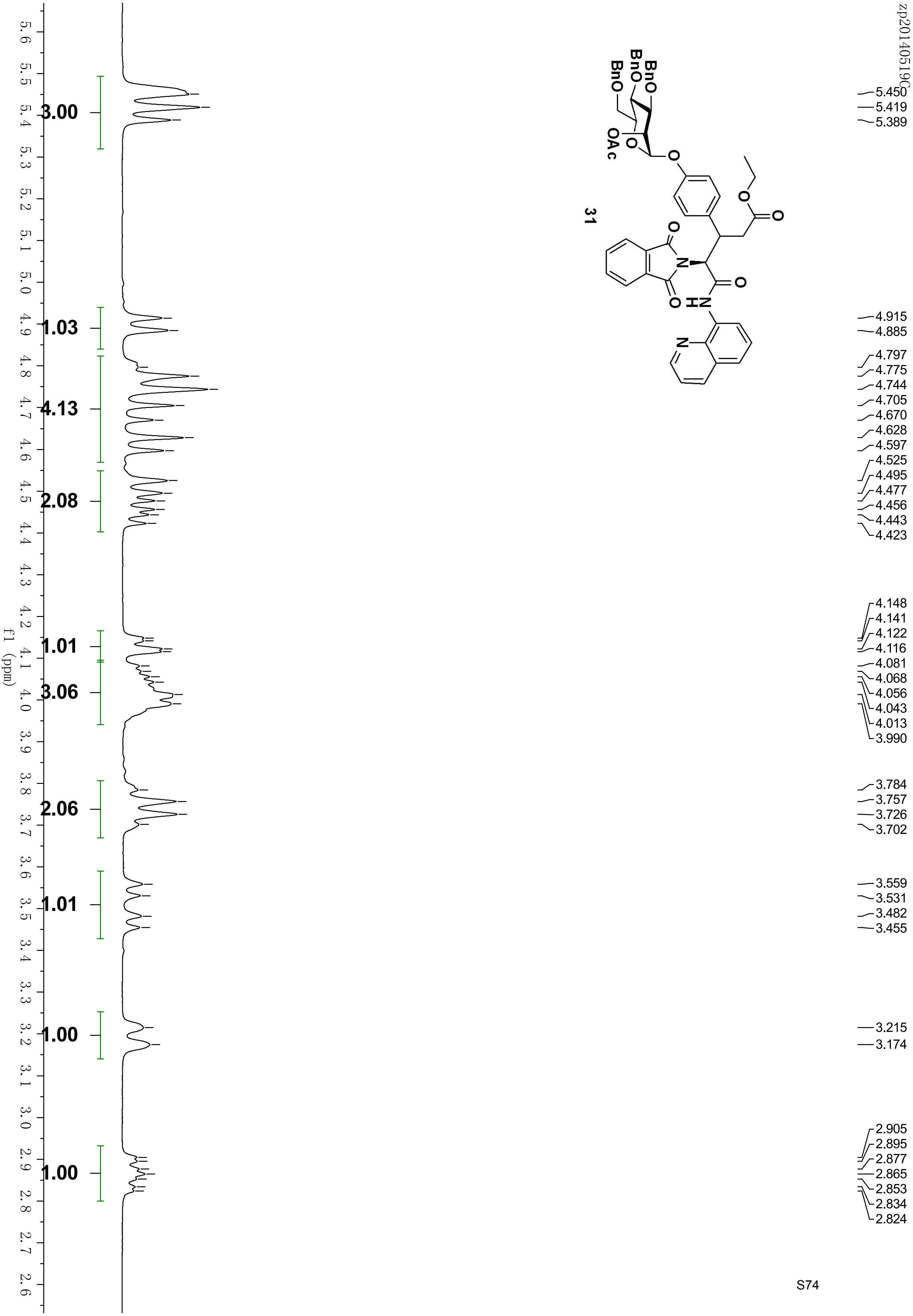
4.122
4.116
4.043
4.013
3.990
3.757
3.726
3.174
2.202
1.120
1.113
1.101
1.093
1.082
1.074
0.97
2.05
1.01
2.10
4.29
1.18
14.24
2.12
2.00
2.00
3.00
1.03
4.13
2.08
1.01
3.06
2.06
1.01
1.00
1.00
3.00
3.06
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

31


zp20140519C
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5.389
4.915
4.885
4.797
4.775
4.744
4.705
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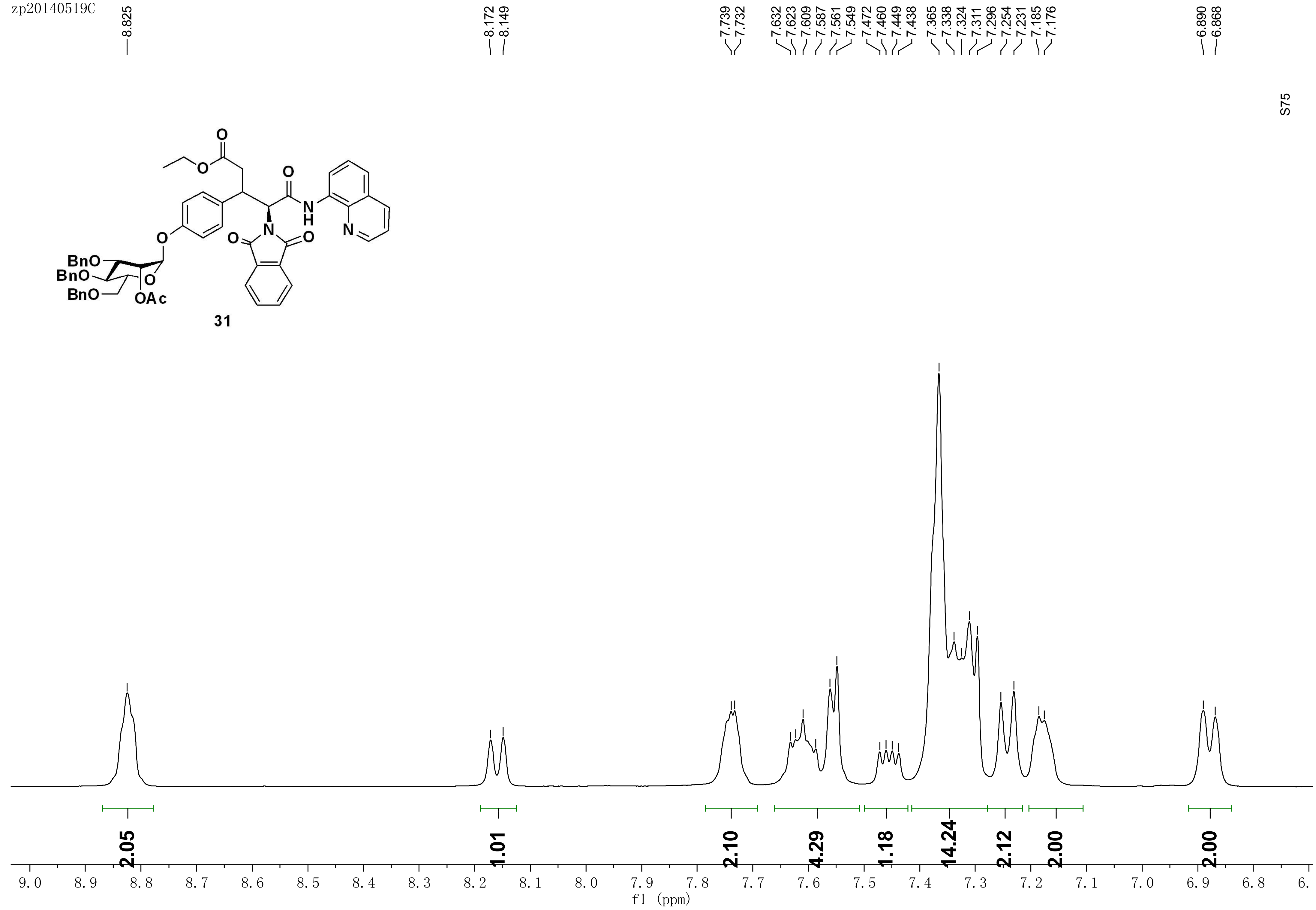
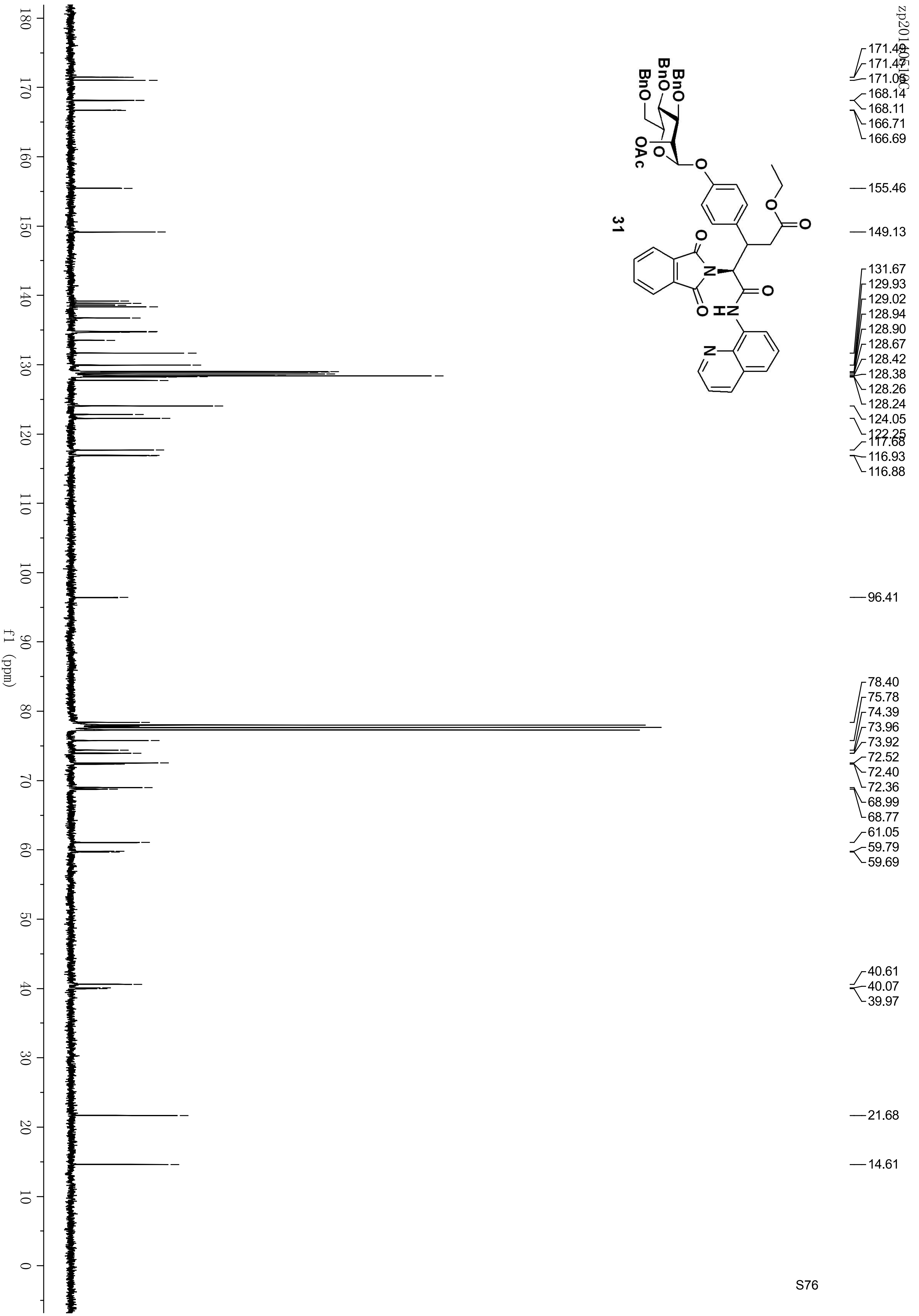
4.628
4.597
4.525
4.495
4.477
4.456
4.443
4.423
4.148
4.141
4.122
4.116
4.081
4.068
4.056
4.043
4.013
3.990
3.784
3.757
3.726
3.702
3.559
3.531
3.482
3.455
3.215
3.174
2.905
2.895
2.877
2.865
2.853
2.834
2.824
3.00
1.03
4.13
2.08
1.01
3.06
2.06
1.01
1.00
1.00
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
f1 (ppm)
BnO
BnO
BnO
OAc
O
O
O
O
O
N
O
O
N
H
N
O

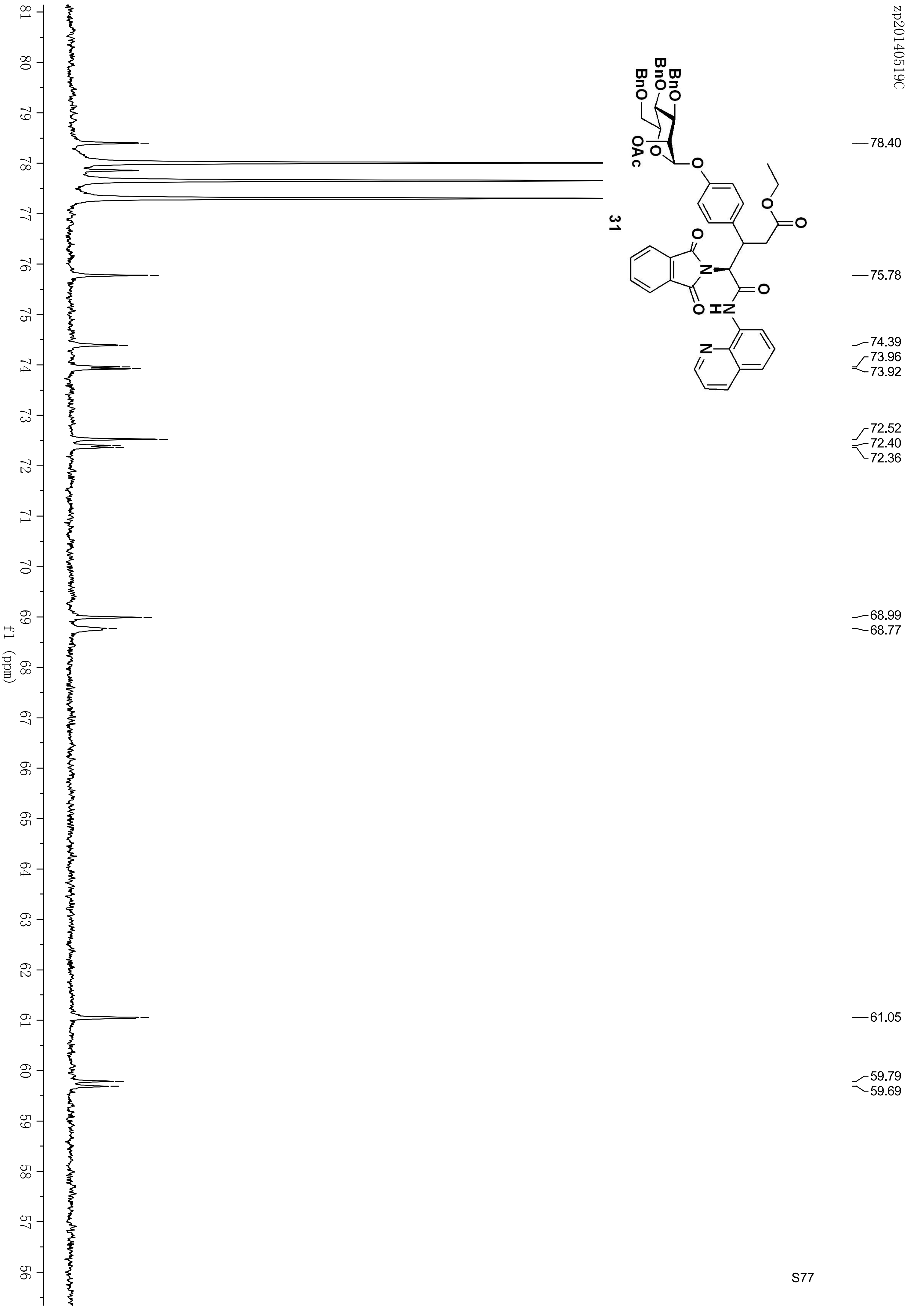
31



31

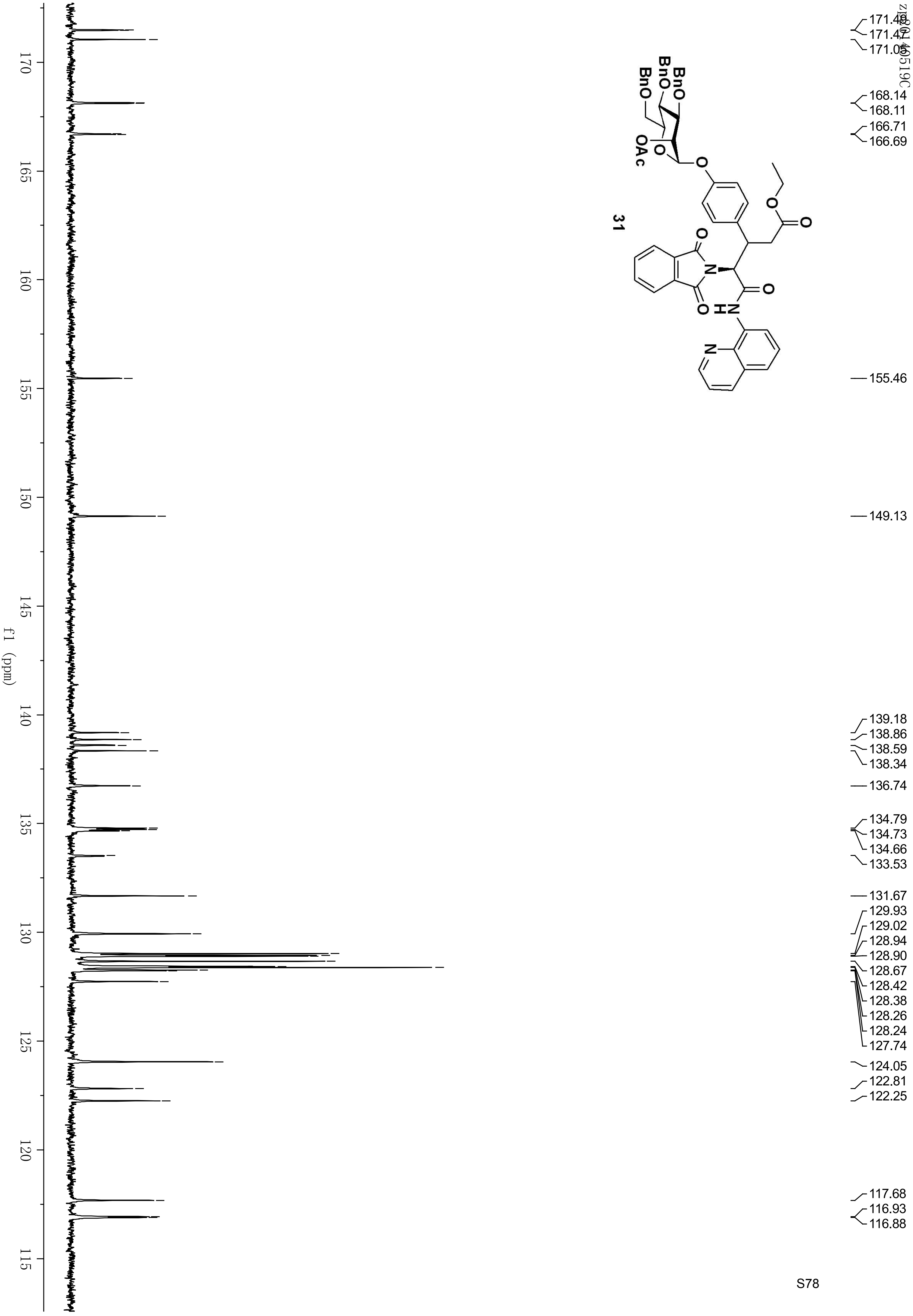
zp20140519C
8.825
8.172
8.149
7.739
7.732
7.632
7.623
7.609
7.587
7.561
7.549
7.472
7.460
7.449
7.438
7.365
7.338
7.324
7.311
7.296
7.254
7.231
7.185
7.176
6.890
6.868
BnO
BnO
BnO
O
OAc
O
O
O
O
N
O
O
N
H
N
2.05
1.01
2.10
4.29
1.18
14.24
2.12
2.00
2.00
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.
f1 (ppm)


zp20140519C
171.49
171.47
171.05
168.14
168.11
166.71
166.69
155.46
149.13
131.67
129.93
129.02
128.94
128.90
128.67
128.42
128.38
128.26
128.24
124.05
122.25
117.68
116.93
116.88
96.41
78.40
75.78
74.39
73.96
73.92
72.52
72.40
72.36
68.99
68.77
61.05
59.79
59.69
40.61
40.07
39.97
21.68
14.61
BnO
BnO
BnO
O
OAc
O
O
O
O
O
N
O
O
N
H
N
31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

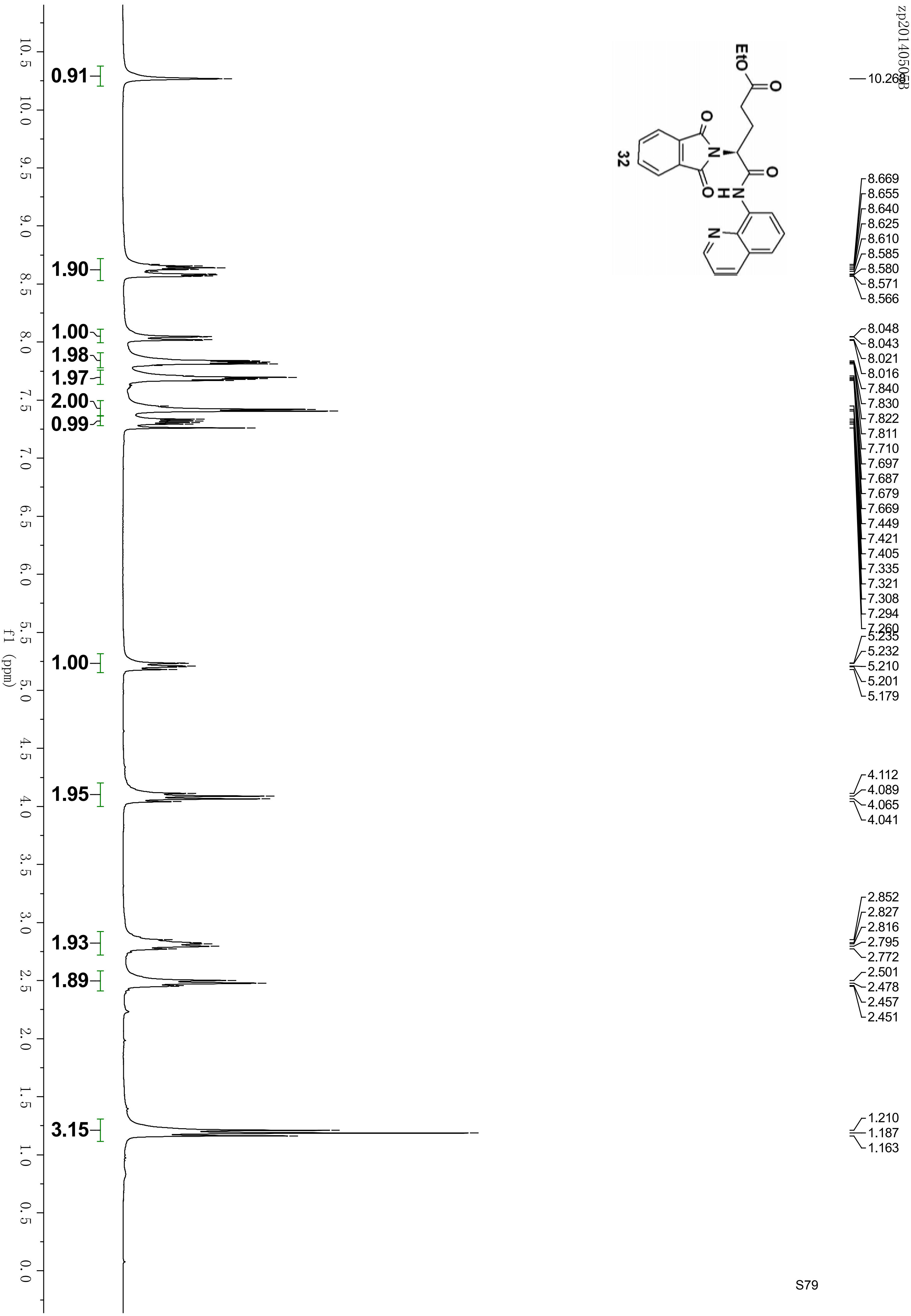


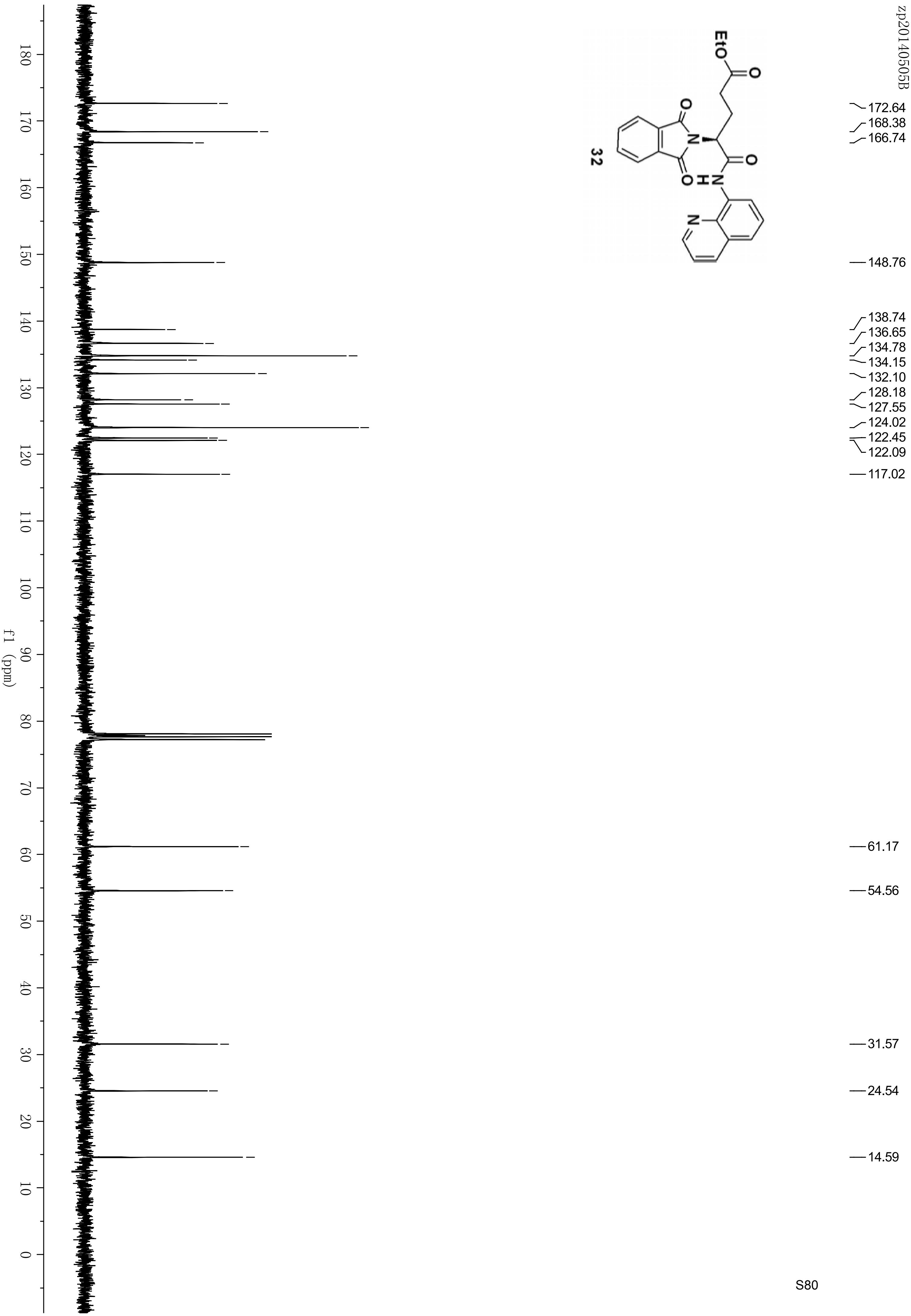
zp20140519C
78.40
75.78
74.39
73.96
73.92
72.52
72.40
72.36
68.99
68.77
61.05
59.79
59.69
81
80
79
78
77
76
75
74
73
72
71
70
69
68
67
66
65
64
63
62
61
60
59
58
57
56
f1 (ppm)
BnO
BnO
BnO
O
OAc
O
O
O
O
N
O
H
N
O
N

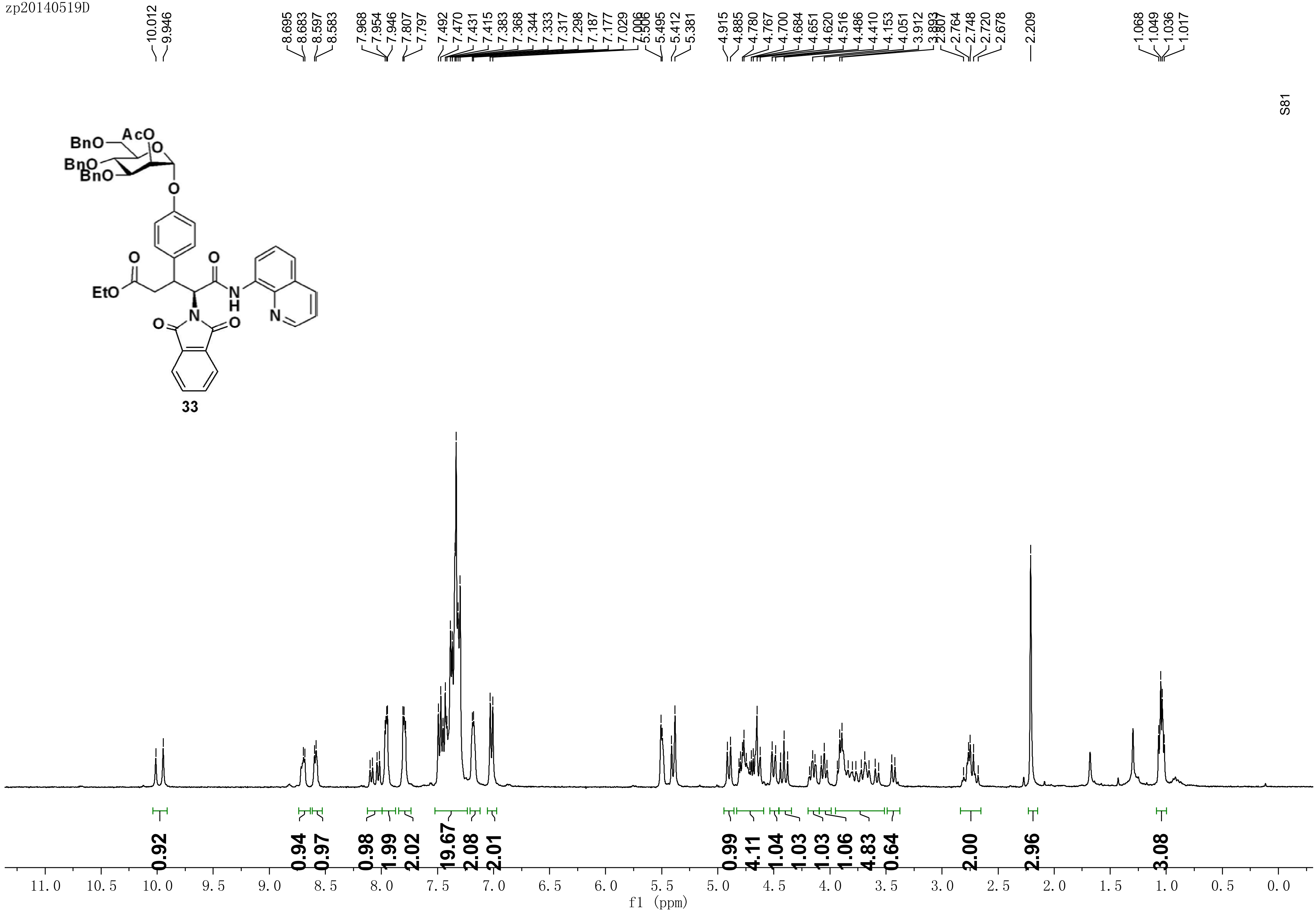
31

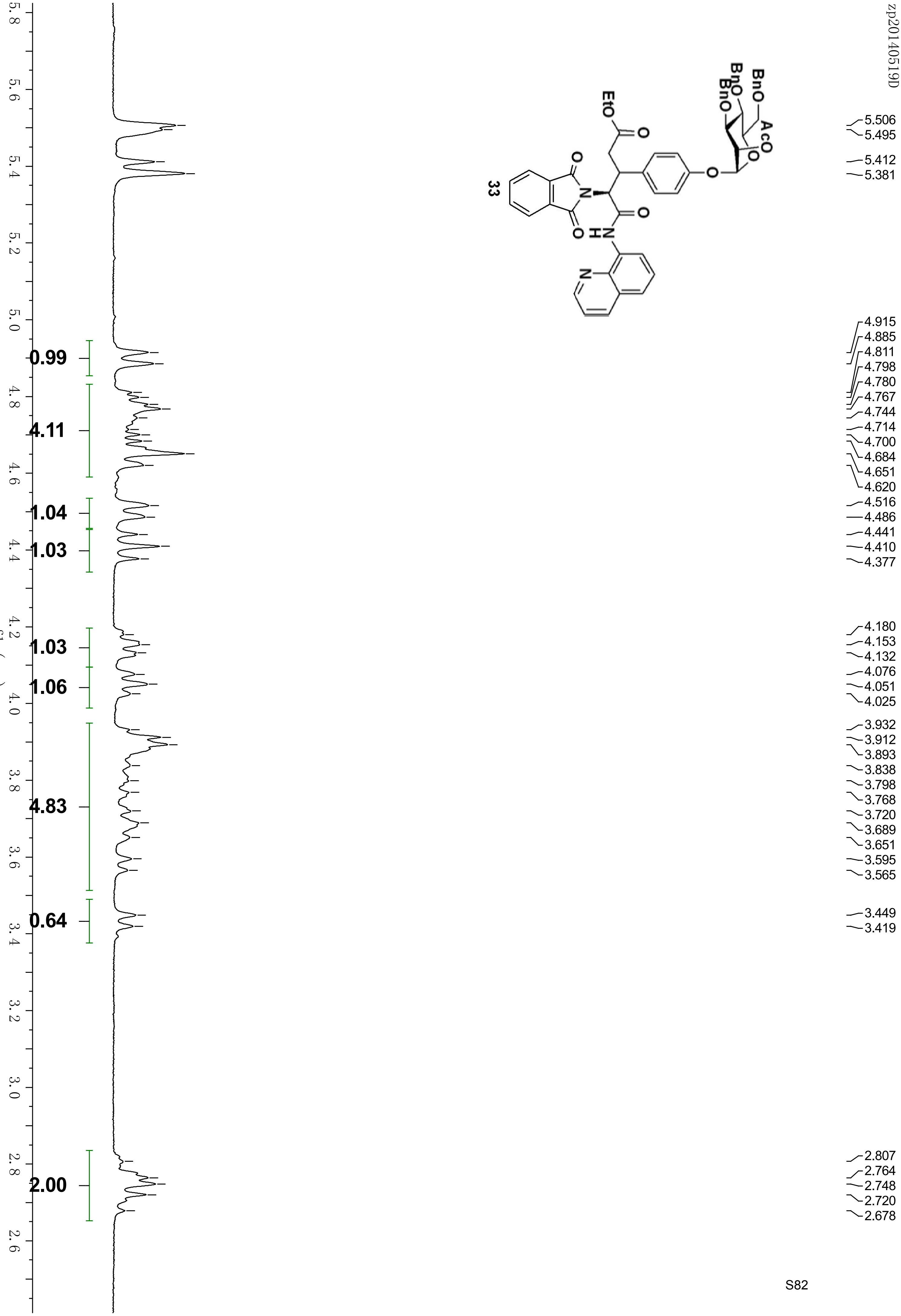

zl20140519C
171.48
171.47
171.05
168.14
168.11
166.71
166.69
155.46
149.13
139.18
138.86
138.59
138.34
136.74
134.79
134.73
134.66
133.53
131.67
129.93
129.02
128.94
128.90
128.67
128.42
128.38
128.26
128.24
127.74
124.05
122.81
122.25
117.68
116.93
116.88
170
165
160
155
150
145
140
135
130
125
120
115
f1 (ppm)
BnO
BnO
BnO
OAc
O
O
O
O
O
O
N
N
H
N
O
O

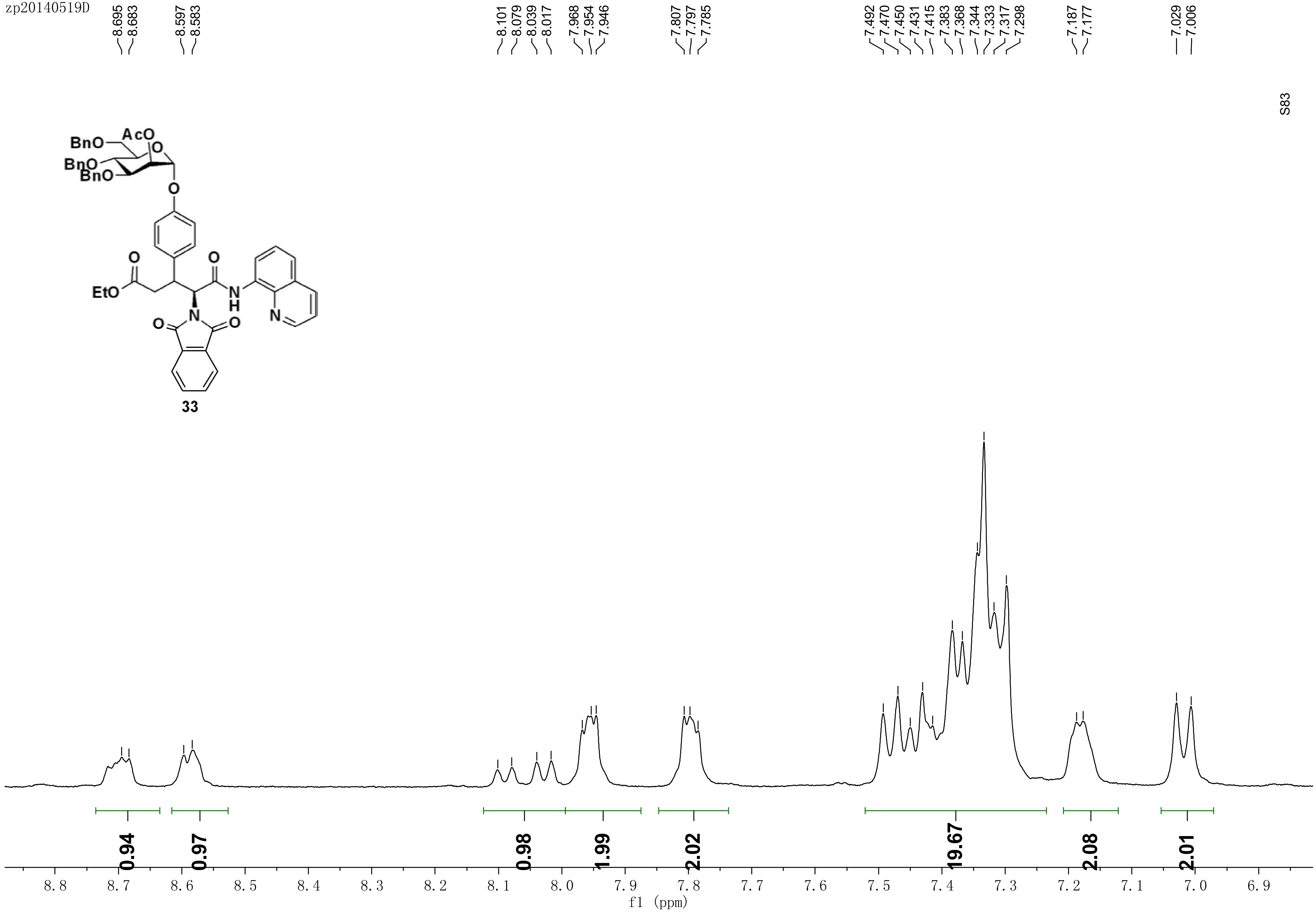
31


zp20140505B
32
EtO
O
N
NH
N
10.5
10.0
9.5
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)
0.91
1.90
1.00
1.98
1.97
2.00
0.99
1.00
1.95
1.93
1.89
3.15
10.268
8.669
8.655
8.640
8.625
8.610
8.585
8.580
8.571
8.566
8.048
8.043
8.021
8.016
7.840
7.830
7.822
7.811
7.710
7.697
7.687
7.679
7.669
7.449
7.421
7.405
7.335
7.321
7.308
7.294
7.260
5.235
5.232
5.210
5.201
5.179
4.112
4.089
4.065
4.041
2.852
2.827
2.816
2.795
2.772
2.501
2.478
2.457
2.451
1.210
1.187
1.163


zp20140505B
32
EtO
O
N
H
172.64
168.38
166.74
148.76
138.74
136.65
134.78
134.15
132.10
128.18
127.55
124.02
122.45
122.09
117.02
61.17
54.56
31.57
24.54
14.59
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

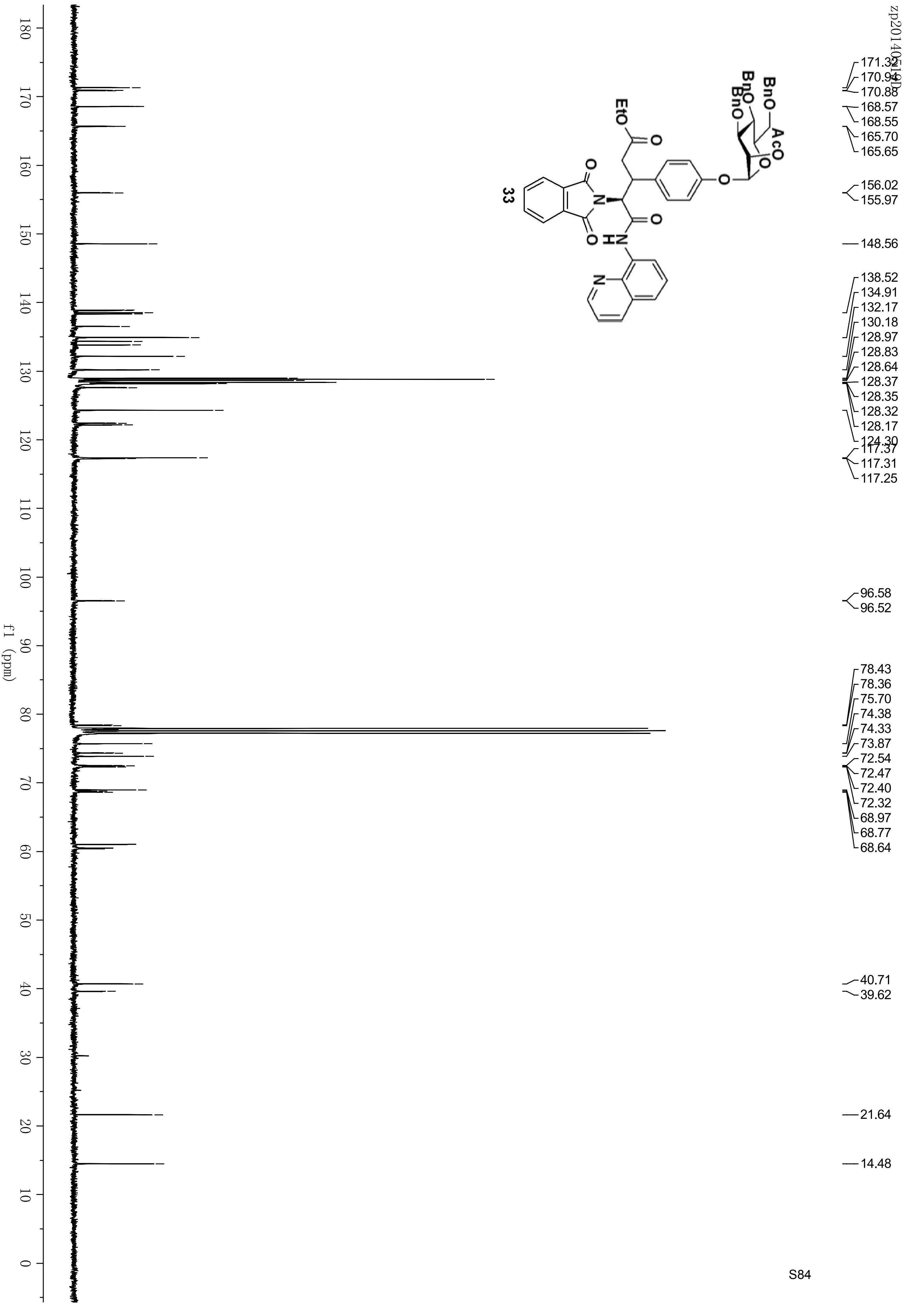

zp20140519D
10.012
9.946
8.695
8.683
8.597
8.583
7.968
7.954
7.946
7.807
7.797
7.492
7.470
7.431
7.415
7.383
7.368
7.344
7.333
7.317
7.298
7.187
7.177
7.029
7.006
5.506
5.495
5.412
5.381
4.915
4.885
4.780
4.767
4.700
4.684
4.651
4.620
4.516
4.486
4.410
4.153
4.051
3.912
3.893
2.807
2.764
2.748
2.720
2.678
2.209
1.068
1.049
1.036
1.017
BnO
AcO
O
BnO
BnO
O
O
EtO
O
N
H
N
N
O
O
33
0.92
0.94
0.97
0.98
1.99
2.02
19.67
2.08
2.01
0.99
4.11
1.04
1.03
1.03
1.06
4.83
0.64
2.00
2.96
3.08
11.0
10.5
10.0
9.5
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)


zp20140519D
5.506
5.495
5.412
5.381
4.915
4.885
4.811
4.798
4.780
4.767
4.744
4.714
4.700
4.684
4.651
4.620
4.516
4.486
4.441
4.410
4.377
4.180
4.153
4.132
4.076
4.051
4.025
3.932
3.912
3.893
3.838
3.798
3.768
3.720
3.689
3.651
3.595
3.565
3.449
3.419
2.807
2.764
2.748
2.720
2.678
0.99
4.11
1.04
1.03
1.03
1.06
4.83
0.64
2.00
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f1 (ppm)
BnO
BnO
BnO
AcO
O
O
EtO
O
O
N
O
H
N
O
N
33



33

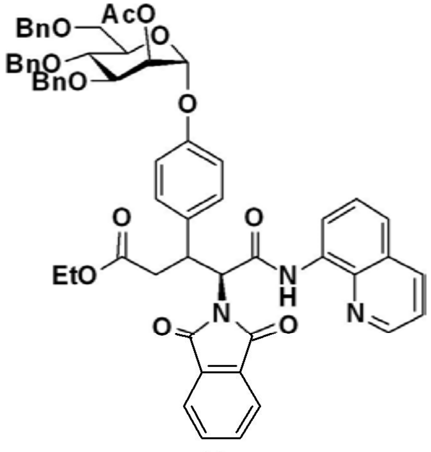
zp20140519D
8.695
8.683
8.597
8.583
8.101
8.079
8.039
8.017
7.968
7.954
7.946
7.807
7.797
7.785
7.492
7.470
7.450
7.431
7.415
7.383
7.368
7.344
7.333
7.317
7.298
7.187
7.177
7.029
7.006
BnO
AcO
O
BnO
BnO
O
O
EtO
O
N
H
N
N
O
O
0.94
0.97
0.98
1.99
2.02
19.67
2.08
2.01
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)



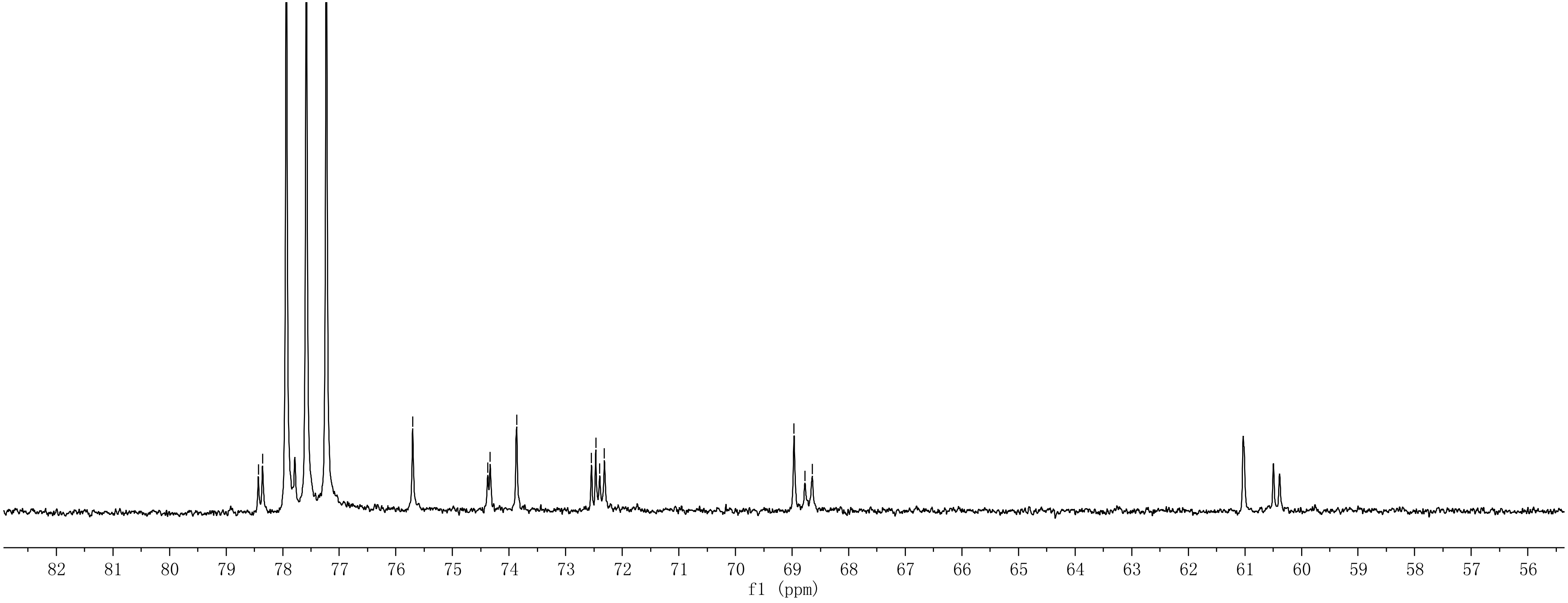
33

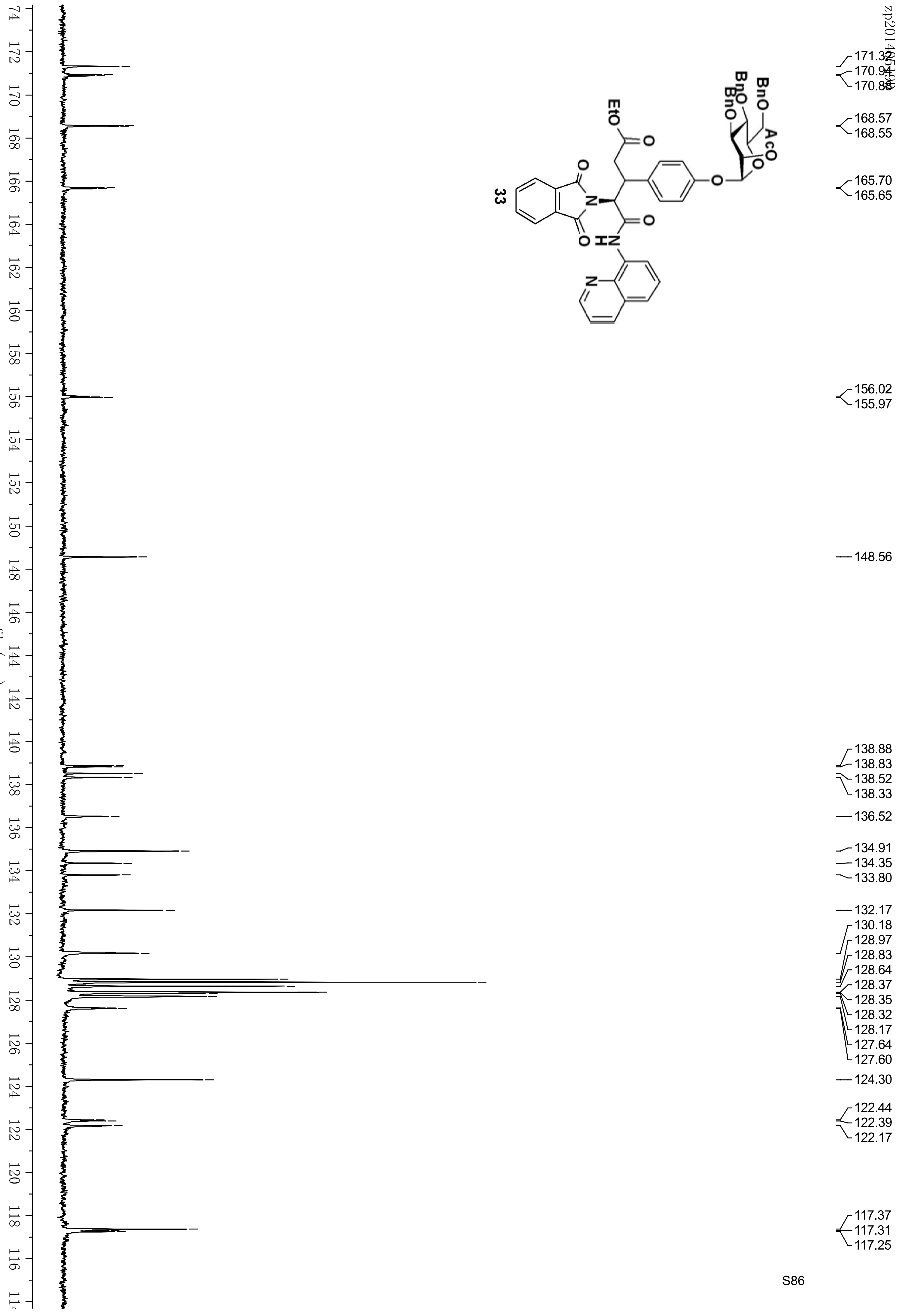
zp20140519D
171.32
170.94
170.88
168.57
168.55
165.70
165.65
156.02
155.97
148.56
138.52
134.91
132.17
130.18
128.97
128.83
128.64
128.37
128.35
128.32
128.17
124.30
117.37
117.31
117.25
96.58
96.52
78.43
78.36
75.70
74.38
74.33
73.87
72.54
72.47
72.40
72.32
68.97
68.77
68.64
40.71
39.62
21.64
14.48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
BnO
BnO
BnO
BnO
AcO
O
O
EtO
O
O
N
O
O
N
H
N

zp20140519D

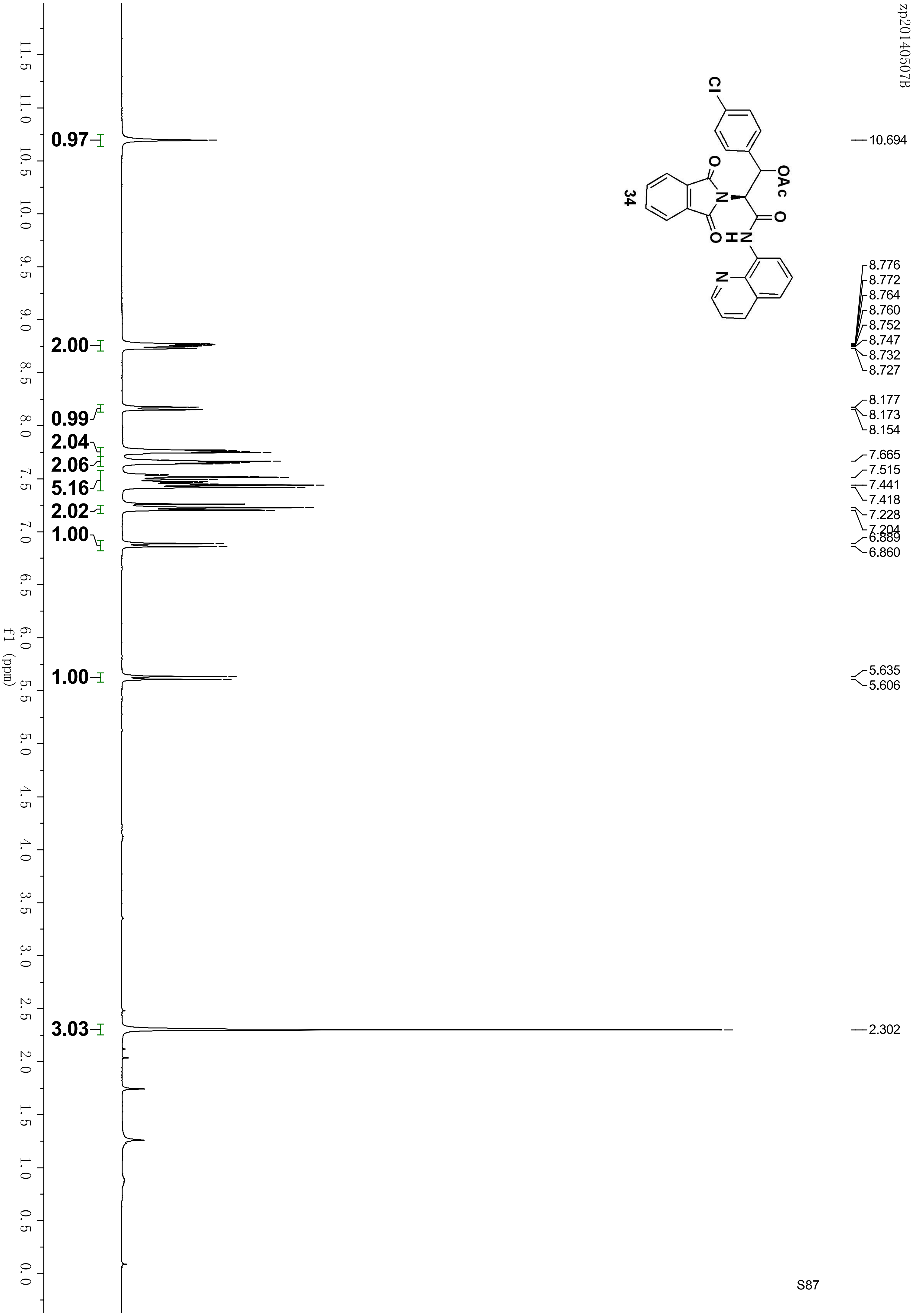


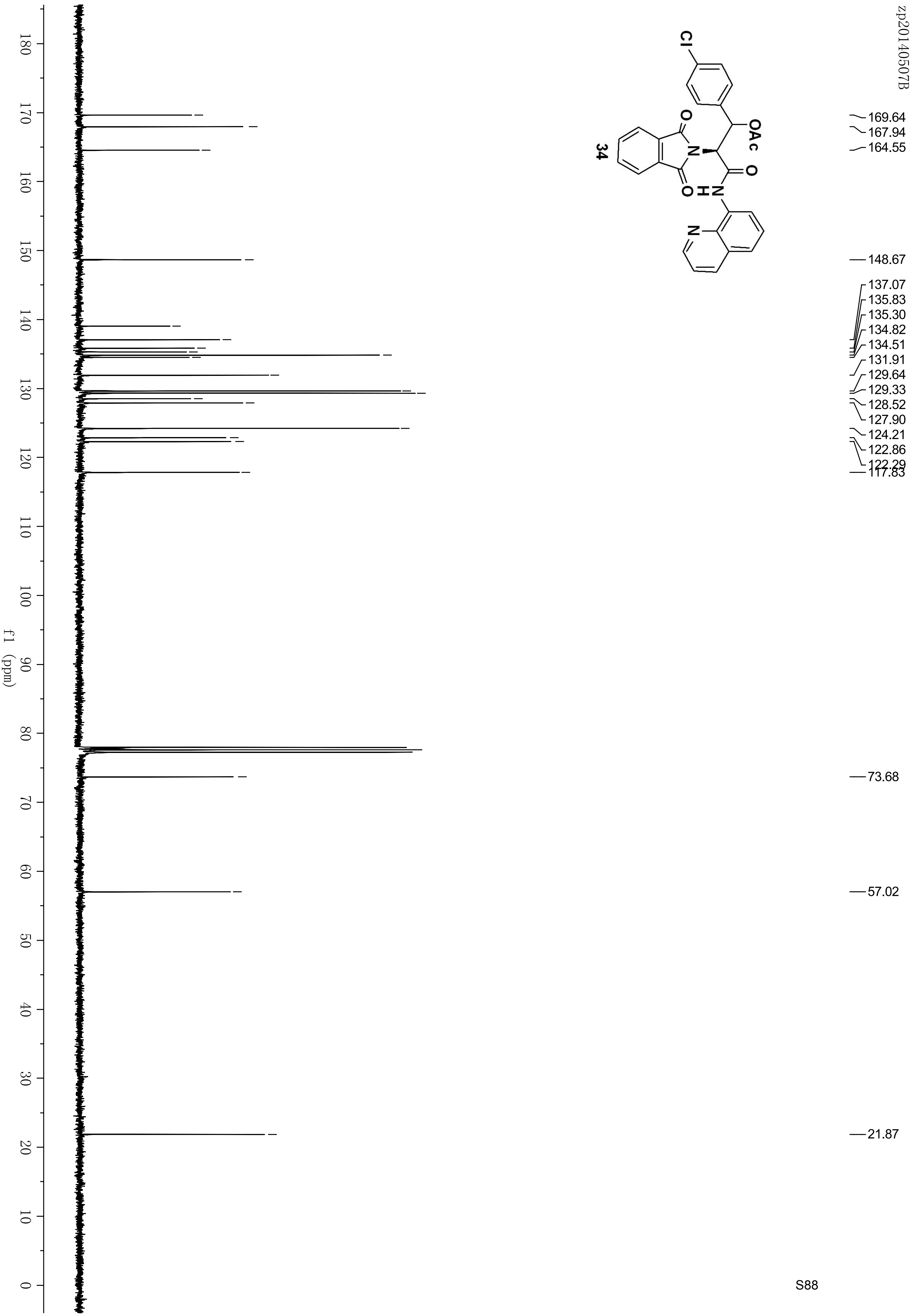
33



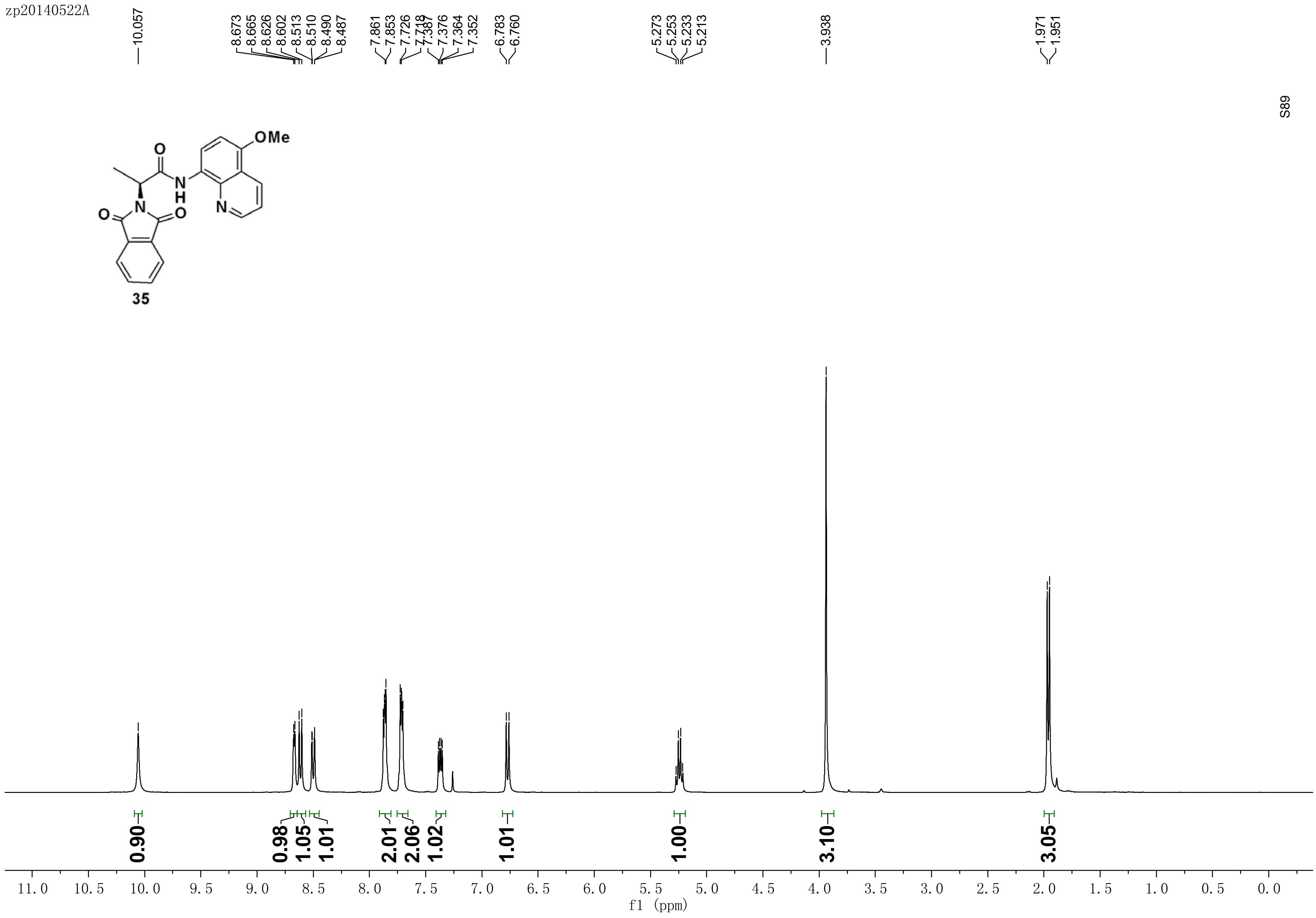

zp20140514-9D
171.32
170.94
170.88
168.57
168.55
165.70
165.65
156.02
155.97
148.56
138.88
138.83
138.52
138.33
136.52
134.91
134.35
133.80
132.17
130.18
128.97
128.83
128.64
128.37
128.35
128.32
128.17
127.64
127.60
124.30
122.44
122.39
122.17
117.37
117.31
117.25
174
172
170
168
166
164
162
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
f1 (ppm)
BnO
AcO
BnO
BnO
O
O
O
EtO
O
O
N
O
N
H
N
O

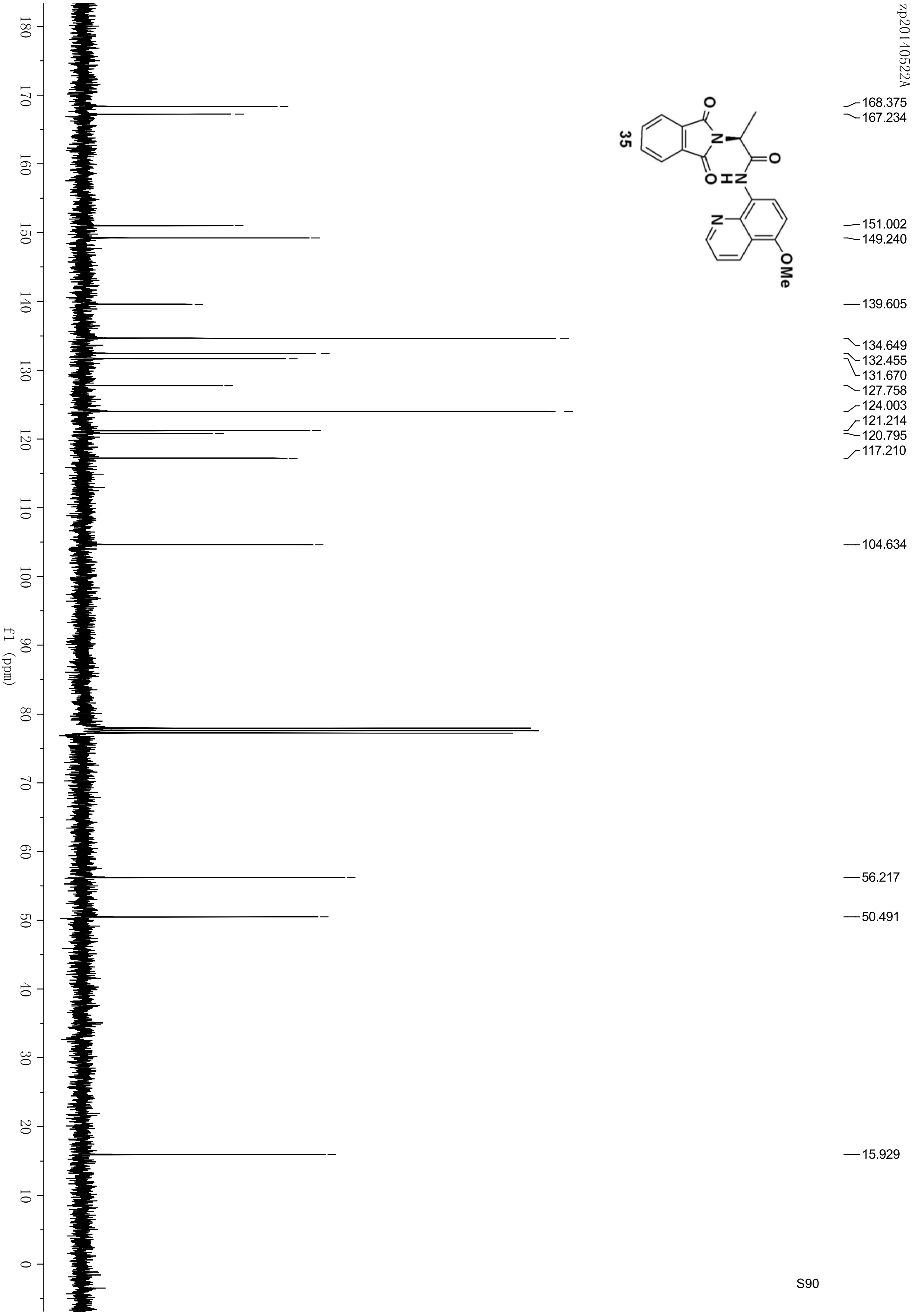
33


zp20140507B
34
Cl
O
N
OAc
O
N
H
O
N
10.694
8.776
8.772
8.764
8.760
8.752
8.747
8.732
8.727
8.177
8.173
8.154
7.665
7.515
7.441
7.418
7.228
7.204
6.889
6.860
5.635
5.606
2.302
0.97
2.00
0.99
2.04
2.06
5.16
2.02
1.00
1.00
3.03
11.5
11.0
10.5
10.0
9.5
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)

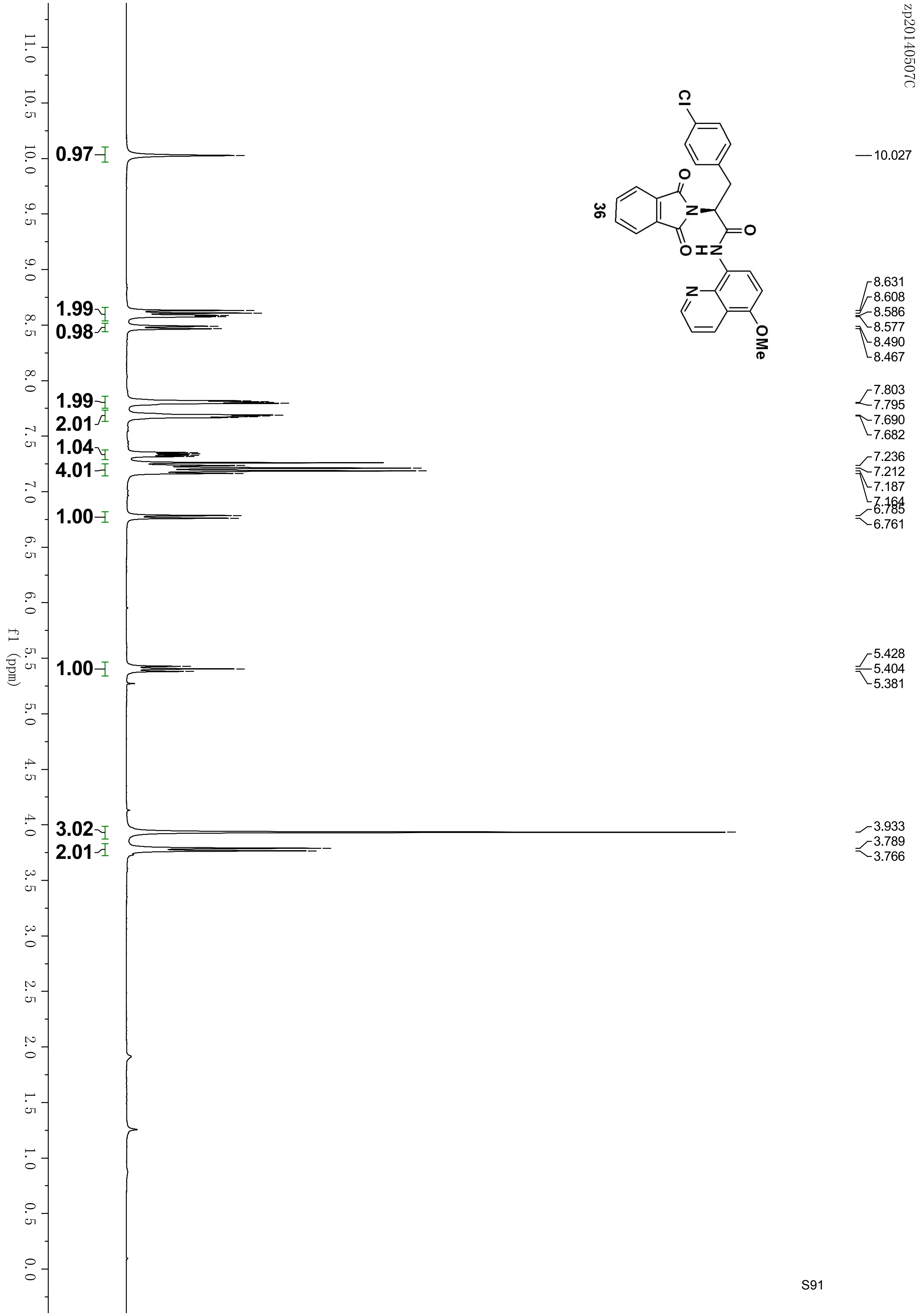

zp20140507B
Cl
OAc
O
N
H
N
O
O
N
169.64
167.94
164.55
148.67
137.07
135.83
135.30
134.82
134.51
131.91
129.64
129.33
128.52
127.90
124.21
122.86
122.29
117.83
73.68
57.02
21.87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

34

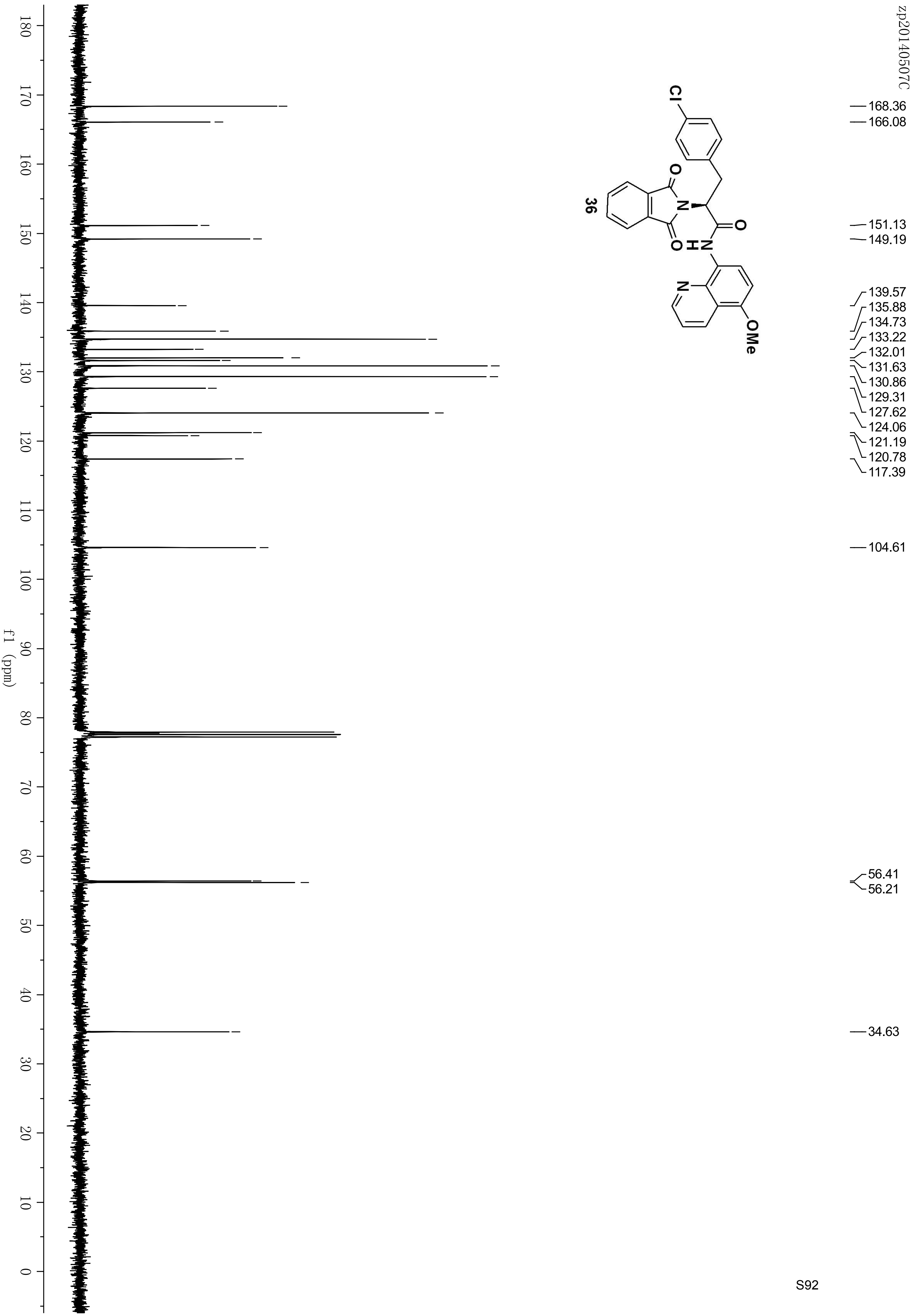

zp20140522A
35
OMe
O
N
H
N
O
O
10.057
8.673
8.665
8.626
8.602
8.513
8.510
8.490
8.487
7.861
7.853
7.726
7.718
7.387
7.376
7.364
7.352
6.783
6.760
5.273
5.253
5.233
5.213
3.938
1.971
1.951
0.90
0.98
1.05
1.01
2.01
2.06
1.02
1.01
1.00
3.10
3.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

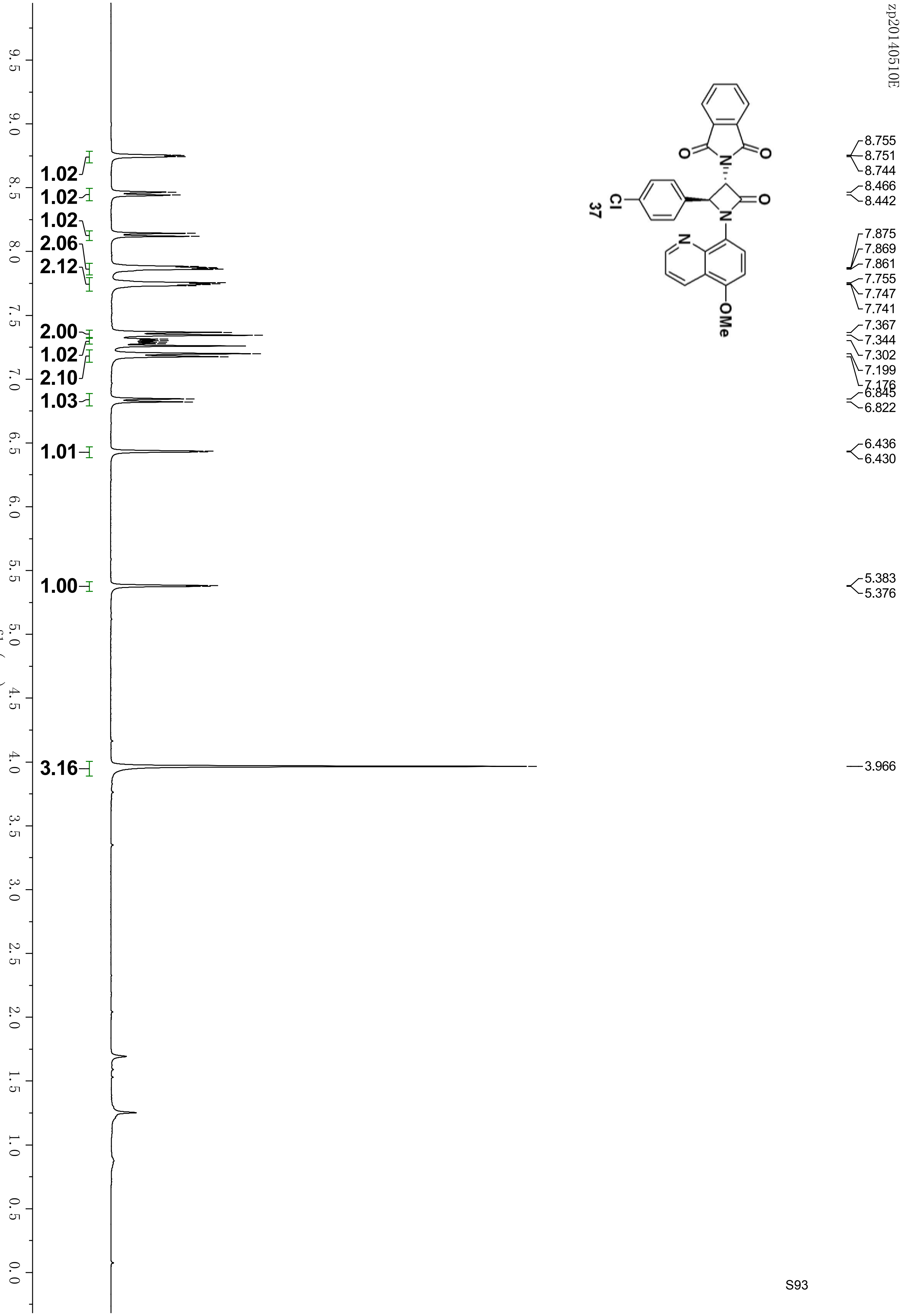


zp20140522A
35
O
O
N
H
N
O
N
OMe
168.375
167.234
151.002
149.240
139.605
134.649
132.455
131.670
127.758
124.003
121.214
120.795
117.210
104.634
56.217
50.491
15.929
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

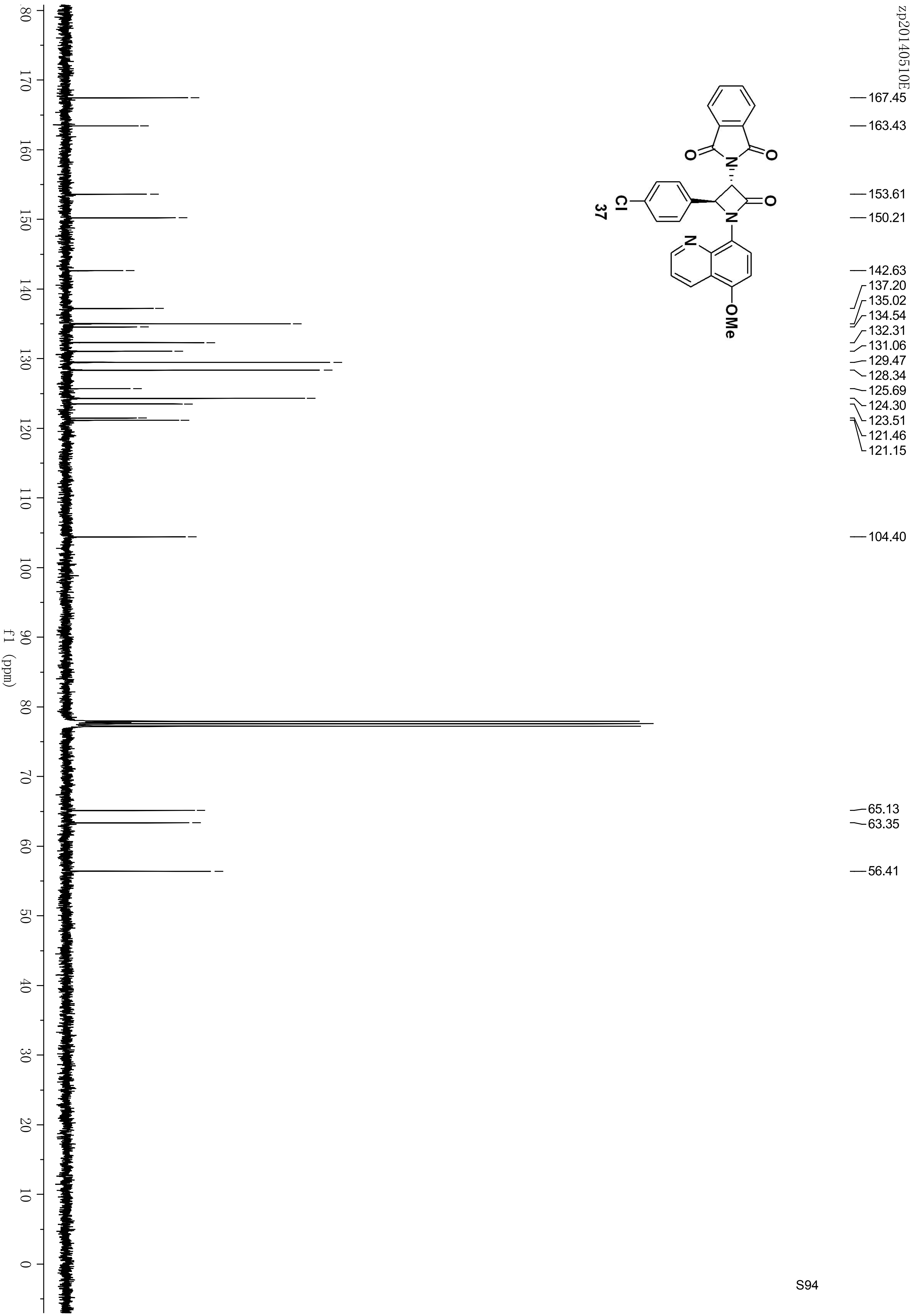

zp20140507C
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.97
1.99
0.98
1.99
2.01
1.04
4.01
1.00
1.00
3.02
2.01
10.027
8.631
8.608
8.586
8.577
8.490
8.467
7.803
7.795
7.690
7.682
7.236
7.212
7.187
7.164
6.785
6.761
5.428
5.404
5.381
3.933
3.789
3.766
Cl
O
N
O
N
H
O
N
OMe

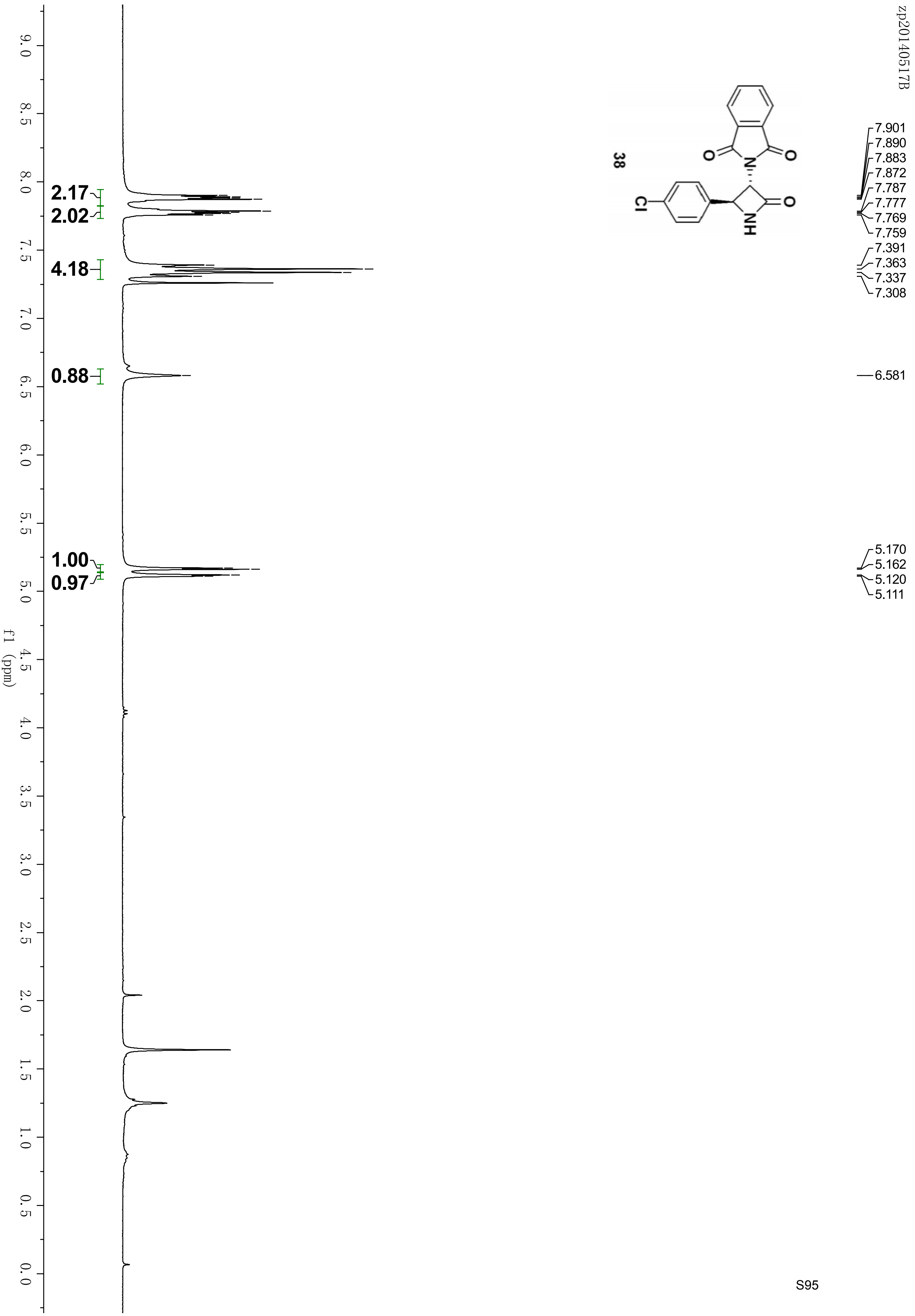
36

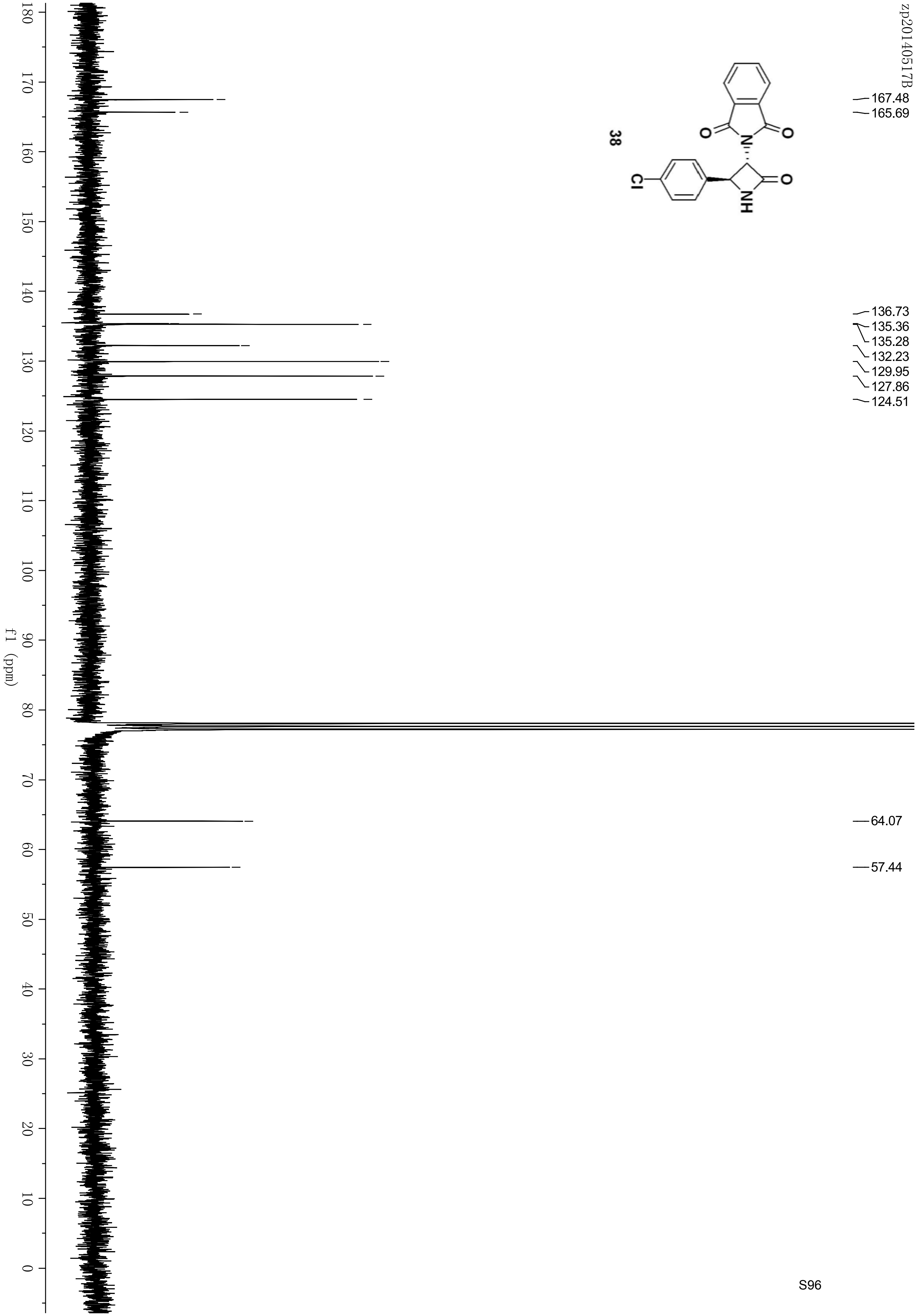

zp20140507C
168.36
166.08
151.13
149.19
139.57
135.88
134.73
133.22
132.01
131.63
130.86
129.31
127.62
124.06
121.19
120.78
117.39
104.61
56.41
56.21
34.63
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl
O
N
O
H
N
O
N
OMe
36


zp20140510E
8.755
8.751
8.744
8.466
8.442
7.875
7.869
7.861
7.755
7.747
7.741
7.367
7.344
7.302
7.199
7.176
6.845
6.822
6.436
6.430
5.383
5.376
3.966
1.02
1.02
1.02
2.06
2.12
2.00
1.02
2.10
1.03
1.01
1.00
3.16
9.5
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)
O
N
O
Cl
O
N
N
OMe

37

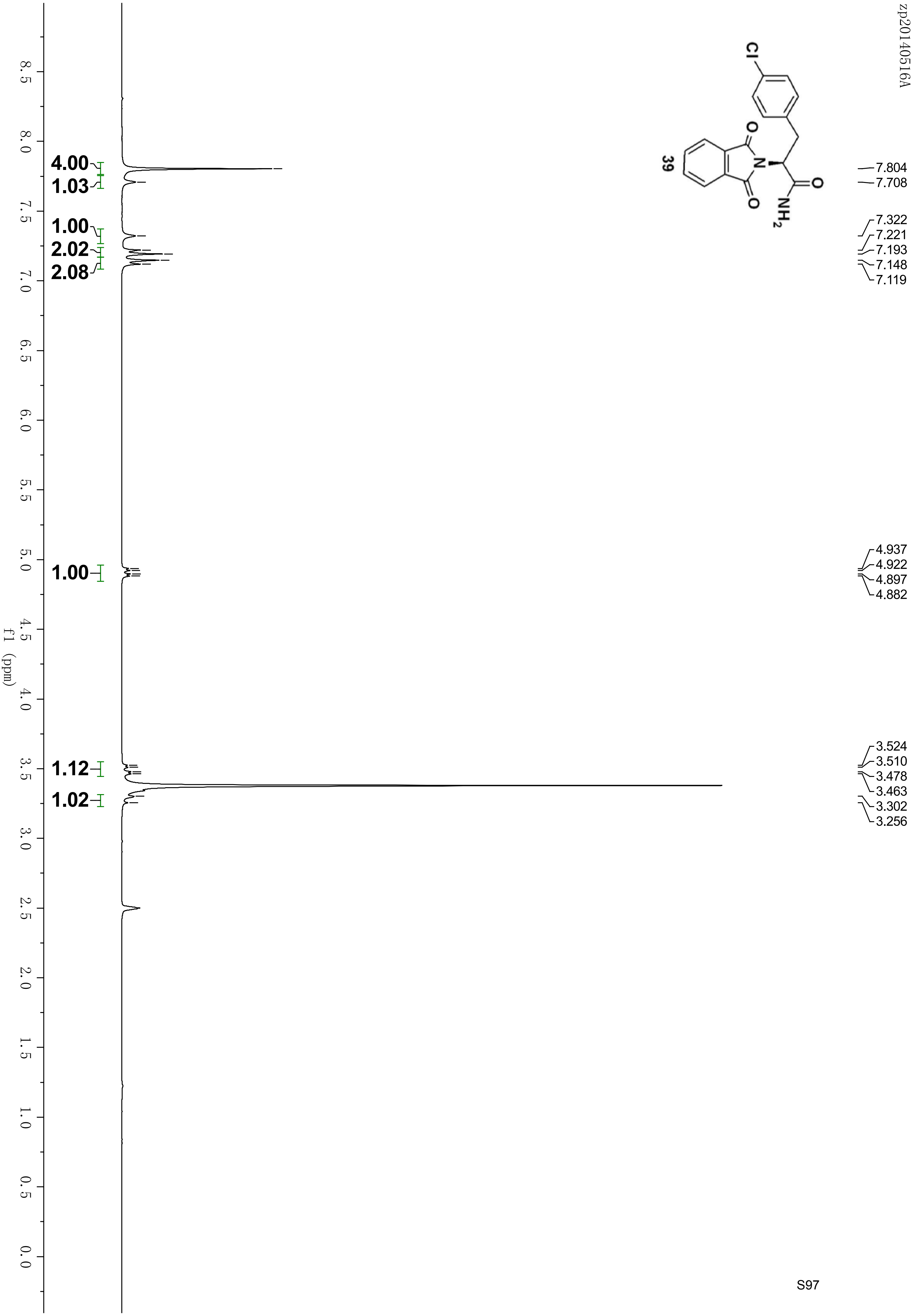

zp20140510E
37
Cl
O
N
O
N
O
N
N
OMe
167.45
163.43
153.61
150.21
142.63
137.20
135.02
134.54
132.31
131.06
129.47
128.34
125.69
124.30
123.51
121.46
121.15
104.40
65.13
63.35
56.41
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

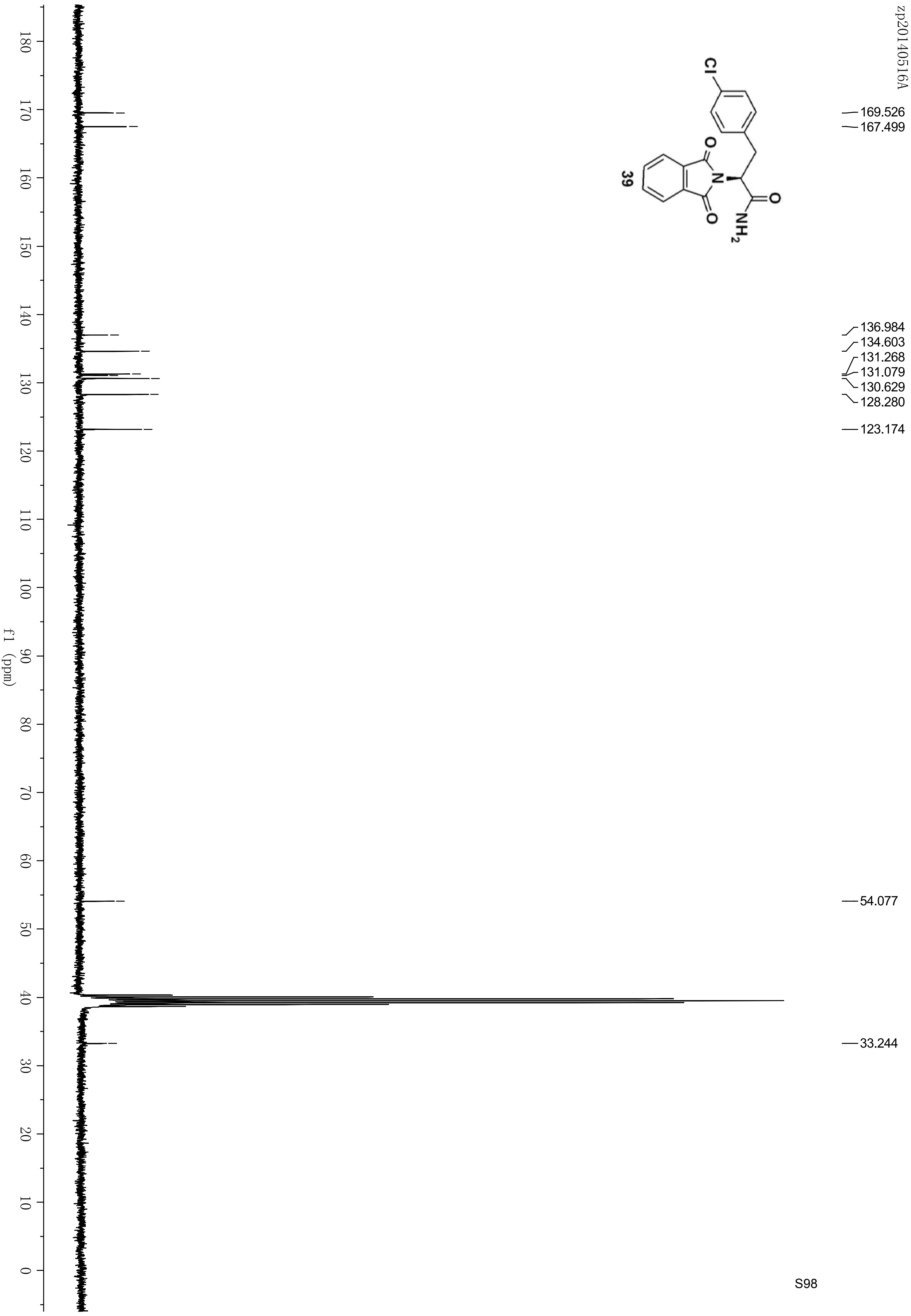

zp20140517B
38
O
N
O
O
Cl
NH
7.901
7.890
7.883
7.872
7.787
7.777
7.769
7.759
7.391
7.363
7.337
7.308
6.581
5.170
5.162
5.120
5.111
2.17
2.02
4.18
0.88
1.00
0.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



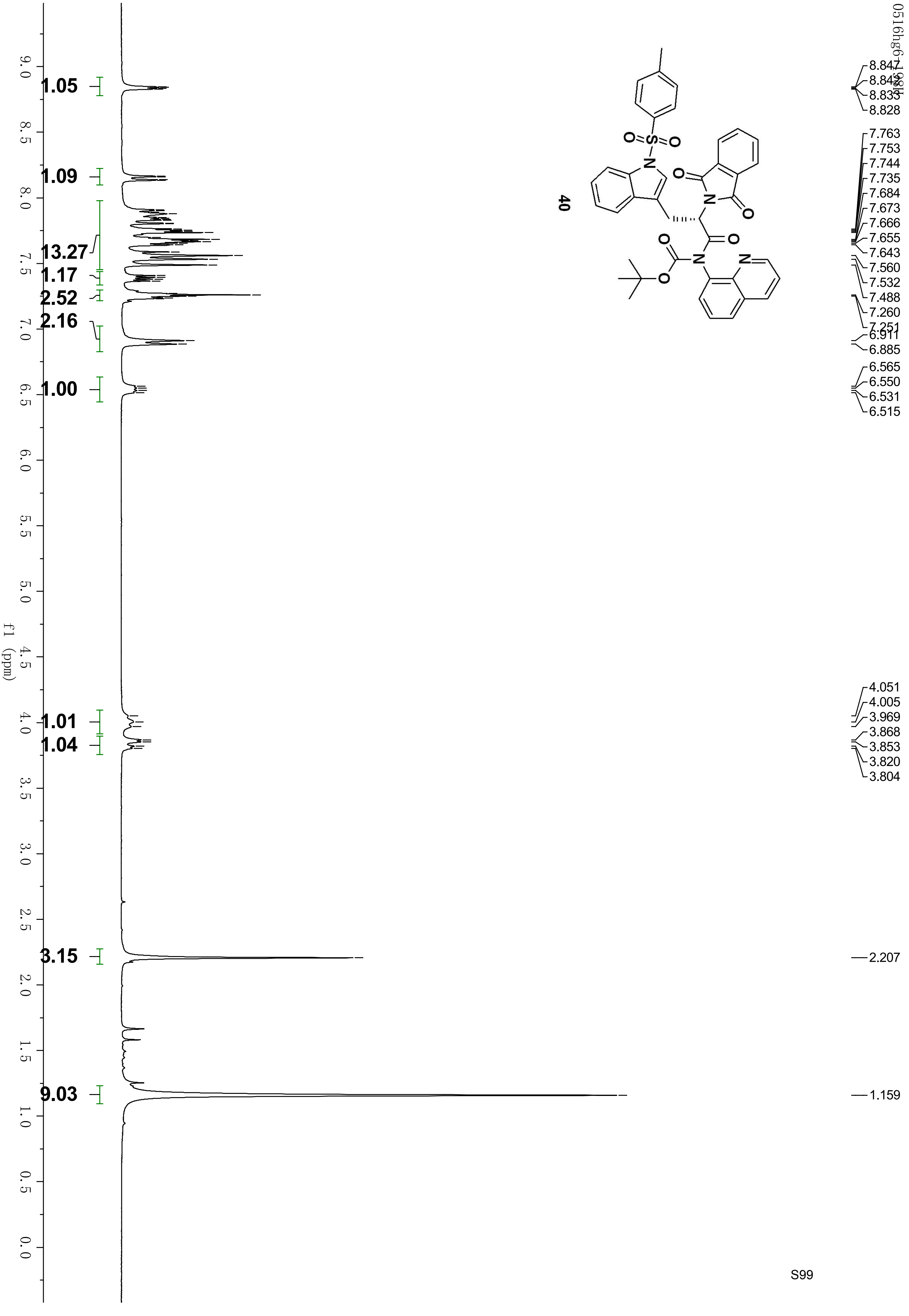
38

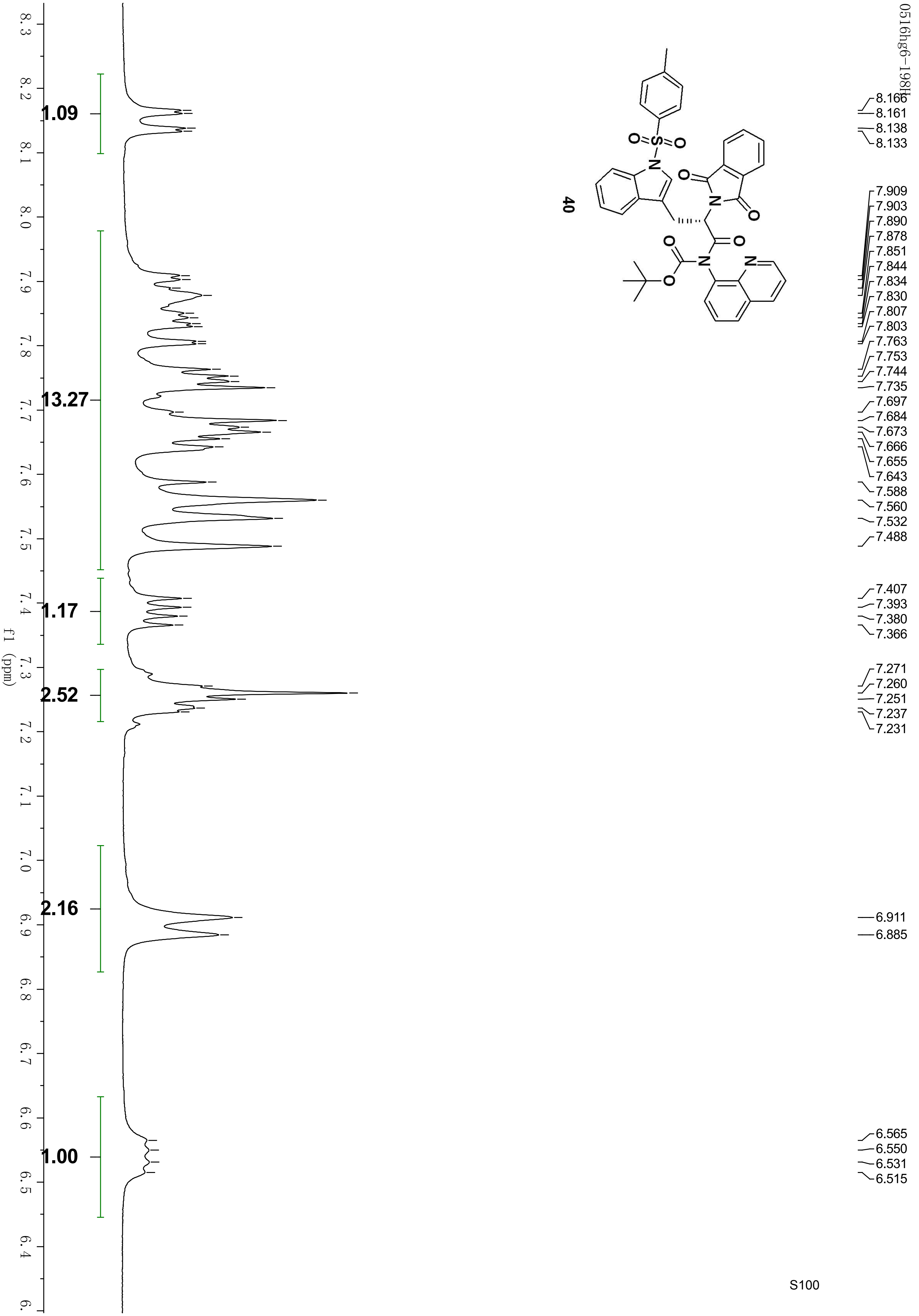
zp20140517B
167.48
165.69
136.73
135.36
135.28
132.23
129.95
127.86
124.51
64.07
57.44
O
N
O
O
Cl
NH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


zp20140516A
39
Cl
O
N
O
O
NH2
7.804
7.708
7.322
7.221
7.193
7.148
7.119
4.937
4.922
4.897
4.882
3.524
3.510
3.478
3.463
3.302
3.256
4.00
1.03
1.00
2.02
2.08
1.00
1.12
1.02
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)


zp20140516A
169.526
167.499
136.984
134.603
131.268
131.079
130.629
128.280
123.174
54.077
33.244
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl
O
N
O
NH2
O

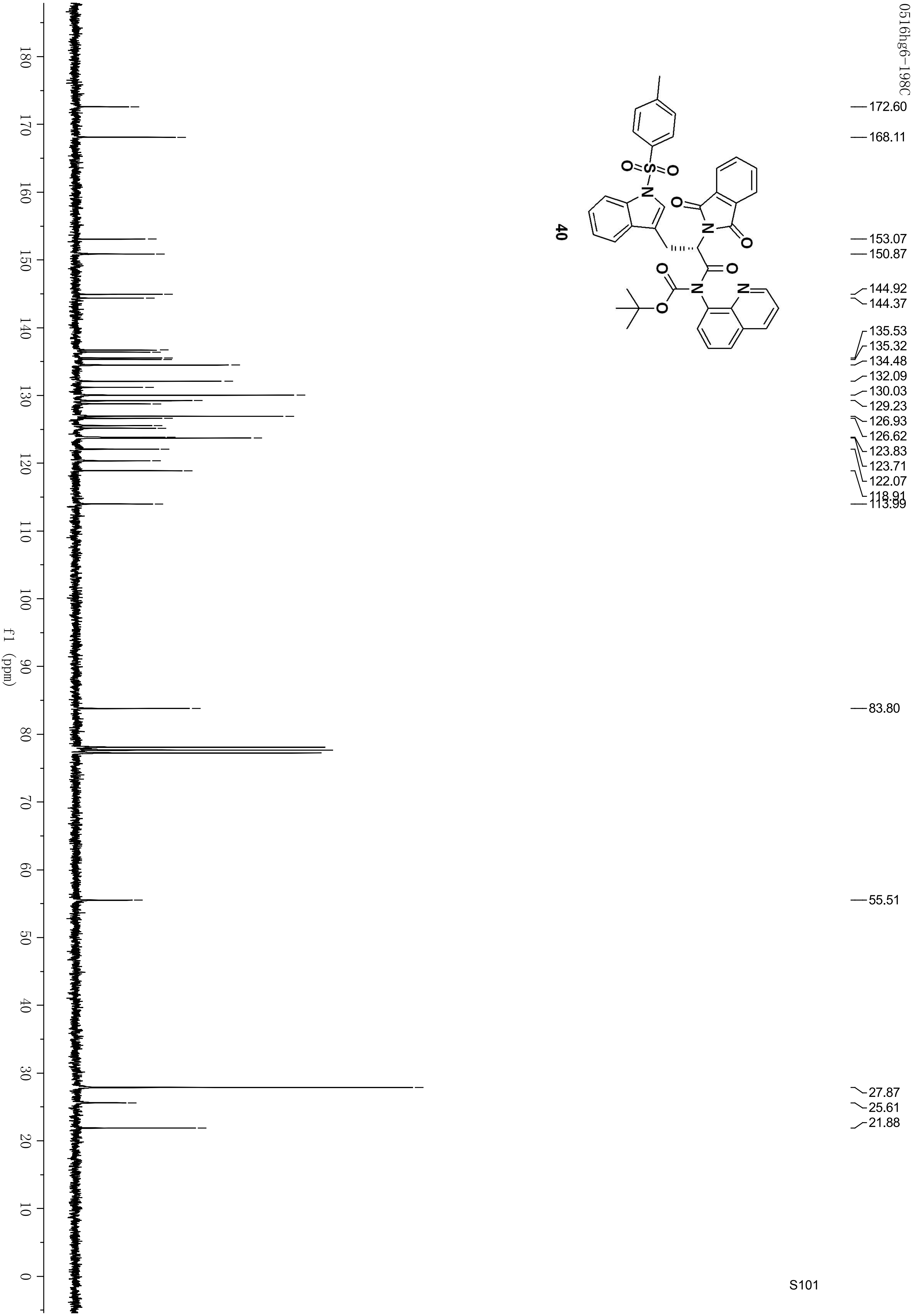
39


0516hg6-1.fid
40
O
S
O
N
N
O
O
O
O
O
N
N
1.05
1.09
13.27
1.17
2.52
2.16
1.00
1.01
1.04
3.15
9.03
8.847
8.842
8.833
8.828
7.763
7.753
7.744
7.735
7.684
7.673
7.666
7.655
7.643
7.560
7.532
7.488
7.260
7.251
6.911
6.885
6.565
6.550
6.531
6.515
4.051
4.005
3.969
3.868
3.853
3.820
3.804
2.207
1.159
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)



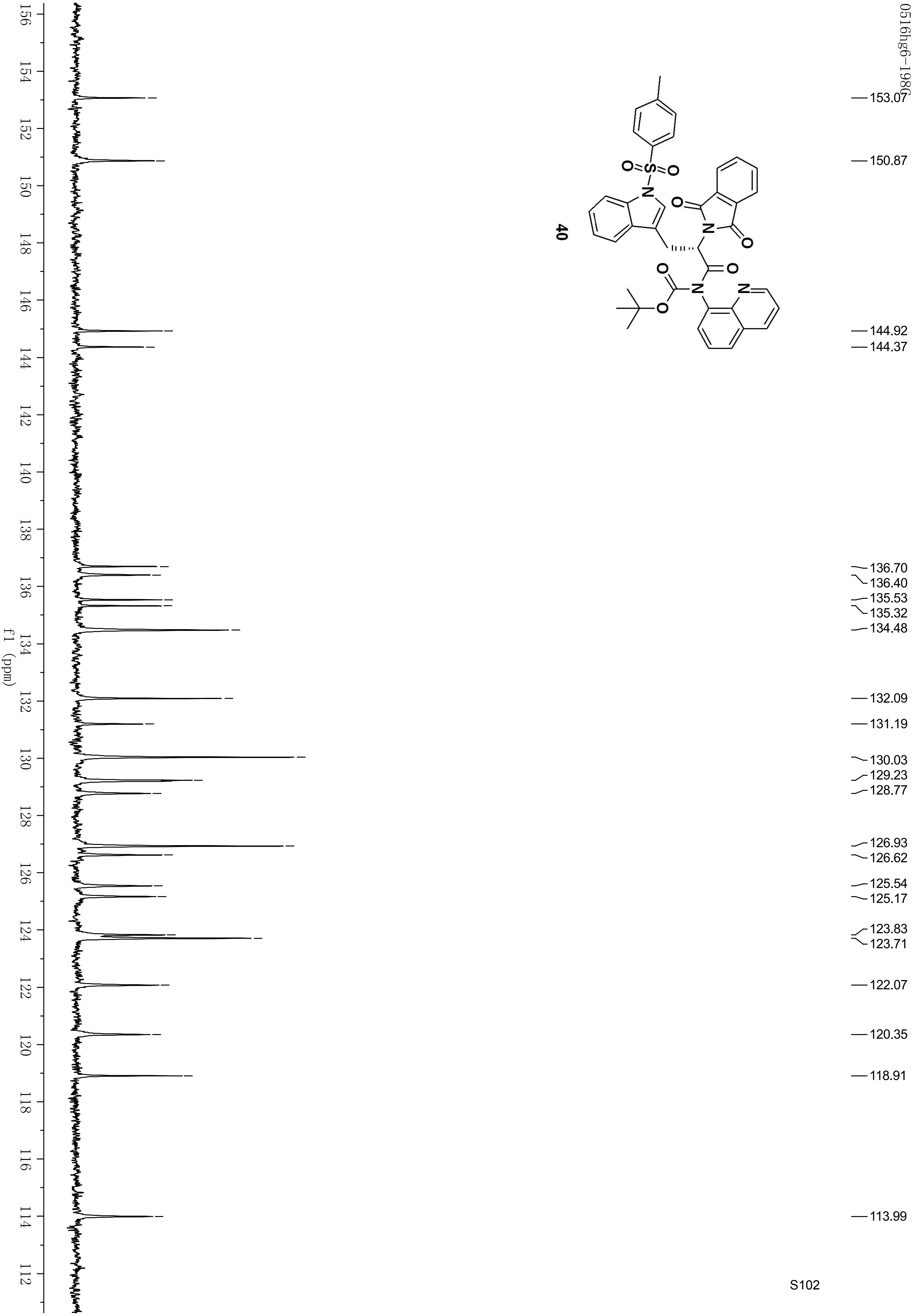
40

0516hg6-198H
f1 (ppm)
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.
1.09
13.27
1.17
2.52
2.16
1.00
8.166
8.161
8.138
8.133
7.909
7.903
7.890
7.878
7.851
7.844
7.834
7.830
7.807
7.803
7.763
7.753
7.744
7.735
7.697
7.684
7.673
7.666
7.655
7.643
7.588
7.560
7.532
7.488
7.407
7.393
7.380
7.366
7.271
7.260
7.251
7.237
7.231
6.911
6.885
6.565
6.550
6.531
6.515

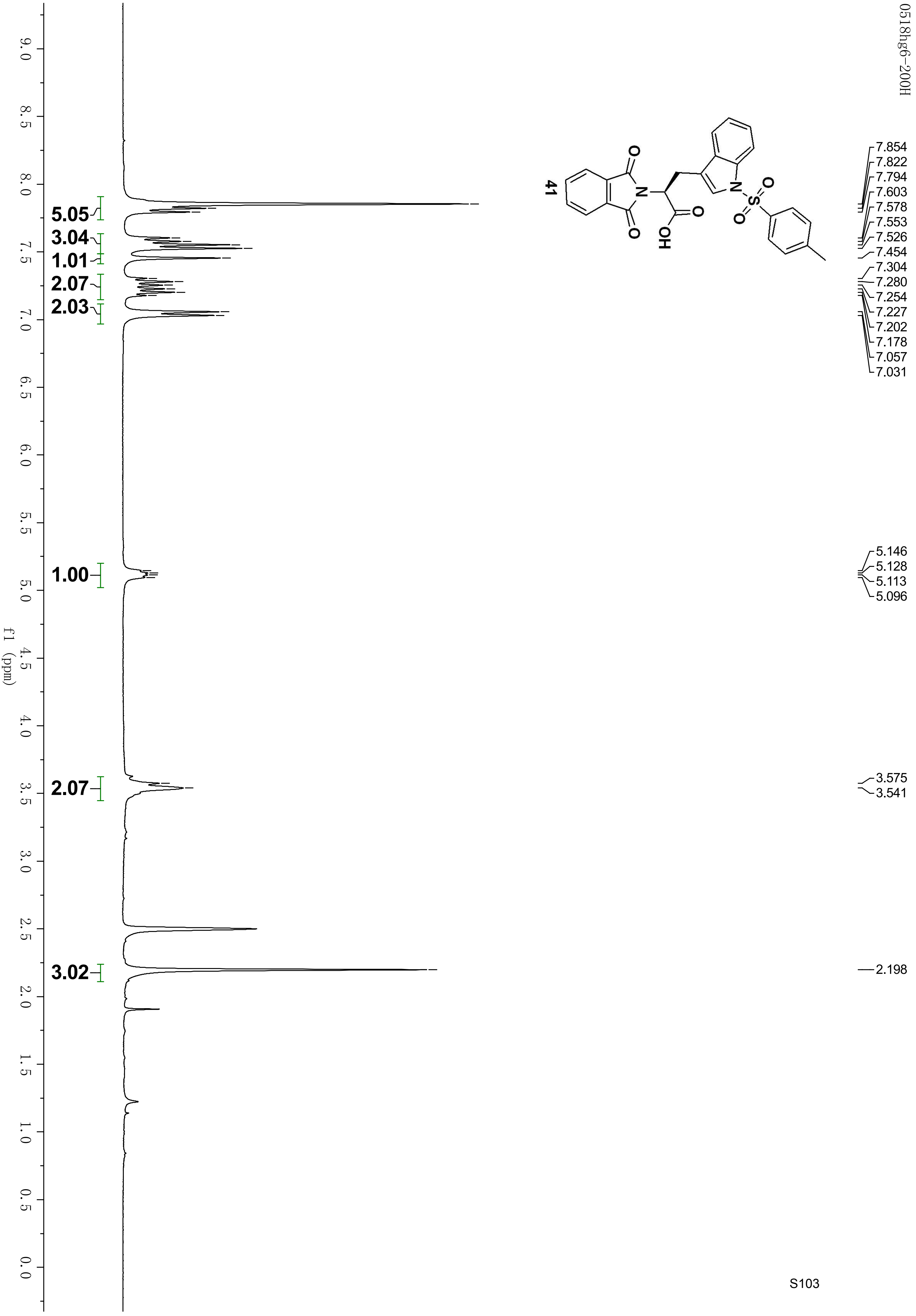


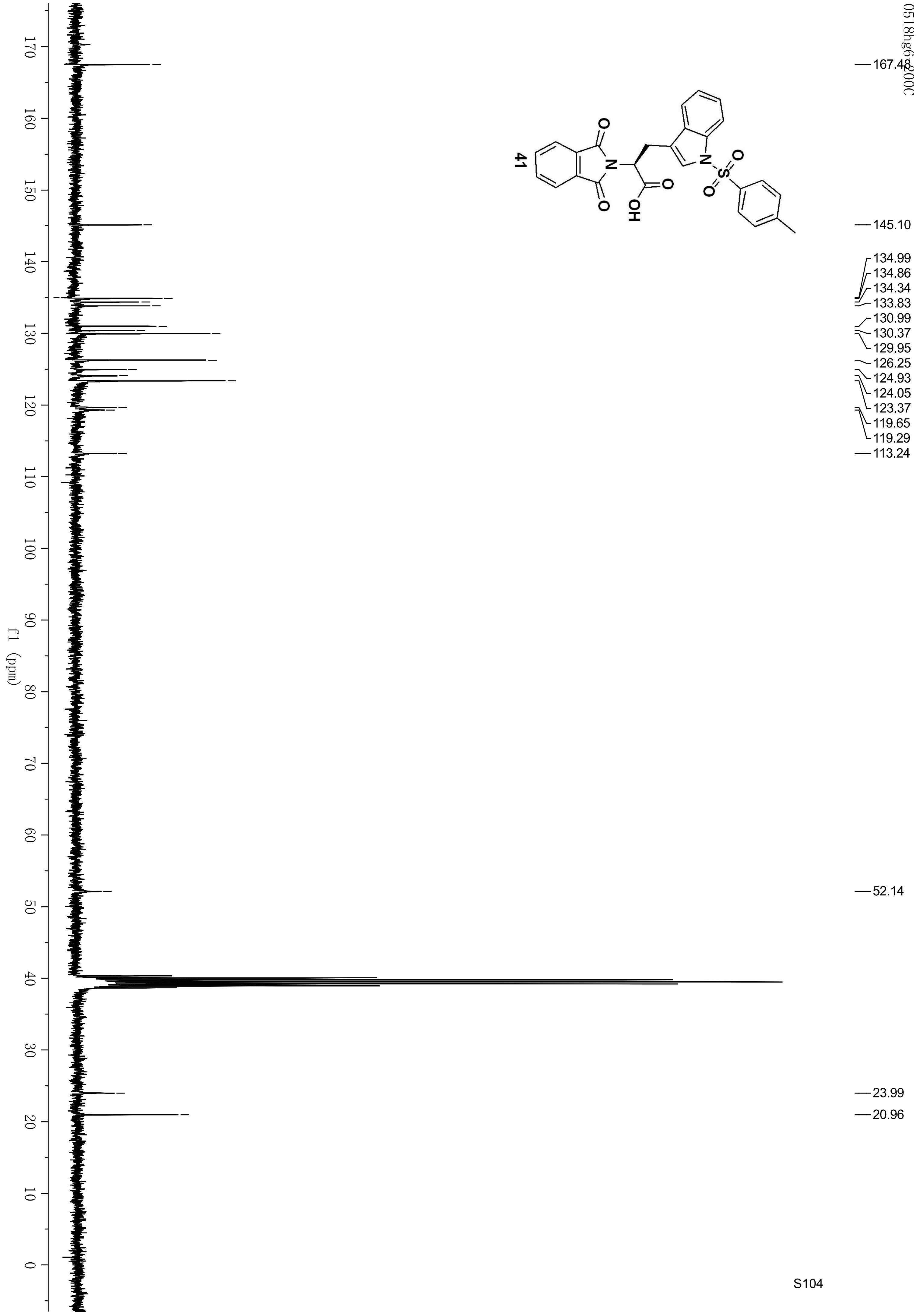
40

0516hg6-198C
172.60
168.11
153.07
150.87
144.92
144.37
135.53
135.32
134.48
132.09
130.03
129.23
126.93
126.62
123.83
123.71
122.07
118.91
113.99
83.80
55.51
27.87
25.61
21.88
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
S
O
N
N
O
O
O
O
N
N

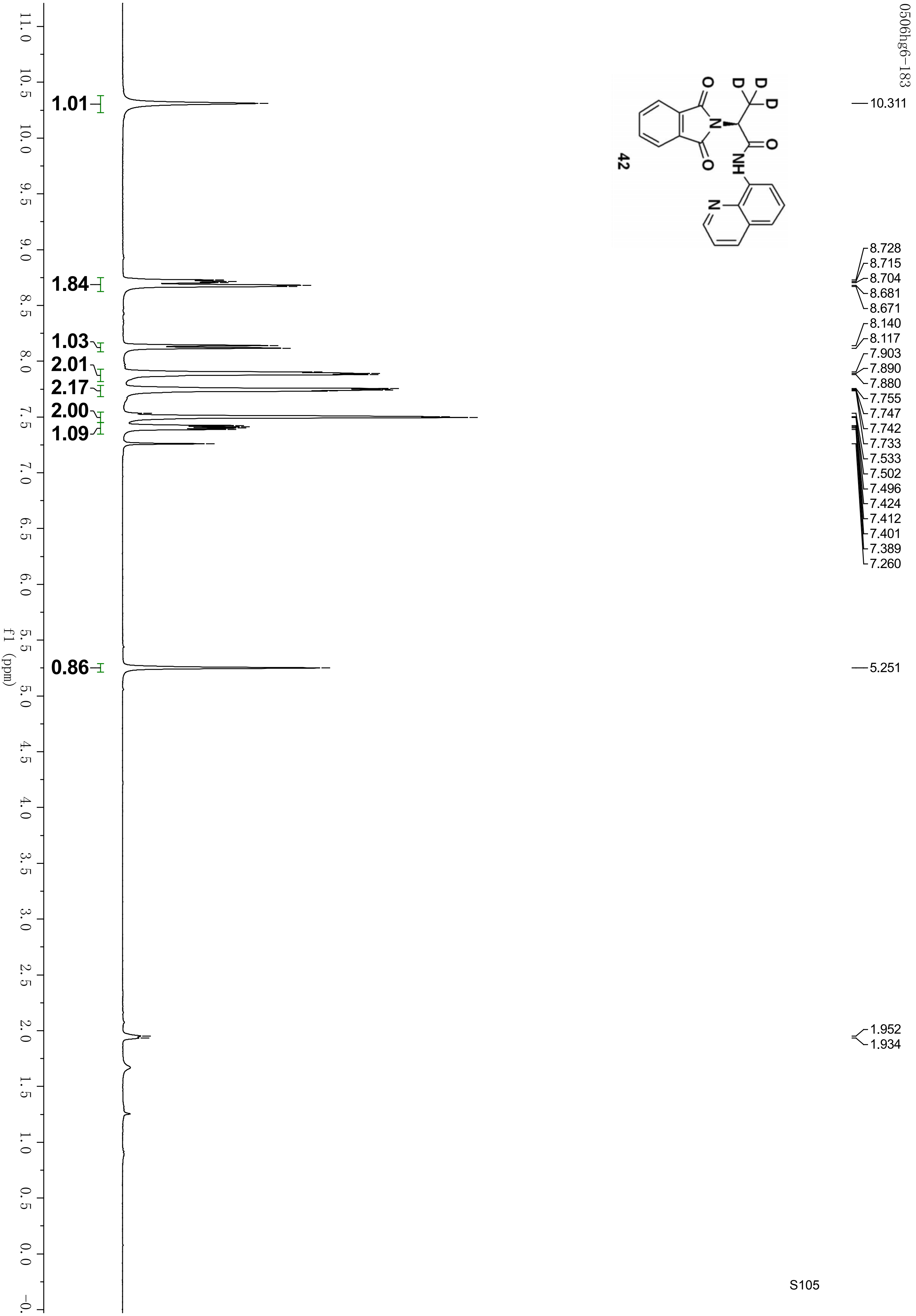

0516hg6-1986
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)
153.07
150.87
144.92
144.37
136.70
136.40
135.53
135.32
134.48
132.09
131.19
130.03
129.23
128.77
126.93
126.62
125.54
125.17
123.83
123.71
122.07
120.35
118.91
113.99
O
S
O
N
O
N
O
O
O
N
O
N

40


0518hg6-200H
41
O
N
O
OH
O
N
S
O
O
7.854
7.822
7.794
7.603
7.578
7.553
7.526
7.454
7.304
7.280
7.254
7.227
7.202
7.178
7.057
7.031
5.146
5.128
5.113
5.096
3.575
3.541
2.198
5.05
3.04
1.01
2.07
2.03
1.00
2.07
3.02
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)



0518hg6-200C
41
O
N
O
OH
O
N
S
O
O
167.48
145.10
134.99
134.86
134.34
133.83
130.99
130.37
129.95
126.25
124.93
124.05
123.37
119.65
119.29
113.24
52.14
23.99
20.96
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0506hg6-183
O
O
N
D
D
D
O
NH
N
10.311
8.728
8.715
8.704
8.681
8.671
8.140
8.117
7.903
7.890
7.880
7.755
7.747
7.742
7.733
7.533
7.502
7.496
7.424
7.412
7.401
7.389
7.260
5.251
1.952
1.934
1.01
1.84
1.03
2.01
2.17
2.00
1.09
0.86
11.0
10.5
10.0
9.5
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
-0.
f1 (ppm)

42