Chiral boron Lewis acid-catalyzed asymmetric synthesis of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines

Yuan Li,[a] Yu-Han Su,[a] De-Jun Dong,[a] Zhao Wu[a] and Shi-Kai Tian*[ab]

[a] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China
[b] Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting information

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General information

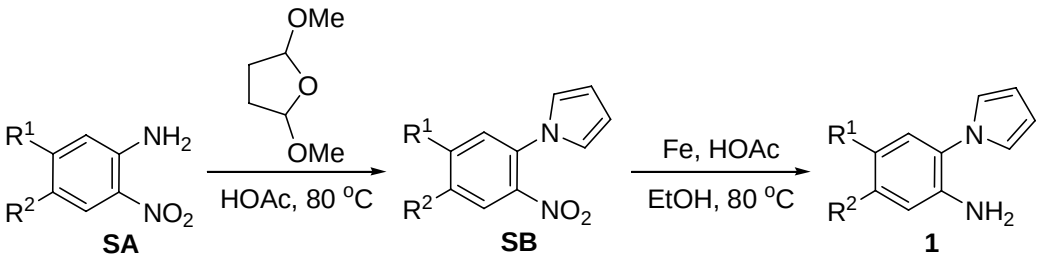
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump, using a Daicel Chiralpak AD or OD column (250 x 4.6 mm), and the UV detection was monitored at 254 nm. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\ ^\circ C}$ (c = g/100 mL, solvent). Single crystal X-ray analysis was performed on a Gemini S Ultra instrument. Melting points were uncorrected.

Catalyst **4a**[1] and ligands **4c-h**[2] were prepared following literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, TCI, and Alfa Aesar, and used as received. The solvents were dried over anhydrous magnesium sulfate prior to use. Molecular sieves were dried overnight under vacuum at 300 ˚C.

Abbreviations: BINOL = 1,1'-binaphthol, DCE = 1,2-dichloroethane, ms = molecular sieves, PMP = *p*-methoxyphenyl, THF = tetrahydrofuran, Ts = *p*-toluenesulfonyl.

Preparation of 2-(1*H*-pyrrol-1-yl)anilines and 2-(1*H*-pyrrol-1-yl)-3-aminopyridine (1h)

2-(1*H*-Pyrrol-1-yl)anilines **1a-f** are known compounds, and they were prepared by modifying literature procedures.[3]



A mixture of 2-nitroaniline **SA** (10.0 mmol) and 2,5-dimethoxytetrahydrofuran (1.32 g, 1.31 mL, 10.0 mmol) in acetic acid (20 mL) was stirred vigorously at 80 °C for 2 h, cooled to room temperature, added saturated aqueous sodium bicarbonate (30 mL), and extracted with ethyl acetate (3 x 40 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, concentrated, and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:50 to 1:20), to give compound **SB**.

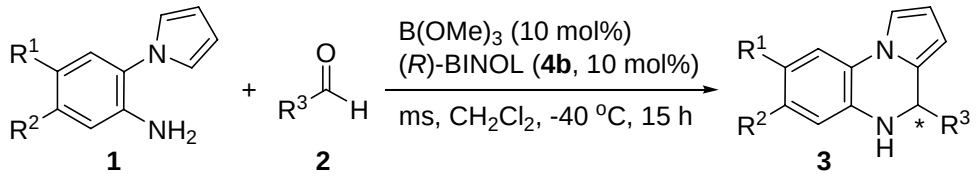
To a solution of compound **SB** (5.00 mmol) in ethanol (10 mL) was added iron

granules (560 mg, 10.0 mmol) and acetic acid (10 mL). The mixture was heated at 80 °C for 4 h, cooled to room temperature, and filtered through celite. The resulting filtrate was added saturated aqueous sodium bicarbonate (30 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, concentrated, and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:30 to 1:5), to give 2-(1*H*-pyrrol-1-yl)aniline **1**.

2-(1*H*-Pyrrol-1-yl)anilines **1a**, **1b**, **1c**, **1d**, **1e**, and **1f** were prepared in 78%, 81%, 80%, 70%, 69%, and 72% yields (two steps), respectively.

Using a similar procedure, 2-(1*H*-pyrrol-1-yl)-3-aminopyridine (**1h**) was prepared in 76 % yield (two steps) from 2-amino-3-nitropyridine.

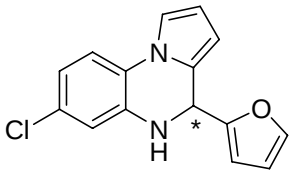
General procedure for the catalytic asymmetric synthesis of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines



To a suspension of powdered 4 Å molecular sieves (50 mg) in dry dichloromethane (0.40 mL) under nitrogen atmosphere were added (*R*)-BINOL (**4b**) (2.9 mg, 0.010 mmol) and a solution of $B(OMe)_3$ in dichloromethane (0.50 M, 20 μL, 0.010 mmol). The mixture was stirred at 40 °C for 1 h, cooled to -40 °C, and a solution of aldehyde **2** (0.11 mmol) in dichloromethane (0.30 mL) was added. After being stirred for 0.5 h at the same temperature, a solution of 2-(1*H*-pyrrol-1-yl)aniline **1** (0.10 mmol) in dichloromethane (0.30 mL) was added. The resulting mixture was stirred at -40 °C for 15 h, and purified directly by silica gel chromatography, eluting with dichloromethane/petroleum ether (1:1 to 8:1), to give 4,5-dihydropyrrolo[1,2-*a*]quinoxaline **3**.

The absolute configuration of compound **3b** was assigned to be *R* by single-crystal X-ray analysis of its *N*-tosyl derivative **5**.

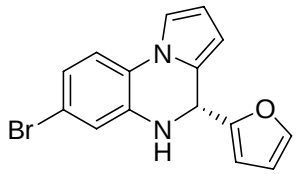
Analytical data for the products



3a

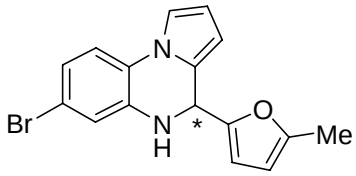
Compound **3a**, light yellow solid, m.p. 103-104 °C; $[\alpha]_D^{20}$ = -84.4 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 1.6, 0.8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.15 (dd, J = 3.2, 1.6 Hz, 1H), 6.78 (dd, J = 8.4, 2.0 Hz, 1H), 6.72 (d, J = 2.0 Hz, 1H), 6.34-6.30 (m, 1H), 6.26 (dd, J = 3.2, 2.0 Hz, 1H), 6.06-6.01 (m, 2H), 5.70 (s,

1H), 4.42 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 142.5, 135.8, 129.7, 125.3, 123.9, 119.3, 115.5, 115.4, 114.5, 110.6, 110.3, 107.1, 106.1, 49.0; HRMS (ESI) calcd for $C_{15}H_{12}ON_2Cl^+$ $(M + H)^+$ 271.0633, found 271.0629. The ee was determined to be 90% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 8.5 min (minor), 11.5 min (major).



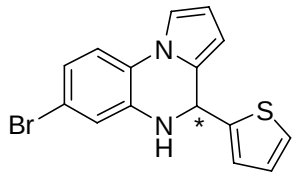
3b

Compound **3b**, light yellow solid, m.p. 135-136 °C; $[\alpha]_D^{20}$ = -50.8 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.16-7.13 (m, 2H), 6.92 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.34-6.30 (m, 1H), 6.26 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.05-6.02 (m, 2H), 5.69 (s, 1H), 4.41 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 141.5, 135.0, 124.3, 123.3, 121.1, 117.2, 116.2, 114.9, 113.5, 109.6, 109.3, 106.1, 105.1, 48.0; HRMS (ESI) calcd for $C_{15}H_{12}ON_2Br^+$ $(M + H)^+$ 315.0128, found 315.0123. The ee was determined to be 94% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 8.6 min (minor), 12.0 min (major).



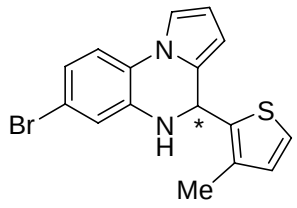
3c

Compound **3c**, light yellow solid, m.p. 98-99 °C; $[\alpha]_D^{20}$ = -84.8 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 2H), 6.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.34-6.30 (m, 1H), 6.03-6.00 (m, 1H), 5.91 (d, *J* = 2.8 Hz, 1H), 5.84 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.63 (s, 1H), 4.39 (s, br, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 152.0, 136.2, 125.6, 124.4, 122.1, 118.2, 117.1, 115.9, 114.4, 110.6, 108.1, 106.2, 106.1, 49.1, 13.6; HRMS (ESI) calcd for $C_{16}H_{14}ON_2Br^+$ $(M + H)^+$ 329.0284, found 329.0279. The ee was determined to be 93% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 7.8 min (minor), 11.7 min (major).



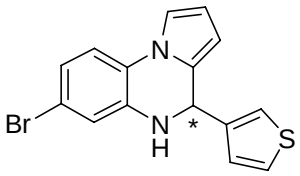
3d

Compound **3d**, light yellow solid, m.p. 75-76 °C; $[\alpha]_D^{20}$ = +15.6 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, J = 5.2, 1.2 Hz, 1H), 7.16 (d, J = 8.8 Hz, 1H), 7.13 (dd, J = 3.2, 1.6 Hz, 1H), 7.05-7.02 (m, 1H), 6.98-6.93 (m, 2H), 6.88 (d, J = 2.0 Hz, 1H), 6.30-6.26 (m, 1H), 5.88 (s, 1H), 5.87-5.84 (m, 1H), 4.34 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 136.4, 128.6, 126.5, 125.8, 125.5, 124.6, 122.4, 118.2, 117.2, 116.0, 114.5, 110.7, 106.3, 51.3; HRMS (ESI) calcd for $C_{15}H_{12}N_2BrS^+$ $(M + H)^+$ 330.9899, found 330.9893. The ee was determined to be 91% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 9.3 min (minor), 13.5 min (major).



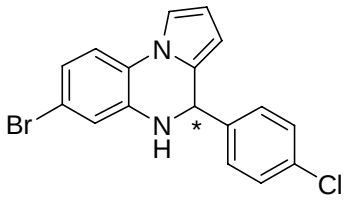
3e

Compound **3e**, light yellow solid, m.p. 108-109 °C; $[\alpha]_D^{20}$ = +38.4 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 5.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.13 (dd, J = 3.2, 1.6 Hz, 1H), 6.96 (dd, J = 8.4, 2.0 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 6.84 (d, J = 5.2 Hz, 1H), 6.29-6.25 (m, 1H), 5.89 (s, 1H), 5.74-5.71 (m, 1H), 4.26 (s, br, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.9, 134.8, 129.9, 128.6, 124.7, 124.4, 122.4, 118.2, 117.2, 116.0, 114.5, 110.6, 106.2, 49.6, 14.0; HRMS (ESI) calcd for $C_{16}H_{14}N_2BrS^+$ $(M + H)^+$ 345.0056, found 345.0053. The ee was determined to be 94% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 6.7 min (minor), 8.6 min (major).



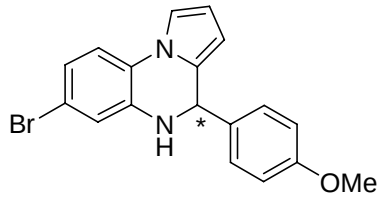
3f

Compound **3f**, light yellow oil, $[\alpha]_D^{20}$ = +39.6 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 4.8, 2.8 Hz, 1H), 7.26-7.24 (m, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.13 (dd, J = 3.2, 1.6 Hz, 1H), 7.11 (dd, J = 4.8, 1.2 Hz, 1H), 6.94 (dd, J = 8.4, 2.0 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 6.29-6.25 (m, 1H), 5.76-5.73 (m, 1H), 5.67 (s, 1H), 4.23 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.0, 128.7, 126.7, 126.6, 124.6, 122.8, 122.1, 117.9, 117.2, 116.0, 114.4, 110.6, 105.9, 51.3; HRMS (ESI) calcd for $C_{15}H_{12}N_2BrS^+$ $(M + H)^+$ 330.9899, found 330.9893. The ee was determined to be 94% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 8.6 min (minor), 12.8 min (major).



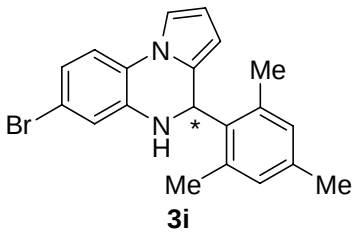
3g

Compound **3g**, light yellow solid, m.p. 103-104 °C; $[\alpha]_D^{20}$ = +78.4 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H), 7.17 (d, J = 8.4 Hz, 1H), 7.14 (dd, J = 3.2, 1.2 Hz, 1H), 6.95 (dd, J = 8.4, 2.0 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 6.28-6.24 (m, 1H), 5.60-5.57 (m, 1H), 5.51 (s, 1H), 4.17 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.0, 134.2, 129.1, 128.9, 124.4, 122.2, 117.9, 117.2, 116.0, 114.5, 110.7, 106.4, 55.4; HRMS (ESI) calcd for $C_{17}H_{13}N_2BrCl^+$ $(M + H)^+$ 358.9945, found 358.9937. The ee was determined to be 80% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 7.7 min (minor), 10.9 min (major).



3h

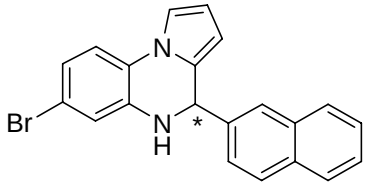
Compound **3h**, light yellow solid, m.p. 108-109 °C; $[\alpha]_D^{20}$ = +30.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 6.8, 2.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 1H), 7.13 (dd, J = 3.2, 1.6 Hz, 1H), 6.93 (dd, J = 8.4, 2.0 Hz, 1H), 6.90 (dd, J = 6.8, 2.0 Hz, 2H), 6.85 (d, J = 2.0 Hz, 1H), 6.27-6.23 (m, 1H), 5.60-5.57 (m, 1H), 5.47 (s, 1H), 4.15 (s, br, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 137.5, 133.2, 129.9, 129.0, 124.5, 121.8, 117.8, 117.1, 115.9, 114.3, 114.1, 110.6, 106.2, 55.4, 55.3; HRMS (ESI) calcd for $C_{18}H_{16}ON_2Br^+$ $(M + H)^+$ 355.0441, found 355.0435. The ee was determined to be 89% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 9.2 min (minor), 13.5 min (major).



3i

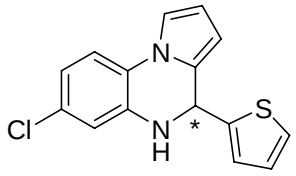
Compound **3i**, white solid, m.p. 150-151 °C; $[\alpha]_D^{20}$ = +50.8 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16-7.11 (m, 2H), 6.90-6.85 (m, 3H), 6.77 (d, J = 2.0 Hz, 1H), 6.24-6.20 (m, 1H), 6.13 (s, 1H), 5.54-5.50 (m, 1H), 3.90 (s, br, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 132.6, 128.4, 123.8, 121.1, 117.1, 115.9, 113.8, 110.7, 105.4, 51.0, 20.9, 20.5; HRMS (ESI) calcd

for $C_{20}H_{20}N_2Br^+$ $(M + H)^+$ 367.0804, found 367.0800. The ee was determined to be 80% by HPLC analysis on a Chiralpak AD column, λ = 254 nm, *n*-hexane/*i*-PrOH (90:10), flow rate = 1.0 mL/min, t_r = 5.6 min (major), 7.2 min (minor).



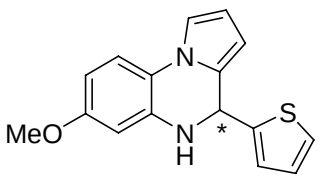
3j

Compound **3j**, light yellow solid, m.p. 120-121 °C; $[\alpha]_D^{20}$ = +53.0 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.49 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 3.2, 1.2 Hz, 1H), 6.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.27-6.23 (m, 1H), 5.69 (s, 1H), 5.61-5.58 (m, 1H), 4.27 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.3, 133.4, 133.2, 129.2, 128.7, 128.0, 127.8, 126.8, 126.4, 126.3, 125.6, 124.4, 121.9, 117.8, 117.2, 115.9, 114.4, 110.7, 106.6, 56.2; HRMS (ESI) calcd for $C_{21}H_{16}N_2Br^+$ $(M + H)^+$ 375.0491, found 375.0487. The ee was determined to be 80% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 16.4 min (minor), 20.4 min (major).



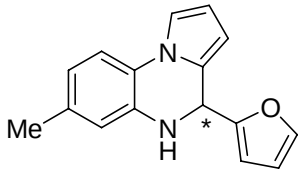
3k

Compound **3k**, light yellow solid, m.p. 139-140 °C; $[\alpha]_D^{20}$ = +20.1 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.14 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.06-7.03 (m, 1H), 6.96 (dd, *J* = 5.2, 3.2 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.30-6.26 (m, 1H), 5.89 (s, 1H), 5.87-5.84 (m, 1H), 4.35 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 136.1, 129.7, 128.6, 126.5, 125.8, 125.5, 124.1, 119.5, 115.6, 115.4, 114.5, 110.6, 106.2, 51.3; HRMS (ESI) calcd for $C_{15}H_{12}N_2ClS^+$ $(M + H)^+$ 287.0404, found 287.0399. The ee was determined to be 89% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 8.8 min (minor), 11.9 min (major).



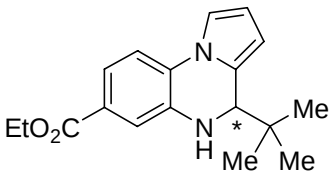
3l

Compound **3l**, light yellow solid, m.p. 107-108 °C; $[\alpha]_D^{20}$ = +23.2 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J = 5.2, 1.2 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.12 (dd, J = 3.2, 1.6 Hz, 1H), 7.05 (dd, J = 3.2, 1.2 Hz, 1H), 6.96 (dd, J = 5.2, 3.2 Hz, 1H), 6.41 (dd, J = 8.8, 2.8 Hz, 1H), 6.32 (d, J = 2.8 Hz, 1H), 6.27-6.23 (m, 1H), 5.87 (s, 1H), 5.83-5.81 (m, 1H), 4.30 (s, br, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 145.5, 136.3, 128.5, 126.4, 125.6, 125.4, 119.8, 115.5, 114.2, 109.7, 105.4, 104.8, 101.6, 55.5, 51.6; HRMS (EI) calcd for $C_{16}H_{14}N_2OS$ (M) 282.0827, found 282.0832. The ee was determined to be 81% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 21.2 min (minor), 30.9 min (major).



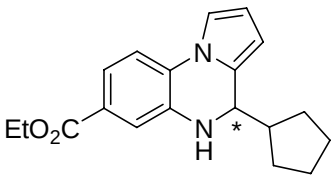
3m

Compound **3m**, light yellow oil, $[\alpha]_D^{20}$ = -67.6 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 1.6, 0.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.16 (dd, J = 3.2, 1.6 Hz, 1H), 6.65-6.61 (m, 1H), 6.55 (d, J = 0.8 Hz, 1H), 6.31-6.27 (m, 1H), 6.26 (dd, J = 3.2, 1.6 Hz, 1H), 6.07-6.04 (m, 1H), 6.01-5.98 (m, 1H), 5.68 (s, 1H), 4.29 (s, br, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.2, 133.6, 133.4, 124.6, 122.2, 119.2, 115.2, 113.4, 113.3, 109.3, 108.8, 105.9, 104.4, 48.3, 20.0; HRMS (EI) calcd for $C_{16}H_{14}N_2O$ (M) 250.1106, found 250.1104. The ee was determined to be 80% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 13.5 min (minor), 23.0 min (major).



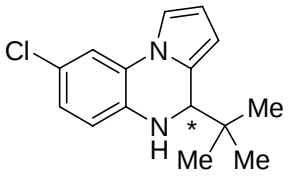
3n

Compound **3n**, white solid, m.p. 123-124 °C; $[\alpha]_D^{20}$ = +52.2 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.4, 2.0 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 3.2, 1.6 Hz, 1H), 6.37-6.33 (m, 1H), 6.03 (dd, J = 3.2, 1.6 Hz, 1H), 4.45 (s, br, 1H), 4.39-4.31 (m, 2H), 4.23 (s, 1H), 1.39 (t, J = 7.2 Hz, 3H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 135.7, 128.2, 126.6, 126.1, 119.6, 114.6, 114.3, 113.8, 110.7, 107.8, 60.8, 60.3, 39.1, 26.2, 14.4; HRMS (EI) calcd for $C_{18}H_{22}N_2O_2$ (M) 298.1681, found 298.1690. The ee was determined to be 95% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (85:15), flow rate = 1.0 mL/min, t_r = 7.8 min (minor), 8.4 min (major).



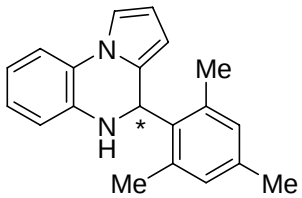
3o

Compound **3o**, light yellow solid, m.p. 140-141 °C; $[\alpha]_D^{20}$ = +30.0 (c = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.4, 1.8 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.16-7.13 (m, 1H), 6.34-6.30 (m, 1H), 6.04-6.00 (m, 1H), 4.40-4.31 (m, 2H), 4.28 (d, J = 8.0 Hz, 1H), 4.24 (s, br, 1H), 2.27-2.12 (m, 1H), 1.85-1.47 (m, 8H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 135.3, 129.3, 128.8, 126.5, 120.7, 116.2, 114.3, 114.1, 110.8, 105.7, 60.8, 55.6, 45.4, 29.8, 29.0, 25.4, 25.3, 14.4; HRMS (EI) calcd for $C_{19}H_{22}N_2O_2$ (M) 310.1681, found 310.1632. The ee was determined to be 72% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (85:15), flow rate = 1.0 mL/min, t_r = 9.1 min (minor), 15.3 min (major).



3p

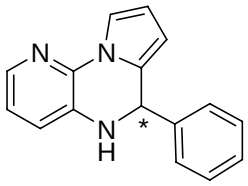
Compound **3p**, white solid, m.p. 107-108 °C; $[\alpha]_D^{20}$ = -94.4 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 2.4 Hz, 1H), 7.10 (dd, J = 3.2, 1.2 Hz, 1H), 6.86 (dd, J = 8.4, 2.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 6.34-6.30 (m, 1H), 6.00 (dd, J = 3.6, 1.2 Hz, 1H), 4.32 (s, br, 1H), 4.19 (s, 1H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 125.7, 125.6, 124.4, 122.1, 114.5, 114.4, 113.9, 110.3, 107.5, 60.3, 39.0, 26.2; HRMS (EI) calcd for $C_{15}H_{17}ClN_2$ (M) 260.1080, found 260.1074. The ee was determined to be 80% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (90:10), flow rate = 1.0 mL/min, t_r = 7.6 min (minor), 11.6 min (major).



3q

Compound **3q**, white solid, m.p. 142-143 °C; $[\alpha]_D^{20}$ = +80.2 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.0, 1.2 Hz, 1H), 7.19-7.16 (m, 1H), 6.97-6.91 (m, 1H), 6.88 (s, 2H), 6.82-6.76 (m, 1H), 6.65 (dd, J = 8.0, 1.2 Hz, 1H), 6.24-6.20 (m, 1H), 6.14 (s, 1H), 5.53-5.50 (m, 1H), 3.85 (s, br, 1H), 2.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.6, 133.0, 128.9, 124.9, 124.6, 118.6, 114.7,

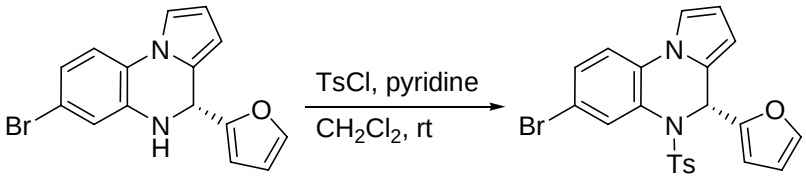
113.8, 110.2, 105.0, 51.2, 20.9; HRMS (EI) calcd for $C_{20}H_{20}N_2$ (M) 288.1626, found 288.1624. The ee was determined to be 80% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (90:10), flow rate = 1.0 mL/min, t_r = 5.3 min (major), 6.2 min (minor).



3r

Compound **3r**, light yellow solid, m.p. 84-85 °C; $[\alpha]_D^{20}$ = +24.4 (c = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.67 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.46-7.41 (m, 2H), 7.40-7.33 (m, 3H), 6.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.90 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.28-6.24 (m, 1H), 5.66-5.63 (m, 1H), 5.62 (s, 1H), 4.16 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 137.7, 131.2, 129.3, 128.8, 128.4, 127.7, 121.0, 120.3, 115.2, 110.7, 107.3, 55.8; HRMS (EI) calcd for $C_{16}H_{13}N_3$ (M) 247.1109, found 247.1102. The ee was determined to be 84% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (80:20), flow rate = 1.0 mL/min, t_r = 9.1 min (major), 13.3 min (minor).

Synthesis of sulfonamide 5



3b **5**

4,5-Dihydropyrrolo[1,2-*a*]quinoxaline **3b** (94% ee, 189 mg, 0.60 mmol) and 4-methylbenzenesulfonyl chloride (137 mg, 0.72 mmol) was dissolved in dichloromethane (2.0 mL) and pyridine (0.10 mL). The mixture was stirred at room temperature overnight and then chromatographed on silica gel, eluting with petroleum ether/ethyl acetate (10:1), to afford sulfonamide **5** (146 mg, 52%) as light yellow solid. m.p. 185-186 °C; $[\alpha]_D^{20}$ = -21.5 (c = 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.4 Hz, 1H), 7.39-7.35 (m, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.67-6.64 (m, 1H), 6.63 (s, 1H), 6.15-6.11 (m, 2H), 6.07-6.04 (m, 1H), 5.73 (d, *J* = 3.2 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 142.6, 142.1, 132.7, 130.9, 130.0, 129.8, 127.9, 125.8, 125.6, 123.0, 115.7, 115.4, 113.7, 109.9, 109.1, 107.9, 106.6, 50.8, 20.4; HRMS (ESI) calcd for $C_{22}H_{18}BrN_2O_3S^+$ $(M + H)^+$ 469.0216, found 469.0207. The ee was determined to be 94% by HPLC analysis on a Chiralpak OD column, λ = 254 nm, *n*-hexane/*i*-PrOH (90:10), flow rate = 1.0 mL/min, t_r = 8.9 min (minor), 10.9 min (major).

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1 D. Uraguchi and M. Terada, *J. Am. Chem. Soc.*, 2004, **126**, 5356.

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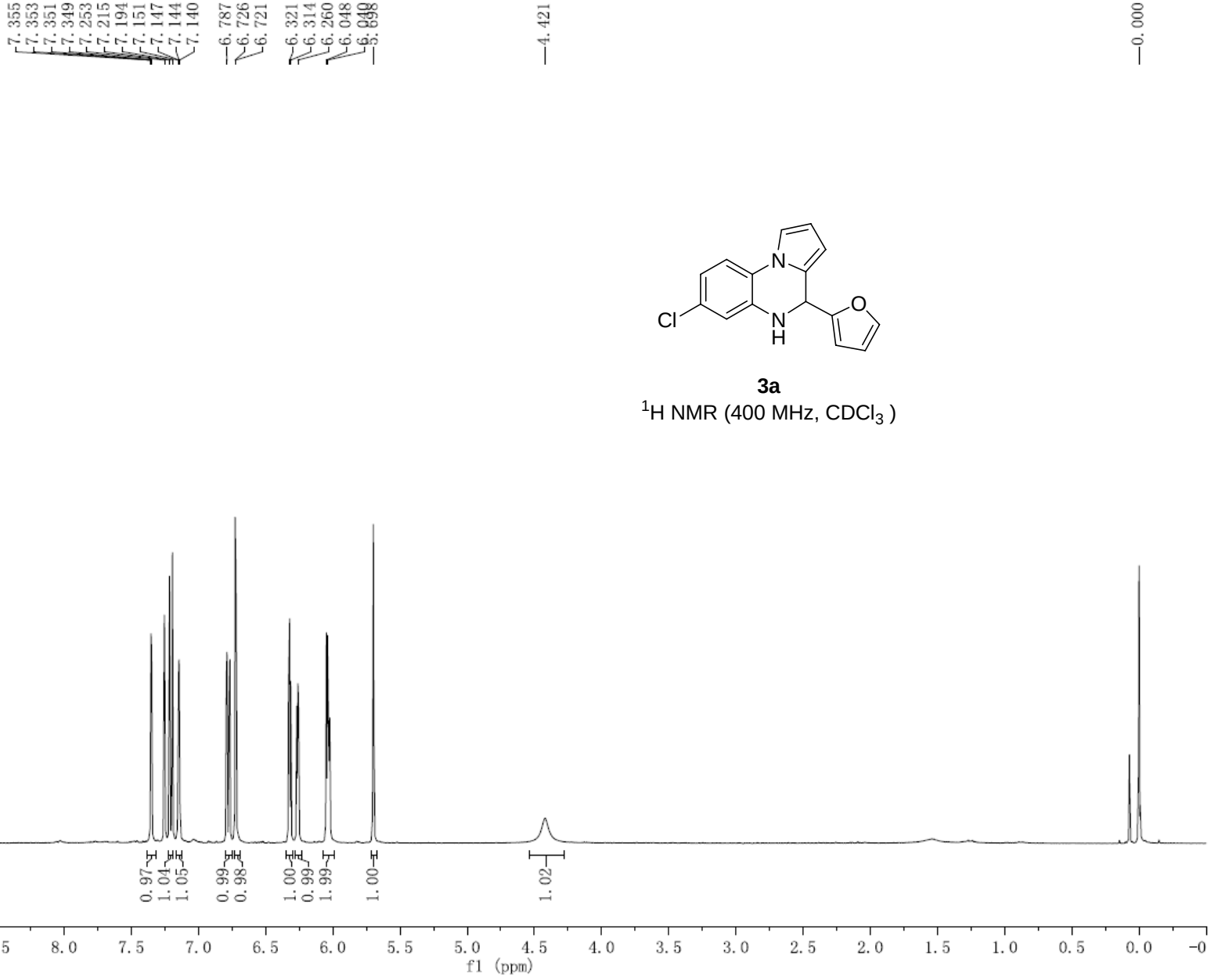
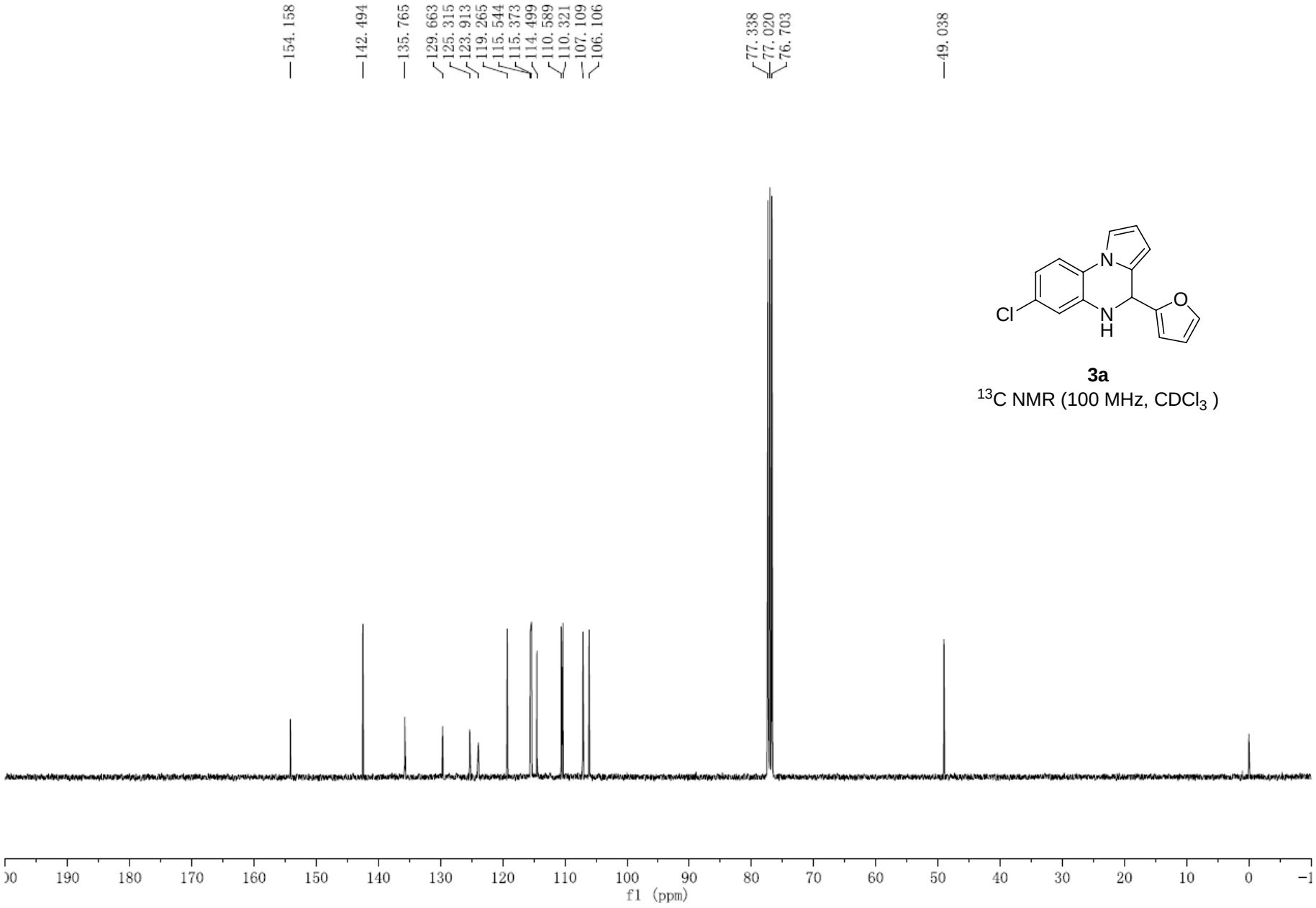
3 (*a*) G. W. H. Cheeseman and A. A. Hawi, *J. Heterocycl. Chem*., 1985, **22**, 423; (*b*) J. P. Sabatucci, F. Ye and P. E. Mahaney, U.S. Patent 0160815, 2006; (*c*) N. T. Patil, P. G. V. V. Lakshmi and V. Singh, *Eur. J. Org. Chem.*, 2010, 4719.



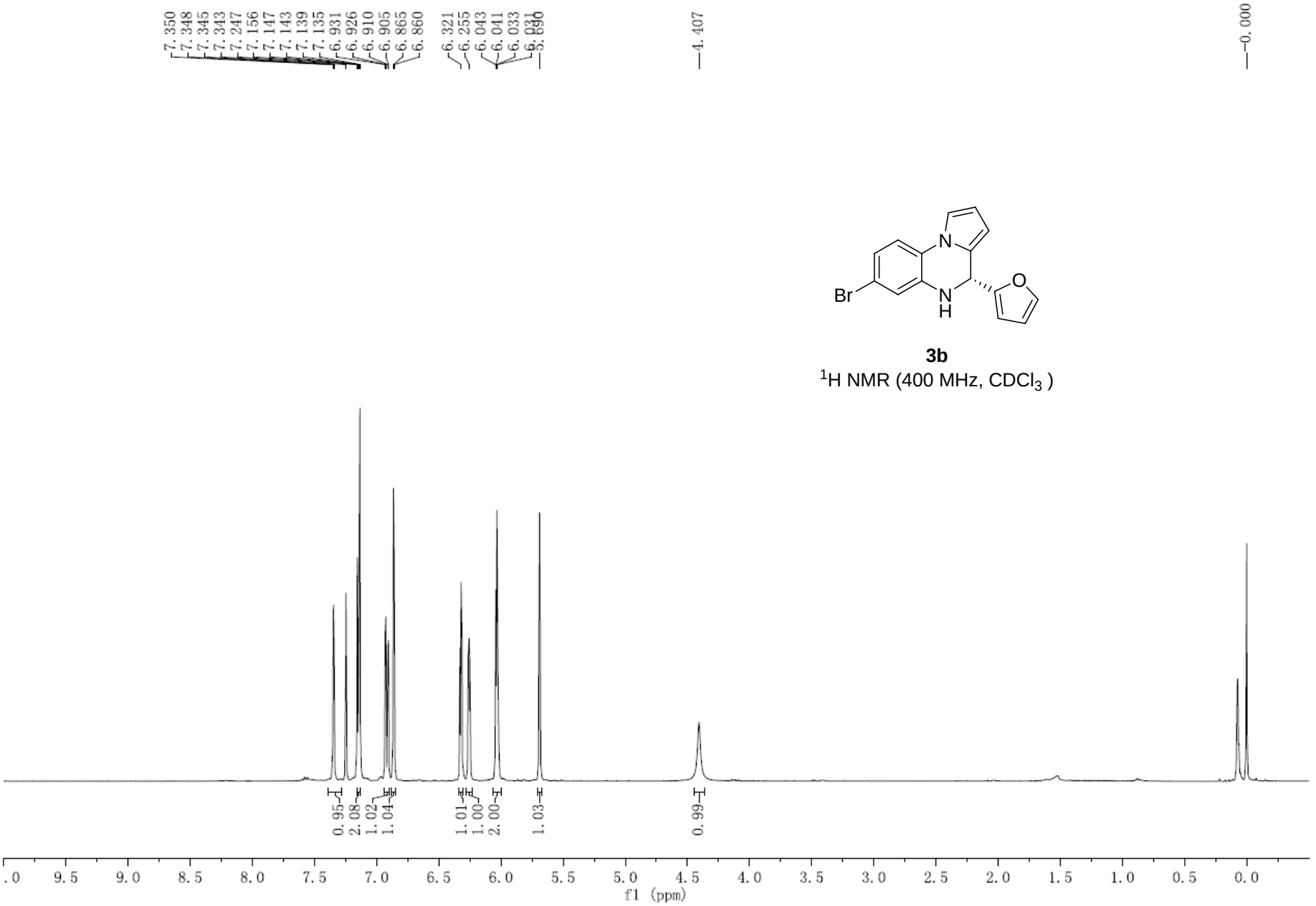
3a

^{1}H NMR (400 MHz, $CDCl_3$)



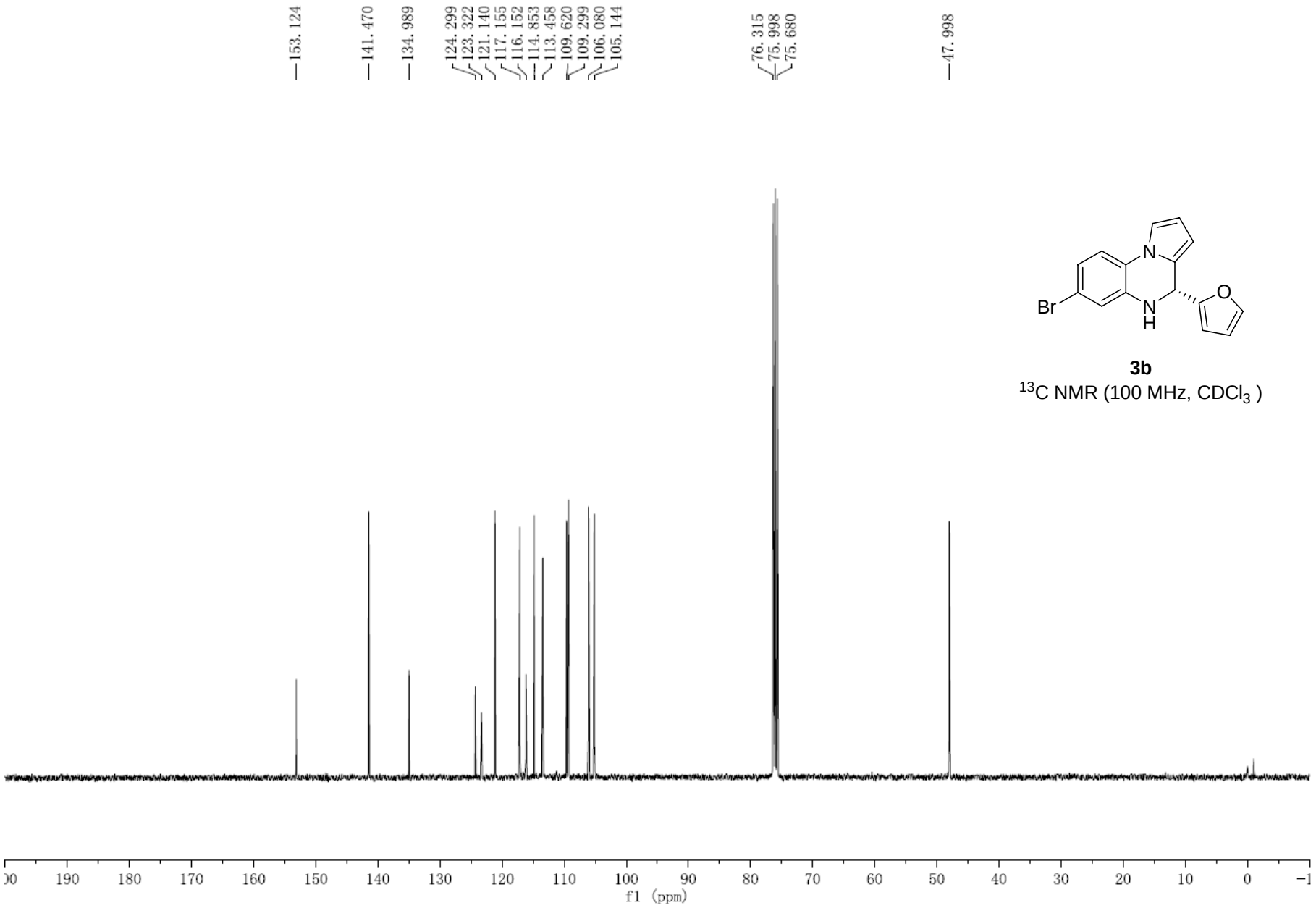
3a

^{13}C NMR (100 MHz, $CDCl_3$)



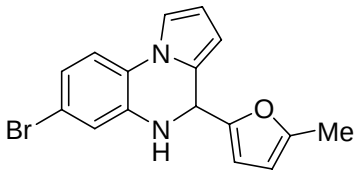
3b

^{1}H NMR (400 MHz, $CDCl_3$)



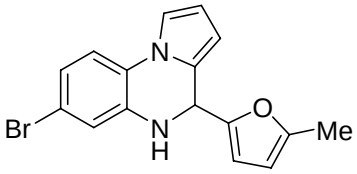
3b

^{13}C NMR (100 MHz, $CDCl_3$)



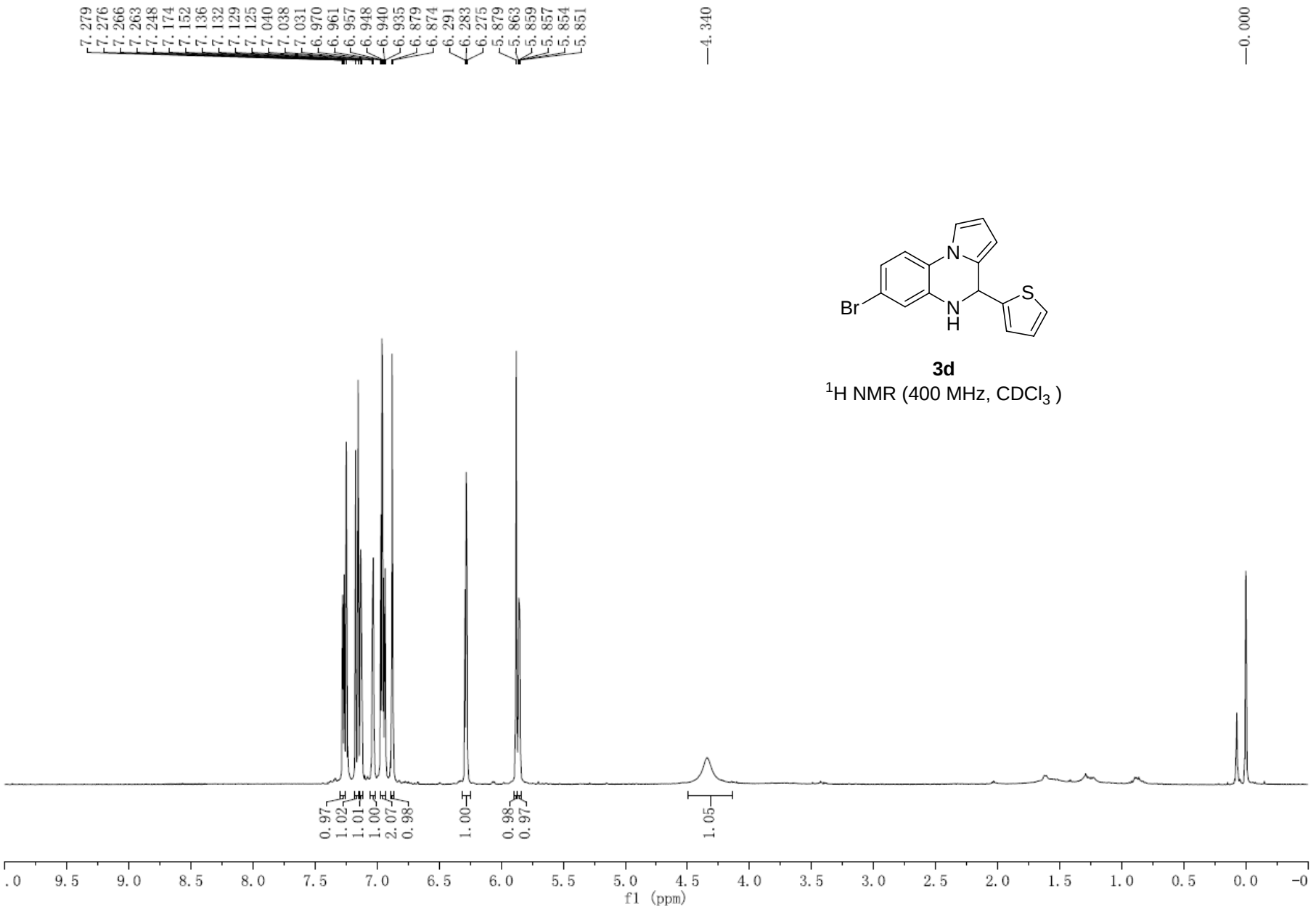
3c

^{1}H NMR (400 MHz, $CDCl_3$)



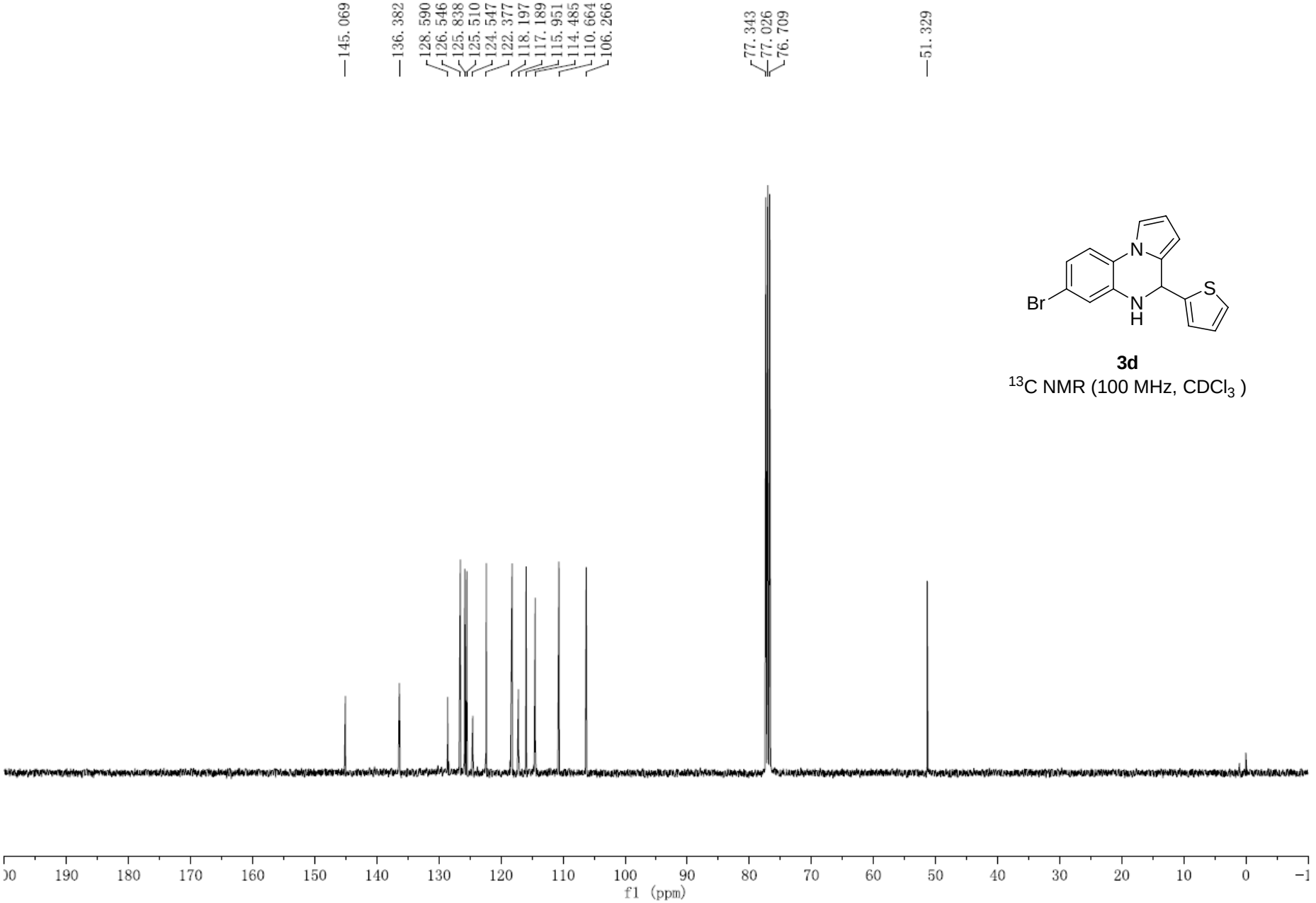
3c

^{13}C NMR (100 MHz, $CDCl_3$)



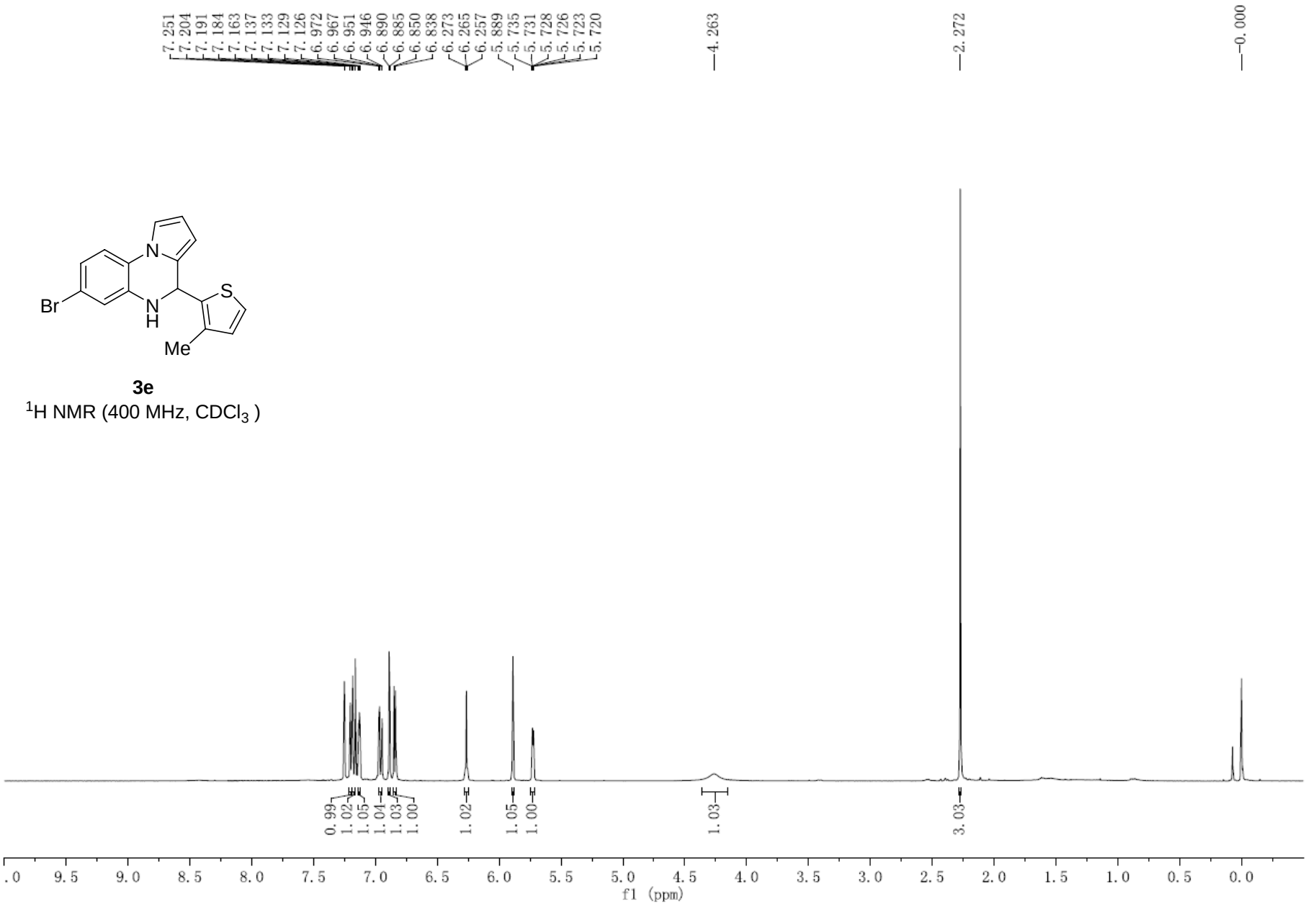
3d

^{1}H NMR (400 MHz, $CDCl_3$)



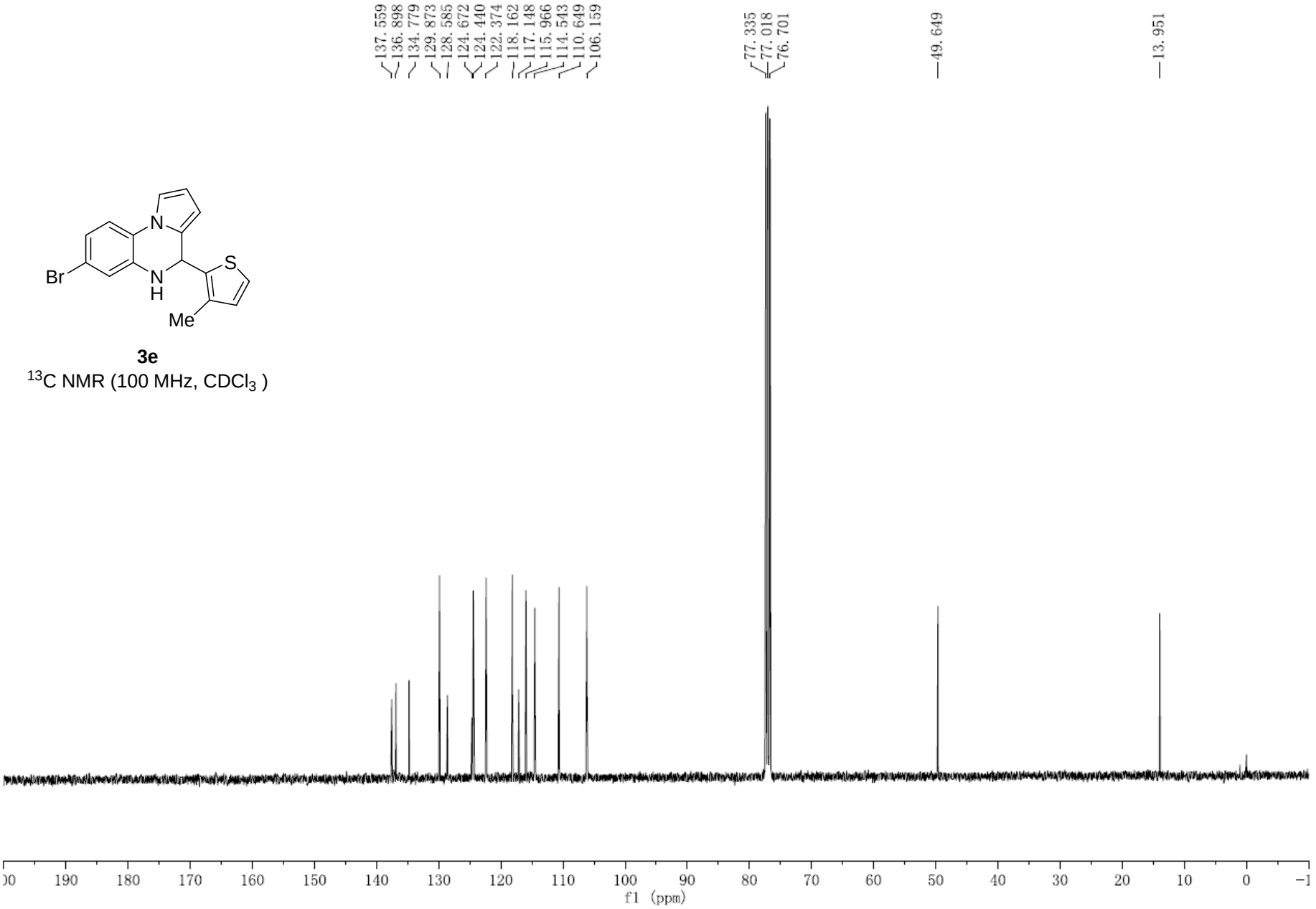
3d

^{13}C NMR (100 MHz, $CDCl_3$)



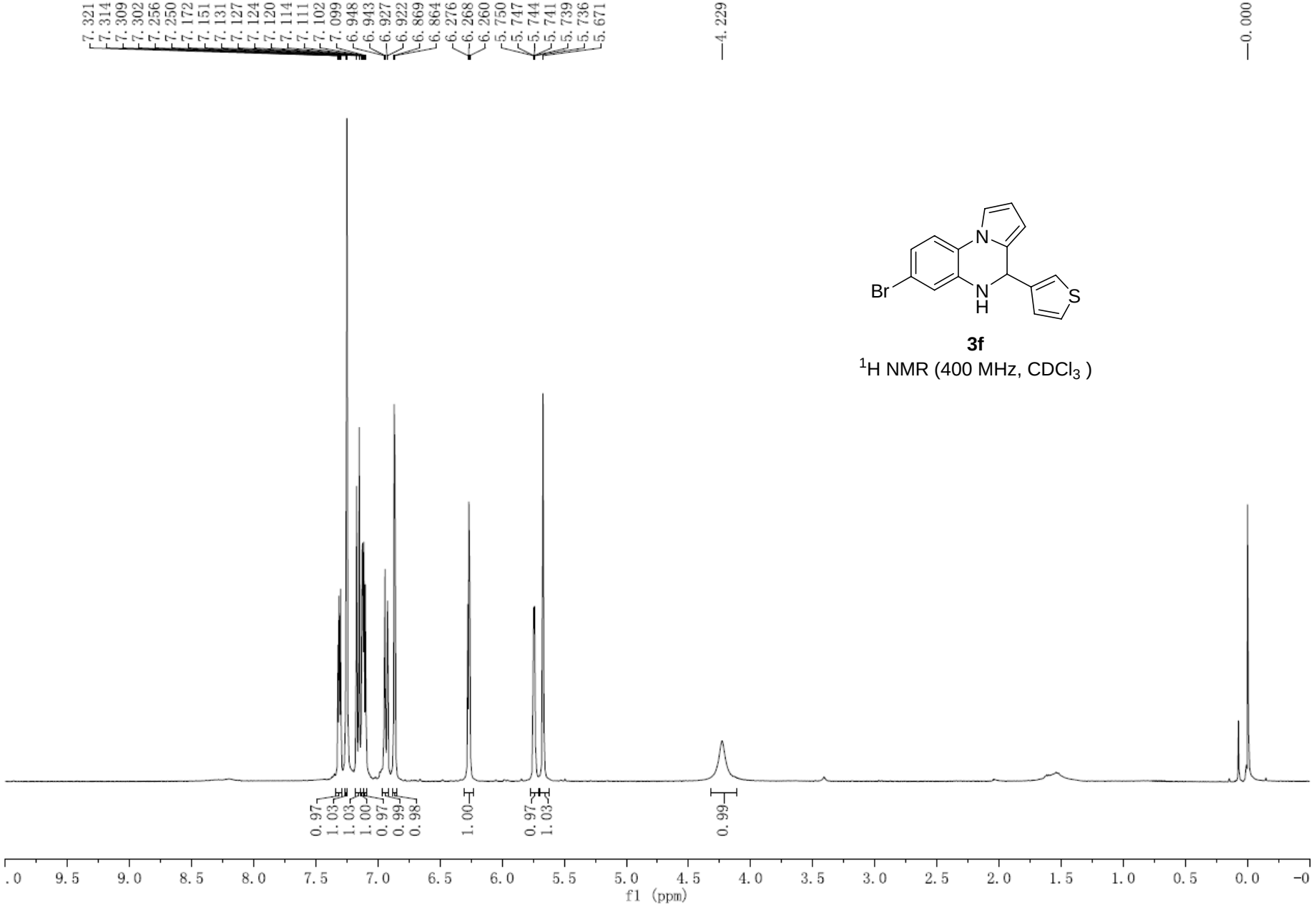
3e

^{1}H NMR (400 MHz, $CDCl_3$)



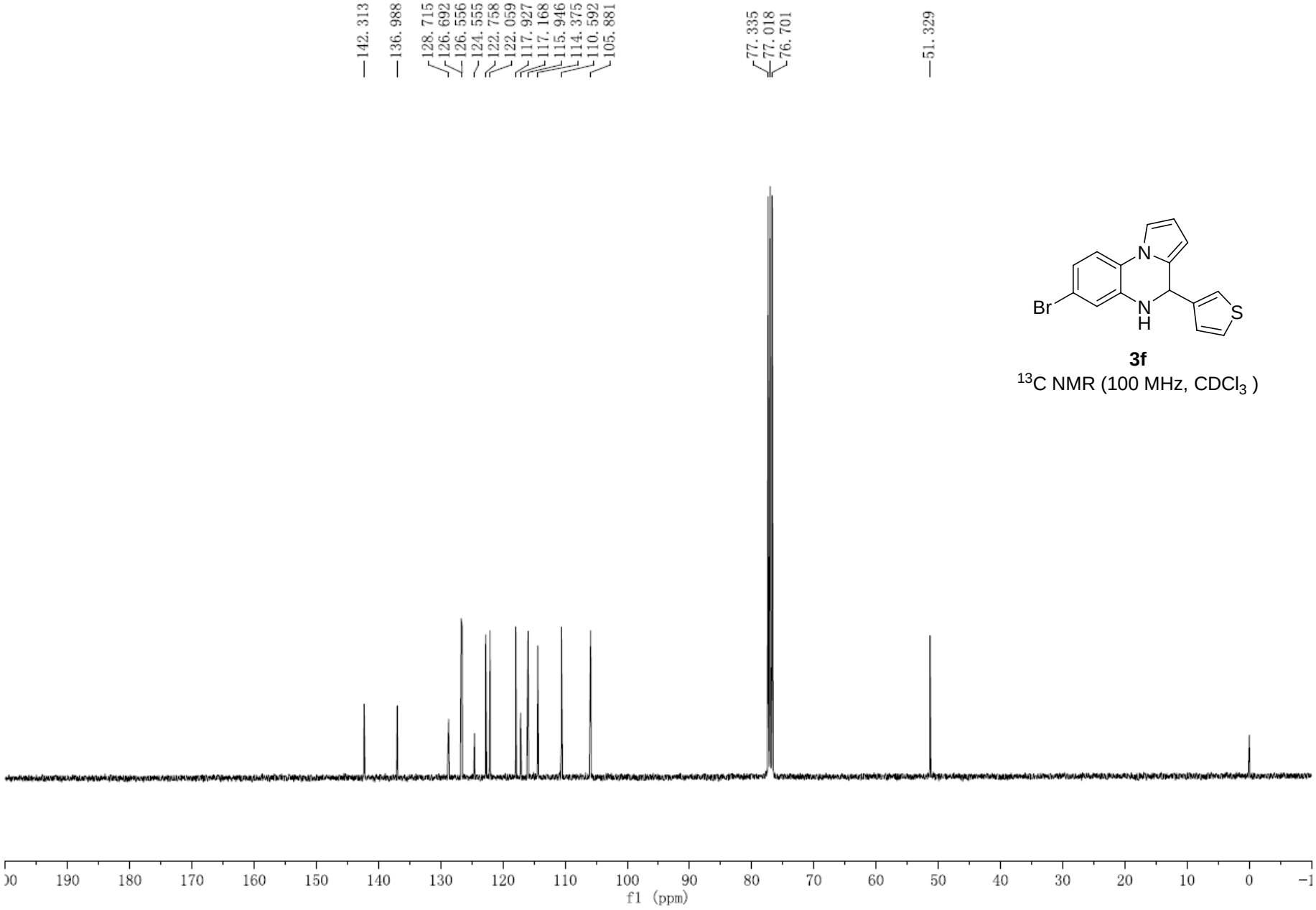
3e

^{13}C NMR (100 MHz, $CDCl_3$)



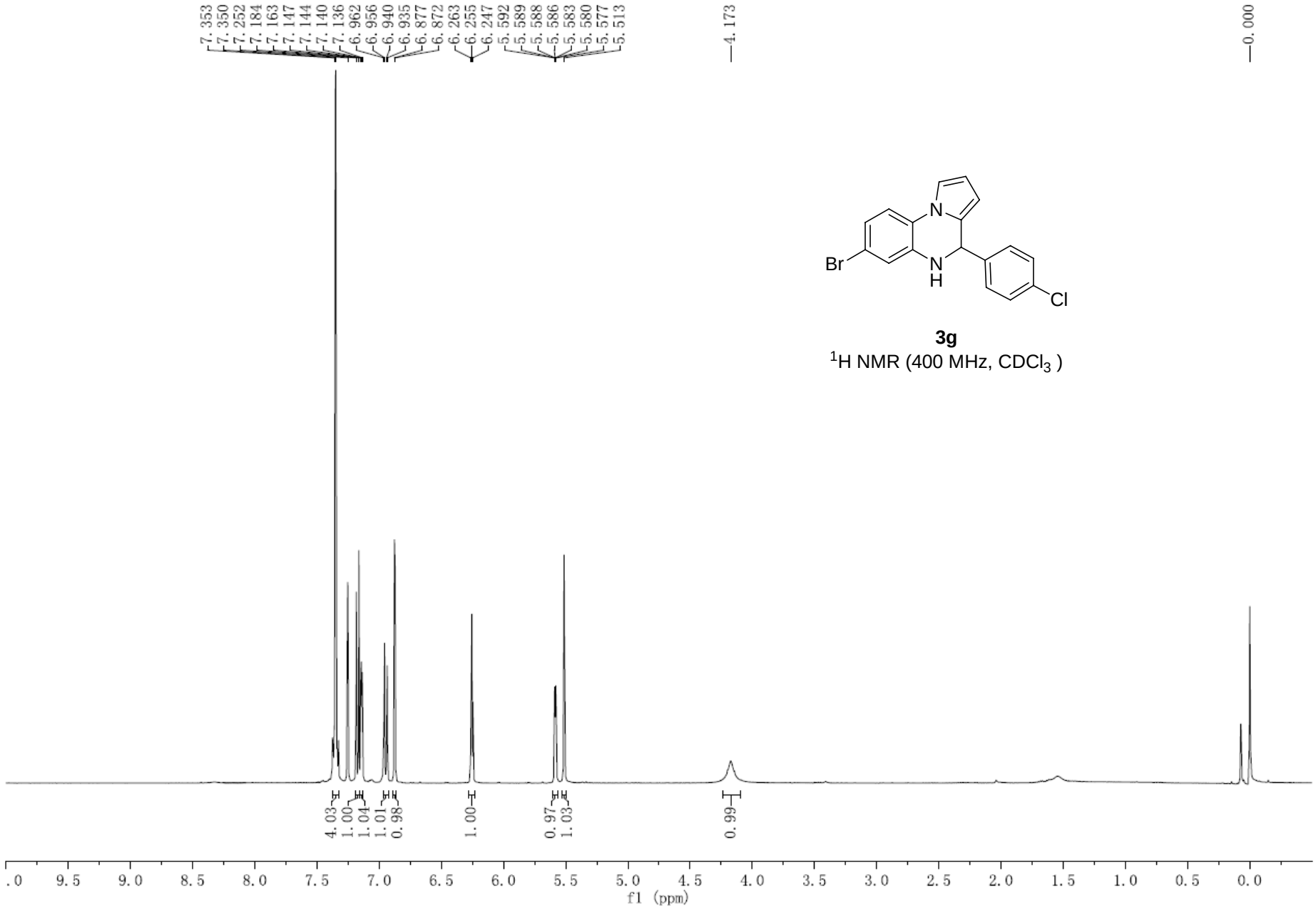
3f

^{1}H NMR (400 MHz, $CDCl_3$)



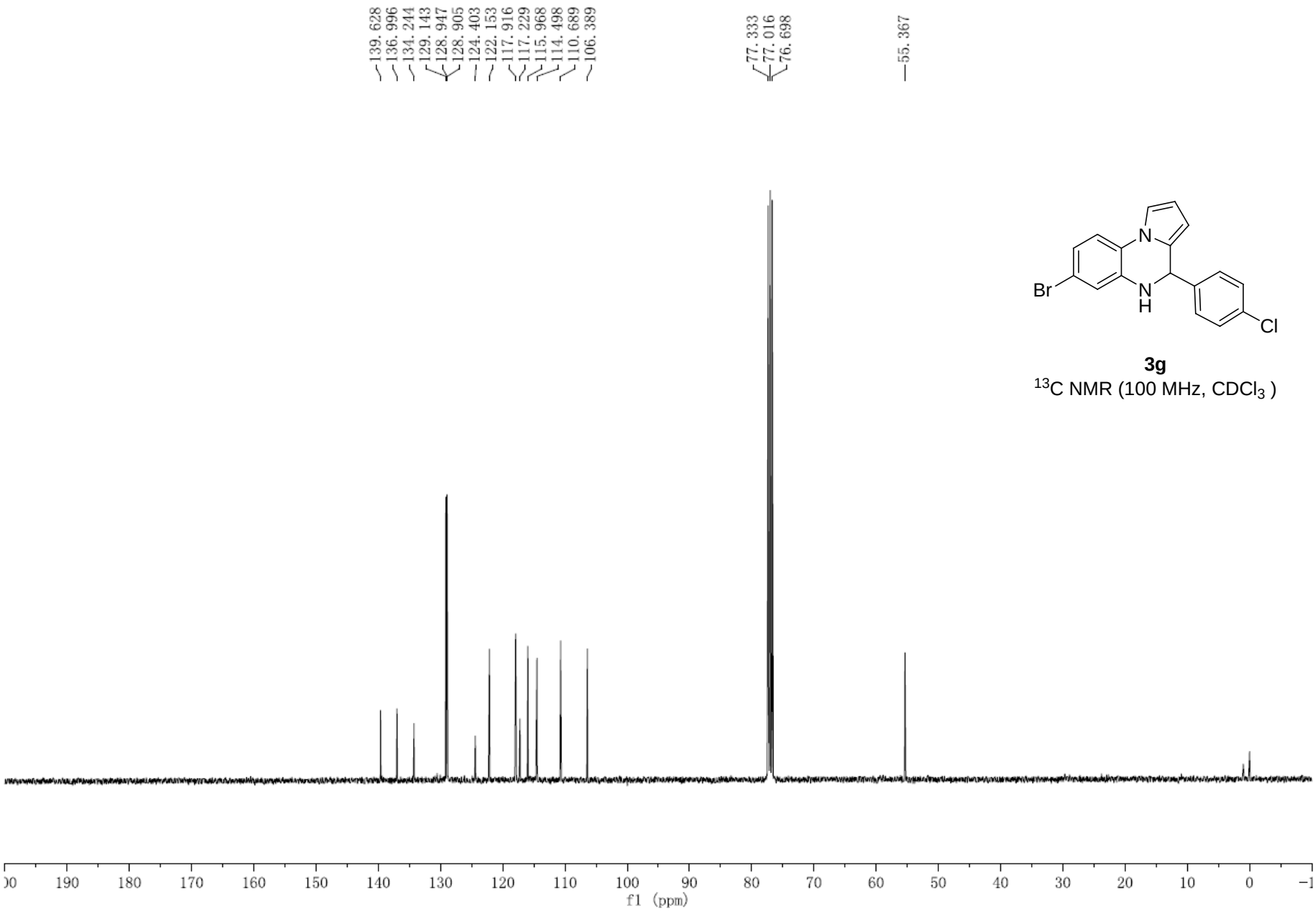
3f

^{13}C NMR (100 MHz, $CDCl_3$)



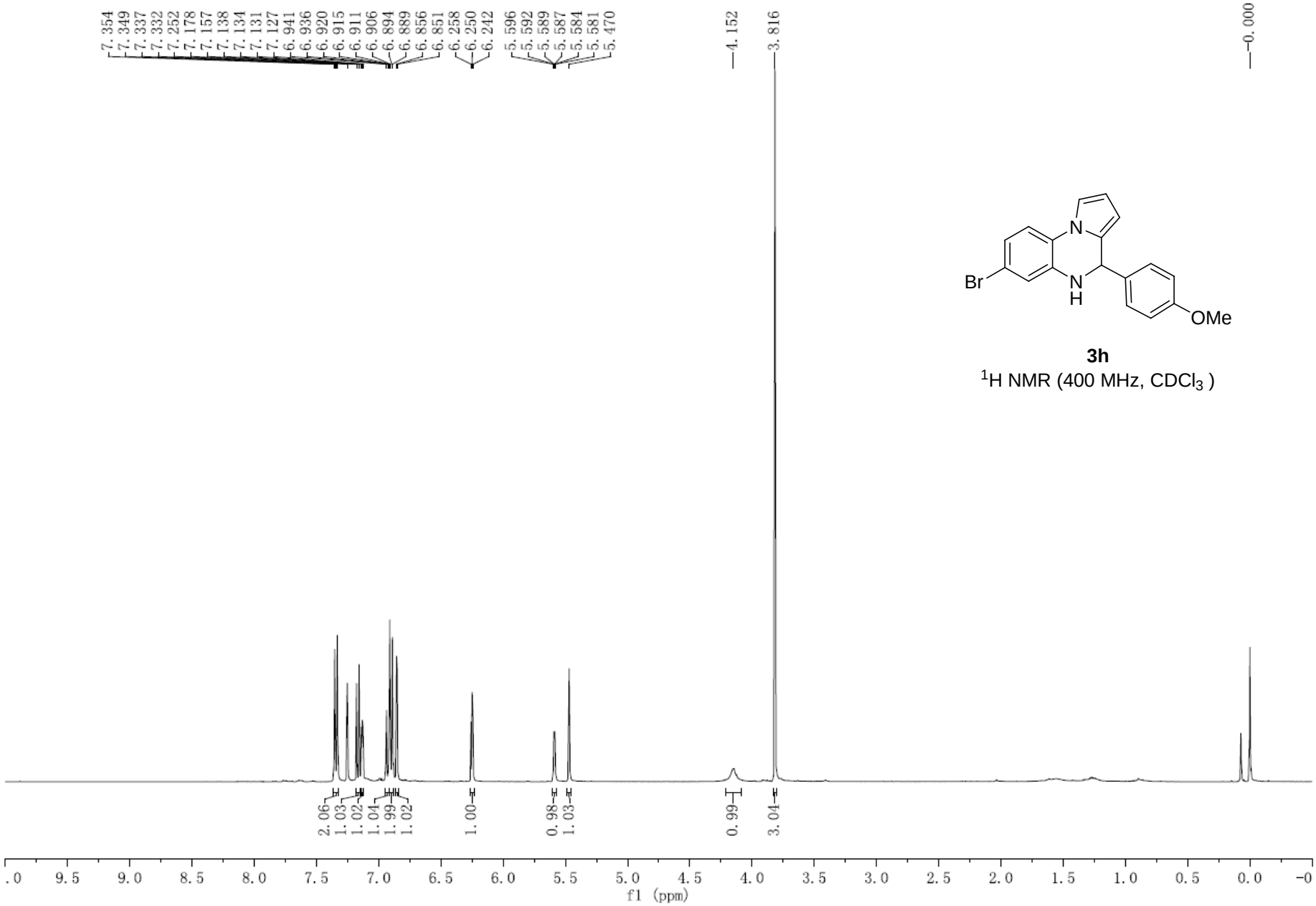
3g

^{1}H NMR (400 MHz, $CDCl_3$)



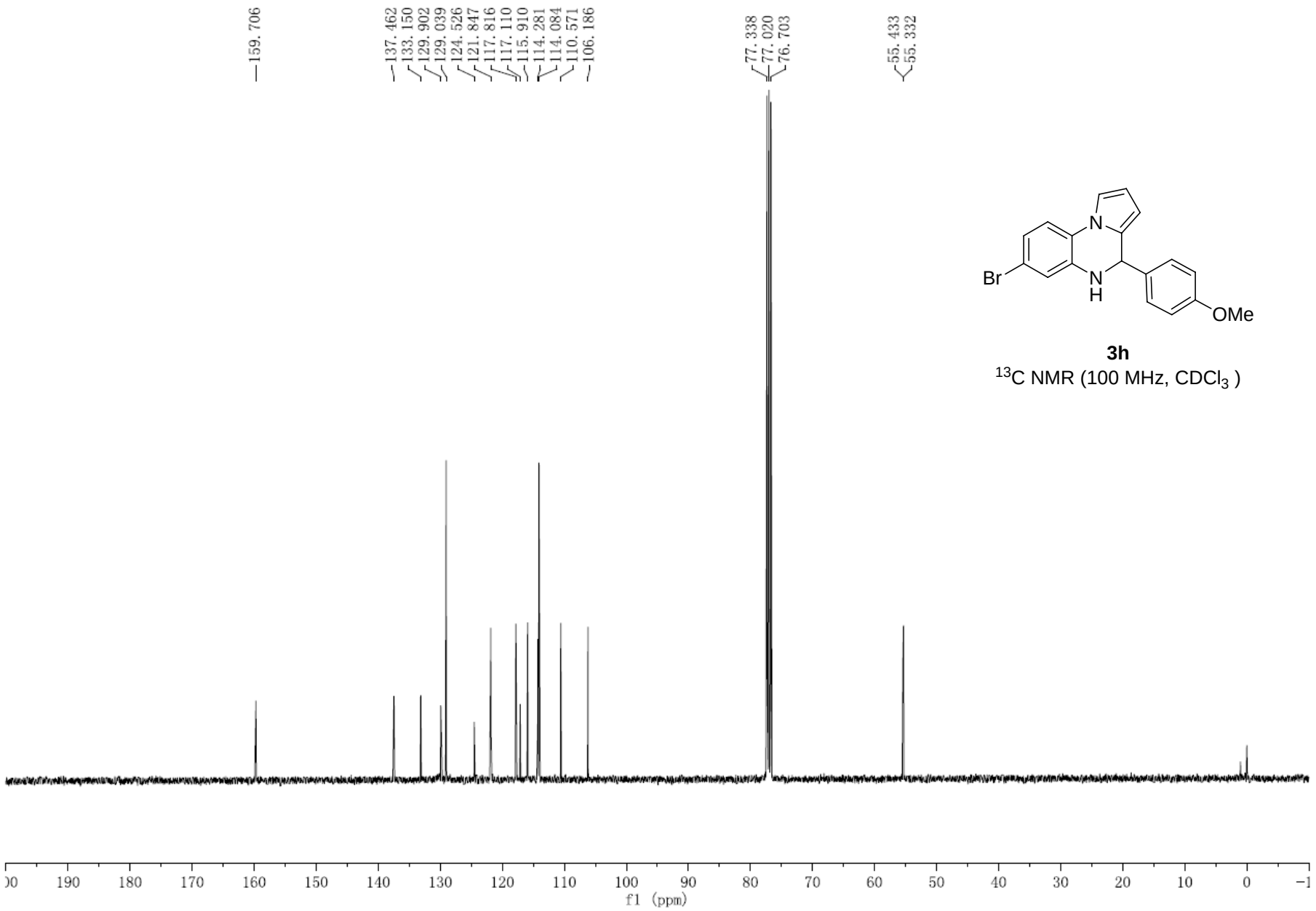
3g

^{13}C NMR (100 MHz, $CDCl_3$)



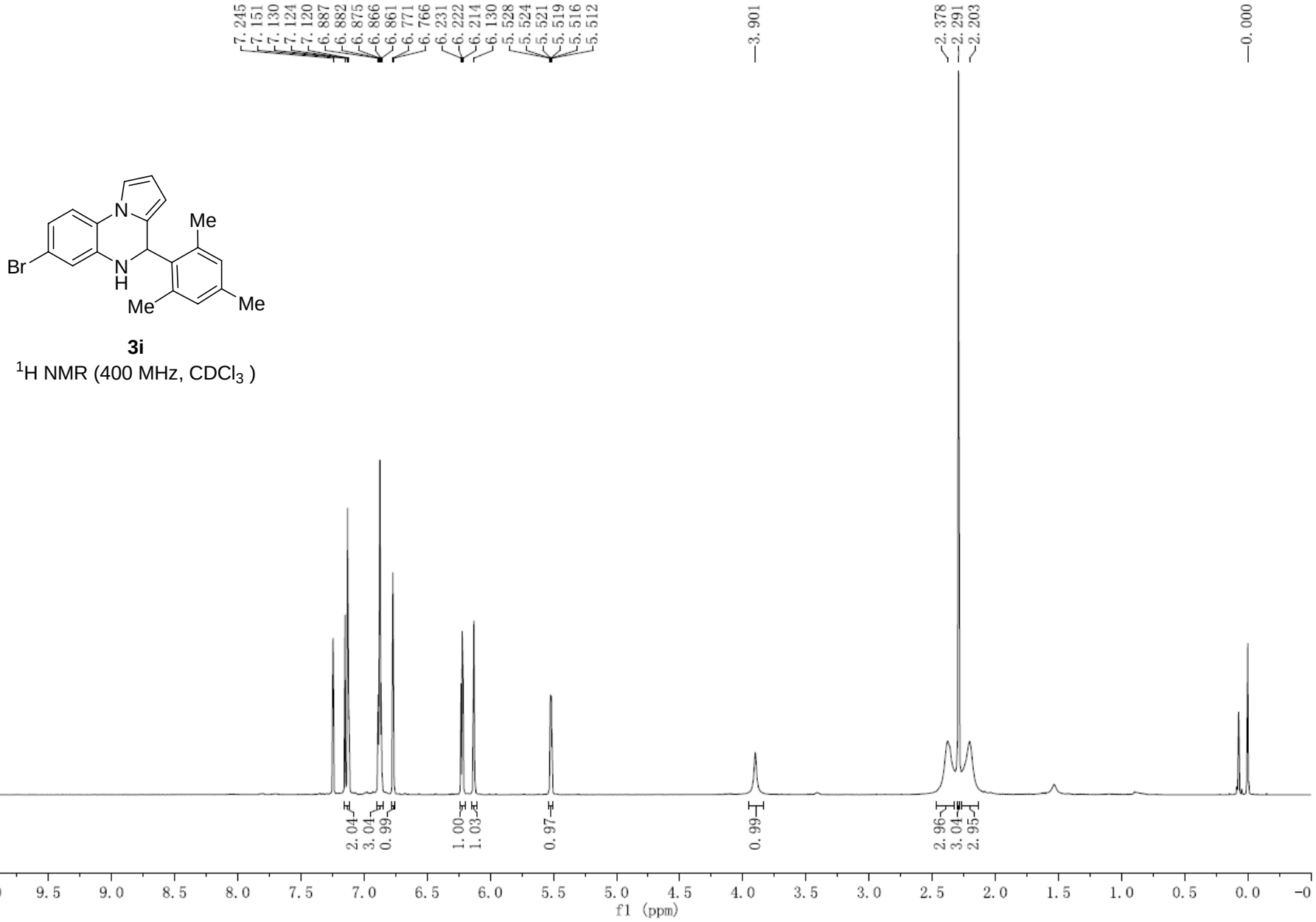
3h

^{1}H NMR (400 MHz, $CDCl_3$)



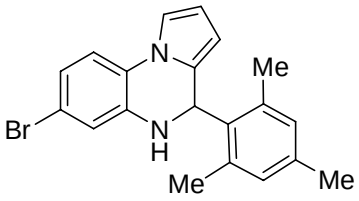
3h

^{13}C NMR (100 MHz, $CDCl_3$)



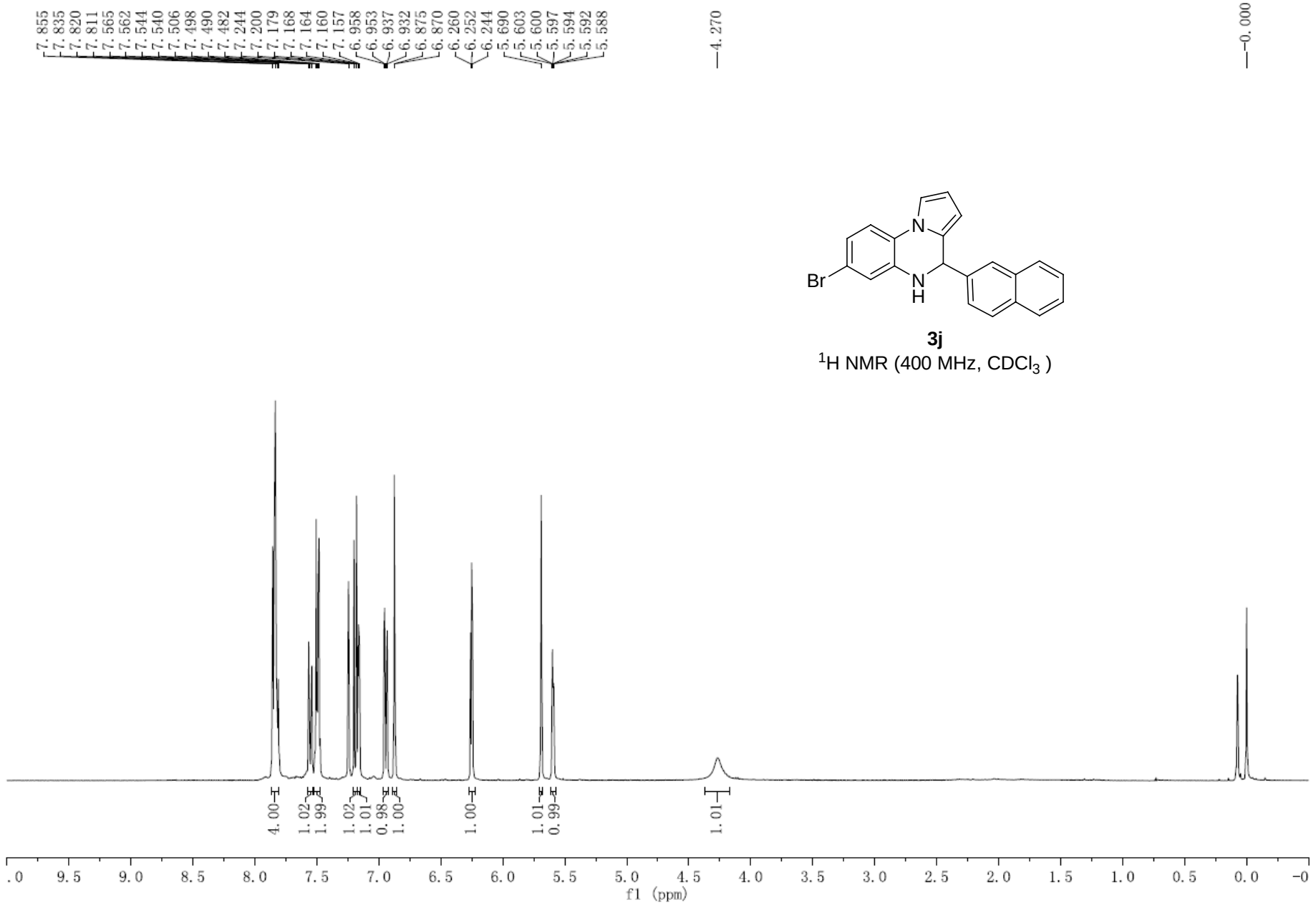
3i

^{1}H NMR (400 MHz, $CDCl_3$)



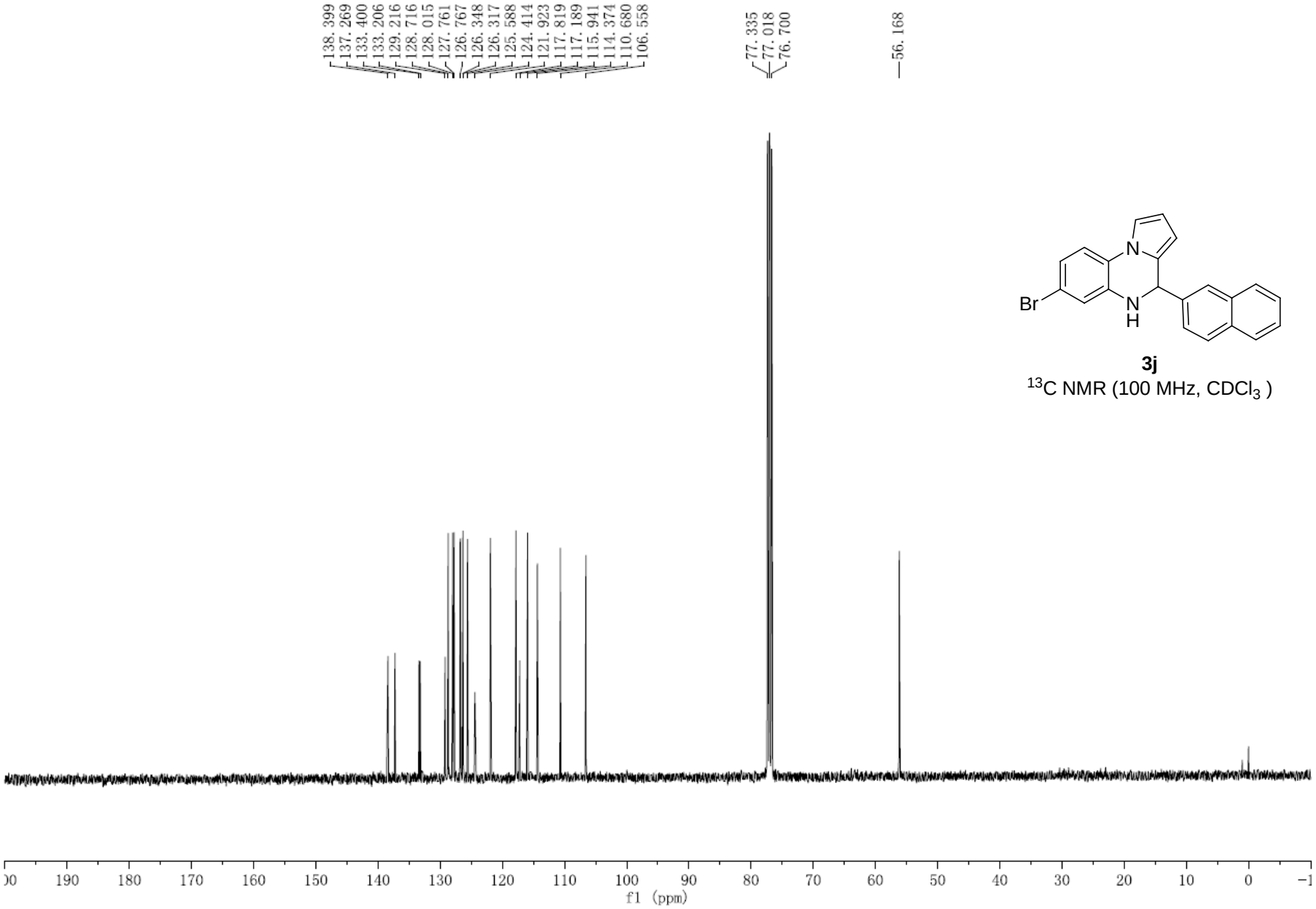
3i

^{13}C NMR (100 MHz, $CDCl_3$)



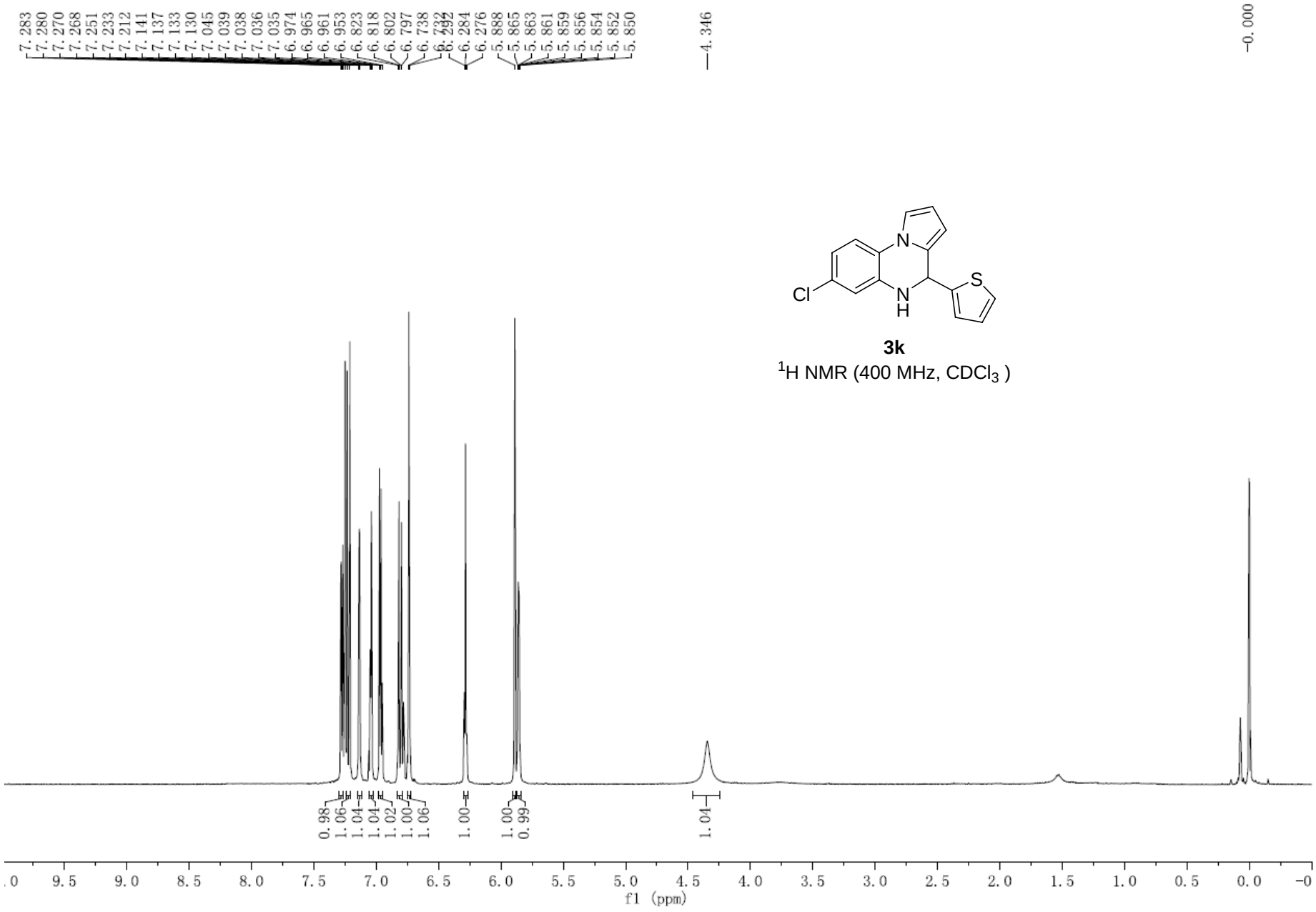
3j

^{1}H NMR (400 MHz, $CDCl_3$)



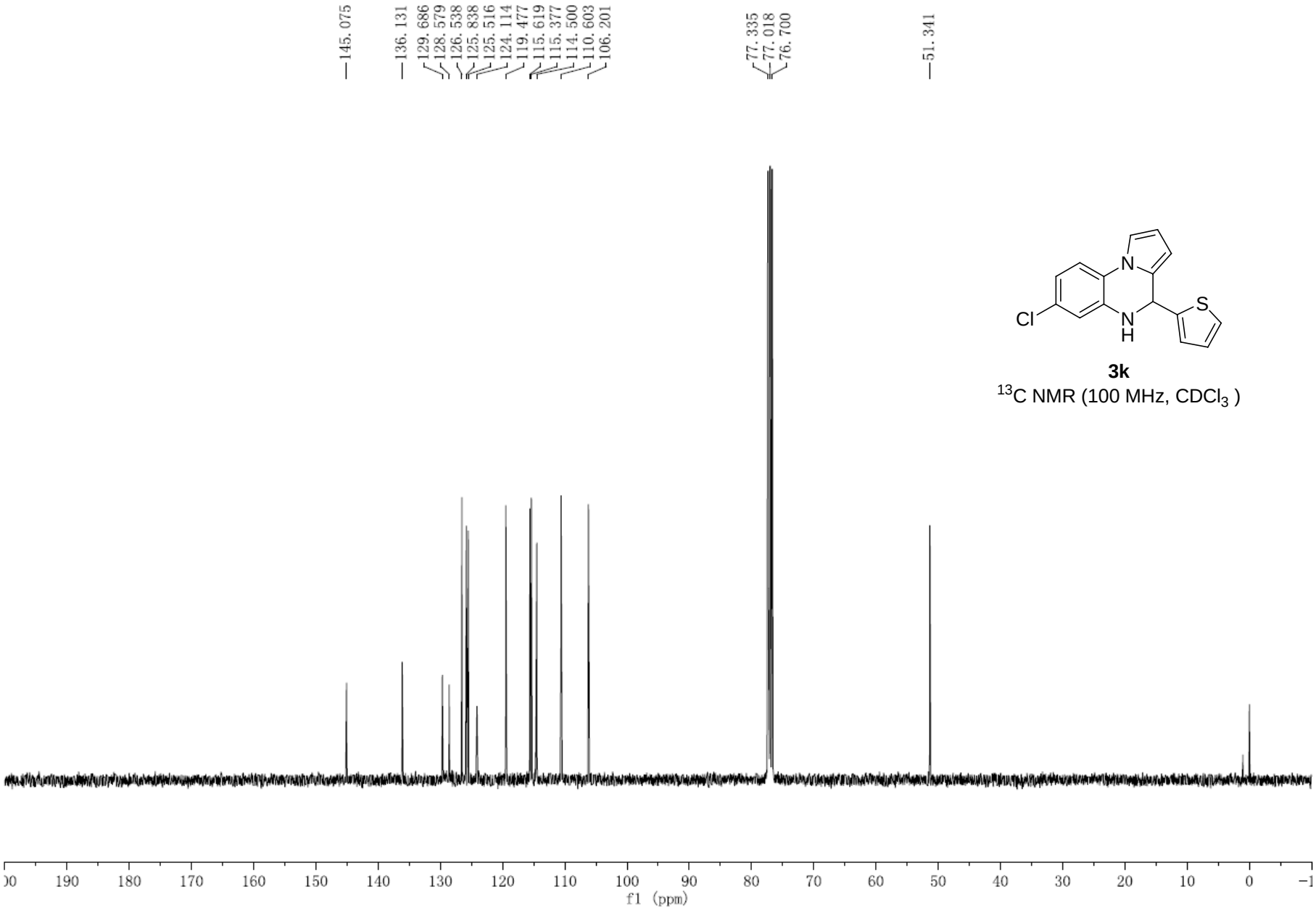
3j

^{13}C NMR (100 MHz, $CDCl_3$)



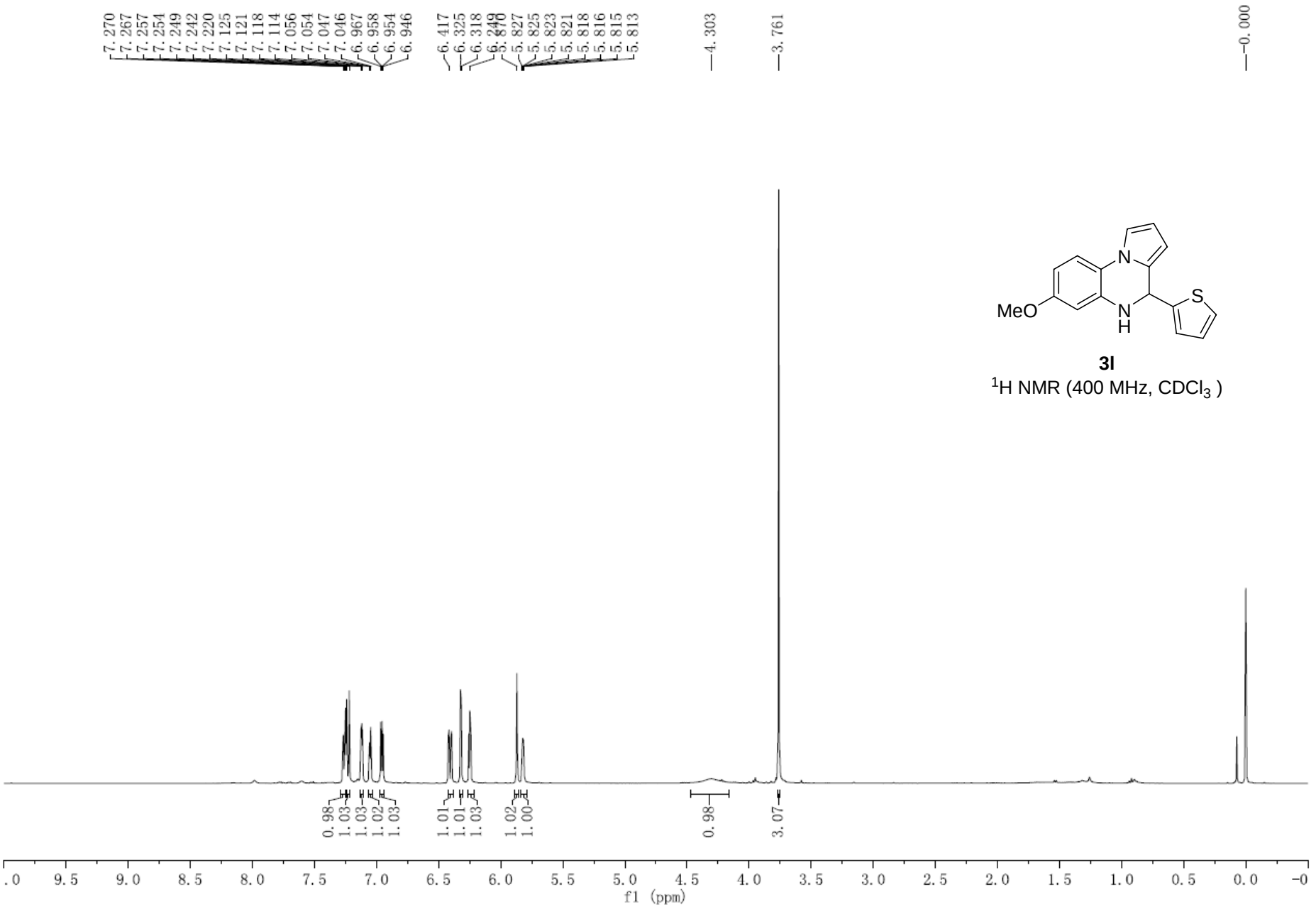
3k

^{1}H NMR (400 MHz, $CDCl_3$)



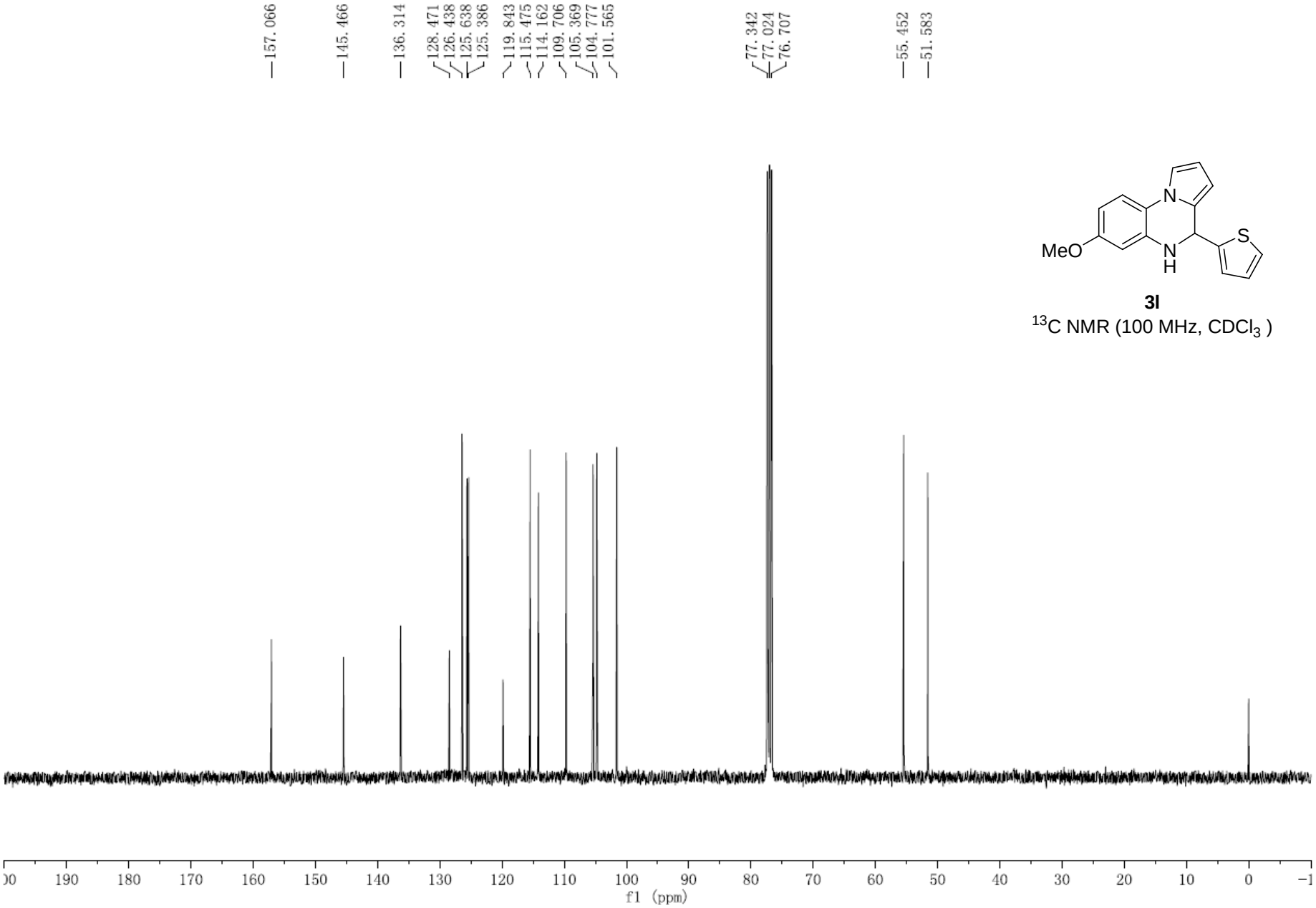
3k

^{13}C NMR (100 MHz, $CDCl_3$)



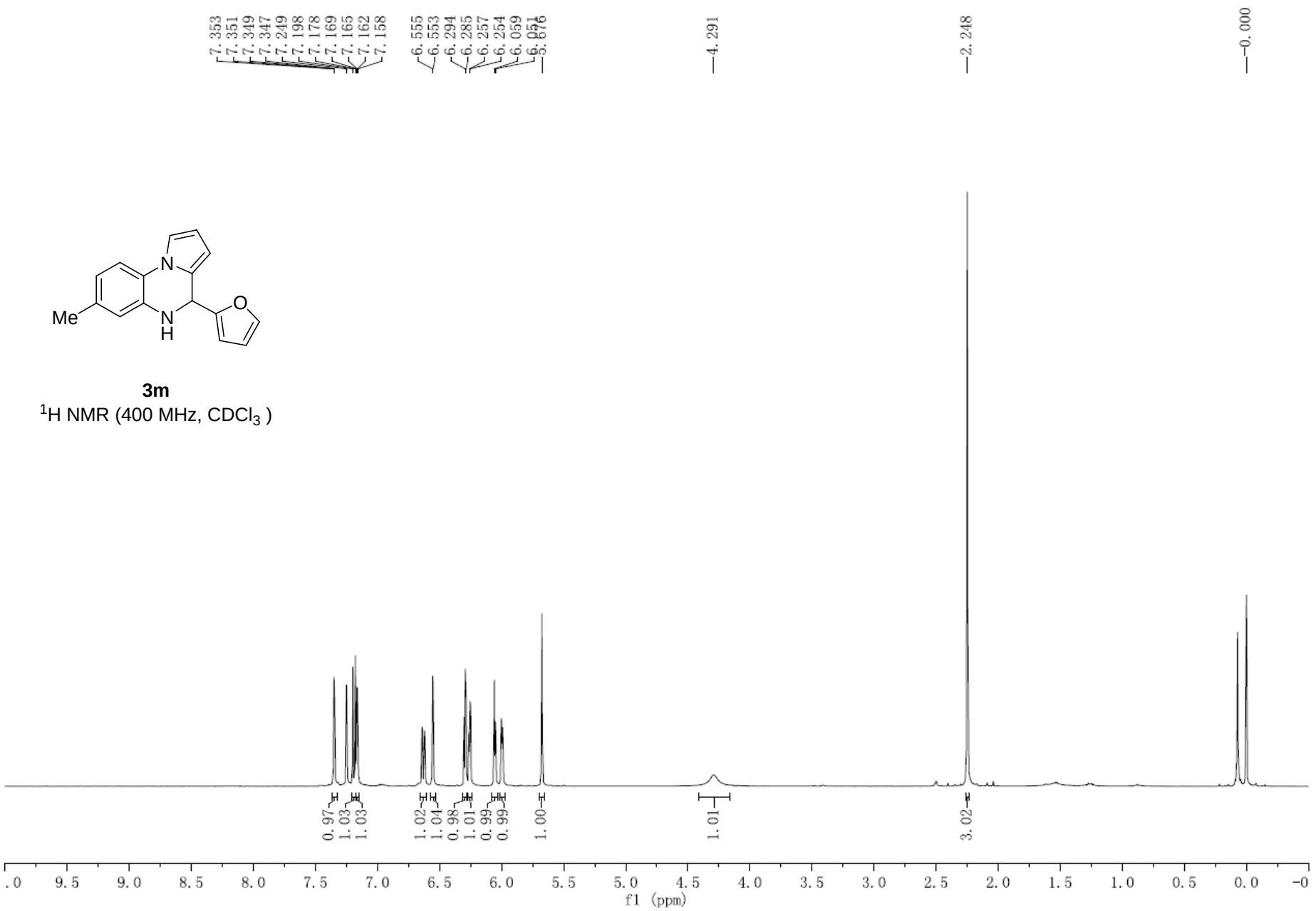
3l

^{1}H NMR (400 MHz, $CDCl_3$)



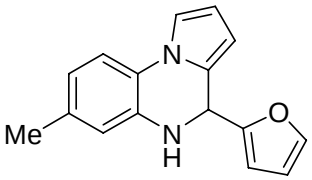
3l

^{13}C NMR (100 MHz, $CDCl_3$)



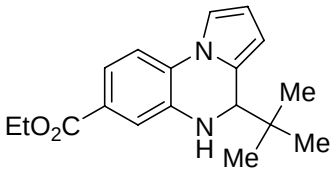
3m

^{1}H NMR (400 MHz, $CDCl_3$)



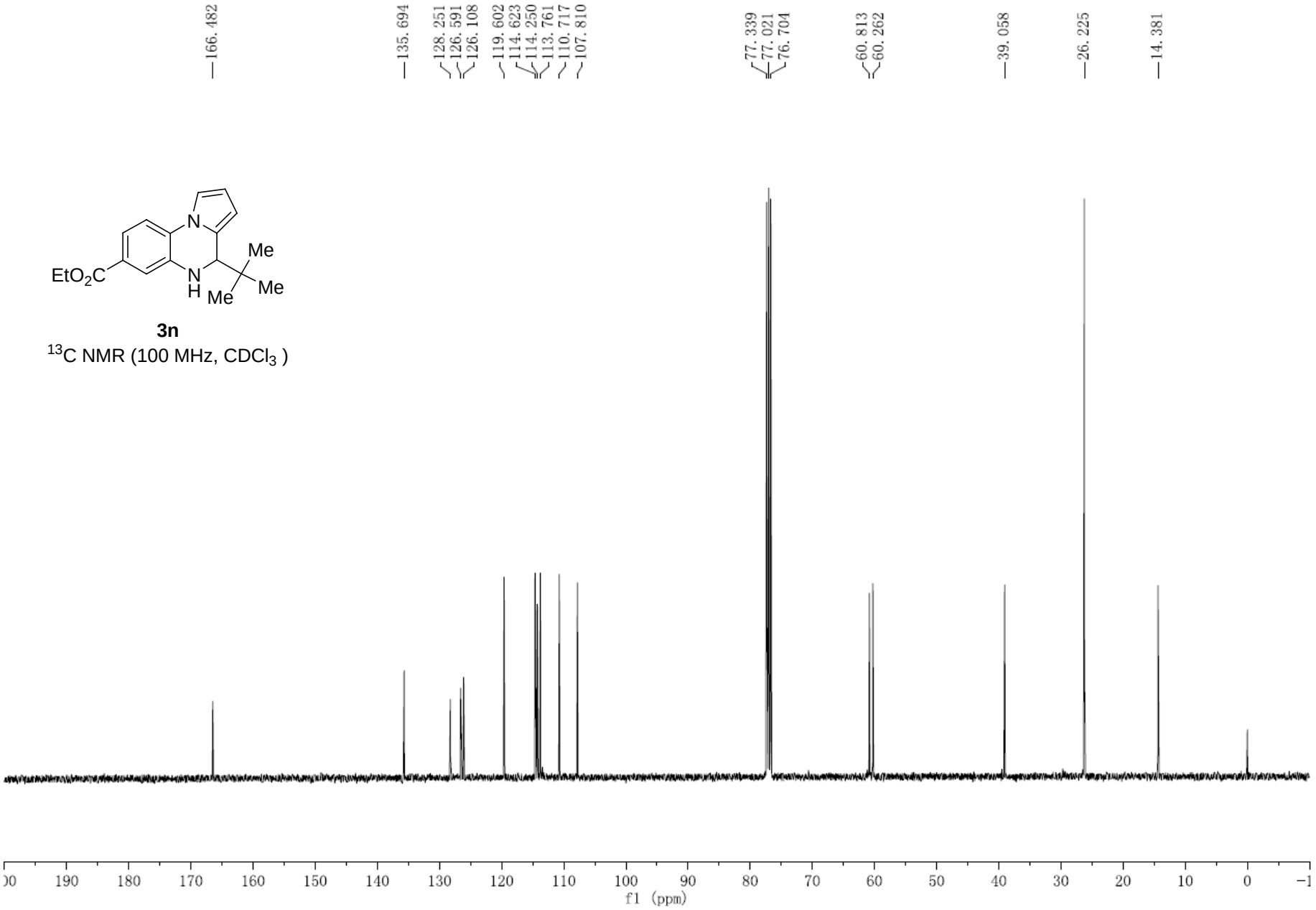
3m

^{13}C NMR (100 MHz, $CDCl_3$)



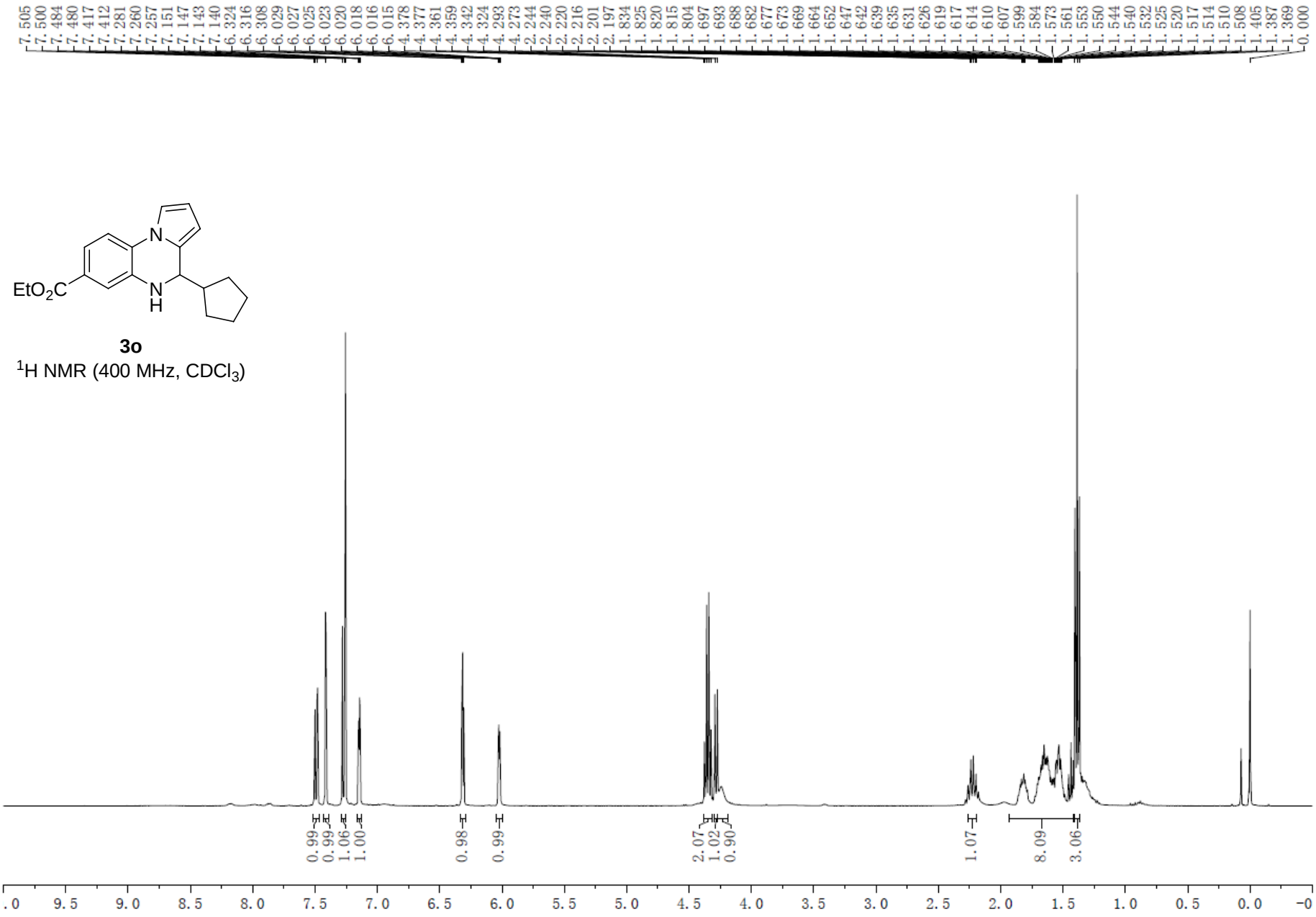
3n

^{1}H NMR (400 MHz, $CDCl_3$)



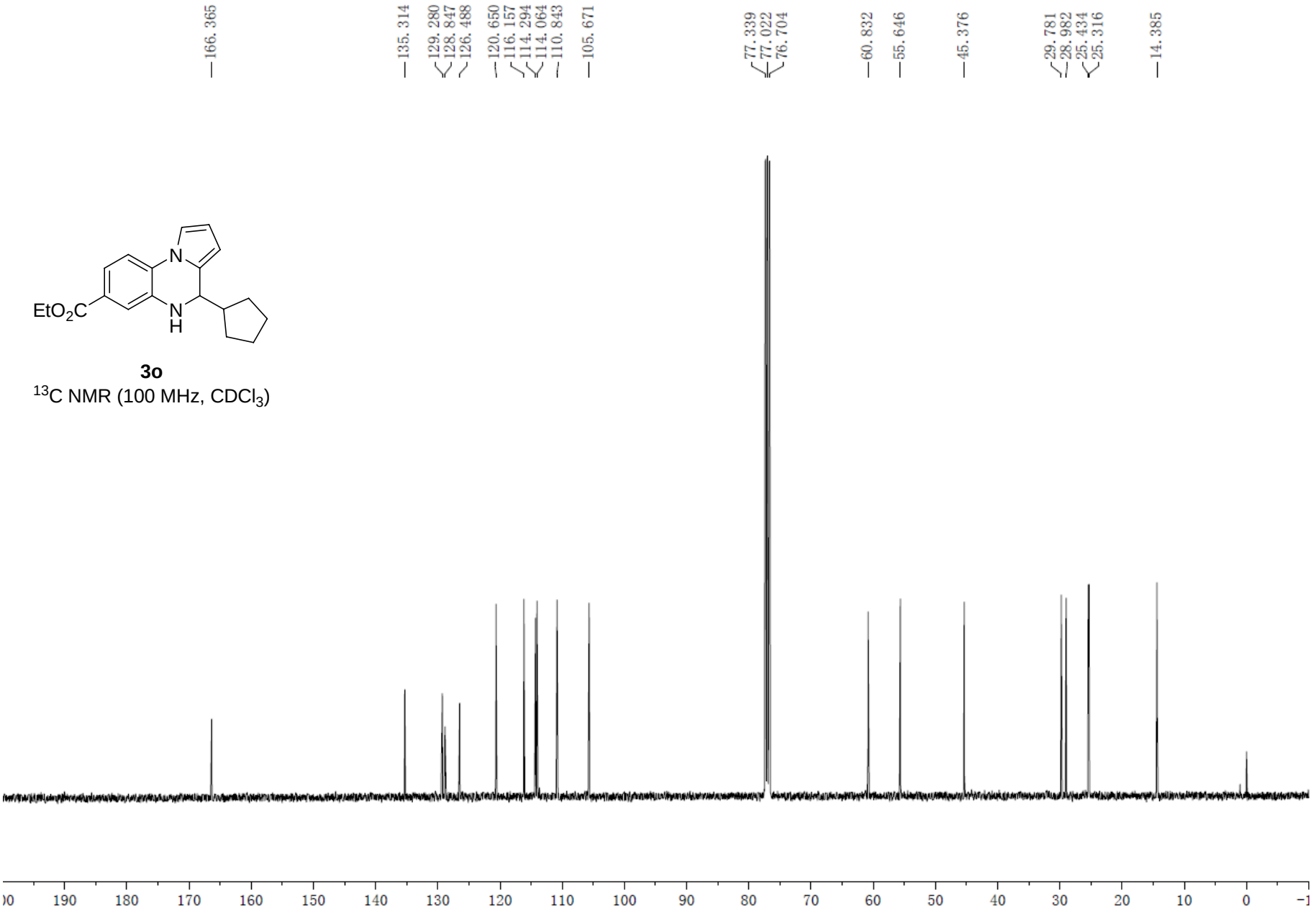
3n

^{13}C NMR (100 MHz, $CDCl_3$)



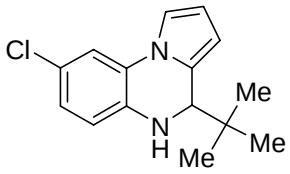
3o

^{1}H NMR (400 MHz, $CDCl_3$)



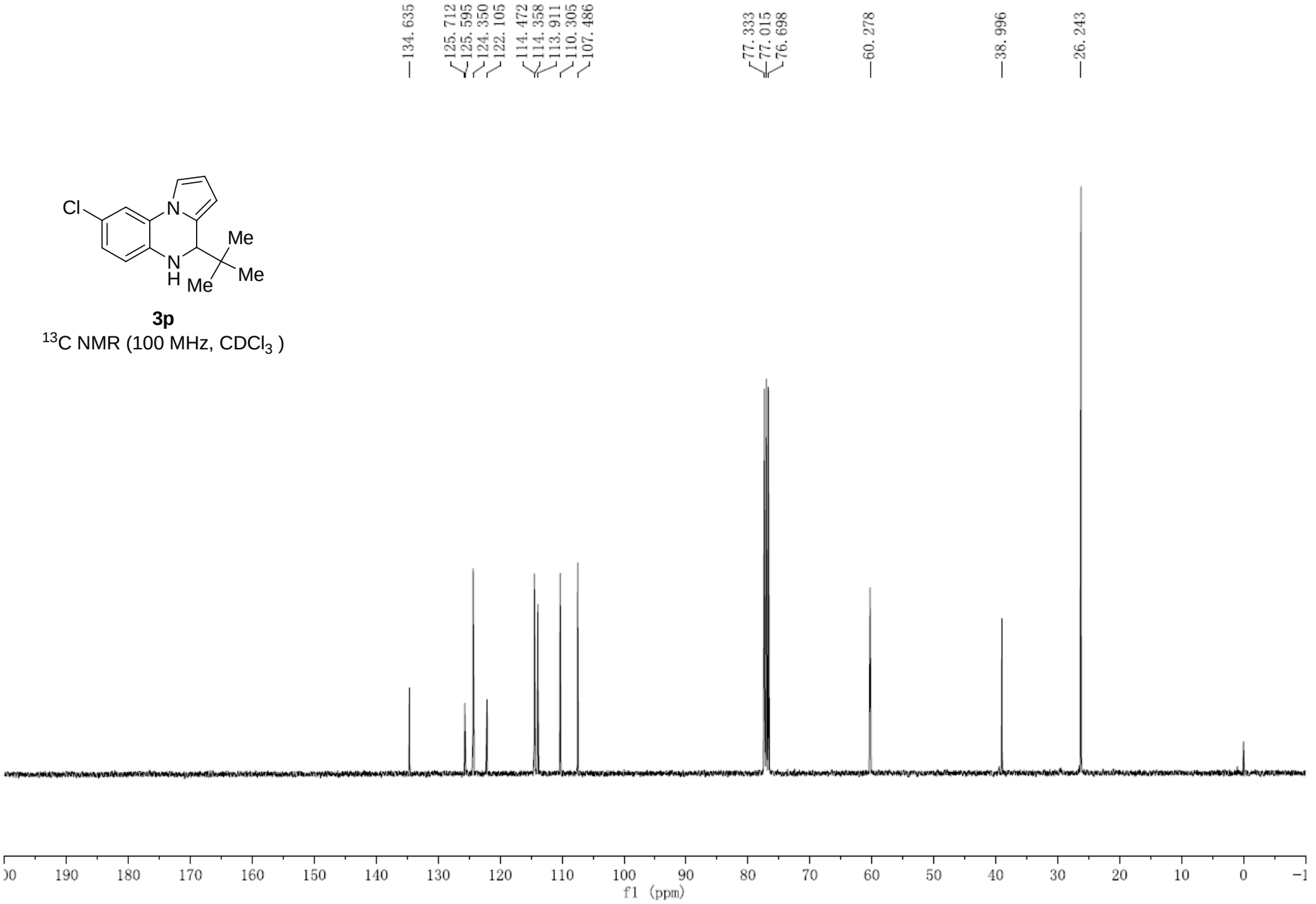
3o

^{13}C NMR (100 MHz, $CDCl_3$)



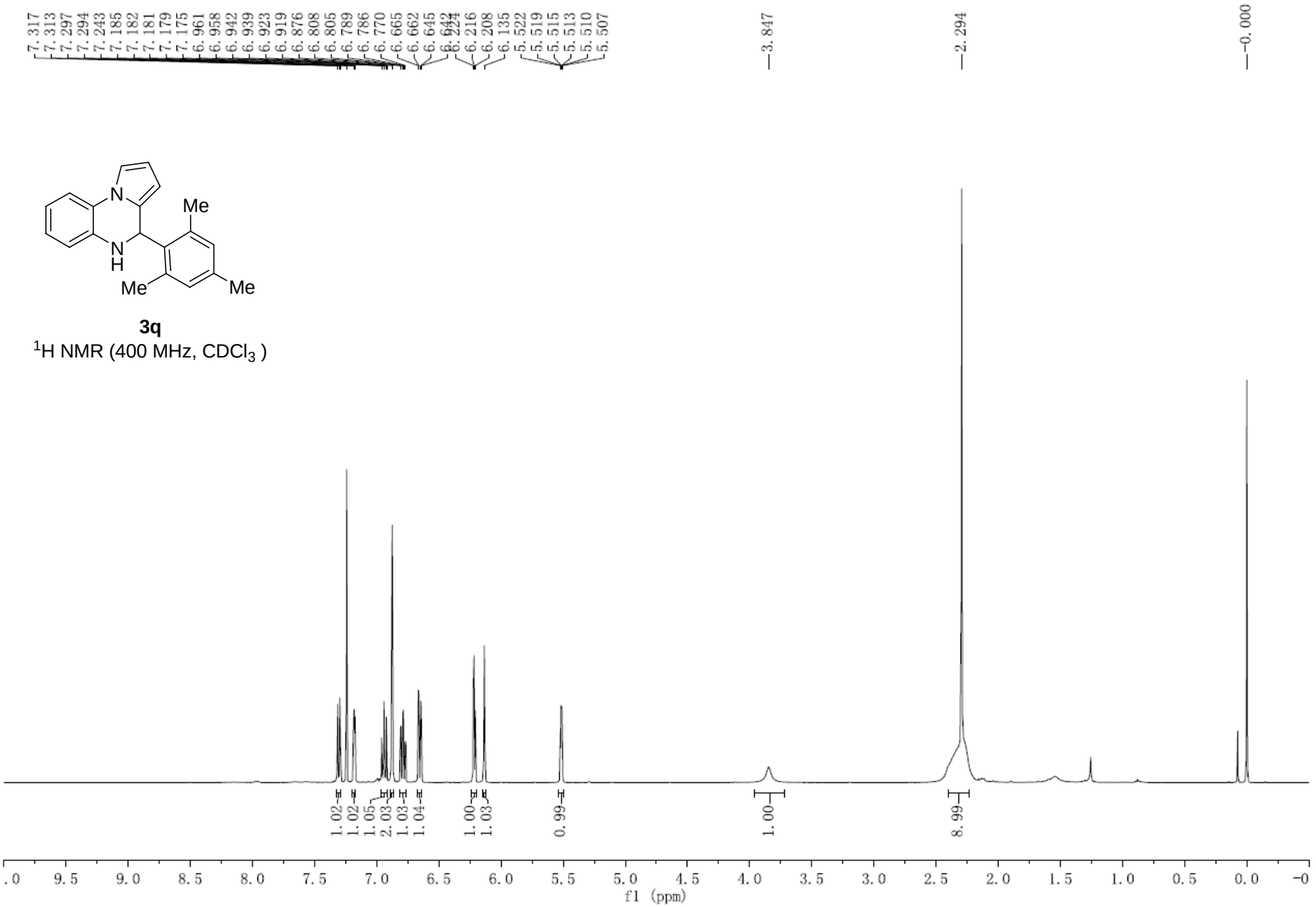
3p

^{1}H NMR (400 MHz, $CDCl_3$)



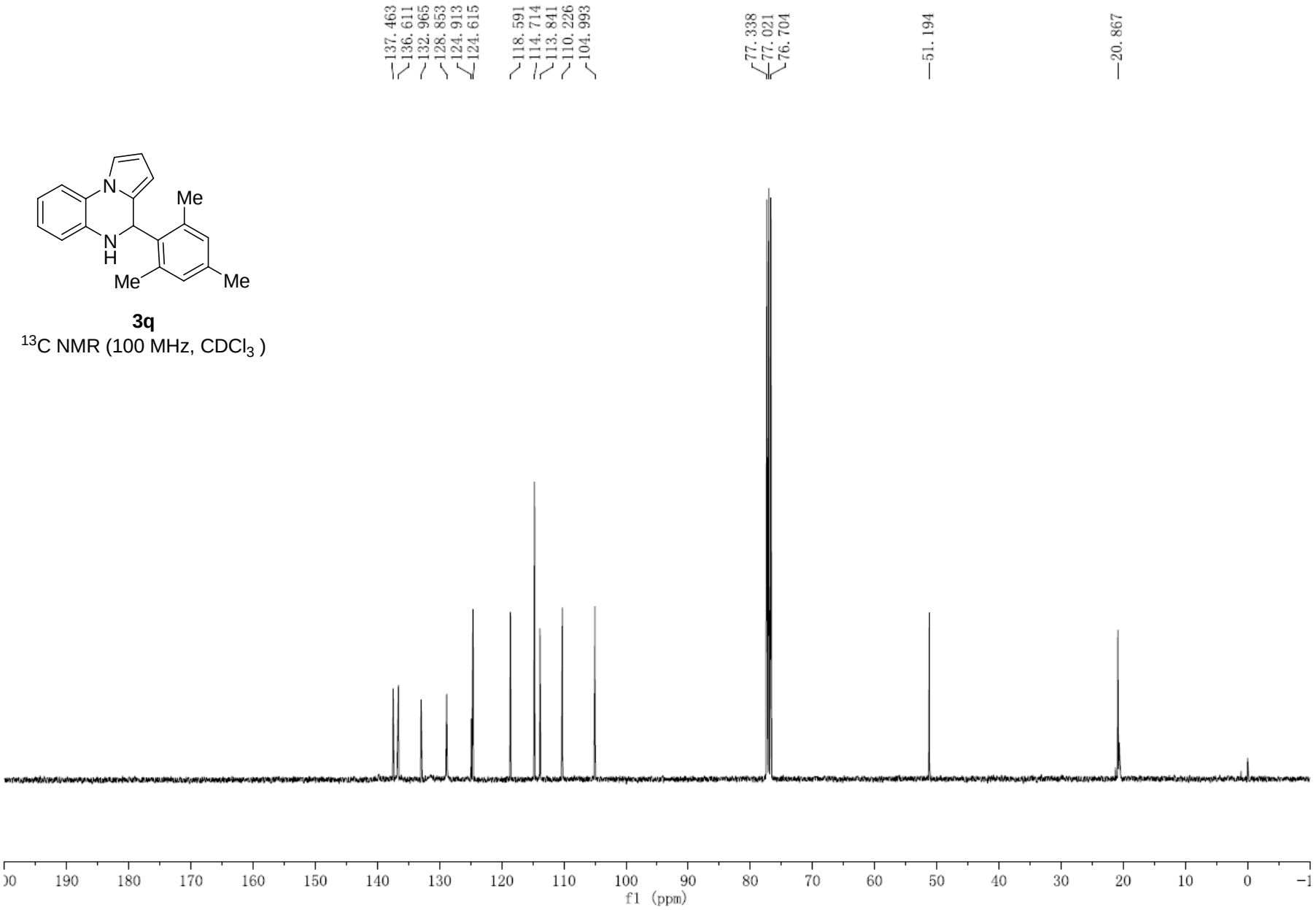
3p

^{13}C NMR (100 MHz, $CDCl_3$)



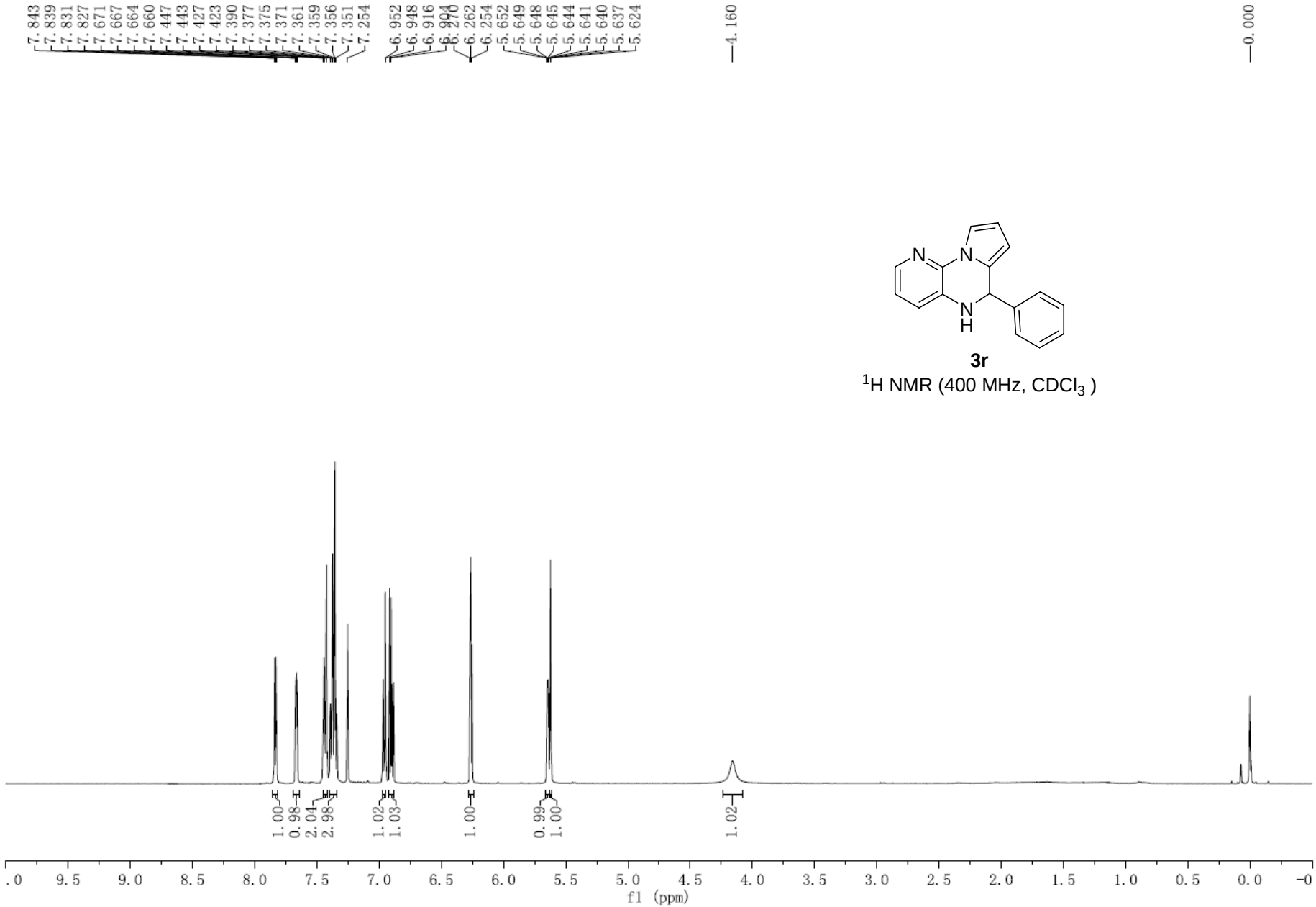
3q

^{1}H NMR (400 MHz, $CDCl_3$)



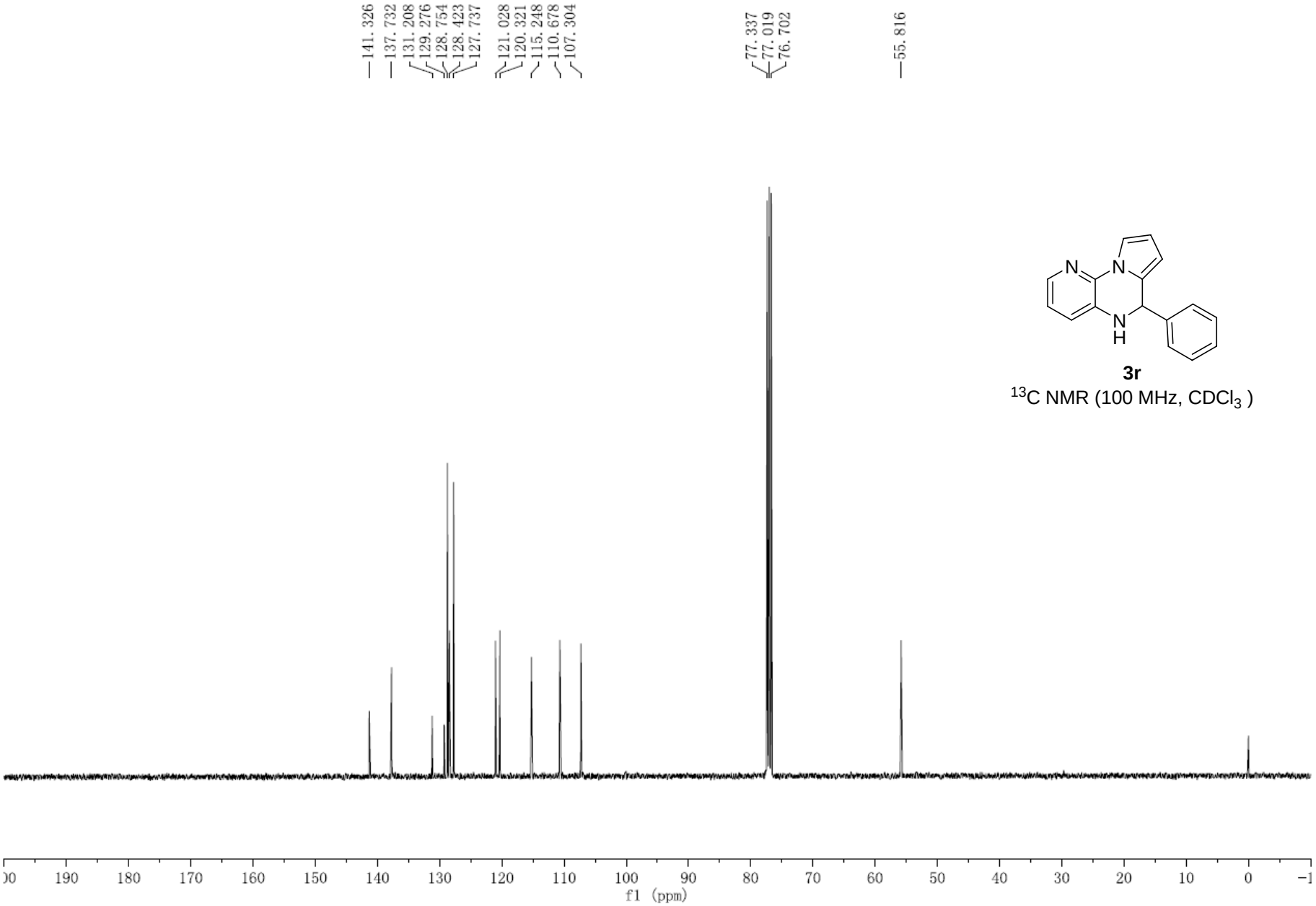
3q

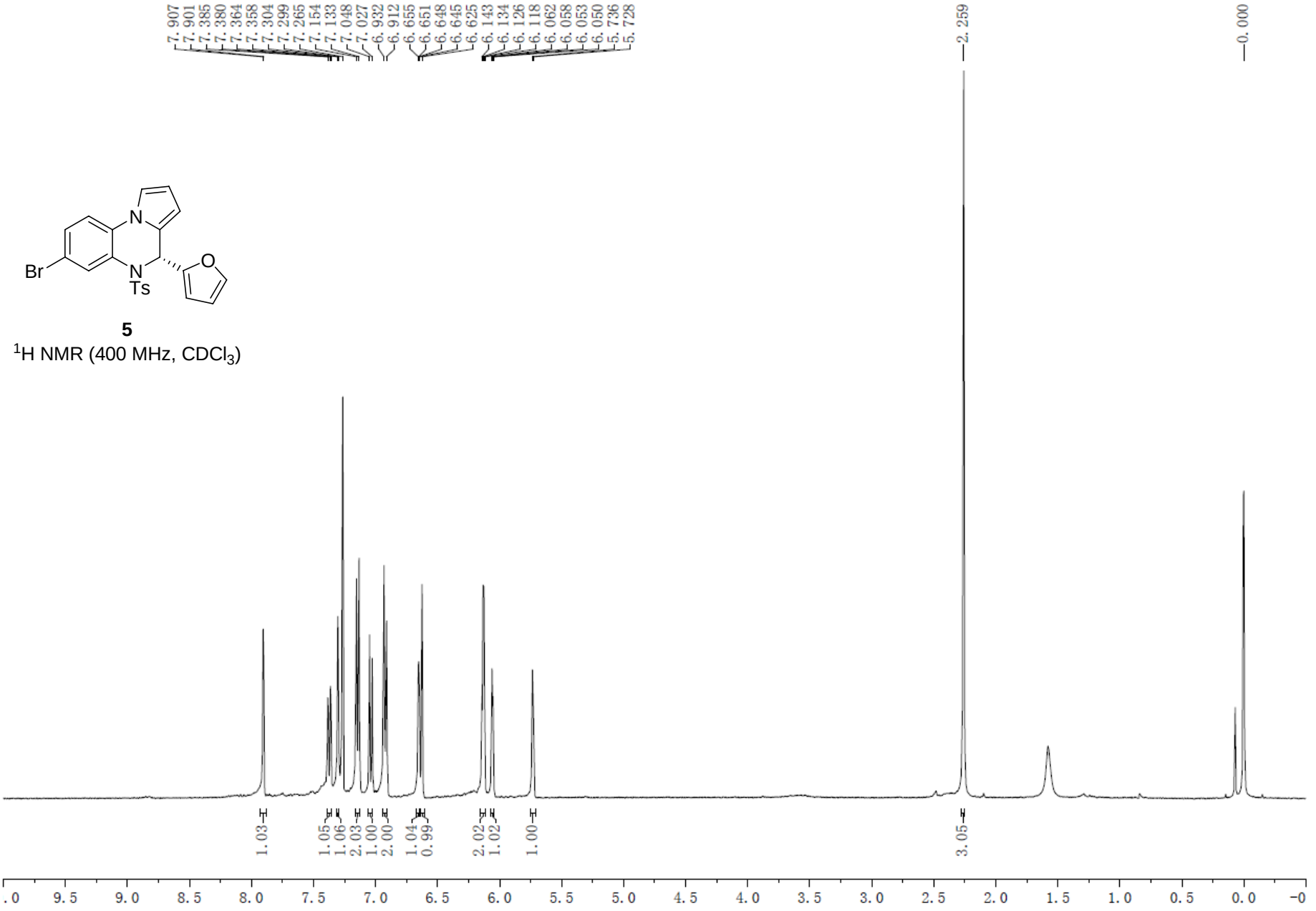
^{13}C NMR (100 MHz, $CDCl_3$)



3r

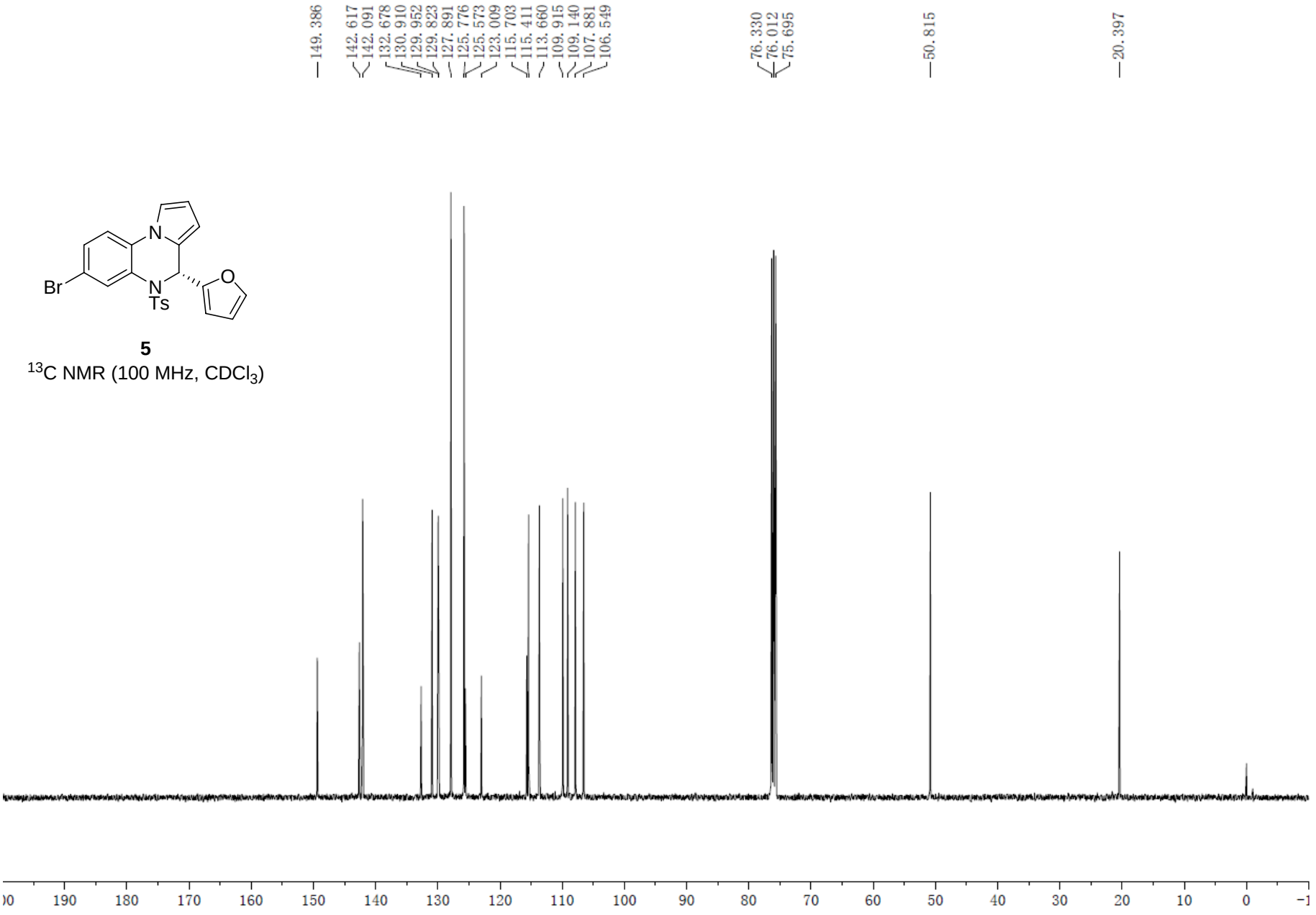
^{1}H NMR (400 MHz, $CDCl_3$)





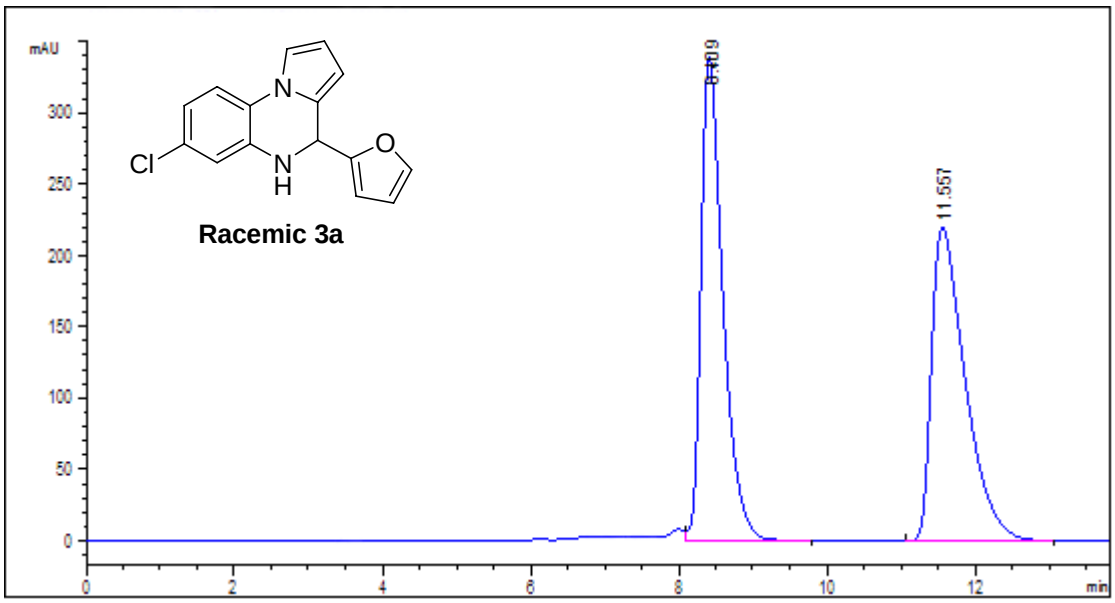
5

^{1}H NMR (400 MHz, $CDCl_3$)

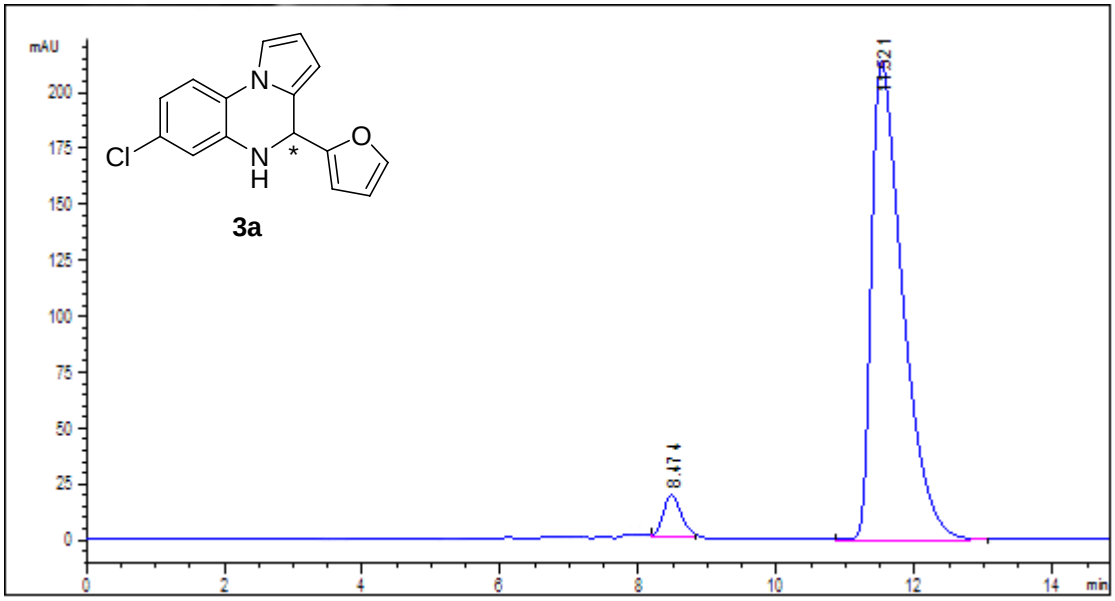


5

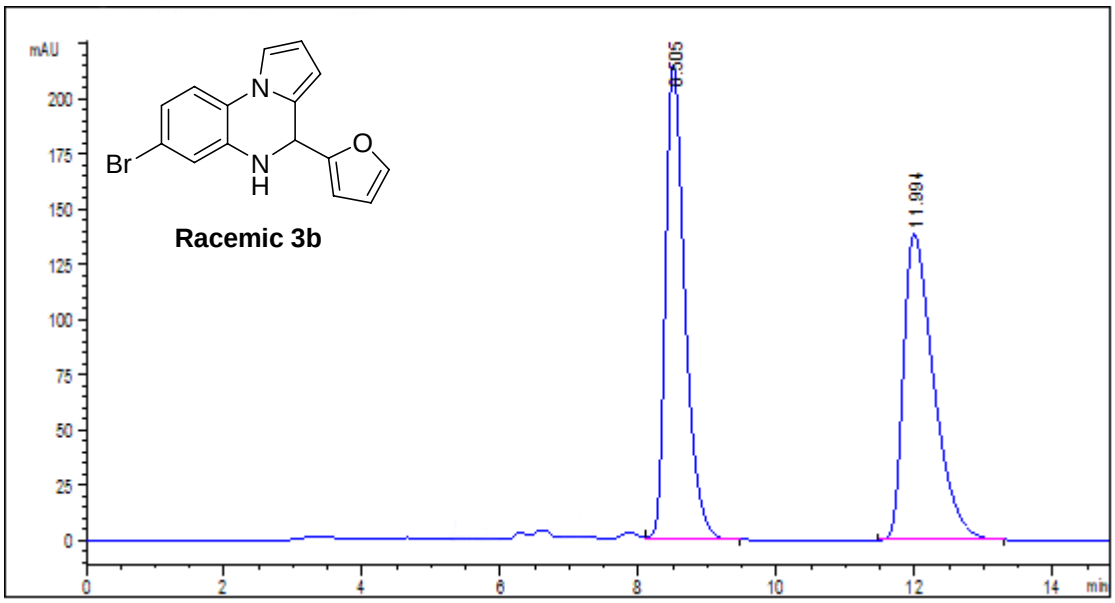
^{13}C NMR (100 MHz, $CDCl_3$)



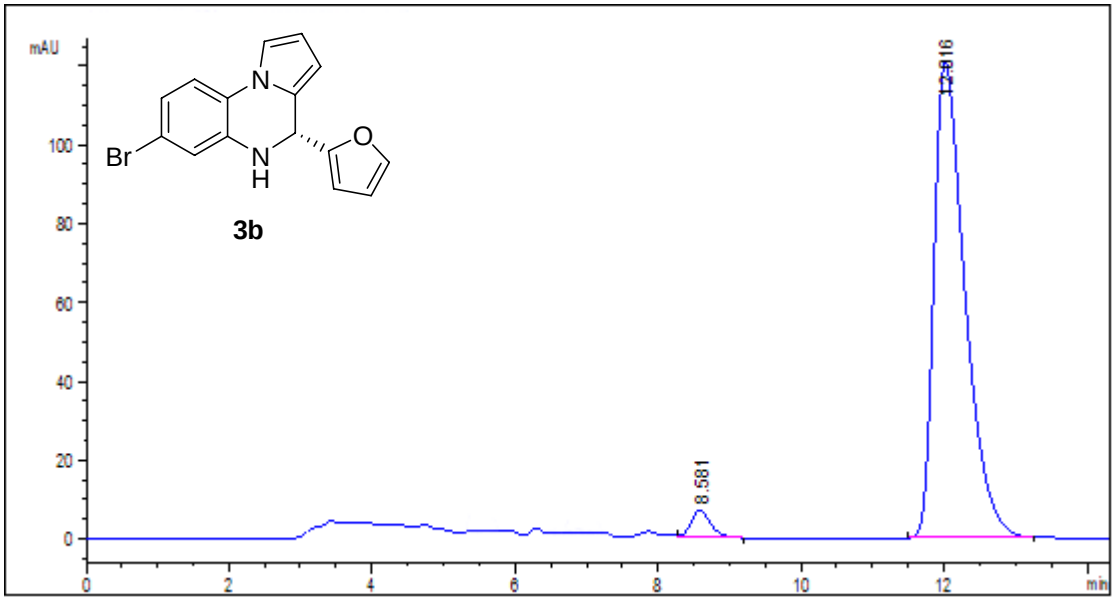
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.409	6981.4	338.8	0.3103	0.559	50.215
2	11.557	6921.7	219.4	0.4729	0.447	49.785



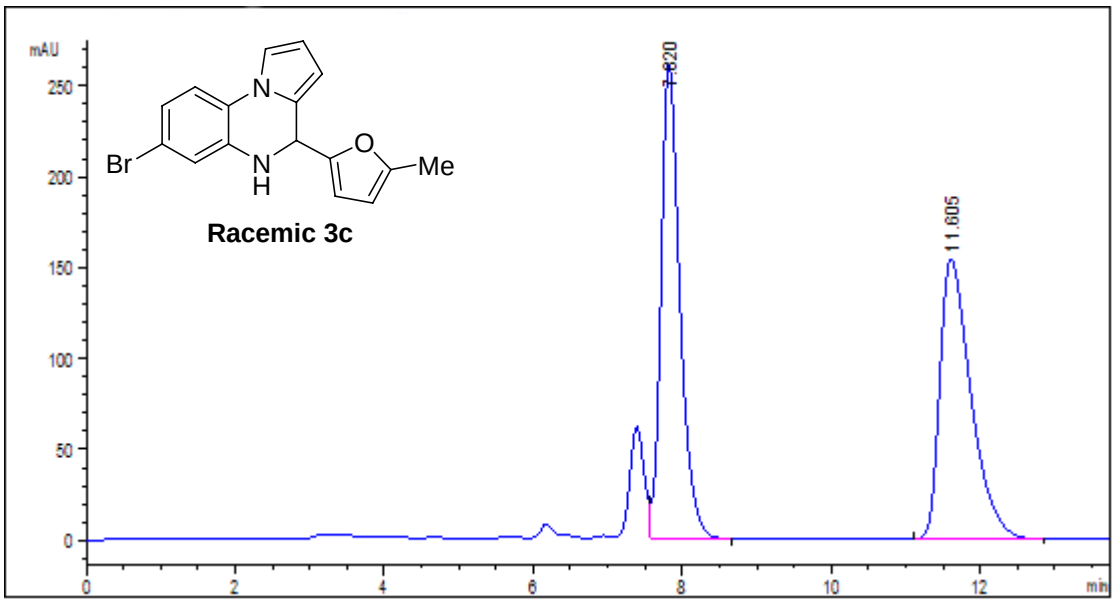
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.474	357.6	19.3	0.3089	0.799	4.996
2	11.521	6800.2	214.4	0.5286	0.471	95.004



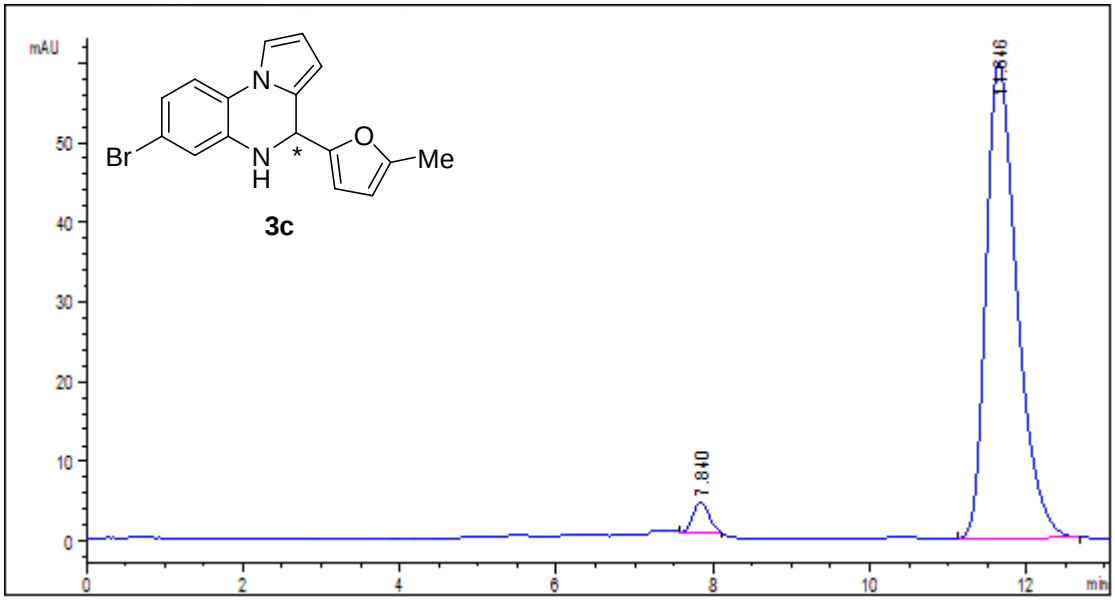
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.505	4217.8	215.4	0.2969	0.627	49.999
2	11.994	4217.9	138.5	0.4617	0.517	50.001



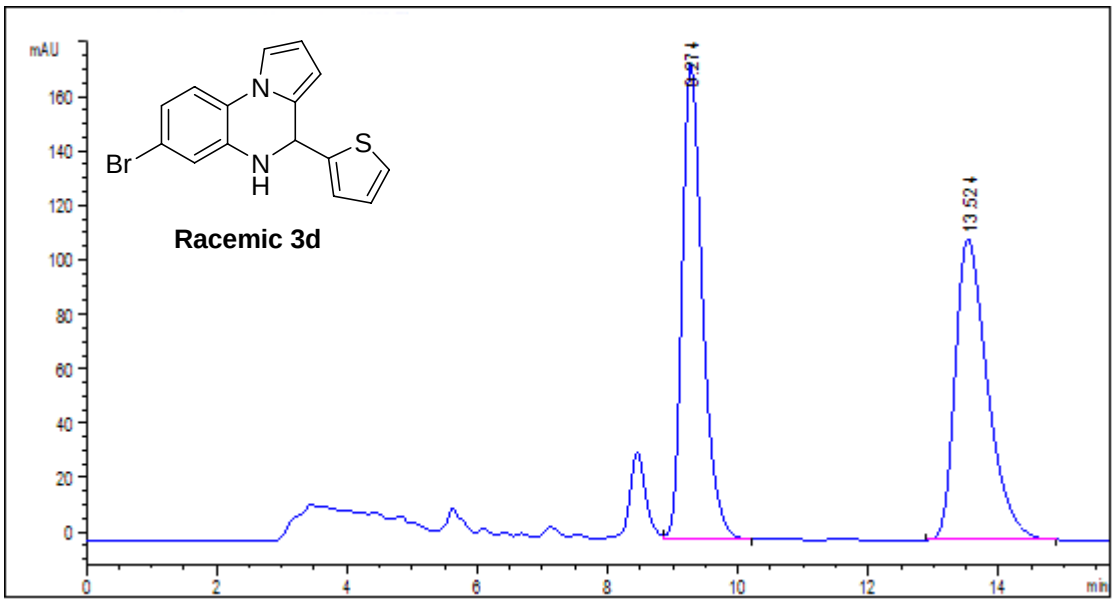
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.581	110.8	6.5	0.2838	0.821	2.961
2	12.016	3632	120.8	0.4571	0.534	97.039



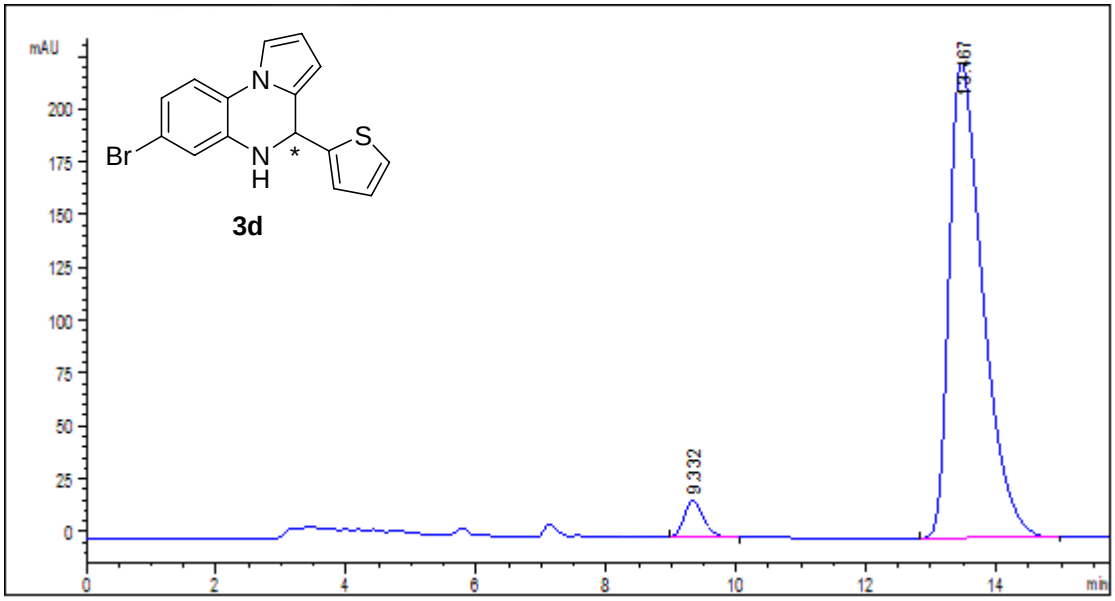
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.82	4582.9	261.3	0.2657	0.679	50.593
2	11.605	4475.4	154.5	0.44	0.531	49.407



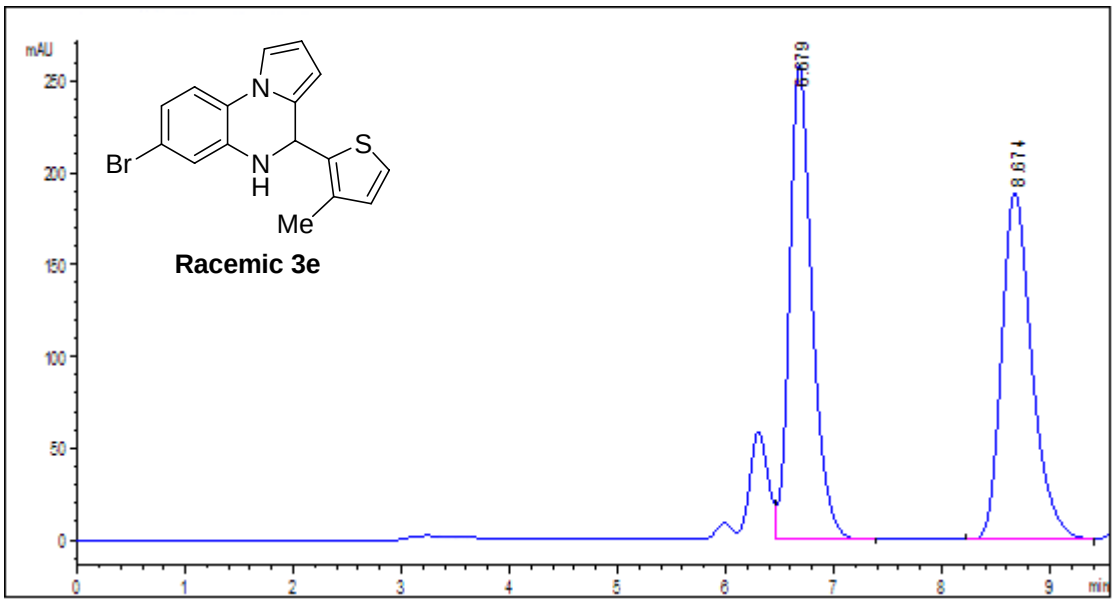
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.84	57.5	3.9	0.2459	0.89	3.399
2	11.646	1634.7	59.7	0.4172	0.642	96.601



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.274	3800.9	174.6	0.3312	0.689	49.964
2	13.524	3806.4	110.5	0.5255	0.612	50.036

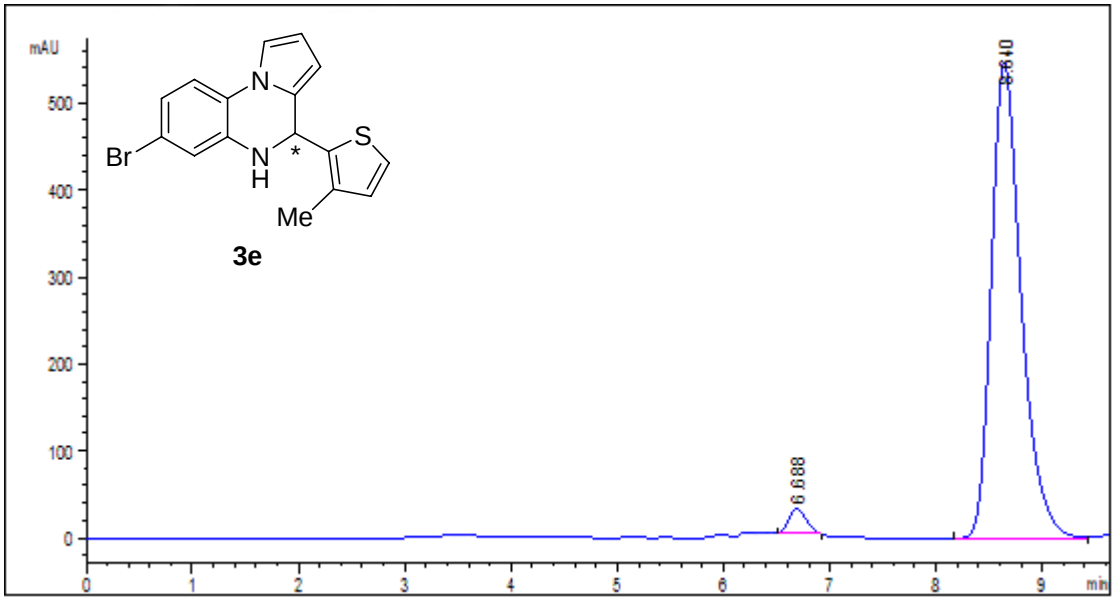


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.332	374.5	17.3	0.3291	0.762	4.432
2	13.467	8074.5	225.2	0.5435	0.532	95.568



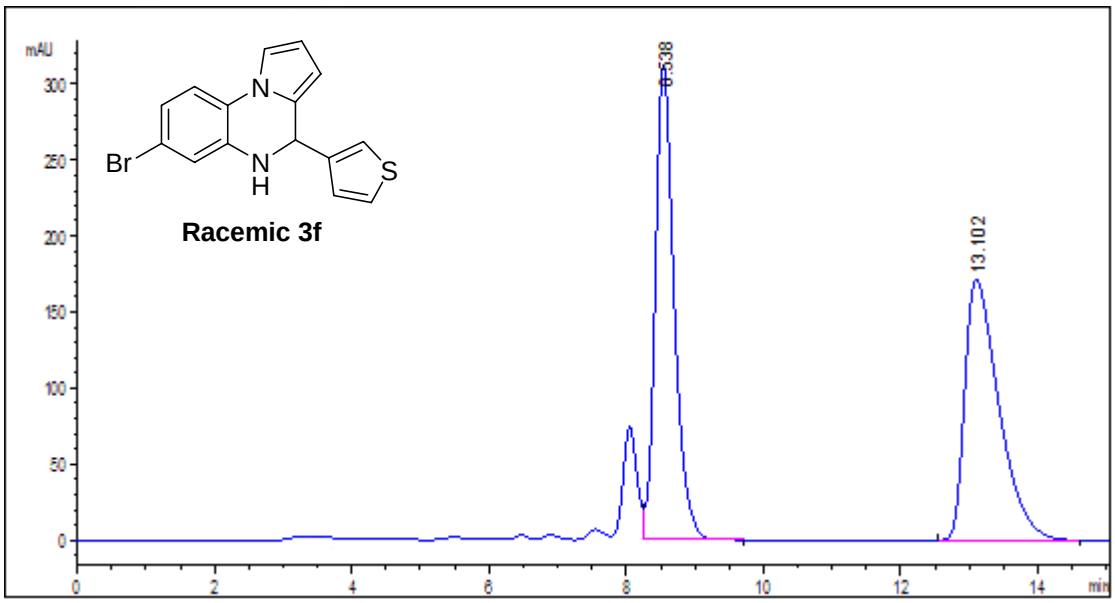
Racemic 3e

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	6.679	3750.1	259	0.2184	0.71	50.386
2	8.674	3692.7	189.4	0.2959	0.727	49.614

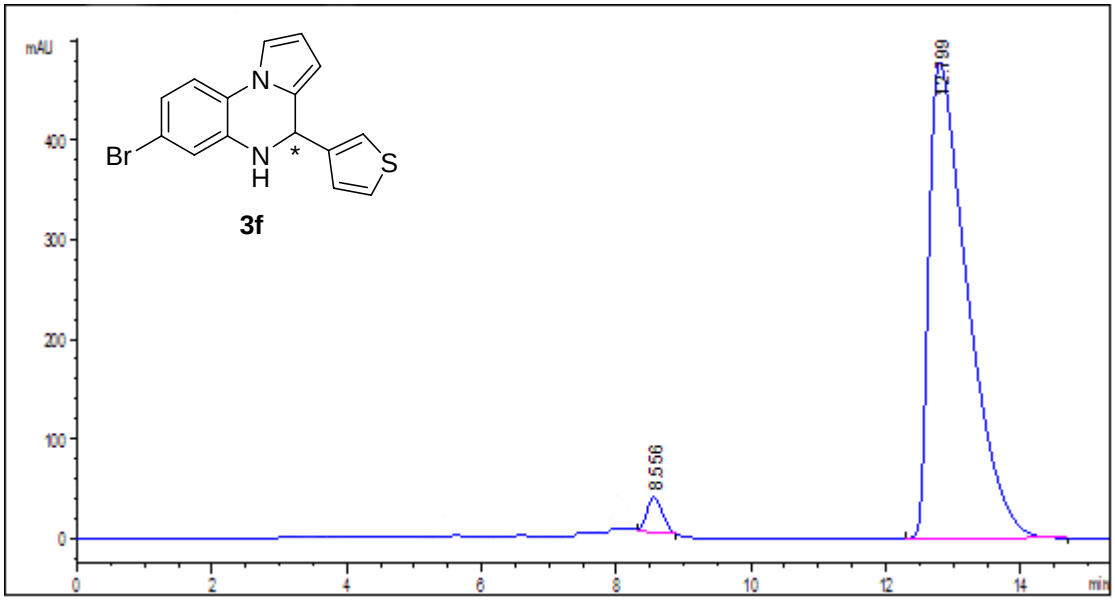


3e

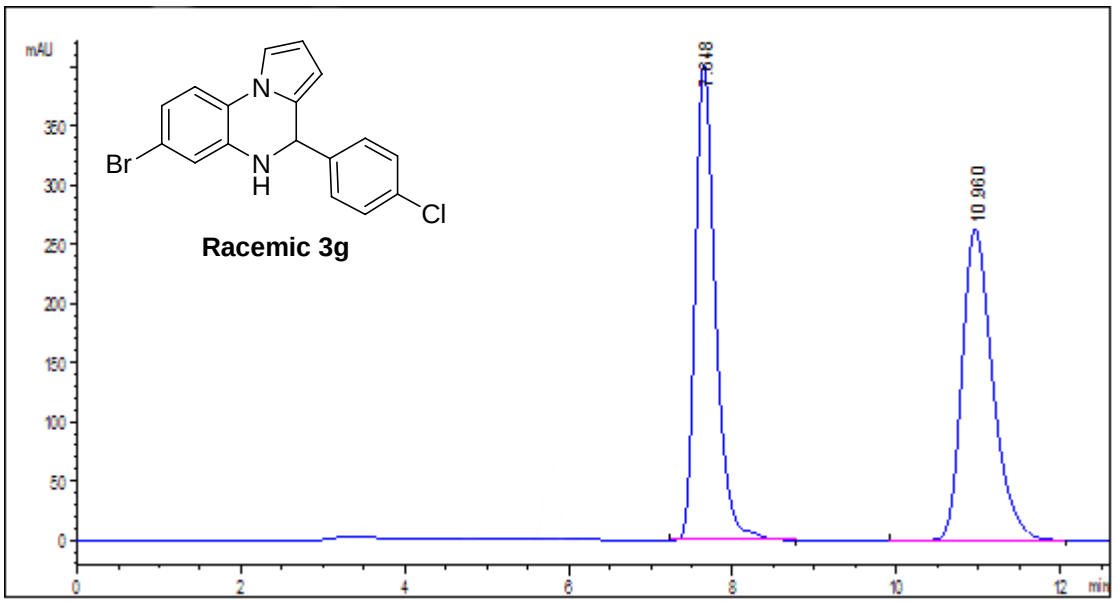
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	6.688	323.9	27.8	0.1938	0.845	2.948
2	8.64	10661.4	547.4	0.2957	0.704	97.052



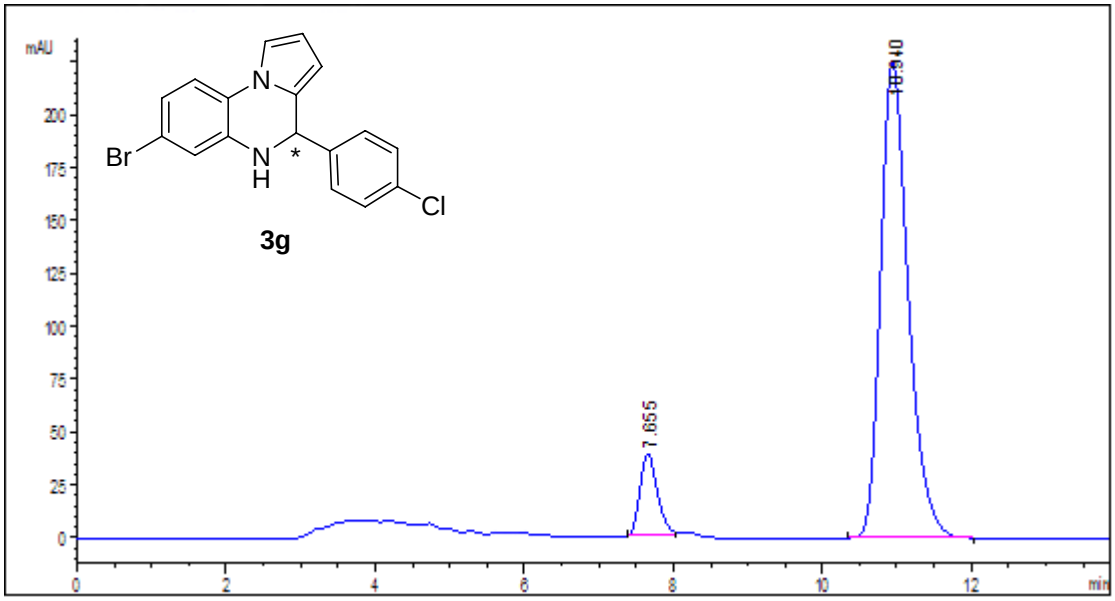
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.538	5980.6	313.2	0.2883	0.702	50.214
2	13.102	5929.5	171.7	0.5238	0.49	49.786



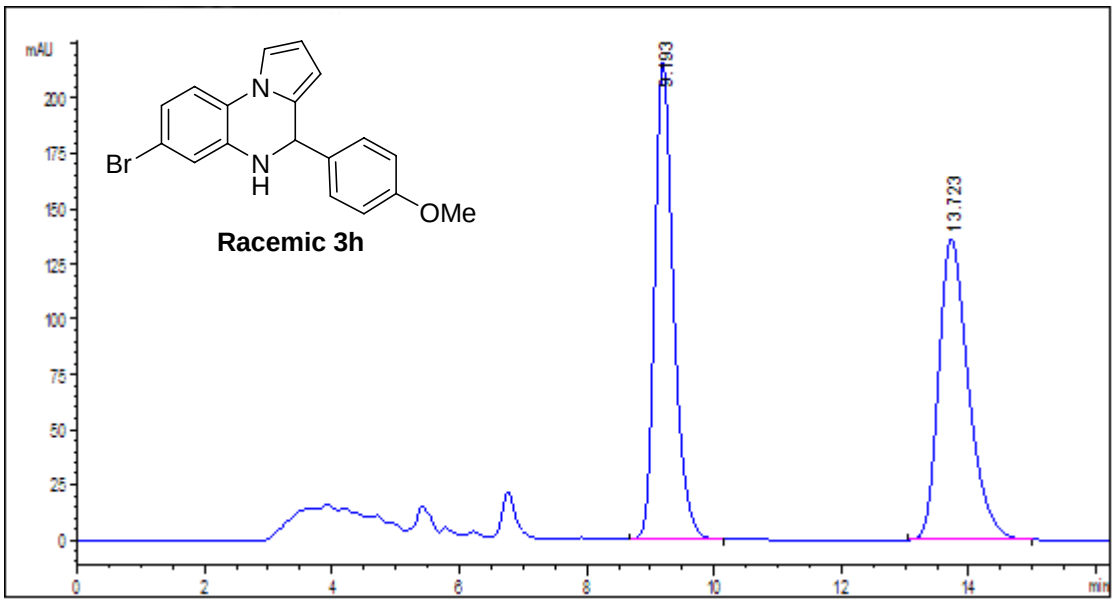
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.556	569.1	35.4	0.2683	0.827	2.907
2	12.799	19005.8	478.4	0.5931	0.365	97.093



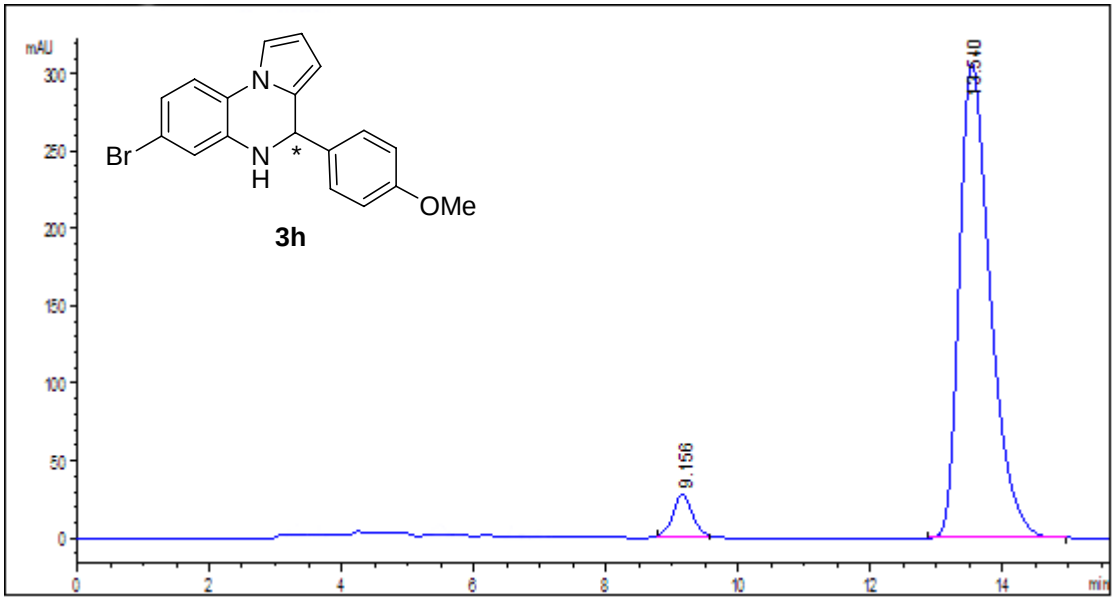
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.648	6913.6	402.6	0.2615	0.687	50.255
2	10.96	6843.4	263.3	0.3964	0.704	49.745



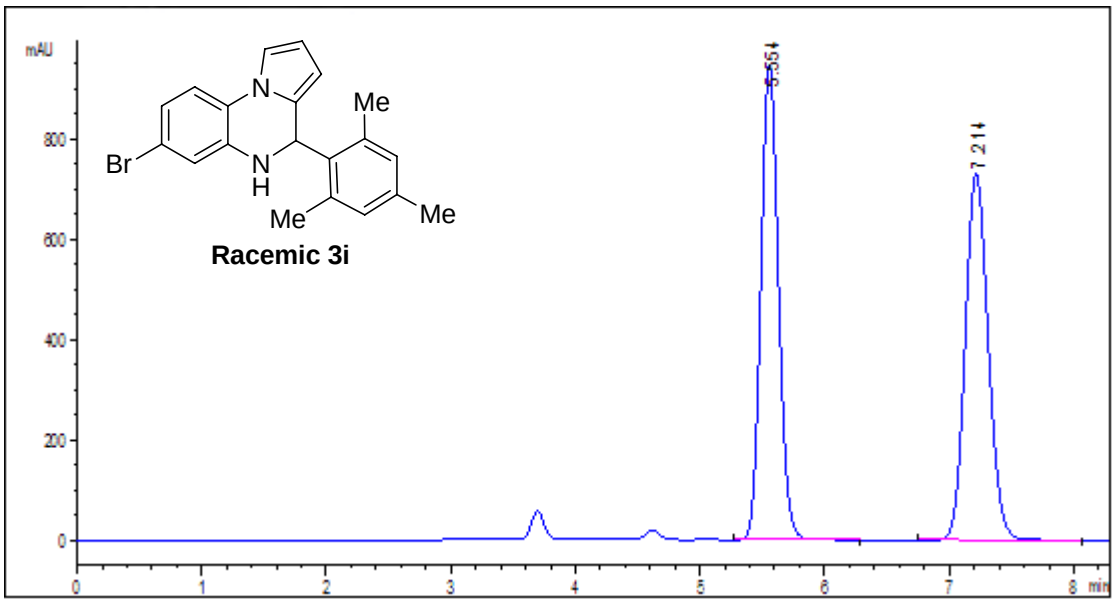
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.655	632.8	38.9	0.2712	0.779	9.843
2	10.94	5795.7	224.8	0.3925	0.711	90.157



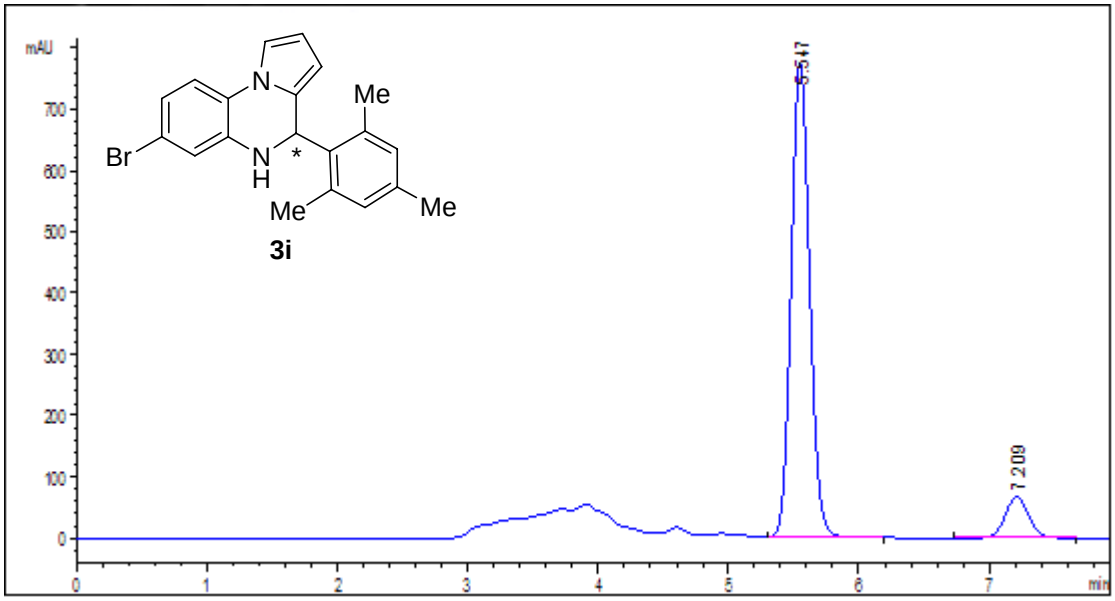
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.193	4464.7	216.3	0.3121	0.718	50.220
2	13.723	4425.6	136.4	0.495	0.693	49.780



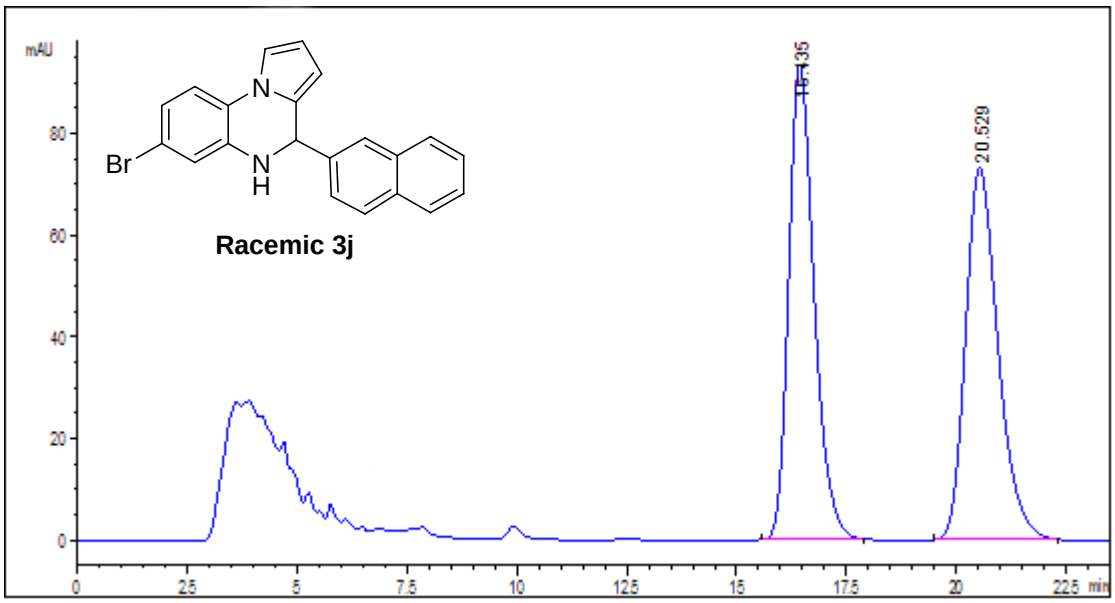
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.156	605.4	28.5	0.3536	0.901	5.707
2	13.54	10003.4	307.4	0.4947	0.638	94.293



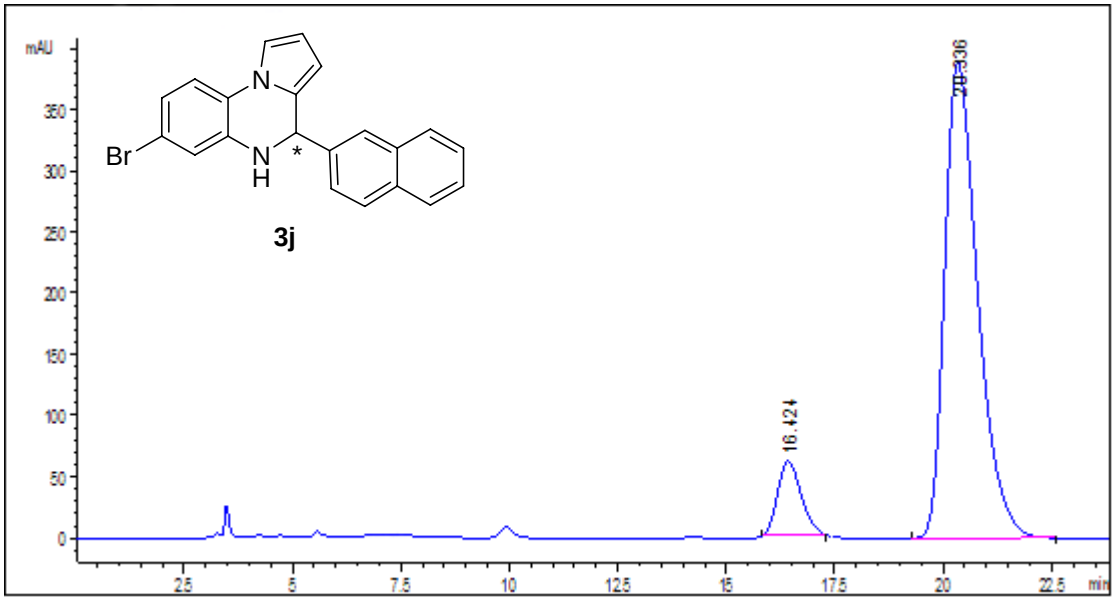
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	5.554	9296.3	950.2	0.152	0.879	49.841
2	7.214	9355.4	730.7	0.1989	0.857	50.159



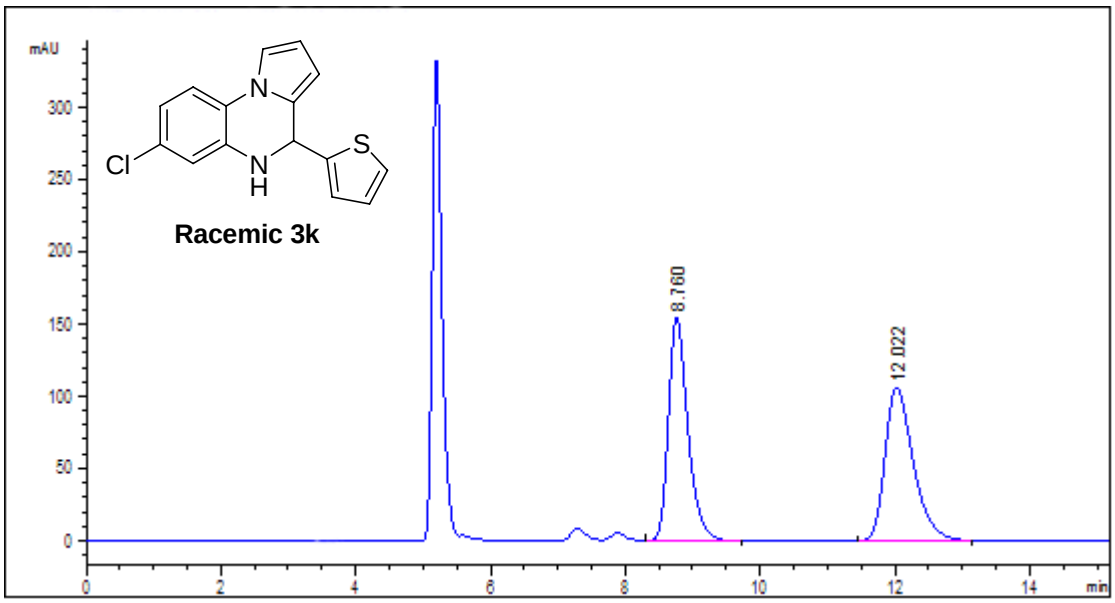
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	5.547	7642	776.6	0.1541	0.884	90.042
2	7.209	845.1	66.9	0.1969	0.919	9.958



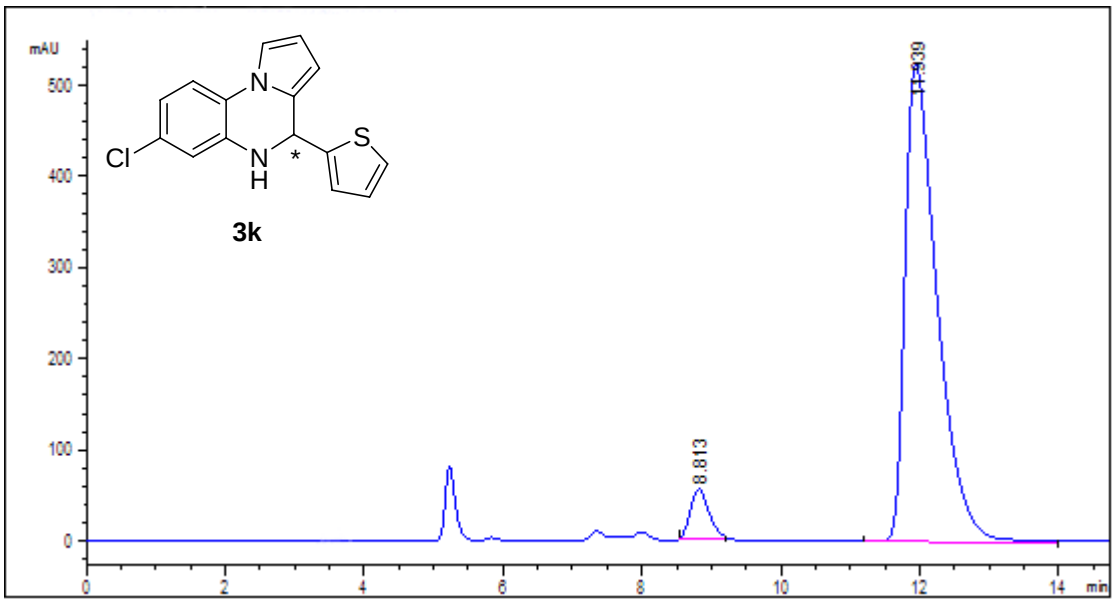
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	16.435	3761.8	93.6	0.6146	0.729	50.008
2	20.529	3760.7	73.2	0.7861	0.734	49.992



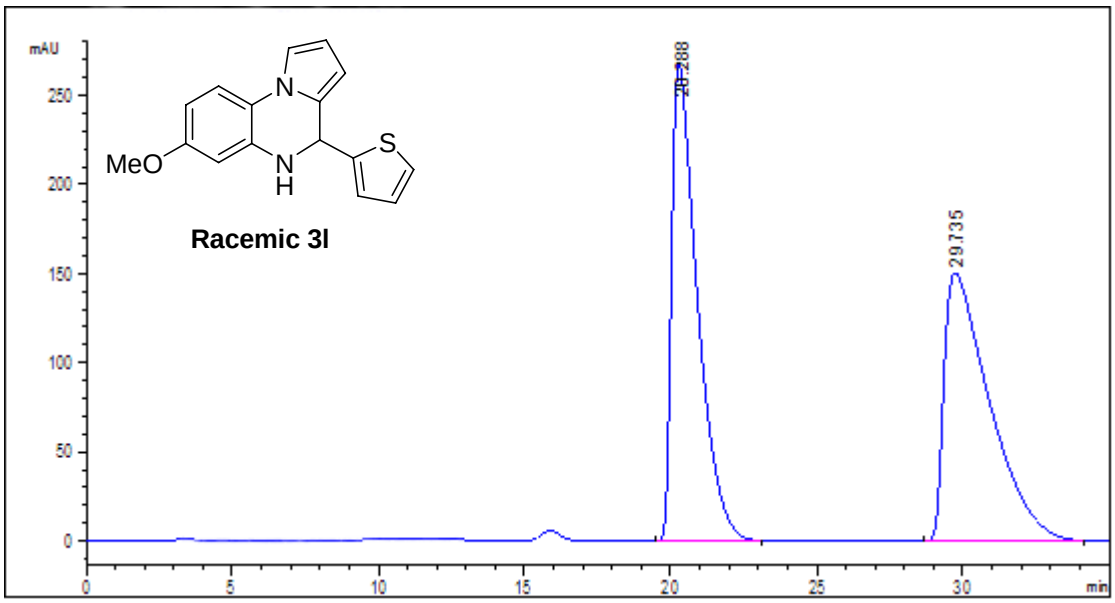
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	16.424	2317.6	61.2	0.6316	0.78	10.133
2	20.336	20554.5	388.8	0.8074	0.625	89.867



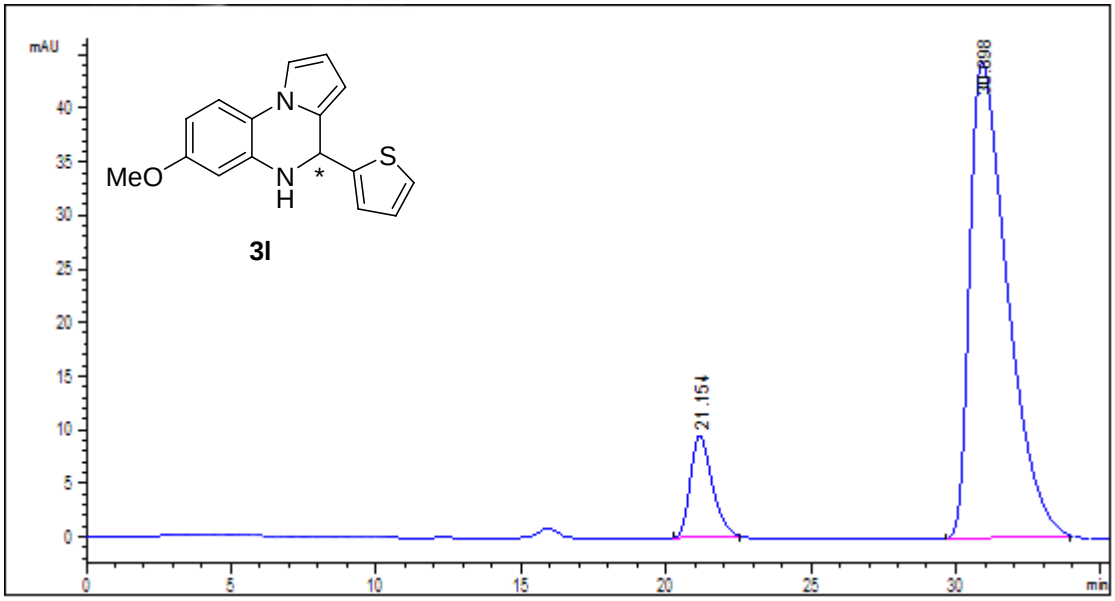
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.76	3091.6	154.5	0.3034	0.694	50.060
2	12.022	3084.2	106.4	0.4402	0.654	49.940



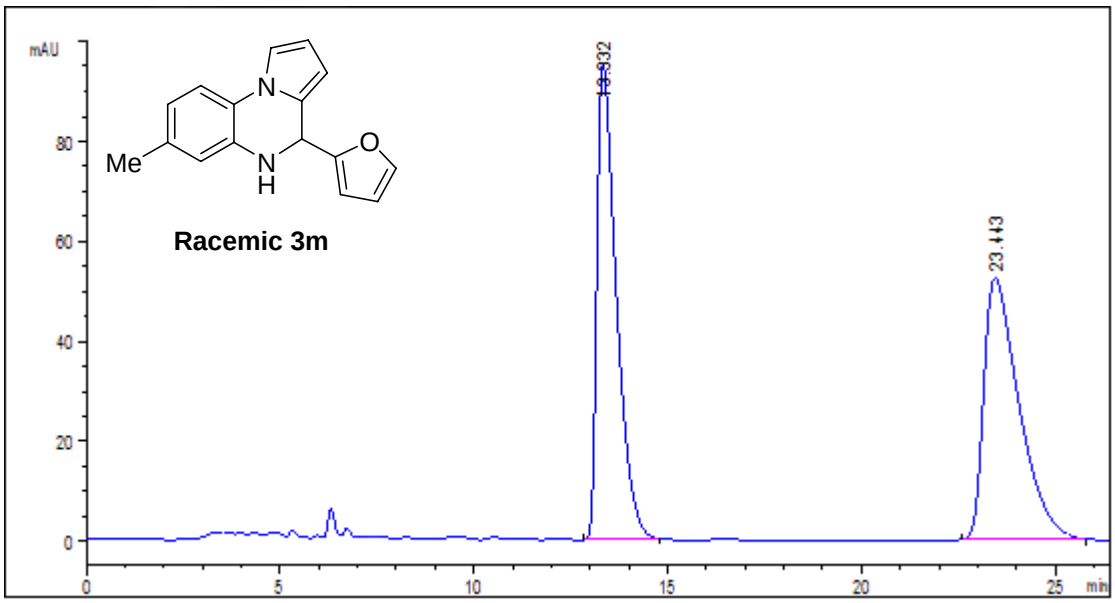
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.813	1032.2	54.9	0.3136	0.768	5.745
2	11.939	16933.9	524.4	0.5382	0.48	94.255



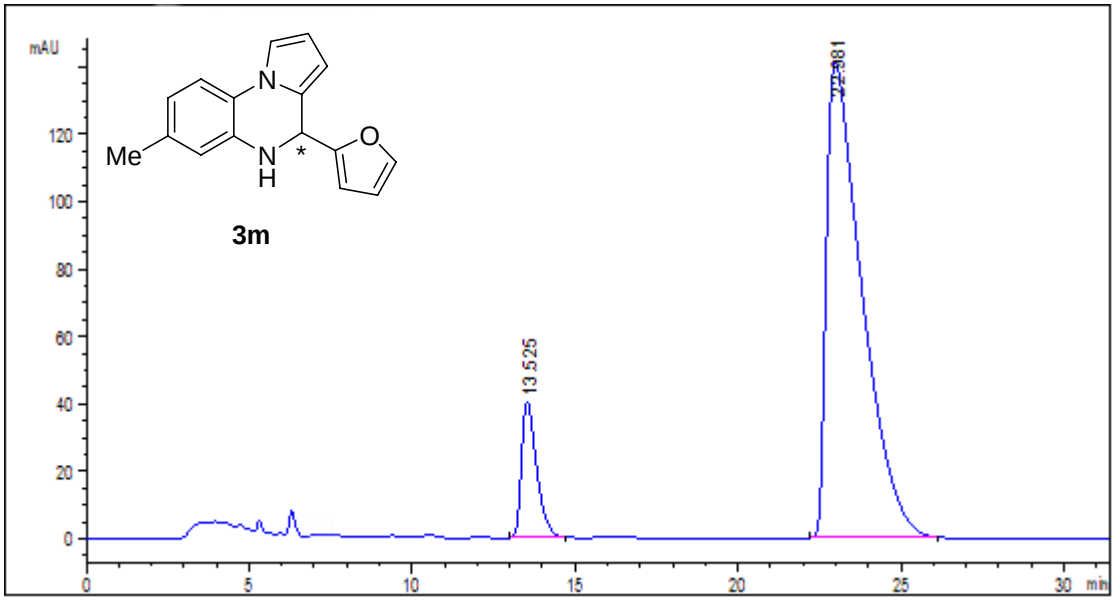
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	20.288	16340.8	268	0.9123	0.37	50.042
2	29.735	16313.4	150.7	1.5657	0.299	49.958



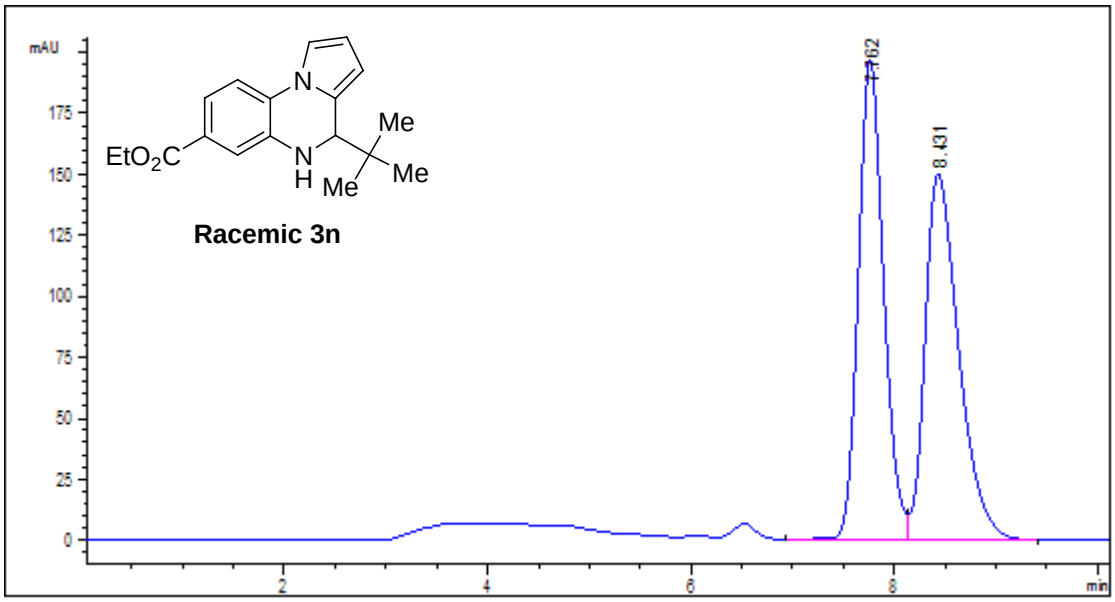
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	21.154	426.3	8.9	0.8001	0.73	9.428
2	30.898	4095.2	44.7	1.5285	0.469	90.572



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	13.332	3304.6	95.1	0.5202	0.427	50.014
2	23.443	3302.8	52.3	0.9358	0.444	49.986

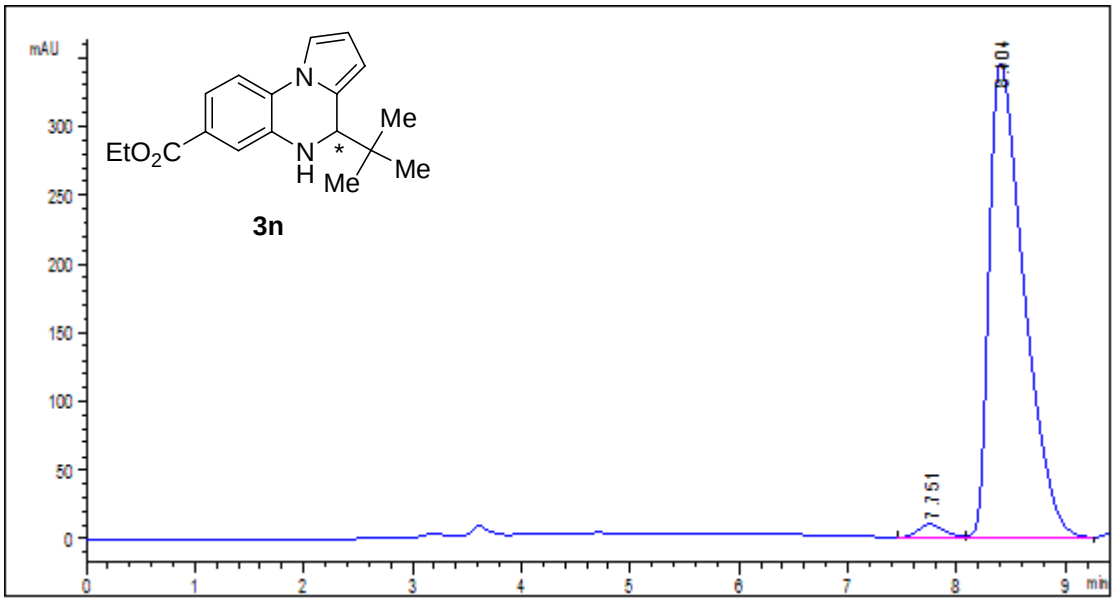


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	13.525	1174.3	38.9	0.5034	0.593	9.881
2	22.981	10710.7	141.2	1.0977	0.308	90.119



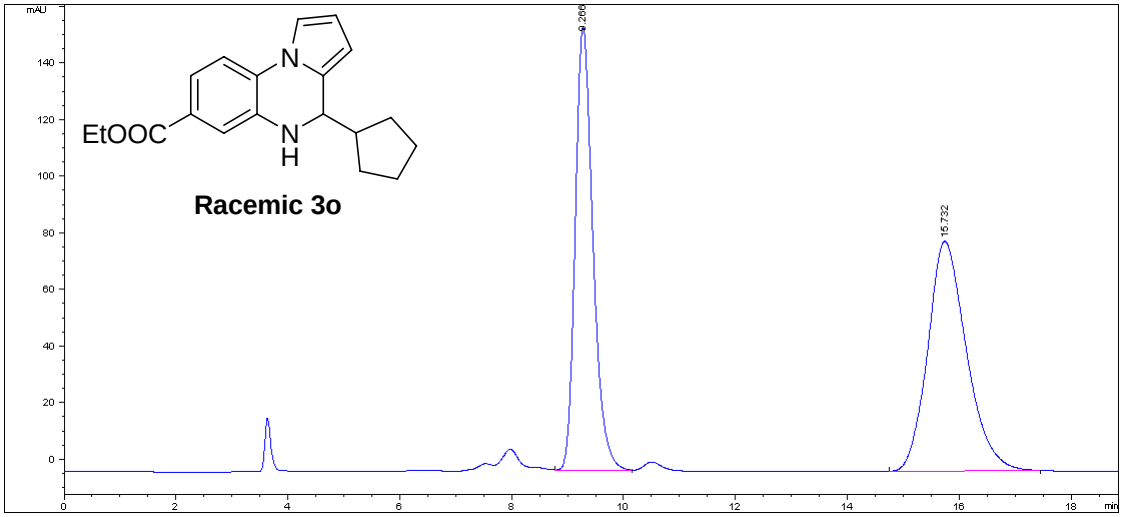
Racemic 3n

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.762	3419	197.1	0.2635	0.845	49.707
2	8.431	3459.3	150.4	0.3513	0.597	50.293

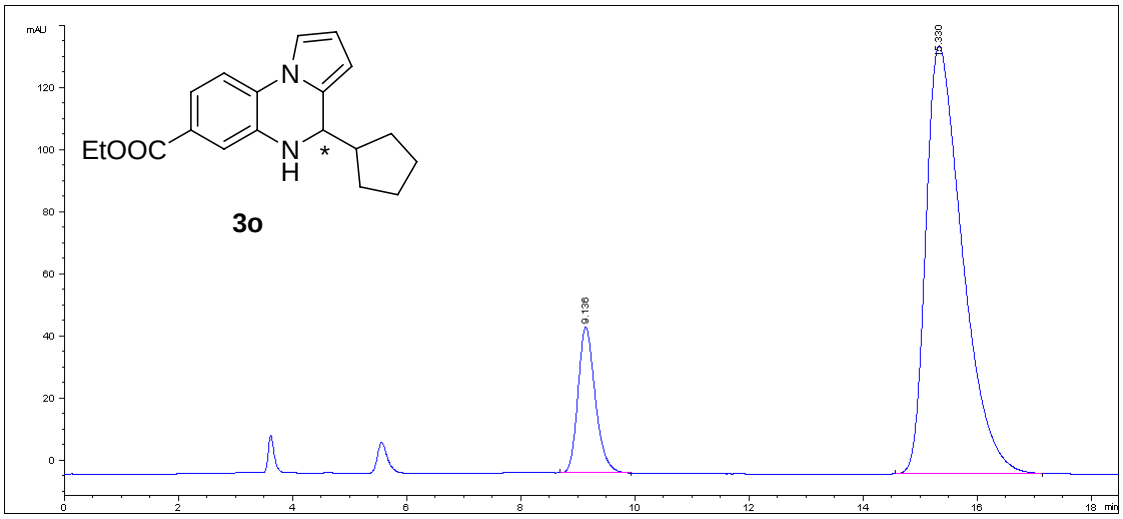


3n

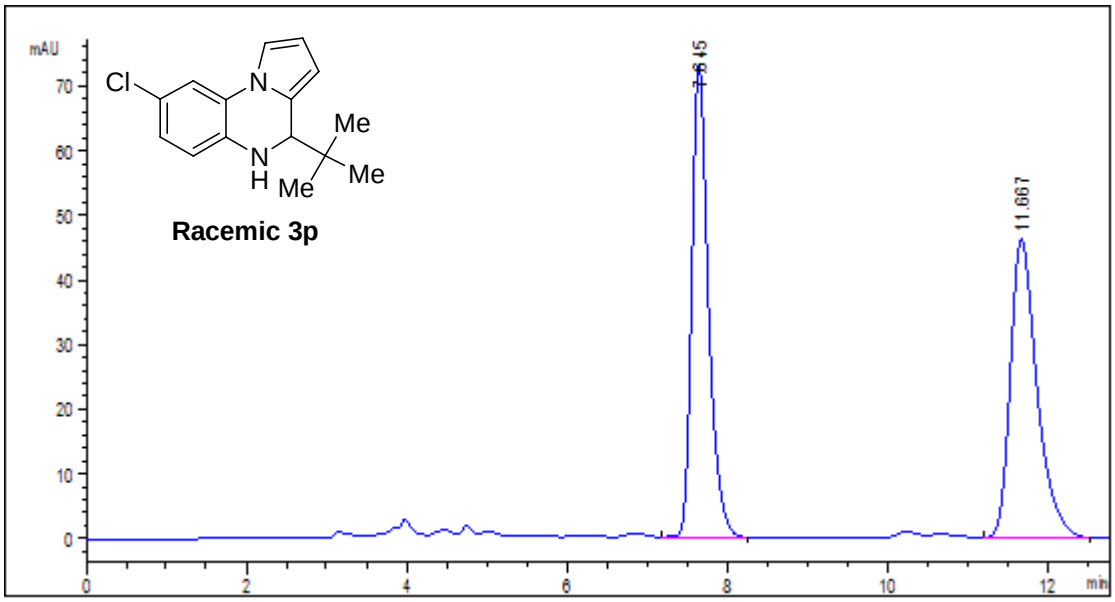
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.751	192.9	10.5	0.272	0.795	2.439
2	8.404	7718	345.9	0.3375	0.461	97.561



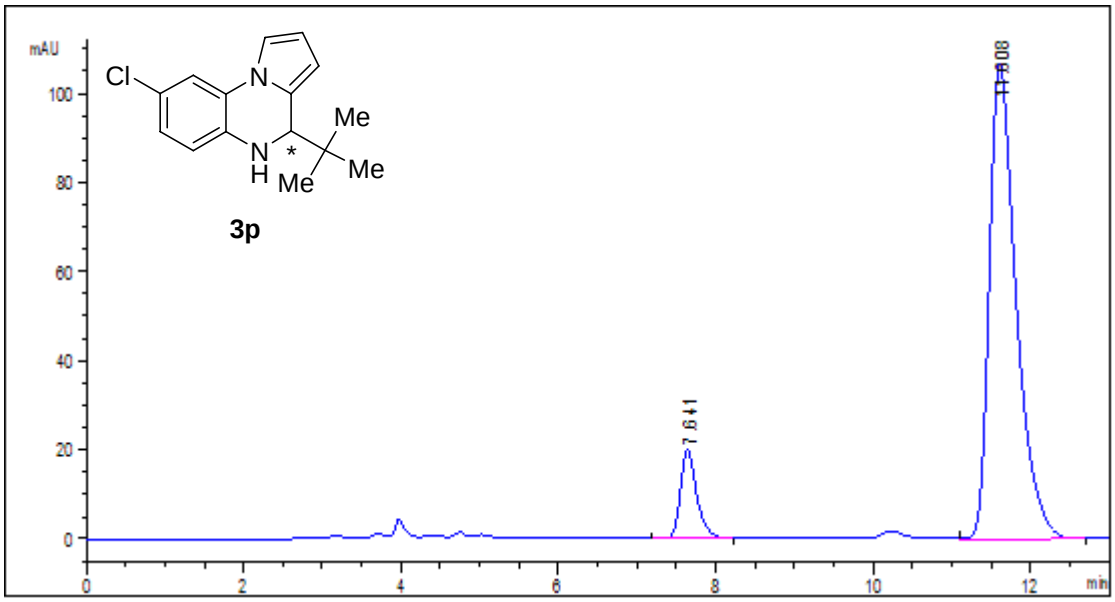
Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.266	3471	157.1	0.3378	0.731	47.012
2	15.732	3912.2	81.2	0.7266	0.750	52.998



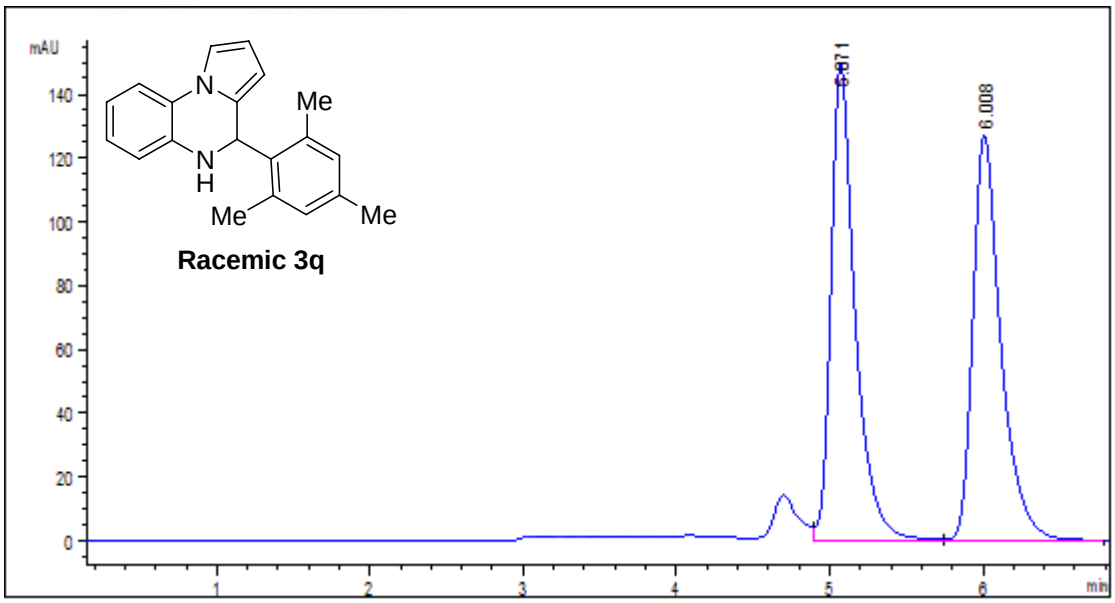
Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.136	991.9	47	0.3206	0.765	13.962
2	15.330	6112.6	137.8	0.6807	0.532	86.038



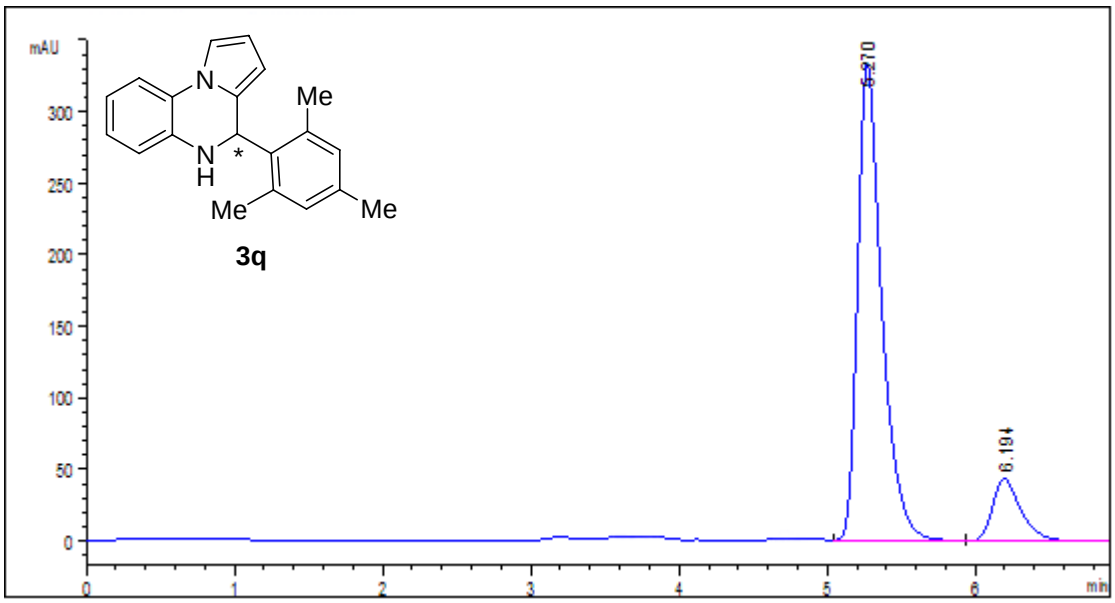
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.645	1051.4	73.2	0.2171	0.71	49.781
2	11.667	1060.7	46.1	0.3483	0.658	50.219



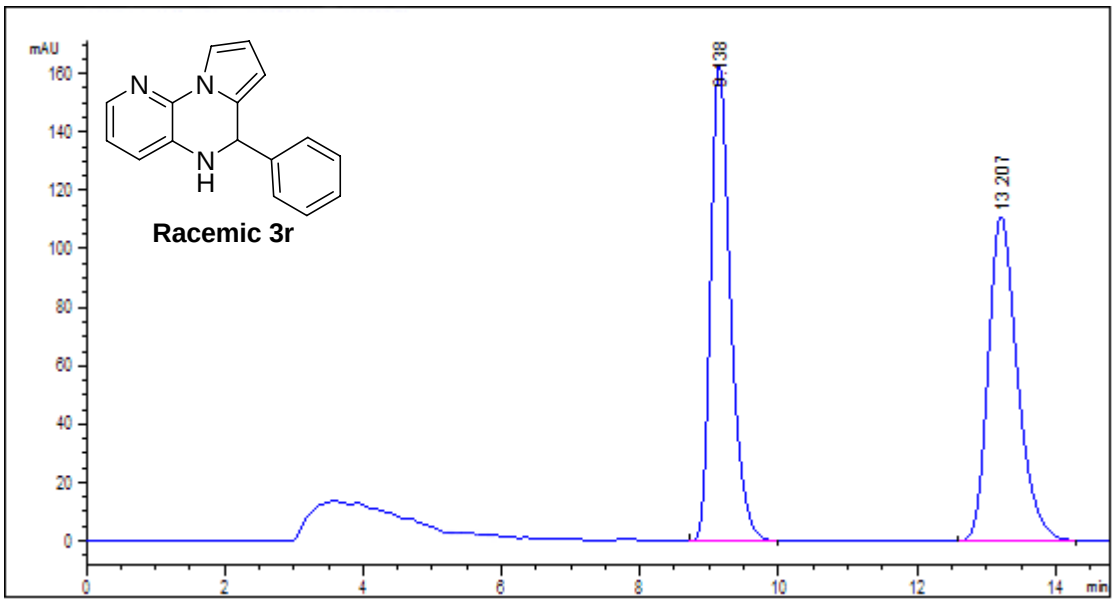
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	7.641	285.2	19.7	0.218	0.722	10.114
2	11.608	2534.9	107	0.3949	0.613	89.886



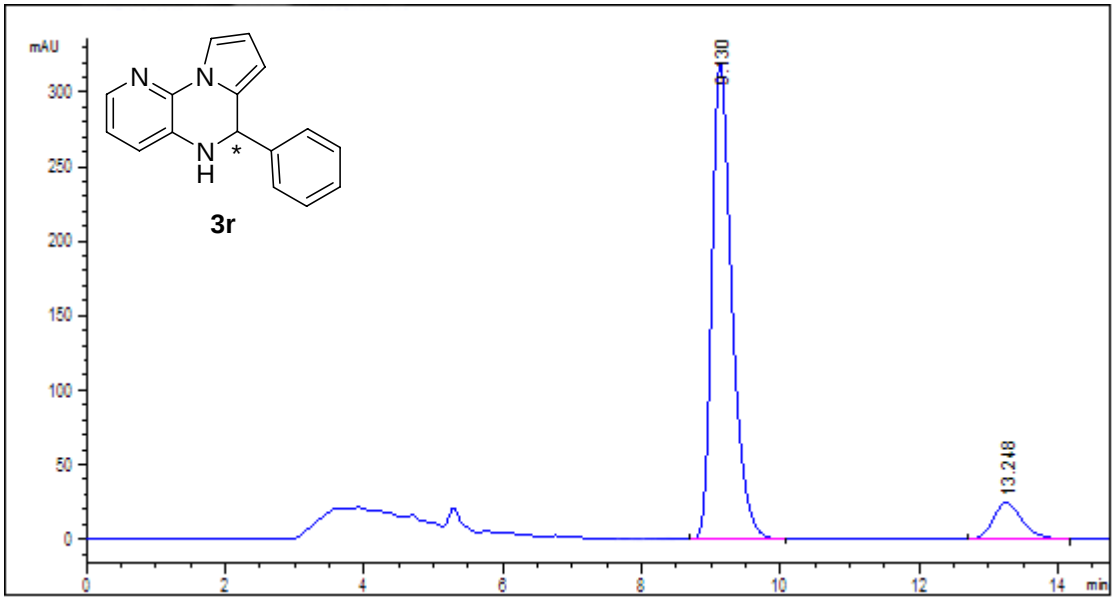
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	5.071	1640.6	149.5	0.163	0.614	50.306
2	6.008	1620.7	127.2	0.1894	0.632	49.694



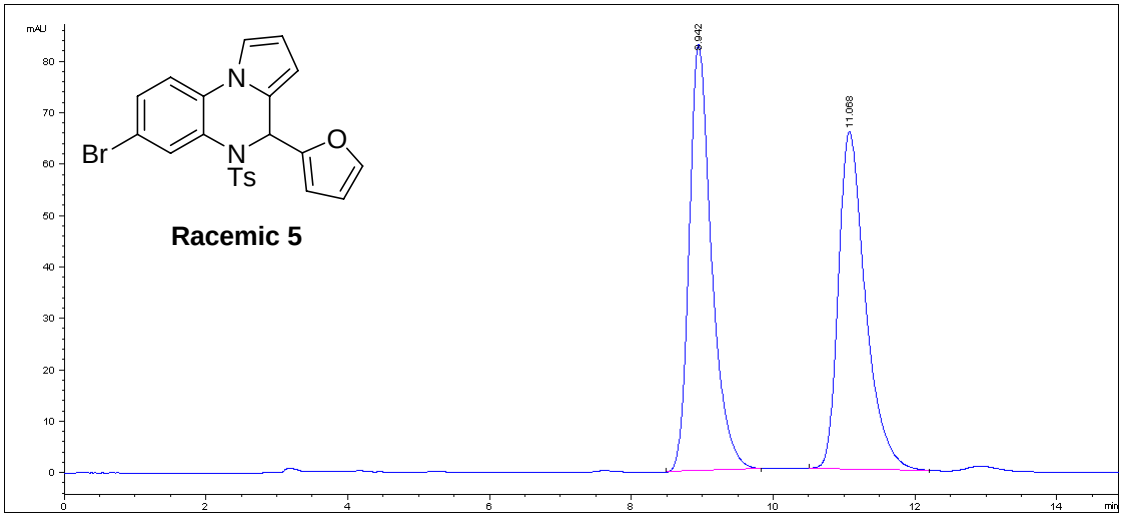
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	5.27	3866.3	333.9	0.193	0.621	89.769
2	6.194	440.6	39.3	0.1867	0.741	10.231



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.138	3253.8	163.3	0.3023	0.69	50.101
2	13.207	3240.7	111	0.444	0.727	49.899



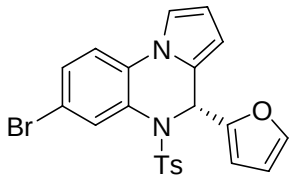
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	9.13	6698.6	323.7	0.3449	0.688	92.073
2	13.248	576.7	22.6	0.4247	0.87	7.927



Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.942	1818.3	82.9	0.3273	0.680	51.044
2	11.068	1744	65.6	0.4002	0.635	48.956

Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area(%)
1	8.929	351.8	16.4	0.3229	0.671	2.798
2	10.891	12221	465.6	0.3965	0.554	97.202

The crystal of compound **5** was obtained by leaving alone its solution in petroleum ether and ethyl acetate at room temperature in the open air for three days. The absolute configuration of compound **5** was assigned to be *R* by the single crystal X-ray analysis. The crystal data of compound **5** have been deposited in CCDC with number 931821.



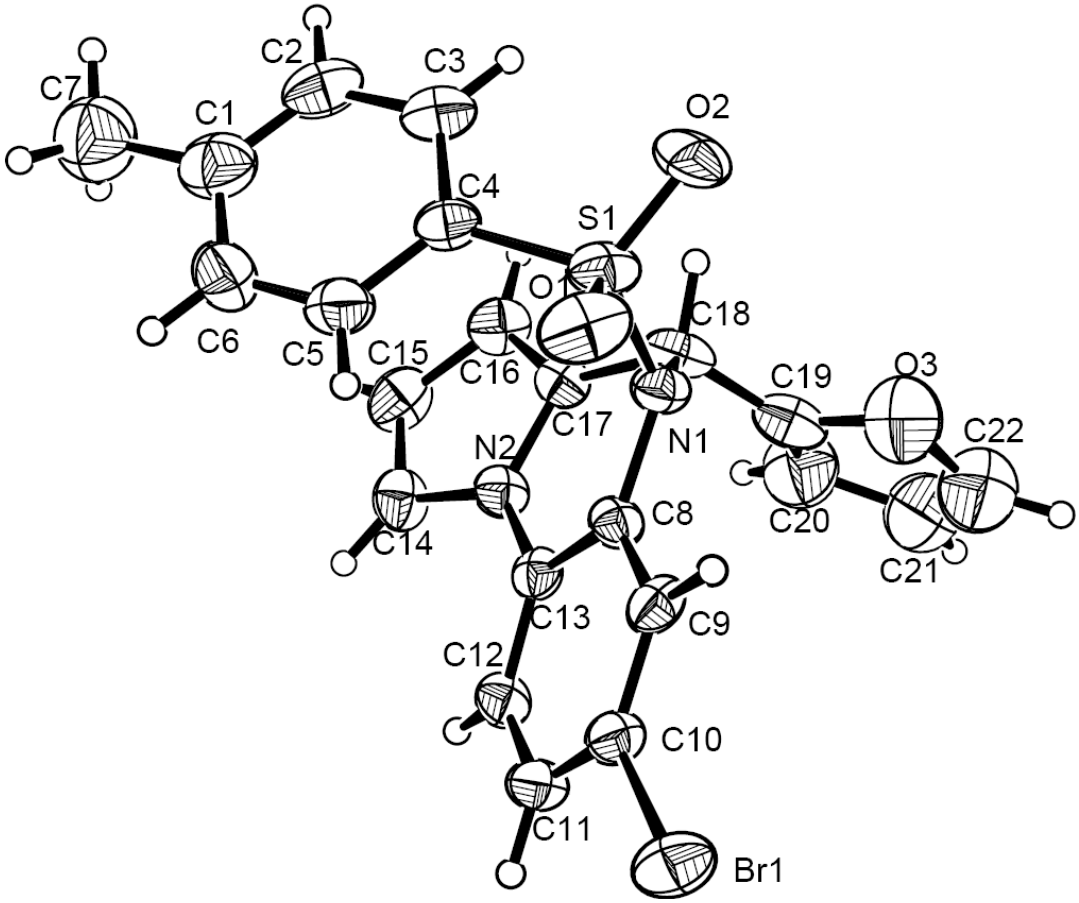


Table 1 Crystal data and structure refinement for 130322

Identification code	130322
Empirical formula	$C_{22}H_{17}BrN_2O_3S$
Formula weight	469.35
Temperature/K	290(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$

a/Å	9.0110(3)
b/Å	10.3134(5)
c/Å	22.7196(9)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2111.42(15)
Z	4
ρ_{calc}mg/mm^3	1.476
m/mm^{-1}	2.071
F(000)	952.0
Crystal size/mm^3	0.35 × 0.31 × 0.3
2Θ range for data collection	5.78 to 52.72°
Index ranges	$-10 \le h \le 11$, $-12 \le k \le 10$, $-28 \le l \le 20$
Reflections collected	8864
Independent reflections	4253[R(int) = 0.0374]
Data/restraints/parameters	4253/42/263
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0578, wR_2 = 0.1241
Final R indexes [all data]	R_1 = 0.0928, wR_2 = 0.1422
Largest diff. peak/hole / e Å^{-3}	0.48/-0.42
Flack parameter	-0.016(14)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 130322. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	10457.1(8)	12698.1(7)	9835.2(3)	69.3(3)
S1	14627.4(17)	14658.8(17)	11692.1(7)	54.1(4)
N1	13309(4)	15579(5)	11403.3(19)	43.7(11)
O1	14586(5)	13455(5)	11385.7(19)	73.8(13)
N2	10740(4)	16005(4)	12038(2)	42.9(11)
C10	10548(6)	13729(6)	10523(2)	46.4(13)
C8	11941(5)	14994(6)	11209(2)	39.5(13)
O2	15943(4)	15429(6)	11685(2)	79.0(16)
C13	10627(6)	15248(5)	11522(2)	39.6(12)
C9	11881(6)	14220(6)	10708(2)	45.5(15)

C18	13087(6)	16902(6)	11675(3)	55.5(14)
C4	14145(5)	14385(6)	12433(3)	47.4(14)
C19	12657(7)	17836(8)	11202(3)	75.1(15)
C11	9244(6)	14006(6)	10826(3)	52.5(16)
C16	11797(6)	17270(7)	12701(3)	57.9(16)
C5	13010(7)	13535(7)	12565(3)	59.9(17)
O3	13494(7)	17866(7)	10697(3)	109.9(16)
C12	9309(6)	14778(6)	11318(2)	45.9(14)
C17	11954(6)	16790(5)	12151(3)	43.4(14)
C14	9836(6)	15986(6)	12518(3)	55.9(16)
C6	12576(8)	13367(8)	13136(4)	76(2)
C3	14847(7)	15076(7)	12875(3)	63.0(18)
C20	11700(10)	18779(10)	11229(5)	103(2)
C22	12762(11)	18873(11)	10379(5)	116(2)
C15	10461(8)	16773(7)	12932(3)	67.3(18)
C2	14381(9)	14890(8)	13450(3)	77(2)
C21	11817(11)	19397(11)	10670(4)	113(2)
C1	13265(9)	14045(9)	13585(4)	82(2)
C7	12717(11)	13881(11)	14228(4)	117(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 130322. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	80.7(5)	70.7(5)	56.4(4)	-18.4(4)	-15.7(3)	-0.8(4)
S1	34.3(7)	73.3(11)	54.7(8)	-15.2(8)	0.0(7)	13.4(8)
N1	34(2)	53(3)	44(3)	-6(2)	-1(2)	0(2)
O1	70(3)	82(3)	69(3)	-27(3)	-7(3)	33(3)
N2	35(3)	48(3)	46(3)	-6(2)	6(2)	6(2)
C10	49(3)	49(3)	41(3)	-1(3)	-7(3)	-3(3)
C8	29(3)	41(3)	48(3)	3(3)	1(2)	5(2)
O2	28(2)	123(5)	86(3)	1(3)	4(2)	-2(2)
C13	38(3)	39(3)	42(3)	6(2)	0(2)	8(3)
C9	46(3)	57(4)	33(3)	1(3)	0(2)	11(3)
C18	33(3)	66(4)	67(4)	-27(2)	0(3)	-4(3)
C4	42(3)	48(4)	52(3)	-4(3)	-9(2)	9(3)
C19	59(4)	73(4)	93(3)	-13(3)	-11(2)	-21(3)
C11	48(4)	54(4)	56(4)	2(3)	-12(3)	-10(3)
C16	60(4)	61(4)	53(3)	-15(4)	2(3)	7(3)

C5	57(4)	60(5)	63(4)	-3(4)	-14(3)	-2(3)
O3	115(2)	109(2)	105(2)	3.2(17)	11.1(16)	0.9(17)
C12	33(3)	54(4)	51(3)	2(3)	6(2)	5(3)
C17	39(3)	37(3)	54(4)	-3(3)	2(2)	9(2)
C14	52(3)	62(4)	54(4)	-1(3)	16(3)	8(3)
C6	70(5)	69(5)	88(6)	12(4)	0(4)	-14(4)
C3	59(4)	66(5)	64(4)	-14(4)	-17(3)	7(3)
C20	103(3)	98(3)	109(2)	5.8(18)	0.8(18)	8.7(18)
C22	122(3)	117(3)	109(2)	8.4(17)	1.1(17)	-2.9(19)
C15	80(4)	75(5)	47(3)	-14(3)	6(4)	12(4)
C2	82(5)	93(6)	57(4)	-16(4)	-24(4)	7(5)
C21	114(3)	110(3)	113(3)	11.4(17)	-4.2(18)	1.1(18)
C1	73(5)	80(6)	93(4)	2(5)	-15(4)	13(4)
C7	119(4)	121(4)	110(3)	4(2)	5(2)	-1(2)

Table 4 Bond Lengths for 130322.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C10	1.891(5)	C4	C5	1.380(8)
S1	N1	1.656(5)	C4	C3	1.386(8)
S1	O1	1.424(5)	C19	O3	1.373(9)
S1	O2	1.427(5)	C19	C20	1.301(11)
S1	C4	1.760(6)	C11	C12	1.375(8)
N1	C8	1.442(7)	C16	C17	1.352(8)
N1	C18	1.511(8)	C16	C15	1.410(9)
N2	C13	1.411(7)	C5	C6	1.365(9)
N2	C17	1.386(7)	O3	C22	1.428(11)
N2	C14	1.362(7)	C14	C15	1.364(8)
C10	C9	1.370(8)	C6	C1	1.384(11)
C10	C11	1.391(8)	C3	C2	1.384(9)
C8	C13	1.406(7)	C20	C21	1.427(12)
C8	C9	1.391(8)	C22	C21	1.206(12)
C13	C12	1.364(7)	C2	C1	1.366(11)
C18	C19	1.495(10)	C1	C7	1.551(12)
C18	C17	1.490(8)			

Table 5 Bond Angles for 130322.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

N1	S1	C4	107.0(2)	C5	C4	S1	119.6(5)
O1	S1	N1	106.7(3)	C5	C4	C3	120.4(6)
O1	S1	O2	120.1(3)	C3	C4	S1	119.9(5)
O1	S1	C4	108.7(3)	O3	C19	C18	118.2(7)
O2	S1	N1	105.8(3)	C20	C19	C18	128.3(8)
O2	S1	C4	107.7(3)	C20	C19	O3	112.8(9)
C8	N1	S1	119.7(4)	C12	C11	C10	119.1(5)
C8	N1	C18	113.0(4)	C17	C16	C15	107.5(6)
C18	N1	S1	116.8(4)	C6	C5	C4	120.0(6)
C17	N2	C13	122.3(4)	C19	O3	C22	100.7(7)
C14	N2	C13	127.9(5)	C13	C12	C11	121.3(5)
C14	N2	C17	109.4(5)	N2	C17	C18	116.8(5)
C9	C10	Br1	120.0(4)	C16	C17	N2	107.6(5)
C9	C10	C11	120.9(5)	C16	C17	C18	135.5(6)
C11	C10	Br1	119.2(4)	N2	C14	C15	107.3(5)
C13	C8	N1	119.2(5)	C5	C6	C1	120.5(7)
C9	C8	N1	121.6(4)	C2	C3	C4	118.3(7)
C9	C8	C13	119.2(5)	C19	C20	C21	104.1(9)
C8	C13	N2	117.5(5)	C21	C22	O3	112.0(11)
C12	C13	N2	122.8(5)	C14	C15	C16	108.2(5)
C12	C13	C8	119.8(5)	C1	C2	C3	121.6(7)
C10	C9	C8	119.8(5)	C22	C21	C20	109.9(11)
C19	C18	N1	108.8(5)	C6	C1	C7	119.8(8)
C17	C18	N1	108.5(5)	C2	C1	C6	119.1(8)
C17	C18	C19	113.1(5)	C2	C1	C7	121.1(8)

Table 6 Torsion Angles for 130322.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C10	C9	C8	179.0(4)	C9	C8	C13	N2	178.1(5)
Br1	C10	C11	C12	-178.6(4)	C9	C8	C13	C12	-2.6(8)
S1	N1	C8	C13	110.8(5)	C18	N1	C8	C13	-32.7(7)
S1	N1	C8	C9	-71.4(6)	C18	N1	C8	C9	145.1(5)
S1	N1	C18	C19	145.3(4)	C18	C19	O3	C22	-178.6(6)
S1	N1	C18	C17	-91.2(5)	C18	C19	C20	C21	176.1(7)
S1	C4	C5	C6	-176.6(6)	C4	S1	N1	C8	-81.0(4)
S1	C4	C3	C2	176.4(5)	C4	S1	N1	C18	61.2(5)
N1	S1	C4	C5	74.3(5)	C4	C5	C6	C1	0.1(11)
N1	S1	C4	C3	-102.2(5)	C4	C3	C2	C1	0.4(11)
N1	C8	C13	N2	-4.1(7)	C19	C18	C17	N2	80.3(7)

N1	C8	C13	C12	175.3(5)	C19	C18	C17	C16	-100.9(8)
N1	C8	C9	C10	-177.1(5)	C19	O3	C22	C21	6.4(11)
N1	C18	C19	O3	-49.0(7)	C19	C20	C21	C22	-1.8(12)
N1	C18	C19	C20	141.5(8)	C11	C10	C9	C8	0.8(8)
N1	C18	C17	N2	-40.5(7)	C5	C4	C3	C2	0.0(9)
N1	C18	C17	C16	138.3(7)	C5	C6	C1	C2	0.3(12)
O1	S1	N1	C8	35.3(5)	C5	C6	C1	C7	177.7(8)
O1	S1	N1	C18	177.5(4)	O3	C19	C20	C21	6.2(10)
O1	S1	C4	C5	-40.6(5)	O3	C22	C21	C20	-3.0(13)
O1	S1	C4	C3	142.9(5)	C17	N2	C13	C8	19.0(7)
N2	C13	C12	C11	-177.7(5)	C17	N2	C13	C12	-160.4(5)
N2	C14	C15	C16	-0.9(7)	C17	N2	C14	C15	0.9(7)
C10	C11	C12	C13	-1.5(9)	C17	C18	C19	O3	-169.7(6)
C8	N1	C18	C19	-70.0(6)	C17	C18	C19	C20	20.8(11)
C8	N1	C18	C17	53.5(6)	C17	C16	C15	C14	0.6(7)
C8	C13	C12	C11	3.0(8)	C14	N2	C13	C8	-152.8(5)
O2	S1	N1	C8	164.3(4)	C14	N2	C13	C12	27.8(8)
O2	S1	N1	C18	-53.5(5)	C14	N2	C17	C18	178.6(5)
O2	S1	C4	C5	-172.3(5)	C14	N2	C17	C16	-0.5(6)
O2	S1	C4	C3	11.3(6)	C3	C4	C5	C6	-0.2(10)
C13	N2	C17	C18	5.5(7)	C3	C2	C1	C6	-0.5(12)
C13	N2	C17	C16	-173.6(5)	C3	C2	C1	C7	-177.9(8)
C13	N2	C14	C15	173.5(5)	C20	C19	O3	C22	-7.6(9)
C13	C8	C9	C10	0.7(8)	C15	C16	C17	N2	-0.1(7)
C9	C10	C11	C12	-0.4(9)	C15	C16	C17	C18	-179.0(7)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 130322.

Atom	*x*	*y*	*z*	U(eq)
H9	12744	14036	10500	55
H18	14027	17186	11850	67
H11	8341	13674	10696	63
H16	12451	17826	12892	69
H5	12541	13077	12266	72
H12	8437	14983	11517	55
H14	8956	15523	12556	67
H6	11812	12793	13224	91
H3	15612	15650	12789	76
H20	11082	18998	11542	124

H22	12988	19099	9993	139
H15	10073	16951	13303	81
H2	14840	15352	13751	93
H21	11249	20100	10547	135
H7A	11864	14422	14292	175
H7B	13493	14129	14495	175
H7C	12454	12992	14295	175