Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Natural Carbolines Inspired the Discovery of Chiral CarOx Ligands for Asymmetric Synthesis and Antifungal Leads

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Content

General Information

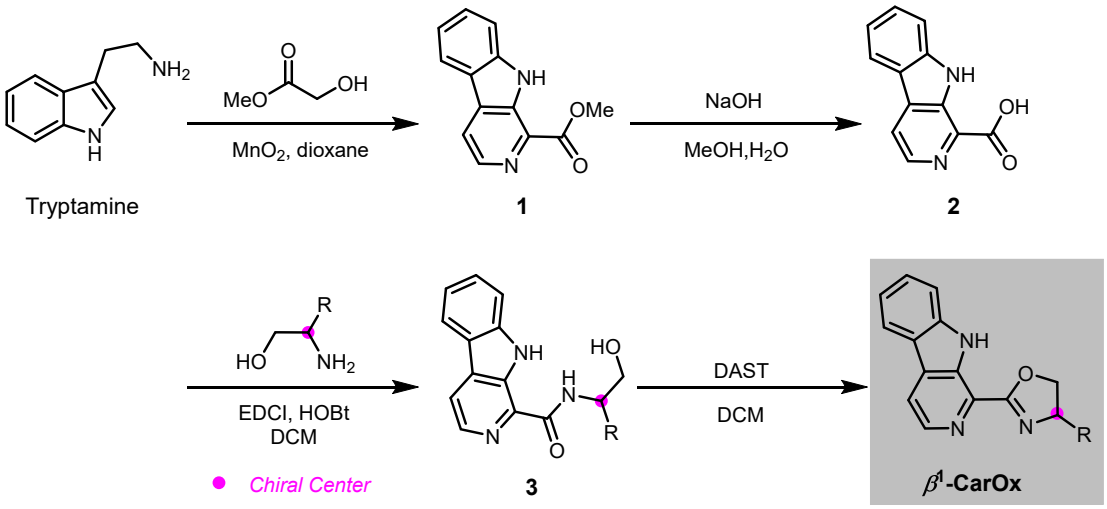
Unless otherwise stated, all solvents and reagents were purchased from commercial sources (Energy or Meryer Chemicals etc.), they were analytically pure and used without further purification. Anhydrous solvents were dried and distilled by standard techniques before use or were purchased from commercial sources (Energy Chemicals etc.).

Silica gel GF_{254} and column chromatography silica gel for isolation (200-300 mesh) were both purchased from Qingdao Broadchem Industrial Co., Ltd. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} with ultraviolet (UV_{254nm} or UV_{365nm}) detection. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker AV 400 or Bruker AV 500 spectrometers with $CDCl_3$ as solvent and tetramethylsilane as the internal standard. The chemical shifts (δ) were recorded in parts per million (ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ: ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet), coupling constant (Hz), integration and assignment (*H*). Data for ^{13}C NMR are reported in terms of chemical shift (δ: ppm). Electrospray ionization high-resolution mass spectrometry (ESI-HRMS) data were also obtained with the Waters XEVO G2-XS Q-TOF mass spectrometer.

The agriculturally important plant pathogens were provided by the College of Plant Protection, Nanjing Agricultural University (Nanjing, China). The in *vitro* antifungal activities of the synthesized natural product alangiobussinine and its analogues were carried out according to the procedures we used previously[1].

Synthesis and Structural Elucidation of β^1-CarOx Ligands

Synthetic Route to the Chiral β^1-CarOx Ligands



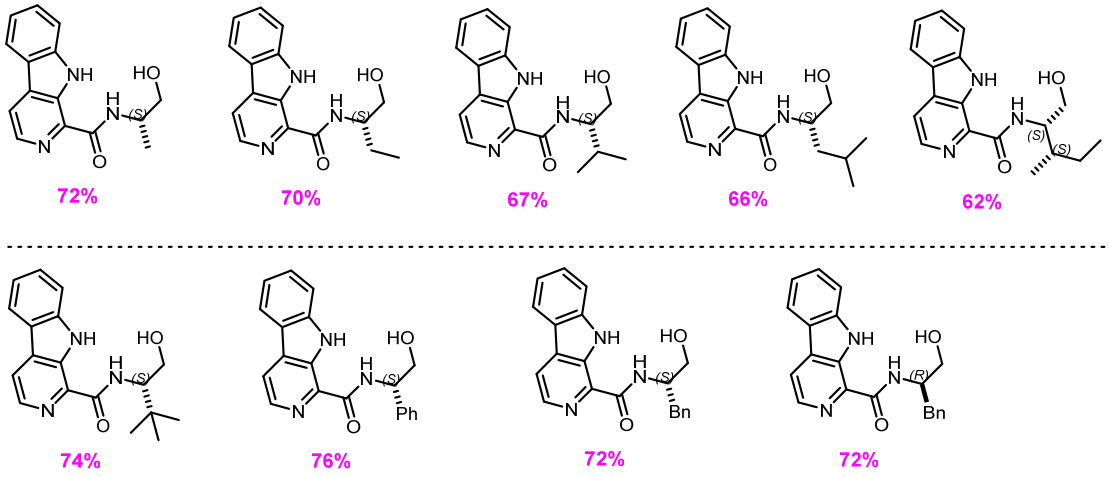
Step 1, Synthesis of the intermediate **1** according to the report by Lang,[2] To a stirred suspension of tryptamine (3.2 g, 20 mmol) and 3A MS (20 g) was added 1,4-dioxane (50 mL). MnO_2 (17 g) and methyl glycolate (2.7 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at room temperature for 3h and then was immersed in a preheated oil bath (110 °C) until the full consumption of the starting material was detected by thin layer chromatography (TLC). The heterogeneous mixture was filtered and rinsed with ethyl acetate. The organic phase concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300m) with hexane/EtOAc (2:1, v/v) as the eluent gave the β-carboline-1-carboxylic methyl ester (intermediate **1**) as yellow solid in 42% yield.

Step 2, To a stirred suspension of β-carboline-1-carboxylic methyl ester **1** (2.26 g, 10 mmol) was added methanol (30 mL). Aqueous sodium hydroxide solution (10 mL, 1 M) was added dropwise at 0 °C. The heterogeneous mixture was immersed in a preheated oil bath (50 °C) and was stirred until the full consumption of the starting material was detected by thin layer chromatography (TLC). The mixture was concentrated under vacuum to remove methanol, and was adjusted to pH 6-7 with hydrochloric acid, from which the β-carboline-1-carboxylic acid (intermediate **2**) was precipitated, the heterogeneous mixture was filtered, and the β-carboline-1-carboxylic

acid intermediate **2** was collected and dried as a yellow solid in 89% yield.

Step 3, ***general procedure of Steglich Condensation*:** To a dried Schlenk flask charged with the synthesized *β*-carboline-1-carboxylic acid, compound **2**, (1 mmol, 212 mg) and the specific chiral amino alcohol (1 mmol), was added anhydrous dichloromethane (5 mL) for dissolution. Hydroxybenzotriazole (HOBt) (175 mg, 1.3 mmol) and *N*-(3-(dimethyl amino)propyl)-*N′*-ethylcarbodiimide hydrochloride (EDCI-HCl) (0.25 g, 1.3 mmol) were then added while the reaction flask was in an ice bath. The mixture was allowed to gradually warm to room temperature, and it was stirred overnight until full consumption of the carboxylic acid detected by thin layer chromatography (TLC). The mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) and separated. The water phase was extracted with dichloromethane (10 mL × 3), and the combined organic phase was sequentially washed with water (10 mL × 2) and saturated aqueous NaCl (10 mL), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300m) with hexane/EtOAc (2:1, v/v) as the eluent gave the amide intermediate **3**.

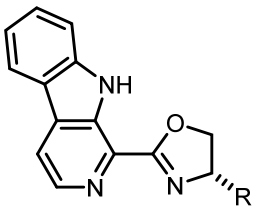
Yields for the intermediate **3** are listed below,



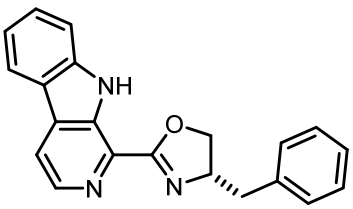
Step 4, *General procedure for the DAST mediated cyclization to produce* ***β*^{1}-CarOx** *Ligand*: To a Schlenk tube charged the amide intermediate **3** (1.0 mmol) was added anhydrous DCM (5.0 mL) under N_2 atmosphere. Diethylaminosulfur trifluoride (DAST) (160mg, 1mmol) was added dropwise at -78 ° C. The reaction mixture was

stirred at -78 °C until the full consumption of the starting material was detected by TLC. The mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (10 mL) and separated, The water phase was extracted with dichloromethane (10 mL × 3), and the combined organic phase was sequentially washed with water (10 mL × 2) and saturated aqueous NaCl (10 mL), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300m) with hexane/EtOAc (2:1, v/v) as the eluent gave the chiral ligand ***β*¹-CarOx**.

Yields for the chiral ligands ***β*¹-CarOx** are listed below,

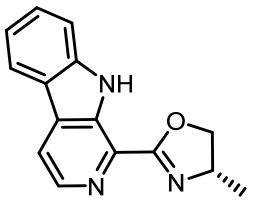


L1: (*S*)-Me-*β*¹CarOx **75%**
L2: (*S*)-Et-*β*¹CarOx **73%**
L3: (*S*)-iPr-*β*¹CarOx **68%**
L4: (*S*)-iBu-*β*¹CarOx **66%**
L5: (*S*)-sBu-*β*¹CarOx **73%**
L6: (*S*)-tBu-*β*¹CarOx **77%**
L7: (*S*)-Ph-*β*¹CarOx **75%**
L8: (*S*)-Bn-*β*¹CarOx **64%**



L9: (*R*)-Bn-*β*¹CarOx **64%**

Characterization of the Synthesized Chiral *β*¹-CarOx Ligands



L1 **(*S*)-Me-*β*¹-CarOx**

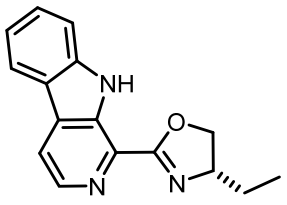
(*S*)-4-methyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

White solid, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.47 (d, J = 6.44 Hz, 3H, *CH₃*), 4.12 (dd, J_1 = 7.60 Hz, J_2 = 7.52 Hz, 1H, O*CH₂*CH), 4.58 (m, 1H, OCH₂*CH*), 4.66 (dd, J_1 = 9.36 Hz, J_2 = 7.84 Hz, 1H, O*CH₂*CH), 7.31 (m, 1H, *H in Benzene Ring*), 7.57-7.60 (m, 2H,

H in Benzene Ring), 8.04 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 8.13 (dd, J_1 = 7.88 Hz, J_2 = 0.96 Hz, 1H, *H in Benzene Ring*), 8.54 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.4 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 62.3, 73.9, 111.9, 116.9, 120.3, 121.3, 121.9, 128.9, 129.0, 129.9, 135.8, 138.7, 140.6, 163.1.

HRESI-MS: calcd for $C_{15}H_{14}N_3O$ $[M+H]^+$: 252.1137, found: 252.1140.

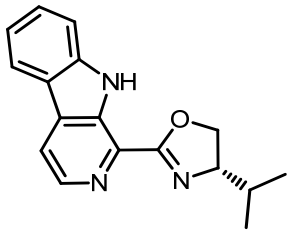
L2  **(*S*)-Et-*β*[1]CarOx**

(*S*)-4-ethyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

White solid, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J = 7.36 Hz, 3H, CH_2CH_3), 1.75 (m, 1H, CH_2CH_3), 1.87 (m, 1H, CH_2CH_3), 4.21 (dd, J_1 = 7.96 Hz, J_2 = 8.00 Hz, 1H, OCH_2CH), 4.46 (m, 1H, OCH_2CH), 4.64 (dd, J_1 = 9.64 Hz, J_2 = 8.00 Hz, 1H, OCH_2CH), 7.31 (m, 1H, *H in Benzene Ring*), 7.56-7.61 (m, 2H, *H in Benzene Ring*), 8.05 (d, J = 5.10 Hz, 1H, *H in Pyridine Ring*), 8.16 (dd, J_1 = 7.92 Hz, J_2 = 1.04 Hz, 1H, *H in Benzene Ring*), 8.54 (d, J = 5.10 Hz, 1H, *H in Pyridine Ring*), 10.4 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 10.3, 28.9, 68.3, 72.1, 112.0, 117.0, 120.3, 121.3, 121.9, 128.9, 129.1, 129.9, 135.9, 138.7, 140.6, 163.1.

HRESI-MS: calcd for $C_{16}H_{16}N_3O$ $[M+H]^+$: 266.1293, found: 266.1576.



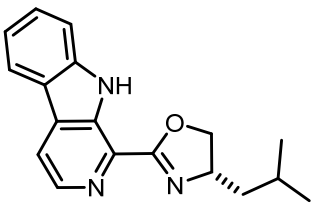
L3 **(*S*)-iPr-*β*[1]CarOx**

(*S*)-4-isopropyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

Pale yellow solid, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.03 (d, *J* = 6.72 Hz, 3H, CH(*CH*$_3$)$_2$), 1.14 (d, *J* = 6.72 Hz, 3H, CH(*CH*$_3$)$_2$), 1.97 (m, 1H, *CH*(CH$_3$)$_2$), 4.28-4.35 (m, 2H, O*CH*$_2$CH), 4.59 (m, 1H, OCH$_2$*CH*), 7.32 (m, 1H, *H in Benzene Ring*), 7.58-7.64 (m, 2H, *H in Benzene Ring*), 8.07 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 8.16 (d, *J* = 7.84 Hz, 1H, *H in Benzene Ring*), 8.55 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.37 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 19.1, 33.1, 70.2, 72.9, 112.0, 117.0, 120.3, 121.4, 121.9, 128.9, 129.0, 129.9, 135.9, 138.7, 140.6.

HRESI-MS: calcd for $C_{17}H_{18}N_3O$ [M+ H] $^{+}$: 280.1483, found: 280.1450.



L4 **(*S*)-iBu-*β*[1]CarOx**

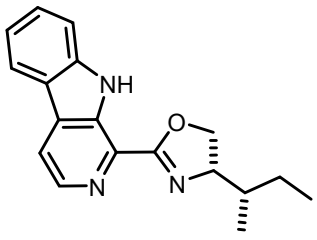
(*S*)-4-isobutyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

Pale yellow solid, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 6H, CH(*CH*$_3$)$_2$), 1.51 (m, 1H, *CH*(CH$_3$)$_2$), 1.82 (m, 1H, *CH*$_2$CH(CH$_3$)$_2$), 1.93 (m, 1H, *CH*$_2$CH(CH$_3$)$_2$), 4.14 (m, 1H, O*CH*$_2$CH), 4.54 (m, 1H, OCH$_2$*CH*), 4.66 (m, 1H, O*CH*$_2$CH), 7.29 (m, 1H, *H in Benzene Ring*), 7.57-7.60 (m, 2H, *H in Benzene Ring*), 8.03 (d, *J* = 5.08 Hz, 1H, *H in Pyridine*

Ring), 8.13 (dd, J_1 = 7.84 Hz, J_2 = 0.96 Hz, 1H, *H in Benzene Ring*), 8.53 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.34 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 22.9, 25.8, 45.8, 65.4, 73.0, 112.0, 116.9, 120.3, 121.3, 121.9, 128.9, 129.1, 129.9, 135.9, 138.7, 140.6, 162.9.

HRESI-MS: calcd for $C_{18}H_{20}N_3O$ $[M+H]^+$: 294.1606, found: 294.1610.



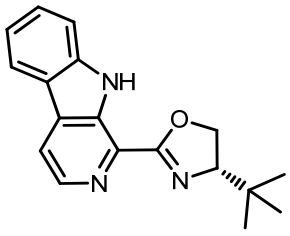
L5 **(*S*)-sBu-*β*^{1}CarOx**

(*S*)-4-((*S*)-sec-butyl)-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

Yellow wax, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.95 (d, J = 6.72 Hz, 3H, CH_2CH_3), 1.02 (t, J = 7.40 Hz, 3H, CH_2CH_3), 1.34 (m, 1H, $CH$$CH_2CH_3$), 1.72 (m, 1H, $CHCH_2CH_3$), 1.82 (m, 1H, $CHCH_2CH_3$), 4.29 (dd, J_1 = 8.08 Hz, J_2 = 8.08 Hz, 1H, OCH_2CH), 4.43 (m, 1H, OCH_2CH), 4.56 (dd, J_1 =9.48 Hz, J_2 = 8.08 Hz, 1H, OCH_2CH), 7.31 (m, 1H, *H in Benzene Ring*), 7.56-7.61 (m, 2H, *H in Benzene Ring*), 8.04 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 8.14 (d, J_1 = 7.20 Hz, 1H, *H in Benzene Ring*), 8.53 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.36 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 14.6, 26.3, 39.4, 69.7, 71.5, 112.0, 117.0, 120.3, 121.3, 121.9, 128.9, 129.0, 129.9, 135.9, 138.7, 140.6, 163.0.

HRESI-MS: calcd for $C_{18}H_{20}N_3O$ $[M+H]^+$: 294.1606, found: 294.1611.



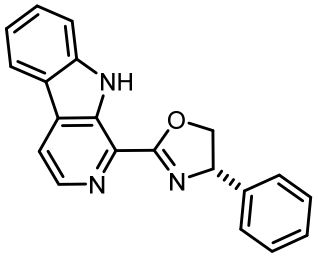
L6 **(*S*)-tBu-*β*[1]CarOx**

(*S*)-4-(tert-butyl)-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

White solid, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H, C(*CH*$_3$)$_3$), 4.28 (dd, J_1 = 10.00 Hz, J_2 = 7.92 Hz, 1H, O*CH*$_2$CH), 4.40 (dd, J_1 = 8.48 Hz, J_2 = 7.92 Hz, 1H, OCH$_2$*CH*), 4.53 (dd, J_1 = 10.00 Hz, J_2 = 8.48 Hz, 1H, O*CH*$_2$CH), 7.32 (m, 1H, *H in Benzene Ring*), 7.59-7.60 (m, 2H, *H in Benzene Ring*), 8.07 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 8.16 (d, *J* = 7.88 Hz, 1H, *H in Benzene Ring*), 8.55 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.37 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1 (3C), 34.1, 68.7, 76.4, 112.0, 117.0, 120.4, 121.4, 122.0, 128.9, 129.0, 129.9, 136.0, 138.7, 140.6, 163.1.

HRESI-MS: calcd for $C_{18}H_{20}N_3O$ $[M+H]^+$: 294.1606, found: 294.1606.



L7 **(*S*)-Ph-*β*[1]CarOx**

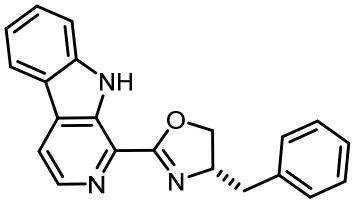
(S)-4-phenyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

Pale yellow solid, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.43 (dd, J_1 = 8.48 Hz, J_2 = 8.44 Hz, 1H, O*CH*$_2$CH), 4.97 (dd, J_1 = 10.08 Hz, J_2 = 8.44 Hz, 1H, OCH$_2$*CH*), 5.61 (J_1 = 10.08 Hz, J_2 = 8.48 Hz, 1H, O*CH*$_2$CH), 7.28-7.38 (m, 2H, *H in Benzene Ring*), 7.38-7.48 (m, 4H, *H in Benzene Ring*), 7.55 (m, 2H, *H in Benzene Ring*), 8.07 (d, *J* = 5.08 Hz, 1H, *H*

in Pyridine Ring), 8.16 (d, *J* = 7.88 Hz, 1H, *H in Benzene Ring*), 8.55 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.37 (s, br, 1H, *NH*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 70.4, 74.8, 112.0, 117.3, 120.4, 121.3, 121.9, 126.9 (2C), 128.0, 128.6, 129.0 (2C), 129.1, 130.1, 136.1, 138.8, 140.6, 142.2, 164.5.

HRESI-MS: calcd for $C_{20}H_{16}N_3O$ $[M+H]^+$: 314.1293, found: 314.1869.

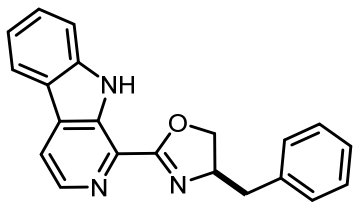
L8  **(*S*)-Bn-*β*^{1}CarOx**

(*S*)-4-benzyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

Yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.92 (dd, J_1 = 13.60 Hz, J_2 = 7.96 Hz, 1H, CH_2Ph), 3.25 (dd, J_1 = 13.60 Hz, J_2 = 6.56 Hz, 1H, CH_2Ph), 4.32 (dd, J_1 = 7.84 Hz, J_2 = 8.04 Hz, 1H), 4.57 (dd, J_1 = 9.12 Hz, J_2 = 8.04 Hz, 1H), 4.79 (m, 1H), 7.29-7.35 (m, 4H, *H in Benzene Ring*), 7.35-7.39 (m, 2H, *H in Benzene Ring*), 7.55-7.62 (m, 2H, *H in Benzene Ring*), 8.07 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 8.16 (d, *J* = 7.88 Hz, 1H, *H in Benzene Ring*), 8.55 (d, *J* = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.34 (s, br, 1H, *NH*).

^{13}C NMR (125 MHz, $CDCl_3$) δ 42.4, 68.2, 72.1, 111.9, 117.1, 120.4, 121.3, 122.0, 126.7, 128.7, 128.9, 129.0, 129.3, 130.0, 136.0, 138.1, 138.7, 140.7, 163.6.

HRESI-MS: calcd for $C_{21}H_{18}N_3O$ $[M+H]^+$: 328.1450, found: 328.1448.

L9  **(*R*)-Bn-*β*^{1}CarOx**

(*R*)-4-benzyl-2-(9H-pyrido[3,4-b]indol-1-yl)-4,5-dihydrooxazole

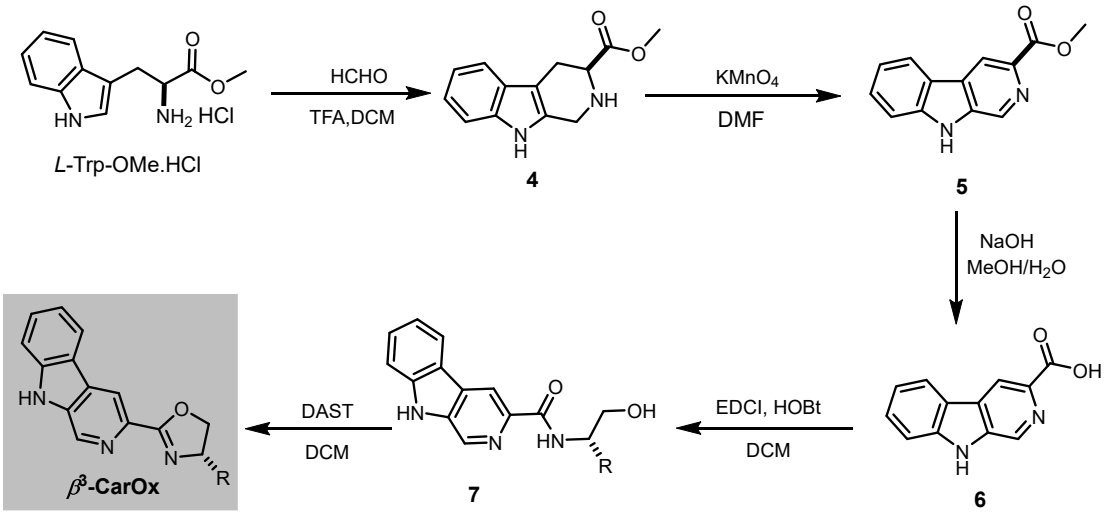
Yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.92 (dd, J_1 = 13.60 Hz, J_2 = 7.96 Hz, 1H, CH_2Ph), 3.25 (dd, J_1 = 13.60 Hz, J_2 = 6.56 Hz, 1H, CH_2Ph), 4.32 (dd, J_1 = 7.84 Hz, J_2 = 8.04 Hz, 1H), 4.56 (dd, J_1 = 9.12 Hz, J_2 = 8.04 Hz, 1H), 4.78 (m, 1H), 7.27-7.35 (m, 4H, *H in Benzene Ring*), 7.35-7.40 (m, 2H, *H in Benzene Ring*), 7.54-7.63 (m, 2H, *H in Benzene Ring*), 8.07 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 8.17 (dd, J_1 = 7.08 Hz, J_1 = 1.08 Hz, 1H, *H in Benzene Ring*), 8.55 (d, J = 5.08 Hz, 1H, *H in Pyridine Ring*), 10.34 (s, br, 1H, *NH*).

^{13}C NMR (100125 MHz, $CDCl_3$) δ 42.3, 68.2, 72.1, 111.9, 117.1, 120.4, 121.3, 122.0, 126.7, 128.7, 128.9, 129.0, 129.3, 130.0, 136.0, 138.1, 138.7, 140.7, 163.6.

HRESI-MS: calcd for $C_{21}H_{18}N_3O$ $[M+H]^+$: 328.1450, found: 328.1448.

Synthesis and Structural Elucidation of *β*^{3}-CarOx Ligands

Synthetic Route to the Chiral *β*^{3}-CarOx Ligands



Step 1, To a stirred suspension of *L*-Tryptophan methyl ester hydrochloride (5.1 g, 20

mmol) and 37% formalin (40 mL) was added anhydrous dichloromethane. Trifluoroacetic acid (TFA) (3.26 mL) was added dropwise at 0 °C. The reaction mixture was stirred until the full consumption of the starting material detected by TLC. The mixture was quenched by the addition of 10% aqueous potassium carbonate solution (20 mL). The water phase was extracted with ethyl acetate (20 mL × 3), dried over anhydrous sodium sulfate, and concentrated under vacuum. This crude (*S*)-*β*-1,2,3,4-tetrahydrocarboline -3-carboxylic acid methyl ester **4** (91% yield) was used for the next step without further purification.

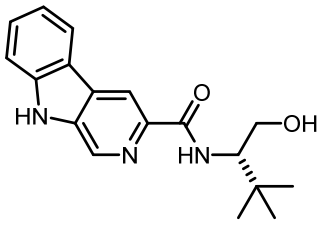
Step 2, To a stirred solution of (*S*)-*β*-1,2,3,4-tetrahydrocarboline-3-carboxylic acid methyl ester **4** (4.6 g, 20 mmol) in DMF (60 mL) was added potassium permanganate ($KMnO_4$) (2.3 g, 20 mmol) in portions while the mixture was in an ice bath. The reaction mixture was stirred vigorously and allowed to gradually warm to room temperature until the full consumption of the starting material was detected by TLC. The heterogeneous mixture was filtered and rinsed with distilled methanol. The *β*-carboline-3-carboxylic acid methyl ester, compound **5**, was collected as yellow solid in 62% yield (2.8 g). Compound **5** was used for the next step without further purification.

Step 3, To a stirred suspension of *β*-carboline-3-carboxylic acid methyl ester **5** (2.80 g, 12 mmol) was added methanol (30 mL). Aqueous sodium hydroxide solution (12 mL, 1 M) was added dropwise at 0 °C. The heterogeneous mixture was immersed in a preheated oil bath (50 ℃) and stirred until the full consumption of the starting material was detected by TLC. The mixture was concentrated under vacuum to remove methanol and was adjusted to pH 6-7 with hydrochloric acid to precipitate the desired product, the heterogeneous mixture was filtered to give *β*-carboline-1-carboxylic acid intermediate **6** as yellow solid in 92% yield (2.34 g). This intermediate was used for the next step without further purification.

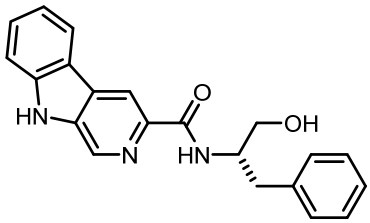
Step 4, *General procedure for Steglich Condensation*: To a dried Schlenk flask charged with the synthesized *β*-carboline-3-carboxylic acid, compound **6**, (1 mmol, 212 mg) and the specific chiral amino alcohol (1 mmol), was added anhydrous dichloromethane (5 mL) for dissolution. Hydroxybenzotriazole (HOBt) (175 mg, 1.3

mmol) and *N*-(3-(dimethyl amino)propyl)-*N*′-ethylcarbodiimide hydrochloride (EDCI-HCl) (0.25 g, 1.3 mmol) were then added while the reaction flask was in an ice bath. The mixture was allowed to gradually warm to room temperature, and it was stirred overnight until full consumption of the carboxylic acid was detected by thin layer chromatography (TLC). The mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) and separated. The water phase was extracted with dichloromethane (10 mL × 3), and the combined organic phase was sequentially washed with water (10 mL × 2) and saturated aqueous NaCl (10 mL), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300m) with hexane/EtOAc (2:1, v/v) as the eluent gave the amide intermediate **7**.

Yields for the intermediate **7** are listed below,



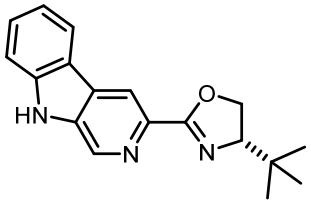
78%



73%

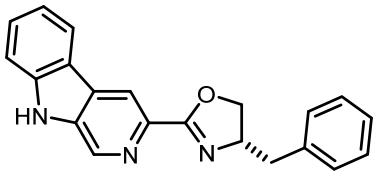
Step 4, General procedure for the DAST mediated cyclization to produce β^3-CarOx Ligand: To a Schlenk tube charged the amide intermediate **7** (1.0 mmol) was added anhydrous DCM (5.0 mL) under N_2 atmosphere. Diethylaminosulfur trifluoride (DAST) (160 mg, 1mmol) was added dropwise at -78 ℃ until the full consumption of the starting material was detected by TLC. The mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (10 mL) and separated, The water phase was extracted with dichloromethane (10 mL × 3), and the combined organic phase was sequentially washed with water (10 mL × 2) and saturated aqueous NaCl (10 mL), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300m) with hexane/EtOAc (2:1, v/v) as the eluent gave the product ***β*^{3}-CarOx** Ligand.

Yields for ***β*^{3}-CarOx** ligands are listed below,



L10: (*S*)-tBu-β^3CarOx

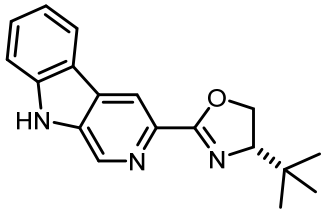
72%



L11: (*S*)-Bn-β^3CarOx

67%

Characterization of the Synthesized Chiral β^3-CarOx Ligands



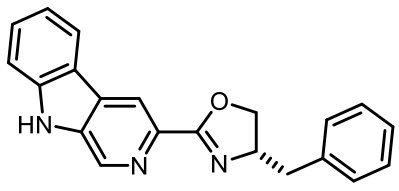
L10 **(*S*)-tBu-β^3CarOx**

(*S*)-4-(tert-butyl)-2-(9H-pyrido[3,4-b]indol-3-yl)-4,5-dihydrooxazole

White solid, ^{1}H-NMR (500MHz, $CDCl_3$) δ 1.00 (s, 9H, C(CH_3)$_3$), 4.18 (dd, J_1 = 10.05 Hz, J_2 = 8.05 Hz, 1H, OCH_2CH), 4.36 (t, J = 8.25 Hz, 1H, OCH$_2$$CH$), 4.50 (dd, J_1 = 9.95 Hz, J_2 = 8.40 Hz, 1H, OCH_2CH), 7.31 (m, 1H, *H in Benzene Ring*), 7.53-7.56 (m, 2H, *H in Benzene Ring*), 8.14 (d, J = 9.90Hz, 1H, *H in Benzene Ring*), 8.78 (s, 1H, *H in Pyridine Ring*), 8.94 (s, 1H, *H in Pyridine Ring*), 9.75 (s, br, 1H, *NH*).

^{13}H-NMR (125 MHz, $CDCl_3$) δ 26.0, 34.1, 63.3, 76.4, 112.0, 116.2, 120.6, 121.5, 122.0, 128.9, 129.1, 133.3, 136.1, 136.9, 140.9, 163.3.

HRESI-MS: calcd for $C_{18}H_{20}N_3O$ [M+ H] $^+$: 294.1606, found: 294.1606.



L11 **(*S*)-Bn-β^3CarOx**

(*S*)-4- Benzyl-2-(9H-pyrido[3,4-b]indol-3-yl)-4,5-dihydrooxazole

White solid, ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.80 (dd, J_1 = 9.15 Hz, J_2 = 13, 85 Hz, 1H,

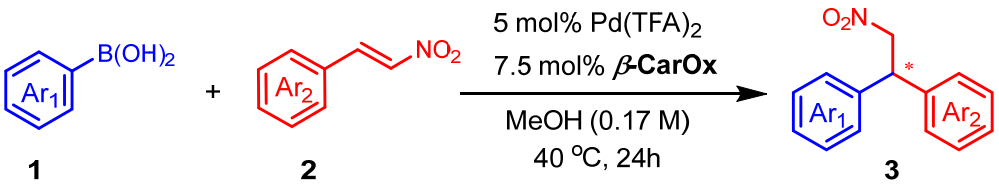
CH$_2$Ph), 3.34 (dd, J_1 = 5.05 Hz, J_2 = 13.80 Hz, 1H, *CH*$_2$Ph), 4.28 (t, *J*= 7.95Hz, 1H), 4.49 (t, *J*= 9.25 Hz, 1H), 4.73 (m, 1H), 7.17-7.20 (s, 1H, *H in Benzene Ring*), 7.25-7.32 (m, 5H, *H in Benzene Ring*), 7.52-7.56 (m, 2H, *H in Benzene Ring*), 8.12 (d, *J* = 7.90 Hz, 1H, *H in Benzene Ring*), 8.78 (s, 1H, *H in Pyridine Ring*), 8.98 (s, 1H, *H in Pyridine Ring*), 10.20 (s, br, 1H, *NH*).

^{13}H-NMR (125 MHz, $CDCl_3$) δ 42.0, 68.0, 72.5, 112.1, 116.2, 120.5, 121.5, 121.9, 126.6, 128.6, 128.8, 129.0, 129.2, 133.6, 135.7, 137.1, 137.9, 141.4, 164.4.

HRESI-MS: calcd for $C_{21}H_{18}N_3O$ $[M+H]^+$: 328.1451, found: 328.1349.

Enantioselective Michael Addition of Arylboronic Acids to Nitroalkenes:

General procedure



1 **2** **3**

To a Schlenk tube charged $Pd(TFA)_2$ (4.15 mg, 0.0125 mmol) and the specific chiral ***β*-CarOx** ligand (0.01875 mmol) was added MeOH (1.0 mL) under N_2 atmosphere. The mixture was stirred at 40 ℃ for 0.5 h to afford the catalyst solution.

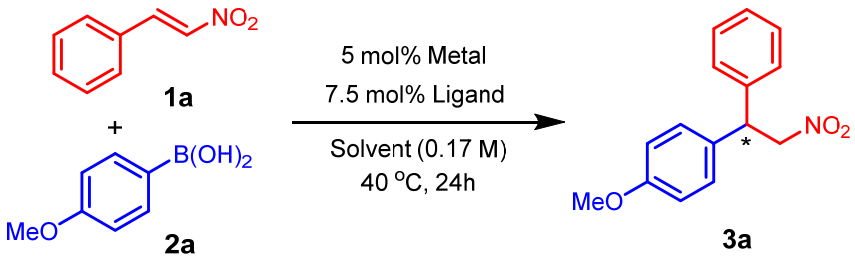
To the above solution was added nitrostyrene **1** (0.25 mmol) and aryl boronic acid **2** (0.375 mmol). The wall of the tube was rinsed with MeOH (0.5 mL) or some oil substrate was dissolved in MeOH (0.5 mL) (The volume of solvent is 1.5 mL). The tube was placed in the modules of the reactor which was set at 40 ℃. After stirring for 24 h, the reaction mixture was cooled to room temperature, and the solvent was removed by

rotary evaporation. The residue was purified by column chromatography (petroleum/ether/EtOAc = 20/1, v/v) to give the product.

2-(isoquinolin-3-yl)-4,5-dihydrooxazole was utilized as a ligand for the preparation of the racemic products.

Optimization of the Reaction Conditions

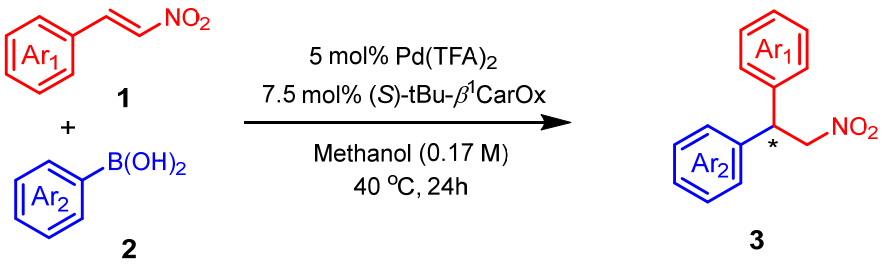
Table 1. Optimization of the Reaction Conditions [a]



Enrty	Metal	Ligand	Solvent	Isolated Yield (%) [b]	ee (%) [c]
1	$Pd(TFA)_2$	$\mathbf{L_1}$	MeOH	81	80（*S*）
2	$Pd(TFA)_2$	$\mathbf{L_2}$	MeOH	82	86（*S*）
3	$Pd(TFA)_2$	$\mathbf{L_3}$	MeOH	88	89（*S*）
4	$Pd(TFA)_2$	$\mathbf{L_4}$	MeOH	78	87（*S*）
5	$Pd(TFA)_2$	$\mathbf{L_5}$	MeOH	78	87（*S*）
6	$Pd(TFA)_2$	$\mathbf{L_6}$	MeOH	92	95（*S*）
7	$Pd(TFA)_2$	$\mathbf{L_7}$	MeOH	86	85（*S*）
8	$Pd(TFA)_2$	$\mathbf{L_8}$	MeOH	84	89（*S*）
9	$Pd(TFA)_2$	$\mathbf{L_9}$	MeOH	81	88（*R*）
10	$Pd(TFA)_2$	$\mathbf{L_{10}}$	MeOH	89	80（*S*）
11	$Pd(TFA)_2$	$\mathbf{L_{11}}$	MeOH	85	73（*S*）
12	$Pd(OAc)_2$	$\mathbf{L_6}$	MeOH	49	83（*S*）
13	$PdCl_2$	$\mathbf{L_6}$	MeOH	<5	n.d.
14	$Pd(TFA)_2$	$\mathbf{L_6}$	EtOH	82	92（*S*）
15	$Pd(TFA)_2$	$\mathbf{L_6}$	^{i}Pr-OH	51	73（*S*）
16	$Pd(TFA)_2$	$\mathbf{L_6}$	^{t}Bu-OH	64	75（*S*）
17	$Pd(TFA)_2$	$\mathbf{L_6}$	2-Methyl-2-butanol	58	66（*S*）
18	$Pd(TFA)_2$	$\mathbf{L_6}$	TFE	51	71（*S*）

[a], unless otherwise mentioned, reactions were carried out on a 0.25 mmol of 2a, 0.375 mmol of *para*-MeO-$C_6H_4B(OH)_2$ using 5 mol % $Pd(TFA)_2$ and 7.5 mol % ligand in 1.5 mL solvent at 40 °C for 24 h under N_2 atmosphere. [b], Isolated yield. [c], Determined by HPLC using a Daicel column (OD-H). The absolute configuration was assigned by comparing the retention time of **3aa** with that reported in the literature.[3] n.d. = not determined.

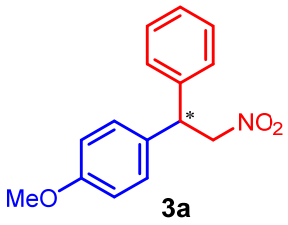
Substrate Scope



NOTE:

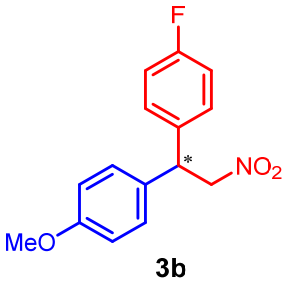
The *nitroalkenes* and *arylboronic acids* *were highlighted by red and blue, respectively.*

Data marked (CC) means that they were reported in "*Chem. Commun.* 2019, 55, 5902-5905."[4]



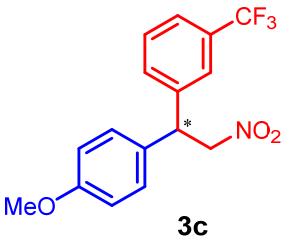
3a

92% yield; 95% ee
84% yield; 93% ee (CC)



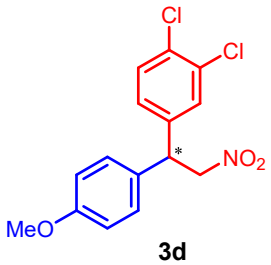
3b

87%yield; 96%ee
75%yield; 76%ee (CC)



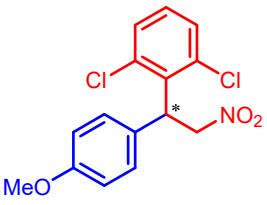
3c

86%yield; 94% ee
73%yield; 80% ee (CC)



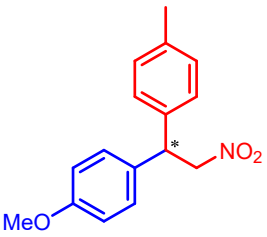
3d

72% yield; 92% ee
67% yield; 82% ee (CC)



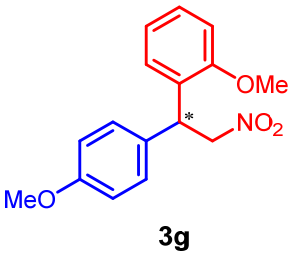
3e

70%yield; 82%ee
64%yield; 64%ee (CC)



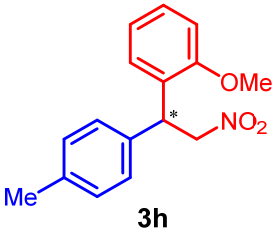
3f

92%yield; 98%ee
74%yield; 80%ee (CC)



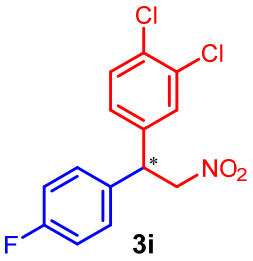
3g

94% yield; 96% ee
70% yield; 87% ee (CC)



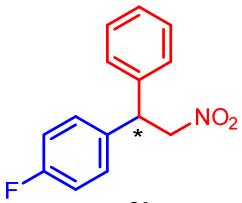
3h

81%yield; 89%ee



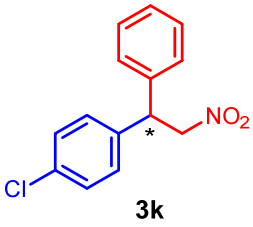
3i

63% yield; 74% ee



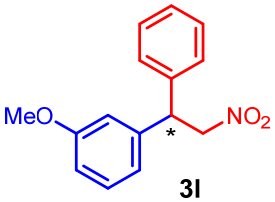
3j

70% yield; 73% ee
65% yield; 77% ee(CC)



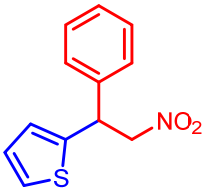
3k

72%yield; 62% ee
65%yield; 70%ee(CC)



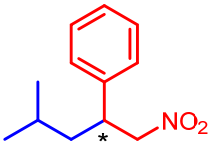
3l

78% yield; 80% ee
71% yield; 82% ee(CC)



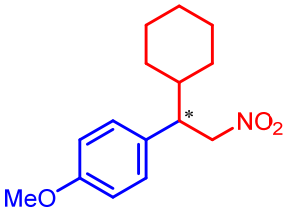
3m

<5% yield; n.d.



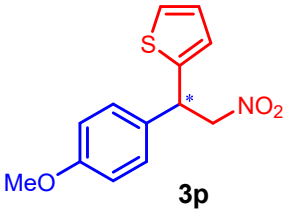
3n

<5% yield; n.d.



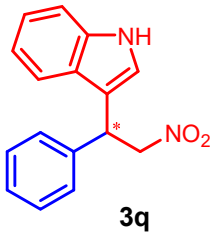
3o

<5% yield; n.d.



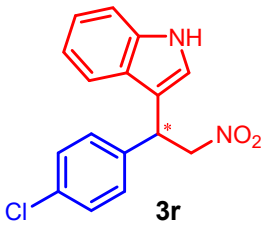
3p

62% yield; 86% ee
57% yield; 84% ee(CC)



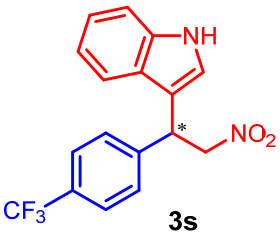
3q

60% yield; 61% ee



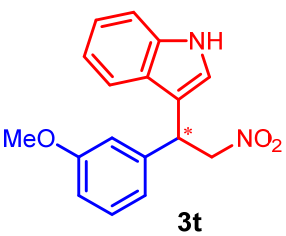
3r

60% yield; 71% ee



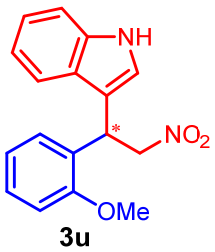
3s

57% yield; 83% ee



3t

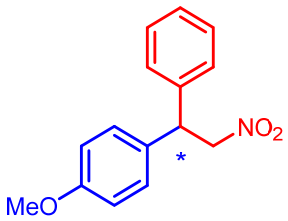
58% yield; 63% ee.



3u

48% yield; 90% ee.

HPLC traces of the Enantioenriched *β*-aryl nitroethanes



3a

Colorless oil, 92% yield.

The NMR data is in accordance with that of previous publications.[4-7]

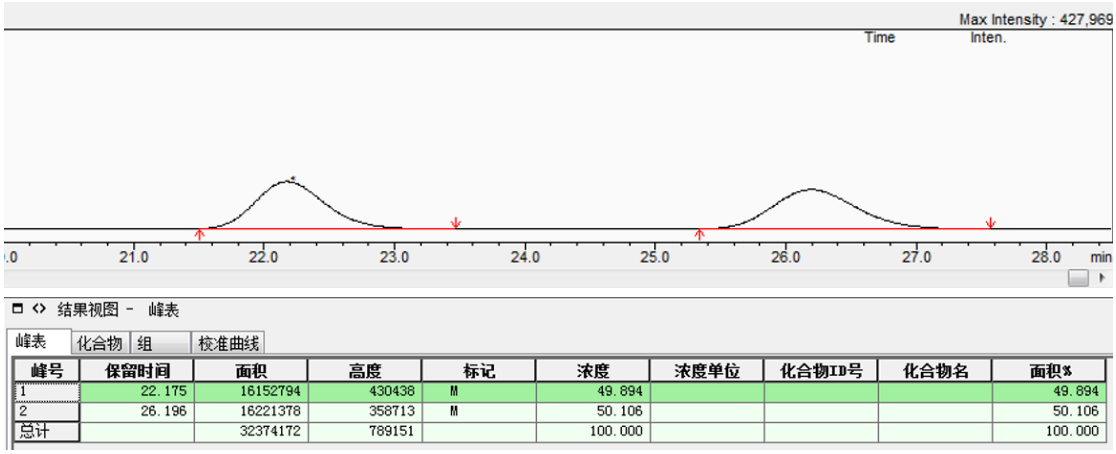
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.78 (s, 3H, OCH_3), 4.86 (m,1H), 4.94-4.96 (m, 2H), 6.84-6.87(m, 2H, Aromatic H), 7.13-7.18 (m, 2H, Aromatic H), 7.20-7.24 (m, 2H, Aromatic H), 7.26 (m, 1H, Aromatic H), 7.29-7.36 (m, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 80/20, 220 nm, 1.0 mL/min.

t_{R1} = 23.4 min (major), t_{R2} = 25.5 min (minor)];

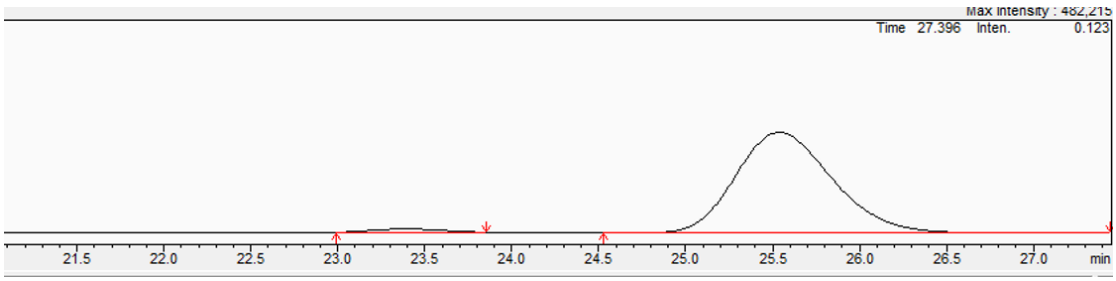
ee = 95.3%.



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

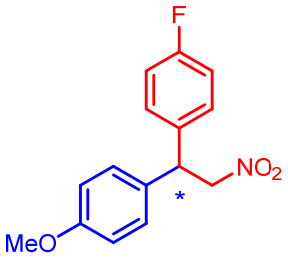
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	22.175	16152794	430438	M	49.894				49.894
2	26.196	16221378	358713	M	50.106				50.106
总计		32374172	789151		100.000				100.000



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	23.393	453753	16200	M	2.375				2.375
2	25.538	18648163	482200		97.625				97.625
总计		19101915	498401		100.000				100.000



3b

Colorless oil, 87% yield.

The NMR data is in accordance with that of previous publications.[4-5]

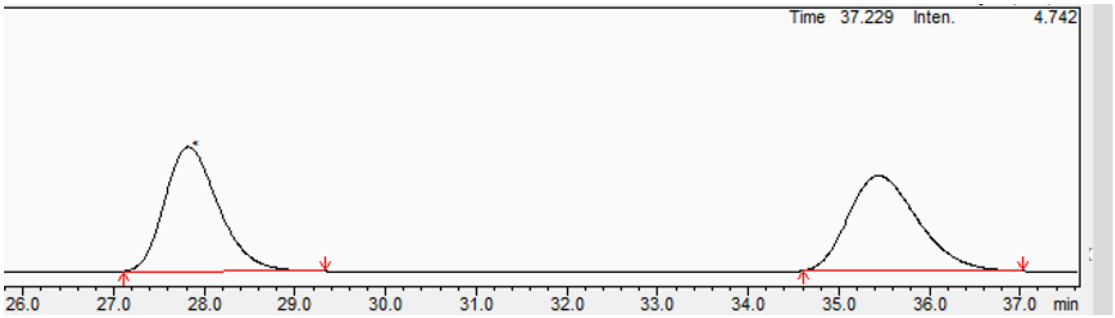
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.78 (s, 3H, OCH_3), 4.84 (m, 1H), 4.89-4.94 (m, 2H), 6.84-6.89 (m, 2H, Aromatic H), 6.99-7.04 (m, 2H, Aromatic H), 7.10-7.15 (m, 2H, Aromatic H), 7.17-7.21 (m, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 60/40, 220 nm, 1.0 mL/min.

t_{R1} = 28.0 min (major), t_{R2} = 35.7 min (minor)

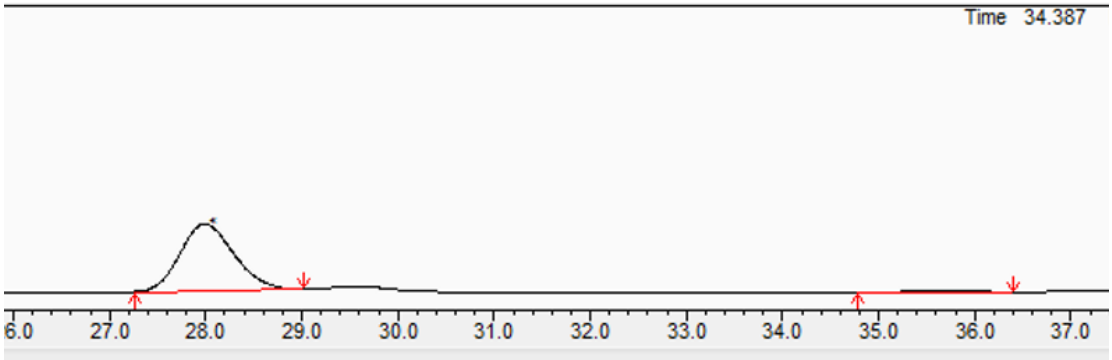
ee = 96.2%.



结果视图 - 峰表

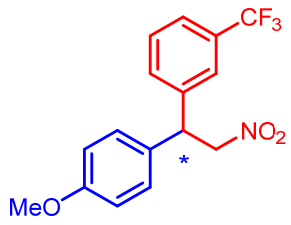
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	27.822	66747221	1619743	M	50.225				50.225
2	35.439	66150033	1240699	M	49.775				49.775
总计		132897254	2860442		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	27.991	14909476	379895	M	98.097				98.097
2	35.691	289180	6290	M	1.903				1.903
总计		15198657	386185		100.000				100.000



3c

Colorless oil, 86% yield.

The NMR data is in accordance with that of previous publication.[4]

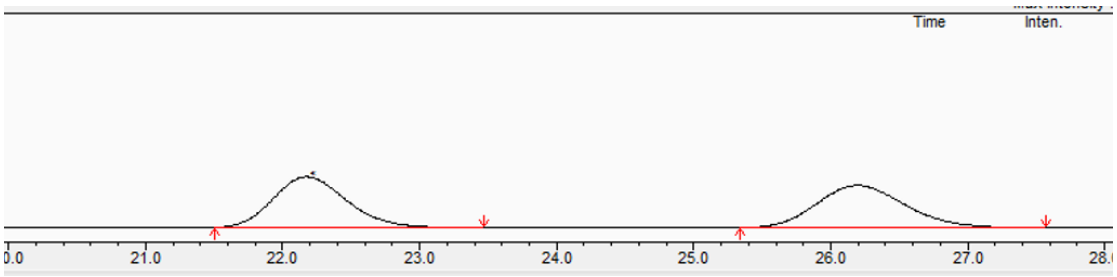
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.79 (s, 3H, OCH_3), 4.92 (m, 1H), 4.95-5.00 (m, 2H), 6.86-6.91 (m, 2H, Aromatic H), 7.12-7.16 (m, 2H, Aromatic H), 7.41-7.50 (m, 3H, Aromatic H), 7.53 (d, J = 7.16 Hz, 1H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 60/40, 220 nm, 1.0 mL/min.

t_{R1} = 19.7 min (major), t_{R2} = 23.3 min (minor)

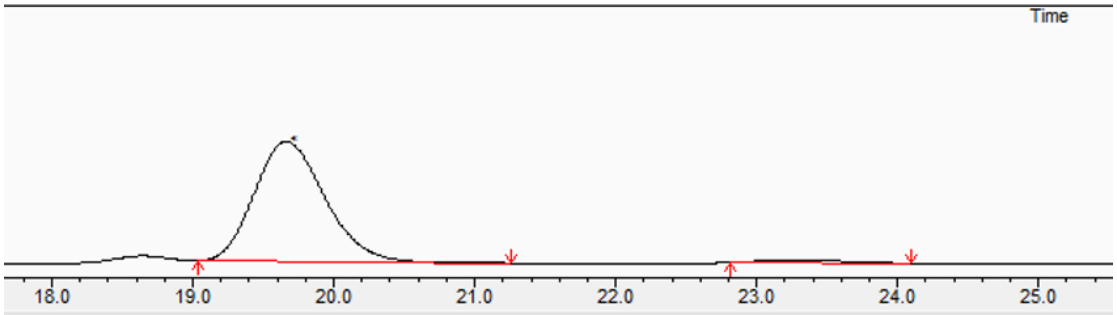
ee = 94.4%.



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

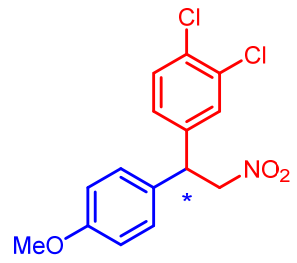
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	22.175	16152794	430438	M	49.894				49.894
2	26.196	16221378	358713	M	50.106				50.106
总计		32374172	789151		100.000				100.000



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	19.663	26903411	775608	M	97.191				97.191
2	23.274	777493	21148	M	2.809				2.809
总计		27680904	796756		100.000				100.000



3d

Colorless oil, 72% yield.

The NMR data is in accordance with that of previous publication.[4]

^{1}H NMR (400 MHz, $CDCl_3$), δ 3.79 (s, 3H, OCH_3), 4.82 (dd, J_1 = 8.76 Hz, J_2 = 7.20 Hz, 1H), 4.92-4.95 (m, 2H), 6.85-6.89 (m, 2H, Aromatic H), 7.08 (dd, J_1 = 8.36 Hz, J_2 = 2.24 Hz, 1H), 7.09-7.13 (m, 2H, Aromatic H), 7.31 (d, J = 2.2 Hz, 1H, Aromatic H), 7.40 (d, J = 8.28 Hz, 1H, Aromatic H).

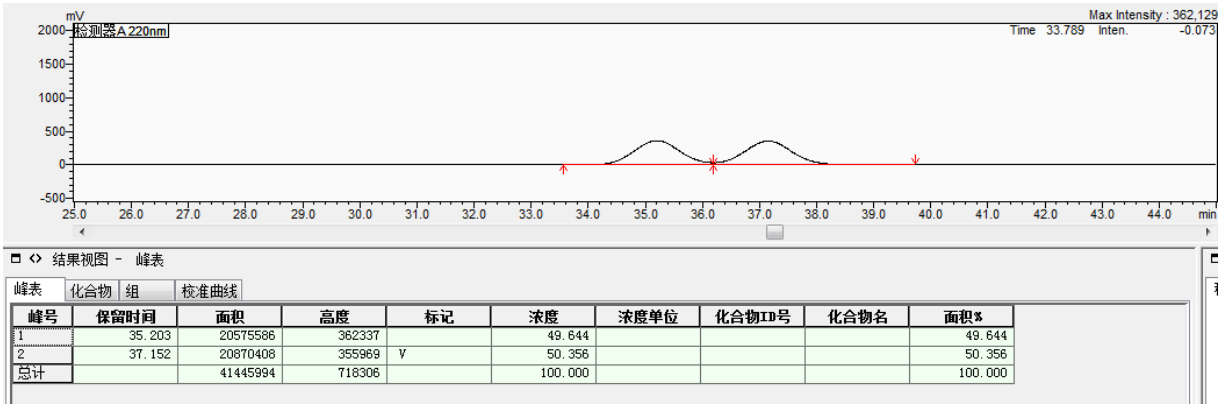
HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 0.8 mL/min.

t_{R1} = 35.2 min (major), t_{R2} = 37.1 min (minor);

ee = 92.4%.

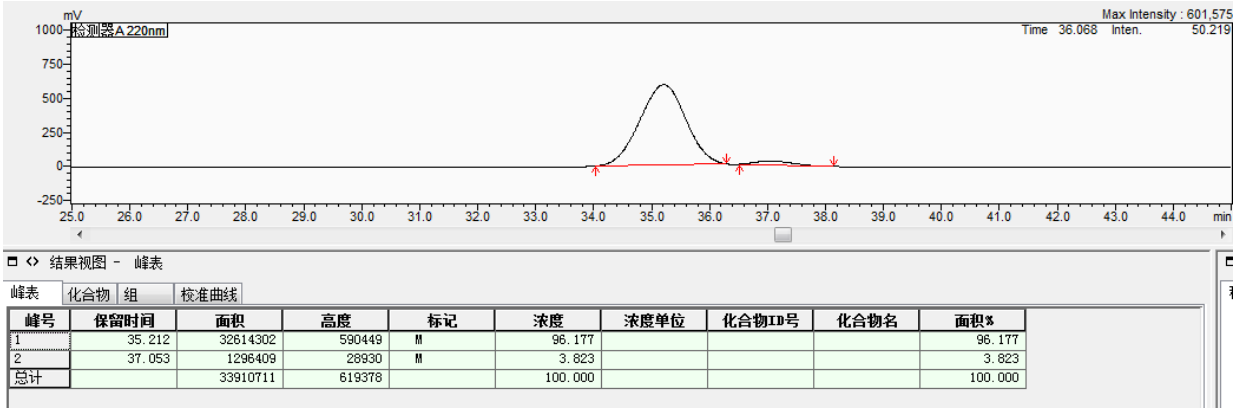
.



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

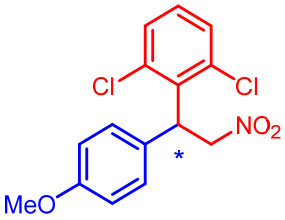
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	35.203	20575586	362337		49.644				49.644
2	37.152	20870408	355969	V	50.356				50.356
总计		41445994	718306		100.000				100.000



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	35.212	32614302	590449	M	96.177				96.177
2	37.053	1296409	28930	M	3.823				3.823
总计		33910711	619378		100.000				100.000



3e

Colorless oil, 70% yield.

The NMR data is in accordance with that of previous publication.[4]

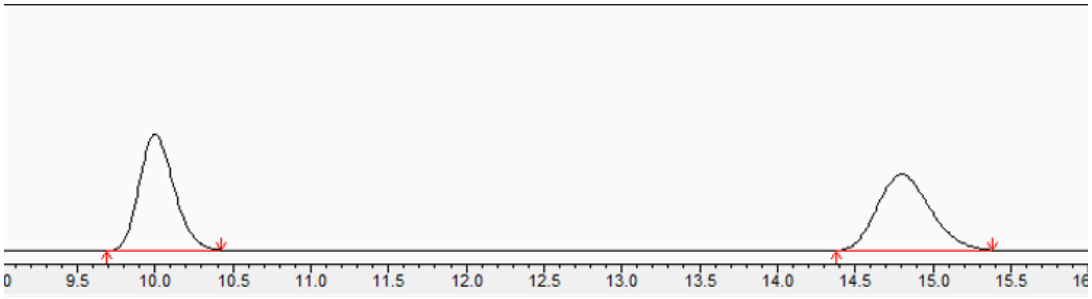
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.78 (s, 3H, OCH_3), 5.26 (dd, J_1 = 13.28 Hz, J_2 = 7.44 Hz, 1H), 5.42 (dd, J_1 = 13.28 Hz, J_2 = 7.44 Hz, 1H), 5.95 (dd, J_1 = J_2 = 7.44 Hz, 1H), 6.82-6.86 (m, 2H, Aromatic H), 7.08-7.14 (m, 2H, Aromatic H), 7.18 (dd, J_1 = J_2 = 8.28 Hz, 1H, Aromatic H), 7.28-7.40 (m, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 80/20, 220 nm, 1.0 mL/min.

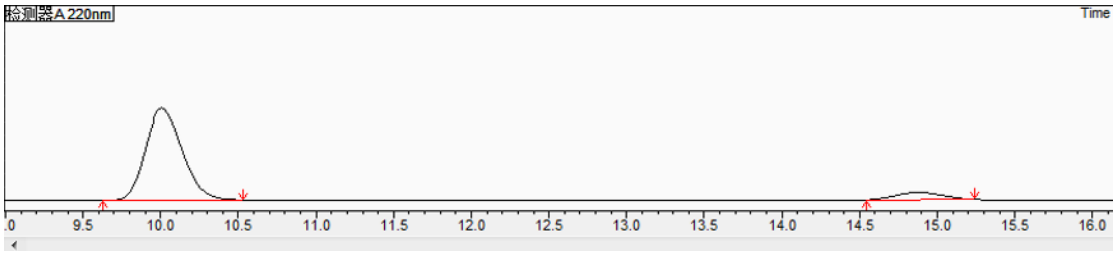
t_{R1} = 10.0 min (major), t_{R2} = 14.9 min (minor);

ee = 81.7%.



峰表 | 化合物 | 组 | 校准曲线

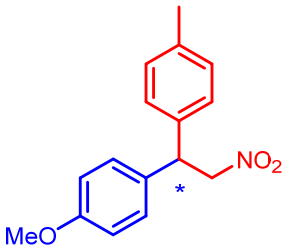
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.999	21783513	1397434	M	50.237				50.237
2	14.799	21578117	913969	M	49.763				49.763
总计		43361630	2311403		100.000				100.000



结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.008	22985275	1405201	M	90.842				90.842
2	14.878	2317212	110417	M	9.158				9.158
总计		25302487	1515618		100.000				100.000



3f

Colorless oil, 92% yield.

The NMR data is in accordance with that of previous publications.[4, 6]

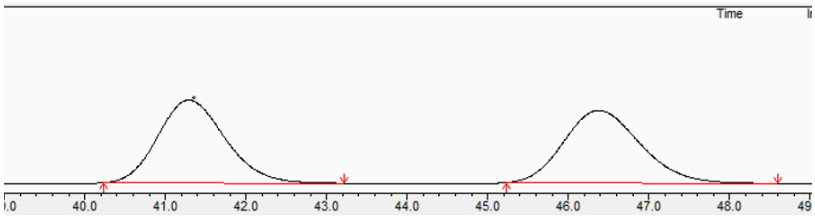
^{1}H NMR (400 MHz, $CDCl_3$), δ 2.31 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.82 (dd, $J_1 = J_2 = 8.16$ Hz, 1H), 4.92-4.94 (m, 2H), 6.82-6.87 (m, 2H, Aromatic H), 7.09-7.17 (m, 6H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 80/20, 220 nm, 1.0 mL/min.

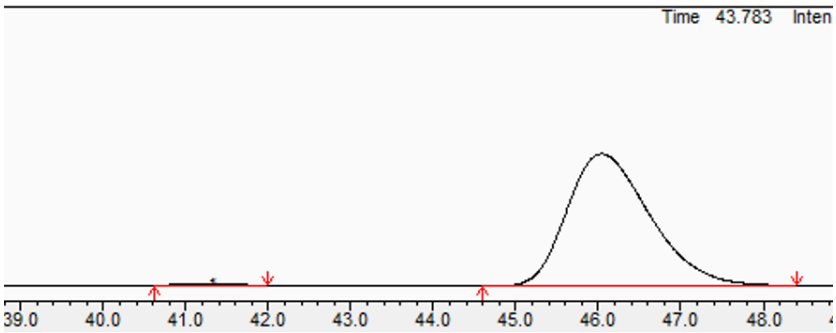
t_{R1} = 41.3 min (major), t_{R2} = 46.0 min (minor)];

ee = 97.9%.



峰表 | 化合物 | 组 | 校准曲线

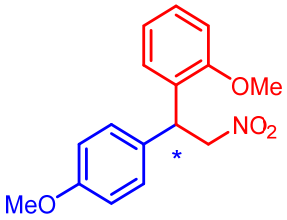
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	41.293	9812310	168850	M	50.158				50.158
2	46.376	9750620	147578	M	49.842				49.842
总计		19562930	316428		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	41.253	1216241	26876	M	1.065				1.065
2	46.041	112934712	1613060	M	98.935				98.935
总计		114150953	1639936		100.000				100.000

3g



Colorless oil, 94% yield.

The NMR data is in accordance with that of previous publication.[4]

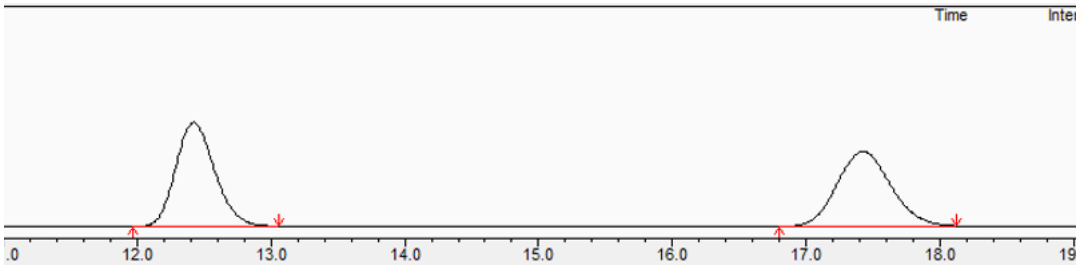
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.77 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.91 (dd, J_1 = 12.76 Hz, J_2 = 9.32 Hz, 1H), 5.01 (dd, J_1 = 12.76 Hz, J_2 = 6.84 Hz, 1H), 5.21 (dd, J_1 = 9.32 Hz, J_2 = 6.84 Hz, 1H), 6.83-6.87 (m, 2H, Aromatic H), 6.87-6.92 (m, 2H, Aromatic H), 7.05 (dd, J_1 = 7.44 Hz, J_2= 1.64 Hz, 1H, Aromatic H), 7.17-7.21 (m, 2H, Aromatic H), 7.22 (dd, J_1 = 7.72 Hz, J_2 = 1.60 Hz, 1H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 80/20, 220 nm, 1.0 mL/min.

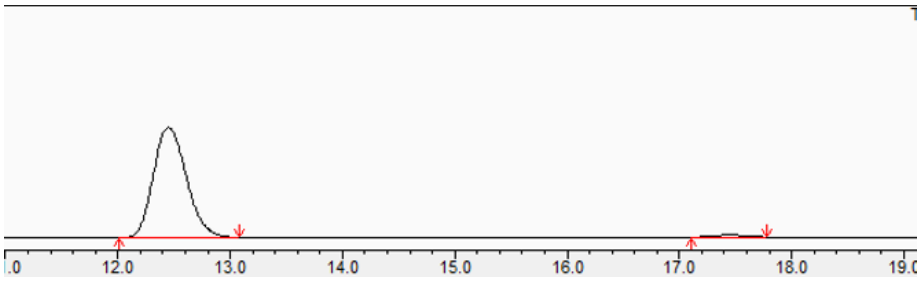
t_{R1} = 12.5 min (major), t_{R2} = 17.5 min (minor)];

ee = 95.7%.



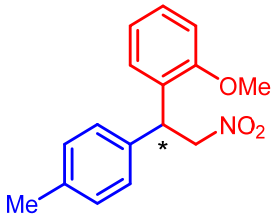
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.424	33190704	1638671	M	50.169				50.169
2	17.424	32966899	1178456	M	49.831				49.831
总计		66157602	2817126		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.451	66673023	3240052	M	97.897				97.897
2	17.444	1432411	64390	M	2.103				2.103
总计		68105435	3304442		100.000				100.000



3h

Colorless oil, 81% yield.

The NMR data is in accordance with that of previous publications.[6, 8]

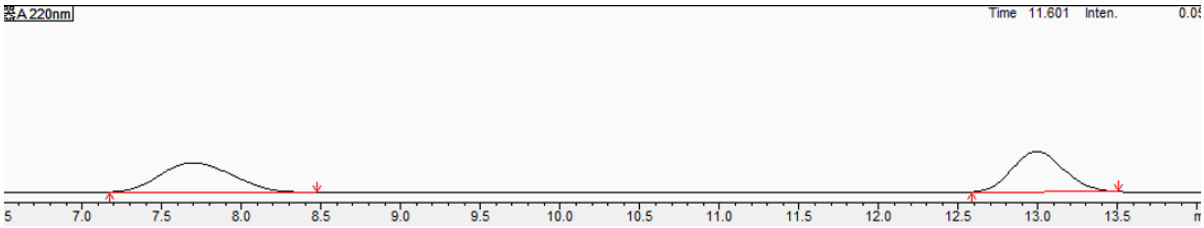
^{1}H NMR (400 MHz, $CDCl_3$), δ 2.31 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 4.90-5.04 (m, 2H), 5.23(m, 1H), 6.88 (t, *J*=8.60 Hz, 2H, Aromatic H), 7.05 (m, 1H, Aromatic H), 7.11(d, *J* =8.12 Hz, 2H, Aromatic H), 7.16 (d, *J* =8.16 Hz, 2H, Aromatic H), 7.23(m, 1H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 90/10, 220 nm, 1.5 mL/min.

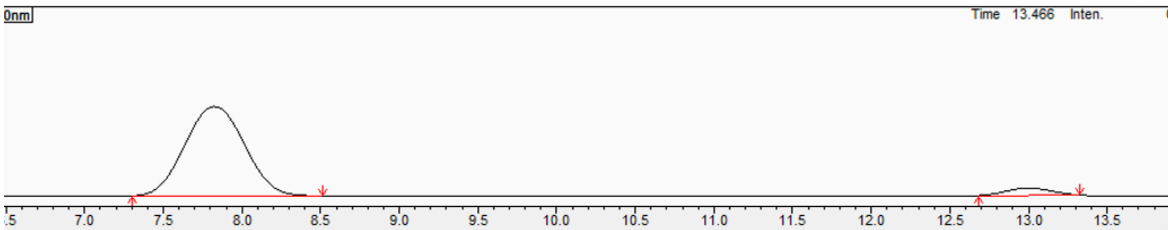
t_{R1} = 7.83 min (major), t_{R2} = 13.0 min (minor)

ee = 88.8%.



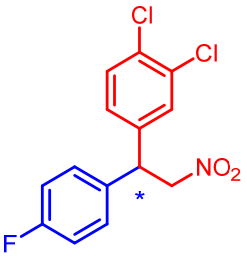
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.696	5910017	187288	M	50.460				50.460
2	12.991	5802165	258236	M	49.540				49.540
总计		11712182	445524		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	7.825	8958936	342260	M	94.374				94.374
2	13.001	534097	27046	M	5.626				5.626
总计		9493032	369306		100.000				100.000



3i

Colorless oil, 63% yield.

^{1}H NMR (500 MHz, $CDCl_3$), δ 4.85 (t, *J*=7.75 Hz, 1H), 4.91-4.93 (m, 2H), 7.03-7.08 (m, 3H, Aromatic H), 7.16-9.19 (m, 2H, Aromatic H), 7.30 (s, 1H, Aromatic H), 7.41 (d, *J*=8.15 Hz, 1H, Aromatic H).

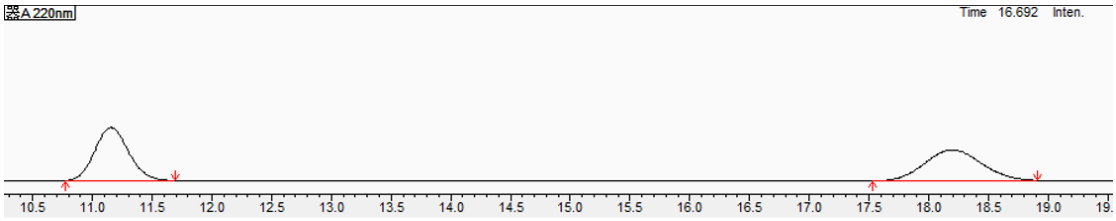
^{13}C NMR (125 MHz, $CDCl_3$), δ 47.3, 78.7, 116.3, 116.4, 126.8, 129.2, 129.3, 129.7, 131.1, 132.9, 133.3, 139.2, 161.3, 163.3.

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.2 mL/min.

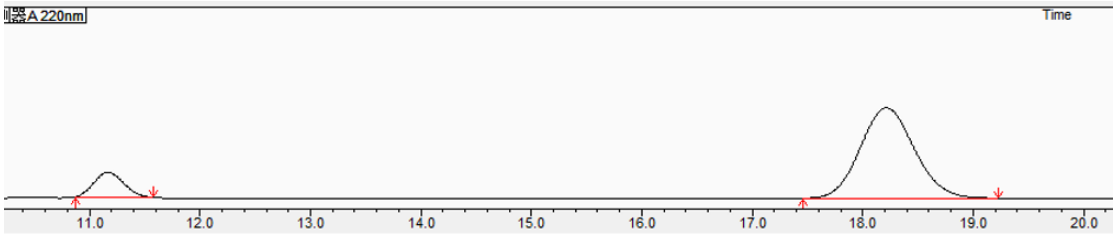
t_{R1} = 18.2 min (major), t_{R2} = 11.2 min (minor)

ee = 73.6%.



峰表 | 化合物 | 组 | 校准曲线

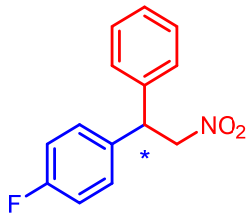
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.155	2295701	116870	M	50.437				50.437
2	18.196	2255936	68187	M	49.563				49.563
总计		4551637	185057		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.167	1500532	80163	M	13.185				13.185
2	18.214	9880402	290313	M	86.815				86.815
总计		11380934	370475		100.000				100.000

3j



Colorless oil, 70% yield.

The NMR data is in accordance with that of previous publications.[4, 8]

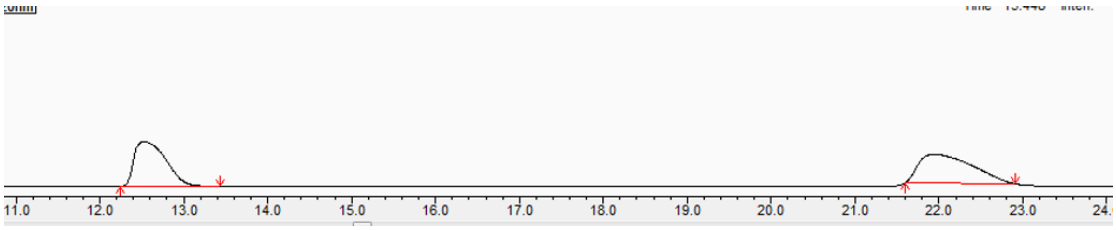
^{1}H NMR (400 MHz, $CDCl_3$), δ 4.88 (m, 1H), 4.91-4.96 (m, 2H), 6.96-7.04 (m, 2H, Aromatic H), 7.16-7.23 (m, 4H, Aromatic H), 7.27 (m, 1H, Aromatic H), 7.29-7.36 (m, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

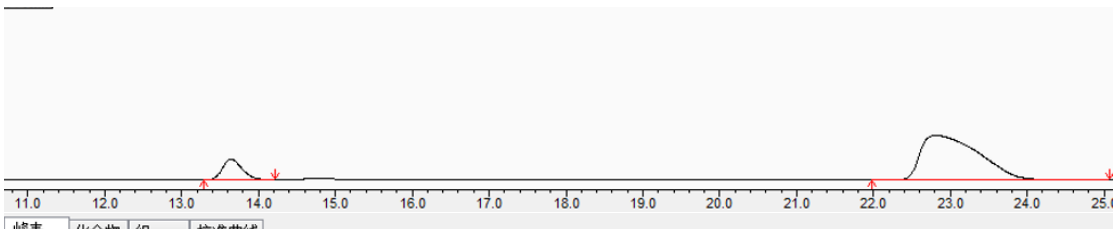
t_{R1} = 13.6min (minor), t_{R2} = 22.8 min (major)

ee = 73.1%.



峰表 | 化合物 | 组 | 校准曲线

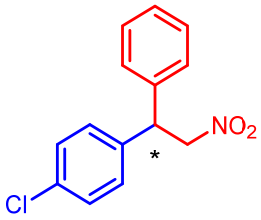
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.525	82331814	3175415	M	47.177				47.177
2	21.945	92186281	2058054	M	52.823				52.823
总计		174518095	5233469		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.640	20255677	1162909	M	13.431				13.431
2	22.814	130561636	2507279	M	86.569				86.569
总计		150817313	3670188		100.000				100.000

3k



Colorless oil, 72% yield.

The NMR data is in accordance with that of previous publications.[4, 6, 8]

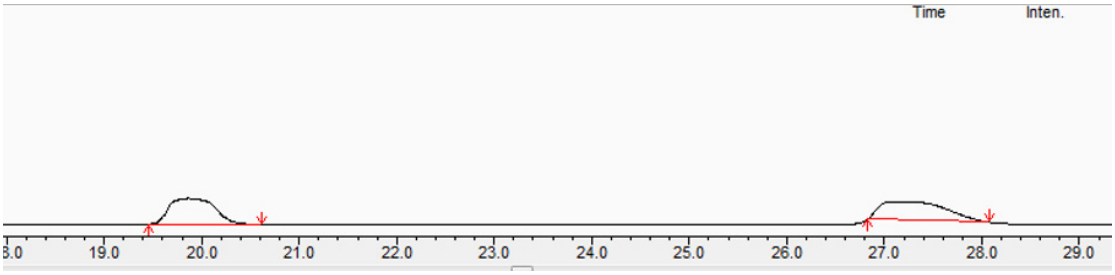
^{1}H NMR (400 MHz, $CDCl_3$), δ 4.88 (m, 1H), 4.92-4.98 (m, 2H), 7.16-7.23 (m, 4H, Aromatic H), 7.27-7.36 (m, 5H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

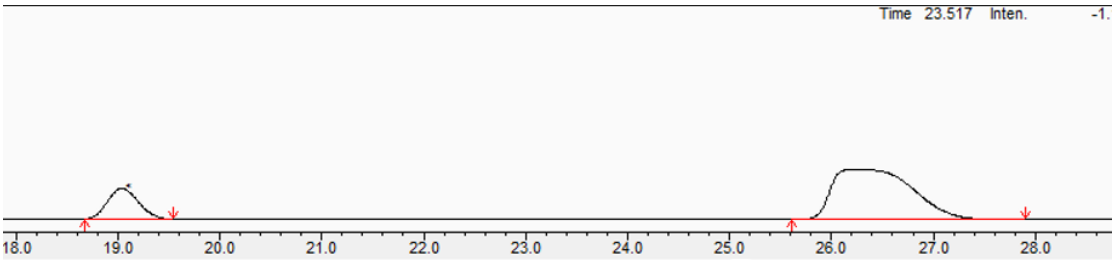
t_{R1} = 17.6 min (minor), t_{R2} = 28.0 min (major)

ee = 61.8%.



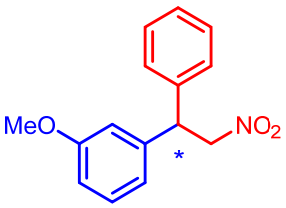
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	19.865	114342747	3536972	M	48.582				48.582
2	27.159	121015176	2557376	M	51.418				51.418
总计		235357922	6094349		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	19.039	41123748	1947397	M	19.105				19.105
2	26.243	174131961	3206748	M	80.895				80.895
总计		215255709	5154145		100.000				100.000



3l

Colorless oil, 78% yield.

The NMR data is in accordance with that of previous publications.[4, 6]

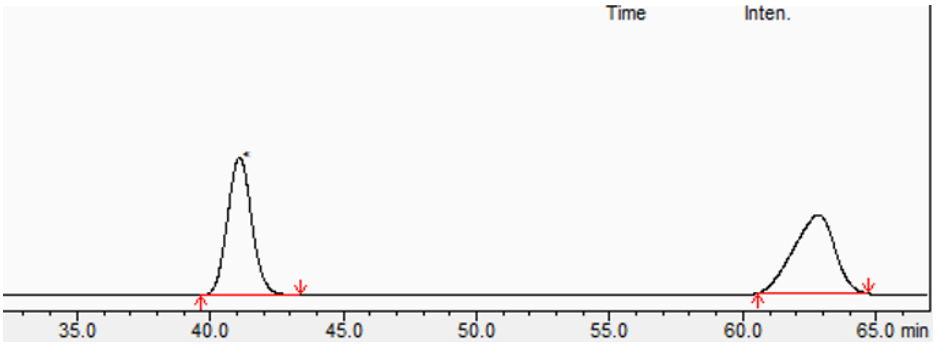
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.77 (s, 3H, OCH_3), 4.87 (m, 1H), 4.94-4.99 (m, 2H), 6.77 (m, 1H, Aromatic H), 6.79 (m, 1H, Aromatic H), 6.84 (d, *J* =7.88 Hz, 1H, Aromatic H), 7.22-7.27 (m, 4H, Aromatic H), 7.30-7.35 (m, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 80/20, 220 nm, 1.0 mL/min.

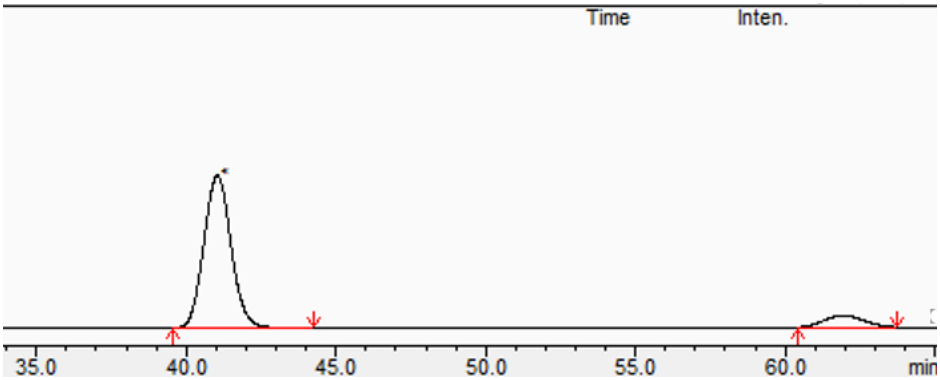
t_{R1} = 41.0 min (minor), t_{R2} = 61.9 min (major)

ee = 79.5%.



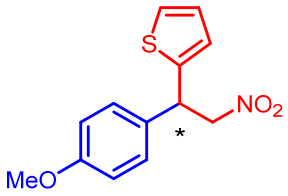
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	41.103	83221152	1310007	M	50.813				50.813
2	62.842	80556923	745155	M	49.187				49.187
总计		163778075	2055162		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	41.040	81822445	1291914	M	89.709				89.709
2	61.927	9386302	101003	M	10.291				10.291
总计		91208748	1392917		100.000				100.000



3p

Colorless oil, 62% yield.

The NMR data is in accordance with that of previous publications.[7-9]

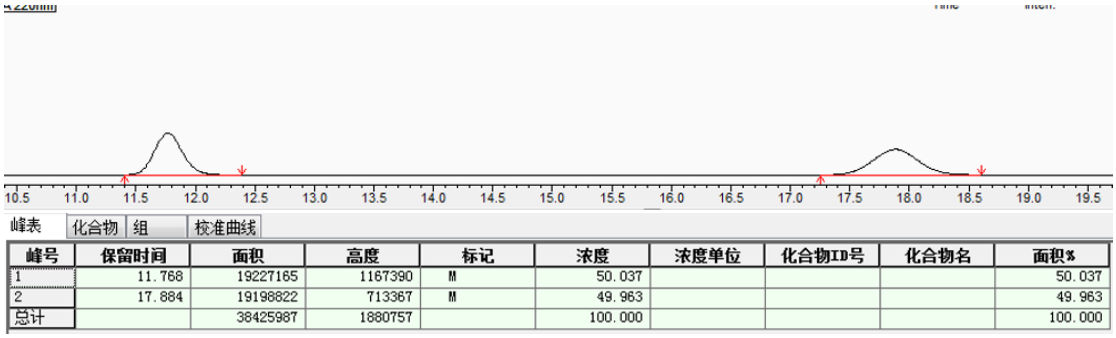
^{1}H NMR (400 MHz, $CDCl_3$), δ 3.79 (s, 3H, OCH_3), 4.89 (dd, J_1 = 12.60 Hz, J_2 = 8.56 Hz, 1H), 4.97 (dd, J_1 = 12.60 Hz, J_2 = 7.52 Hz, 1H), 5.08 (dd, J_1 = 8.56 Hz, J_2 = 7.52 Hz, 1H), 6.86-6.90 (m, 3H, Aromatic H), 6.95 (dd, J_1 = 5.12 Hz, J_2 = 3.52 Hz, 1H, Aromatic H), 7.19-7.24 (m, 3H, Aromatic H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 60/40, 220 nm, 1.0 mL/min.

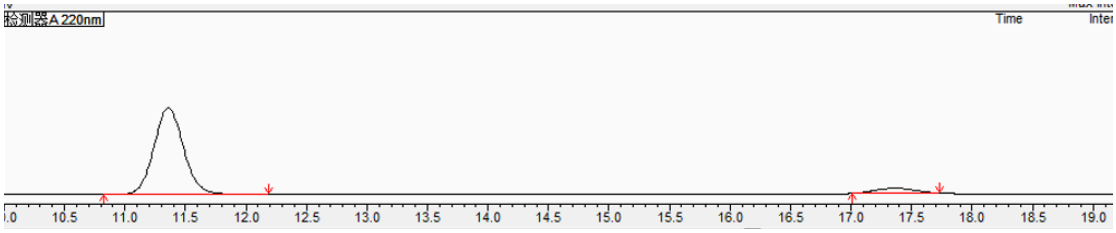
t_{R1} = 11.4 min (major), t_{R2} = 17.4 min (minor)

ee = 85.5%.



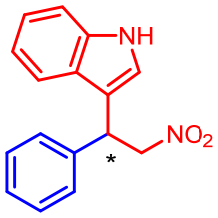
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.768	19227165	1167390	M	50.037				50.037
2	17.884	19198822	713367	M	49.963				49.963
总计		38425987	1880757		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.359	32580408	1931371	M	92.799				92.799
2	17.362	2528025	111278	M	7.201				7.201
总计		35108433	2042649		100.000				100.000



3q

Colorless solid, 62% yield.

The NMR data is in accordance with that of previous publications.[10-11]

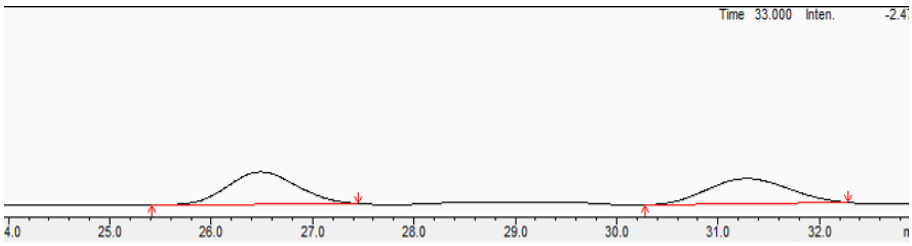
^{1}H NMR (400 MHz, $CDCl_3$), δ 4.97 (dd, J_1 = 12.48 Hz, J_2 = 8.36 Hz, 1H), 4.99 (dd, J_1 = 12.48 Hz, J_2 = 7.68 Hz, 1H), 5.22 (t, J =8.04 Hz, 1H), 7.05 (d, J = 2.20 Hz, 1H, Aromatic H), 7.11 (m, 1H, Aromatic H), 7.24 (m, 1H, Aromatic H), 7.29 (m, 1H, Aromatic H), 7.33-7.39 (m, 5H, Aromatic H), 7.48 (d, J = 8.04 Hz, 1H, Aromatic H), 8.12 (s, 1H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

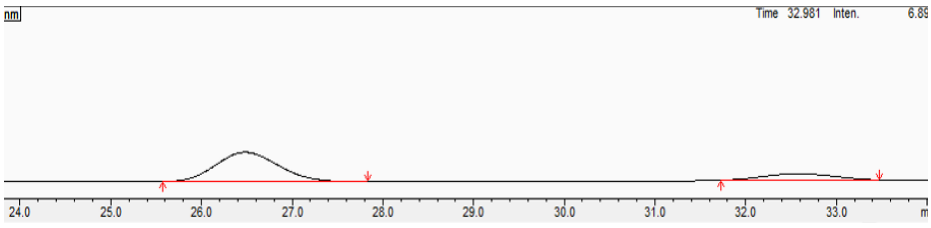
t_{R1} = 26.5 min (major), t_{R2} = 32.6 min (minor)

ee = 61.1%



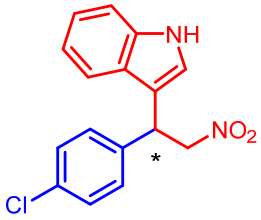
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	26.487	6170740	130018	M	52.029				52.029
2	31.283	5689485	101511	M	47.971				47.971
总计		11860225	231529		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	26.483	2348781	48454	M	80.550				80.550
2	32.577	567149	10536	M	19.450				19.450
总计		2915929	58990		100.000				100.000



3r

Colorless solid, 60% yield.

The NMR data is in accordance with that of previous publications.[10-11]

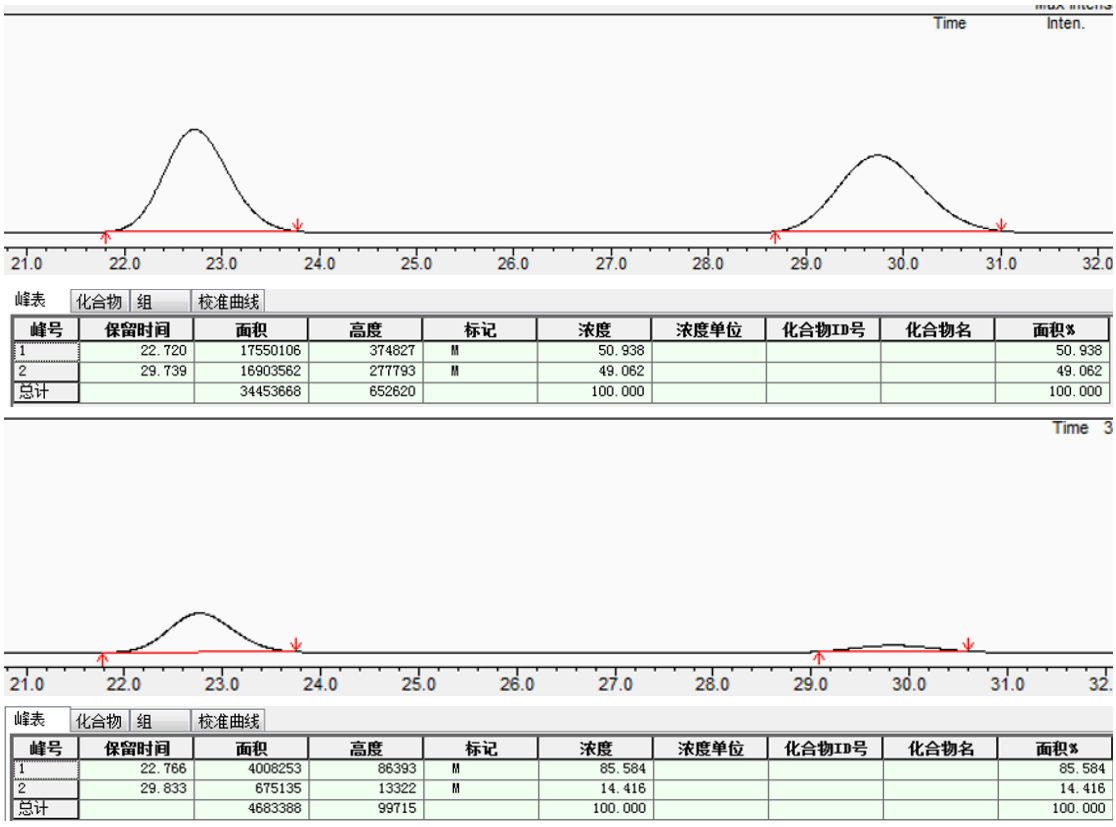
^{1}H NMR (500 MHz, $CDCl_3$), δ 4.85 (t, J = 110.25 Hz, 1H), 5.00 (dd, J_1= 10.25 Hz, J_2=7.55 Hz, 1H), 5.12 (t, J=7.60 Hz, 1H), 6.6.97-7.01 (m, 3H, Aromatic H), 7.04 (t, J=7.30 Hz, 1H, Aromatic H), 7.16 (t, J=7.20 Hz, 1H, Aromatic H), 77.27-7.30 (m, 2H, Aromatic H), 7.31 (d, J = 8.00 Hz, 1H, Aromatic H) 7.36 (d, J = 7.85 Hz, 1H, Aromatic H), 8.08 (s, 1H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

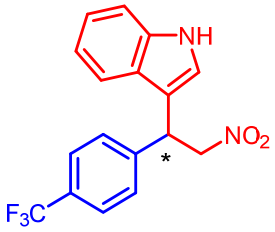
t_{R1} = 22.8 min (major), t_{R2} = 29.8 min (minor)

ee = 71.1%.



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	22.720	17550106	374827	M	50.938				50.938
2	29.739	16903562	277793	M	49.062				49.062
总计		34453668	652620		100.000				100.000

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	22.766	4008253	86393	M	85.584				85.584
2	29.833	675135	13322	M	14.416				14.416
总计		4683388	99715		100.000				100.000



3s

Colorless solid, 57% yield.

The NMR data is in accordance with that of previous publications.[12-13]

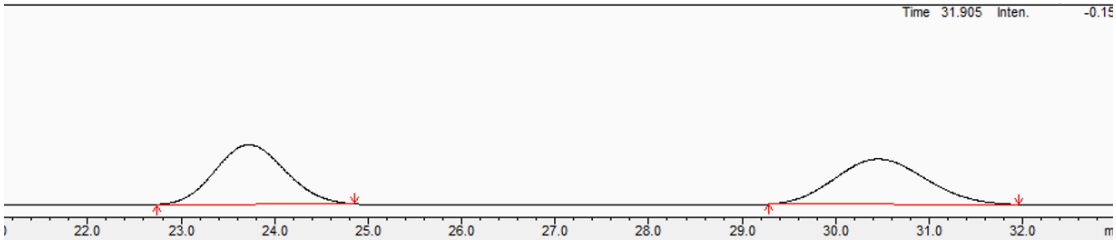
^{1}H NMR (500 MHz, $CDCl_3$), δ 4.97 (dd, J_1 = 11.75 Hz, J_2 = 8.85Hz, 1H), 5.09 (dd, J_1 = 12.10 Hz, J_2 = 7.20 Hz, 1H), 5.26 (t, J=8.05 Hz, 1H), 7.04 (m, 1H, Aromatic H), 7.09 (m, 1H, Aromatic H), 7.22 (t, J= 7.80 Hz, 1H, Aromatic H), 7.35-7.42 (m, 2H, Aromatic H), 7.47 (d, J= 7.90 Hz, 2H, Aromatic H), 7.58 (d, J= 7.95 Hz, 2H, Aromatic H), 8.17 (s, 1H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

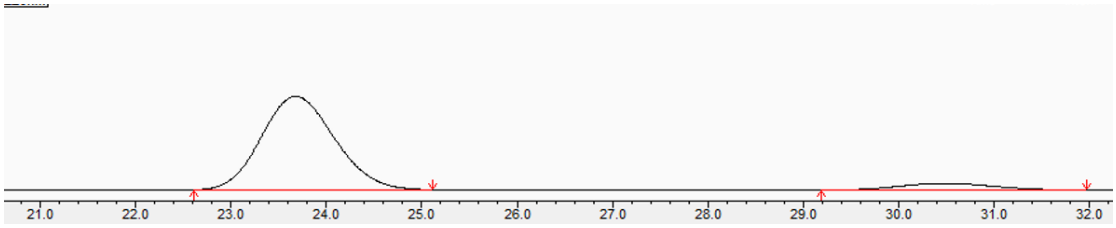
t_{R1} = 23.7 min (major), t_{R2} = 30.5 min (minor)

ee = 82.9%.



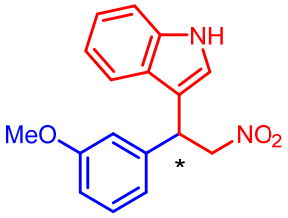
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	23.724	3980734	76098	M	50.284				50.284
2	30.455	3935837	57956	M	49.716				49.716
总计		7916571	134054		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	23.677	30612941	571405	M	91.416				91.416
2	30.483	2874464	41905	M	8.584				8.584
总计		33487405	613310		100.000				100.000



3t

Colorless solid, 58% yield.

The NMR data is in accordance with that of previous publications.[10-11]

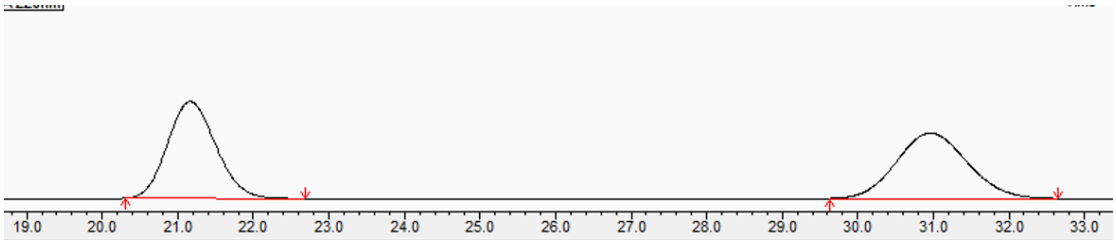
^{1}H NMR (500 MHz, $CDCl_3$), δ 3,76 (s, 3H, OMe), 4.93 (dd, J_1=9.90 Hz, J_2=7.15 Hz, 1H), 5.04 t, J = 10.30 Hz, 1H), 5.16 (t, J=8.15 Hz, 1H), 6.79 (d, J= 8.40 Hz, 1H, Aromatic H), 6.86 (s,1H, Aromatic H), 6.93 (d, J= 7.80 Hz, 1H, Aromatic H), 7.04 (s, 1H, Aromatic H), 7.08 (t, J= 7.70 Hz, 1H, Aromatic H), 7.18-7.24 (m, 2H, Aromatic H), 7.35 (d, J= 8.25 Hz, 1H, Aromatic H), 7.47 (d, J= 8.00 Hz, 1H, Aromatic H), 8.10 (s, 1H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

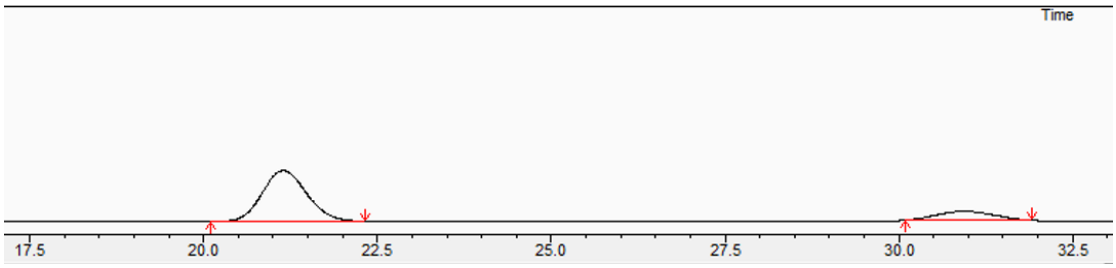
t_{R1} = 21.1min (major), t_{R2} = 30.9 min (minor)

ee = 63.3%.



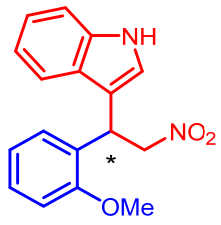
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	21.164	14914052	336508	M	50.044				50.044
2	30.962	14887958	227336	M	49.956				49.956
总计		29802010	563844		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	21.145	17900431	404116	M	81.632				81.632
2	30.940	4027729	70767	M	18.368				18.368
总计		21928160	474883		100.000				100.000



3u

Colorless solid, 48% yield.

The NMR data is in accordance with that of previous publications.[10-11]

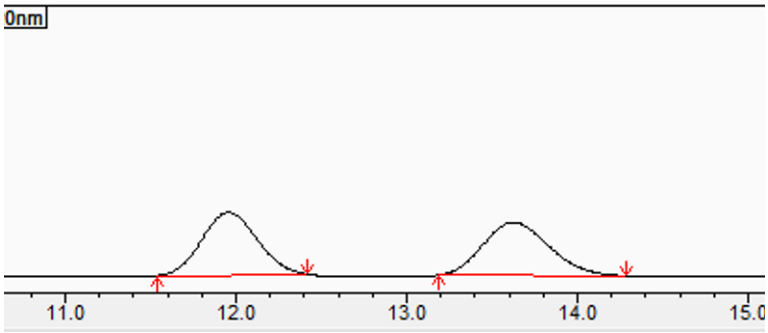
^{1}H NMR (500 MHz, $CDCl_3$), δ 3,87 (s, 3H, OMe), 4.92 -5.03 (m, 2H), 5.57 (t, *J* =7.50 Hz, 1H), 6.80 (t, *J*= 7.10 Hz, 1H, Aromatic H), 6.89 (d, *J*= 8.10 Hz 1H, Aromatic H), 7.03 -7.07 (m, 3H, Aromatic H), 7.15 (t, *J*= 7.10 Hz, 1H, Aromatic H), 7.20 (t, *J*= 6.40 Hz, 1H, Aromatic H), 7.28 (d, *J*= 8.05 Hz, 1H, Aromatic H), 7.44 (d, *J*= 7.75 Hz, 1H, Aromatic H), 8.03 (s, 1H).

HPLC trace:

Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.0 mL/min.

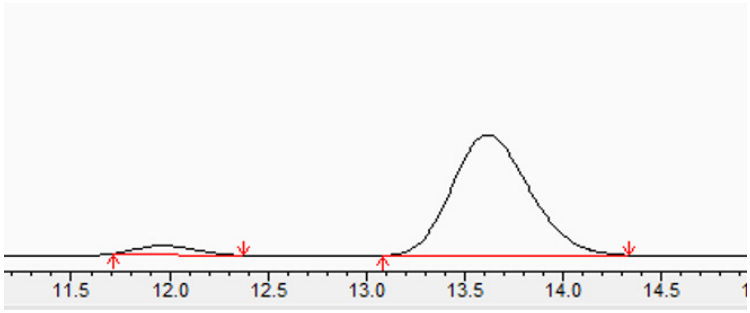
t_{R1} = 12.0 min (minor), t_{R2} = 13.6 min (minor)

ee = 90.3%.



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.956	11991712	531127	M	49.657				49.657
2	13.623	12157530	451501	M	50.343				50.343
总计		24149242	982628		100.000				100.000

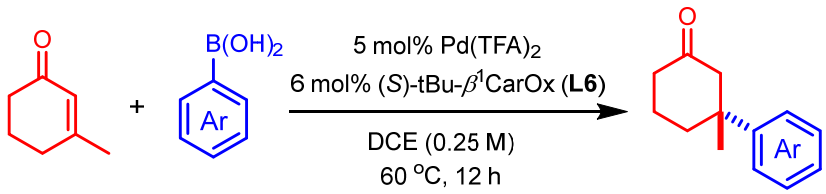


峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.967	752266	38218	M	4.852				4.852
2	13.619	14750866	536766	M	95.148				95.148
总计		15503131	574984		100.000				100.000

Enantioselective Addition of Arylboronic Acids to *β*-substituted Cyclic Enones

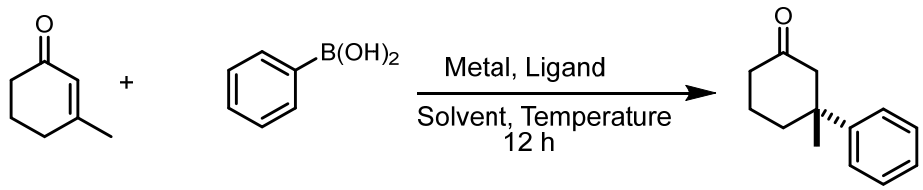
General procedure



To a Schlenck tube charged with $Pd(TFA)_2$ (4.15 mg, 0.0125 mmol), (*S*)-tBu-β^1CarOx (4.4 mg, 0.015 mmol) and aryl boronic acid (0.5 mmol), was added dichloroethane (0.5 mL) for dissolution and then *β*-substituted cyclic enones (0.25 mmol) was added. The walls of the vial were rinsed with an additional portion of dichloroethane (0.5 mL). The vial was capped with a Teflon/silicone septum and stirred in a 60 °C oil bath for 12 h. The reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography (petroleumether/EtOAc = 20/1, v/v) to give the product.

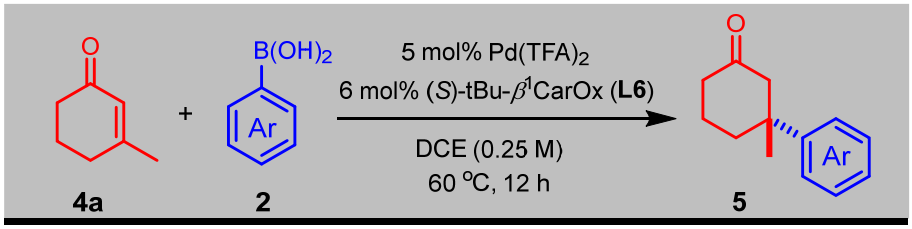
Racemic products were synthesized in a manner analogous to the general procedure using bipyridine (2.1 mg, 0.015 mmol, 6 mol%) as an achiral ligand.

Concise optimization

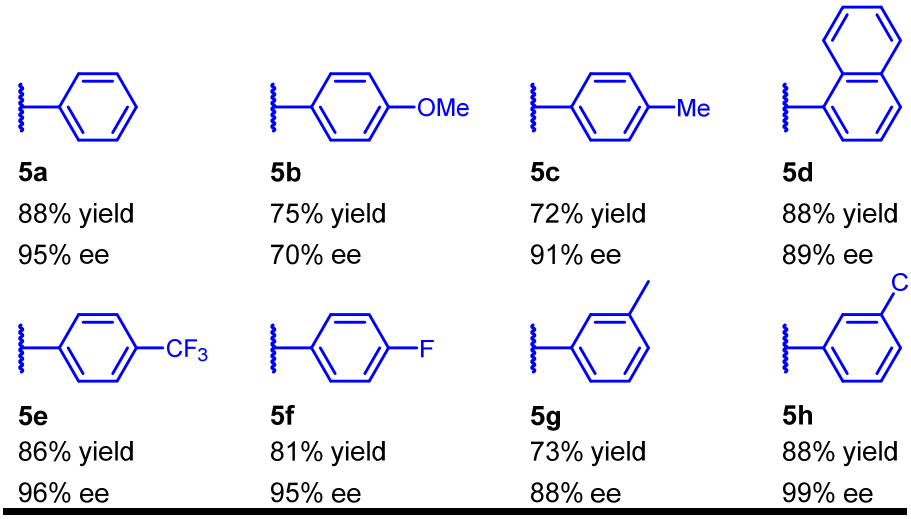


Entry	Metal	*β*-CarOx	Solvent	Temperature	Yield(%)	ee(%)
1	$Pd(TFA)_2$	**L3**	DCE	60 °C	78	50
2	$Pd(TFA)_2$	**L6**	DCE	60 °C	88	94
3	$Pd(TFA)_2$	**L7**	DCE	60 °C	76	91
4	$Pd(TFA)_2$	**L8**	DCE	60 °C	73	32
5	$Pd(TFA)_2$	**L10**	DCE	60 °C	56	93
6	$PdCl_2$	**L6**	DCE	60 °C	<5	n.d.
7	$Pd(OAc)_2$	**L6**	DCE	60 °C	67	89
8	$Pd(TFA)_2$	**L6**	DCM	40 °C	49	90
9	$Pd(TFA)_2$	**L6**	MeOH	60 °C	<5	n.d.
10	$Pd(TFA)_2$	**L6**	DCE	40 °C	72	90
11	$Pd(TFA)_2$	**L6**	DCE	80 °C	86	87

Substrate Scope

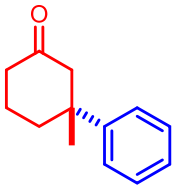


4a **2** **5**



5a	**5b**	**5c**	**5d**
88% yield	75% yield	72% yield	88% yield
95% ee	70% ee	91% ee	89% ee
5e	**5f**	**5g**	**5h**
86% yield	81% yield	73% yield	88% yield
96% ee	95% ee	88% ee	99% ee

HPLC traces of the Enantioenriched *β*-aryl ketones



5a

Colorless oil, 88% yield.

The NMR data is in accordance with that of previous publication.[14]

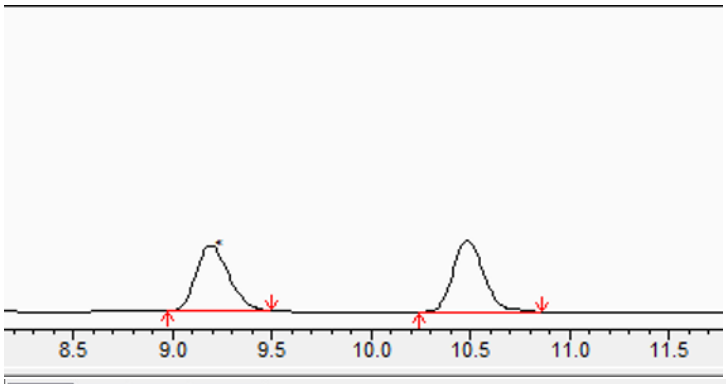
^{1}H NMR (400 MHz, $CDCl_3$), δ 1.35(s, 3H, CH_3), 1.67 (m, 1H), 1.87-1.98 (m, 2H), 2.21 (m, 1H), 2.2.31-2.42 (m, 2H), 2.46 (d, *J*=14.12 Hz, 1H), 2.91 (d, *J*=14.20 Hz, 1H), 7.20-7.25 (m, 1H, Aromatic H), 7.32-7.37 (m, 4H, Aromatic H).

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 1.0 mL/min.

t_{R1} = 9.1 min (major), t_{R2} = 10.5 min (minor)

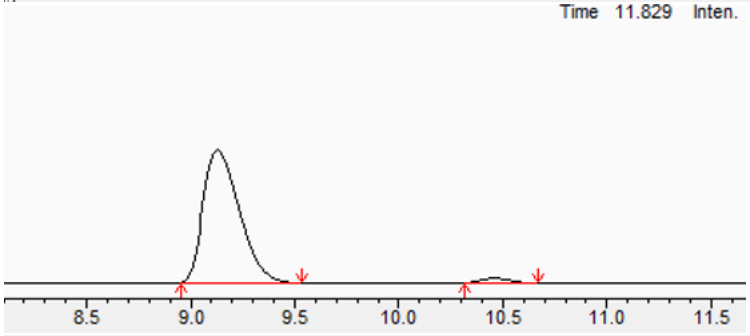
ee = 94.9%.



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.191	2074354	179682	M	49.252				49.252
2	10.483	2137331	197131	M	50.748				50.748
总计		4211686	376813		100.000				100.000

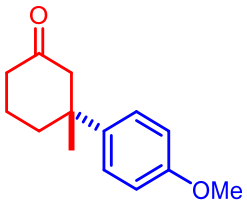
Time 11.829 Inten.



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.132	5491306	447375	M	97.413				97.413
2	10.459	145827	15224	M	2.587				2.587
总计		5637134	462599		100.000				100.000

5b



Colorless oil, 75% yield.

The NMR data is in accordance with that of previous publications.[14-16]

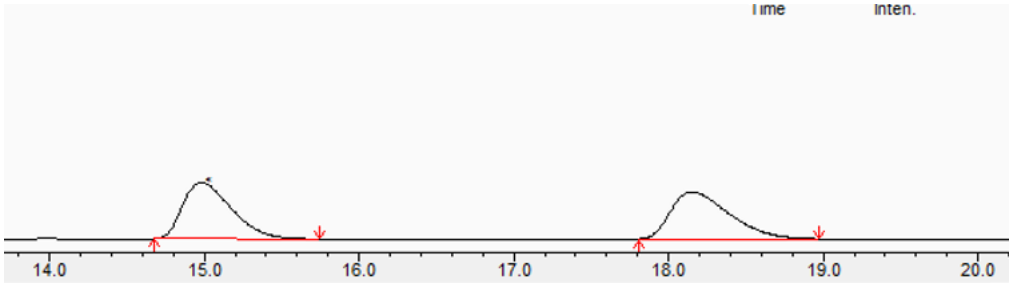
^{1}H NMR (400 MHz, $CDCl_3$), δ 1.31(s, 3H, CH_3), 1.68 (m, 1H), 1.85-1.94 (m, 2H), 2.2.21 (m, 1H), 2.30-2.32 (m, 2H), 2.43 (d, *J*=14.12 Hz, 1H), 2.87 (d, *J*=14.16 Hz, 1H), 3.79 (s, 3H), 6.85-6.89 (m, 2H, Aromatic H), 7.23-7.27 (m, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 1.0 mL/min.

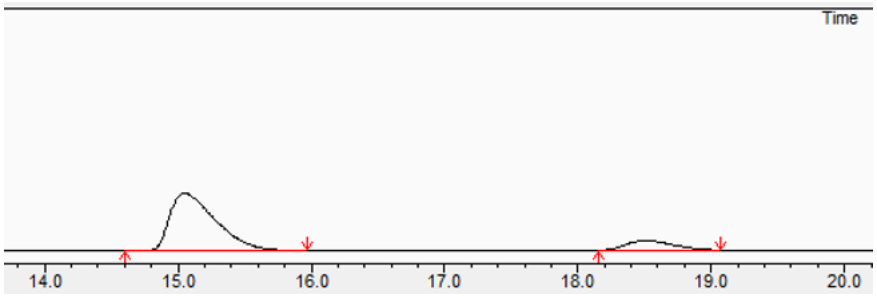
t_{R1} = 15.0 min (major), t_{R2} = 18.5 min (minor)

ee = 70.2%.



峰表 | 化合物 | 组 | 校准曲线

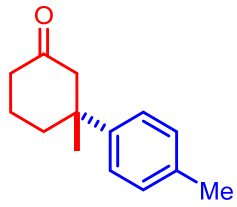
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.980	11820971	543550	M	50.135				50.135
2	18.151	11757375	451541	M	49.865				49.865
总计		23578346	995091		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.050	25896596	1098923	M	85.087				85.087
2	18.507	4538757	185622	M	14.913				14.913
总计		30435353	1284545		100.000				100.000

5c



Colorless oil, 72% yield.

The NMR data is in accordance with that of previous publications. [14-16]

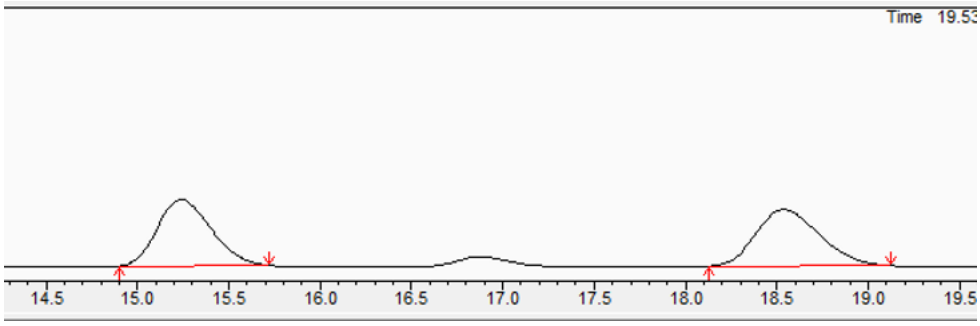
^{1}H NMR (400 MHz, $CDCl_3$), δ 1.33(s, 3H, CH_3), 1.1.70 (m, 1H), 1.86-1.95 (m, 2H), 2.12.19 (m, 1H),2.28-2.32 (m, 2H), 2.34 (s, 3H, CH_3), 2.44 (d, *J*=8.12 Hz, 1H), 2.89 (d, *J*=9.80 Hz, 1H), 7.16 (d, *J*=8.16 Hz, 2H, Aromatic H), 7.23 (d, *J*=8.28 Hz, 2H, Aromatic H).

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 1.0 mL/min.

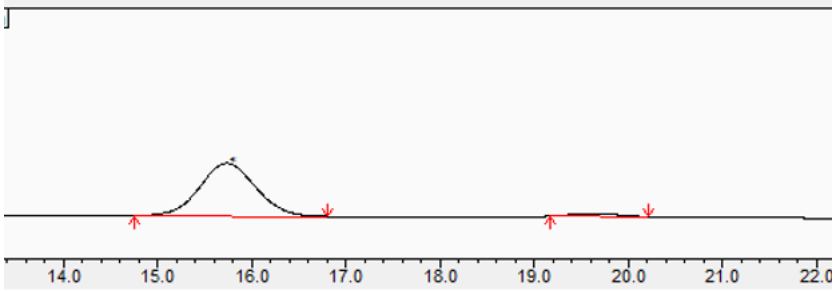
t_{R1} = 15.7 min (major), t_{R2} = 19.5 min (minor)

ee = 91.2%.



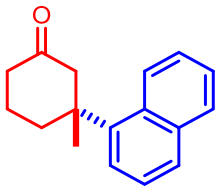
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.240	2277992	111201	M	49.809				49.809
2	18.538	2295487	94554	M	50.191				50.191
总计		4573479	205755		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.732	334782	8057	M	95.626				95.626
2	19.551	15314	433	M	4.374				4.374
总计		350096	8490		100.000				100.000



5d

Colorless oil, 88% yield.

The NMR data is in accordance with that of previous publication.[17]

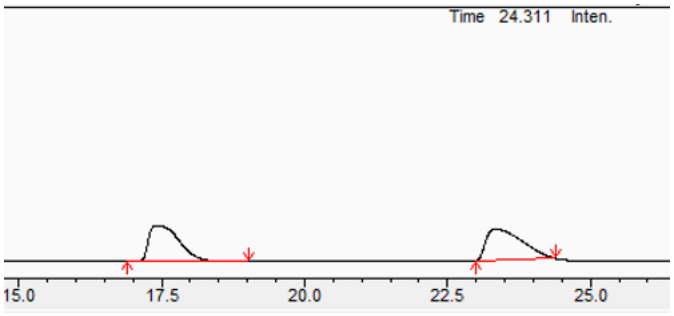
^{1}H NMR (400 MHz, $CDCl_3$), δ 1.44 (s, 3H, CH_3), 1.67 (m, 1H), 1.89-2.05 (m, 2H), 2.31-2.38 (m, 3H), 2.55 (d, *J*=14.24 Hz, 1H), 3.05 (d, *J*=14.32 Hz, 1H), 7.46-7.52 (m, 3H, Aromatic H), 7.73 (d, *J*=1.64 Hz, 1H, Aromatic H), 7.82-7.86 (m, 3H, Aromatic H) .

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 1.0 mL/min.

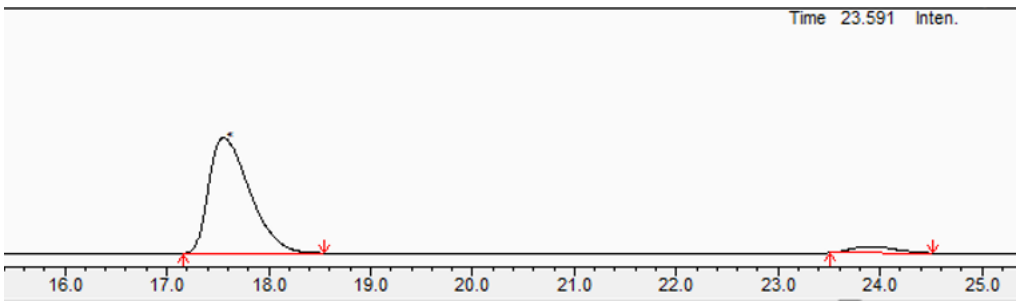
t_{R1} = 17.5 min (major), t_{R2} = 23.9 min (minor)

ee = 88.8%.



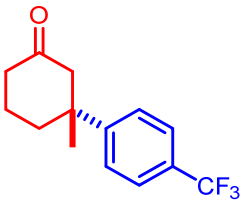
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	17.428	108316047	2955125	M	49.015				49.015
2	23.347	112667848	2565653	M	50.985				50.985
总计		220983896	5520778		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	17.559	51900871	1855385	M	94.409				94.409
2	23.908	3073584	104045	M	5.591				5.591
总计		54974455	1959430		100.000				100.000



5e

Colorless oil, 86% yield.

The NMR data is in accordance with that of previous publications.[14, 16]

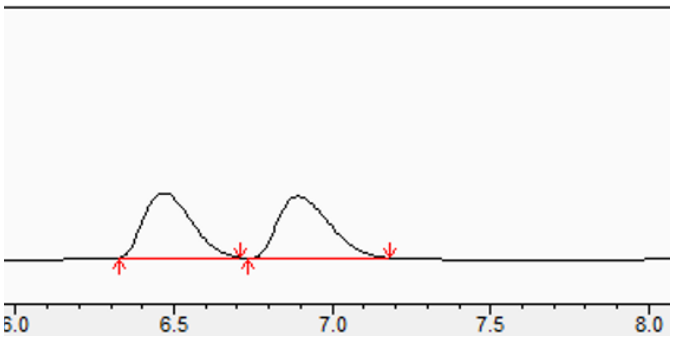
^{1}H NMR (500 MHz, $CDCl_3$), δ 1.34 (s, 3H, CH_3), 1.62-1.67 (m, 2H), 1.89-1.98 (m, 2H), 2.19 (m, 1H), 2.32-2.36 (m, 2H), 2.48 (d, *J*=14.20 Hz, 1H), 2.88 (d, *J*=14.20 Hz, 1H), 7.44 (d, *J*=8.10 Hz, 2H, Aromatic H), 7.58 (d, *J*=7.75 Hz, 2H, Aromatic H) .

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 1.0 mL/min.

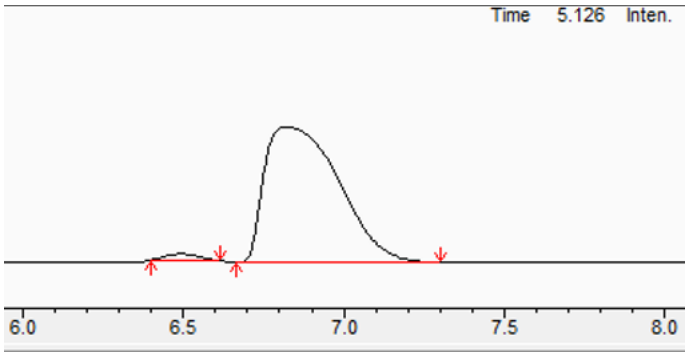
t_{R1} = 6.82 min (major), t_{R2} = 6.49 min (minor)];

ee = 95.8%.



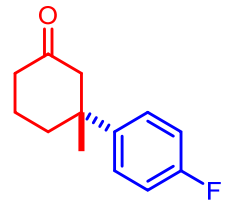
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.467	12334370	1182439	M	49.220				49.220
2	6.893	12725158	1120766	M	50.780				50.780
总计		25059528	2303205		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.489	758881	103889	M	2.100				2.100
2	6.822	35374690	2218226	M	97.900				97.900
总计		36133572	2322115		100.000				100.000



5f

Colorless oil, 81% yield.

The NMR data is in accordance with that of previous publications.[14, 18]

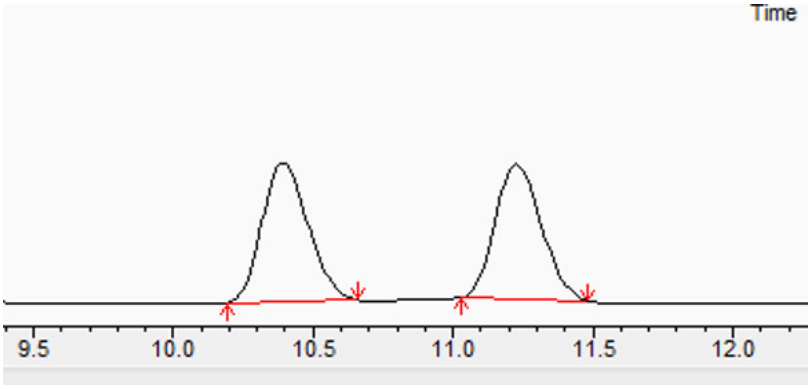
^{1}H NMR (400 MHz, $CDCl_3$), δ 1.32 (s, 3H, CH_3), 1.61-1.69 (m, 1H), 1.84-1.95 (m, 2H), 2.13-2.19 (m, 1H), 2.32 (t, J_1=13.48 Hz, J_2=6.74 Hz, 2H), 2.44 (d, J=10.12 Hz, 1H), 2.85 (d, J=14.20 Hz, 1H), 7.23-7.31 (m, 4H, Aromatic H).

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 0.9 mL/min.

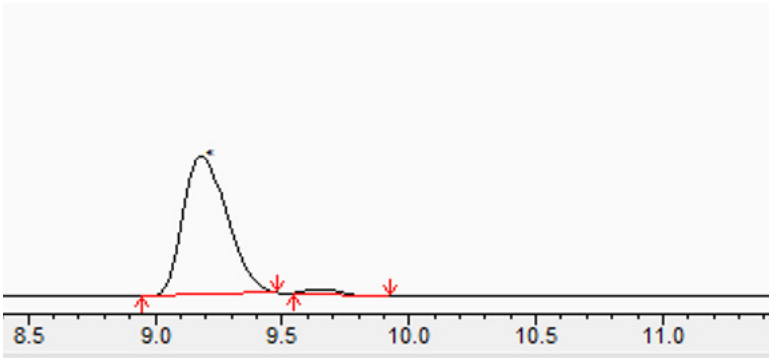
t_{R1} = 9.18 min (major), t_{R2} = 10.8 min (minor)];

ee = 95.2%.



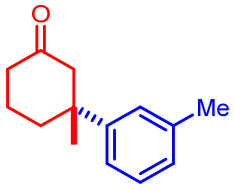
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.391	1174490	102700	M	50.556				50.556
2	11.225	1148652	100320	M	49.444				49.444
总计		2323142	203020		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.183	2896918	239620	M	97.600				97.600
2	9.649	71223	8649	M	2.400				2.400
总计		2968141	248269		100.000				100.000



5g

Colorless oil, 73% yield.

The NMR data is in accordance with that of previous publication.[14]

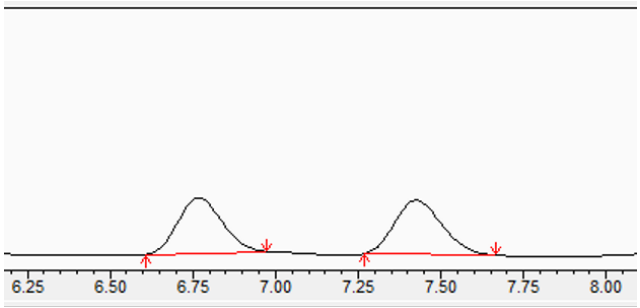
^{1}H NMR (500 MHz, $CDCl_3$), δ 1.31 (s, 3H, CH_3), 1.70 (m, 1H), 1.85-1.93 (m, 2H), 2.18 (m, 1H), 2.30-2.34 (m, 5H), 2.42 (d, *J*=14.15 Hz, 1H), 2.87 (d, *J*=14.20 Hz, 1H), 7.02 (d, *J*=7.60 Hz ,1H, Aromatic H), 7.11 (d, *J*=8.80 Hz, 2H, Aromatic H), 7.21 (m, 1H, Aromatic H).

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 1.0 mL/min.

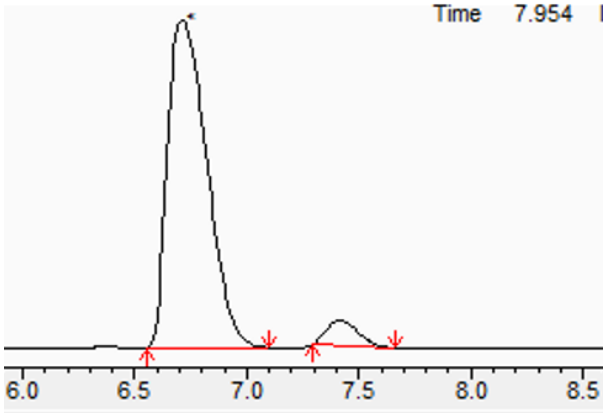
t_{R1} = 6.71 min (major), t_{R2} = 7.42 min (minor)];

ee = 88.4%.



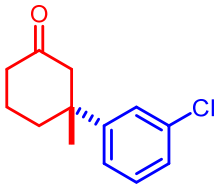
峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.768	250555	26714	M	48.798				48.798
2	7.425	262901	26292	M	51.202				51.202
总计		513456	53006		100.000				100.000



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.711	24673517	2021794	M	94.225				94.225
2	7.416	1512188	156852	M	5.775				5.775
总计		26185705	2178646		100.000				100.000



5h

Colorless oil, 88% yield.

The NMR data is in accordance with that of previous publications.[14-15]

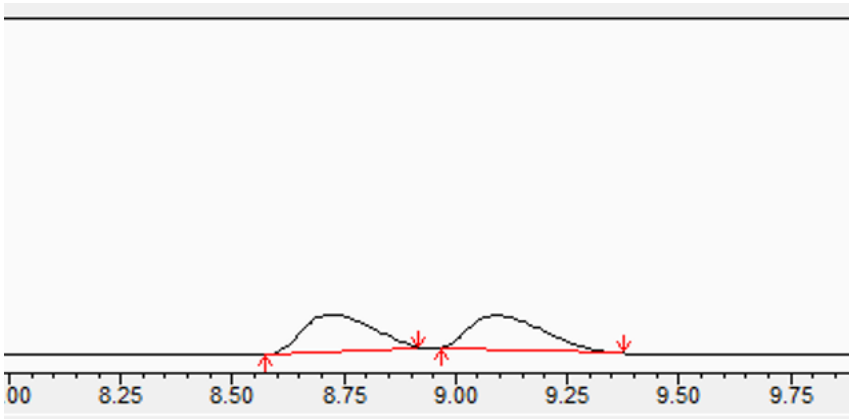
^{1}H NMR (500 MHz, $CDCl_3$), δ 1.31 (s, 3H, CH_3), 1.69 (m, 1H), 1.87-1.94 (m, 2H), 2.15 (m, 1H), 2.31-2.34 (m, 2H), 2.43 (d, *J*=14.15 Hz, 1H), 2.84 (d, *J*=14.15 Hz, 1H), 7.18-7.20 (m, 2H, Aromatic H), 7.25 (m, 1H, Aromatic H) 7.30 (s, 1H, Aromatic H).

HPLC trace:

Daicel chiralcel OJ-H, hexane/i-PrOH = 95/5, 220 nm, 0.9 mL/min.

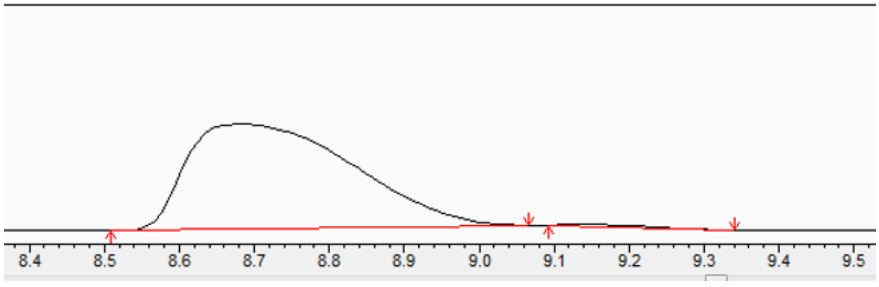
t_{R1} = 8.68 min (major), t_{R2} = 9.14 min (minor)];

ee = 98.6%.



峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.722	17233770	1622842	M	49.360				49.360
2	9.094	17680500	1522708	M	50.640				50.640
总计		34914270	3145550		100.000				100.000

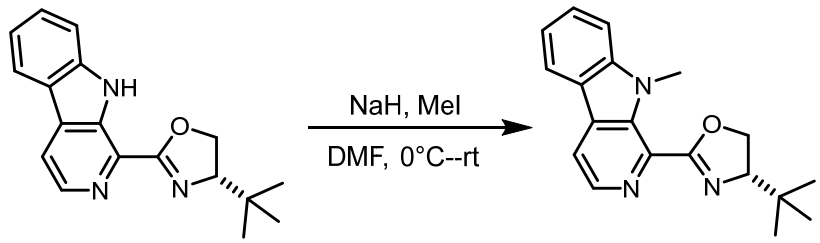


峰表 | 化合物 | 组 | 校准曲线

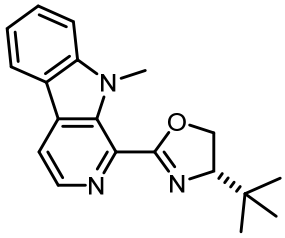
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.681	36838698	2402542	M	99.300				99.300
2	9.143	259805	36243	M	0.700				0.700
总计		37098503	2438785		100.000				100.000

Synthesis and Application of Chiral Ligands L12 and L13

Synthesis of *N*-Methylated (*S*)-tBu-β^1-CarOx **L12**



L12 was synthesized following the reported procedure.[19] To a suspended solution of NaH (4.8 mg, 0.2 mmol) in DMF (1 mL), (S)-tBu-***β*^{1}-CarOx** (29.3 mg, 0.1 mmol) in DMF (1 mL) was added dropwise at 0 ° C. The heterogeneous mixture was stirred at 0 °C for 15 min and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (10 μL, 0.15 mmol), and allowed to warm to room temperture. After 6 h, the reaction mixture was cooled to 0 °C, quenched with saturated aqueous NH_4Cl (3 mL), and extracted with ethyl acetate (3×5 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel to give product *N*-Methylated (*S*)-tBu-***β*^{1}-CarOx L12** as a white solid (56% yield).



L12

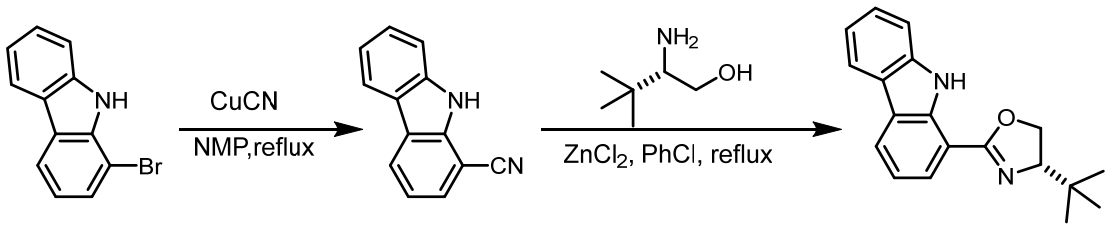
(*S*)-4-(tert-butyl)-2-(9-methyl-9H-pyrido[3,4-b]indol-3-yl)-4,5-dihydrooxazole

^{1}H NMR (500 MHz, $CDCl_3$), δ 1.07 (s, 9H, 3 × *CH*$_3$), 4.09 (s, 3H, N-*CH*$_3$), 4.28 (dd, J_1 =9.95 Hz, J_2 =9.95 Hz, 1H), 4.35 (dd, J_1 =9.95 Hz, J_2 = 8.7 Hz, 1H), 4.57 (dd, J_1 = 9.95 Hz, J_2 = 8.7 Hz, 1H), 7.32 (m, 1H), 7.48 (d, J = 8.20 Hz, 1H) 7.62 (dd, J_1 = 7.85 Hz, J_2 = 6.90 Hz, 1H), 8.06 (s, 1H), 8.14 (d, J = 7.90 Hz 1H), 8.54 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$), δ 26.3, 32.9, 33.9, 68.9, 77.4, 109.8, 116.2, 120.2, 120.8, 121.5, 129.0, 131.1, 131.3, 135.8, 138.3, 143.1, 162.3.

HRESI-MS: calcd for $C_{19}H_{22}N_3O$ $[M+H]^+$: 308.1764, found: 308.1658.

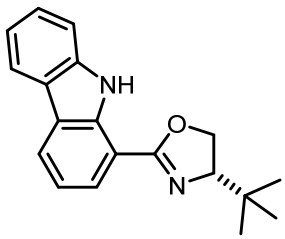
Synthesis of Carbazole-Oxazoline Ligand **L13**



L13 was synthesized following the reported procedure. [6], [20]

Step 1, To a suspended solution of CuCN (182 mg, 2.0 mmol) in NMP (3 mL), 1-Bromocarbazole (246 mg, 1.0 mmol) in 2 ml NMP was added dropwise , the reaction mixture was heated to reflux for 2h. The reaction mixture was then cooled to ambient temperature, quenched with H_2O (3 mL), and extracted with ethyl acetate (3×5 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel to give product 1-cyanide carbazole (yield: 68%, as white solid).

Step 2, To a suspended solution of *S*-tert-Leucinol (140 mg, 1.2 mmol) and $ZnCl_2$(8.3 mg, 0.06 mmol) in PhCl (3 mL), 1-Cyanide carbazole (115 mg, 0.6 mmol) in 2 ml in PhCl was added dropwise , the reaction mixture was heated to reflux for 12h. The reaction mixture was then cooled to ambient temperature, quenched with H_2O (3 mL), and extracted with ethyl acetate (3×5 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel to give product C_1-*S*-^{t}Bu-Carbazole-Oxazoline Ligand (**L13**) (yield: 48 %, as white solid).



L13

(*S*)-4-(tert-butyl)-2-(9H-carbazol-3-yl)-4,5-dihydrooxazole

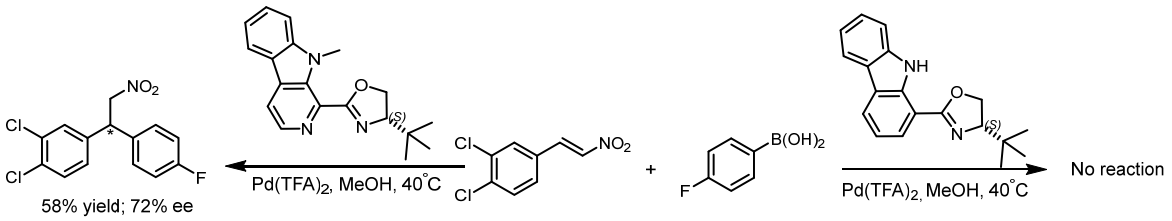
^{1}H NMR (500 MHz, $CDCl_3$), δ 1.03 (s, 9H, 3 × *CH₃*), 4.20 (dd, J_1 = 9.95 Hz, J_2 = 7.75 Hz, 1H), 4.28 (t, J_1 = 7.75 Hz, J_2 = 8.25 Hz, 1H), 4.40 (dd, J_1 = 9.95 Hz, J_2 = 8.25 Hz, 1H), 7.23 -7.27 (m, 2H), 7.46 (m, 1H), 7.54 (d, J = 8.05 Hz, 1H), 7.86 (d, dd, J_1 =

7.60 Hz, J_2 = 1.10 Hz, 1H), 8.10 (d, J = 7.75 Hz, 1H), 8.19 (d, J = 7.75 Hz, 1H), 10.55 (s, 1H).

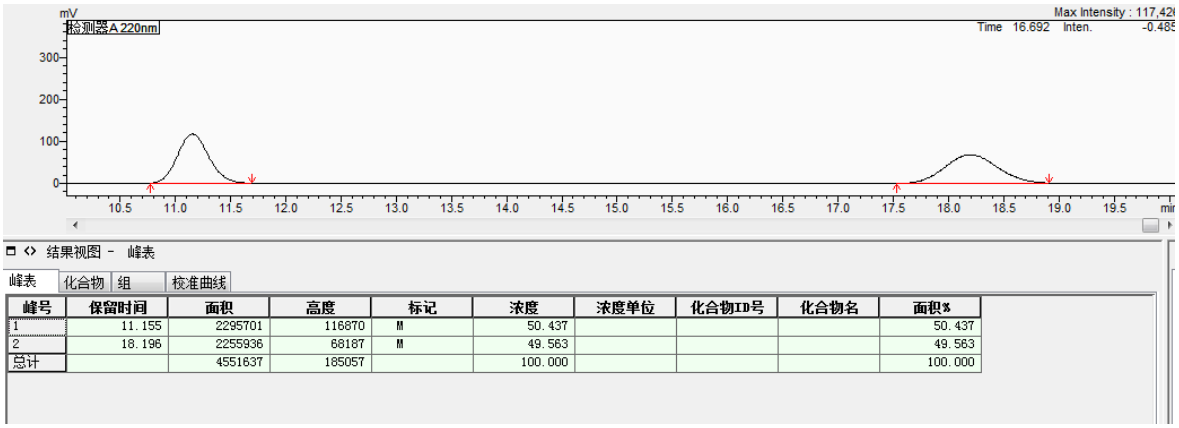
^{13}C NMR (125 MHz, $CDCl_3$), δ 26.0, 34.1, 68.1, 76.2, 109.5, 111.3, 118.3, 119.6, 120.5, 122.9, 123.4, 123.6, 125.3, 126.2, 139.2, 139.6, 163.1.

HRESI-MS: calcd for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1655, found:.293.1658.

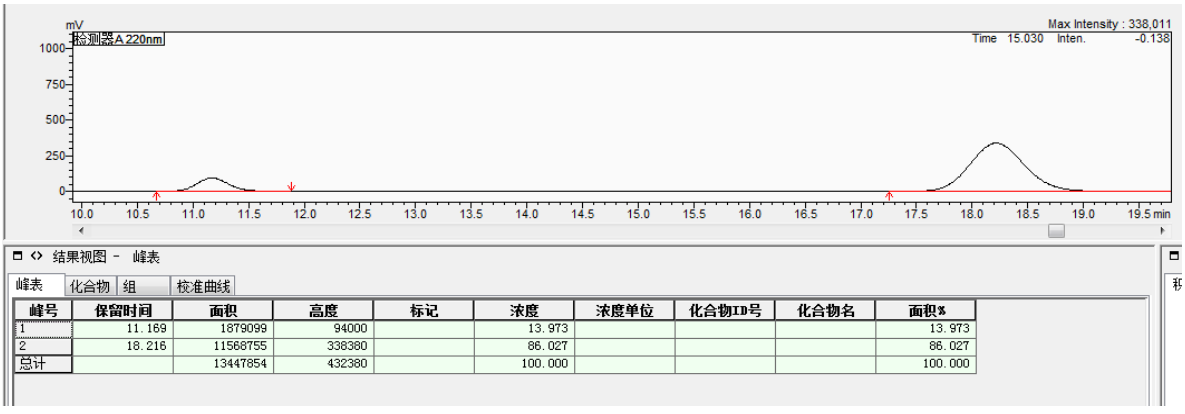
Application of **L12** and **L13** in the enantioselective synthesis of compound **3i**



HPLC traces for the chiral ligand **L12**,



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.155	2295701	116870	M	50.437				50.437
2	18.196	2255936	68187	M	49.563				49.563
总计		4551637	185057		100.000				100.000

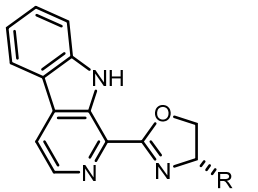


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	11.169	1879099	94000		13.973				13.973
2	18.216	11568755	338380		86.027				86.027
总计		13447854	432380		100.000				100.000

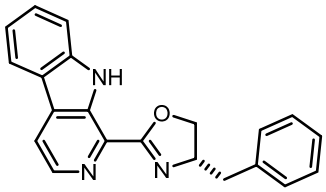
HPLC [Daicel chiralcel OD-H, hexane/i-PrOH = 70/30, 220 nm, 1.2 mL/min. t_{R1} = 11.17 min (major), t_{R2} = 18.22 min (minor)]; ee = 72.0%.

Antifungal Bioassay of CarOx Ligands

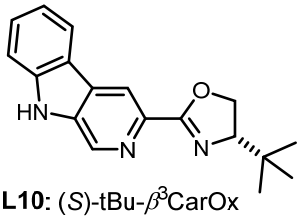
Compounds Selected for Biotest



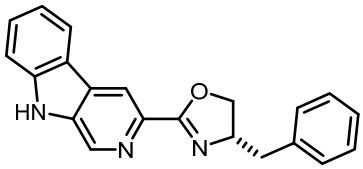
L1: (*S*)-Me-β^1CarOx
L2: (*S*)-Et-β^1CarOx
L3: (*S*)-iPr-β^1CarOx
L4: (*S*)-iBu-β^1CarOx
L5: (*S*)-sBu-β^1CarOx
L6: (*S*)-tBu-β^1CarOx
L7: (*S*)-Ph-β^1CarOx
L8: (*S*)-Bn-β^1CarOx



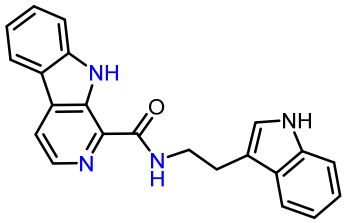
L9: (*R*)-Bn-β^1CarOx



L10: (*S*)-tBu-β^3CarOx



L11: (*S*)-Bn-β^3CarOx



alangiobussinine

Initial Screening

The antifungal activity of the target compounds was tested in *vitro* against the plant pathogenic fungi using the mycelium growth rate test. All the tested compounds were dissolved in DMSO at a concentration of μg/mL. The media containing compounds at a concentration of 50 μg/mL were then poured into Petri dishes for initial screening.

$$\text{Inhibition rate (\%)} = (C-T) / (C-5\text{ mm}) \times 100\%$$

Where *C*: The average diameter (in mm) of mycelia in the blank test, *T*: The average diameter (in mm) of mycelia on treated PDA with tested compounds.

Compd.	Inhibitory Rate at 50 μg/mL (%)					
	Rhizoctonia solani	*Sclerotinia scleotiorum*	*Botrytis cinerea*	*Fusarium graminearum*	*Phytophthora capsici*	*Magnaporthe oryzae*
L1	39.2	63.5	57.8	56.8	65.1	64.7
L2	66.3	86.5	83.1	71.4	80.8	87.2
L3	70.4	86.5	98.0	69.1	87.8	82.1
L4	94.9	70.2	78.2	45.5	52.9	57.1
L5	86.8	74.0	71.7	67.0	63.9	66.7
L6	69.4	92.3	72.3	66.7	77.3	70.5
L7	75.5	90.9	59.4	53.8	55.8	65.8
L8	61.8	54.5	31.5	52.9	56.4	51.9
L9	71.5	88.5	61.2	54.8	74.4	83.3
L10	64.2	47.8	37.9	60.0	46.5	63.5
L11	78.1	92.5	63.7	60.0	62.1	61.5
alangiobussinine	33.5	48.9	52.6	52.3	34.5	52.5

Precise Antifungal Test

In the precision antifungal test, the 20 mg/mL stock solution was diluted to 50, 25, 12.5, 6.25, 3.125,1.5625, 0.78125 μg/mL and the above experiments were repeated for three times, the inhibition rates were calculated separately. The statistical analyses were performed by SPSS software version 20.0. Inhibition rate was calculated as follows,

Inhibition rate (%) = (C−T) / (C−5 mm) × 100%

Where C: The average diameter (in mm) of mycelia in the blank test, T: The average diameter (in mm) of mycelia on treated PDA with tested compounds.

EC_{50} values (μM) of the Selected Antifungal *β*-CarOx Ligands

Compd.	*Rhizoctonia solani*	*Sclerotinia scleotiorum*	*Botrytis cinerea*	*Fusarium graminearum*	*Phytophthora capsici*	*Magnaporthe oryzae*
L2	57.7	22.4	72.5	66.4	55.4	55.5
L3	50.3	15.5	37.7	60.9	40.5	54.1
L5	28.7	17.7	56.2	67.3	92.9	47.5
L6	35.7	13.0	45.7	92.9	26.9	42.7
L7	57.5	17.3	65.3	104.8	109.1	38.6
L9	16.4	12.0	75.5	84.5	17.4	36.6
alangiobussinine	>141.6	>141.6	>141.6	>141.6	>141.6	>141.6
Boscalid	4.6	0.9	4.9	165.3	7.4	3.3

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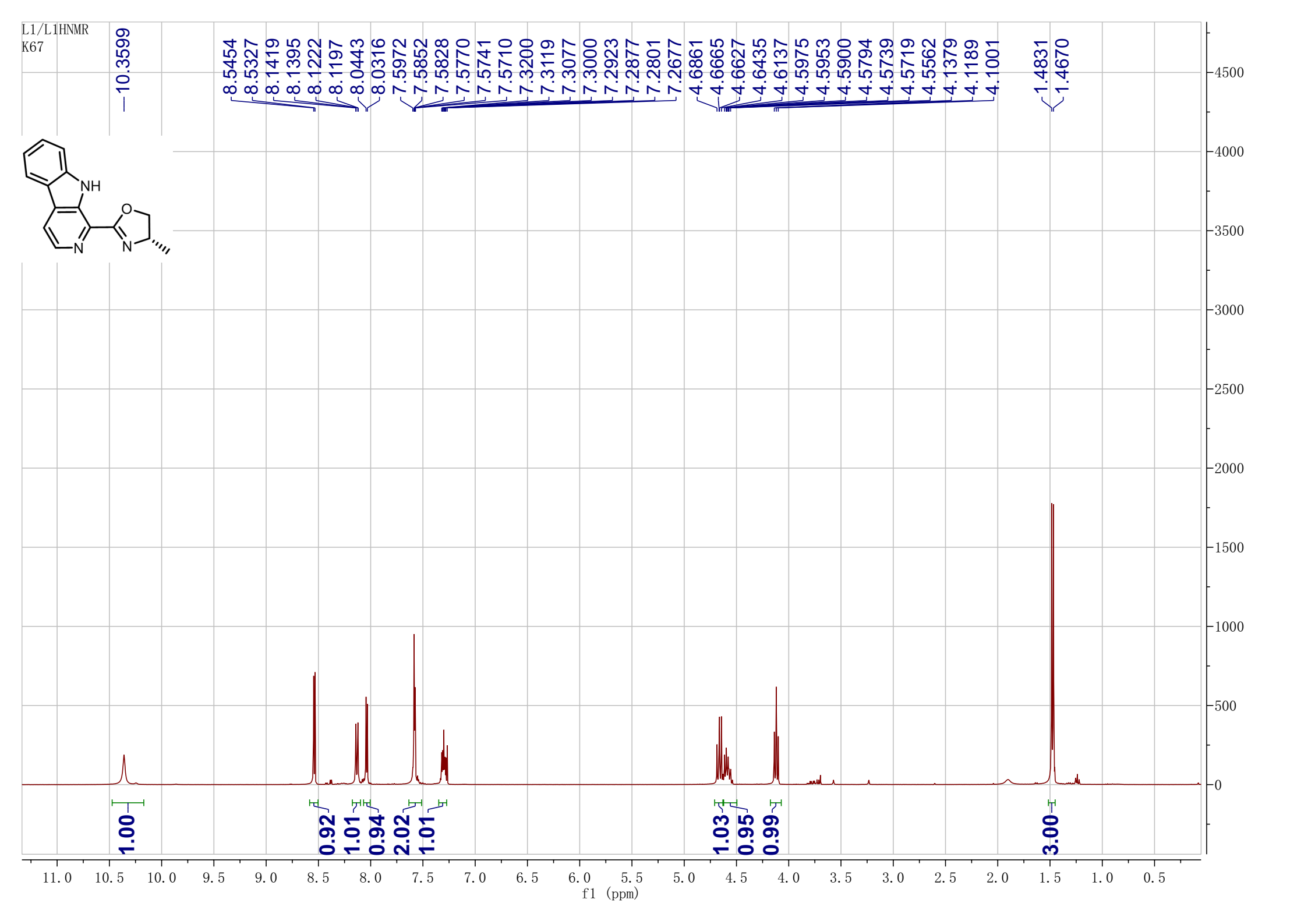
[20] Alicia Regueiro-Ren.; Qiufen M Xue.; Jacob J Swidorski.; Yi-Fei Gong.; Inhibitors of Human Immunodeficiency Virus Type 1 (HIV-1) Attachment. 12.Structure−Activity Relationships Associated with 4-Fluoro-6-azaindole Derivatives Leading to the Identification of 1-(4-Benzoylpiperazin-1-yl)-2-(4-fluoro-7-[1,2,3]triazol-1-yl-1H-pyrrolo[2,3-c]pyridin-3-yl)ethane-1,2-dione (BMS-585248). *J. Med. Chem*. **2013**, *56*, 4, 1656–1669.

NMR Spectra Traces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K67
10.3599
8.5454
8.5327
8.1419
8.1395
8.1222
8.1197
8.0443
8.0316
7.5972
7.5852
7.5828
7.5770
7.5741
7.5710
7.3200
7.3119
7.3077
7.3000
7.2923
7.2877
7.2801
7.2677
4.6861
4.6665
4.6627
4.6435
4.6137
4.5975
4.5953
4.5900
4.5794
4.5739
4.5719
4.5562
4.1379
4.1189
4.1001
1.4831
1.4670
NH
O
N
N
1.00
0.92
1.01
0.94
2.02
1.01
1.03
0.95
0.99
3.00
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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
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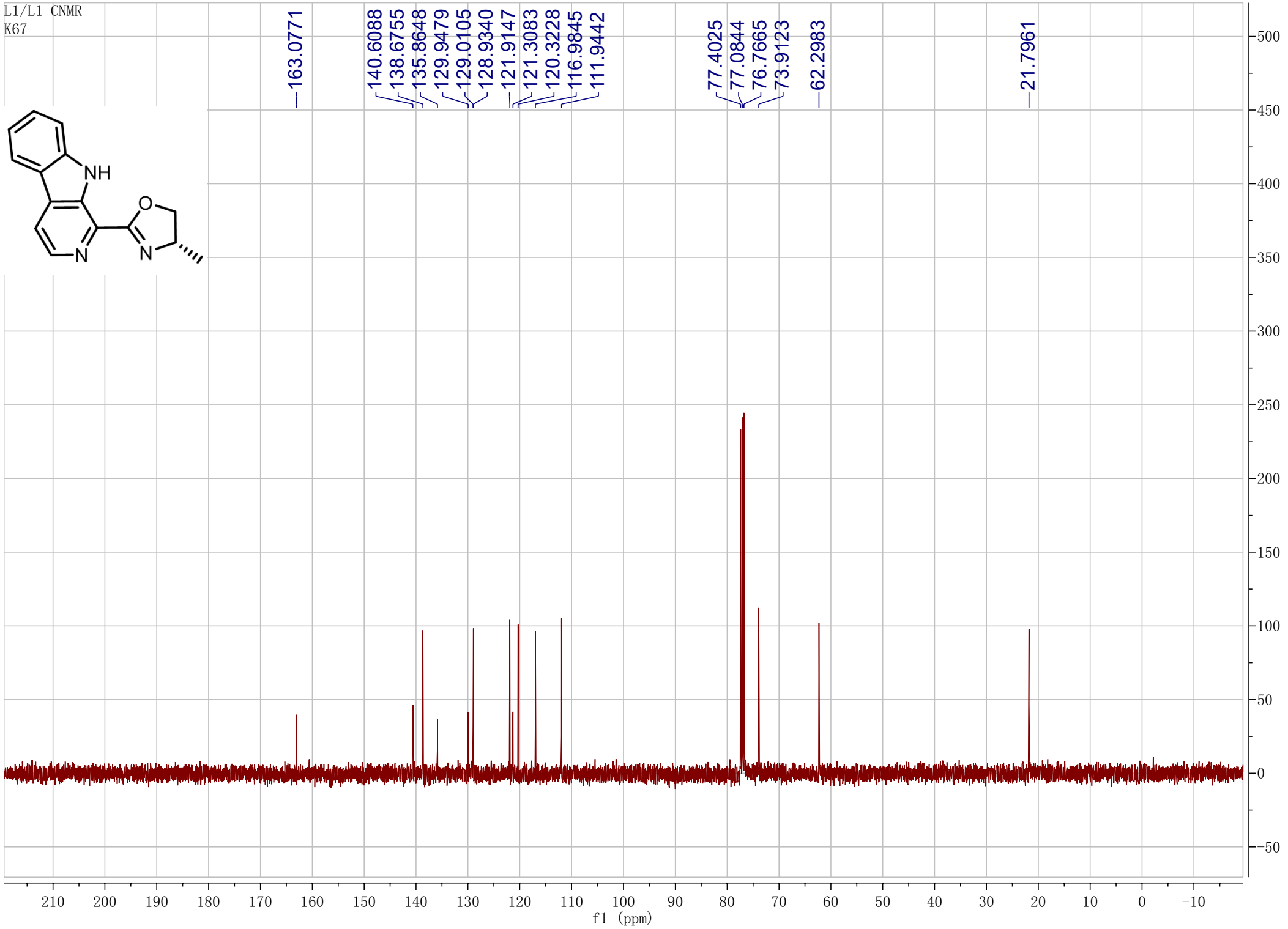
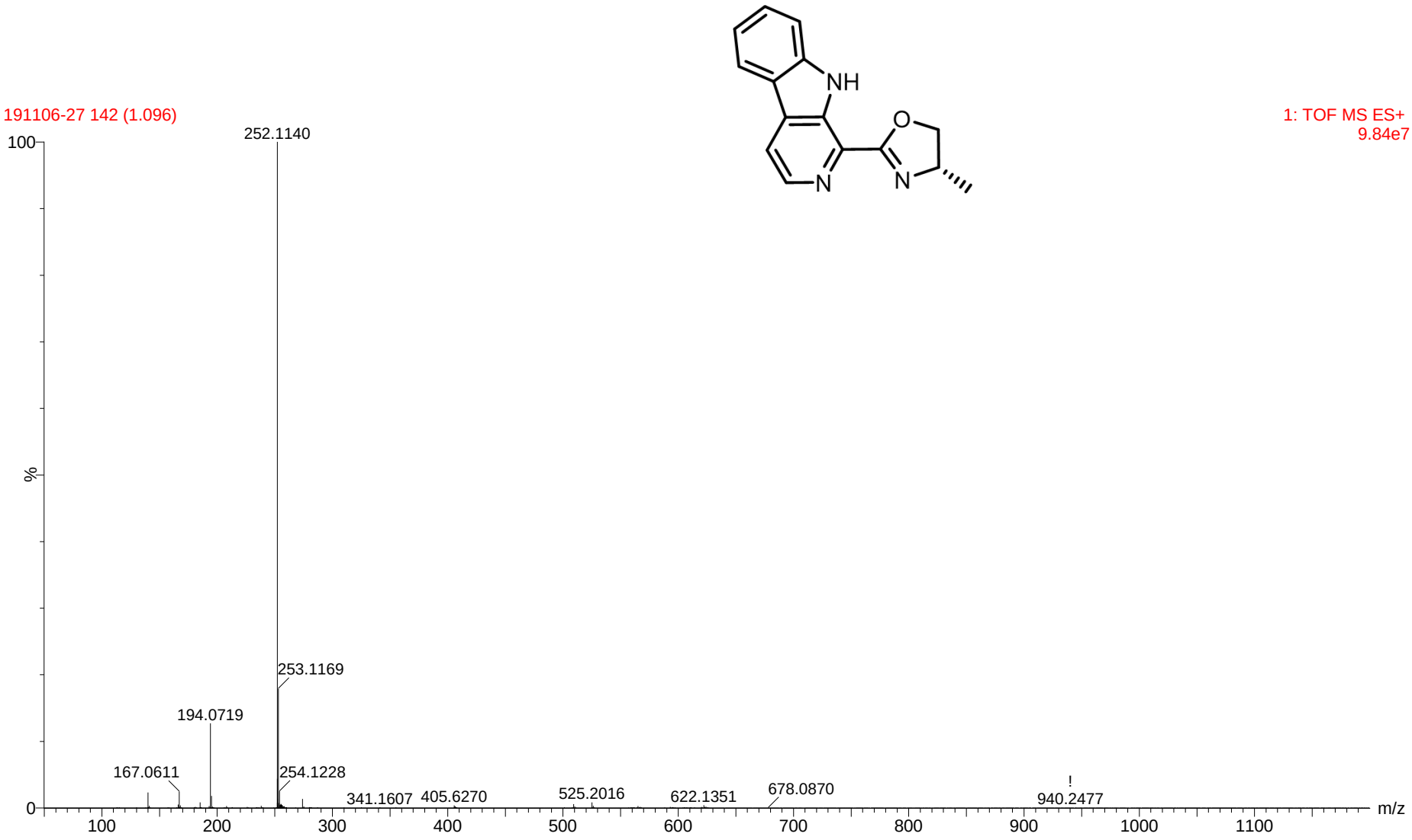
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


L1/L1 CNMR
K67
163.0771
140.6088
138.6755
135.8648
129.9479
129.0105
128.9340
121.9147
121.3083
120.3228
116.9845
111.9442
77.4025
77.0844
76.7665
73.9123
62.2983
21.7961
NH
O
N
N
f1 (ppm)


191106-27 142 (1.096)
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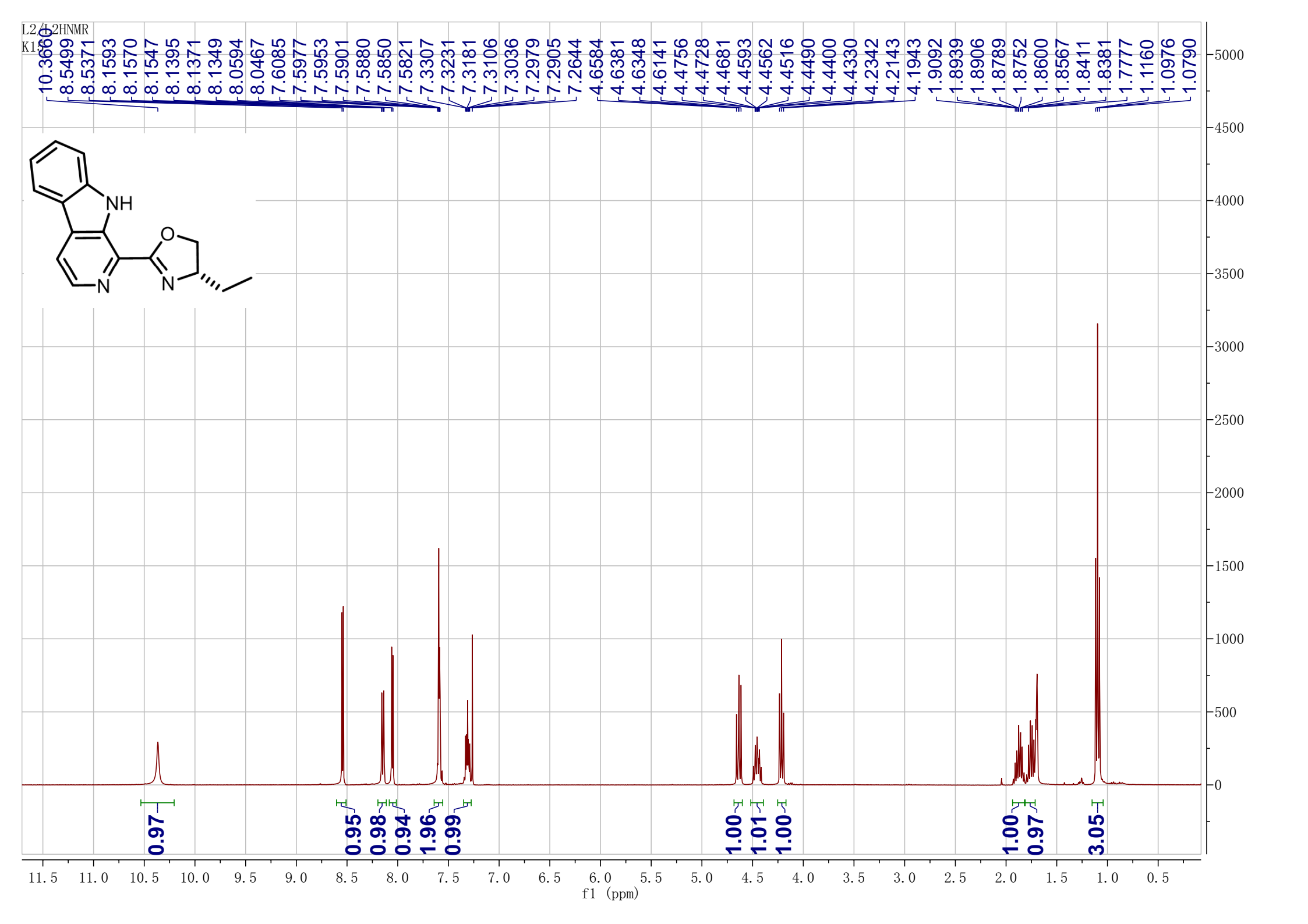
100
%
0
252.1140
253.1169
194.0719
167.0611
254.1228
341.1607
405.6270
525.2016
622.1351
678.0870
940.2477
m/z
100
200
300
400
500
600
700
800
900
1000
1100
NH
O
N
N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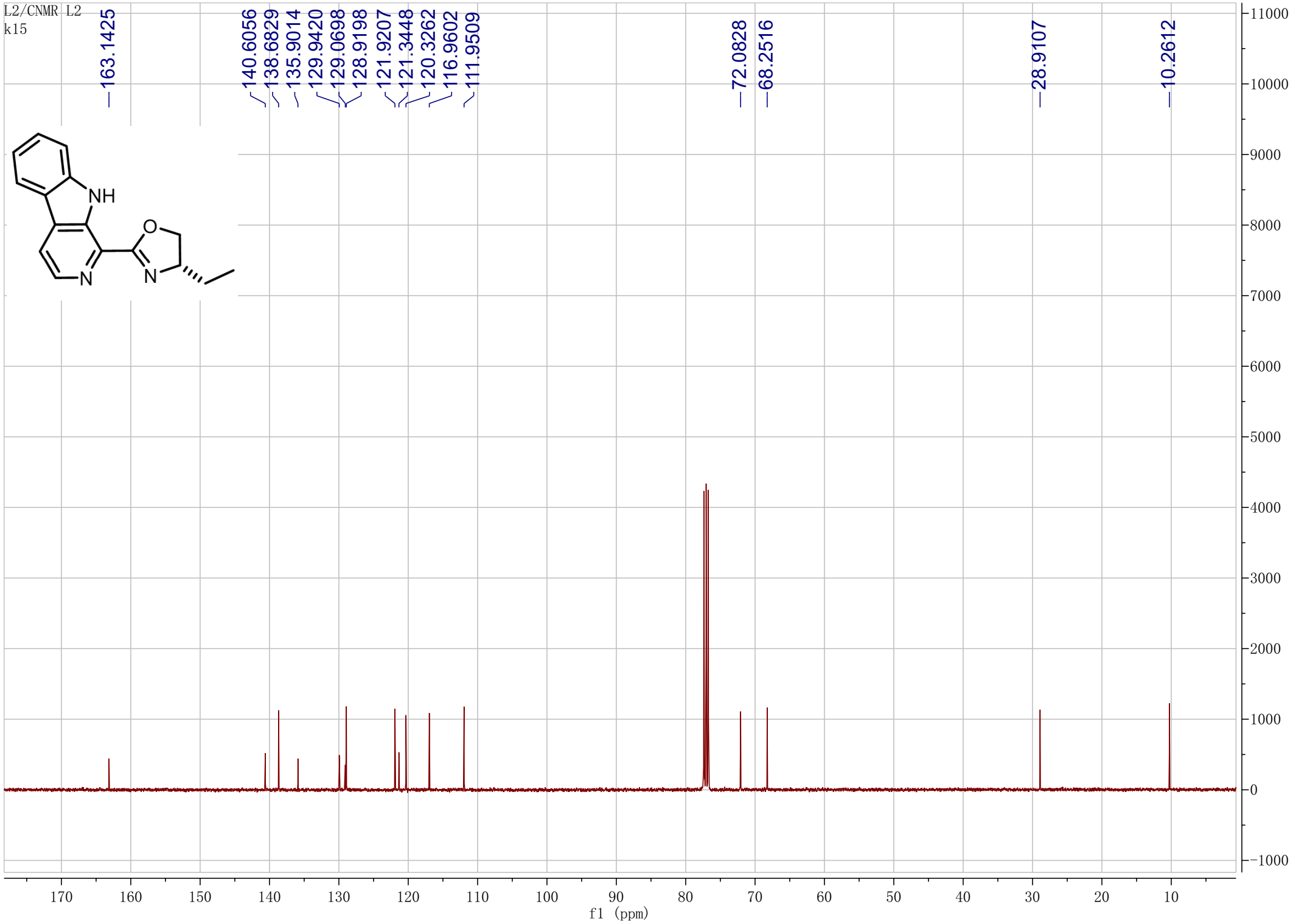
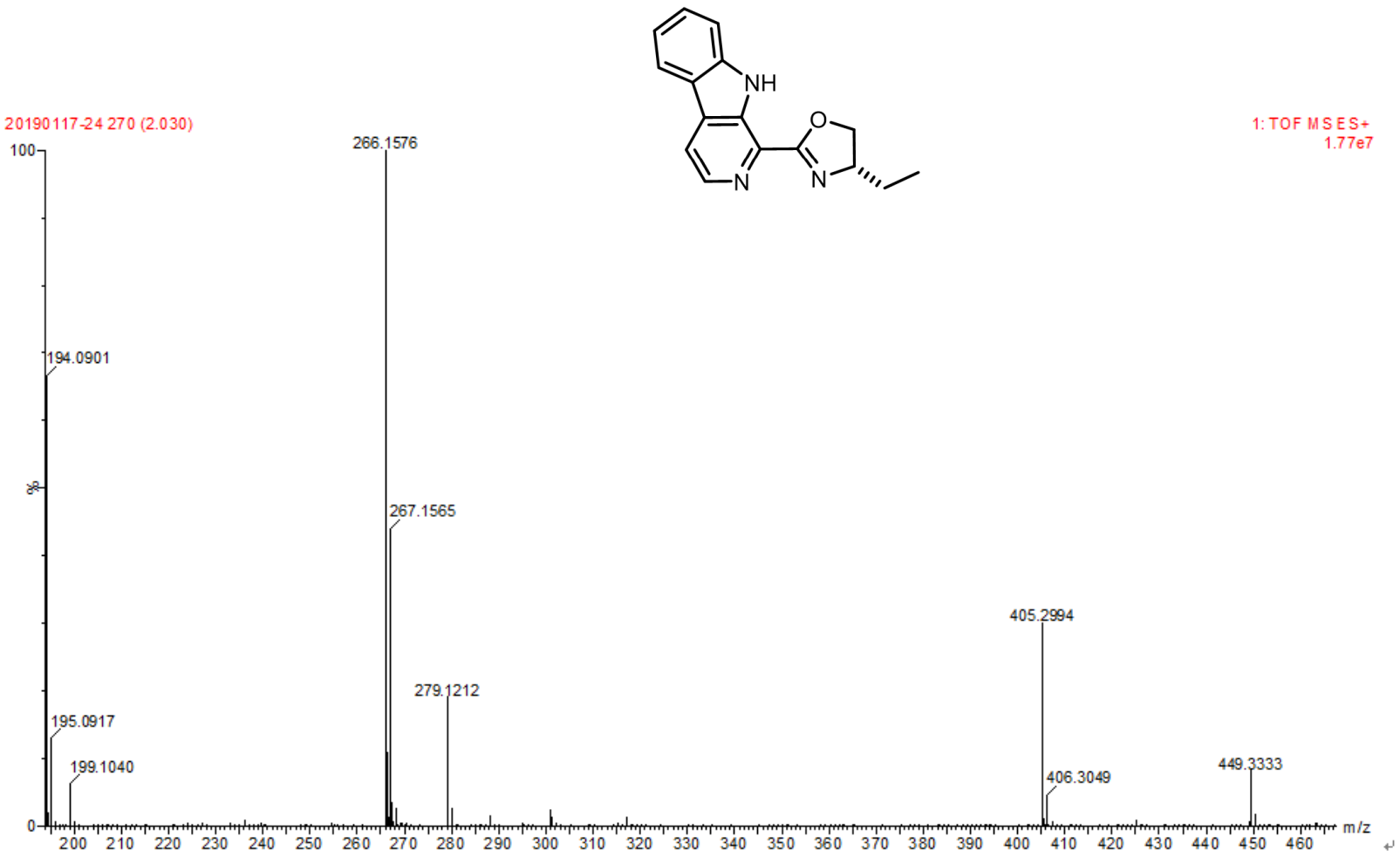
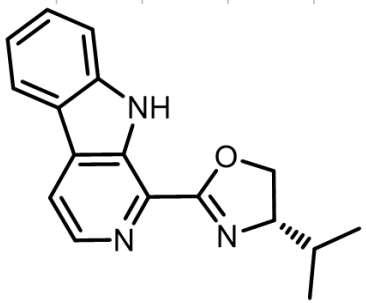
8.1570
8.1547
8.1395
8.1371
8.1349
8.0594
8.0467
7.6085
7.5977
7.5953
7.5901
7.5880
7.5850
7.5821
7.3307
7.3231
7.3181
7.3106
7.3036
7.2979
7.2905
7.2644
4.6584
4.6381
4.6348
4.6141
4.4756
4.4728
4.4681
4.4593
4.4562
4.4516
4.4490
4.4400
4.4330
4.2342
4.2143
4.1943
1.9092
1.8939
1.8906
1.8789
1.8752
1.8600
1.8567
1.8411
1.8381
1.7777
1.1160
1.0976
1.0790
NH
O
N
N
0.97
0.95
0.98
0.94
1.96
0.99
1.00
1.01
1.00
1.00
0.97
3.05
f1 (ppm)


L2/CNMR L2
k15
163.1425
140.6056
138.6829
135.9014
129.9420
129.0698
128.9198
121.9207
121.3448
120.3262
116.9602
111.9509
72.0828
68.2516
28.9107
10.2612
NH
O
N
N
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


20190117-24 270 (2.030)
1: TOF MS ES+
1.77e7
100
%
0
266.1576
194.0901
267.1565
405.2994
279.1212
195.0917
199.1040
406.3049
449.3333
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460
m/z
NH
O
N
N

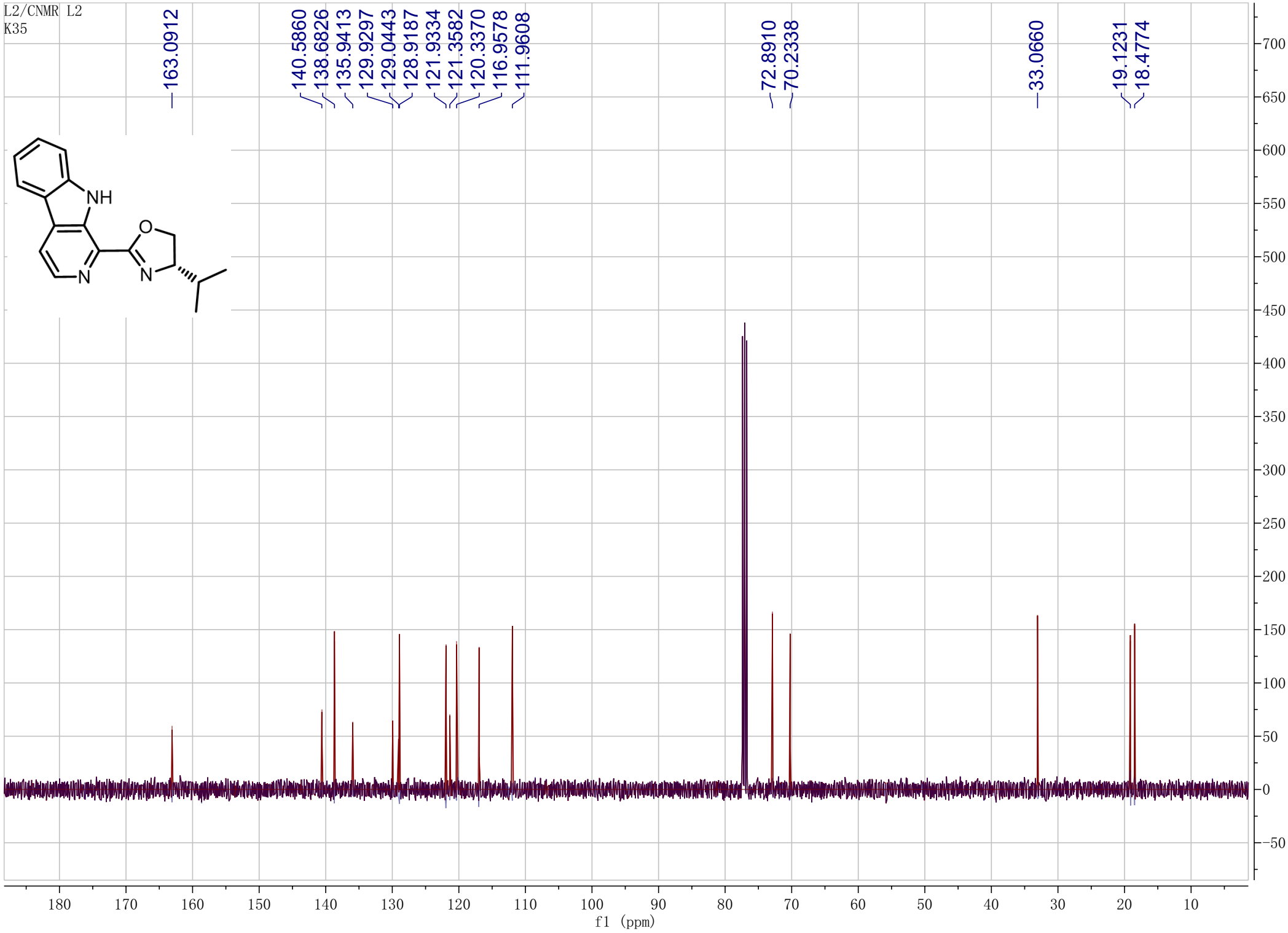
L2/L2-HNMR
K34

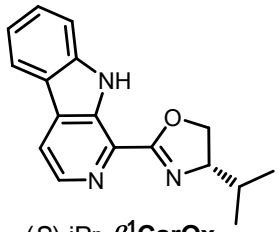


10.3742
8.5552
8.5425
8.1707
8.1511
8.0723
8.0597
7.6187
7.6074
7.6051
7.5990
7.5956
7.5924
7.3406
7.3326
7.3282
7.3205
7.3131
7.3080
7.3005
7.2640
4.6212
4.6036
4.5919
4.5882
4.5758
4.5593
4.5546
4.3466
4.3311
4.3268
4.3104
4.3066
4.2980
4.2775
1.9964
1.9798
1.9636
1.9477
1.9470
1.1465
1.1297
1.0374
1.0206

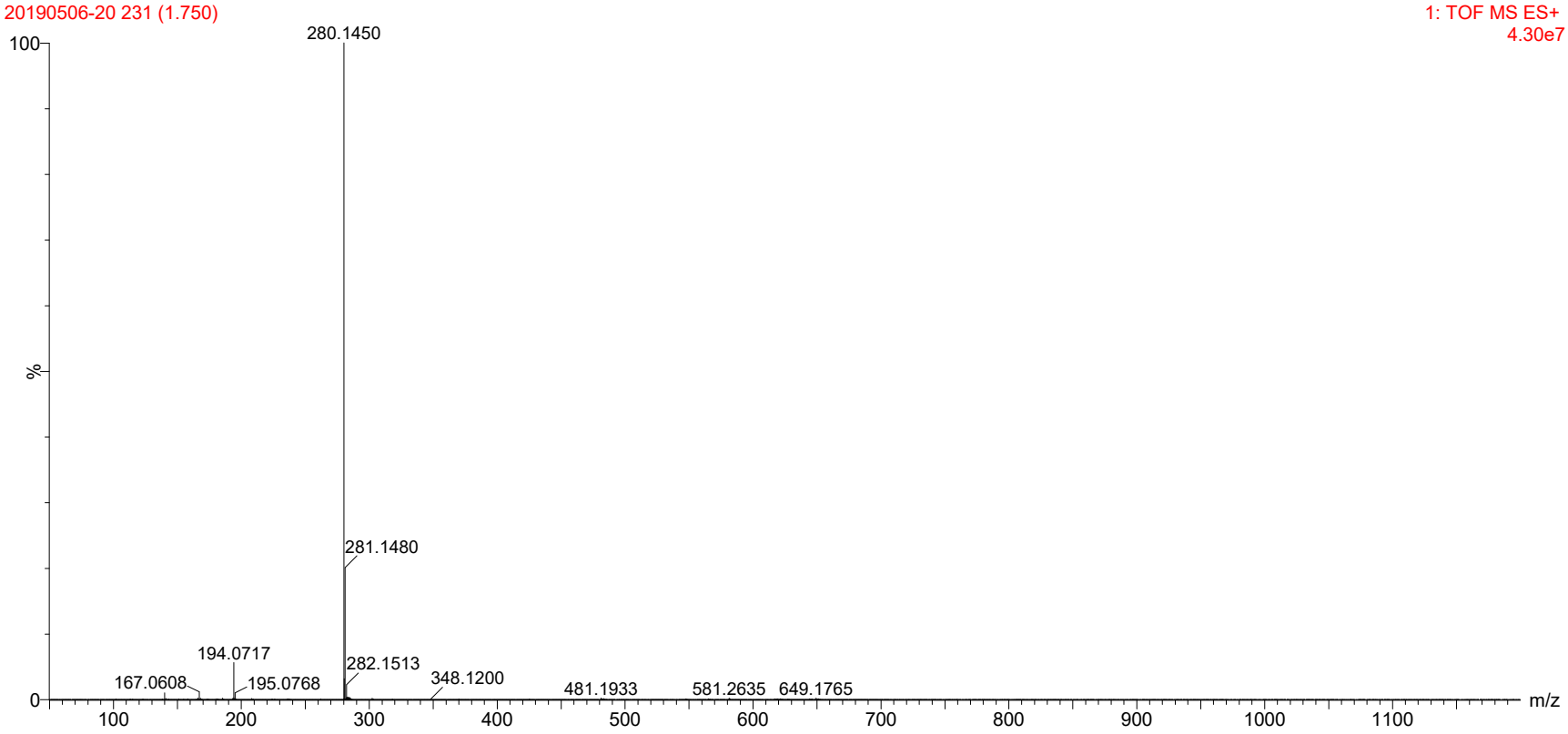
0.93
1.02
0.99
0.98
1.99
1.03
1.02
2.07
1.01
3.00
3.04

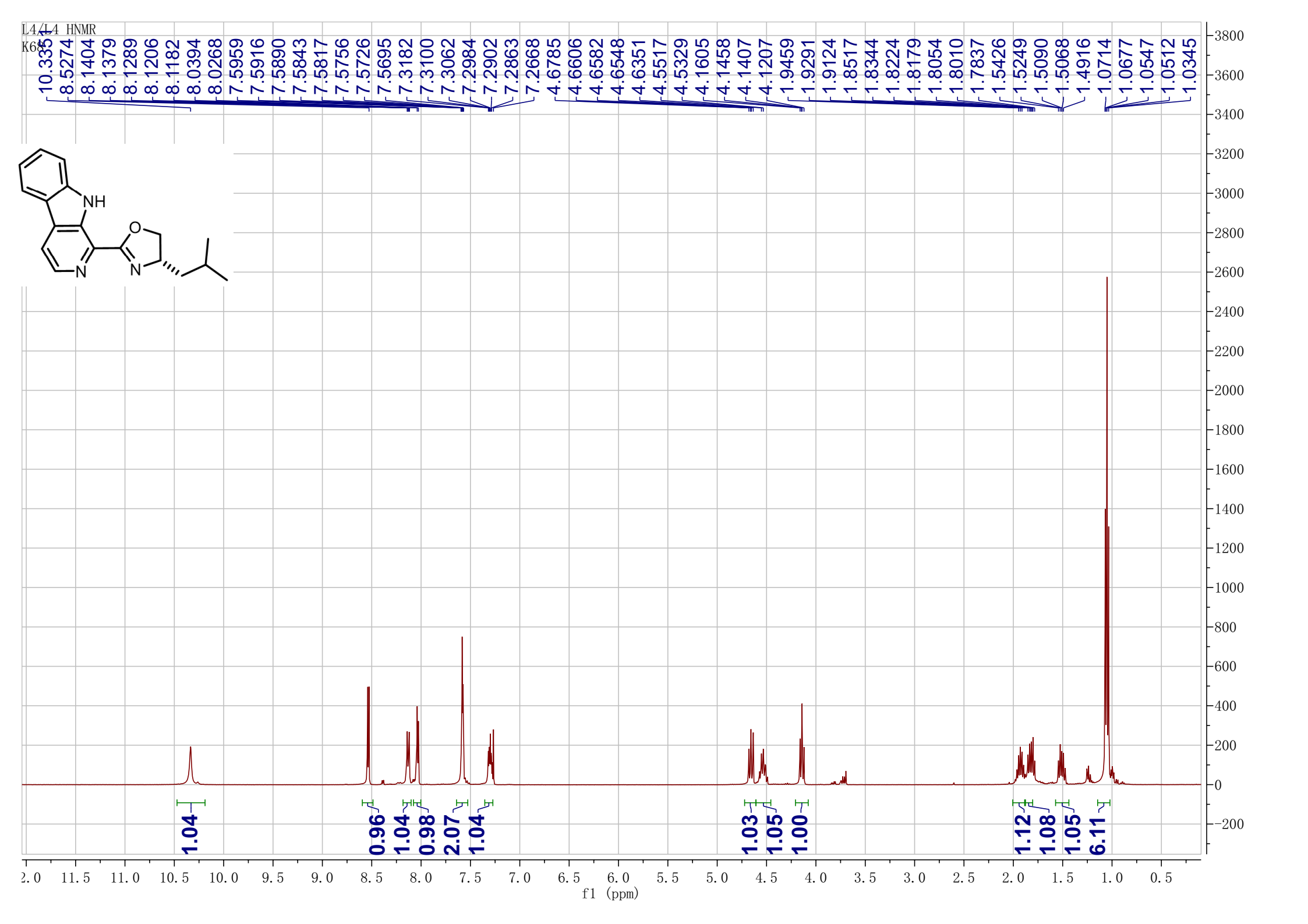
f1 (ppm)

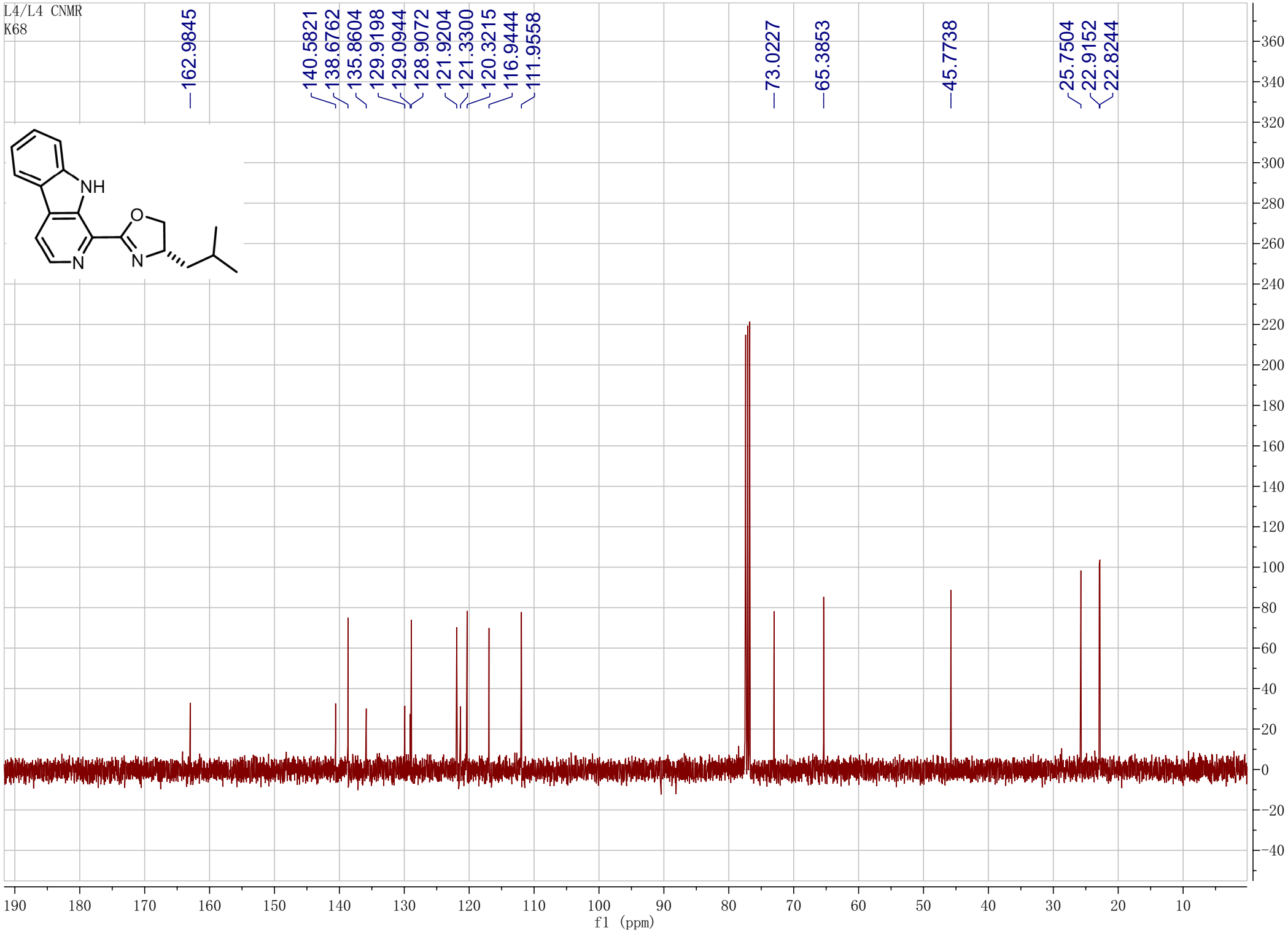

L2/CNMR L2
K35
163.0912
140.5860
138.6826
135.9413
129.9297
129.0443
128.9187
121.9334
121.3582
120.3370
116.9578
111.9608
72.8910
70.2338
33.0660
19.1231
18.4774
NH
O
N
N
f1 (ppm)

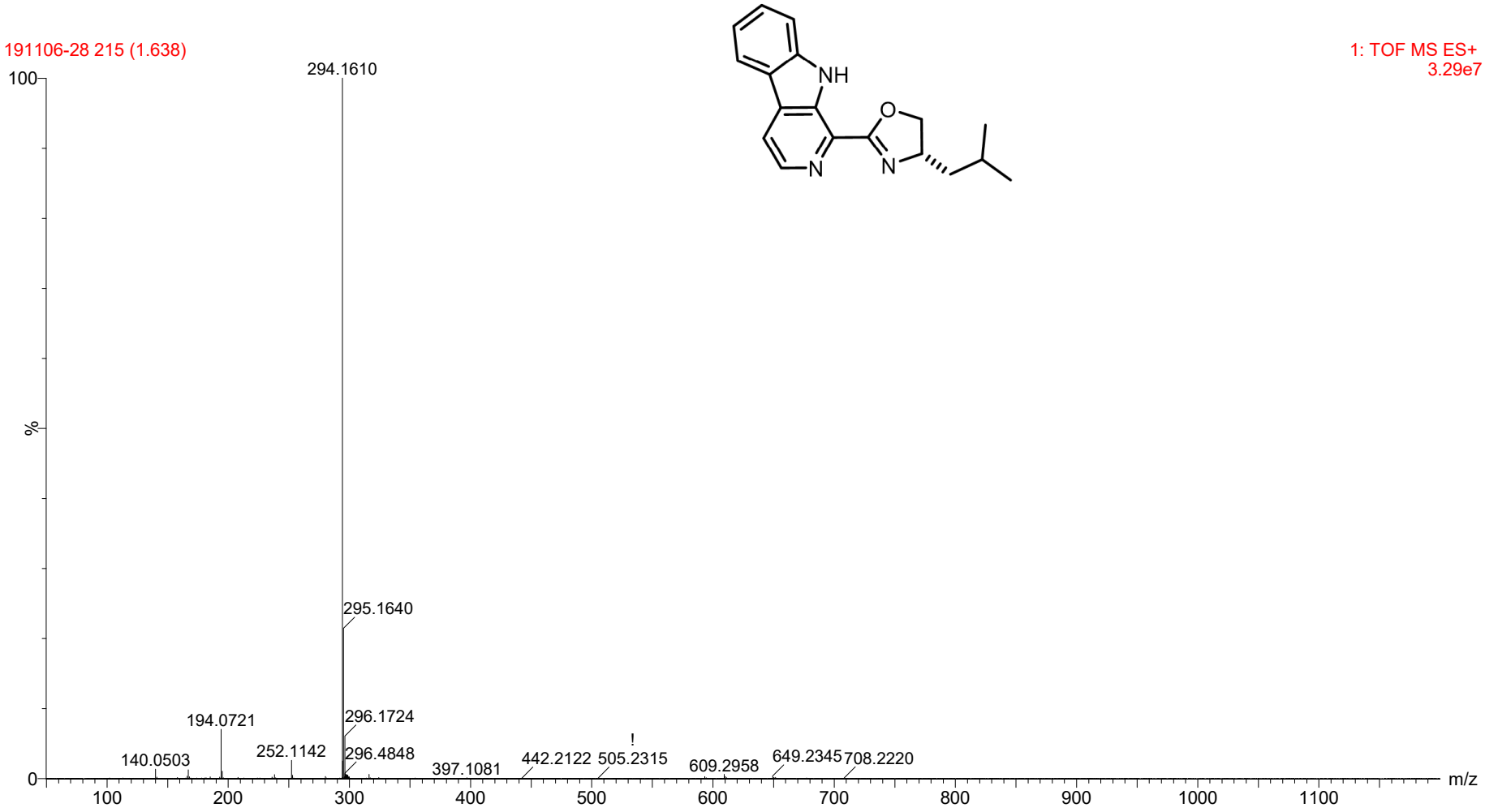


(*S*)-iPr-β^1**CarOx**

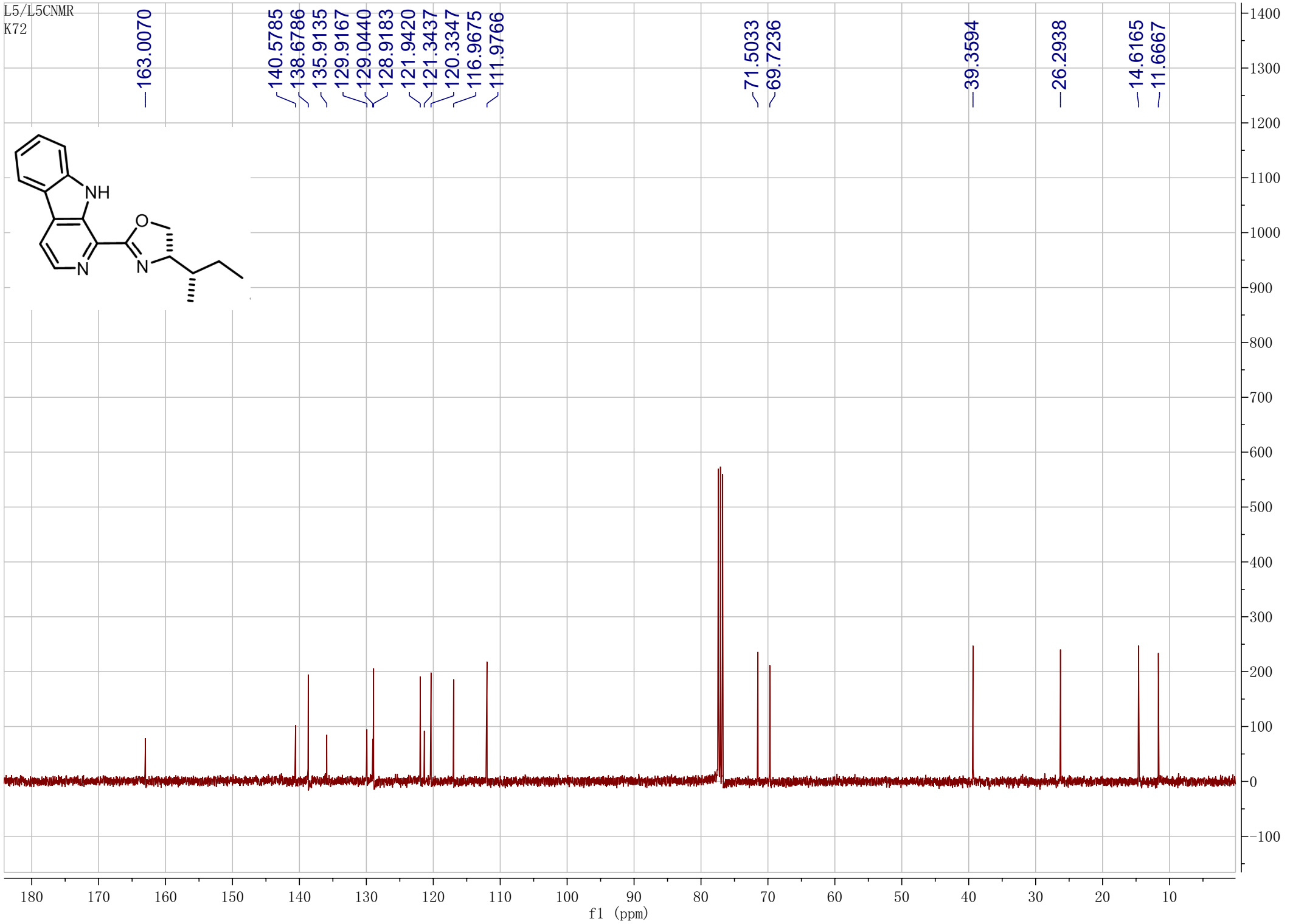


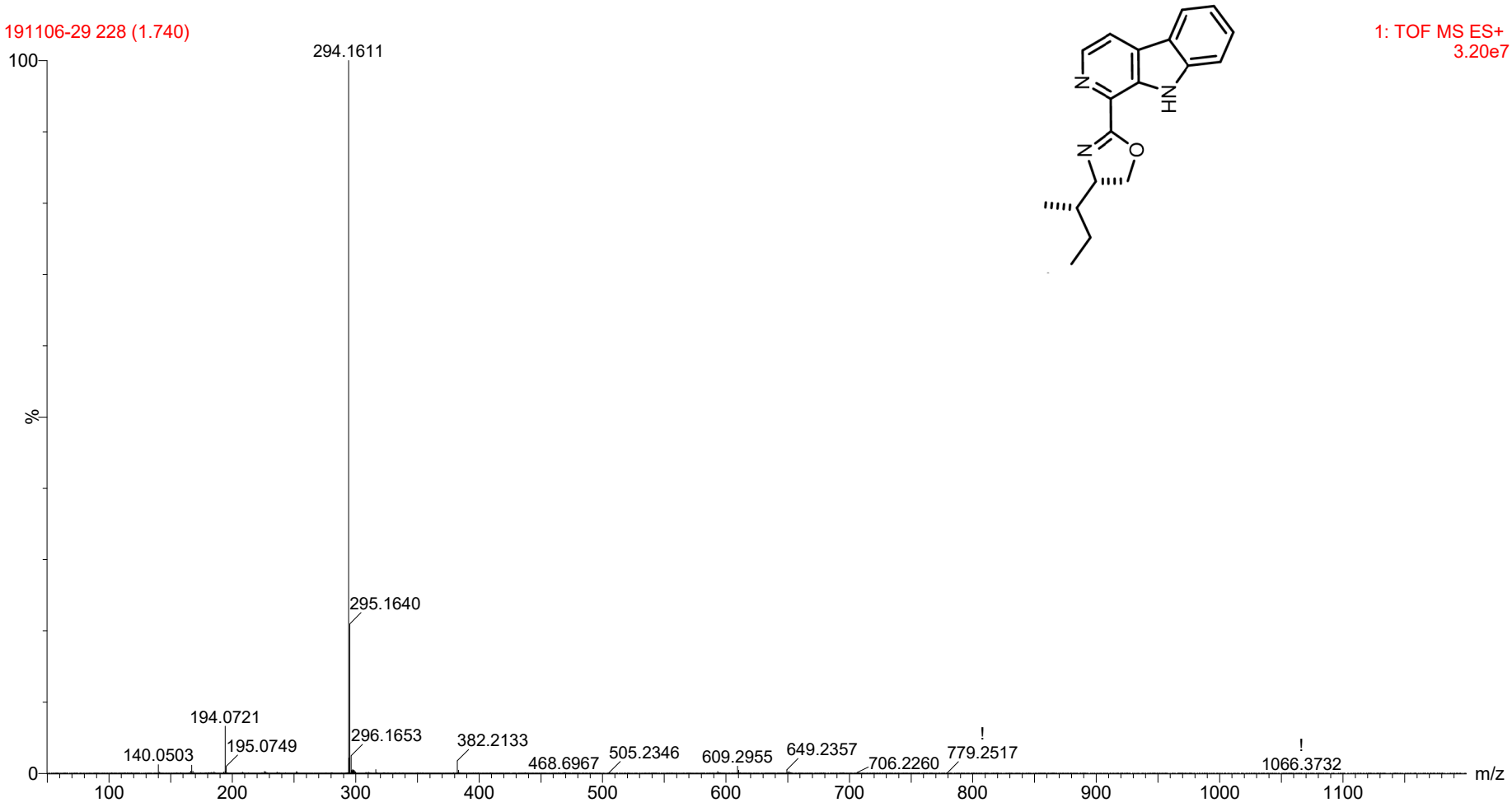

L4/L4 HNMR
K68
10.335
8.5274
8.1404
8.1379
8.1289
8.1206
8.1182
8.0394
8.0268
7.5959
7.5916
7.5890
7.5843
7.5817
7.5756
7.5726
7.5695
7.3182
7.3100
7.3062
7.2984
7.2902
7.2863
7.2668
4.6785
4.6606
4.6582
4.6548
4.6351
4.5517
4.5329
4.1605
4.1458
4.1407
4.1207
1.9459
1.9291
1.9124
1.8517
1.8344
1.8224
1.8179
1.8054
1.8010
1.7837
1.5426
1.5249
1.5090
1.5068
1.4916
1.0714
1.0677
1.0547
1.0512
1.0345
NH
O
N
N
1.04
0.96
1.04
0.98
2.07
1.04
1.03
1.05
1.00
1.12
1.08
1.05
6.11
f1 (ppm)

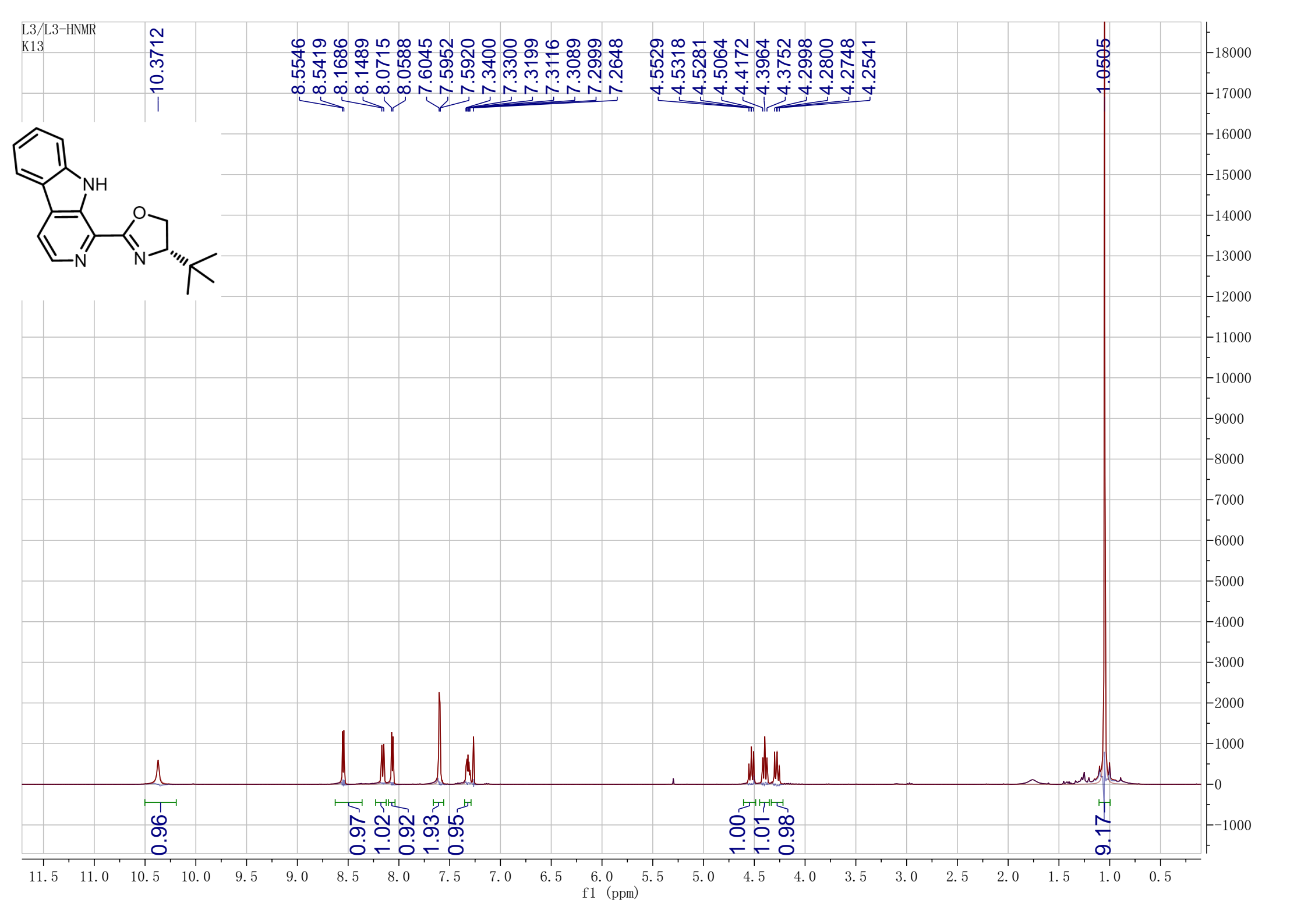

L4/L4 CNMR
K68
162.9845
140.5821
138.6762
135.8604
129.9198
129.0944
128.9072
121.9204
121.3300
120.3215
116.9444
111.9558
73.0227
65.3853
45.7738
25.7504
22.9152
22.8244
NH
O
N
N
f1 (ppm)


191106-28 215 (1.638)
1: TOF MS ES+
3.29e7
294.1610
295.1640
296.1724
296.4848
194.0721
140.0503
252.1142
397.1081
442.2122
505.2315
609.2958
649.2345
708.2220
NH
O
N
N
%
m/z
100
0
100
200
300
400
500
600
700
800
900
1000
1100

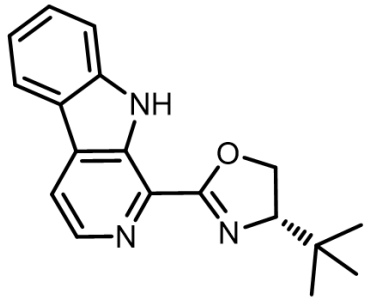

L5/L5 HNMR
K726
10.3566
8.5468
8.5341
8.1484
8.1288
8.0514
8.0480
8.0386
8.0352
7.5939
7.5914
7.5881
7.5846
7.5810
7.5780
7.5750
7.3251
7.3179
7.3119
7.3050
7.3022
7.2985
7.2919
7.2849
7.2660
4.5800
4.5603
4.5563
4.5357
4.4497
4.4349
4.4302
4.4262
4.4147
4.4116
4.4055
4.3104
4.2902
4.2700
1.8314
1.8263
1.8094
1.7405
1.7259
1.7064
1.3516
1.3484
1.3337
1.3299
1.3156
1.0402
1.0217
1.0032
0.9596
0.9428
NH
O
N
N
1.02
0.95
0.98
1.00
1.99
1.00
1.00
1.01
1.02
1.11
1.08
1.08
3.13
3.14
f1 (ppm)


L5/L5CNMR
K72
163.0070
140.5785
138.6786
135.9135
129.9167
129.0440
128.9183
121.9420
121.3437
120.3347
116.9675
111.9766
71.5033
69.7236
39.3594
26.2938
14.6165
11.6667
NH
O
N
N
f1 (ppm)


191106-29 228 (1.740)
1: TOF MS ES+
3.20e7
100
%
0
294.1611
295.1640
194.0721
195.0749
140.0503
296.1653
382.2133
468.6967
505.2346
609.2955
649.2357
706.2260
779.2517
1066.3732
m/z
100
200
300
400
500
600
700
800
900
1000
1100

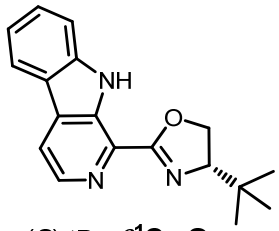

L3/L3-HNMR
K13
10.3712
8.5546
8.5419
8.1686
8.1489
8.0715
8.0588
7.6045
7.5952
7.5920
7.3400
7.3300
7.3199
7.3116
7.3089
7.2999
7.2648
4.5529
4.5318
4.5281
4.5064
4.4172
4.3964
4.3752
4.2998
4.2800
4.2748
4.2541
1.0505
NH
O
N
N
0.96
0.97
1.02
0.92
1.93
0.95
1.00
1.01
0.98
9.17
f1 (ppm)

L3/L3-CNMR
K36

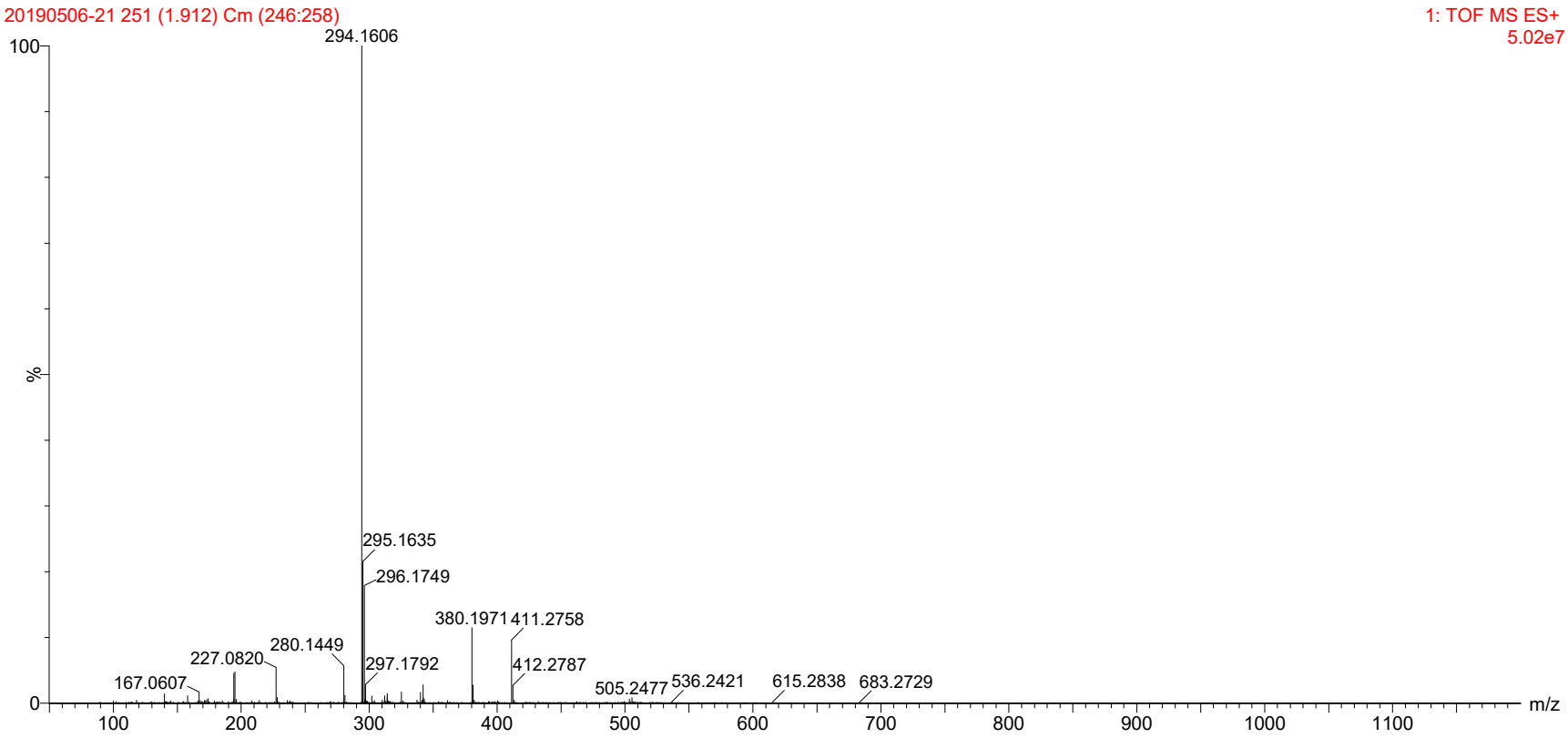


163.0793
140.5675
138.7020
136.0016
129.9225
129.0324
128.9273
121.9570
121.3810
120.3590
116.9735
111.9766
76.4154
68.6983
34.0663
26.0718

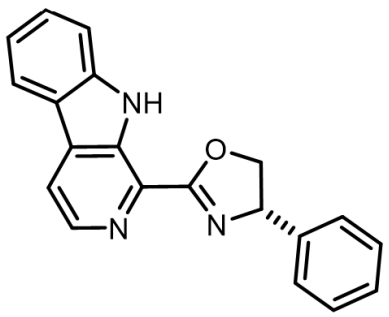
f1 (ppm)



(*S*)-tBu-β^1**CarOx**



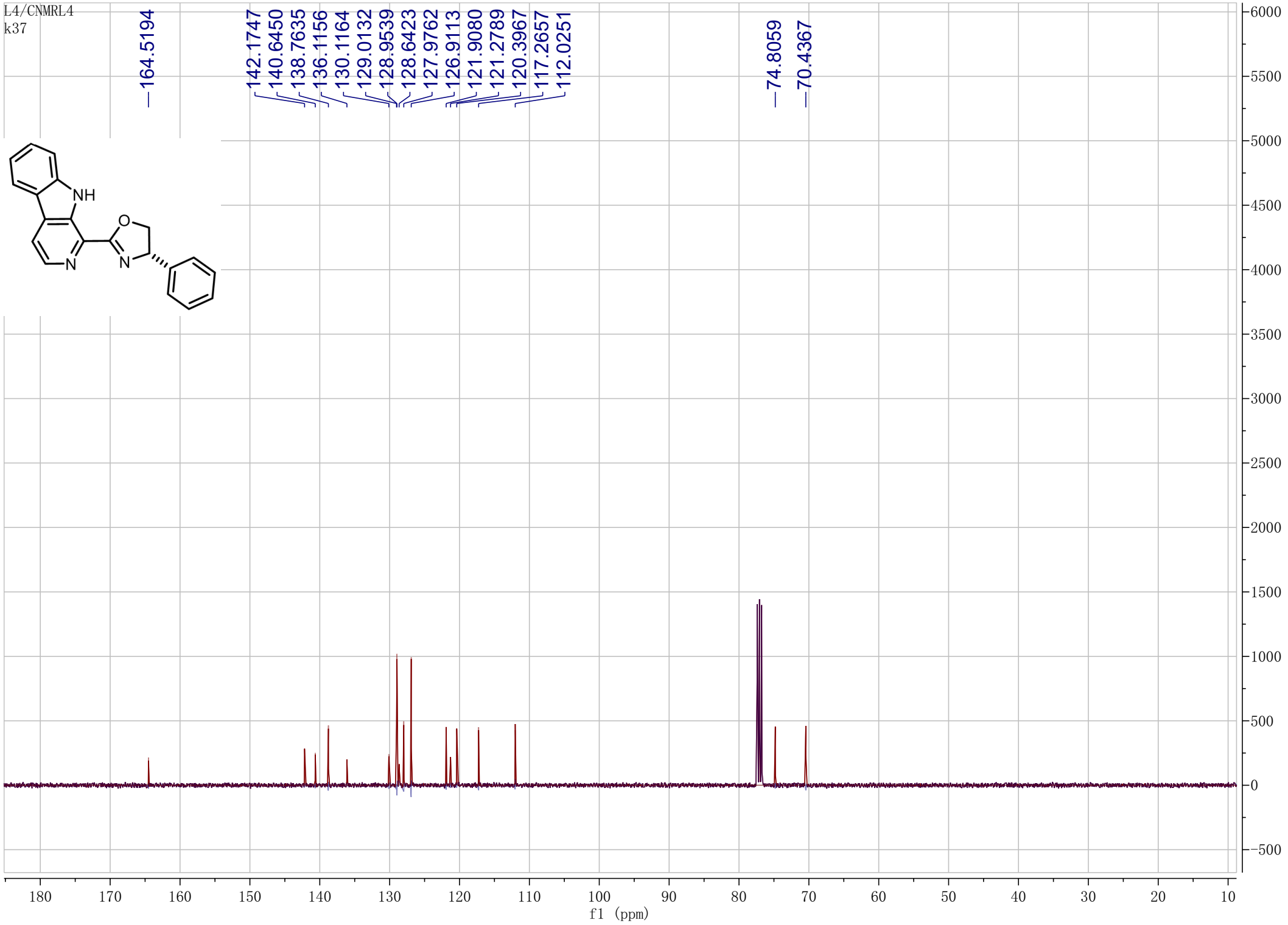
L4/L4-HNMR
K14

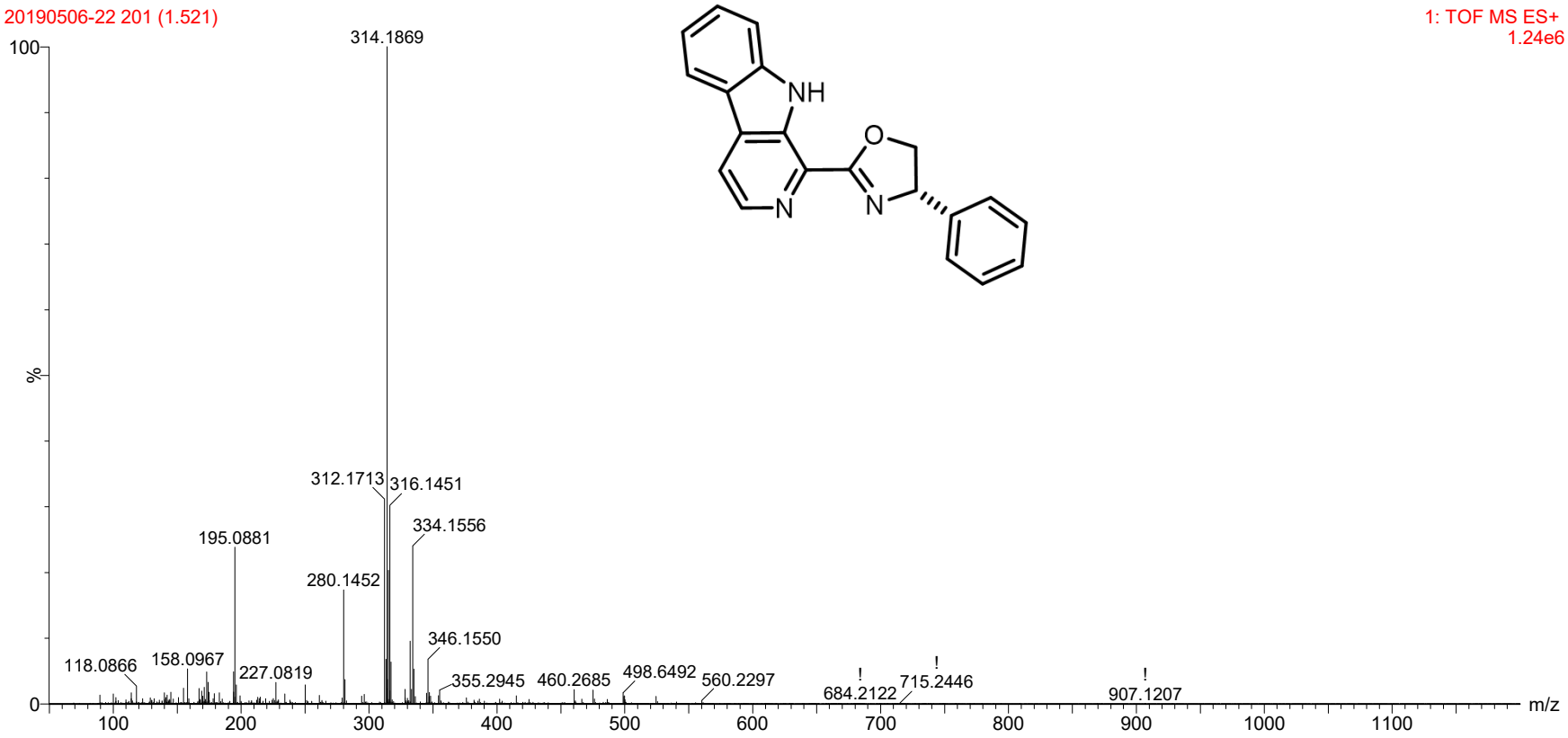


10.3826
8.5965
8.5837
8.1674
8.1477
8.1053
8.0926
7.5719
7.5687
7.5546
7.5516
7.5374
7.5173
7.4166
7.4060
7.3944
7.3721
7.3617
7.3505
7.3313
7.3282
7.3118
7.3082
7.2948
7.2914
7.2607
5.6299
5.6092
5.6048
5.5834
4.9881
4.9671
4.9629
4.9413
4.4464
4.4252
4.4041

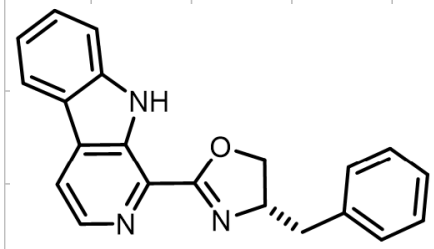
0.98
1.00
1.07
1.00
2.15
4.19
2.00
1.00
1.02
1.03

f1 (ppm)


L4/CNMRL4
k37
164.5194
142.1747
140.6450
138.7635
136.1156
130.1164
129.0132
128.9539
128.6423
127.9762
126.9113
121.9080
121.2789
120.3967
117.2657
112.0251
74.8059
70.4367
NH
O
N
N
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


20190506-22 201 (1.521)
1: TOF MS ES+
1.24e6
100
%
0
314.1869
312.1713
316.1451
334.1556
195.0881
280.1452
346.1550
118.0866
158.0967
227.0819
355.2945
460.2685
498.6492
560.2297
684.2122
715.2446
907.1207
NH
O
N
N
100
200
300
400
500
600
700
800
900
1000
1100
m/z

L8/HNMR-L8
K38

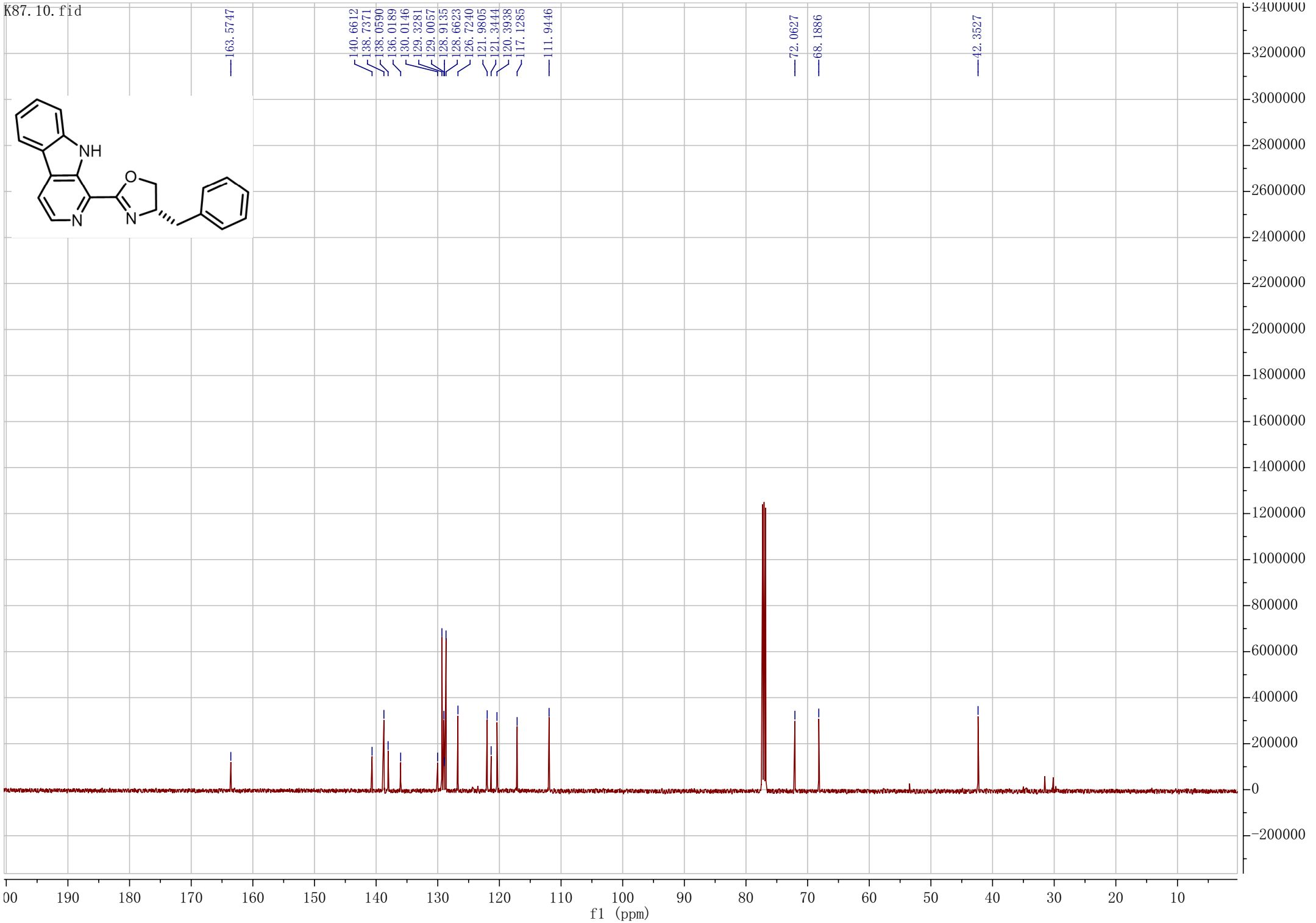


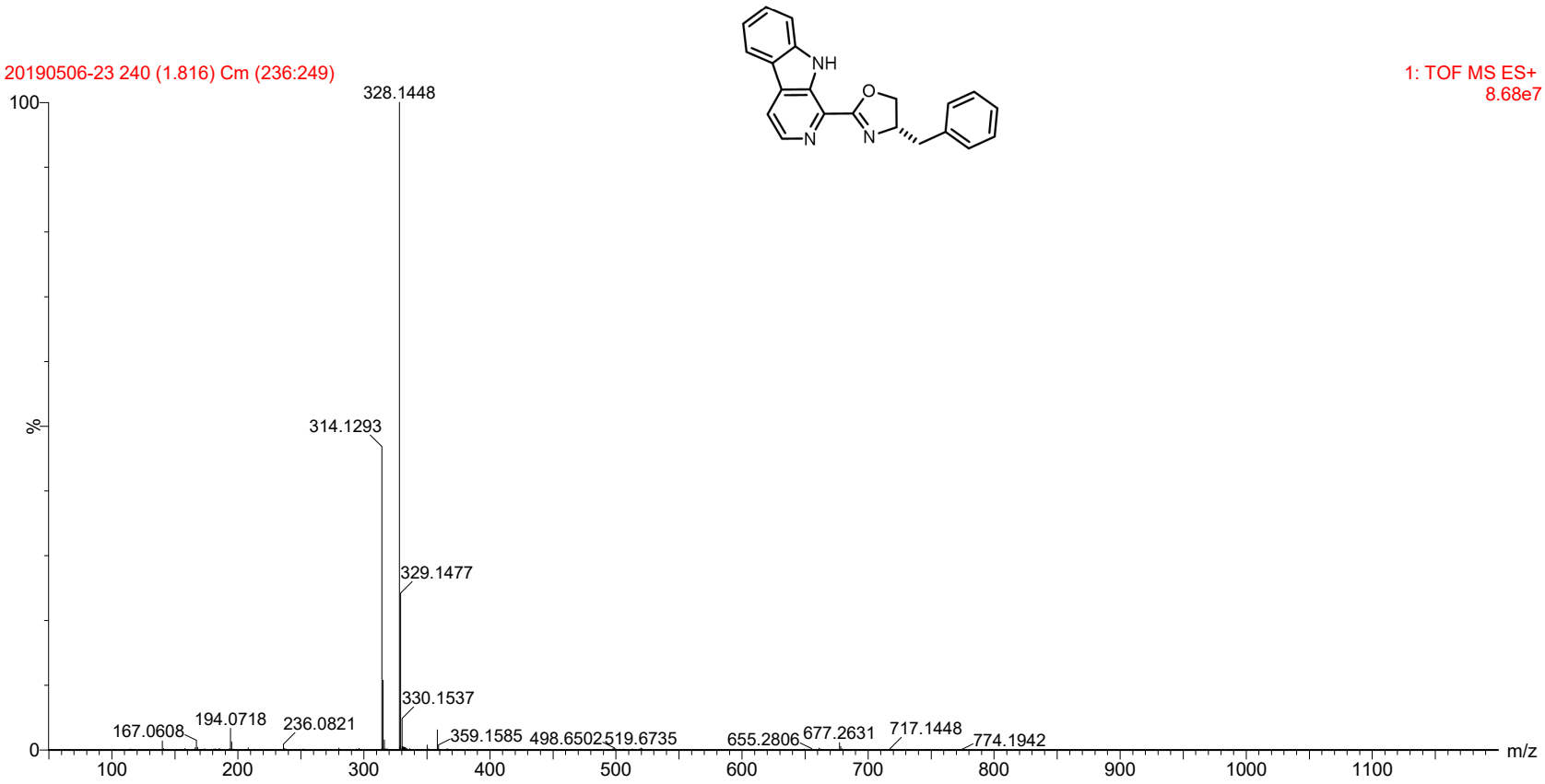
10.3461

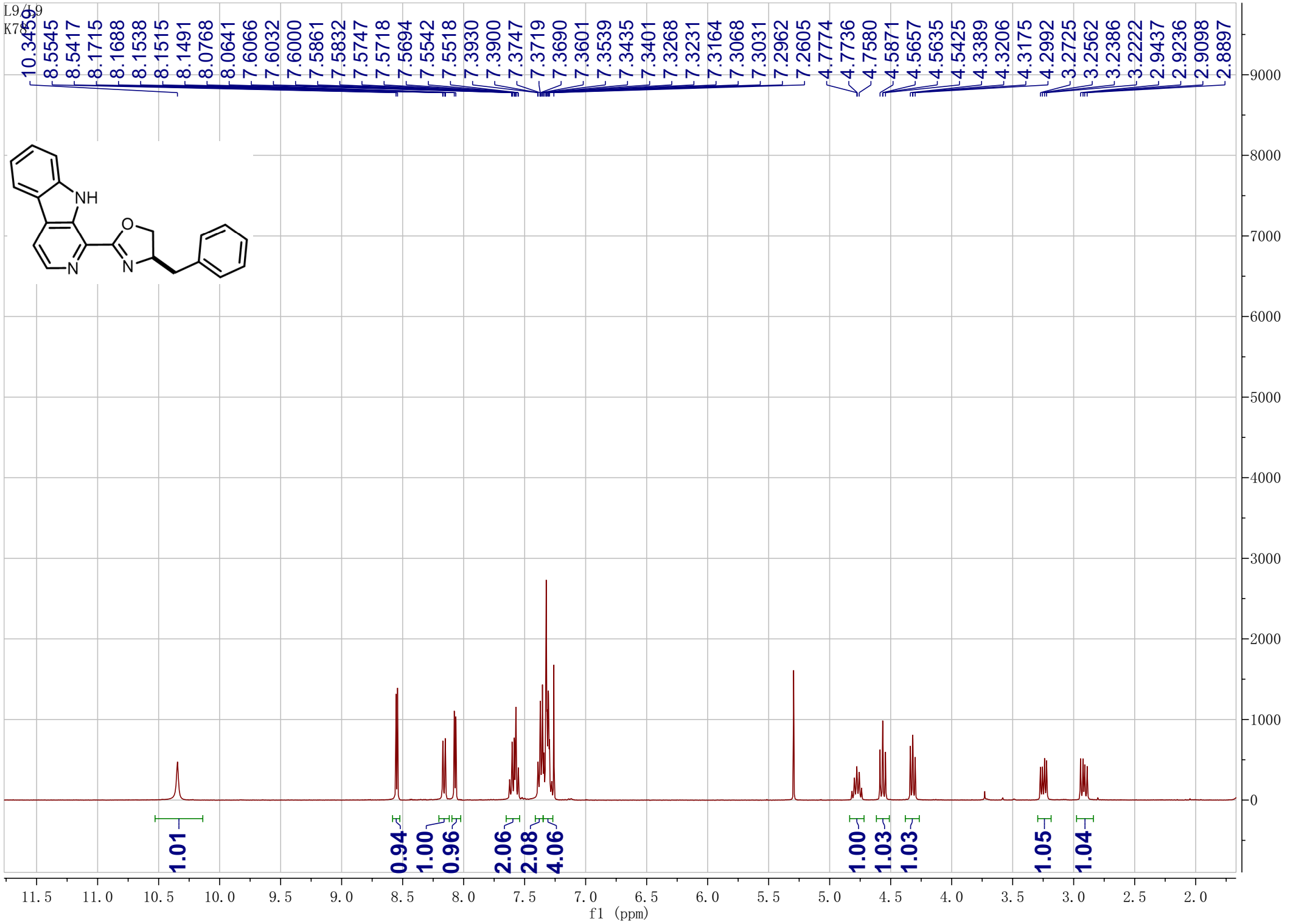
8.5529 8.5400 8.1707 8.1510 8.0771 8.0644 7.6018 7.5843 7.5717 7.5517 7.3893 7.3707 7.3523 7.3426 7.3396 7.3236 7.3145 7.3057 7.2944 7.2762 7.2609 4.7991 4.7821 4.7775 4.7581 4.5888 4.5667 4.5440 4.3388 4.3192 4.2991 3.2694 3.2531 3.2355 3.2191 2.9479 2.9279 2.9138 2.8938

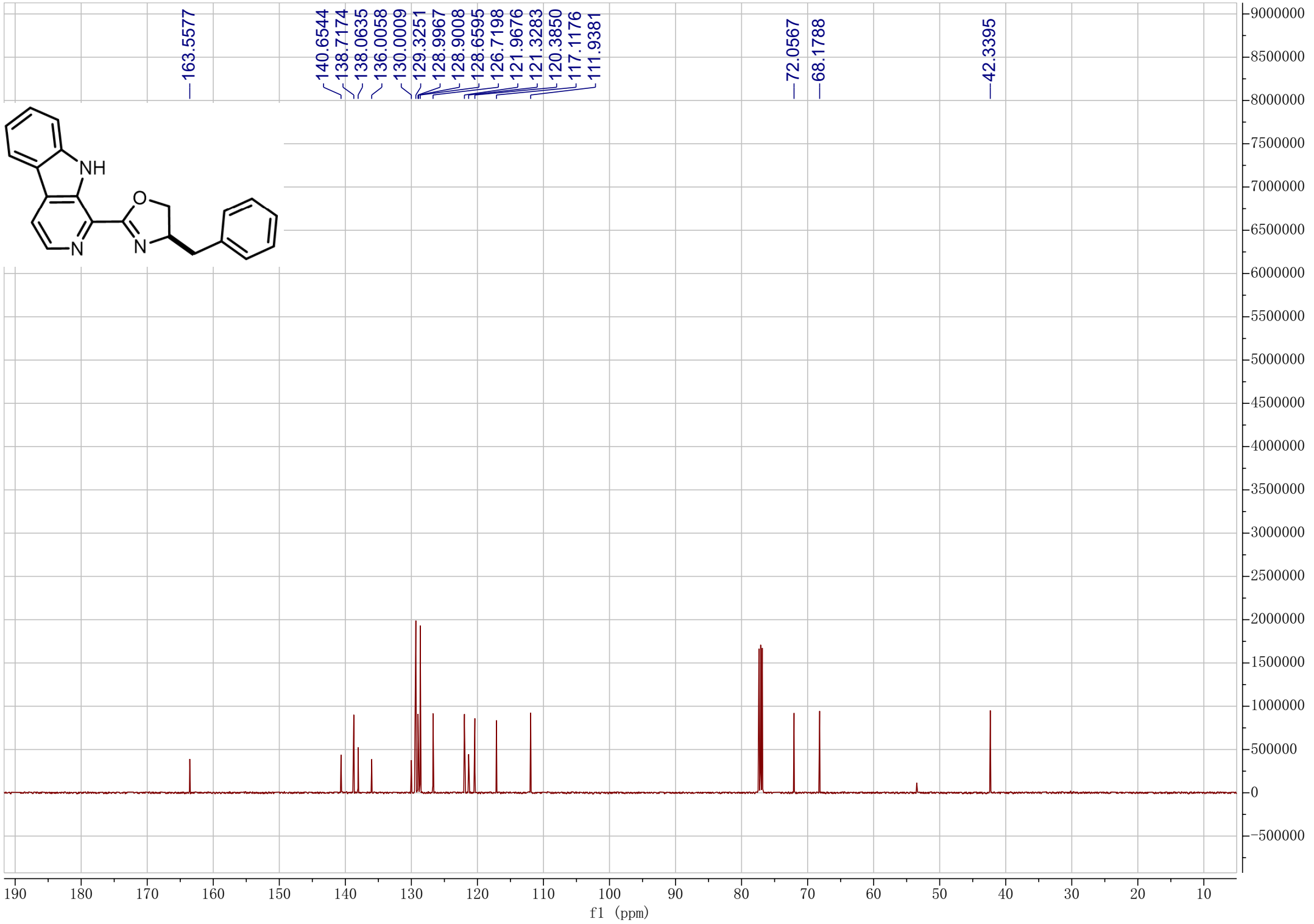
1.09 0.99 1.07 0.99 2.20 2.22 4.14 1.00 1.04 1.06 1.00 1.07

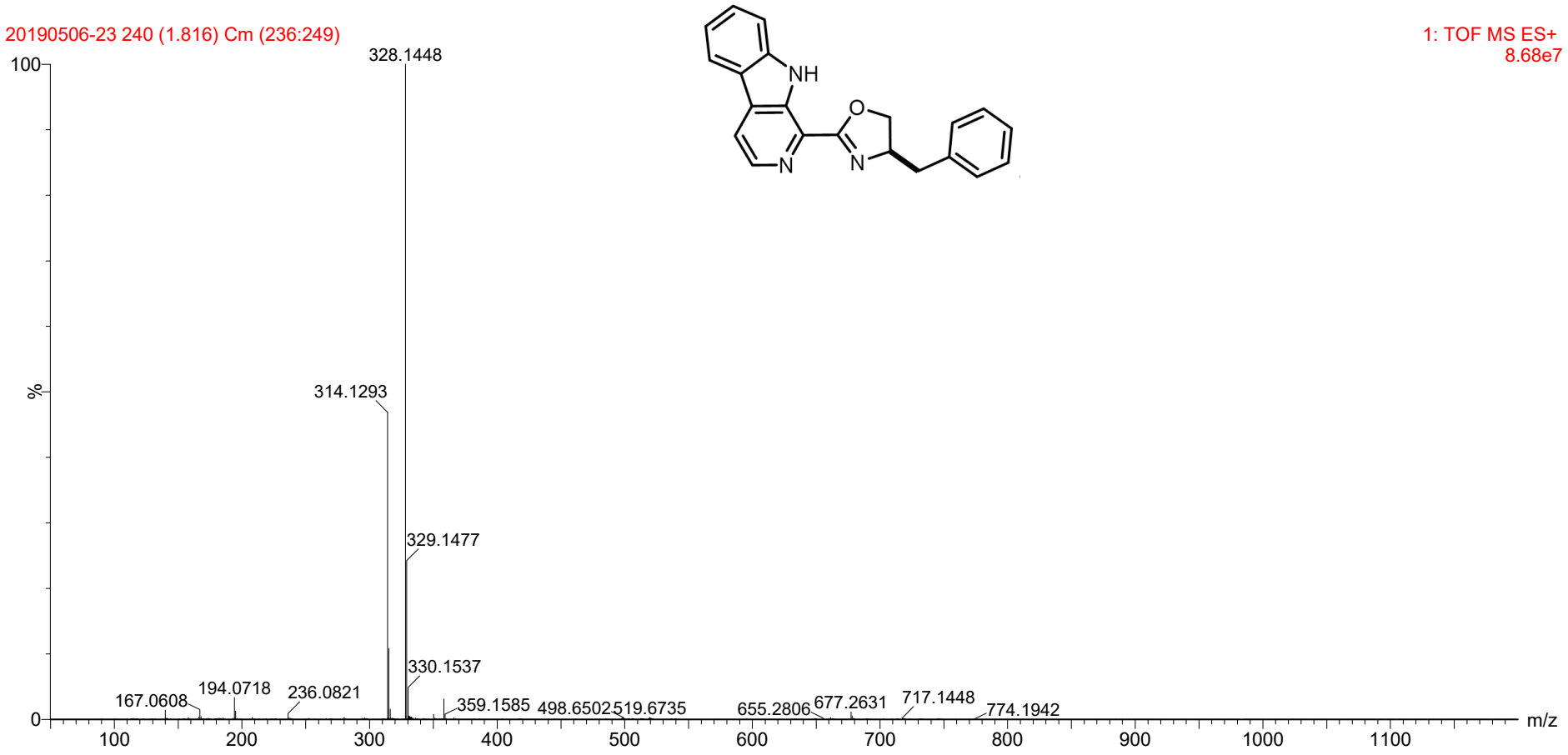
f1 (ppm)

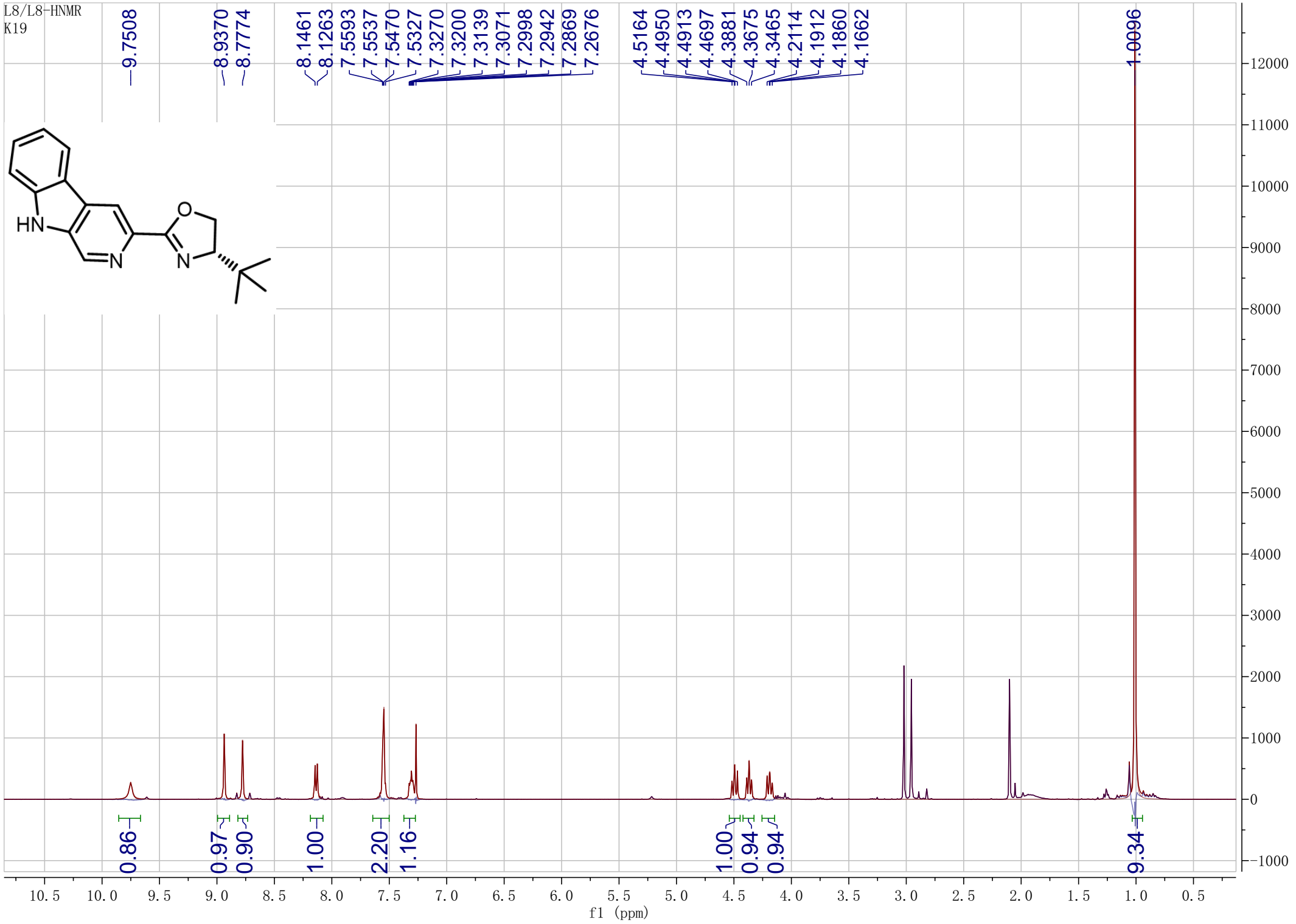

K87.10.fid
163.5747
140.6612
138.7371
138.0590
136.0189
130.0146
129.3281
129.0057
128.9135
128.6623
126.7240
121.9805
121.3444
120.3938
117.1285
111.9446
72.0627
68.1886
42.3527
NH
O
N
N
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

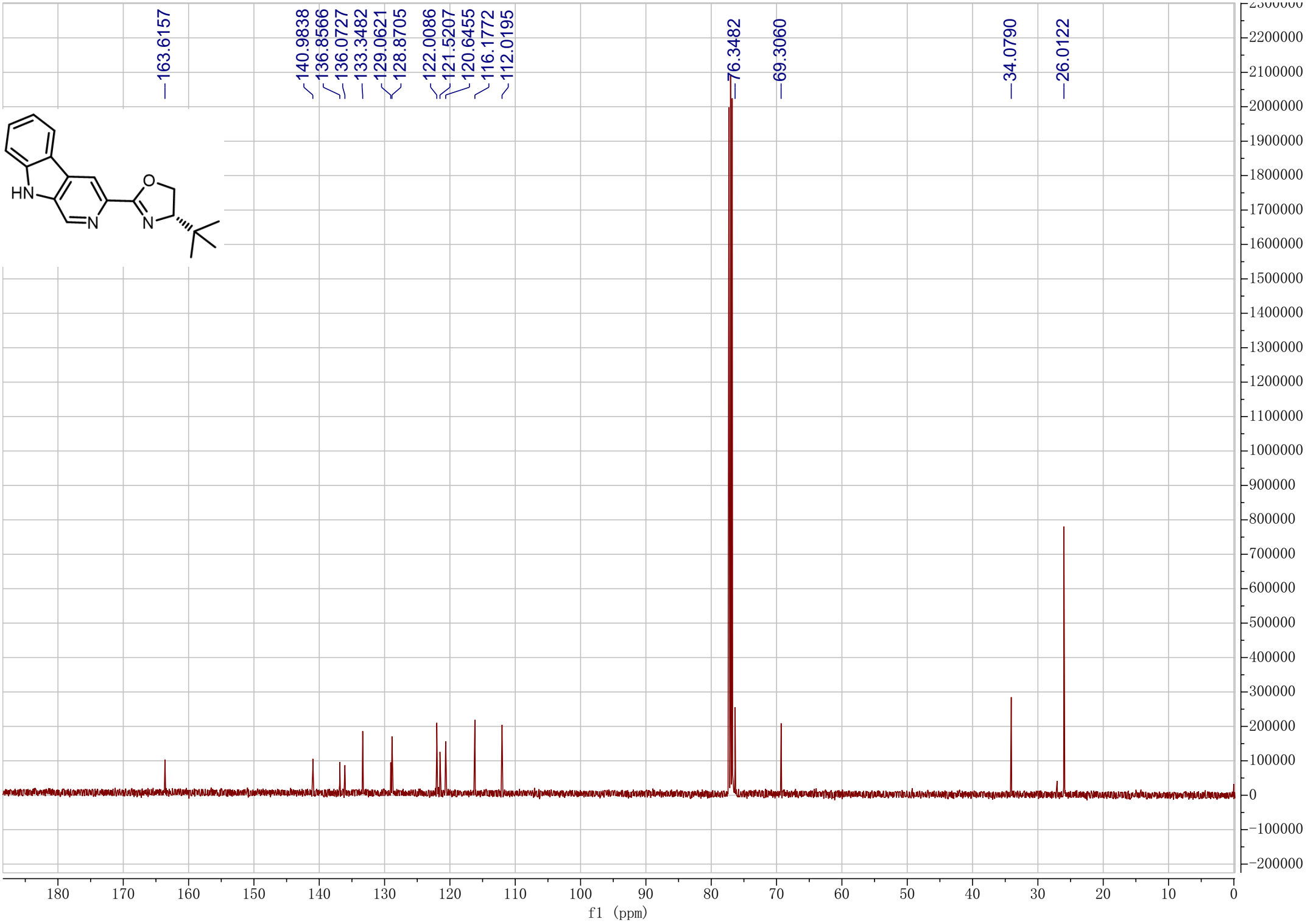

20190506-23 240 (1.816) Cm (236:249)
1: TOF MS ES+
8.68e7
100
%
0
328.1448
314.1293
329.1477
330.1537
167.0608
194.0718
236.0821
359.1585
498.6502
519.6735
655.2806
677.2631
717.1448
774.1942
m/z
100
200
300
400
500
600
700
800
900
1000
1100
NH
O
N
N

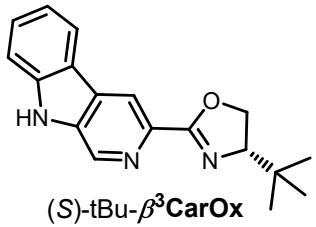

L9719
K78-9
10.3459
8.5545
8.5417
8.1715
8.1688
8.1538
8.1515
8.1491
8.0768
8.0641
7.6066
7.6032
7.6000
7.5861
7.5832
7.5747
7.5718
7.5694
7.5542
7.5518
7.3930
7.3900
7.3747
7.3719
7.3690
7.3601
7.3539
7.3435
7.3401
7.3268
7.3231
7.3164
7.3068
7.3031
7.2962
7.2605
4.7774
4.7736
4.7580
4.5871
4.5657
4.5635
4.5425
4.3389
4.3206
4.3175
4.2992
3.2725
3.2562
3.2386
3.2222
2.9437
2.9236
2.9098
2.8897
NH
O
N
N
1.01
0.94
1.00
0.96
2.06
2.08
4.06
1.00
1.03
1.03
1.05
1.04
f1 (ppm)


163.5577
140.6544
138.7174
138.0635
136.0058
130.0009
129.3251
128.9967
128.9008
128.6595
126.7198
121.9676
121.3283
120.3850
117.1176
111.9381
72.0567
68.1788
42.3395
NH
O
N
N
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

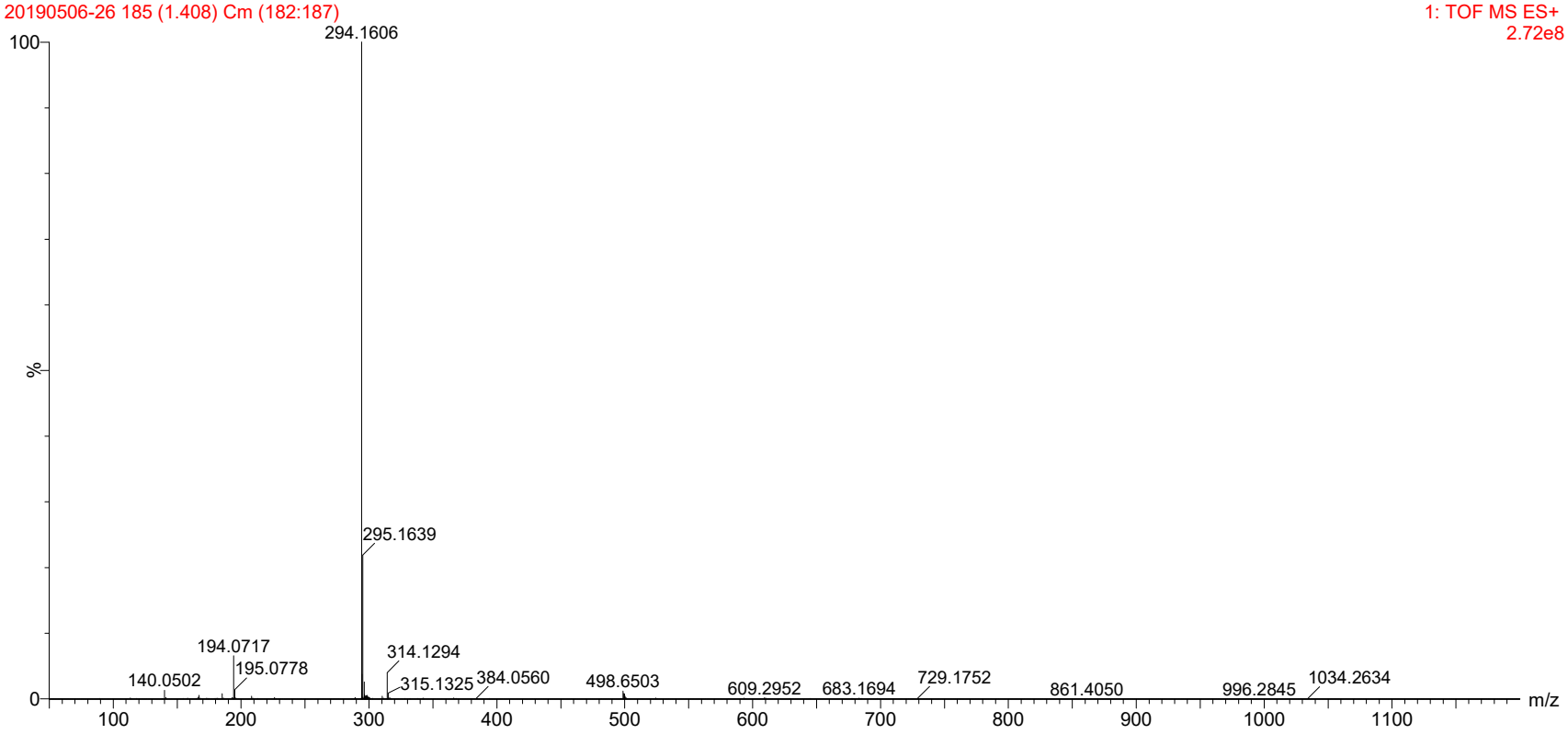

20190506-23 240 (1.816) Cm (236:249)
1: TOF MS ES+
8.68e7
100
%
0
328.1448
314.1293
329.1477
330.1537
167.0608
194.0718
236.0821
359.1585
498.6502
519.6735
655.2806
677.2631
717.1448
774.1942
m/z
100
200
300
400
500
600
700
800
900
1000
1100
NH
O
N
N

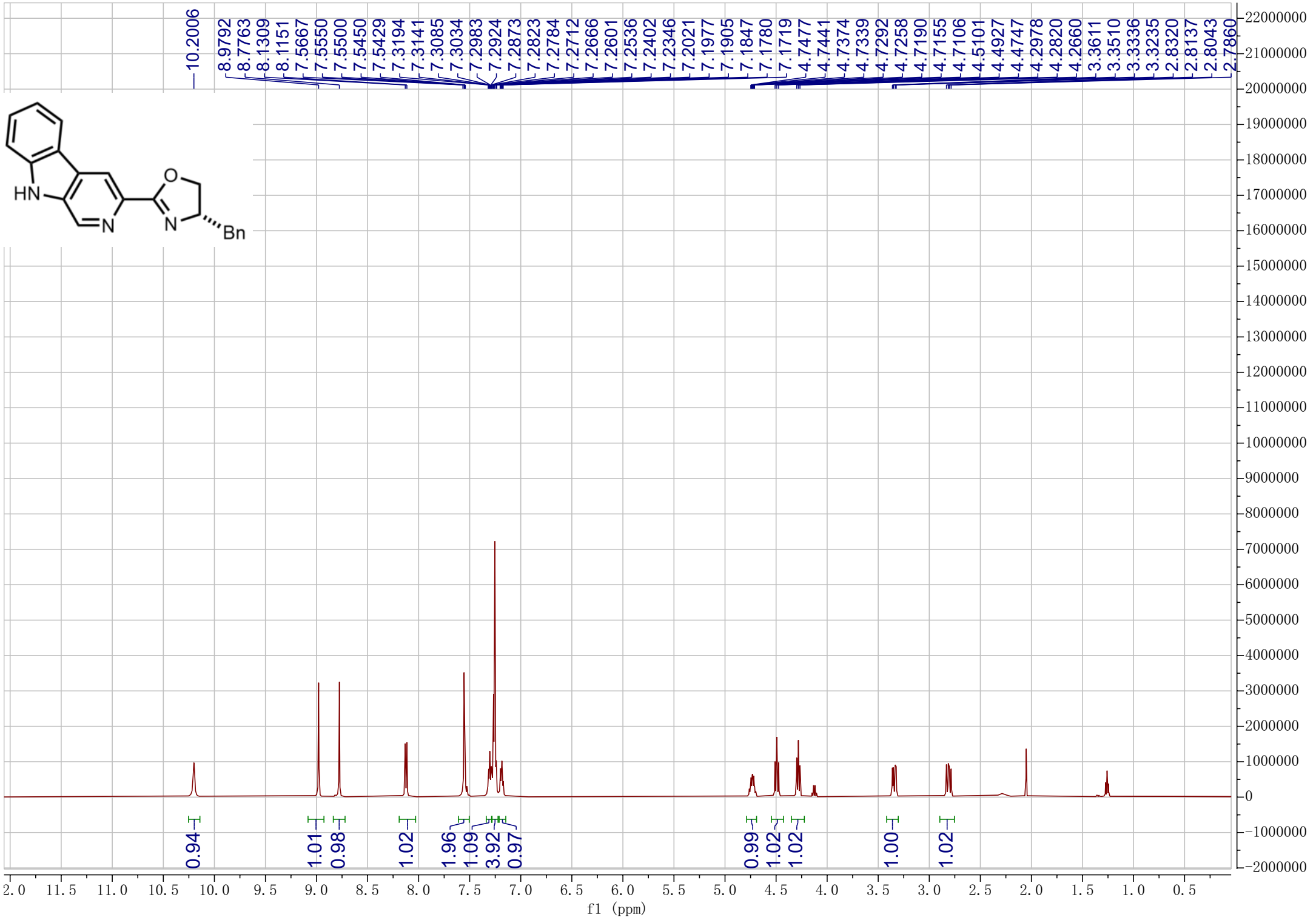

L8/L8-HNMR
K19
9.7508
8.9370
8.7774
8.1461
8.1263
7.5593
7.5537
7.5470
7.5327
7.3270
7.3200
7.3139
7.3071
7.2998
7.2942
7.2869
7.2676
4.5164
4.4950
4.4913
4.4697
4.3881
4.3675
4.3465
4.2114
4.1912
4.1860
4.1662
1.0096
HN
O
N
N
0.86
0.97
0.90
1.00
2.20
1.16
1.00
0.94
0.94
9.34
f1 (ppm)

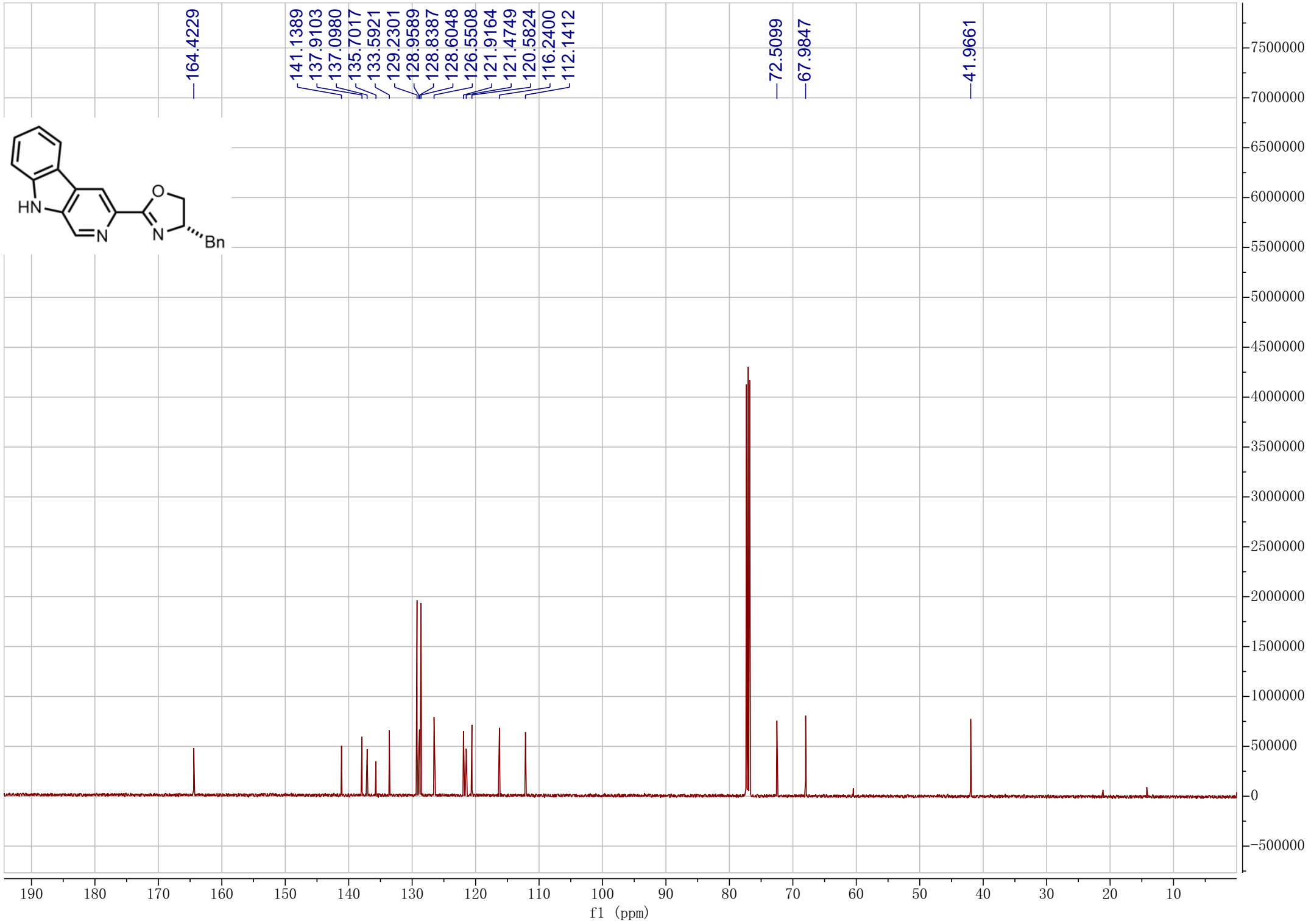

163.6157
140.9838
136.8566
136.0727
133.3482
129.0621
128.8705
122.0086
121.5207
120.6455
116.1772
112.0195
76.3482
69.3060
34.0790
26.0122
HN
N
O
N
f1 (ppm)

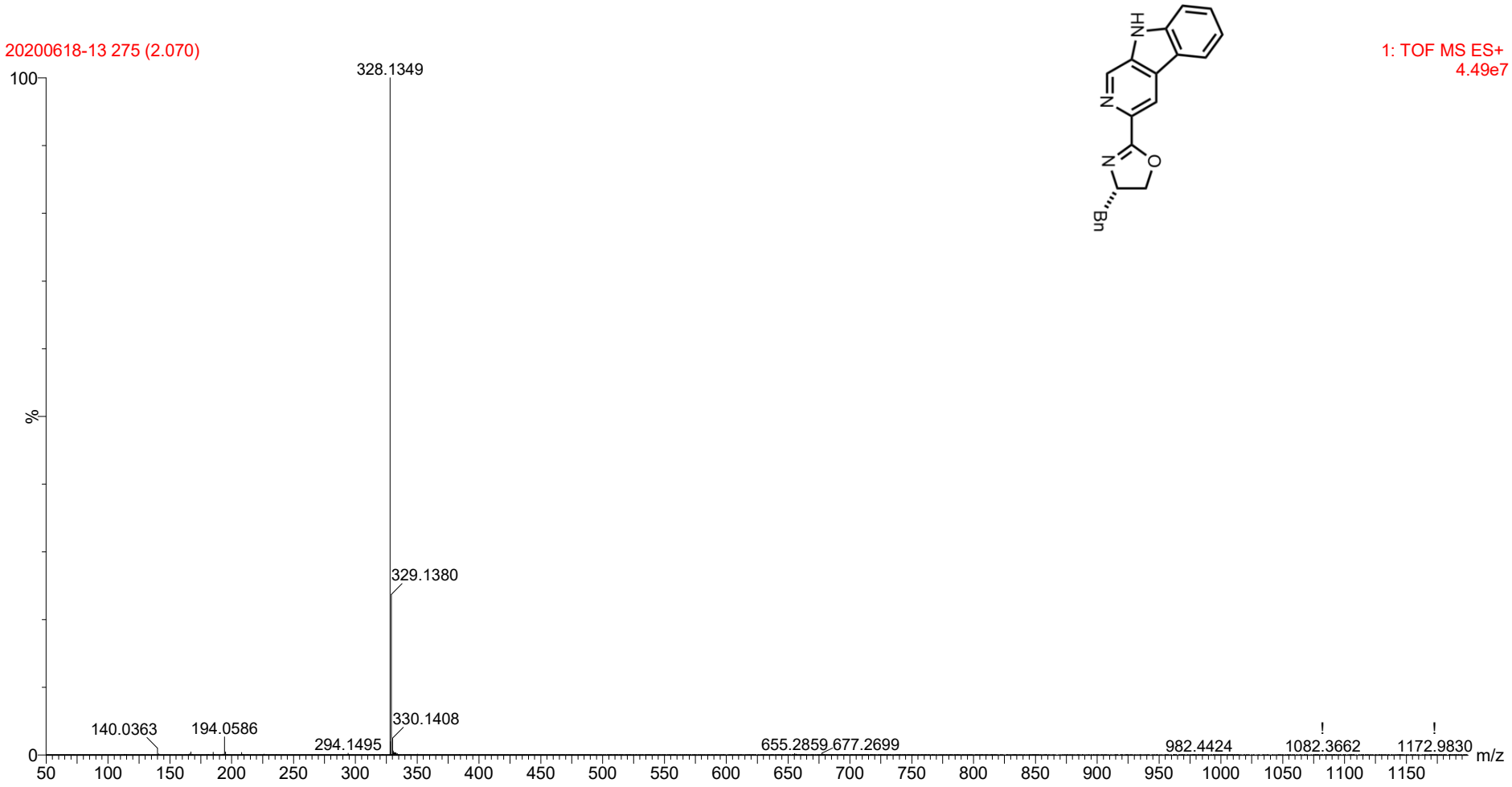


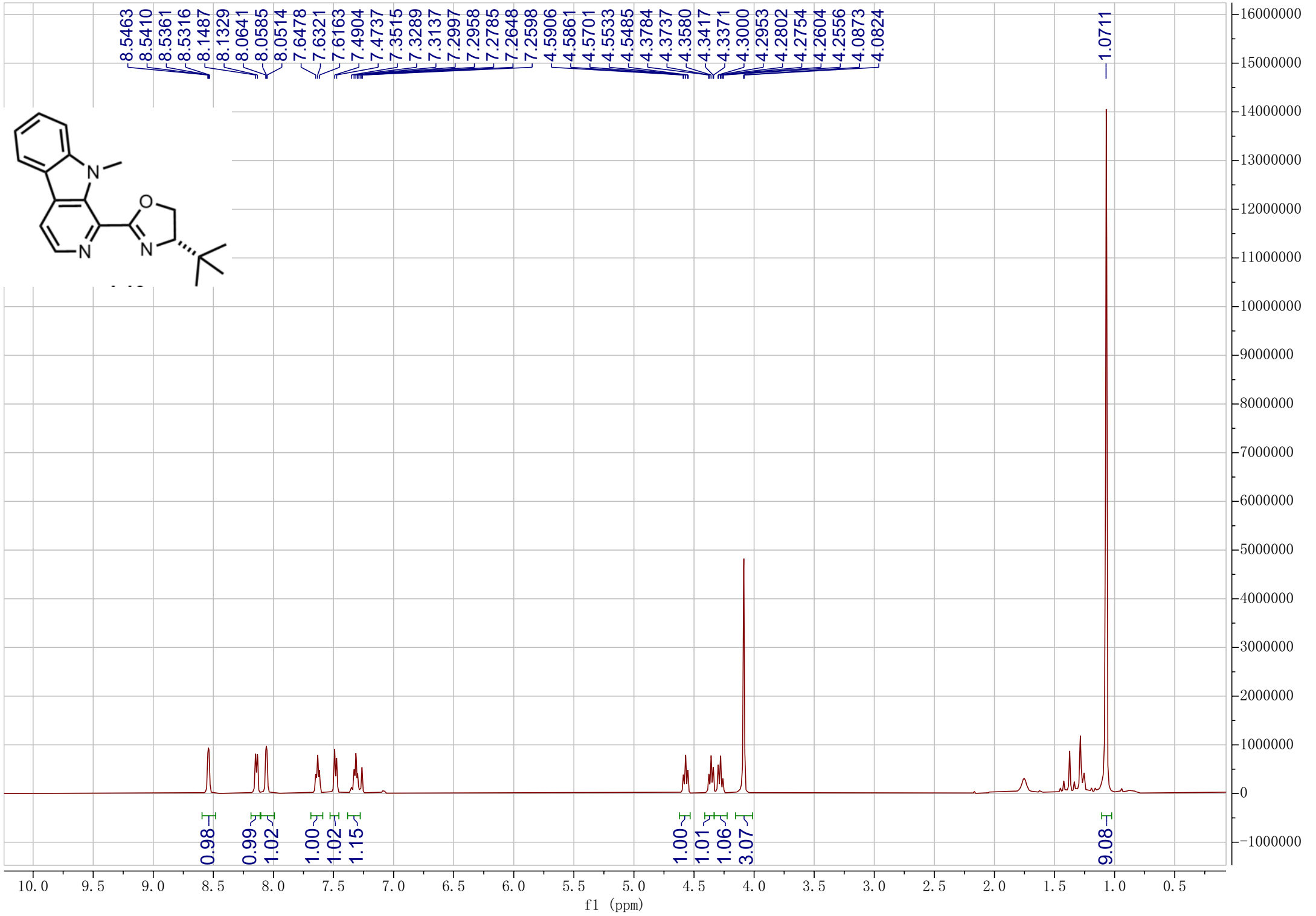
(*S*)-tBu-β^3**CarOx**

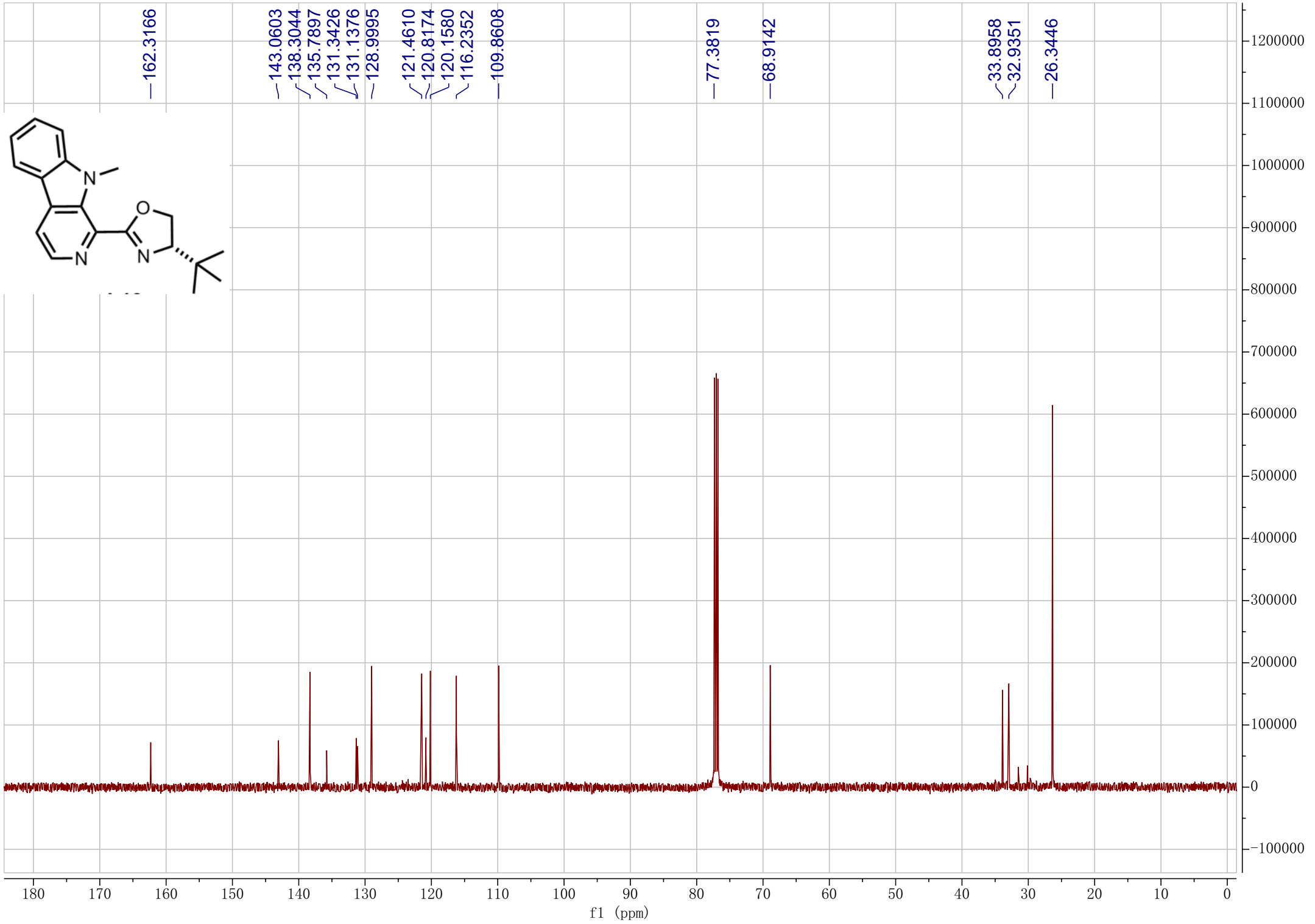


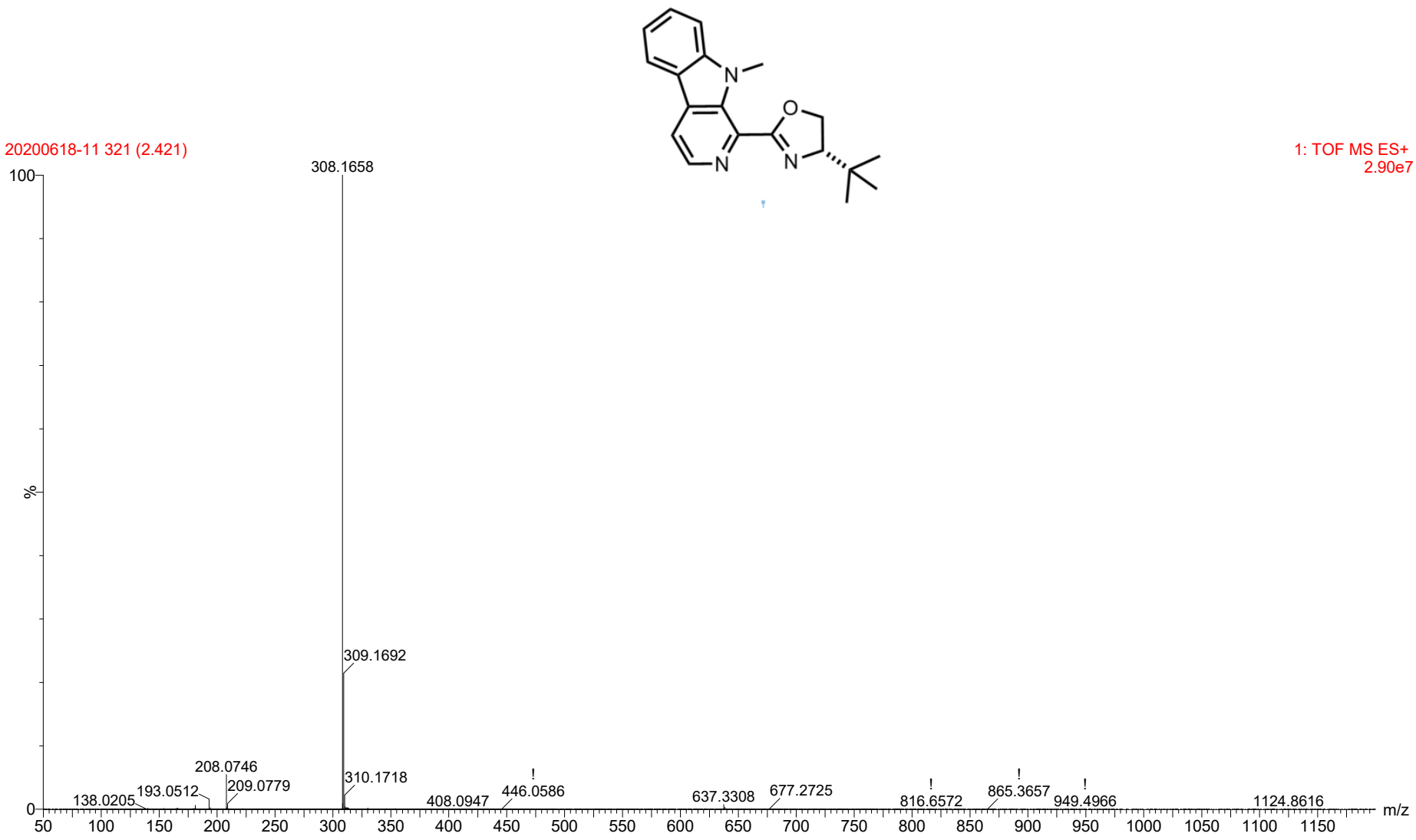

10.2006
8.9792
8.7763
8.1309
8.1151
7.5667
7.5550
7.5500
7.5450
7.5429
7.3194
7.3141
7.3085
7.3034
7.2983
7.2924
7.2873
7.2823
7.2784
7.2712
7.2666
7.2601
7.2536
7.2402
7.2346
7.2021
7.1977
7.1905
7.1847
7.1780
7.1719
4.7477
4.7441
4.7374
4.7339
4.7292
4.7258
4.7190
4.7155
4.7106
4.5101
4.4927
4.4747
4.2978
4.2820
4.2660
3.3611
3.3510
3.3336
3.3235
2.8320
2.8137
2.8043
2.7860
HN
N
O
N
Bn
0.94
1.01
0.98
1.02
1.96
1.09
3.92
0.97
0.99
1.02
1.02
1.00
1.02
f1 (ppm)

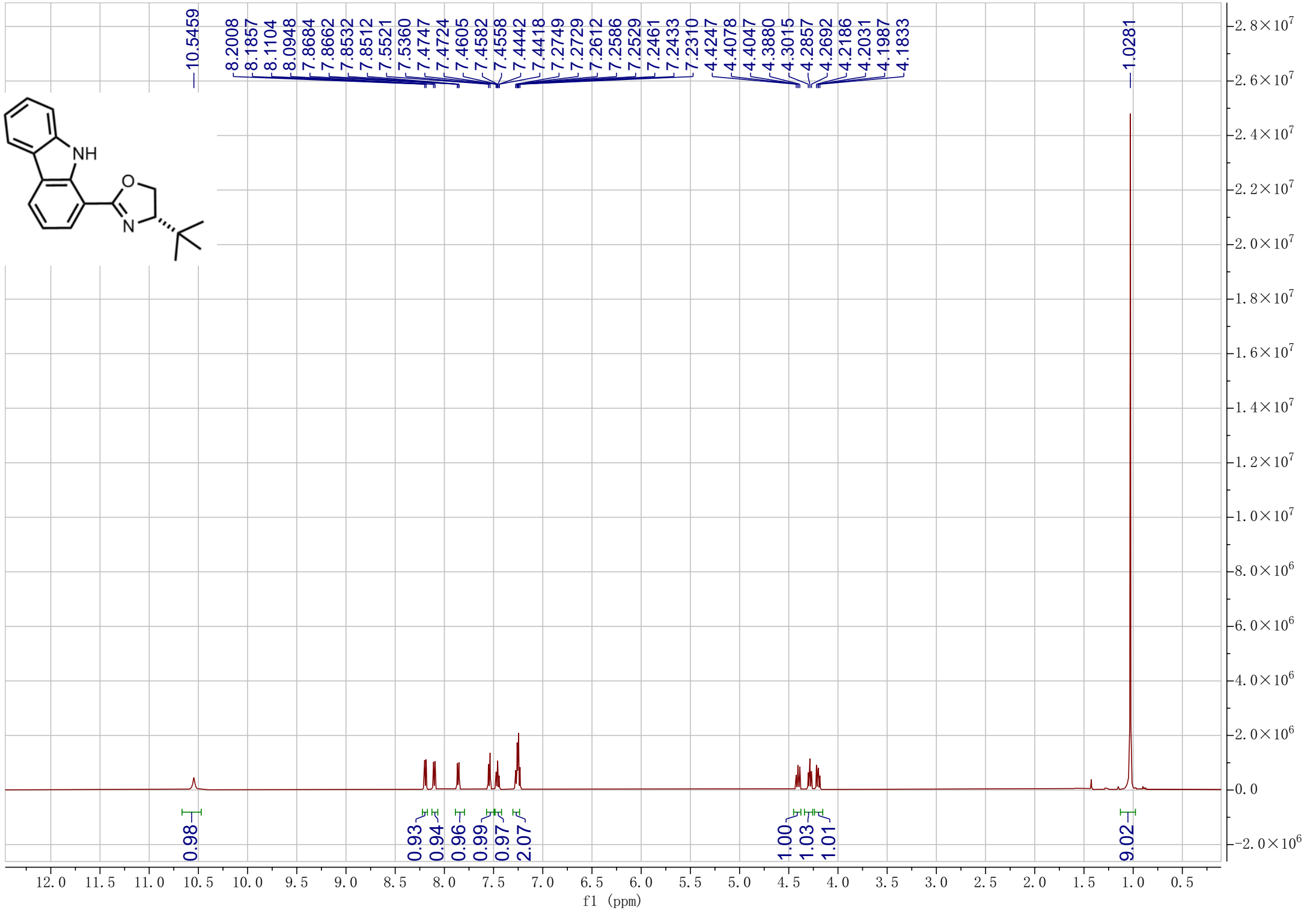

164.4229
141.1389
137.9103
137.0980
135.7017
133.5921
129.2301
128.9589
128.8387
128.6048
126.5508
121.9164
121.4749
120.5824
116.2400
112.1412
72.5099
67.9847
41.9661
HN
N
O
N
Bn
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

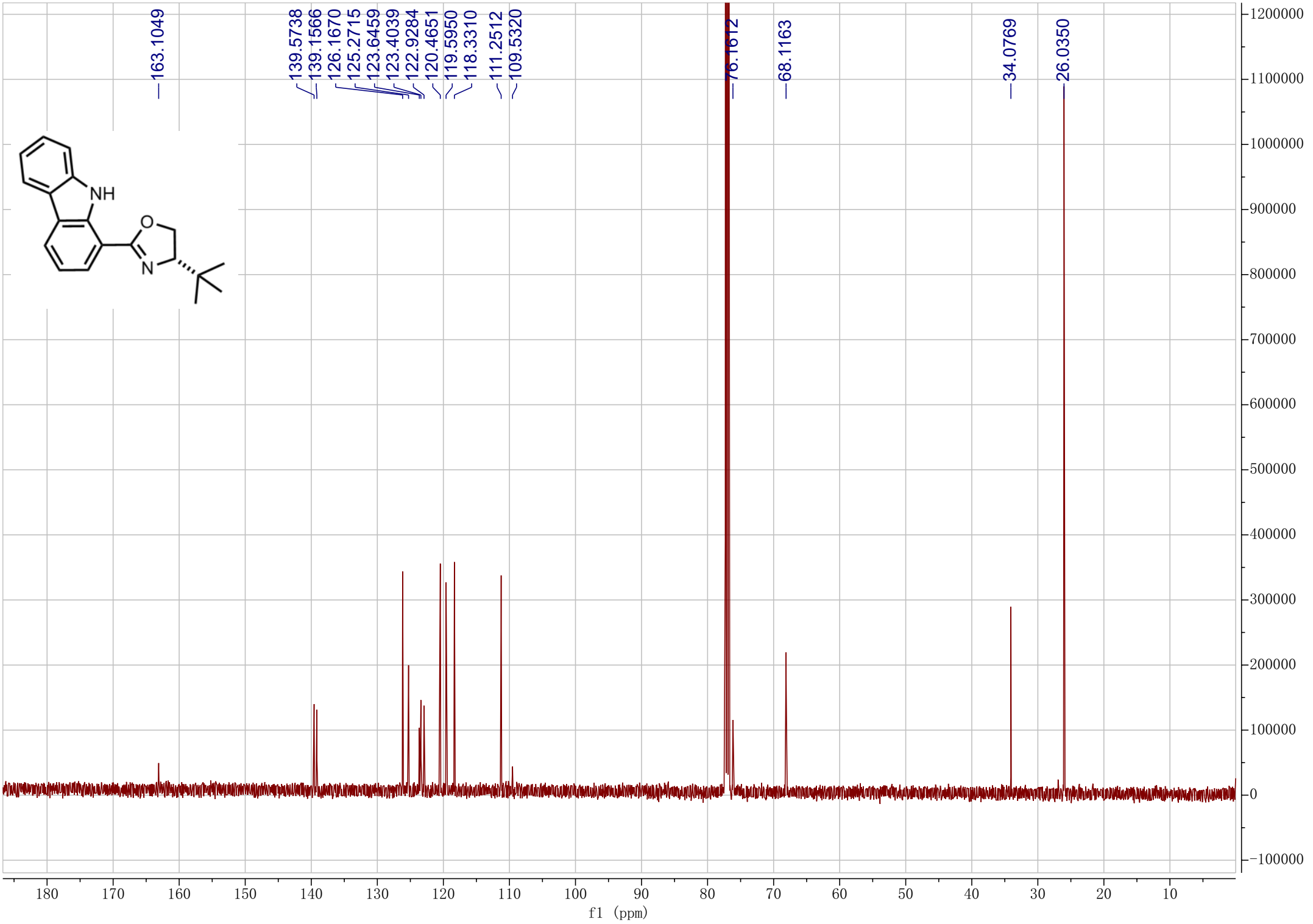

20200618-13 275 (2.070)
1: TOF MS ES+
4.49e7
100
%
0
328.1349
329.1380
330.1408
140.0363
194.0586
294.1495
655.2859
677.2699
982.4424
1082.3662
1172.9830
m/z
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
NH
N
N
O
Bn


8.5463
8.5410
8.5361
8.5316
8.1487
8.1329
8.0641
8.0585
8.0514
7.6478
7.6321
7.6163
7.4904
7.4737
7.3515
7.3289
7.3137
7.2997
7.2958
7.2785
7.2648
7.2598
4.5906
4.5861
4.5701
4.5533
4.5485
4.3784
4.3737
4.3580
4.3417
4.3371
4.3000
4.2953
4.2802
4.2754
4.2604
4.2556
4.0873
4.0824
1.0711
0.98
0.99
1.02
1.00
1.02
1.15
1.00
1.01
1.06
3.07
9.08
f1 (ppm)

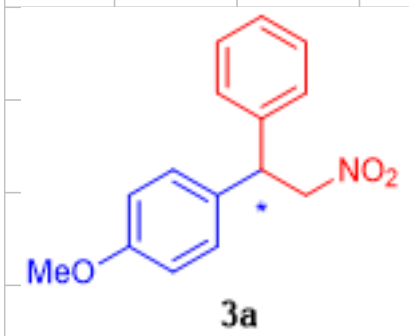

162.3166
143.0603
138.3044
135.7897
131.3426
131.1376
128.9995
121.4610
120.8174
120.1580
116.2352
109.8608
77.3819
68.9142
33.8958
32.9351
26.3446
N
O
N
N
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


20200618-11 321 (2.421)
1: TOF MS ES+
2.90e7
100
%
0
308.1658
309.1692
310.1718
208.0746
209.0779
193.0512
138.0205
408.0947
446.0586
637.3308
677.2725
816.6572
865.3657
949.4966
1124.8616
m/z
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150


10.5459
8.2008
8.1857
8.1104
8.0948
7.8684
7.8662
7.8532
7.8512
7.5521
7.5360
7.4747
7.4724
7.4605
7.4582
7.4558
7.4442
7.4418
7.2749
7.2729
7.2612
7.2586
7.2529
7.2461
7.2433
7.2310
4.4247
4.4078
4.4047
4.3880
4.3015
4.2857
4.2692
4.2186
4.2031
4.1987
4.1833
1.0281
NH
O
N
0.98
0.93
0.94
0.96
0.99
0.97
2.07
1.00
1.03
1.01
9.02
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
−2.0×10^6
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
f1 (ppm)

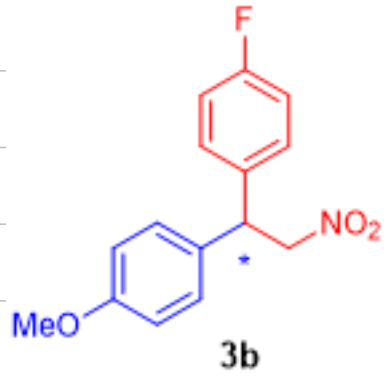

163.1049
139.5738
139.1566
126.1670
125.2715
123.6459
123.4039
122.9284
120.4651
119.5950
118.3310
111.2512
109.5320
76.1612
68.1163
34.0769
26.0350
NH
O
N
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

加成谱图/3aa
L-42



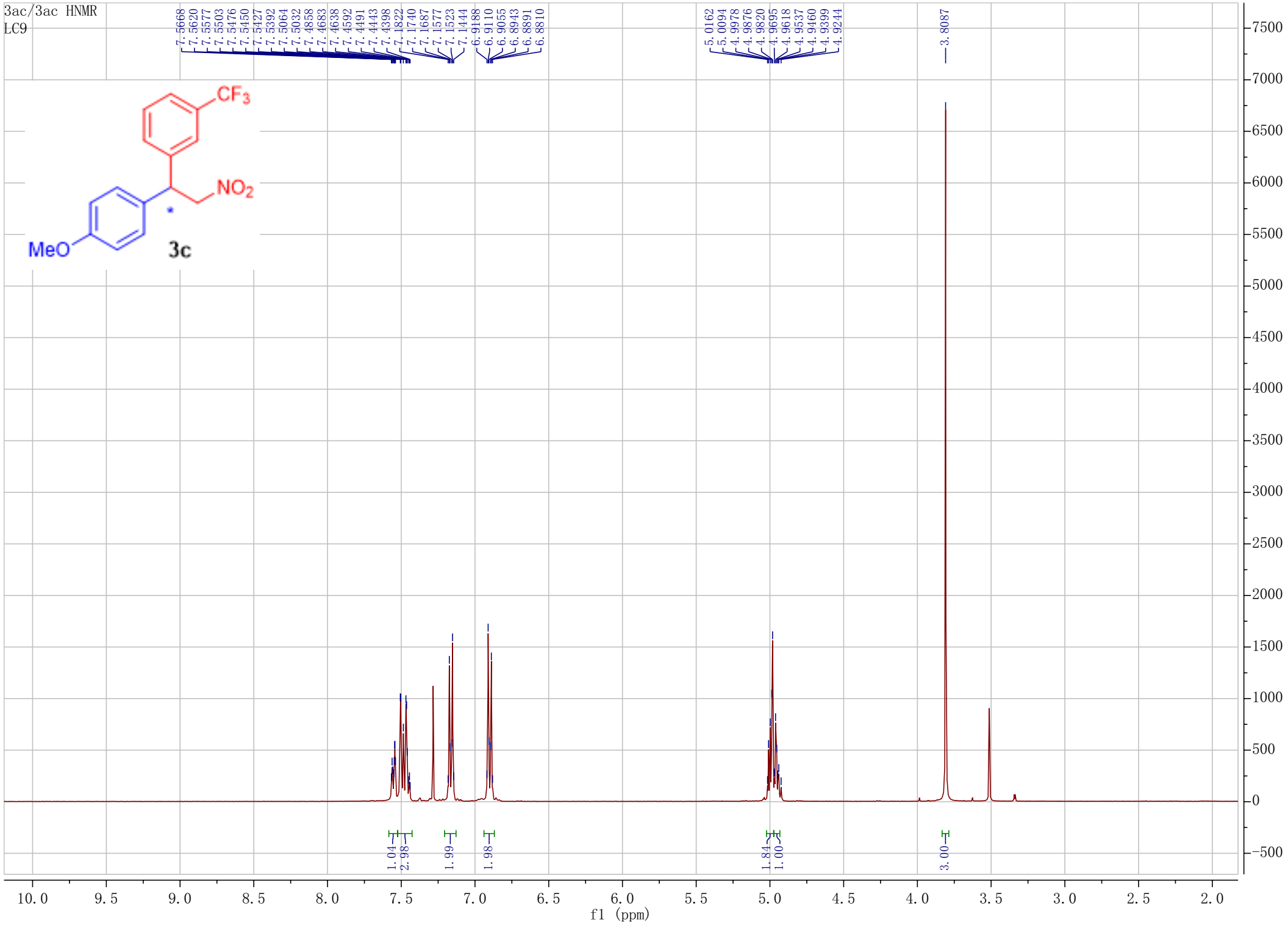
3a

3ab/3ab HNMR
LC3

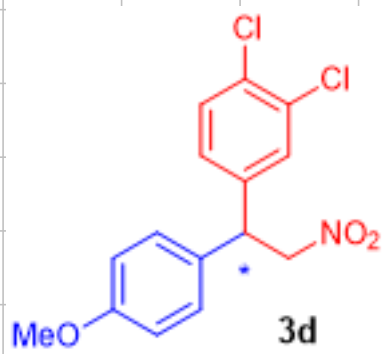


3b

f1 (ppm)


3ac/3ac HNMR
LC9
7.5668
7.5620
7.5577
7.5503
7.5476
7.5450
7.5427
7.5392
7.5064
7.5032
7.4858
7.4683
7.4638
7.4592
7.4491
7.4443
7.4398
7.1822
7.1740
7.1687
7.1577
7.1523
7.1444
6.9188
6.9110
6.9055
6.8943
6.8891
6.8810
5.0162
5.0094
4.9978
4.9876
4.9820
4.9695
4.9618
4.9537
4.9460
4.9399
4.9244
3.8087
CF3
NO2
MeO
3c
1.04
2.98
1.99
1.98
1.84
1.00
3.00
f1 (ppm)

3ag/3ag HNMR
LC-17



7.4123
7.3916
7.3115
7.3061
7.1248
7.1195
7.1086
7.1031
7.0945
7.0888
7.0735
7.0680
6.8858
6.8805
6.8693
6.8639
4.9279
4.9227
4.9050
4.8348
4.8168
4.8121
4.7942
3.7893

0.91
0.90
0.85
1.88
1.84
1.81
1.00
2.81

f1 (ppm)

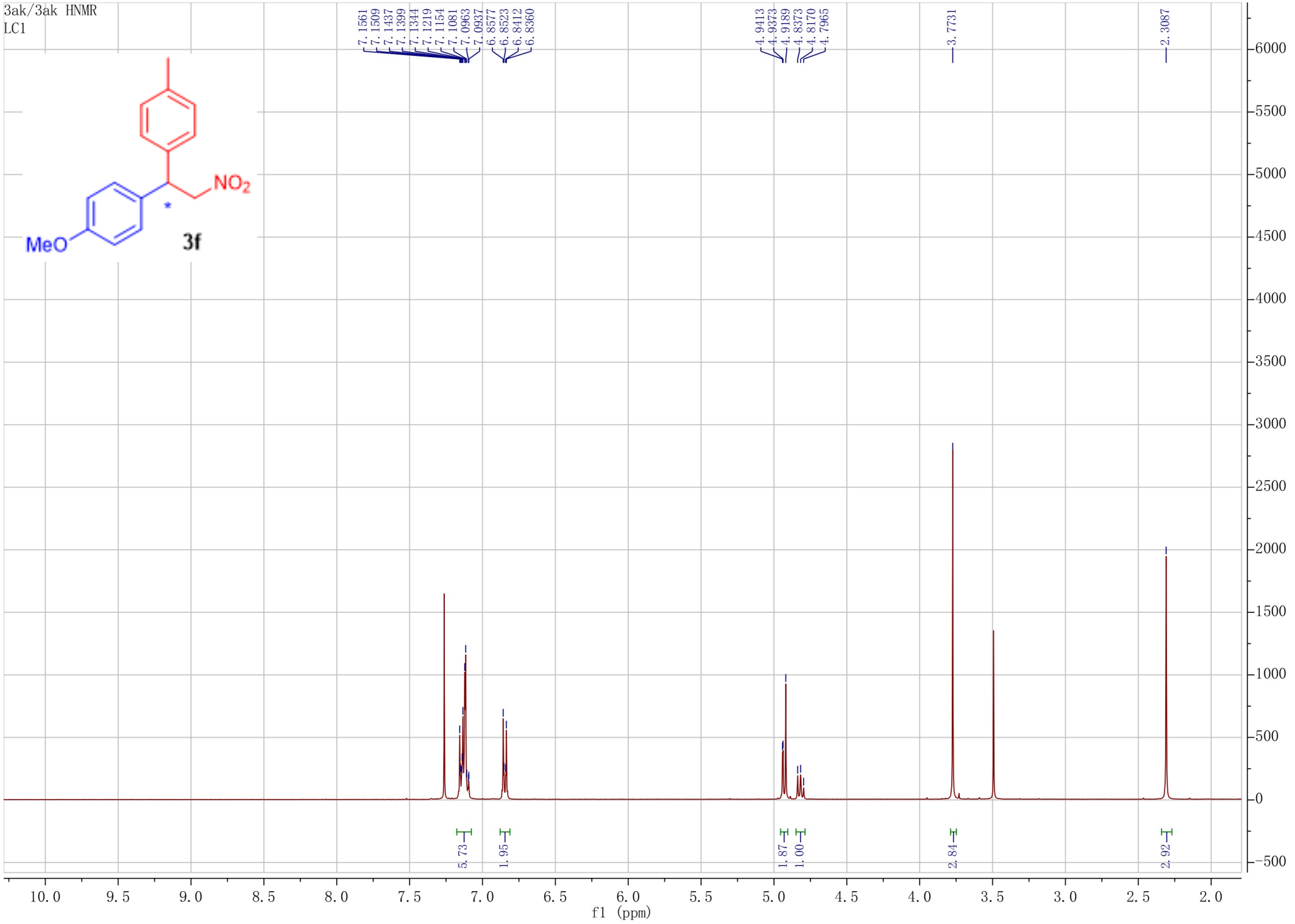
3ah/3ah HNMR
LC5

3e

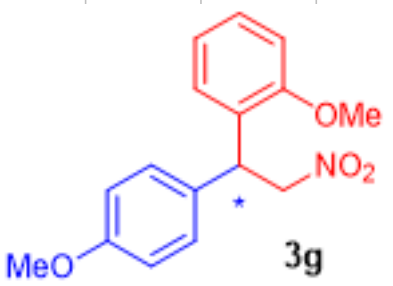
7.3373
7.1974
7.1773
7.1573
7.1273
7.1252
7.1206
7.1107
7.1087
7.1050
7.1027
6.8587
6.8507
6.8454
6.8340
6.8285
6.8205
5.9704
5.9518
5.9331
5.4504
5.4318
5.4173
5.3986
5.2926
5.2740
5.2595
5.2409
3.7817

1.71
1.00
1.89
1.90
0.93
0.97
1.00
2.83

f1 (ppm)


3ak/3ak HNMR
LC1
7.1561
7.1509
7.1437
7.1399
7.1344
7.1219
7.1154
7.1081
7.0963
7.0937
6.8577
6.8523
6.8412
6.8360
4.9413
4.9373
4.9189
4.8373
4.8170
4.7965
3.7731
2.3087
NO2
MeO
3f
5.73
1.95
1.87
1.00
2.84
2.92
f1 (ppm)

3ai/3ai HNMR
LC11



7.2395 7.2377 7.2342 7.2189 7.2146 7.2088 7.2033 7.1926 7.1873 7.1791

5.2337 5.2166 5.2103 5.1932 5.0344 5.0173 5.0024 4.9853 4.9413 4.9180 4.9094 4.8859

3.8386 3.7748

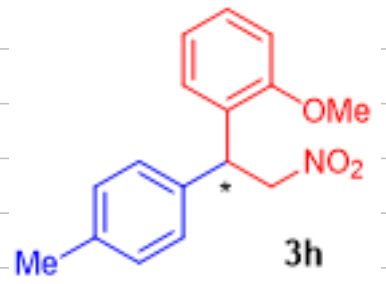
0.89 1.88 1.03 2.08 1.85

1.00 1.04 1.03

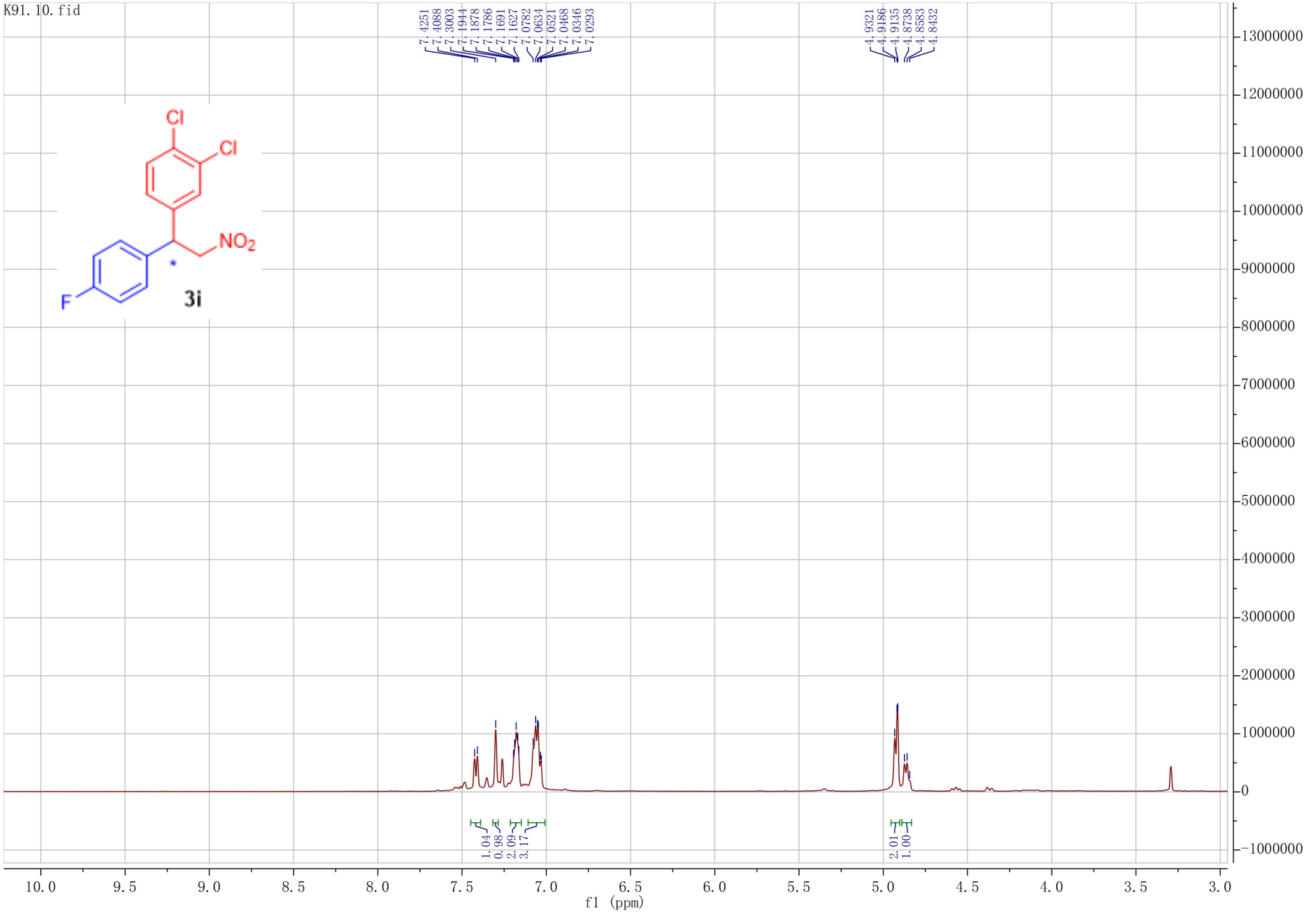
3.03 3.10

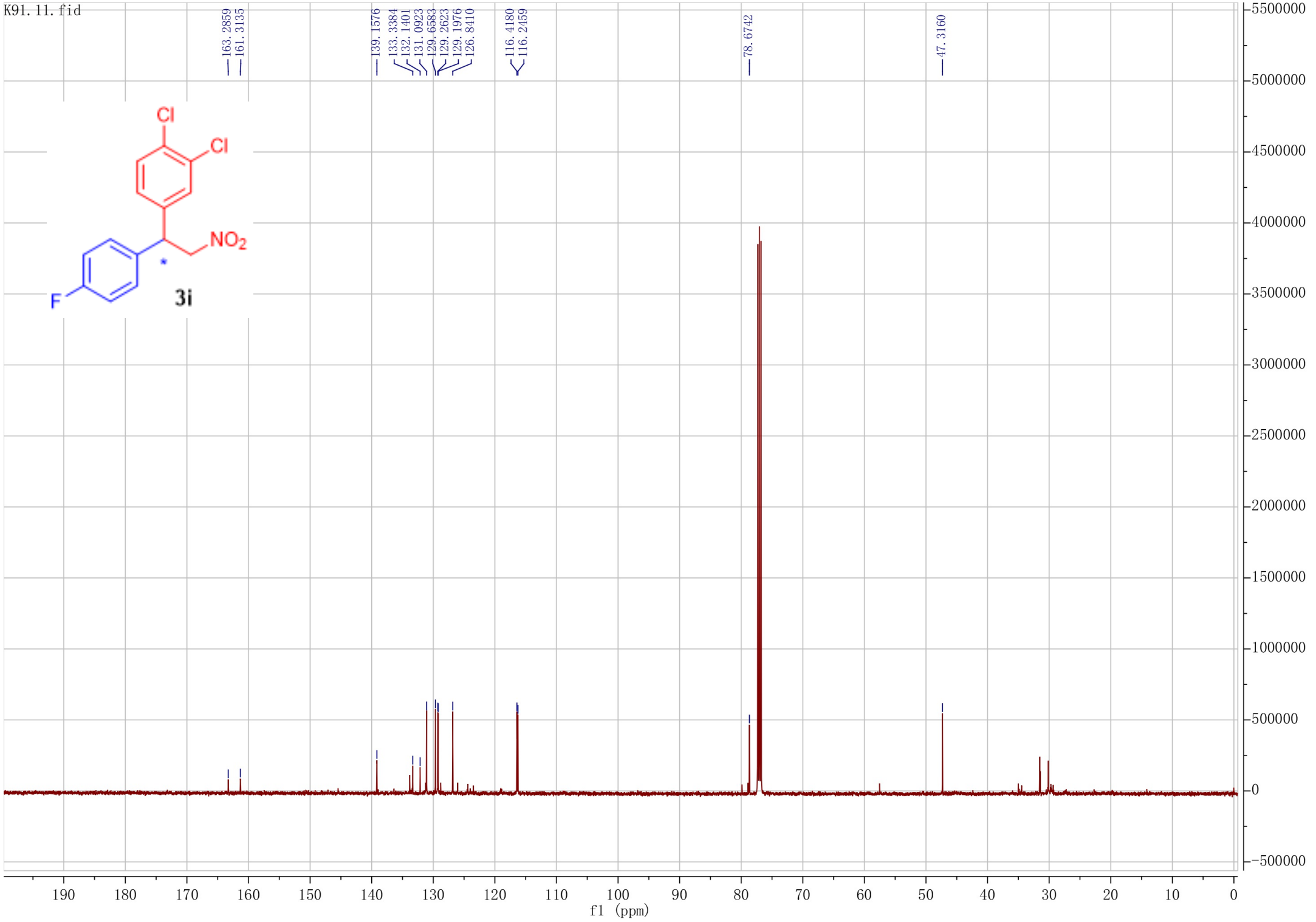
f1 (ppm)

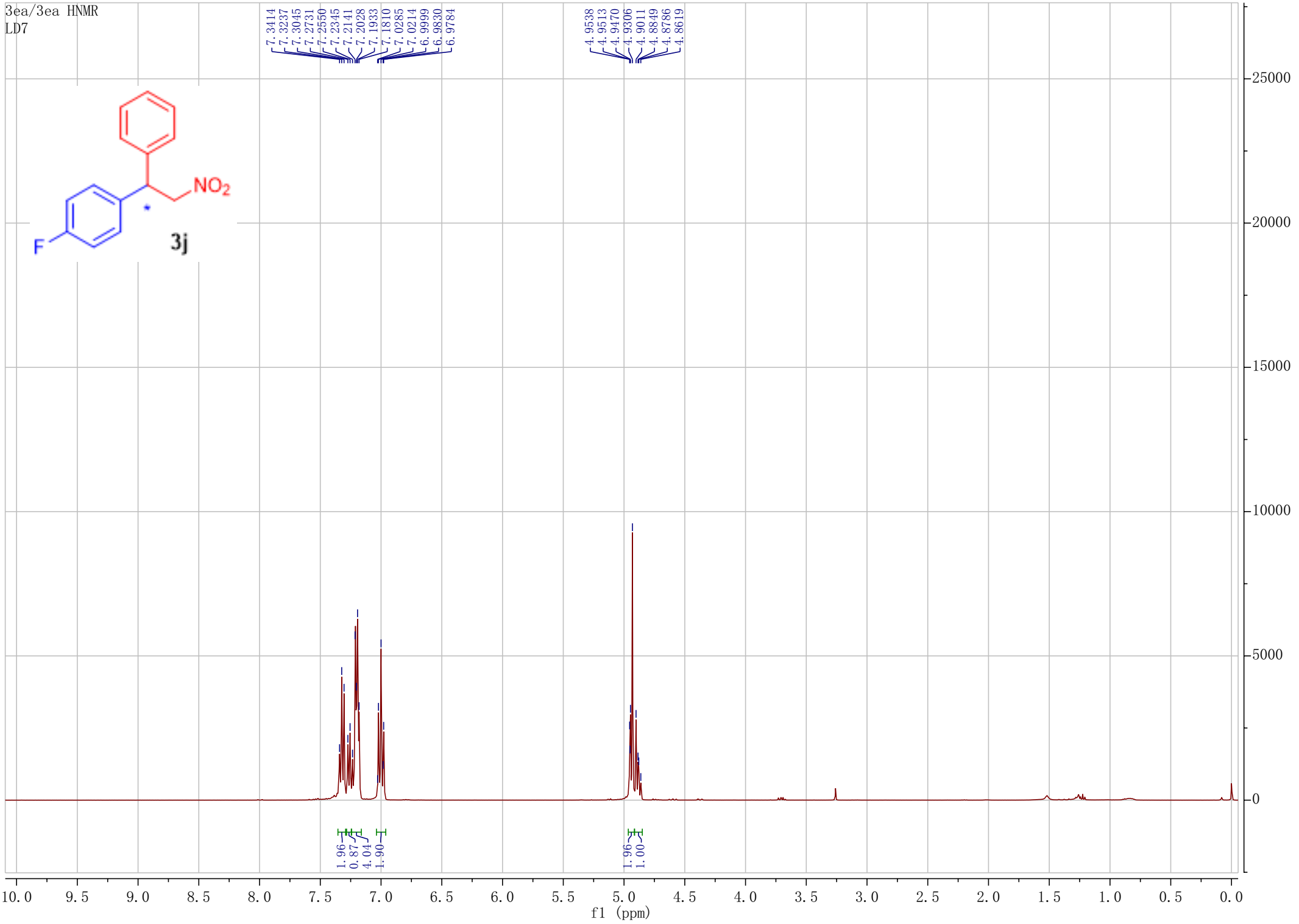
3ae/3ae-HNMR
K45

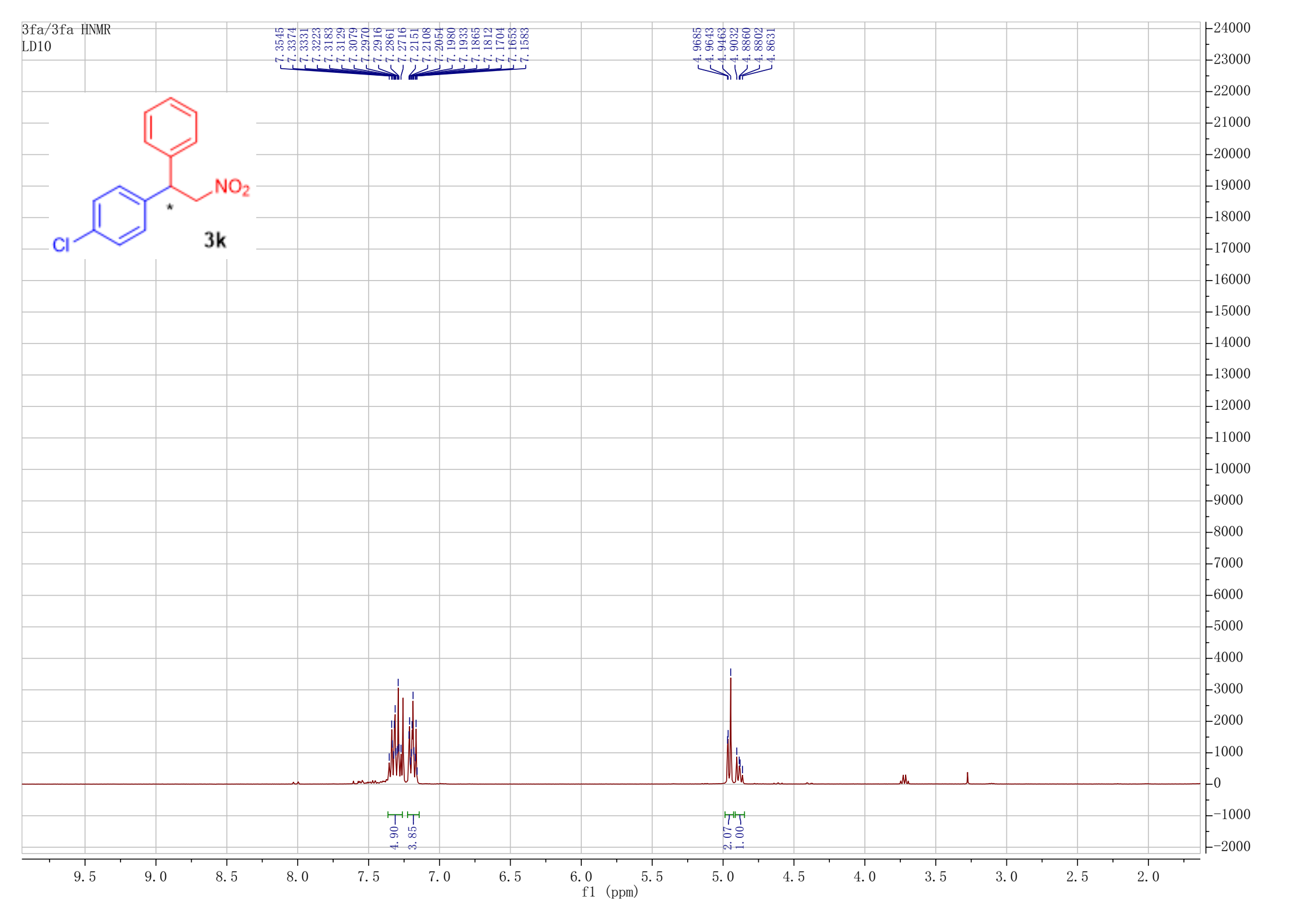


f1 (ppm)

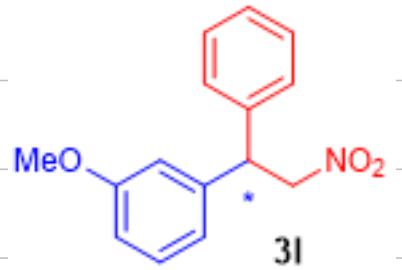

K91.10.fid
7.4251
7.4088
7.3003
7.1944
7.1878
7.1786
7.1691
7.1627
7.0782
7.0634
7.0521
7.0468
7.0346
7.0293
4.9321
4.9186
4.9135
4.8738
4.8583
4.8432
Cl
Cl
NO2
F
3i
1.04
0.98
2.09
3.17
2.01
1.00
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
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
f1 (ppm)


K91.11.fid
163.2859
161.3135
139.1576
133.3384
132.1401
131.0923
129.6583
129.2623
129.1976
126.8410
116.4180
116.2459
78.6742
47.3160
Cl
Cl
NO2
F
3i
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3ea/3ea HNMR
LD7
7.3414
7.3237
7.3045
7.2731
7.2550
7.2345
7.2141
7.2028
7.1933
7.1810
7.0285
7.0214
6.9999
6.9830
6.9784
4.9538
4.9513
4.9470
4.9306
4.9011
4.8849
4.8786
4.8619
NO2
F
3j
1.96
0.87
4.04
1.90
1.96
1.00
25000
20000
15000
10000
5000
0
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)


3fa/3fa HNMR
LD10
7.3545
7.3374
7.3331
7.3223
7.3183
7.3129
7.3079
7.2970
7.2916
7.2861
7.2716
7.2151
7.2108
7.2054
7.1980
7.1933
7.1865
7.1812
7.1704
7.1653
7.1583
4.9685
4.9643
4.9463
4.9032
4.8860
4.8802
4.8631
NO2
Cl
*
3k
4.90
3.85
2.07
1.00
f1 (ppm)

3ba/3ba HNMR
LD5



3l

7.3480 7.3446 7.3408 7.3322 7.3274 7.3239 7.3188 7.3126 7.3089 7.3065 7.3027 7.2741 7.2704 7.2679 7.2557 7.2487 7.2370 7.2322 7.2287 6.8416 6.8223 6.8064 6.8042 6.8001 6.7977 6.7863 6.7839 6.7799 6.7776 6.7695 6.7645 6.7590

4.9824 4.9792 4.9606 4.8929 4.8749 4.8706 4.8525

3.7707

2.01 4.51 0.97 1.93 1.95 1.00 2.96

f1 (ppm)

3an/3an HNMR
LC10

3p

7.2363
7.2285
7.2256
7.2226
7.2126
7.2097
7.2066
7.1987
6.9582
6.9493
6.9453
6.9366
6.8952
6.8925
6.8892
6.8837
6.8808
6.8726
6.8672
6.8592
5.0999
5.0799
5.0598
4.9913
4.9724
4.9598
4.9410
4.9132
4.8918
4.8817
4.8603
3.7915

2.88
0.98
2.88
1.00
1.05
1.04
3.02

f1 (ppm)

3cf
K79

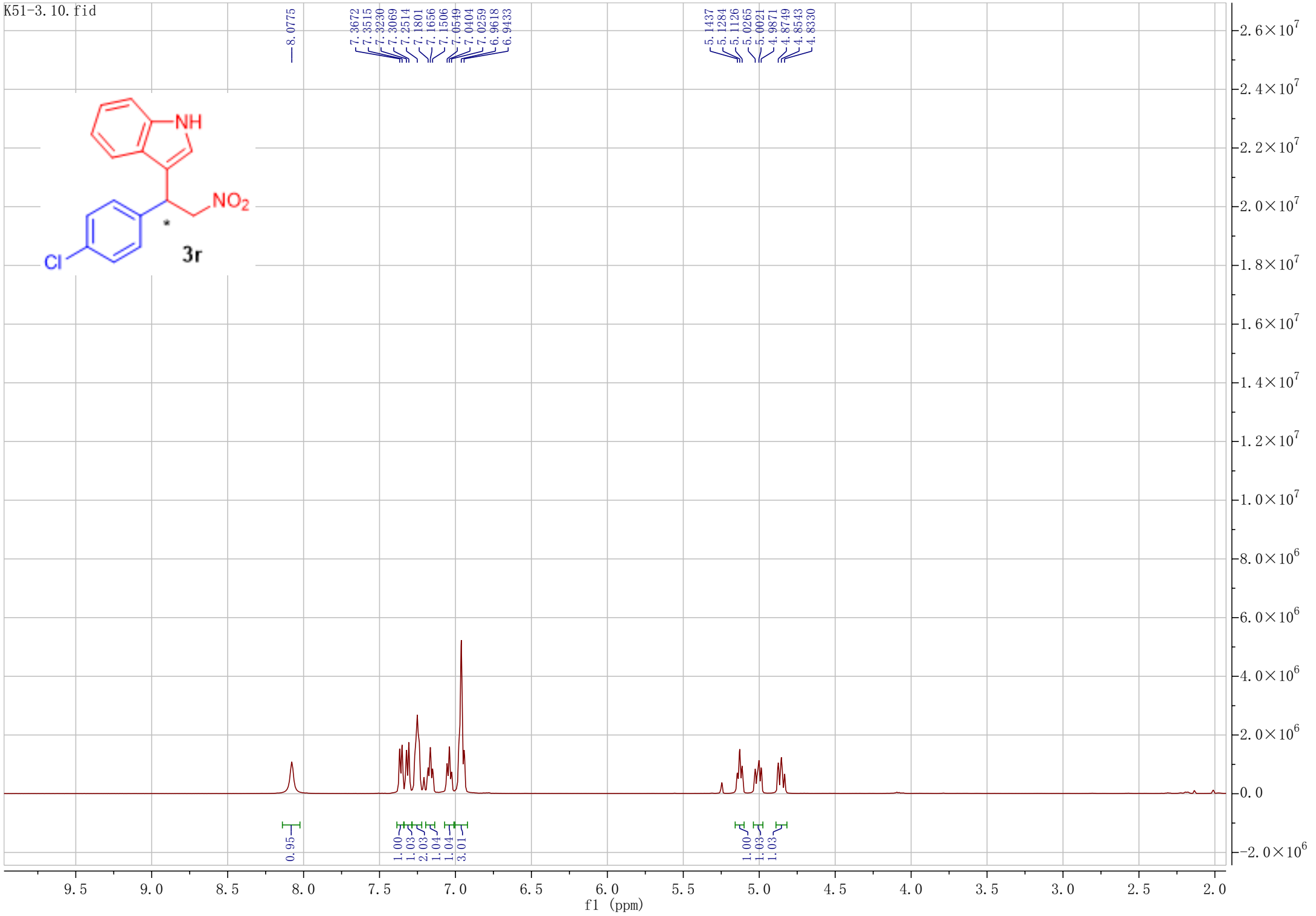
3q

8.0783 7.4484 7.4284 7.3510 7.3393 7.3251 7.3191 7.3100 7.2949 7.2897 7.2689 7.2628 7.2557 7.2472 7.2404 7.2104 7.2084 7.1905 7.1724 7.0897 7.0878 7.0699 7.0520 7.0504 7.0093 7.0033

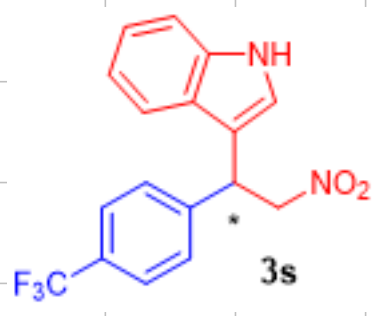
5.2032 5.1831 5.1632 5.0804 5.0612 5.0492 5.0300 4.9568 4.9359 4.9257 4.9047

0.94 1.06 5.03 1.07 0.98 1.05 0.95 1.00 1.05 1.06

f1 (ppm)


K51-3.10.fid
8.0775
7.3672
7.3515
7.3230
7.3069
7.2514
7.1801
7.1656
7.1506
7.0549
7.0404
7.0259
6.9618
6.9433
5.1437
5.1284
5.1126
5.0265
5.0021
4.9871
4.8749
4.8543
4.8330
NH
NO2
Cl
3r
0.95
1.00
1.03
2.03
1.04
1.04
3.01
1.00
1.03
1.03
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
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
f1 (ppm)

K51-6.10.fid



3s

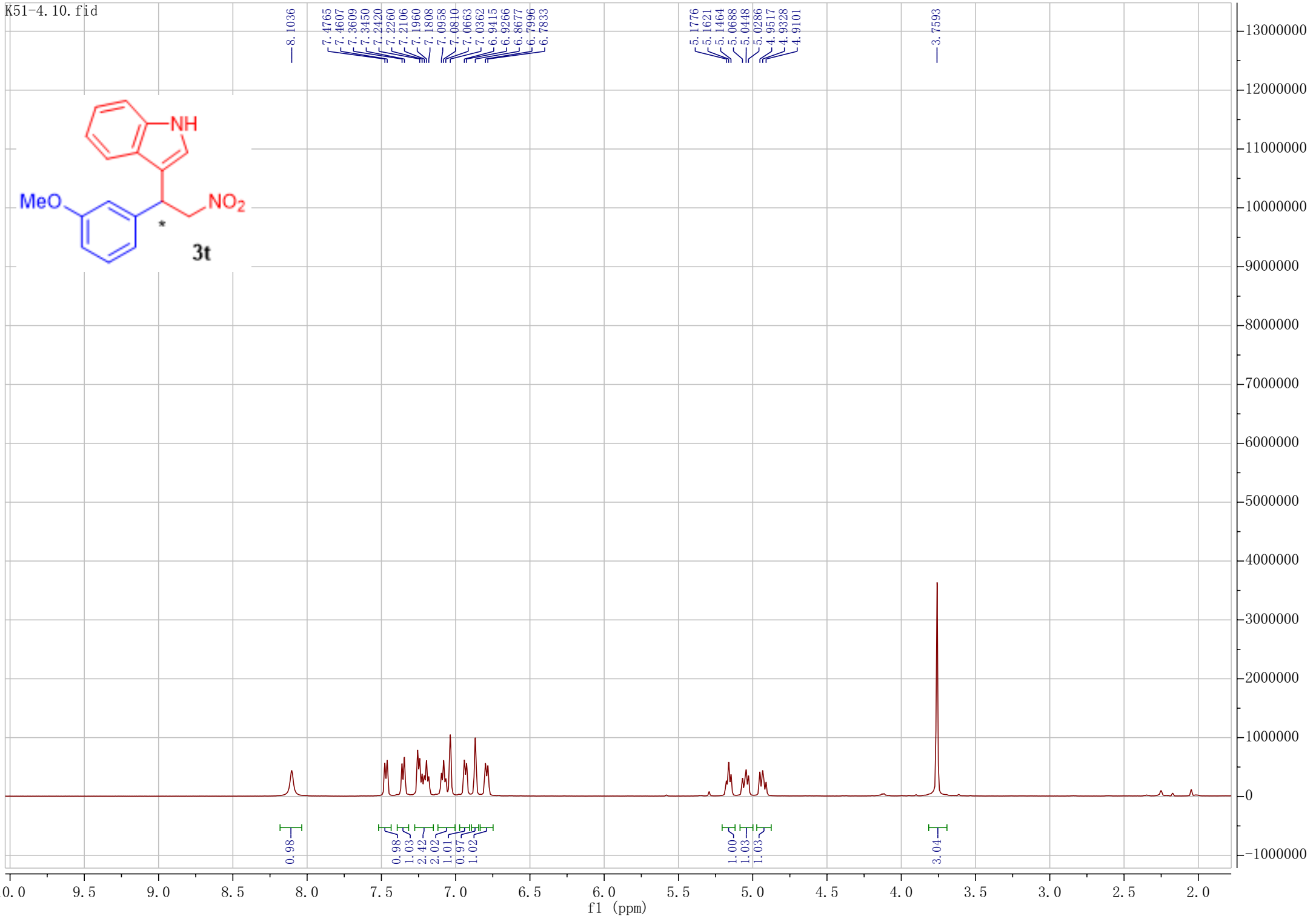
8.1744
7.5951
7.5798
7.4775
7.4622
7.4184
7.4010
7.3962
7.3775
7.3513
7.2389
7.2237
7.2088
7.1134
7.0972
7.0856
7.0440
5.2784
5.2623
5.2463
5.1125
5.0977
5.0886
5.0743
4.9911
4.9730
4.9705
4.9497

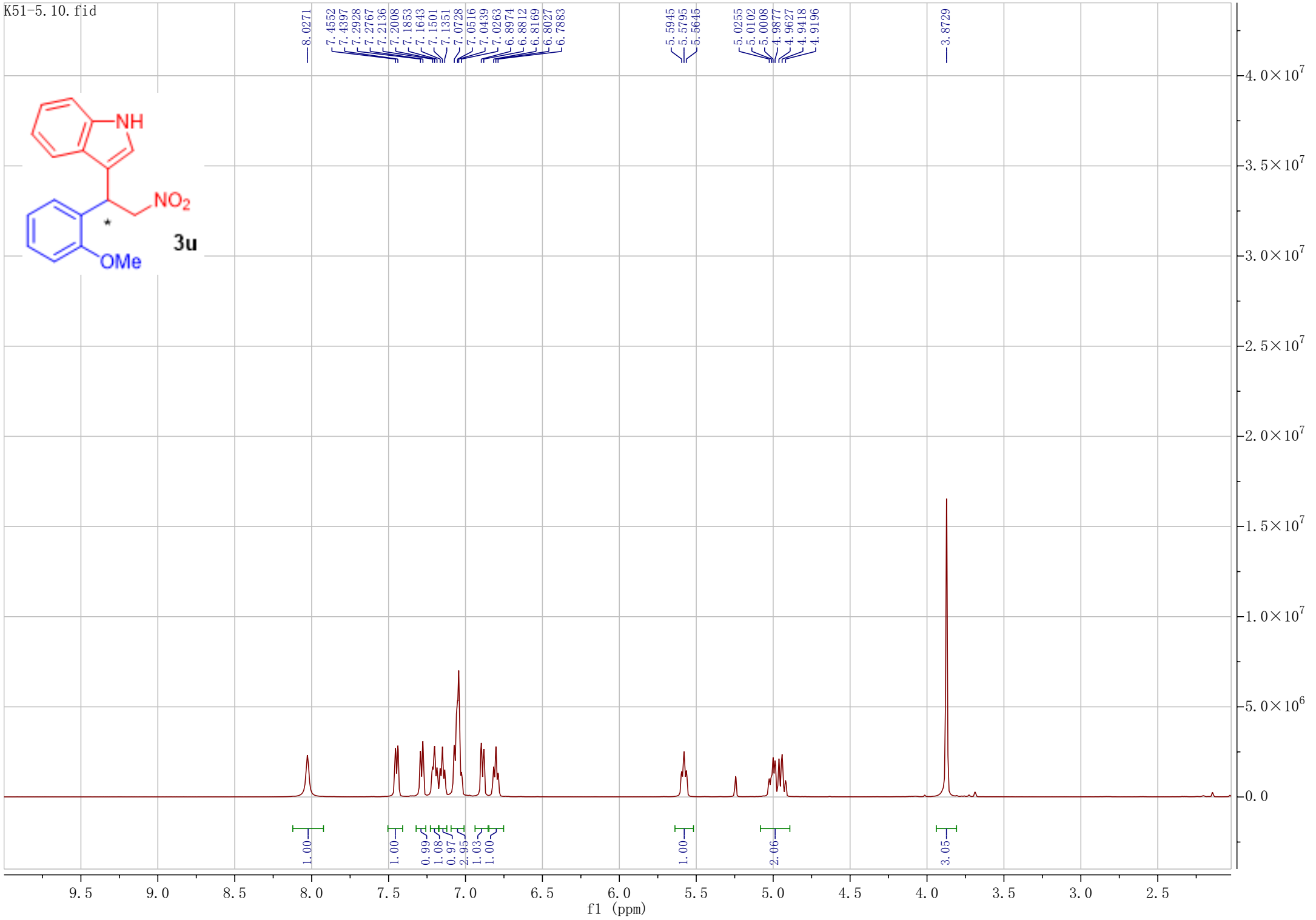
1.08
1.77
1.81
2.35
1.00
1.32
0.92
1.00
1.10
1.06

6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000

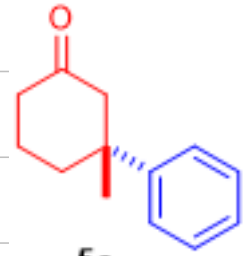
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

f1 (ppm)


K51-4.10.fid
8.1036
7.4765
7.4607
7.3609
7.3450
7.2420
7.2260
7.2106
7.1960
7.1808
7.0958
7.0810
7.0663
7.0362
6.9415
6.9266
6.8677
6.7996
6.7833
5.1776
5.1621
5.1464
5.0688
5.0448
5.0286
4.9517
4.9328
4.9101
3.7593
NH
MeO
NO2
*
3t
0.98
0.98
1.03
2.42
2.02
1.01
0.97
1.02
1.00
1.03
1.03
3.04
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
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
f1 (ppm)


K51-5.10.fid
8.0271
7.4552
7.4397
7.2928
7.2767
7.2136
7.2008
7.1853
7.1643
7.1501
7.1351
7.0728
7.0516
7.0439
7.0263
6.8974
6.8812
6.8169
6.8027
6.7883
5.5945
5.5795
5.5645
5.0255
5.0102
5.0008
4.9877
4.9627
4.9418
4.9196
3.8729
NH
NO2
OMe
3u
1.00
1.00
0.99
1.08
0.97
2.95
1.03
1.00
1.00
2.06
3.05
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
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
f1 (ppm)

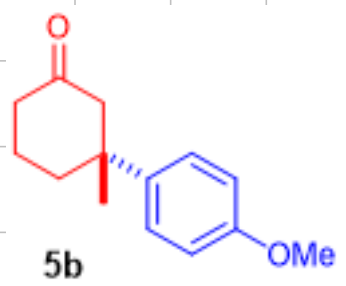
新建文件夹.19.fid
K81-1



5a

f1 (ppm)

新建文件夹.20.fid
K81-2

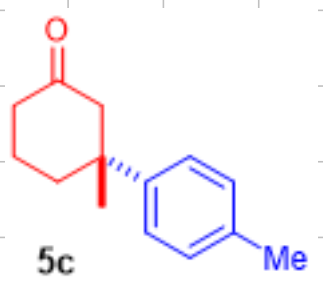


7.2527 7.2443 7.2387 7.2275 7.2220 7.2137 6.8761 6.8677 6.8621 6.8508 6.8456 6.8371 3.7869 2.8702 2.8348 2.4328 2.3975 2.3185 2.3014 2.2847 2.1885 2.1844 2.1804 2.1767 2.1699 2.1660 2.1608 2.1559 2.1509 2.1454 2.1415 2.1363 2.1326 2.1254 2.1215 1.9246 1.9223 1.9157 1.9134 1.9082 1.9023 1.8998 1.8924 1.8880 1.8829 1.8798 1.8727 1.8675 1.8645 1.8570 1.8479 1.8411 1.8385 1.8320 1.8294 1.8227 1.6902 1.6836 1.6777 1.6729 1.6681 1.6658 1.6597 1.6553 1.6506 1.6482 1.6416 1.6386 1.6346 1.6320 1.6297 1.6242 1.6204 1.6164 1.2991

1.90 1.87 2.94 1.00 1.00 2.01 1.04 2.05 1.05 3.07

f1 (ppm)

新建文件夹.21.fid
K81-3

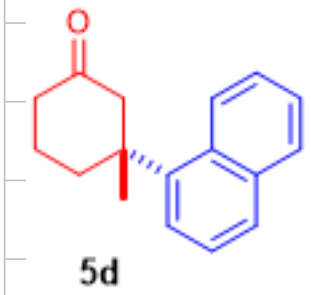


5c

f1 (ppm)

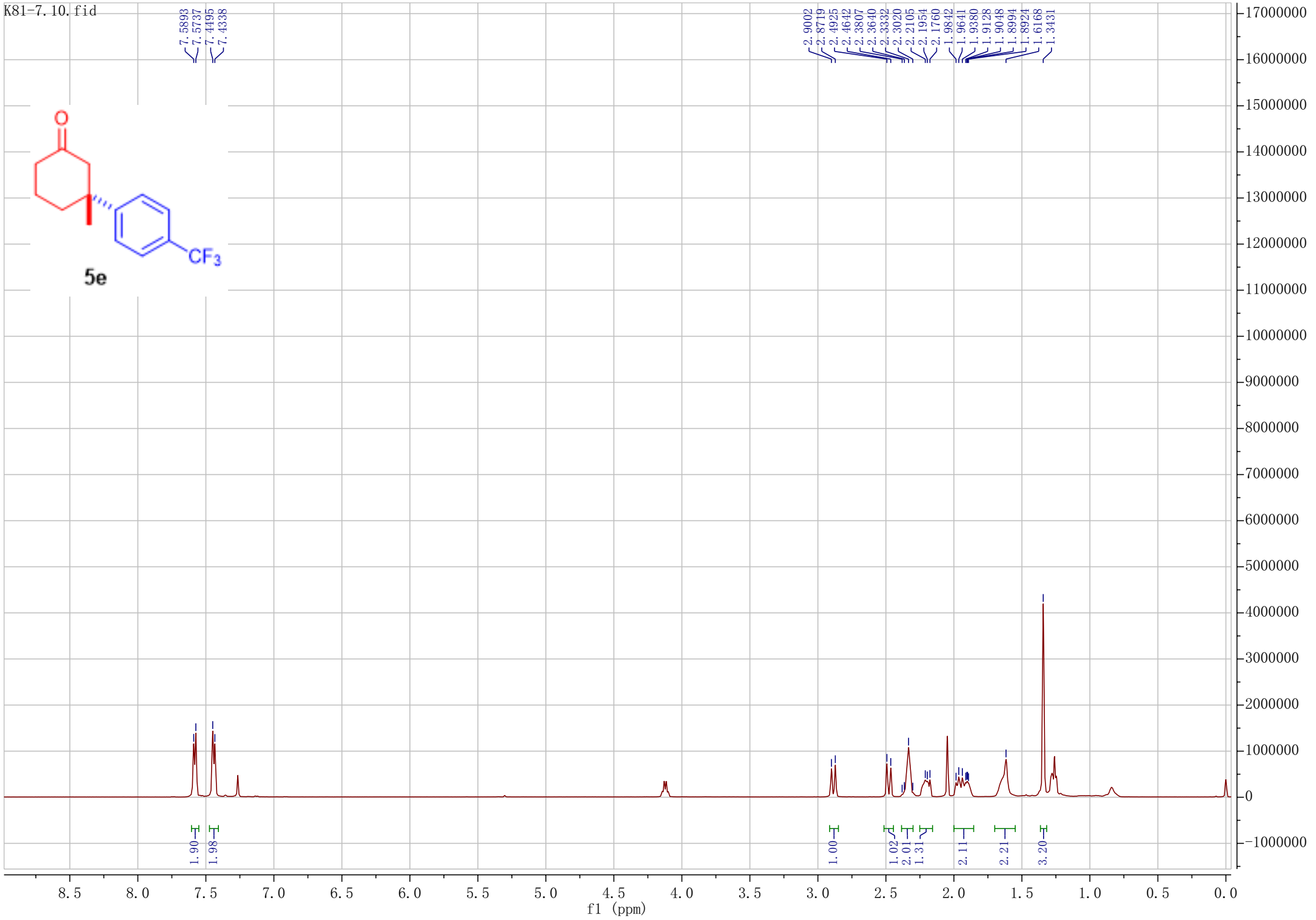
新建文件夹/K81-5H.NMR

K81-5

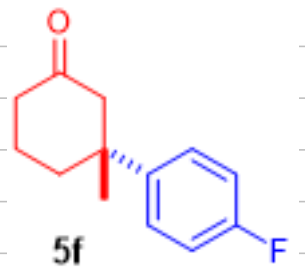


5d

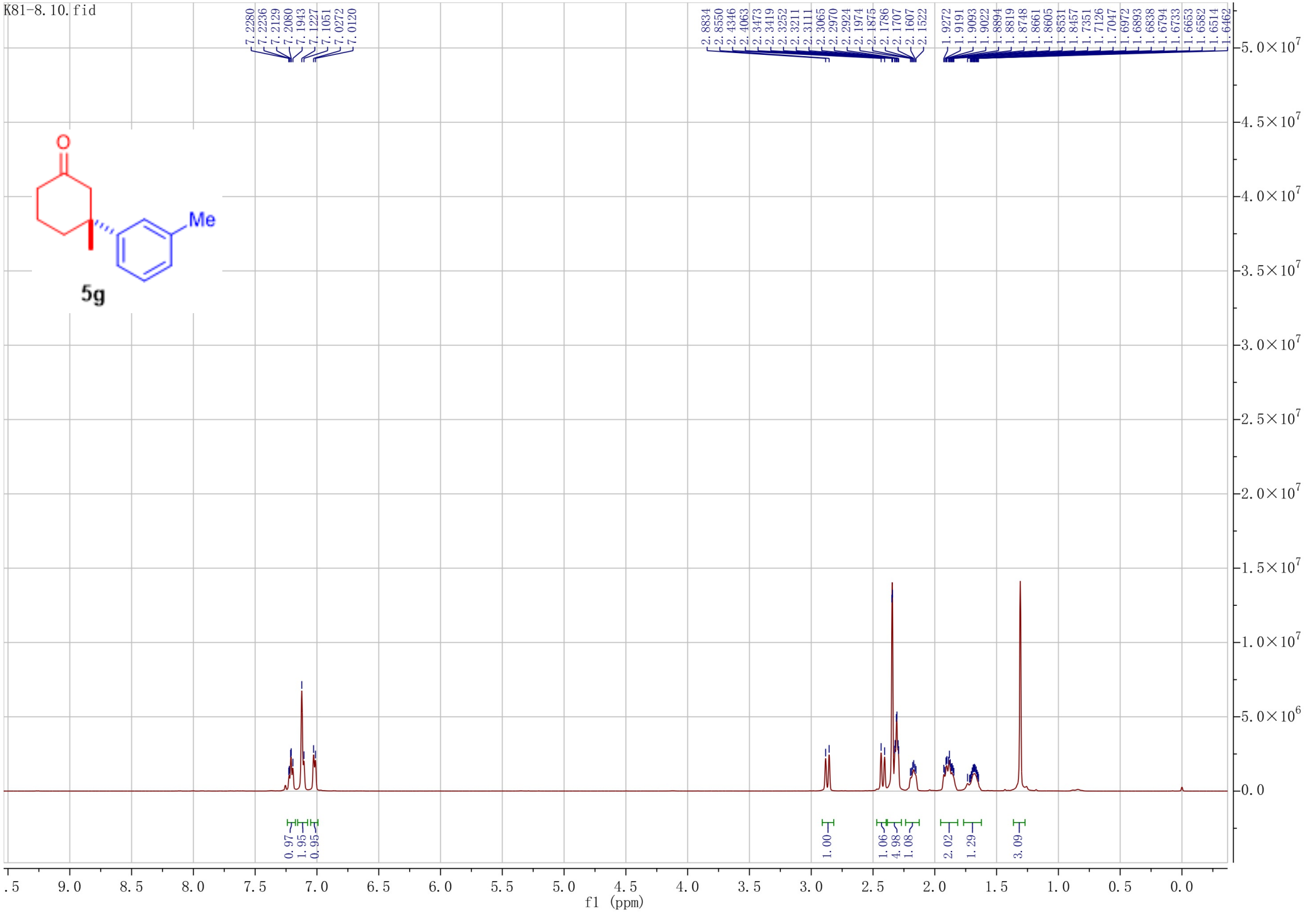
f1 (ppm)

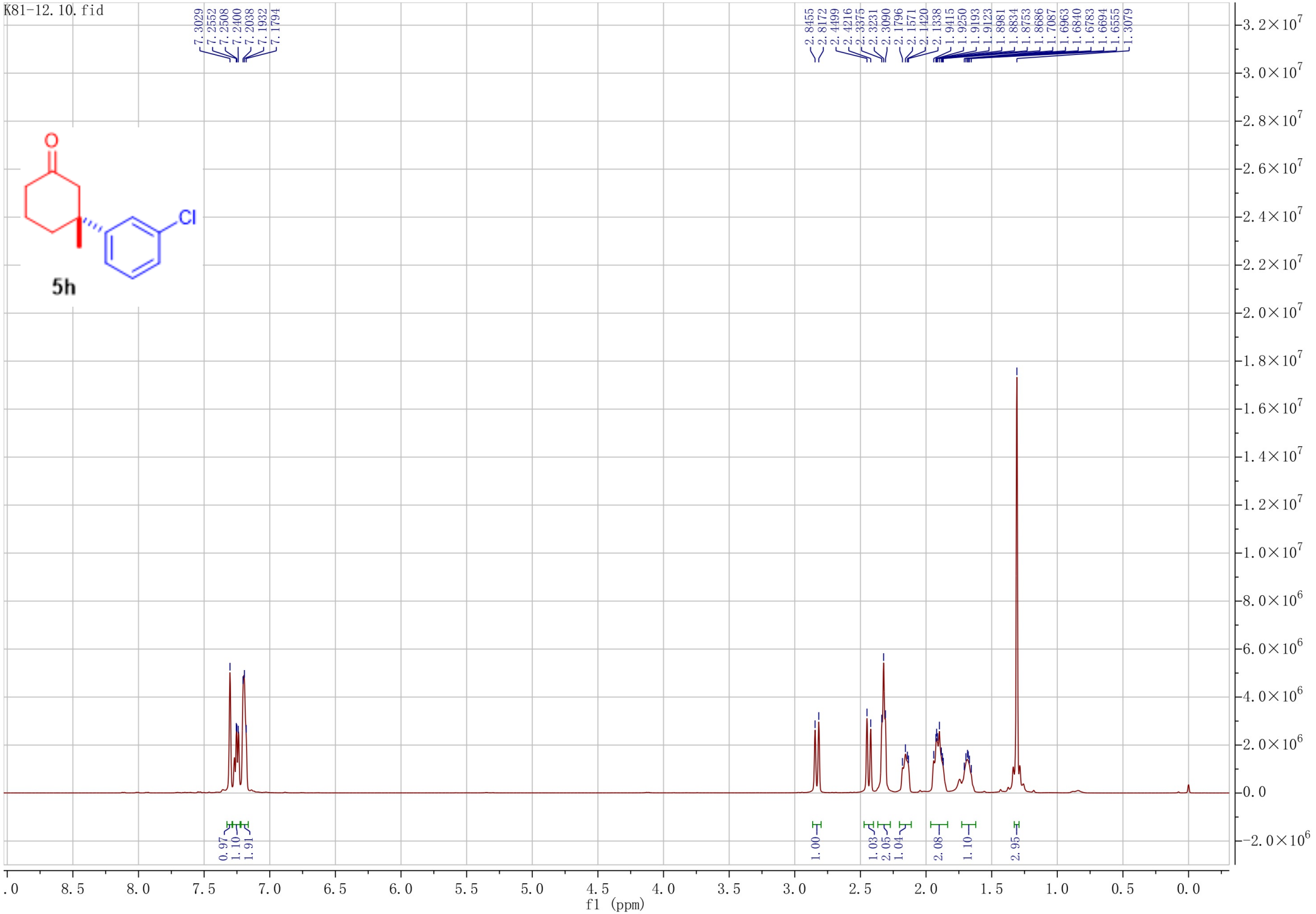

K81-7.10.fid
7.5893
7.5737
7.4495
7.4338
2.9002
2.8719
2.4925
2.4642
2.3807
2.3640
2.3332
2.3020
2.2105
2.1954
2.1760
1.9842
1.9641
1.9380
1.9128
1.9048
1.8994
1.8924
1.6168
1.3431
CF3
5e
1.90
1.98
1.00
1.02
2.01
1.31
2.11
2.21
3.20
f1 (ppm)

新建文件夹.22.fid
K81-4



f1 (ppm)


K81-8.10.fid
7.2280
7.2236
7.2129
7.2080
7.1943
7.1227
7.1051
7.0272
7.0120
2.8834
2.8550
2.4346
2.4063
2.3473
2.3419
2.3252
2.3211
2.3111
2.3065
2.2970
2.2924
2.1974
2.1875
2.1786
2.1707
2.1607
2.1522
1.9272
1.9191
1.9093
1.9022
1.8894
1.8819
1.8748
1.8661
1.8605
1.8531
1.8457
1.7351
1.7126
1.7047
1.6972
1.6893
1.6838
1.6794
1.6733
1.6653
1.6582
1.6514
1.6462
O
Me
5g
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
0.97
1.95
0.95
1.00
1.06
4.98
1.08
2.02
1.29
3.09
.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)


K81-12.10.fid
7.3029
7.2552
7.2508
7.2400
7.2038
7.1932
7.1794
2.8455
2.8172
2.4499
2.4216
2.3375
2.3231
2.3090
2.1796
2.1571
2.1420
2.1338
1.9415
1.9250
1.9193
1.9123
1.8981
1.8834
1.8753
1.8686
1.7087
1.6963
1.6840
1.6783
1.6694
1.6555
1.3079
Cl
5h
0.97
1.10
1.91
1.00
1.03
2.05
1.04
2.08
1.10
2.95
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
.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)