**Supporting Information**

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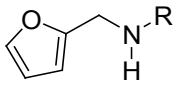
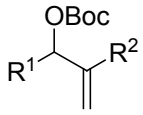
## I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), $KMnO_4$, *p*-anisaldehyde stain, and phosphomolybdic acid (PMA) stain; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a 300 or 500 MHz spectrometer in $CDCl_3$, and carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on 75 or 125 MHz spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Infrared (IR) spectra were recorded on a spectrometer. Mass spectra were recorded on the Bruker MicrOTOF Q II. Melting points were measured on a melting point apparatus and were uncorrected. The enantiomeric excesses of products were determined by chiral phase HPLC analysis at 30$^o$C.

## II Preparation of Substrates



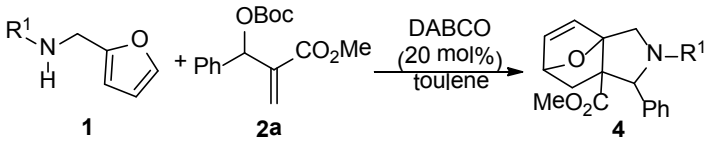

Furfurylamines were prepared according to a published procedure,[1, 2] the spectral data were in agreement with literature values.




MBH carbonates were prepared according to a published procedure,[3, 4] the spectral data were in agreement with literature values.

## III. Reaction Condition Screening

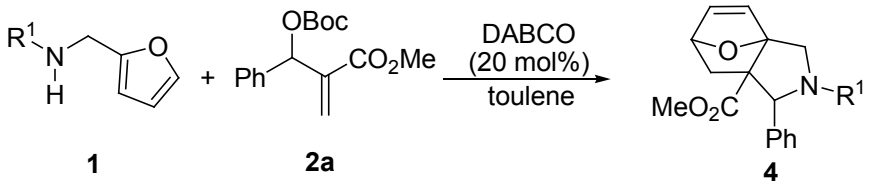
**Representative procedure for the synthesis of compounds 4 (Procedure A)**




1 2a 4

A mixture of sulfonamide **1** (0.1 mmol), MBH carbonate **2a** (0.13 mmol), and catalyst (0.02 mmol or 0.01 mmol), was dissolved in toluene (1.0 mL). Reaction mixture was stirred at room temperature and the reaction was monitored by TLC. Upon completion, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, EtOAc/petroleum ether) to provide the desired product **4**. The major disteroisomers were characterizated, unless otherwise noted.

Table 1. Protecting group $R^1$ screening. [a]

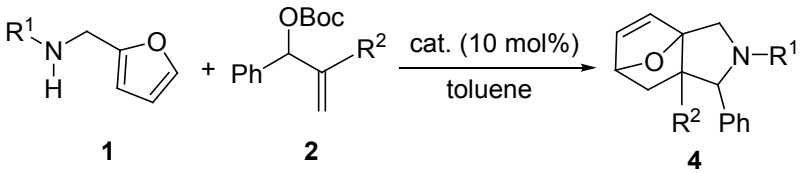



1 2a 4

| Entry | $R^1$ | 1 | d.r. [b] | Yield (%) [c] |
|---|---|---|---|---|
| 1 | PhCO | **1a** | 1:1.1 | 80 (**4aa**) |
| 2 | Ms | **1b** | >20/1 | 89 (**4ba**) |
| 3 | Tf | **1c** | >20/1 | 94 (**4ca**) |
| 4 | Ts | **1d** | >20/1 | 92 (**4da**) |
| 5 | 4-Ns | **1f** | >20/1 | 93 (**4fa**) |
| 6 | 2-Ns | **1g** | >20/1 | 95 (**4ga**) |
| 7 | $CF_3CO$ | **1j** | 4/1 | 92 (**4ja**) |
| 8 | Boc | **1e** | - | < 1 |
| 9 | CBz | **1k** | 1.5/1 | 56 (**4ka**) |

[a] Unless otherwise noted, reactions were performed with **1** (0.1 mmol), **2** (0.13 mmol) and DABCO (20 mol %) in solvent (1 mL) at 30℃. [b] Determined by NMR analysis. [c] Isolated yields.

Table 2. Screening of Catalysts for Asymmetric Cascade Reaction of Compound **1a.** [a]



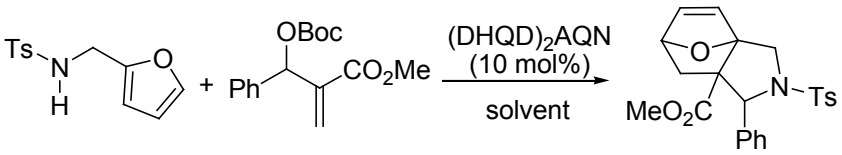

1 2 4

**2a**: $R^2$ = $CO_2Me$; **2b**: $R^2$ =$CO_2Et$; **2c**: $R^2$ = $CO_2Bu$*t*; **2d**: $R^2$ = CN;

| Entry | Cat. | R[1] | 2 | Yield (%) [b] | d.r. [c] | ee [%] [d] |
|---|---|---|---|---|---|---|
| 1 | quinidine | Ts | **2a** | 84 (**4da**) | >20/1 | 67 |
| 2 | quinidine | Ts | **2b** | 78 (**4db**) | >20/1 | 62 |
| 3 | quinidine | Ts | **2c** | 25 (**4dc**) | >20/1 | 62 |
| 4[e] | quinidine | Ts | **2d** | 97 (**4dd**) | 1.1/1 | 33(51) |
| 5 | hydroquinidine | Ts | **2a** | 75 (**4da**) | >20/1 | 76 |
| 6 | quinine | Ts | **2a** | 80 (**4da**) | >20/1 | -30 |
| 7 | cinchonine | Ts | **2a** | 10 (**4da**) | >20/1 | 52 |
| 8 | cinchonidine | Ts | **2a** | 68 (**4da**) | >20/1 | 20 |
| 9 | $(DHQ)_2PHAL$ | Ts | **2a** | 38 (**4da**) | >20/1 | -50 |
| 10 | $(DHQD)_2PHAL$ | Ts | **2a** | 43 (**4da**) | 18/1 | 58 |
| 11 | $(DHQ)_2PYR$ | Ts | **2a** | 54 (**4da**) | >20/1 | -49 |
| 12 | $(DHQD)_2PYR$ | Ts | **2a** | 31 (**4da**) | >20/1 | 72 |
| 13 | $(DHQ)_2AQN$ | Ts | **2a** | 54 (**4da**) | 19/1 | -39 |
| 14 | $(DHQD)_2AQN$ | Ts | **2a** | 46 (**4da**) | >20/1 | 89 |
| 15 | $(DHQD)_2AQN$ | Ms | **2a** | 65 (**4ba**) | 15/1 | 79 |
| 16 | $(DHQD)_2AQN$ | Tf | **2a** | <1 (**4ca**) | - | - |
| 17 | $(DHQD)_2AQN$ | 4-Ns | **2a** | 70 (**4fa**) | 15/1 | 87 |
| 18 | $(DHQD)_2AQN$ | 2-Ns | **2a** | 70 (**4ga**) | 9/1 | 85 |

[a] Unless otherwise noted, reactions were performed with **1** (0.1 mmol), **2** (0.13 mmol), and catalyst (10 mol %) in toluene (0.5 mL, c = 0.2 M) at 25 °C for 24 hours. [b] Isolated yields. [c] Determined by $^1$HNMR analysis. [d] Determined by chiral HPLC analysis. [e] The d.r. value was calculated by isolated yields.

Table 3. Solvents screening. [a]

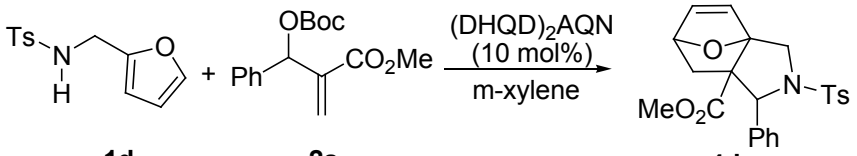



**1d** **2a** **4da**

| Entry | Solvent | Yield (%) [b] | d.r. [c] | ee(%) [c] |
|---|---|---|---|---|
| 1 | toluene | 46 | 24/1 | 89 |
| 2 | xylene | 52 | 18/1 | 90 |
| 3 | $CHCl_3$ | 87 | 24/1 | 68 |
| 4 | DCE | 86 | 19/1 | 71 |
| 5 | $PhCF_3$ | 84 | 21/1 | 83 |
| 6 | benzene | 72 | 18/1 | 82 |
| 7 | 1,4-dioxane | 54 | 32/1 | 79 |
| 8 | DCM | 86 | 16/1 | 70 |
| 9 | THF | 85 | 17/1 | 66 |
| 10 | *o*-xylene | 50 | 20/1 | 89 |
| 11 | *m*-xylene | 50 | 20/1 | 91 |
| 12 | *p*-xylene | 57 | 17/1 | 86 |

[a] Unless otherwise noted, reactions were performed with **1d** (0.1 mmol), **2a** (0.13 mmol), and catalyst (10 mol %) in toluene (0.5 mL, c = 0.2 M) at 25°C for 48 hours. [b] Isolated yields. [c] Determined by chiral HPLC analysis.

Table 4. Additives screening. [a]



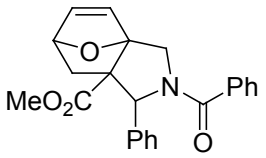

**1d** **2a** **4da**

| Entry | Additives | T (℃) | *t* (d) | Yield (%) [b] | d.r.[c] | Ee[%] [c] |
|---|---|---|---|---|---|---|
| 1 | no | 25 | 2 | 50 | 20/1 | 91 |
| 2 | $FeCl_2$ | 25 | 2 | n.r. | - | - |
| 3 | $FeCl_3$ | 25 | 2 | n.r. | - | - |
| 4 | $CuSO_4$ | 25 | 2 | 49 | 20/1 | 91 |
| 5 | CuI | 25 | 2 | 43 | 23/1 | 91 |
| 6 [d] | CuI /L | 25 | 2 | 52 | 23/1 | 87 |
| 7 [d] | $CuCl_2$ /L | 25 | 2 | 51 | 23/1 | 90 |
| 8 | (s)-(-)BINOL | 25 | 2 | 35 | 23/1 | 91 |
| 9 | 4ÅMS | 25 | 2 | 47 | 27/1 | 91 |
| 10 | 4ÅMS | 35 | 3 | 61 | 22/1 | 91 |
| 11 | 4ÅMS | 50 | 2 | 93 | 7/1 | 89 |
| 12 [e] | 4ÅMS | 25 | 2 | 73 | 26/1 | 90 |
| 13 [e] | 4ÅMS | 25 | 4 | 95 | 29/1 | 90 |

[a] Unless otherwise noted, reactions were performed with **1d** (0.1 mmol), **2a** (0.13 mmol), catalyst (10 mol %) and additives (10 mol%) in toluene (0.5 mL, c = 0.2 M) at 25°C for 48 hours. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] Ligand (1,10-phenanthroline, 10 mol%) was added. [e] Reaction was carried out in solvent (c = 0.4 M)

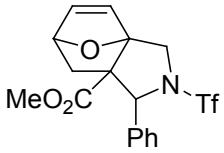
## IV. General Procedure and Experimental Details of the Formation of Azapolyheterocycle Compounds 4

### Preparation of compound 4 by Procedure A:



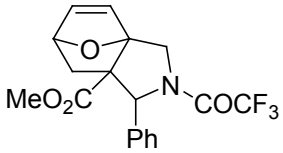

**4aa**

According to the general procedure in which DABCO (20 mol%) was used, colourless oil was obtained as inseparate mixture of **4aa** *(endo-/exo-)* in 80% yield (30 mg, dr =1/1.1). Major isomer: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.58 –6.95 (m, 10H), 6.49 (dd, *J* = 5.7, 1.4 Hz, 1H ), 6.41 (d, *J* = 5.7 Hz, 1H), 5.02 (s, 1H), 4.77 (dd, *J* = 4.5, 1.6 Hz, 1H), 4.70 (d, *J* = 14.0 Hz, 1H), 4.31 (d, *J* = 14.1 Hz, 1H), 3.74 (s, 3H), 1.85-1.71 (m, 1H), 1.64 – 1.59 (m, 1H). Minor isomer: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.58 –6.95 (m, 10H), 6.45 (dd, *J* = 5.7, 1.5 Hz, 1H), 6.30 (d, *J* = 5.7 Hz, 1H), 5.74 (s, 1H), 4.77 (dd, *J* = 4.5, 1.6 Hz, 1H), 4.22 (s, 2H), 3.74 (s, 3H), 1.85-1.71 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.76, 173.37, 171.92, 140.39, 139.72, 139.64, 139.59, 137.10, 136.92, 134.49, 134.07, 131.29, 129.94, 129.29, 128.56, 128.47, 128.37, 128.24, 127.95, 127.88, 127.44,127.34, 126.85, 126.12, 97.61, 97.35, 80.52, 80.18, 69.33, 66.63, 64.80, 63.27, 52.72, 51.90, 51.62, 49.02,33.60, 33.55. HRMS (ESI): calcd. for $C_{23}H_{22}NO_4$ ($[M+H]^+$): 376.1543, found 376.1544.



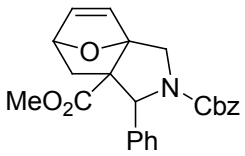

**4ca**

According to the general procedure in which DABCO (20 mol%) was used, white solid was obtained in 94% yield (38 mg), mp: 101.4-103.8℃. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 6.53 (dd, *J* = 5.7, 1.6 Hz, 1H), 6.37 (d, *J* = 5.7 Hz, 1H), 5.36 (s, 1H), 4.82 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.53 (d, *J* = 11.2 Hz, 1H), 4.25 (d, *J* = 11.3 Hz, 1H), 3.79 (s, 3H), 1.84 (d, *J* = 12.4 Hz, 1H), 1.62 (dd, *J* = 12.5, 4.8 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 172.78, 140.57, 133.56, 128.36, 80.63, 70.62, 53.07, 51.55, 34.26. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -77.43 (s). HRMS (ESI): calcd. for $C_{17}H_{17}F_3NO_5S$ ($[M+H]^+$): 404.0774, found 404.0775.




**4ja**

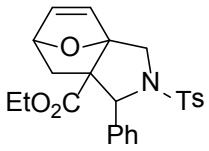
According to the general procedure in which DABCO (20 mol%) was used, colorless oil was obtained as inseparate mixture of **4ja** *(endo-/exo-)* obtained in 92% yield (33.8 mg, dr =4/1). Major isomer: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 3H), 7.17 – 7.11 (m, 2H), 6.51 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.40-6.34 (m, 1H), 5.50 (s, 1H), 4.80 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 12.2 Hz, 1H), 3.73 (s, 3H), 1.83 (d, *J* = 12.3 Hz, 1H), 1.75-1.67 (m, 1H). Minor isomer: δ 7.35 – 7.25 (m, 3H), 7.17 – 7.11 (m, 2H), 6.51 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.40-6.34 (m, 1H), 5.47 (s, 1H), 4.77 (dd, *J* = 4.5, 1.9 Hz, 1H), 4.55 (d, *J* = 14.4 Hz, 1H), 4.26 (d, *J* = 14.4 Hz, 1H), 3.74 (s, 3H), 1.88 (d, *J* = 12.4 Hz, 1H), 1.75-1.67 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.31, 140.34, 137.90, 134.33, 133.62, 128.61, 128.08, 128.05, 127.99, 127.80, 97.93, 80.84, 80.63, 68.78, 62.75, 53.09, 50.91, 49.31, 49.28, 49.24,49.21,33.86,33.72. $^{19}$FNMR (471 MHz, $CDCl_3$) δ -70.76, -72.70. HRMS (ESI): calcd. for $C_{18}H_{17}F_3NO_4$ ($[M+H]^+$): 368.1104, found 368.1105.




**4ka**

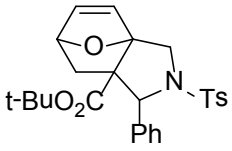
According to the general procedure in which DABCO (20 mol%) was used, colorless oil was obtained as inseparate mixture of **4ka** *(endo-/exo-)* in 56% yield (22.7 mg, dr =1.5/1). Major isomer: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 7.22-7.10 (m, 4H), 6.71 (d, *J* = 7.1 Hz, 1H), 6.48-6.44 (m, 1H), 6.40-6.36 (m, 1H), 5.21 (s, 1H), 5.12-5.05 (m, 1H), 4.90 (d, *J* = 12.6 Hz, 1H), 4.78-4.75 (m, 1H), 4.36-4.30 (m, 1H), 4.23-4.15 (m, 1H), 3.70 (s, 3H), 1.81-1.75 (m, 1H), 1.67-1.61 (m, 1H). Minor isomer: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 7.22-7.10 (m, 4H), 6.71 (d, *J* = 7.1 Hz, 1H), 6.48-6.44 (m, 1H), 6.40-6.36 (m, 1H), 5.29 (s, 1H), 5.12-5.05 (m, 2H), 4.78-4.75 (m, 1H), 4.36-4.30 (m, 1H), 4.23-4.15 (m, 1H), 3.70 (s, 3H), 1.81-1.75 (m, 1H), 1.67-1.61 (m, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.94, 173.90, 154.99, 154.98, 140.87, 139.98, 139.88, 139.81, 139.25, 136.93, 136.49, 136.16, 134.31, 133.64, 128.65, 128.36, 128.33, 128.29, 128.15,

128.08, 127.95, 127.62, 127.52, 127.40, 127.29, 127.06, 97.73, 96.96, 95.07, 80.29, 80.09, 71.47, 71.14, 67.70, 67.44, 67.29, 67.21, 66.99, 64.88, 63.89, 52.82, 52.79, 51.69, 50.48, 50.05, 49.44, 49.17, 37.95, 34.16, 33.94. HRMS (ESI): calcd. for $C_{24}H_{24}NO_5$ ($[M+H]^+$): 406.1649, found 406.1650.



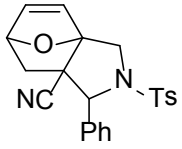

**4db**

According to the general procedure, quinidine (10 mol%) was used. White solid (34.3 mg, 78 %), mp: 103.2-105.0℃, 62 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 25.7 min (minor) and $t_R$ = 27.5 min (major), minor diastereomer: $t_R$ =33.5 min (major). [ α ] $_D^{25}$ = -33 (C = 1.06, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 2H), 7.26-7.19 (m,, 7H), 6.43 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.28 (d, *J* = 5.7 Hz, 1H), 5.06 (s, 1H), 4.75 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.17 (d, *J* = 10.7 Hz, 1H), 4.08 (d, *J* = 10.8 Hz, 1H), 4.09 – 3.98 (m, 1H), 3.73 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.40 (s, 3H), 1.69 (d, *J* = 12.4 Hz, 1H), 1.51 (dd, *J* = 12.4, 4.8 Hz, 1H), 1.12 (t, *J* =7.4 Hz,3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.72, 143.34, 139.85, 139.79, 135.18, 133.53, 129.36, 127.73, 127.49, 96.96, 79.94, 68.82, 65.12, 61.32, 50.21, 34.60, 21.50, 13.98. HRMS (ESI): calcd. for $C_{24}H_{26}NO_5S$ ($[M+H]^+$): 440.1526, found 440.1529.




**4dc**

According to the general procedure, quinidine (10 mol%) was used. Colorless oil (11.7 mg, 25 %), 62 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 11.4 min (major) and $t_R$ = 12.8 min (minor). [ α ] $_D^{21}$ = -12 (C = 0.49, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.25 – 7.01 (m, 7H), 6.44 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.37 (d, *J* = 5.7 Hz, 1H), 5.11 (s, 1H), 4.72 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.28 (d, *J* = 10.6 Hz, 1H), 3.99 (d, *J* = 10.6 Hz, 1H), 2.37 (s, 3H), 1.65 (d, *J* = 12.4 Hz, 1H), 1.46 (dd, *J* = 12.4, 4.8 Hz, 1H), 1.41 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.01, 143.15, 139.52, 139.50, 136.05, 133.88, 129.29, 127.50, 127.37, 96.84, 82.11, 79.76, 68.95, 65.94, 50.36, 34.64, 27.79, 21.44.



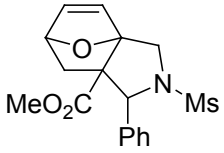

**4dd**

According to the general procedure, quinidine (10 mol%) was used. The disteroisomers can be separated by column. White solid **4dd** (minor isomer A: 18.1 mg, 46 %), mp: 117.0-119.3℃, 51 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 35.5 min (major) and $t_R$ = 40.5

min (minor)). [ α ] $_D^{21}$ = +9 (C = 0.52, $CHCl_3$). Isomer A: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.32-7.24 (m, 7H), 6.59 (dd, *J* = 5.7, 1.6 Hz, 1H), 6.51 (d, *J* = 5.7 Hz, 1H), 5.32 (s, 1H), 4.88 (dd, *J* = 4.5, 1.6 Hz, 1H), 4.22 (d, *J* = 11.7 Hz, 1H), 4.04 (d, *J* = 11.8 Hz, 1H), 2.43 (s, 3H), 1.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.52 (d, *J* = 12.4 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.20, 140.47, 137.80, 133.99, 133.84, 129.81, 128.46, 128.35, 128.21, 127.67, 121.91, 98.11, 80.85, 69.49, 51.21, 48.80, 37.63, 21.61. HRMS (ESI): calcd. for $C_{22}H_{21}N_2O_3S$ ($[M+H]^+$): 393.1267, found 393.1267.
Major isomer B: white solid (20.0 mg, 51 %), mp: 111.3-113.1℃, 33 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 24.0 min (minor) and $t_R$ = 30.6 min (major). [ α ] $_D^{25}$ = +79 (C = 0.88, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.43-7.42 (m, 2H), 7.36-7.33 (m, 3H), 7.27 – 7.22 (m, 2H), 6.61 (dd, *J* = 5.8, 1.7 Hz, 1H), 6.55 (d, *J* = 5.8 Hz, 1H), 5.09 (dd, *J* = 4.4, 1.7 Hz, 1H), 4.37 (d, *J* = 13.2 Hz, 1H), 4.27 (s, 1H), 4.19 (d, *J* = 13.3 Hz, 1H), 2.41 (s, 1H), 2.34 (dd, *J* = 12.2, 4.5 Hz, 1H), 1.64 (d, *J* = 12.3 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 144.30, 140.57, 137.91, 134.09, 133.95, 129.92, 128.57, 128.46, 128.32, 127.77, 122.02, 98.22, 80.96, 69.60, 51.32, 48.91, 37.73, 21.71. HRMS (ESI): calcd. for $C_{22}H_{21}N_2O_3S$ ($[M+H]^+$): 393.1267, found 393.1266.

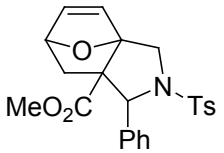
**Preparation of compound 4 by Procedure B:**

A mixture of sulfonamide **1** (0.1 mmol), MBH carbonate **2** (0.13 mmol), 4Å molecular sieves (20 mg) and $(DHQD)_2AQN$ (0.01 mmol), was dissolved in *m*-xylene (0.25 mL). Reaction mixture was stirred at 25 ℃ for 96 hrs. Upon completion, the mixture was filtrated through a pad of Celite and the precipitate washed with dichloromethane. The organic phase was evaporated and the residue was purified by flash chromatography (silica gel, EtOAc/petroleum ether) to provide the desired product **4**. The major disteroisomers were characterizated, unless otherwise noted.




**4ba**

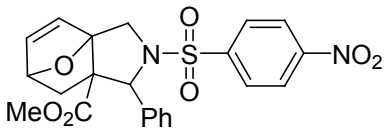
White solid (23 mg, 65%), mp: 149.2-151.5℃, 79 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 45.2 min (minor) and $t_R$ = 48.0 min (major). [ α ] $_D^{25}$ = -20 (C = 1.16, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H), 6.50 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.36 (d, *J* = 5.7 Hz, 1H), 5.20 (s, 1H), 4.83 (dd, *J* = 4.8, 1.7 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.08 (d, *J* = 11.0 Hz, 1H), 3.76 (s, 3H), 2.79 (s, 3H), 1.80 (d, *J* = 12.4 Hz, 1H), 1.57 (dd, *J* = 12.4, 4.8 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.83, 140.21, 139.79, 133.68, 128.65, 128.10, 97.93, 80.35, 69.01, 65.06, 52.98, 50.17, 38.68, 34.32. HRMS (ESI): calcd. for $C_{17}H_{20}NO_5S$ ($[M+H]^+$): 350.1057, found 350.1056.




**4da**

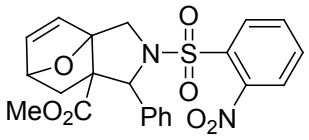
White solid (40.5 mg, 95%), mp: 167.9-168.5℃, 90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 30.0 min (minor) and $t_R$ = 36.7 min (major), minor diastereomer: $t_R$ = 46.1min (major). [ α ] $_D^{25}$ = -75 (C = 1.00, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.20 (m, 7H), 6.43 (dd, *J* = 5.7, 1.7 Hz,

1H), 6.25 (d, *J* = 5.7 Hz, 1H), 5.01 (s, 1H), 4.76 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.12 (s, 2H), 3.32 (s, 3H), 2.43 (s, 3H), 1.69 (d, *J* = 12.4 Hz, 1H), 1.52 (dd, *J* = 12.4, 4.8 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.34, 143.57, 140.14, 140.11, 134.90, 133.57, 129.59, 128.03, 127.72, 97.18, 80.18, 68.95, 65.25, 52.46, 50.36, 34.69, 21.69. HRMS (ESI): calcd. for $C_{23}H_{24}NO_5S$ ($[M+H]^+$): 426.1370, found 426.1378.



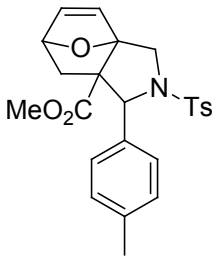
**4fa**

White solid (32.0 mg, 70%), mp: 39.6-42.1℃, 87 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 37.1 min (major) and $t_R$ = 43.9 min (major), minor diastereomer: $t_R$ =50.3min (major). [ α ] $_D^{25}$ = -30 (C = 1.05, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.20 (m, 2H), 7.80 – 7.76 (m, 2H), 7.22-7.11 (m, 5H), 6.47 (dd, *J* = 5.7, 1.6 Hz, 1H), 6.29 (d, *J* = 5.7 Hz, 1H), 5.17 (s, 1H), 4.78 (dd, *J* = 4.7, 1.6 Hz, 1H), 4.30 (d, *J* = 10.9 Hz, 1H), 4.11 (d, *J* = 10.9 Hz, 1H), 3.55 (s, 3H), 1.74 (d, *J* = 12.4 Hz, 1H), 1.53 (dd, *J* = 12.4, 4.7 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.17, 150.04, 144.42, 140.24, 138.68, 133.42, 128.78, 128.38, 128.11, 124.03, 97.41, 80.29, 69.41, 65.07, 52.82, 50.49, 34.33. HRMS (ESI): calcd. for $C_{22}H_{21}N_2O_7S$ ($[M+H]^+$): 457.1064, found 457.1066.



**4ga**

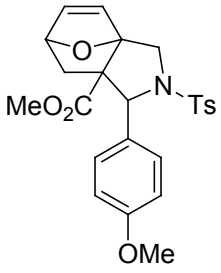
Colorless oil (31.5 mg, 70%), 85 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 29.2 min (major) and $t_R$ = 41.8 min (minor). [ α ] $_D^{25}$ = -127 (C = 1.04, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.31-7.26 (m, 1H), 7.17-7.10 (m, 5H), 6.48 (d, *J* = 5.8 Hz, 1H), 6.35 (d, *J* = 5.7 Hz, 1H), 5.42 (s, 1H), 4.80 (d, *J* = 4.4 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 3.63 (s, 3H), 1.78 (d, *J* = 12.3 Hz, 1H), 1.57 (dd, *J* = 12.3, 4.7 Hz, 1H, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.25, 140.06, 138.50, 133.66, 133.36, 132.42, 131.26, 131.02, 128.89, 128.21 (brs), 127.86, 123.68, 97.39, 80.27, 69.06, 65.23, 52.80, 50.68, 34.27. HRMS (ESI): calcd. for $C_{22}H_{21}N_2O_7S$ ($[M+H]^+$): 457.1064, found 457.1061.



**4de**

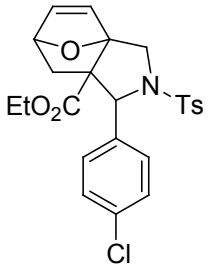
White solid (37.8 mg, 86 %), mp: 151.5-153.7℃, 95 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 27.0 min (minor) and $t_R$ = 36.1 min (major), minor diastereomer: $t_R$ = 44.4min (major). [ α ] $_D^{25}$ = -83 (C = 1.00, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.29

(d, *J* = 7.9 Hz, 2H), 7.09 (m, 4H), 6.42 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.23 (d, *J* = 5.7 Hz, 1H), 4.95 (s, 1H), 4.76 (dd, *J* = 4.6, 1.7 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.29 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H), 1.68 (d, *J* = 12.3 Hz, 1H), 1.55 (dd, *J* = 12.4, 4.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.20, 143.35, 139.91, 137.13, 137.07, 134.63, 133.39, 129.40, 127.88, 96.89, 80.00, 68.62, 65.08, 52.22, 50.18, 34.55, 21.51, 21.17. HRMS (ESI): calcd. for $C_{24}H_{26}NO_5S$ ($[M+H]^+$): 440.1526, found 440.1522.




**4df**

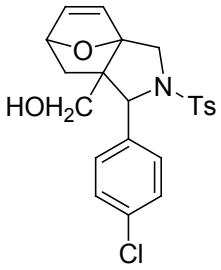
White solid (41.0 mg, 90 %), mp: 148.2-150.1℃, 94 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 37.8 min (minor) and $t_R$ = 56.7 min (major), minor diastereomer: $t_R$ = 73.9 min (major). [ α ] $_D^{21}$ = -73 (C = 0.56, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.25 (m, 4H), 6.81 (dd, *J* = 7.5, 1.4 Hz, 2H), 6.42 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.24 (d, *J* = 5.7 Hz, 1H), 4.94 (s, 1H), 4.77 (dd, *J* = 4.6, 1.6 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.80 (s, 3H), 3.29 (s, 3H), 2.42 (s, 3H), 1.68 (d, *J* = 12.3 Hz, 1H), 1.56 (dd, *J* = 12.3, 4.7 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.35, 159.06, 143.47, 140.05, 134.88, 133.55, 132.28, 129.53, 127.96, 96.98, 80.13, 68.52, 65.27, 55.36, 52.37, 50.29, 34.68, 21.64. HRMS (ESI): calcd. for $C_{24}H_{26}NO_6S$ ($[M+H]^+$): 456.1475, found 456.1473.




**4dg**

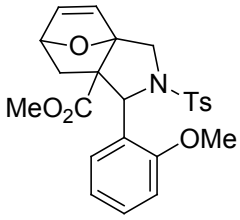
White solid (46.3 mg, 98 %), mp: 123.3-125.0℃. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.22 (m, 6H), 6.44 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.28 (d, *J* = 5.7 Hz, 1H), 5.02 (s, 1H), 4.76 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.15 (d, *J* = 10.7 Hz, 1H), 4.07 (d, *J* = 10.7 Hz, 1H), 4.06-3.97 (m, 1H), 3.78 – 3.67 (m, 1H), 2.42 (s, 3H), 1.70 (d, *J* = 12.4 Hz, 1H), 1.50 (dd, *J* = 12.4, 4.8 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 172.62, 143.76, 140.02, 138.75, 135.11, 133.51, 133.43, 129.60, 127.86, 97.09, 80.08, 68.31, 65.11, 61.56, 50.27, 34.80, 21.66, 14.11. HRMS (ESI): calcd. for $C_{24}H_{25}ClNO_5S$ ($[M+H]^+$): 474.1136, found 474.1138.

Ee of enantiomers of **4dg** can not be separated by chiral HPLC columns. Therefore, compound **4dg'** was prepared for chiral HPLC analysis. A mixture of sulfonamide **1d** (0.1 mmol), MBH carbonate **2g** (0.13 mmol), 4Å molecular sieves (20 mg) and $(DHQD)_2AQN$ (0.01 mmol), was dissolved in *m*-xylene (0.25 mL). After reaction mixture was stirred at 25 ℃ for 96 hrs, DIBAL-H (0.25 mL, 1.0 M in hexane) was added dropwise. The solution was stirred at rt for 10hrs. Upon completion, cold water (5 mL) was added at 0℃ and the aqueous phase extracted with ethyl acetate (3×8 mL). The combined organic solvent was dried with $Na_2SO_4$, filtered, concentrated in *vacuo* and purified by flash chromatography to give **4dg'**, which is analyzed by chiral HPLC.



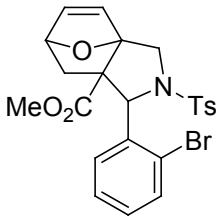

**4dg'**

Colorless oil (32.4 mg, 75 %), 93 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 27.1 min (major) and $t_R$ = 22.4 min (minor), minor diastereomer: $t_R$ =21.0min (major) and $t_R$ = 19.7 min (minor). [ α ] $_D^{25}$ = -43 (C = 1.08, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19-7.09 (m, 4H), 6.41 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.34 (d, *J* = 5.8 Hz, 1H), 5.01 (s, 1H), 4.70 (dd, *J* = 4.9, 1.4 Hz, 1H), 4.01 (d, *J* = 10.8 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.42 (d, *J* = 10.6 Hz, 1H), 3.03 (d, *J* = 10.5 Hz, 1H), 2.40 (s, 3H), 1.41 (dd, *J* = 12.2, 4.9 Hz, 1H), 0.69 (d, *J* = 12.2 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 143.75, 140.15, 138.63, 135.21, 133.48, 132.83, 129.56, 127.94, 96.71, 79.44, 69.61, 68.10, 60.54, 50.73, 33.79, 21.73. HRMS (ESI): calcd. for $C_{22}H_{23}ClNO_4S$ ($[M+H]^+$): 432.1031, found 432.1038.




**4dh**

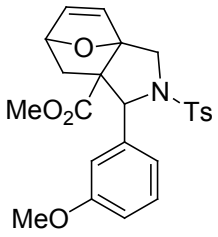
White solid (37.8 mg, 83 %), mp: 182.7-185.0℃, 88 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 24.6 min (minor) and $t_R$ = 35.5 min (major), minor diastereomer: $t_R$ = 27.2 min (major). [ α ] $_D^{25}$ = -128 (C = 0.84, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.18 (m, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.42 (dd, *J* = 5.7, 1.6 Hz, 1H), 6.14 (d, *J* = 5.8 Hz, 1H), 5.36 (s, 1H), 4.70 (dd, *J* = 4.8, 1.6 Hz, 1H), 4.13 (d, *J* = 10.6 Hz, 1H), 4.02 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 3.19 (s, 3H), 2.45 (s, 3H), 1.82 (d, *J* = 12.3 Hz, 1H), 1.36 (dd, *J* = 12.3, 4.8 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.84, 155.62, 143.31, 140.12, 134.35, 132.65, 129.44, 129.31, 128.59, 128.36, 128.17, 120.50, 109.38, 97.09, 80.03, 64.34, 62.98, 55.37, 51.95, 50.05, 34.03, 21.52. HRMS (ESI): calcd. for $C_{24}H_{26}NO_6S$ ($[M+H]^+$): 456.1475, found 456.1481.




**4di**

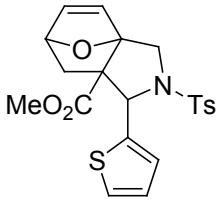
White solid (48.9 mg, 97 %), mp: 182.3-184.5℃, 91 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 34.7 min (minor) and $t_R$ =

46.3 min (major). [ α ] $_D^{25}$ = -75 (C = 1.00, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.67 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 1H), 7.16 – 7.11 (m, 1H), 6.47 (dd, *J* = 5.8, 1.7 Hz, 1H), 6.12 (d, *J* = 5.7 Hz, 1H), 5.39 (s, 1H), 4.76 (dd, *J* = 4.8, 1.7 Hz, 1H), 4.22 (d, *J* = 10.7 Hz, 1H), 3.99 (d, *J* = 10.6 Hz, 1H), 3.16 (s, 3H), 2.46 (s, 3H), 1.94 (d, *J* = 12.5 Hz, 1H), 1.36 (dd, *J* = 12.4, 4.9 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 172.32, 143.79, 140.59, 139.57, 133.76, 132.16, 131.91, 131.52, 129.71, 129.07, 128.38, 127.49, 123.27, 97.54, 80.32, 67.53, 64.37, 52.31, 50.20, 34.21, 21.65. HRMS (ESI): calcd. for $C_{23}H_{23}BrNO_5S$ ($[M+H]^+$): 504.0475, found 504.0477.



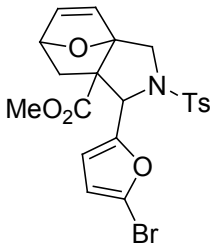

**4dj**

White solid (44.2 mg, 97 %), mp: 65.1-67.3℃, 90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 31.4 min (minor) and $t_R$ = 40.8 min (major), minor diastereomer: $t_R$ = 44.5 min (major). [ α ] $_D^{25}$ = -72 (C = 0.93, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.94-6.63 (m,3H), 6.43 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.24 (d, *J* = 5.7 Hz, 1H), 4.98 (s, 1H), 4.77 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.11 (s, 2H), 3.72 (s,3H), 3.34 (s, 3H), 2.42 (s, 3H), 1.70 (d, *J* = 12.4 Hz, 1H), 1.54 (dd, *J* = 12.4, 4.7 Hz, 1H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.11, 143.39, 141.46, 139.94, 133.31, 129.43, 129.39, 127.82, 113.63, 96.90, 79.95, 68.65, 65.04, 55.12, 52.30, 50.19, 34.49, 21.49. HRMS (ESI): calcd. for $C_{24}H_{26}NO_6S$ ($[M+H]^+$): 456.1475, found 456.1479.



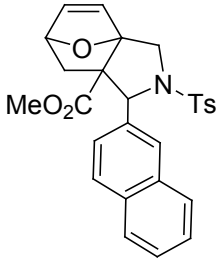

**4dk**

White solid (42.3 mg, 98 %), mp: 149.6-151.9℃, 86 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 54.4 min (minor) and $t_R$ = 87.6 min (major). [ α ] $_D^{25}$ = -14 (C = 0.73, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.25 – 7.20 (m, 3H), 6.93 – 6.878 (m, 2H), 6.49 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.27 (d, *J* = 5.7 Hz, 1H), 5.39 (s, 1H), 4.89 (dd, *J* = 3.7, 1.3 Hz, 1H), 4.13 (d, *J* = 10.7 Hz, 1H), 4.00 (d, *J* = 10.7 Hz, 1H), 3.43 (s, 3H), 2.40 (s, 3H), 1.82-1.79 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 172.91, 143.92, 143.45, 140.18, 135.63, 133.33, 129.53, 127.74, 127.56, 126.62, 126.31, 97.18, 80.24, 64.90, 64.72, 52.66, 49.73, 34.67, 21.70. HRMS (ESI): calcd. for $C_{21}H_{22}NO_5S_2$ ($[M+H]^+$): 432.0934, found 432.0935.



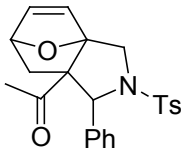

**4dl**

White solid (46.5 mg, 94 %), mp: 145.2-147.0℃, 81 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 30.2 min (minor) and $t_R$ = 46.0 min (major), minor diastereomer: $t_R$ = 36.1min (major) and $t_R$ = 42.7 min (minor). [ α ] $_D^{25}$ = -74 (C = 1.02, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.32(d, *J* = 8.3 Hz, 2H), 6.48 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.29 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.23 (dd, *J* = 3.4, 0.4 Hz, 1H), 6.20 (d, *J* = 5.8 Hz, 1H), 5.07 (s, 1H), 4.88 (dd, *J* = 4.7, 1.7 Hz, 1H), 4.02 (m, 2H), 3.31 (s, 3H), 2.44 (s, 3H), 1.86 (d, *J* = 12.5 Hz, 1H), 1.63 (dd, *J* = 12.5, 4.8 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.11, 155.14, 143.65, 140.01, 134.66, 132.63, 129.55, 127.77, 120.50, 112.62, 112.31, 97.12, 80.09, 64.23, 62.24, 52.40, 49.31, 34.16, 21.55. HRMS (ESI): calcd. for $C_{21}H_{21}BrNO_6S$ ([M+H]$^+$): 494.0267, found 494.0257.




**4dm**

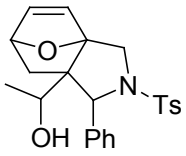
White solid (47.0 mg, 99 %), mp: 152.6-154.7℃, 94 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 38.5 min (minor) and $t_R$ = 50.0 min (major), minor diastereomer: $t_R$ =56.6min (major). [ α ] $_D^{21}$ = -99 (C = 0.74, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 3H), 7.64 (d, *J* = 7.9 Hz, 3H), 7.46-7.43 (m, 2H), 7.24-7.21 (m, 3H), 6.41 (dd, *J* = 5.7, 1.4 Hz, 1H), 6.26 (d, *J* = 5.7 Hz, 1H), 5.18 (s, 1H), 4.71 (brs, 1H), 4.19 (s, 2H), 3.35 (s, 3H), 2.36 (s, 3H), 1.69 (d, *J* = 12.4 Hz, 1H), 1.51 (dd, *J* = 12.4, 4.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.26, 143.57, 140.06, 133.41, 133.06, 129.51, 128.12, 128.08, 128.05, 128.04, 127.92, 127.83, 127.71, 126.07, 80.09, 69.00, 52.47, 50.39, 34.69, 21.56. HRMS (ESI): calcd. for $C_{27}H_{26}NO_5S$ ([M+H]$^+$): 476.1526, found 476.1529.




**4do**

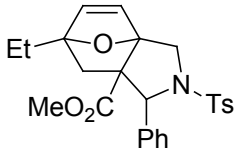
According to the general procedure, compound **4do** was isolated as an unstable compound which resulted in a endo-/exo-mixture of **4do** at room temperature. Therefore, compound **4do'** was prepared for characterization and chiral HPLC analysis. A mixture of sulfonamide **1d** (0.1 mmol), MBH carbonate **2o** (0.13 mmol), 4Å molecular sieves (20 mg) and $(DHQD)_2AQN$ (0.01 mmol), was dissolved in *m*-xylene (0.25 mL). After reaction mixture was stirred at 25 ℃ for 48 hrs, DIBAL-H (0.25 mL, 1.0 M in hexane) was added dropwise. The solution was stirred at rt

for 10hrs. Upon completion, cold water (5 mL) was added at 0℃ and the aqueous phase extracted with ethyl acetate (3×8 mL). The combined organic solvent was dried with $Na_2SO_4$, filtered, concentrated in *vacuo* and purified by flash chromatography to give **4do'**, which is stable and analyzed by chiral HPLC.



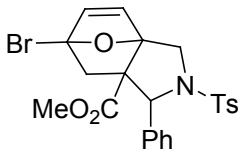

**4do'**

Yellow oil (28.8 mg, 70 %), 91 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 17.5 min (minor) and $t_R$ = 22.5 min (major). [ α ] $_D^{25}$ = -49 (C = 0.95, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 6.6 Hz, 1H), 7.25 – 7.14 (m, 5H), 6.99 (d, *J* = 6.1 Hz, 1H), 6.42 (d, *J* = 5.7 Hz, 1H), 6.38 (d, *J* = 5.7 Hz, 1H), 4.99 (s, 1H), 4.64 (d, *J* = 4.8 Hz, 1H), 4.04 (d, *J* = 10.2 Hz, 1H), 3.96 (d, *J* = 10.2 Hz, 1H), 3.23-3.18 (m, 1H), 2.37 (s, 3H), 1.38 (dd, *J* = 12.1, 4.9 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 0.54 (d, *J* = 12.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 143.33, 141.70, 138.24, 135.40, 133.92, 129.41, 129.33, 128.52, 128.01, 127.60, 127.31, 126.83, 97.83, 78.81, 73.90, 64.10, 63.49, 51.09, 34.60, 21.65, 21.02. HRMS (ESI): calcd. for $C_{23}H_{26}NO_4S$ ($[M+H]^+$): 412.1577, found 412.1577.



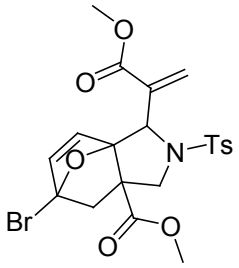

**4ha**

White solid (39.5 mg, 87 %), mp: 118.5-120.2℃, 89 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 33.9 min (minor) and $t_R$ = 37.2 min (major), minor diastereomer: $t_R$ =45.3min (major). [ α ] $_D^{25}$ = -48 (C = 0.95, $CHCl_3$). $^1$H NMR (300 MHz,$CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.35 – 7.15 (m, 7H), 6.32 (d, *J* = 5.7 Hz, 1H), 6.24 (d, *J* = 5.7 Hz, 1H), 5.00 (s, 1H), 4.10 (s, 2H), 3.32 (s, 3H), 2.42 (s, 3H), 1.70 (d, *J* = 12.3 Hz, 1H), 1.60 (q, *J* = 7.2, 2H), 1.27 (d, *J* = 12.3 Hz, 1H), 0.73 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.24, 143.33, 142.00, 139.97, 134.83, 133.76, 129.39, 127.82, 127.51, 96.37, 92.11, 68.80, 67.55, 52.22, 50.41, 38.01, 25.18, 21.50, 8.69. HRMS (ESI): calcd. for $C_{25}H_{28}NO_5S$ ($[M+H]^+$): 454.1683, found 454.1684.



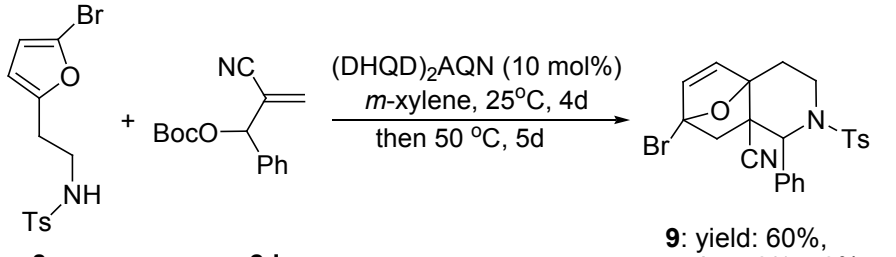

**4ia**

White solid (50.0 mg, 99 %), mp: 164.7-167.1℃, 91 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 18.7 min (minor) and $t_R$ = 25.6 min (major), minor diastereomer: $t_R$ =24.3min (major) and $t_R$ = 27.4 min (minor). [ α ] $_D^{25}$ = -42 (C = 0.86, $CHCl_3$). $^1$H NMR (300 MHz,$CDCl_3$) δ 7.65 – 7.53 (m, 2H), 7.37 – 7.17 (m, 7H), 6.45 (d, *J* = 5.5 Hz, 1H), 6.30 (d, *J* = 5.5 Hz, 1H), 4.19 – 4.06 (m, 2H), 3.42 (s, 3H), 2.42 (s, 3H), 2.30 (d, *J* = 12.6 Hz, 1H), 1.80 (d, *J* = 12.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 171.96, 143.59, 143.42, 138.99, 134.77, 134.34, 129.44, 128.06, 127.75, 95.54, 88.95, 68.76, 68.13, 52.67, 49.96, 45.36, 21.52. HRMS (ESI): calcd. for $C_{23}H_{23}BrNO_5S$ ($[M+H]^+$): 504.0475, found 504.0478.



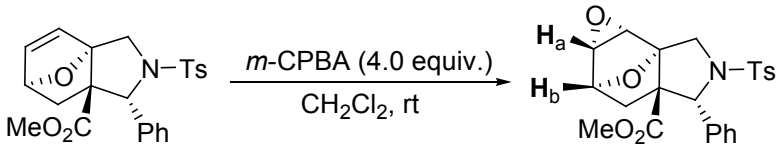
**7**

Yellow oil (28.2 mg, 55 %), 83 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 43.5 min (major) and $t_R$ = 49.7 min (minor). [ α ] $_D^{21}$ = +2 (C = 0.3, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 1H), 6.34 (d, *J* = 5.7 Hz, 1H), 6.29 (d, *J* = 0.7 Hz, 1H), 6.04 (d, *J* = 5.7 Hz, 1H), 4.82 (s, 1H), 4.47 (d, *J* = 9.4 Hz, 1H), 3.81 (s, 3H), 3.60 (s, 3H), 3.11 (d, *J* = 9.4 Hz, 1H), 2.45 (s, 3H), 2.33 (d, *J* = 12.0 Hz, 1H), 2.27 (d, *J* = 11.9 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 171.15, 165.91, 144.34, 139.33, 136.03, 133.62, 131.96, 130.55, 129.85, 128.04, 97.98, 88.21, 60.36, 59.92, 56.75, 52.55, 52.23, 50.40, 21.63. HRMS (ESI): calcd. for $C_{21}H_{23}BrNO_7S$ ($[M+H]^+$): 512.0373, found 512.0378.




A mixture of sulfonamide **8** (0.1 mmol),[5] MBH carbonate **2d** (0.13 mmol), 4Å molecular sieves (20 mg) and $(DHQD)_2AQN$ (0.01 mmol), was dissolved in *m*-xylene (0.25 mL). After reaction mixture was stirred at 25 ℃ for 4 days, the reaction was allowed to warm to 50 ℃ for 5 days. The mixture was filtrated through a pad of Celite and the precipitate washed with dichloromethane. The organic phase was evaporated in vapor and the residue was purified by flash chromatography (silica gel, EtOAc/petroleum ether) to provide the desired product **9**.

Light yellow oil (29.0 mg, 60 %, dr = 6/1), 59 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 27.3 min (minor) and $t_R$ = 30.1 min (major). minor diastereomer: $t_R$ =45.7 min (the peaks of minor diastereomer are overlapped). [ α ] $_D^{25}$ = +14 (C = 1.11, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.16 (m, 7H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 5.5 Hz, 1H), 6.42 (d, *J* = 5.5 Hz, 1H), 4.23 (s, 1H), 4.31 – 4.19 (m, 1H), 3.60 – 3.51 (m, 1H), 2.75-2.66 (m, 1H), 2.39 (s, 3H), 2.45 – 2.35 (m, 1H), 2.22 (d, *J* = 12.6 Hz, 1H), 2.13 (d, *J* = 12.6 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 143.68, 143.45, 138.02, 136.89, 133.70, 130.93, 129.52, 129.27, 128.16, 127.51, 120.52, 88.24, 88.05, 67.45, 50.53, 48.81, 44.47, 27.60, 21.71. HRMS (ESI): calcd. for $C_{23}H_{22}BrN_2O_3S$ ($[M+H]^+$): 485.0529, found 485.0535.




**4da** (90%ee)

**10**: yield: 88%, d.r.>20/1, 90%ee

A solution of **4da** (42.6 mg, 0.1 mmol) and *m*-CPBA (69.0 mg, 0.4 mmol) in $CH_2Cl_2$ (2 mL) was stirred at 25℃ for 16 hrs. [6] Upon completion, the reaction mixture was poured into water (30 mL) and basified with sa. $NaHCO_3$ (aq.) to pH=9-10.The organic layer was separated and the water layer was extracted with $CH_2Cl_2$ (3*30 mL). The combined organic layers were washed with water (2*20 mL). Then the organic phase was dried by anhydrous $Na_2SO_4$ and evaporated in vapor. The residue was purified by flash chromatography (silica gel, petroleum ether/ EtOAc: 10/1 to 3/1 gradient) to provide the desired product **10**.

White solid (38.6 mg, 88%), mp: 118.4-120 ℃, 90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 70/30, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 43.3 min (minor) and $t_R$ = 53.9 min (major). [ α ] $_D^{25}$ = -129 (C = 1.10, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.13 (m, 7H), 4.94 (s, 1H), 4.26 (d, *J* = 5.3 Hz, 1Ha), 4.11 (d, *J* = 10.9 Hz, 1H), 4.02 (d, *J* = 10.9 Hz, 1H), 3.48 (s, 3H), 3.35 (d, *J* = 3.3 Hz, 1H), 3.30 (d, *J* = 3.3 Hz, 1H), 2.43 (s, 3H), 1.90 (d, *J* = 13.4 Hz, 1H), 1.49 (dd, *J* = 13.4, 5.4 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 172.20, 143.64, 139.16, 134.71, 129.52, 128.48, 127.90, 127.85, 92.27, 75.96, 69.34, 67.22, 52.81, 49.80, 49.16, 48.29, 34.99, 21.59. HRMS (ESI): calcd. for $C_{23}H_{24}NO_6S$ ($[M+H]^+$): 442.1319, found 442.1319.

Because the corresponding $J_{Ha\text{-}Hb}$ value is really small (the bridged $H_b$ is a doublet), the relative stereochemistry between $H_a$ and $H_b$ could be assigned to be syn, which is also confirmed by NOESY-spectrum.

## Reference

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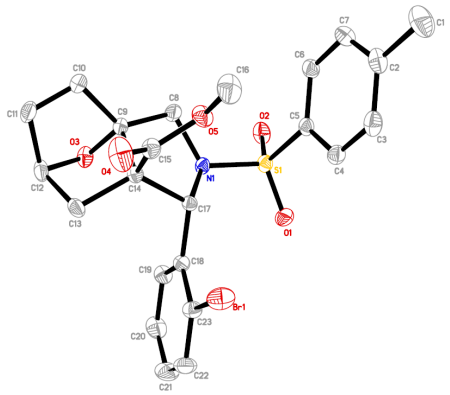
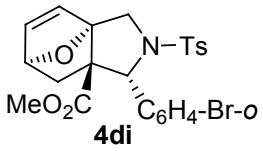
## V. Crystal data and structure refinement for enantiopure 4df





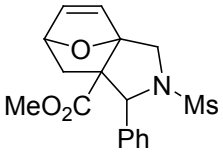

**4di**

Table 1. Crystal data and structure refinement for compound **4di**.

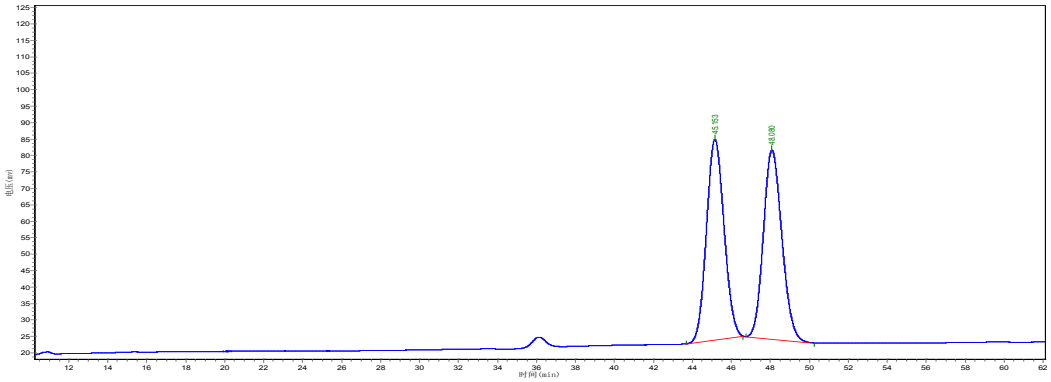
| | |
|---|---|
| Identification code | **4di** |
| Empirical formula | $C_{23}$ $H_{22}$ Br N $O_5$ S |
| Formula weight | 504.39 |
| Temperature | 291(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Orthorhombic, P2(1)2(1)2(1) |
| Unit cell dimensions | a = 7.7952(16) A alpha = 90 deg.<br>b = 13.733(3) A beta = 90 deg.<br>c = 21.171(4) A gamma = 90 deg. |
| Volume | 2266.4(8) A^3 |
| Z, Calculated density | 4, 1.478 Mg/m^3 |
| Absorption coefficient | 1.940 mm^-1 |
| F(000) | 1032 |
| Crystal size | 0.45 x 0.32 x 0.31 mm |
| Theta range for data collection | 3.00 to 27.47 deg. |

| | |
|---|---|
| Limiting indices | -10<=h<=9, -17<=k<=17, -27<=l<=27 |
| Reflections collected / unique | 21522 / 5156 [R(int) = 0.0416] |
| Completeness to theta = 27.47 | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.5837 and 0.4776 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 5156 / 0 / 282 |
| Goodness-of-fit on F^2 | 1.039 |
| Final R indices [I>2sigma(I)] | R1 = 0.0357, wR2 = 0.0870 |
| R indices (all data) | R1 = 0.0475, wR2 = 0.0922 |
| Absolute structure parameter | 0.008(7) |
| Largest diff. peak and hole | 0.724 and -0.408 e.A^-3 |

**VI. HPLC Spectra**

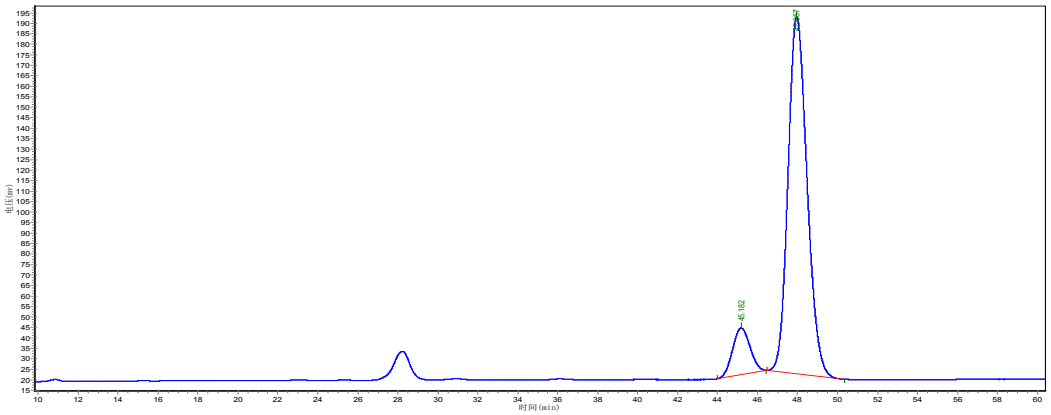



4ba




Result Table

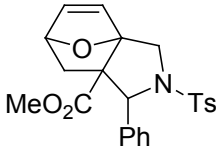
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 45.153 | 60984.555 | 3832883.000 | 50.2898 |
| 2 | 48.080 | 57498.477 | 3788711.000 | 49.7102 |
| total | | 118483.031 | 7621594.000 | 100.0000 |



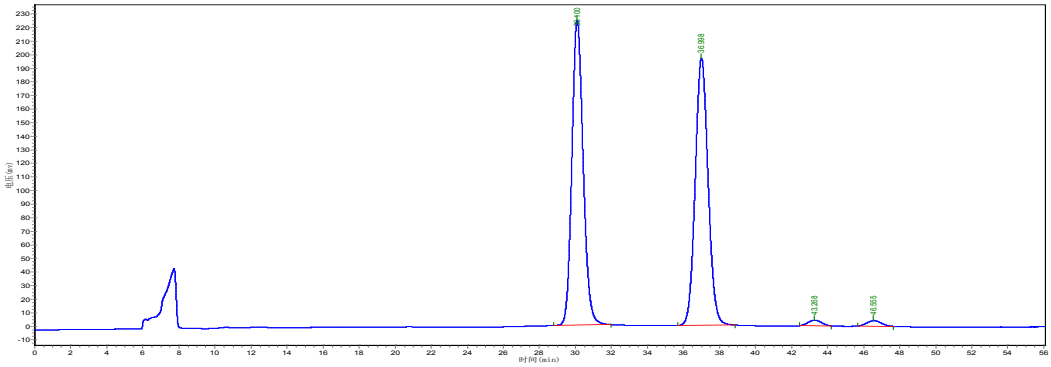

Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 45.182 | 22255.029 | 1347499.375 | 10.6944 |
| 2 | 47.957 | 170169.313 | 11252524.000 | 89.3056 |
| total | | 192424.342 | 12600023.375 | 100.0000 |

79 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, $t_R$ = 45.2 min (minor) and $t_R$ = 48.0 min (major).

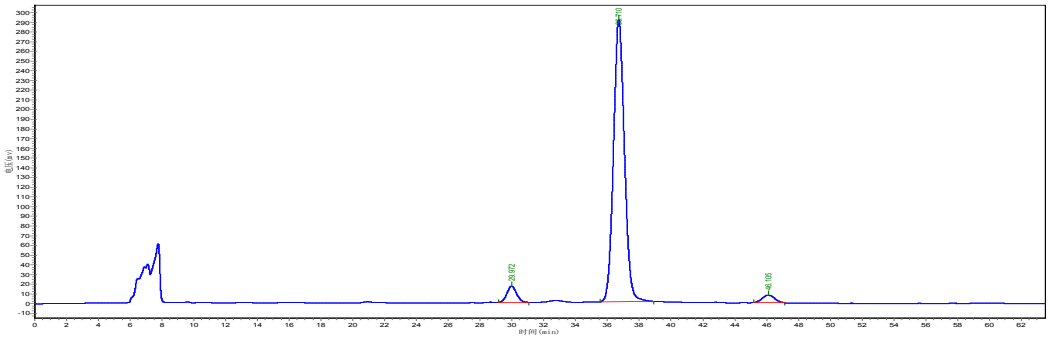



4da



Result Table

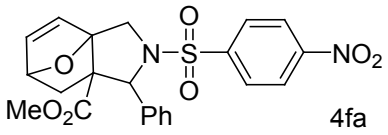
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 30.100 | 224475.453 | 9761292.000 | 48.8656 |
| 2 | 36.998 | 196715.766 | 9773942.000 | 48.9289 |
| 3 | 43.268 | 4145.165 | 213888.891 | 1.0707 |
| 4 | 46.555 | 4099.804 | 226685.203 | 1.1348 |
| total | | 429436.188 | 19975808.094 | 100.0000 |



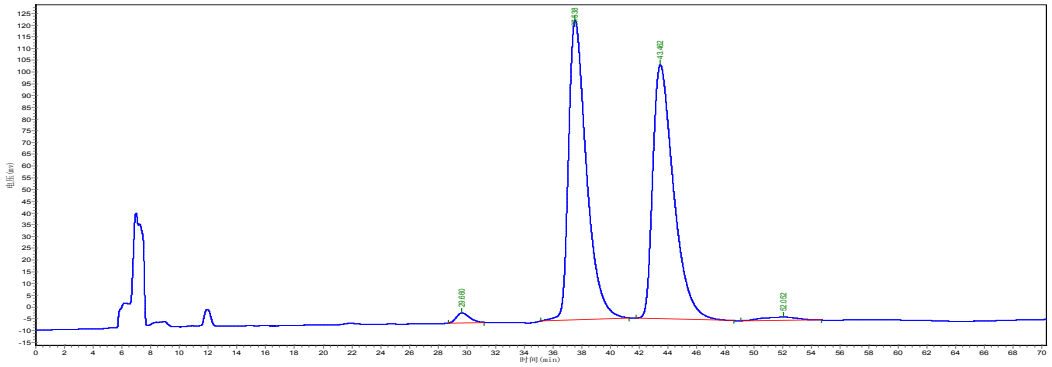
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 29.972 | 16721.637 | 701972.500 | 4.6784 |
| 2 | 36.710 | 290777.656 | 13876680.000 | 92.4830 |
| 3 | 46.105 | 7802.701 | 425918.031 | 2.8386 |
| total | | 315301.994 | 15004570.531 | 100.0000 |

90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 30.0 min (minor) and $t_R$ = 36.7 min (major); minor diastereomer: $t_R$ = 46.1 min (major)).

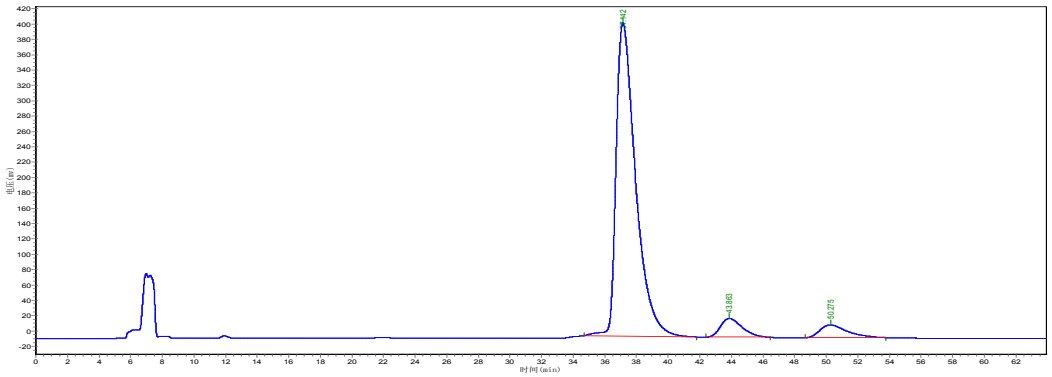



4fa



Result Table

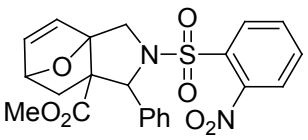
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 29.660 | 4213.453 | 266619.219 | 1.1923 |
| 2 | 37.538 | 127425.555 | 11010751.000 | 49.2391 |
| 3 | 43.462 | 108030.078 | 10845840.000 | 48.5016 |
| 4 | 52.052 | 1387.826 | 238592.203 | 1.0670 |
| total | | 241056.912 | 22361802.422 | 100.0000 |



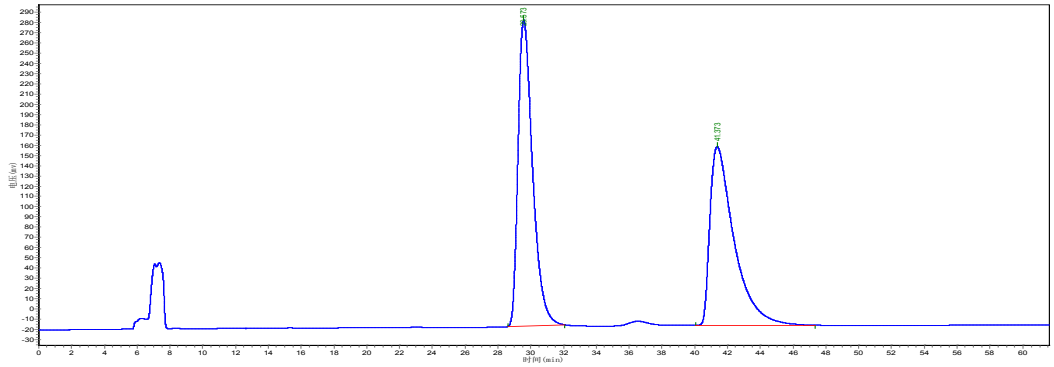
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 37.142 | 408497.094 | 34997016.000 | 88.9544 |
| 2 | 43.863 | 24291.643 | 2333555.000 | 5.9314 |
| 3 | 50.275 | 16680.131 | 2012056.000 | 5.1142 |
| total | | 449468.867 | 39342627.000 | 100.0000 |

87 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 37.1 min (major) and $t_R$ = 43.9 min (major); minor diastereomer: $t_R$ = 50.3 min (major)).

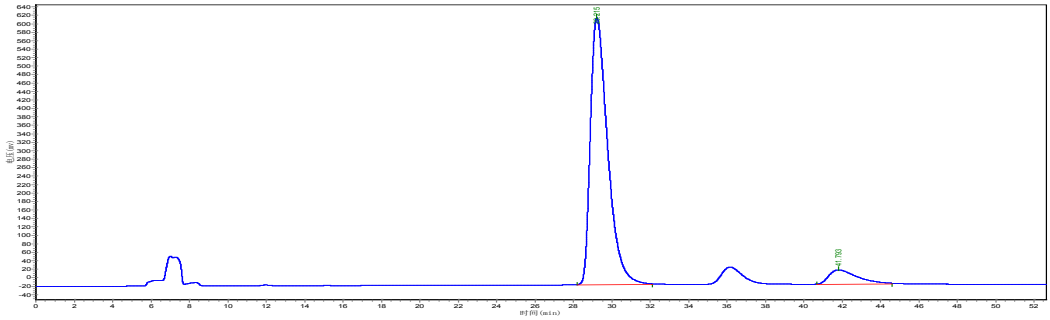



4ga



Result Table

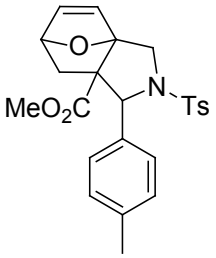
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 29.573 | 299217.594 | 18426690.000 | 50.8677 |
| 2 | 41.373 | 174693.813 | 17798062.000 | 49.1323 |
| total | | 473911.406 | 36224752.000 | 100.0000 |



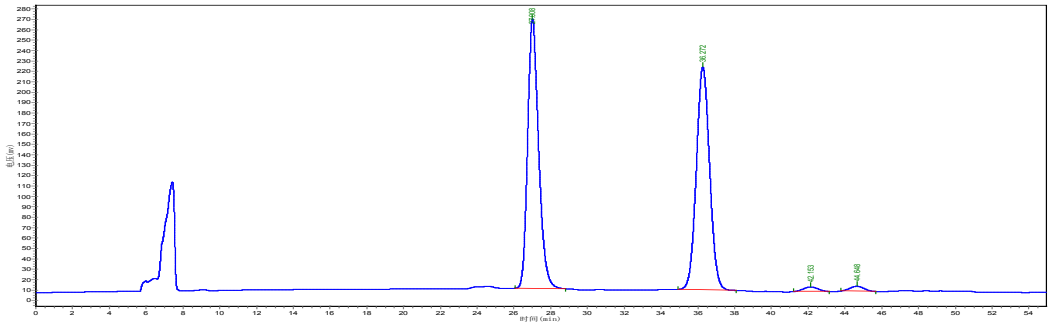
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 29.215 | 629436.125 | 39220368.000 | 92.3797 |
| 2 | 41.793 | 32800.453 | 3235267.750 | 7.6203 |
| total | | 662236.578 | 42455635.750 | 100.0000 |

85 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, $t_R$ = 29.2 min (major) and $t_R$ = 41.8 min (minor)).

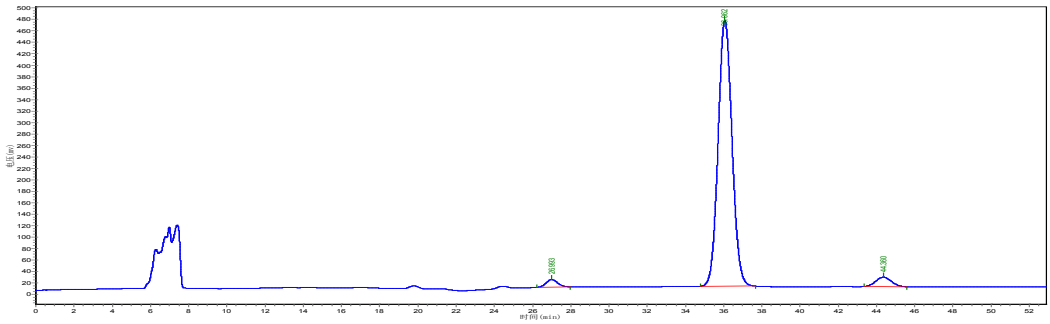



4de



Result Table

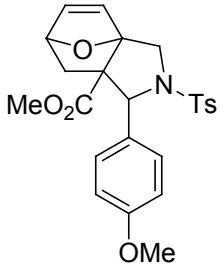
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 27.008 | 258501.453 | 10723273.000 | 48.7726 |
| 2 | 36.272 | 214068.125 | 10758660.000 | 48.9335 |
| 3 | 42.153 | 4482.442 | 248310.031 | 1.1294 |
| 4 | 44.648 | 4759.710 | 256029.219 | 1.1645 |
| total | | 481811.730 | 21986272.250 | 100.0000 |



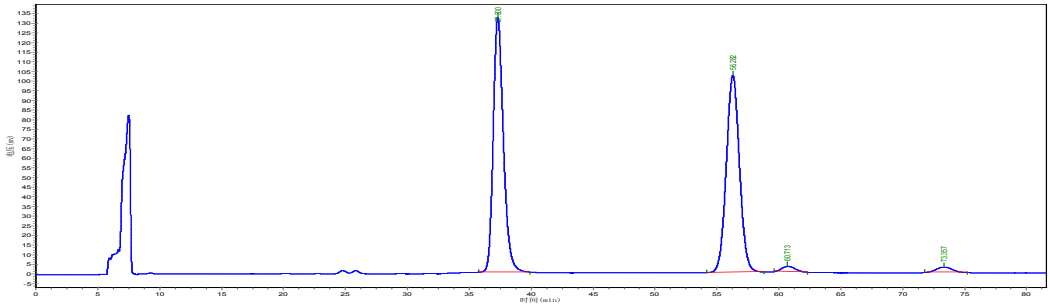
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 26.993 | 13086.258 | 550023.625 | 2.2093 |
| 2 | 36.062 | 463819.813 | 23418028.000 | 94.0623 |
| 3 | 44.360 | 16390.871 | 928247.625 | 3.7285 |
| total | | 493296.941 | 24896299.250 | 100.0000 |

95 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 27.0 min (minor) and $t_R$ = 36.1 min (major); minor diastereomer: $t_R$ = 44.4 min (major)).



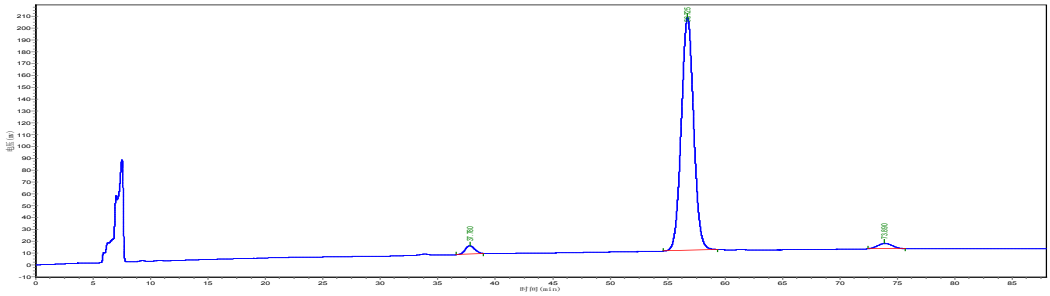

4df



Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 37.300 | 132017.641 | 7532526.000 | 48.3792 |
| 2 | 56.282 | 102076.305 | 7555149.500 | 48.5245 |
| 3 | 60.713 | 2912.635 | 221037.266 | 1.4197 |
| 4 | 73.357 | 2862.256 | 261049.281 | 1.6766 |
| total | | 239868.836 | 15569762.047 | 100.0000 |

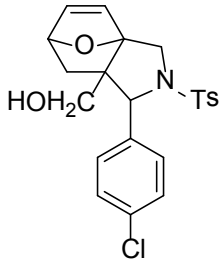
Result Table



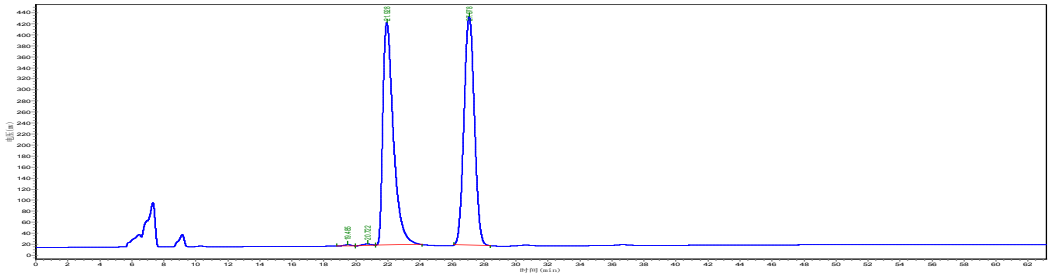
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 37.780 | 7094.938 | 406248.281 | 2.6130 |
| 2 | 56.725 | 196767.266 | 14738271.000 | 94.7969 |
| 3 | 73.890 | 4484.458 | 402686.406 | 2.5901 |
| 4 | | 208346.662 | 15547205.688 | 100.0000 |

94 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 37.8 min (minor) and $t_R$ = 56.7 min (major); minor diastereomer: $t_R$ = 73.9 min (major)).

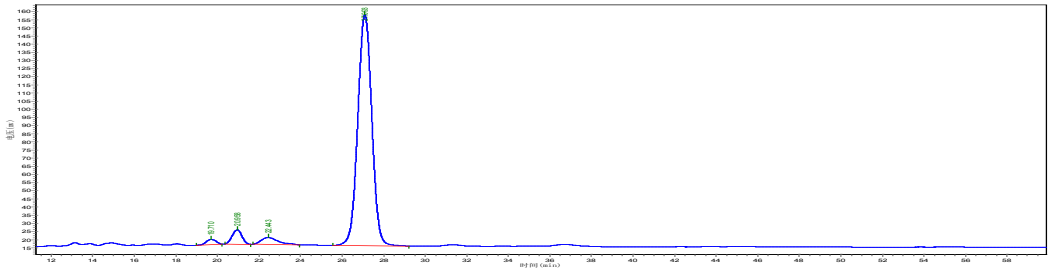



4dg’



Result Table

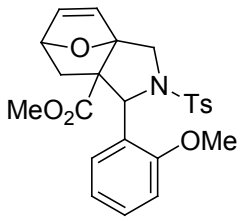
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 19.485 | 2112.966 | 66047.438 | 0.1766 |
| 2 | 20.722 | 2721.152 | 99710.469 | 0.2667 |
| 3 | 21.928 | 403420.156 | 18443324.000 | 49.3228 |
| 4 | 27.078 | 415135.719 | 18784038.000 | 50.2339 |
| total | | 823389.993 | 3733119.906 | 100.0000 |



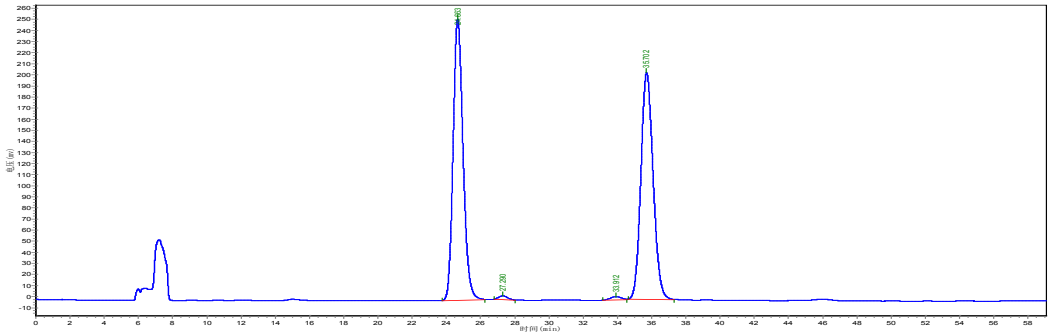
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 19.710 | 3094.359 | 102536.203 | 1.4100 |
| 2 | 20.958 | 8720.529 | 284160.594 | 3.9076 |
| 3 | 22.443 | 4277.871 | 242337.578 | 3.3325 |
| 4 | 27.093 | 141614.375 | 6642964.000 | 91.3499 |
| total | | 157707.134 | 7271998.375 | 100.0000 |

93 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 27.1 min (major) and $t_R$ = 22.4 min (minor); minor diastereomer: $t_R$ = 19.7 min (minor) and $t_R$ = 21.0 min (major)).

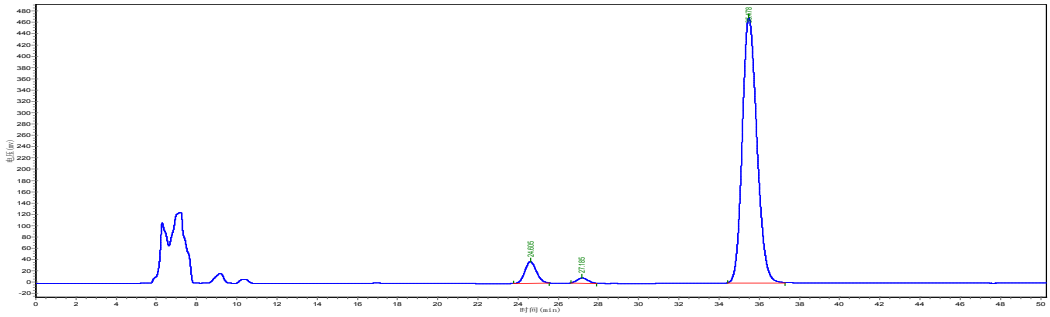



4dh



Result Table

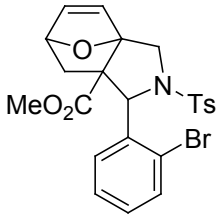
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 24.663 | 253327.984 | 10177489.000 | 49.6329 |
| 2 | 27.290 | 3184.516 | 114296.797 | 0.5574 |
| 3 | 33.912 | 2674.826 | 111681.203 | 0.5446 |
| 4 | 35.702 | 204266.109 | 10102049.000 | 49.2650 |
| total | | 463453.436 | 20505516.000 | 100.0000 |



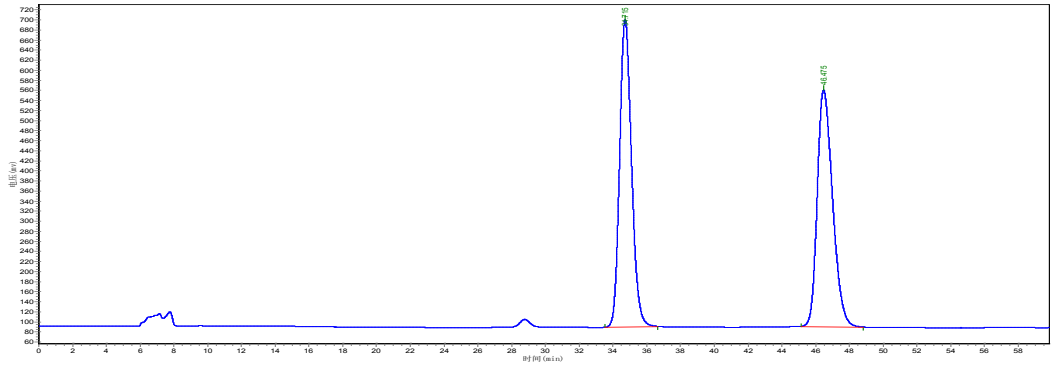
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 24.605 | 38109.066 | 1518231.000 | 5.9731 |
| 2 | 27.185 | 8802.259 | 323236.688 | 1.2717 |
| 3 | 35.478 | 469468.875 | 23576374.000 | 92.7552 |
| total | | 516380.875 | 25417841.688 | 100.0000 |

88 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 24.6 min (minor) and $t_R$ = 35.5 min (major); minor diastereomer: $t_R$ = 27.2 min (major)).

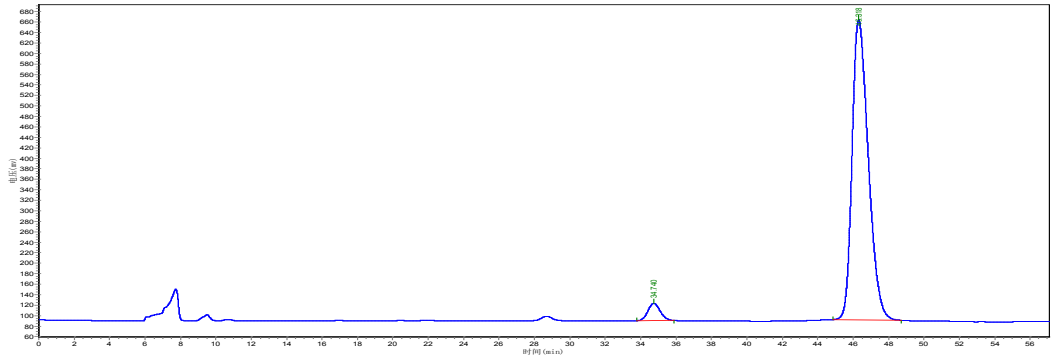



4di



Result Table

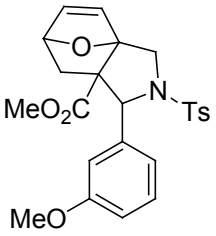
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 34.715 | 610399.938 | 29920894.000 | 50.2445 |
| 2 | 46.475 | 470414.875 | 29629650.000 | 49.7555 |
| total | | 1080814.813 | 59550544.000 | 100.0000 |



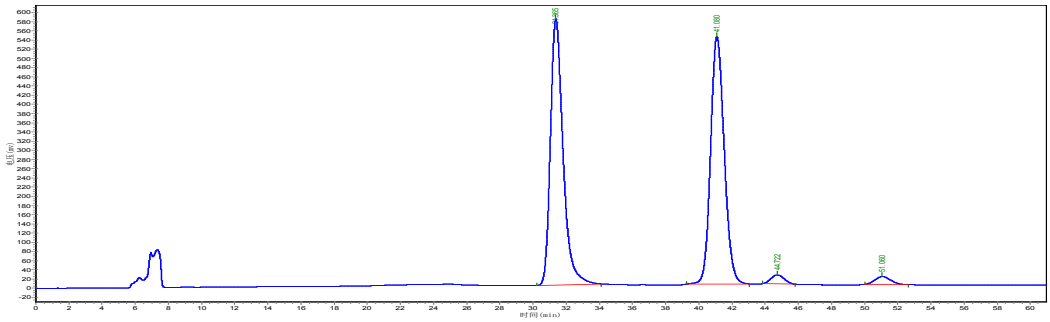
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 34.740 | 32734.779 | 1579884.375 | 4.1597 |
| 2 | 46.318 | 572155.875 | 36401096.000 | 95.8403 |
| total | | 604890.654 | 37980980.375 | 100.0000 |

91 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, $t_R$ = 34.7 min (minor) and $t_R$ = 46.3 min (major)).

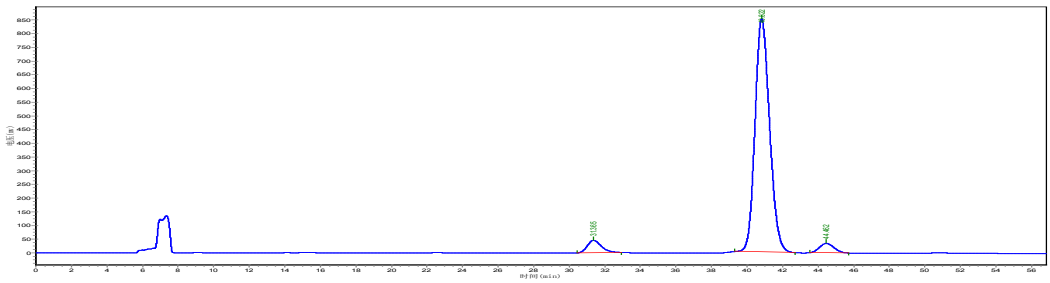



4dj



Result Table

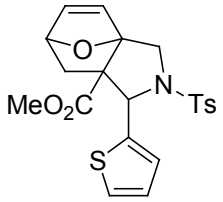
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 31.365 | 578819.938 | 30616952.000 | 48.2379 |
| 2 | 41.080 | 538235.125 | 30640518.000 | 48.2750 |
| 3 | 44.722 | 19419.924 | 1081257.375 | 1.7036 |
| 4 | 51.060 | 17128.479 | 1132018.750 | 1.7835 |
| total | | 1153603.465 | 63470746.125 | 100.0000 |



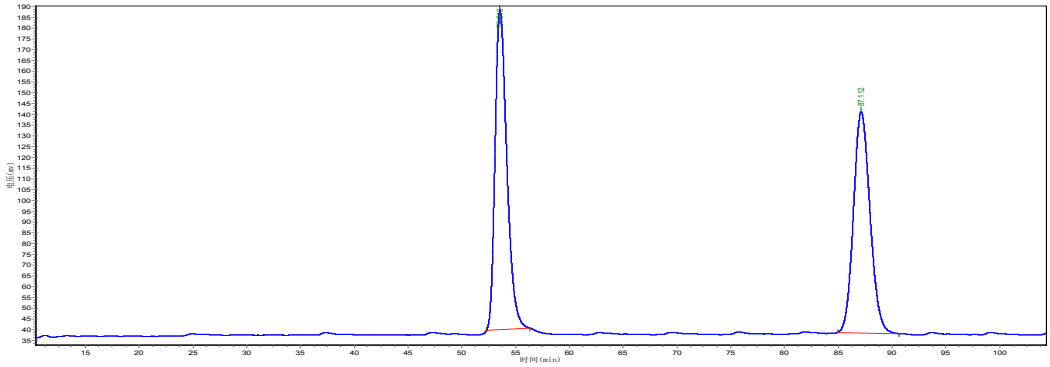
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 31.365 | 45572.168 | 2497960.000 | 4.7241 |
| 2 | 40.822 | 850890.875 | 48434696.000 | 91.5996 |
| 3 | 44.462 | 34233.177 | 1943899.750 | 3.6763 |
| total | | 930696.160 | 52876555.750 | 100.0000 |

90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 31.4 min (minor) and $t_R$ = 40.8 min (major); minor diastereomer: $t_R$ = 44.5 min (major)).

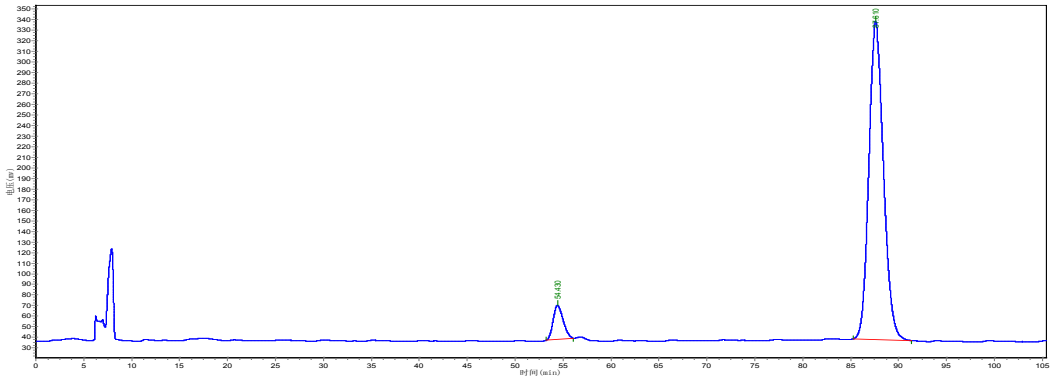



4dk



Result Table

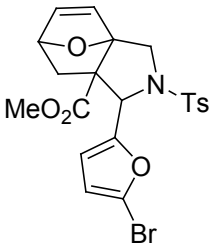
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 53.540 | 148364.063 | 11283139.000 | 50.7498 |
| 2 | 87.112 | 102508.305 | 10949733.000 | 49.2502 |
| total | | 250872.367 | 22232872.000 | 100.000 |



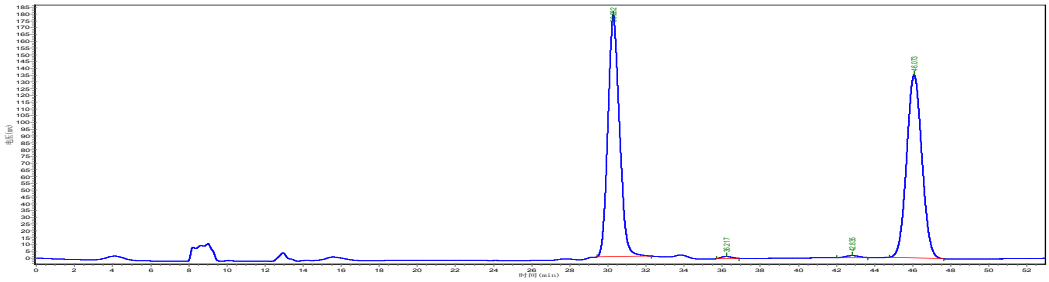
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 54.430 | 32077.158 | 2317846.750 | 6.8096 |
| 2 | 87.610 | 300495.281 | 31720076.000 | 93.1904 |
| total | | 332572.439 | 34037922.750 | 100.0000 |

86 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate: 0.5 ml/min, λ= 210 nm, $t_R$ = 54.4 min (minor) and $t_R$ = 87.6 min (major)).

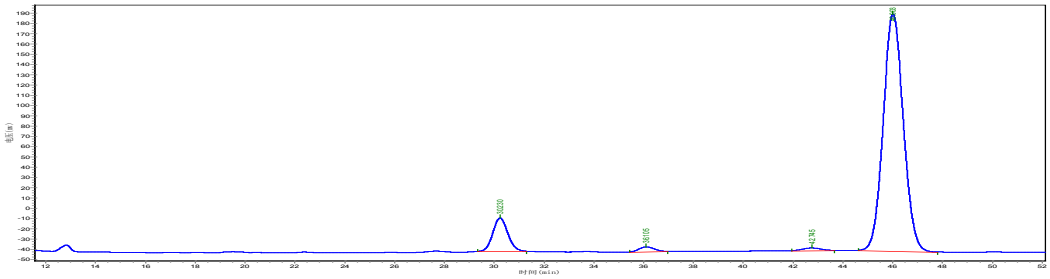



4dl



Result Table

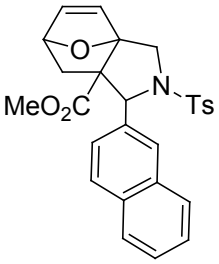
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 30.282 | 178655.906 | 7489916.000 | 49.5436 |
| 2 | 36.217 | 1543.372 | 58134.750 | 0.3845 |
| 3 | 42.835 | 1474.556 | 69844.195 | 0.4620 |
| 4 | 46.073 | 135068.125 | 7499939.500 | 49.6099 |
| total | | 316741.959 | 15117834.445 | 100.0000 |



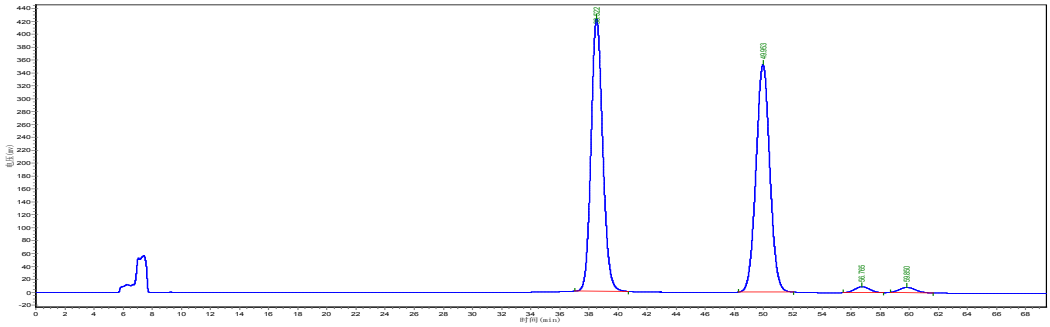
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 30.230 | 32380.061 | 1344509.250 | 9.2305 |
| 2 | 36.105 | 4739.546 | 197958.500 | 1.3590 |
| 3 | 42.745 | 2483.156 | 121434.477 | 0.8337 |
| 4 | 46.003 | 230777.391 | 12902113.000 | 88.5768 |
| total | | 270380.154 | 14566015.227 | 100.0000 |

81 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 30.2 min (minor) and $t_R$ = 46.0 min (major); minor diastereomer: $t_R$ = 36.1 min (major) and $t_R$ = 42.7 min (minor)).

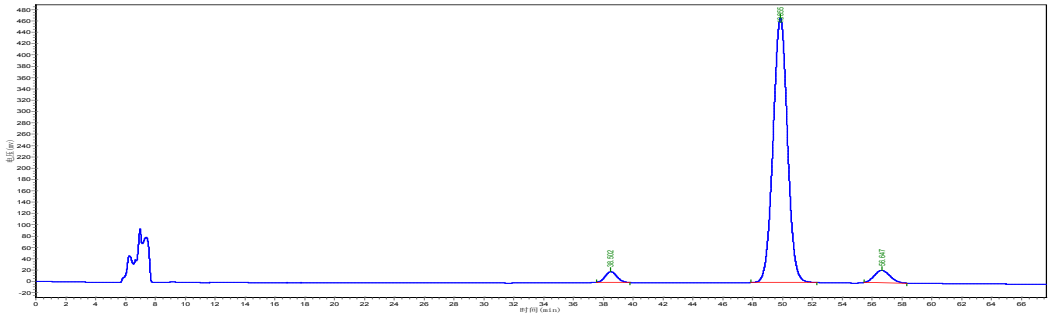



4dm



Result Table

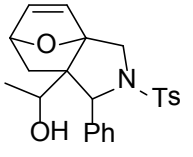
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 38.522 | 422599.250 | 23426912.000 | 48.8033 |
| 2 | 49.953 | 352864.875 | 23305530.000 | 48.5505 |
| 3 | 56.765 | 9136.372 | 659178.250 | 1.3732 |
| 4 | 59.850 | 8024.069 | 611074.188 | 1.2730 |
| total | | 792624.069 | 48002694.438 | 100.0000 |



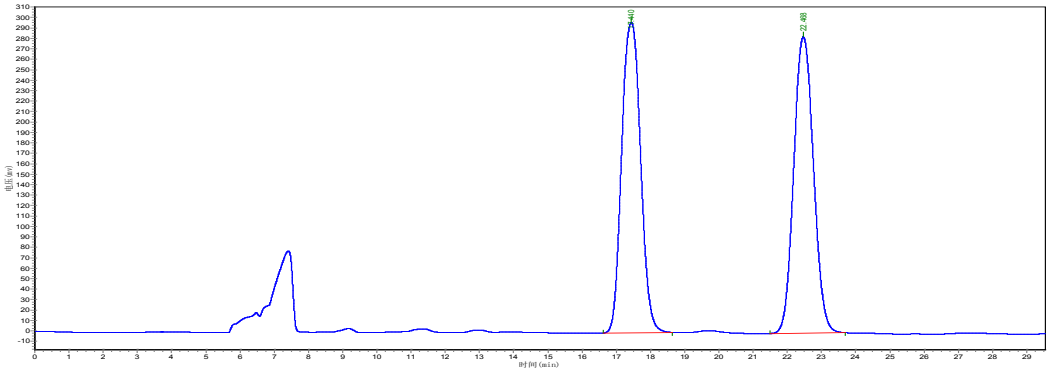
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 38.502 | 18786.201 | 1016015.938 | 3.0096 |
| 2 | 49.855 | 467070.719 | 31172042.000 | 92.3356 |
| 3 | 56.647 | 21705.254 | 1571458.750 | 4.6549 |
| total | | 507562.174 | 33759516.688 | 100.0000 |

94 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 38.5 min (minor) and $t_R$ = 50.0 min (major); minor diastereomer: $t_R$ = 56.6 min (major)).

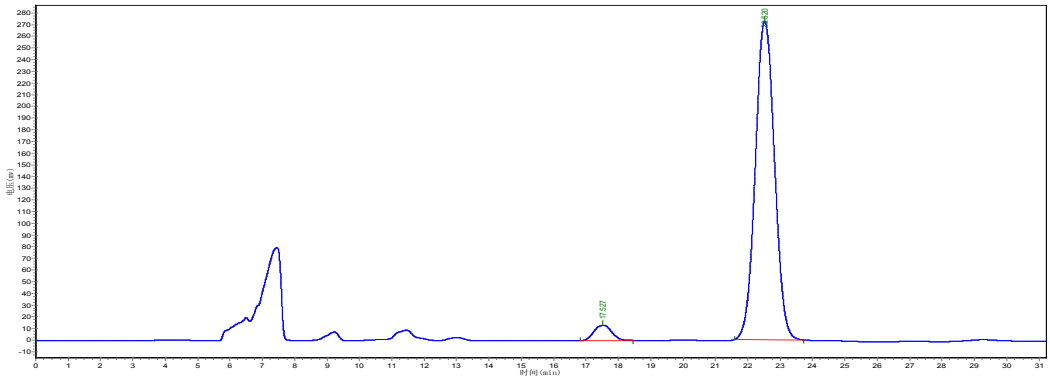



4do‘



Result Table

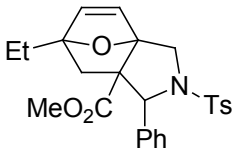
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 17.440 | 297114.000 | 11404918.000 | 50.0760 |
| 2 | 22.468 | 283792.656 | 11370318.000 | 49.9240 |
| total | | 580906.656 | 22775236.000 | 100.0000 |



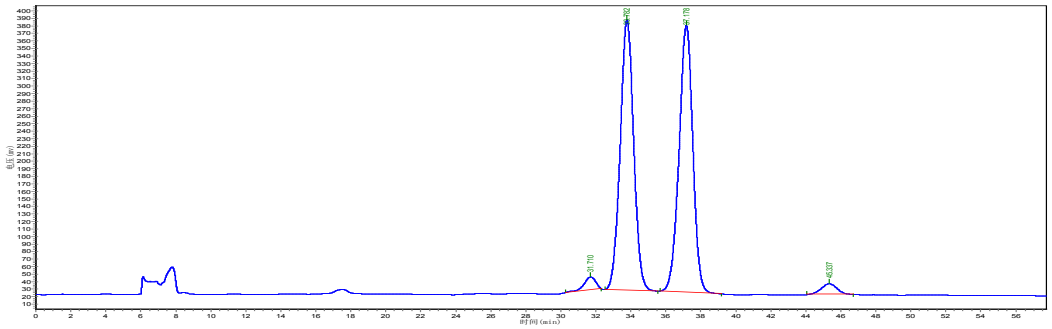
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 17.527 | 13095.306 | 500193.094 | 4.2651 |
| 2 | 22.520 | 272274.219 | 11227432.000 | 95.7349 |
| total | | 285369.524 | 11727625.094 | 100.0000 |

91 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, $t_R$ = 17.5 min (minor) and $t_R$ = 22.5 min (major).

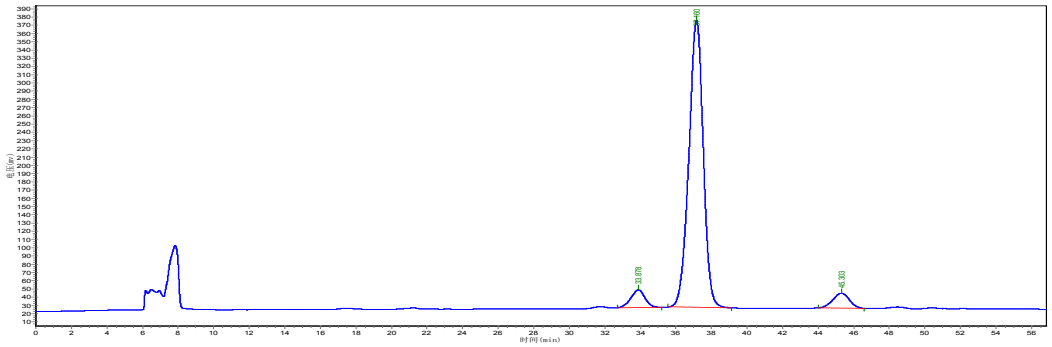



4ha



Result Table

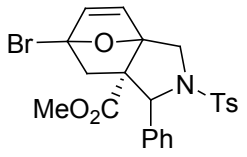
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 31.710 | 17012.391 | 783076.313 | 1.9390 |
| 2 | 33.782 | 359628.750 | 19255998.000 | 47.6802 |
| 3 | 37.178 | 354992.469 | 19433048.000 | 48.1186 |
| 4 | 45.337 | 14255.497 | 913584.625 | 2.2621 |
| total | | 745889.106 | 40385706.938 | 100.0000 |



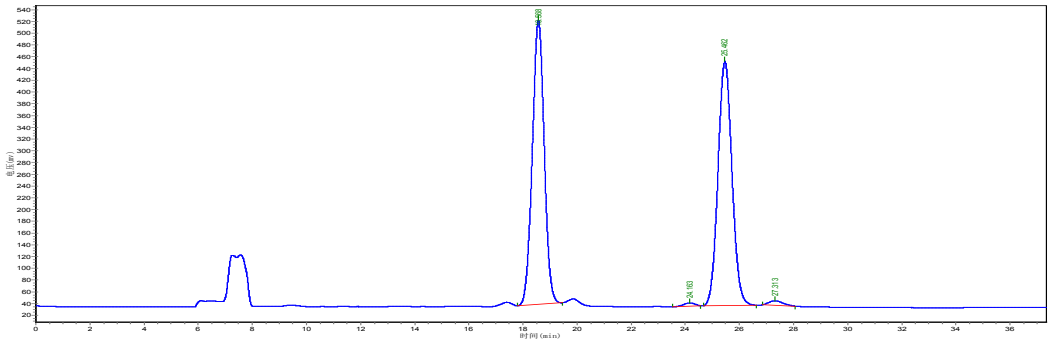
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 33.878 | 21337.295 | 1154179.750 | 5.2665 |
| 2 | 37.160 | 348337.438 | 19600382.000 | 89.4369 |
| 3 | 45.303 | 18176.340 | 1160754.625 | 5.2965 |
| total | | 387851.072 | 21915316.375 | 100.0000 |

89 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 33.9 min (minor) and $t_R$ = 37.2 min (major); minor diastereomer: $t_R$ = 45.3 min (major)).

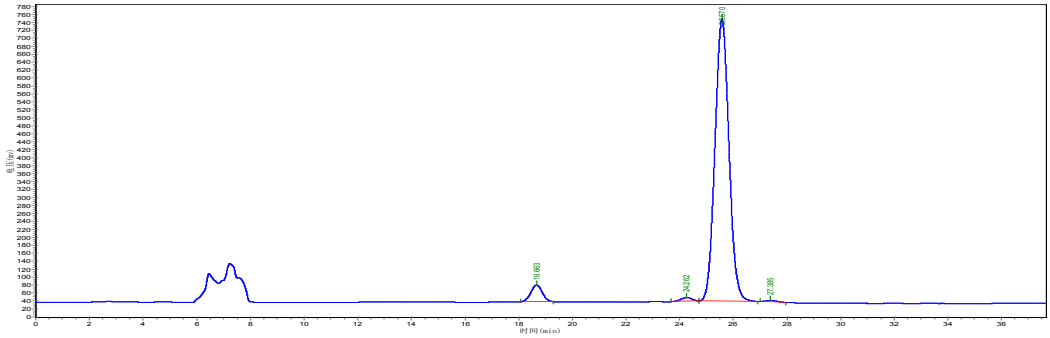



4ia



Result Table

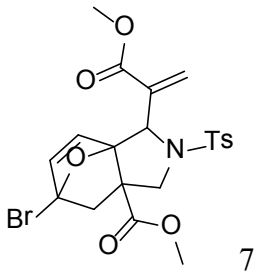
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 18.568 | 483812.250 | 14752231.000 | 49.0348 |
| 2 | 24.163 | 5627.479 | 166542.219 | 0.5536 |
| 3 | 25.462 | 415208.063 | 14897884.000 | 49.5190 |
| 4 | 27.313 | 7560.078 | 268557.563 | 0.8927 |
| total | | 912207.870 | 30085214.781 | 100.0000 |



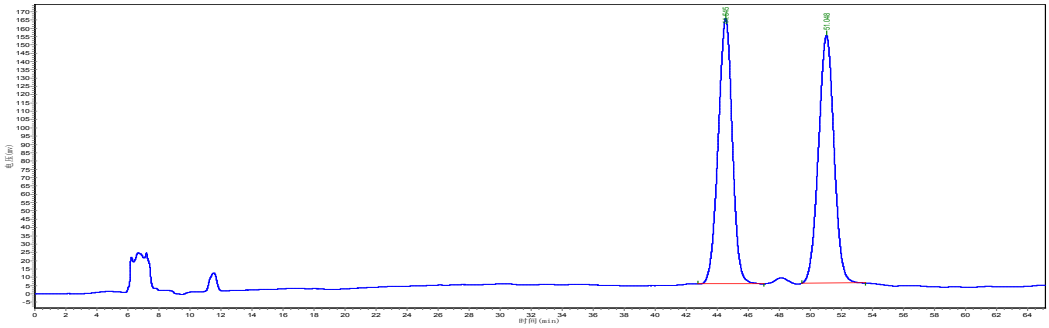
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 18.663 | 41877.977 | 1234057.375 | 4.5217 |
| 2 | 24.262 | 8924.072 | 263707.813 | 0.9662 |
| 3 | 25.570 | 708686.875 | 25689556.000 | 94.1287 |
| 4 | 27.385 | 3427.698 | 104617.617 | 0.3833 |
| total | | 762916.622 | 27291938.805 | 100.0000 |

91 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 18.7 min (minor) and $t_R$ = 25.6 min (major); minor diastereomer: $t_R$ = 24.3 min (major) and $t_R$ = 27.4 min (minor)).

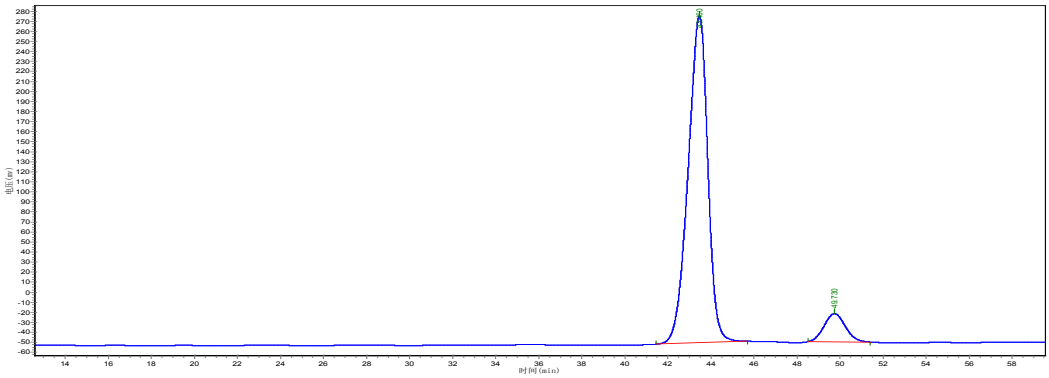



7



Result Table

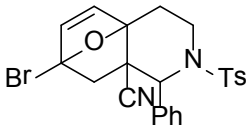
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 44.545 | 159841.859 | 10143288.000 | 49.3813 |
| 2 | 51.048 | 149367.132 | 10397460.000 | 50.6187 |
| total | | 309209.031 | 20540748.000 | 100.0000 |



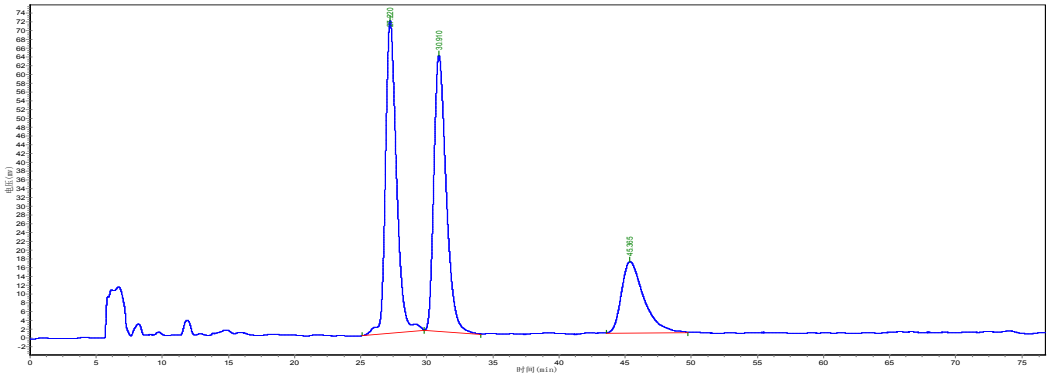
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 43.460 | 325604.250 | 20670614.000 | 91.5229 |
| 2 | 49.730 | 28011.938 | 1914563.125 | 8.4771 |
| total | | 353616.188 | 22585177.125 | 100.0000 |

-83 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 43.5 min (major) and $t_R$ = 49.7 min (minor).

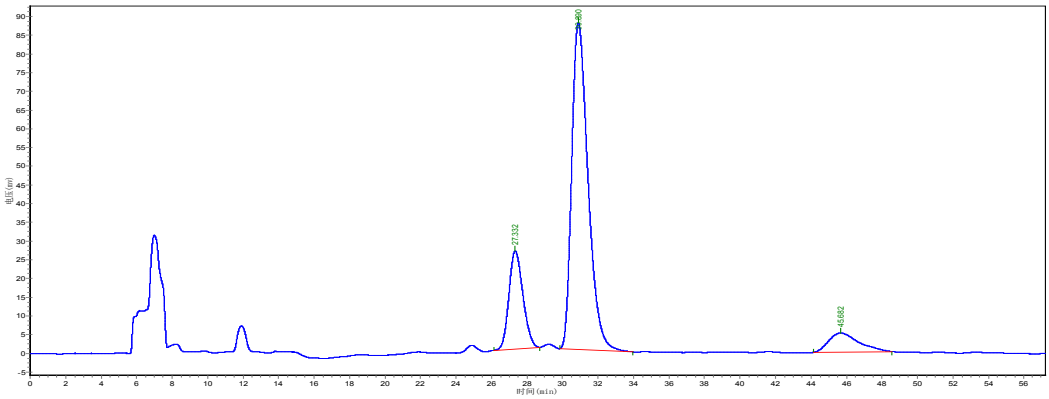



9



Result Table

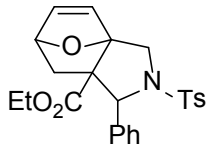
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 27.220 | 71196.828 | 4114852.250 | 41.0202 |
| 2 | 30.910 | 62805.309 | 4028233.750 | 40.1567 |
| 3 | 45.365 | 16216.535 | 1888201.375 | 18.8231 |
| total | | 150218.672 | 10031287.375 | 100.0000 |



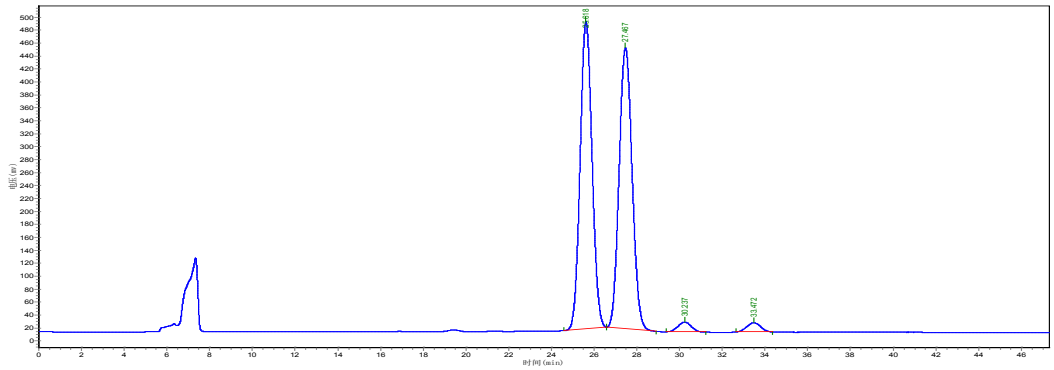
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 27.332 | 26144.596 | 1429539.250 | 18.8184 |
| 2 | 30.890 | 87343.570 | 5568706.000 | 73.3064 |
| 3 | 45.682 | 5067.264 | 598237.188 | 7.8752 |
| total | | 118555.430 | 7596482.438 | 100.0000 |

59 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 27.3 min (minor) and $t_R$ = 30.1 min (major). minor diastereomer: $t_R$ =45.7 min (the peaks of minor diastereomer are overlapped).

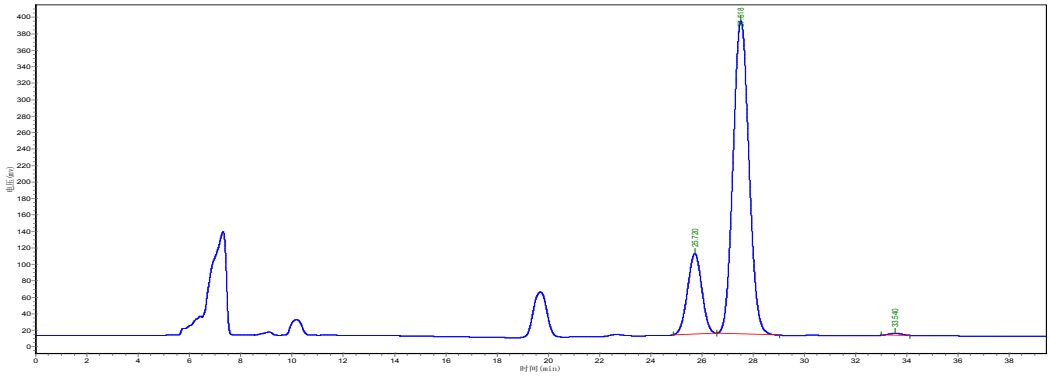



4db



Result Table

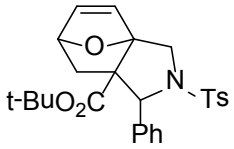
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 25.618 | 474526.219 | 18382238.000 | 48.2814 |
| 2 | 27.467 | 433443.406 | 18378514.000 | 48.2716 |
| 3 | 30.237 | 15385.043 | 663340.500 | 1.7423 |
| 4 | 33.472 | 14424.449 | 649025.688 | 1.7047 |
| total | | 937779.117 | 38073118.188 | 100.0000 |



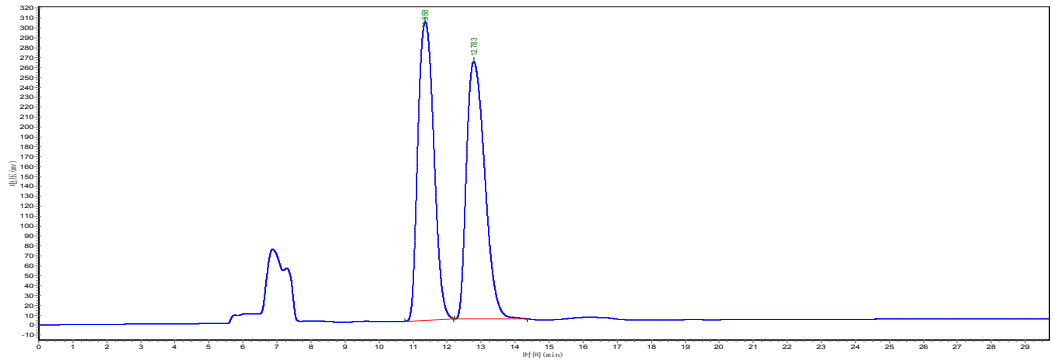
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 25.720 | 97901.484 | 3769689.750 | 18.6831 |
| 2 | 27.518 | 380256.375 | 16317654.000 | 80.8727 |
| 3 | 33.540 | 2395.879 | 89626.766 | 0.4442 |
| total | | 480553.739 | 20176970.516 | 100.0000 |

62 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 25.7 min (minor) and $t_R$ = 27.5 min (major); minor diastereomer: $t_R$ = 33.5 min (major)) .

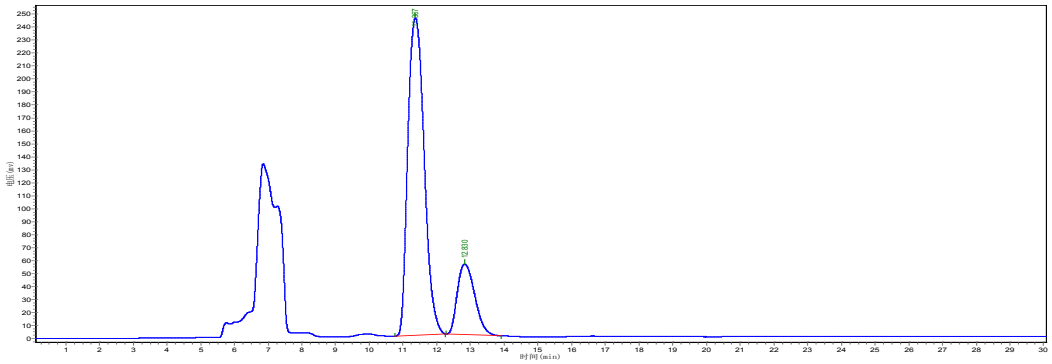



4dc



Result Table

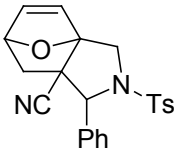
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 11.538 | 301177.906 | 9784586.000 | 50.1941 |
| 2 | 12.783 | 259598.828 | 9708902.000 | 49.8059 |
| total | | 560776.734 | 19493488.000 | 100.0000 |



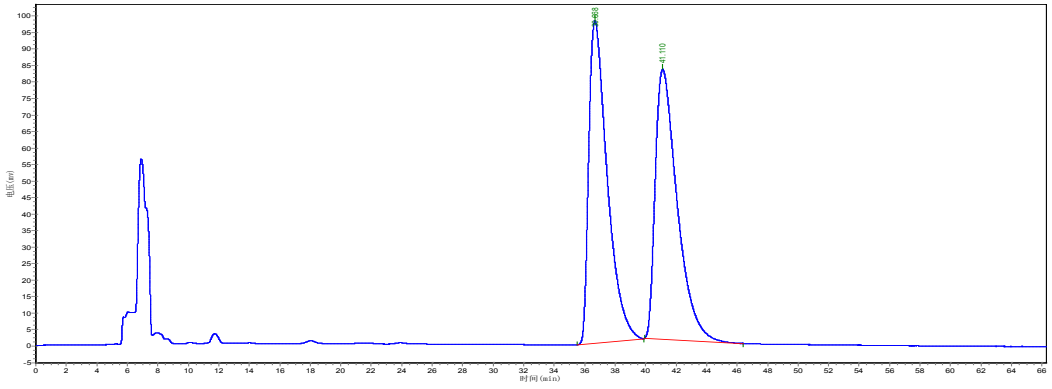
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 11.367 | 244207.453 | 8227607.000 | 80.7897 |
| 2 | 12.830 | 54377.145 | 1956376.000 | 19.2103 |
| total | | 298584.598 | 10183983.000 | 100.0000 |

62 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 11.4 min (major) and $t_R$ = 12.8 min (minor).

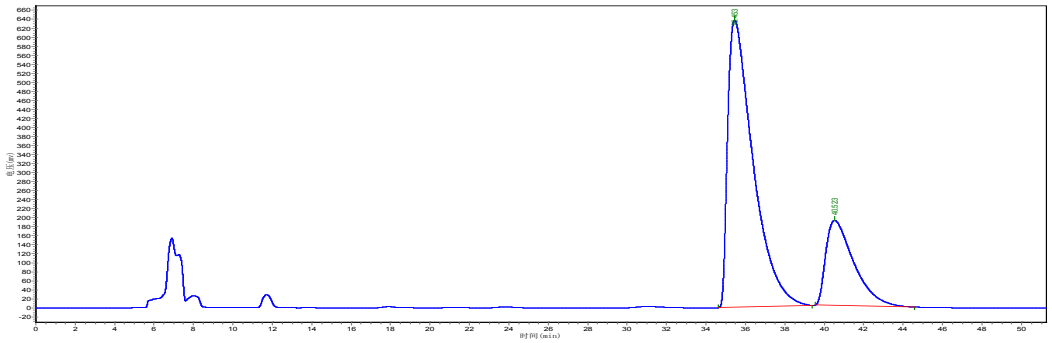



4dd (isomer A)



Result Table

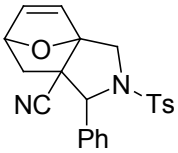
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 36.668 | 97655.555 | 8225971.000 | 50.2043 |
| 2 | 41.110 | 81767.148 | 8159028.000 | 49.7957 |
| total | | 179422.703 | 16384999.000 | 100.0000 |



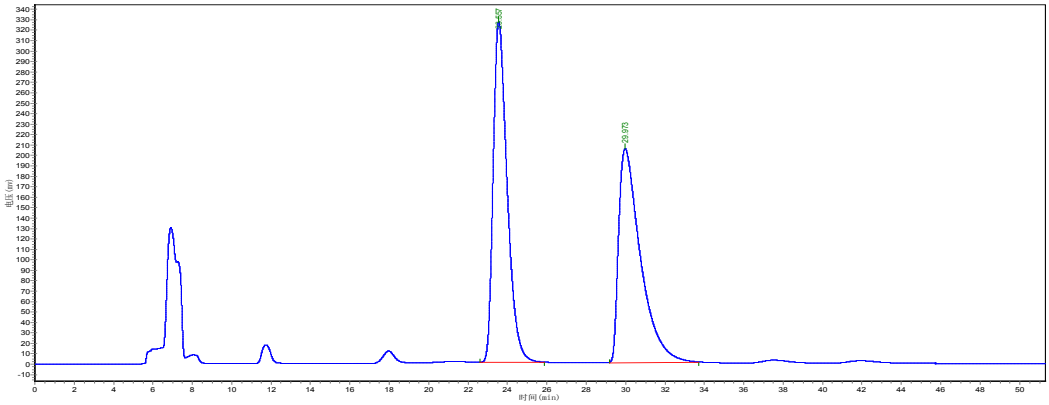
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 35.453 | 636859.875 | 56993408.000 | 75.3692 |
| 2 | 40.523 | 188398.703 | 18625568.000 | 24.6308 |
| total | | 825258.578 | 75618976.000 | 100.0000 |

51 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 35.5 min (major) and $t_R$ = 40.5 min (minor)).

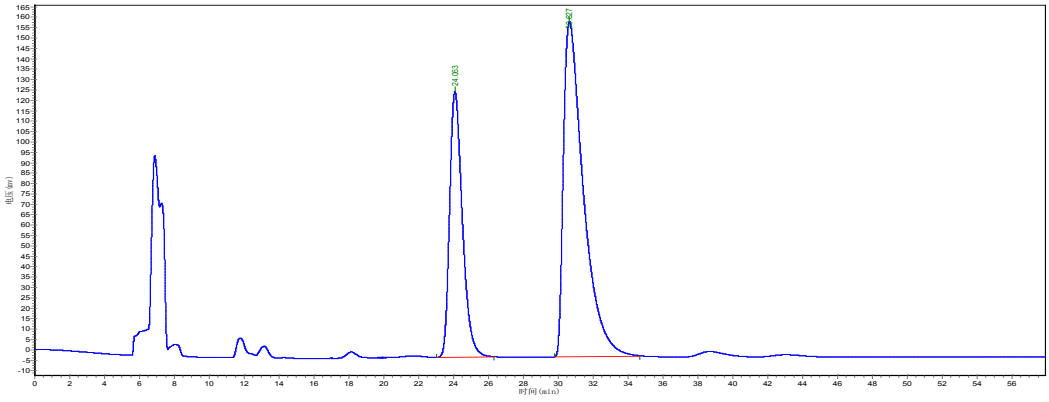



4dd (isomer B)



Result Table

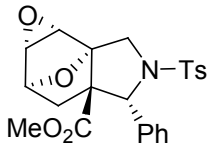
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 23.557 | 326284.188 | 16041656.000 | 50.5284 |
| 2 | 29.973 | 204694.266 | 15706119.000 | 49.4716 |
| toal | | 530978.453 | 31747775.000 | 100.0000 |



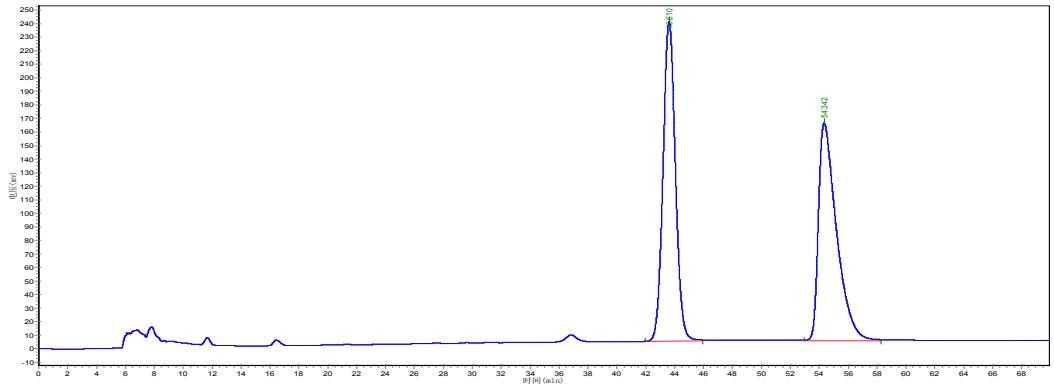
Result Table

| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 24.063 | 127796.508 | 6464587.000 | 33.6380 |
| 2 | 30.627 | 161091.859 | 12753523.000 | 66.3620 |
| total | | 288888.367 | 19218110.000 | 100.0000 |

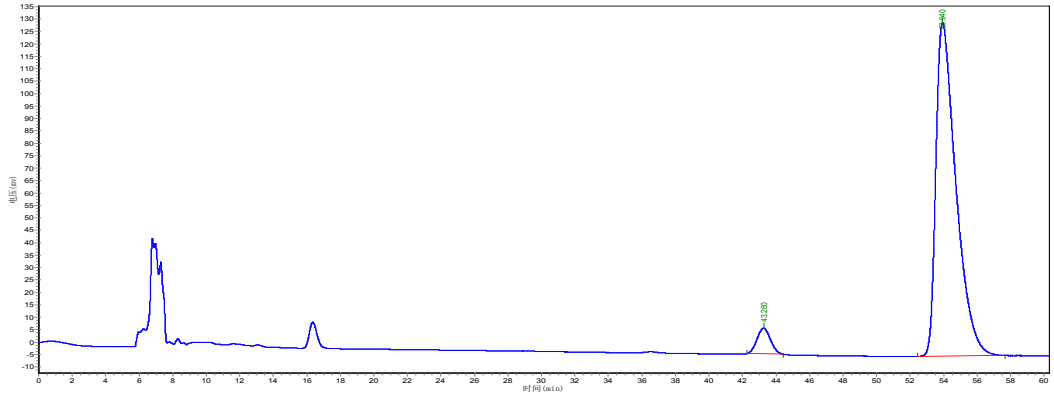
33 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 80/20, flow rate: 0.5 ml/min, λ= 210 nm, major diastereomer: $t_R$ = 24.0 min (minor) and $t_R$ = 30.6 min (major)).




10



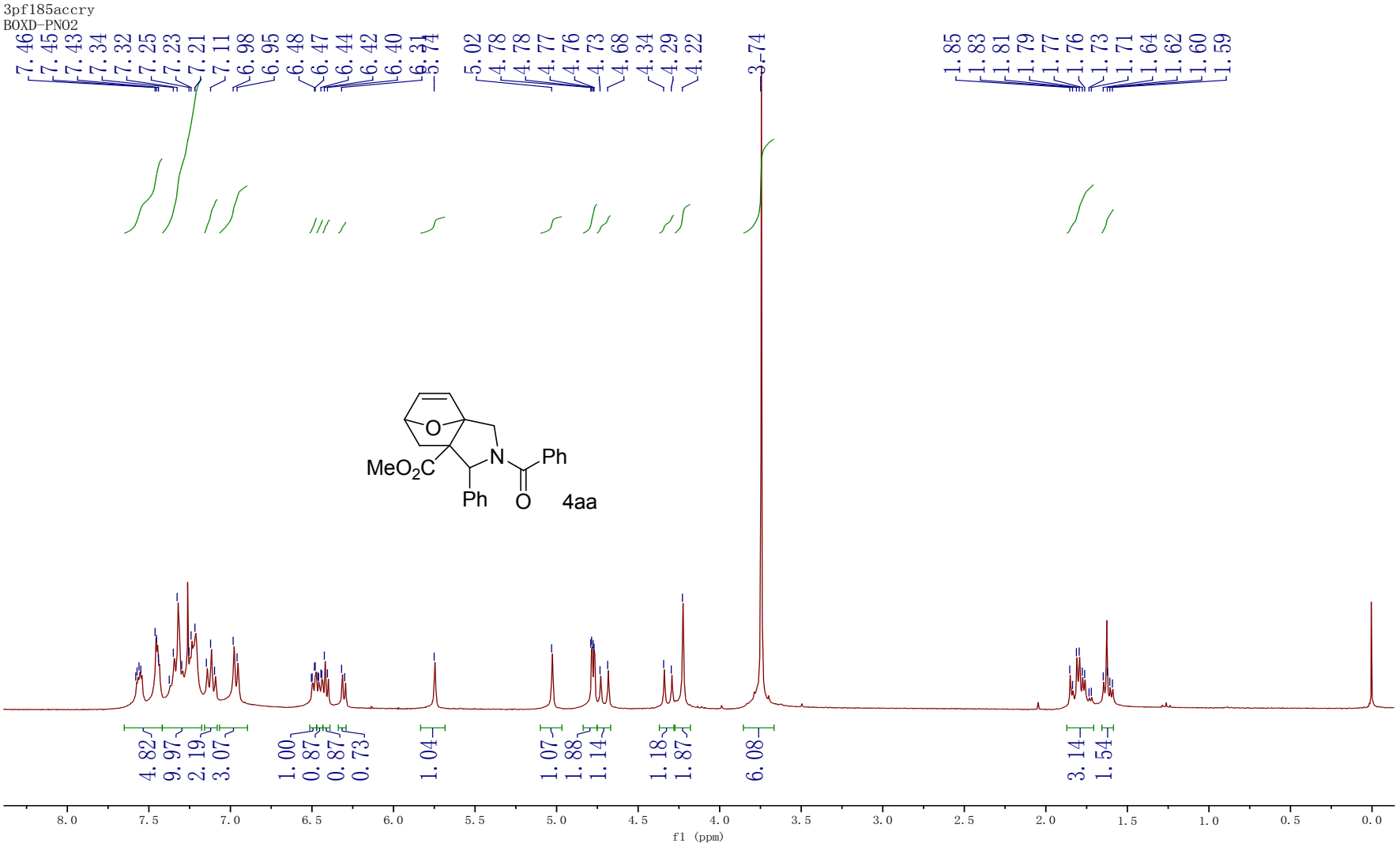
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 43.610 | 235477.750 | 13945985.000 | 50.3629 |
| 2 | 54.342 | 160254.109 | 13744978.000 | 49.6371 |
| total | | 395731.859 | 27690963.000 | 100.0000 |



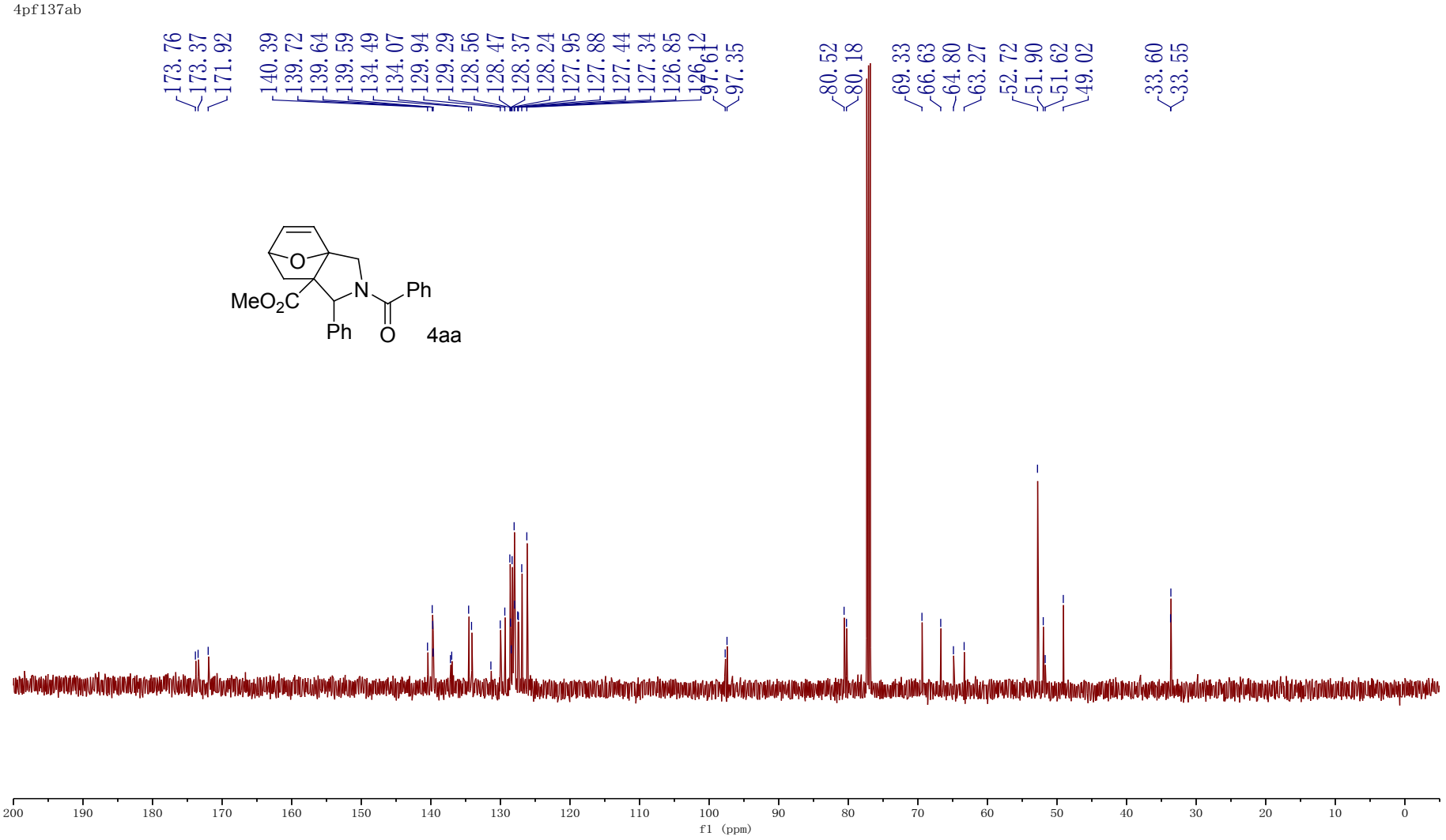
| Peak# | Ret. Time/min | Height/μV | Area/μV·s | Area% |
|---|---|---|---|---|
| 1 | 43.260 | 10379.087 | 581593.125 | 4.9692 |
| 2 | 53.940 | 134120.984 | 11122454.000 | 95.0308 |
| total | | 144500.071 | 11704047.125 | 100.0000 |

90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 70/30, flow rate 0.5 ml/min, λ= 210 nm, $t_R$ = 43.3 min (minor) and $t_R$ = 53.9 min (major).

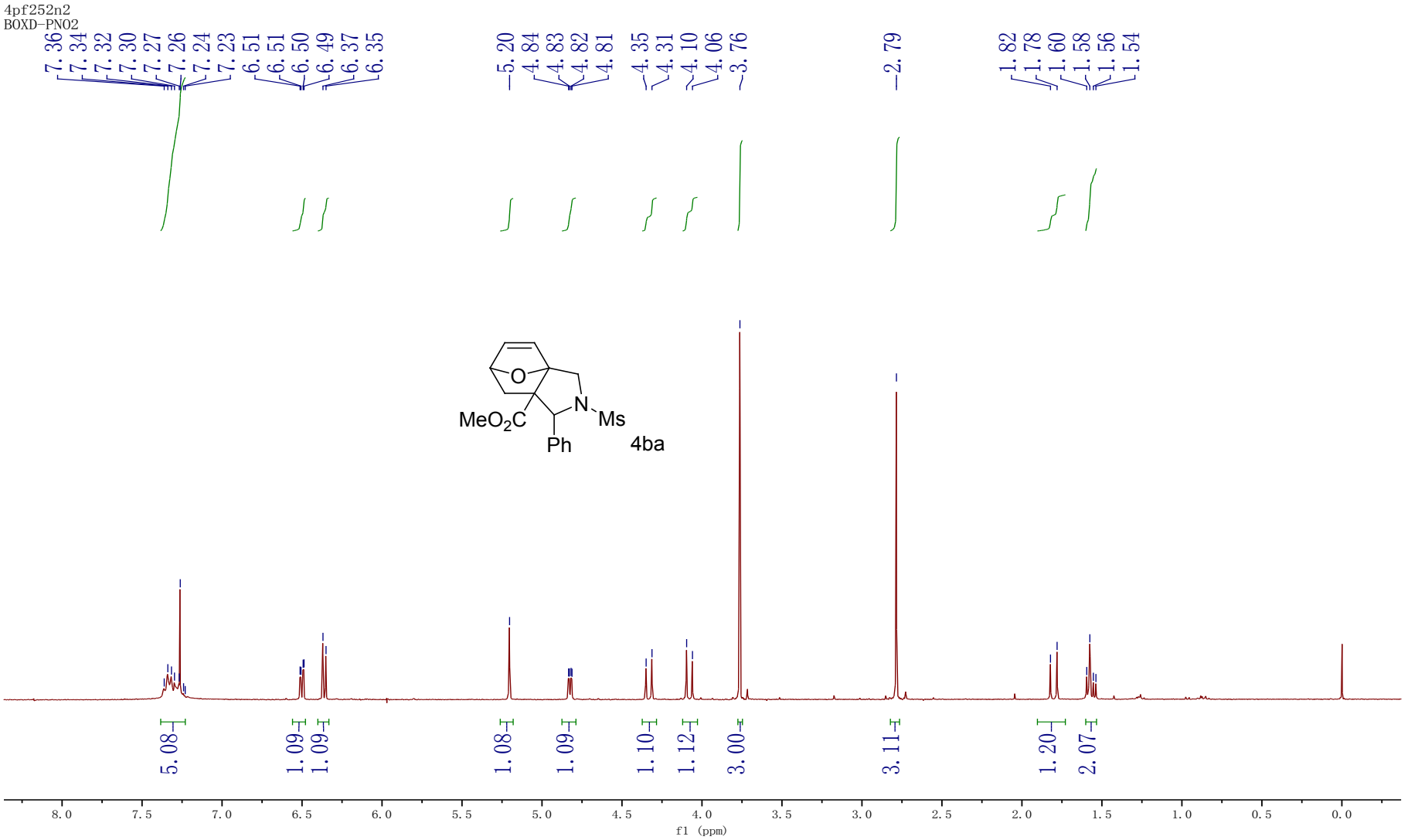
**Spectra of NMR:**



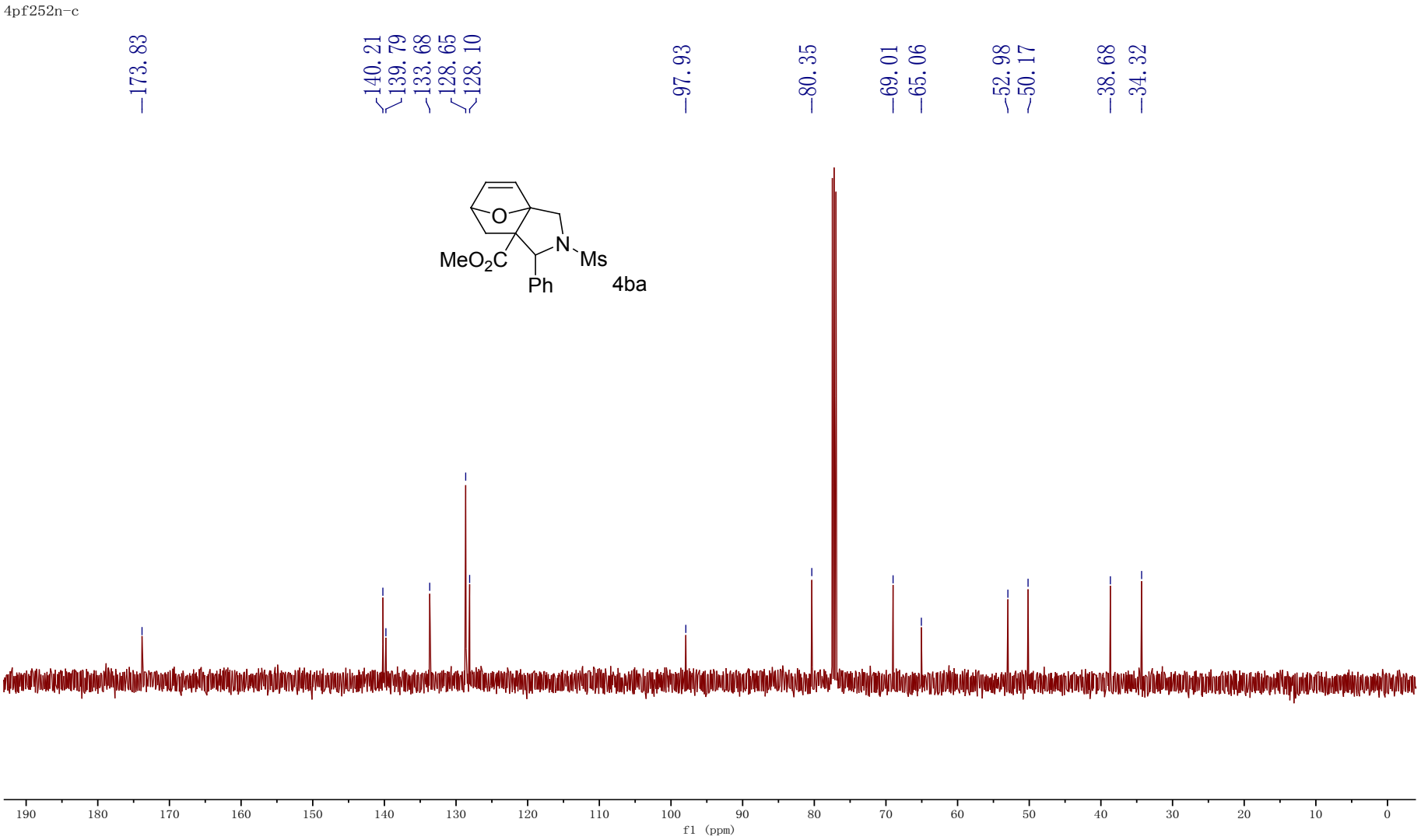

Spectra-42



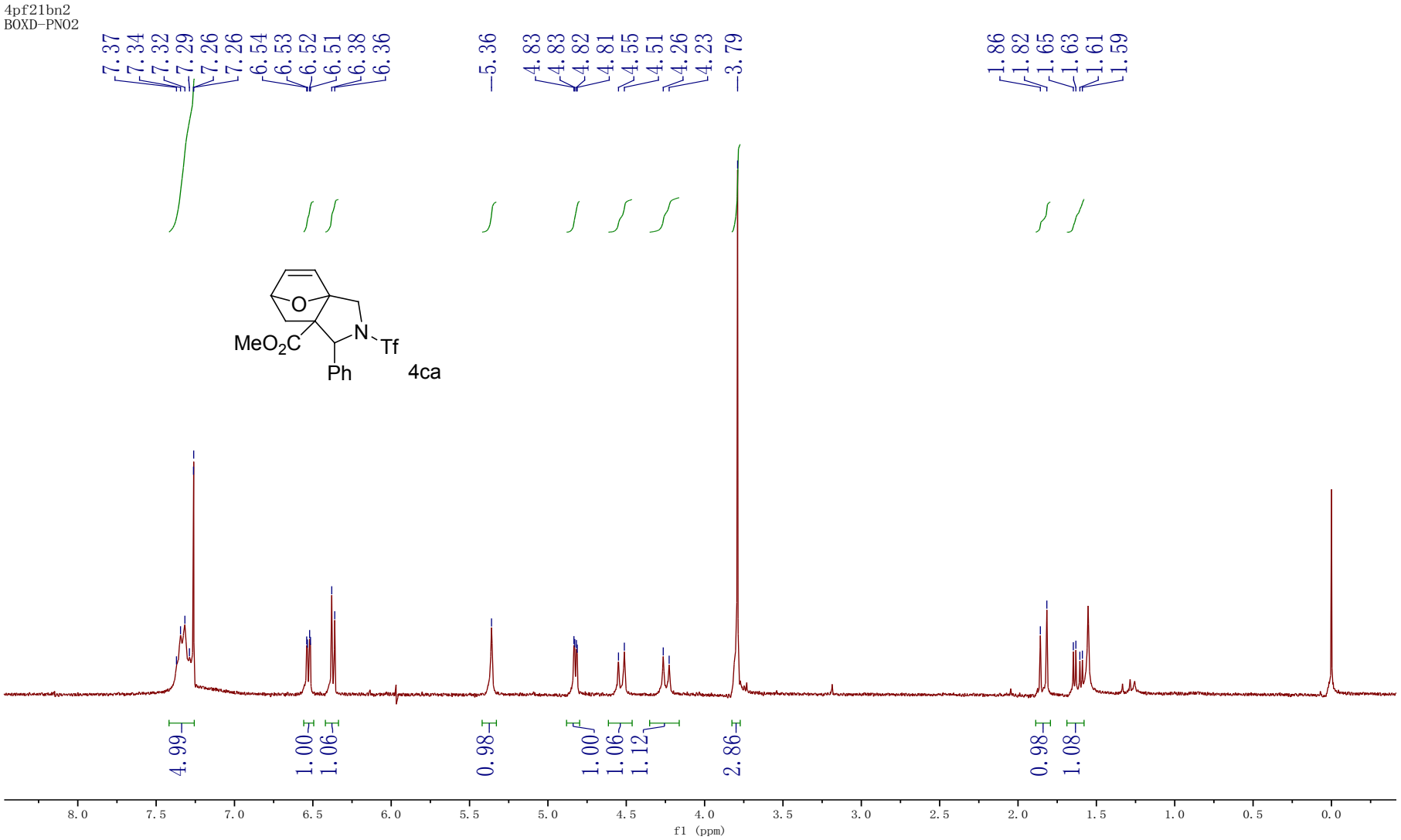

Spectra-43



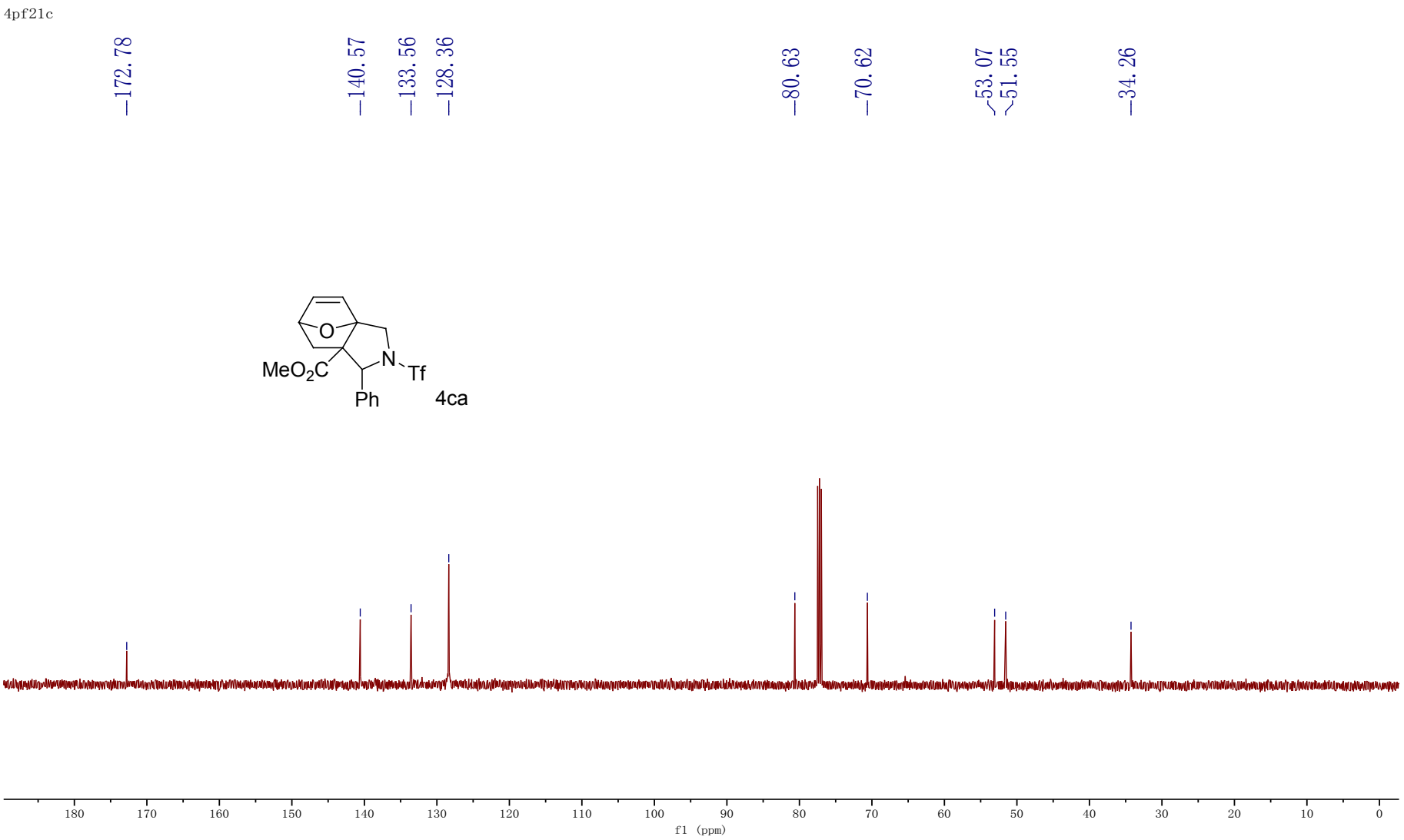

Spectra-44



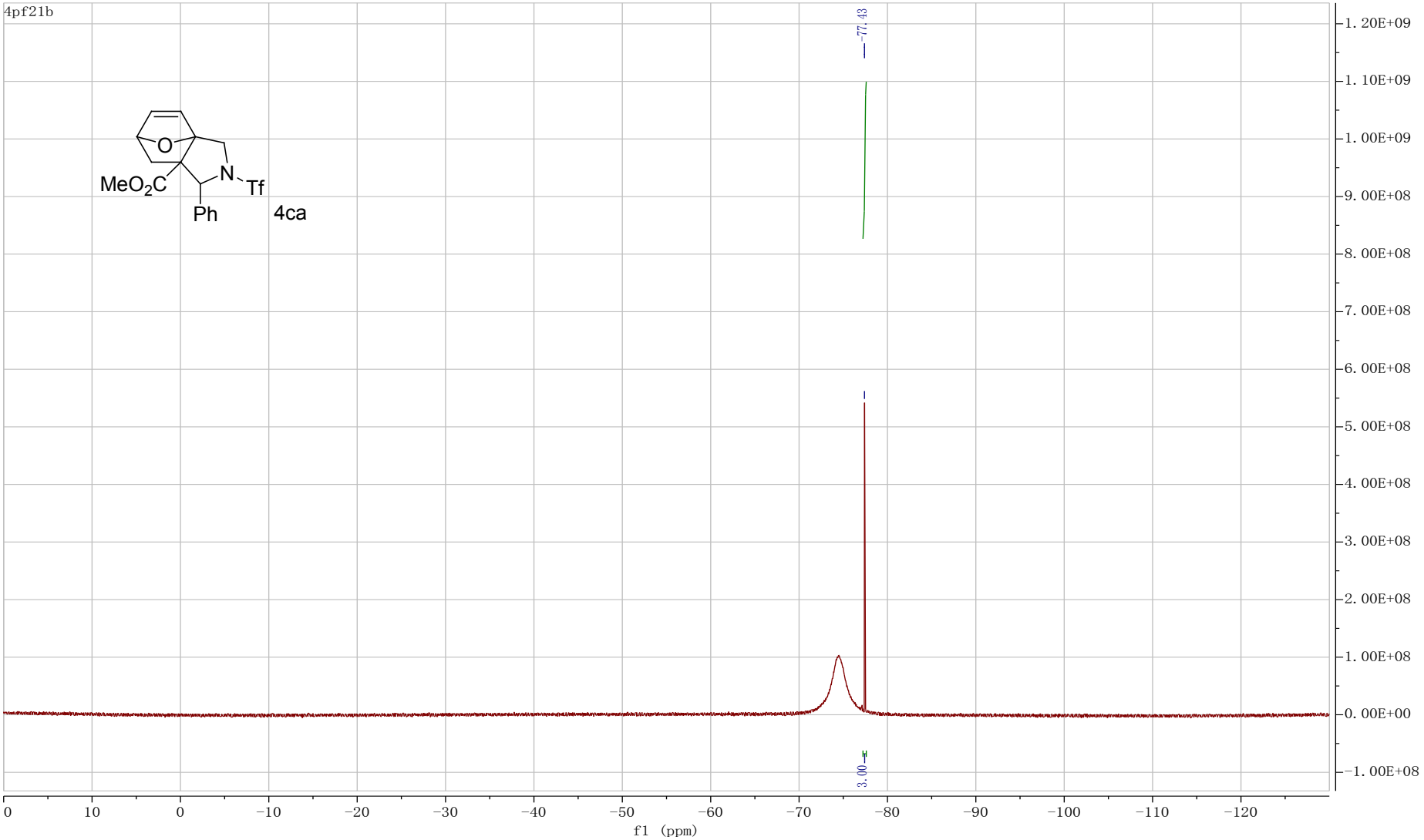

Spectra-45



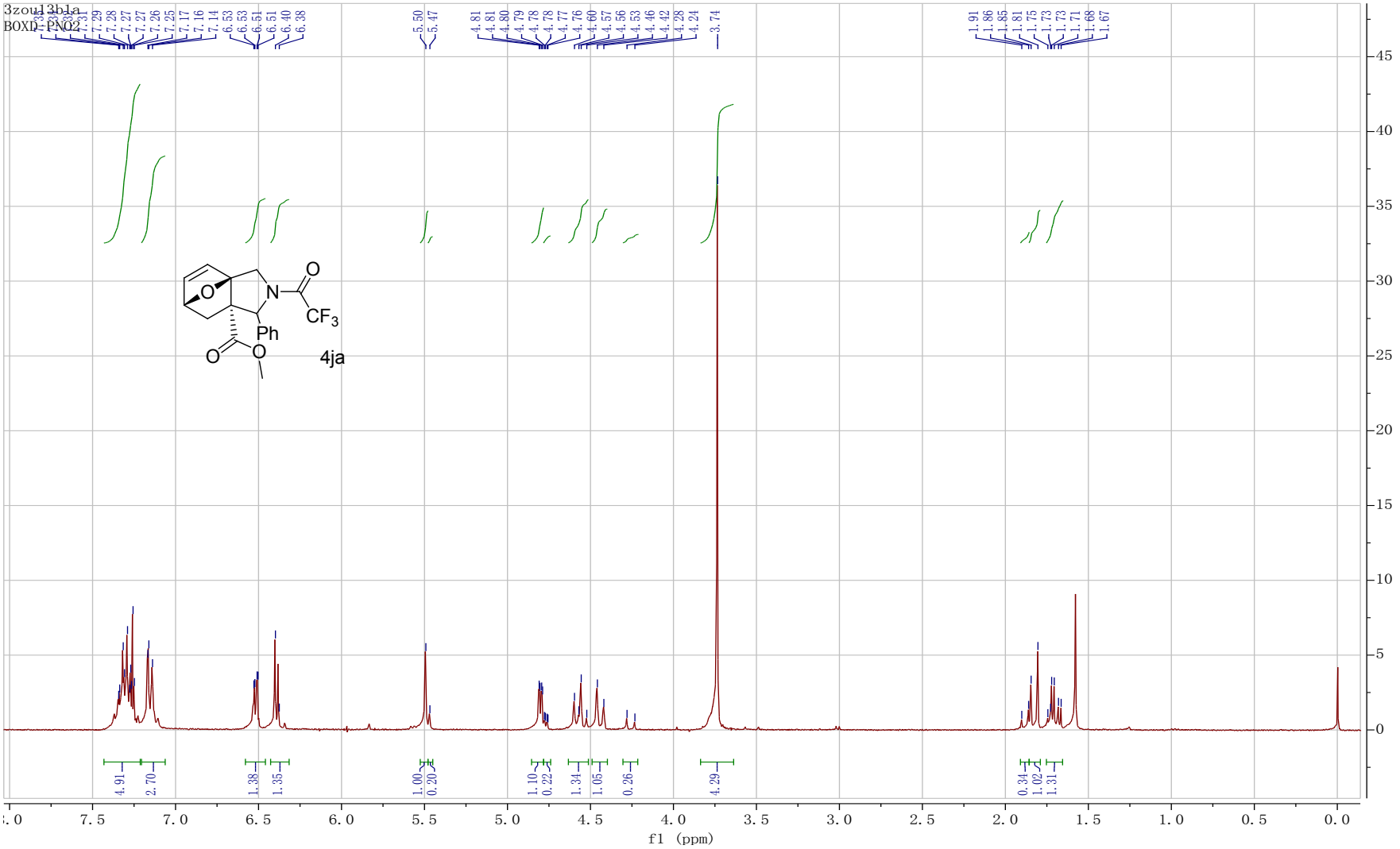

Spectra-46



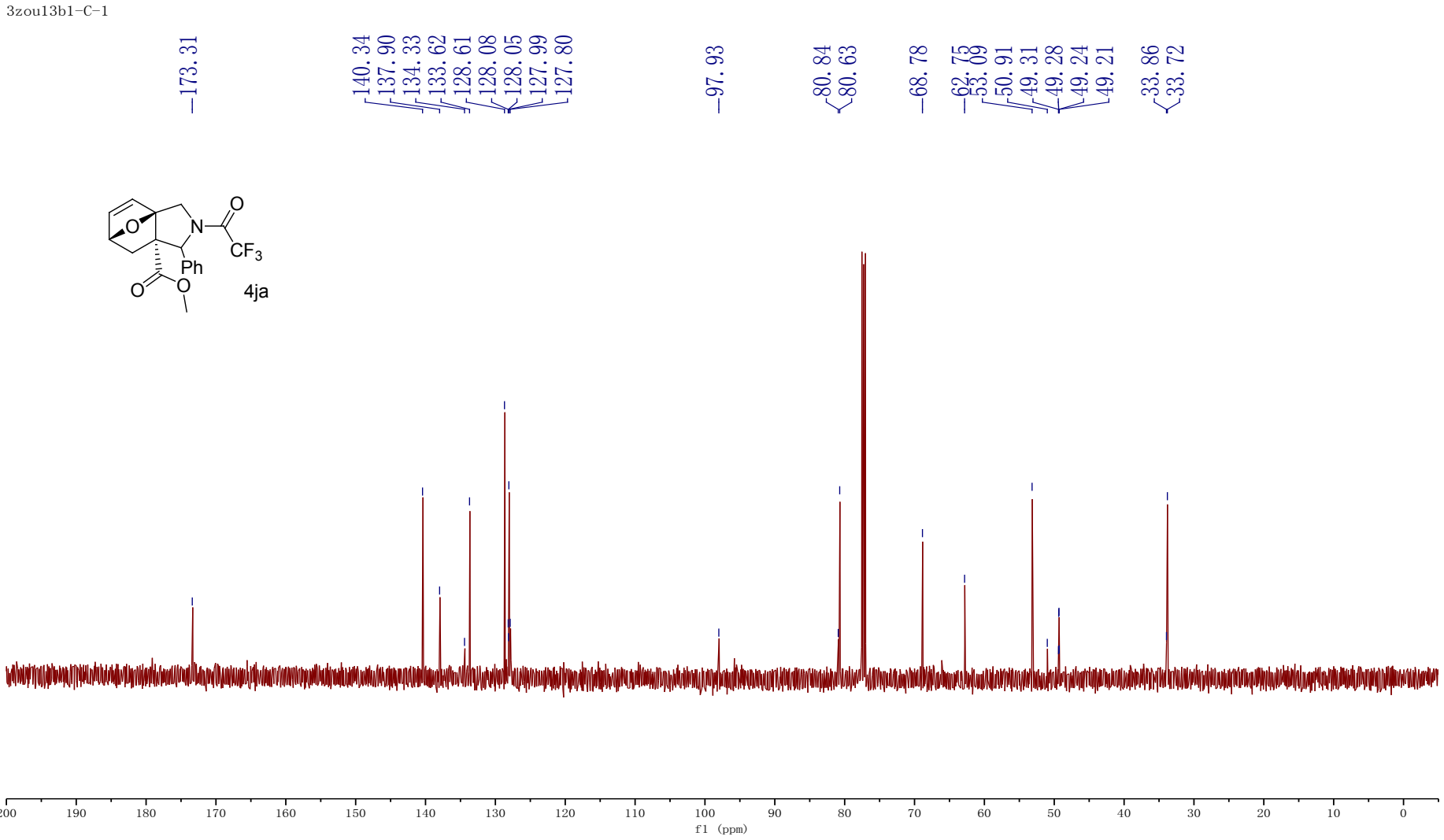

Spectra-47



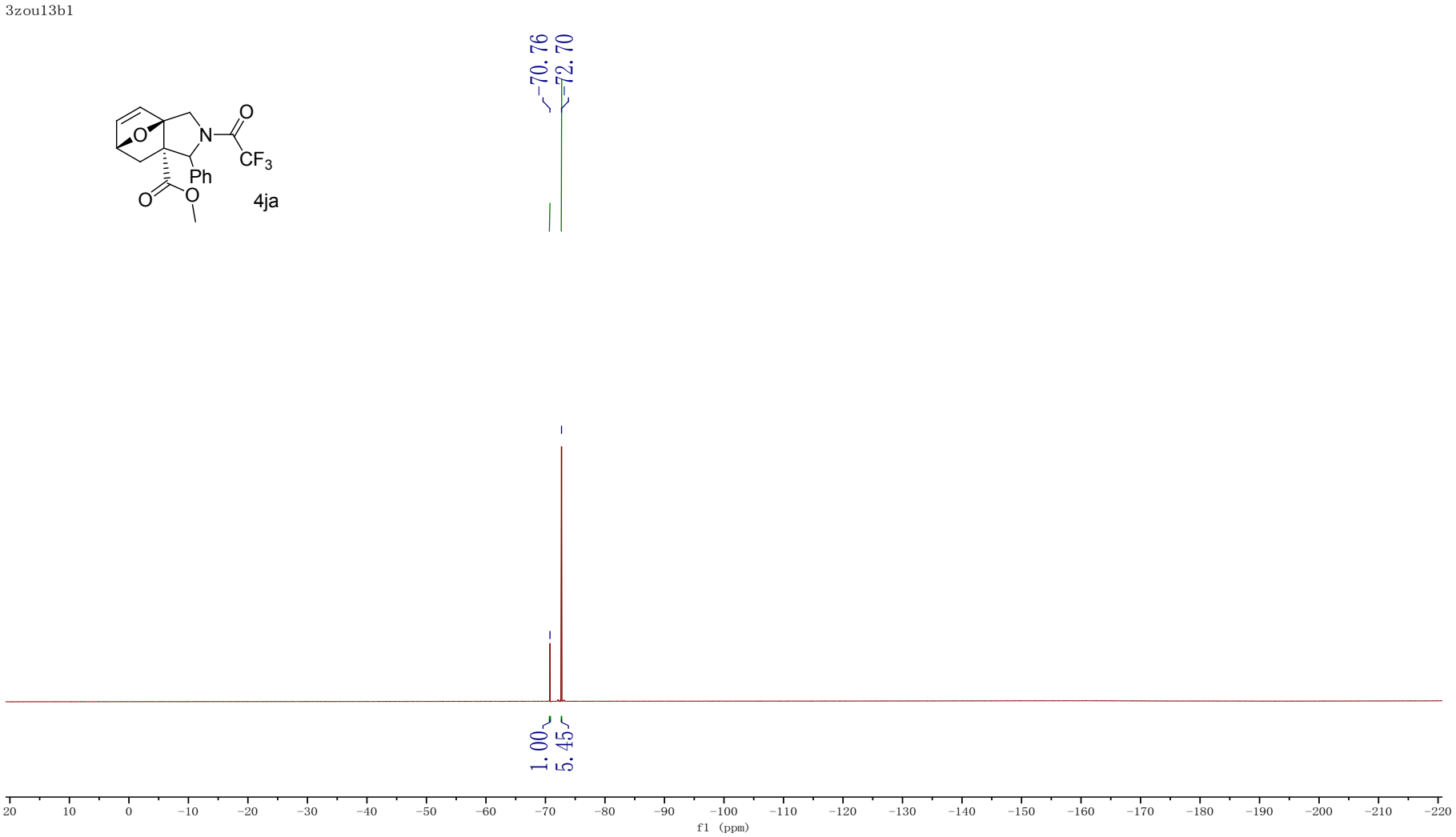

Spectra-48

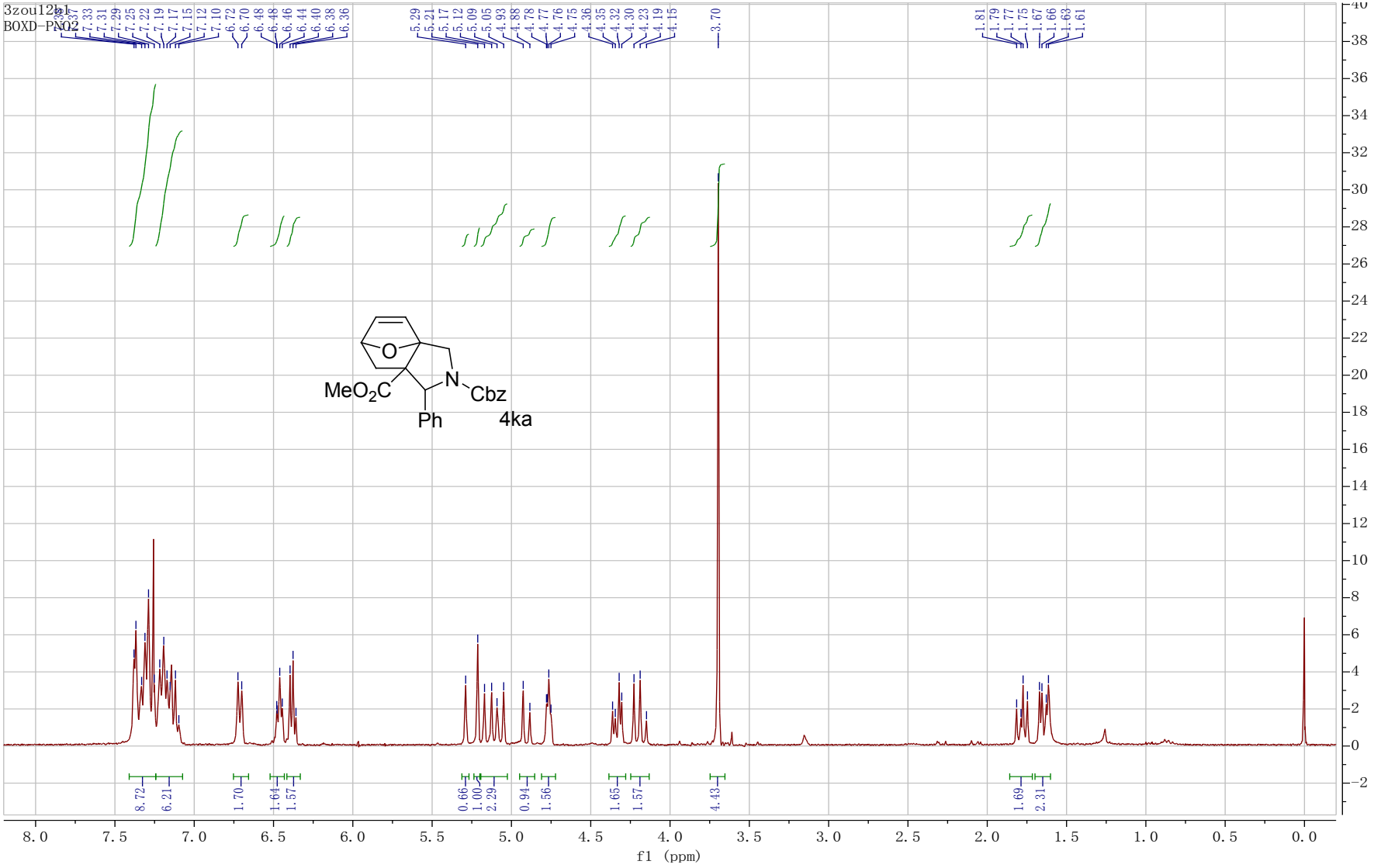



Spectra-49

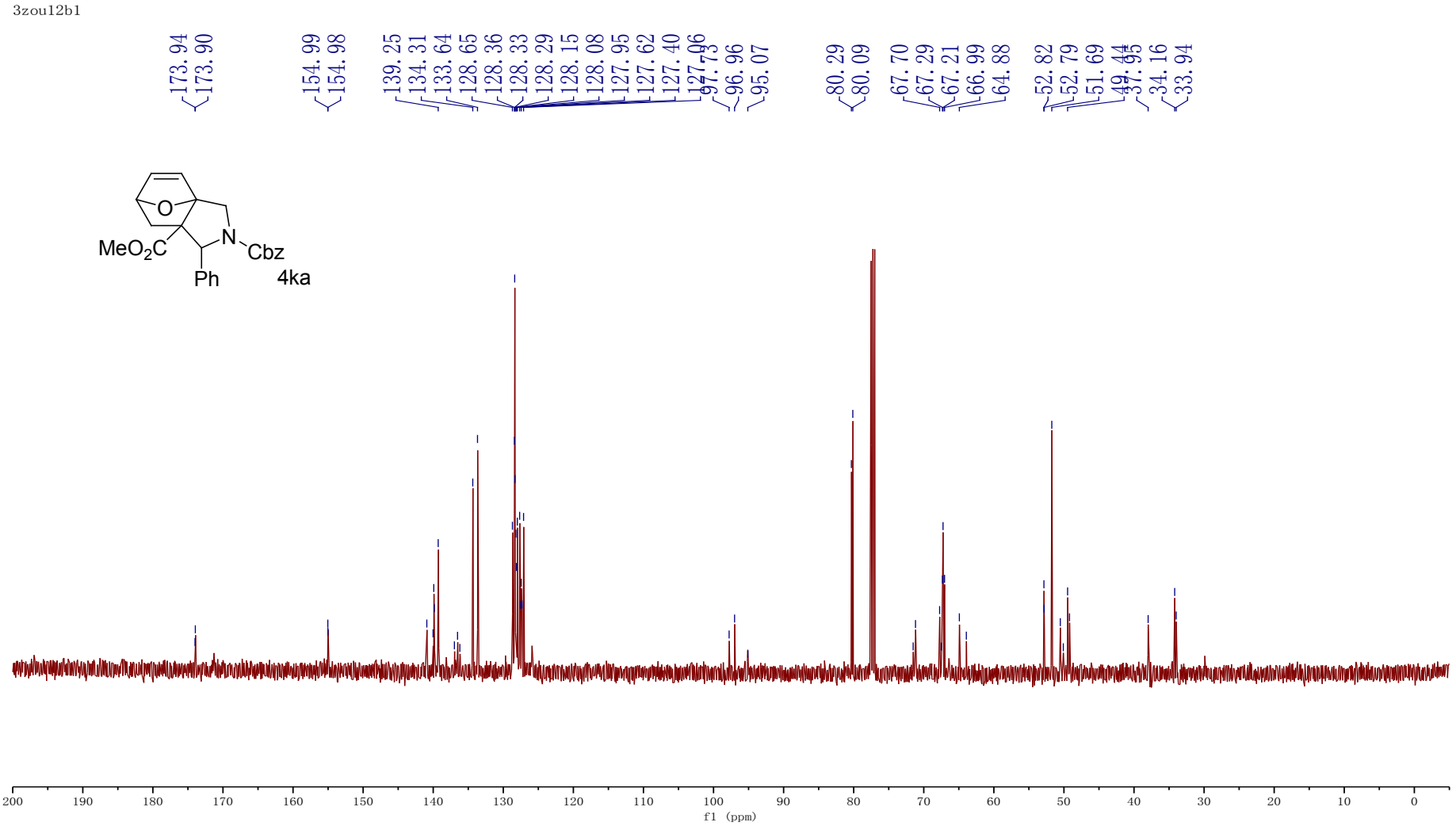



Spectra-50

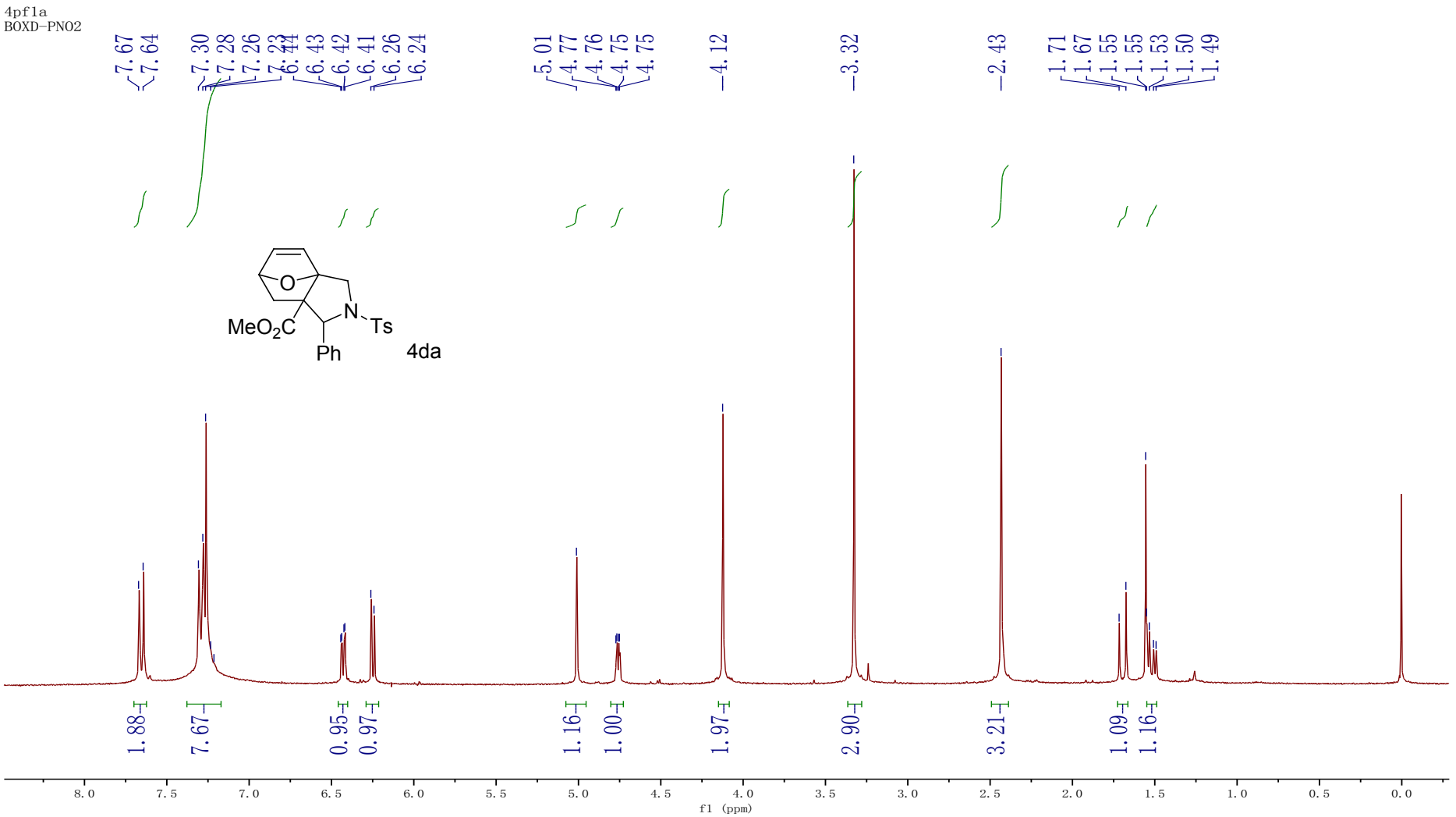




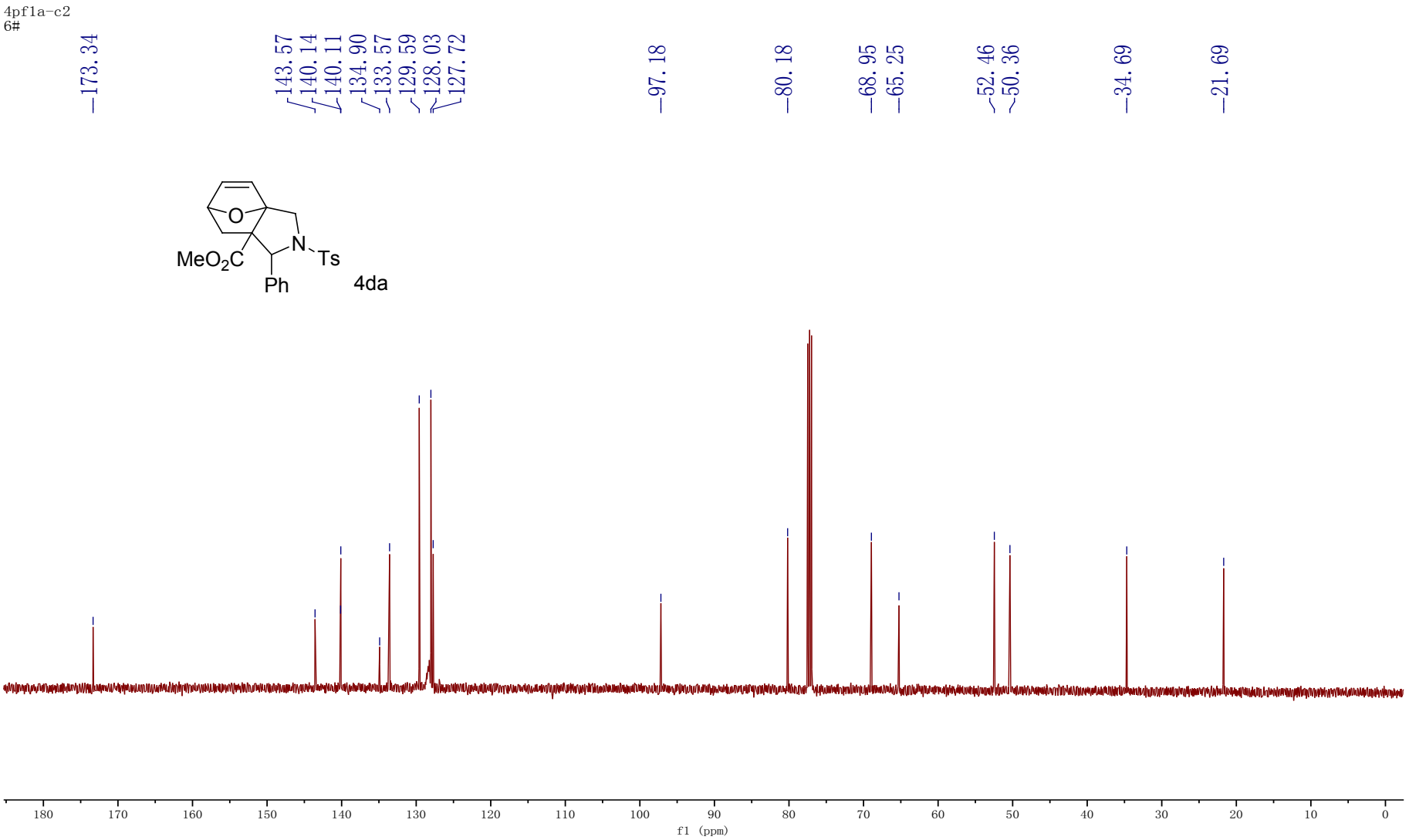

Spectra-52



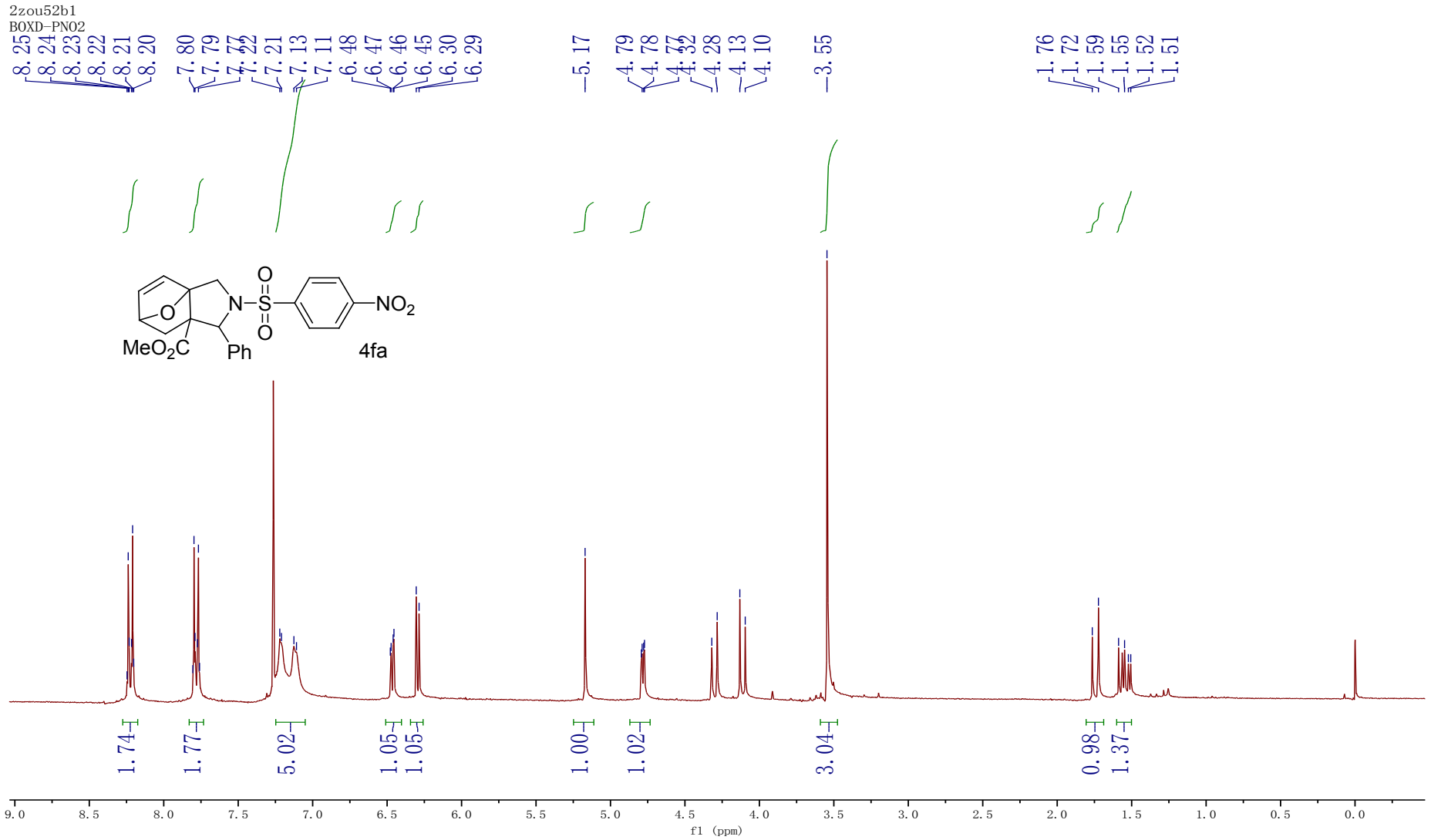

Spectra-53



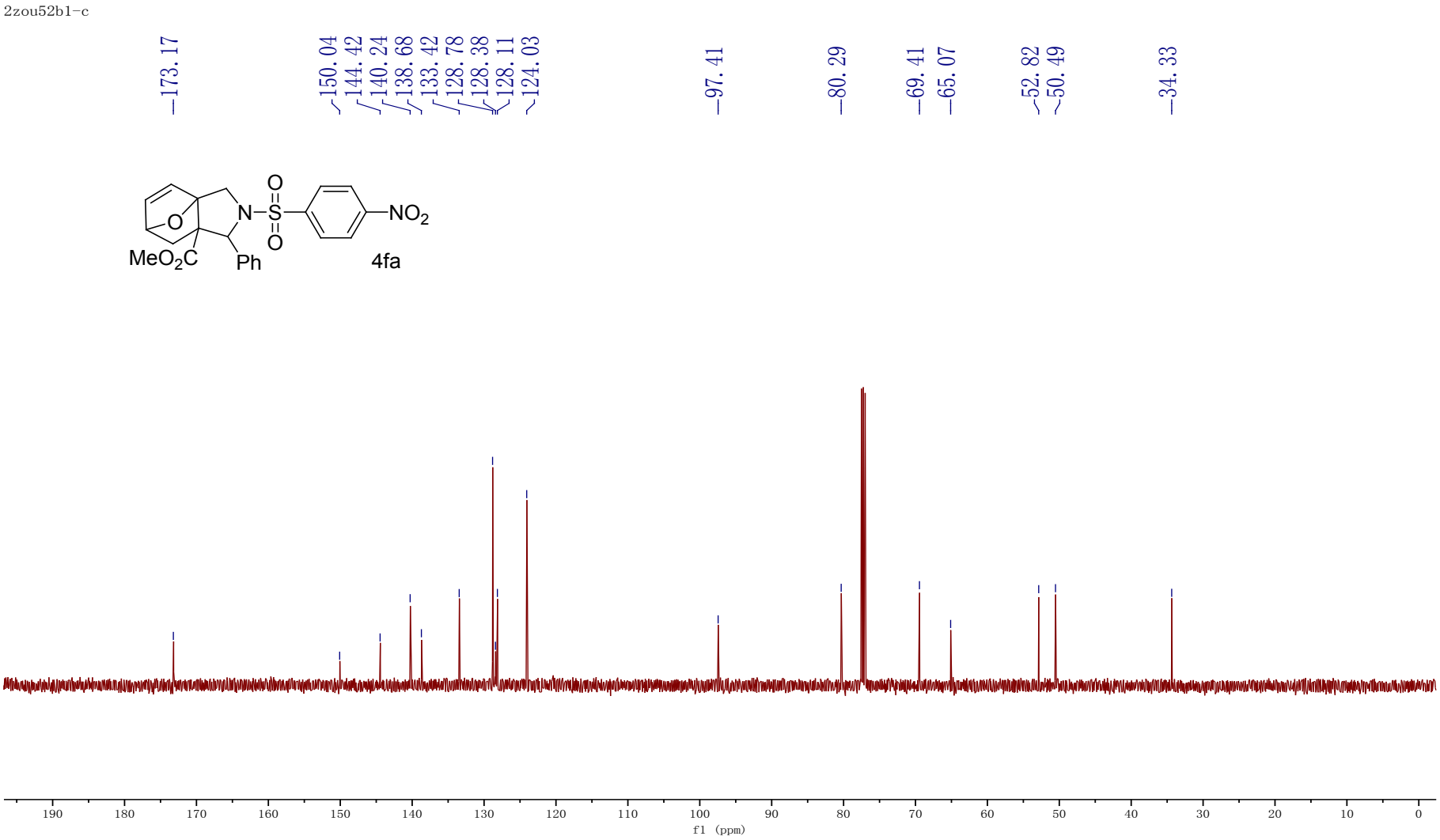

Spectra-54



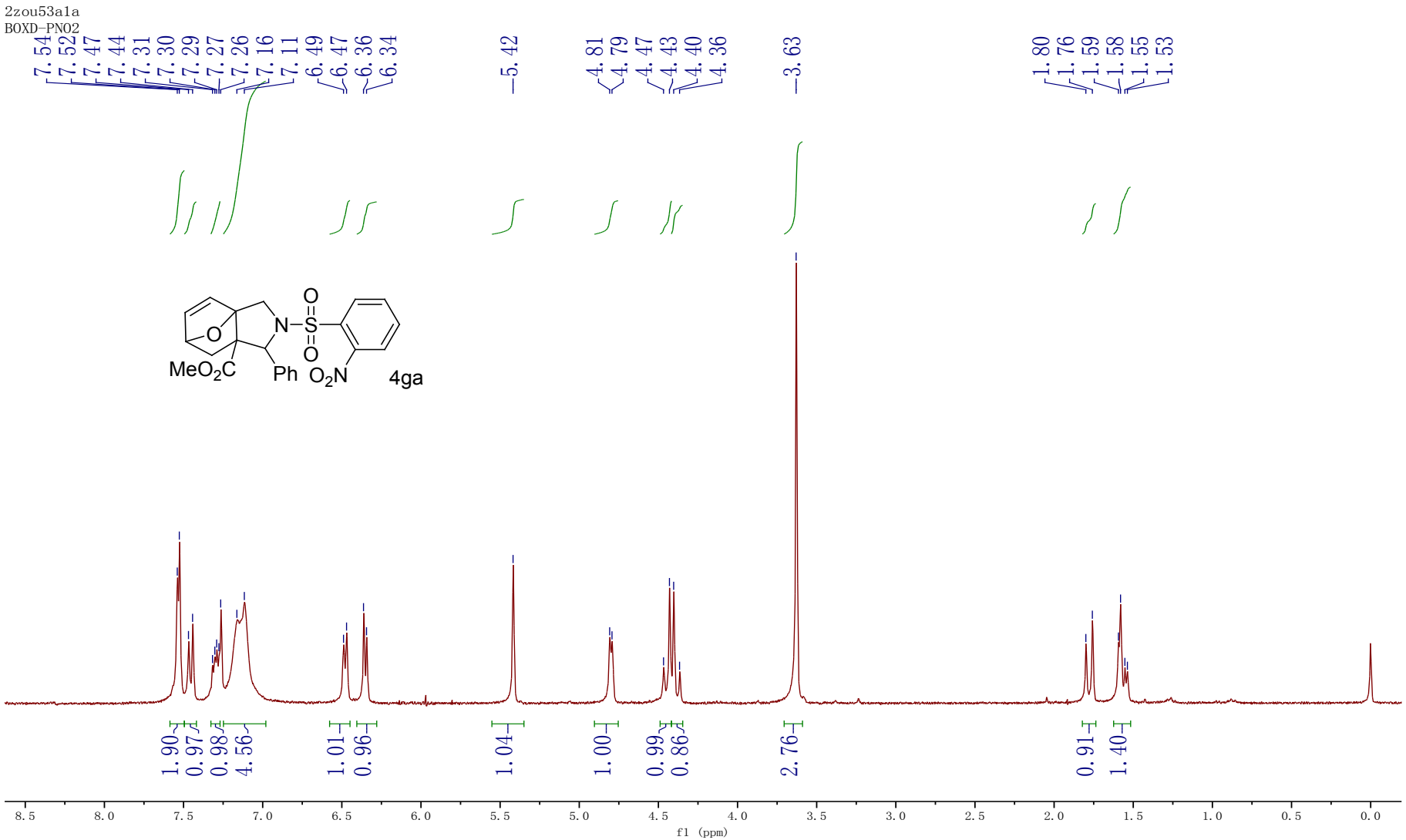

Spectra-55




Spectra-56

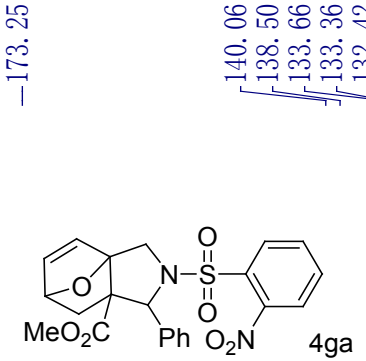


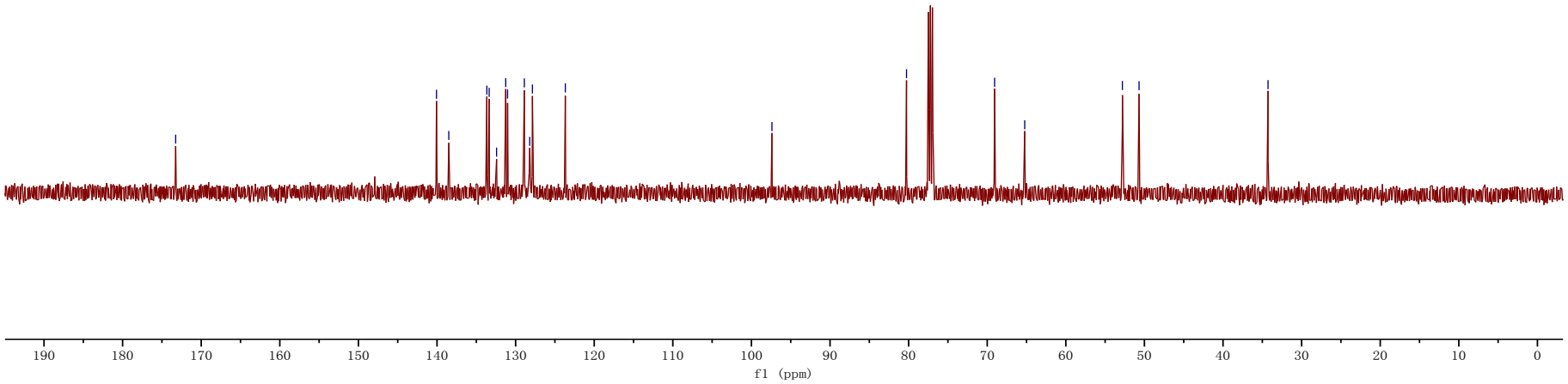

Spectra-57



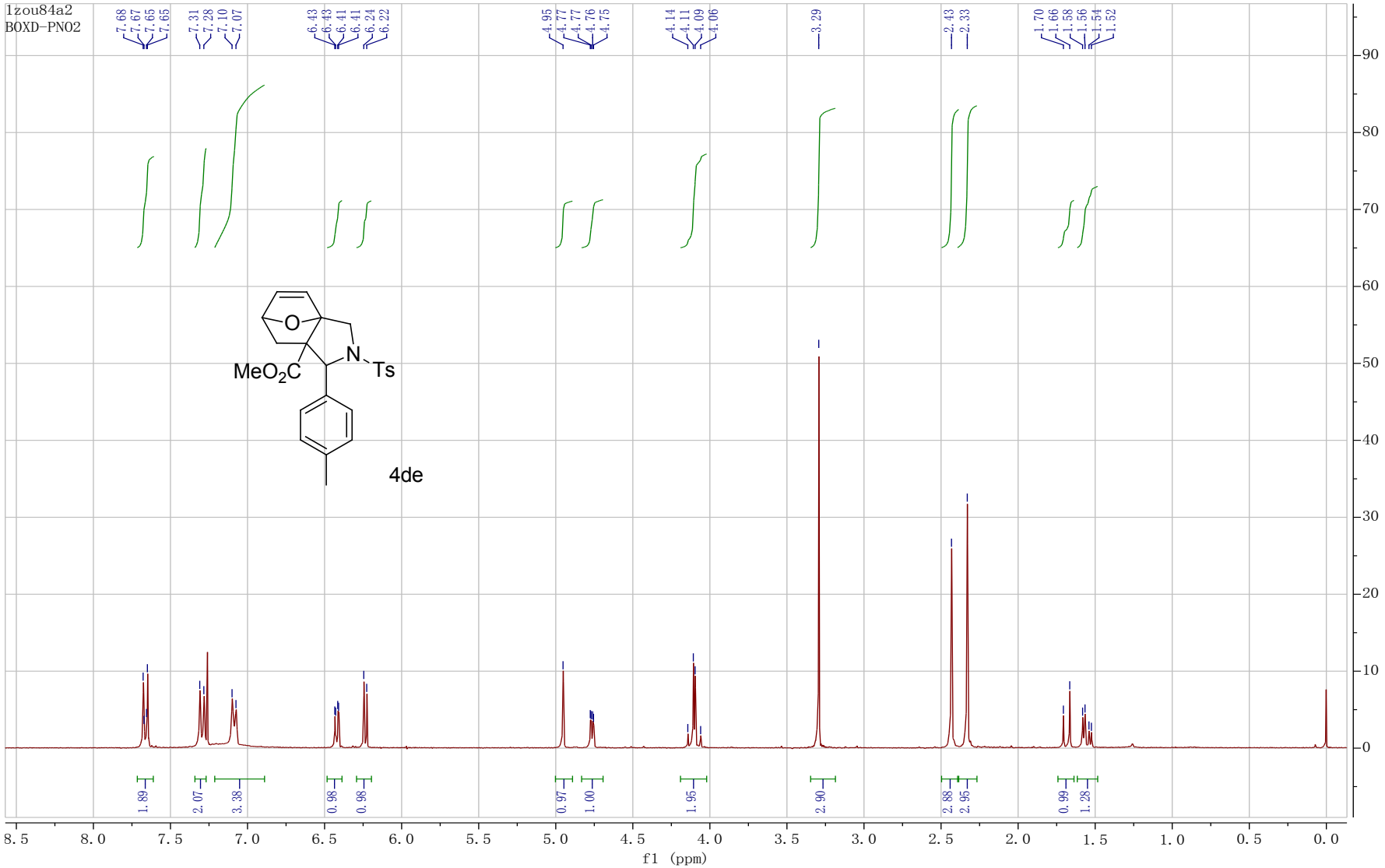

Spectra-58

2zou531a

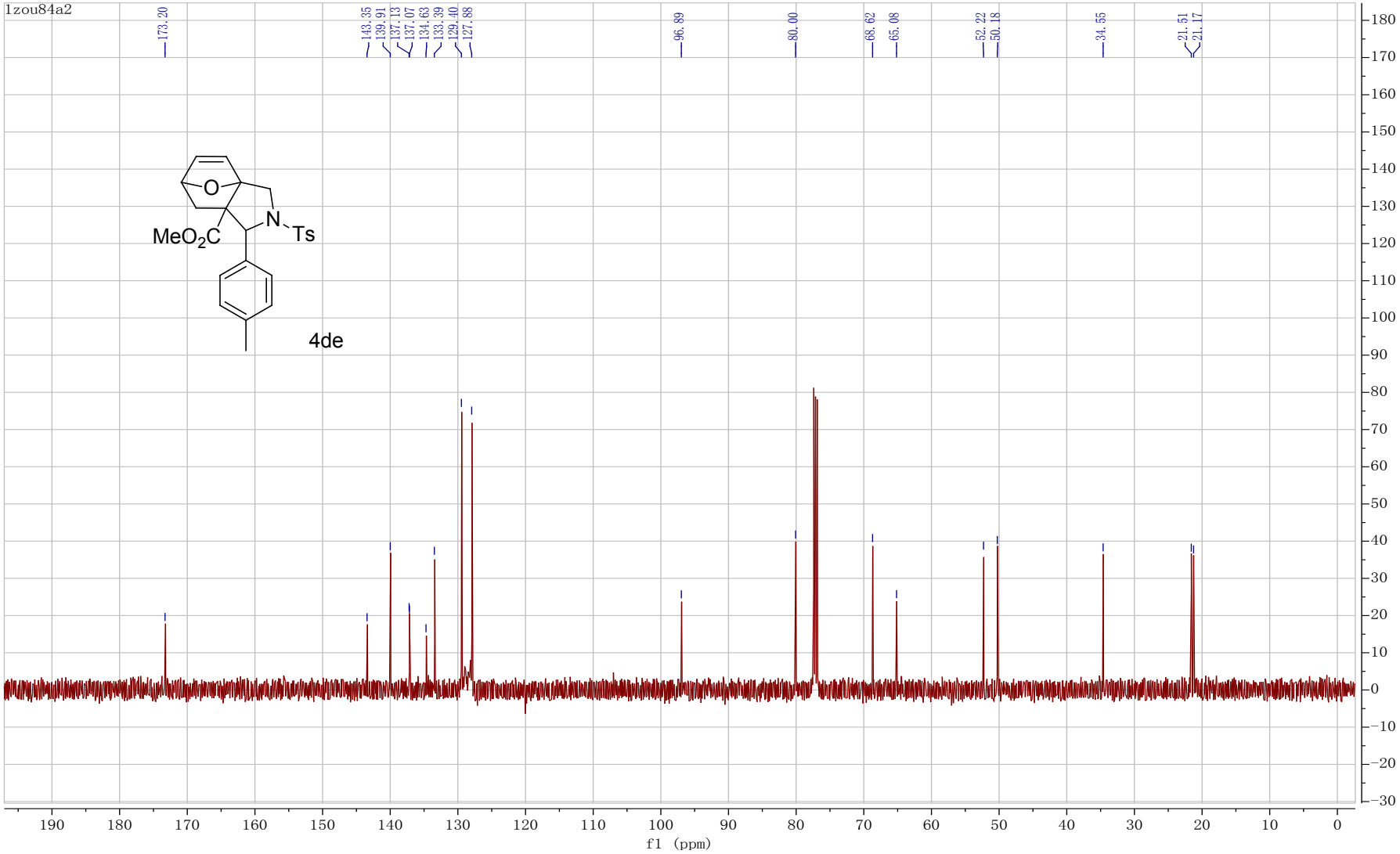


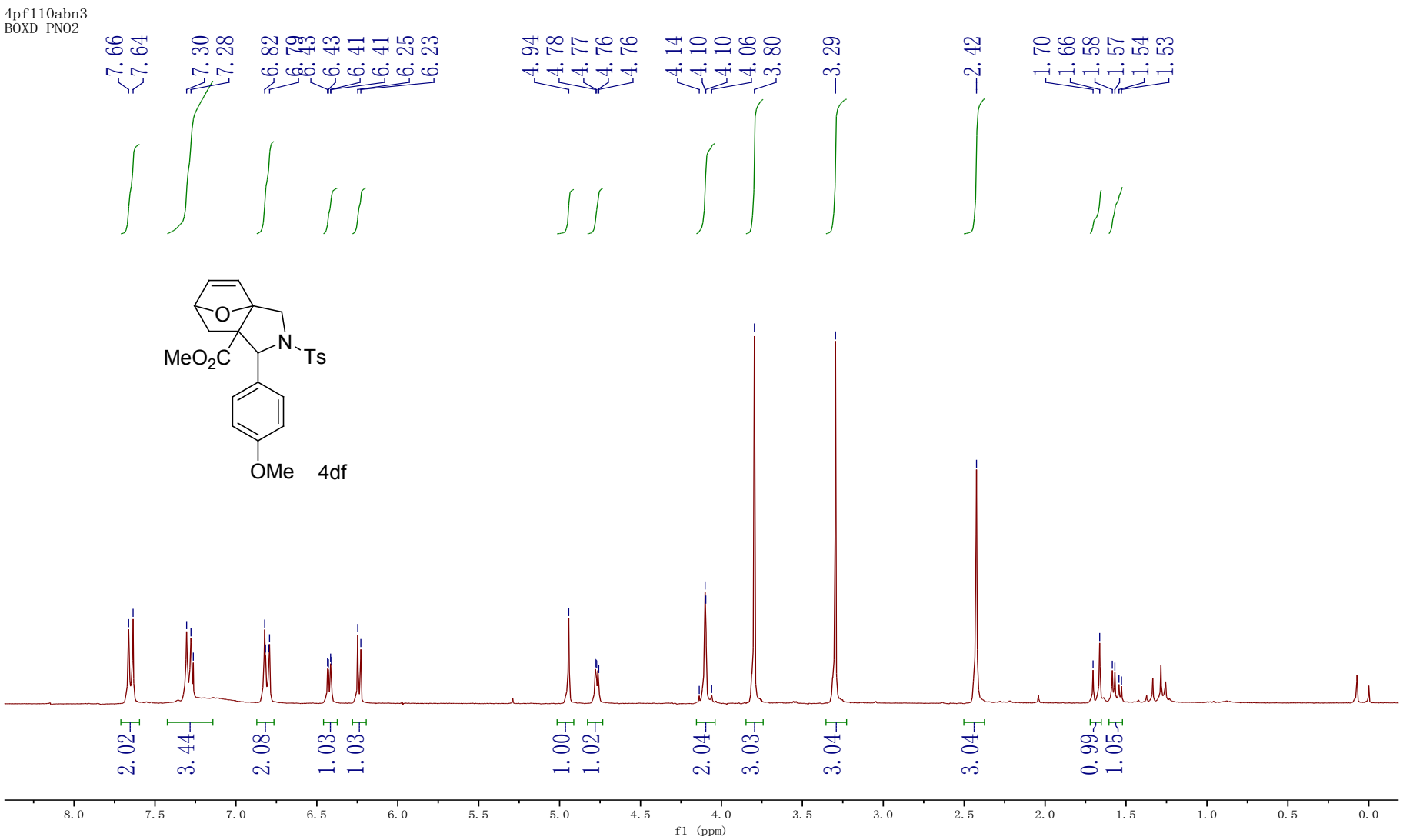

Spectra-59



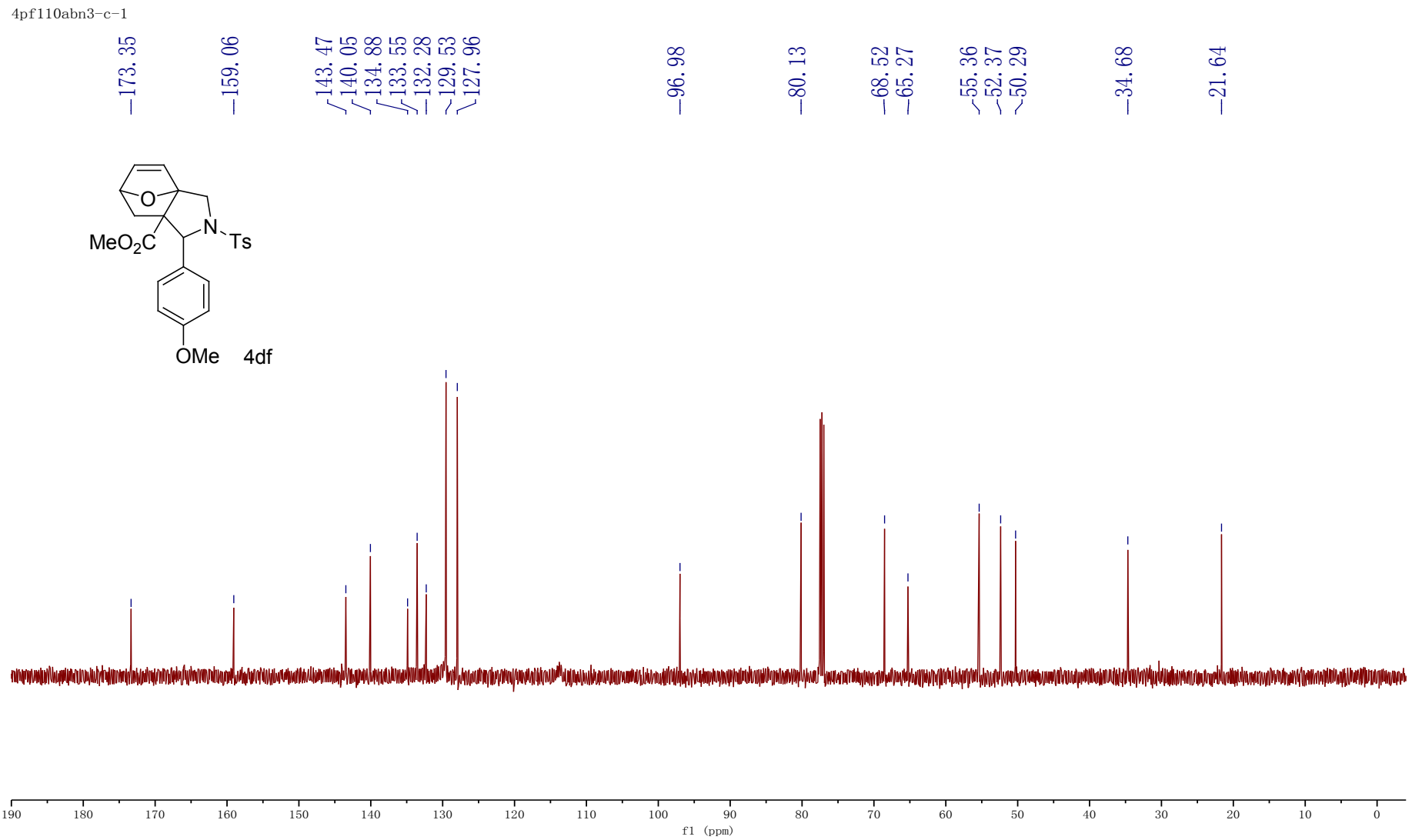

Spectra-60



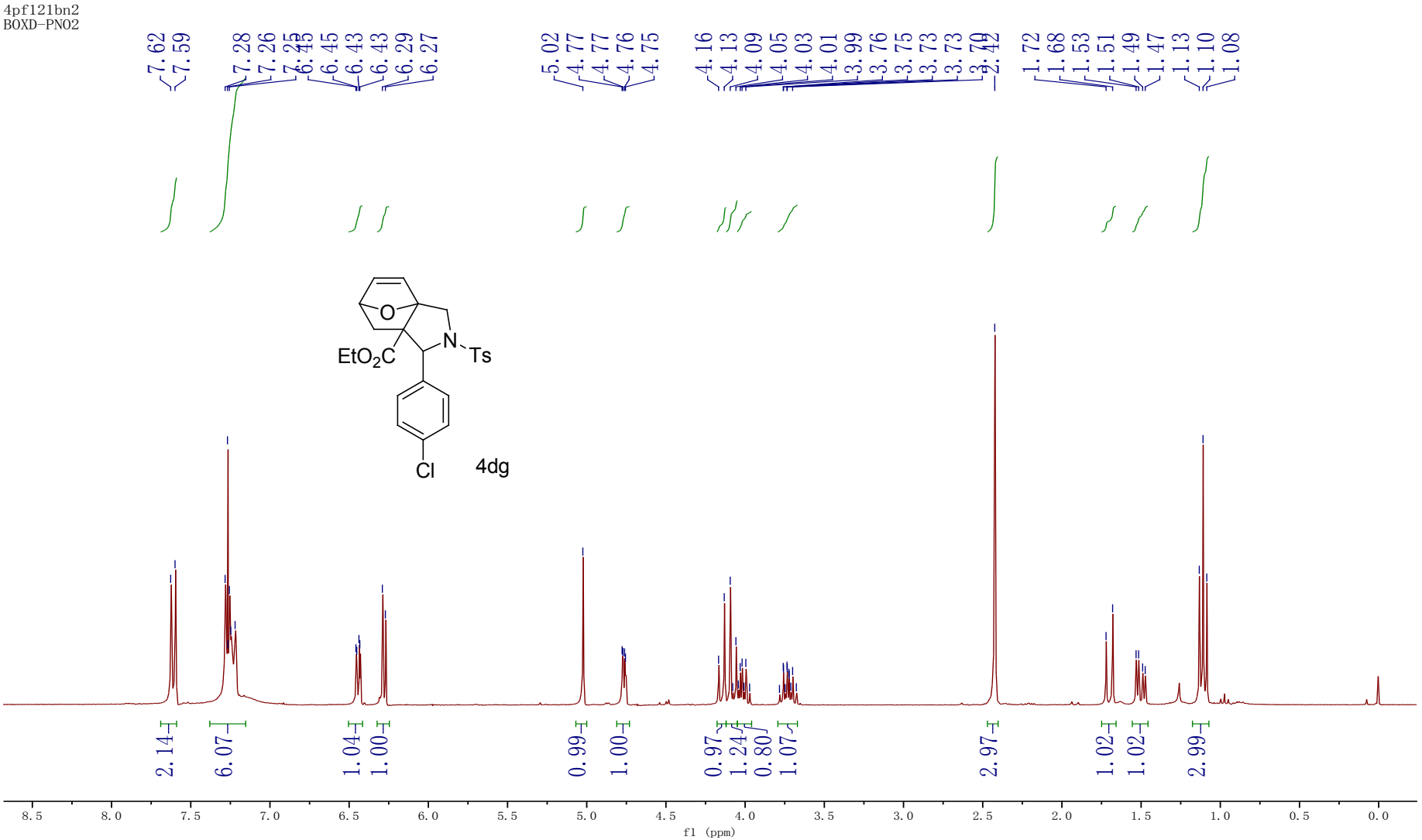

Spectra-61



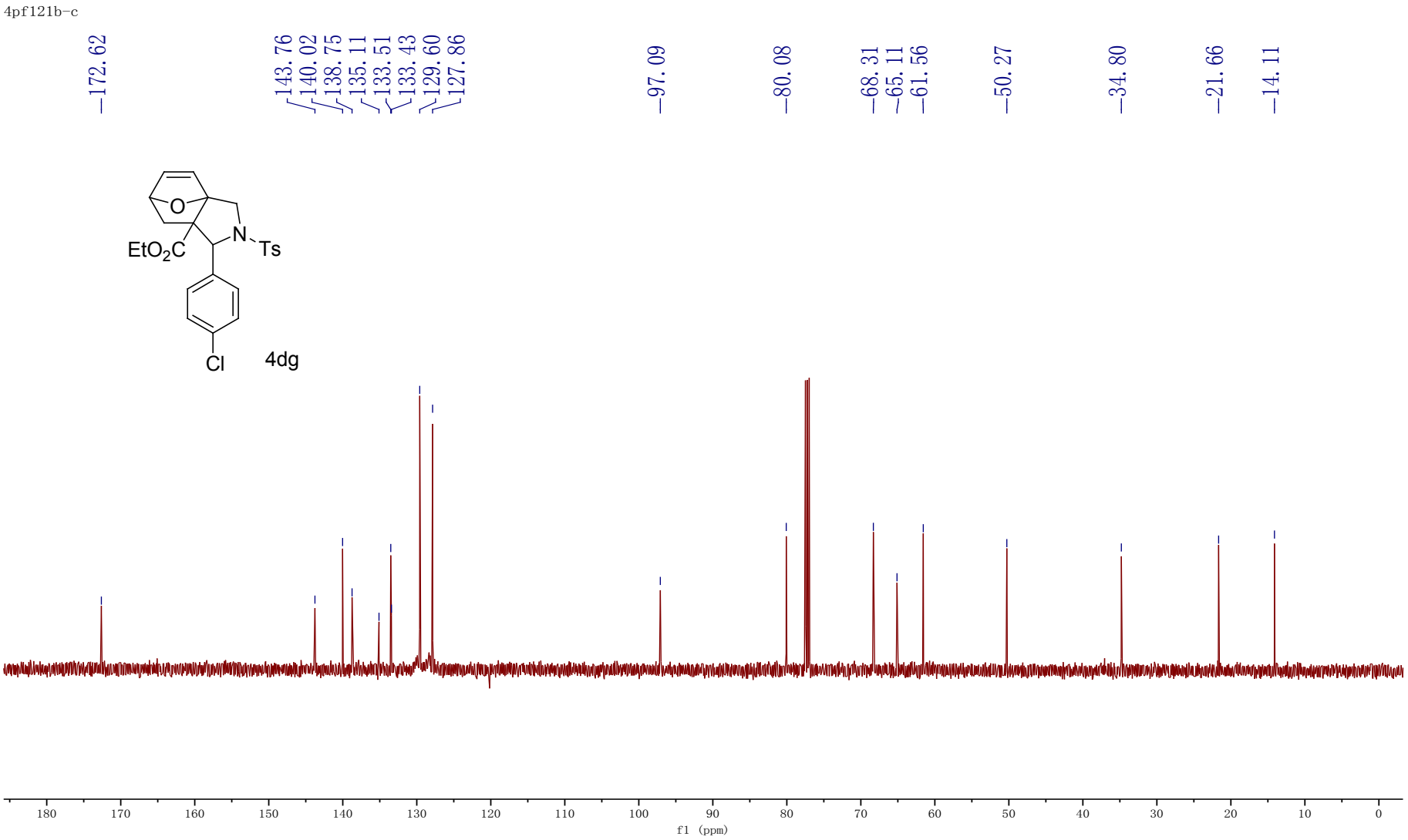

Spectra-62



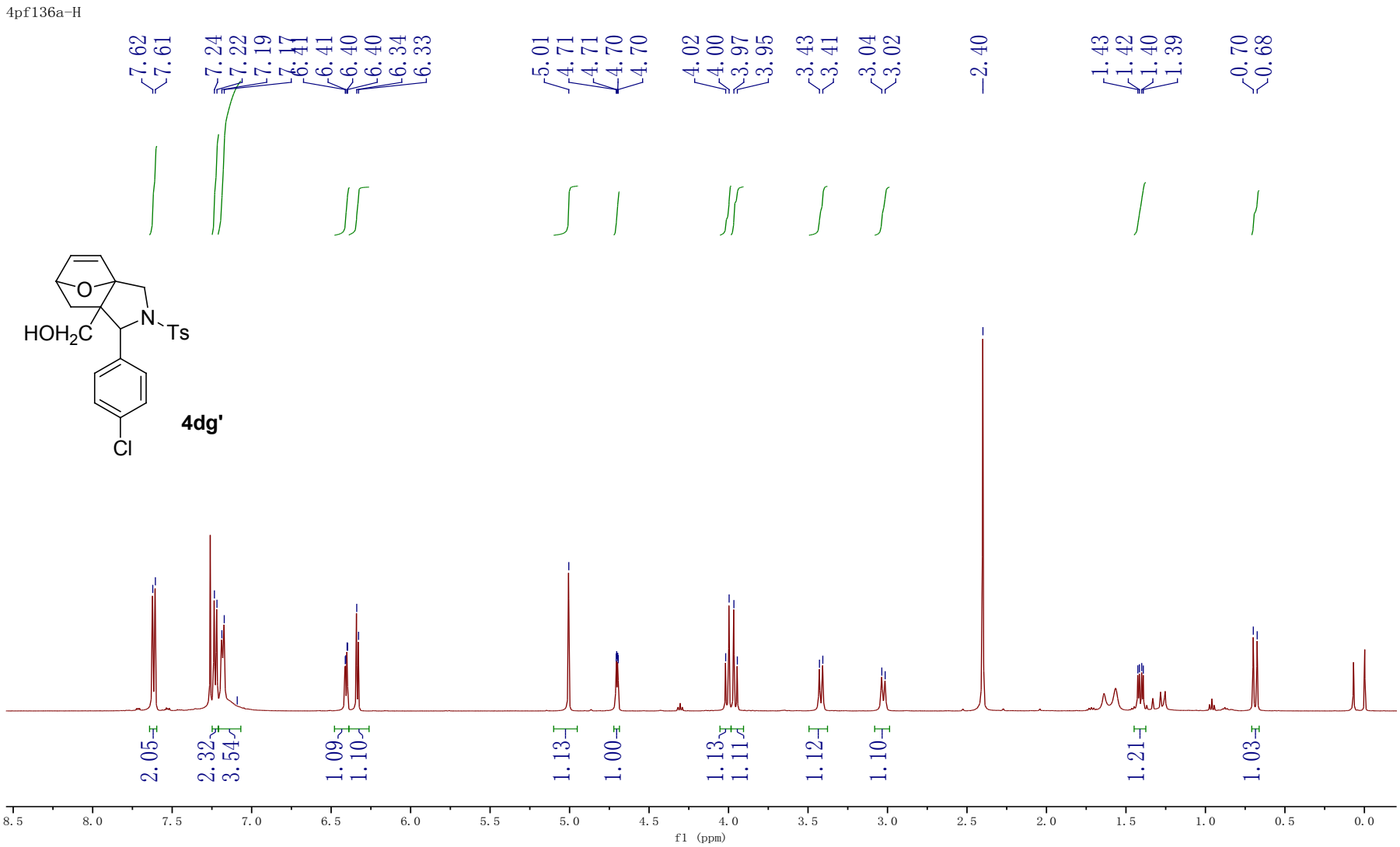

Spectra-63



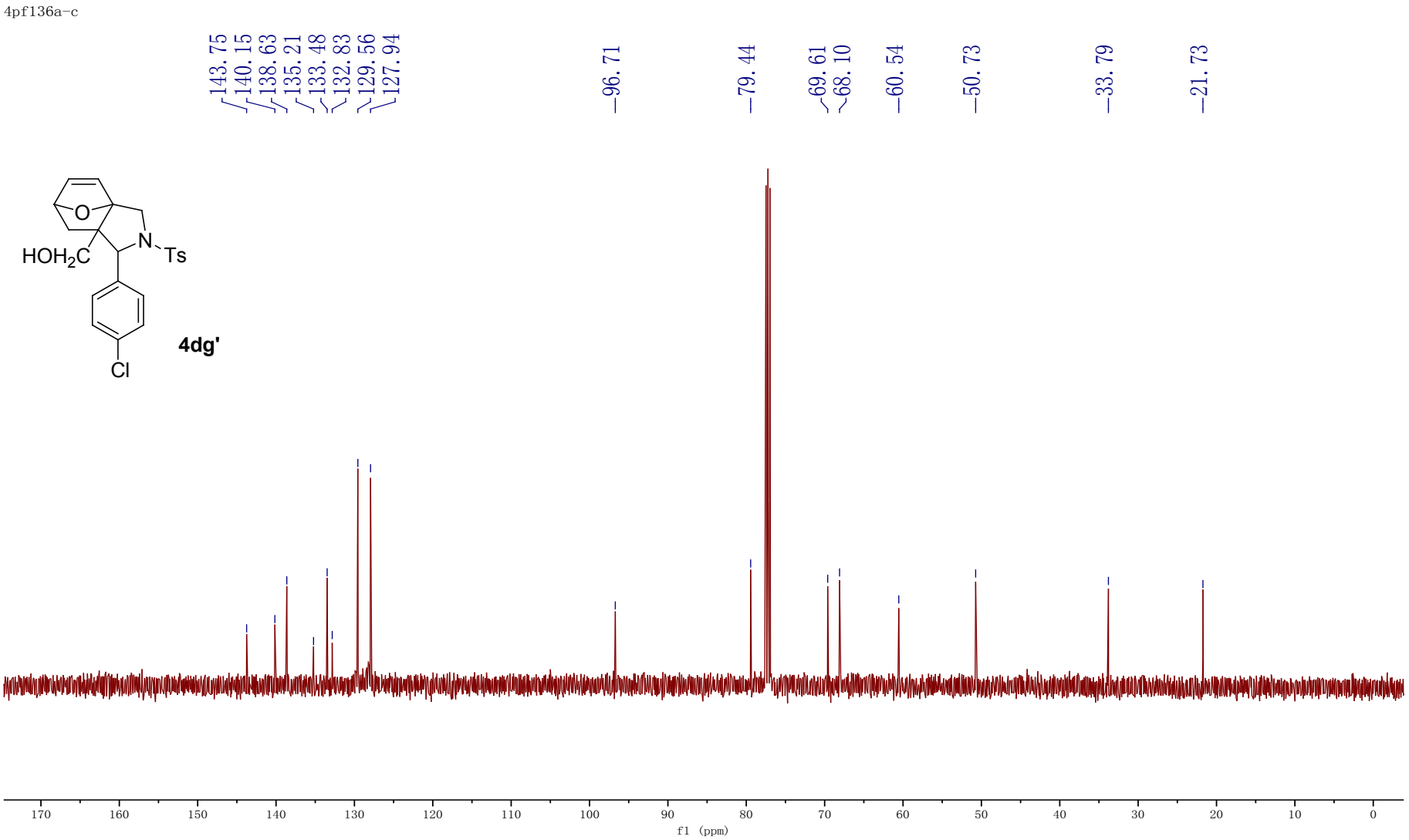

Spectra-64



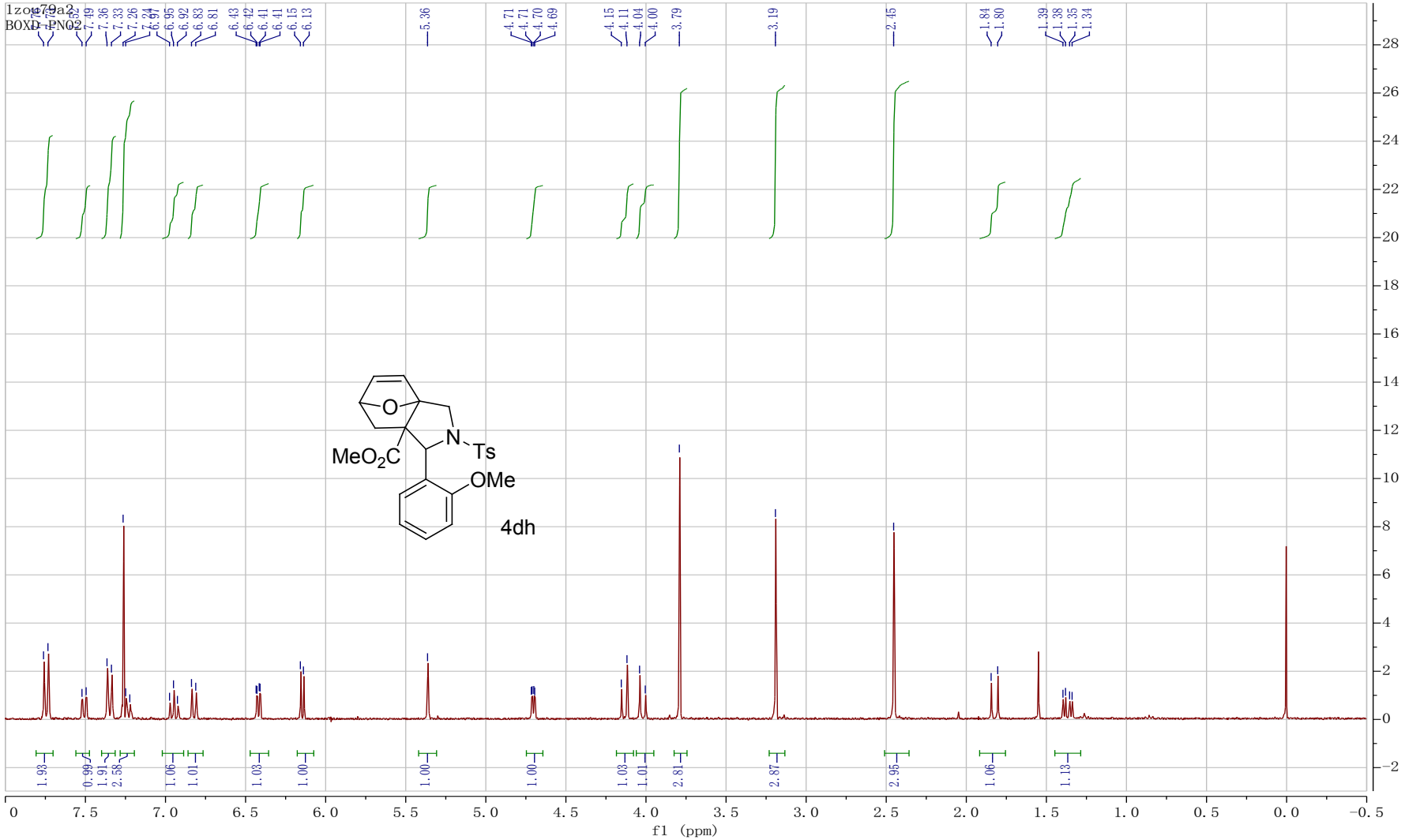

Spectra-65



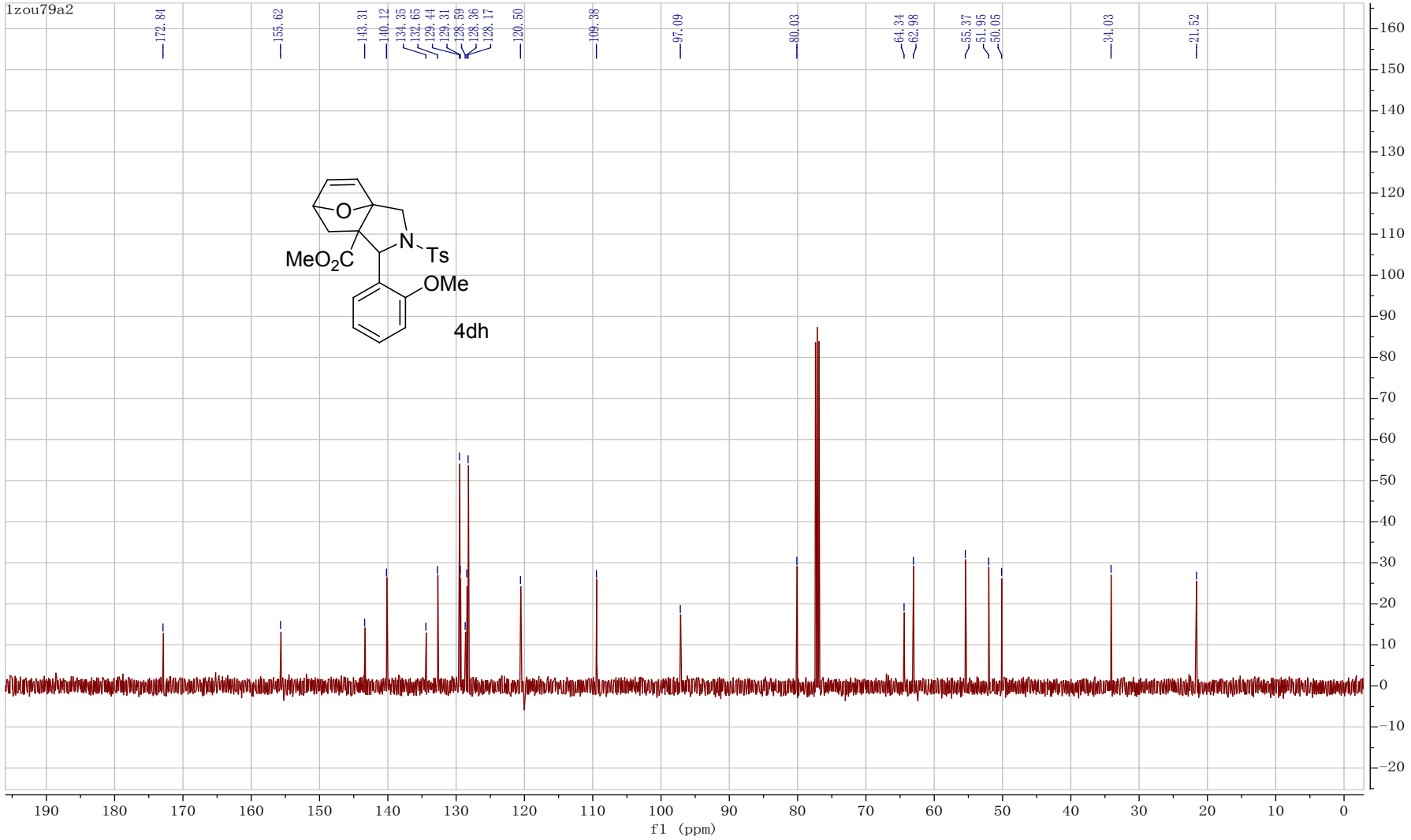

Spectra-66



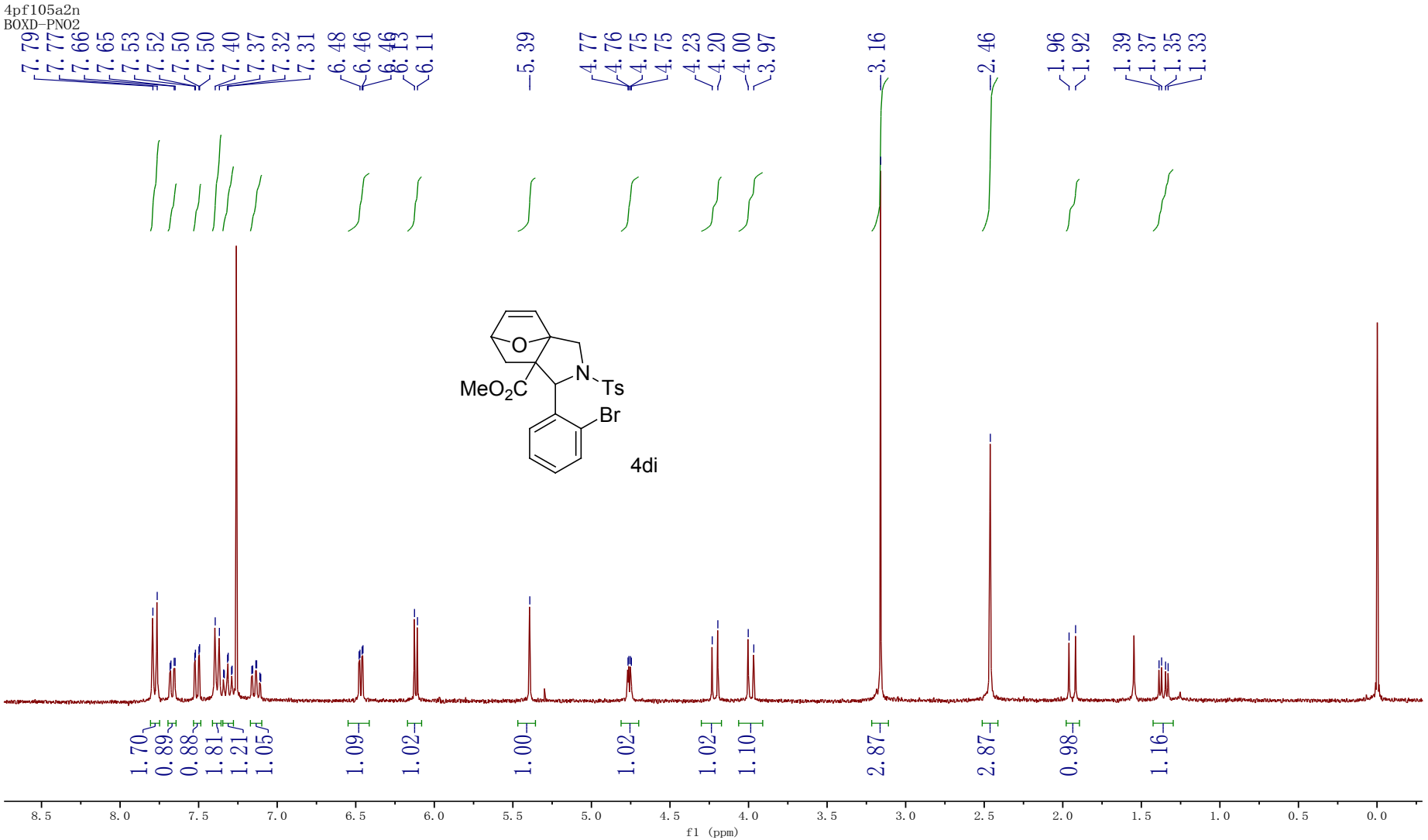

Spectra-67



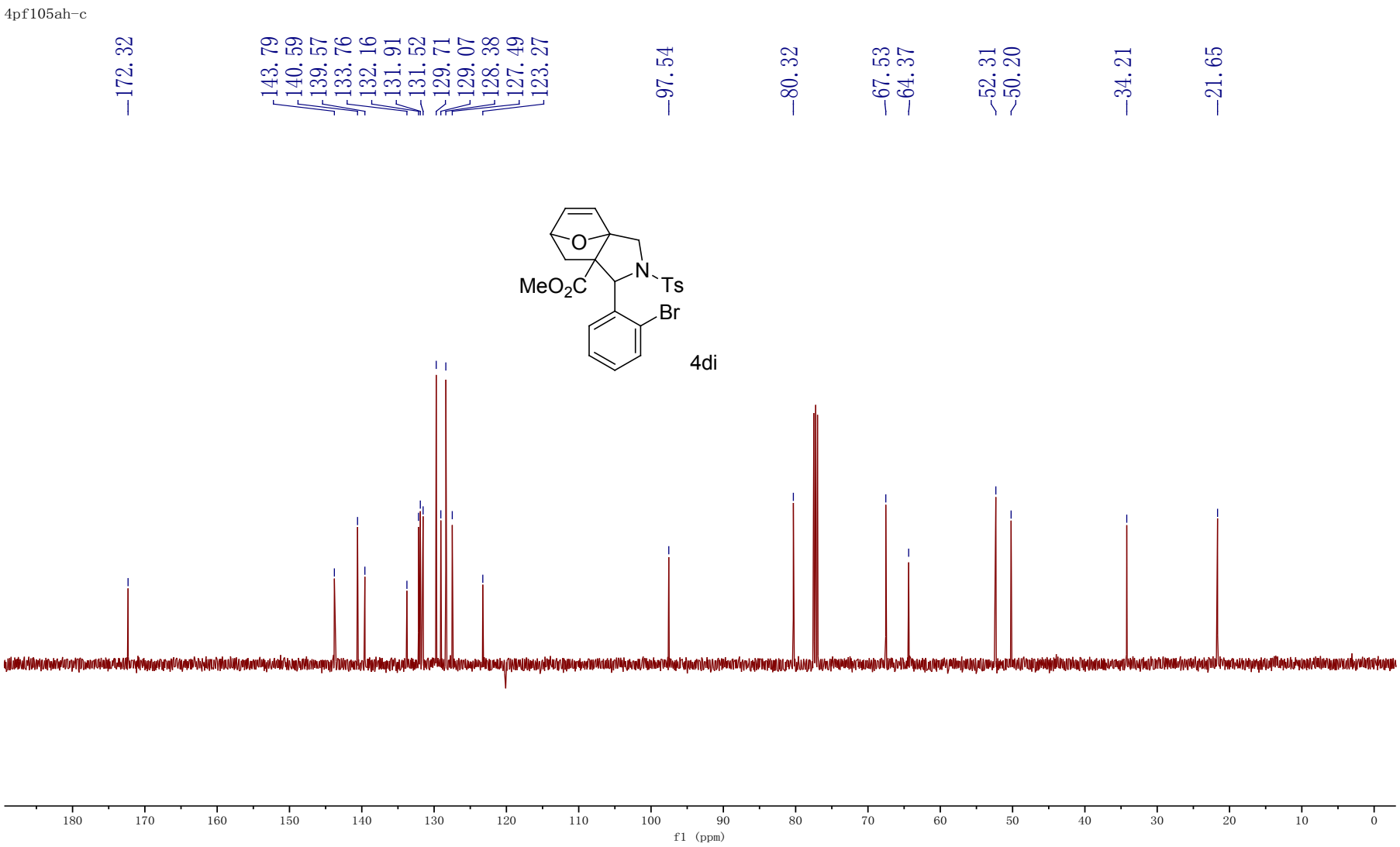

Spectra-68



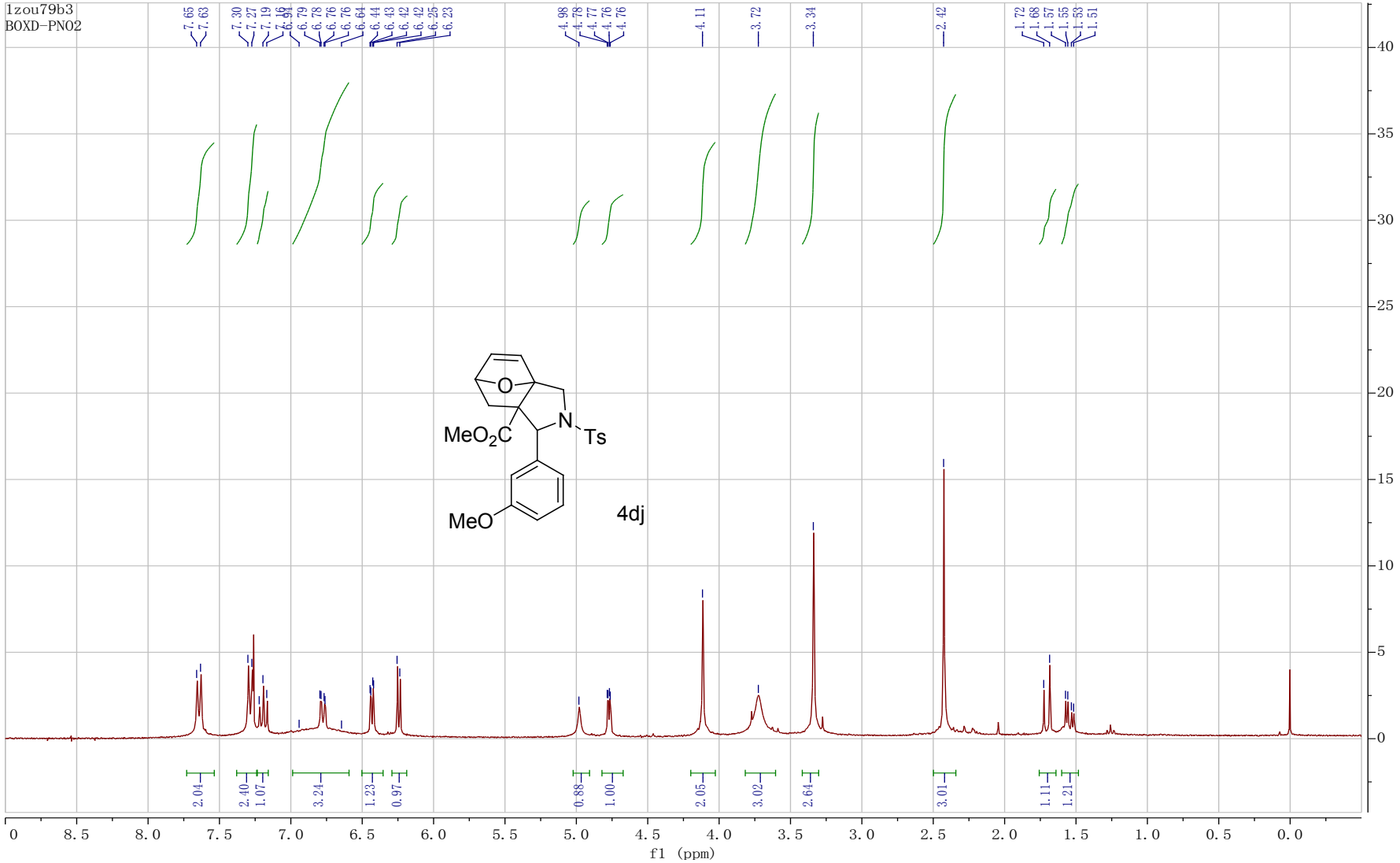

Spectra-69



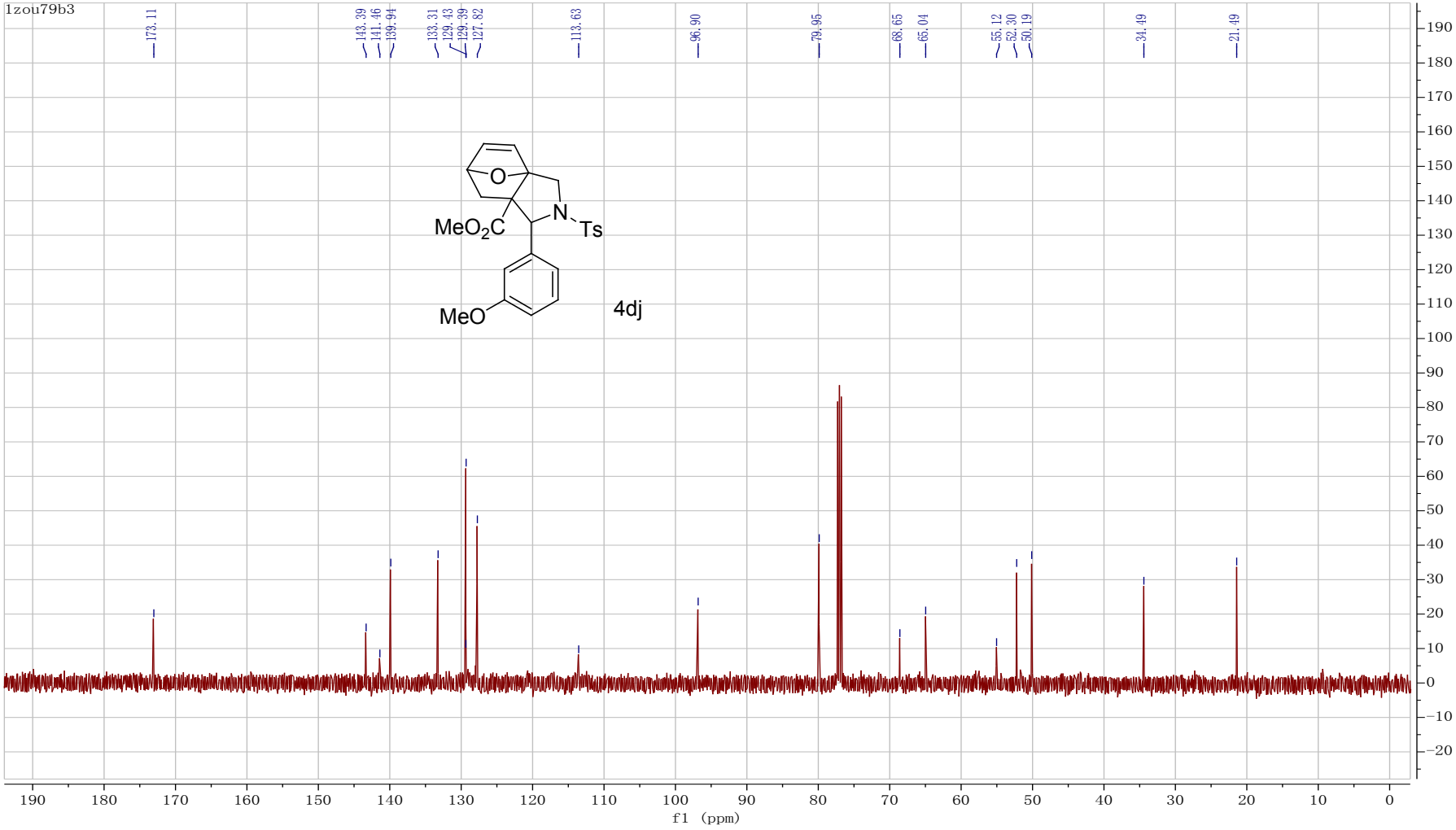

Spectra-70



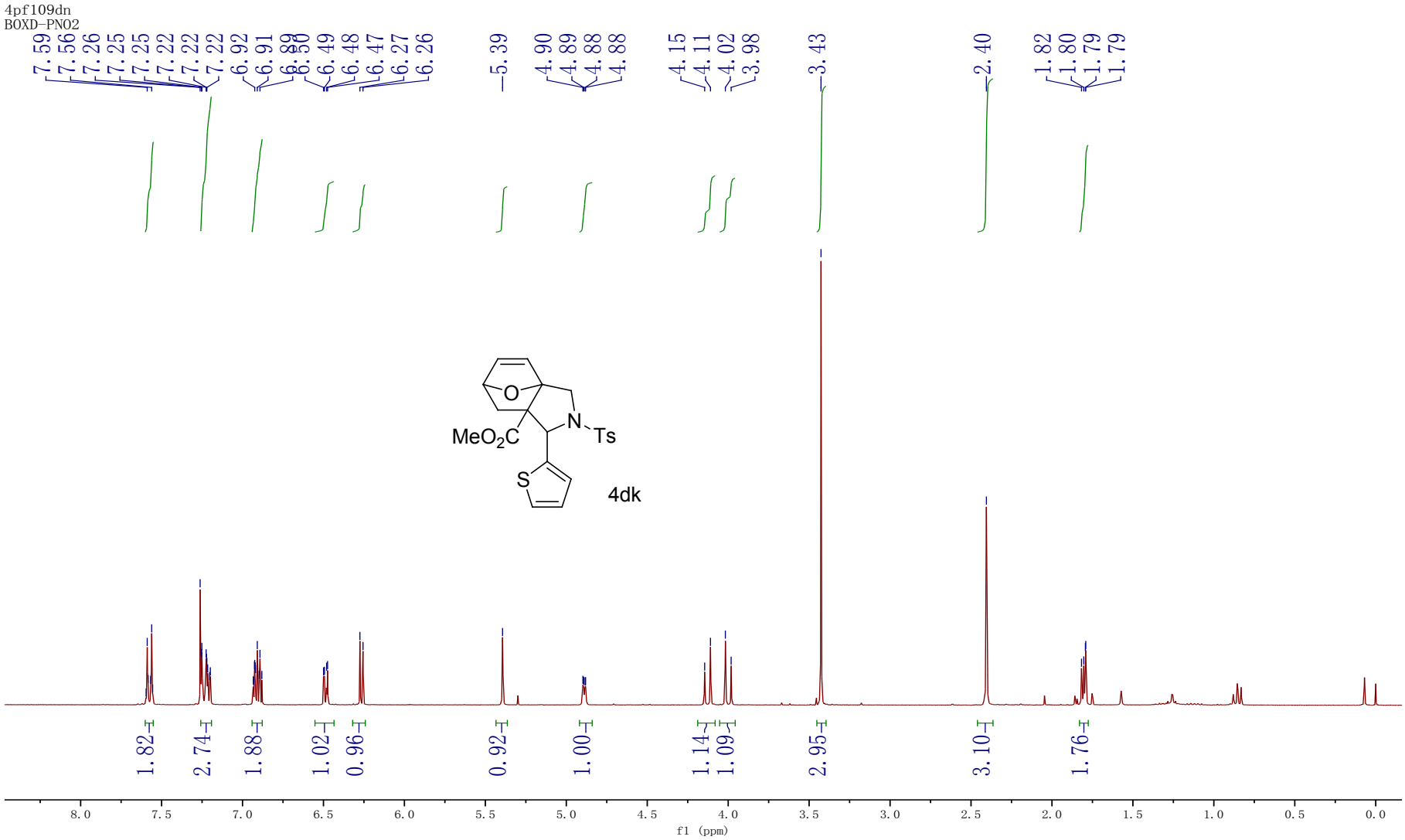

Spectra-71



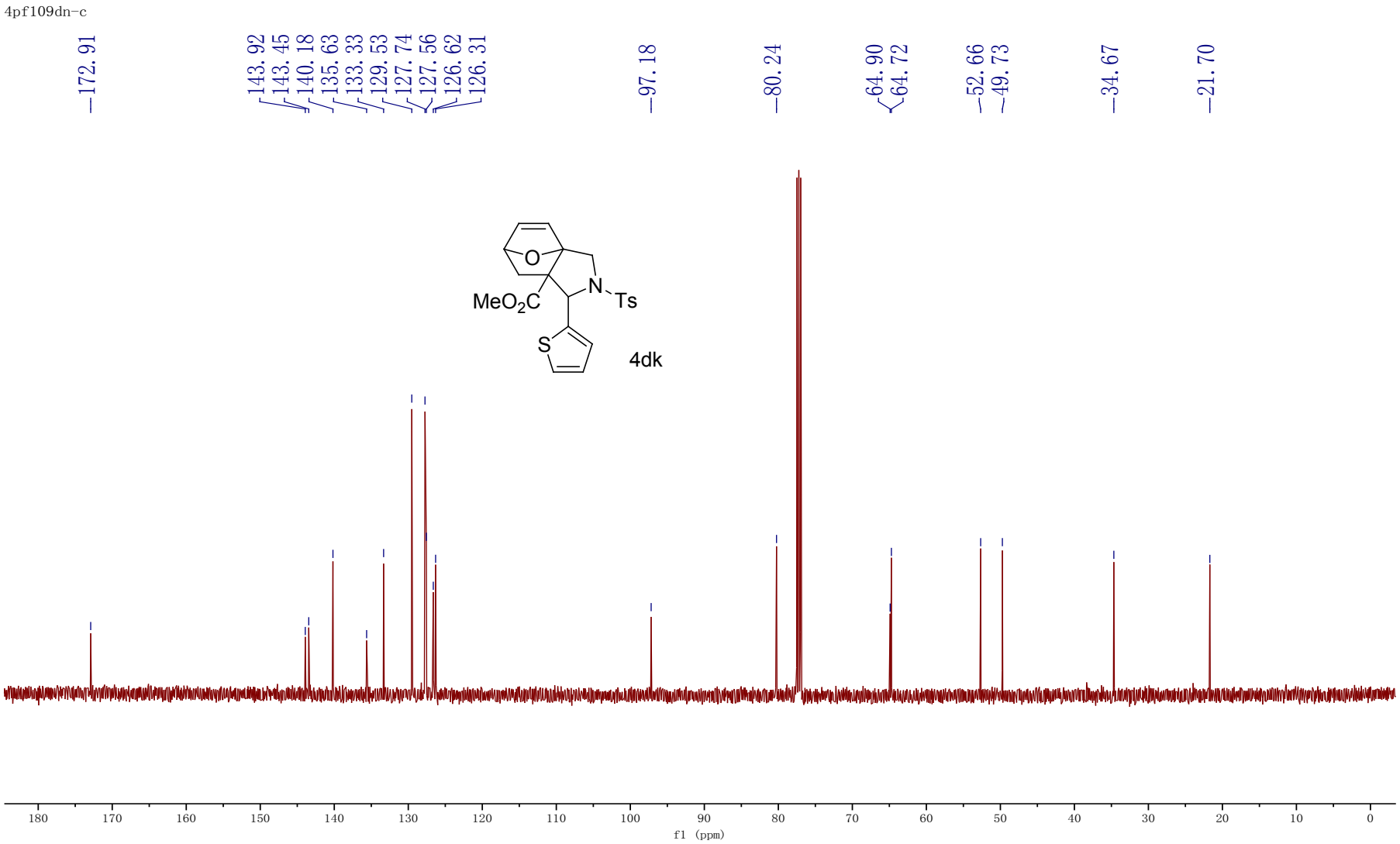

Spectra-72



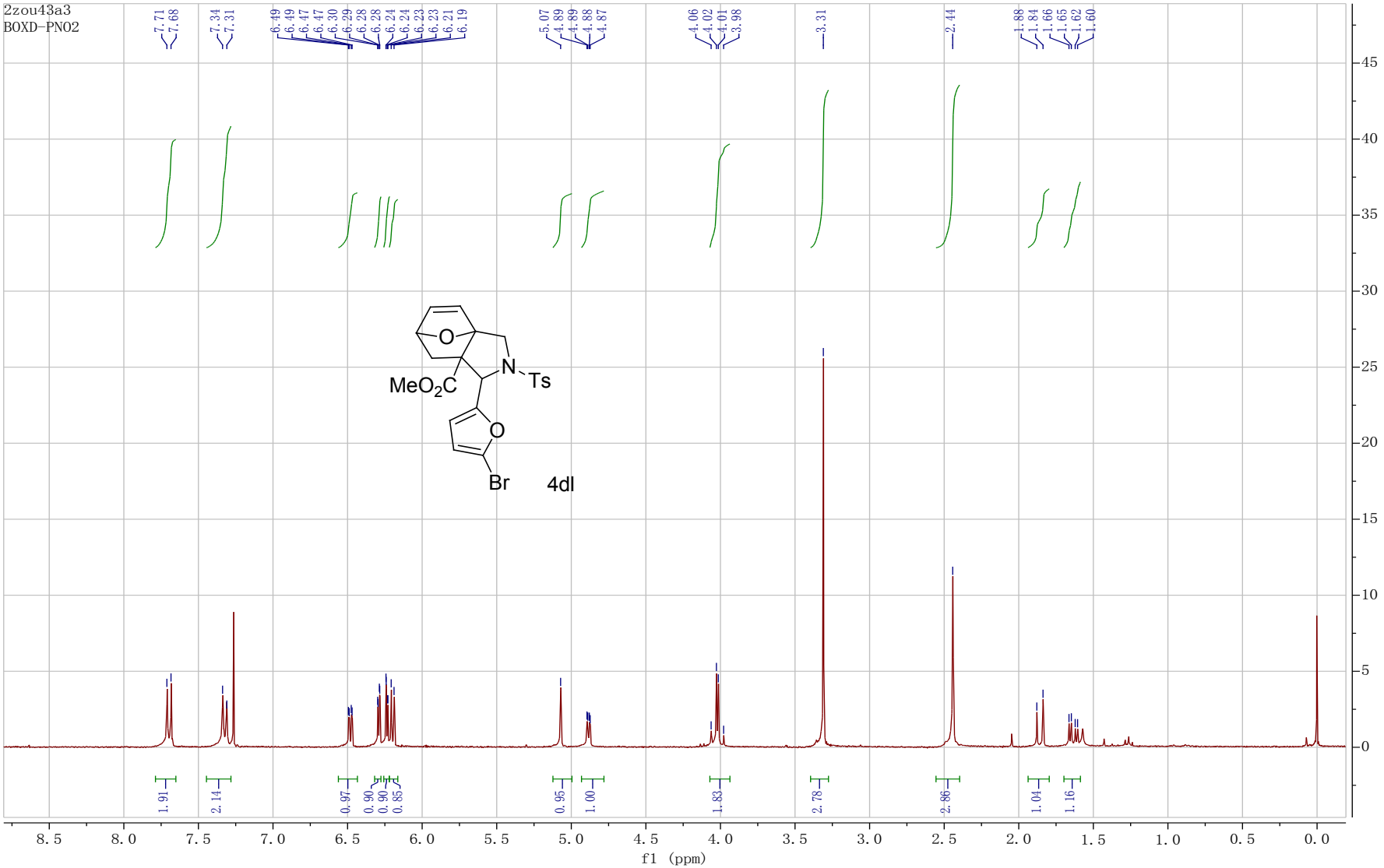

Spectra-73



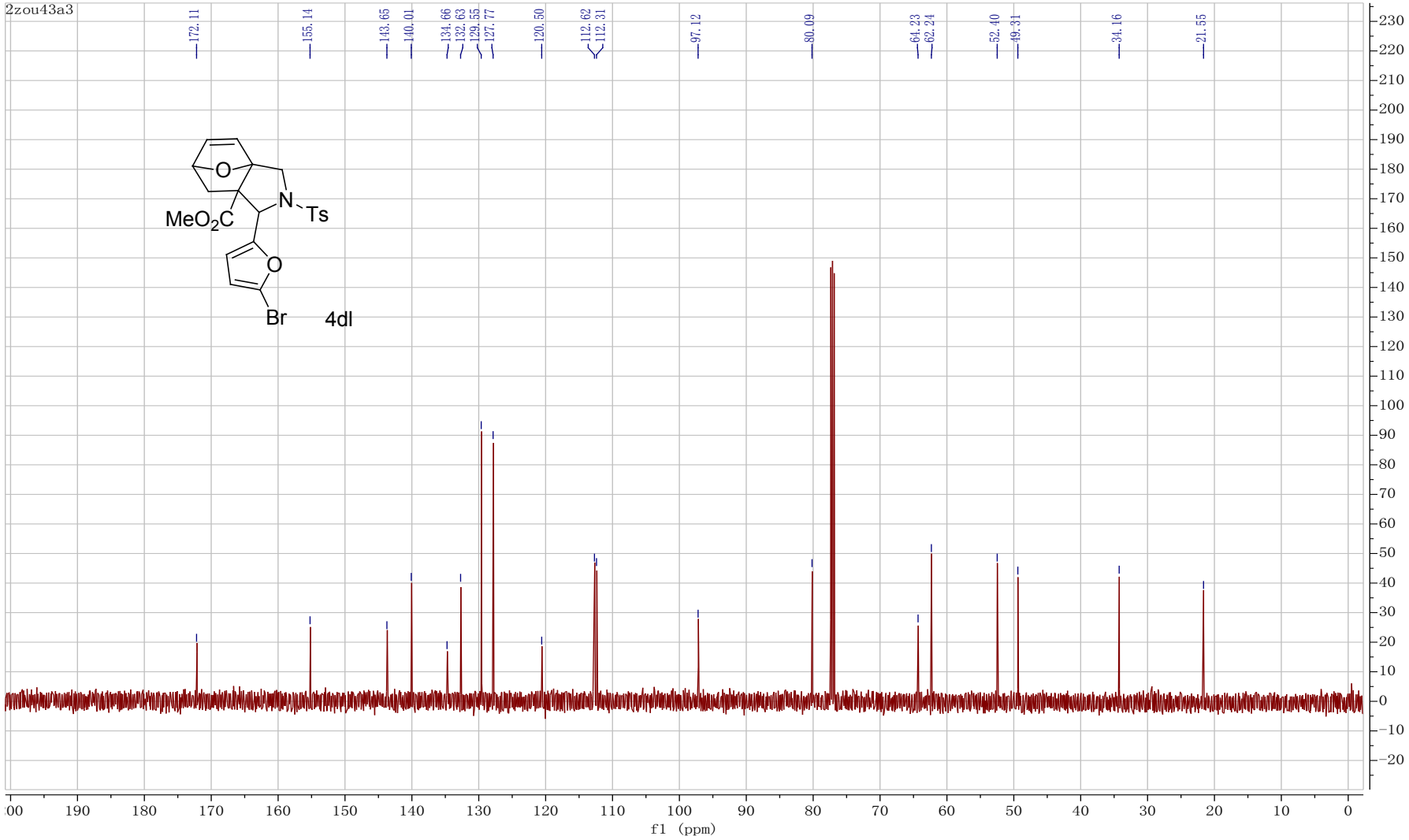

Spectra-74



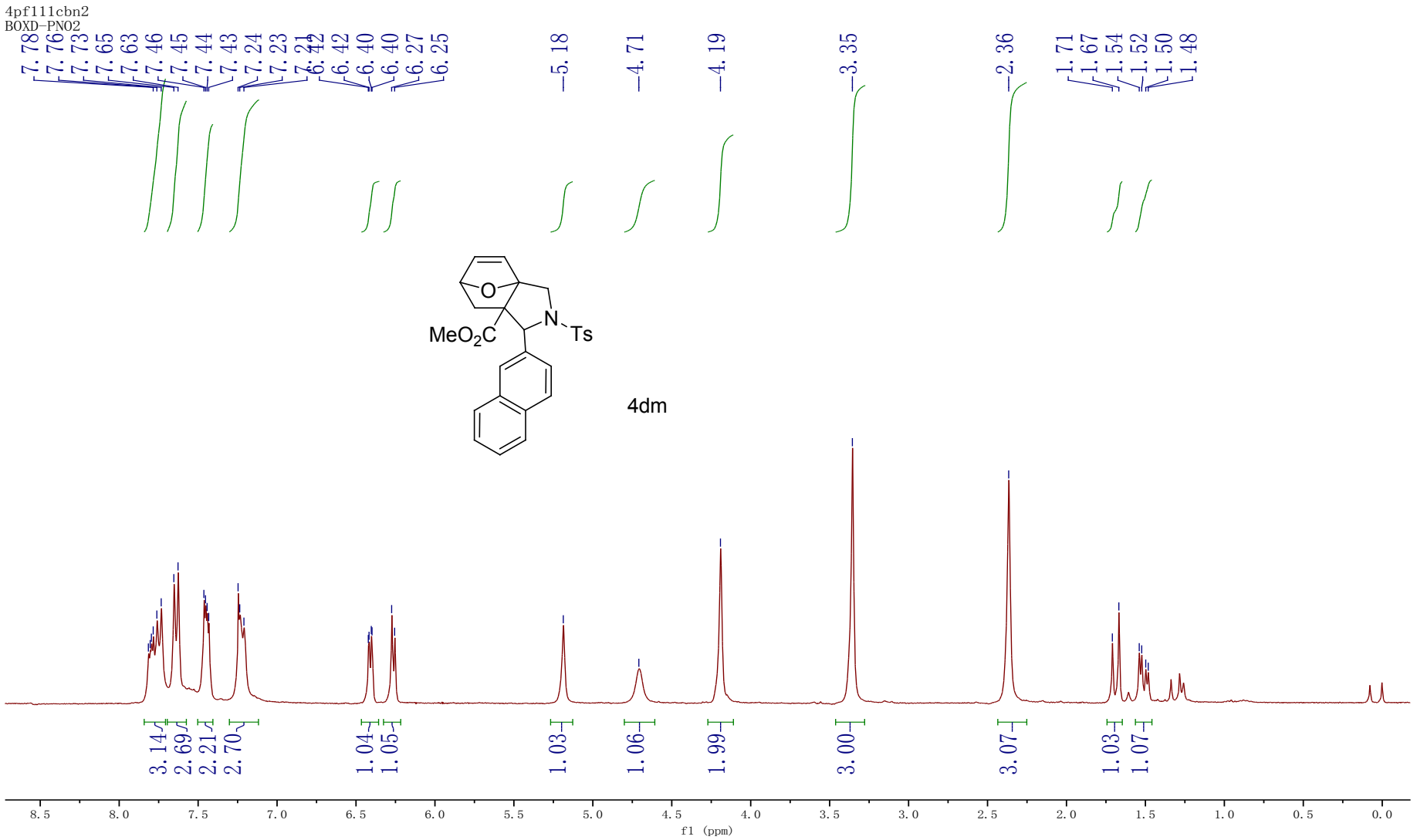

Spectra-75



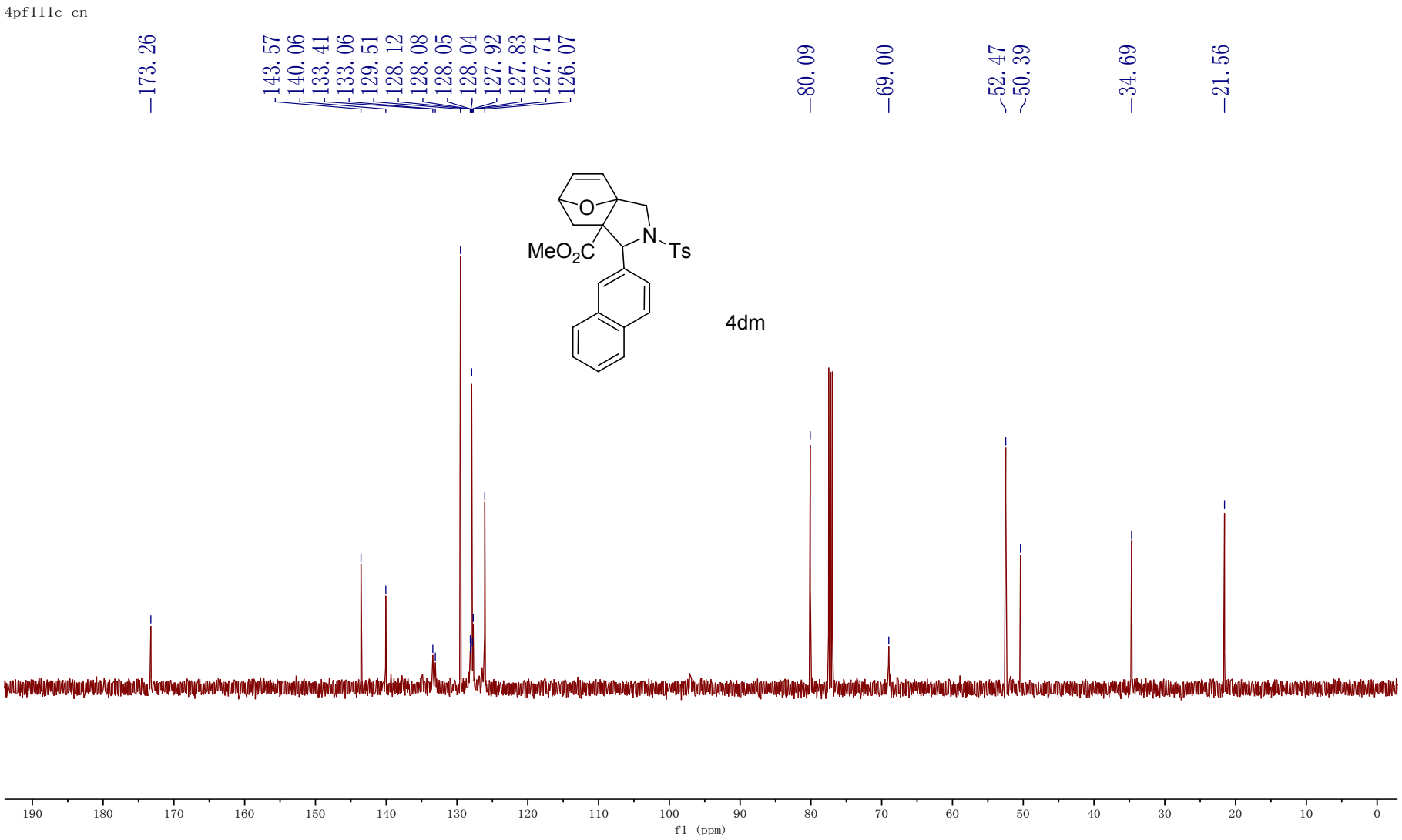

Spectra-76



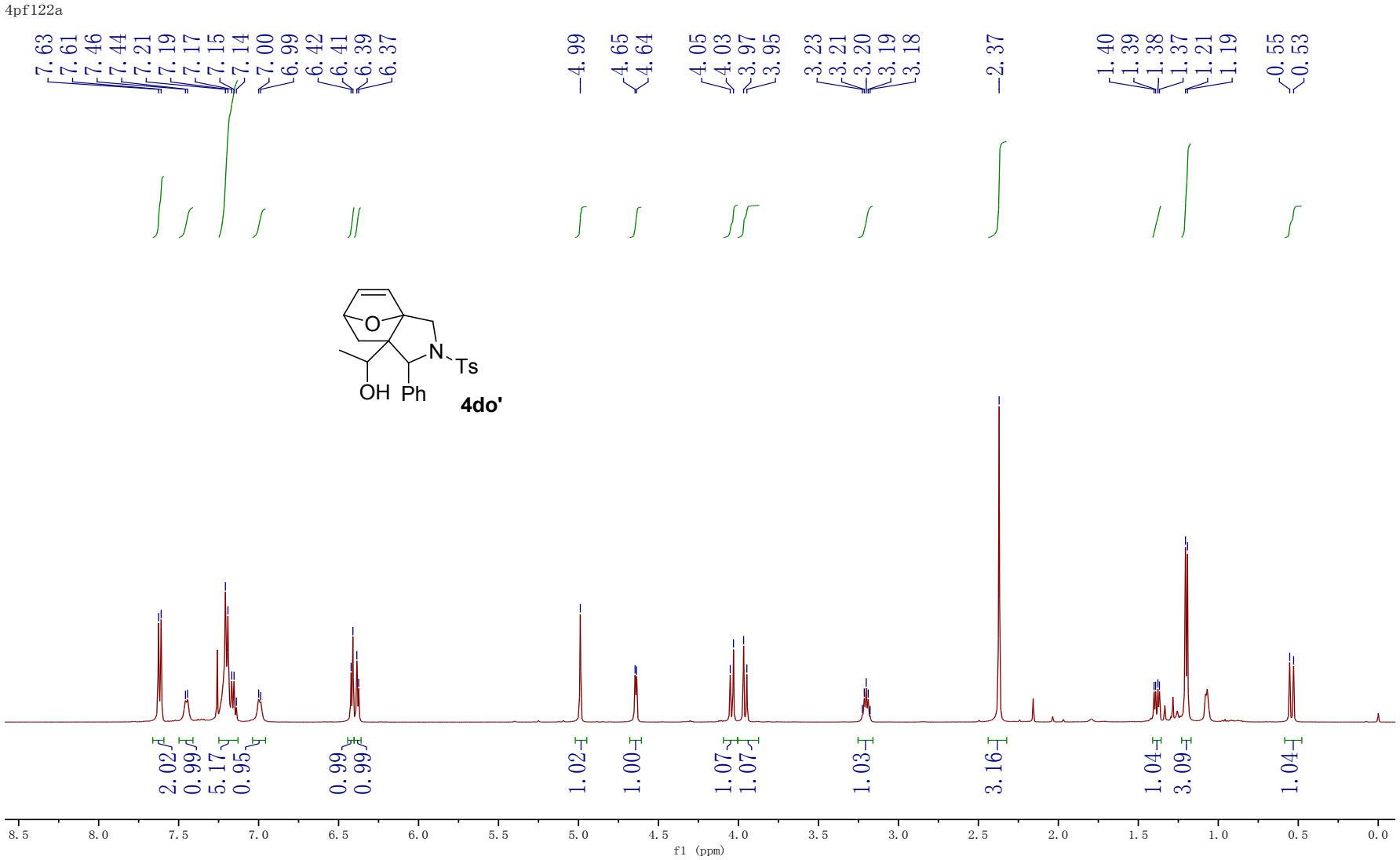

Spectra-77



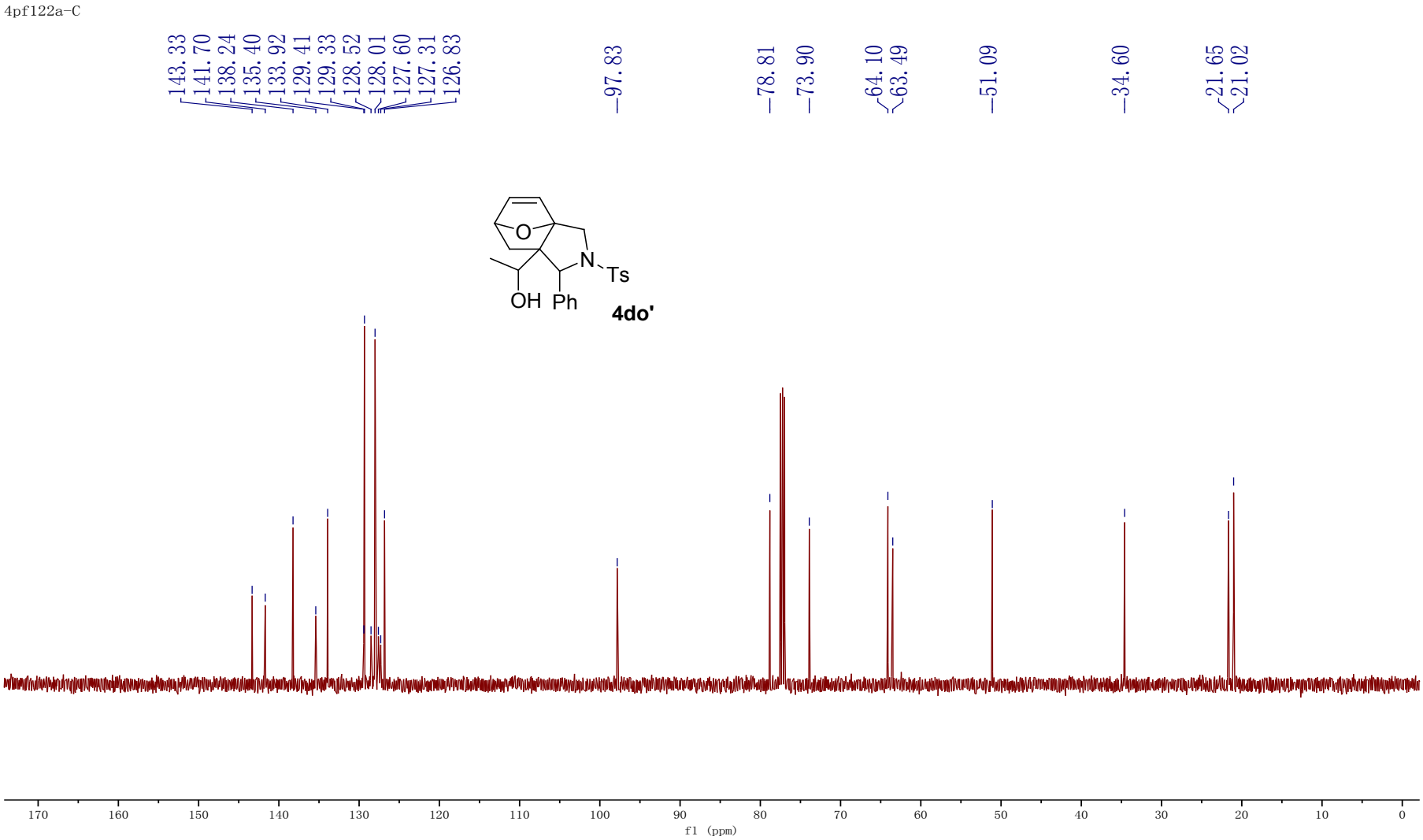

Spectra-78



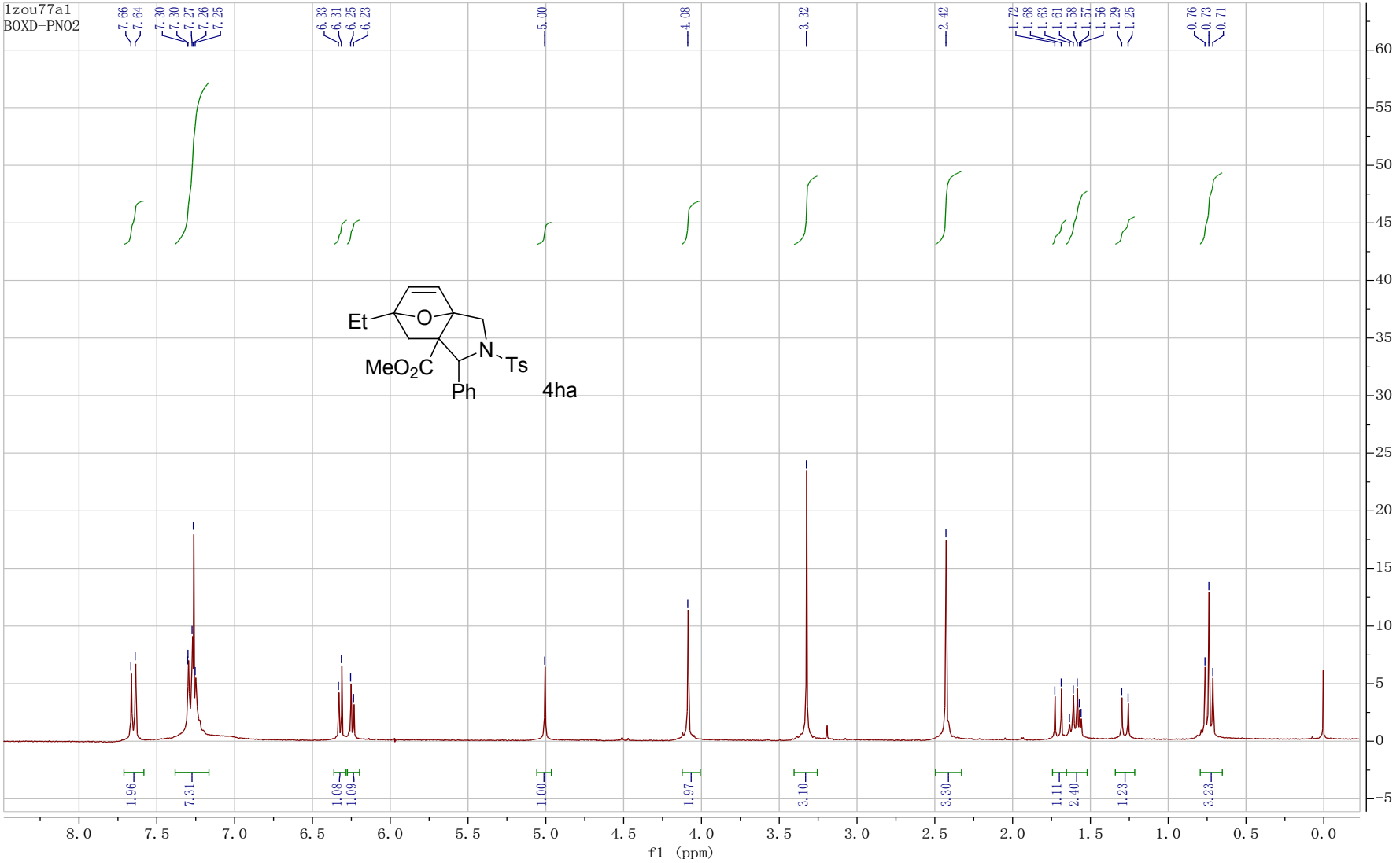

Spectra-79



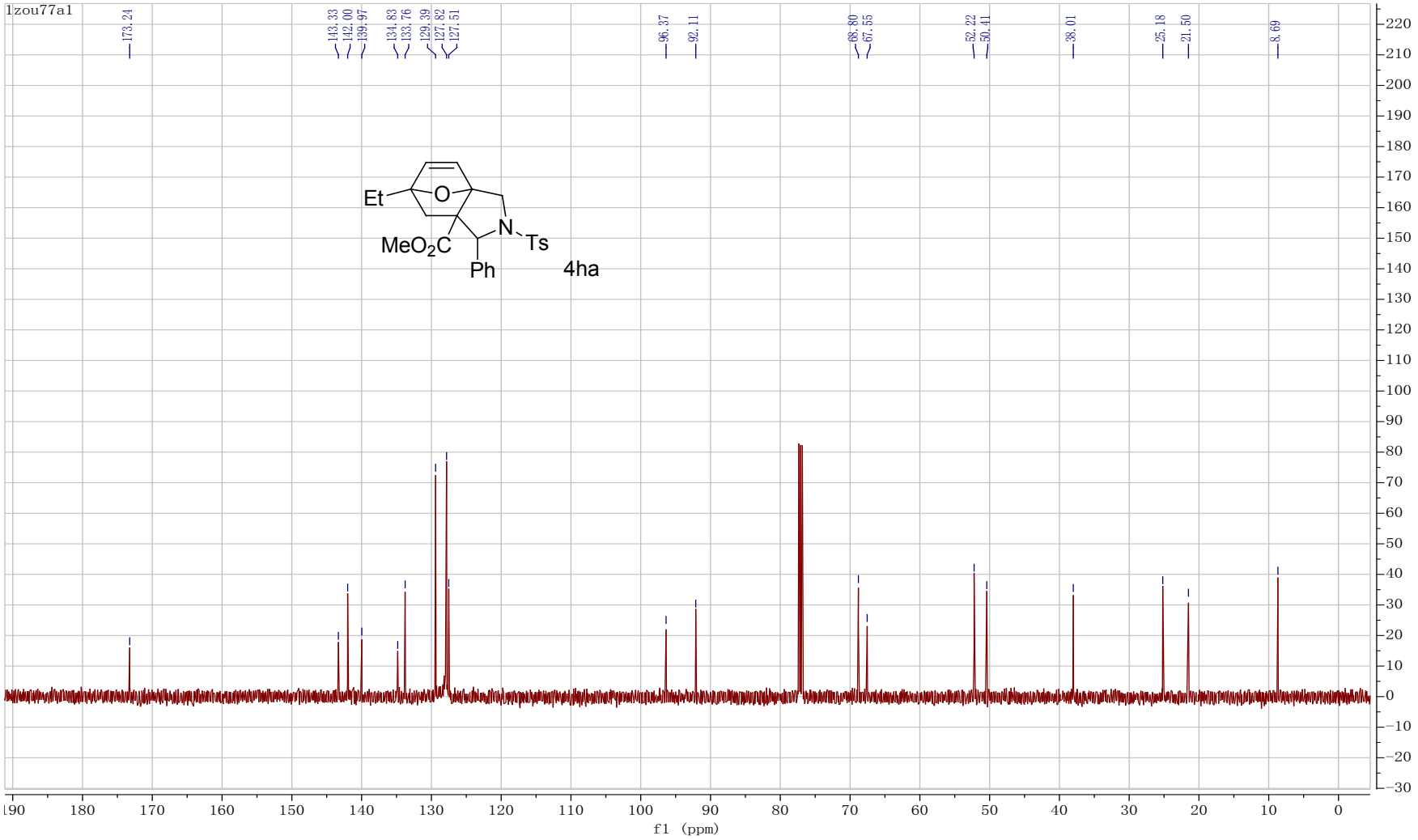

Spectra-80



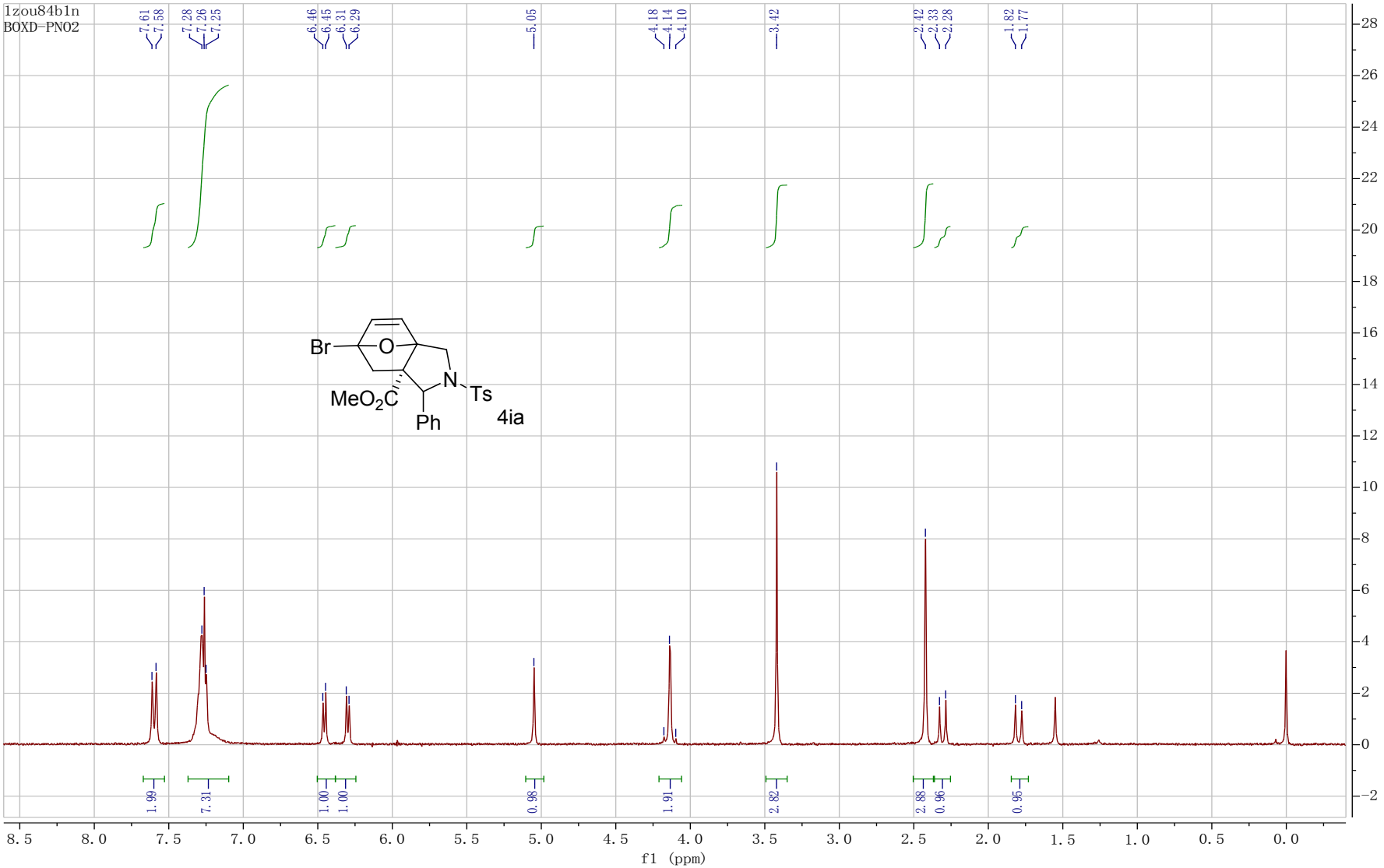

Spectra-81



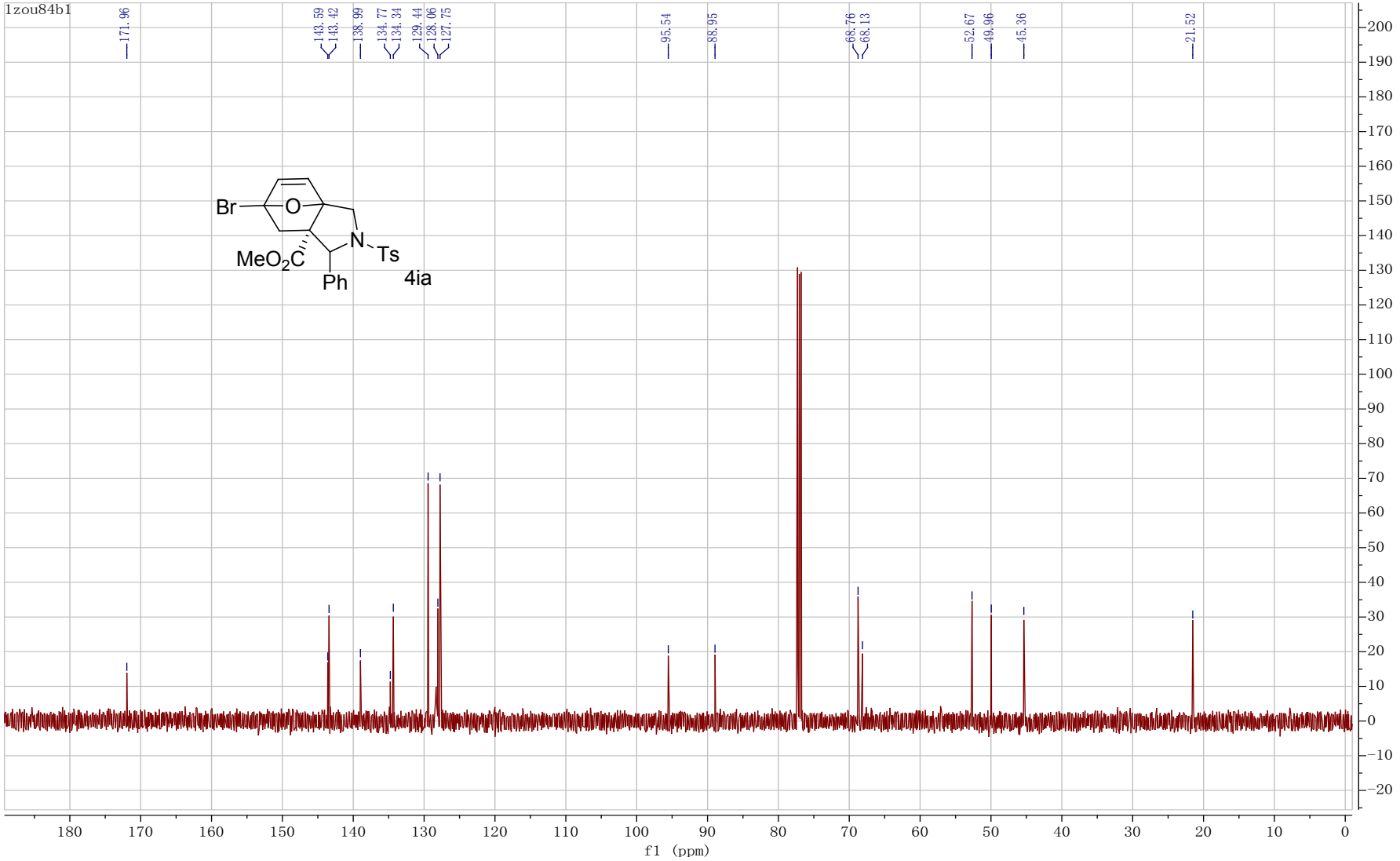

Spectra-82



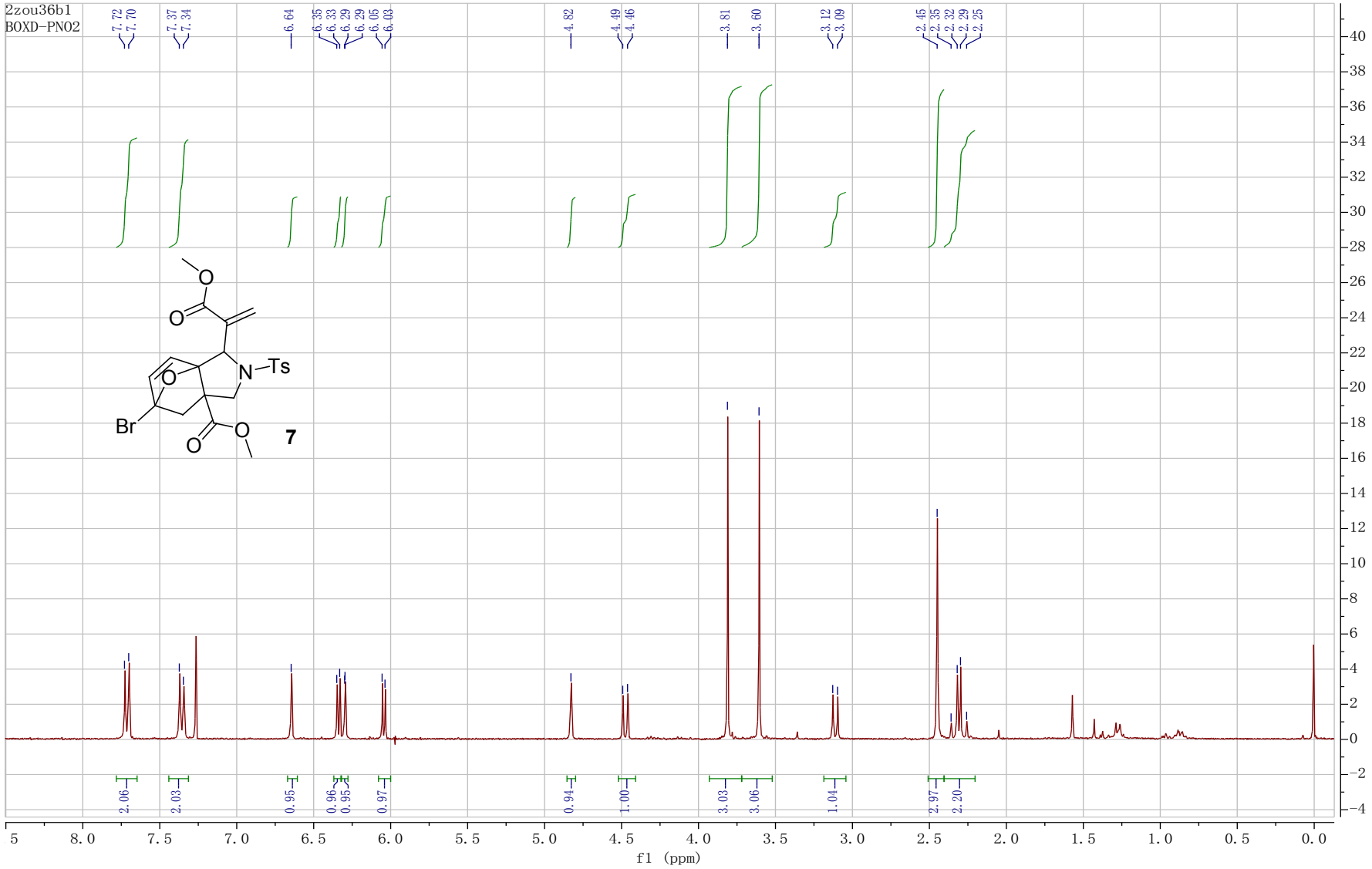

Spectra-83



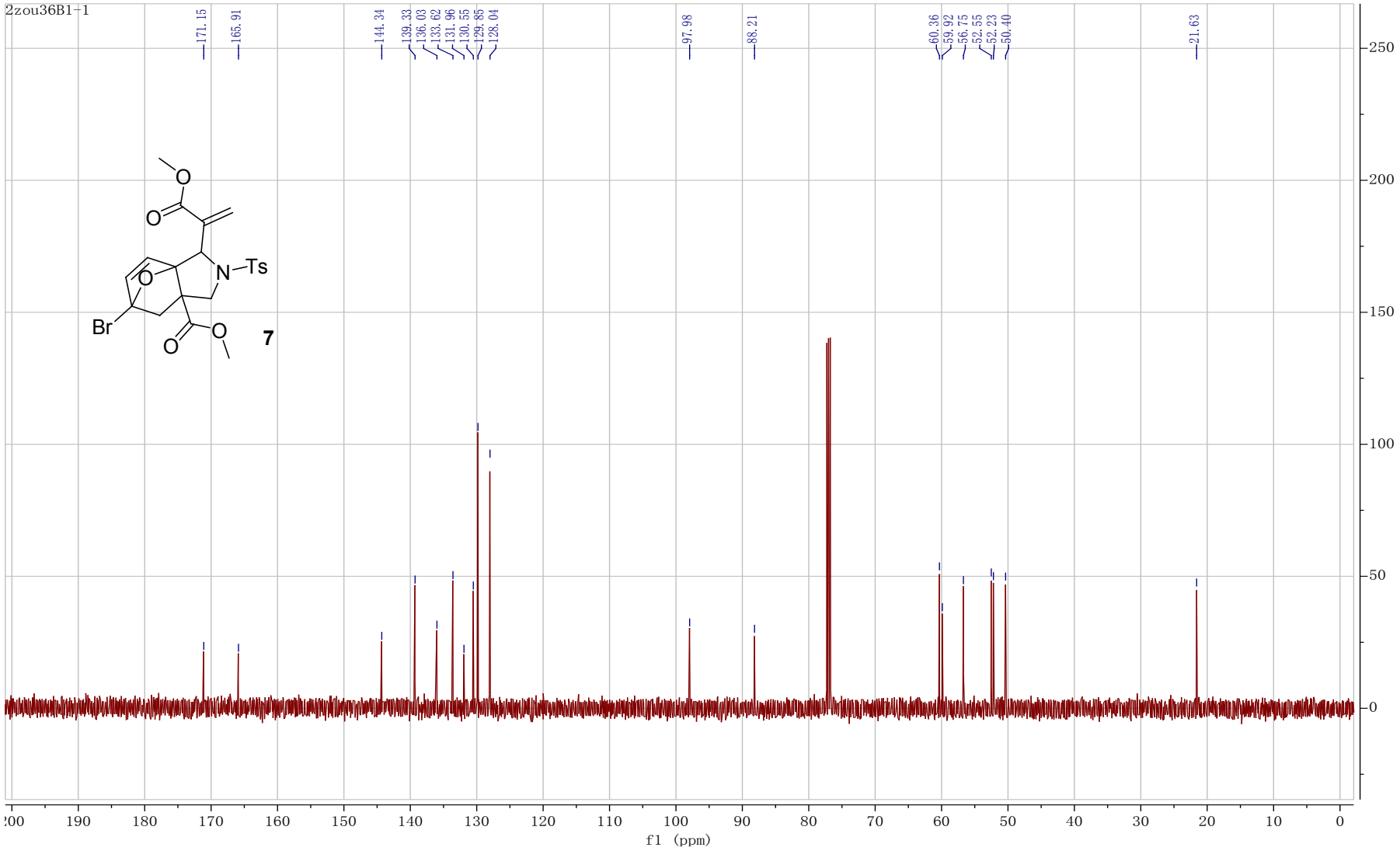

Spectra-84



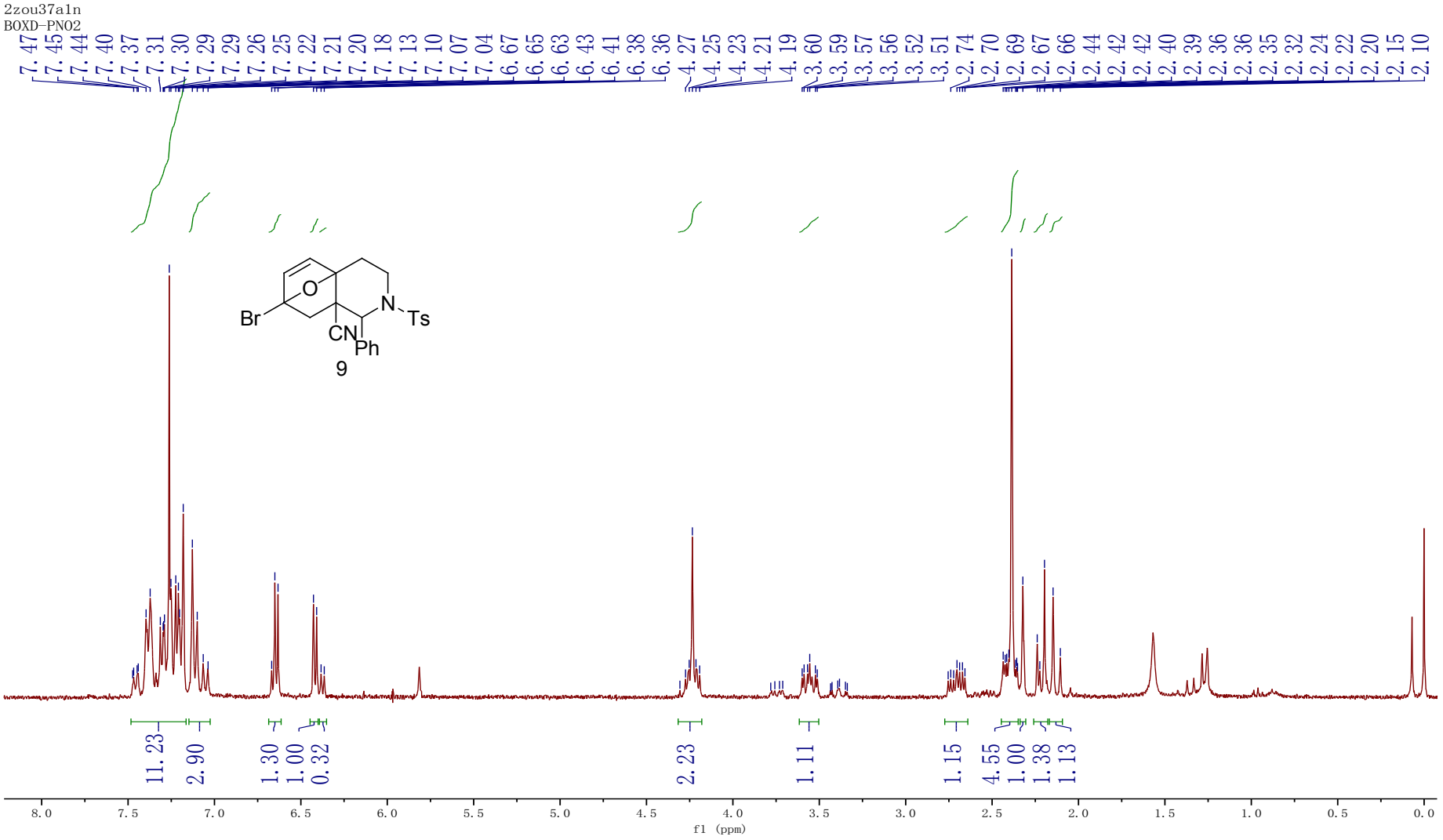

Spectra-85




Spectra-86

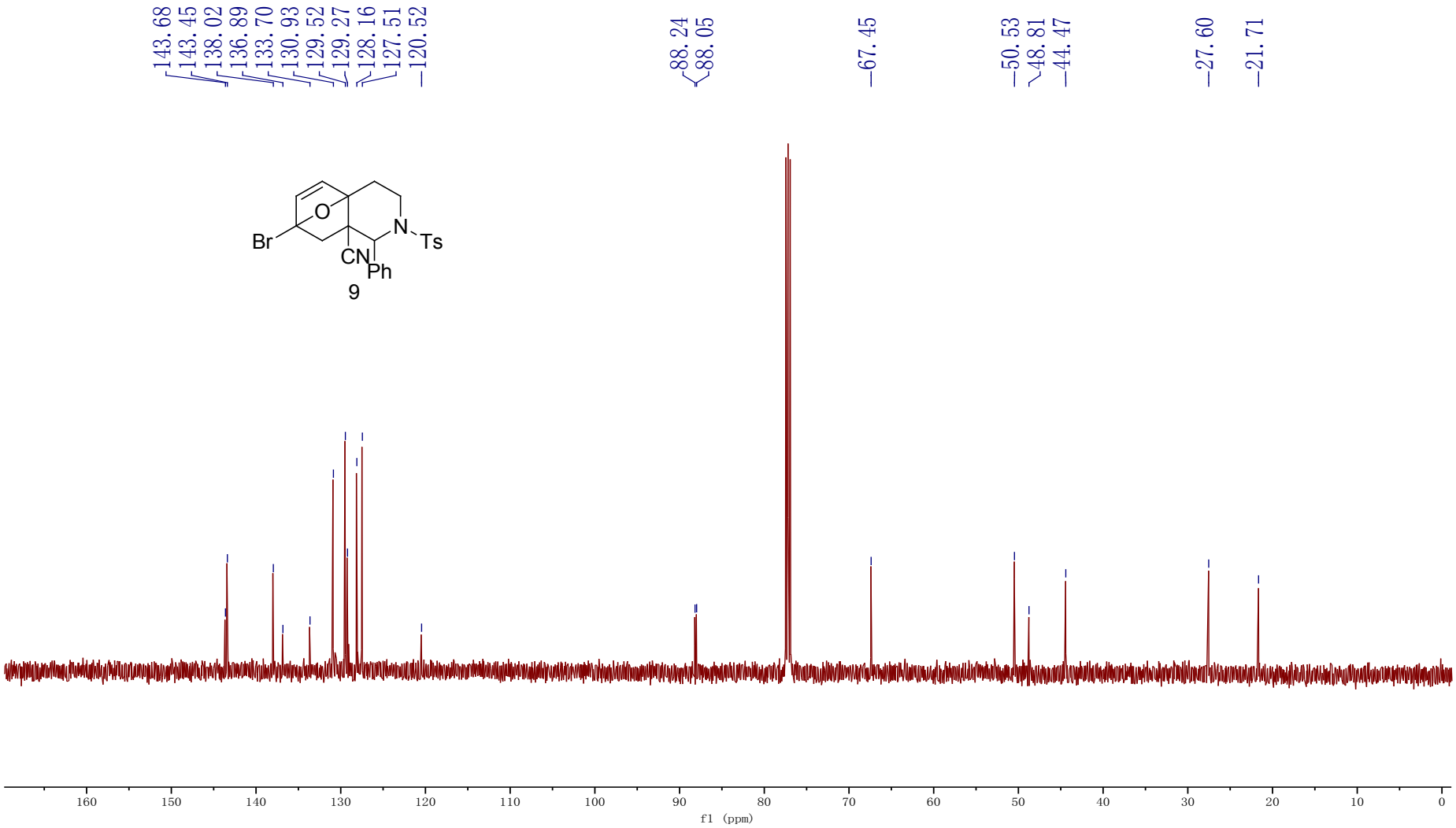



Spectra-87

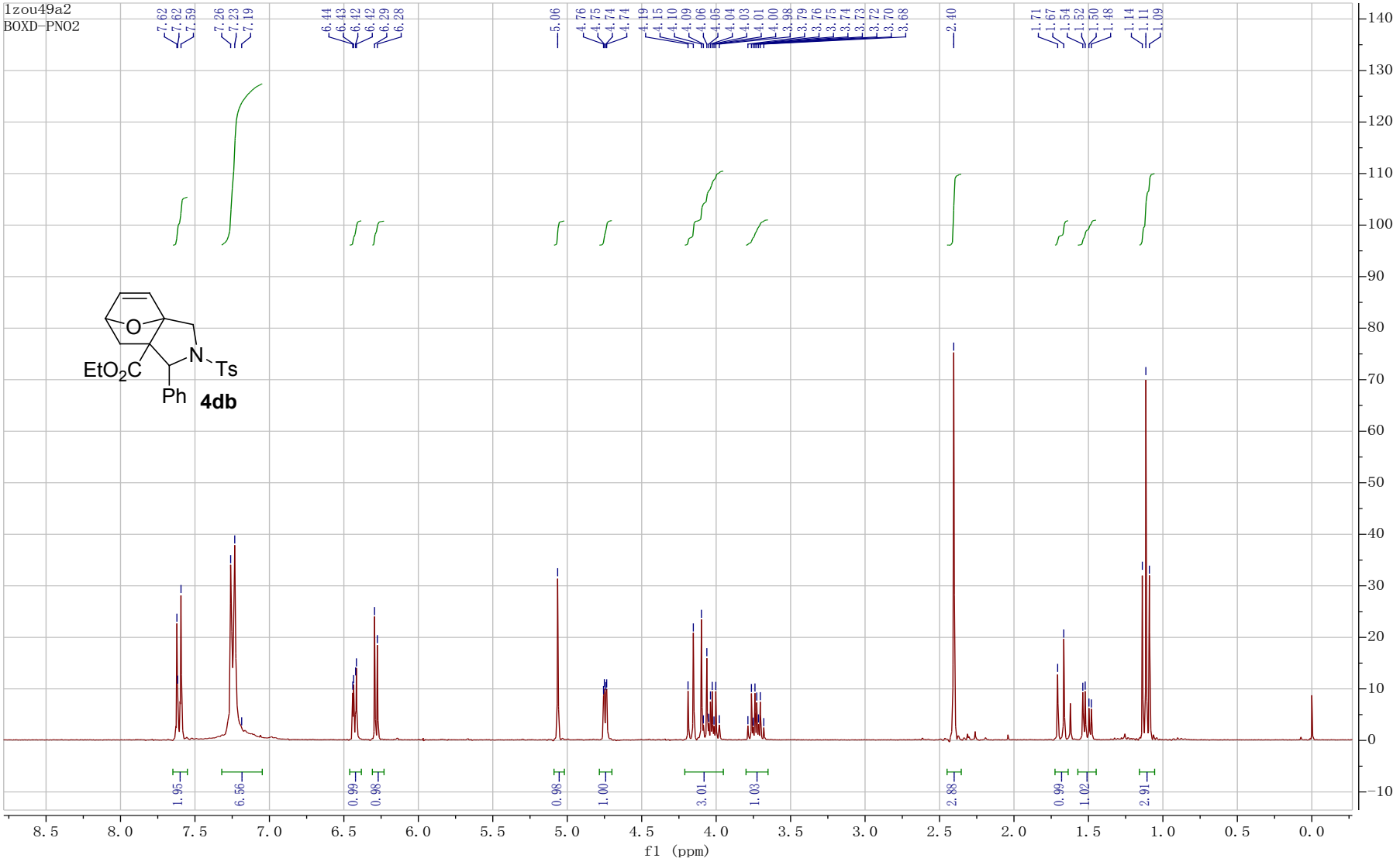



Spectra-88

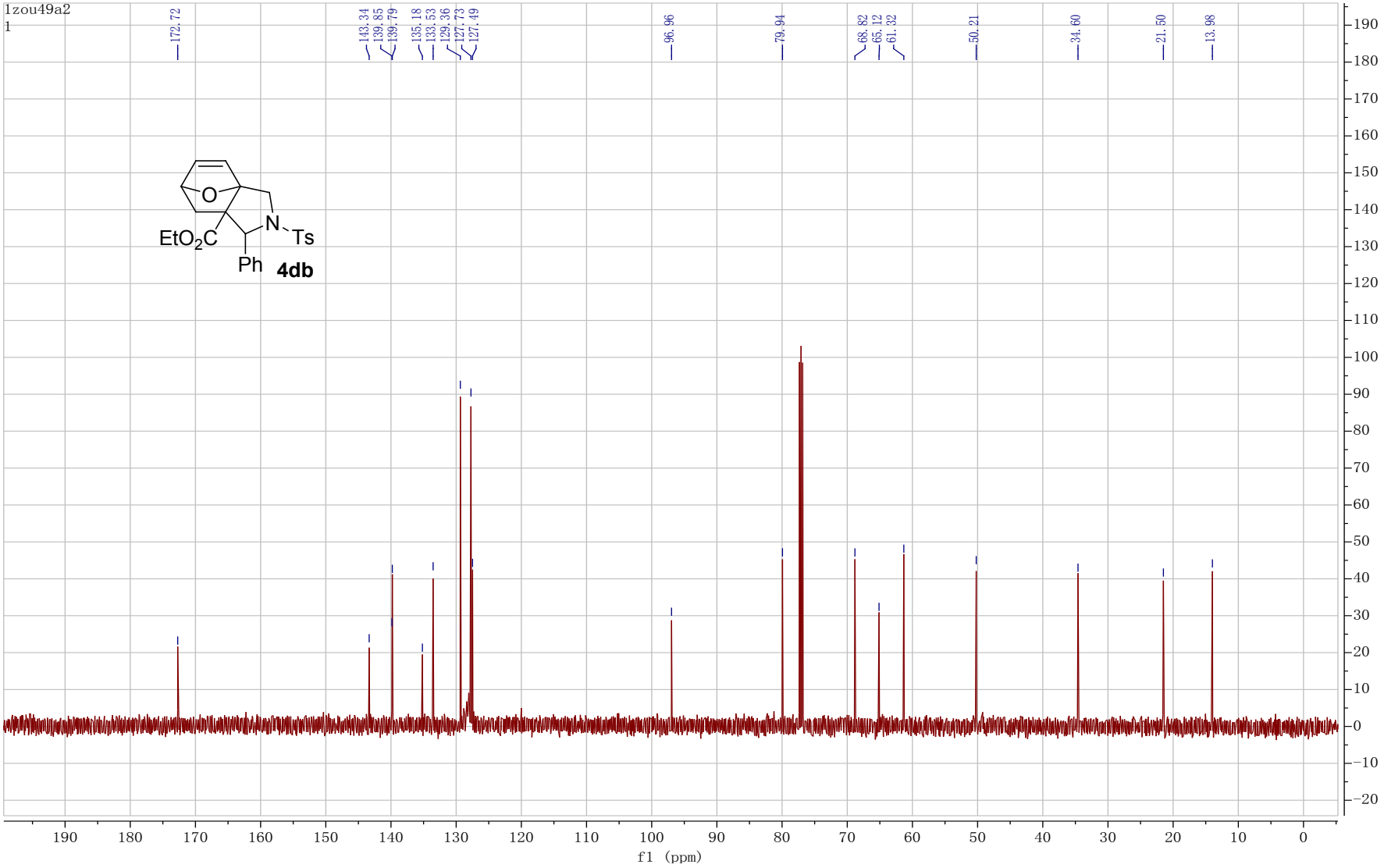
桌面




Spectra-89




Spectra-90

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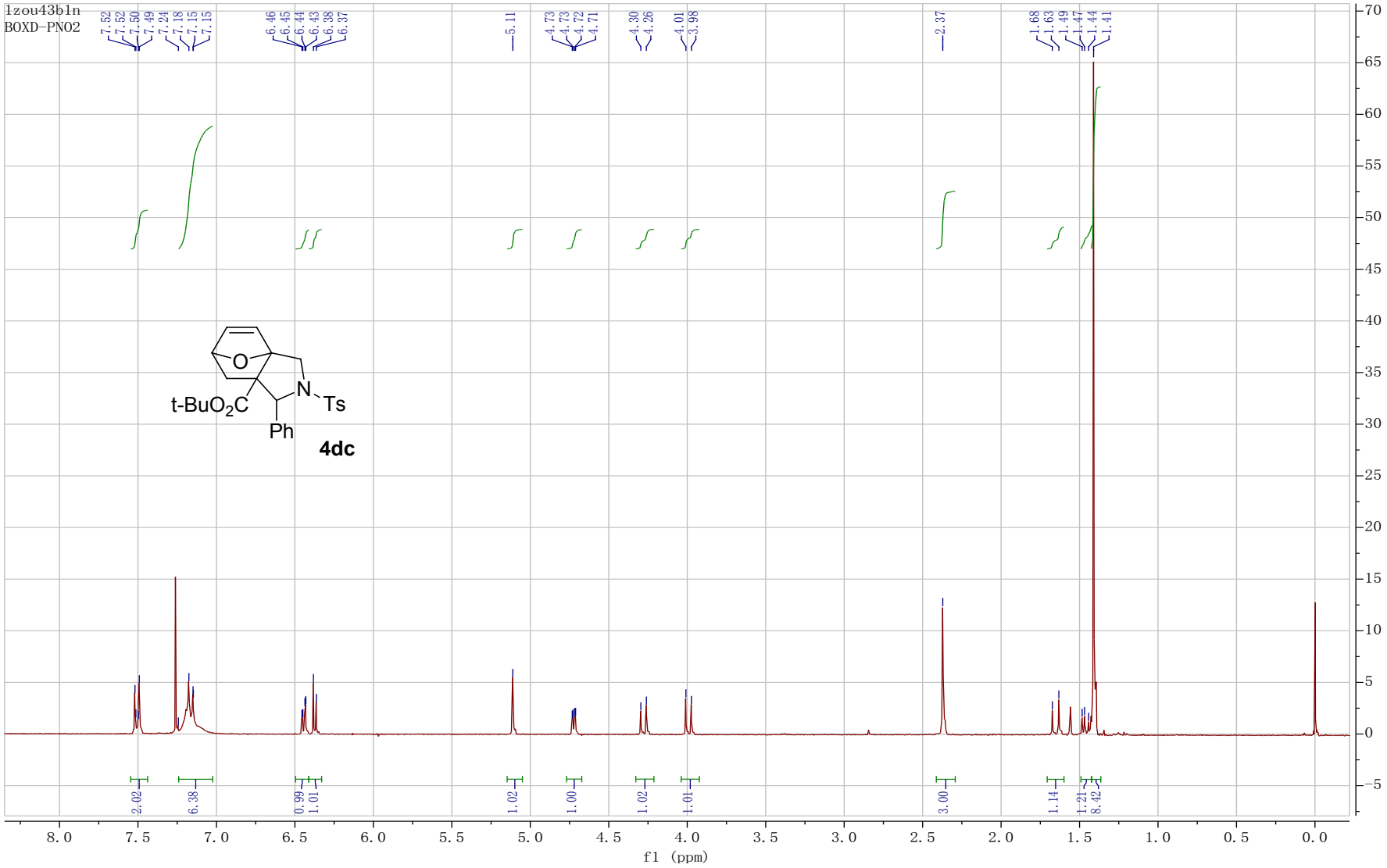


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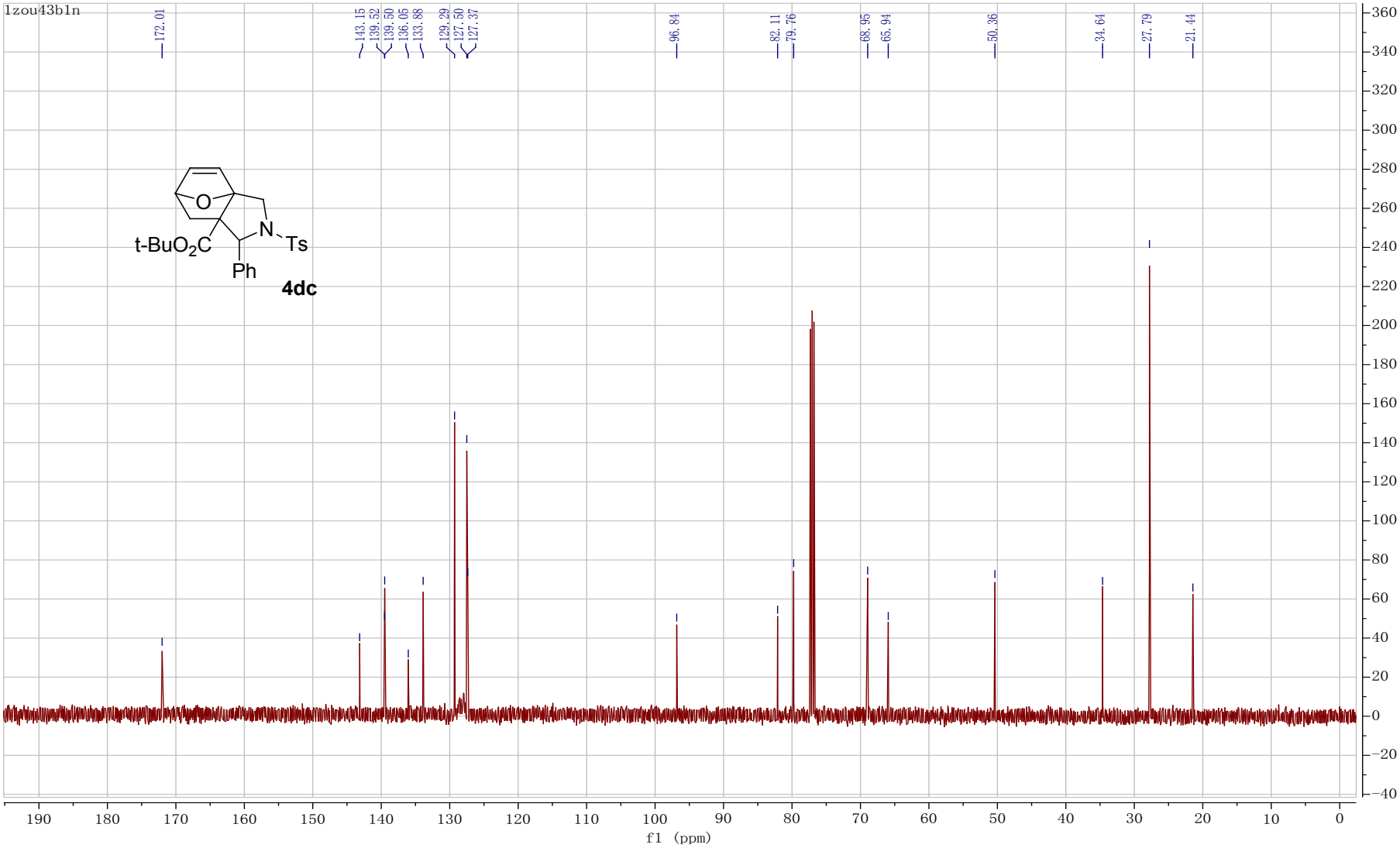


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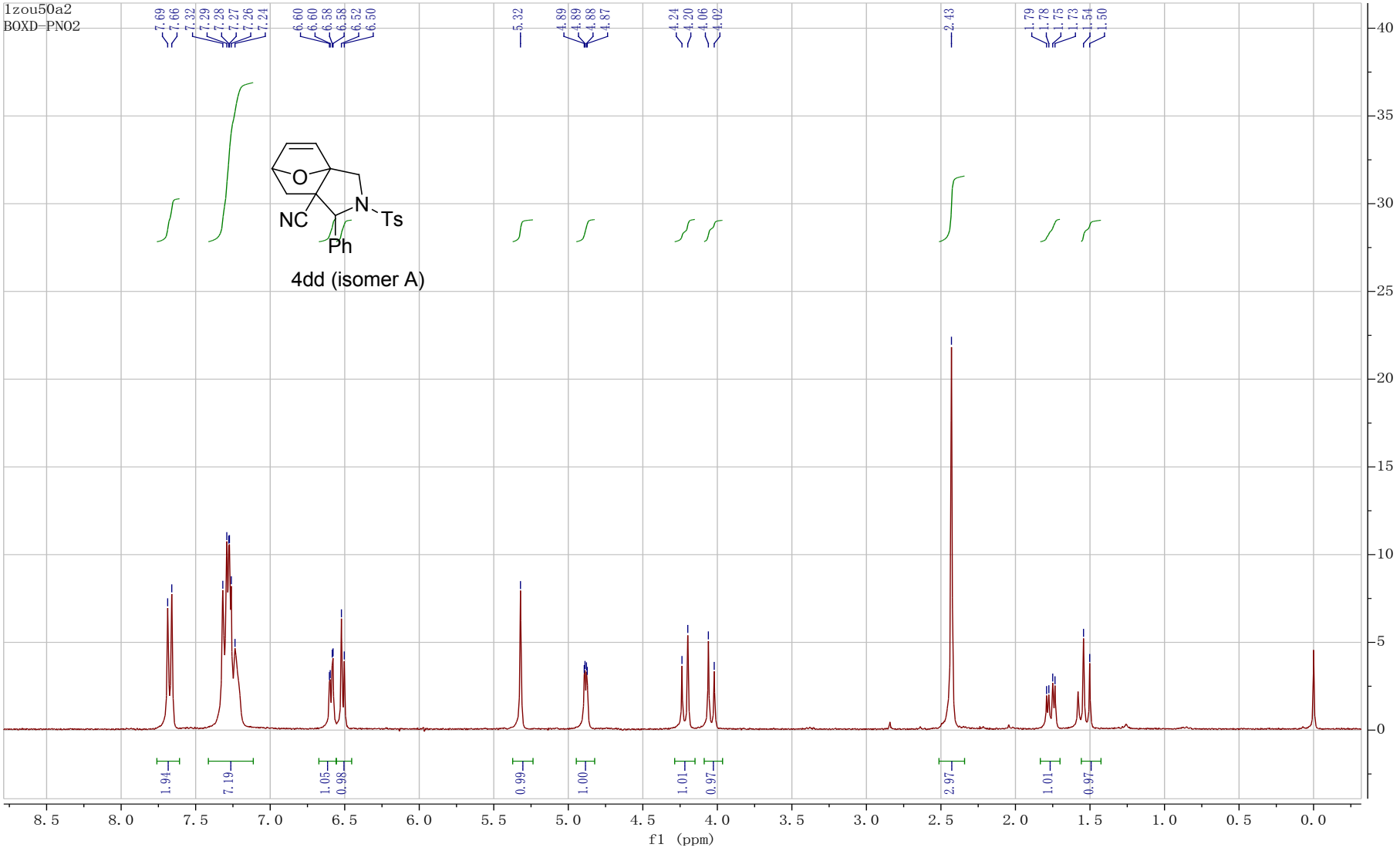


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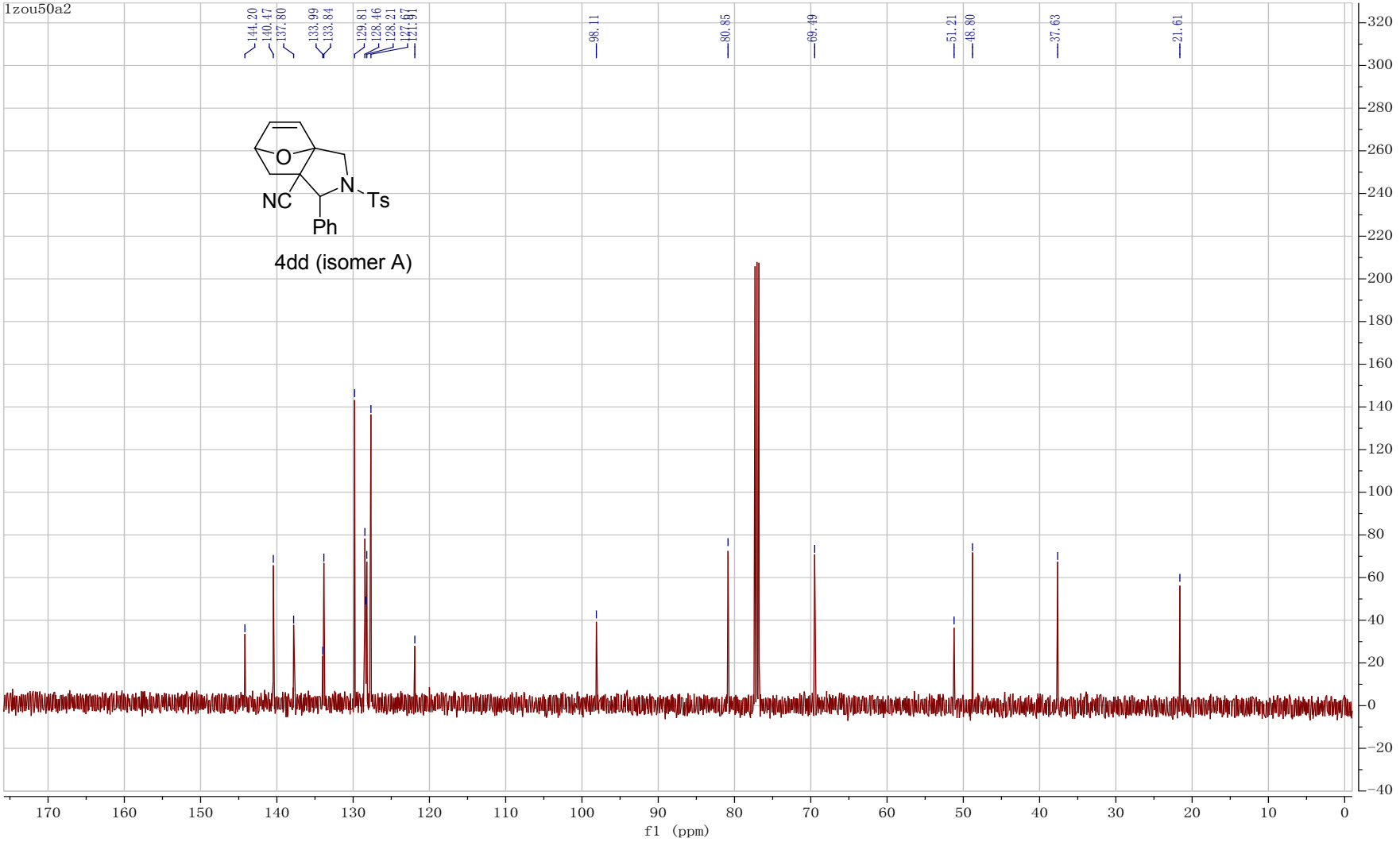


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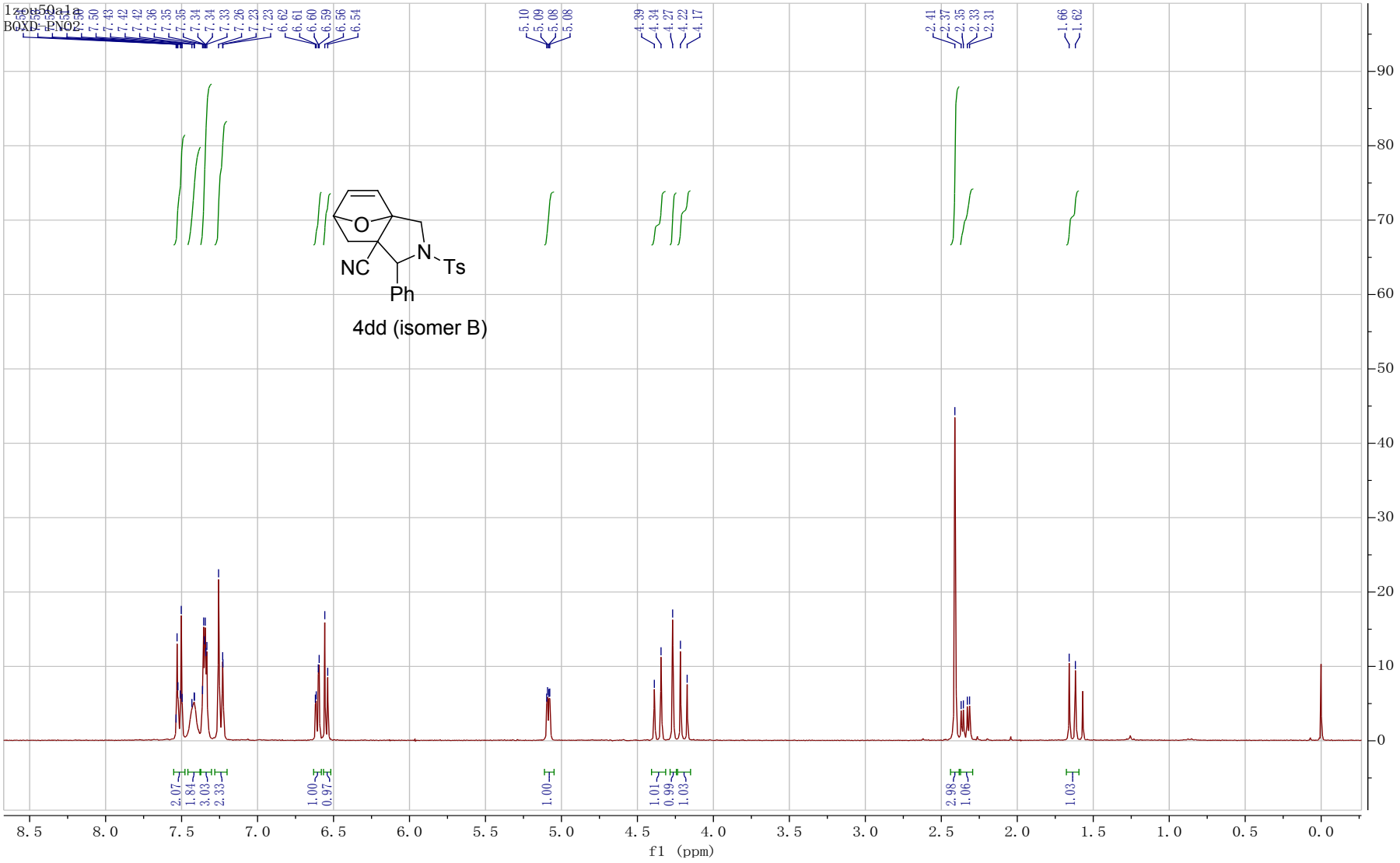


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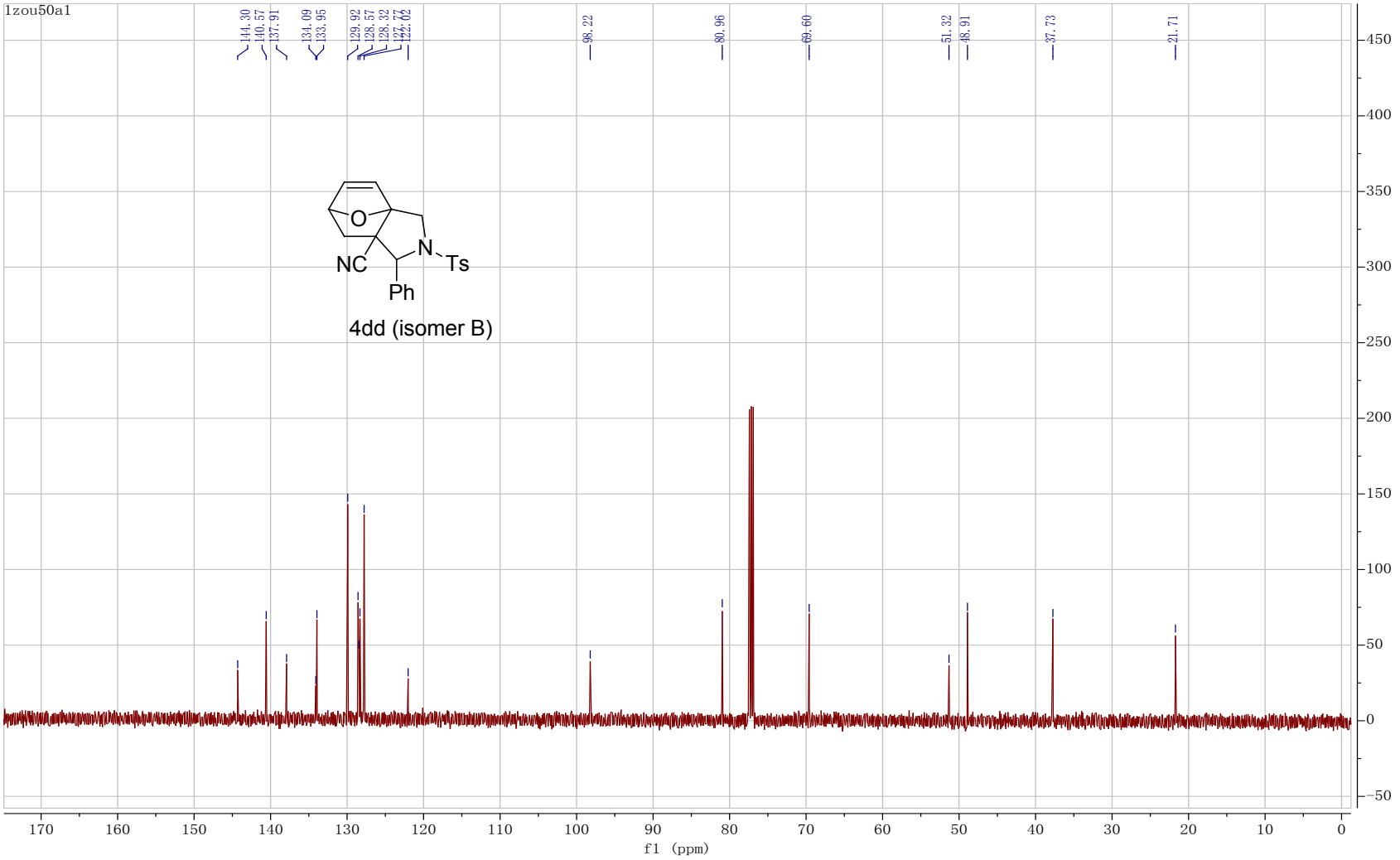

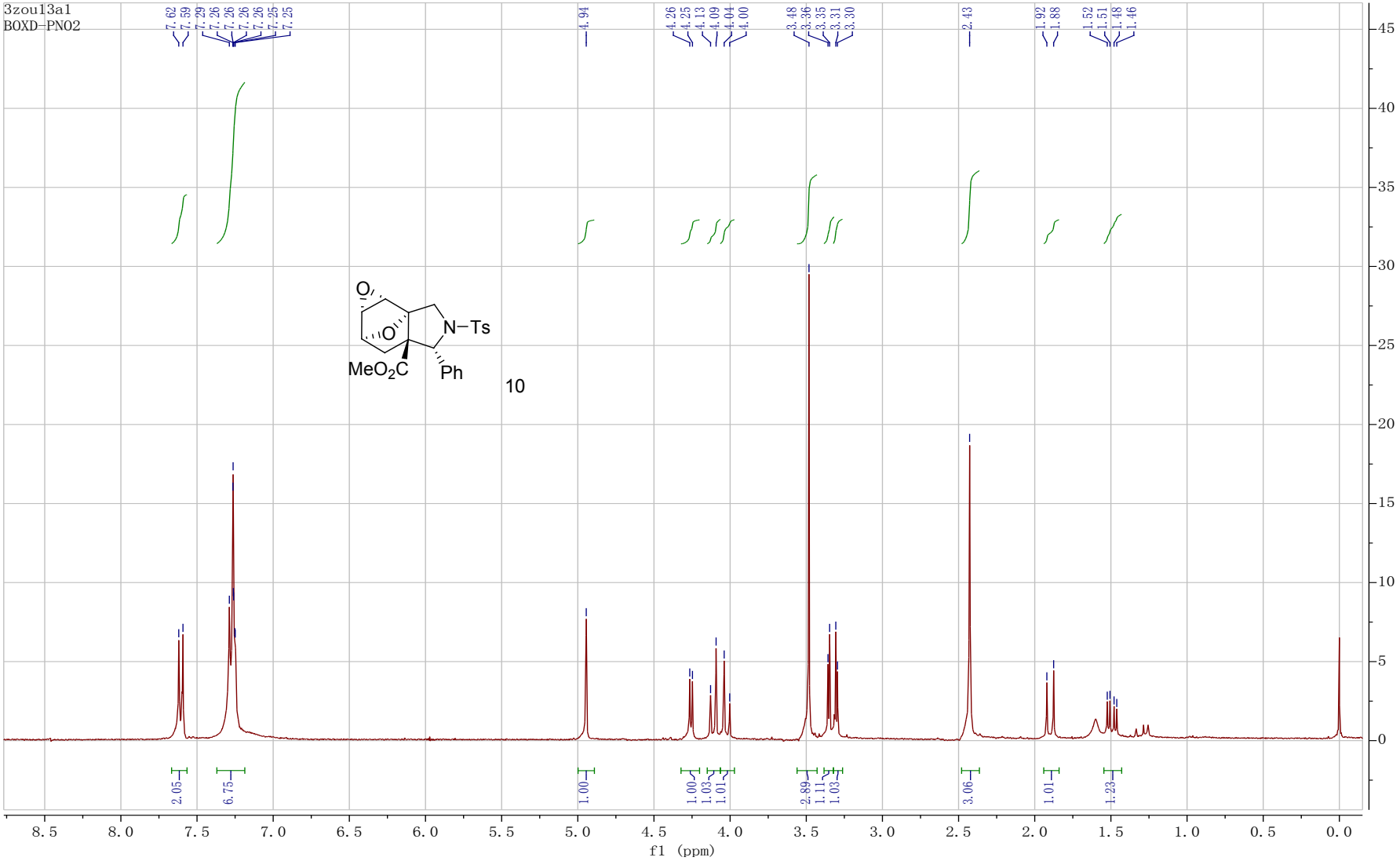


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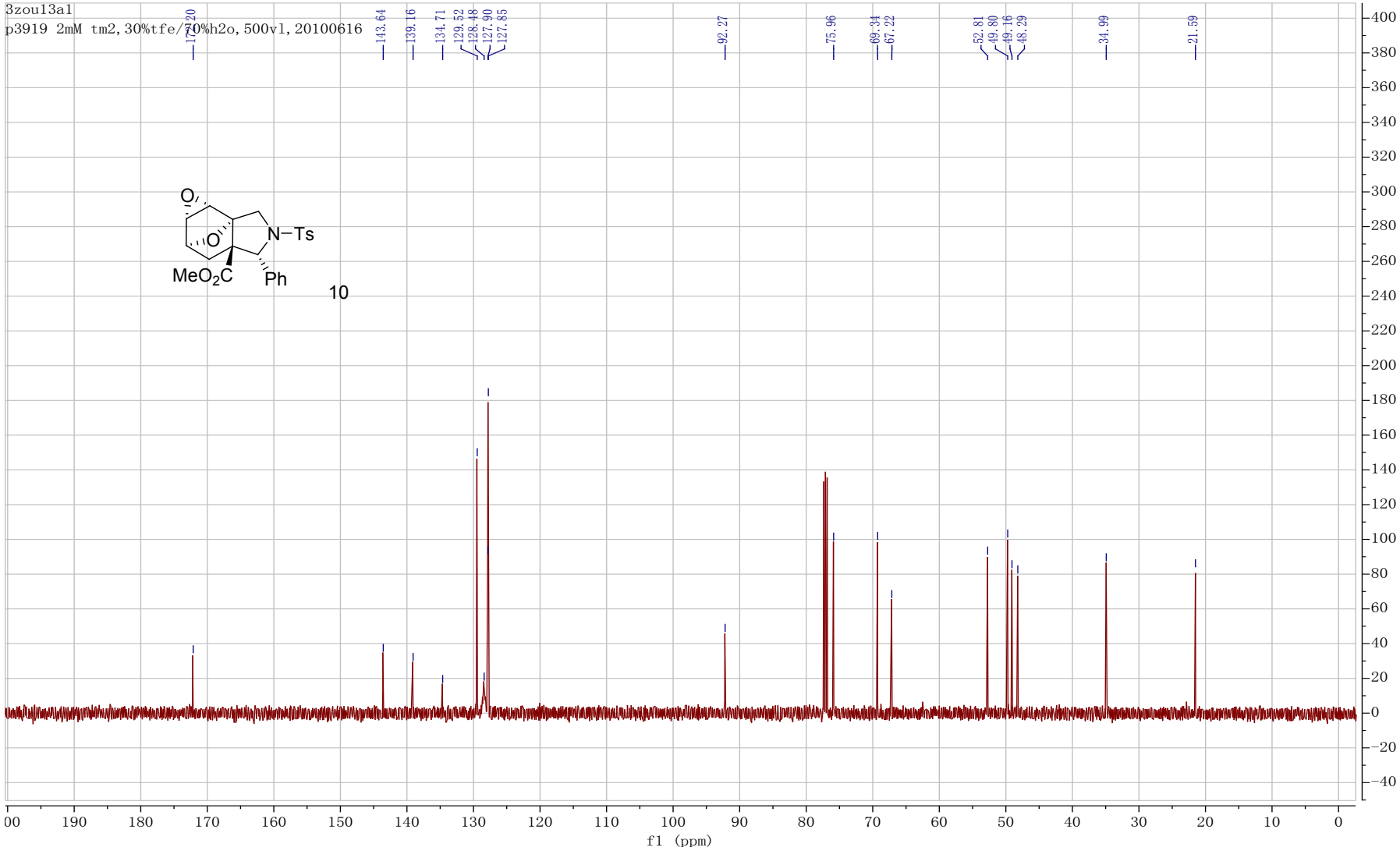


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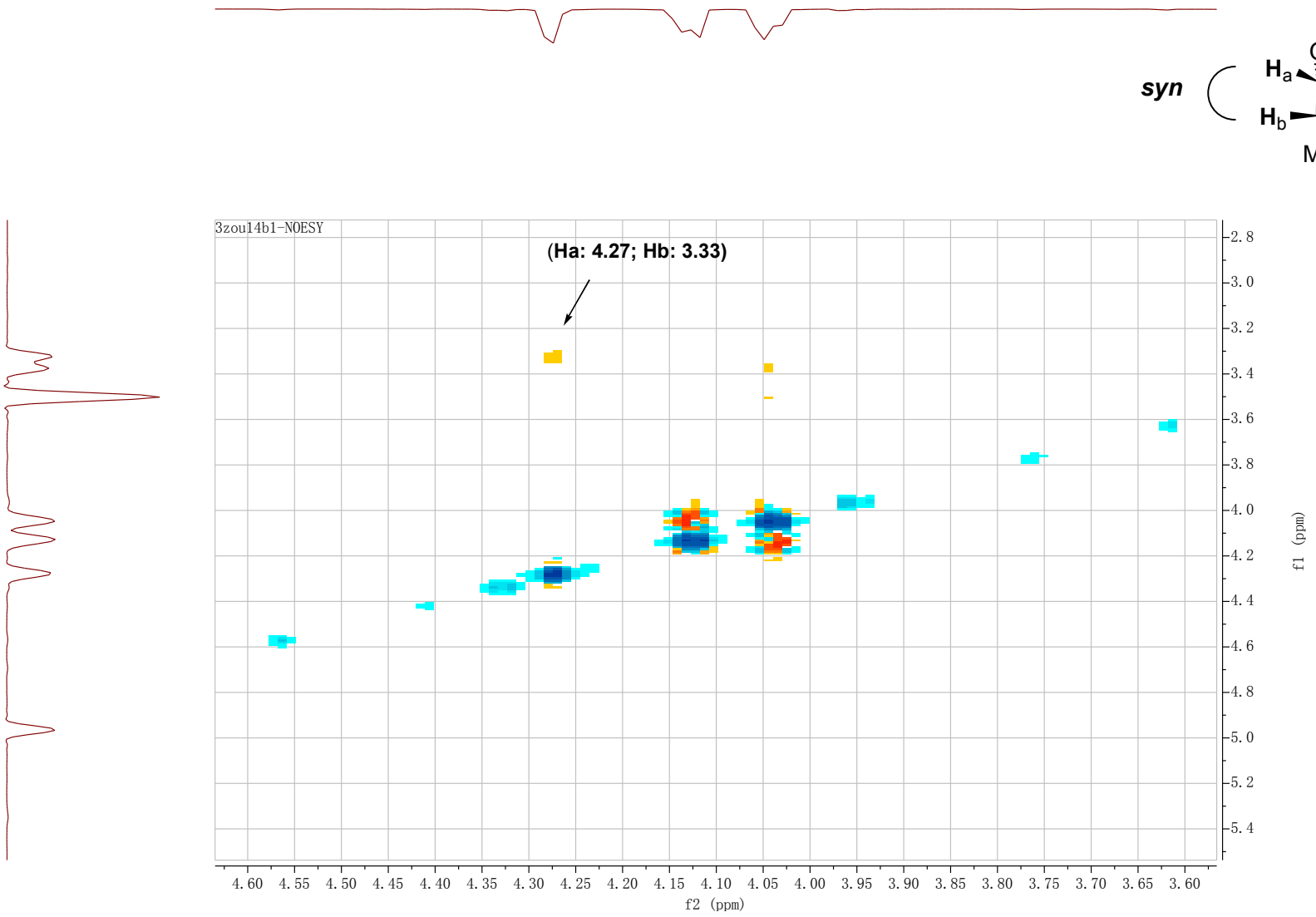





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Spectra-100