

Stereoselective Synthesis of α -(Dichloromethyl)amines, α -(Chloromethyl)amines, and α -Chloroaziridines

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333 Longteng Road, Shanghai 201620, China

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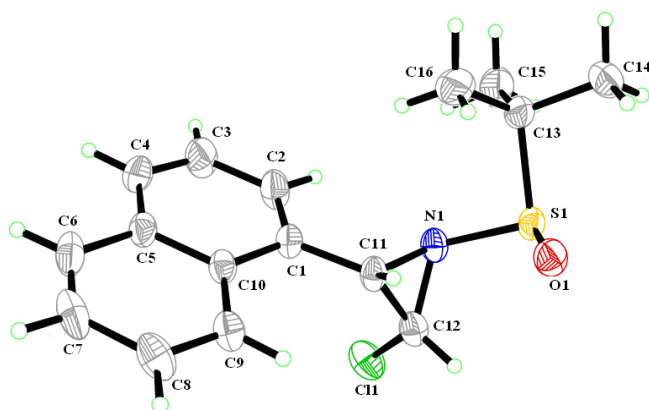
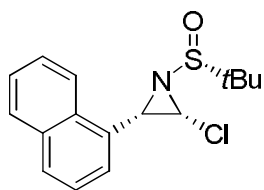
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General Procedures.

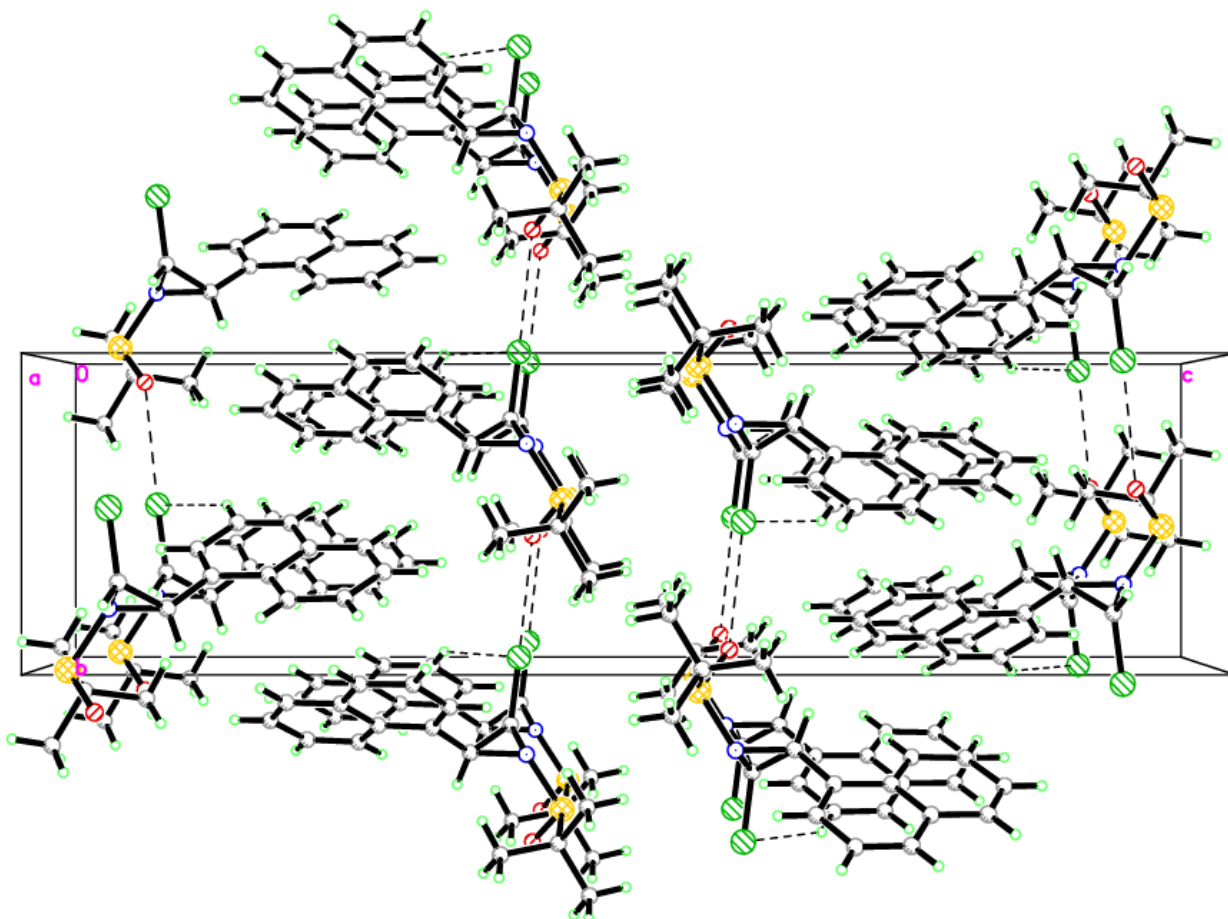
All commercial reagents and solvents were used directly as purchased without further purification. THF was distilled from sodium/benzophenone. N,N-Dimethylformamide was distilled from CaH₂. Flash chromatography was performed on silica gel with petroleum ether (PE)/EtOAc as the eluent. Melting points were uncorrected. Optical rotations were measured with a sodium lamp. ¹H NMR spectra were recorded at 400 MHz. Decoupled ¹³C NMR spectra were recorded at 100 MHz at the given temperatures. Chemical shifts (δ) are reported in parts per million and referenced to the residual solvent peak, and *J* values are given in hertz (Hz).

Determination of the configuration of compound 5c



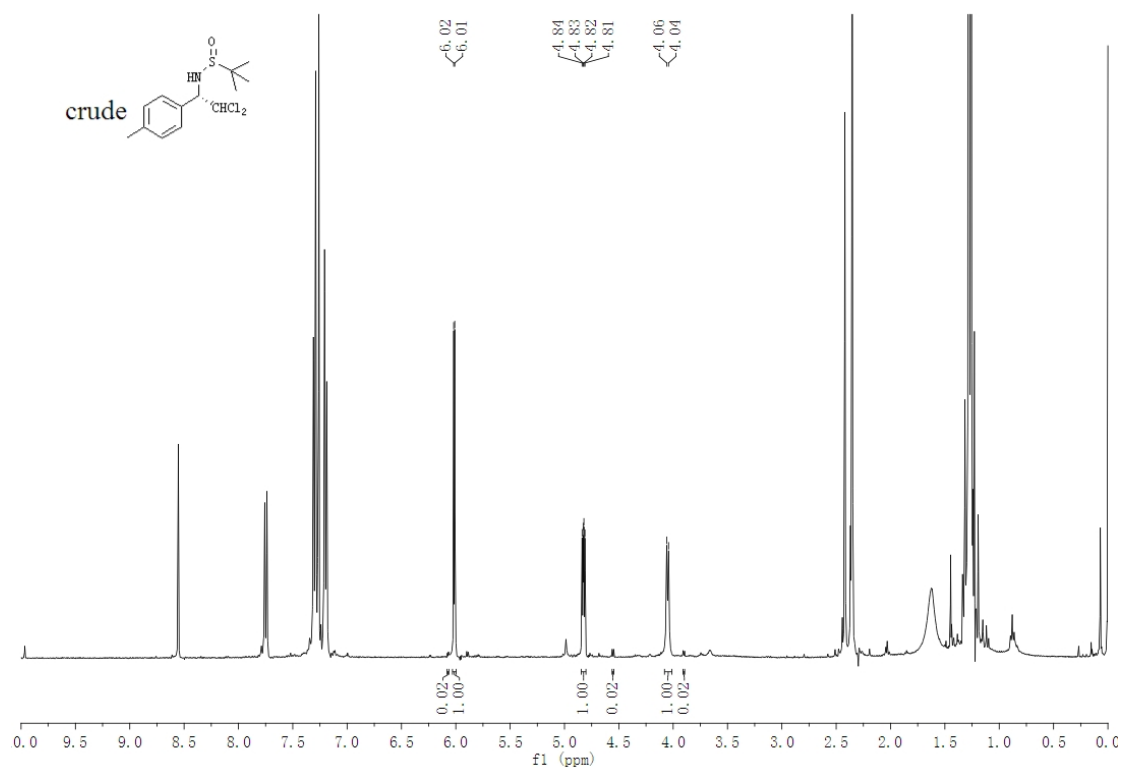
Packing view of compound 5c

The Cl \cdots O distance is 3.183Å

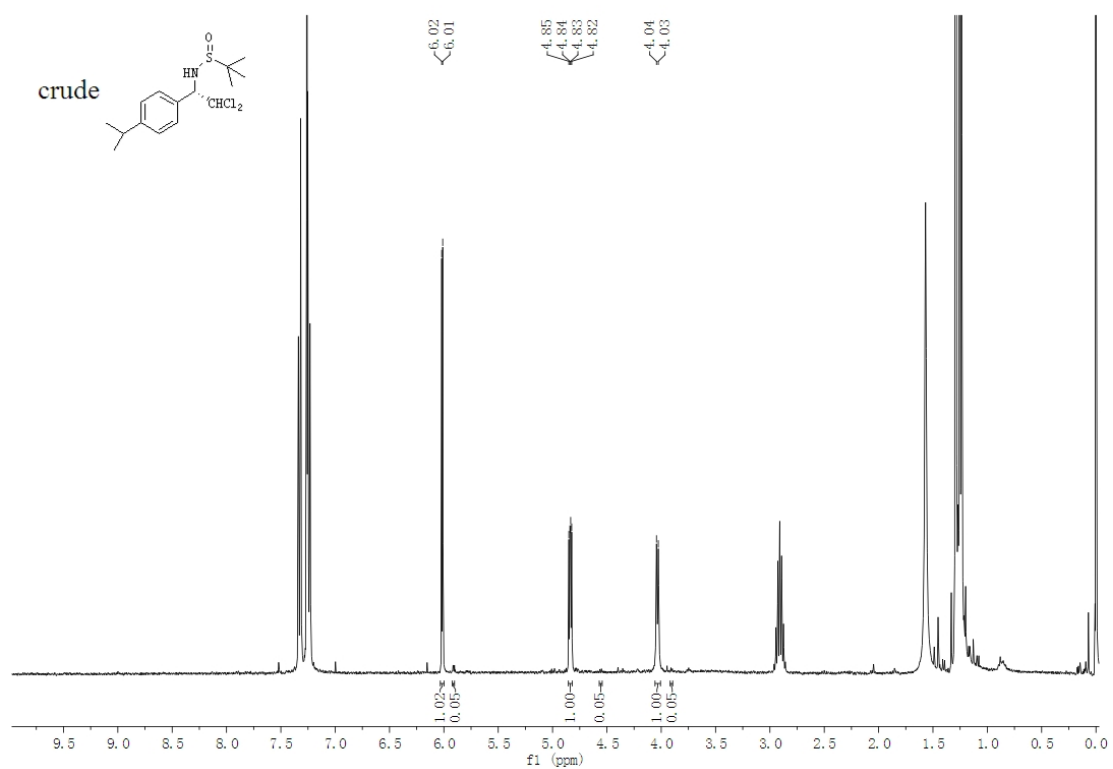


¹H NMR Spectra of the crude products 3

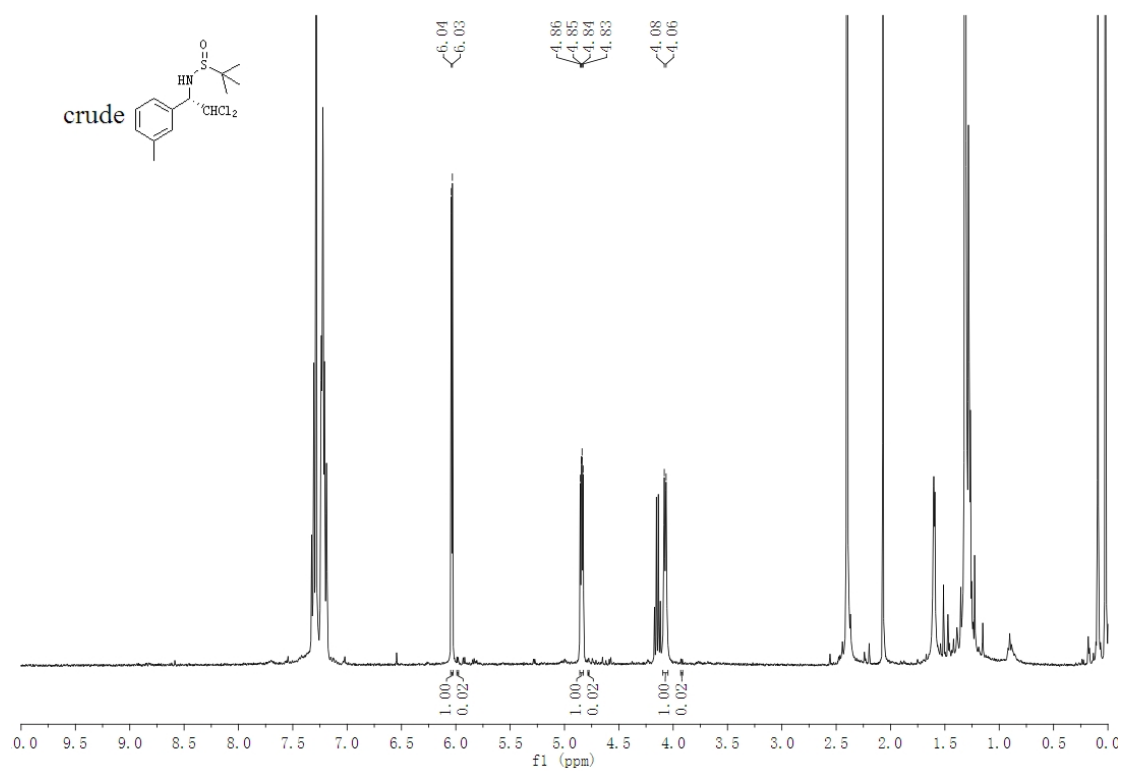
¹H NMR of crude product 3a



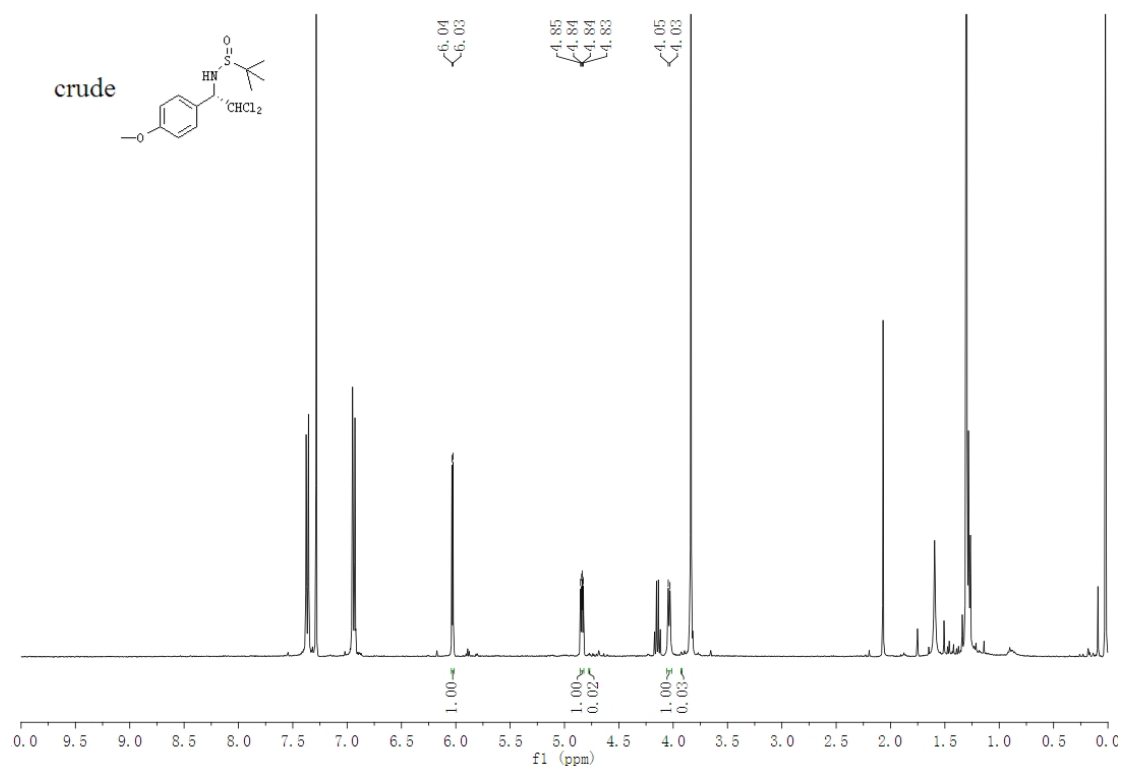
¹H NMR of crude product 3b



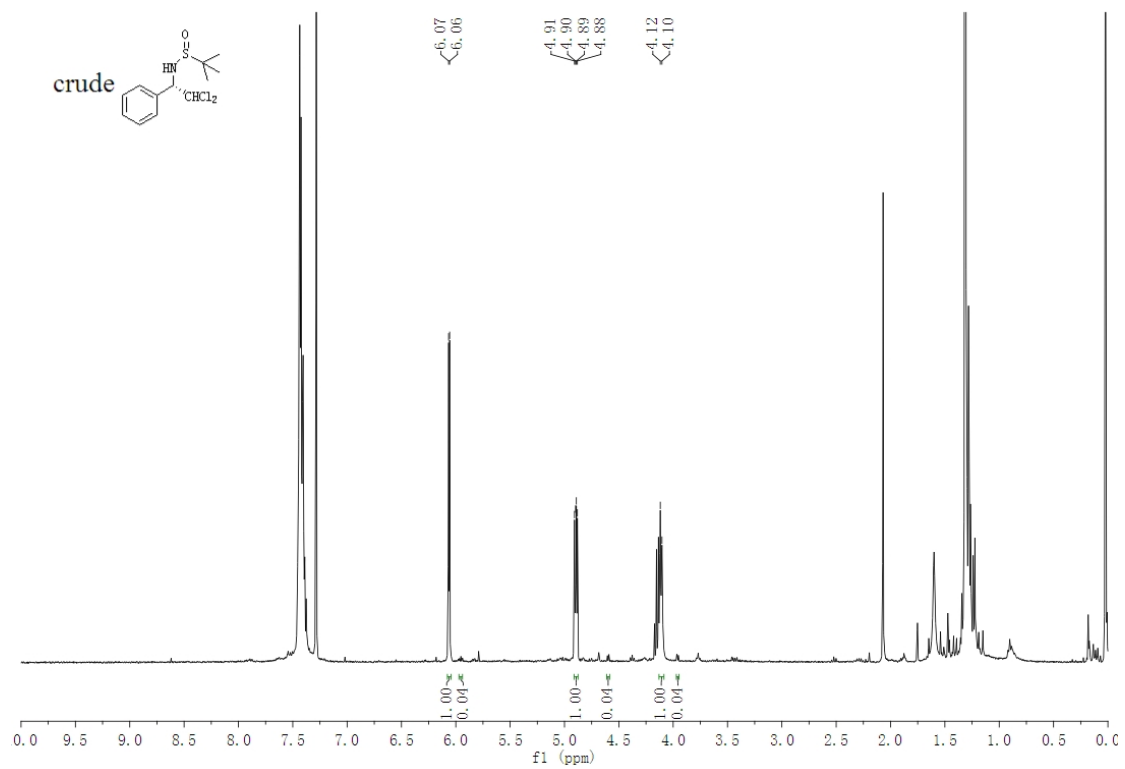
¹H NMR of crude product **3c**



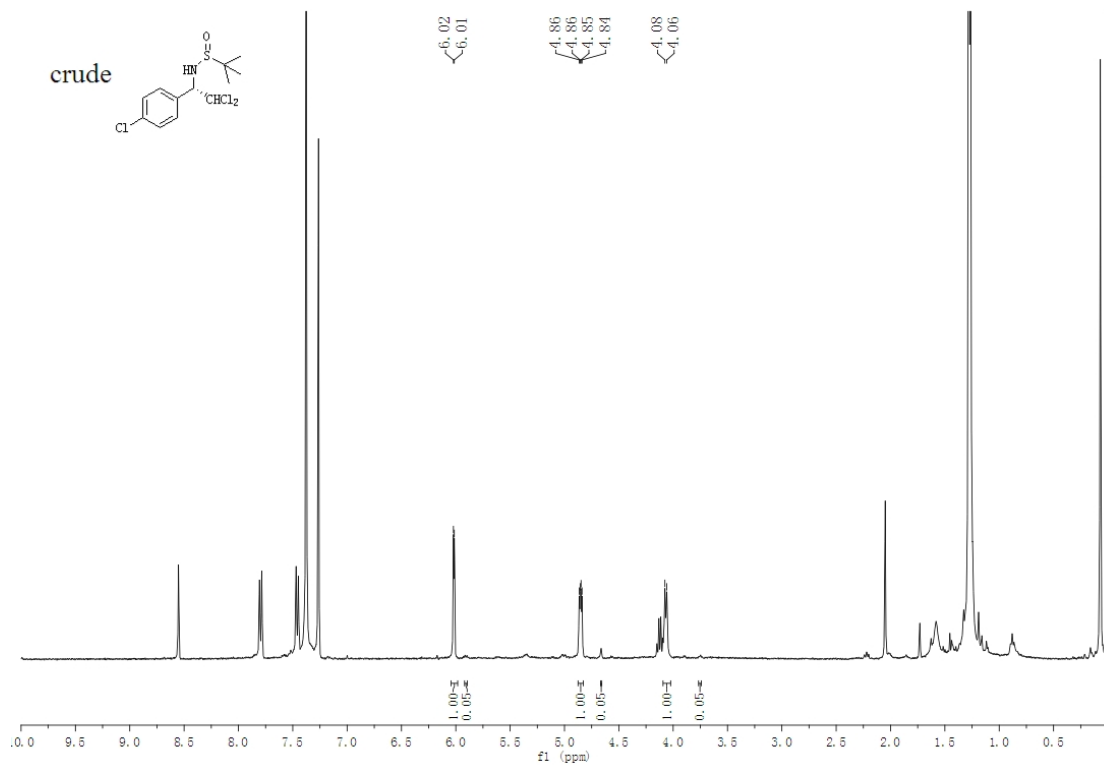
¹H NMR of crude product **3d**



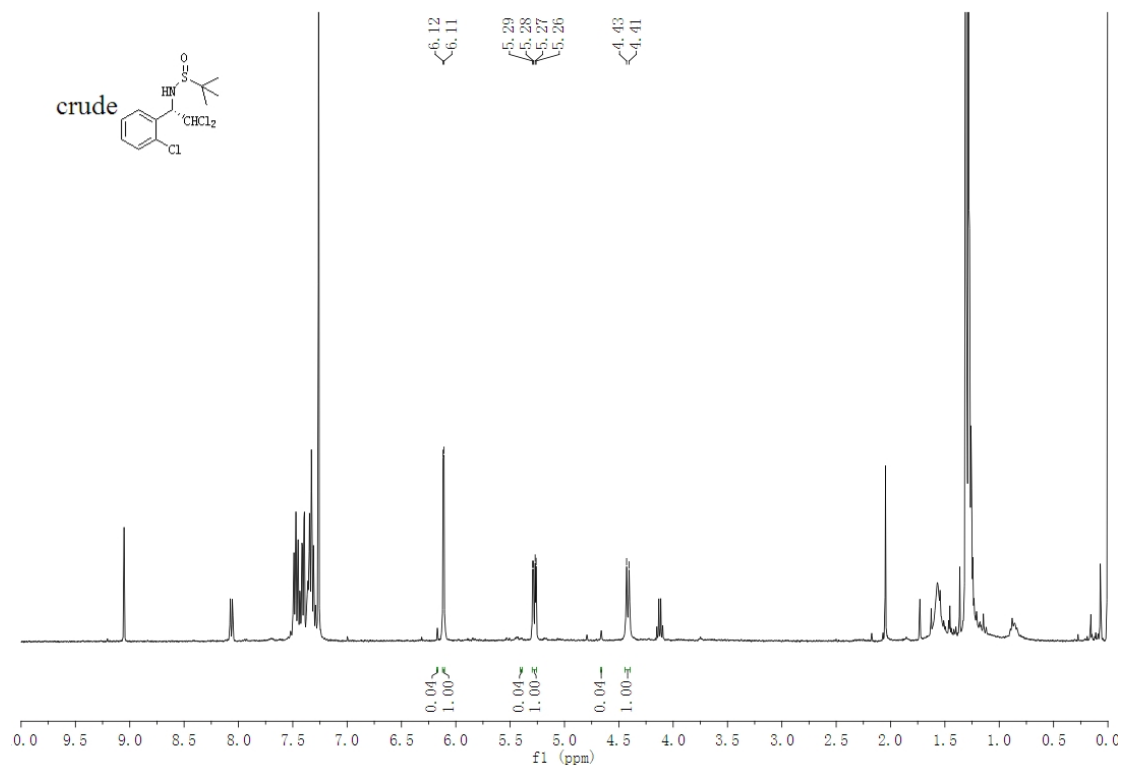
¹H NMR of crude product 3e



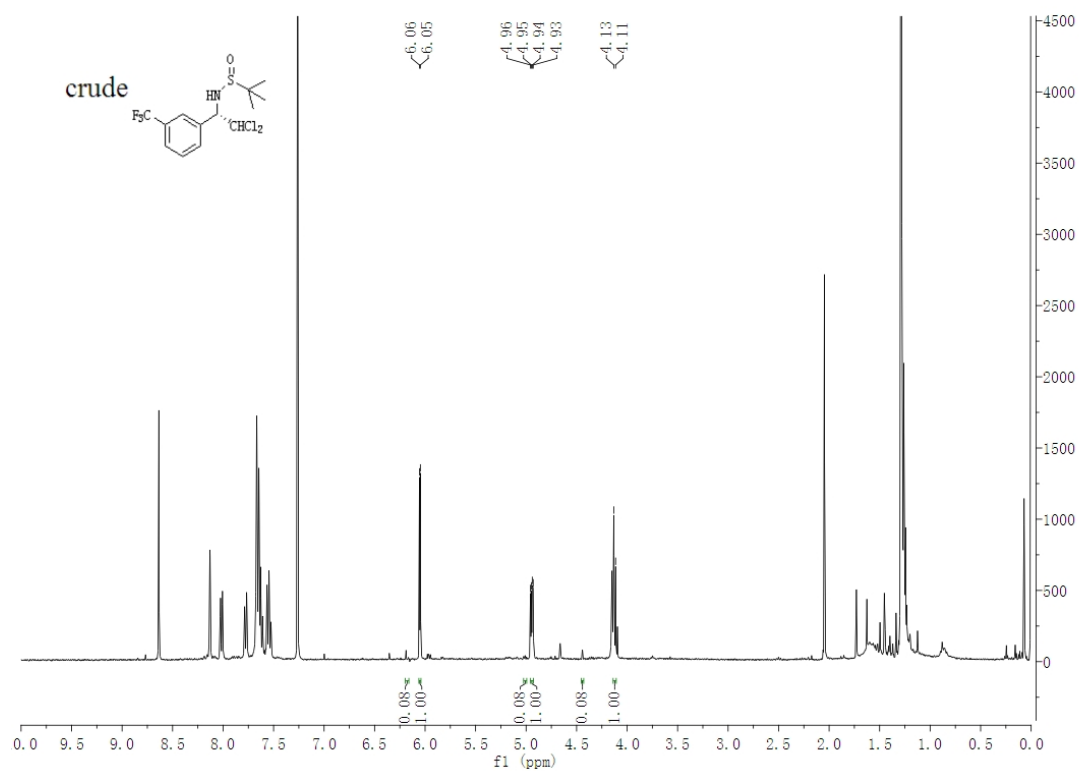
¹H NMR of crude product 3f



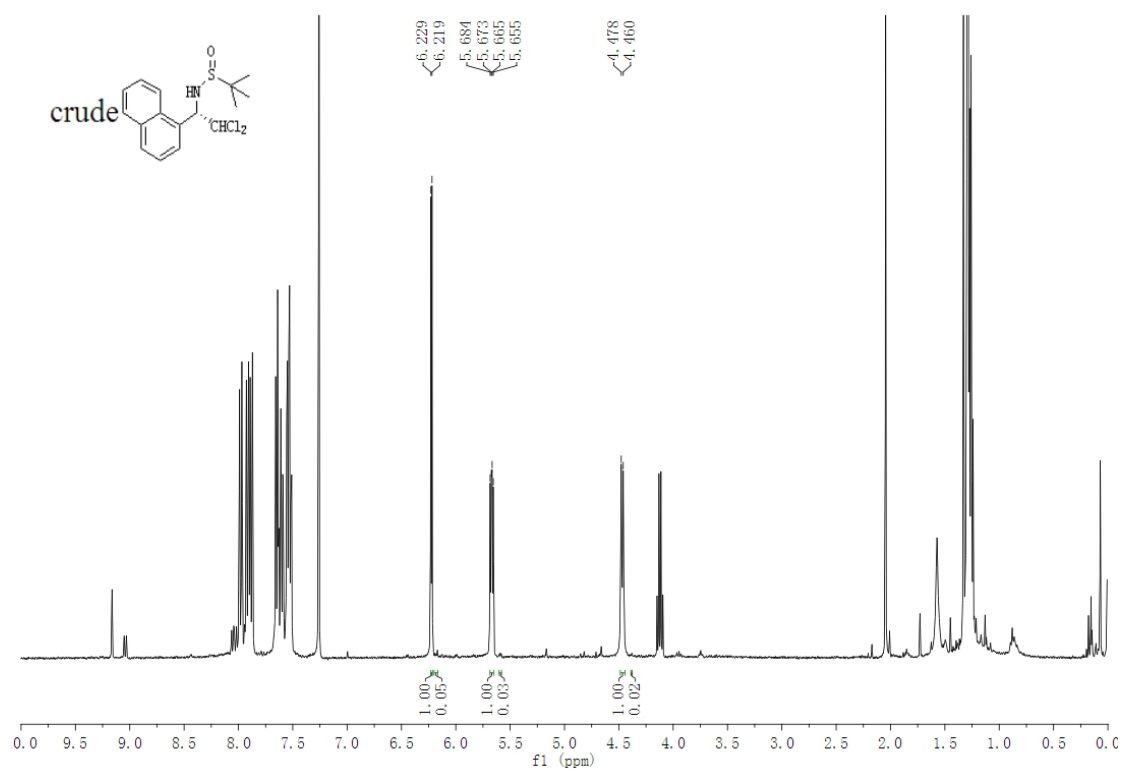
¹H NMR of crude product **3g**



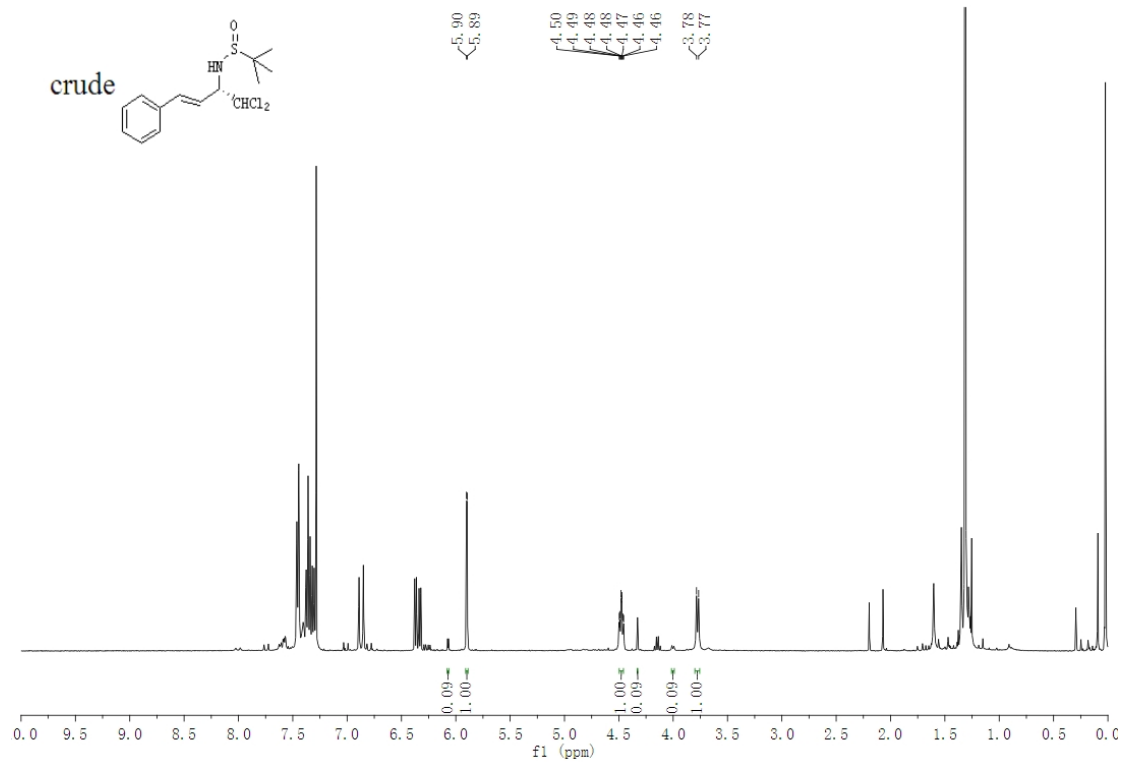
¹H NMR of crude product **3h**



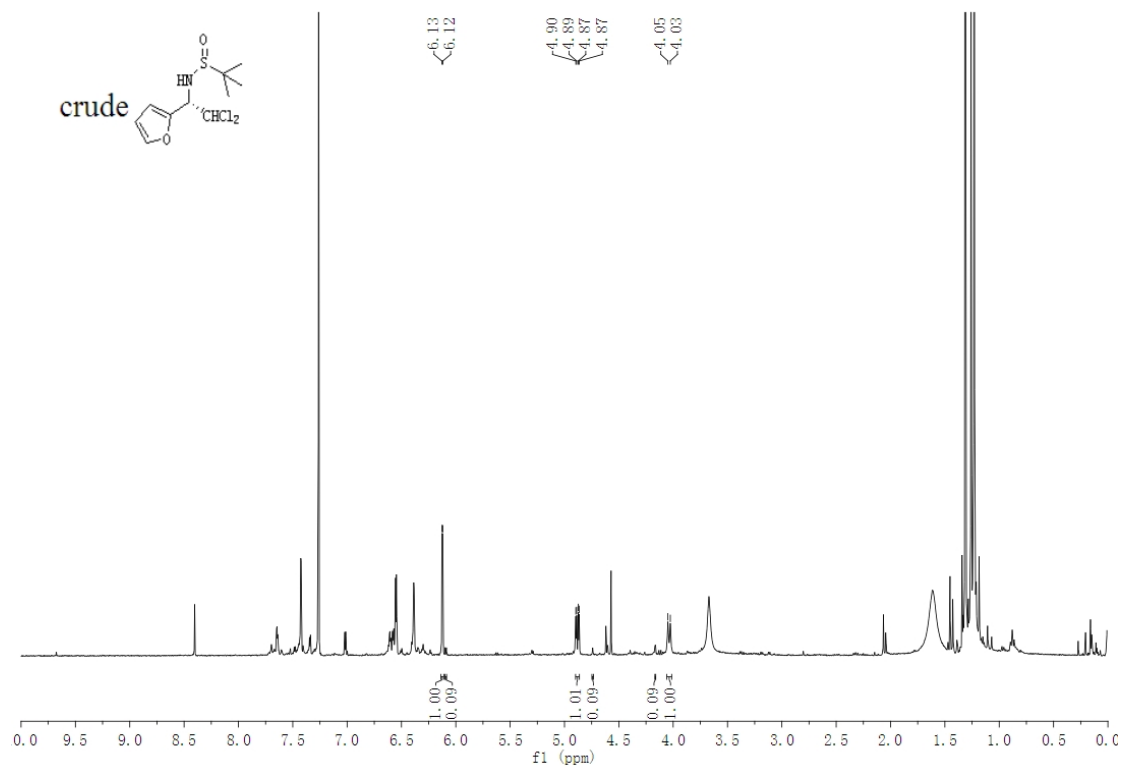
¹H NMR of crude product 3i



¹H NMR of crude product 3j

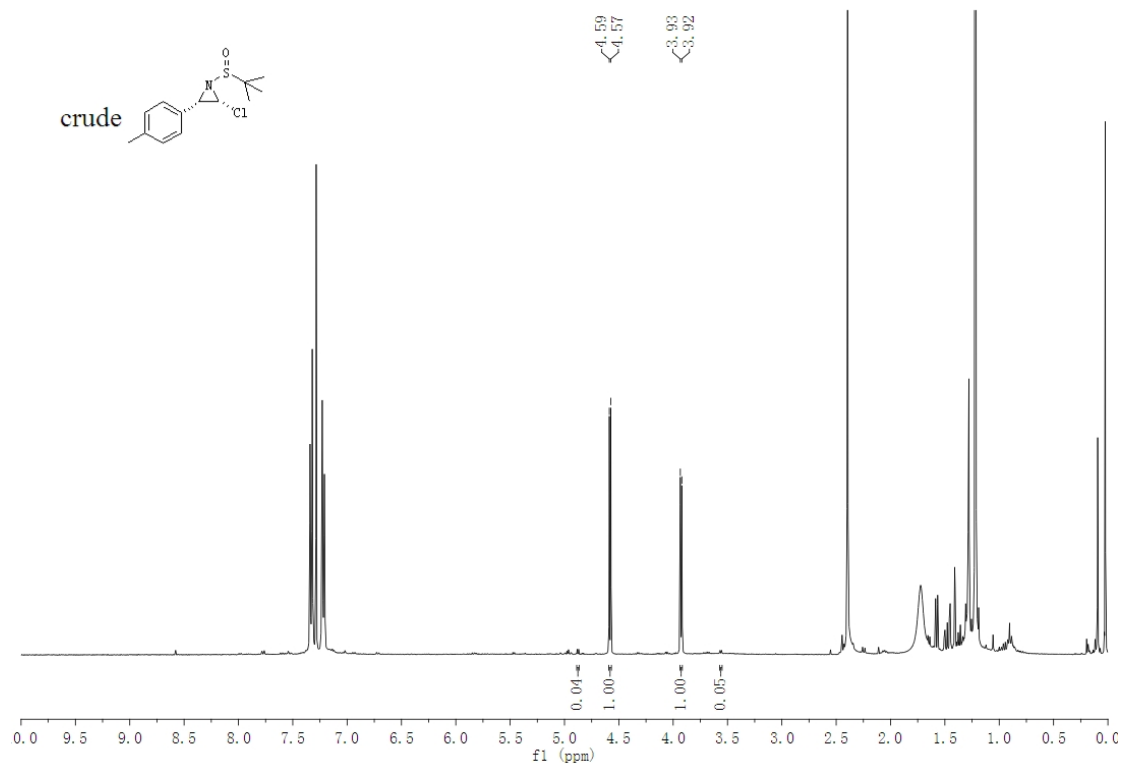


¹H NMR of crude product **3k**

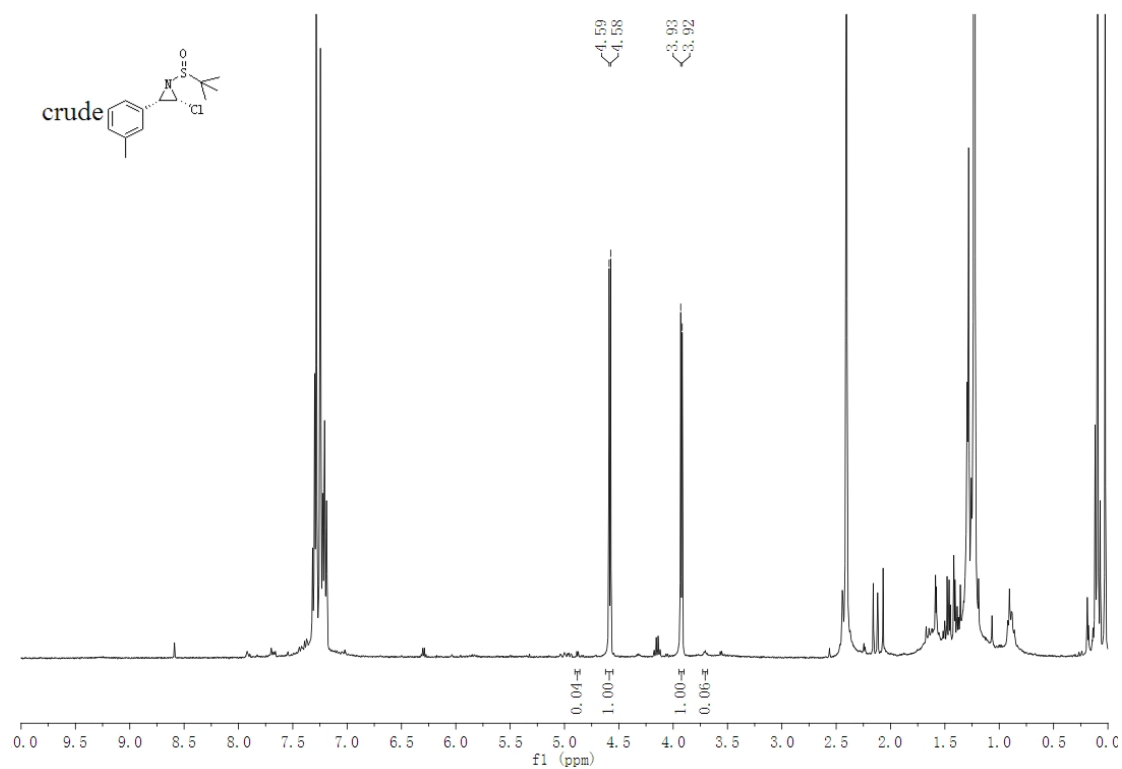


¹H NMR Spectra of the crude products **5**

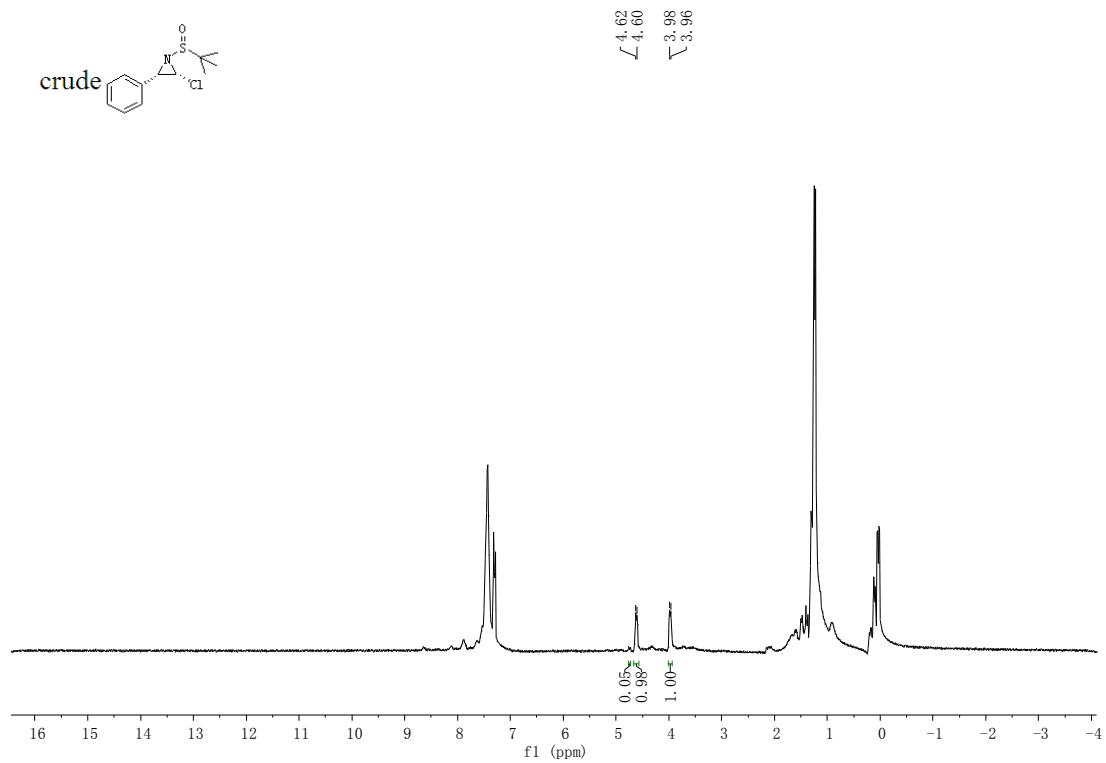
¹H NMR of crude product **5a**



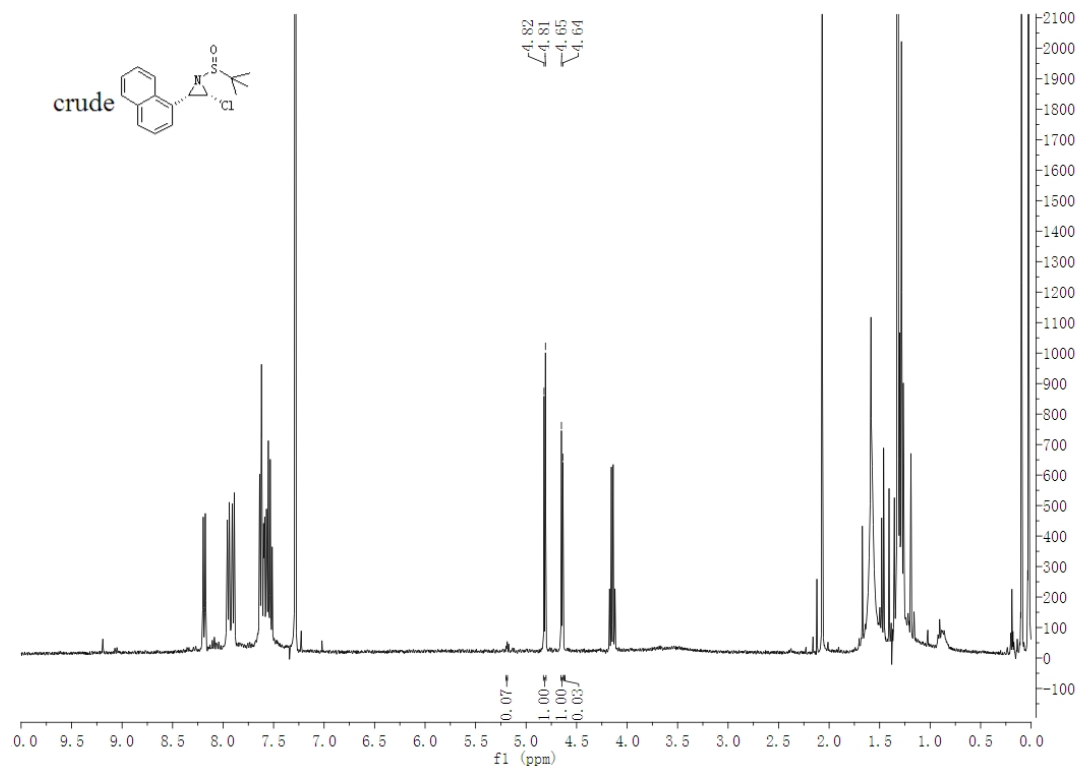
¹H NMR of crude product **5b**



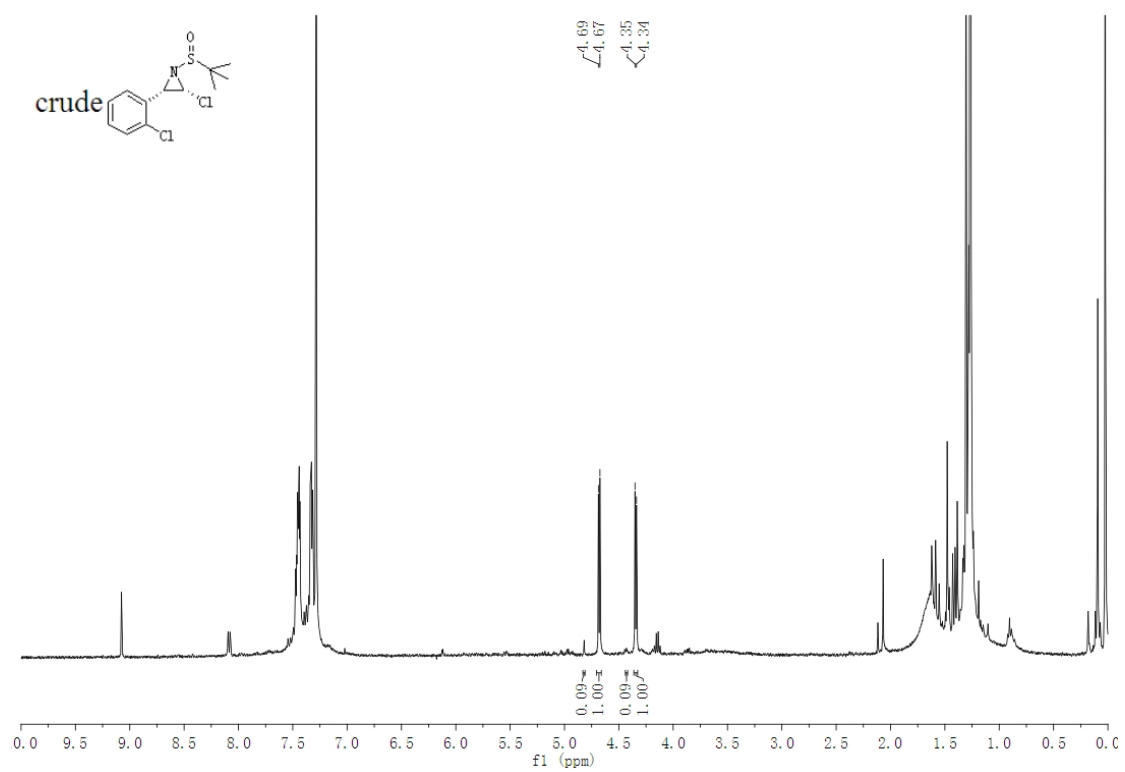
¹H NMR of crude product **5c**



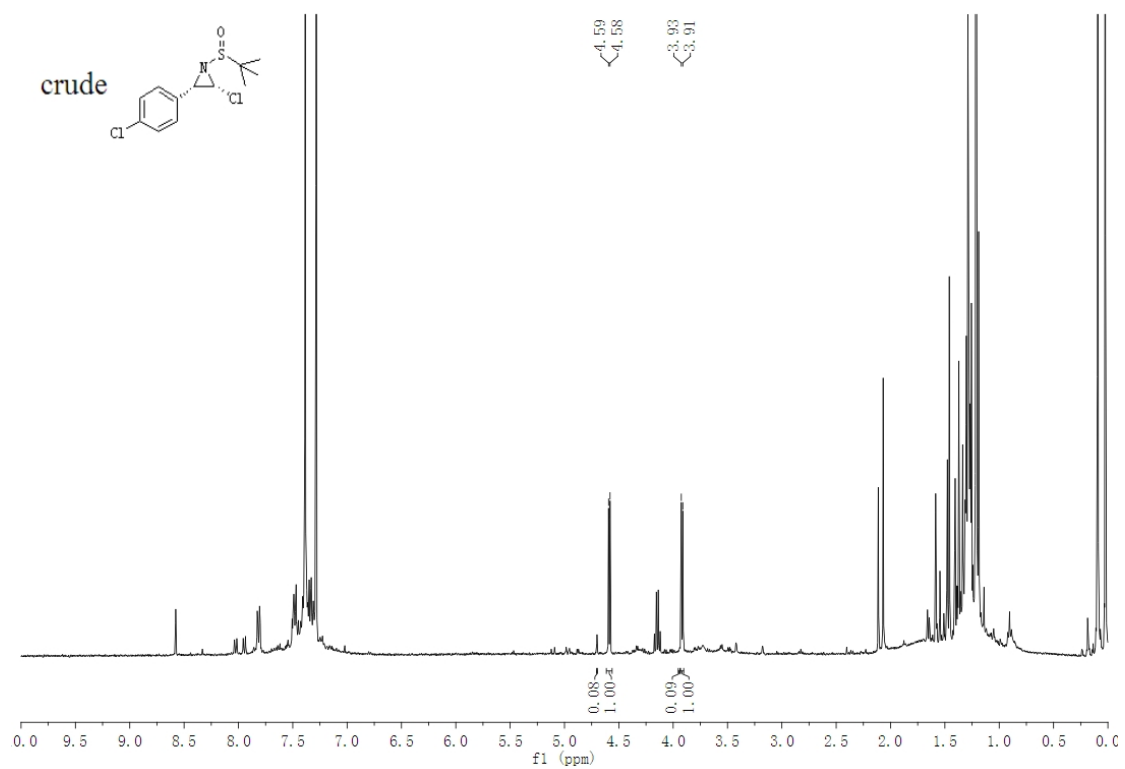
¹H NMR of crude product **5d**



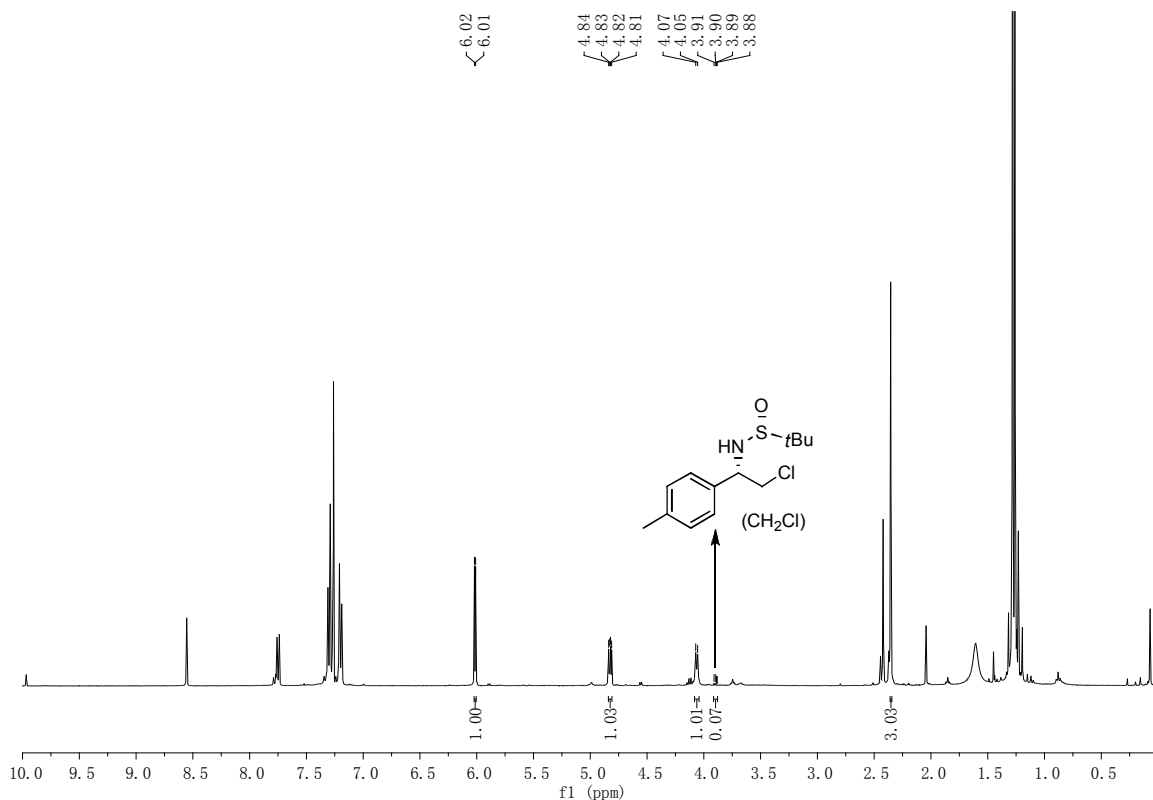
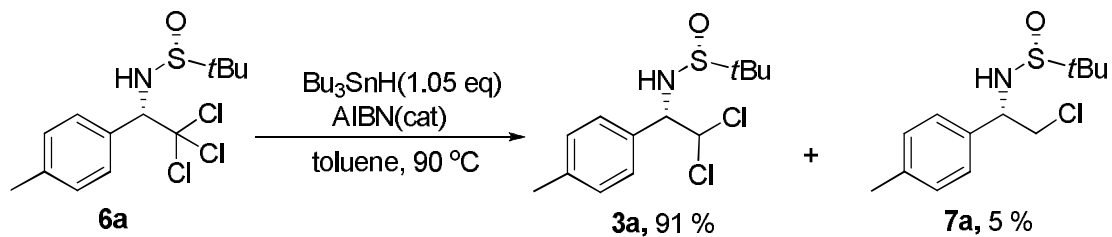
¹H NMR of crude product **5e**



¹H NMR of crude product **5f**



¹H NMR of crude product 3a via radical mono-dechlorination of compound 6a

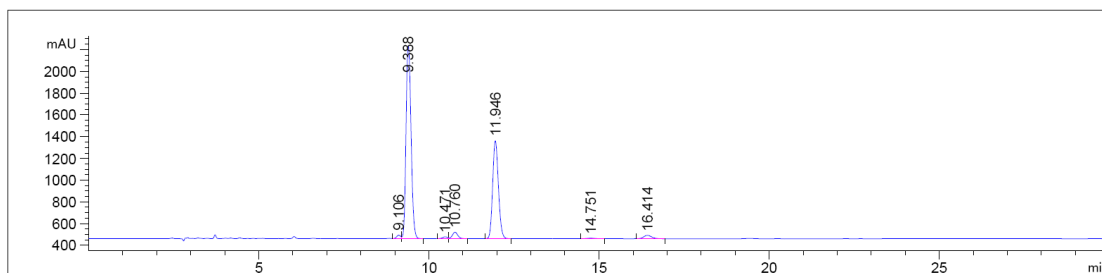


LC-MS spectra of the crude products 3

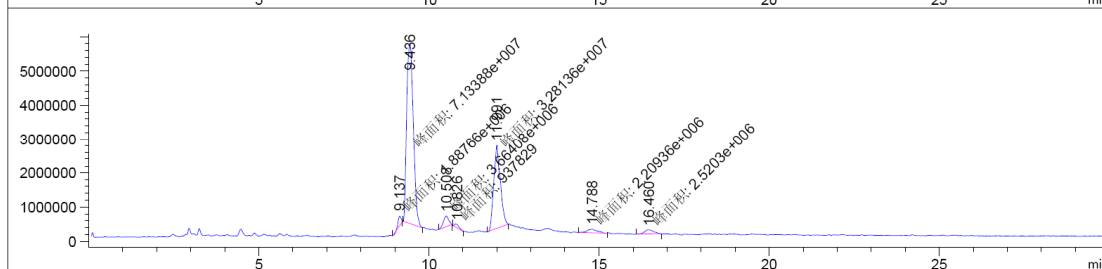
3a, $rt = 9.38$ min; the other diastereomer, $rt = 9.10$ min

$dr = 59.7 : 0.9 = 98 : 2$

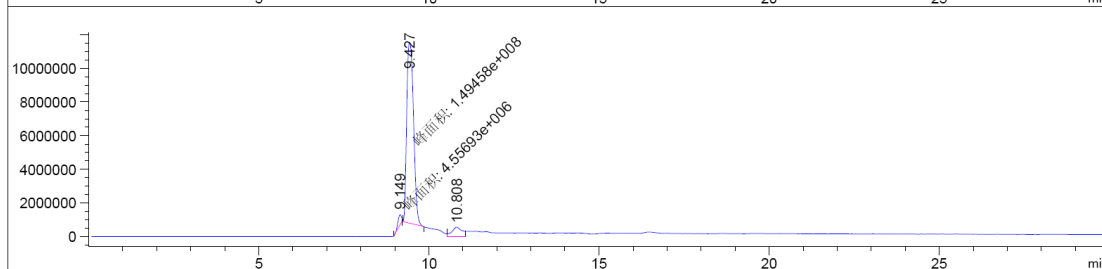
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram



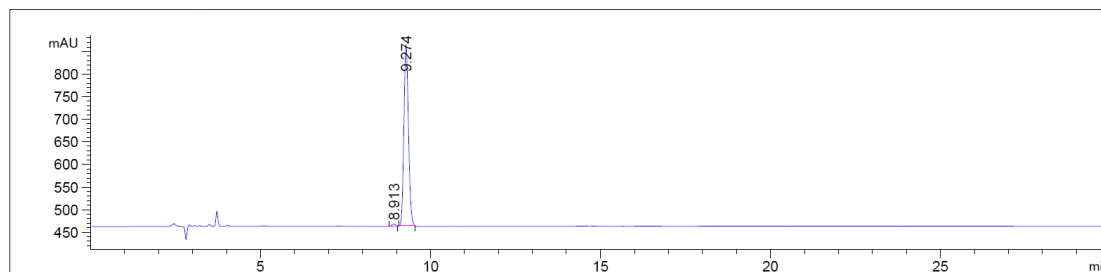
1c) Selected ion



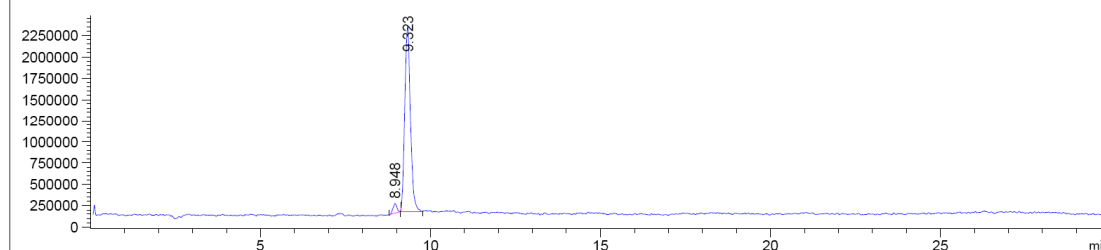
3c, $rt = 9.27$ min; the other diastereomer, $rt = 8.91$ min

$dr = 98.8 : 1.11 = 98 : 2$

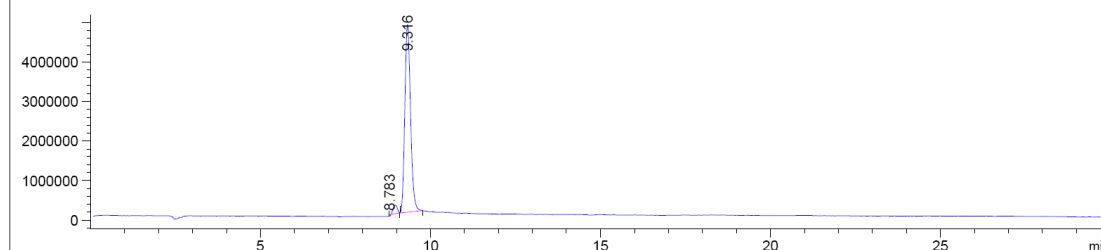
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram



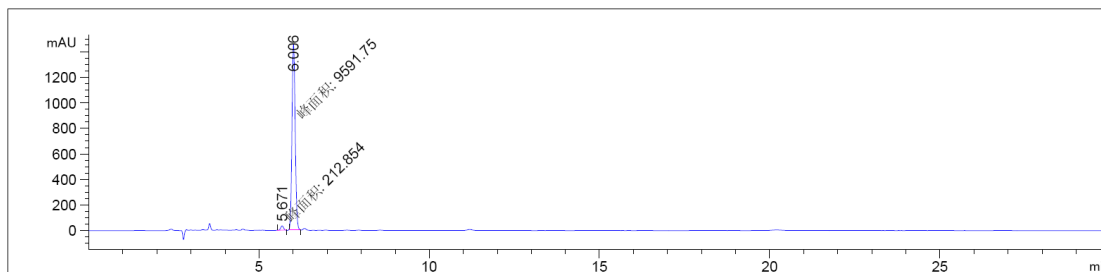
1c) Selected ion



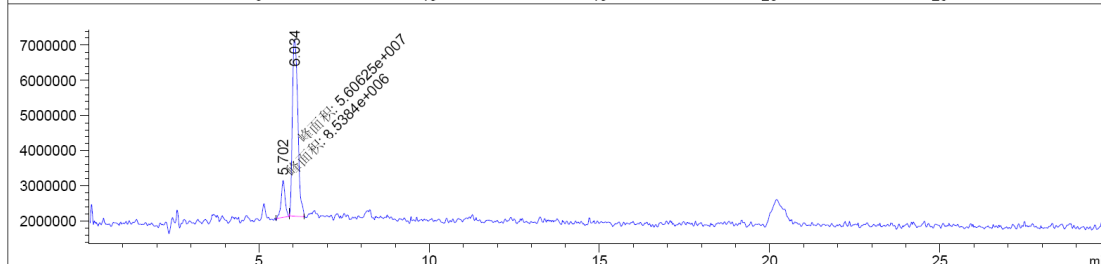
3d, $rt = 6.00$ min; the other diastereomer, $rt = 5.67$ min

$dr = 9591 : 212 = 98 : 2$

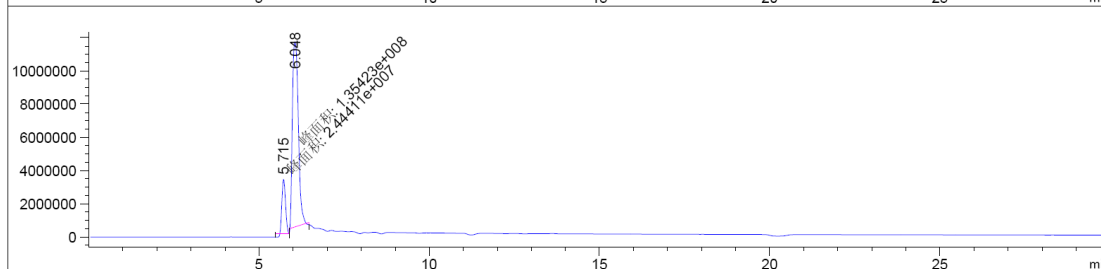
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram

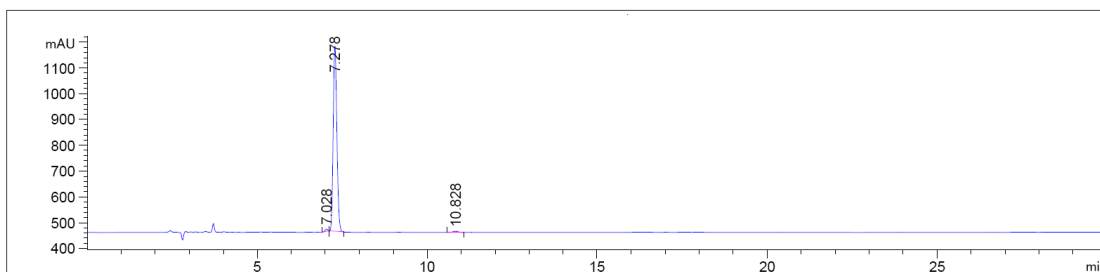


1c) Selected ion

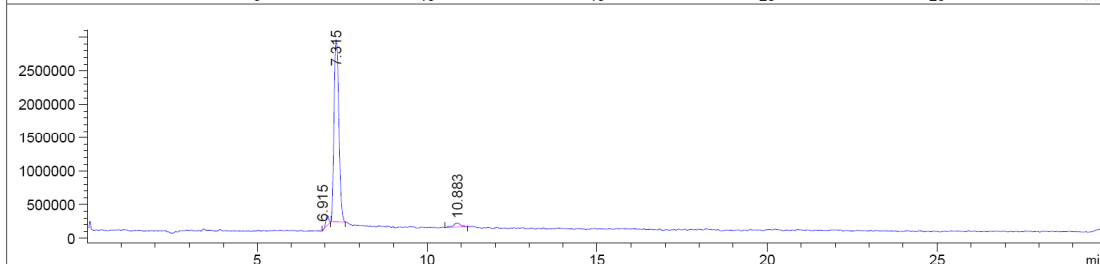


3e, $rt = 7.27$ min; the other diastereomer, $rt = 7.02$ min
 $dr = 98.06 : 1.06 = 98 : 2$

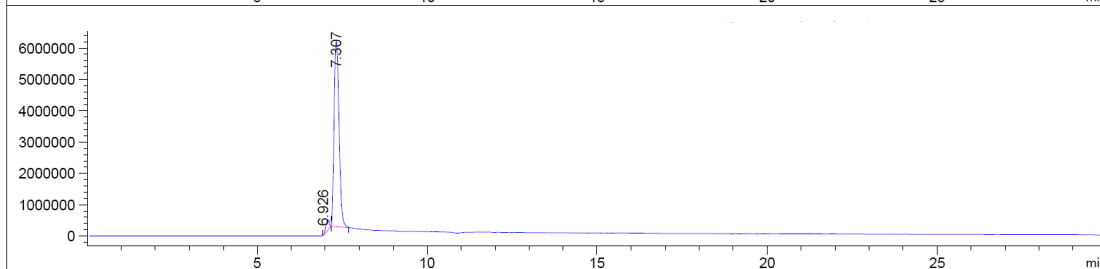
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram

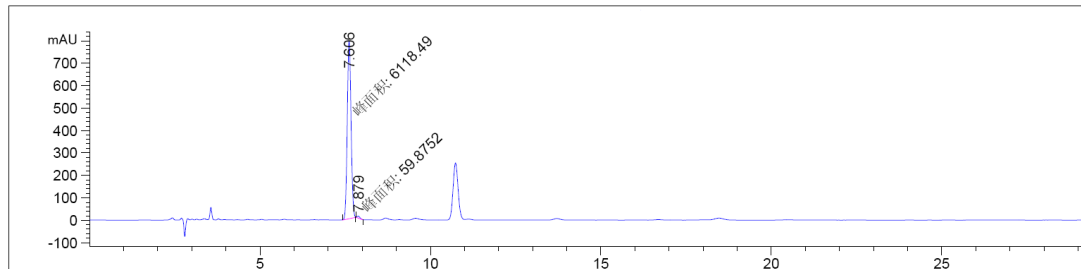


1c) Selected ion

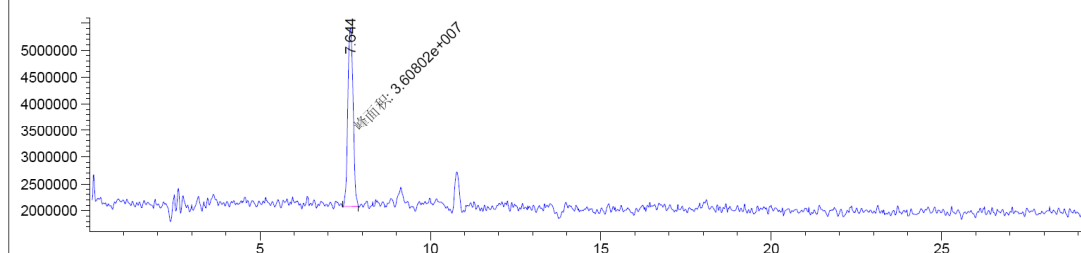


3f, $rt = 7.60$ min; the other diastereomer, $rt = 7.87$ min
 $dr = 6118 : 59.8 = 98 : 2$

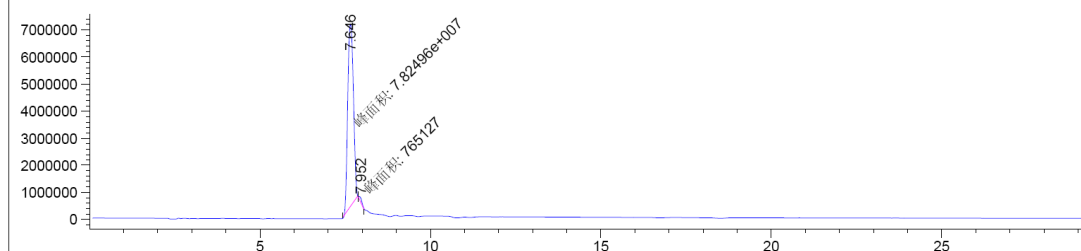
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram

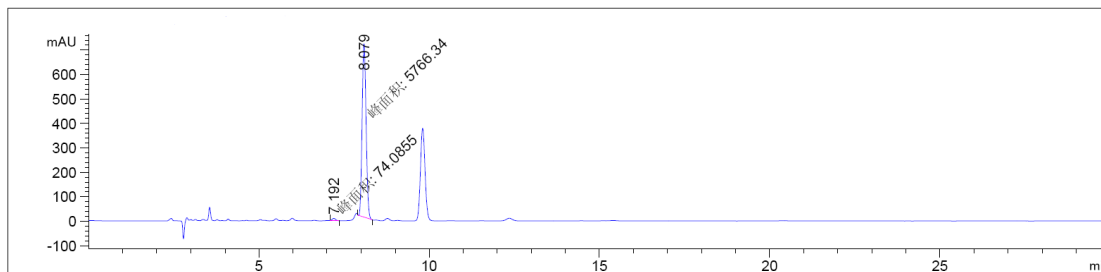


1c) Selected ion

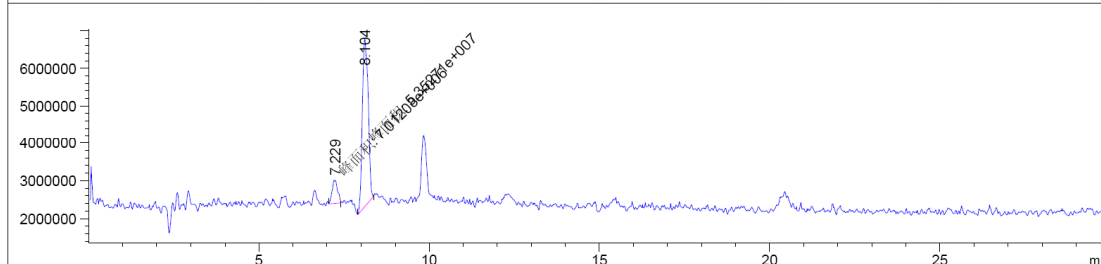


3g, $rt = 8.07$ min; the other diastereomer, $rt = 7.19$ min
 $dr = 5766 : 74 = 98 : 2$

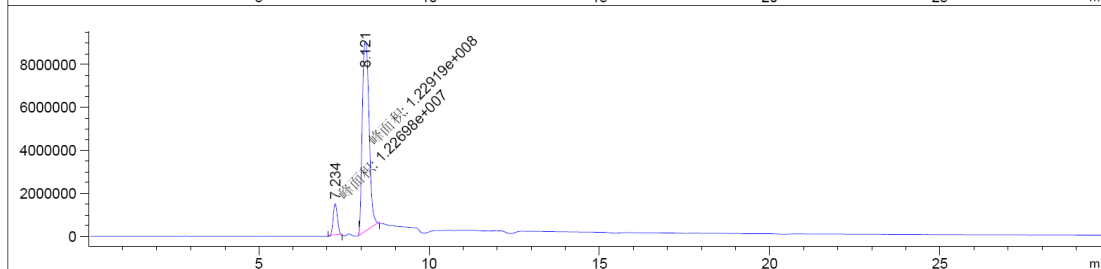
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram



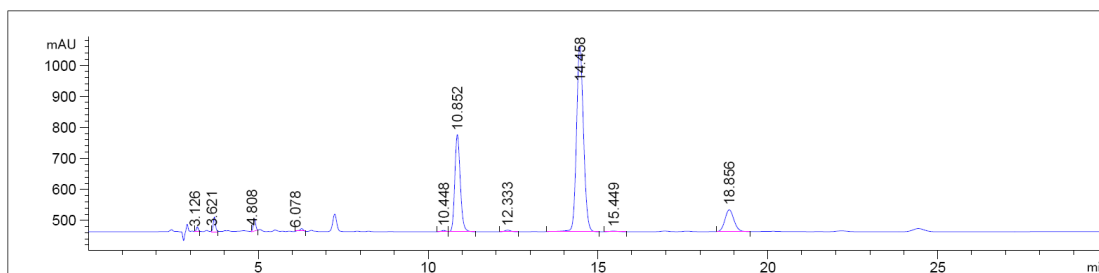
1c) Selected ion



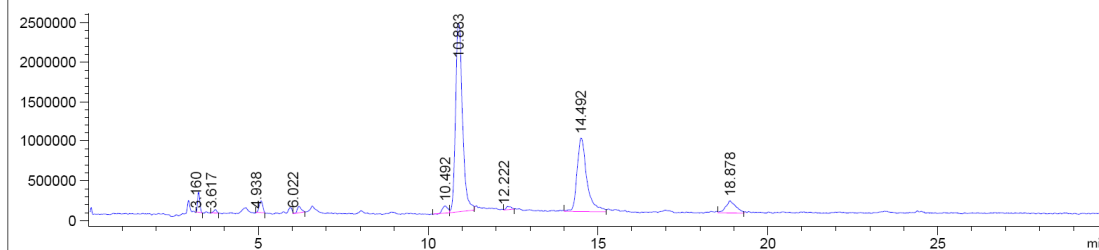
3h, $rt = 10.85$ min; the other diastereomer, $rt = 10.44$ min

$dr = 24.8 : 0.29 = 98 : 2$

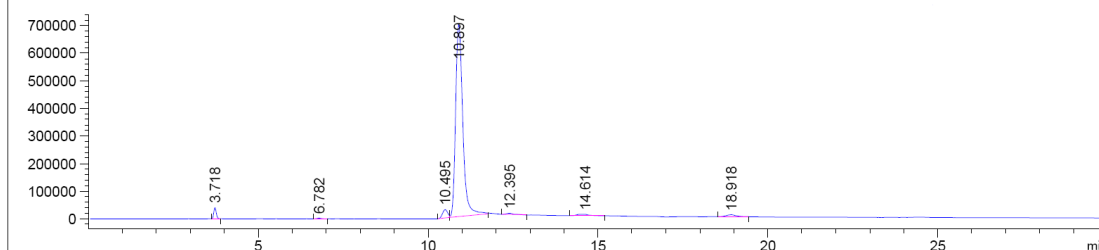
1a) HPLC
spectroscopy



1b) Total ion
current
chromatogram



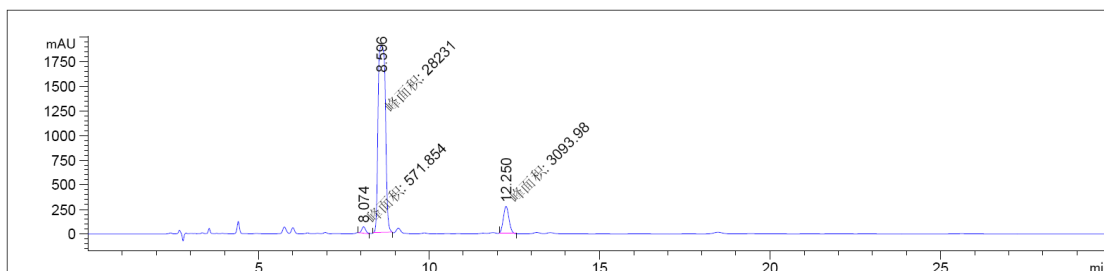
1c) Selected ion



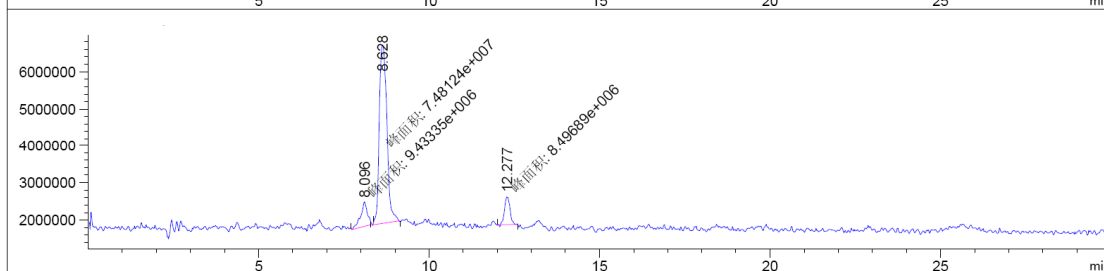
3i, $rt = 8.59$ min; the other diastereomer, $rt = 8.07$ min

$dr = 28231 : 571 = 98 : 2$

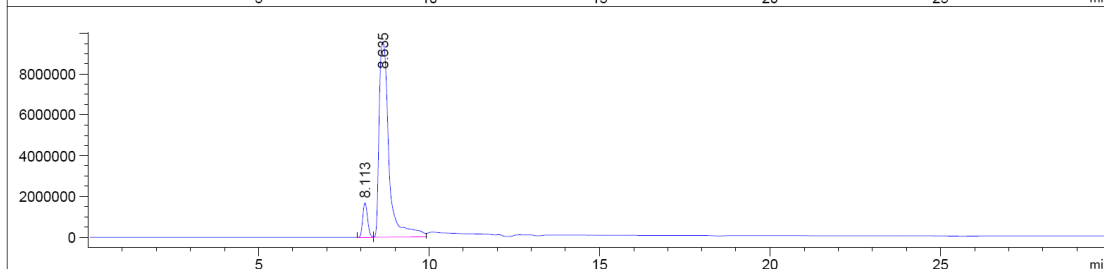
1a) HPLC
spectroscopy



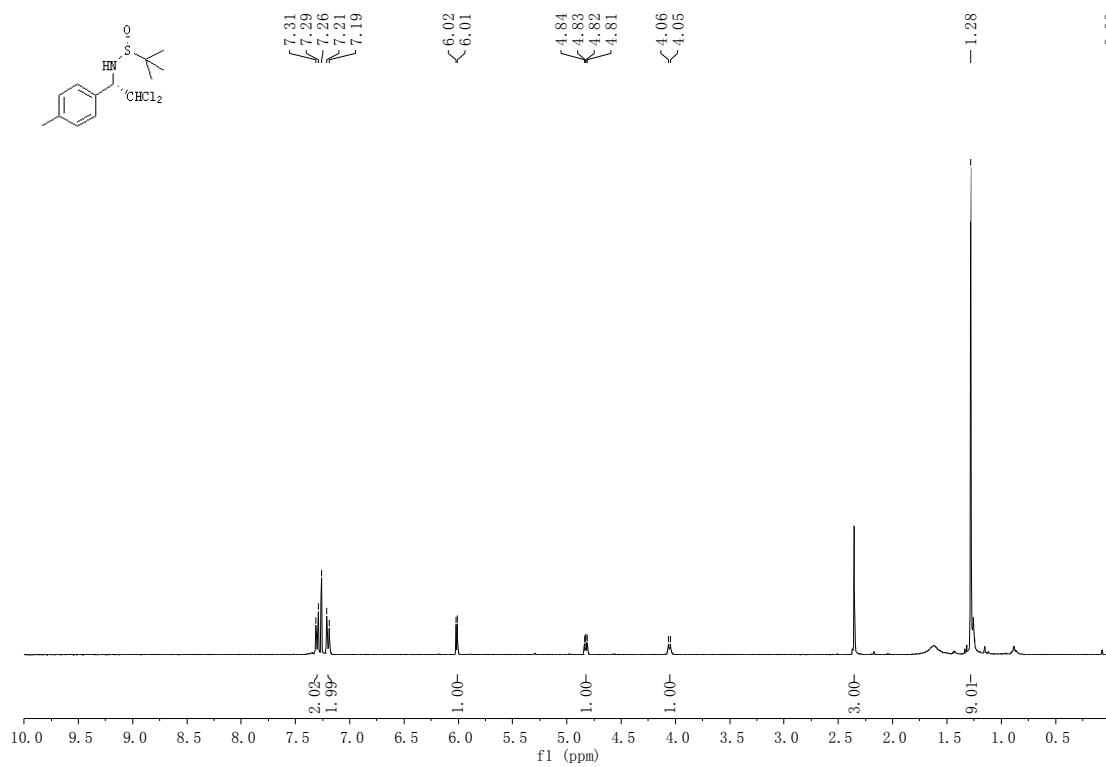
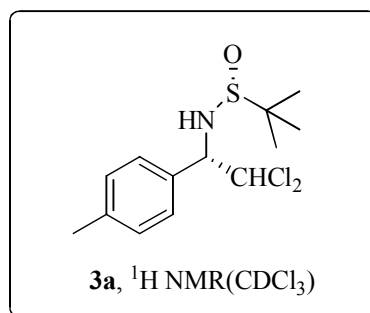
1b) Total ion
current
chromatogram

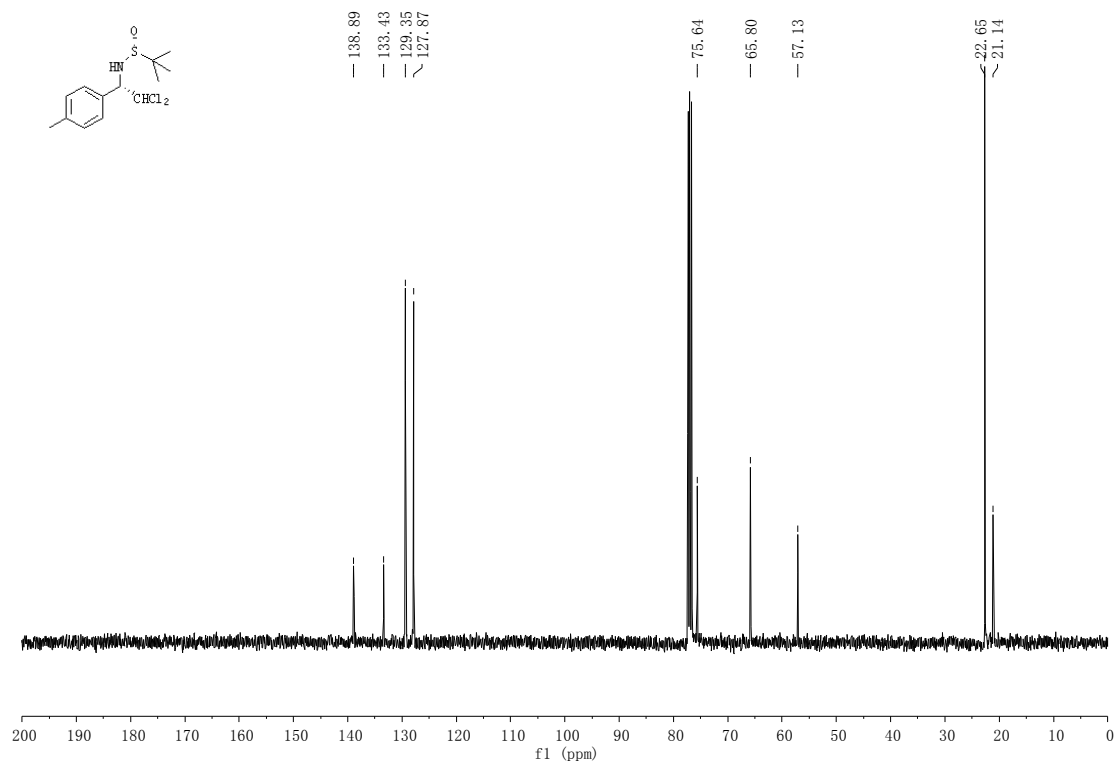
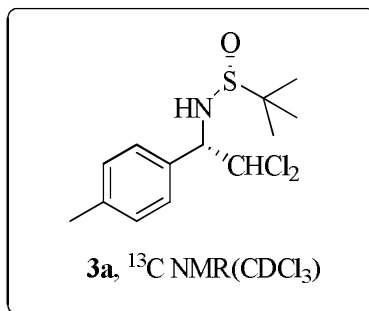


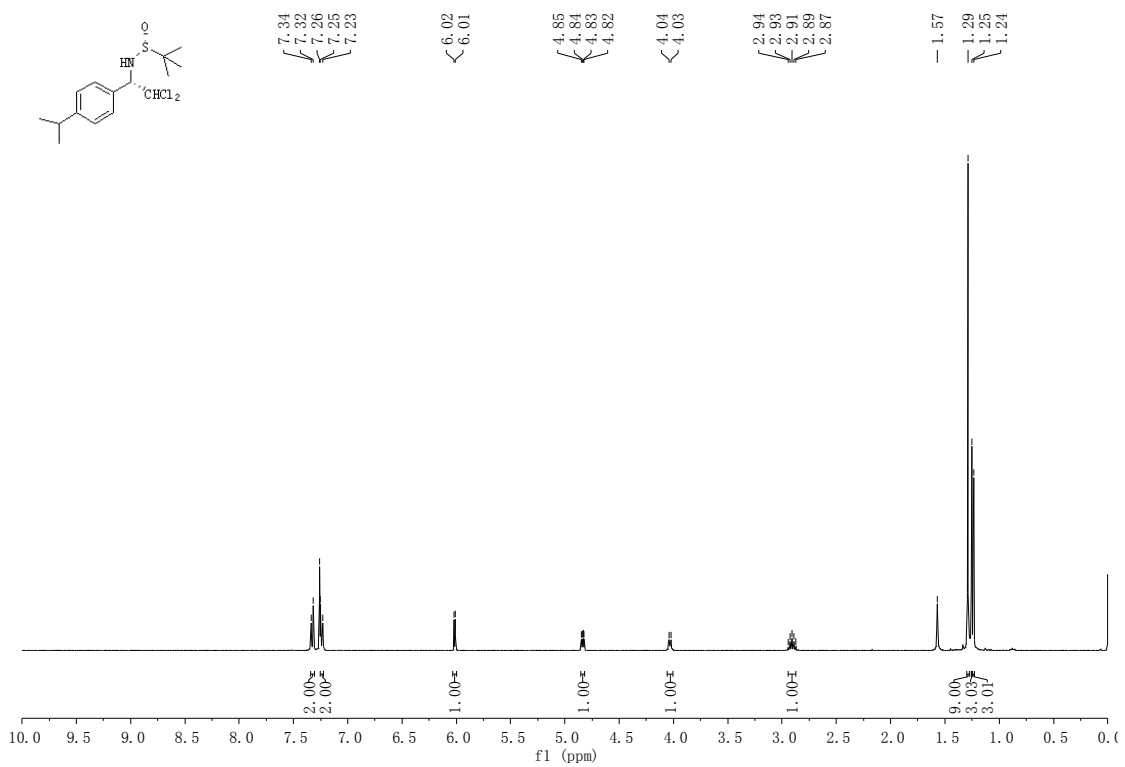
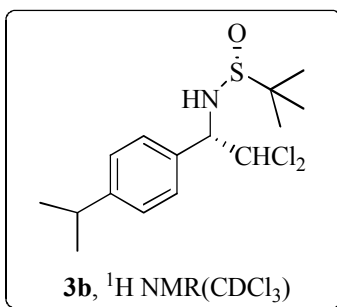
1c) Selected ion

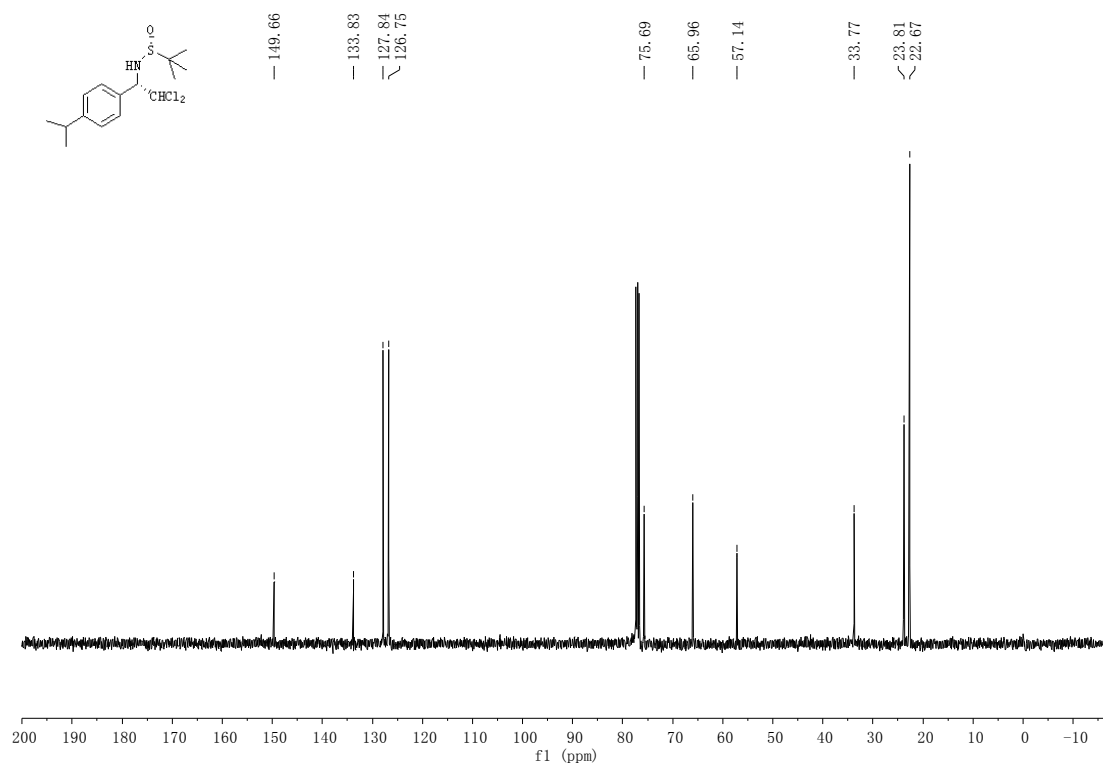
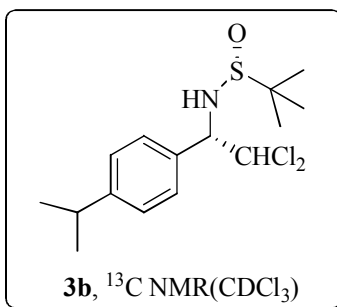


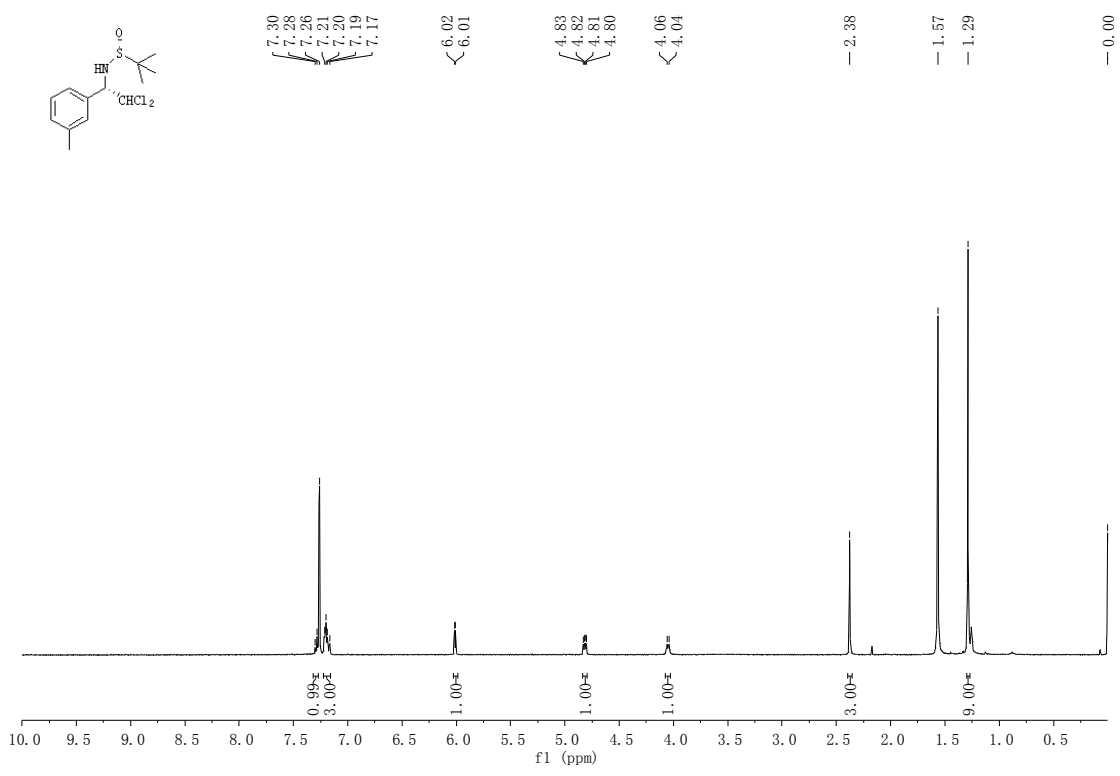
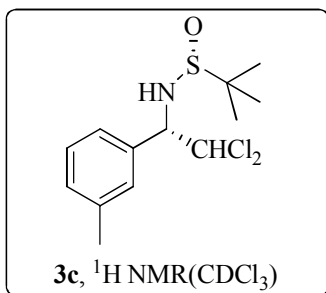
NMR Spectra for all new products

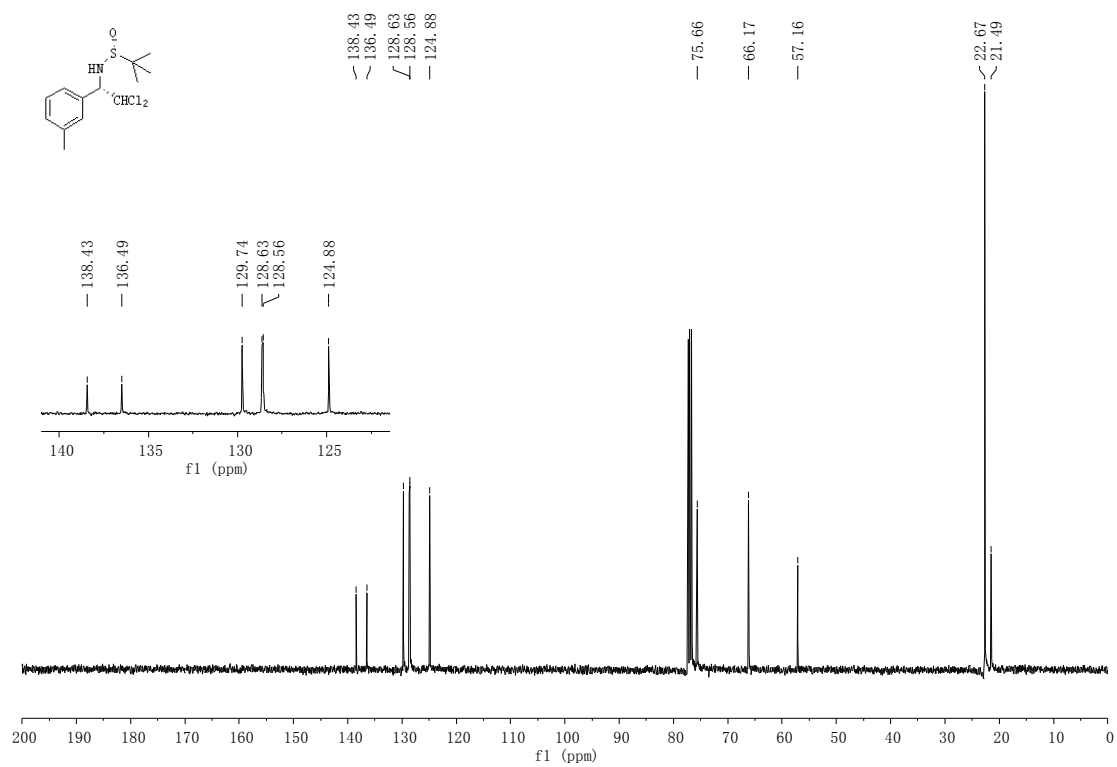
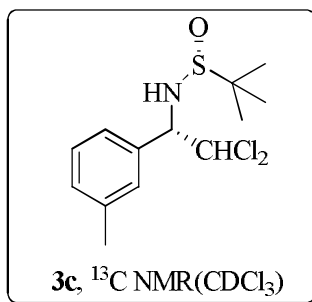


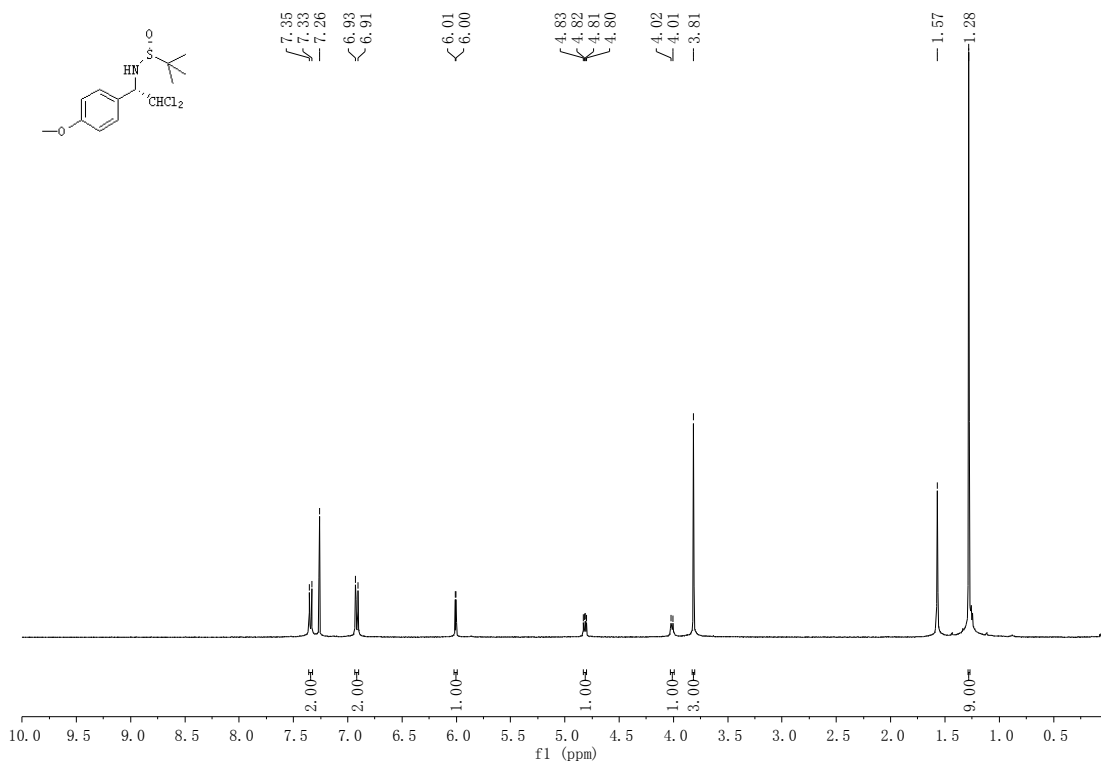
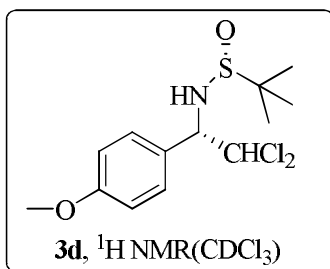


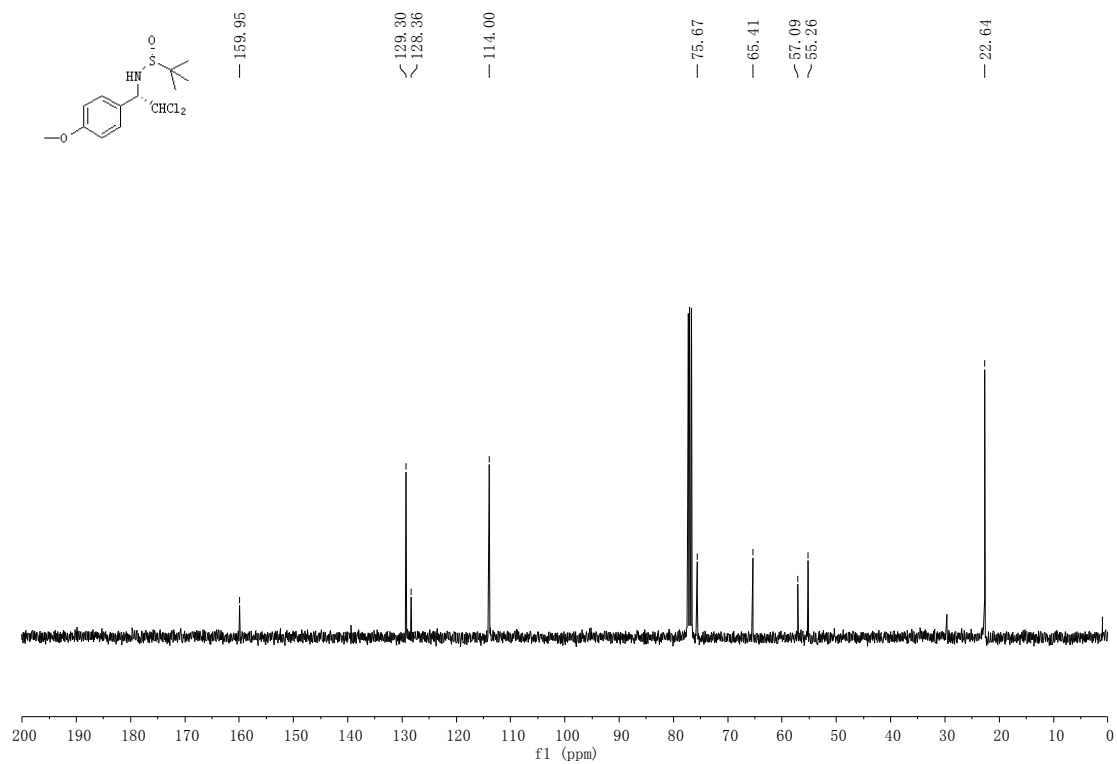
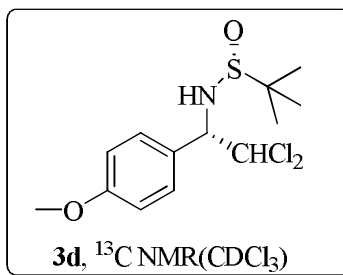


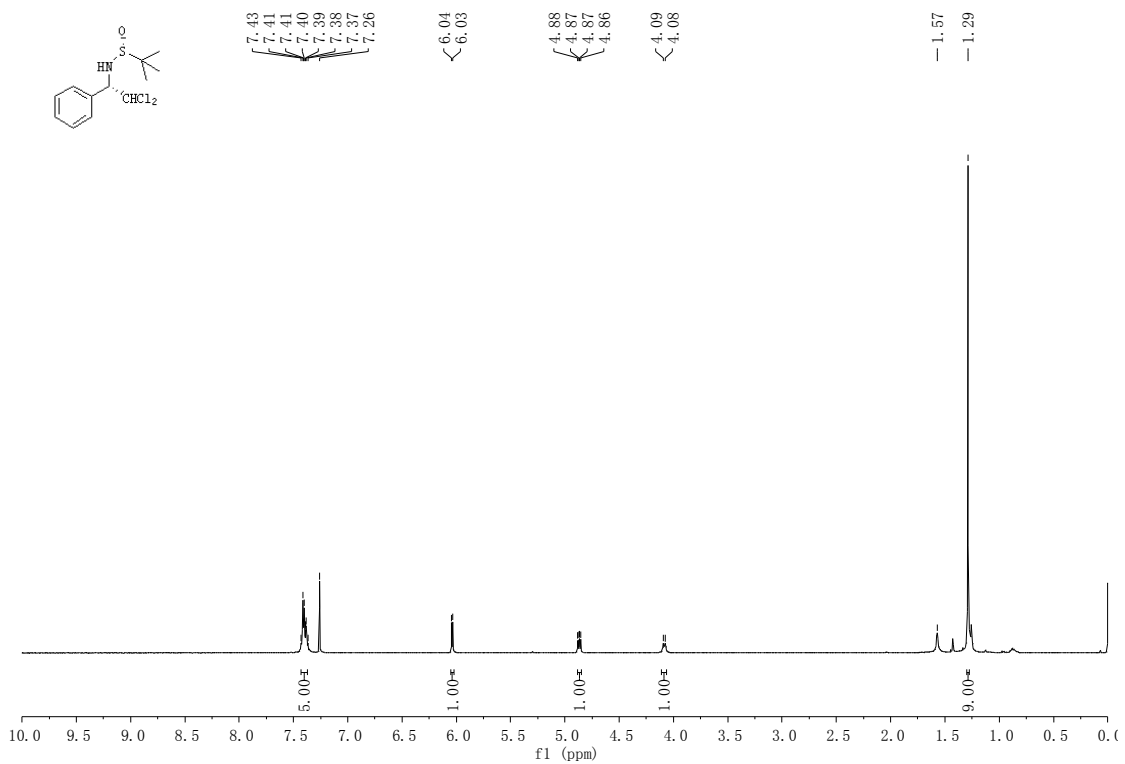
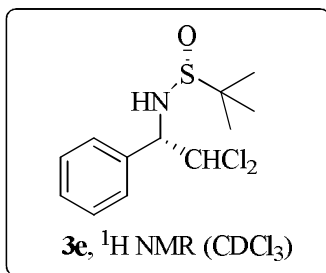


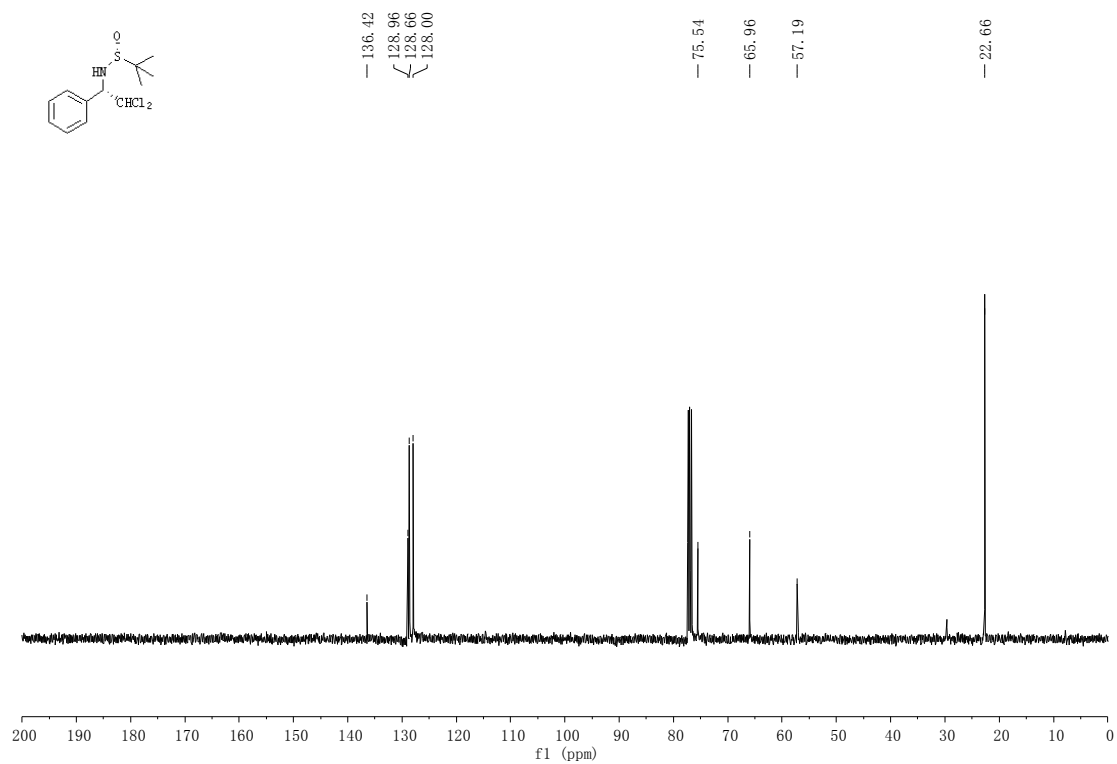
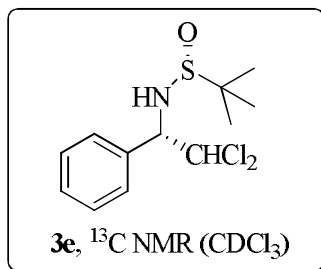


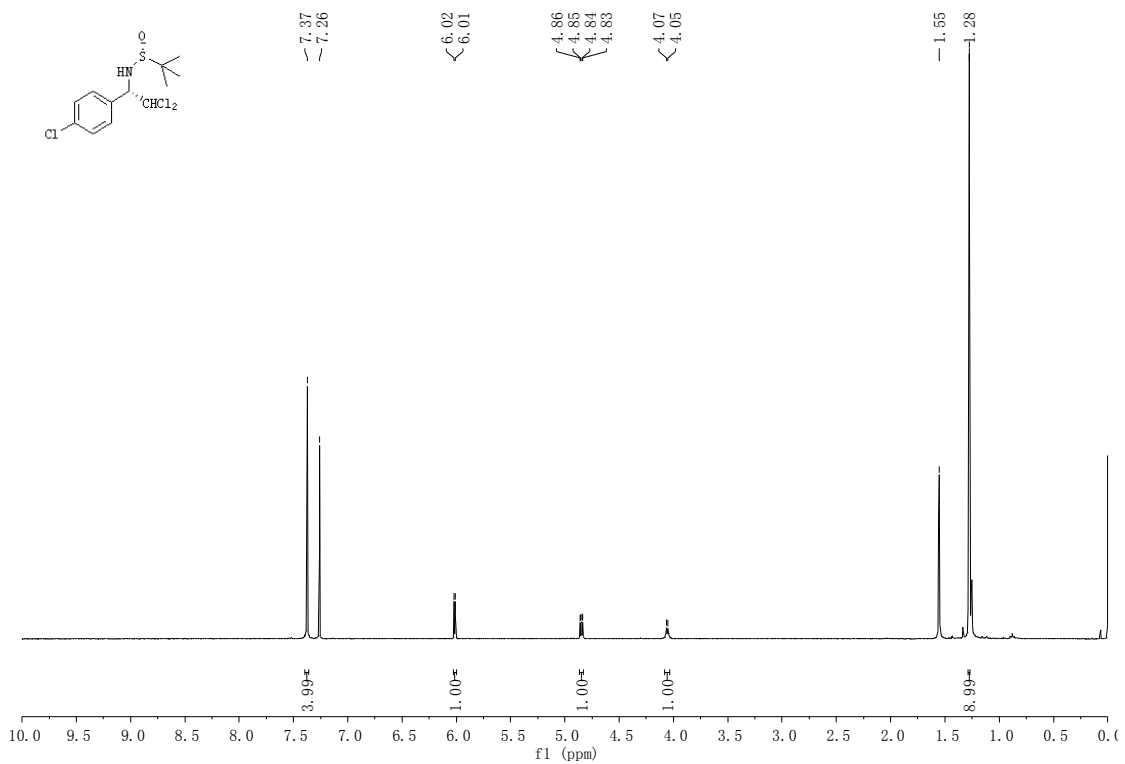
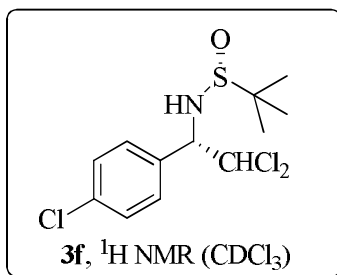


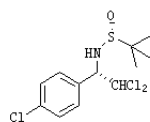
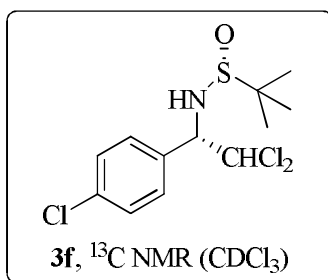








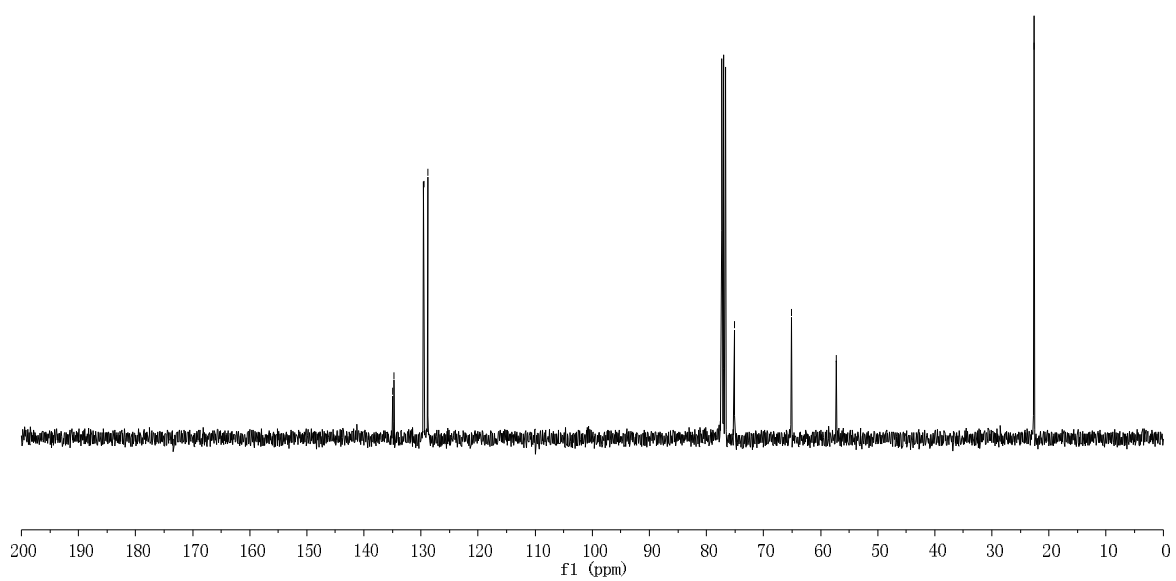


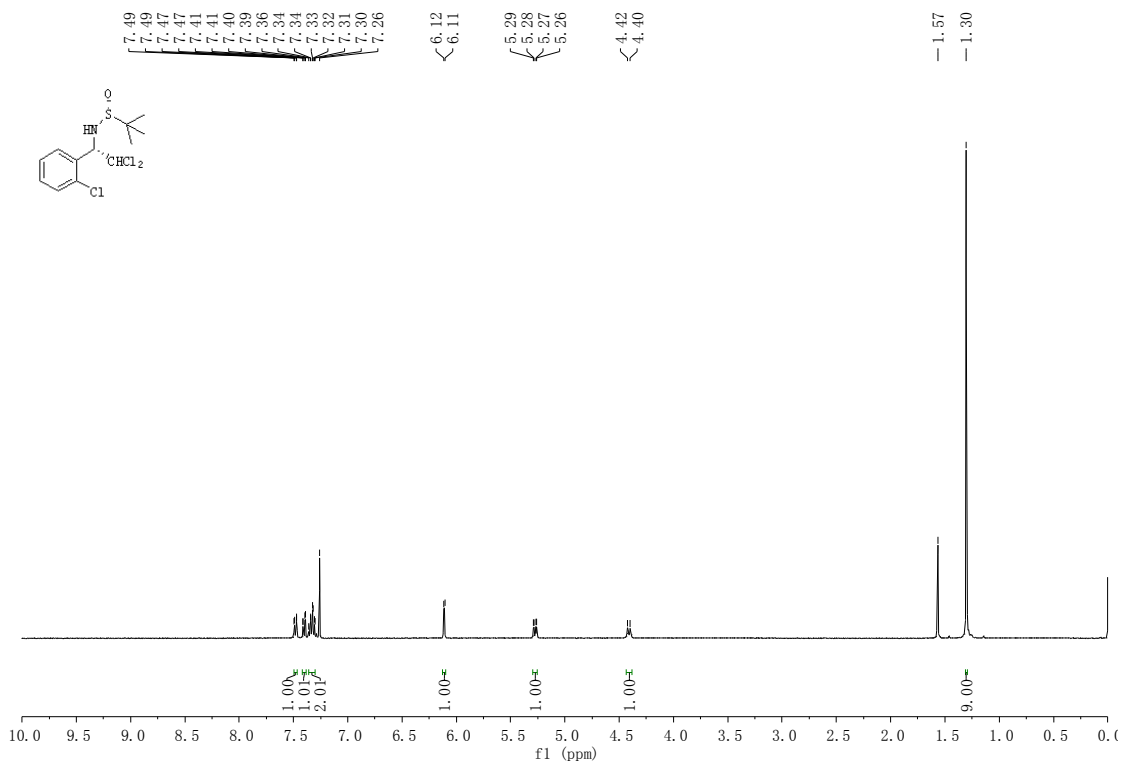
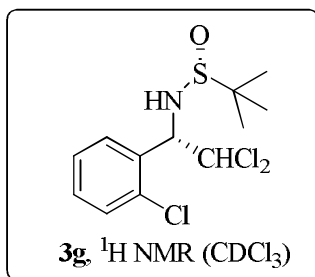


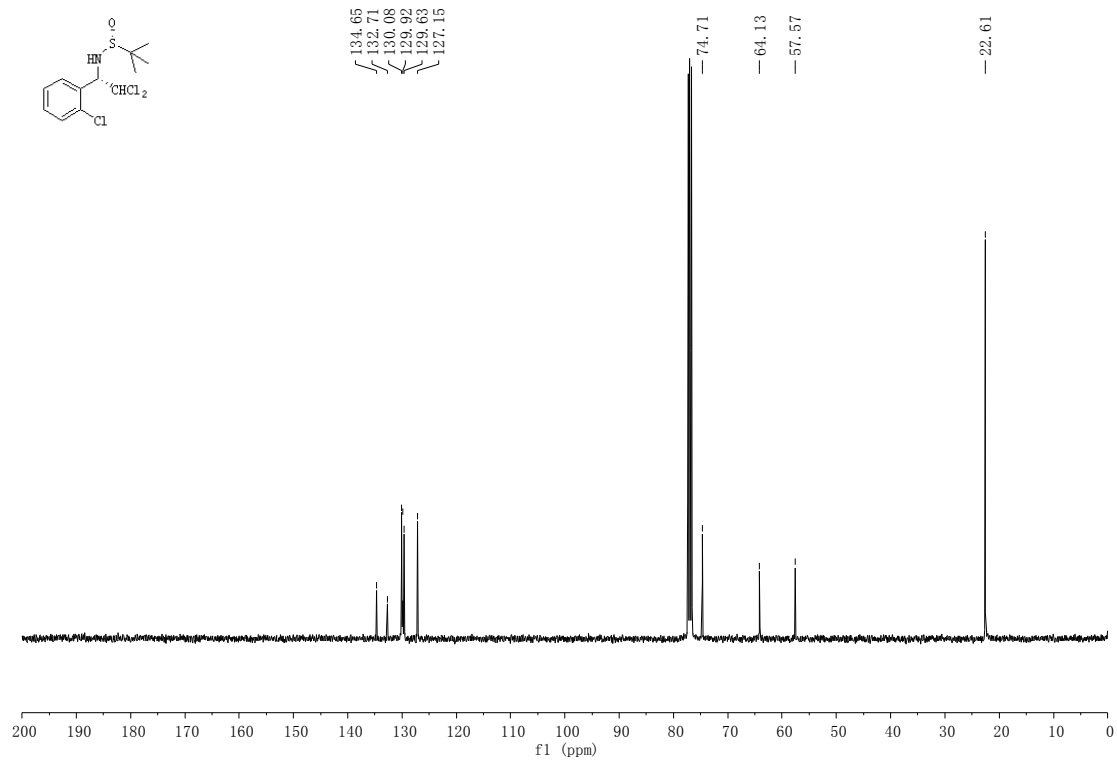
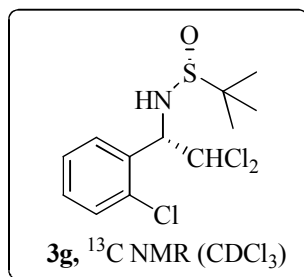
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128.83

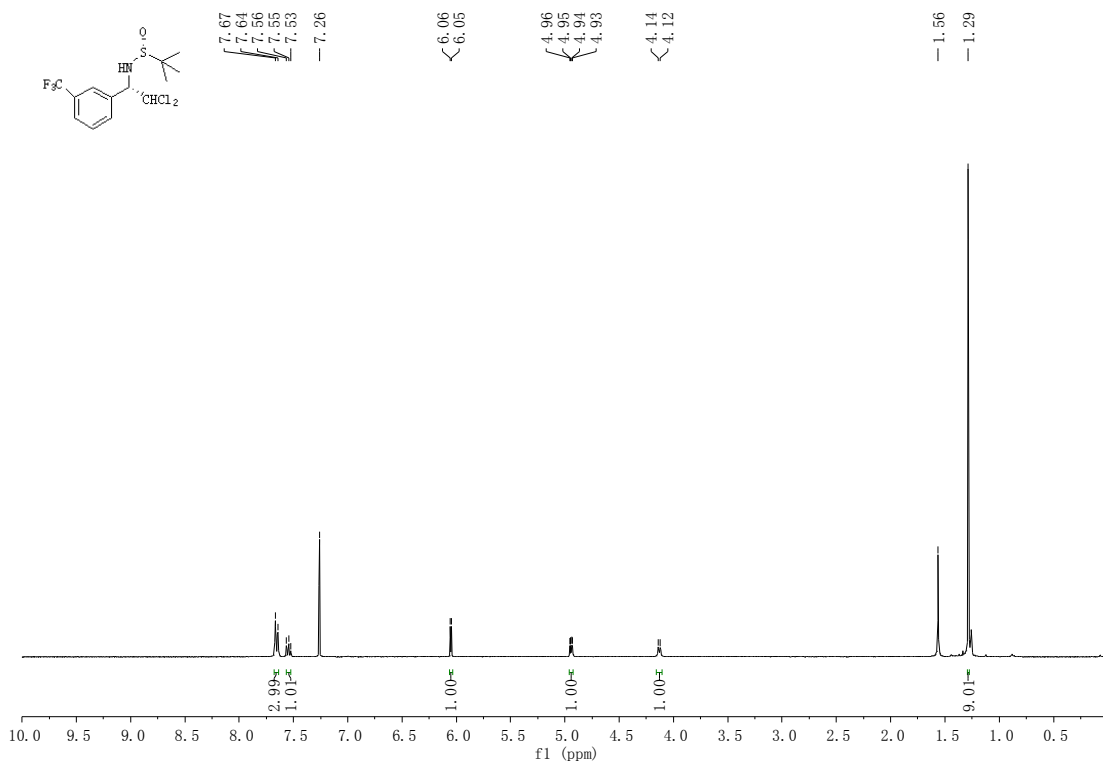
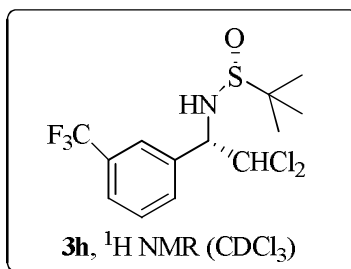
75.11
65.14
57.26

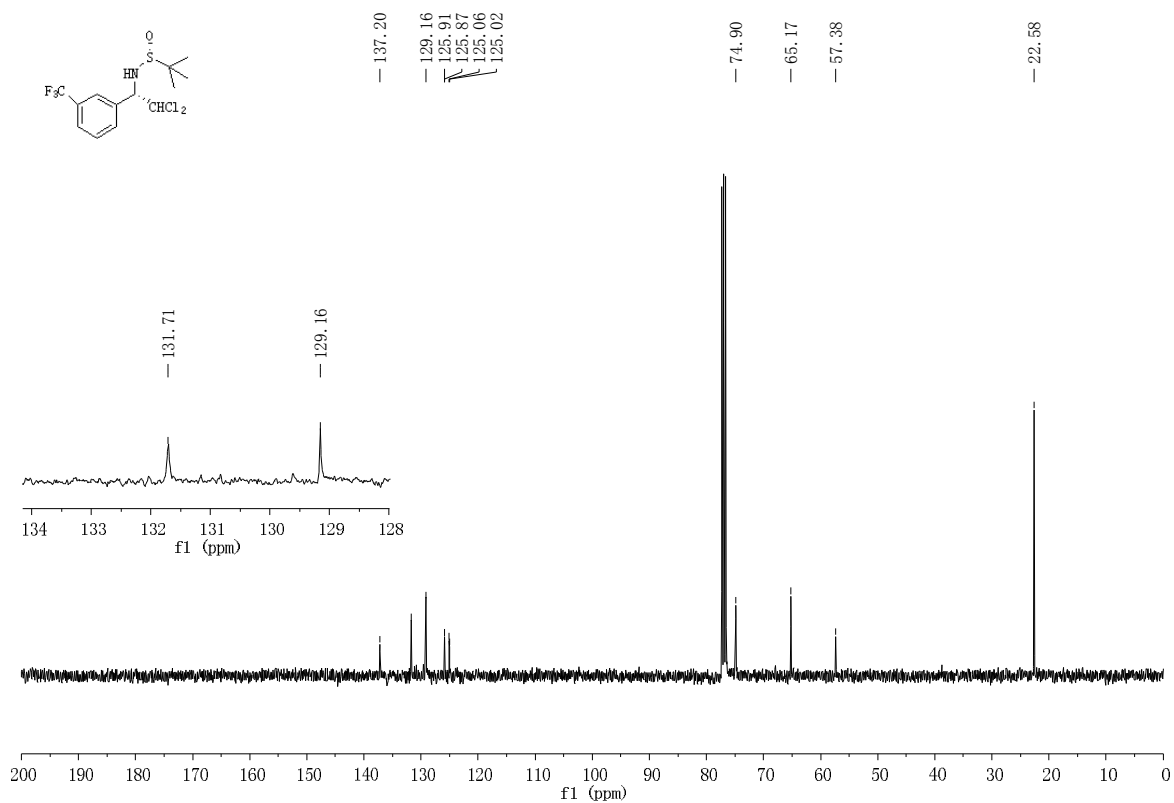
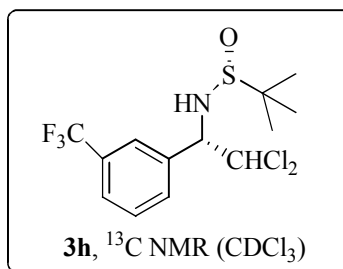
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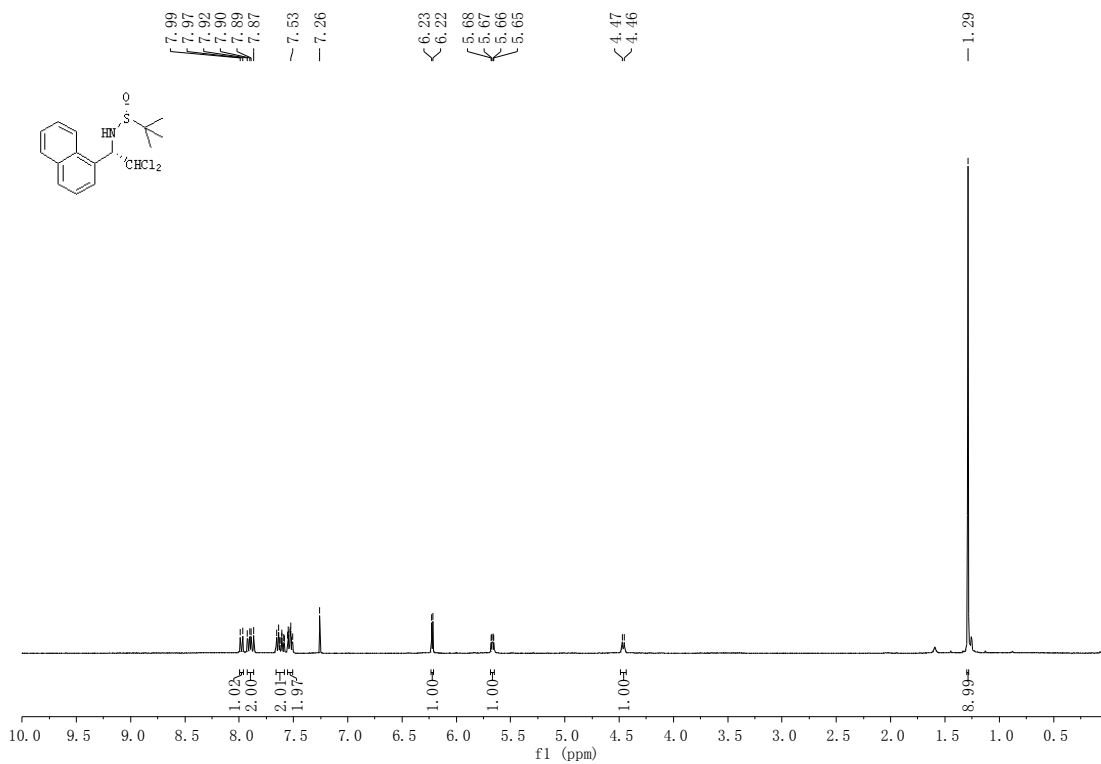
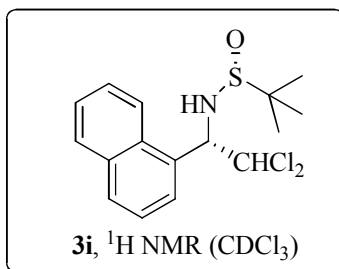


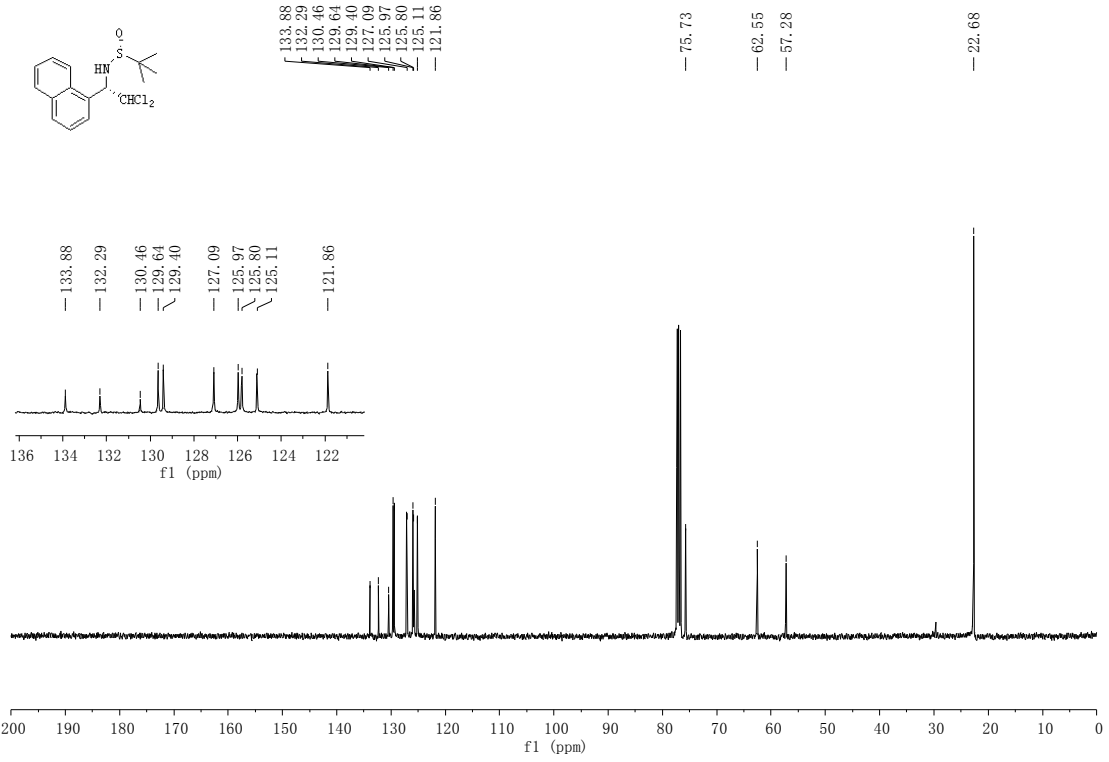
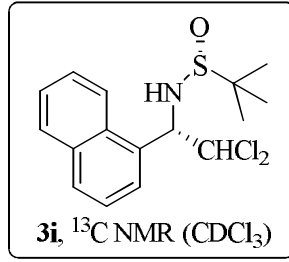


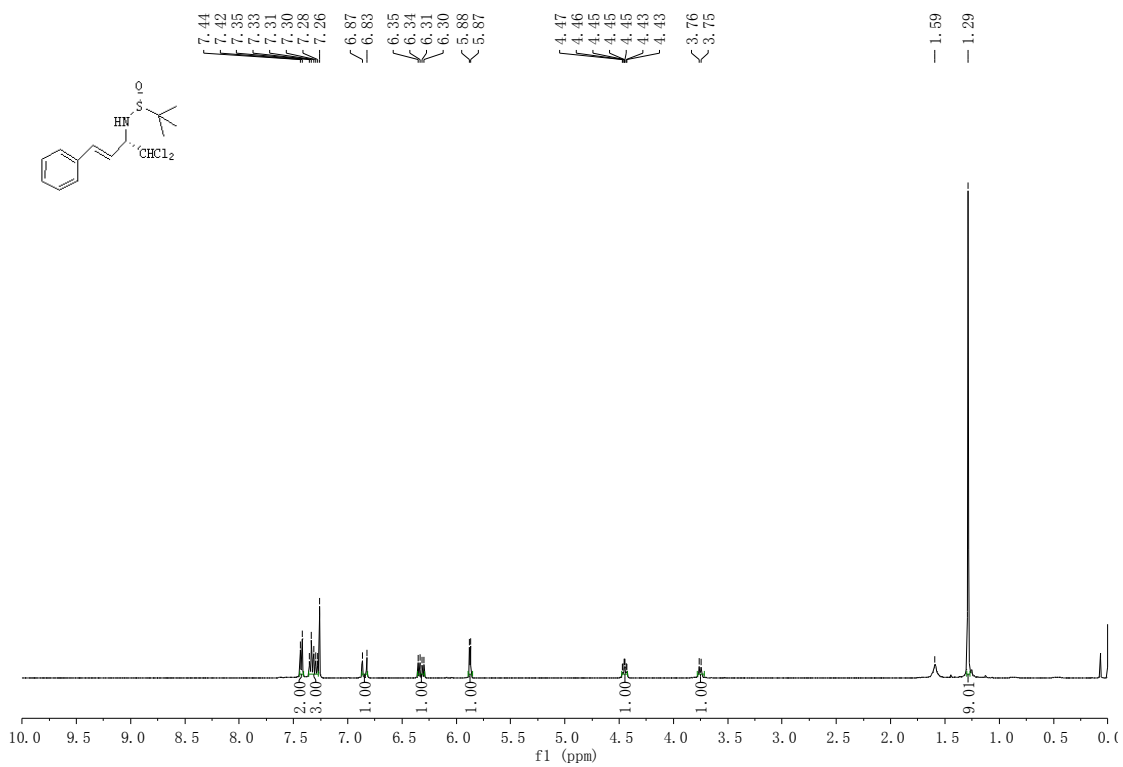
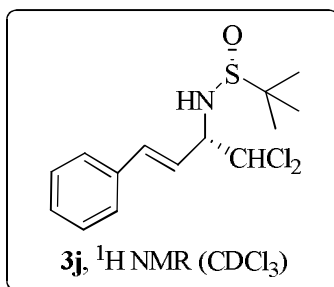


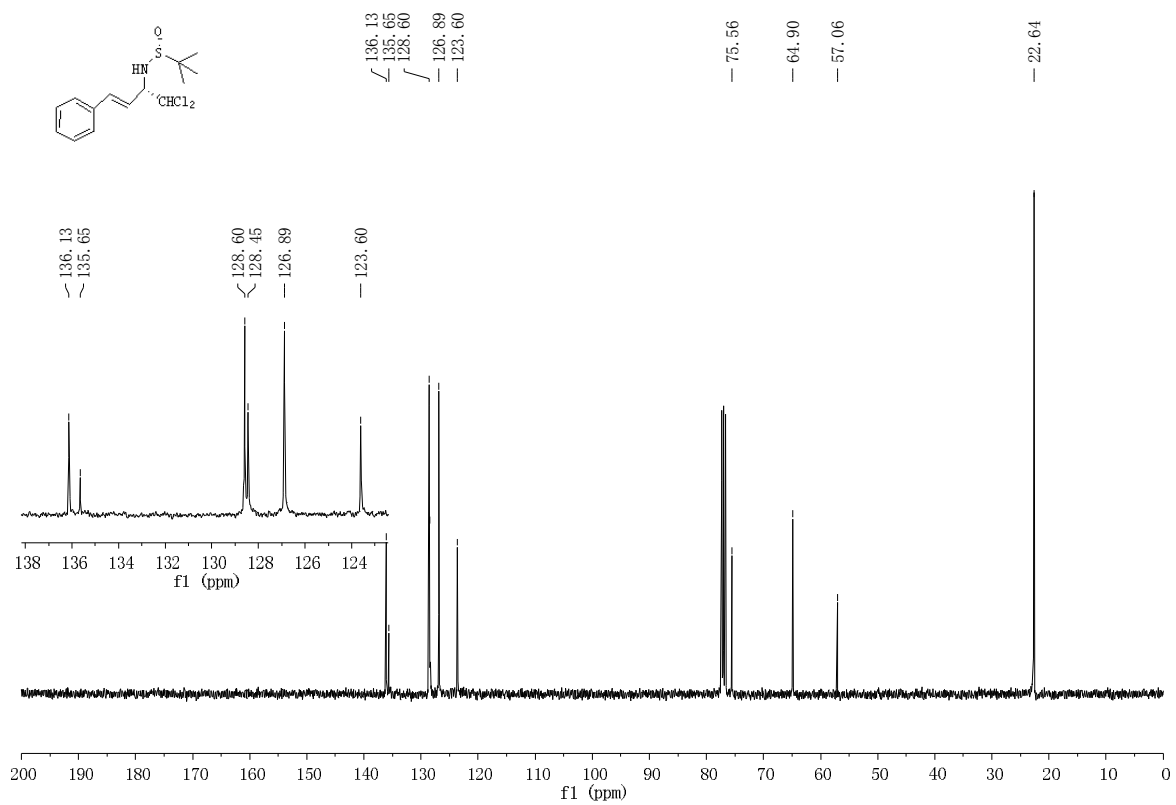
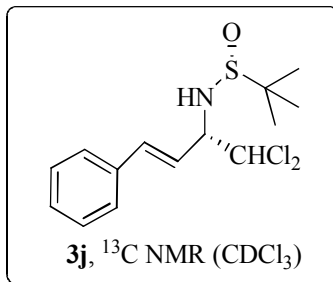


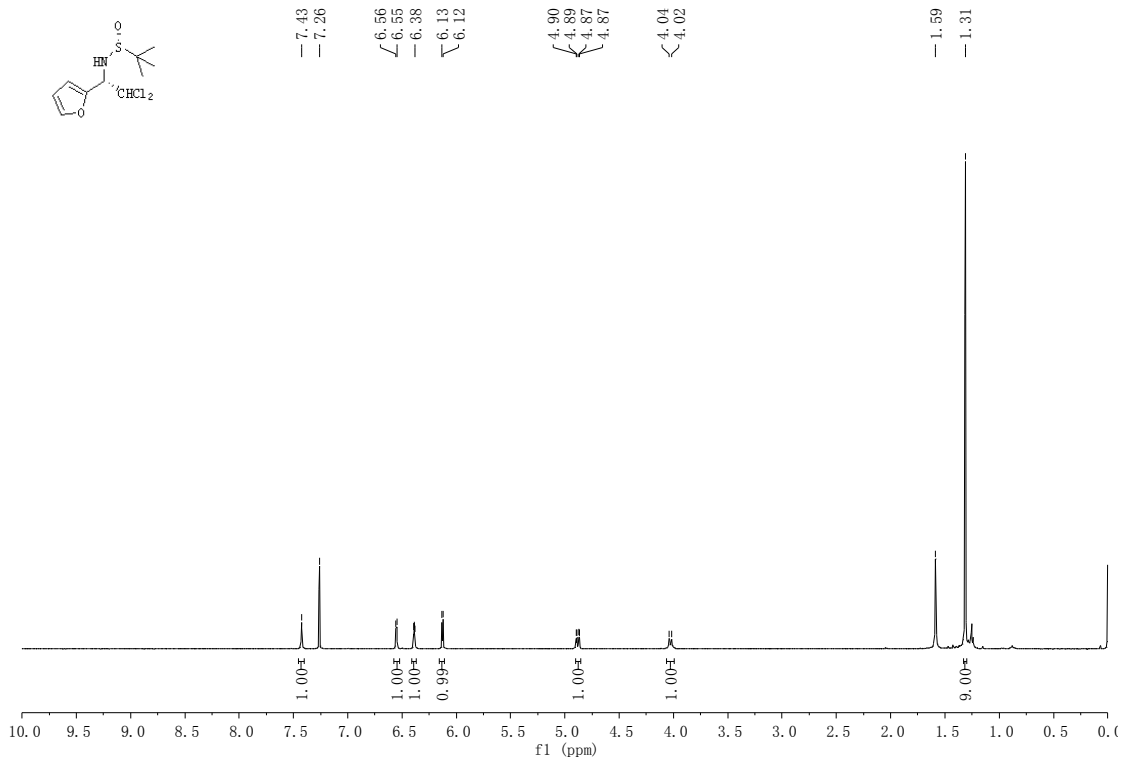
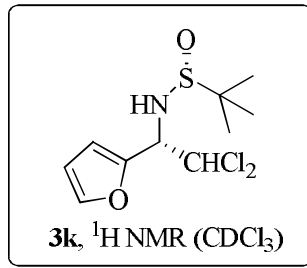


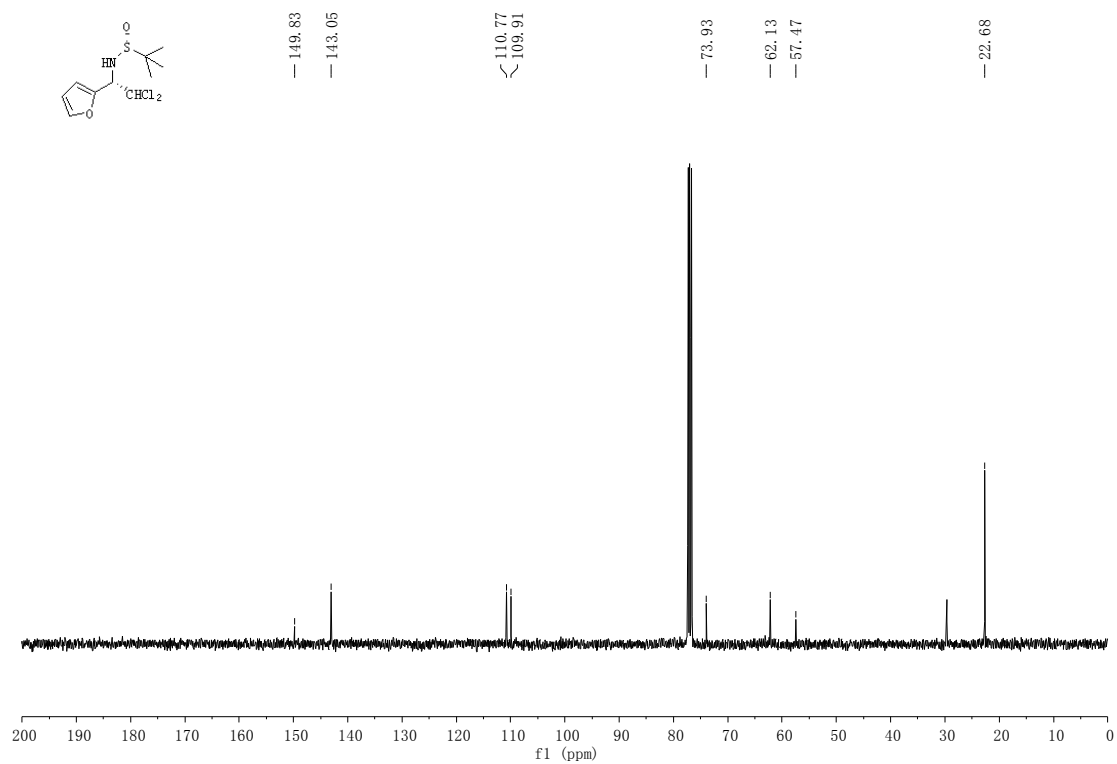
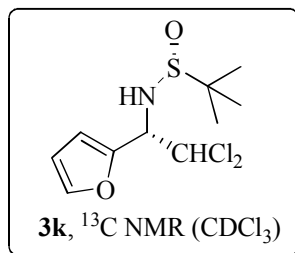


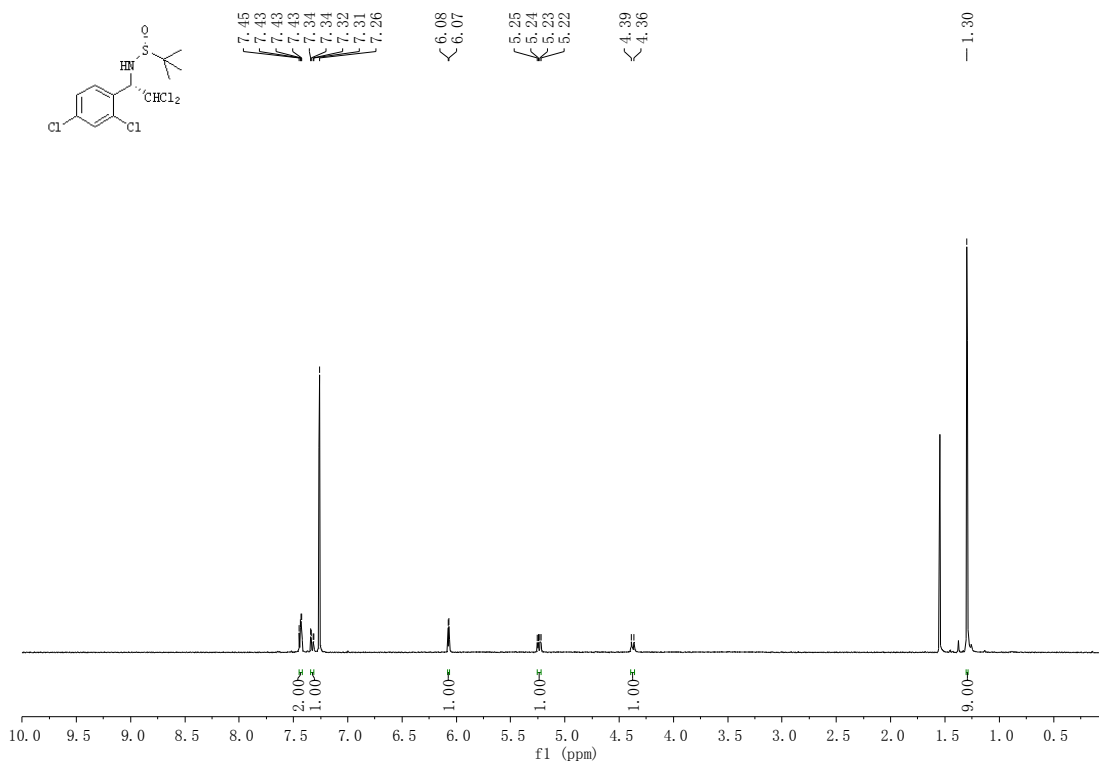
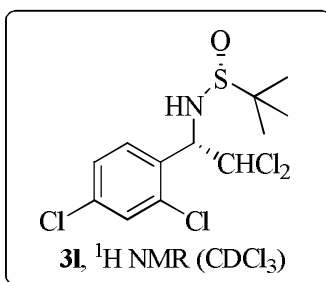


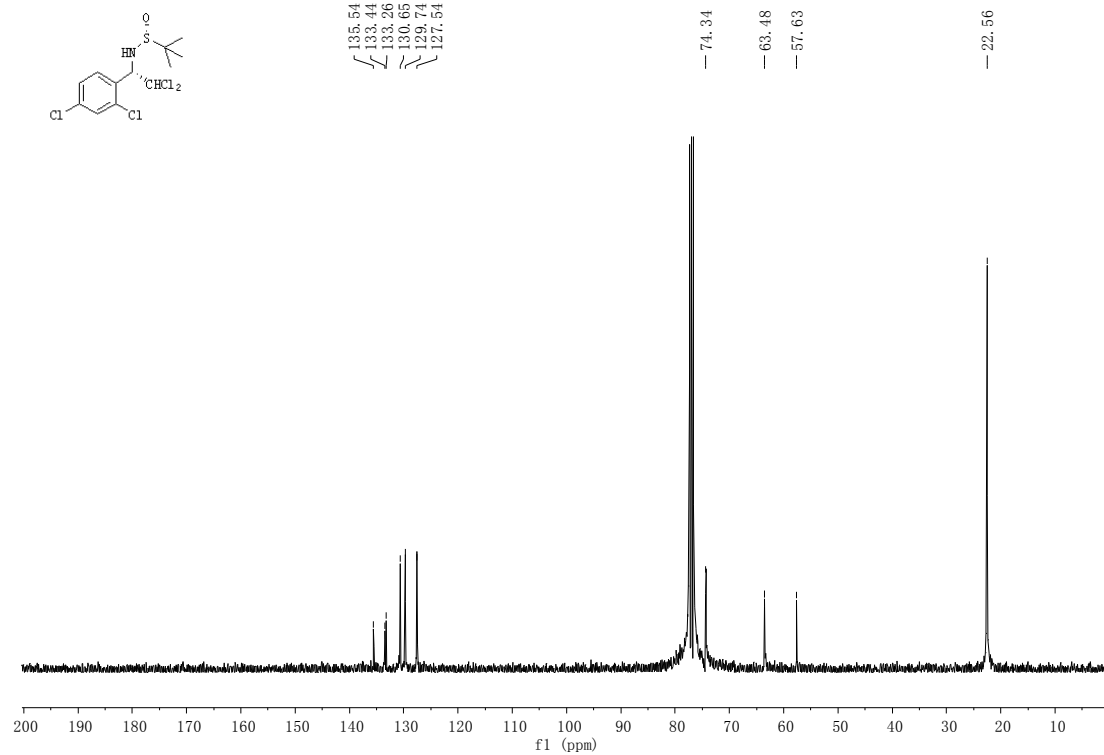
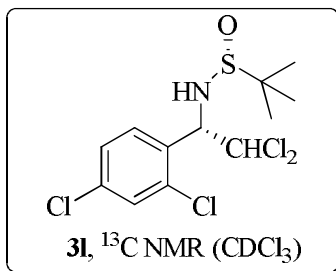


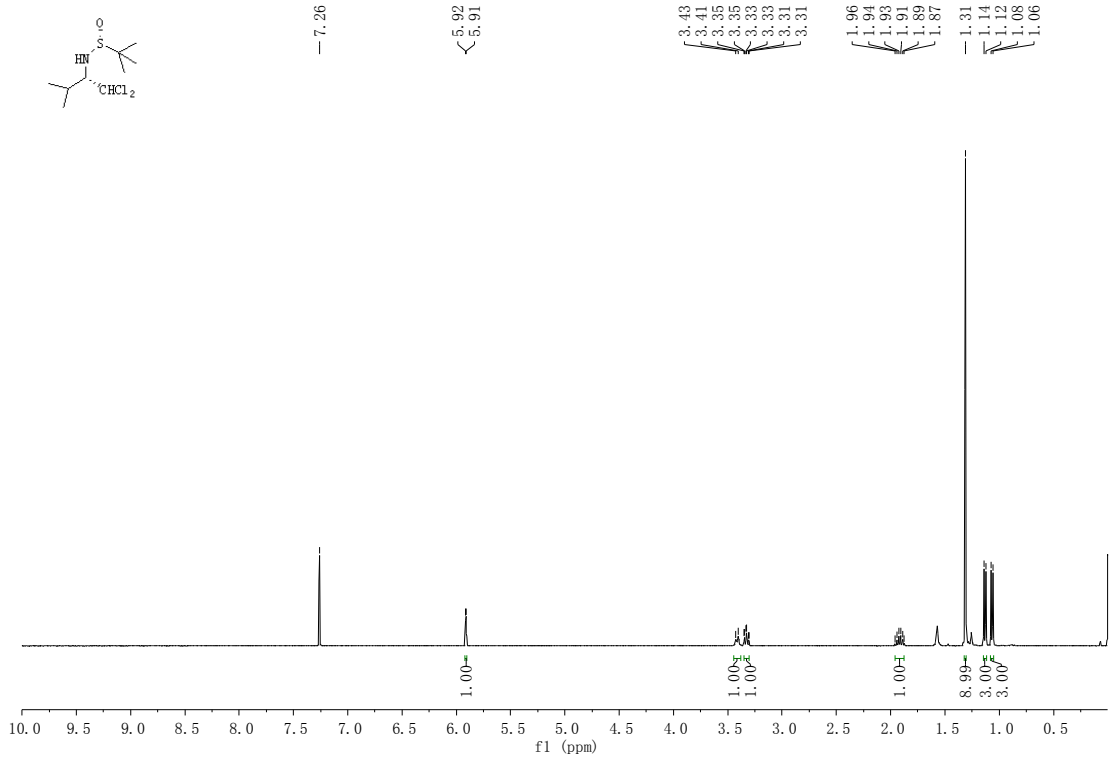
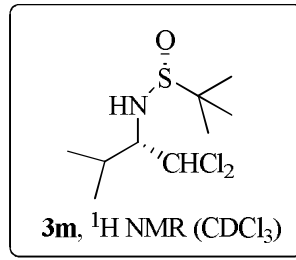


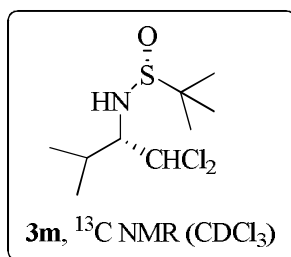




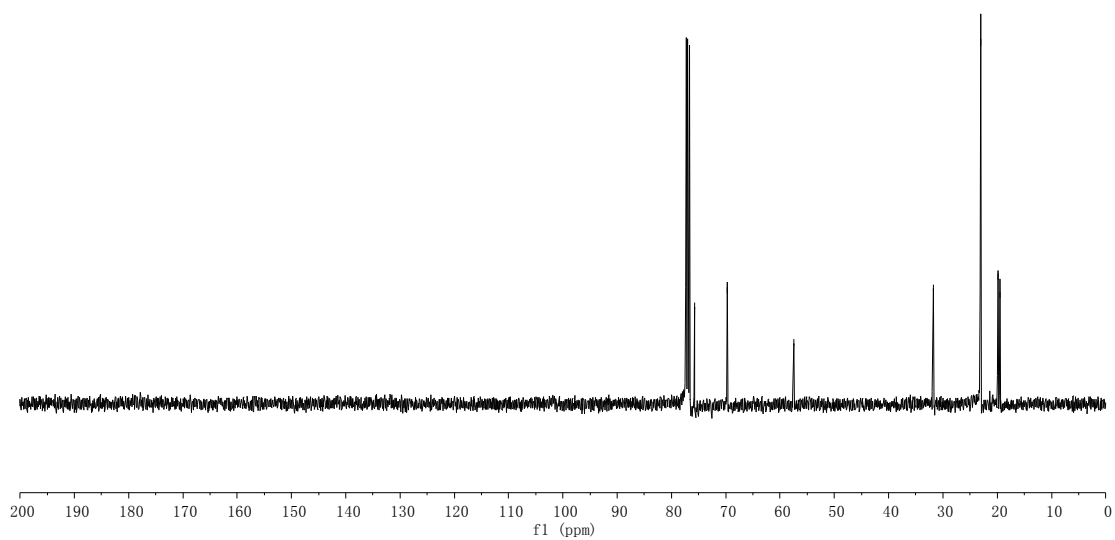


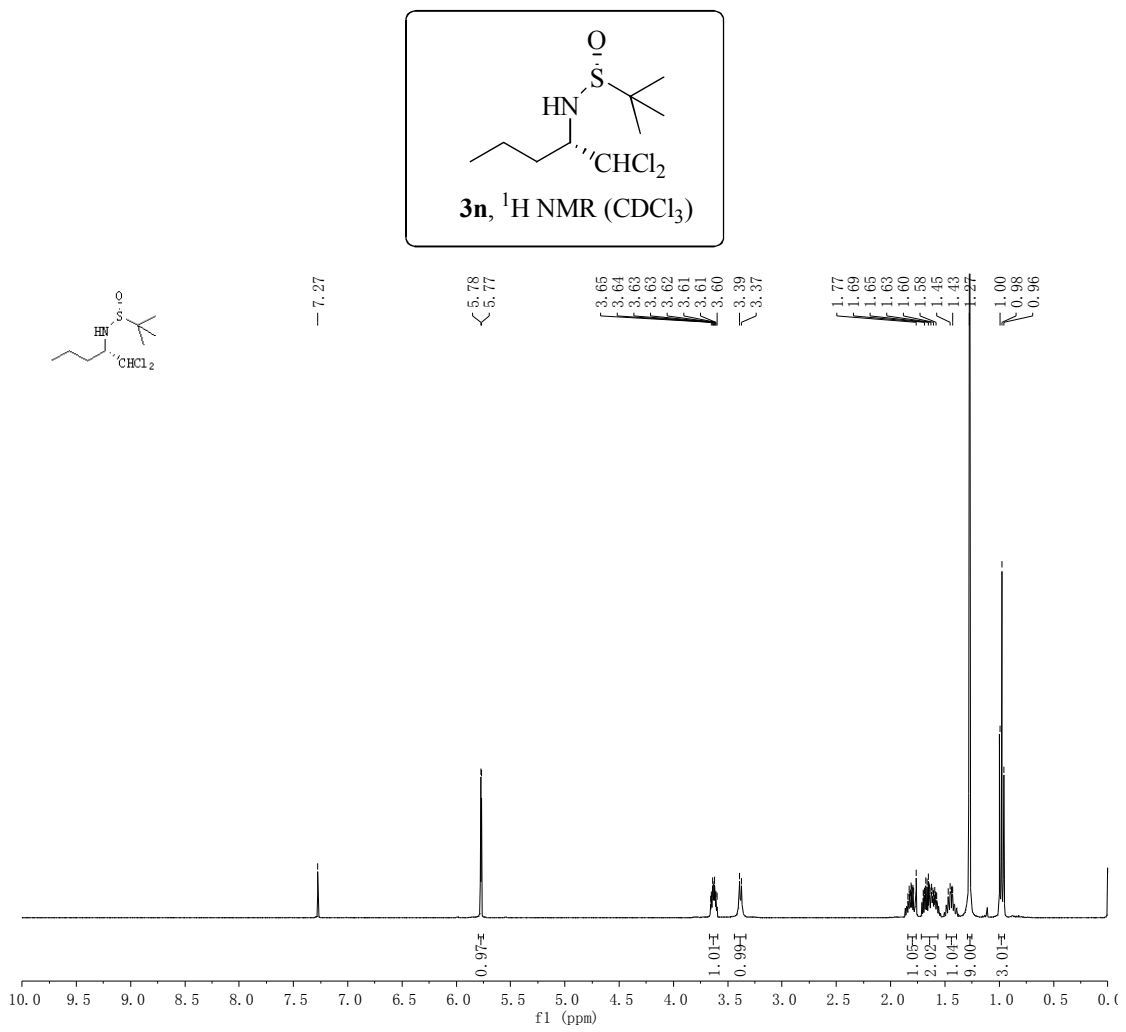


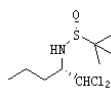
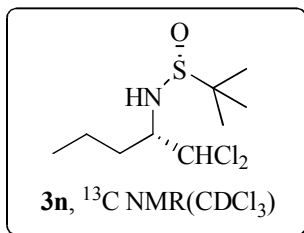




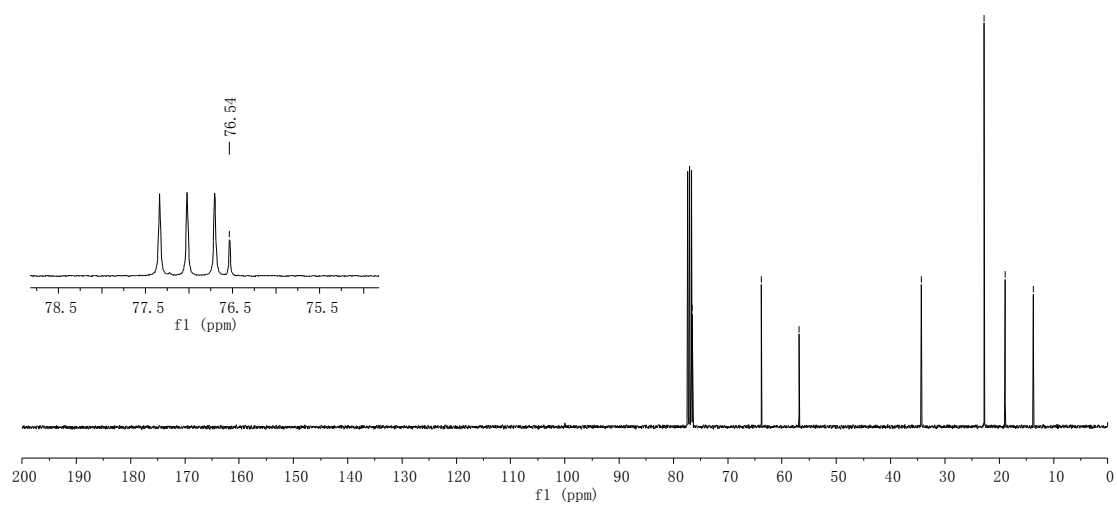
- 75.77
 - 69.69
 - 57.44
 - 31.77
 - 23.06
 - 19.86
 - 19.44

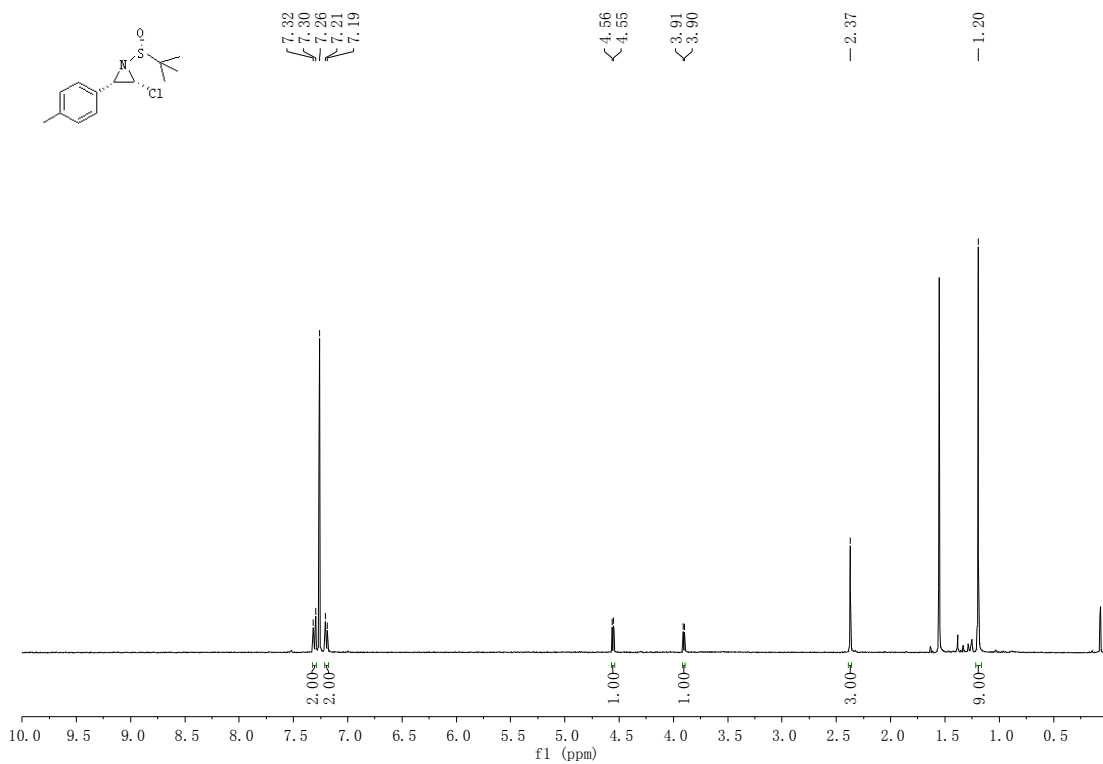
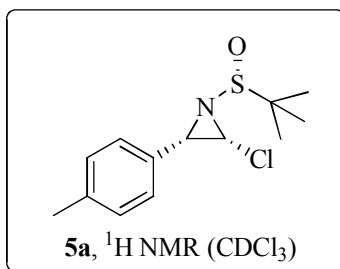


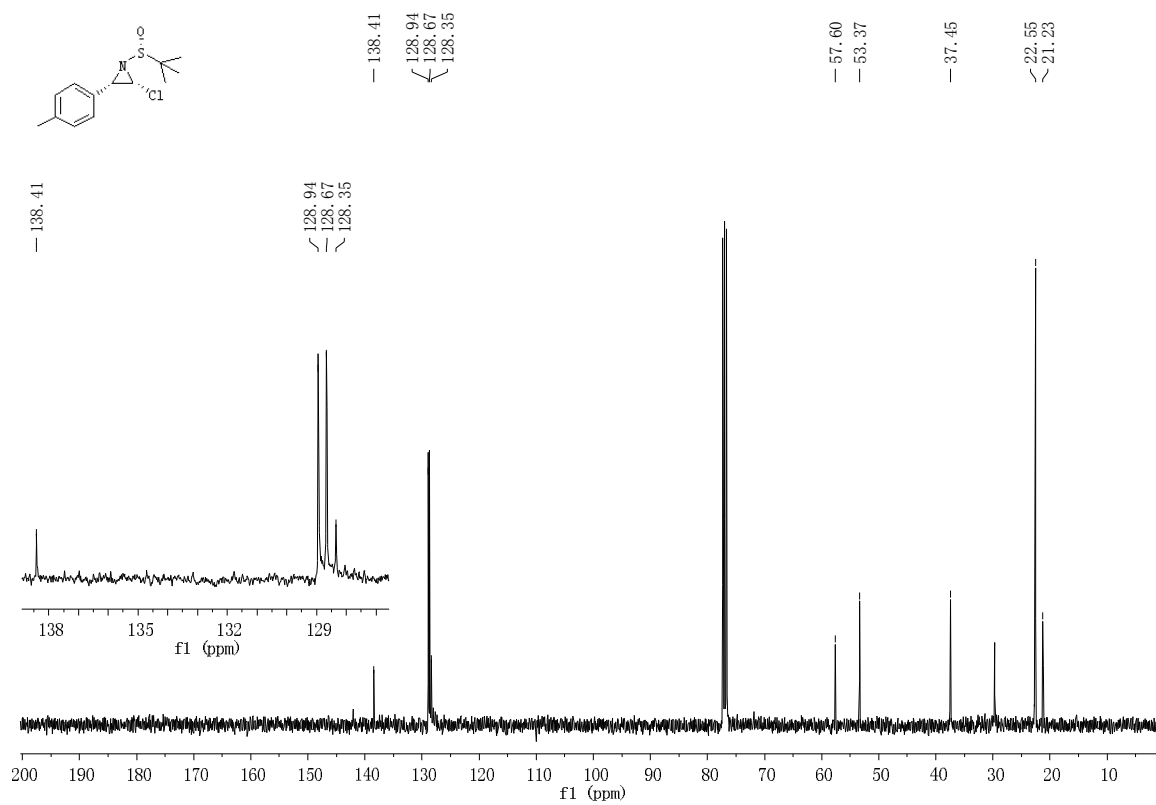
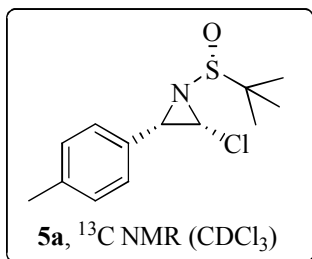


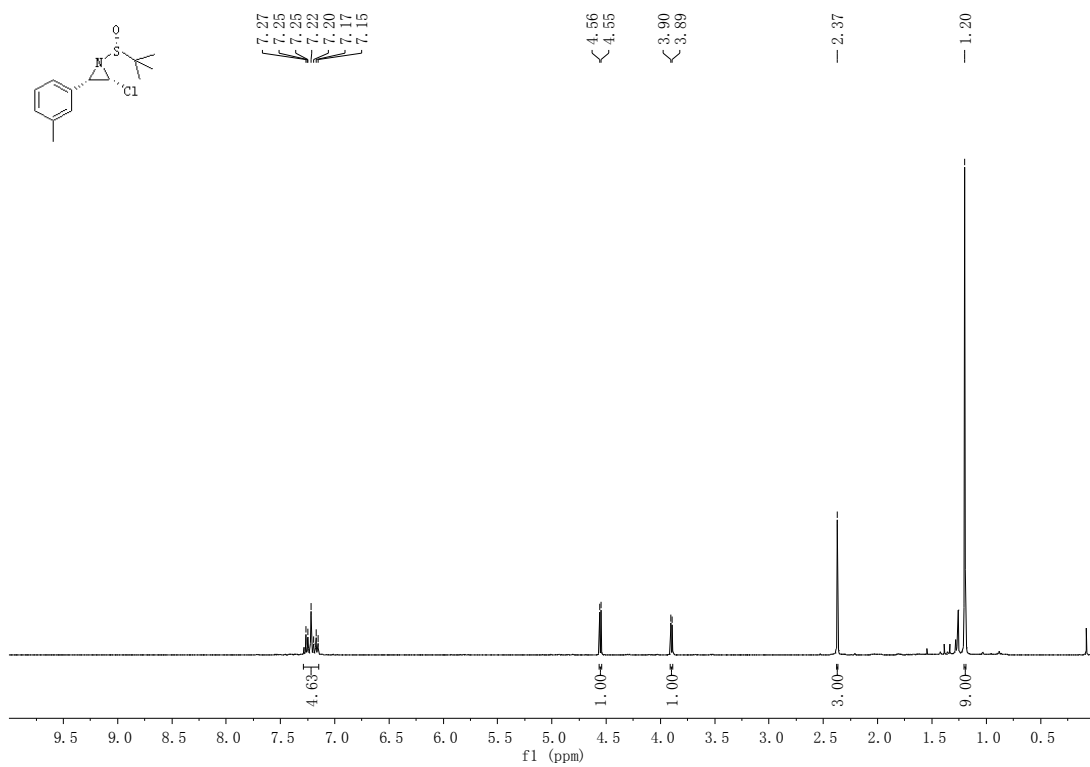
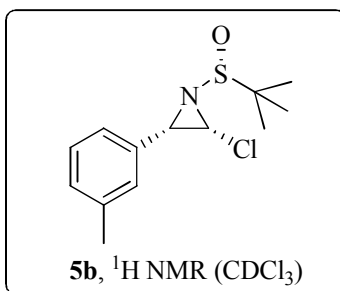


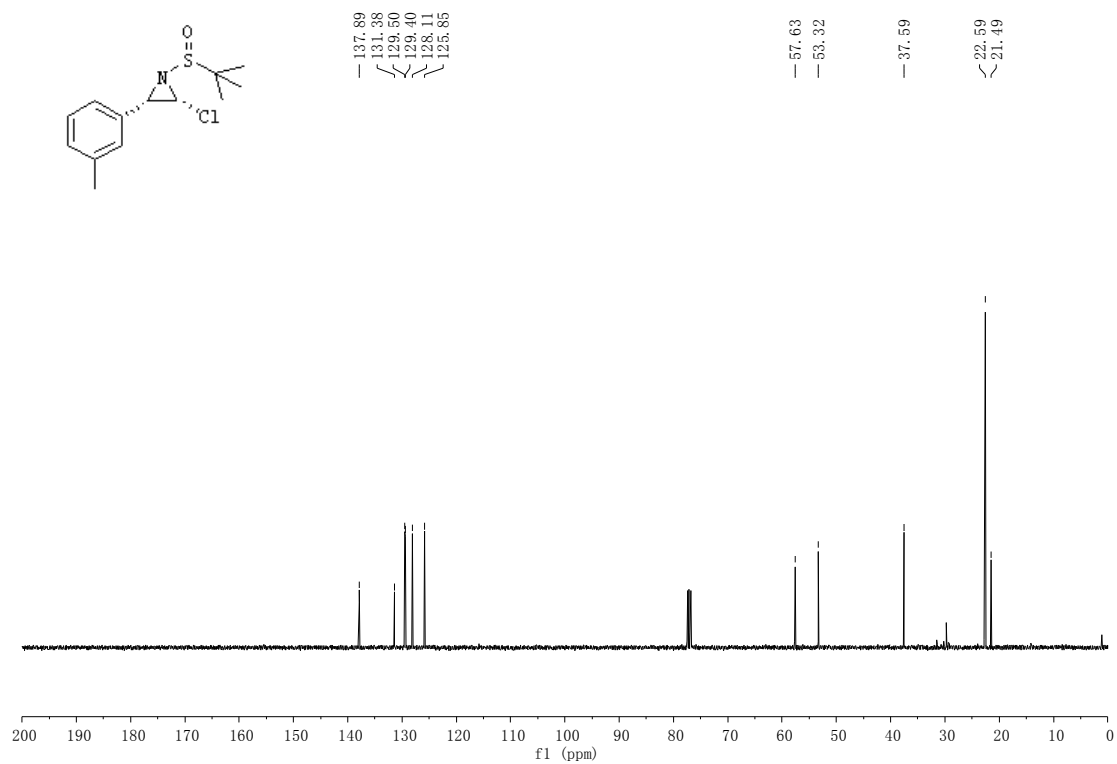
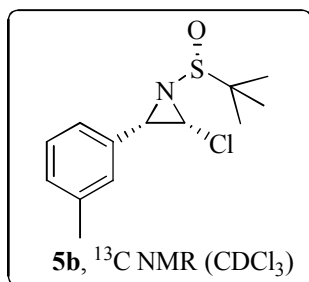
— 76.54
 — 63.78
 — 56.89
 — 34.37
 — 22.76
 — 18.94
 — 13.69

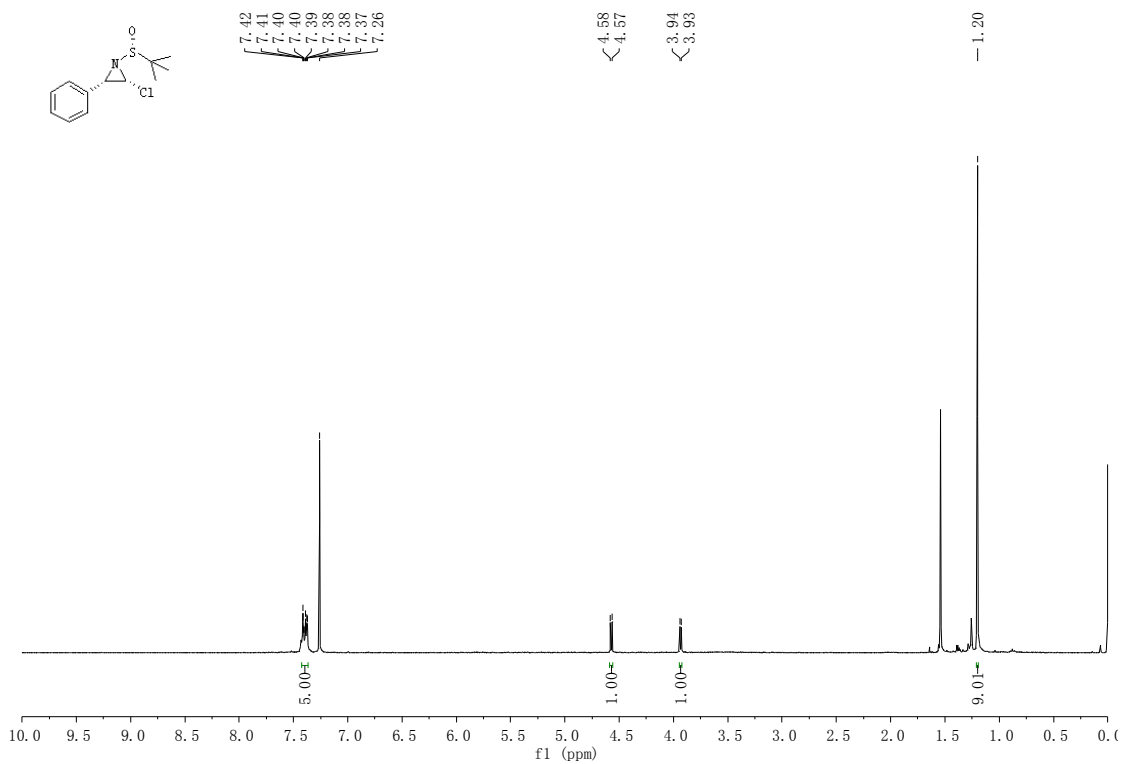
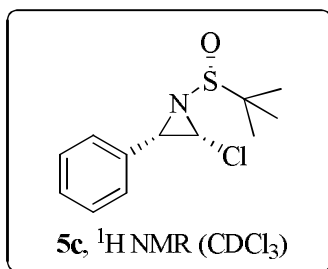


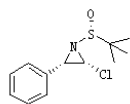
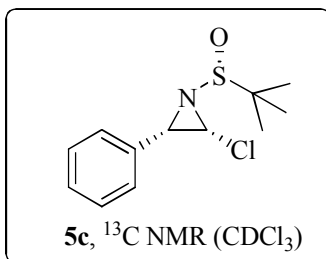










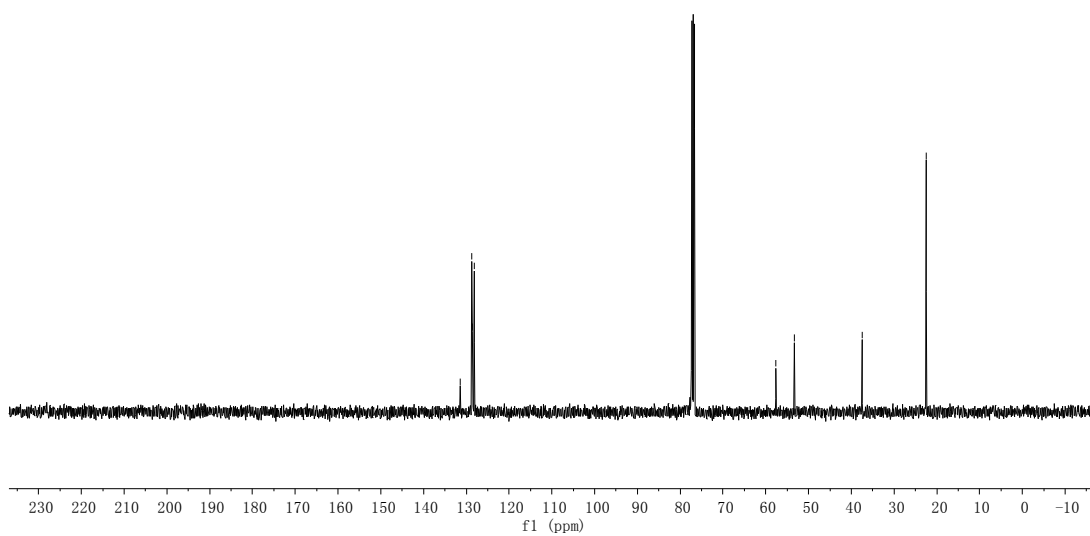


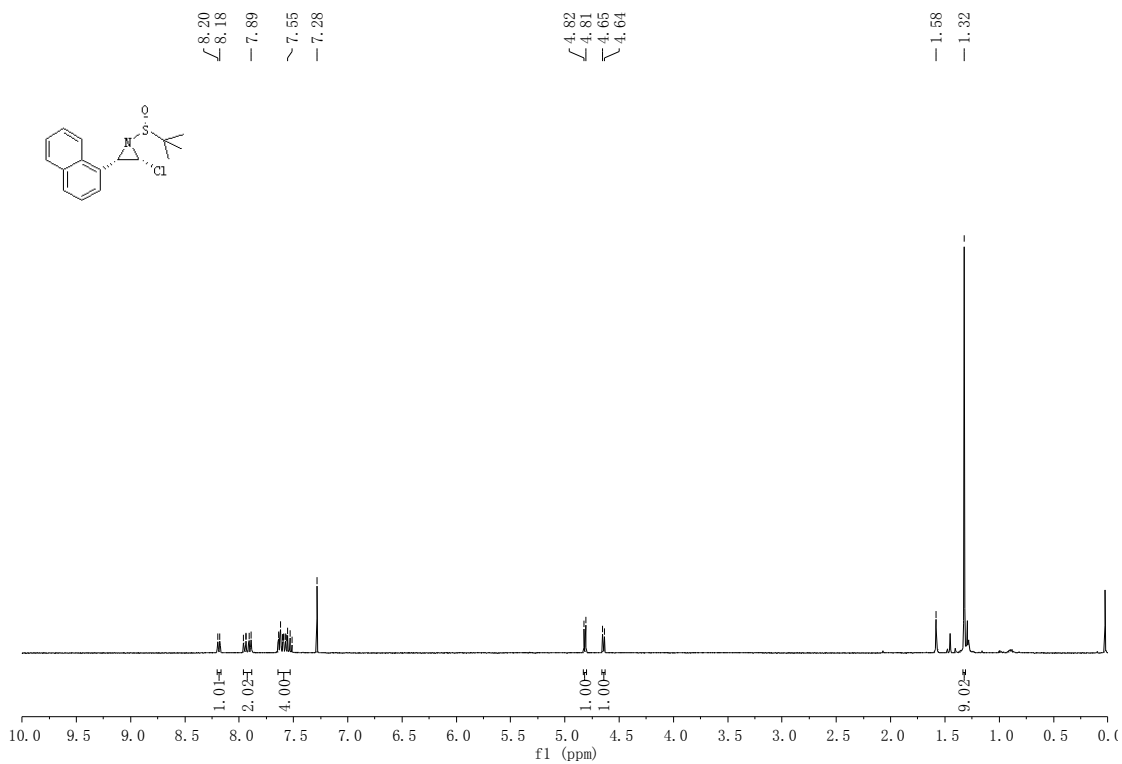
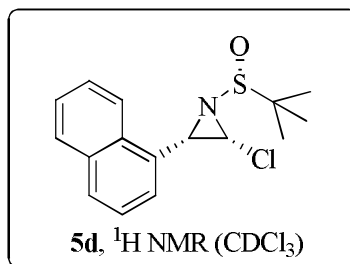
131.42
128.77
128.53
128.18

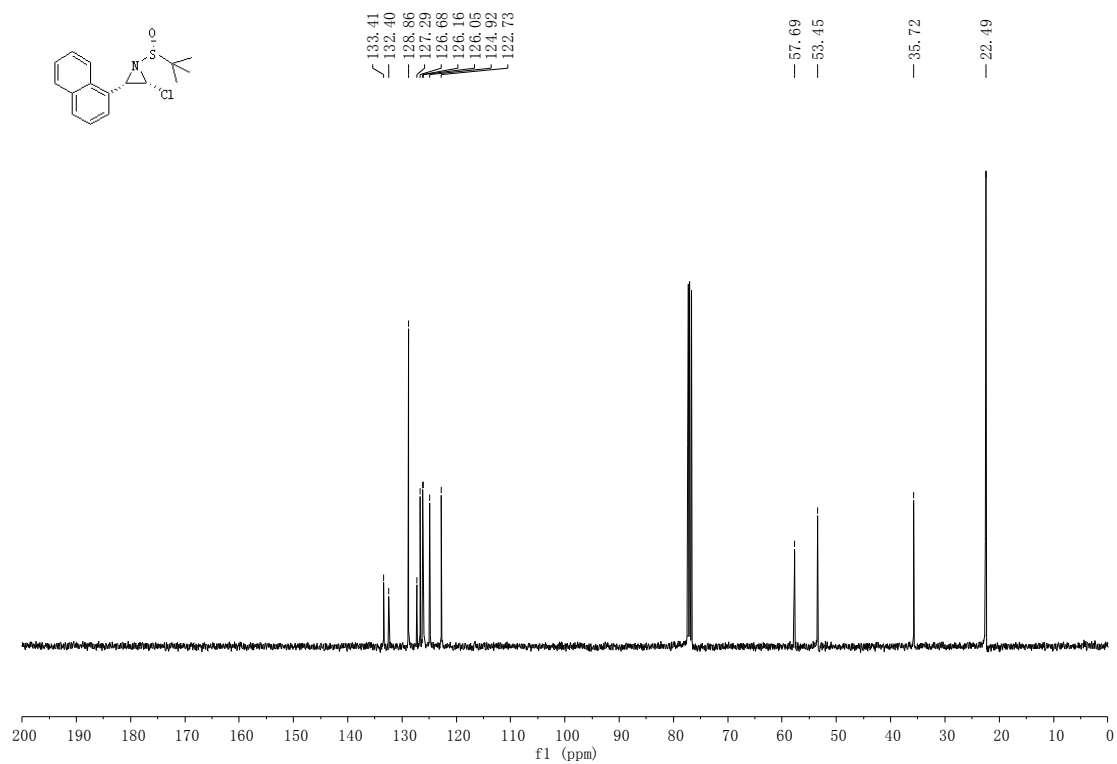
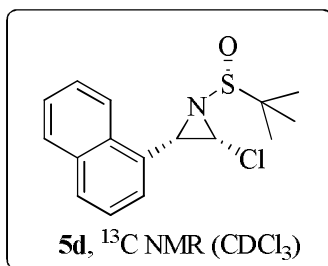
57.64
53.30

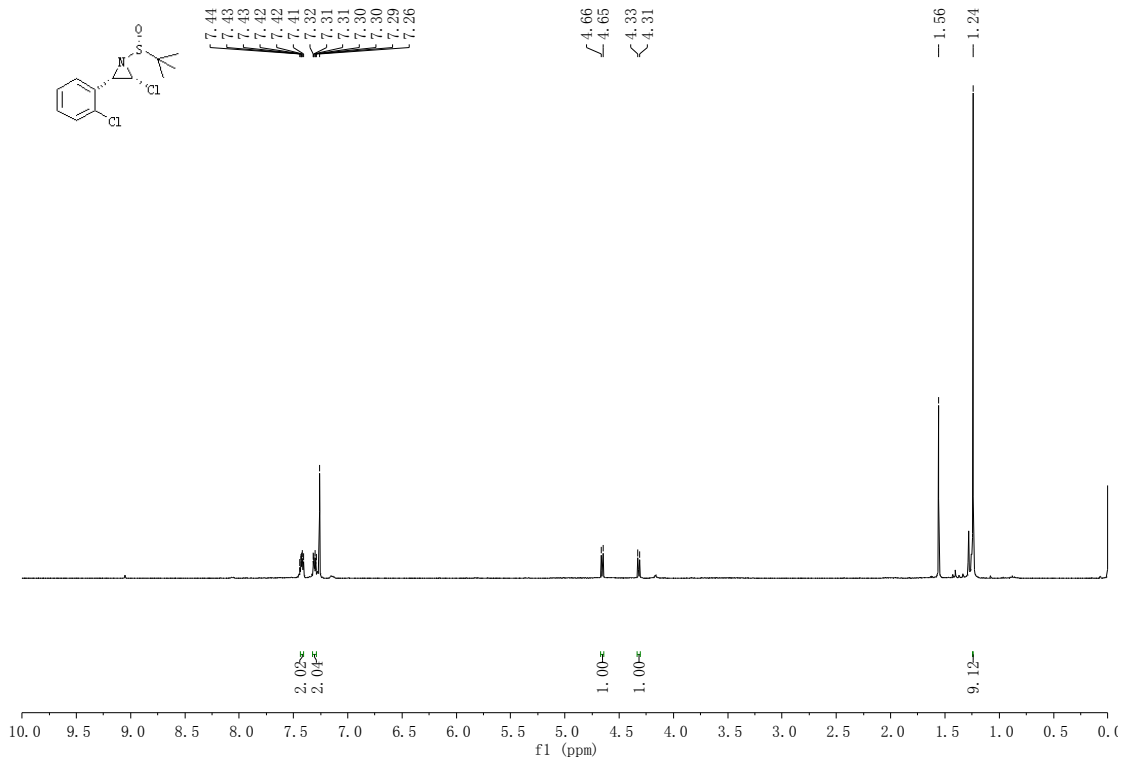
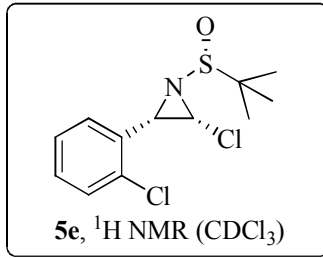
37.51

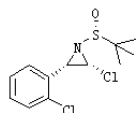
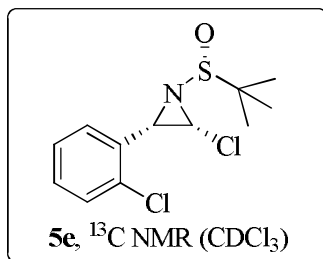
22.53









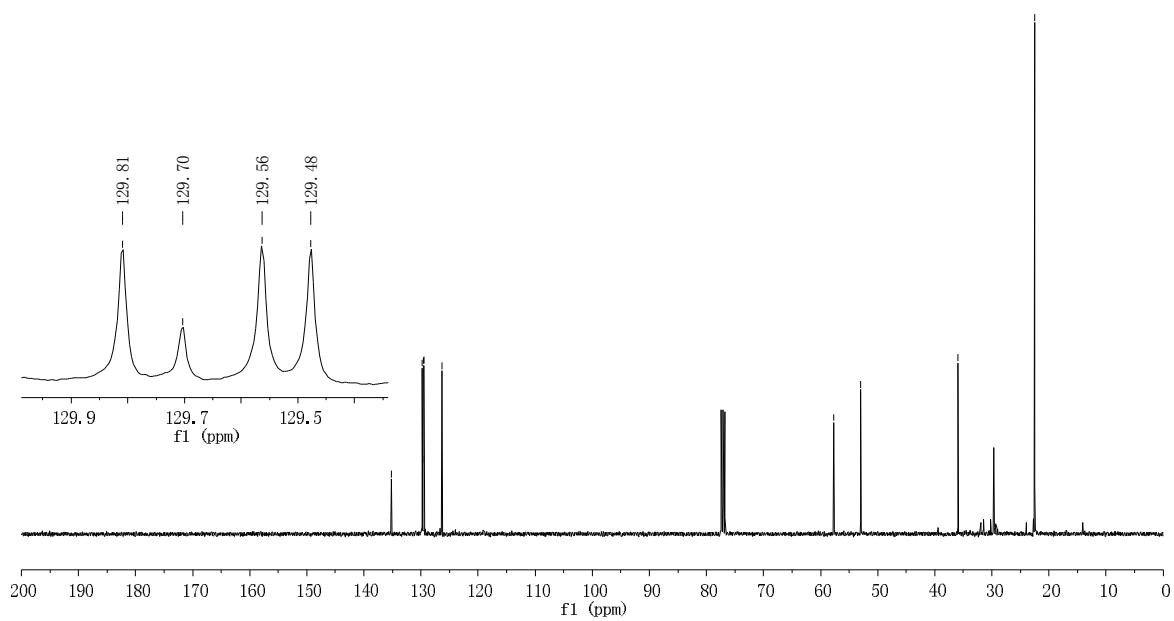


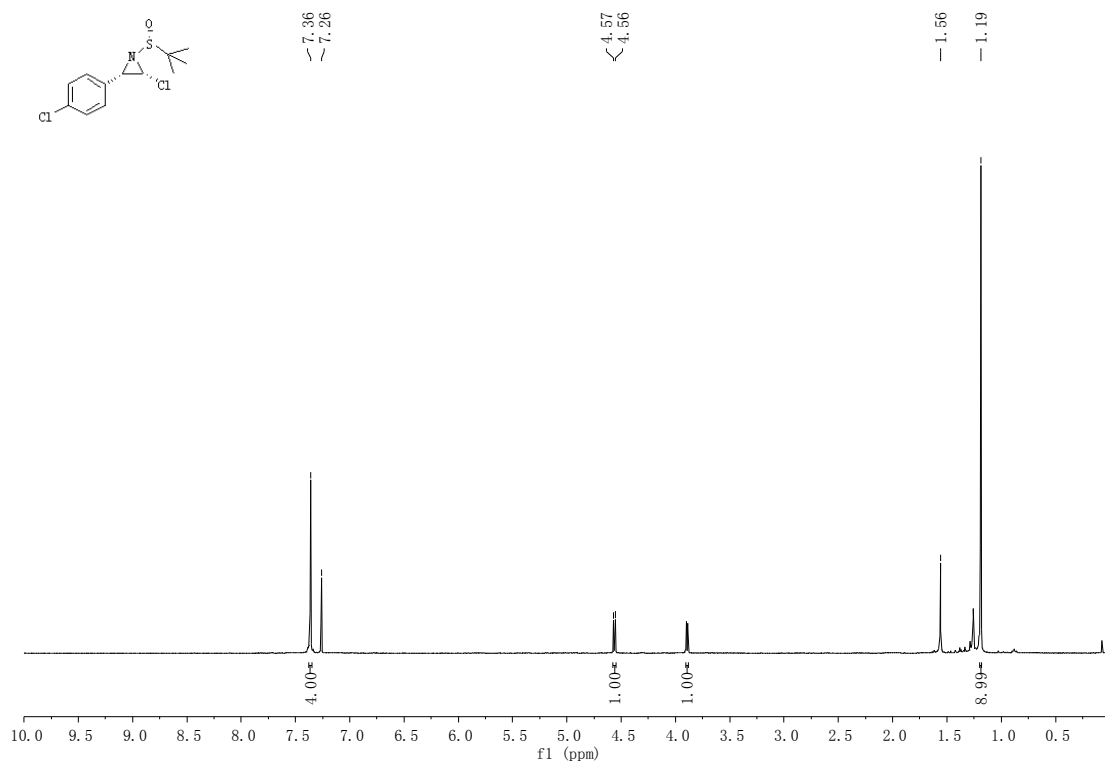
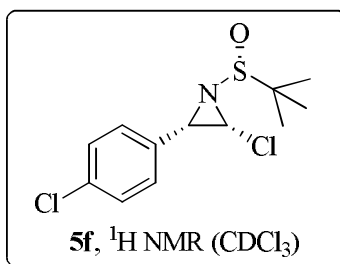
— 135.21
 — 129.48
 — 126.37

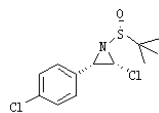
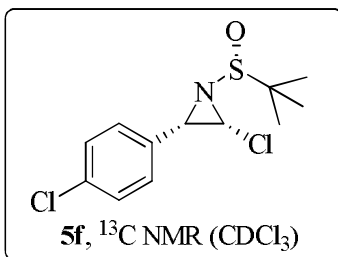
— 57.70
 — 52.94

— 35.91

— 22.50





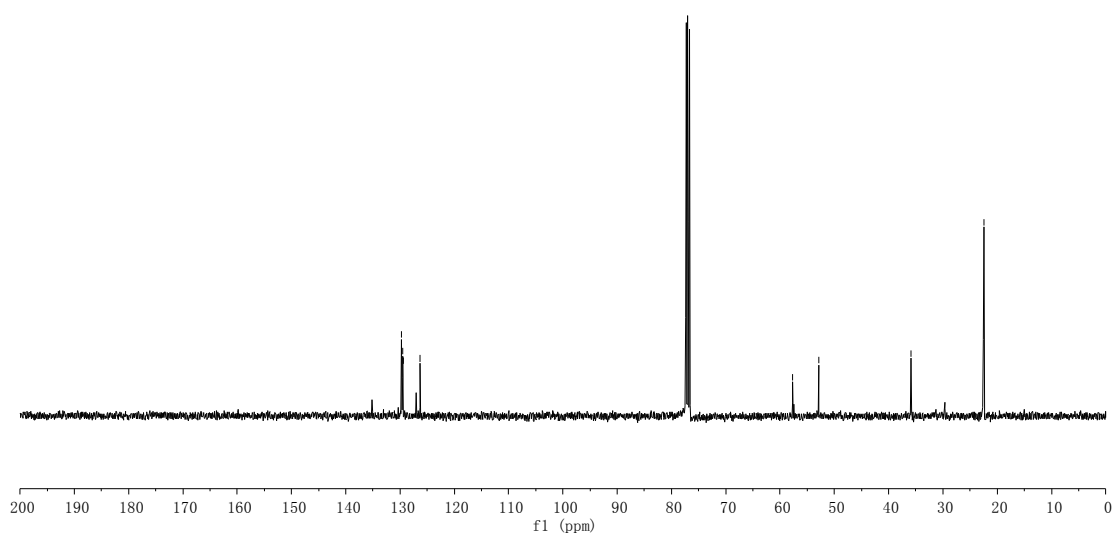


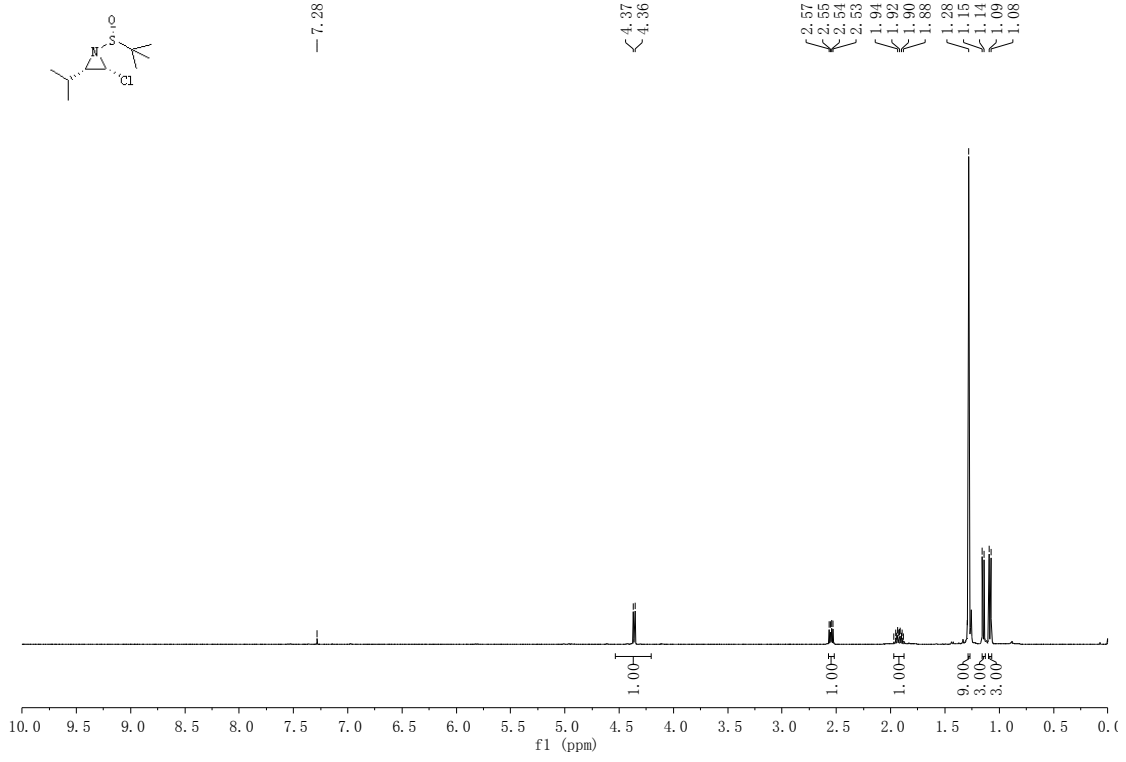
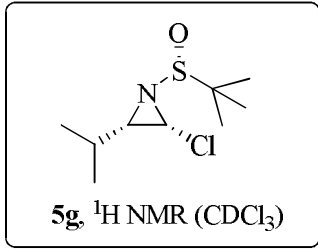
129.75
129.52
129.44
126.31

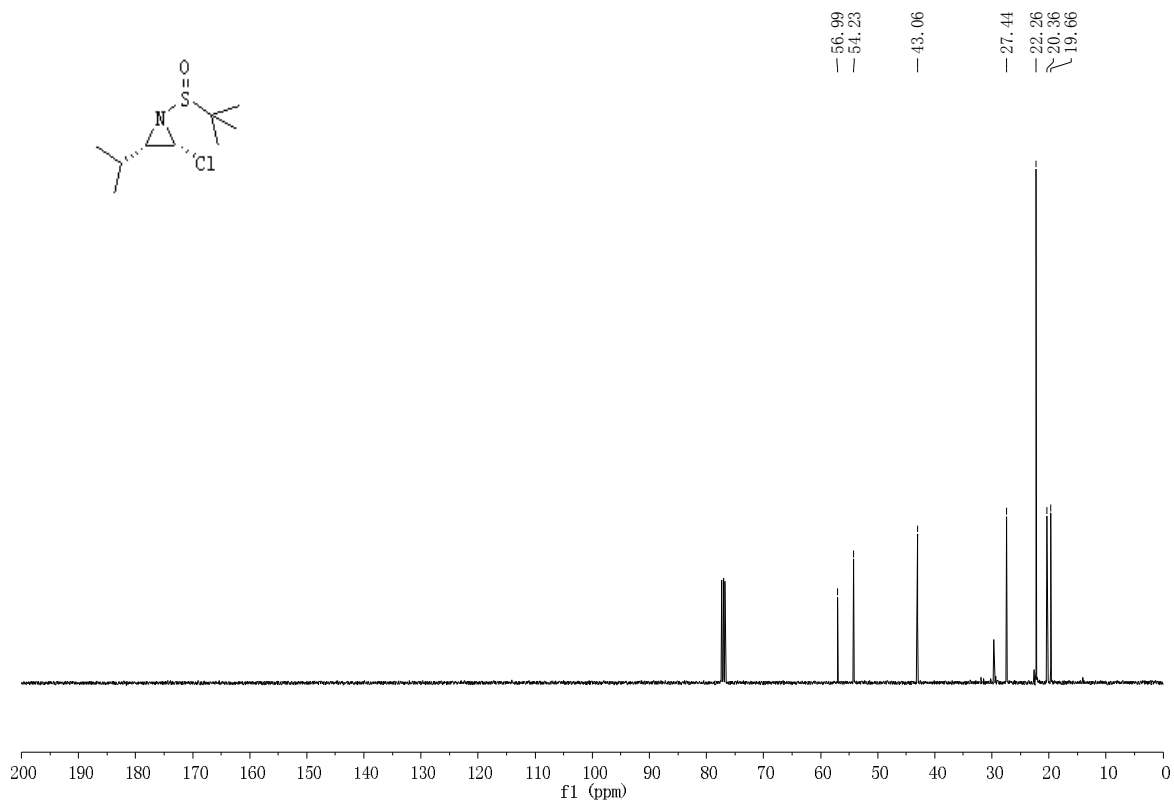
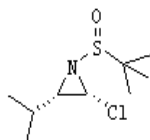
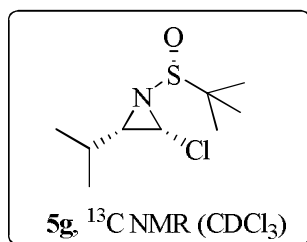
57.68
52.90

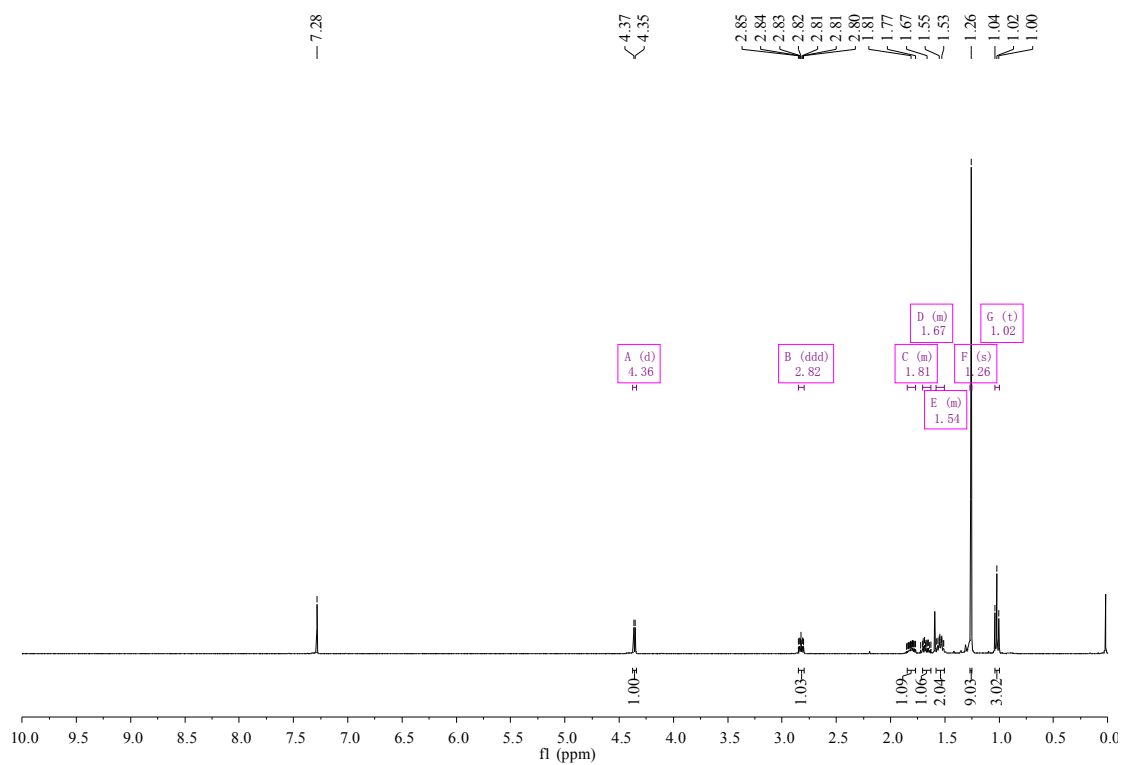
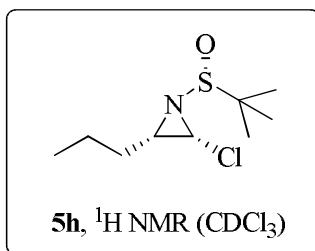
35.88

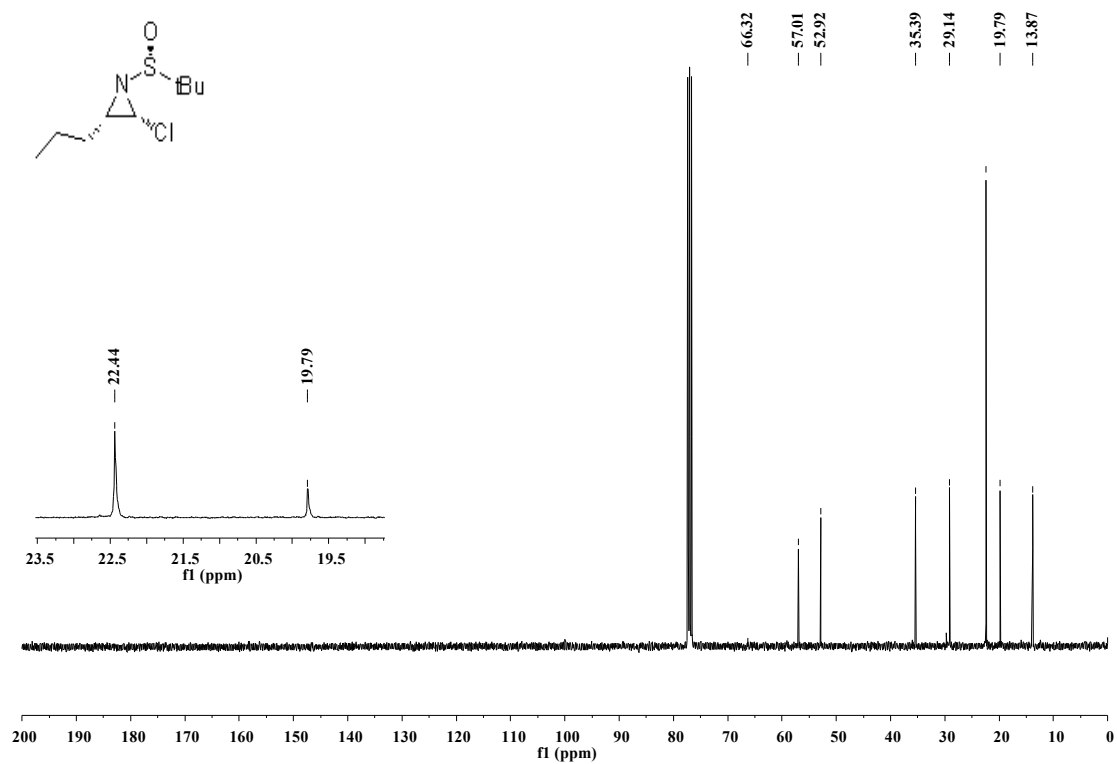
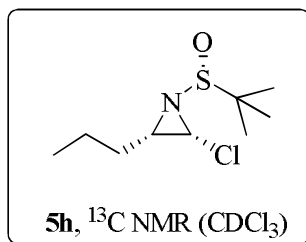
22.48

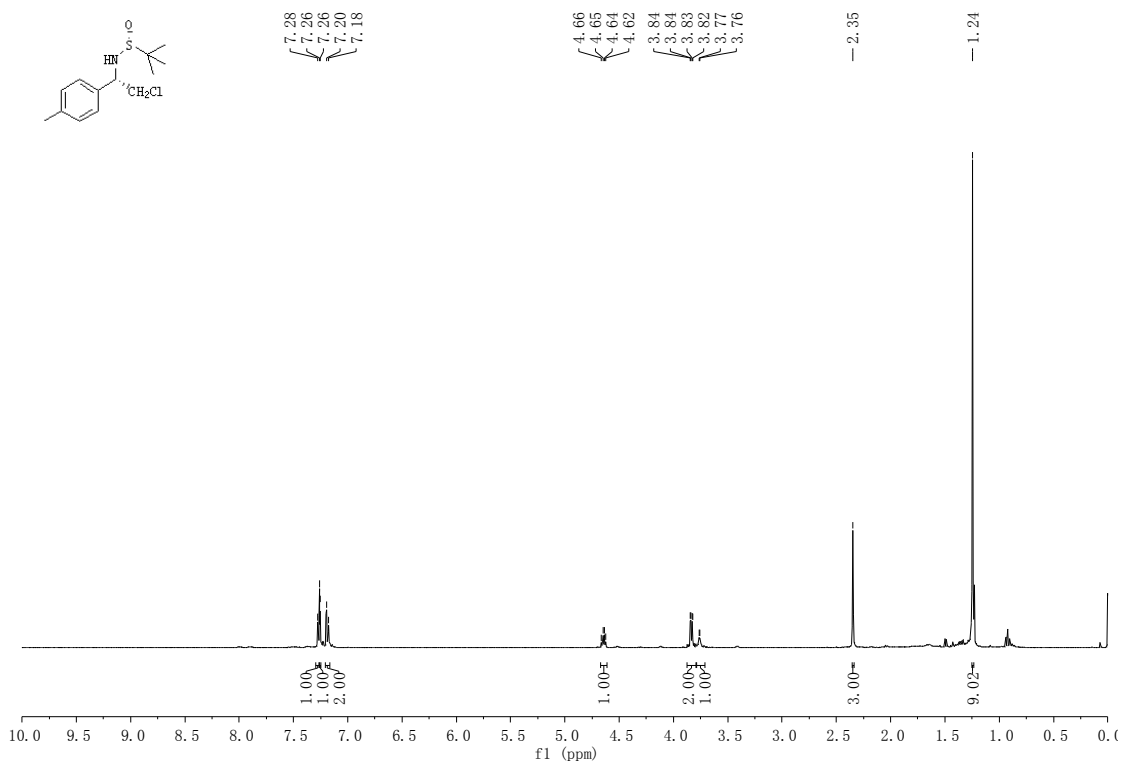
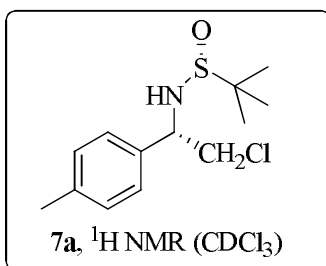


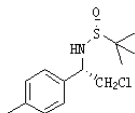
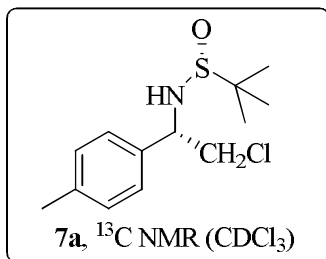












< 138.41
 < 135.96
 < 129.51
 < 127.16

< 59.37
 < 56.41
 < 48.41

< 22.56
 < 21.12

