Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ir/BiphPHOX-Catalyzed Asymmetric Hydrogenation of 3-Substituted 2,5-Dihydropyrroles and 2,5-Dihydrothiophene 1,1-Dioxides

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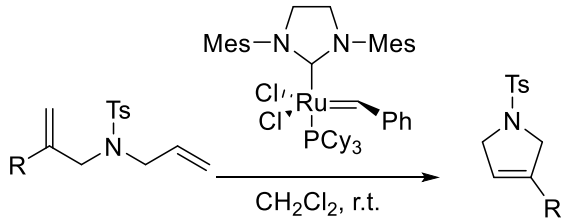
1. General Details.

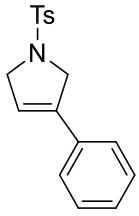
All reactions were performed in flame-dried glassware under an atmosphere of dried argon, and the workup was carried out in air, unless otherwise noted. Solvents were dried and distilled through standard procedures. Commercially available reagents were used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer. HRMS was performed on a Waters Micromass Q-TOF Premier Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. The *ee* values were determined by HPLC using Daicel chiral columns. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. The absolute configuration of hydrogenated products was determined by the single crystal of **2a** and **4a**.

2. Preparation of Starting Materials.

2.1. General Procedure for the Synthesis of the Substrates.[1]

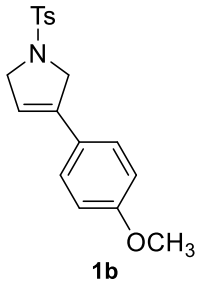


Procedure 1: Diene (xx mmol) and Grubbs 2:nd generation catalyst (4 mol%) were dissolved in dry dichloromethane (70 ml/mmol) and the solution stirred at room temperature over night. The reaction was quenched with water (20 mL), and extracted with DCM (30 mL×3). The organic layers were combined, washed with brine (10 mL), dried by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was purified with 200-300 mesh silica gel column chromatography to give the corresponding products.



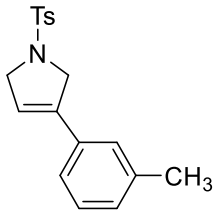
1a

3-Phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (1a). White soild, 77% yield, mp = 137.4 – 139.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.34 – 7.26 (m, 7H), 6.02 – 6.00 (m, 1H), 4.50 – 4.47 (m, 2H), 4.32 – 4.29 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 137.5, 134.2, 132.7, 130.1, 128.9, 128.7, 127.7, 125.6, 119.1, 55.9, 55.1, 21.8. HRMS (FT-MS) calcd for $C_{17}H_{17}NO_2S$ $(M + Na)^+$: 322.0878; found: 322.0878.



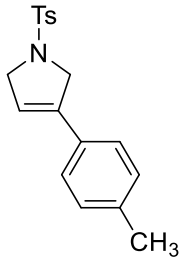
1b

3-(4-Methoxyphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1b). White soild, 48% yield, mp = 138.0 – 138.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 2H), 6.87 – 6.83 (m, 2H), 5.86 – 5.85 (m, 1H), 4.46 – 4.43 (m, 2H), 4.29 – 4.27 (m, 2H), 3.80 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 143.5, 136.7, 134.1, 129.8, 127.5, 126.7, 125.3, 116.6, 114.1, 55.7, 55.3, 55.0, 21.5. HRMS (FT-MS) calcd for $C_{18}H_{19}NO_3S$ $(M+Na)^+$: 352.0983; found: 352.0986.



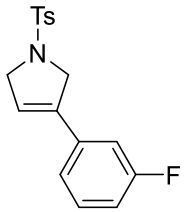
1c

3-(*m*-Tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1c). White soild, 50% yield, mp = 112.5 – 114.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 3H), 5.99 – 5.97 (m, 1H), 4.49 – 4.46 (m, 2H), 4.31 – 4.28 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.3, 137.4, 134.0, 132.4, 129.8, 129.2, 128.6, 127.5, 126.1, 122.5, 118.7, 55.7, 55.0, 21.5, 21.4. HRMS (FT-MS) calcd for $C_{18}H_{19}NO_2S$ $(M + Na)^+$: 336.1034; found: 336.1035.



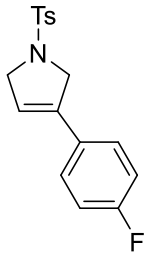
1d

3-(*p*-Tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1d). White soild, 55% yield, mp = 143.1 – 144.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.94 – 5.93 (m, 1H), 4.47 – 4.45 (m, 2H), 4.30 – 4.27 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.4, 137.2, 134.1, 129.8, 129.7, 129.4, 127.5, 125.3, 117.8, 55.7, 55.0, 21.5, 21.2. HRMS (FT-MS) calcd for $C_{18}H_{19}NO_2S$ $(M + Na)^+$: 336.1034; found: 336.1032.



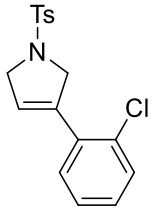
1e

3-(3-Fluorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1e). White soild, 48% yield, mp = 144.6 – 146.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.05 – 6.02 (m, 1H), 4.46 – 4.43 (m, 2H), 4.32 – 4.29 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 244.9 Hz), 143.9, 136.6, 134.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 134.1, 130.5 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.1, 127.7, 121.3 (d, $J_{C\text{-}F}$ = 1.8 Hz), 120.6, 115.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 112.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 55.8, 55.0, 21.8. HRMS (FT-MS) calcd for $C_{17}H_{16}FNO_2S$ $(M + Na)^+$: 340.0783; found: 340.0783.



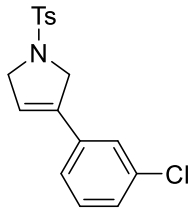
1f

3-(4-Fluorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1f). White soild, 46% yield, mp = 117.2 – 119.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.04 – 6.99 (m, 2H), 5.95 – 5.93 (m, 1H), 4.46 – 4.43 (m, 2H), 4.31 – 4.28 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, $J_{C\text{-}F}$ = 247.2 Hz), 143.7, 136.3, 134.0, 129.9, 128.7 (d, $J_{C\text{-}F}$ = 3.4 Hz), 127.5, 127.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 118.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.6 Hz), 55.6, 54.9, 21.5. HRMS (FT-MS) calcd for $C_{17}H_{16}FNO_2S$ $(M + Na)^+$: 340.0783; found: 340.0782.



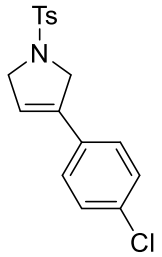
1g

3-(2-Chlorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1g). White soild, 41% yield, mp = 142.5 – 144.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.34 – 7.28 (m, 4H), 7.22 – 7.19 (m, 2H), 6.01 – 5.99 (m, 1H), 4.46 – 4.43 (m, 2H), 4.31 – 4.28 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.3, 134.2, 134.0, 131.0, 129.9, 128.9, 127.5, 126.7, 119.6, 55.6, 54.8, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{16}ClNO_2S$ $(M + Na)^+$: 356.0488; found: 356.0487.



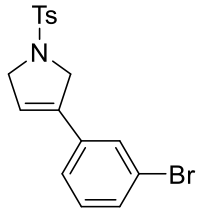
1h

3-(3-Chlorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1h). White soild, 46% yield, mp = 128.8 – 130.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 4.0 Hz, 3H), 7.17 – 7.14 (m, 1H), 6.05 – 6.03 (m, 1H), 4.46 – 4.43 (m, 2H), 4.32 – 4.29 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.2, 134.7, 134.2, 134.0, 129.9, 129.9, 128.4, 127.5, 125.6, 123.5, 120.5, 55.6, 54.8, 21.6 .HRMS (FT-MS) calcd for $C_{17}H_{16}ClNO_2S$ $(M + Na)^+$: 356.0488; found: 356.0489.



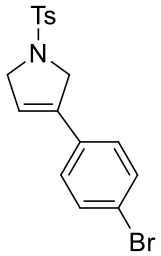
1i

3-(4-Chlorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1i). White soild, 49% yield, mp = 130.0 – 131.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.34 – 7.28 (m, 4H), 7.22 – 7.19 (m, 2H), 6.01 – 5.99 (m, 1H), 4.46 – 4.43 (m, 2H), 4.31 – 4.28 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.3, 134.2, 134.0, 131.0, 130.0, 128.9, 127.5, 126.7, 119.6, 55.6, 54.8, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{16}ClNO_2S$ $(M + Na)^+$: 356.0488; found: 356.0485.



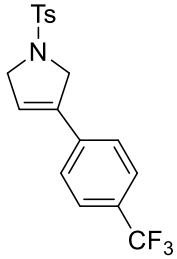
1j

3-(3-Bromophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1j). White soild, 56% yield, mp = 127.2 – 128.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 2H), 7.41 – 7.39 (m, 2H), 7.34 – 7.32 (m, 2H), 7.21 – 7.17 (m, 2H), 6.04 – 6.02 (m, 1H), 4.45 – 4.42 (m, 2H), 4.32 – 4.29 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.1, 134.5, 133.9, 131.3, 130.2, 129.9, 128.5, 127.5, 124.0, 122.9, 120.6, 55.6, 54.7, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{16}BrNO_2S$ $(M + Na)^+$: 399.9983; found: 399.9984.



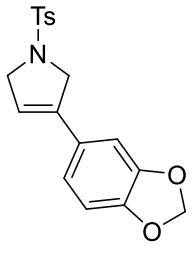
1k

3-(4-Bromophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1k) white soild, 57% yield, mp = 136.9 – 138.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.03 – 6.01 (m, 1H), 4.46 – 4.43 (m, 2H), 4.30 – 4.27 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.4, 134.0, 131.8, 131.4, 129.9, 127.5, 126.9, 122.4, 119.8, 55.7, 54.7, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{16}BrNO_2S$ $(M+Na)^+$: 399.9983; found: 399.9983.



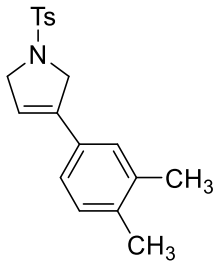
1l

1-Tosyl-3-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1*H*-pyrrole (1l). white soild, 42% yield, mp = 157.8 – 158.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 6.15 – 6.13 (m, 1H), 4.51 – 4.48 (m, 2H), 4.35 – 4.32 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 136.3, 135.8 (q, J_{C-F} = 1.3 Hz), 134.0, 130.3 (q, J_{C-F} = 32.4 Hz), 129.9, 127.5, 125.7 (q, J_{C-F} = 3.7 Hz), 125.7, 123.9 (q, J_{C-F} = 270.3 Hz), 121.7, 55.7, 54.7, 21.6. HRMS (FT-MS) calcd for $C_{18}H_{16}F_3NO_2S$ $(M + Na)^+$: 390.0752; found: 390.0753.

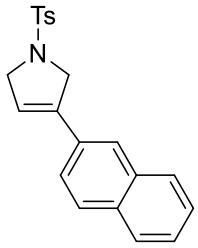


1m

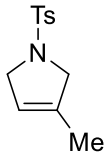
3-(Benzo[d][1,3]dioxol-5-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1m). White soild, 60% yield, mp = 145.5 – 147.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.71 – 6.69 (m, 1H), 5.96 (s, 2H), 5.84 – 5.83 (m, 1H), 4.42 – 4.40 (m, 2H), 4.29 – 4.27 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 148.0, 143.8, 137.0, 134.2, 130.1, 127.7, 127.0, 119.6, 117.6, 108.5, 105.8, 101.5, 55.8, 55.2, 21.8. HRMS (FT-MS) calcd for $C_{18}H_{17}NO_4S$ $(M + Na)^+$: 366.0776; found: 366.0775.



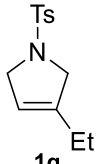
1n **3-(3,4-Dimethylphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1n).** White soild, 66% yield, mp = 157.8 – 159.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.01 (m, 3H), 5.93 – 5.92 (m, 1H), 4.47 – 4.44 (m, 2H), 4.29 – 4.27 (m, 2H), 2.41 (s, 3H), 2.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.3, 137.2, 136.9, 134.1, 130.1, 129.9, 129.8, 127.5, 126.6, 122.8, 117.6, 55.7, 55.0, 21.5, 19.8, 19.6. HRMS (FT-MS) calcd for $C_{19}H_{21}NO_2S$ $(M + Na)^+$: 350.1191; found: 350.1193.



1o **3-(Naphthalen-2-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1o).** White soild, 68% yield, mp = 178.6 – 179.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 5H), 7.57 (s, 1H), 7.53 – 7.45 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.14 – 6.13 (m, 1H), 4.63 – 4.60 (m, 2H), 4.37 – 4.34 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.3, 134.1, 133.2, 133.1, 129.9, 129.8, 128.4, 128.2, 127.7, 127.5, 126.7, 126.5, 124.6, 123.1, 119.5, 55.8, 55.0, 21.5. HRMS (FT-MS) calcd for $C_{21}H_{19}NO_2S$ $(M + Na)^+$: 372.1034; found: 372.1035.

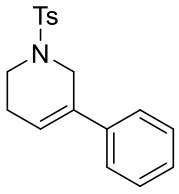


1p **3-Methyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (1p).** White soild, 60% yield, mp = 94.0 – 94.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.33 – 7.31 (m, 2H), 5.26 – 5.24 (m, 1H), 4.07 – 4.06 (m, 2H), 3.97 – 3.96 (m, 2H), 2.43 (s, 3H), 1.66 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 135.3, 134.4, 130.0, 127.7, 119.3, 57.9, 55.4, 21.8, 14.3. HRMS (FT-MS) calcd for $C_{12}H_{15}NO_2S$ $(M + Na)^+$: 260.0721; found: 260.0721.



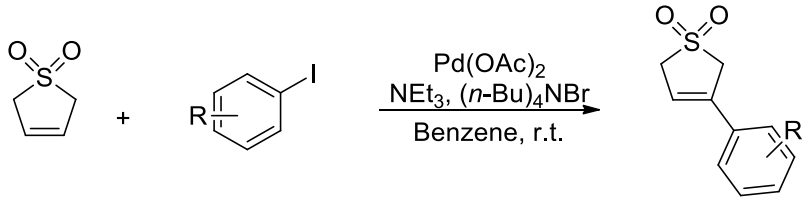
1q **3-Ethyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (1q).** White soild, 37% yield, mp = 79.2 – 81.2 ℃. ^{1}H NMR (400 MHz, CDCl3) δ 7.73 – 7.71 (m, 2H), 7.33 – 7.31 (m, 2H), 5.26 – 5.24 (m, 1H), 4.10 – 4.05 (m, 2H), 4.02 – 3.99 (m, 2H), 2.43 (s, 3H), 2.02 – 1.96 (m, 2H), 1.00 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.2, 134.3, 129.7, 127.5, 117.0, 56.5, 55.1, 21.7,

21.5, 11.7. HRMS (FT-MS) calcd for $C_{13}H_{17}NO_2S$ (M + Na)$^+$: 274.0878; found: 274.0875.

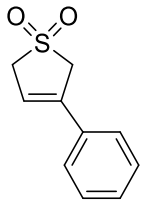


1r

5-Phenyl-1-tosyl-1,2,3,6-tetrahydropyridine(1r). White soild, 63% yield, mp = 111.8 – 112.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.34 – 7.24 (m, 7H), 6.08 – 6.06 (m, 1H), 3.95 – 3.94 (m, 2H), 3.25 – 3.22 (m, 2H), 2.42 (s, 3H), 2.41 – 2.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.7, 133.5, 133.4, 129.7, 128.5, 127.7, 125.2, 122.2, 46.4, 42.4, 25.7, 21.6. HRMS (FT-MS) calcd for $C_{18}H_{19}NO_2S$ (M + Na)$^+$: 336.1034; found: 336.1035.

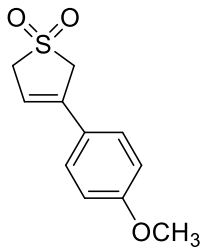


Procedure 2: A mixture of 2.04 g (10.0 mmol) iodobenzene, 1.24 g (10.5 mmol) sulfolene, 1.26 g (12.5 mmol) triethylamine, 3.22 g (10.0 mmol) tetrabutylammonium bromide, 112 mg (5%) $Pd(OAc)_2$, and 5 ml of benzene was stirred in a foil-covered, stoppered flask for 24 h. The solvent was removed in vacuum, quenched with water (20 mL), and extracted with DCM (30 mL×3). The organic layers were combined, washed with brine (10 mL), dried by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was purified with 200 – 300 mesh silica gel column chromatography to give the corresponding product[2].



3a

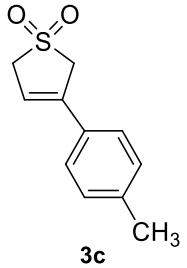
3-Phenyl-2,5-dihydrothiophene 1,1-dioxide (3a). White soild, 91% yield, mp = 122.0 – 124.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 5H), 6.36 – 6.34 (m, 1H), 4.16 – 4.15 (m, 2H), 4.05 – 4.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 133.9, 129.3, 129.0, 125.5, 117.1, 57.7, 56.7. HRMS (FT-MS) calcd for $C_{10}H_{10}SO_2$ (M + Na)$^+$: 217.0299; found: 217.0294.



3b

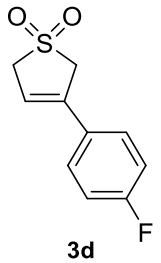
3-(4-Methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (3b). White soild, 83% yield, mp = 91.6 – 92.8 ℃. ^{1}H NMR (400 MHz, CDCl3) δ 7.31 – 7.28 (m, 2H), 6.93 – 6.89 (m, 2H), 6.22 – 6.20 (m, 1H), 4.11 (d, *J* = 1.6 Hz, 2H), 4.02 – 4.01 (m, 2H), 3.83 (s, 3H). ^{13}C

NMR (100 MHz, CDCl3) δ 160.3, 135.6, 126.8, 126.6, 114.9, 114.3, 57.7, 56.7, 55.4. HRMS (FT-MS) calcd for $C_{11}H_{12}SO_3$ $(M + Na)^+$: 247.0405; found: 247.0407.



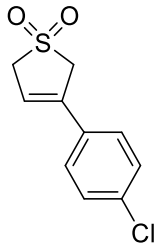
3c

3-(*p*-Tolyl)-2,5-dihydrothiophene 1,1-dioxide (3c). White soild, 90% yield, mp = 146.6 – 148.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 4H), 6.30 – 6.28 (m, 1H), 4.12 (d, *J* = 1.6 Hz, 2H), 4.02 – 4.01 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 132.4, 129.2, 126.7, 117.8, 57.7, 56.5. HRMS (FT-MS) calcd for $C_{11}H_{12}SO_2$ $(M + Na)^+$: 231.0456; found: 231.0460.



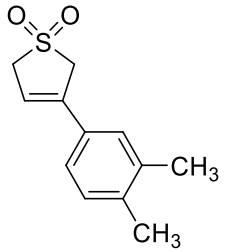
3d

3-(4-Fluorophenyl)-2,5-dihydrothiophene 1,1-dioxide (3d). White soild, 81% yield, mp = 103.1 – 105.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.12 – 7.06 (m, 2H), 6.30 – 6.28 (m, 1H), 4.12 (dd, *J* = 3.2, 1.2 Hz, 2H), 4.03 (d, *J* = 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 248.5 Hz), 135.2, 130.2 (d, $J_{C\text{-}F}$ = 3.4 Hz), 127.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 117.1 (d, $J_{C\text{-}F}$ = 1.8 Hz), 116.1 (d, $J_{C\text{-}F}$ = 21.7 Hz), 57.7, 56.6. HRMS (FT-MS) calcd for $C_{10}H_9FSO_2$ $(M + Na)^+$: 235.0205; found: 235.0200.



3e

3-(4-Chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (3e). White soild, 88% yield, mp = 148.0 – 149.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.31 – 7.28 (m, 2H), 6.36 – 6.34 (m, 1H), 4.12 – 4.11 (m, 2H), 4.04 – 4.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 132.4, 129.2, 126.7, 117.8, 57.7, 56.5. HRMS (FT-MS) calcd for $C_{10}H_9ClSO_2$ $(M + Na)^+$: 250.9909; found: 250.9916.

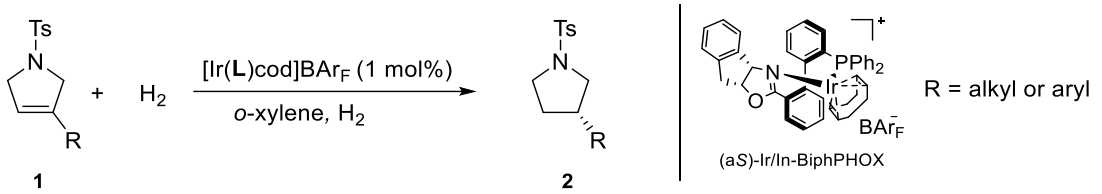


3f

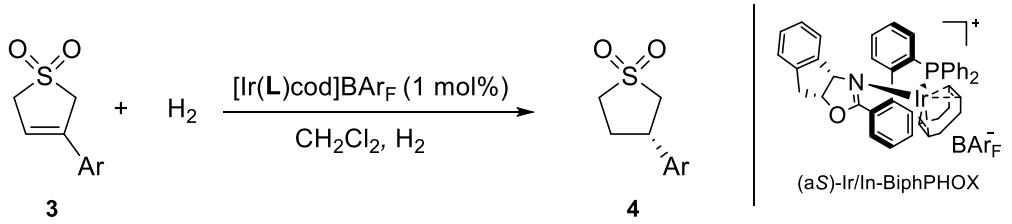
3-(3,4-Dimethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (3f). White soild,

87% yield, mp = 103.3 – 105.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 3H), 6.29 – 6.26 (m, 1H), 4.13 – 4.11 (m, 2H), 4.01 – 4.00 (m, 2H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.2, 136.2, 131.6, 130.1, 126.6, 122.9, 115.9, 57.7, 56.7, 19.9, 19.6. HRMS (FT-MS) calcd for $C_{12}H_{14}SO_2$ $(M + Na)^+$: 245.0612; found: 245.0611.

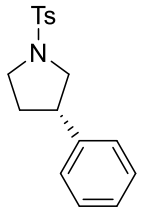
3. General Procedure for Asymmetric Hydrogenation.



The catalyst[3] (1.0 mg, 0.0006 mmol) and substrate **1** (0.06 mmol) were placed in a 5 mL tube equipped with a magnetic stirrer bar. This tube was then put into an argon-filled autoclave. Solvent (2.0 mL) was added to the mixture under argon atmosphere. The autoclave was then closed, purged three times with hydrogen (less than the pressure needed), and finally pressurized to 2.5 bar. The reaction mixture was stirred at r.t. for 1 h, and the hydrogen gas was slowly released. The conversion of the product **2** was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture and isolated by chromatography. The *ee* was determined by chiral HPLC.



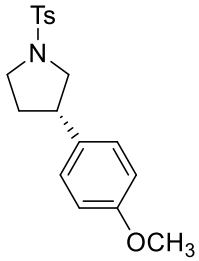
The catalyst (1.0 mg, 0.0006 mmol) and substrate **3** (0.06 mmol) were placed in a 5 mL tube equipped with a magnetic stirrer bar. This tube was then put into an argon-filled autoclave. Solvent (2.0 mL) was added to the mixture under argon atmosphere. The autoclave was then closed, purged three times with hydrogen (less than the pressure needed), and finally pressurized to 60 bar. The reaction mixture was stirred at 50 ℃ for 48 h, and the hydrogen gas was slowly released. The conversion of the product **4** was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture and isolated by chromatography. The *ee* was determined by chiral HPLC.



2a

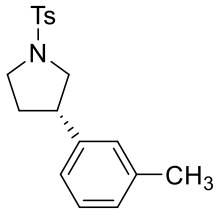
(*S*)-3-Phenyl-1-tosylpyrrolidine (2a). White soild, 99% yield, mp = 87.8 – 89.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.19 (m, 3H), 7.11 – 7.08 (m, 2H), 3.74 – 3.71 (m, 1H), 3.55 – 3.50 (m, 1H), 3.39 – 3.32 (m, 1H), 3.27 – 3.17 (m, 2H), 2.45 (s, 3H), 2.24 – 2.17 (m, 1H), 1.91 – 1.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.7, 133.9, 129.7, 128.7, 127.8, 127.0, 127.0, 54.1, 47.8, 43.8, 32.9, 21.6. HRMS (FT-MS) calcd

for $C_{17}H_{19}NO_2S$ (M + Na)$^+$: 324.1034; found: 324.1035. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 40.4 min (minor), t_{R2} = 42.4 min (major)]; *ee* = 98% $[\alpha]^{20}_D$ = -5.00 (c = 0.90, $CHCl_3$).



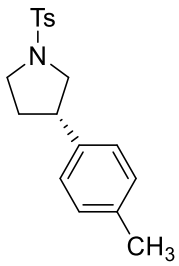
2b

(*S*)-3-(4-Methoxyphenyl)-1-tosylpyrrolidine (2b). White soild, 97% yield, mp = 82.8 – 84.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.03 – 7.01 (m, 2H), 6.82 – 6.79 (m, 2H), 3.77 (s, 3H), 3.71 – 3.66 (m, 1H), 3.54 – 3.49 (m, 1H), 3.37 – 3.31 (m, 1H), 3.22 – 3.11 (m, 2H), 2.45 (s, 3H), 2.20 – 2.13 (m, 1H), 1.87 – 1.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 143.5, 133.9, 132.6, 129.7, 127.9, 127.6, 114.0, 55.3, 54.3, 47.8, 43.1, 33.1, 21.6. HRMS (FT-MS) calcd for $C_{18}H_{21}NO_3S$ (M + Na)$^+$: 354.1140; found: 354.1141. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 68.8 min (minor), t_{R2} = 71.2 min (major)]; *ee* = 98%, $[\alpha]^{20}_D$ = -6.59 (c = 0.99, $CHCl_3$).



2c

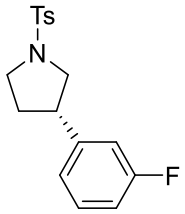
(*S*)-3-(*m*-Tolyl)-1-tosylpyrrolidine (2c). White soild, 97% yield, mp = 48.8 – 49.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.10 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 2.0 Hz, 2H), 3.75 – 3.68 (m, 1H), 3.55 – 3.50 (m, 1H), 3.38 – 3.32 (m, 1H), 3.23 – 3.14 (m, 2H), 2.45 (s, 3H), 2.29 (s, 3H), 2.22 – 2.15 (m, 1H), 1.90 – 1.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.6, 138.3, 134.0, 129.7, 128.5, 127.7, 127.6, 124.0, 54.1, 47.9, 43.8, 32.9, 21.6, 21.4. HRMS (FT-MS) calcd for $C_{18}H_{21}NO_2S$ (M + Na)$^+$: 338.1191; found: 338.1191. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 31.0 min (minor), t_{R2} = 33.3 min (major)]; *ee* = 98% , $[\alpha]^{20}_D$ = -8.88 (c = 0.95, $CHCl_3$).



2d

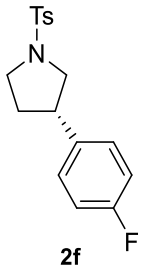
(*S*)-3-(*p*-Tolyl)-1-tosylpyrrolidine (2d). Colorless viscous liquid, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.75 – 3.65 (m, 1H), 3.54 – 3.49 (m, 1H), 3.38 – 3.31 (m, 1H), 3.23 – 3.13 (m, 2H), 2.45 (s, 3H), 2.30 (s, 3H), 2.24 – 2.14 (m, 1H), 1.88 – 1.78 (m, 1H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 143.5, 137.6, 136.6, 133.9, 129.7, 129.3, 127.6, 126.8, 54.2, 47.9, 43.5, 33.0, 21.6, 21.0. HRMS (FT-MS) calcd for $C_{18}H_{21}NO_2S$ $(M + Na)^+$: 338.1191; found: 338.1193. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 20.6 min (minor), t_{R2} = 23.0 min (major)]; *ee* = 97%, $[\alpha]^{20}_D$ = -5.66 (c = 0.95, $CHCl_3$).



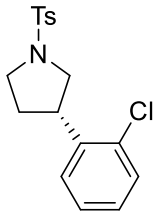
2e

(*S*)-3-(3-Fluorophenyl)-1-tosylpyrrolidine (2e). White soild, 97% yield, mp = 53.5 – 54.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.93 – 6.88 (m, 2H), 6.77 – 6.74 (m, 1H), 3.74 – 3.69 (m, 1H), 3.54 – 3.49 (m, 1H), 3.37 – 3.33 (m, 1H), 3.28 – 3.16 (m, 2H), 2.46 (s, 3H), 2.25 – 2.17 (m, 1H), 1.89 – 1.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 244.7 Hz), 143.6, 143.4 (d, $J_{C\text{-}F}$ = 7.1 Hz), 133.8, 130.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 129.8, 127.5, 122.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 113.9 (d, $J_{C\text{-}F}$ = 21.2 Hz), 53.9, 47.7, 43.5, 43.5, 32.8, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}FNO_2S$ $(M + Na)^+$: 342.0940; found: 342.0940. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 26.7 min (minor), t_{R2} = 28.3 min (major)]; *ee* = 96% $[\alpha]^{20}_D$ = 2.92 (c = 0.96, $CHCl_3$).



2f

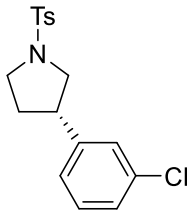
(*S*)-3-(4-Fluorophenyl)-1-tosylpyrrolidine (2f). White soild, 97% yield, mp = 72.0 – 73.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.07 – 7.04 (m, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 3.71 – 3.67 (m, 1H), 3.54 – 3.49 (m, 1H), 3.37 – 3.30 (m, 1H), 3.25 – 3.13 (m, 2H), 2.45 (s, 3H), 2.21 – 2.15 (m, 1H), 1.87 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 243.9 Hz), 143.6, 136.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 133.9, 129.8, 128.4 (d, $J_{C\text{-}F}$ = 7.9 Hz), 127.6, 115.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 54.2, 47.7, 43.1, 33.1, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}FNO_2S$ $(M + Na)^+$: 342.0940; found: 342.0942. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 49.8 min (minor), t_{R2} = 51.7 min (major)]; *ee* = 97%, $[\alpha]^{20}_D$ = -8.97 (c = 0.96, $CHCl_3$).



2g

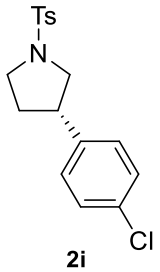
(*S*)-3-(2-Chlorophenyl)-1-tosylpyrrolidine (2g). White soild, 95% yield, mp = 60.5 – 62.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.18 – 7.13 (m, 3H), 3.71 – 3.60 (m, 2H), 3.55 – 3.49 (m, 1H), 3.36 – 3.26 (m, 2H), 2.46 (s, 3H), 2.20 – 2.13 (m, 1H), 1.95 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.3, 134.0, 133.8,

129.8, 129.7, 128.1, 127.6, 127.2, 127.0, 52.9, 47.4, 40.3, 31.5, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}ClNO_2S$ $(M + Na)^+$: 358.0644; found: 358.0645. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 33.5 min (minor), t_{R2} = 38.9 min (major)]; *ee* = 93%, $[\alpha]^{20}_D$ = -20.81 (c = 1.01, $CHCl_3$).



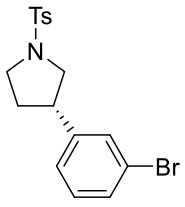
2h

(*S*)-3-(3-Chlorophenyl)-1-tosylpyrrolidine (2h). Colorless viscous liquid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.19 (m, 2H), 7.04 (s, 1H), 7.01 – 6.98 (m, 1H), 3.75 – 3.67 (m, 1H), 3.55 – 3.49 (m, 1H), 3.39 – 3.32 (m, 1H), 3.25 – 3.15 (m, 2H), 2.46 (s, 3H), 2.24 – 2.17 (m, 1H), 1.89 – 1.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.9, 134.5, 133.8, 129.9, 129.8, 127.5, 127.2, 127.1, 125.2, 53.9, 47.7, 43.5, 32.8, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}ClNO_2S$ $(M + Na)^+$: 358.0644; found: 358.0646. HPLC [DAICEL CHIRALPAK OJ-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 42.8min (major), t_{R2} = 49.7 min (minor)]; *ee* = 96%, $[\alpha]^{20}_D$ = -11.99 (c = 1.01, $CHCl_3$).



2i

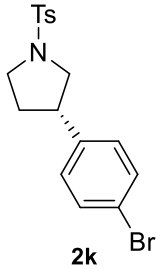
(*S*)-3-(4-Chlorophenyl)-1-tosylpyrrolidine (2i). White soild, 96% yield, mp = 60.6 – 62.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.04 – 7.01 (m, 2H), 3.72 – 3.66 (m, 1H), 3.54 – 3.49 (m, 1H), 3.37 – 3.31 (m, 1H), 3.25 – 3.14 (m, 2H), 2.46 (s, 3H), 2.23 – 2.16 (m, 1H), 1.88 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.3, 133.8, 132.7, 129.7, 128.8, 128.3, 127.6, 54.0, 47.7, 43.2, 32.9, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}ClNO_2S$ $(M + Na)^+$: 358.0644; found: 358.0642. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 45.6 min (minor), t_{R2} = 47.2 min (major)]; *ee* = 98%, $[\alpha]^{20}_D$ = -9.57 (c = 1.01, $CHCl_3$).



2j

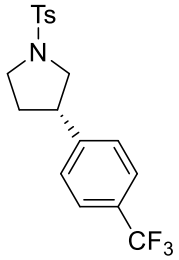
(*S*)-3-(3-Bromophenyl)-1-tosylpyrrolidine (2j). White soild, 97% yield, mp = 71.5 – 72.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.20 (s, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 3.73 – 3.67 (m, 1H), 3.55 – 3.49 (m, 1H), 3.38 – 3.31 (m, 1H), 3.24 – 3.14 (m, 2H), 2.45 (s, 3H), 2.23 – 2.16 (m, 1H), 1.88 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.2, 133.8, 130.2, 130.1, 130.1, 129.8, 127.5, 125.67, 122.7, 53.9, 47.7, 43.5, 32.8, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}BrNO_2S$ $(M + Na)^+$: 402.0139;

found: 402.0147. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 98/2, 210 nm, 1.0 mL/min. t_{R1} = 56.0 min (major), t_{R2} = 58.7 min (minor)]; *ee* = 97%, $[\alpha]^{20}_D$ = -8.12 (c = 1.14, $CHCl_3$).



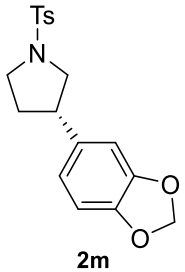
2k

(*S*)-3-(4-Bromophenyl)-1-tosylpyrrolidine (2k). White soild, 98% yield, mp = 60.1 – 61.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.33 (m, 4H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.72 – 3.65 (m, 1H), 3.53 – 3.49 (m, 1H), 3.37 – 3.31 (m, 1H), 3.23 – 3.14 (m, 2H), 2.46 (s, 3H), 2.23 – 2.16 (m, 1H), 1.87 – 1.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.8, 133.8, 131.7, 129.8, 128.7, 127.6, 120.7, 53.9, 47.7, 43.3, 32.8, 21.6. HRMS (FT-MS) calcd for $C_{17}H_{18}BrNO_2S$ $(M + Na)^+$: 402.0139; found: 402.0144. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 38.8 min (minor), t_{R2} = 40.5 min (major)]; *ee* = 98%, $[\alpha]^{20}_D$ = -10.54 (c = 1.14, $CHCl_3$).



2l

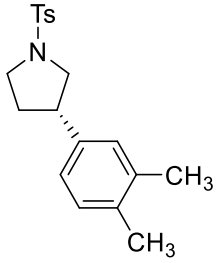
(*S*)-1-Tosyl-3-(4-(trifluoromethyl)phenyl)pyrrolidine **(2l)**. White soild, 95% yield, mp = 91.7 – 93.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.74 – 3.70 (m, 1H), 3.57 – 3.51 (m, 1H), 3.40 – 3.20 (m, 3H), 2.46 (s, 3H), 2.28 – 2.20 (m, 1H), 1.93-1.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (q, *J* = 1.1 Hz), 143.7, 133.7, 129.8, 129.0 (q, *J* = 32.4 Hz), 127.6, 127.3, 125.6 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 270.3 Hz), 53.8, 47.7, 43.6, 32.8, 21.6. HRMS (FT-MS) calcd for $C_{18}H_{18}F_3NO_2S$ $(M + Na)^+$: 392.0908; found: 392.0906. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 27.2 min (minor), t_{R2} = 29.0 min (major)]; *ee* = 97%, $[\alpha]^{20}_D$ = -12.11 (c = 1.11, $CHCl_3$).



2m

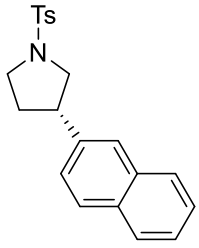
(*S*)-3-(Benzo[d][1,3]dioxol-5-yl)-1-tosylpyrrolidine (2m). White soild, 98% yield, mp = 117.0 – 119.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.70 – 6.68 (m, 1H), 6.56 – 6.54 (m, 2H), 5.92 (s, 2H), 3.71 – 3.64 (m, 1H), 3.53 – 3.48 (m, 1H), 3.36 – 3.30 (m, 1H), 3.19 – 3.09 (m, 2H), 2.45 (s, 3H), 2.17 – 2.12 (m, 1H), 1.84 – 1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 146.4, 143.5, 134.4, 133.8, 129.7, 127.6, 120.0,

108.3, 107.2, 101.0, 54.3, 47.8, 43.6, 33.1, 21.6. HRMS (FT-MS) calcd for $C_{18}H_{19}NO_4S$ (M + Na)$^+$: 368.0932; found: 368.0933. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 41.2 min (minor), t_{R2} = 45.1 min (major)]; *ee* = 98%, $[\alpha]^{20}_D$ = -8.17 (c = 1.04, $CHCl_3$).



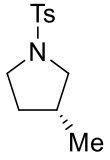
2n

(*S*)-3-(3,4-Dimethylphenyl)-1-tosylpyrrolidine (2n). White soild, 96% yield, mp = 65.4 – 67.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.81 (m, 2H), 3.74 – 3.67 (m, 1H), 3.54 – 3.49 (m, 1H), 3.38 – 3.31 (m, 1H), 3.21 – 3.12 (m, 2H), 2.45 (s, 3H), 2.21(s, 3H), 2.20 (s, 3H), 2.18 – 2.14 (m, 1H), 1.88 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.1, 136.8, 135.3, 134.0, 129.8, 129.7, 128.3, 127.6, 124.2, 54.2, 47.9, 43.5, 33.0, 21.6, 19.8, 19.3. HRMS (FT-MS) calcd for $C_{19}H_{23}NO_2S$ (M + Na)$^+$: 352.1347; found: 352.1348. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 21.5 min (minor), t_{R2} = 23.8 min (major)]; *ee* = 97%, $[\alpha]^{20}_D$ = -5.94 (c = 0.99, $CHCl_3$).



2o

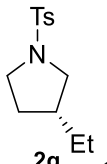
(*S*)-3-(Naphthalen-2-yl)-1-tosylpyrrolidine (2o). White soild, 95% yield, mp = 102.3 – 103.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 4H), 7.72 – 7.70 (m, 1H), 7.50 – 7.42 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.21 (m, 1H), 3.82 – 3.78 (m, 1H), 3.60 – 3.55 (m, 1H), 3.44 – 3.37 (m, 2H), 3.35 – 3.31 (m, 1H), 2.45 (s, 3H), 2.32 – 2.17 (m, 1H), 2.03 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.1, 133.9, 133.3, 132.4, 129.8, 128.4, 127.6, 126.3, 125.8, 125.3, 54.0, 47.9, 43.9, 32.9, 21.6. HRMS (FT-MS) calcd for $C_{21}H_{21}NO_2S$ (M + Na)$^+$: 374.1191; found: 374.1190. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 47.1 min (minor), t_{R2} = 51.7 min (major)]; *ee* = 98%, $[\alpha]^{20}_D$ = -13.27 (c = 1.05, $CHCl_3$).



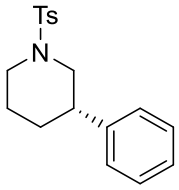
2p

(*R*)-3-Methyl-1-tosylpyrrolidine (2p). White soild, 97% yield, mp = 74.0 – 74.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.44 – 3.40 (m, 1H), 3.37 – 3.32 (m, 1H), 3.25 – 3.19 (m, 1H), 2.77 – 2.73 (m, 1H), 2.43 (s, 3H), 2.16 – 2.07 (m, 1H), 1.94 – 1.87 (m, 1H), 1.40 – 1.31 (m, 1H), 0.92 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

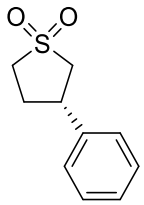
143.2, 134.0, 129.6, 127.5, 54.8, 47.6, 33.3, 33.2, 21.5, 17.6. HRMS (FT-MS) calcd for $C_{12}H_{17}NO_2S$ $(M + Na)^+$: 262.0878; found: 262.0878. HPLC [DAICEL CHIRALPAK OZ-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 84.8 min (major), t_{R2} = 93.7 min (minor)]; *ee* = 83%, $[\alpha]^{20}_D$ = -7.98 (c = 0.72, $CHCl_3$).



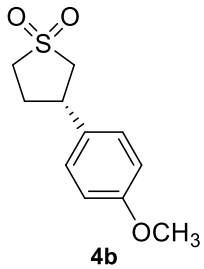
2q **(*R*)-3-Ethyl-1-tosylpyrrolidine (2q).** Colorless viscous liquid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.33 – 7.31 (m, 2H), 3.45 – 3.41 (m, 1H), 3.36 – 3.31 (m, 1H), 3.22 – 3.15 (m, 1H), 2.80 – 2.76 (m, 1H), 2.43 (s, 3H), 1.97 – 1.88 (m, 2H), 1.43 – 1.31 (m, 1H), 1.30 – 1.28 (m, 1H), 1.26 – 1.23 (m, 1H) 0.84 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 133.9, 129.6, 127.5, 53.1, 47.7, 40.6, 31.2, 26.0, 21.5, 12.5. HRMS (FT-MS) calcd for $C_{13}H_{19}NO_2S$ $(M + Na)^+$: 276.1034; found: 276.1029. HPLC [DAICEL CHIRALPAK OZ-H, hexane/*i*PrOH = 98/2, 210 nm, 0.5 mL/min. t_{R1} = 119.7 min (major), t_{R2} = 127.4 min (minor)]; *ee* = 80%. $[\alpha]^{20}_D$ = 9.65 (c = 0.36, $CHCl_3$).



2r **(*S*)-3-Phenyl-1-tosylpiperidine (2r)**. White soild, 95% yield, mp = 116.4 – 117.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 4H), 7.25 – 7.21 (m, 1H), 7.18 – 7.16 (m, 2H), 3.89 – 3.84 (m, 2H), 2.91 – 2.85 (m, 1H), 2.43 (s, 3H), 2.30 – 2.19 (m, 2H), 1.94 (d, *J* = 13.2 Hz, 1H), 1.87 – 1.72 (m, 2H), 1.47 – 1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.6, 133.2, 129.6, 128.6, 127.7, 127.2, 126.9, 52.70, 46.4, 42.1, 30.5, 25.1, 21.6. HRMS (FT-MS) calcd for $C_{18}H_{21}NO_2S$ $(M + Na)^+$: 338.1191; found: 338.1191. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 97/3, 210 nm, 1.0 mL/min. t_{R1} = 19.6 min (minor), t_{R2} = 23.1 min (major)]; *ee* = 86%. $[\alpha]^{20}_D$ = 96.17 (c = 0.95, $CHCl_3$).

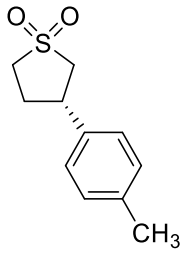


4a **(*S*)-3-Phenyltetrahydrothiophene 1,1-dioxide (4a).** White soild, 97% yield, mp = 103.6 – 105.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 7.28 – 7.26 (m, 2H), 3.68 – 3.60 (m, 1H), 3.51 – 3.46 (m, 1H), 3.41 – 3.35 (m, 1H), 3.26 – 3.01 (m, 2H), 2.60 – 2.52 (m, 1H), 2.38 – 2.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 129.4, 128.1, 127.0, 57.8, 53.1, 42.0, 31.0. HRMS (FT-MS) calcd for $C_{10}H_{12}SO_2$ $(M + Na)^+$: 219.0456; found: 219.0461. HPLC [DAICEL CHIRALPAK OJ-H, hexane/*i*PrOH = 60/40, 210 nm, 1.0 mL/min. t_{R1} = 16.8 min (minor), t_{R2} = 19.6 min (major)]; *ee* = 89%, $[\alpha]^{20}_D$ = 11.59 (c = 0.59, $CHCl_3$).



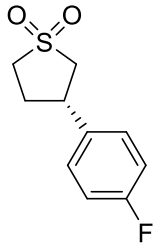
4b

(*S*)-3-(4-Methoxyphenyl)tetrahydrothiophene 1,1-dioxide (4b). White soild, 97% yield, mp = 97.0 – 98.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.17 (m, 2H), 6.92 – 6.89 (m, 2H), 3.81 (s, 3H), 3.63 – 3.54 (m, 1H), 3.48 – 3.43 (m, 1H), 3.40 – 3.34 (m, 1H), 3.21 – 3.04 (m, 2H), 2.56 – 2.48 (m, 1H), 2.34 – 2.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 131.6, 128.0, 114.7, 58.0, 55.6, 53.2, 41.4, 31.2. HRMS (FT-MS) calcd for $C_{11}H_{14}SO_3$ $(M + Na)^+$: 249.0561; found: 249.0557. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 90/10, 210 nm, 1.0 mL/min. t_{R1} = 23.5 min (major), t_{R2} = 25.9 min (minor)]; *ee* = 84%, $[\alpha]^{20}_D$ = 16.84 (c = 0.68, $CHCl_3$).



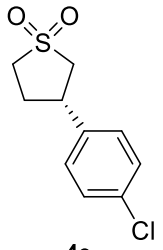
4c

(*S*)-3-(*p*-Tolyl)tetrahydrothiophene 1,1-dioxide (4c). White soild, 95% yield, mp = 95.4 – 97.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 4H), 3.64 – 3.55 (m, 1H), 3.49 – 3.44 (m, 1H), 3.40 – 3.34 (m, 1H), 3.22 – 3.07 (m, 2H), 2.57 – 2.50 (m, 1H), 2.35 (s, 3H), 2.33 – 2.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.7, 130.0, 126.8, 57.9, 53.1, 41.7, 31.1, 21.3. HRMS (FT-MS) calcd for $C_{11}H_{14}SO_2$ $(M + Na)^+$: 233.0612; found: 233.0606. HPLC [DAICEL CHIRALPAK OJ-H, hexane/*i*PrOH = 60/40, 210 nm, 1.0 mL/min. t_{R1} = 13.8 min (minor), t_{R2} = 15.1 min (major)]; *ee* = 84%, $[\alpha]^{20}_D$ = 18.13 (c = 0.63, $CHCl_3$).



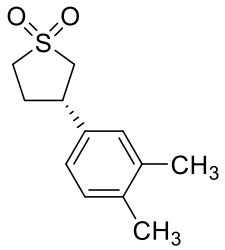
4d

(*S*)-3-(4-Fluorophenyl)tetrahydrothiophene 1,1-dioxide (4d). White soild, 95% yield, mp = 88.5 – 89.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 3.67 – 3.58 (m, 1H), 3.50 – 3.45(m, 1H), 3.41 – 3.35 (m, 1H), 3.23 – 3.05 (m, 2H), 2.58 – 2.52 (m, 1H), 2.34 – 2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 245.5 Hz), 135.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 57.8, 53.0, 41.3, 31.1. HRMS (FT-MS) calcd for $C_{10}H_{11}SFO_2$ $(M + Na)^+$: 237.0361; found: 237.0365. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 90/10, 210 nm, 1.0 mL/min. t_{R1} = 20.5 min (major), t_{R2} = 26.8 min (minor)]; *ee* = 71%, $[\alpha]^{20}_D$ = 14.67 (c = 0.64, $CHCl_3$).



4e

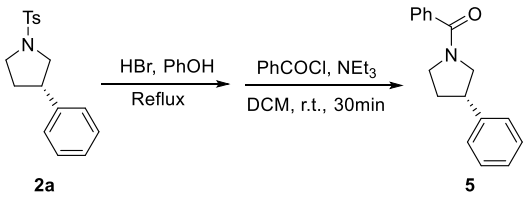
(*S*)-3-(4-Chlorophenyl)tetrahydrothiophene 1,1-dioxide (4e). White soild, 94% yield, mp = 97.3 – 98.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.66 – 3.57 (m, 1H), 3.50 – 3.45 (m, 1H), 3.40 – 3.35 (m, 1H), 3.23 – 3.05 (m, 2H), 2.59 – 2.52 (m, 1H), 2.34 – 2.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 133.9, 129.5, 128.3, 57.6, 52.9, 41.4, 30.9. HRMS (FT-MS) calcd for $C_{10}H_{11}ClSO_2$ $(M + Na)^+$: 253.0066; found: 253.0072. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 90/10, 210 nm, 1.0 mL/min. t_{R1} = 22.3 min (major), t_{R2} = 26.2 min (minor)]; *ee* = 72%, $[\alpha]^{20}_D$ = 11.87 (c = 0.69, $CHCl_3$).



4f

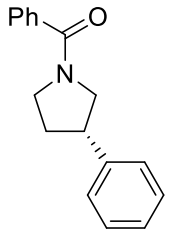
(*S*)-3-(3,4-Dimethylphenyl)tetrahydrothiophene 1,1-dioxide (4f). White soild, 97% yield, mp = 117.5 – 118.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.98 (m, 2H), 3.61 – 3.52 (m, 1H), 3.48 – 3.42 (m, 1H), 3.39 – 3.34 (m, 1H), 3.21 – 3.07 (m, 2H), 2.55 – 2.48 (m, 1H), 2.35 – 2.29 (m, 1H), 2.27 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.1, 136.5, 130.5, 128.2, 124.2, 57.9, 53.2, 41.8, 31.1, 20.1, 19.6. HRMS (FT-MS) calcd for $C_{12}H_{16}SO_2$ $(M + Na)^+$: 247.0769; found: 247.0765. HPLC [DAICEL CHIRALPAK OJ-H, hexane/*i*PrOH = 60/40, 210 nm, 1.0 mL/min. t_{R1} = 12.8 min (minor), t_{R2} = 16.6 min (major)]; *ee* = 86%, $[\alpha]^{20}_D$ = 11.92 (c = 0.67, $CHCl_3$).

4. Transformation of Hydrogenation Product 2a.



2a **5**

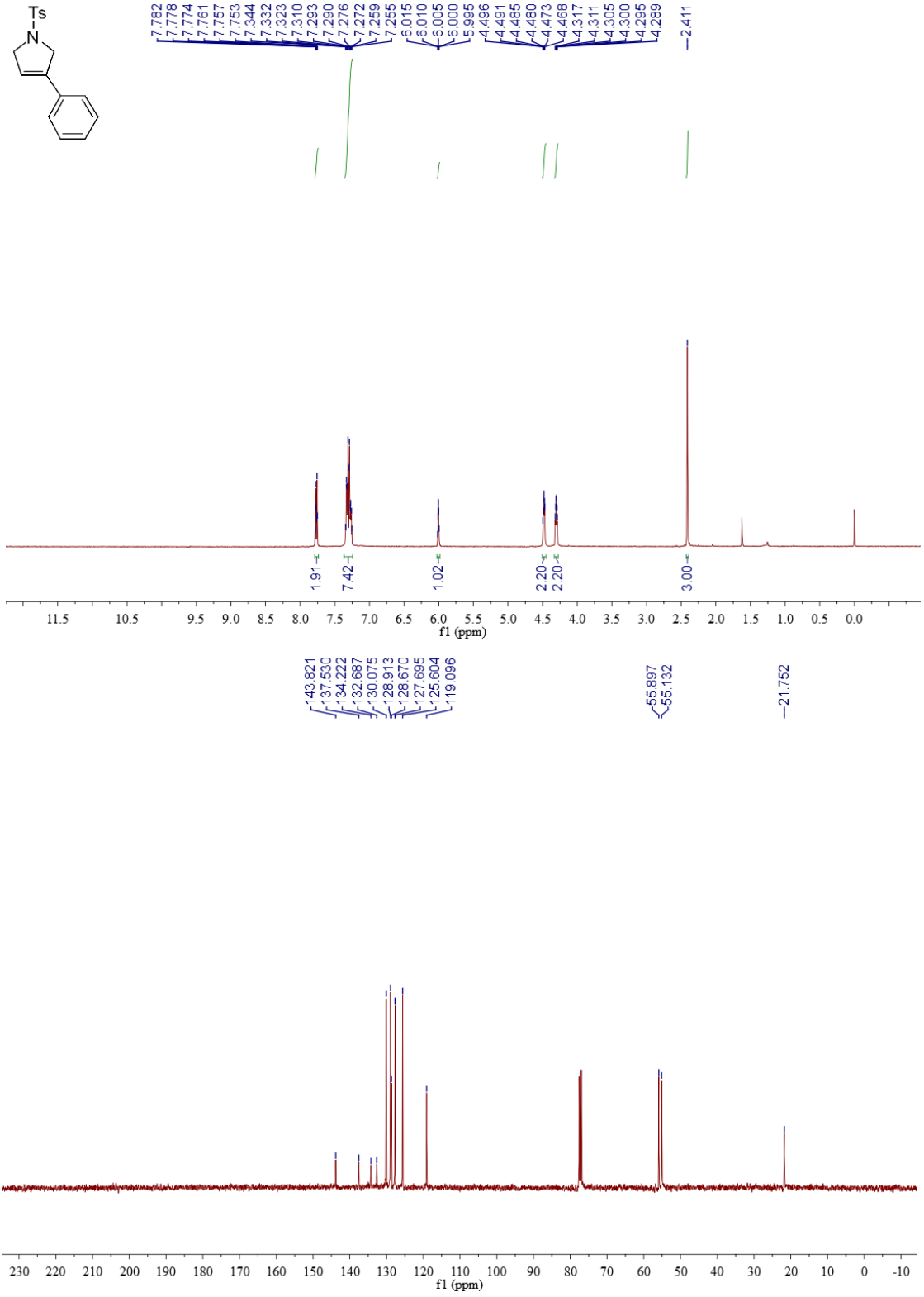
The reaction was conducted following literature procedure[4-5]. To a solution of (*S*)-3-Phenyl-1-tosylpyrrolidine **2a** (120.4 mg, 0.4 mmol, 98% ee) was added phenol (0.1 g) and 48% HBr (0.7 mL). The mixture was heated to 120 ℃ for 2 h. The acidic mixture was cooled to room temperature and was washed with diethyl ether. It was made alkaline with 30% sodium hydroxide solution and extracted with diethyl ether. The combined diethyl ether extracts of the alkaline solution were dried over Na_2SO_4 and concentrated. The residue was redissolved in DCM (5 mL). Benzoyl chloride (92 μL, 0.8 mmol) and NEt_3 (166 μL, 1.2 mmol) were added, and the mixture was stirred for 30 min at room temperature. The solvent was removed under vacuum, and the residue was purified by silica gel preparative TLC with petroleum ether/EtOAc = 2/1 to afford **5** as white soild (84.4 mg, 0.34 mmol, 84% yield over 2 steps).

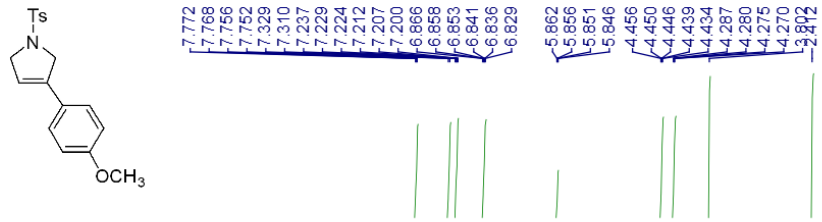


5

(*S*)-Phenyl(3-phenylpyrrolidin-1-yl)methanone (5). White soild, 84% yield, mp = 81.5 – 83.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) mixture of rotamers, δ 7.56 – 7.53 (m, 4H), 7.45 – 7.37 (m, 6H), 7.35 – 7.28 (m, 5H), 7.26 – 7.18 (m, 5H), 4.14 (dd, *J* = 12.0, 7.6 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.83 – 3.75 (m, 2H), 3.73 – 3.65 (m, 1H), 3.63 – 3.53 (m, 2H), 3.51 – 3.44 (m, 2H), 3.40 – 3.32 (m, 1H), 2.42 – 2.36 (m, 1H), 2.32 – 2.25 (m, 1H), 2.21 – 2.09 (m, 1H), 2.06 – 1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 169.7, 141.0, 140.3, 136.8, 136.8, 132.9, 130.0, 128.7, 128.3, 127.2, 127.1, 127.0, 126.9, 56.1, 52.3, 49.4, 46.3, 44.7, 42.8, 33.9, 31.6. HRMS (FT-MS) calcd for $C_{17}H_{17}NO$ $(M + Na)^+$: 247.1208; found: 247.1202. HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*PrOH = 95/5, 210 nm, 1.0 mL/min. t_{R1} = 29.8 min (major), t_{R2} = 35.6 min (minor)]; *ee* = 98%, $[\alpha]^{20}_D$ = 10.20 (c = 0.62, $CHCl_3$).

5. NMR Spectra and HPLC Charts.

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7.229
7.224
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7.207
7.200
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6.858
6.853
6.841
6.836
6.829
5.862
5.856
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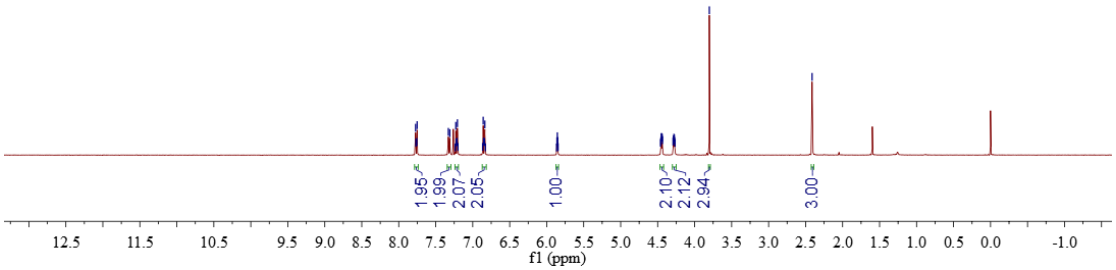
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11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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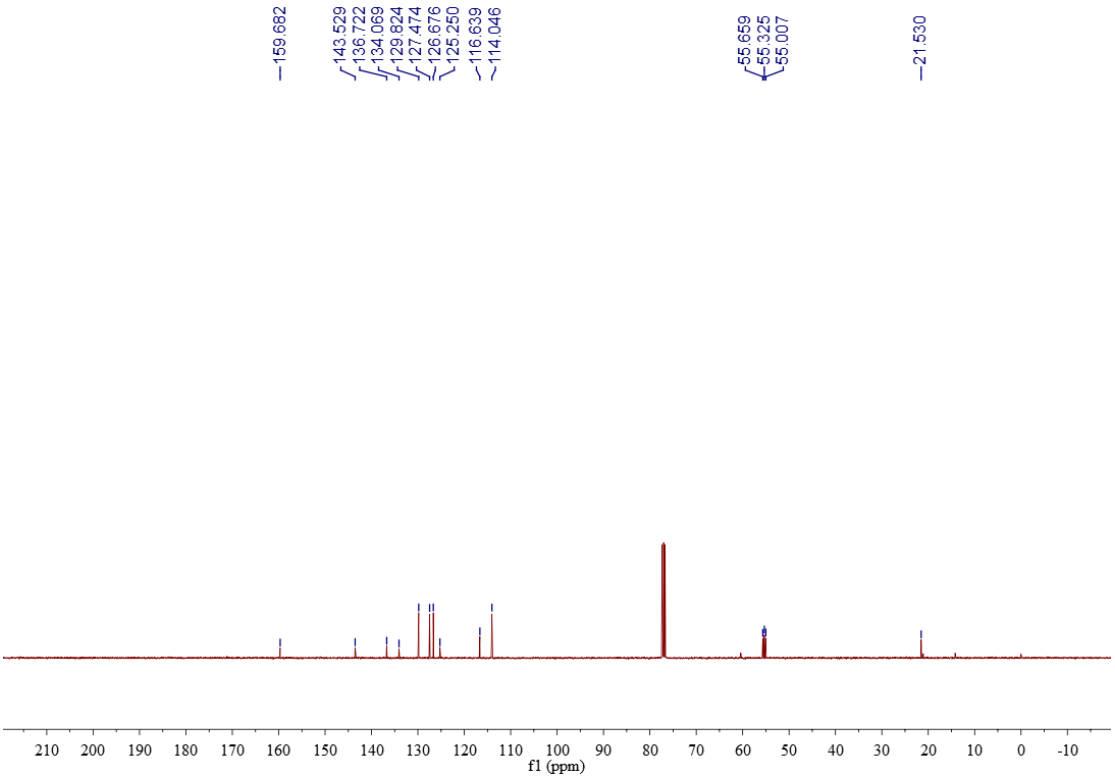
f1 (ppm)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21.530
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200
190
180
170
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150
140
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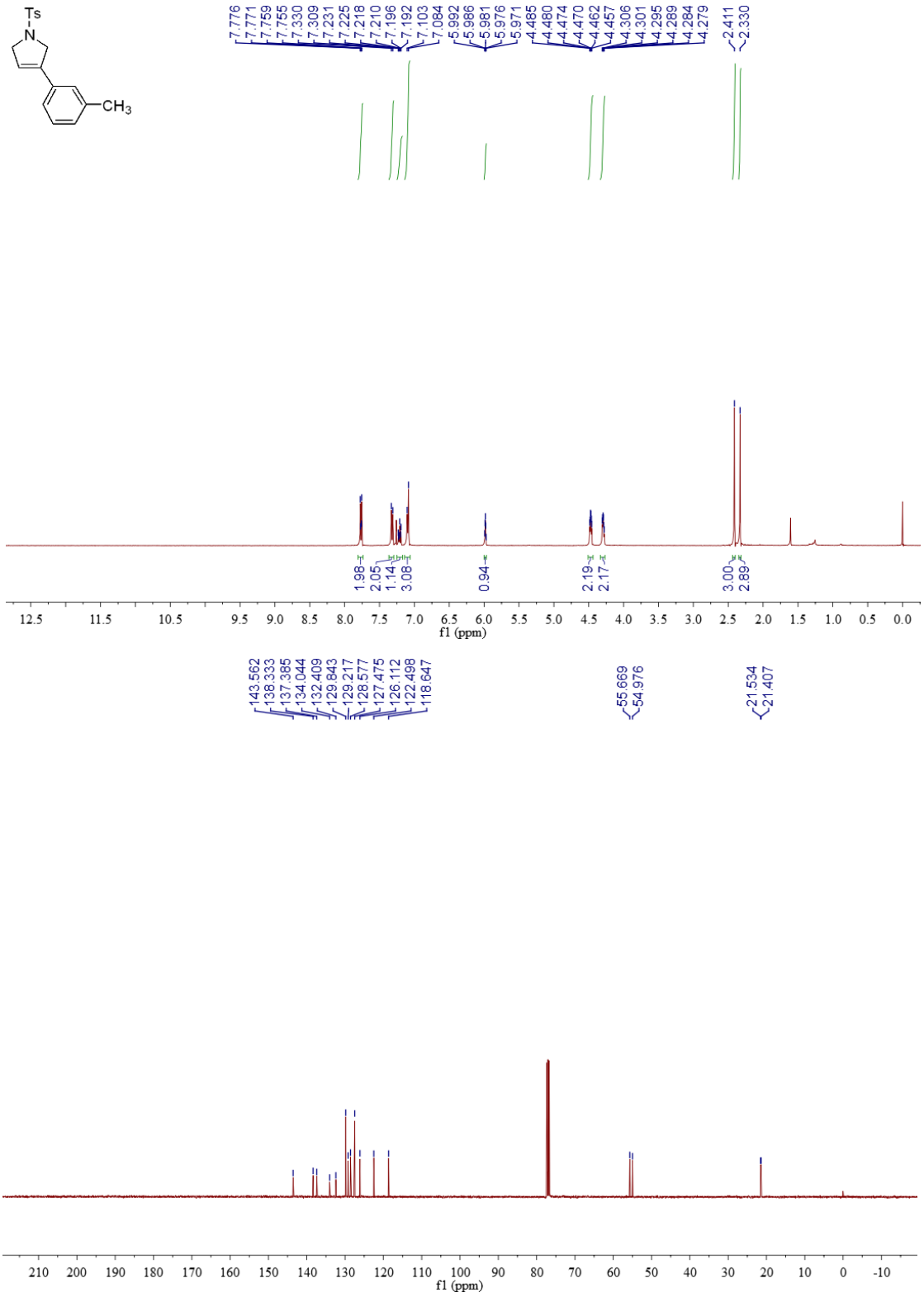
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.192
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7.084
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5.986
5.981
5.976
5.971
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4.480
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4.470
4.462
4.457
4.306
4.301
4.295
4.289
4.284
4.279
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2.330
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2.05
1.14
3.08
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2.19
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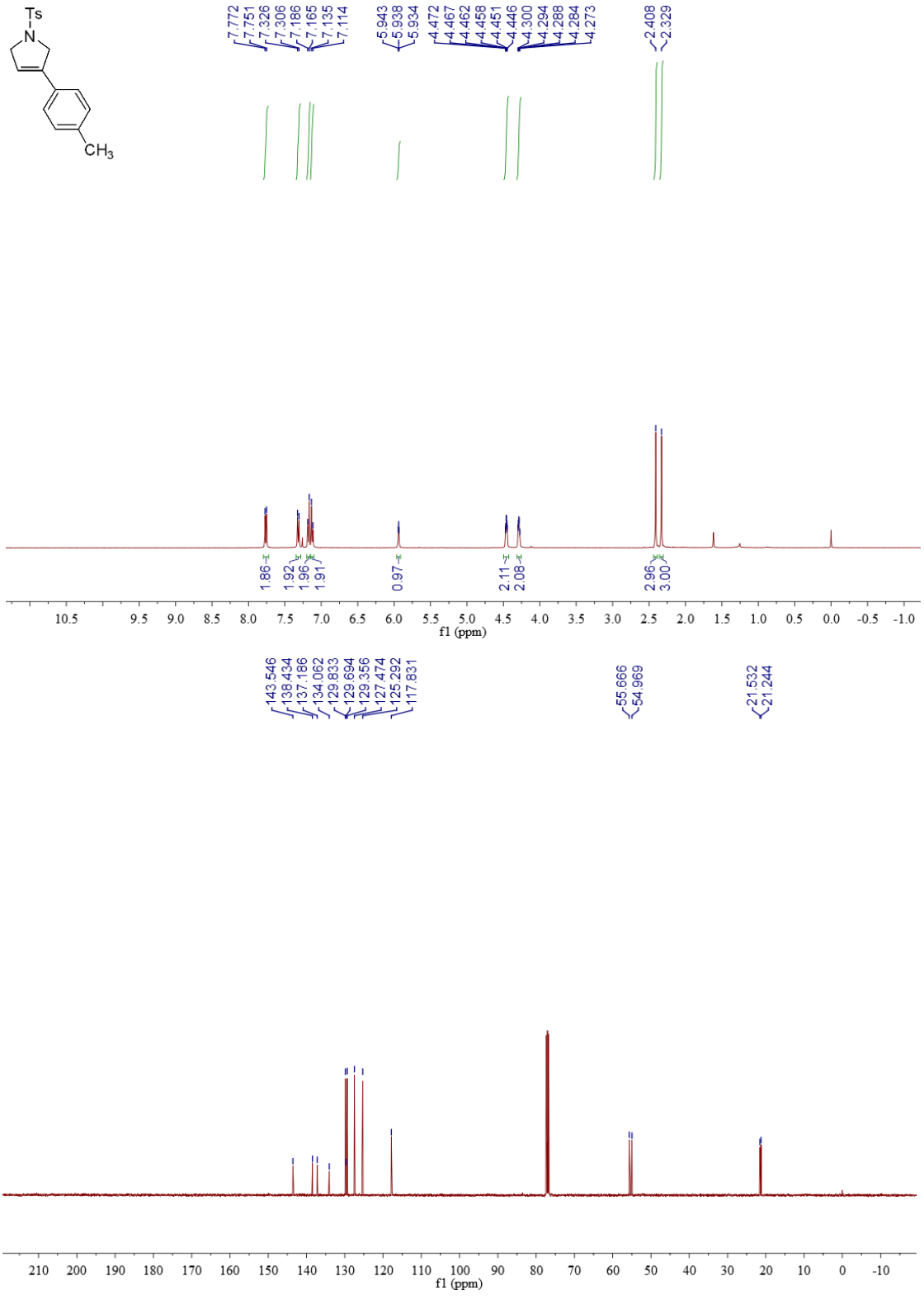
f1 (ppm)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4.294
4.288
4.284
4.273
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1.96
1.91
0.97
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2.08
2.96
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f1 (ppm)
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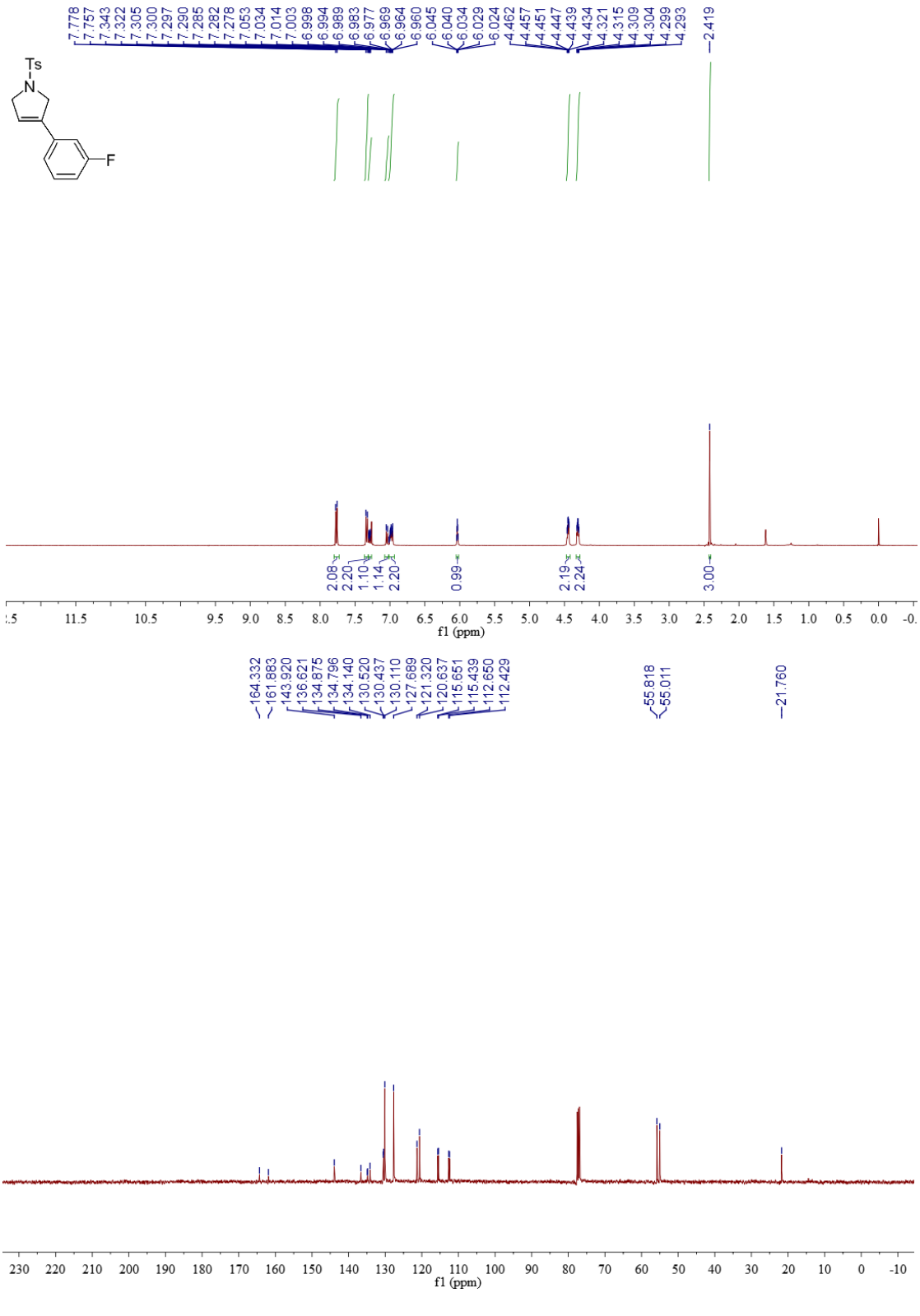
21.244
f1 (ppm)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7.014
7.003
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6.994
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6.983
6.977
6.969
6.964
6.960
6.045
6.040
6.034
6.029
6.024
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4.439
4.434
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4.315
4.309
4.304
4.299
4.293
2.419
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F
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1.10
1.14
2.20
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2.19
2.24
3.00
f1 (ppm)
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134.875
134.796
134.140
130.520
130.437
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120.637
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55.011
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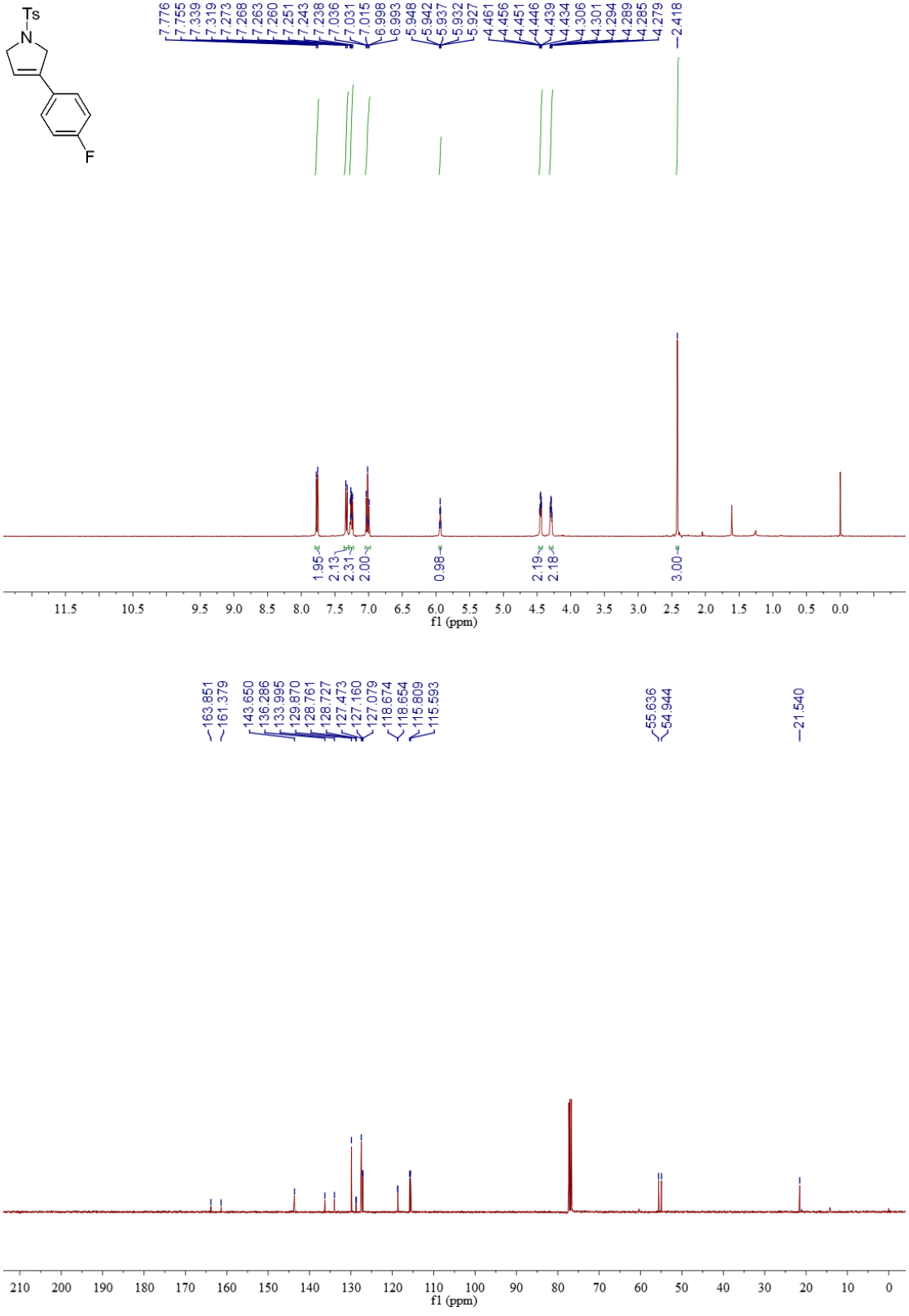
f1 (ppm)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7.031
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6.993
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5.942
5.937
5.932
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4.456
4.451
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4.439
4.434
4.306
4.301
4.294
4.289
4.285
4.279
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3.00
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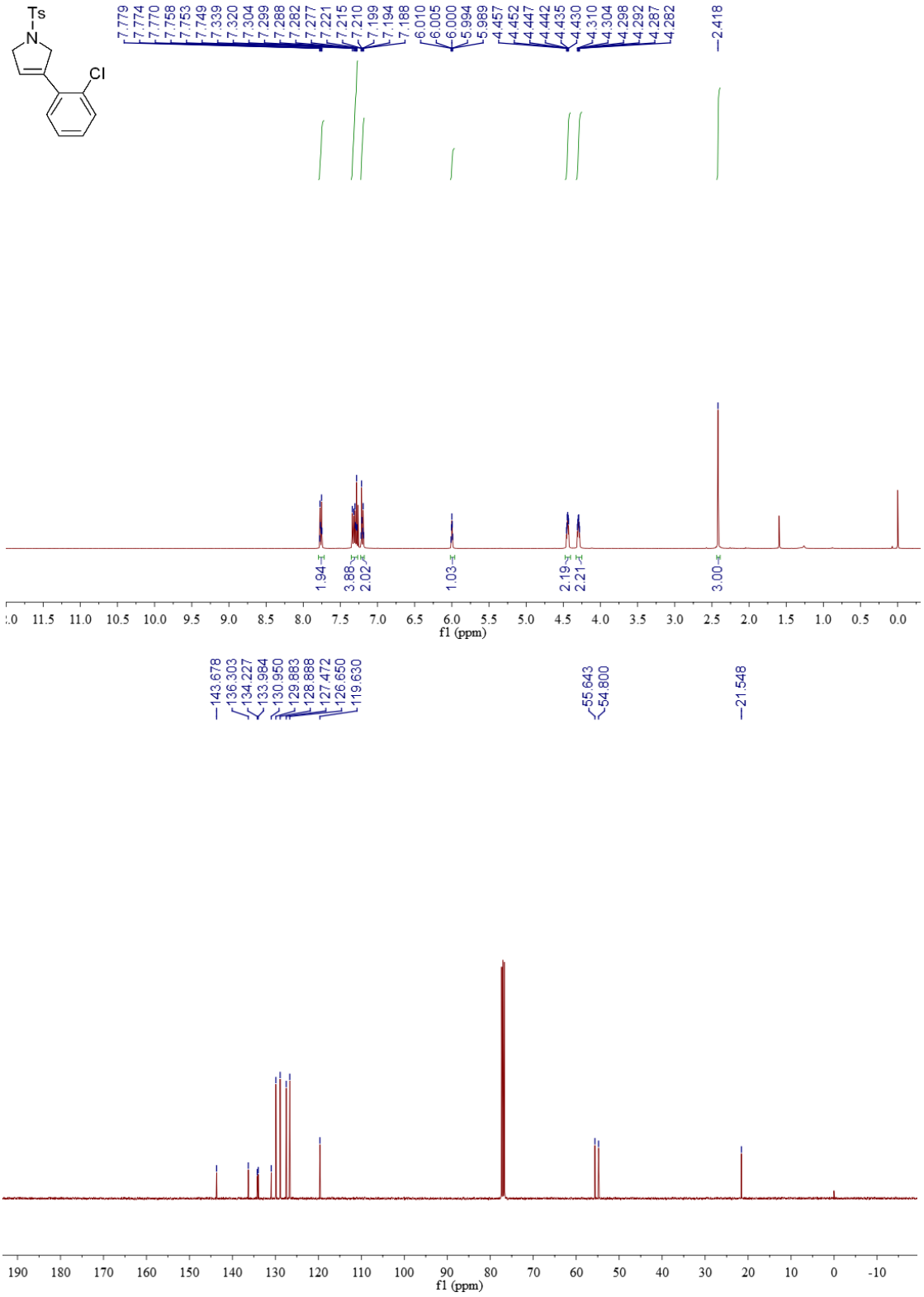
f1 (ppm)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7.282
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7.215
7.210
7.199
7.194
7.188
6.010
6.005
6.000
5.994
5.989
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4.447
4.442
4.435
4.430
4.310
4.304
4.298
4.292
4.287
4.282
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1.94
3.88
2.02
1.03
2.19
2.21
3.00
f1 (ppm)
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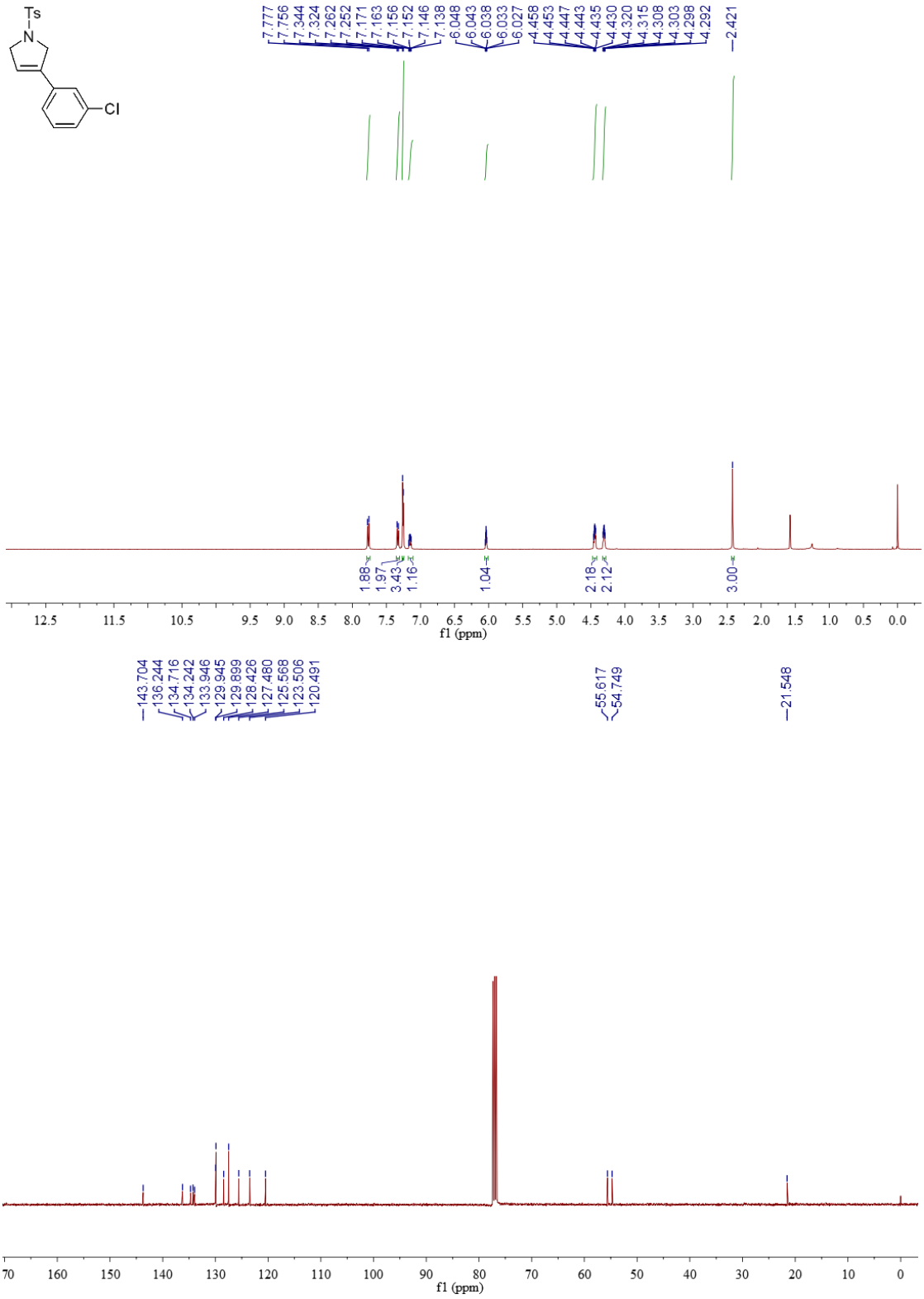
f1 (ppm)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6.038
6.033
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3.43
1.16
1.04
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2.12
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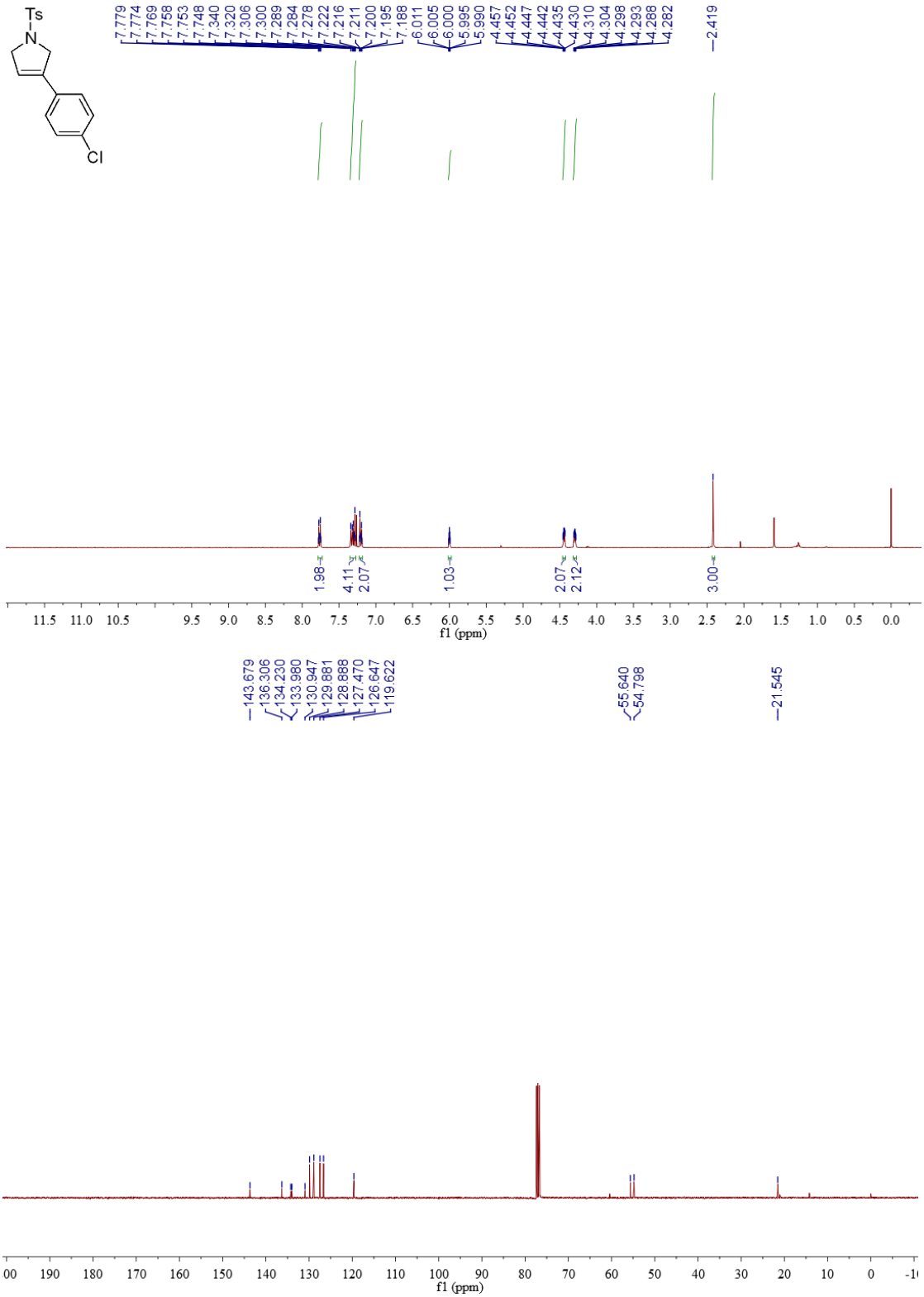
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7.200
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7.188
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6.000
5.995
5.990
4.457
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4.447
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4.304
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4.293
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4.282
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2.07
1.03
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3.00
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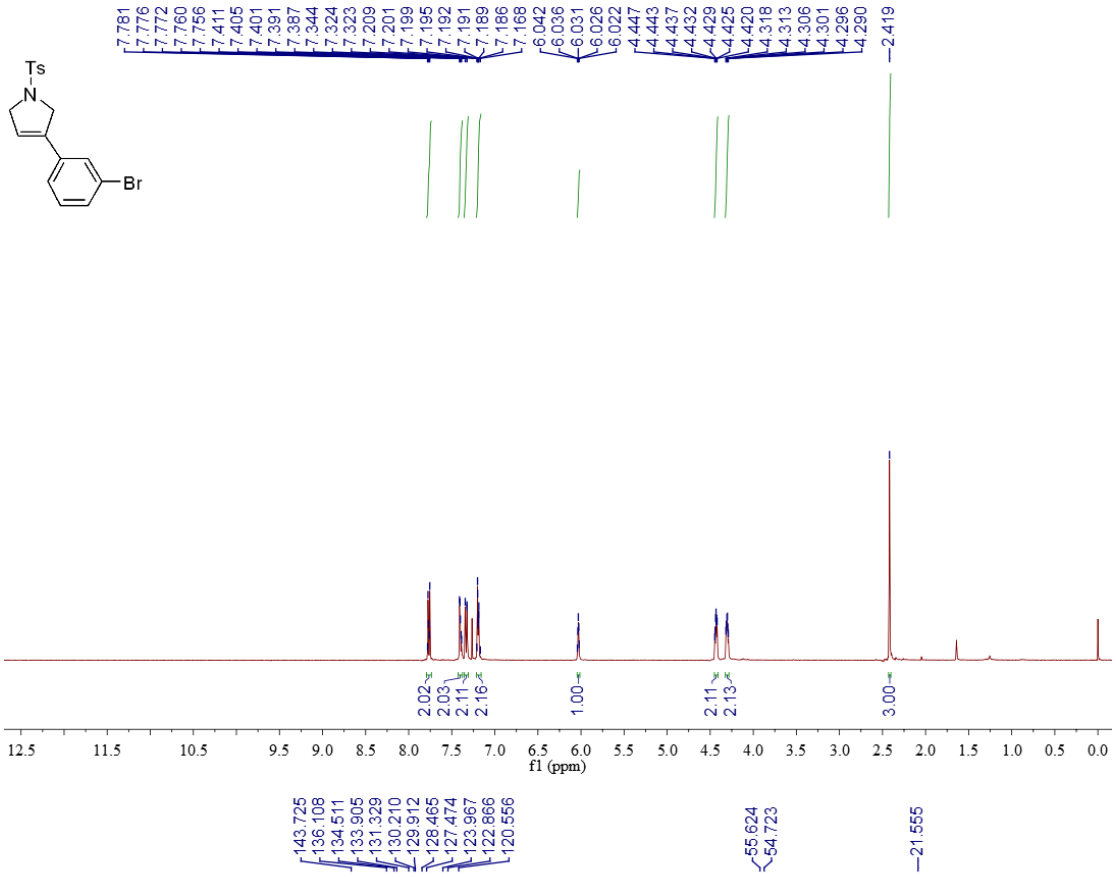
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7.323
7.209
7.201
7.199
7.195
7.192
7.191
7.189
7.186
7.168
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6.036
6.031
6.026
6.022
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4.429
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4.420
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4.313
4.306
4.301
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2.02
2.03
2.11
2.16
1.00
2.11
2.13
3.00
f1 (ppm)
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134.511
133.905
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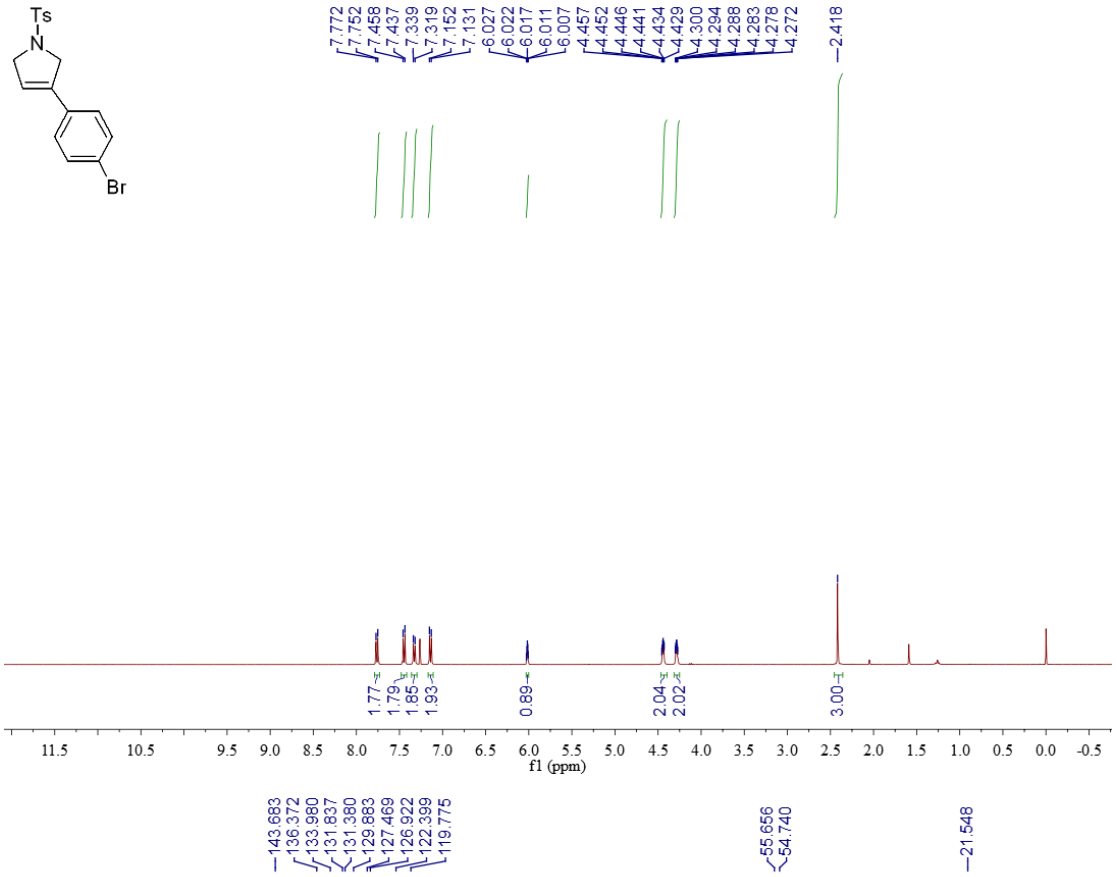
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6.011
6.007
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4.446
4.441
4.434
4.429
4.300
4.294
4.288
4.283
4.278
4.272
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1.79
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1.93
0.89
2.04
2.02
3.00
f1 (ppm)
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133.980
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127.469
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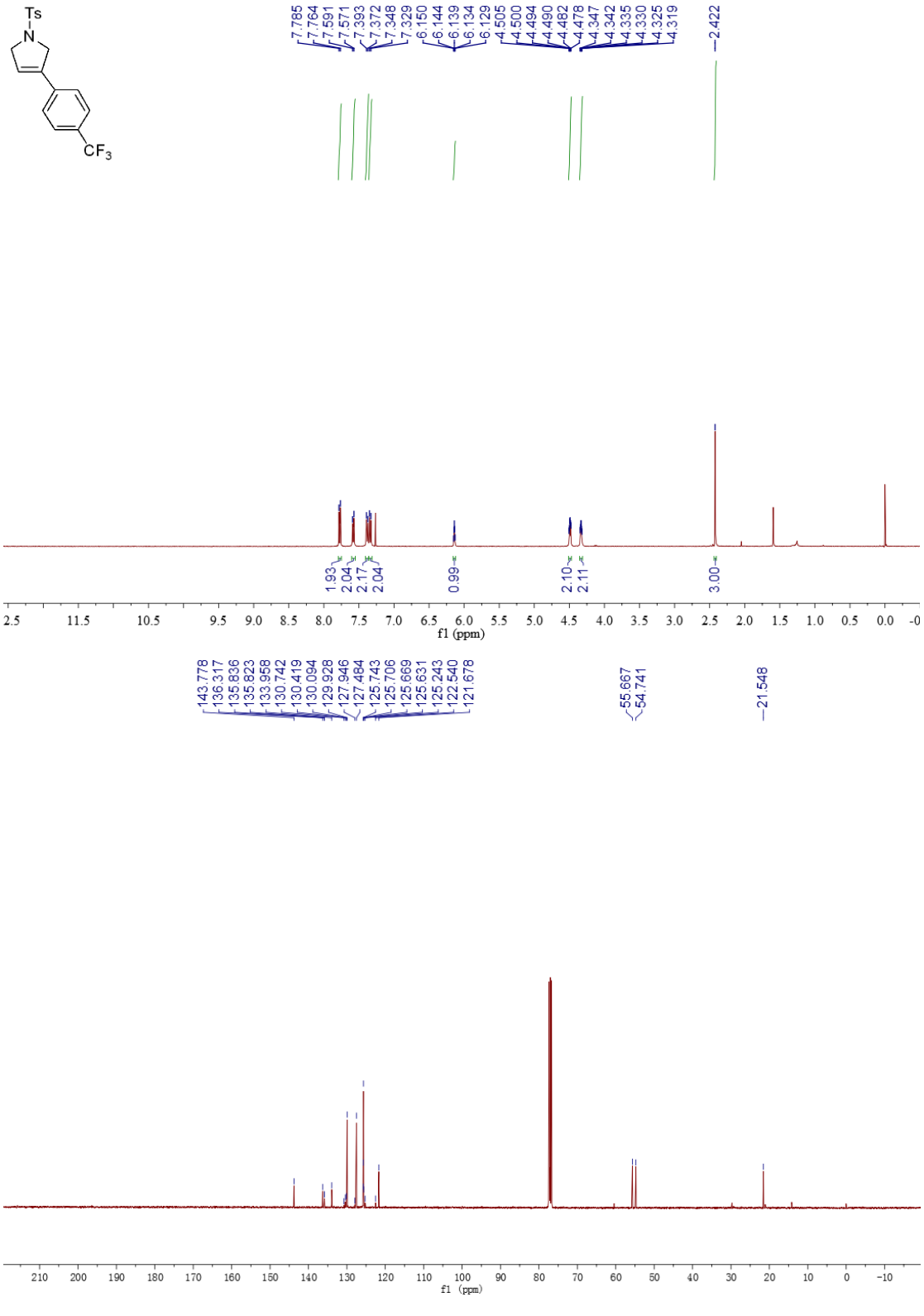
f1 (ppm)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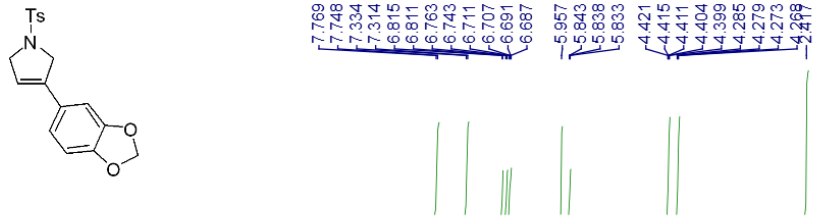
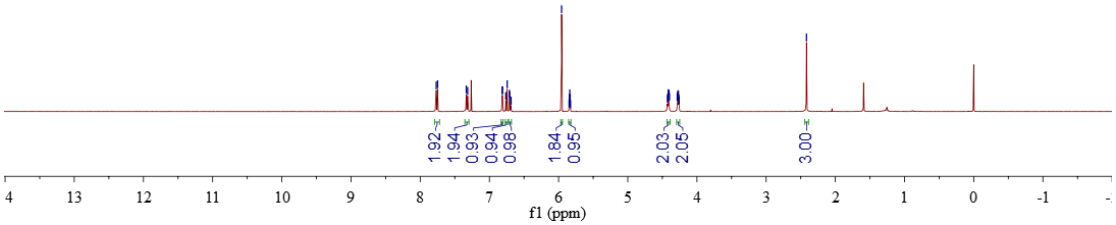
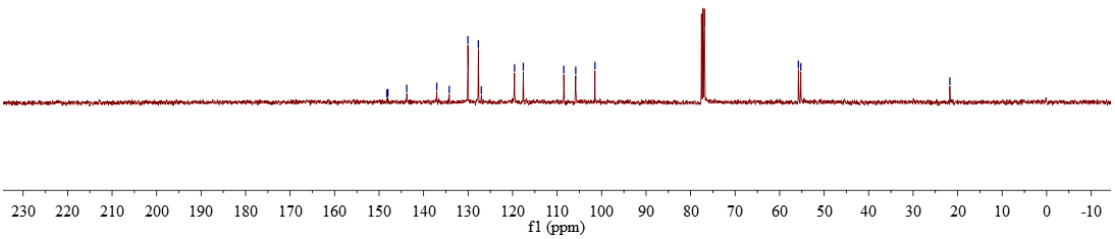
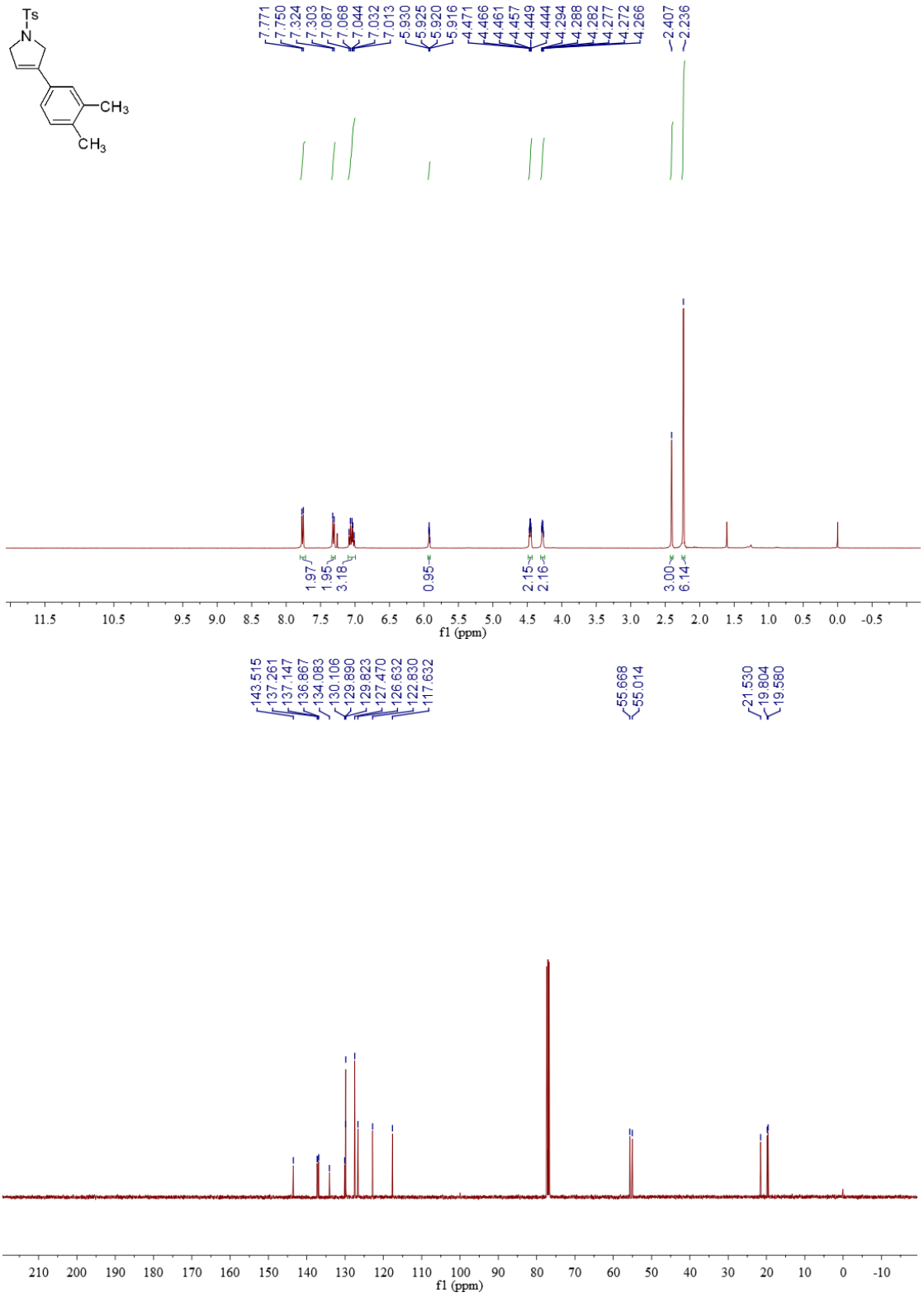
N
CF3
7.785
7.764
7.591
7.571
7.393
7.372
7.348
7.329
6.150
6.144
6.139
6.134
6.129
4.505
4.500
4.494
4.490
4.482
4.478
4.347
4.342
4.335
4.330
4.325
4.319
2.422
1.93
2.04
2.17
2.04
0.99
2.10
2.11
3.00
f1 (ppm)
143.778
136.317
135.836
135.823
133.958
130.742
130.419
130.094
129.928
127.946
127.484
125.743
125.706
125.669
125.631
125.243
122.540
121.678
55.667
54.741
21.548
f1 (ppm)

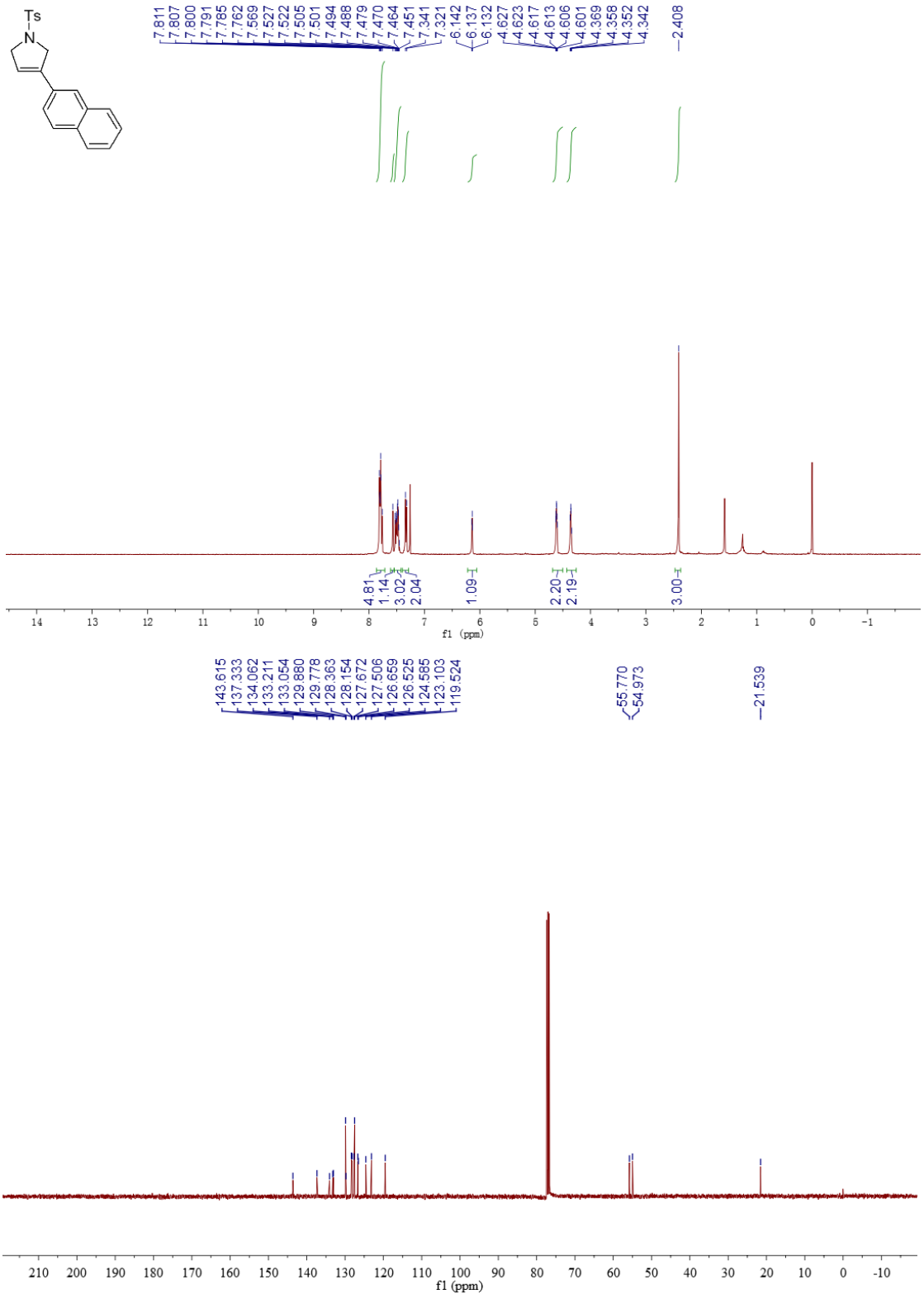

Ts
N
O
O
7.769
7.748
7.334
7.314
6.815
6.811
6.763
6.743
6.711
6.707
6.691
6.687
5.957
5.843
5.838
5.833
4.421
4.415
4.411
4.404
4.399
4.285
4.279
4.273
4.268
2.417

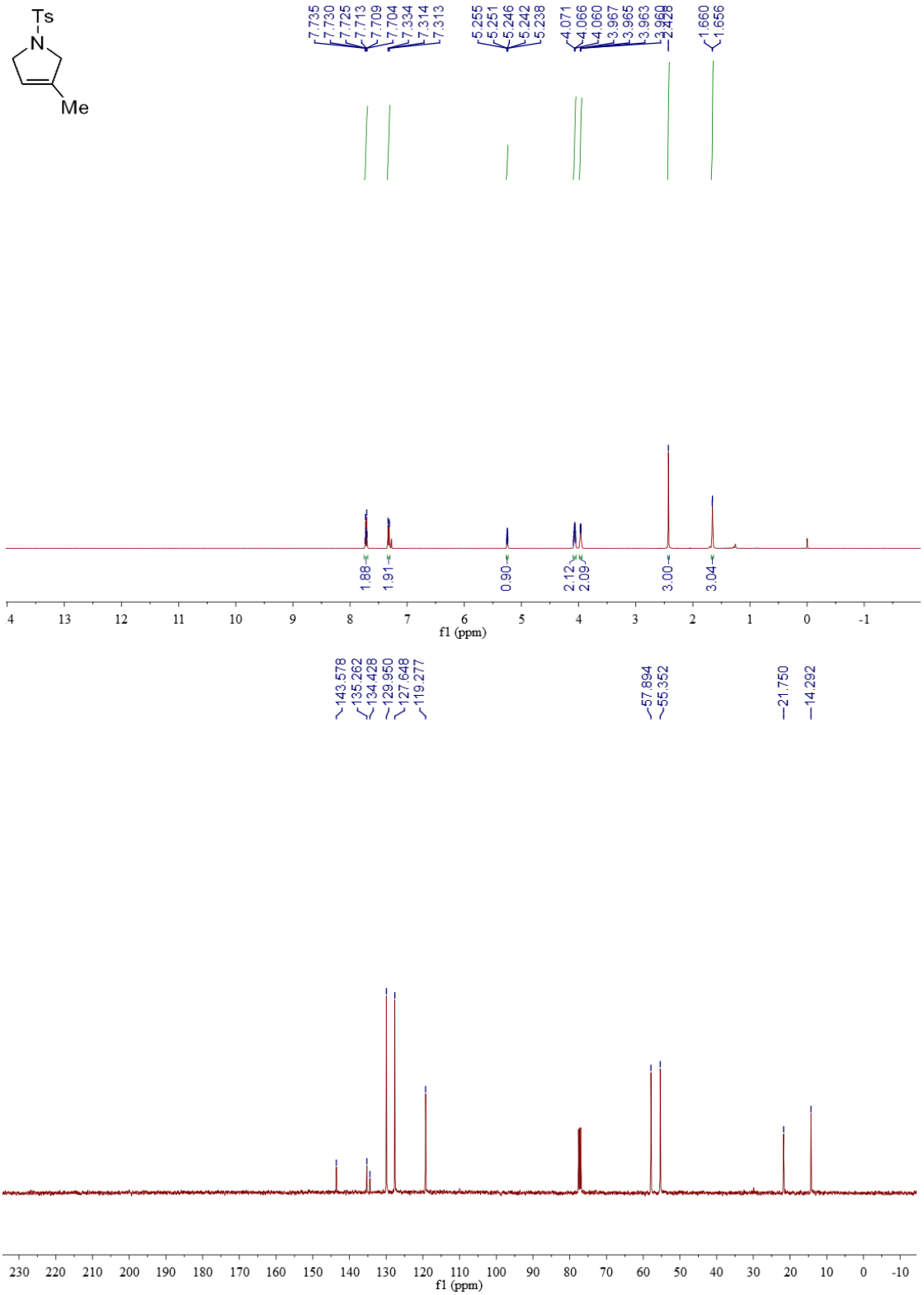

1.92
1.94
0.93
0.94
0.98
1.84
0.95
2.03
2.05
3.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

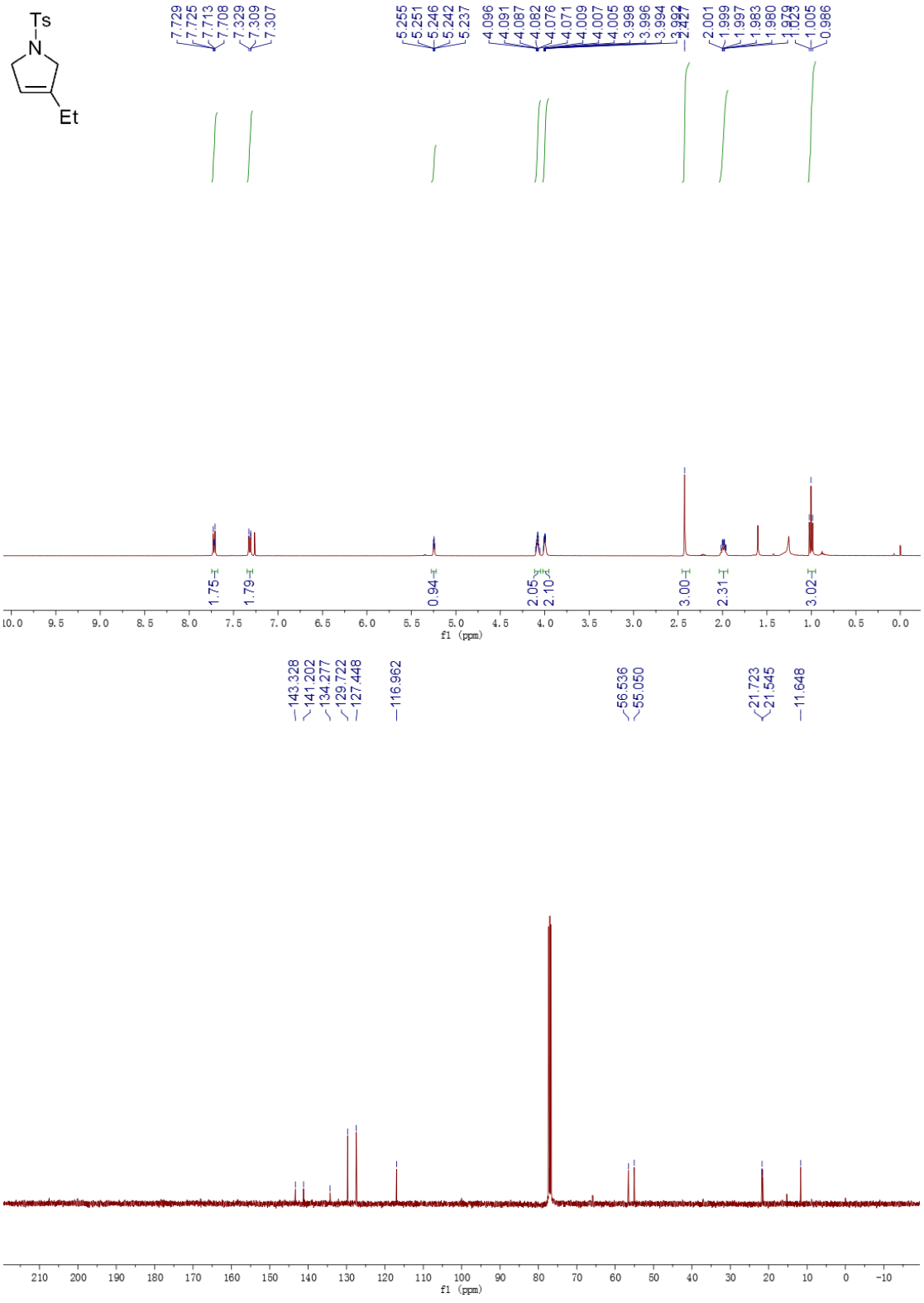

148.263
148.016
143.794
137.044
134.236
130.057
127.693
127.028
119.564
117.599
108.509
105.817
101.489
55.780
55.242
21.748

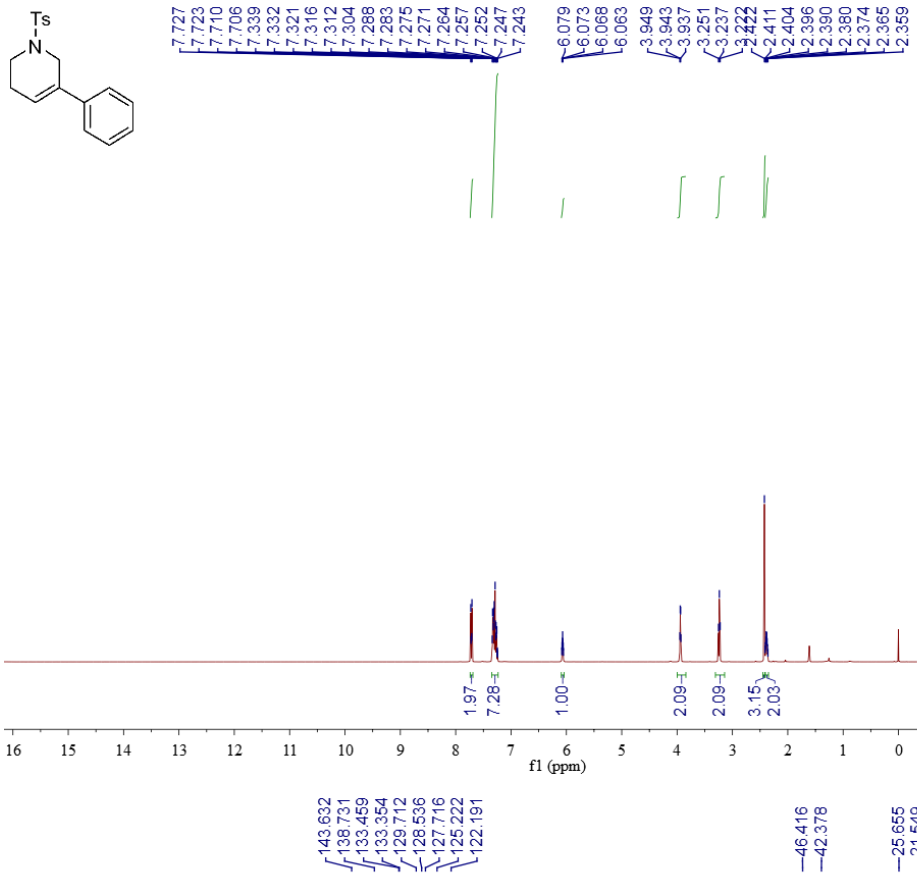

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ts
N
CH3
CH3
7.771
7.750
7.324
7.303
7.087
7.068
7.044
7.032
7.013
5.930
5.925
5.920
5.916
4.471
4.466
4.461
4.457
4.449
4.444
4.294
4.288
4.282
4.277
4.272
4.266
2.407
2.236
1.97
1.95
3.18
0.95
2.15
2.16
3.00
6.14
f1 (ppm)
143.515
137.261
137.147
136.867
134.083
130.106
129.890
129.823
127.470
126.632
122.830
117.632
55.668
55.014
21.530
19.804
19.580
f1 (ppm)


Ts
N
7.811
7.807
7.800
7.791
7.785
7.762
7.569
7.527
7.522
7.505
7.501
7.494
7.488
7.479
7.470
7.464
7.451
7.341
7.321
6.142
6.137
6.132
4.627
4.623
4.617
4.613
4.606
4.601
4.369
4.358
4.352
4.342
2.408
4.81
1.14
3.02
2.04
1.09
2.20
2.19
3.00
f1 (ppm)
143.615
137.333
134.062
133.211
133.054
129.880
129.778
128.363
128.154
127.672
127.506
126.659
126.525
124.585
123.103
119.524
55.770
54.973
21.539
f1 (ppm)


Ts
N
Me
7.735
7.730
7.725
7.713
7.709
7.704
7.334
7.314
7.313
5.255
5.251
5.246
5.242
5.238
4.071
4.066
4.060
3.967
3.965
3.963
3.960
2.428
1.660
1.656
1.88
1.91
0.90
2.12
2.09
3.00
3.04
f1 (ppm)
143.578
135.262
134.428
129.950
127.648
119.277
57.894
55.352
21.750
14.292
f1 (ppm)


Ts
N
Et
7.729
7.725
7.713
7.708
7.329
7.309
7.307
5.255
5.251
5.246
5.242
5.237
4.096
4.091
4.087
4.082
4.076
4.071
4.009
4.007
4.005
3.998
3.996
3.994
2.427
2.001
1.999
1.997
1.983
1.980
1.005
0.986
1.75
1.79
0.94
2.05
2.10
3.00
2.31
3.02
f1 (ppm)
143.328
141.202
134.277
129.722
127.448
116.962
56.536
55.050
21.723
21.545
11.648
f1 (ppm)


Ts
N
7.727
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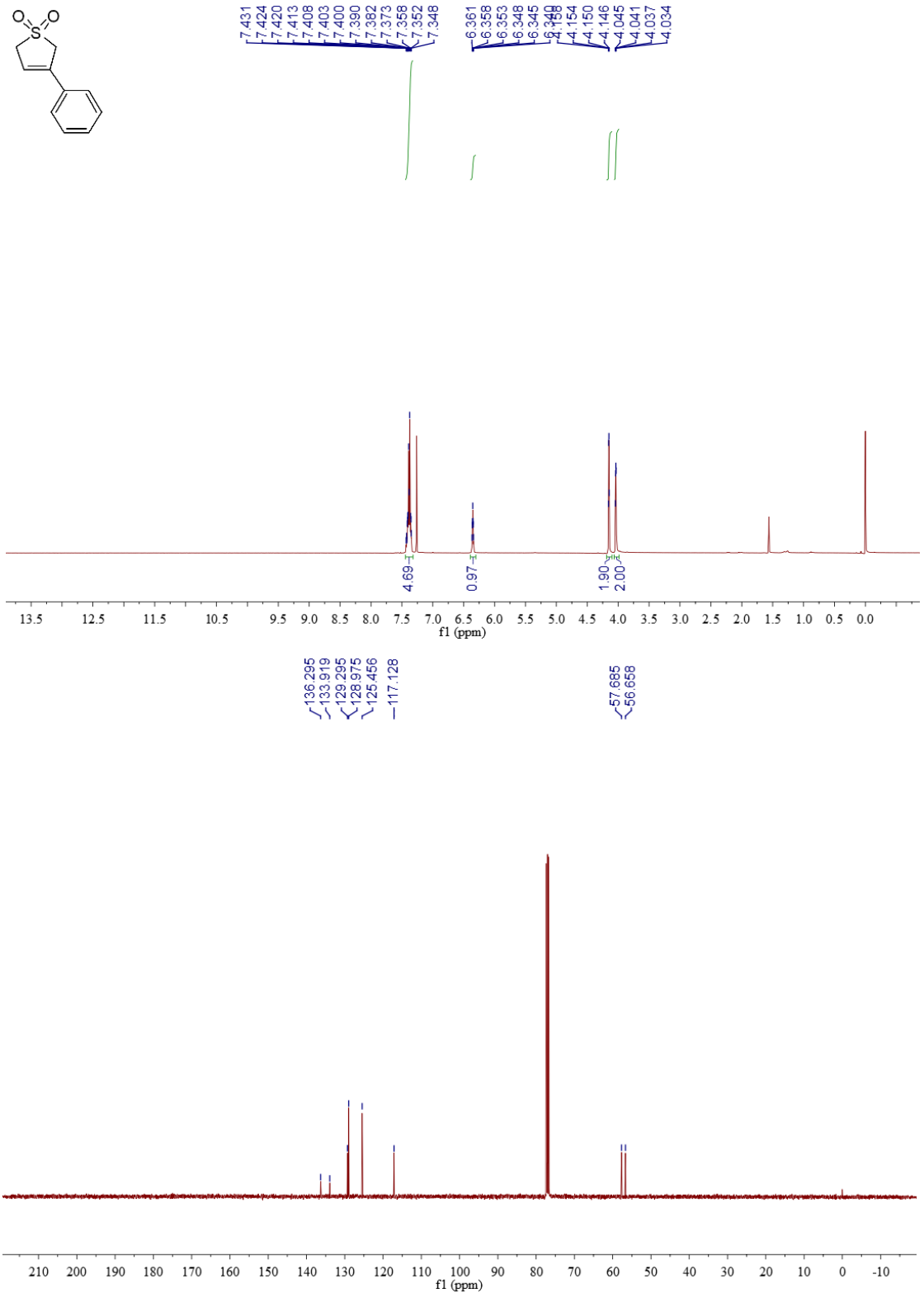
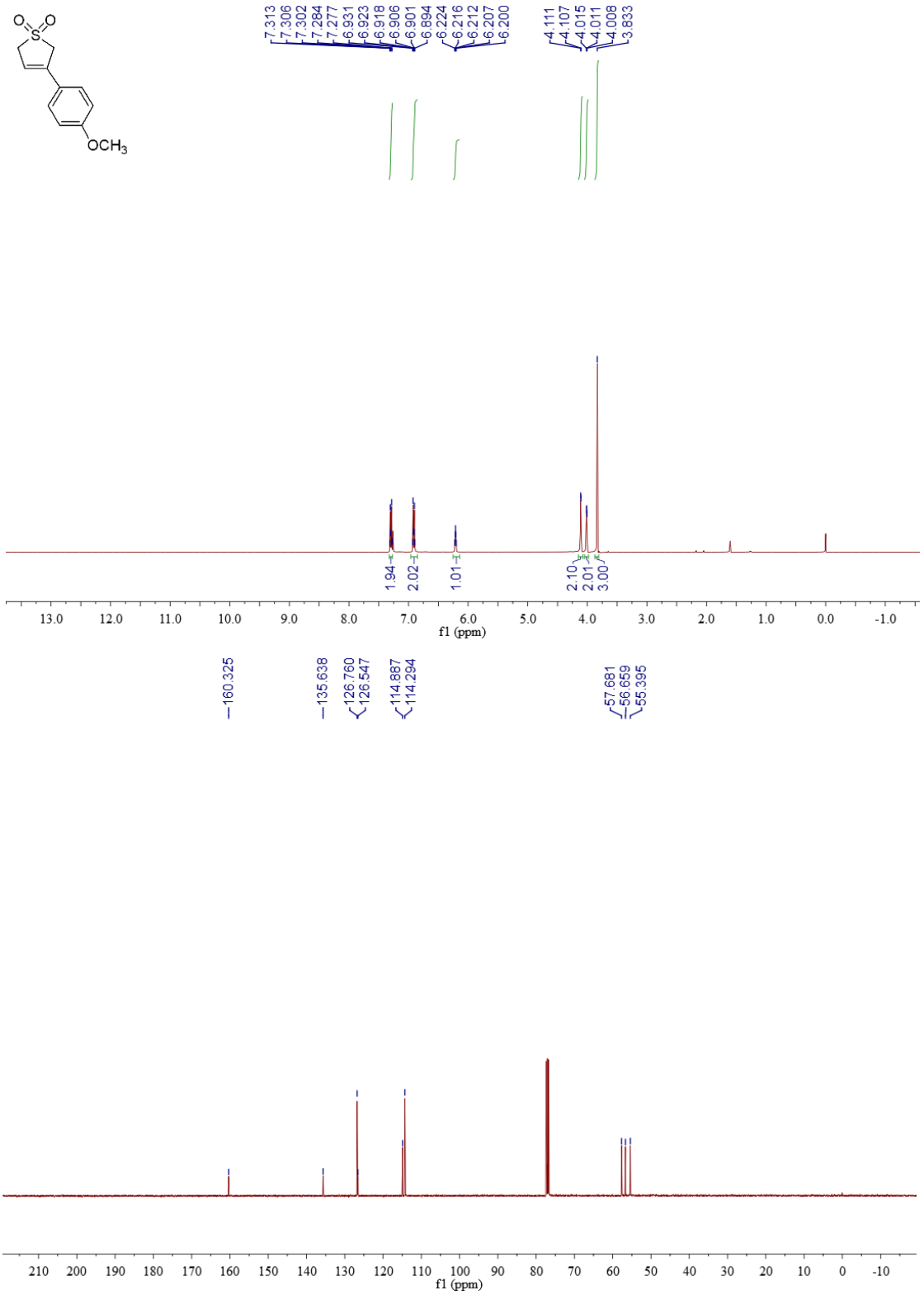
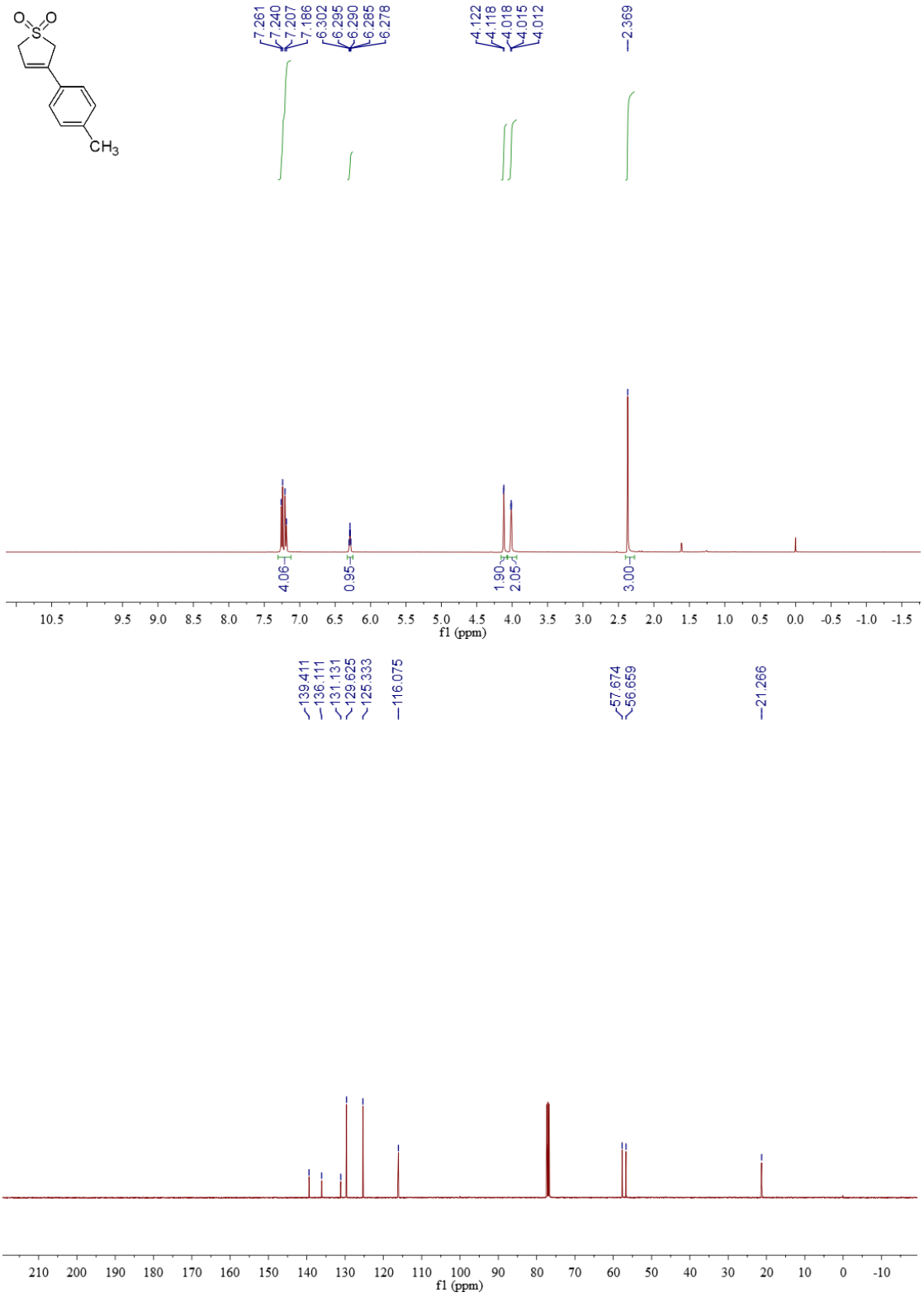
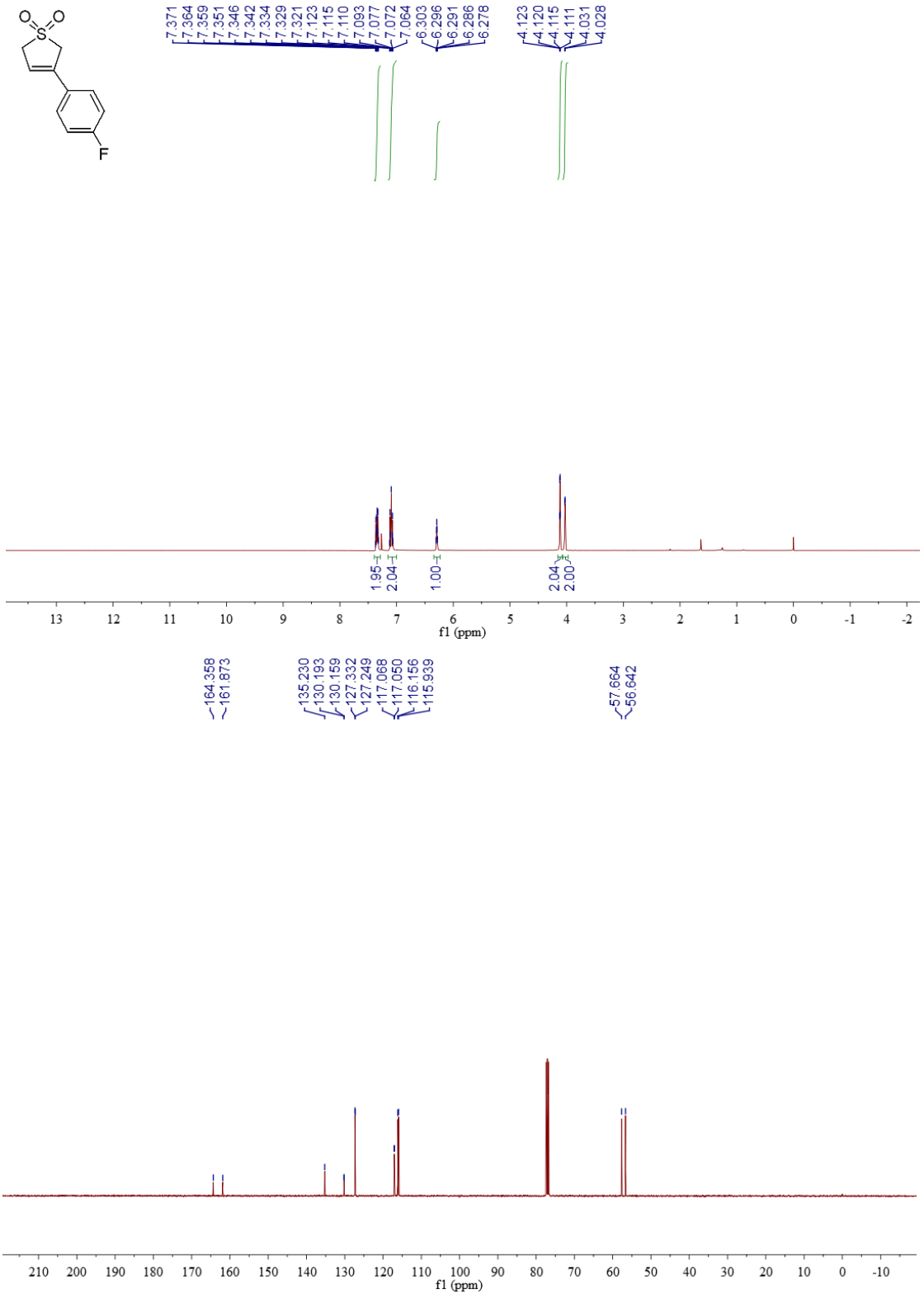
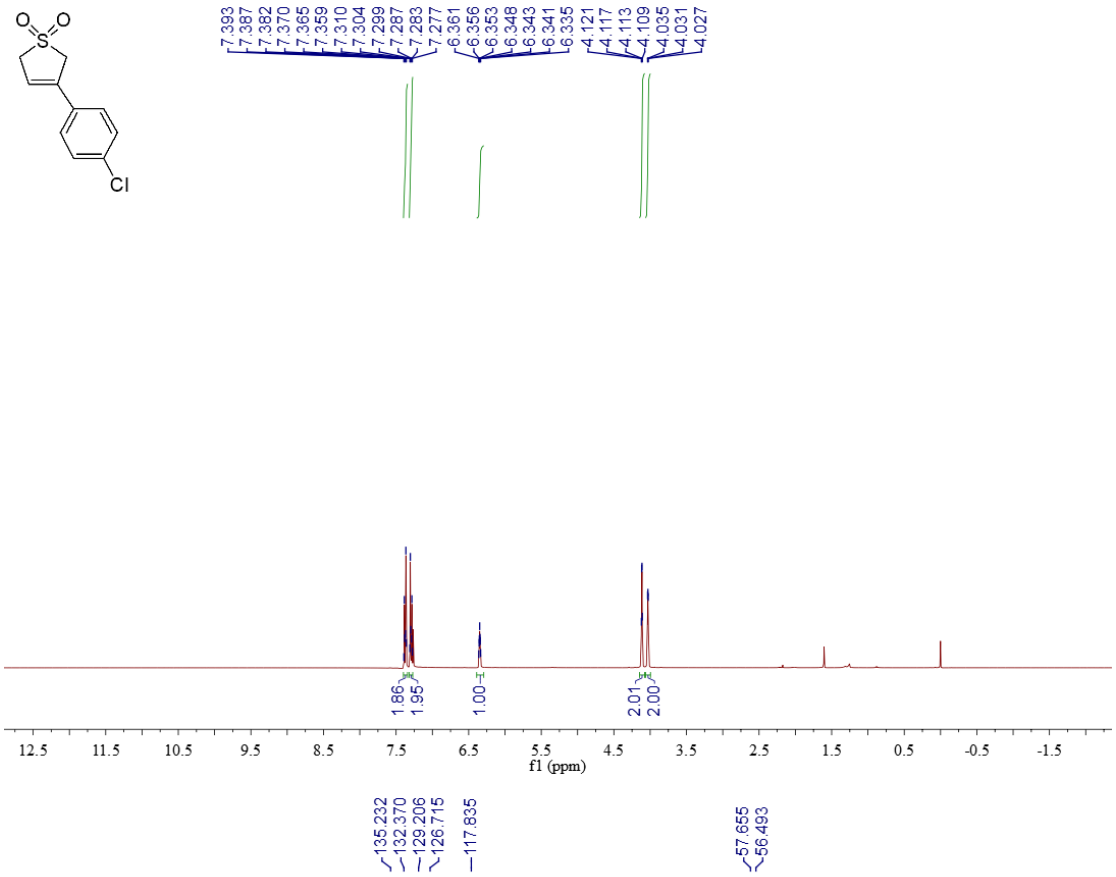
7.710
7.706
7.339
7.332
7.321
7.316
7.312
7.304
7.288
7.283
7.275
7.271
7.264
7.257
7.252
7.247
7.243
6.079
6.073
6.068
6.063
3.949
3.943
3.937
3.251
3.237
2.411
2.404
2.396
2.390
2.380
2.374
2.365
2.359
1.97
7.28
1.00
2.09
2.09
3.15
2.03
f1 (ppm)
143.632
138.731
133.459
133.354
129.712
128.536
127.716
125.222
122.191
46.416
42.378
25.655
21.549
f1 (ppm)


7.431
7.424
7.420
7.413
7.408
7.403
7.400
7.390
7.382
7.373
7.358
7.352
7.348
6.361
6.358
6.353
6.348
6.345
4.154
4.150
4.146
4.045
4.041
4.037
4.034
4.69
0.97
1.90
2.00
f1 (ppm)
136.295
133.919
129.295
128.975
125.456
117.128
57.685
56.658
f1 (ppm)


7.313
7.306
7.302
7.284
7.277
6.931
6.923
6.918
6.906
6.901
6.894
6.224
6.216
6.212
6.207
6.200
4.111
4.107
4.015
4.011
4.008
3.833
OCH3
1.94
2.02
1.01
2.10
2.01
3.00
f1 (ppm)
160.325
135.638
126.760
126.547
114.887
114.294
57.681
56.659
55.395
f1 (ppm)


7.261
7.240
7.207
7.186
6.302
6.295
6.290
6.285
6.278
4.122
4.118
4.018
4.015
4.012
2.369
4.06
0.95
1.90
2.05
3.00
f1 (ppm)
139.411
136.111
131.131
129.625
125.333
116.075
57.674
56.659
21.266
f1 (ppm)


7.371
7.364
7.359
7.351
7.346
7.342
7.334
7.329
7.321
7.123
7.115
7.110
7.093
7.077
7.072
7.064
6.303
6.296
6.291
6.286
6.278
4.123
4.120
4.115
4.111
4.031
4.028
1.95
2.04
1.00
2.04
2.00
f1 (ppm)
164.358
161.873
135.230
130.193
130.159
127.332
127.249
117.068
117.050
116.156
115.939
57.664
56.642
f1 (ppm)


O
O
S
Cl
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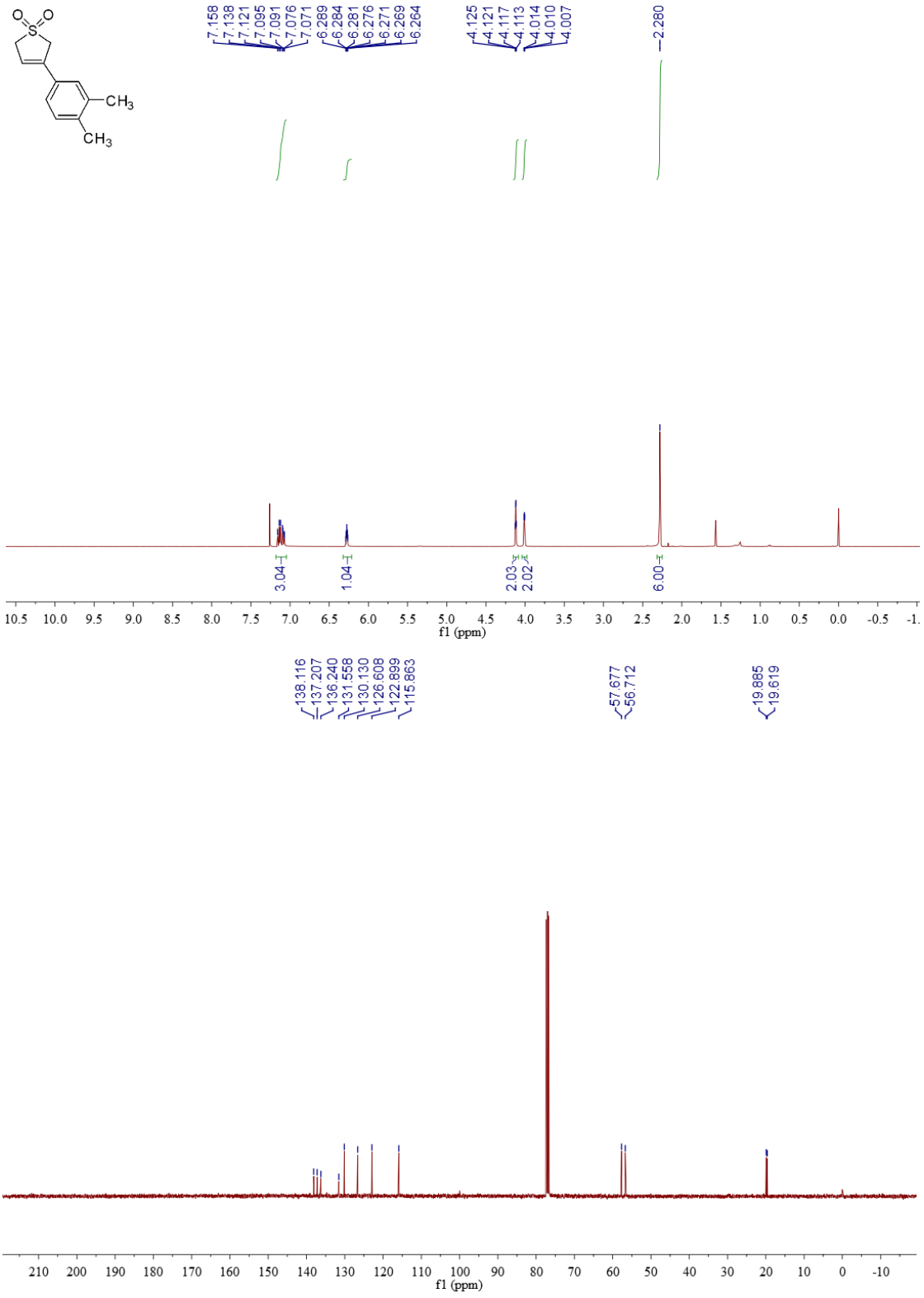
7.359
7.310
7.304
7.299
7.287
7.283
7.277
6.361
6.356
6.353
6.348
6.343
6.341
6.335
4.121
4.117
4.113
4.109
4.035
4.031
4.027
1.86
1.95
1.00
2.01
2.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)
135.232
132.370
129.206
126.715
117.835
57.655
56.493
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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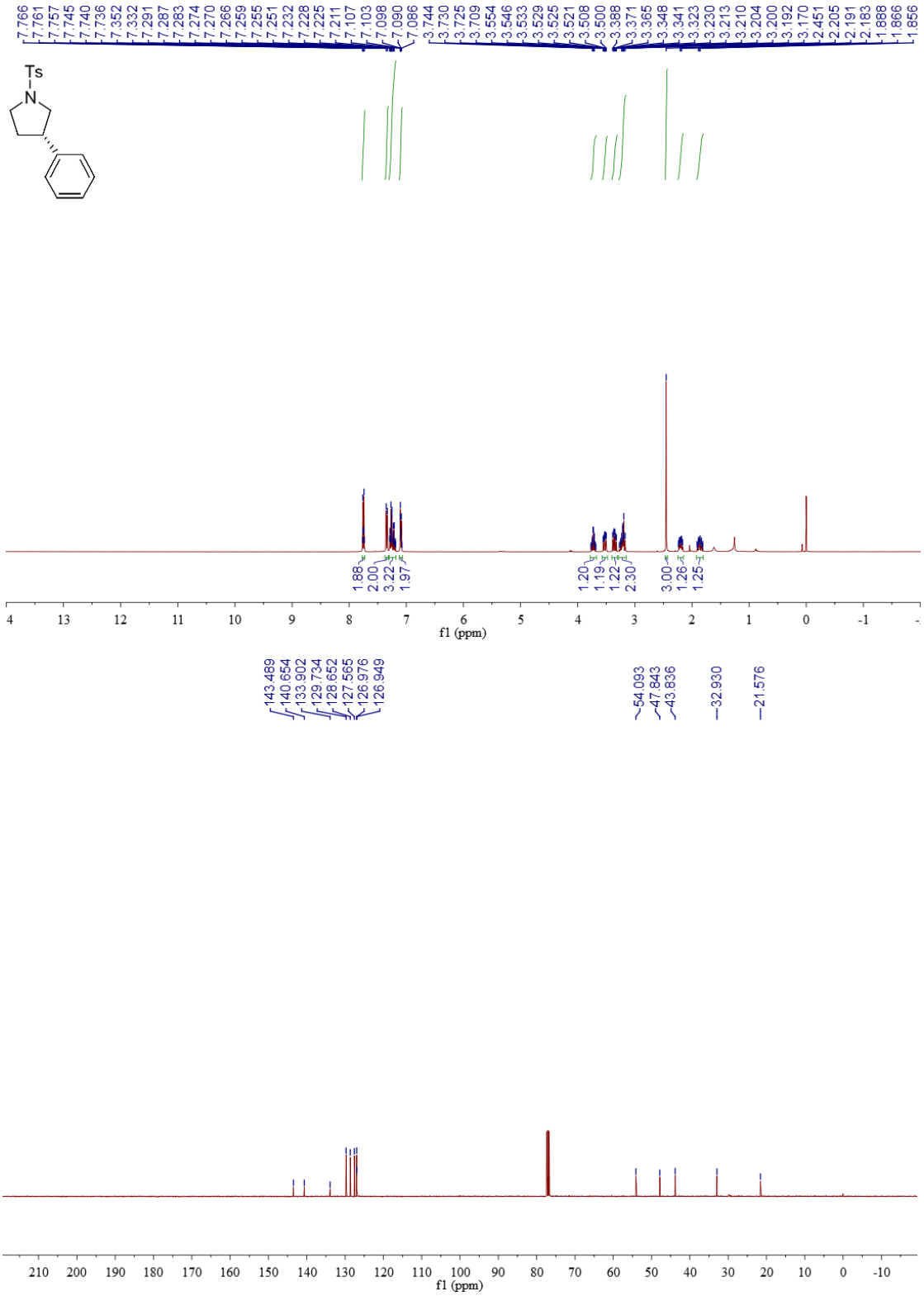
7.138
7.121
7.095
7.091
7.076
7.071
6.289
6.284
6.281
6.276
6.271
6.269
6.264
4.125
4.121
4.117
4.113
4.014
4.010
4.007
2.280
3.04
1.04
2.03
2.02
6.00
f1 (ppm)
138.116
137.207
136.240
131.558
130.130
126.608
122.899
115.863
57.677
56.712
19.885
19.619
f1 (ppm)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7.745
7.740
7.736
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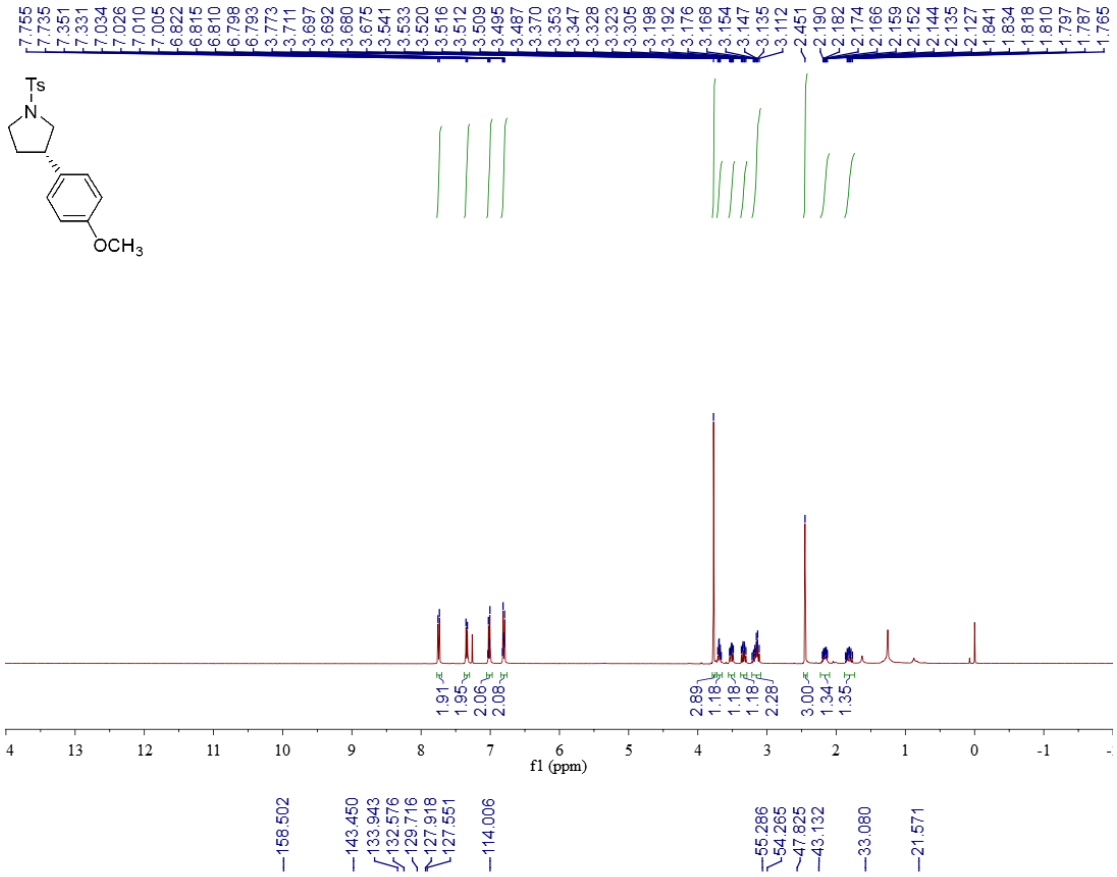
7.332
7.291
7.287
7.283
7.274
7.270
7.266
7.259
7.255
7.251
7.232
7.228
7.225
7.211
7.107
7.103
7.098
7.090
7.086
3.744
3.730
3.725
3.709
3.554
3.546
3.533
3.529
3.525
3.521
3.508
3.500
3.388
3.371
3.365
3.348
3.341
3.323
3.230
3.213
3.210
3.204
3.200
3.192
3.170
2.451
2.205
2.191
2.183
1.888
1.866
1.856
Ts
N
1.88
2.00
3.22
1.97
1.20
1.19
1.22
2.30
3.00
1.26
1.25
f1 (ppm)
143.489
140.654
133.902
129.734
128.652
127.565
126.976
126.949
54.093
47.843
43.836
32.930
21.576
f1 (ppm)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7.331
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7.026
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7.005
6.822
6.815
6.810
6.798
6.793
3.773
3.711
3.697
3.692
3.680
3.675
3.541
3.533
3.520
3.516
3.512
3.509
3.495
3.487
3.370
3.353
3.347
3.328
3.323
3.305
3.198
3.192
3.176
3.168
3.154
3.147
3.135
3.112
2.451
2.190
2.182
2.174
2.166
2.159
2.152
2.144
2.135
2.127
1.841
1.834
1.818
1.810
1.797
1.787
1.765
Ts
N
OCH3
1.91
1.95
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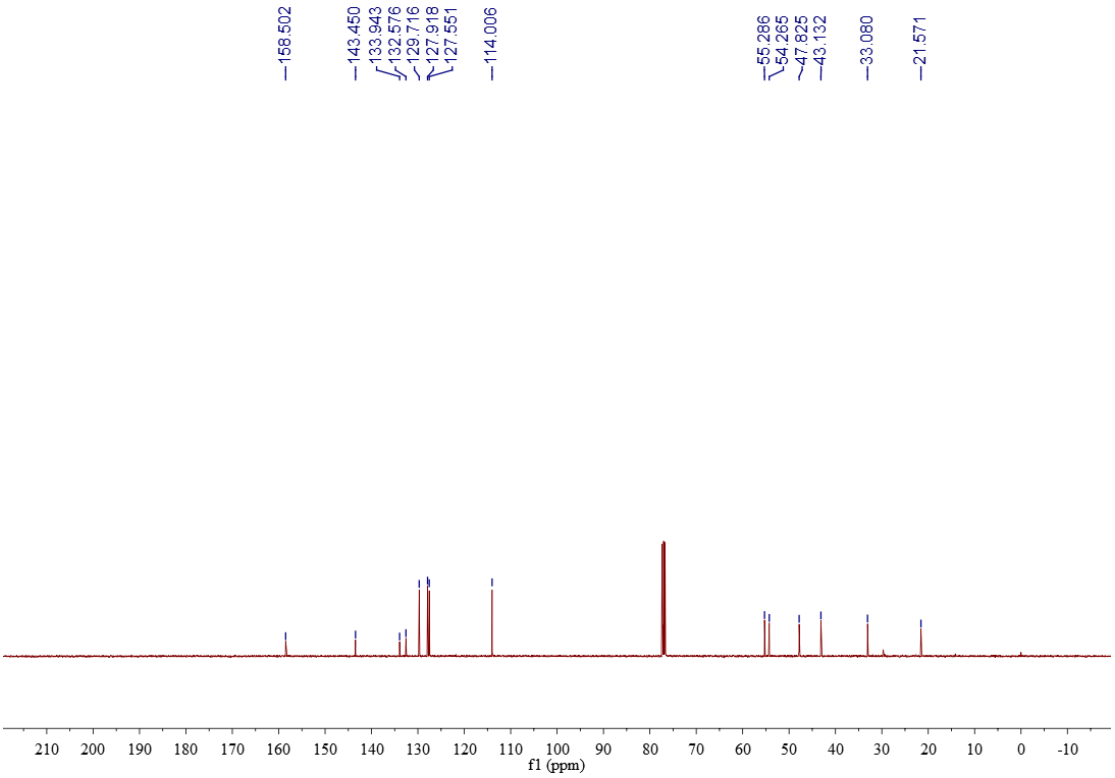
2.08
2.89
1.18
1.18
1.18
2.28
3.00
1.34
1.35
f1 (ppm)


158.502
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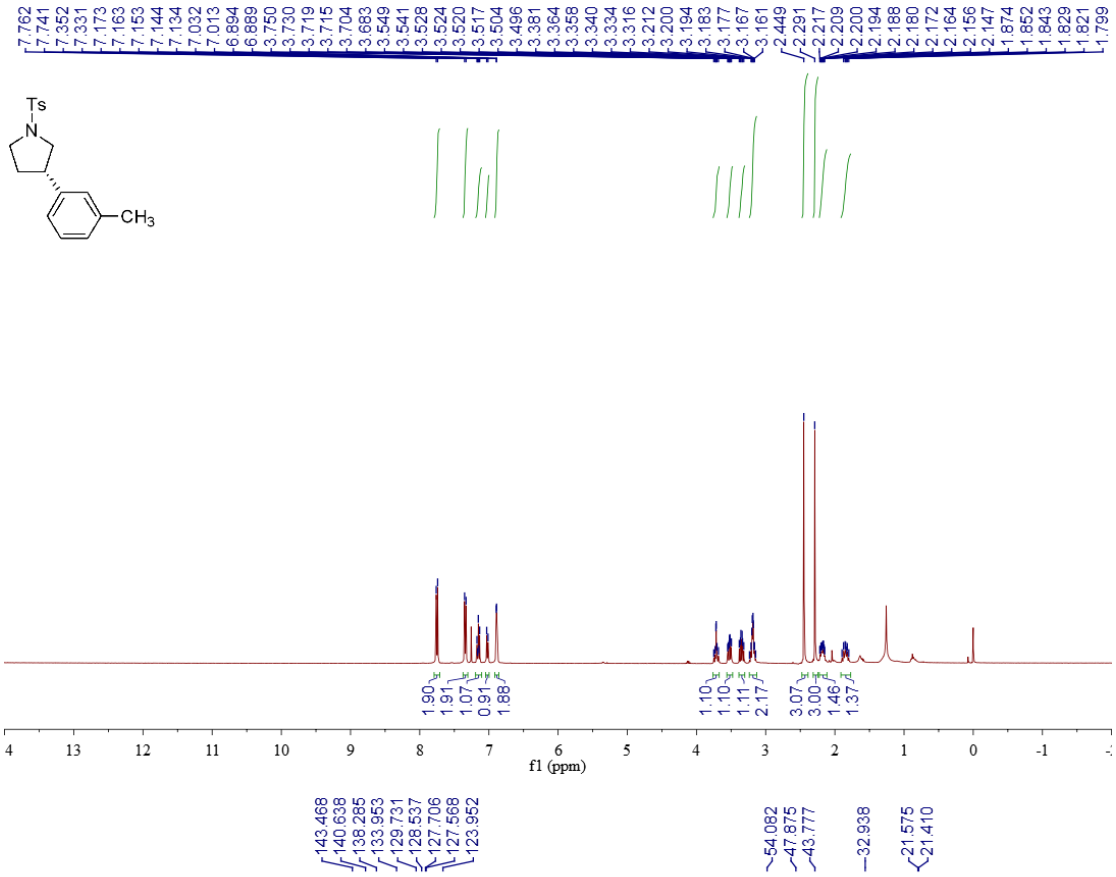
133.943
132.576
129.716
127.918
127.551
114.006
55.286
54.265
47.825
43.132
33.080
21.571
f1 (ppm)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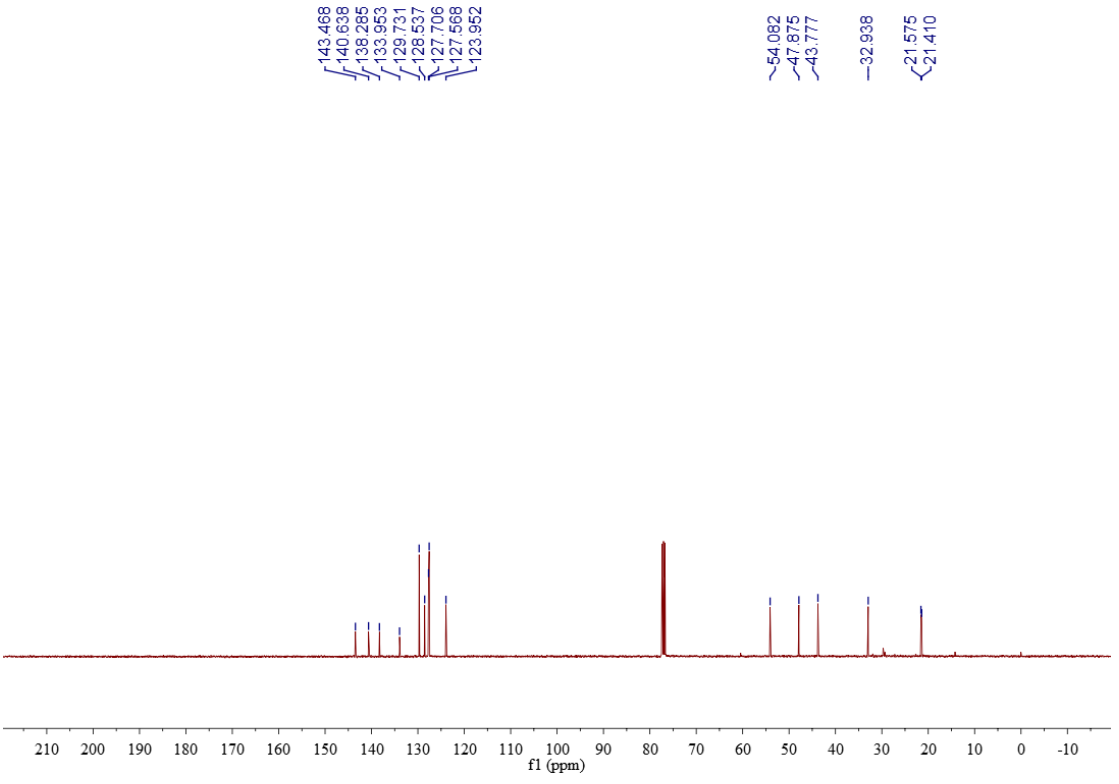
7.352
7.331
7.173
7.163
7.153
7.144
7.134
7.032
7.013
6.894
6.889
3.750
3.730
3.719
3.715
3.704
3.683
3.549
3.541
3.528
3.524
3.520
3.517
3.504
3.496
3.381
3.364
3.358
3.340
3.334
3.316
3.212
3.200
3.194
3.183
3.177
3.167
3.161
2.449
2.291
2.217
2.209
2.200
2.194
2.188
2.180
2.172
2.164
2.156
2.147
1.874
1.852
1.843
1.829
1.821
1.799
Ts
N
CH3
1.90
1.91
1.07
0.91
1.88
1.10
1.10
1.11
2.17
3.07
3.00
1.46
1.37
f1 (ppm)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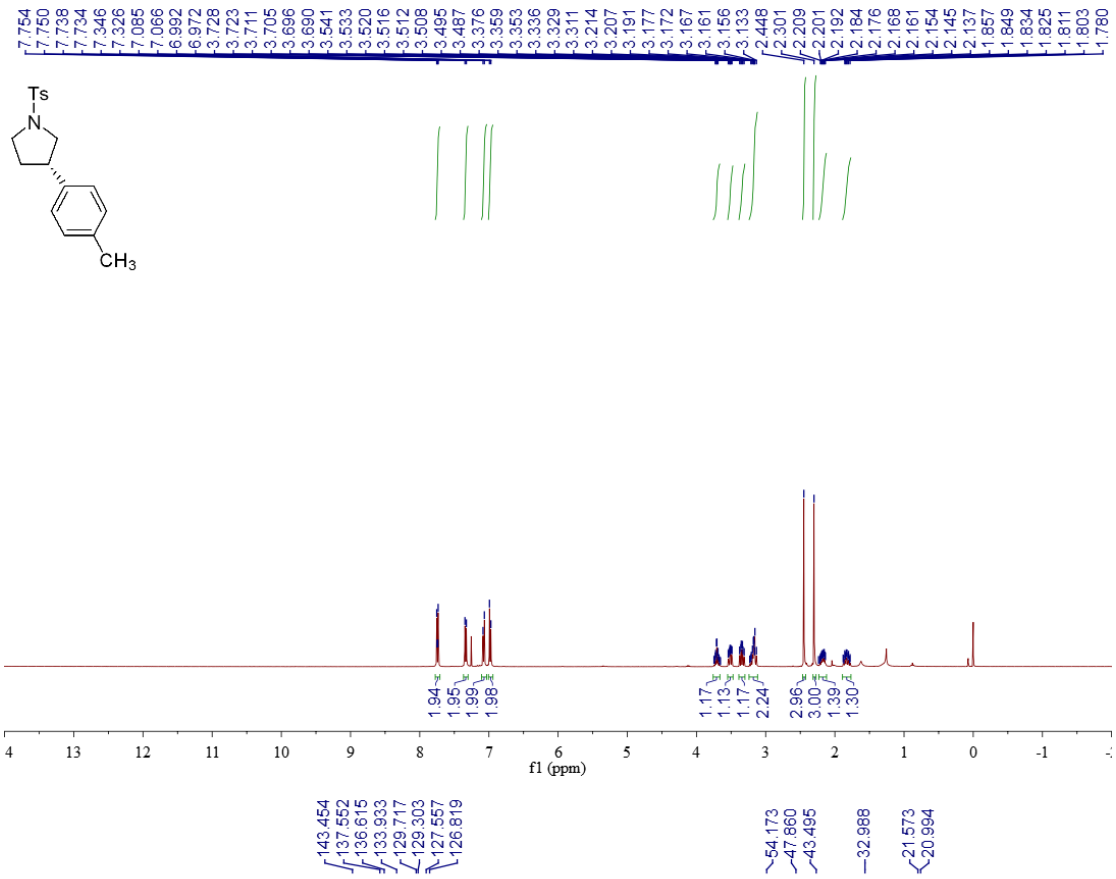
138.285
133.953
129.731
128.537
127.706
127.568
123.952
54.082
47.875
43.777
32.938
21.575
21.410
f1 (ppm)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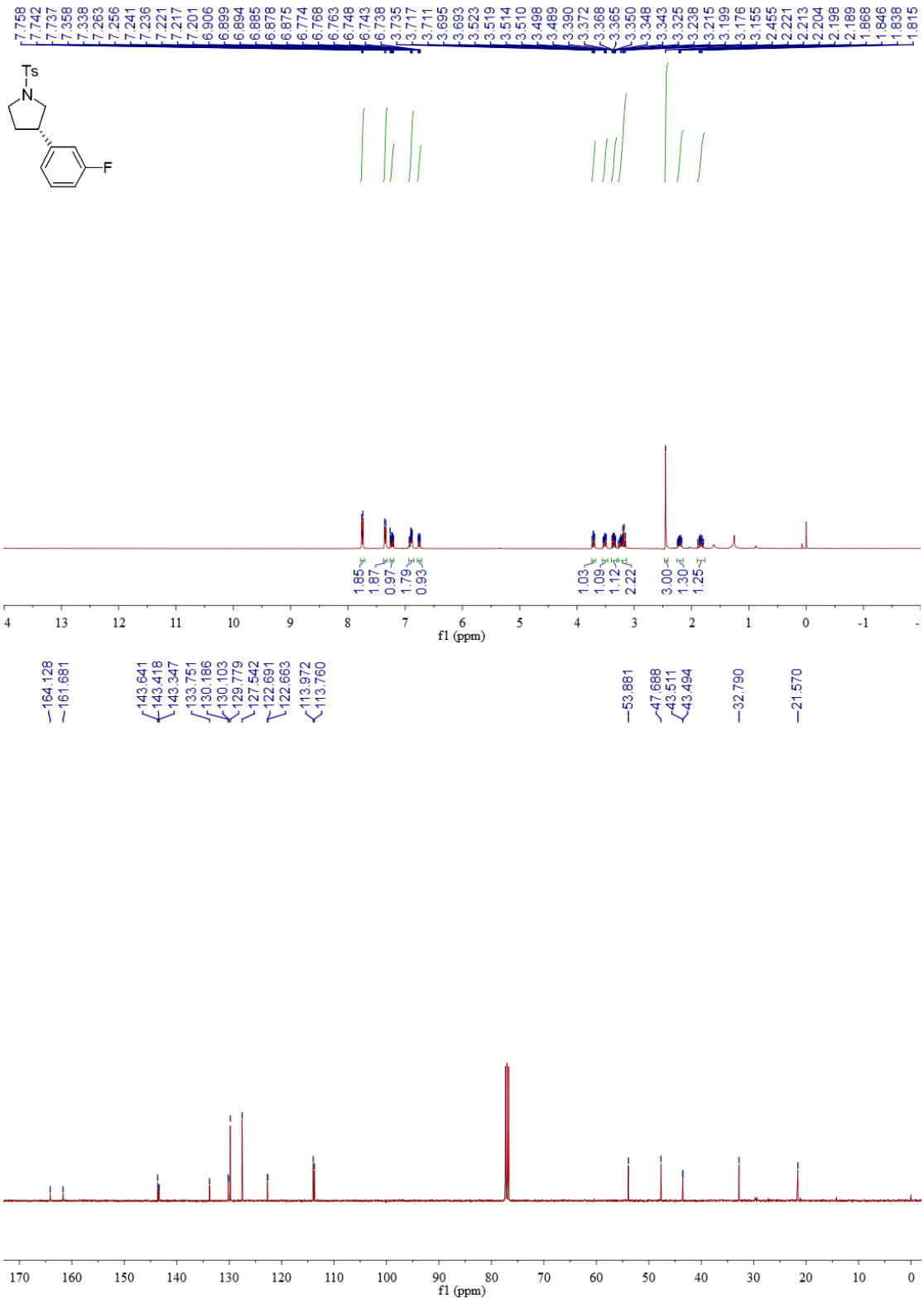
7.346
7.326
7.085
7.066
6.992
6.972
3.728
3.723
3.711
3.705
3.696
3.690
3.541
3.533
3.520
3.516
3.512
3.508
3.495
3.487
3.376
3.359
3.353
3.336
3.329
3.311
3.214
3.207
3.191
3.177
3.172
3.167
3.161
3.156
3.133
2.448
2.301
2.209
2.201
2.192
2.184
2.176
2.168
2.161
2.154
2.145
2.137
1.857
1.849
1.834
1.825
1.811
1.803
1.780
Ts
N
CH3
1.94
1.95
1.99
1.98
1.17
1.13
1.17
2.24
2.96
3.00
1.39
1.30
f1 (ppm)
143.454
137.552
136.615
133.933
129.717
129.303
127.557
126.819
54.173
47.860
43.495
32.988
21.573
20.994
f1 (ppm)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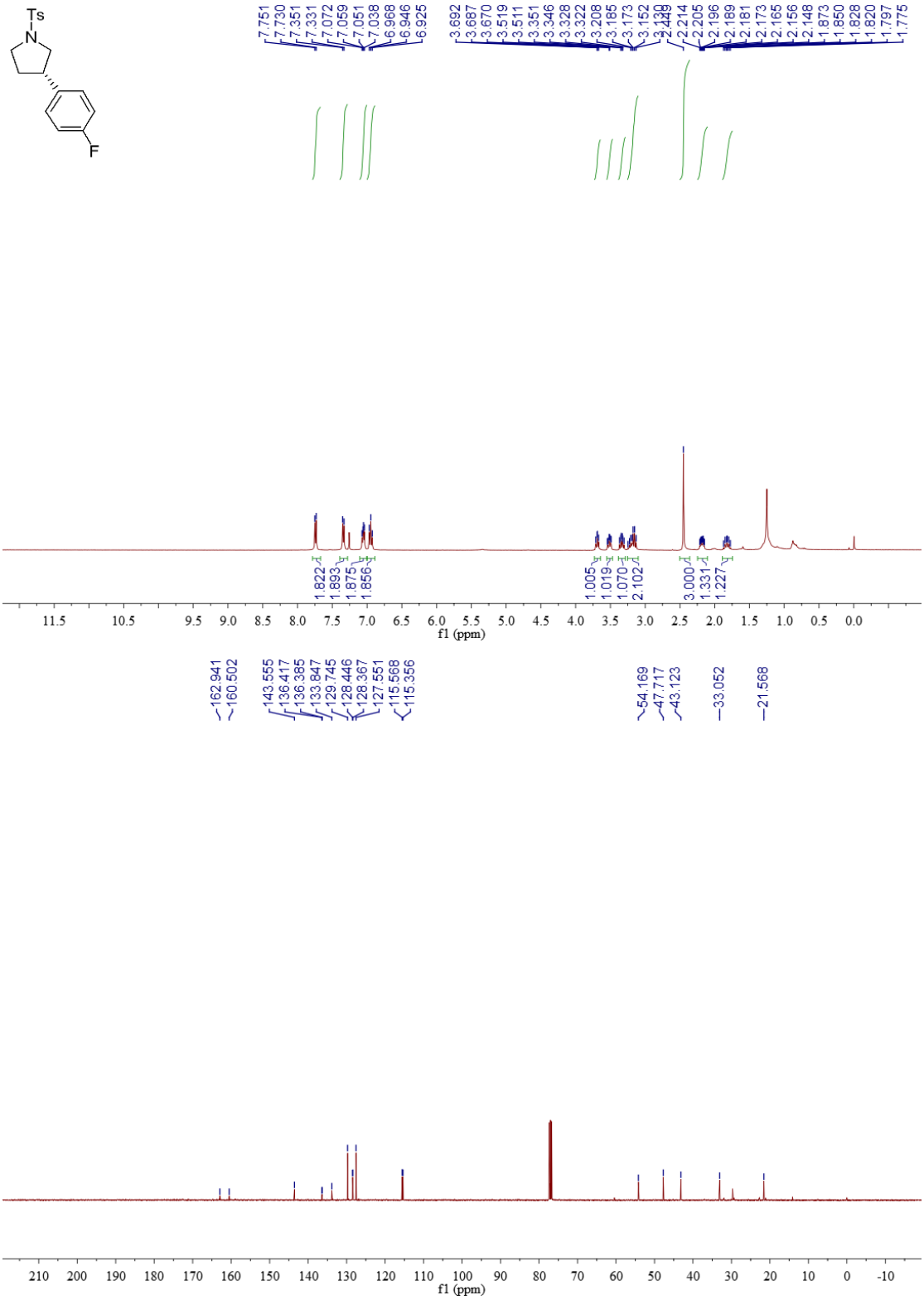
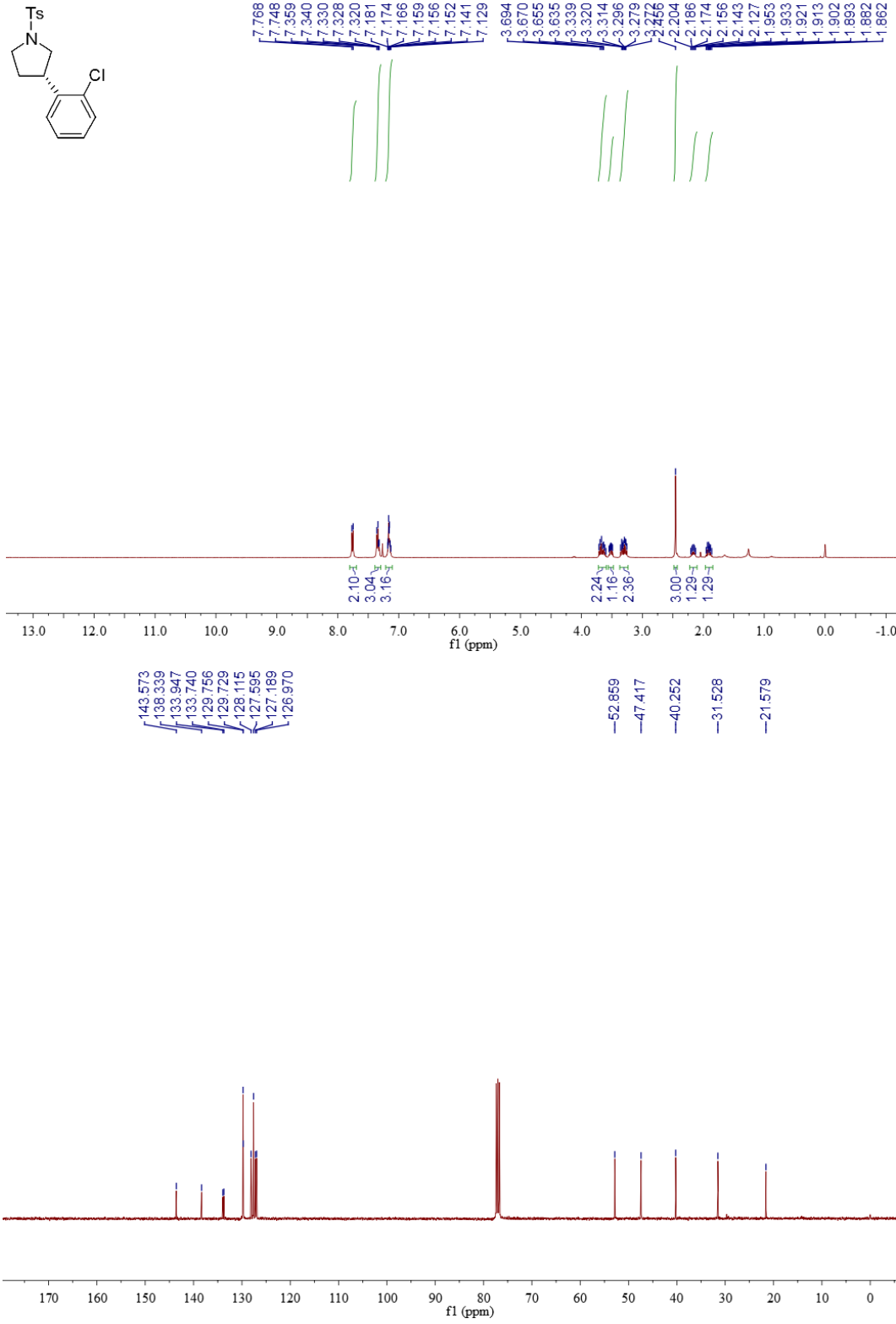
7.256
7.241
7.236
7.221
7.217
7.201
6.906
6.899
6.894
6.885
6.878
6.875
6.774
6.768
6.763
6.748
6.743
6.738
3.735
3.717
3.711
3.695
3.693
3.523
3.519
3.514
3.510
3.498
3.489
3.390
3.372
3.368
3.365
3.350
3.348
3.343
3.325
3.238
3.215
3.199
3.176
3.155
2.455
2.221
2.213
2.204
2.198
2.189
1.868
1.846
1.838
1.815
Ts
N
F
1.85
1.87
0.97
1.79
0.93
1.03
1.09
1.12
2.22
3.00
1.30
1.25
f1 (ppm)
164.128
161.681
143.641
143.418
143.347
133.751
130.186
130.103
129.779
127.542
122.691
122.663
113.972
113.760
53.881
47.688
43.511
43.494
32.790
21.570
f1 (ppm)


Ts
N
F
7.751
7.730
7.351
7.331
7.072
7.059
7.051
7.038
6.968
6.946
6.925
3.692
3.687
3.670
3.519
3.511
3.351
3.346
3.328
3.322
3.208
3.185
3.173
3.152
2.214
2.205
2.196
2.189
2.181
2.173
2.165
2.156
2.148
1.873
1.850
1.828
1.820
1.797
1.775
1.822
1.893
1.875
1.856
1.005
1.019
1.070
2.102
3.000
1.331
1.227
f1 (ppm)
162.941
160.502
143.555
136.417
136.385
133.847
129.745
128.446
128.367
127.551
115.568
115.356
54.169
47.717
43.123
33.052
21.568
f1 (ppm)


Ts
N
Cl
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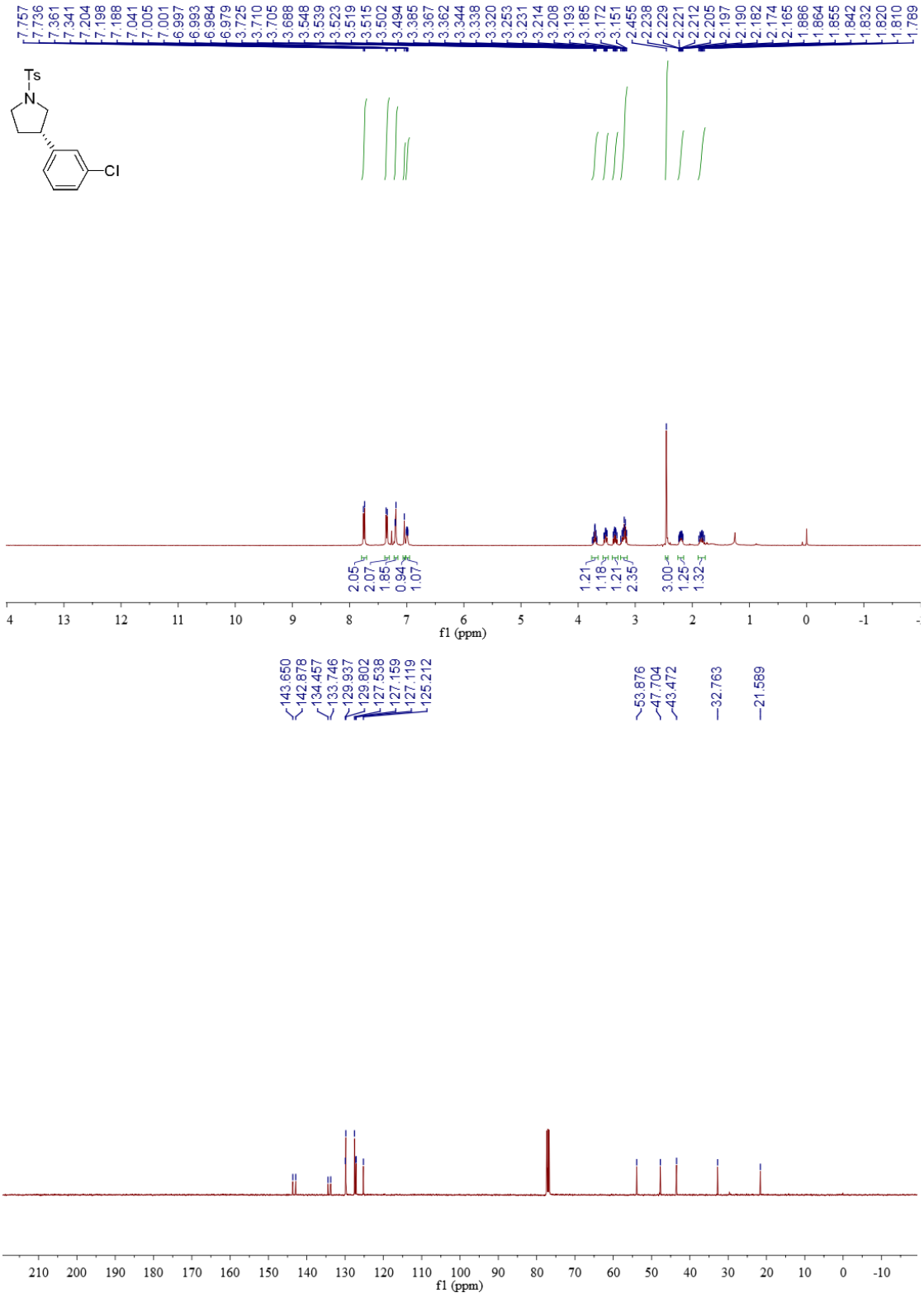
7.330
7.328
7.320
7.181
7.174
7.166
7.159
7.156
7.152
7.141
7.129
3.694
3.670
3.655
3.635
3.339
3.320
3.314
3.296
3.279
3.272
2.204
2.186
2.174
2.156
2.143
2.127
1.953
1.933
1.921
1.913
1.902
1.893
1.882
1.862
2.10
3.04
3.16
2.24
1.16
2.36
3.00
1.29
1.29
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
143.573
138.339
133.947
133.740
129.756
129.729
128.115
127.595
127.189
126.970
52.859
47.417
40.252
31.528
21.579
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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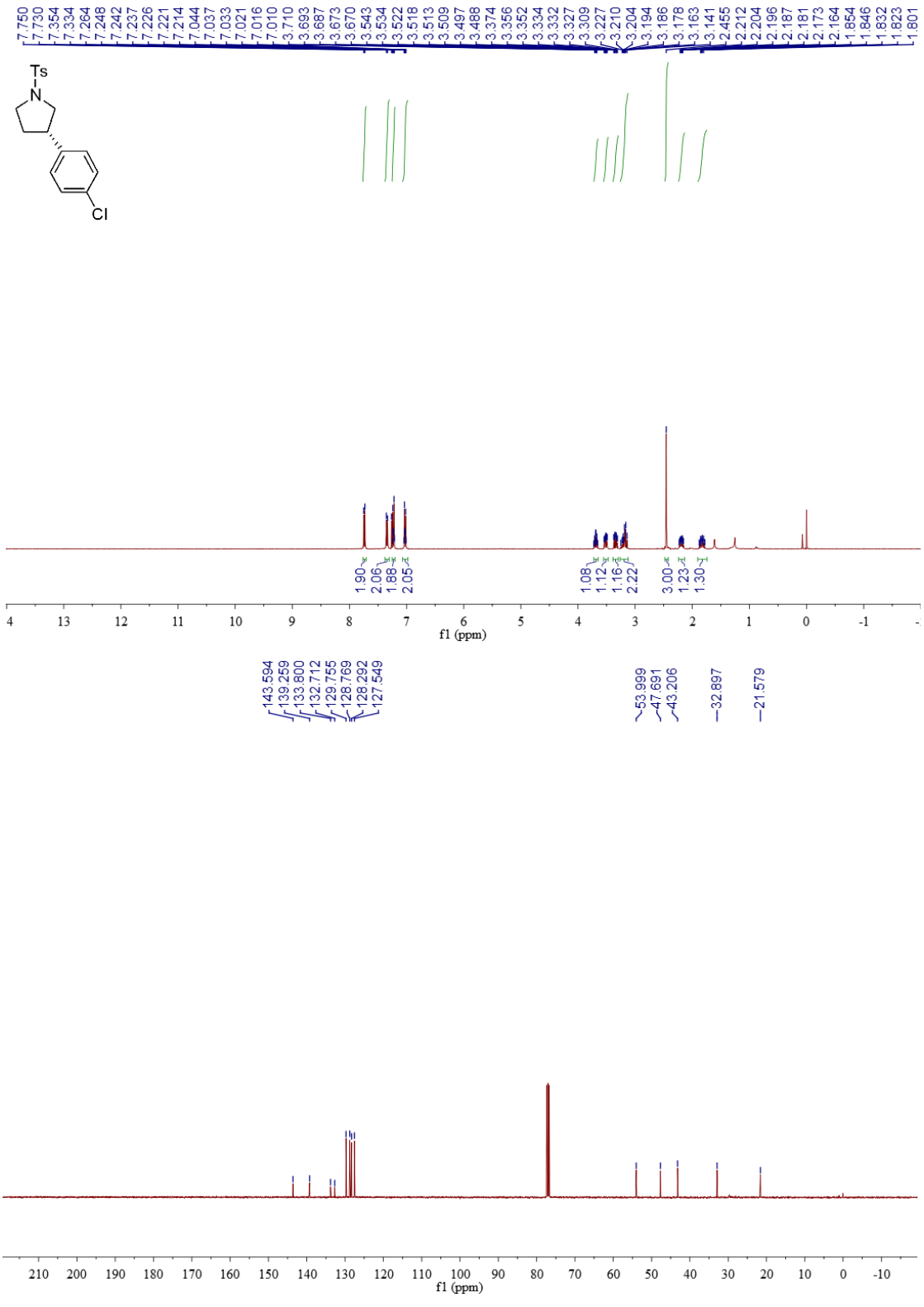
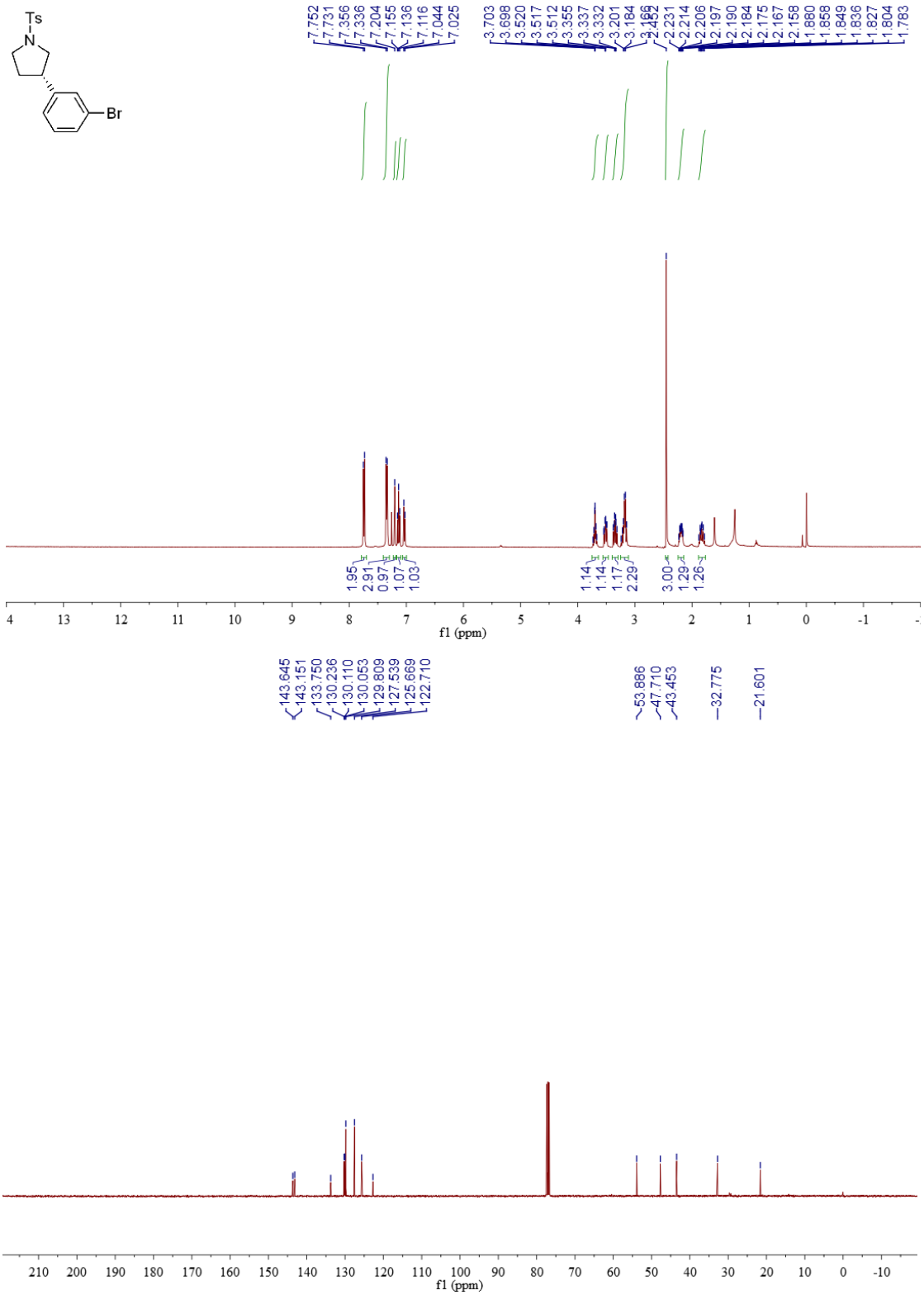
7.736
7.361
7.341
7.204
7.198
7.188
7.041
7.005
7.001
6.997
6.993
6.984
6.979
3.725
3.710
3.705
3.688
3.548
3.539
3.523
3.519
3.515
3.502
3.494
3.385
3.367
3.362
3.344
3.338
3.320
3.253
3.231
3.214
3.208
3.193
3.185
3.172
3.151
2.455
2.238
2.229
2.221
2.212
2.205
2.197
2.190
2.182
2.174
2.165
1.886
1.864
1.855
1.842
1.832
1.820
1.810
1.789
Ts
N
Cl
2.05
2.07
1.85
0.94
1.07
1.21
1.18
1.21
2.35
3.00
1.25
1.32
f1 (ppm)
143.650
142.878
134.457
133.746
129.937
129.802
127.538
127.159
127.119
125.212
53.876
47.704
43.472
32.763
21.589
f1 (ppm)


7.750
7.730
7.354
7.334
7.264
7.248
7.242
7.237
7.226
7.221
7.214
7.044
7.037
7.033
7.021
7.016
7.010
3.710
3.693
3.687
3.673
3.670
3.543
3.534
3.522
3.518
3.513
3.509
3.497
3.488
3.374
3.356
3.352
3.334
3.332
3.327
3.309
3.227
3.210
3.204
3.194
3.186
3.178
3.163
3.141
2.455
2.212
2.204
2.196
2.187
2.181
2.173
2.164
1.854
1.846
1.832
1.823
1.801
Ts
N
Cl
1.90
2.06
1.88
2.05
1.08
1.12
1.16
2.22
3.00
1.23
1.30
f1 (ppm)
143.594
139.259
133.800
132.712
129.755
128.769
128.292
127.549
53.999
47.691
43.206
32.897
21.579
f1 (ppm)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N
Br
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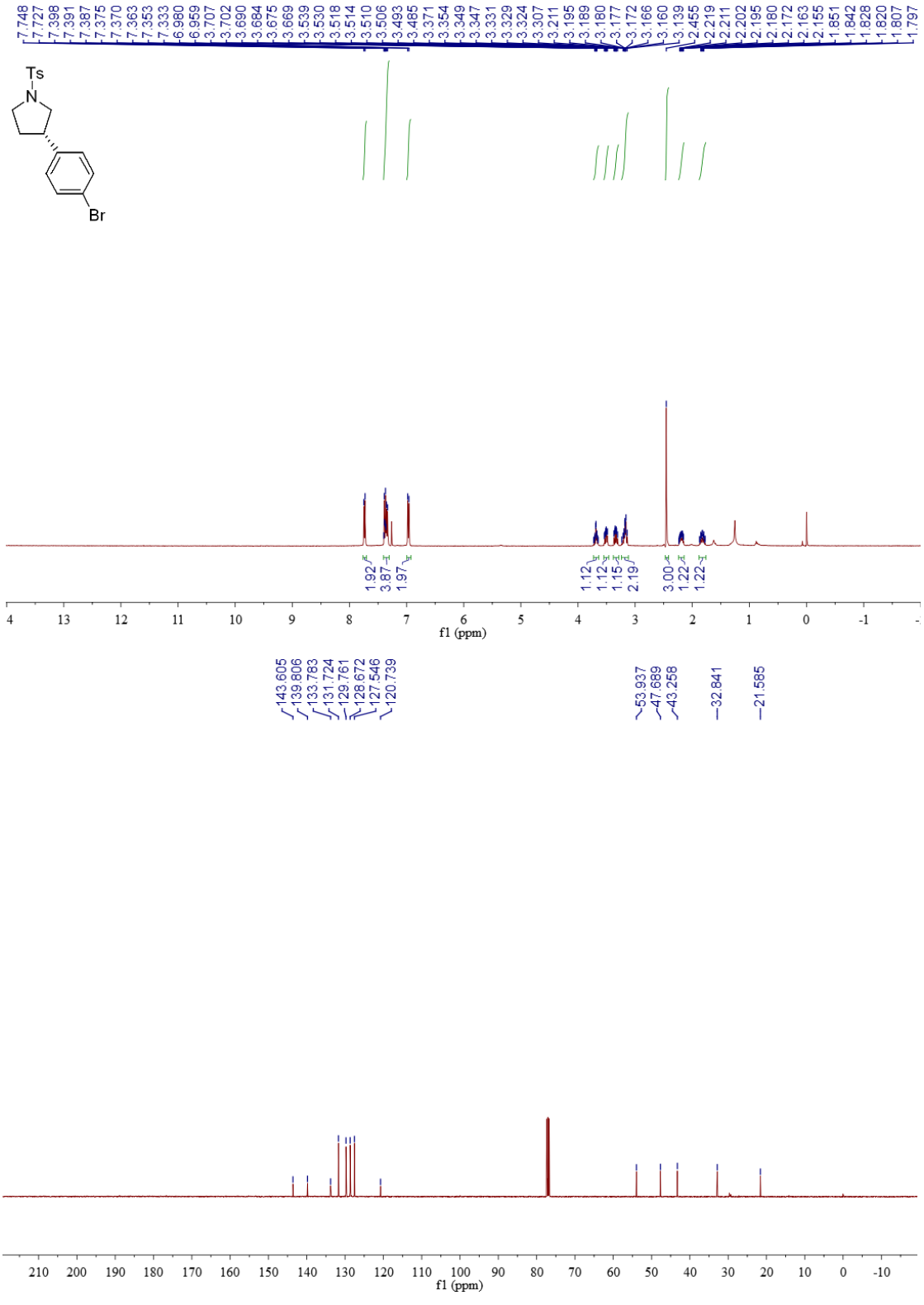
7.731
7.356
7.336
7.204
7.155
7.136
7.116
7.044
7.025
3.703
3.698
3.520
3.517
3.512
3.355
3.337
3.332
3.201
3.184
2.231
2.214
2.206
2.197
2.190
2.184
2.175
2.167
2.158
1.880
1.858
1.849
1.836
1.827
1.804
1.783
1.95
2.91
0.97
1.07
1.03
1.14
1.14
1.17
2.29
3.00
1.29
1.26
f1 (ppm)
143.645
143.151
133.750
130.236
130.110
130.053
129.809
127.539
125.669
122.710
53.886
47.710
43.453
32.775
21.601
f1 (ppm)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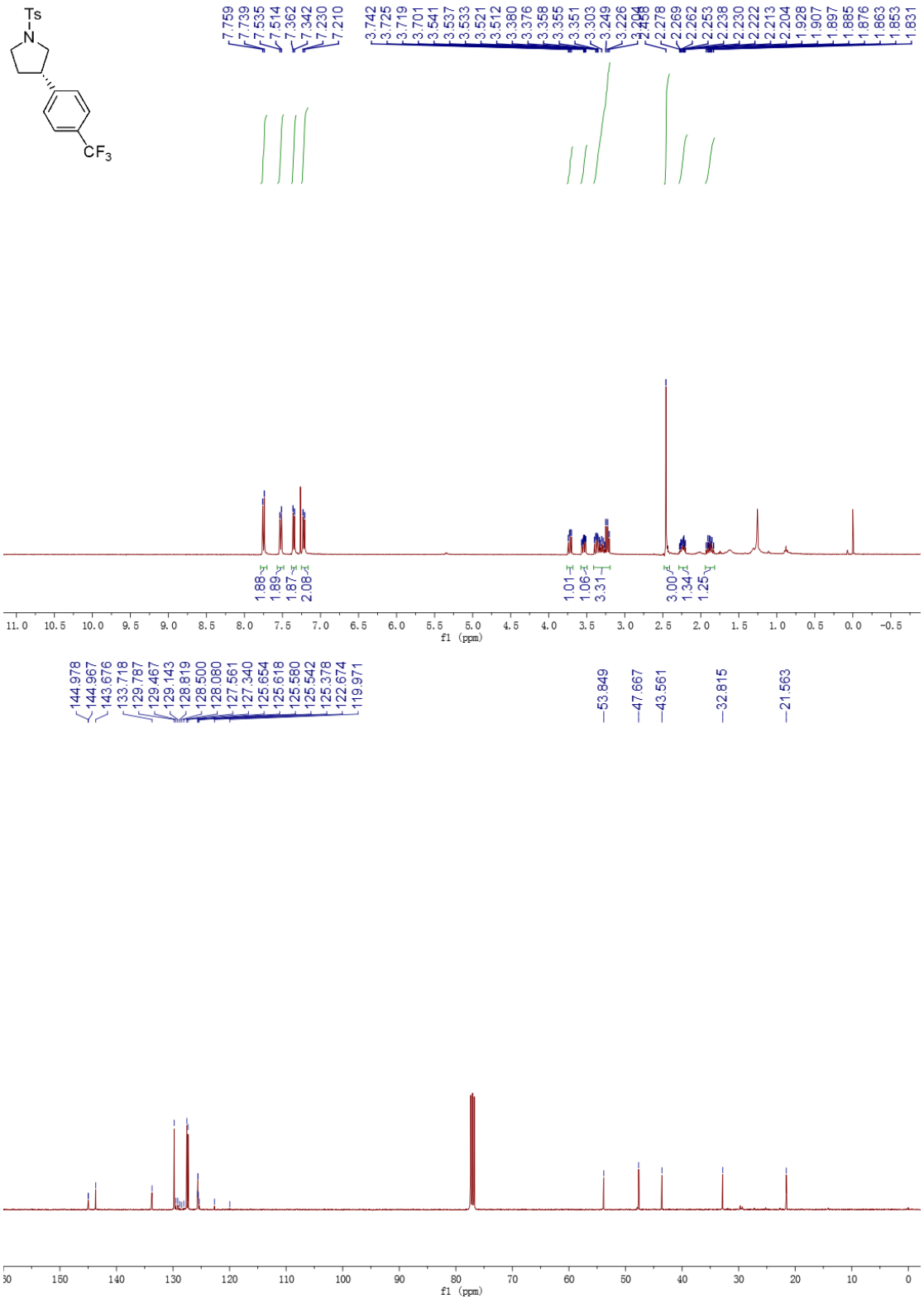
7.370
7.363
7.353
7.333
6.980
6.959
3.707
3.702
3.690
3.684
3.675
3.669
3.539
3.530
3.518
3.514
3.510
3.506
3.493
3.485
3.371
3.354
3.349
3.347
3.331
3.329
3.324
3.307
3.211
3.195
3.189
3.180
3.177
3.172
3.166
3.160
3.139
2.455
2.219
2.211
2.202
2.195
2.180
2.172
2.163
2.155
1.851
1.842
1.828
1.820
1.807
1.797
Ts
N
Br
1.92
3.87
1.97
1.12
1.12
1.15
2.19
3.00
1.22
1.22
f1 (ppm)
143.605
139.806
133.783
131.724
129.761
128.672
127.546
120.739
53.937
47.689
43.258
32.841
21.585
f1 (ppm)


Ts
N
CF3
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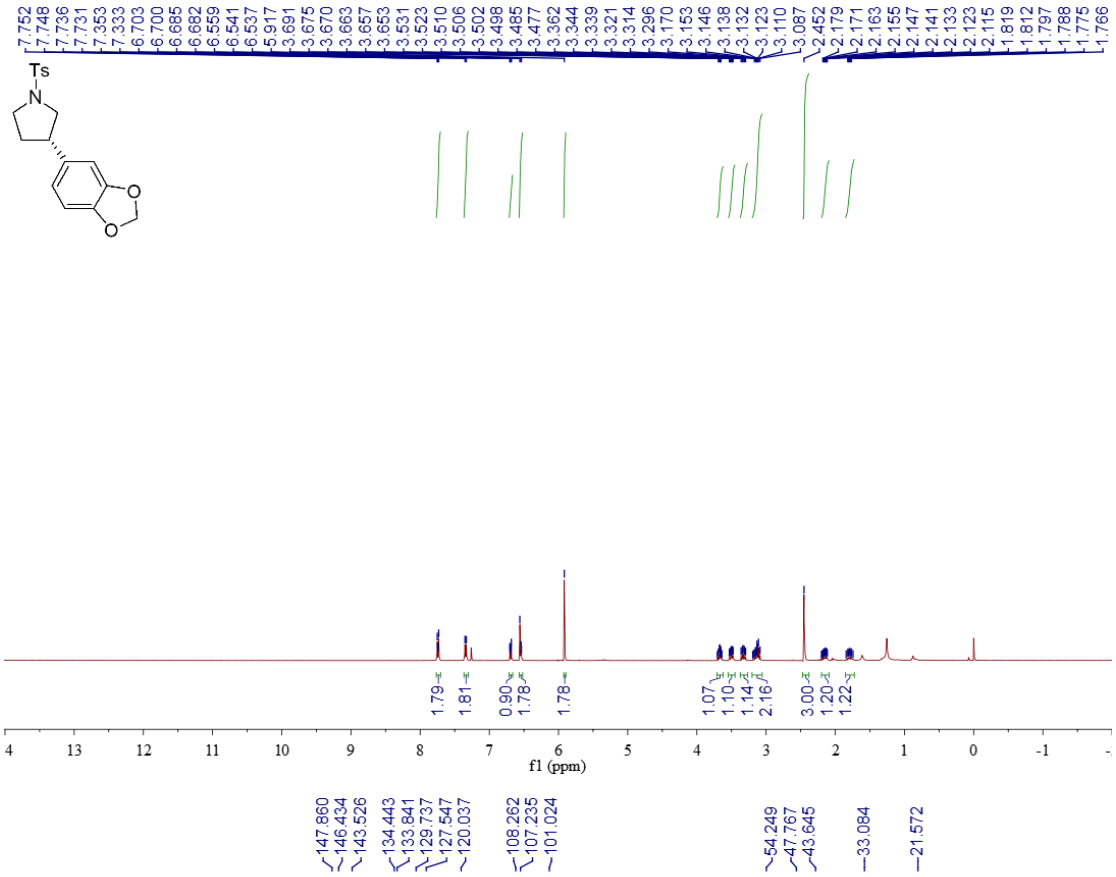
7.739
7.535
7.514
7.362
7.342
7.230
7.210
3.742
3.725
3.719
3.701
3.541
3.537
3.533
3.521
3.512
3.380
3.376
3.358
3.355
3.351
3.303
3.249
3.226
2.278
2.269
2.262
2.253
2.238
2.230
2.222
2.213
2.204
1.928
1.907
1.897
1.885
1.876
1.863
1.853
1.831
1.88
1.89
1.87
2.08
1.01
1.06
3.31
3.00
1.34
1.25
f1 (ppm)
144.978
144.967
143.676
133.718
129.787
129.467
129.143
128.819
128.500
128.080
127.561
127.340
125.654
125.618
125.580
125.542
125.378
122.674
119.971
53.849
47.667
43.561
32.815
21.563
f1 (ppm)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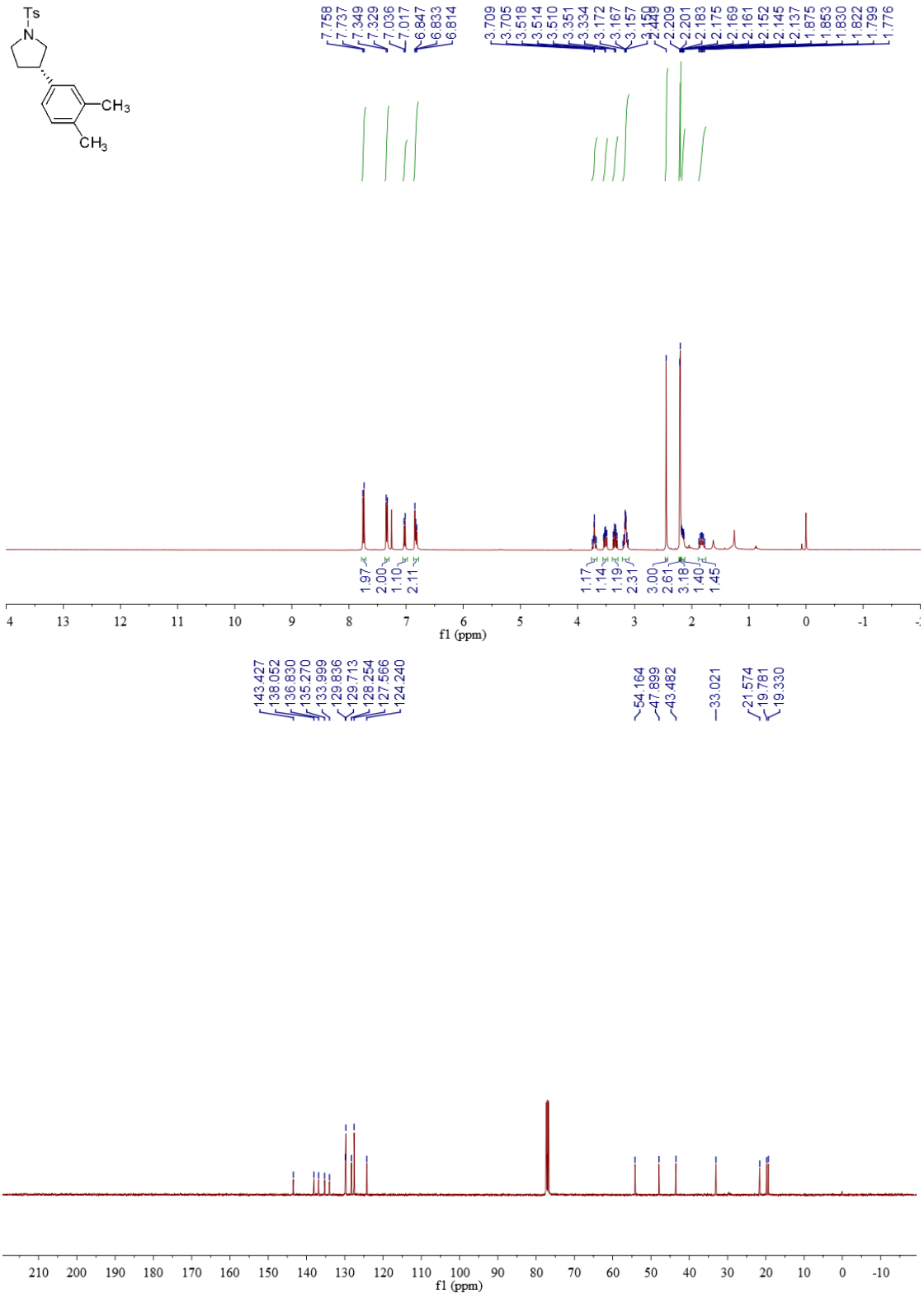
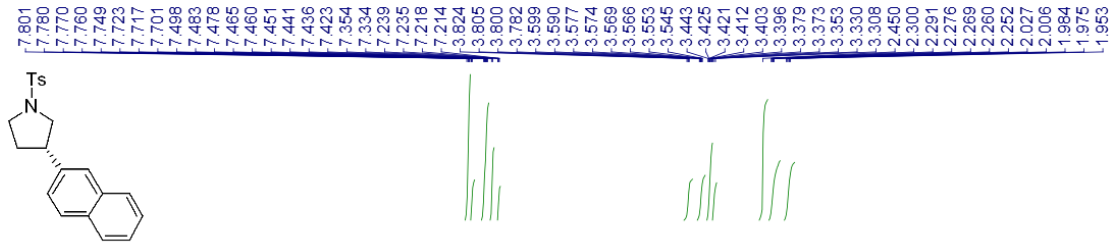
7.736
7.731
7.353
7.333
6.703
6.700
6.685
6.682
6.559
6.541
6.537
5.917
3.691
3.675
3.670
3.663
3.657
3.653
3.531
3.523
3.510
3.506
3.502
3.498
3.485
3.477
3.362
3.344
3.339
3.321
3.314
3.296
3.170
3.153
3.146
3.138
3.132
3.123
3.110
3.087
2.452
2.179
2.171
2.163
2.155
2.147
2.141
2.133
2.123
2.115
1.819
1.812
1.797
1.788
1.775
1.766
Ts
N
O
O
1.79
1.81
0.90
1.78
1.78
1.07
1.10
1.14
2.16
3.00
1.20
1.22
f1 (ppm)
147.860
146.434
143.526
134.443
133.841
129.737
127.547
120.037
108.262
107.235
101.024
54.249
47.767
43.645
33.084
21.572
f1 (ppm)


Ts
N
CH3
CH3
7.758
7.737
7.349
7.329
7.036
7.017
6.847
6.833
6.814
3.709
3.705
3.518
3.514
3.510
3.351
3.334
3.172
3.167
3.157
2.209
2.201
2.183
2.175
2.169
2.161
2.152
2.145
2.137
1.875
1.853
1.830
1.822
1.799
1.776
1.97
2.00
1.10
2.11
1.17
1.14
1.19
2.31
3.00
2.61
3.18
1.40
1.45
f1 (ppm)
143.427
138.052
136.830
135.270
133.999
129.836
129.713
128.254
127.566
124.240
54.164
47.899
43.482
33.021
21.574
19.781
19.330
f1 (ppm)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7.760
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7.723
7.717
7.701
7.498
7.483
7.478
7.465
7.460
7.451
7.441
7.436
7.423
7.354
7.334
7.239
7.235
7.218
7.214
3.824
3.805
3.800
3.782
3.599
3.590
3.577
3.574
3.569
3.566
3.553
3.545
3.443
3.425
3.421
3.412
3.403
3.396
3.379
3.373
3.353
3.330
3.308
2.450
2.300
2.291
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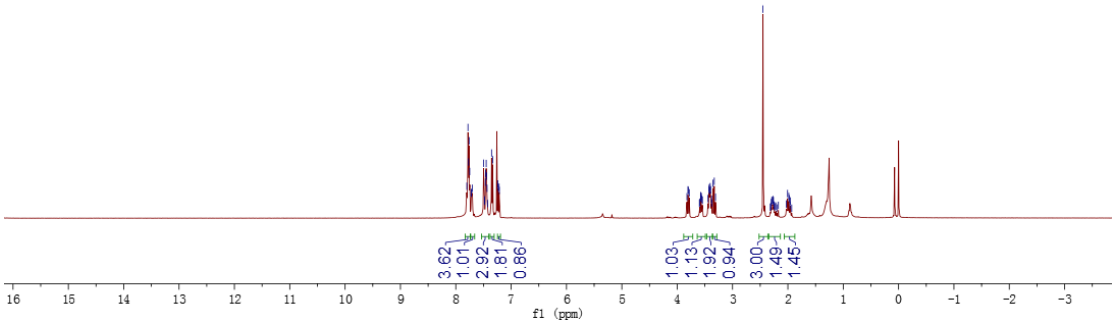
2.269
2.260
2.252
2.027
2.006
1.984
1.975
1.953
Ts
N


3.62
1.01
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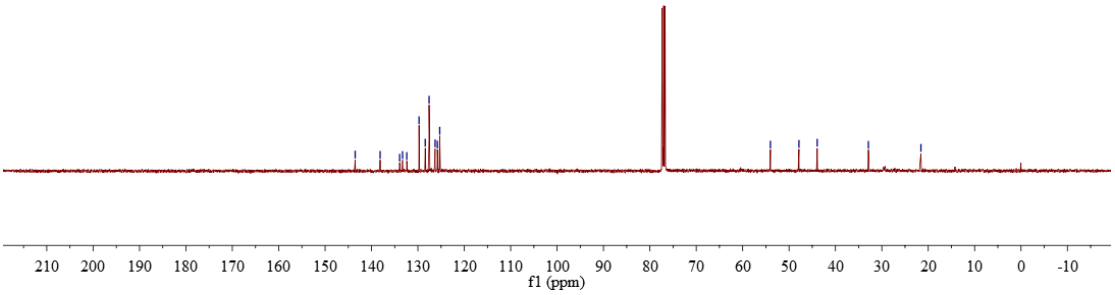
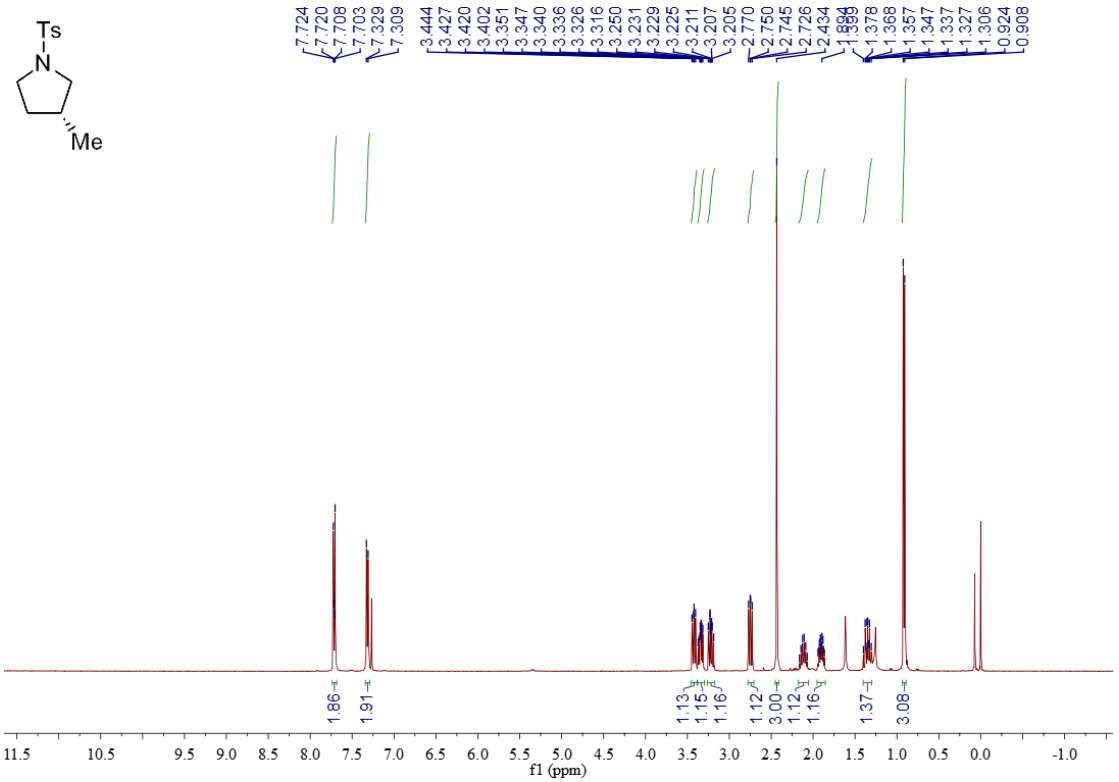
1.81
0.86
1.03
1.13
1.92
0.94
3.00
1.49
1.45
f1 (ppm)


143.518
138.140
133.936
133.309
132.397
129.752
128.419
127.587
126.289
125.803
125.296
54.017
47.862
43.933
32.897
21.576


f1 (ppm)


Ts
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Me
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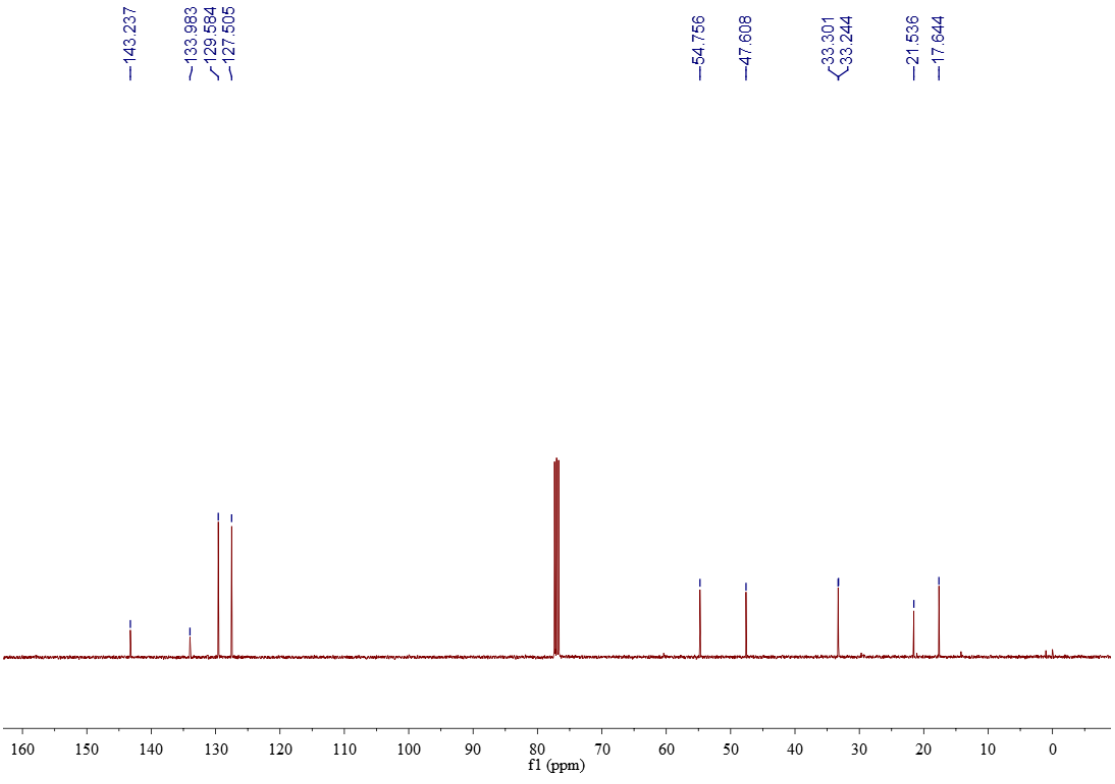
7.703
7.329
7.309
3.444
3.427
3.420
3.402
3.351
3.347
3.340
3.336
3.326
3.316
3.250
3.231
3.229
3.225
3.211
3.207
3.205
2.770
2.750
2.745
2.726
2.434
1.894
1.378
1.368
1.357
1.347
1.337
1.327
1.306
0.924
0.908
1.86
1.91
1.13
1.15
1.16
1.12
3.00
1.12
1.16
1.37
3.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)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127.505
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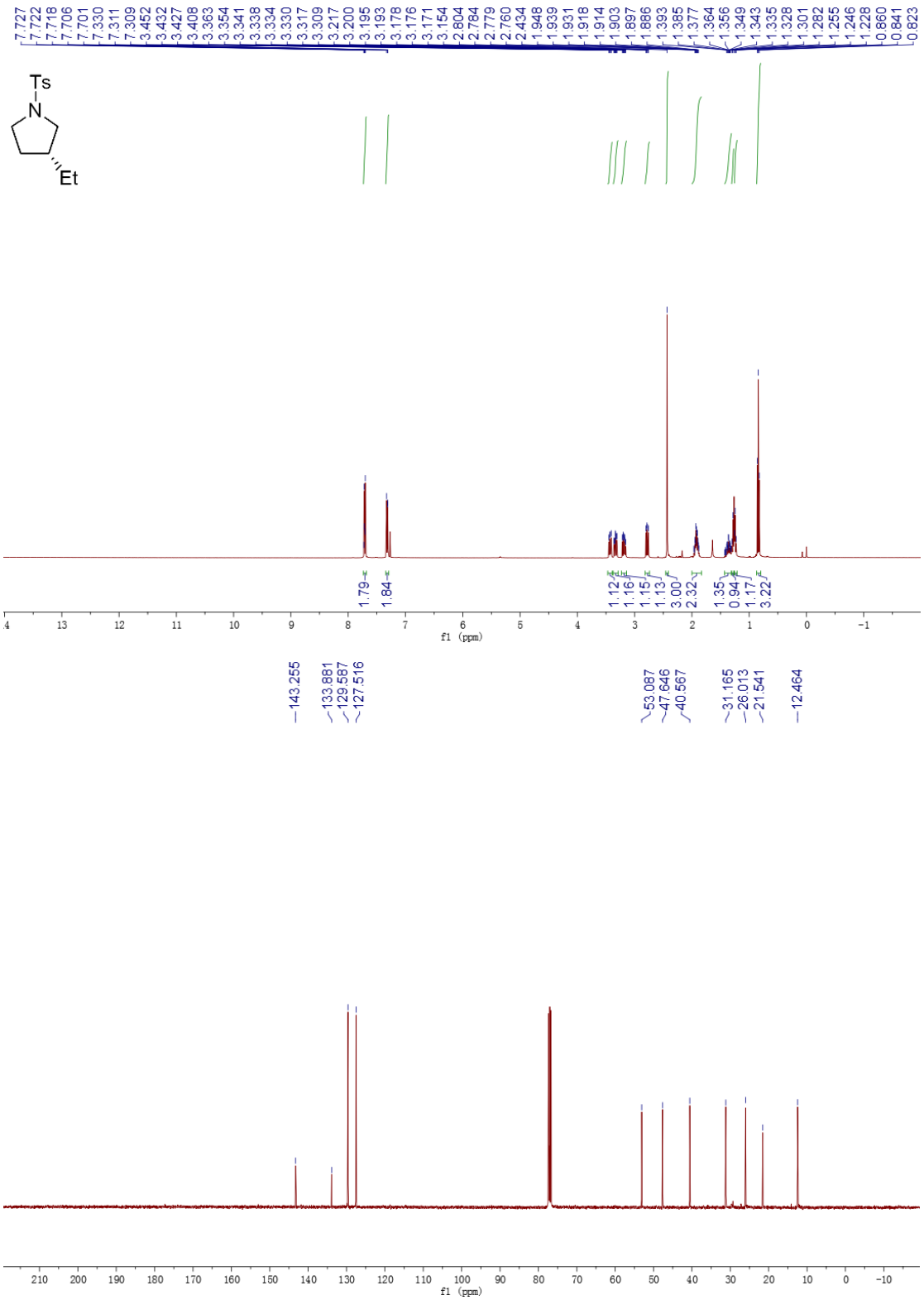
33.244
21.536
17.644
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.718
7.706
7.701
7.330
7.311
7.309
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3.432
3.427
3.408
3.363
3.354
3.341
3.338
3.334
3.330
3.317
3.309
3.217
3.200
3.195
3.193
3.178
3.176
3.171
3.154
2.804
2.784
2.779
2.760
2.434
1.948
1.939
1.931
1.918
1.914
1.903
1.897
1.886
1.393
1.385
1.377
1.364
1.356
1.349
1.343
1.335
1.328
1.301
1.282
1.255
1.246
1.228
0.860
0.841
0.823
Ts
N
Et
1.79
1.84
1.12
1.16
1.15
1.13
3.00
2.32
1.35
0.94
1.17
3.22
f1 (ppm)
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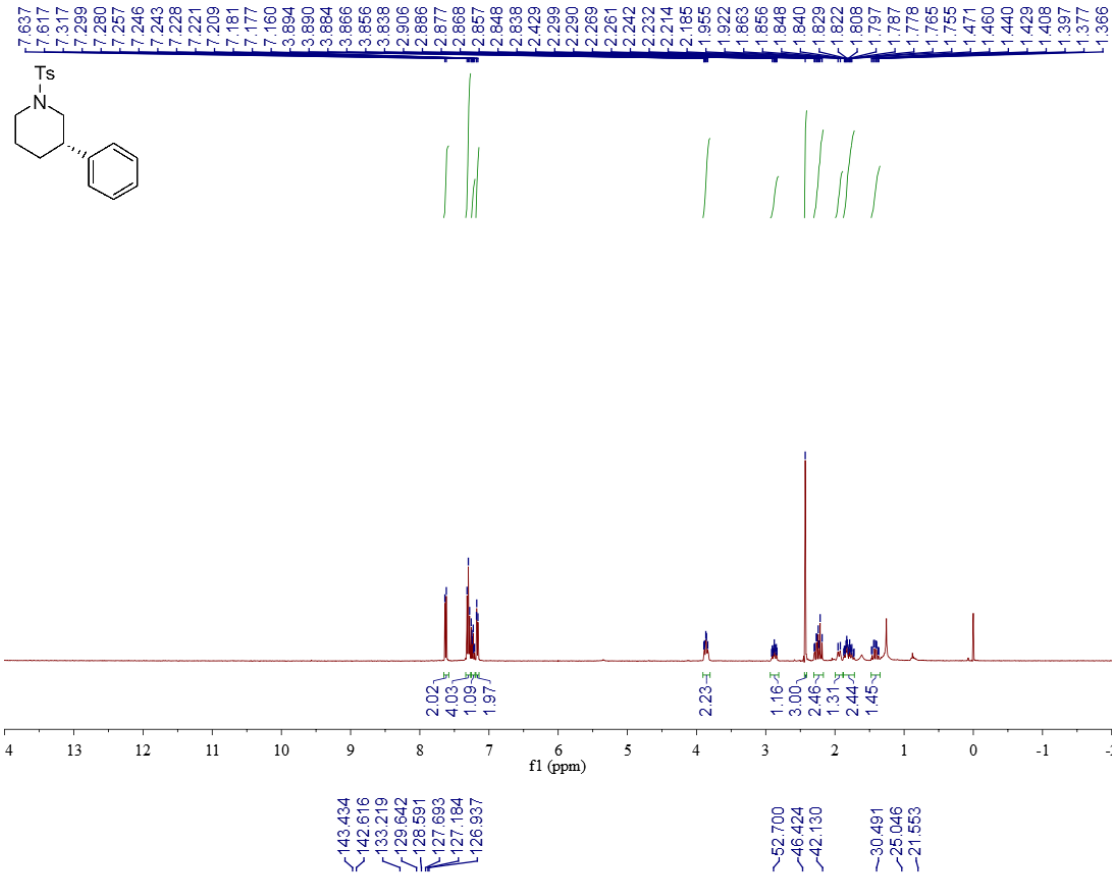
127.516
53.087
47.646
40.567
31.165
26.013
21.541
12.464
f1 (ppm)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7.280
7.257
7.246
7.243
7.228
7.221
7.209
7.181
7.177
7.160
3.894
3.890
3.884
3.866
3.856
3.838
2.906
2.886
2.877
2.868
2.857
2.848
2.838
2.429
2.299
2.290
2.269
2.261
2.242
2.232
2.214
2.185
1.955
1.922
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1.856
1.848
1.840
1.829
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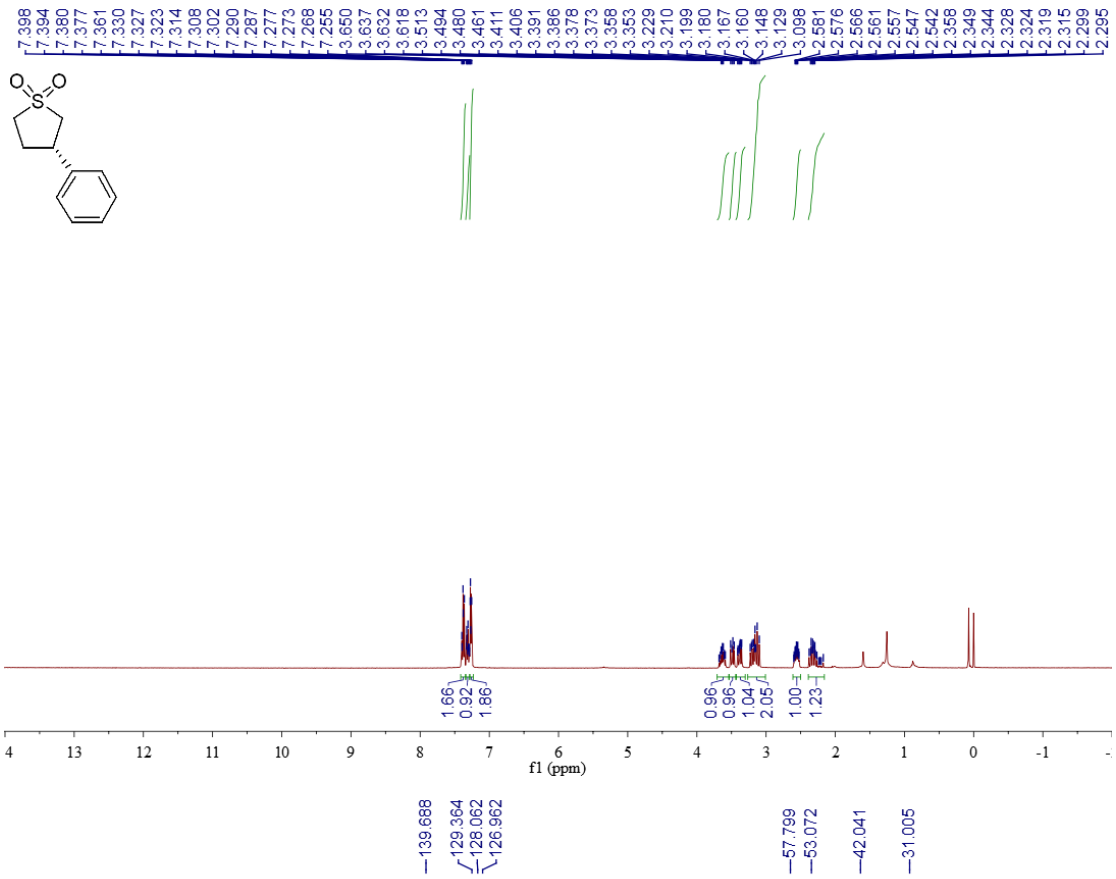
1.808
1.797
1.787
1.778
1.765
1.755
1.471
1.460
1.440
1.429
1.408
1.397
1.377
1.366
Ts
N
2.02
4.03
1.09
1.97
2.23
1.16
3.00
2.46
1.31
2.44
1.45
f1 (ppm)
143.434
142.616
133.219
129.642
128.591
127.693
127.184
126.937
52.700
46.424
42.130
30.491
25.046
21.553
f1 (ppm)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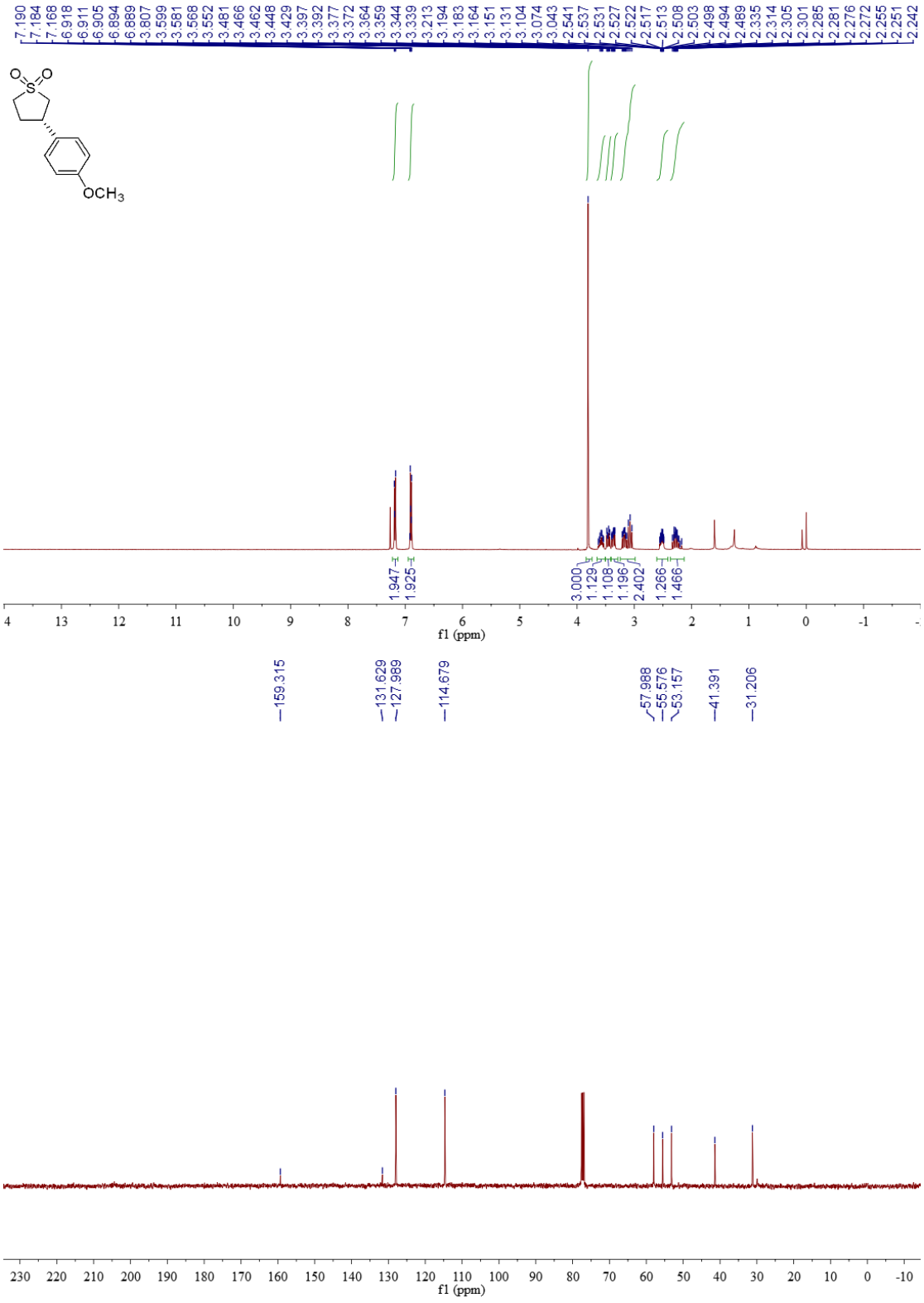
7.361
7.330
7.327
7.323
7.314
7.308
7.302
7.290
7.287
7.277
7.273
7.268
7.255
3.650
3.637
3.632
3.618
3.513
3.494
3.480
3.461
3.411
3.406
3.391
3.386
3.378
3.373
3.358
3.353
3.229
3.210
3.199
3.180
3.167
3.160
3.148
3.129
3.098
2.581
2.576
2.566
2.561
2.557
2.547
2.542
2.358
2.349
2.344
2.328
2.324
2.319
2.315
2.299
2.295
O
O
S
1.66
0.92
1.86
0.96
0.96
1.04
2.05
1.00
1.23
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
139.688
129.364
128.062
126.962
57.799
53.072
42.041
31.005
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.889
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3.599
3.581
3.568
3.552
3.481
3.466
3.462
3.448
3.429
3.397
3.392
3.377
3.372
3.364
3.359
3.344
3.339
3.213
3.194
3.183
3.164
3.151
3.131
3.104
3.074
3.043
2.541
2.537
2.531
2.527
2.522
2.517
2.513
2.508
2.503
2.498
2.494
2.489
2.335
2.314
2.305
2.301
2.285
2.281
2.276
2.272
2.255
2.251
2.242
O
S
O
OCH3
1.947
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3.000
1.129
1.108
1.196
2.402
1.266
1.466
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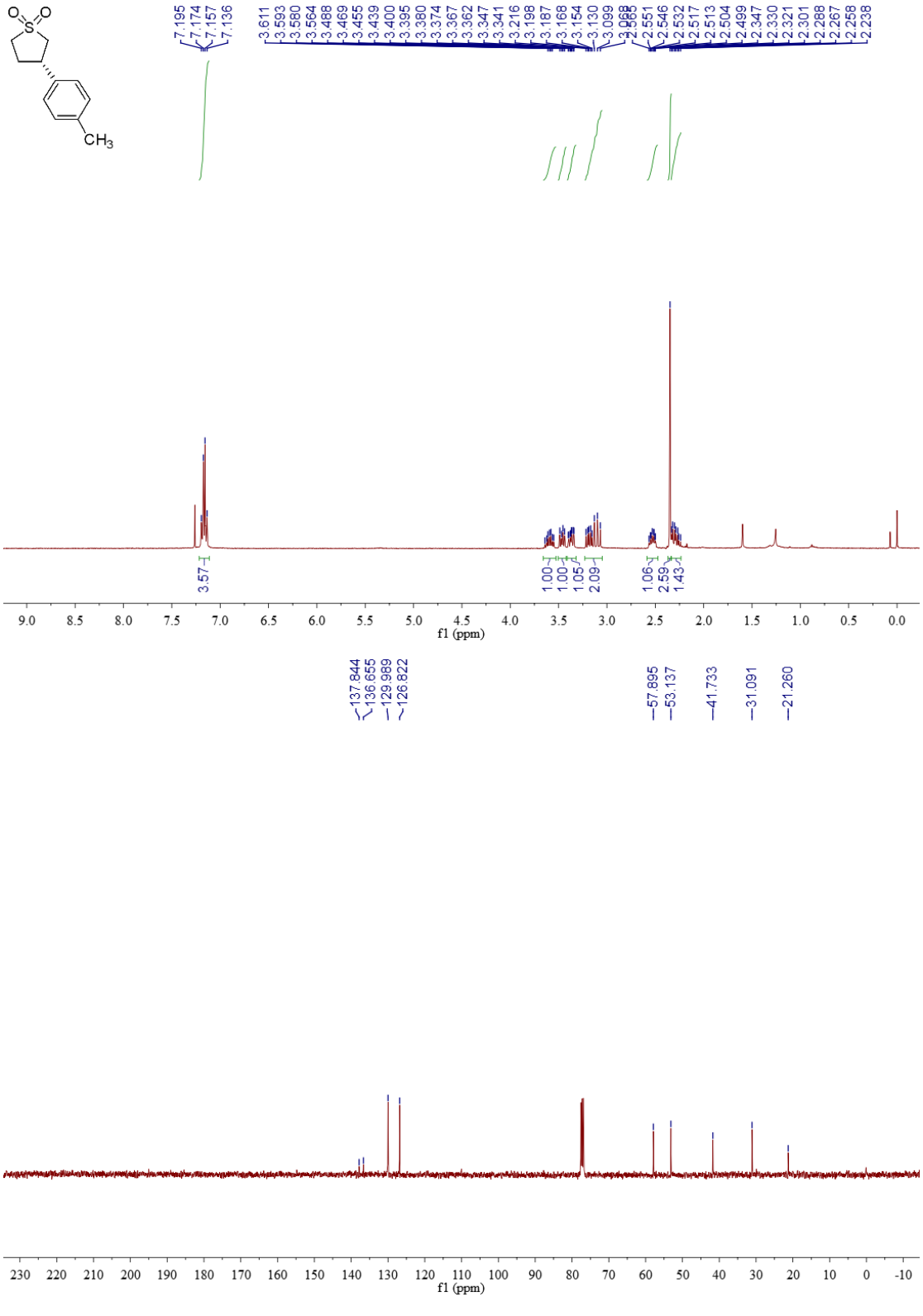
127.989
114.679
57.988
55.576
53.157
41.391
31.206
f1 (ppm)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7.157
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3.593
3.580
3.564
3.488
3.469
3.455
3.439
3.400
3.395
3.380
3.374
3.367
3.362
3.347
3.341
3.216
3.198
3.187
3.168
3.154
3.130
3.099
2.551
2.546
2.532
2.517
2.513
2.504
2.499
2.347
2.330
2.321
2.301
2.288
2.267
2.258
2.238
CH3
3.57
1.00
1.00
1.05
2.09
1.06
2.59
1.43
f1 (ppm)
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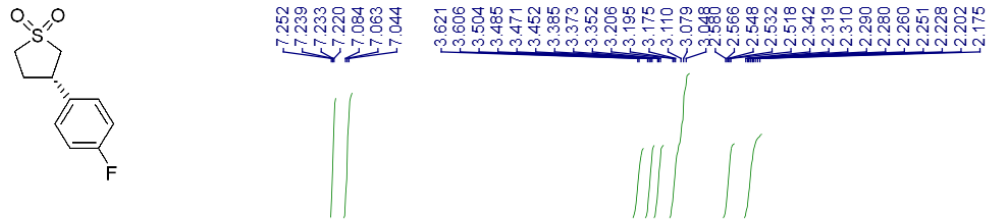
136.655
129.989
126.822
57.895
53.137
41.733
31.091
21.260
f1 (ppm)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7.233
7.220
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7.063
7.044
3.621
3.606
3.504
3.485
3.471
3.452
3.385
3.373
3.352
3.206
3.195
3.175
3.110
3.079
2.566
2.548
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2.518
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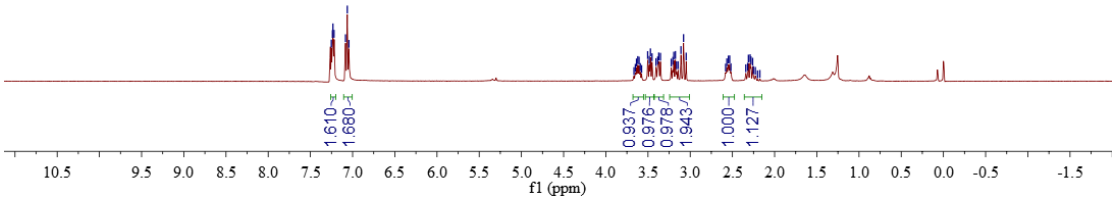
2.310
2.290
2.280
2.260
2.251
2.228
2.202
2.175
F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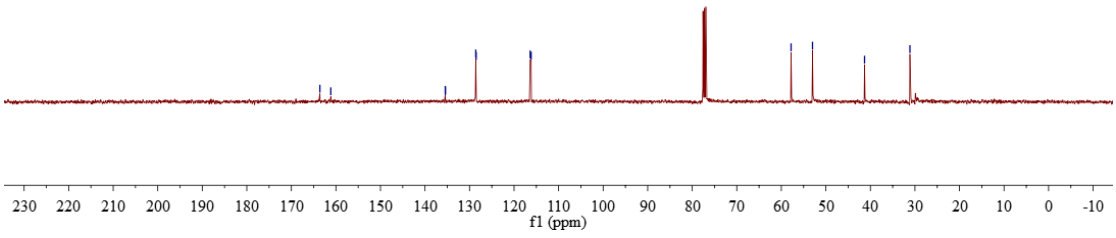
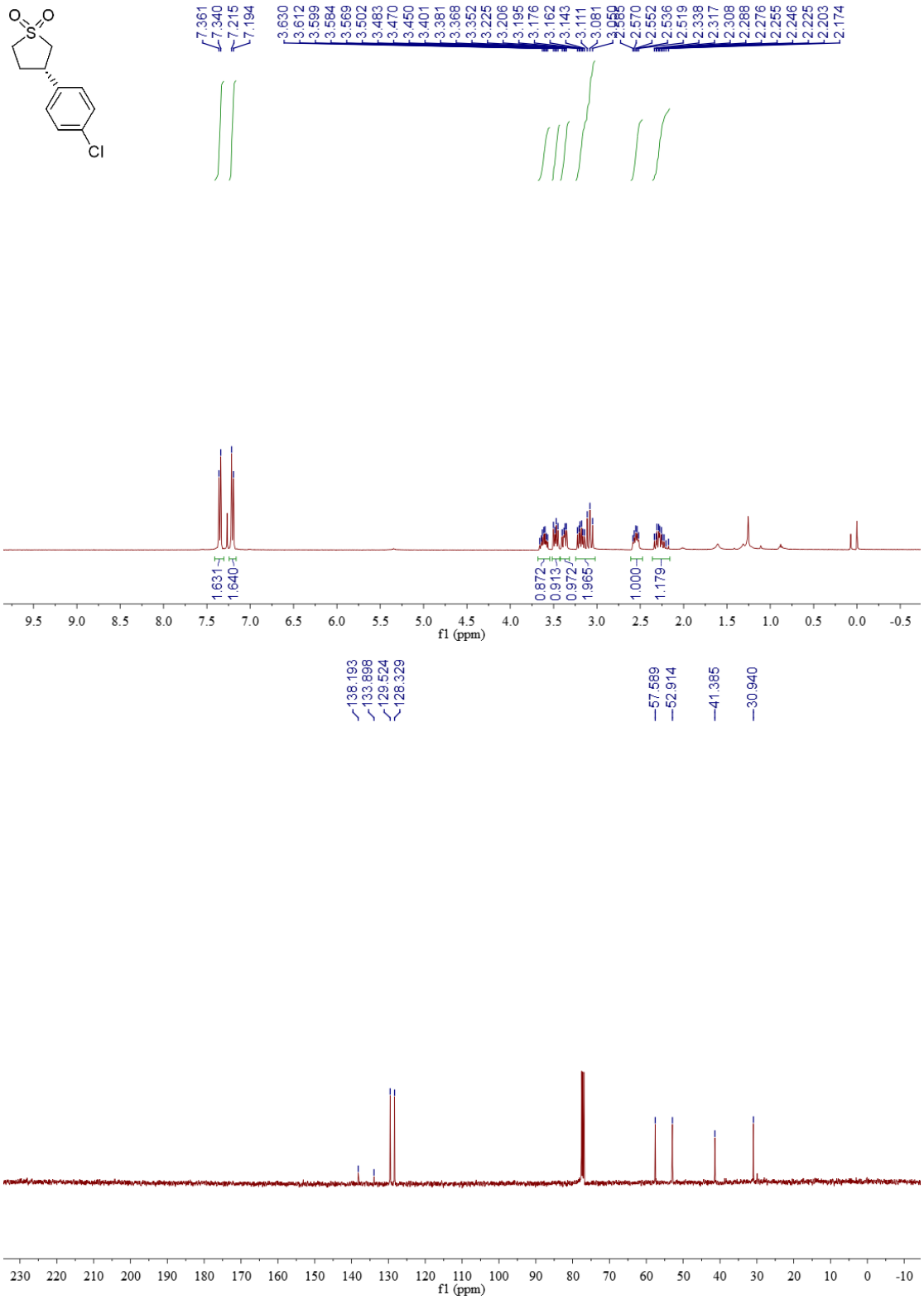
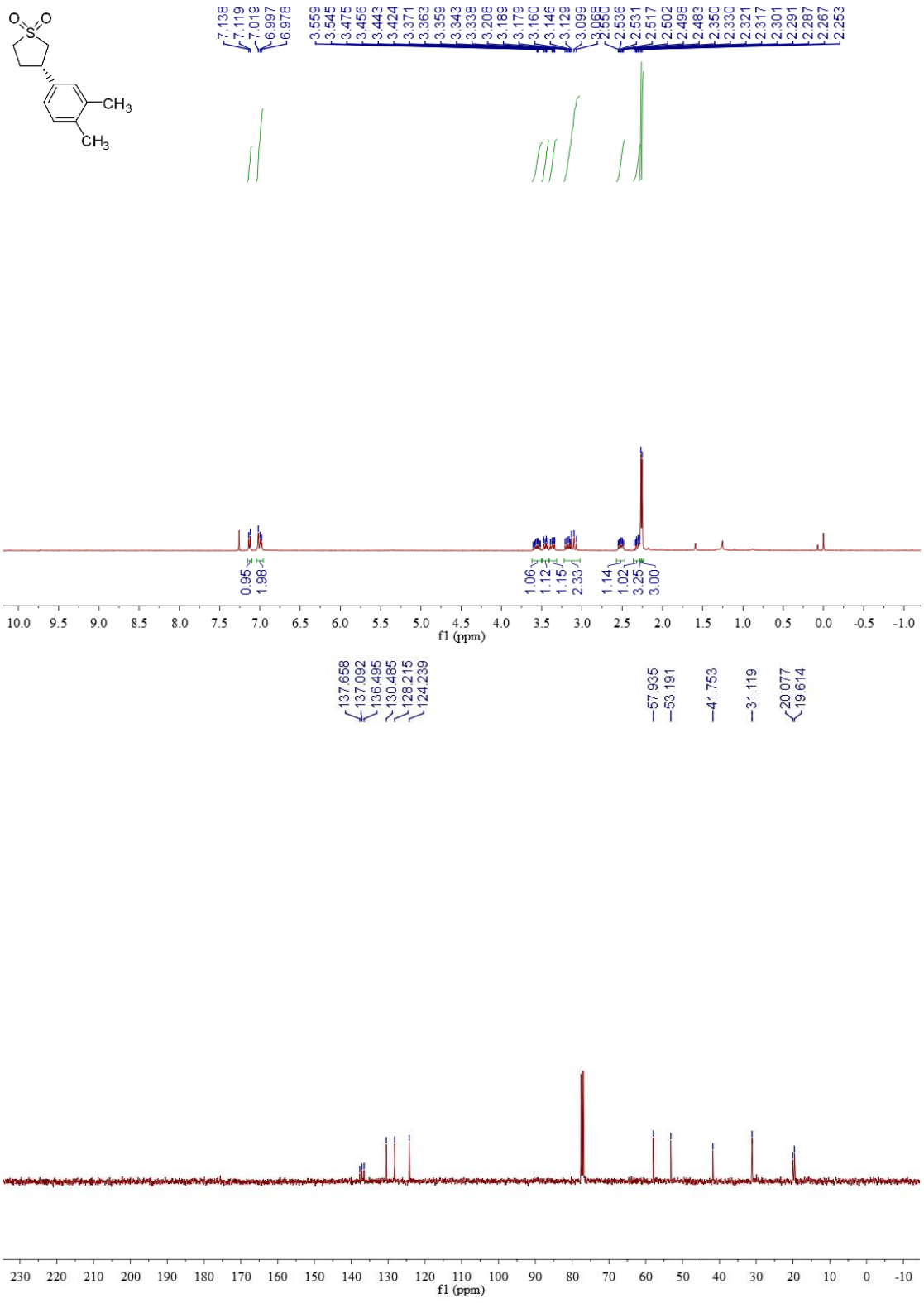
1.680
0.937
0.976
0.978
1.943
1.000
1.127
f1 (ppm)


163.597
161.142
135.452
135.423
128.599
128.519
116.386
116.172
57.810
52.999
41.316
31.126


f1 (ppm)


O
O
S
Cl
7.361
7.340
7.215
7.194
3.630
3.612
3.599
3.584
3.569
3.502
3.483
3.470
3.450
3.401
3.381
3.368
3.352
3.225
3.206
3.195
3.176
3.162
3.143
3.111
3.081
2.570
2.552
2.536
2.519
2.338
2.317
2.308
2.288
2.276
2.255
2.246
2.225
2.203
2.174
1.631
1.640
0.872
0.913
0.972
1.965
1.000
1.179
f1 (ppm)
138.193
133.898
129.524
128.329
57.589
52.914
41.385
30.940
f1 (ppm)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6.978
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3.545
3.475
3.456
3.443
3.424
3.371
3.363
3.359
3.343
3.338
3.208
3.189
3.179
3.160
3.146
3.129
3.099
2.536
2.531
2.517
2.502
2.498
2.483
2.350
2.330
2.321
2.317
2.301
2.291
2.287
2.267
2.253
CH3
CH3
0.95
1.98
1.06
1.12
1.15
2.33
1.14
1.02
3.25
3.00
f1 (ppm)
137.658
137.092
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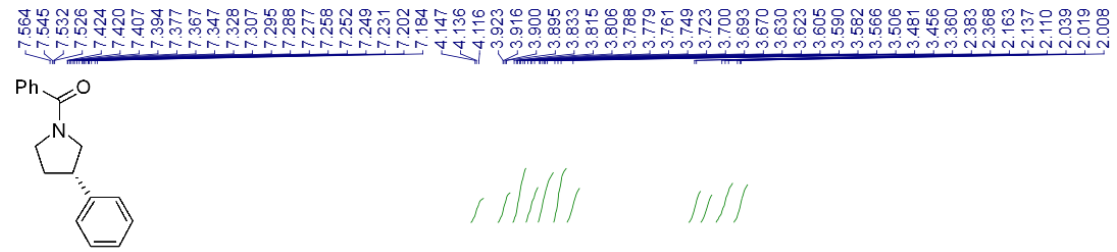
130.485
128.215
124.239
57.935
53.191
41.753
31.119
20.077
19.614
f1 (ppm)


7.564
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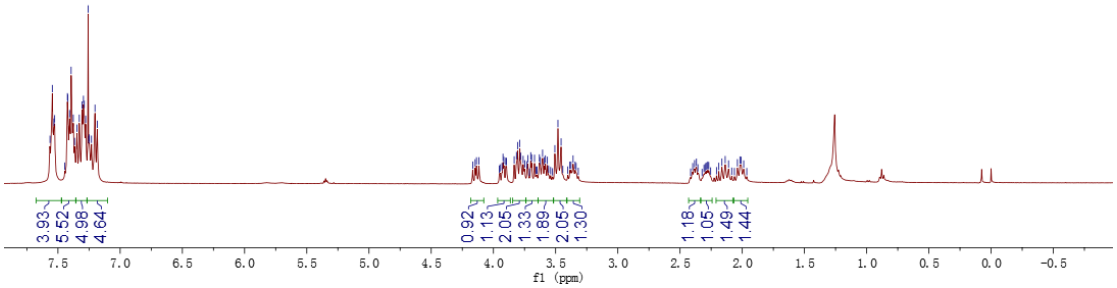
7.307
7.295
7.288
7.277
7.258
7.252
7.249
7.231
7.202
7.184
4.147
4.136
4.116
3.923
3.916
3.900
3.895
3.833
3.815
3.806
3.788
3.779
3.761
3.749
3.723
3.700
3.693
3.670
3.630
3.623
3.605
3.590
3.582
3.566
3.506
3.481
3.456
3.360
2.383
2.368
2.163
2.137
2.110
2.039
2.019
2.008

Ph
O
N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2.05
1.33
1.89
2.05
1.30
1.18
1.05
1.49
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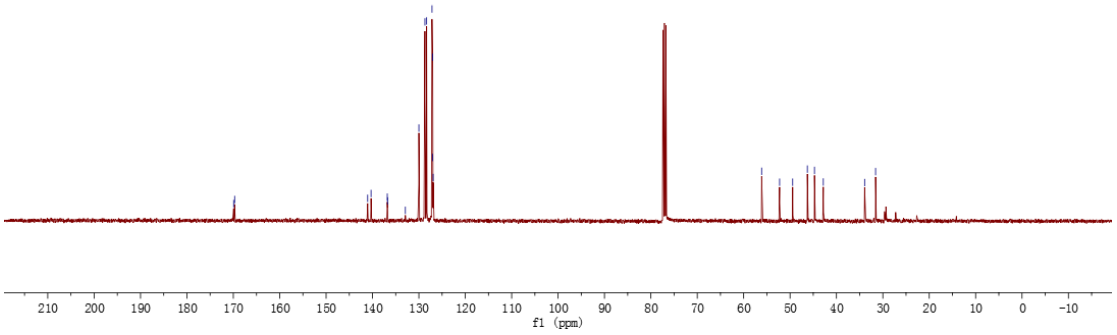
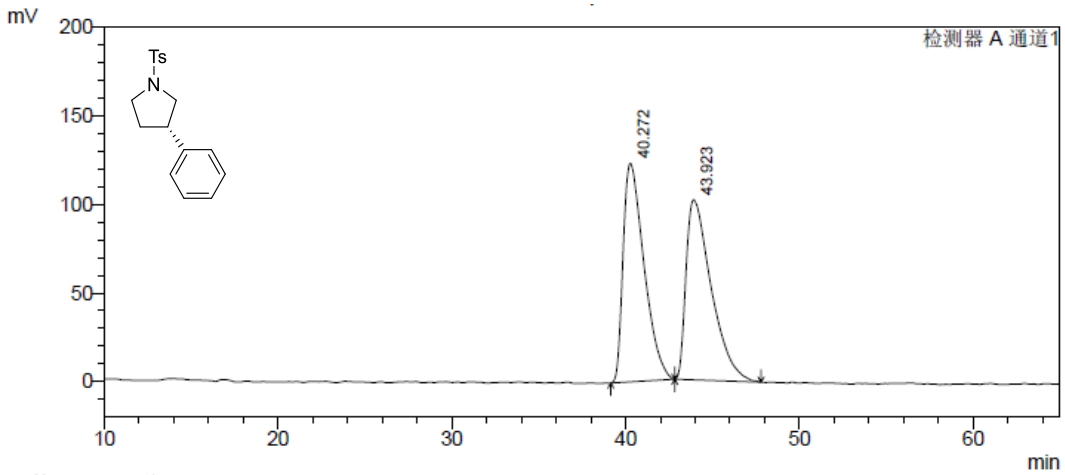
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


169.934
169.711
141.042
140.308
136.816
136.751
132.915
129.999
128.700
128.329
127.173
127.074
127.019
126.929
56.128
52.252
49.432
46.271
44.736
42.831
33.928
31.565


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

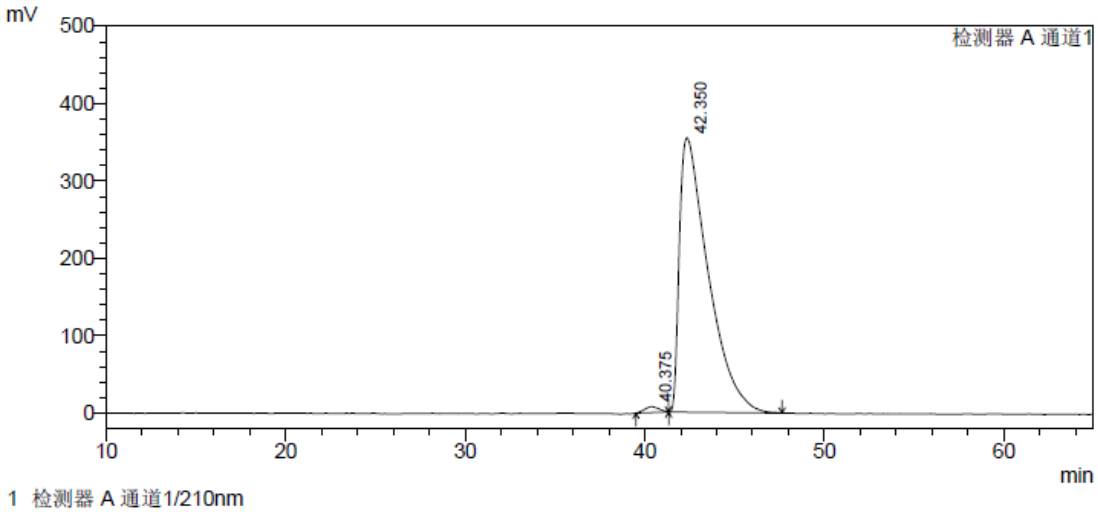


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	40.272	10316756	123449	50.088	54.807
2	43.923	10280339	101794	49.912	45.193
总计		20597095	225243	100.000	100.000

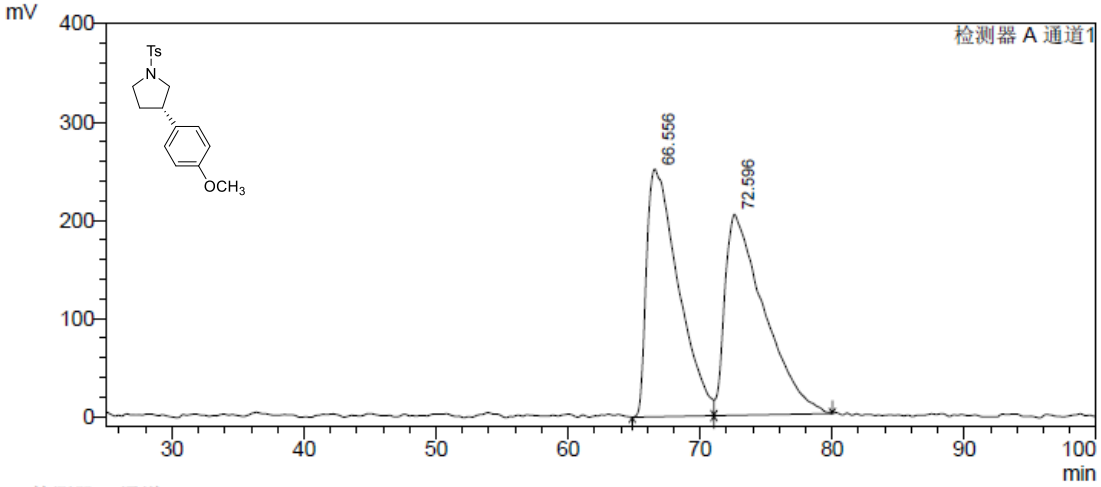


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	40.375	419006	7573	1.049	2.090
2	42.350	39543451	354751	98.951	97.910
总计		39962458	362323	100.000	100.000

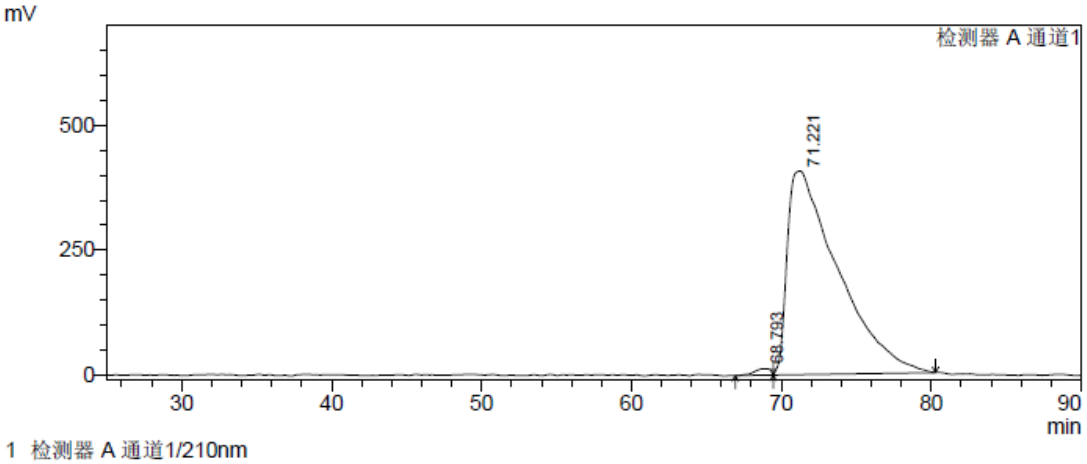


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	66.556	42183512	252183	49.756	55.196
2	72.596	42597592	204703	50.244	44.804
总计		84781104	456886	100.000	100.000

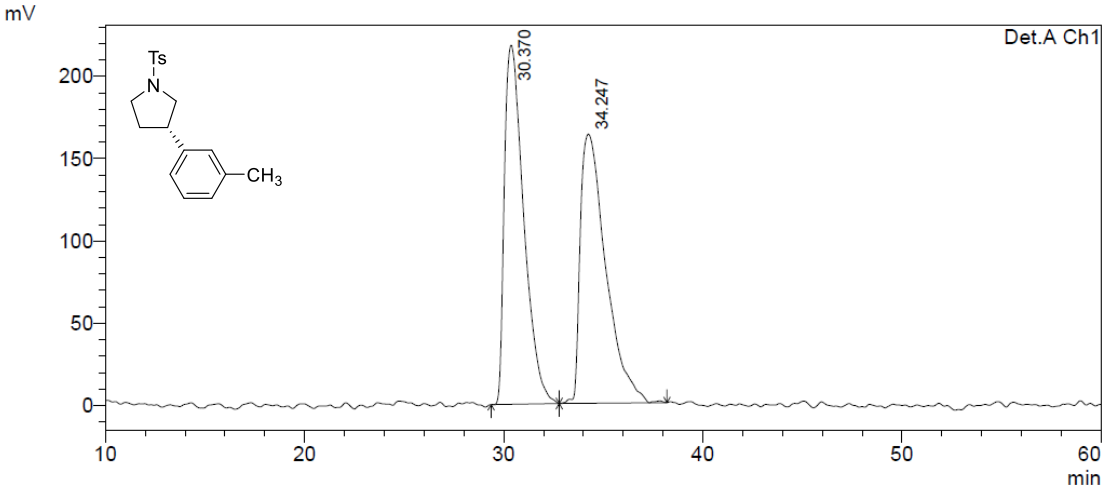


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	68.793	1041296	13188	1.068	3.127
2	71.221	96483774	408521	98.932	96.873
总计		97525070	421709	100.000	100.000

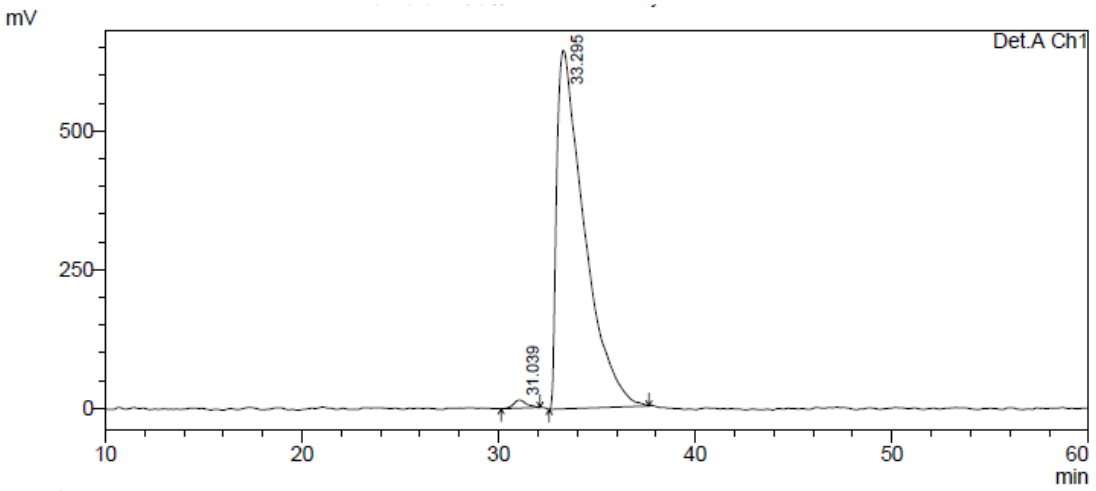


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.370	14731454	218067	50.242	57.147
2	34.247	14589830	163526	49.758	42.853
Total		29321284	381594	100.000	100.000

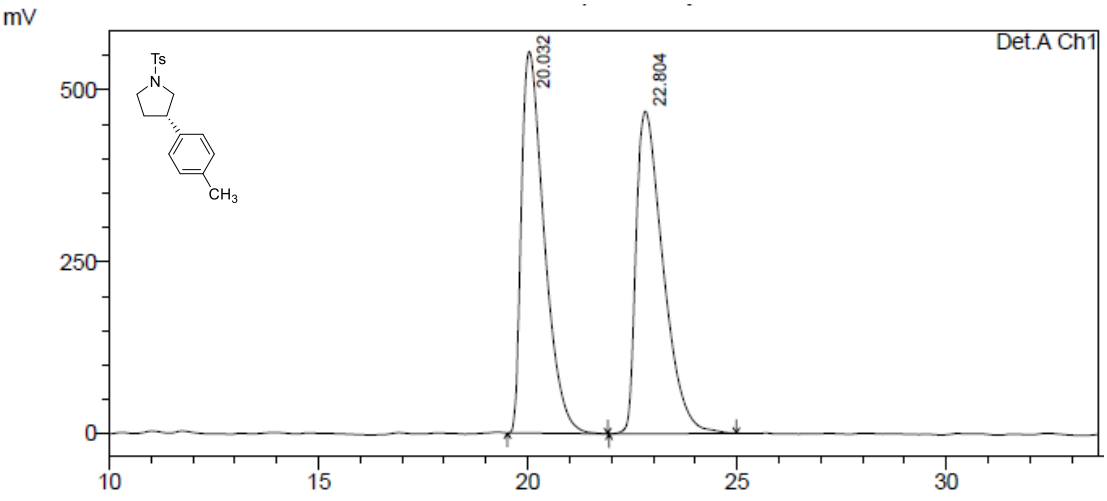


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.039	670389	14639	1.056	2.215
2	33.295	62830812	646248	98.944	97.785
Total		63501201	660887	100.000	100.000

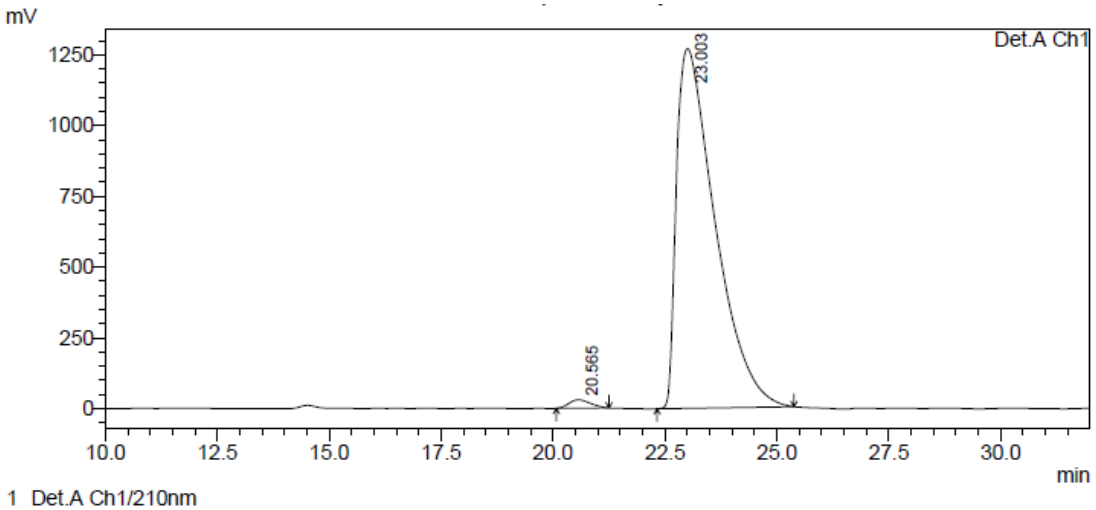


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.032	21011656	554485	49.892	54.201
2	22.804	21103002	468532	50.108	45.799
Total		42114658	1023017	100.000	100.000

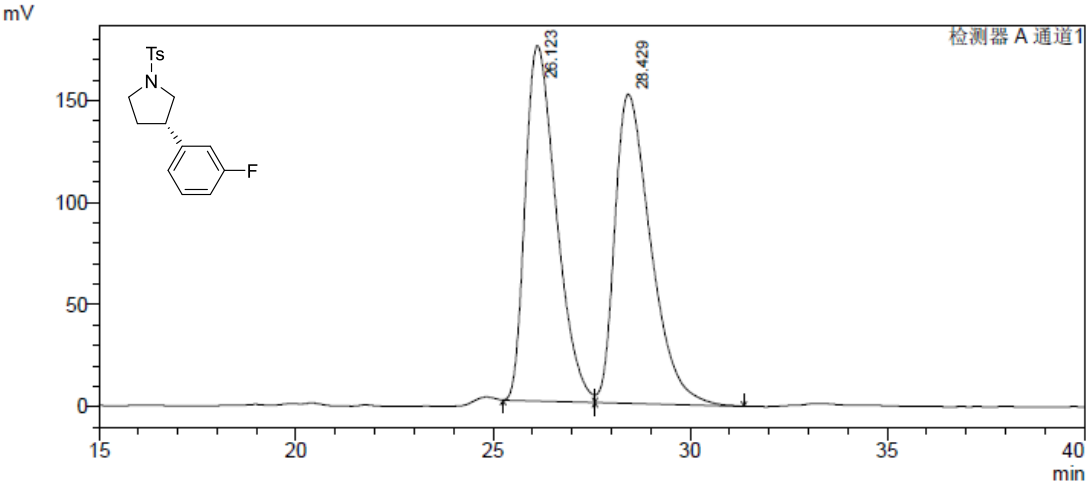


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.565	986414	29421	1.273	2.261
2	23.003	76482245	1271616	98.727	97.739
Total		77468660	1301037	100.000	100.000

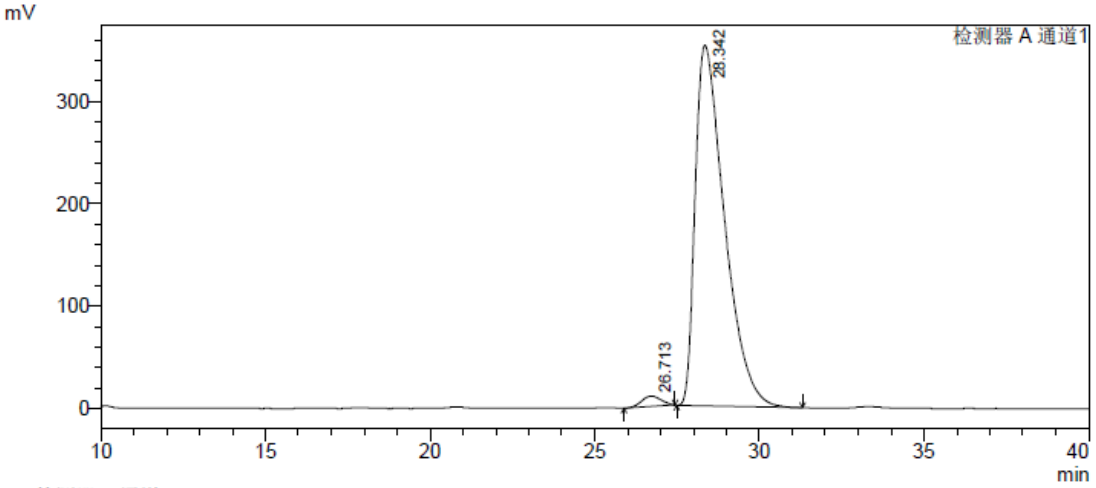


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.123	9552059	174148	49.851	53.473
2	28.429	9609166	151527	50.149	46.527
总计		19161225	325676	100.000	100.000

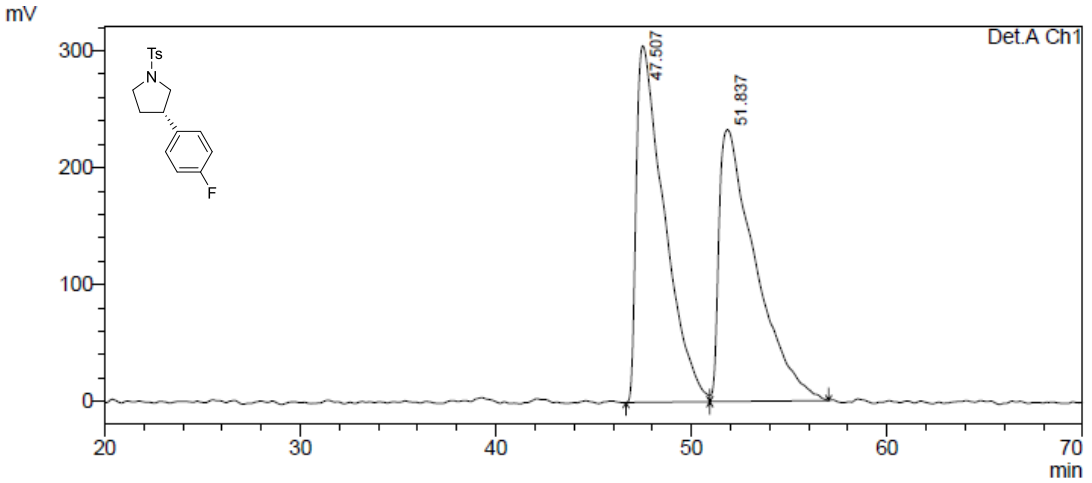


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.713	413429	10054	1.864	2.776
2	28.342	21766352	352092	98.136	97.224
总计		22179781	362146	100.000	100.000

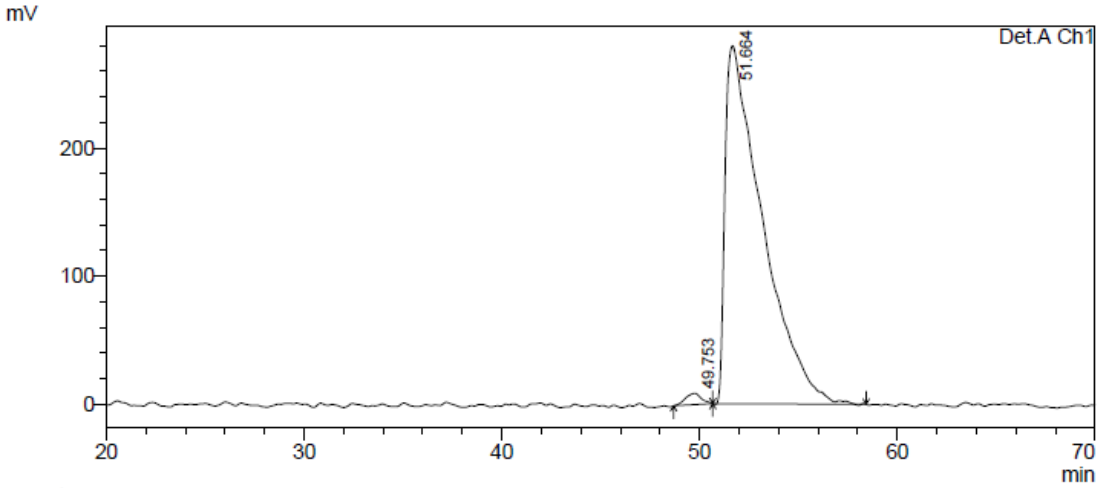


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.507	30371052	304735	50.158	56.738
2	51.837	30180242	232352	49.842	43.262
Total		60551294	537088	100.000	100.000

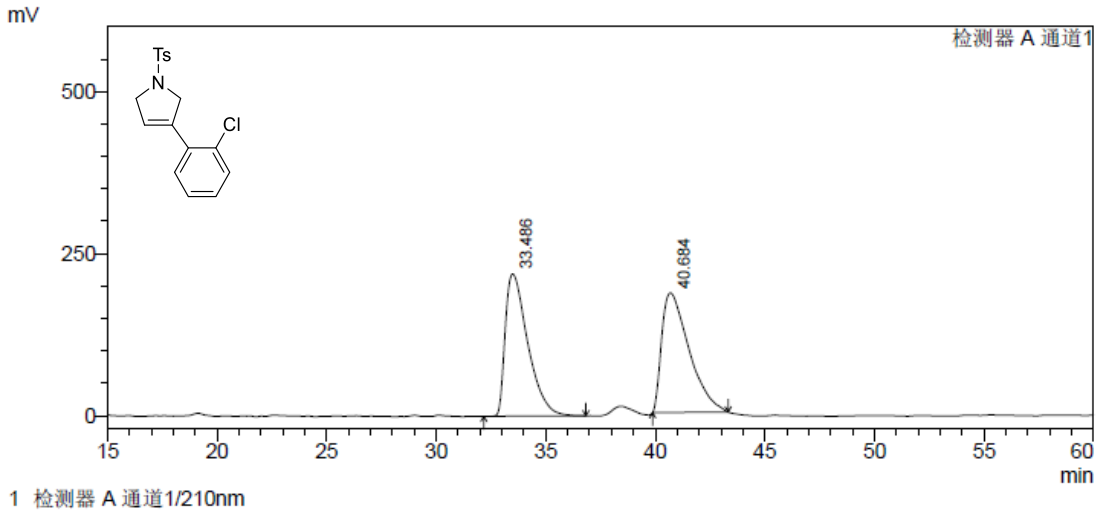


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.753	497119	8779	1.333	3.044
2	51.664	36790800	279651	98.667	96.956
Total		37287919	288430	100.000	100.000

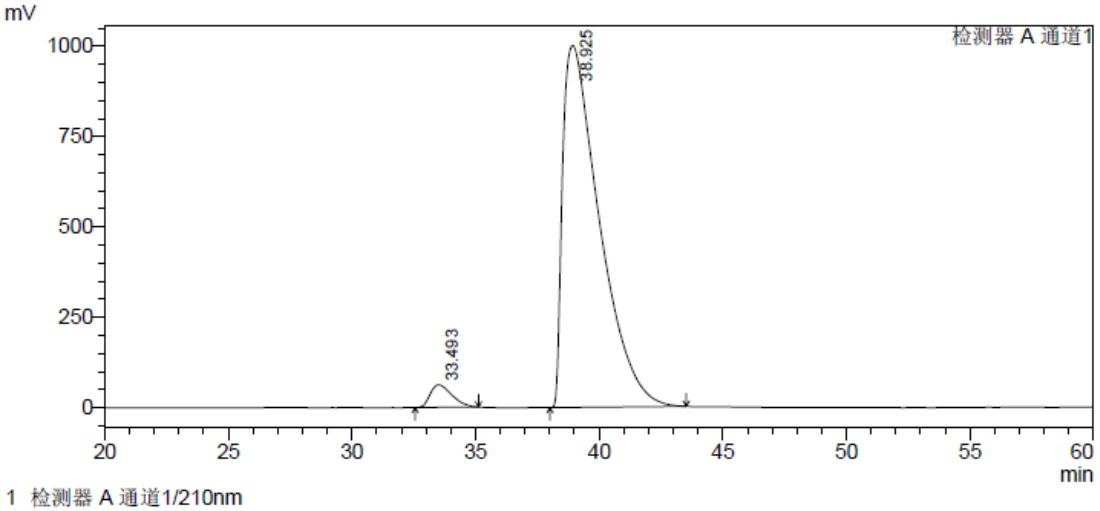


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	33.486	15679636	219338	49.426	54.327
2	40.684	16043656	184399	50.574	45.673
总计		31723293	403737	100.000	100.000

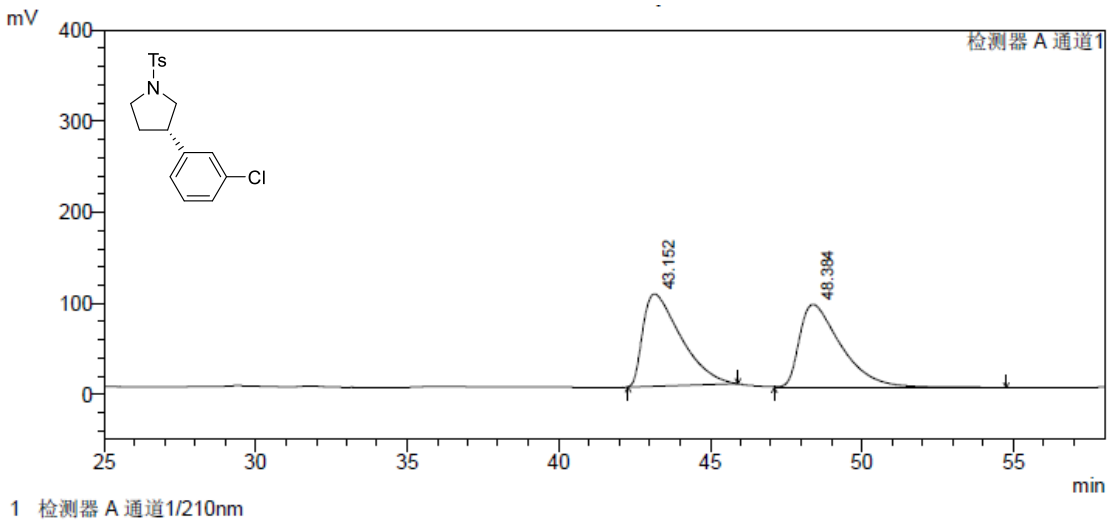


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	33.493	3802053	62418	3.537	5.869
2	38.925	103677199	1001071	96.463	94.131
总计		107479251	1063489	100.000	100.000

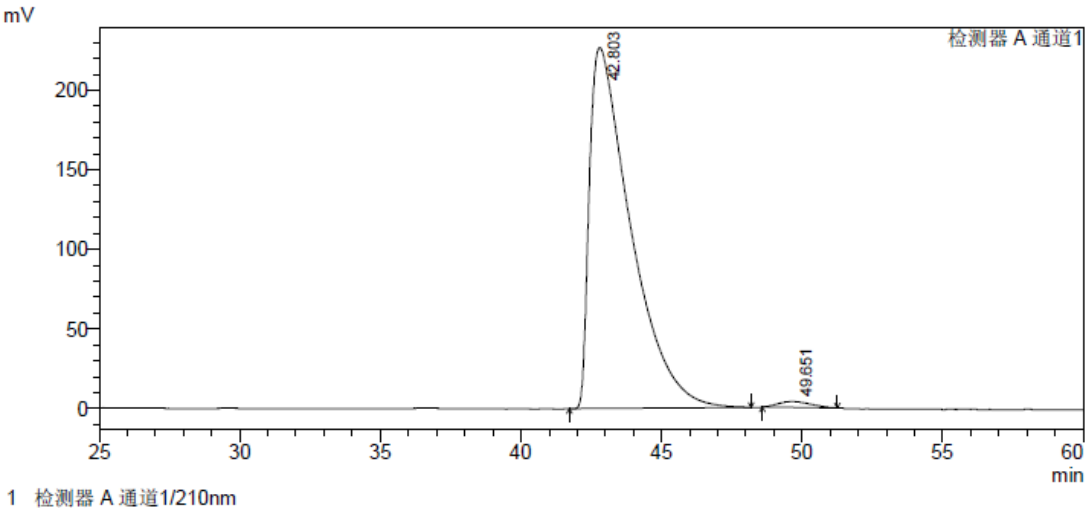


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	43.152	8847206	101218	49.813	52.484
2	48.384	8913745	91635	50.187	47.516
总计		17760951	192852	100.000	100.000

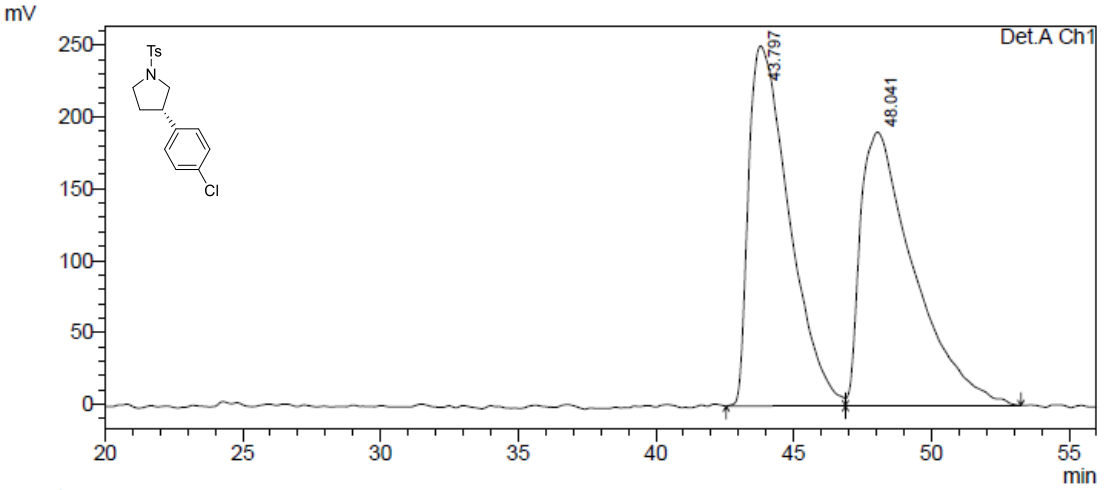


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	42.803	23147305	226834	98.718	98.368
2	49.651	300485	3764	1.282	1.632
总计		23447791	230597	100.000	100.000

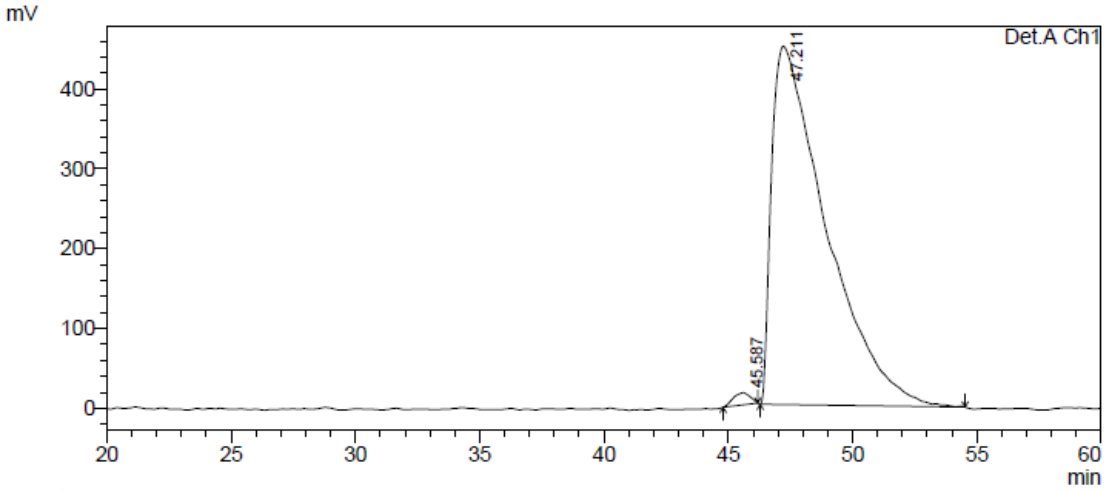


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.797	25724680	250874	49.843	56.822
2	48.041	25886909	190631	50.157	43.178
Total		51611589	441504	100.000	100.000

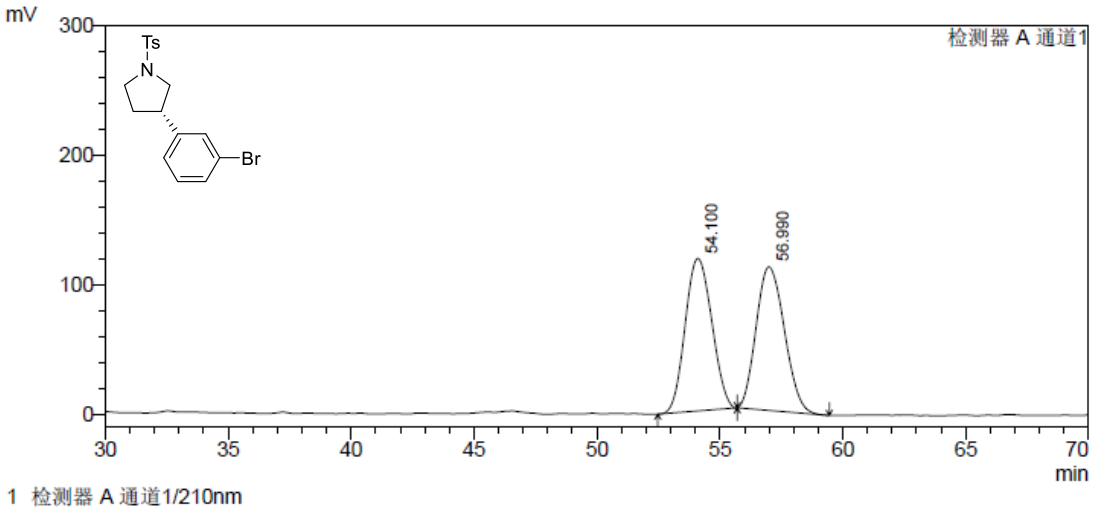


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.587	720616	15177	1.042	3.269
2	47.211	68431046	449166	98.958	96.731
Total		69151662	464343	100.000	100.000

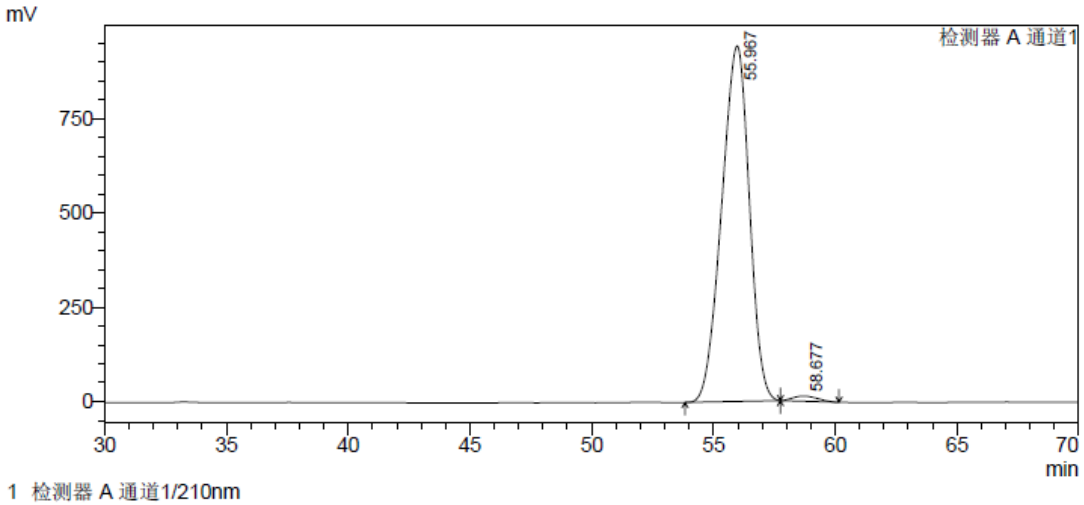


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	54.100	8897587	117946	49.999	51.481
2	56.990	8897819	111158	50.001	48.519
总计		17795406	229103	100.000	100.000

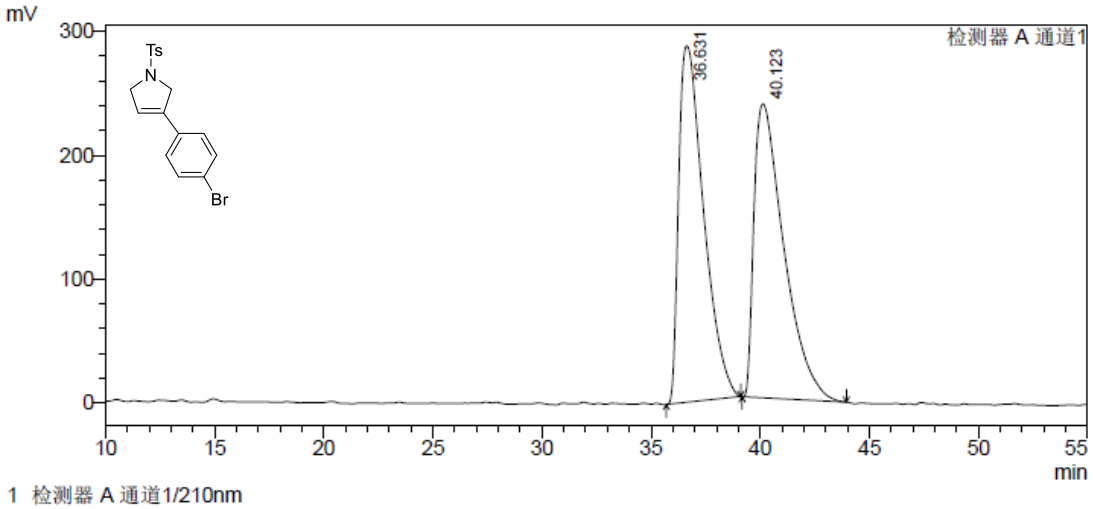


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	55.967	74554727	943392	98.713	98.544
2	58.677	972324	13939	1.287	1.456
总计		75527051	957331	100.000	100.000

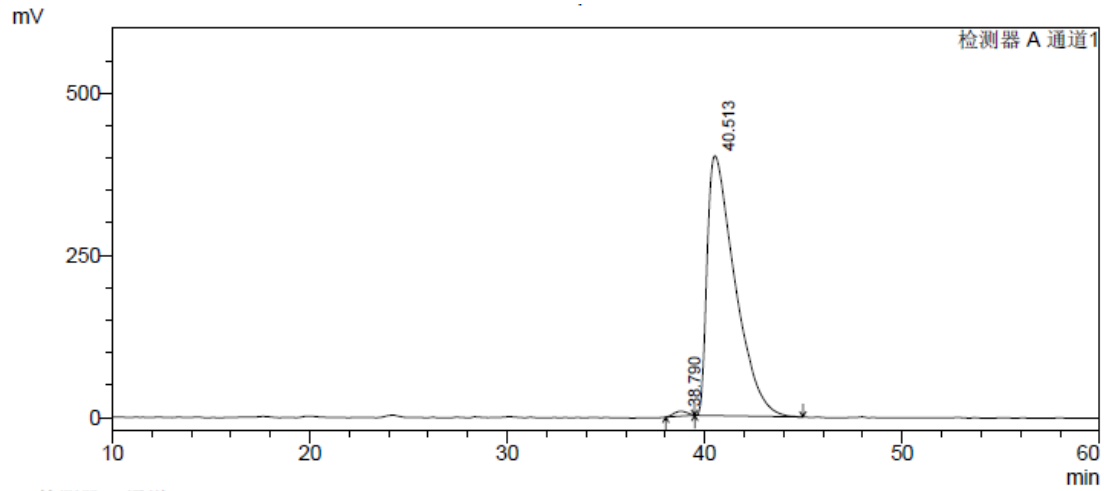


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	36.631	22864345	287697	50.267	54.799
2	40.123	22621187	237309	49.733	45.201
总计		45485532	525005	100.000	100.000

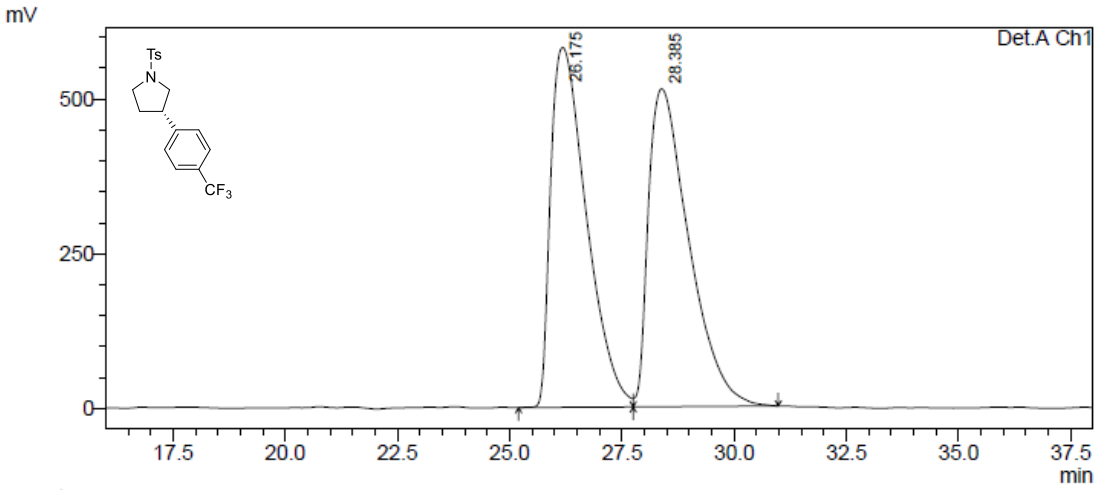


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	38.790	352047	7438	0.893	1.823
2	40.513	39089495	400484	99.107	98.177
总计		39441542	407922	100.000	100.000

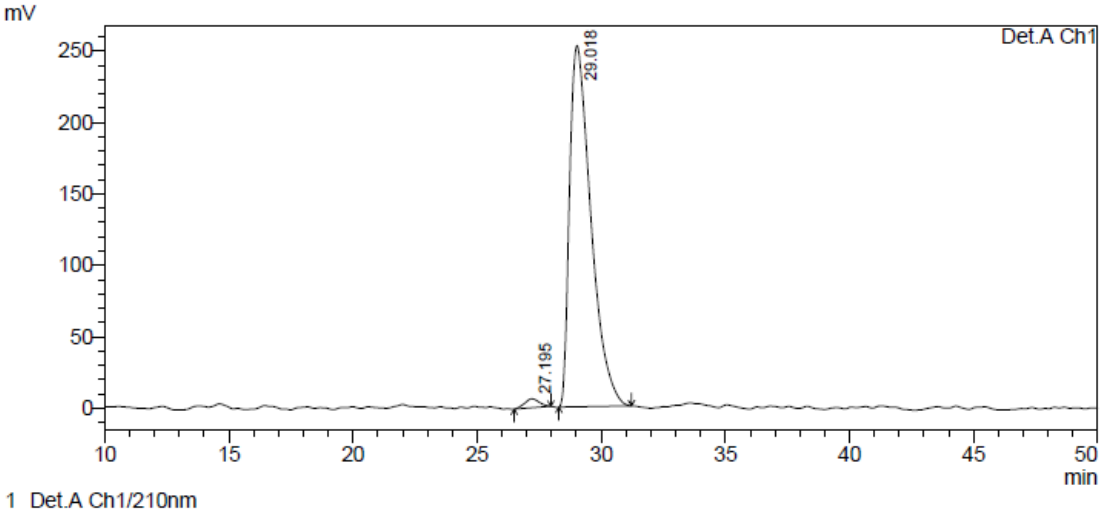


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.175	32299062	581789	49.990	53.092
2	28.385	32312196	514033	50.010	46.908
Total		64611259	1095821	100.000	100.000

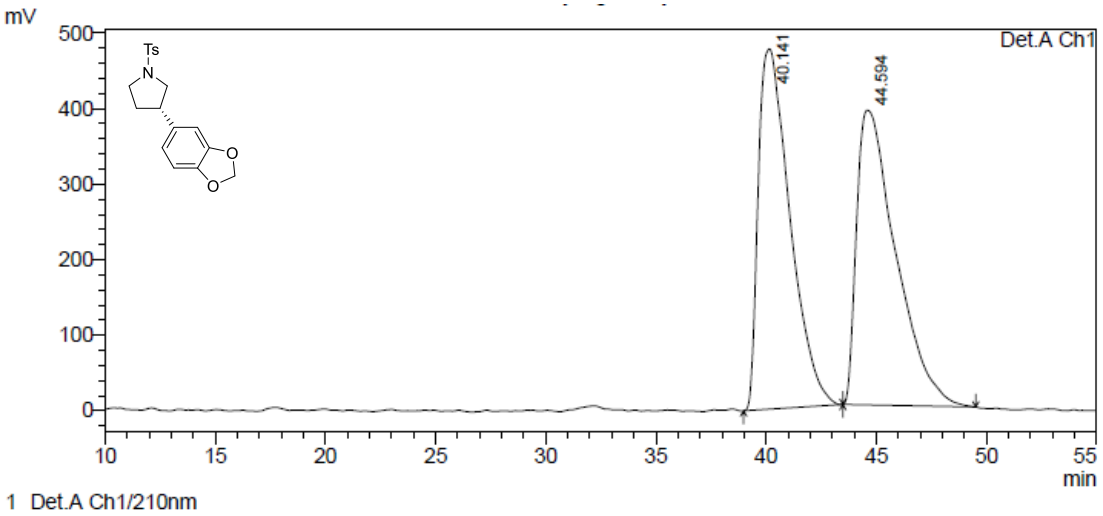


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.195	256918	6276	1.669	2.422
2	29.018	15133694	252873	98.331	97.578
Total		15390612	259150	100.000	100.000

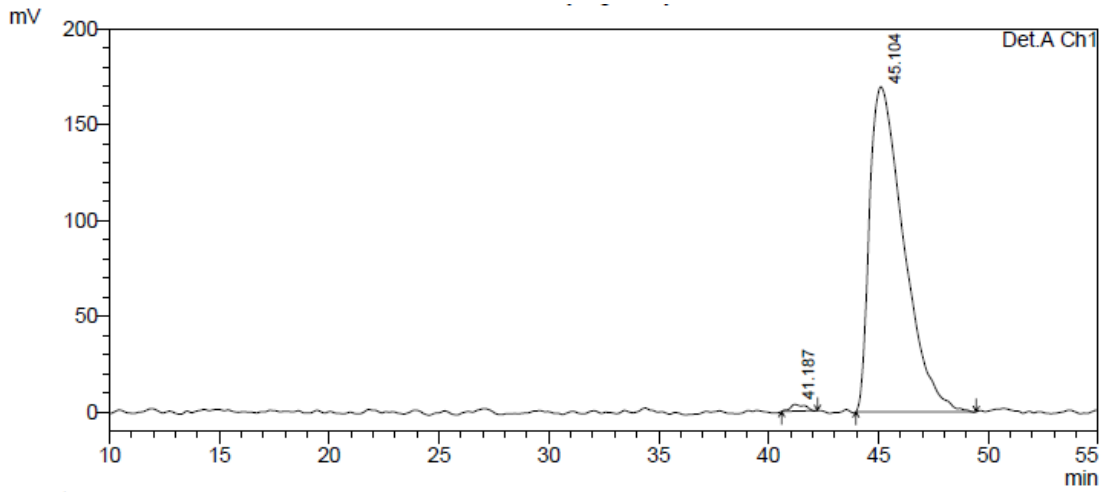


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.141	47706568	476817	49.687	54.999
2	44.594	48308539	390144	50.313	45.001
Total		96015107	866961	100.000	100.000

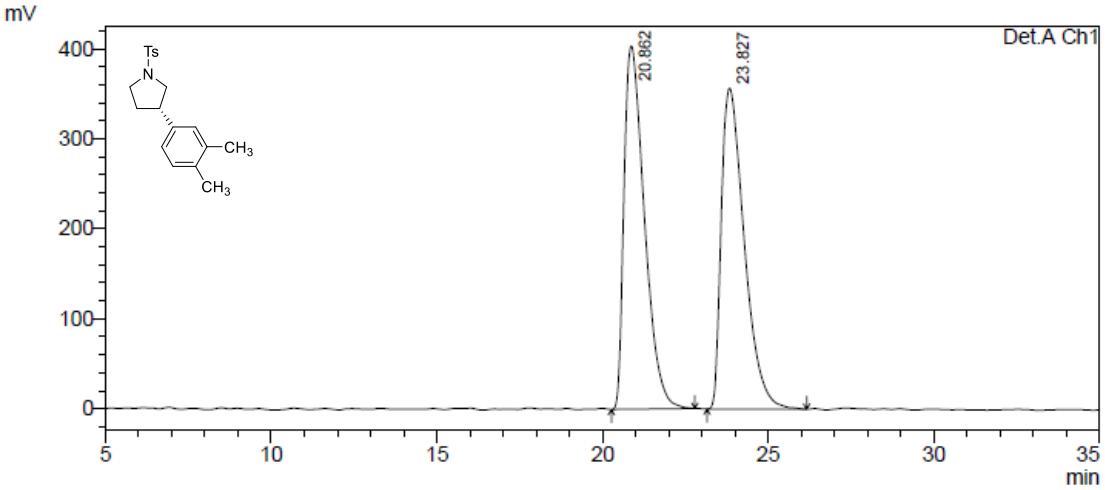


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.187	161999	3486	0.877	2.016
2	45.104	18319850	169450	99.123	97.984
Total		18481850	172936	100.000	100.000

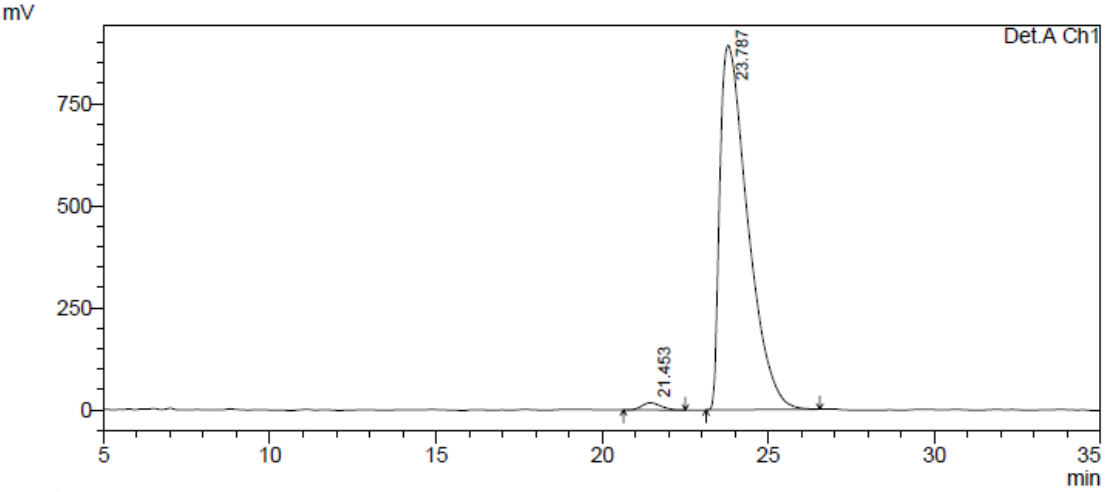


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.862	17280360	403484	50.095	53.092
2	23.827	17214619	356482	49.905	46.908
Total		34494978	759966	100.000	100.000

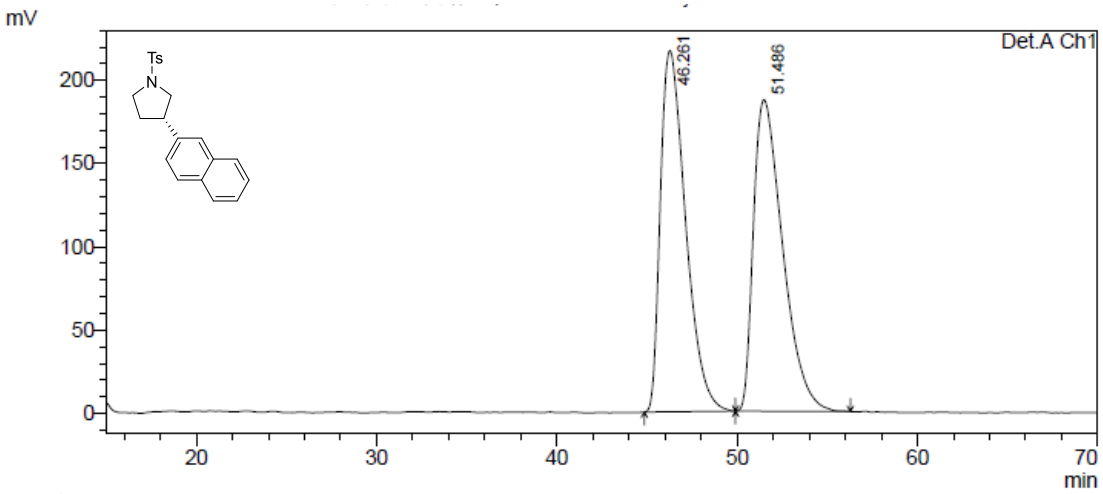


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.453	697610	17625	1.324	1.936
2	23.787	51986101	892628	98.676	98.064
Total		52683712	910253	100.000	100.000

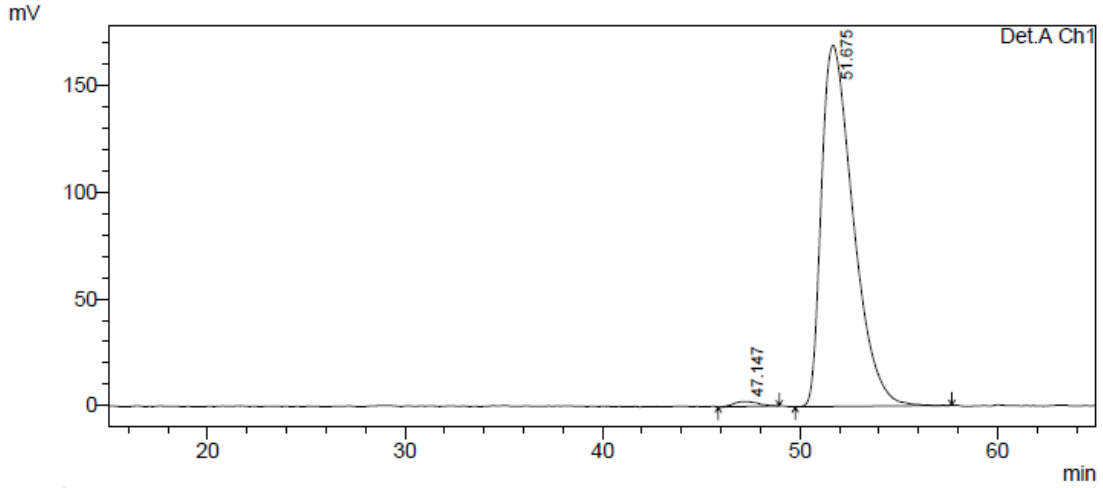


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.261	21052121	216910	49.938	53.699
2	51.486	21104539	187027	50.062	46.301
Total		42156660	403937	100.000	100.000

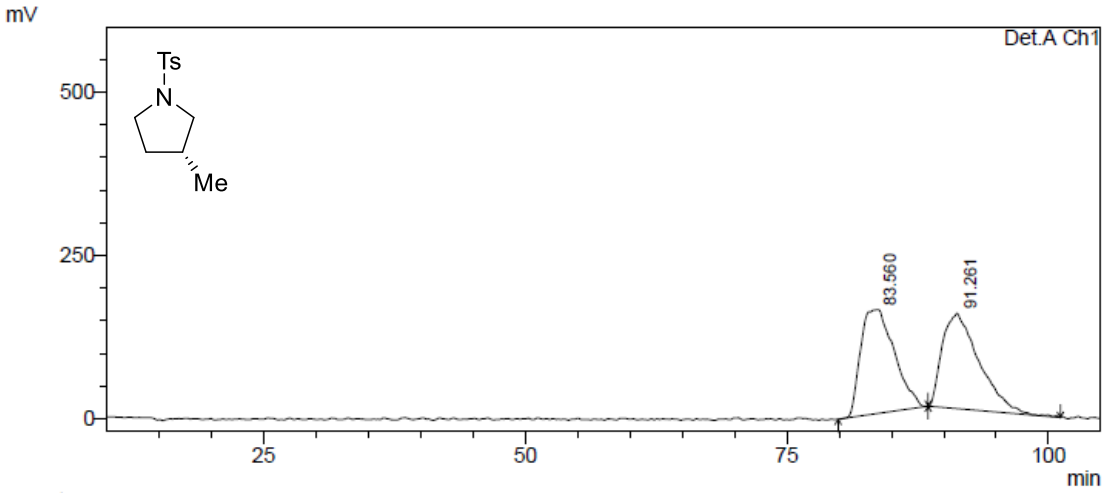


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.147	196387	2258	1.029	1.317
2	51.675	18891059	169115	98.971	98.683
Total		19087446	171373	100.000	100.000

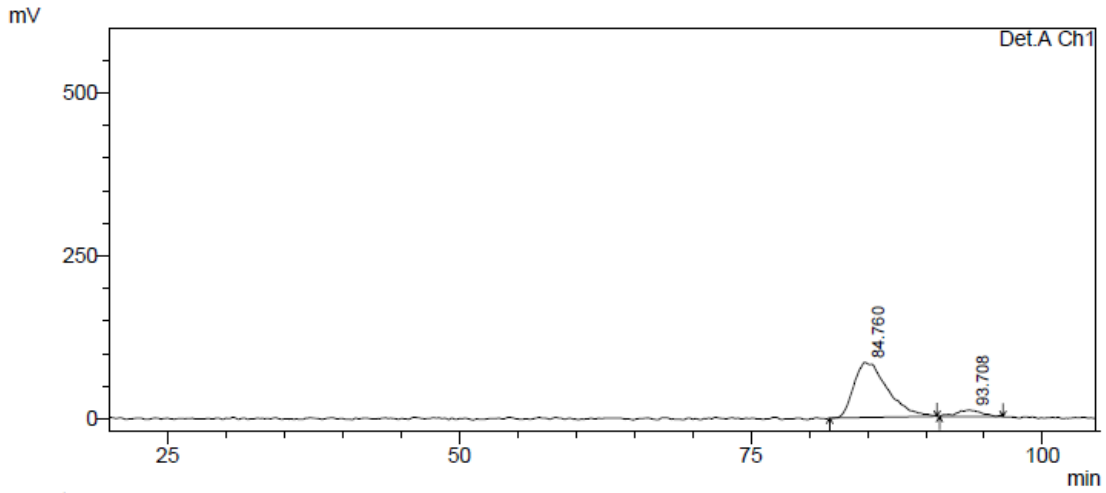


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	83.560	35671312	159253	49.907	52.171
2	91.261	35804713	146000	50.093	47.829
Total		71476025	305253	100.000	100.000

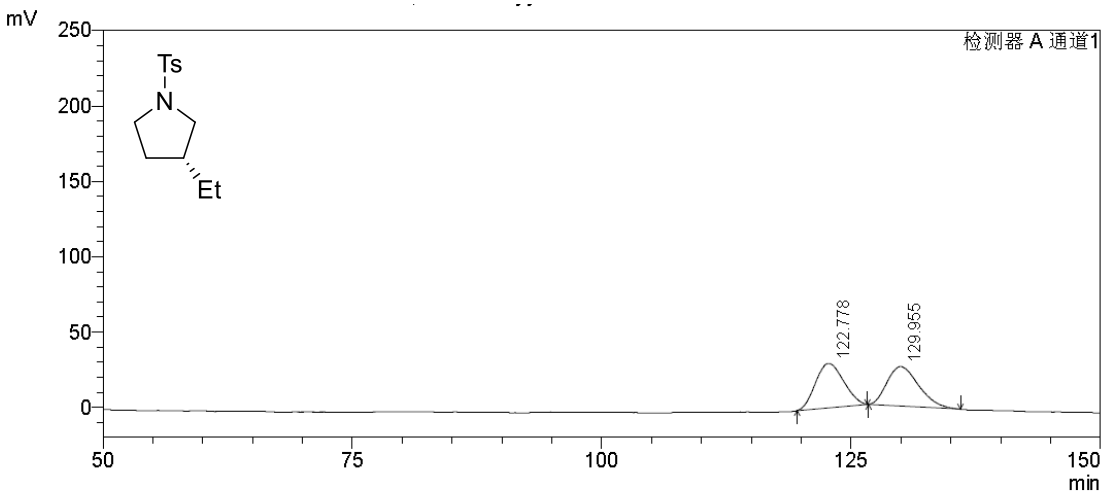


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	84.760	16966846	84580	91.683	89.507
2	93.708	1539099	9915	8.317	10.493
Total		18505945	94495	100.000	100.000

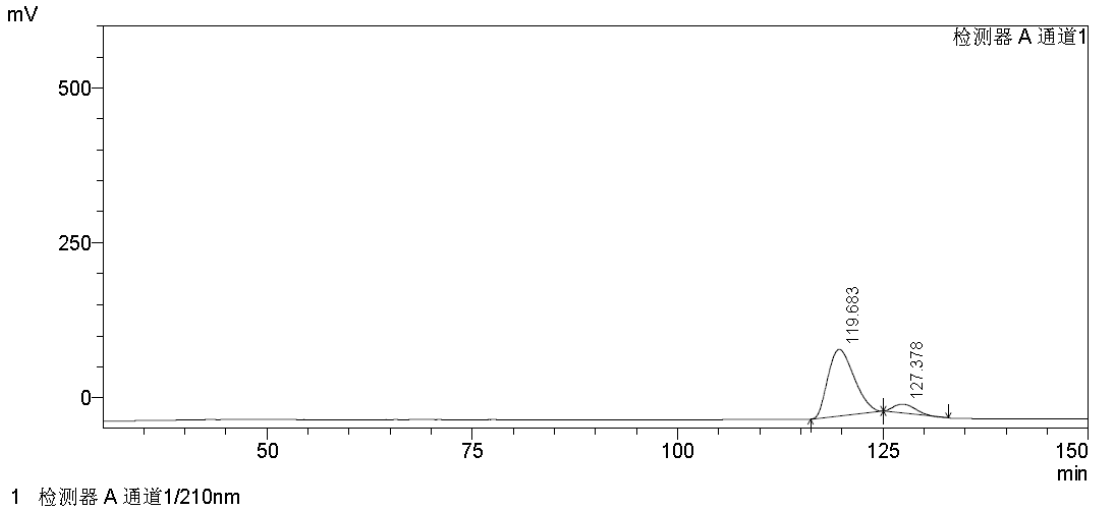


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	122.778	5770289	29408	49.924	52.927
2	129.955	5787886	26156	50.076	47.073
总计		11558175	55564	100.000	100.000

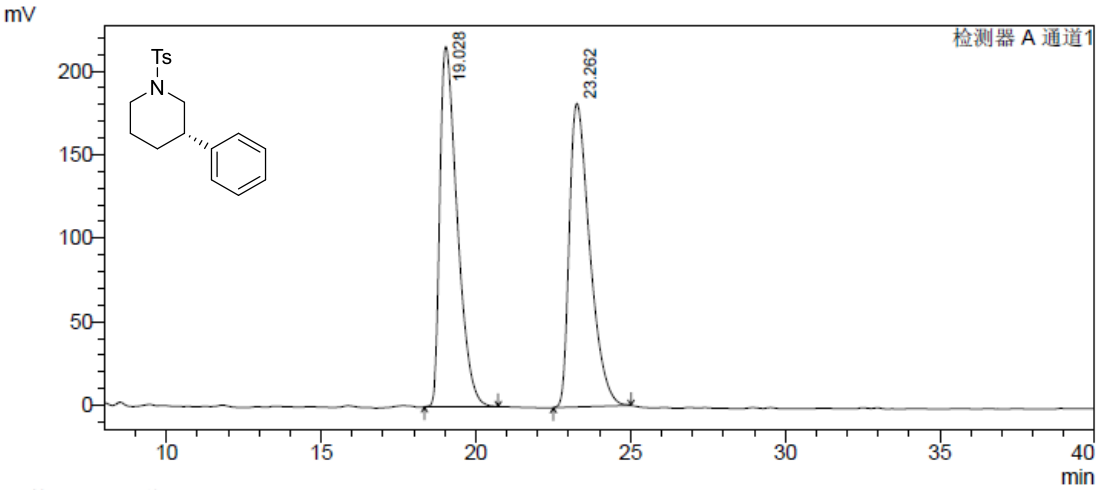


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	119.683	23907489	107735	89.832	88.039
2	127.378	2706041	14638	10.168	11.961
总计		26613529	122373	100.000	100.000

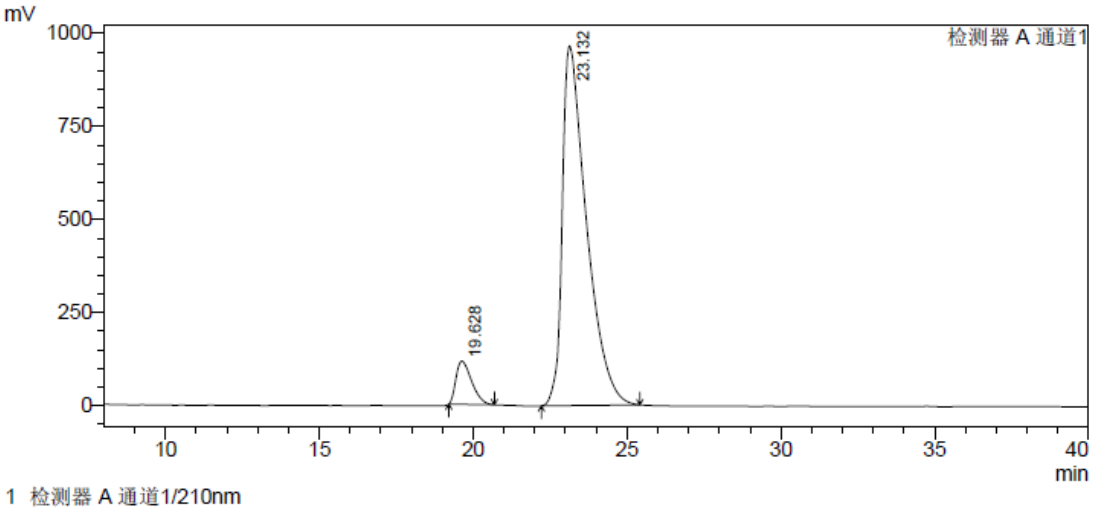


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	19.028	8417396	215480	50.175	54.268
2	23.262	8358520	181588	49.825	45.732
总计		16775916	397068	100.000	100.000

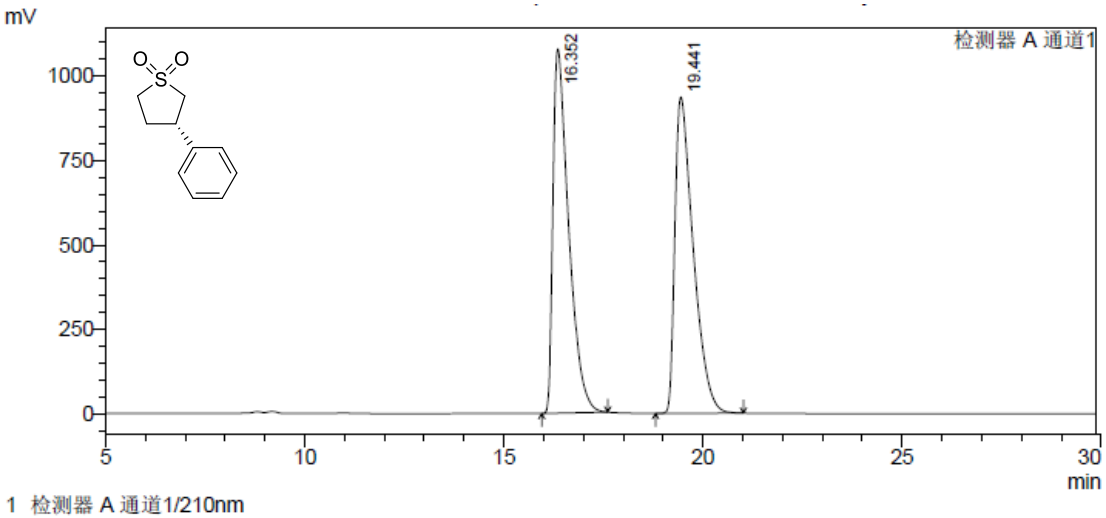


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	19.628	4113863	115973	7.220	10.712
2	23.132	52865876	966667	92.780	89.288
总计		56979739	1082640	100.000	100.000

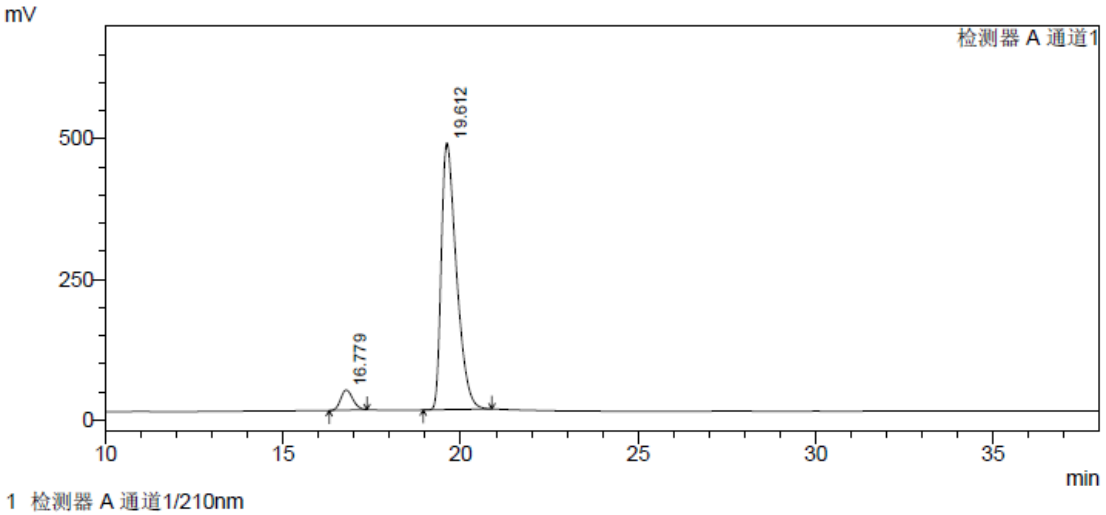


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.352	29604716	1079468	49.637	53.532
2	19.441	30037781	937031	50.363	46.468
总计		59642497	2016499	100.000	100.000

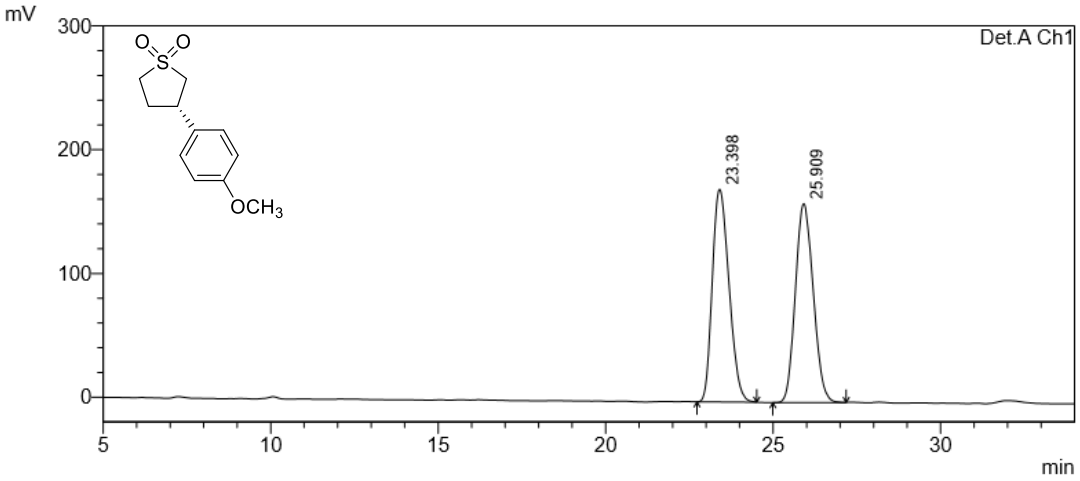


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.779	851048	36099	5.717	7.067
2	19.612	14034199	474677	94.283	92.933
总计		14885247	510775	100.000	100.000

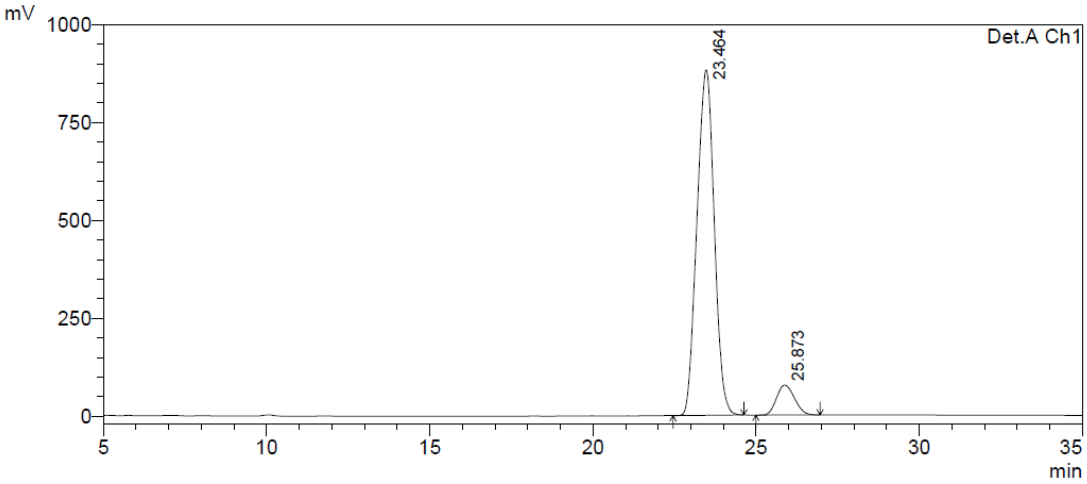


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.398	5941315	171665	49.868	51.648
2	25.909	5972726	160710	50.132	48.352
Total		11914041	332375	100.000	100.000

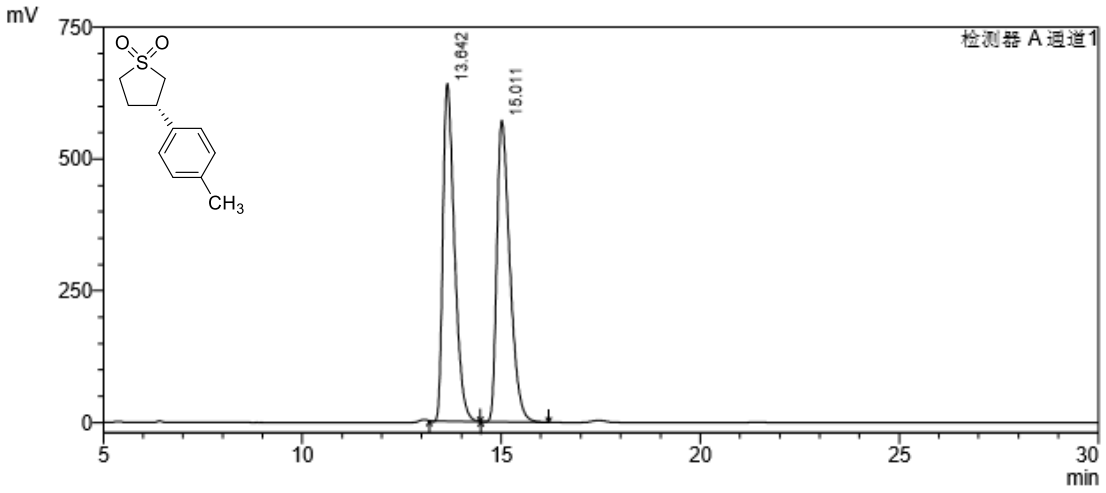


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.464	32534211	882222	91.774	92.037
2	25.873	2915977	76324	8.226	7.963
Total		35450188	958546	100.000	100.000

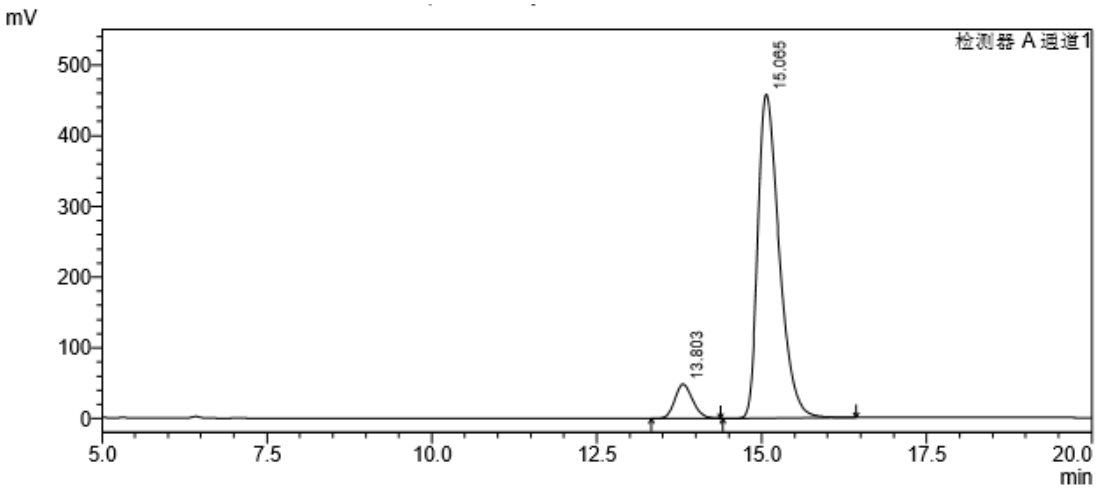


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	13.642	12898671	640804	49.771	52.845
2	15.011	13017158	571806	50.229	47.155
总计		25915829	1212610	100.000	100.000

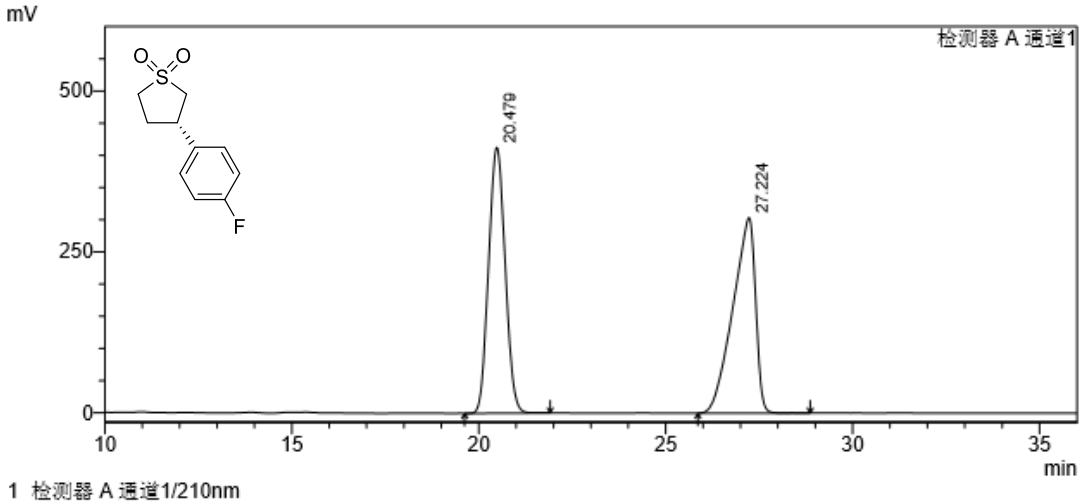


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	13.803	921134	48617	8.218	9.603
2	15.065	10287172	457658	91.782	90.397
总计		11208306	506275	100.000	100.000

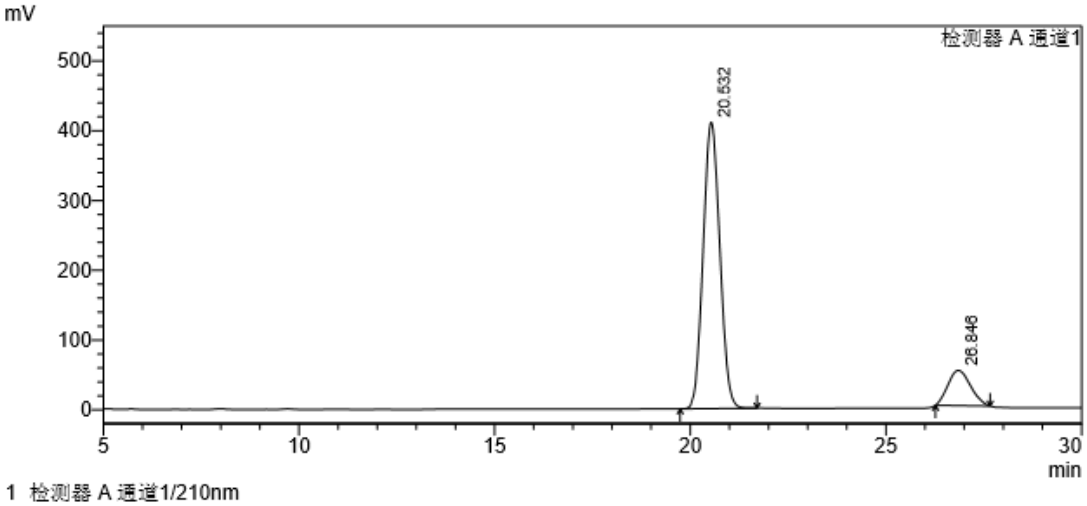


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	20.479	12719718	412945	49.839	57.620
2	27.224	12801844	303721	50.161	42.380
总计		25521561	716666	100.000	100.000

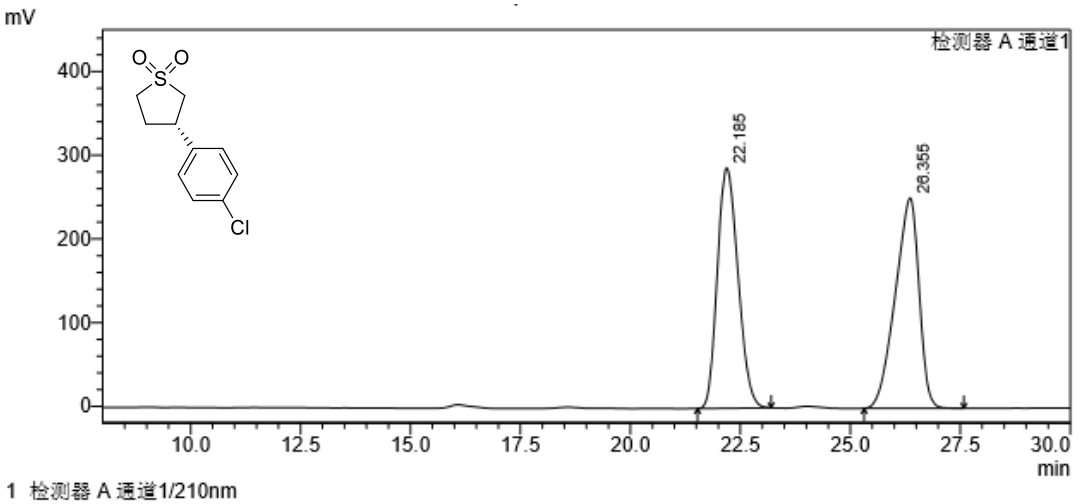


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	20.532	12190924	410554	85.713	89.054
2	26.846	2031992	50460	14.287	10.946
总计		14222916	461014	100.000	100.000

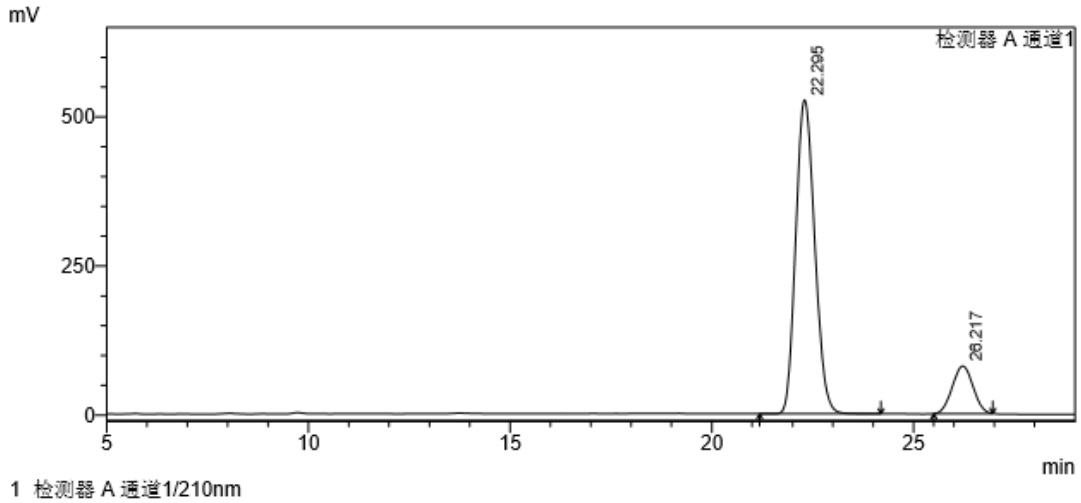


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	22.185	9404398	287262	49.897	53.327
2	26.355	9443077	251416	50.103	46.673
总计		18847475	538678	100.000	100.000

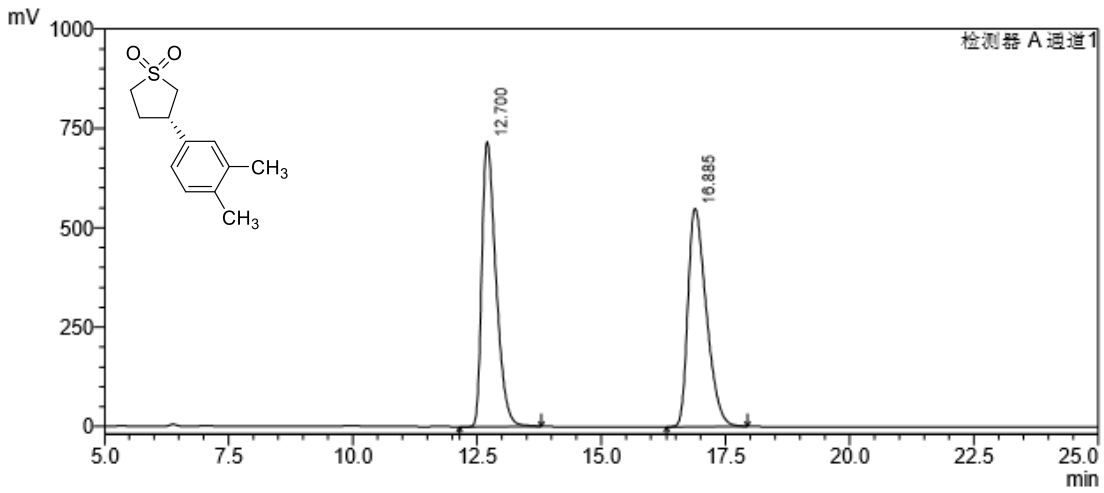


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	22.295	17197268	526261	85.761	86.801
2	26.217	2855369	80025	14.239	13.199
总计		20052637	606286	100.000	100.000

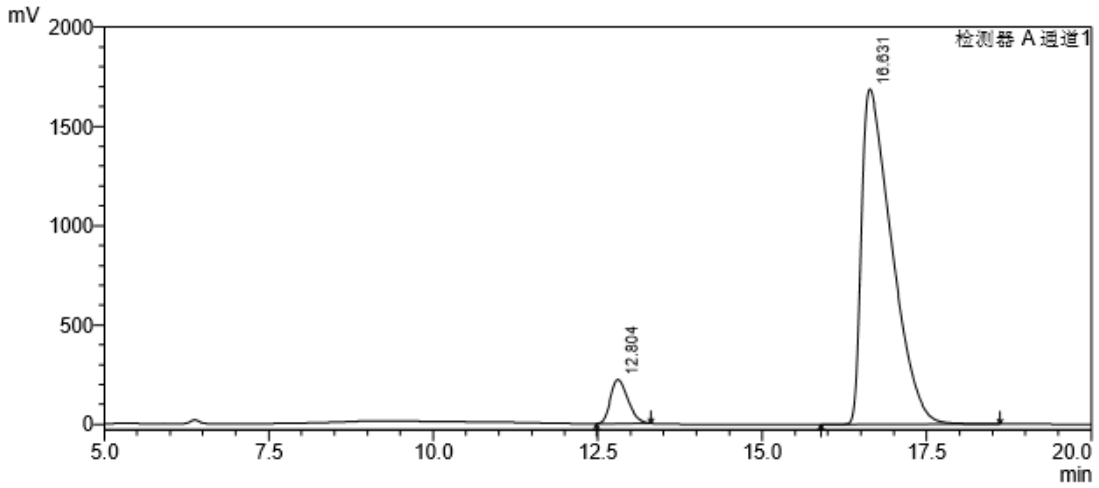


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.700	14167408	716678	50.023	56.635
2	16.885	14154493	548759	49.977	43.365
总计		28321900	1265437	100.000	100.000

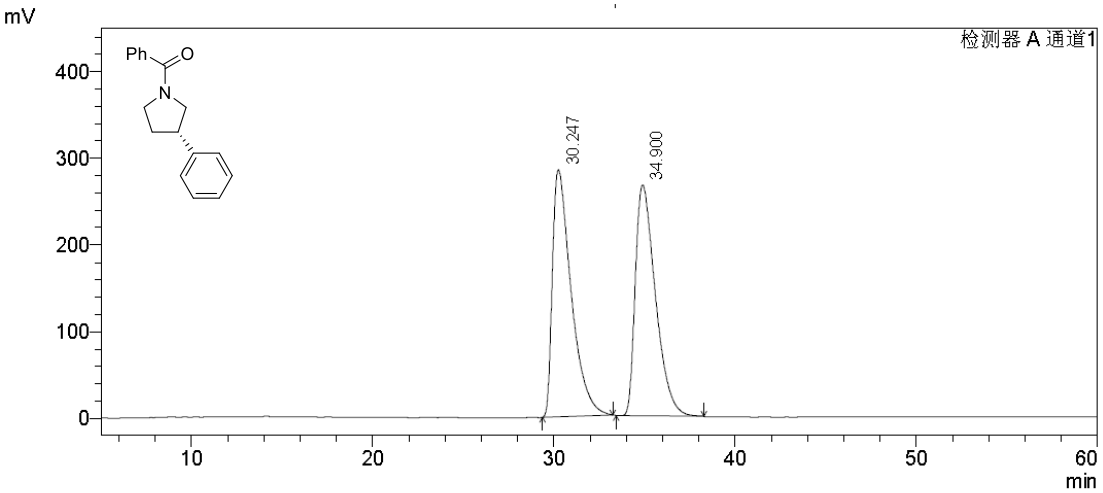


1 检测器 A 通道1/210nm

峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.804	4091996	221449	7.071	11.601
2	16.631	53780950	1687392	92.929	88.399
总计		57872946	1908841	100.000	100.000

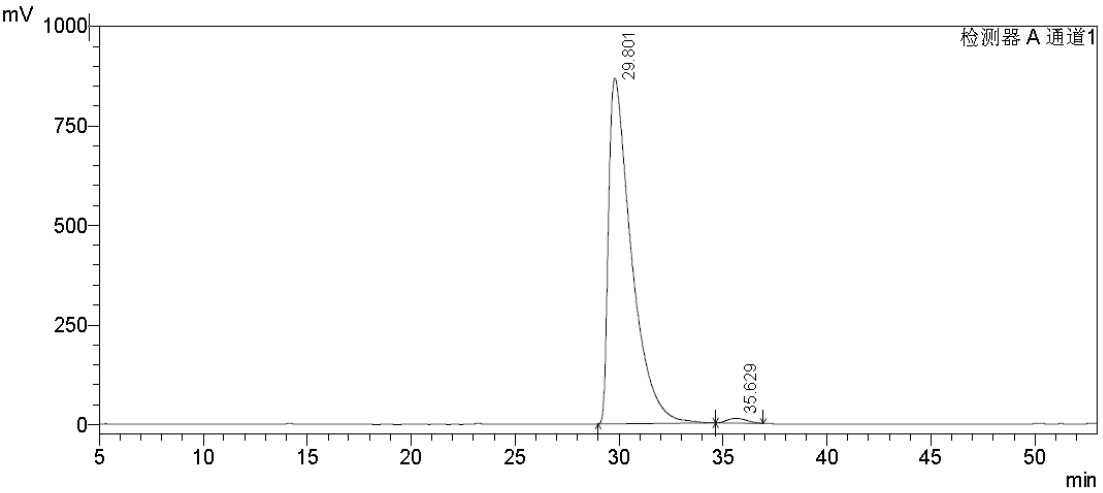


1 检测器 A 通道1/210nm

峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	30.247	20517347	285140	49.961	51.698
2	34.900	20548976	266411	50.039	48.302
总计		41066323	551552	100.000	100.000



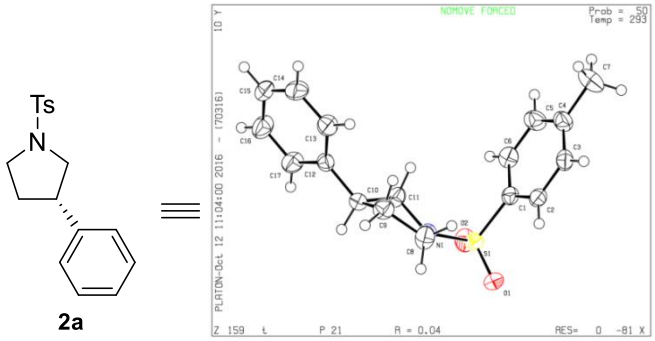
1 检测器 A 通道1/210nm

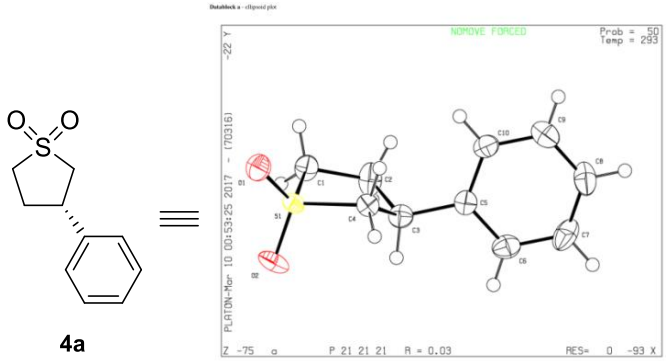
峰表

检测器 A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	29.801	66398522	867849	98.801	98.608
2	35.629	805754	12255	1.199	1.392
总计		67204277	880104	100.000	100.000

6. Single Crystal of Enantioenriched 2a and 4a.





The crystal data of compound **(2a, 4a)** have been deposited in CCDC with numbers 1538195 and 1538169, respectively. Chemical Formula: $C_{17}H_{19}NO_2S$ (**2a**), $C_{10}H_{12}O_2S$ (**4a**); Molecular Weight: 301.4040 (**2a**), 196.2640 (**4a**); Crystal Color: Colorless. The crystal was obtained from an EtOAc/PE system at room temperature.

7. References.

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