Supporting Information for

Catalytic Asymmetric [3+2] Annulation of Hantzsch Esters with Racemic *N*-Sulfonylaziridines

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General Information

Commercial reagents and solvents were purified prior to use following the guidelines of Perrin and Armarego.[1] $[(CH_3CN)_4Cu]PF_6$, chiral diphosphine ligands were purchased from commercial vendors and used as received. Chromatographic purification of products was accomplished by using forced-flow chromatography on Silicycle SiliaFlash® F60 40–63 μm, 60 Å silica gel. Thin-layer chromatography (TLC) was performed on silica gel plates (HSGF 254). Visualization of the developed chromatogram was performed by UV light, staining with iodine (dispersed in silica gel), or by $KMnO_4$ stain.

^1H NMR spectra (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra data were recorded on Bruker AVANCE-500 spectrometers. ^1H NMR chemical shifts are reported in parts per million (ppm) and are referenced to residual protium in the NMR solvent (δ 7.26 for $CHCl_3$, δ 7.16 for C_6D_5H). ^{13}C NMR chemical shifts are reported in parts per million (ppm) and are referenced to are referenced to the carbon resonances of the solvent residual peak (δ 77.16 for $CDCl_3$, δ 128.06 for C_6D_6). ^{19}F NMR data recorded are listed by using $CFCl_3$ as external reference. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are recorded with broad-band proton decoupling technique and are reported in terms of chemical shift. Single crystal x-ray crystallographic analyses were performed on a Bruker APEX-II CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (I = 0.71073 Å). Melting points were determined on a SGW X-4 melting apparatus and are uncorrected. Mass spectra were obtained on a Bruker Apex IV RTMS and a TOF analyzer. High performance liquid chromatography (HPLC) was performed on a DIONEX UltiMate 3000 LC systems using Daicel CHIRALPAK® columns as noted.

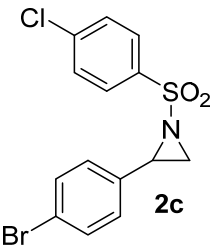
Sources of Hantzsch Esters (HEs) 1 and Aziridines 2 Used in This Study

Hantzsch esters **1a**, **1e**, **1h** and **1i** were purchased from commercial vendors and were used as received; **1b**–**1d**, **1f** and **1g** were prepared following literature methods.[2]

Aziridines **2** were prepared from the corresponding alkenes (8 mmol) with the corresponding PhI=NSO_2Ar (4 mmol) following Evans' procedure by using $Cu(acac)_2$ (8 mol%) as catalyst in 30 mL of CH_3CN.[3a]

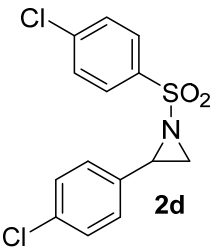
The spectroscopic data of all known compounds are in agreement with those previously reported.

Analytical data for aziridine substrates previously not reported:



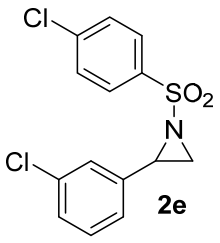
2c

2-(4-Bromophenyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2c**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (1.04 g, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.76 (dd, *J* = 7.1, 4.4 Hz, 1H), 3.01 (d, *J* = 7.1 Hz, 1H), 2.38 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.6, 136.5, 133.9, 131.9, 129.7, 129.4, 128.3, 122.6, 40.7, 36.4; **HRMS** (ESI-TOF) Calculated for $C_{14}H_{12}BrClNO_2S$ ($[M+H]^+$): 371.9455, found: 371.9452.



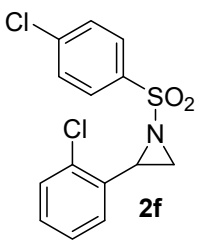
2d

2-(4-Chloromophenyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2d**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.94 g, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 3.77 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.00 (d, *J* = 7.2 Hz, 1H), 2.38 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.6, 136.5, 134.5, 133.4, 129.6, 129.4, 129.0, 128.0, 40.6, 36.4; **HRMS** (ESI-TOF) Calculated for $C_{14}H_{12}Cl_2NO_2S$ ($[M+H]^+$): 327.9960, found: 327.9962.

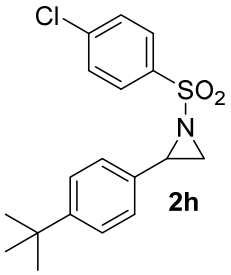


2e

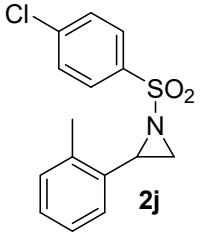
2-(3-Chloromophenyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2e**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.81 g, 62% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.26–7.21 (m, 2H), 7.19 (s, 1H), 7.11 (m, 1H), 3.78 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.00 (d, *J* = 7.2 Hz, 1H), 2.38 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.7, 137.0, 136.5, 134.8, 130.1, 129.7, 129.5, 128.9, 126.6, 125.0, 40.5, 36.5; **HRMS** (ESI-TOF) Calculated for $C_{14}H_{12}Cl_2NO_2S$ ($[M+H]^+$): 327.9960, found: 327.9961.



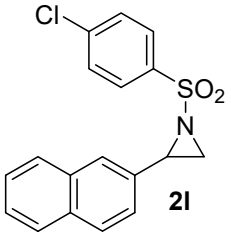
2-(2-Chloromophenyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2f**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.86 g, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.53 (m, 2H), 7.33 (m, 1H), 7.24–7.15 (m, 3H), 4.09 (dd, *J* = 7.1, 4.4 Hz, 1H), 3.07 (m, 1H), 2.37 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.6, 136.4, 133.9, 132.8, 129.7, 129.6, 129.4, 127.4, 127.2, 39.4, 35.9; **HRMS** (ESI-TOF) Calculated for $C_{14}H_{12}Cl_2NO_2S$ ($[M+H]^+$): 327.9960, found: 327.9951.



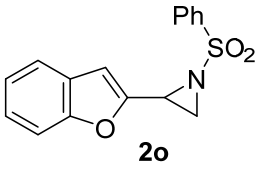
2-(4-*tert*-Butylphenyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2h**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (1.09 g, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 3.31 (dd, *J* = 7.1, 4.4 Hz, 1H), 3.01 (d, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 5.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.8, 140.4, 136.8, 131.7, 129.6, 129.5, 126.4, 125.7, 41.5, 36.1, 34.7, 31.3; **HRMS** (ESI-TOF) Calculated for $C_{18}H_{21}ClNO_2S$ ($[M+H]^+$): 350.0976, found: 350.0978.



2-(2-Methylphenyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2j**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.99 g, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.22–7.09 (m, 4H), 3.93 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.03 (d, *J* = 7.1 Hz, 1H), 2.40 (s, 3H), 2.37 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.4, 136.8, 136.6, 132.9, 130.1, 129.6, 129.5, 128.3, 126.3, 125.8, 39.9, 35.4, 19.1; **HRMS** (ESI-TOF) Calculated for $C_{14}H_{12}Cl_2NO_2S$ ($[M+H]^+$): 327.9960, found: 327.9951.

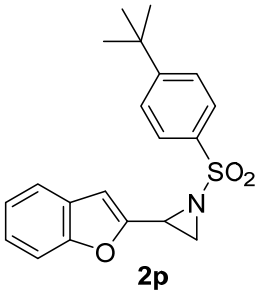


2-(2-Naphthyl)-1-((4-chlorophenyl)sulfonyl)aziridine (**2l**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (1.01 g, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.22–7.09 (m, 4H), 3.93 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.03 (d, *J* = 7.1 Hz, 1H), 2.40 (s, 3H), 2.37 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.4, 136.7, 133.3, 133.1, 132.1, 129.6, 129.4, 128.7, 127.9, 127.8, 126.7, 126.5, 126.3, 123.6, 41.7, 36.3; **HRMS** (ESI-TOF) Calculated for $C_{18}H_{15}ClNO_2S$ ($[M+H]^+$): 344.0507, found: 344.0505.



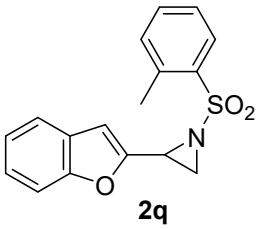
2o

2-(Benzofuran-2-yl)-1-(phenylsulfonyl)aziridine (**2o**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.91 g, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.64 (m, 1H), 7.57–7.50 (m, 3H), 7.39 (m, 1H), 7.27–7.21 (m, 2H), 6.74 (s, 1H), 3.98 (dd, *J* = 7.2, 4.9 Hz, 1H), 3.08 (d, *J* = 7.1 Hz, 1H), 2.86 (d, *J* = 4.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 155.0, 150.6, 137.8, 134.0, 129.4, 128.1, 128.0, 125.0, 123.2, 121.2, 111.5, 106.8, 35.5, 33.7; **HRMS** (ESI-TOF) Calculated for $C_{16}H_{14}NO_3S$ ($[M+H]^+$): 300.0689, found: 300.0692.



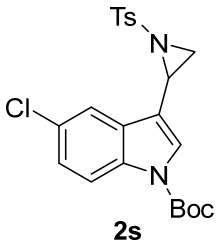
2p

2-(Benzofuran-2-yl)-1-(4-*tert*-butylphenylsulfonyl)aziridine (**2p**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). Pink solid (0.99 g, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.27 (pseudo t, *J* = 7.2 Hz, 1H), 7.21 (pseudo t, *J* = 7.7 Hz, 1H), 6.75 (s, 1H), 3.98 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.05 (d, *J* = 7.2 Hz, 1H), 2.84 (d, *J* = 4.4 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.9, 155.0, 150.8, 134.6, 128.0, 126.4, 124.9, 123.2, 121.2, 111.4, 106.7, 35.4, 35.3, 33.7, 31.1; **HRMS** (ESI-TOF) Calculated for $C_{20}H_{22}NO_3S$ ($[M+H]^+$): 356.1315, found: 356.1313.



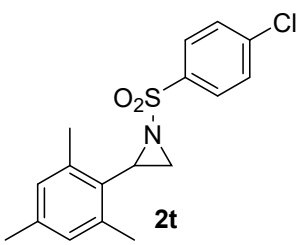
2q

2-(Benzofuran-2-yl)-1-(2-methylphenylsulfonyl)aziridine (**2q**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.94 g, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.51 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.34 (m, 2H), 7.28 (m, 1H), 7.21 (pseudo t, *J* = 7.7 Hz, 1H), 6.71 (s, 1H), 3.98 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.10 (d, *J* = 7.2 Hz, 1H), 2.82 (d, *J* = 4.4 Hz, 1H), 2.78 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 155.0, 151.0, 139.3, 136.2, 133.9, 132.8, 129.4, 128.0, 126.2, 124.9, 123.2, 121.2, 111.4, 106.5, 35.3, 33.9, 20.8; **HRMS** (ESI-TOF) Calculated for $C_{17}H_{16}NO_3S$ ($[M+H]^+$): 314.0845, found: 314.0839.



2s

tert-Butyl 5-chloro-3-(1-tosylaziridin-2-yl)-1H-indole-1-carboxylate (**2s**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (1.39 g, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.01 (brs, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.47 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.23 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.19 (d, *J* = 2.2 Hz, 1H), 3.77 (dd, *J* = 6.6, 4.4 Hz, 1H), 3.06 (d, *J* = 6.6 Hz, 1H), 2.62 (d, *J* = 4.4 Hz, 1H), 2.46 (s, 3H), 1.63 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.1, 145.3, 134.8, 134.0, 130.1, 128.8, 128.3, 125.7, 125.2, 118.9, 116.5, 114.9, 84.7, 34.9, 33.8, 28.2, 21.9; **HRMS** (ESI-TOF) Calculated for $C_{22}H_{24}ClN_2O_4S$ ($[M+H]^+$): 447.1140, found: 447.1145.

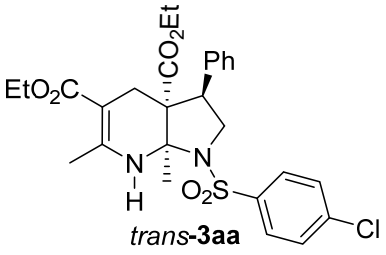


1-((4-Chlorophenyl)sulfonyl)-2-mesitylaziridine (**2t**). Purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1 (v/v)). White solid (0.94 g, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 6.81 (s, 2H), 3.92 (pseudo t, *J* = 5.0 Hz, 1H), 2.97 (d, *J* = 7.1 Hz, 1H), 2.32 (s, 6H), 2.25 (s, 3H), 2.21 (d, *J* = 5.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.4, 137.8, 137.4, 136.8, 129.7, 129.5, 129.4, 128.1, 39.8, 35.9, 20.9, 20.2; **HRMS** (ESI-TOF) Calculated for $C_{17}H_{19}ClNO_2S$ ([M+H]$^+$): 336.0820, found: 336.0811.

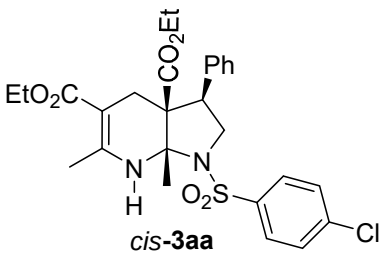
Typical Procedure for the Enantioselective [3+2] Annulations of Aziridines with HEs.

Under argon atmosphere, to an oven-dried Schlenk tube was added $[(CH_3CN)_4Cu]PF_6$ (0.9 mg, 0.0025 mmol) and (*S*)-BINAP (1.9 mg, 0.003 mmol). The system was evacuated under vacuum and back-filled with argon (repeated twice). Then 1.0 mL of toluene was added and the resulting mixture was stirred at rt for 20 mins to give a white suspension, followed by the sequential addition of the Hantzsch ester **1** (0.1 mmol), aziridine **2** (0.22 mmol) and 1.0 mL of toluene. The reaction mixture was stirred at 35±2 °C or the temperature as specified in tables 2–3 until the disappearance of **1** as monitored by TLC (visualized by staining with iodine and UV light). Then 10 mL of saturated aqueous $NaHCO_3$ solution and 10 mL of ethyl acetate (EtOAc) were added, and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated via rotary evaporation under reduced pressure to provide the crude mixture, which was analyzed by ^{1}H NMR analysis to estimate the diastereomeric ratio wherever applicable. Then the crude mixture was purified by column chromatography (eluting with petroleum ether/EtOAc (v/v): 10:1–1:1 containing 0.5 v% triethylamine) to furnish the desired products.

The corresponding racemic products for HPLC assay were prepared following a similar procedure with $[(CH_3CN)_4Cu]PF_6$ (5 mol%), *rac*-BINAP (6 mol%), 0.12 mmol of the HE **1** and 0.1 mmol of aziridine **2** in toluene.



Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-phenyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3aa**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3aa** was obtained as a white solid following the general procedure (42.6 mg, 78% yield). ee = 96%, $[\alpha]_D^{23}$ = +70.4 (*c* = 1.04, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I ＝254 nm): t_R = 7.673 min (minor), 13.3 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.30–7.25 (m, 5H), 4.75 (s, 1H), 4.30 (dd, *J* = 10.5, 8.4 Hz, 1H), 4.10–3.98 (m, 4H), 3.89 (pseudo t, *J* = 8.8 Hz, 1H), 3.58 (pseudo t, *J* = 10.5 Hz, 1H), 2.38 (d, *J* = 17.0 Hz, 1H), 2.12 (s, 3H), 1.82 (d, *J* = 17.0 Hz, 1H), 1.80 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.1, 167.9, 146.7, 139.1, 139.0, 134.7, 129.4, 129.2, 128.5, 128.1, 127.9, 94.8, 78.8, 61.3, 59.3, 53.3, 47.1, 44.7, 27.6, 24.3, 20.8, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{32}ClN_2O_6S$ ([M+H]$^+$): 547.1664, found: 547.1660.

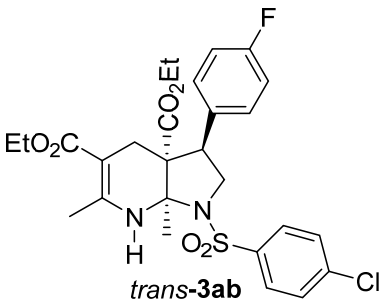


cis-**3aa**

Diethyl (3*R*, 3a*S*, 7a*S*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-phenyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3aa**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3aa** was obtained as a white solid following the general procedure (11.5 mg, 21% yield). ee = 95%, $[\alpha]_D^{23}$ = -16.1 (*c* = 1.04, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I＝254 nm): t_R = 19.3 min (minor), 25.0 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.30–7.25 (m, 5H), 4.75 (s, 1H), 4.30 (dd, *J* = 10.5, 8.4 Hz, 1H), 4.10–3.98 (m, 4H), 3.89 (pseudo t, *J* = 8.8 Hz, 1H), 3.58 (pseudo t, *J* = 10.5 Hz, 1H), 2.38 (d, *J* = 17.0 Hz, 1H), 2.12 (s, 3H), 1.82 (d, *J* = 17.0 Hz, 1H), 1.49 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.2, 168.5, 149.2, 140.5, 139.2, 134.2, 129.4, 128.9, 128.6, 128.4, 128.1, 88.7, 79.1, 61.1, 60.4, 59.2, 51.1, 44.6, 24.5, 23.5, 21.1, 14.9, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{32}ClN_2O_6S$ ($[M+H]^+$): 547.1664, found: 547.1658.

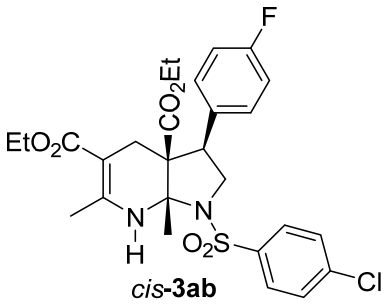
The gram-scale run (Scheme 2) was performed following the general procedure to provide *trans*-**3aa** in 72% yield, 95% ee, *cis*-**3aa** in 25% yield, 95% ee and the aziridine (*S*)-**2a** was recovered (48% yield, 87% ee). After a single recrystallization from *n*-hexane/ethyl acetate, (*S*)-**2a** with 98% ee was obtained, $[\alpha]_D^{23}$ = 31.1 (*c* = 0.93, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I＝254 nm): t_R = 20.5 min (minor), 25.6 min (major).

The crystals of *cis*-**3aa** suitable for x-ray crystallographic analysis was obtained by recrystallization from petroleum ether-ethyl acetate to provide colorless crystals, m.p. = 140–141 °C, ee > 99%.



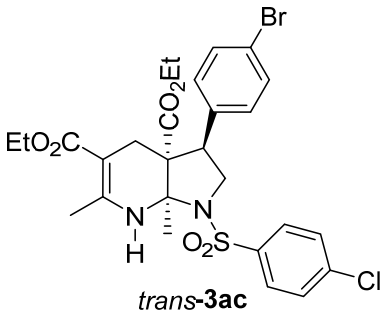
trans-**3ab**

Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(4-fluorophenyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ab**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ab** was obtained as a white solid following the general procedure (46.3 mg, 82% yield). ee = 98%, $[\alpha]_D^{23}$ = +48.9 (*c* = 1.10, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I＝254 nm): t_R = 20.1 min (major), 26.9 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.28–7.25 (m, 2H), 6.99 (m, 2H), 4.77 (s, 1H), 4.59 (pseudo t, *J* = 9.9 Hz, 1H), 4.10–3.98 (m, 4H), 3.88 (pseudo t, *J* = 8.8 Hz, 1H), 3.52 (pseudo t, *J* = 9.9 Hz, 1H), 2.33 (d, *J* = 17.0 Hz, 1H), 2.13 (s, 3H), 1.82 (d, *J* = 17.0 Hz, 1H), 1.80 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 167.8, 162.4 (d, $^1J_{C-F}$ = 247.4 Hz), 146.8, 139.2, 138.9, 131.0 (d, $^3J_{C-F}$ = 8.1 Hz), 130.3 (d, $^4J_{C-F}$ = 3.5 Hz), 129.3, 128.1, 115.3 (d, $^2J_{C-F}$ = 20.8 Hz), 94.6, 78.6, 61.3, 59.4, 53.2, 47.1, 44.1, 27.5, 24.2, 20.8, 14.6, 14.0; **^{19}F NMR** (470 MHz, $CDCl_3$): δ -114.5 (m); **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}ClFN_2O_6S$ ($[M+H]^+$): 565.1570, found: 565.1577.



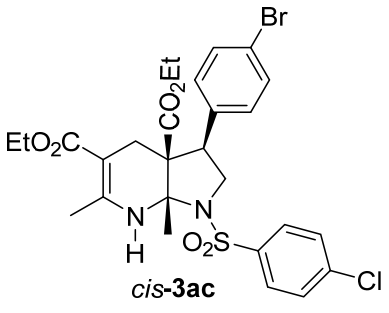
cis-**3ab**

Diethyl (3*R*, 3a*S*, 7a*S*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(fluorophenyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ab**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ab** was obtained as a white solid following the general procedure (10.2 mg, 18% yield). ee = 95%, $[\alpha]_D^{23}$ = -6.2 (*c* = 0.22, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AD-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 12.7 min (minor), 17.9 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 5.47 (s, 1H), 4.31–4.25 (m, 1H), 4.19–4.09 (m, 3H), 3.89–3.75 (m, 2H), 3.59 (pseudo t, *J* = 10.4 Hz, 1H), 2.80 (d, *J* = 17.0 Hz, 1H), 2.38 (d, *J* = 17.1 Hz, 1H), 2.31 (s, 3H), 1.47 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.1, 168.4, 162.0 (d, $^1J_{C-F}$ = 247.4 Hz), 149.2, 140.4, 139.3, 130.5 (d, $^3J_{C-F}$ = 8.1 Hz), 129.9 (d, $^4J_{C-F}$ = 3.4 Hz), 129.5, 128.3, 115.4 (d, $^2J_{C-F}$ = 22.0 Hz), 88.6, 79.0, 61.1, 60.4, 59.3, 51.2, 43.9, 24.5, 23.4, 21.1, 14.9, 13.8; **^{19}F NMR** (470 MHz, $CDCl_3$): δ -114.1 (m); **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}ClFN_2O_6S$ ($[M+H]^+$): 565.1570, found: 565.1579.



trans-**3ac**

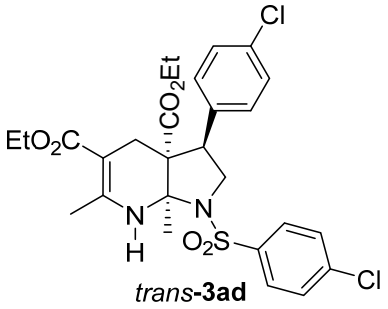
Diethyl (3*R*, 3a*R*, 7a*R*)-3-(4-bromophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl--1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ac**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ac** was obtained as a white solid following the general procedure (51.9 mg, 83% yield). ee = 98%, $[\alpha]_D^{23}$ = +70.5 (*c* = 1.28, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 7.6 min (major); 9.5 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.43 (m, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.76 (s, 1H), 4.26 (pseudo t, *J* = 9.9 Hz, 1H), 4.11–3.98 (m, 4H), 3.88 (pseudo t, *J* = 9.4 Hz, 1H), 3.52 (pseudo t, *J* = 9.9 Hz, 1H), 2.33 (d, *J* = 17.0 Hz, 1H), 2.13 (s, 3H), 1.82 (d, *J* = 17.0 Hz, 1H), 1.79 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 167.8, 146.8, 139.3, 138.9, 133.8, 131.6, 131.1, 129.3, 128.1, 122.1, 94.6, 78.6, 61.4, 59.4, 53.2, 46.9, 44.3, 27.4, 24.2, 20.8, 14.7, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}BrClN_2O_6S$ ($[M+H]^+$): 625.0769, found: 625.0761.



cis-**3ac**

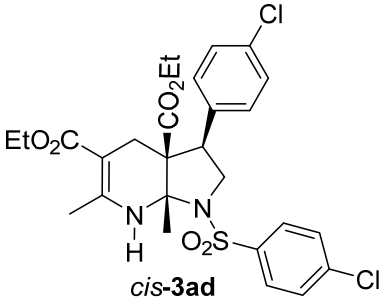
Diethyl (3*R*, 3a*S*, 7a*S*)- 3-(4-bromophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ac**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ac** was obtained as a white solid following the general procedure (10.0 mg, 16% yield). ee = 96%, $[\alpha]_D^{23}$ = +17.2 (*c* = 0.51, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AD-H column,

isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 18.8 min (minor), 24.5 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 5.47 (s, 1H), 4.31–4.25 (m, 1H), 4.19–4.09 (m, 3H), 3.89–3.75 (m, 2H), 3.59 (pseudo t, *J* = 10.4 Hz, 1H), 2.80 (d, *J* = 17.0 Hz, 1H), 2.38 (d, *J* = 17.1 Hz, 1H), 2.31 (s, 3H), 1.47 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.0, 168.3, 149.2, 140.3, 139.3, 133.3, 131.6, 130.6, 129.4, 128.3, 122.1, 88.5, 79.0, 61.2, 60.3, 59.3, 51.0, 44.0, 24.5, 23.4, 21.1, 14.9, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}BrClN_2O_6S$ ($[M+H]^+$): 625.0769, found: 625.0765.



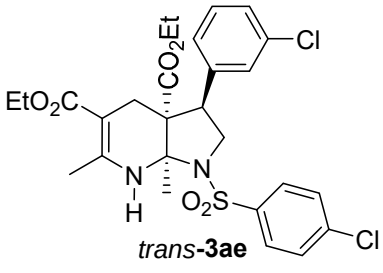
trans-**3ad**

Diethyl (3*R*, 3a*R*, 7a*R*)-3-(4-chlorophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ad**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ad** was obtained as a white solid following the general procedure (47.0 mg, 81% yield). ee = 99%, $[\alpha]_D^{23}$ = +61.1 (*c* = 0.62, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 7.4 min (major), 9.3 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.24 (AB, *J* = 8.8 Hz, 4H), 4.77 (s, 1H), 4.28 (dd, *J* = 10.5, 9.4 Hz, 1H), 4.11–3.98 (m, 4H), 3.88 (pseudo t, *J* = 9.4 Hz, 1H), 3.52 (pseudo t, *J* = 10.5 Hz, 1H), 2.33 (d, *J* = 17.0 Hz, 1H), 2.13 (s, 3H), 1.81 (d, *J* = 17.0 Hz, 1H), 1.79 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 167.8, 146.8, 139.2, 138.9, 133.9, 133.2, 130.8, 129.3, 128.6, 128.1, 94.5, 78.6, 61.4, 59.4, 53.2, 46.9, 44.2, 27.5, 24.2, 20.8, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}Cl_2N_2O_6S$ ($[M+H]^+$): 581.1274, found: 581.1273.



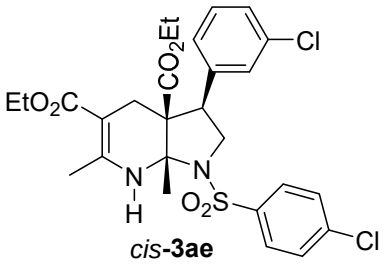
cis-**3ad**

Diethyl (3*R*, 3a*S*, 7a*S*)-3-(4-chloromophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ad**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ad** was obtained as a white solid following the general procedure (8.7 mg, 15% yield). ee = 98%, $[\alpha]_D^{23}$ = -32.6 (*c* = 0.23, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AD-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 13.4 min (minor), 15.2 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 5.48 (s, 1H), 4.32–4.25 (m, 1H), 4.20–4.09 (m, 3H), 3.89–3.76 (m, 2H), 3.61 (pseudo t, *J* = 10.5 Hz, 1H), 2.81 (d, *J* = 17.6 Hz, 1H), 2.37 (d, *J* = 17.6 Hz, 1H), 2.32 (s, 3H), 1.48 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.0, 168.3, 149.3, 140.3, 139.3, 134.0, 132.7, 130.3, 129.4, 128.7, 128.3, 88.5, 79.0, 61.2, 60.3, 59.3, 51.0, 43.9, 24.4, 23.4, 21.1, 14.9, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}Cl_2N_2O_6S$ ($[M+H]^+$): 581.1274, found: 581.1269.



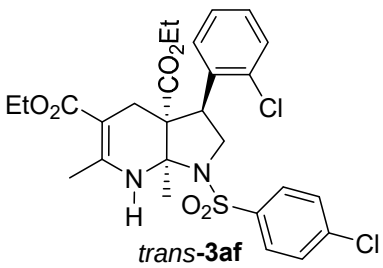
trans-**3ae**

Diethyl (3*R*, 3a*R*, 7a*R*)-3-(3-chlorophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ae**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ae** was obtained as a white solid following the general procedure (40.0 mg, 69% yield). ee = 98%, $[\alpha]_D^{23}$ = 53.2 (*c* = 0.69, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I＝254 nm): t_R = 13.1 min (minor), 24.2 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.29 (m, 1H), 7.27–7.22 (m, 2H), 7.16 (m, 1H), 4.76 (s, 1H), 4.27 (pseudo t, *J* = 10.5 Hz, 1H), 4.14–4.01 (m, 4H), 3.89 (pseudo t, *J* = 9.3 Hz, 1H), 3.53 (pseudo t, *J* = 10.5 Hz, 1H), 2.37 (d, *J* = 17.1 Hz, 1H), 2.13 (s, 3H), 1.82 (d, *J* = 17.1 Hz, 1H), 1.80 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 167.8, 146.8, 139.3, 138.9, 136.9, 134.4, 129.8, 129.7, 129.3, 128.2, 127.3, 94.6, 78.6, 61.5, 59.4, 53.3, 46.9, 44.4, 27.4, 24.3, 20.8, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}Cl_2N_2O_6S$ ($[M+H]^+$): 581.1274, found: 581.1271.



cis-**3ae**

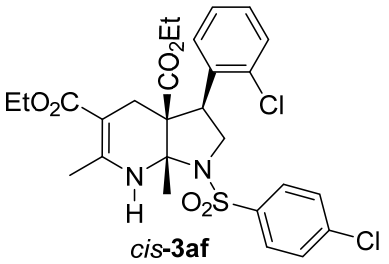
Diethyl (3*R*, 3a*S*, 7a*S*)-3-(3-chloromophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ad**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ae** was obtained as a white solid following the general procedure (16.2 mg, 28% yield). ee = 98%, $[\alpha]_D^{23}$ = -32.7 (*c* = 0.63, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AD-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I ＝254 nm): t_R = 10.7 min (minor), 15.9 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.26–7.20 (m, 2H), 7.14 (s, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 5.48 (s, 1H), 4.30–4.24 (m, 1H), 4.20–4.12 (m, 3H), 3.90–3.78 (m, 2H), 3.61 (pseudo t, *J* = 9.9 Hz, 1H), 2.83 (d, *J* = 17.1 Hz, 1H), 2.37 (d, *J* = 17.1 Hz, 1H), 2.32 (s, 3H), 1.49 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.0, 168.3, 149.4, 140.3, 139.3, 136.4, 134.5, 129.8, 129.5, 128.9, 128.3, 127.4, 88.5, 79.0, 61.3, 60.3, 59.4, 50.9, 44.2, 24.5, 23.4, 21.0, 14.8, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}Cl_2N_2O_6S$ ($[M+H]^+$): 581.1274, found: 581.1267.



trans-**3af**

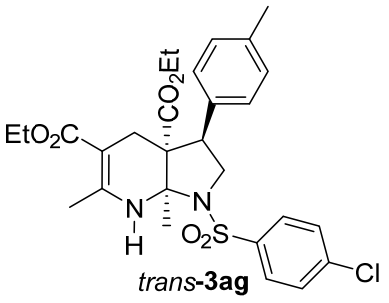
Diethyl (3*R*, 3a*R*, 7a*R*)-3-(2-chlorophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3af**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3af** was obtained as a white solid following the general procedure (35.4 mg, 61% yield). ee = 98%, $[\alpha]_D^{23}$ = +54.6

(*c* = 0.94, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 17.5 min (minor), 23.2 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.38–7.34 (m, 2H), 7.23–7.18 (m, 2H), 4.94 (s, 1H), 4.63 (pseudo t, *J* = 9.4 Hz, 1H), 4.03–3.90 (m, 5H), 3.56 (pseudo t, *J* = 9.9 Hz, 1H), 2.68 (d, *J* = 16.5 Hz, 1H), 2.15 (m, 4H), 1.90 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.3, 167.5, 148.8, 139.2, 139.1, 136.2, 133.7, 129.9, 129.3, 129.2, 128.9, 128.2, 126.6, 92.5, 79.5, 61.3, 59.3, 53.7, 48.9, 40.8, 26.8, 25.0, 20.8, 14.6, 13.7; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}Cl_2N_2O_6S$ ($[M+H]^+$): 581.1274, found: 581.1275.



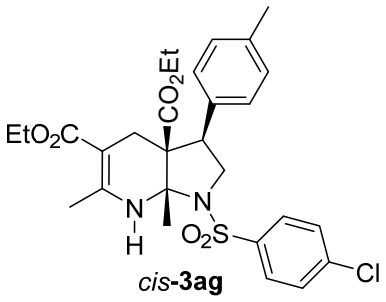
cis-**3af**

Diethyl (3*R*, 3a*S*, 7a*S*)- 3-(2-chloromophenyl)-1-((4-chlorophenyl) sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3af**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3af** was obtained as a white solid following the general procedure (14.5 mg, 25% yield). ee = 98%, $[\alpha]_D^{23}$ = -61 (*c* = 0.41, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I =254 nm): t_R = 10.6 min (minor), 25.8 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.38 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.25 (m, 1H), 7.21–7.15 (m, 2H), 5.32 (s, 1H), 4.38 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.20–4.07 (m, 2H), 4.01–3.94 (m, 2H), 3.89–3.82 (m, 1H), 2.66 (d, *J* = 17.6 Hz, 1H), 2.45 (d, *J* = 17.6 Hz, 1H), 2.31 (s, 3H), 1.47 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 168.7, 147.1, 140.5, 139.2, 136.5, 132.5, 130.5, 129.4, 129.2, 128.43, 128.4, 126.7, 89.6, 78.3, 61.2, 60.0, 59.1, 52.5, 40.6, 23.8, 23.6, 21.1, 14.8, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{31}Cl_2N_2O_6S$ ($[M+H]^+$): 581.1274, found: 581.1277.



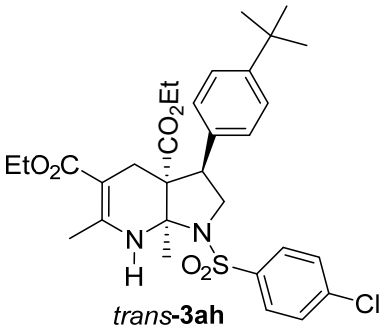
trans-**3ag**

Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(*p*-tolyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ag**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ag** was obtained as a white solid following the general procedure (46.0 mg, 82% yield). ee = 97%, $[\alpha]_D^{23}$ = +57.2 (*c* = 0.69, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 10/90, flow rate =1.0 mL/min, I=254 nm): t_R = 21.2 min (major), 28.2 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.13 (AB, *J* = 8.3 Hz, 4H), 4.76 (s, 1H), 4.28 (pseudo t, *J* = 9.9 Hz, 1H), 4.11–3.98 (m, 4H), 3.88 (pseudo t, *J* = 9.4 Hz, 1H), 3.56 (pseudo t, *J* = 9.9 Hz, 1H), 2.38 (d, *J* = 17.1 Hz, 1H), 2.31 (s, 3H), 1.82 (d, *J* = 17.1 Hz, 1H), 1.80 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 167.9, 146.6, 139.1, 139.0, 137.6, 131.5, 129.2, 129.18, 129.15, 128.1, 94.8, 78.7, 61.2, 59.3, 53.2, 47.1, 44.4, 27.6, 24.2, 21.1, 20.8, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{28}H_{34}ClN_2O_6S$ ($[M+H]^+$): 561.1821, found: 561.1812.



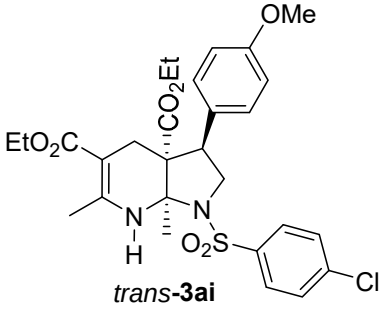
cis-**3ag**

Diethyl (3*R*, 3a*S*, 7a*S*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(*p*-tolyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ag**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ag** was obtained as a white solid following the general procedure (6.7 mg, 12% yield). ee = 94%, $[\alpha]_D^{23}$ = -23.3 (*c* = 0.89, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 9.3 min (minor), 14.7 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.04 (AB, *J* = 8.3 Hz, 4H), 5.46 (s, 1H), 4.32–4.26 (m, 1H), 4.18–4.09 (m, 3H), 3.88–3.75 (m, 2H), 3.60 (pseudo t, *J* = 9.9 Hz, 1H), 2.85 (d, *J* = 17.0 Hz, 1H), 2.35 (d, *J* = 17.1 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.49 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.3, 168.5, 149.2, 140.5, 139.2, 137.8, 131.0, 129.4, 129.2, 128.7, 128.3, 88.7, 79.0, 61.0, 60.3, 59.2, 51.2, 44.3, 24.5, 23.4, 21.2, 21.1, 14.9, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{28}H_{34}ClN_2O_6S$ ($[M+H]^+$): 561.1821, found: 561.1830.



trans-**3ah**

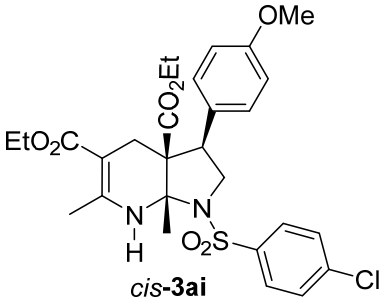
Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(4-*tert*-butylphenyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ah**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ah** was obtained as a white solid following the general procedure (53.0 mg, 88% yield). ee = 99%, $[\alpha]_D^{23}$ = +50.6 (*c* = 1.09, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AD-H column, 10% IPA in hexanes, flow rate = 1.0 mL/min, I=254 nm): t_R = 9.2 min (minor), 15.7 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.25 (AB, *J* = 8.3 Hz, 4H), 4.74 (s, 1H), 4.29 (dd, *J* = 10.5, 9.4 Hz, 1H), 4.13–4.00 (m, 4H), 3.89 (pseudo t, *J* = 9.4 Hz, 1H), 3.58 (pseudo t, *J* = 10.5 Hz, 1H), 2.41 (d, *J* = 17.0 Hz, 1H), 2.12 (s, 3H), 1.82 (d, *J* = 17.0 Hz, 1H), 1.80 (s, 3H), 1.29 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.8, 168.0, 150.8, 146.5, 139.1, 139.0, 131.6, 129.2, 129.0, 128.1, 125.4, 94.9, 78.7, 61.2, 59.4, 53.2, 47.2, 44.2, 34.6, 31.4, 27.6, 24.3, 20.9, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{31}H_{40}ClN_2O_6S$ ($[M+H]^+$): 603.2290, found: 603.2286.



trans-**3ai**

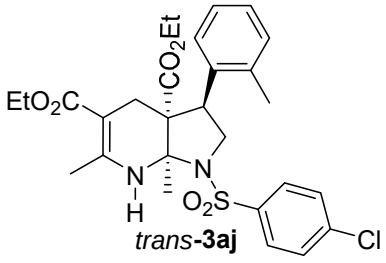
Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(4-methoxyphenyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ai**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ai** was obtained as a white solid following the general procedure (40.9 mg, 71% yield). ee = 97%, $[\alpha]_D^{23}$ = +62.2 (*c* = 0.90, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I=254 nm): t_R = 10.3 min (minor), 20.6 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* =

8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.77 (s, 1H), 4.26 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.10–3.97 (m, 4H), 3.86 (pseudo t, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 3.53 (pseudo t, *J* = 10.4 Hz, 1H), 2.35 (d, *J* = 17.1 Hz, 1H), 2.12 (s, 3H), 1.81 (d, *J* = 17.1 Hz, 1H), 1.80 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 167.9, 159.2, 146.7, 139.1, 139.0, 130.0, 129.2, 128.1, 126.4, 113.8, 94.7, 78.7, 61.2, 59.3, 55.3, 53.2, 47.2, 44.1, 27.6, 24.2, 20.8, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{28}H_{34}ClN_2O_7S$ ($[M+H]^+$): 577.1770, found: 577.1765.



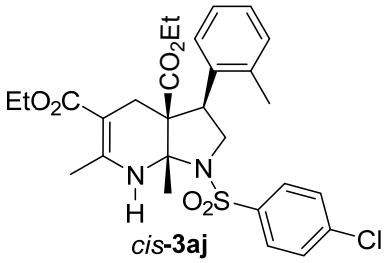
cis-**3ai**

Diethyl (3*R*, 3a*S*, 7a*S*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(4-methoxyphenyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ai**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ai** was obtained as a white solid following the general procedure (6.3 mg, 11% yield). ee = 93%, $[\alpha]_D^{23}$ = -12.3 (*c* = 0.69, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I＝254 nm): t_R = 13.1 min (minor), 20.2 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.46 (s, 1H), 4.31–4.26 (m, 1H), 4.17–4.08 (m, 3H), 3.88–3.73 (m, 2H), 3.76 (s, 3H), 3.57 (pseudo t, *J* = 10.5 Hz, 1H), 2.82 (d, *J* = 17.1 Hz, 1H), 2.34 (d, *J* = 17.0 Hz, 1H), 2.31 (s, 3H), 1.47 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.2, 168.4, 159.3, 149.1, 140.4, 139.1, 129.9, 129.3, 128.3, 125.9, 113.8, 88.6, 78.9, 61.0, 60.3, 59.1, 55.3, 51.2, 43.9, 24.4, 23.3, 21.0, 14.8, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{28}H_{34}ClN_2O_7S$ ($[M+H]^+$): 577.1770, found: 577.1772.



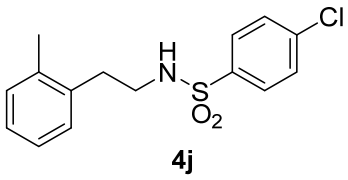
trans-**3aj**

Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(*o*-tolyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3aj**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3aj** was obtained as a white solid following the general procedure (35.3 mg, 63% yield). ee = 97%, $[\alpha]_D^{23}$ = +73.3 (*c* = 0.70, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IA column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I＝254 nm): t_R = 5.7 min (minor), 7.1 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.27 (m, 1H), 7.16 (m, 3H), 4.88 (s, 1H), 4.37 (dd, *J* = 10.5, 8.8 Hz, 1H), 4.08–4.00 (m, 2H), 3.97–3.88 (m, 2H), 3.84 (pseudo t, *J* = 8.8 Hz, 1H), 3.45 (pseudo t, *J* = 10.5 Hz, 1H), 2.74 (d, *J* = 15.9 Hz, 1H), 2.42 (s, 3H), 2.17 (s, 3H), 2.10 (d, *J* = 15.9 Hz, 1H), 1.90 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 167.7, 147.8, 139.1, 138.9, 138.5, 133.6, 131.1, 129.2, 128.1, 127.9, 127.6, 125.8, 93.5, 79.5, 61.1, 59.3, 53.4, 49.1, 40.3, 27.7, 24.7, 20.7, 20.5, 14.6, 13.7; **HRMS** (ESI-TOF) Calculated for $C_{28}H_{34}ClN_2O_6S$ ($[M+H]^+$): 561.1821, found: 561.1822.



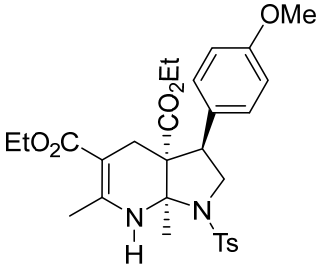
cis-**3aj**

Diethyl (3*R*, 3a*S*, 7a*S*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(*o*-tolyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3aj**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3aj** was obtained as a white solid following the general procedure (6.7 mg, 12% yield). ee = 97%, $[\alpha]_D^{23}$ = -57.4 (*c* = 0.1, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IC column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 7.2 min (minor), 16.9 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.15 (m, 3H), 7.11–7.07 (m, 1H), 5.44 (s, 1H), 4.22 (m, 1H), 4.19–4.07 (m, 2H), 4.05–3.94 (m, 3H), 3.90–3.84 (m, 1H), 2.51 (AB, *J* = 18.2 Hz, 2H), 2.32 (s, 3H), 2.23 (s, 3H), 1.48 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 168.5, 147.8, 140.5, 139.1, 138.8, 132.6, 131.3, 129.4, 128.4, 127.8, 126.6, 125.9, 88.6, 78.3, 61.1, 59.9, 59.1, 53.0, 40.4, 23.6, 23.5, 21.3, 19.8, 14.8, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{28}H_{34}ClN_2O_6S$ ($[M+H]^+$): 561.1821, found: 561.1828.



4j

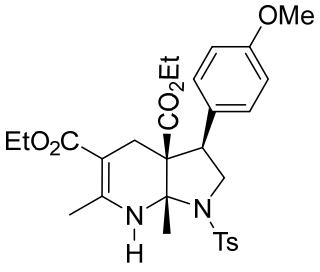
4-Chloro-*N*-(2-methylphenethyl) benzenesulfonamide (**4j**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound **4j** was obtained as a primrose solid following the general procedure (6.8 mg, 22% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.15–7.09 (m, 3H), 7.02 (m, 1H), 4.85 (brs, 1H), 3.18 (m, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.23 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.2, 138.5, 136.4, 135.7, 130.7, 129.5, 129.4, 128.6, 127.1, 126.4, 43.1, 33.4, 19.3; **HRMS** (ESI-TOF) Calculated for $C_{15}H_{17}ClNO_2S$ ($[M+H]^+$): 310.0663, found: 310.0657.



trans-**3ak**

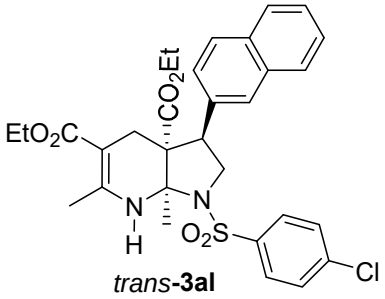
Diethyl (3*R*, 3a*R*, 7a*R*)-3-(4-methoxyphenyl)-6, 7a-dimethyl-1-tosyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ak**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ak** was obtained as a white solid following the general procedure (40.1 mg, 72% yield). ee = 94%; The run with 0.12 mmol of **1a** and 0.1 mmol of (±)-**2k** under the otherwise same reaction conditions provided the same product in 75% yield (95% ee). $[\alpha]_D^{23}$ = 78.5 (*c* = 0.68, $CHCl_3$) for 95% ee, **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 8.4 min (minor), 11.8 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.86 (s, 1H), 4.24 (pseudo t, *J* = 10.5 Hz, 1H), 4.09–3.97 (m, 4H), 3.83 (pseudo t, *J* = 9.4 Hz, 1H), 3.77 (s, 3H), 3.52 (dd, *J* = 10.5, 9.4 Hz, 1H), 2.39 (s, 3H), 2.33 (d, *J* = 16.5 Hz, 1H), 2.13 (s, 3H), 1.85 (d, *J* = 16.5 Hz, 1H), 1.79 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.9, 168.1, 159.2, 147.1, 143.4, 137.6, 130.5, 129.6, 126.8, 126.7, 113.8, 94.3, 78.5, 61.1, 59.1, 55.3, 53.4, 47.1, 44.2, 27.6, 24.1, 21.6, 20.9, 14.7, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{29}H_{37}N_2O_7S$ ($[M+H]^+$): 557.2316, found: 557.2313.

The crystals of *trans*-**3ak** suitable for x-ray crystallographic analysis was obtained by recrystallization from petroleum ether-ethyl acetate to provide colorless crystals, m.p. = 183–184 °C, ee > 99%.



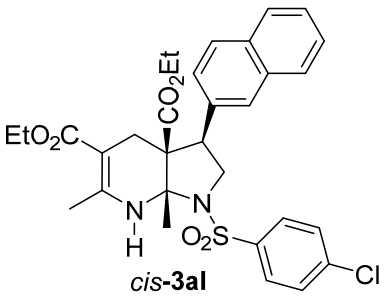
cis-**3ak**

Diethyl (3*R*, 3a*S*, 7a*S*)-3-(4-methoxyphenyl)-6, 7a-dimethyl-1-tosyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3ak**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3ak** was obtained as a white solid following the general procedure (5.6 mg, 10% yield). ee = 85%; The run with 0.12 mmol of **1a** and 0.1 mmol of (±)-**2k** under the otherwise same reaction conditions provided the same product in 12% yield (85% ee). $[\alpha]_D^{23}$ = -10.9 (*c* = 0.46, $CHCl_3$) for 85% ee, **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I=254 nm): t_R = 10.9 min (major), 14.9 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.53 (s, 1H), 4.32–4.25 (m, 1H), 4.17–4.09 (m, 3H), 3.88–3.76 (m, 2H), 3.77 (s, 3H), 3.57 (pseudo t, *J* = 10.5 Hz, 1H), 2.83 (d, *J* = 17.0 Hz, 1H), 2.44 (s, 3H), 2.36 (d, *J* = 17.1 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.4, 168.5, 159.3, 149.4, 143.5, 139.0, 130.0, 129.7, 126.9, 126.2, 113.8, 88.6, 78.9, 60.9, 60.4, 59.1, 55.3, 51.2, 43.8, 24.7, 23.5, 21.7, 21.1, 14.9, 13.8; **HRMS** (ESI-TOF) Calculated for $C_{29}H_{37}N_2O_7S$ ($[M+H]^+$): 557.2316, found: 557.2309.



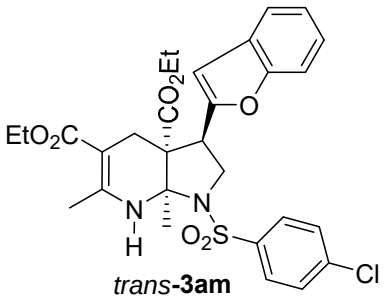
trans-**3al**

Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(2-naphthyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3al**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3al** was obtained as a white solid following the general procedure (48.3 mg, 81% yield). ee = 94%, $[\alpha]_D^{23}$ = +76.2 (*c* = 0.52, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 8.9 min (major), 10.8 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.82–7.77 (m, 3H), 7.73–7.71 (m, 3H), 7.48–7.45 (m, 4H), 7.41 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.80 (s, 1H), 4.49 (pseudo t, *J* = 10.5 Hz, 1H), 4.13–3.97 (m, 5H), 3.74 (pseudo t, *J* = 10.5 Hz, 1H), 2.42 (d, *J* = 17.1 Hz, 1H), 2.14 (s, 3H), 1.96 (d, *J* = 17.1 Hz, 1H), 1.86 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.8, 167.8, 146.8, 139.2, 139.0, 133.2, 132.9, 132.3, 129.3, 128.6, 128.2, 128.1, 128.0, 127.6, 127.1, 126.4, 126.3, 94.8, 78.8, 61.3, 59.3, 53.6, 47.1, 44.9, 27.6, 24.4, 20.8, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{31}H_{34}ClN_2O_6S$ ($[M+H]^+$): 597.1821, found: 597.1823.



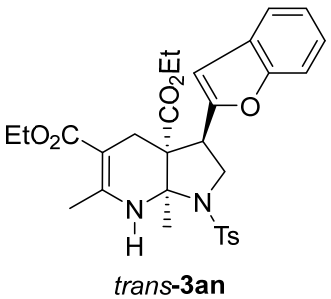
cis-**3al**

Diethyl (3*R*, 3a*S*, 7a*S*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(2-naphthyl) -1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*cis*-**3al**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *cis*-**3al** was obtained as a white solid following the general procedure (10.7 mg, 18% yield). ee = 92%, $[\alpha]_D^{23}$ = -20.1 (*c* = 0.47, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AS-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 10.9 min (minor), 17.4 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.80 (m, 1H), 7.76 (m, 2H), 7.61 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.47 (m, 2H), 7.26 (m, 1H), 5.53 (s, 1H), 4.38–4.26 (m, 3H), 4.22–4.15 (m, 1H), 3.88–3.81 (m, 2H), 3.76–3.70 (m, 1H), 2.92 (d, *J* = 17.1 Hz, 1H), 2.40 (d, *J* = 17.1 Hz, 1H), 2.37 (s, 3H), 1.52 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.2, 168.5, 149.3, 140.5, 139.2, 133.3, 133.1, 131.7, 129.5, 128.4, 128.1, 128.0, 127.9, 127.7, 126.9, 126.4, 126.3, 88.7, 79.1, 61.1, 60.5, 59.3, 51.3, 44.8, 24.5, 23.5, 21.1, 14.9, 13.7; **HRMS** (ESI-TOF) Calculated for $C_{31}H_{34}ClN_2O_6S$ ($[M+H]^+$): 597.1821, found: 597.1817.



trans-**3am**

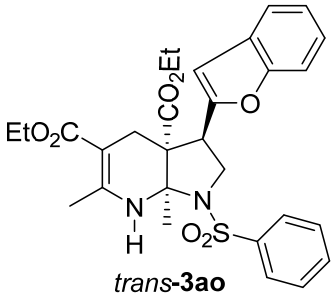
Diethyl (3*R*, 3a*R*, 7a*R*)-1-((4-chlorophenyl)sulfonyl)-6, 7a-dimethyl-3-(2-benzofuranyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3am**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3am** was obtained as a white solid following the general procedure (56.9 mg, 97% yield). ee = 99%, $[\alpha]_D^{23}$ = +96.5 (*c* = 1.59, $CHCl_3$), **HPLC** (Daicel CHIRALPAK AD-H column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 20.3 min (minor), 35.1 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42 (m, 3H), 7.27–7.19 (m, 2H), 6.62 (s, 1H), 4.79 (s, 1H), 4.50 (pseudo t, *J* = 9.9 Hz, 1H), 4.19–4.08 (m, 2H), 4.06–3.98 (m, 3H), 3.75 (pseudo t, *J* = 9.9 Hz, 1H), 2.50 (d, *J* = 17.6 Hz, 1H), 2.11 (s, 3H), 1.98 (d, *J* = 17.6 Hz, 1H), 1.79 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.2, 167.7, 154.8, 152.6, 146.7, 139.1, 139.0, 129.2, 128.1, 128.0, 124.2, 122.9, 120.8, 111.2, 106.2, 94.6, 77.9, 61.4, 59.3, 52.9, 45.3, 39.9, 27.0, 24.6, 20.7, 14.5, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{29}H_{32}ClN_2O_7S$ ($[M+H]^+$): 587.1613, found: 587.1605.



trans-**3an**

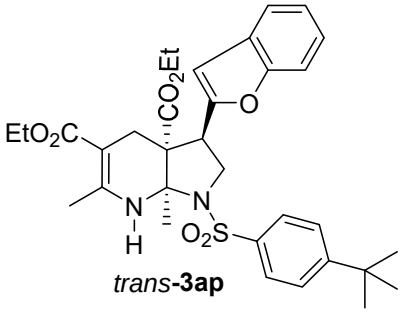
Diethyl (3*R*, 3a*R*, 7a*R*)-3-(2-benzofuranyl)-6, 7a-dimethyl-1-tosyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3an**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3an** was obtained as a white solid following the general procedure (53.8 mg, 95% yield). ee = 98%, $[\alpha]_D^{23}$ = +81.3 (*c* = 1.34, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I=254 nm): t_R = 14.0 min (major), 19.2 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.7 Hz,

1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.25–7.17 (m, 4H), 6.60 (s, 1H), 4.86 (s, 1H), 4.48 (pseudo t, *J* = 9.9 Hz, 1H), 4.18–4.08 (m, 2H), 4.03–3.95 (m, 3H), 3.72 (pseudo t, *J* = 9.9 Hz, 1H), 2.48 (d, *J* = 17.6 Hz, 1H), 2.39 (s, 3H), 2.12 (s, 3H), 2.01 (d, *J* = 17.1 Hz, 1H), 1.79 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.5, 167.9, 154.8, 153.0, 147.1, 143.5, 137.6, 129.6, 128.2, 126.7, 124.2, 122.9, 120.8, 111.2, 106.0, 94.2, 77.7, 61.4, 59.1, 53.0, 45.3, 40.1, 27.0, 24.6, 21.6, 20.8, 14.6, 14.1; **HRMS** (ESI-TOF) Calculated for $C_{30}H_{35}N_2O_7S$ ([M+H]$^+$): 567.2159, found: 567.2156.



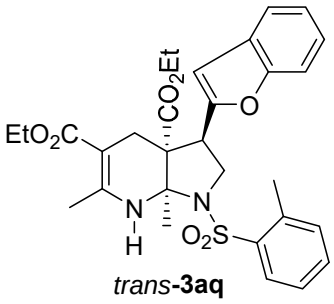
trans-**3ao**

Diethyl (3*R*, 3a*R*, 7a*R*)-3-(2-benzofuranyl)-6, 7a-dimethyl-1-(phenylsulfonyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ao**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ao** was obtained as a white solid following the general procedure (51.4 mg, 93% yield). ee = 98%, $[\alpha]_D^{23}$ = +66.8 (*c* = 1.02, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I ＝254 nm): t_R = 9.0 min (major), 11.9 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.54–7.40 (m, 5H), 7.26–7.18 (m, 2H), 6.61 (s, 1H), 4.82 (s, 1H), 4.49 (pseudo t, *J* = 9.9 Hz, 1H), 4.18–4.08 (m, 2H), 4.03–3.96 (m, 3H), 3.77 (pseudo t, *J* = 9.9 Hz, 1H), 2.48 (d, *J* = 17.6 Hz, 1H), 2.08 (s, 3H), 2.02 (d, *J* = 17.6 Hz, 1H), 1.80 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.4, 167.8, 154.8, 152.9, 147.0, 140.6, 132.7, 129.0, 128.1, 126.6, 124.2, 122.9, 120.8, 111.2, 106.1, 94.3, 77.7, 61.4, 59.1, 52.9, 45.4, 40.0, 27.0, 24.5, 20.7, 14.6, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{29}H_{33}N_2O_7S$ ([M+H]$^+$): 553.2003, found: 553.2005.



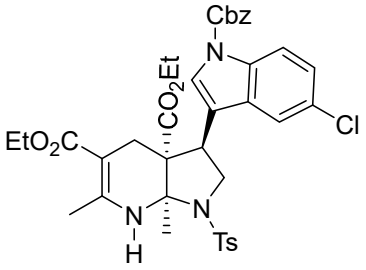
trans-**3ap**

Diethyl (3*R*, 3a*R*, 7a*R*)-3-(2-benzofuranyl)-1-((4-*tert*-butylphenyl)sulfonyl)-6, 7a-dimethyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3ap**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ap** was obtained as a white solid following the general procedure (56.0 mg, 92% yield). ee = 98%, $[\alpha]_D^{23}$ = +74.2 (*c* = 1.19, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I＝254 nm): t_R = 7.8 min (major), 9.3 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.26–7.18 (m, 2H), 6.61 (s, 1H), 4.80 (s, 1H), 4.49 (pseudo t, *J* = 9.9 Hz, 1H), 4.19–4.08 (m, 2H), 4.03–3.94 (m, 3H), 3.78 (pseudo t, *J* = 9.9 Hz, 1H), 2.50 (d, *J* = 17.6 Hz, 1H), 2.05 (m, 4H), 1.79 (s, 3H), 1.32 (s, 9H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.5, 167.8, 156.5, 154.8, 153.0, 147.1, 137.1, 128.2, 126.5, 125.9, 124.1, 122.9, 120.8, 111.2, 106.0, 94.1, 77.6, 61.3, 59.1, 52.8, 45.4, 40.0, 35.2, 31.1, 26.9, 24.5, 20.8, 14.5, 14.0; **HRMS** (ESI-TOF) Calculated for $C_{33}H_{41}N_2O_7S$ ([M+H]$^+$): 609.2629, found: 609.2634.



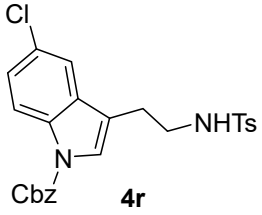
trans-**3aq**

Diethyl (3*R*, 3a*R*, 7a*R*)-3-(2-benzofuranyl)-6, 7a-dimethyl-1-(*o*-tosyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3aq**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3aq** was obtained as a white solid following the general procedure (54.4 mg, 96% yield). ee = 99%, $[\alpha]_D^{23}$ = +51.0 (*c* = 1.02, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I＝254 nm): t_R = 12.9 min (major), 15.6 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.49–7.45 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.30–7.17 (m, 4H), 6.59 (s, 1H), 4.86 (s, 1H), 4.54 (pseudo t, *J* = 9.9 Hz, 1H), 4.21–4.11 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.90 (pseudo t, *J* = 9.9 Hz, 1H), 3.53 (pseudo t, *J* = 9.9 Hz, 1H), 2.58 (s, 3H), 2.56 (d, *J* = 17.6 Hz, 1H), 2.40 (d, *J* = 17.1 Hz, 1H), 2.03 (s, 3H), 1.86 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 168.1, 154.8, 153.1, 147.6, 138.4, 138.1, 133.3, 132.8, 129.7, 128.1, 126.2, 124.1, 122.9, 120.8, 111.2, 106.1, 94.3, 78.0, 61.4, 59.2, 53.5, 45.0, 40.0, 25.2, 25.16, 20.5, 19.5, 14.6, 14.1; **HRMS** (ESI-TOF) Calculated for $C_{30}H_{35}N_2O_7S$ ([M+H]$^+$): 567.2159, found: 567.2161.



trans-**3ar**

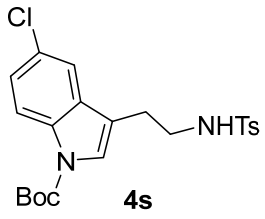
Diethyl (3R,3aR,7aR)-3-(1-((benzyloxy)carbonyl)-5-chloro-1*H*-indol-3-yl)-6,7a-dimethyl-1-tosyl-1,2,3,4,7,7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**3ar**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3ar** was obtained as a yellow solid following the general procedure (13.9 mg, 19% yield). ee = 91%, $[\alpha]_D^{23}$ = +87.8 (*c* = 0.28, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I＝254 nm): t_R = 15.1 min (major), 19.2 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (brs, 1H), 7.69 (m, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.53 (s, 1H), 7.47 (m, 2H), 7.43–7.37 (m, 3H), 7.25 (m, 3H), 5.45 (AB, *J* = 12.1 Hz, 2H), 4.87 (s, 1H), 4.37 (dd, *J* = 11.0, 9.3 Hz, 1H), 4.05–3.94 (m, 4H), 3.87 (pseudo t, *J* = 9.4 Hz, 1H), 3.38 (pseudo t, *J* = 10.5 Hz, 1H), 2.52 (d, *J* = 16.6 Hz, 1H), 2.40 (s, 3H), 2.16 (s, 3H), 2.01 (d, *J* = 16.6 Hz, 1H), 1.85 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.6, 167.8, 150.6, 147.5, 143.7, 137.3, 134.9, 133.5, 131.9, 129.7, 129.1, 129.0, 128.9, 128.8, 126.8, 125.3, 120.1, 116.3, 115.4, 94.0, 78.6, 69.3, 61.5, 59.1, 52.3, 48.2, 37.0, 27.3, 25.1, 21.7, 20.8, 14.6, 13.9; **HRMS** (ESI-TOF) Calculated for $C_{38}H_{41}ClN_3O_8S$ ([M+H]$^+$): 734.2297, found: 734.2289.



4r

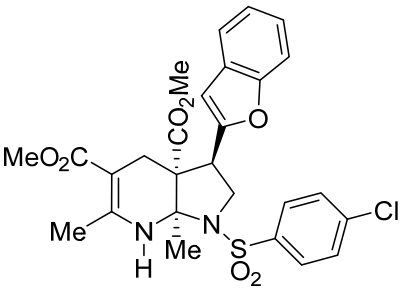
Benzyl 5-chloro-3-(2-((4-methylphenyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (**4r**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound **4r** was obtained as a white solid following the general procedure (38.6 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.04 (brs, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.49–7.38 (m, 6H), 7.26–7.23 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 2H), 5.41 (s, 2H), 4.80 (t, *J* = 6.6 Hz, 1H), 3.24 (m, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.4, 143.6, 136.7, 134.9, 134.1, 131.2, 129.7, 129.0, 128.9, 128.8, 127.0,

125.1, 124.7, 118.5, 116.8, 116.5, 69.1, 42.3, 25.3, 21.6; **HRMS** (ESI-TOF) Calculated for $C_{25}H_{24}ClN_2O_4S$ ([M+H]$^+$): 483.1140, found: 483.1142.



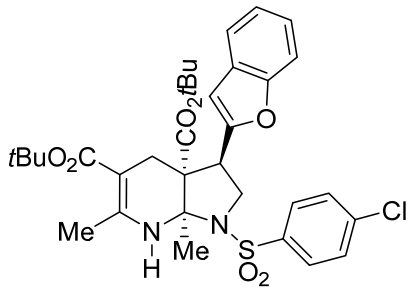
4s

tert-Butyl 5-chloro-3-(2-((4-methylphenyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (**4s**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound **4s** was obtained as a yellow solid following the general procedure (39.4 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.04 (brs, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.37 (s, 1H), 7.25–7.20 (m, 4H), 4.63 (t, *J* = 6.6 Hz, 1H), 3.26 (m, 2H), 2.80 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 1.66 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.3, 143.7, 136.6, 134.1, 131.1, 129.8, 128.4, 127.1, 125.1, 124.8, 118.4, 116.5, 115.8, 84.3, 42.3, 28.3, 25.4, 21.7; **HRMS** (ESI-TOF) Calculated for $C_{17}H_{18}ClN_2O_2S$ ([M+2H-Boc]$^+$): 349.0772, found: 349.0775.



trans-**3bm**

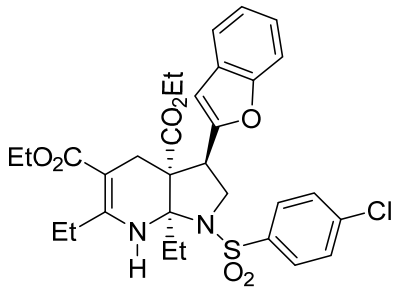
Dimethyl (3*R*,3a*R*,7a*R*)-3-(benzofuran-2-yl)-1-((4-chlorophenyl) sulfonyl)-6,7a-dimethyl-1,2,3,4,7,7a-hexahydro-3a*H*-pyrrolo [2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**3bm**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3bm** was obtained as a white solid following the general procedure (53.6 mg, 96% yield). ee = 99%, $[\alpha]_D^{23}$ = +80.2 (*c* = 1.06, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, I=254 nm): t_R = 8.9 min (major), 10.9 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.43 (m, 3H), 7.28–7.20 (m, 2H), 6.61 (s, 1H), 4.84 (s, 1H), 4.51 (pseudo t, *J* = 9.9 Hz, 1H), 3.99 (pseudo t, *J* = 9.4 Hz, 1H), 3.73 (pseudo t, *J* = 9.9 Hz, 1H), 3.69 (s, 3H), 3.55 (s, 3H), 2.48 (d, *J* = 17.6 Hz, 1H), 2.15 (s, 3H), 1.98 (d, *J* = 17.6 Hz, 1H), 1.78 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.9, 168.0, 154.8, 152.5, 147.2, 139.2, 138.9, 129.3, 128.1, 128.0, 124.3, 123.0, 120.9, 111.3, 106.2, 94.1, 77.9, 53.1, 52.7, 50.8, 45.1, 40.1, 27.0, 24.4, 20.7; **HRMS** (ESI-TOF) Calculated for $C_{27}H_{28}ClN_2O_7S$ ([M+H]$^+$): 559.1300, found: 559.1309.



trans-**3cm**

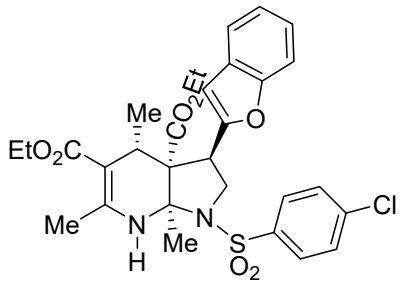
Di-*tert*-butyl (3*R*,3a*R*,7a*R*)-3-(benzofuran-2-yl)-1-((4-chloro phenyl)sulfonyl)-6,7a-dimethyl-1,2,3,4,7,7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**3cm**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3cm** was obtained as a white solid following the general procedure (60.4 mg, 94% yield). ee = 99%, $[\alpha]_D^{23}$ = +83.4 (*c* = 1.20, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, I=254 nm): t_R = 10.7 min (minor), 21.5 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 1H), 7.40 (m, 3H), 7.24–7.16 (m, 2H), 6.59 (s, 1H), 4.62 (s, 1H), 4.43 (pseudo t, *J* = 9.9 Hz, 1H), 3.99 (pseudo t, *J* = 9.4 Hz, 1H), 3.72 (pseudo t, *J* = 9.9 Hz, 1H), 2.43 (d, *J* = 17.6 Hz, 1H), 2.00 (s, 3H), 1.85 (d, *J* = 17.6 Hz, 1H), 1.80 (s, 3H), 1.37 (s, 18H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.2, 167.4, 154.7, 153.0, 145.1, 139.3, 138.9, 129.1, 128.1, 128.0, 124.1, 122.8,

120.8, 111.1, 105.8, 96.3, 81.8, 79.0, 77.9, 53.0, 45.4, 39.8, 28.5, 27.8, 27.0, 24.9, 21.1; **HRMS** (ESI-TOF) Calculated for $C_{33}H_{40}ClN_2O_7S$ ($[M+H]^+$): 643.2239, found: 643.2232.



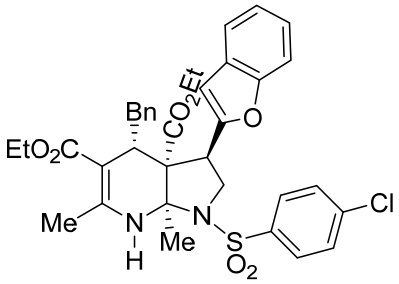
trans-**3dm**

Diethyl (3*R*,3a*R*,7a*R*)-3-(benzofuran-2-yl)-1-((4-chloro phenyl) sulfonyl)-6,7a-diethyl-1,2,3,4,7,7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**3dm**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3dm** was obtained as a white solid following the general procedure (55.3 mg, 90% yield). ee = 99%, $[\alpha]_D^{23}$ = +128.5 (*c* = 0.94, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IB column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I = 254 nm): t_R = 8.4 min (minor), 14.8 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (m, 3H), 7.26–7.17 (m, 2H), 6.59 (s, 1H), 4.89 (s, 1H), 4.58 (pseudo t, *J* = 9.9 Hz, 1H), 4.12–3.95 (m, 4H), 3.92 (pseudo t, *J* = 9.4 Hz, 1H), 3.70 (pseudo t, *J* = 9.9 Hz, 1H), 3.16–3.09 (m, 1H), 2.38 (d, *J* = 17.1 Hz, 1H), 2.22–2.06 (m, 3H), 1.78 (d, *J* = 17.1 Hz, 1H), 1.19–1.12 (m, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.5, 167.2, 154.7, 152.7, 152.5, 139.2, 138.2, 129.1, 128.4, 128.1, 124.2, 122.9, 120.9, 111.2, 106.4, 93.5, 81.2, 61.5, 59.2, 52.8, 45.6, 40.2, 33.6, 27.6, 25.2, 14.5, 14.0, 13.0, 9.2; **HRMS** (ESI-TOF) Calculated for $C_{31}H_{36}ClN_2O_7S$ ($[M+H]^+$): 615.1926, found: 615.1928.



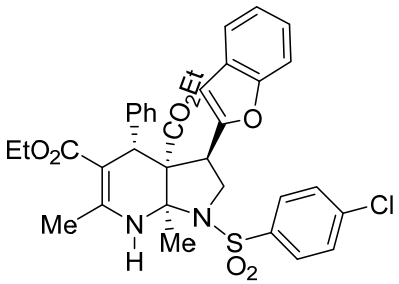
trans-**3em**

Diethyl (3*R*, 3a*R*, 4*S*, 7a*R*)-3-(benzofuran-2-yl)-1-((4-chloro phenyl)sulfonyl)-4,6,7a-trimethyl-1,2,3,4,7,7a-Hexahydro-3a*H*-pyrrolo [2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**3em**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3em** was obtained as a white solid following the general procedure (56.4 mg, 94% yield). ee = 99%, $[\alpha]_D^{23}$ = +47.4 (*c* = 1.11, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IB column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I = 254 nm): t_R = 9.8 min (minor), 17.9 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.27–7.19 (m, 2H), 6.82 (s, 1H), 4.54 (s, 1H), 4.42 (pseudo t, *J* = 9.9 Hz, 1H), 4.23–4.01 (m, 5H), 3.92 (pseudo t, *J* = 9.3 Hz, 1H), 3.04 (q, *J* = 6.6 Hz, 1H), 1.86 (s, 3H), 1.73 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.46 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.0, 167.6, 154.9, 152.1, 143.9, 139.8, 139.0, 129.1, 128.2, 128.0, 124.3, 123.0, 121.0, 111.2, 107.7, 102.6, 61.1, 60.2, 59.4, 45.8, 39.4, 28.5, 26.2, 20.5, 15.7, 14.6, 14.2; **HRMS** (ESI-TOF) Calculated for $C_{30}H_{34}ClN_2O_7S$ ($[M+H]^+$): 601.1770, found: 601.1767.



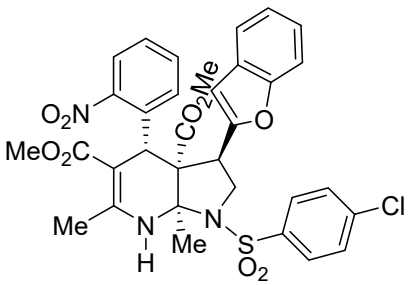
trans-**3fm**

Diethyl (3*R*, 3a*R*, 4*S*, 7a*R*)-3-(benzofuran-2-yl)-4-benzyl-1-((4-chloro phenyl)sulfonyl)-6,7a-dimethyl-1,2,3,4,7,7a-Hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**3fm**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3fm** was obtained as a white solid following the general procedure (55.7 mg, 82% yield). ee = 99%, $[\alpha]_D^{23}$ = +30.5 (*c* = 1.08, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IB column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I=254 nm): t_R = 11.7 min (minor), 24.8 min (major); **^{1}H NMR** (500 MHz, C_6D_6): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.31 (m, 1H), 7.26 (m, 1H), 7.13 (m, 2H), 7.04–6.91 (m, 7H), 6.35 (s, 1H), 5.02 (s, 1H), 3.97–3.84 (m, 3H), 3.81–3.72 (m, 3H), 3.13–3.07 (m, 1H), 2.93 (dd, *J* = 12.6, 2.7 Hz, 1H), 2.90–2.83 (m, 1H), 2.66 (dd, *J* = 12.7, 10.5 Hz, 1H), 2.17 (s, 3H), 1.85 (s, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.3, 167.2, 154.8, 153.0, 149.5, 140.5, 139.9, 139.6, 129.5, 129.4, 128.6, 128.2, 127.8, 125.8, 124.2, 122.8, 120.8, 111.1, 106.2, 99.5, 80.4, 64.7, 61.6, 58.6, 49.4, 44.4, 39.0, 38.1, 26.0, 20.4, 14.3, 13.3; **HRMS** (ESI-TOF) Calculated for $C_{36}H_{38}ClN_2O_7S$ ($[M+H]^+$): 677.2083, found: 677.2090.



trans-**3gm**

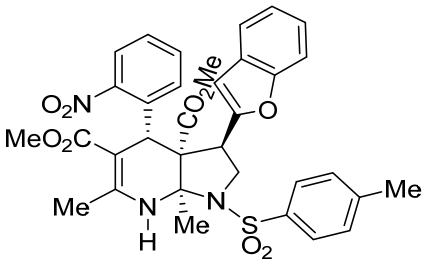
Diethyl (3*R*, 3a*R*, 4*S*, 7a*R*)-3-(benzofuran-2-yl)-1-((4-chlorophenyl)sulfonyl)-6,7a-dimethyl-4-phenyl-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2, 3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3gm**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3gm** was obtained as a white solid following the general procedure (64.9 mg, 98% yield). ee = 99%, $[\alpha]_D^{23}$ = +119.1 (*c* = 1.40, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 25/75, flow rate = 1.0 mL/min, I=254 nm): t_R = 11.1 min (major), 14.1 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.52–7.45 (m, 4H), 7.31–7.22 (m, 2H), 6.84 (pseudo t, *J* = 7.2 Hz, 1H), 6.80 (s, 1H), 6.67 (pseudo t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.7 Hz, 2H), 4.90 (s, 1H), 4.38 (pseudo t, *J* = 9.4 Hz, 1H), 4.31 (s, 1H), 4.16 (pseudo t, *J* = 9.9 Hz, 1H), 3.94–3.88 (m, 2H), 3.72–3.63 (m, 3H), 2.15 (s, 3H), 1.82 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.9, 167.0, 154.4, 152.2, 147.8, 141.1, 139.3, 139.27, 129.3, 128.6, 128.4, 127.0, 126.3, 124.4, 123.1, 121.0, 111.3, 108.4, 102.1, 79.4, 62.2, 61.1, 59.1, 46.2, 41.0, 40.9, 26.0, 20.7, 13.8, 13.77; **HRMS** (ESI-TOF) Calculated for $C_{35}H_{36}ClN_2O_7S$ ($[M+H]^+$): 663.1926, found: 663.1930.



trans-**3hm**

Dimethyl (3*R*, 3a*R*, 4*S*, 7a*R*)-3-(benzofuran-2-yl)-1-((4-chlorophenyl)sulfonyl)-6,7a-dimethyl-4-(2-nitrophenyl)-1,2,3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2, 3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3hm**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3hm** was obtained as a yellow solid following the general procedure (66.8 mg, 98% yield). ee = 99%, $[\alpha]_D^{23}$ = +174.9 (*c* =

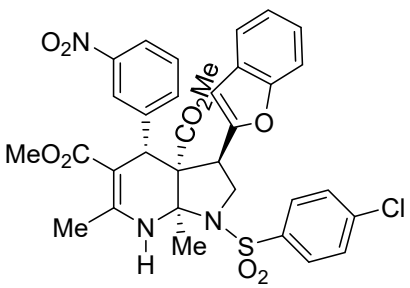
0.76, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IB column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I＝254 nm): t_R = 20.8 min (minor), 30.7 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.37–7.29 (m, 3H), 7.23–7.13 (m, 3H), 6.62 (s, 1H), 5.41 (s, 1H), 4.93 (s, 1H), 4.72 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.38 (dd, *J* = 9.4, 5.0 Hz, 1H), 4.16 (pseudo t, *J* = 9.4 Hz, 1H), 3.39 (s, 3H), 2.83 (s, 3H), 2.09 (s, 3H), 1.56 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.4, 166.4, 154.6, 154.4, 150.8, 149.4, 140.0, 139.6, 139.5, 132.3, 130.3, 129.4, 128.2, 128.1, 127.0, 124.3, 124.1, 122.9, 120.5, 110.9, 106.7, 96.0, 77.6, 62.9, 52.6, 50.1, 42.2, 37.9, 27.2, 21.5; **HRMS** (ESI-TOF) Calculated for $C_{33}H_{31}ClN_3O_9S$ ($[M+H]^+$): 680.1464, found: 680.1459.



trans-**3hn**

Dimethyl (3*R*, 3a*R*, 4*S*, 7a*R*)-3-(benzofuran-2-yl)-1-((4-methylphenyl)sulfonyl)-6, 7a-dimethyl-4-(2-nitrophenyl)-1, 2, 3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2, 3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3hn**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3hn** was obtained as a yellow solid following the general procedure (63.4 mg, 96% yield). ee = 93%, $[\alpha]_D^{23}$ = +184.8 (*c* = 1.17, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IB column, flow rate = isopropanol/*n*-hexane = 25/75, 1.0 mL/min, I＝254 nm): t_R = 10.6 min (minor), 11.4 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.74 (m, 3H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.36–7.28 (m, 5H), 7.22–7.18 (m, 2H), 7.14 (pseudo t, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 5.48 (s, 1H), 4.92 (s, 1H), 4.75 (dd, *J* = 8.8, 5.0 Hz, 1H), 4.35 (dd, *J* = 9.9, 4.9 Hz, 1H), 4.17 (pseudo t, *J* = 9.4 Hz, 1H), 3.38 (s, 3H), 2.80 (s, 3H), 2.39 (s, 3H), 2.08 (s, 3H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.4, 166.5, 154.9, 154.7, 151.3, 149.5, 144.0, 139.9, 138.7, 132.3, 130.5, 129.8, 128.1, 126.9, 126.89, 124.2, 124.1, 122.8, 120.5, 111.0, 106.5, 95.6, 63.2, 52.6, 50.2, 50.0, 42.3, 38.1, 27.2, 21.6, 21.5; **HRMS** (ESI-TOF) Calculated for $C_{34}H_{34}N_3O_9S$ ($[M+H]^+$): 660.2010, found: 660.2011.

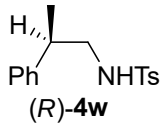
The crystals of *trans*-**3hn** suitable for x-ray crystallographic analysis was obtained by recrystallization from petroleum ether-ethyl acetate to provide colorless crystals, m.p. = 160–161 °C, ee > 99%.



trans-**3im**

Dimethyl (3*R*, 3a*R*, 4*S*, 7a*R*)-3-(benzofuran-2-yl)-1-((4-chlorophenyl)sulfonyl)-6,7a-dimethyl-4-(3-nitrophenyl)-1,2,3, 4, 7, 7a-hexahydro-3a*H*-pyrrolo[2, 3-b]pyridine-3a, 5-dicarboxylate (*trans*-**3im**). Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound *trans*-**3im** was obtained as a yellow solid following the general procedure (62.5 mg, 92% yield). ee = 99%, $[\alpha]_D^{23}$ = +123.6 (*c* = 1.12, $CHCl_3$), **HPLC** (Daicel CHIRALPAK IB column, isopropanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, I＝254 nm): t_R = 15.9 min (minor), 28.5 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.51–7.47 (m, 5H), 7.32 (pseudo t, *J* = 7.2 Hz, 1H), 7.26 (pseudo t, *J* = 7.2 Hz, 1H), 6.77 (s, 1H), 6.76–6.68 (m,

2H), 5.02 (s, 1H), 4.41 (pseudo t, *J* = 9.4 Hz, 1H), 4.30 (s, 1H), 4.19 (pseudo t, *J* = 9.9 Hz, 1H), 3.95 (pseudo t, *J* = 8.8 Hz, 1H), 3.53 (s, 3H), 3.20 (s, 3H), 2.16 (s, 3H), 1.79 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.9, 167.0, 154.3, 151.2, 149.0, 147.5, 143.6, 139.6, 139.2, 135.9, 129.5, 128.3, 127.7, 124.8, 123.8, 123.5, 121.7, 121.1, 111.5, 108.7, 100.6, 78.7, 62.1, 52.1, 50.5, 45.8, 41.1, 40.7, 26.0, 21.3; **HRMS** (ESI-TOF) Calculated for $C_{33}H_{31}ClN_3O_9S$ ($[M+H]^+$): 680.1464, found: 680.1471.

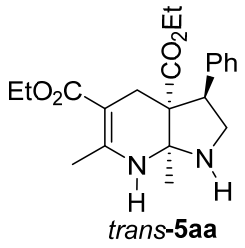


(*R*)-**4w**

(R)-4-Methyl-N-(2-phenylpropyl)benzenesulfonamide (**4w**).[4] Purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1→1:1 (v/v) containing 0.5 v% Et_3N). Compound **4s** was obtained as a white solid following the general procedure after a reaction time of 32 h (39.4 mg, 60% yield, 36% ee). **HPLC** (Daicel CHIRALPAK IC column, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, I＝254 nm): t_R = 15.9 min (major), 28.5 min (minor). The spectroscopic data agree with those of literature data.[4]

Procedure for the Transformation of *trans*-3aa to *trans*-5aa

Under argon atmosphere, to a stirred solution of the *trans*-**3aa** (136.7 mg, 0.25 mmol, 99% ee) in dry methanol (10.0 mL) was added magnesium turnings (600 mg, 25 mmol) at 25 °C, and the resulting reaction mixture was sonicated at 25±3 °C in a water bath for 4 h (monitored by TLC). The reaction mixture was filtered through a short pad of Celite and the filter cake was washed with EtOAc (10 mL x 2). The combined filtrate was concentrated in vacuo by rotary evaporation, and the residue was purified by flash chromatography on silica gel (eluting with CH_2Cl_2/CH_3OH/Et_3N (v/v) = 100:10:0.5) to afford the product *trans*-**5aa** as a yellow oil in 75% yield (70.1 mg).



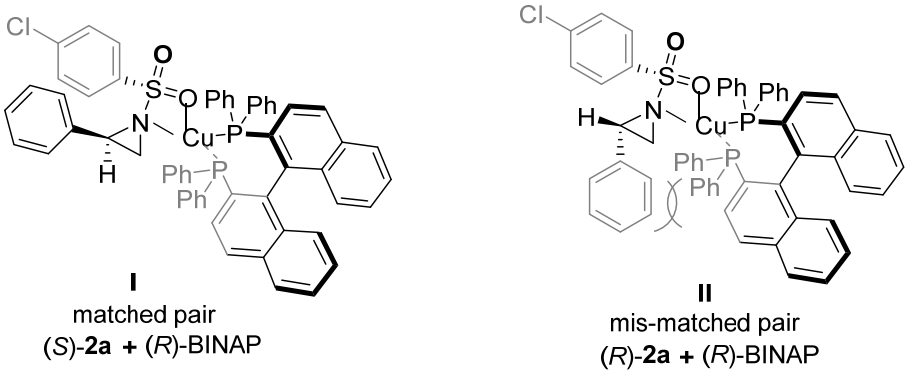
trans-**5aa**

Diethyl (3*R*,3a*R*,7a*S*)-6,7a-dimethyl-3-phenyl-1,2,3,4,7,7a-hexahydro-3a*H*-pyrrolo[2,3-b]pyridine-3a,5-dicarboxylate (*trans*-**5aa**). Compound *trans*-**5aa**. ee = 99%, $[\alpha]_D^{23}$ = -43.0 (*c* = 1.32, $CHCl_3$), **HPLC** (Daicel CHIRALPAK ID column, isopropanol/*n*-hexane = 25/75, flow rate = 1.0 mL/min, I＝254 nm): t_R = 8.3 min (minor), 9.4 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.23–7.15 (m, 5H), 4.25 (s, 1H), 4.24–4.15 (m, 2H), 4.03 (pseudo t, *J* = 8.8 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.45 (dd, *J* = 12.1, 8.3 Hz, 1H), 3.37 (m, 1H), 2.60 (brs, 1H), 2.41 (AB, *J* = 17.0 Hz, 2H), 2.14 (s, 3H), 1.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 175.3, 168.0, 150.1, 138.0, 129.2, 127.8, 127.0, 91.9, 77.6, 61.3, 58.7, 56.6, 52.0, 47.5, 25.3, 24.5, 21.2, 14.6, 14.3; **HRMS** (ESI-TOF) Calculated for $C_{21}H_{29}N_2O_4$ ($[M+H]^+$): 373.2122, found: 373.2129.

Tentative Stereochemical Models to Explain the Observed Enantio- and Diastereoselectivity (Figure S1)

Previous studies form our group and others (see refs. 7–9 in the main text) have shown that Cu(I)/Ag(I)-chiral diphosphine–catalyzed transformations of racemic 2-(hetero)aryl aziridines via kinetic resolution (KR) most probably proceed via a S_N2-type mechanism, as originally proposed by Ghorai and coworkers for general Lewis acid-catalyzed nucleophilic ring openings of aziridines.[5] Based on the experimental results and these previous studies, we have proposed a simplified stereochemical model to rationalize the matched/mis-matched effect (Table 1, entries 9–10) between the aziridine (*R/S*)-**2a** and Cu(I)-(*S*)-BINAP (Figure S1a). In this proposed model, the mis-matched pair is presumed to be less favored due to the steric repulsion between the 2-phenyl group of the aziridine and the two phenyl groups of the ligand. As confirmed by the x-ray structures of *cis*-**3aa** and *trans*-**3ak**, the major enantiomers of both the *trans*- and *cis*-products **3** derived from (*S*)-aziridine only. We thus propose that the diastereoselectivity of the reaction depends on the approaching face of the nucleophile HE **1a** (*Re vs Si*); the *Re*-face attack of HE **1a** leading to the major product is favored probably due to the reduced steric repulsion between the HE ring and the Ar group of the sulfonyl group and the two phenyl groups of the ligand (Figure S1b).

a) tentative explaination for the enantioselective kinetic resolution



b) tentative explaination for the diastereoselectivity

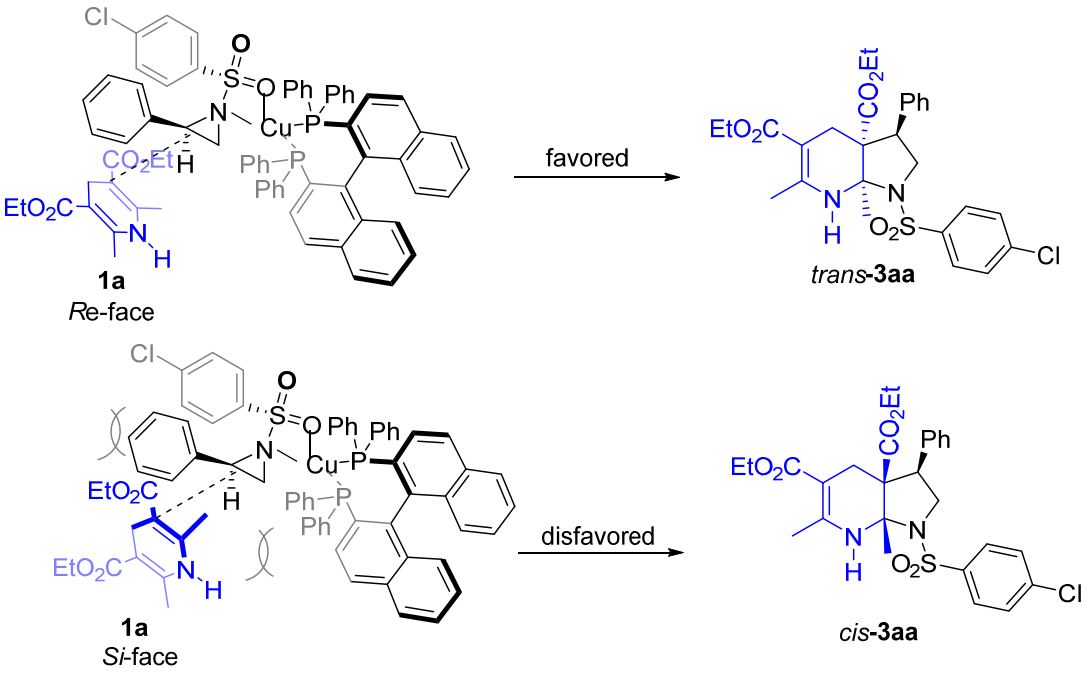
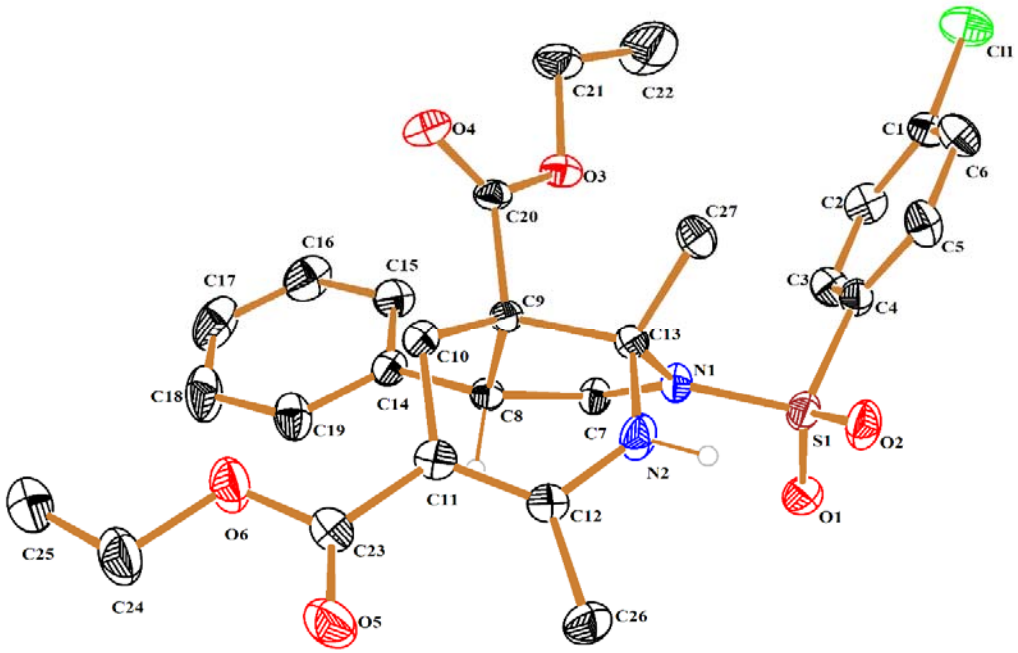


Figure S1. Tentative Stereochemical Models

X-ray Crystal Data and Structures for *cis*-3aa, *trans*-3ak and *trans*-3hn

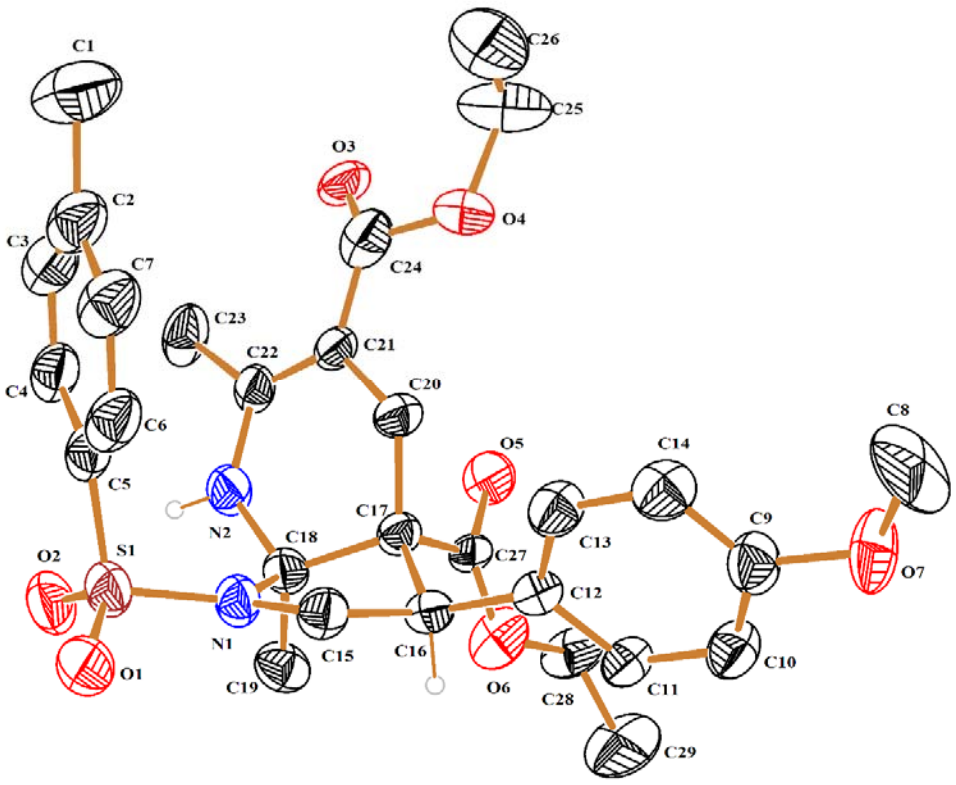


Thermal ellipsoids are set at the 30% probability level (*cis*-**3aa**)

Table S1. Crystal data and structure refinement for *cis*-3aa.

Identification code	mo_20200926c_0m
Empirical formula	$C_{27}H_{31}ClN_2O_6S$
Formula weight	547.05
Temperature/K	273
Crystal system	orthorhombic
Space group	P 21 21 21
a/Å	9.8557(5)
b/Å	11.1093(6)
c/Å	24.7877(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2714.0(3)
Z	4
ρ_{calc}g/cm^3	1.339
μ /mm^{-1}	0.261

F(000)	1152
Crystal size/mm^3	0.23 × 0.22 × 0.21
Radiation	MoKα (I ＝ 0.71073 Å)
2θ range for data collection/°	2.882 to 27.539
Index range	-12⩽ h ≤12, -14≤ k ≤14, -31≤ l ≤32
Reflections collected	208112
Independent reflections	6261
Data/restraints/parameters	6261/0/339
Goodness of fit on F2	1.053
Final R indexes [I>=2 σ (I)]	R1 = 0.0568, wR2 = 0.1721
Final R indexes [all data]	R1 = 0.0754, wR2 = 0.1964
Largest diff. peak/hole / e Å^3	0.496/-0.262
Flack parameter	-0.004(13)

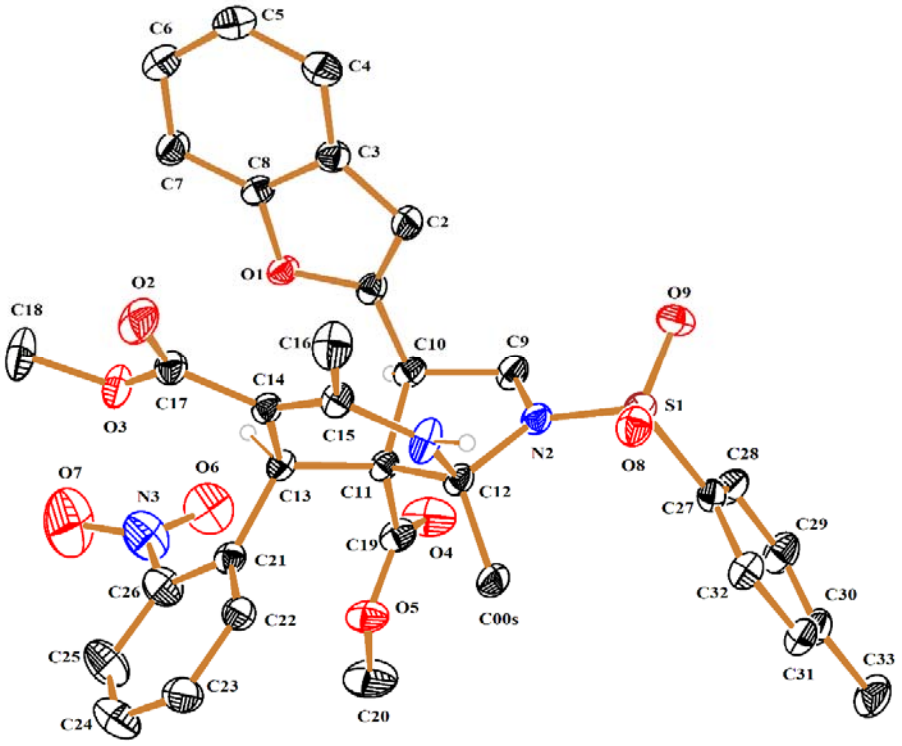


Thermal ellipsoids are set at the 30% probability level (*trans*-**3ak**)

Table S2. Crystal data and structure refinement for *trans*-3ak.

Identification code	190508b_0m_a
Empirical formula	$C_{29}H_{36}N_2OS$
Formula weight	556.66
Temperature/K	293

Crystal system	orthorhombic
Space group	P 21 21 21
a/Å	8.771(2)
b/Å	11.110(3)
c/Å	29.992(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2922.5(13)
Z	4
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.158
F(000)	1184
Crystal size/mm^3	0.24 × 0.23 × 0.2
Radiation	MoKα (I ＝ 0.71073 Å)
2θ range for data collection/°	1.955 to 27.506
Index range	-10≤ h ≤11, -14≤ k ≤14, -38≤ l ≤33
Reflections collected	25643
Independent reflections	6635
Data/restraints/parameters	6635/6/463
Goodness of fit on F2	0.972
Final R indexes [I>=2σ (I)]	R1 = 0.0606, wR2 = 0.1111
Final R indexes [all data]	R1 = 0.1867, wR2 = 0.1538
Largest diff. peak/hole / e Å^3	0.126/-0.177
Flack parameter	-0.04(9)



Thermal ellipsoids are set at the 30% probability level (*trans*-**3hn**)

Table S3. Crystal data and structure refinement for *trans*-3hn.

Identification code	210310b_0m_a
Empirical formula	$C_{34}H_{33}N_3O_9S$
Formula weight	659.69
Temperature/K	293
Crystal system	orthorhombic
Space group	P 21 21 21
a/Å	7.6574(18)
b/Å	14.452(3)
c/Å	29.482(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3262.5(13)
Z	4
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	0.159
F(000)	1384
Crystal size/mm^3	0.23 × 0.21 × 0.2

Radiation	MoKα (I ＝ 0.71073 Å)
2θ range for data collection/°	1.569 to 27.751
Index range	-9≤ h ≤9, -18≤ k ≤18, -34≤ l ≤38
Reflections collected	28149
Independent reflections	7545
Data/restraints/parameters	7545/0/429
Goodness of fit on F2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0574, wR2 = 0.1376
Final R indexes [all data]	R1 = 0.0769, wR2 = 0.1475
Largest diff. peak/hole / e Å^3	0.248/-0.393
Flack parameter	0.06(4)

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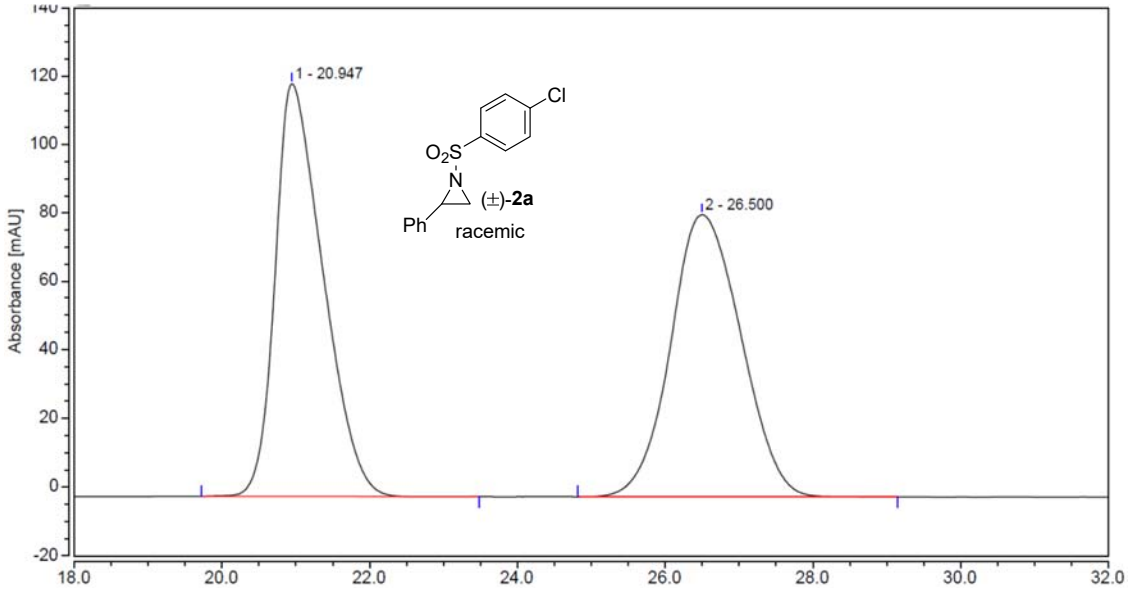

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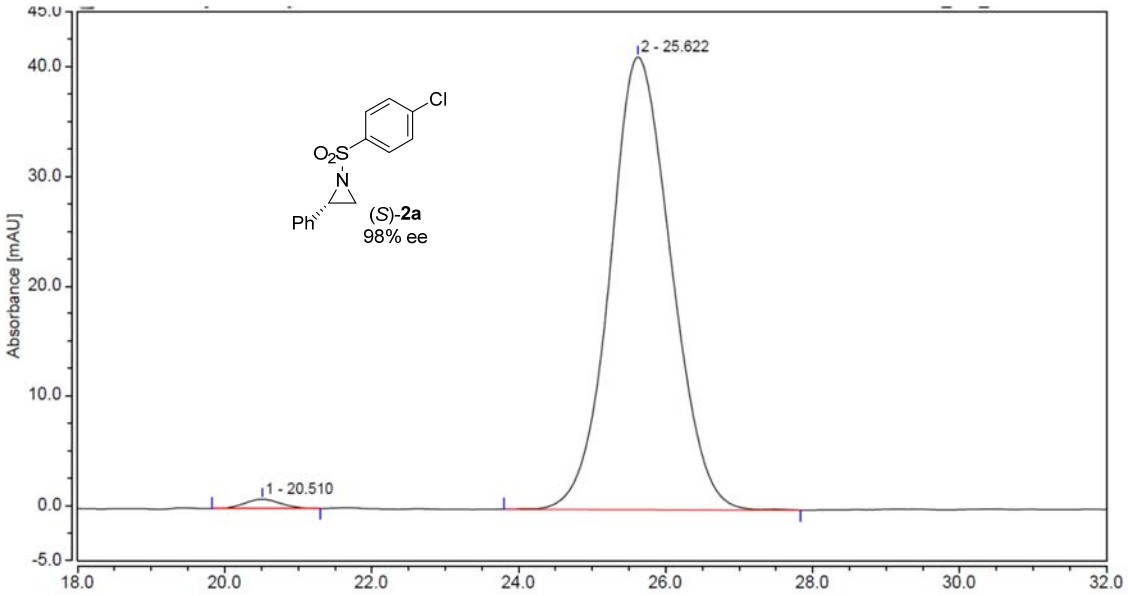

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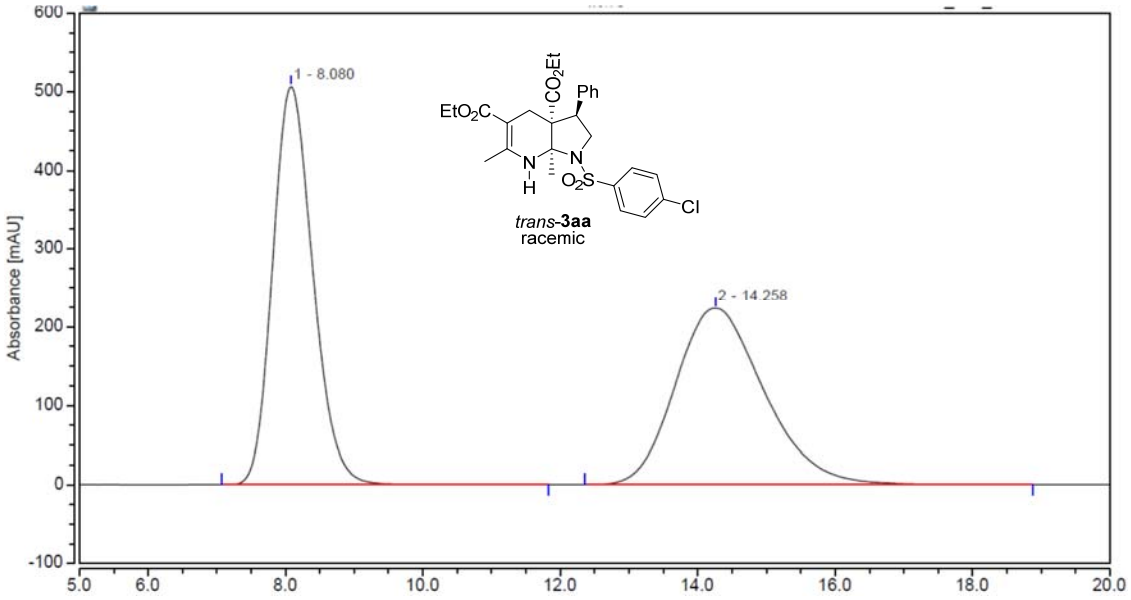

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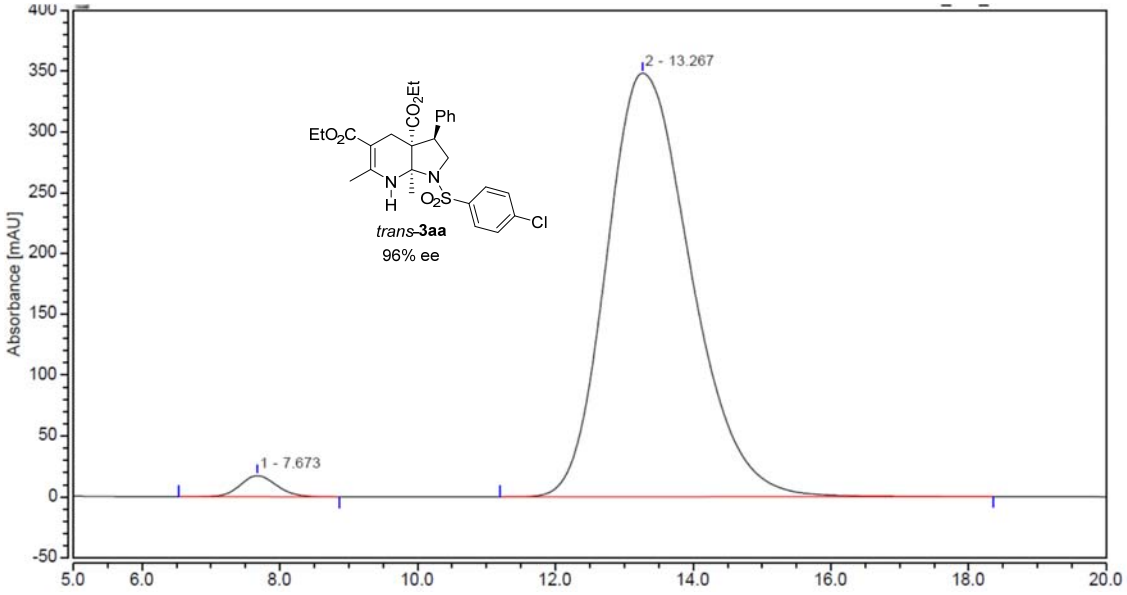

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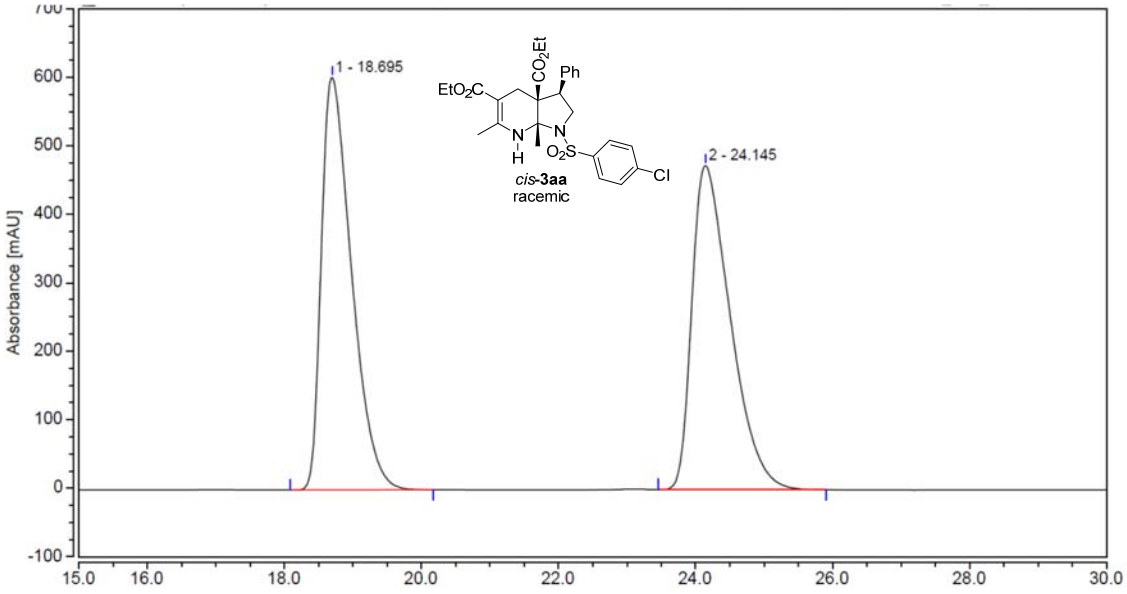

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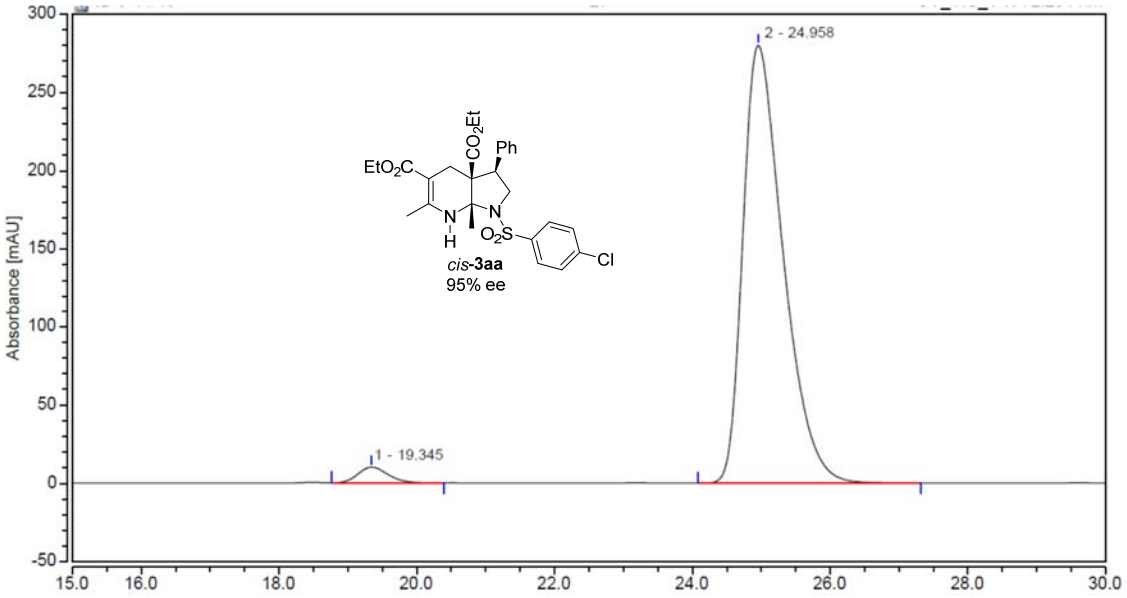

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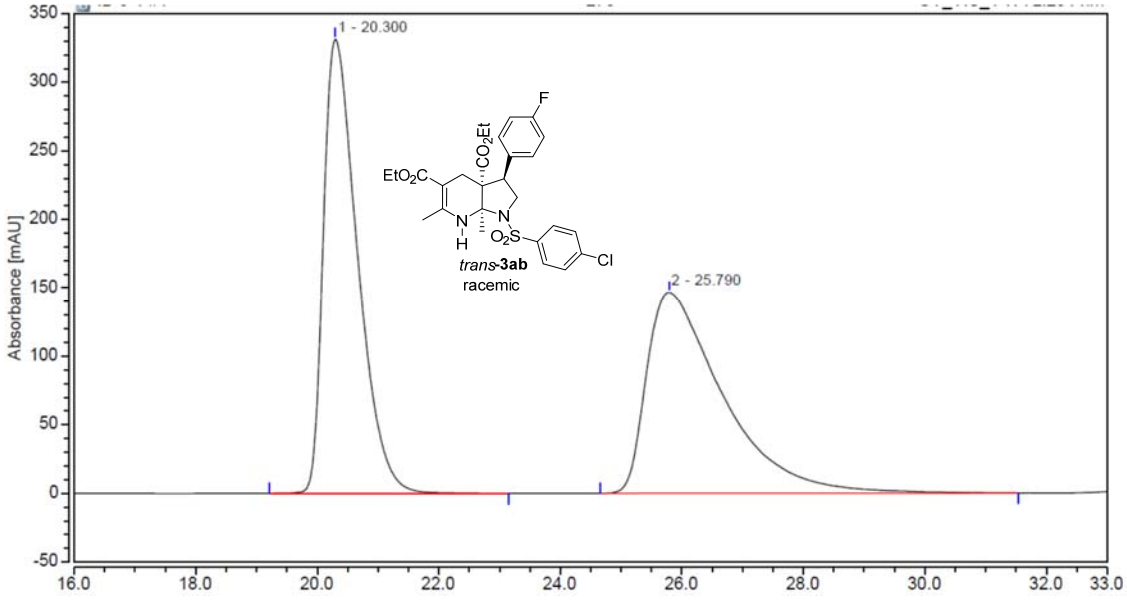

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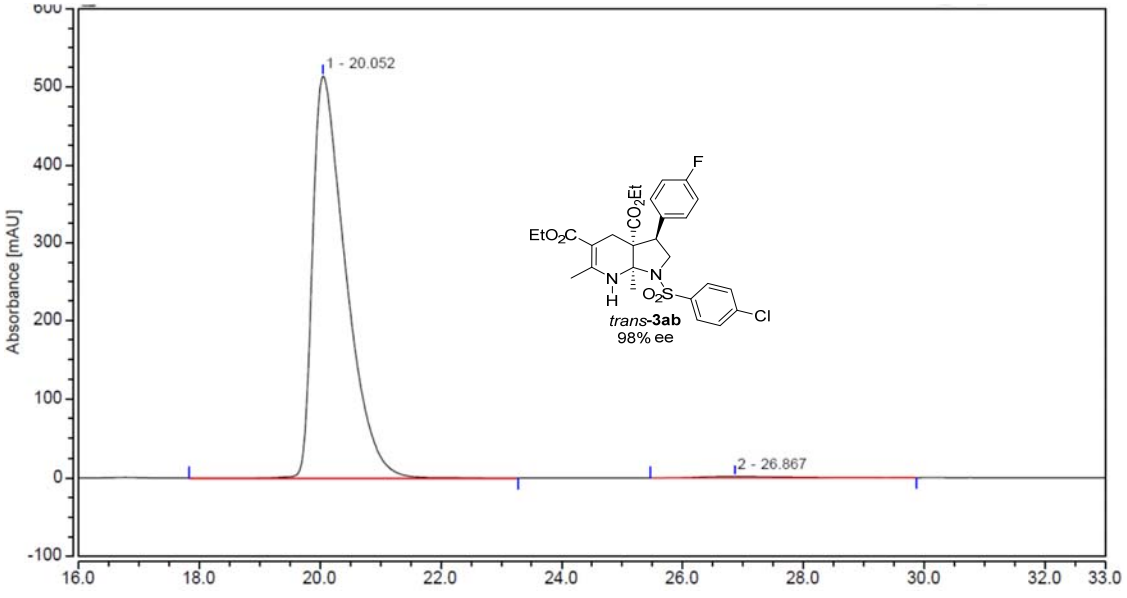

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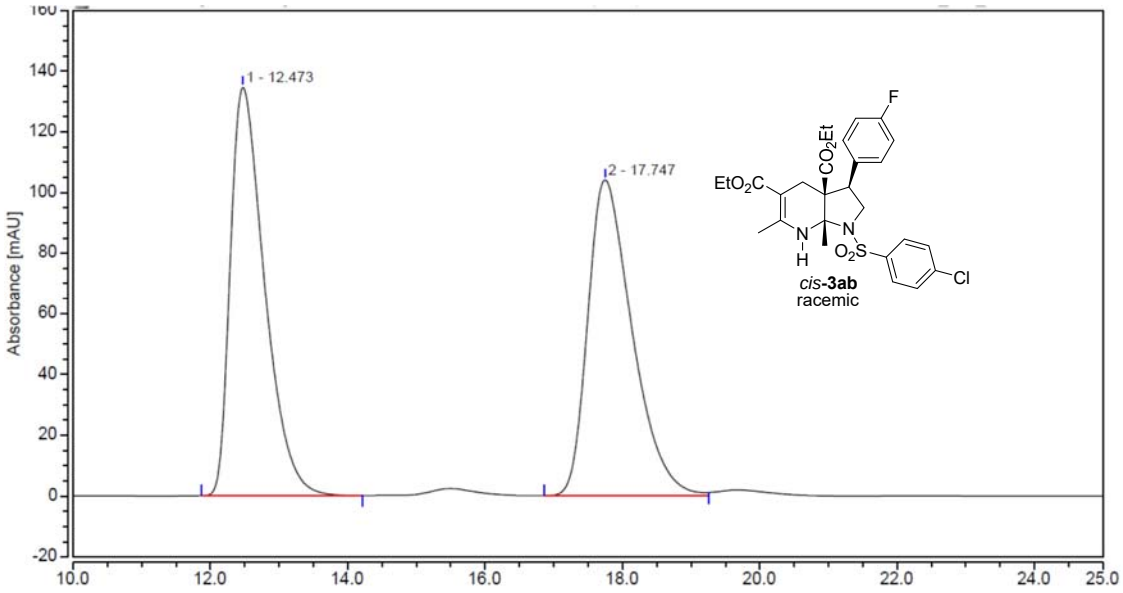
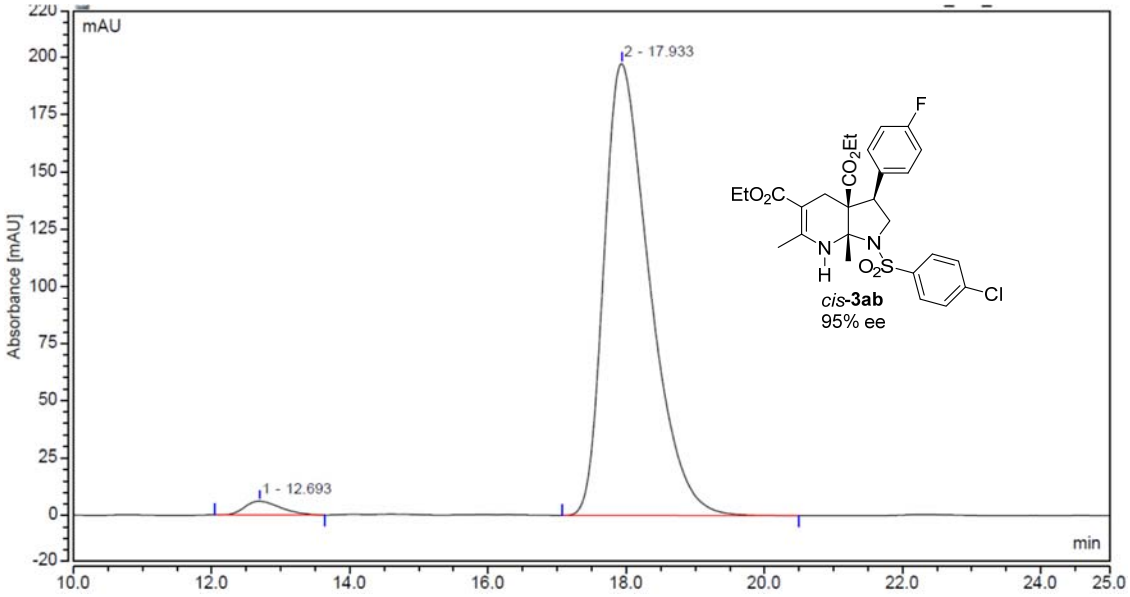


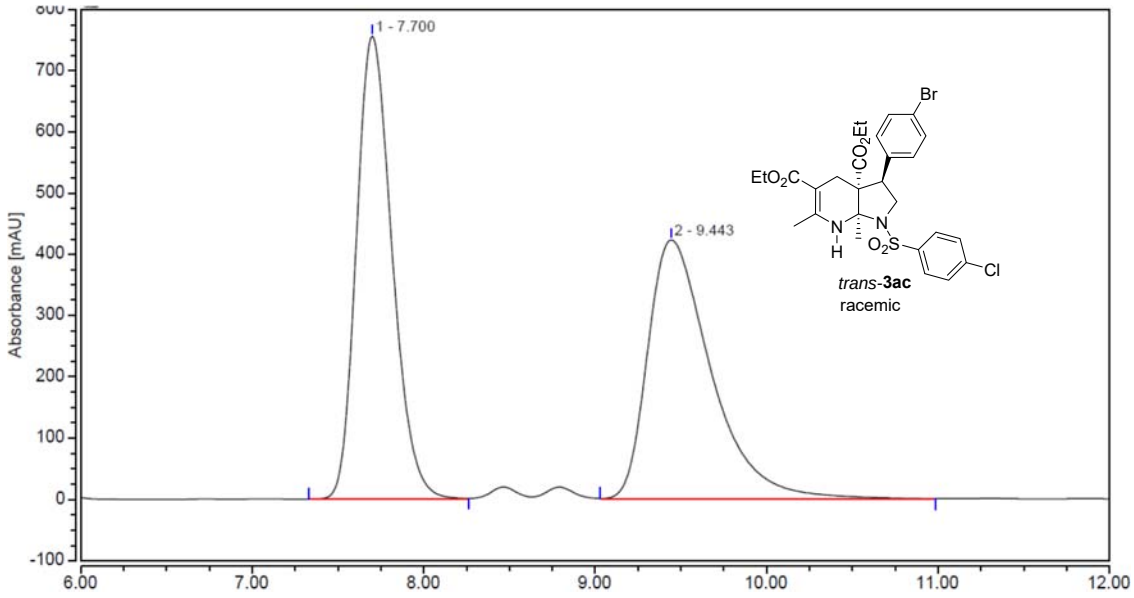
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	12.473	77.555	134.583	49.92	56.39
2	17.747	77.804	104.079	50.08	43.61



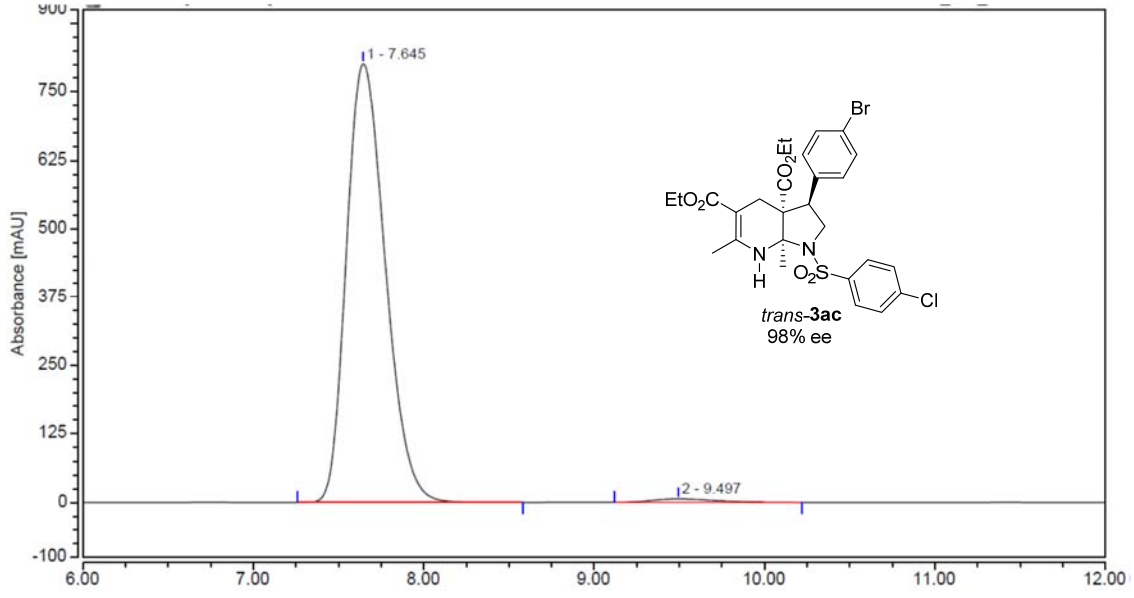
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	12.693	3.579	5.996	2.32	2.95
2	17.933	150.758	197.226	97.68	97.05



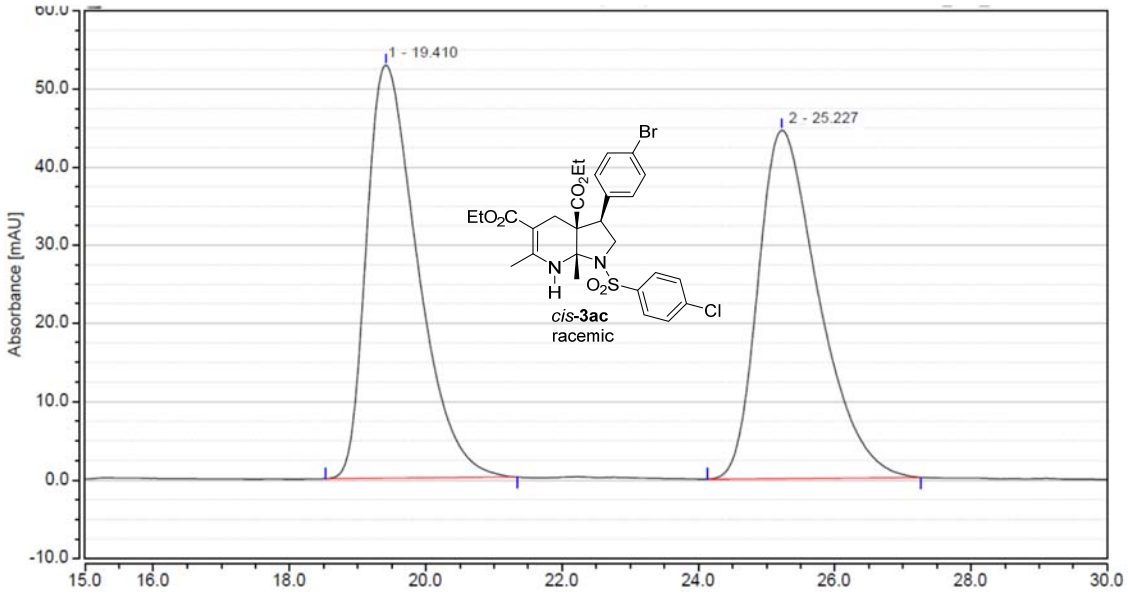
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	7.700	182.787	756.259	50.40	64.18
2	9.443	179.911	422.172	49.60	35.82



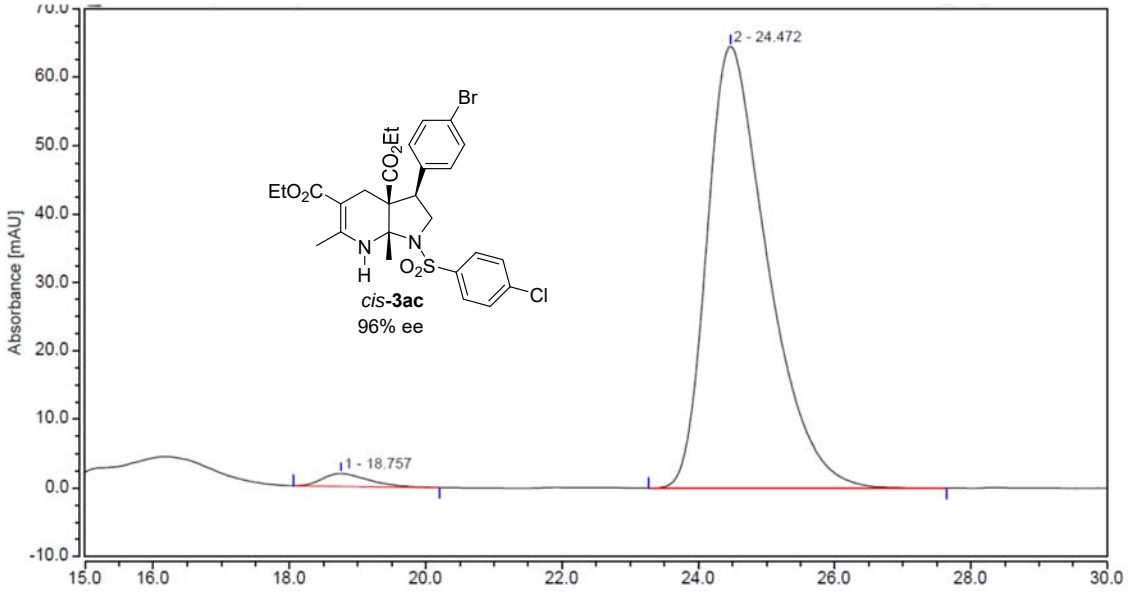
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	7.645	212.039	800.911	98.75	99.23
2	9.497	2.678	6.252	1.25	0.77



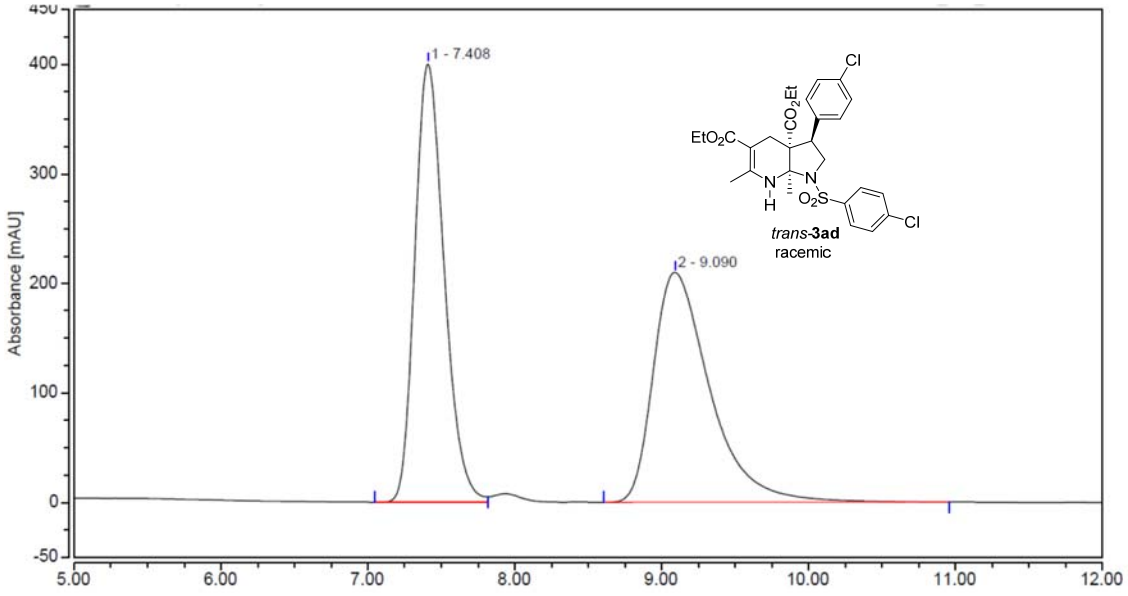
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	19.410	45.742	52.786	49.89	54.25
2	25.227	45.936	44.514	50.11	45.75



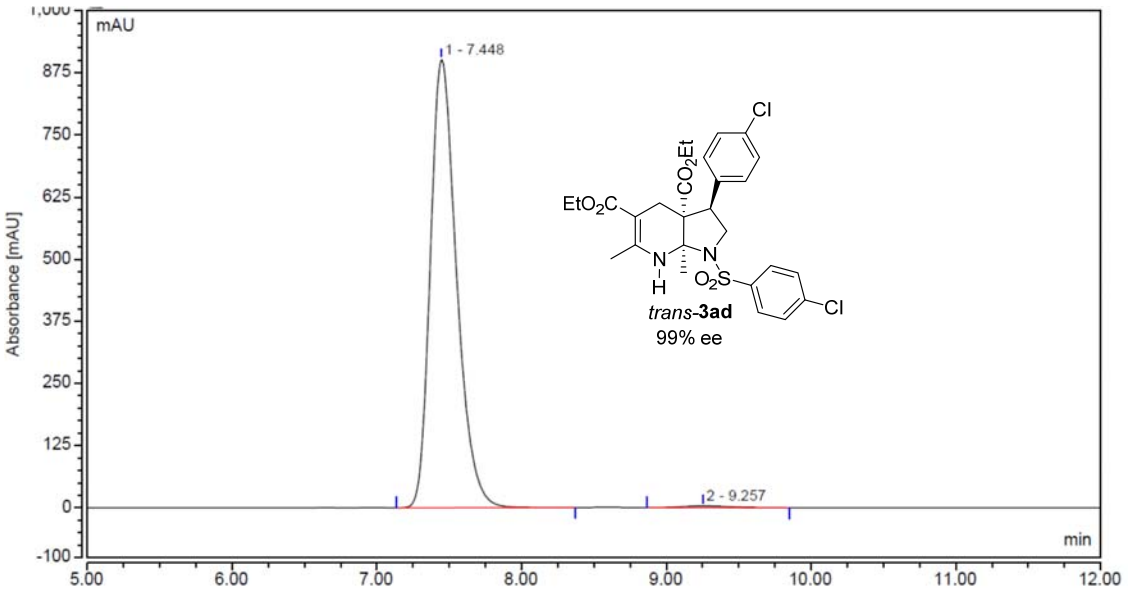
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	18.757	1.470	1.875	2.17	2.82
2	24.472	66.248	64.500	97.83	97.18



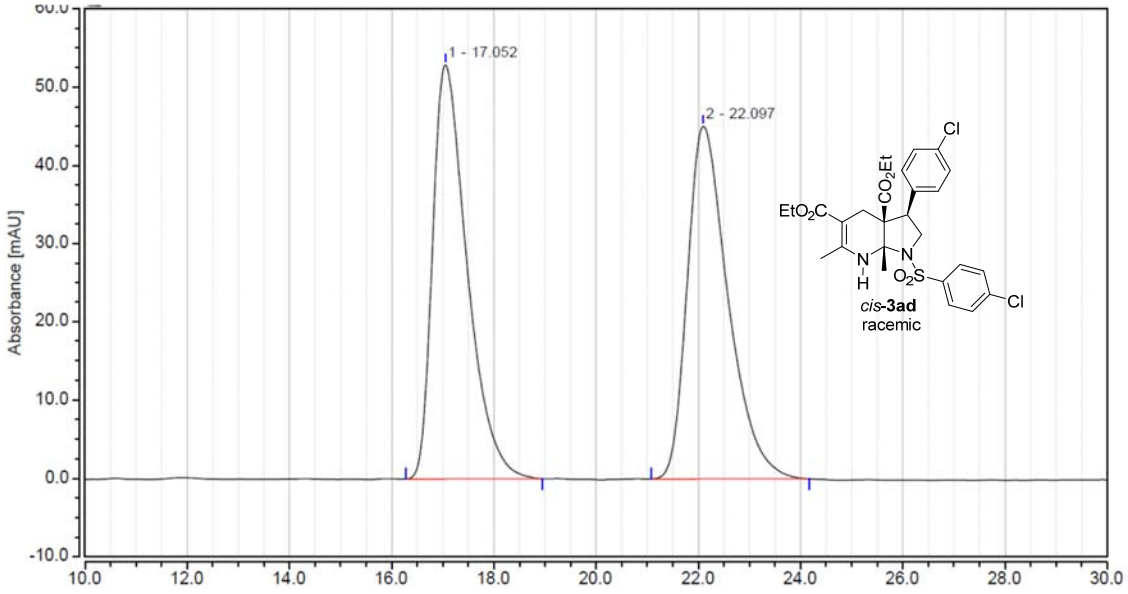
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	7.408	92.652	399.899	49.68	65.55
2	9.090	93.834	210.126	50.32	34.45



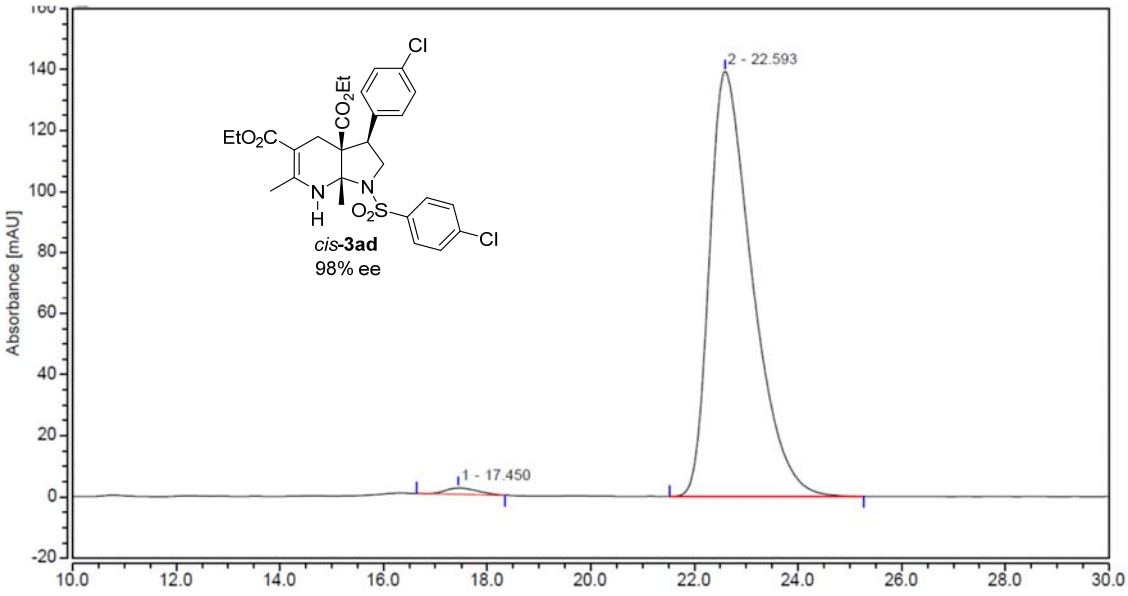
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	7.448	189.268	901.152	99.29	99.61
2	9.257	1.356	3.488	0.71	0.39



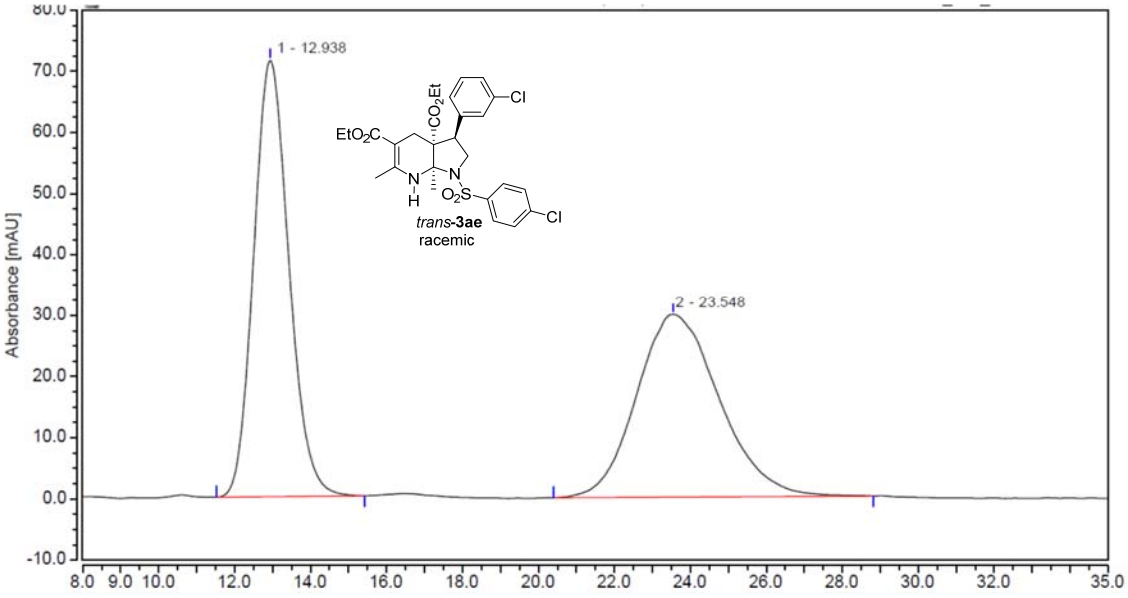
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	17.052	41.365	52.898	49.86	53.99
2	22.097	41.590	45.078	50.14	46.01



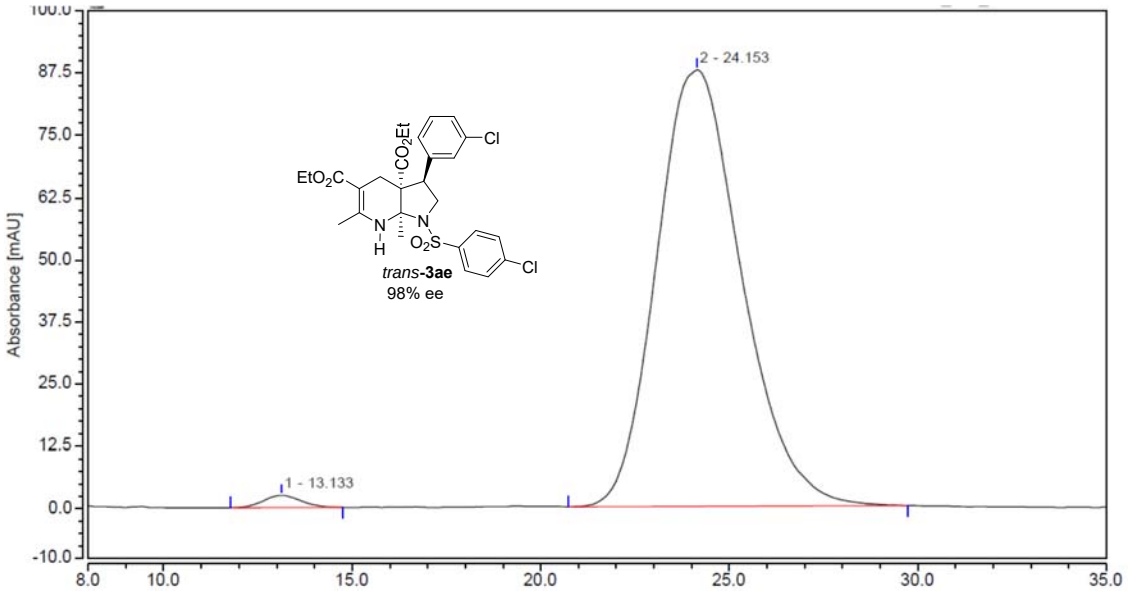
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	17.450	1.482	2.074	1.11	1.47
2	22.593	132.669	139.274	98.89	98.53



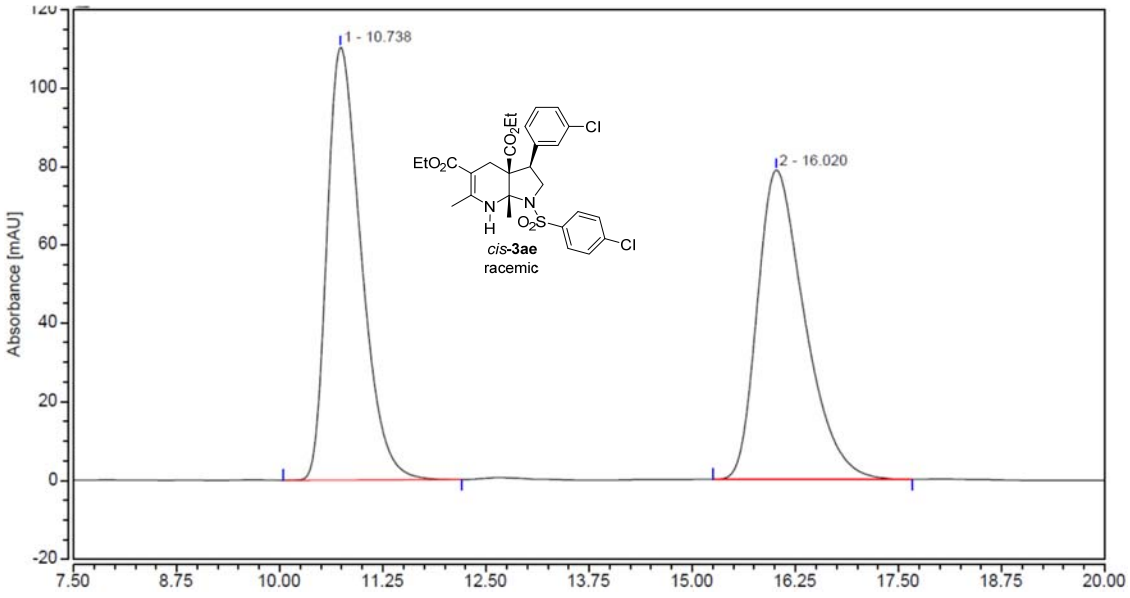
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	12.938	76.855	71.474	50.43	70.51
2	23.548	75.554	29.888	49.57	29.49



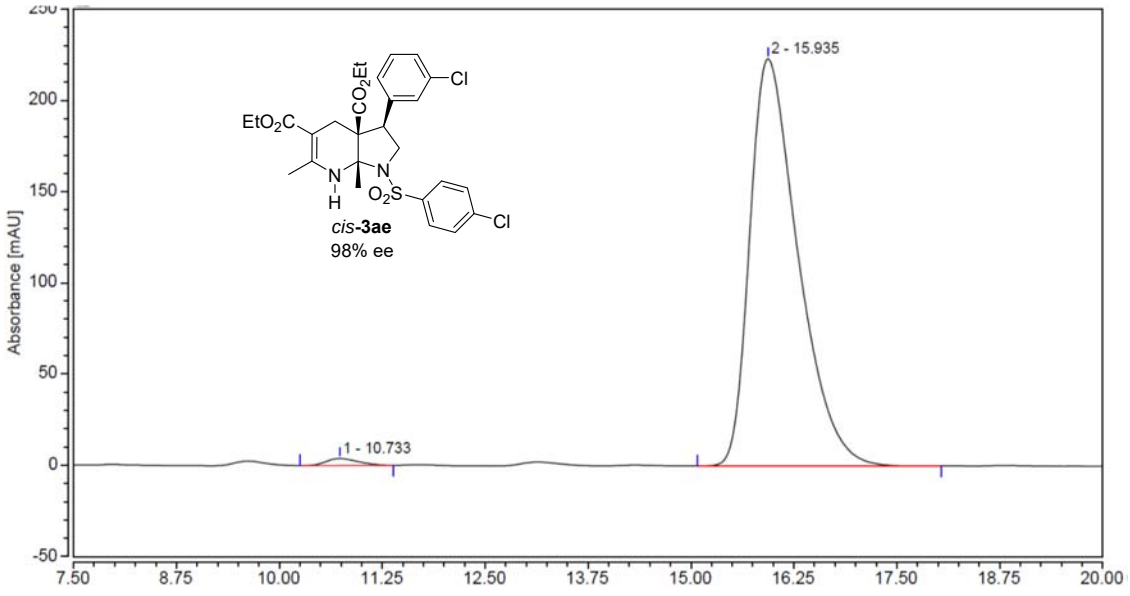
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	13.133	2.841	2.453	1.22	2.72
2	24.153	229.447	87.627	98.78	97.28



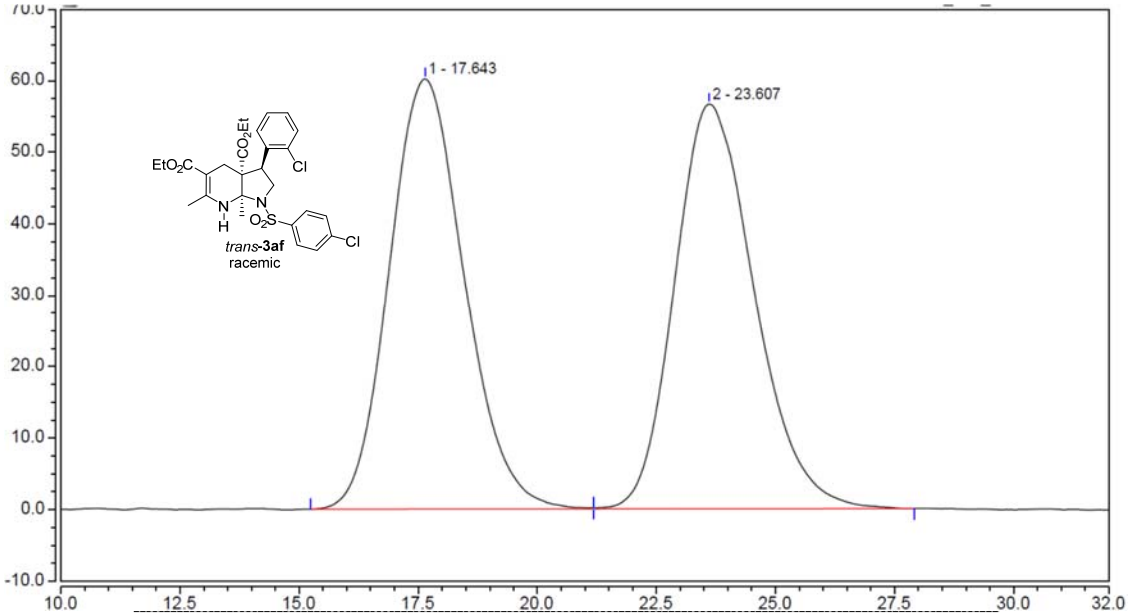
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	10.738	52.838	110.321	50.26	58.34
2	16.020	52.295	78.793	49.74	41.66



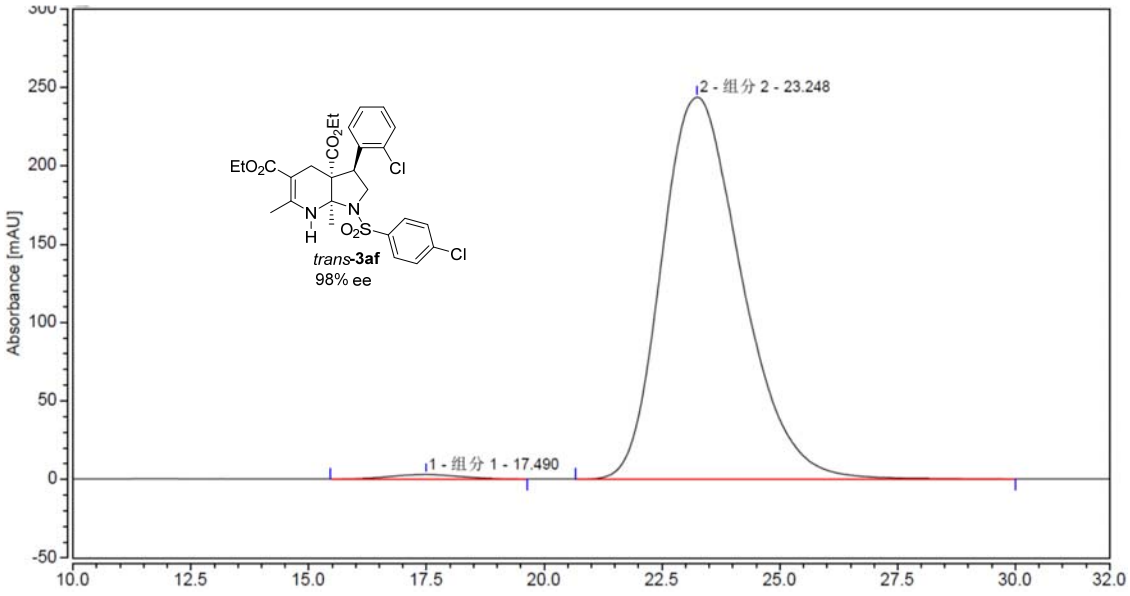
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	10.733	1.675	3.756	1.10	1.66
2	15.935	151.221	223.103	98.90	98.34



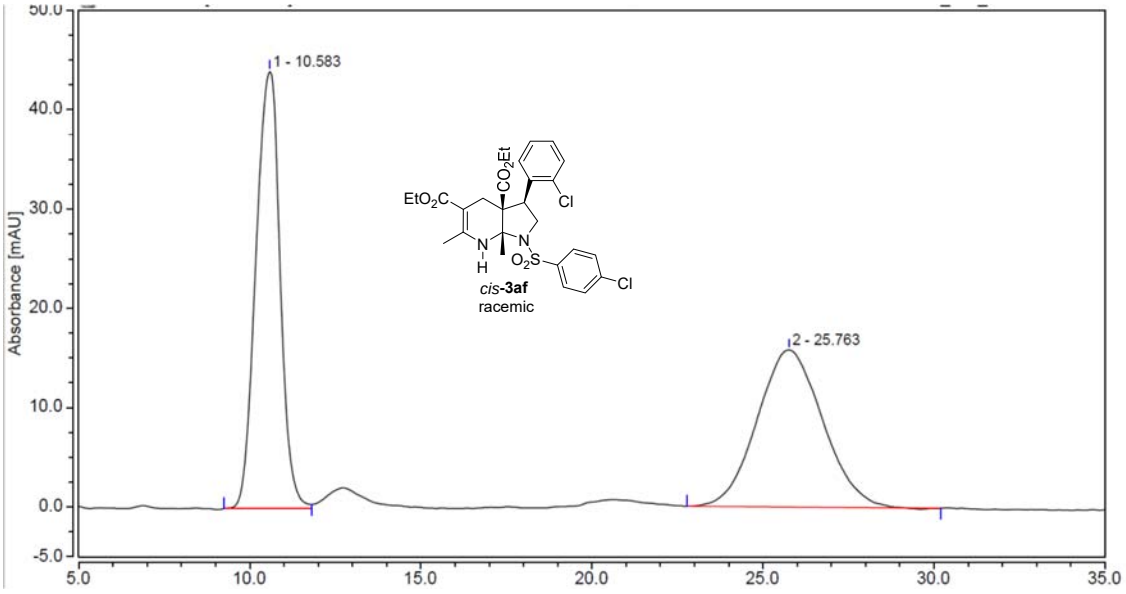
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	17.643	110.097	60.220	50.01	51.53
2	23.607	110.055	56.642	49.99	48.47



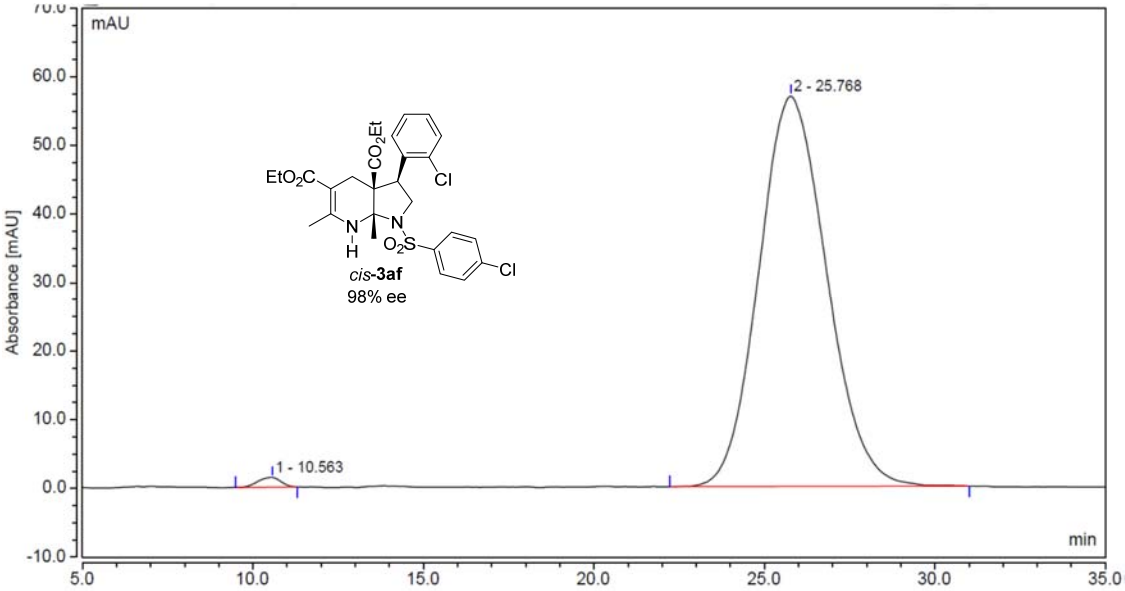
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area%	Height%
1	17.490	4.928	2.865	1.02	1.16
2	23.248	479.986	243.487	98.98	98.84



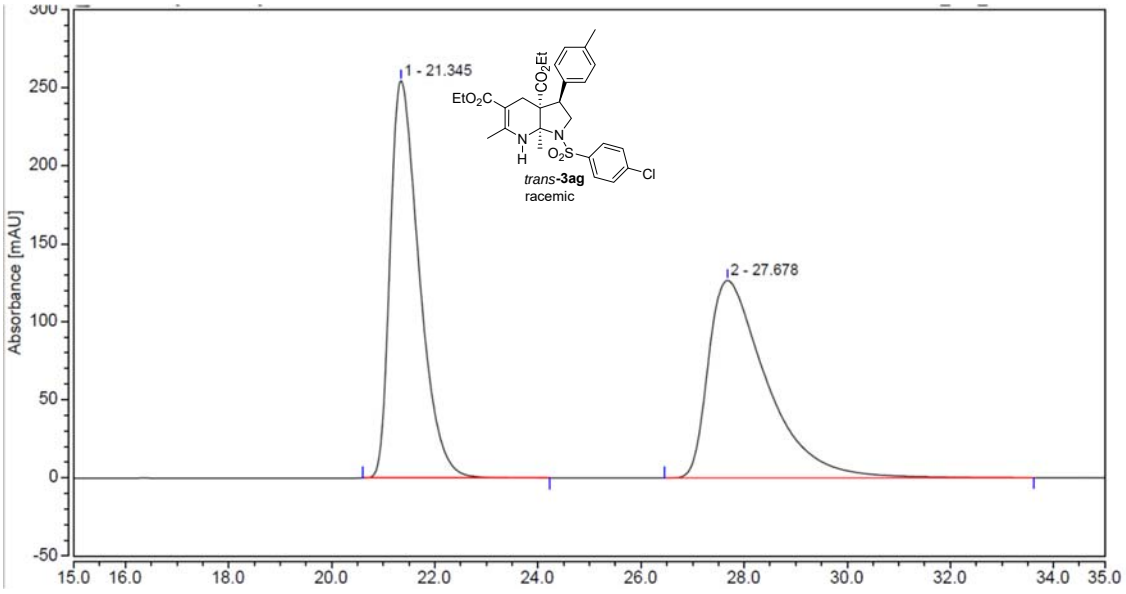
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.583	36.059	44.004	50.70	73.58
2	25.763	35.064	15.800	49.30	26.42



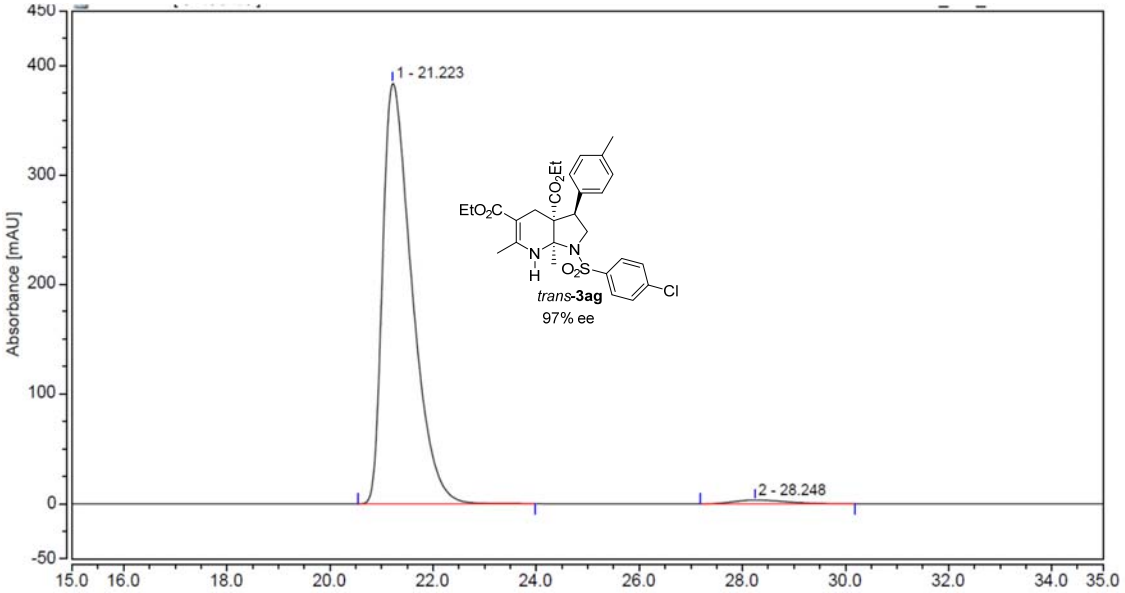
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.563	1.098	1.424	0.83	2.44
2	25.768	131.100	56.911	99.17	97.56



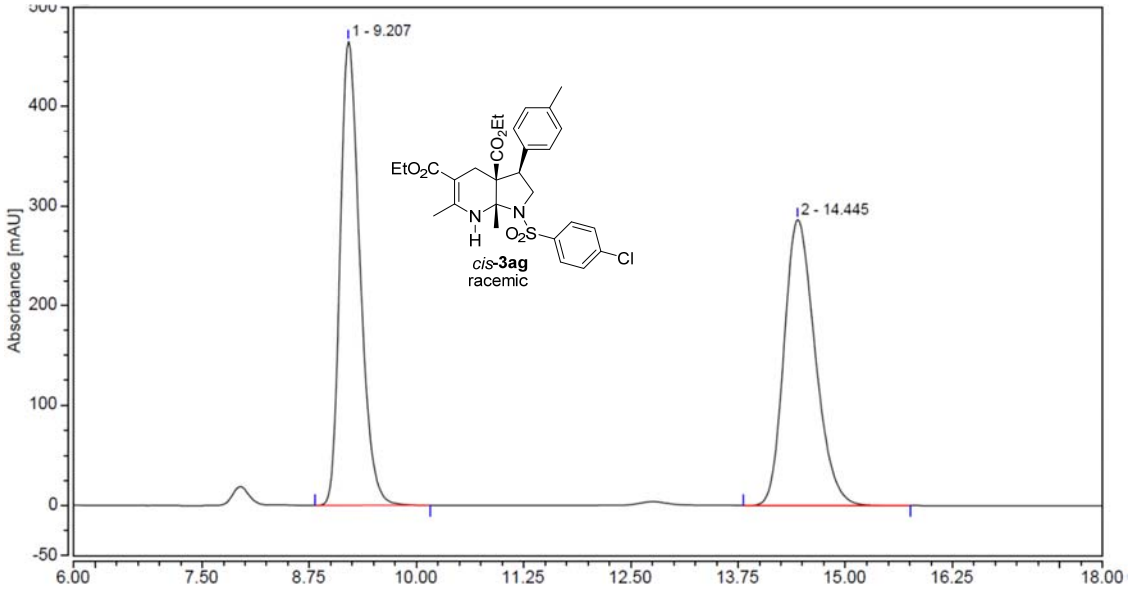
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	21.345	166.531	254.630	50.07	66.78
2	27.678	166.092	126.653	49.93	33.22



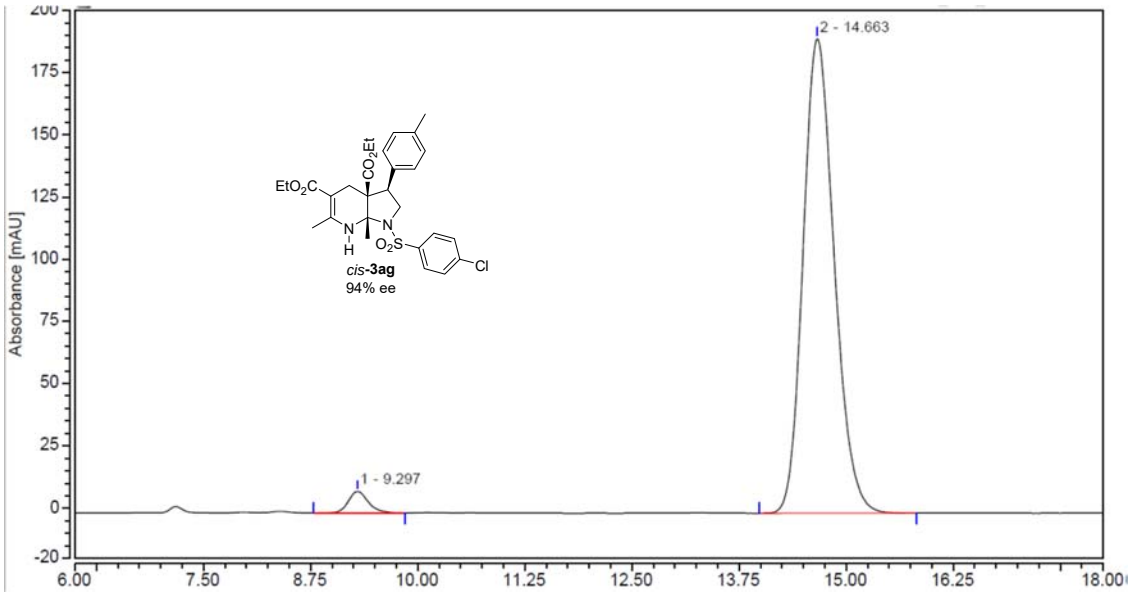
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	21.223	251.565	384.139	98.35	99.11
2	28.248	4.212	3.454	1.65	0.89



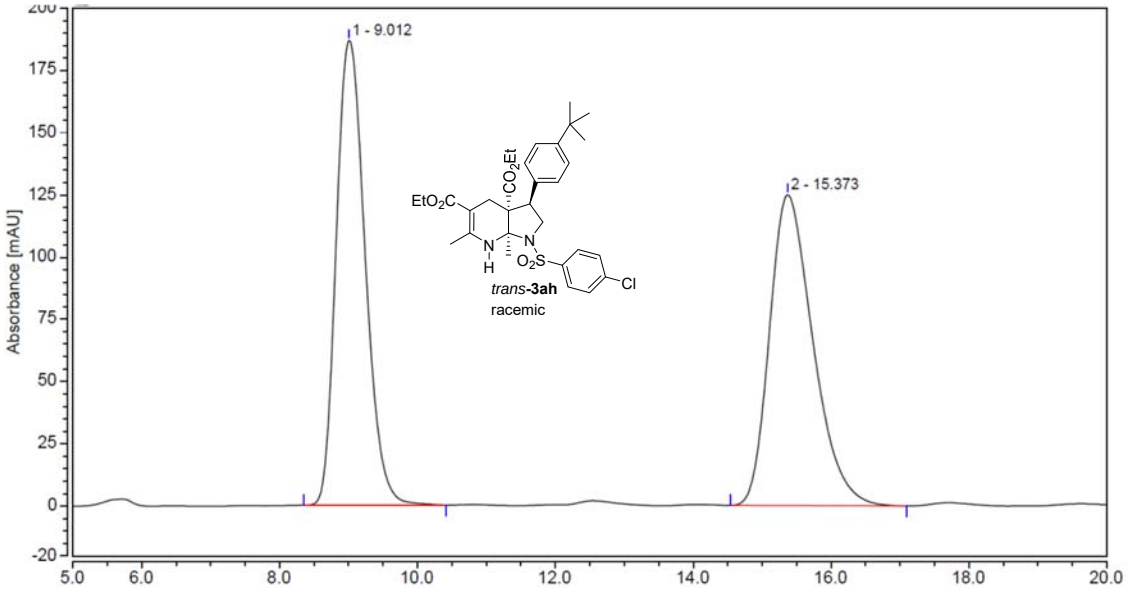
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.207	124.370	465.506	50.89	61.89
2	14.445	120.024	286.616	49.11	38.11



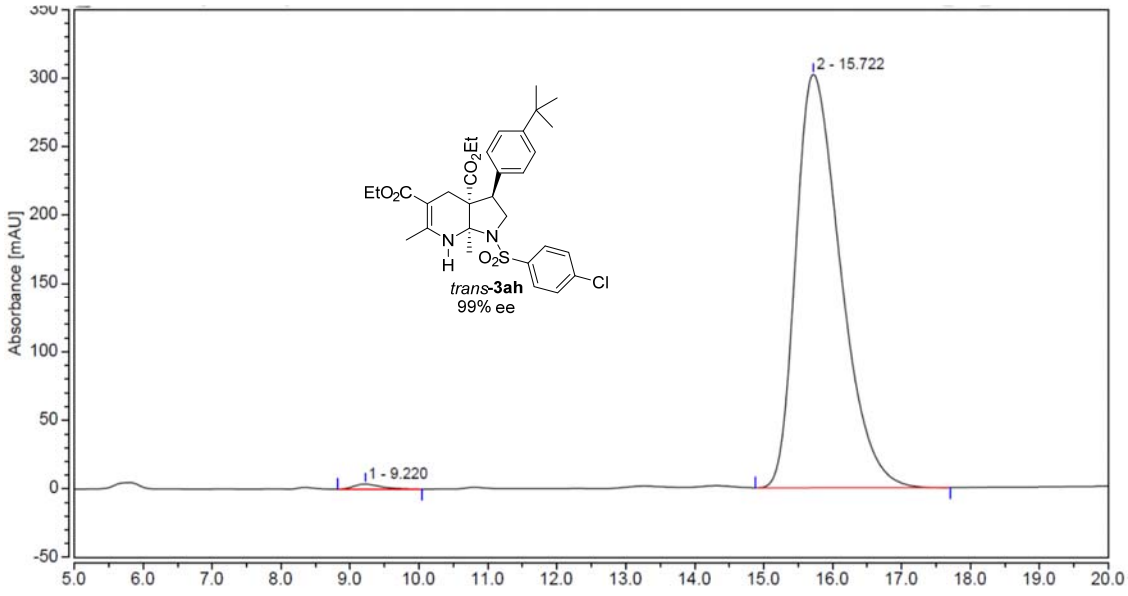
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.297	2.352	8.651	2.85	4.34
2	14.663	80.120	190.606	97.15	95.66



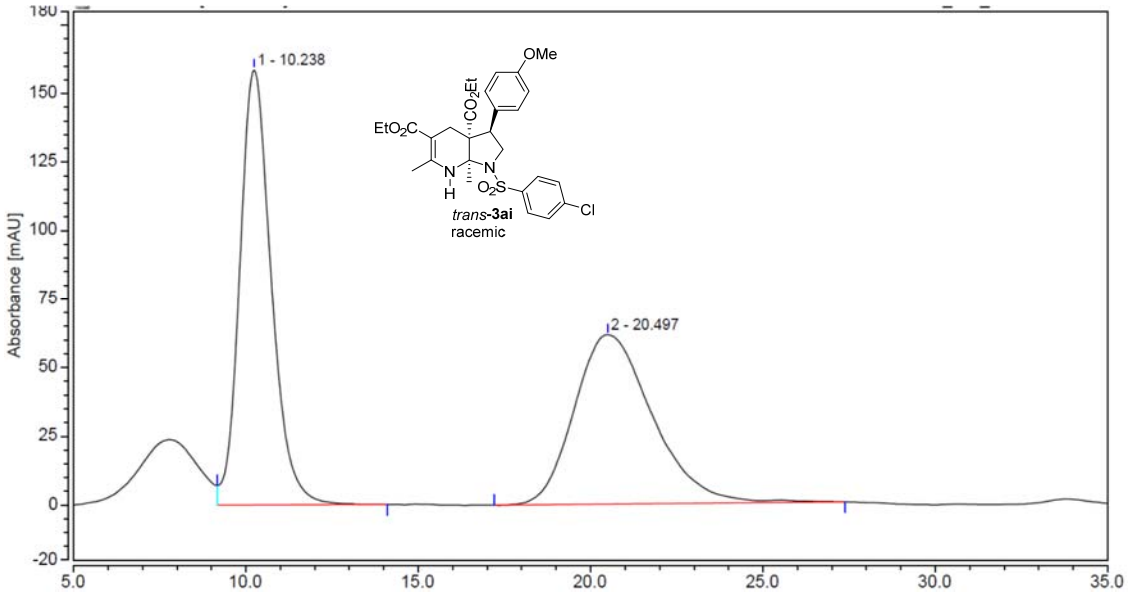
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.012	90.648	186.713	49.89	59.92
2	15.373	91.036	124.881	50.11	40.08



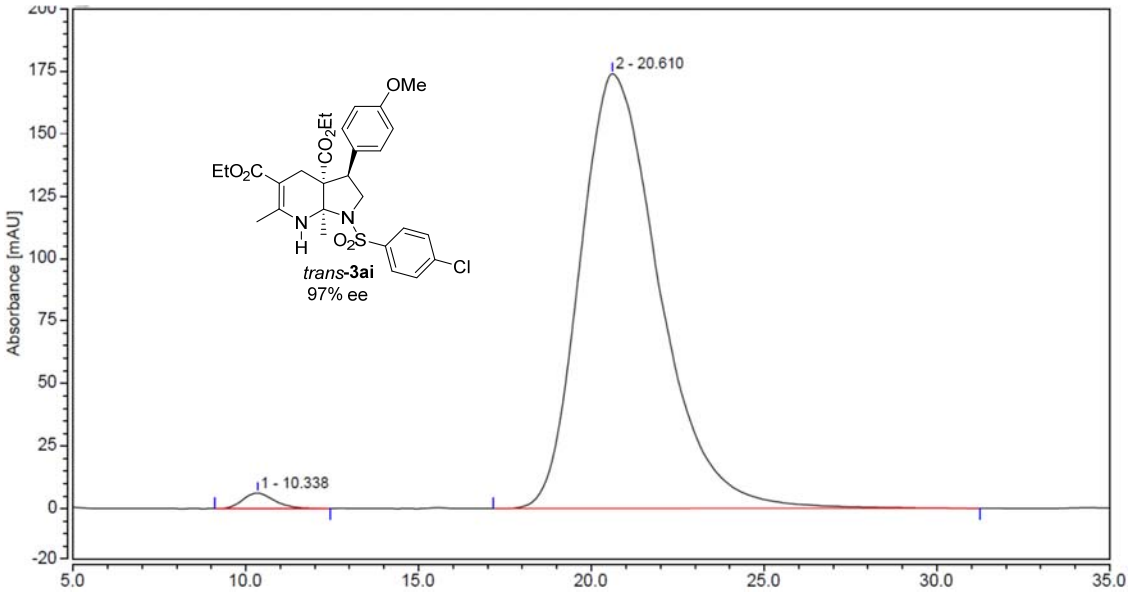
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.220	1.645	3.664	0.72	1.20
2	15.722	227.178	302.016	99.28	98.80



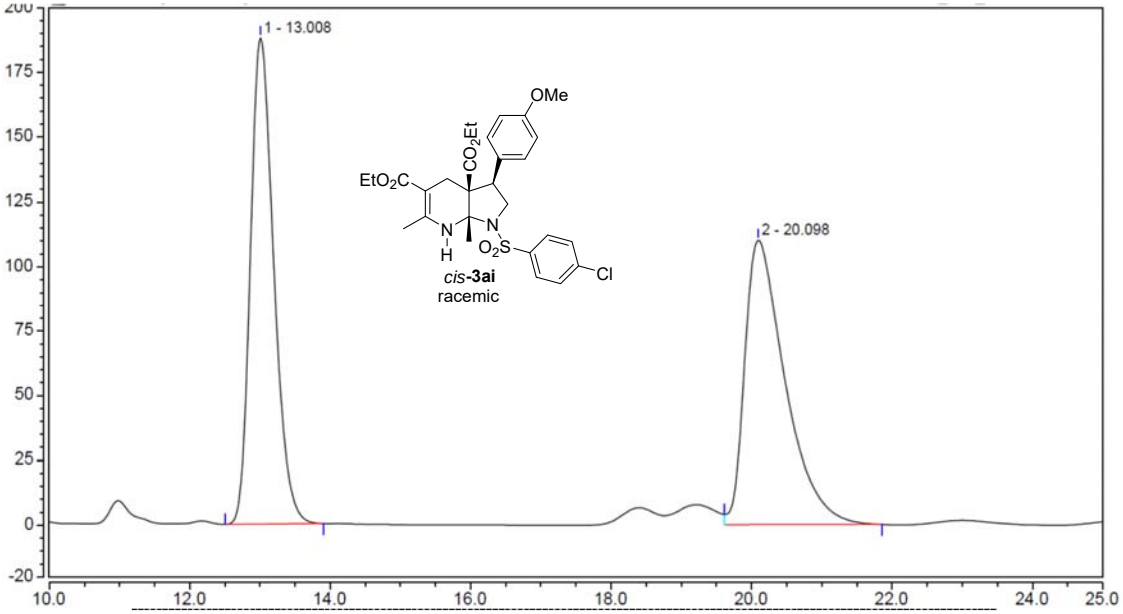
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.238	167.981	158.585	50.89	72.03
2	20.497	162.091	61.590	49.11	27.97



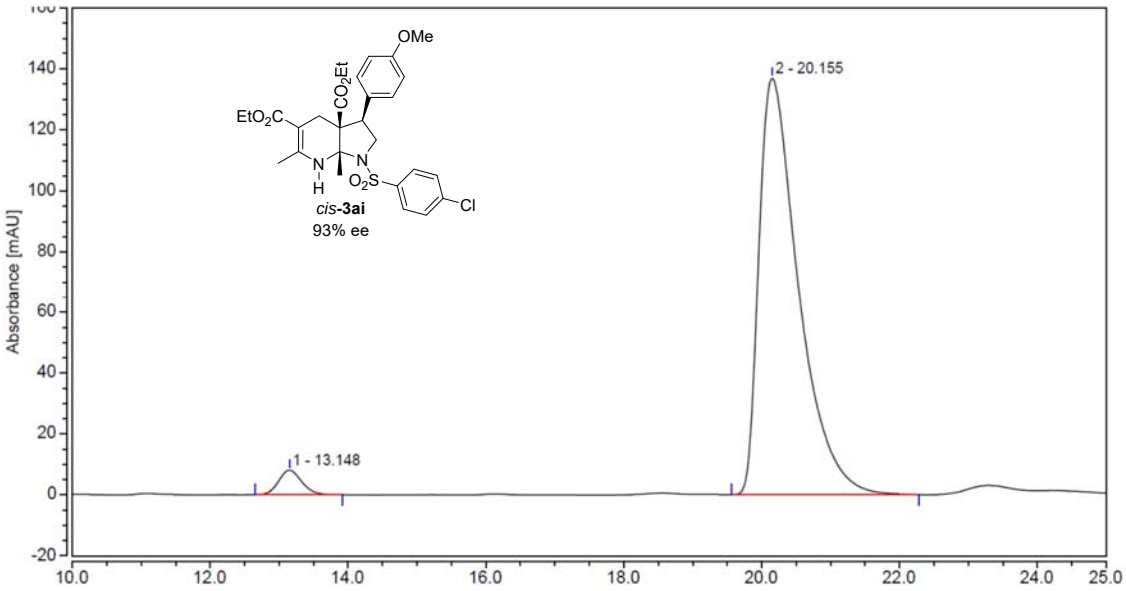
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.338	6.542	6.171	1.39	3.43
2	20.610	462.466	173.971	98.61	96.57



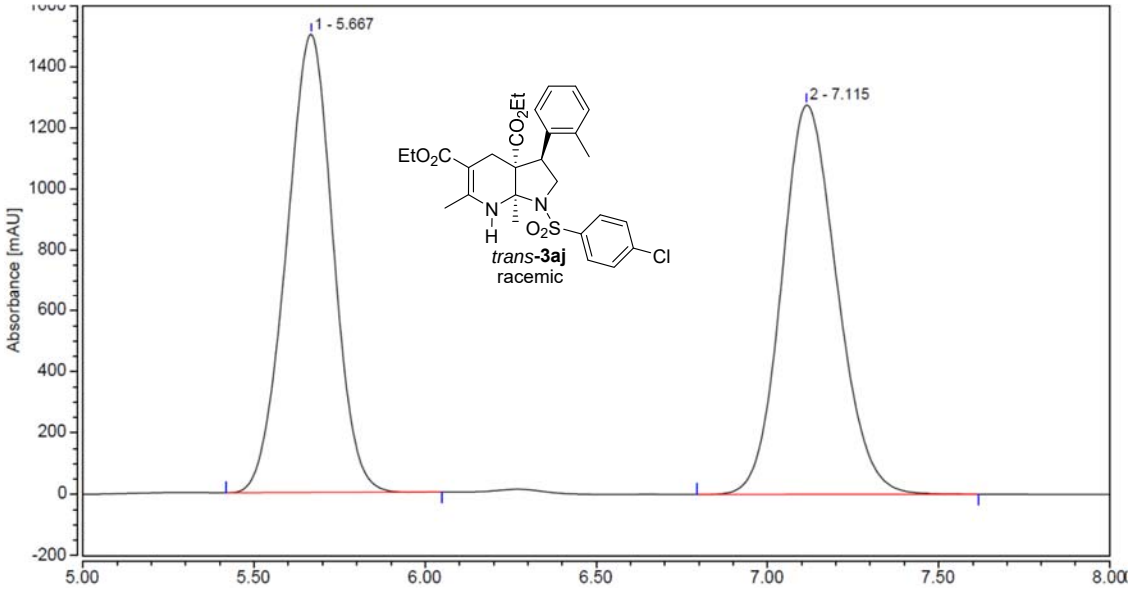
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	13.008	72.265	188.057	49.71	63.10
2	20.098	73.096	109.995	50.29	36.90



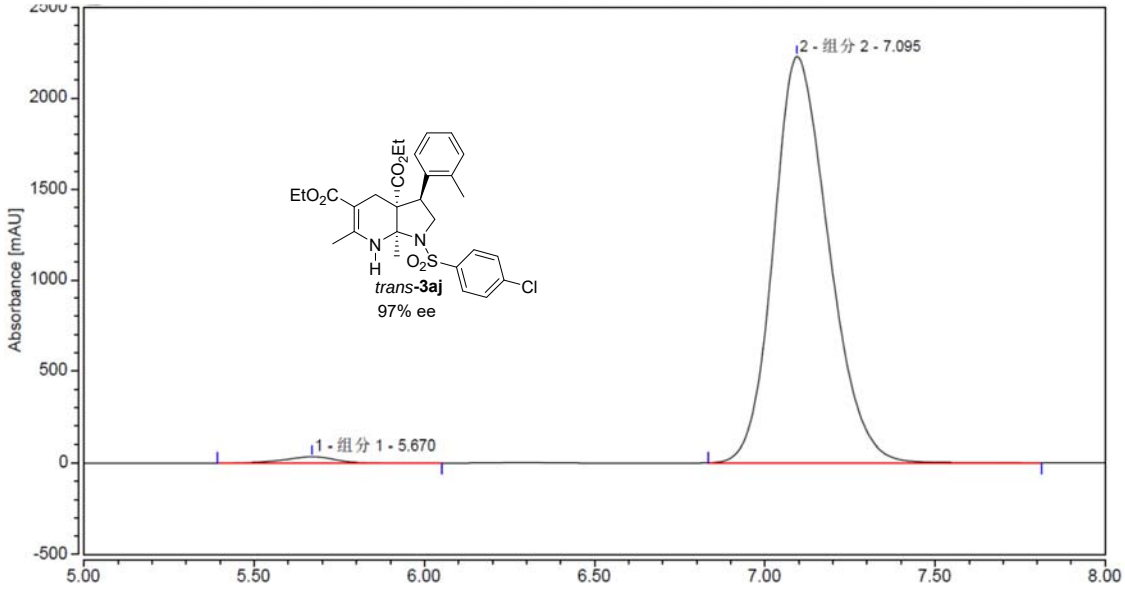
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	13.148	3.092	8.019	3.29	5.54
2	20.155	90.885	136.772	96.71	94.46



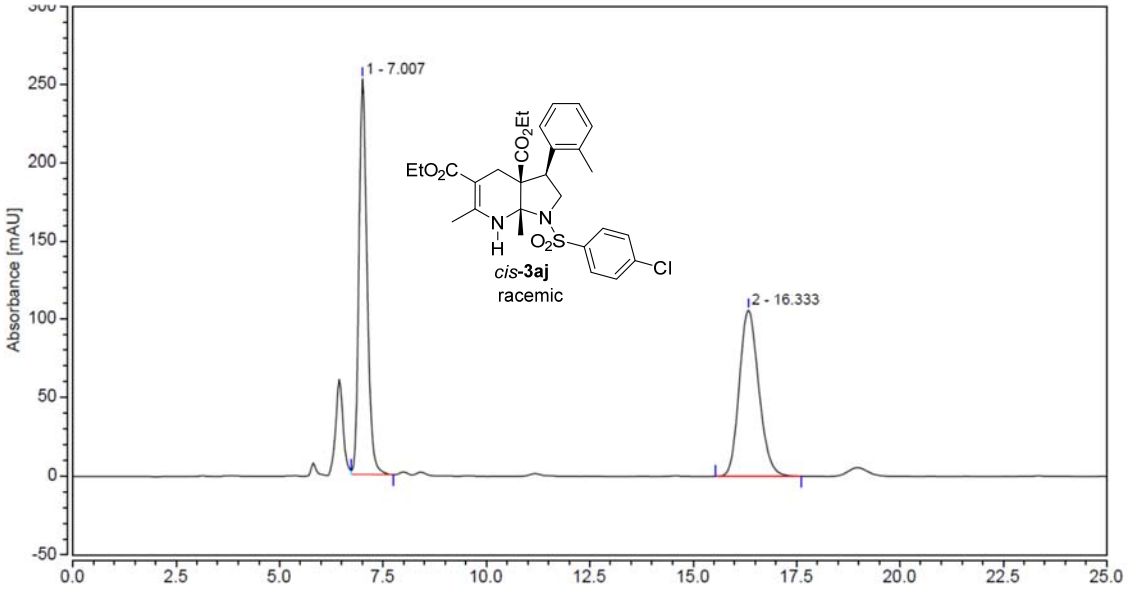
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	5.667	236.304	1500.320	49.70	54.06
2	7.115	239.158	1274.856	50.30	45.94



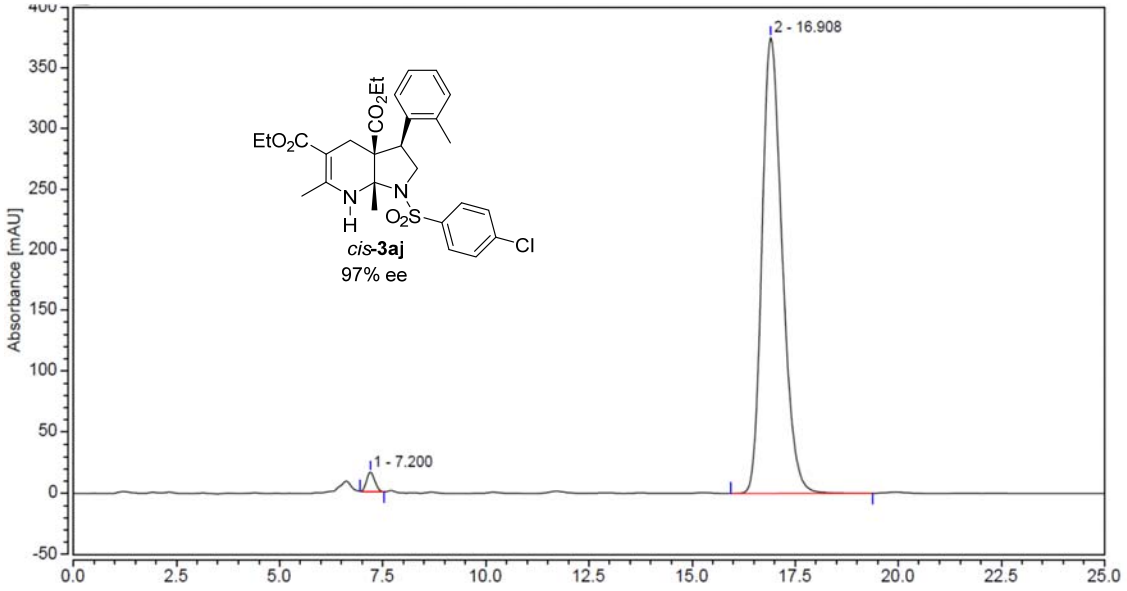
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	5.670	5.957	34.376	1.41	1.52
2	7.095	417.953	2228.125	98.59	98.48



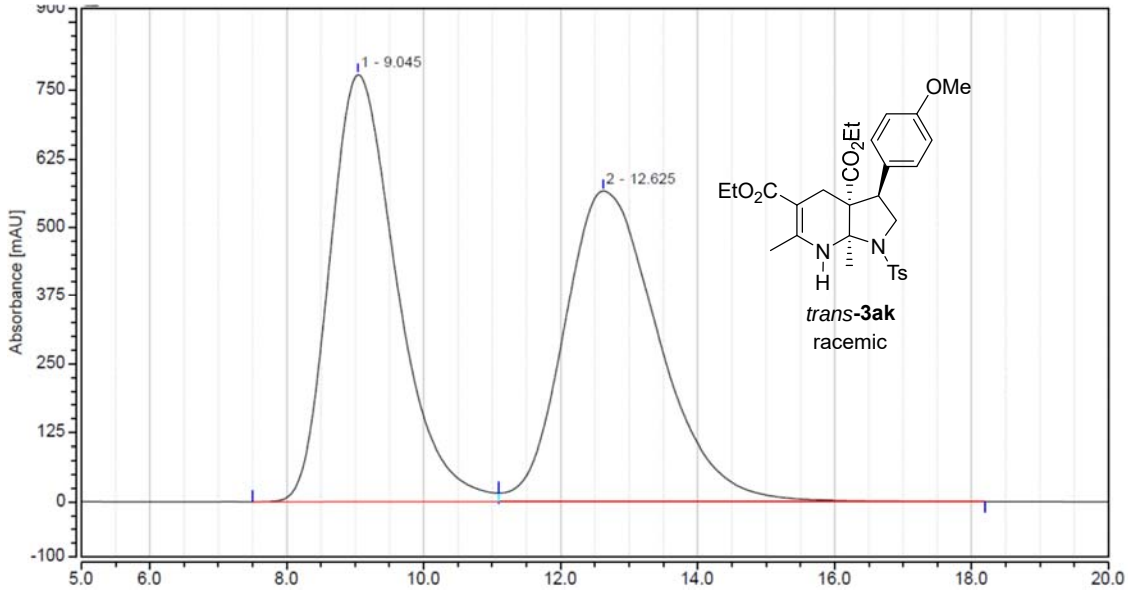
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	7.007	57.515	252.438	50.01	70.54
2	16.333	57.489	105.419	49.99	29.46



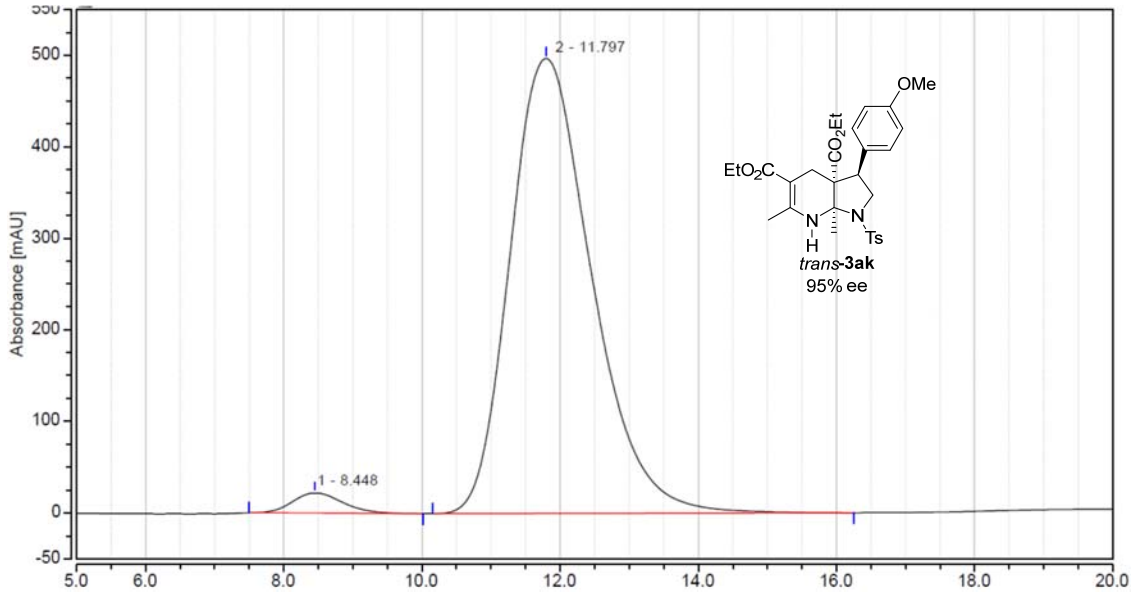
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	7.200	3.789	16.229	1.75	4.15
2	16.908	212.169	374.996	98.25	95.85



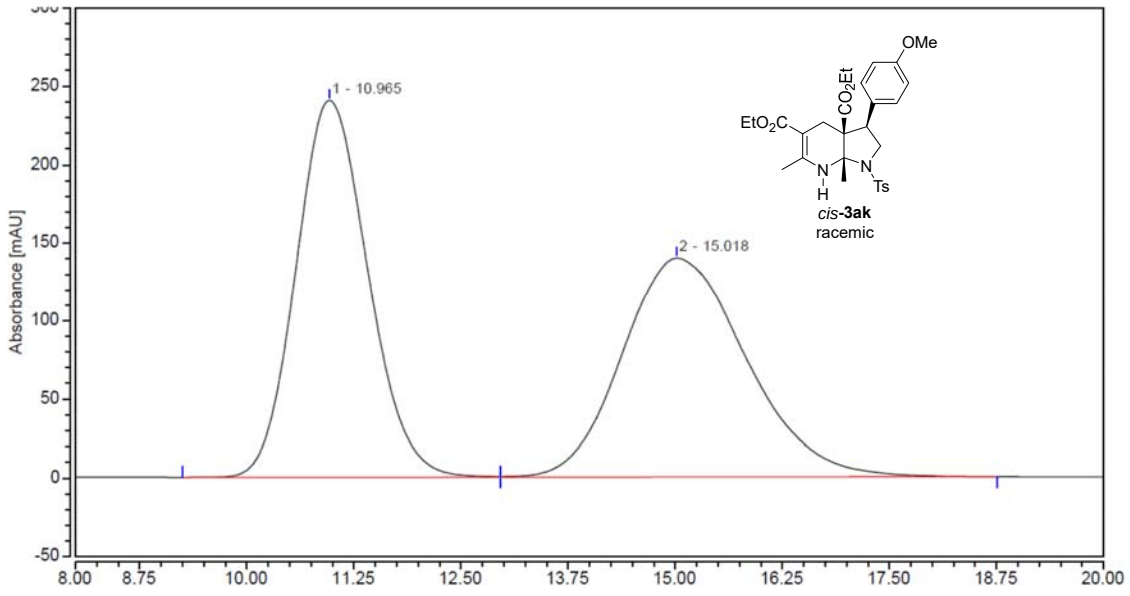
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.045	881.187	778.119	49.41	57.89
2	12.625	902.064	566.110	50.59	42.11



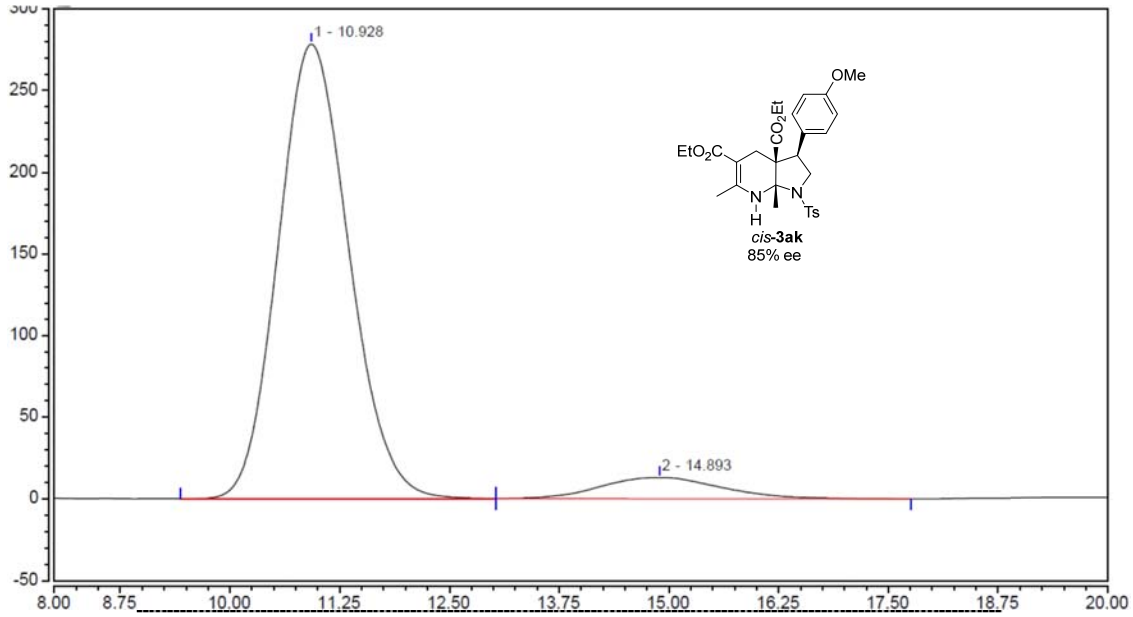
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.448	18.413	21.869	2.64	4.22
2	11.797	679.722	496.766	97.36	95.78



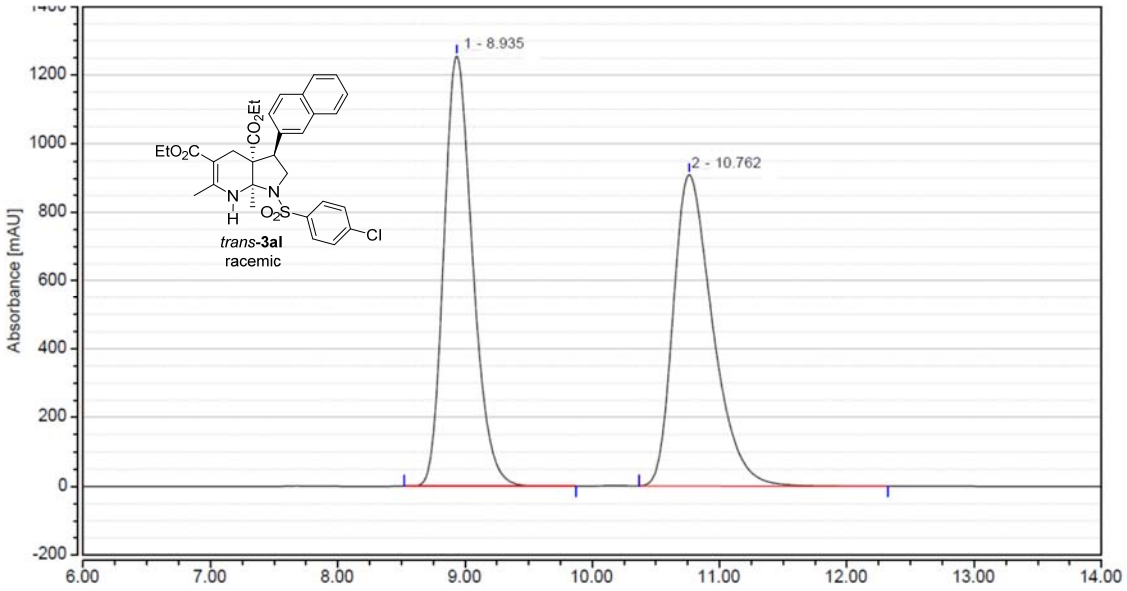
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.965	233.705	240.333	50.01	63.23
2	15.018	233.573	139.740	49.99	36.77



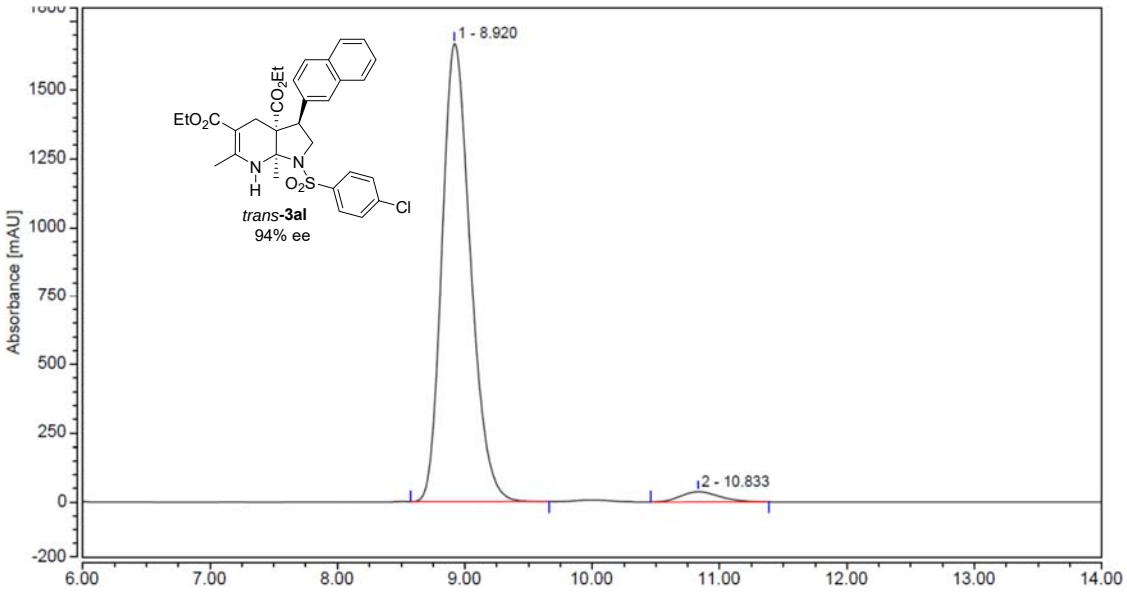
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.928	260.133	278.049	92.49	95.51
2	14.893	21.137	13.067	7.51	4.49



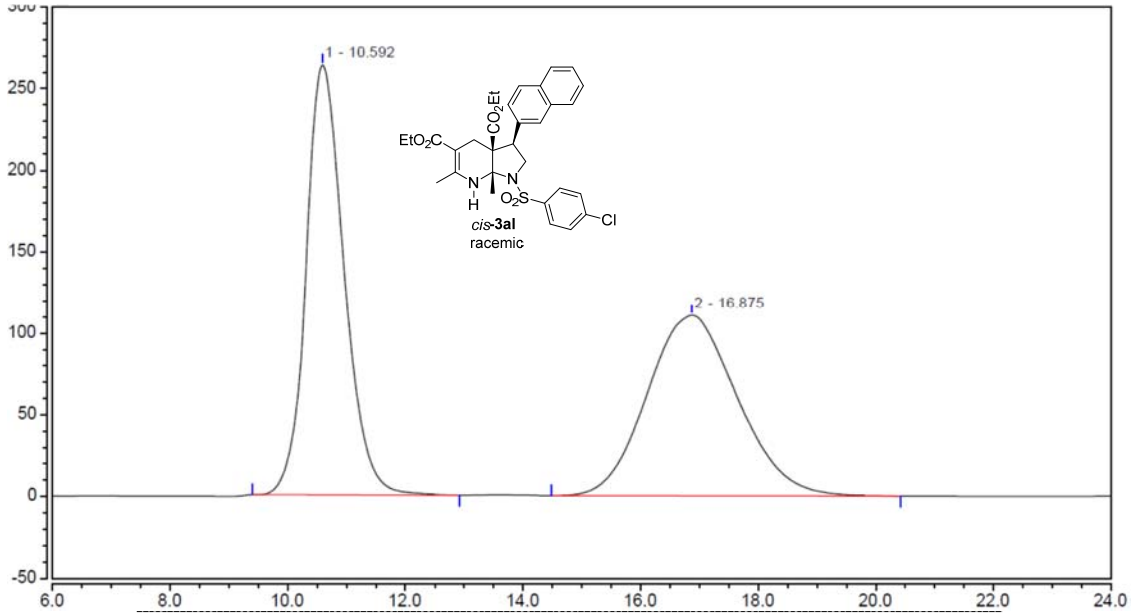
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.935	328.584	1255.296	50.25	58.00
2	10.762	325.372	908.892	49.75	42.00



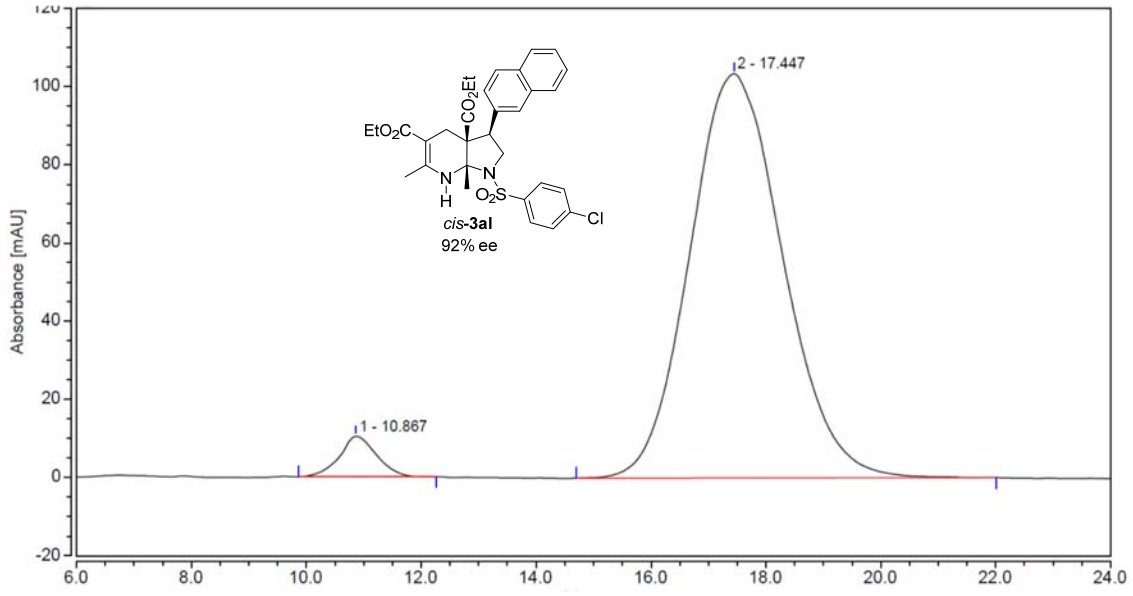
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.920	432.925	1668.631	97.05	97.83
2	10.833	13.162	37.075	2.95	2.17



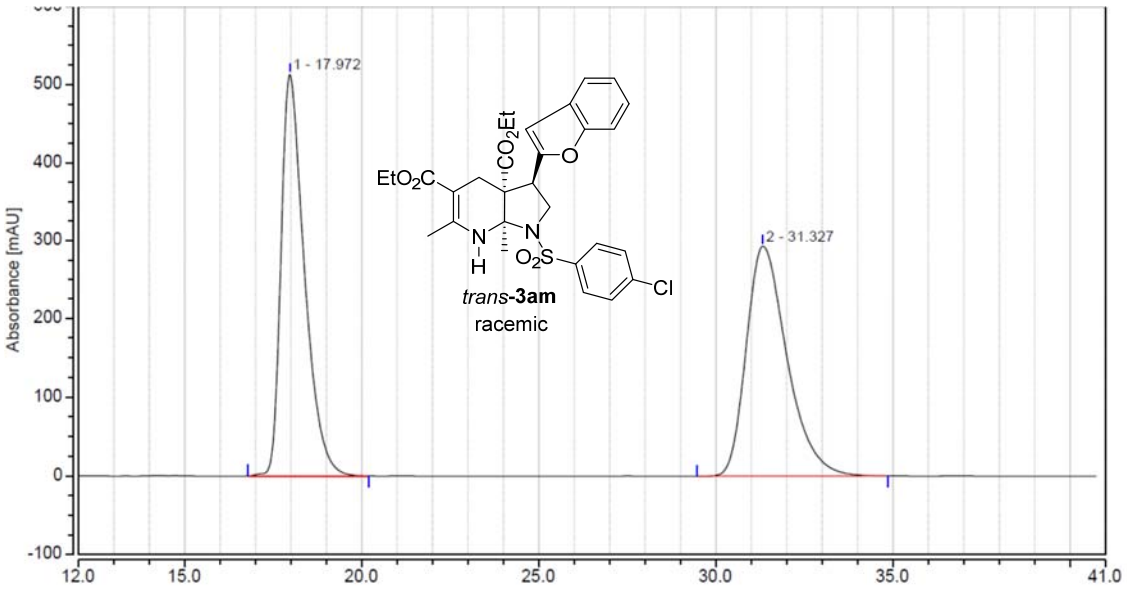
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.592	197.446	263.283	50.09	70.44
2	16.875	196.709	110.511	49.91	29.56



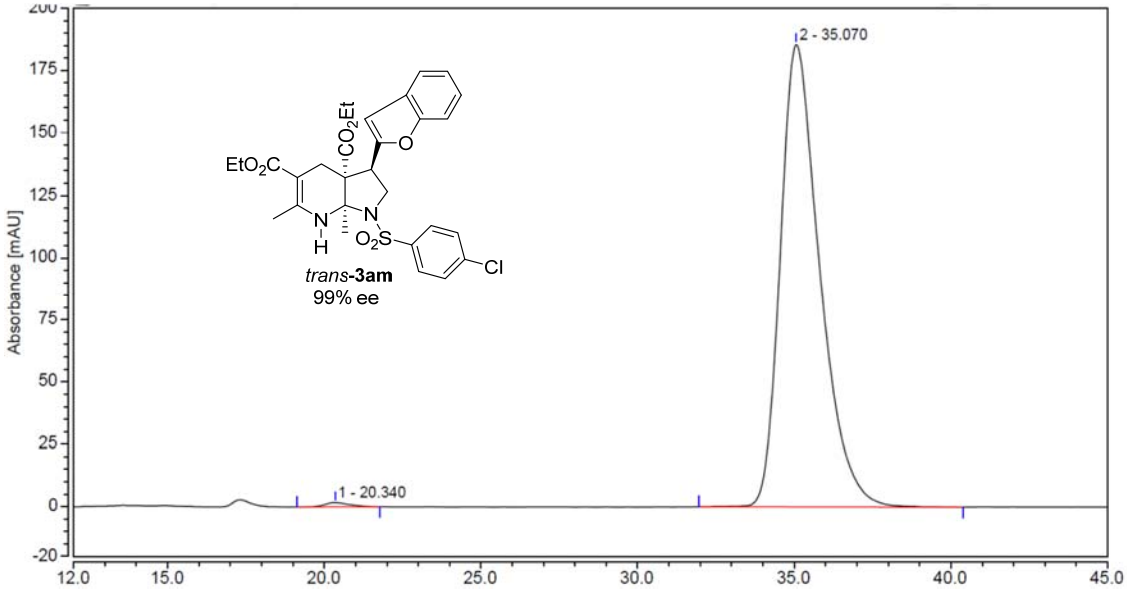
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.867	7.756	10.293	3.84	9.06
2	17.447	194.271	103.367	96.16	90.94



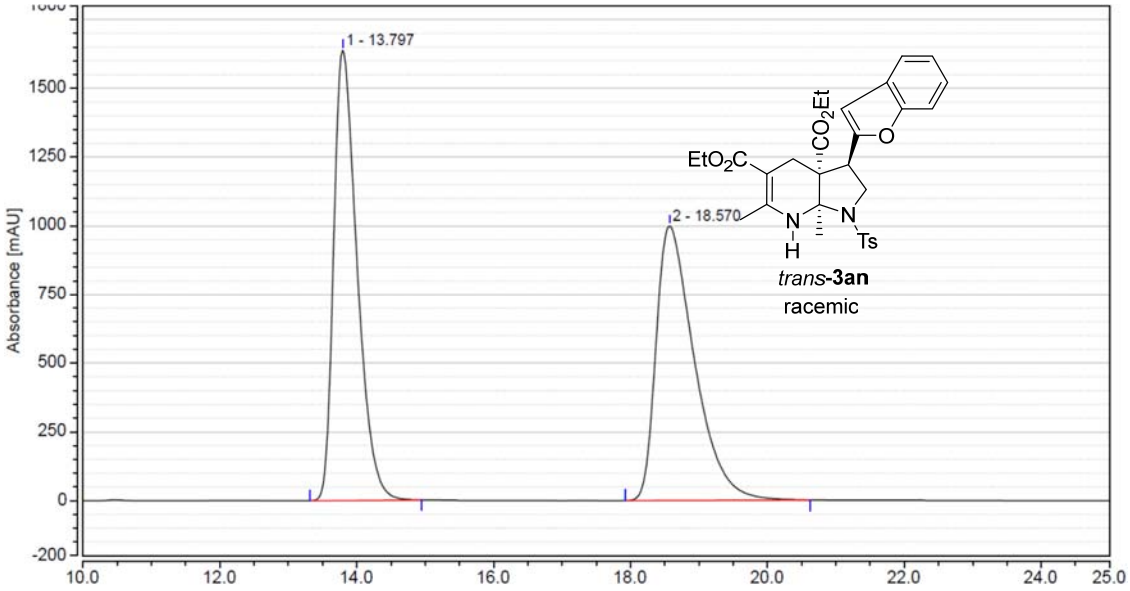
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	17.972	392.838	513.560	50.15	63.64
2	31.327	390.530	293.442	49.85	36.36



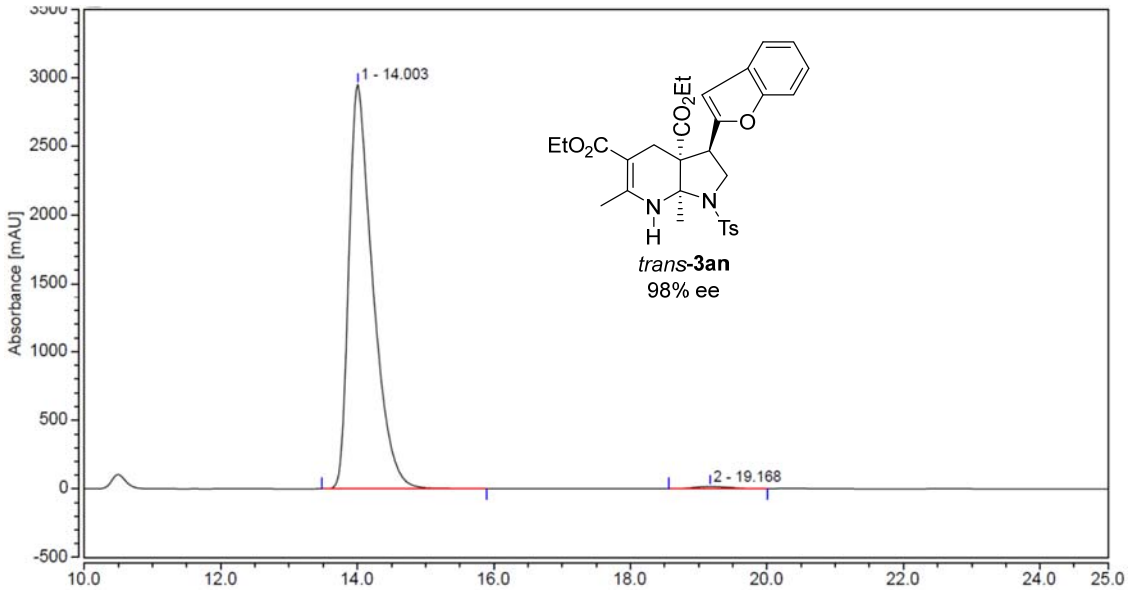
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	20.340	1.592	1.747	0.58	0.93
2	35.070	270.739	185.484	99.42	99.07



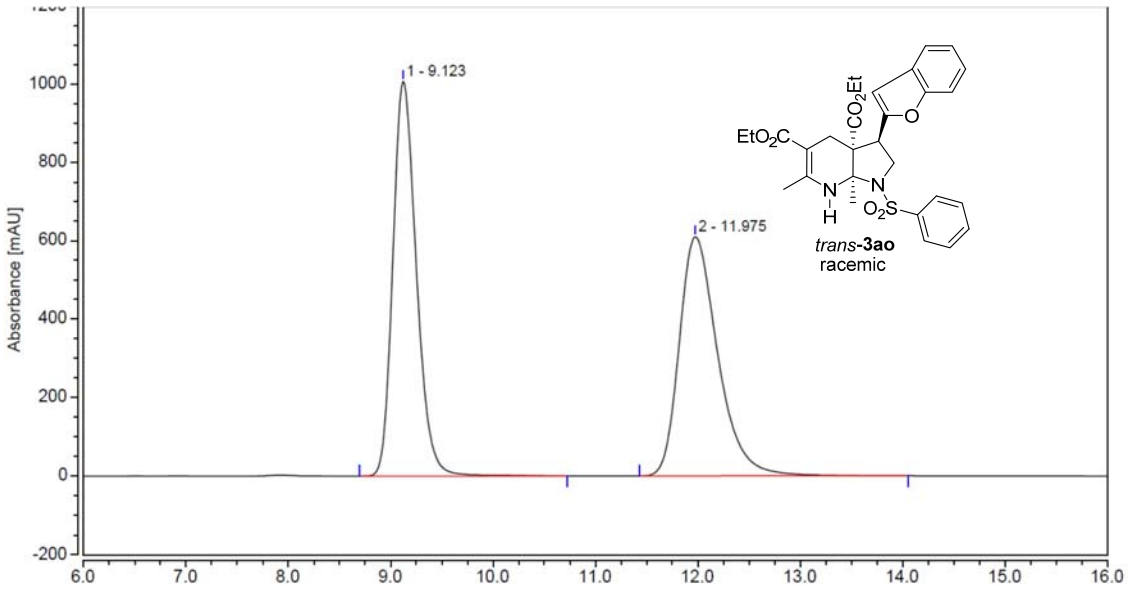
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	13.797	648.924	1638.188	50.07	62.12
2	18.570	647.157	999.098	49.93	37.88



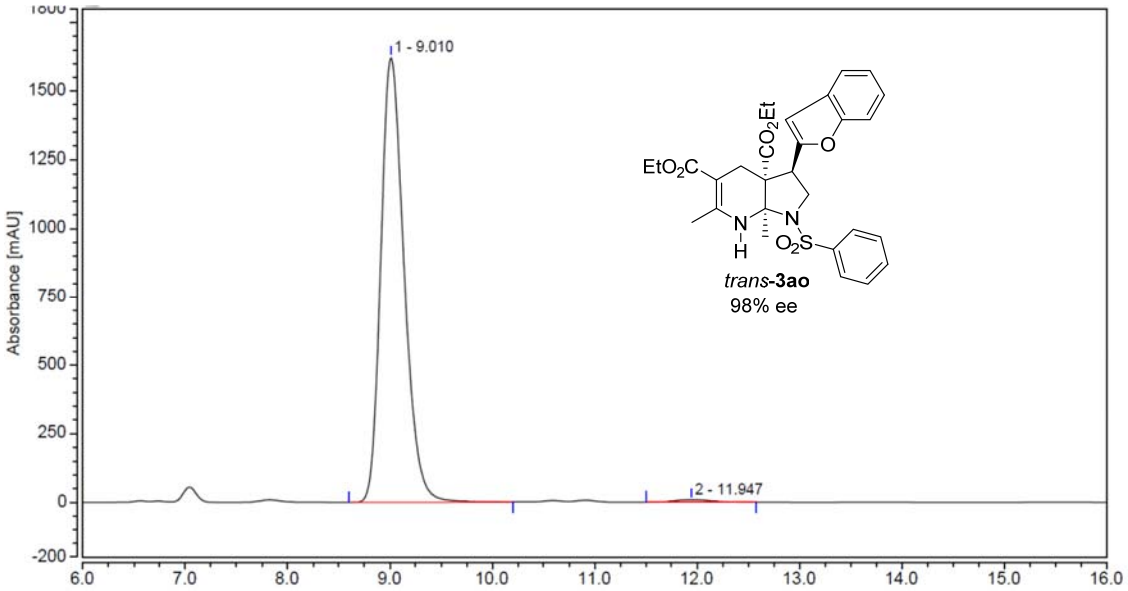
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	14.003	1194.908	2952.216	99.23	99.48
2	19.168	9.285	15.333	0.77	0.52



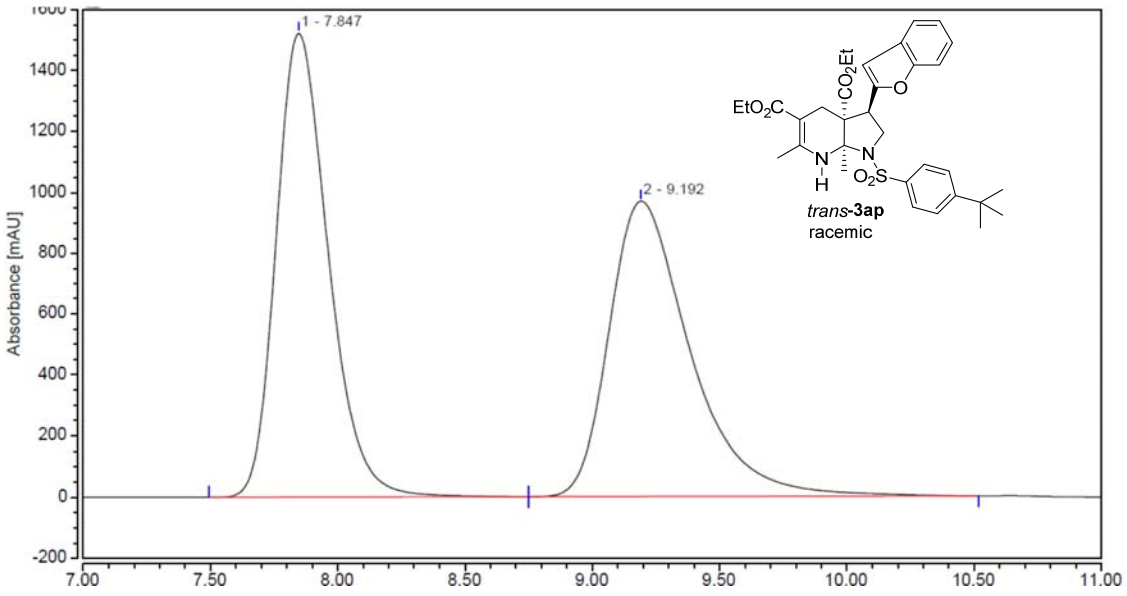
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.123	267.363	1007.653	50.15	62.29
2	11.975	265.762	609.951	49.85	37.71



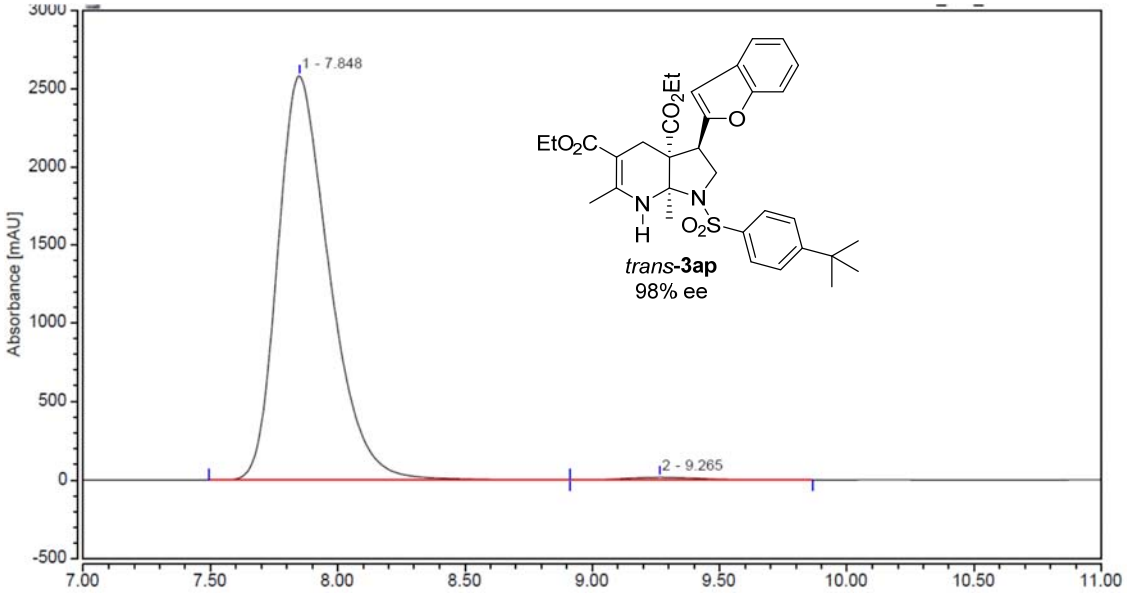
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.010	427.523	1623.522	99.03	99.40
2	11.947	4.185	9.752	0.97	0.60



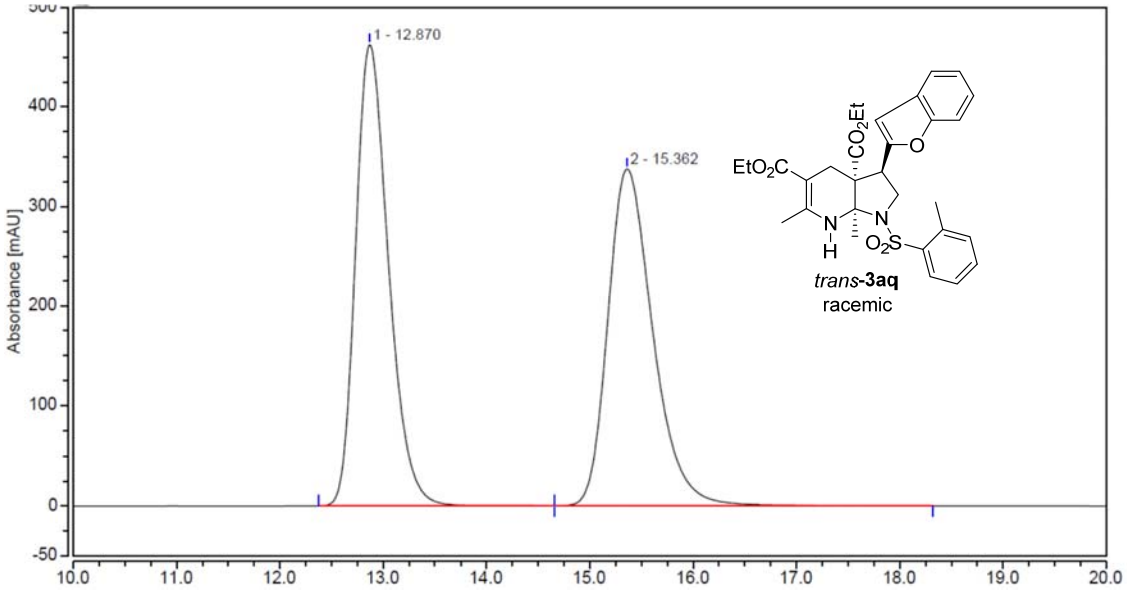
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	7.847	361.124	1522.225	50.24	61.08
2	9.192	357.721	969.951	49.76	38.92



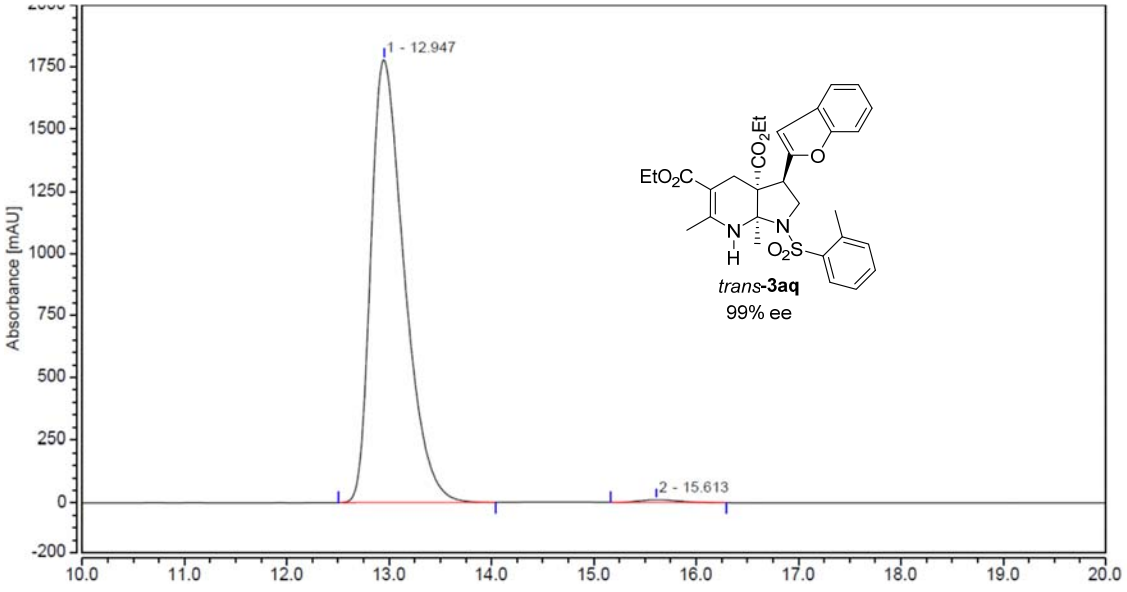
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	7.848	606.820	2581.342	99.01	99.36
2	9.265	6.076	16.701	0.99	0.64



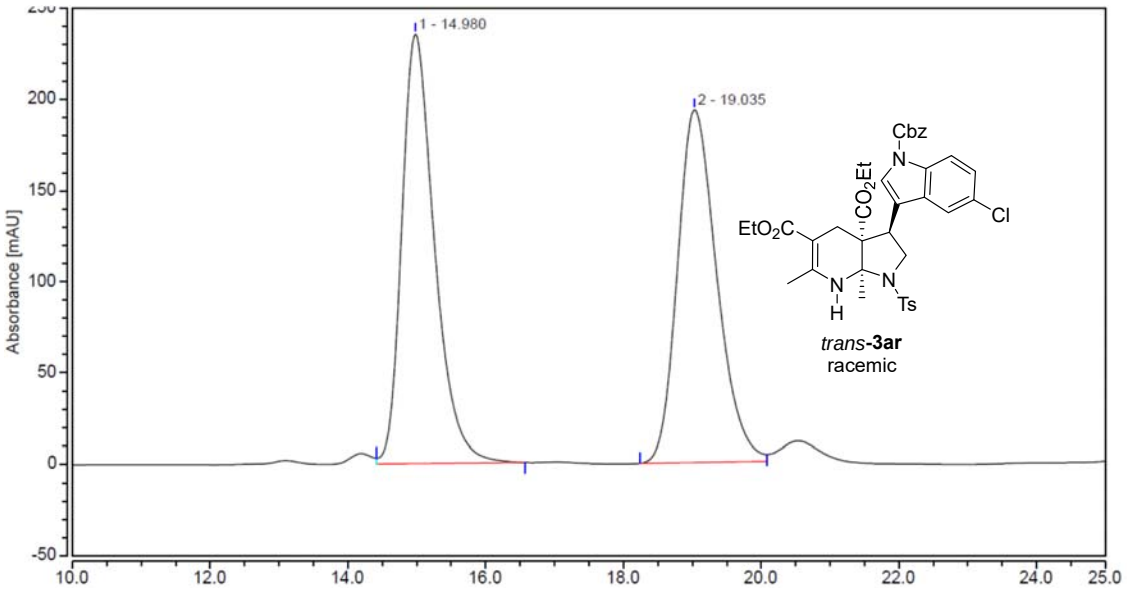
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	12.870	170.548	462.564	50.03	57.78
2	15.362	170.347	337.980	49.97	42.22



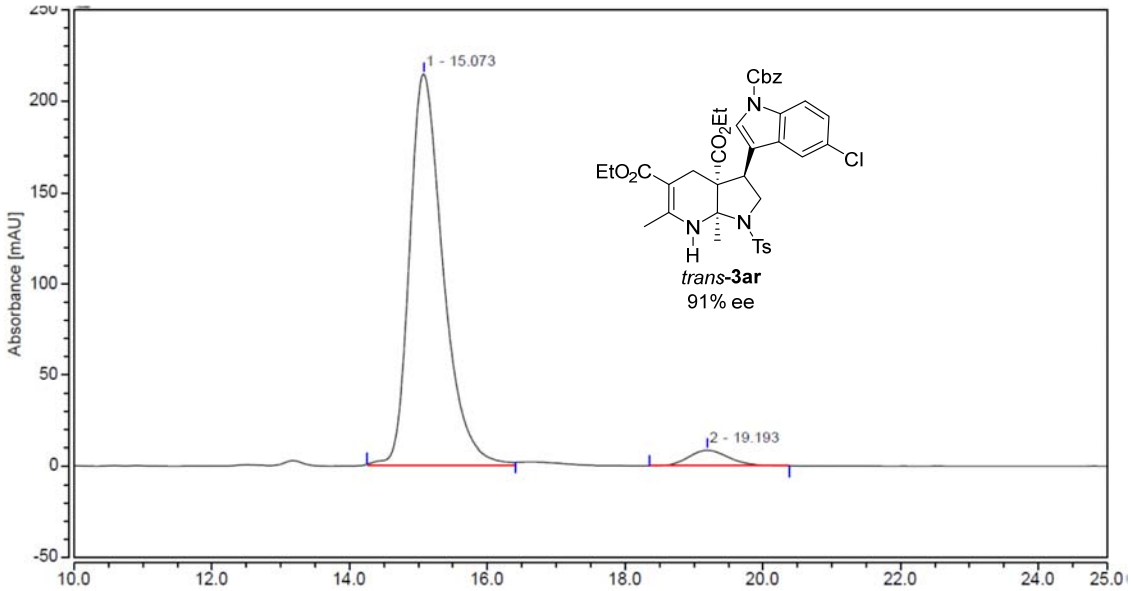
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	12.947	669.915	1778.731	99.25	99.39
2	15.613	5.080	10.949	0.75	0.61



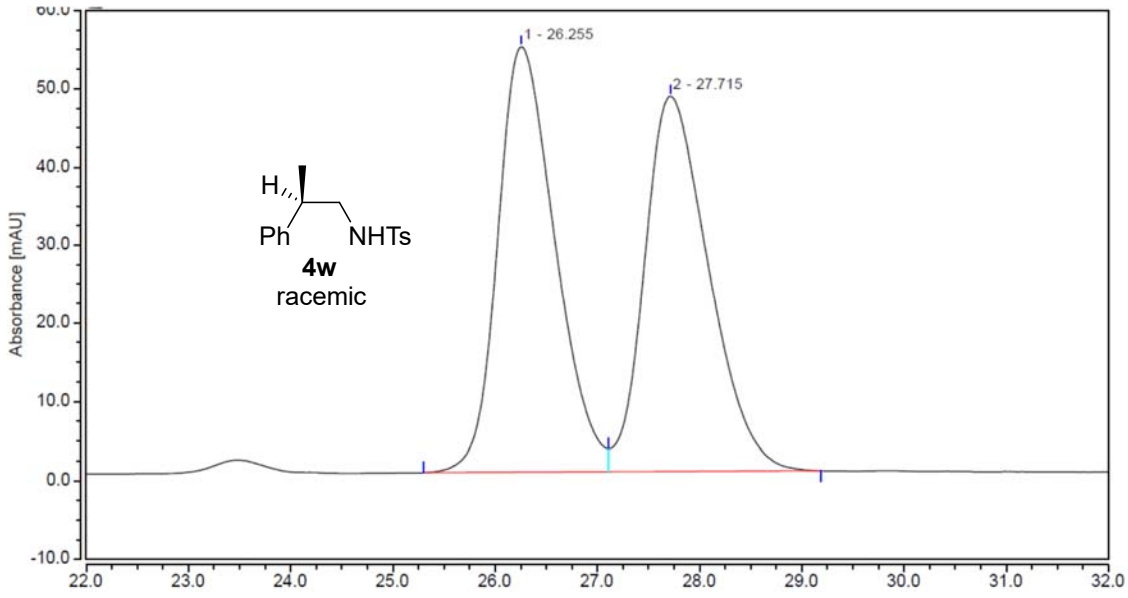
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	14.980	129.214	235.222	50.34	54.92
2	19.035	127.490	193.109	49.66	45.08



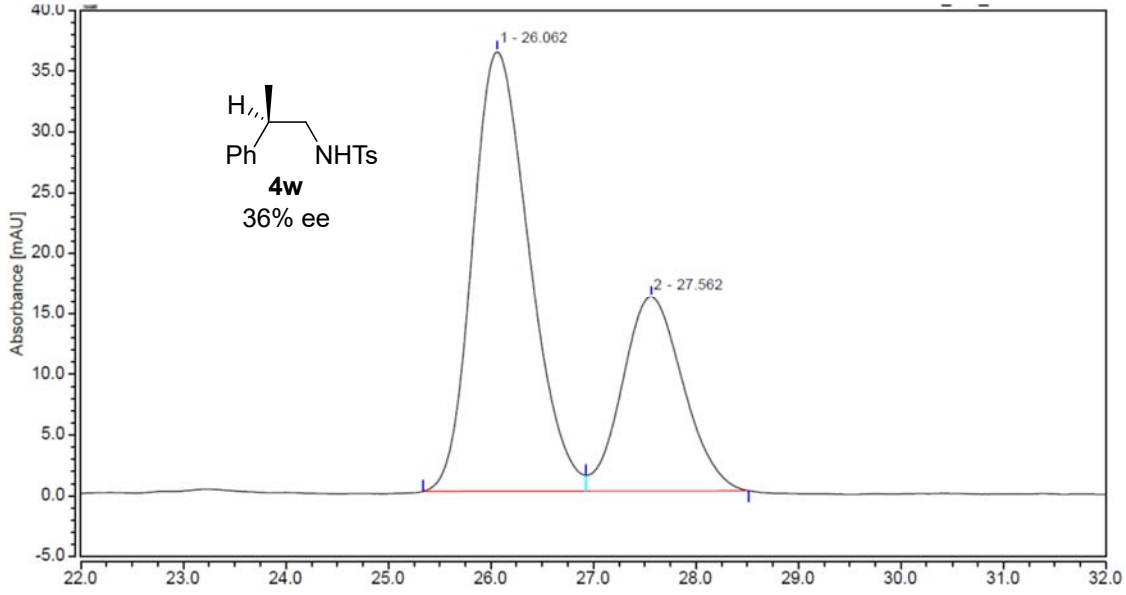
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	15.073	120.893	214.256	95.37	96.15
2	19.193	5.874	8.575	4.63	3.85



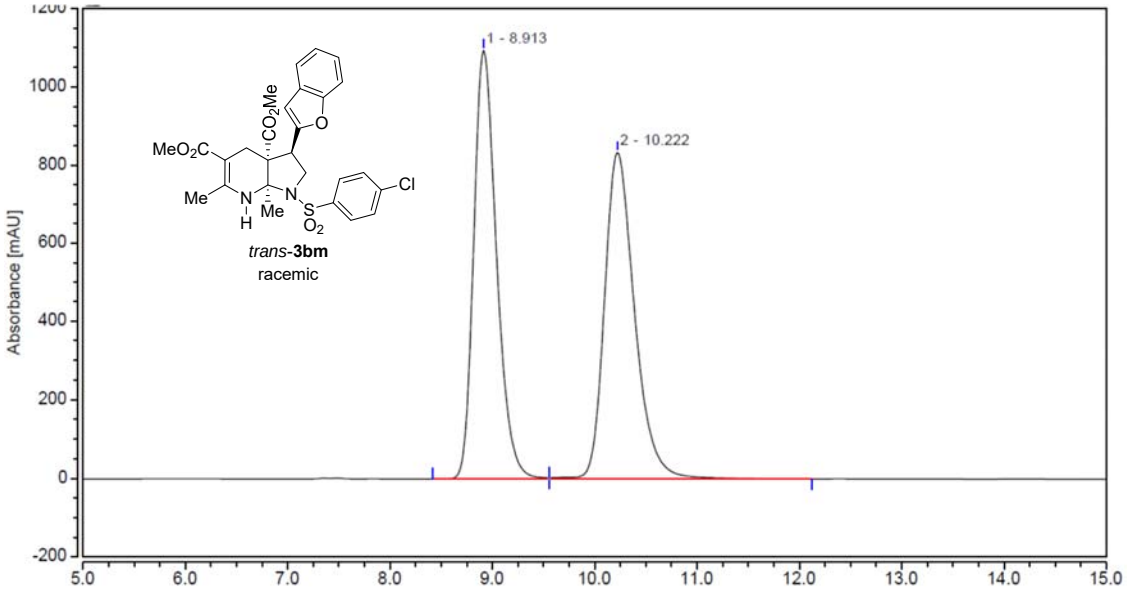
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	26.255	35.216	54.292	50.36	53.15
2	27.715	34.720	47.862	49.64	46.85



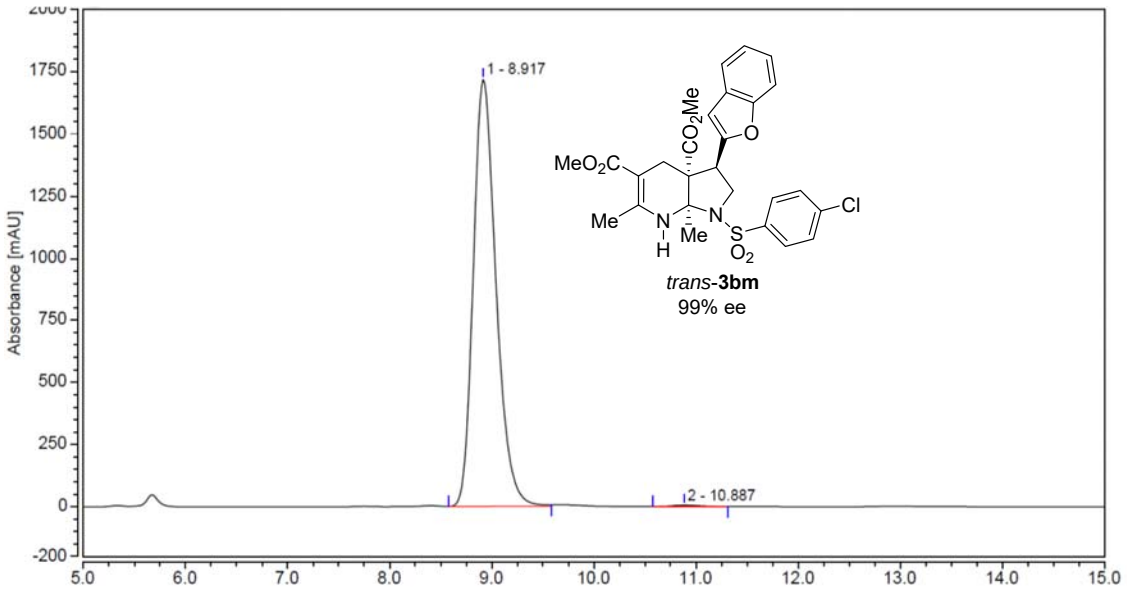
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	26.062	23.236	36.222	67.93	69.35
2	27.562	10.970	16.007	32.07	30.65



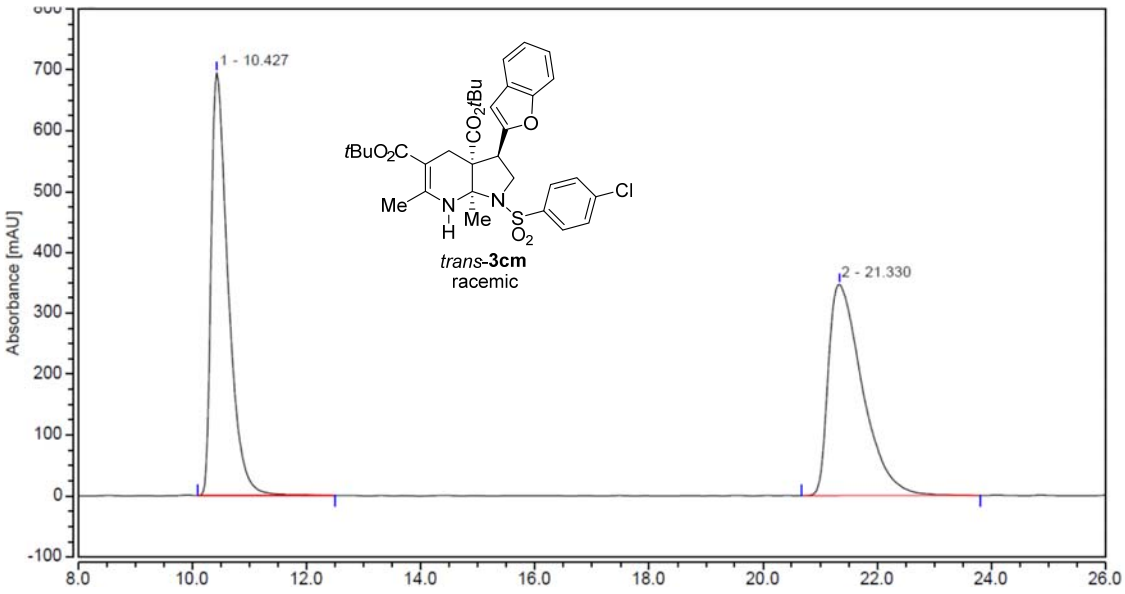
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.913	282.412	1094.750	49.85	56.78
2	10.222	284.157	833.422	50.15	43.22



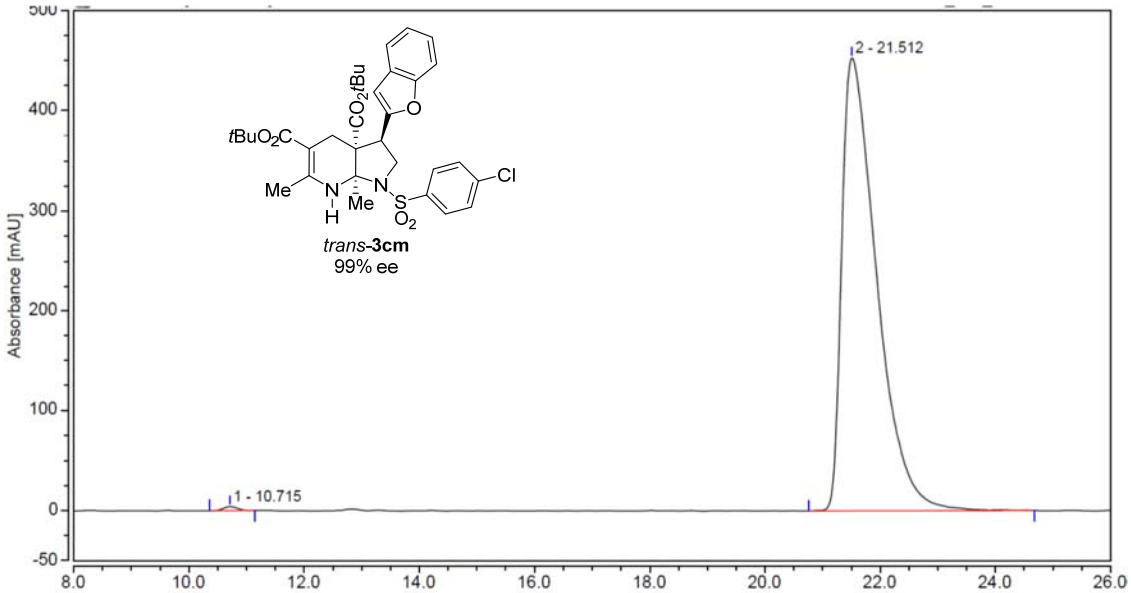
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.917	442.808	1716.907	99.66	99.71
2	10.887	1.526	4.983	0.34	0.29



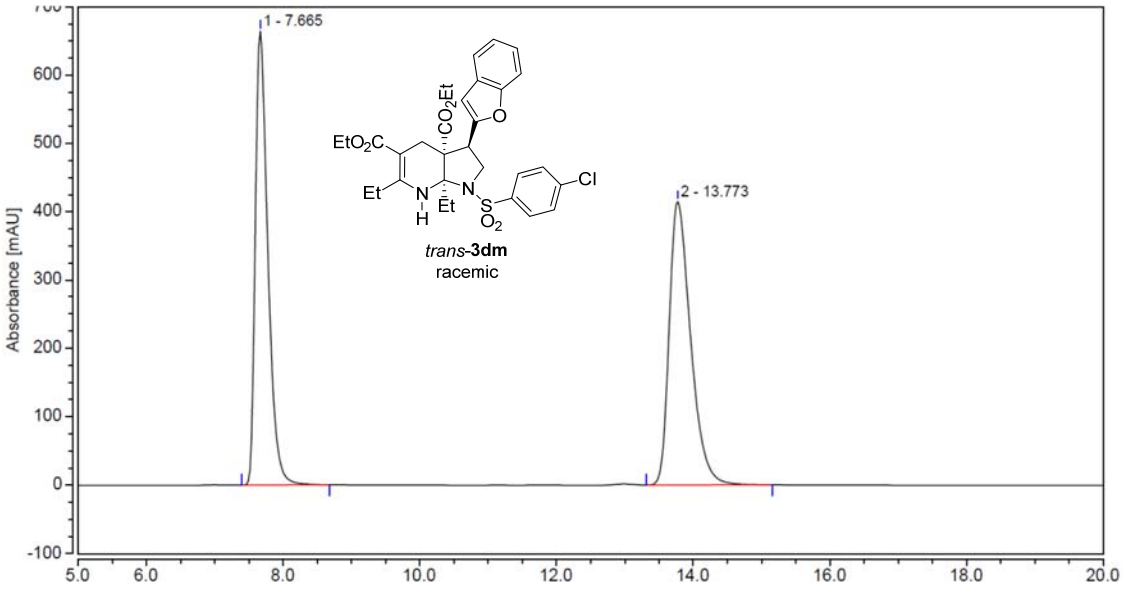
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.427	240.469	694.888	50.05	66.63
2	21.330	240.014	347.993	49.95	33.37



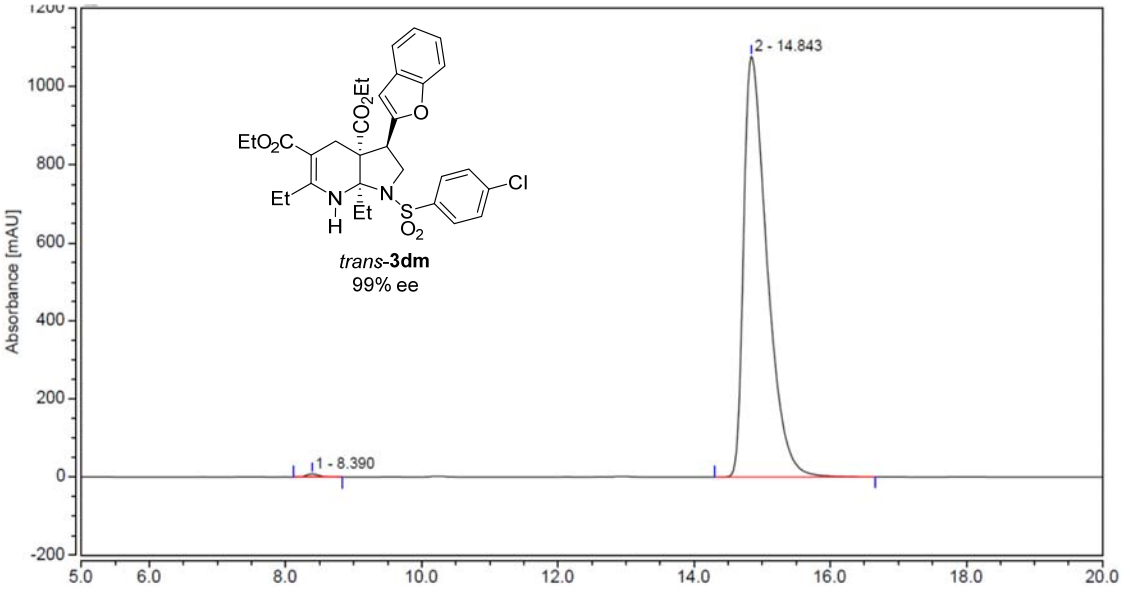
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.715	1.169	4.150	0.37	0.91
2	21.512	317.686	452.593	99.63	99.09



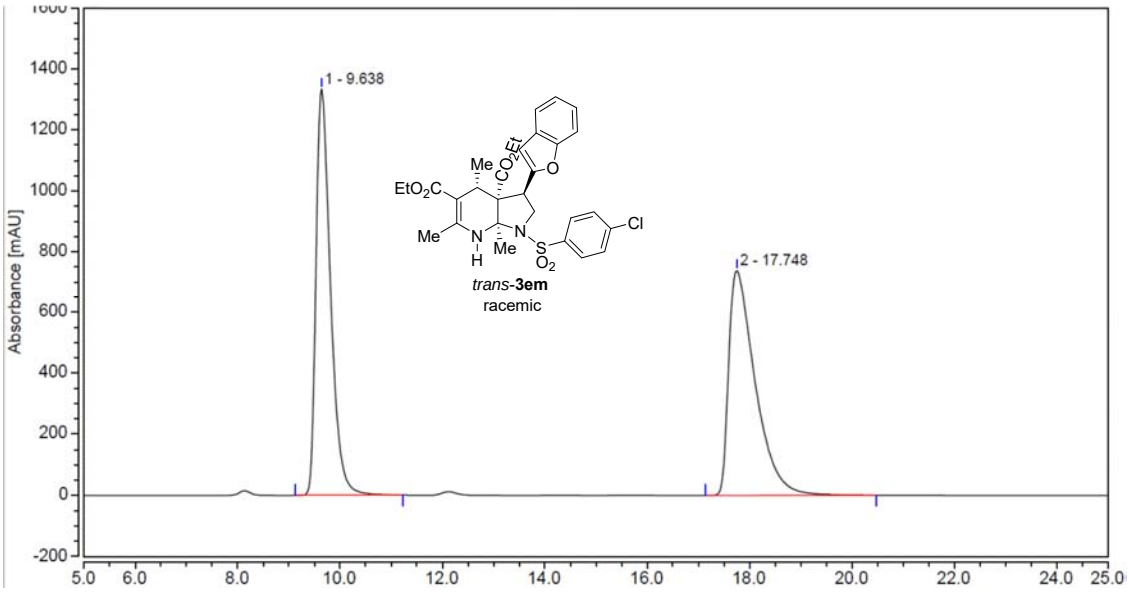
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	7.665	141.337	664.588	48.47	61.56
2	13.773	150.250	414.927	51.53	38.44



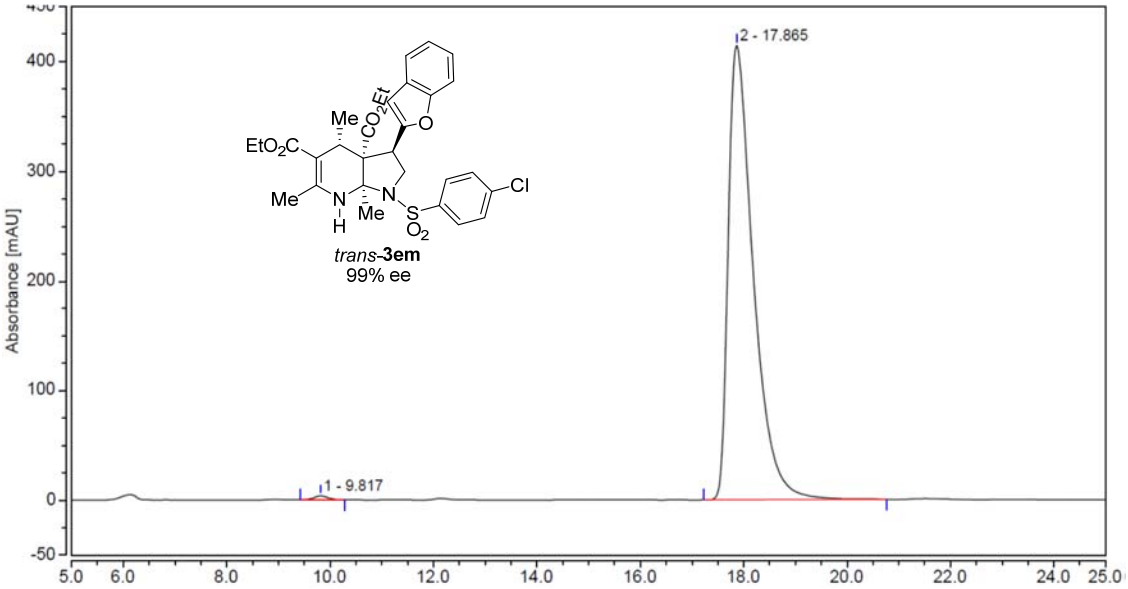
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.390	1.741	8.147	0.40	0.75
2	14.843	428.548	1077.670	99.60	99.25



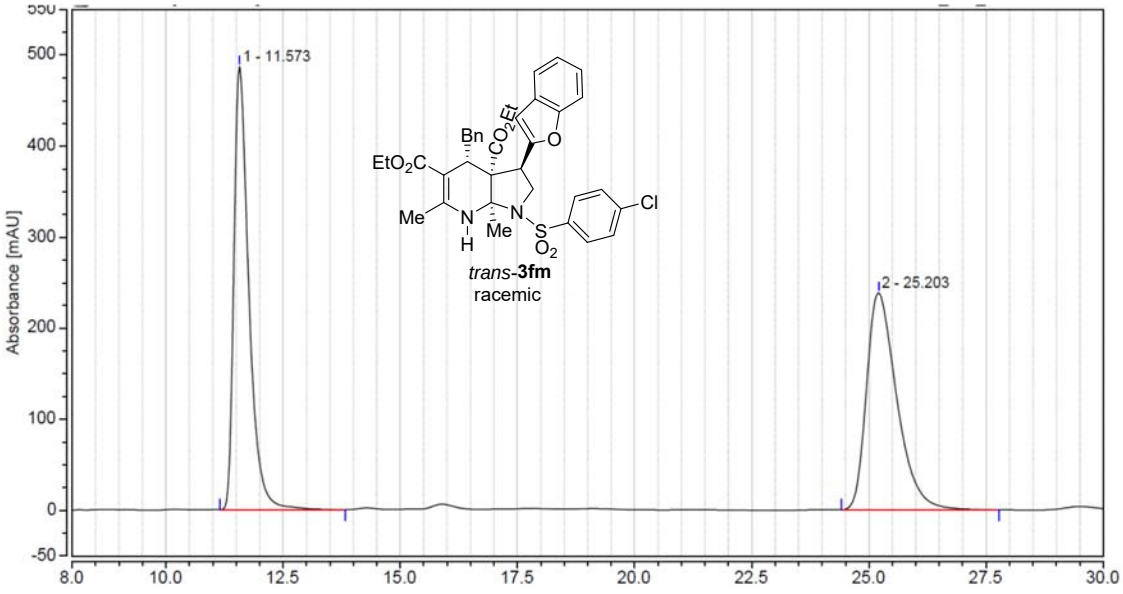
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.638	436.165	1332.694	49.81	64.38
2	17.748	439.570	737.261	50.19	35.62



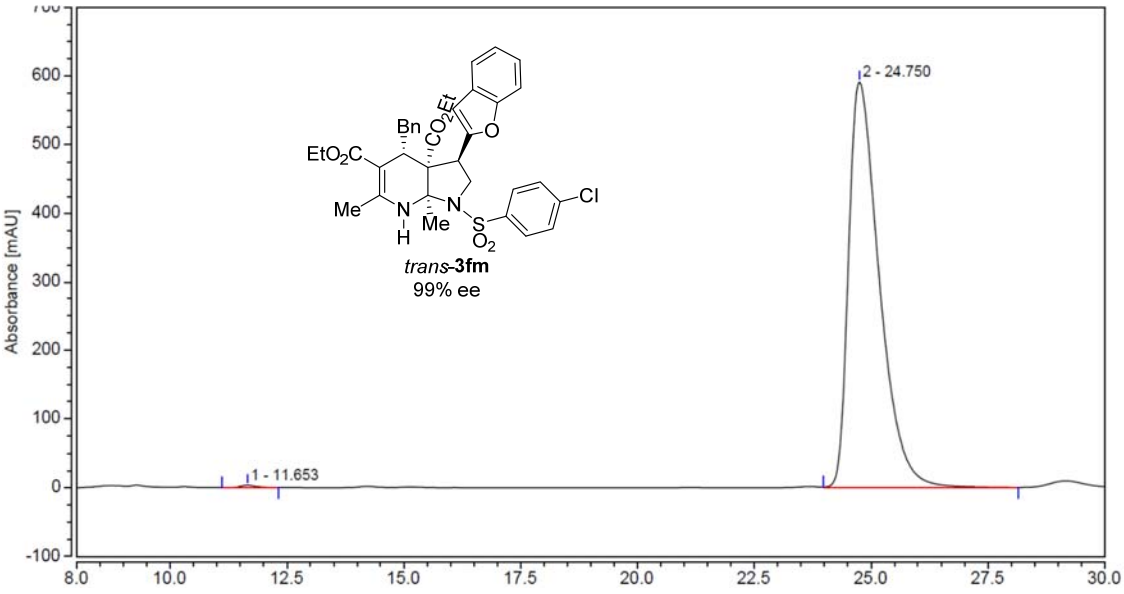
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	9.817	1.089	3.494	0.46	0.84
2	17.865	233.189	414.173	99.54	99.16



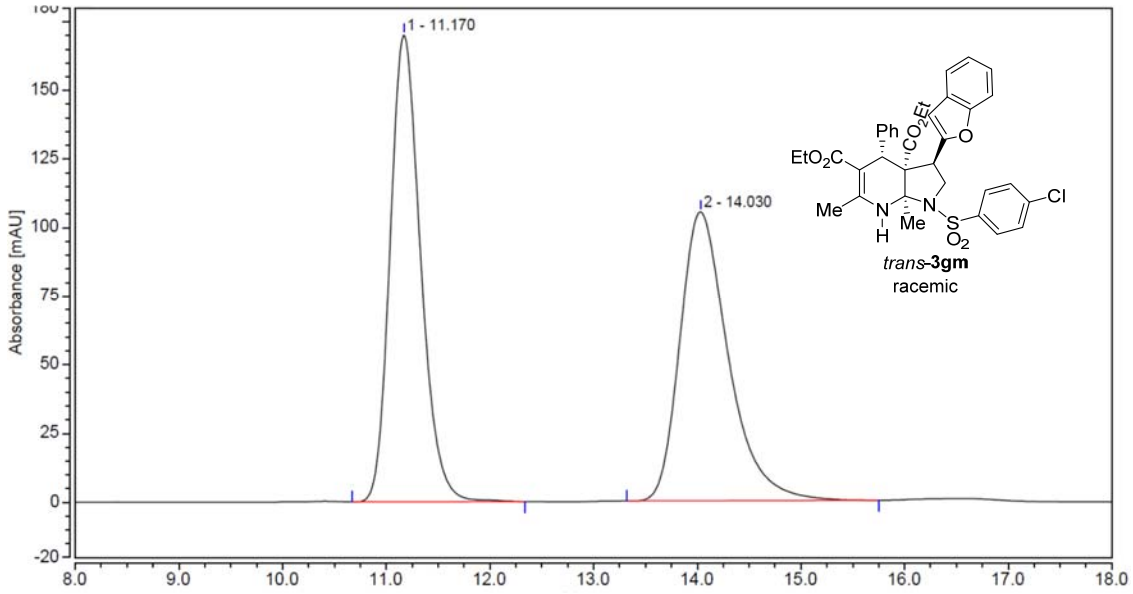
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	11.573	180.260	486.684	50.27	67.10
2	25.203	178.302	238.636	49.73	32.90



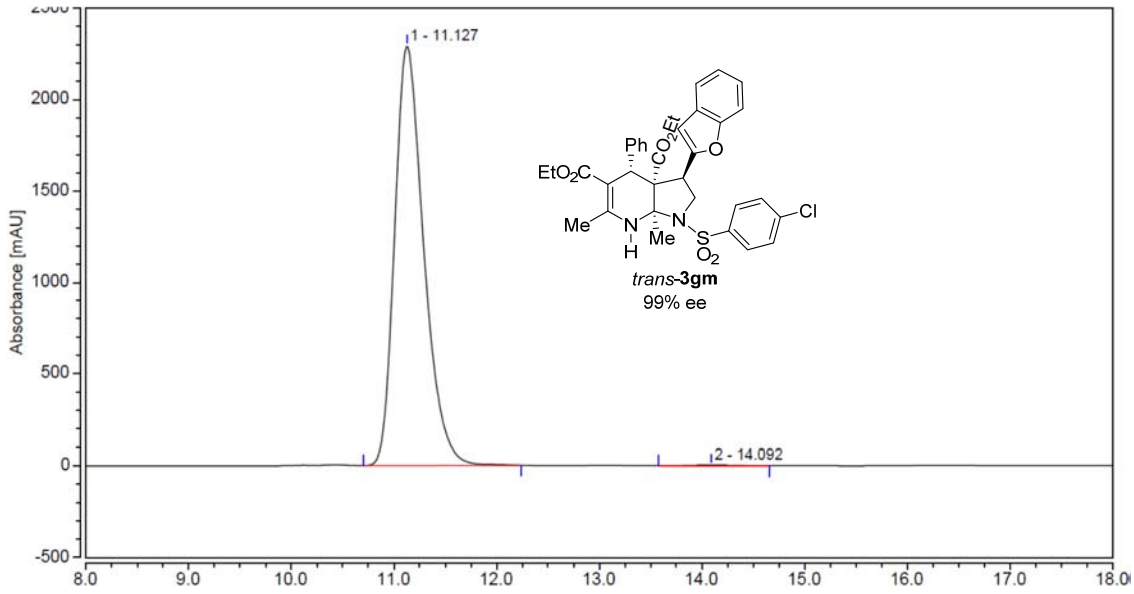
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	11.653	1.316	3.467	0.29	0.58
2	24.750	449.192	590.574	99.71	99.42



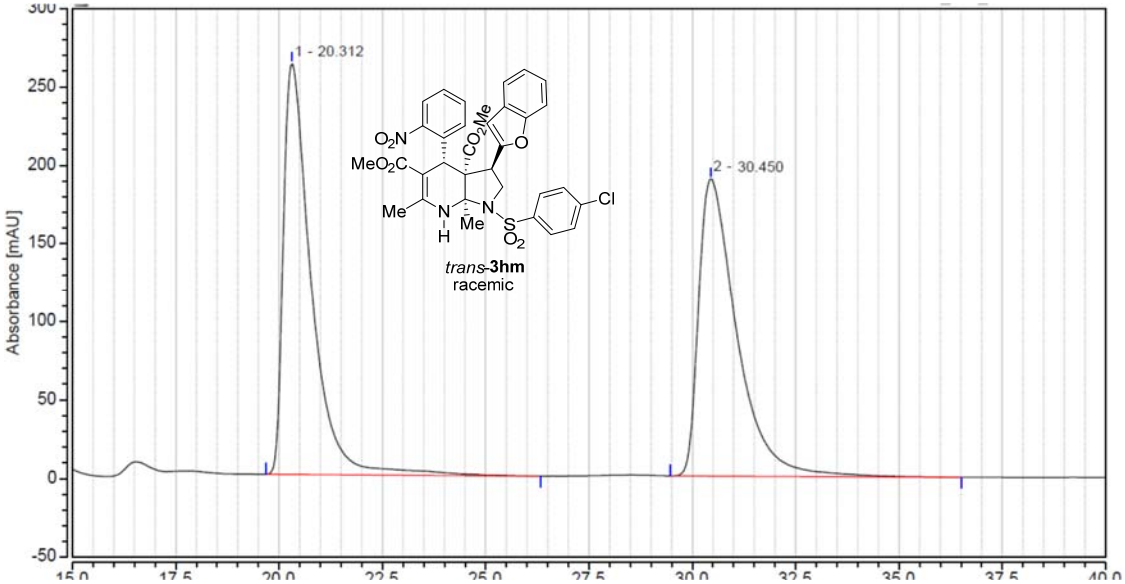
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	11.170	57.990	170.067	50.53	61.78
2	14.030	56.772	105.226	49.47	38.22



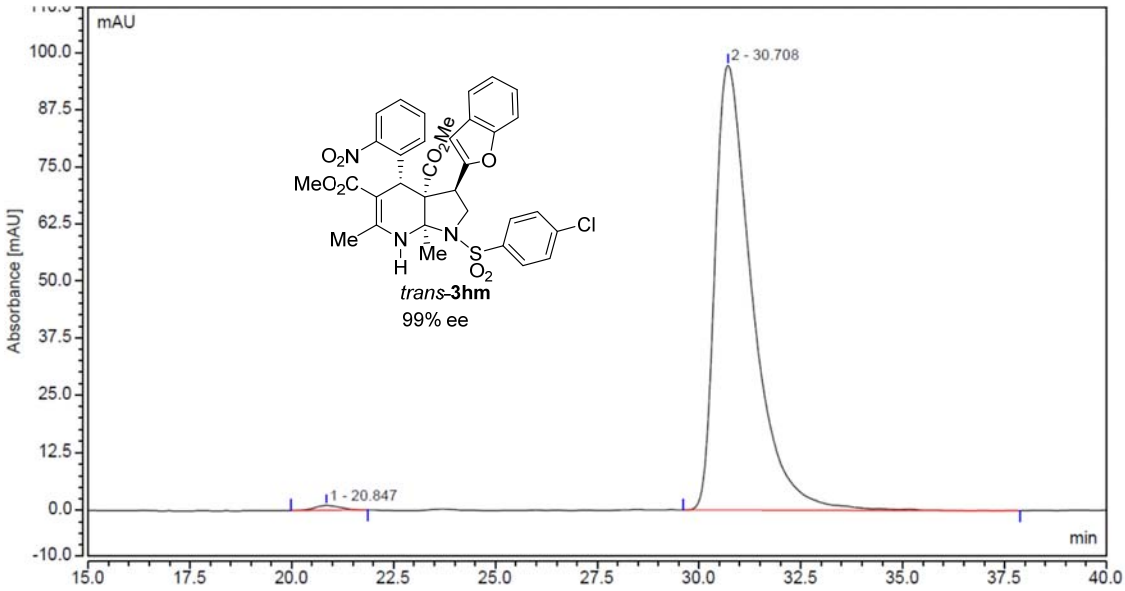
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	11.127	750.167	2291.634	99.78	99.85
2	14.092	1.638	3.505	0.22	0.15



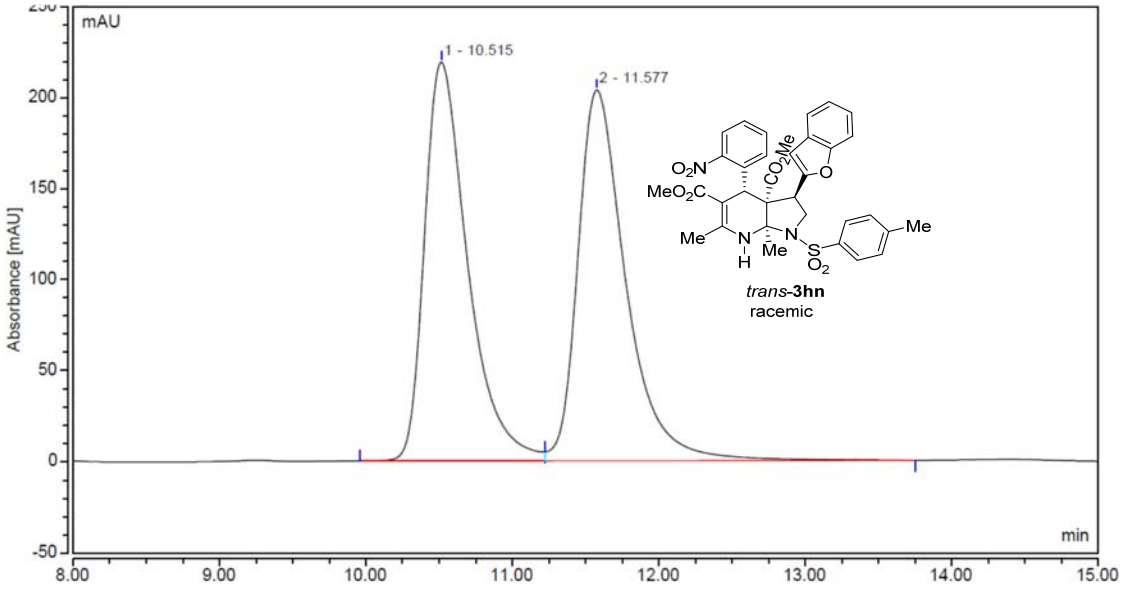
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	20.312	205.747	262.332	50.34	58.03
2	30.450	202.975	189.754	49.66	41.97



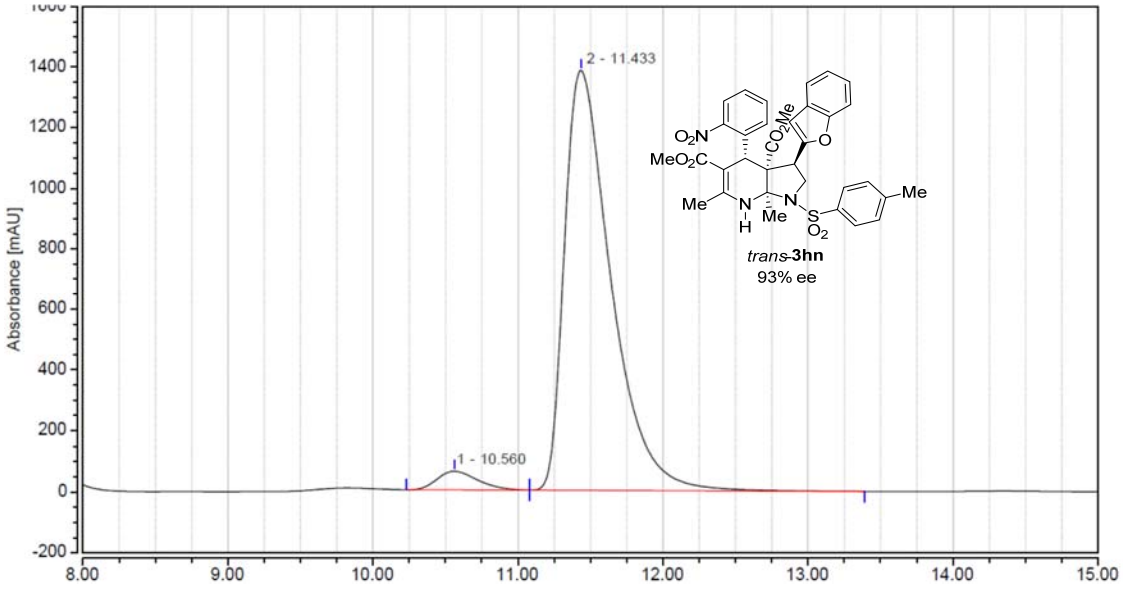
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	20.847	0.768	1.052	0.74	1.07
2	30.708	102.645	97.242	99.26	98.93



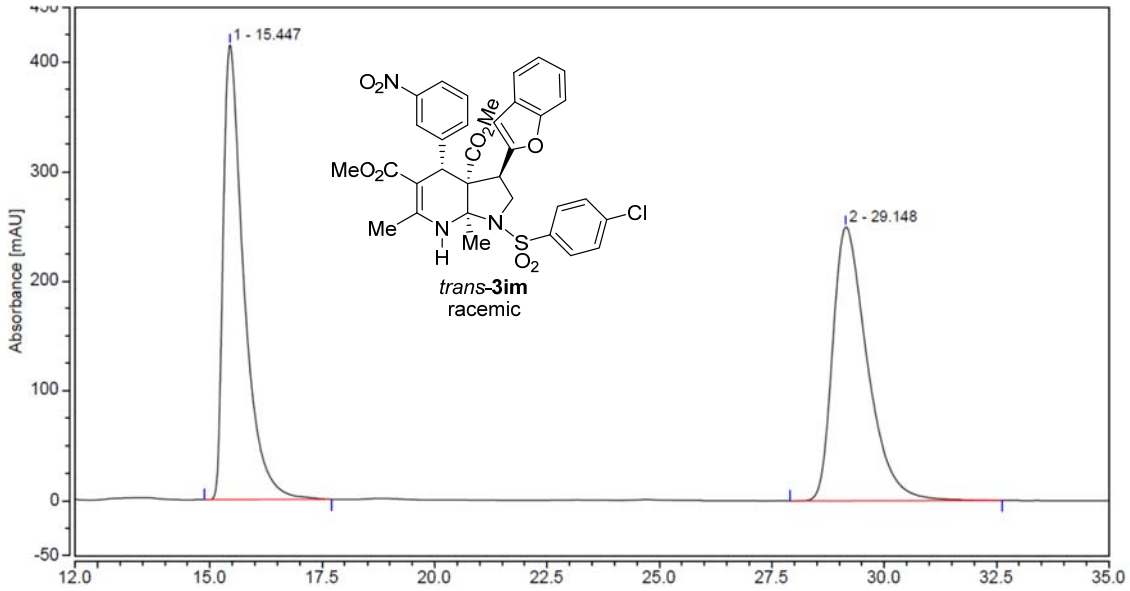
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.515	74.672	219.081	49.17	51.83
2	11.577	77.181	203.643	50.83	48.17



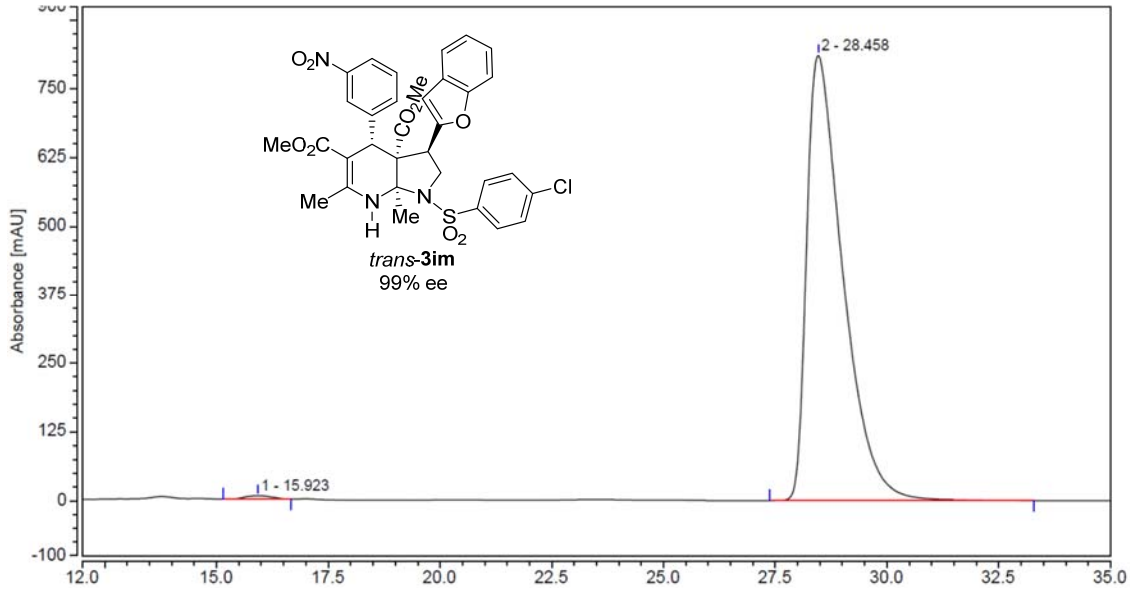
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	10.560	19.936	61.509	3.73	4.26
2	11.433	514.446	1383.909	96.27	95.74



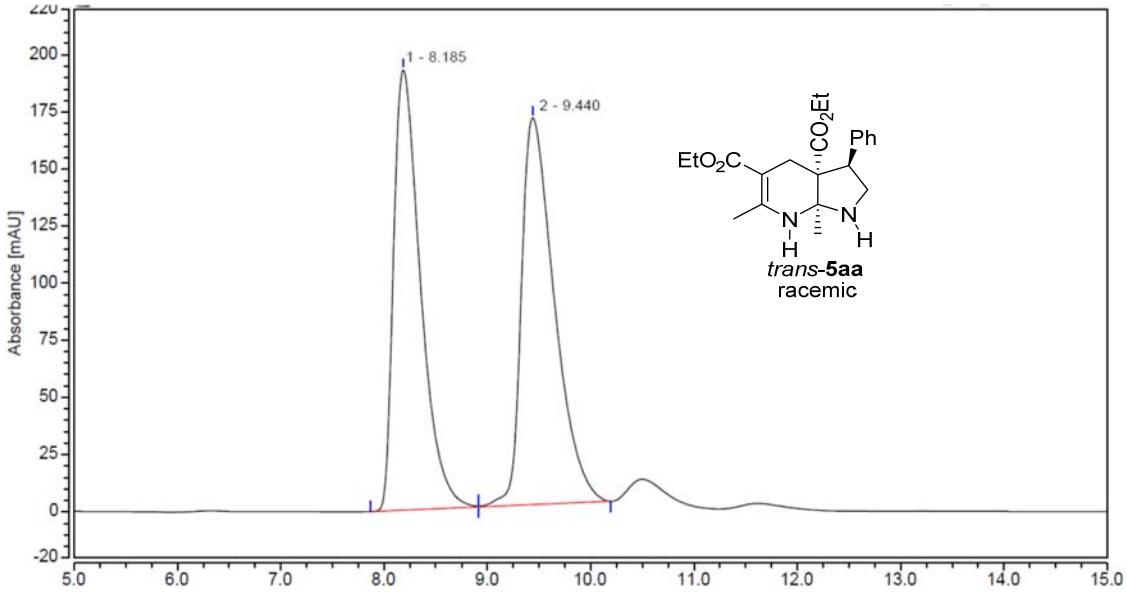
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	15.447	219.918	414.476	49.76	62.40
2	29.148	222.057	249.778	50.24	37.60



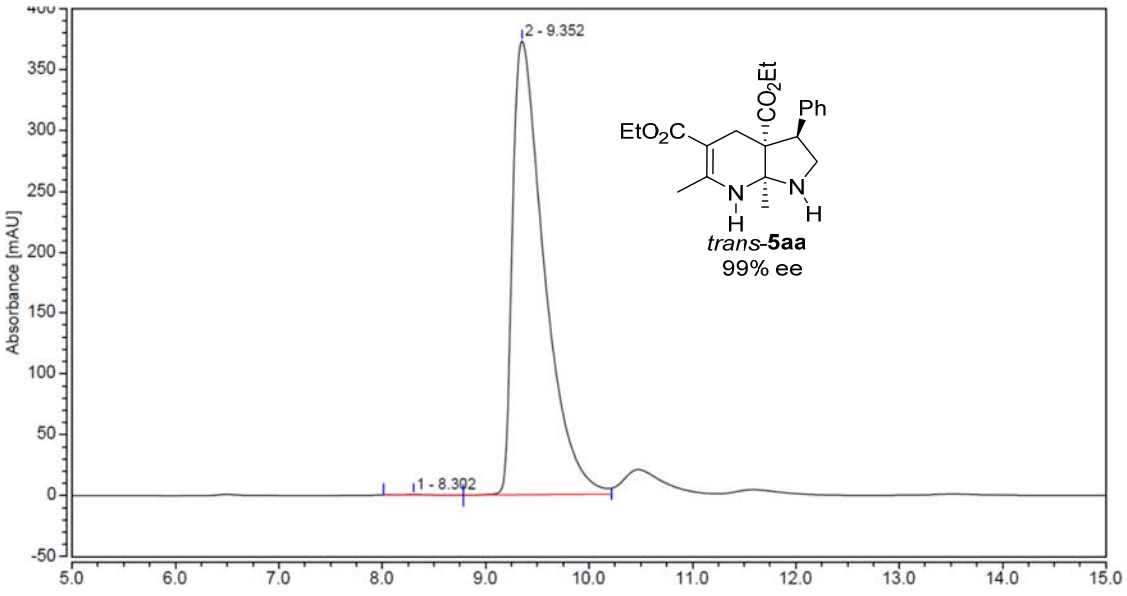
Area Percent Report

Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	15.923	4.406	6.243	0.58	0.76
2	28.458	759.782	810.662	99.42	99.24



Area Percent Report

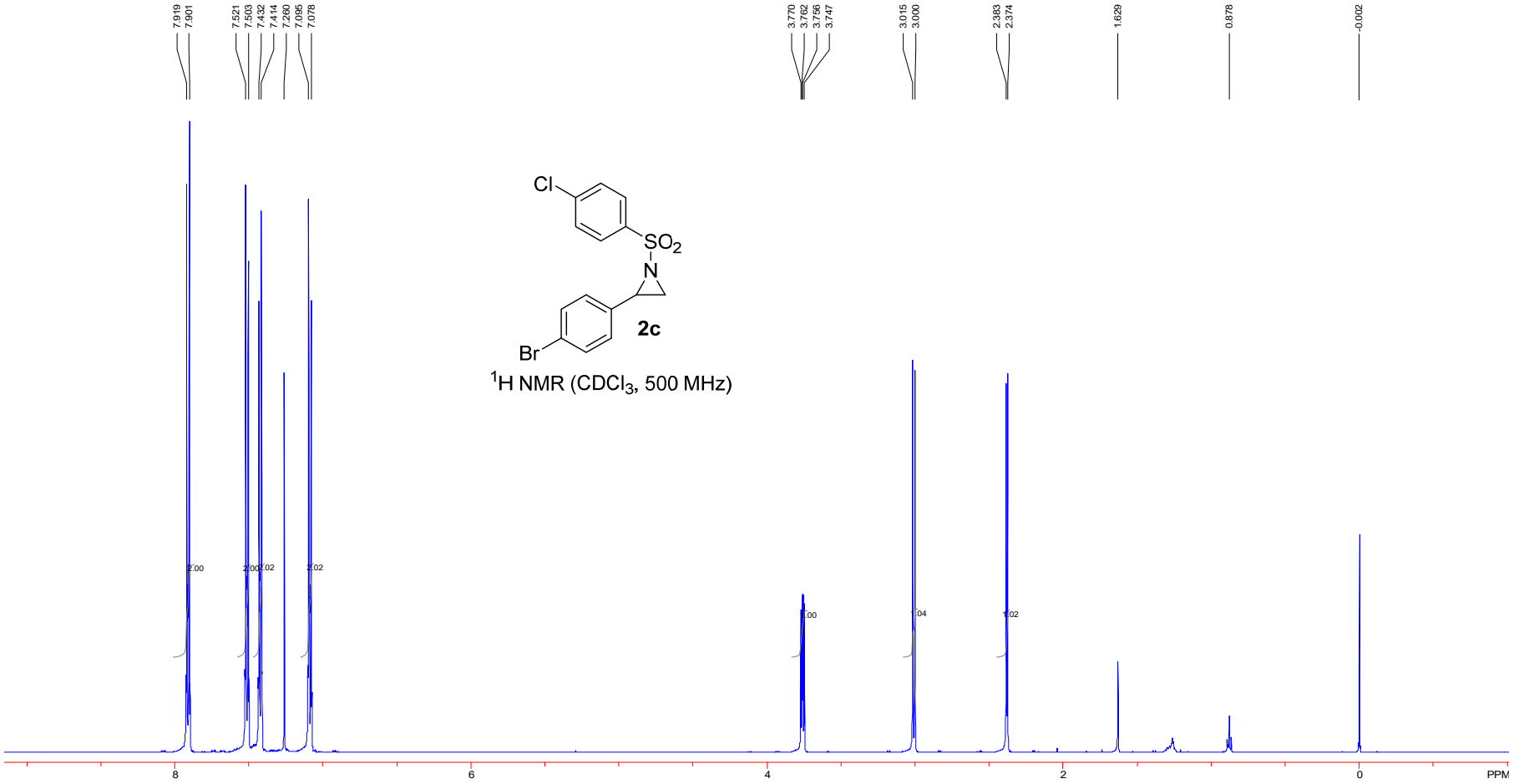
Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.185	58.106	192.783	48.11	53.23
2	9.440	62.674	169.410	51.89	46.77

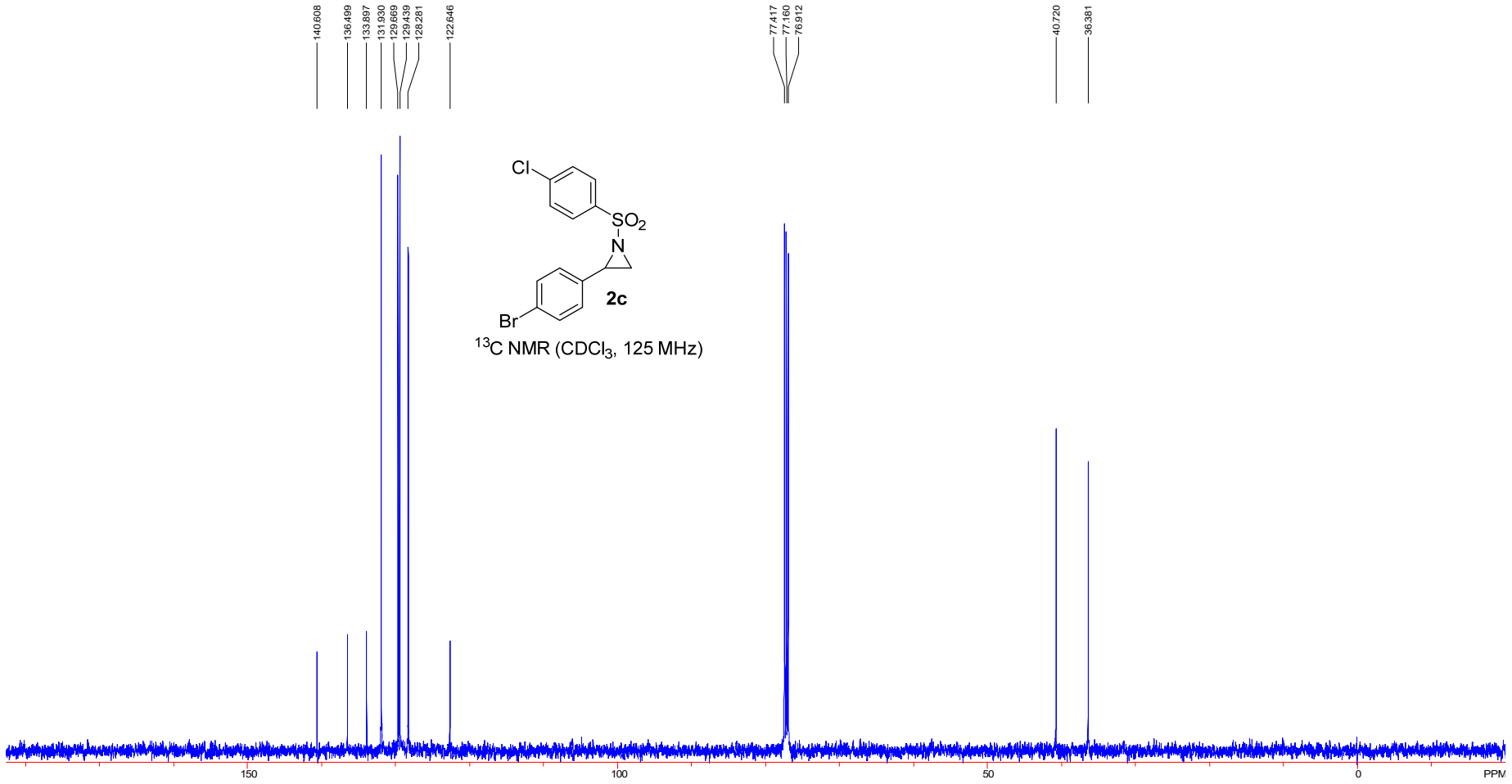


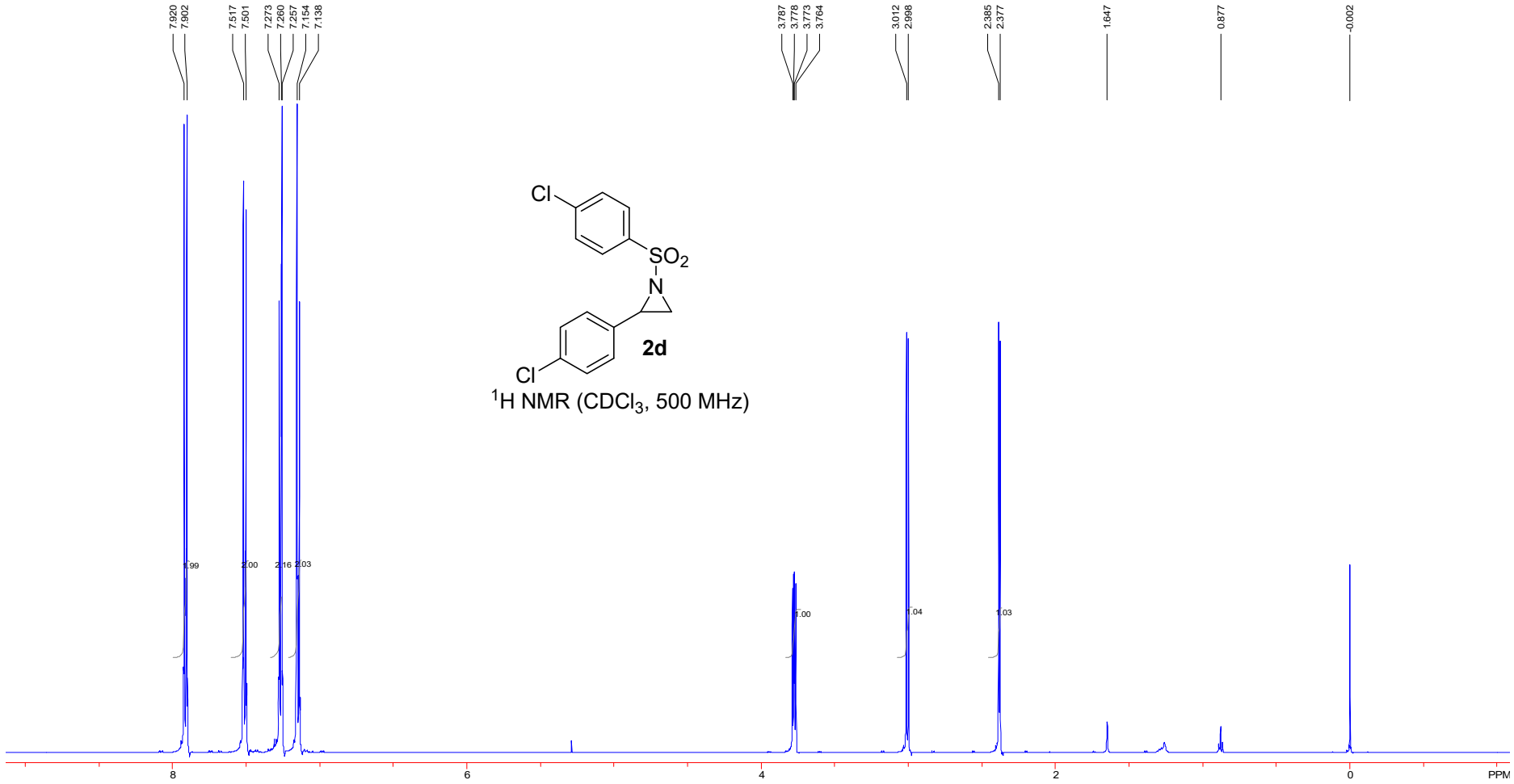
Area Percent Report

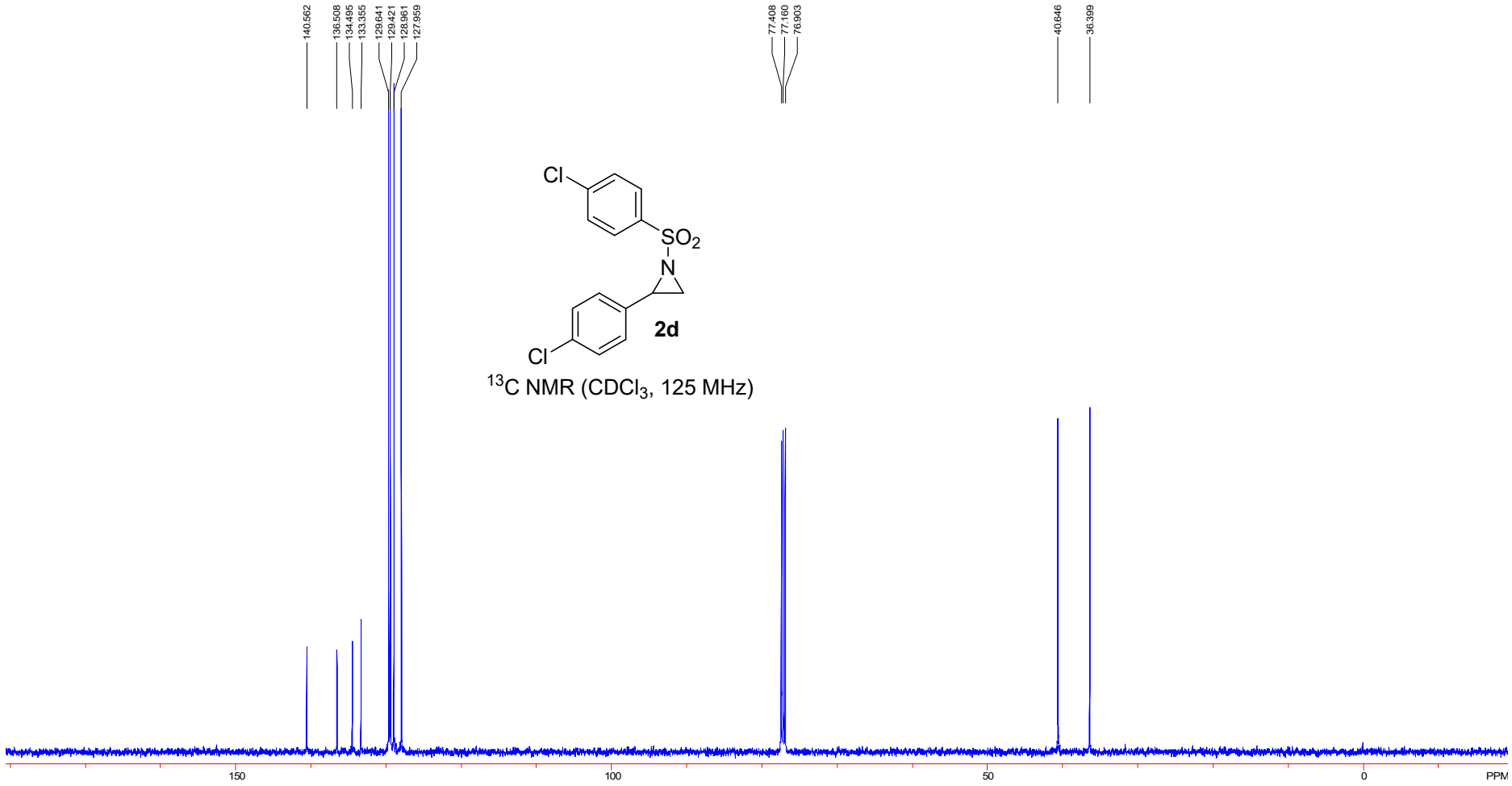
Peak #	RetTime [min]	Area [mAU *min]	Height [mAU]	Area %	Height %
1	8.302	0.110	0.405	0.08	0.11
2	9.352	132.396	372.842	99.92	99.89

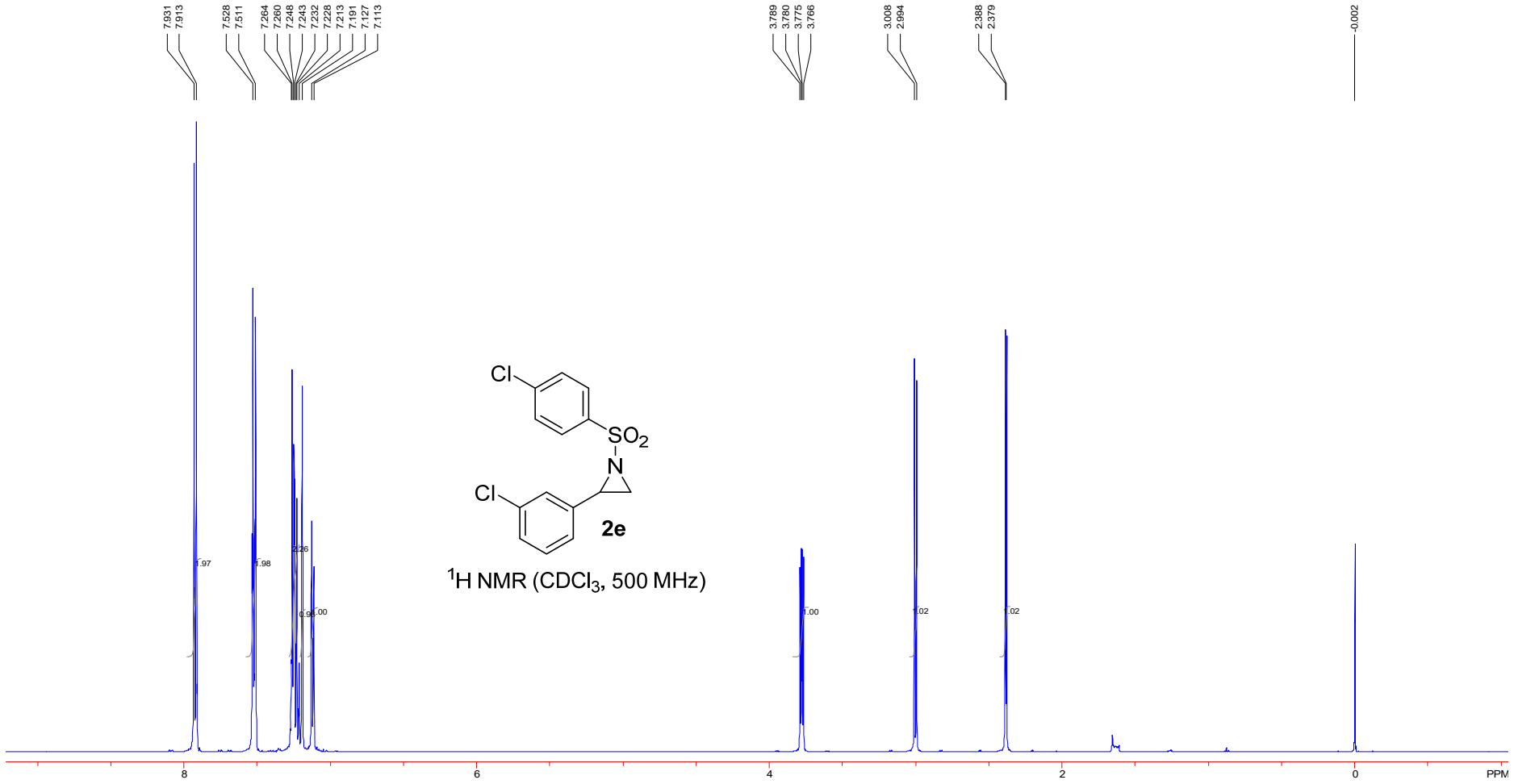
Copies of ^{1}H NMR and ^{13}C NMR Spectra for All New Compounds

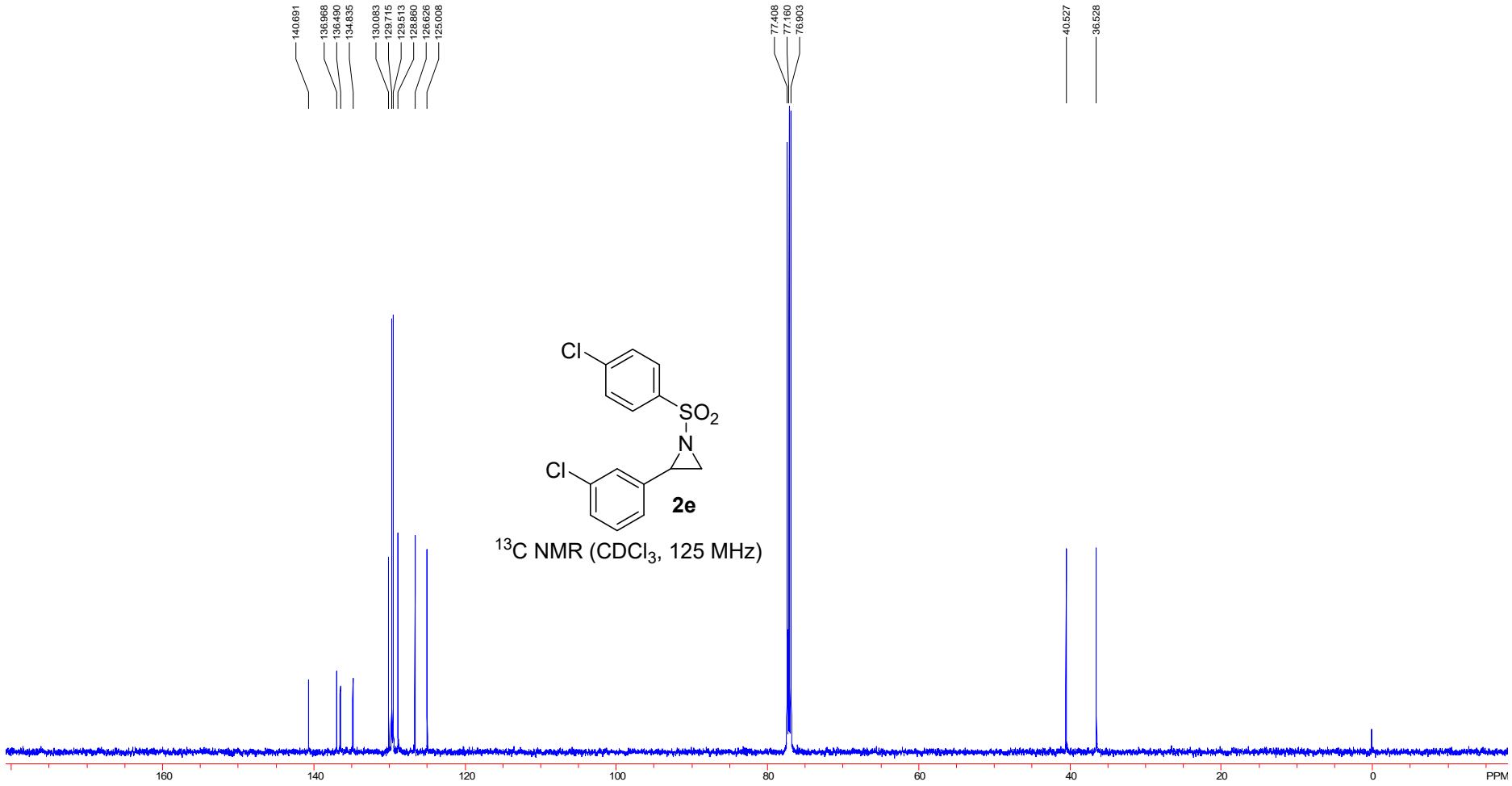


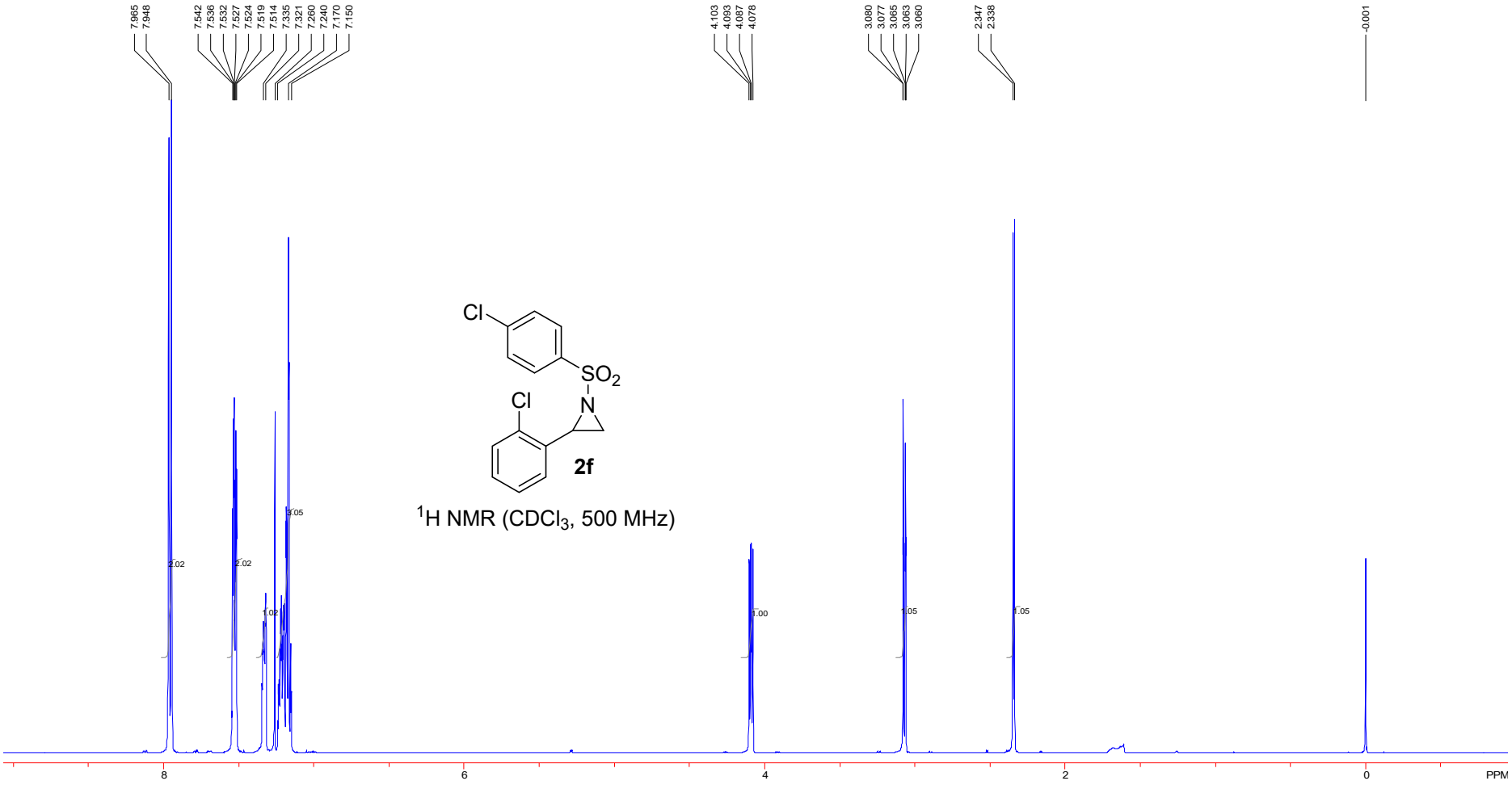

140.608
136.499
133.897
131.930
129.669
129.439
128.281
122.646
77.417
77.160
76.912
40.720
36.381
Cl
SO2
N
Br
2c
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

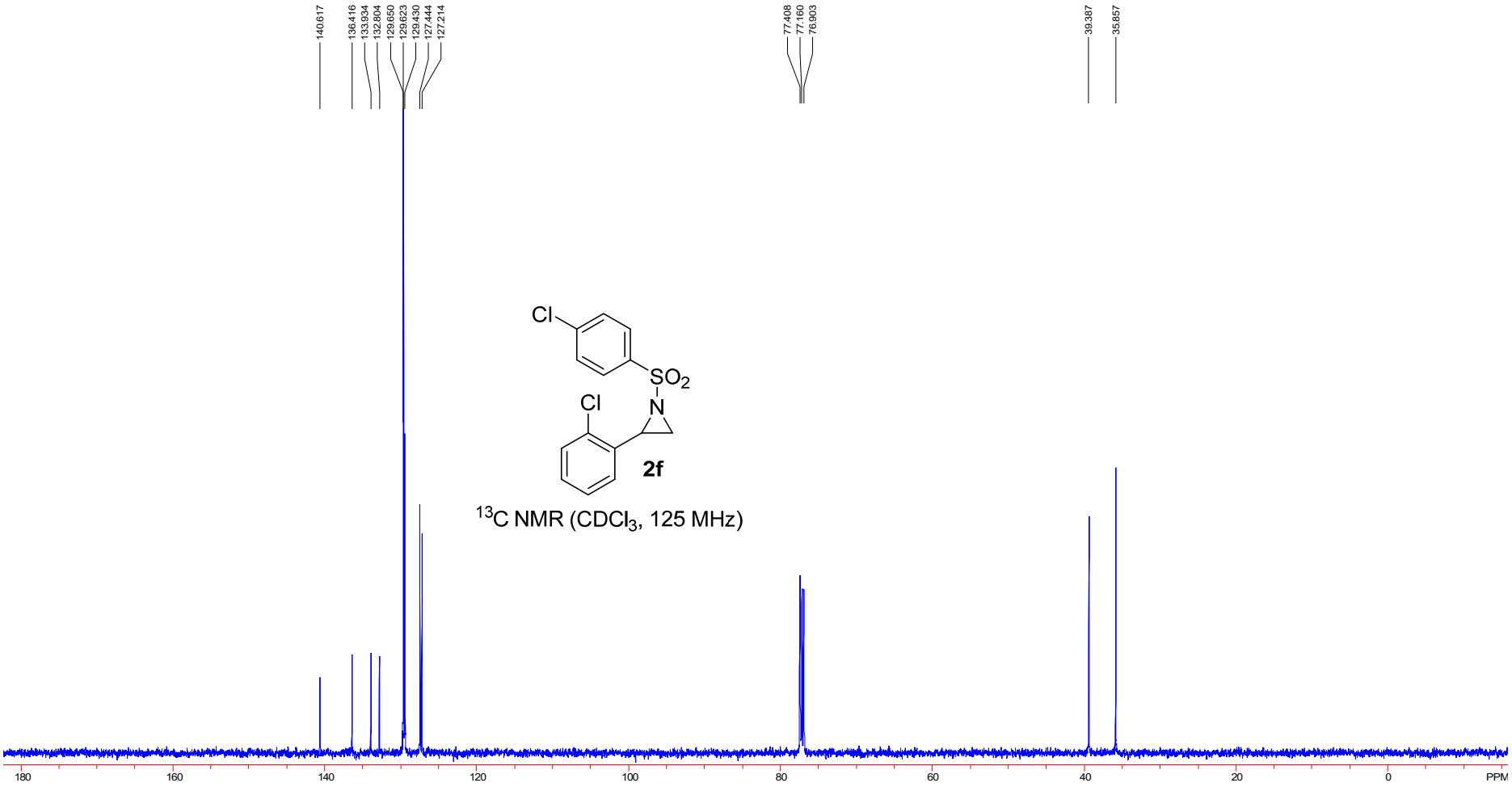

7.920
7.902
7.517
7.501
7.273
7.260
7.257
7.154
7.138
3.787
3.778
3.773
3.764
3.012
2.998
2.385
2.377
1.647
0.877
-0.002
Cl
SO2
N
Cl
2d
1H NMR (CDCl3, 500 MHz)
1.99
2.00
2.16
2.03
1.00
1.04
1.03
8
6
4
2
0
PPM

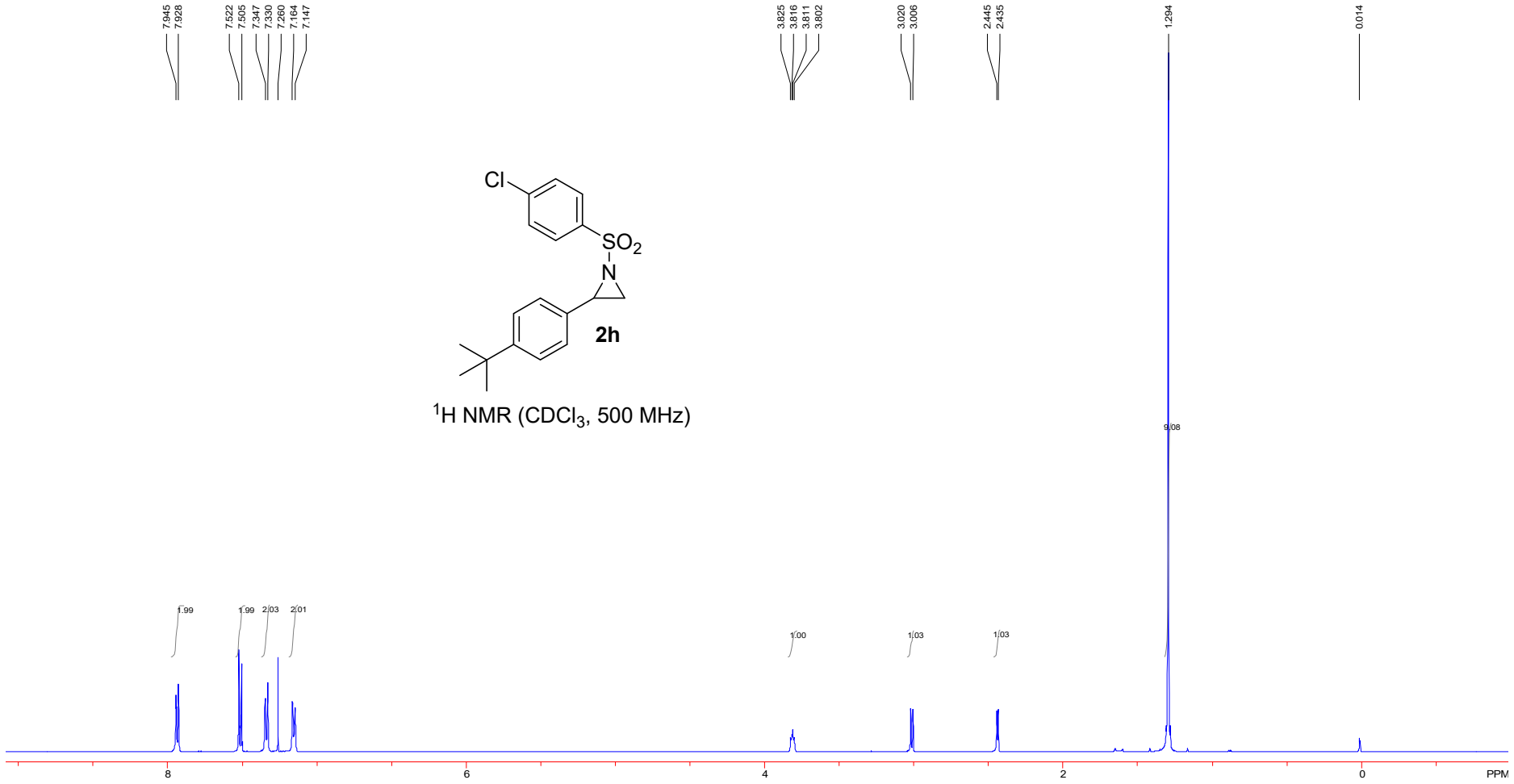

140.562
136.508
134.495
133.355
129.641
129.421
128.961
127.959
77.408
77.160
76.903
40.646
36.399
Cl
SO2
N
Cl
2d
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

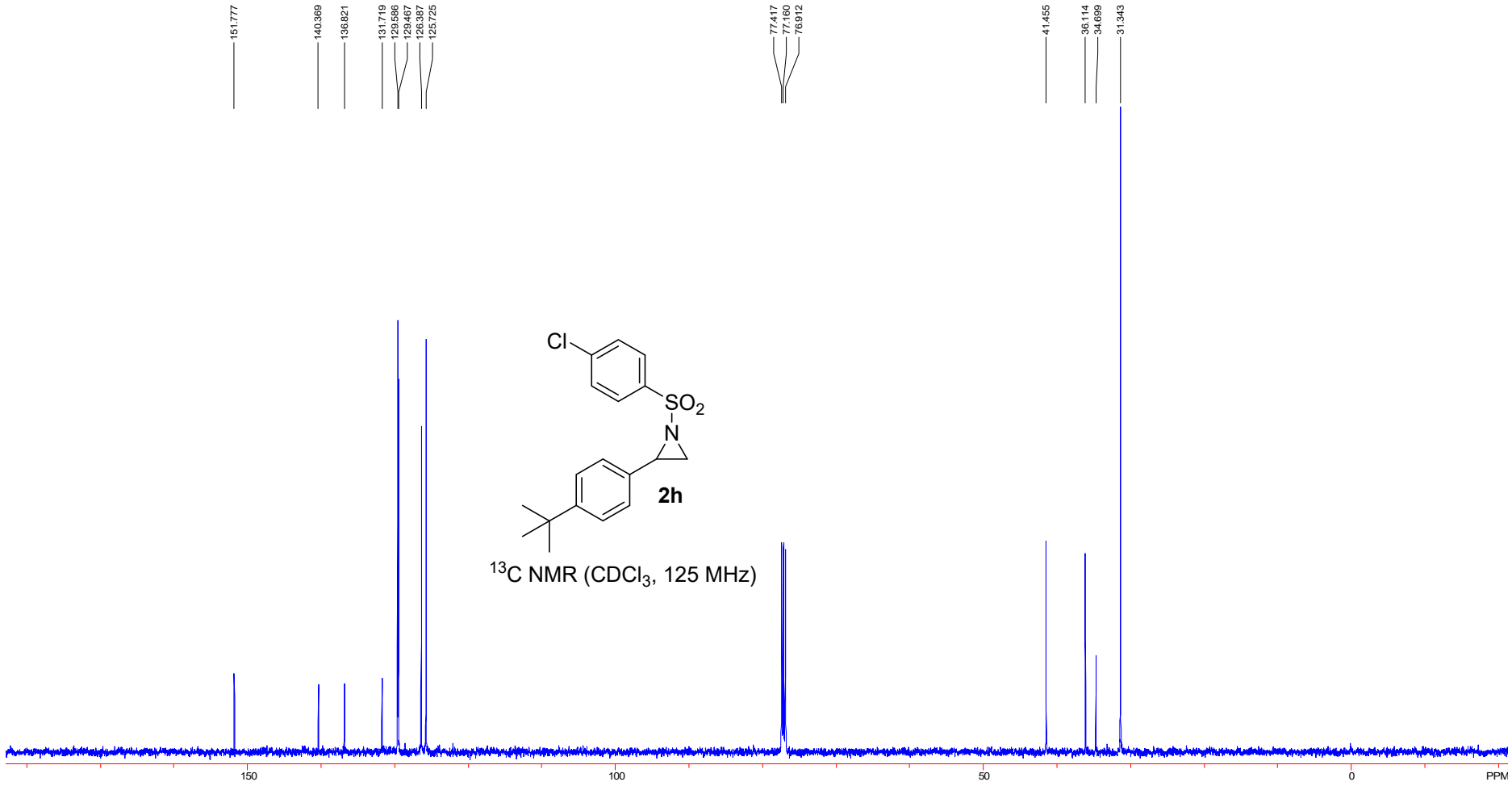

7.931
7.913
7.528
7.511
7.264
7.260
7.248
7.243
7.232
7.228
7.213
7.191
7.127
7.113
3.789
3.780
3.775
3.766
3.008
2.994
2.388
2.379
-0.002
Cl
SO2
N
Cl
2e
1H NMR (CDCl3, 500 MHz)
1.97
1.98
2.26
0.96
1.00
1.00
1.02
1.02
8
6
4
2
0
PPM

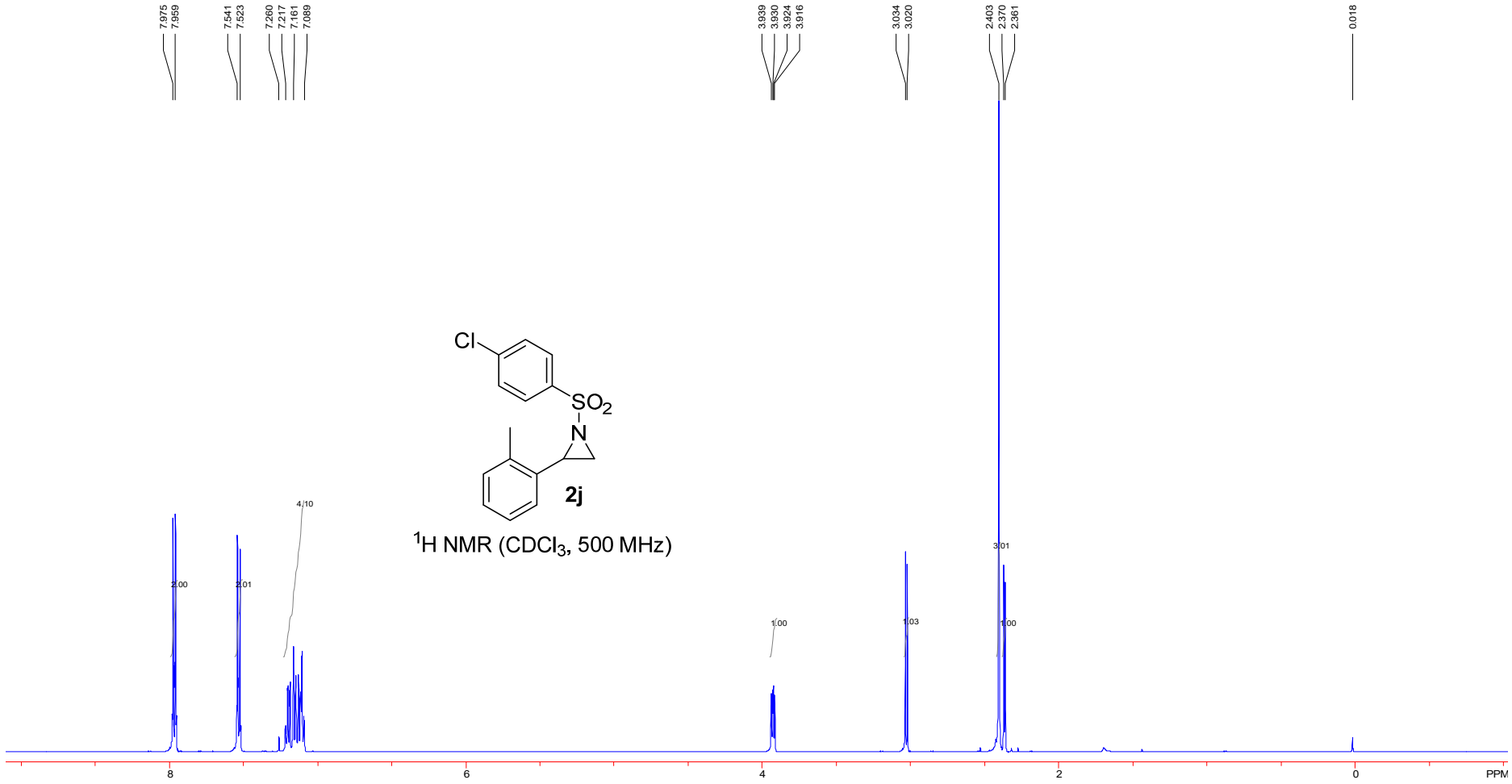

140.691
136.968
136.490
134.835
130.083
129.715
129.513
128.860
126.626
125.008
77.408
77.160
76.903
40.527
36.528
Cl
SO2
N
Cl
2e
13C NMR (CDCl3, 125 MHz)
160
140
120
100
80
60
40
20
0
PPM

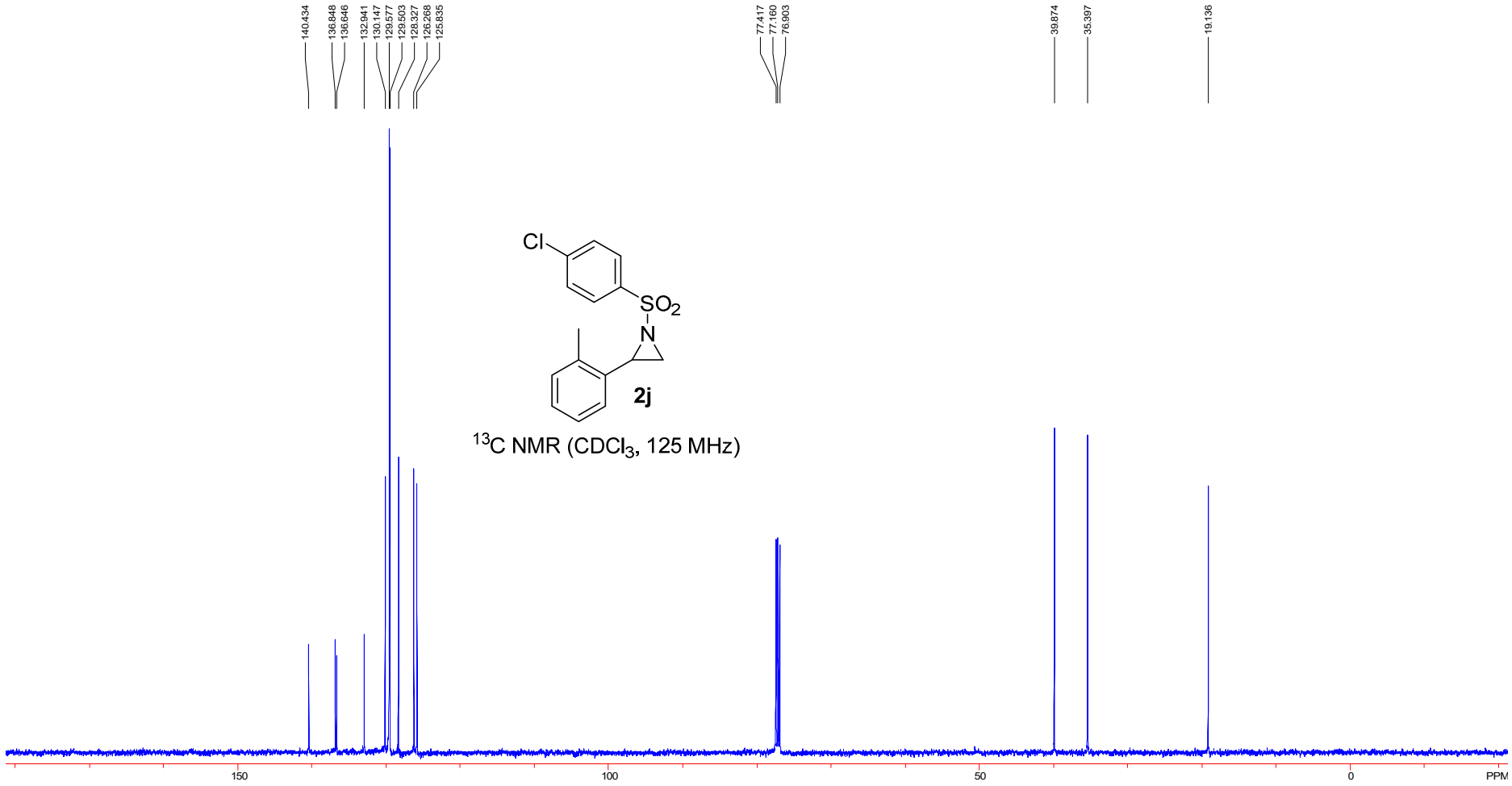

7.965
7.948
7.542
7.536
7.532
7.527
7.524
7.519
7.514
7.335
7.321
7.260
7.240
7.170
7.150
4.103
4.093
4.087
4.078
3.080
3.077
3.065
3.063
3.060
2.347
2.338
-0.001
Cl
SO2
N
Cl
2f
1H NMR (CDCl3, 500 MHz)
2.02
2.02
1.02
3.05
1.00
3.05
1.05
8
6
4
2
0
PPM

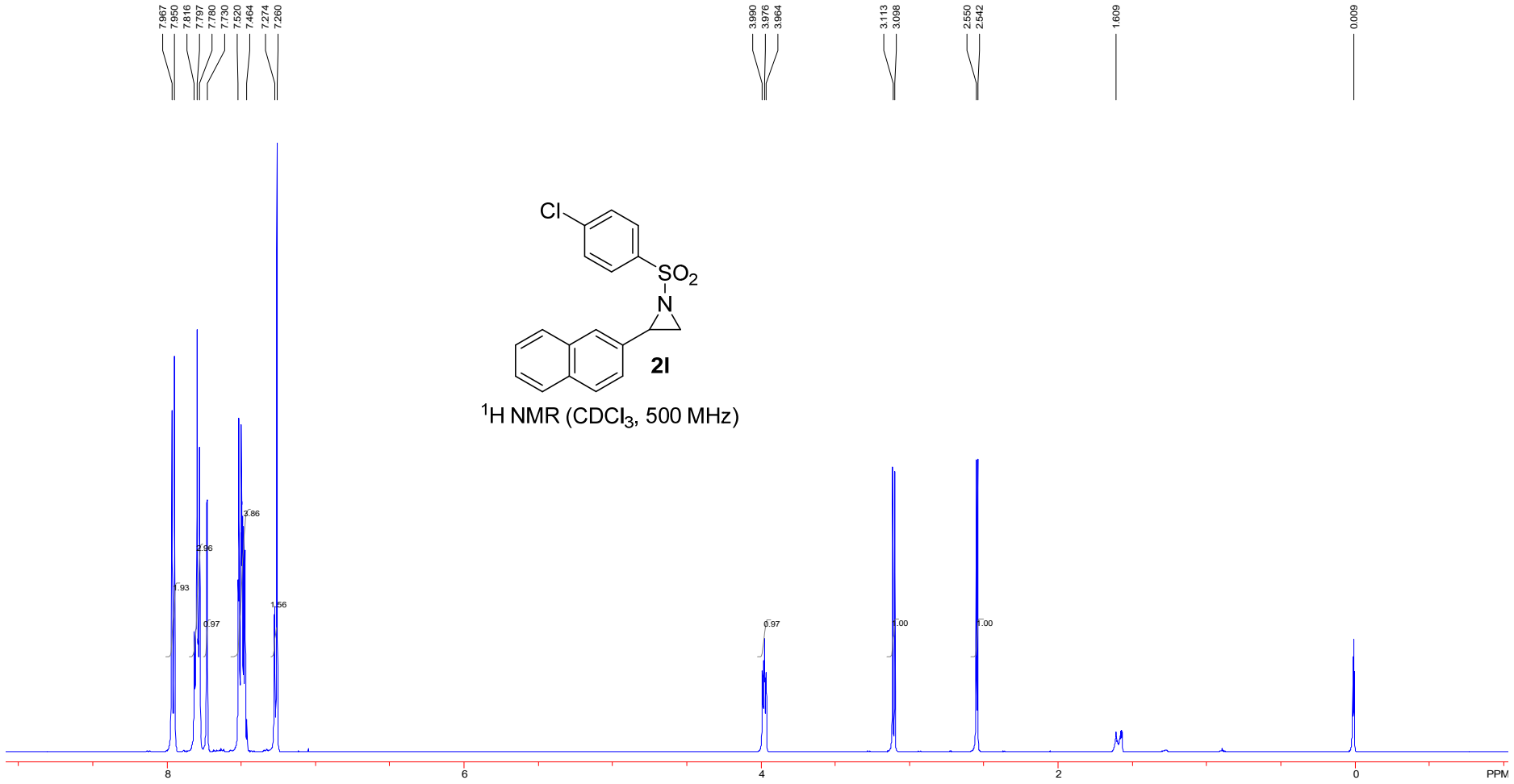

140.617
136.416
133.934
132.804
129.650
129.623
129.430
127.444
127.214
77.408
77.160
76.903
39.387
35.857
Cl
SO2
N
Cl
2f
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

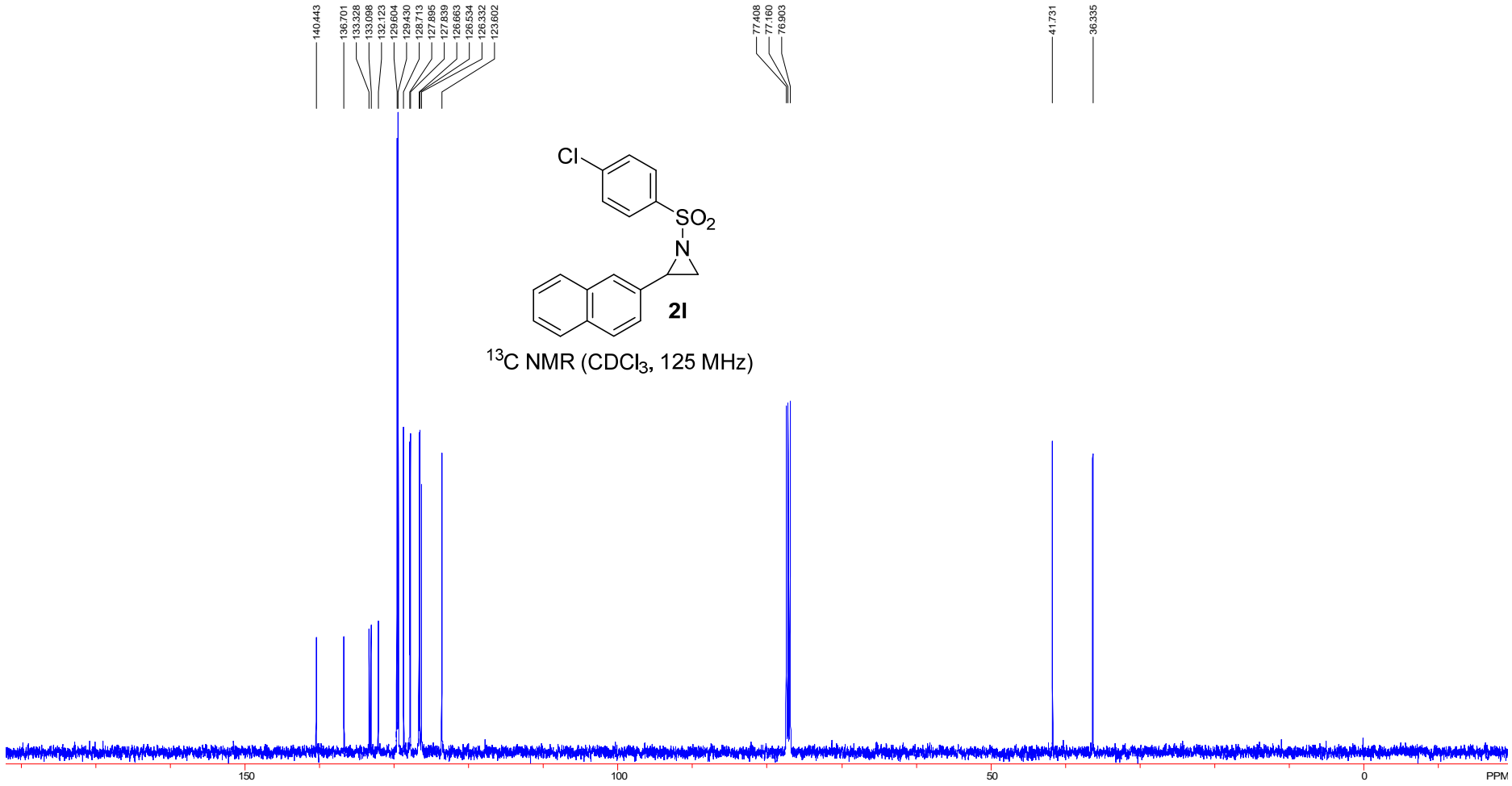

7.945
7.928
7.522
7.505
7.347
7.330
7.260
7.164
7.147
3.825
3.816
3.811
3.802
3.020
3.006
2.445
2.435
1.294
0.014
Cl
SO2
N
2h
1H NMR (CDCl3, 500 MHz)
9.08
1.99
1.99
2.03
2.01
1.00
1.03
1.03
8
6
4
2
0
PPM

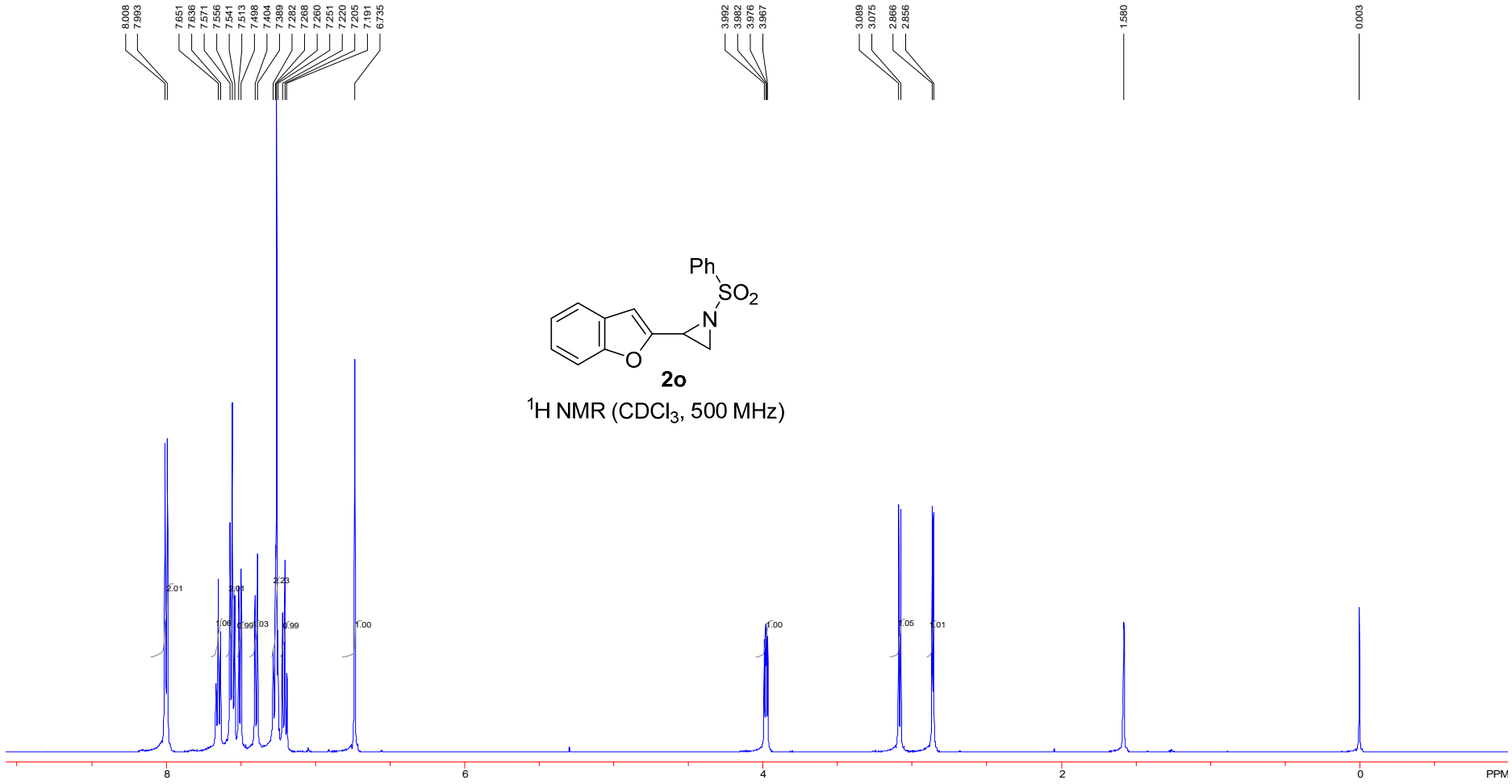

151.777
140.369
136.821
131.719
129.586
129.467
126.387
125.725
77.417
77.160
76.912
41.455
36.114
34.699
31.343
Cl
SO2
N
2h
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

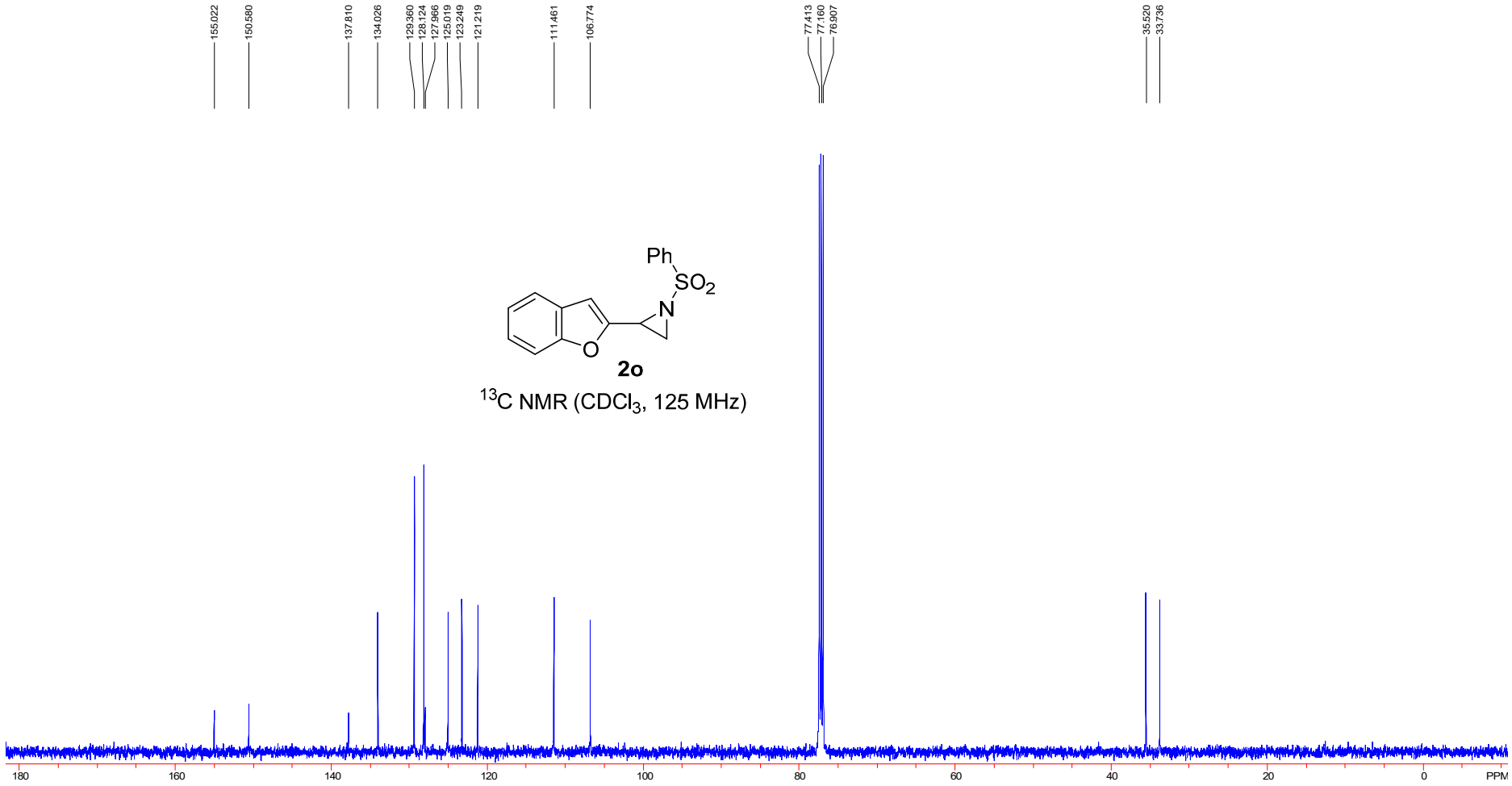

7.975
7.959
7.541
7.523
7.260
7.217
7.161
7.089
3.939
3.930
3.924
3.916
3.034
3.020
2.403
2.370
2.361
0.018
Cl
SO2
N
2j
1H NMR (CDCl3, 500 MHz)
2.00
2.01
4.10
1.00
1.03
3.01
1.00
8
6
4
2
0
PPM

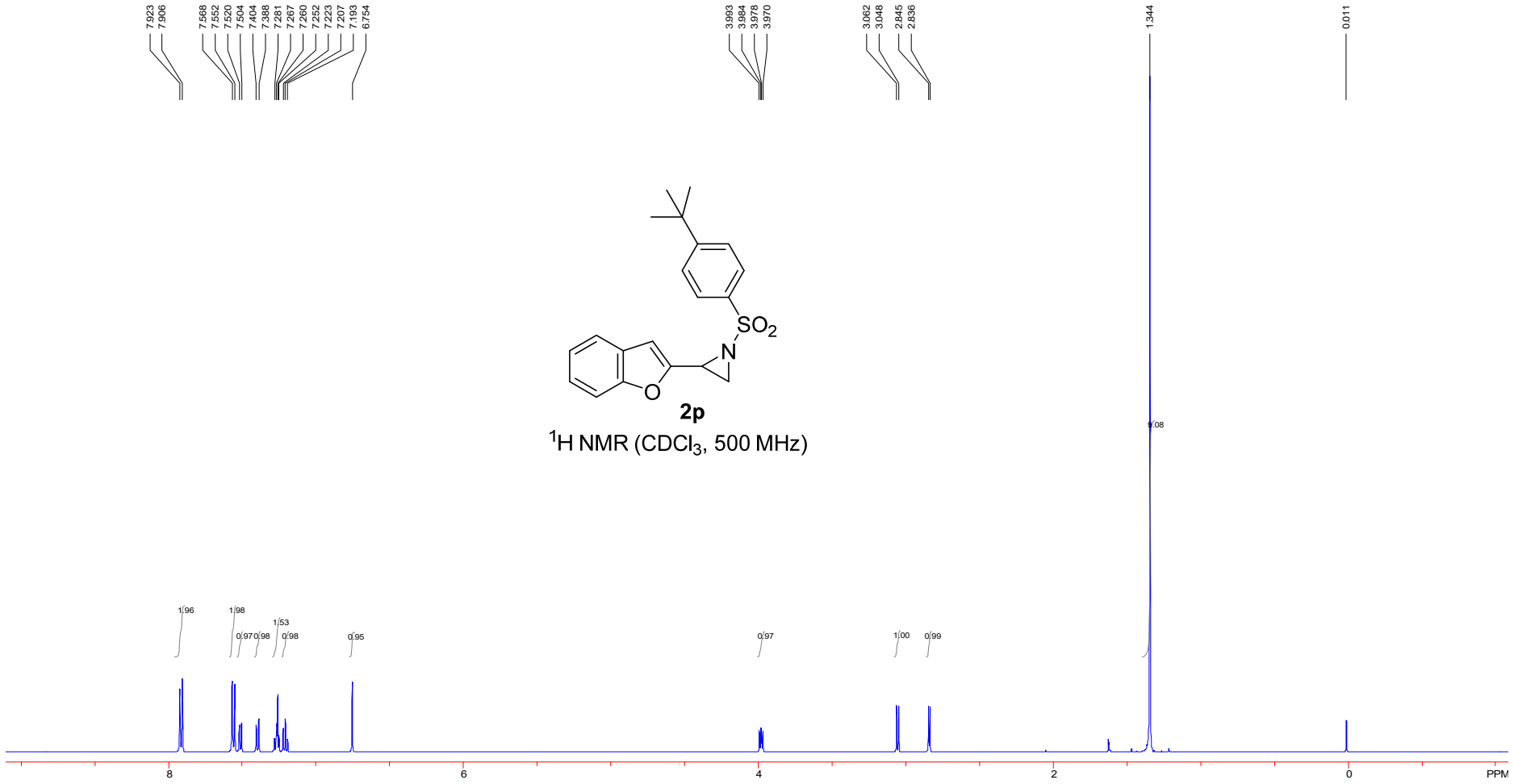

140.434
136.848
136.646
132.941
130.147
129.577
129.503
128.327
126.268
125.635
77.417
77.160
76.903
39.874
35.397
19.136
Cl
SO2
N
2j
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

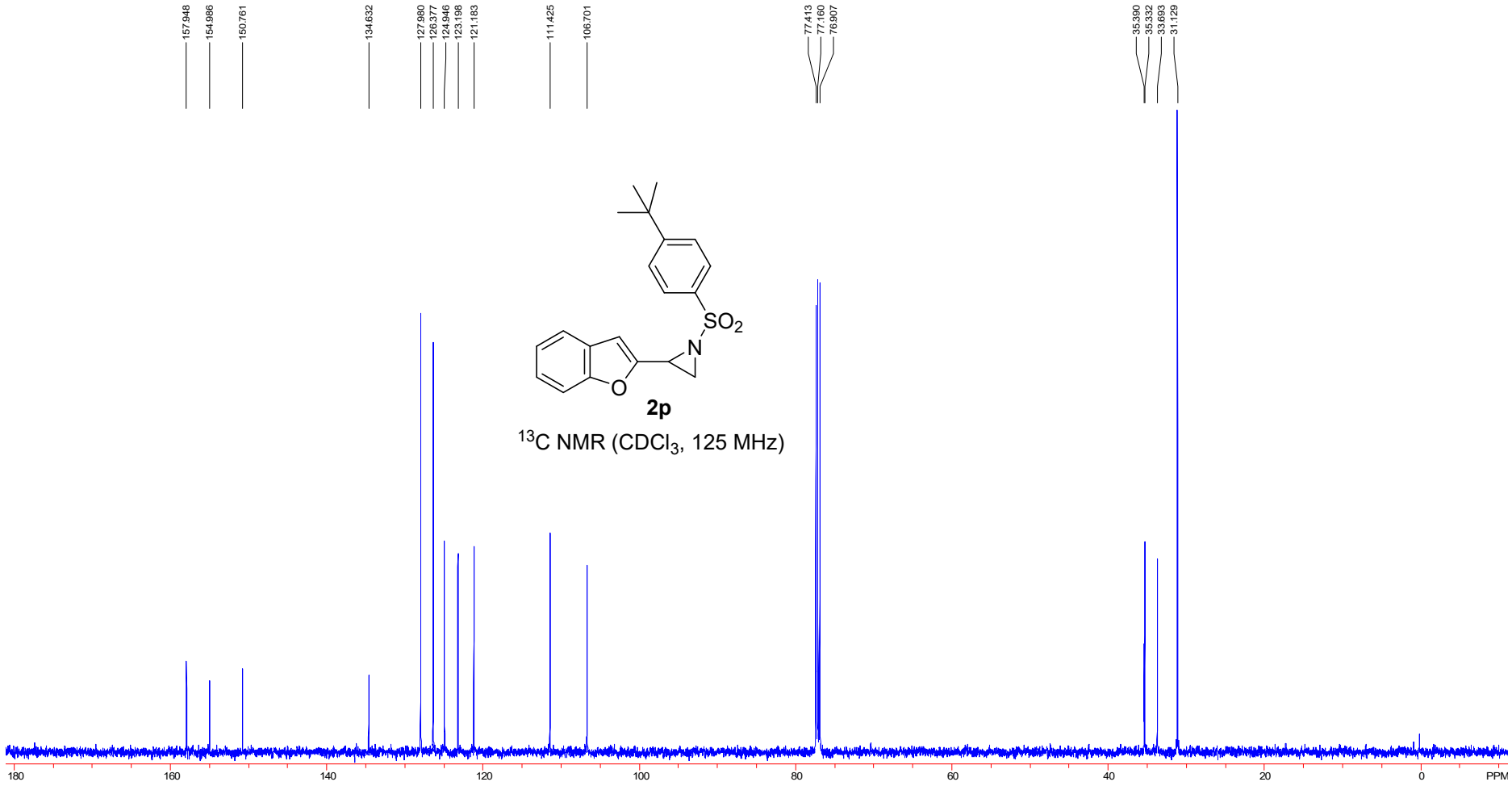

7.967
7.950
7.816
7.797
7.780
7.730
7.520
7.464
7.274
7.260
3.990
3.976
3.964
3.113
3.098
2.550
2.542
1.609
0.009
Cl
SO2
N
2l
1H NMR (CDCl3, 500 MHz)
1.93
2.96
0.97
3.86
1.56
0.97
3.00
3.00
8
6
4
2
0
PPM

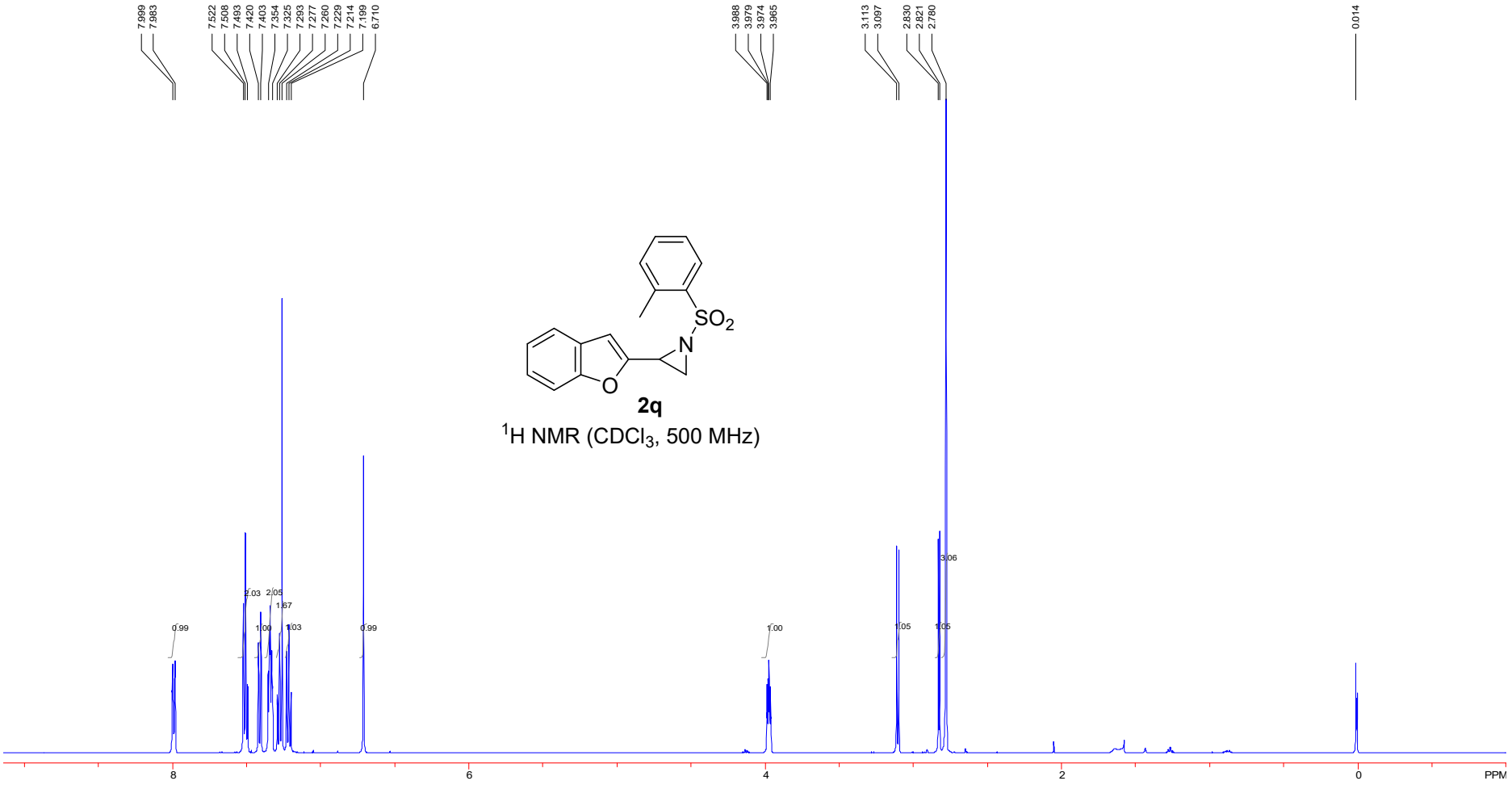

140.443
136.701
133.328
133.098
132.123
129.604
129.430
128.713
127.895
127.839
126.663
126.534
126.332
123.602
77.408
77.160
76.903
41.731
36.335
Cl
SO2
N
2l
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM


8.008
7.993
7.651
7.636
7.571
7.556
7.541
7.513
7.498
7.404
7.389
7.282
7.268
7.260
7.251
7.220
7.205
7.191
6.735
3.992
3.982
3.976
3.967
3.089
3.075
2.866
2.856
1.580
0.003
Ph
SO2
N
O
2o
1H NMR (CDCl3, 500 MHz)
2.01
2.00
2.23
1.06
0.99
1.03
0.99
1.00
1.00
1.05
1.01
8
6
4
2
0
PPM


155.022
150.580
137.810
134.026
129.360
128.124
127.966
125.019
123.249
121.219
111.461
106.774
77.413
77.160
76.907
35.520
33.736
Ph
SO2
N
O
2o
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

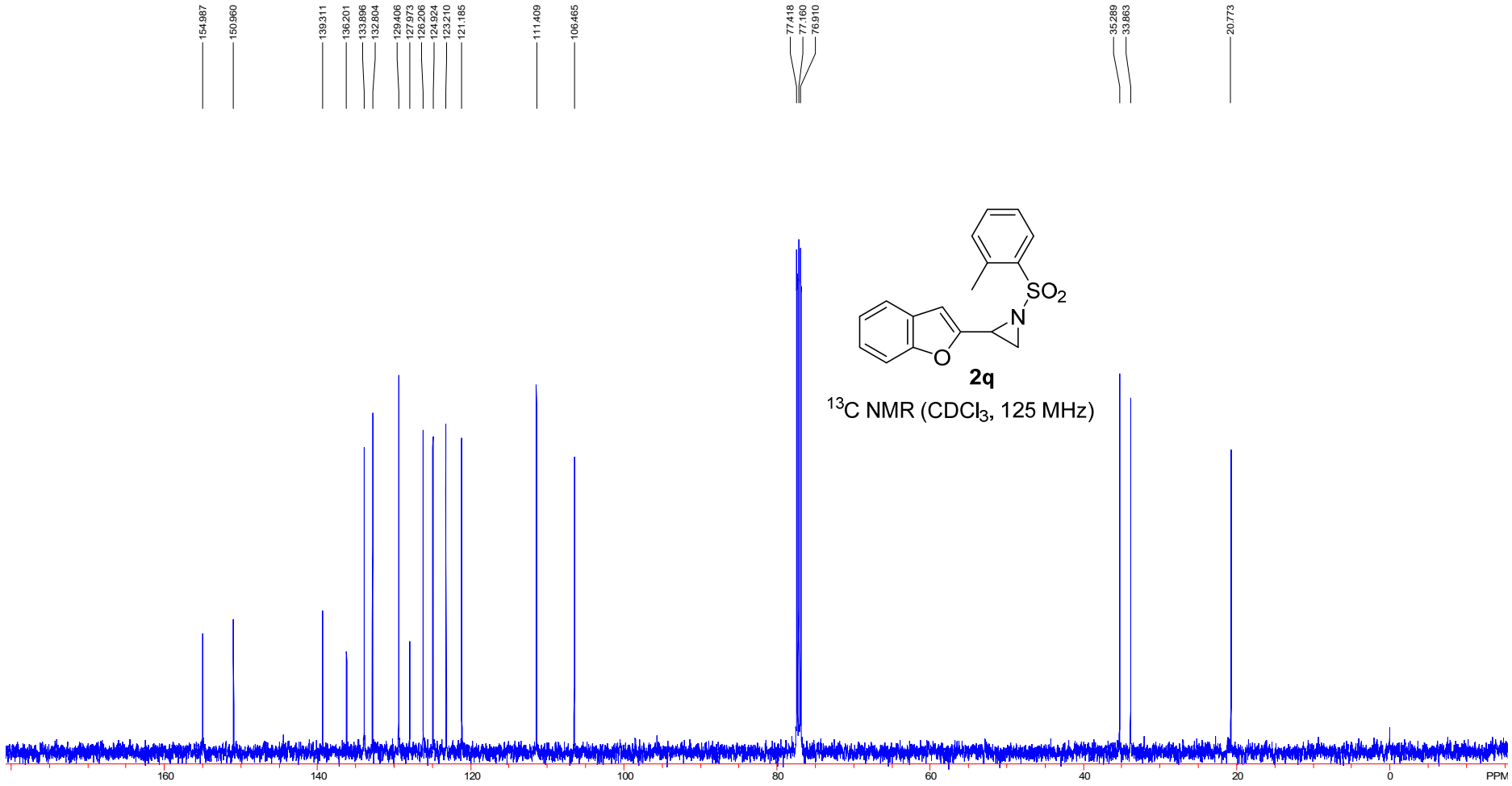

7.923
7.906
7.568
7.552
7.520
7.504
7.404
7.388
7.281
7.267
7.260
7.252
7.223
7.207
7.193
6.754
3.993
3.984
3.978
3.970
3.062
3.048
2.845
2.836
1.344
0.011
SO2
N
O
2p
1H NMR (CDCl3, 500 MHz)
9.08
1.96
1.98
1.53
0.97
0.98
0.98
0.95
0.97
1.00
0.99
8
6
4
2
0
PPM

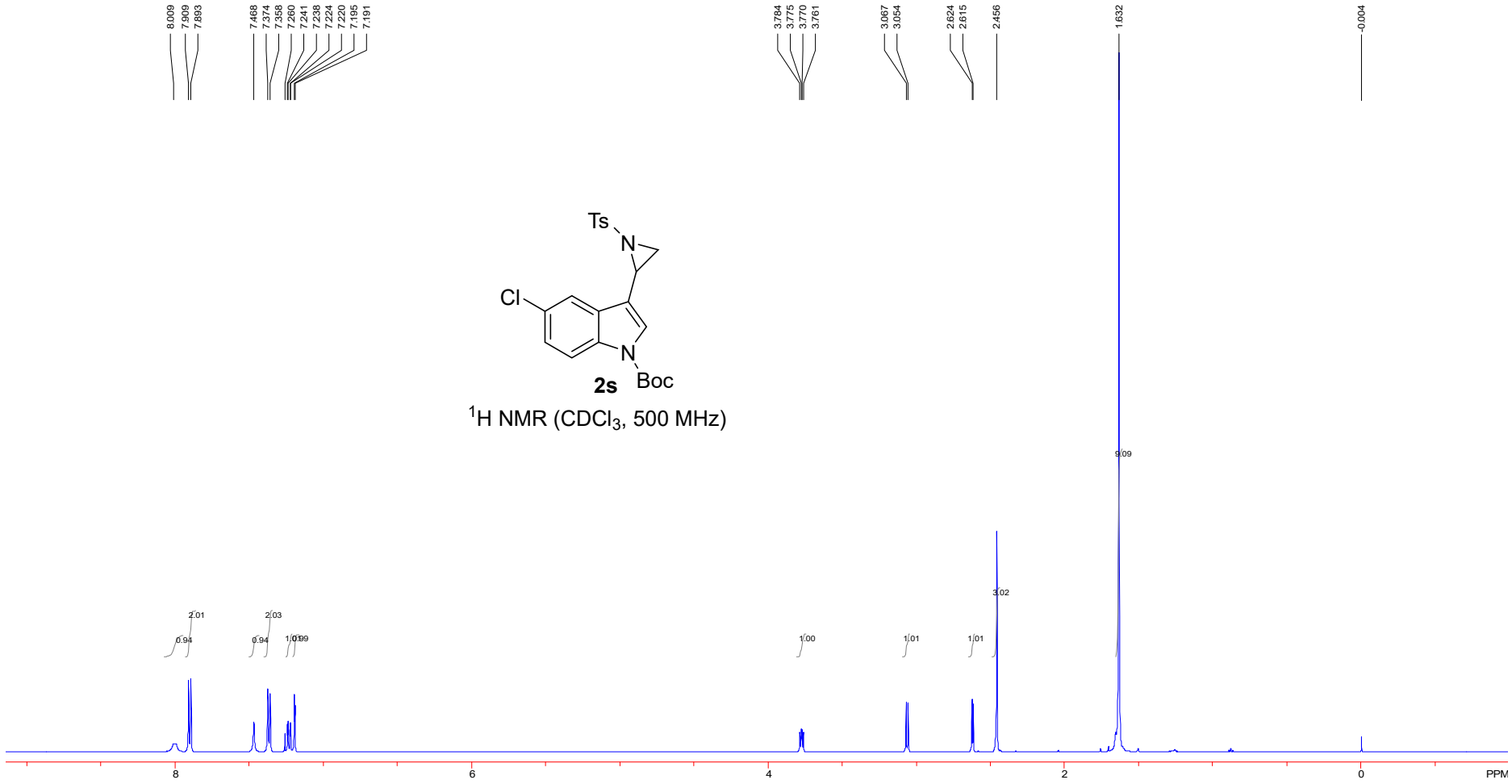

157.948
154.986
150.761
134.632
127.980
126.377
124.946
123.198
121.183
111.425
106.701
77.413
77.160
76.907
35.390
35.332
33.693
31.129
SO2
N
O
2p
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

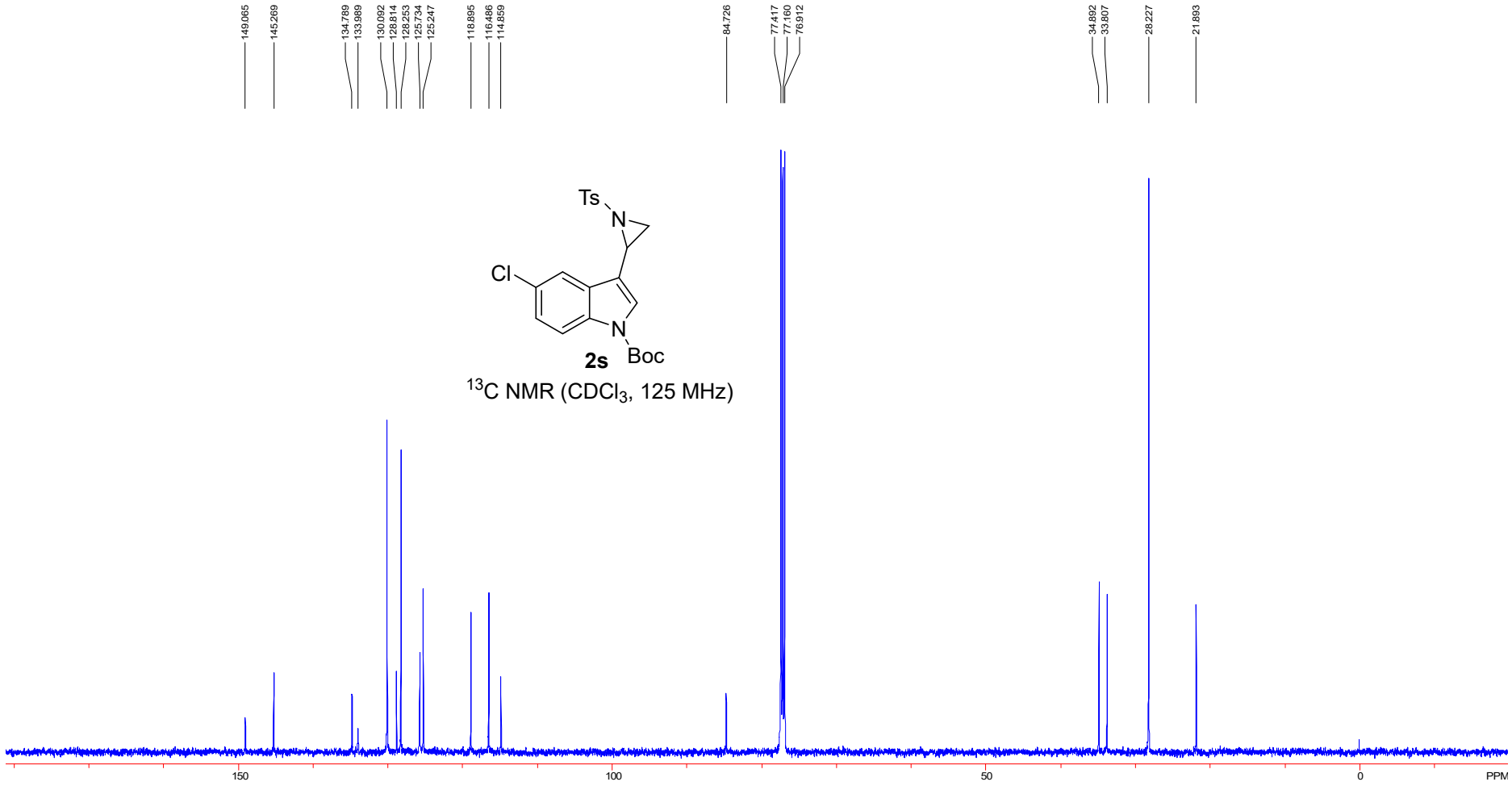


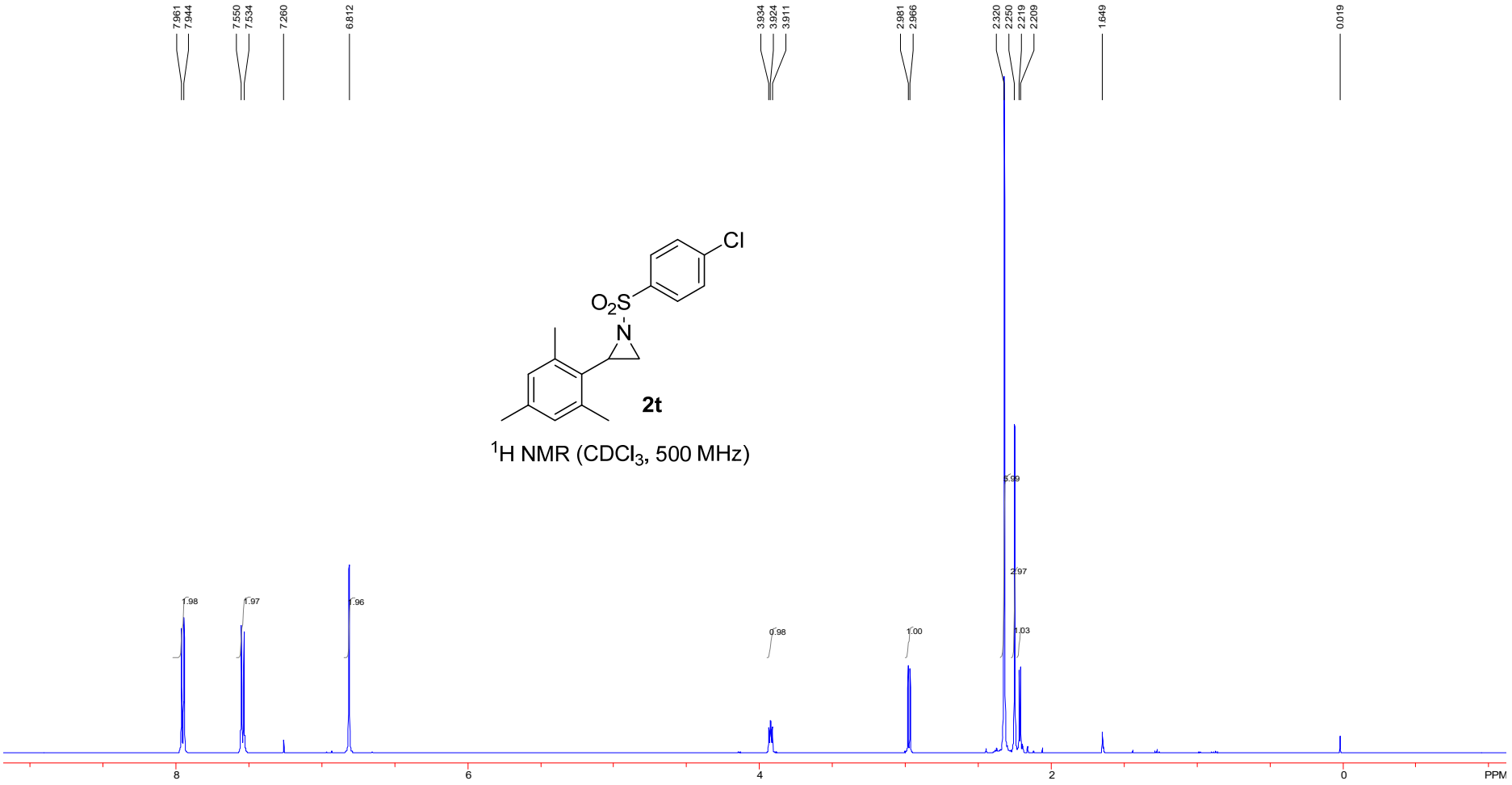
2q

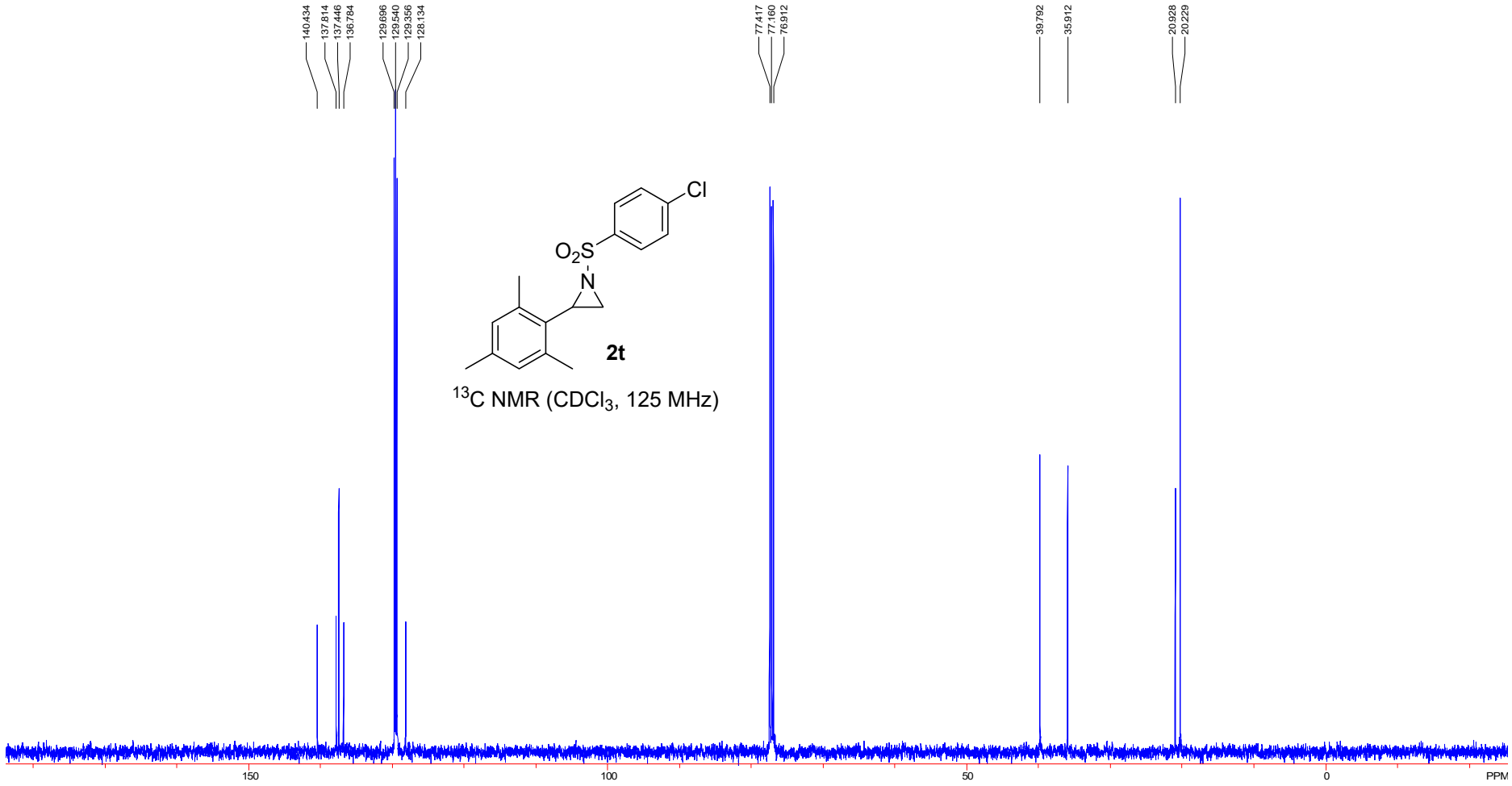
^{1}H NMR ($CDCl_3$, 500 MHz)

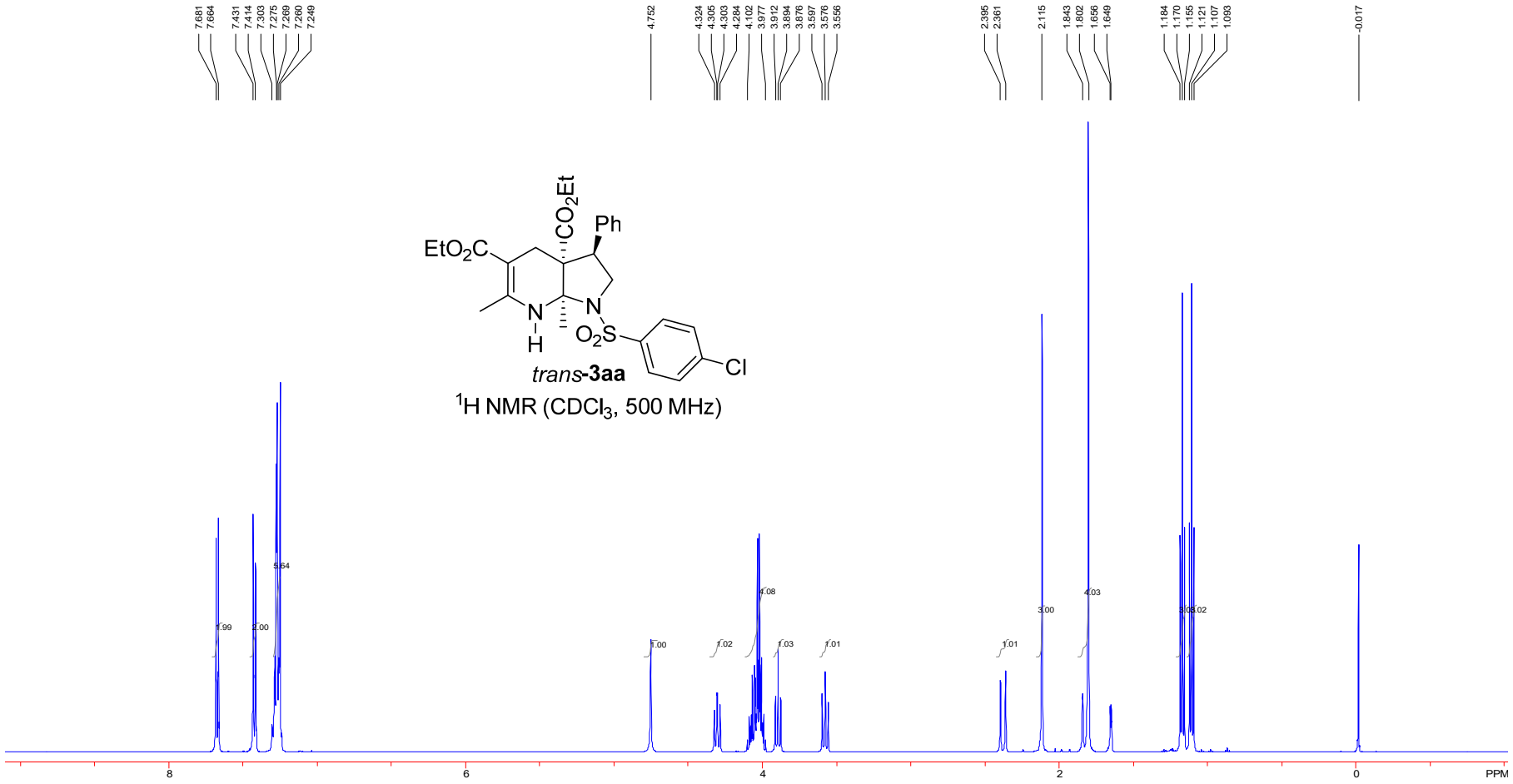

154.987
150.960
139.311
136.201
133.896
132.804
129.406
127.973
126.206
124.924
123.210
121.185
111.409
106.465
77.418
77.160
76.910
35.289
33.863
20.773
SO2
N
O
2q
13C NMR (CDCl3, 125 MHz)
160
140
120
100
80
60
40
20
0
PPM

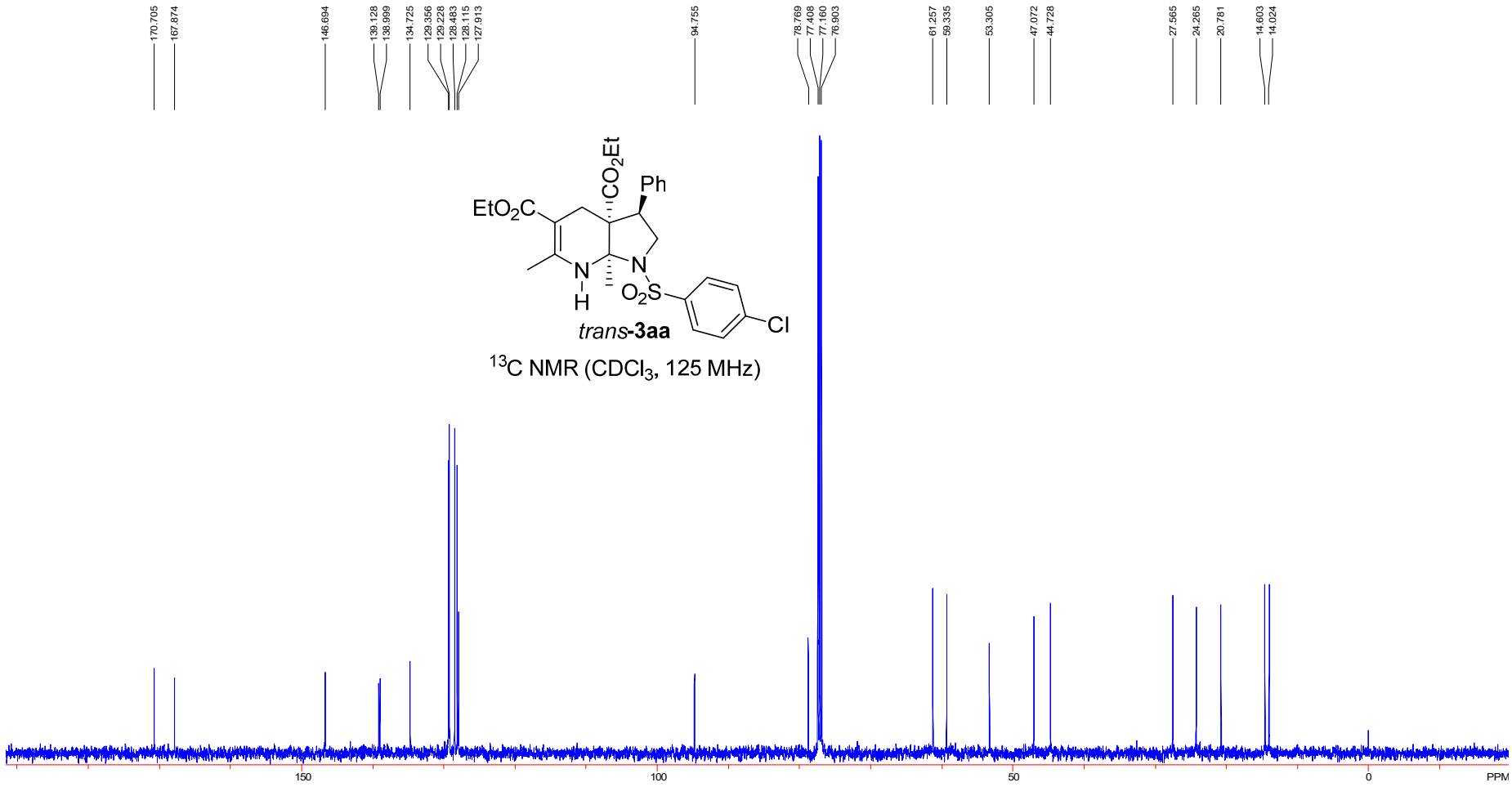

8.009
7.909
7.893
7.468
7.374
7.358
7.260
7.241
7.238
7.224
7.220
7.195
7.191
3.784
3.775
3.770
3.761
3.067
3.054
2.624
2.615
2.456
1.632
-0.004
Ts
N
Cl
N
Boc
2s
1H NMR (CDCl3, 500 MHz)
9.09
3.02
2.01
2.03
0.94
0.94
1.00
1.01
1.01
8
6
4
2
0
PPM

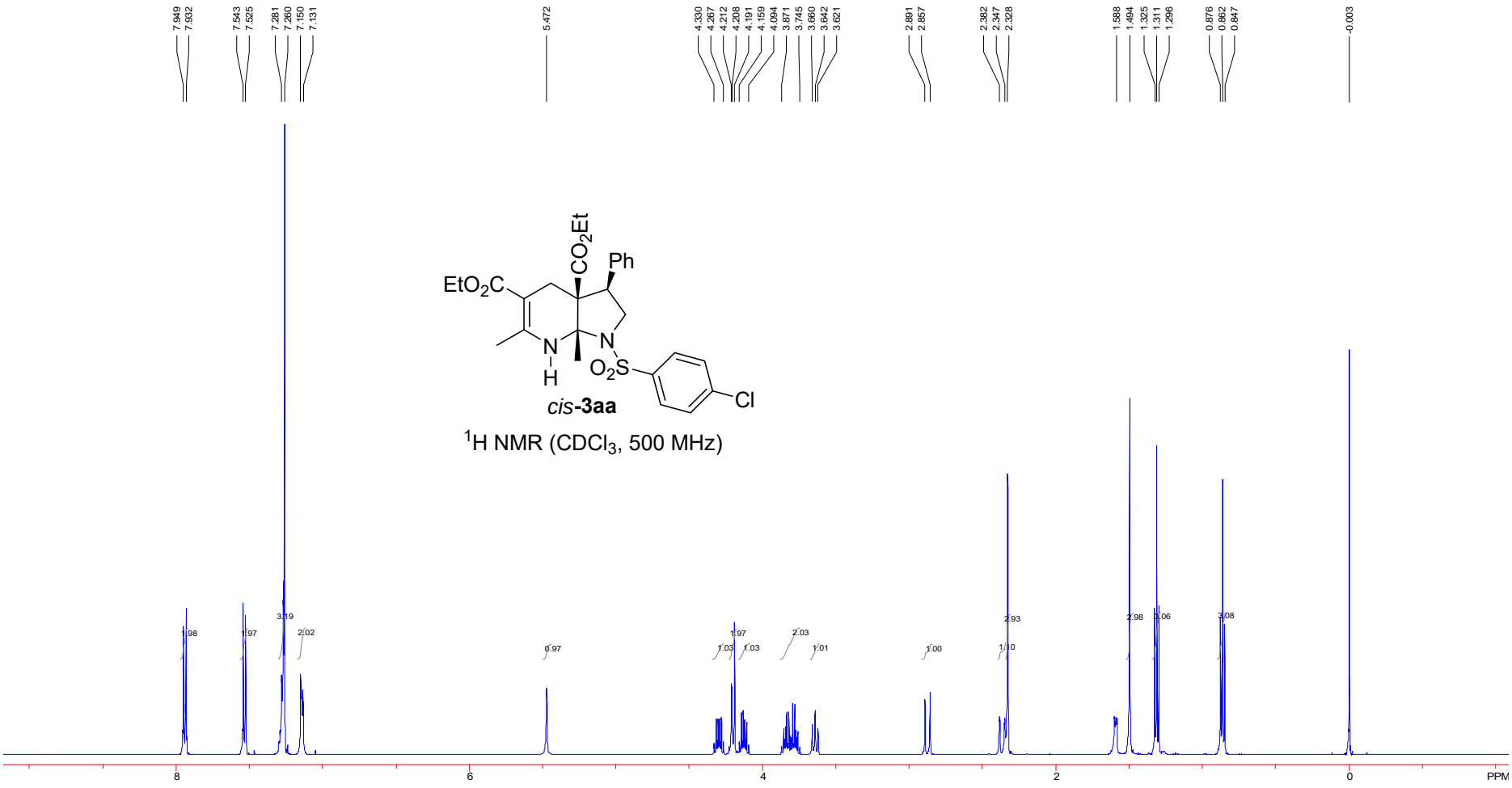

149.065
145.269
134.789
133.989
130.092
128.814
128.253
125.734
125.247
118.895
116.486
114.859
84.726
77.417
77.160
76.912
34.892
33.807
28.227
21.893
Ts
N
Cl
N
Boc
2s
^{13}C NMR ($CDCl_3$, 125 MHz)
150
100
50
0
PPM

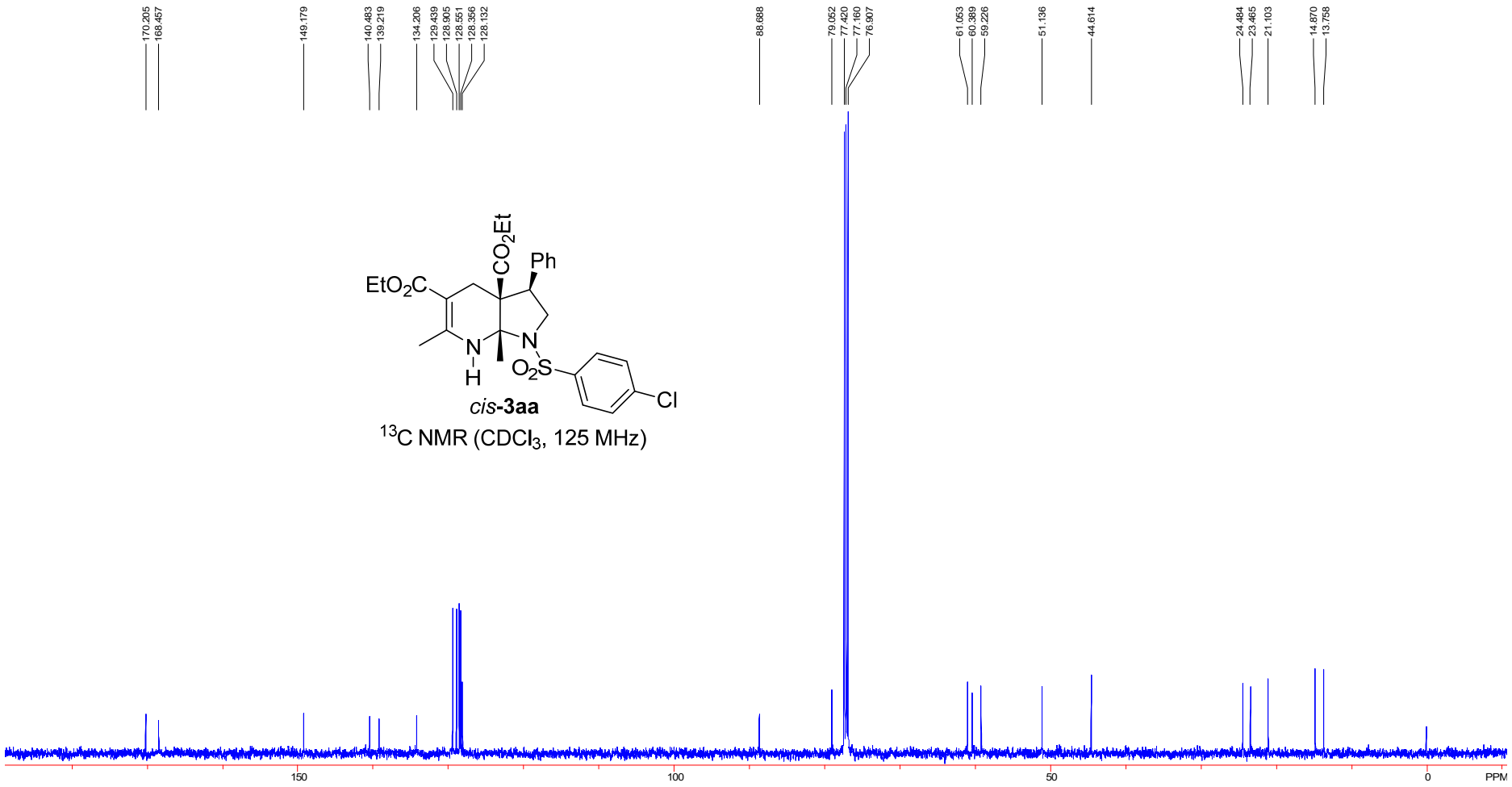

7.961
7.944
7.550
7.534
7.260
6.812
3.934
3.924
3.911
2.981
2.966
2.320
2.250
2.219
2.209
1.649
0.019
Cl
O2S
N
2t
1H NMR (CDCl3, 500 MHz)
1.98
1.97
1.96
0.98
1.00
5.99
2.97
1.03
8
6
4
2
0
PPM

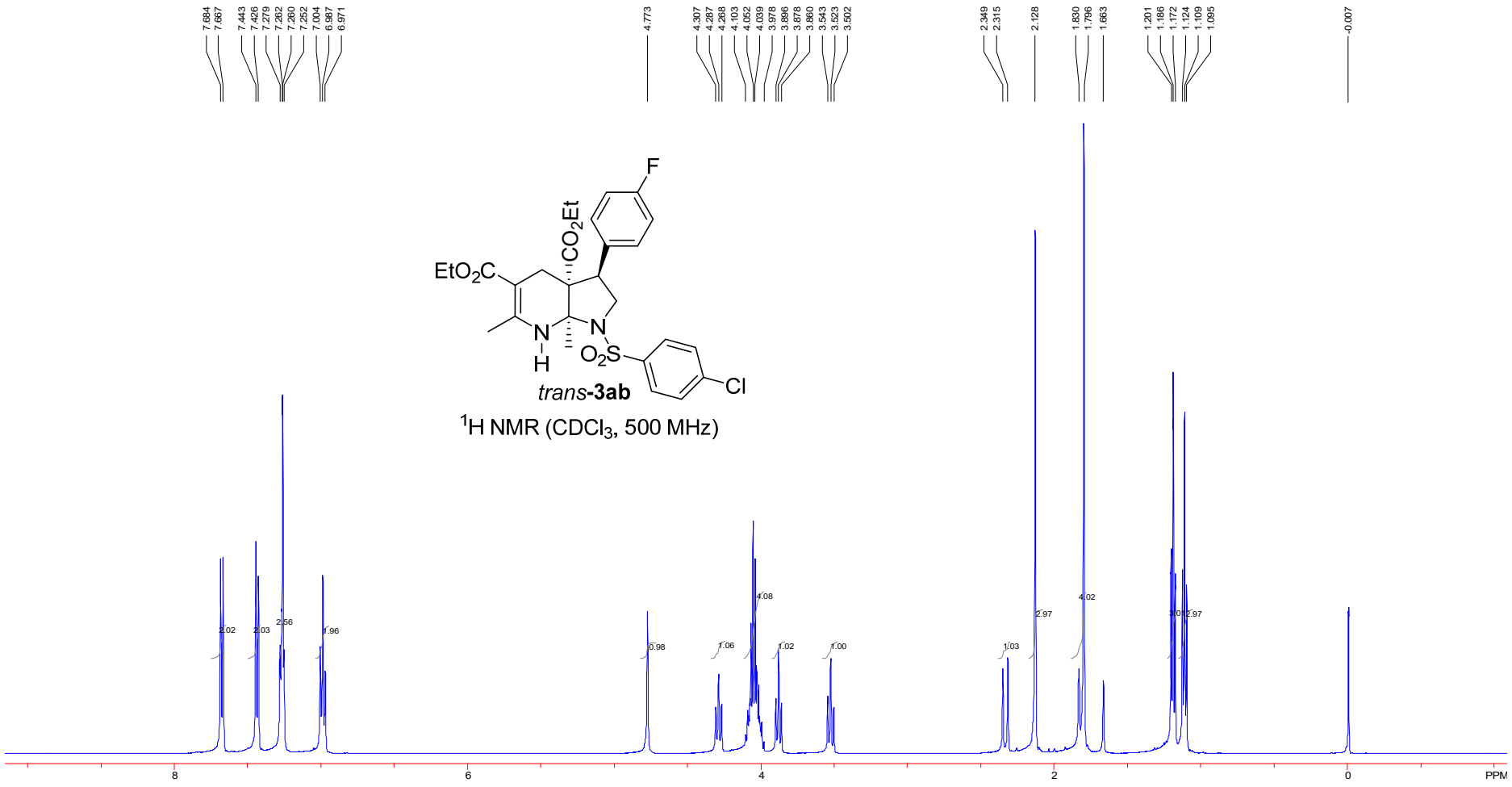

140.434
137.814
137.446
136.784
129.696
129.540
129.356
128.134
77.417
77.160
76.912
39.792
35.912
20.928
20.229
Cl
O2S
N
2t
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM


7.681
7.664
7.431
7.414
7.303
7.275
7.269
7.260
7.249
4.752
4.324
4.305
4.303
4.284
4.102
3.977
3.912
3.894
3.876
3.597
3.576
3.556
2.395
2.361
2.115
1.843
1.802
1.656
1.649
1.184
1.170
1.155
1.121
1.107
1.093
-0.017
EtO2C
CO2Et
Ph
N
H
N
O2S
Cl
trans-3aa
1H NMR (CDCl3, 500 MHz)
1.99
2.00
5.64
1.00
1.02
4.08
1.03
1.01
1.01
3.00
4.03
3.03
3.02
8
6
4
2
0
PPM


170.705
167.874
146.694
139.128
138.999
134.725
129.356
129.228
128.483
128.115
127.913
94.755
78.769
77.408
77.160
76.903
61.257
59.335
53.305
47.072
44.728
27.565
24.265
20.781
14.603
14.024
CO2Et
Ph
EtO2C
N
H
N
O2S
Cl
trans-3aa
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM


7.949
7.932
7.543
7.525
7.281
7.260
7.150
7.131
5.472
4.330
4.267
4.212
4.208
4.191
4.159
4.094
3.871
3.745
3.660
3.642
3.621
2.891
2.857
2.382
2.347
2.328
1.588
1.494
1.325
1.311
1.296
0.876
0.862
0.847
-0.003
EtO2C
CO2Et
Ph
N
H
N
O2S
Cl
cis-3aa
1H NMR (CDCl3, 500 MHz)
1.98
1.97
3.19
2.02
0.97
1.97
1.03
1.03
2.03
1.01
1.00
2.93
1.10
2.98
3.06
3.08
8
6
4
2
0
PPM


170.205
168.457
149.179
140.483
139.219
134.206
129.439
128.905
128.551
128.356
128.132
88.688
79.052
77.420
77.160
76.907
61.053
60.389
59.226
51.136
44.614
24.484
23.465
21.103
14.870
13.758
CO2Et
Ph
EtO2C
N
H
N
O2S
Cl
cis-3aa
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM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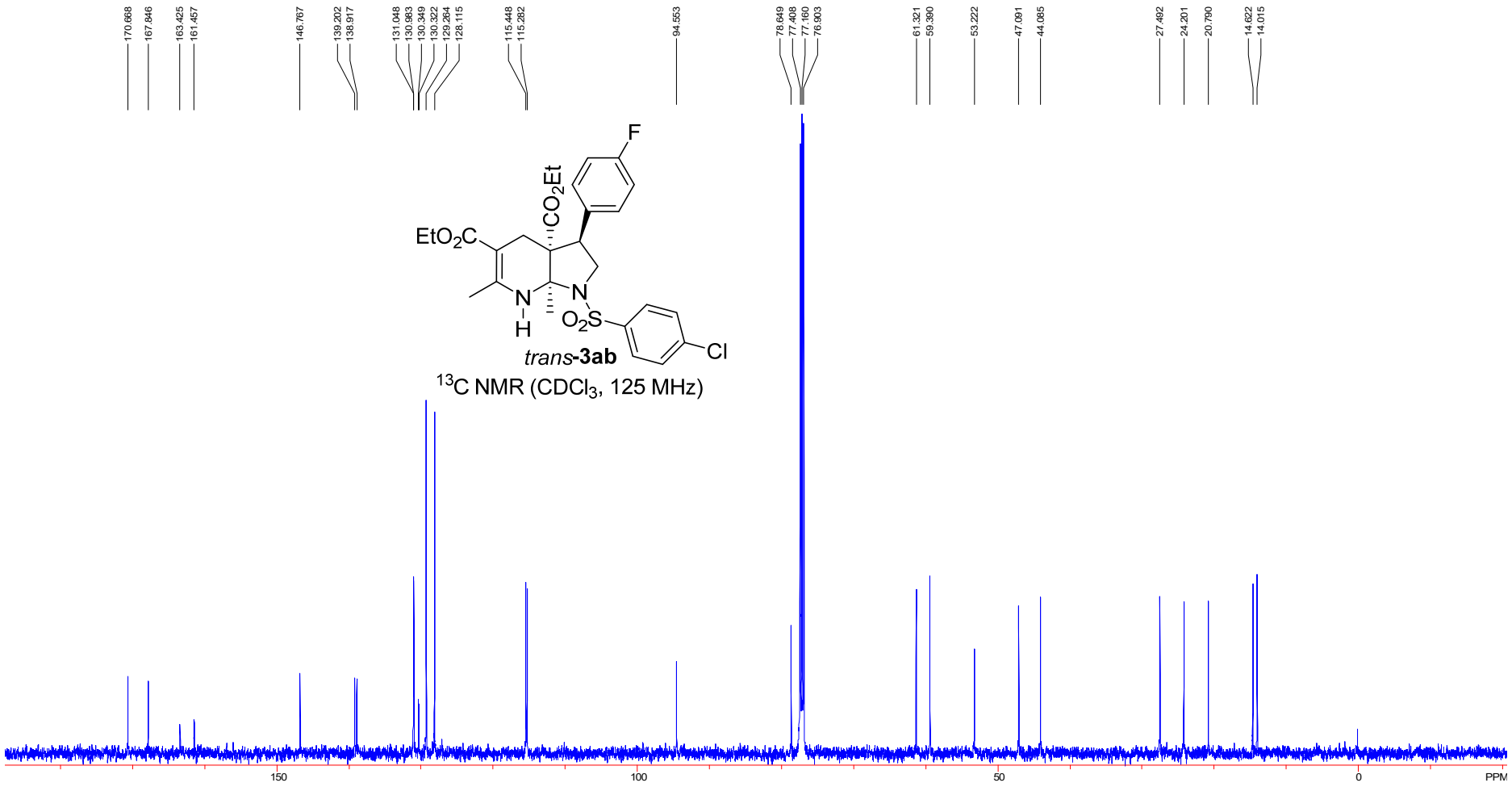
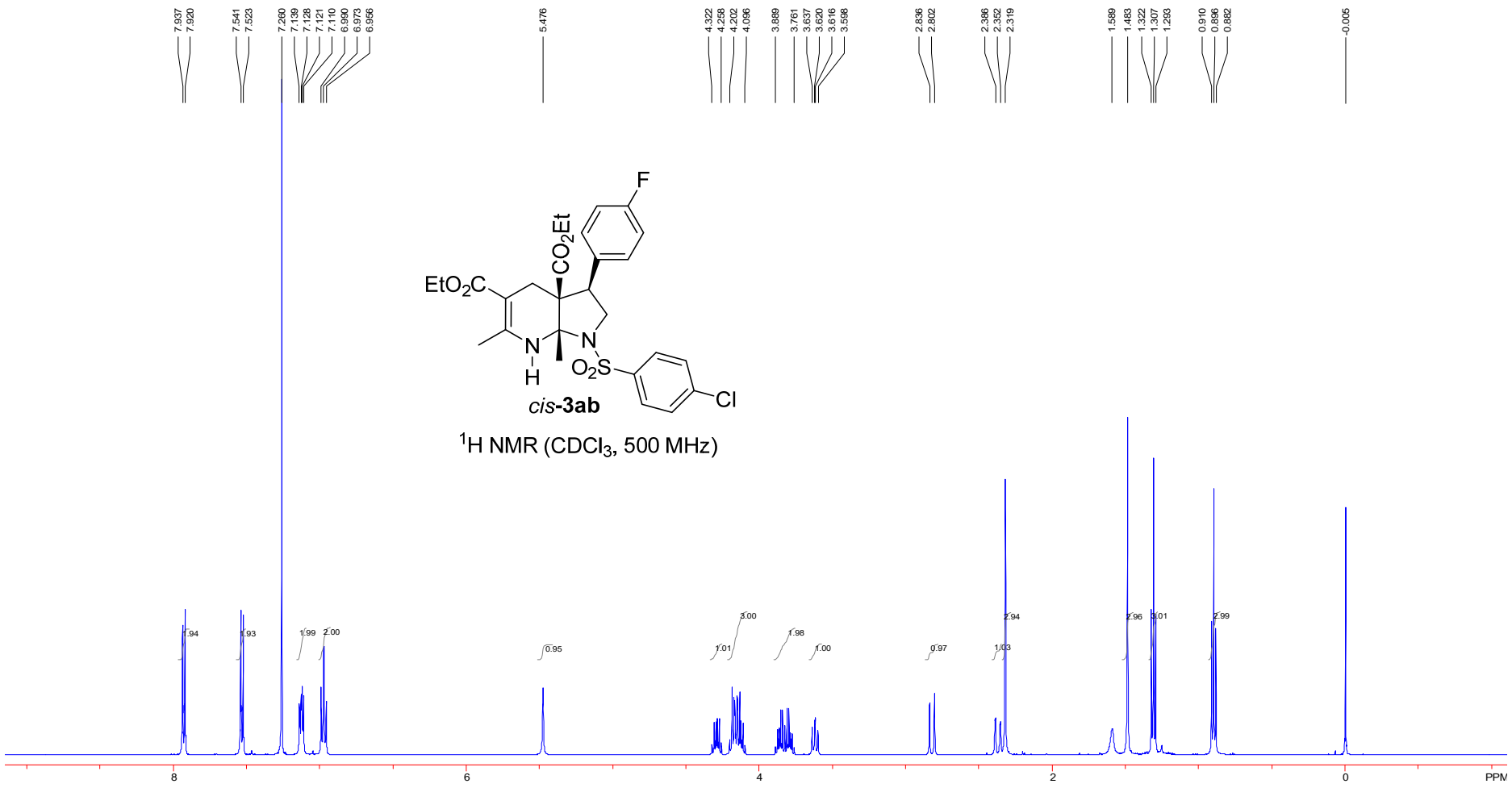
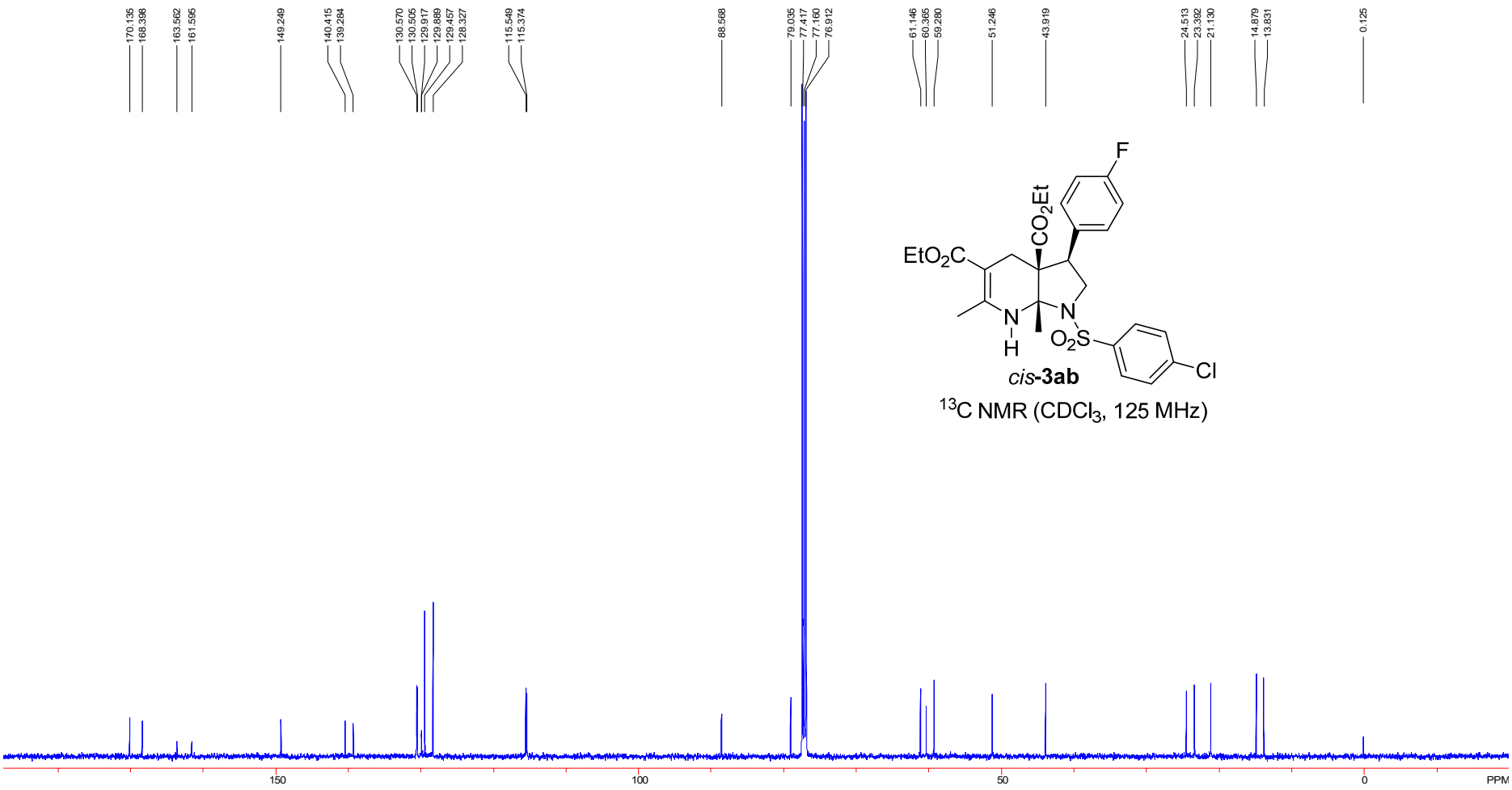
7.667
7.443
7.426
7.279
7.262
7.260
7.252
7.004
6.987
6.971
4.773
4.307
4.287
4.268
4.103
4.052
4.039
3.978
3.896
3.878
3.860
3.543
3.523
3.502
2.349
2.315
2.128
1.830
1.796
1.663
1.201
1.186
1.172
1.124
1.109
1.095
-0.007
F
CO2Et
EtO2C
N
H
N
O2S
Cl
trans-3ab
1H NMR (CDCl3, 500 MHz)
2.02
2.03
2.56
1.96
0.98
1.06
4.08
1.02
1.00
1.03
2.97
4.02
3.01
2.97
8
6
4
2
0
PPM

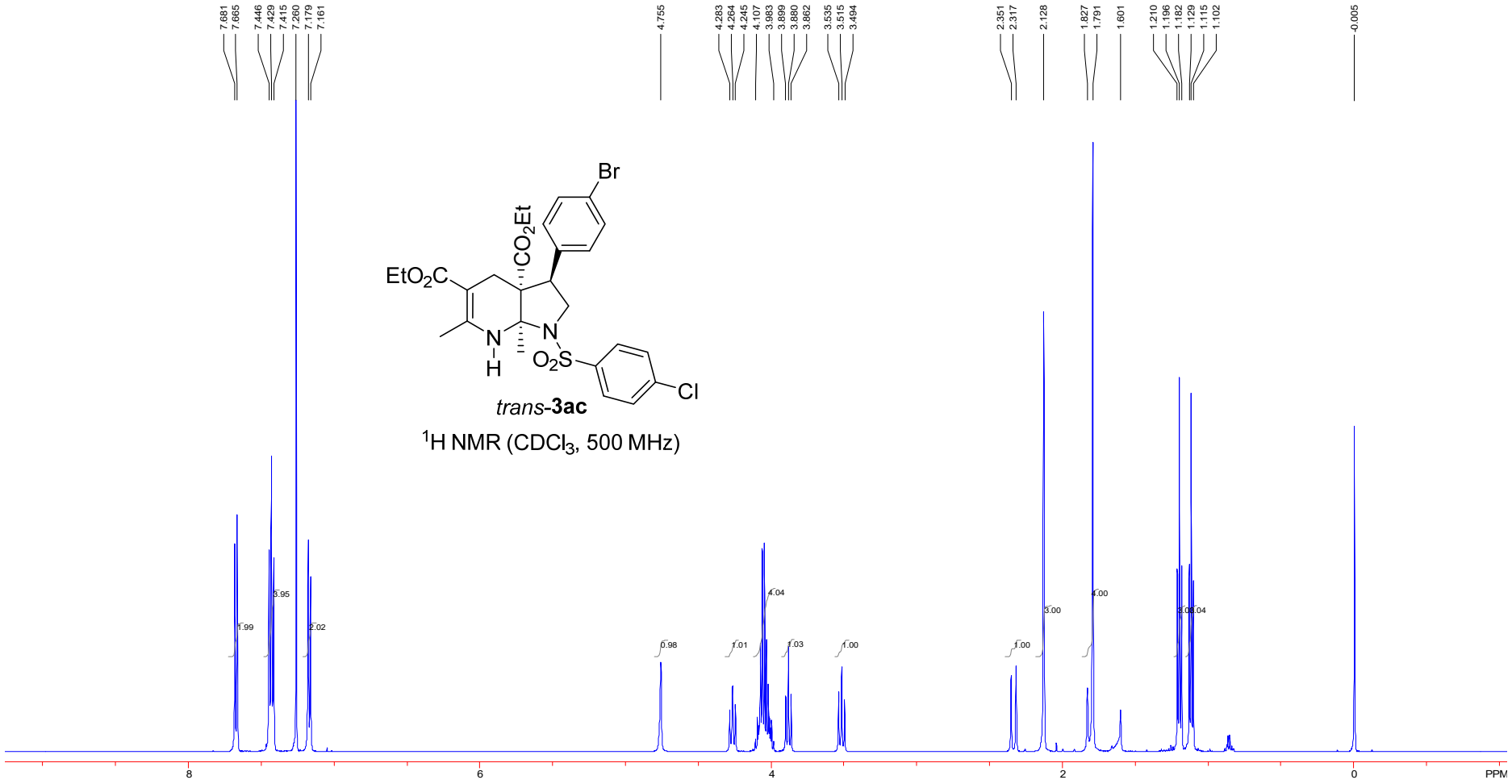


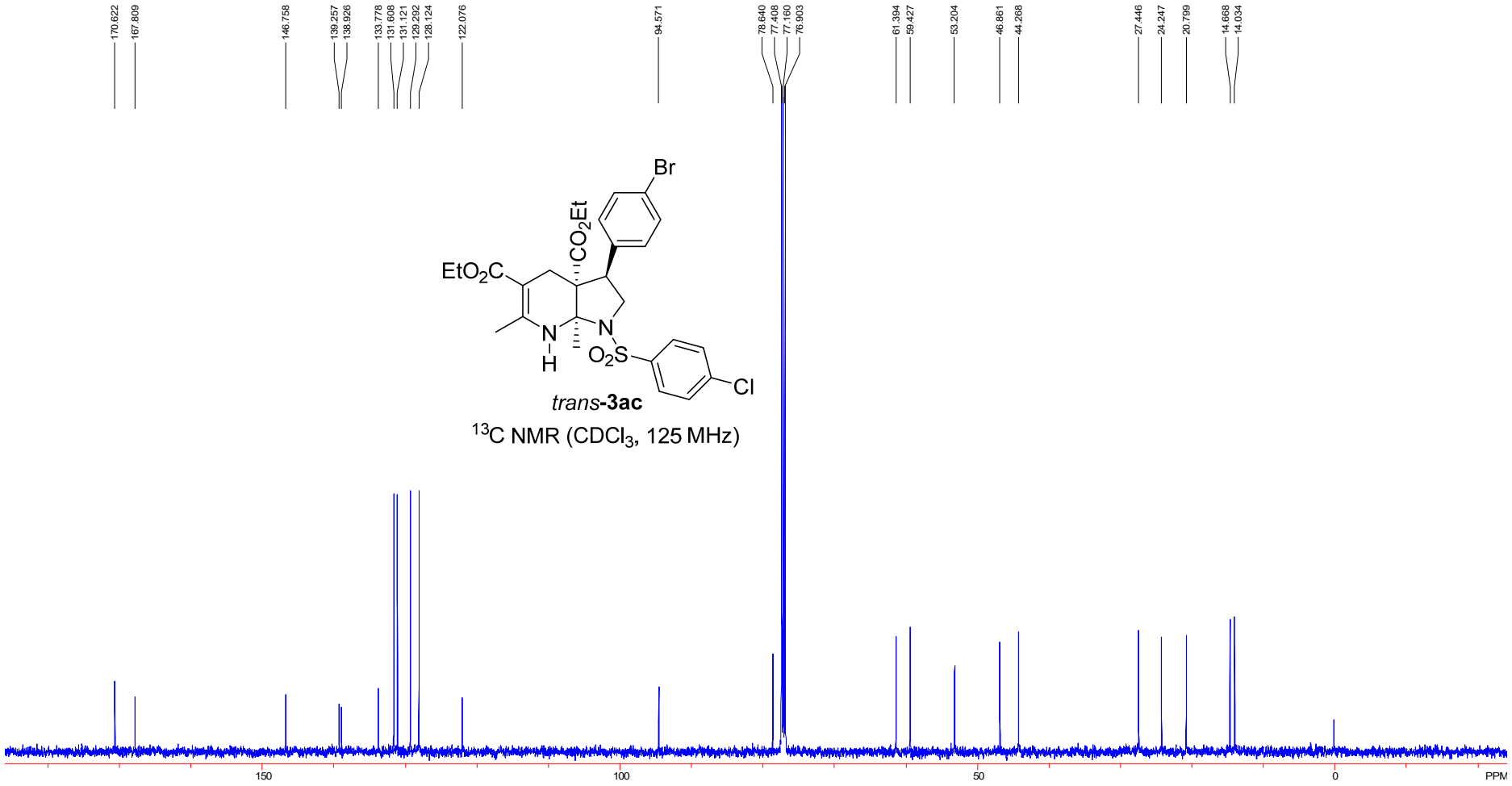
trans-**3ab**

^{13}C NMR ($CDCl_3$, 125 MHz)


7.937
7.920
7.541
7.523
7.260
7.139
7.128
7.121
7.110
6.990
6.973
6.956
5.476
4.322
4.258
4.202
4.096
3.889
3.761
3.637
3.620
3.616
3.598
2.836
2.802
2.386
2.352
2.319
1.589
1.483
1.322
1.307
1.293
0.910
0.896
0.882
-0.005
F
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ab
1H NMR (CDCl3, 500 MHz)
1.94
1.93
1.99
2.00
0.95
3.00
1.01
1.98
1.00
0.97
2.94
1.03
2.96
3.01
2.99
8
6
4
2
0
PPM

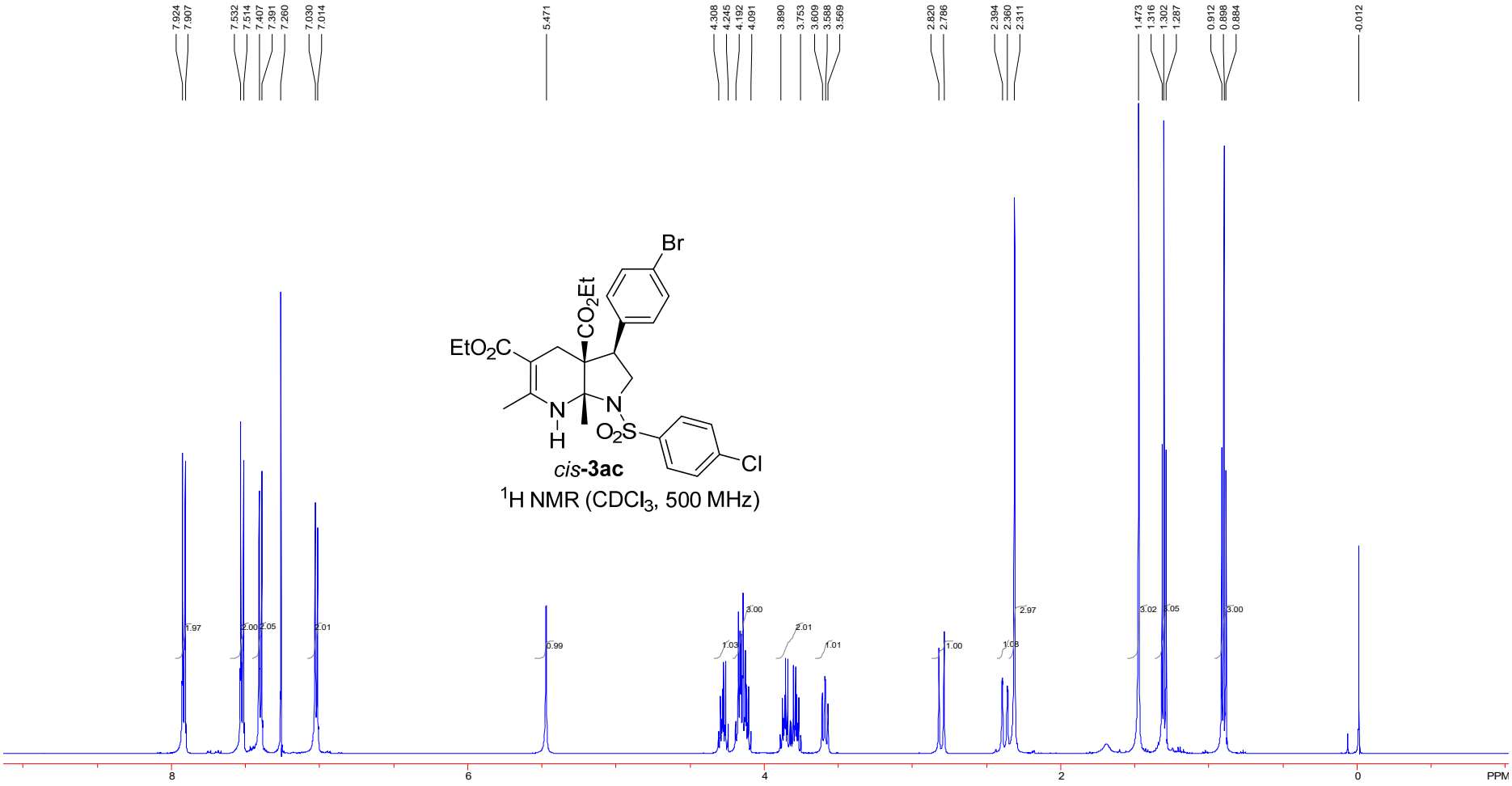

170.135
168.398
163.562
161.595
149.249
140.415
139.284
130.570
130.505
129.917
129.889
129.457
128.327
115.549
115.374
88.568
79.035
77.417
77.160
76.912
61.146
60.365
59.280
51.246
43.919
24.513
23.392
21.130
14.879
13.831
0.125
F
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ab
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

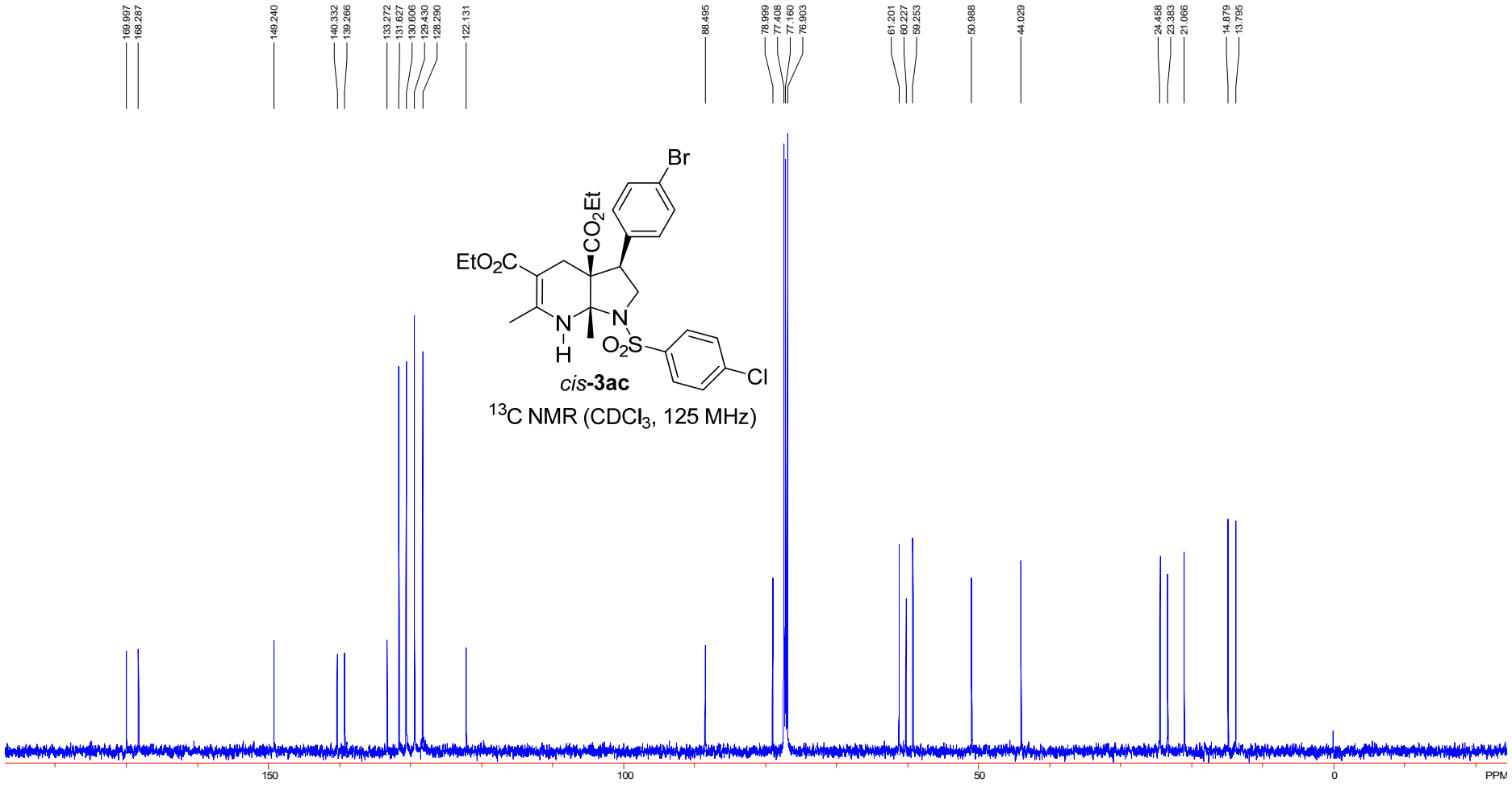

7.681
7.665
7.446
7.429
7.415
7.260
7.179
7.161
4.755
4.283
4.264
4.245
4.107
3.983
3.899
3.880
3.862
3.535
3.515
3.494
2.351
2.317
2.128
1.827
1.791
1.601
1.210
1.196
1.182
1.129
1.115
1.102
0.005
Br
CO2Et
EtO2C
N
H
N
O2S
Cl
trans-3ac
1H NMR (CDCl3, 500 MHz)
1.99
3.95
2.02
0.98
1.01
4.04
1.03
1.00
1.00
3.00
4.00
3.08
4.04
8
6
4
2
0
PPM

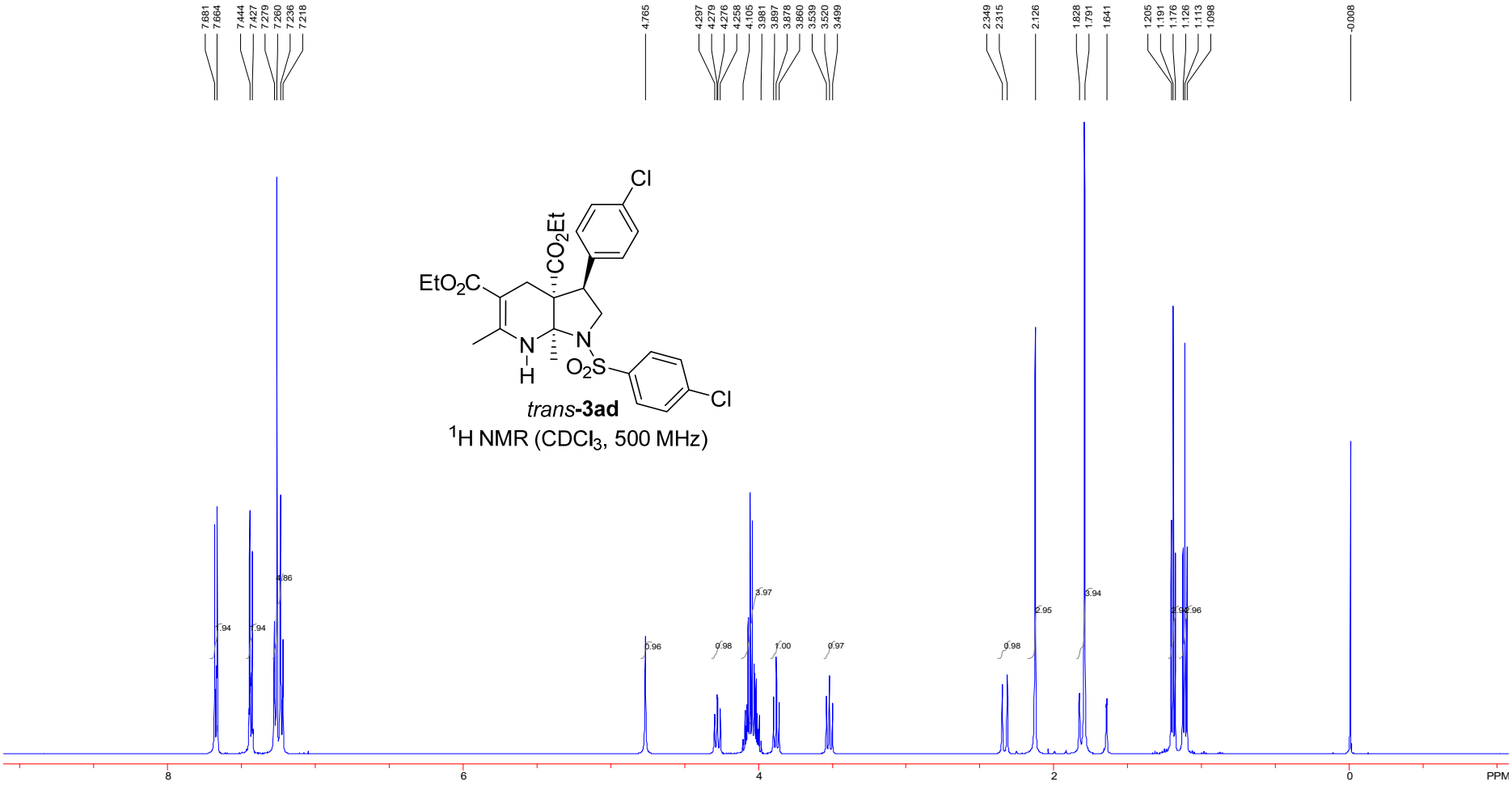


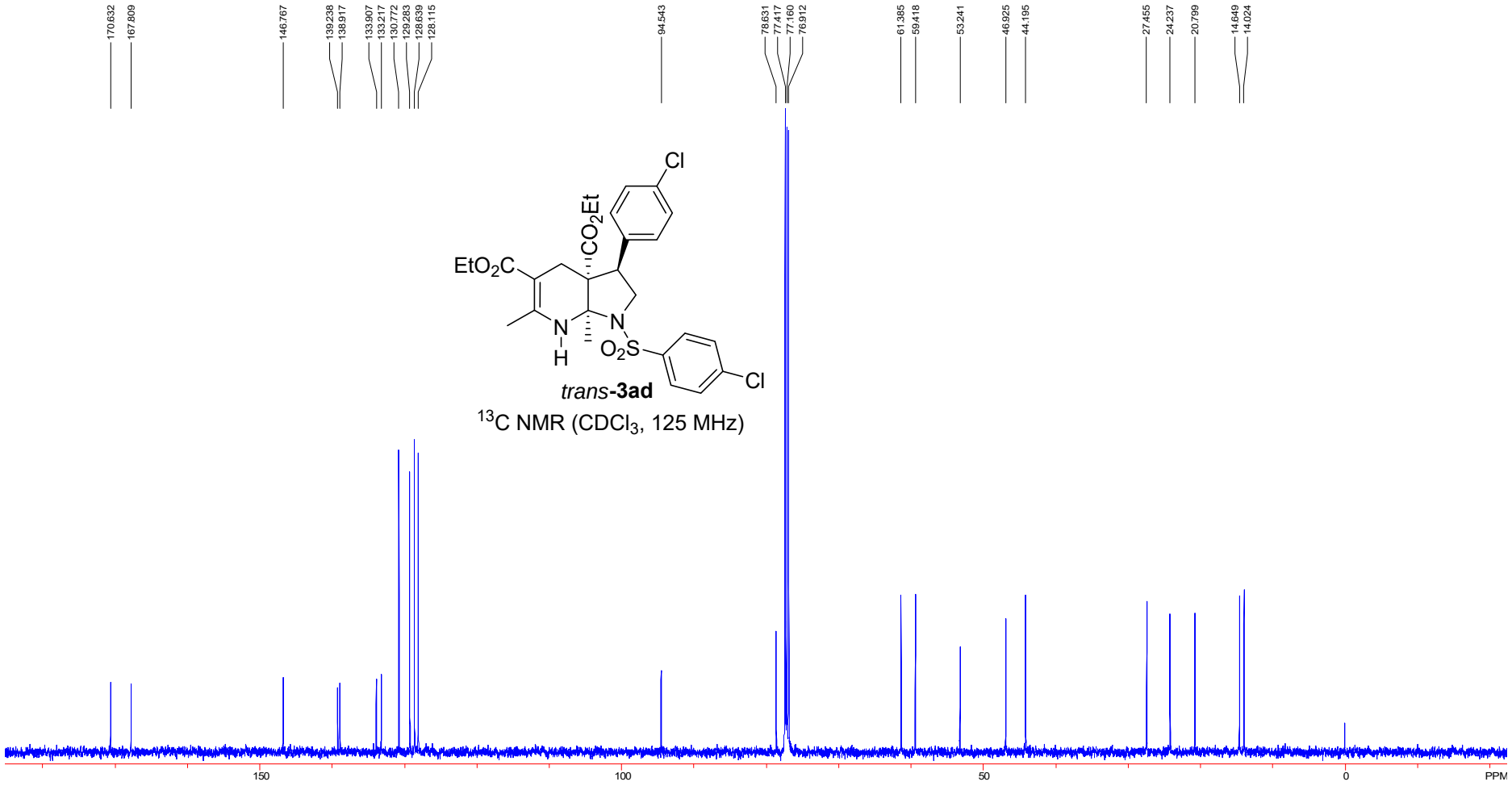
trans-**3ac**

^{13}C NMR ($CDCl_3$, 125 MHz)


7.924
7.907
7.532
7.514
7.407
7.391
7.260
7.030
7.014
5.471
4.308
4.245
4.192
4.091
3.890
3.753
3.609
3.588
3.569
2.820
2.786
2.394
2.360
2.311
1.473
1.316
1.302
1.287
0.912
0.898
0.884
0.012
Br
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ac
1H NMR (CDCl3, 500 MHz)
1.97
2.00
2.05
2.01
0.99
3.00
1.03
2.01
1.01
1.00
2.97
1.08
3.02
3.05
3.00
8
6
4
2
0
PPM

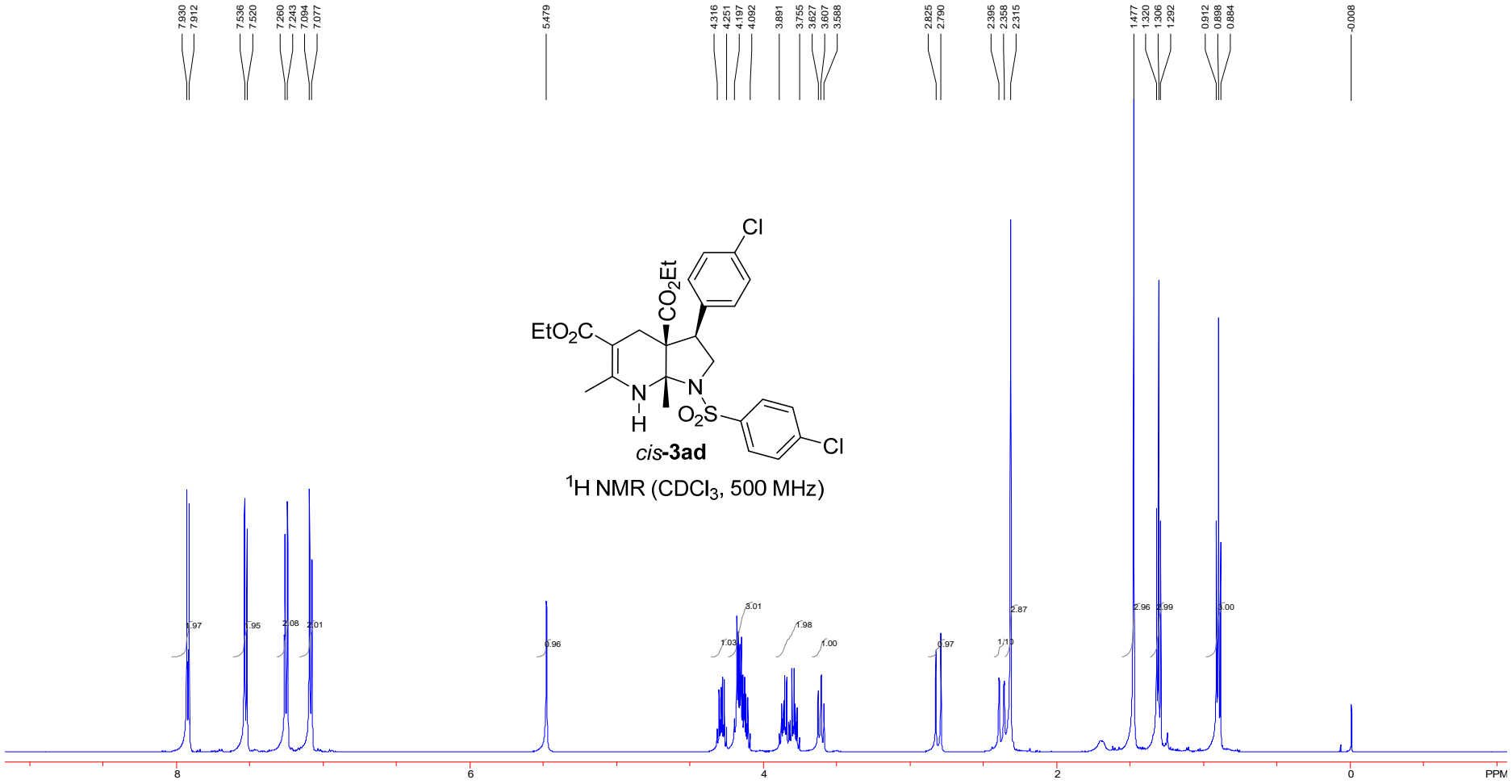

169.997
168.287
149.240
140.332
139.266
133.272
131.627
130.606
129.430
128.290
122.131
88.495
78.999
77.408
77.160
76.903
61.201
60.227
59.253
50.988
44.029
24.458
23.383
21.066
14.879
13.795
Br
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ac
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

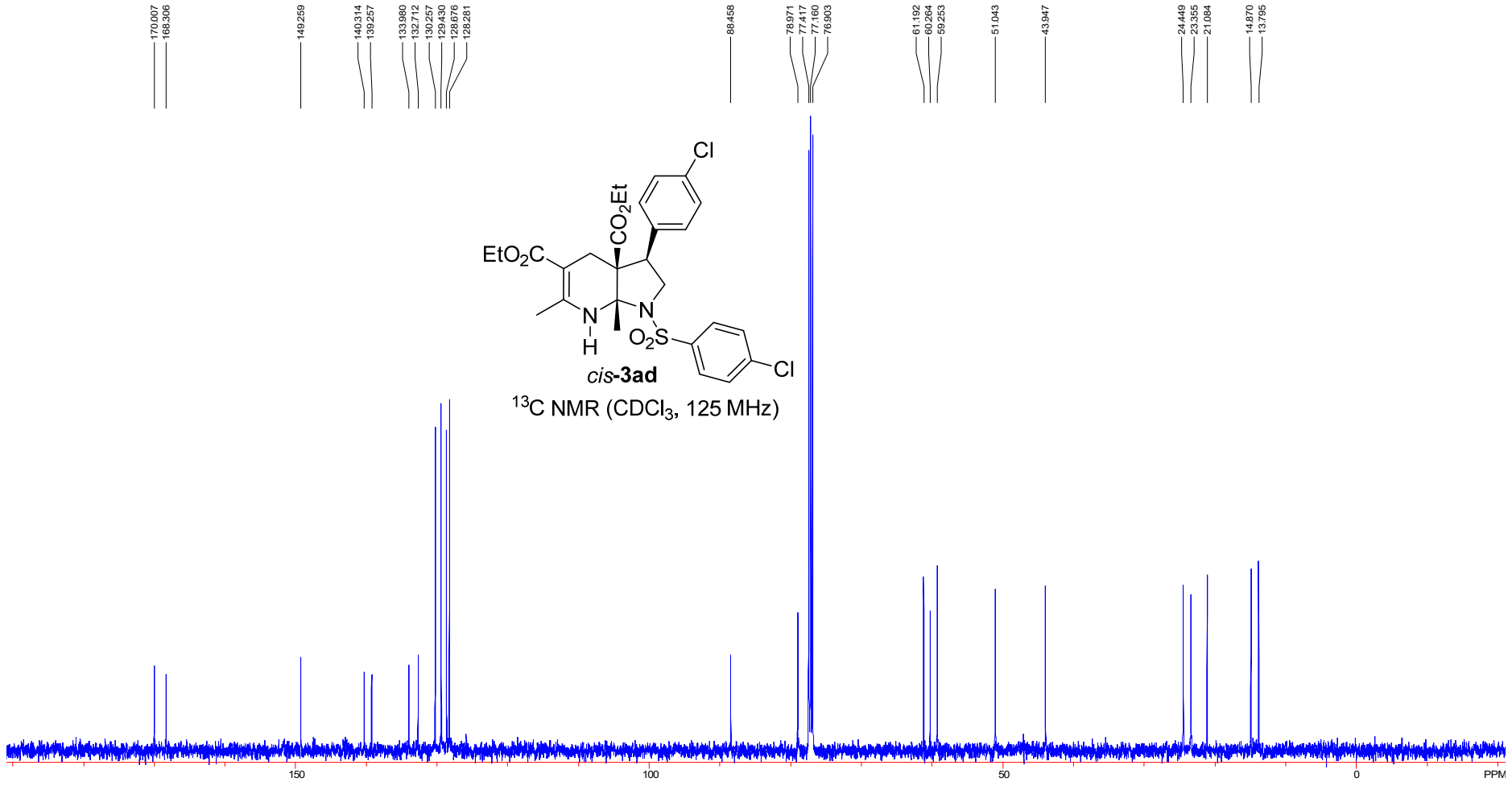

7.681
7.664
7.444
7.427
7.279
7.260
7.236
7.218
4.765
4.297
4.279
4.276
4.258
4.105
3.981
3.897
3.878
3.860
3.539
3.520
3.499
2.349
2.315
2.126
1.828
1.791
1.641
1.205
1.191
1.176
1.126
1.113
1.098
-0.008
Cl
CO2Et
EtO2C
N
H
N
O2S
Cl
trans-3ad
1H NMR (CDCl3, 500 MHz)
1.94
1.94
4.86
0.96
0.98
3.97
1.00
0.97
0.98
2.95
3.94
2.92
2.96
8
6
4
2
0
PPM

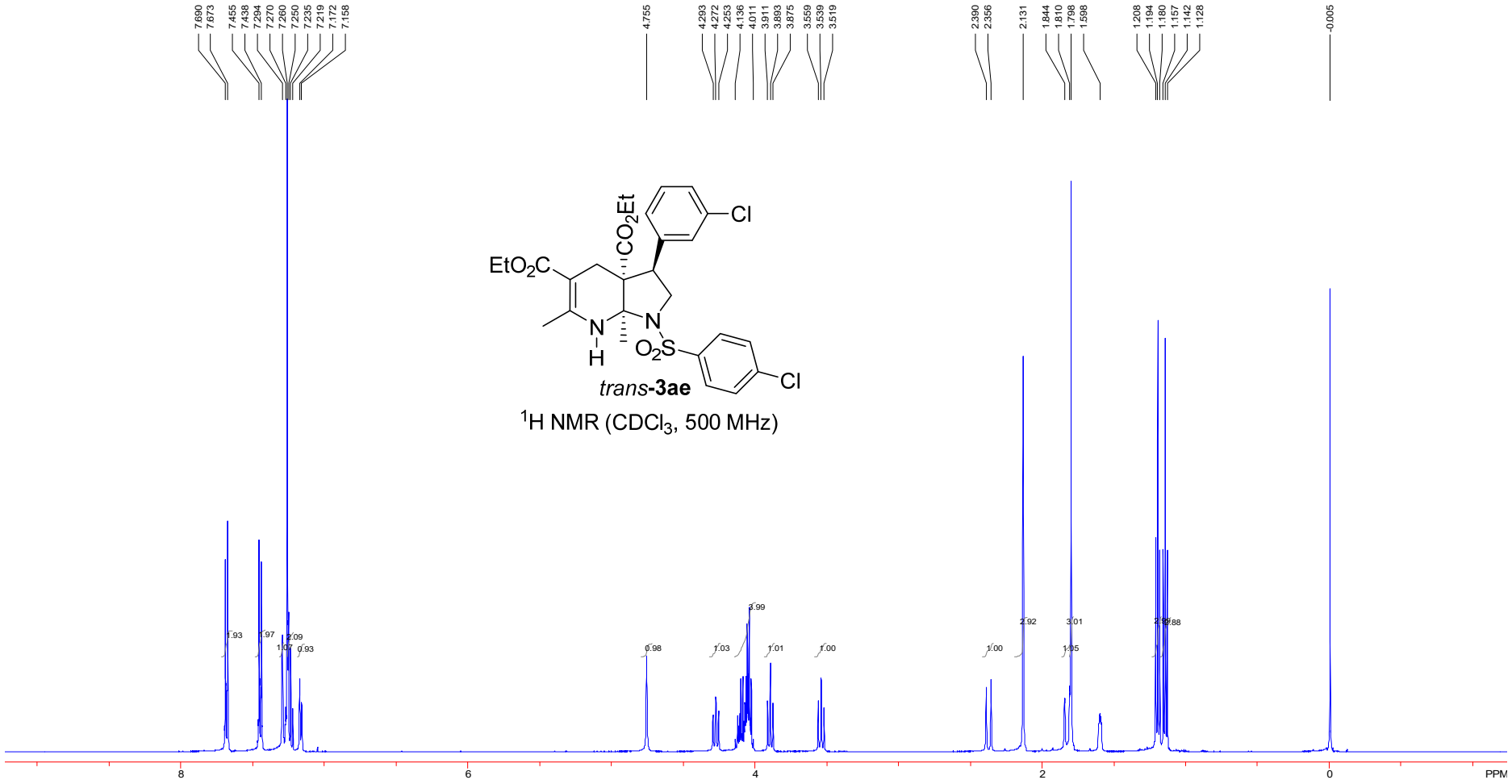


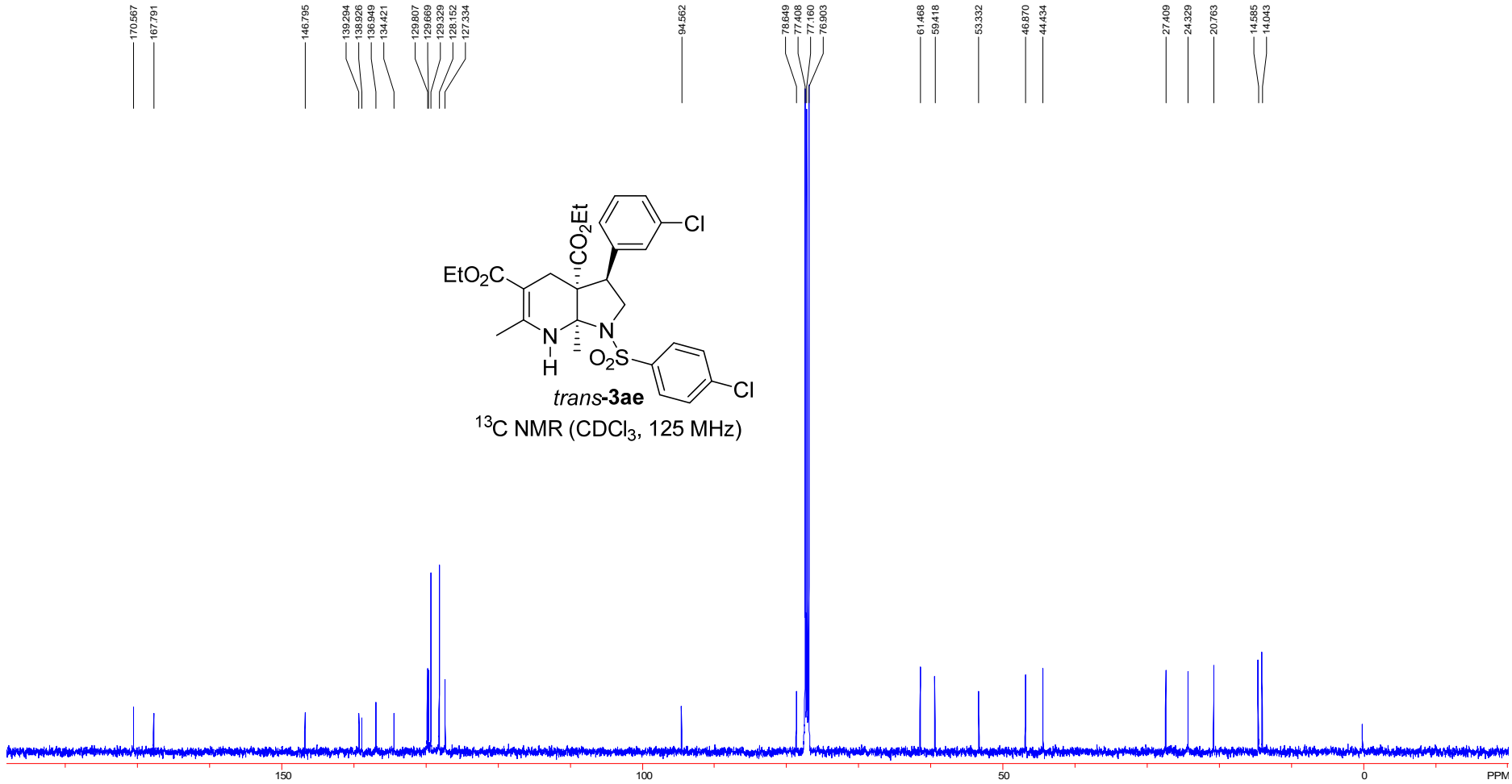
trans-**3ad**

^{13}C NMR ($CDCl_3$, 125 MHz)


7.930
7.912
7.536
7.520
7.260
7.243
7.094
7.077
5.479
4.316
4.251
4.197
4.092
3.891
3.755
3.627
3.607
3.588
2.825
2.790
2.395
2.358
2.315
1.477
1.320
1.306
1.292
0.912
0.898
0.884
0.008
Cl
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ad
1H NMR (CDCl3, 500 MHz)
1.97
1.95
2.08
2.01
0.96
3.01
1.03
1.98
1.00
0.97
1.10
2.87
2.96
2.99
3.00
8
6
4
2
0
PPM

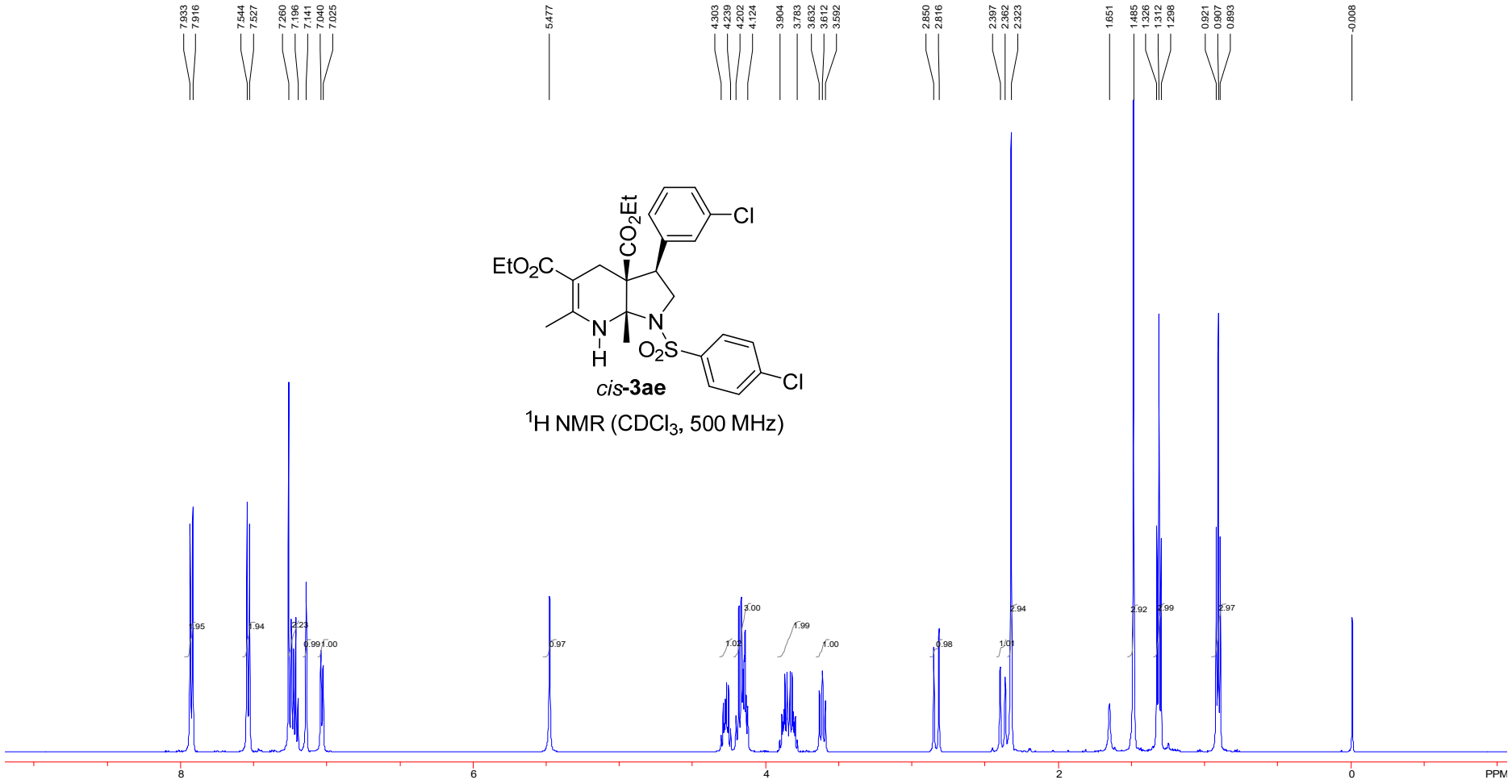

170.007
168.306
149.259
140.314
139.257
133.980
132.712
130.257
129.430
128.676
128.281
88.458
78.971
77.417
77.160
76.903
61.192
60.264
59.253
51.043
43.947
24.449
23.355
21.084
14.870
13.795
Cl
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ad
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

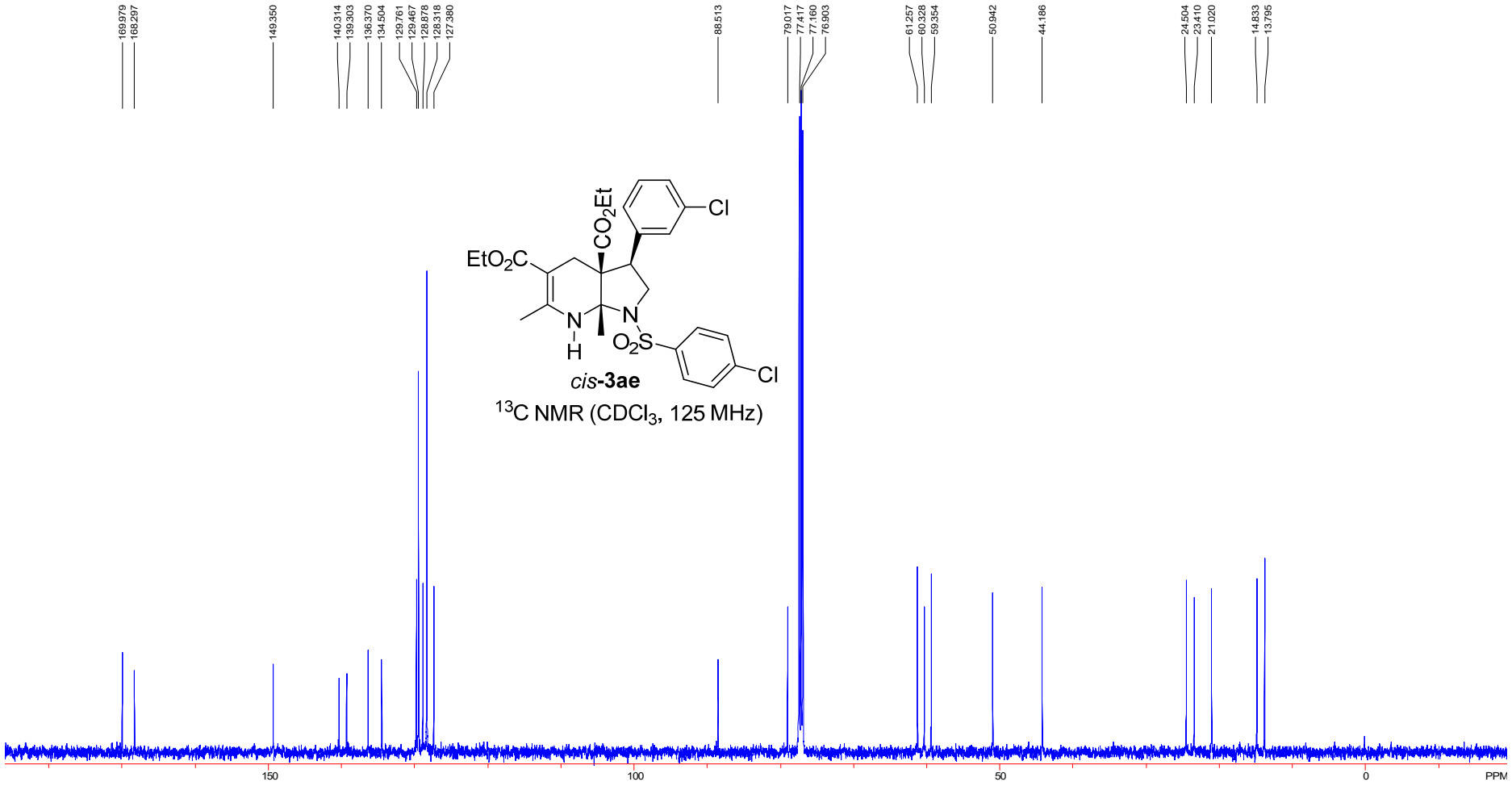

7.690
7.673
7.455
7.438
7.294
7.270
7.260
7.250
7.235
7.219
7.172
7.158
4.755
4.293
4.272
4.253
4.136
4.011
3.911
3.893
3.875
3.559
3.539
3.519
2.390
2.356
2.131
1.844
1.810
1.798
1.598
1.208
1.194
1.180
1.157
1.142
1.128
-0.005
EtO2C
CO2Et
Cl
N
H
N
O2S
Cl
trans-3ae
1H NMR (CDCl3, 500 MHz)
1.93
1.97
2.09
1.07
0.93
0.98
1.03
3.99
1.01
1.00
1.00
2.92
3.01
1.05
2.88
8
6
4
2
0
PPM



trans-**3ae**

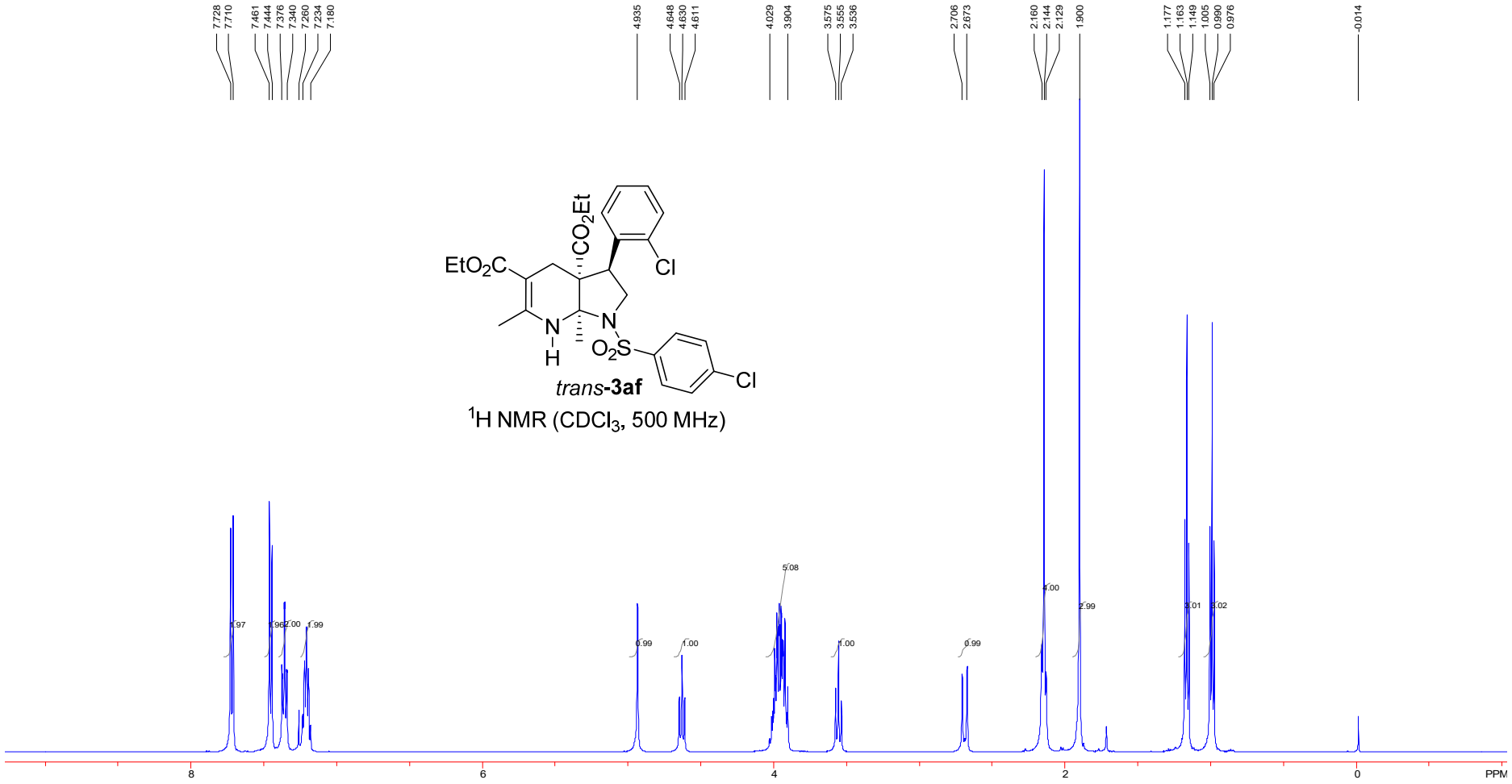
^{13}C NMR ($CDCl_3$, 125 MHz)

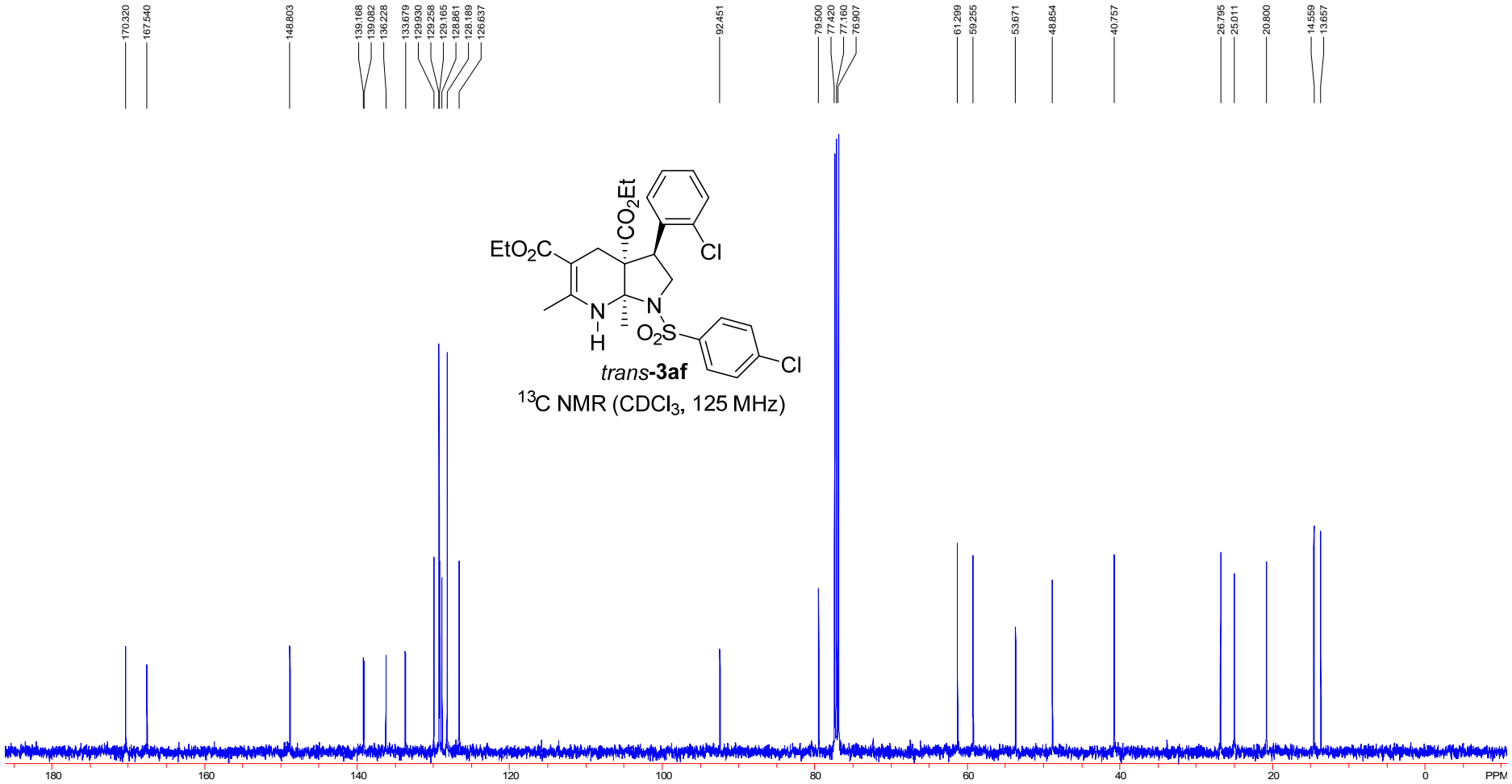

7.933
7.916
7.544
7.527
7.260
7.196
7.141
7.040
7.025
5.477
4.303
4.239
4.202
4.124
3.904
3.783
3.632
3.612
3.592
2.850
2.816
2.397
2.362
2.323
1.651
1.485
1.326
1.312
1.298
0.921
0.907
0.893
0.008
CO2Et
EtO2C
Cl
N
H
N
O2S
Cl
cis-3ae
1H NMR (CDCl3, 500 MHz)
1.95
1.94
2.23
0.99
1.00
0.97
1.02
3.00
1.99
1.00
0.98
1.01
2.94
2.92
2.99
2.97
8
6
4
2
0
PPM

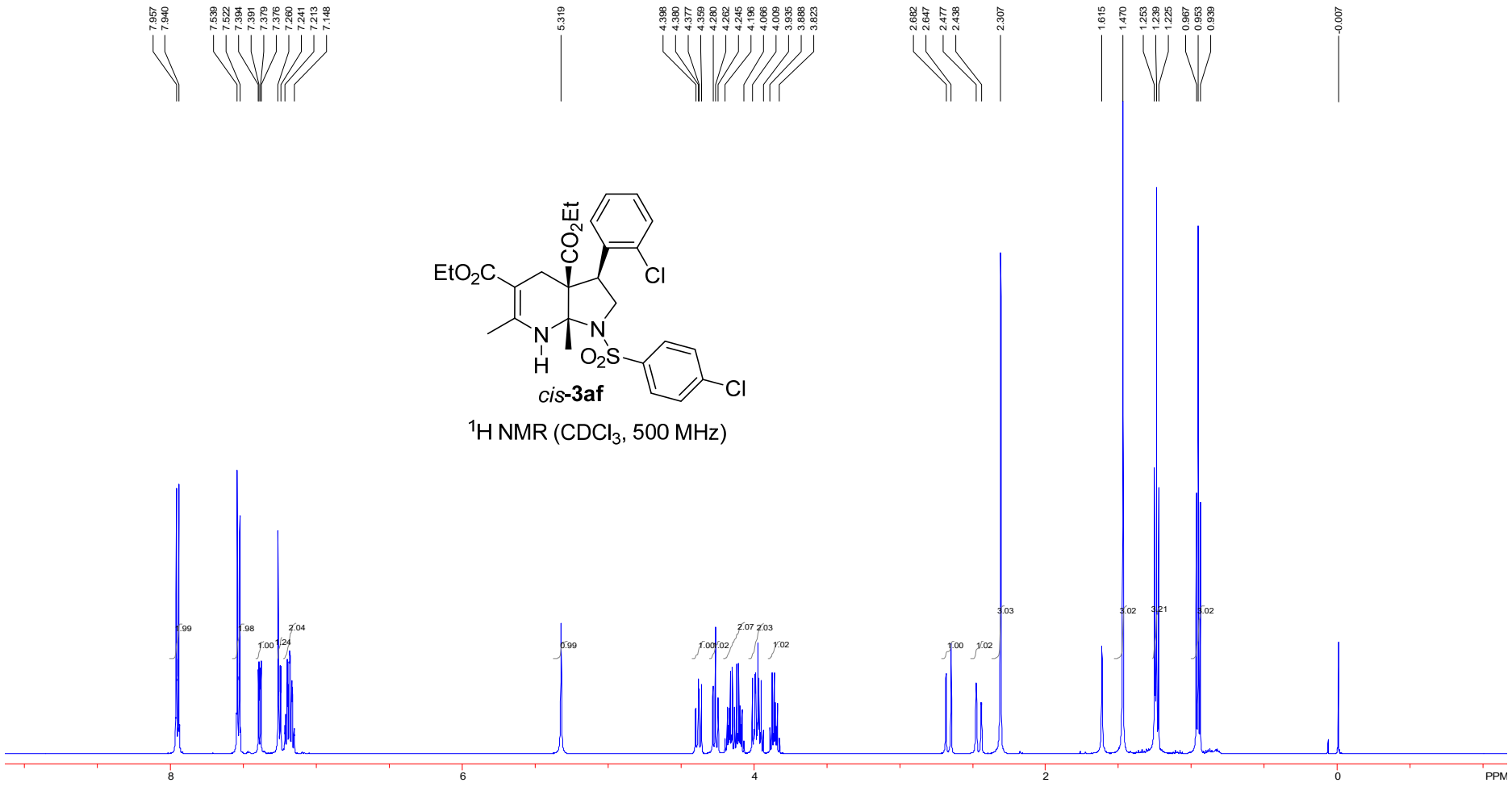


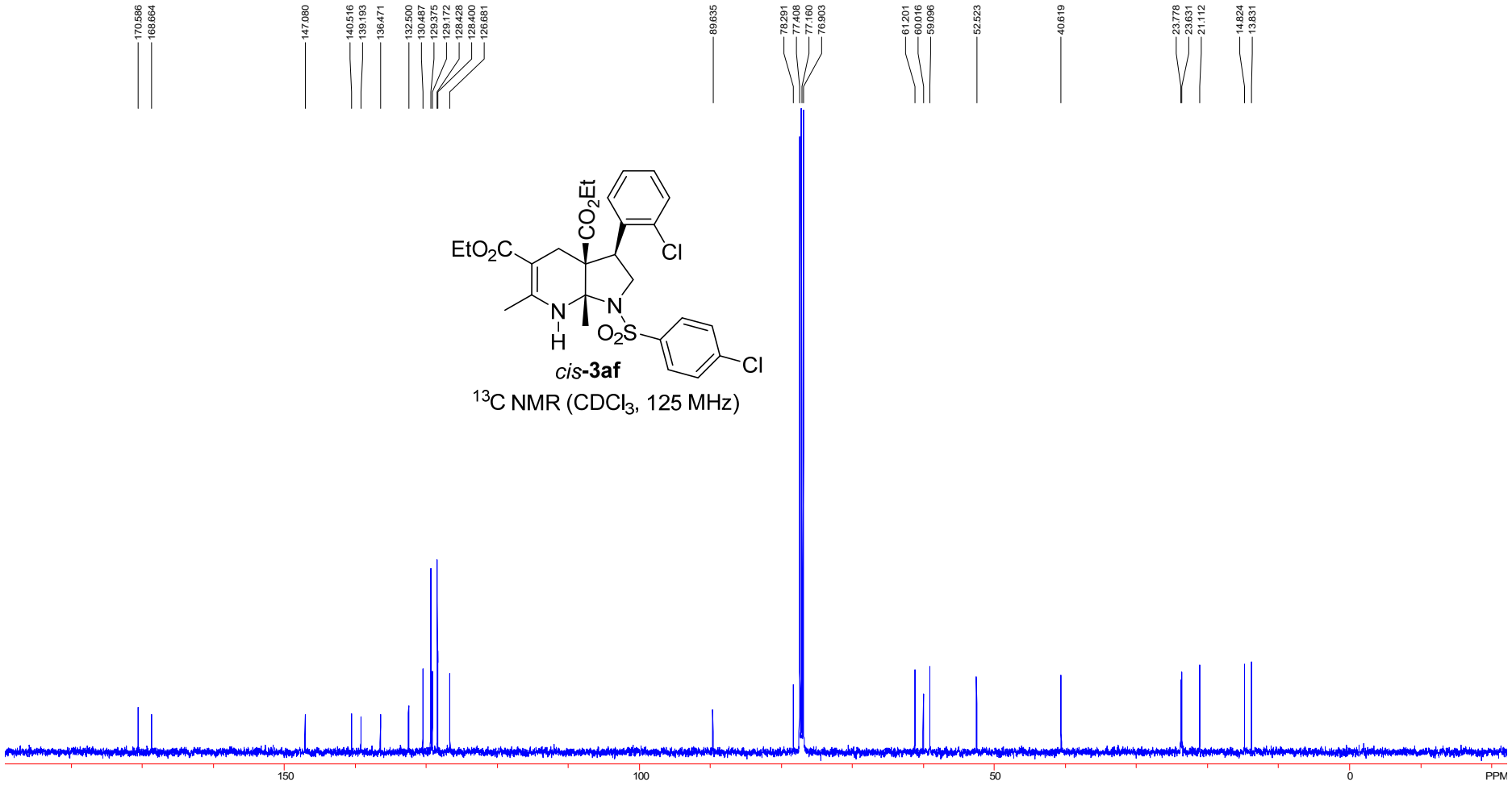
cis-**3ae**

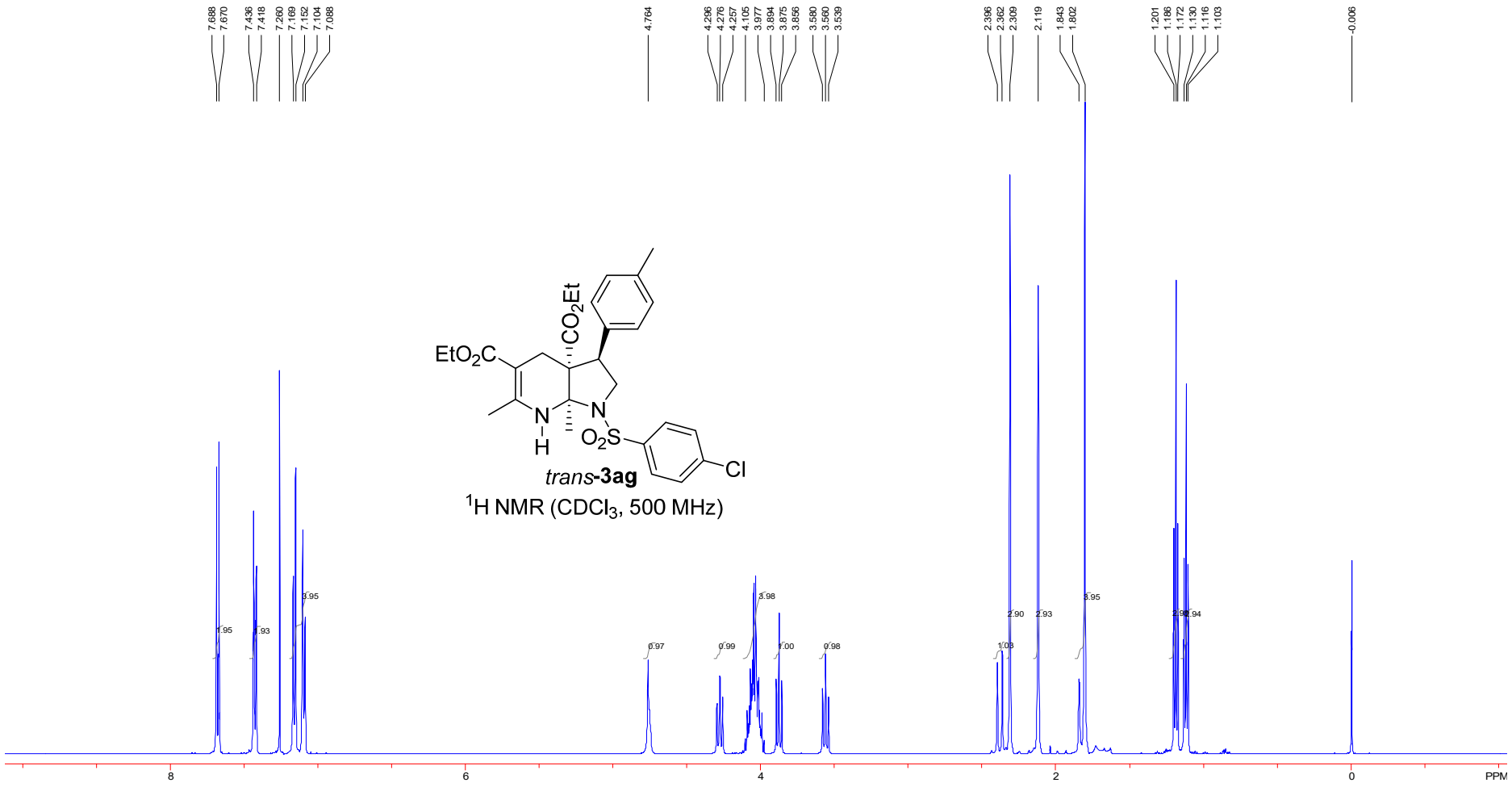
^{13}C NMR ($CDCl_3$, 125 MHz)

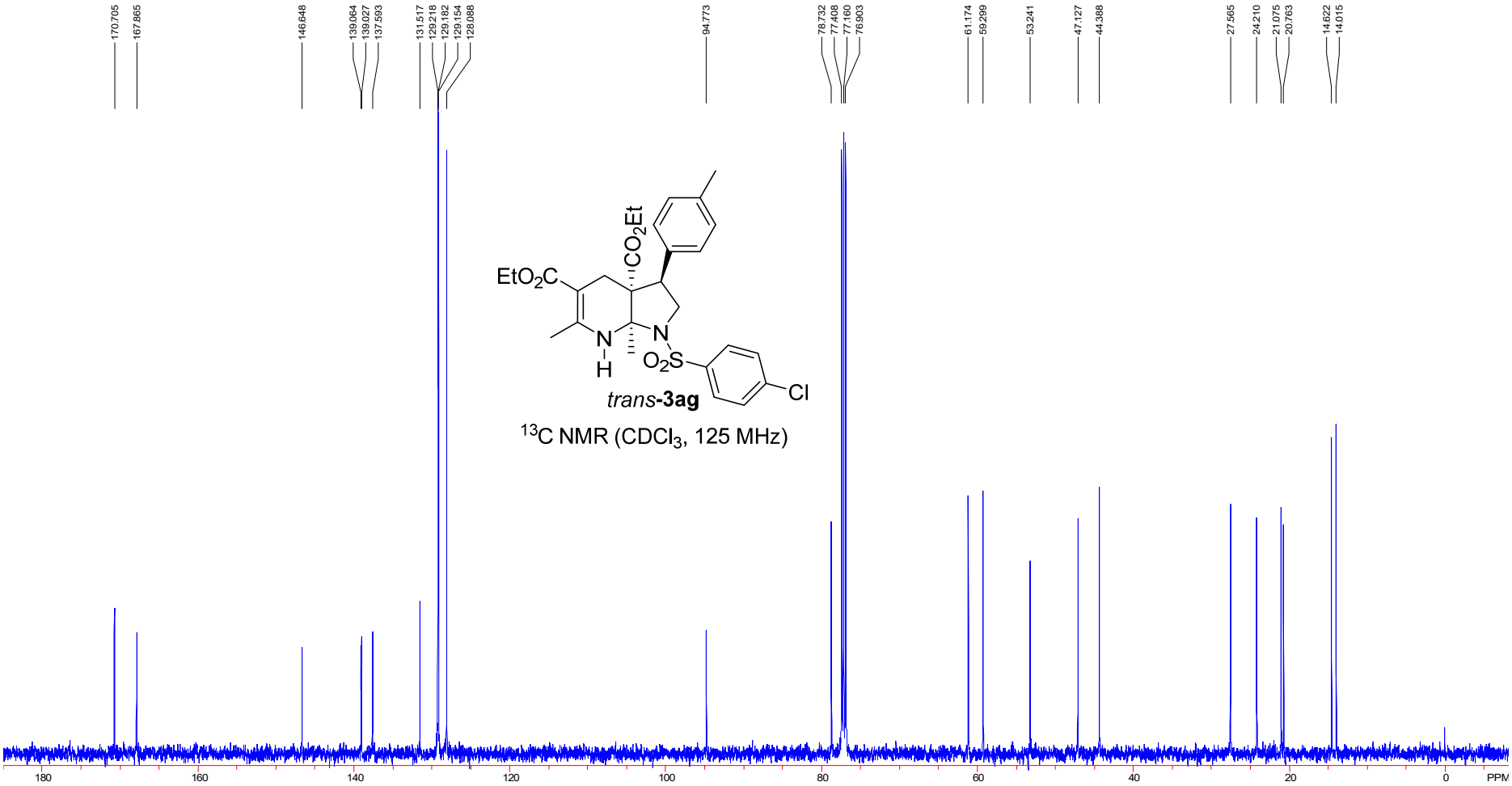

7.728
7.710
7.461
7.444
7.376
7.340
7.260
7.234
7.180
4.935
4.648
4.630
4.611
4.029
3.904
3.575
3.555
3.536
2.706
2.673
2.160
2.144
2.129
1.900
1.177
1.163
1.149
1.005
0.990
0.976
-0.014
EtO2C
CO2Et
Cl
N
H
N
O2S
Cl
trans-3af
1H NMR (CDCl3, 500 MHz)
1.97
1.96
2.00
1.99
0.99
1.00
5.08
1.00
0.99
4.00
2.99
2.01
3.02
8
6
4
2
0
PPM

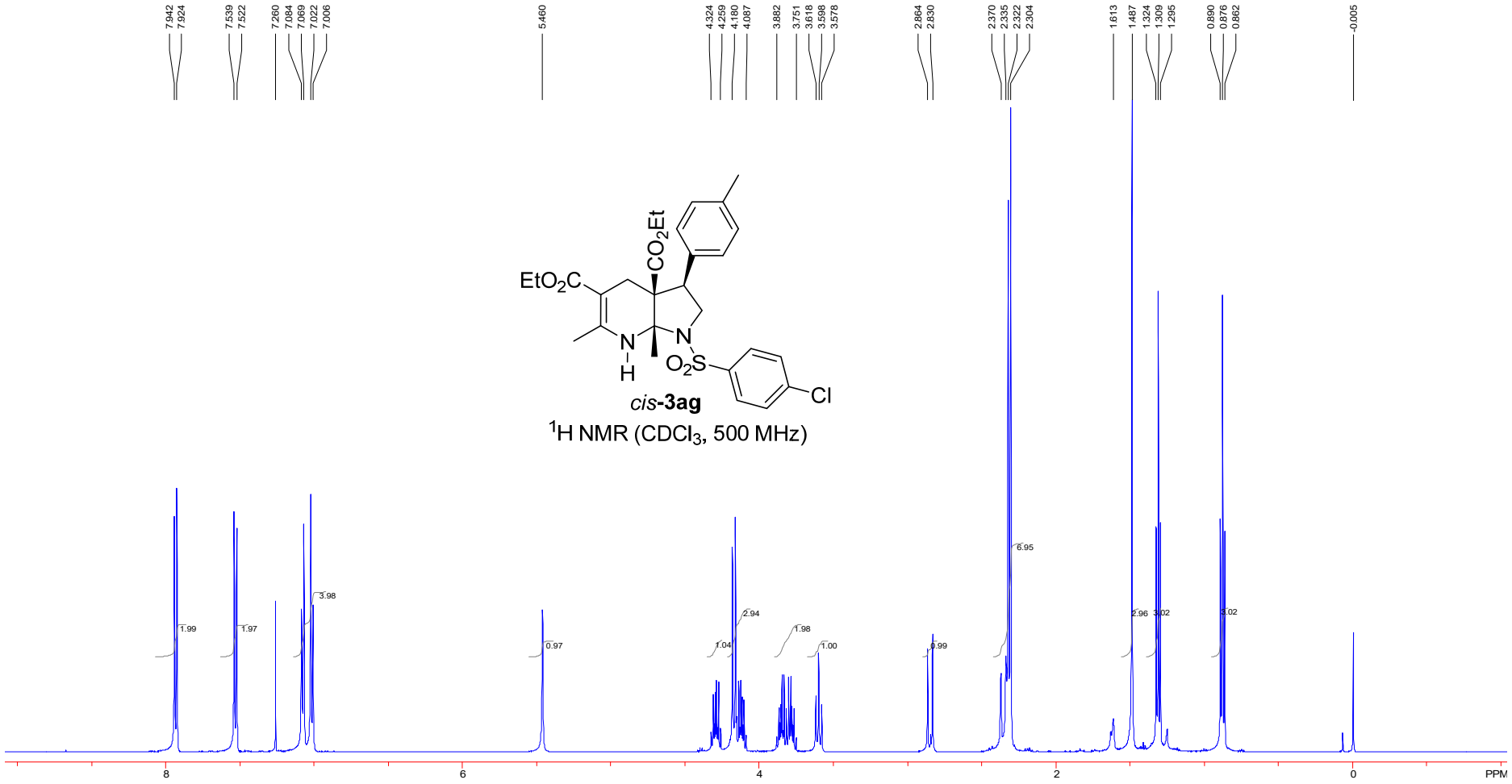

170.320
167.540
148.803
139.168
139.082
136.228
133.679
129.930
129.258
129.165
128.861
128.189
126.637
92.451
79.500
77.420
77.160
76.907
61.299
59.255
53.671
48.854
40.757
26.795
25.011
20.800
14.559
13.657
EtO2C
CO2Et
Cl
N
H
N
O2S
Cl
trans-3af
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

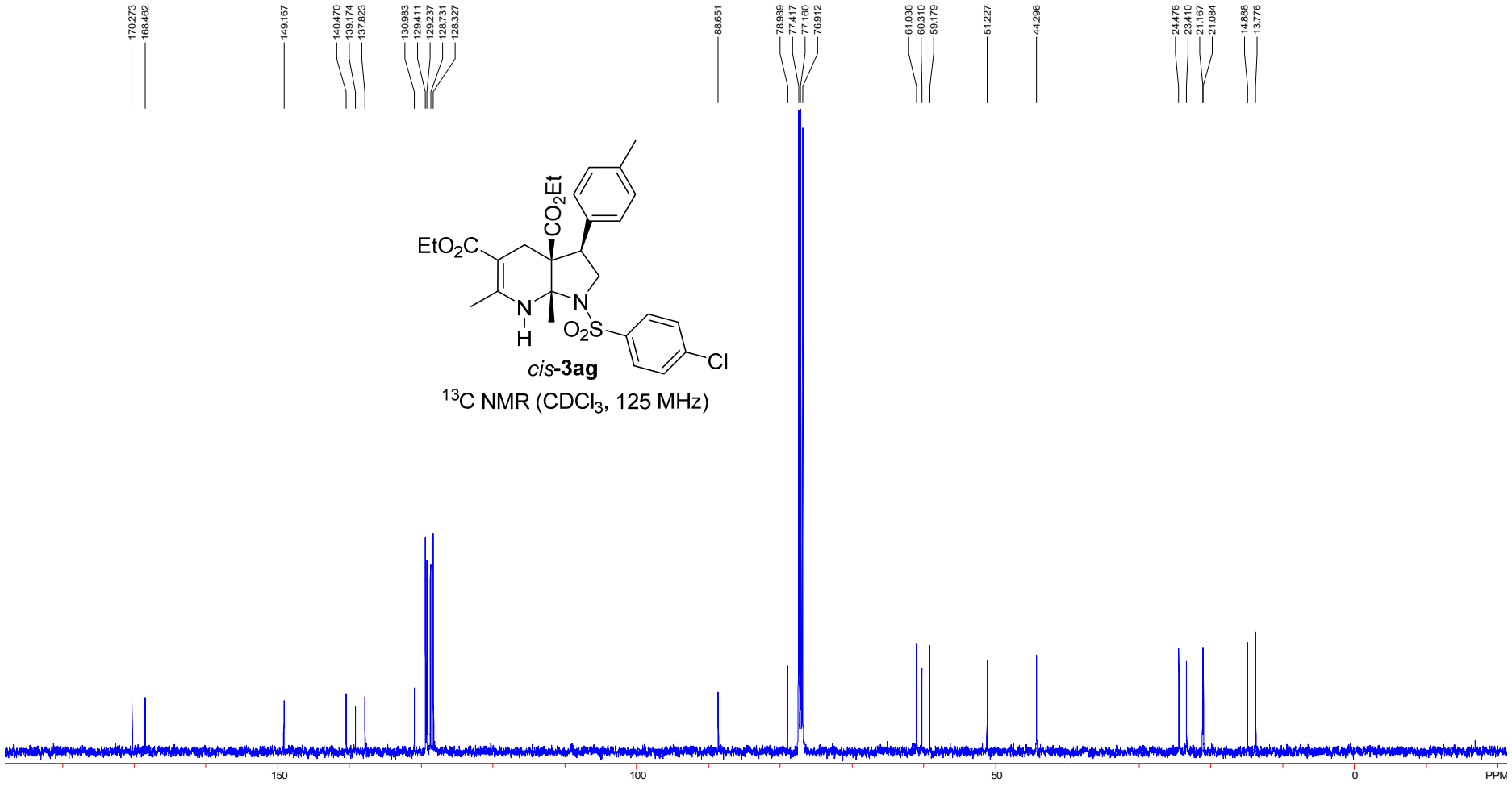

7.957
7.940
7.539
7.522
7.394
7.391
7.379
7.376
7.280
7.241
7.213
7.148
5.319
4.398
4.380
4.377
4.359
4.280
4.262
4.245
4.196
4.066
4.009
3.935
3.888
3.823
2.682
2.647
2.477
2.438
2.307
1.615
1.470
1.253
1.239
1.225
0.967
0.953
0.939
-0.007
EtO2C
CO2Et
Cl
N
H
N
O2S
Cl
cis-3af
1H NMR (CDCl3, 500 MHz)
1.99
1.98
1.00
1.24
2.04
0.99
1.00
1.02
2.07
2.03
1.02
1.00
1.02
3.03
3.02
3.21
3.02
8
6
4
2
0
PPM


170.586
168.664
147.080
140.516
139.193
136.471
132.500
130.487
129.375
129.172
128.428
128.400
126.681
89.635
78.291
77.408
77.160
76.903
61.201
60.016
59.096
52.523
40.619
23.778
23.631
21.112
14.824
13.831
EtO2C
CO2Et
Cl
N
H
N
O2S
Cl
cis-3af
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM


7.688
7.670
7.436
7.418
7.260
7.169
7.152
7.104
7.088
4.764
4.296
4.276
4.257
4.105
3.977
3.894
3.875
3.856
3.580
3.560
3.539
2.396
2.362
2.309
2.119
1.843
1.802
1.201
1.186
1.172
1.130
1.116
1.103
0.006
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3ag
1H NMR (CDCl3, 500 MHz)
1.95
1.93
3.95
0.97
0.99
3.98
1.00
0.98
2.90
2.93
3.95
1.03
2.98
2.94
8
6
4
2
0
PPM

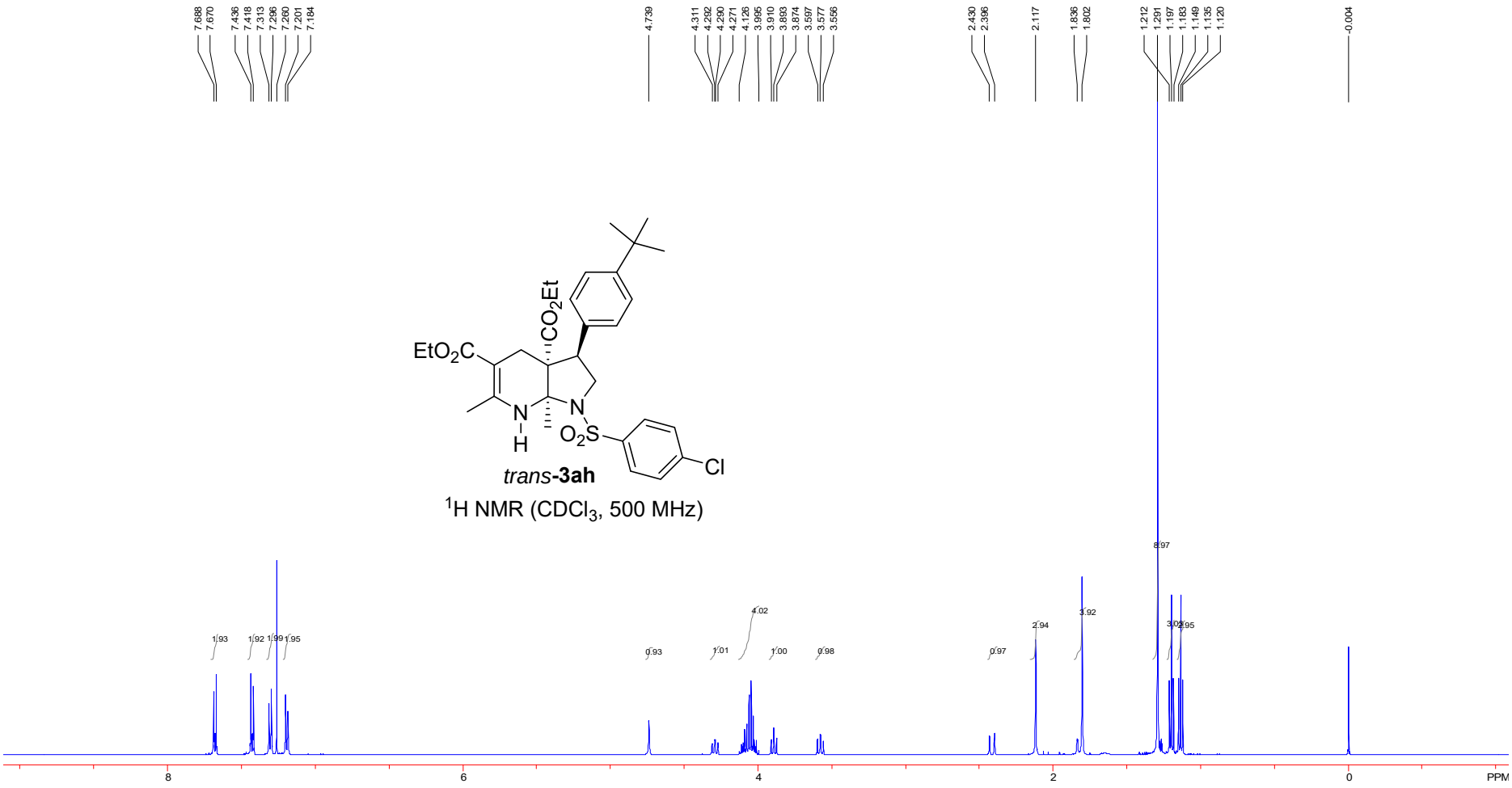

170.705
167.865
146.648
139.064
139.027
137.593
131.517
129.218
129.182
129.154
128.088
94.773
78.732
77.408
77.160
76.903
61.174
59.299
53.241
47.127
44.388
27.565
24.210
21.075
20.763
14.622
14.015
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3ag
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

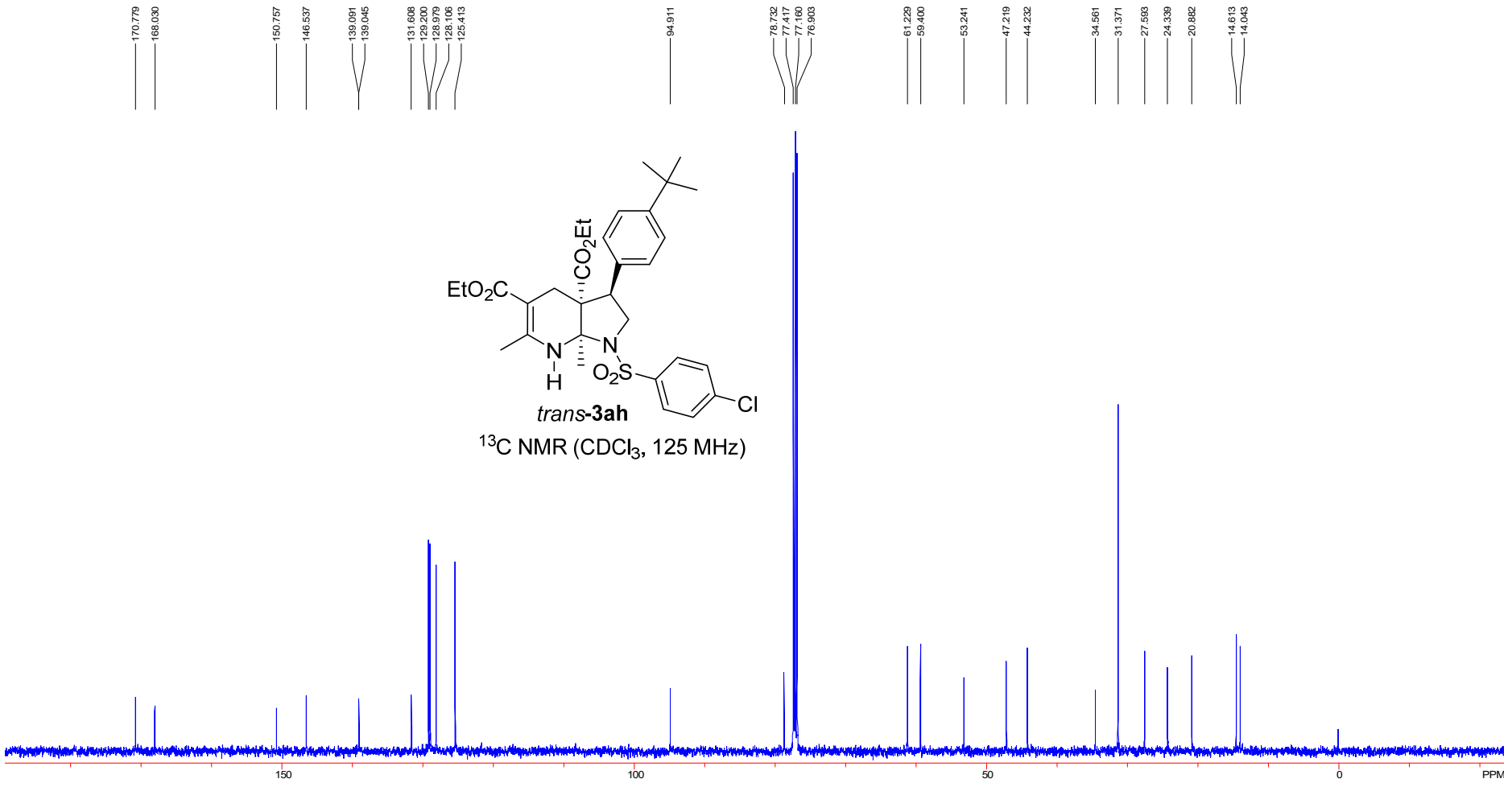

7.942
7.924
7.539
7.522
7.260
7.084
7.069
7.022
7.006
5.460
4.324
4.259
4.180
4.087
3.882
3.751
3.618
3.598
3.578
2.864
2.830
2.370
2.335
2.322
2.304
1.613
1.487
1.324
1.306
1.295
0.890
0.876
0.862
0.005
EtO2C
CO2Et
N
H
N
O2S
Cl
cis-3ag
1H NMR (CDCl3, 500 MHz)
1.99
1.97
3.98
0.97
1.04
2.94
1.98
1.00
0.99
6.95
2.96
3.02
3.02
8
6
4
2
0
PPM

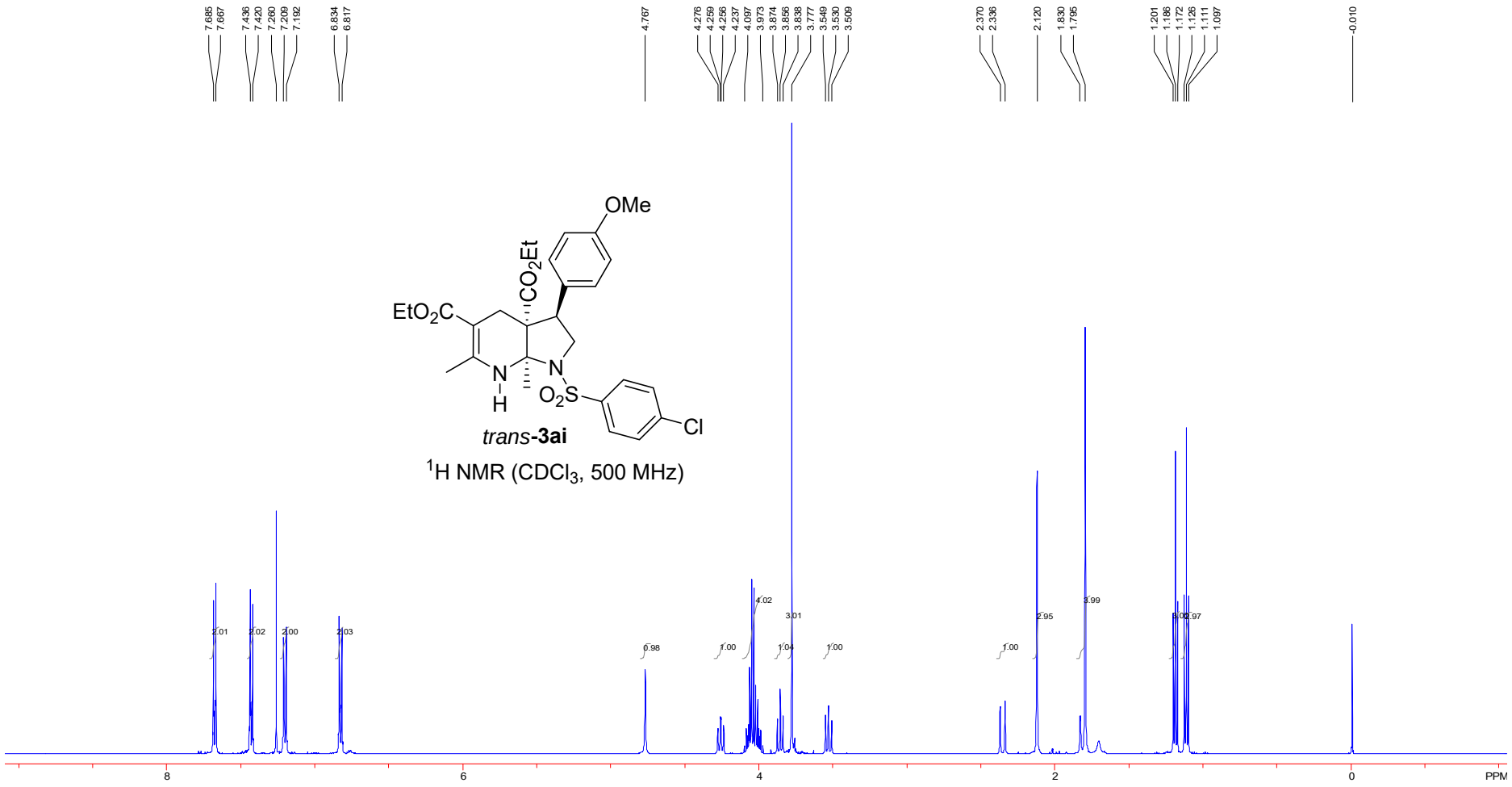


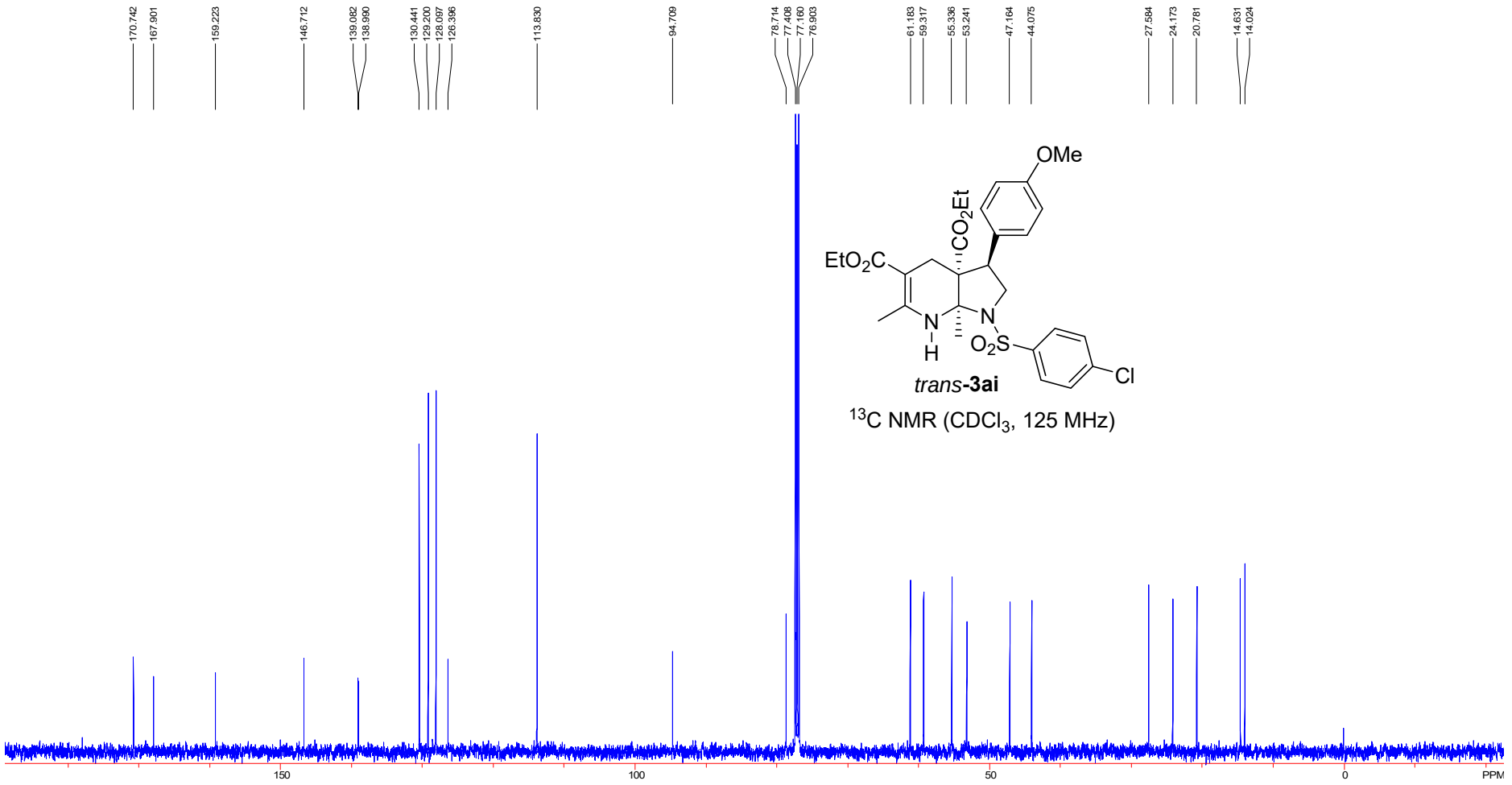
cis-**3ag**

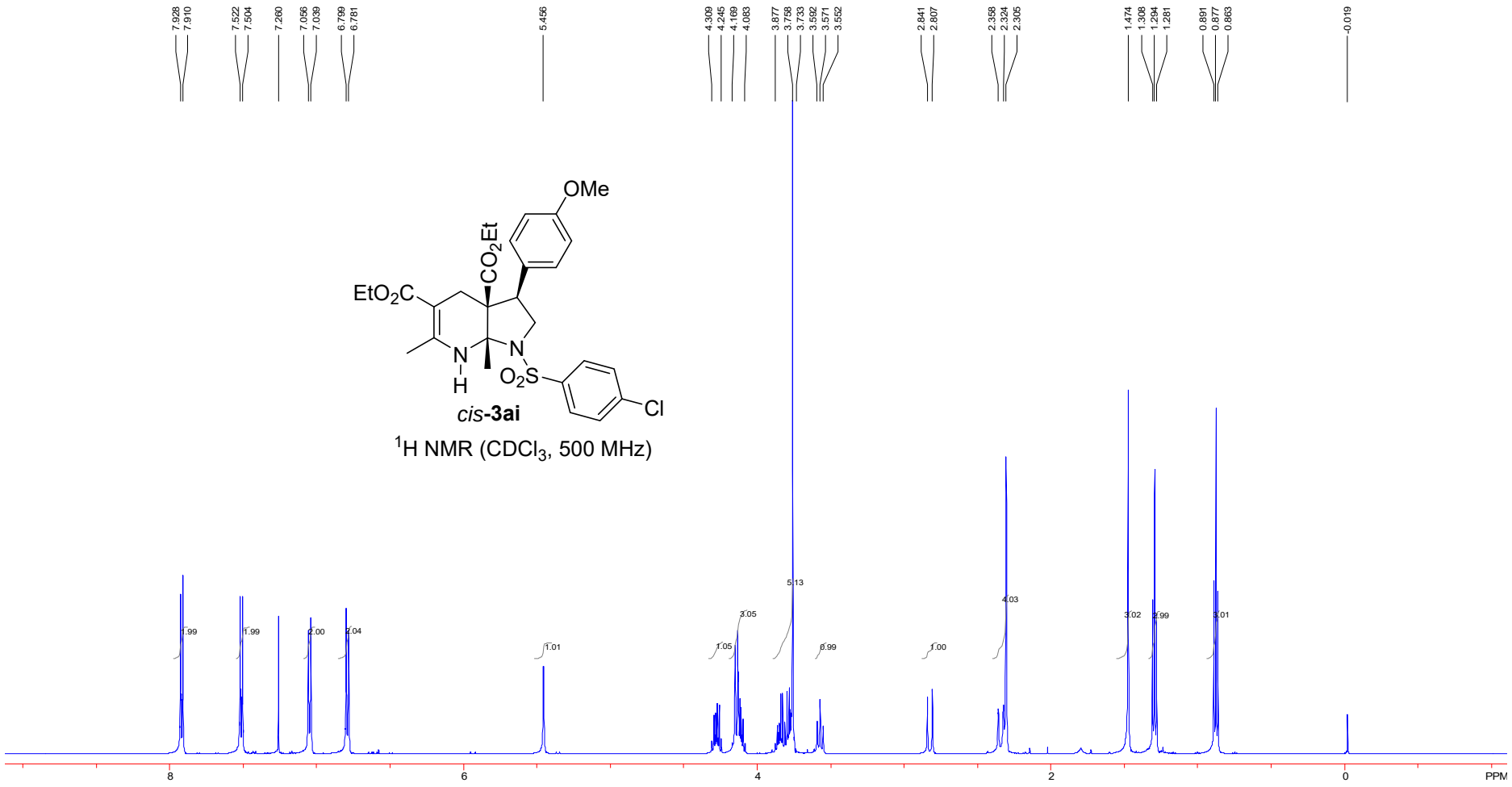
^{13}C NMR ($CDCl_3$, 125 MHz)

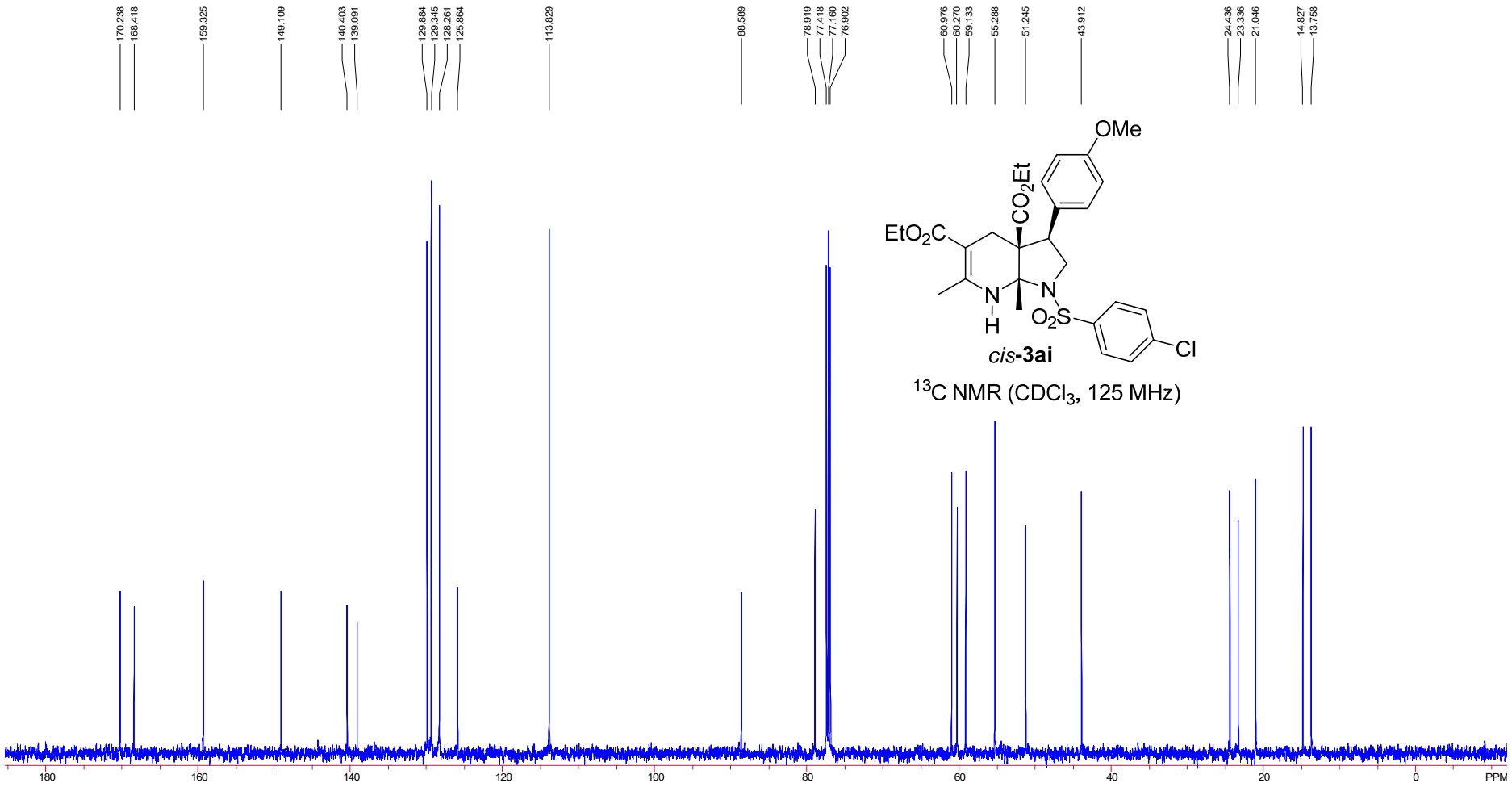

7.688
7.670
7.436
7.418
7.313
7.296
7.260
7.201
7.184
4.739
4.311
4.292
4.290
4.271
4.126
3.995
3.910
3.893
3.874
3.597
3.577
3.556
2.430
2.396
2.117
1.836
1.802
1.212
1.291
1.197
1.183
1.149
1.135
1.120
-0.004
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3ah
1H NMR (CDCl3, 500 MHz)
1.93
1.92
1.99
1.95
0.93
1.01
4.02
1.00
0.98
0.97
2.94
3.92
8.97
3.02
2.95
8
6
4
2
0
PPM

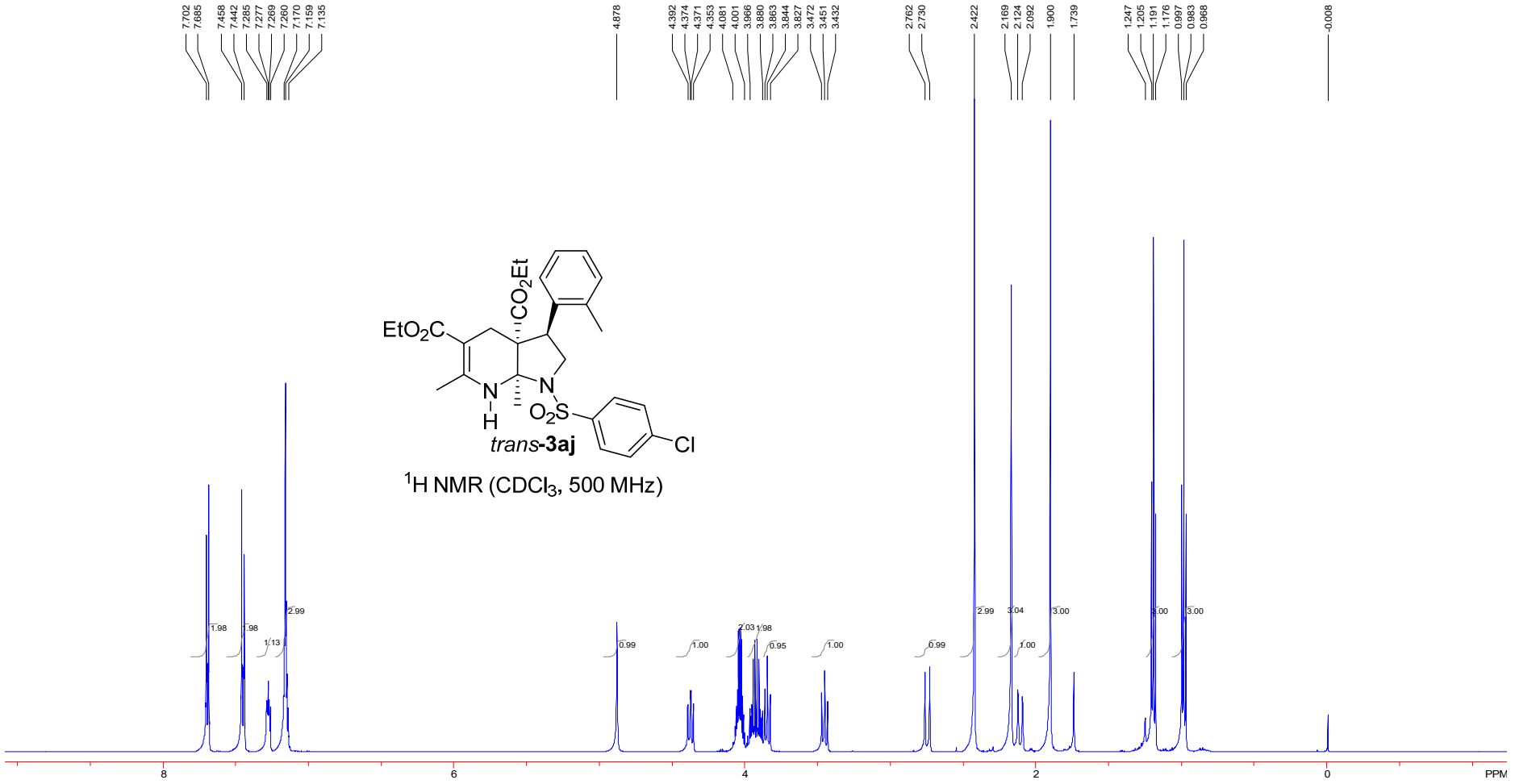

170.779
168.030
150.757
146.537
139.091
139.045
131.608
129.200
128.979
128.106
125.413
94.911
78.732
77.417
77.160
76.903
61.229
59.400
53.241
47.219
44.232
34.561
31.371
27.593
24.339
20.882
14.613
14.043
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3ah
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

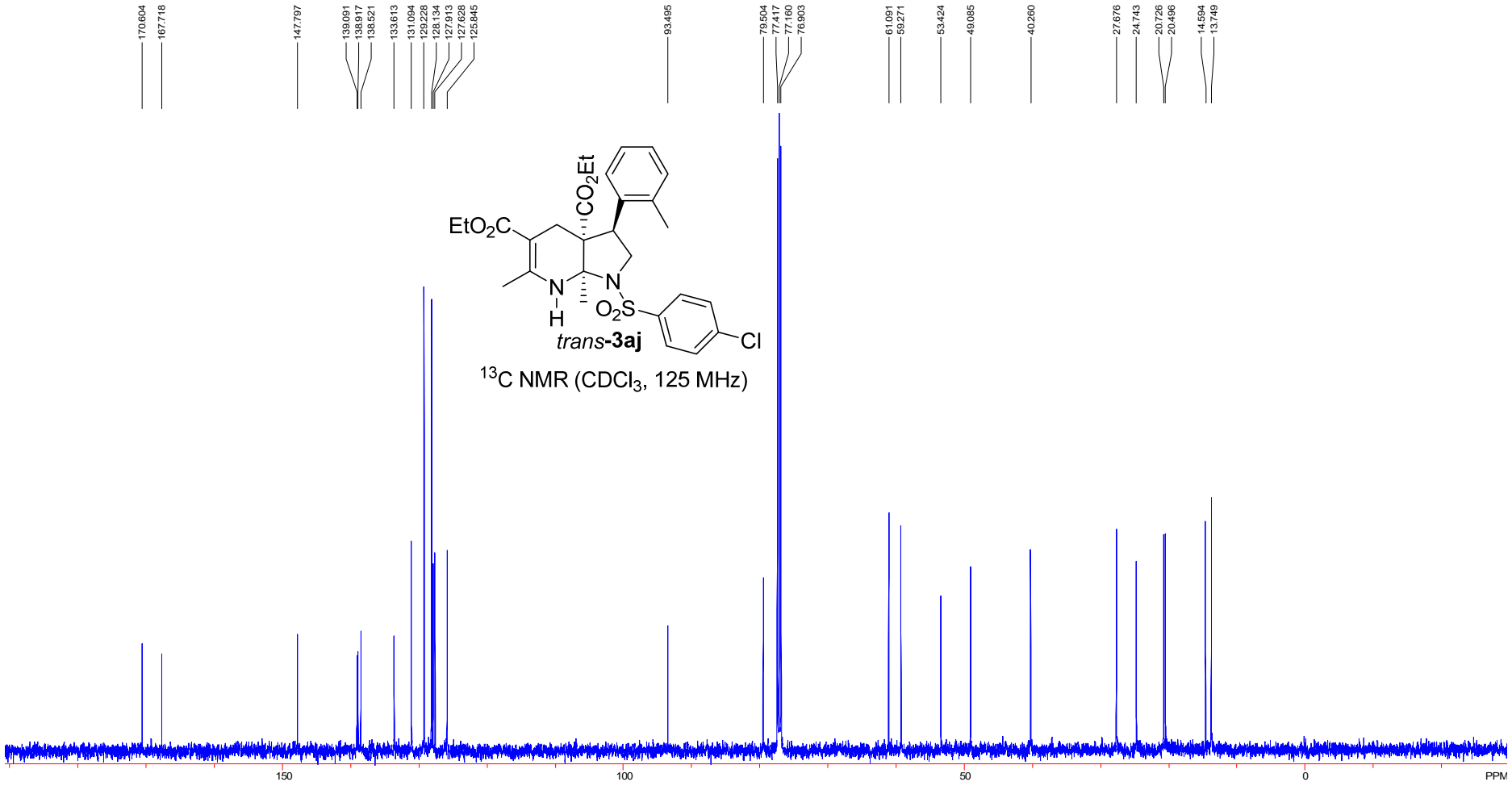

7.685
7.667
7.436
7.420
7.260
7.209
7.192
6.834
6.817
4.767
4.276
4.259
4.256
4.237
4.097
3.973
3.874
3.856
3.838
3.777
3.549
3.530
3.509
2.370
2.336
2.120
1.830
1.795
1.201
1.186
1.172
1.126
1.111
1.097
-0.010
OMe
CO2Et
EtO2C
N
H
N
O2S
Cl
trans-3ai
1H NMR (CDCl3, 500 MHz)
2.01
2.02
2.00
2.03
0.98
1.00
4.02
3.01
1.04
1.00
1.00
2.95
3.99
2.02
2.97
8
6
4
2
0
PPM

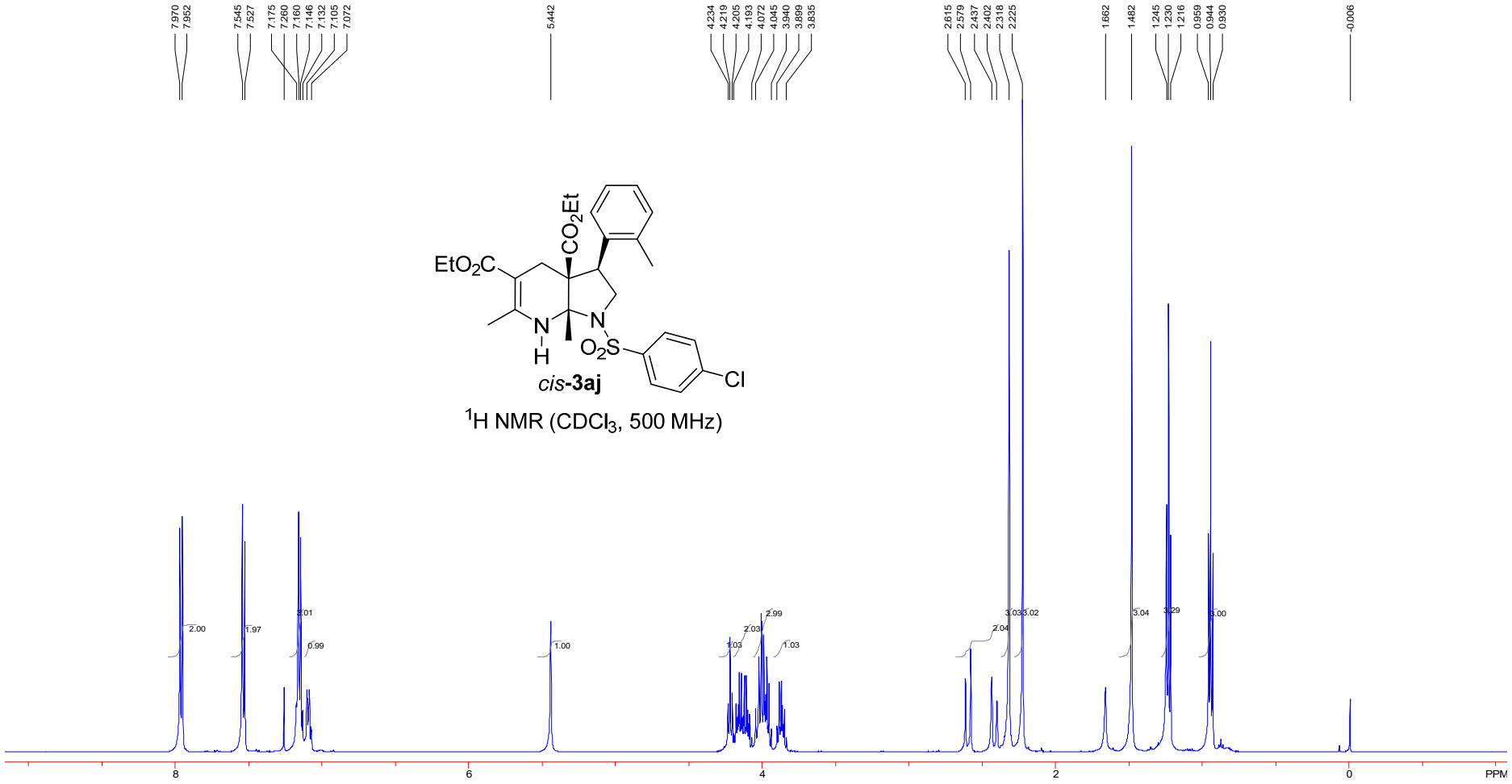

170.742
167.901
159.223
146.712
139.082
138.990
130.441
129.200
128.097
126.396
113.830
94.709
78.714
77.408
77.160
76.903
61.183
59.317
55.336
53.241
47.164
44.075
27.584
24.173
20.781
14.631
14.024
OMe
CO2Et
EtO2C
N
H
N
O2S
Cl
trans-3ai
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

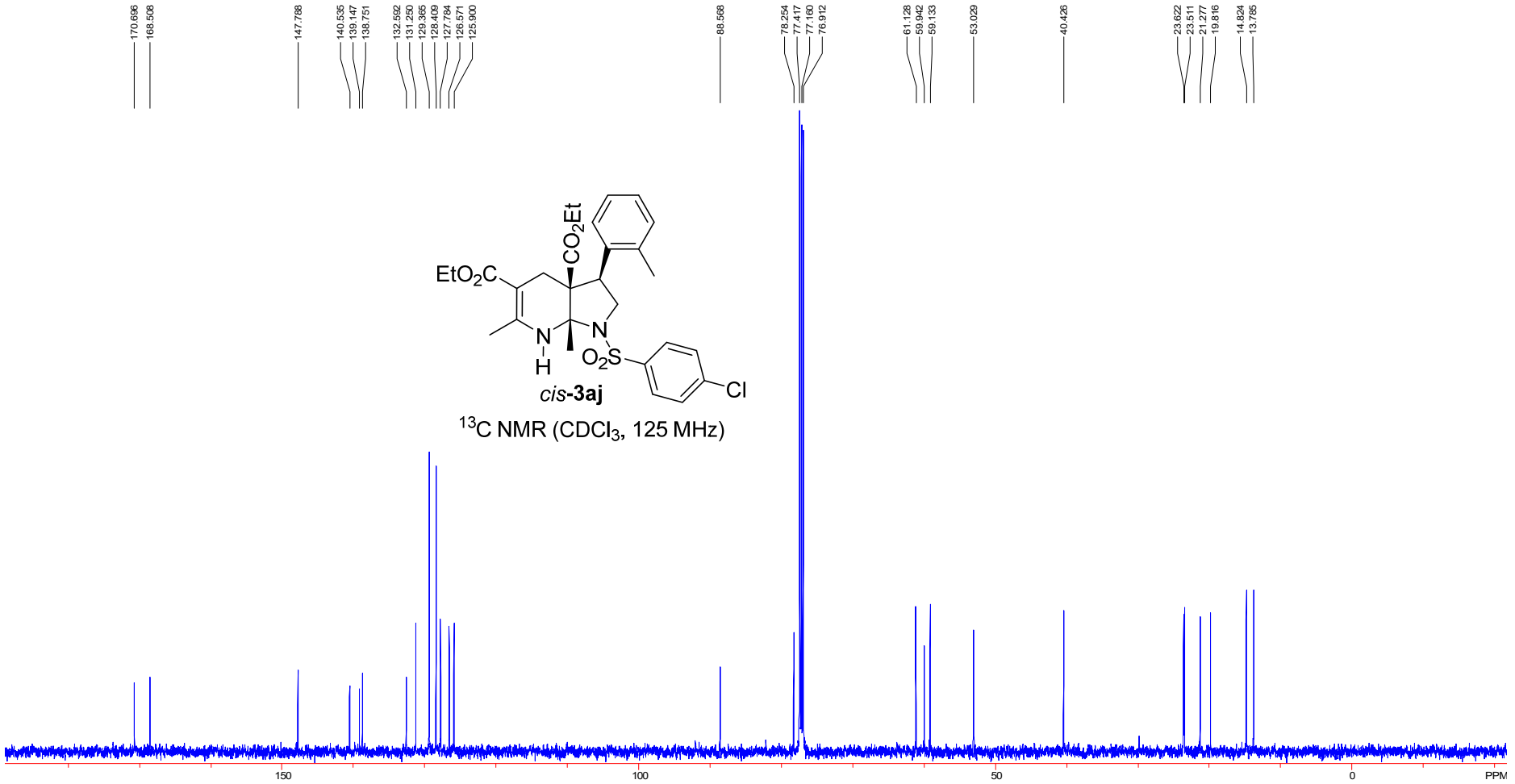

7.928
7.910
7.522
7.504
7.260
7.056
7.039
6.799
6.781
5.456
4.309
4.245
4.169
4.083
3.877
3.758
3.733
3.592
3.571
3.552
2.841
2.807
2.358
2.324
2.305
1.474
1.308
1.294
1.281
0.891
0.877
0.863
-0.019
OMe
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ai
1H NMR (CDCl3, 500 MHz)
1.99
1.99
2.00
2.04
1.01
1.05
3.05
5.13
0.99
1.00
4.03
3.02
2.99
3.01
8
6
4
2
0
PPM

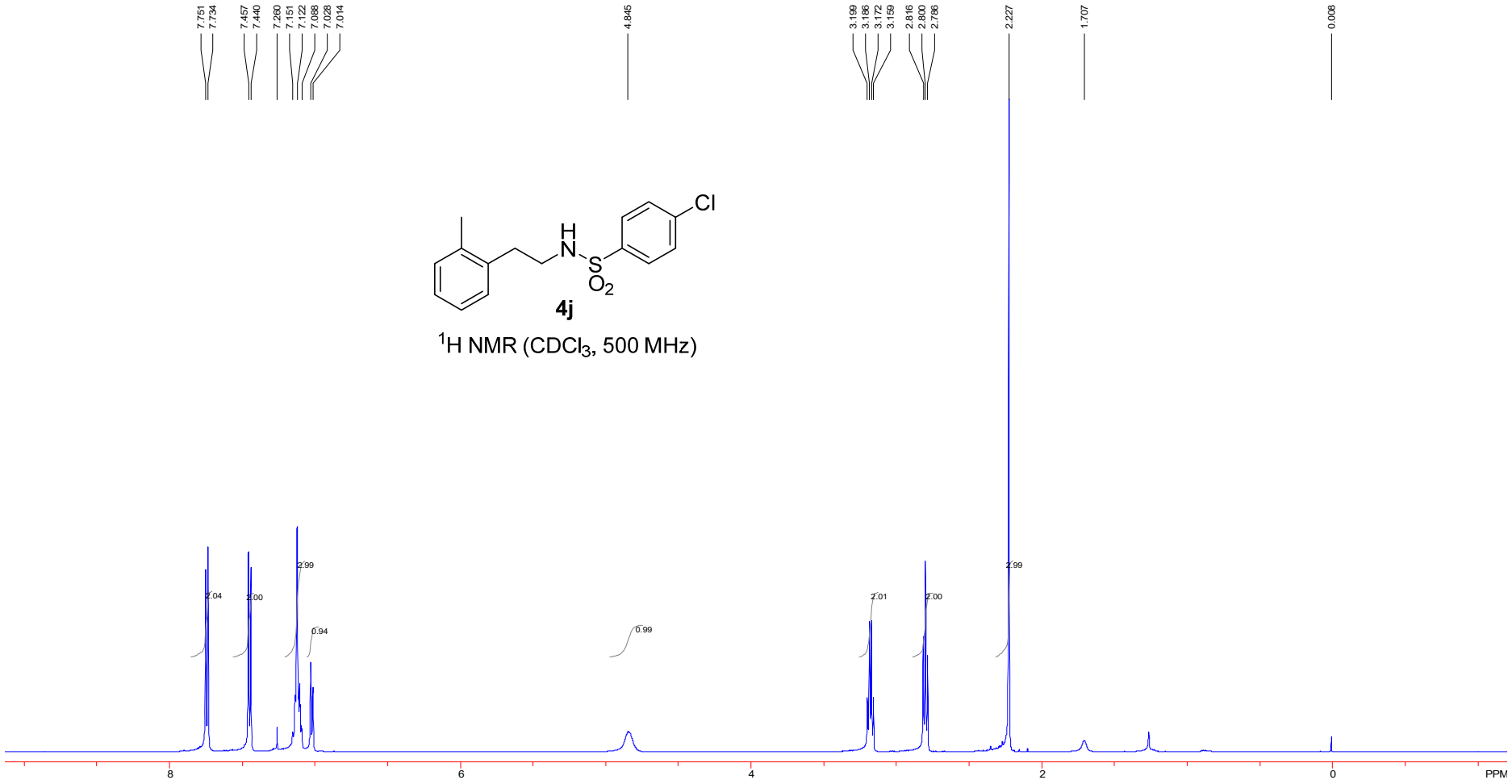

170.238
168.418
159.325
149.109
140.403
139.091
129.884
129.345
128.261
125.864
113.829
88.589
78.919
77.418
77.160
76.902
60.976
60.270
59.133
55.288
51.245
43.912
24.436
23.306
21.046
14.827
13.758
OMe
CO2Et
EtO2C
N
H
N
O2S
Cl
cis-3ai
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

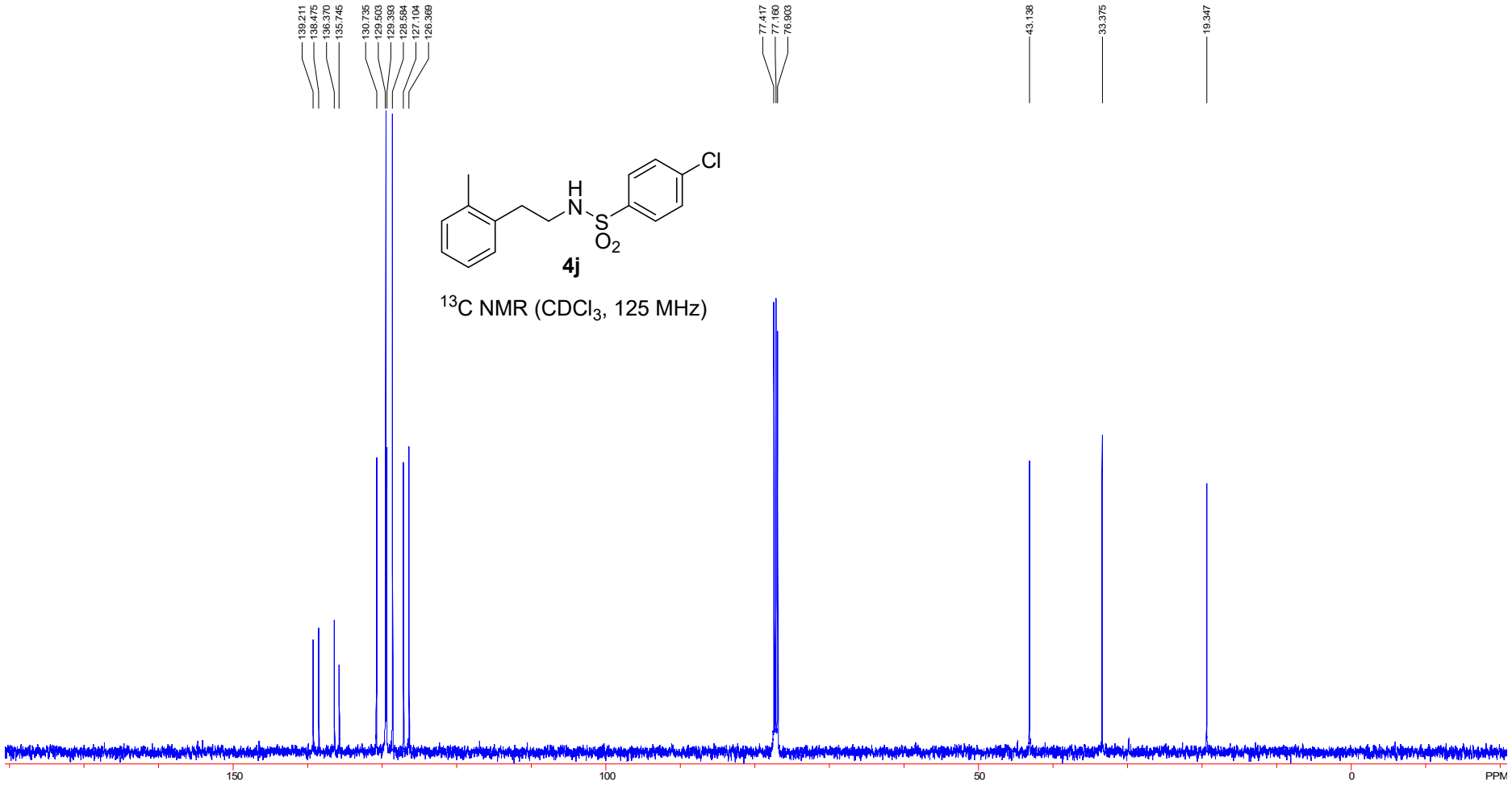

7.702
7.685
7.458
7.442
7.285
7.277
7.269
7.260
7.170
7.159
7.135
4.878
4.392
4.374
4.371
4.353
4.081
4.001
3.966
3.880
3.863
3.844
3.827
3.472
3.451
3.432
2.762
2.730
2.422
2.169
2.124
2.092
1.900
1.739
1.247
1.205
1.191
1.176
0.997
0.983
0.968
0.008
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3aj
1H NMR (CDCl3, 500 MHz)
1.98
1.98
1.13
2.99
0.99
1.00
2.03
1.98
0.95
1.00
0.99
2.99
3.04
1.00
3.00
3.00
3.00
8
6
4
2
0
PPM

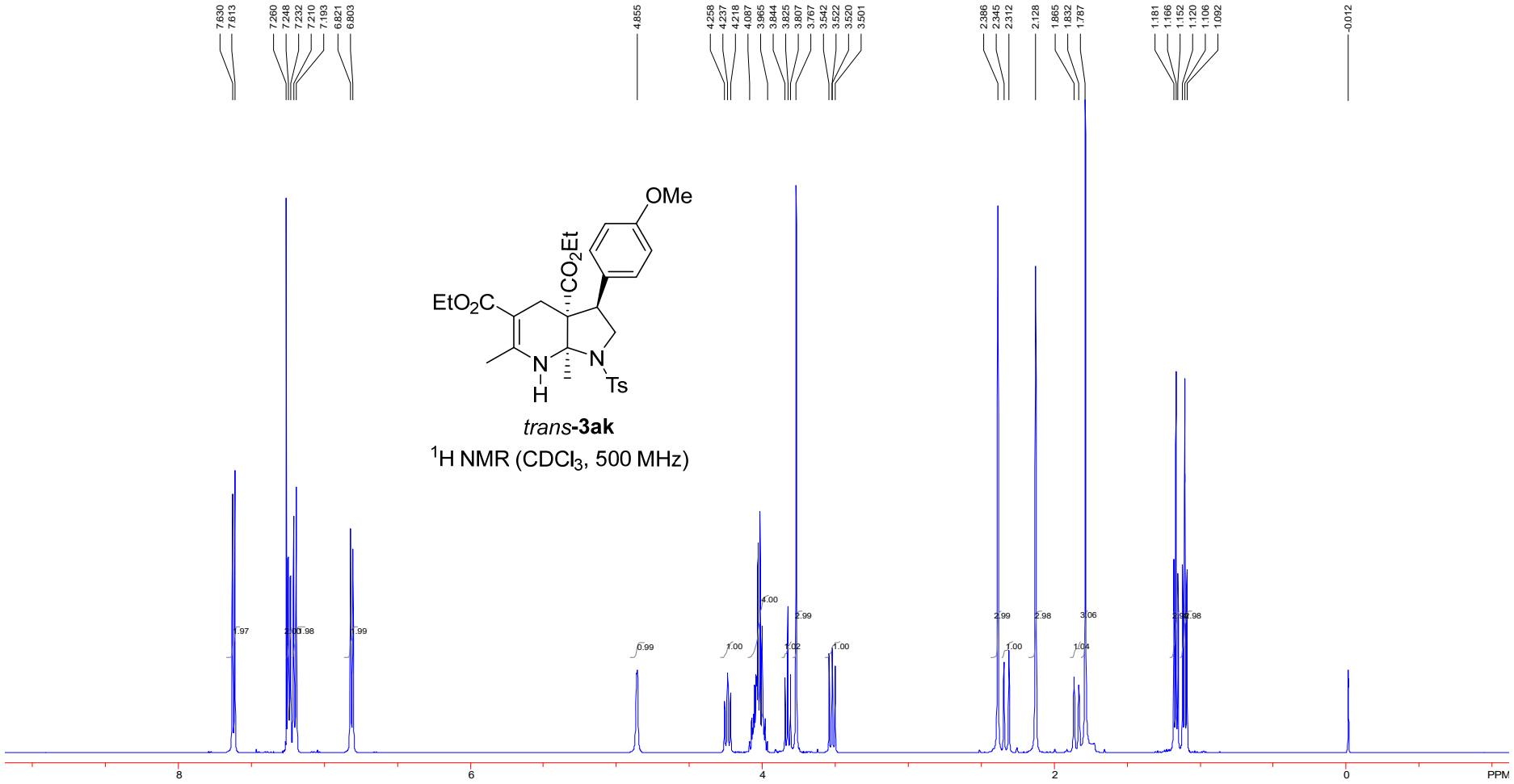

170.604
167.718
147.797
139.091
138.917
138.521
133.613
131.094
129.226
128.134
127.913
127.628
125.845
93.495
79.504
77.417
77.160
76.903
61.091
59.271
53.424
49.085
40.260
27.676
24.743
20.726
20.496
14.594
13.749
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3aj
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

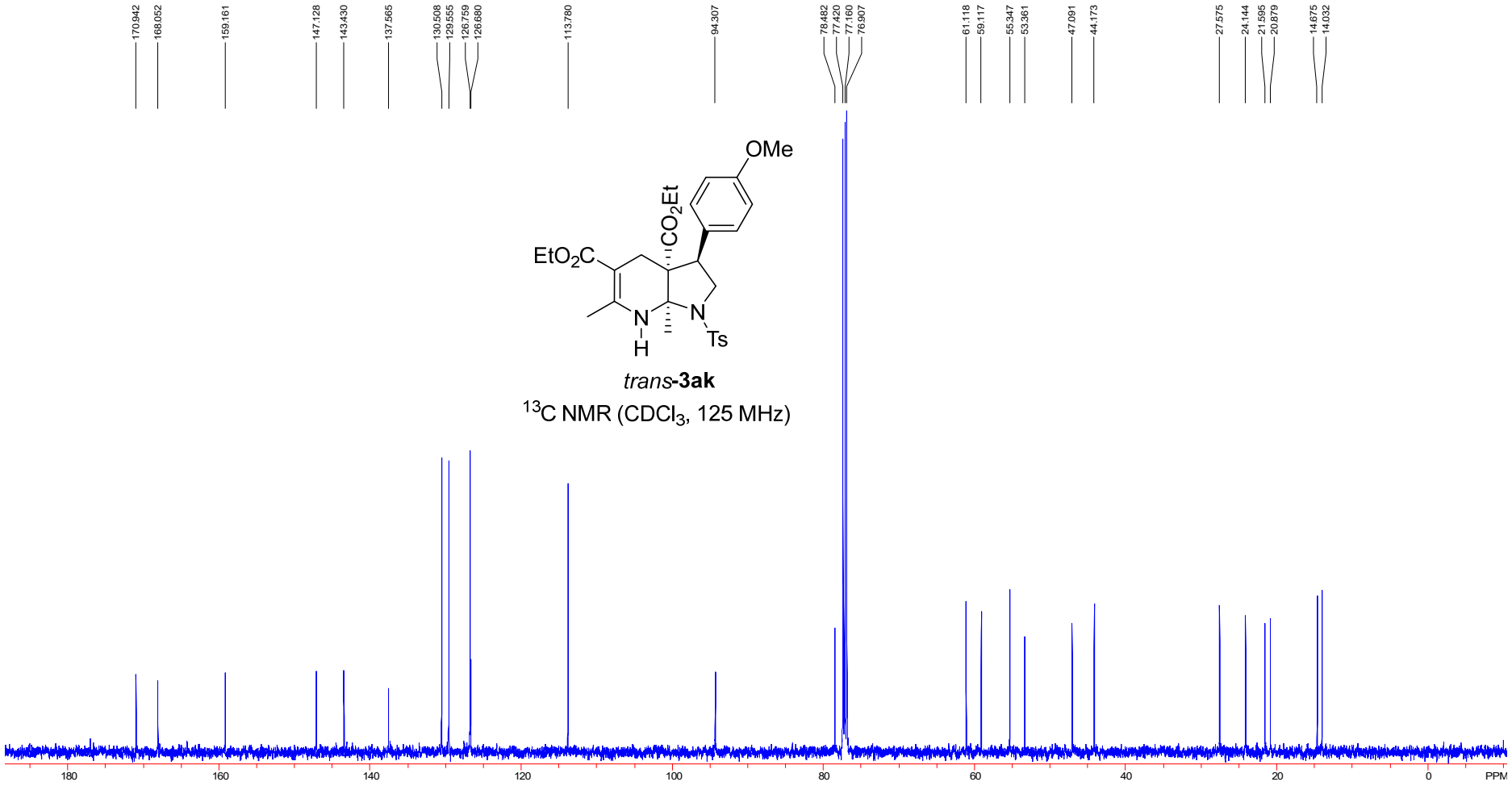

7.970
7.952
7.545
7.527
7.175
7.260
7.160
7.146
7.132
7.105
7.072
5.442
4.234
4.219
4.205
4.193
4.072
4.045
3.940
3.899
3.835
2.615
2.579
2.437
2.402
2.318
2.225
1.662
1.482
1.245
1.230
1.216
0.959
0.944
0.930
-0.006
EtO2C
CO2Et
N
H
N
O2S
Cl
cis-3aj
1H NMR (CDCl3, 500 MHz)
2.00
1.97
3.01
0.99
1.00
1.03
2.03
2.99
1.03
2.04
3.03
3.02
3.04
3.29
3.00
8
6
4
2
0
PPM

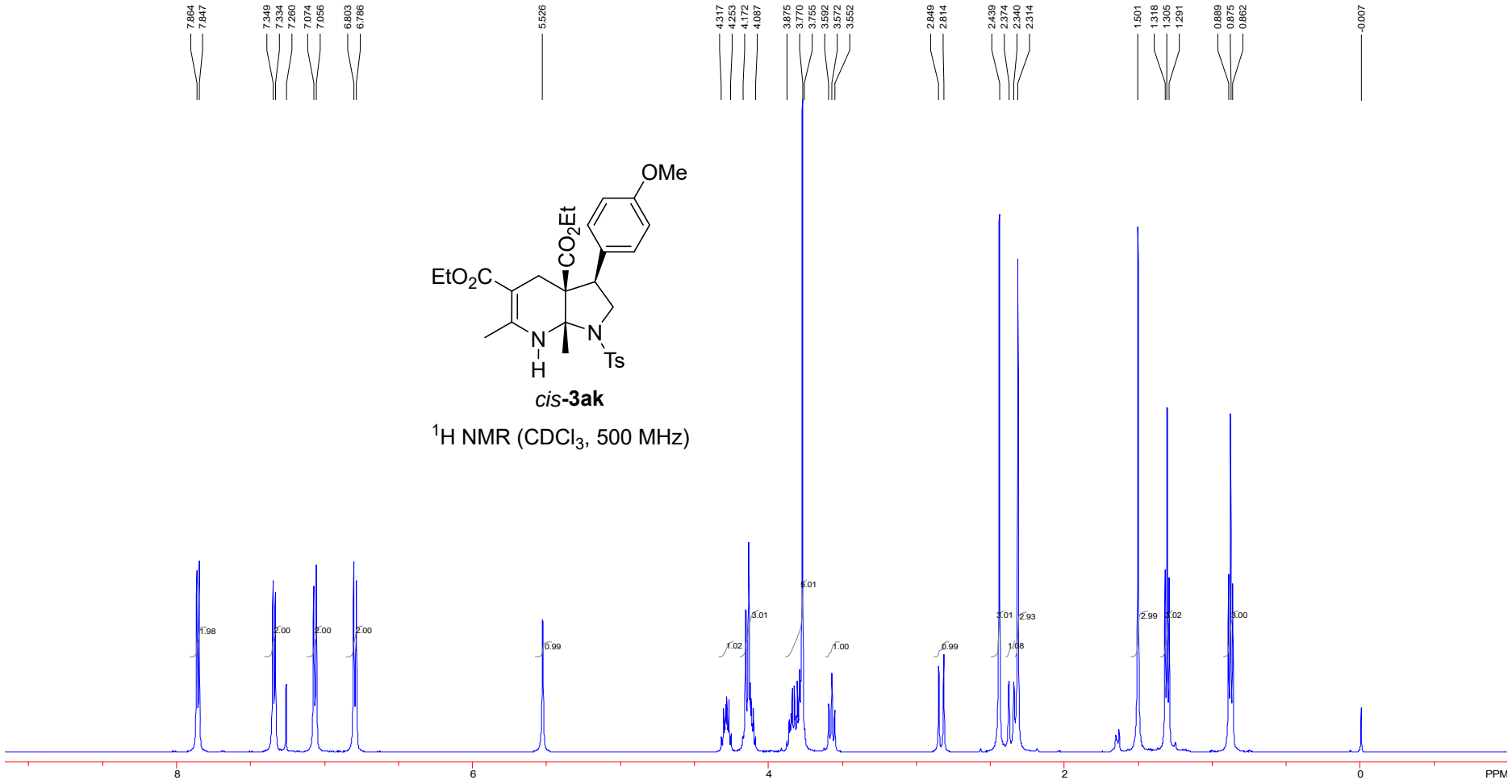

170.696
168.508
147.788
140.535
139.147
138.751
132.592
131.250
129.365
128.409
127.784
126.571
125.900
88.568
78.254
77.417
77.160
76.912
61.128
59.942
59.133
53.029
40.426
23.622
23.511
21.277
19.816
14.824
13.785
EtO2C
CO2Et
N
H
N
O2S
Cl
cis-3aj
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

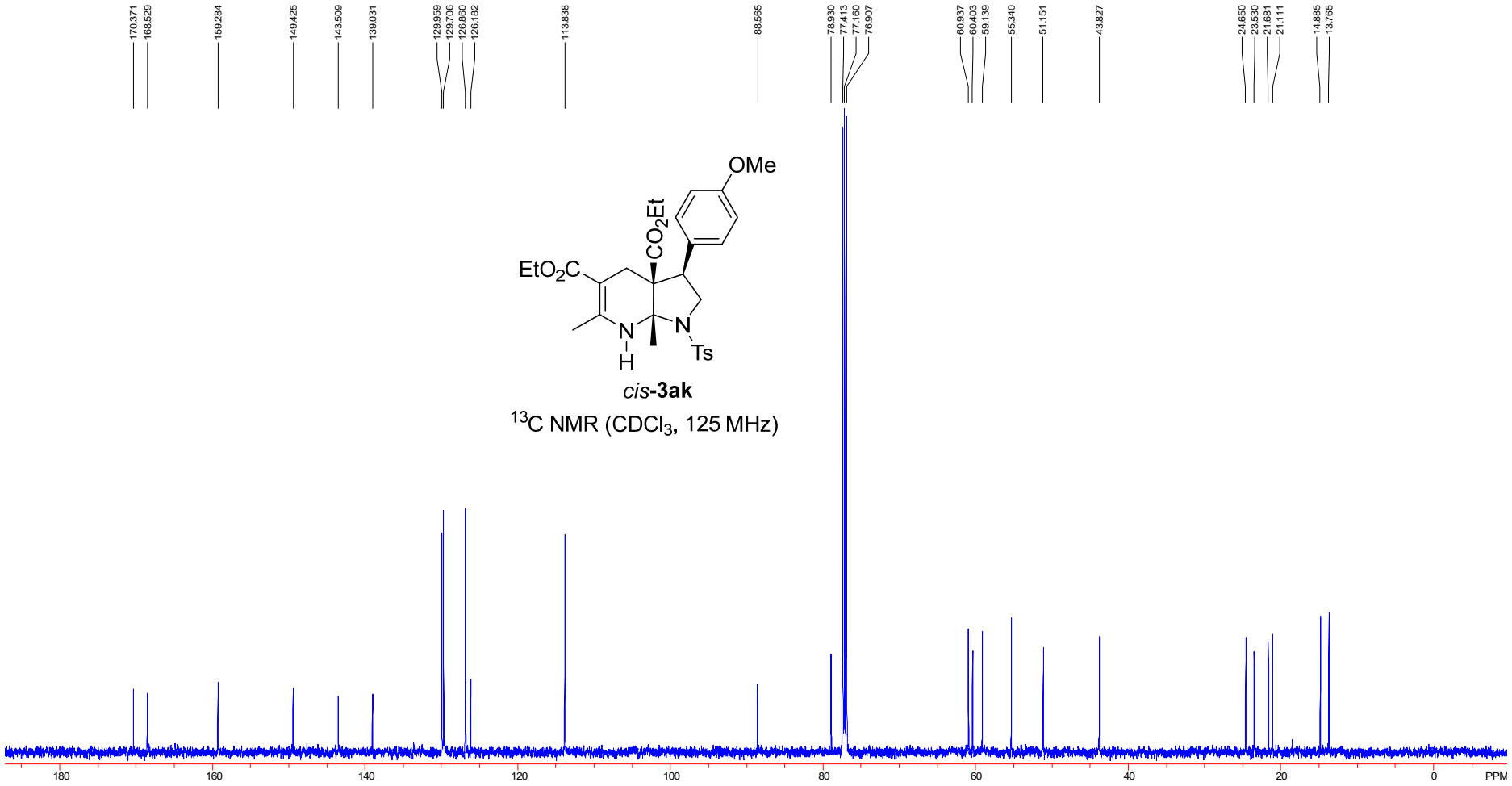

7.751
7.734
7.457
7.440
7.260
7.151
7.122
7.088
7.028
7.014
4.845
3.199
3.186
3.172
3.159
2.816
2.800
2.786
2.227
1.707
0.008
Cl
H
N
S
O2
4j
1H NMR (CDCl3, 500 MHz)
2.04
2.00
2.99
0.94
0.99
2.01
2.00
2.99
8
6
4
2
0
PPM

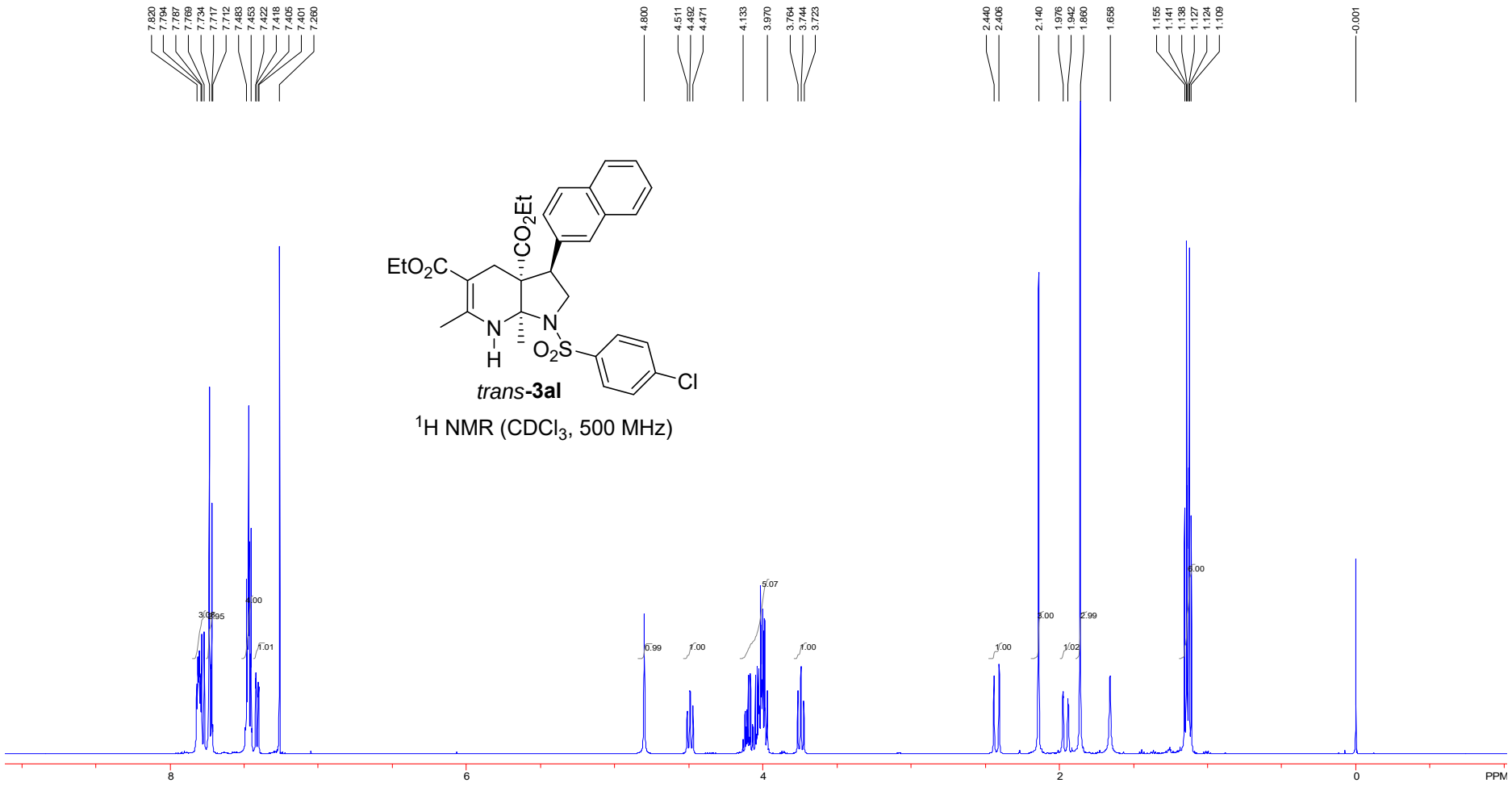

139.211
138.475
136.370
135.745
130.735
129.503
129.393
128.584
127.104
126.369
77.417
77.160
76.903
43.138
33.375
19.947
Cl
H
N
S
O2
4j
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

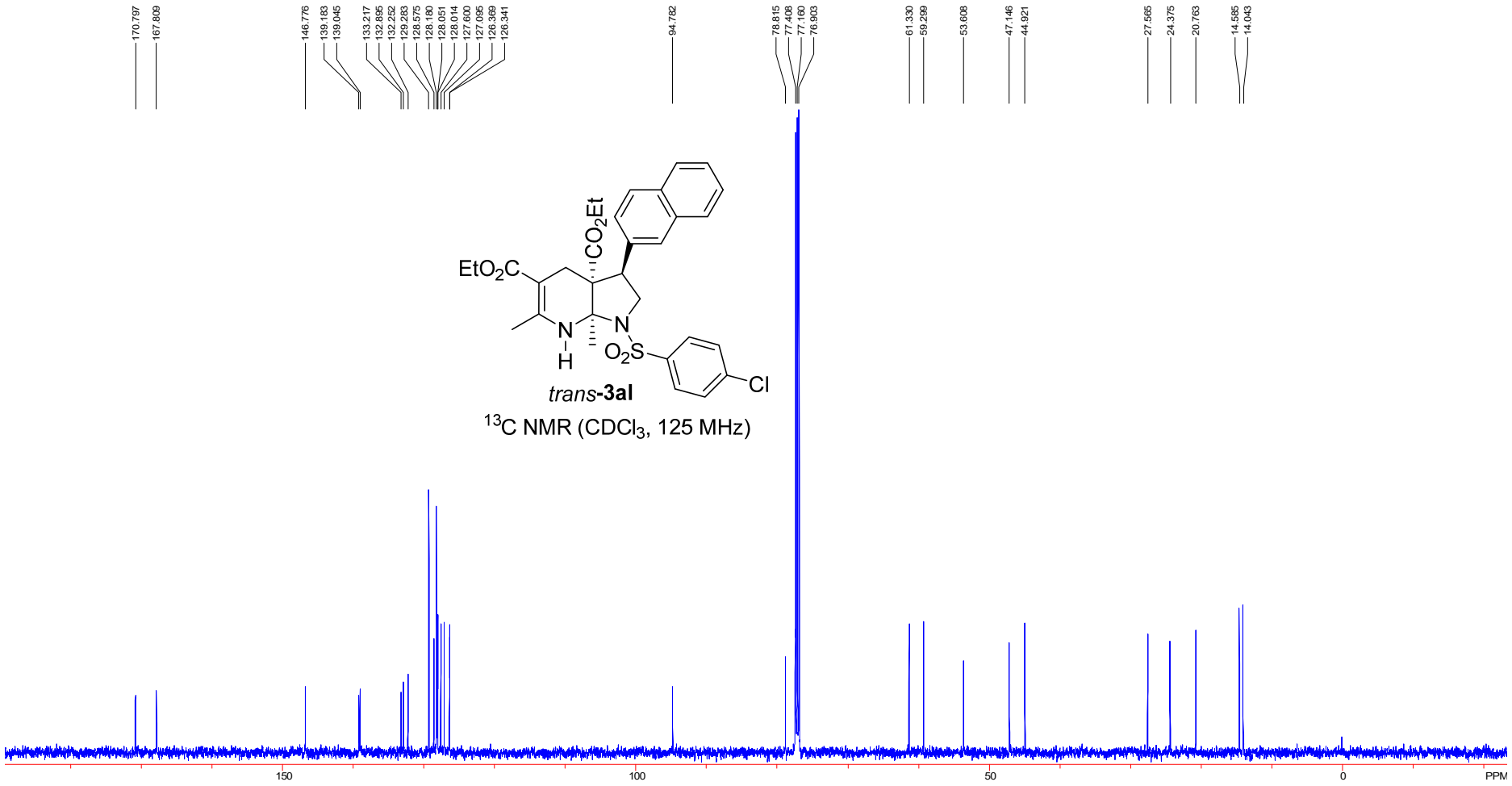

7.630
7.613
7.260
7.248
7.232
7.210
7.193
6.821
6.803
4.855
4.258
4.237
4.218
4.087
3.965
3.844
3.825
3.807
3.767
3.542
3.522
3.520
3.501
2.386
2.345
2.312
2.128
1.865
1.832
1.787
1.181
1.166
1.152
1.120
1.106
1.092
-0.012
OMe
CO2Et
EtO2C
N
H
N
Ts
trans-3ak
1H NMR (CDCl3, 500 MHz)
1.97
2.00
0.98
1.99
0.99
1.00
4.00
2.99
1.02
1.00
2.99
1.00
2.98
3.06
1.04
2.00
2.02
0.98
8
6
4
2
0
PPM


170.942
168.052
159.161
147.128
143.430
137.565
130.508
129.555
126.759
126.680
113.780
94.307
78.482
77.420
77.160
76.907
61.118
59.117
55.347
53.361
47.091
44.173
27.575
24.144
21.595
20.879
14.675
14.032
OMe
CO2Et
EtO2C
N
H
N
Ts
trans-3ak
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM


7.864
7.847
7.349
7.334
7.280
7.074
7.056
6.803
6.786
5.526
4.317
4.253
4.172
4.087
3.875
3.770
3.755
3.592
3.572
3.552
2.849
2.814
2.439
2.374
2.340
2.314
1.501
1.318
1.305
1.291
0.889
0.875
0.862
-0.007
OMe
CO2Et
EtO2C
N
H
N
Ts
cis-3ak
1H NMR (CDCl3, 500 MHz)
1.98
2.00
2.00
2.00
0.99
1.02
3.01
5.01
1.00
0.99
3.01
2.93
1.08
2.99
3.02
3.00
8
6
4
2
0
PPM

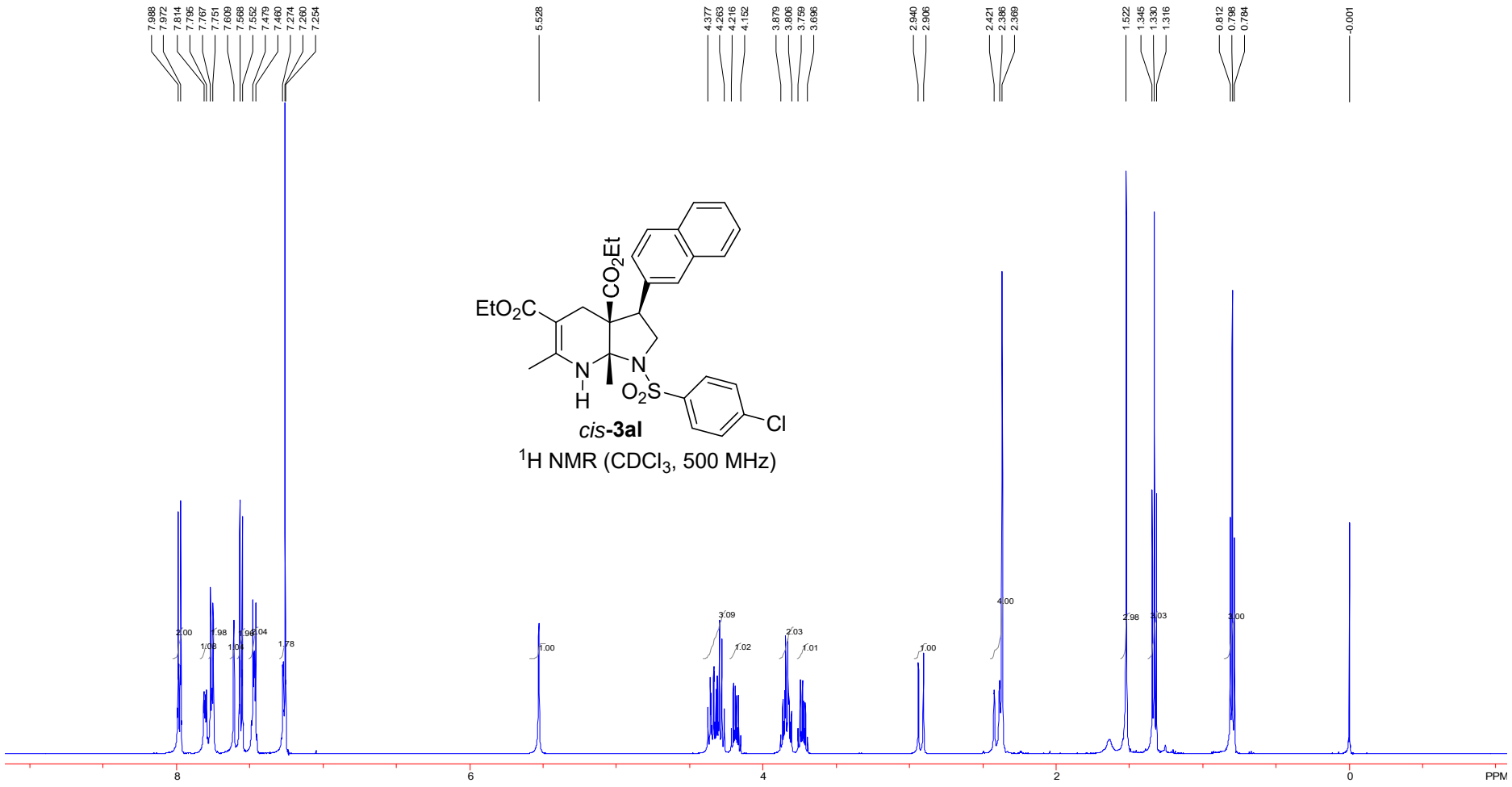

170.371
168.529
159.284
149.425
143.509
139.031
129.959
129.706
126.860
126.182
113.838
88.565
78.930
77.413
77.160
76.907
60.937
60.403
59.139
55.340
51.151
43.827
24.650
23.530
21.681
21.111
14.885
13.765
OMe
CO2Et
EtO2C
N
H
N
Ts
cis-3ak
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

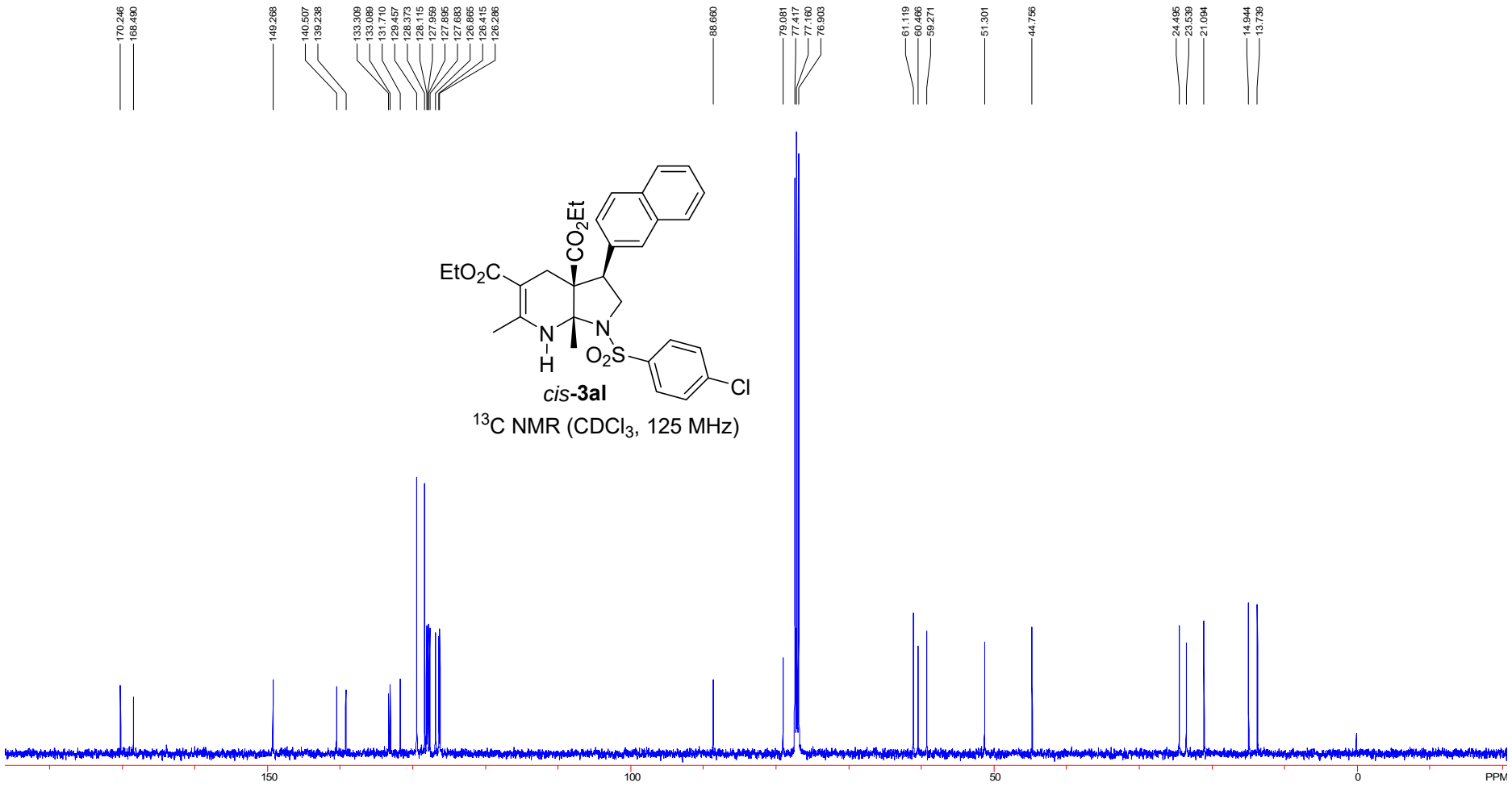

7.820
7.794
7.787
7.769
7.734
7.717
7.712
7.483
7.453
7.422
7.418
7.405
7.401
7.260
4.800
4.511
4.492
4.471
4.133
3.970
3.764
3.744
3.723
2.440
2.406
2.140
1.976
1.942
1.860
1.658
1.155
1.141
1.138
1.127
1.124
1.109
-0.001
EtO2C
CO2Et
N
H
N
O2S
Cl
trans-3al
1H NMR (CDCl3, 500 MHz)
3.00
2.95
4.00
1.01
6.99
1.00
5.07
1.00
1.00
3.00
1.02
2.99
6.00
8
6
4
2
0
PPM

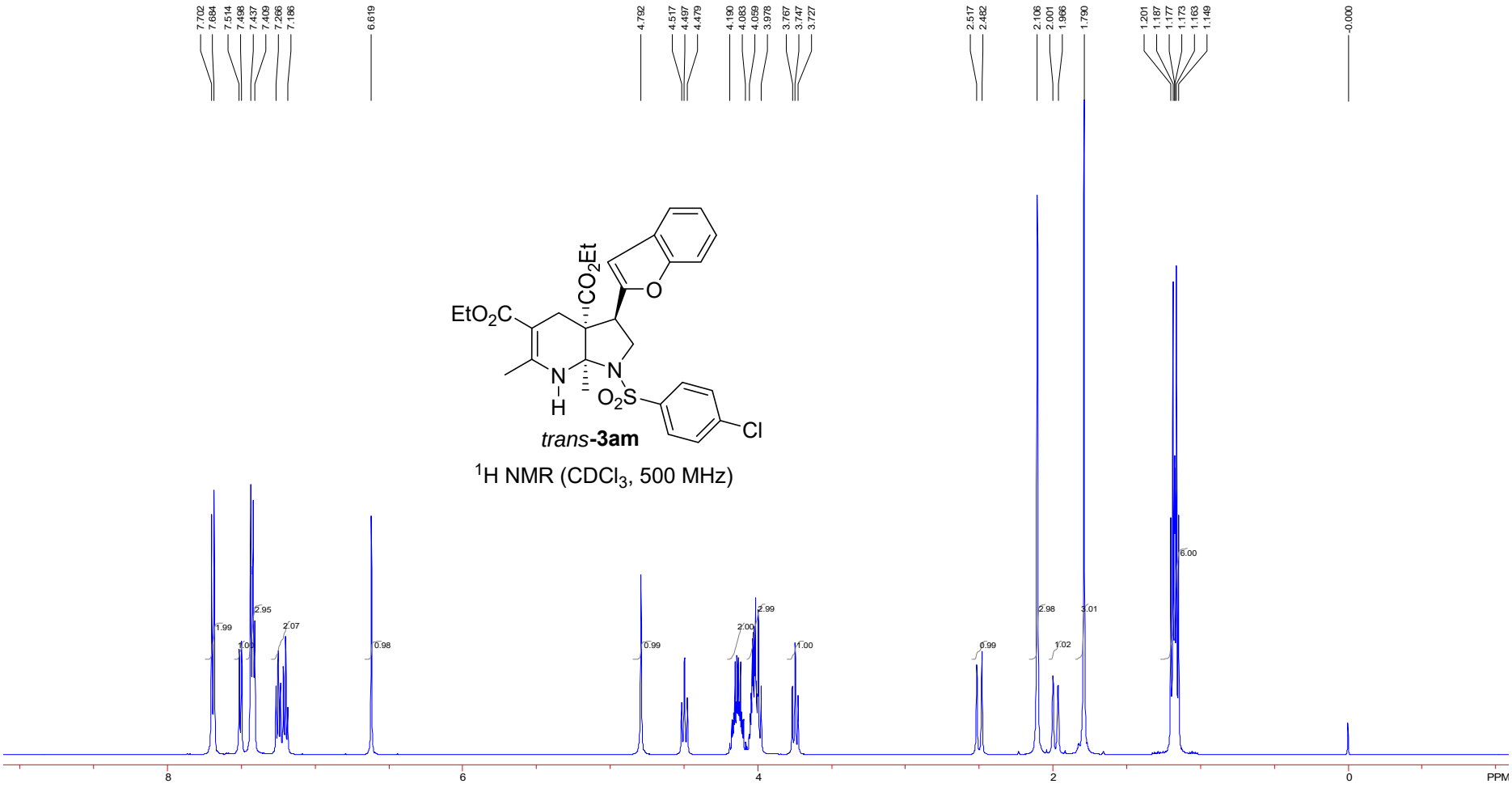


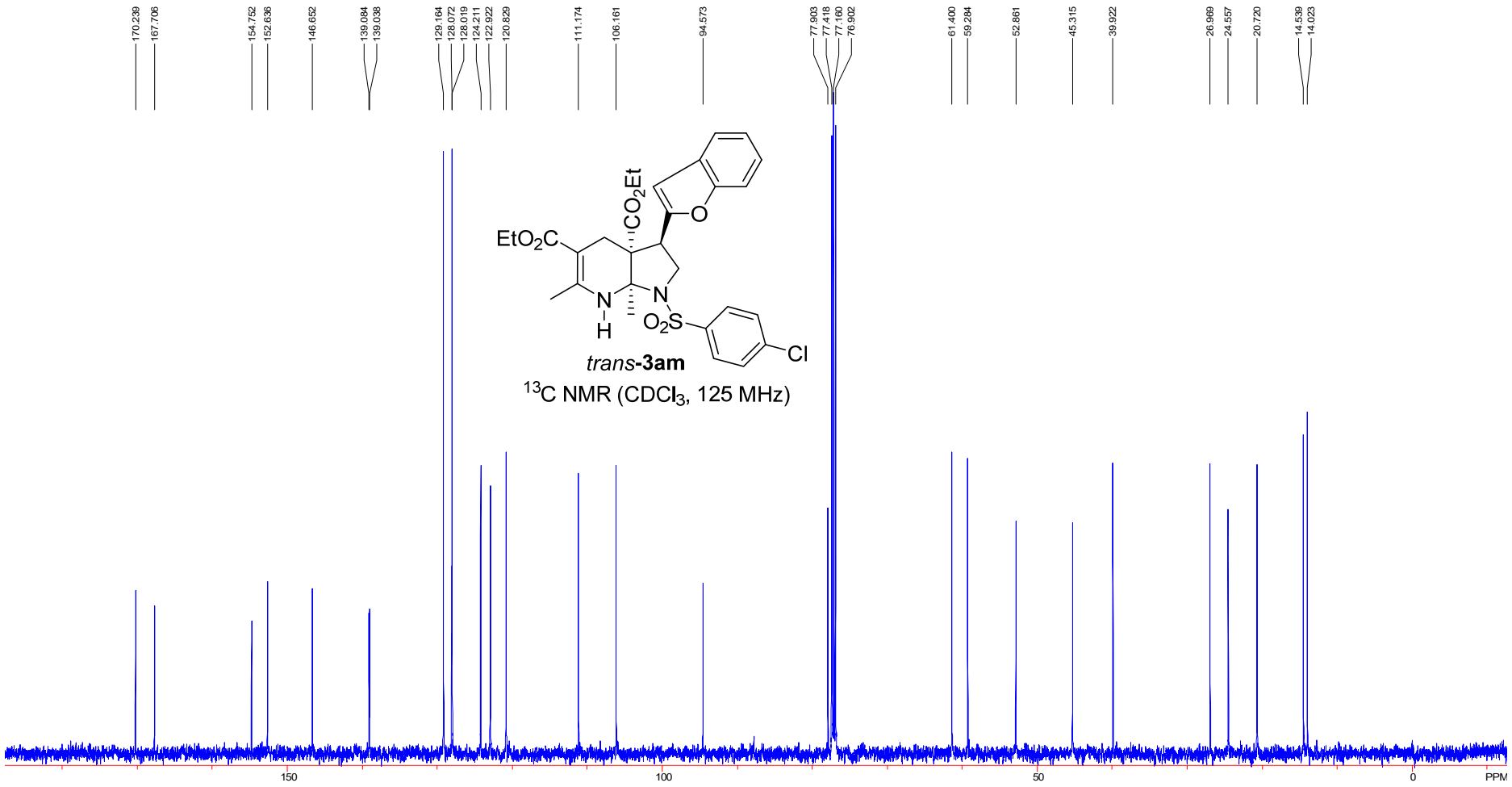
trans-**3al**

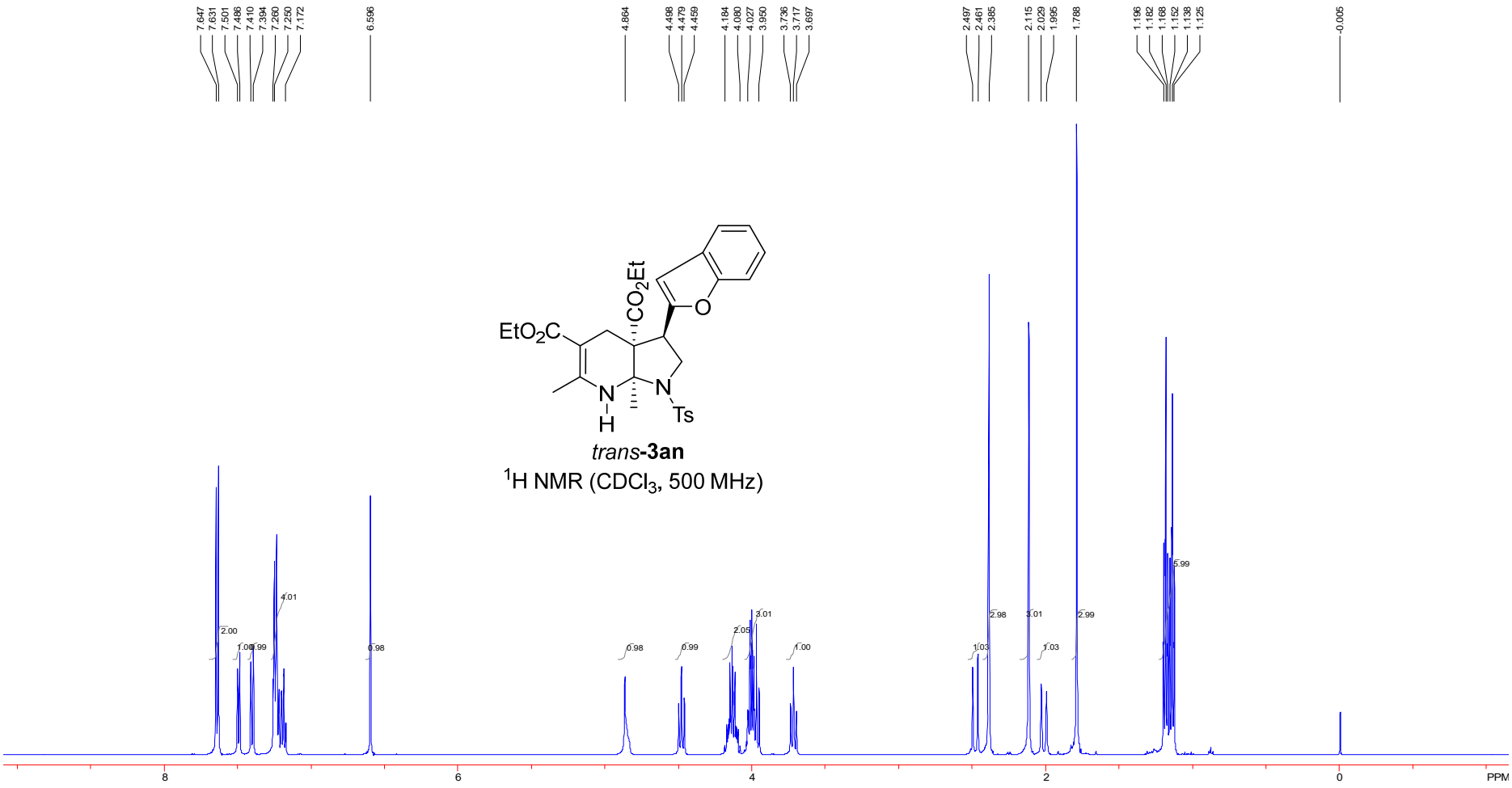
^{13}C NMR ($CDCl_3$, 125 MHz)

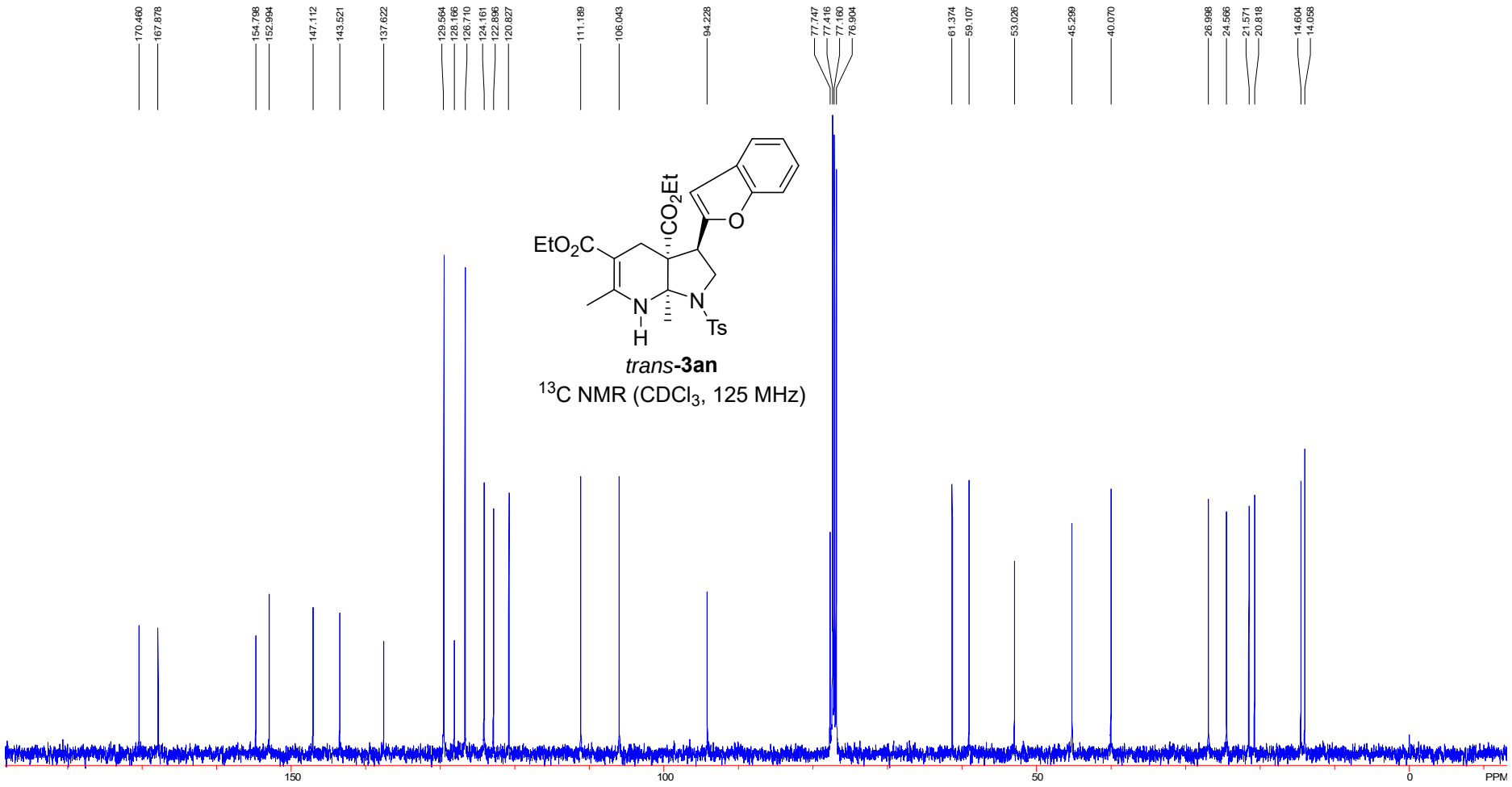

7.988
7.972
7.814
7.795
7.767
7.751
7.609
7.568
7.552
7.479
7.460
7.274
7.260
7.254
5.528
4.377
4.263
4.216
4.152
3.879
3.806
3.759
3.696
2.940
2.906
2.421
2.386
2.369
1.522
1.345
1.330
1.316
0.812
0.798
0.784
-0.001
EtO2C
CO2Et
N
H
N
O2S
Cl
cis-3al
1H NMR (CDCl3, 500 MHz)
2.00
1.98
1.08
1.04
1.04
1.78
1.00
3.09
1.02
2.03
1.01
1.00
4.00
2.98
3.03
3.00
8
6
4
2
0
PPM


170.246
168.490
149.268
140.507
139.238
133.309
133.089
131.710
129.457
128.373
128.115
127.959
127.895
127.683
126.865
126.415
126.286
88.660
79.081
77.417
77.160
76.903
61.119
60.466
59.271
51.301
44.756
24.495
23.539
21.094
14.944
13.739
EtO2C
CO2Et
N
H
N
O2S
Cl
cis-3al
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM


7.702
7.684
7.514
7.498
7.437
7.409
7.266
7.186
6.619
4.792
4.517
4.497
4.479
4.190
4.083
4.059
3.978
3.767
3.747
3.727
2.517
2.482
2.106
2.001
1.966
1.790
1.201
1.187
1.177
1.173
1.163
1.149
-0.000
EtO2C
CO2Et
O
N
H
N
O2S
Cl
trans-3am
1H NMR (CDCl3, 500 MHz)
1.99
2.95
1.00
2.07
0.98
0.99
2.00
2.99
1.00
0.99
2.98
1.02
3.01
6.00
8
6
4
2
0
PPM

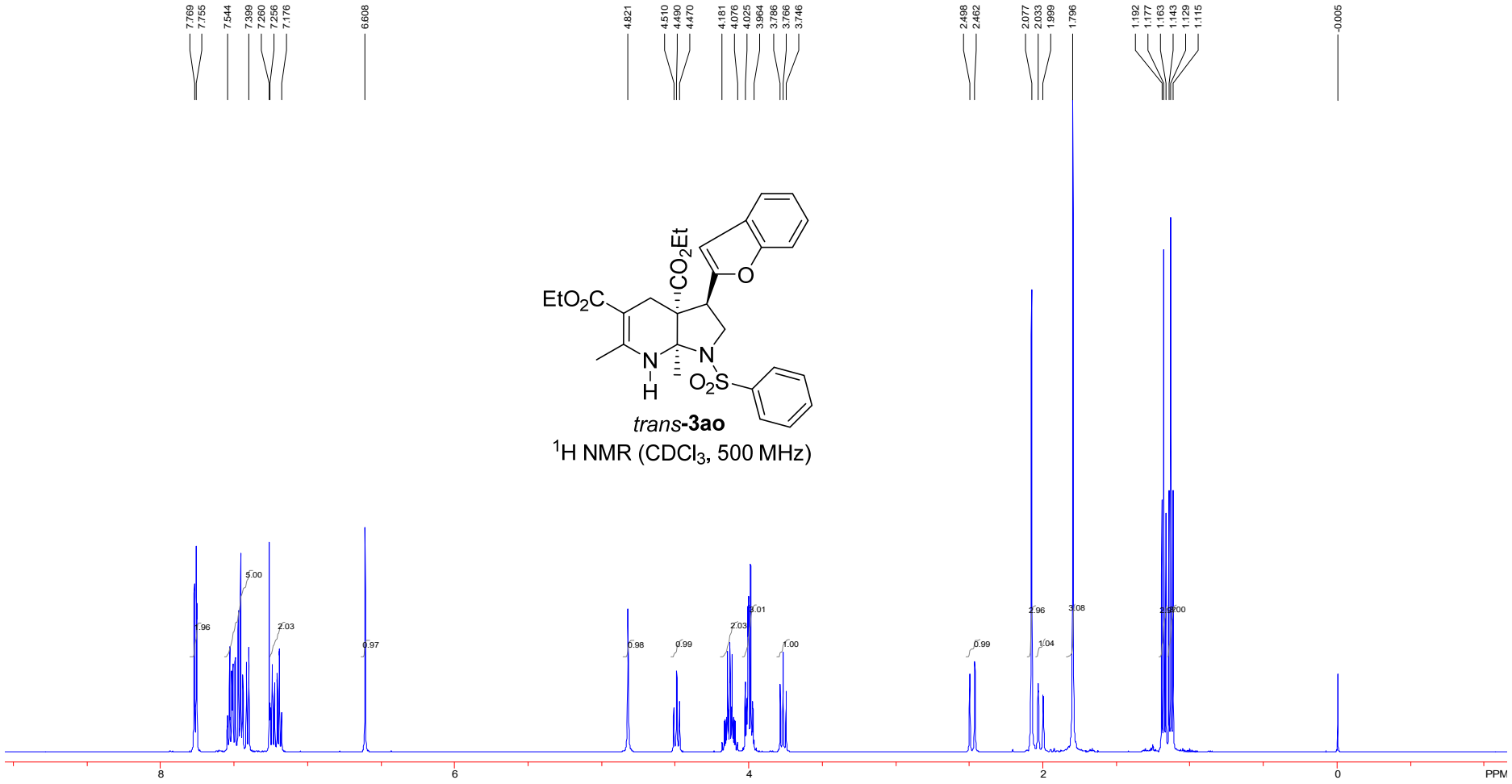

170.239
167.706
154.752
152.636
146.652
139.084
139.038
129.164
128.072
128.019
124.211
122.922
120.829
111.174
106.161
94.573
77.903
77.418
77.160
76.902
61.400
59.284
52.861
45.315
39.922
26.969
24.557
20.720
14.539
14.023
EtO2C
CO2Et
O
N
H
N
O2S
Cl
trans-3am
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

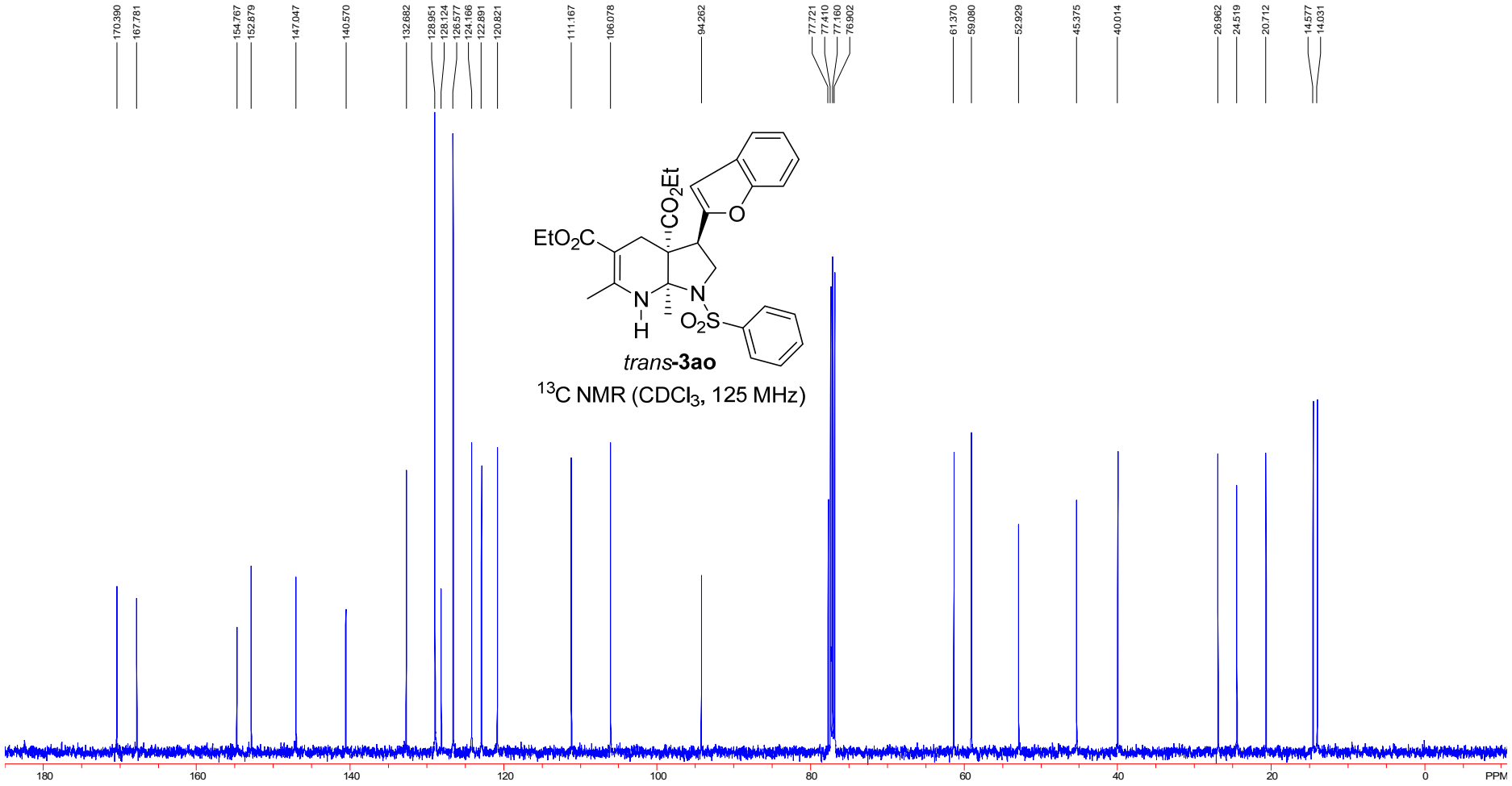

7.647
7.631
7.501
7.486
7.410
7.394
7.280
7.250
7.172
6.596
4.864
4.498
4.479
4.459
4.184
4.080
4.027
3.950
3.736
3.717
3.697
2.497
2.461
2.385
2.115
2.029
1.995
1.788
1.196
1.182
1.168
1.152
1.138
1.125
-0.005
EtO2C
CO2Et
O
N
H
N
Ts
trans-3an
1H NMR (CDCl3, 500 MHz)
2.00
1.00
0.99
4.01
0.98
0.98
0.99
2.05
3.01
1.00
1.03
2.98
3.01
1.03
2.99
5.99
8
6
4
2
0
PPM

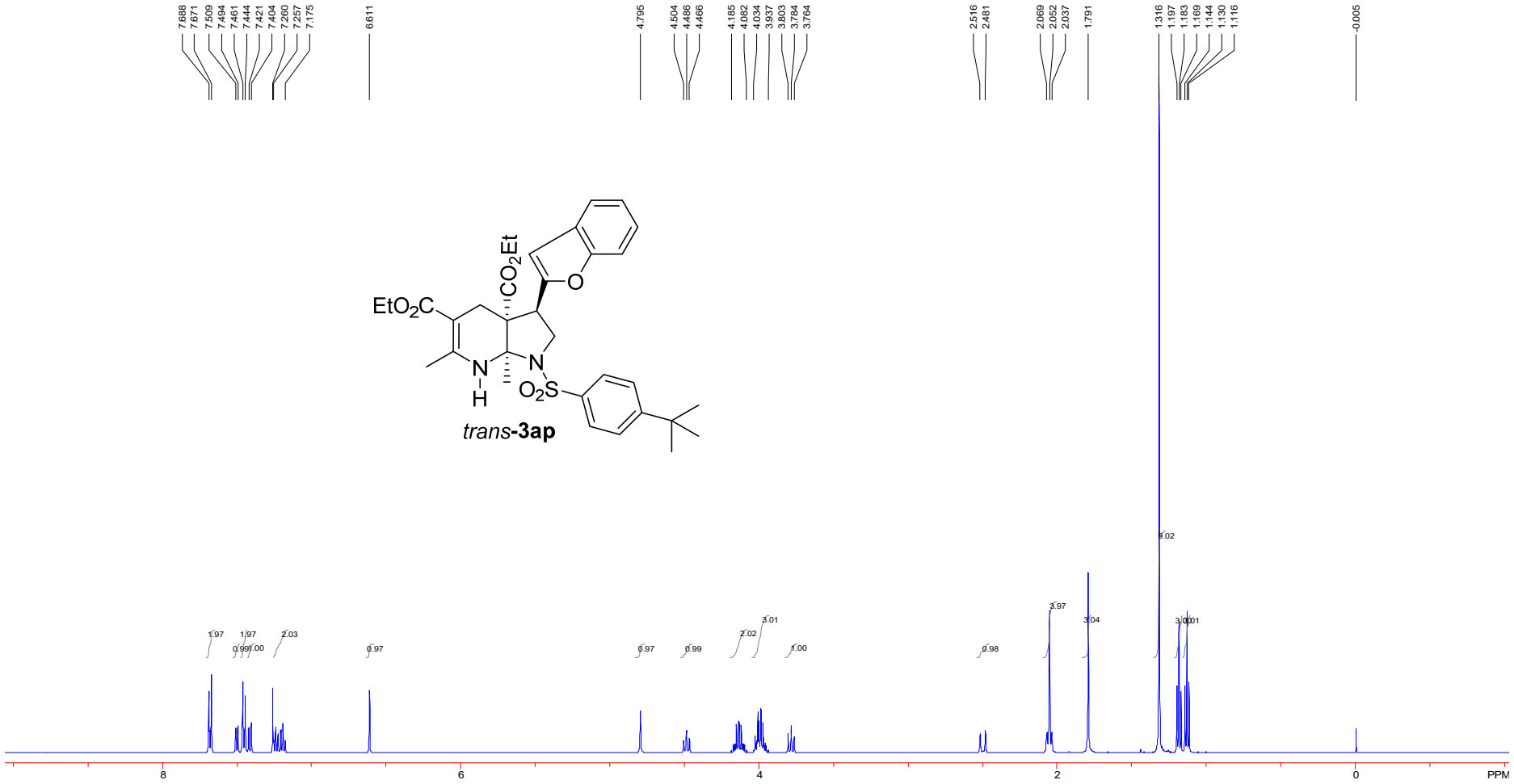


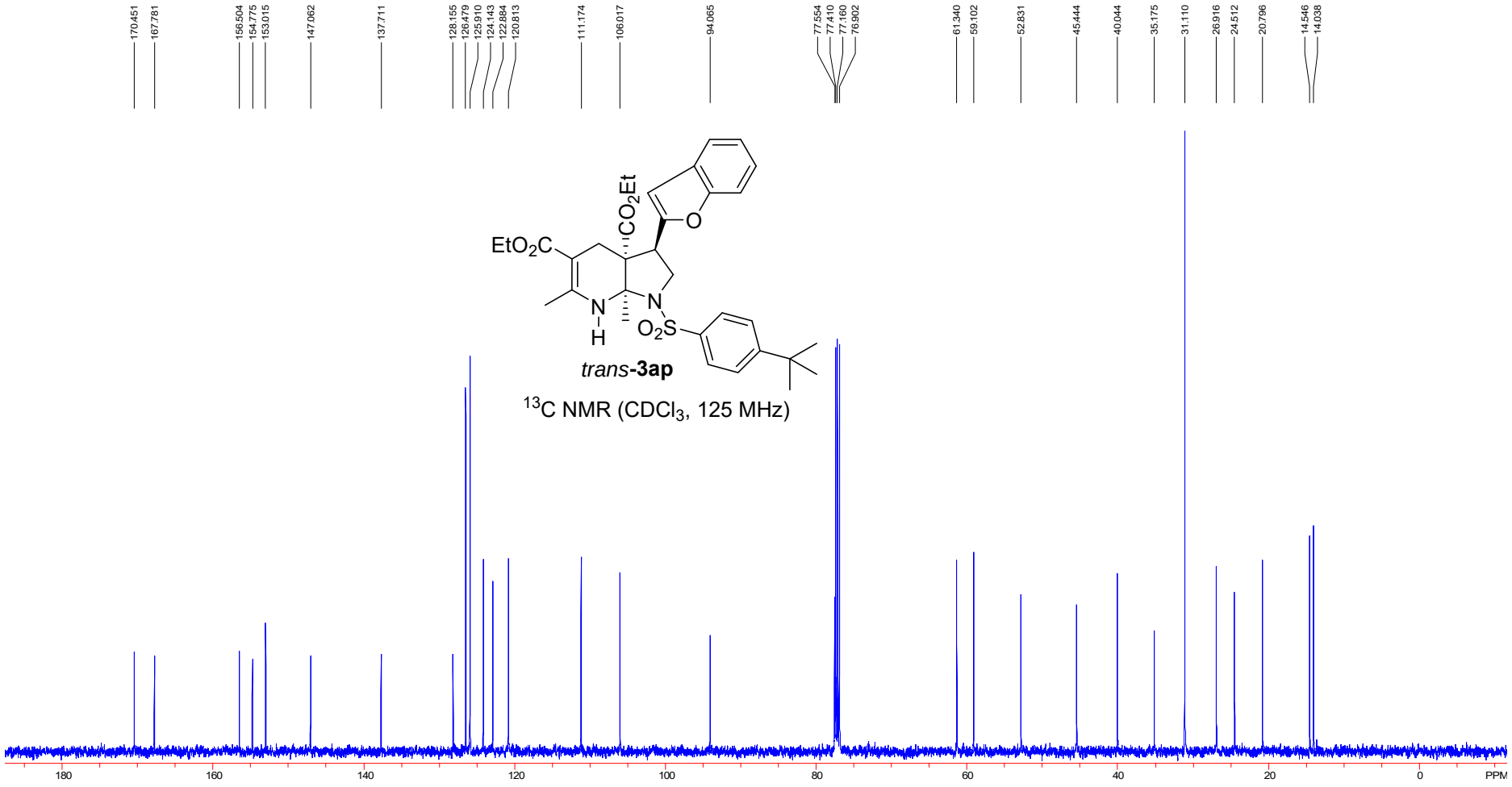
trans-**3an**

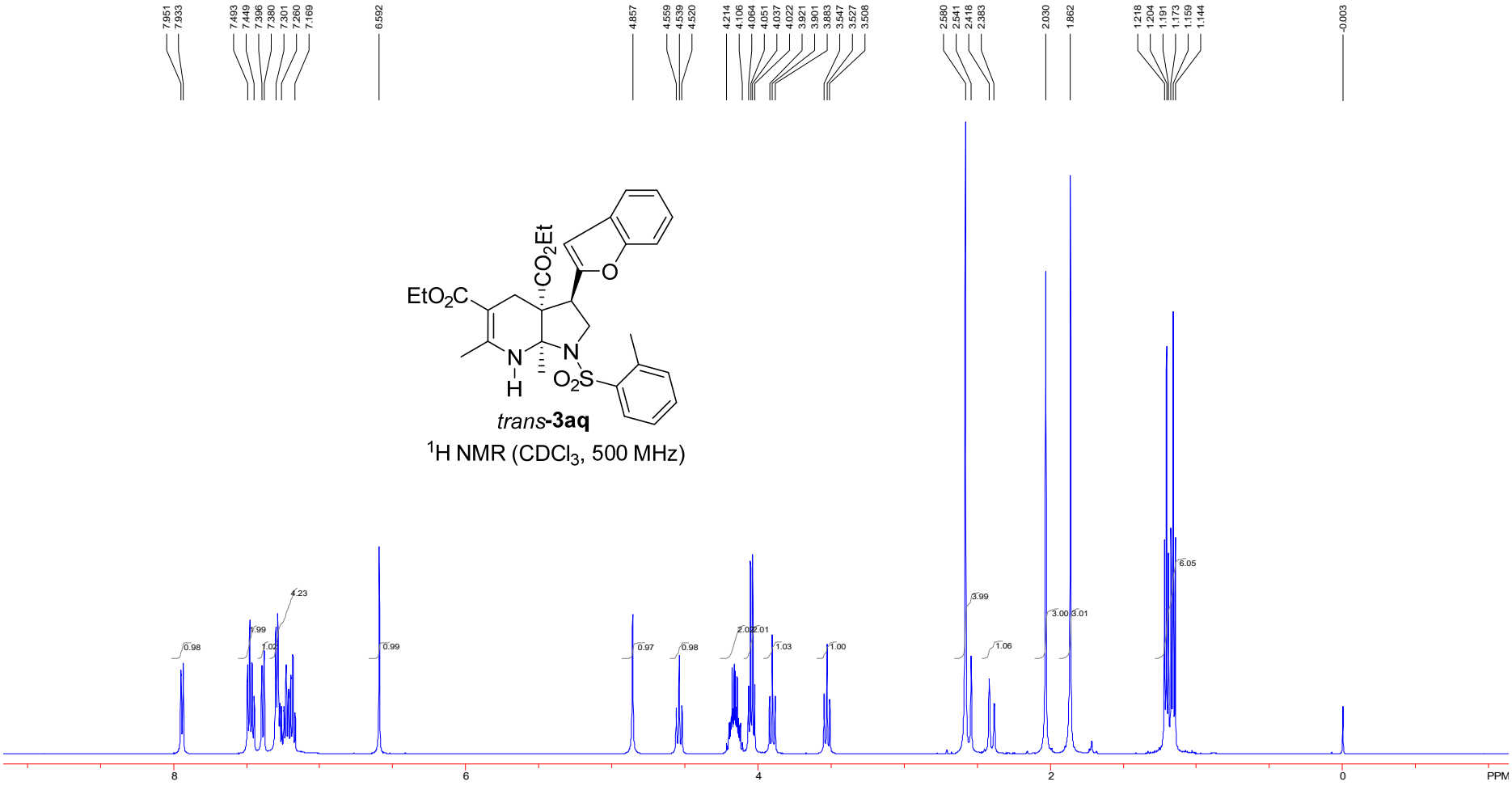
^{13}C NMR ($CDCl_3$, 125 MHz)

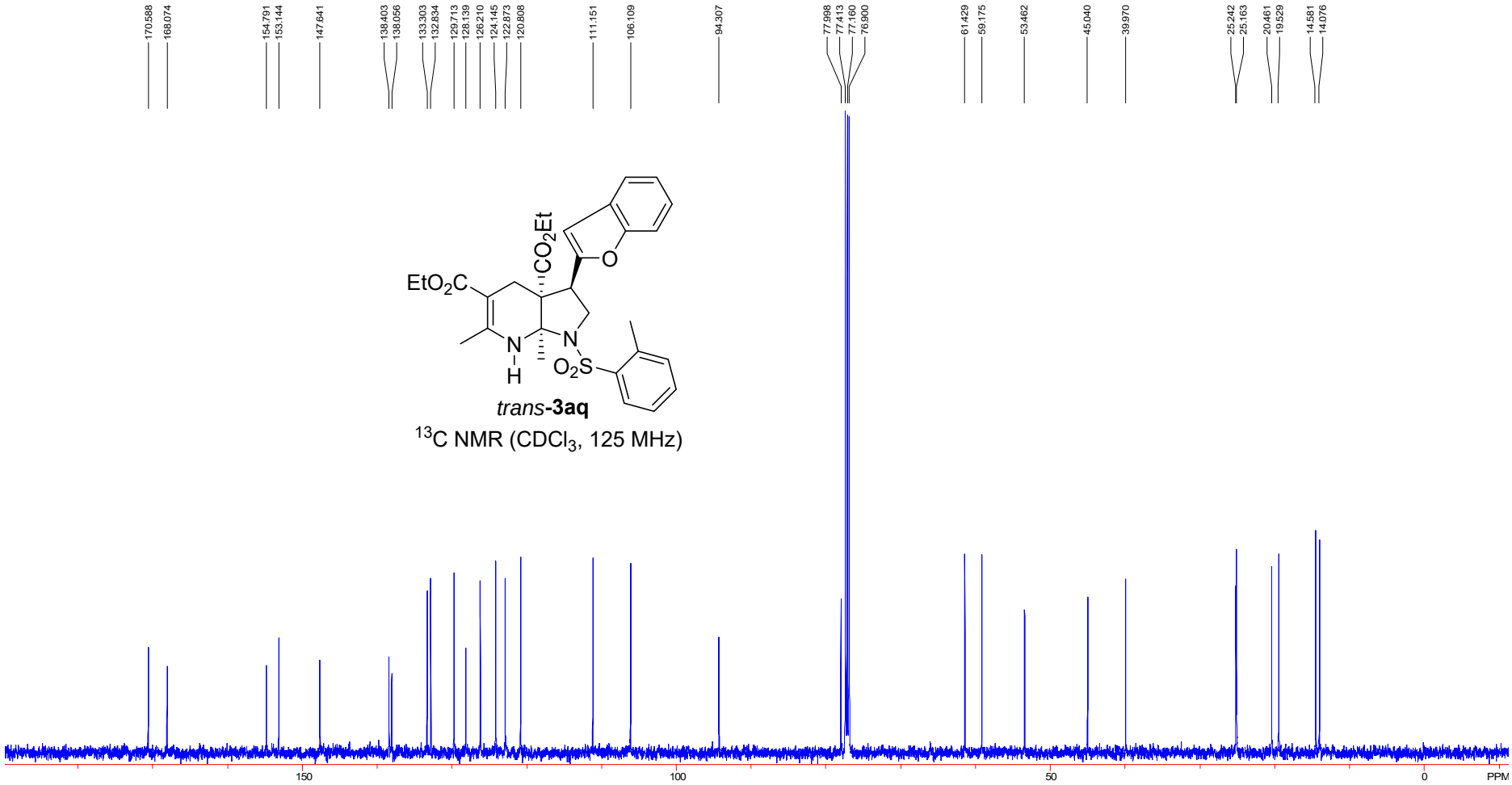

7.769
7.755
7.544
7.399
7.260
7.256
7.176
6.608
4.821
4.510
4.490
4.470
4.181
4.076
4.025
3.964
3.786
3.766
3.746
2.498
2.462
2.077
2.033
1.999
1.796
1.192
1.177
1.163
1.143
1.129
1.115
-0.005
EtO2C
CO2Et
O
N
H
N
O2S
trans-3ao
1H NMR (CDCl3, 500 MHz)
5.00
2.03
0.97
0.98
0.99
2.03
3.01
1.00
0.99
2.96
1.04
3.08
8
6
4
2
0
PPM


170.390
167.781
154.767
152.879
147.047
140.570
132.682
128.951
128.124
126.577
124.166
122.891
120.821
111.167
106.078
94.262
77.721
77.410
77.160
76.902
61.370
59.080
52.929
45.375
40.014
26.962
24.519
20.712
14.577
14.031
EtO2C
CO2Et
O
N
H
N
O2S
trans-3ao
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM


7.688
7.671
7.509
7.494
7.461
7.444
7.421
7.404
7.260
7.257
7.175
6.611
4.795
4.504
4.486
4.466
4.185
4.082
4.034
3.937
3.803
3.784
3.764
2.516
2.481
2.069
2.052
2.037
1.791
1.316
1.197
1.183
1.169
1.144
1.130
1.116
-0.005
EtO2C
CO2Et
O
N
H
N
O2S
trans-3ap
1.97
1.97
2.03
0.99
1.00
0.97
0.97
0.99
2.02
3.01
1.00
0.98
3.97
3.04
9.02
3.00
3.01
8
6
4
2
0
PPM

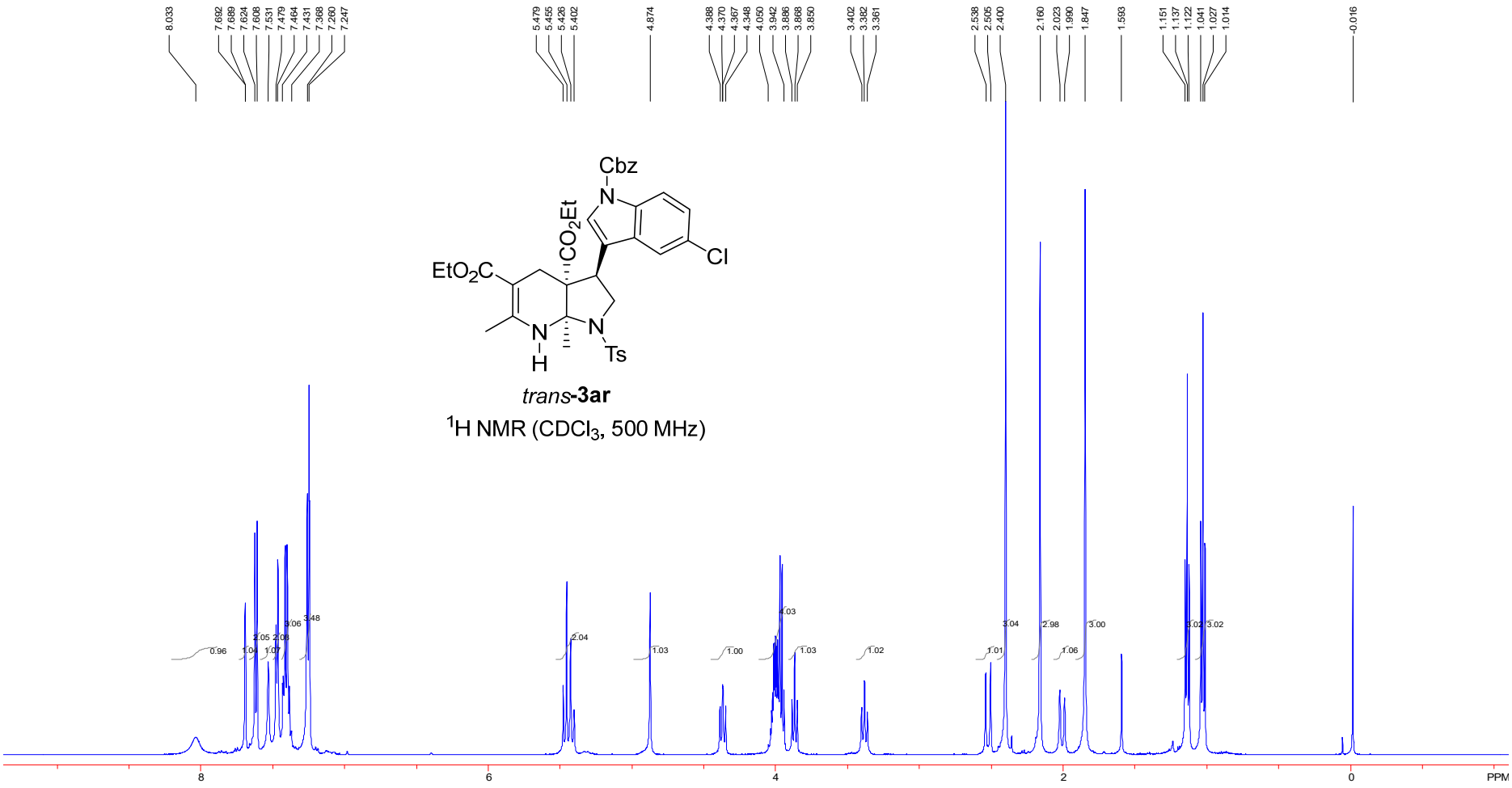

170.451
167.781
156.504
154.775
153.015
147.062
137.711
128.155
126.479
125.910
124.143
122.884
120.813
111.174
106.017
94.065
77.554
77.410
77.160
76.902
61.340
59.102
52.831
45.444
40.044
35.175
31.110
26.916
24.512
20.796
14.546
14.038
EtO2C
CO2Et
O
N
H
N
O2S
trans-3ap
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

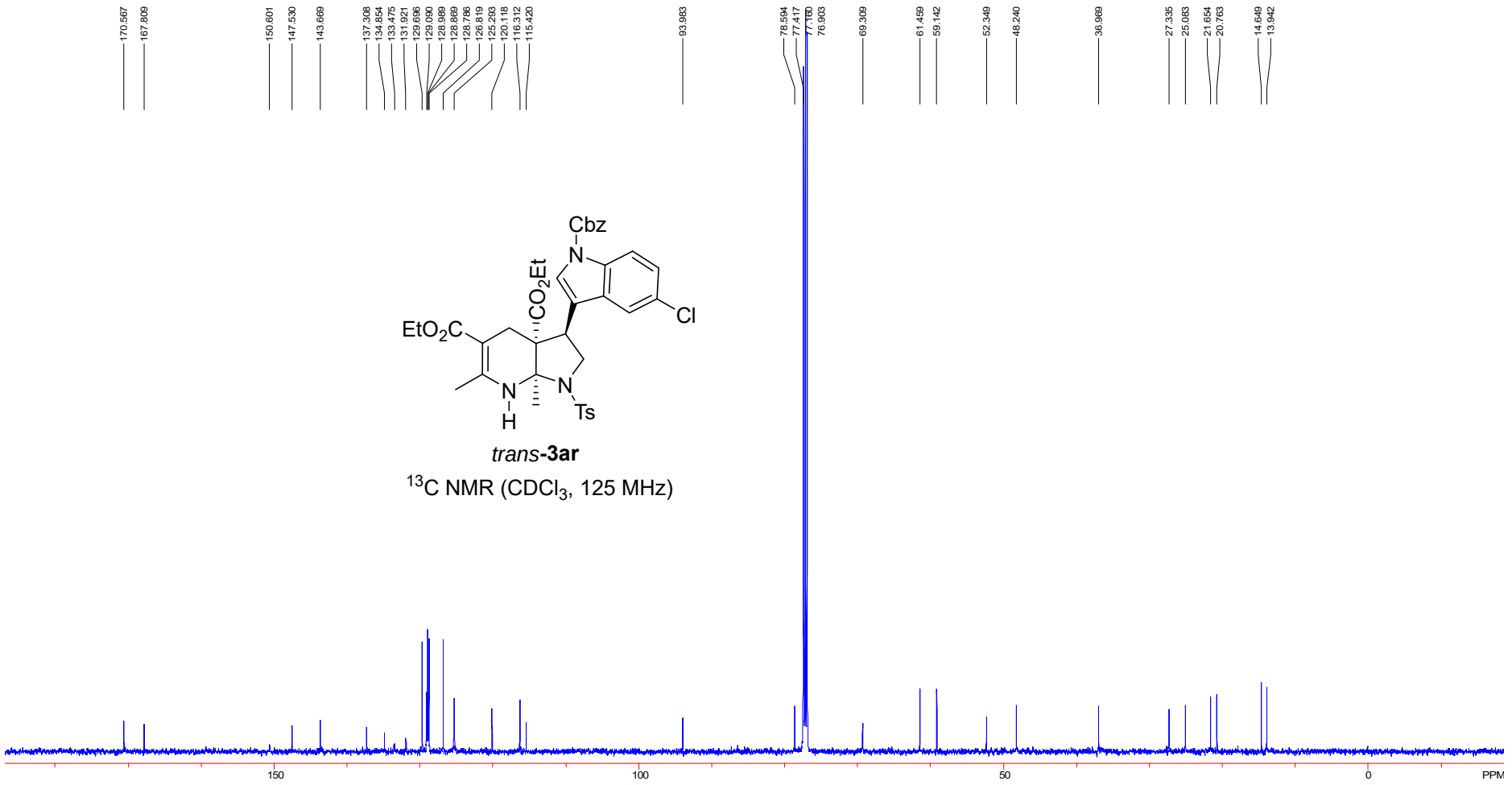

7.951
7.933
7.493
7.449
7.396
7.380
7.301
7.260
7.169
6.592
4.857
4.559
4.539
4.520
4.214
4.106
4.064
4.051
4.037
4.022
3.921
3.901
3.883
3.547
3.527
3.508
2.580
2.541
2.418
2.383
2.030
1.862
1.218
1.204
1.191
1.173
1.159
1.144
-0.003
EtO2C
CO2Et
O
N
H
N
O2S
trans-3aq
1H NMR (CDCl3, 500 MHz)
0.98
1.99
1.02
4.23
0.99
0.97
0.98
2.02
2.01
1.03
1.00
3.99
1.06
3.00
3.01
6.05
8
6
4
2
0
PPM



trans-**3aq**

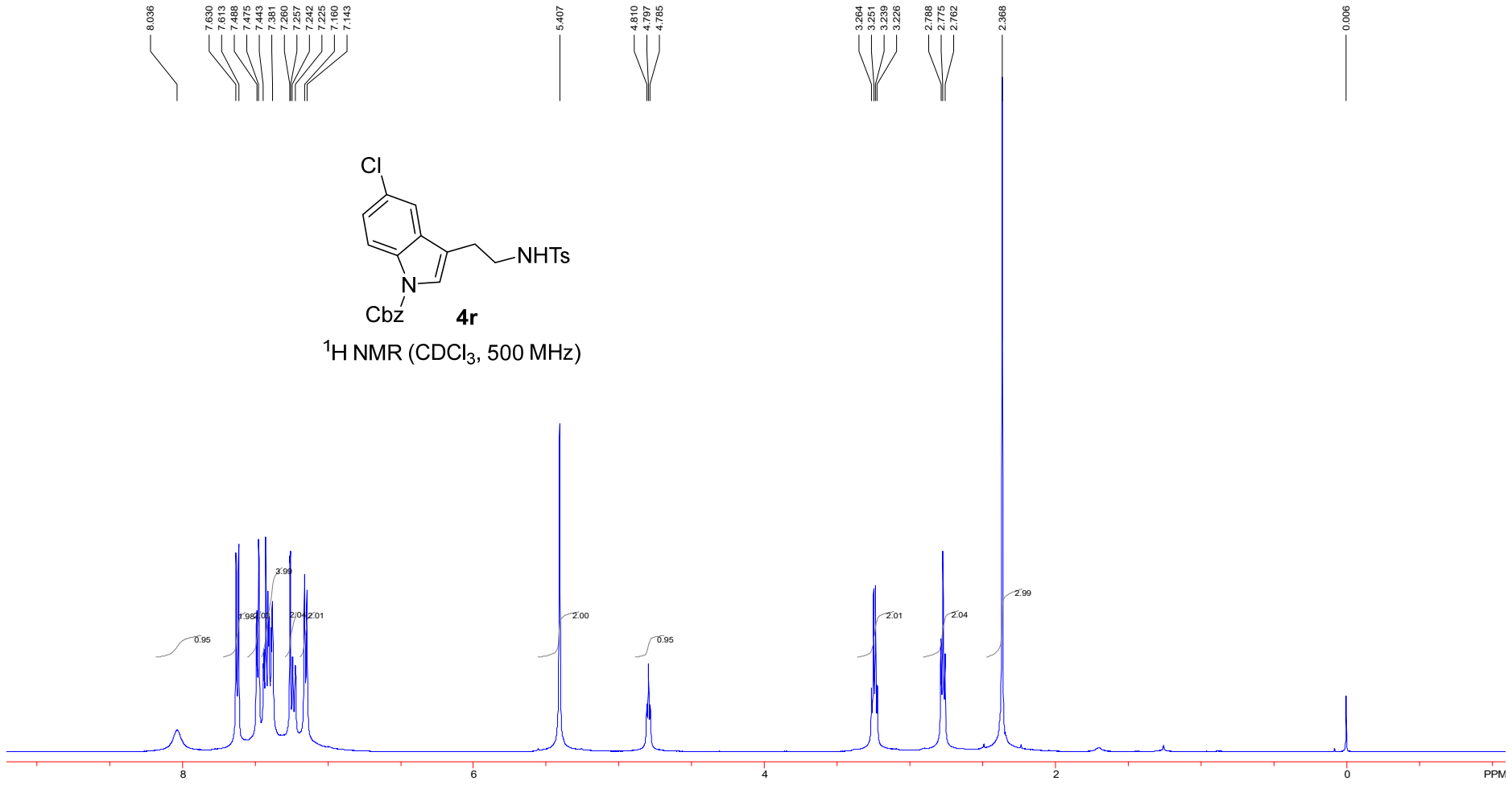
^{13}C NMR ($CDCl_3$, 125 MHz)

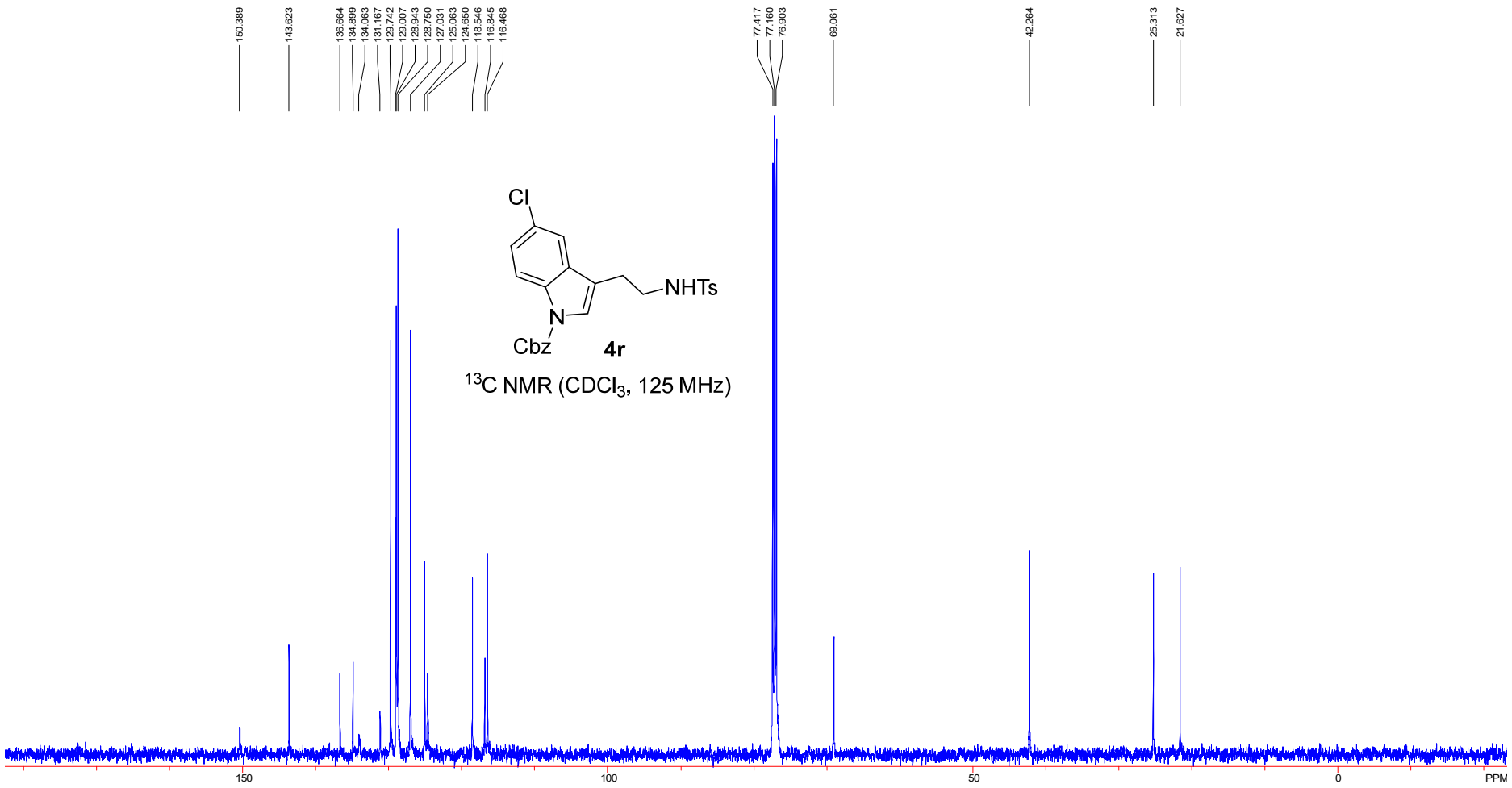

8.033
7.692
7.688
7.624
7.608
7.531
7.479
7.464
7.431
7.368
7.280
7.247
5.479
5.455
5.426
5.402
4.874
4.388
4.370
4.367
4.348
4.050
3.942
3.886
3.868
3.850
3.402
3.382
3.361
2.538
2.505
2.400
2.160
2.023
1.990
1.847
1.593
1.151
1.137
1.122
1.041
1.027
1.014
0.016
Cbz
N
CO2Et
Cl
EtO2C
N
N
Ts
H
trans-3ar
1H NMR (CDCl3, 500 MHz)
0.96
1.04
1.07
2.05
2.09
3.06
3.48
2.04
1.03
1.00
4.03
1.03
1.02
1.01
3.04
2.98
1.06
3.00
3.02
3.02
8
6
4
2
0
PPM

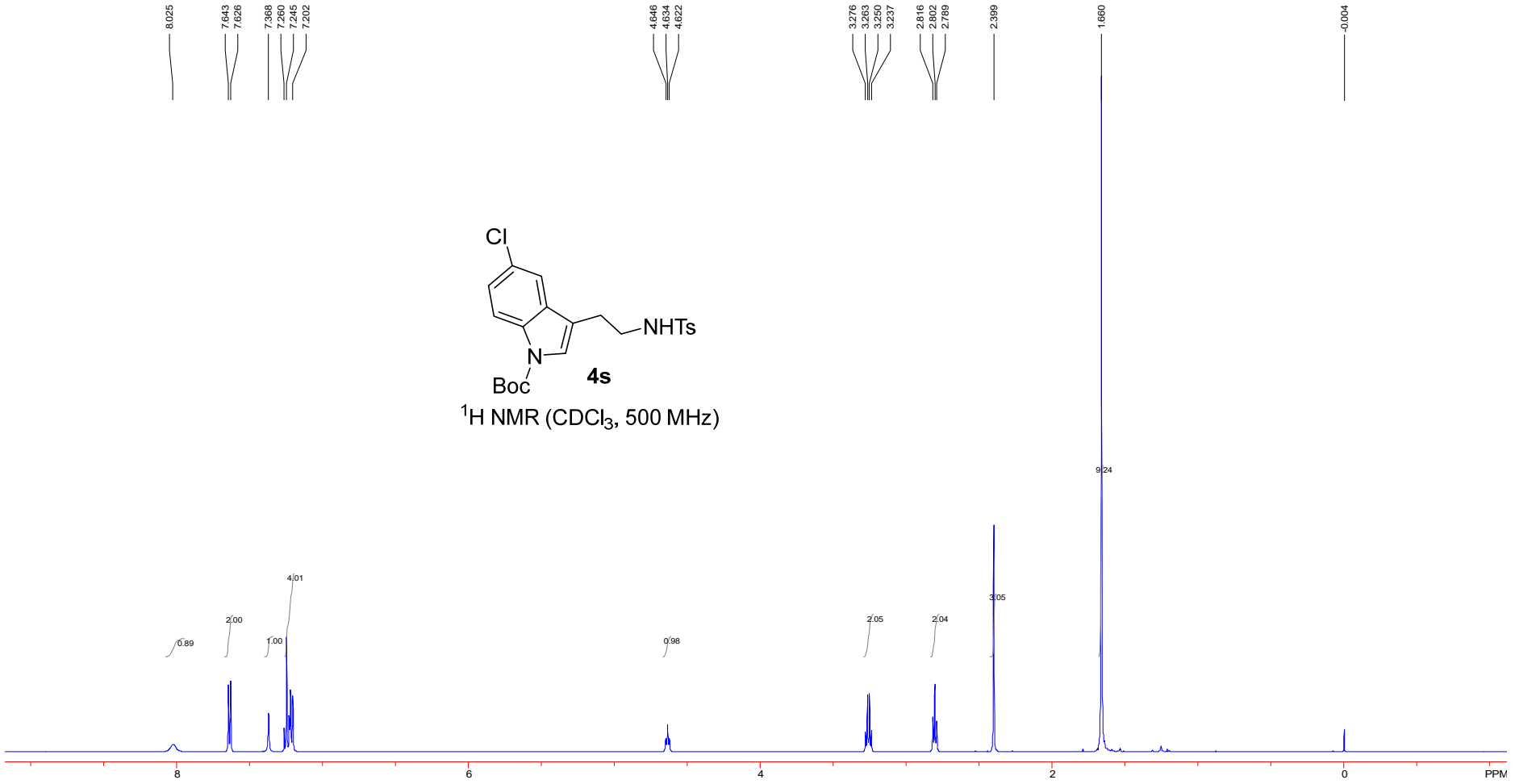


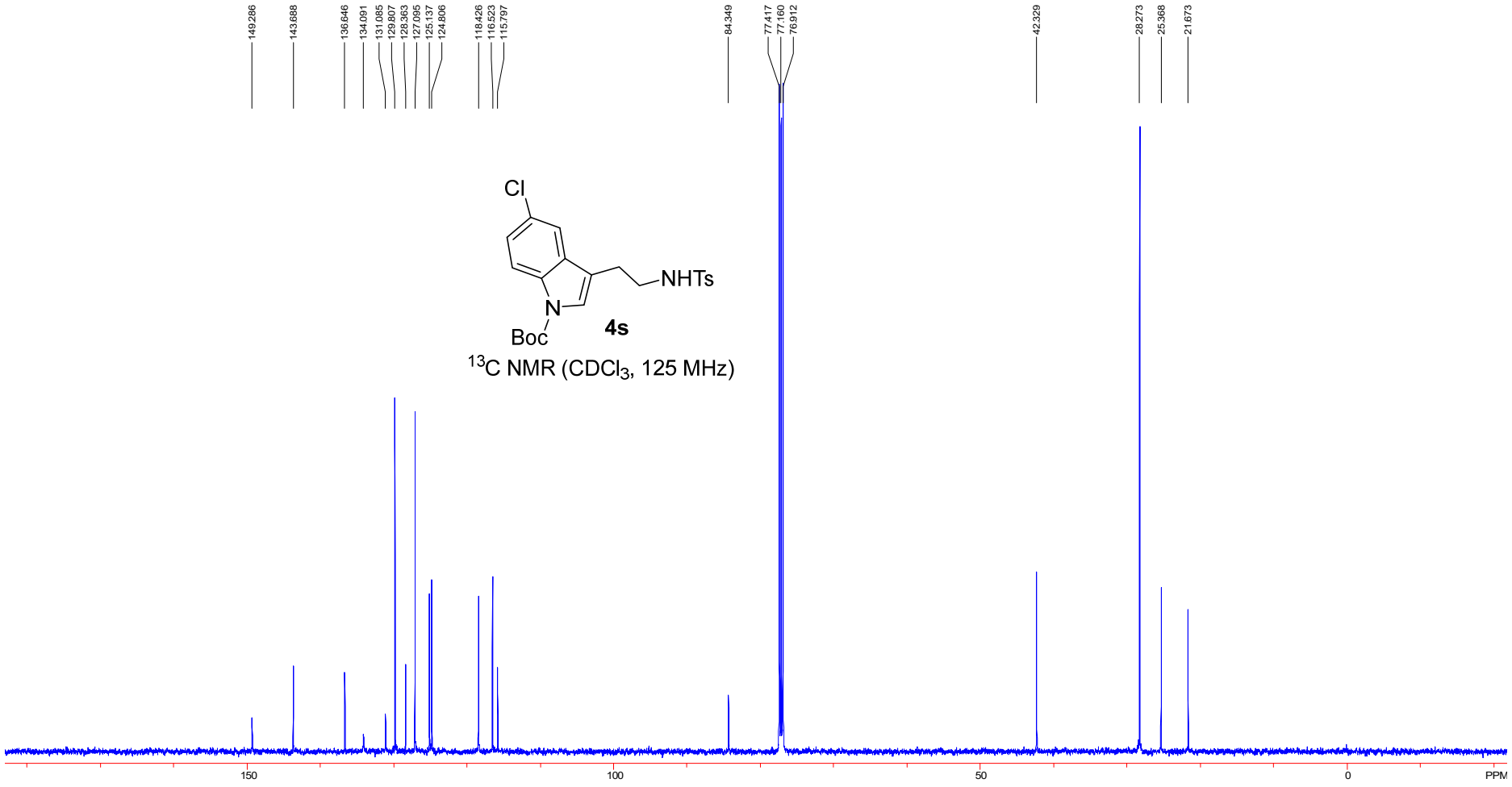
trans-**3ar**

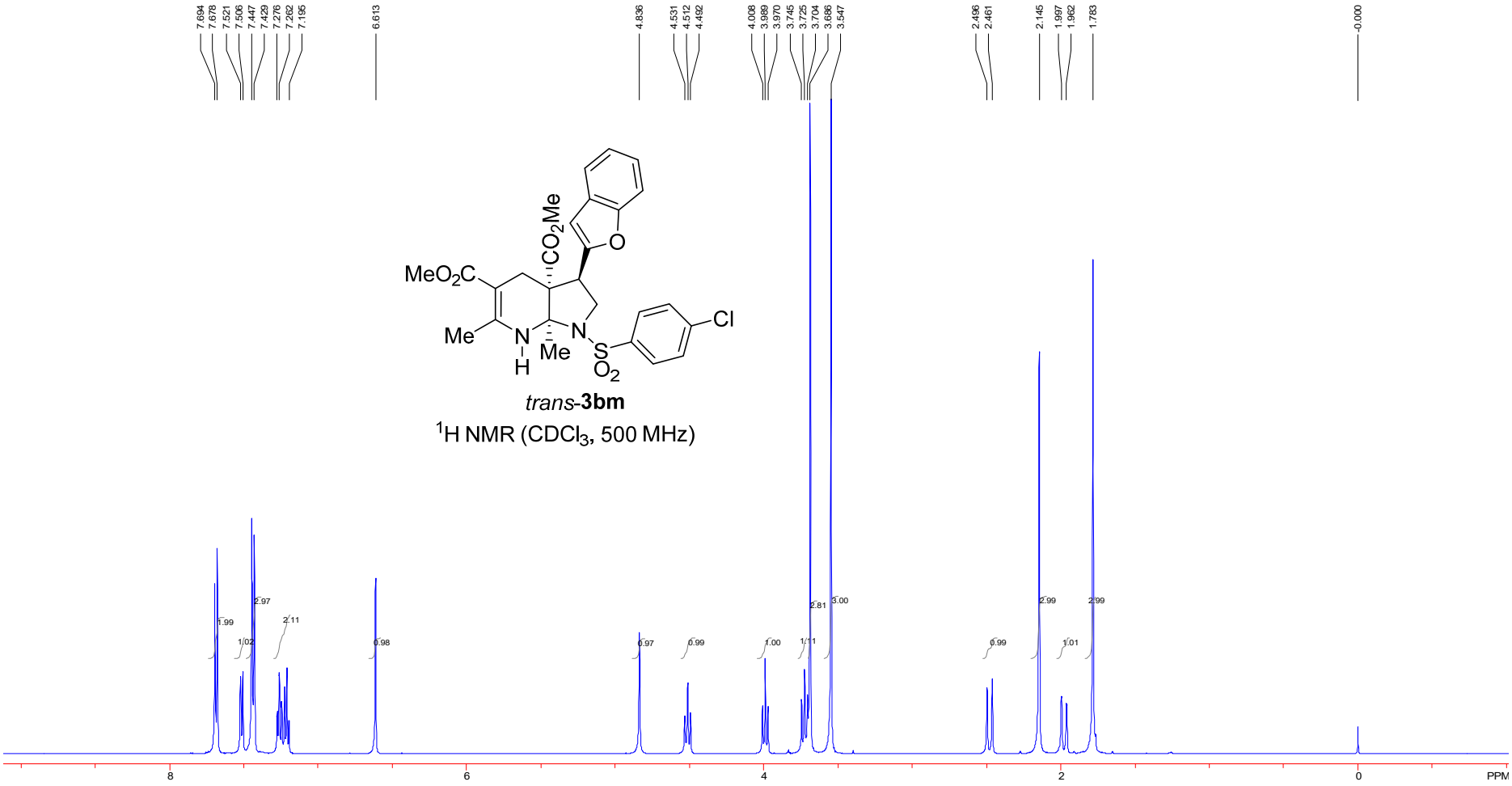
^{13}C NMR ($CDCl_3$, 125 MHz)


8.036
7.630
7.613
7.488
7.475
7.443
7.381
7.260
7.257
7.242
7.225
7.160
7.143
5.407
4.810
4.797
4.785
3.264
3.251
3.239
3.226
2.788
2.775
2.762
2.368
0.006
Cl
NHTs
N
Cbz
4r
1H NMR (CDCl3, 500 MHz)
0.95
1.98
1.00
3.99
2.04
2.01
2.00
0.95
2.01
2.04
2.99
8
6
4
2
0
PPM


150.389
143.623
136.664
134.899
134.063
131.167
129.742
129.007
128.943
128.750
127.031
125.063
124.650
118.546
116.845
116.468
77.417
77.160
76.903
69.061
42.264
25.313
21.627
Cl
NHTs
N
Cbz
4r
13C NMR (CDCl3, 125 MHz)
150
100
50
0
PPM

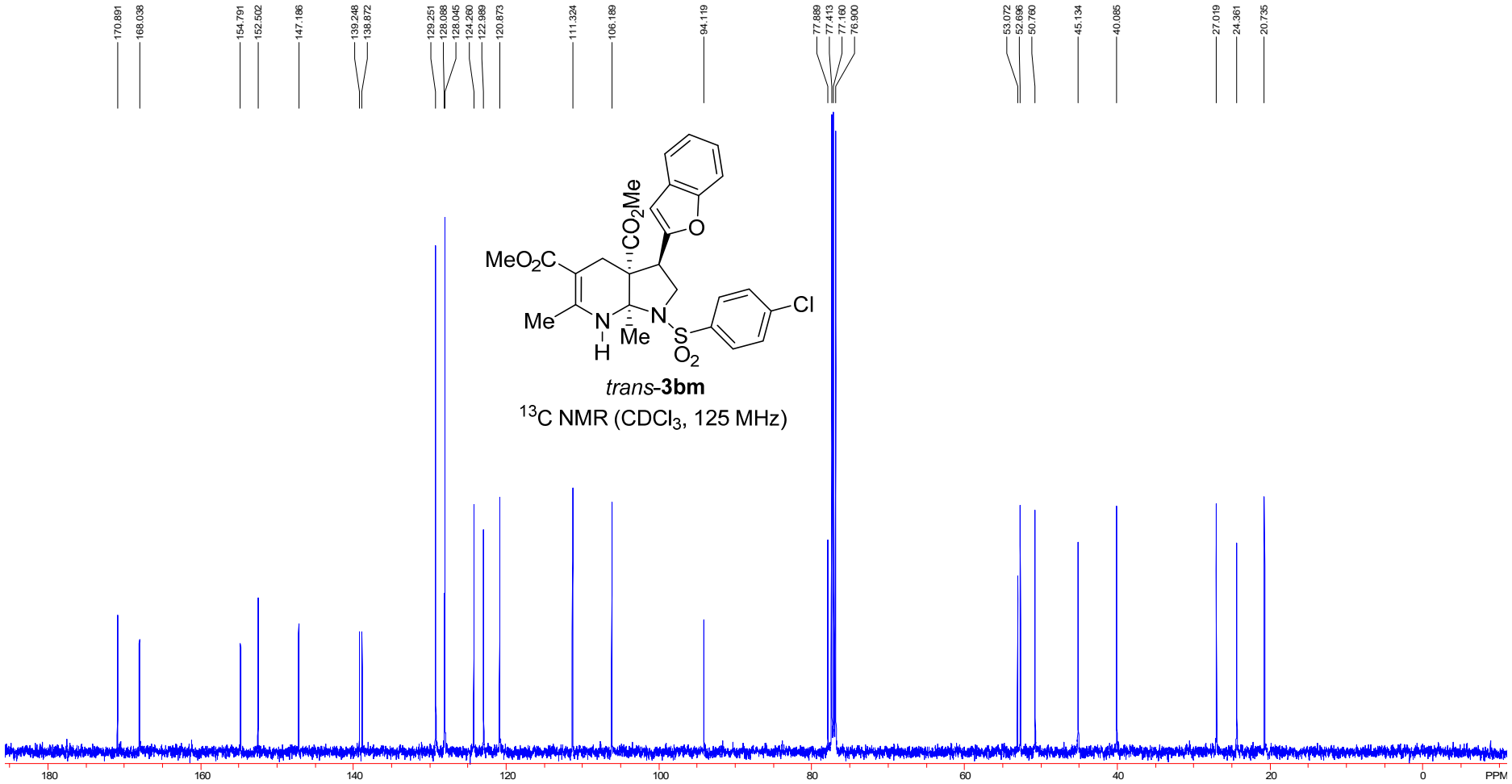

8.025
7.643
7.626
7.368
7.260
7.245
7.202
4.646
4.634
4.622
3.276
3.263
3.250
3.237
2.816
2.802
2.789
2.399
1.660
-0.004
Cl
NHTs
N
Boc
4s
1H NMR (CDCl3, 500 MHz)
0.89
2.00
1.00
4.01
0.98
2.05
2.04
3.05
9.24
8
6
4
2
0
PPM

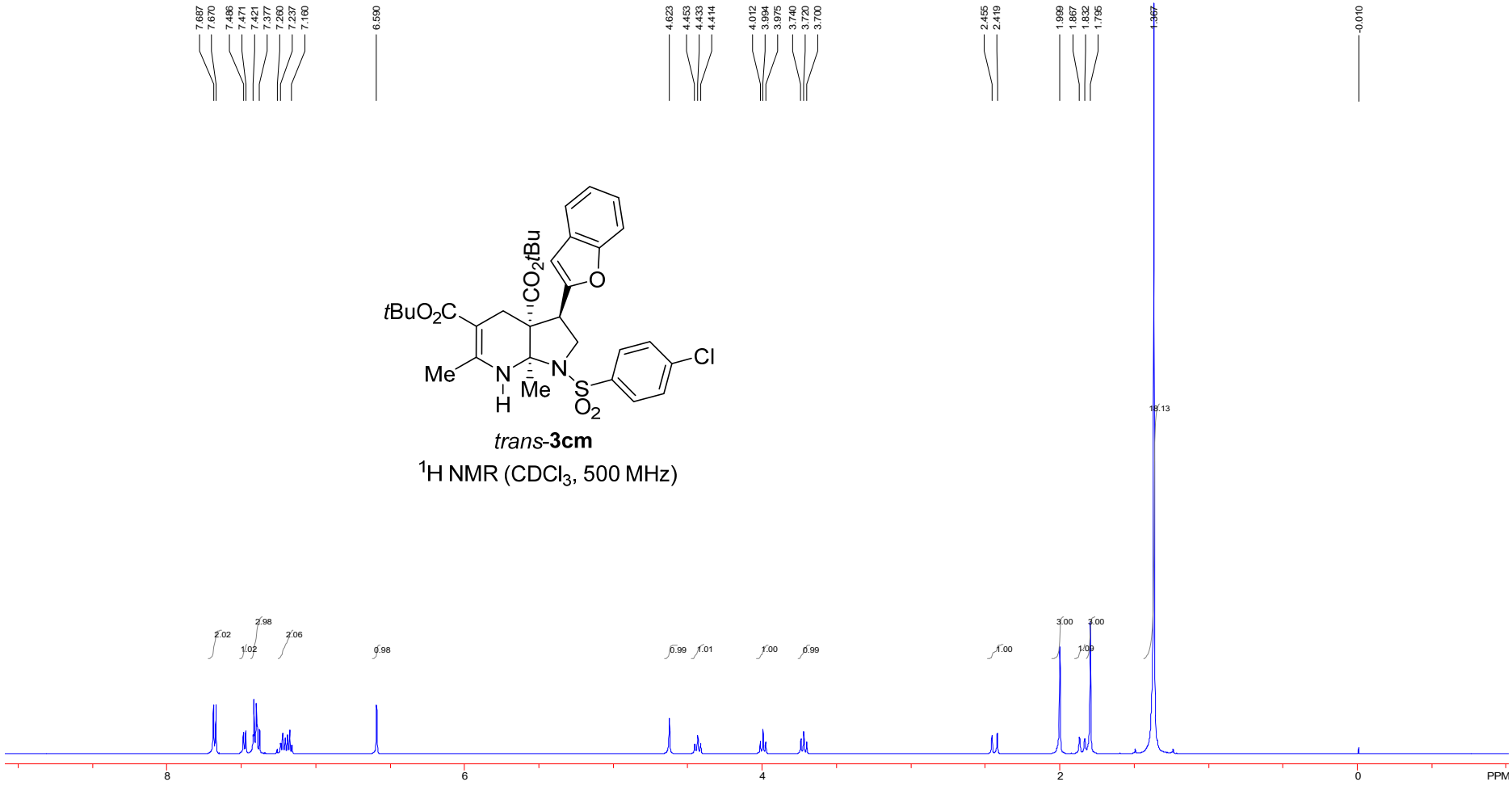

149.286
143.688
136.646
134.091
131.085
129.807
128.363
127.095
125.137
124.806
118.426
116.523
115.797
84.349
77.417
77.160
76.912
42.329
28.273
25.368
21.673
Cl
NHTs
N
Boc
4s
^{13}C NMR ($CDCl_3$, 125 MHz)
150
100
50
0
PPM



trans-**3bm**

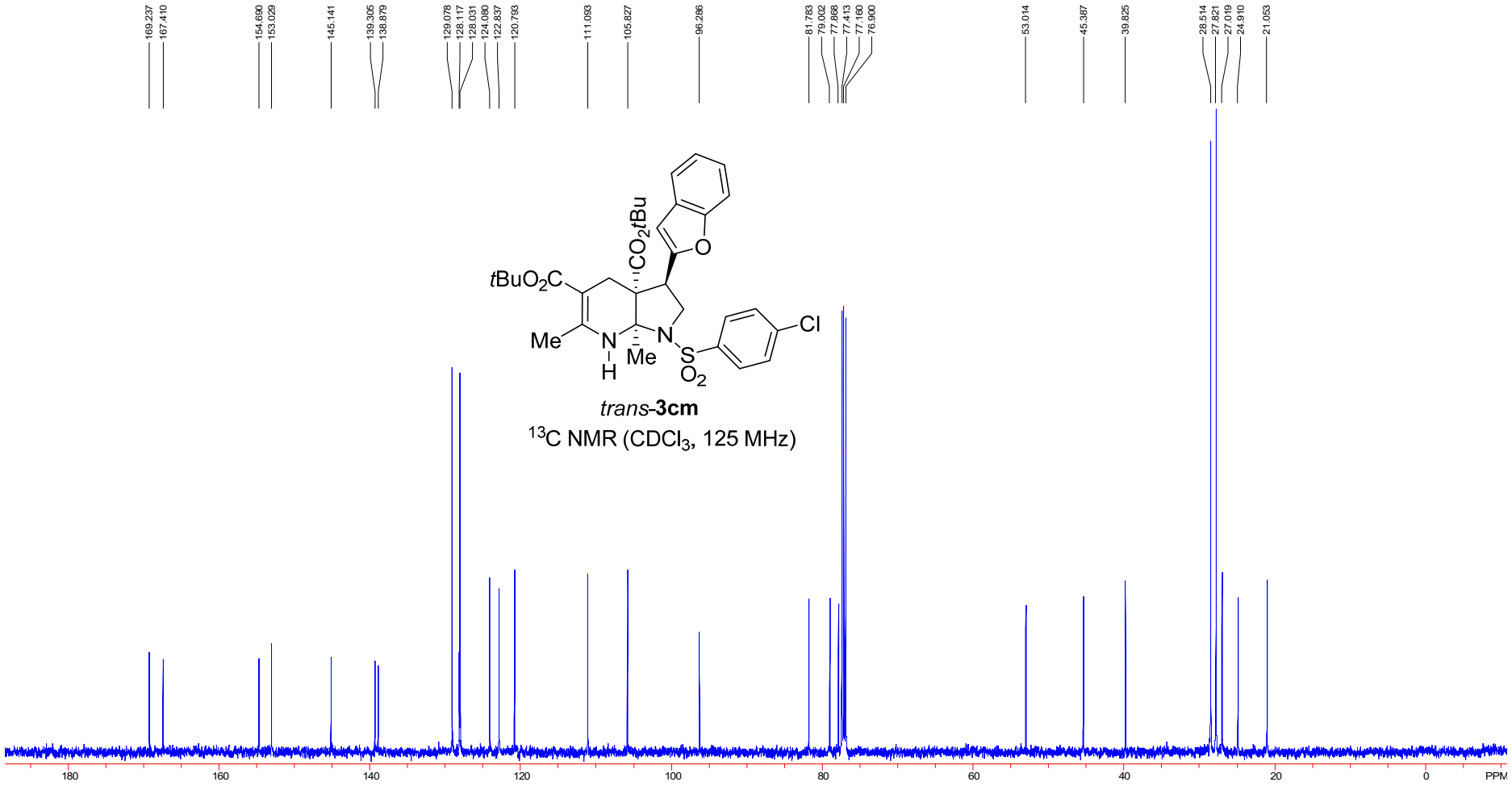
^{1}H NMR ($CDCl_3$, 500 MHz)

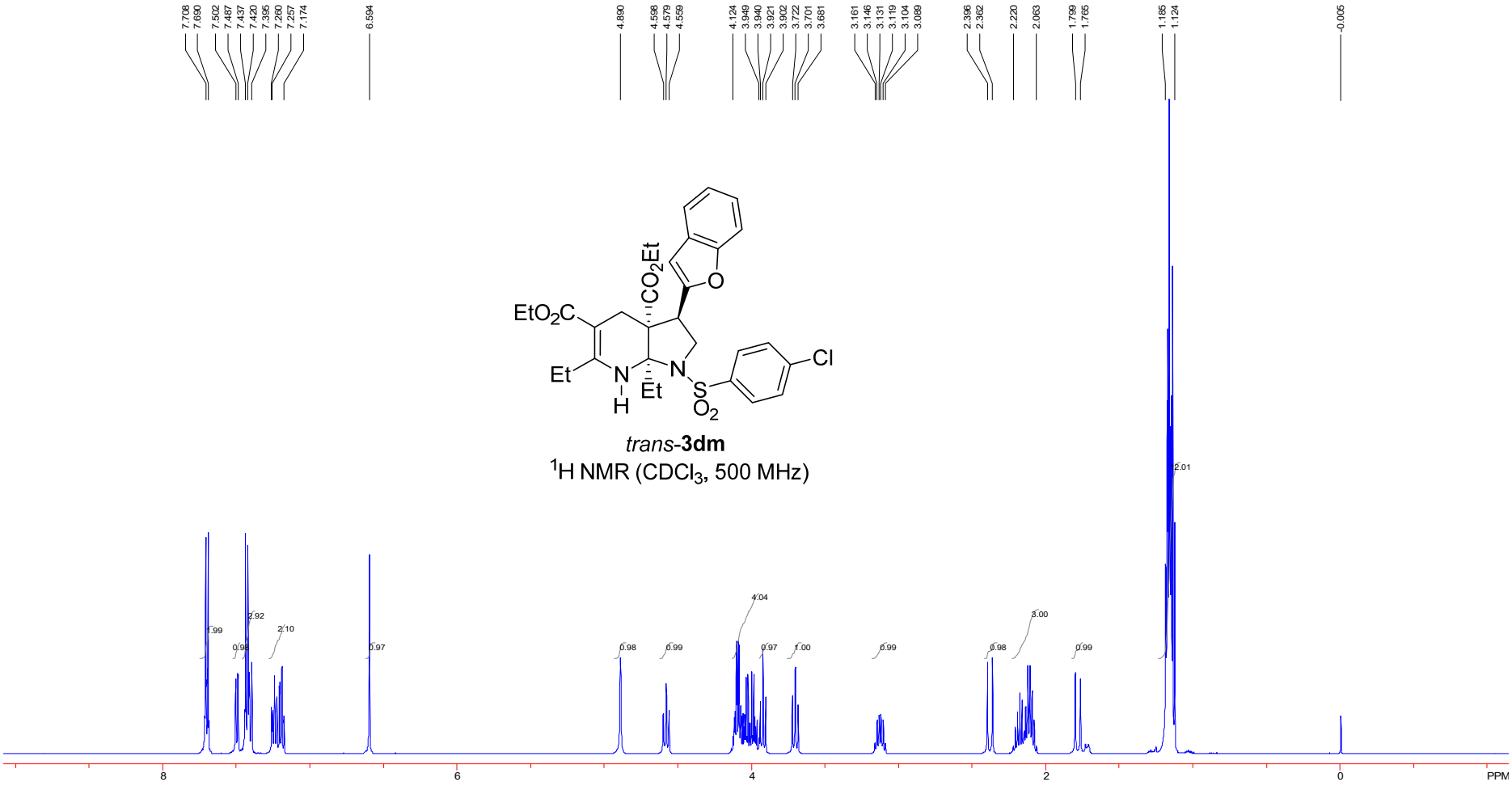

170.891
168.038
154.791
152.502
147.186
139.248
138.872
129.251
128.088
128.045
124.260
122.989
120.873
111.324
106.189
94.119
77.889
77.413
77.160
76.900
53.072
52.696
50.760
45.134
40.085
27.019
24.361
20.735
MeO2C
CO2Me
O
Me
N
H
N
Me
S
O2
Cl
trans-3bm
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

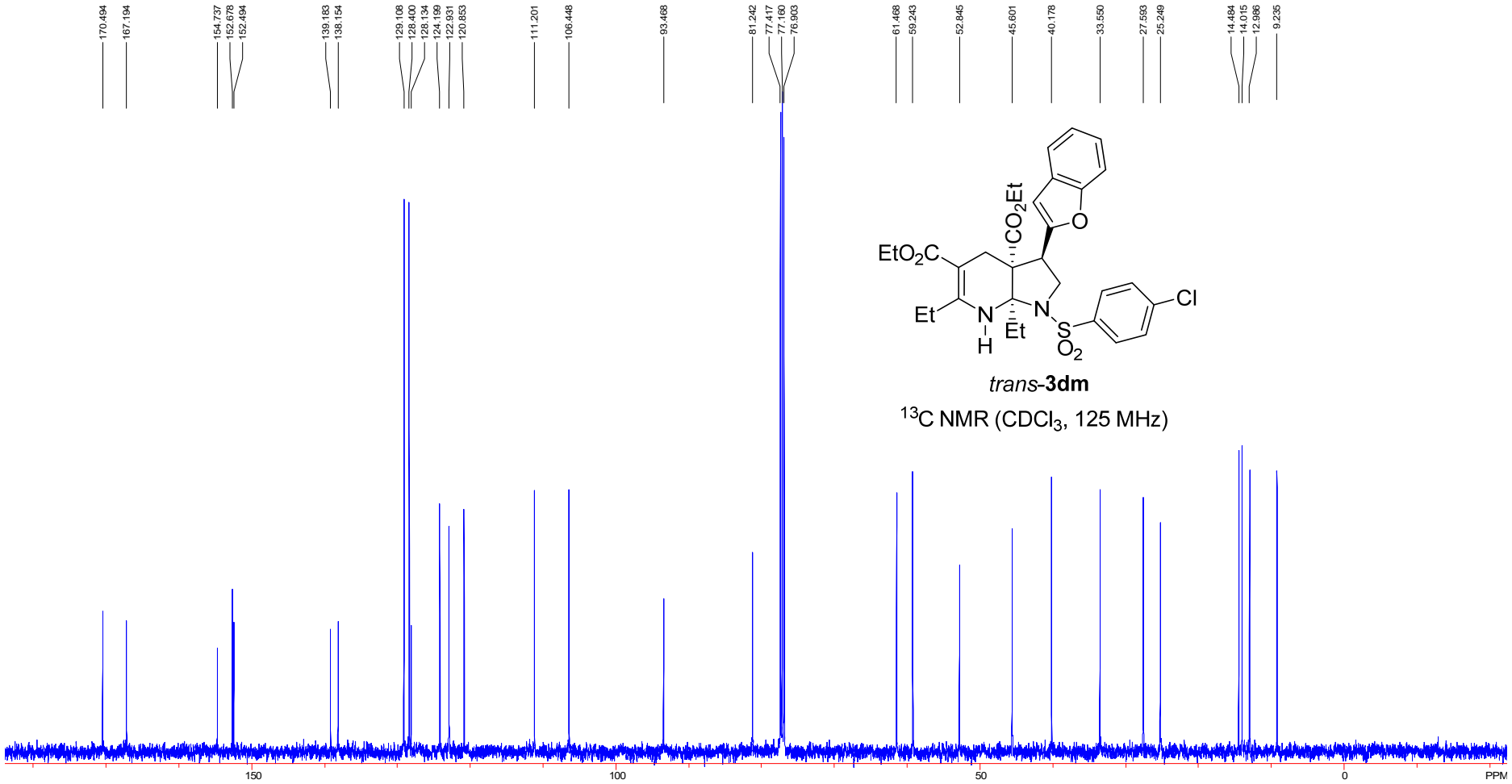


trans-**3cm**

^{1}H NMR ($CDCl_3$, 500 MHz)

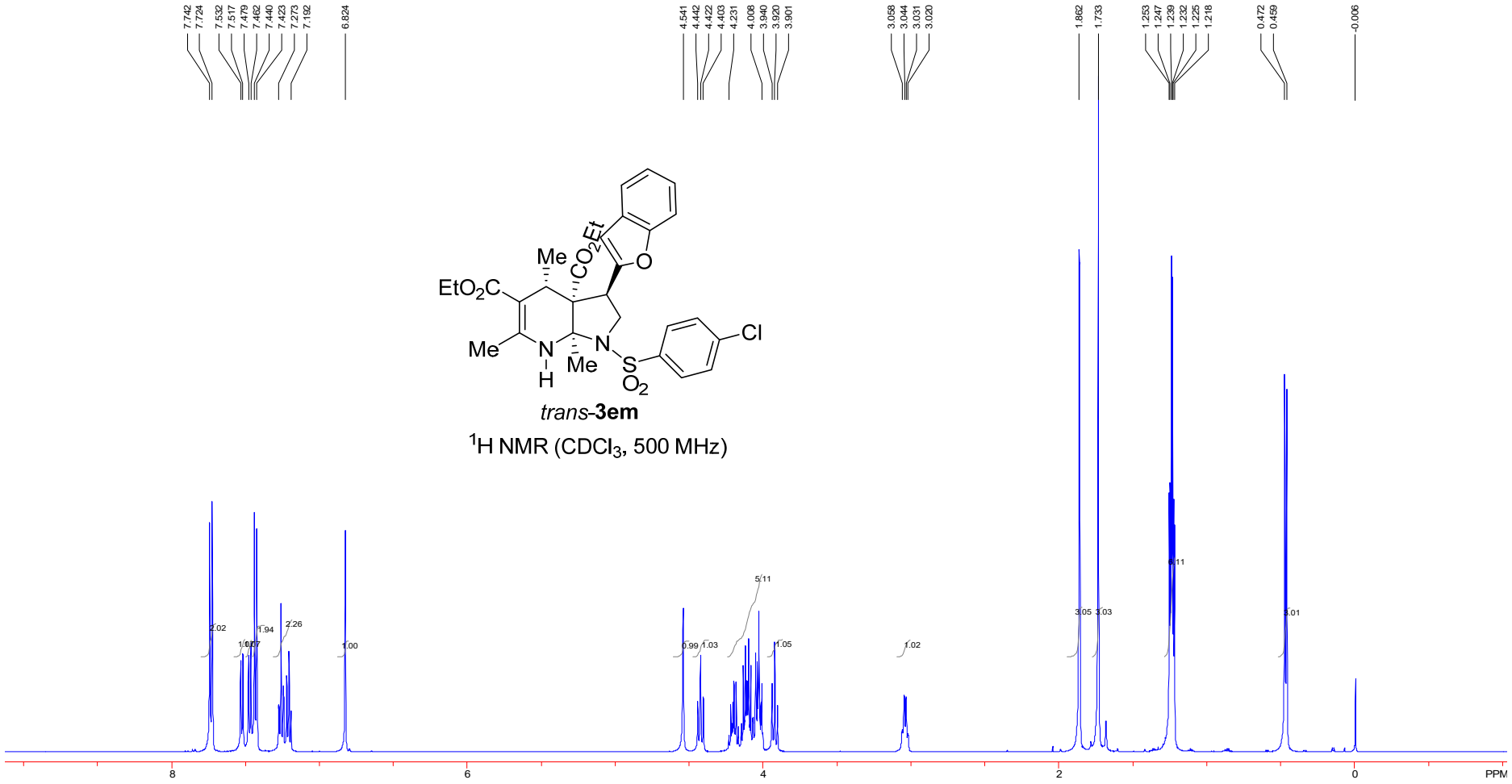

169.237
167.410
154.690
153.029
145.141
139.305
138.879
129.078
128.117
128.031
124.080
122.837
120.793
111.093
105.827
96.286
81.783
79.002
77.868
77.413
77.160
76.900
53.014
45.387
39.825
28.514
27.821
27.019
24.910
21.053
tBuO2C
CO2tBu
O
Me
N
H
N
Me
S
O2
Cl
trans-3cm
13C NMR (CDCl3, 125 MHz)
180
160
140
120
100
80
60
40
20
0
PPM

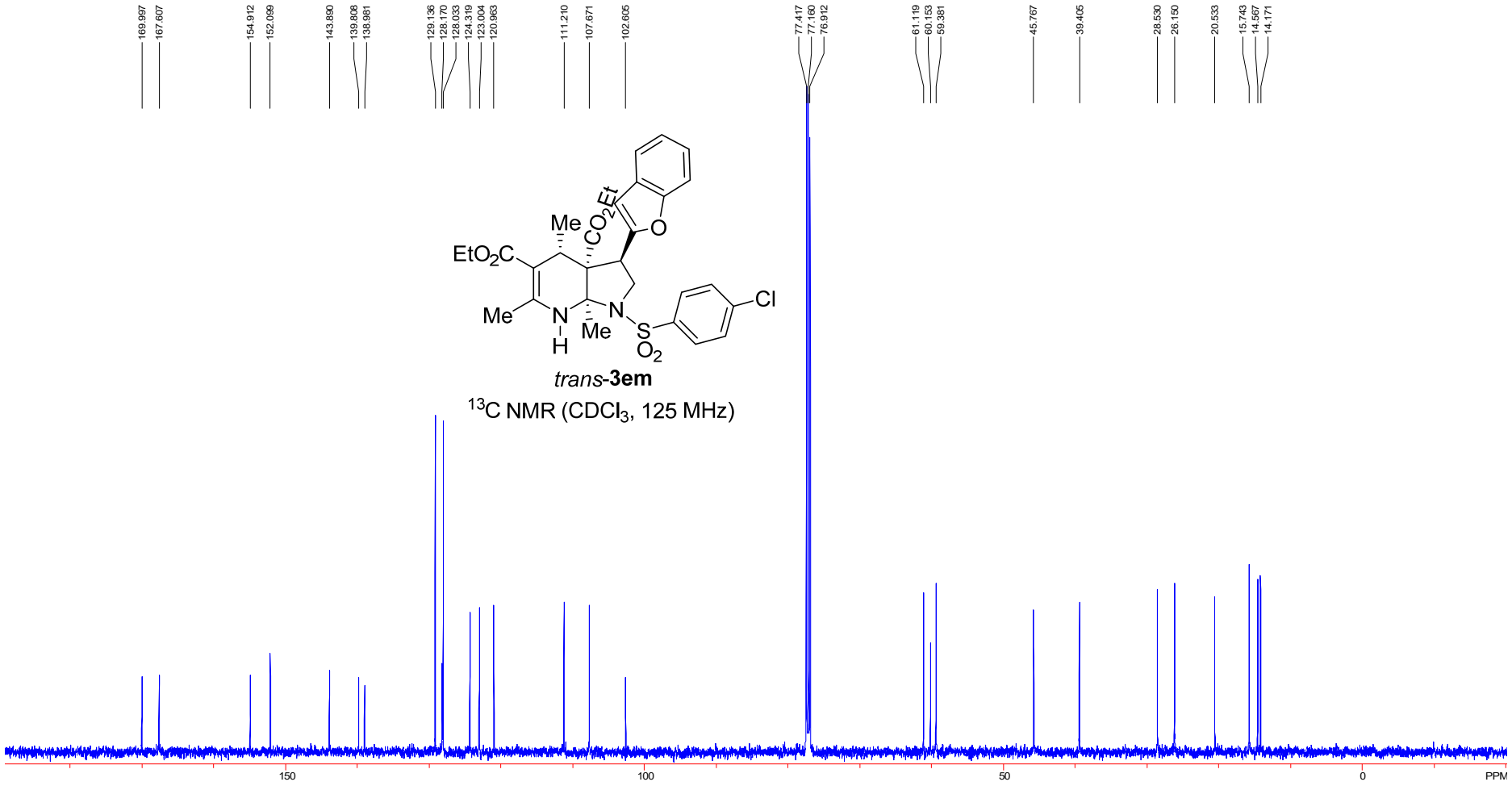

7.708
7.690
7.502
7.487
7.437
7.420
7.395
7.260
7.257
7.174
6.594
4.890
4.598
4.579
4.559
4.124
3.949
3.940
3.921
3.902
3.722
3.701
3.681
3.161
3.146
3.131
3.119
3.104
3.089
2.396
2.362
2.220
2.063
1.799
1.765
1.185
1.124
-0.005
EtO2C
CO2Et
O
Et
N
H
Et
N
S
O2
Cl
trans-3dm
1H NMR (CDCl3, 500 MHz)
1.99
2.92
0.98
2.10
0.97
0.98
0.99
4.04
0.97
1.00
0.99
0.98
3.00
0.99
2.01
8
6
4
2
0
PPM



trans-**3dm**

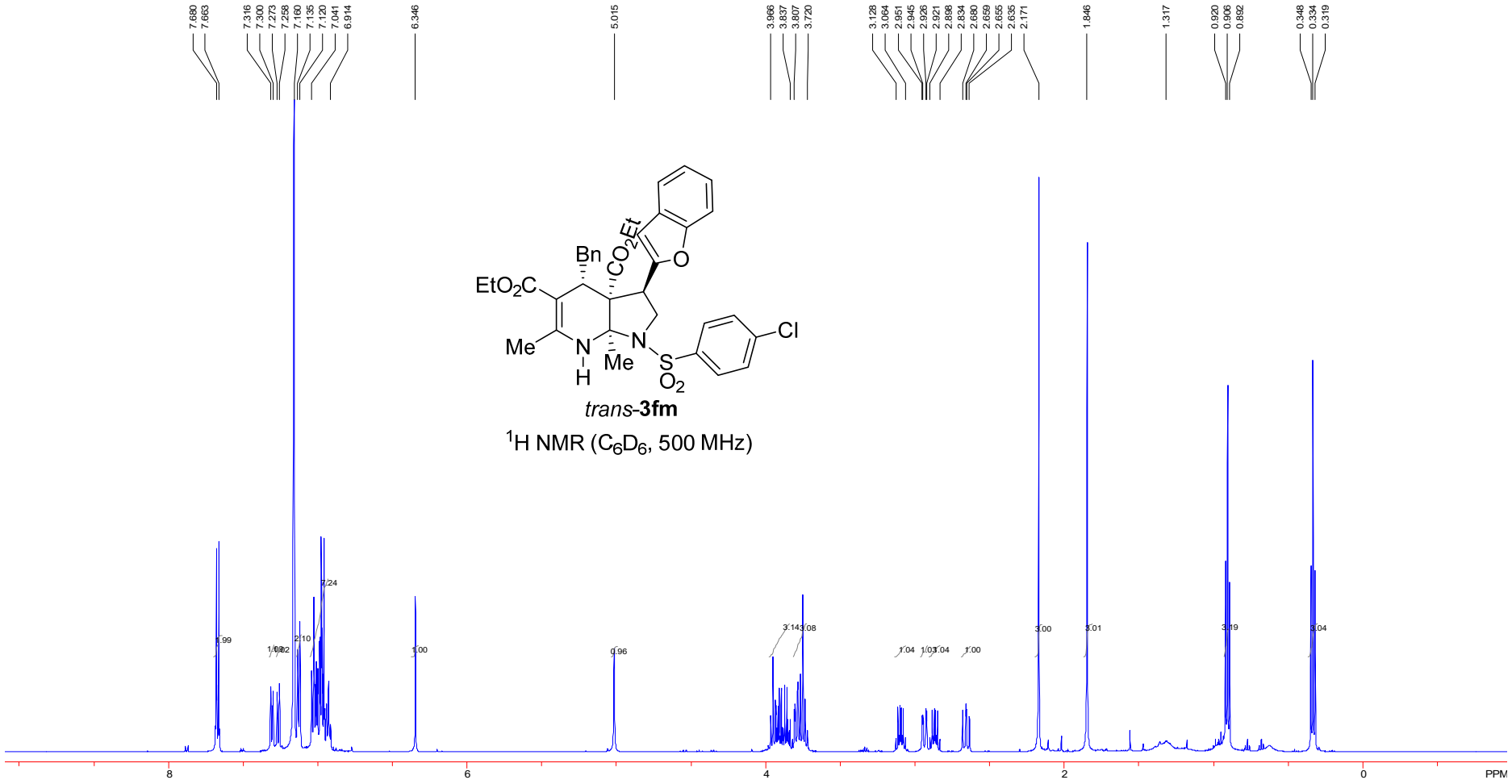
^{13}C NMR ($CDCl_3$, 125 MHz)

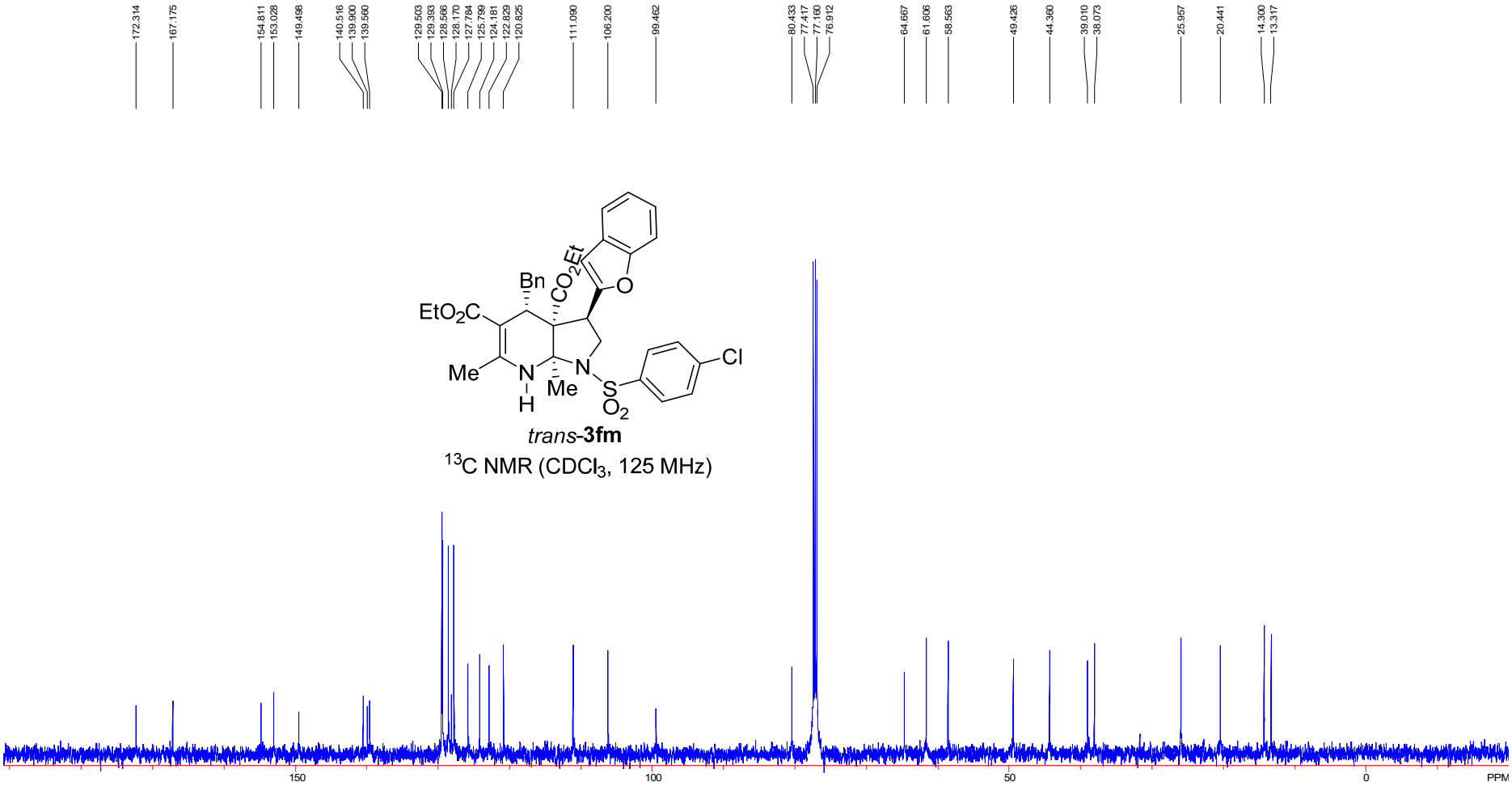

7.742
7.724
7.532
7.517
7.479
7.462
7.440
7.423
7.273
7.192
6.824
4.541
4.442
4.422
4.403
4.231
4.008
3.940
3.920
3.901
3.058
3.044
3.031
3.020
1.862
1.733
1.253
1.247
1.239
1.232
1.225
1.218
0.472
0.459
-0.006
Me
CO2Et
O
EtO2C
Me
N
H
N
Me
S
O2
Cl
trans-3em
1H NMR (CDCl3, 500 MHz)
2.02
1.94
2.26
1.00
0.99
1.03
5.11
1.05
1.02
3.05
3.03
6.11
3.01
8
6
4
2
0
PPM



trans-**3em**

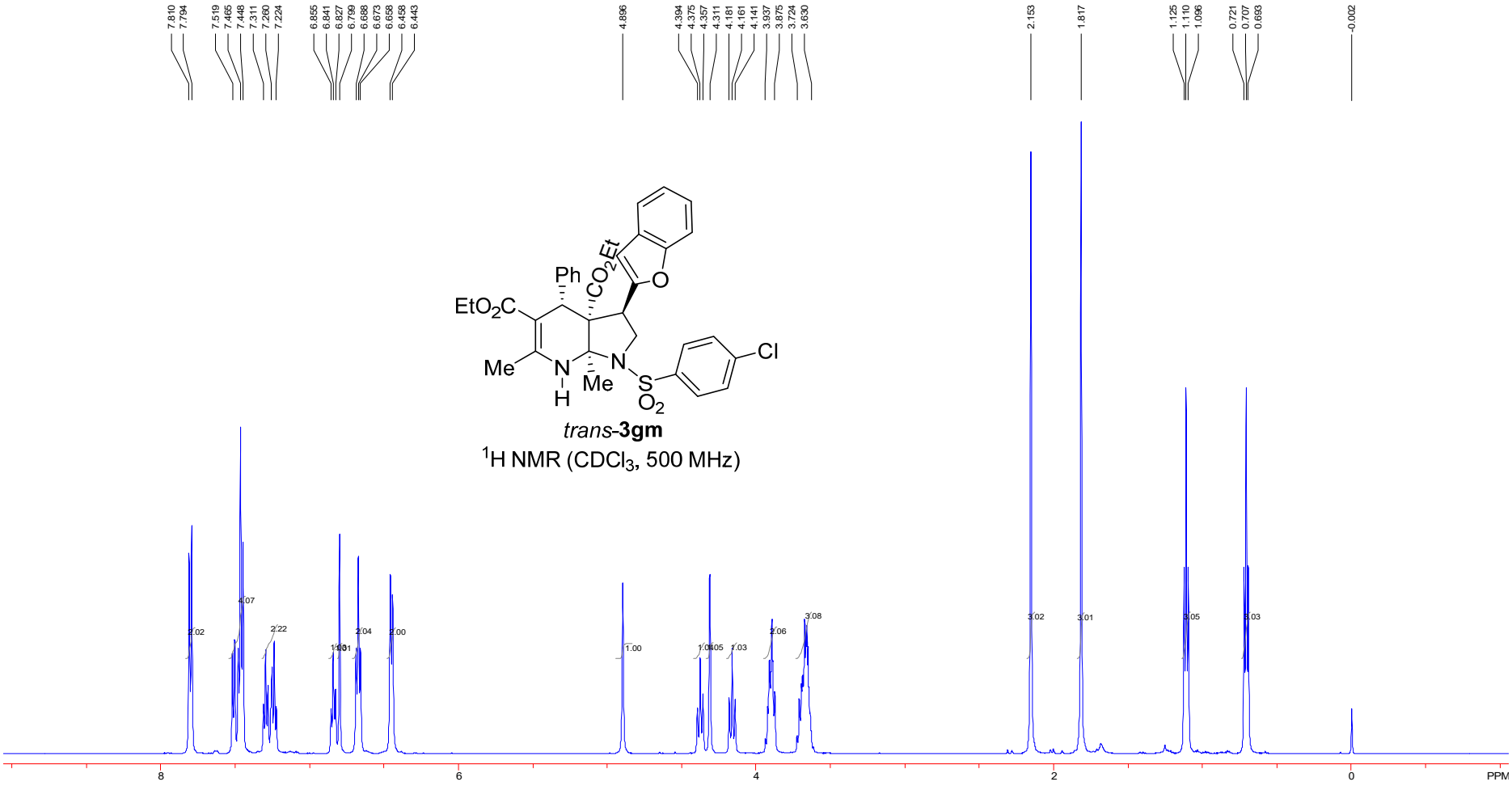
^{13}C NMR ($CDCl_3$, 125 MHz)

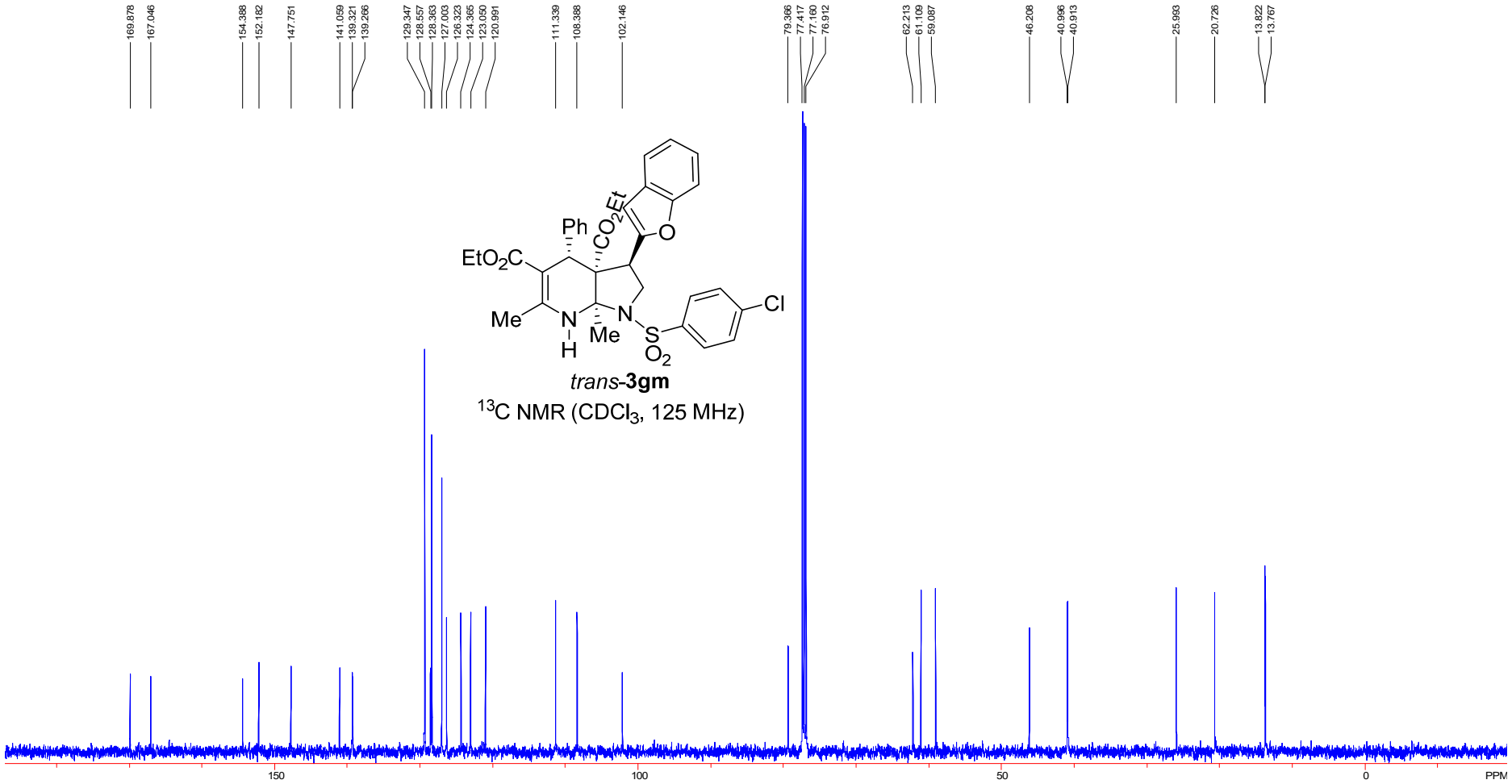

7.680
7.663
7.316
7.300
7.273
7.258
7.160
7.135
7.120
7.041
6.914
6.346
5.015
3.966
3.837
3.807
3.720
3.128
3.064
2.951
2.945
2.926
2.921
2.898
2.834
2.680
2.659
2.655
2.635
2.171
1.846
1.317
0.920
0.906
0.892
0.348
0.334
0.319
Bn
CO2Et
O
EtO2C
Me
N
H
N
Me
S
O2
Cl
trans-3fm
1H NMR (C6D6, 500 MHz)
8
6
4
2
0
PPM



trans-**3fm**

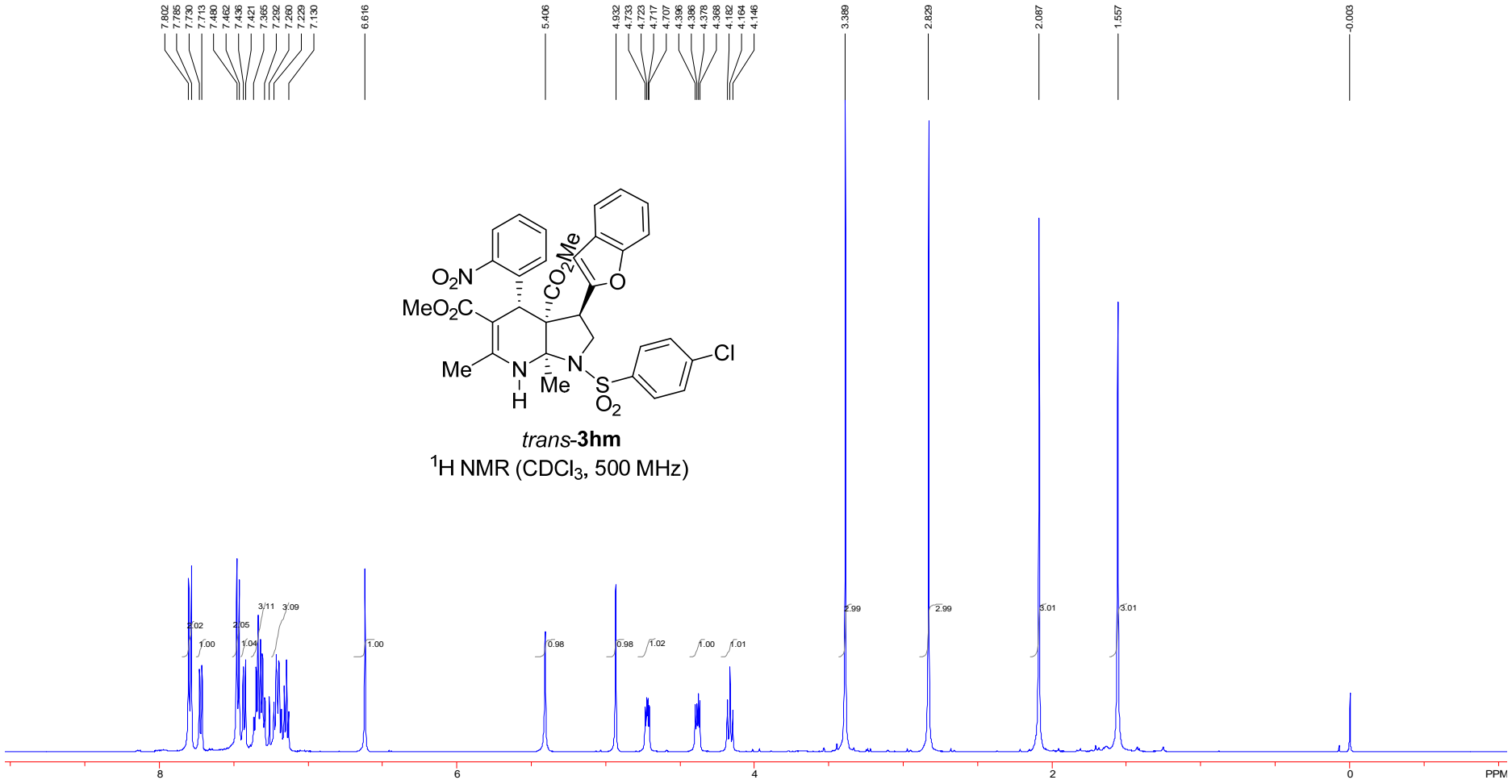
^{13}C NMR ($CDCl_3$, 125 MHz)


7.810
7.794
7.519
7.465
7.448
7.311
7.280
7.224
6.855
6.841
6.827
6.799
6.688
6.673
6.658
6.458
6.443
4.896
4.394
4.375
4.357
4.311
4.181
4.161
4.141
3.937
3.875
3.724
3.630
2.153
1.817
1.125
1.110
1.096
0.721
0.707
0.693
-0.002
Ph
CO2Et
EtO2C
O
Me
N
H
N
Me
S
O2
Cl
trans-3gm
1H NMR (CDCl3, 500 MHz)
2.02
4.07
2.22
1.01
1.01
2.04
2.00
1.00
1.05
1.03
2.06
3.08
3.02
3.01
3.05
3.03
8
6
4
2
0
PPM



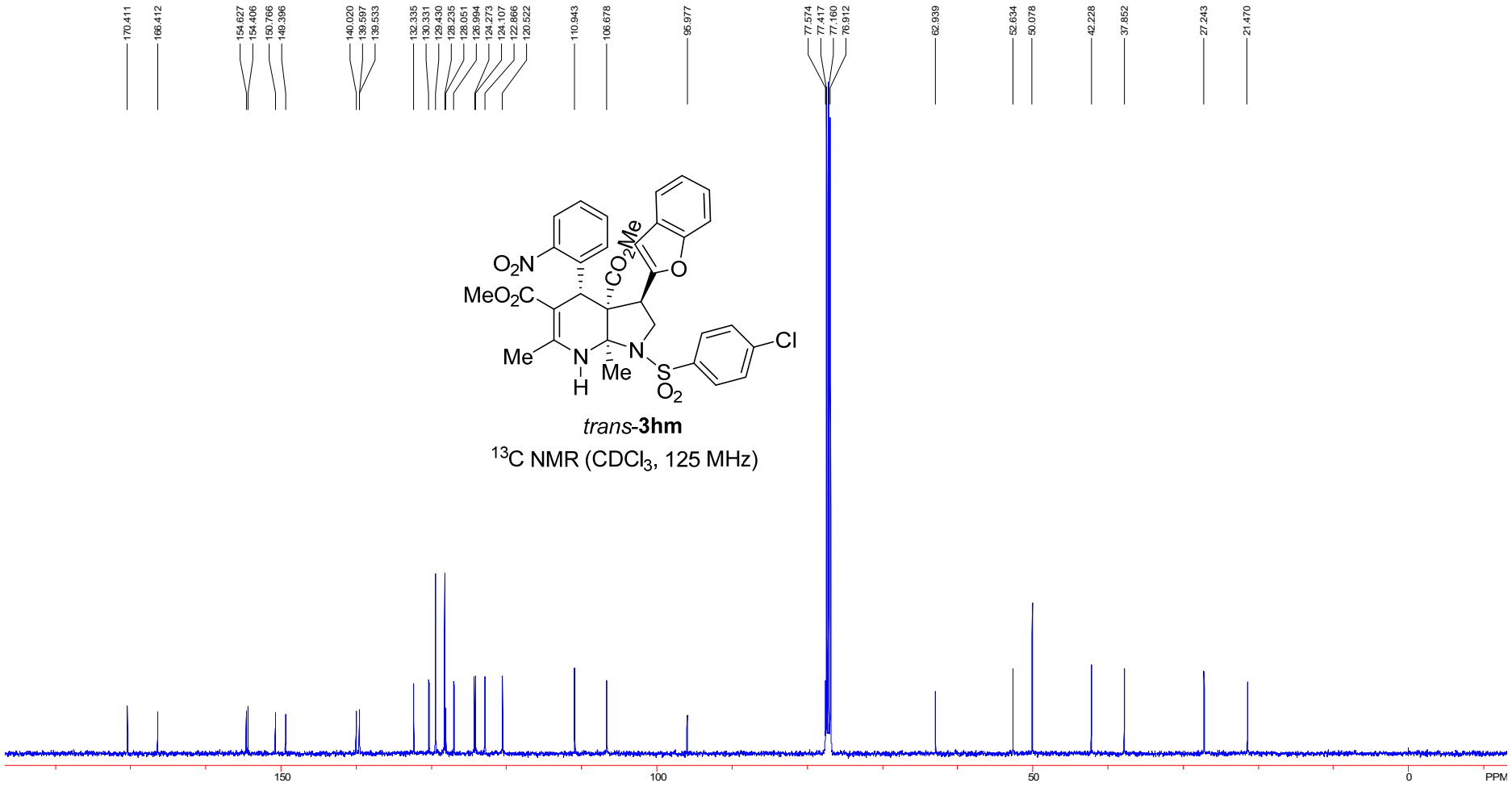
trans-**3gm**

^{13}C NMR ($CDCl_3$, 125 MHz)



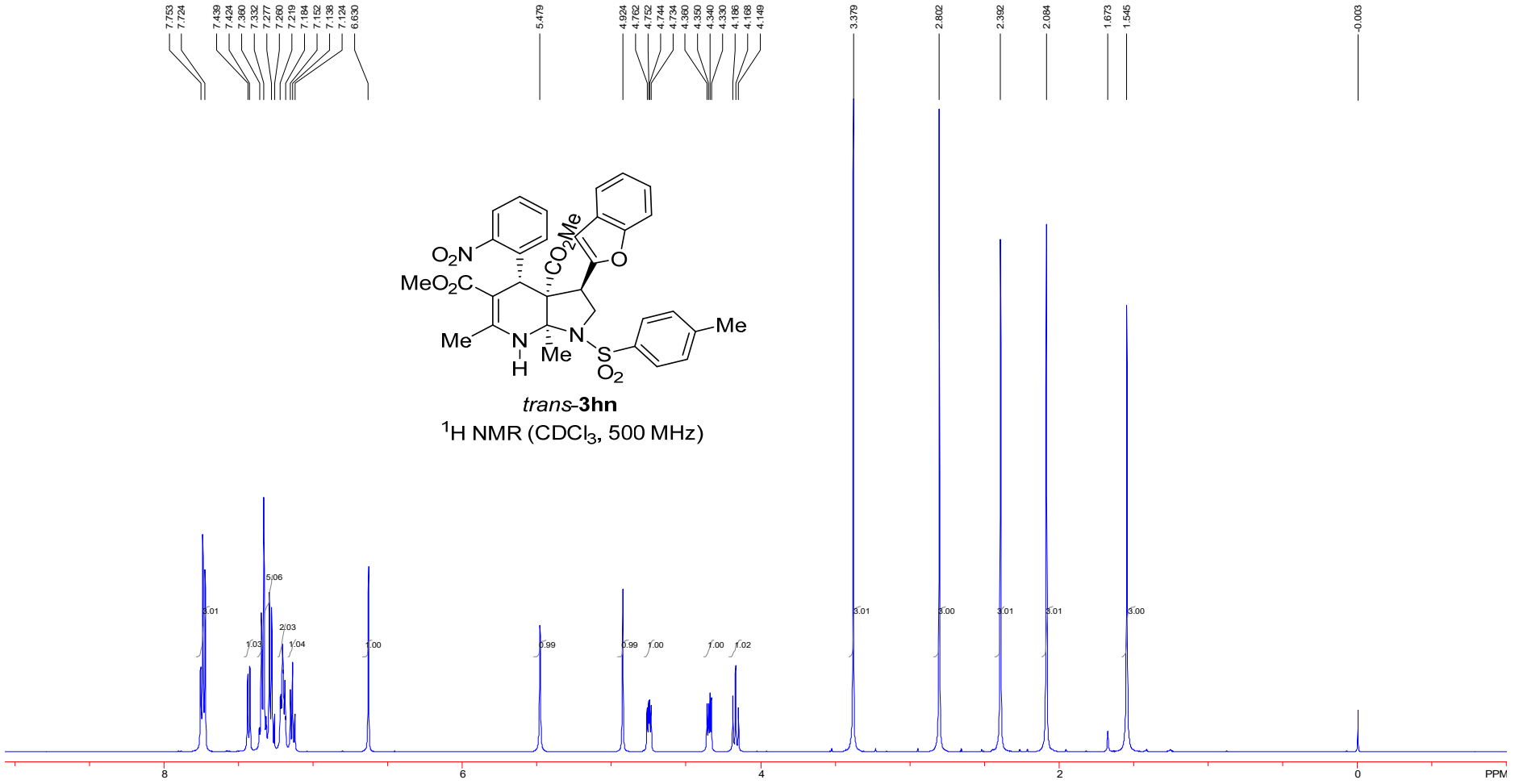
trans-**3hm**

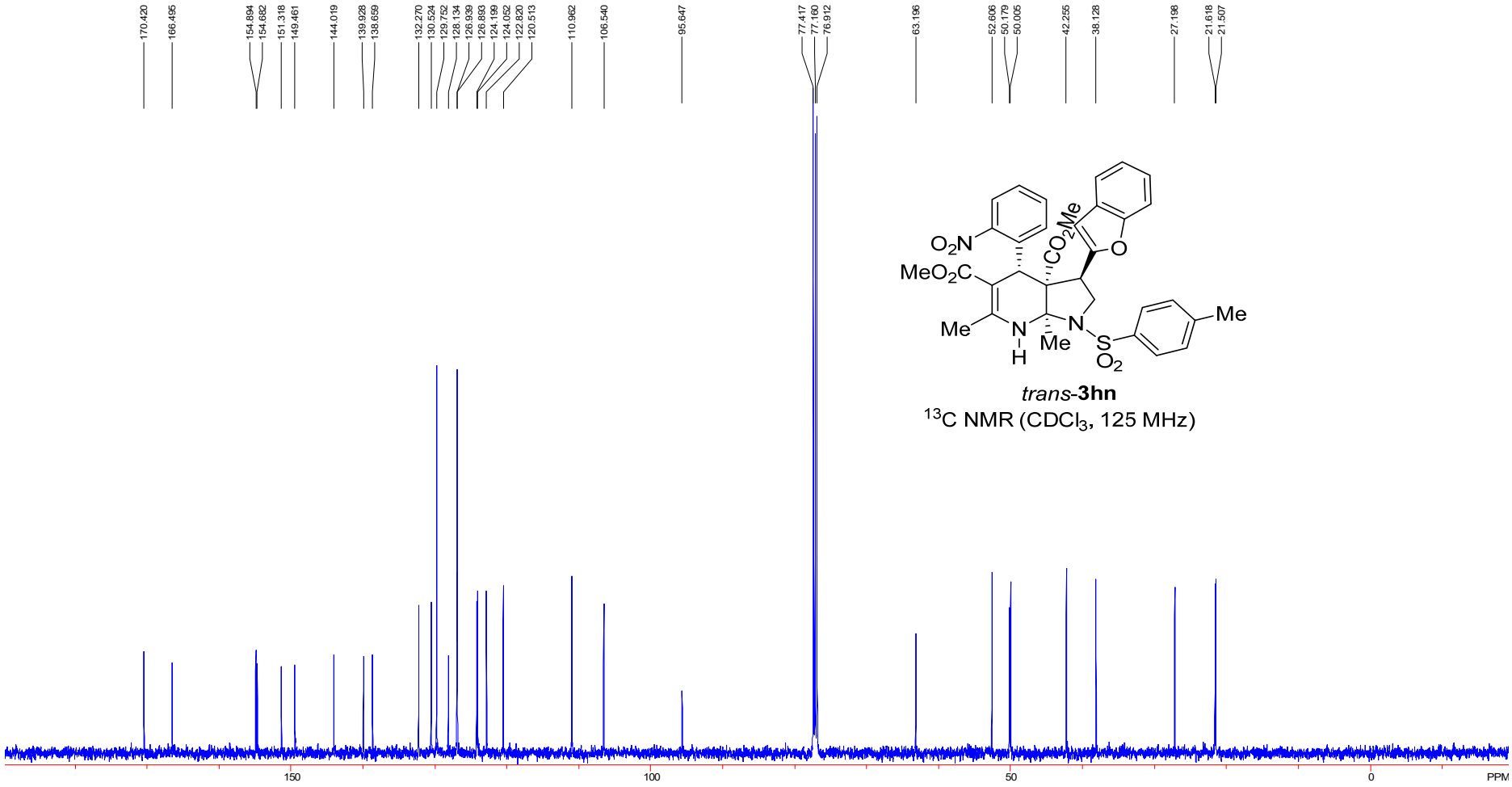
^{1}H NMR ($CDCl_3$, 500 MHz)



trans-**3hm**

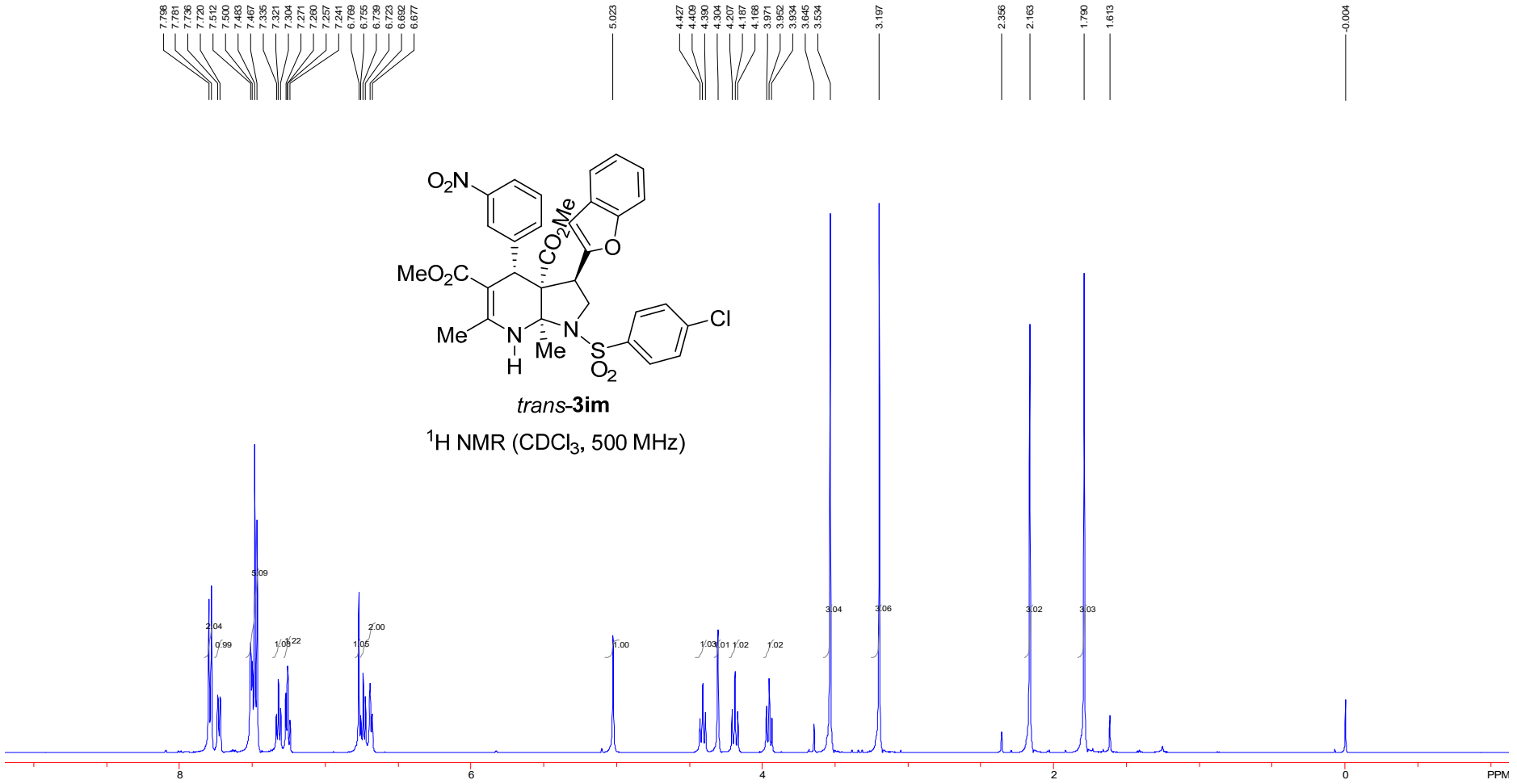
^{13}C NMR ($CDCl_3$, 125 MHz)

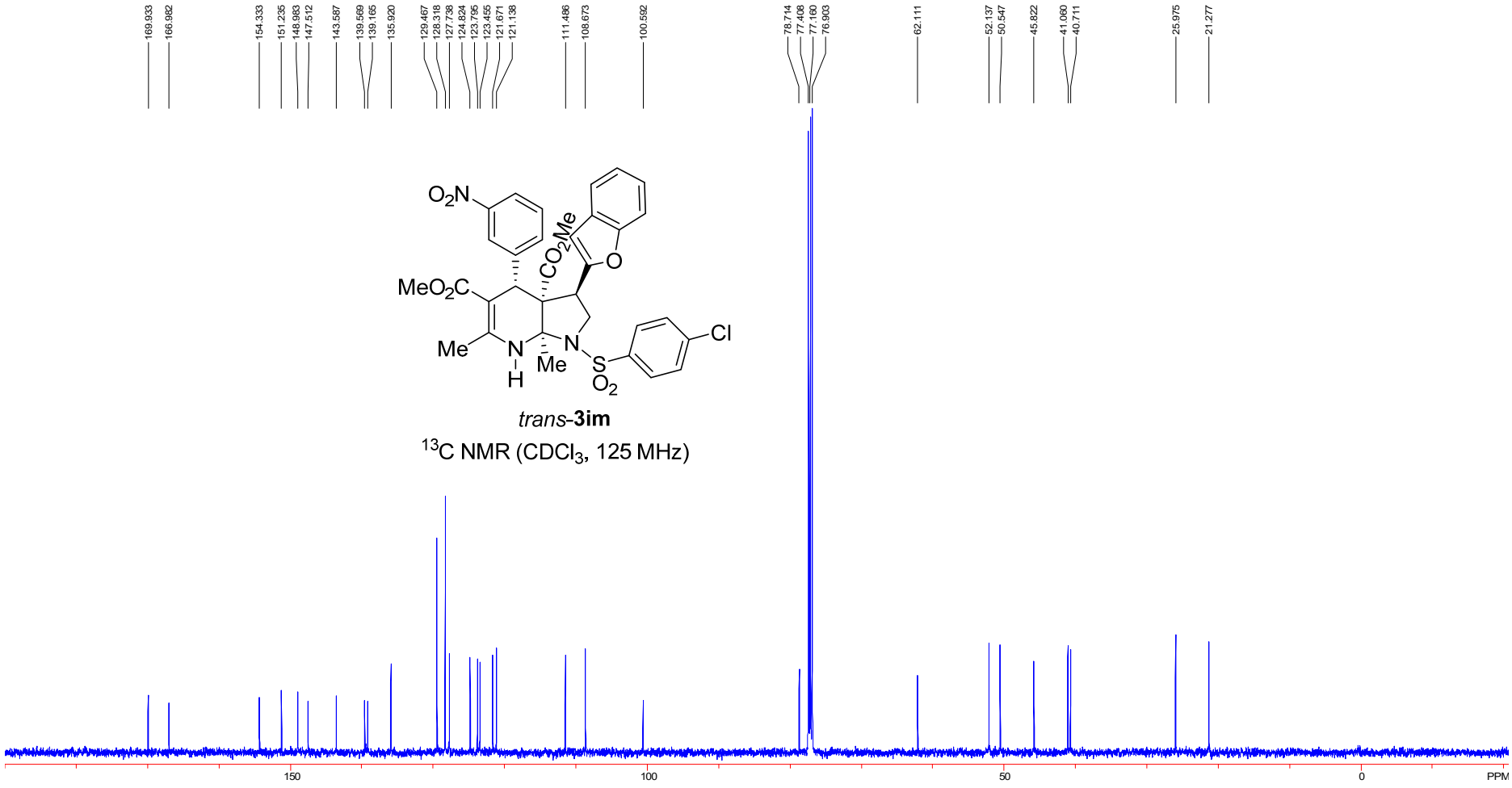

7.753
7.724
7.439
7.424
7.380
7.332
7.277
7.260
7.219
7.184
7.152
7.138
7.124
6.630
5.479
4.924
4.762
4.752
4.744
4.734
4.360
4.350
4.340
4.330
4.186
4.168
4.149
3.379
2.802
2.392
2.084
1.673
1.545
-0.003
O2N
MeO2C
CO2Me
O
Me
N
H
Me
N
S
O2
Me
trans-3hn
1H NMR (CDCl3, 500 MHz)
3.01
5.06
2.03
1.03
1.04
1.00
0.99
0.99
1.00
1.00
1.02
3.01
3.00
3.01
3.01
3.00
8
6
4
2
0
PPM



trans-**3hn**

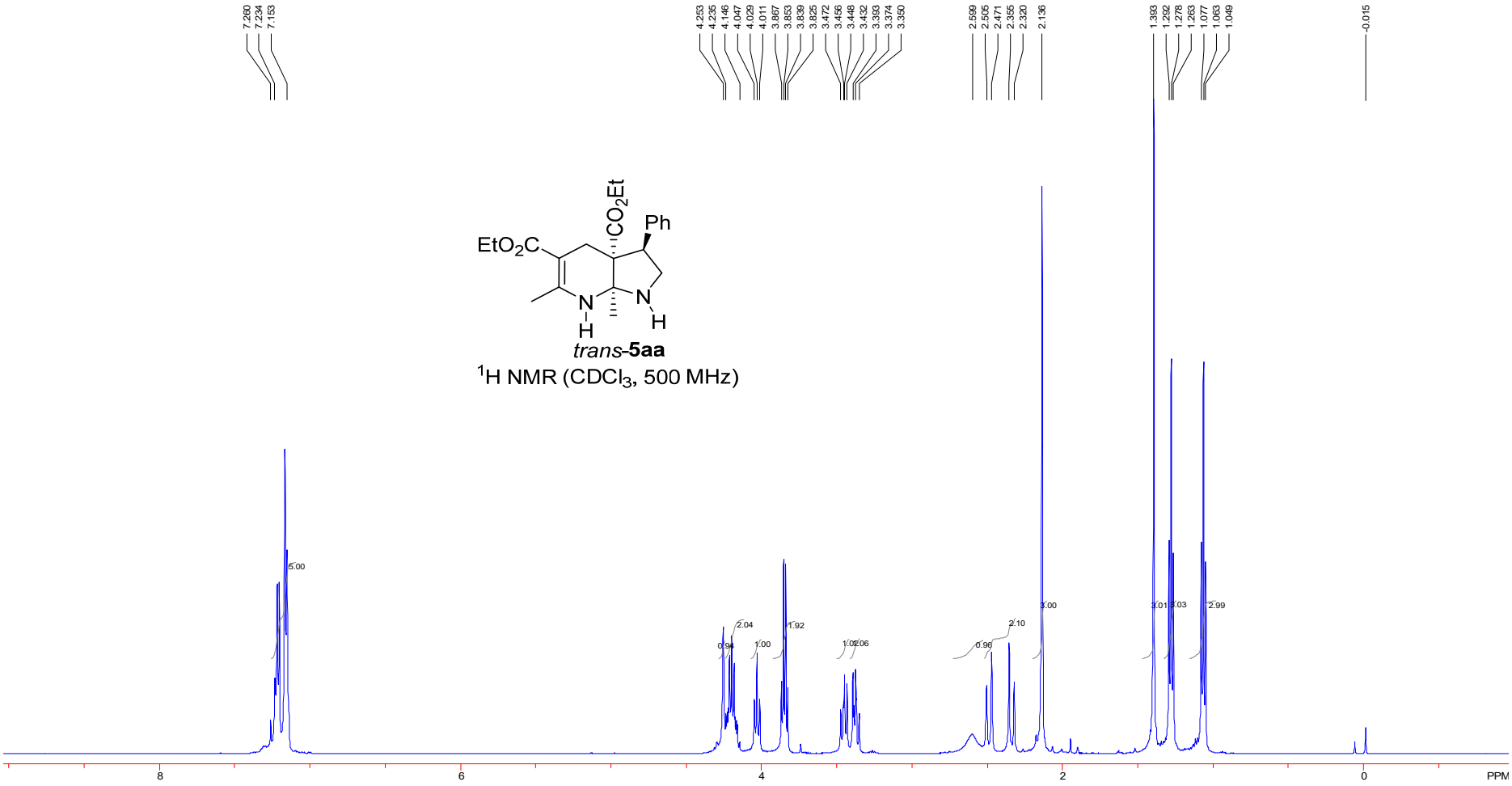
^{13}C NMR ($CDCl_3$, 125 MHz)

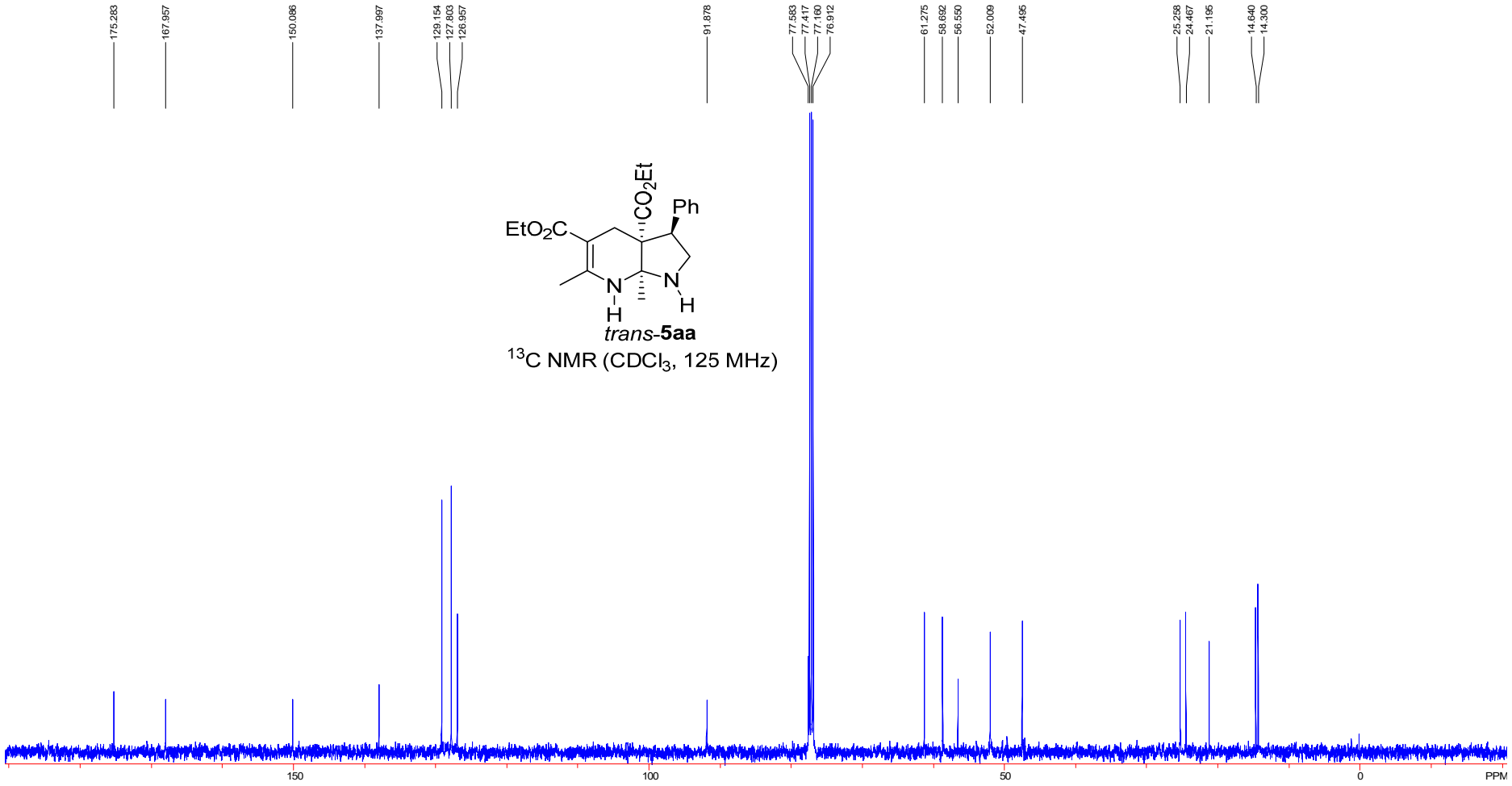

7.798
7.781
7.736
7.720
7.512
7.500
7.483
7.467
7.335
7.321
7.304
7.271
7.260
7.257
7.241
6.769
6.755
6.739
6.723
6.692
6.677
5.023
4.427
4.409
4.390
4.304
4.207
4.187
4.168
3.971
3.962
3.934
3.645
3.534
3.197
2.355
2.163
1.790
1.613
-0.004
O2N
CO2Me
O
MeO2C
Me
N
H
N
Me
S
O2
Cl
trans-3im
1H NMR (CDCl3, 500 MHz)
2.04
0.99
5.09
1.03
1.22
1.05
2.00
1.00
1.03
1.01
1.02
1.02
3.04
3.06
3.02
3.03
8
6
4
2
0
PPM



trans-**3im**

^{13}C NMR ($CDCl_3$, 125 MHz)


7.260
7.234
7.153
4.253
4.235
4.146
4.047
4.029
4.011
3.867
3.853
3.839
3.825
3.472
3.456
3.448
3.432
3.393
3.374
3.350
2.599
2.505
2.471
2.355
2.320
2.136
1.393
1.292
1.278
1.263
1.077
1.063
1.049
-0.015
EtO2C
CO2Et
Ph
N
H
N
H
trans-5aa
1H NMR (CDCl3, 500 MHz)
5.00
0.94
2.04
1.00
1.92
1.02
2.06
0.96
2.10
3.00
3.01
3.03
2.99
8
6
4
2
0
PPM



trans-**5aa**

^{13}C NMR ($CDCl_3$, 125 MHz)