

Supporting Information

Planar chiral [2.2]paracyclophane-based phosphine-phenols: Use in enantioselective [3+2] annulations of allenoates and *N*-tosylimines

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Contents

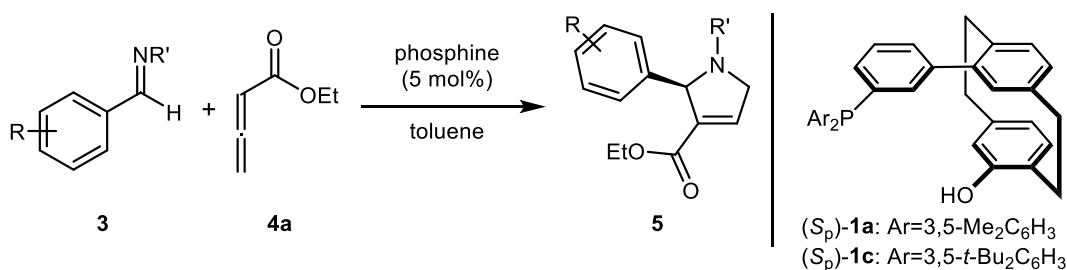
(1)	General Information	S2
(2)	Effects of the substituent on the imine nitrogen atom	S2
(3)	Preparation of catalyst (<i>S_p</i>)- 1c	S2
(4)	Determination of the absolute configuration for 5j and 5m	S4
(5)	¹ H and ¹³ C NMR Spectra	S5
(6)	HPLC Data	S29

(1) General Information

Melting point (mp) was measured by Yanaco melting point apparatus MP-500D and uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded by a Bruker Avance III 600 spectrometer operating at 600 MHz (150 MHz for ^{13}C NMR) at 25 °C with tetramethylsilane ($\delta = 0.0$ ppm) as an internal standard. The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant (Hz). ^{31}P NMR spectra were recorded with 85% H_3PO_4 ($\delta = 0.0$ ppm) as an external standard. High resolution mass spectra were measured with a JEOL JMS-3000. Analytical thin-layer chromatography (TLC) was performed on MERCK silica gel, grade 60 F₂₅₄. The spots and bands were detected by UV light of irradiation (254 nm) and/or by staining with 5% phosphomolybdic acid followed by heating. Column chromatography for isolation of the products was carried out on KANTO Sillica Gel 60 (230-400 mesh). HPLC analyses were performed using Interigent UV/VIS Detector JASCO UV-7500. The chiral columns included CHIRALCEL OD-H and CHIRALPAK AD-H (Daicel Chemical Industries, Ltd., 0.46 $\Phi \times 25$ cm).

Materials Aldimines **3a–o** were prepared by using reported methods.¹ Allenates **4b–d** were prepared from the appropriate phosphorane according to the literature.² Commercially available reagents were used throughout without purification unless otherwise stated. Catalysts (*S_p*)-**1a**³ and **1b**⁴ were prepared using reported method in our previous paper.

(2) Effects of the substituent on the imine nitrogen atom.^a



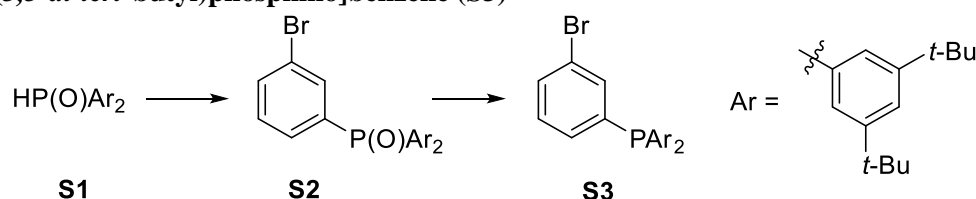
Entry	R	R'	Phosphine	Temp.	<i>t</i>	Yield (%) ^b	Ee (%) ^c
1	4-Cl	Ts	(<i>S_p</i>)- 1a	rt	25 min	96	40
2	4-Cl	Ms	(<i>S_p</i>)- 1a	rt	40 min	95	37
3	4-Cl	2-Naphthalene-sulfonyl	(<i>S_p</i>)- 1a	rt	20 min	90	39
4	4-Cl	DPP	(<i>S_p</i>)- 1a	rt	48 h	10	37
5	4-Cl	Ts	(<i>S_p</i>)- 1c	-30 °C	7 h	99	80
6	4-Cl	Ms	(<i>S_p</i>)- 1c	-30 °C	6 h	88	78
7	4-Cl	2-Naphthalene-sulfonyl	(<i>S_p</i>)- 1c	-30 °C	6 h	99	73

^a Reaction conditions: **3** (0.05 mmol), **4a** (0.11 mmol), catalyst (2.5×10^{-3} mmol) in toluene (0.5 mL) at room temperature.

^b Isolated yield. ^c Determined by HPLC analysis using a chiral stationary phase.

(3) Preparation of catalyst (*S_p*)-1c

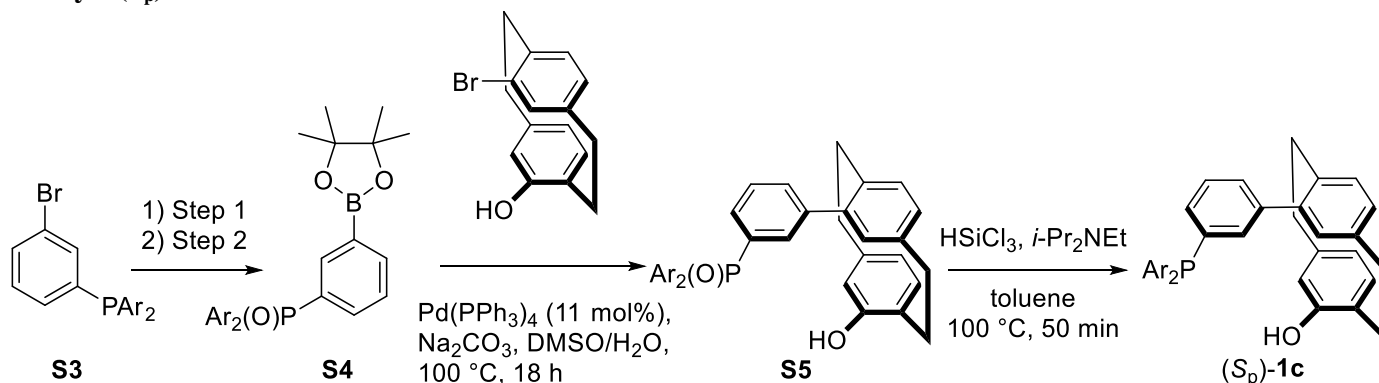
1-Bromo-3-[bis(3,5-di-*tert*-butyl)phosphino]benzene (**S3**)



This reaction was carried out under Ar. To a solution of phosphine oxide **S1**⁵ (2.03 g, 4.76 mmol), DPPP (176 mg, 0.426 mmol) and Pd(OAc)₂ (107 mg, 0.475 mmol) in DMSO (54.2 mL) were added 3-bromoiodobenzene (0.55 mL, 4.33 mL) and *i*-Pr₂NEt (2.28 mL, 13.1 mmol). After being stirred for 10 h at 100 °C, the reaction mixture was quenched with 10% aqueous HCl (26.7 mL), and extracted with EtOAc (50 mL x 3). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography (EtOAc/hexane, 5:1) on silica gel to provide 1.73 g (65%) of **S2** as a yellow oil.

To a cooled (0 °C) stirred solution of the phosphine oxide **S2** (1.73 g, 2.97 mmol) in toluene (26 mL) were added HSiCl₃ (3.0 mL, 30 mmol) and *i*-Pr₂NEt (10 mL, 57 mmol). After being stirred for 2 h at 80 °C, the mixture was quenched with 25% aqueous NaOH (70 mL). The precipitated solids were removed by filtration through a pad of Celite and washed well with EtOAc. The filtrate was extracted with EtOAc (30 mL × 3). The combined extracts were washed with water (100 mL) and saturated brine (100 mL), respectively. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane only) to provide 1.44 g (86%) of **S3** as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 1.25 (s, 36H), 7.14 (d, 2H, *J* = 1.8 Hz), 7.15 (d, 2H, *J* = 1.8 Hz), 7.16-7.21 (m, 2H), 7.39-7.41 (m, 2H), 7.42 (dt, 1H, *J* = 5.4, 1.8 Hz), 7.46 (dt, 1H, *J* = 6.6, 1.8 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 31.4 (12C), 34.9 (4C), 122.7, 122.9 (4C), 128.2 (d, 4C, *J*_{c-p} = 21.0 Hz), 129.7 (d, *J*_{c-p} = 21.0 Hz), 131.2 (2C), 131.8 (d, *J*_{c-p} = 18.0 Hz), 135.4 (d, *J*_{c-p} = 9.0 Hz), 135.9 (d, *J*_{c-p} = 19.5 Hz), 142.0 (d, *J*_{c-p} = 16.5 Hz), 150.8 (d, 2C, *J*_{c-p} = 6.0 Hz). HRMS (MALDI) calcd for C₃₄H₄₇PBr [*M*+H]⁺: 565.2593, found: 565.2611.

Catalyst (*S_p*)-1c



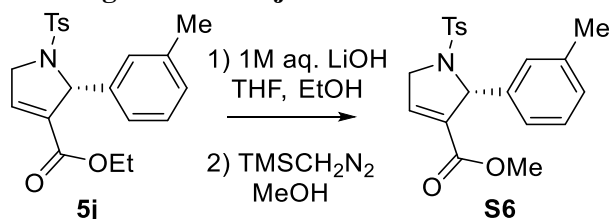
Procedure for preparation of **S4** from **S3**: The following reaction was carried out under Ar. (**Step 1**) To a cooled (−78 °C) solution of **S3** (200 mg, 0.354 mmol) in THF (2.1 mL) was slowly added *n*-BuLi (0.29 mL, 0.46 mmol, 1.6 M in hexane solution). After stirring for 30 min at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.22 mL, 1.1 mmol) was added to the mixture at that temperature. Then the reaction mixture was stirred for 14.3 h at room temperature, quenched with water, and extracted with CH₂Cl₂ (15 mL × 4). The combined extracts were washed with water (30 mL) and brine (30 mL), dried over Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography (EtOAc/hexane, 1:80) on silica gel to provide 100.5 mg (46%) of borylated compound as white solids.

(**Step 2**) A stirred solution of the compound obtained in **step 1** (135 mg, 0.221 mmol), FeCl₃·6H₂O (6.0 mg, 0.022 mmol), KSCN (10.8 mg, 0.111 mmol) and I₂ (cat. amount) in dry MeCN (2.4 mL) was heated at 80 °C with vigorous O₂ bubbling. After being stirred for 1 h at 80 °C, the mixture was cooled to room temperature, and concentrated under reduced pressure. The residue was extracted with EtOAc (40 mL × 3). The combined extracts were washed with saturated aqueous Na₂S₂O₃ (30 mL), water (30 mL) and brine (30 mL), dried over Na₂SO₄ and concentrated to provide 140.9 mg (quant.) of **S4** as light green solids.

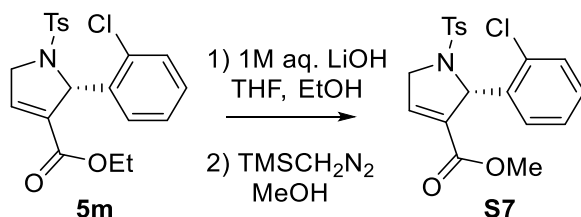
Procedure for preparation of (*S_p*)-1c: To a solution of **S4** (126 mg, 0.200 mmol) in DMSO (3.0 mL) and H₂O (0.3 mL) were added (*S_p*)-12-bromo[2.2]paracyclophan-4-ol (60.6 mg, 0.200 mmol), Na₂CO₃ (63.6 mg, 0.600 mmol) and Pd(PPh₃)₄ (26.3 mg, 0.0228 mmol, 11 mol%). After being stirred for 18 h at 100 °C, the mixture was diluted with water and extracted with EtOAc (30 mL × 2). The combined extracts were washed with saturated brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH₂Cl₂/EtOAc/hexane, 2:1:4) to provide **S5** (116 mg, 80%) as yellow solids. To a solution of **S5** (114 mg, 0.157 mmol) in toluene (1.4 mL) were added HSiCl₃ (0.16 mL, 1.6 mmol) and *i*-Pr₂NEt (0.55 mL, 3.2 mmol) at 0 °C. After being stirred for 50 min at 100 °C, the reaction mixture was quenched with saturated aqueous NaHCO₃ (9 mL) and extracted with EtOAc (40 mL × 2). The combined extracts were washed with saturated brine (40 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 70.8 mg (63%) of (*S_p*)-1c as colorless solids: mp 163-164 °C; [α]_D²⁵ = +7.85 (*c* = 0.46 in CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ 1.24 (s, 18H), 1.26 (s, 18H), 2.26 (m, 1H), 2.56 (m, 1H), 2.70-2.92 (m, 2H), 2.85-2.95 (m, 2H), 3.03 (t, 1H, *J* = 11.4 Hz), 3.25-3.39 (m, 2H), 5.13 (d, 1H, *J* = 1.2 Hz), 6.18 (dd, 1H, *J* = 7.8, 1.2 Hz), 6.37 (dd, 1H, *J* = 7.8, 1.2 Hz), 6.40 (d, 1H, *J* = 7.8 Hz), 6.60 (d, 1H, *J* = 7.8 Hz), 6.78 (d, 1H, *J* = 1.8 Hz), 7.10 (d, 1H, *J* = 5.4 Hz), 7.20-7.25 (m, 4H), 7.34 (d, 1H, *J* = 7.8 Hz), 7.38 (td, 1H, *J* = 7.8, 1.8 Hz), 7.41-7.50 (m, 2H), 7.54 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 31.1, 31.4 (6C), 31.5 (6C), 33.1, 33.9, 34.2, 34.9 (2C), 35.0 (2C), 118.0, 123.0 (d, *J*_{c-p} = 18.0 Hz), 124.5, 125.4, 128.1, 128.2, 128.3, 130.8, 132.2, 132.5, 132.7 (d, *J*_{c-p} = 4.5 Hz), 135.1, 135.3, 135.8 (d, *J*_{c-p} = 9.0 Hz), 136.1, 136.8 (d, *J*_{c-p} = 9.0 Hz), 138.9 (d, *J*_{c-p} = 12.0 Hz), 140.0, 141.2, 141.3,

141.7, 151.0 (d, $J_{c-p} = 7.5$ Hz), 153.1; ^{31}P NMR (242 MHz, CDCl_3): $\delta -3.21$. HRMS (MALDI) calcd for $\text{C}_{50}\text{H}_{62}\text{OP}$ $[M+H]^+$: 709.4528, found: 709.4533.

(4) Determination of the absolute configuration for **5j** and **5m**



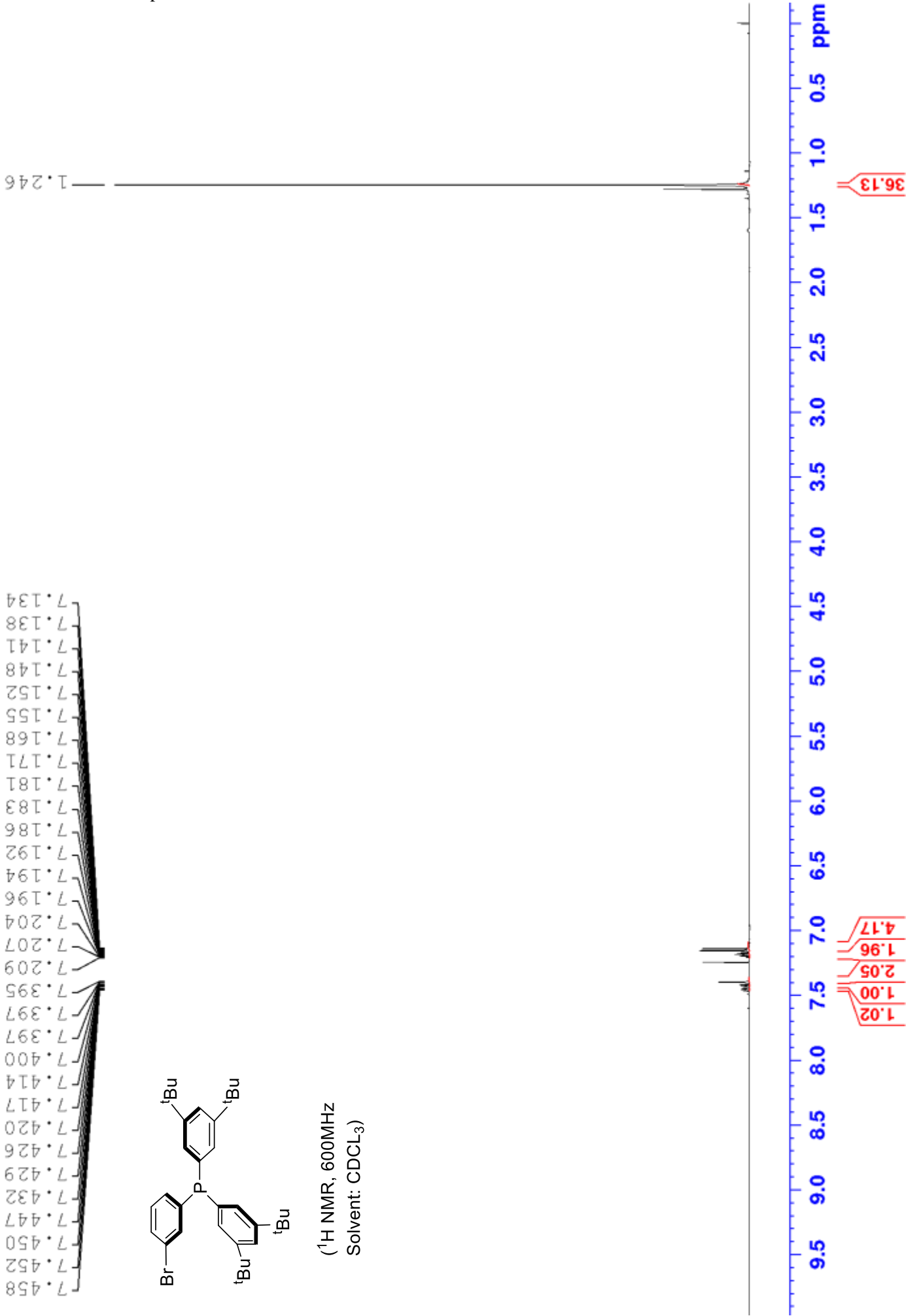
To a cooled ($0\text{ }^\circ\text{C}$) stirred solution of **5j** (18.0 mg, 0.0467 mmol, 84% *ee*) in THF (0.9 mL) and EtOH (0.9 mL) was added 1M aqueous LiOH (0.9 mL) slowly. After being stirred at room temperature for 1.5 h, the mixture was quenched with 2M aqueous HCl (2 mL) and extracted with EtOAc (30 mL \times 3). The combined extracts were washed with saturated brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure to provide the crude product (18.3 mg), which was used in the next step without further purification. To a cooled ($0\text{ }^\circ\text{C}$) stirred solution of the crude product (13.5 mg) in MeOH (0.5 mL) was added TMSCH_2N_2 (0.6 M in hexane) (0.38 mL, 0.23 mmol). After being stirred for 20 min at $0\text{ }^\circ\text{C}$, the mixture was concentrated under reduced pressure. The residue was purified by PTLTC (EtOAc/hexane, 1:2) to provide 9.9 mg (70%) of **S6** as a colorless oil: $[\alpha]_{\text{D}}^{26} = -120$ ($c = 0.49$ in CHCl_3); {ref. 6 (*S*)-**S6**; $[\alpha]_{\text{D}}^{26} = -157$ ($c = 1.02$ in CHCl_3) for 87% *ee*}. ^1H NMR (600 MHz, CDCl_3): δ 2.23 (s, 3H), 2.37 (s, 3H), 3.59 (s, 3H), 4.43-4.55 (m, 2H), 5.70 (dt, 1H, $J = 5.4, 1.8$ Hz), 6.77 (q, 1H, $J = 1.8$ Hz), 6.90 (s, 1H), 7.03 (d, 2H, $J = 7.8$ Hz), 7.10-7.15 (m, 3H), 7.60 (d, 2H, $J = 7.8$ Hz).

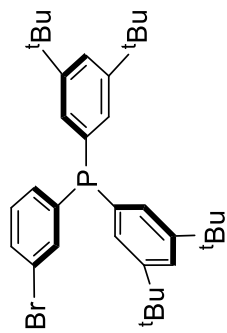


To a cooled ($0\text{ }^\circ\text{C}$) stirred solution of **5m** (15.8 mg, 0.0389 mmol, 90% *ee*) in THF (0.8 mL) and EtOH (0.8 mL) was added 1M aqueous LiOH (0.8 mL) slowly. After being stirred at room temperature for 1.5 h, the mixture was quenched with 2M aqueous HCl (2 mL) and extracted with EtOAc (30 mL \times 3). The combined extracts were washed with saturated brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure to provide the crude product (18.1 mg), which was used in the next step without further purification. To a cooled ($0\text{ }^\circ\text{C}$) stirred solution of the crude product (18.1 mg) in MeOH (0.5 mL) was added TMSCH_2N_2 (0.6 M in hexane) (0.38 mL, 0.23 mmol). After being stirred for 20 min at $0\text{ }^\circ\text{C}$, the mixture was concentrated under reduced pressure. The residue was purified by PTLTC (EtOAc/hexane, 1:2) to provide 10.5 mg (68%) of **S7** as a colorless oil: $[\alpha]_{\text{D}}^{26} = -240$ ($c = 0.51$ in CHCl_3); {ref. 6 (*S*)-**S7**; $[\alpha]_{\text{D}}^{26} = -206$ ($c = 0.98$ in CHCl_3) for 83% *ee*}. ^1H NMR (600 MHz, CDCl_3): δ 2.39 (s, 3H), 3.57 (s, 3H), 4.43-4.55 (m, 2H), 6.14 (m, 1H), 6.79 (q, 1H, $J = 1.8$ Hz), 7.13-7.19 (m, 3H), 7.21 (d, 2H, $J = 8.4$ Hz), 7.30 (m, 1H), 7.60 (d, 2H, $J = 8.4$ Hz).

References

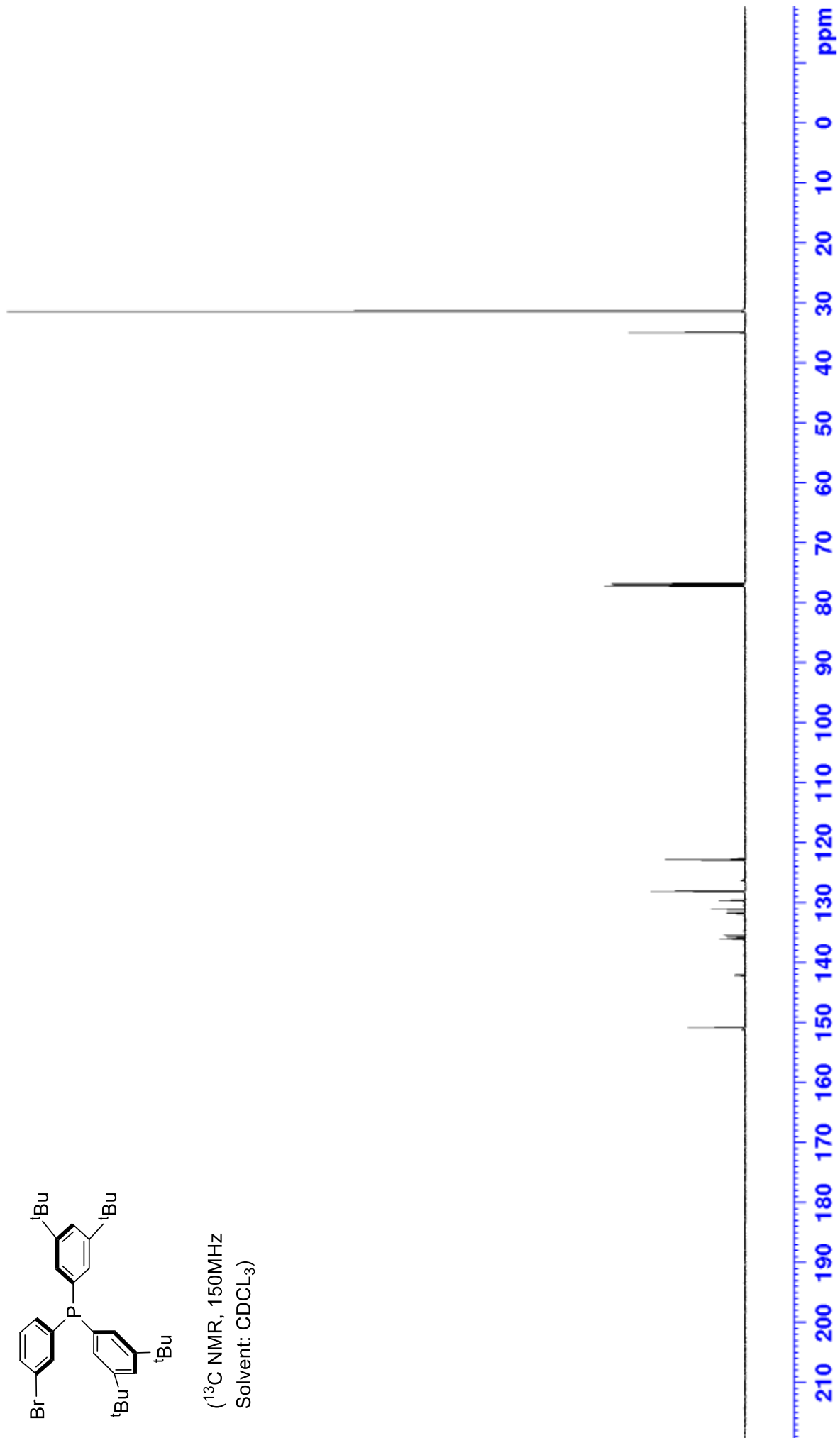
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2. a) G. Wang, X. Liu, Y. Chen, J. Yang, J. Li, L. Lin, X. Feng, *ACS Catal.* **2016**, *6*, 2482. b) B. J. Cowen, L. B. Saunders, S. J. Miller, *J. Am. Chem. Soc.* **2009**, *131*, 6105. c) C.-Y. Li, X.-B. Wang, X.-L. Sun, Y. Tang, J.-C. Zheng, Z.-H. Xu, Y.-G. Zhou, L.-X. Dai, *J. Am. Chem. Soc.* **2007**, *129*, 1494.
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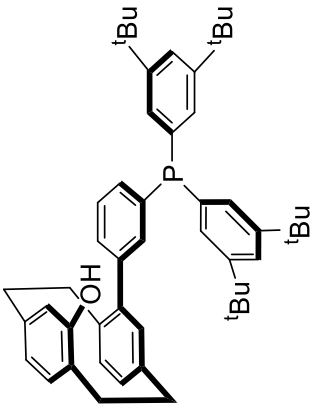


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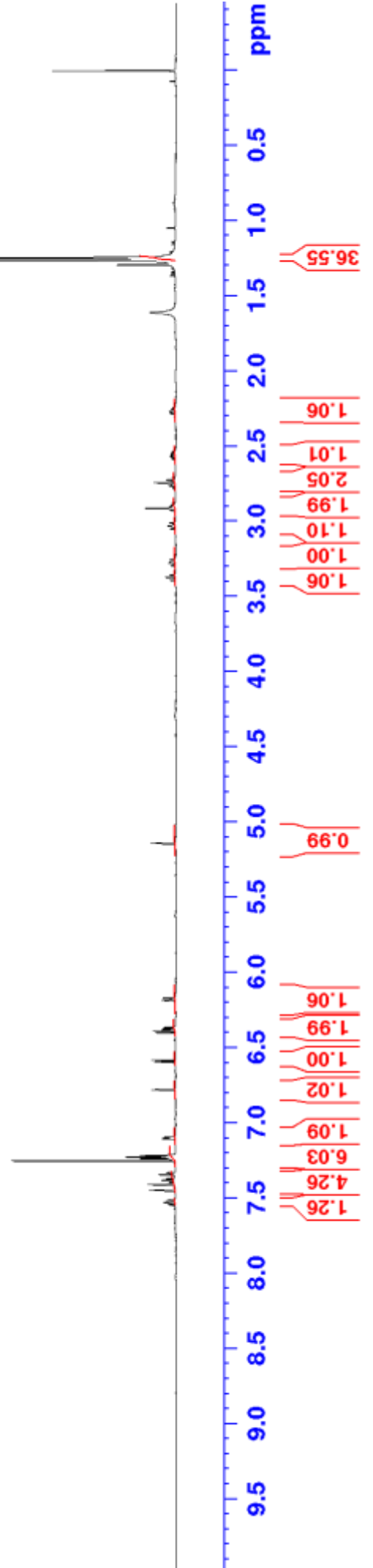
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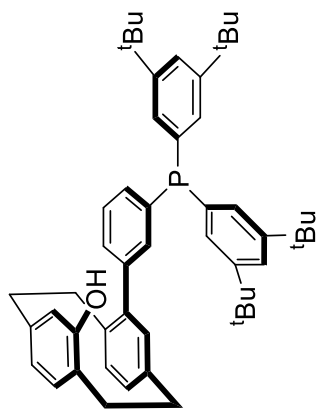


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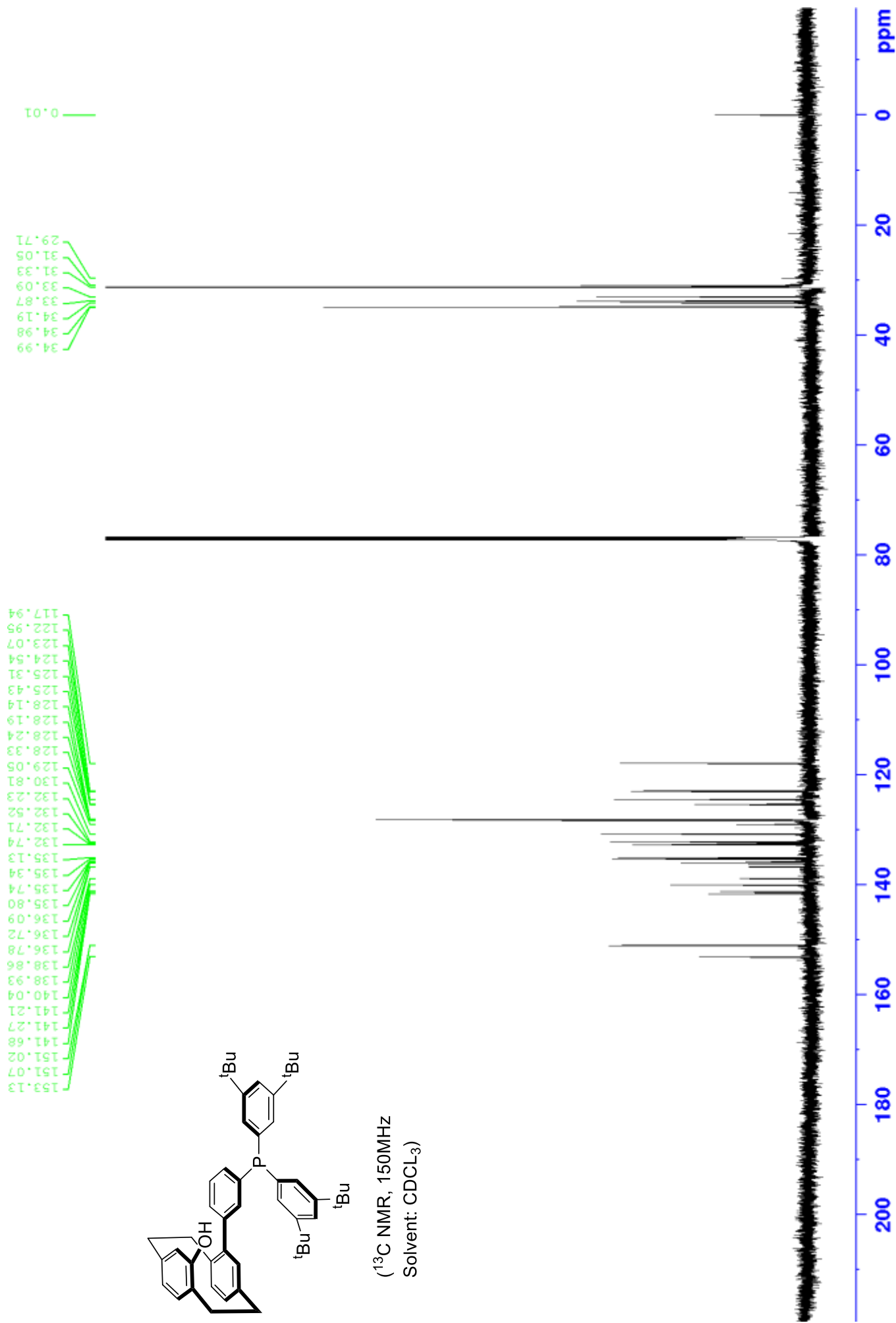


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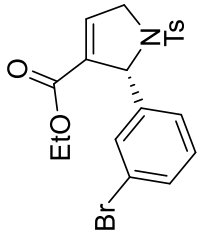




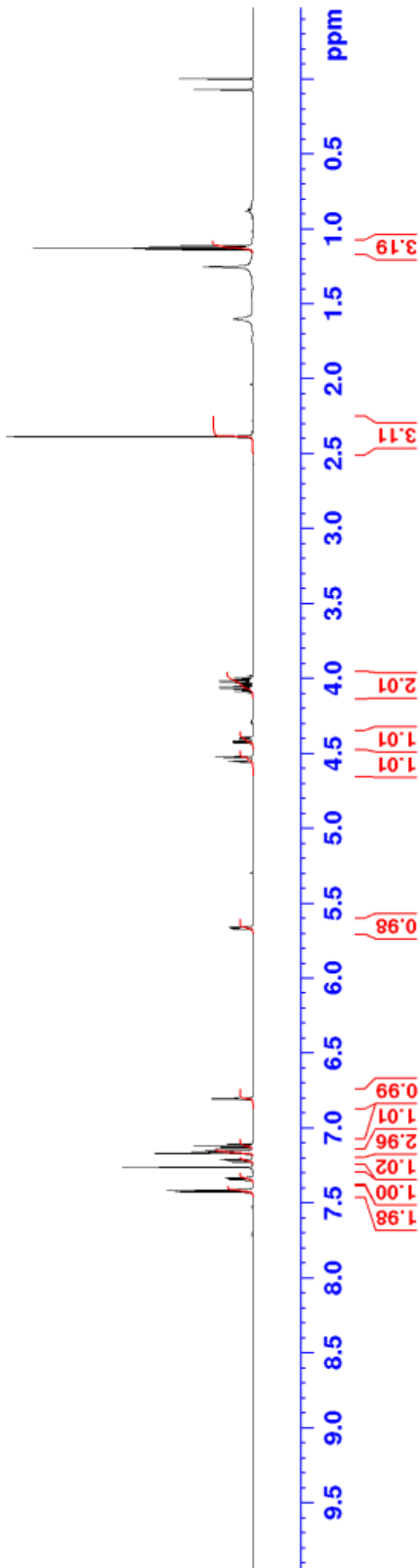
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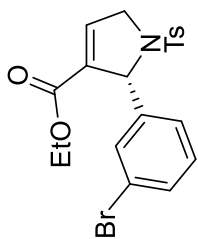


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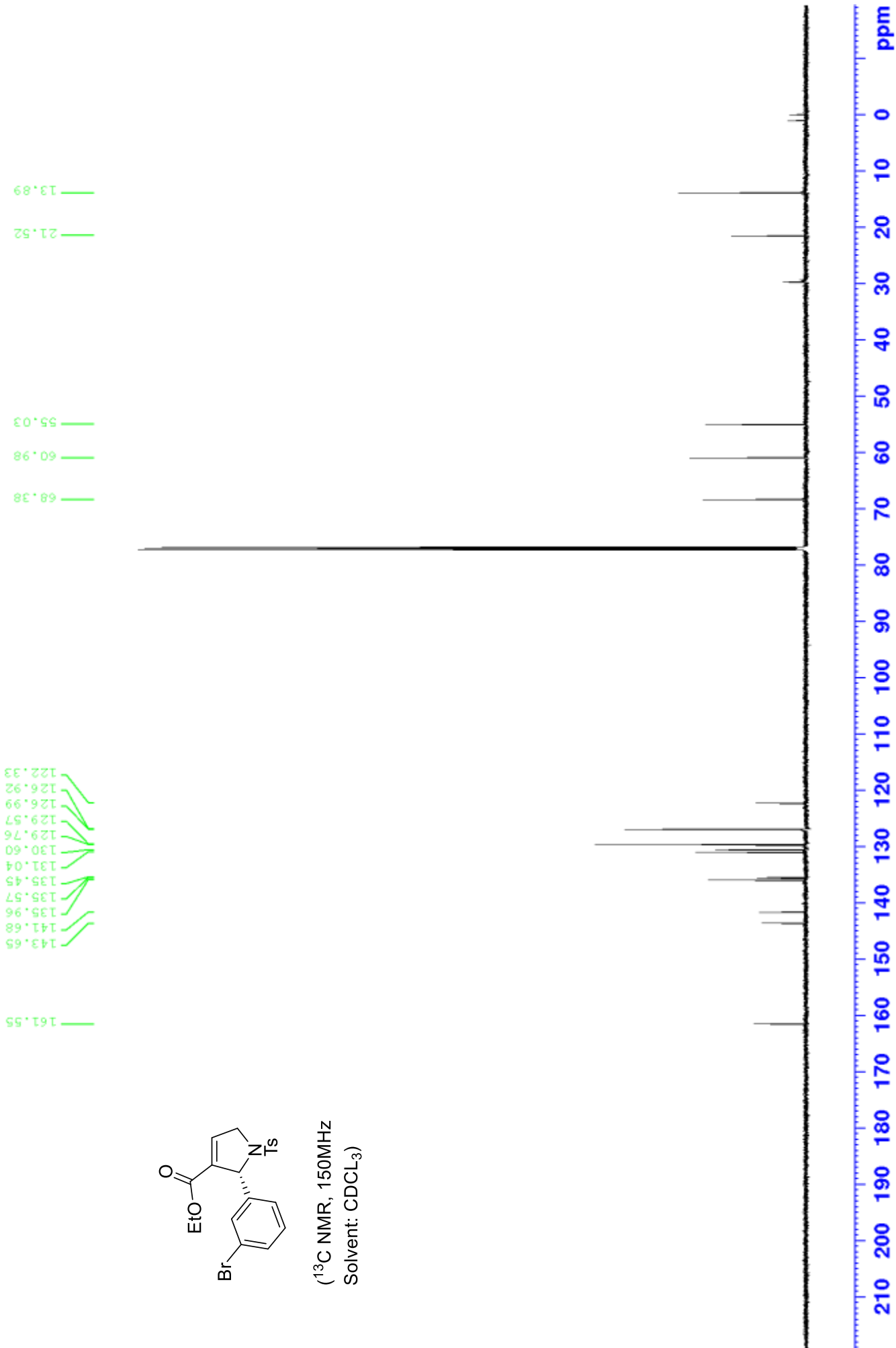


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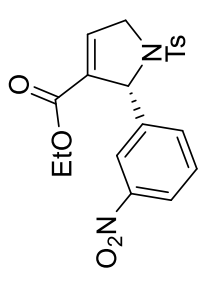




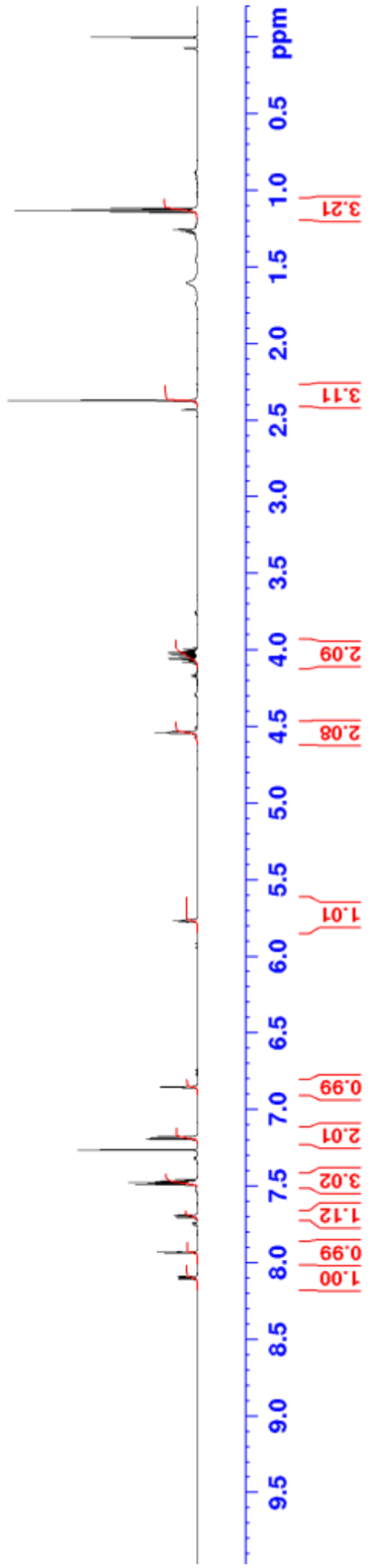
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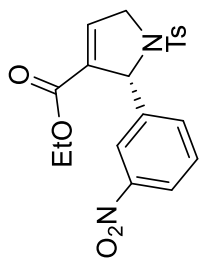


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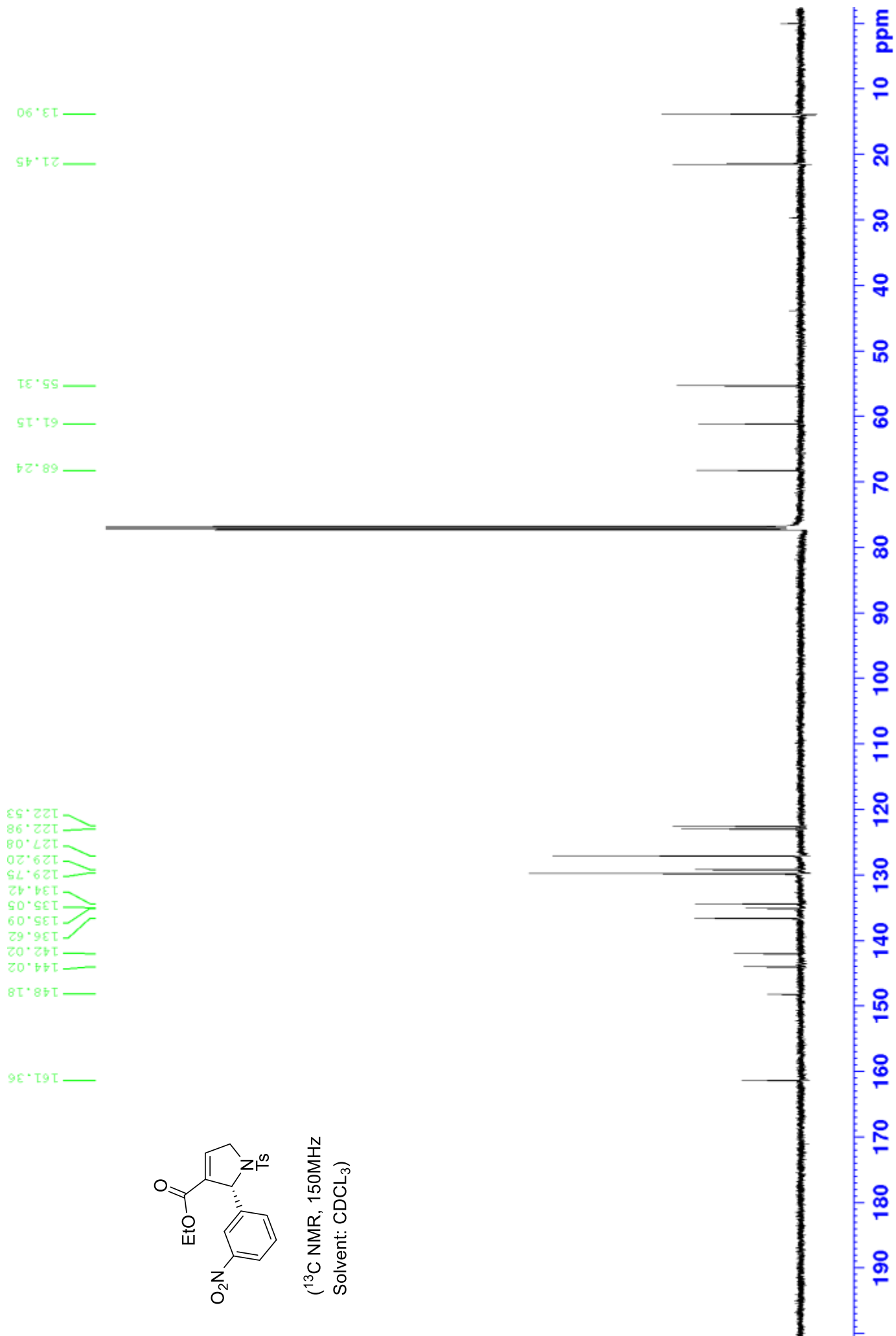


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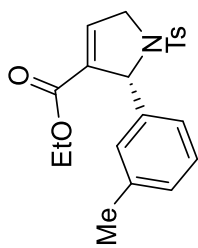




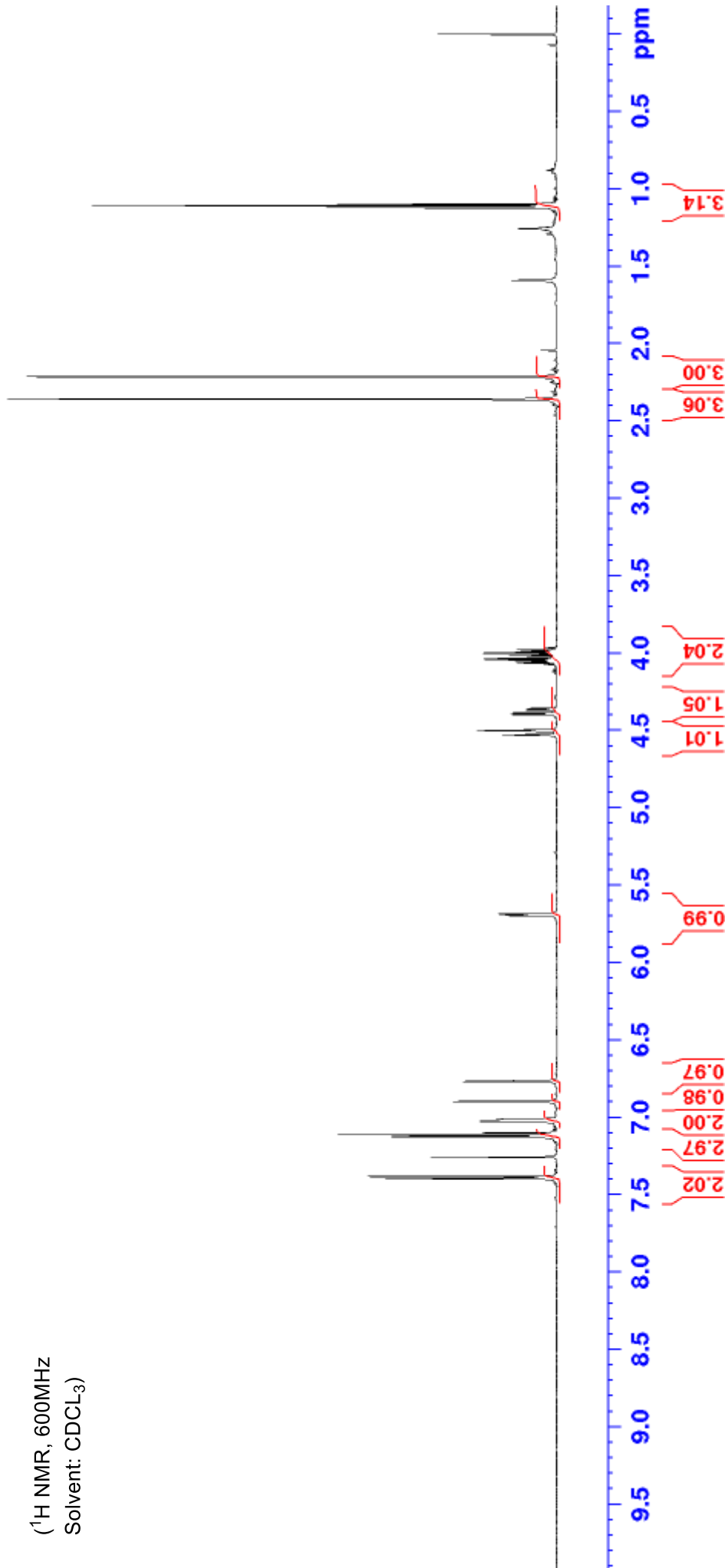
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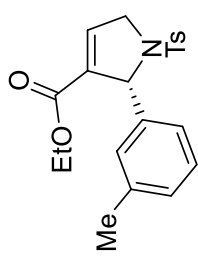


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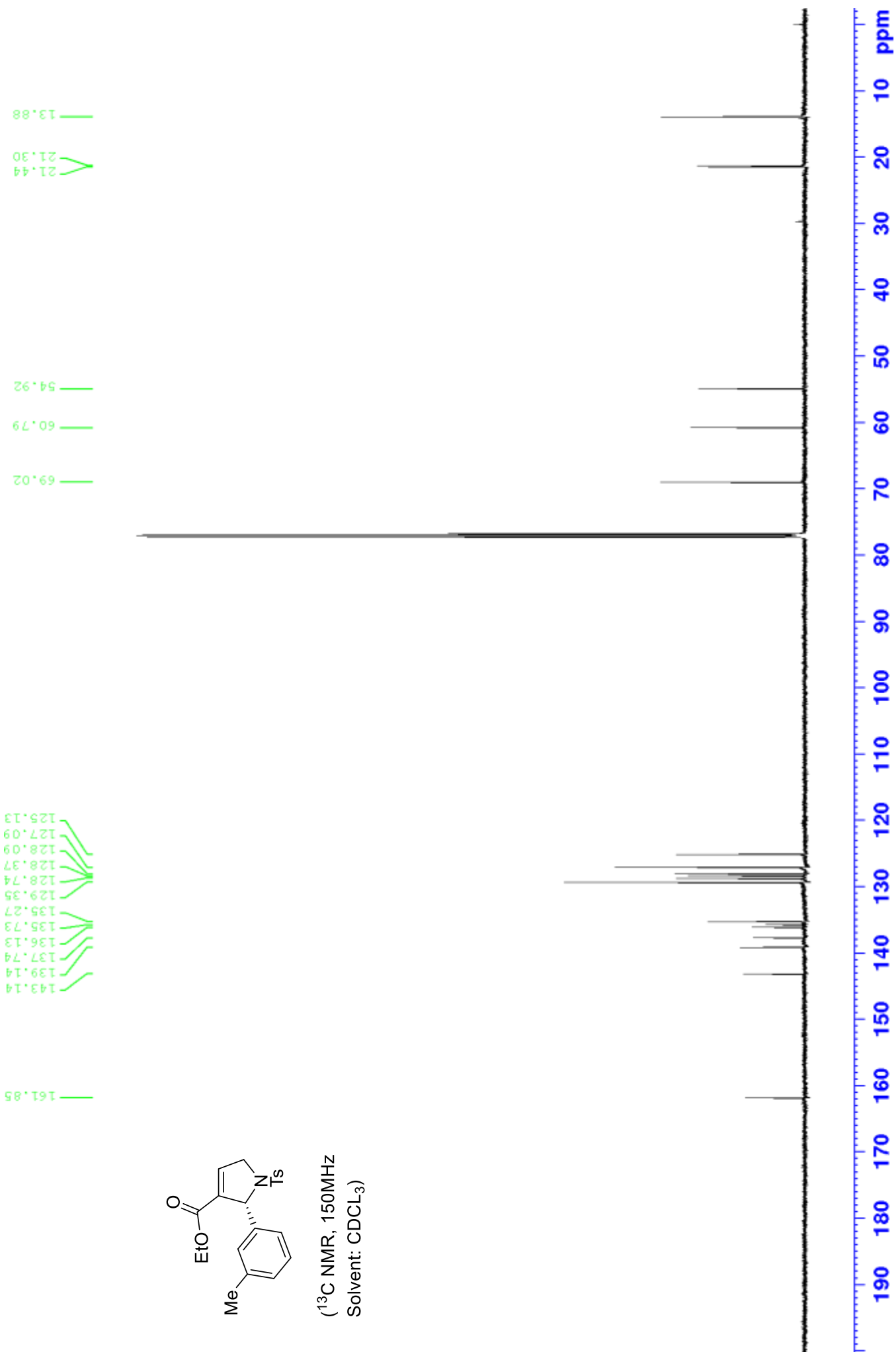


¹H NMR, 600MHz
 Solvent: CDCl₃

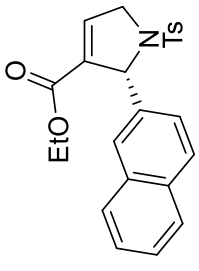




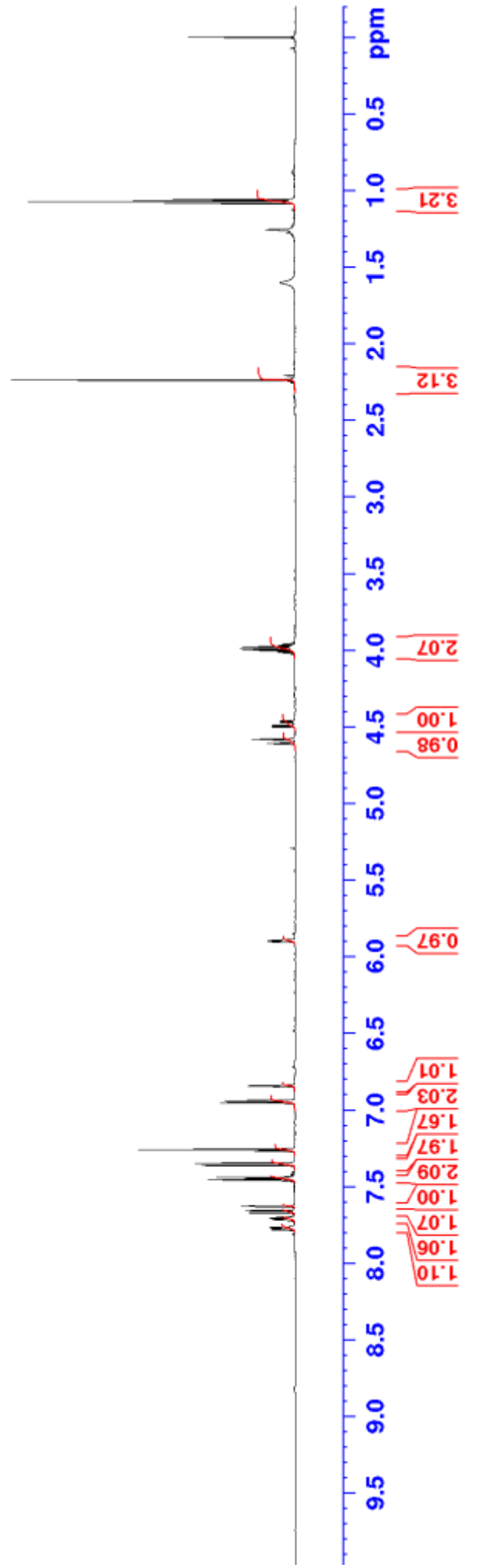
(¹³C NMR, 150MHz
Solvent: CDCL₃)

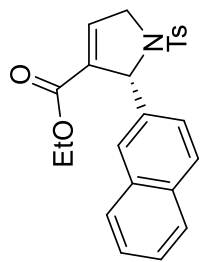


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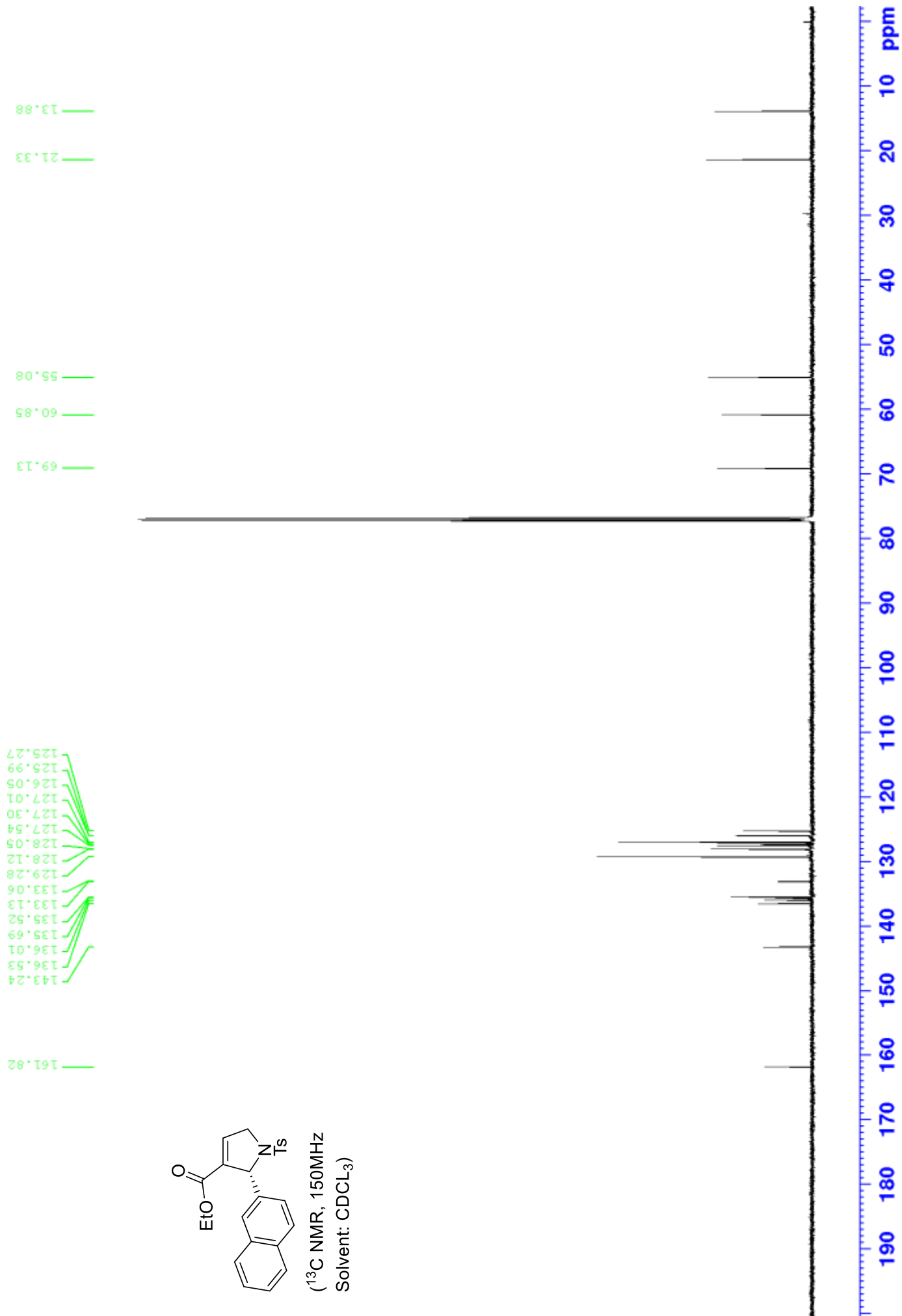


¹H NMR, 600MHz
 Solvent: CDCl₃

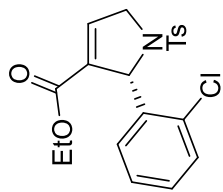




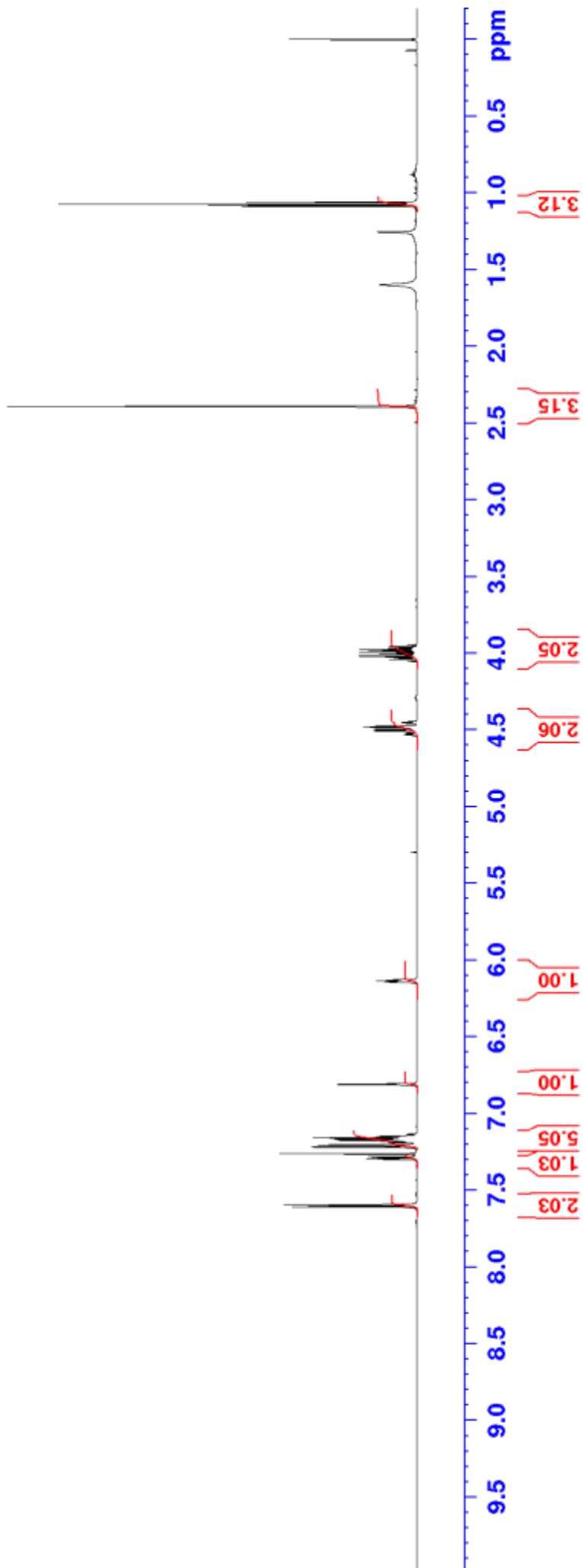
¹³C NMR, 150MHz
Solvent: CDCl₃

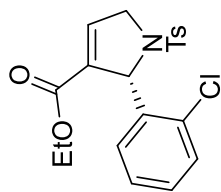


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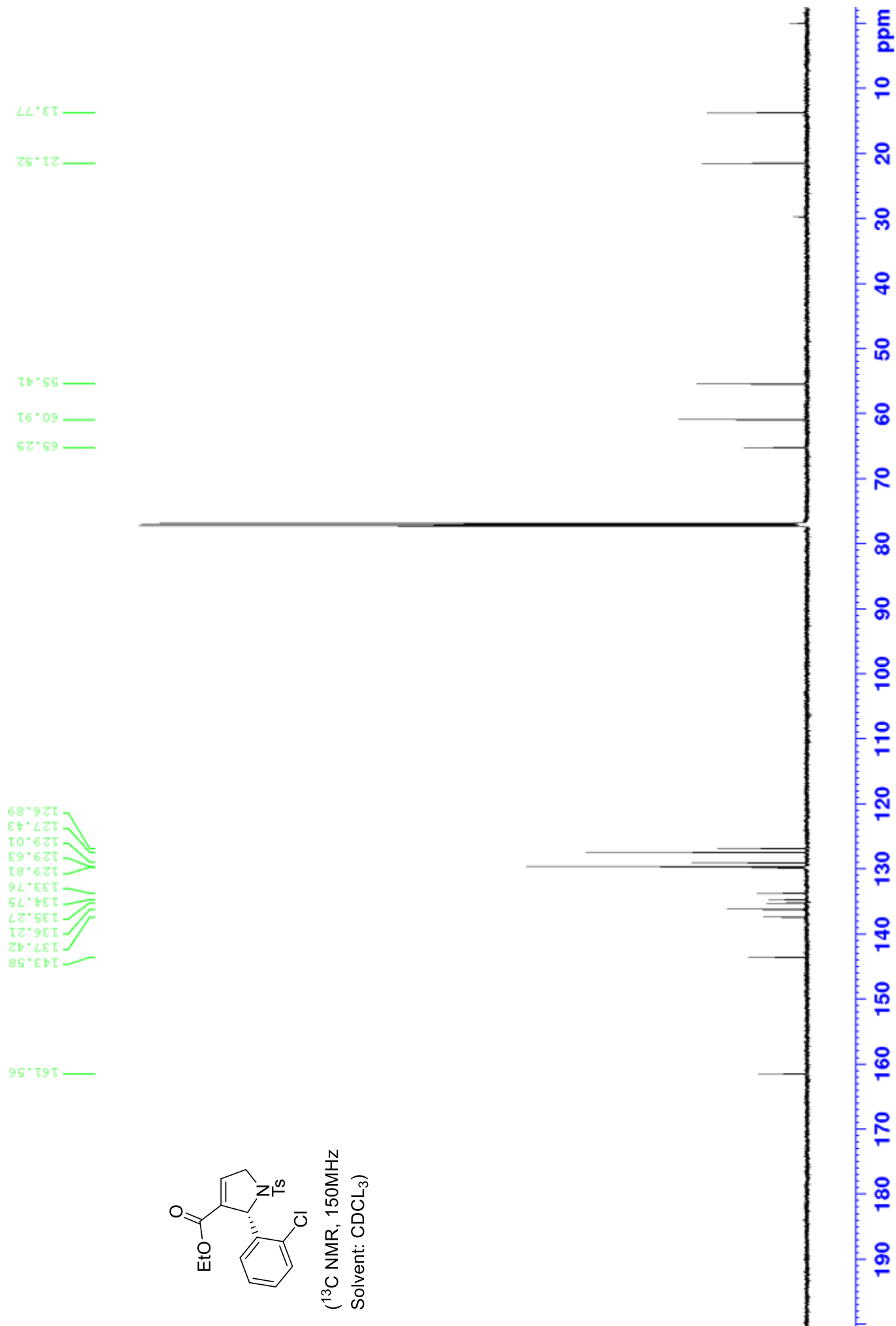


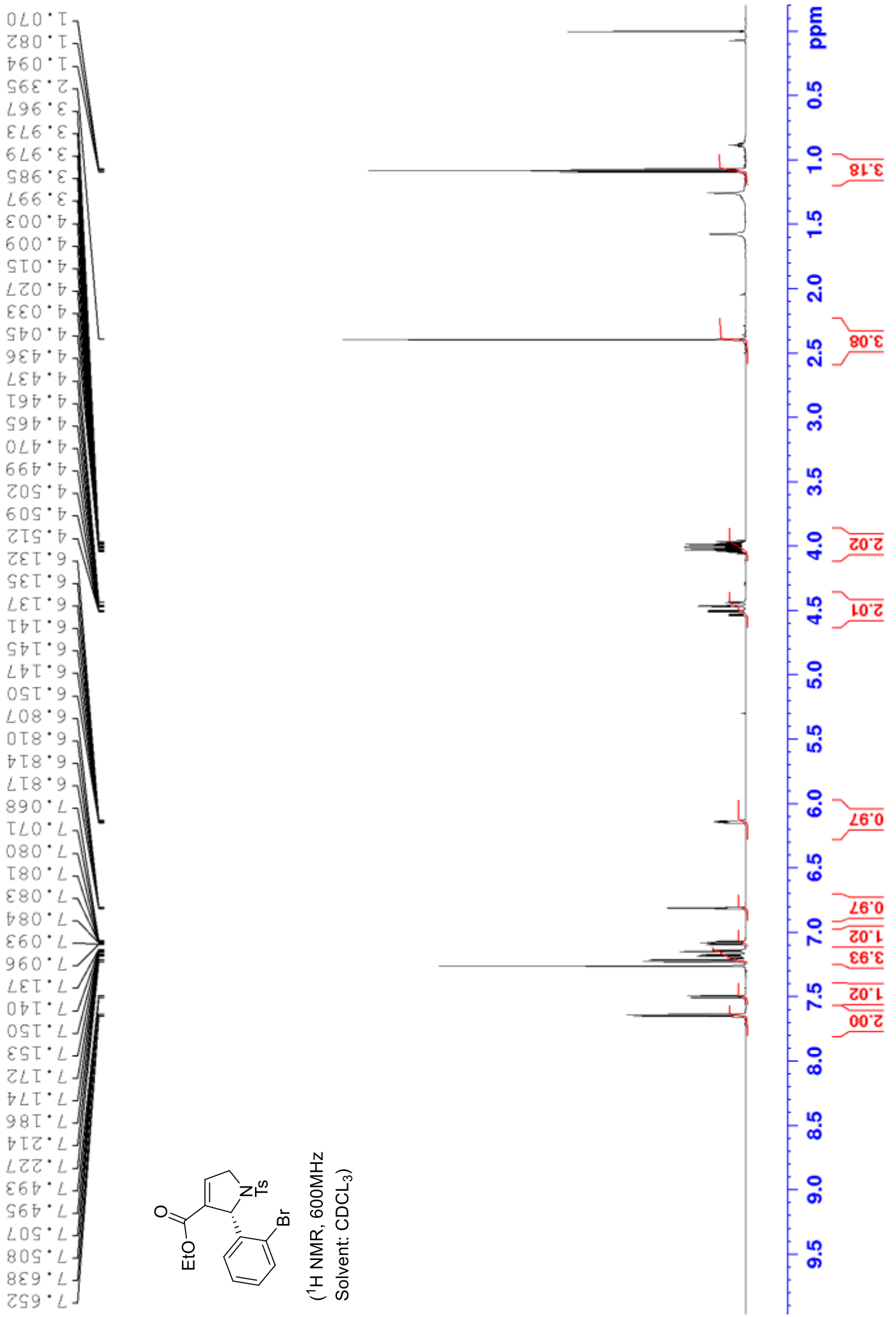
¹H NMR, 600MHz
 Solvent: CDCl₃

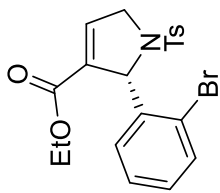




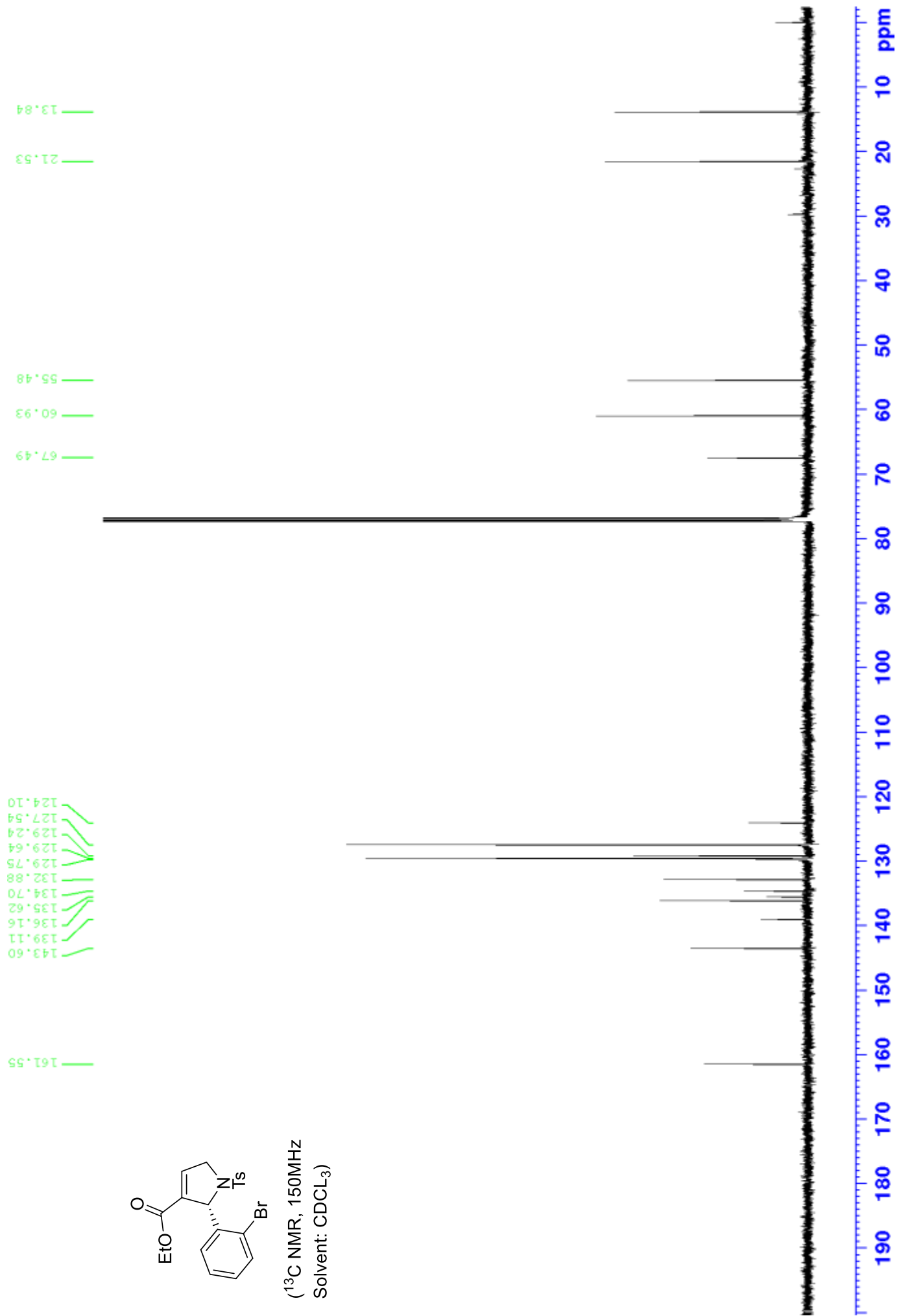
¹³C NMR, 150MHz
Solvent: CDCL₃

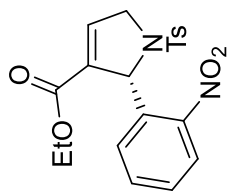




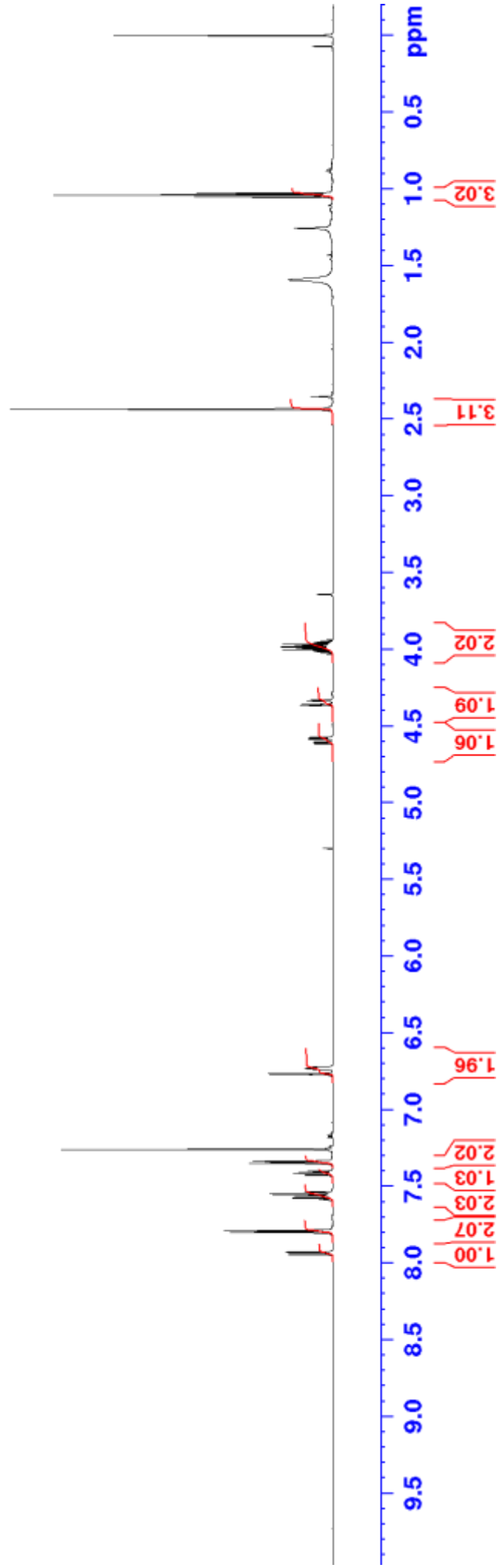
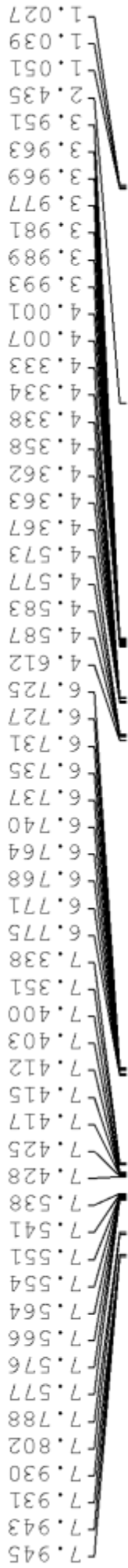


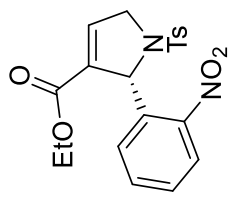
(¹³C NMR, 150MHz
Solvent: CDCl₃)



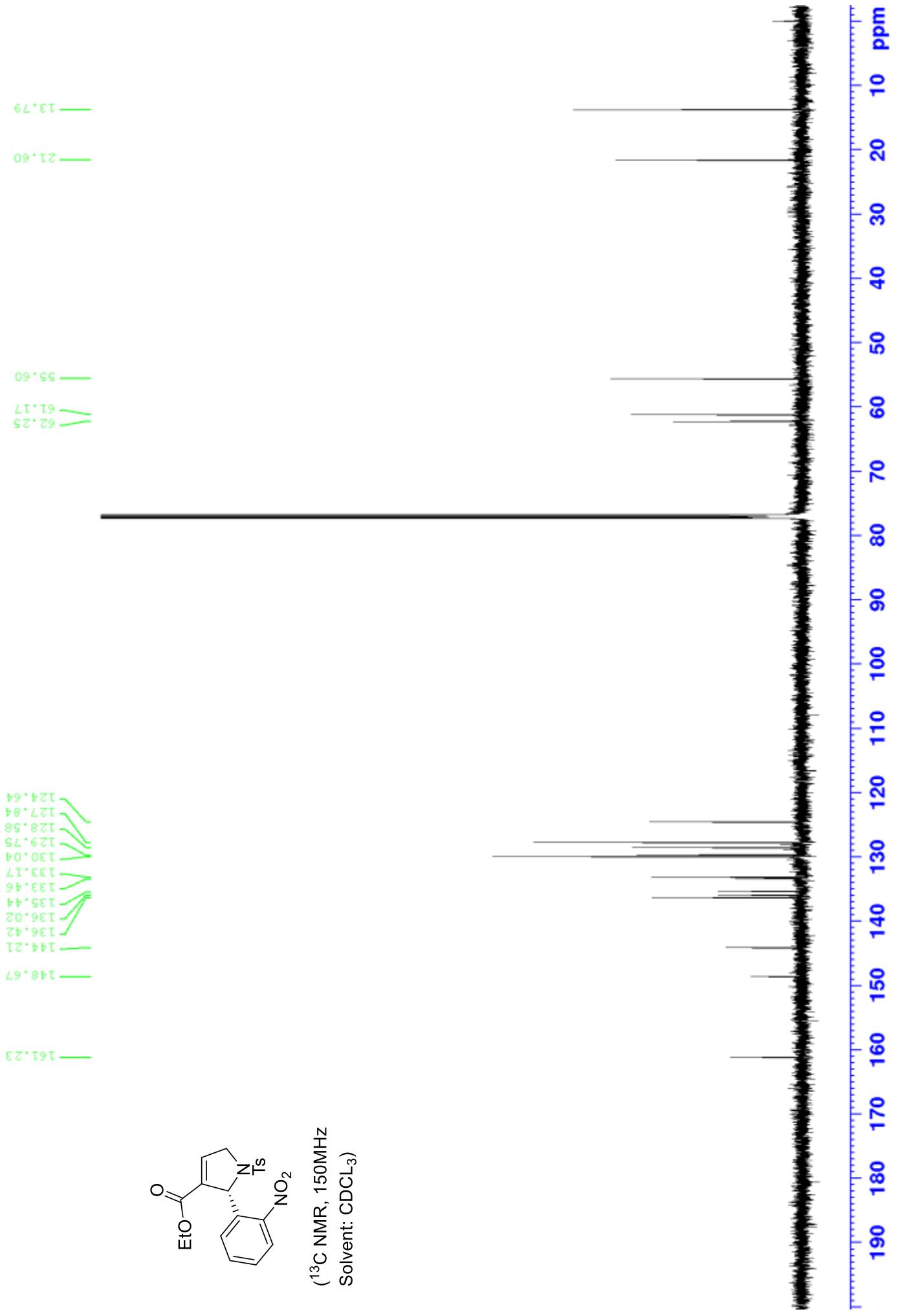


¹H NMR, 600MHz
Solvent: CDCl₃

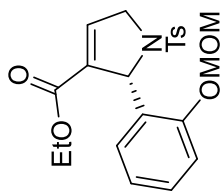




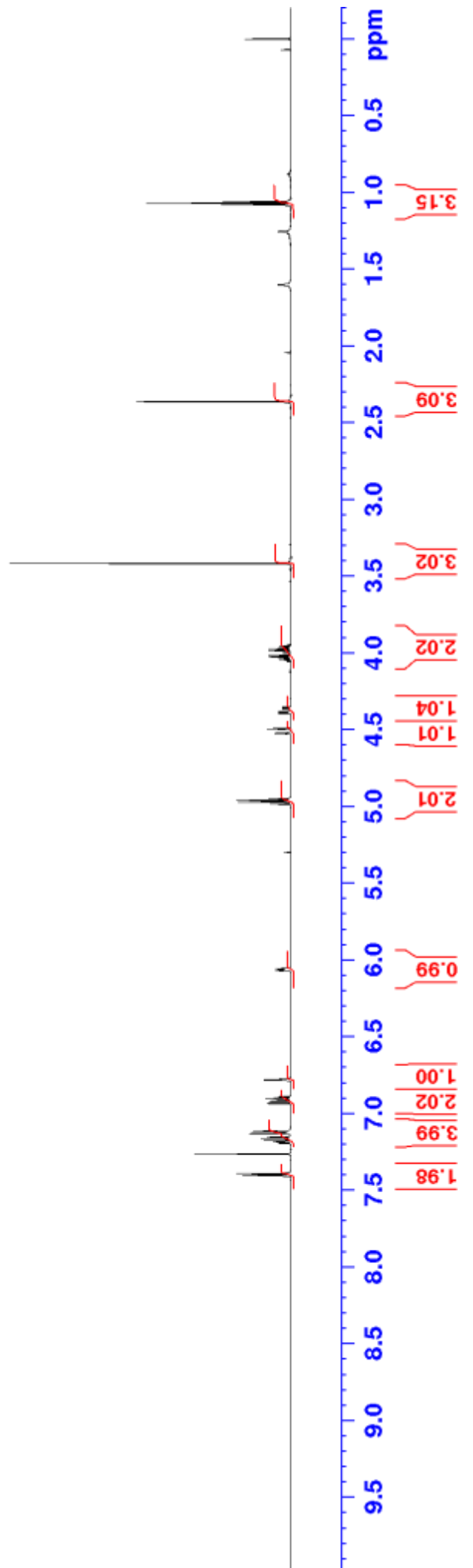
(¹³C NMR, 150MHz
Solvent: CDCL₃)

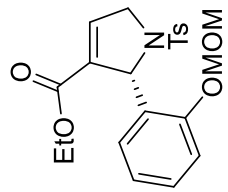


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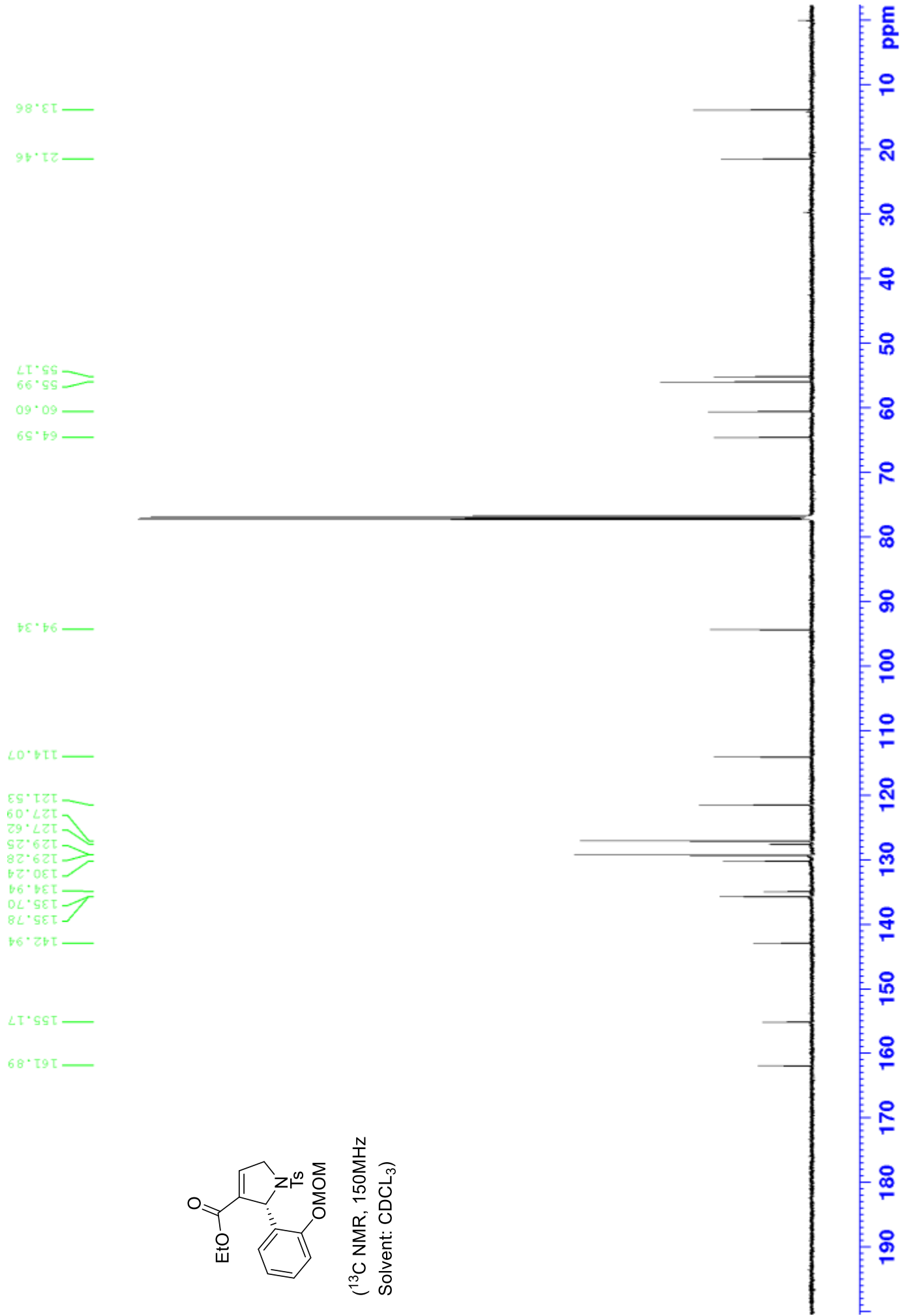


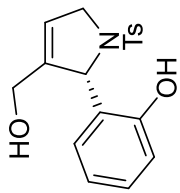
¹H NMR, 600MHz
 Solvent: CDCl₃





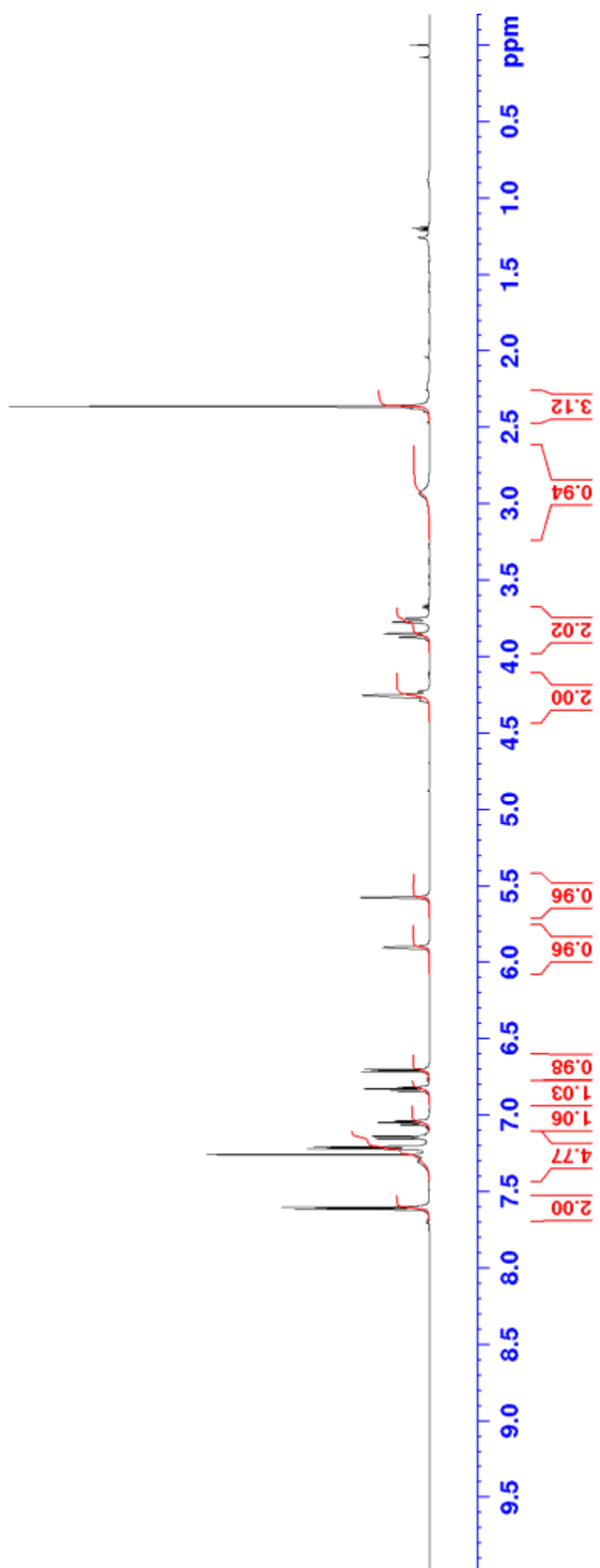
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Solvent: CDCl₃)

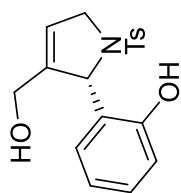




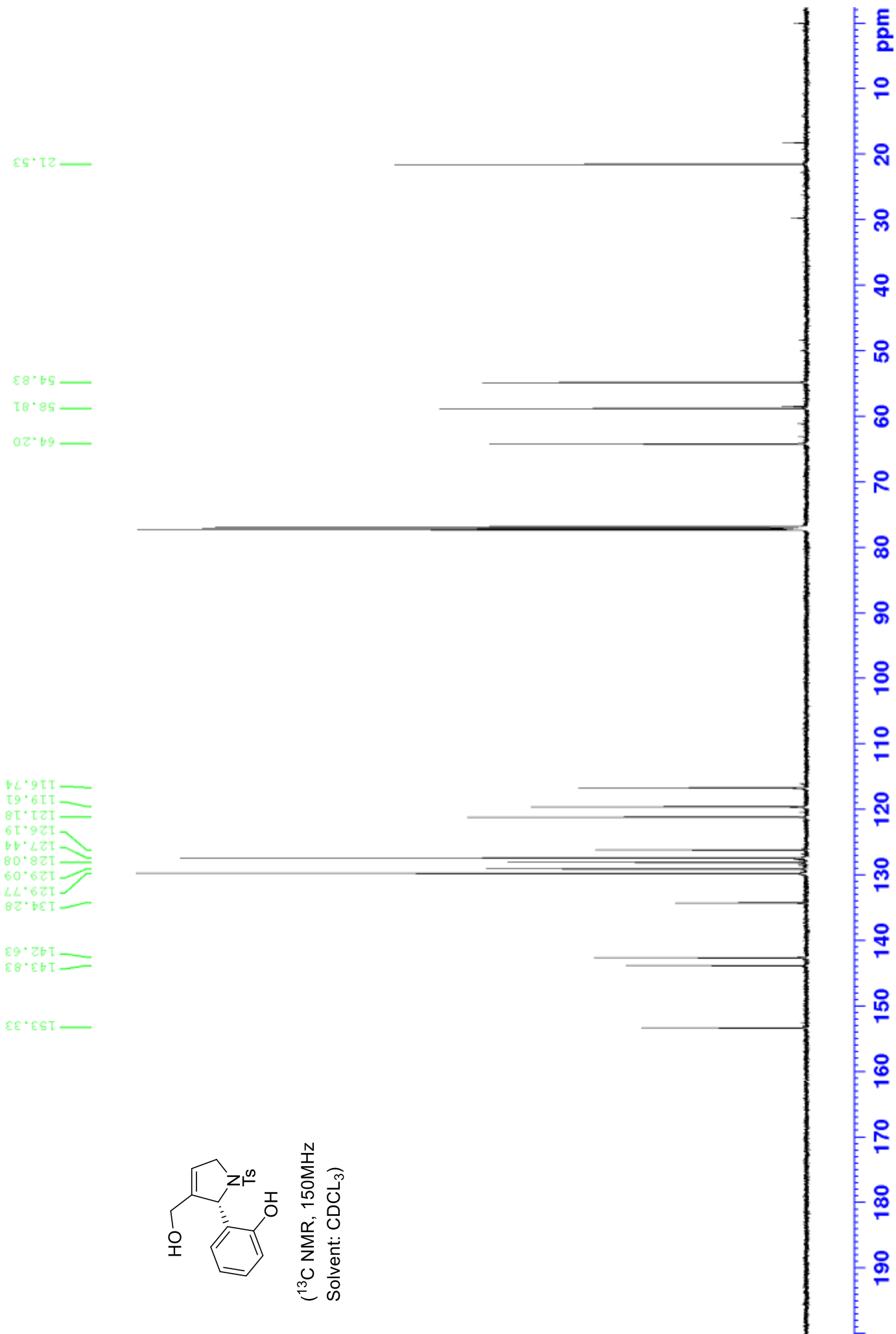
¹H NMR, 600MHz
Solvent: CDCl₃

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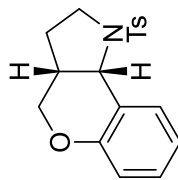




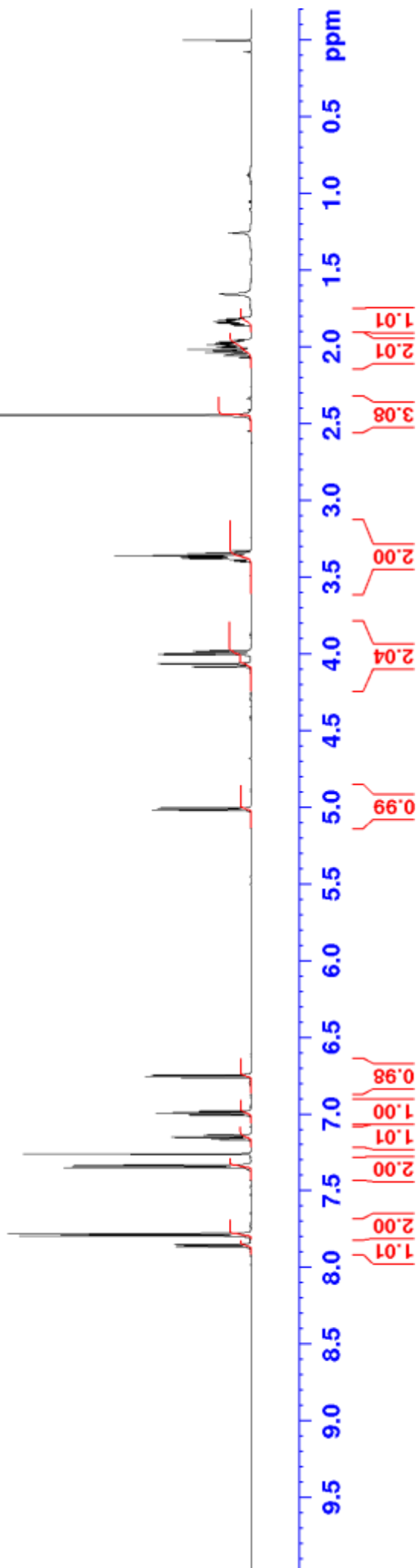
(¹³C NMR, 150MHz
Solvent: CDCL₃)

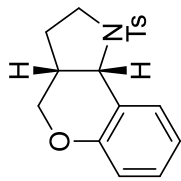


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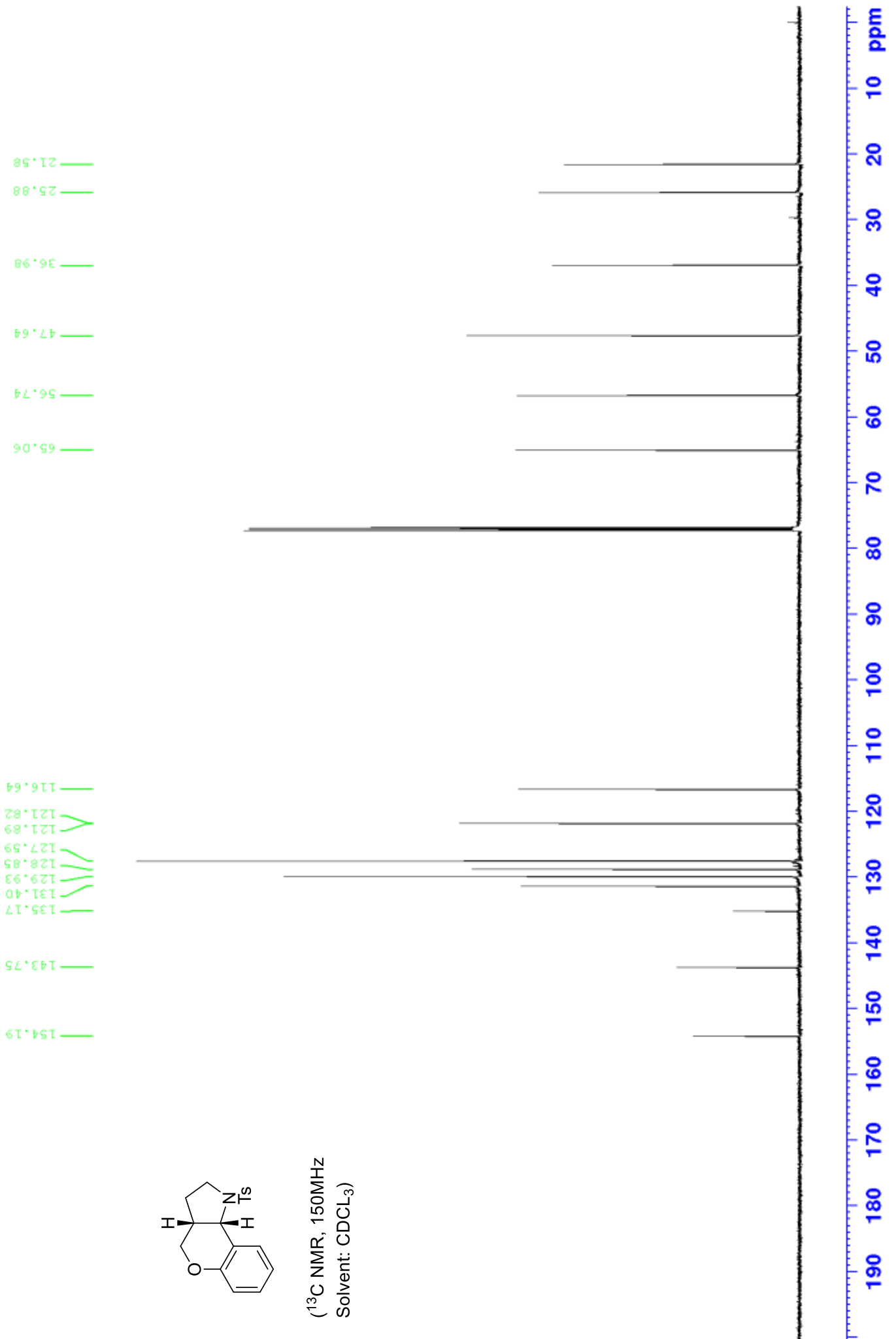


¹H NMR, 600MHz
 Solvent: CDCL₃

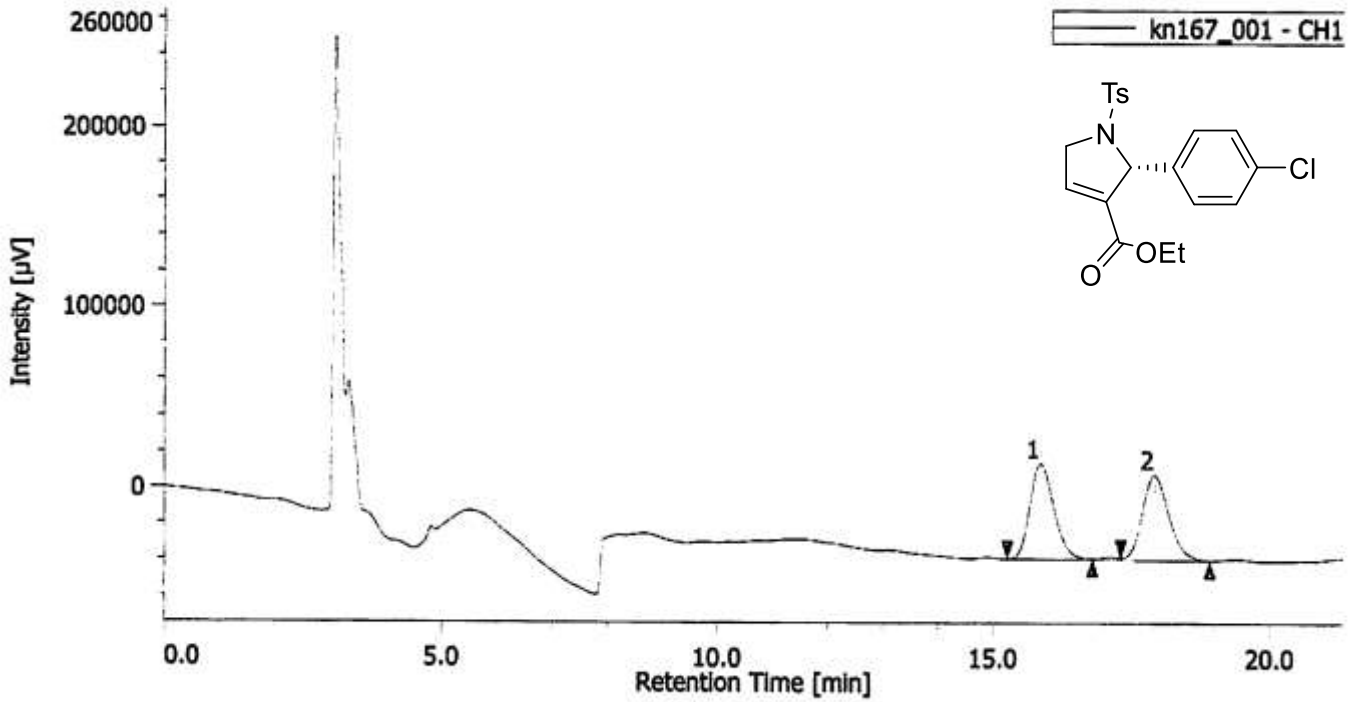




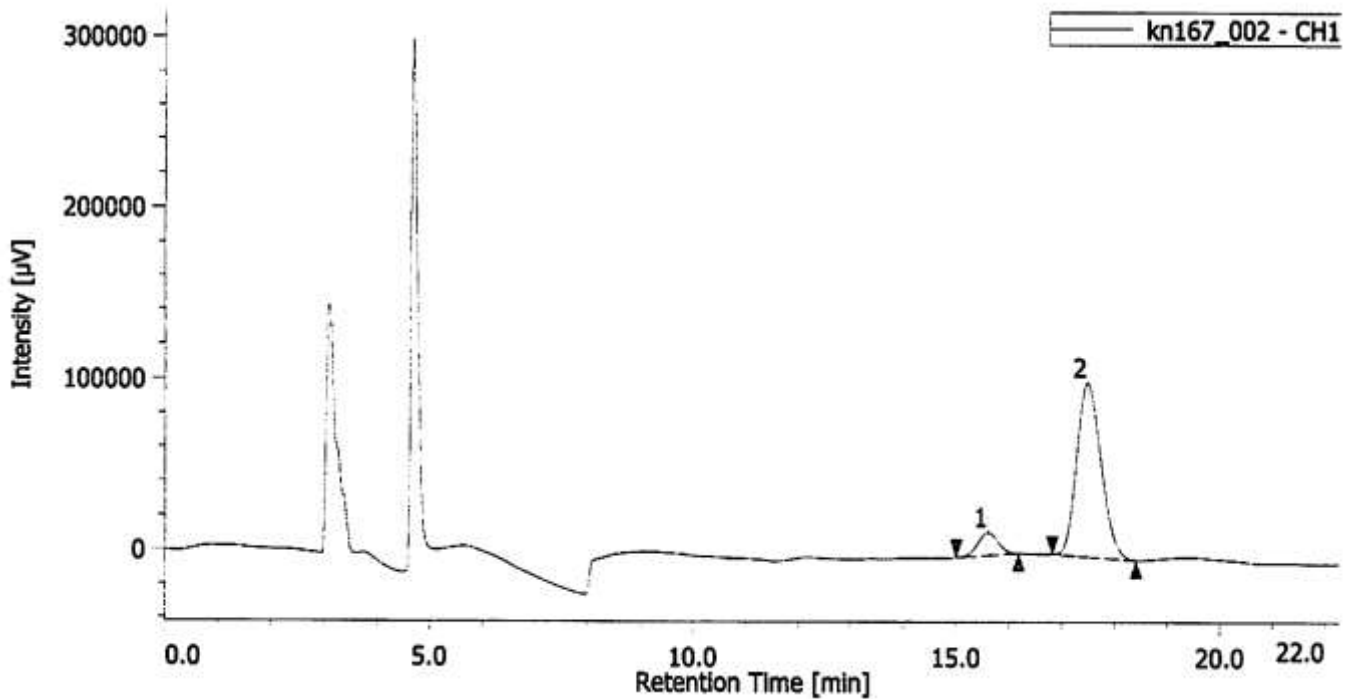
^{13}C NMR, 150MHz
Solvent: CDCl_3



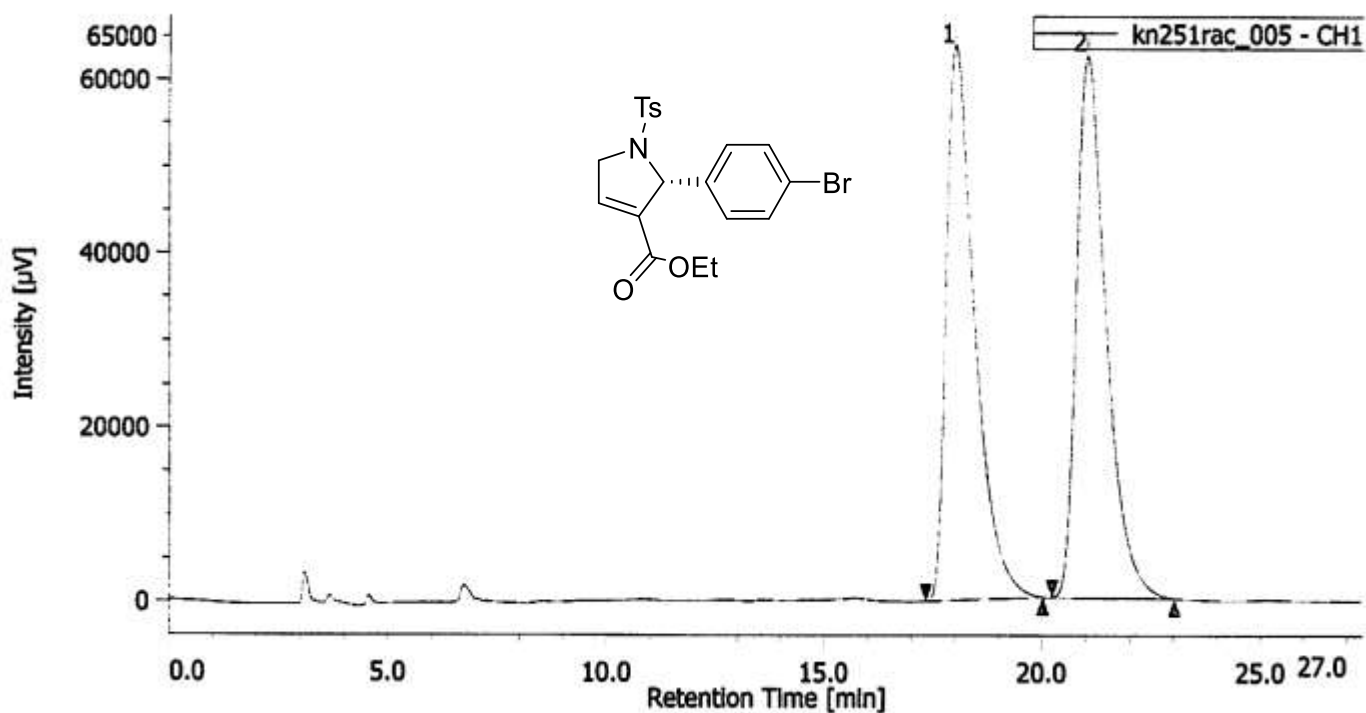
HPLC Data



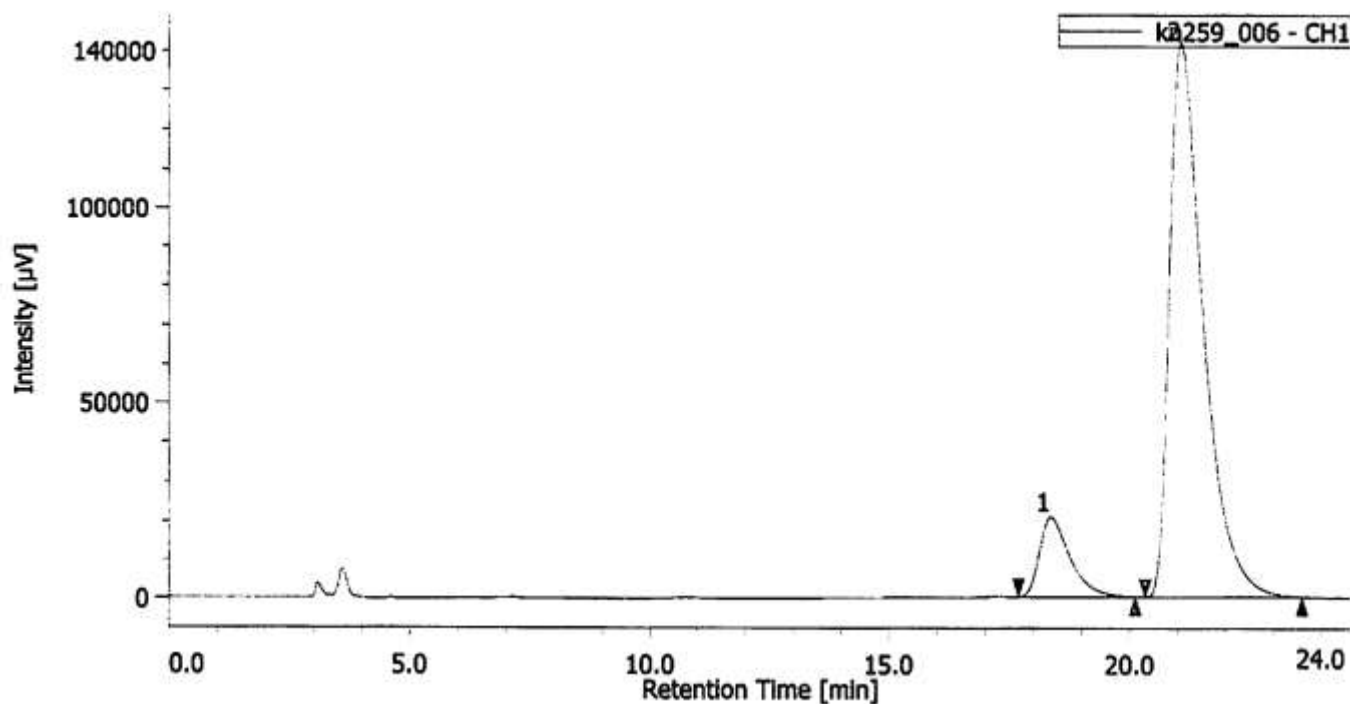
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	1	15.850	1576787	52585	50.122	52.867	N/A	6532	2.482	1.225	
2	Unknown	1	17.900	1569115	48863	49.878	47.133	N/A	6745	N/A	1.194	



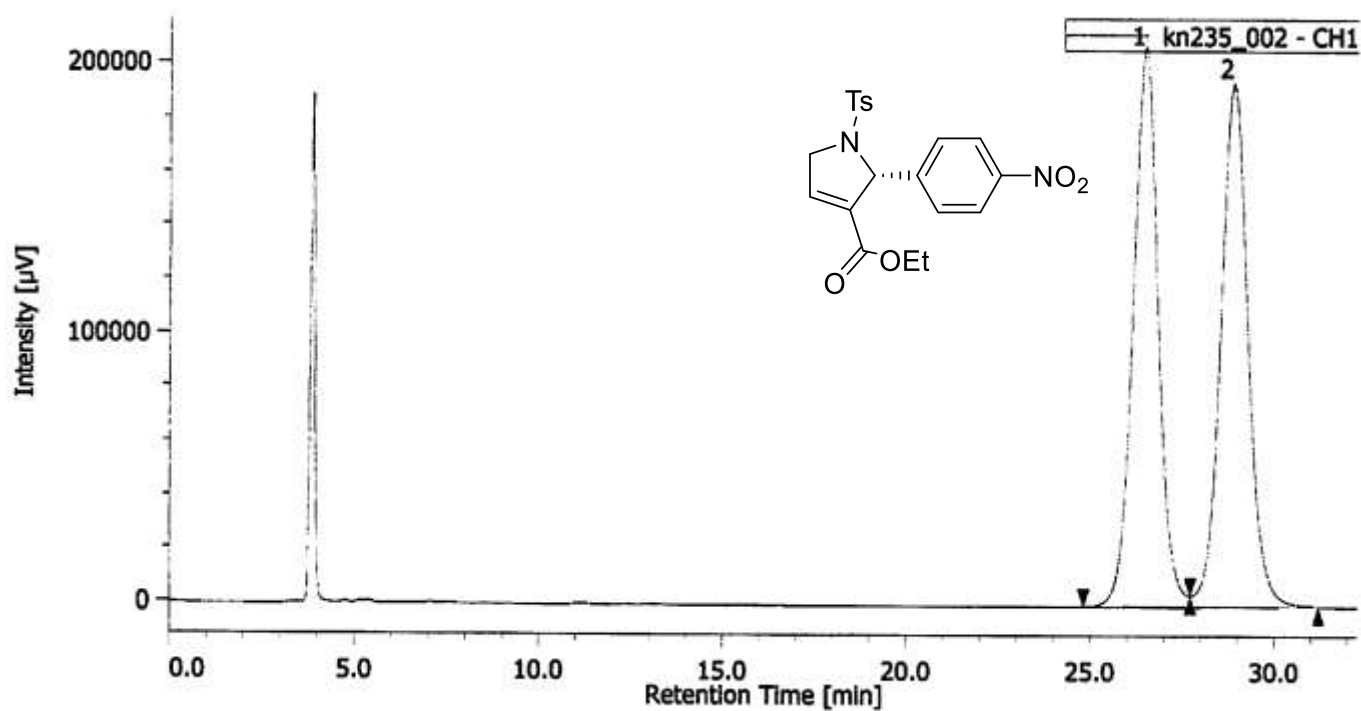
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1	Unknown	1	15.608	365024	13389	10.158	11.641	N/A	7352	2.393	1.016	
2	Unknown	1	17.483	3229124	101629	89.844	88.359	N/A	6884	N/A	1.201	



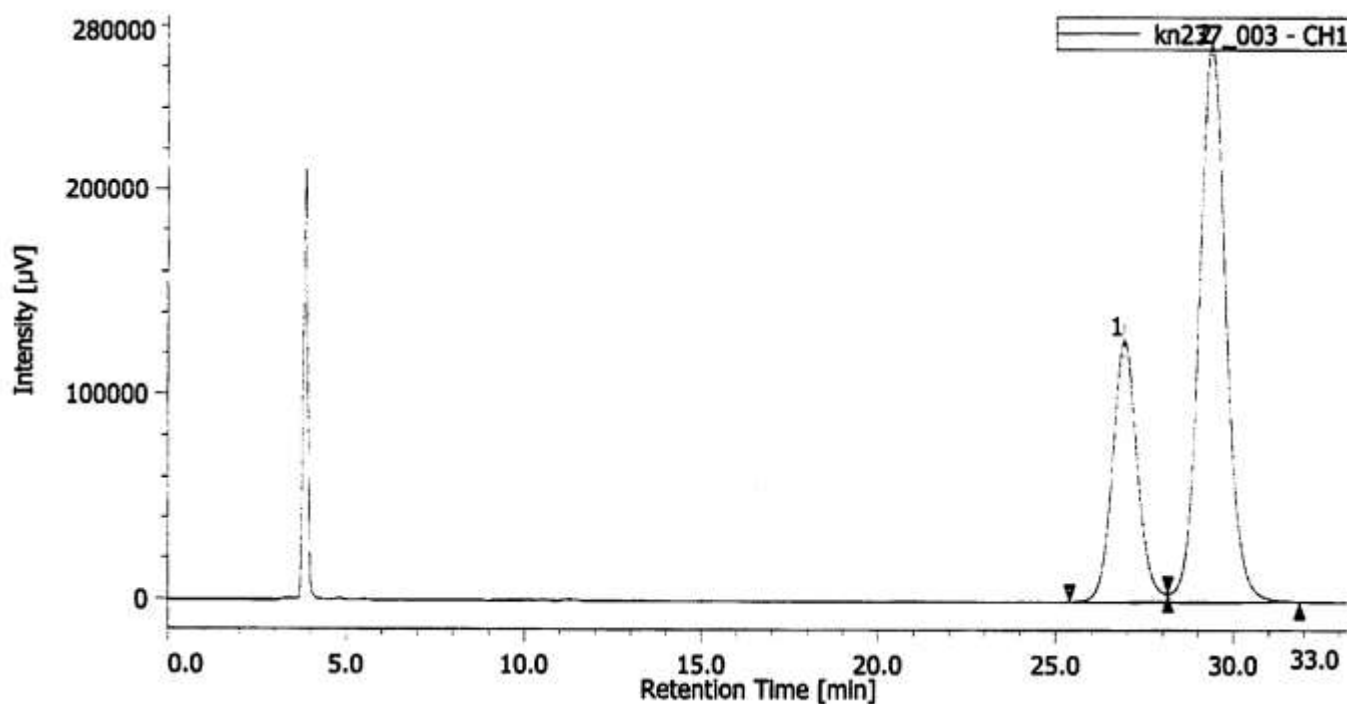
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1	Unknown	1	18.017	2902351	63978	49.707	50.645	N/A	3994	2.587	1.863	
2	Unknown	1	21.033	2936539	62349	50.293	49.355	N/A	4930	N/A	1.583	



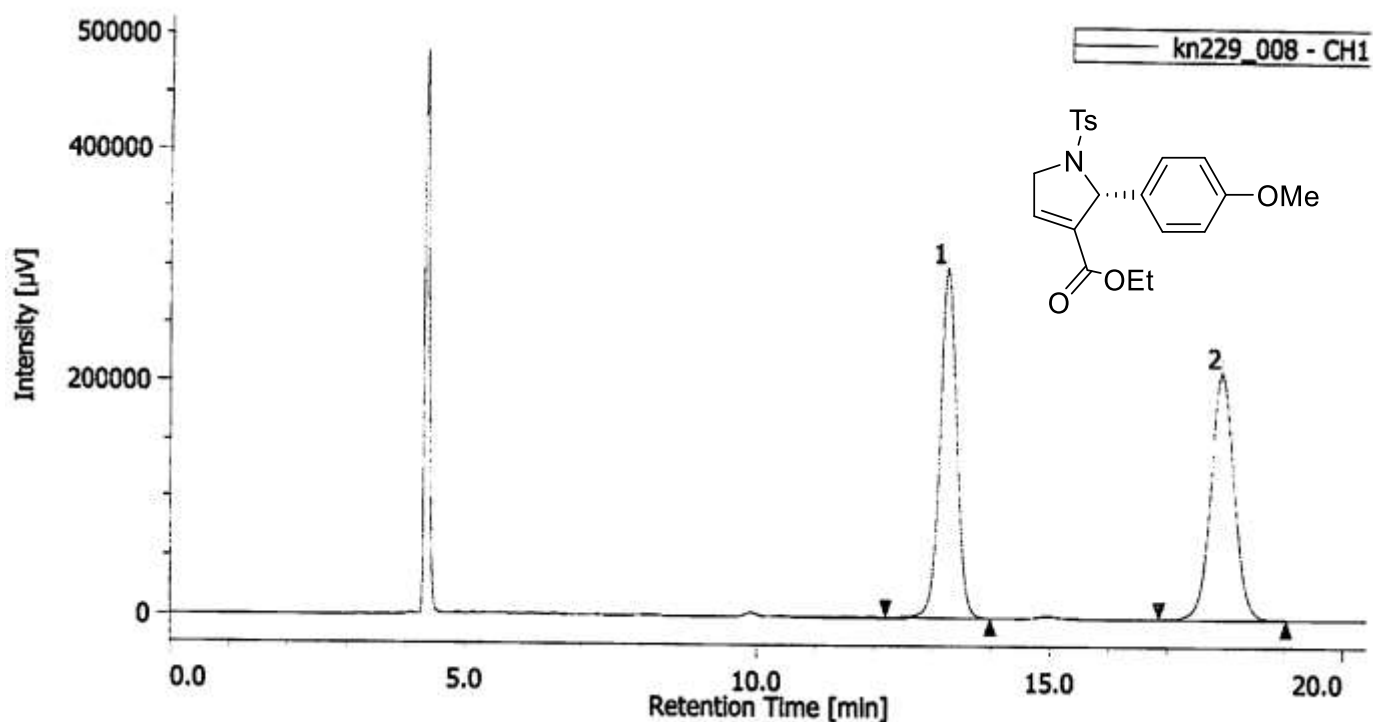
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1	Unknown	1	18.367	907849	20829	11.554	12.799	N/A	4497	2.329	1.624	
2	Unknown	1	21.075	6949577	141913	88.446	87.201	N/A	4649	N/A	1.793	



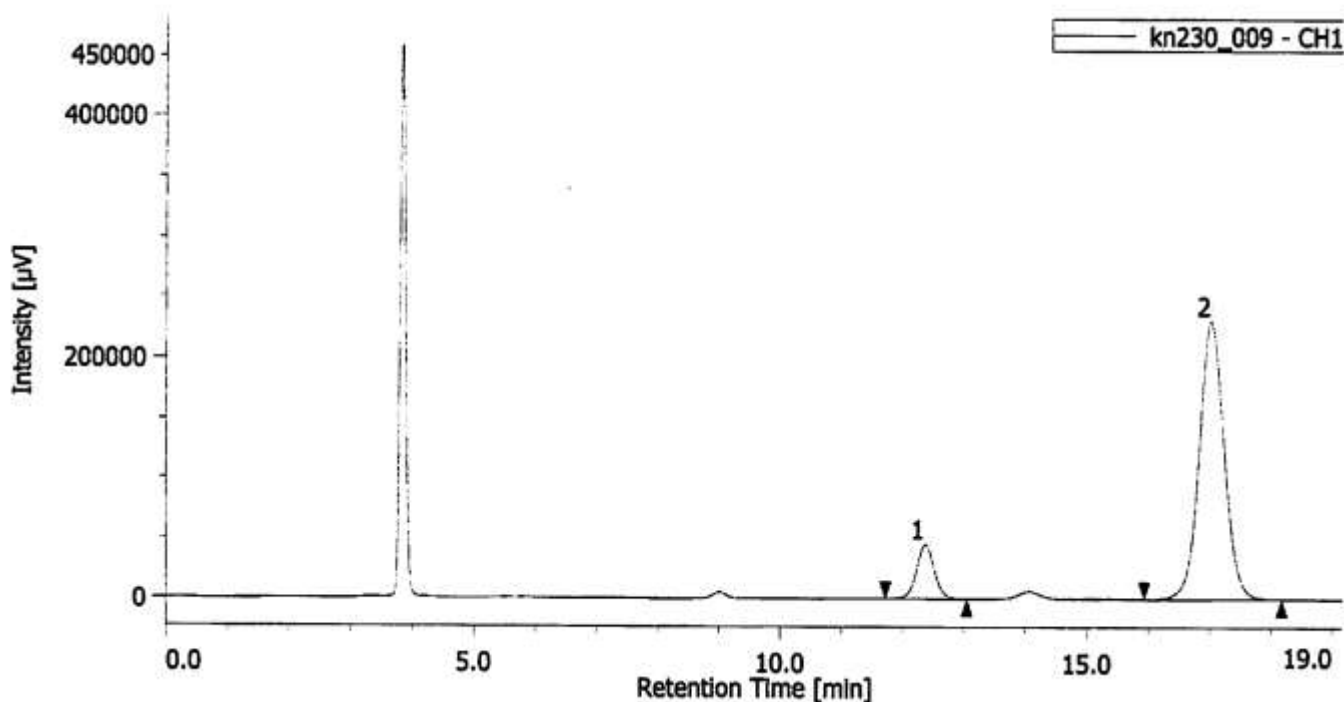
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1	Unknown	1	26.475	9924648	207892	49.815	51.686	N/A	7483	1.898	1.049	
2	Unknown	1	28.875	9998334	194330	50.185	48.314	N/A	7748	N/A	1.074	



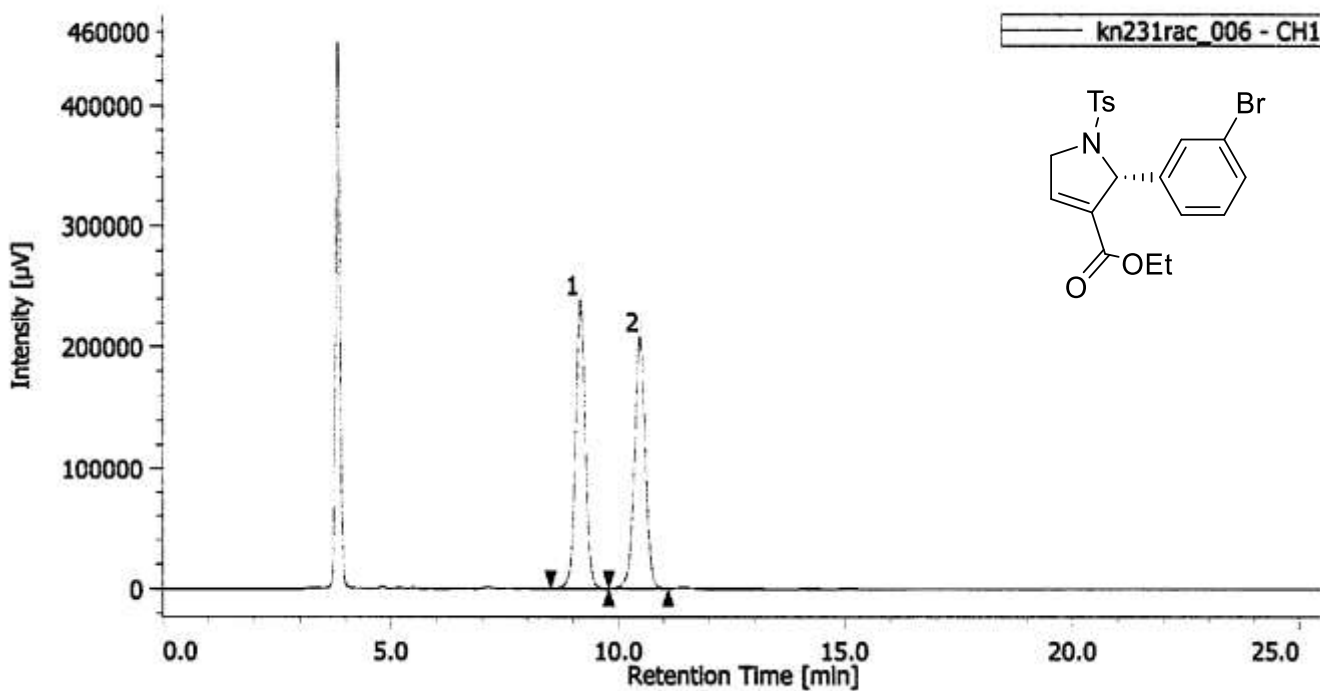
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1	Unknown	1	26.917	6198298	127472	30.192	31.941	N/A	7525	1.900	1.111	
2	Unknown	1	29.375	14326452	271617	69.808	68.059	N/A	7543	N/A	1.098	



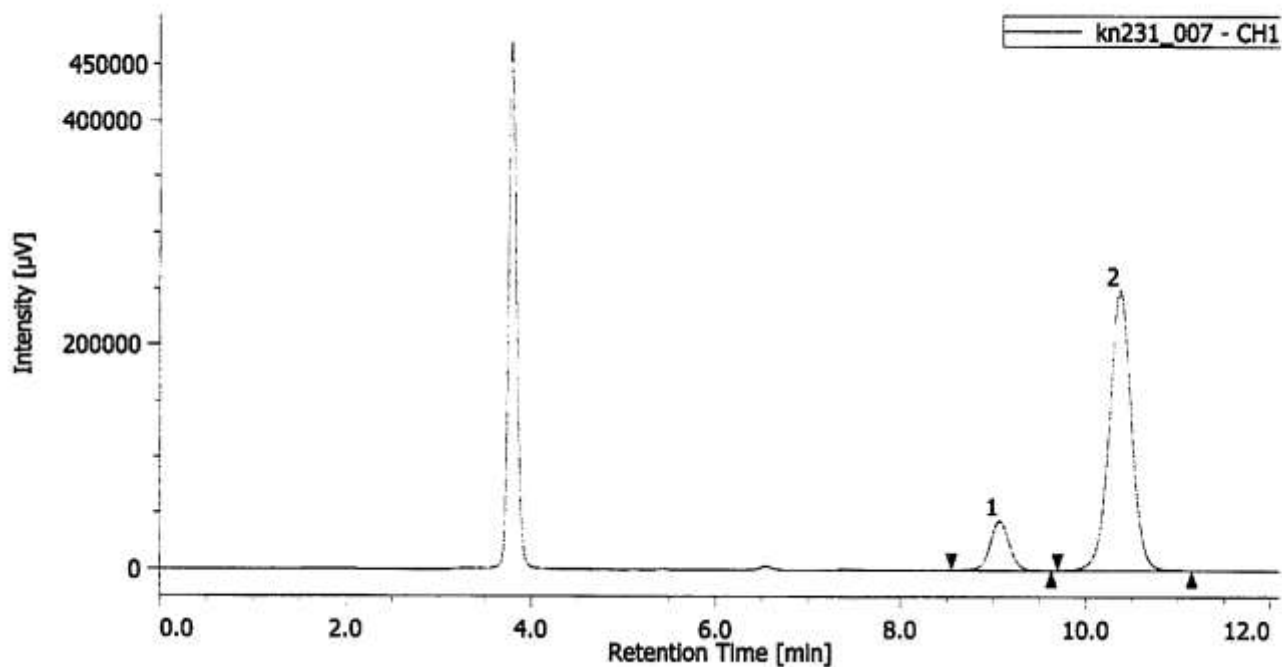
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1	Unknown	1	13.258	5976307	303654	49.797	58.610	N/A	11072	7.630	1.024	
2	Unknown	1	17.925	6025084	214435	50.203	41.390	N/A	9850	N/A	1.045	



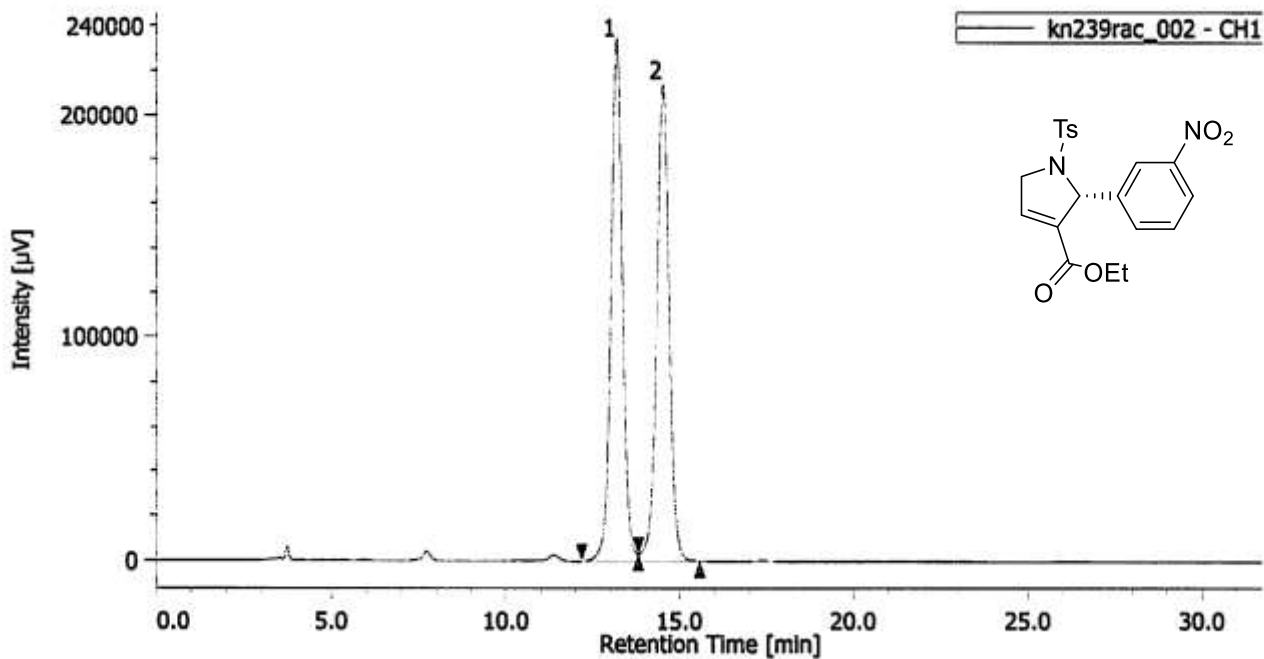
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1	Unknown	1	12.367	917537	45905	12.248	16.568	N/A	9253	7.492	1.038	
2	Unknown	1	17.017	6573872	231168	87.752	83.432	N/A	8683	N/A	1.055	



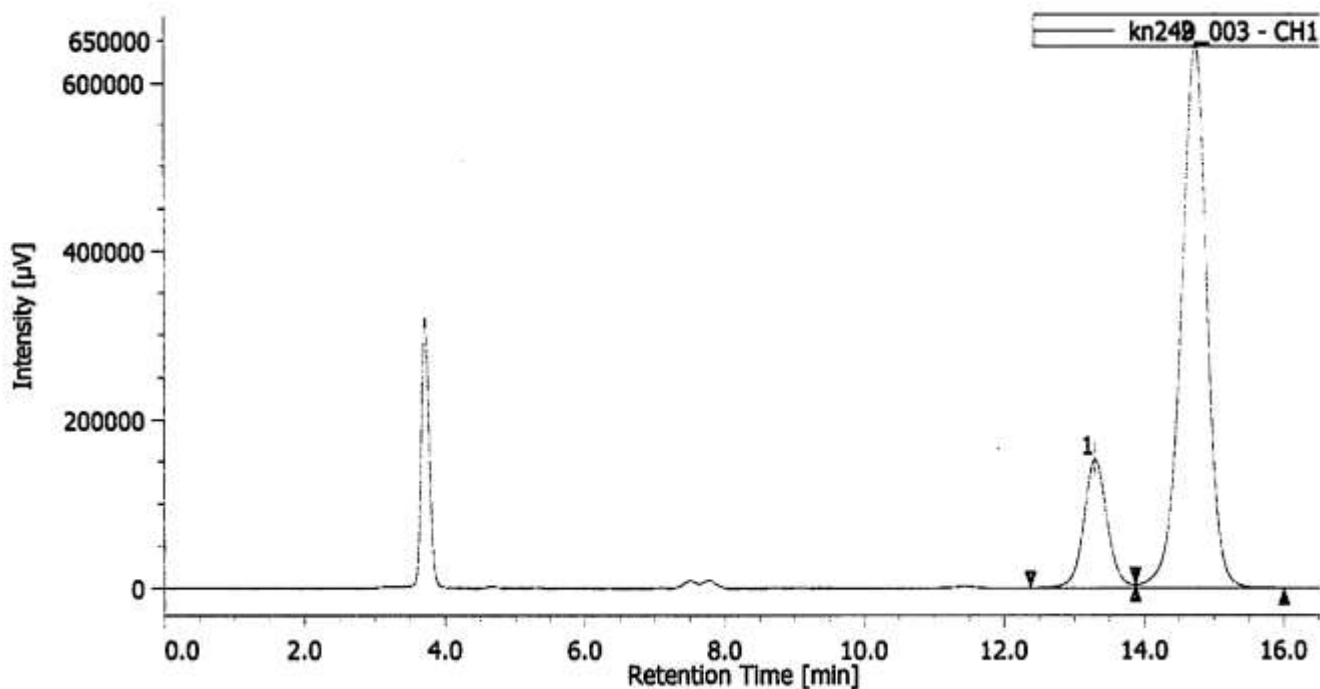
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1	Unknown	1	9.158	3509253	239086	50.093	53.457	N/A	9808	3.288	1.021	
2	Unknown	1	10.475	3498180	208163	49.907	46.543	N/A	9529	N/A	0.973	



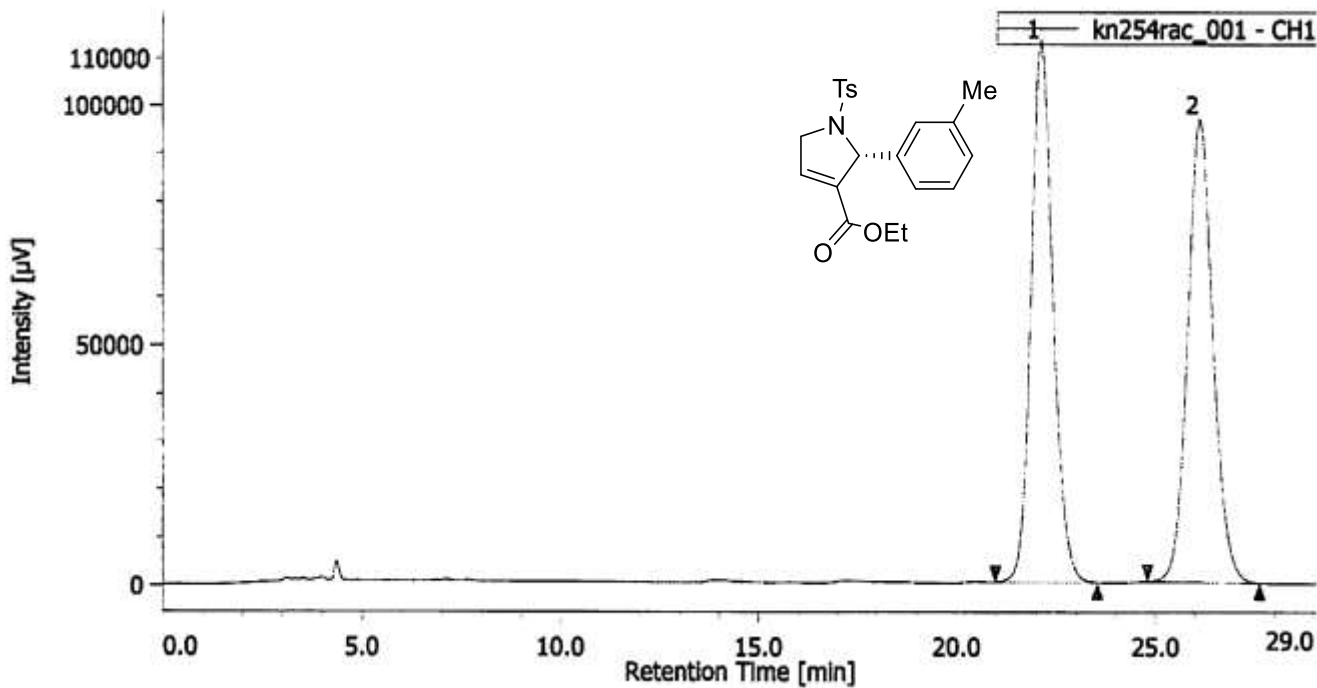
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1	Unknown	1	9.067	631288	43662	13.088	14.888	N/A	9611	3.260	1.034	
2	Unknown	1	10.367	4191944	249619	86.912	85.112	N/A	9307	N/A	1.007	



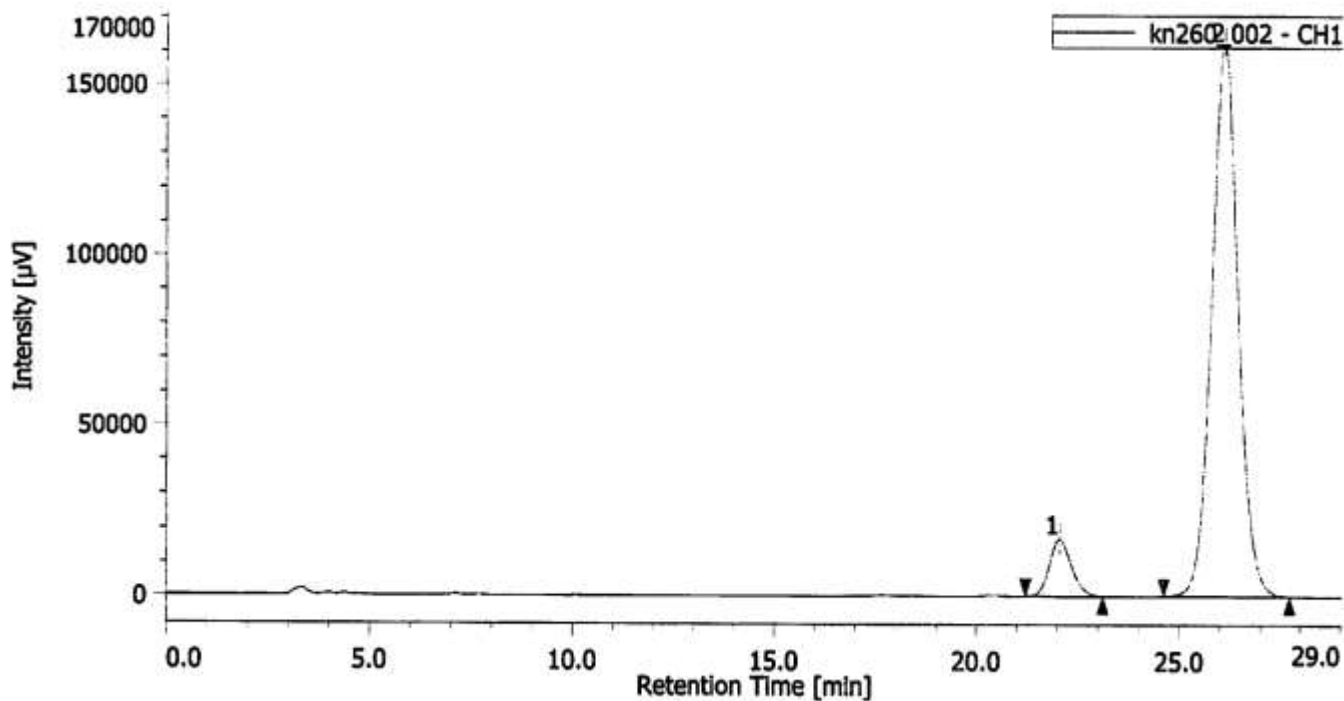
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1	Unknown	1	13.175	5319440	234301	50.089	52.253	N/A	8450	2.241	1.031	
2	Unknown	1	14.517	5304818	214096	49.931	47.747	N/A	8565	N/A	0.995	



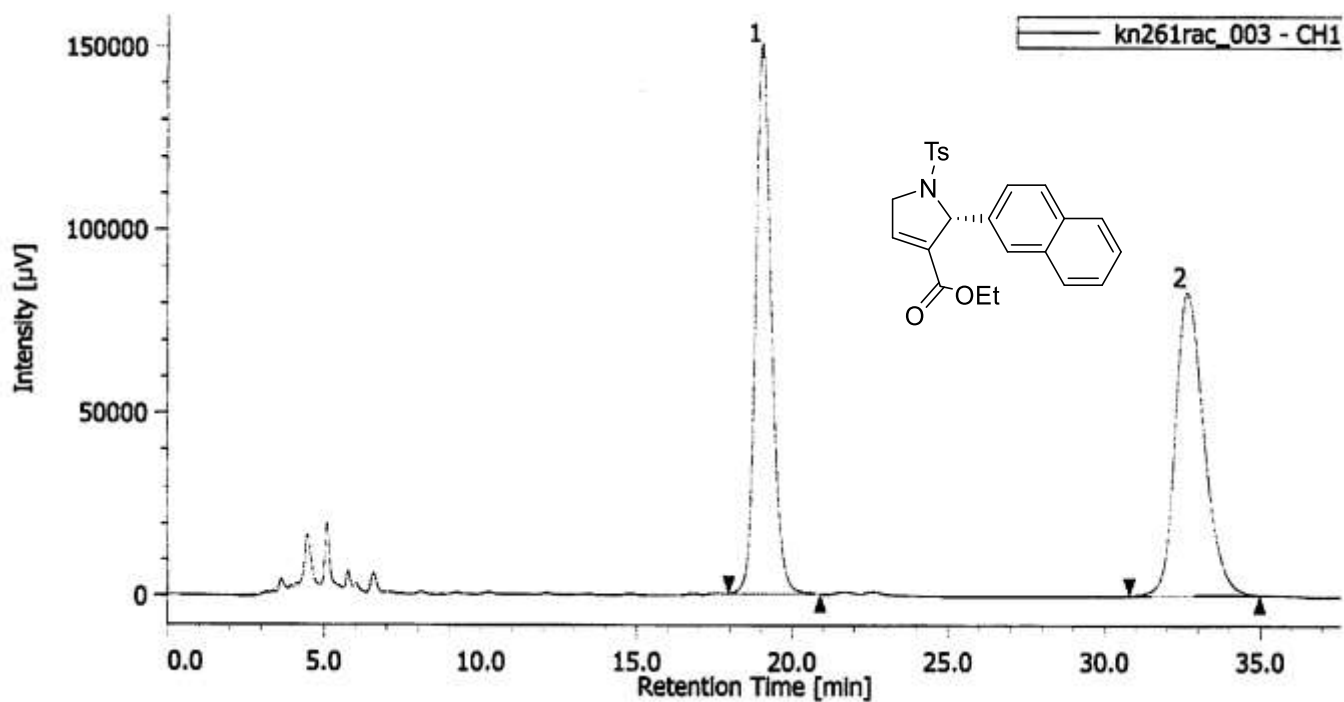
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1	Unknown	1	13.292	3549396	151978	17.698	19.019	N/A	8107	2.335	1.062	
2	Unknown	1	14.733	18507869	647122	82.304	80.981	N/A	8280	N/A	0.917	



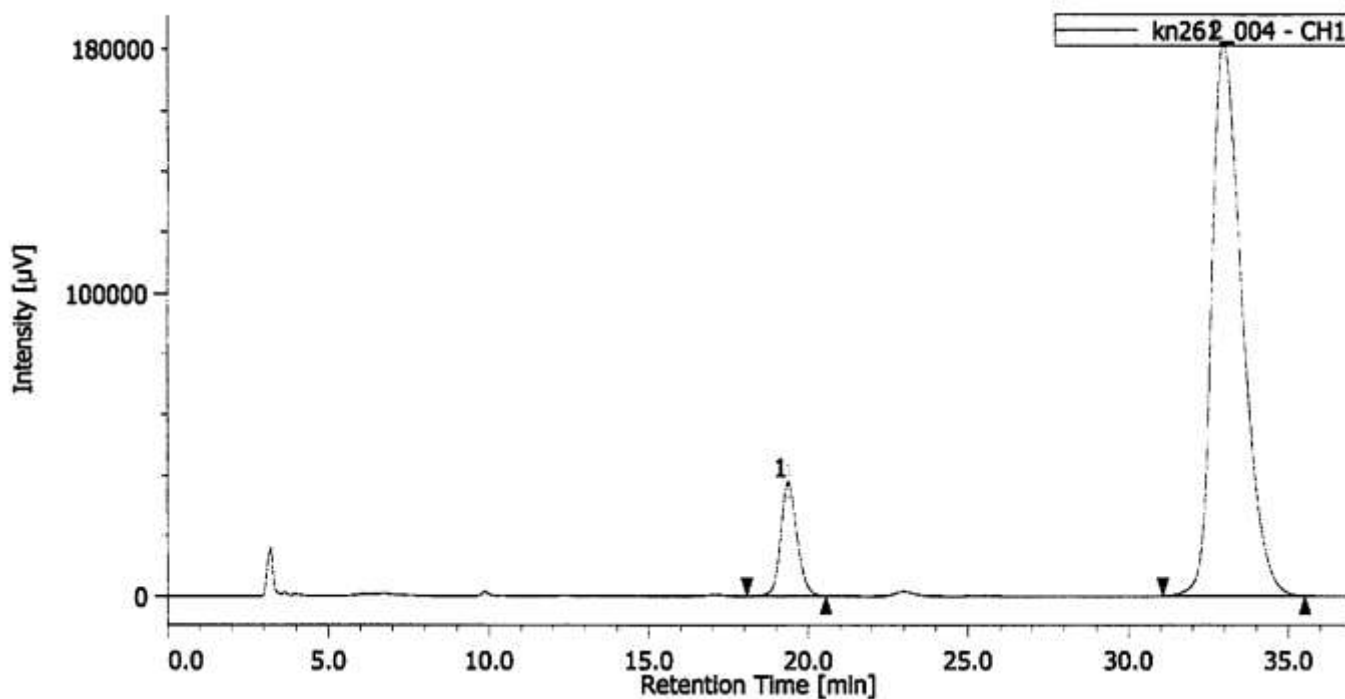
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1	Unknown	1	22.117	4310372	113060	50.098	53.960	N/A	8158	3.773	1.147	
2	Unknown	1	26.108	4293512	96467	49.902	46.040	N/A	8361	N/A	1.097	



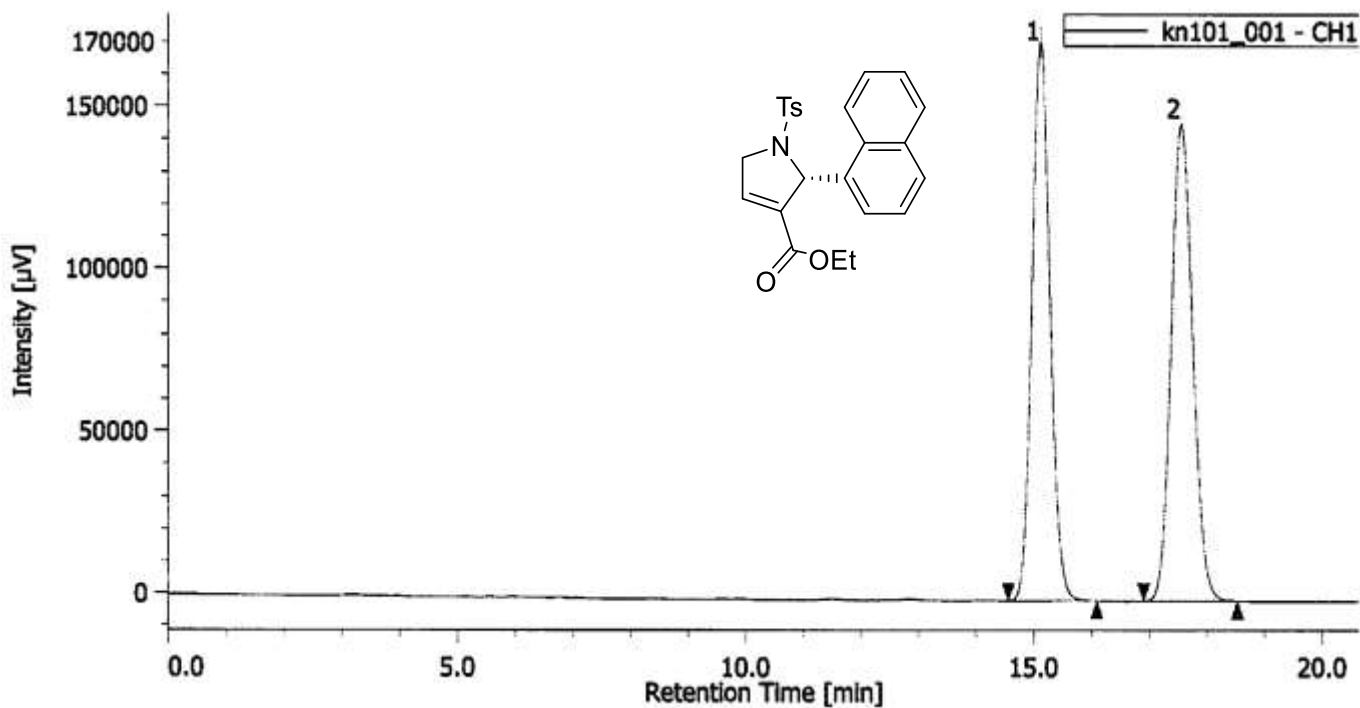
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1	Unknown	1	22.042	642925	18997	8.004	9.462	N/A	8018	3.786	1.172	
2	Unknown	1	26.100	7389528	162645	91.996	90.538	N/A	8034	N/A	1.075	



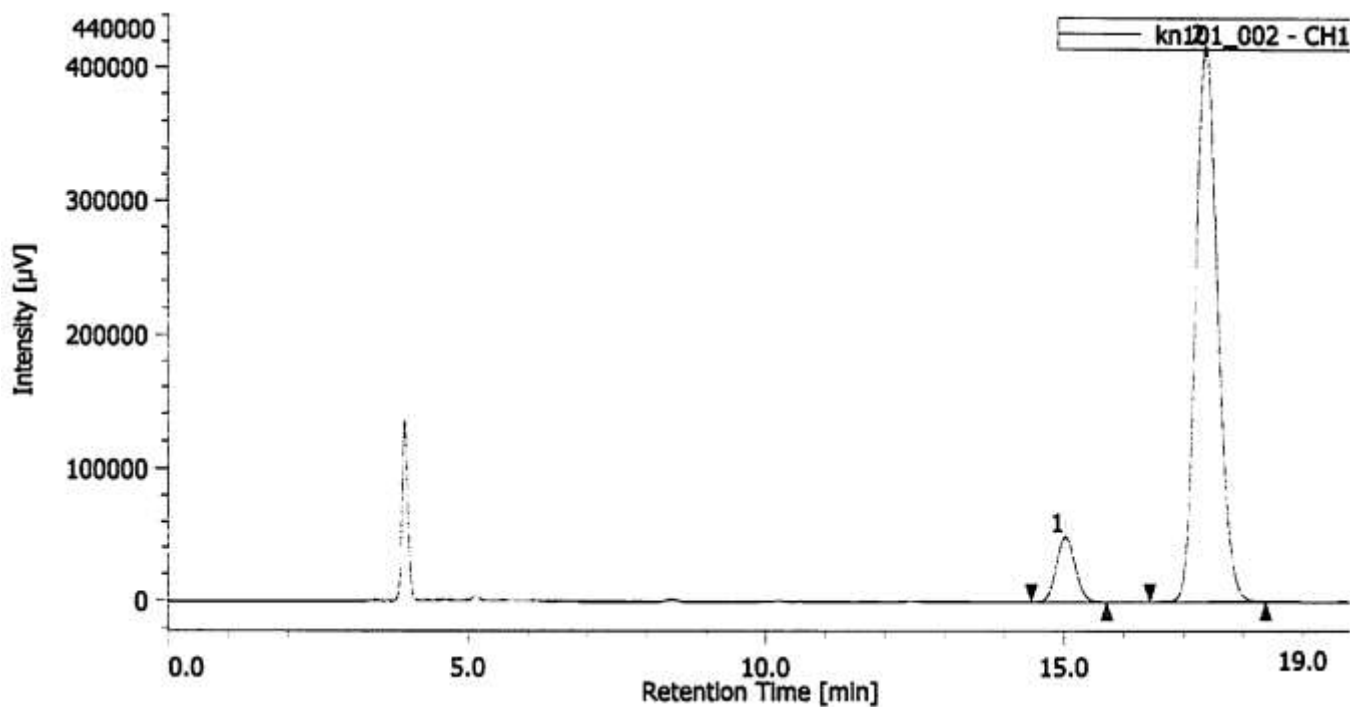
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1	Unknown	1	19.033	5320905	150414	49.962	64.405	N/A	7152	10.705	1.218	
2	Unknown	1	32.642	5328980	83130	50.038	35.595	N/A	6270	N/A	1.281	



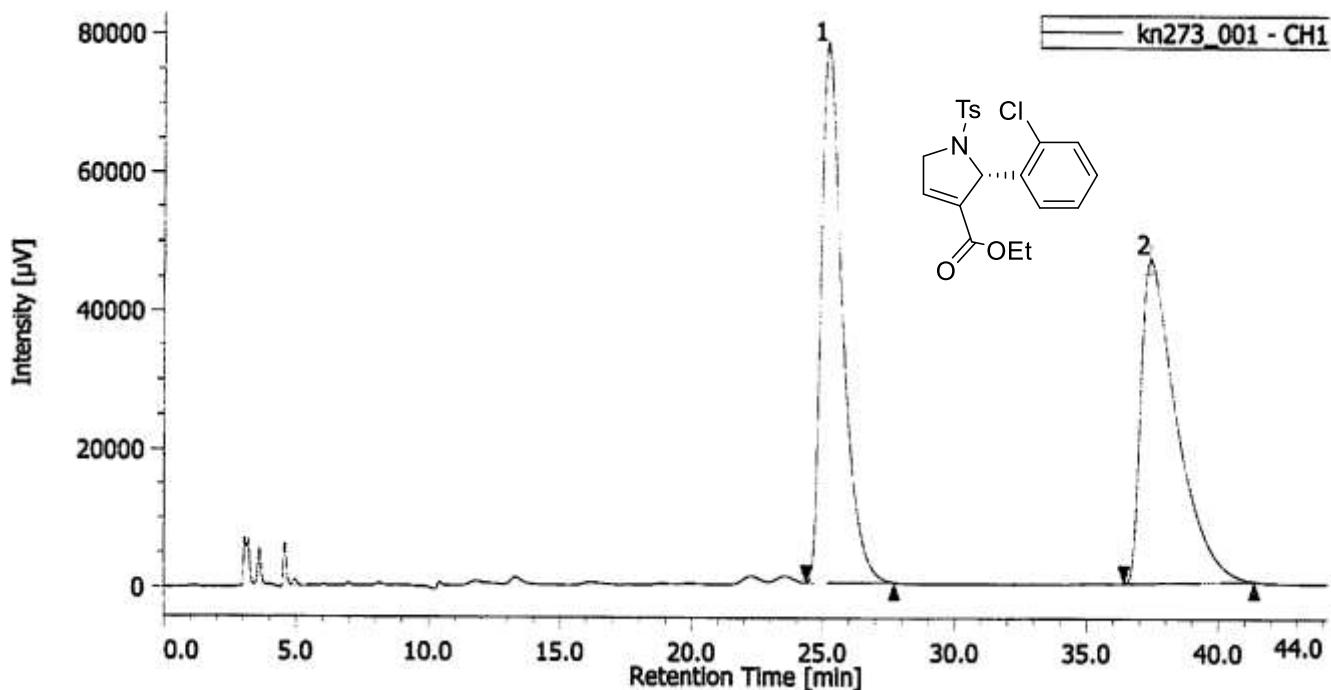
#	ピーク名	CH	tR [min]	面積 [$\mu\text{V}\cdot\text{sec}$]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	1	19.367	1339881	37800	9.980	17.169	N/A	7364	10.398	1.159	
2	Unknown	1	32.975	12072191	182365	80.010	82.831	N/A	5869	N/A	1.411	



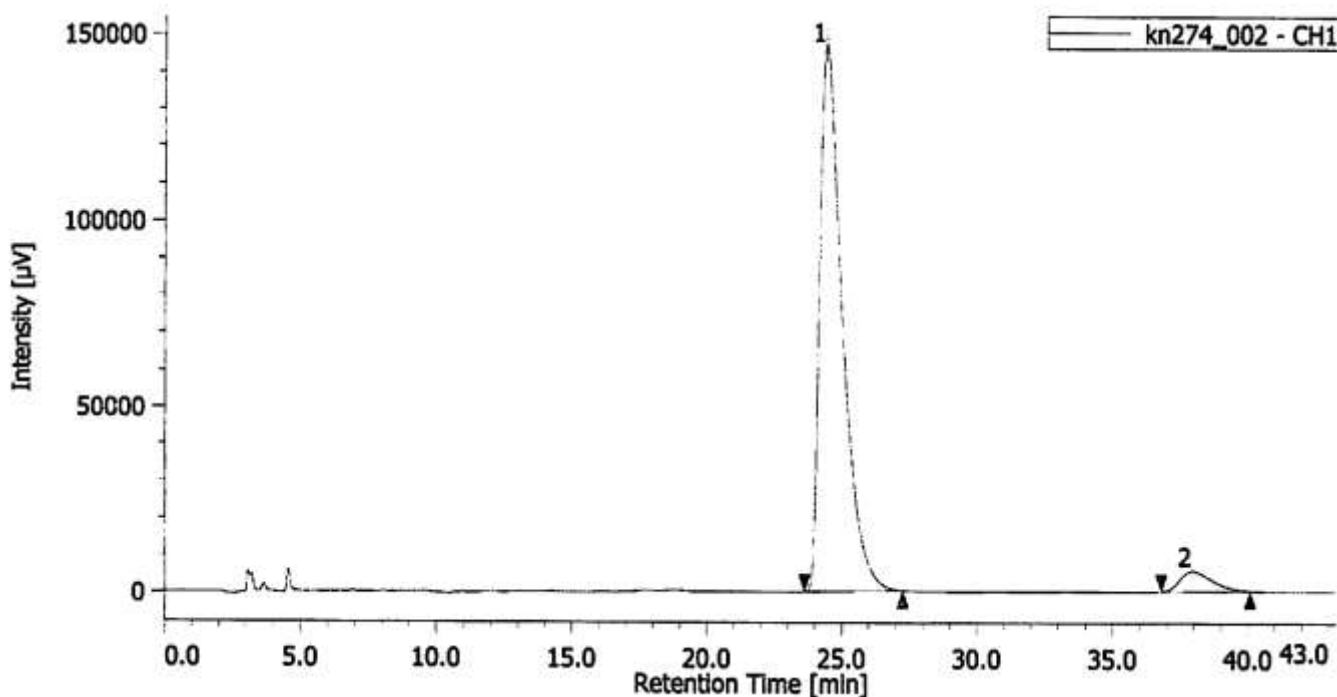
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1	Unknown	1	15.108	3829515	172732	49.953	53.958	N/A	10752	3.846	1.119	
2	Unknown	1	17.542	3836741	147393	50.047	46.042	N/A	10468	N/A	1.122	



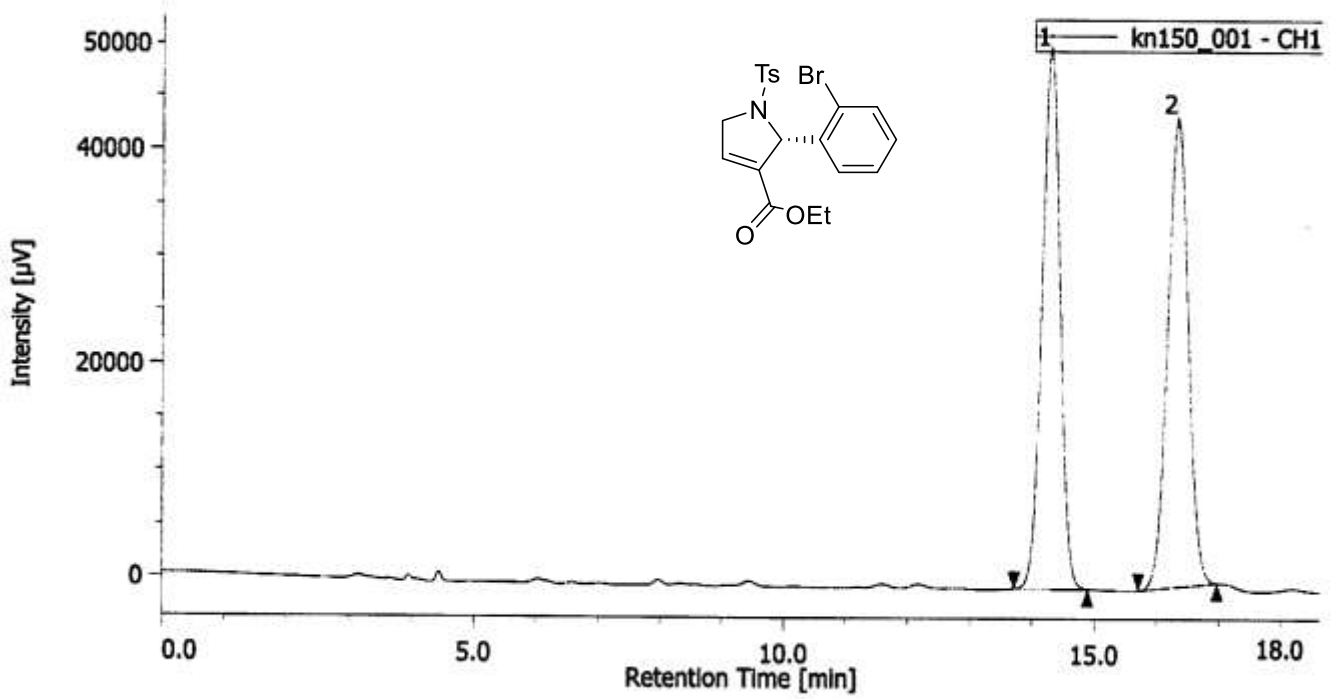
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1	Unknown	1	15.025	1078761	49570	9.018	10.542	N/A	11015	3.745	1.083	
2	Unknown	1	17.367	10883897	420654	90.982	89.458	N/A	10399	N/A	1.171	



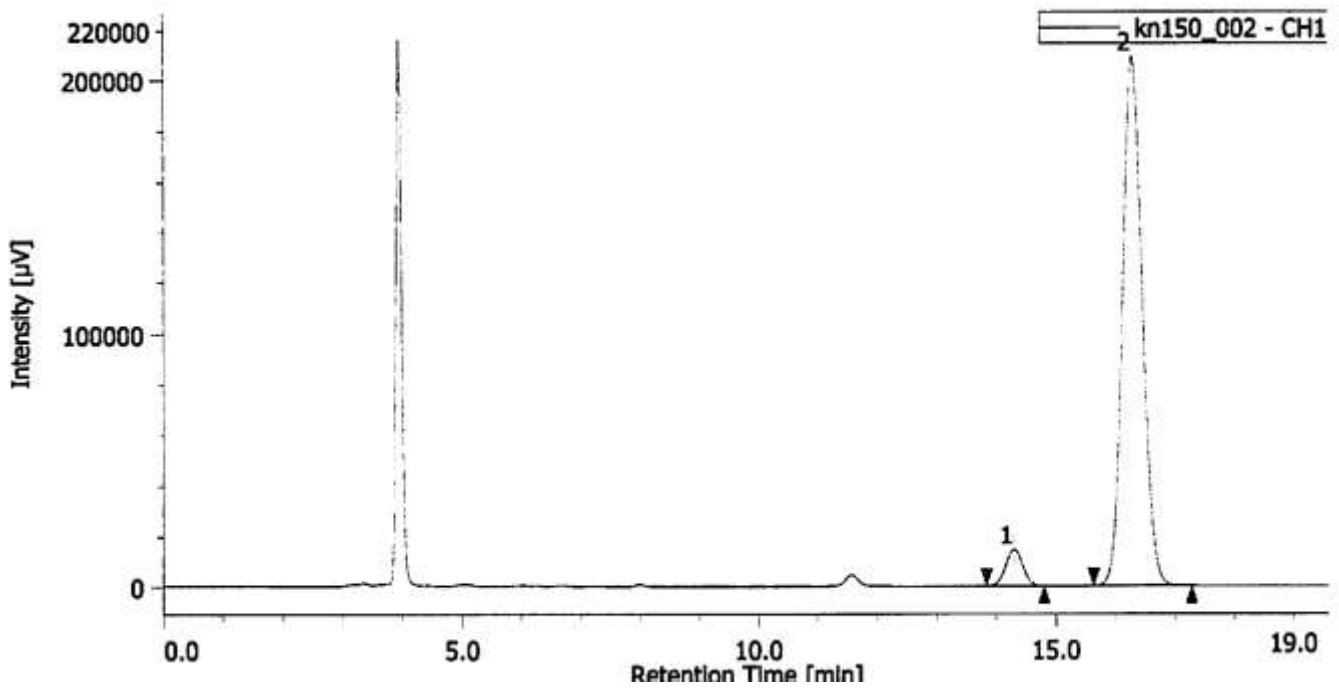
#	ピーク名	CH	tR [min]	面積: [μV·sec]	高さ: [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	1	25.175	4458177	78056	50.014	82.443	N/A	4784	6.346	1.809	
2	Unknown	1	37.400	4455756	46949	49.986	37.557	N/A	3883	N/A	2.407	



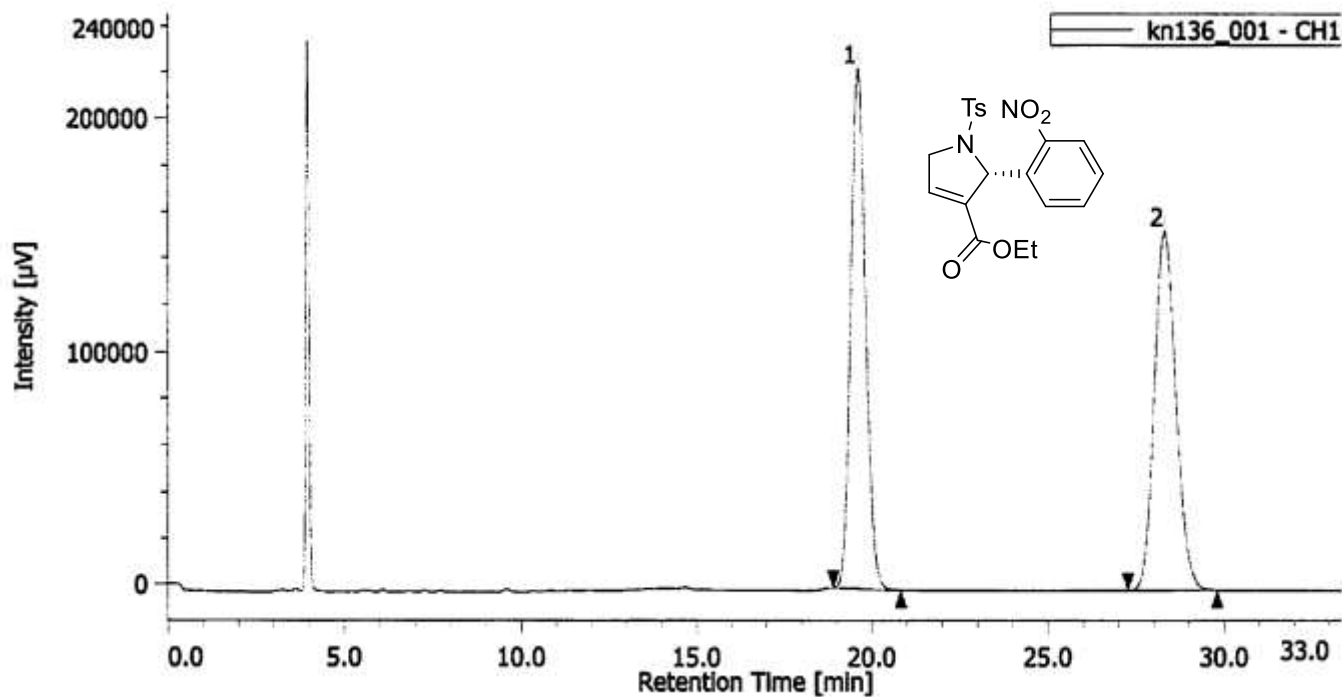
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1	Unknown	1	24.408	8566828	147383	94.922	98.382	N/A	4403	7.394	2.087	
2	Unknown	1	37.933	458263	5532	5.078	3.618	N/A	4770	N/A	1.468	



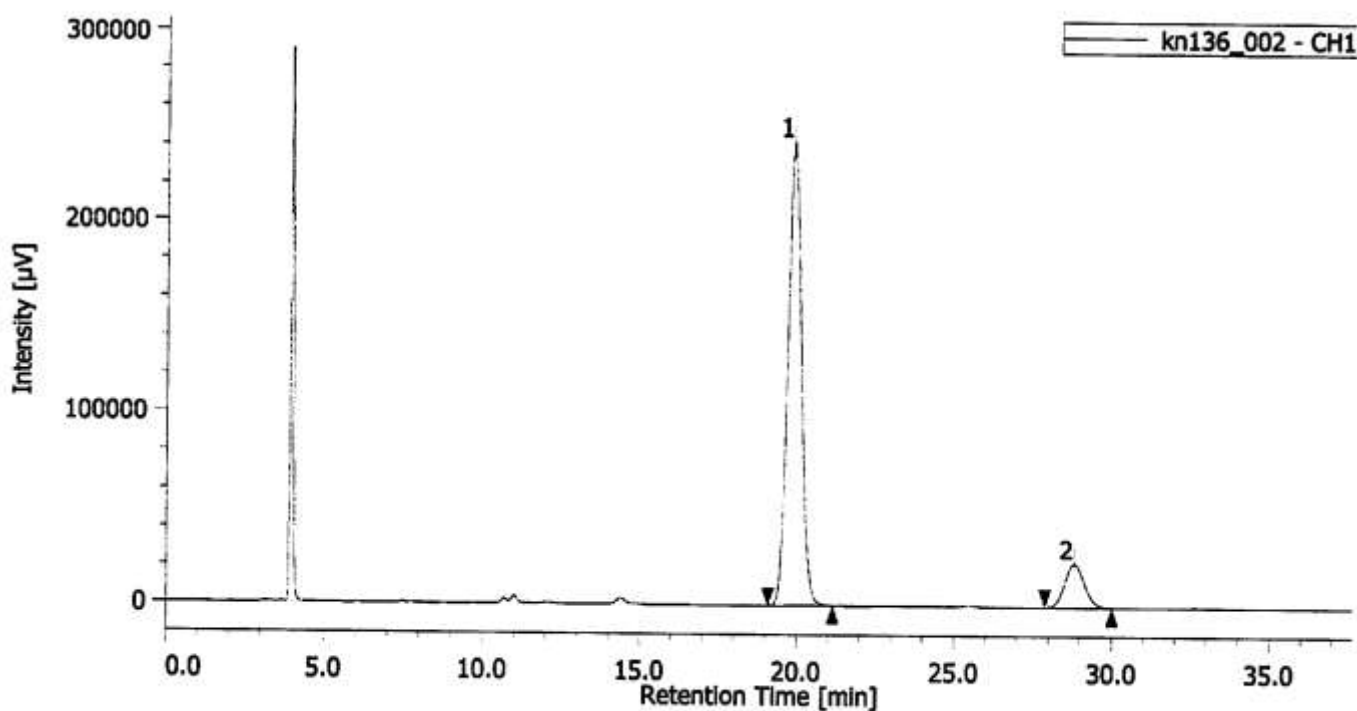
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1	Unknown	1	14.283	1021684	50840	50.148	53.641	N/A	11653	3.598	1.022	
2	Unknown	1	16.325	1015669	43937	49.852	48.359	N/A	11512	N/A	1.044	



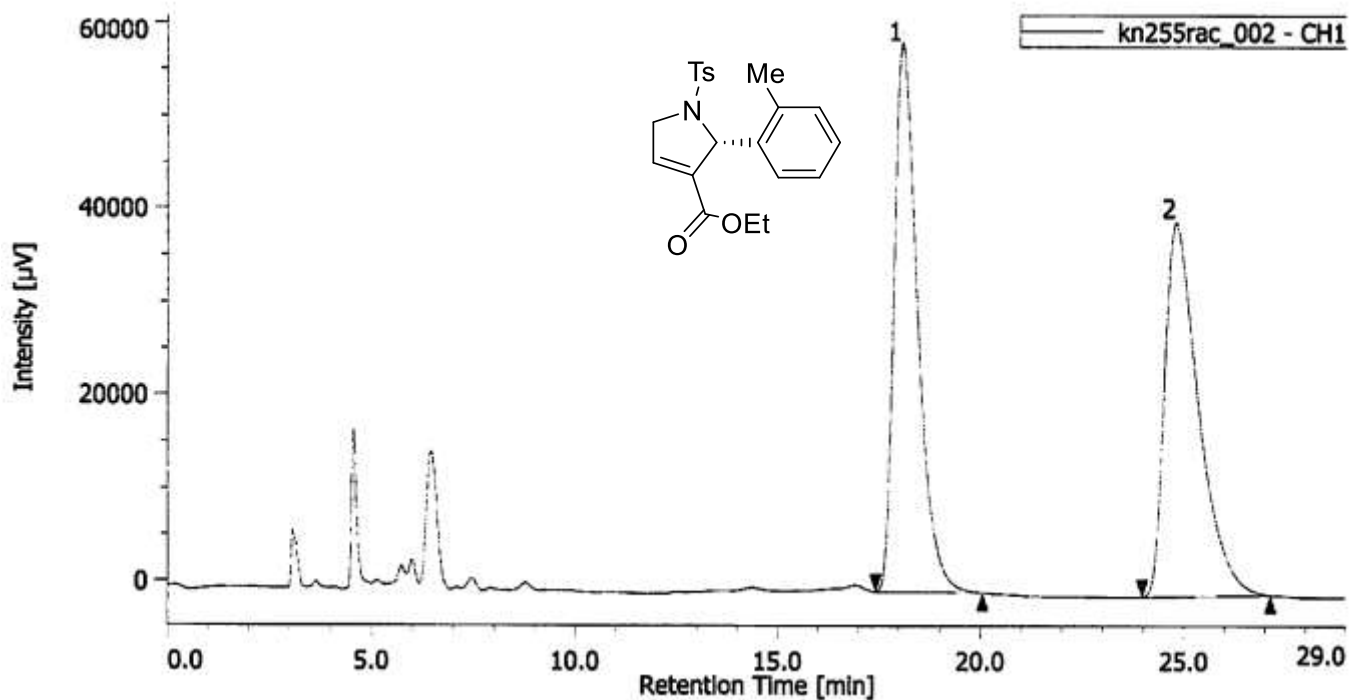
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1	Unknown	1	14.300	291941	14830	5.635	6.617	N/A	12013	3.484	1.008	
2	Unknown	1	16.275	4888769	209272	94.365	93.383	N/A	11209	N/A	1.103	



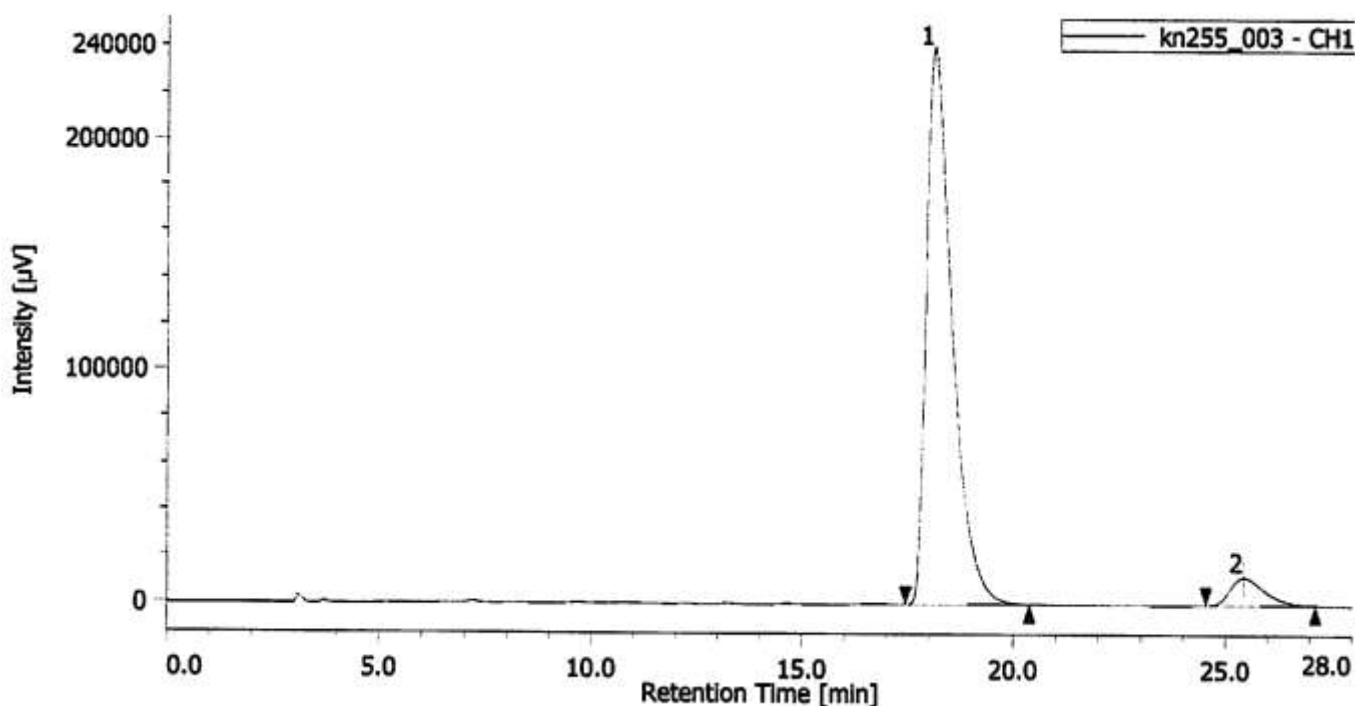
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1	Unknown	1	19.592	6557252	223460	49.835	59.168	N/A	10312	9.191	1.124	
2	Unknown	1	28.292	6600622	154208	50.165	40.832	N/A	10092	N/A	1.136	



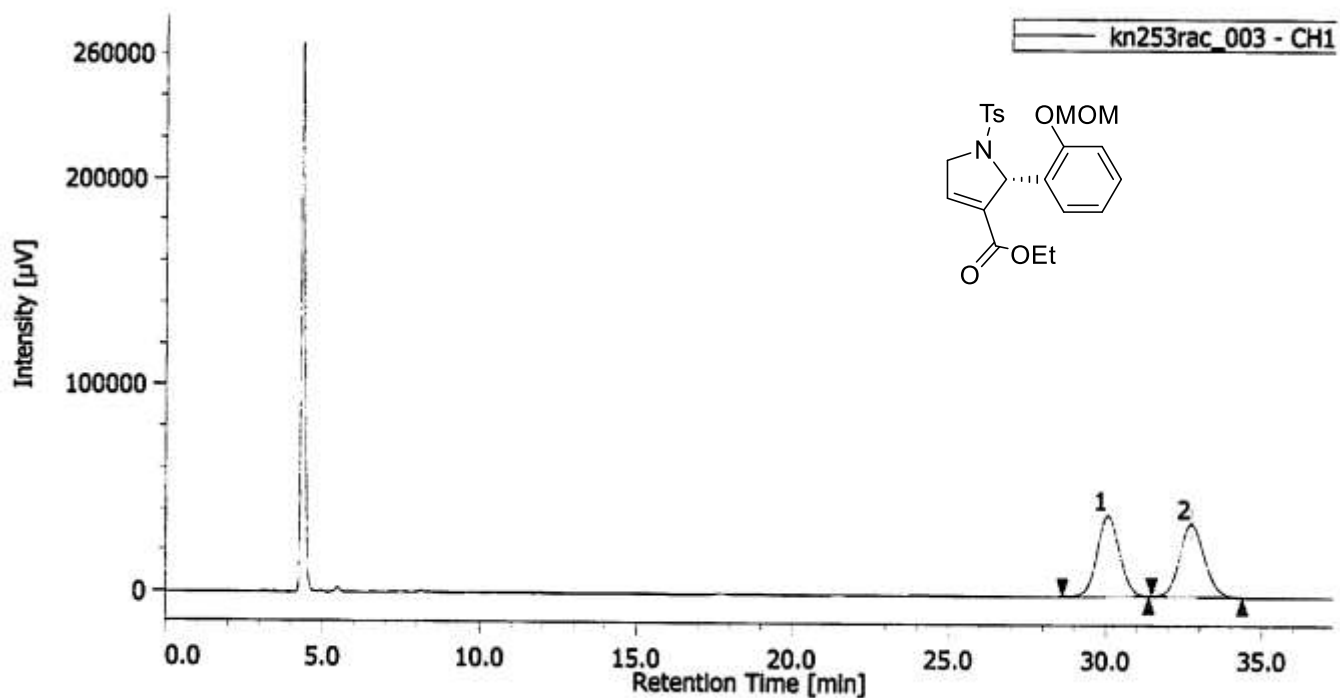
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1	Unknown	1	19.867	7275855	242980	88.010	91.382	N/A	10229	9.305	1.123	
2	Unknown	1	28.800	991180	22974	11.990	8.638	N/A	10221	N/A	1.106	



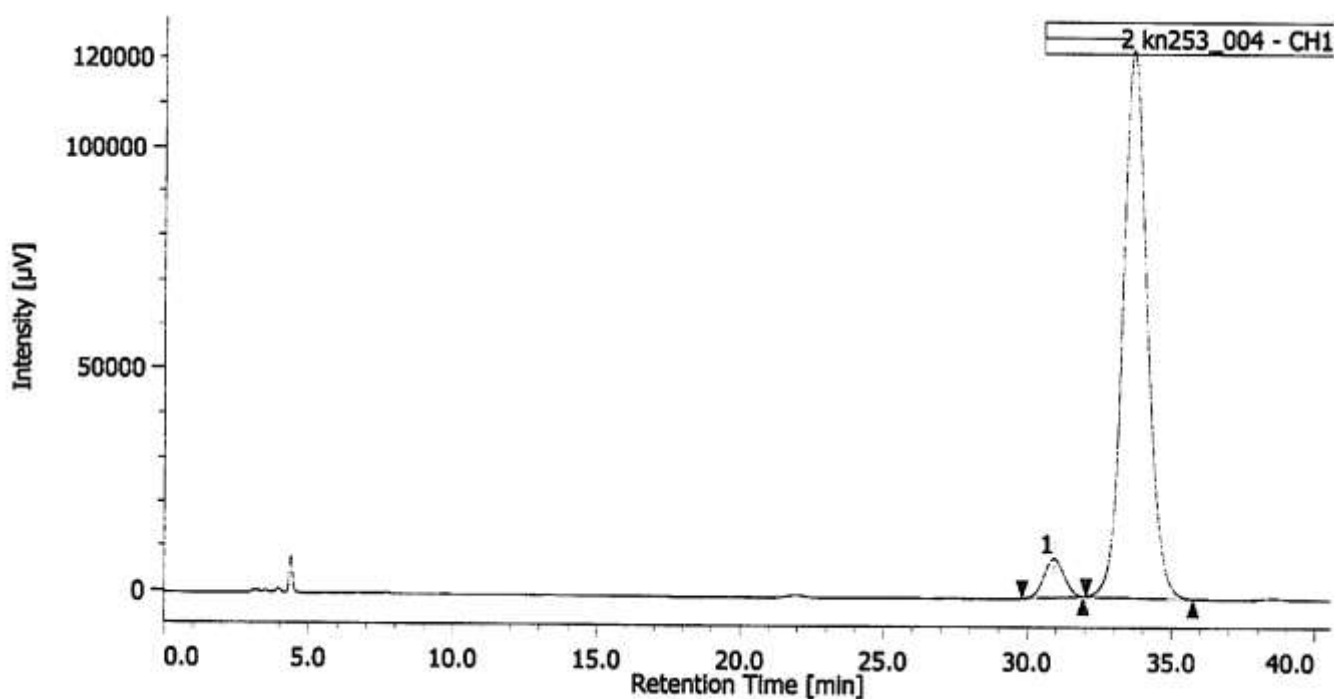
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1	Unknown	1	18.092	2385358	58951	50.227	59.581	N/A	4984	5.321	1.551	
2	Unknown	1	24.800	2343997	40026	49.773	40.439	N/A	4388	N/A	1.783	



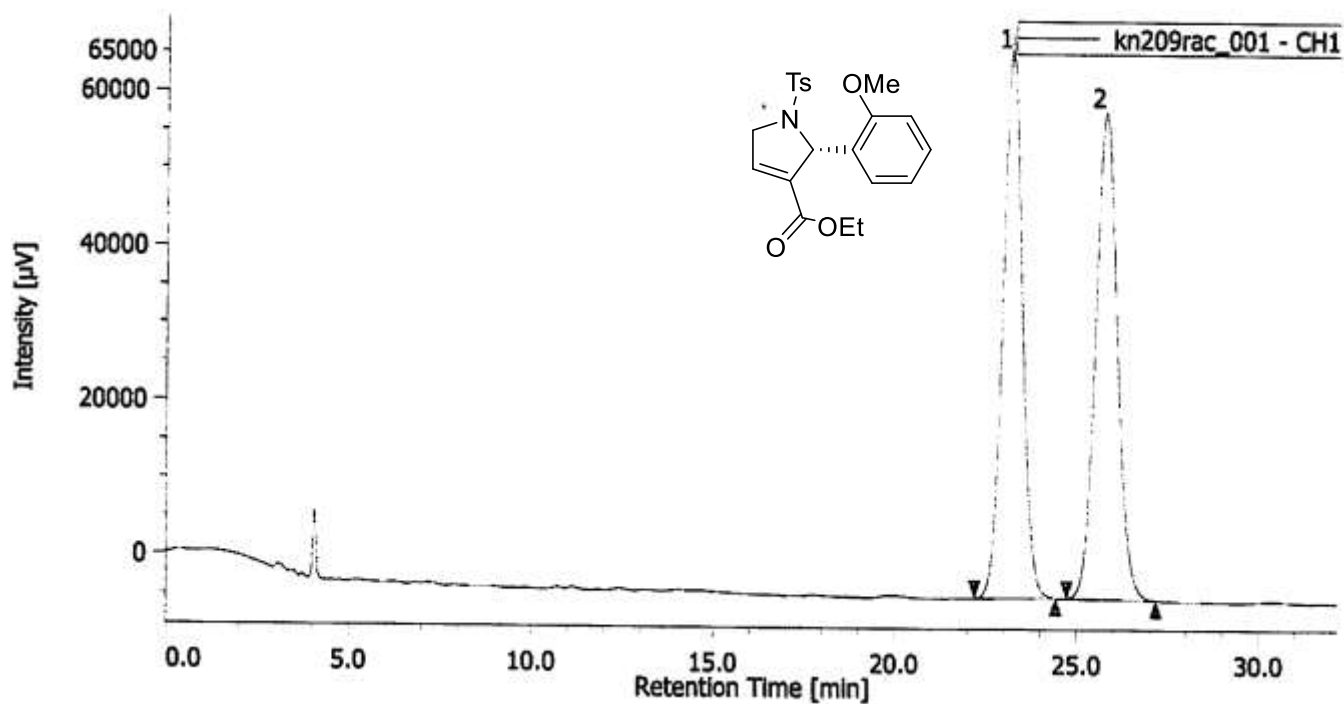
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1	Unknown	1	18.108	10157053	240529	93.779	95.329	N/A	4555	5.723	1.951	
2	Unknown	1	25.433	673833	11787	6.221	4.671	N/A	4841	N/A	1.458	



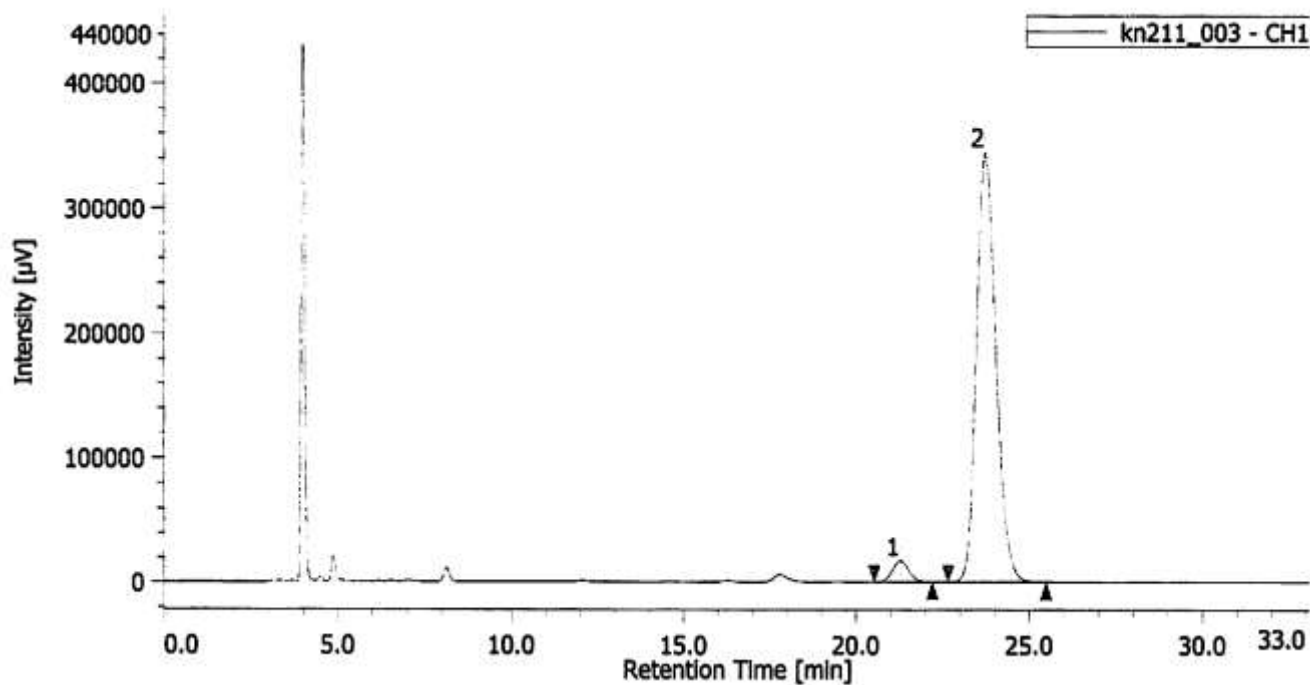
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1	Unknown	1	30.067	1932979	39200	50.179	52.732	N/A	8852	1.977	1.049	
2	Unknown	1	32.725	1919220	35137	49.821	47.268	N/A	8516	N/A	1.113	



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	1	30.917	412638	8511	5.421	6.463	N/A	9208	1.938	1.012	
2	Unknown	1	33.617	7199635	123177	94.579	93.537	N/A	7983	N/A	1.174	



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	1	23.175	2602269	70837	50.051	52.940	N/A	9394	2.536	1.093	
2	Unknown	1	25.742	2596929	62969	49.949	47.080	N/A	9200	N/A	1.133	



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	1	21.275	573945	17336	4.089	4.783	N/A	9571	2.595	1.084	
2	Unknown	1	23.725	13528908	345133	95.931	95.217	N/A	8594	N/A	1.198	