

**Stereoselective Construction of All-Carbon Quaternary Center by
Means of Chiral Phosphoric Acid: Highly Enantioselective
Friedel-Crafts Reaction of Indoles with β,β -Disubstituted Nitroalkenes**

Keiji Mori, Manari Wakazawa, and Takahiko Akiyama^{†*}

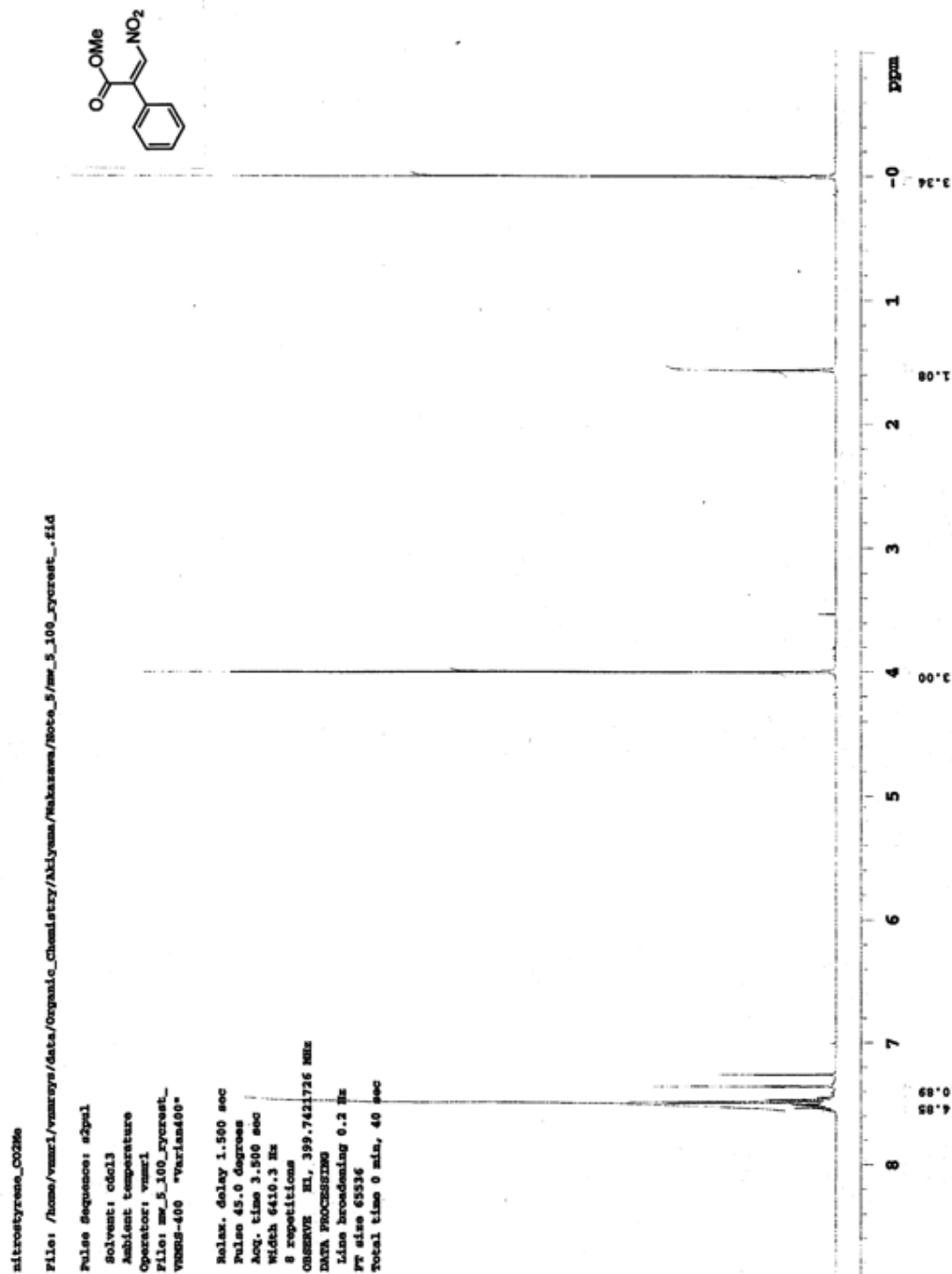
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1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan*

takahiko.akiyama@gakushuin.ac.jp

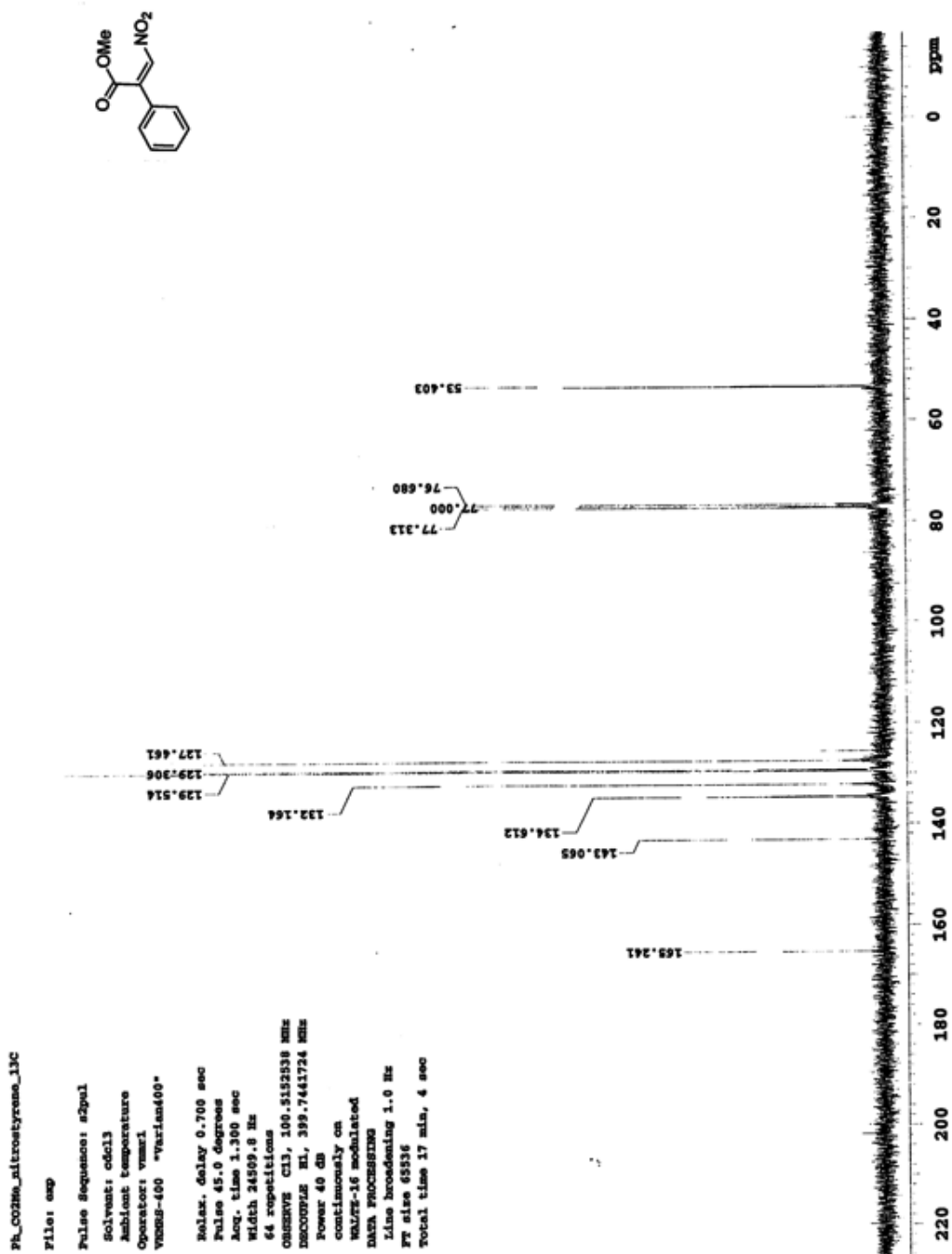
Supporting Information

Scanned images of ¹H-, ¹³C-NMR, and HPLC chart of new compounds S1

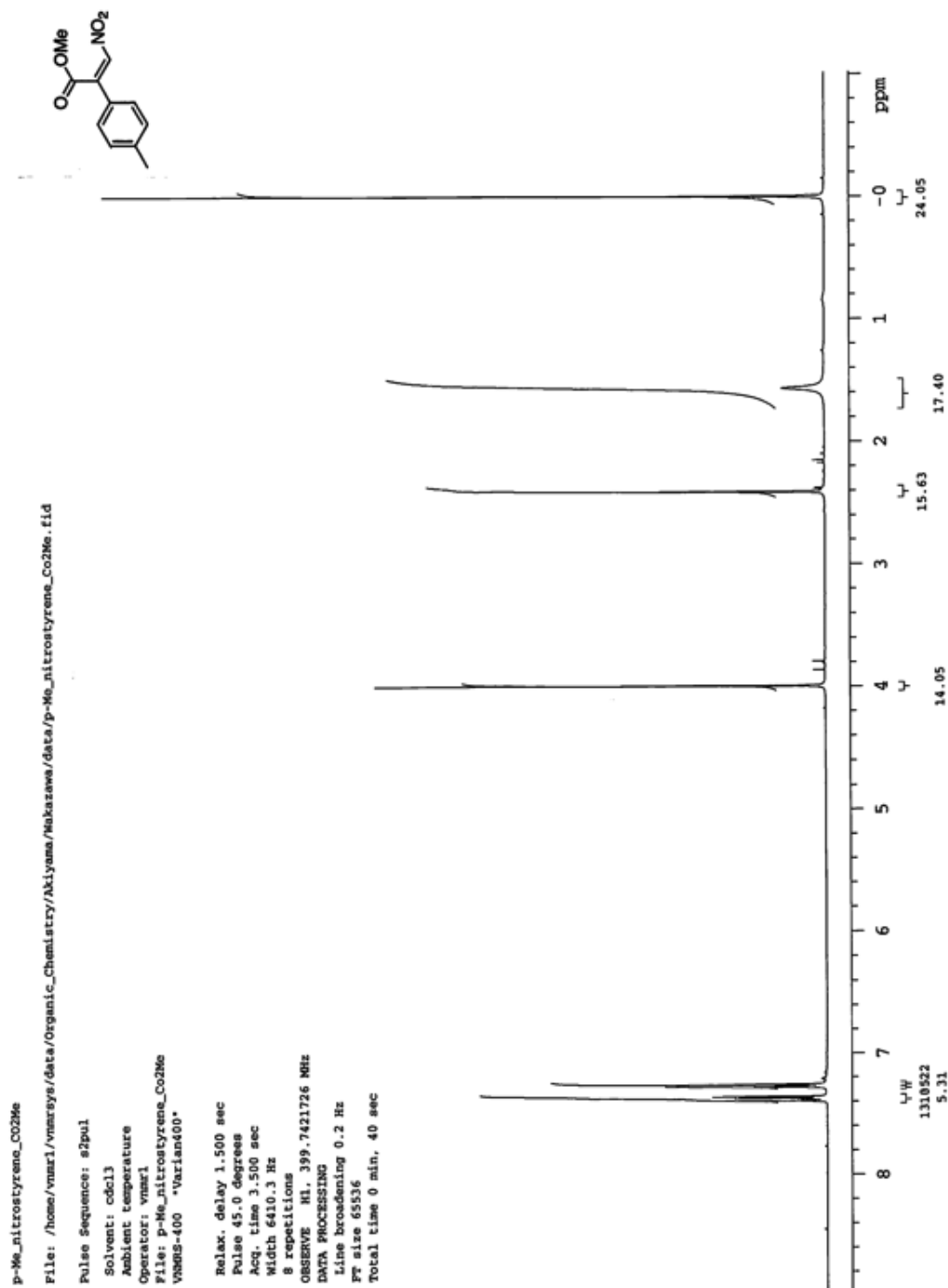
¹H NMR spectrum of **5a**.



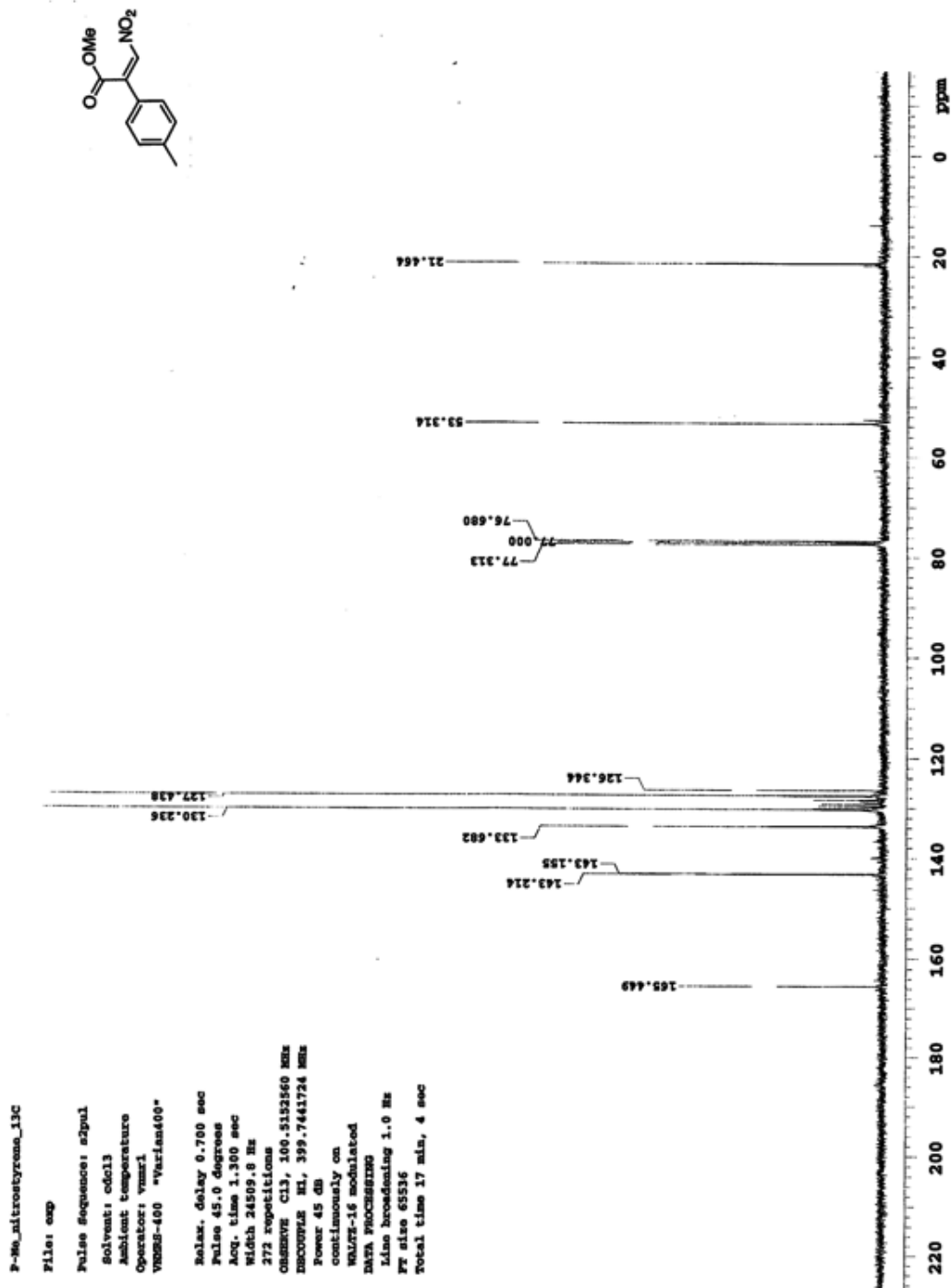
¹³C NMR spectrum of 5a.



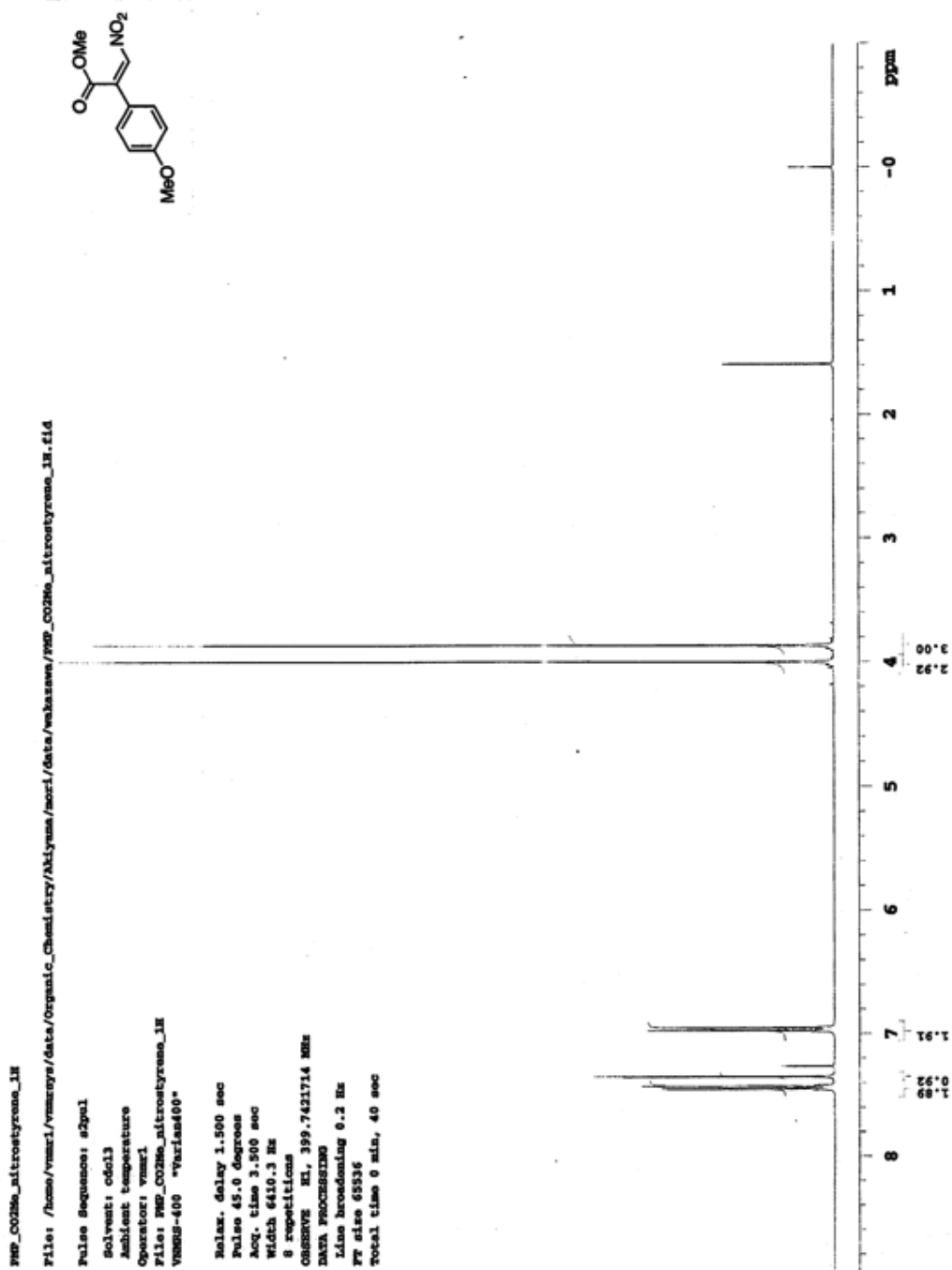
^1H NMR spectrum of **5f**.



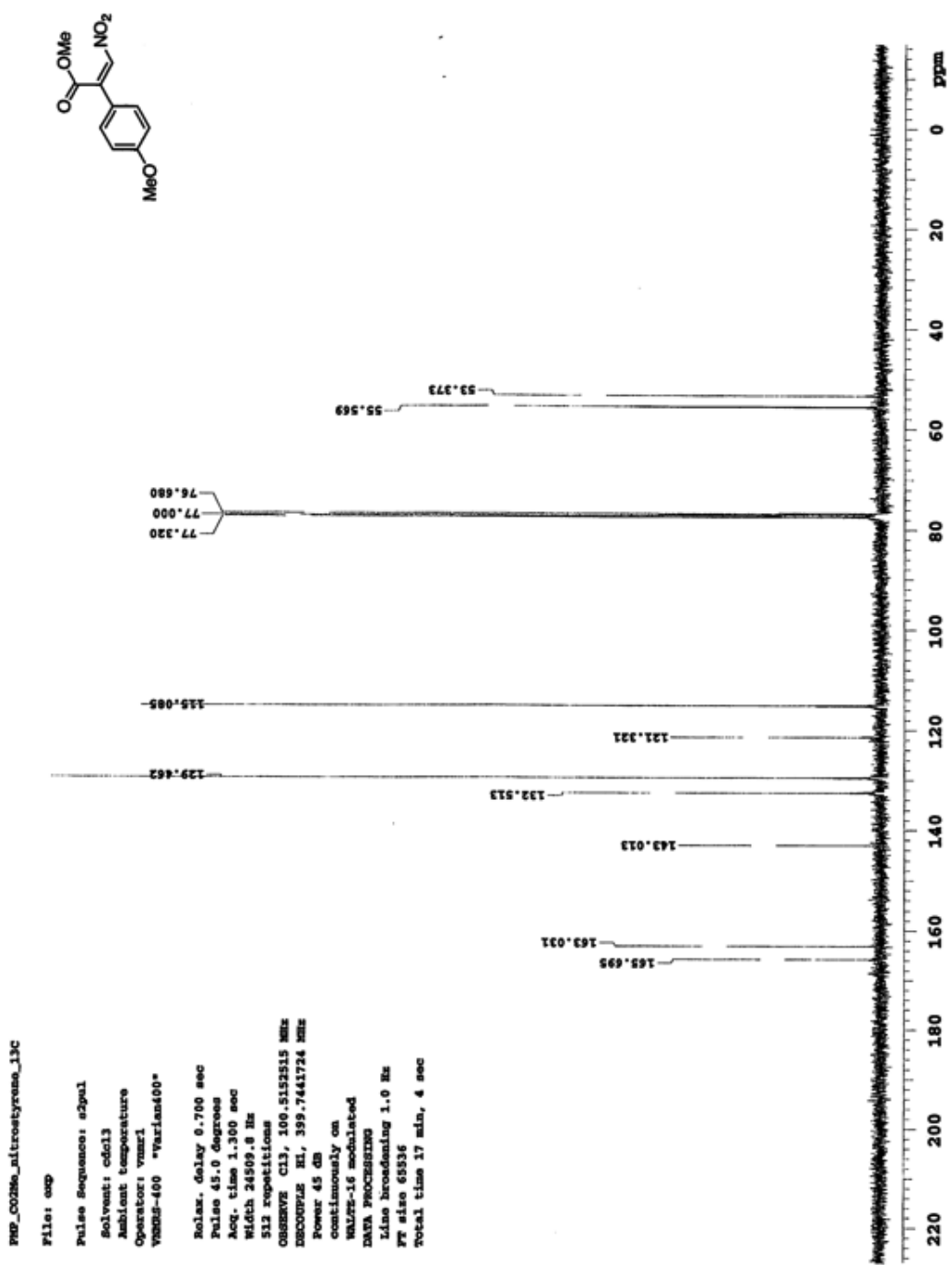
¹³C NMR spectrum of **5f**.



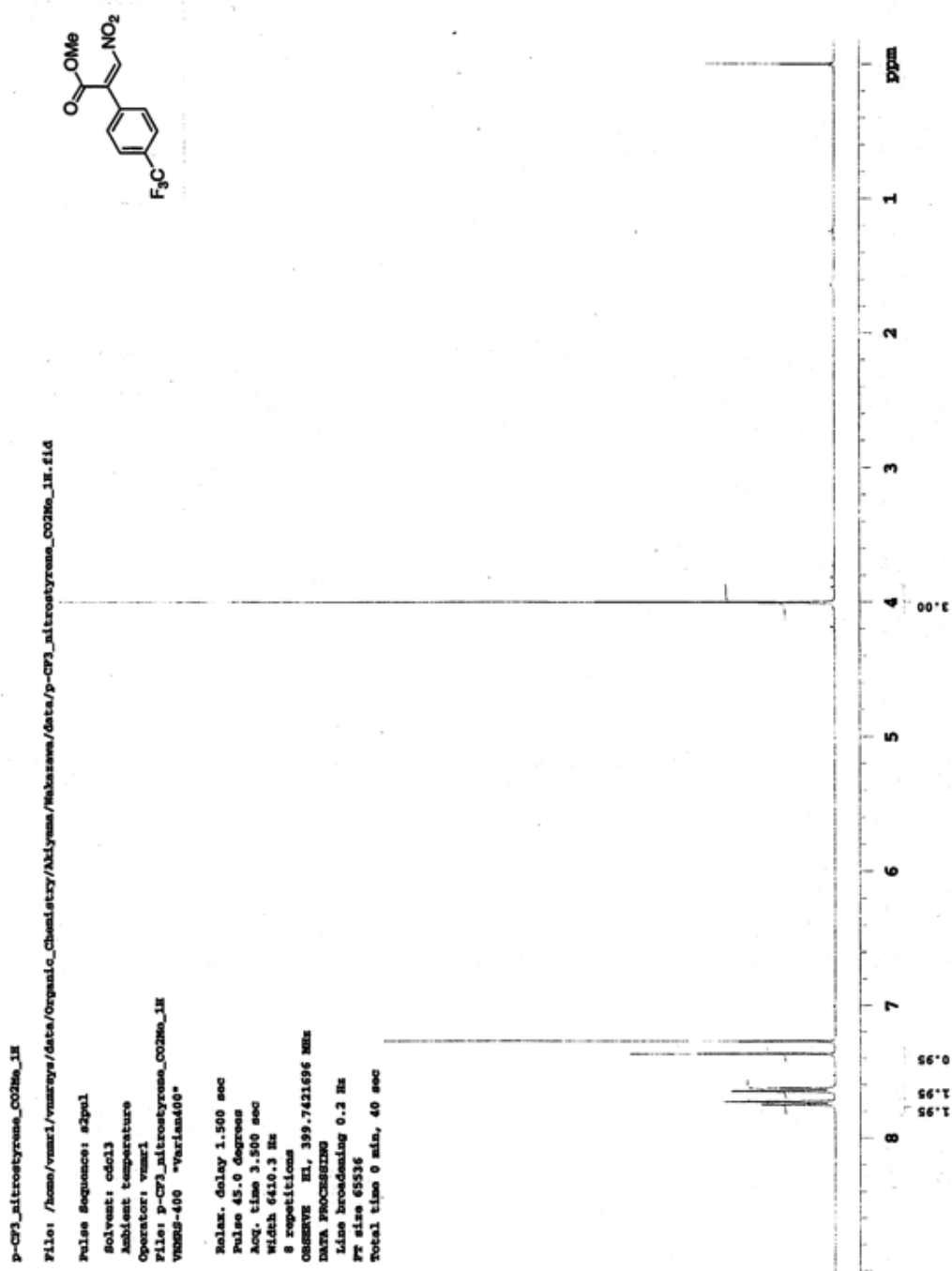
¹H NMR spectrum of **5g**.



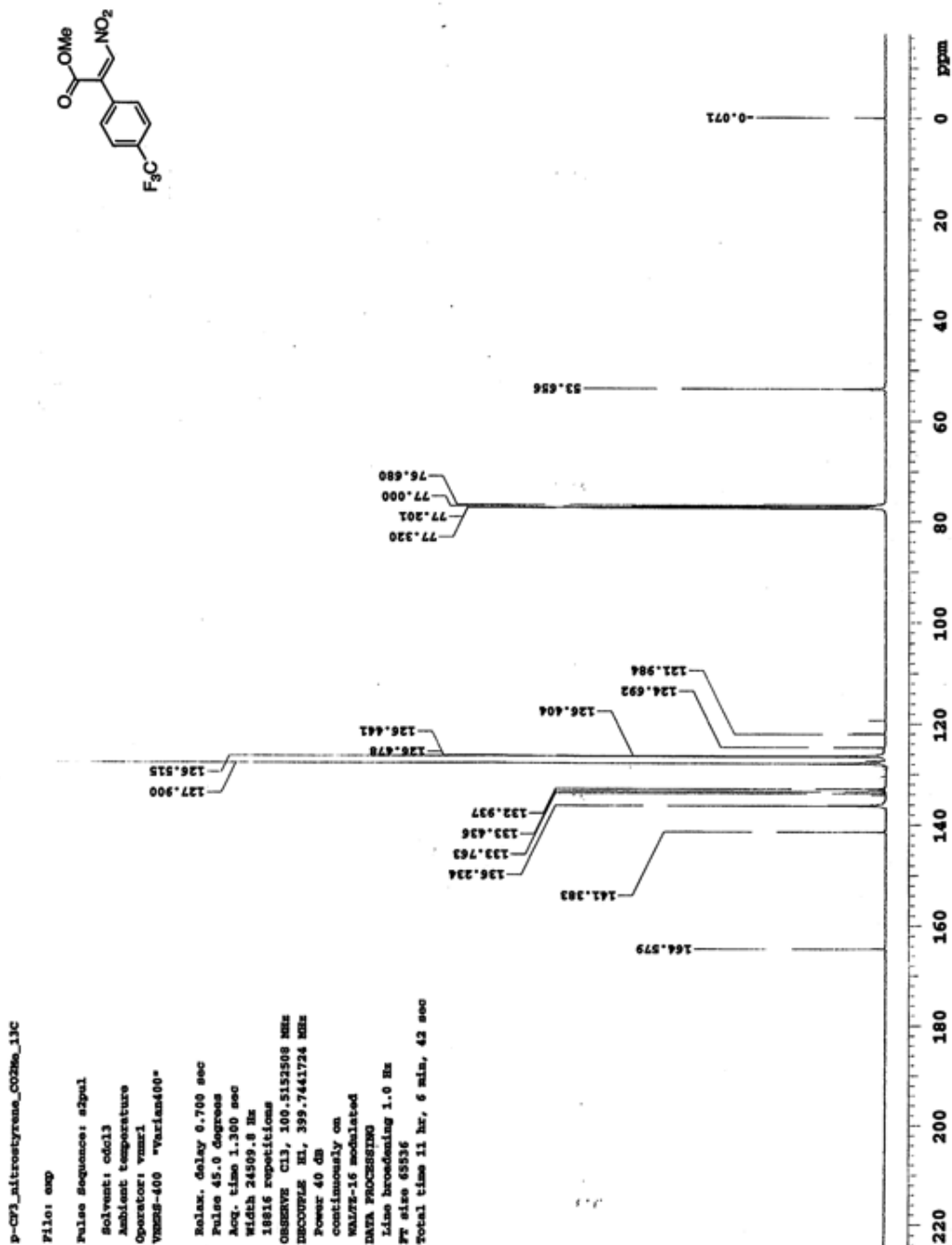
¹³C NMR spectrum of **5g**.



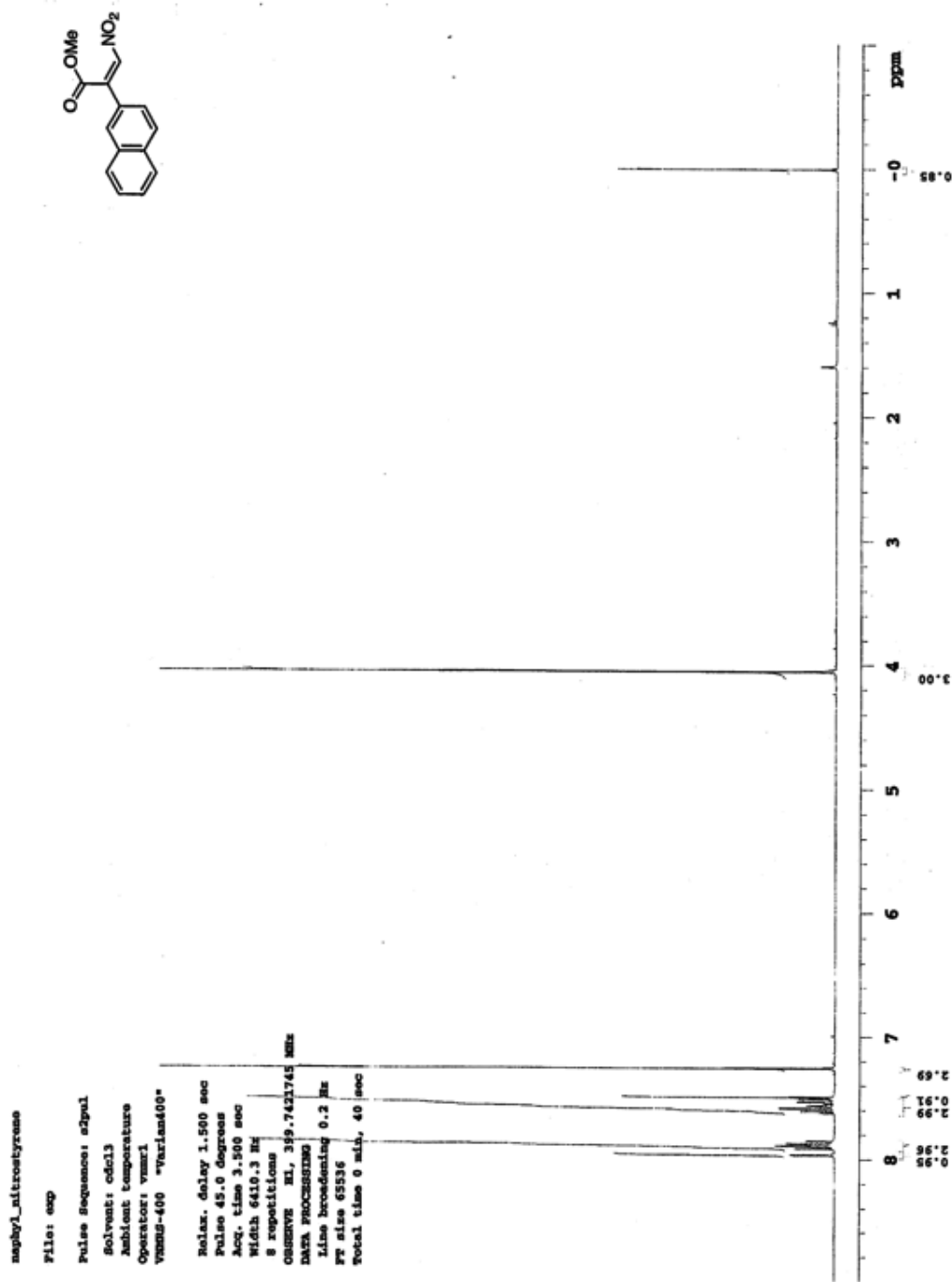
¹H NMR spectrum of **5h**.



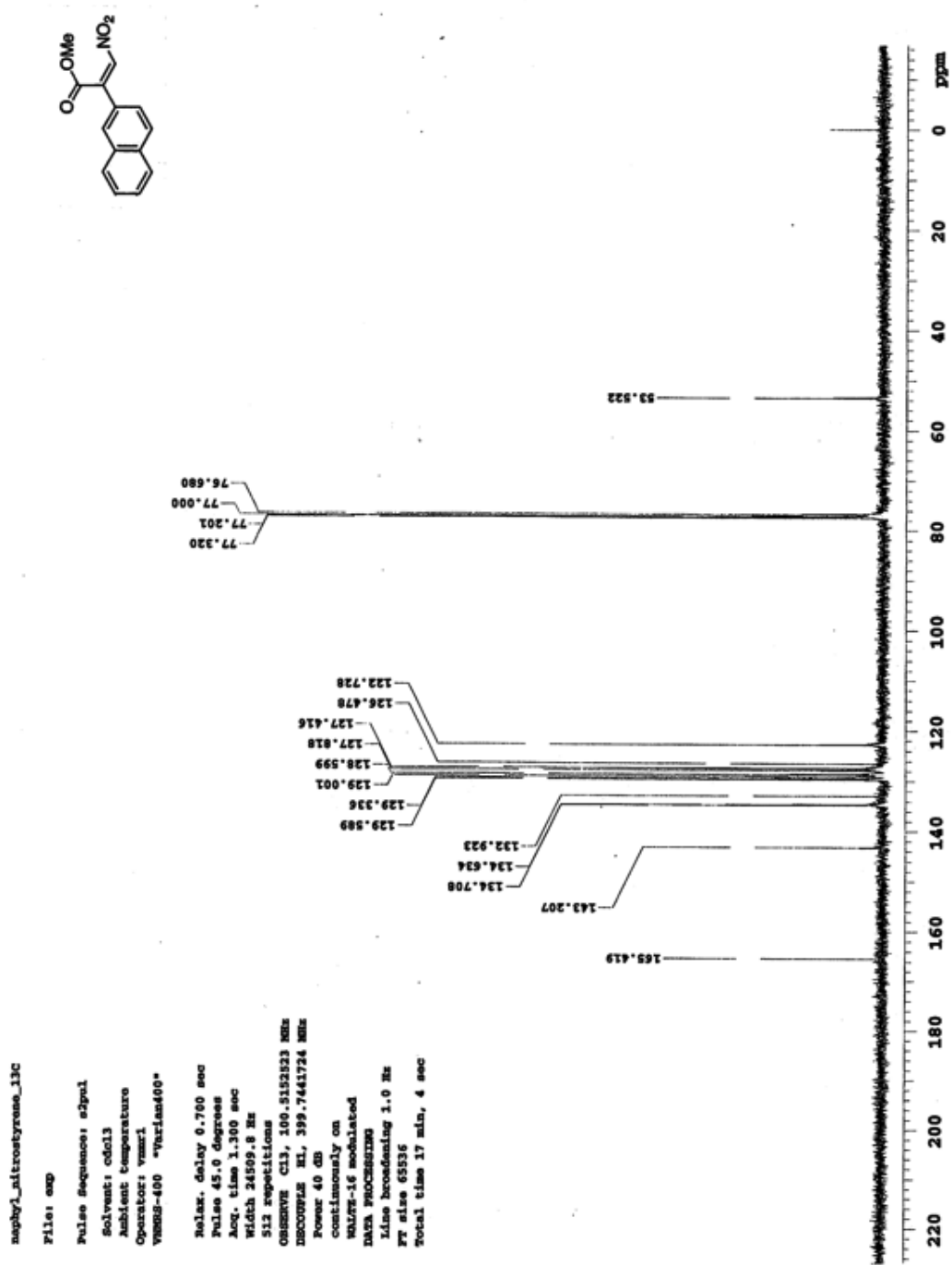
¹³C NMR spectrum of **5h**.



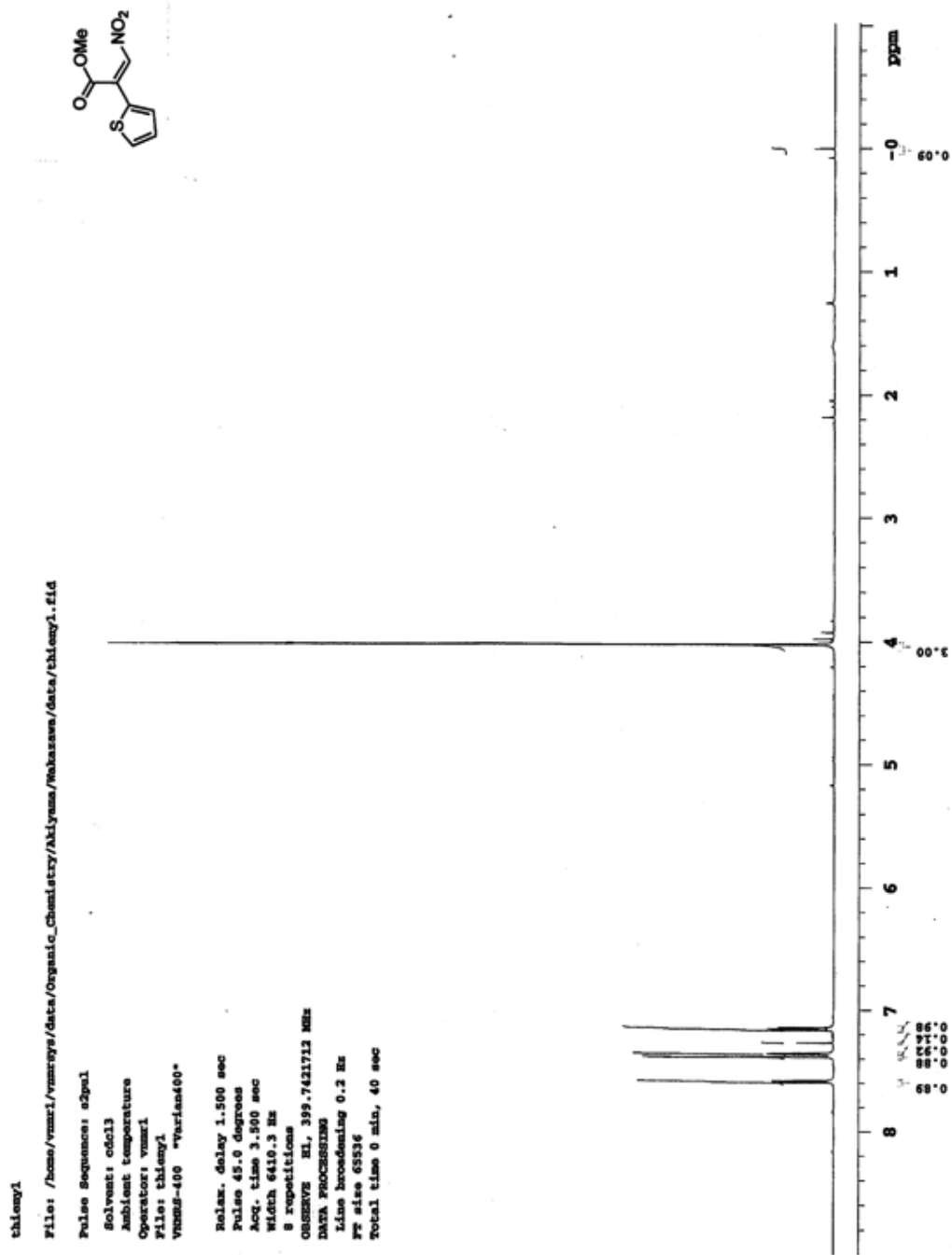
¹H NMR spectrum of **5i**.



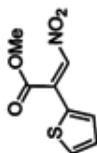
¹³C NMR spectrum of **5i**.



¹H NMR spectrum of **5j**.



¹³C NMR spectrum of **5j**.



thiemy_13C

File: exp

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vnmr1

VNMR-400 *Varian400*

Relax. delay 0.700 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 24509.6 Hz

304 repetitions

CUSERVE C13, 100.5152515 MHz

INCOUPLE H1, 399.7441724 MHz

Power 45 dB

continuously on

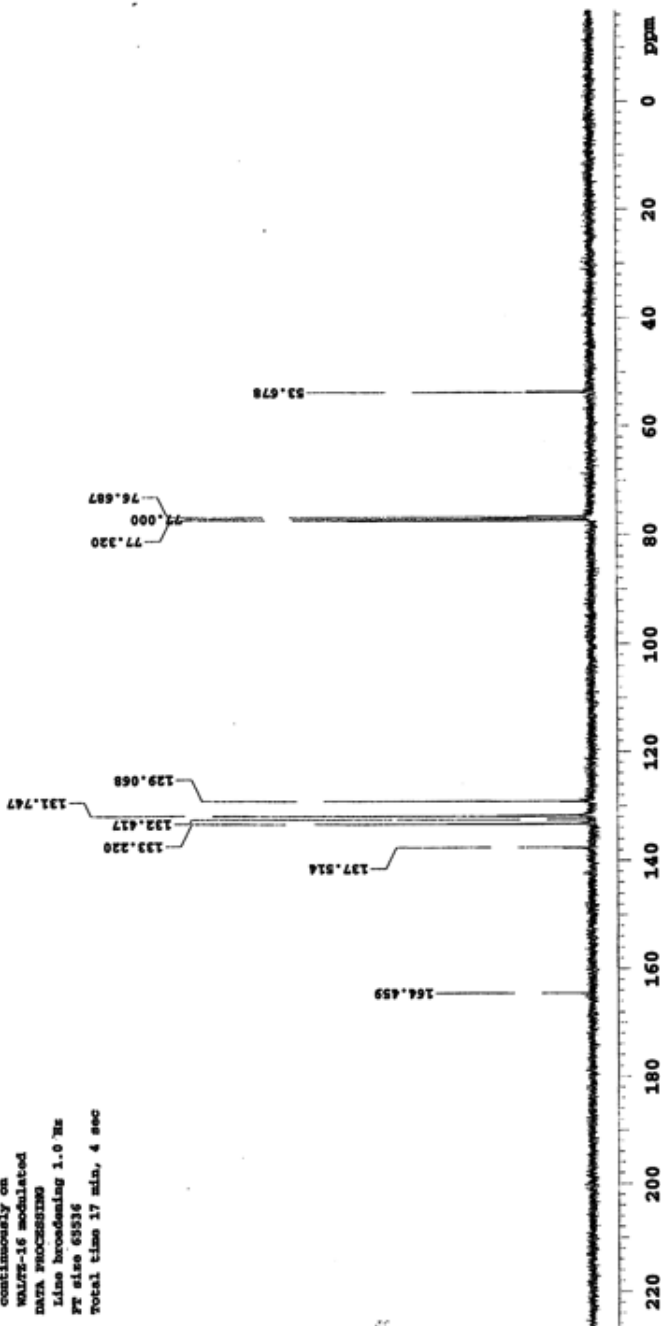
WALTZ-16 modulated

DATA PROCESSING

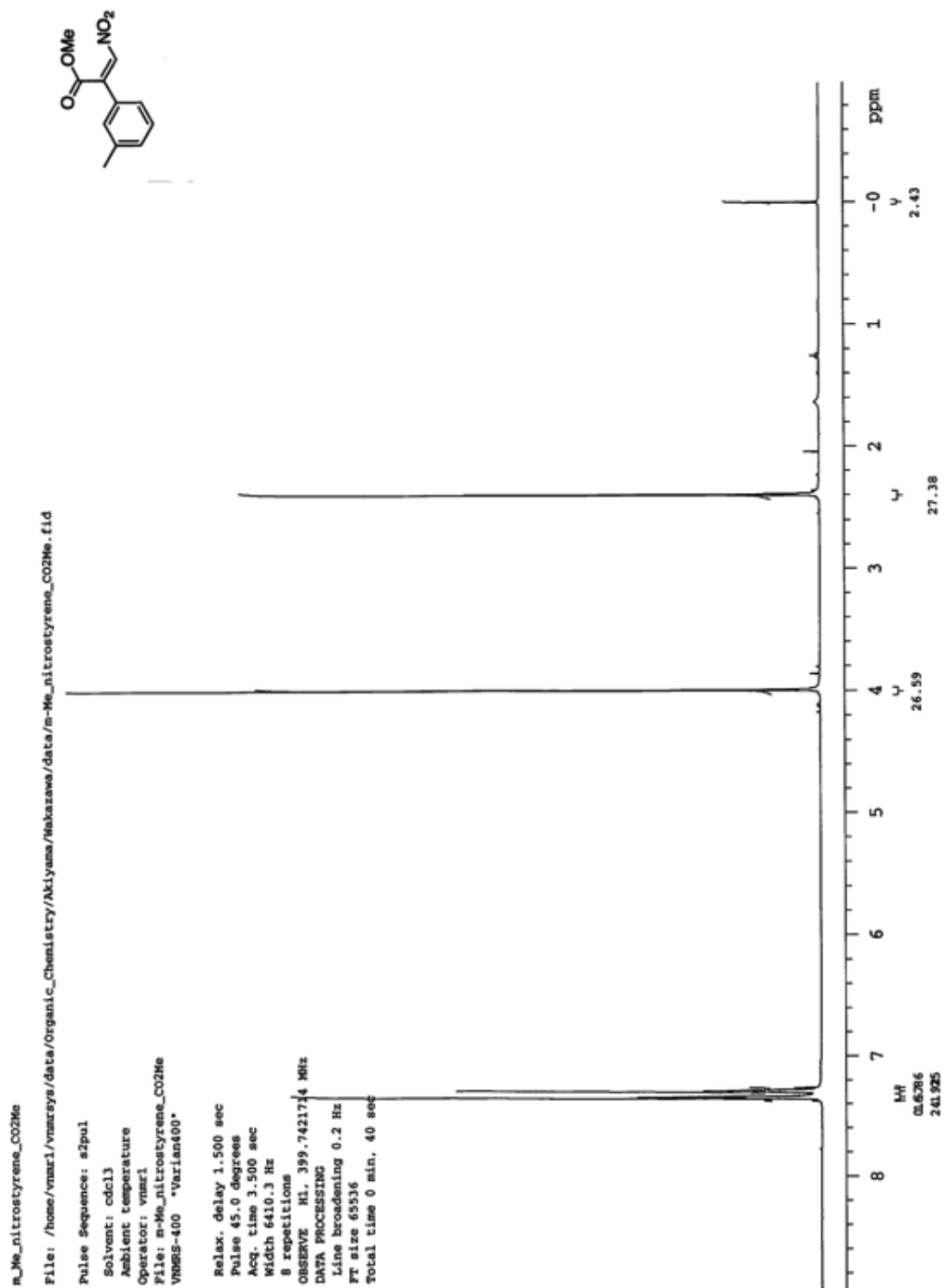
Line broadening 1.0 Hz

FT size 65536

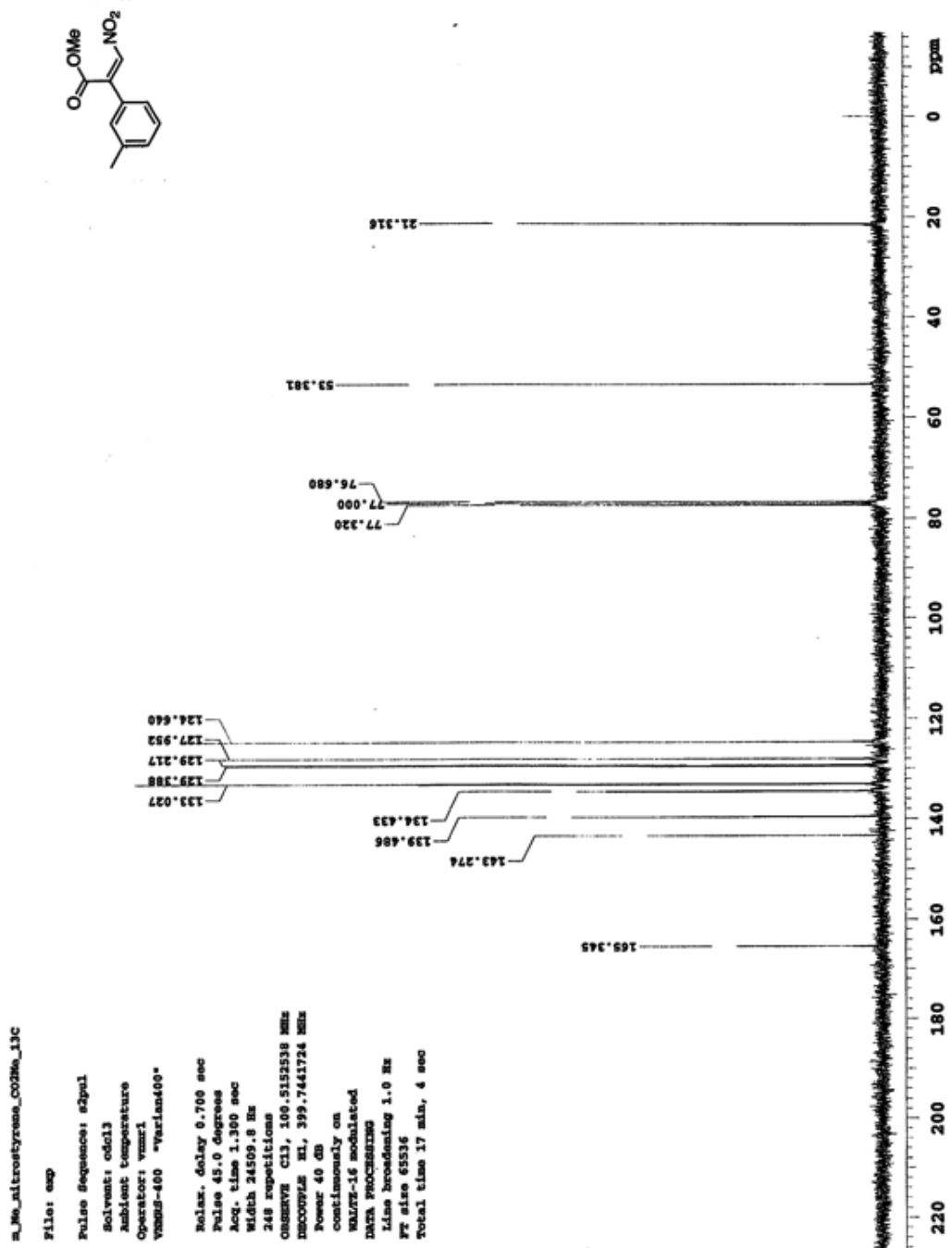
Total time 17 min, 4 sec



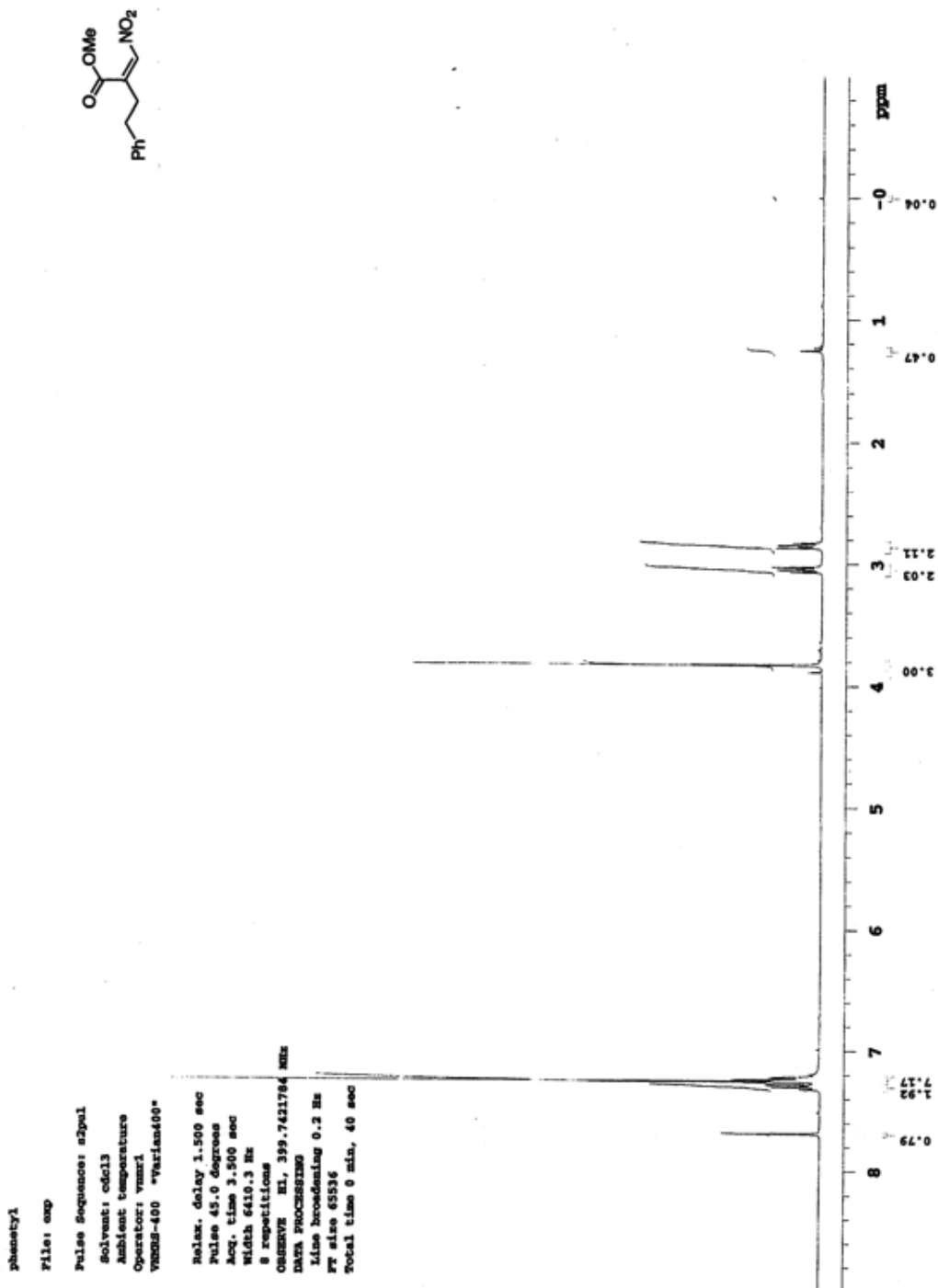
¹H NMR spectrum of **5k**.



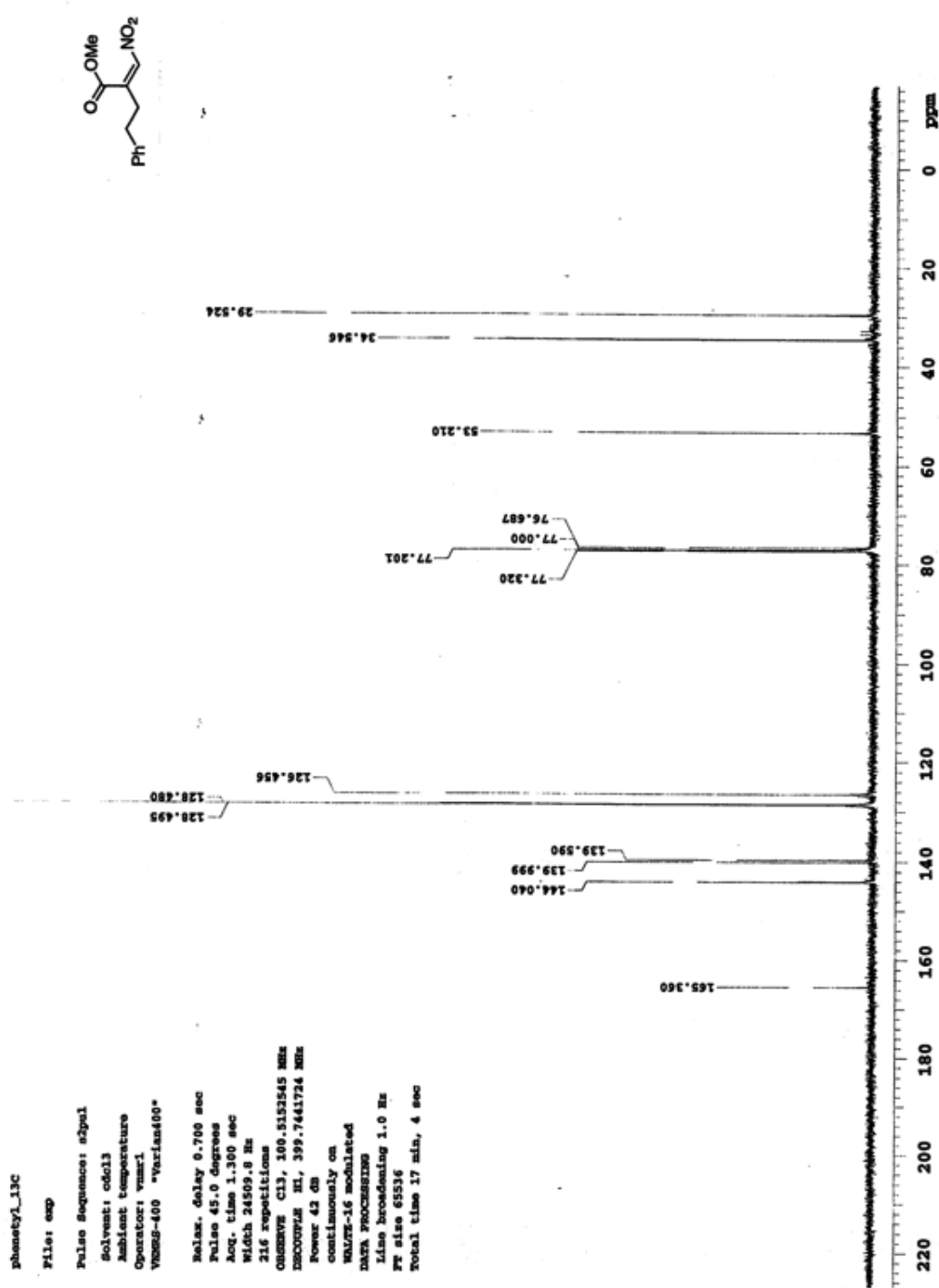
¹³C NMR spectrum of **5k**.



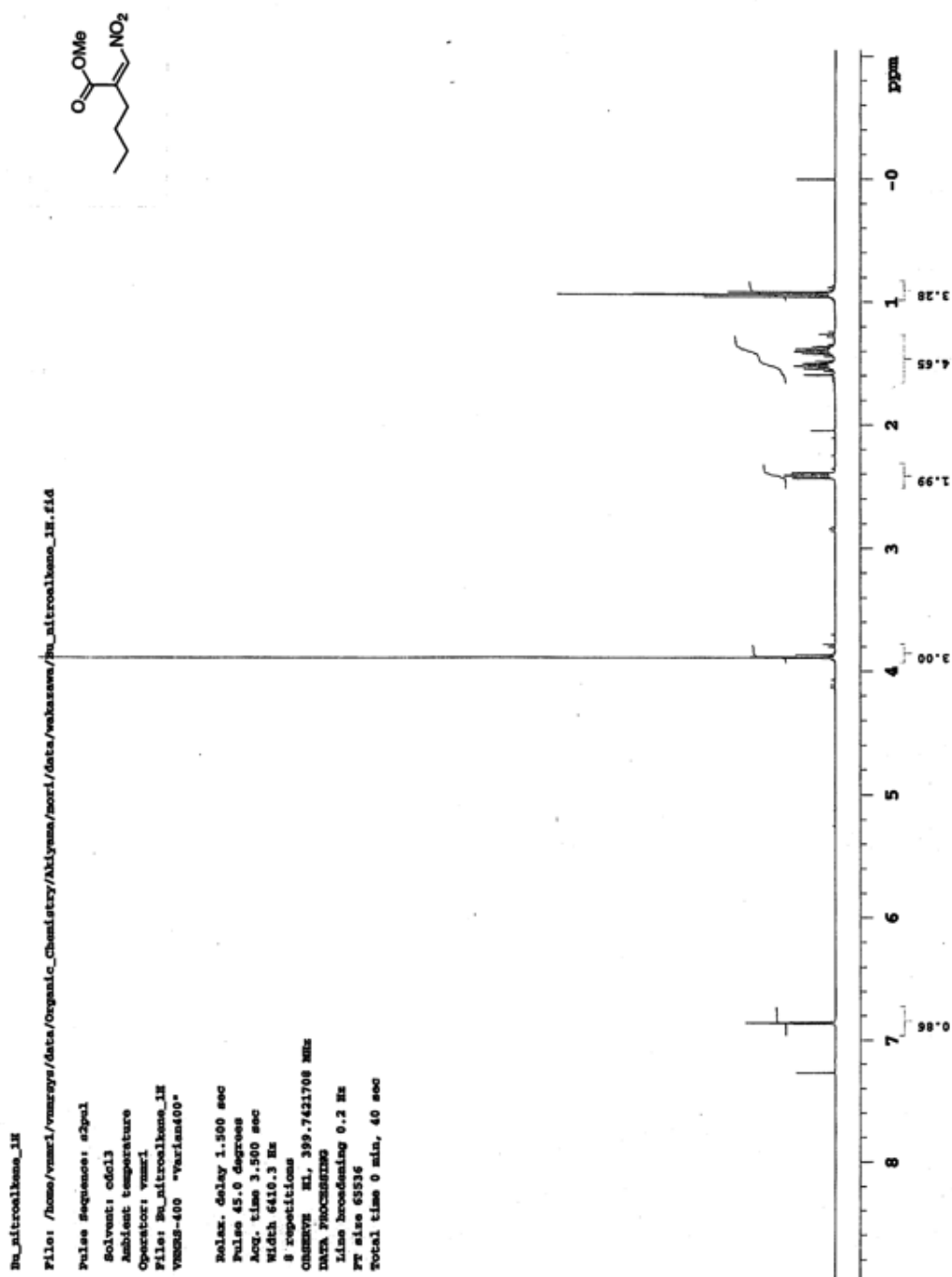
¹H NMR spectrum of **5m**.



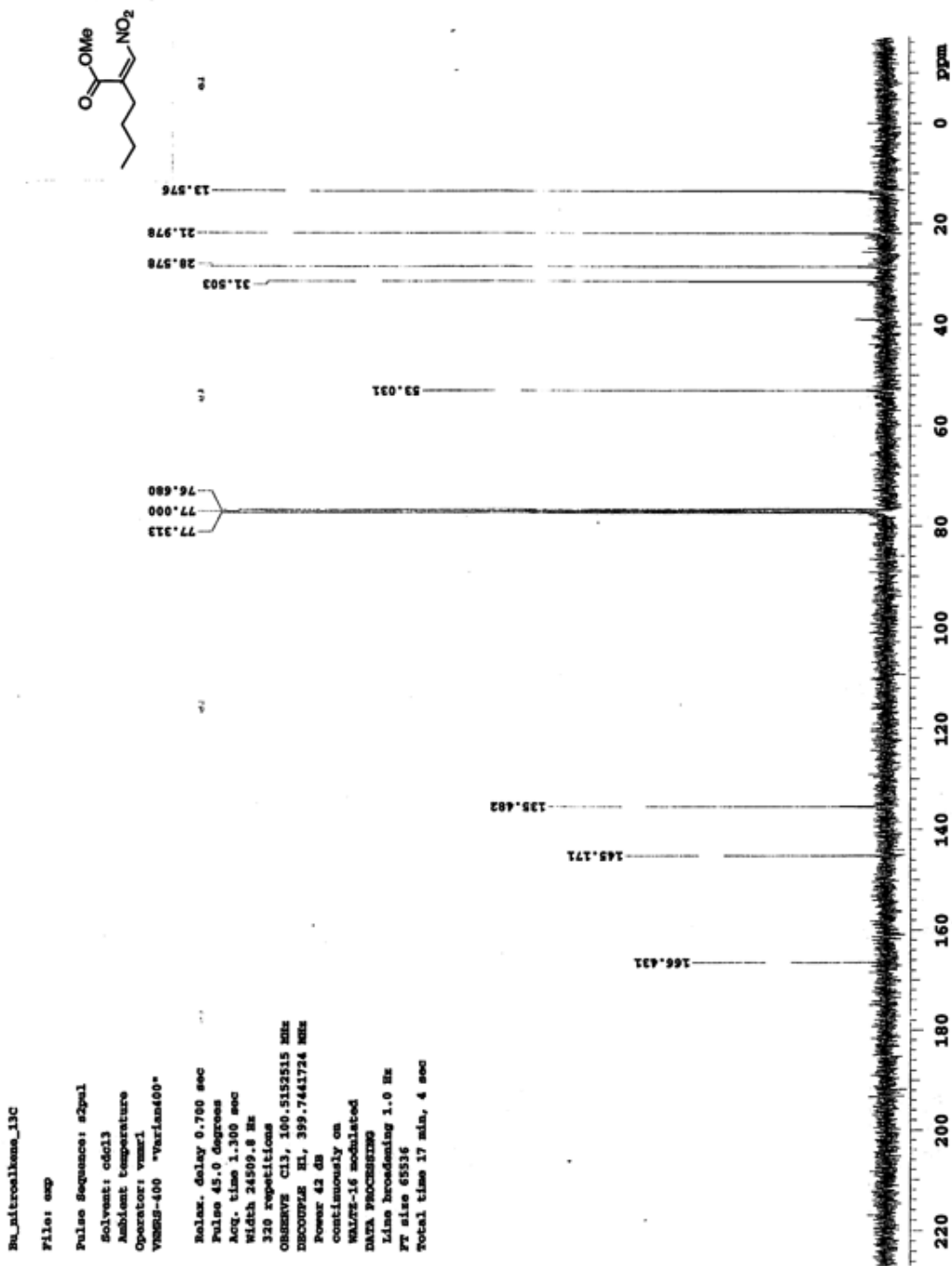
¹³C NMR spectrum of **5m**.



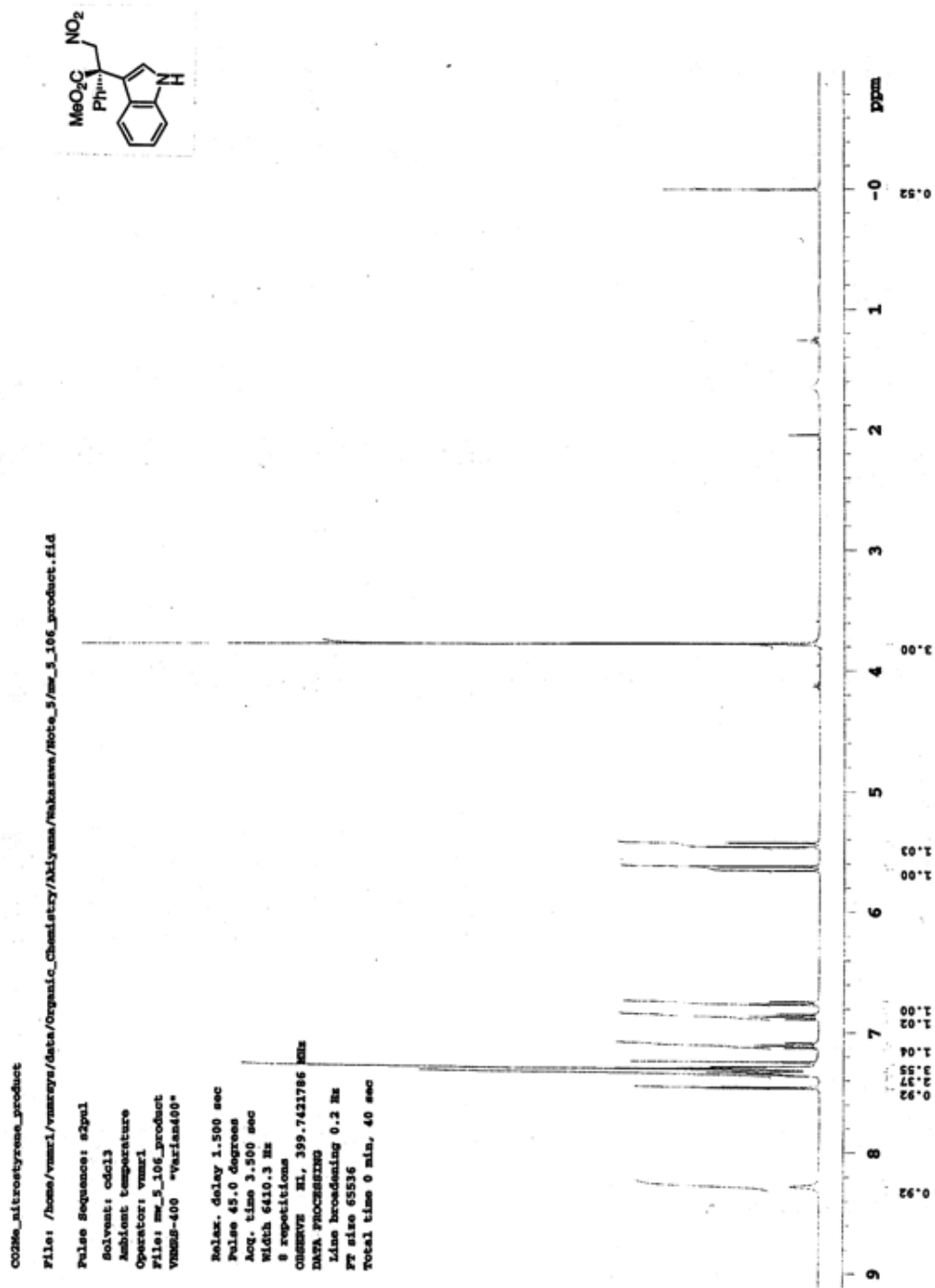
^1H NMR spectrum of **5n**.



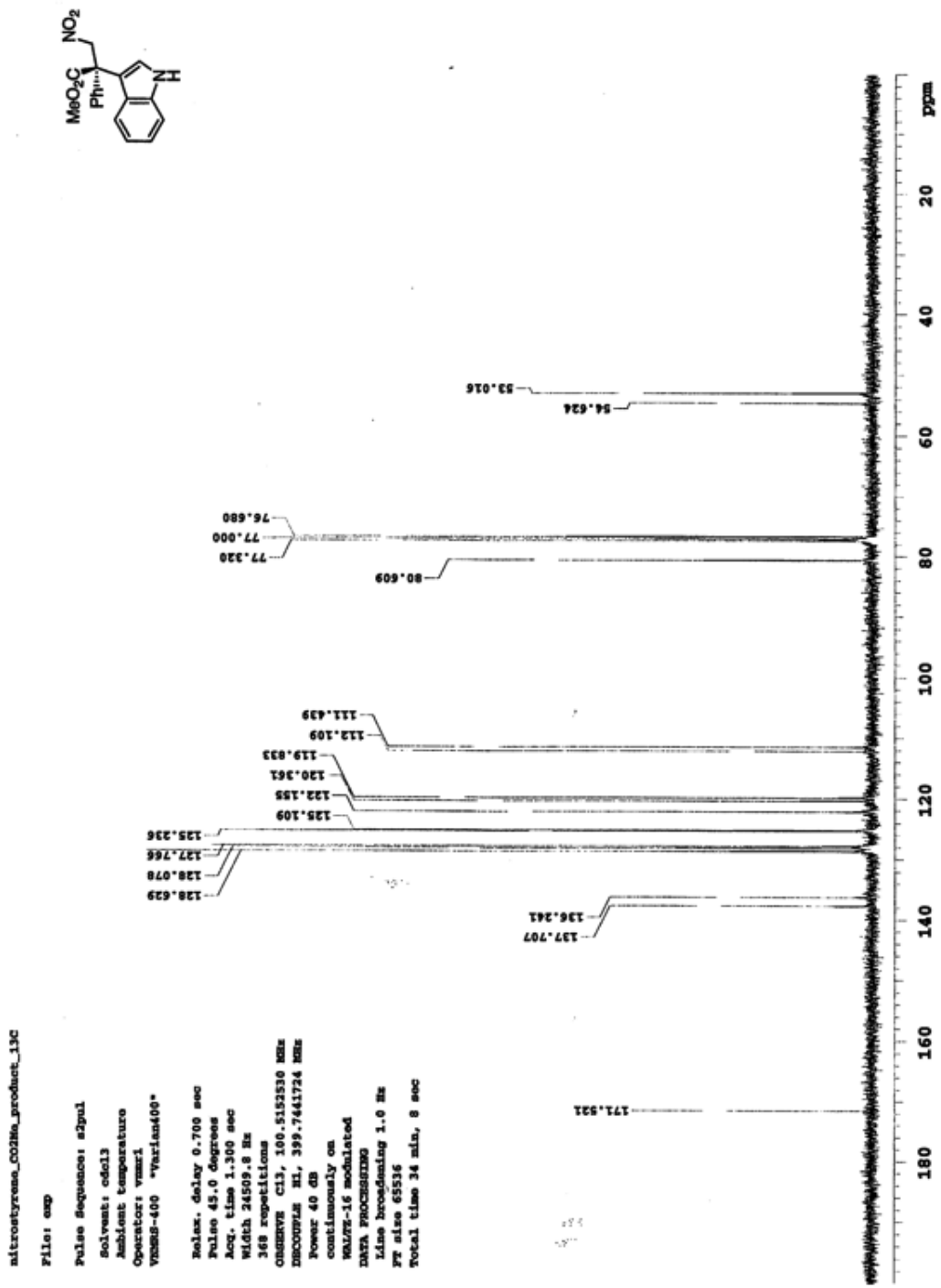
¹³C NMR spectrum of **5n**.



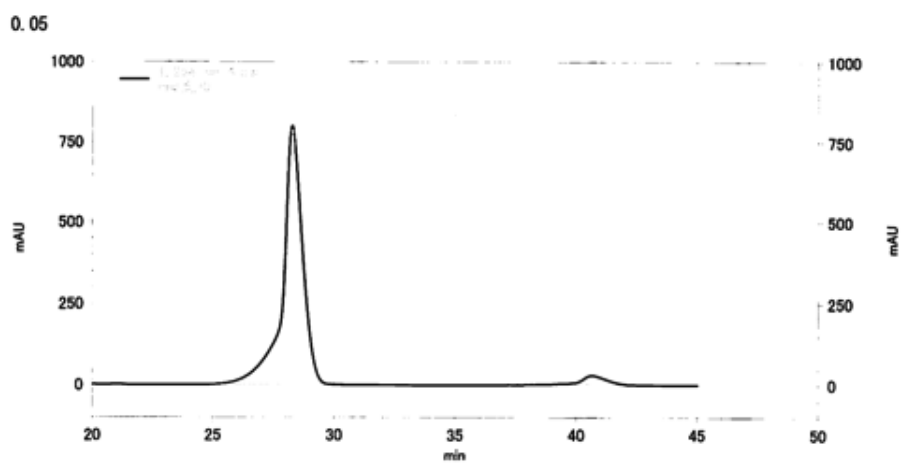
¹H NMR spectrum of **6a**.



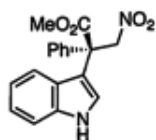
¹³C NMR spectrum of 6a.



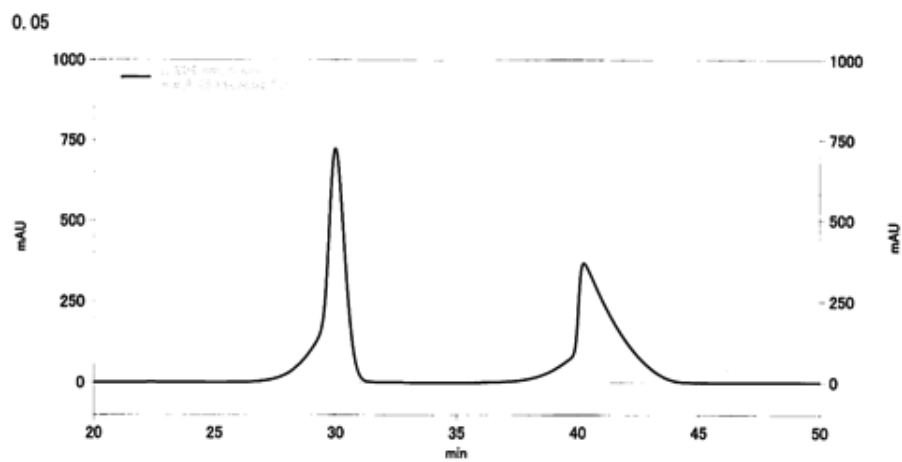
HPLC chart of **6a**.



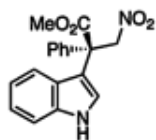
Peak #	Retention time	Type	Area	Area %
1	28.27	BB	183153378	96.243
2	40.66	BB	7149680	3.757



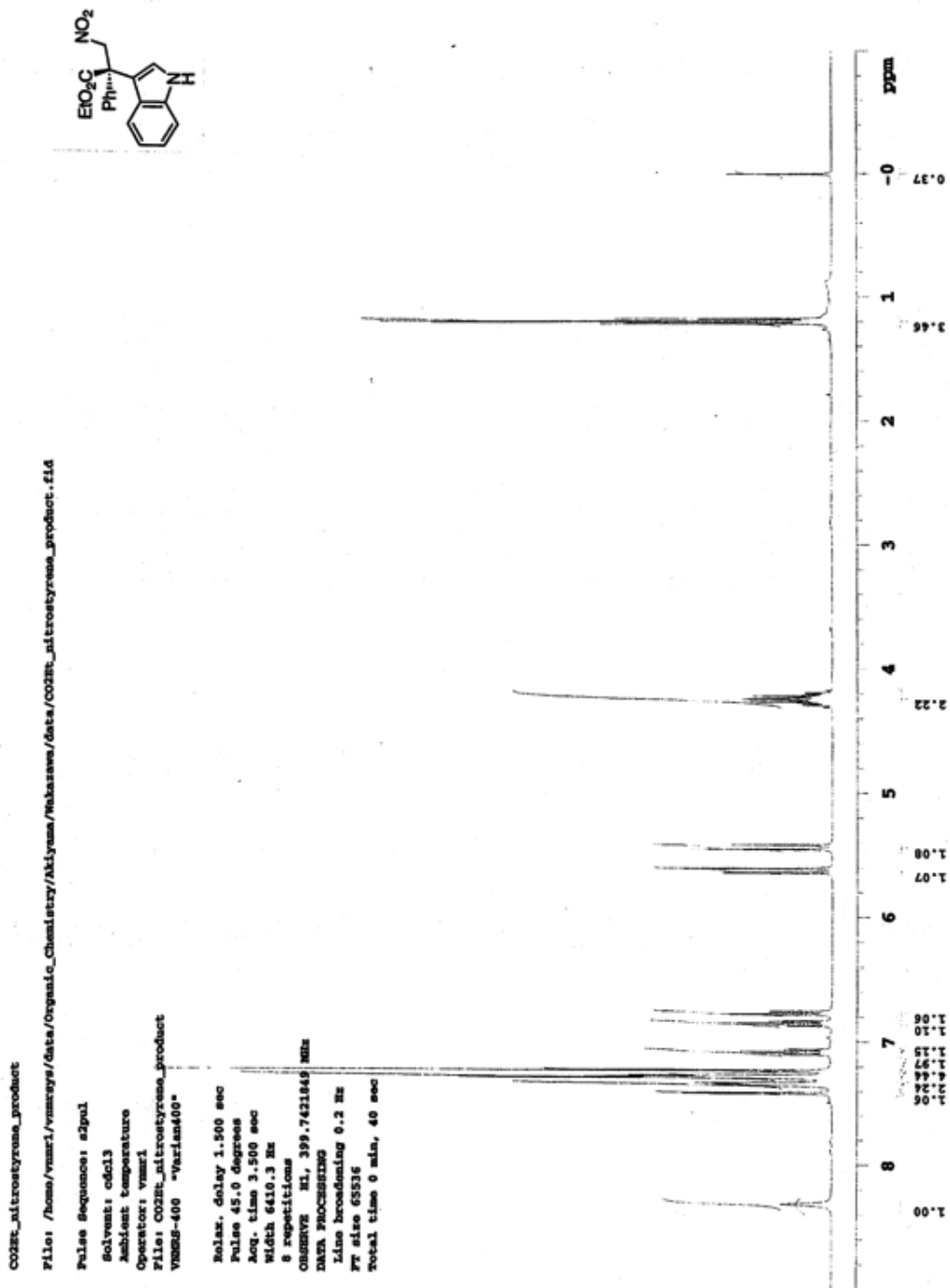
HPLC chart of **6a** (racemic).



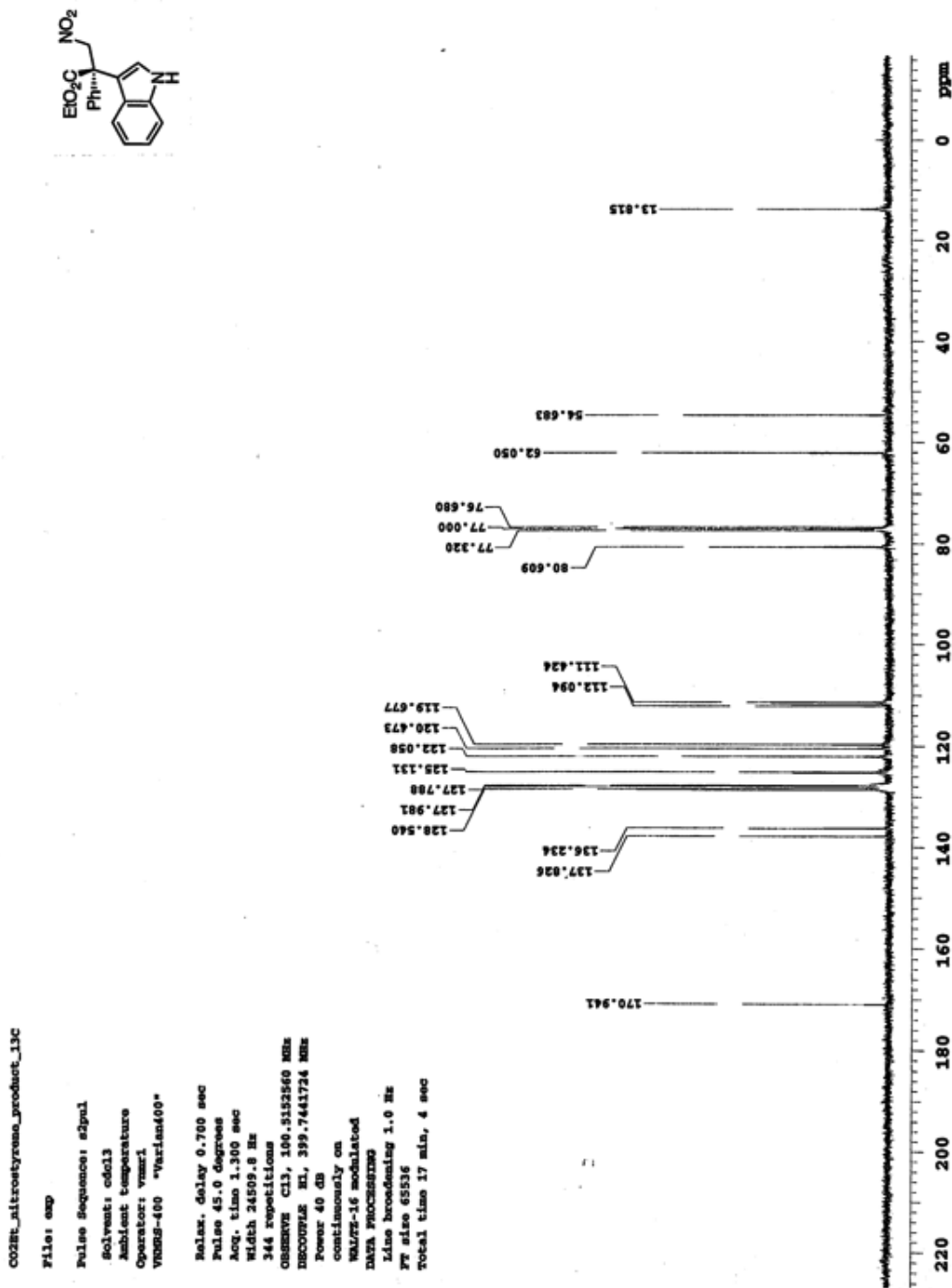
Peak #	Retention time	Type	Area	Area %
1	29.99	BB	168964803	50.074
2	40.25	BB	168464751	49.926



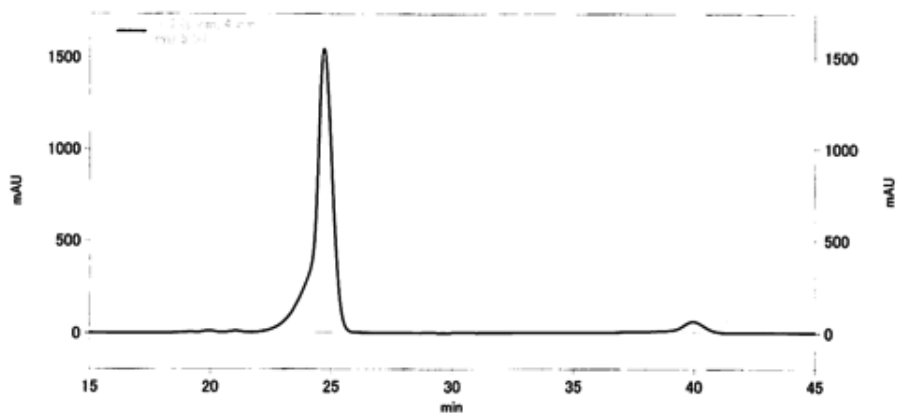
^1H NMR spectrum of **6b**.



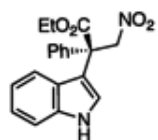
¹³C NMR spectrum of **6b**.



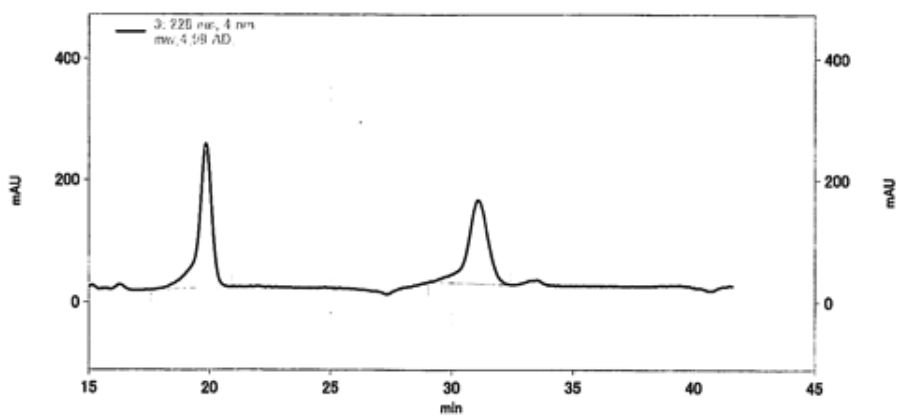
HPLC chart of **6b**.



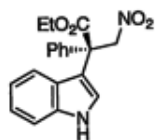
Peak #	Retention time	Type	Area	Area %
1	24.71	BB	313402971	95.760
2	39.97	BB	13876097	4.240



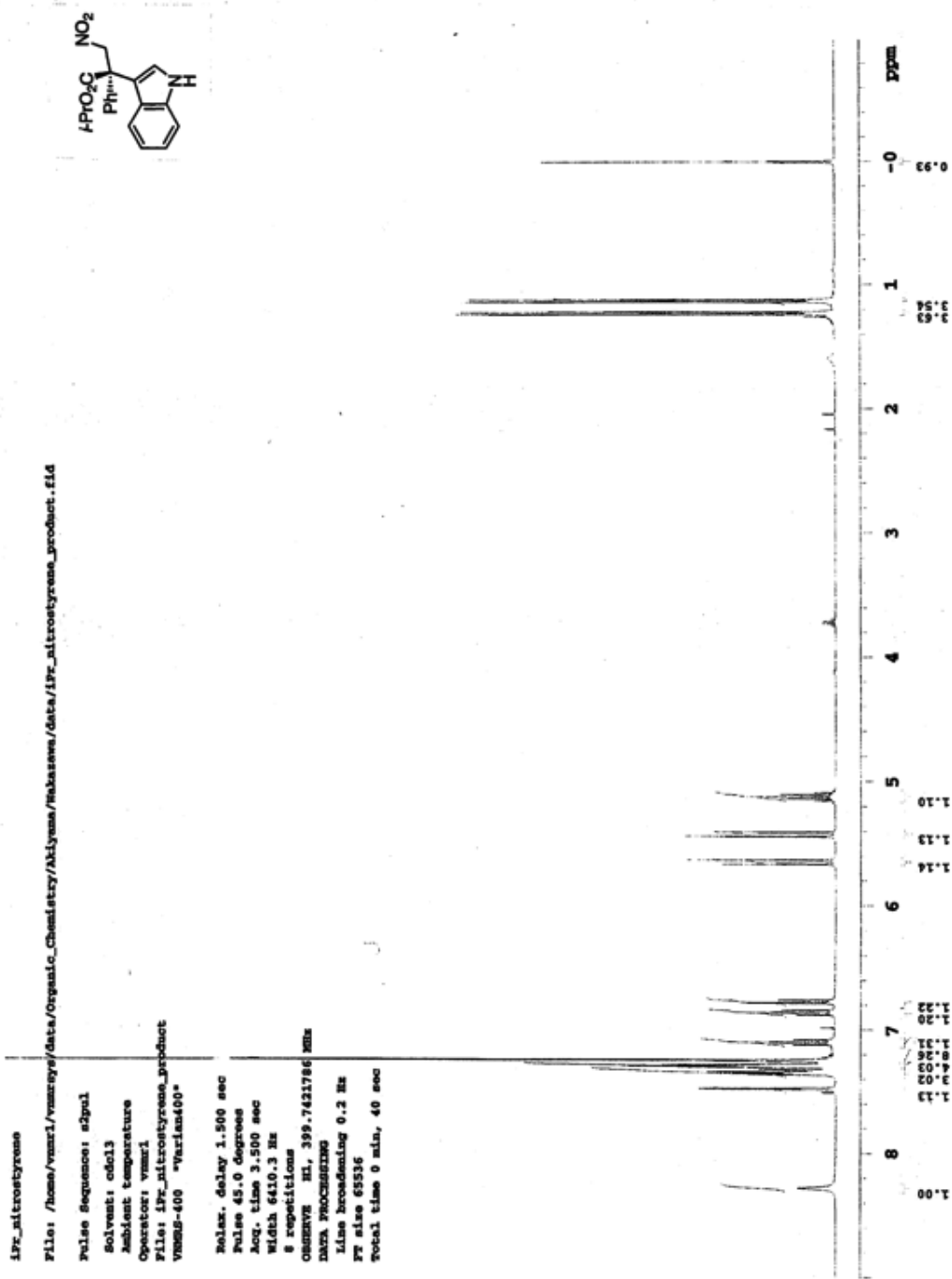
HPLC chart of **6b** (racemic).



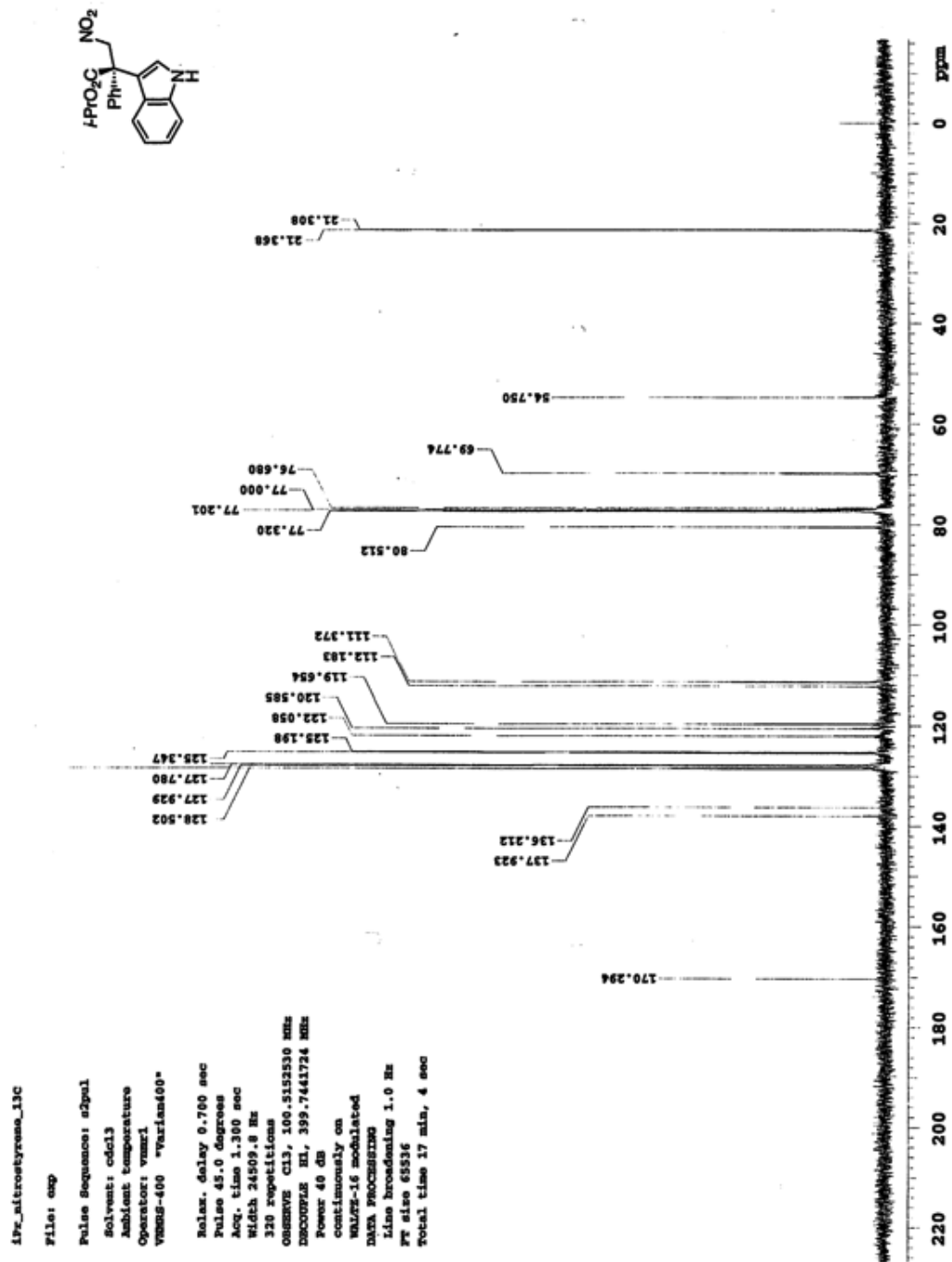
Peak #	Retention time	Type	Area	Area %
1	19.85	BB	36451723	52.941
2	31.07	1B	32401152	47.059



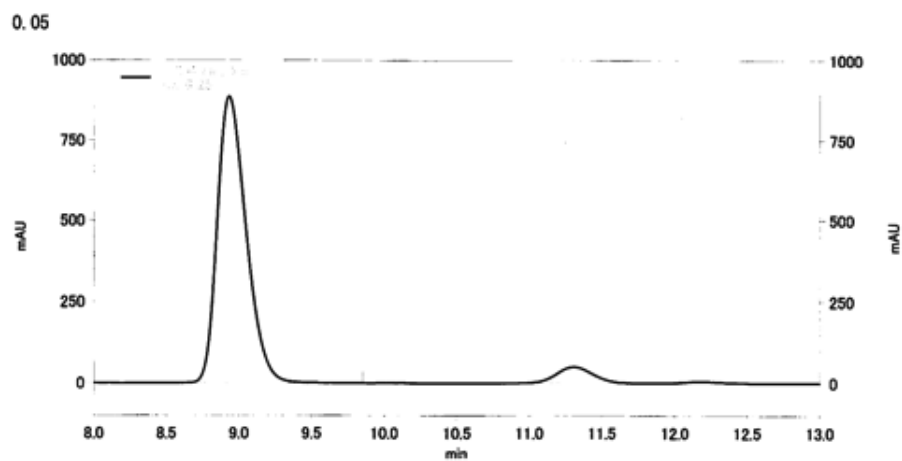
^1H NMR spectrum of **6c**.



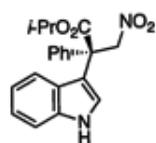
¹³C NMR spectrum of **6c**.



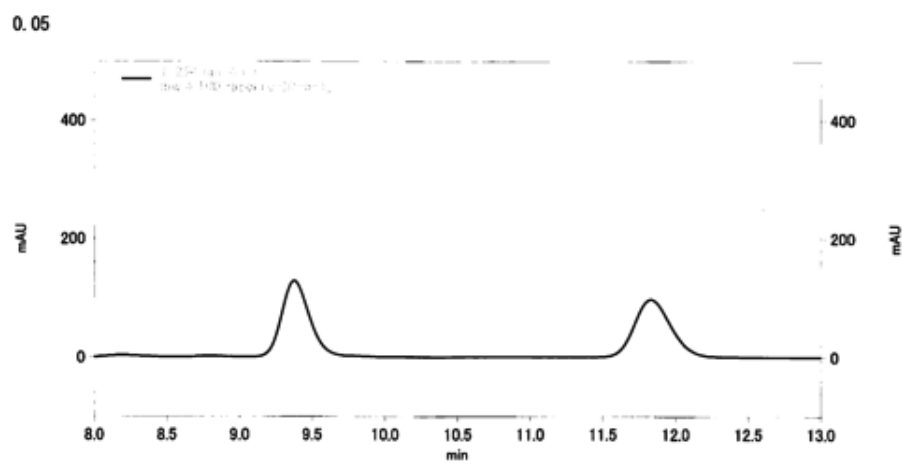
HPLC chart of **6c**.



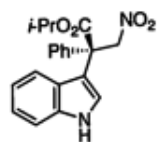
Peak #	Retention time	Type	Area	Area %
1	8.93	BB	48718933	93.207
2	11.31	BB	3550396	6.793



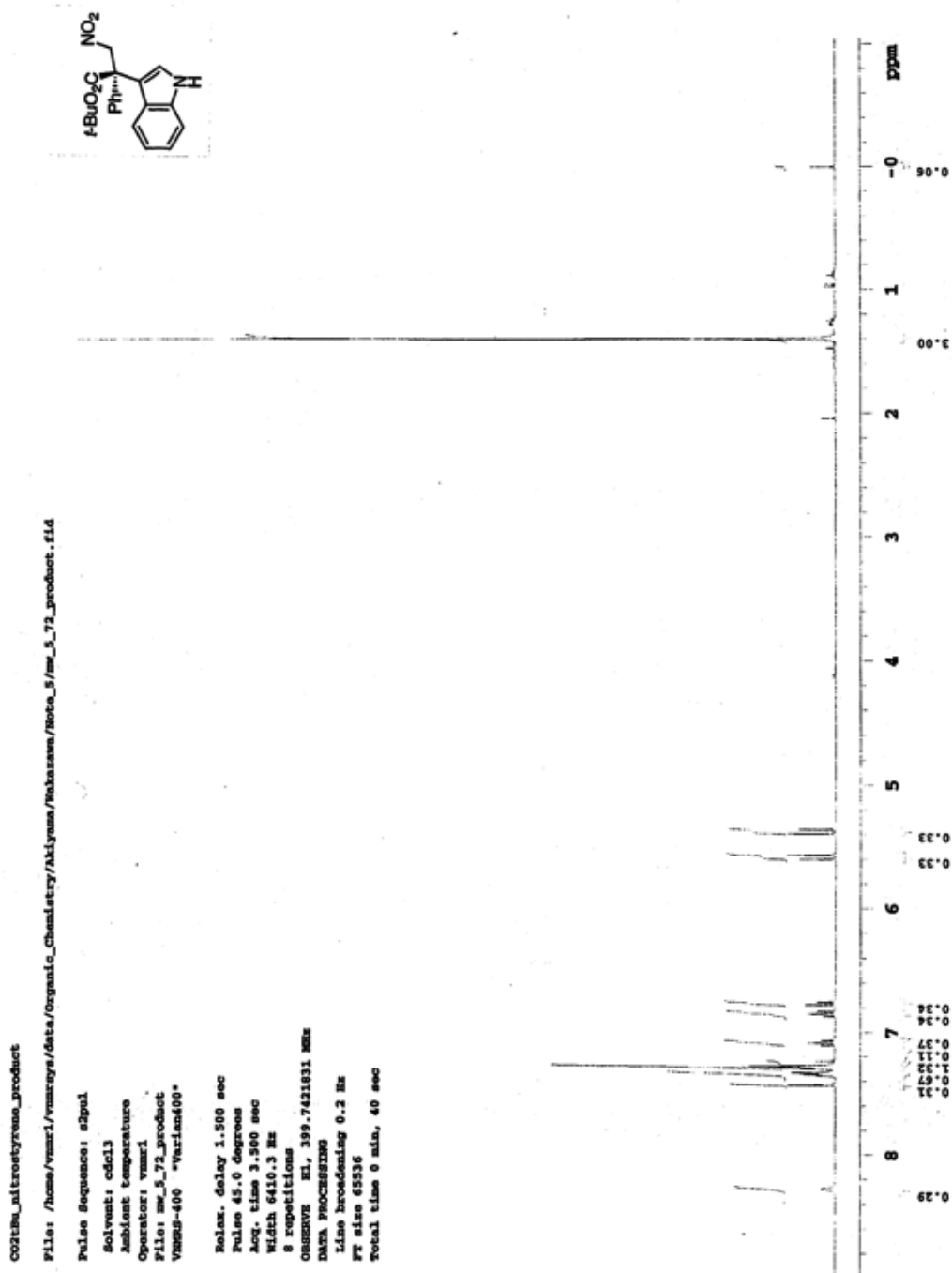
HPLC chart of **6c** (racemic).



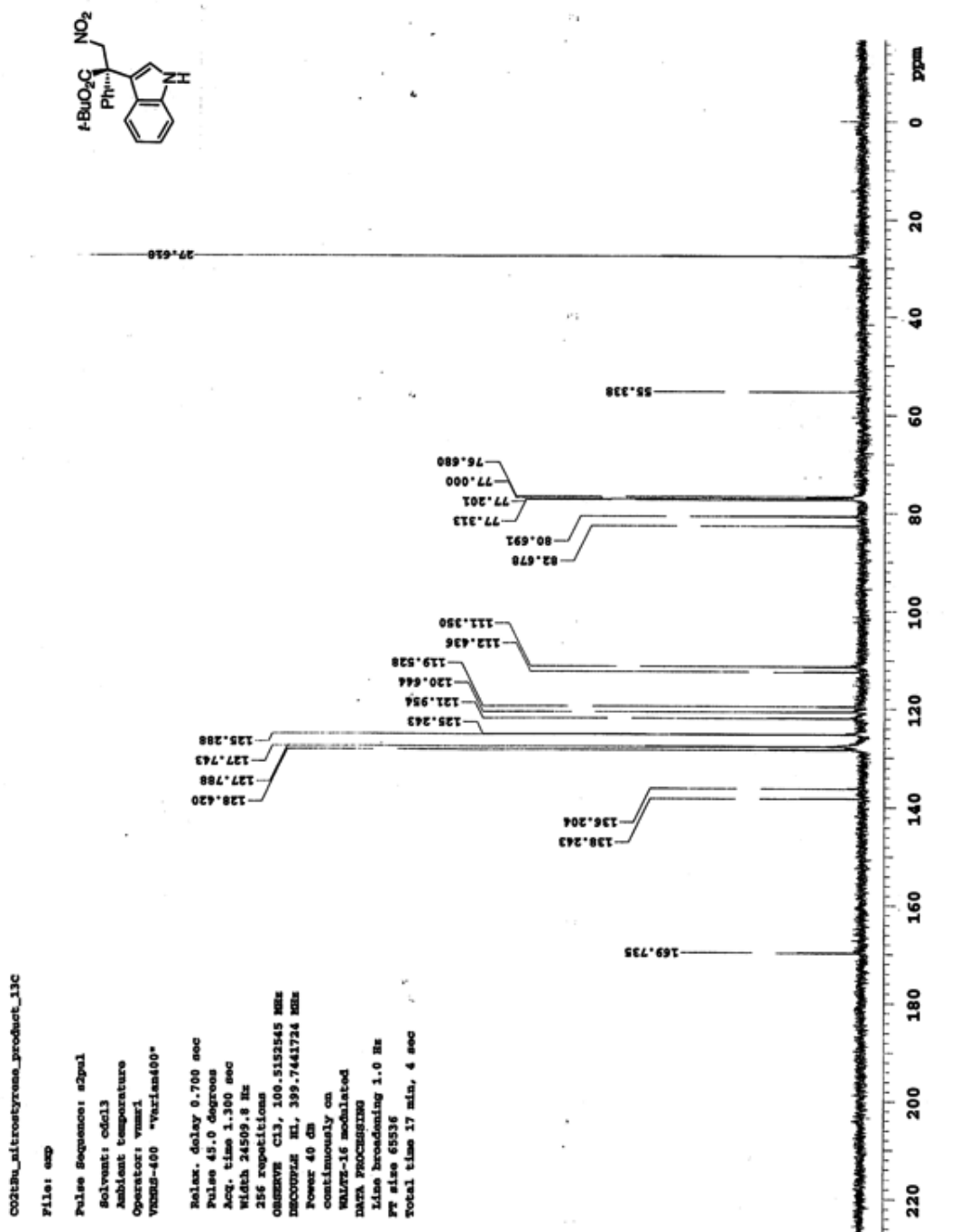
Peak #	Retention time	Type	Area	Area %
1	9.37	BB	6942670	50.549
2	11.83	BB	6791941	49.451



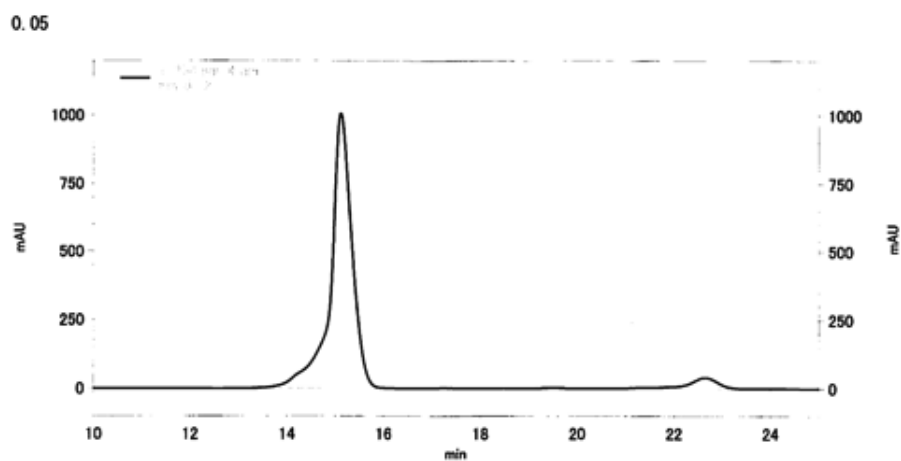
¹H NMR spectrum of **6d**.



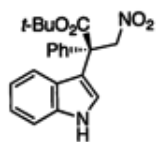
¹³C NMR spectrum of **6d**.



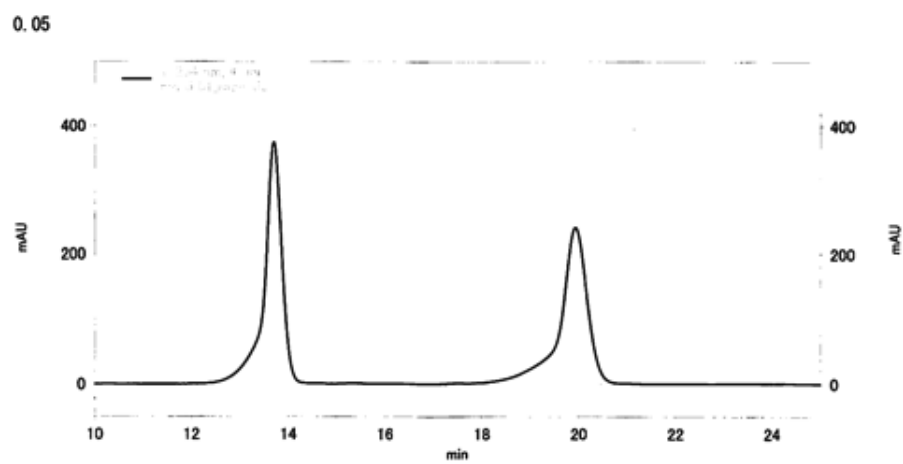
HPLC chart of **6d**.



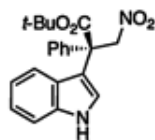
Peak #	Retention time	Type	Area	Area %
1	15.12	BB	122715275	95.708
2	22.65	BB	5503141	4.292



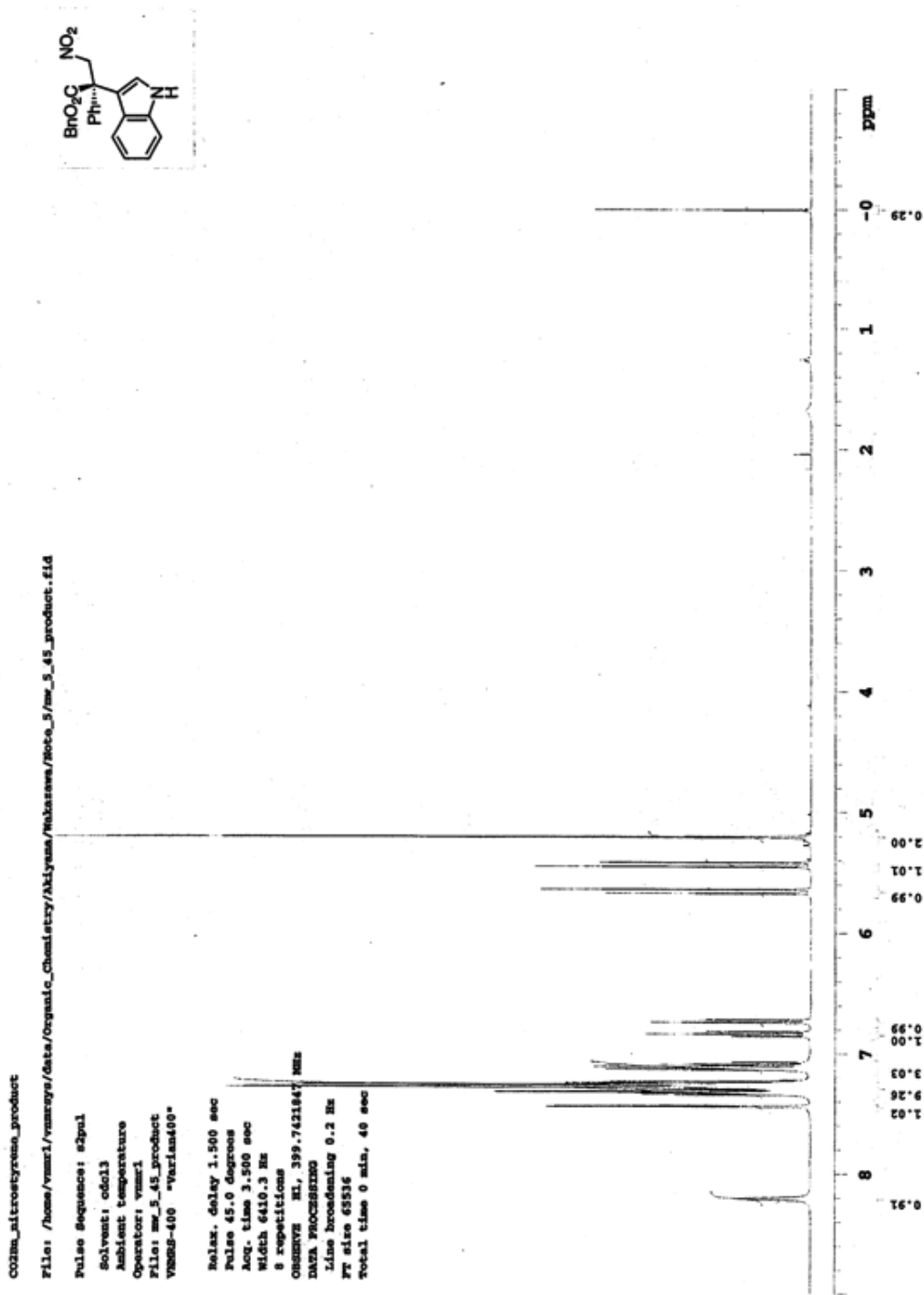
HPLC chart of **6b** (racemic).



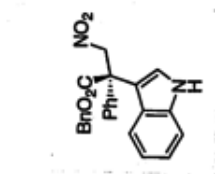
Peak #	Retention time	Type	Area	Area %
1	13.70	BB	38080391	50.115
2	19.93	BB	37905135	49.885



¹H NMR spectrum of **6e**.



¹³C NMR spectrum of **6e**.



nitrostyrene_CO2In_product_13C

File: exp

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vmmz

VMSS-400 *Varian400*

Relax. delay 0.700 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

336 repetitions

OBSERVE C13, 100.6152523 MHz

DECOUPLE H1, 399.7441724 MHz

Power 45.00

continuously on

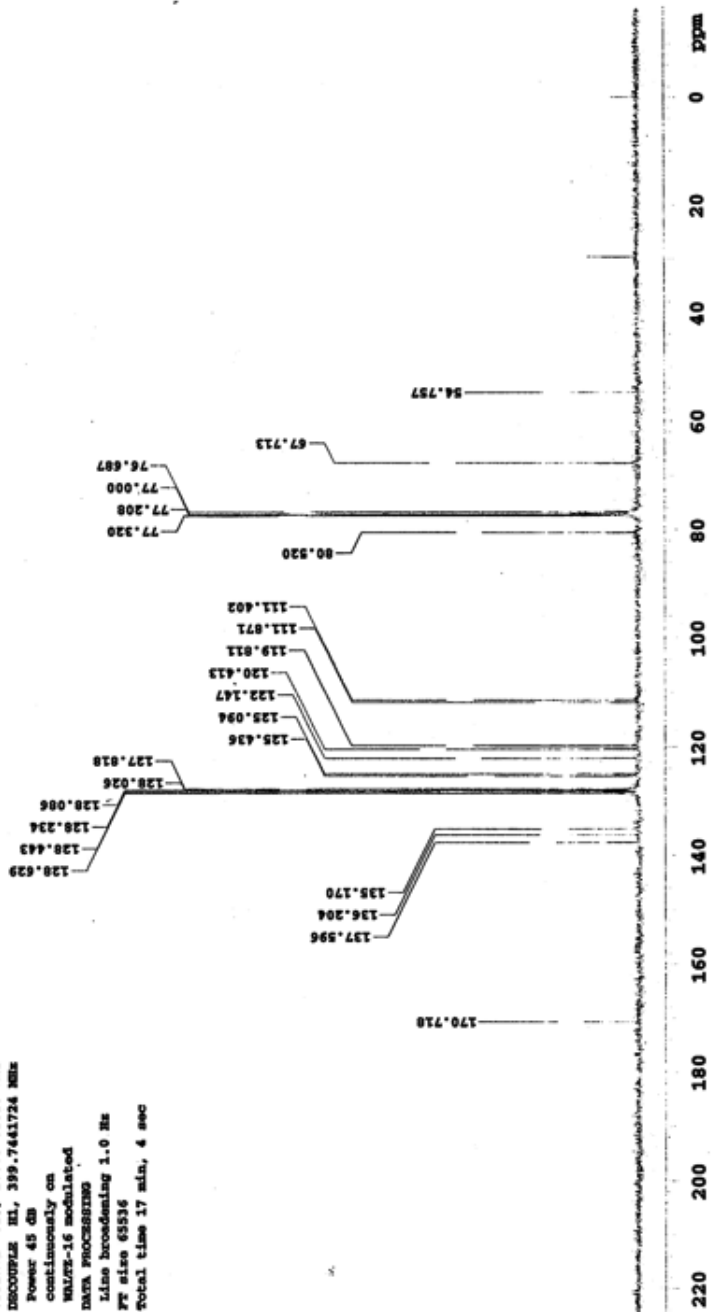
NUC13-16 modulated

DATA PROCESSING

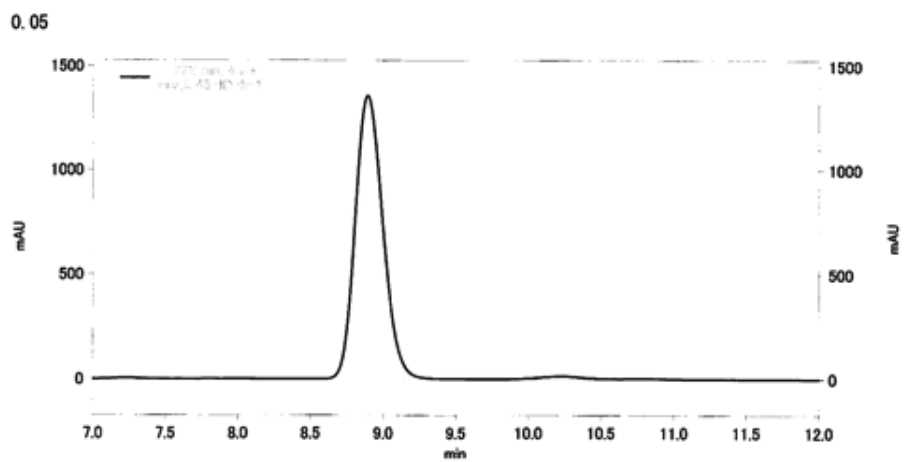
Line broadening 1.0 Hz

FT size 65536

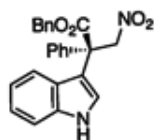
Total time 17 min, 4 sec



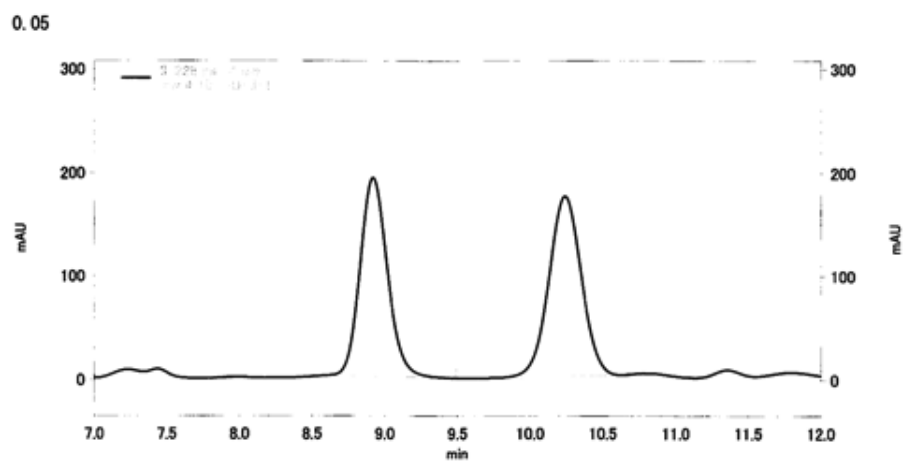
HPLC chart of **6e**.



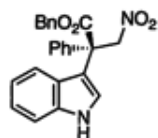
Peak #	Retention time	Type	Area	Area %
1	8.89	BB	72011617	98.553
2	10.23	BB	1057652	1.447



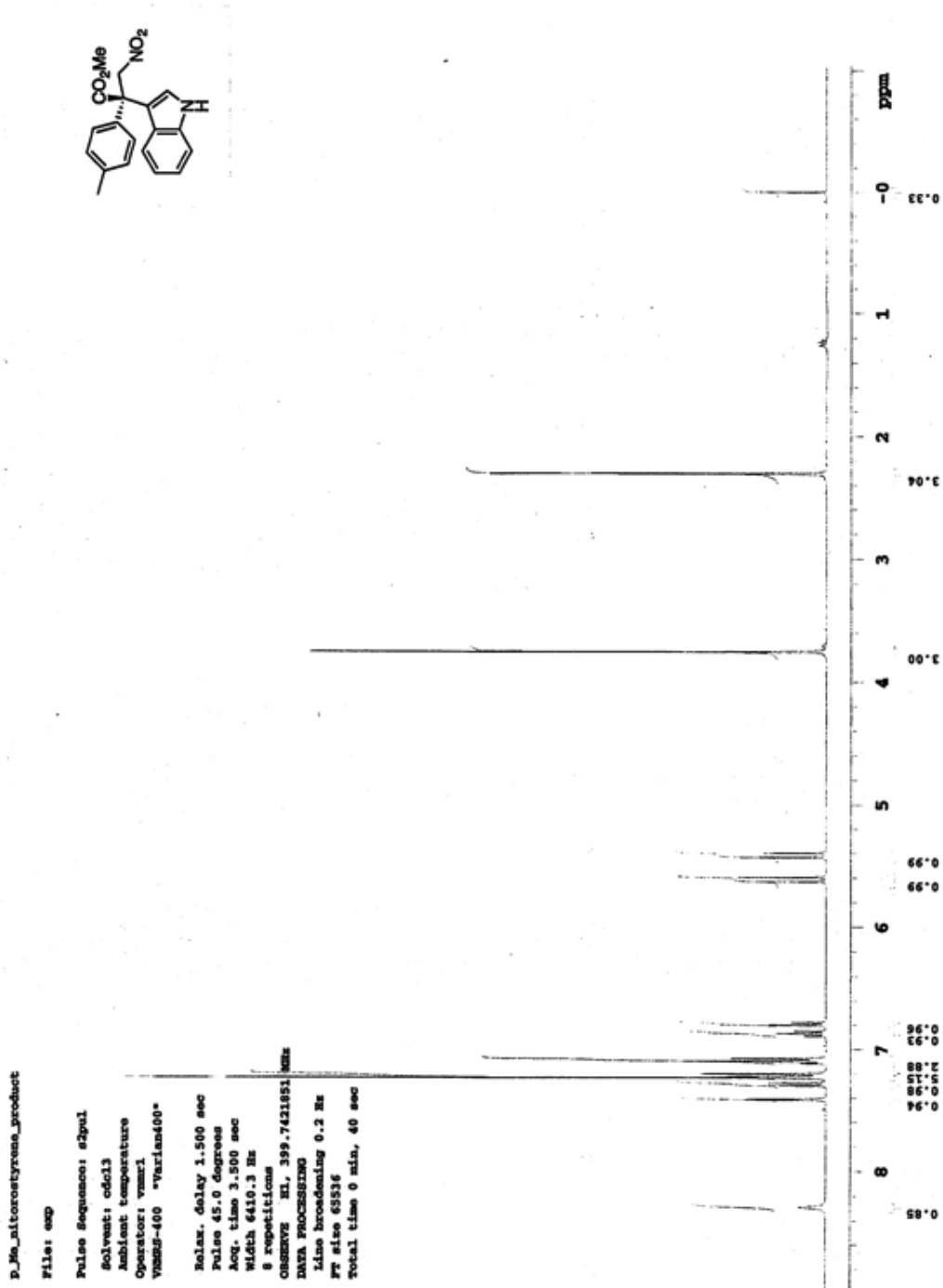
HPLC chart of **6e** (racemic).



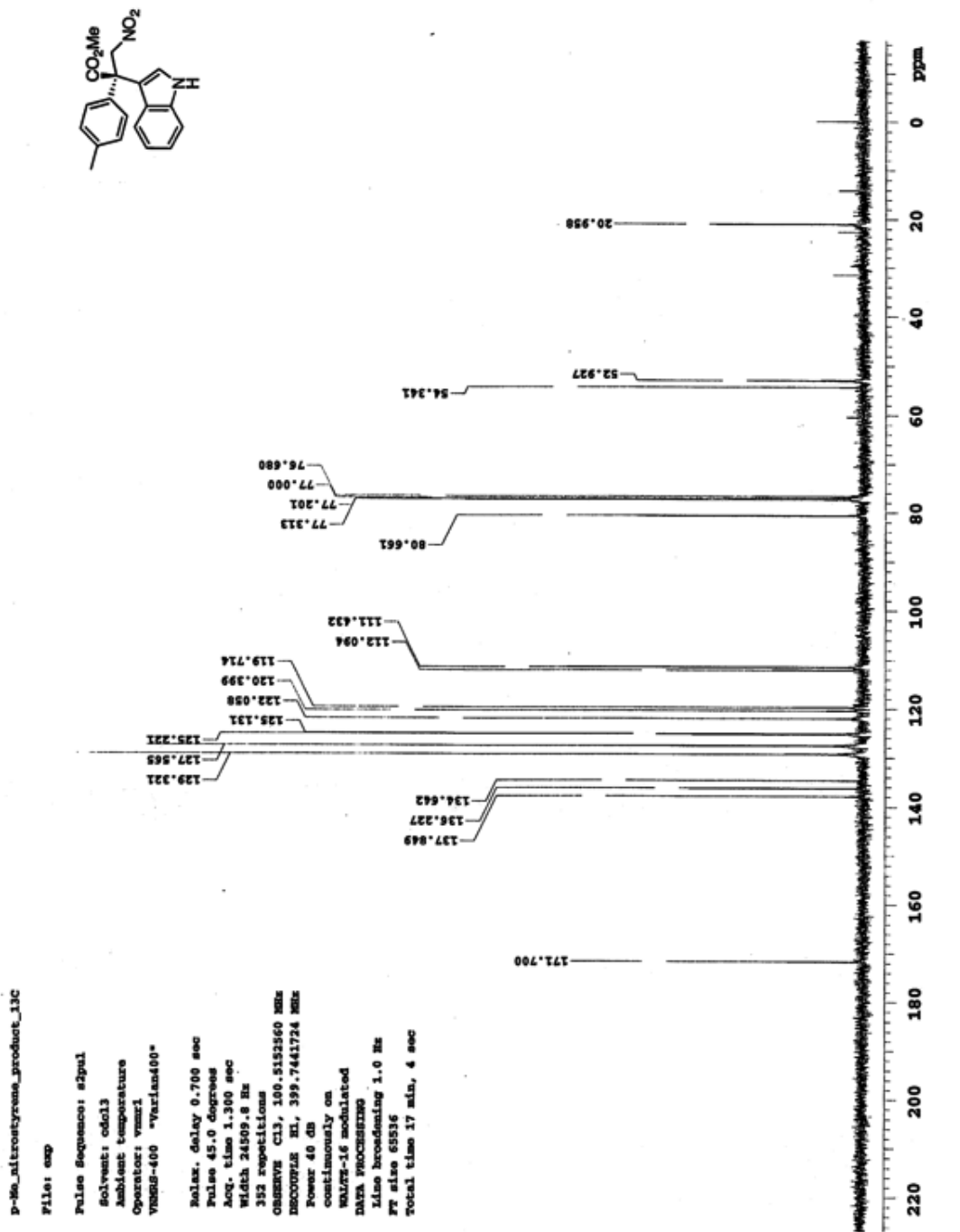
Peak #	Retention time	Type	Area	Area %
1	8.92	BB	10069417	48.210
2	10.24	BB	10817300	51.790



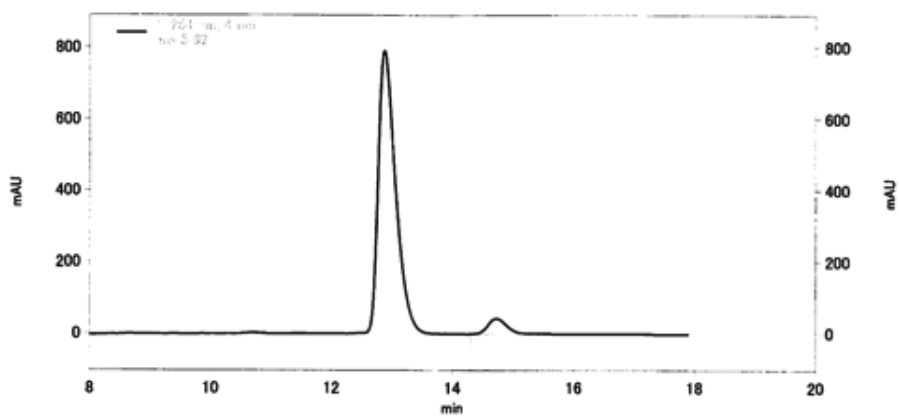
¹H NMR spectrum of **6f**.



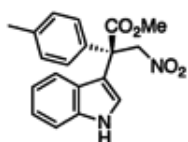
¹³C NMR spectrum of **6f**.



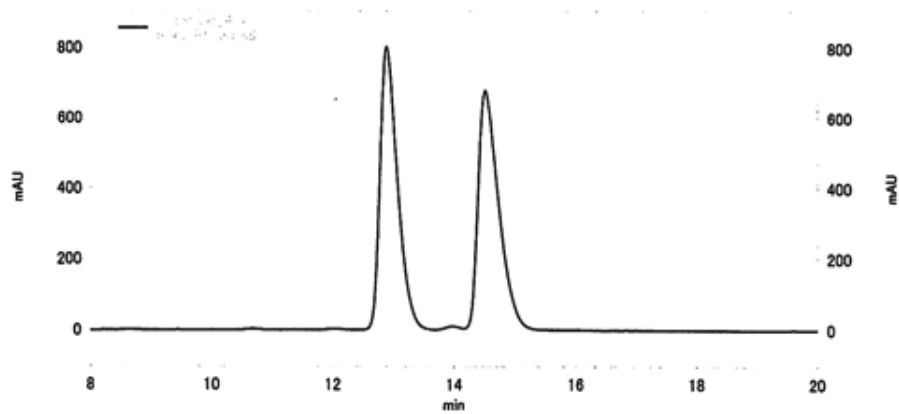
HPLC chart of **6f**.



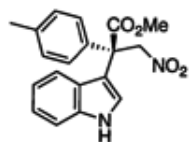
Peak #	Retention time	Type	Area	Area %
1	12.87	BB	63712546	94.495
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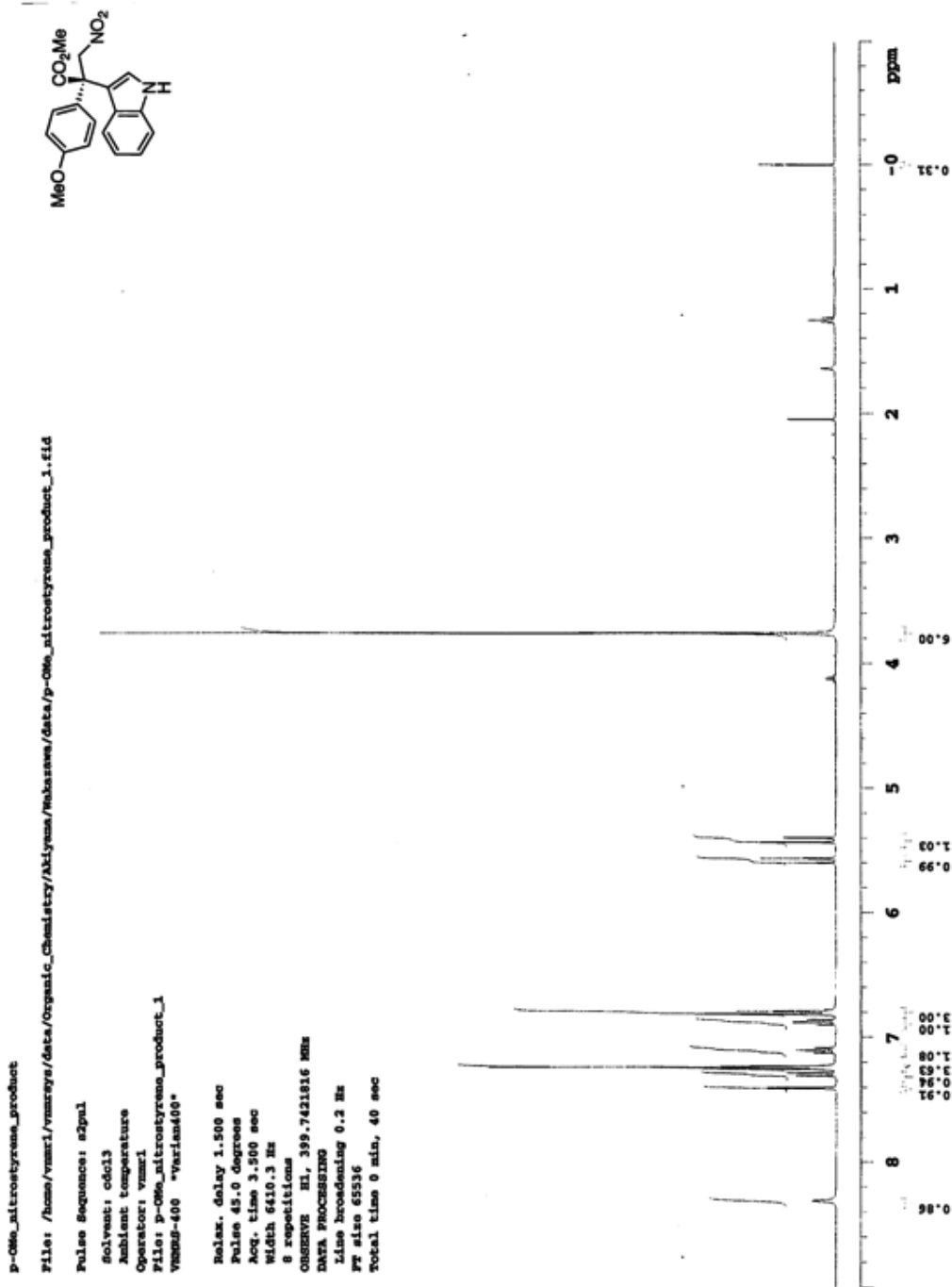
HPLC chart of **6f** (racemic).



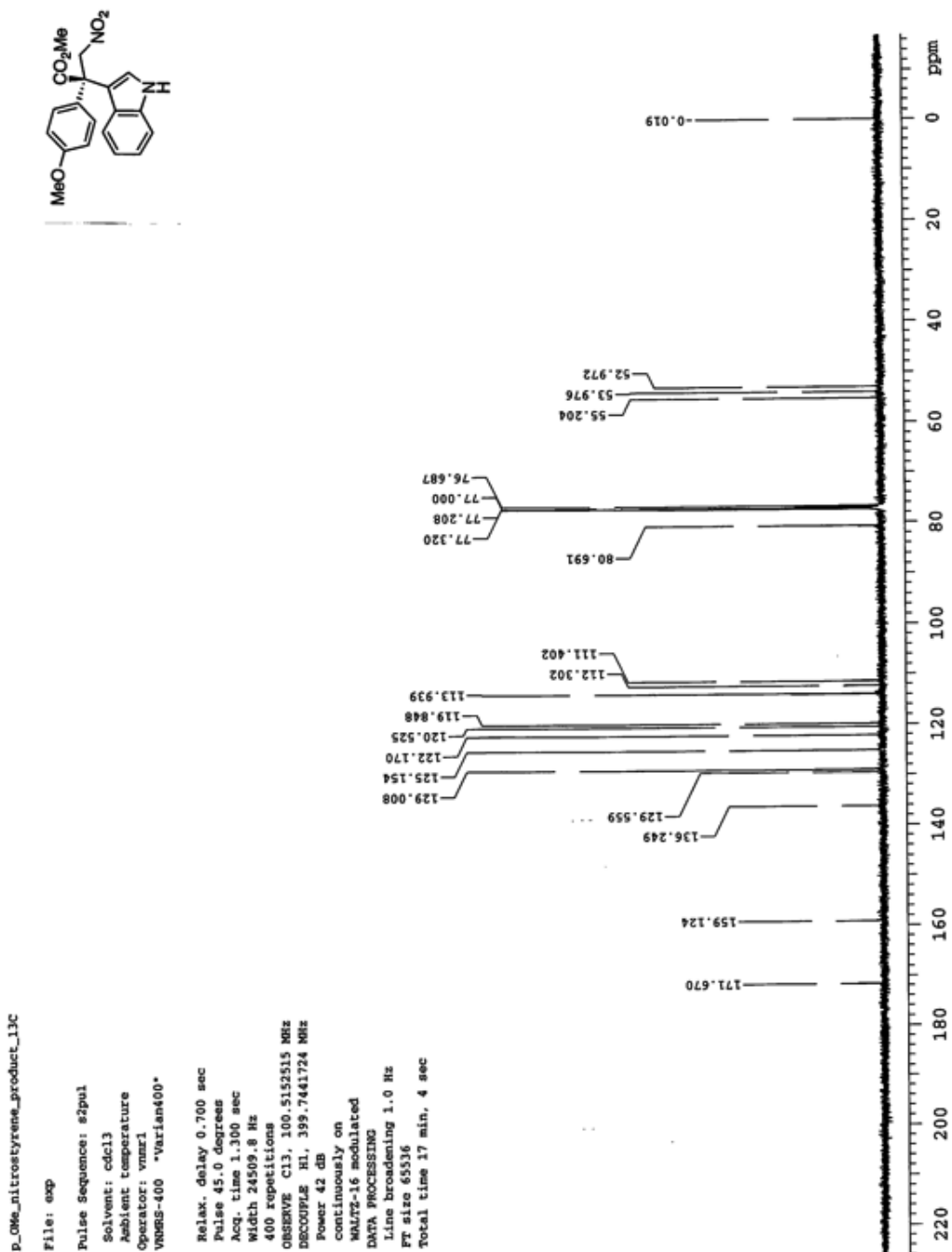
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2	14.51	BB	63838042	49.522



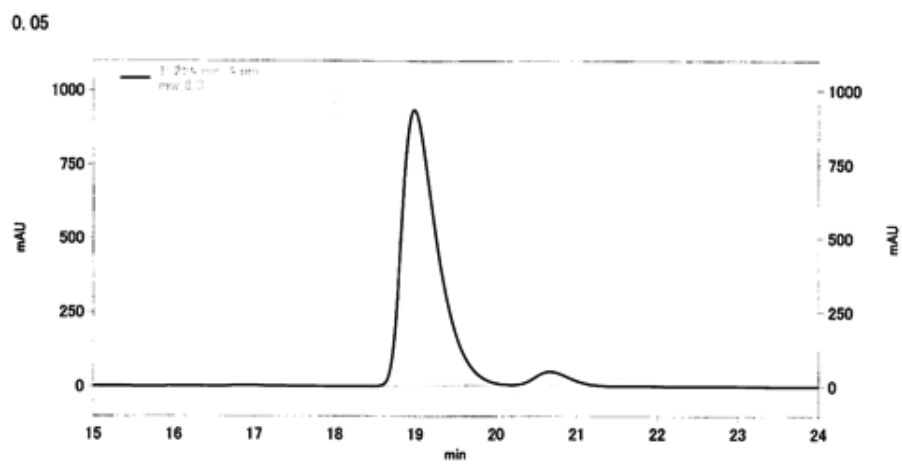
^1H NMR spectrum of **6g**.



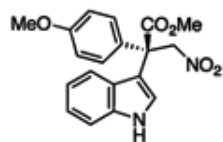
¹³C NMR spectrum of **6g**.



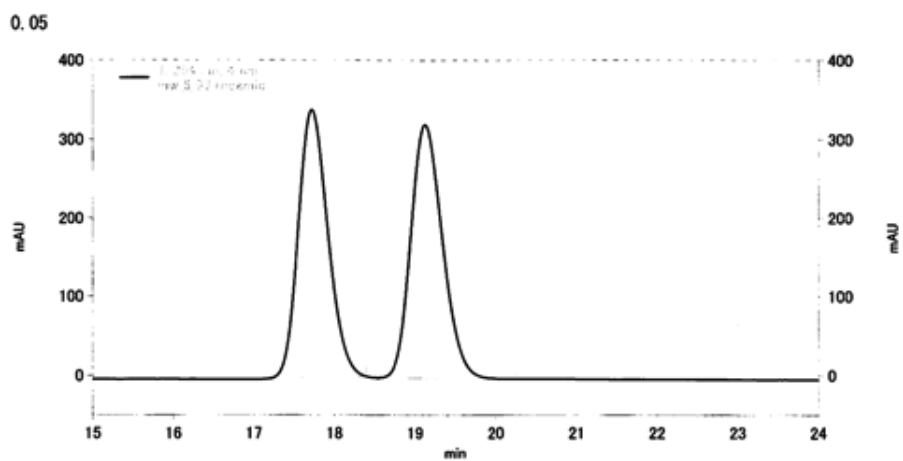
HPLC chart of **6g**.



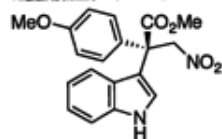
Peak #	Retention time	Type	Area	Area %
1	18.99	BB	113864178	95.573
2	20.67	IB	5274109	4.427



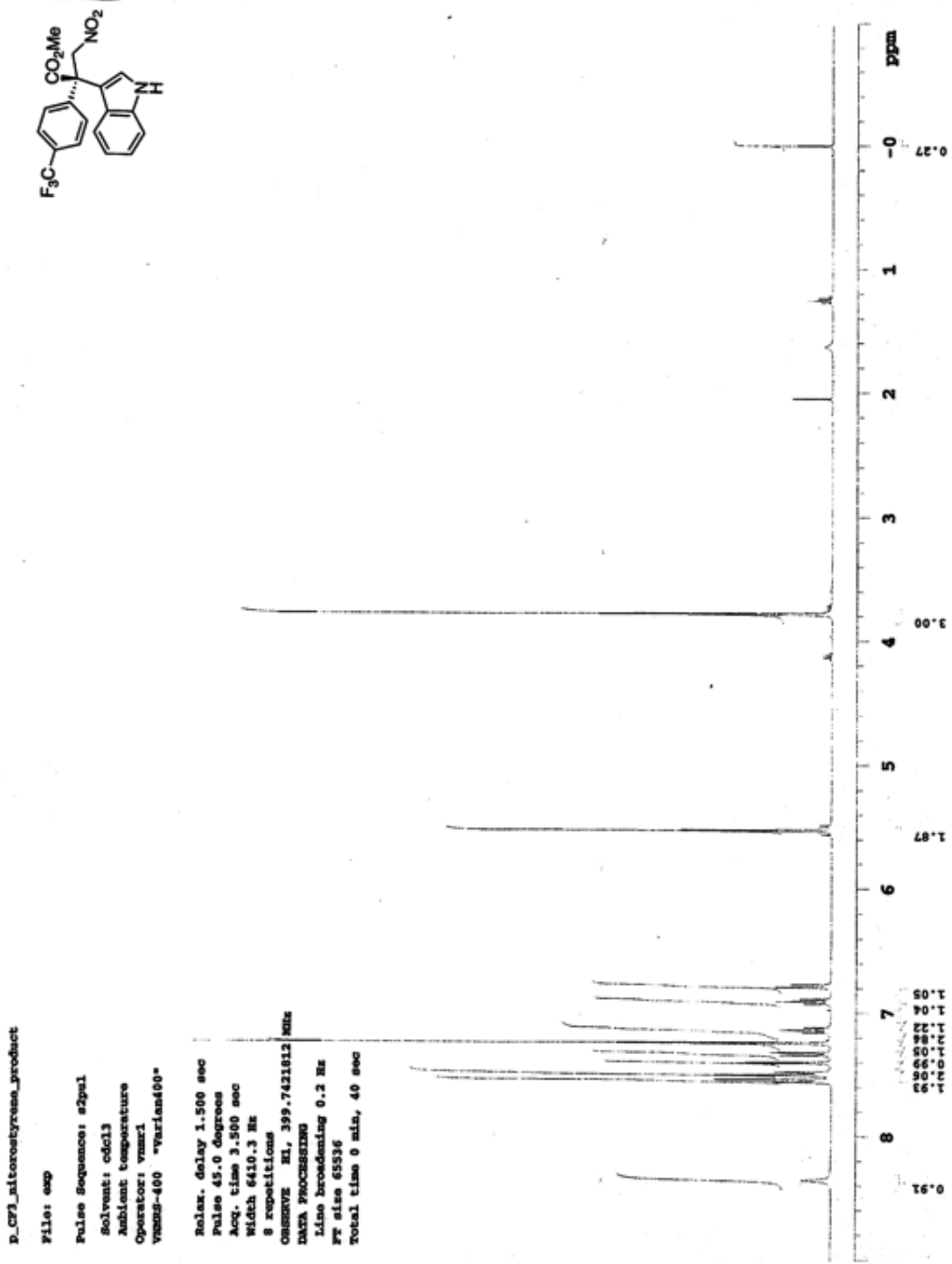
HPLC chart of **6b** (racemic).



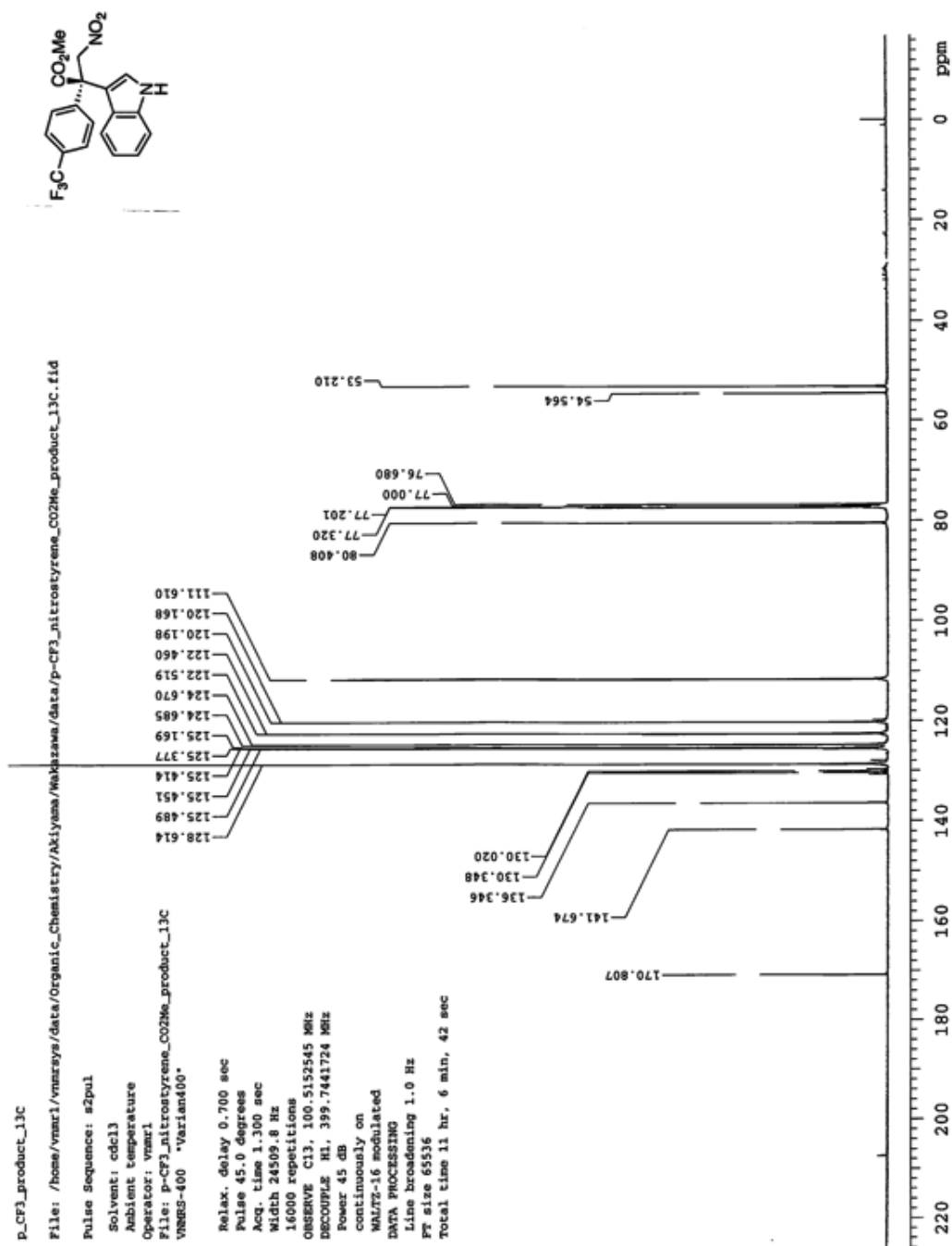
Peak #	Retention time	Type	Area	Area %
1	17.72	B1	34673972	49.706
2	19.12	BB	35084595	50.294



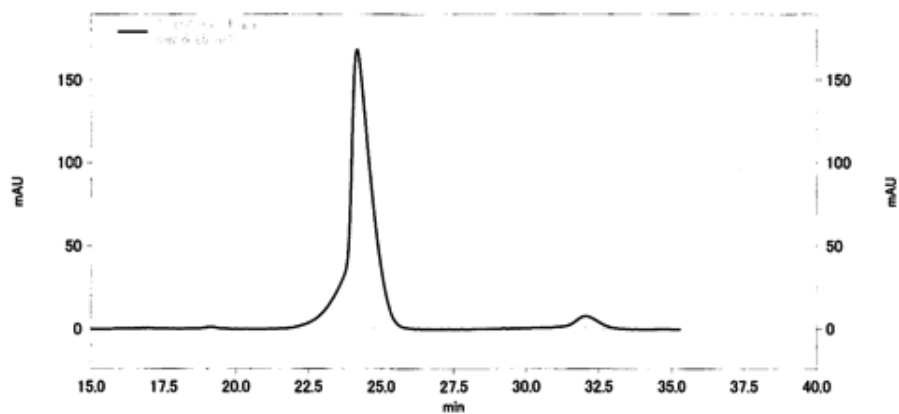
¹H NMR spectrum of **6h**.



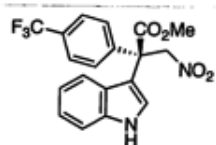
¹³C NMR spectrum of **6h**.



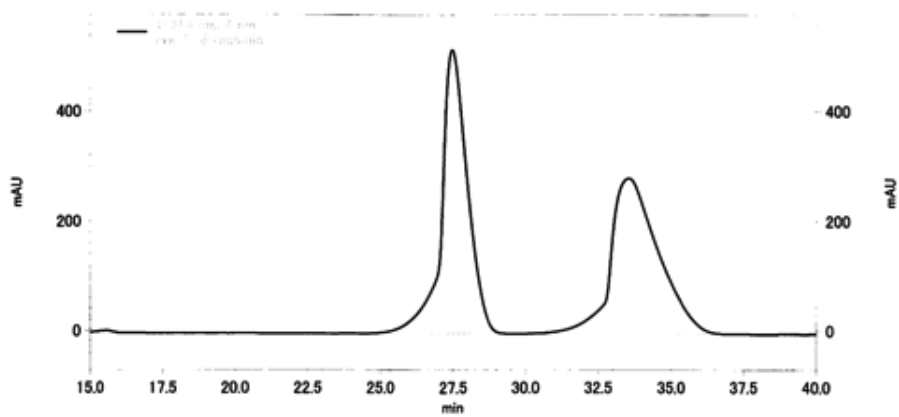
HPLC chart of **6h**.



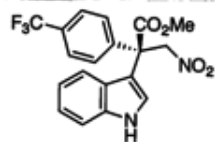
Peak #	Retention time	Type	Area	Area %
1	24.17	BB	36299034	96.309
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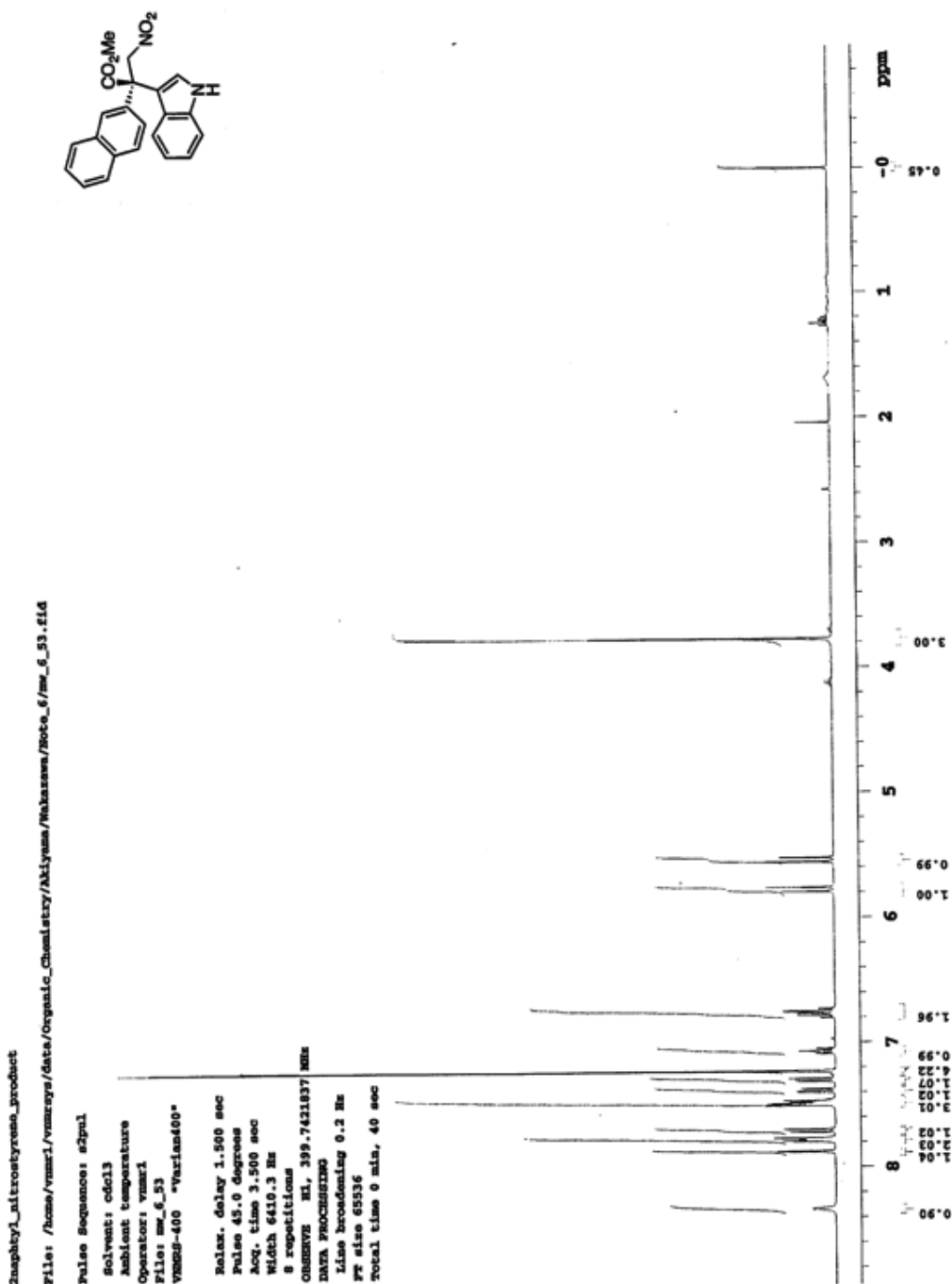
HPLC chart of **6h** (racemic).



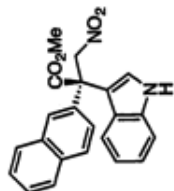
Peak #	Retention time	Type	Area	Area %
1	27.47	BB	128886934	49.817
2	33.55	BB	129831902	50.183



¹H NMR spectrum of **6i**.



¹³C NMR spectrum of **6i**.



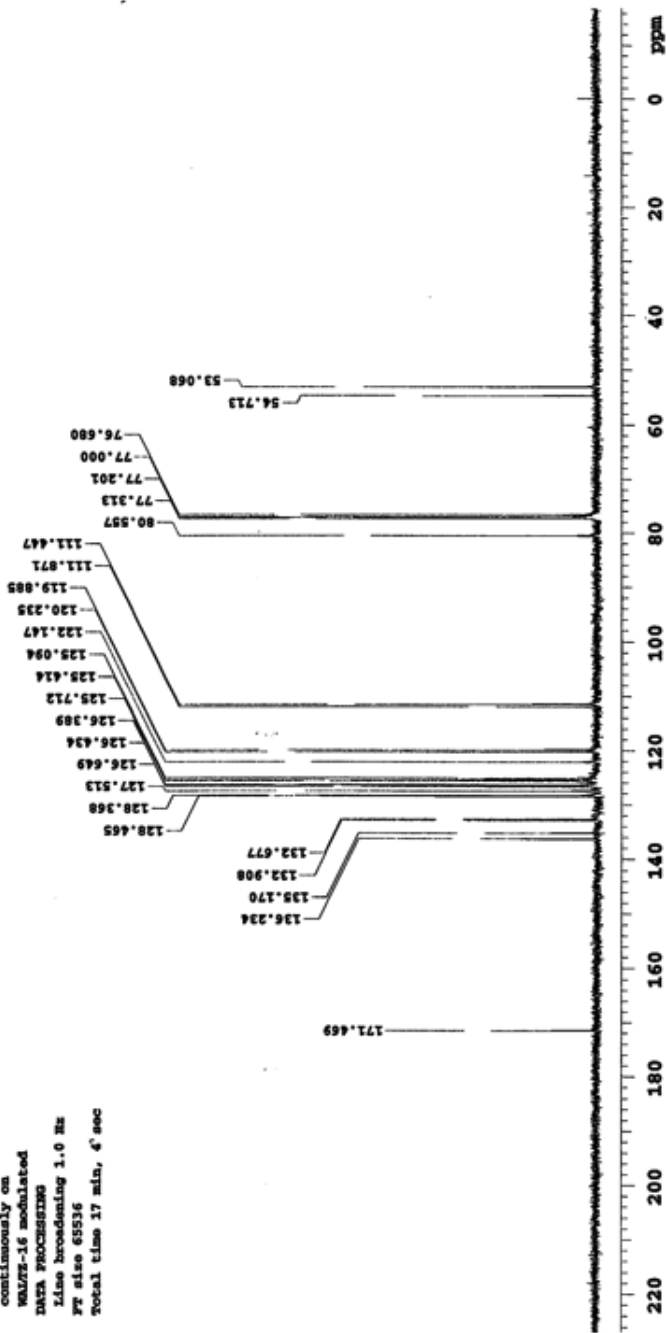
2naphthyl_nitrotryptamine_product_13C

File: exp

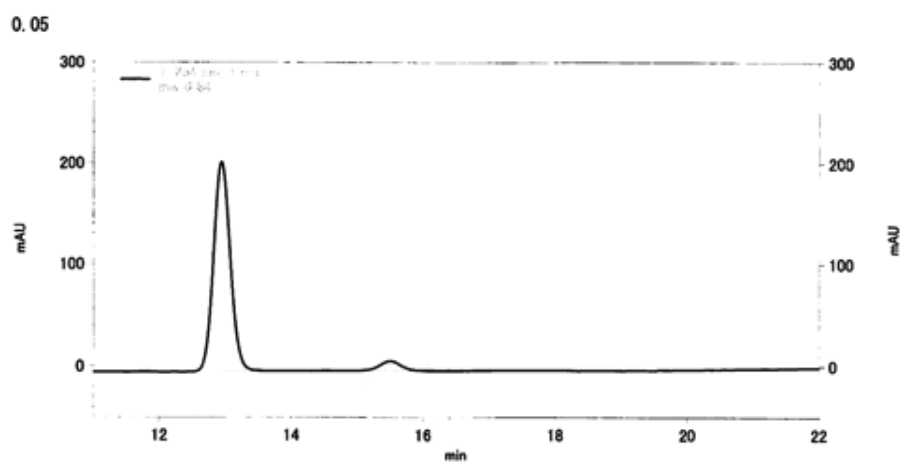
Pulse sequence: #2pul
 Solvent: cdcl3
 Ambient temperature
 Operator: vmer1
 VMS-400 *Varian400*

Relax. delay 0.700 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 344 repetitions

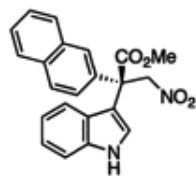
CHANNELS C13, 100.5152553 MHz
 RECOUPLE H1, 399.7441724 MHz
 Power 45 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min, 4 sec



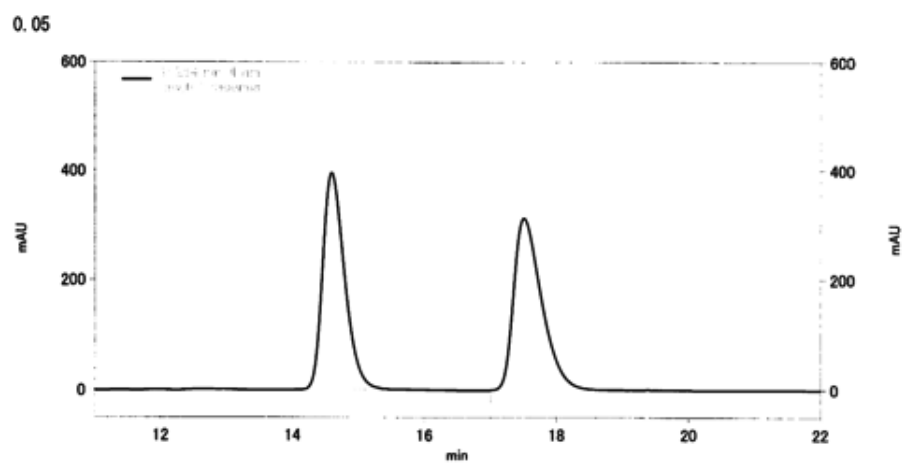
HPLC chart of **6i**.



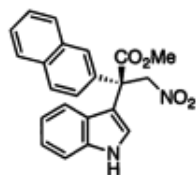
Peak #	Retention time	Type	Area	Area %
1	12.95	BI	14500748	94.936
2	15.50	BB	773472	5.064



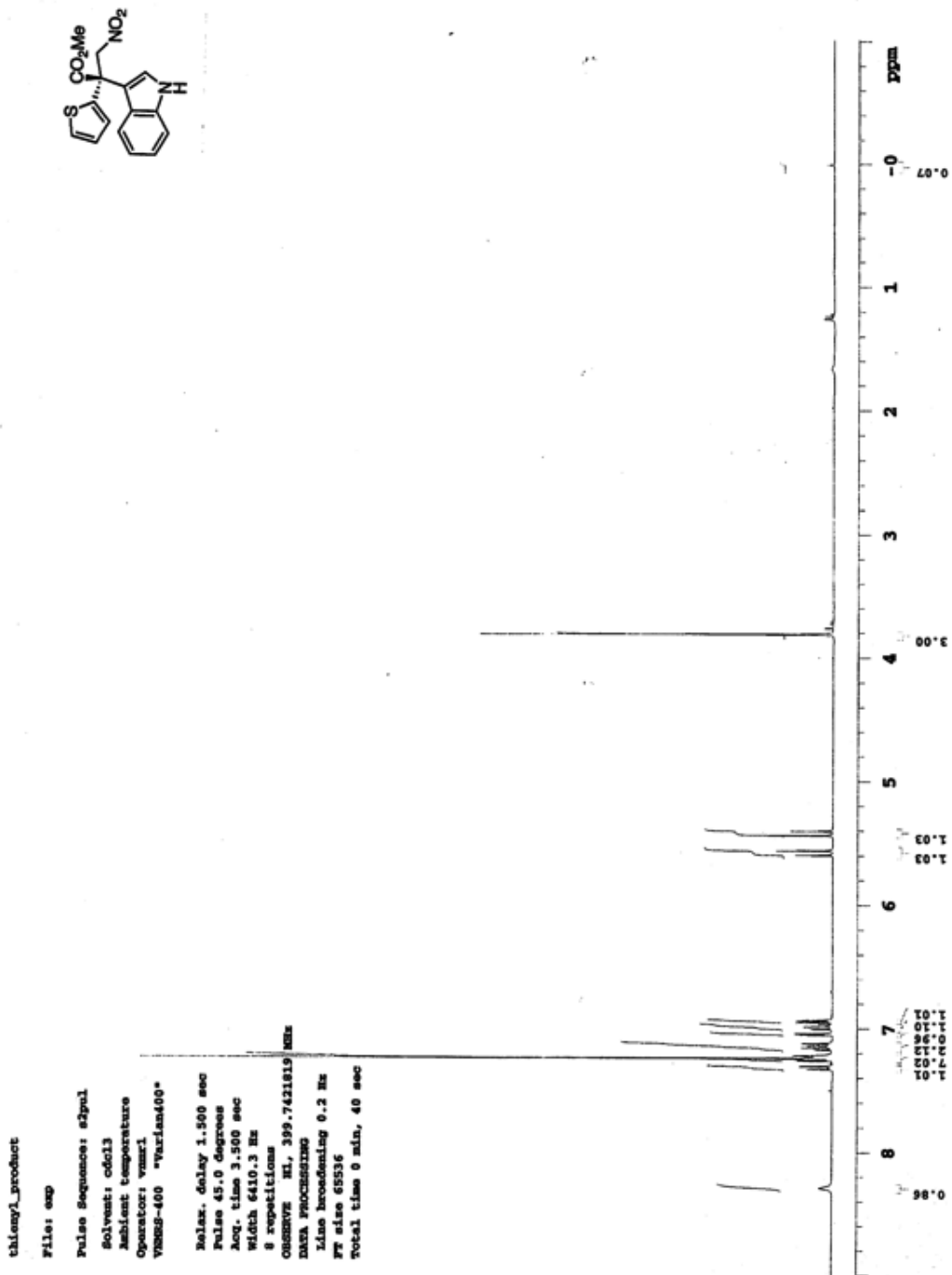
HPLC chart of **6i** (racemic).



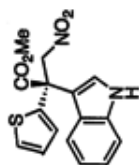
Peak #	Retention time	Type	Area	Area %
1	14.59	BB	36489774	49.775
2	17.51	BB	36818977	50.225



¹H NMR spectrum of **6j**.



¹³C NMR spectrum of 6j.



thioxy1_product_13C

File: exp

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

Operator: vmar1

VMRS-400 "Varian400"

Relax. delay 0.700 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Wdth 24509.8 Hz

328 repetitions

OBSERVE C13, 100.5152568 MHz

RECOUPLE H1, 399.7441724 MHz

Power 45 dB

continuously on

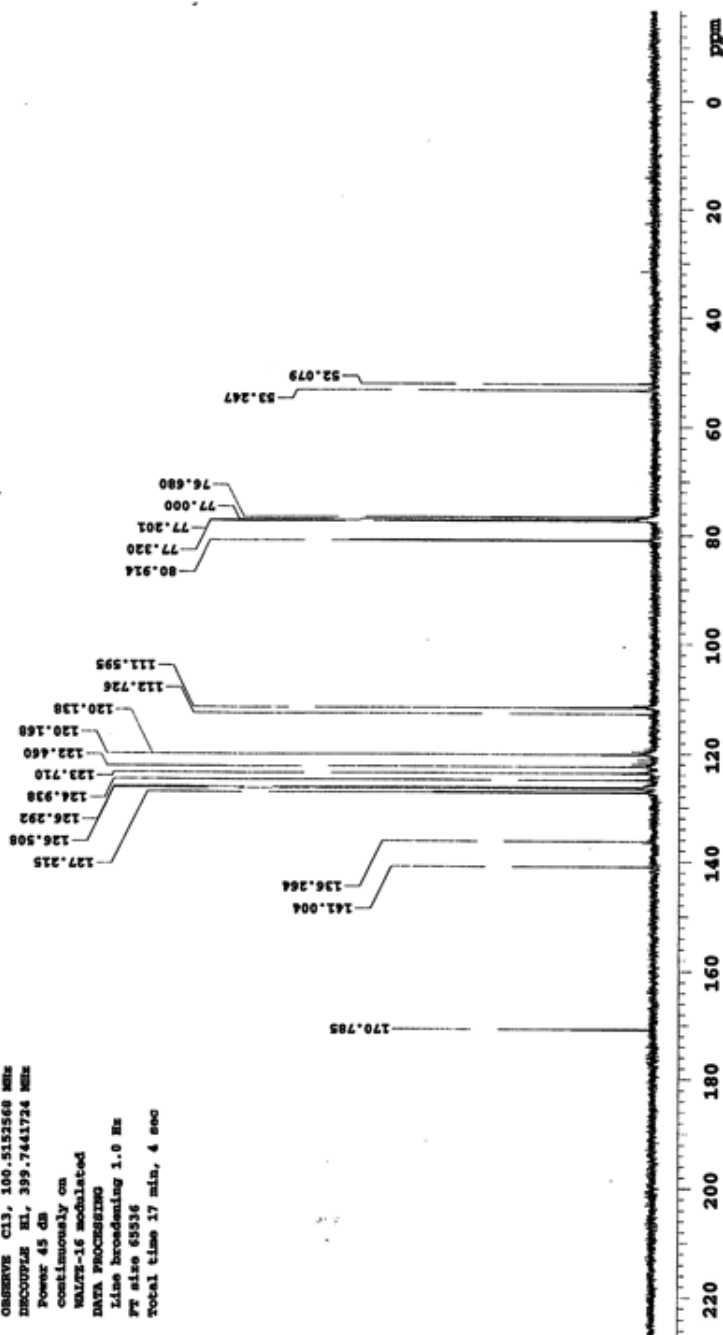
WALTZ-16 modulated

DATA PROCESSING

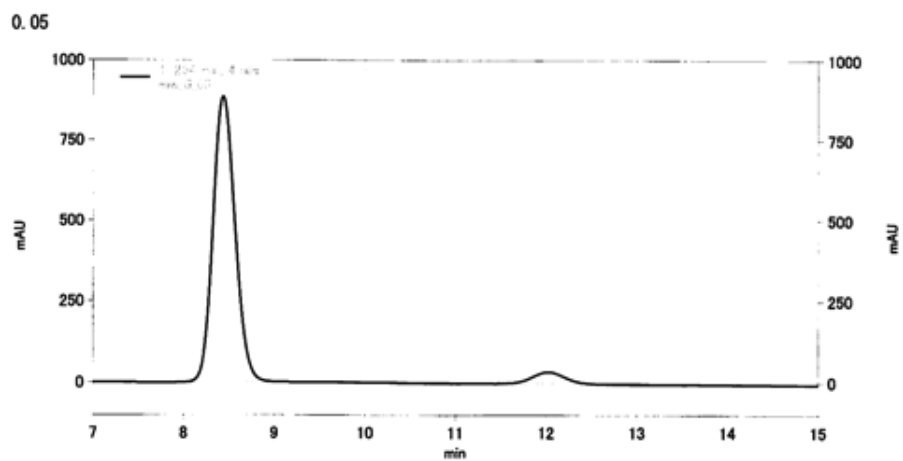
Line broadening 1.0 Hz

FT size 65536

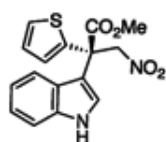
Total time 17 min, 4 sec



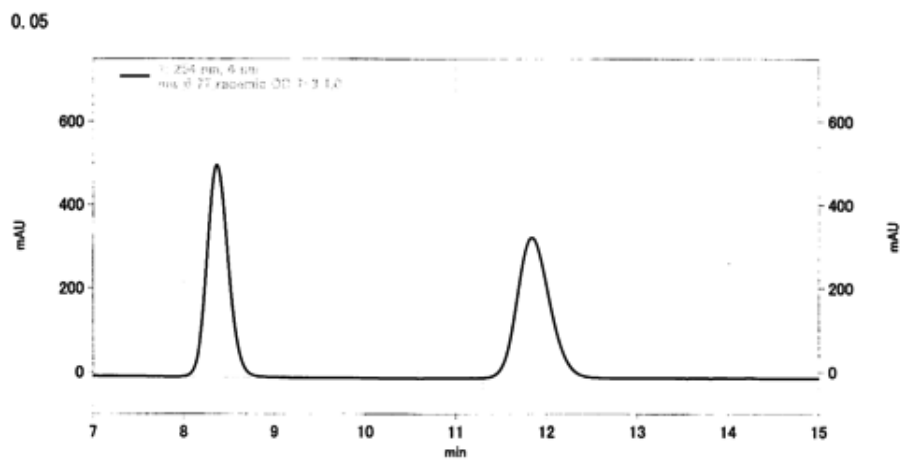
HPLC chart of **6j**.



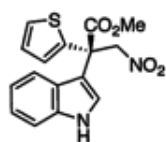
Peak #	Retention time	Type	Area	Area %
1	8.44	BB	59835567	94.362
2	12.02	BB	3575009	5.638



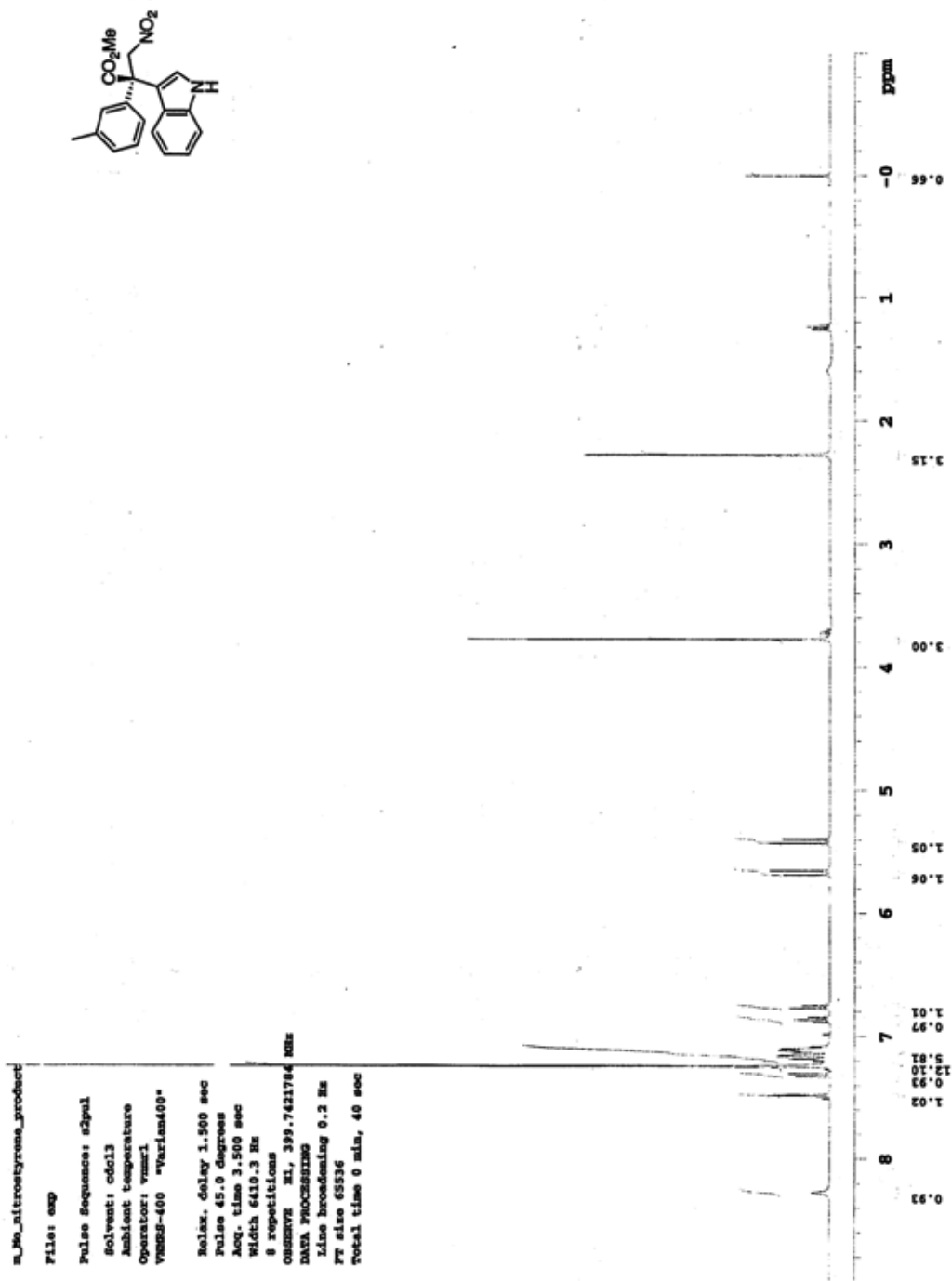
HPLC chart of **6j** (racemic).



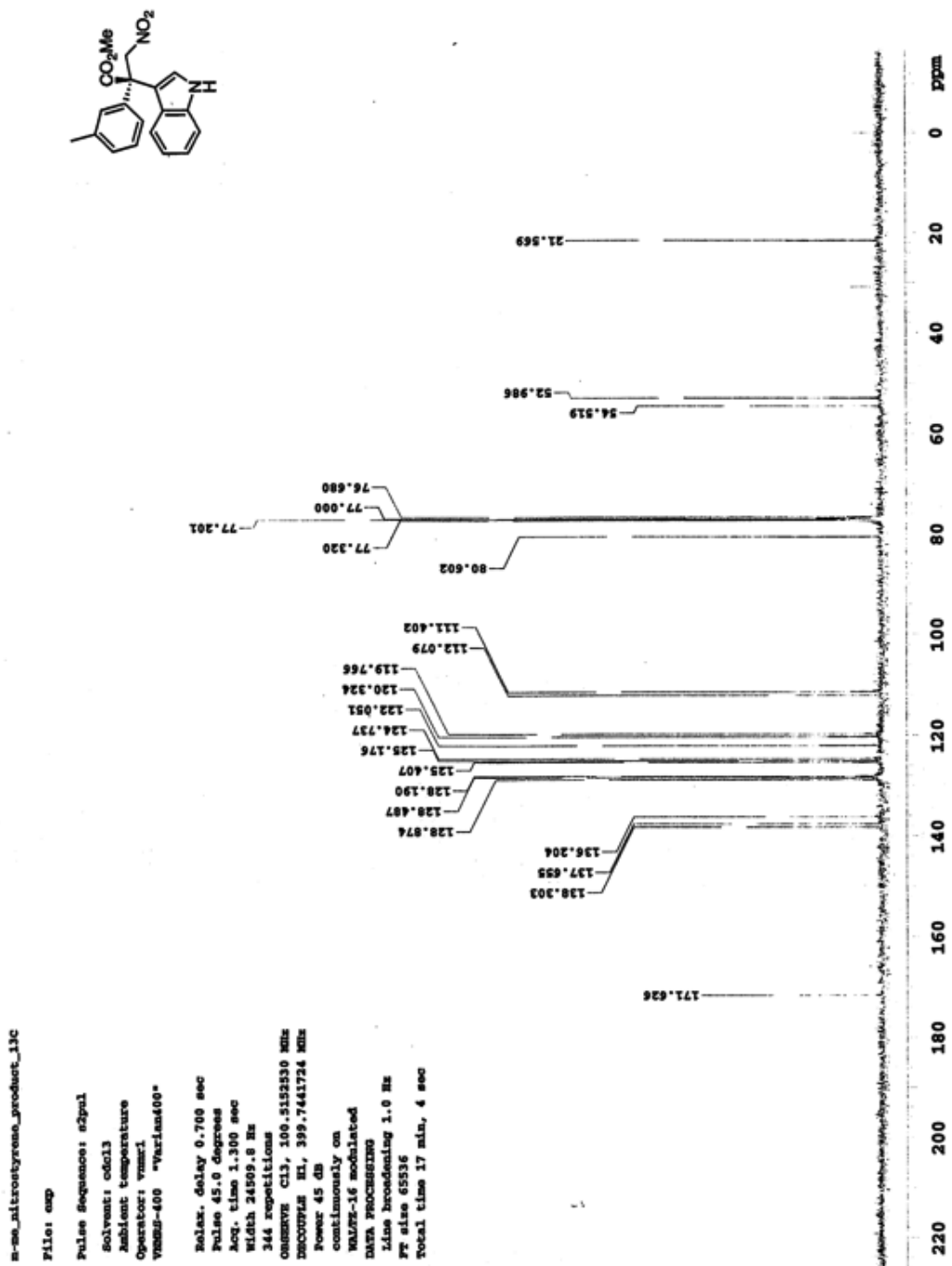
Peak #	Retention time	Type	Area	Area %
1	8.37	BB	33311330	50.004
2	11.84	BB	33305698	49.996



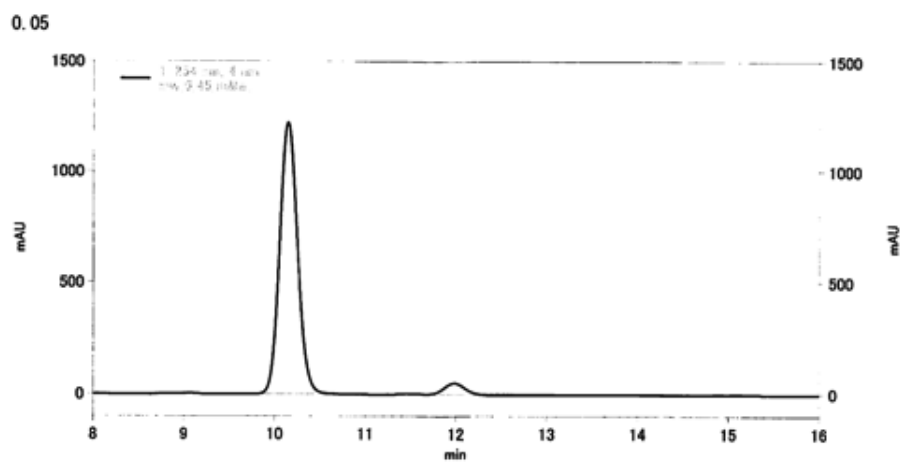
¹H NMR spectrum of **6k**.



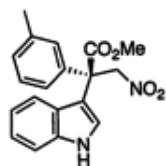
¹³C NMR spectrum of **6k**.



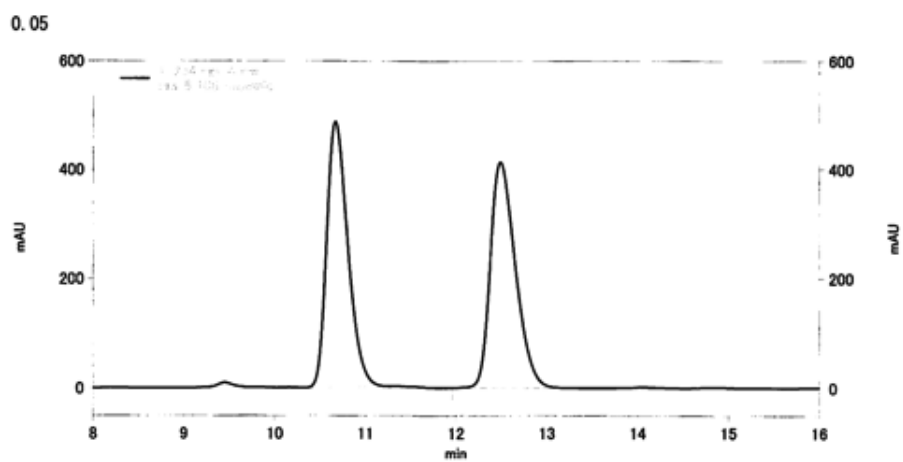
HPLC chart of **6k**.



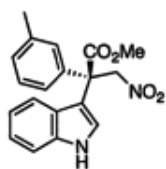
Peak #	Retention time	Type	Area	Area %
1	10.15	BB	67384856	95.447
2	11.98	BB	3214525	4.553



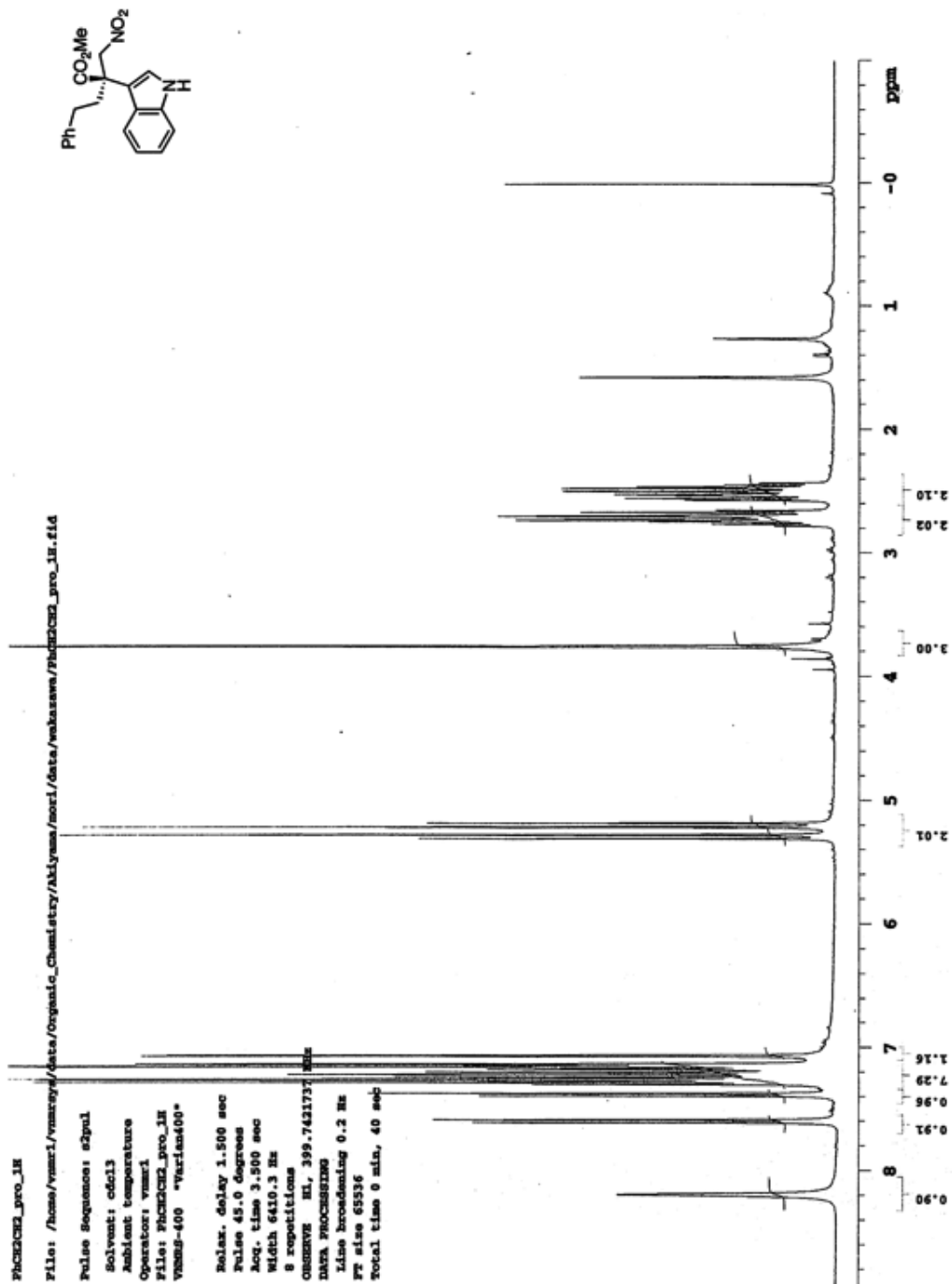
HPLC chart of **6k** (racemic).



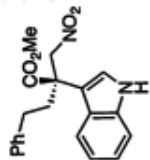
Peak #	Retention time	Type	Area	Area %
1	10.67	BB	31430820	49.647
2	12.49	BB	31877522	50.353



^1H NMR spectrum of **6m**.



¹³C NMR spectrum of 6m.



PMR2002_pfo_13C

File: emp

Pulse Sequence: sfpul

Solvent: cdcl3

Ambient temperature

Operator: vmm1

VNMR-400 "varian400"

Relax. delay 0.700 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

384 repetitions

OBSERVE CH1, 100.5152530 MHz

RECOVERIE HL, 399.7441724 MHz

Power 43 dB

continuously on

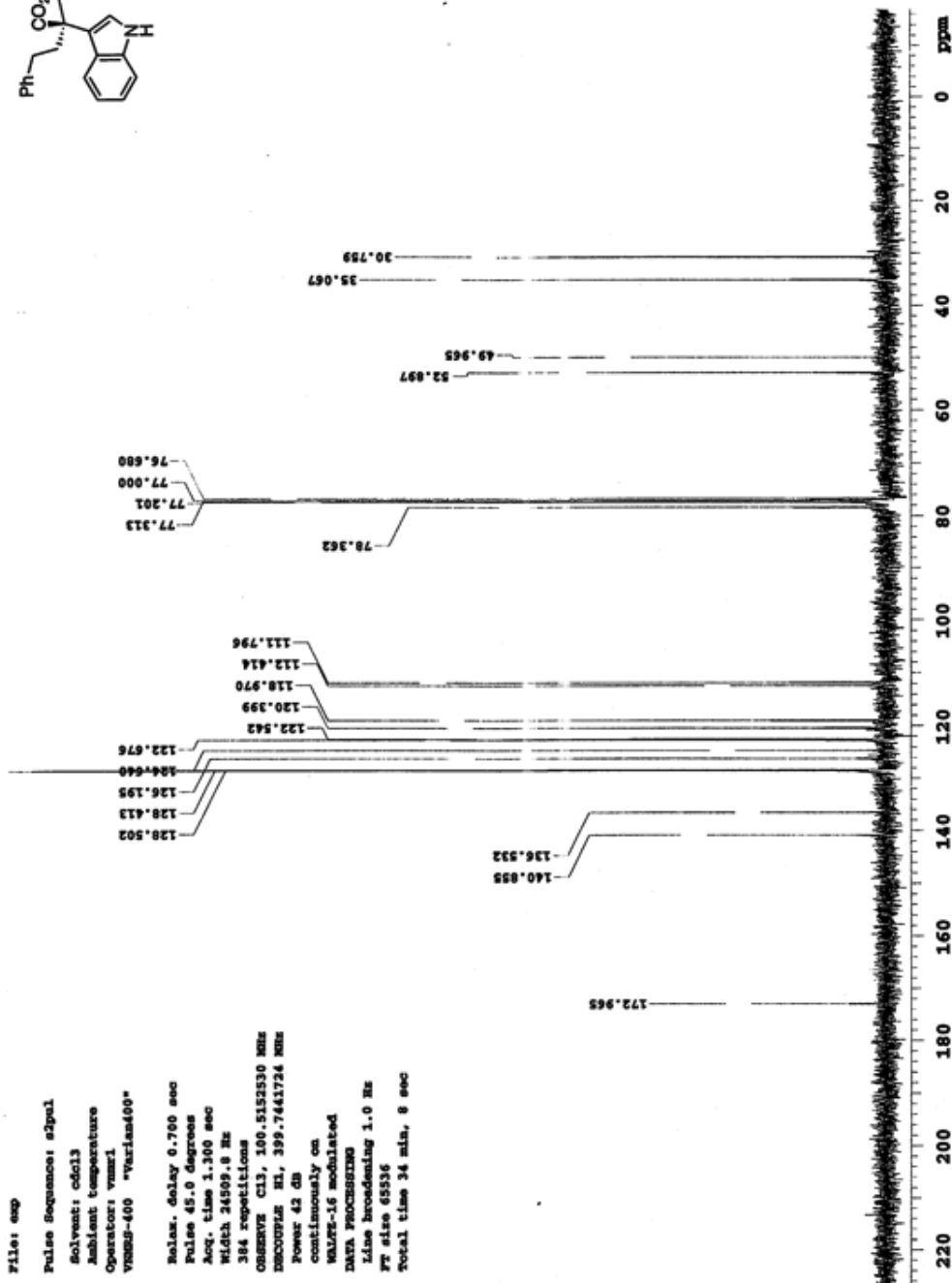
WALTZ-16 modulated

DATA PROCESSING

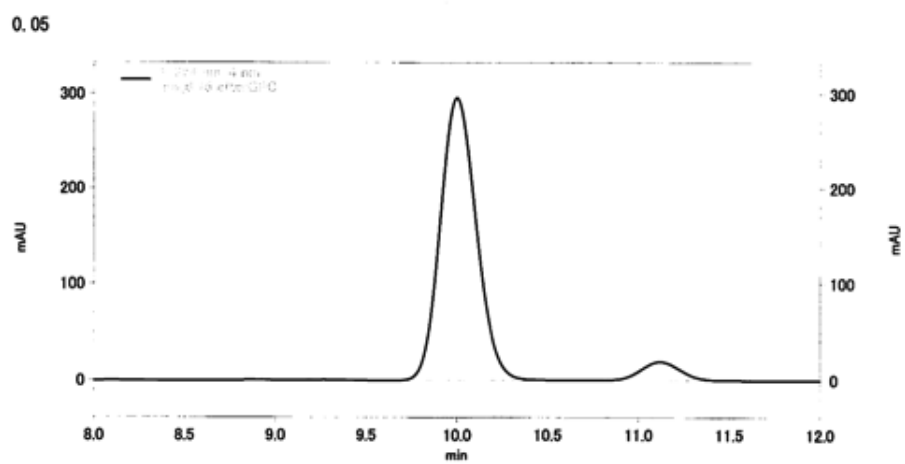
Line broadening 1.0 Hz

FT size 65536

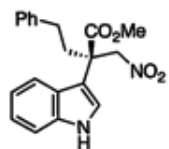
Total time 34 min, 8 sec



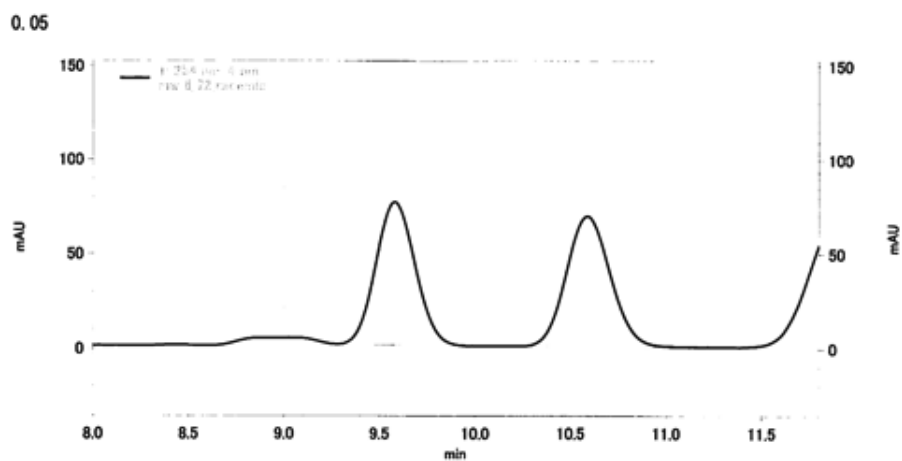
HPLC chart of 6m.



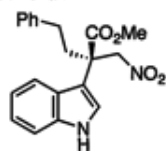
Peak #	Retention time	Type	Area	Area %
1	10.00	BB	16267772	93.359
2	11.12	BB	1157158	6.641



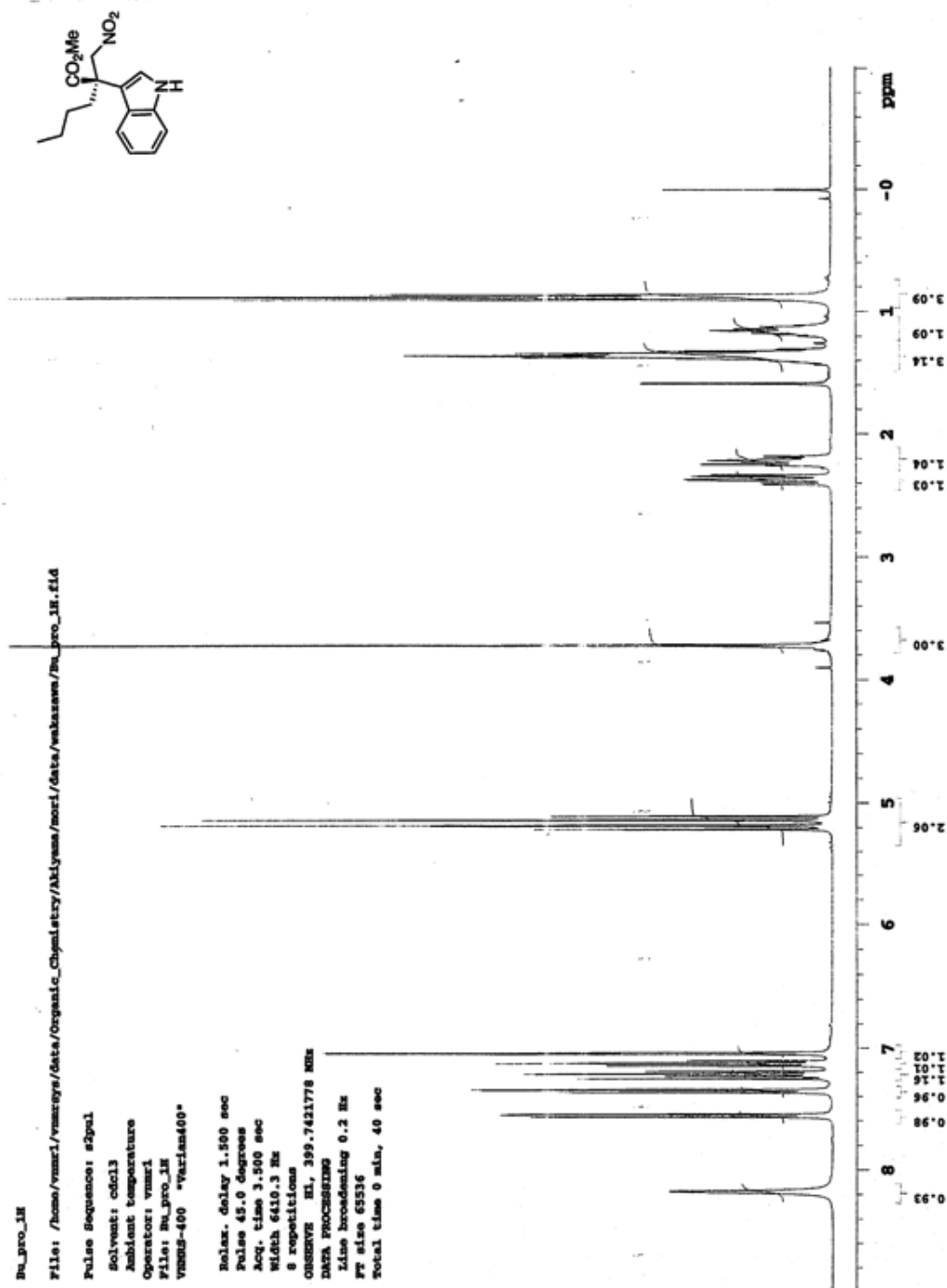
HPLC chart of **6m** (racemic).



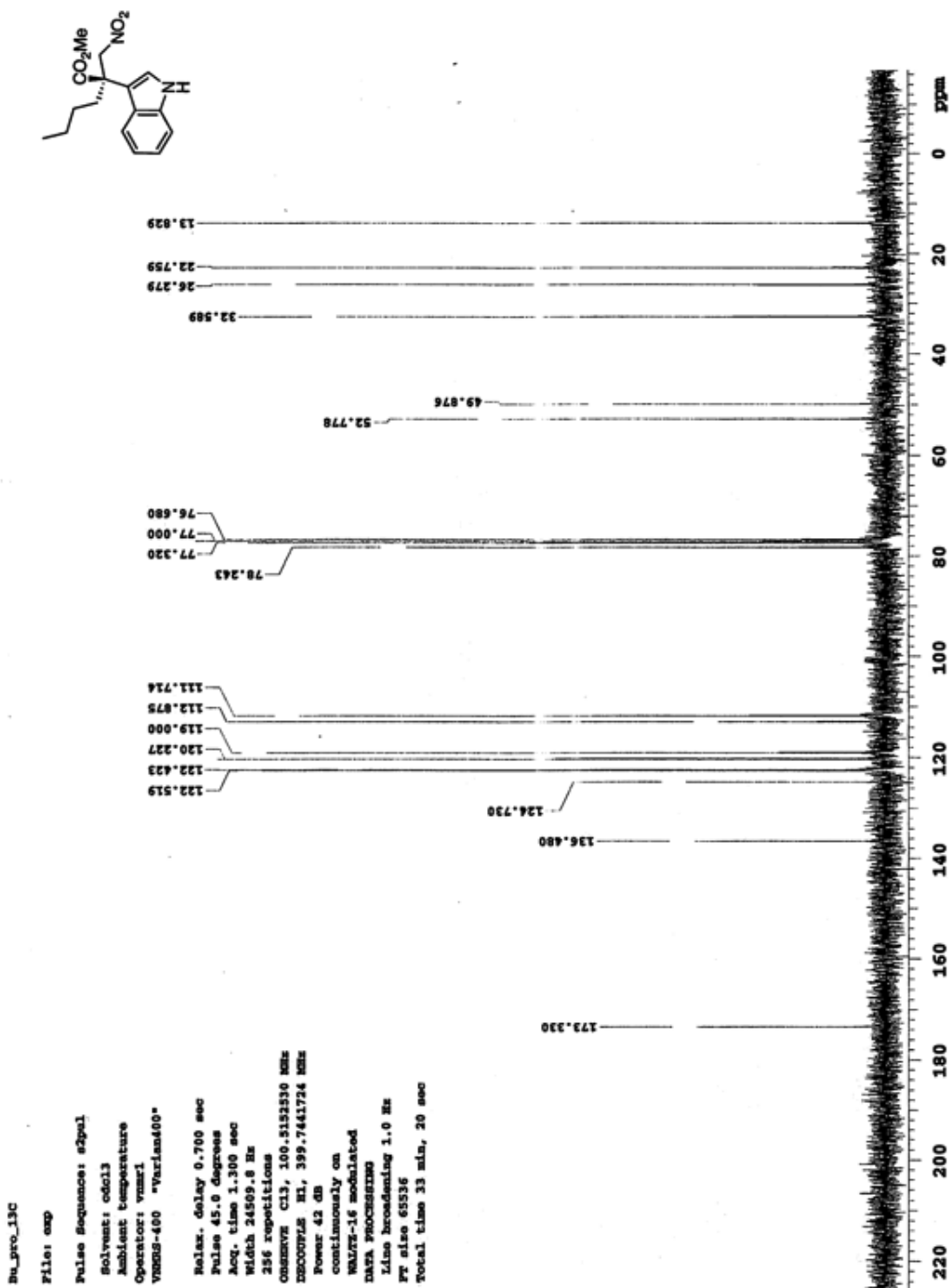
Peak #	Retention time	Type	Area	Area %
1	9.58	BB	4356463	49.595
2	10.59	BB	4427571	50.405



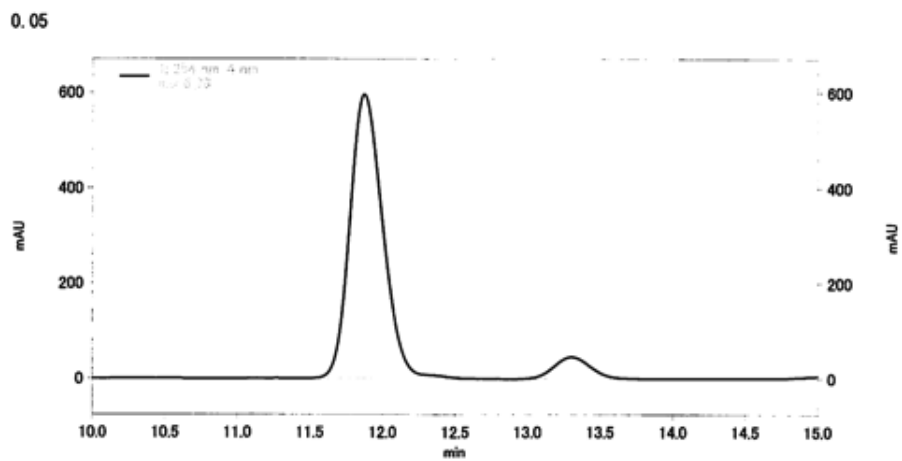
^1H NMR spectrum of **6n**.



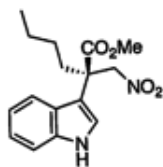
¹³C NMR spectrum of **6n**.



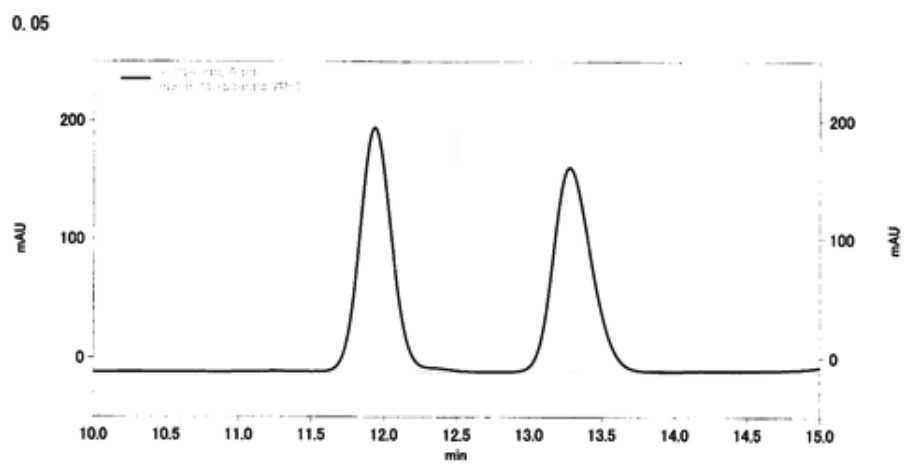
HPLC chart of **6n**.



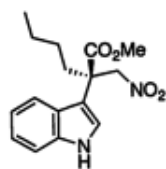
Peak #	Retention time	Type	Area	Area %
1	11.87	BI	37414699	92.582
2	13.30	BI	2993647	7.408



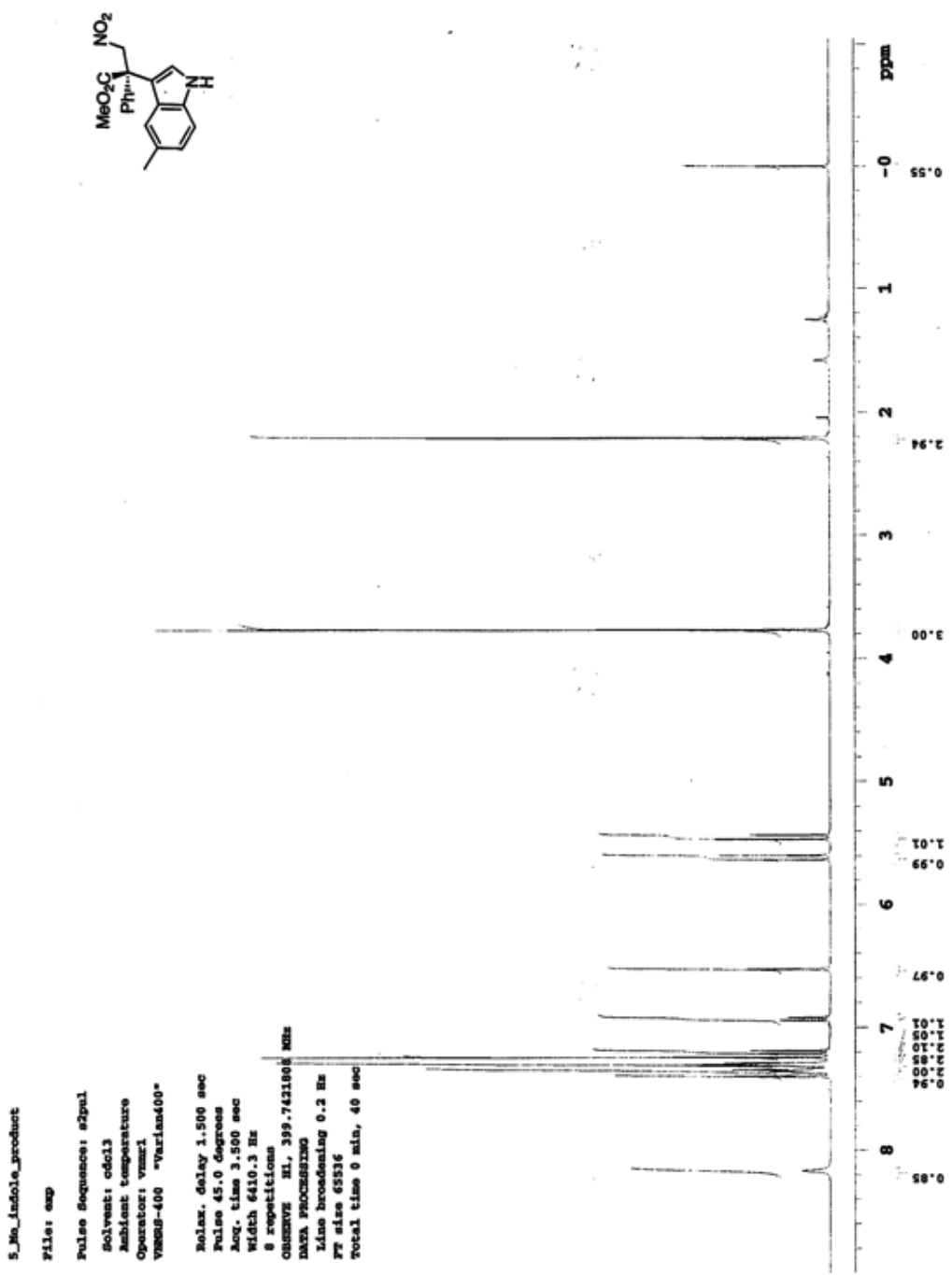
HPLC chart of **6n** (racemic).



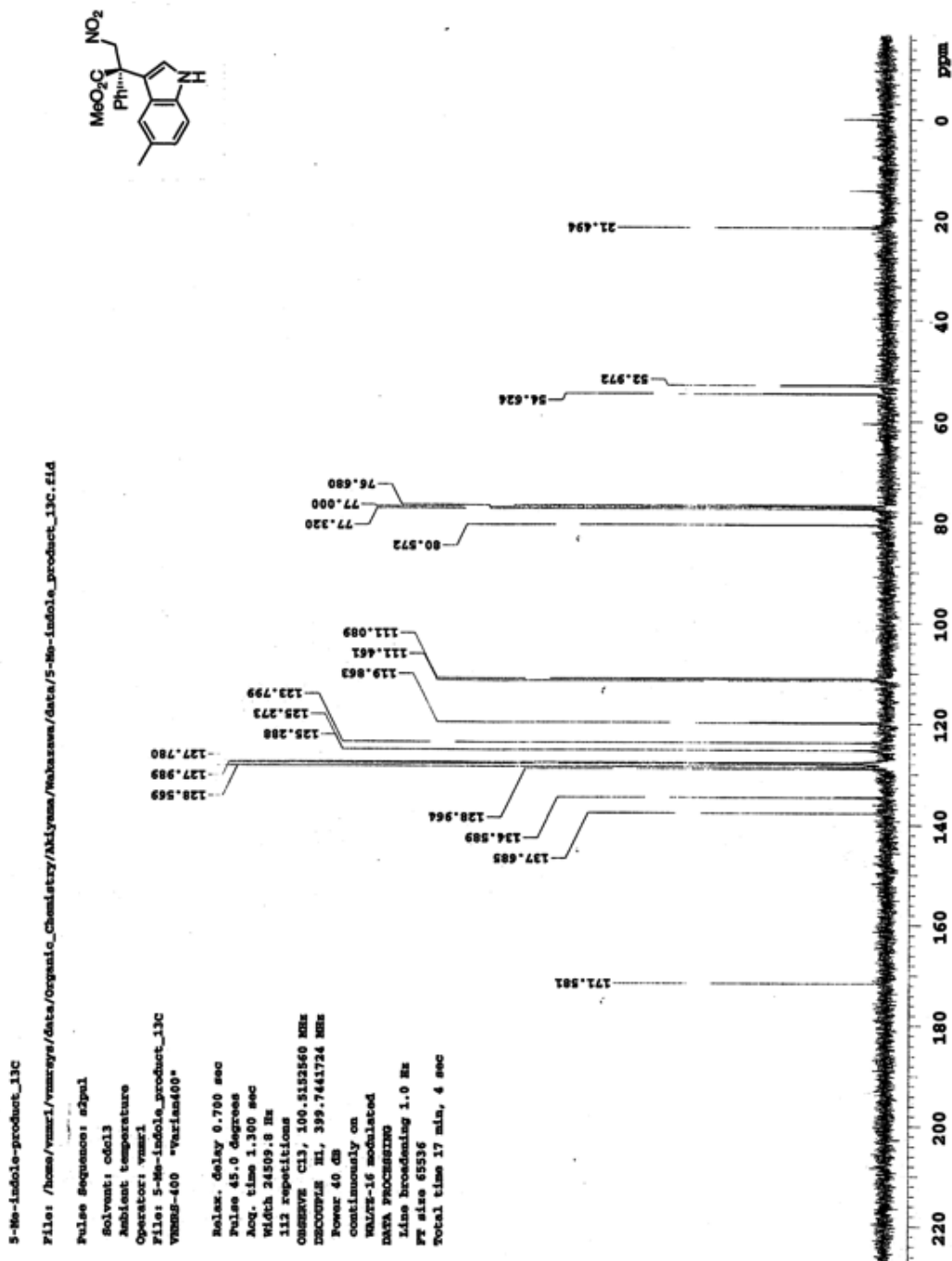
Peak #	Retention time	Type	Area	Area %
1	11.93	BB	12745602	50.363
2	13.28	BB	12561781	49.637



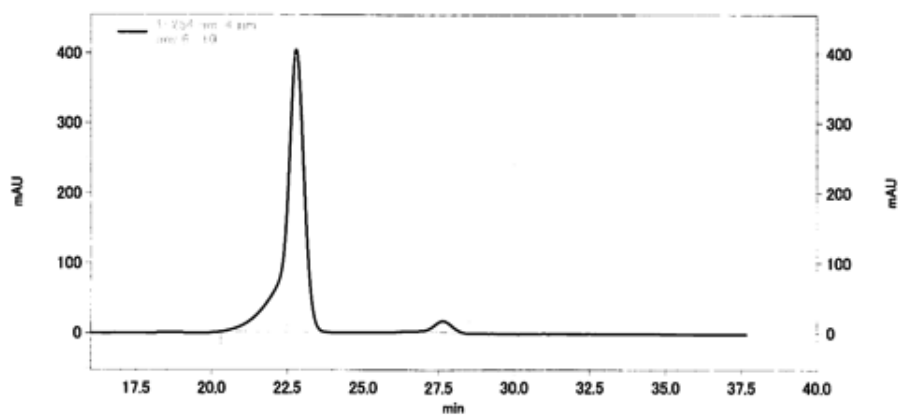
¹H NMR spectrum of **60**.



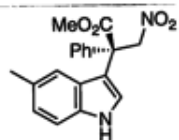
¹³C NMR spectrum of **60**.



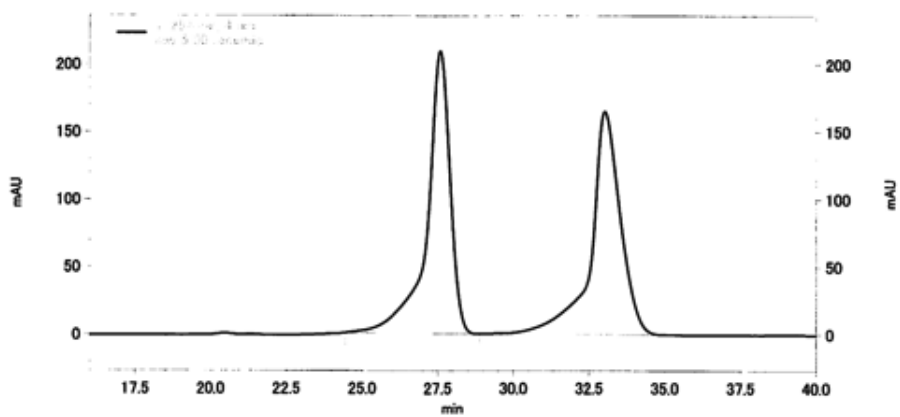
HPLC chart of **60**.



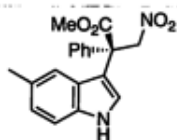
Peak #	Retention time	Type	Area	Area %
1	22.80	BB	69956621	96.581
2	27.65	BB	2476322	3.419



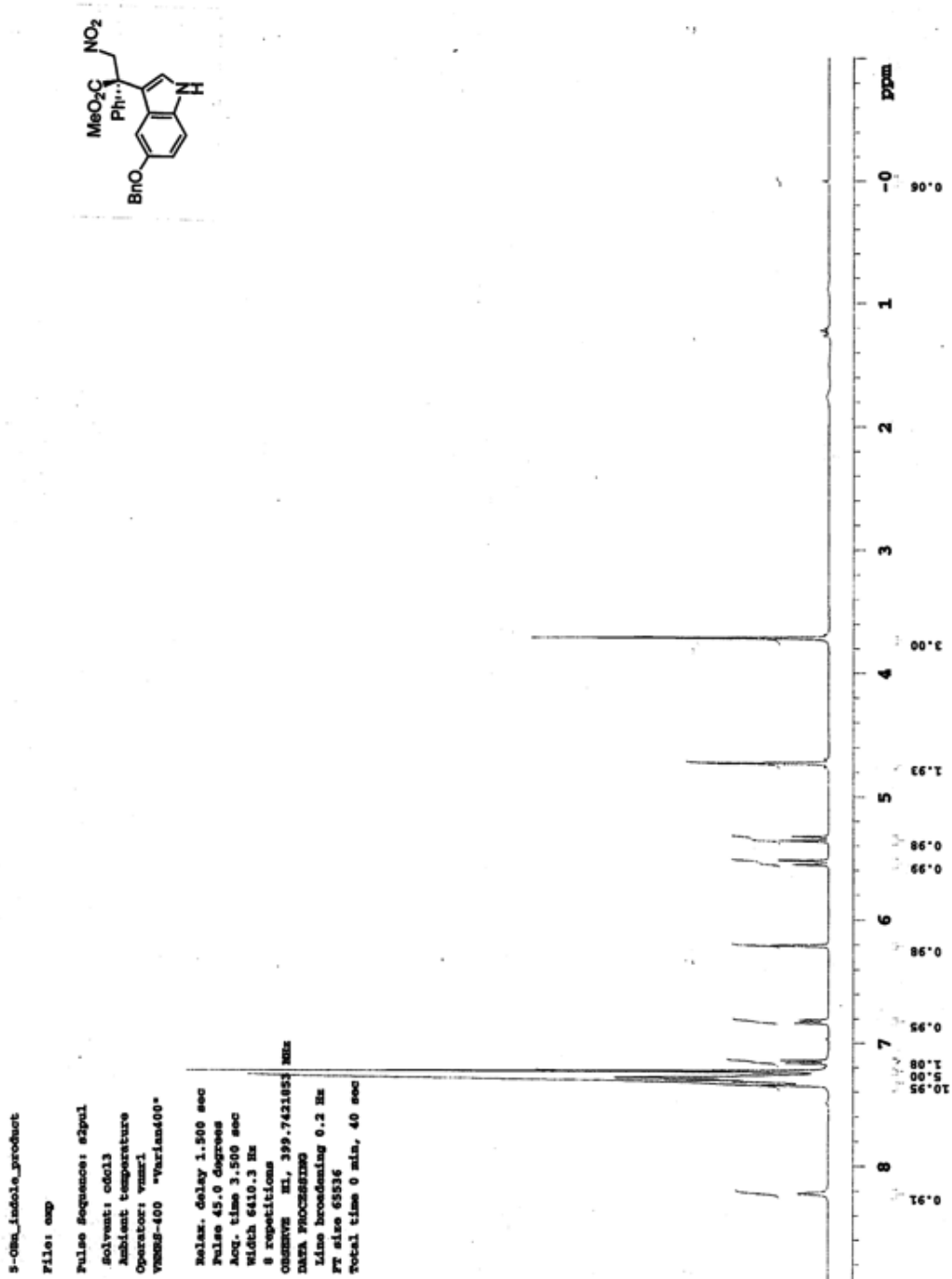
HPLC chart of **60** (racemic).



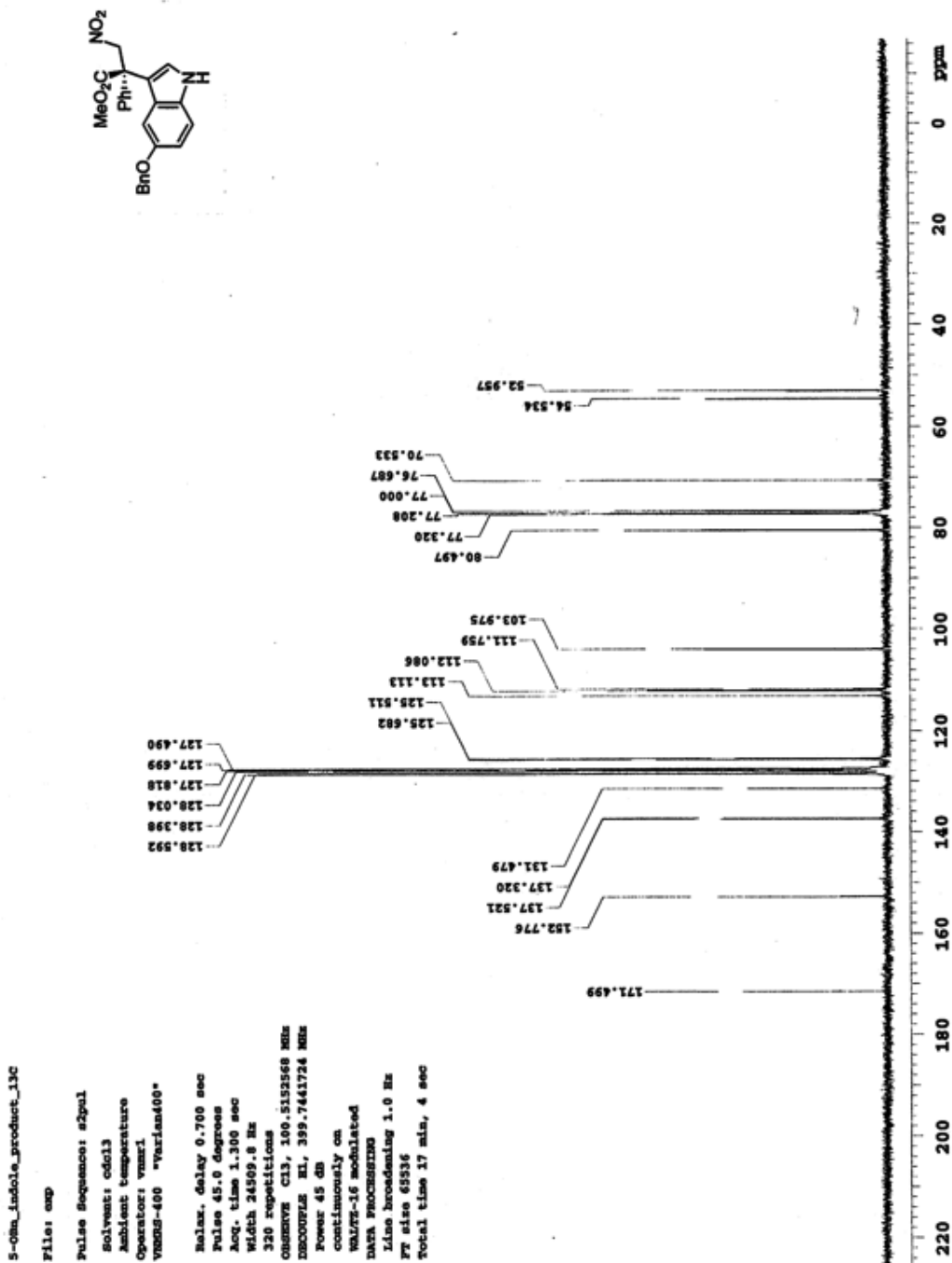
Peak #	Retention time	Type	Area	Area %
1	27.59	BB	44411986	49.766
2	33.03	BB	44828870	50.234



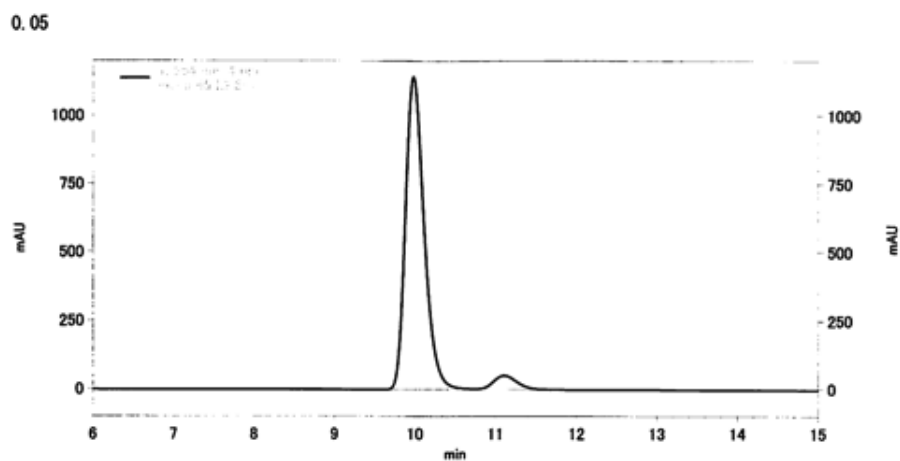
^1H NMR spectrum of **6p**.



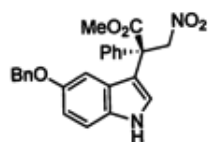
¹³C NMR spectrum of 6p.



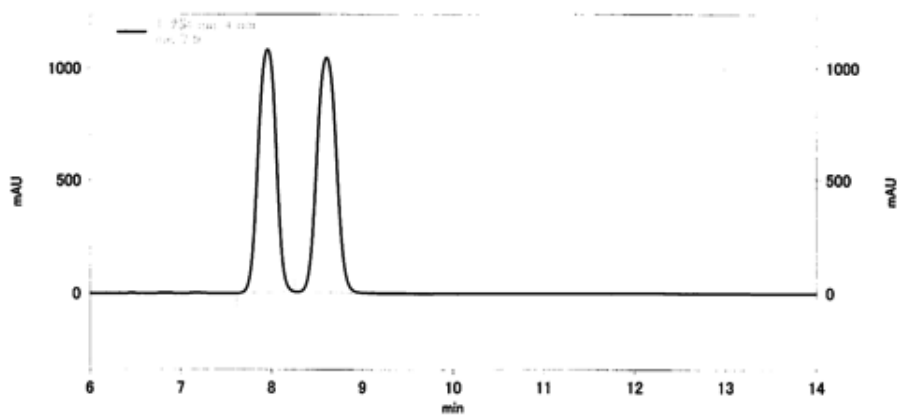
HPLC chart of **6p**.



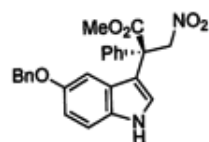
Peak #	Retention time	Type	Area	Area %
1	9.98	BB	73410536	94.883
2	11.11	IB	3958801	5.117



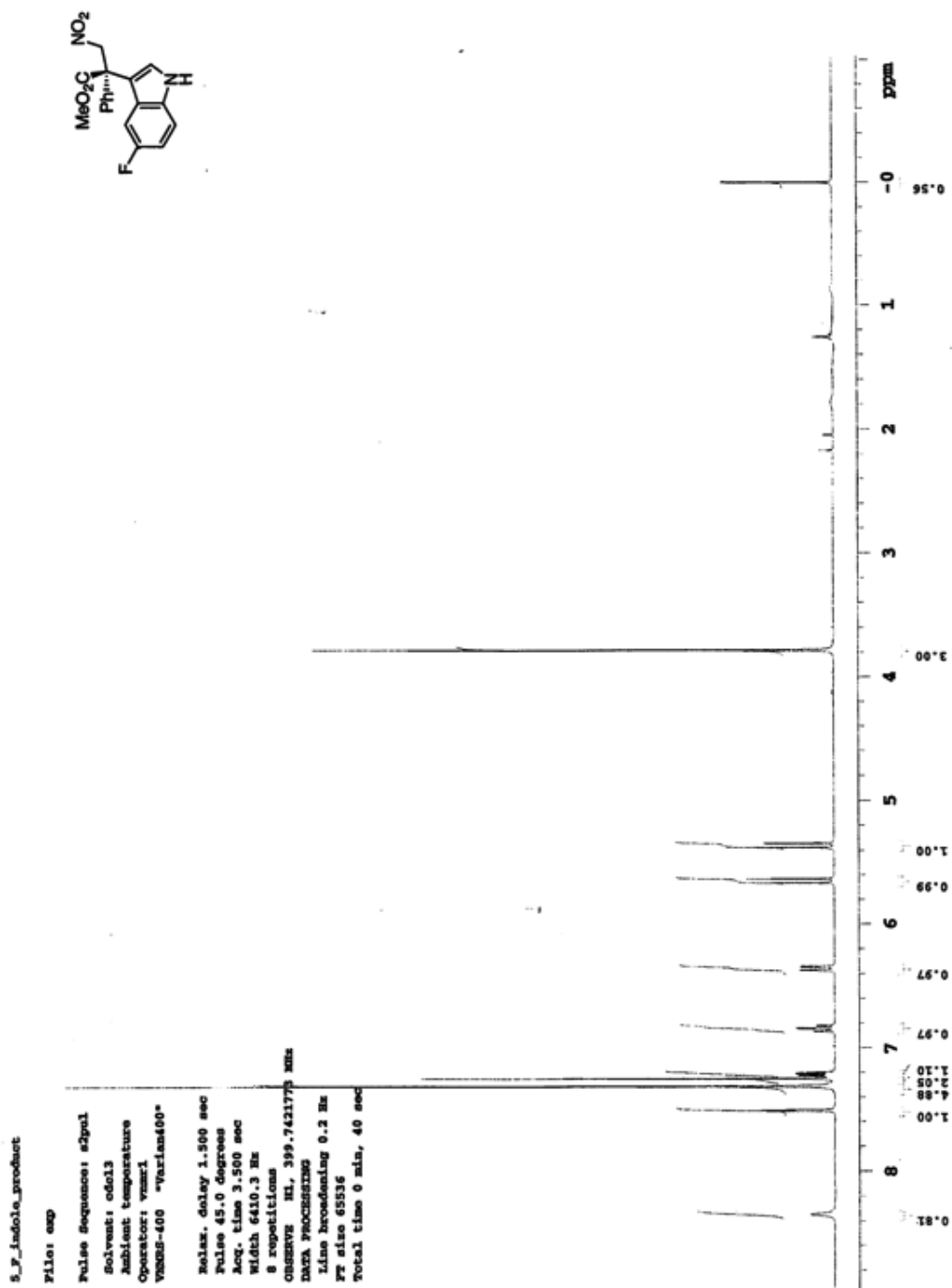
HPLC chart of **6p** (racemic).



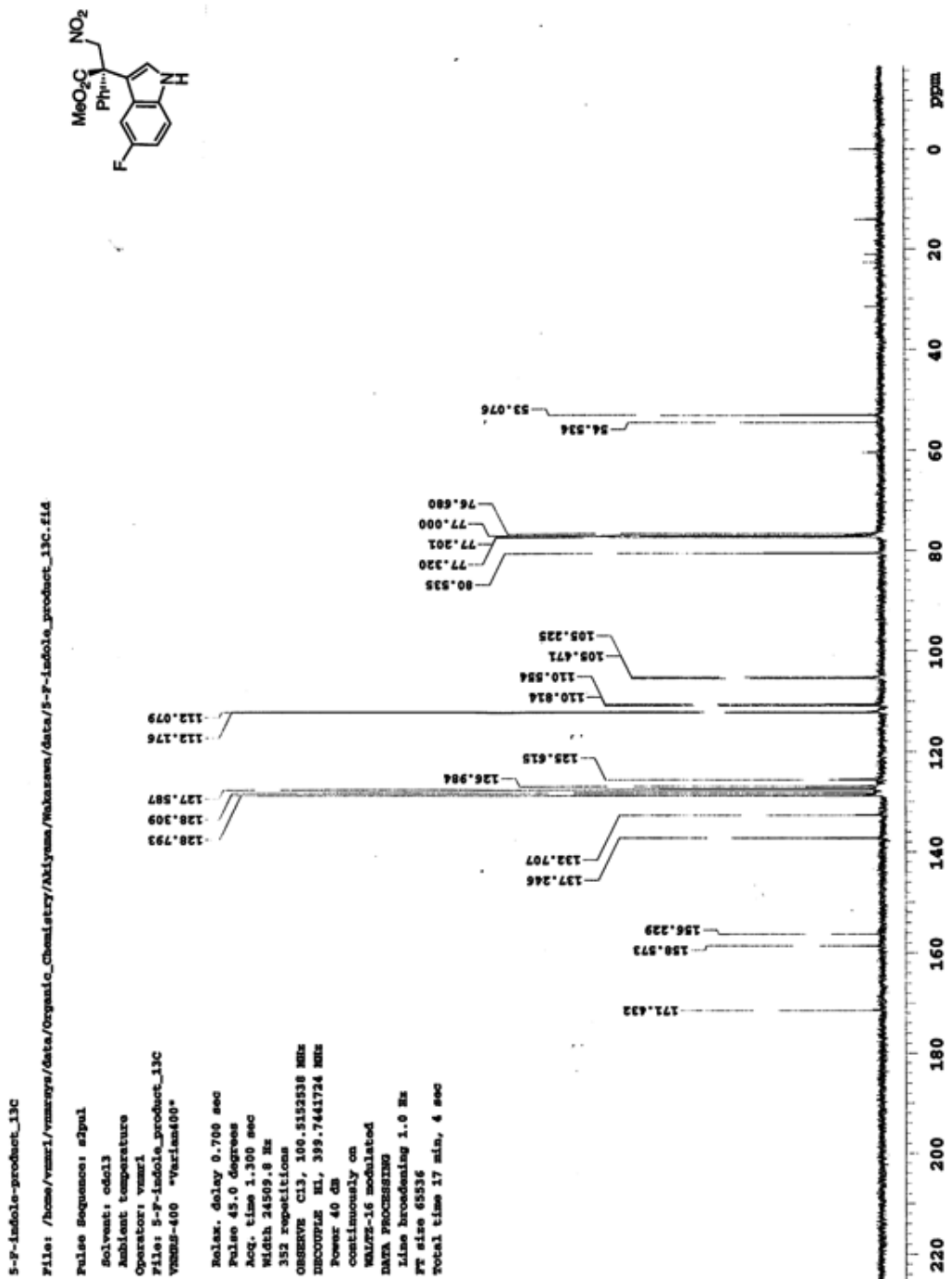
Peak #	Retention time	Type	Area	Area %
1	7.96	B1	58701246	48.950
2	8.61	B	61220060	51.050



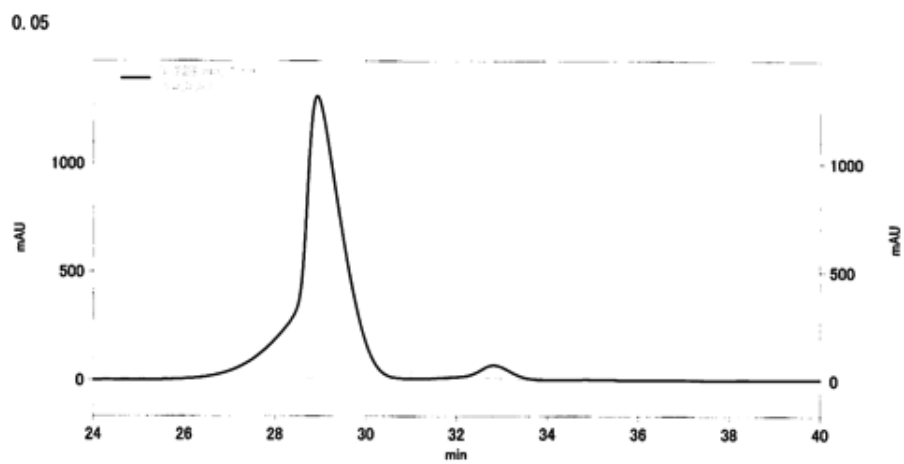
¹H NMR spectrum of **6q**.



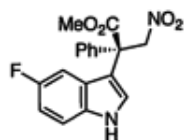
¹³C NMR spectrum of 6q.



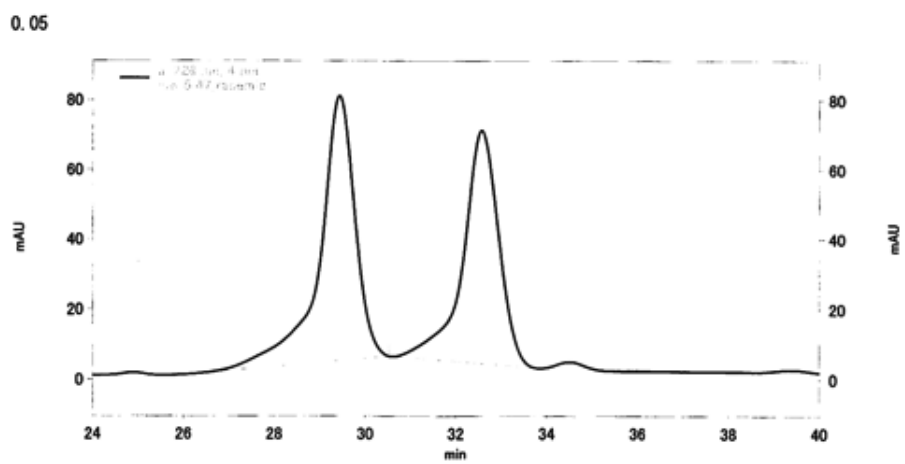
HPLC chart of **6q**.



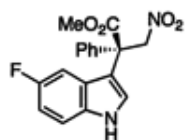
Peak #	Retention time	Type	Area	Area %
1	28.93	BB	333613049	96.906
2	32.82	BB	10652161	3.094



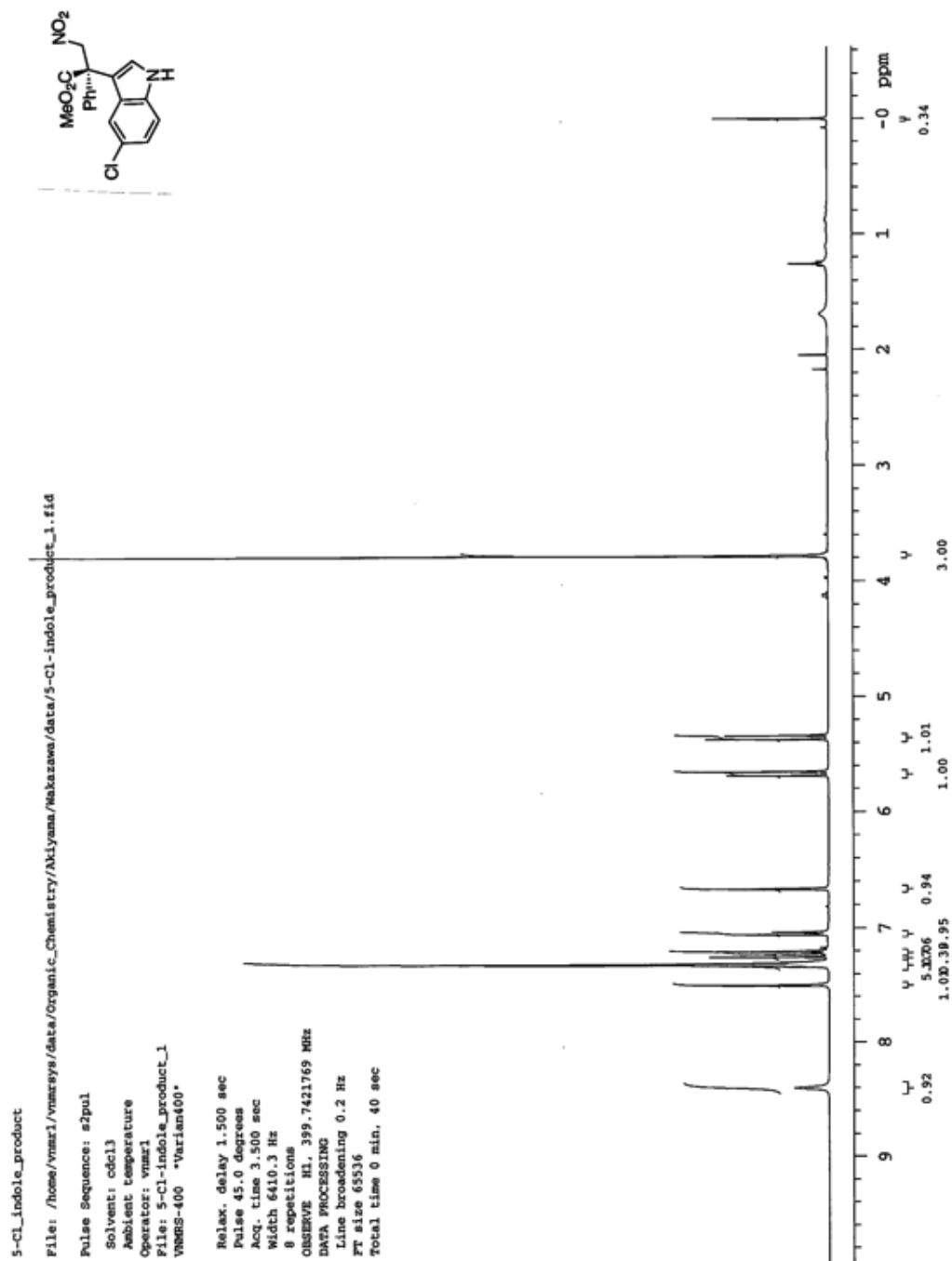
HPLC chart of **6q** (racemic).



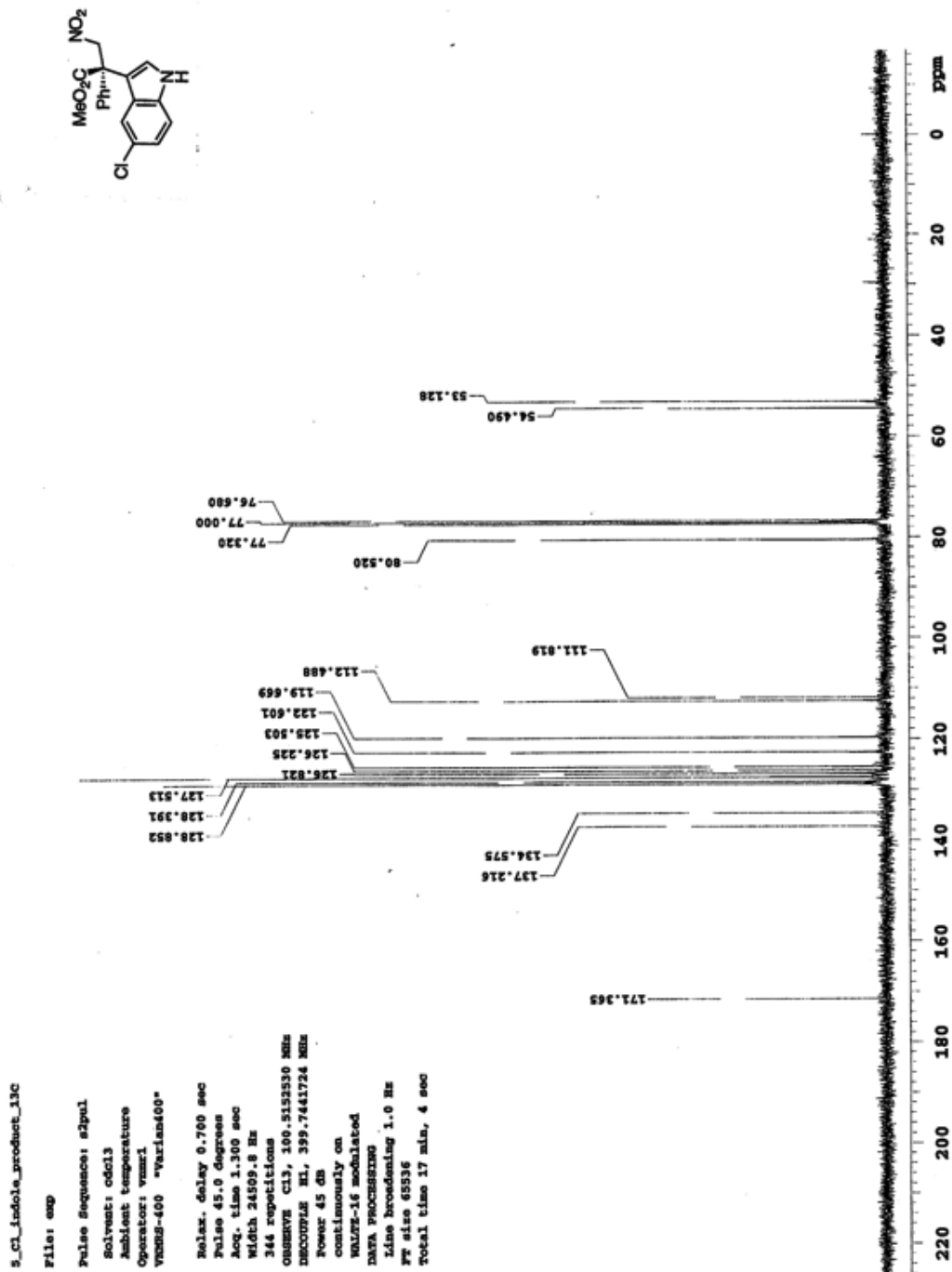
Peak #	Retention time	Type	Area	Area %
1	29.44	B1	16382562	52.733
2	32.57	BB	14684383	47.267



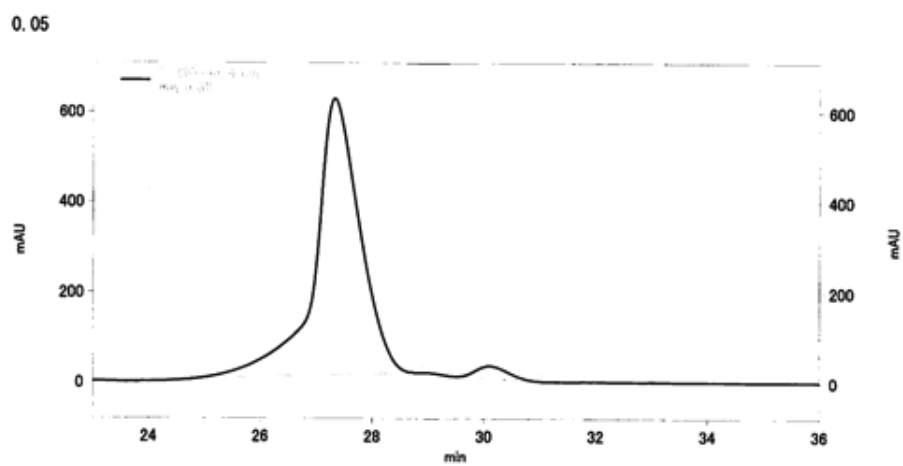
¹H NMR spectrum of **6r**.



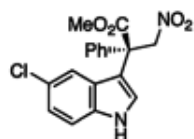
¹³C NMR spectrum of **6r**.



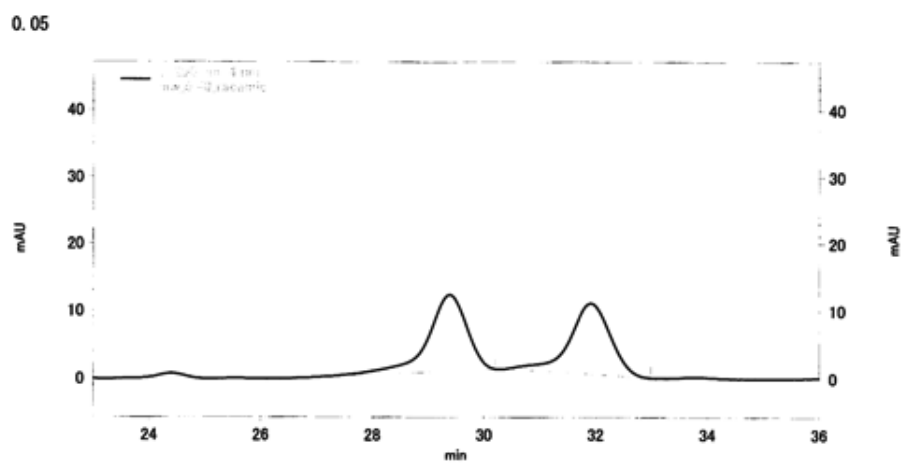
HPLC chart of **6r**.



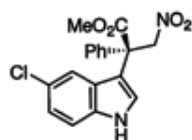
Peak #	Retention time	Type	Area	Area %
1	27.33	BB	137170194	96.985
2	30.09	BB	4264282	3.015



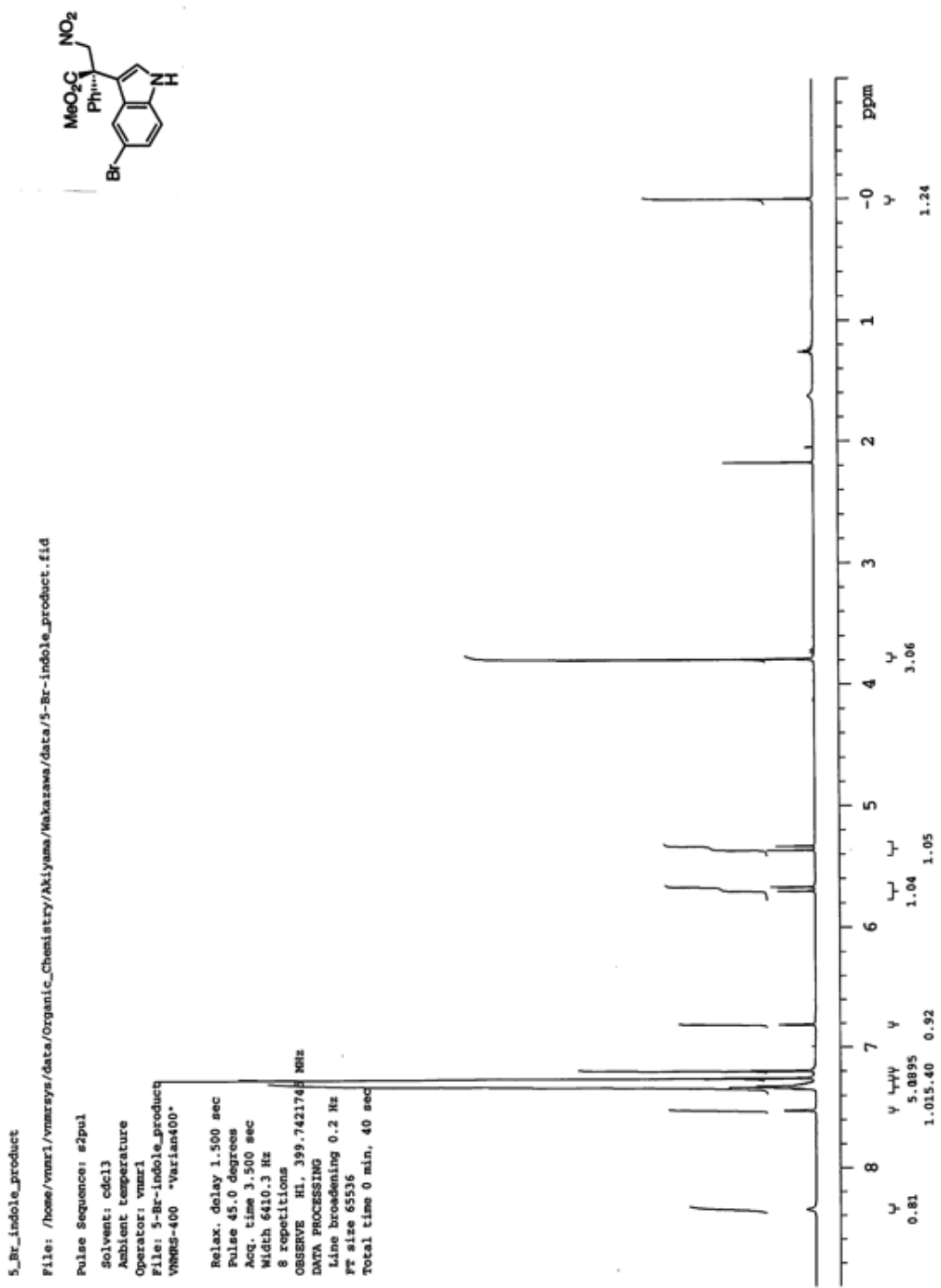
HPLC chart of **6b** (racemic).



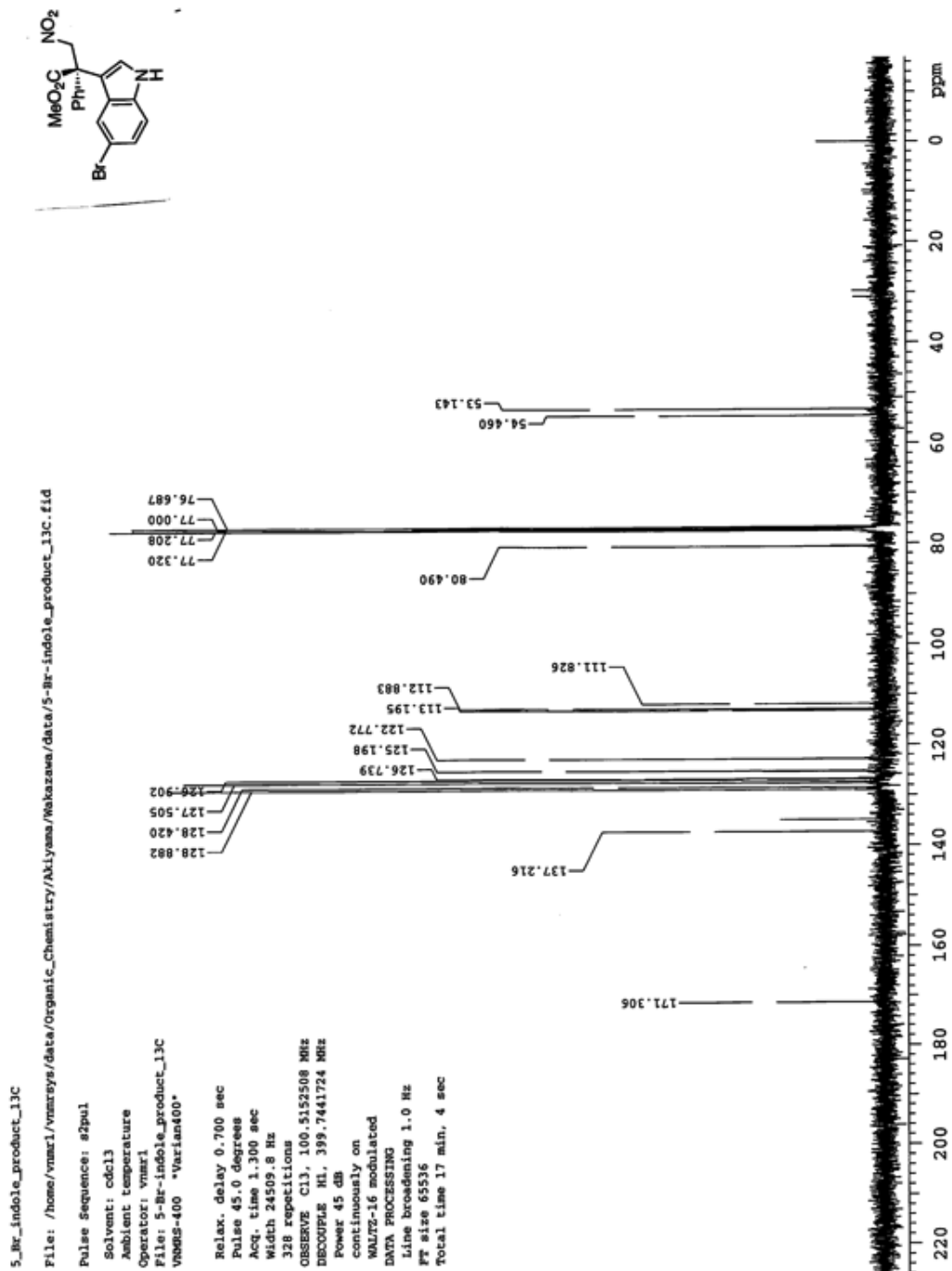
Peak #	Retention time	Type	Area	Area %
1	29.39	BI	2177871	50.583
2	31.91	BB	2127686	49.417



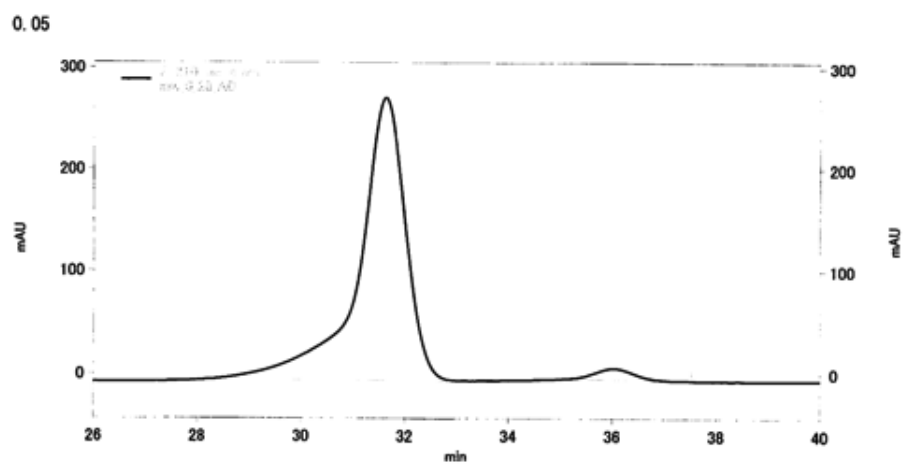
^1H NMR spectrum of **6s**.



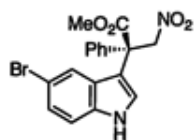
¹³C NMR spectrum of **6s**.



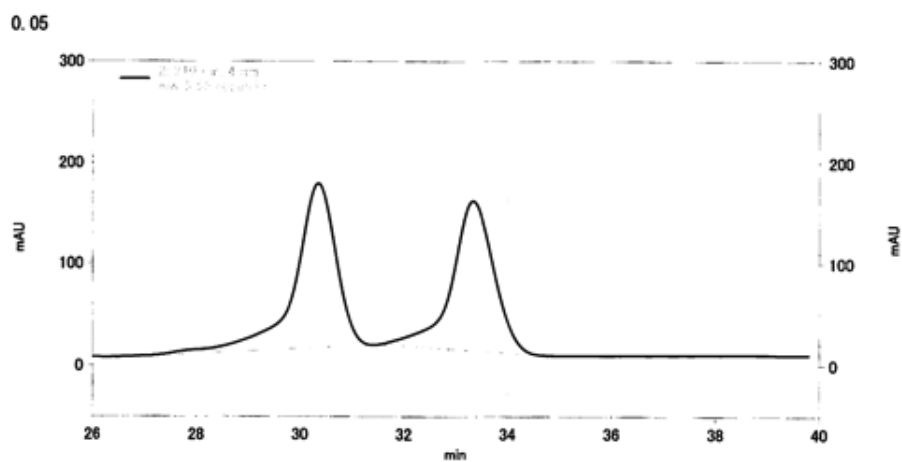
HPLC chart of **6s**.



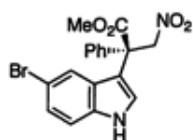
Peak #	Retention time	Type	Area	Area %
1	31.63	BB	69919498	96.891
2	36.03	BB	2243579	3.109



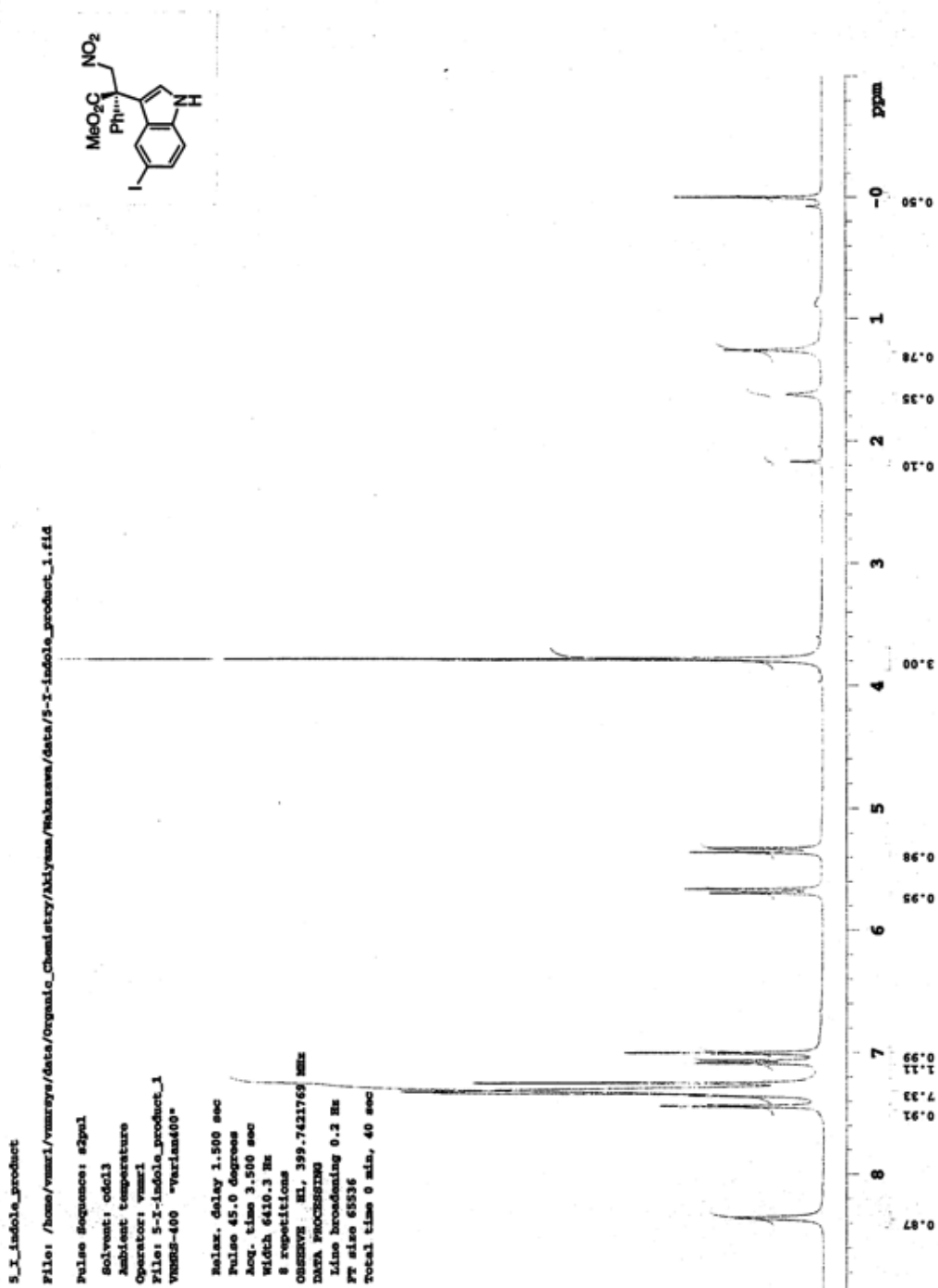
HPLC chart of **6s** (racemic).



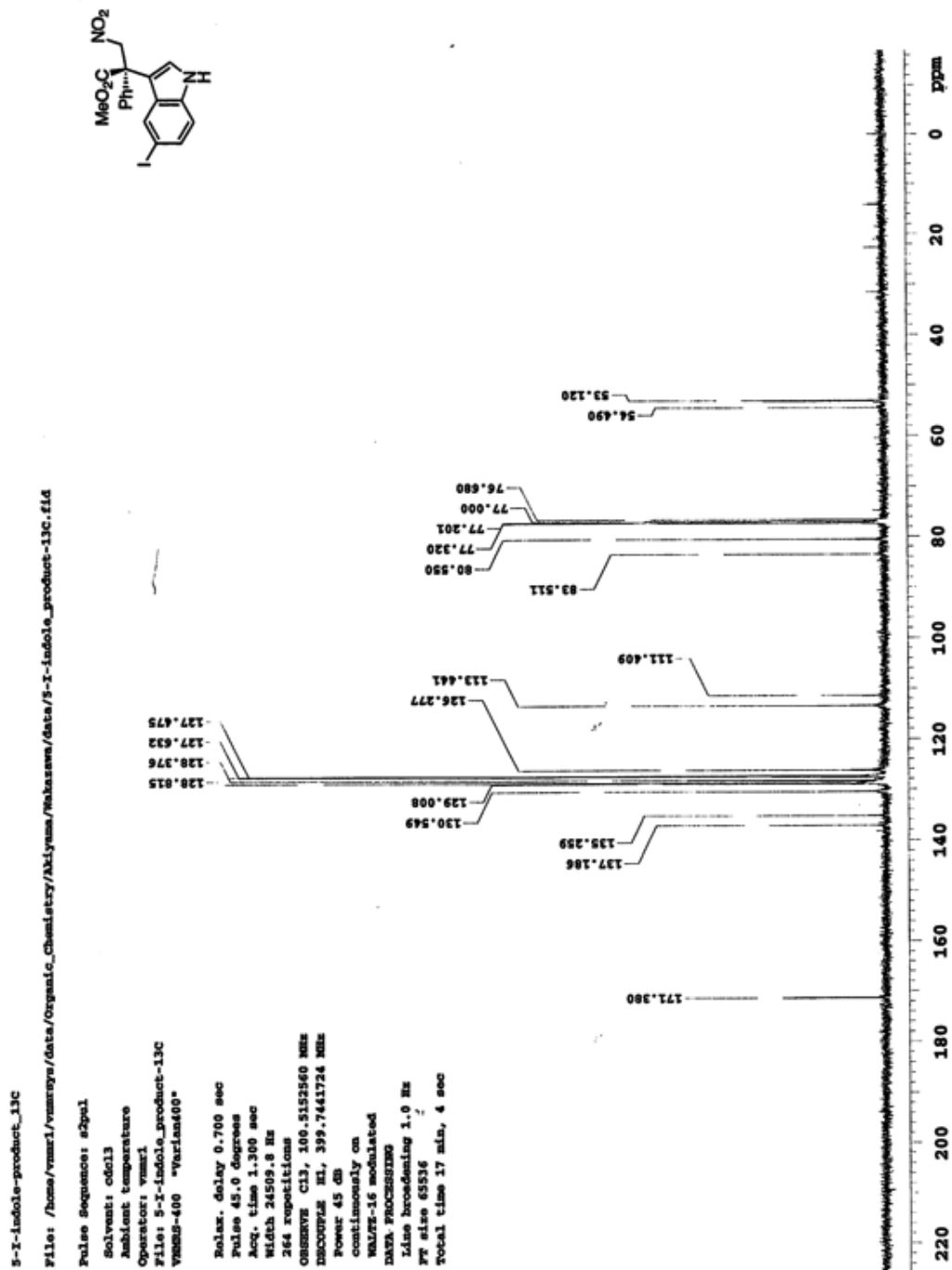
Peak #	Retention time	Type	Area	Area %
1	30.35	BB	35527470	51.640
2	33.33	IB	33271168	48.360



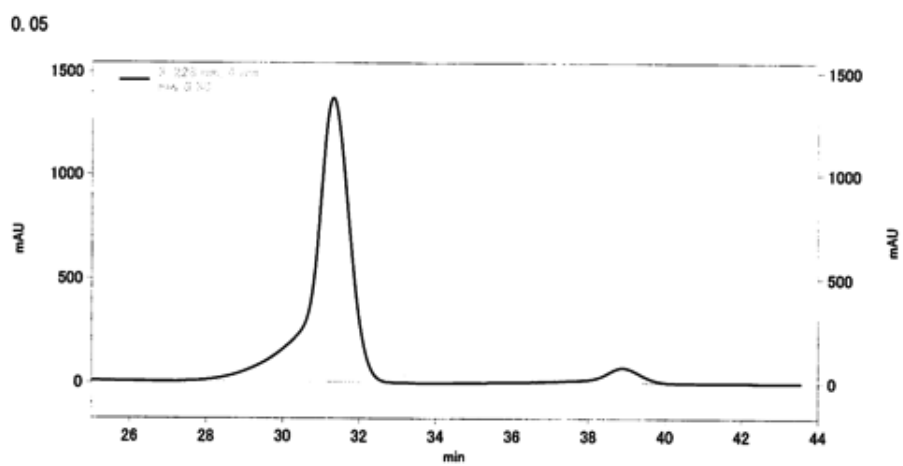
¹H NMR spectrum of **6t**.



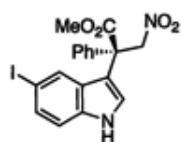
¹³C NMR spectrum of **6t**.



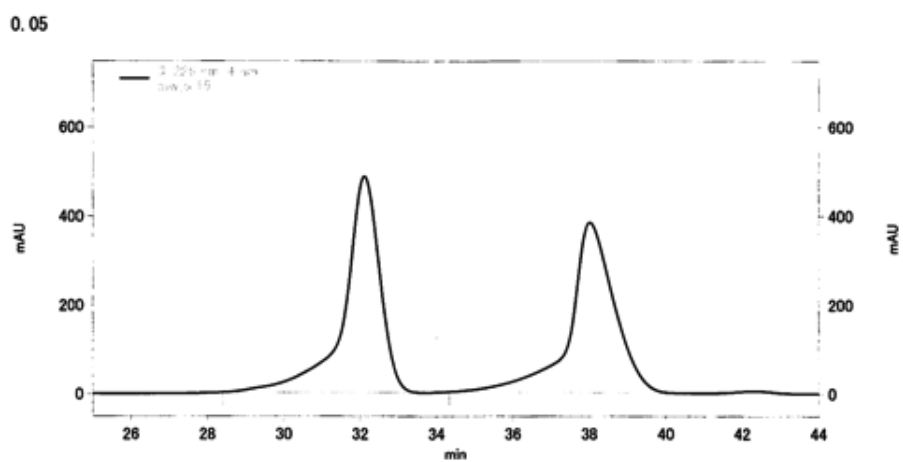
HPLC chart of **6t**.



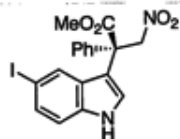
Peak #	Retention time	Type	Area	Area %
1	31.31	BB	359547761	95.278
2	38.89	BB	17820061	4.722



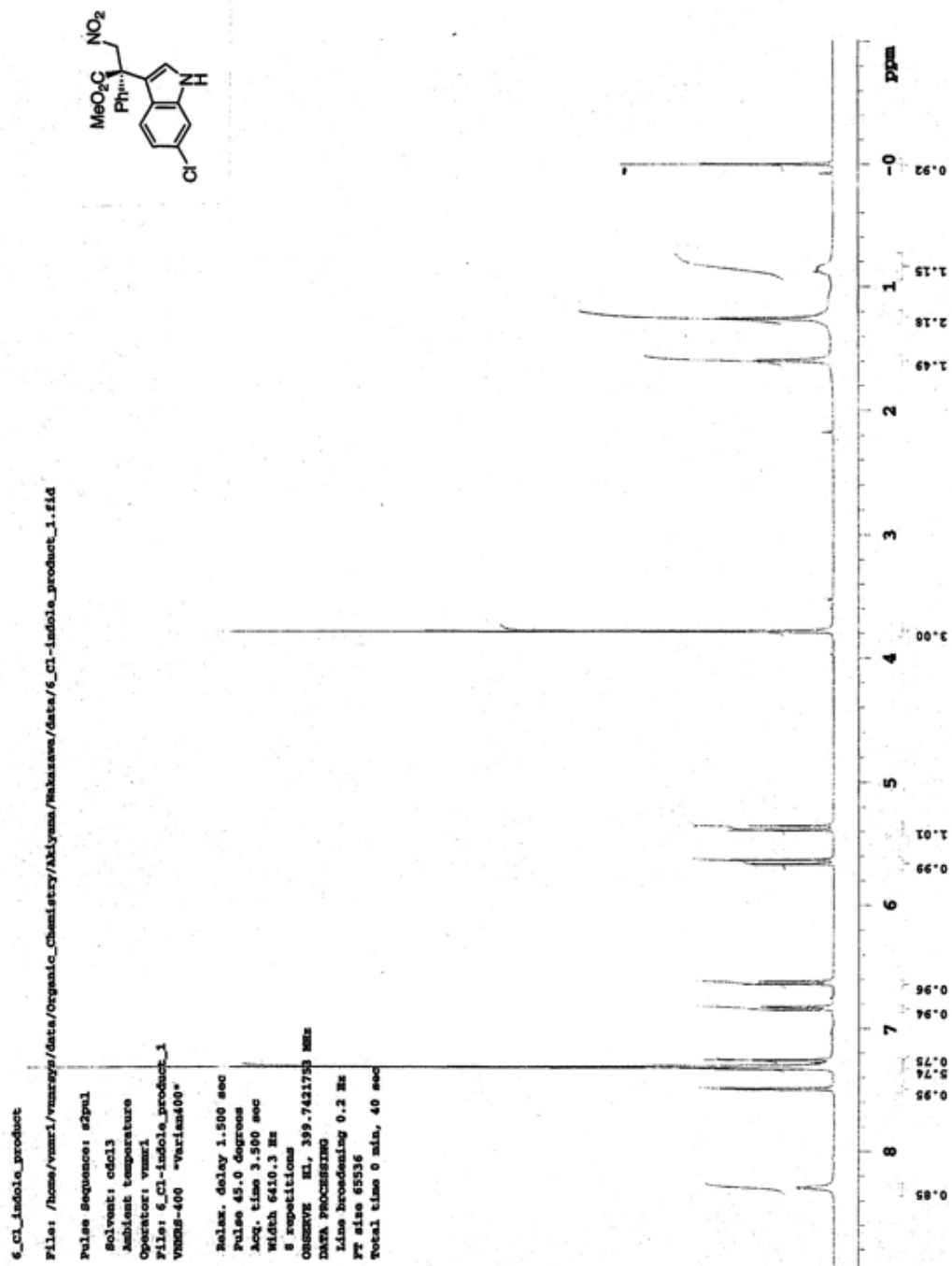
HPLC chart of **6t** (racemic).



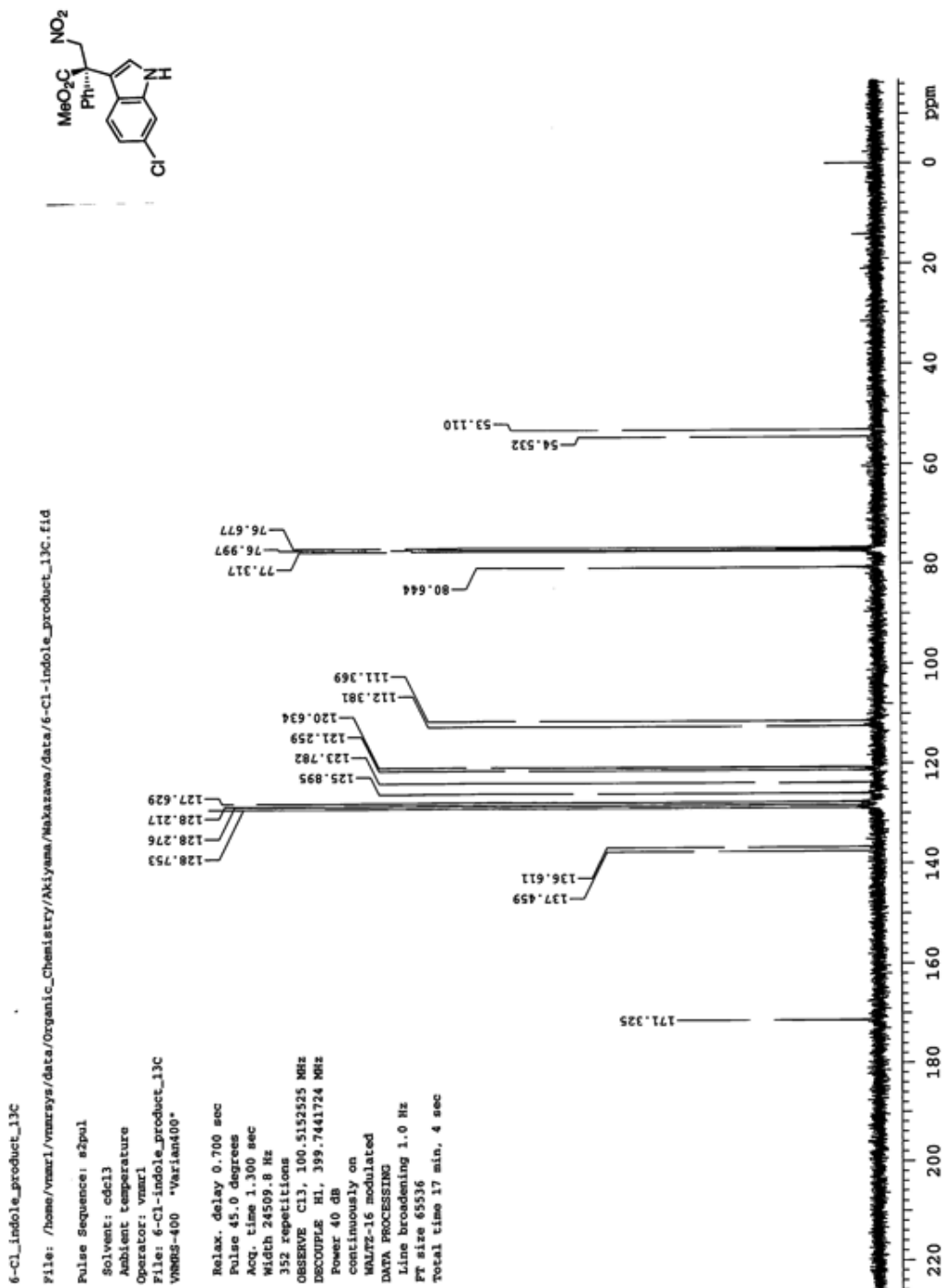
Peak #	Retention time	Type	Area	Area %
1	32.11	BB	126299300	50.471
2	38.01	BB	123941629	49.529



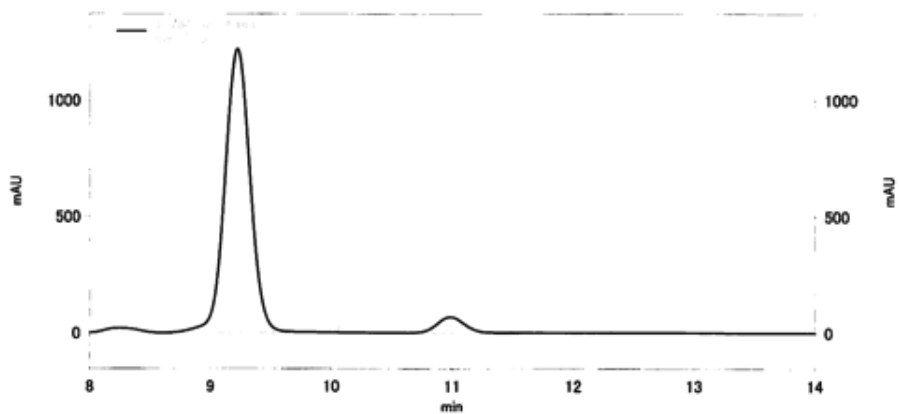
^1H NMR spectrum of **6u**.



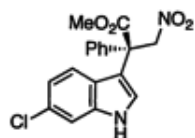
¹³C NMR spectrum of **6u**.



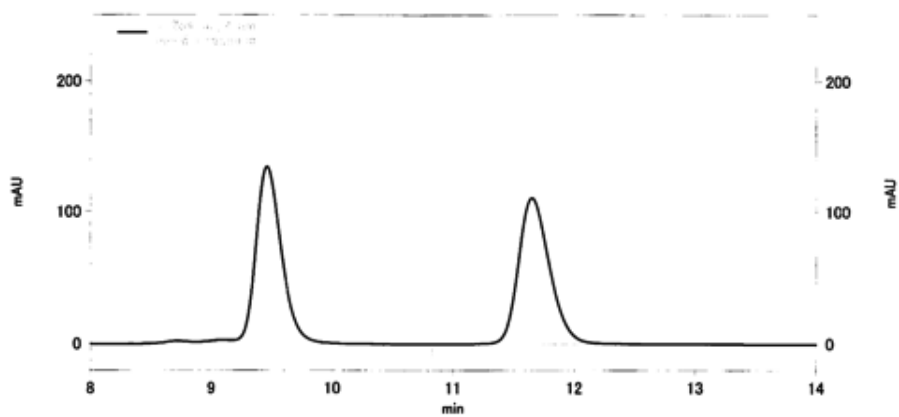
HPLC chart of **6u**.



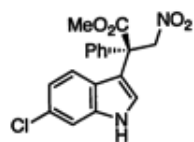
Peak #	Retention time	Type	Area	Area %
1	9.23	BB	70763602	94.270
2	10.99	BB	4301559	5.730



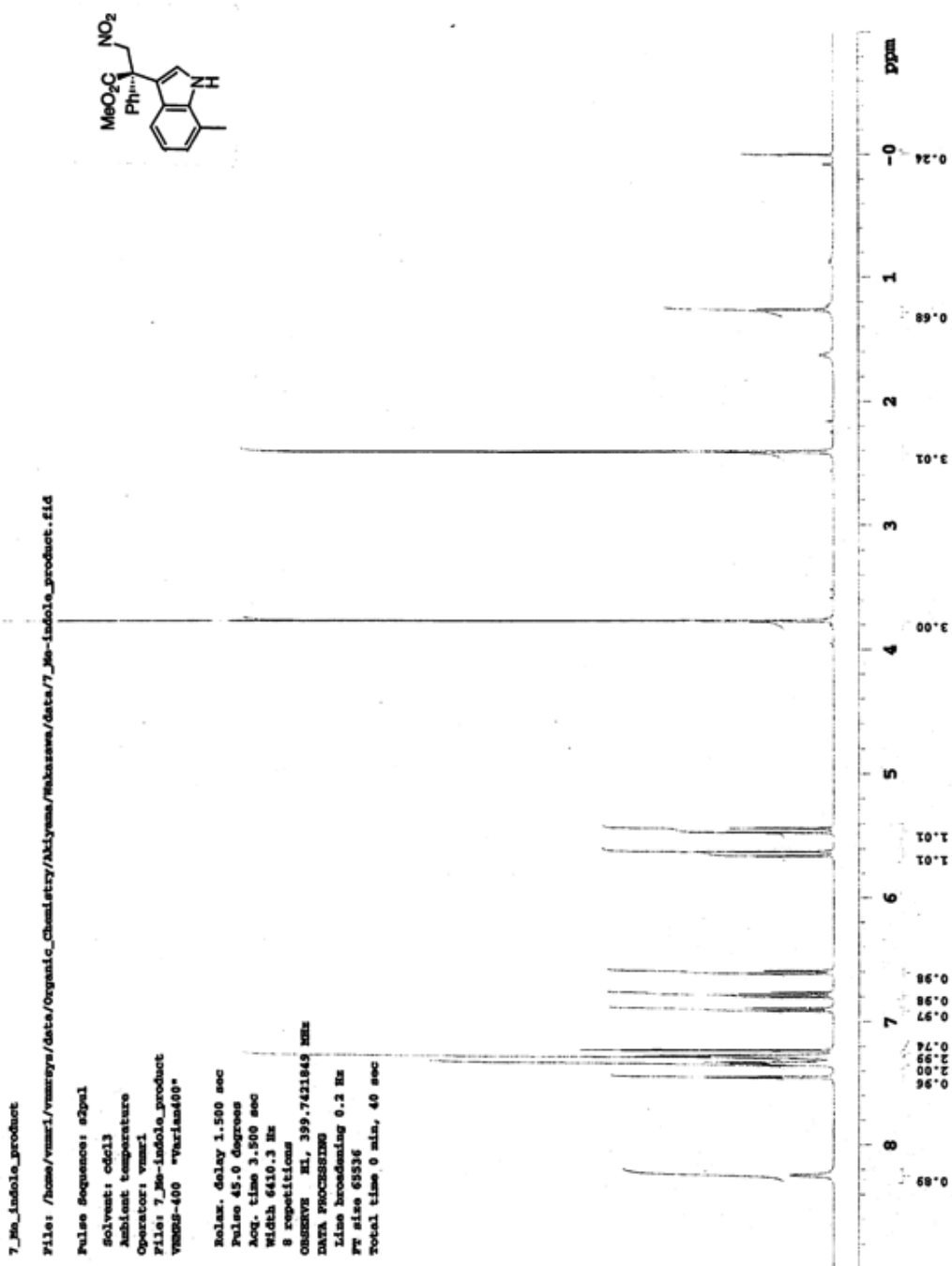
HPLC chart of **6u** (racemic).



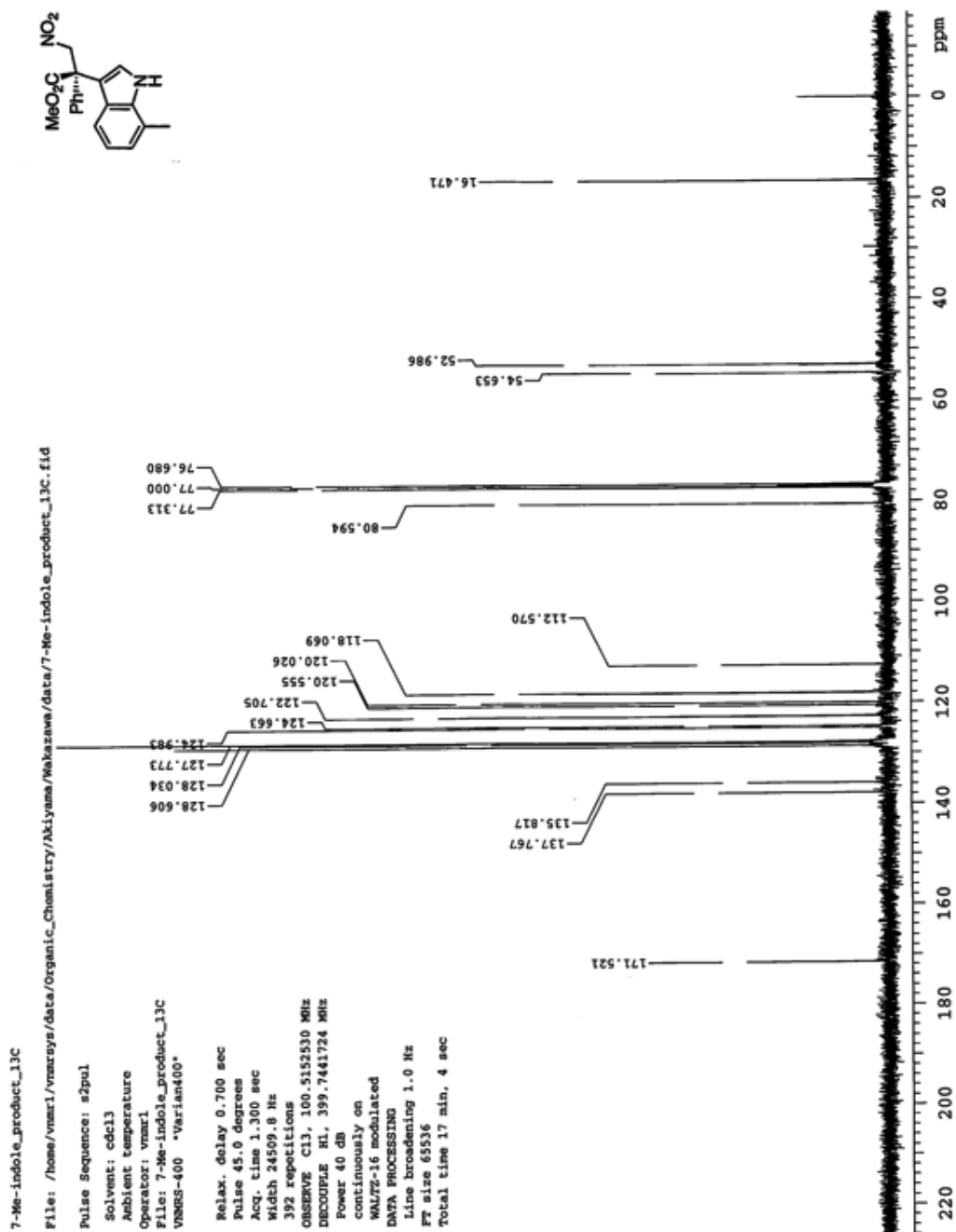
Peak #	Retention time	Type	Area	Area %
1	9.46	BB	7852327	49.777
2	11.65	BB	7922785	50.223



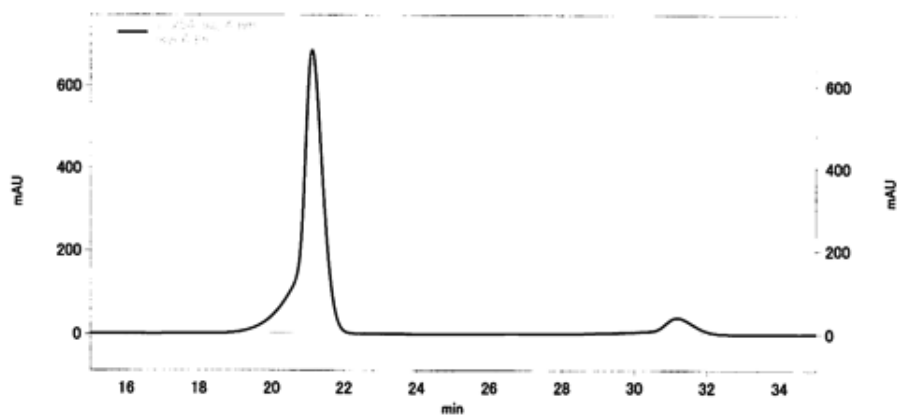
^1H NMR spectrum of **6v**.



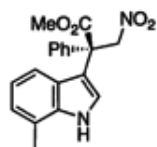
¹³C NMR spectrum of **6v**.



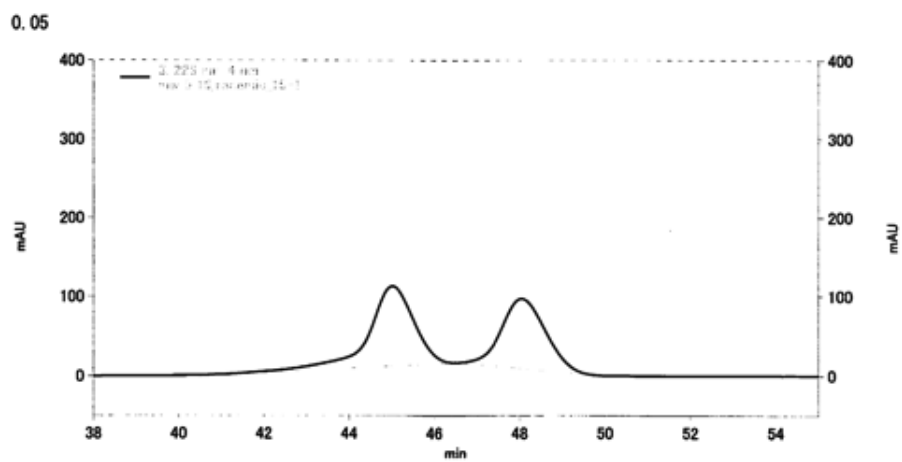
HPLC chart of **6v**.



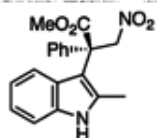
Peak #	Retention time	Type	Area	Area %
1	21.11	BB	112567507	93.872
2	31.18	BB	7348668	6.128



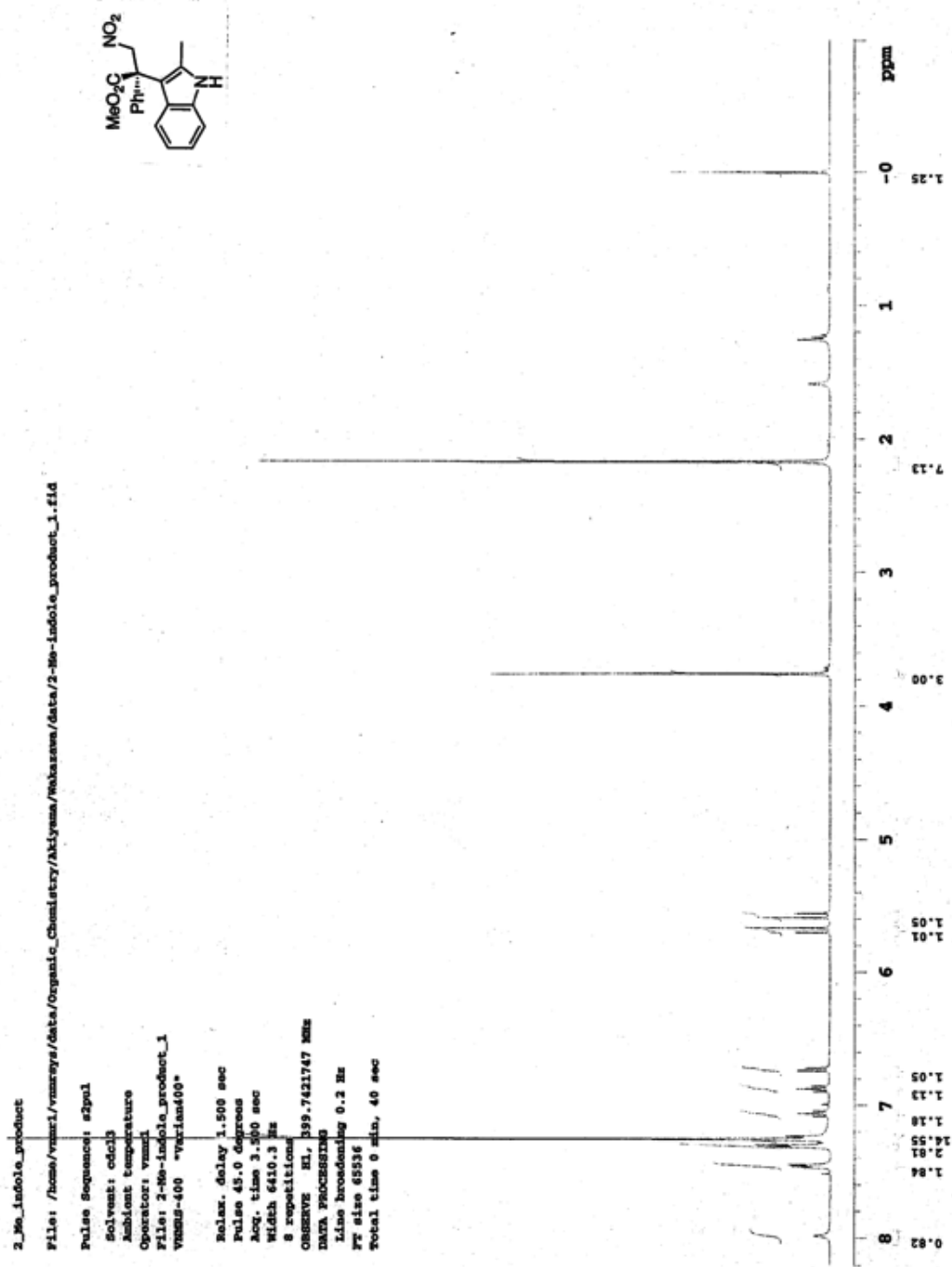
HPLC chart of **6v** (racemic).



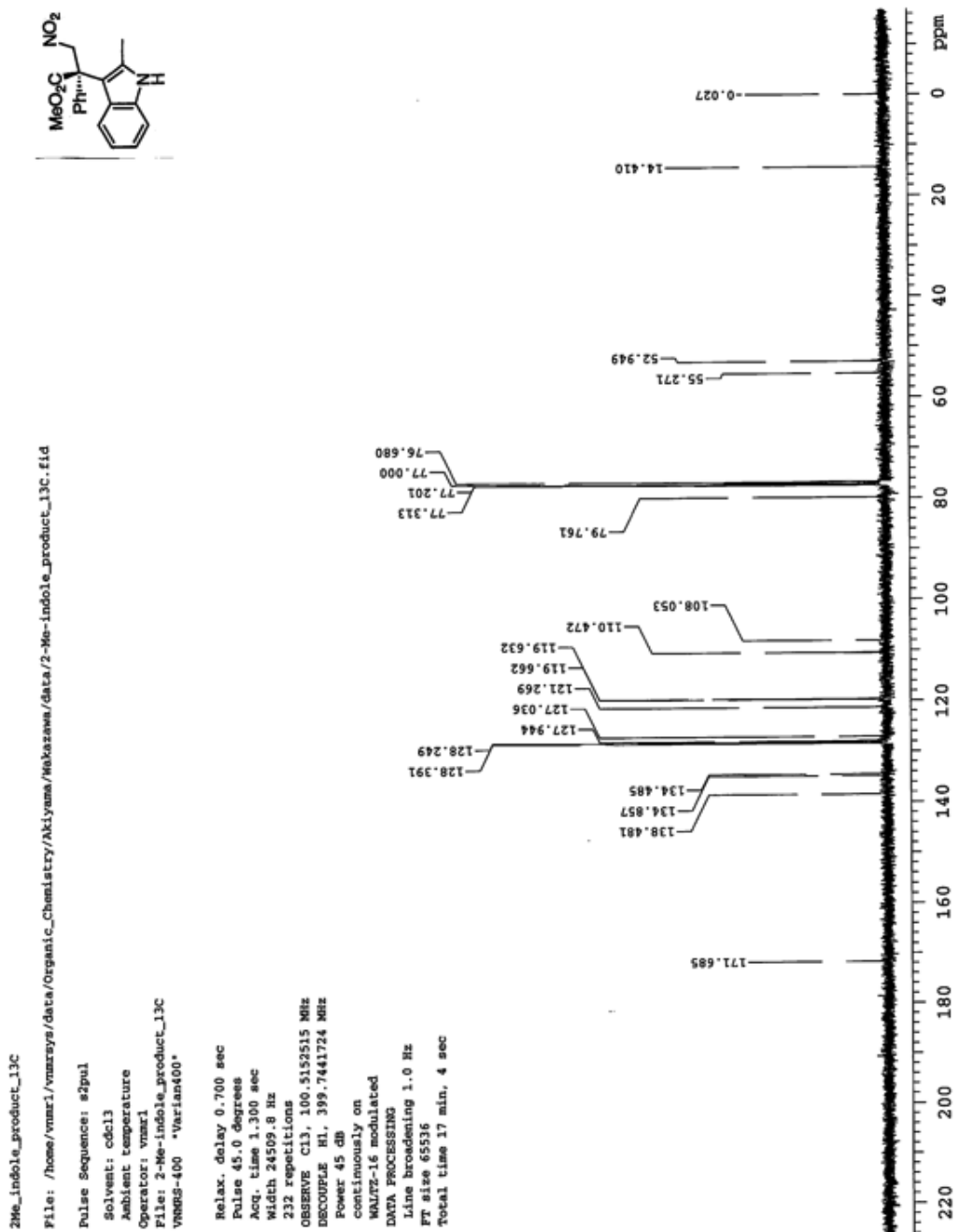
Peak #	Retention time	Type	Area	Area %
1	45.01	BB	29537646	53.976
2	48.05	BB	25186044	46.024



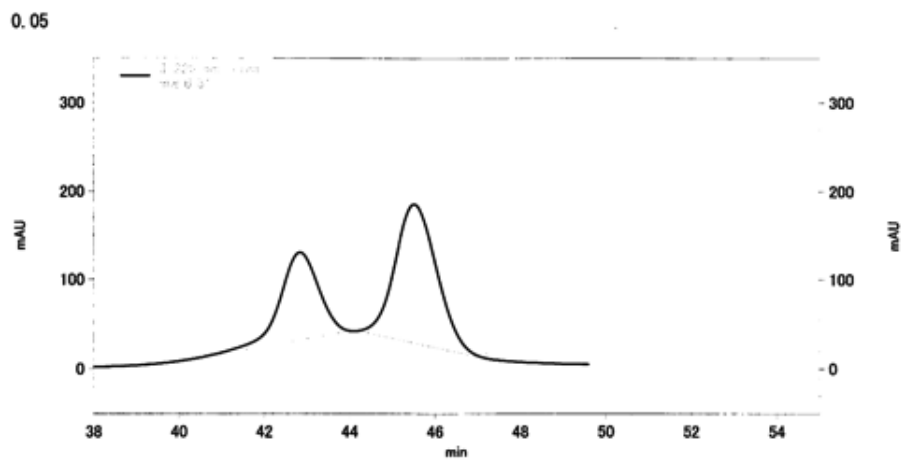
¹H NMR spectrum of **6w**.



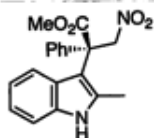
¹³C NMR spectrum of **6w**.



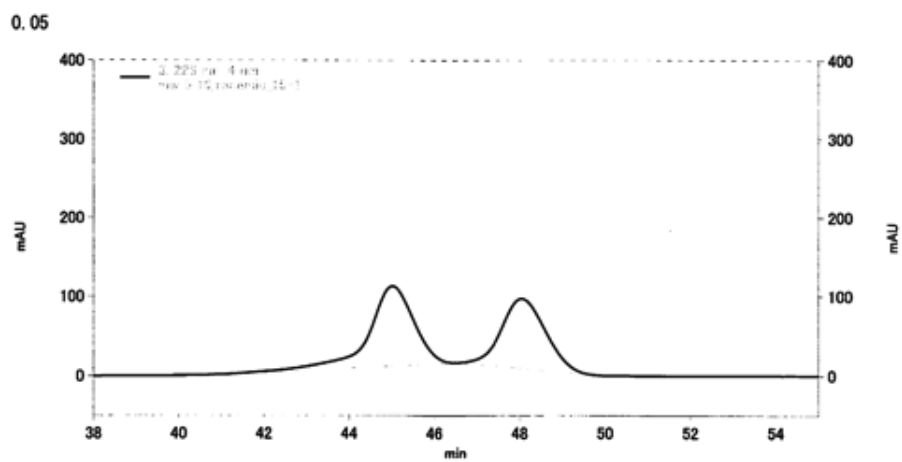
HPLC chart of 6w.



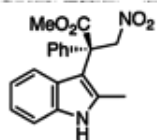
Peak #	Retention time	Type	Area	Area %
1	42.83	BI	24768624	36.861
2	45.51	BB	42425537	63.139



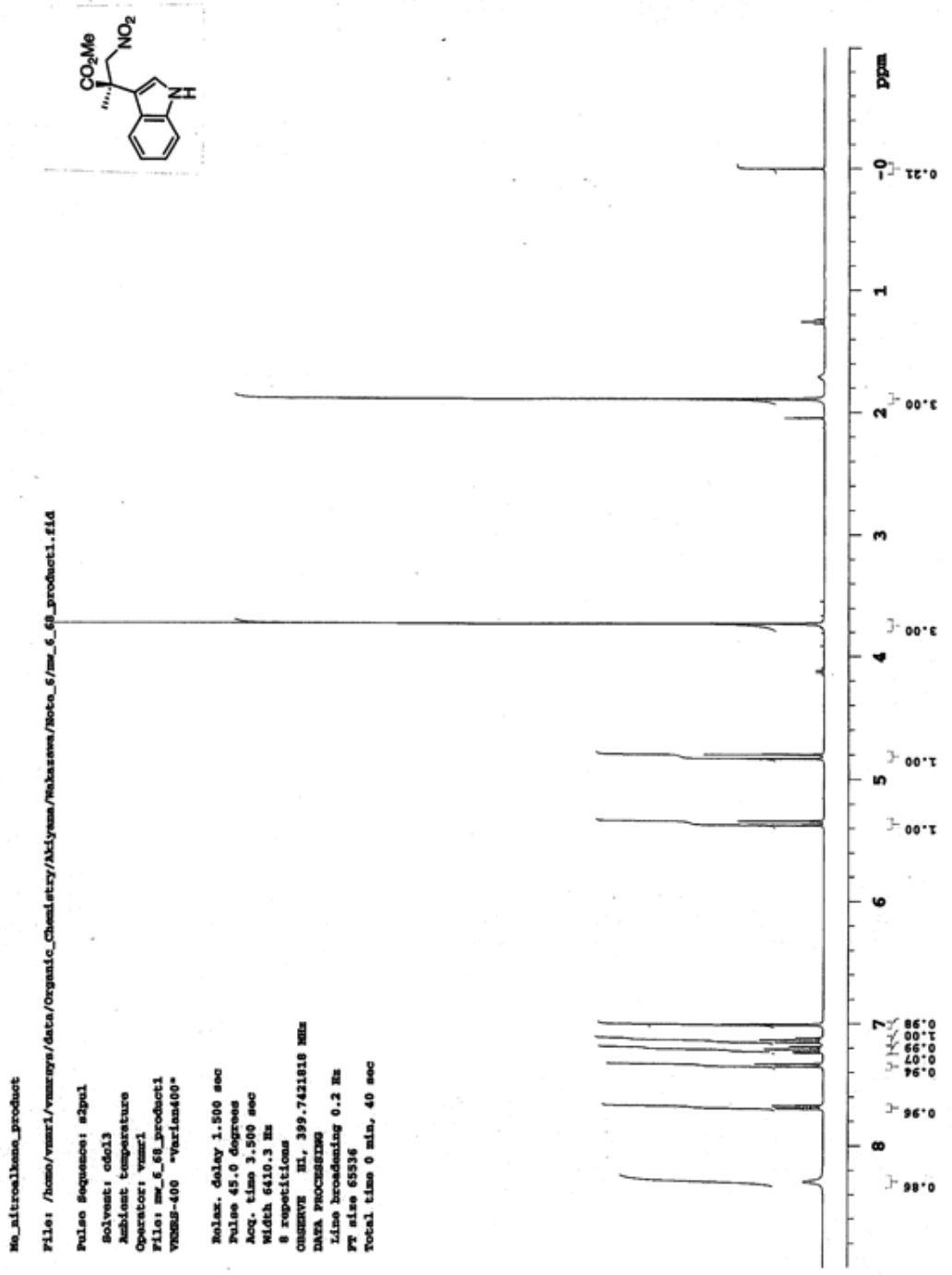
HPLC chart of **6w** (racemic).



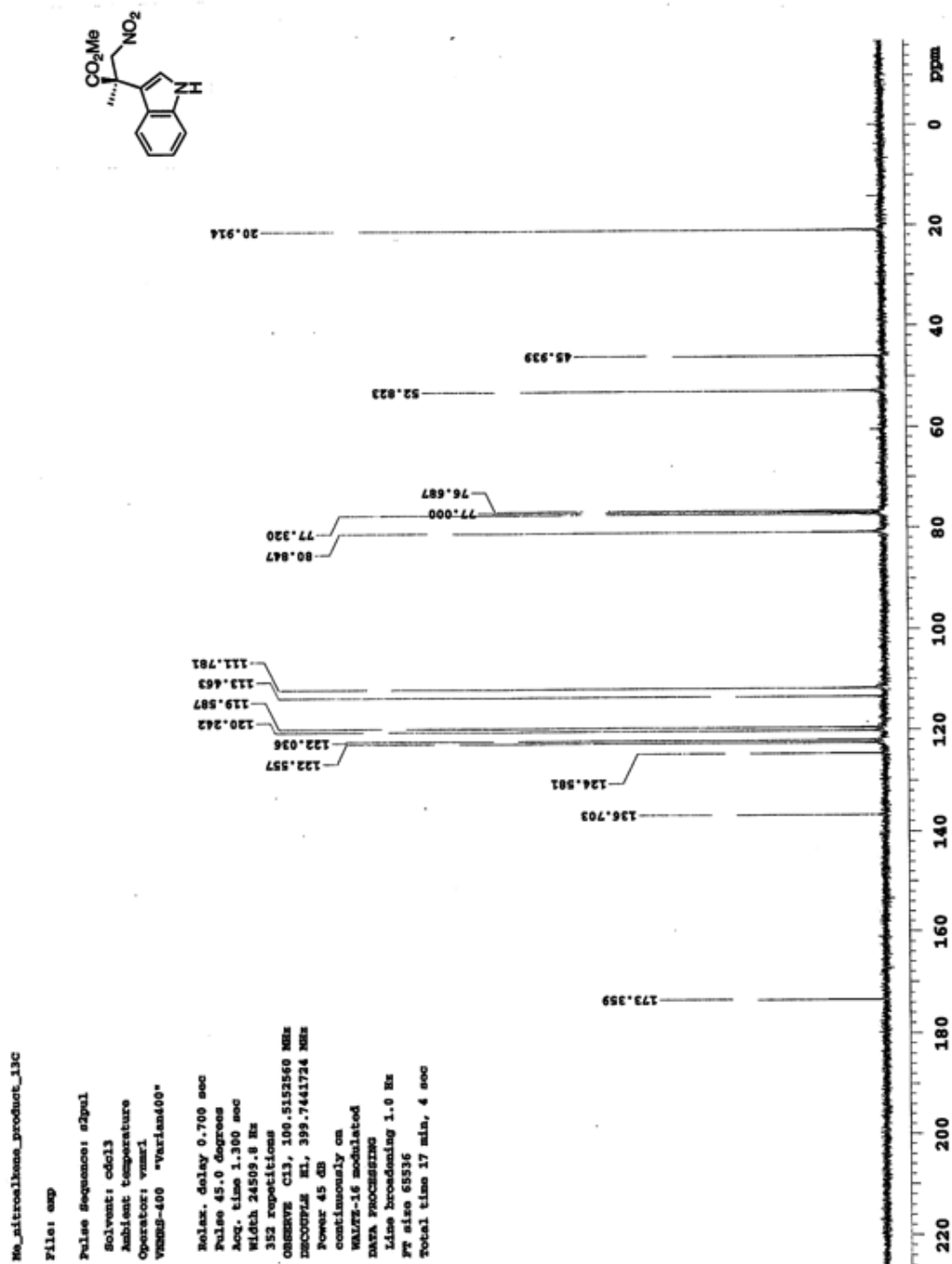
Peak #	Retention time	Type	Area	Area %
1	45.01	BB	29537646	53.976
2	48.05	BB	25186044	46.024



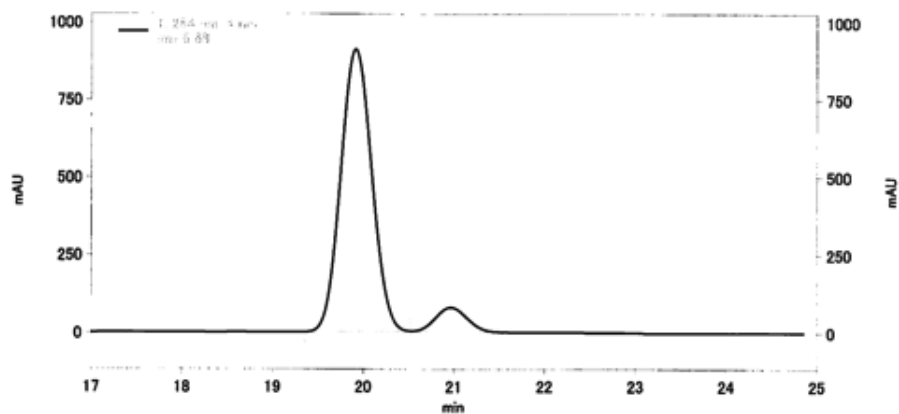
¹H NMR spectrum of **6x**.



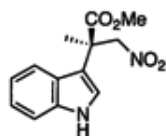
¹³C NMR spectrum of 6x.



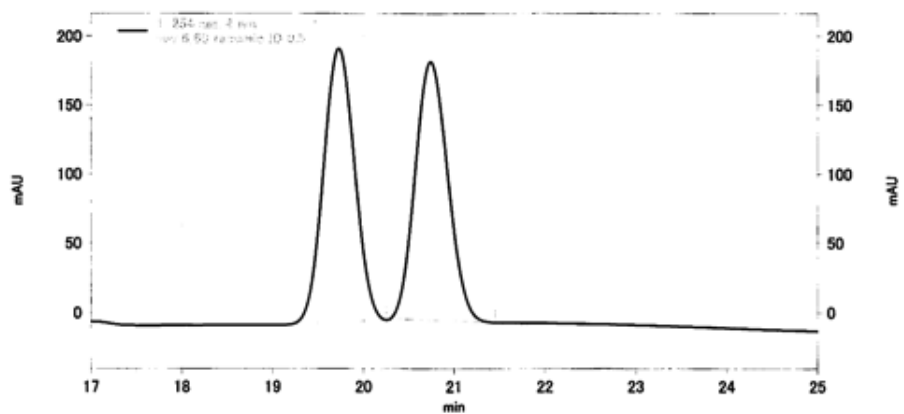
HPLC chart of **6x**.



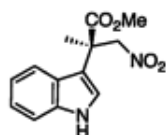
Peak #	Retention time	Type	Area	Area %
1	19.91	BI	86301065	92.098
2	20.97	BB	7404481	7.902



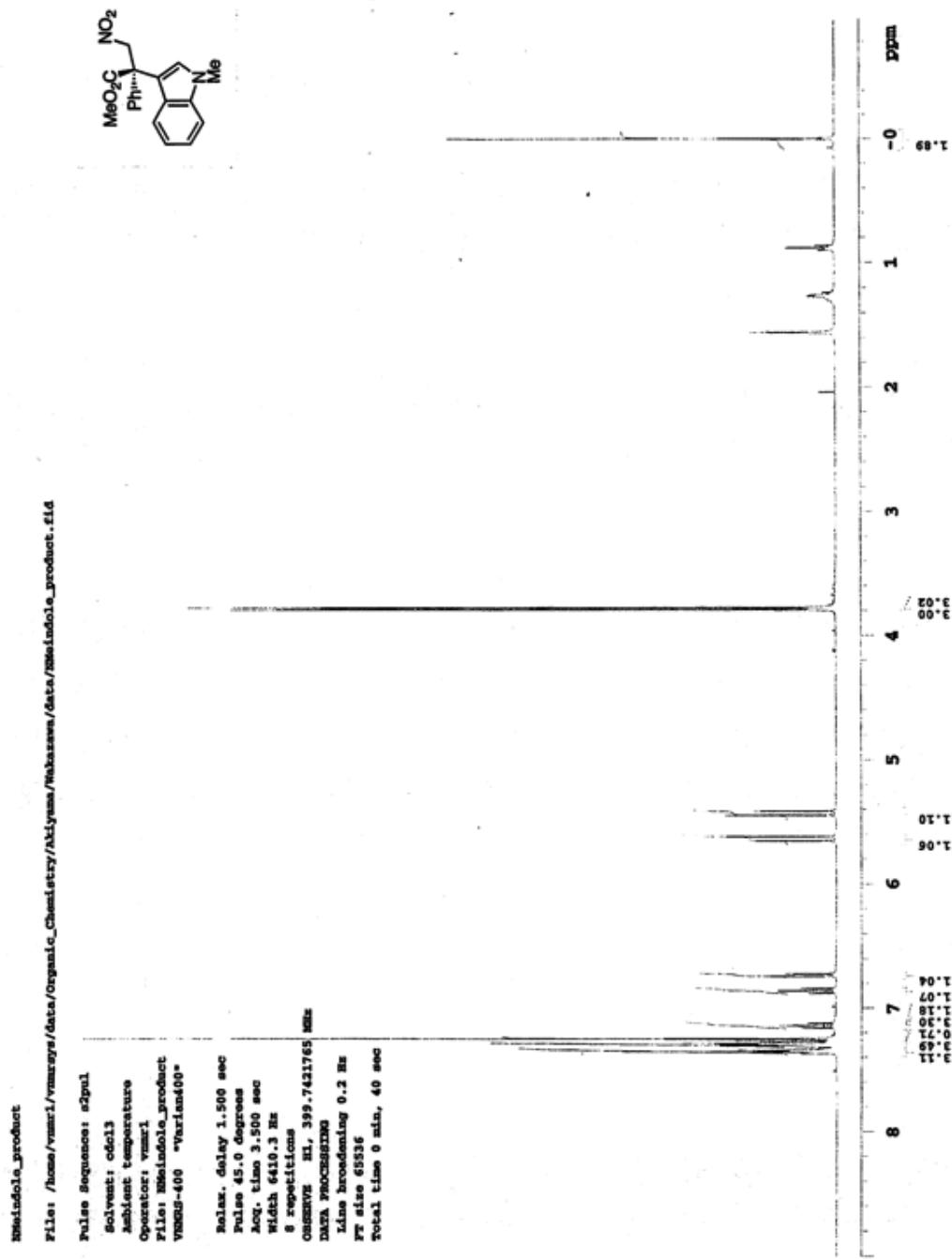
HPLC chart of **6x** (racemic).



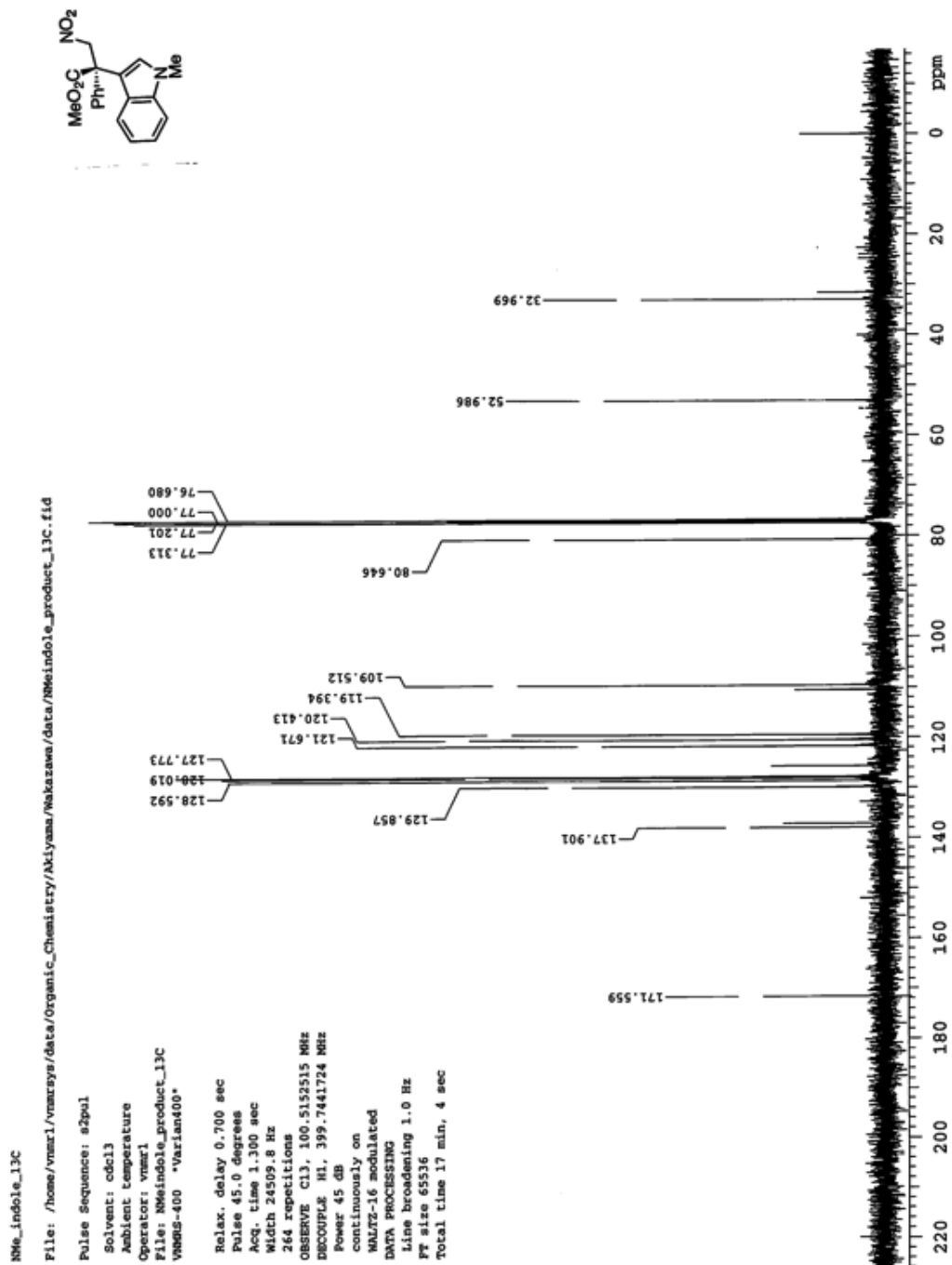
Peak #	Retention time	Type	Area	Area %
1	19.73	BB	18692462	50.211
2	20.74	IB	18535453	49.789



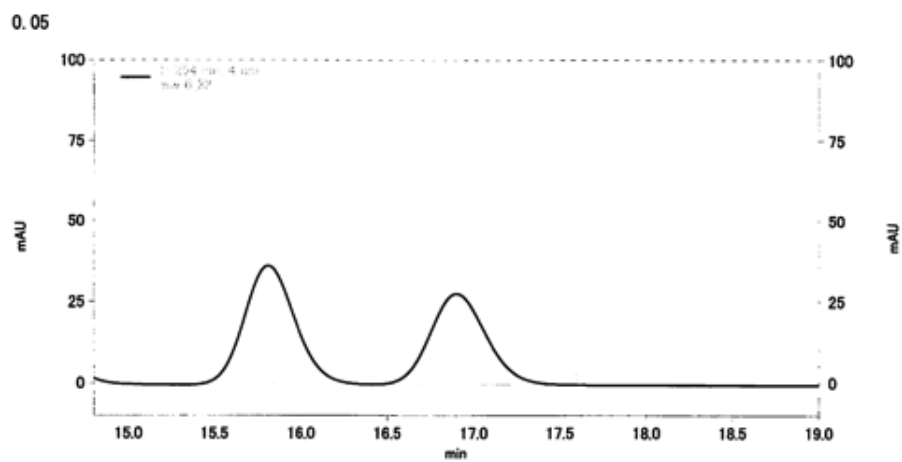
¹H NMR spectrum of 13.



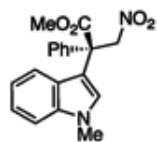
¹³C NMR spectrum of **13**.



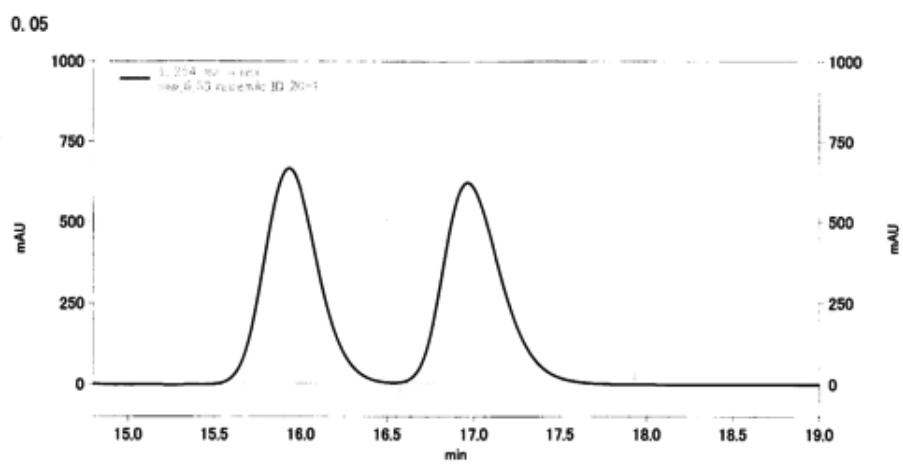
HPLC chart of 13.



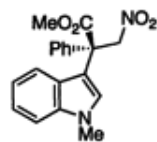
Peak #	Retention time	Type	Area	Area %
1	15.81	BB	2951666	53.958
2	16.90	BB	2518641	46.042



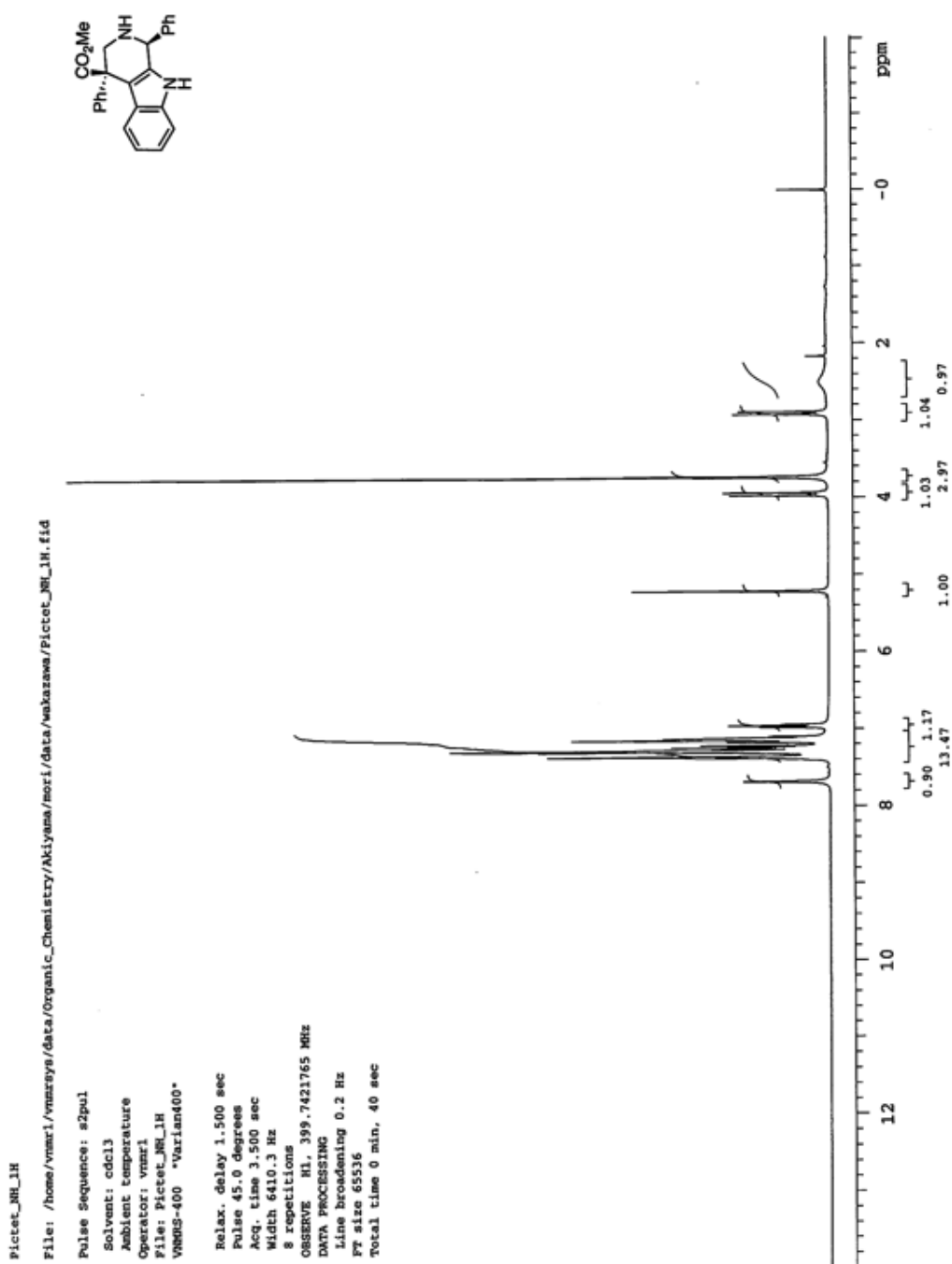
HPLC chart of **13** (racemic).



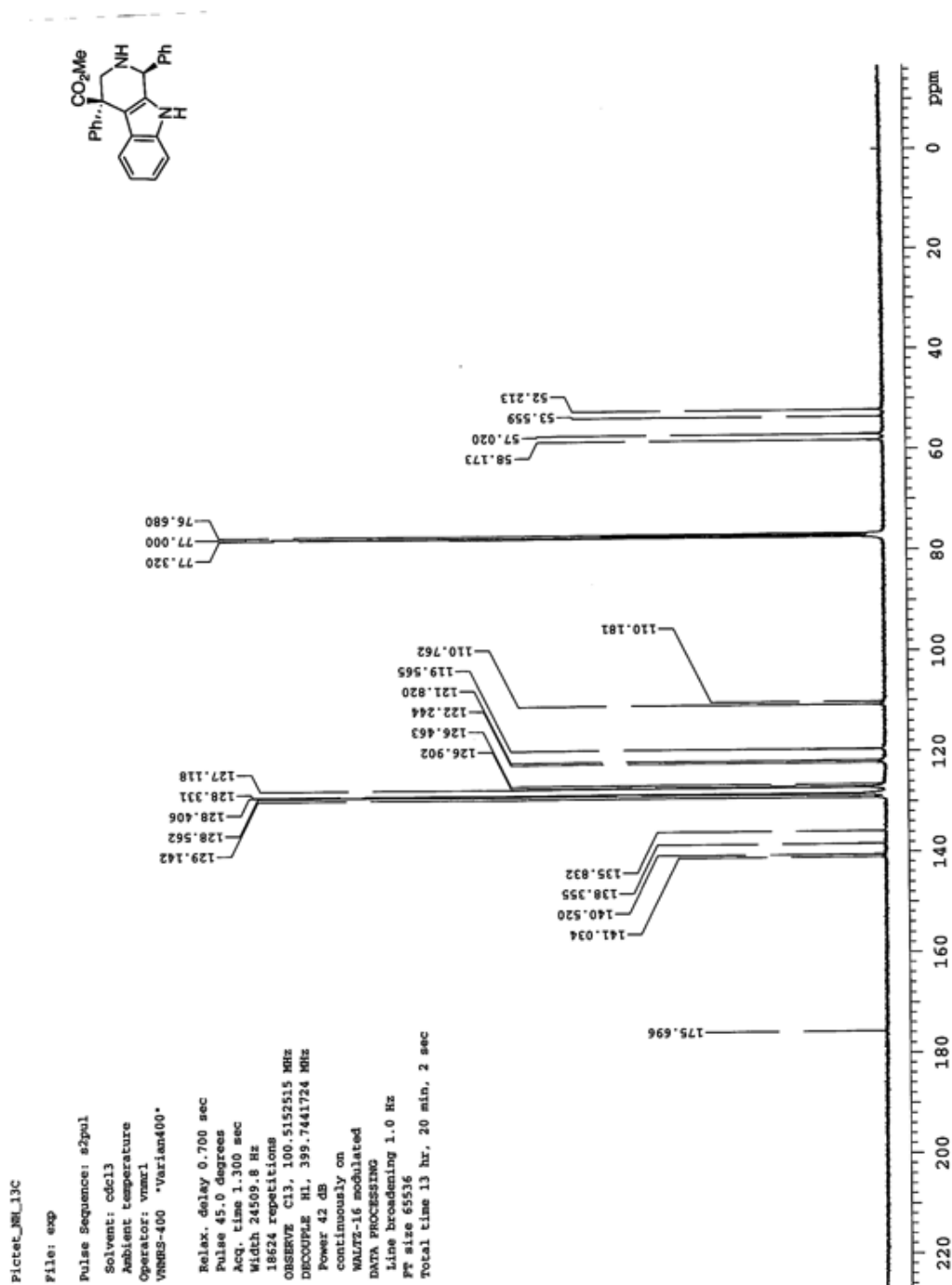
Peak #	Retention time	Type	Area	Area %
1	15.93	BI	57490187	50.054
2	16.97	IB	57366745	49.946



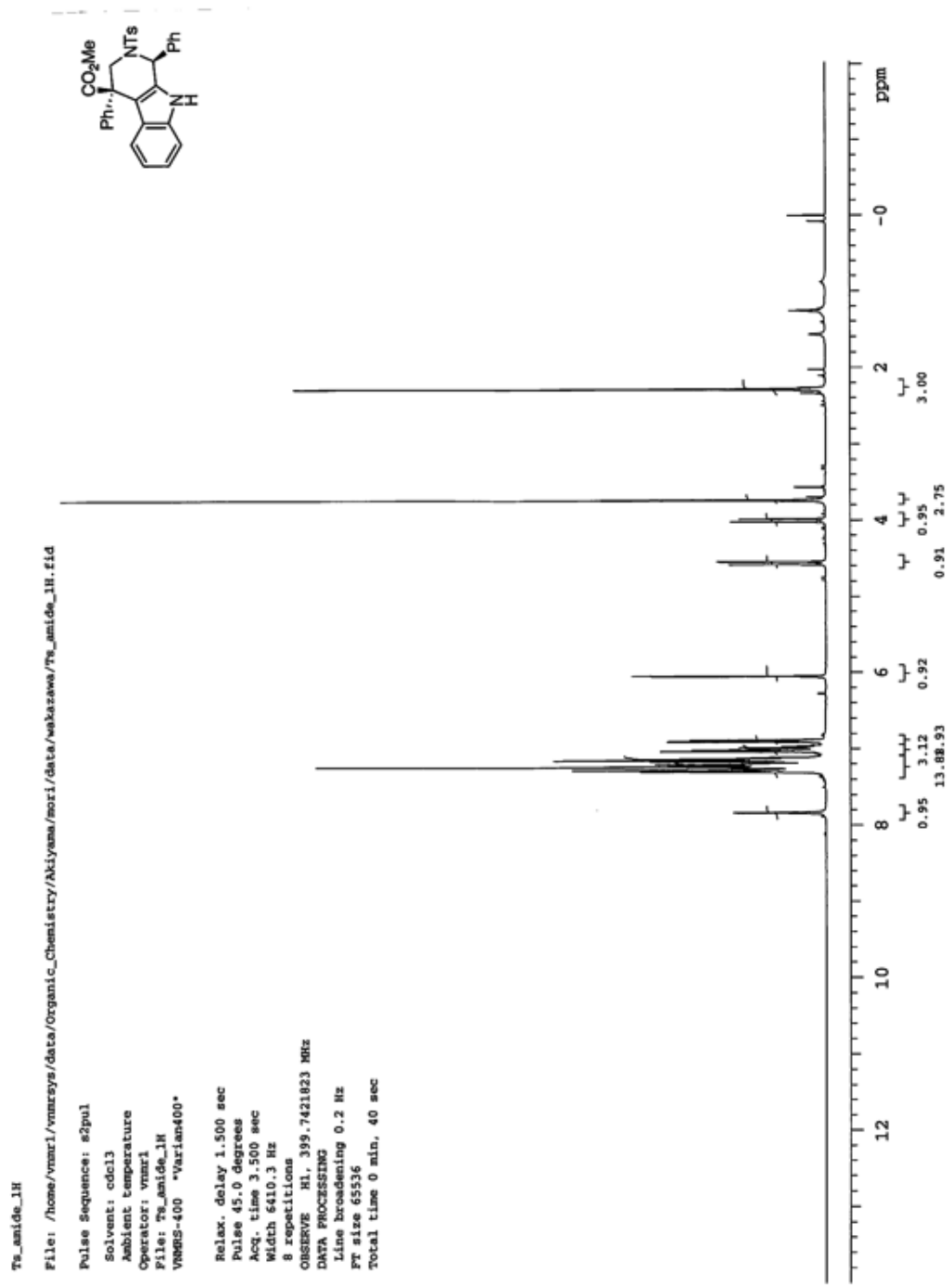
^1H NMR spectrum of **s18**.



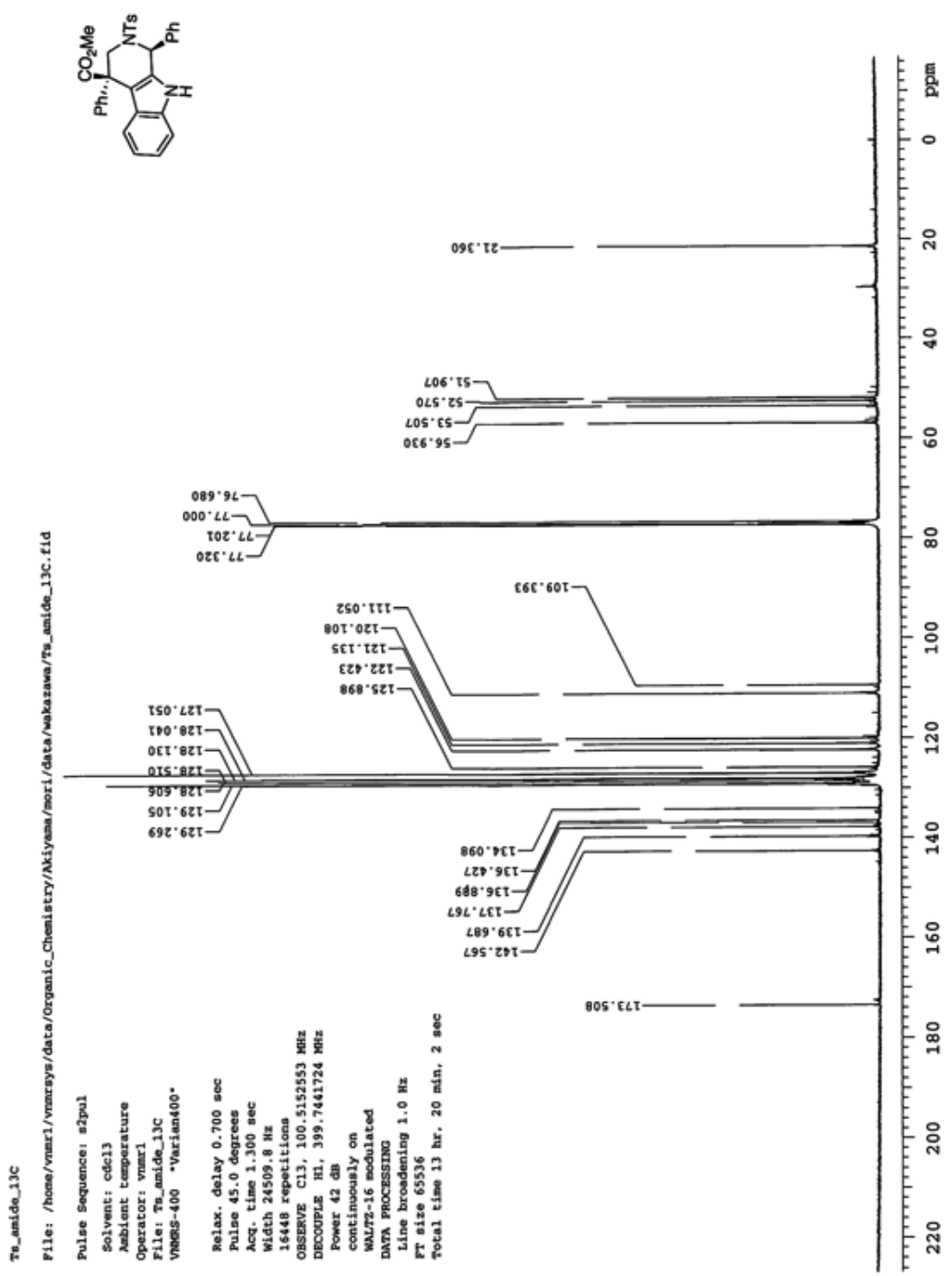
^{13}C NMR spectrum of **s18**.



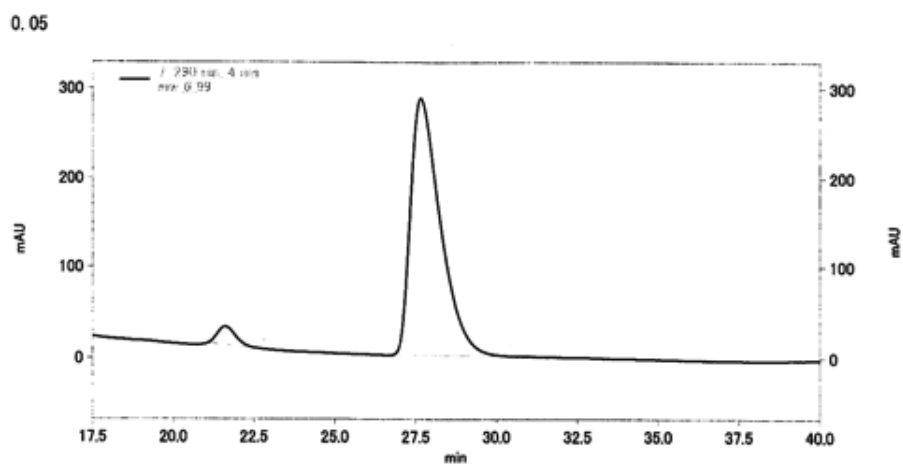
¹H NMR spectrum of **8**.



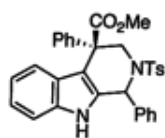
¹³C NMR spectrum of **8**.



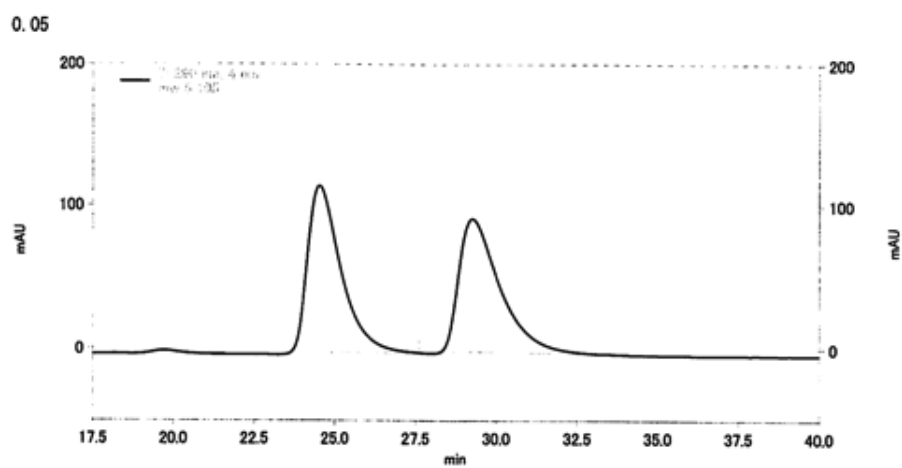
HPLC chart of **8**.



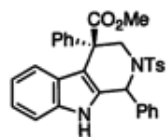
Peak #	Retention time	Type	Area	Area %
1	21.62	BB	3113220	4.067
2	27.66	BB	73433769	95.933



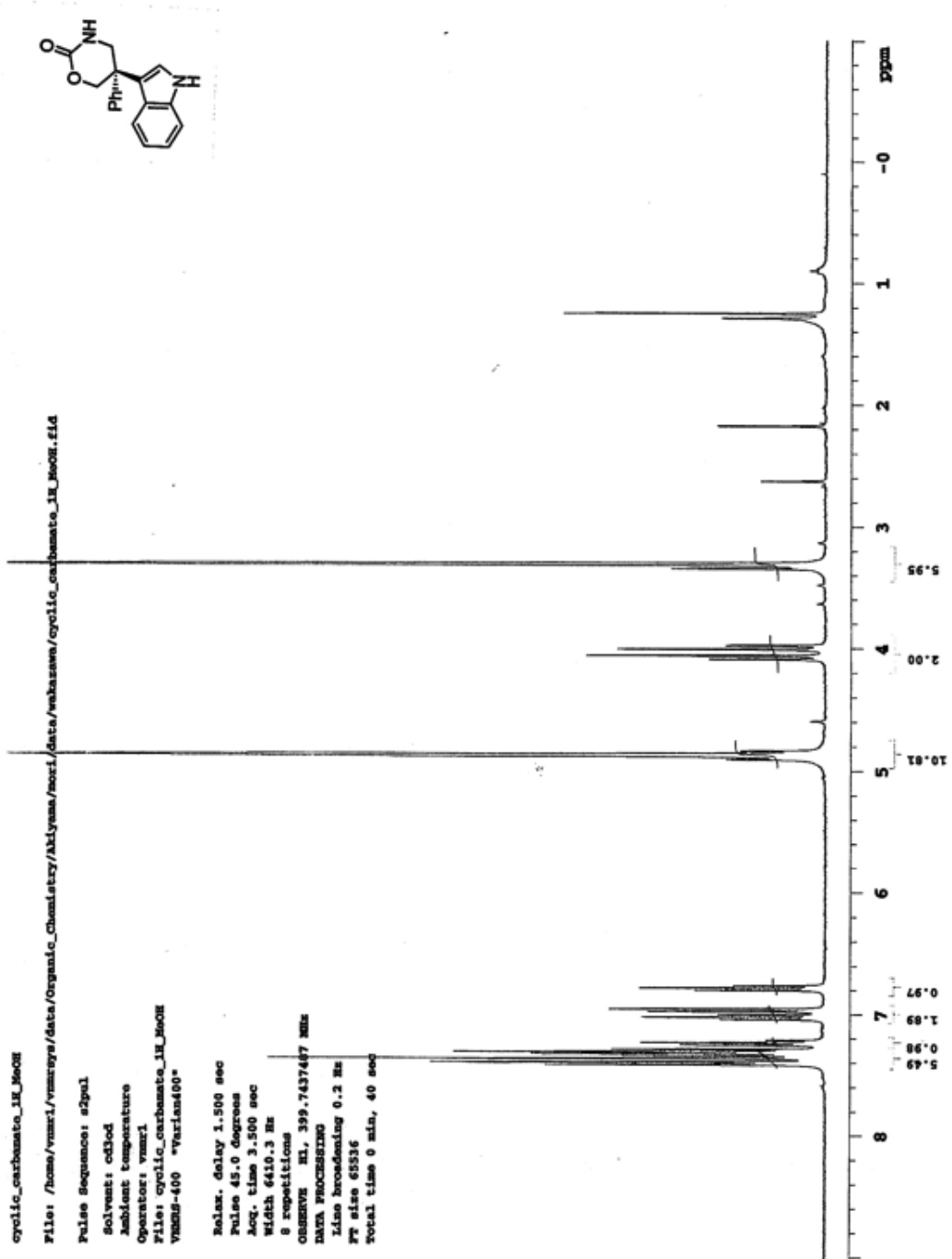
HPLC chart of **8** (racemic).



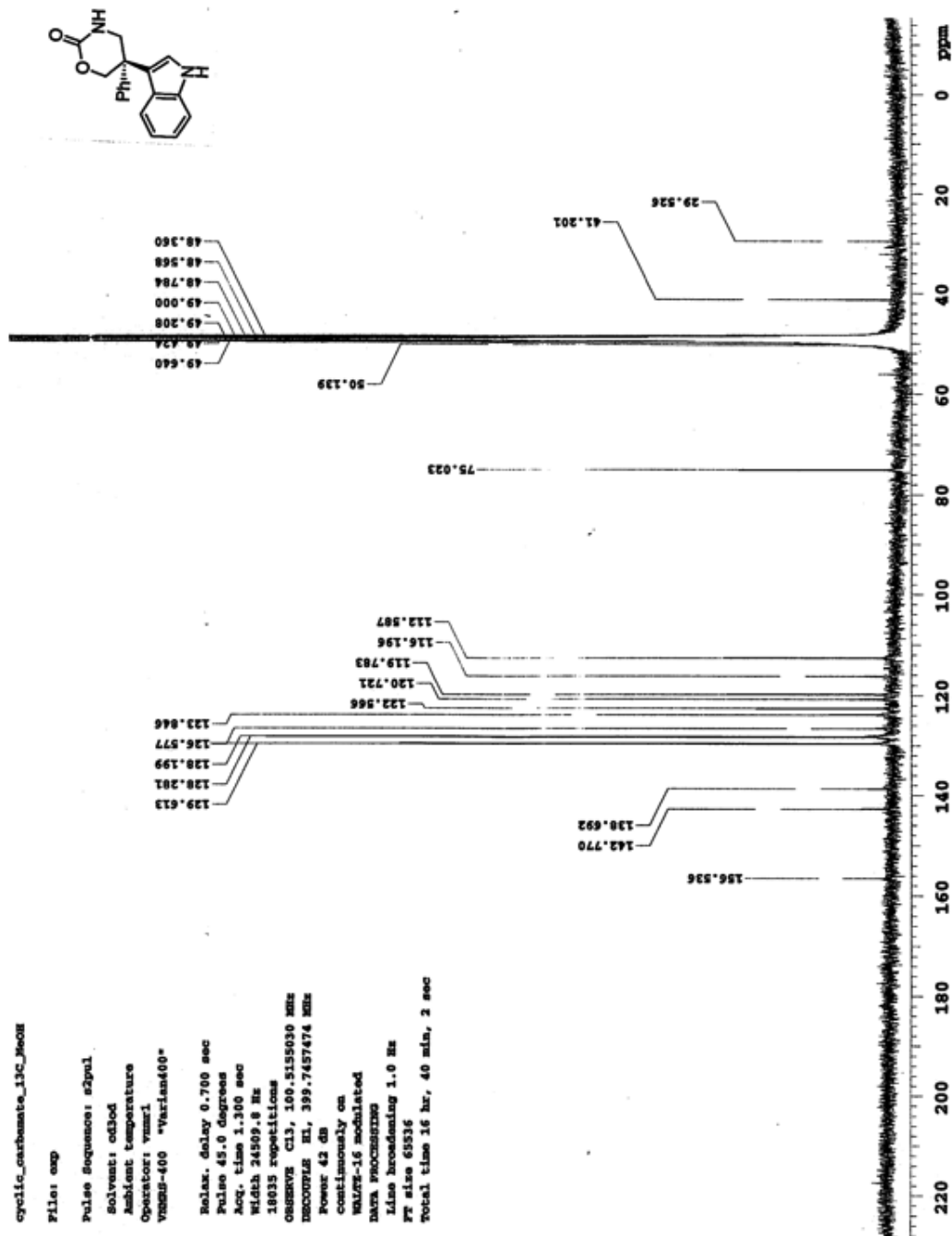
Peak #	Retention time	Type	Area	Area %
1	24.53	BI	33412090	50.520
2	29.25	BB	32724109	49.480



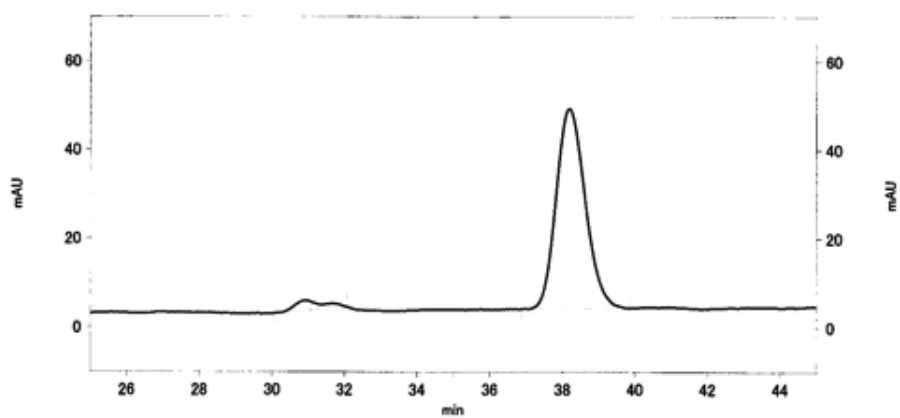
¹H NMR spectrum of **9**.



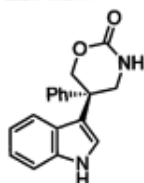
¹³C NMR spectrum of 9.



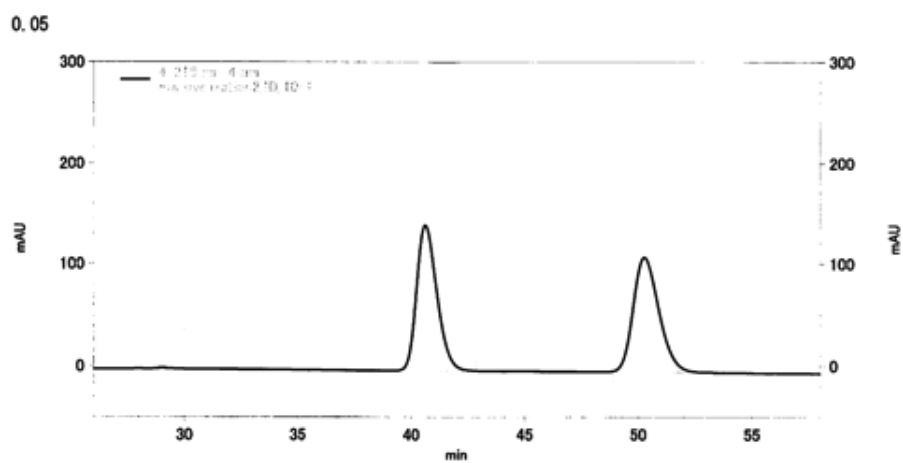
HPLC chart of **9**.



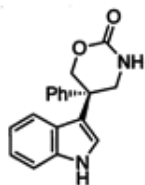
Peak #	Retention time	Type	Area	Area %
1	30.93	BI	487916	4.633
2	38.19	BB	10043105	95.367



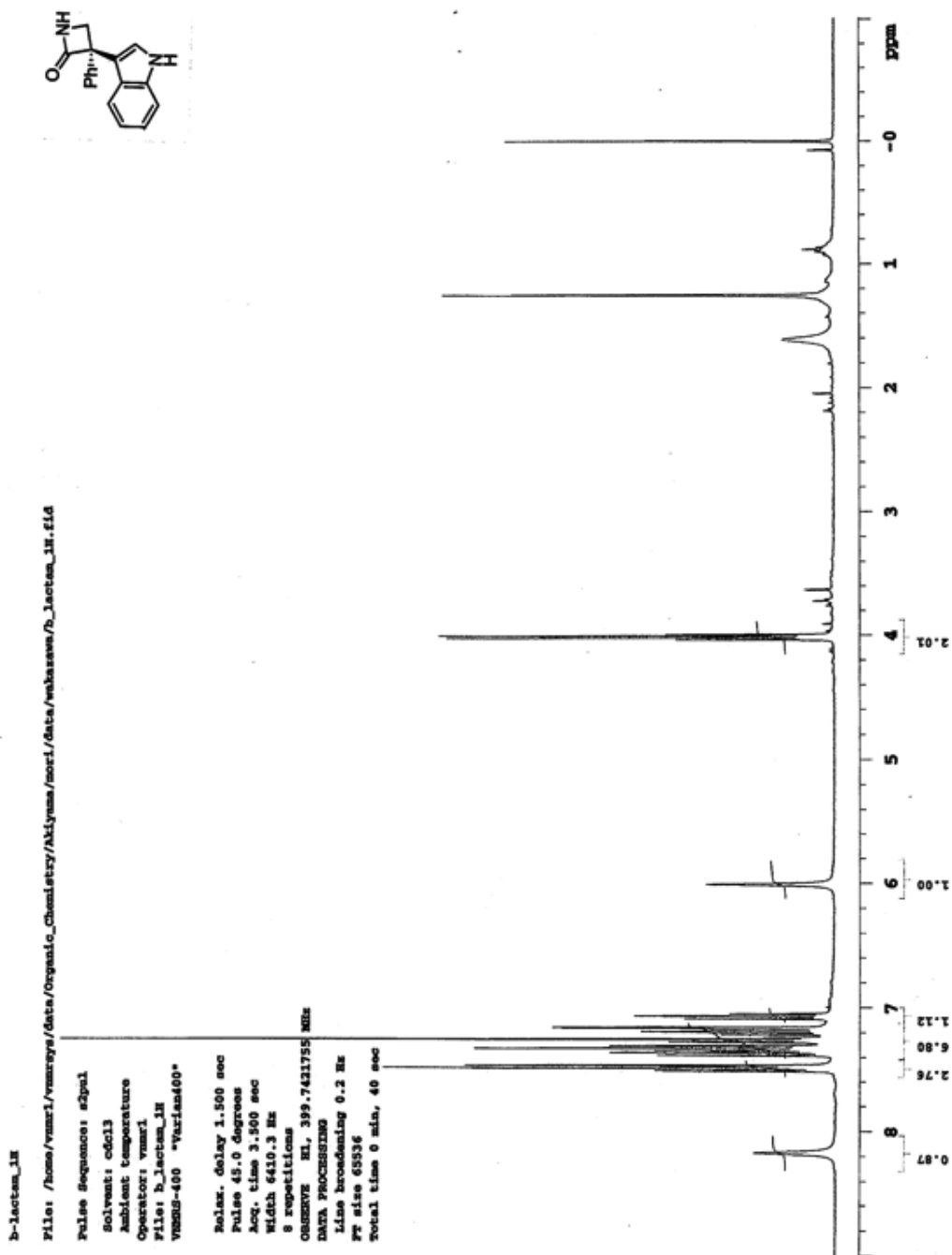
HPLC chart of **9** (racemic).



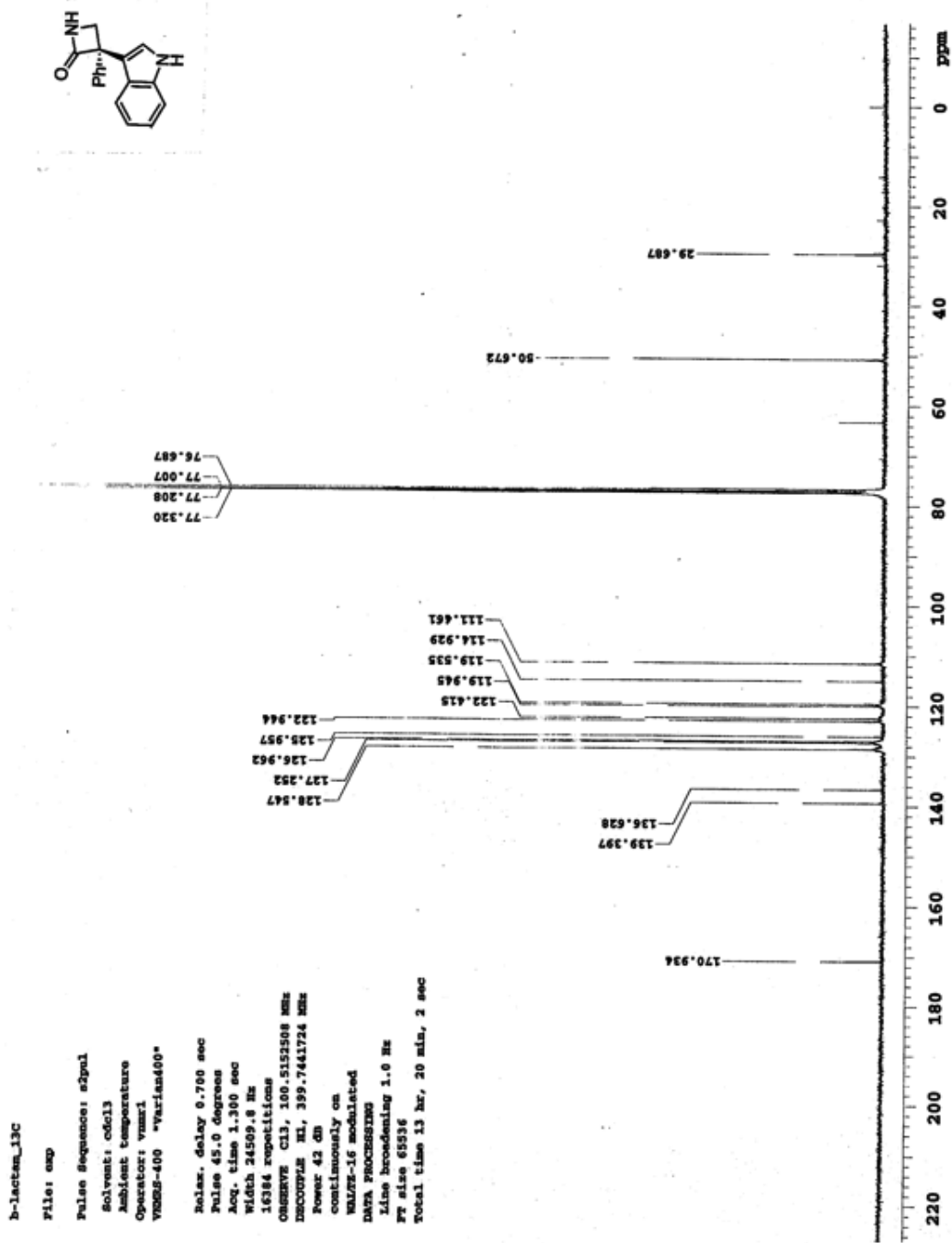
Peak #	Retention time	Type	Area	Area %
1	40.62	BB	35214712	50.200
2	50.26	BB	34934487	49.800



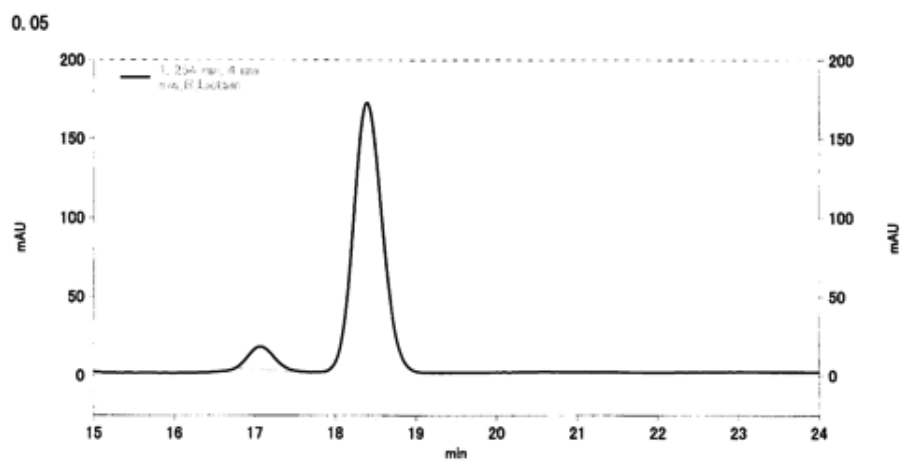
^1H NMR spectrum of **10**.



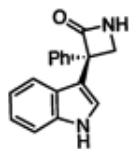
¹³C NMR spectrum of 10.



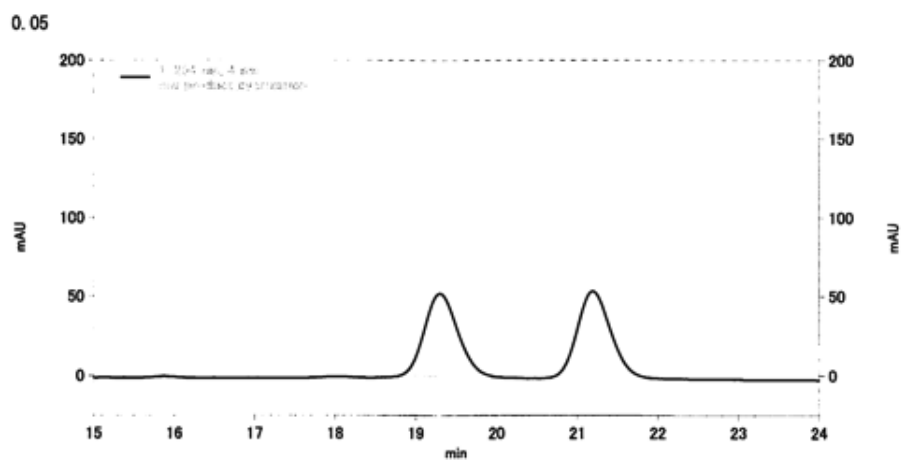
HPLC chart of **10**.



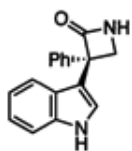
Peak #	Retention time	Type	Area	Area %
1	17.07	BB	1270074	6.950
2	18.39	BB	17005093	93.050



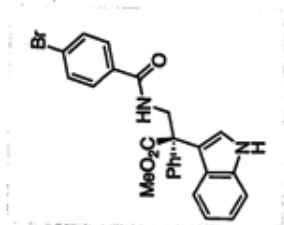
HPLC chart of **10** (racemic).



Peak #	Retention time	Type	Area	Area %
1	19.30	BB	6040546	48.408
2	21.19	BB	6437978	51.592



^1H NMR spectrum of **11**.

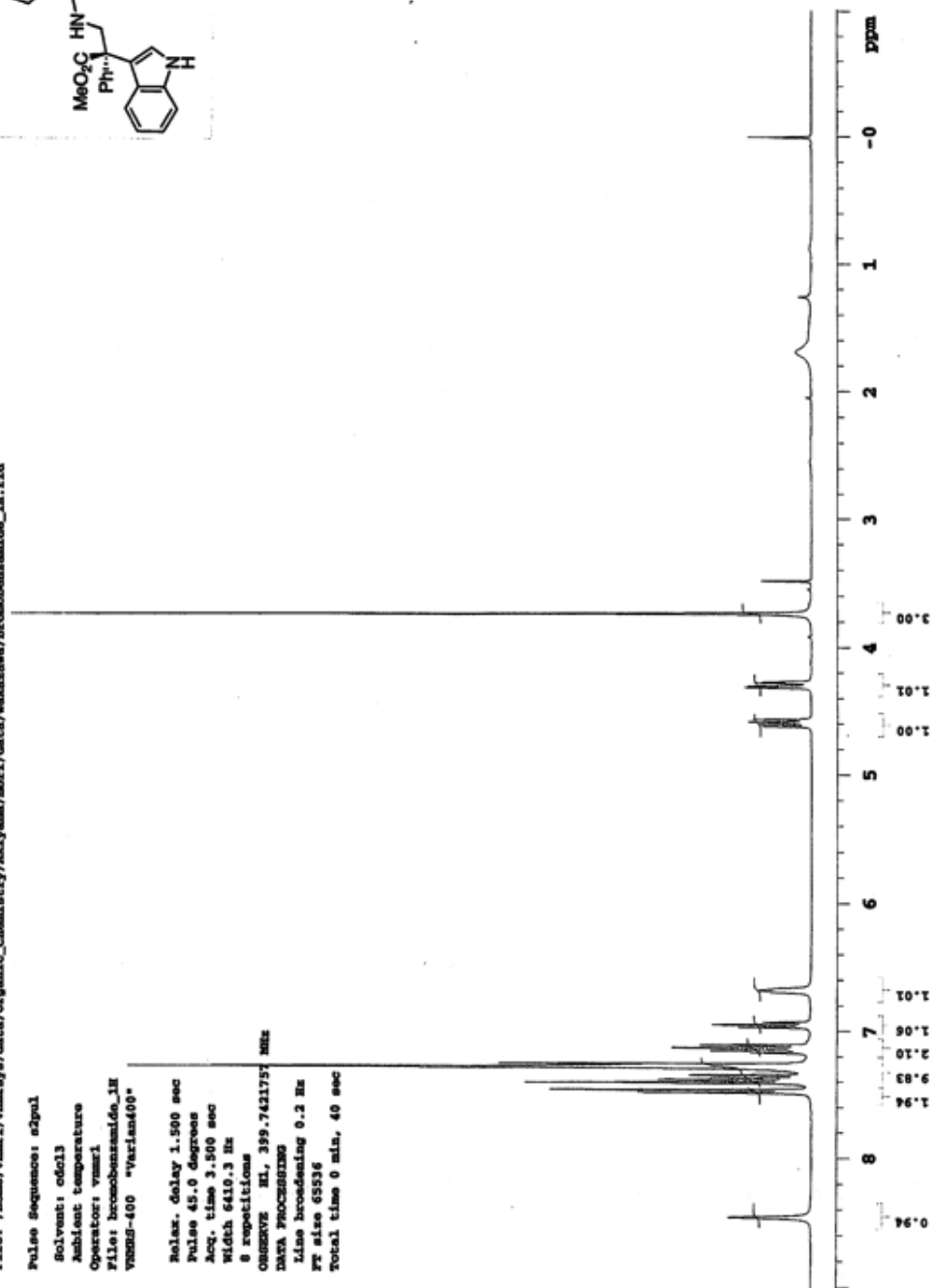


hrcmbozsmid6_1H
File: /home/vmr1/vmrays/data/organic_chemistry/Akiyama/mori/data/wakazawa/hrcmbozsmid6_1H.fid

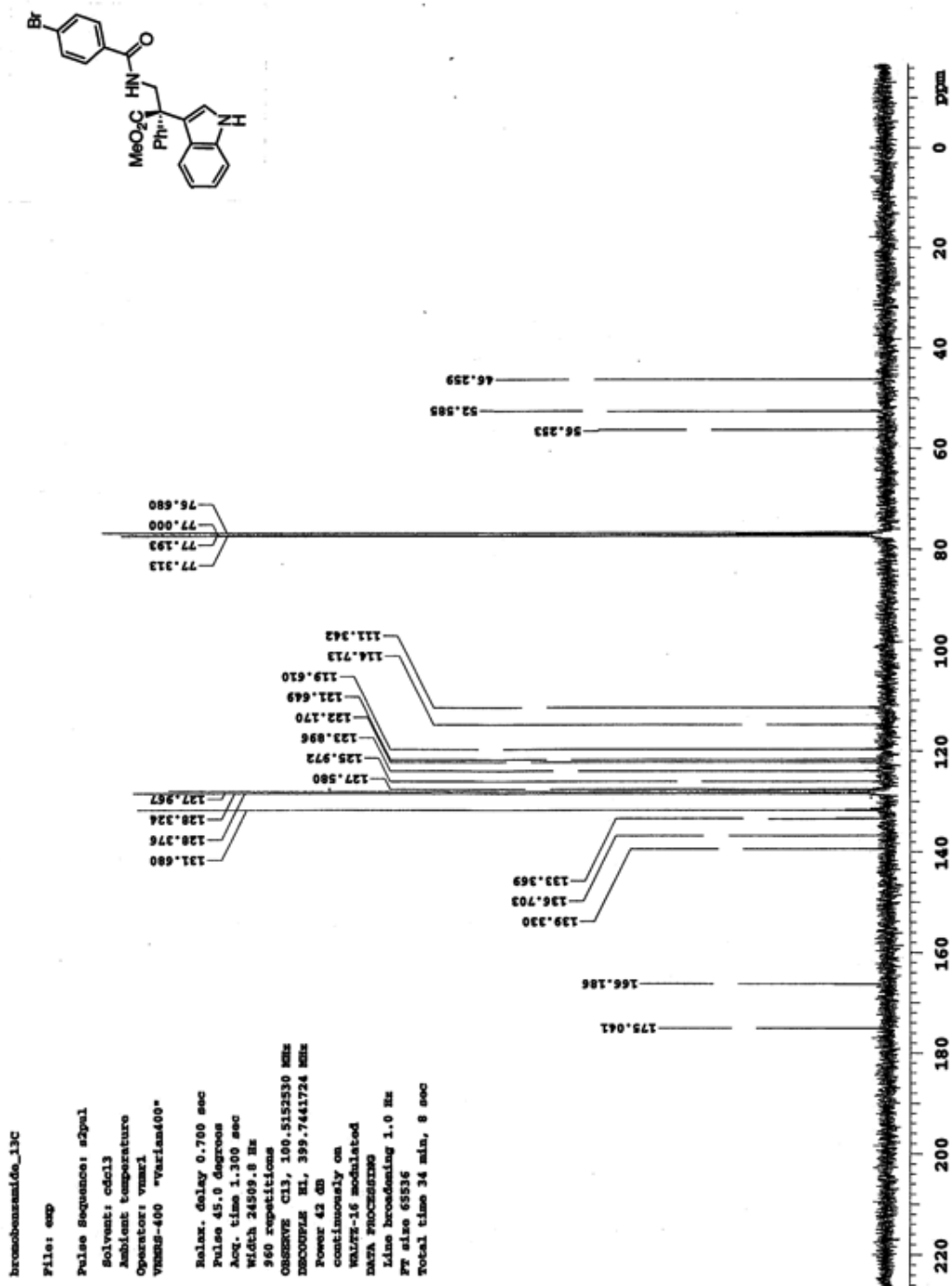
Pulse Sequence: zgpg30
Solvent: cdcl3
Ambient Temperature
Operator: vmr1
File: hrcmbozsmid6_1H
VMSR-400 "Varian400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
8 repetitions

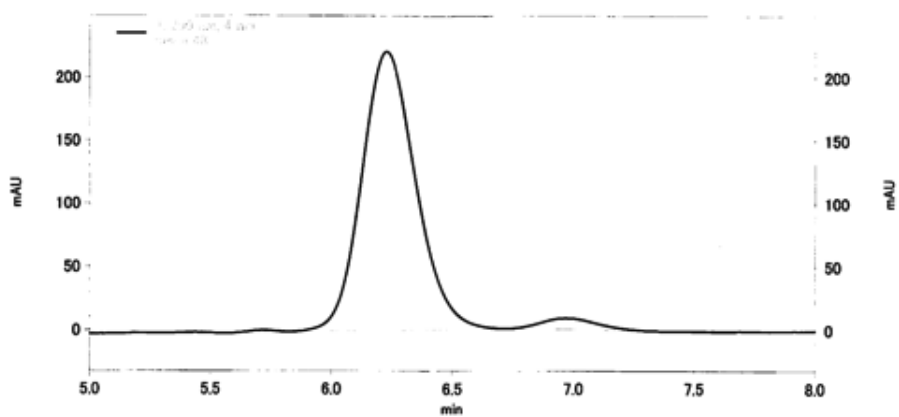
OBSERVE ML 399.742175 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 40 sec



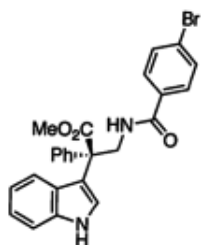
¹³C NMR spectrum of **11**.



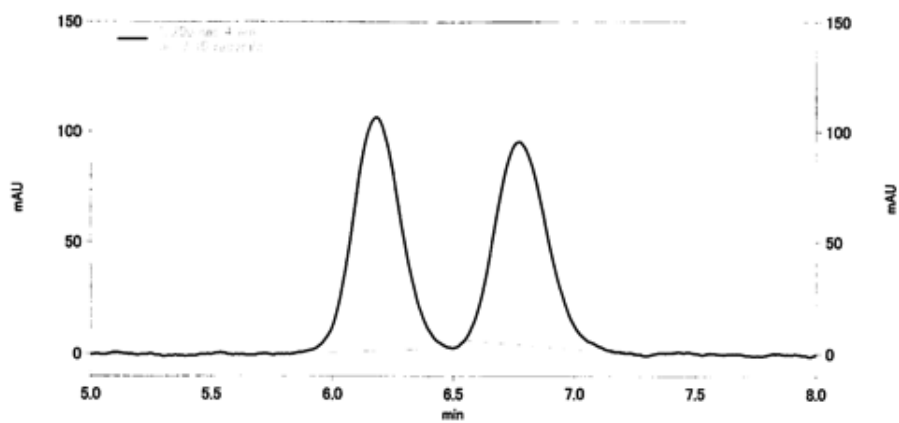
HPLC chart of 11.



Peak #	Retention time	Type	Area	Area %
1	6.23	BI	13735870	96.057
2	6.97	IB	563810	3.943



HPLC chart of **11** (racemic).



Peak #	Retention time	Type	Area	Area %
1	6.18	BB	5817390	51.425
2	6.77	IB	5495030	48.575

