Enantioselective Allylation of Imines Catalyzed by Newly Developed (–)-β-Pinene-based π-Allylpalladium Catalyst: An Efficient Synthesis of (*R*)-α-Propylpiperonylamine and (*R*)-Pipecolic Acid

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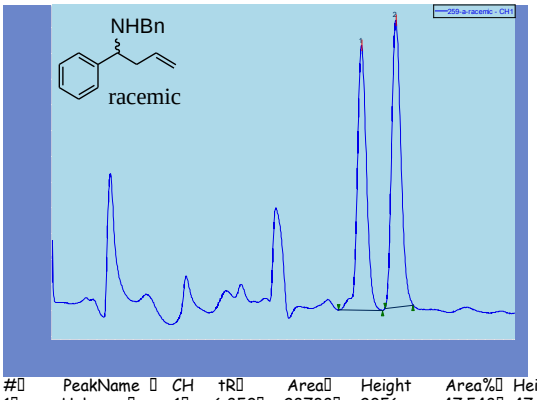
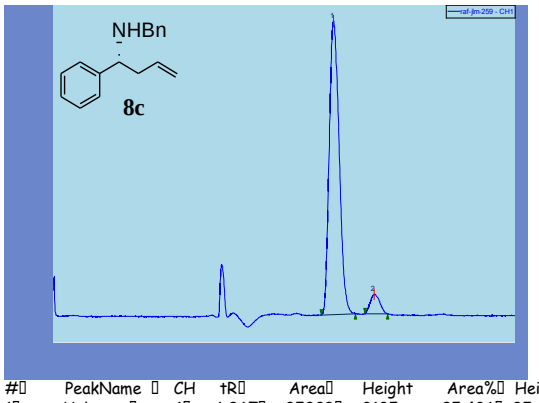
SUPPORTING INFORMATION

HPLC chromatograms of homoallylamines (8a-8s)

(*R*)-*N*-Benzyl-1-phenyl-3-butenylamine 8c

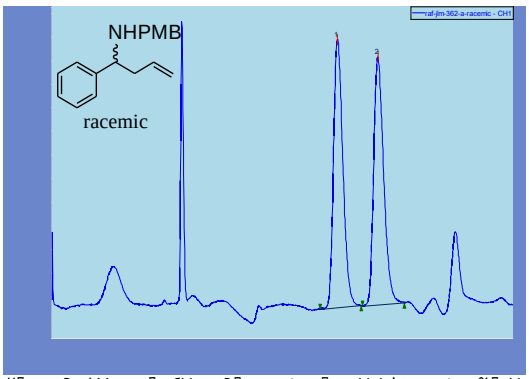


#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	6.850□	28738□	2056	47.548□	47.983
2□	Unknown□	1□	7.608	□31702□	2228□	52.452	52.017



#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	6.967□	35383□	2105	95.406□	95.628
2□	Unknown□	1□	7.975	□1704□	96 □	4.594	4.372

(*R*)-*N*-(4-Methoxybenzyl)-1-phenyl-3-butenylamine 8d



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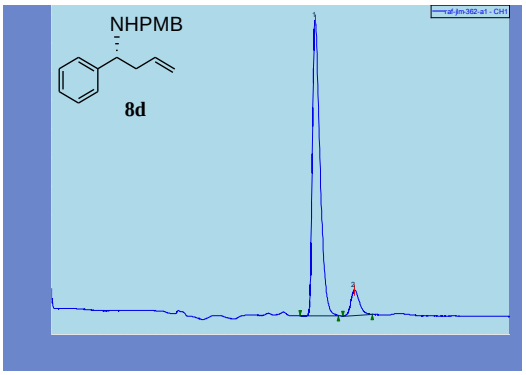
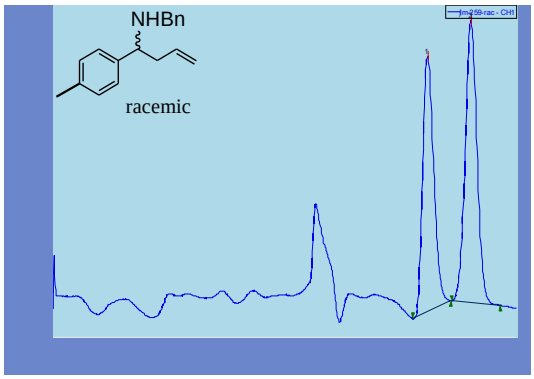
1□	Unknown□	1□	8.208□	21208□	1133	50.423□	51.931
2□	Unknown□	1□	9.367	□20852□	1049□	49.577	48.069

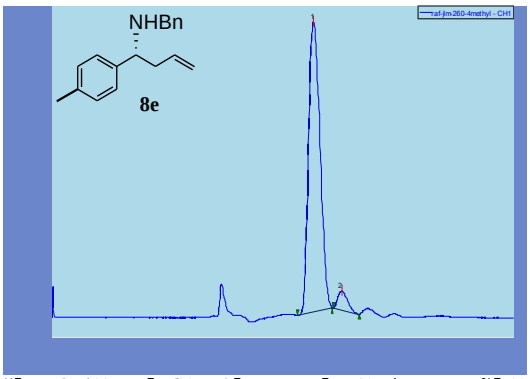


#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	7.600□	79062□	5205	94.457□	94.598
2□	Unknown□	1□	8.733	□4640□	297 □	5.543	5.402

(*R*)-*N*-Benzyl-1-(4-methylphenyl)-3-butenylamine 8e

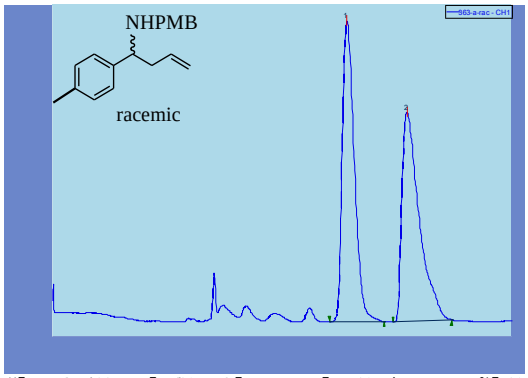


#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	8.008□	30852□	1880	45.786□	47.513
2□	Unknown□	1□	8.942	□36531□	2077□	54.214	52.487

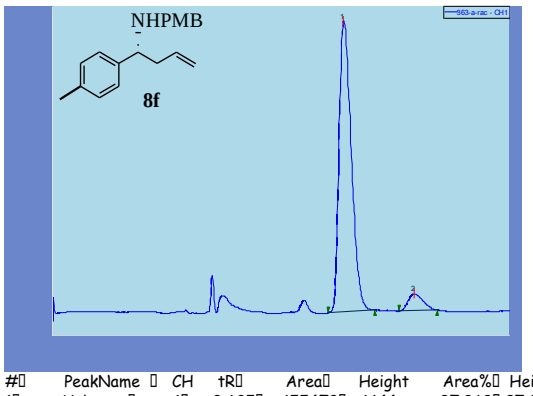


#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	7.517□	87699□	3863	95.915□	95.524
2□	Unknown□	1□	8.325	□3735□	181 □	4.085	4.476

(*R*)-*N*-(4-Methoxybenzyl)-1-(4-methylphenyl)-3-butenylamine 8f

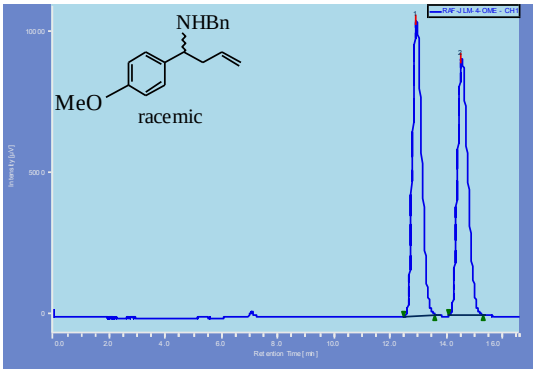


#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	8.600□	125352□	5133	50.034□	59.001
2□	Unknown□	1□	10.358	125184□	3567□	49.966	40.999

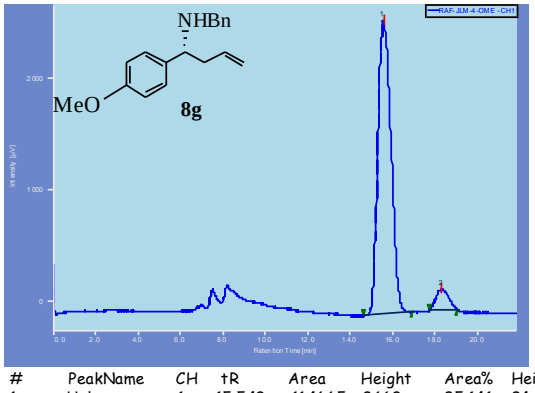


#□	PeakName □	CH	tR□	Area□	Height	Area%□	Height%
1□	Unknown□	1□	8.625□	155479□	6144	97.869□	97.138
2□	Unknown□	1□	10.717	□3385□	181 □	2.131	2.862

(*R*)-*N*-Benzyl-1-(4-methoxyphenyl)-3-butenylamine 8g

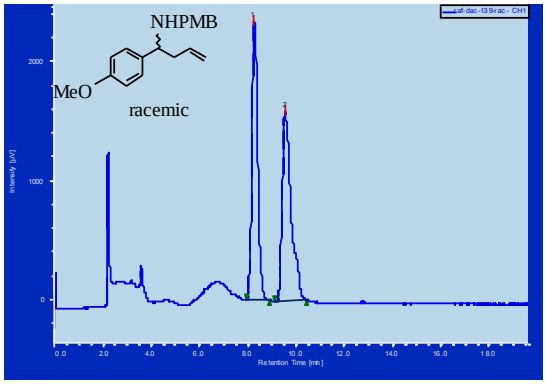


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	12.925	241264	10450	50.509	53.615
2	Unknown	1	14.533	236400	9041	49.491	46.385

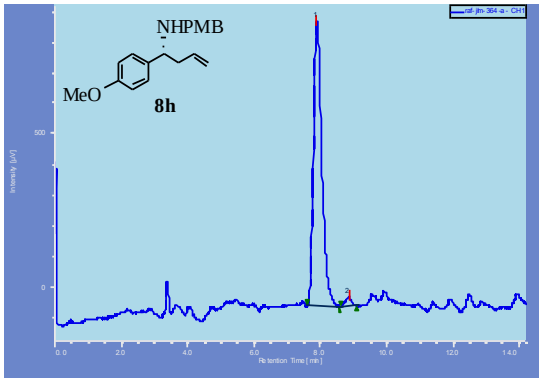


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	15.542	114665	2663	95.141	94.485
2	Unknown	1	18.267	5856	155	4.859	5.515

(*R*)-*N*-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-3-butenylamine 8h

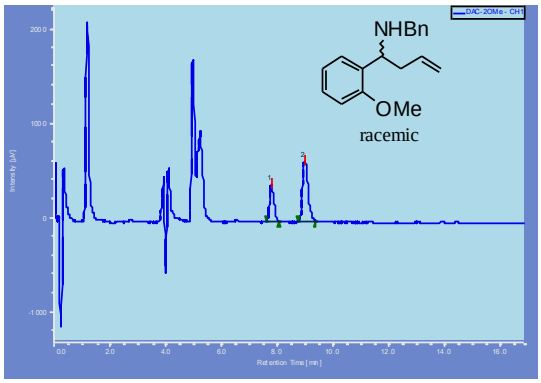


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	8.275	38940	2340	48.920	59.541
2	Unknown	1	9.550	40660	1590	51.080	40.459

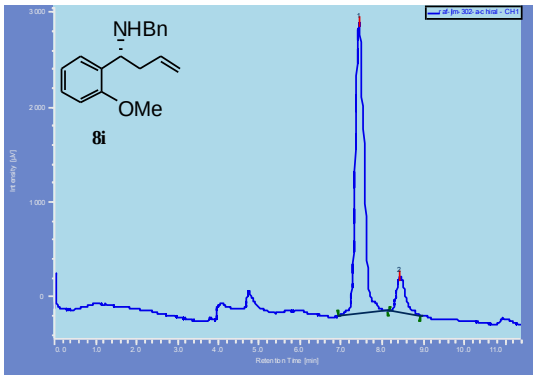


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	7.892	16254	930	98.844	97.786
2	Unknown	1	8.850	190	21	1.156	2.214

(*R*)-*N*-Benzyl-1-(2-methoxyphenyl)-3-butenylamine 8i

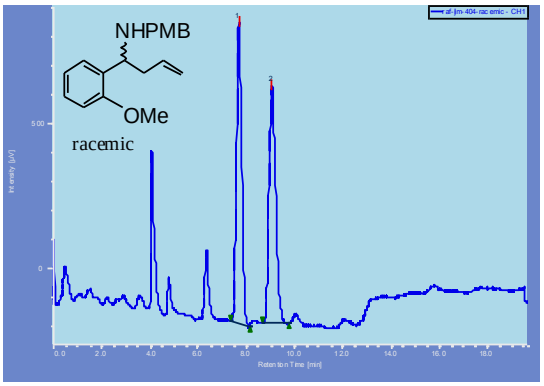


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	7.775	6324	380	47.524	41.151
2	Unknown	1	8.975	7116	543	53.476	58.849

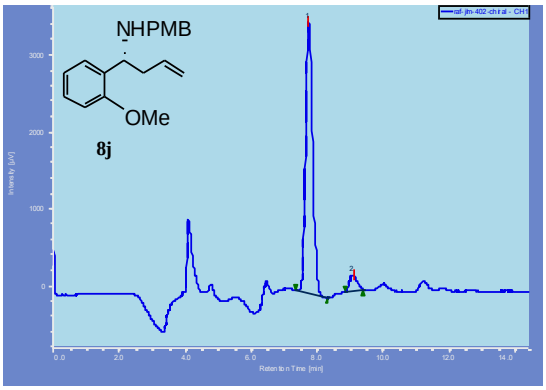


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	7.425	45039	3075	95.217	92.949
2	Unknown	1	8.425	2262	233	4.783	7.051

(*R*)-*N*-(4-Methoxybenzyl-1-(2-methoxyphenyl)-3-butenylamine 8j

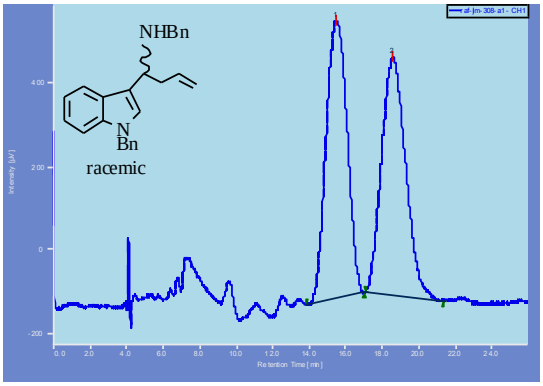


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	7.675	15582	1042	49.514	55.908
2	Unknown	1	9.050	15888	822	50.486	44.092

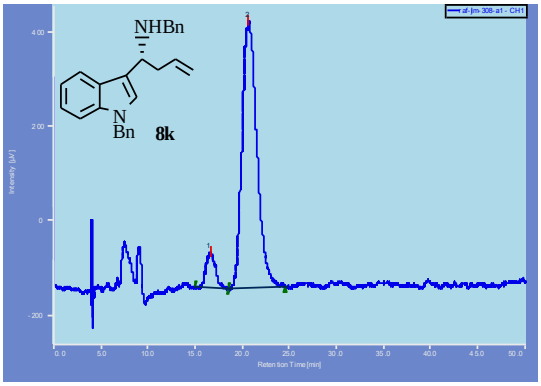


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	7.725	51404	3526	95.086	95.229
2	Unknown	1	9.075	2657	177	4.914	4.771

(*R*)-*N*-benzyl-1-(1-benzylindol-3-yl)but-3-en-1-amine 8k

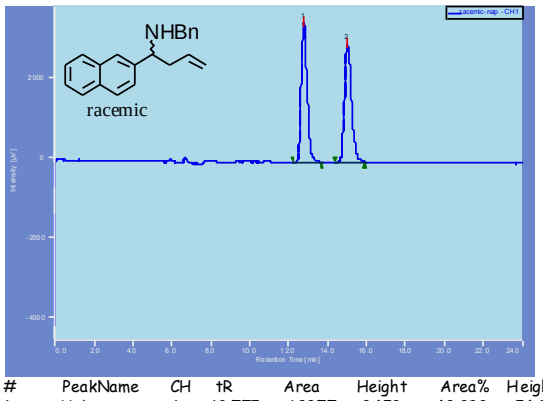


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	15.467	53490	667	50.470	53.816
2	Unknown	1	18.558	52494	572	49.530	46.184

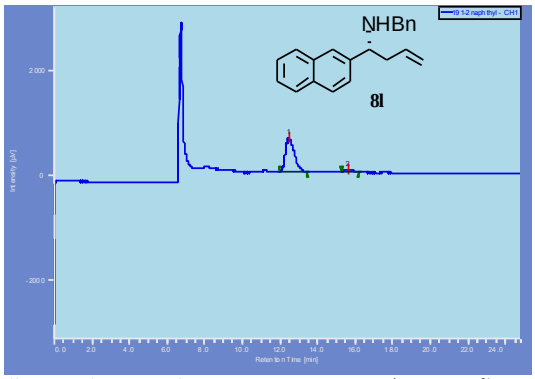


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	16.567	4270	75	6.510	11.713
2	Unknown	1	20.617	61329	565	93.490	88.287

(*R*)-*N*-Benzyl-1-(2-naphthyl)-3-butenylamine 8l

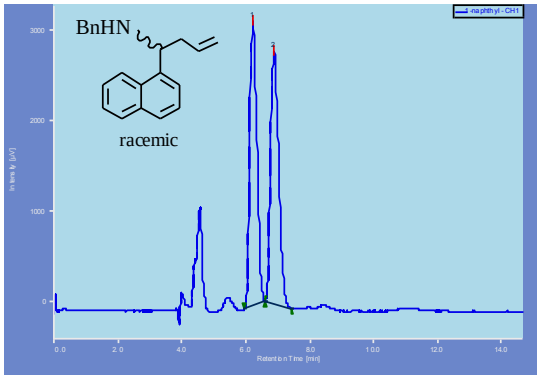


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	12.775	69877	3459	49.993	54.234
2	Unknown	1	15.008	69897	2919	50.007	45.766

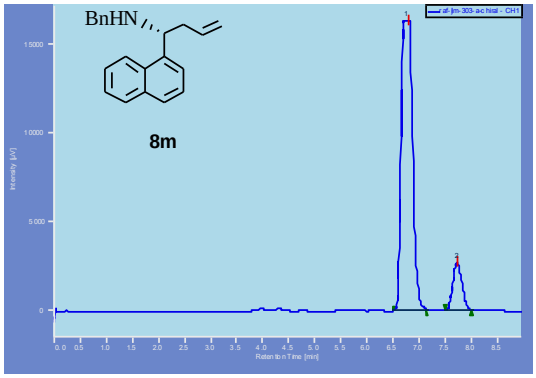


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	12.467	20451	631	97.863	96.225
2	Unknown	1	15.625	447	25	2.137	3.775

(*R*)-*N*-Benzyl-1-(1-naphthyl)-3-butenylamine 8m

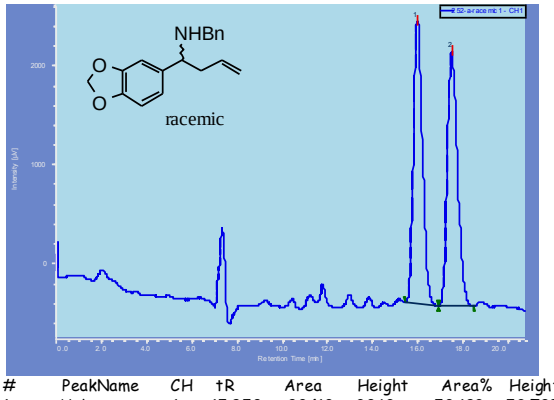


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	6.208	48758	3150	49.693	53.052
2	Unknown	1	6.867	49362	2788	50.307	46.948

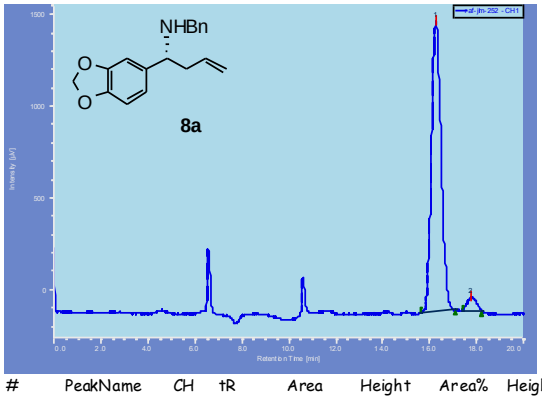


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	6.783	245105	16289	90.857	88.185
2	Unknown	1	7.725	24665	2182	9.143	11.815

(*R*)-*N*-Benzyl-1-piperonyl-3-butenylamine 8a

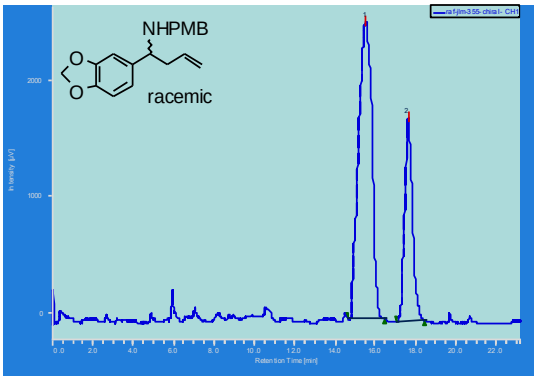


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	15.958	80410	2862	50.192	52.733
2	Unknown	1	17.475	79795	2566	49.808	47.267

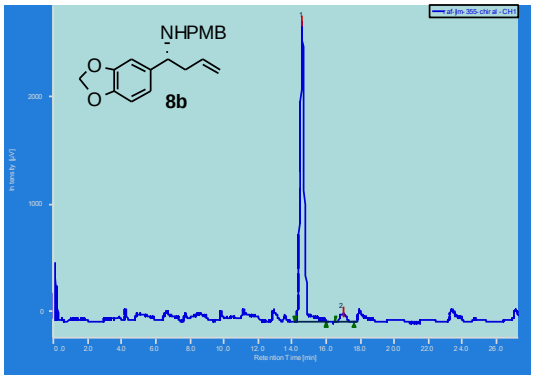


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	16.258	45159	1569	97.556	96.053
2	Unknown	1	17.775	1131	64	2.444	3.947

(*R*)-*N*-(4-Methoxybenzyl)-1-piperonyl-3-butenylamine 8b

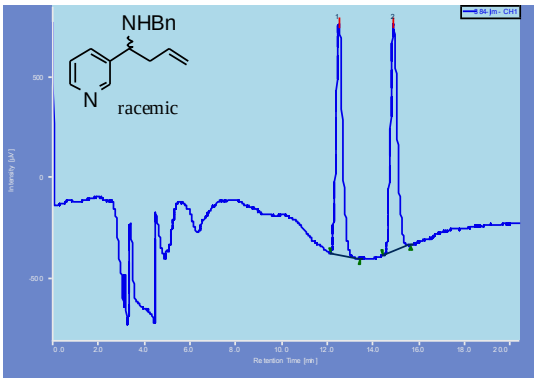


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	15.517	84333	2539	51.447	59.355
2	Unknown	1	17.617	79589	1739	48.553	40.645

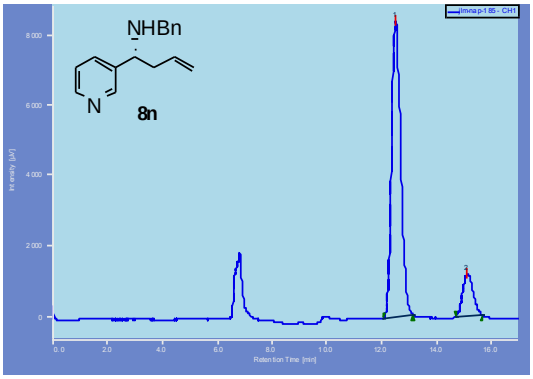


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	14.558	45096	2774	97.546	97.862
2	Unknown	1	17.000	1134	61	2.454	2.138

(*R*)-*N*-Benzyl-1-(3-pyridyl)-3-butenylamine 8n

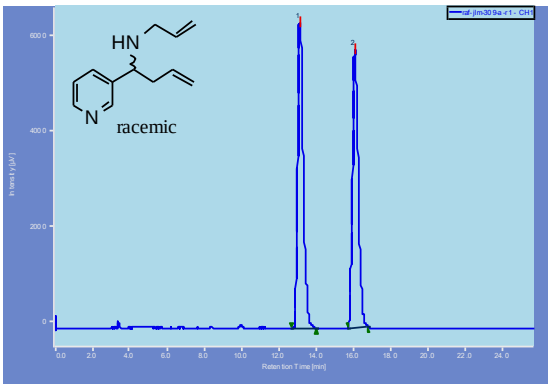


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	12.500	22804	1147	49.453	50.376
2	Unknown	1	14.875	23309	1130	50.547	49.624

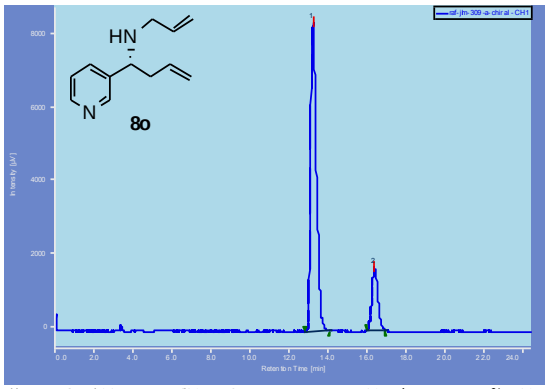


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	12.508	193388	8392	85.870	87.420
2	Unknown	1	15.125	31822	1208	14.130	12.580

(*R*)-*N*-Allyl-1-(3-pyridyl)-3-butenylamine 8o

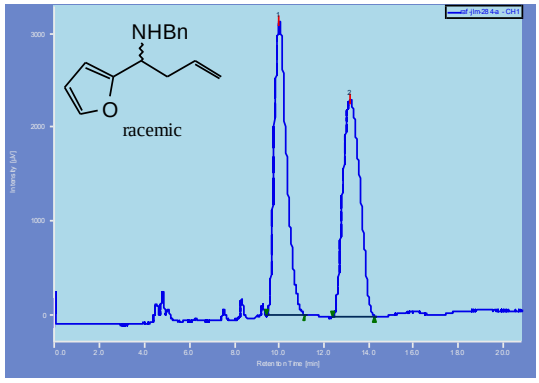


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	13.125	130494	6408	51.088	52.450
2	Unknown	1	16.083	124935	5809	48.912	47.550

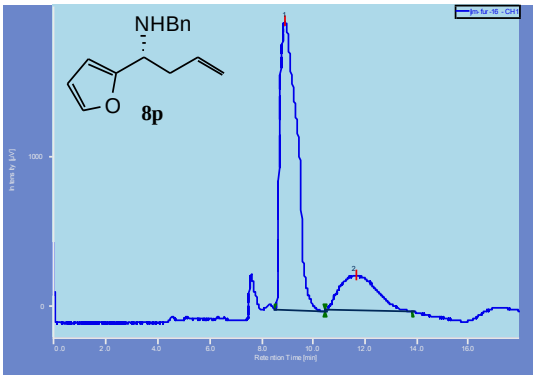


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	13.183	174498	8445	85.485	84.352
2	Unknown	1	16.342	29629	1567	14.515	15.648

(*R*)-*N*-Benzyl-1-(2-furfuryl)-3-butenylamine 8p

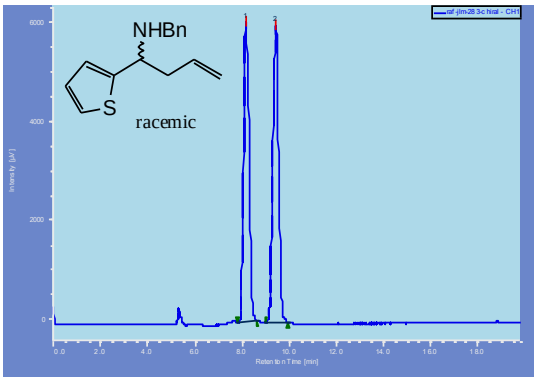


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	10.000	120363	3136	49.674	57.472
2	Unknown	1	13.158	121943	2320	50.326	42.528

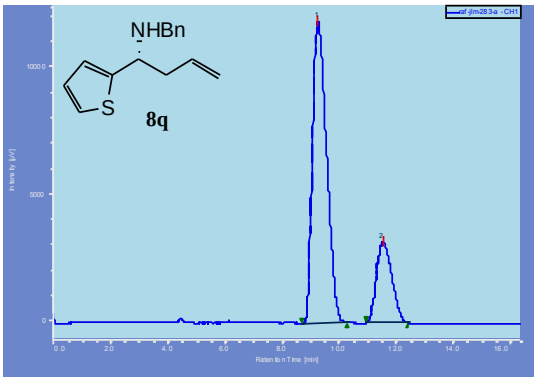


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	8.892	84055	1897	85.158	90.968
2	Unknown	1	11.633	14650	188	14.842	9.032

(*R*)-*N*-Benzyl-1-(2-thiophenyl)-3-butenylamine 8q

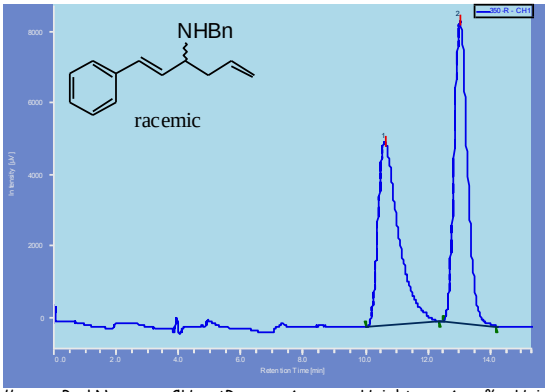


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	9.250	97967	6054	48.868	50.337
2	Unknown	1	11.517	102505	5973	51.132	49.663

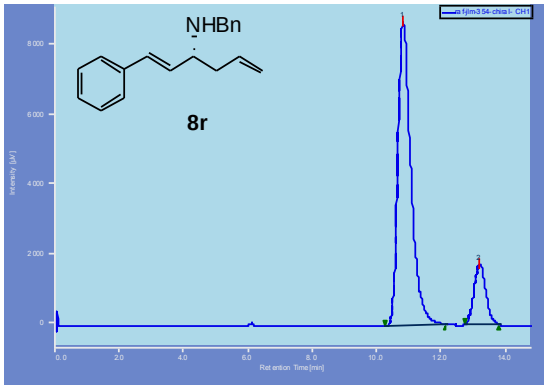


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	9.250	410523	11893	80.481	79.548
2	Unknown	1	11.517	99564	3058	19.519	20.452

(*R*,*E*)-*N*-benzyl-1-phenylhexa-1,5-diene-3-amine 8r



#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	10.608	237196	5129	48.907	37.896
2	Unknown	1	13.017	247801	8405	51.093	62.104



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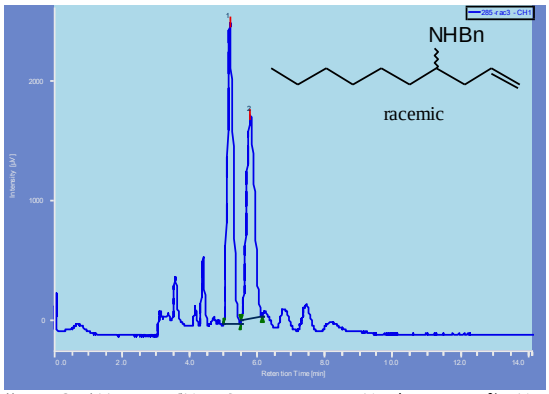
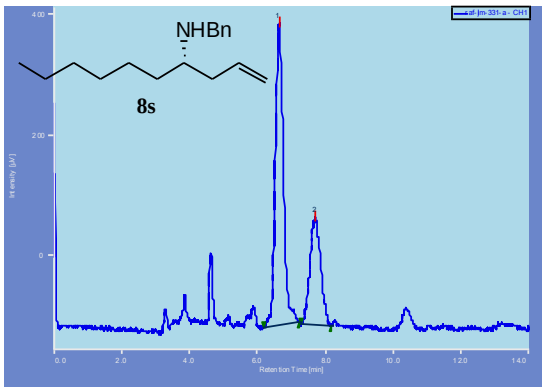
1	Unknown	1	10.808	248882	8671	85.926	83.292
2	Unknown	1	13.192	40765	1739	14.074	16.708

(*R*)-*N*-Benzyl-1-heptyl-3-butenylamine 8s

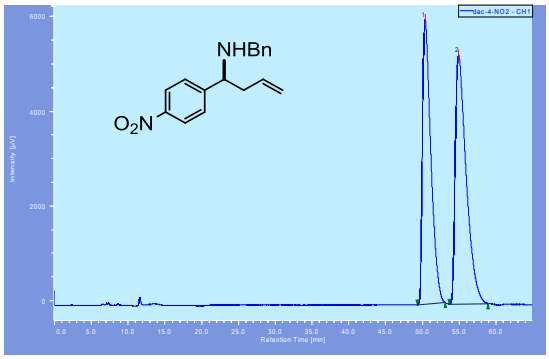


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	5.167	29137	2514	50.822	59.543
2	Unknown	1	5.775	28194	1708	49.178	40.457

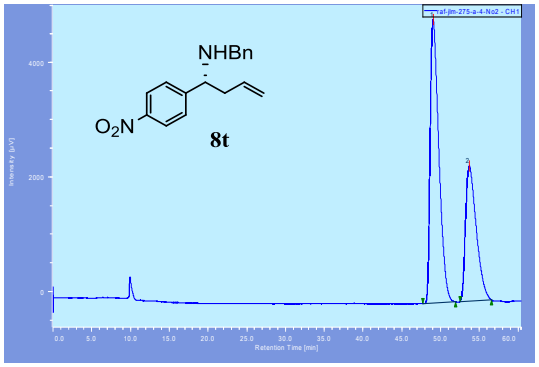


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	6.633	8591	499	70.471	73.947
2	Unknown	1	7.692	3600	297	29.529	26.053

(*R*)-*N*–Benzyl–1–(4–nitrophenyl)–3–butenylamine (8t)

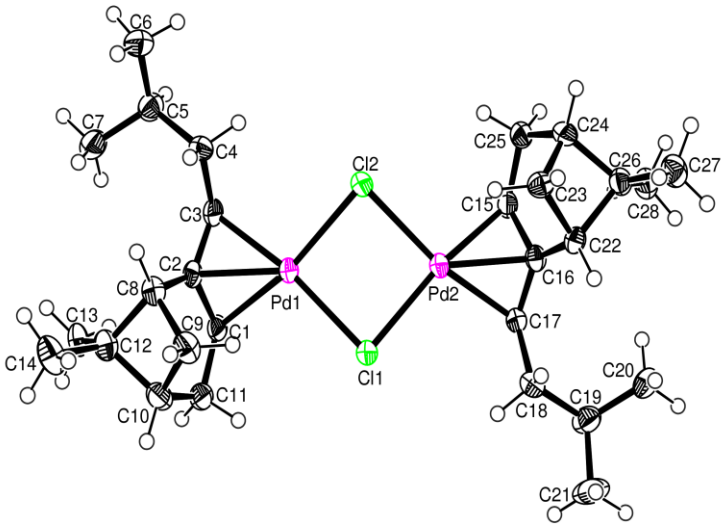


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	50.317	474410	60007	46.674	53.358
2	Unknown	1	54.875	542017	5251	53.326	56.642

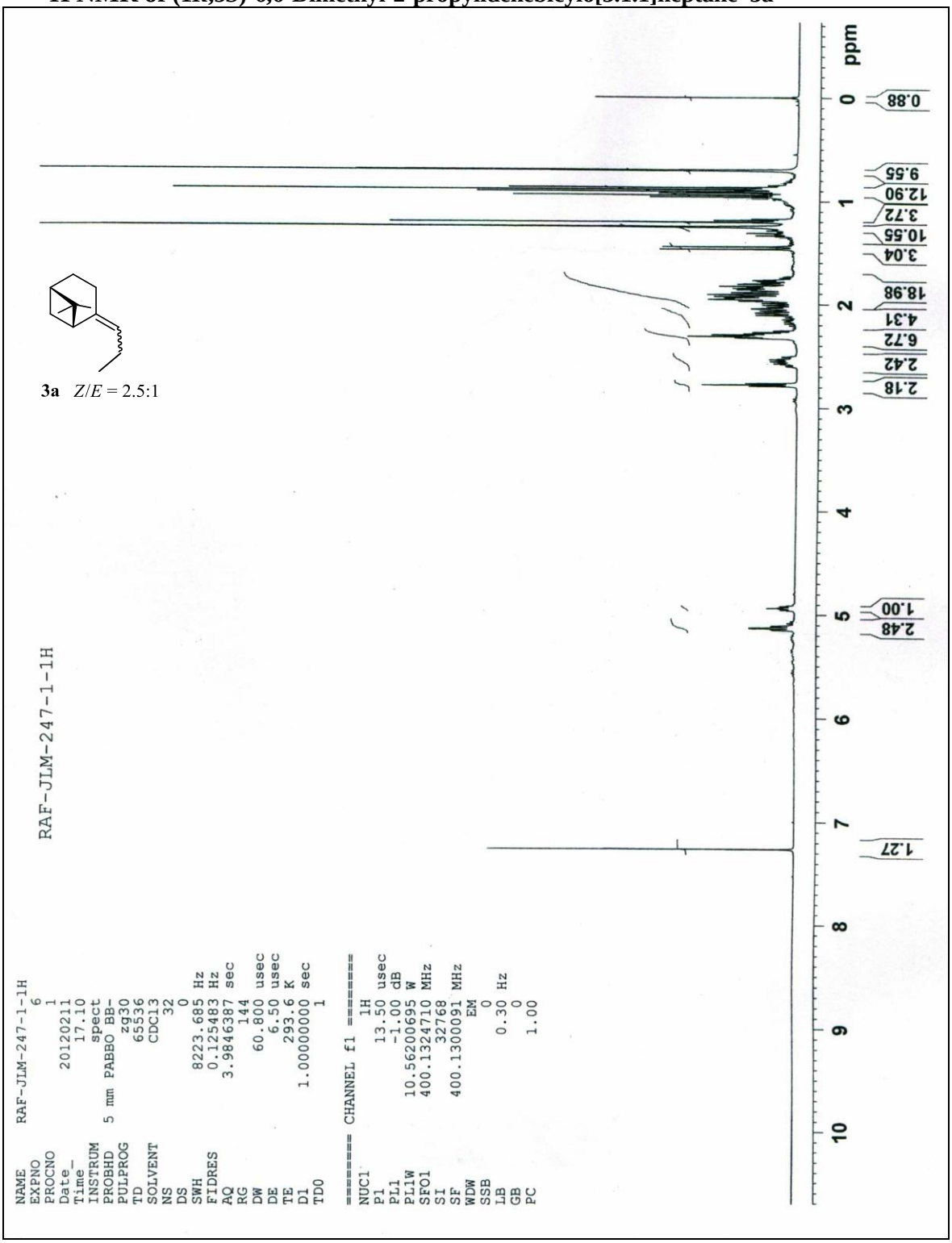


#	PeakName	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	48.983	384120	21480	69.850	68.449
2	Unknown	1	53.625	165801	9901	30.150	31.551

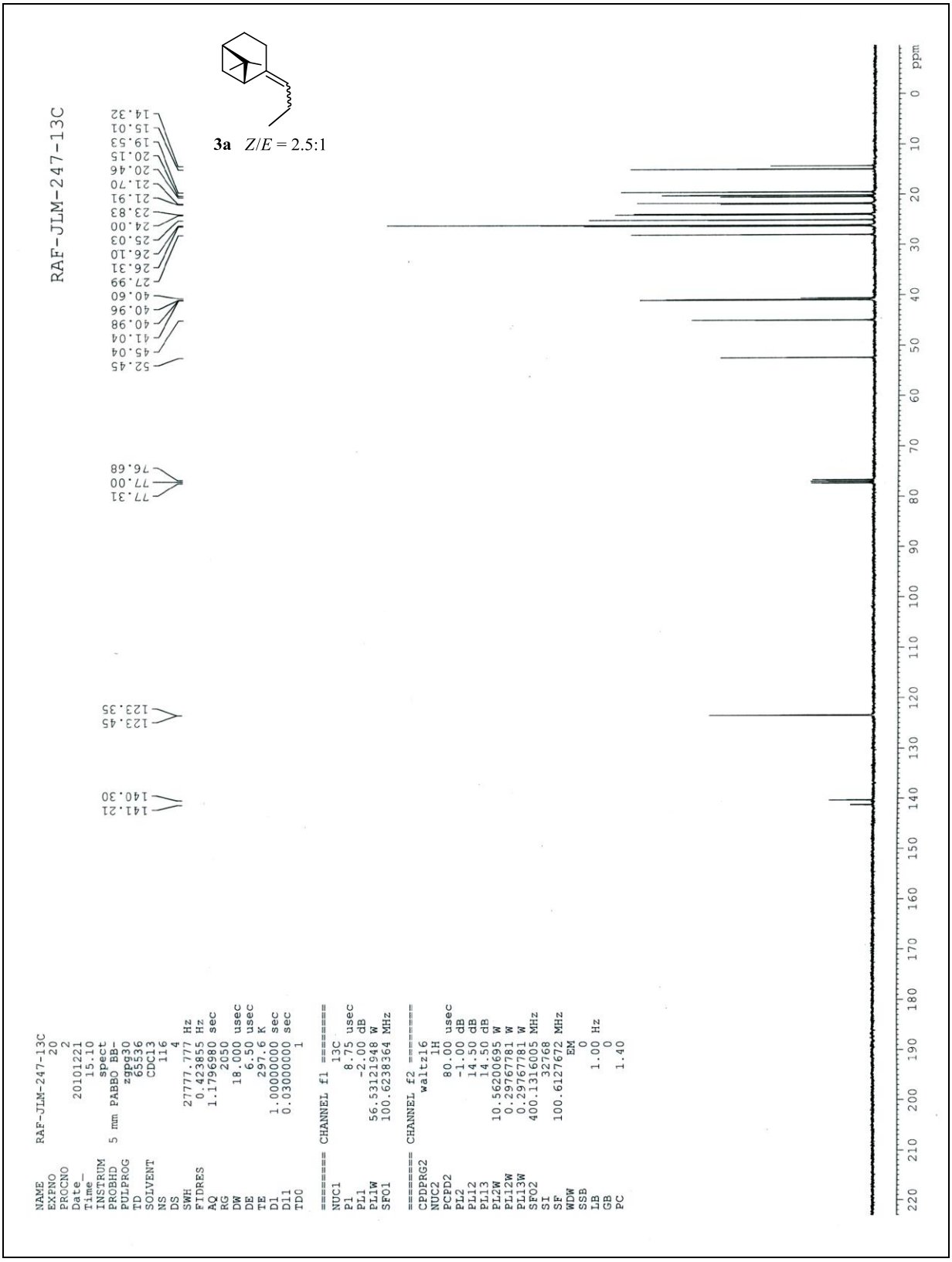
X-Ray Crystallographic Structure of 4c:



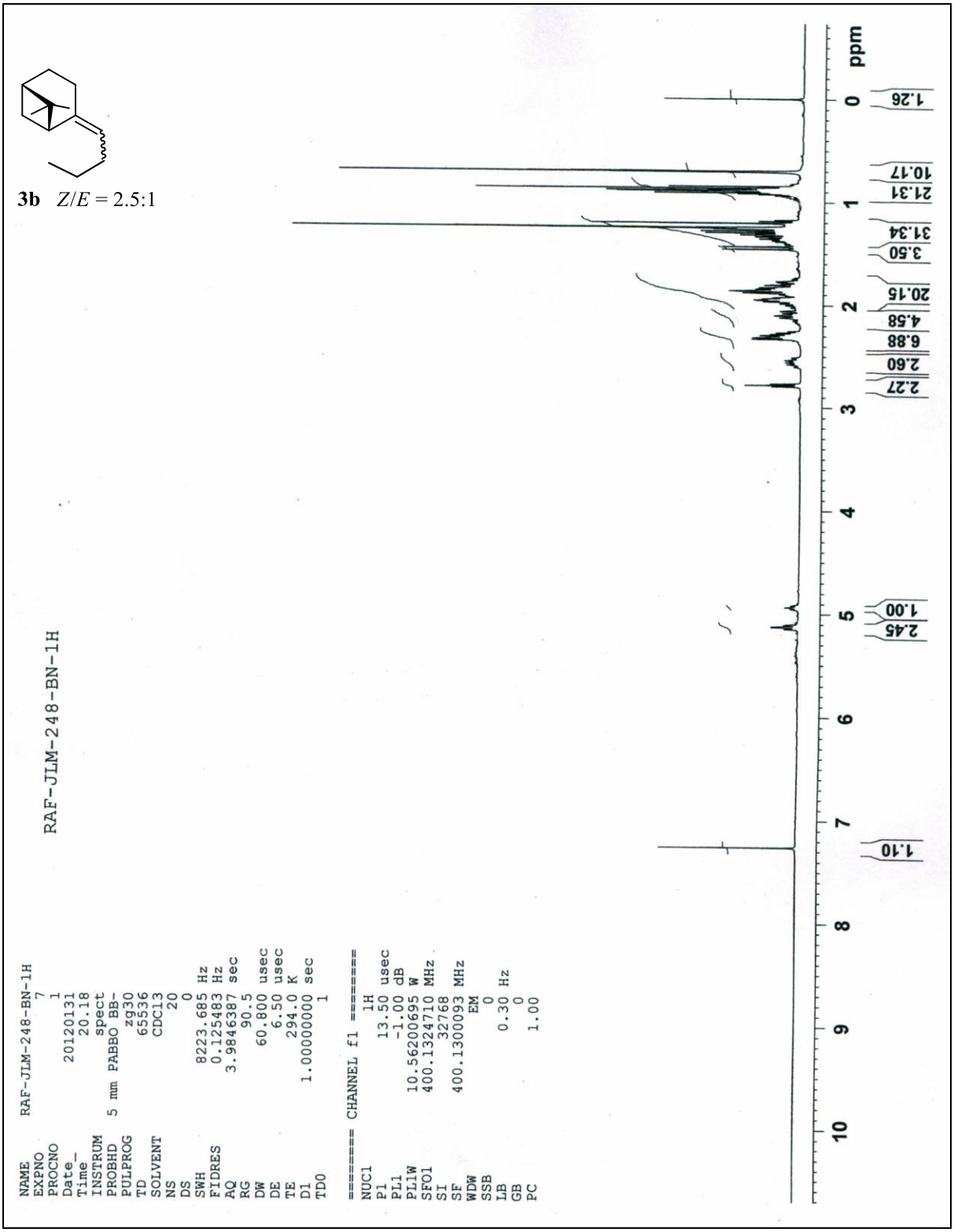
^{1}H NMR of (1*R*,5*S*)-6,6-Dimethyl-2-propylidenebicylo[3.1.1]heptane 3a



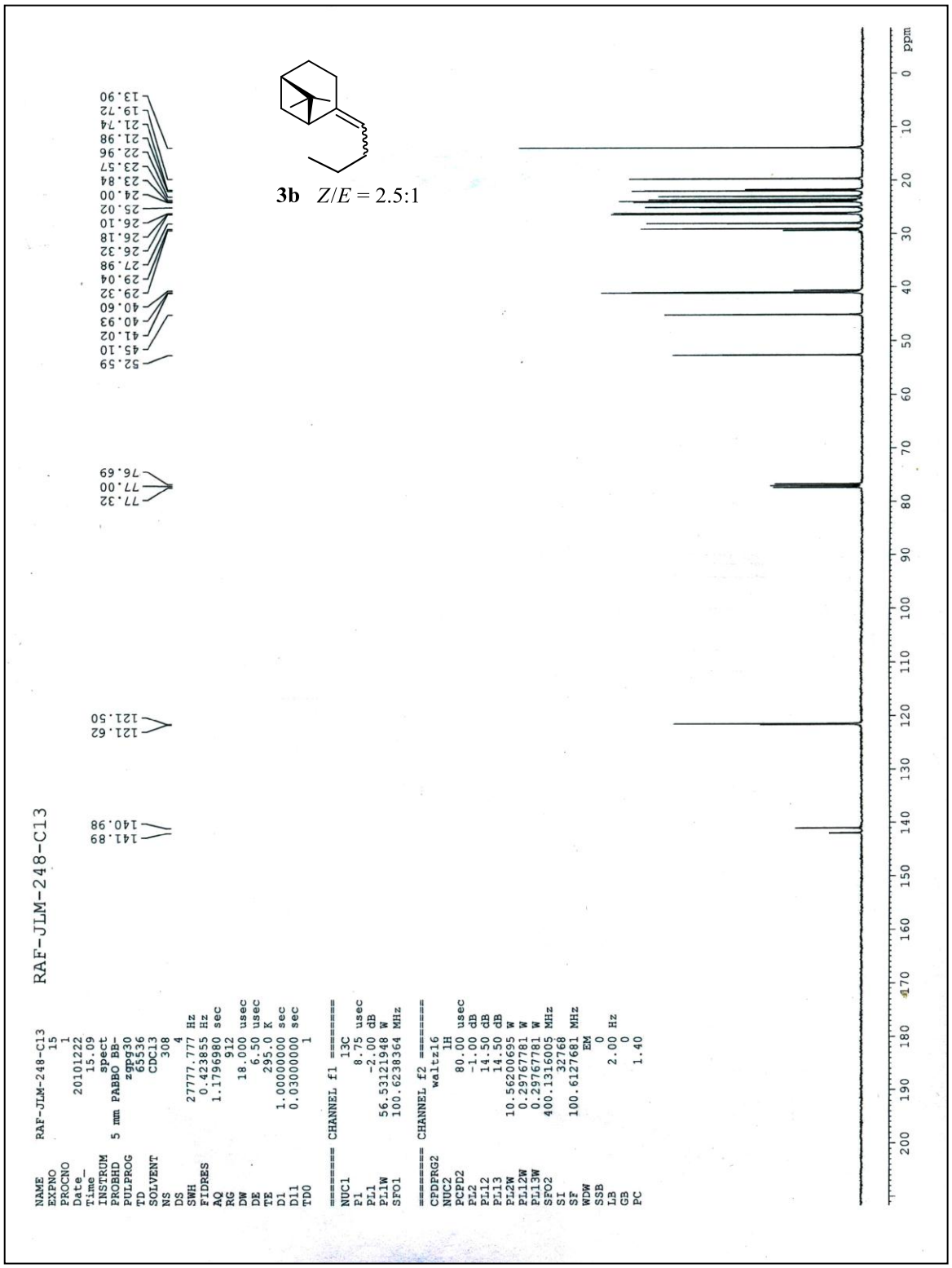
^{13}C NMR of (1*R*,5*S*)-6,6-Dimethyl-2-propylidenebicylo[3.1.1]heptane 3a



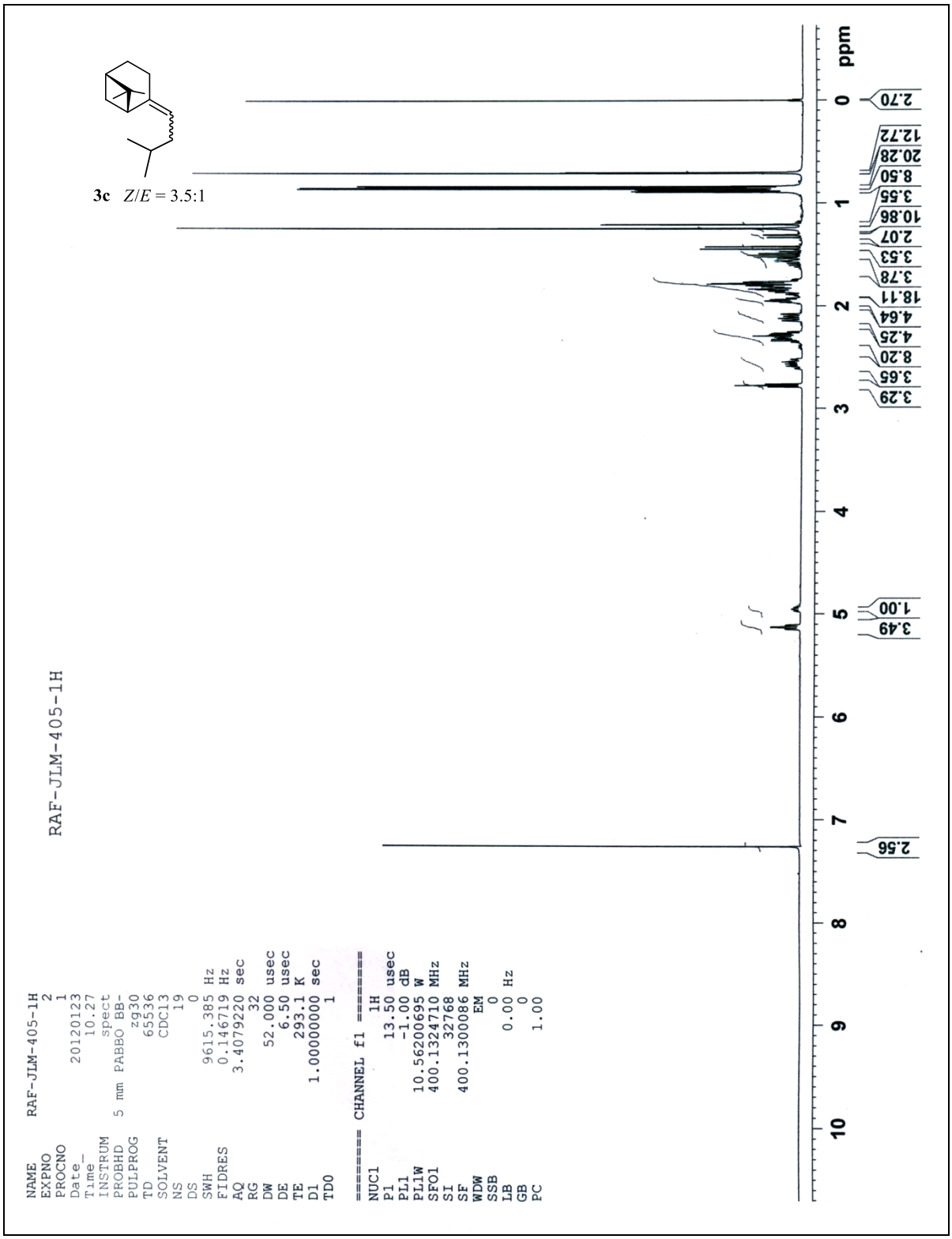
^{1}H NMR of (1*R*,5*S*)-2-Butylidene-6,6-dimethylbicyclo[3.1.1]heptane 3b



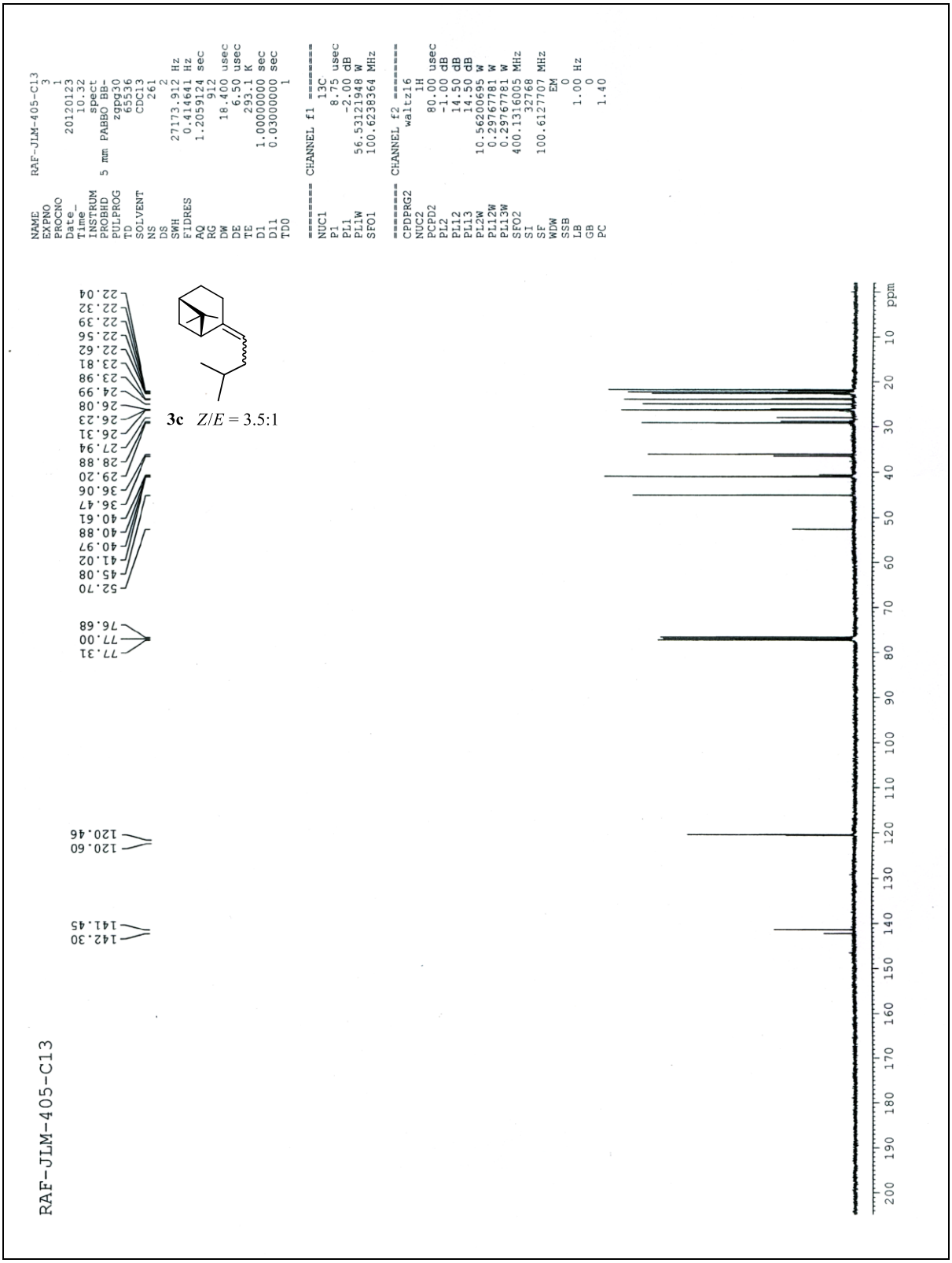
^{13}C NMR of (1*R*,5*S*)-2-Butylidene-6,6-dimethylbicyclo[3.1.1]heptane 3b



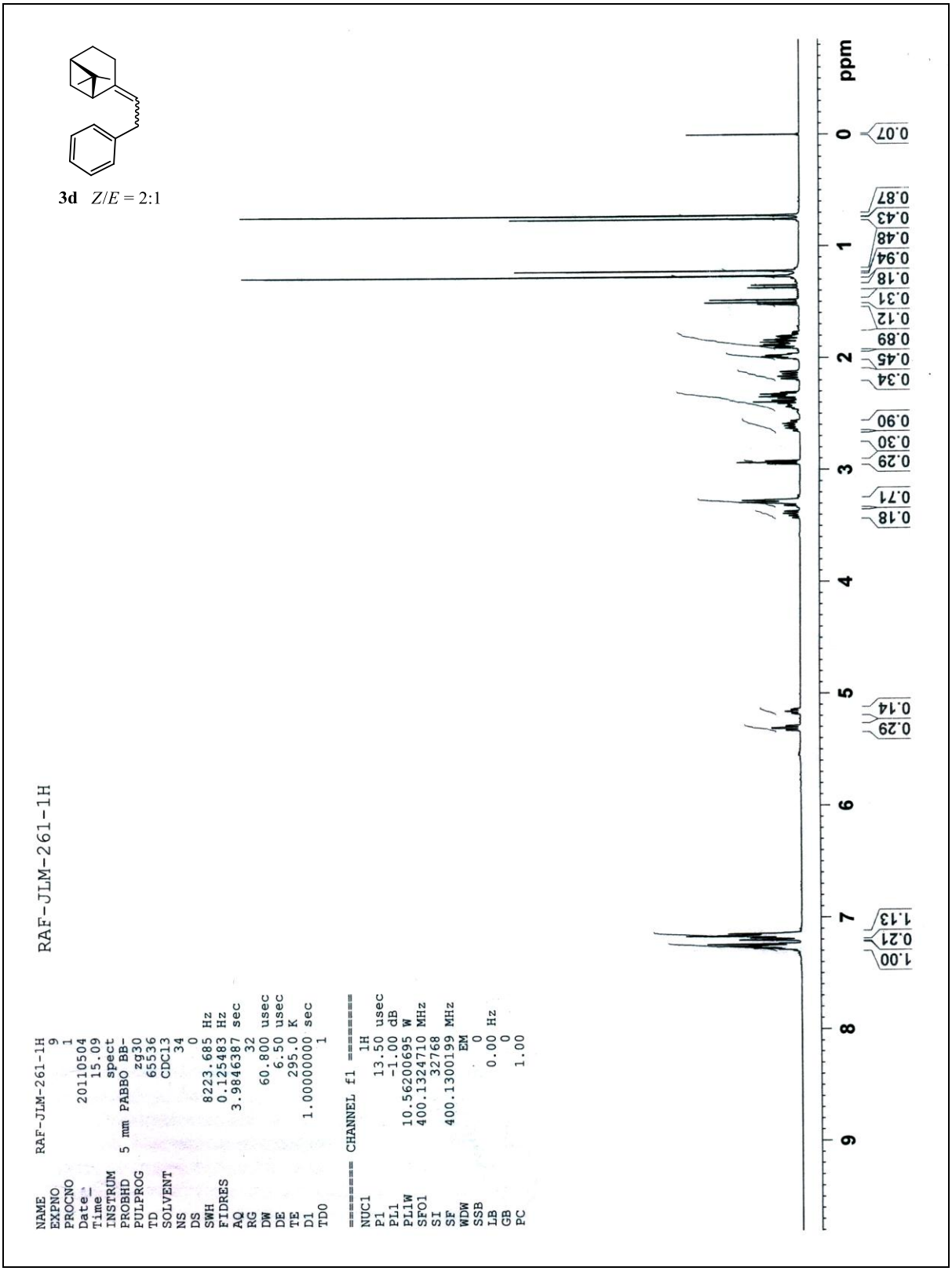
^{1}H NMR of (1*R*,5*S*)-6,6-Dimethyl-2-(3-methylbutylidene)bicyclo[3.1.1]heptane 3c



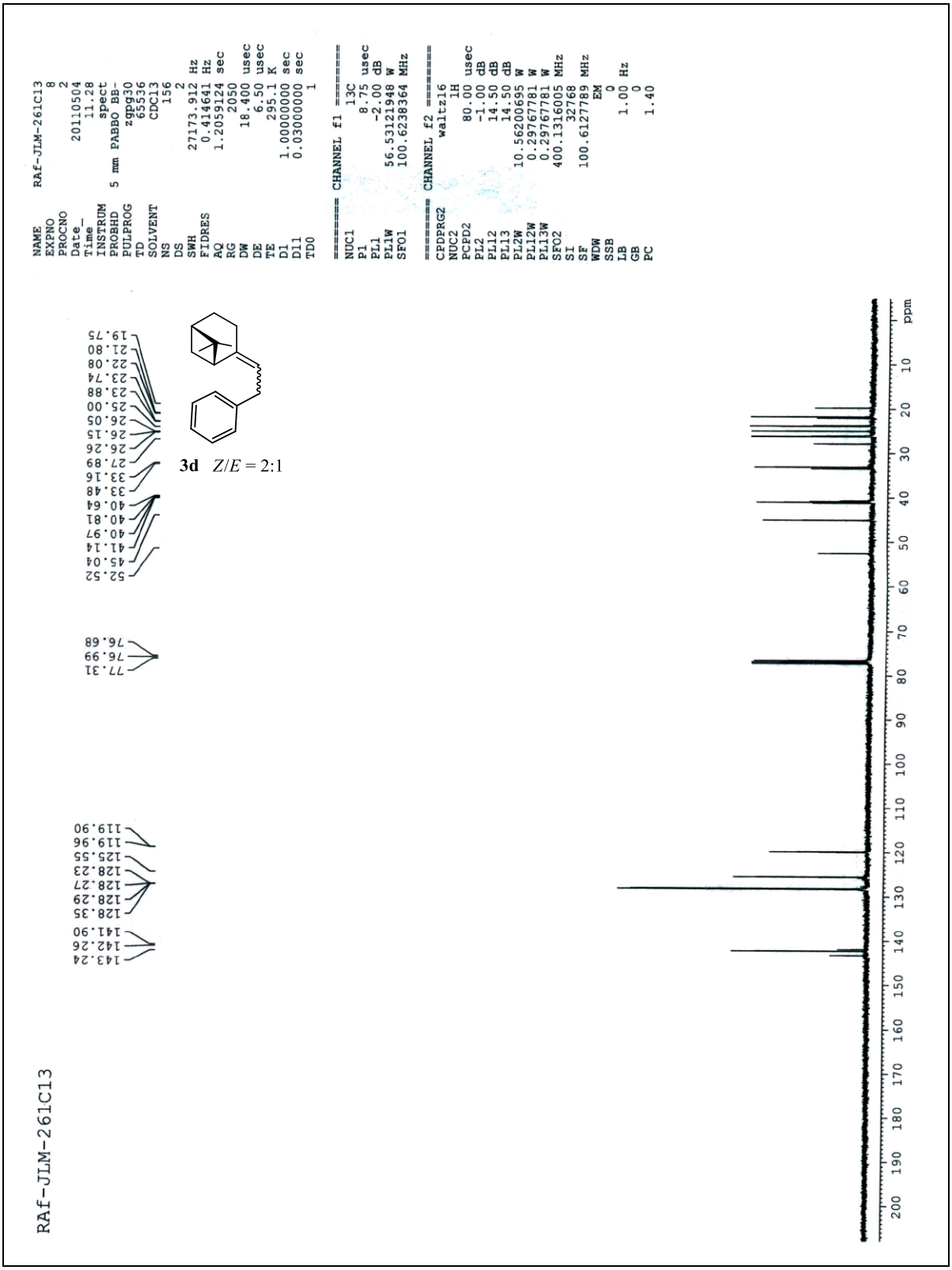
^{13}C NMR of (1*R*,5*S*)-6,6-Dimethyl-2-(3-methylbutylidene)bicyclo[3.1.1]heptane 3c



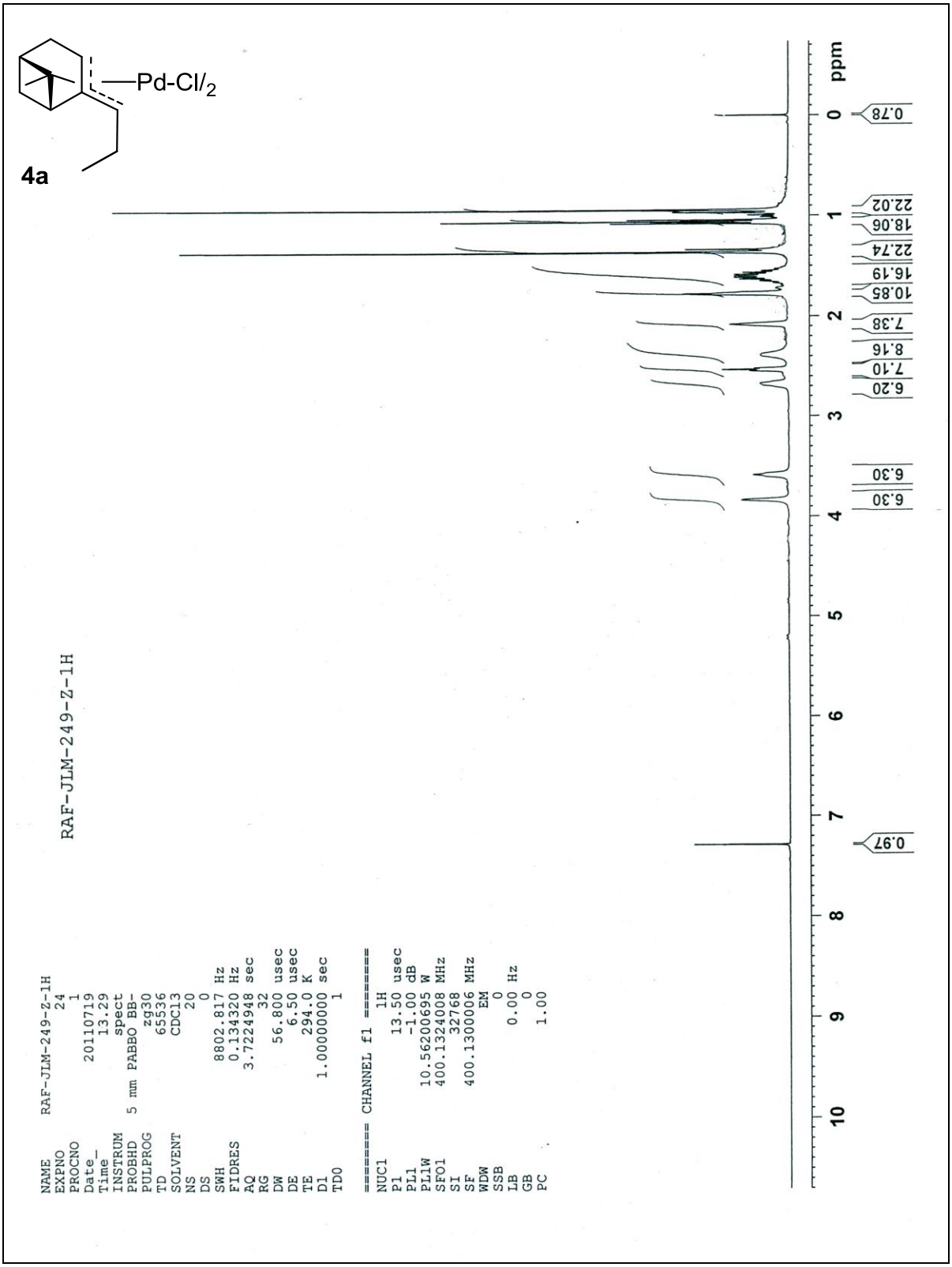
^{1}H NMR of (1*R*,5*S*)-6,6-Dimethyl-2-(2-phenylethylidene)bicyclo[3.1.1]heptane 3d



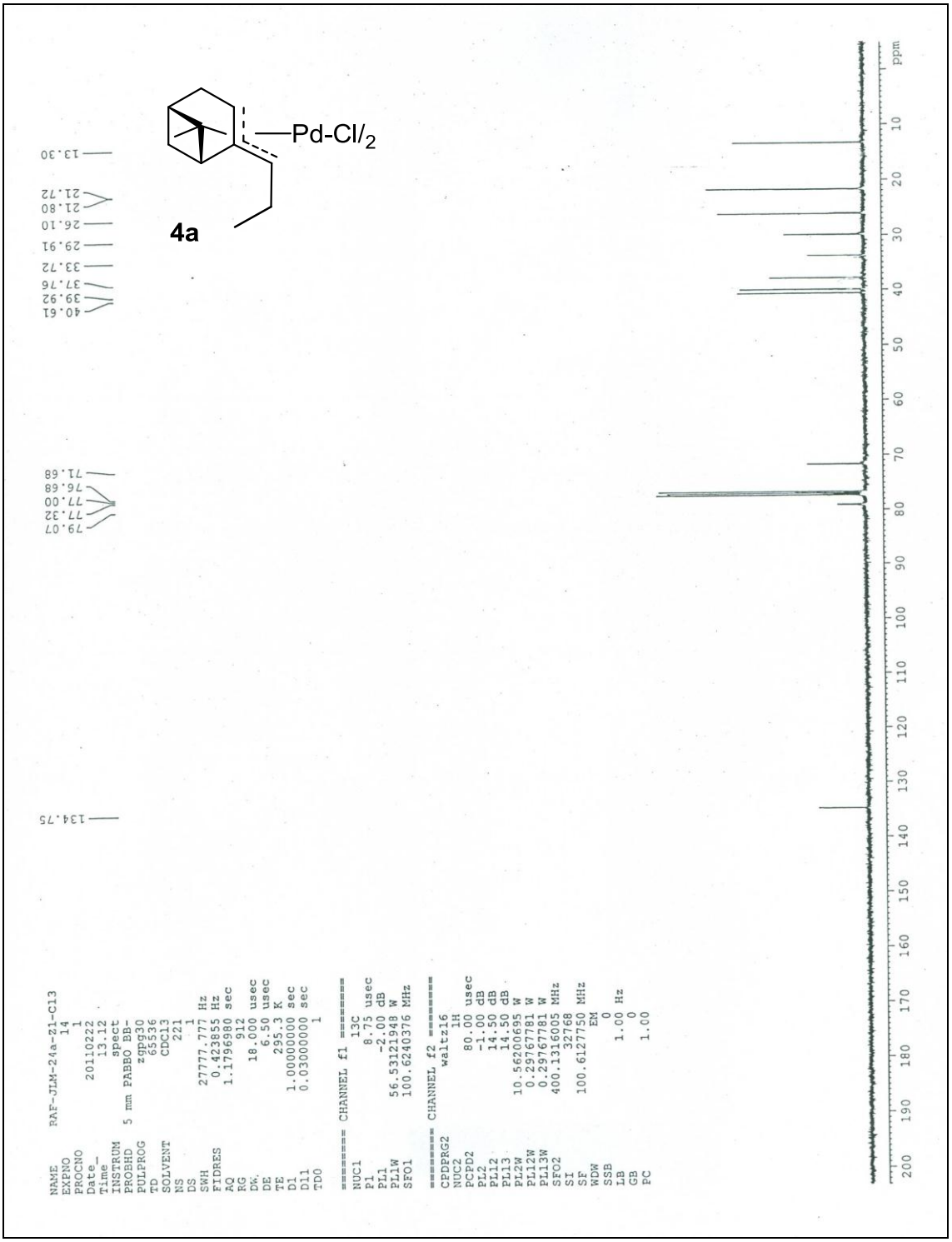
^{13}C NMR of (1*R*,5*S*)-6,6-Dimethyl-2-(2-phenylethylidene)bicyclo[3.1.1]heptane 3d



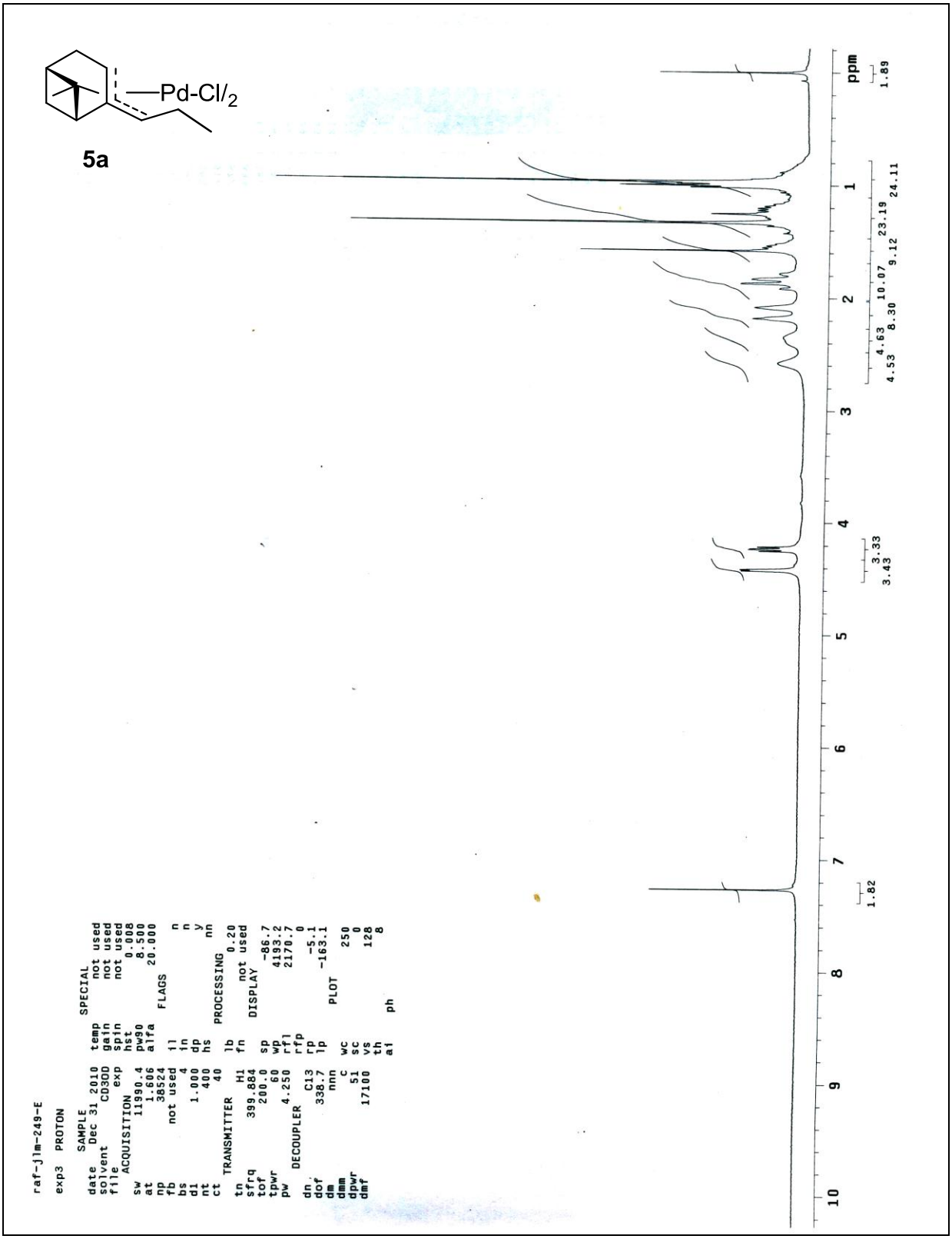
^{1}H NMR of π–Allylpalladium chloride complex 4a



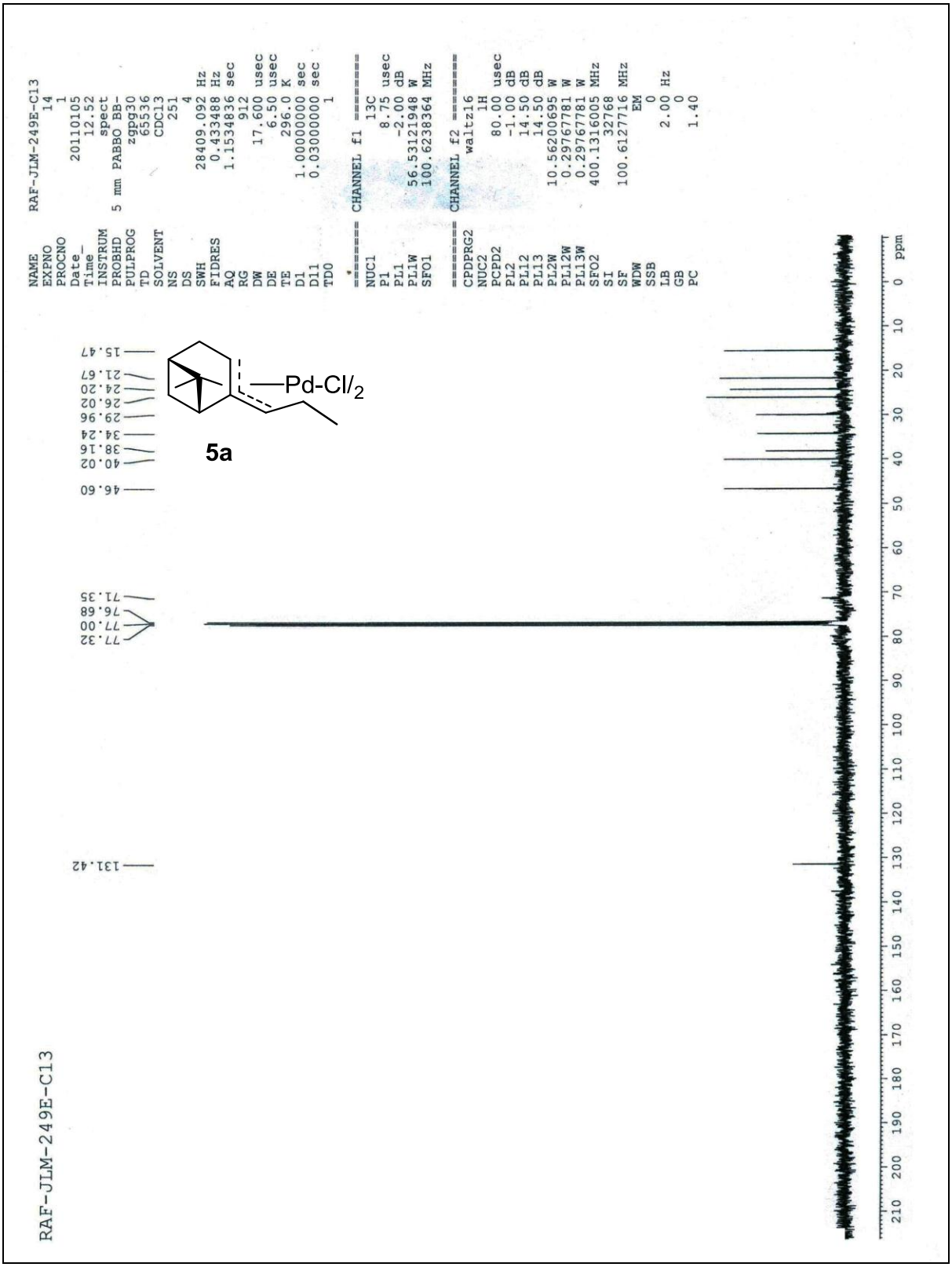
^{13}C NMR of π–Allylpalladium chloride complex 4a



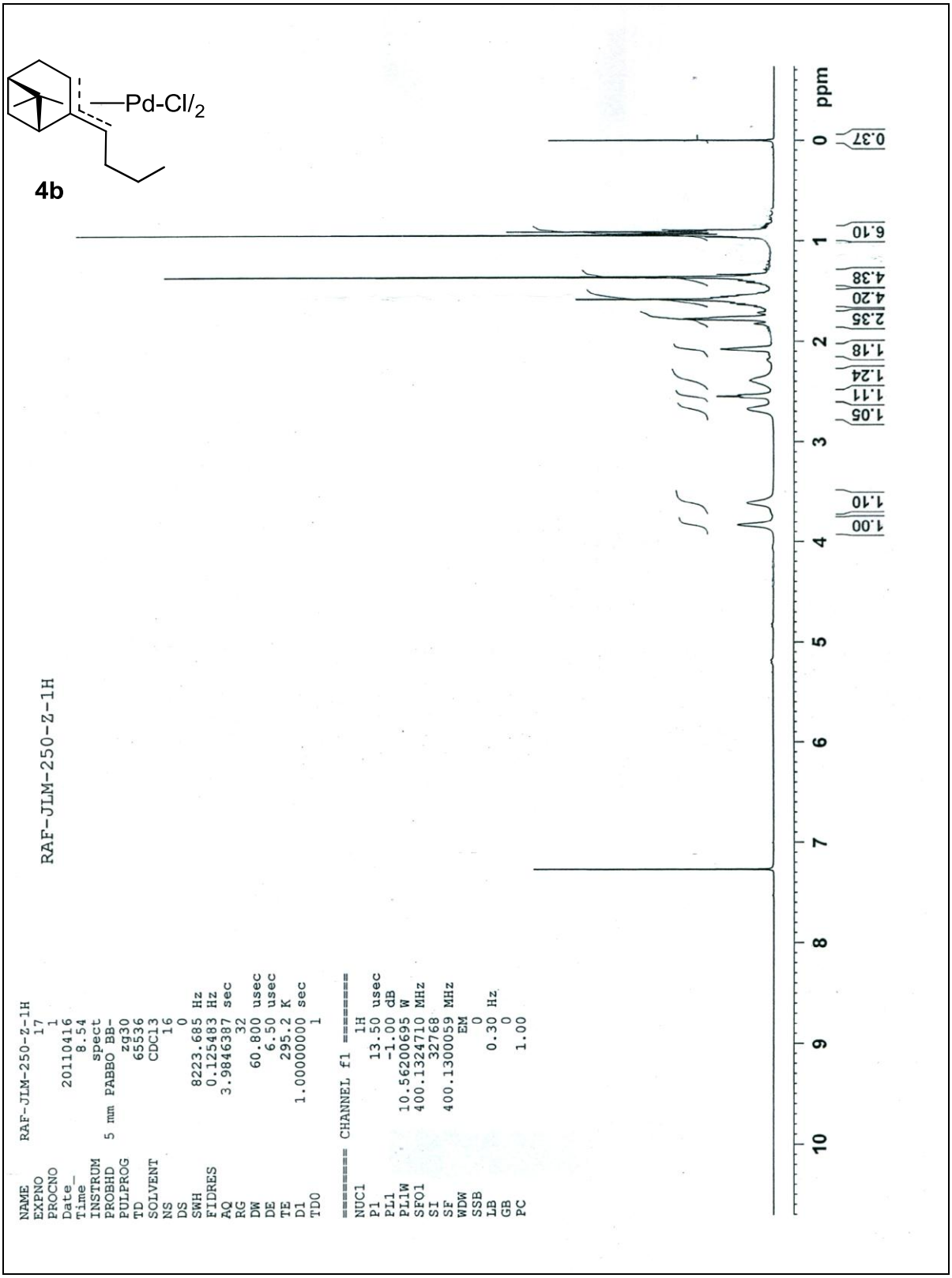
^{1}H NMR of π–Allylpalladium chloride complex 5a



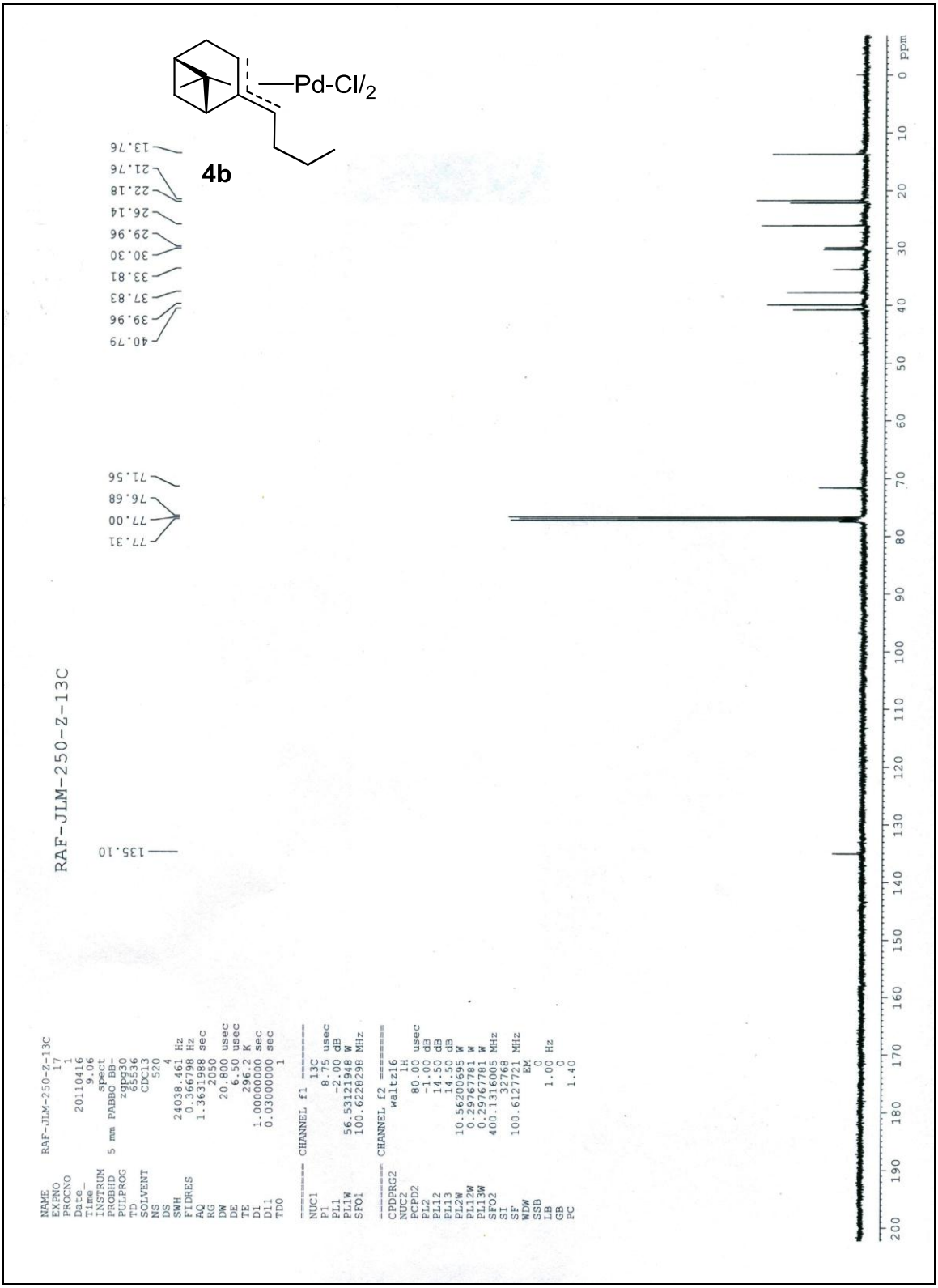
^{13}C NMR of π–Allylpalladium chloride complex 5a



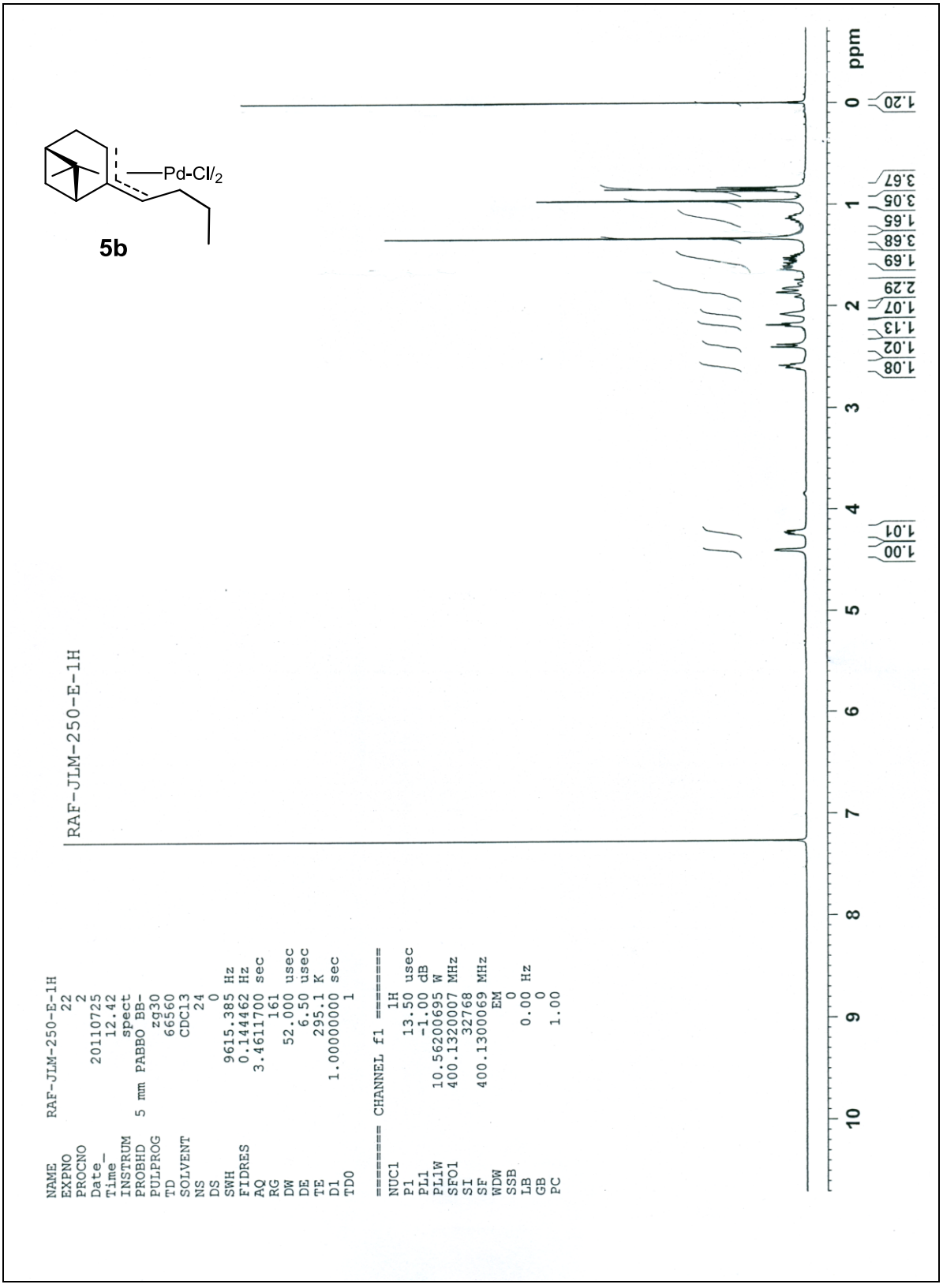
^{1}H NMR of π–Allylpalladium chloride complex 4b



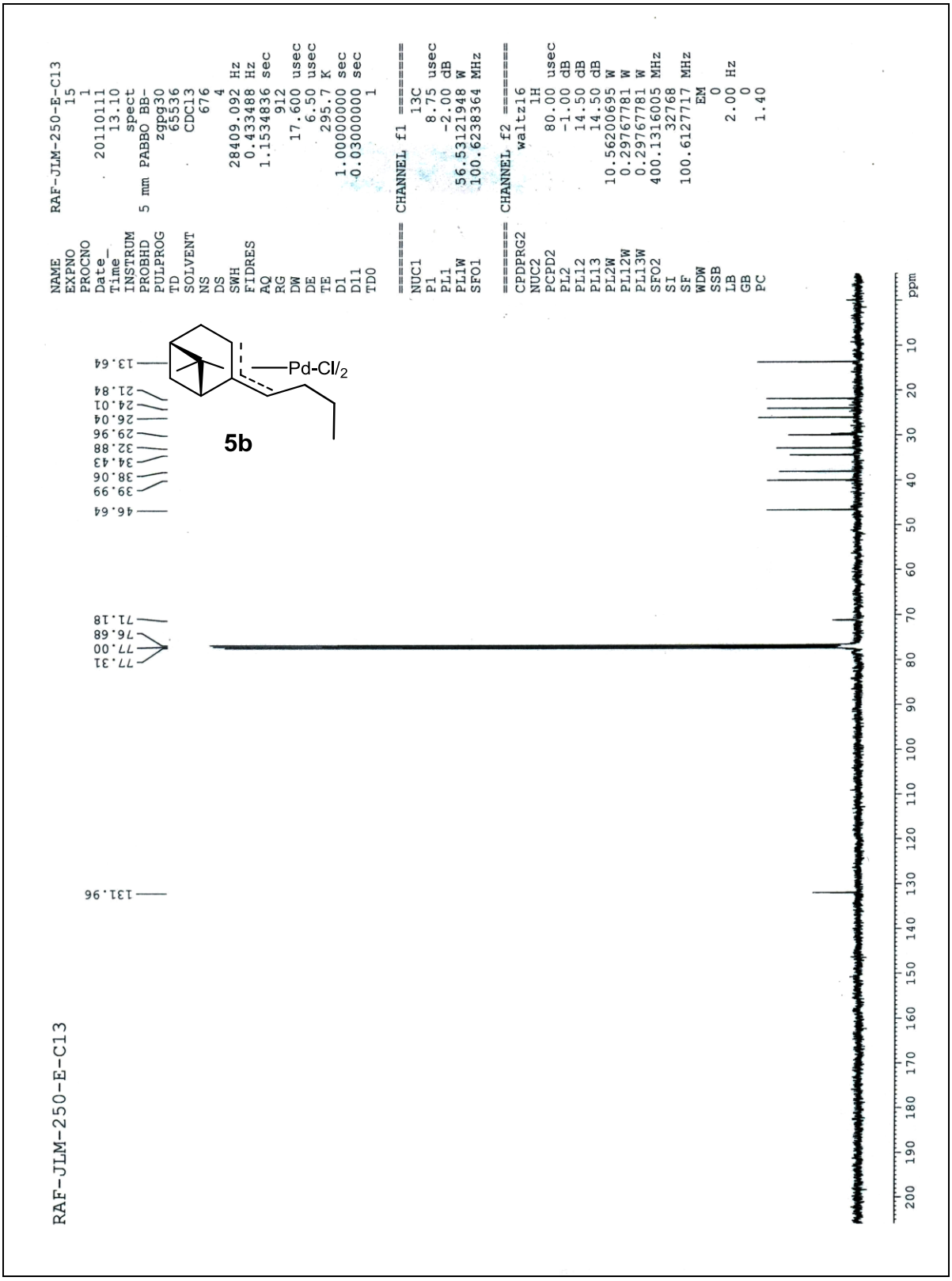
^{13}C NMR of π–Allylpalladium chloride complex 4b



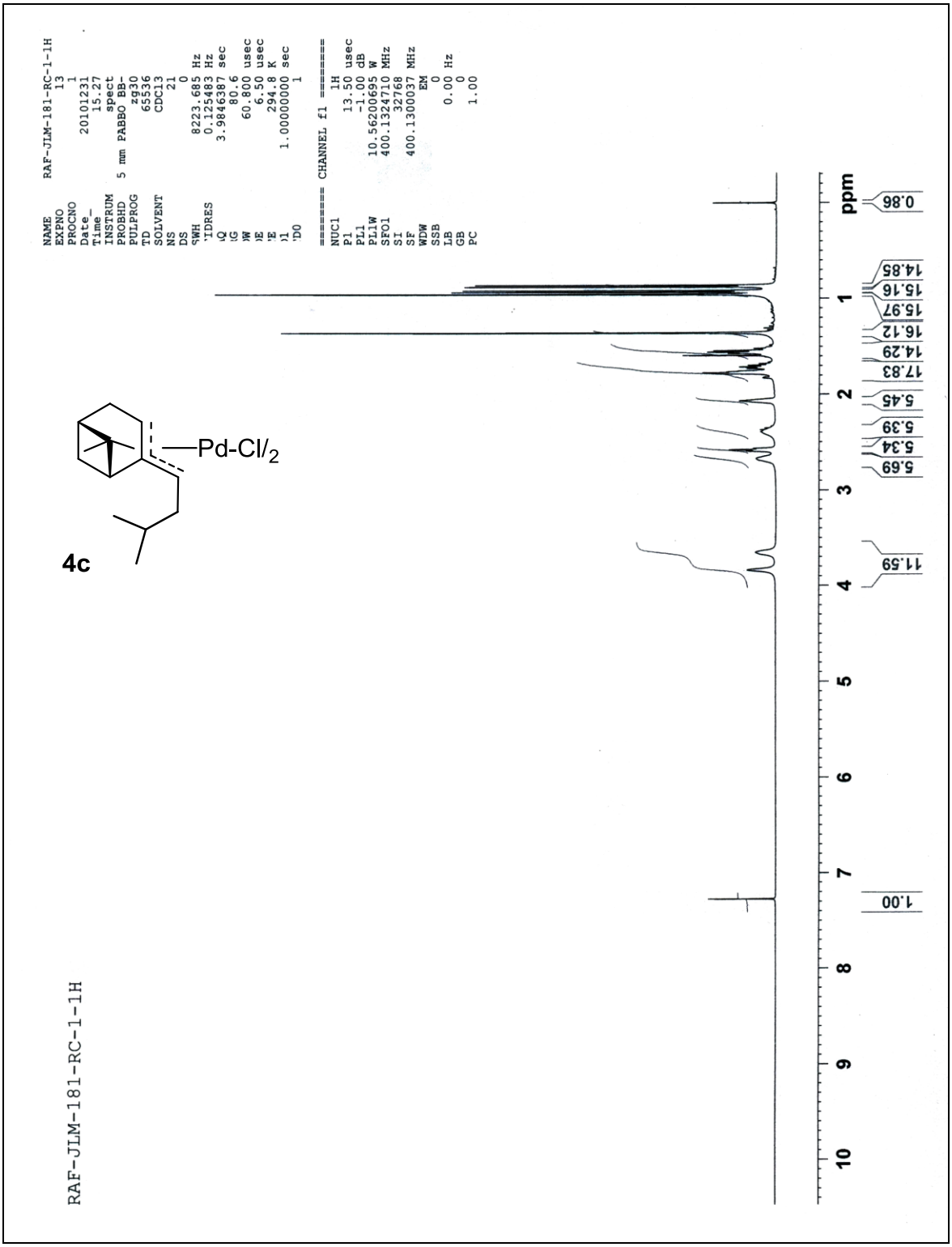
^{1}H NMR of π–Allylpalladium chloride complex 5b



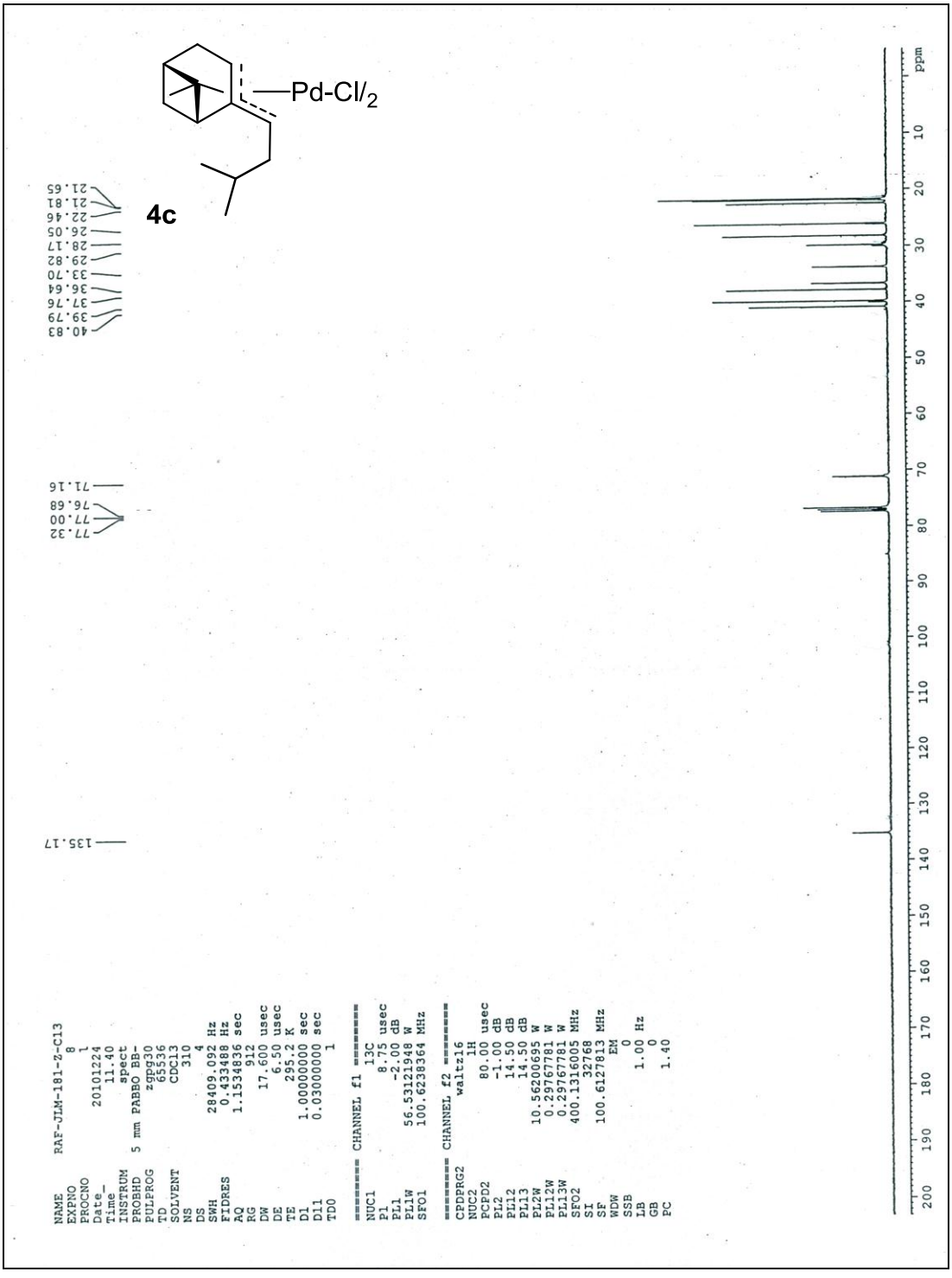
^{13}C NMR of π–Allylpalladium chloride complex 5b



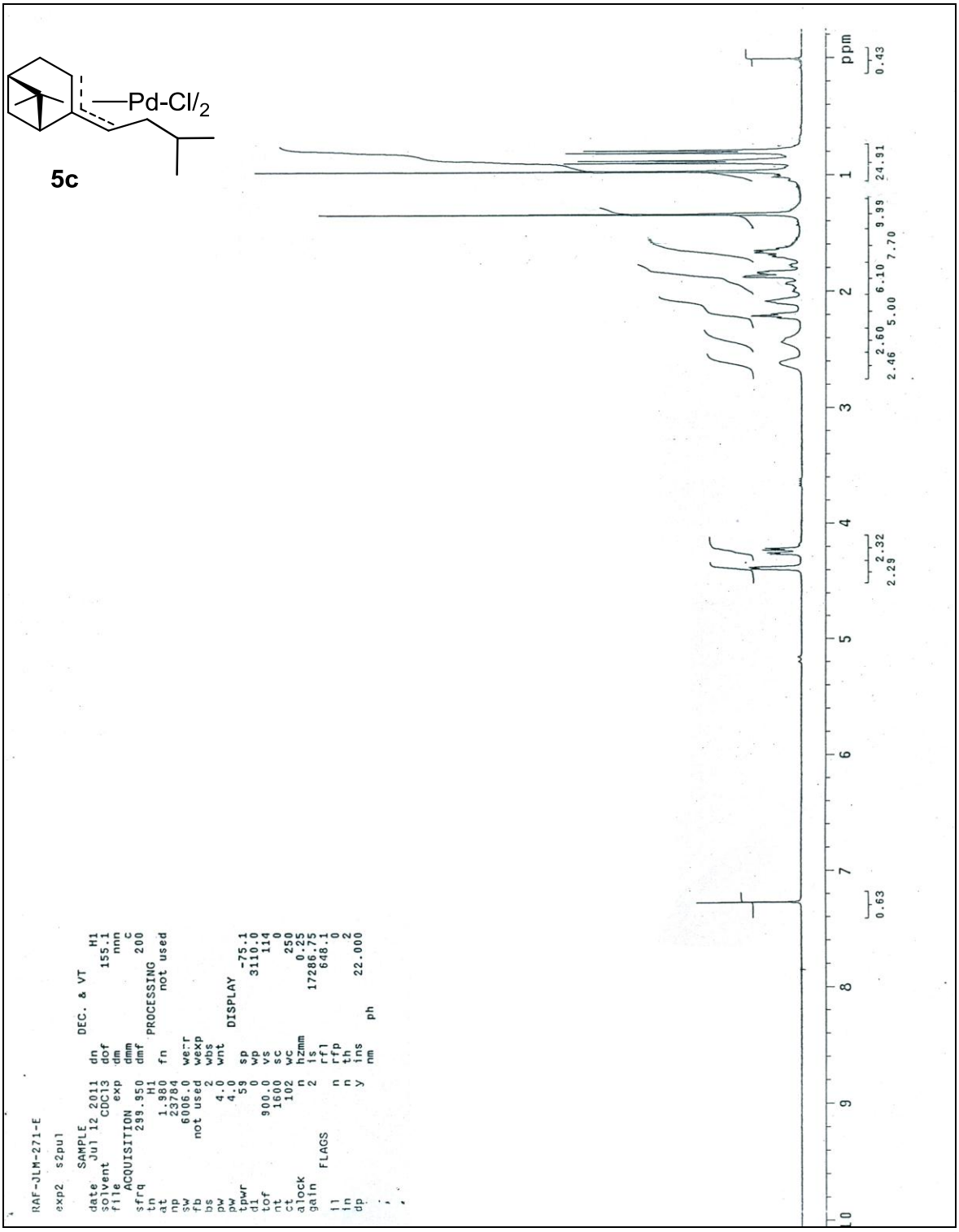
^{1}H NMR of π–Allylpalladium chloride complex 4c



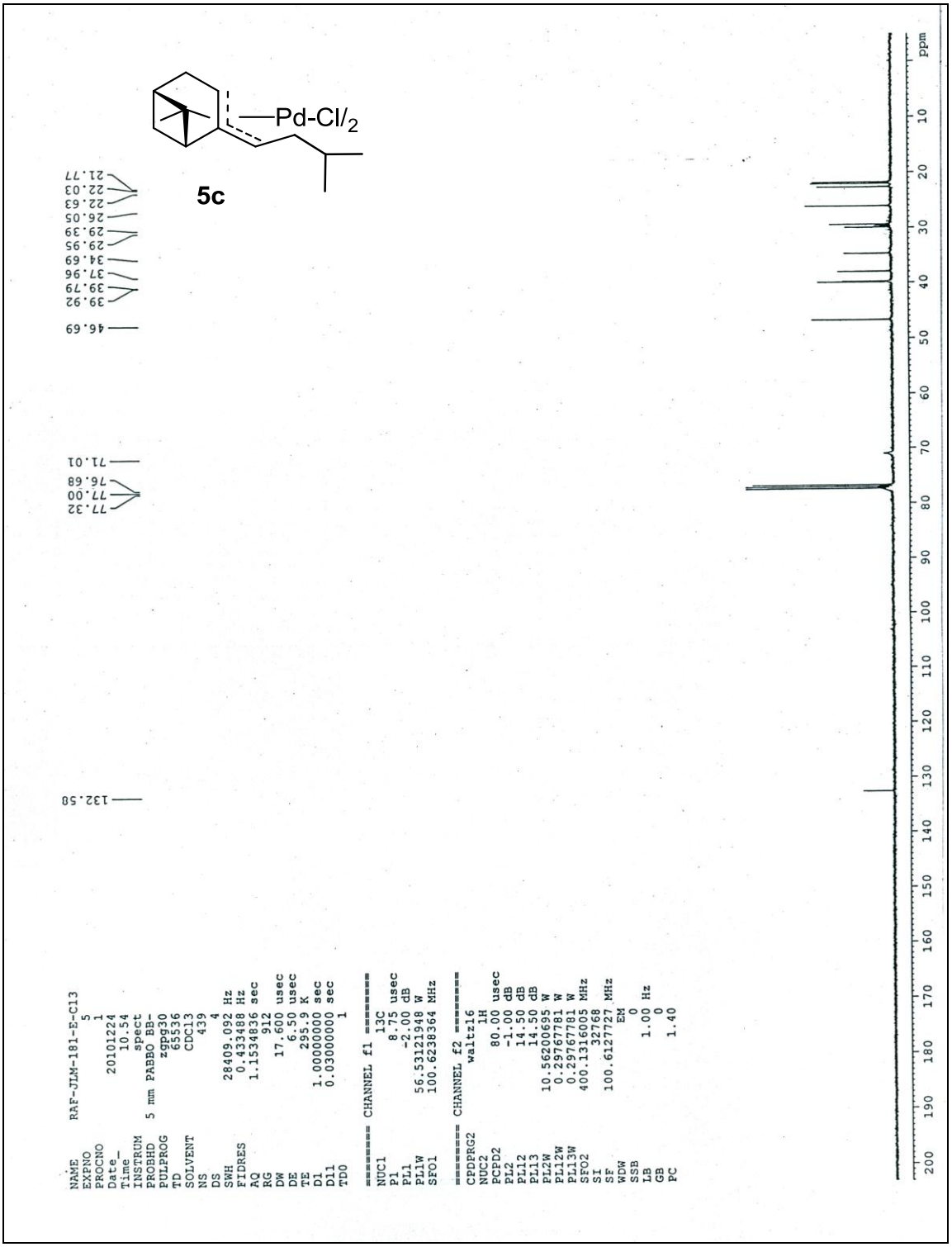
^{13}C NMR of π–Allylpalladium chloride complex 4c



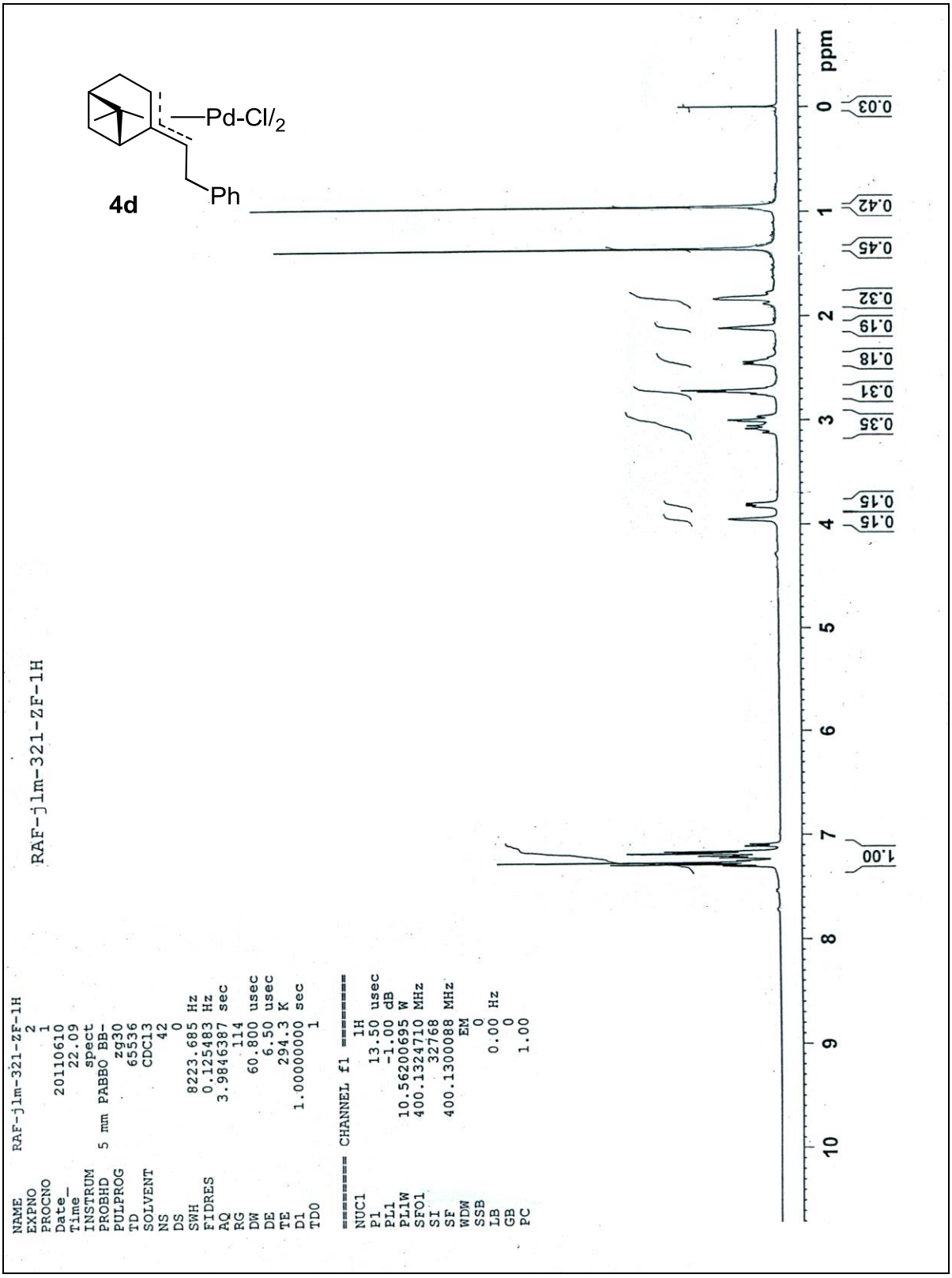
^{1}H NMR of π–Allylpalladium chloride complex 5c



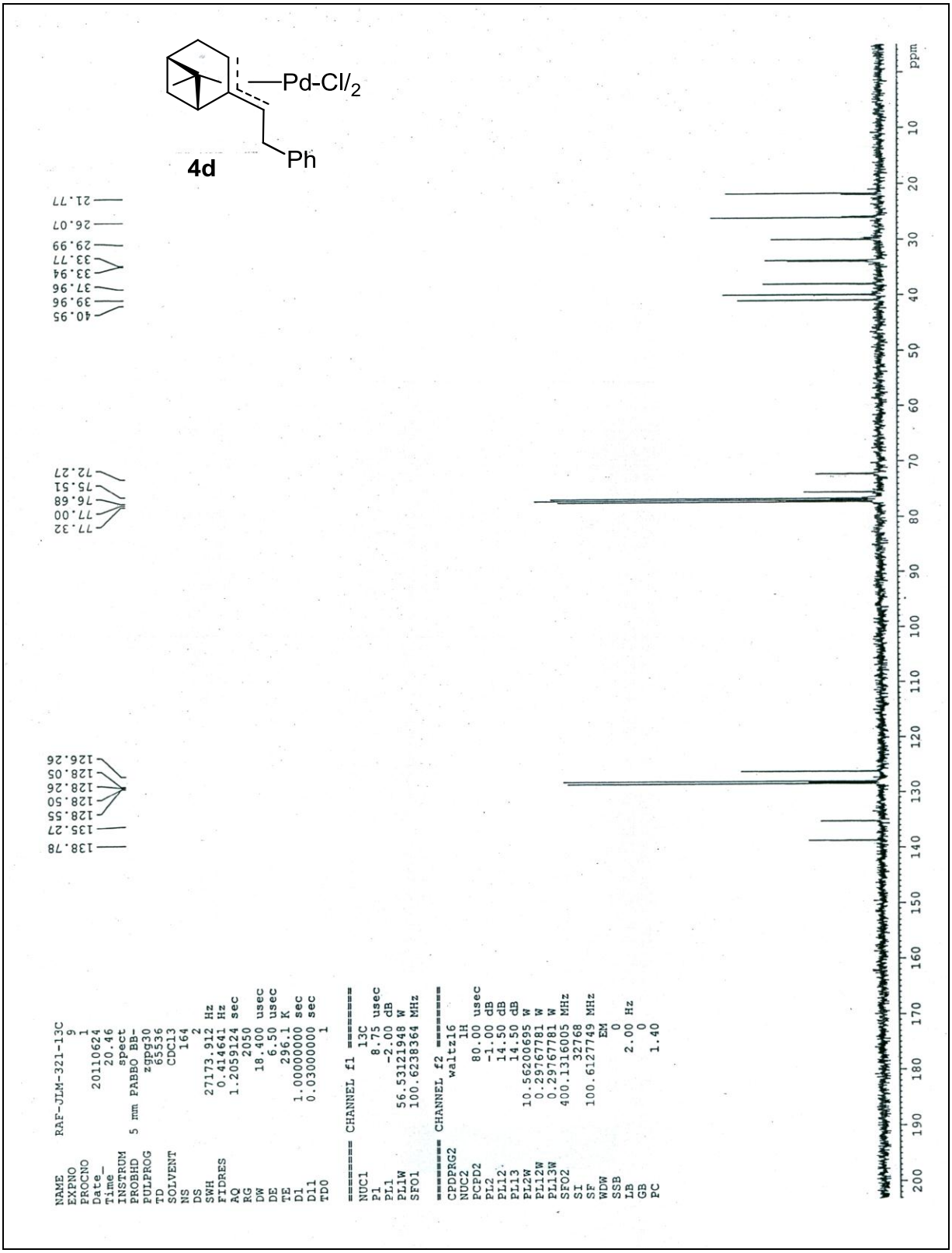
^{13}C NMR of π–Allylpalladium chloride complex 5c



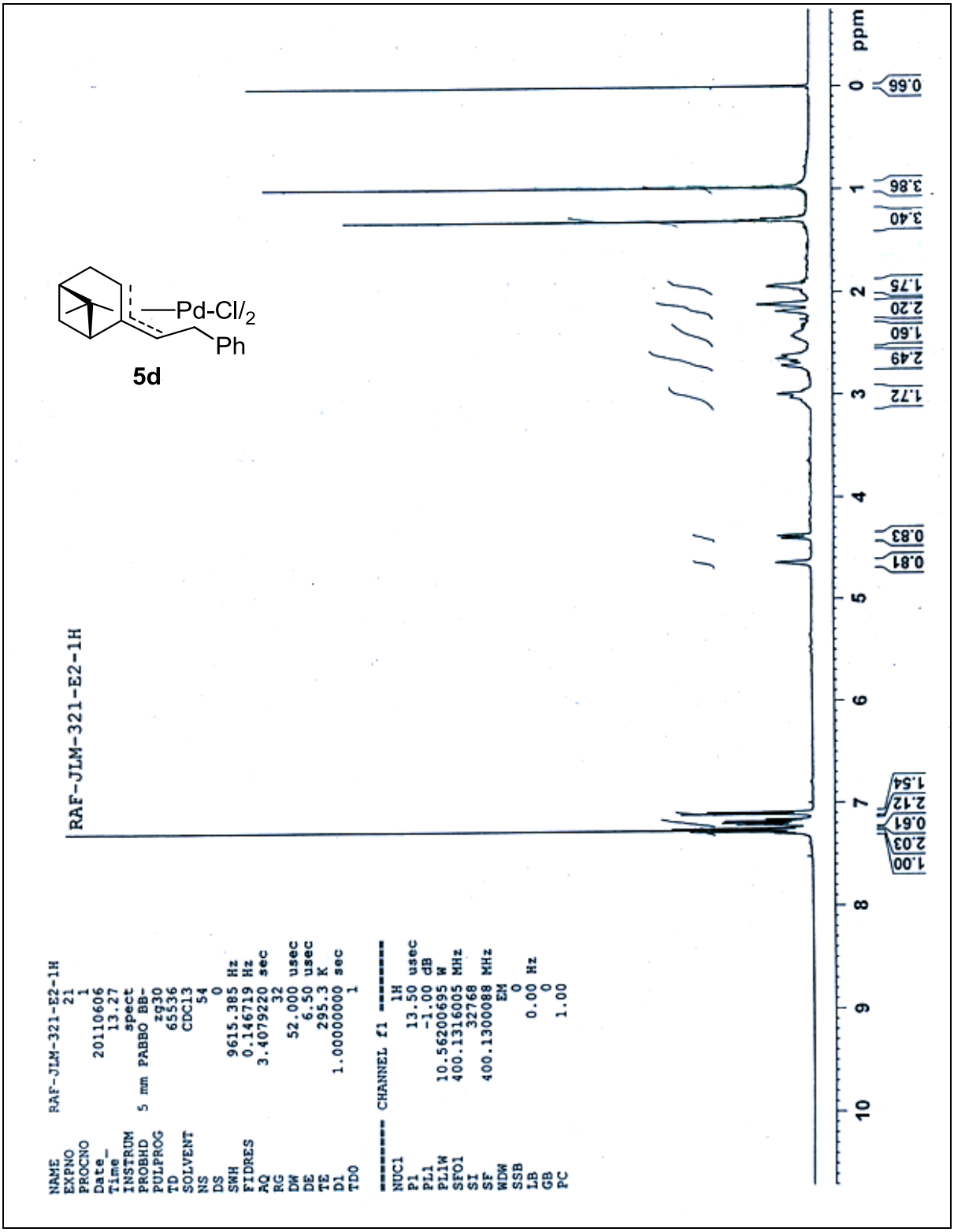
^{1}H NMR of π–Allylpalladium chloride complex 4d



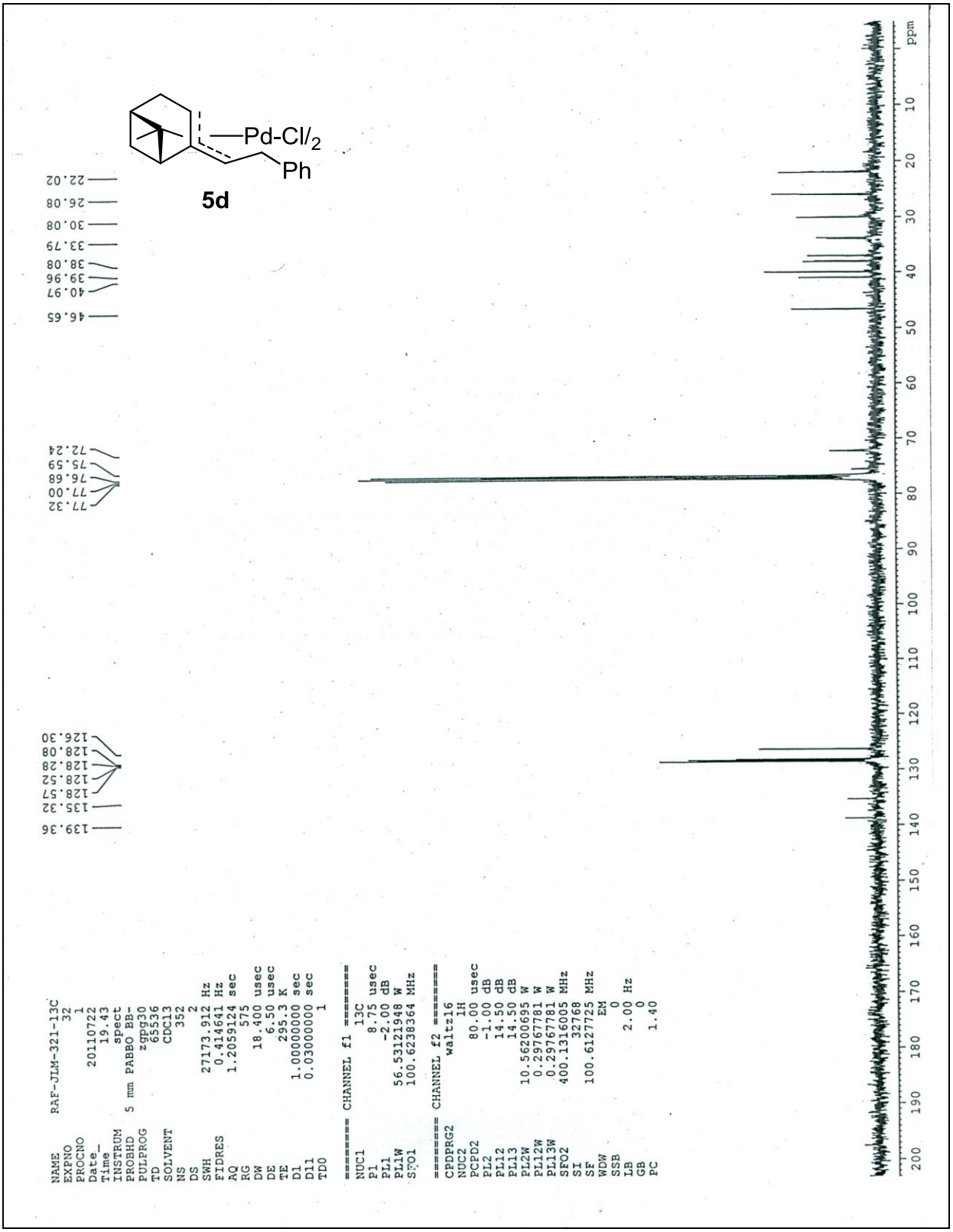
^{13}C NMR of π–Allylpalladium chloride complex 4d



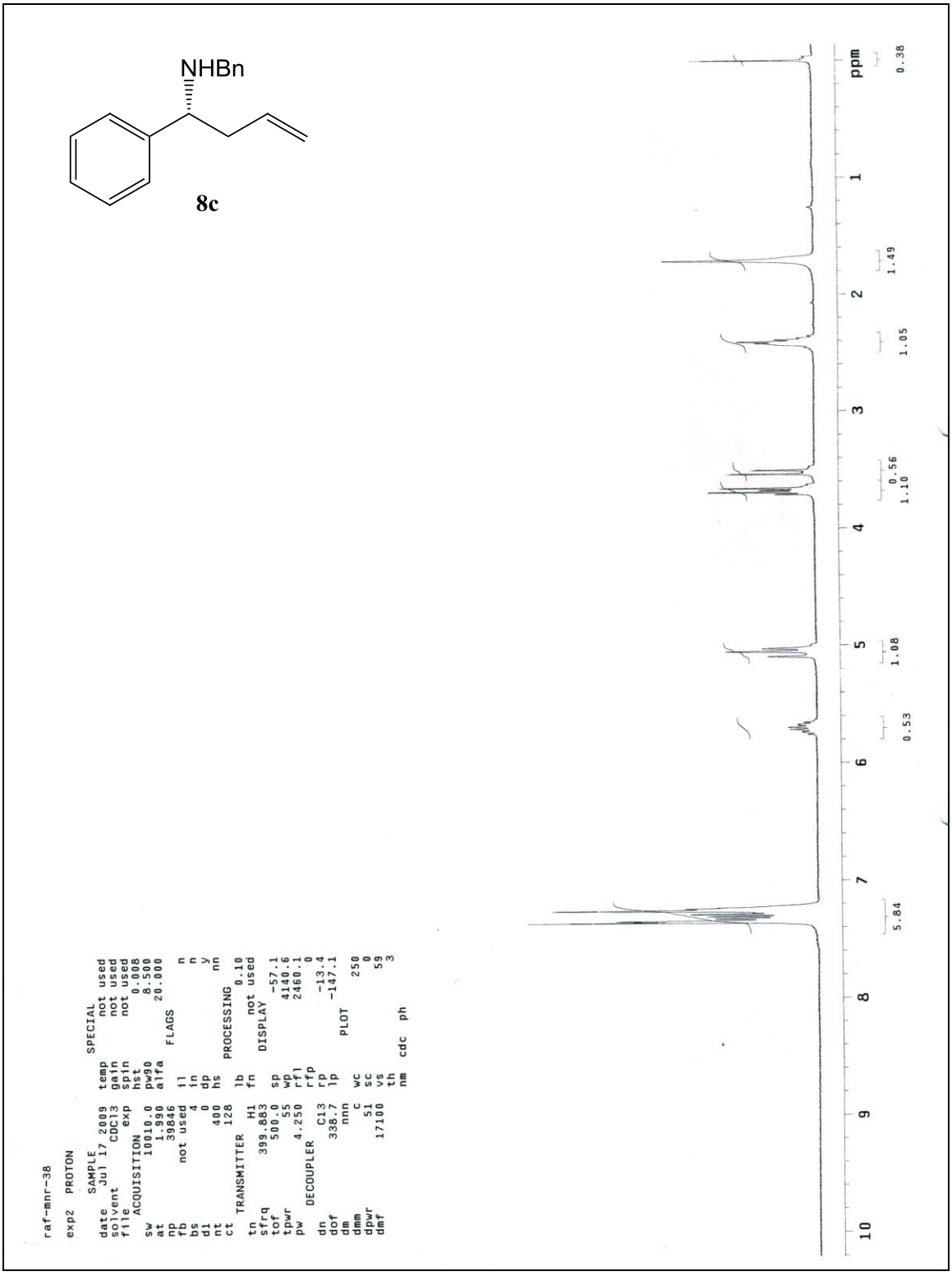
^{1}H NMR of π–Allylpalladium chloride complex 5d



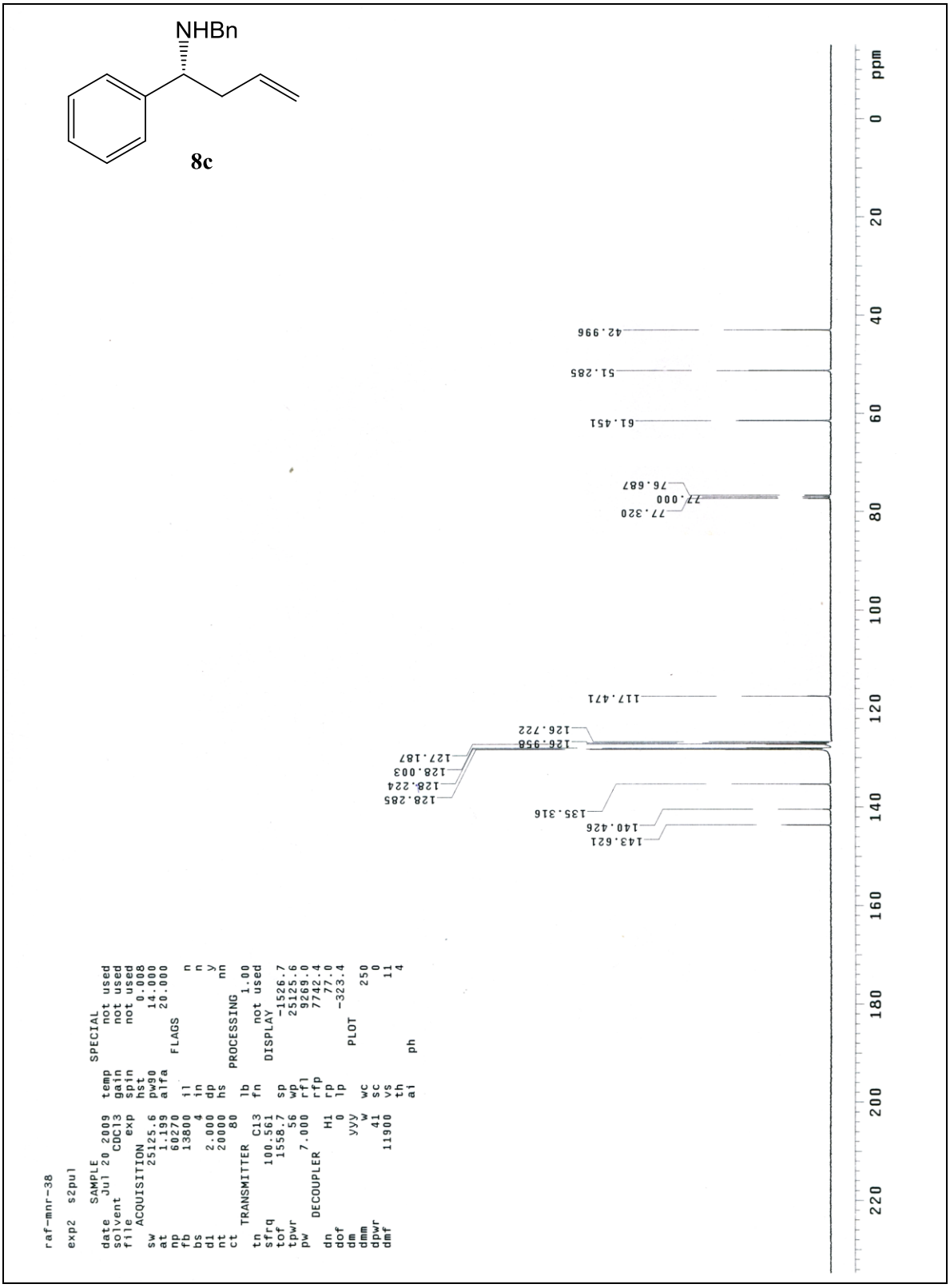
^{13}C NMR of π–Allylpalladium chloride complex 5d



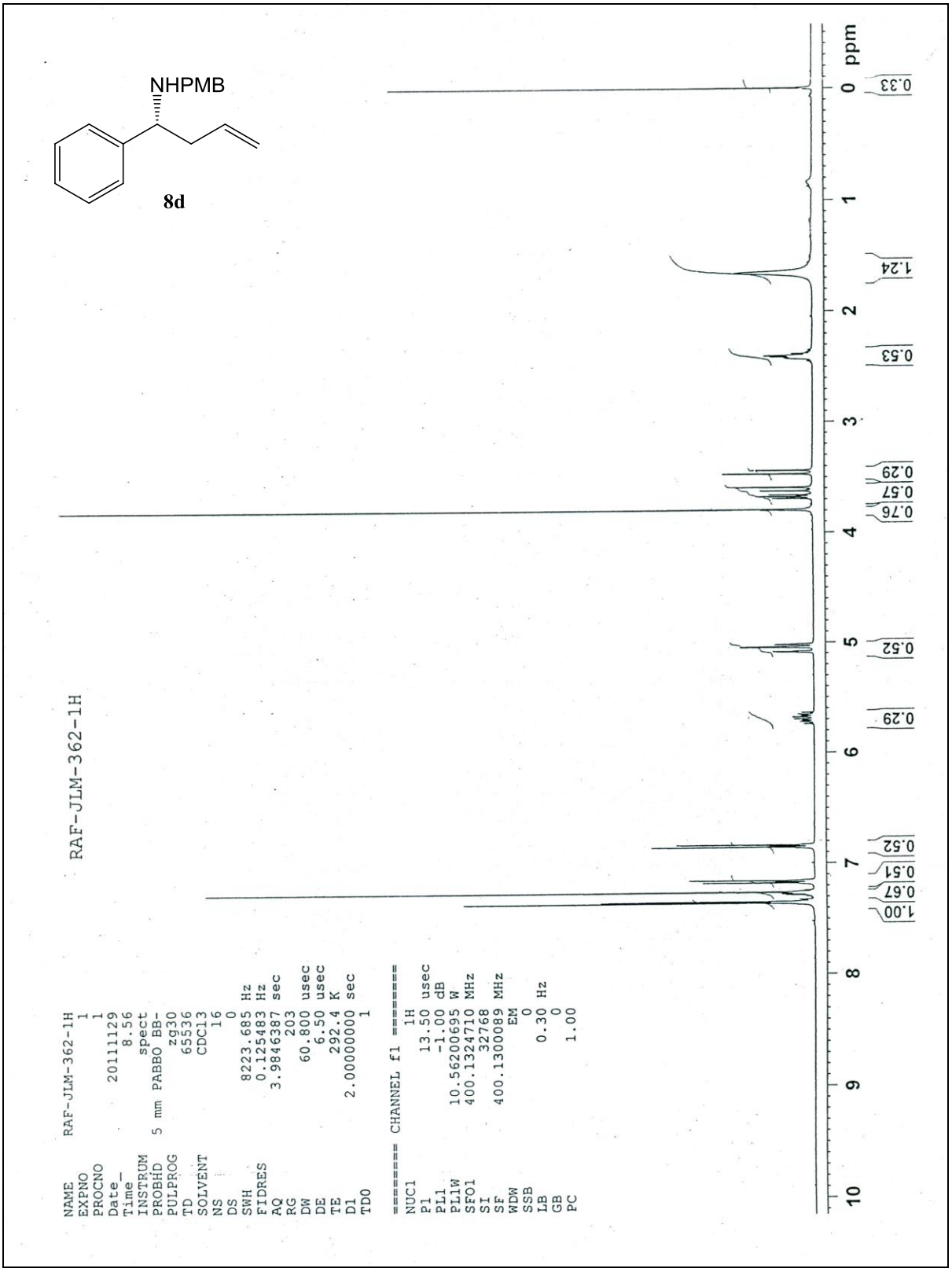
^{1}H NMR of (*R*)-*N*-Benzyl-1-phenyl-3-butenylamine 8c



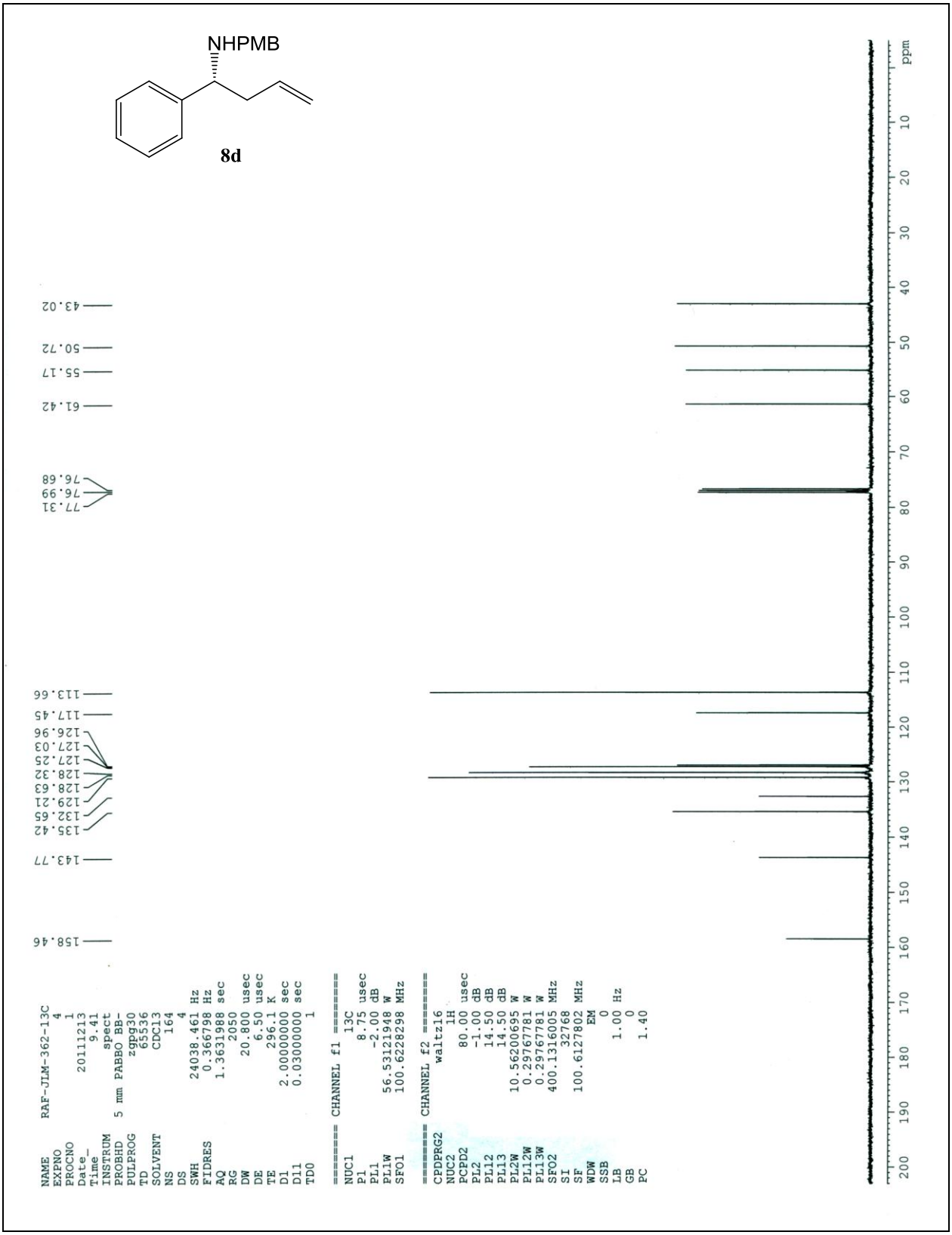
^{13}C NMR of (*R*)-*N*-Benzyl-1-phenyl-3-butenylamine 8c



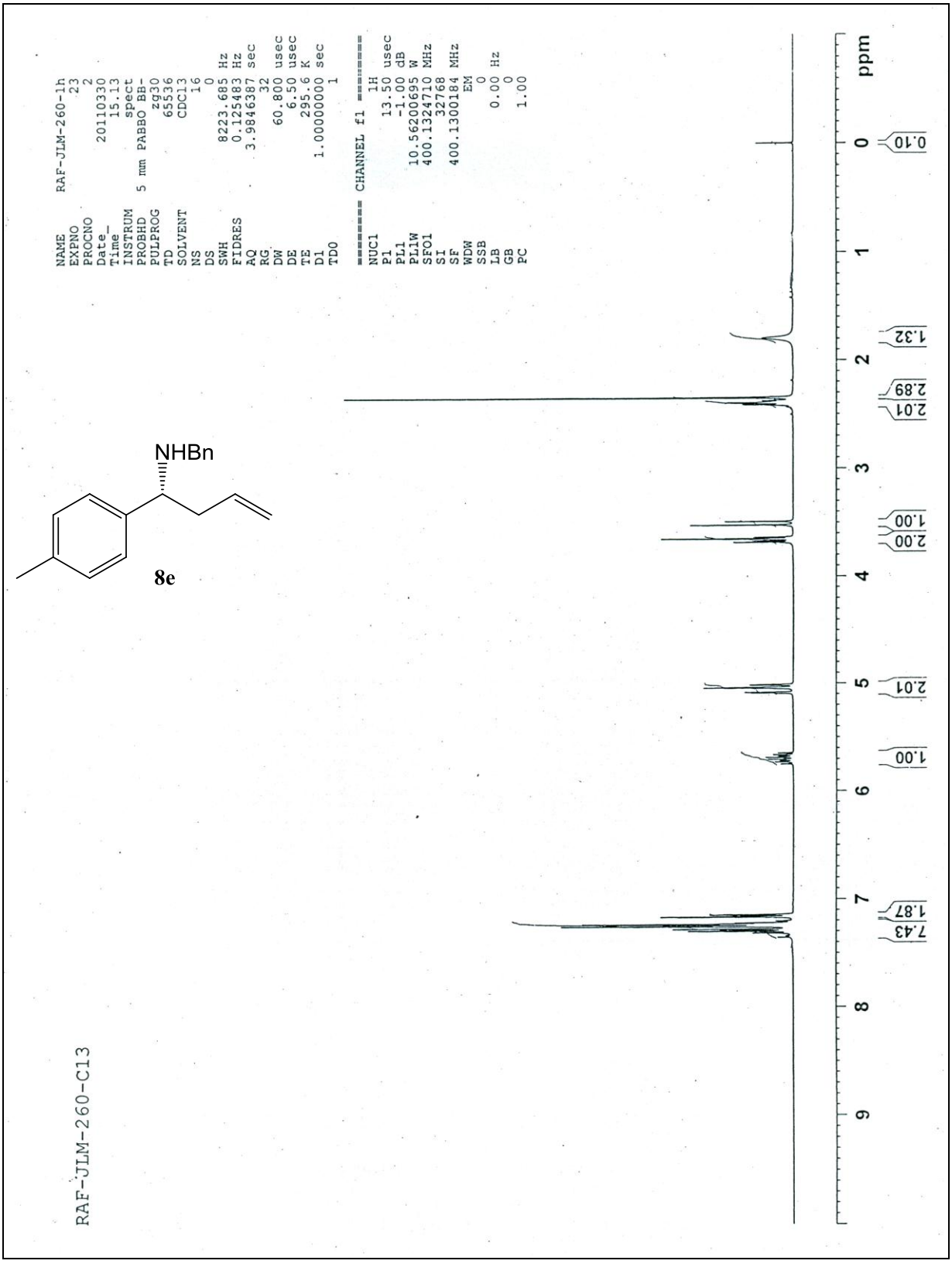
^{1}H NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-phenyl-3-butenylamine 8d



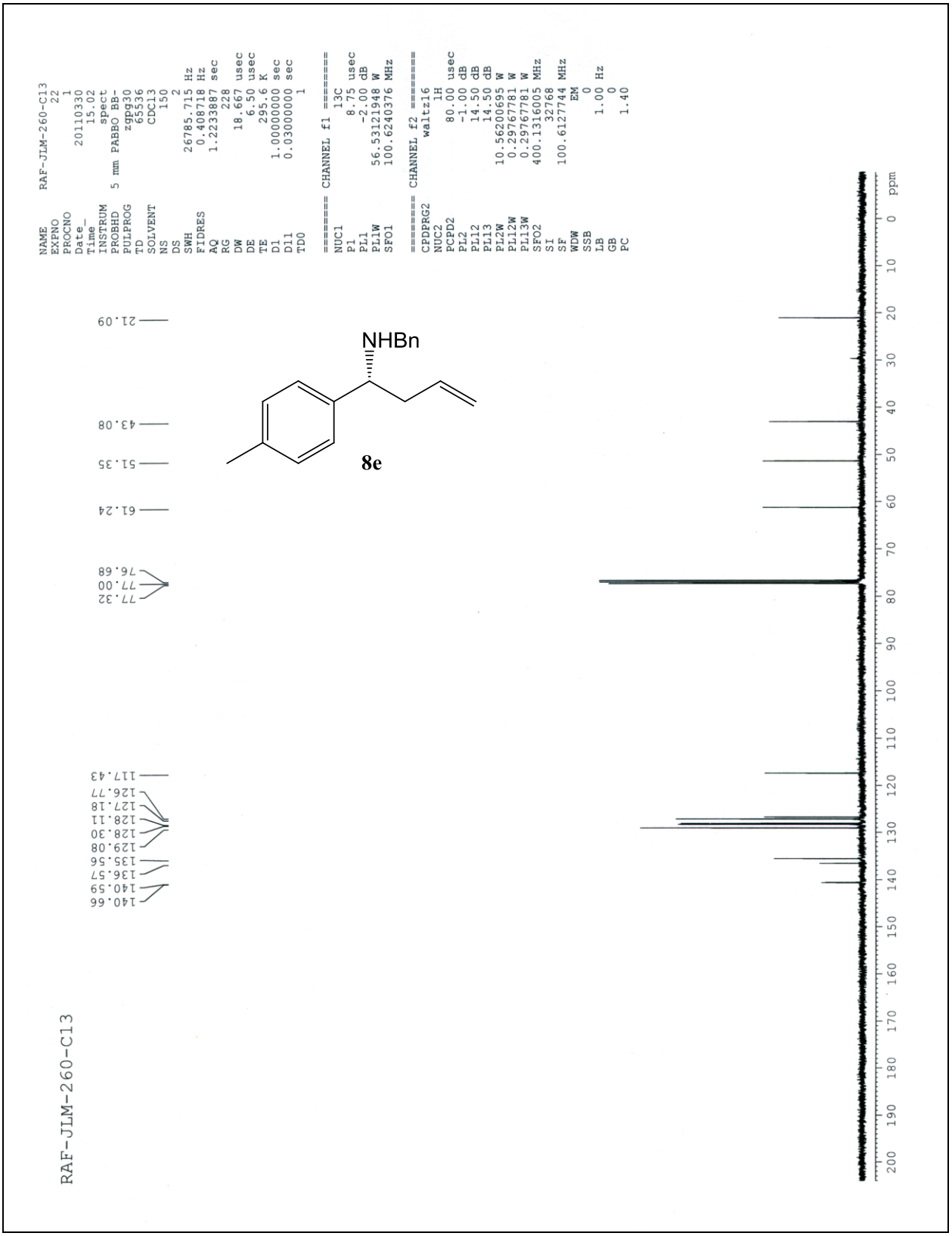
^{13}C NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-phenyl-3-butenylamine 8d



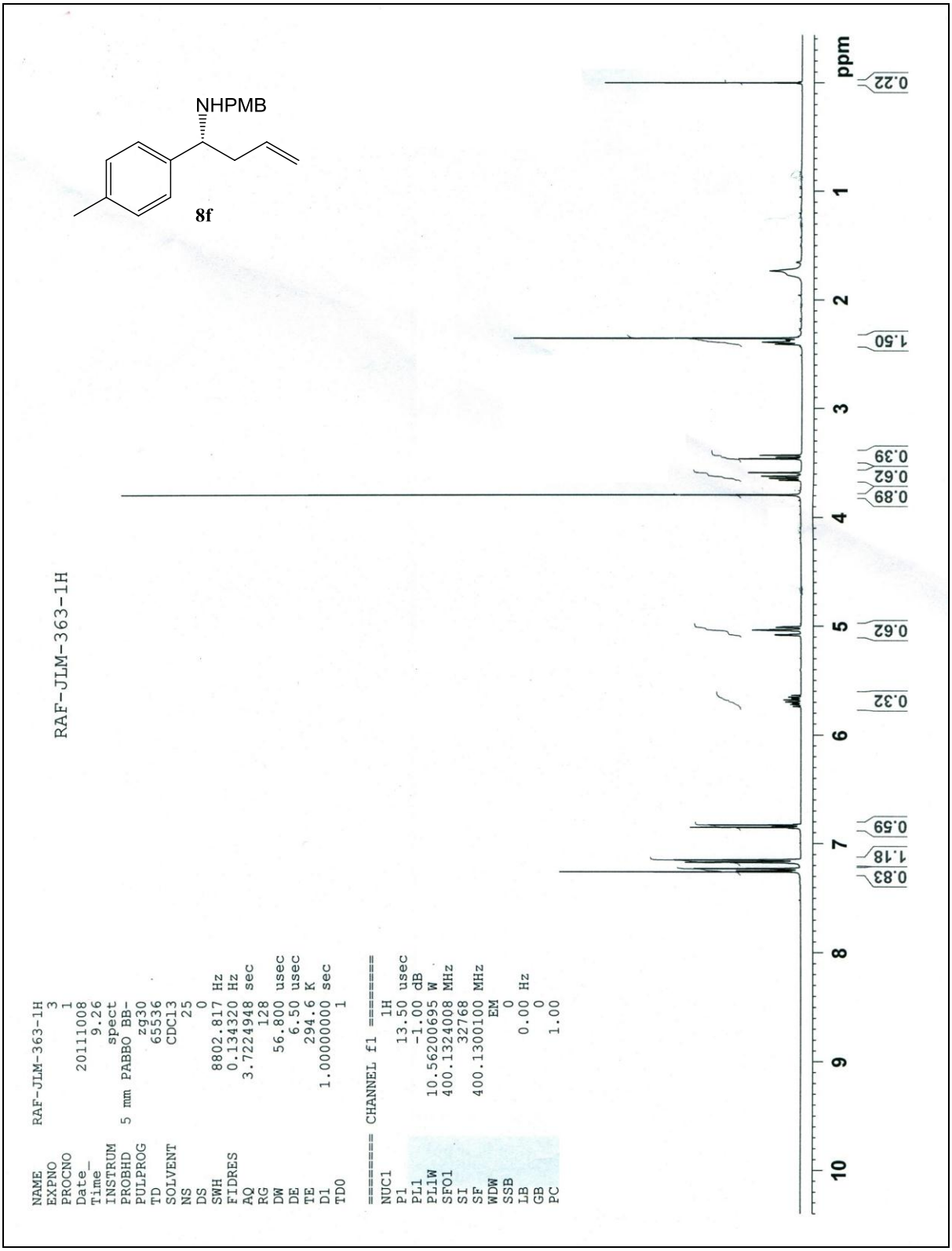
^{1}H NMR of (*R*)-*N*-Benzyl-1-(4-methylphenyl)-3-butenylamine 8e



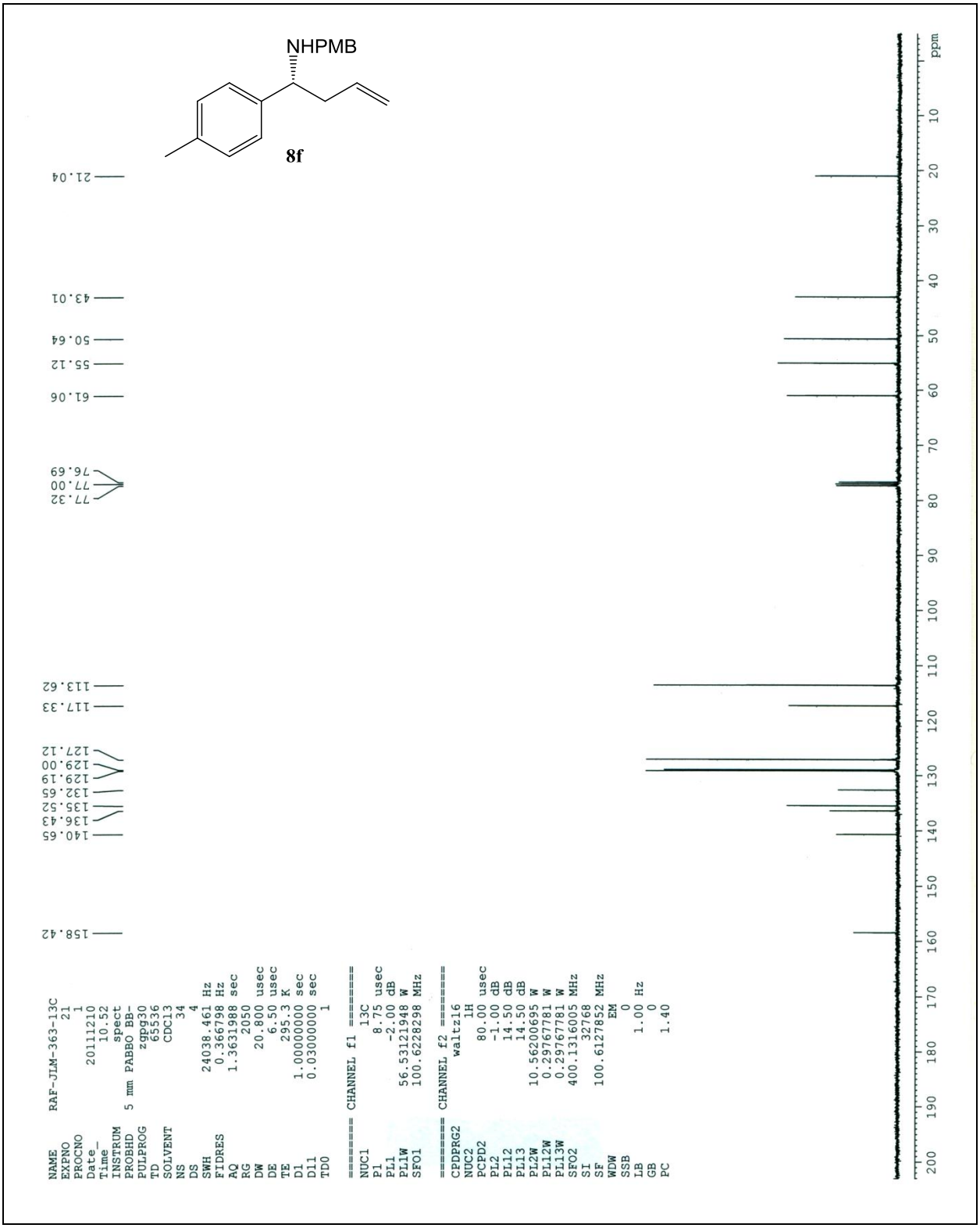
^{13}C NMR of (*R*)-*N*-Benzyl-1-(4-methylphenyl)-3-butenylamine 8e



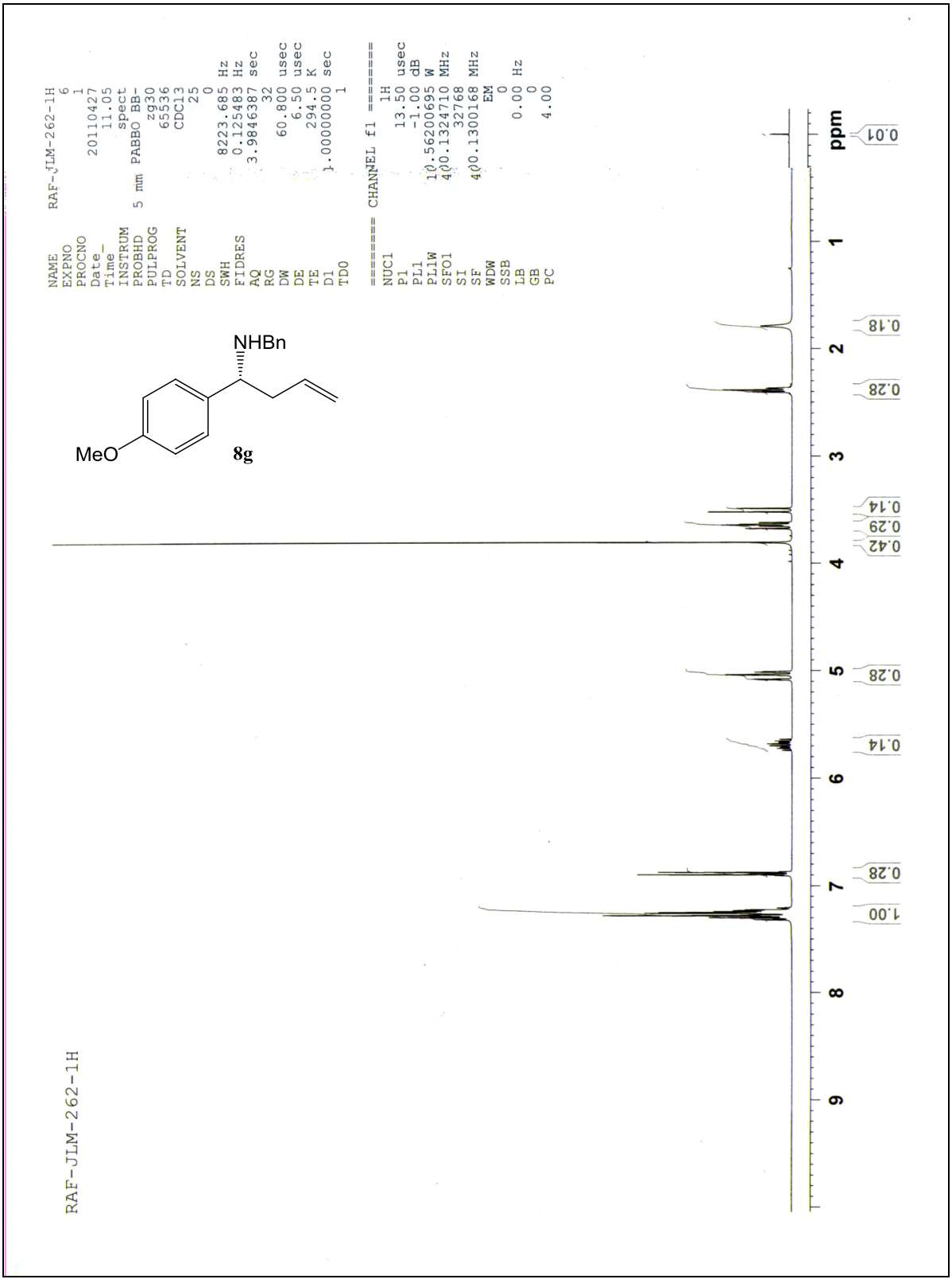
^{1}H NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-(4-methylphenyl)-3-butenylamine 8f



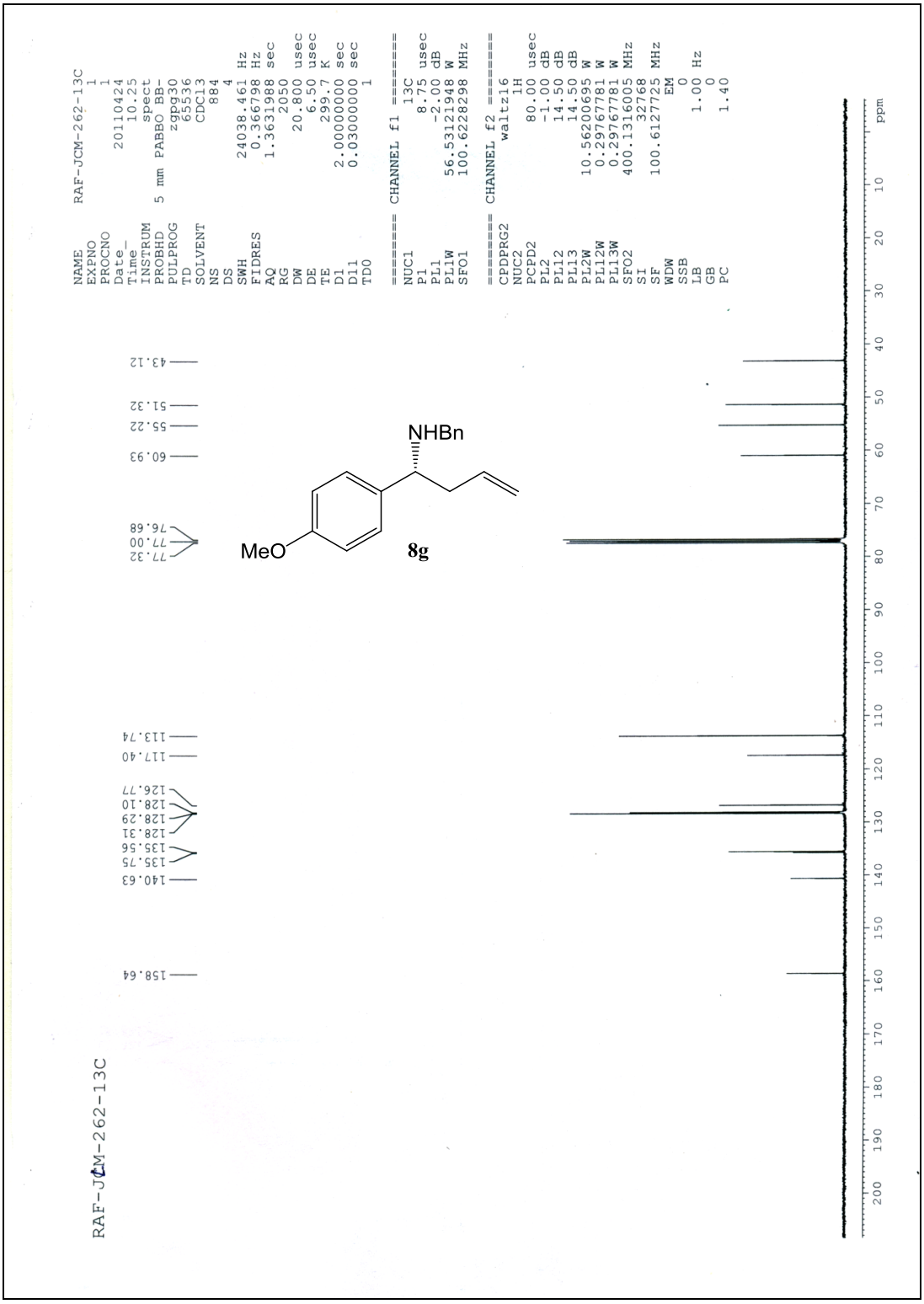
^{13}C NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-(4-methylphenyl)-3-butenylamine 8f



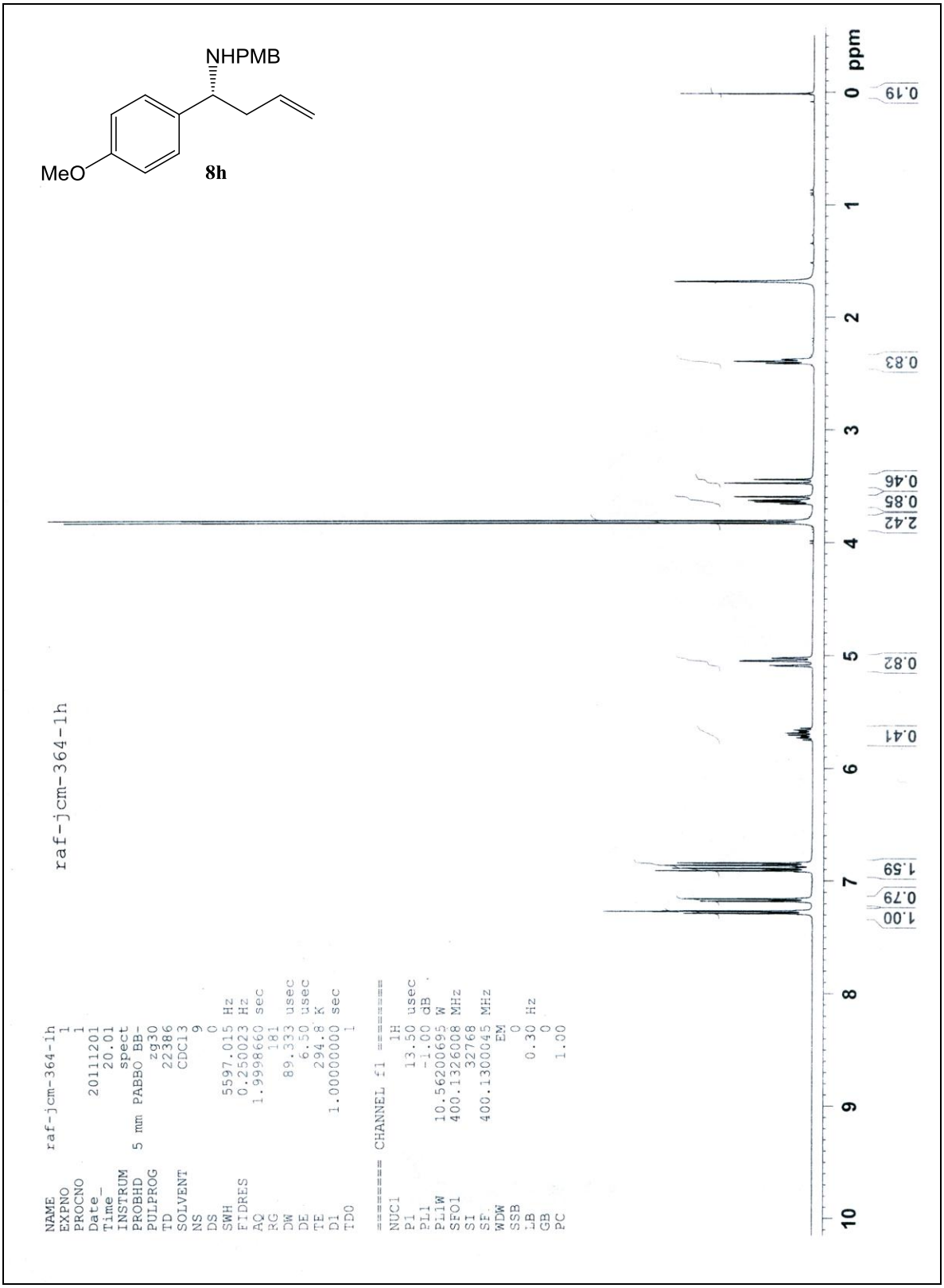
^{1}H NMR of (*R*)-*N*-Benzyl-1-(4-methoxyphenyl)-3-butenylamine 8g



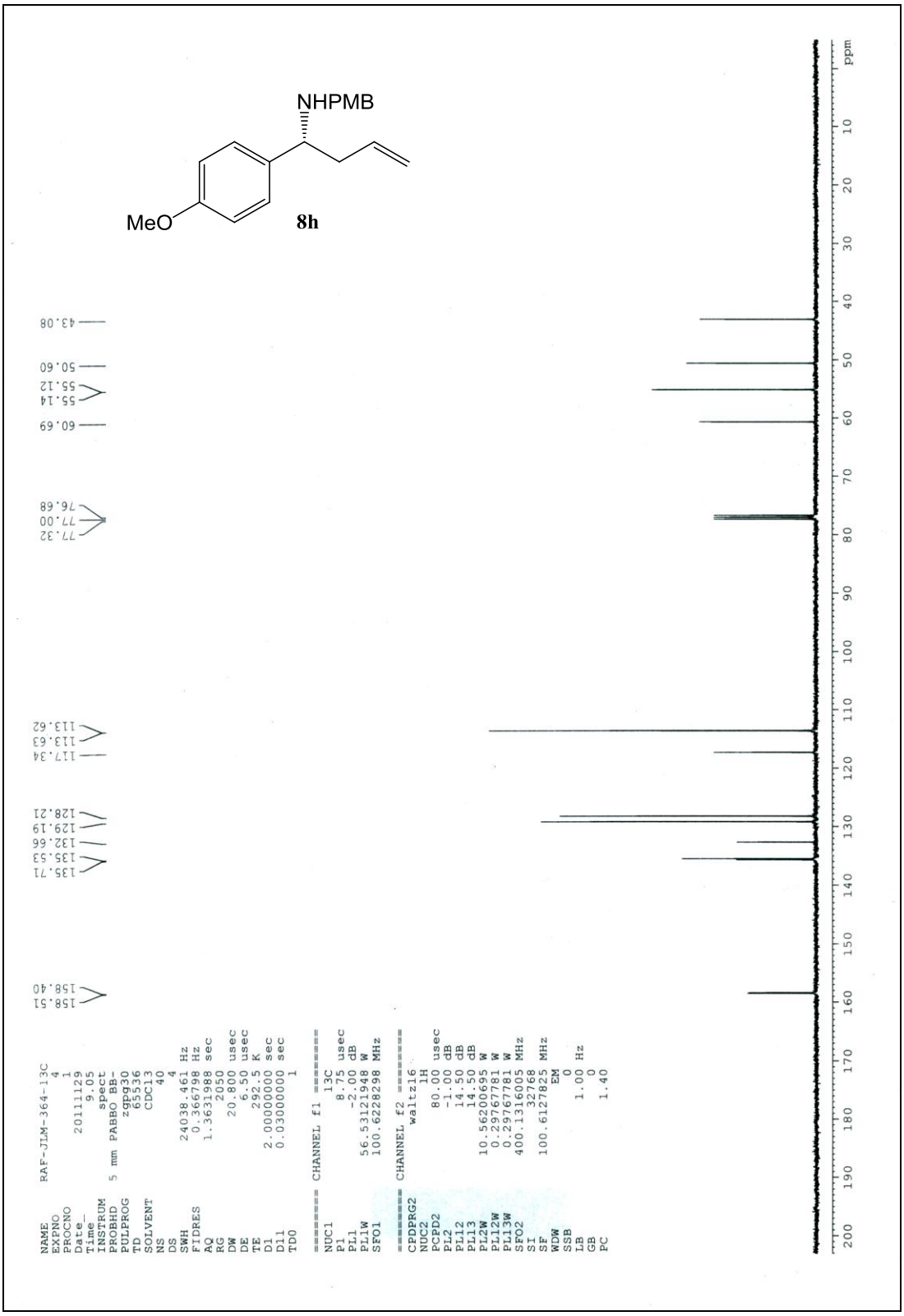
^{13}C NMR of (*R*)-*N*-Benzyl-1-(4-methoxyphenyl)-3-butenylamine 8g



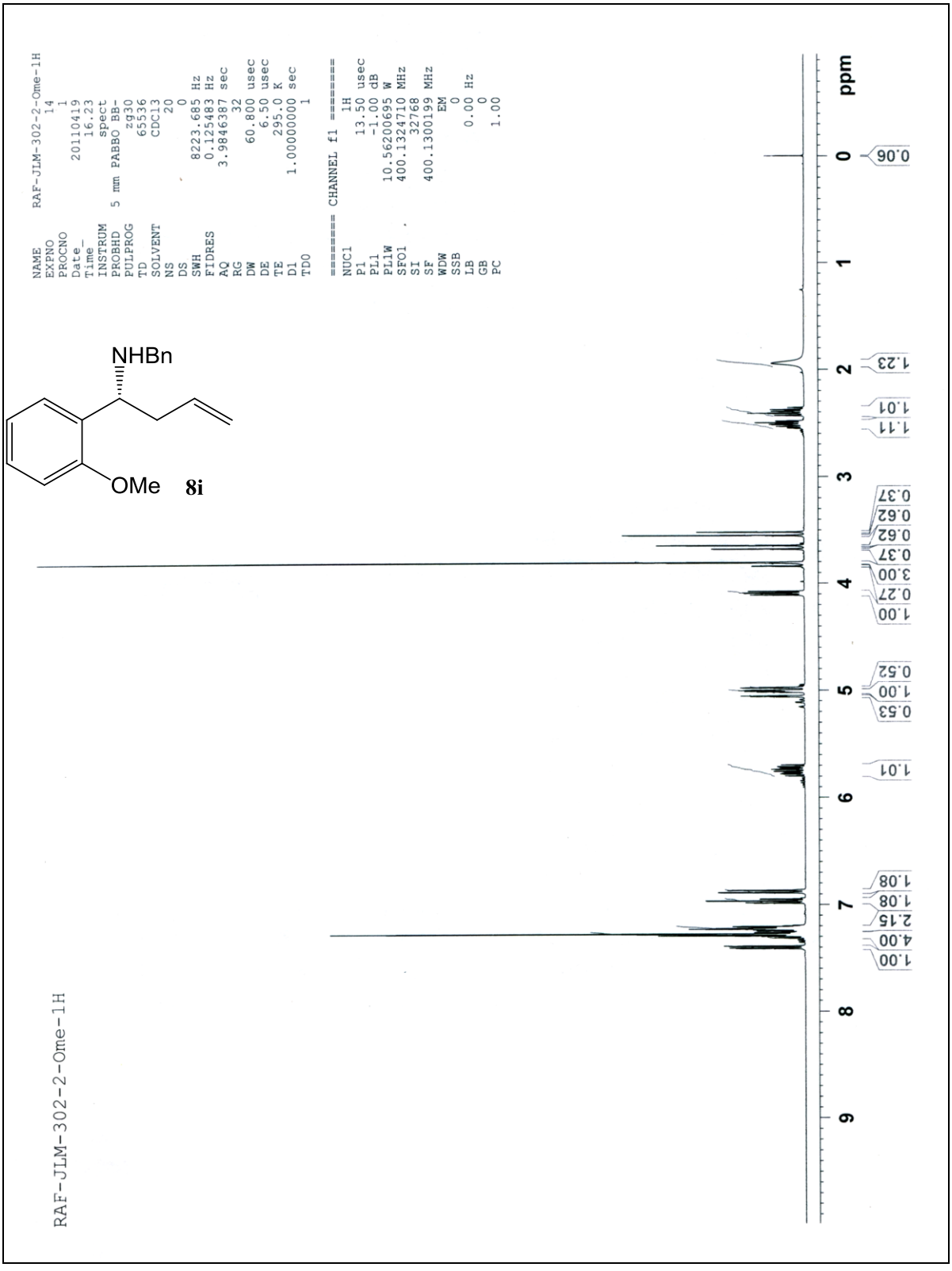
^{1}H NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-3-butenylamine 8h



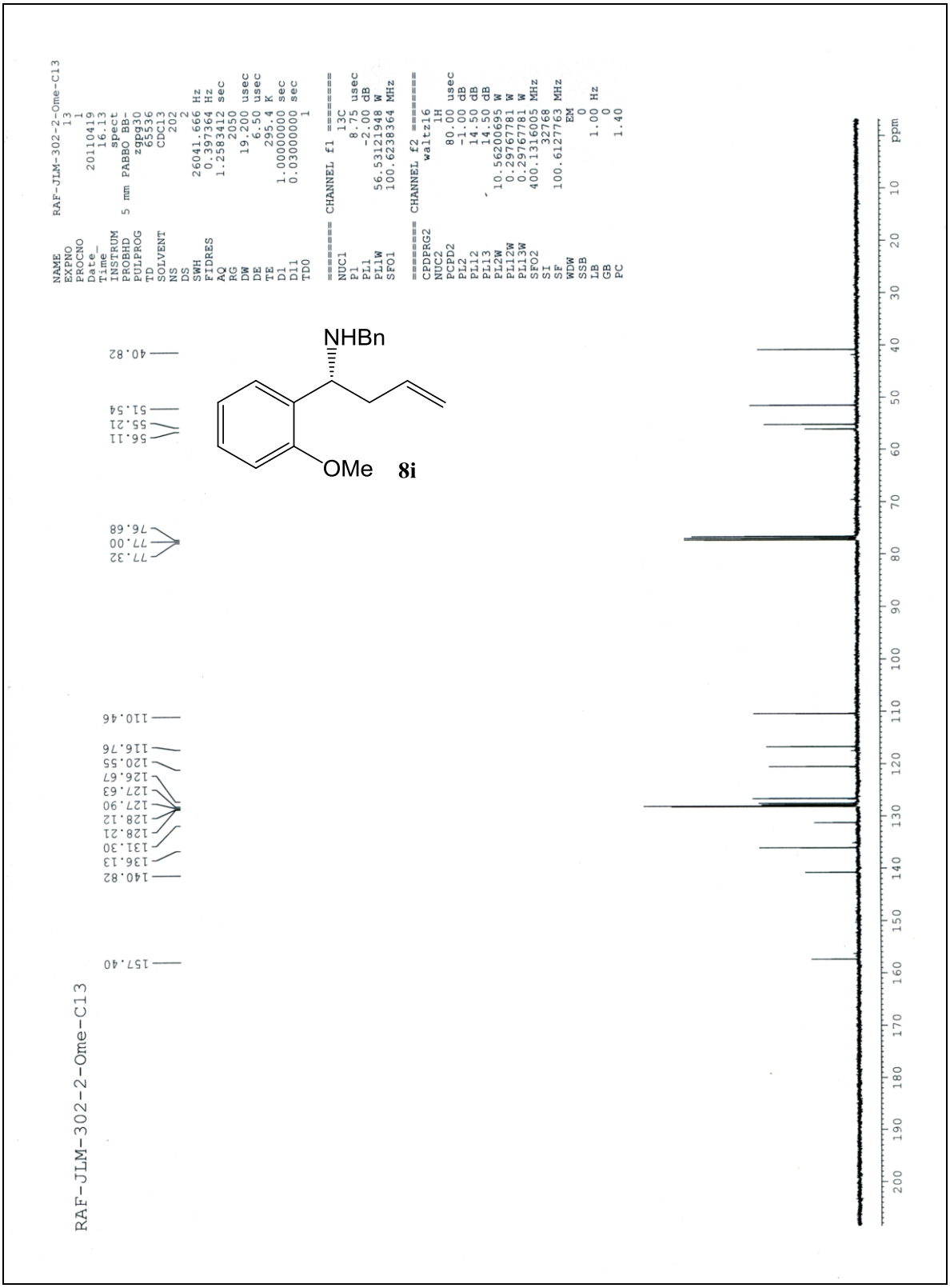
^{13}C NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-3-butenylamine 8h



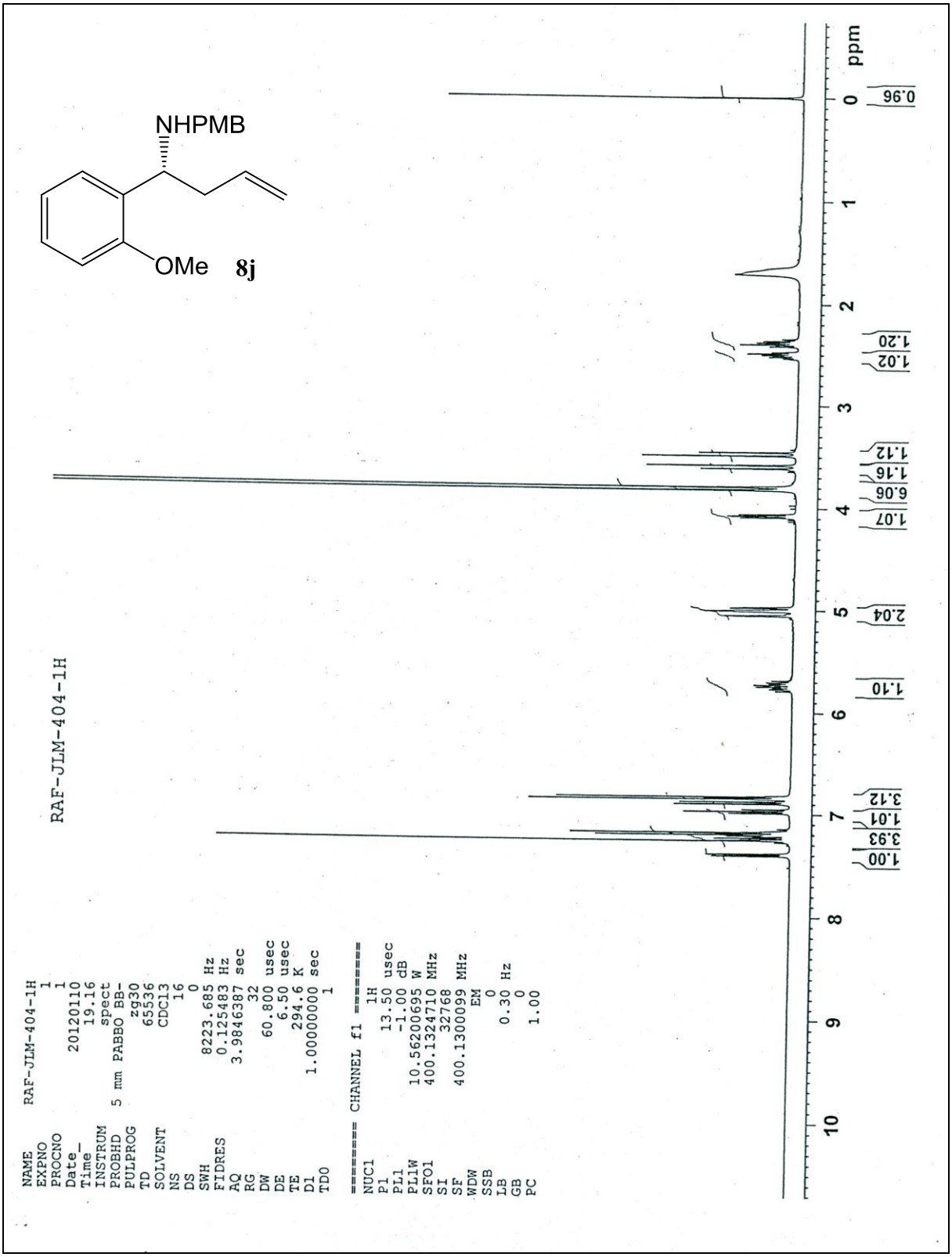
^{1}H NMR of (*R*)-*N*-Benzyl-1-(2-methoxyphenyl)-3-butenylamine 8i



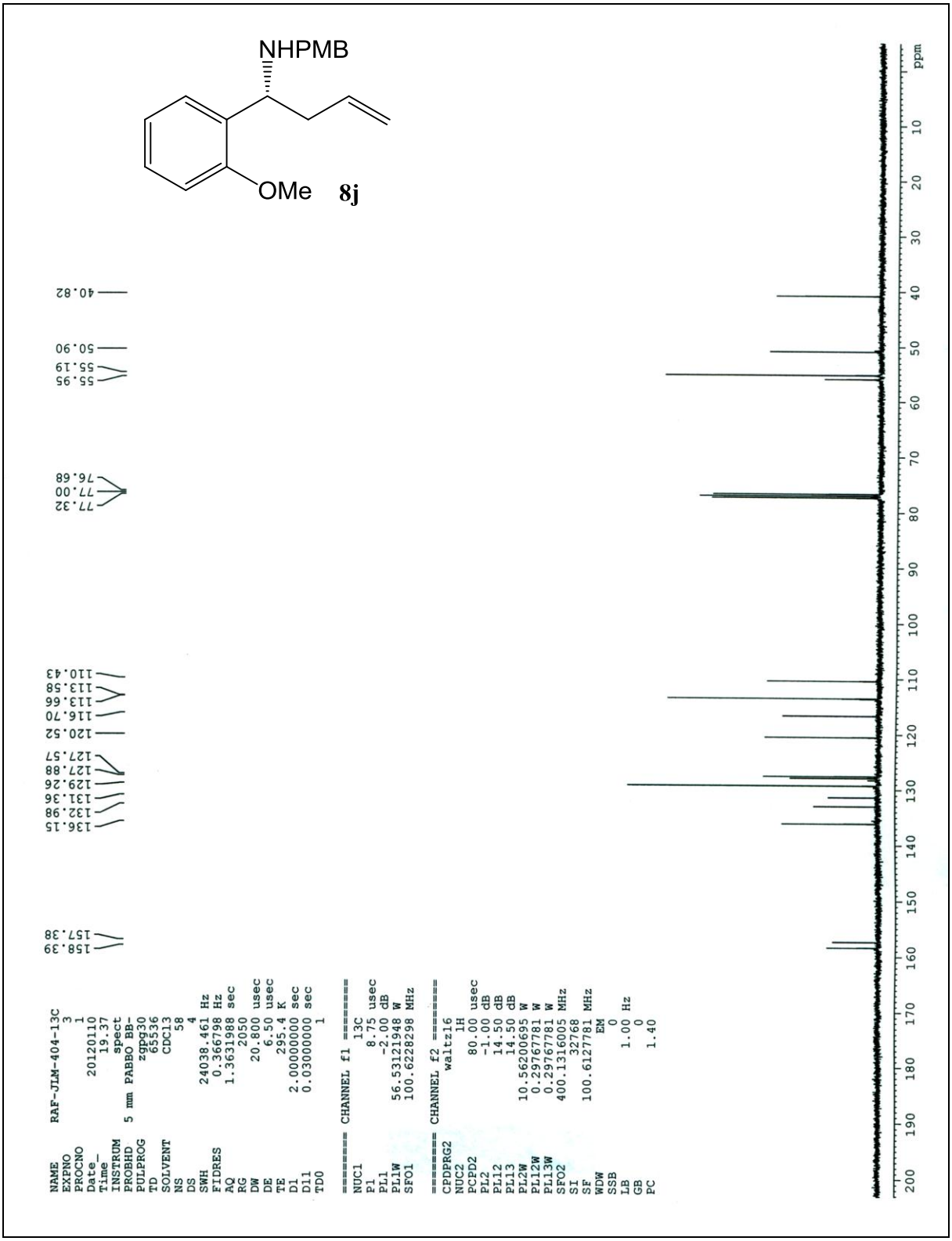
^{13}C NMR of (*R*)-*N*-Benzyl-1-(2-methoxyphenyl)-3-butenylamine 8i



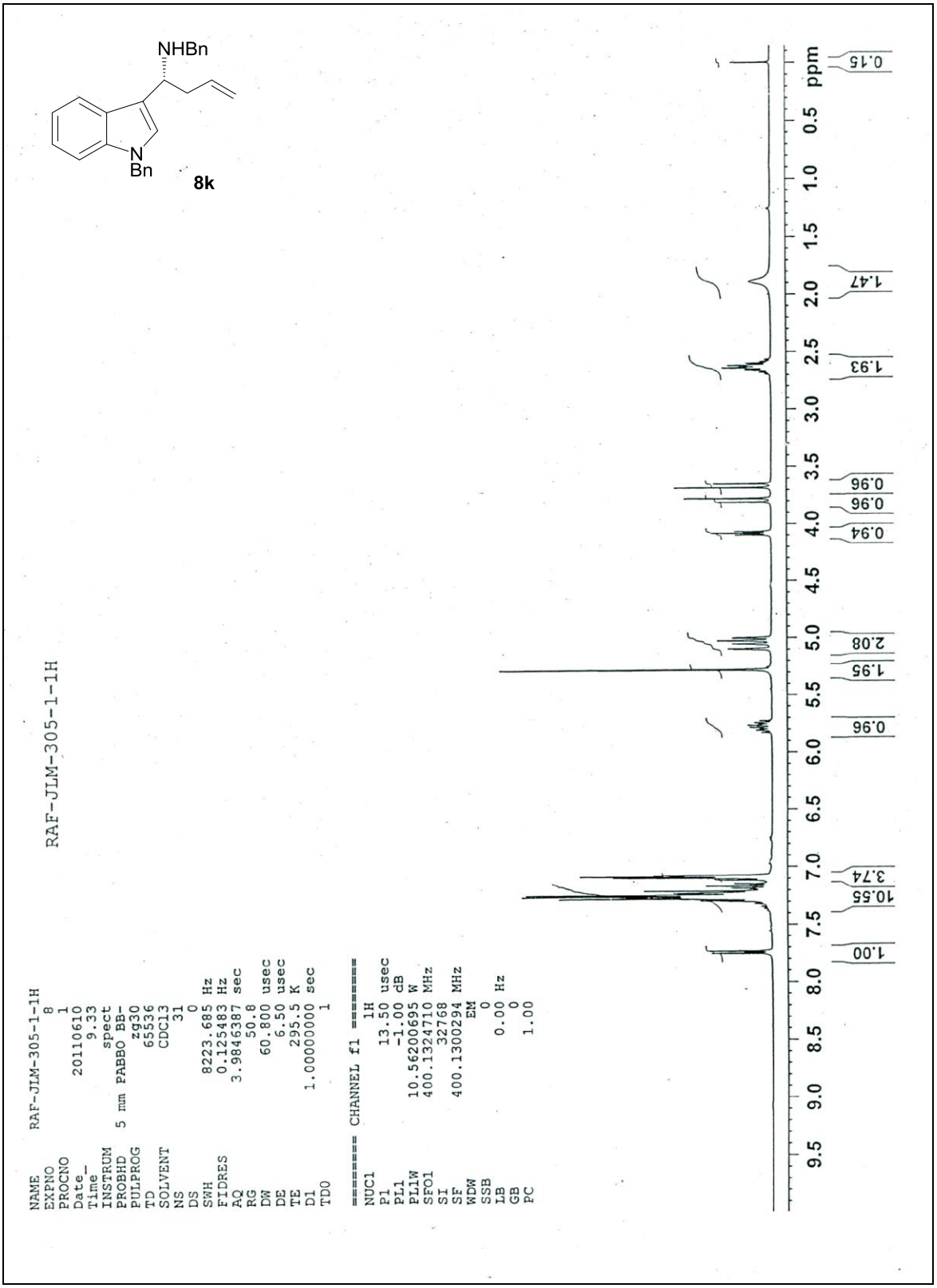
^{1}H NMR of (*R*)-*N*-(4-Methoxybenzyl-1-(2-methoxyphenyl)-3-butenylamine 8j



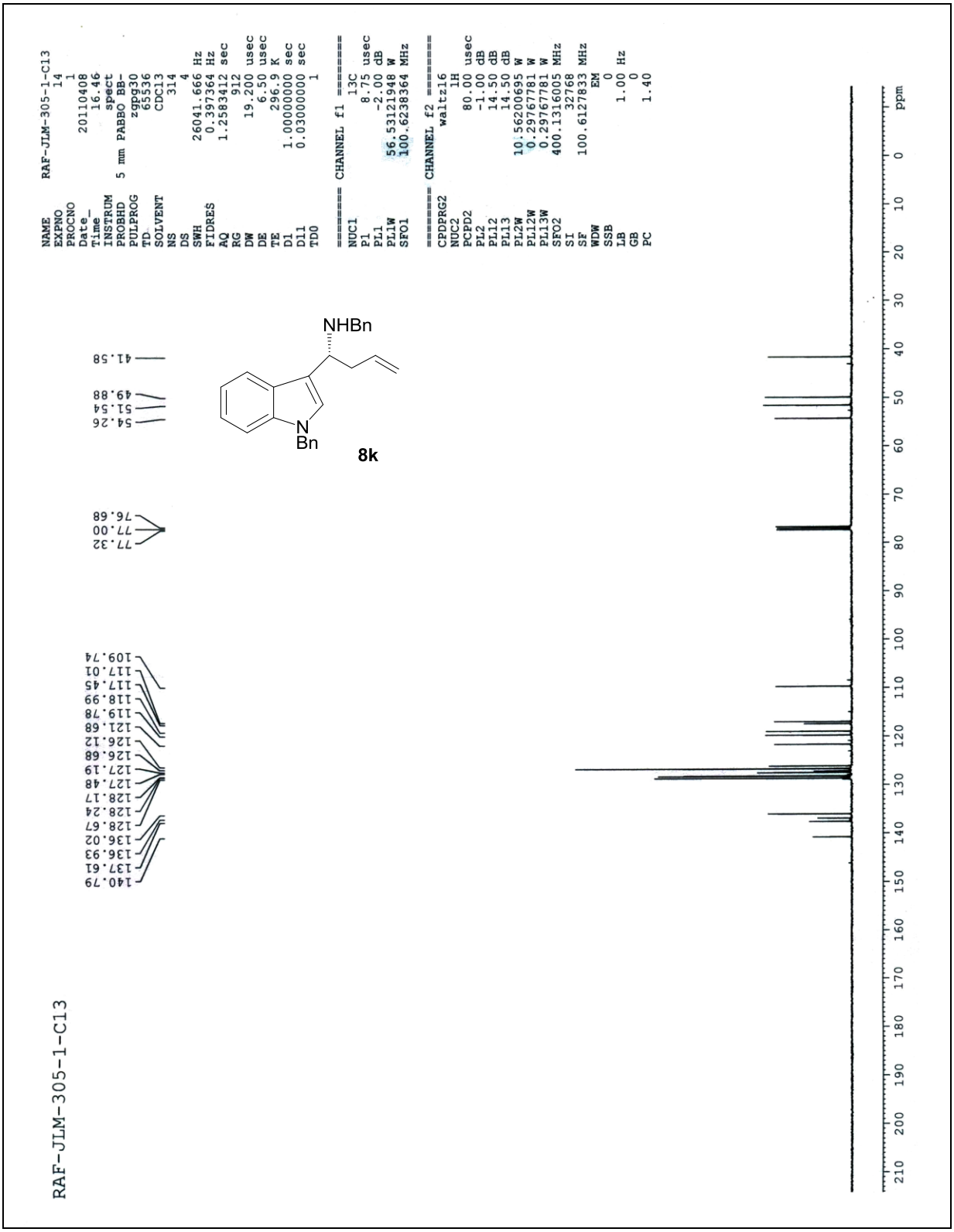
^{13}C NMR of (*R*)-*N*-(4-Methoxybenzyl-1-(2-methoxyphenyl)-3-butenylamine 8j



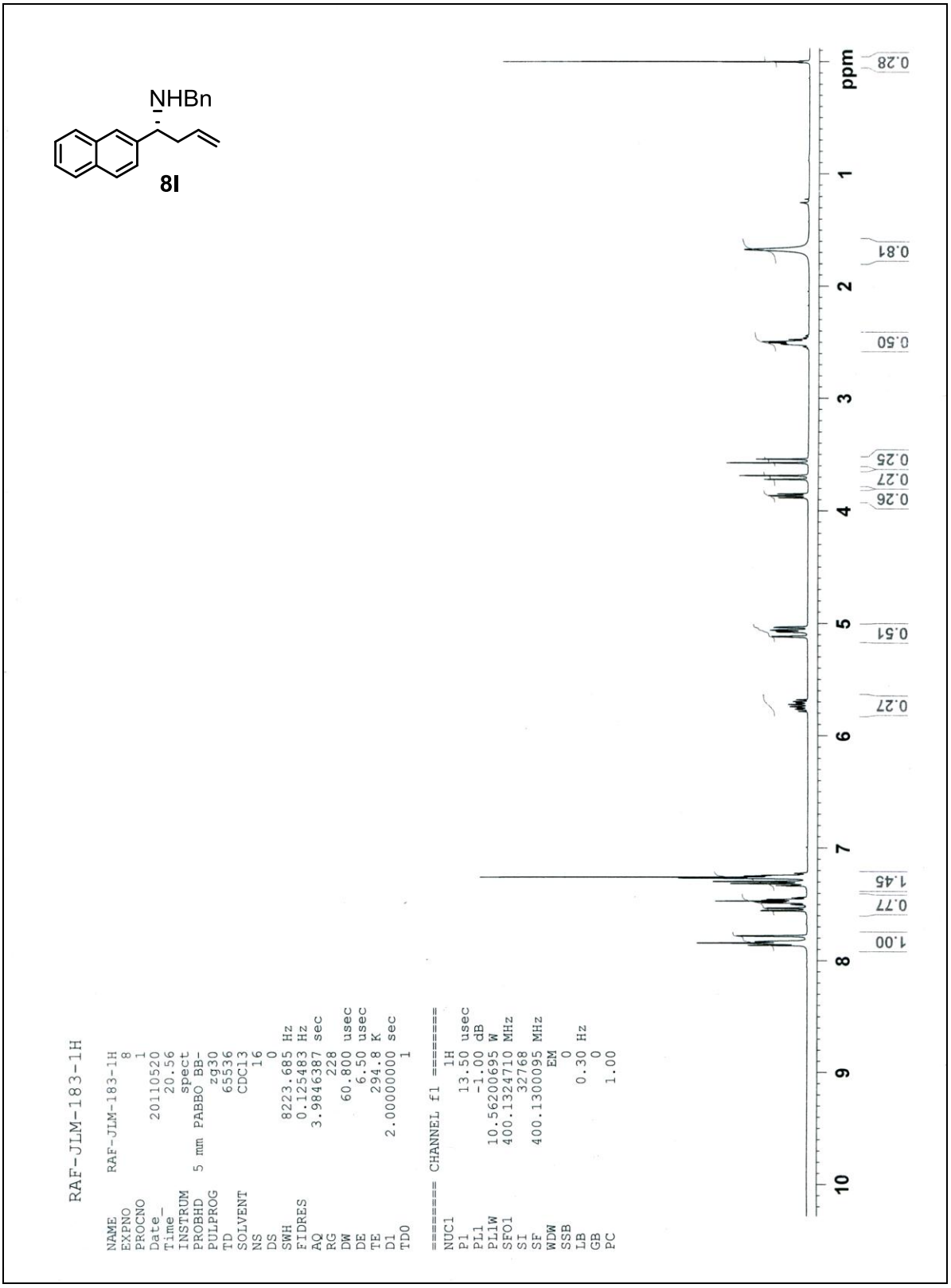
^{1}H NMR of (*R*)-*N*-benzyl-1-(1-benzylindol-3-yl)but-3-en-1-amine 8k



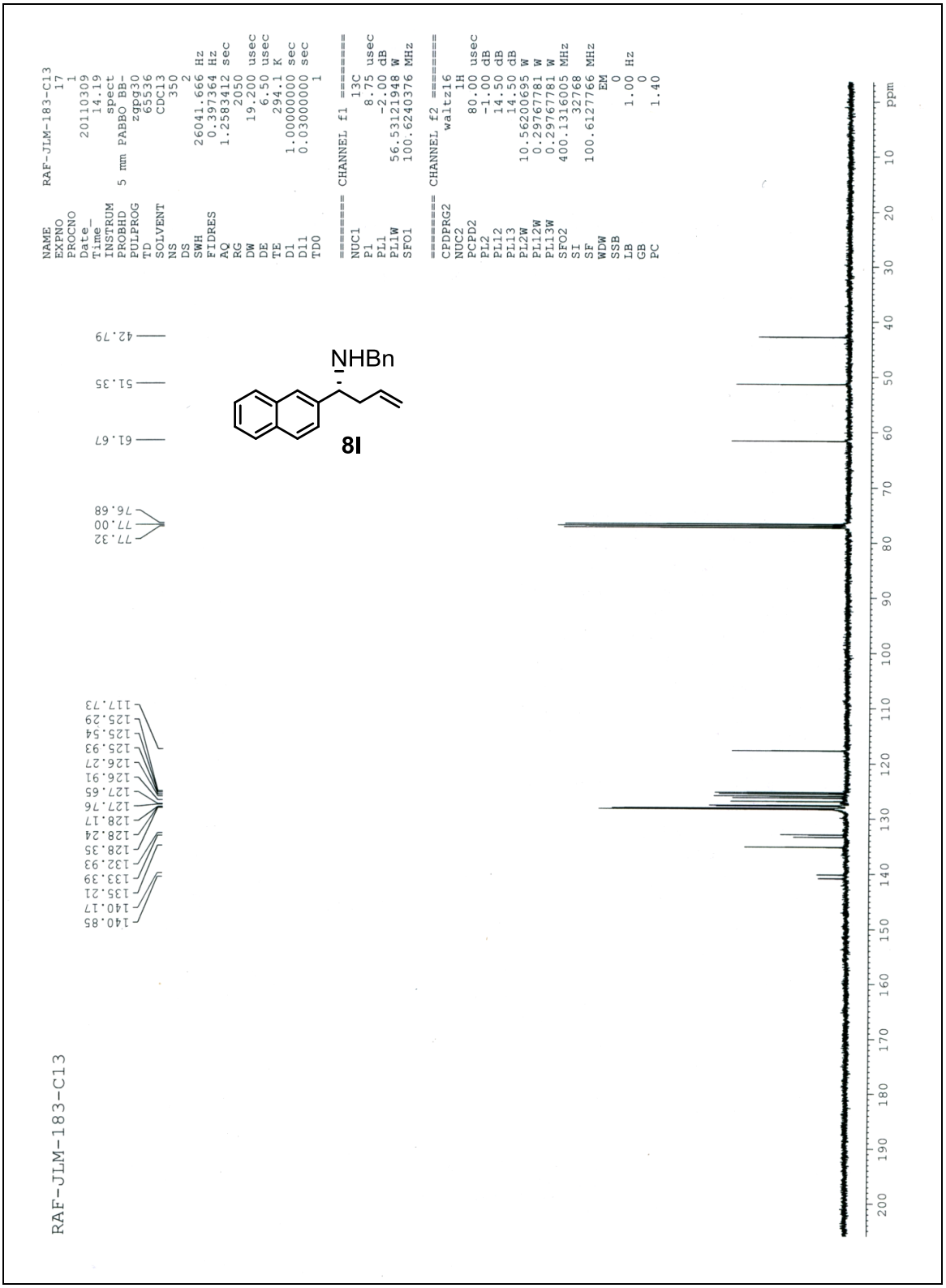
^{13}C NMR of (*R*)-*N*-benzyl-1-(1-benzylindol-3-yl)but-3-en-1-amine 8k



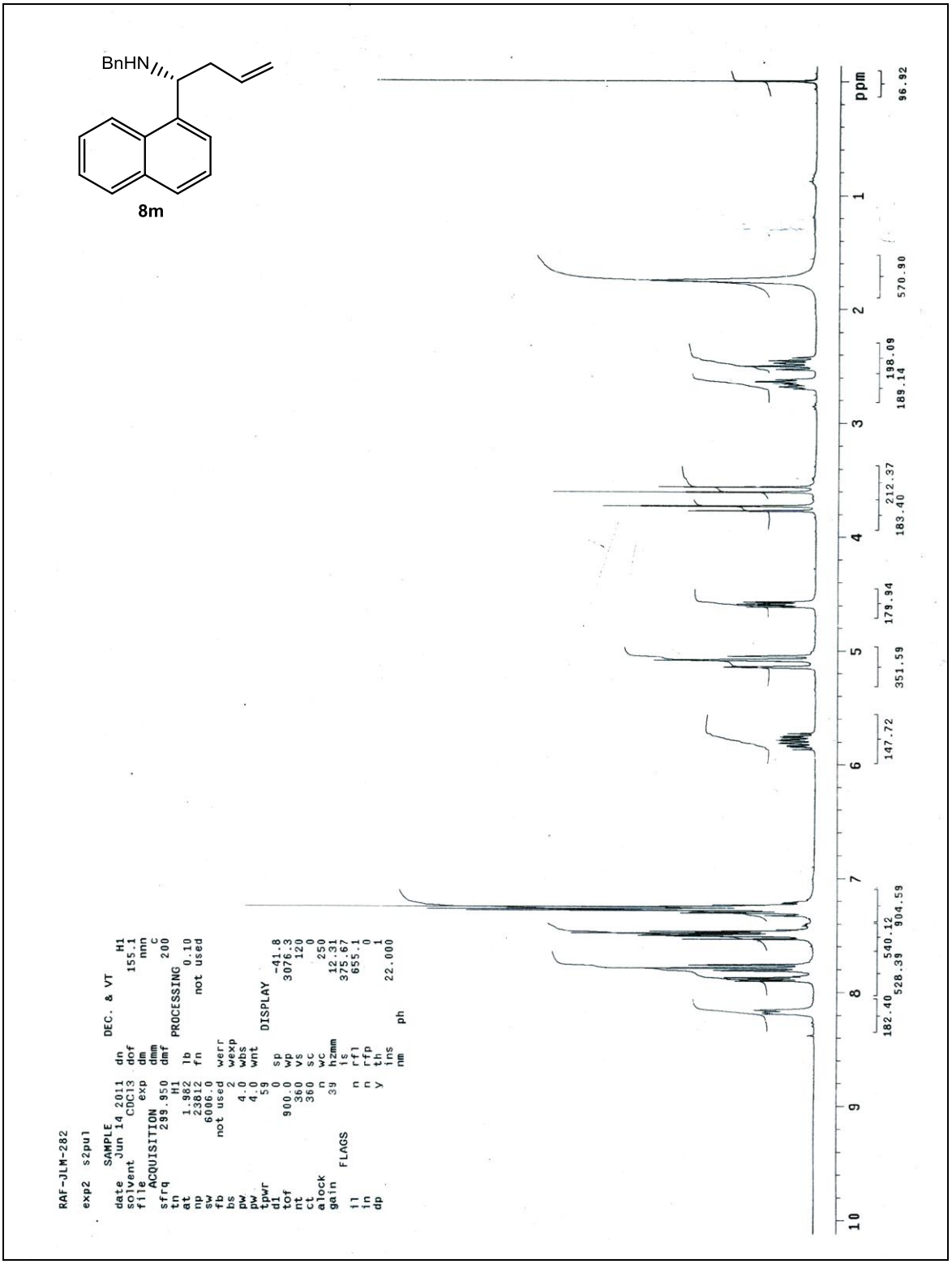
^{1}H NMR of (*R*)-*N*-Benzyl-1-(2-naphthyl)-3-butenylamine 8l



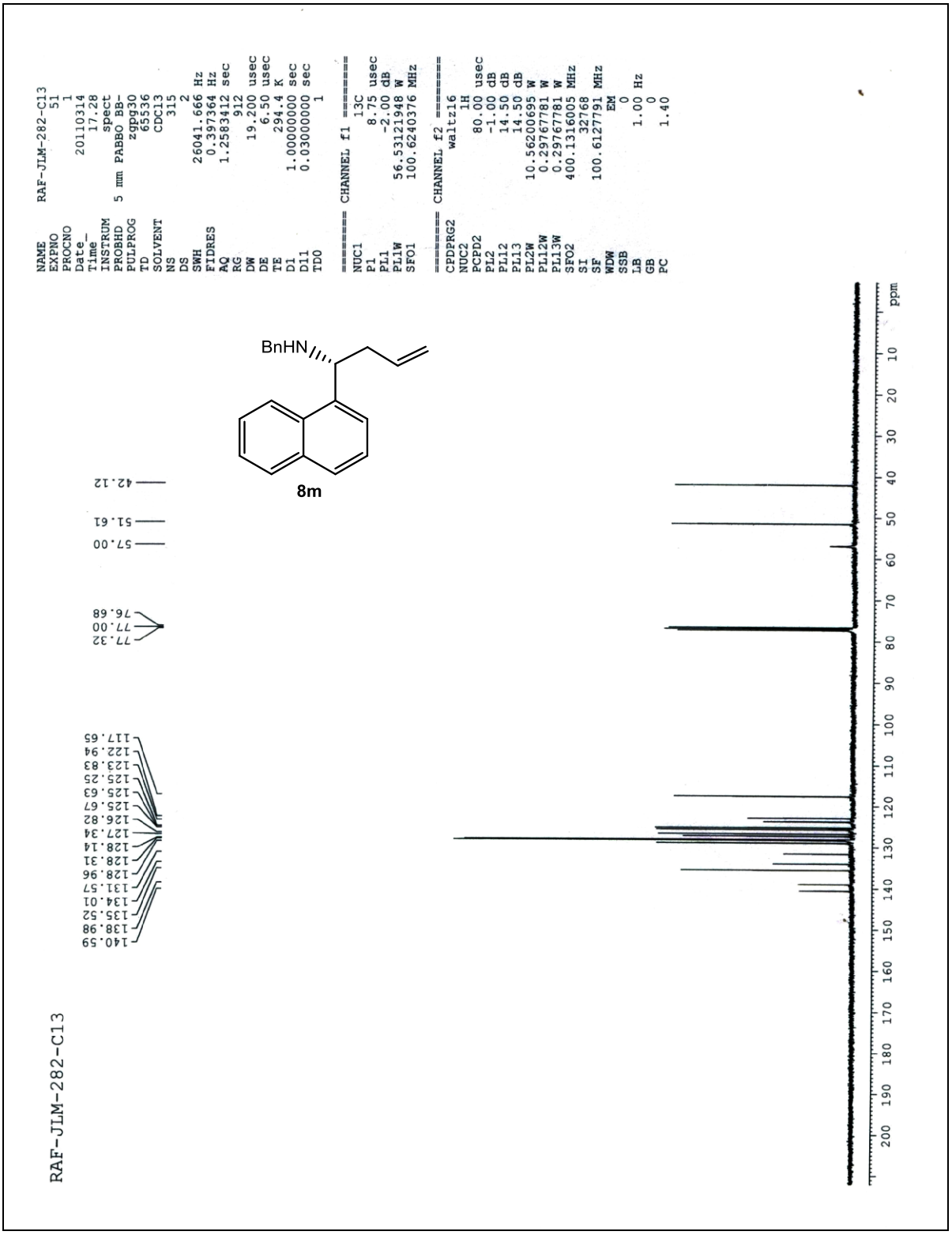
^{13}C NMR of (*R*)-*N*-Benzyl-1-(2-naphthyl)-3-butenylamine 8l



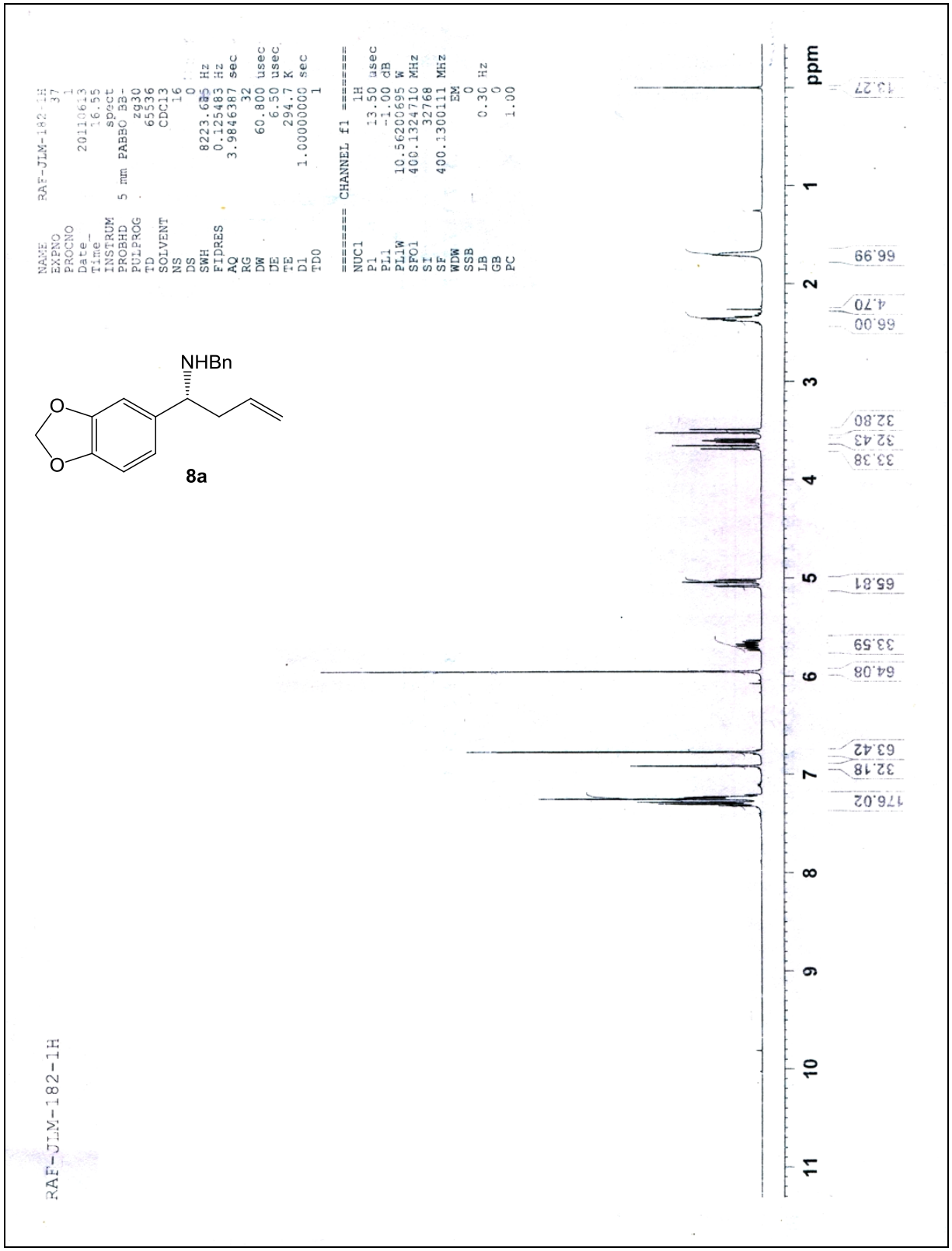
^{1}H NMR of (*R*)-*N*-Benzyl-1-(1-naphthyl)-3-butenylamine 8m



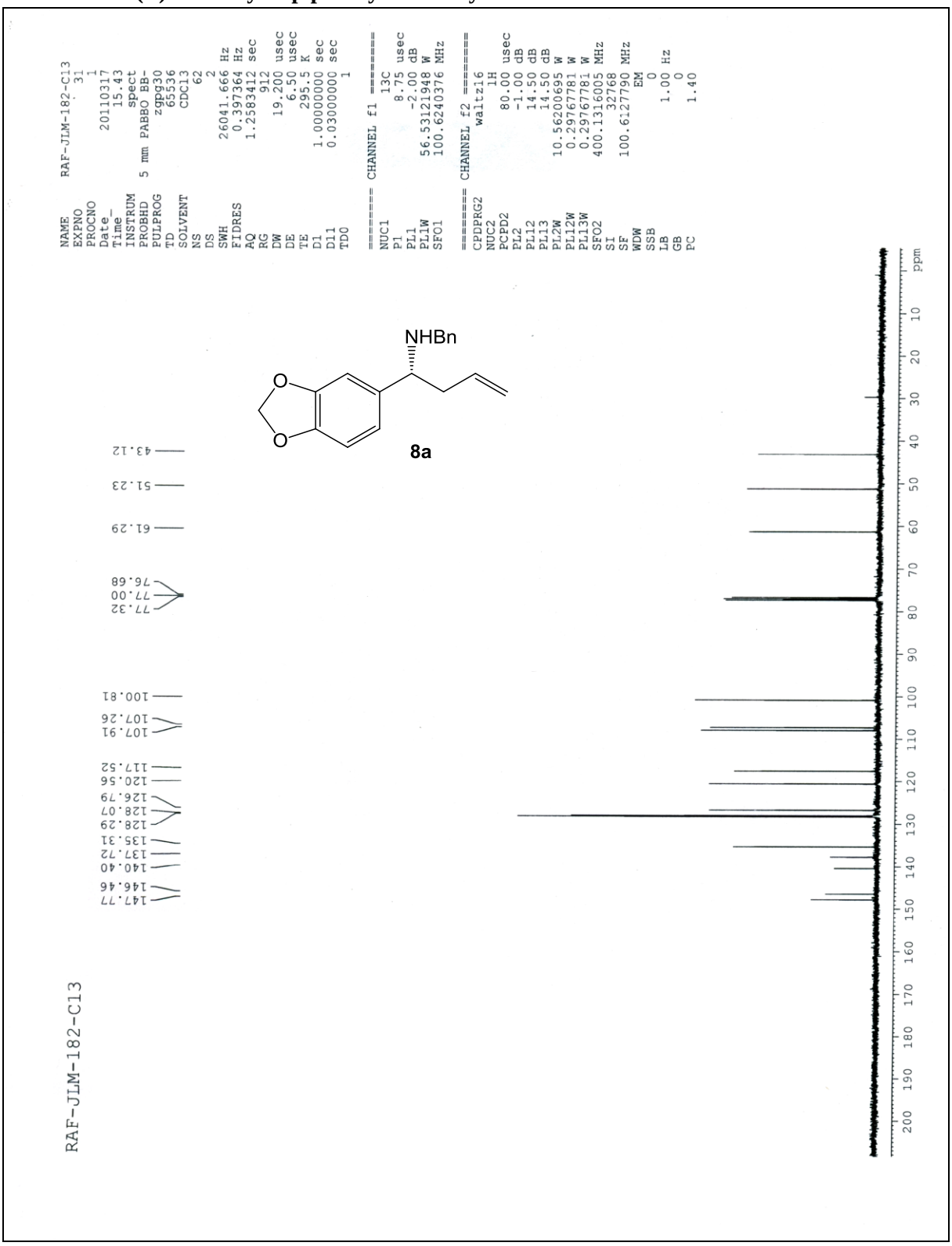
^{13}C NMR of (*R*)-*N*-Benzyl-1-(1-naphthyl)-3-butenylamine 8m



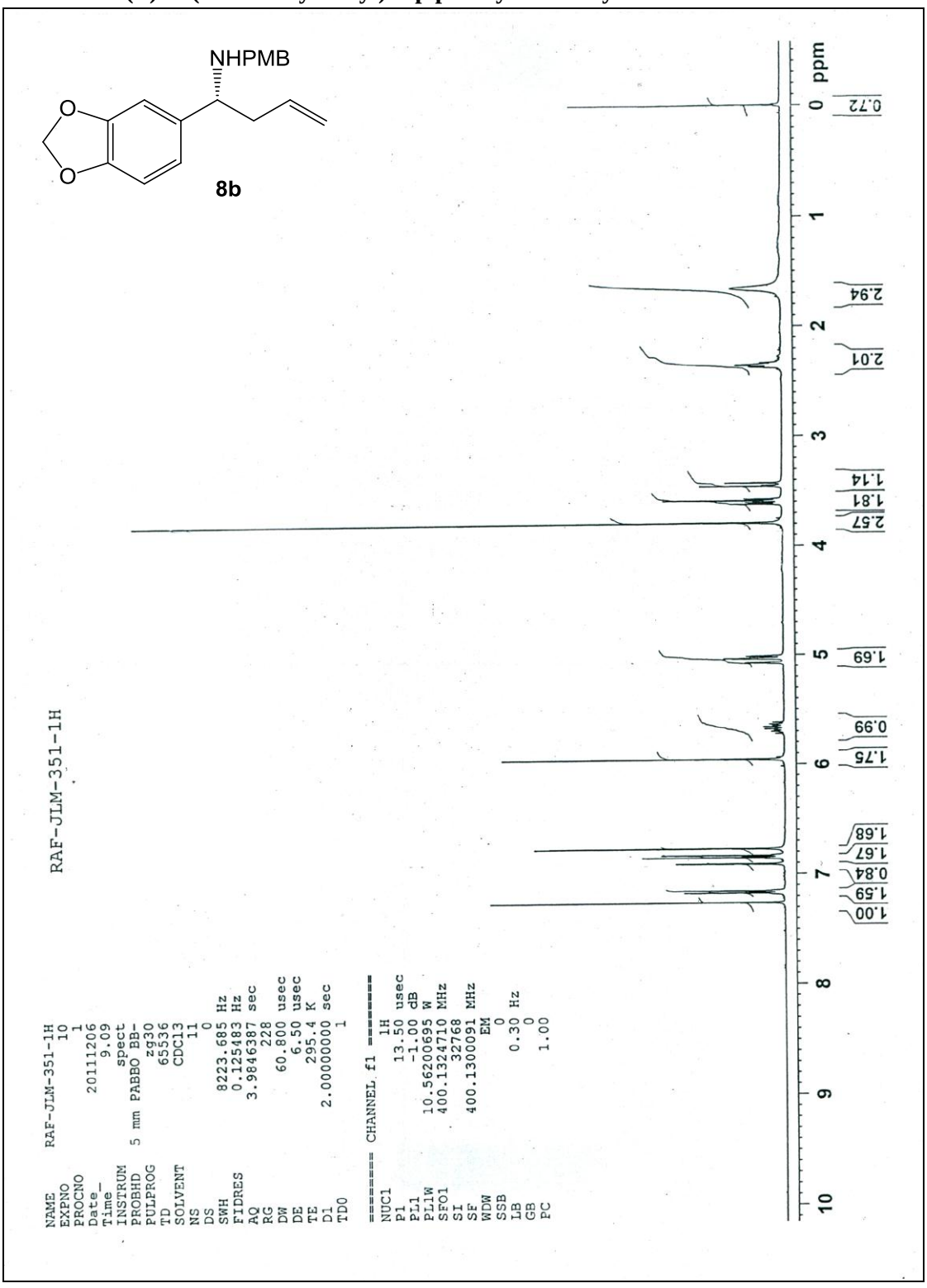
^{1}H NMR of (*R*)-*N*-Benzyl-1-piperonyl-3-butenylamine 8a



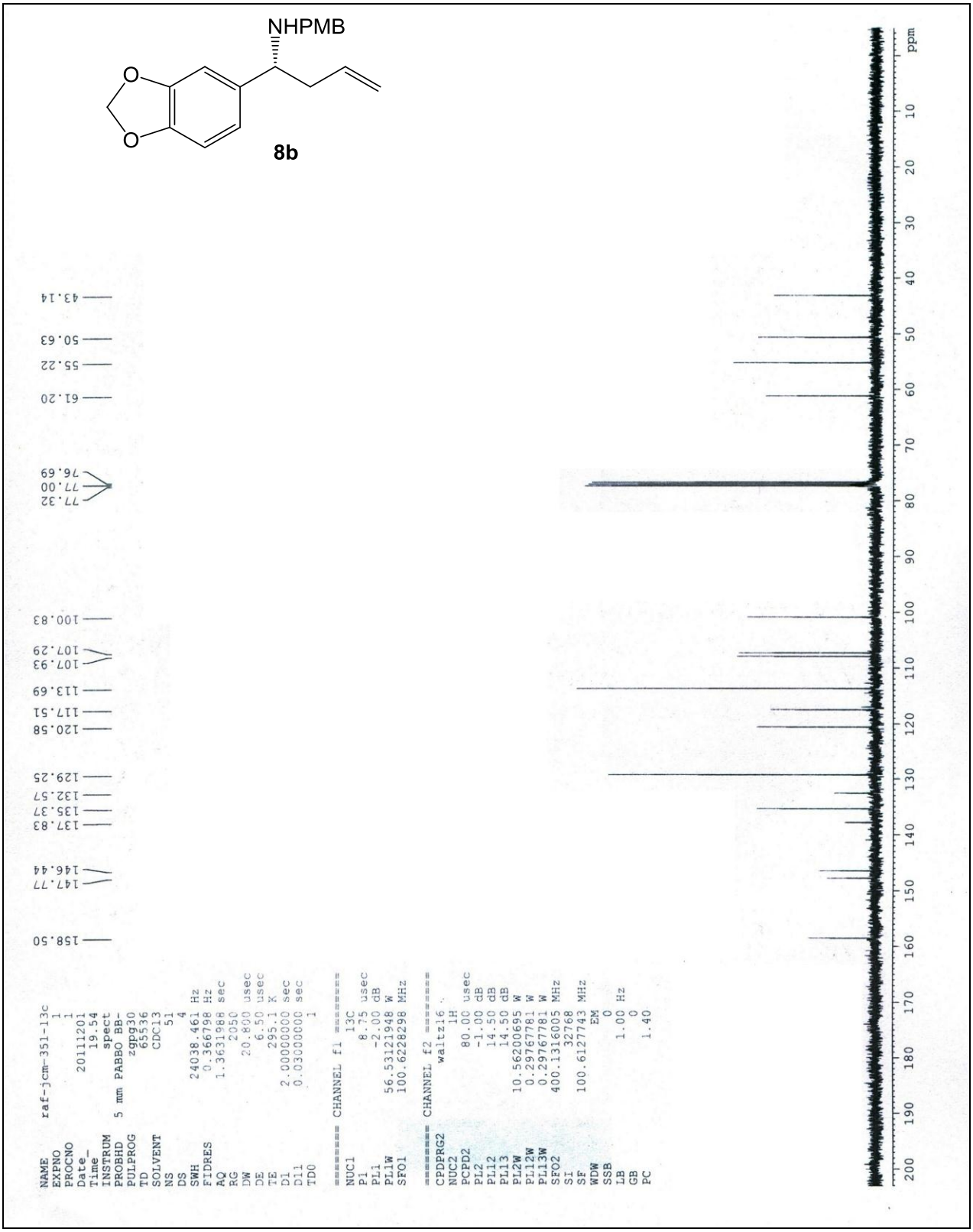
^{13}C NMR of (*R*)-*N*-Benzyl-1-piperonyl-3-butenylamine 8a



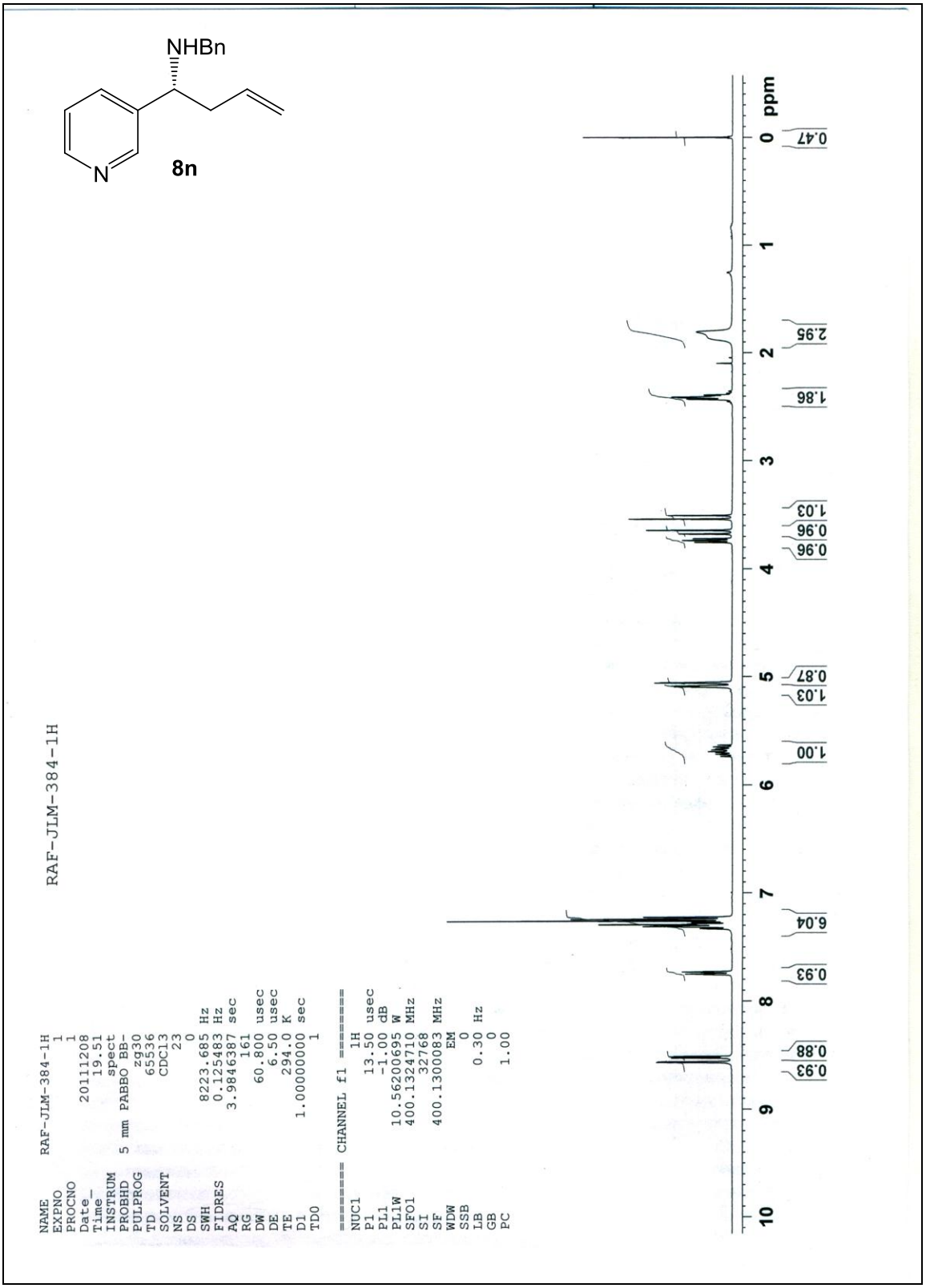
^{1}H NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-piperonyl-3-butenylamine 8b



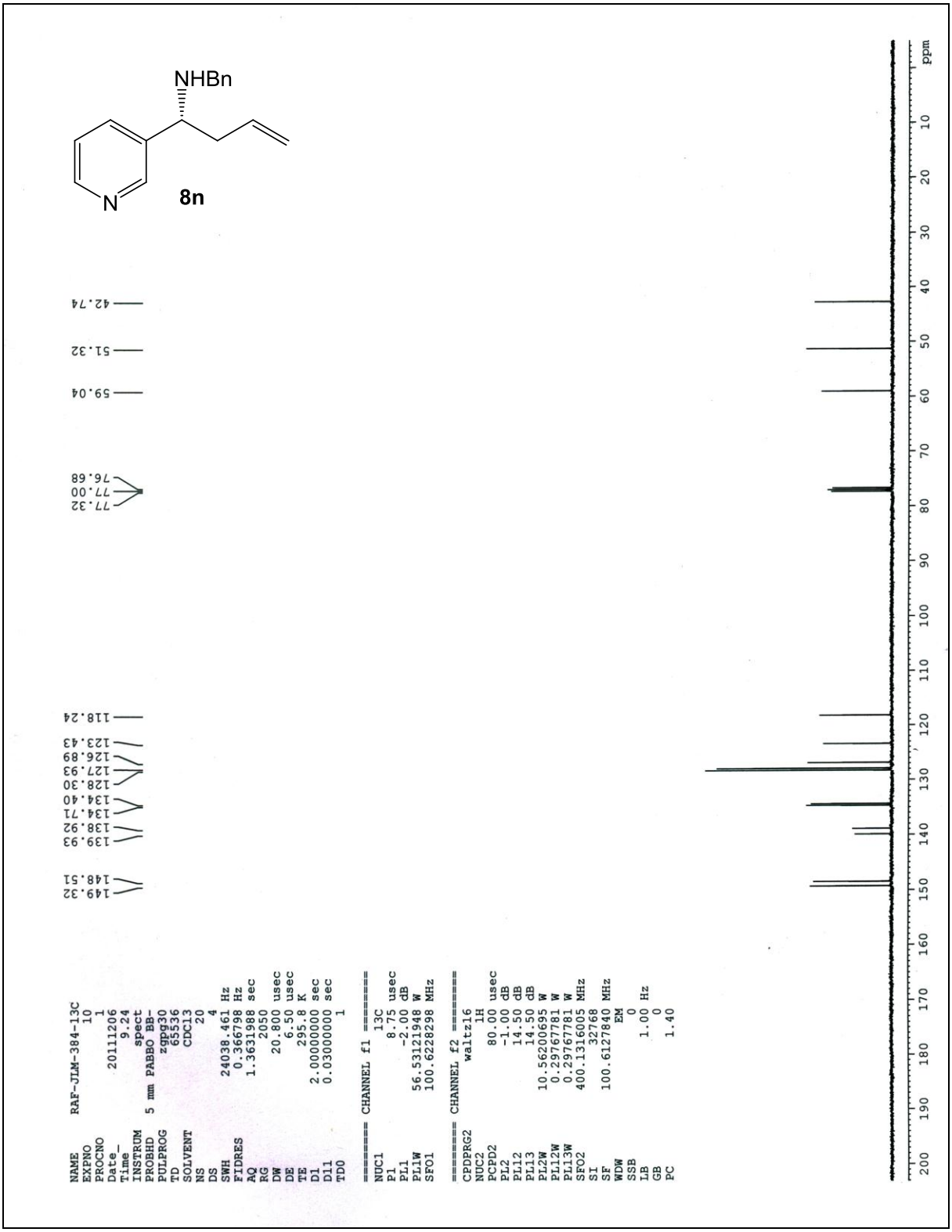
^{13}C NMR of (*R*)-*N*-(4-Methoxybenzyl)-1-piperonyl-3-butenylamine 8b



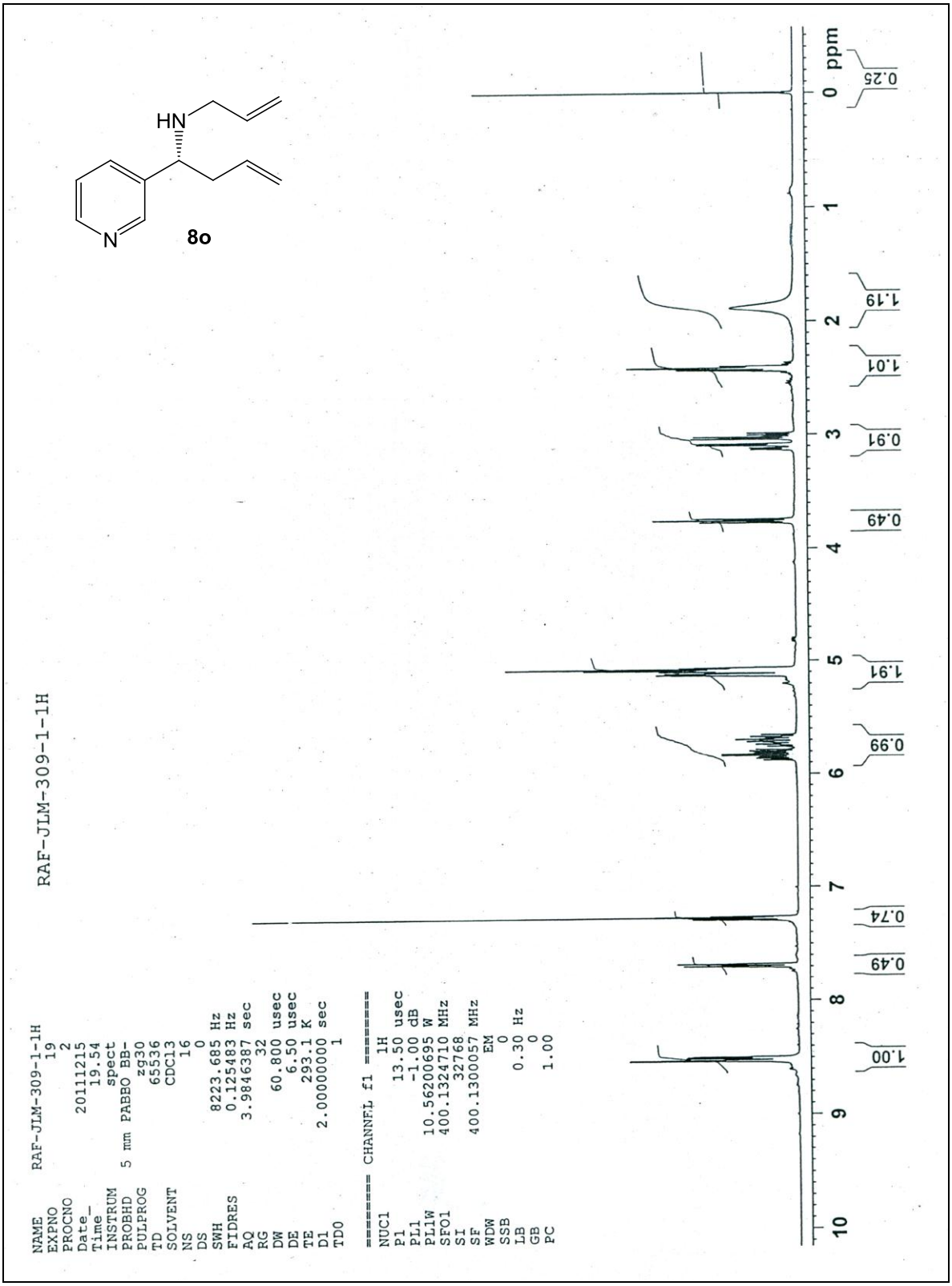
^{1}H NMR of (*R*)-*N*-Benzyl-1-(3-pyridyl)-3-butenylamine 8n



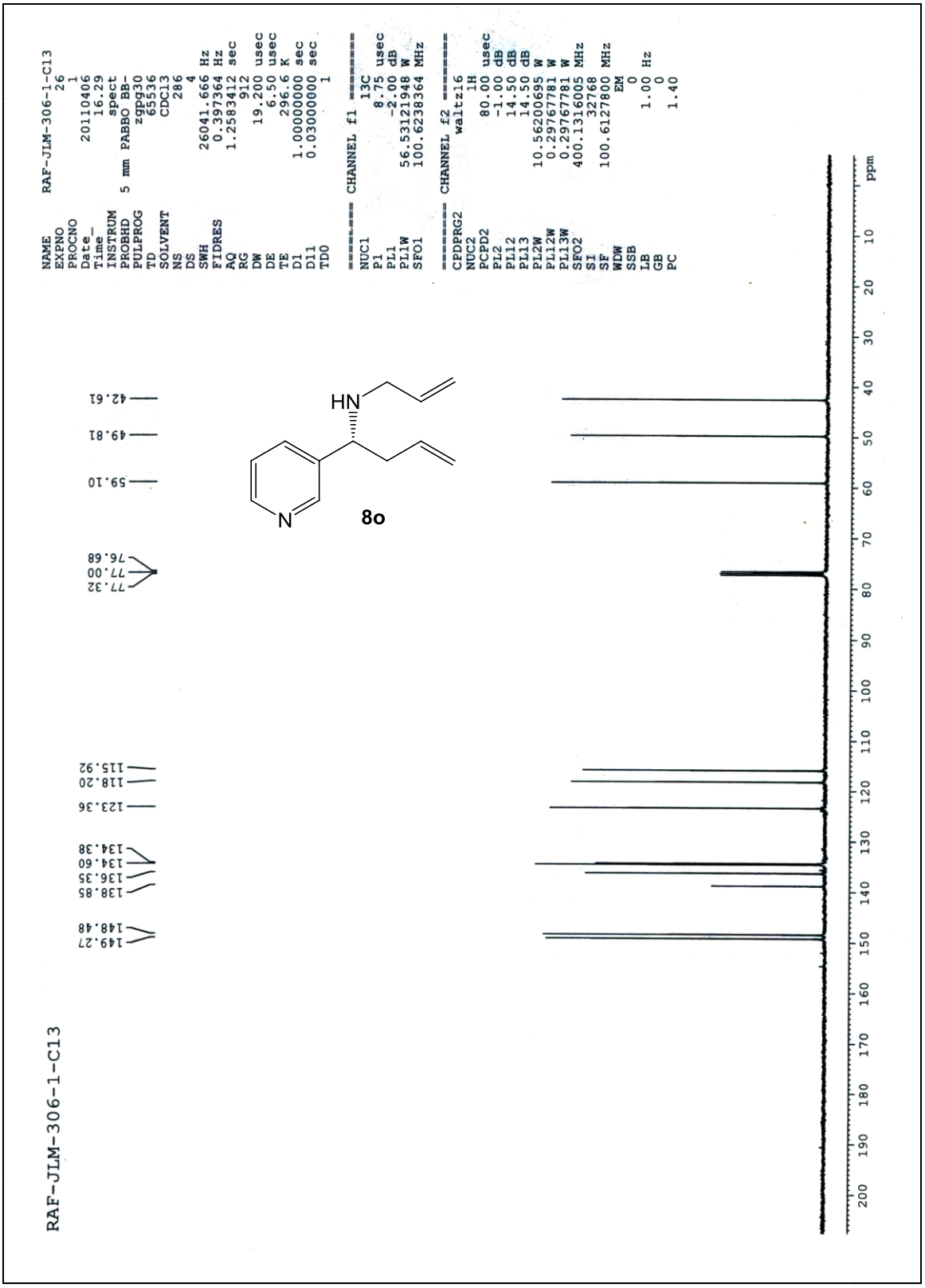
^{13}C NMR of (*R*)-*N*-Benzyl-1-(3-pyridyl)-3-butenylamine 8n



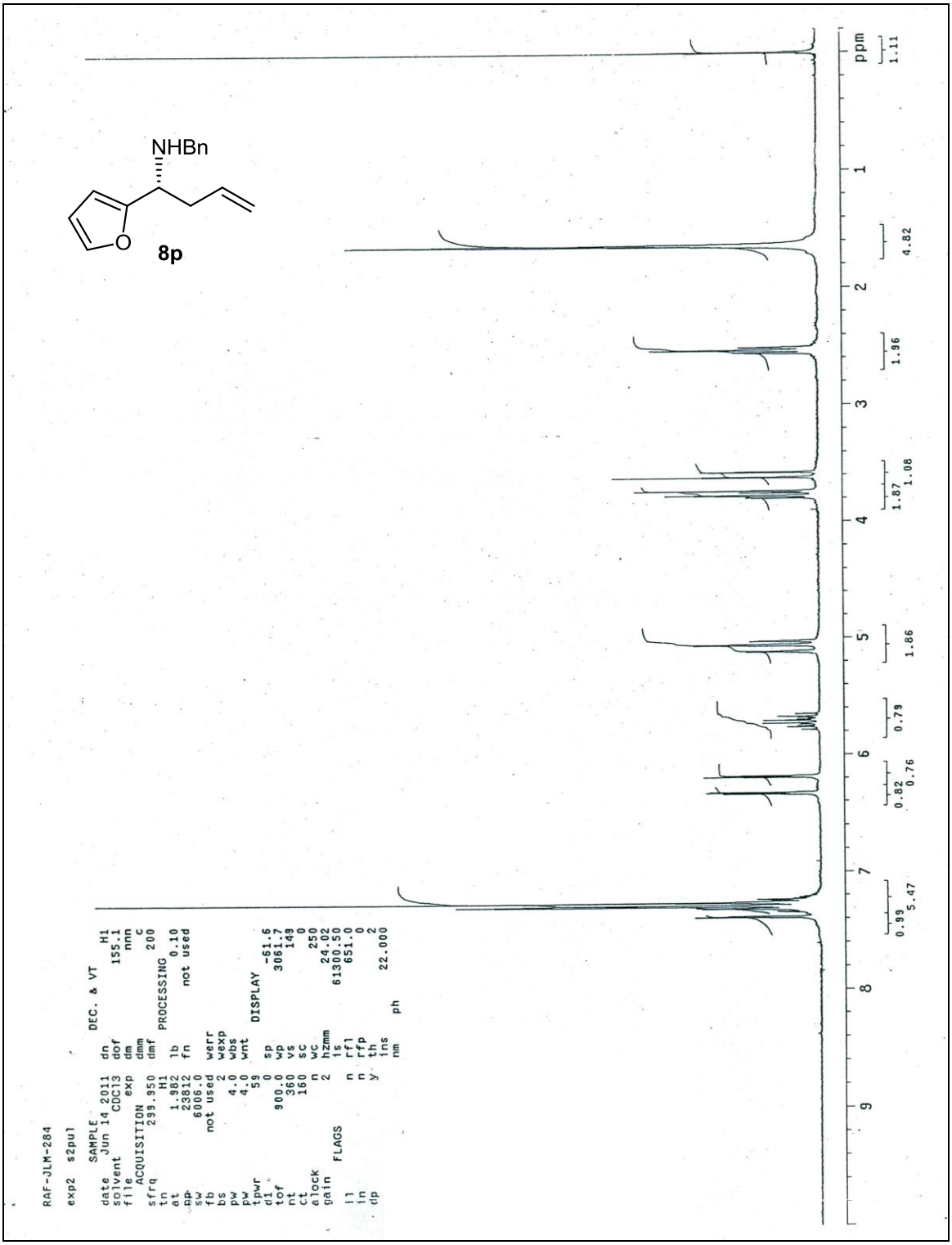
^{1}H NMR of (*R*)-*N*-Allyl-1-(3-pyridyl)-3-butenylamine 8o



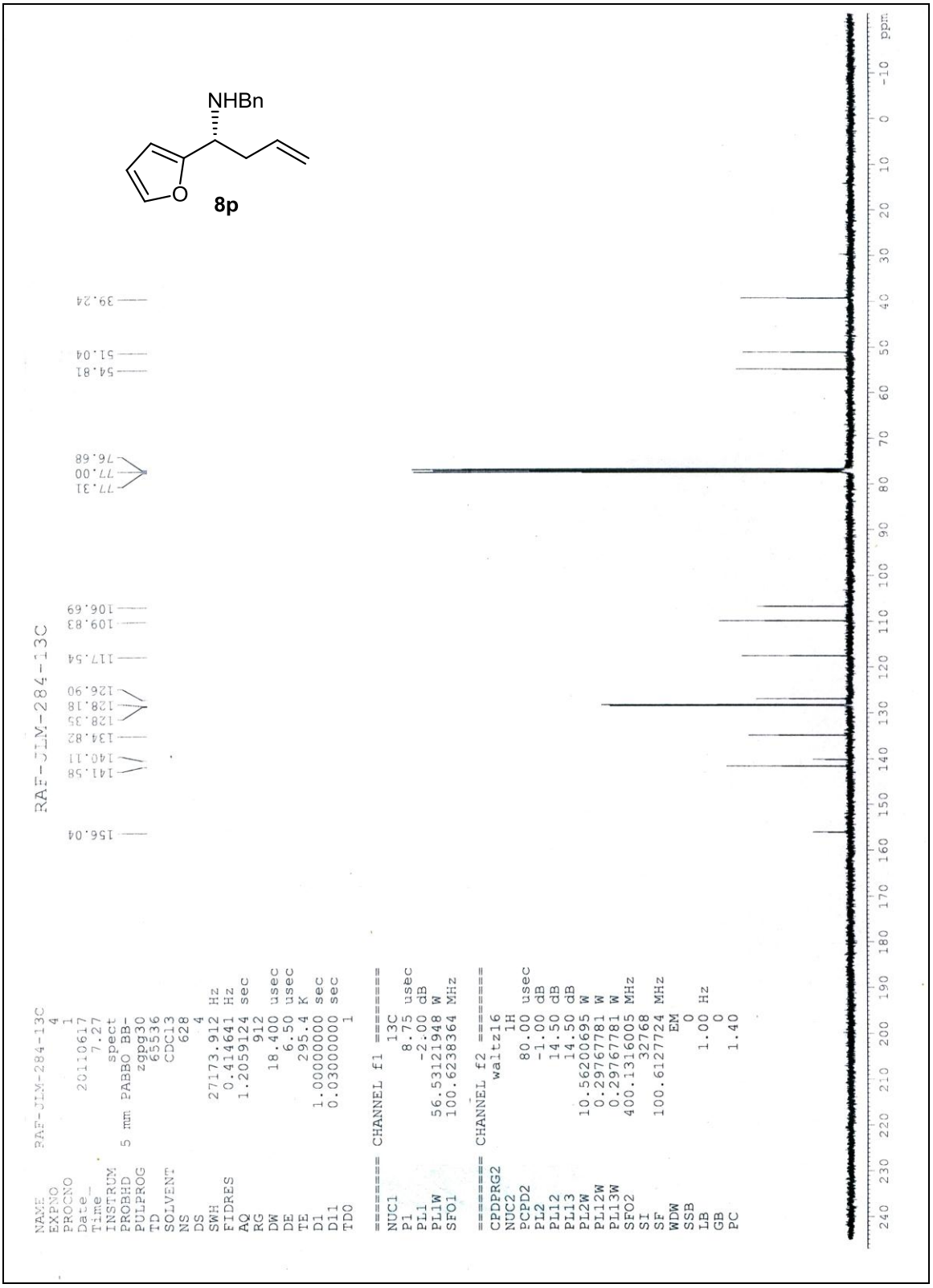
^{13}C NMR of (*R*)-*N*-Allyl-1-(3-pyridyl)-3-butenylamine 8o



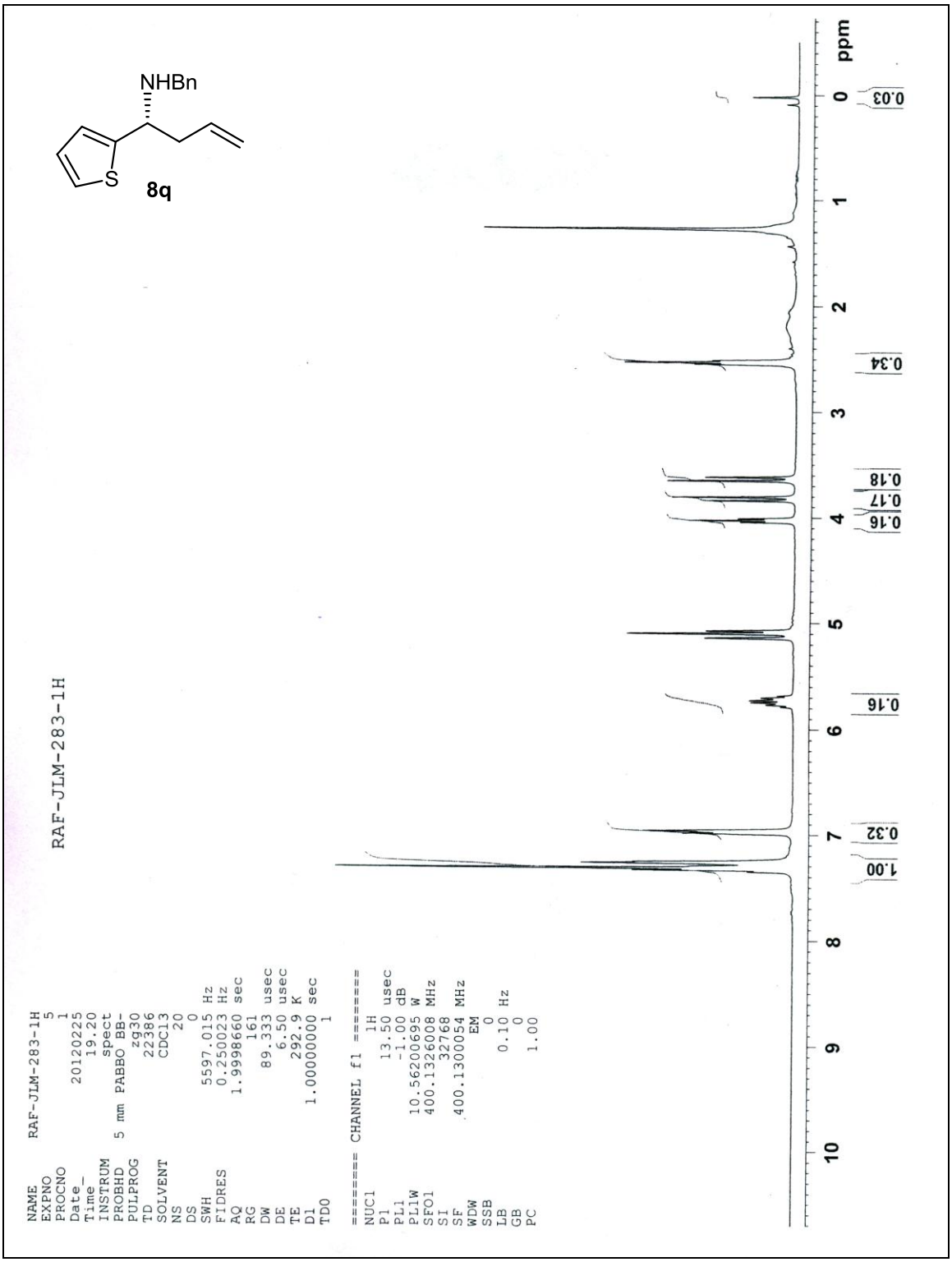
^{1}H NMR of (*R*)-*N*-Benzyl-1-(2-furfuryl)-3-butenylamine 8p



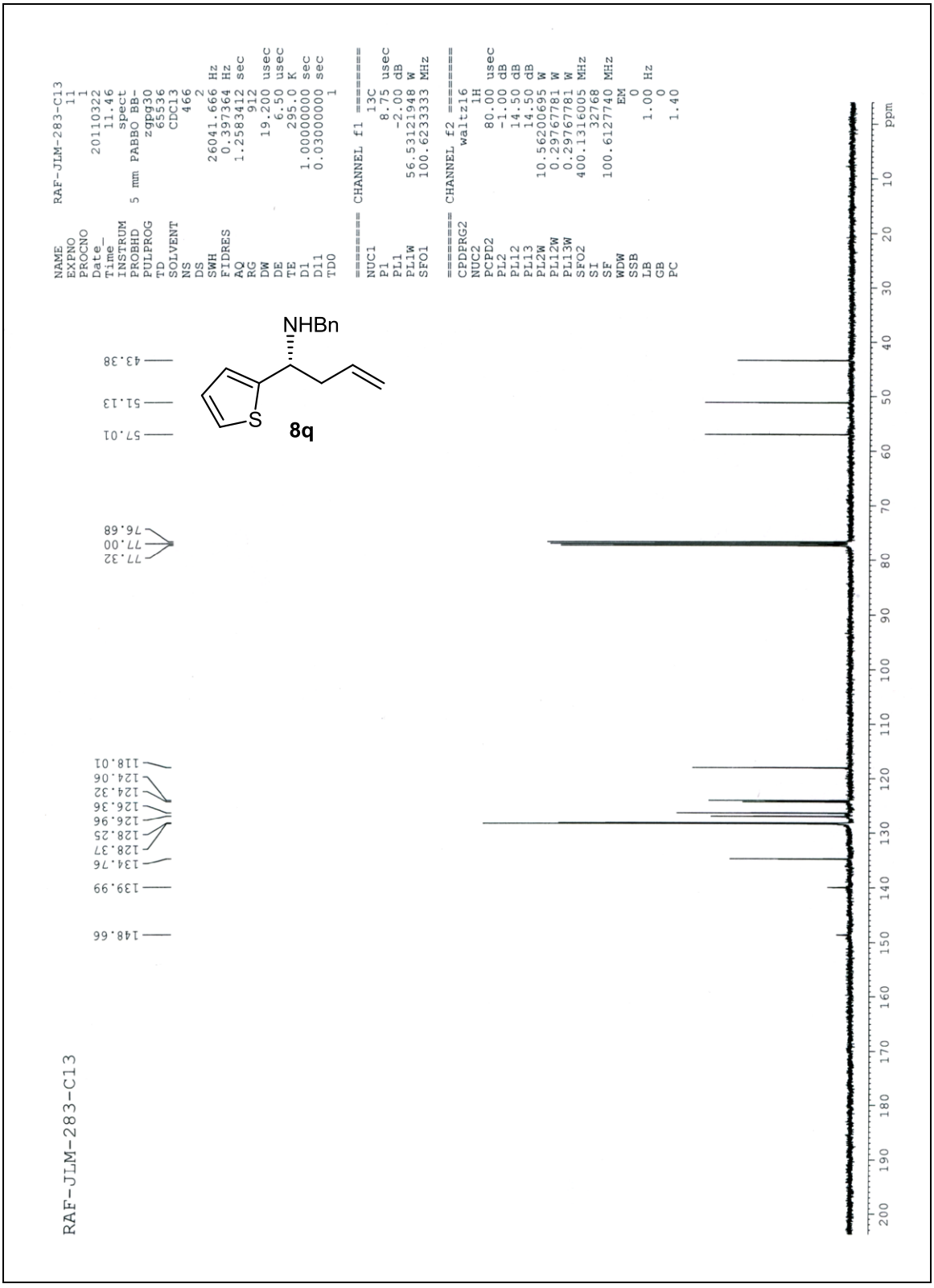
^{13}C NMR of (*R*)-*N*-Benzyl-1-(2-furfuryl)-3-butenylamine 8p



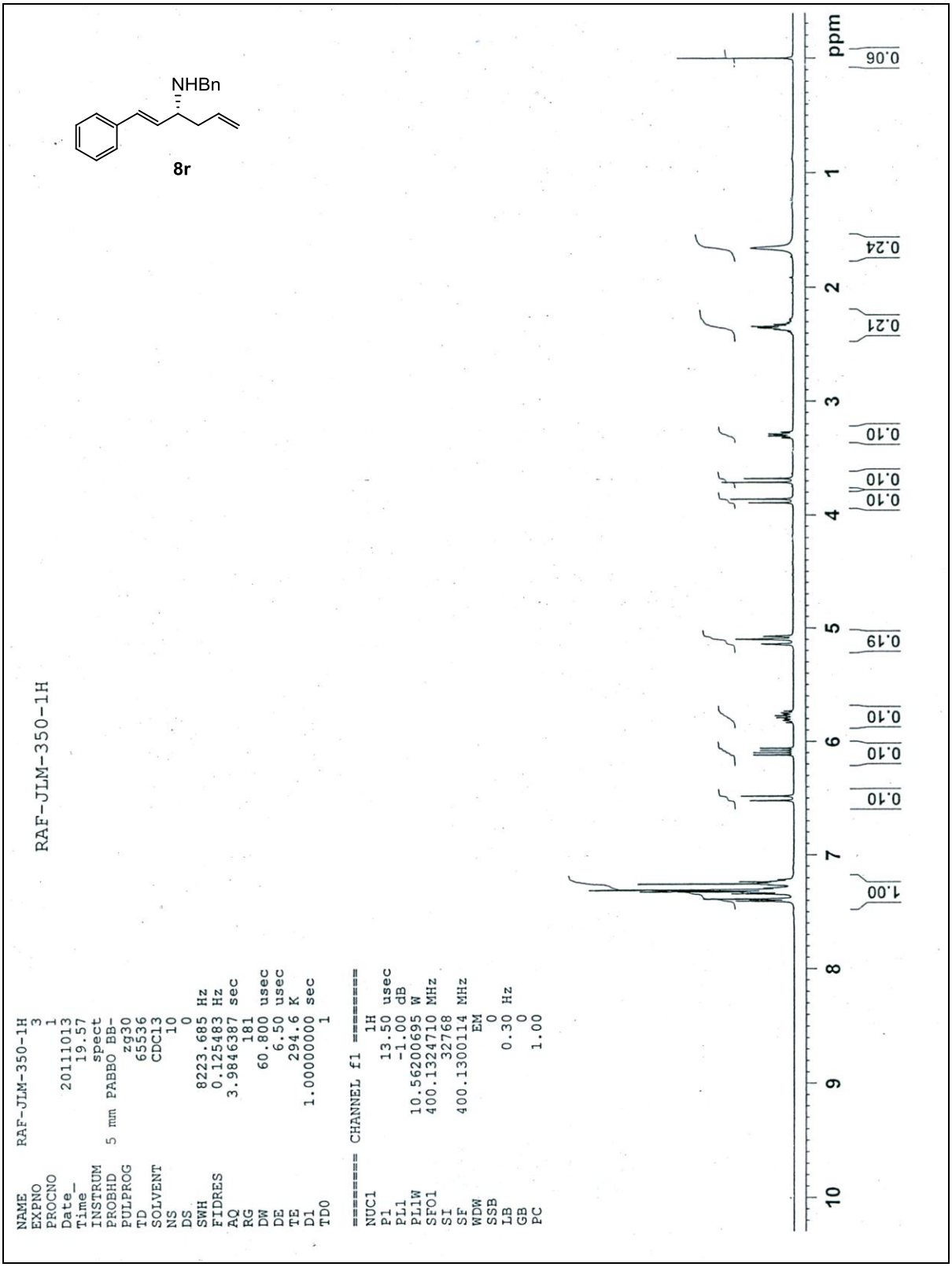
^{1}H NMR of (*R*)-*N*-Benzyl-1-(2-thiophenyl)-3-butenylamine 8q



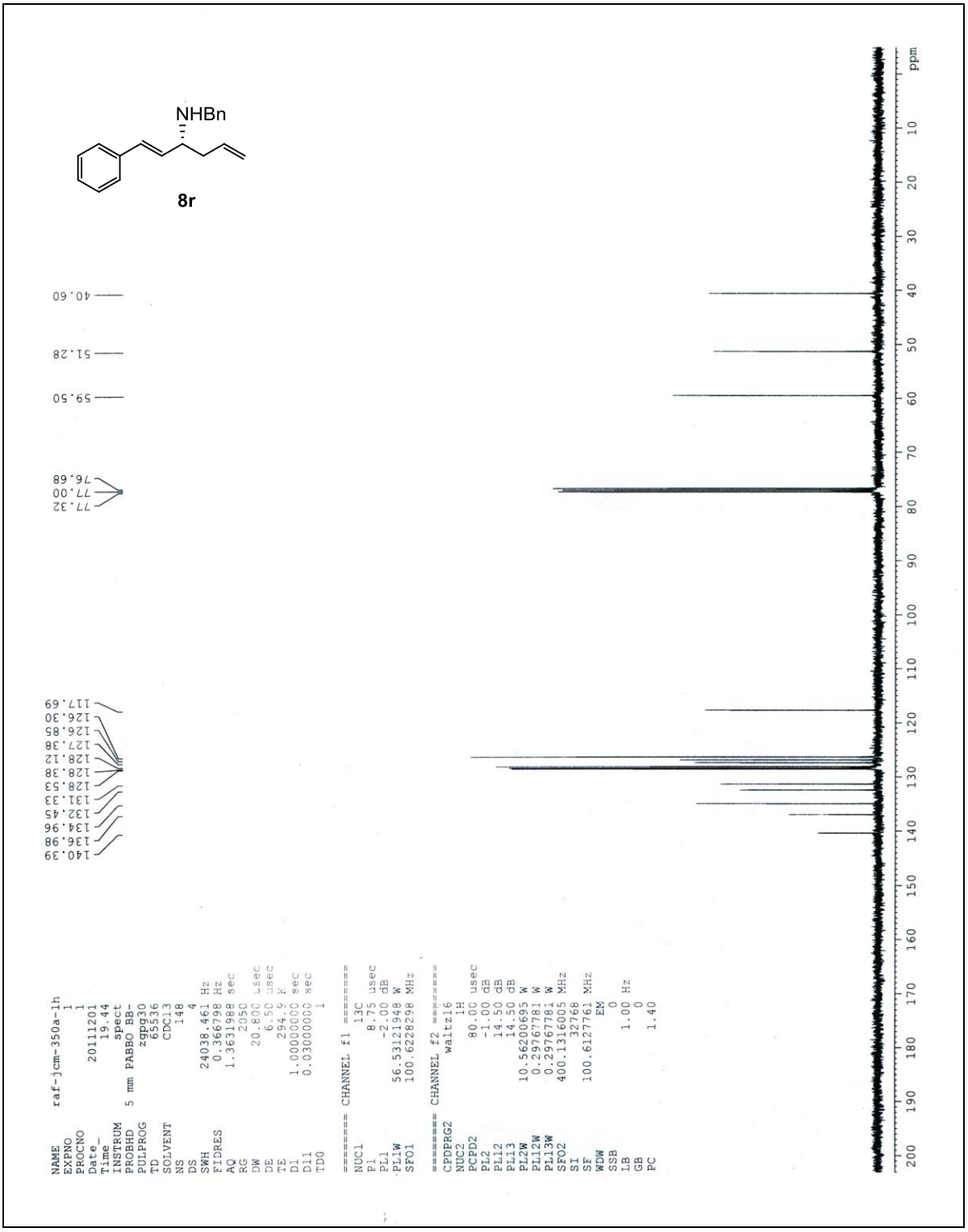
^{13}C NMR of (*R*)-*N*-Benzyl-1-(2-thiophenyl)-3-butenylamine 8q



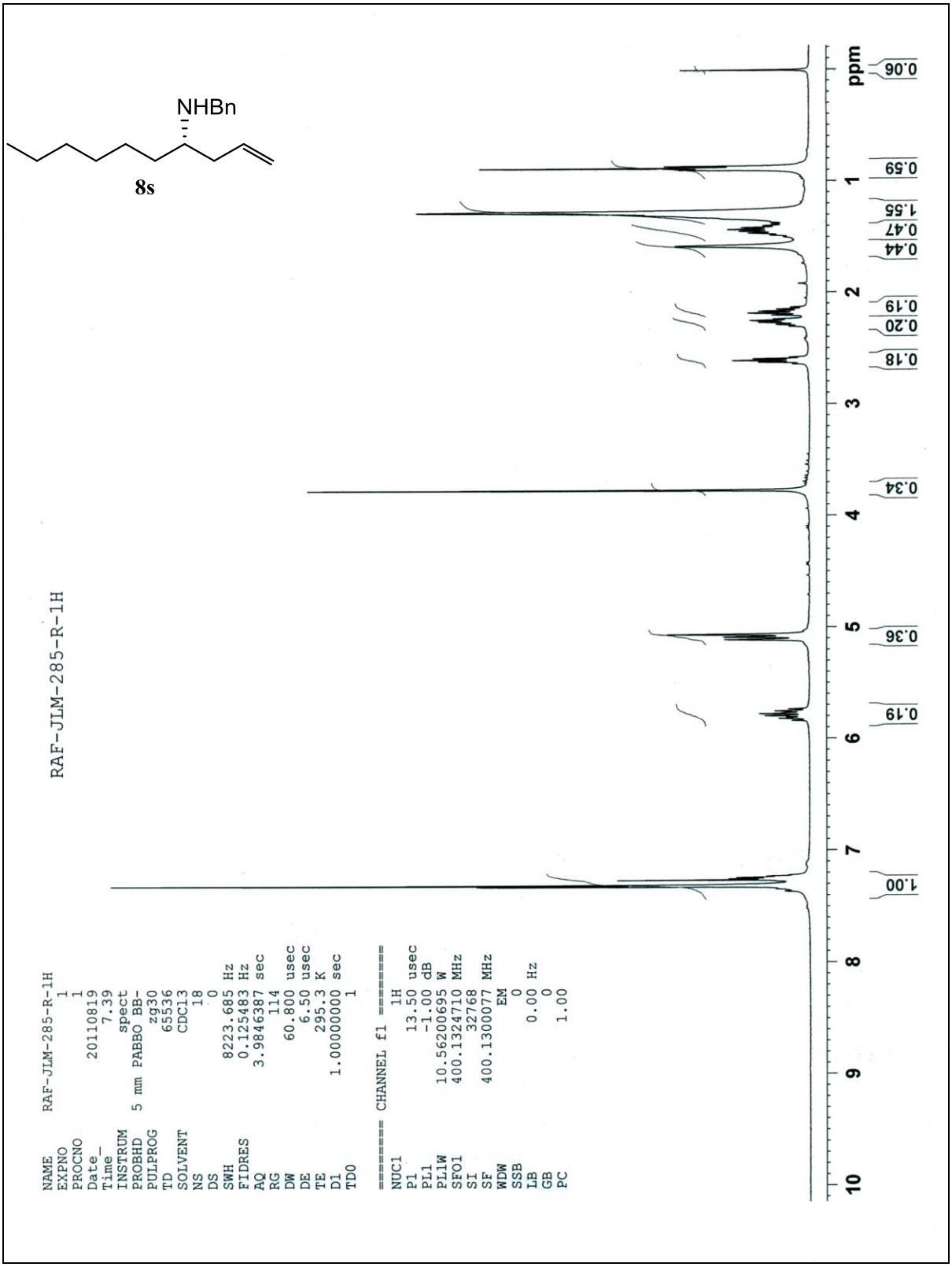
^{1}H NMR of (*R*,*E*)-*N*-benzyl-1-phenylhexa-1,5-diene-3-amine 8r



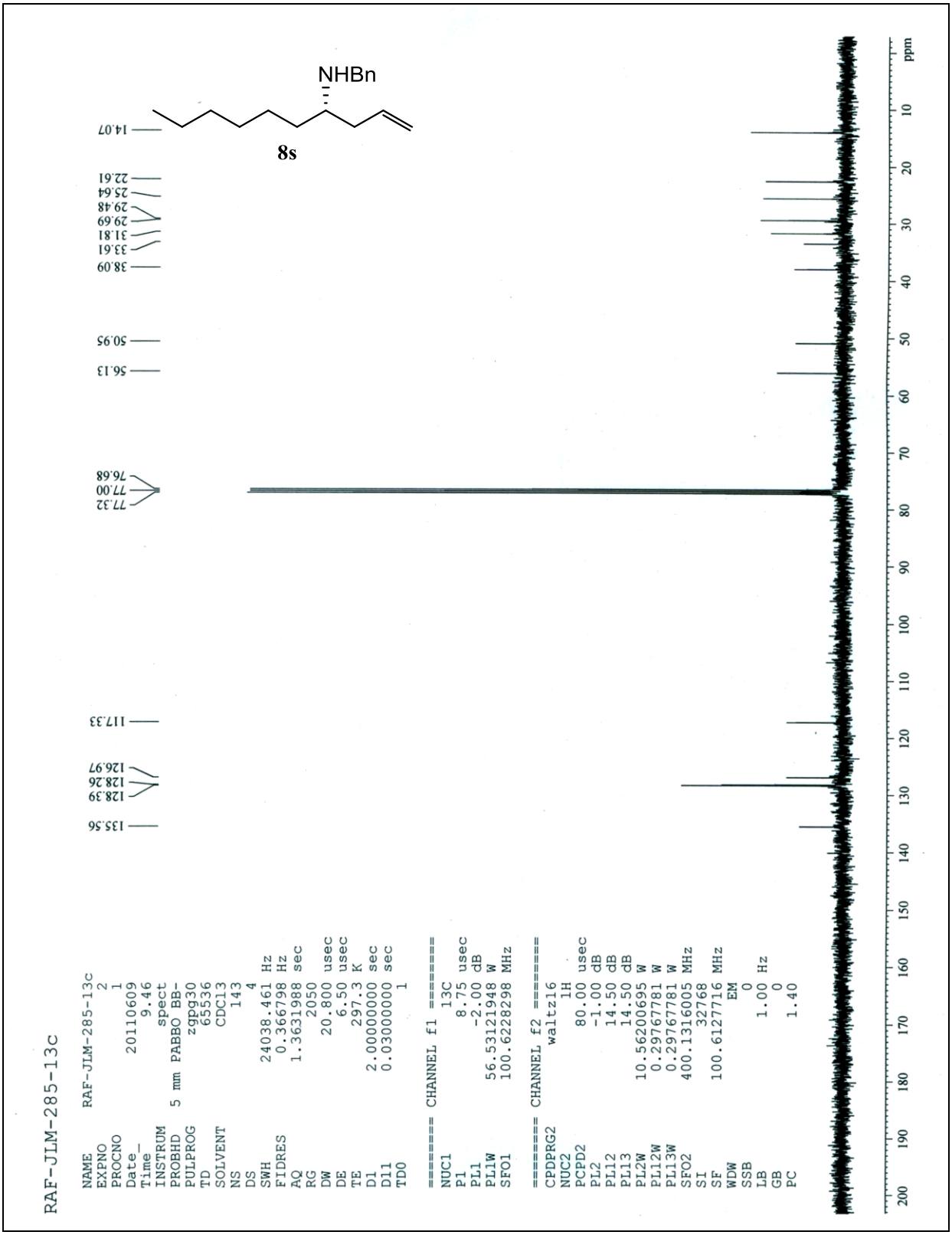
^{13}C NMR of (*R*,*E*)-*N*-benzyl-1-phenylhexa-1,5-diene-3-amine 8r



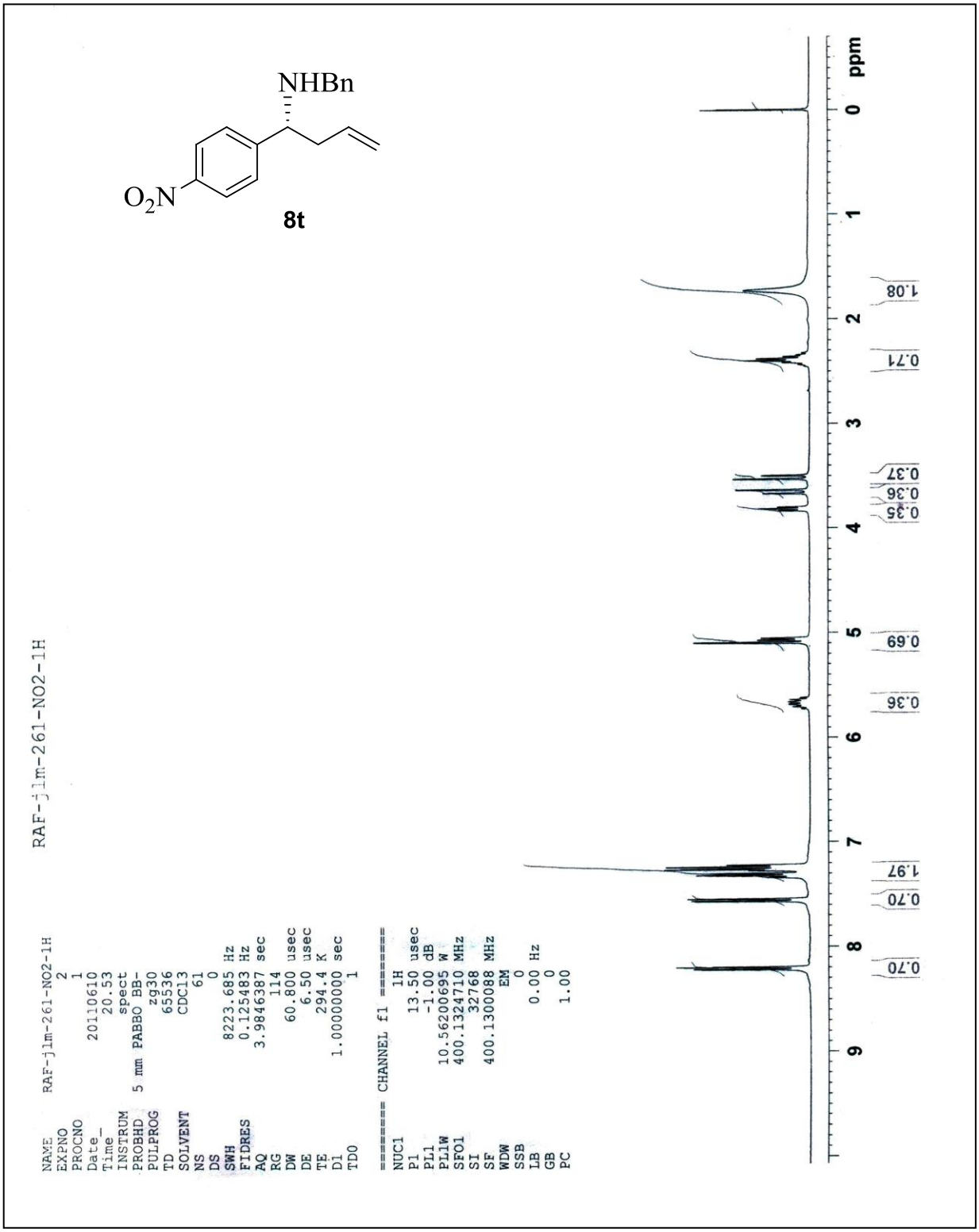
^{1}H NMR of (*R*)-*N*-Benzyl-1-heptyl-3-butenylamine 8s



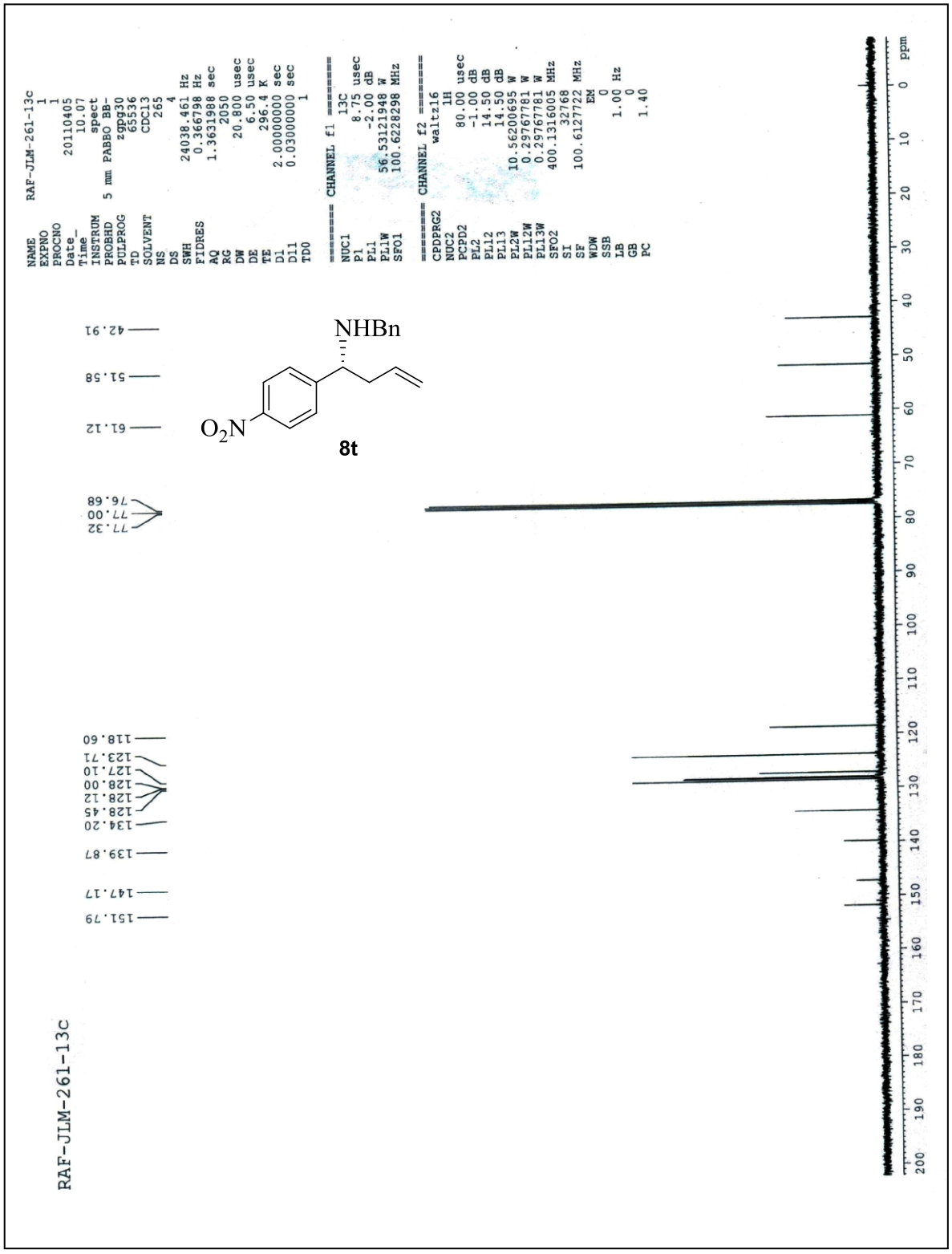
^{13}C NMR of (*R*)-*N*-Benzyl-1-heptyl-3-butenylamine 8s



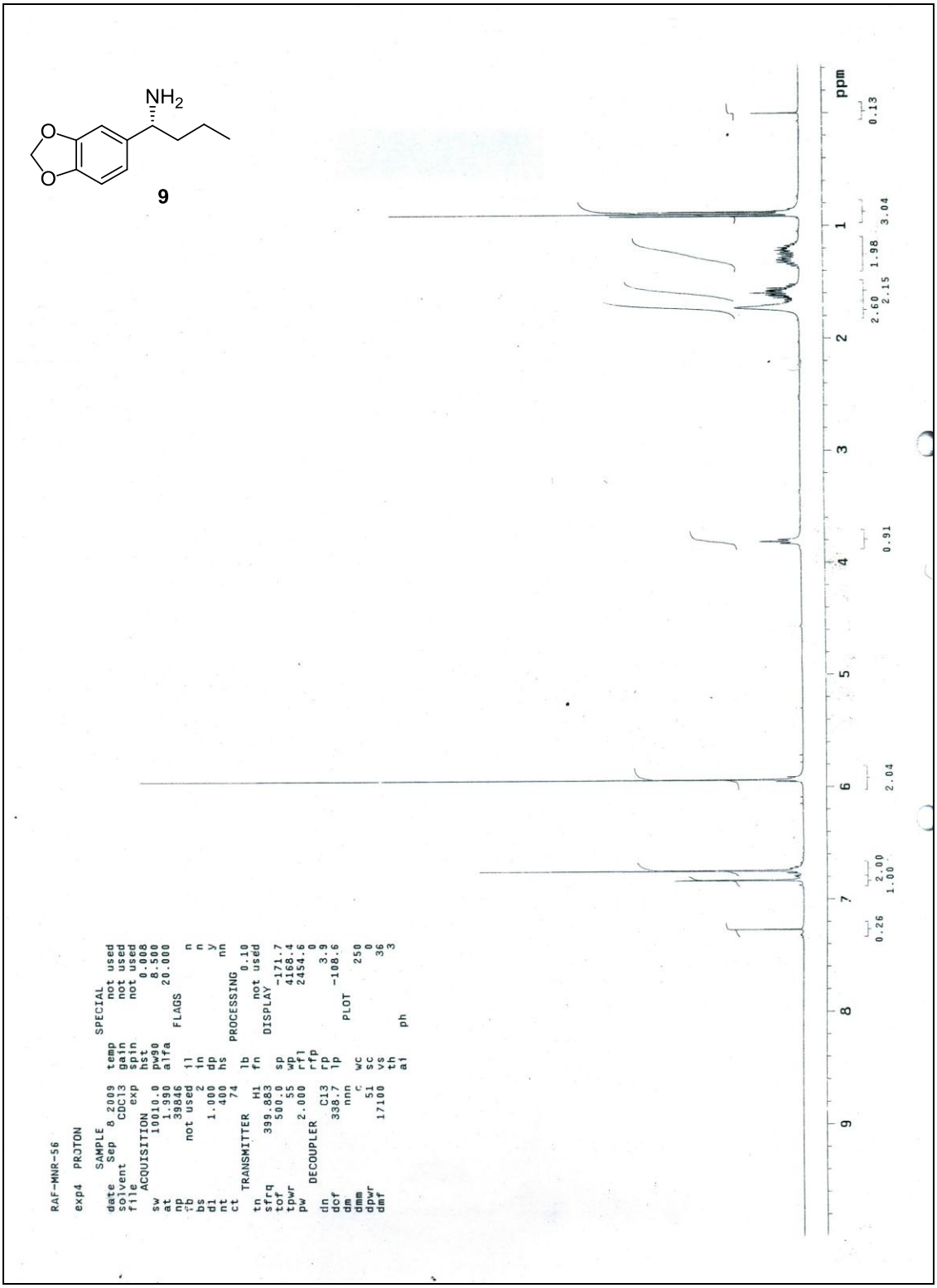
^{1}H NMR of (*R*)-*N*–Benzyl–1–(4–nitrophenyl)–3–butenylamine 8t



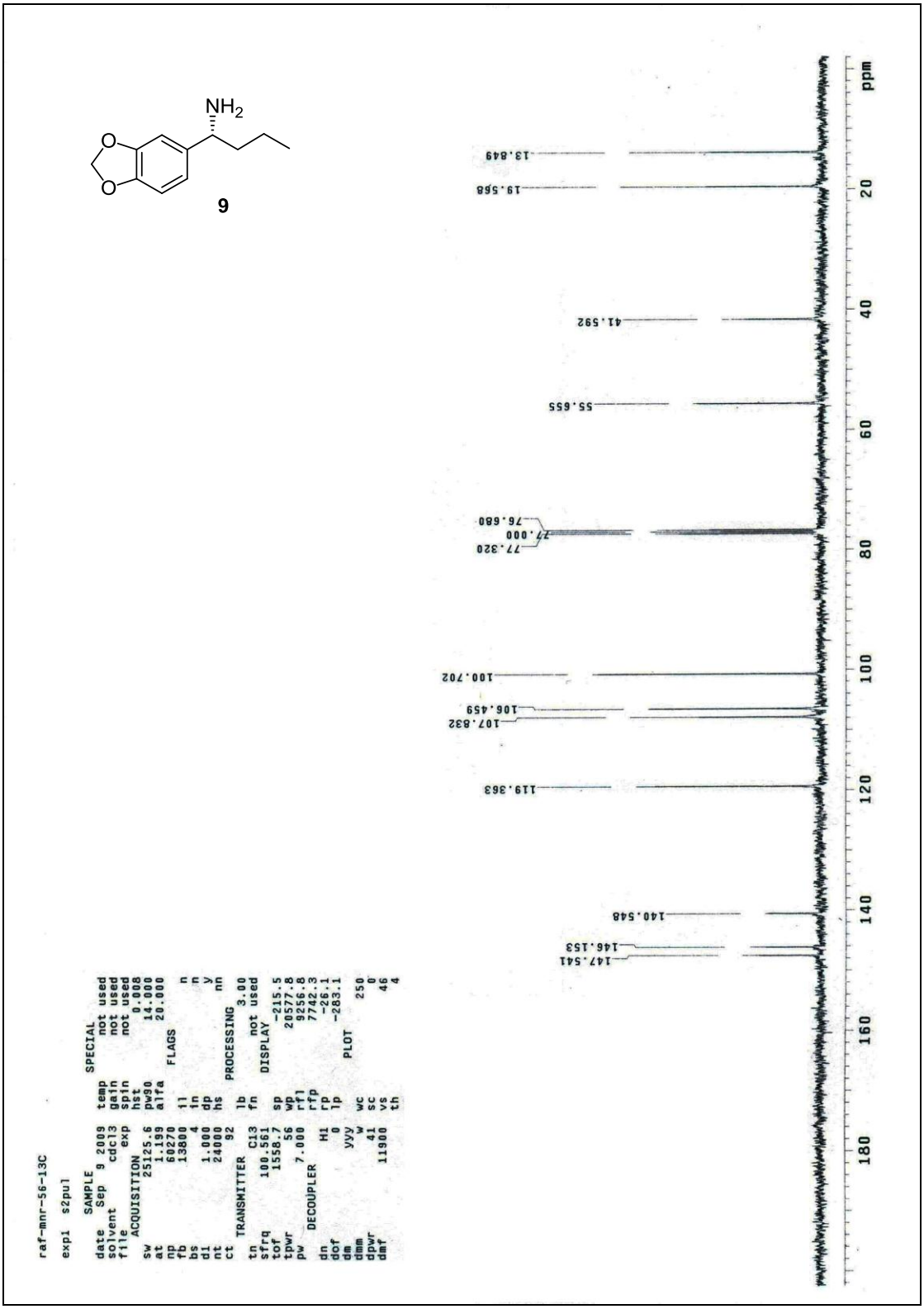
^{13}C NMR of (*R*)-*N*–Benzyl–1–(4–nitrophenyl)–3–butenylamine 8t



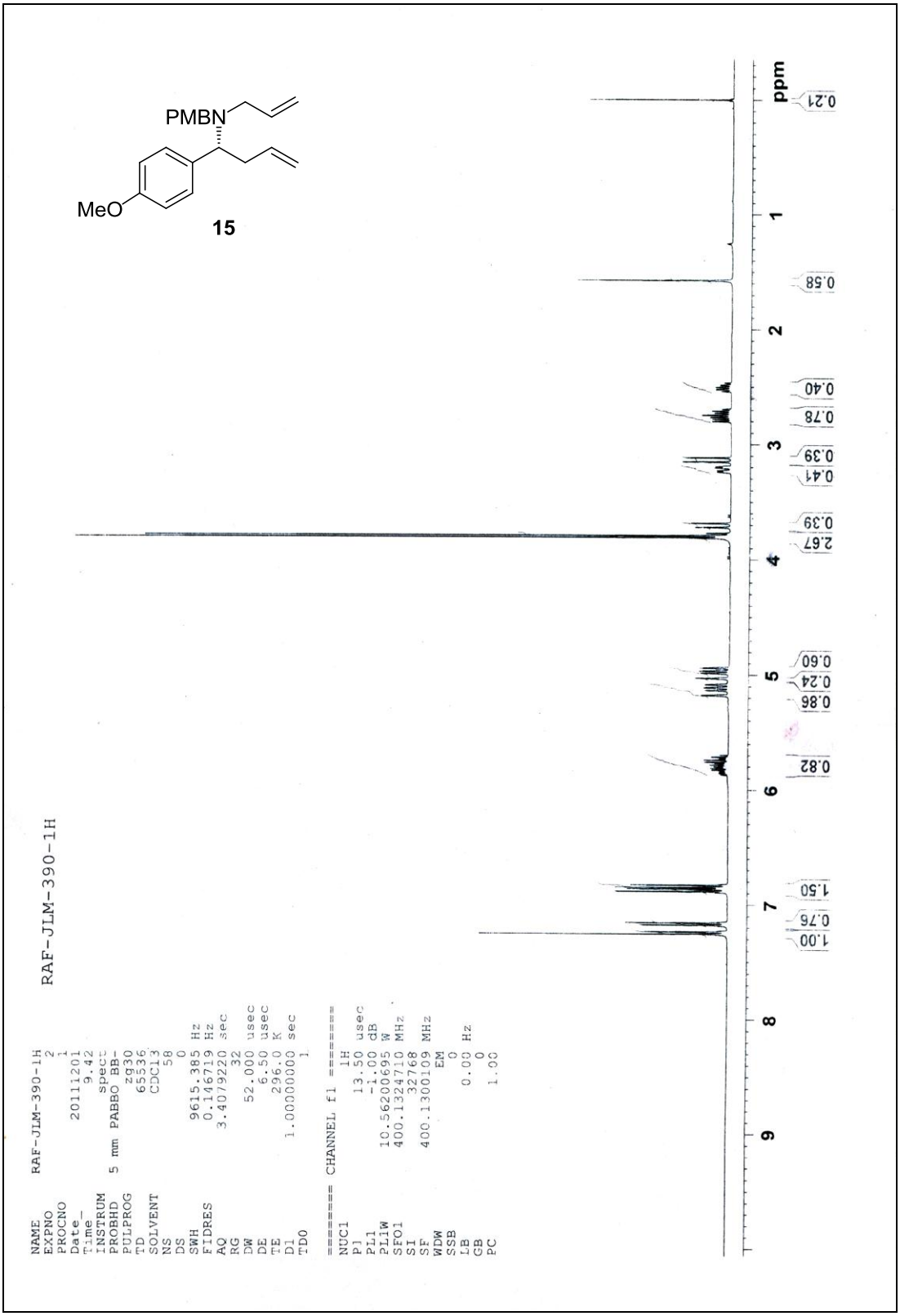
^{1}H NMR of (*R*)-α-Propylpiperonylamine 9



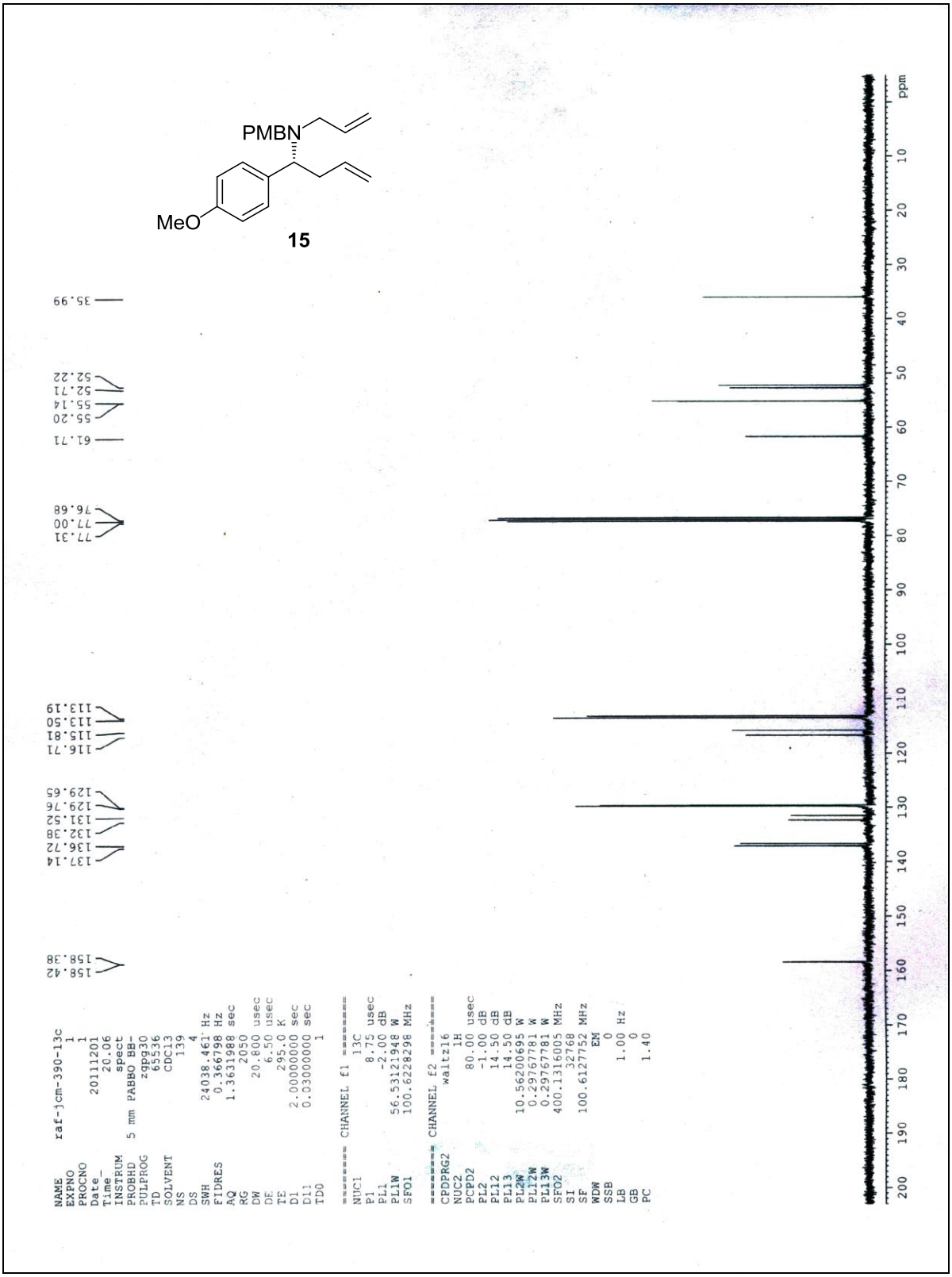
^{13}C NMR of (*R*)-α-Propylpiperonylamine 9



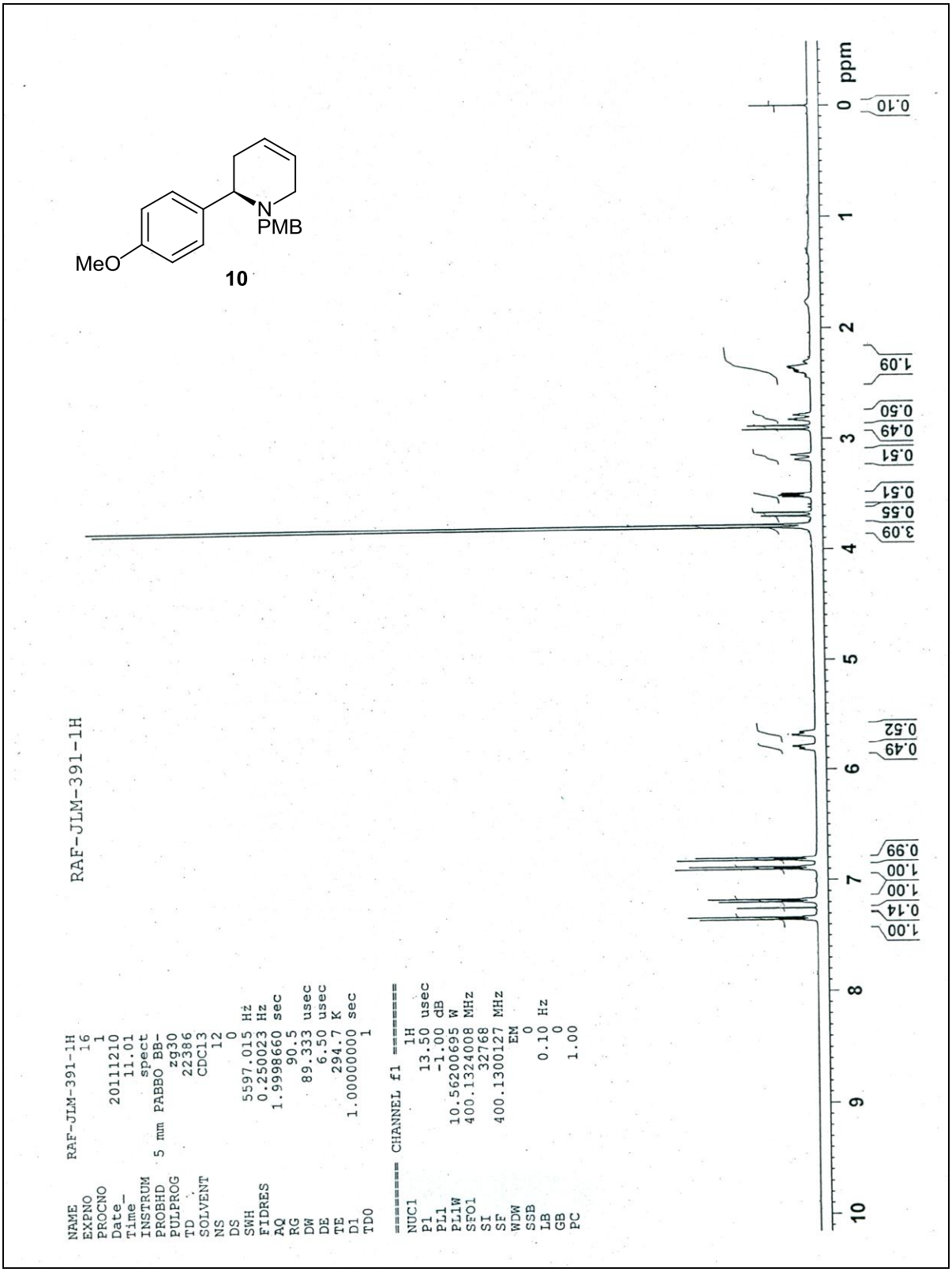
^{1}H NMR of (*R*)-*N*-allyl-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)but-3-en-1-amine 15



^{13}C NMR of (*R*)-*N*-allyl-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)but-3-en-1-amine 15

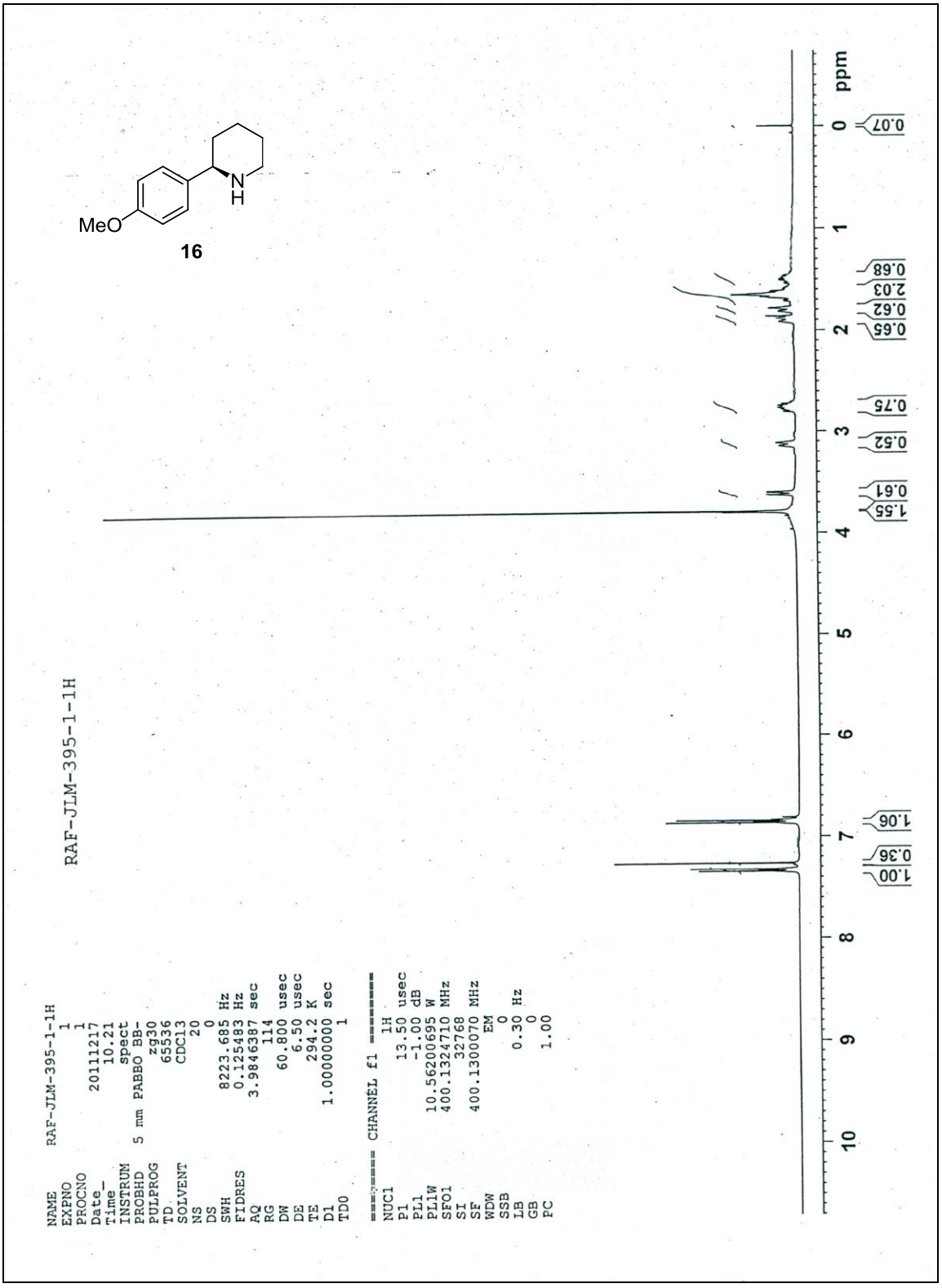


^{1}H NMR of (*R*)-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1,2,3,6-tetrahydropyridine 10

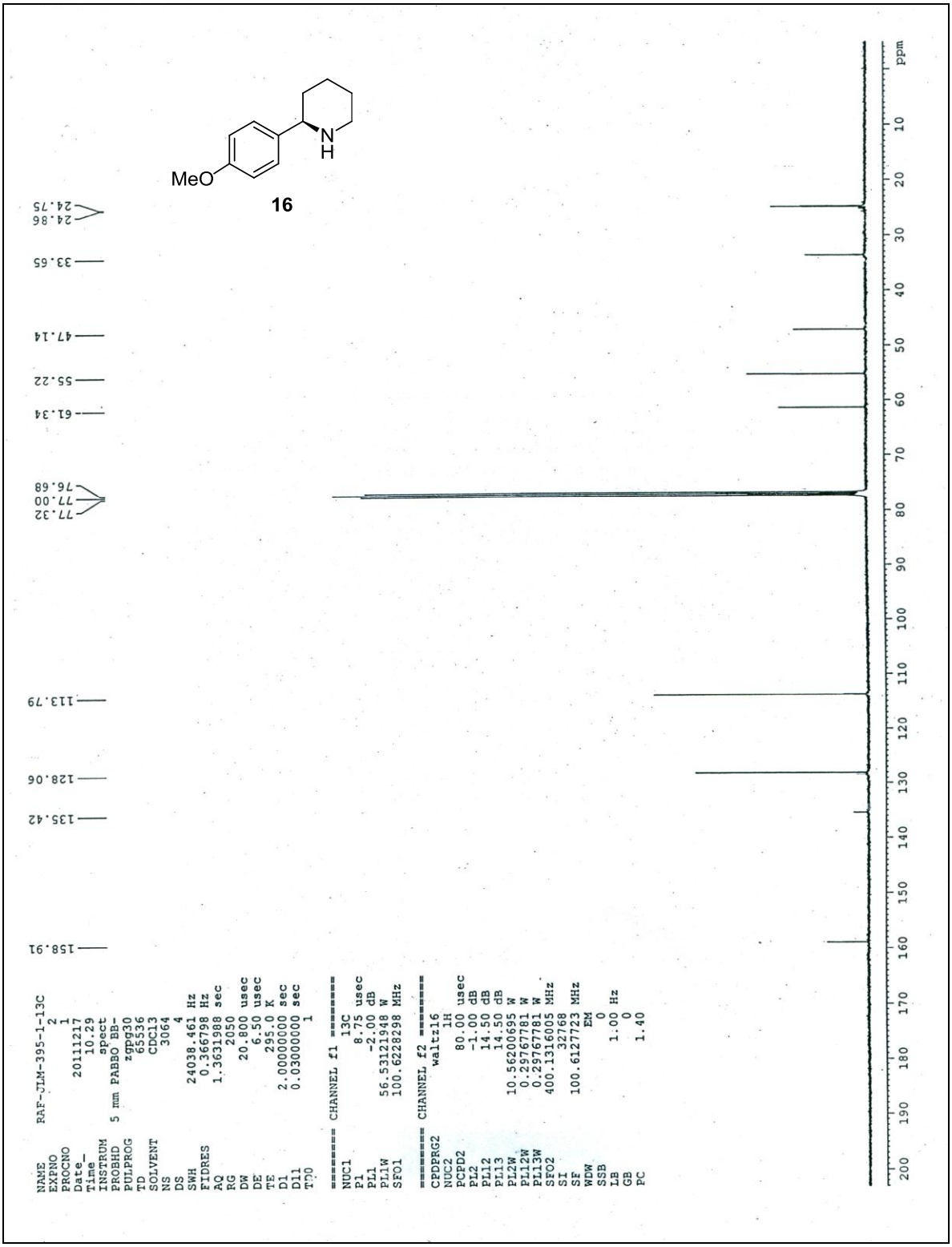


^{13}C NMR of (*R*)-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1,2,3,6-tetrahydropyridine 10

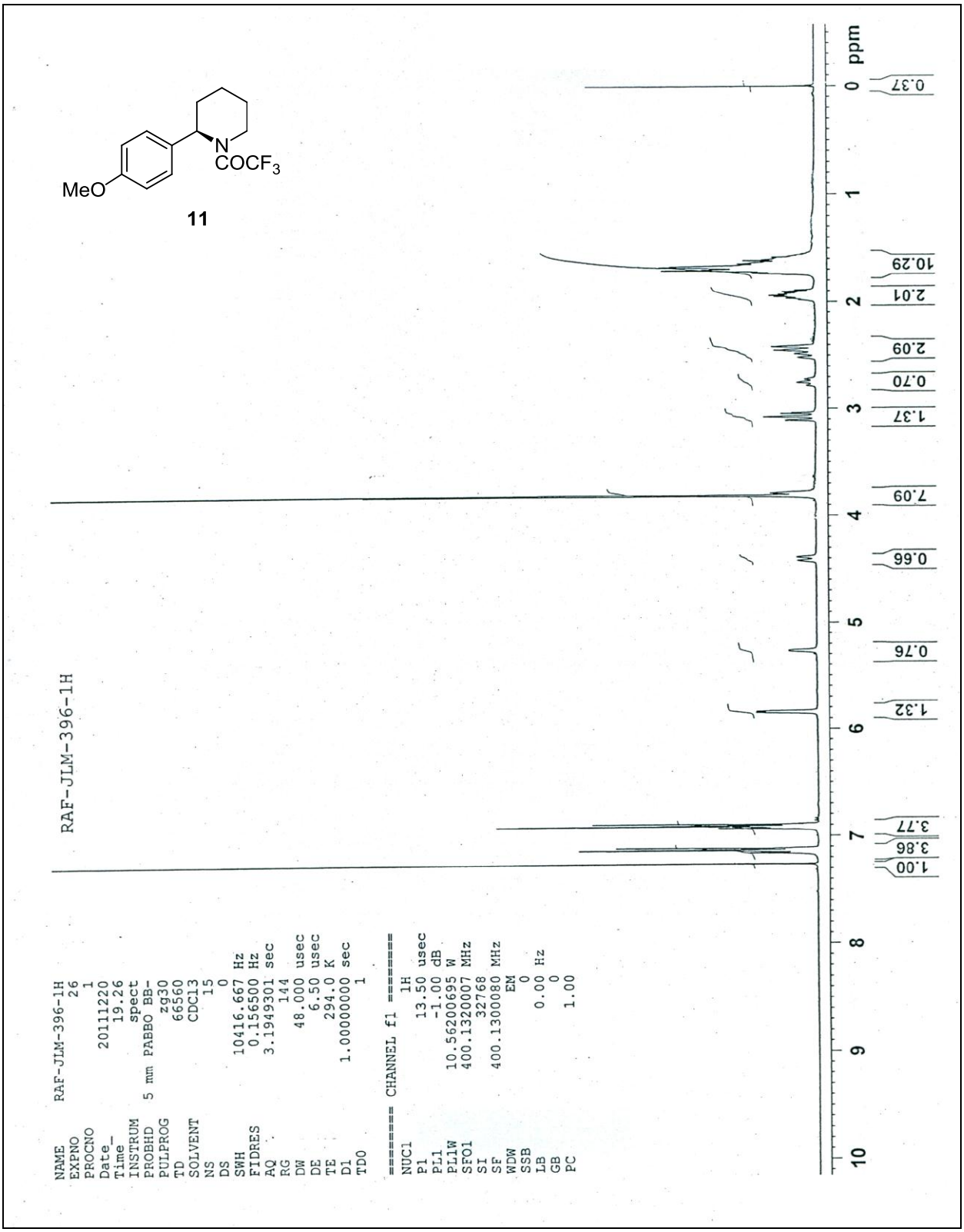
^{1}H NMR of (*R*)-2-(4-Methoxyphenyl)piperidine 16



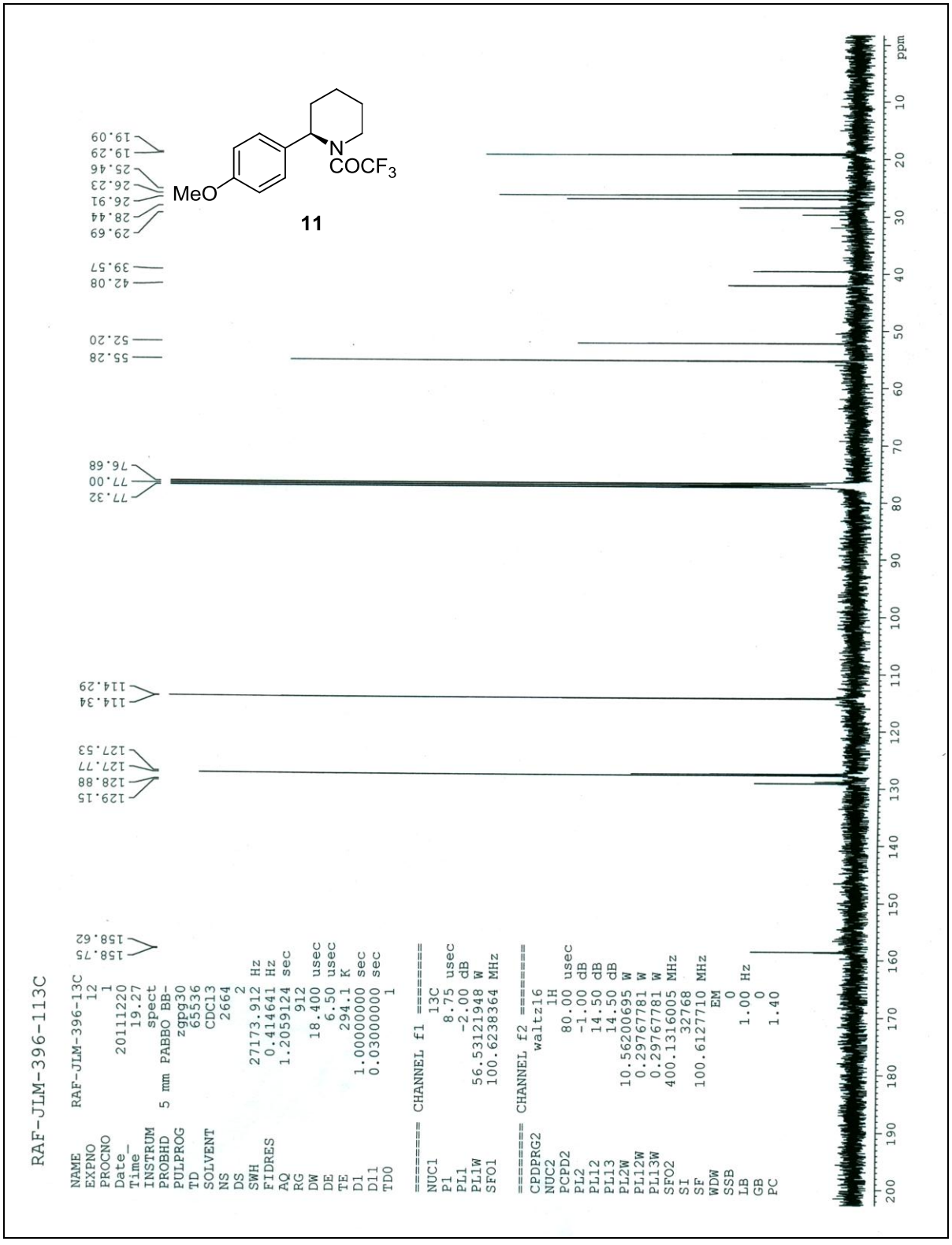
^{13}C NMR of (*R*)-2-(4-Methoxyphenyl)piperidine 16



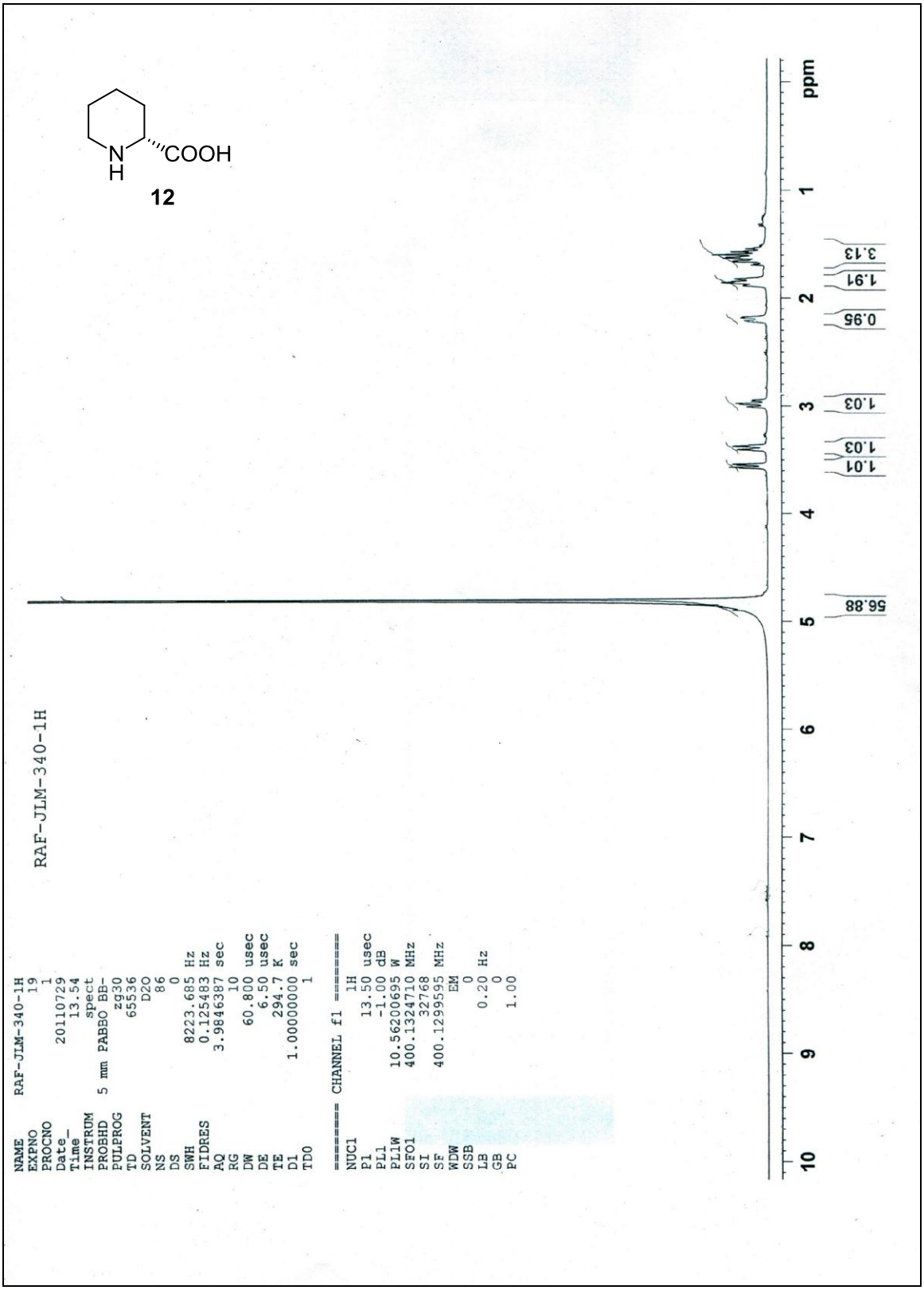
^{1}H NMR of (*R*)-*N*-Trifluroacetyl-2-(4-methoxyphenyl)piperidine 11



^{13}C NMR of (*R*)-*N*-Trifluroacetyl-2-(4-methoxyphenyl)piperidine 11



^{1}H NMR of (*R*)-Pipecolic acid 12



^{13}C NMR of (*R*)-Pipecolic acid 12