Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2018

Diastereo- and Enantioselective Additions of α-Nitro Esters to Imines for *anti*-α,β-Diamino Acid Synthesis with α-Alkyl-Substitution

Daniel J. Sprague, Anand Singh, and Jeffrey N. Johnston*

Department of Chemistry & Vanderbilt Institute of Chemical Biology

Vanderbilt University

2301 Vanderbilt Place, Nashville, TN 37235-1822

S-II-X

Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$) of **12e**

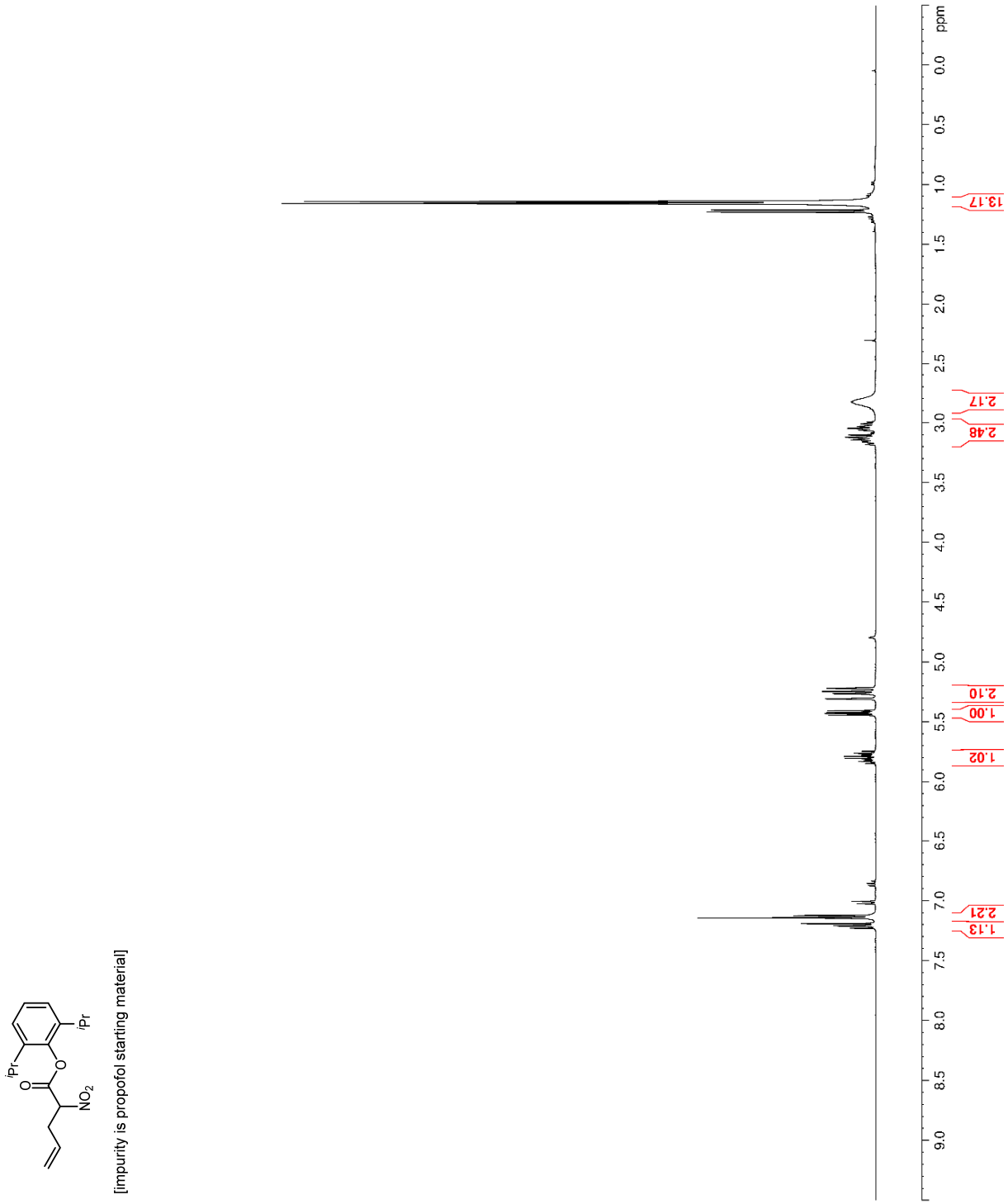


Figure 2. ^{13}C NMR (100 MHz, $CDCl_3$) of **12e**

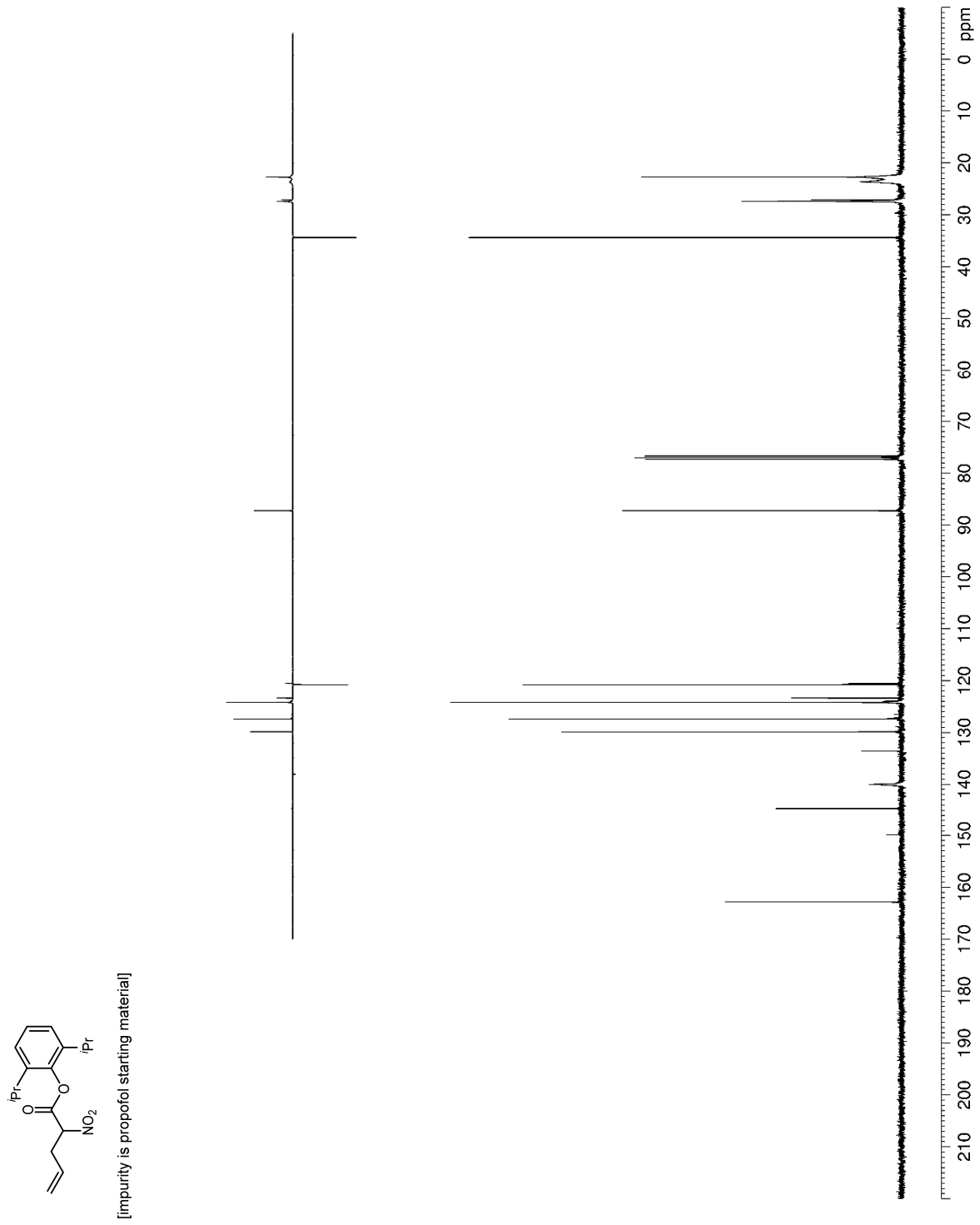


Figure 3. ^{1}H NMR (500 MHz, $CDCl_3$) of **12f**

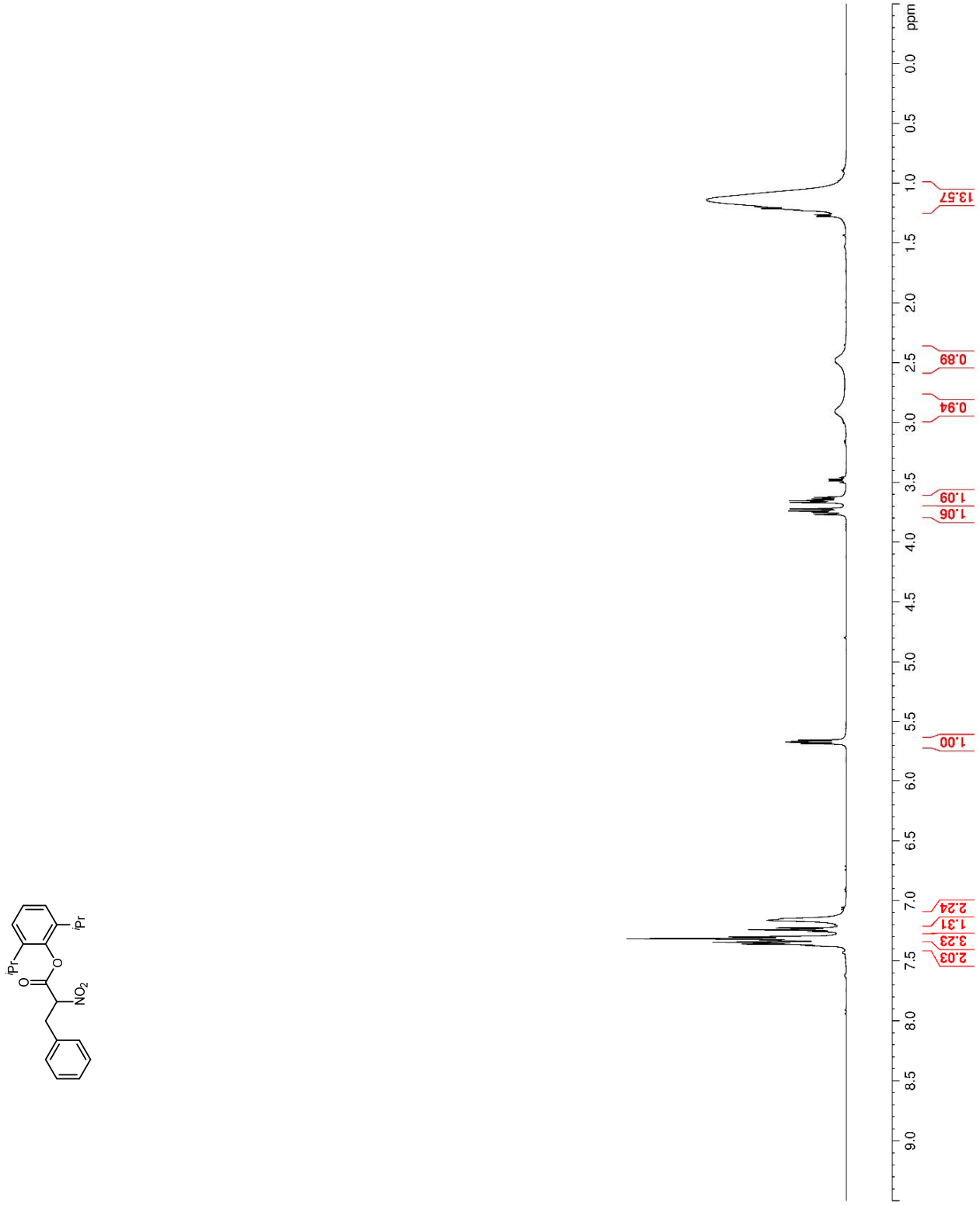


Figure 4. ^{13}C NMR (125 MHz, $CDCl_3$) of **12f**

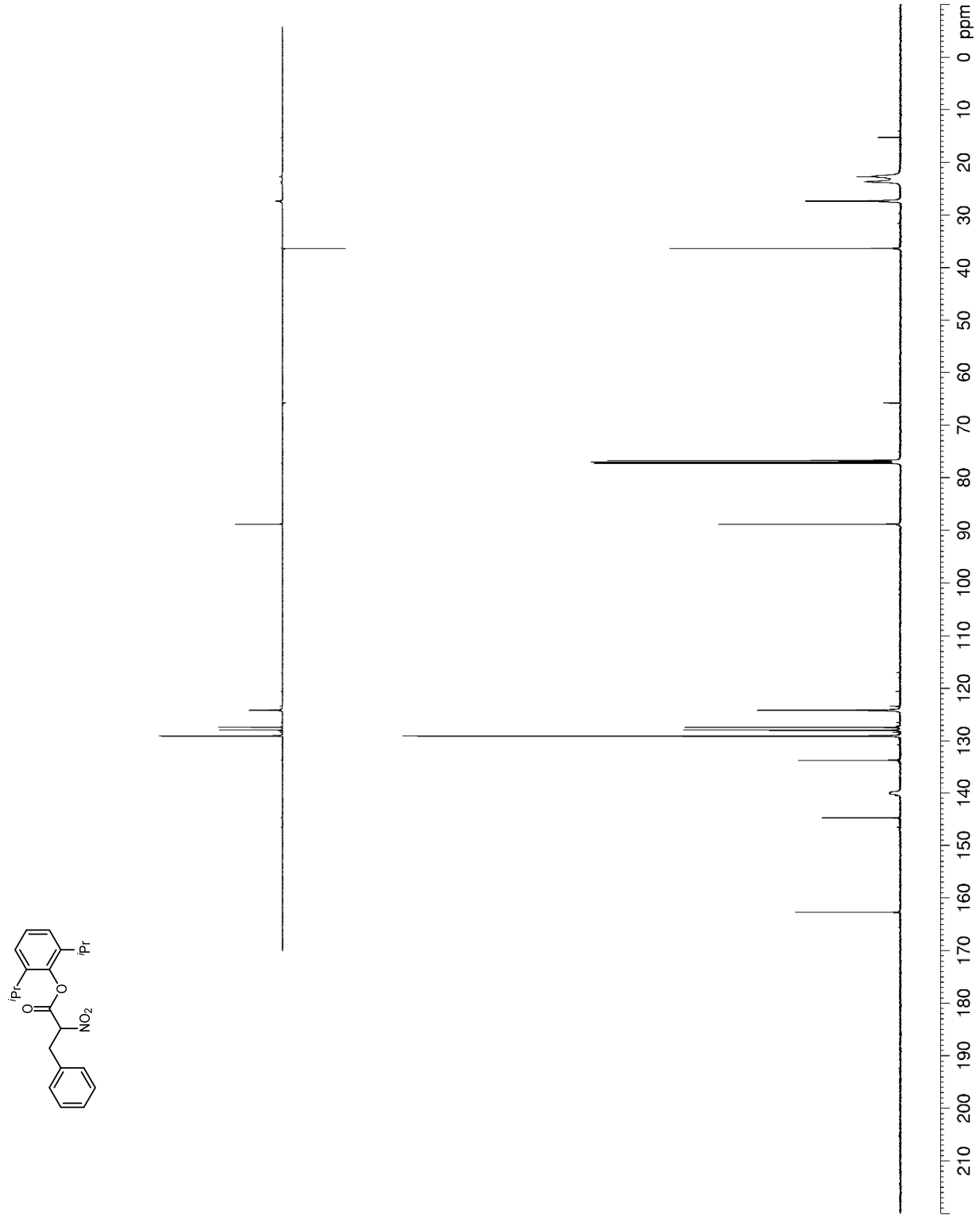


Figure 5. ^{1}H NMR (500 MHz, $CDCl_3$) of **12g**

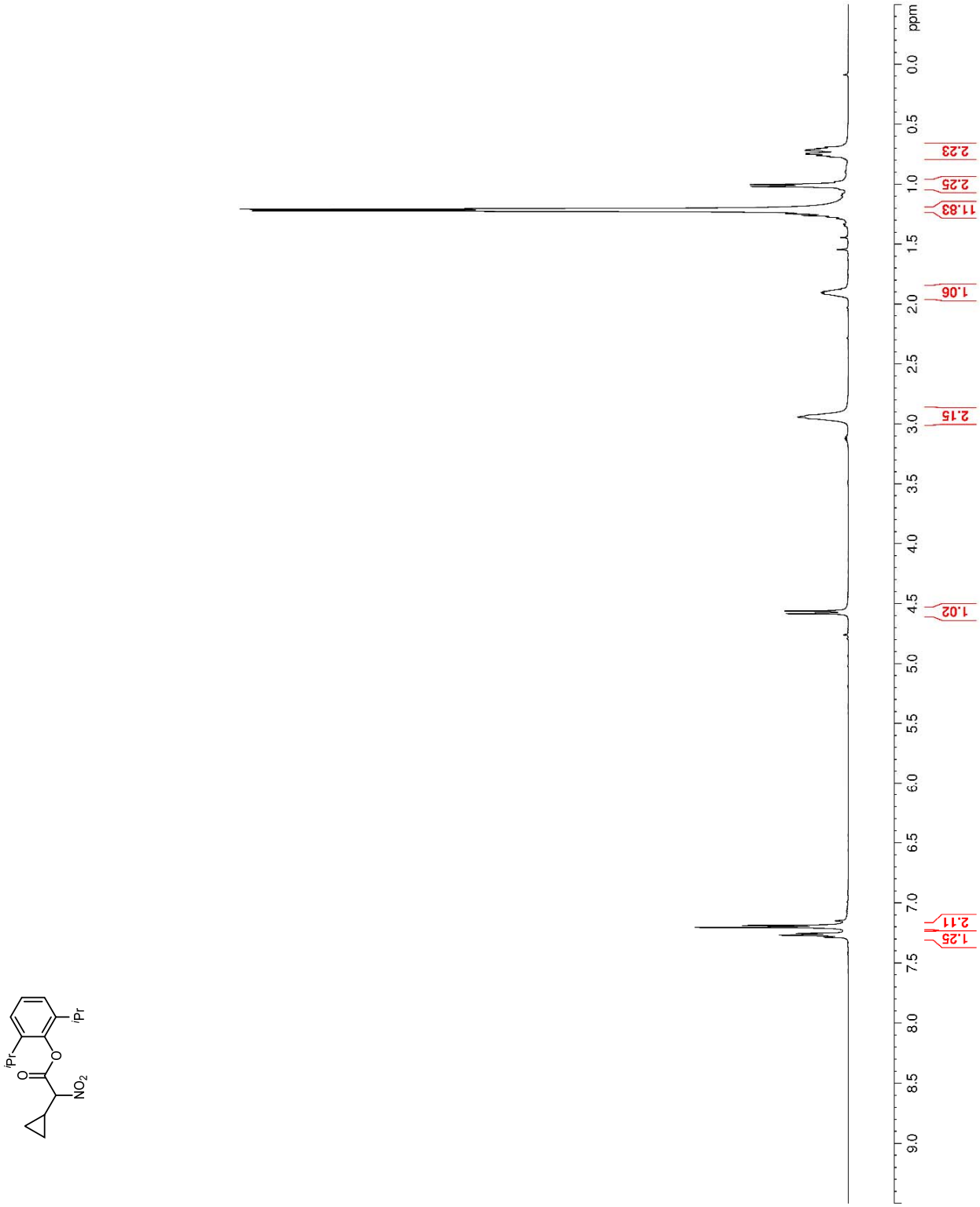


Figure 6. ^{13}C NMR (125 MHz, $CDCl_3$) of **12g**

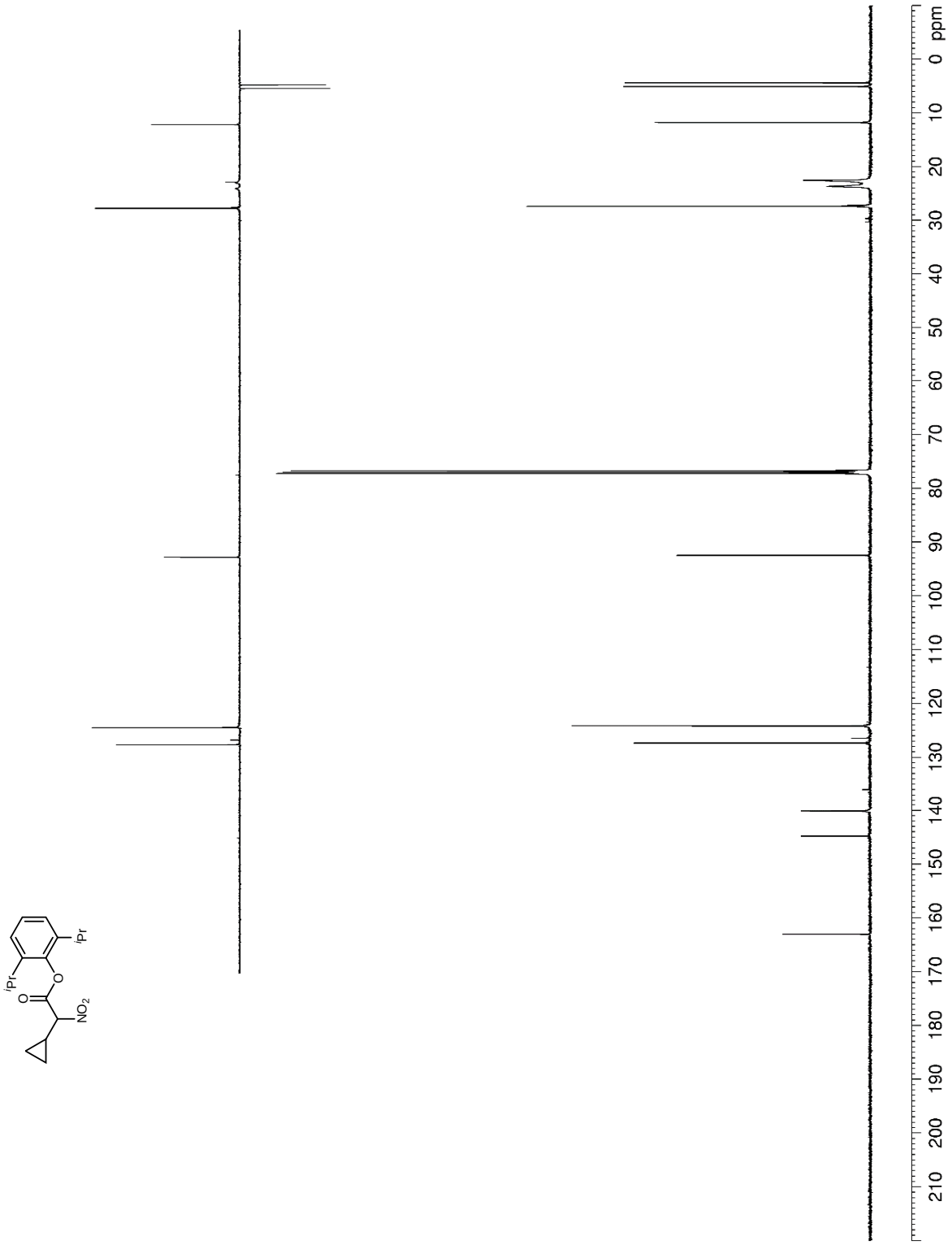


Figure 7. ^{1}H NMR (400 MHz, $CDCl_3$) of **12i**

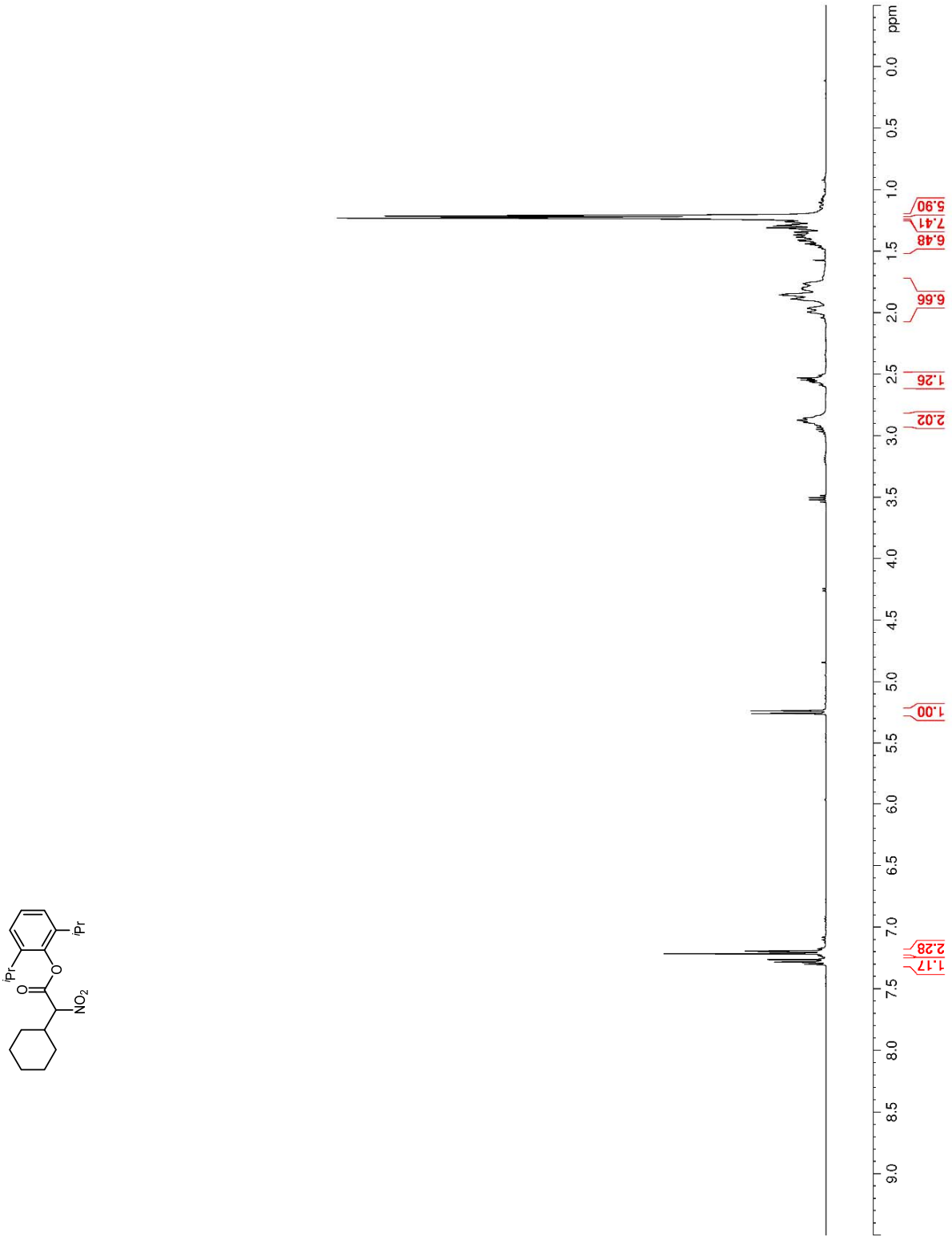


Figure 8. ^{13}C NMR (100 MHz, $CDCl_3$) of **12i**

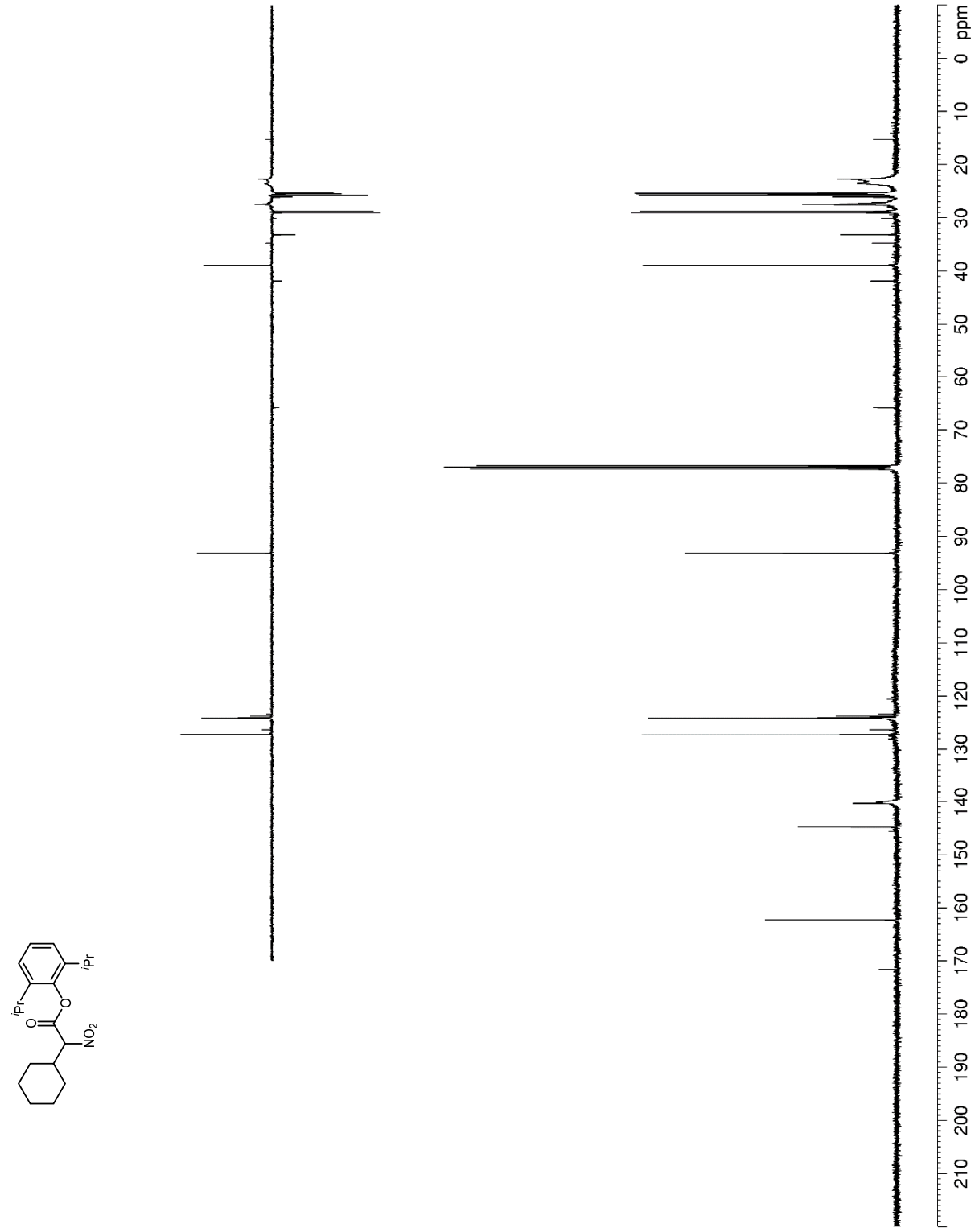


Figure 9. ^{1}H NMR (400 MHz, $CDCl_3$) of **13a**

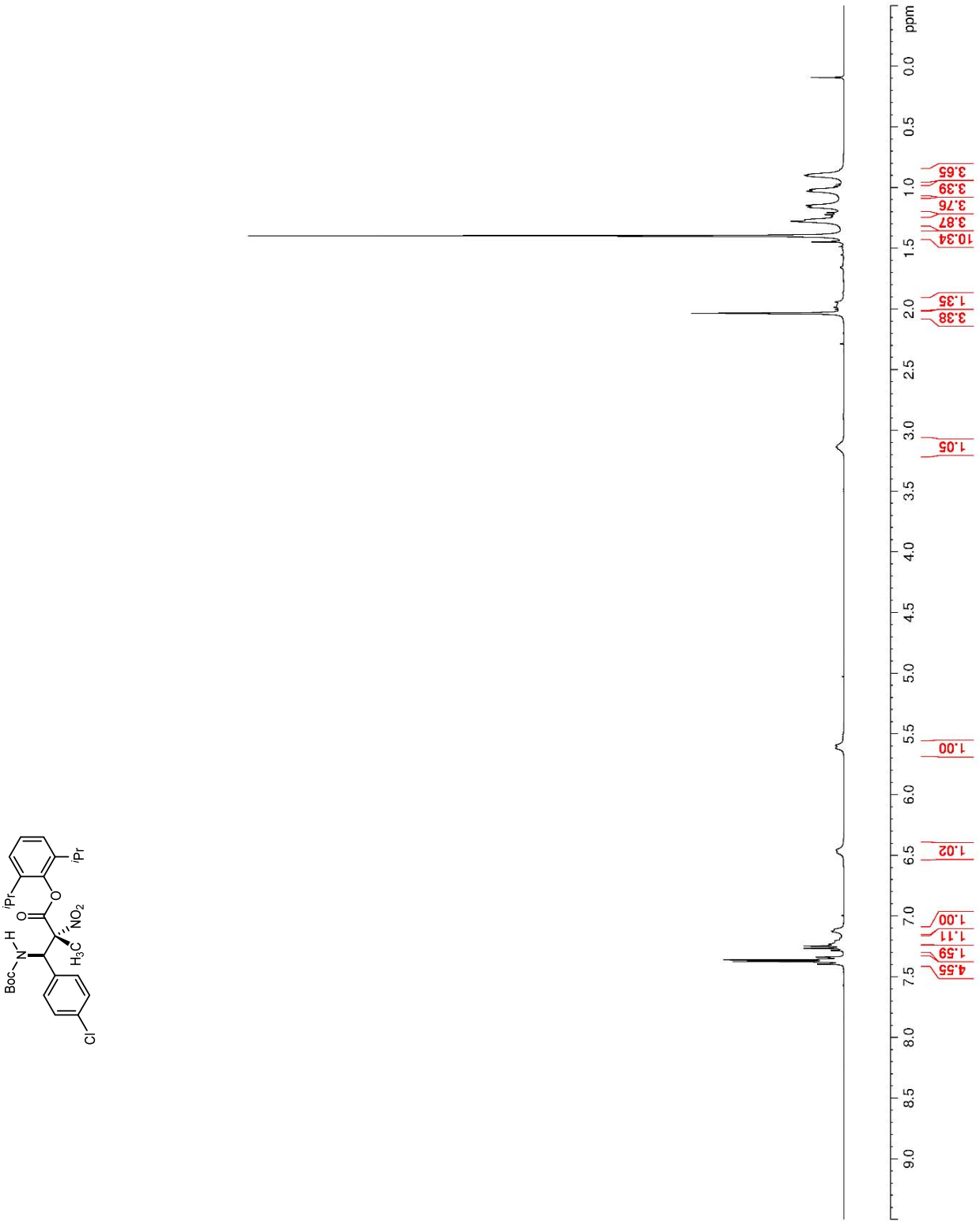


Figure 10. ^{13}C NMR (100 MHz, $CDCl_3$) of **13a**

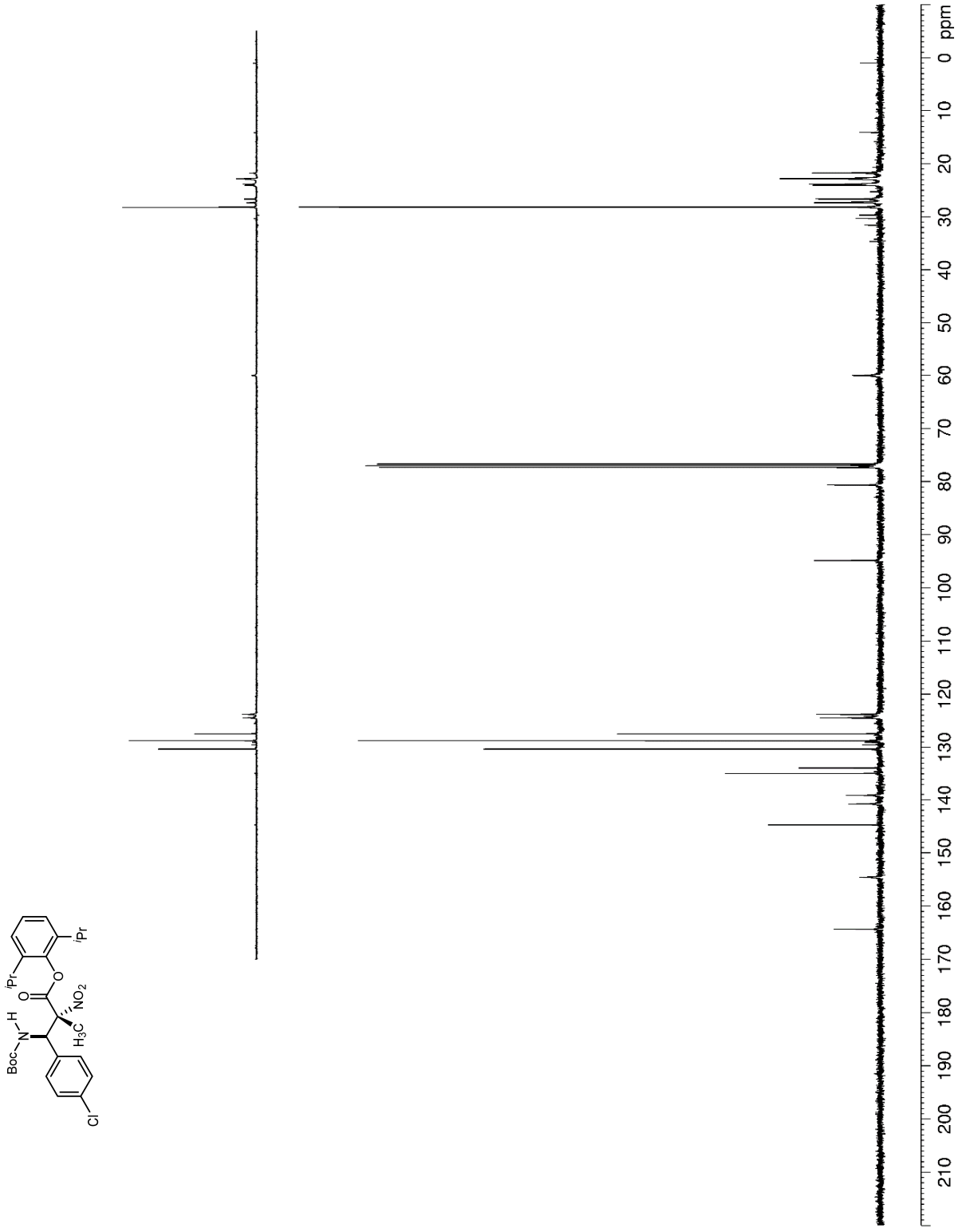


Figure 11. ^{1}H NMR (400 MHz, $CDCl_3$) of **13b**

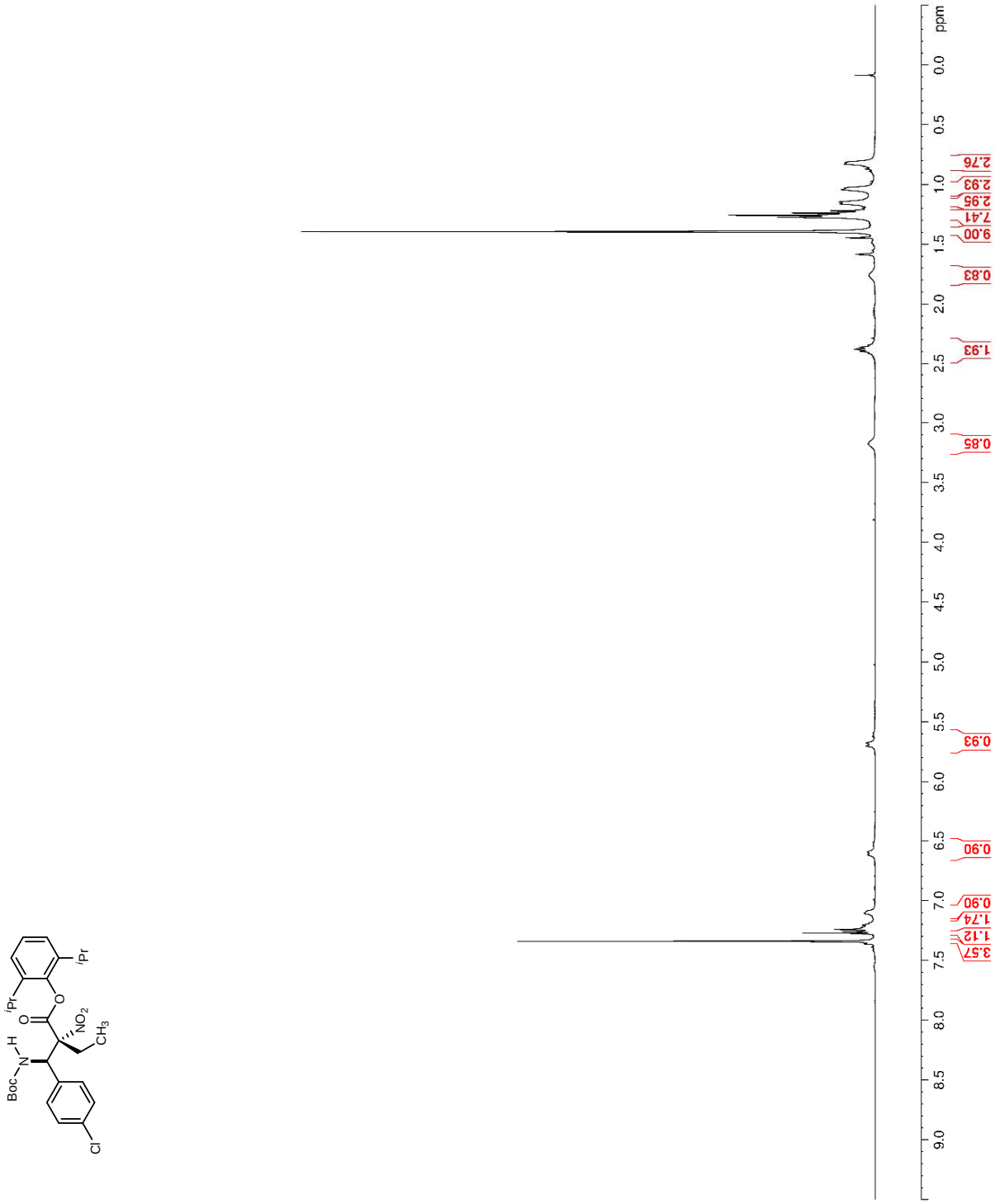


Figure 12. ^{13}C NMR (100 MHz, $CDCl_3$) of **13b**

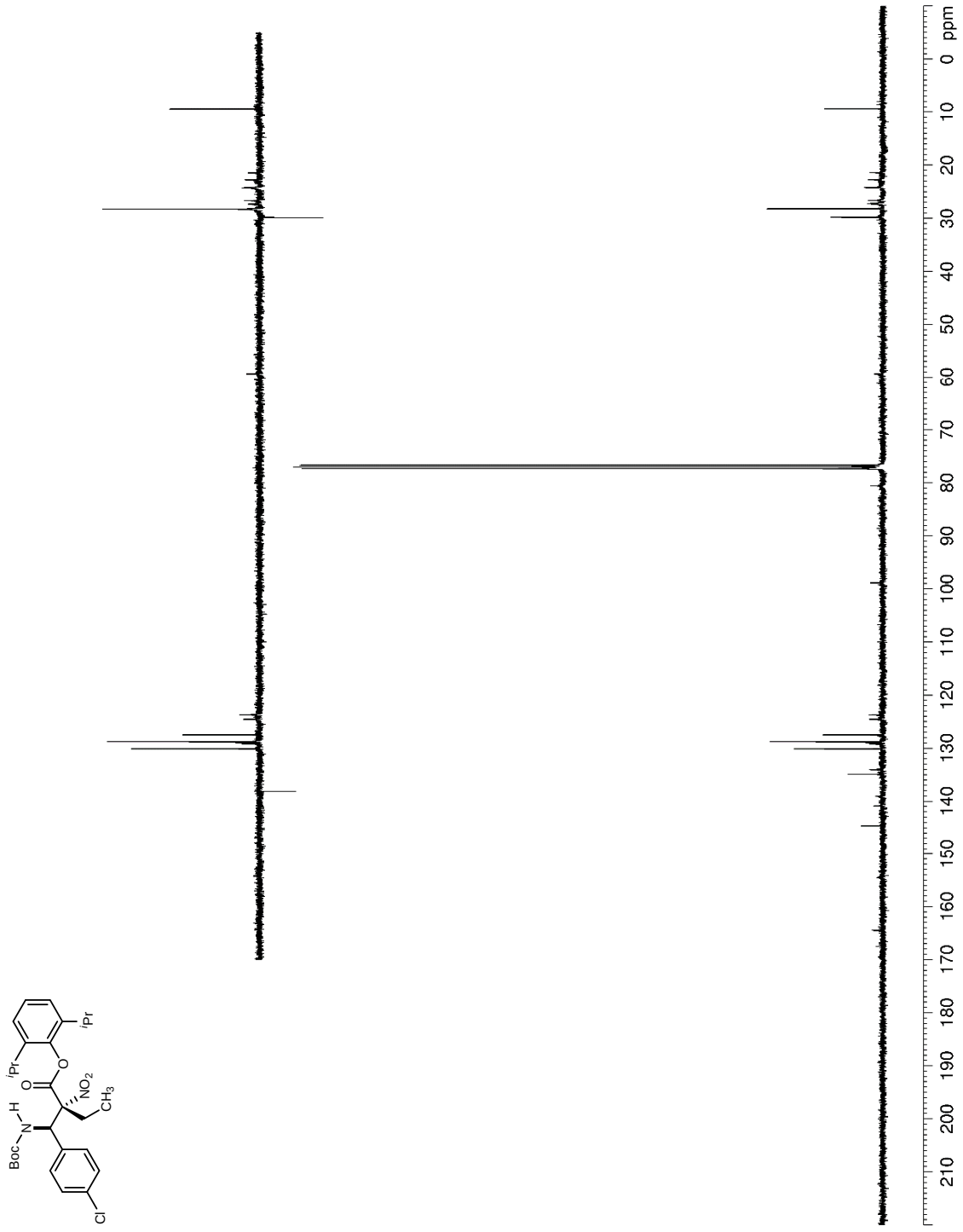


Figure 13. ^{1}H NMR (400 MHz, $CDCl_3$) of **13c**

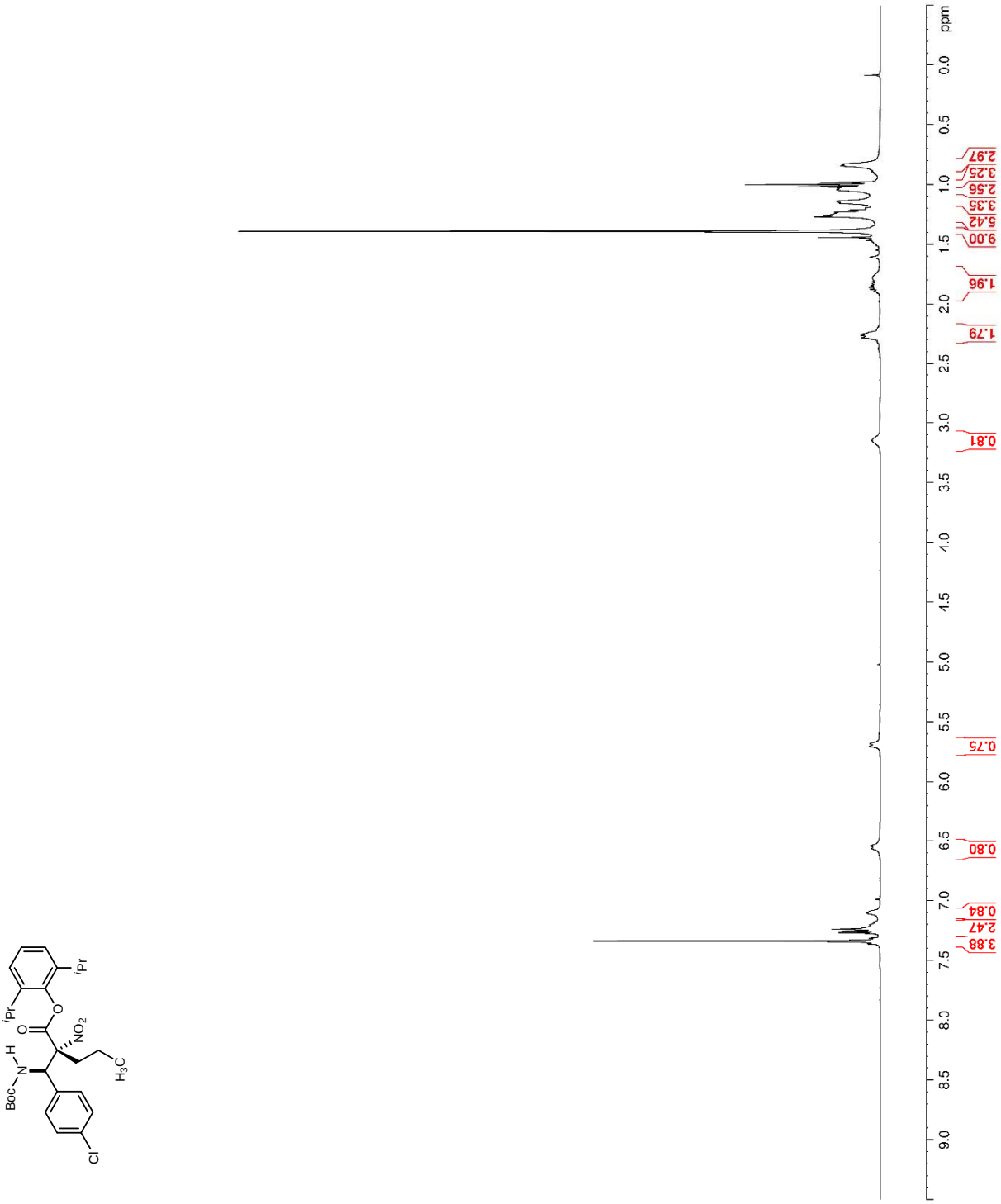


Figure 14. ^{13}C NMR (100 MHz, $CDCl_3$) of **13c**

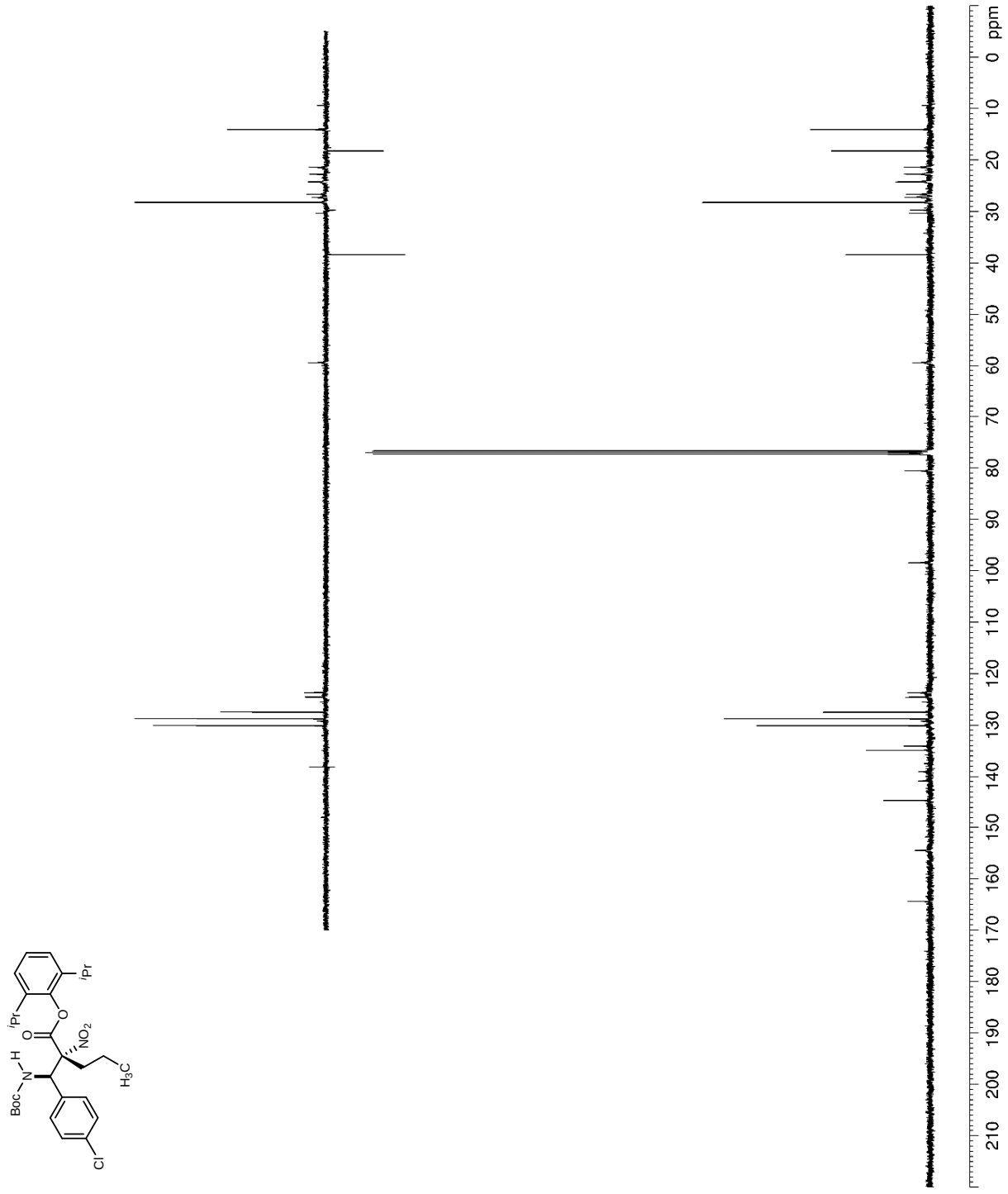


Figure 15. ^{1}H NMR (400 MHz, $CDCl_3$) of **13d**

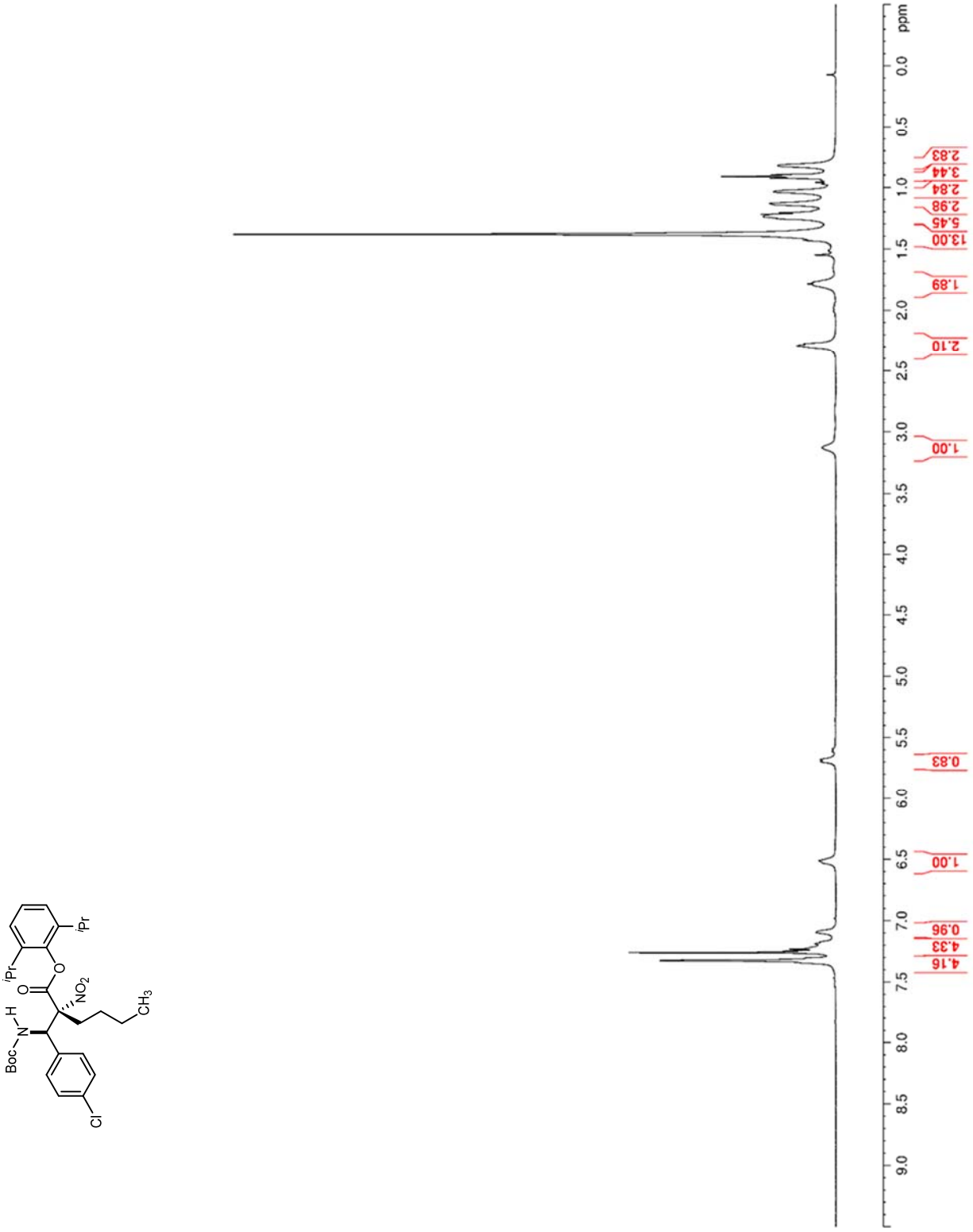


Figure 16. ^{13}C NMR (100 MHz, $CDCl_3$) of **13d**

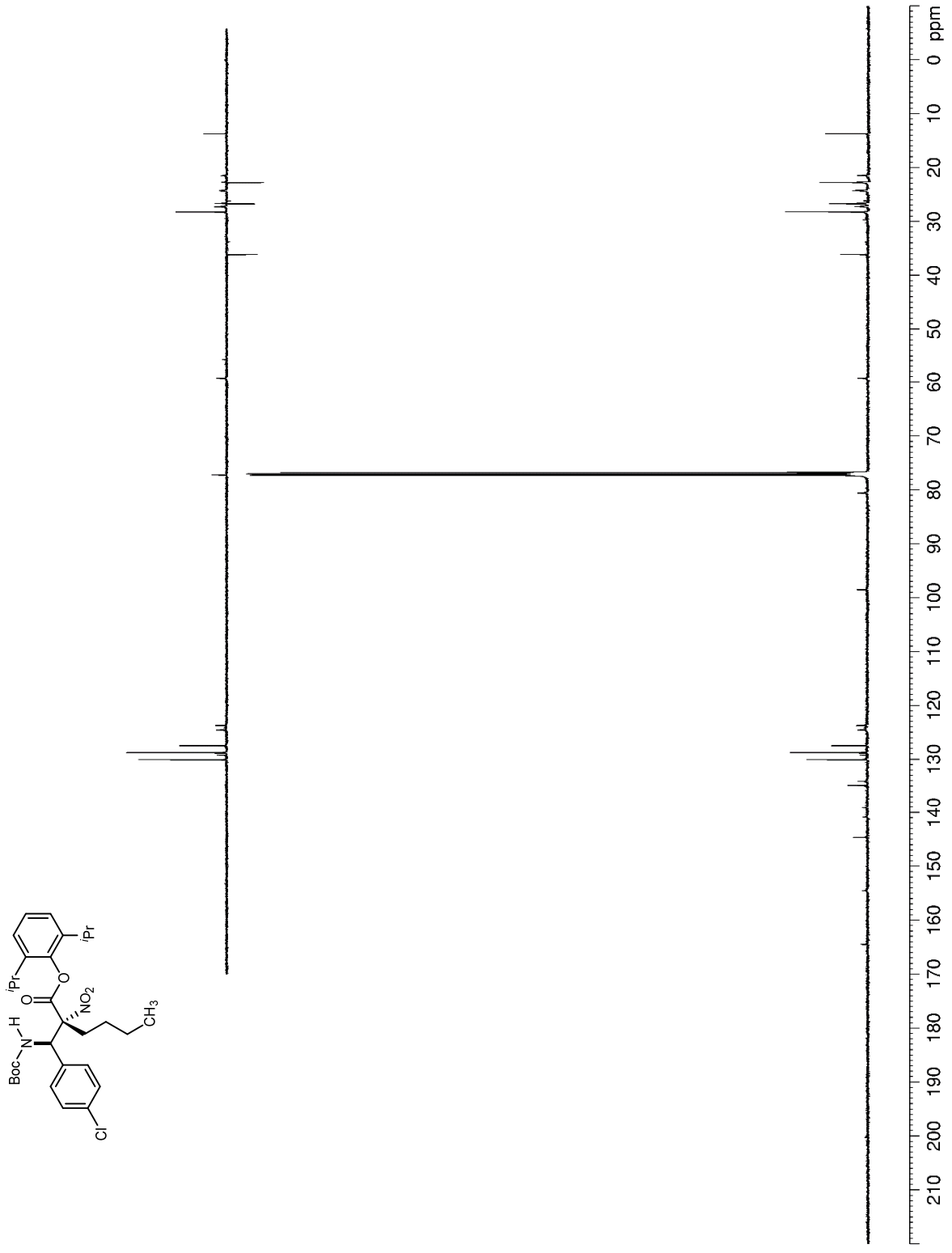


Figure 17. ^{1}H NMR (400 MHz, $CDCl_3$) of **13e**

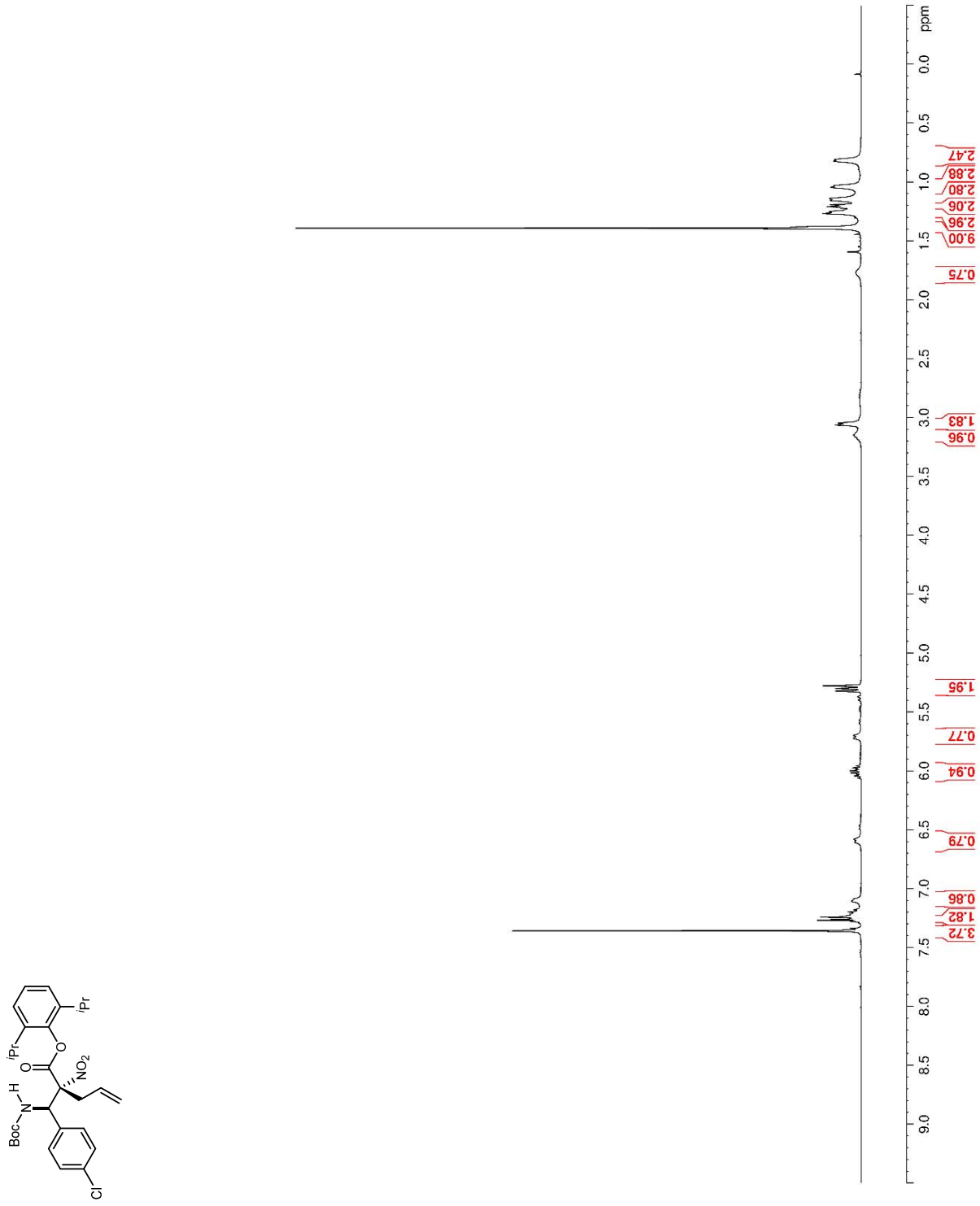


Figure 18. ^{13}C NMR (100 MHz, $CDCl_3$) of **13e**

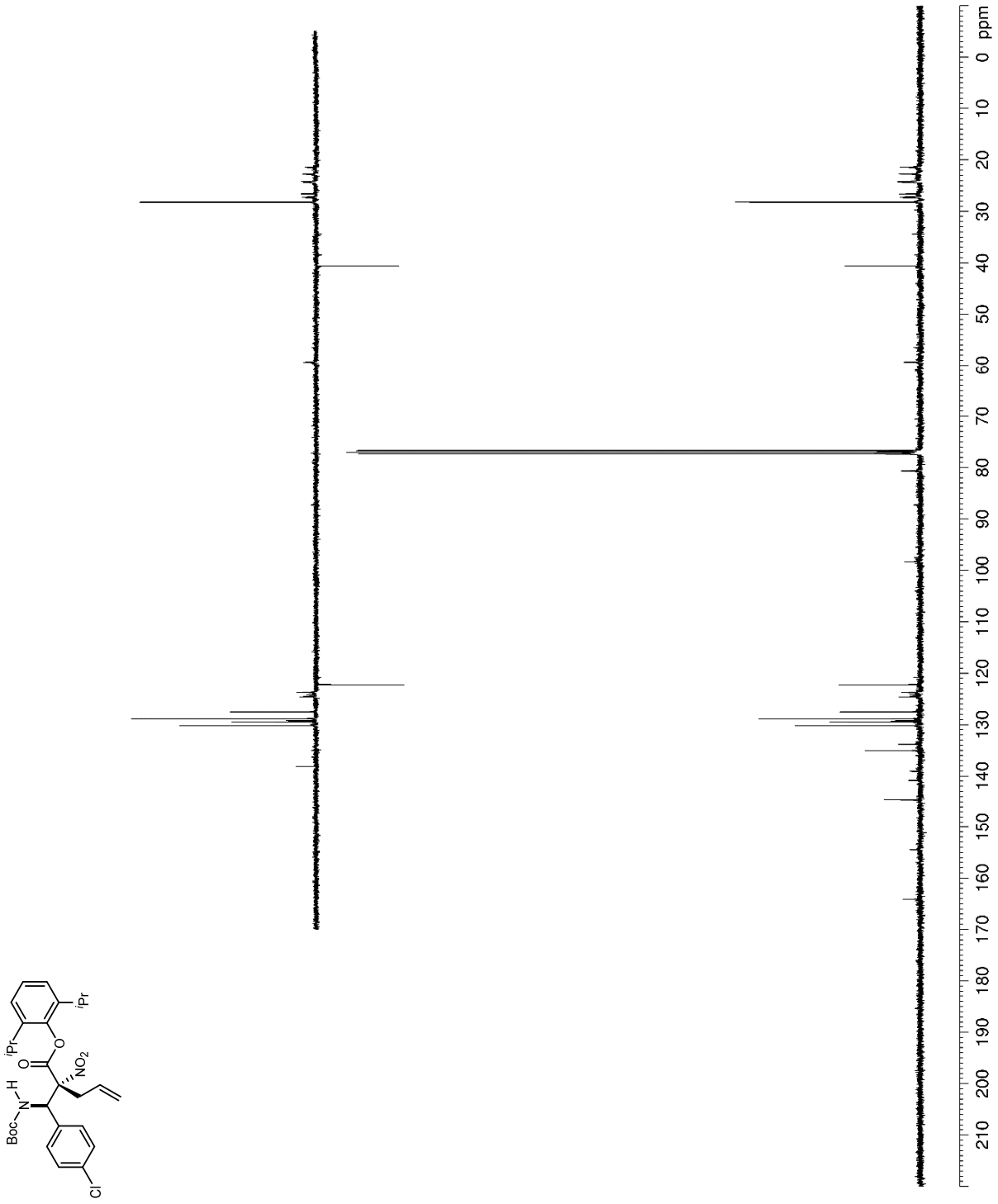


Figure 19. ^{1}H NMR (400 MHz, $CDCl_3$) of **13f**

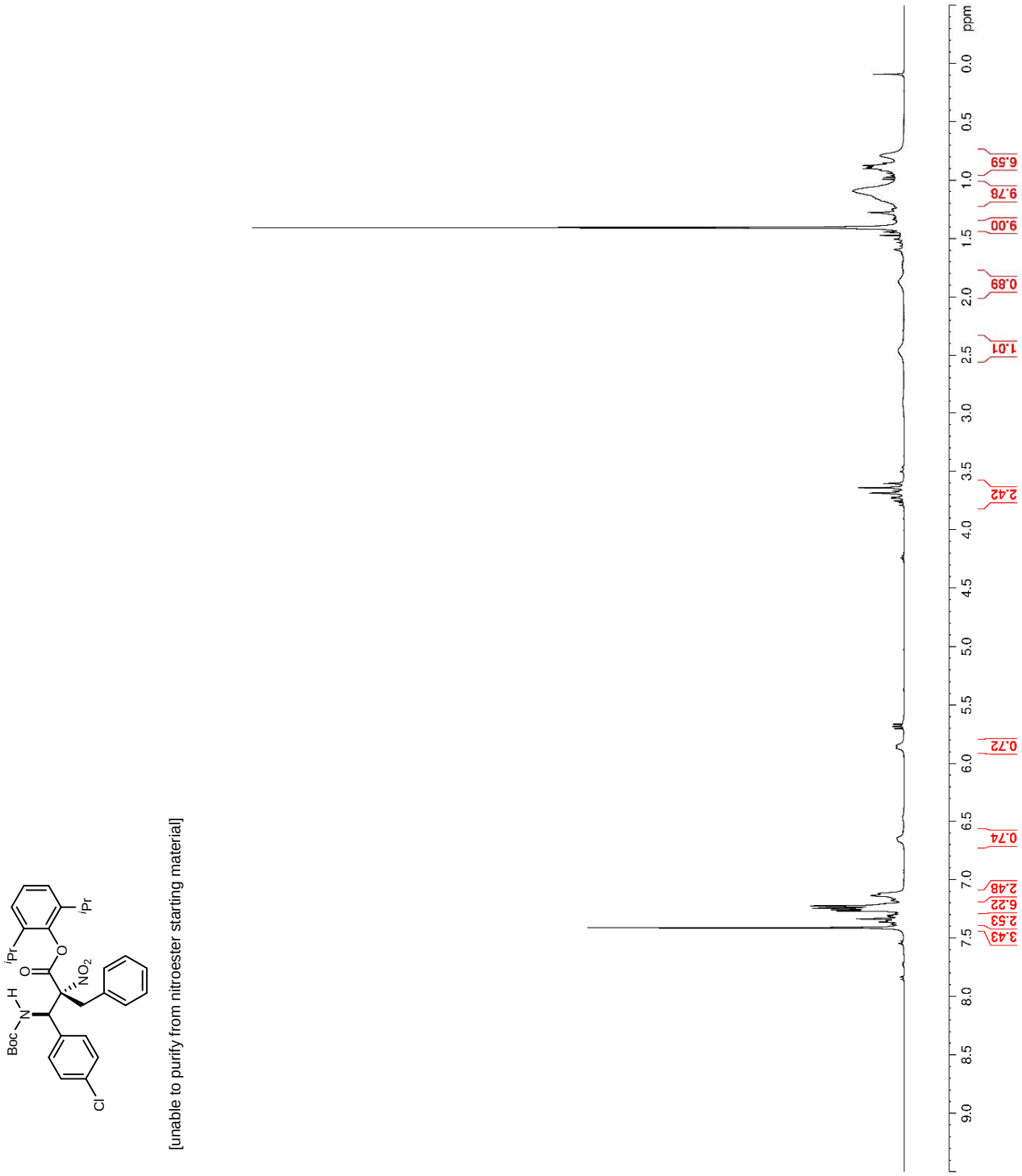


Figure 20. ^{13}C NMR (100 MHz, $CDCl_3$) of **13f**

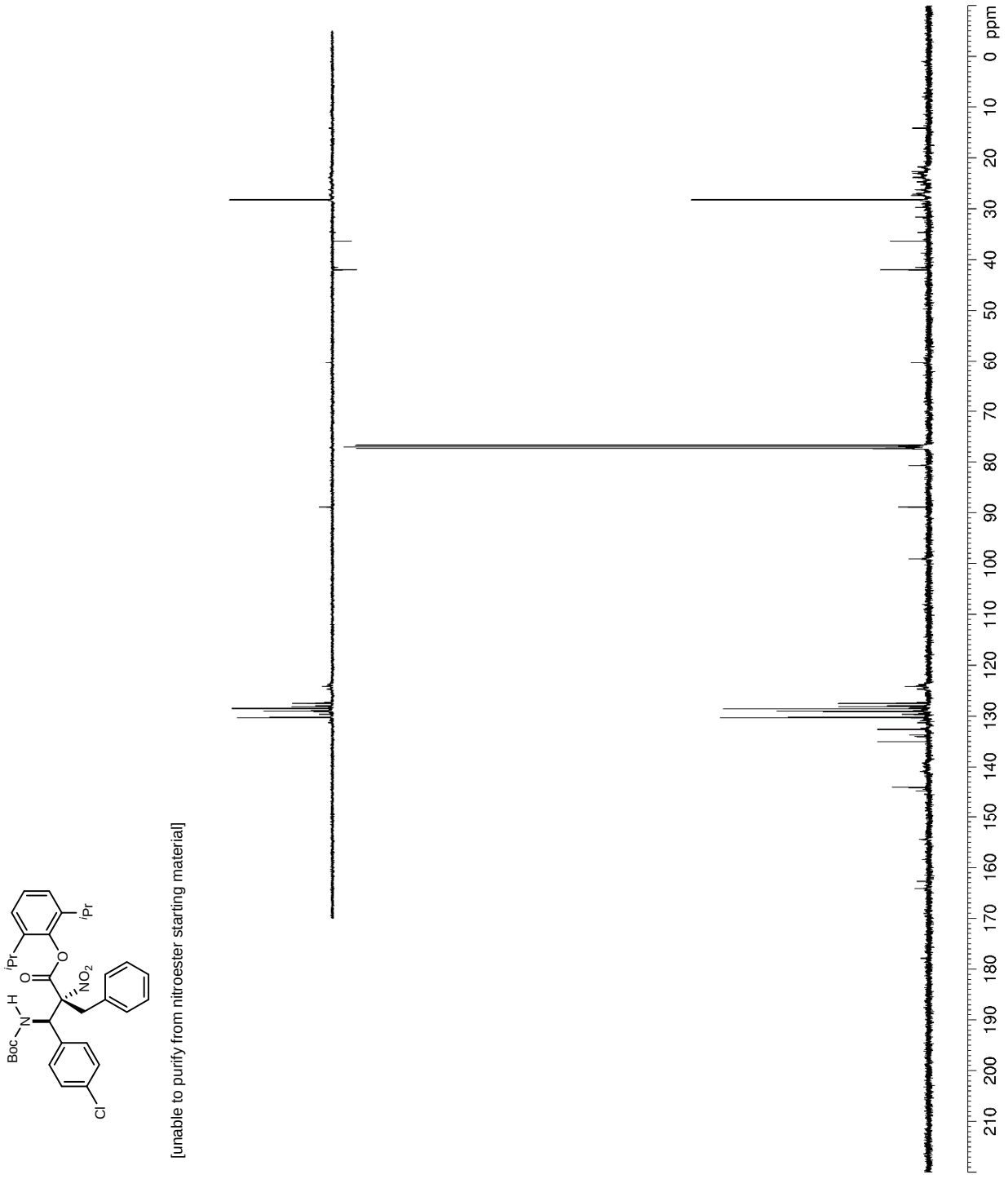


Figure 21. ^{1}H NMR (400 MHz, $CDCl_3$) of **13g**

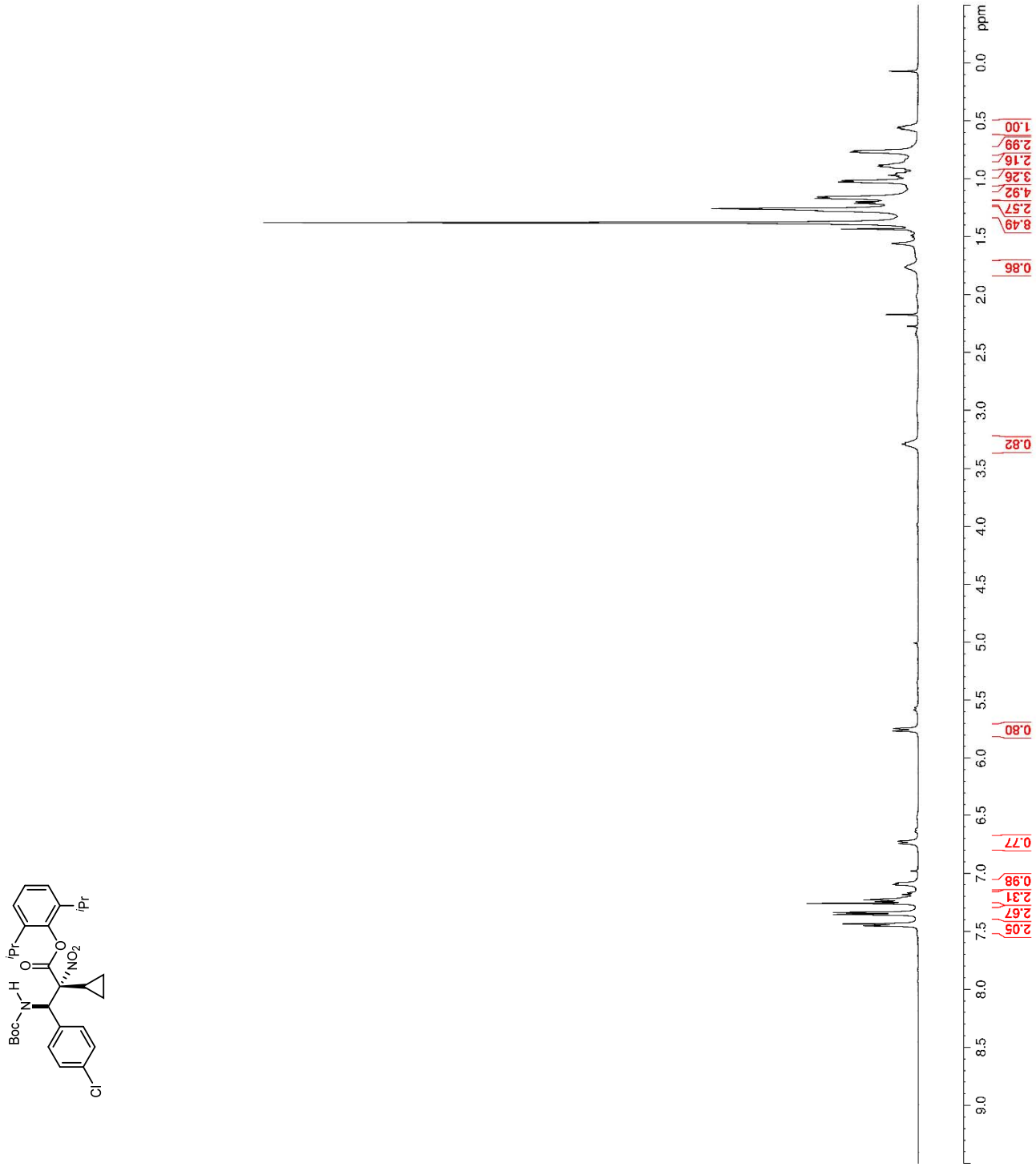


Figure 22. ^{13}C NMR (100 MHz, $CDCl_3$) of **13g**

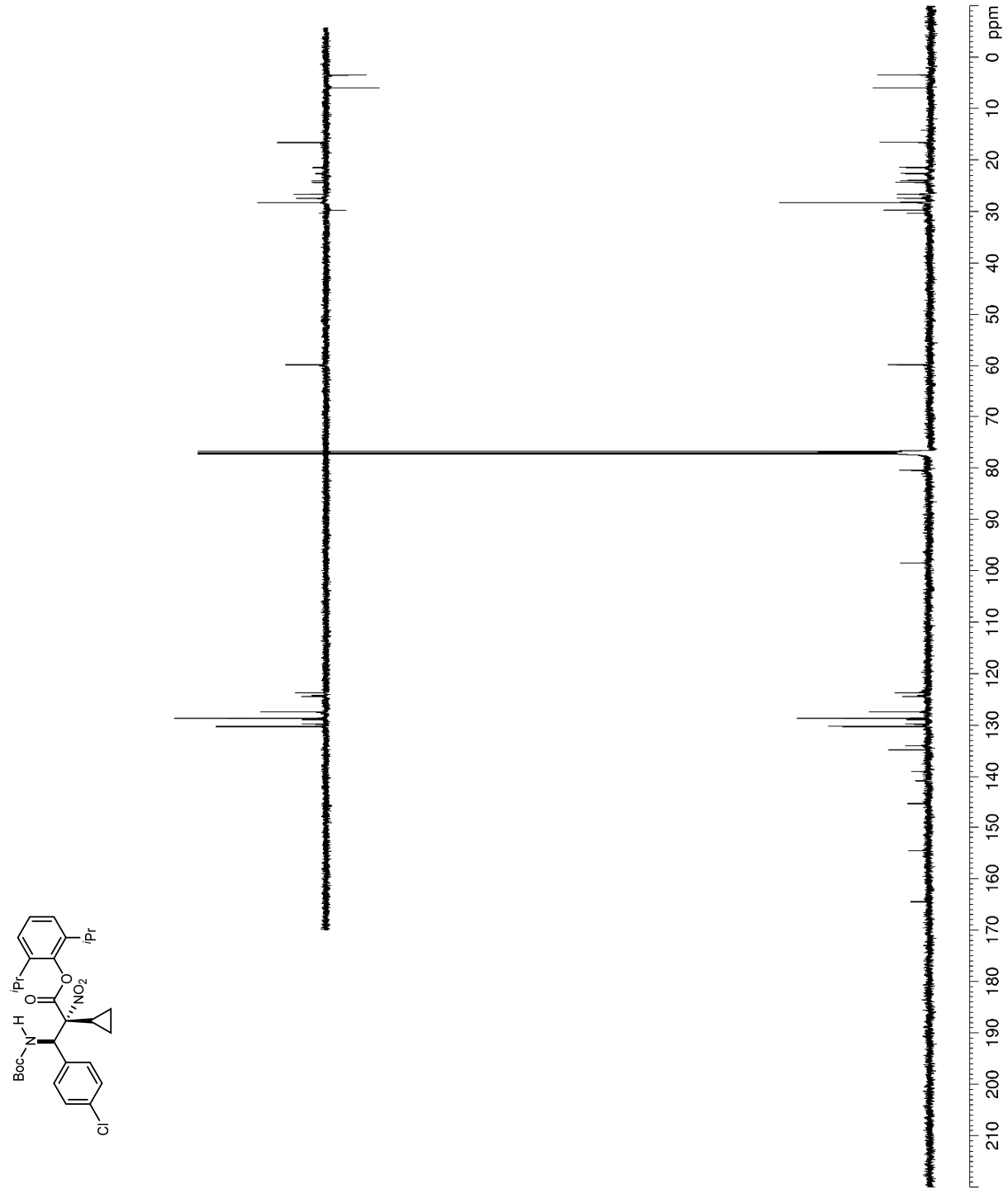


Figure 23. ^{1}H NMR (400 MHz, $CDCl_3$) of **13h**

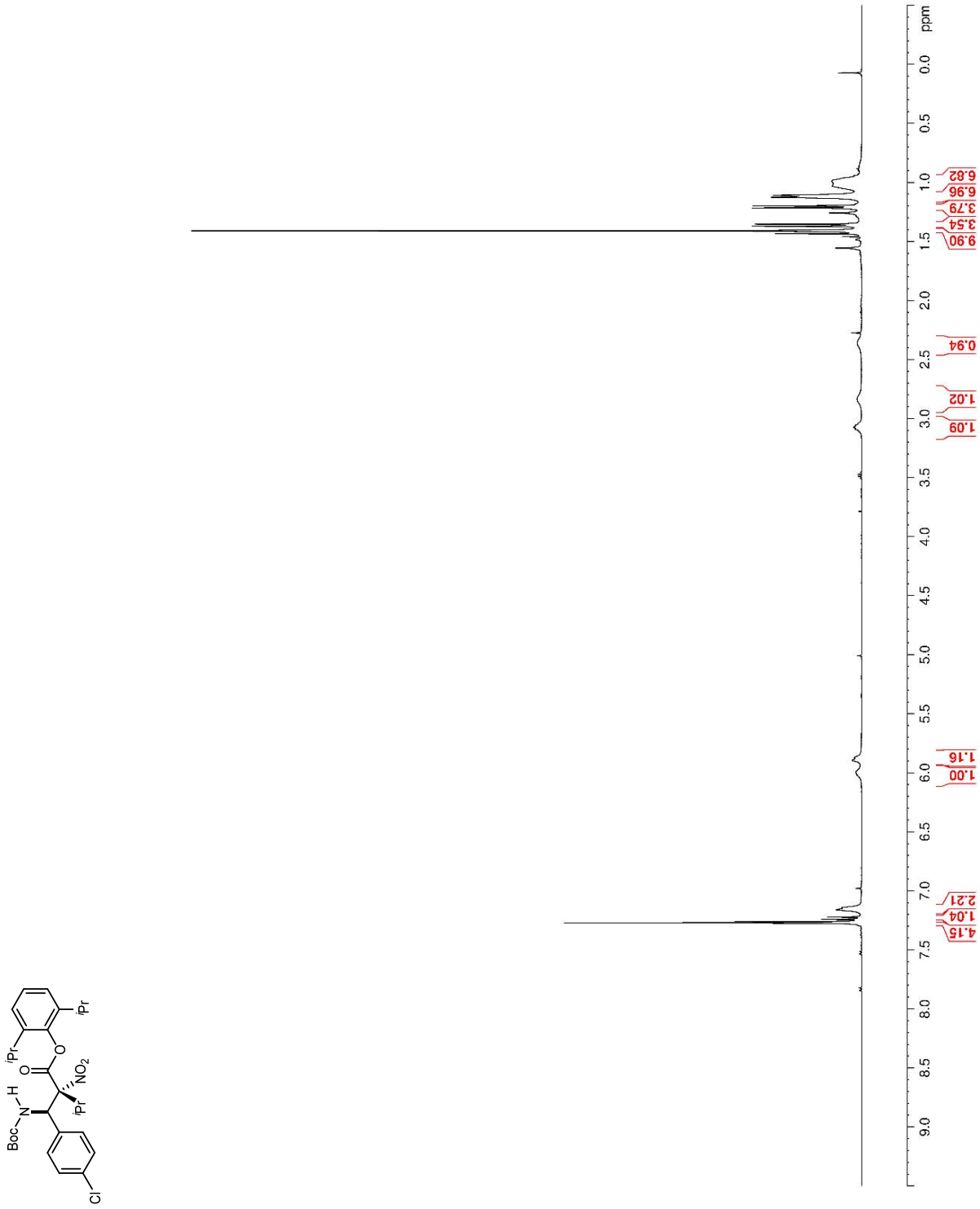


Figure 24. ^{13}C NMR (100 MHz, $CDCl_3$) of **13h**

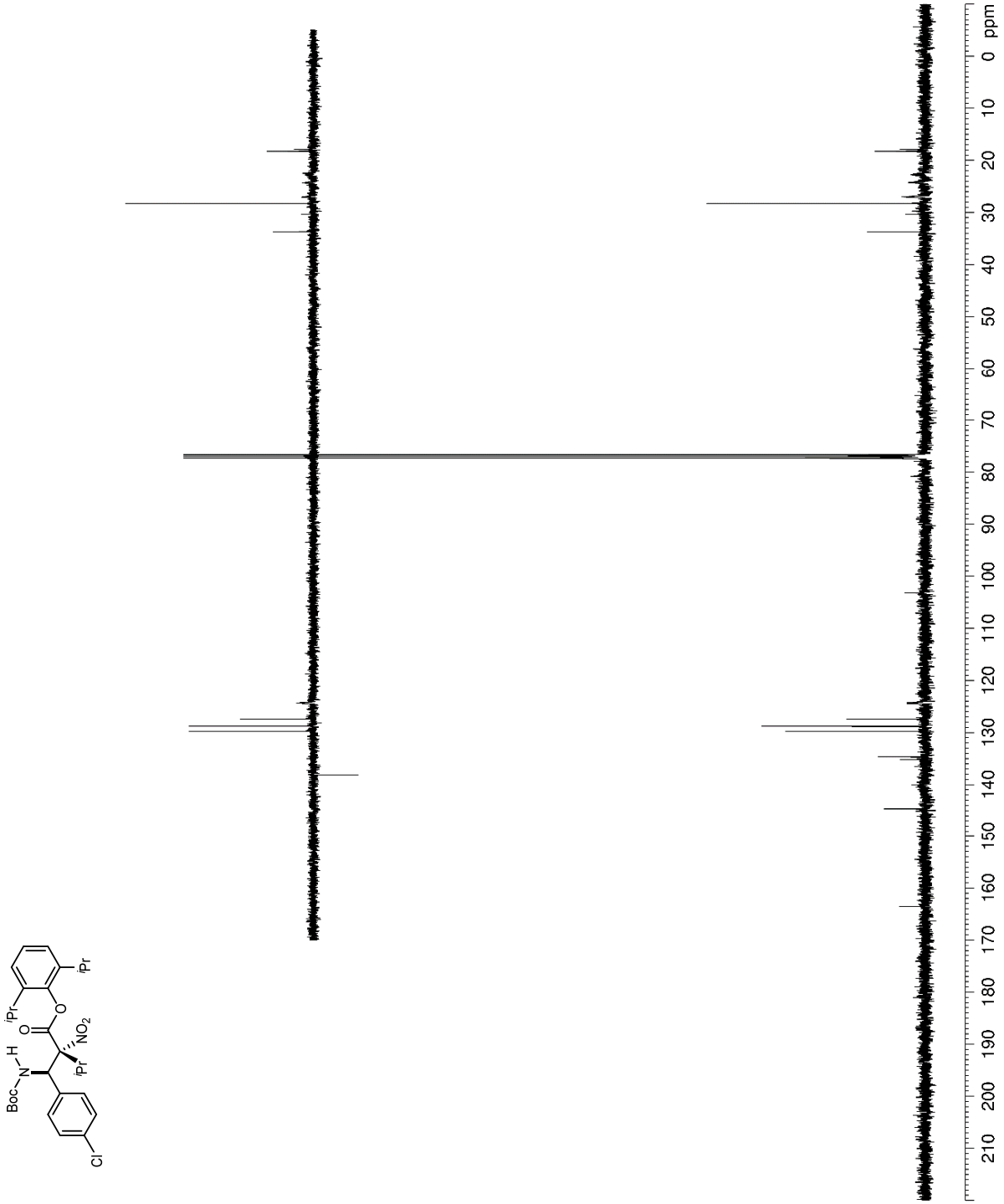


Figure 25. ^{1}H NMR (400 MHz, $CDCl_3$) of **13i**

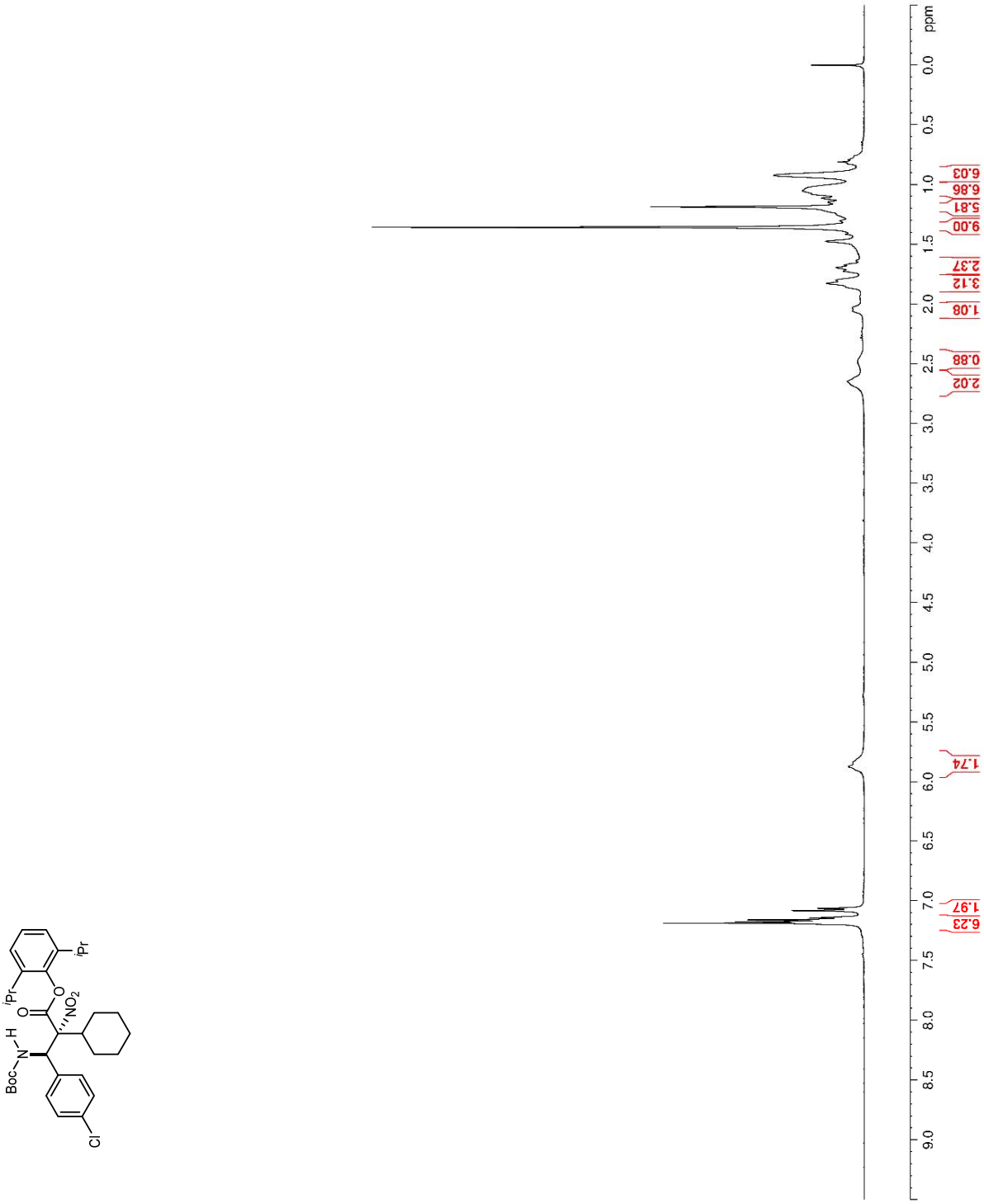


Figure 26. ^{13}C NMR (100 MHz, $CDCl_3$) of **13i**

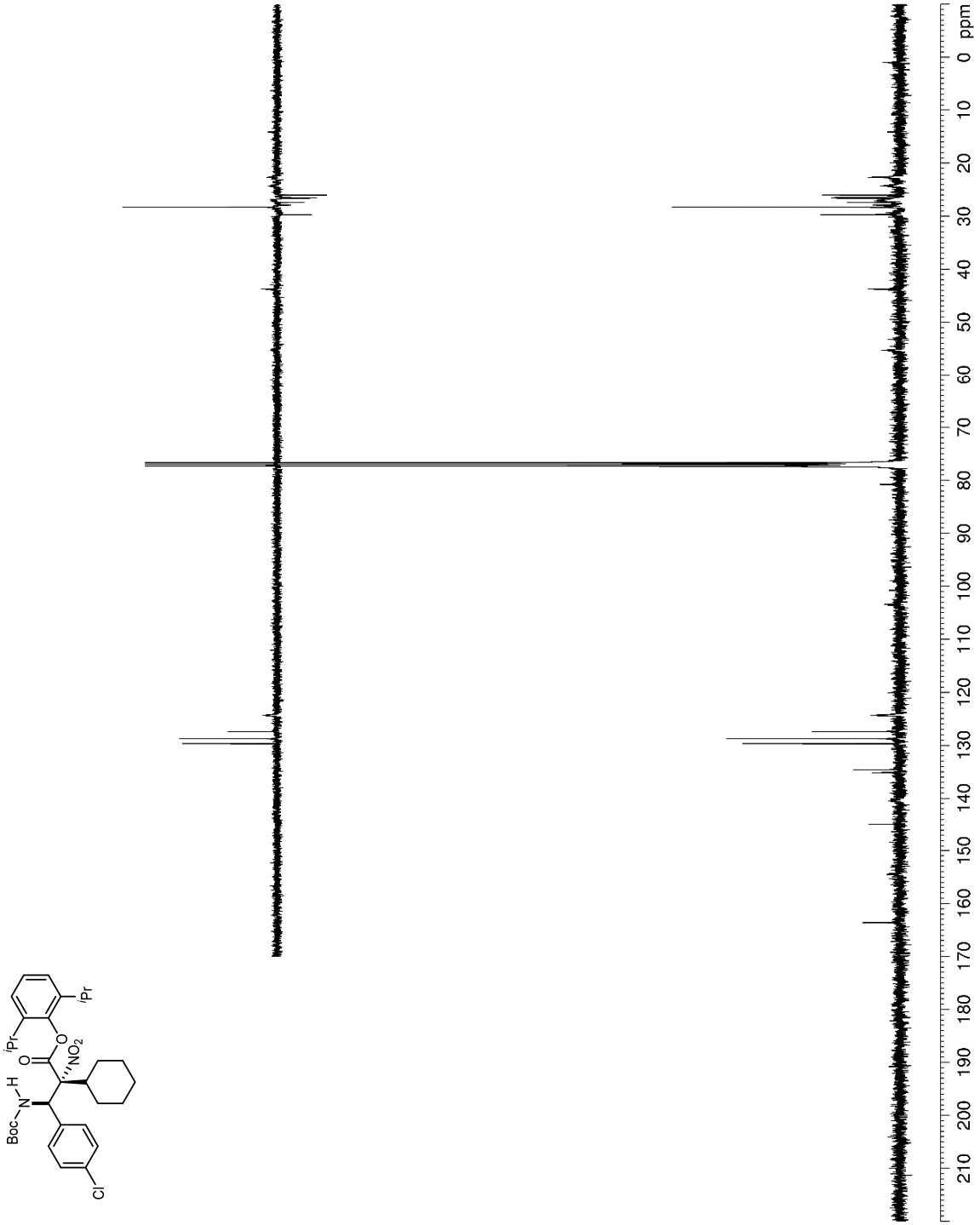


Figure 27. ^{1}H NMR (500 MHz, DMSO-d_6) of **13j**

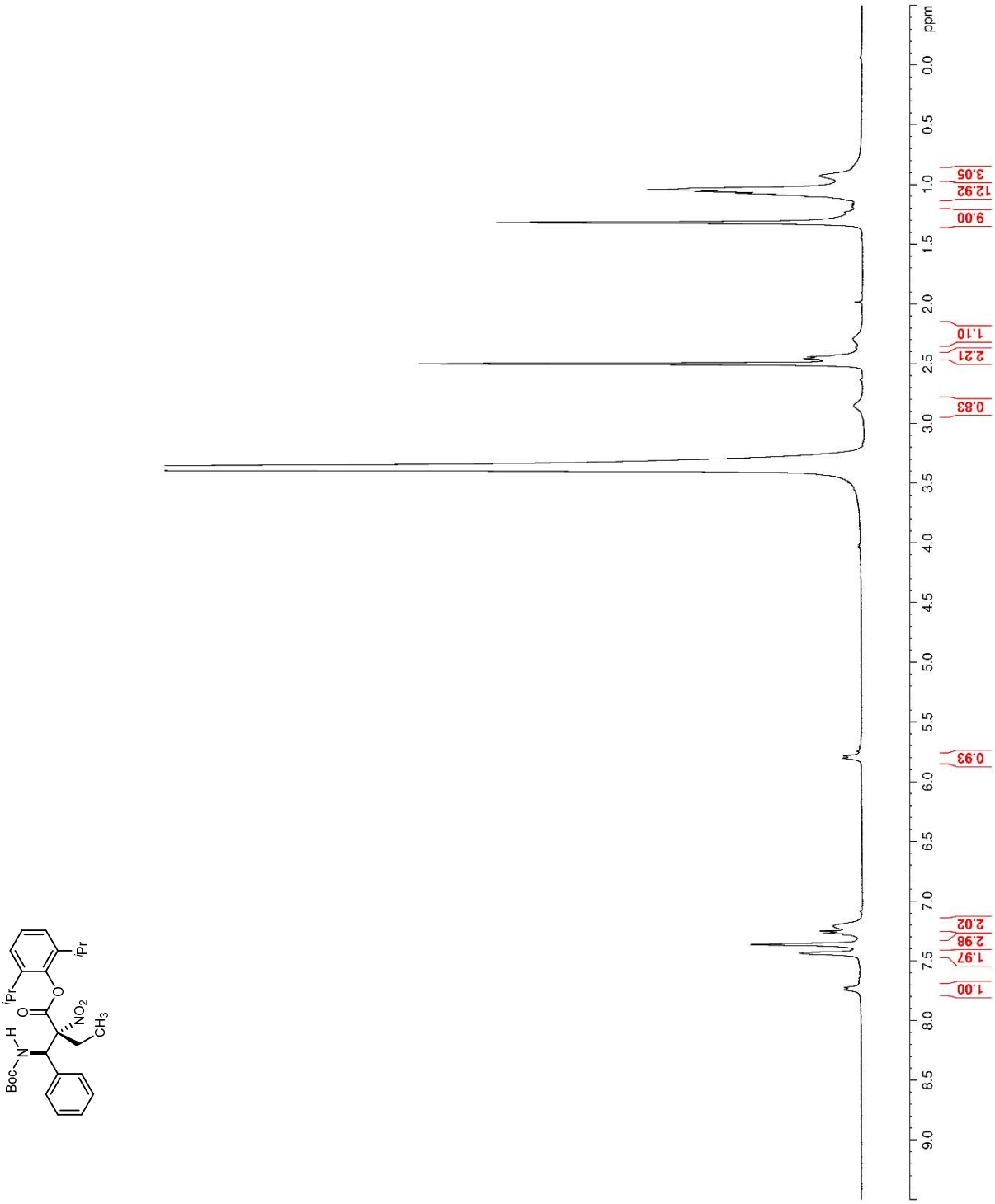


Figure 28. ^{13}C NMR (125 MHz, DMSO-d_6) of **13j**

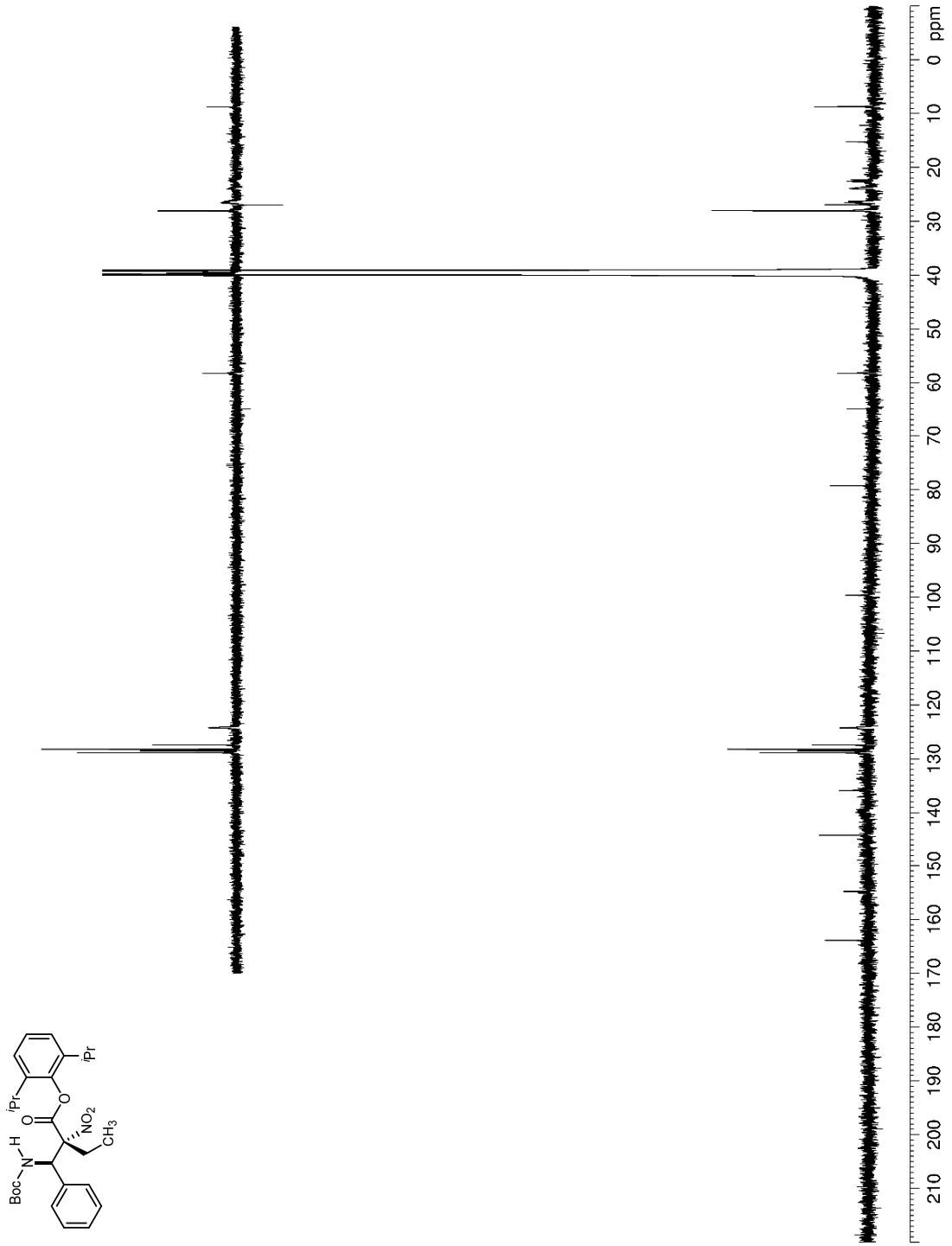


Figure 29. ^{1}H NMR (400 MHz, $CDCl_3$) of **13k**

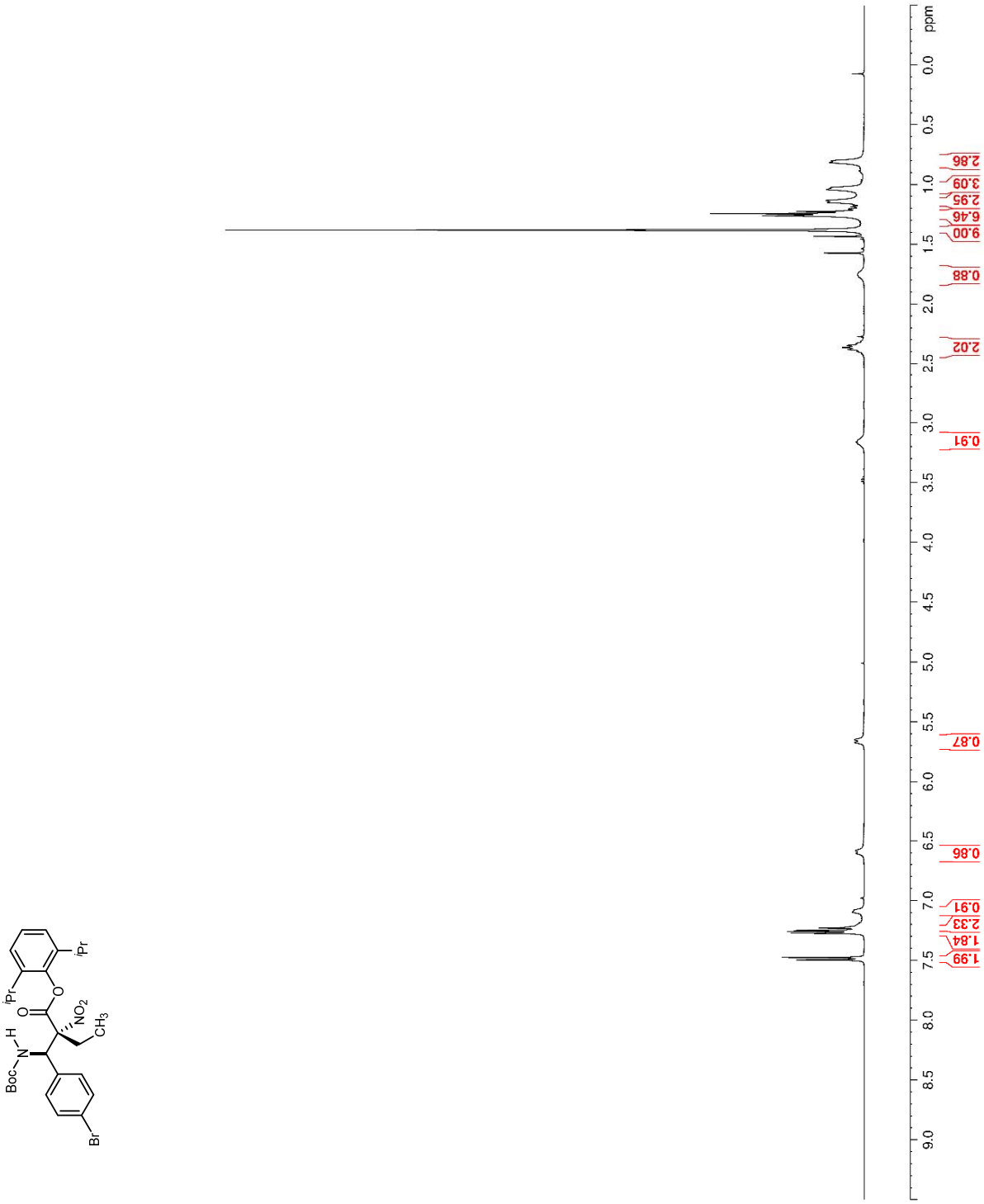


Figure 30. ^{13}C NMR (100 MHz, $CDCl_3$) of **13k**

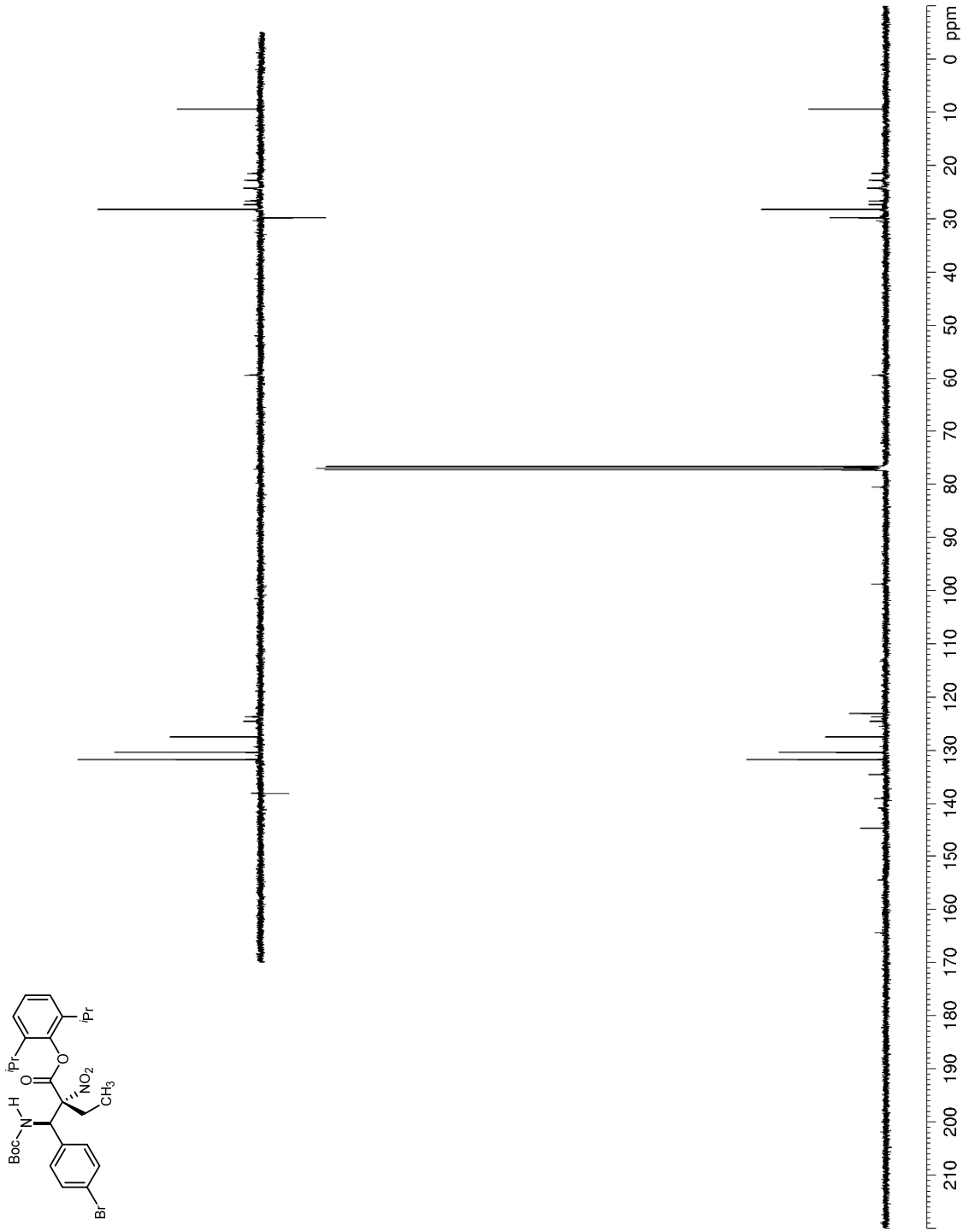


Figure 31. ^{1}H NMR (400 MHz, $CDCl_3$) of **13l**

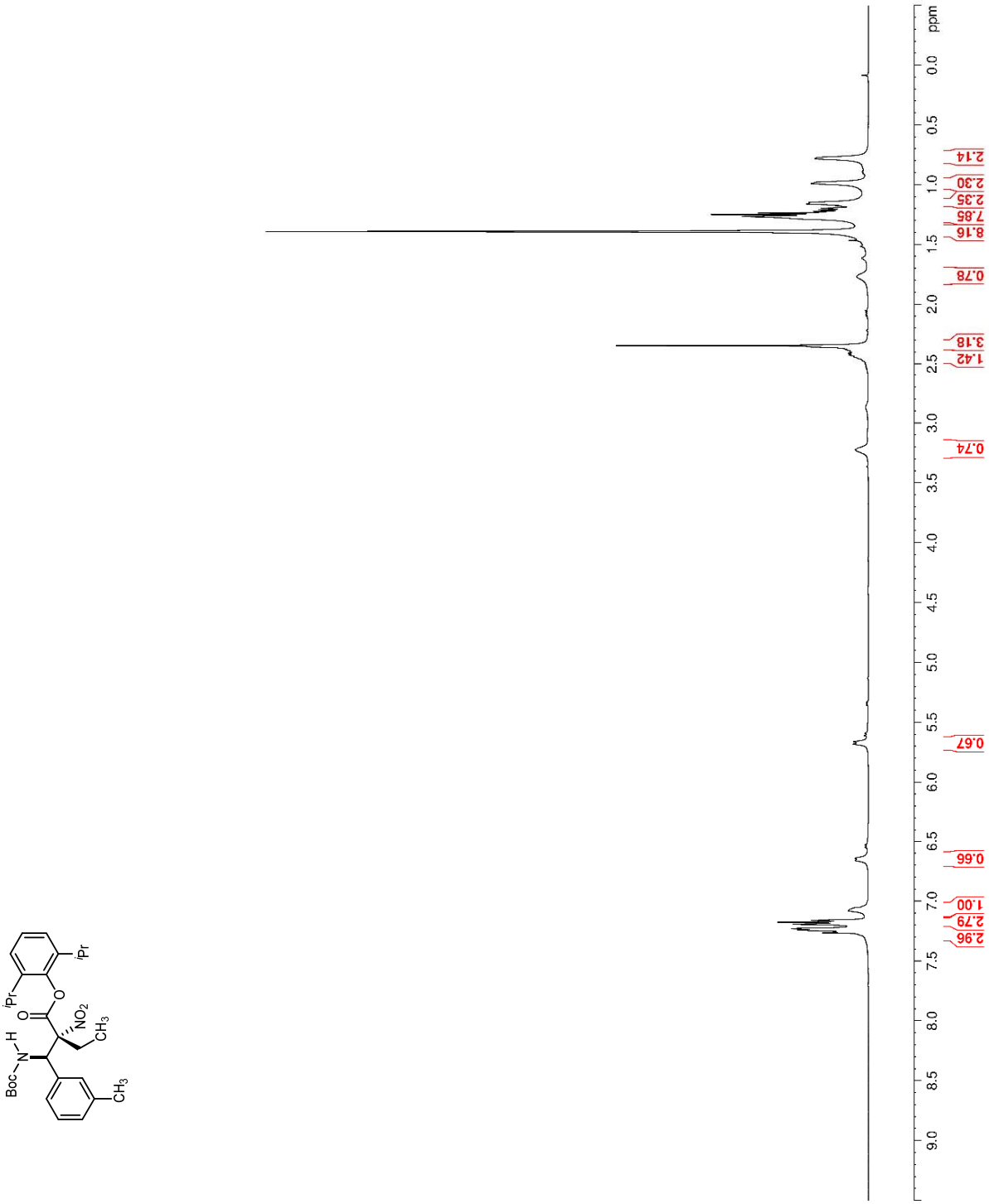


Figure 32. ^{13}C NMR (100 MHz, $CDCl_3$) of **13l**

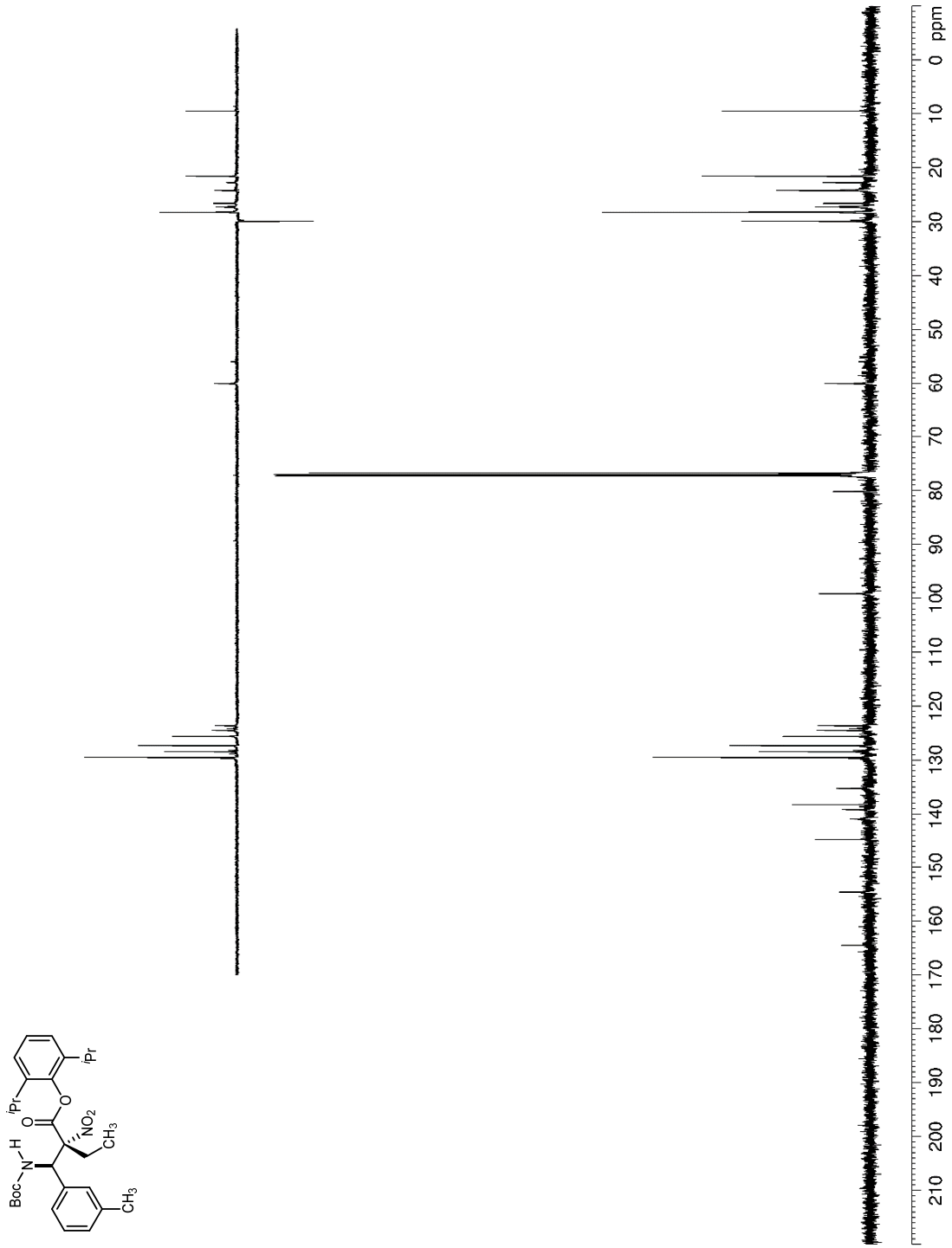


Figure 33. ^{1}H NMR (400 MHz, $CDCl_3$) of **13m**

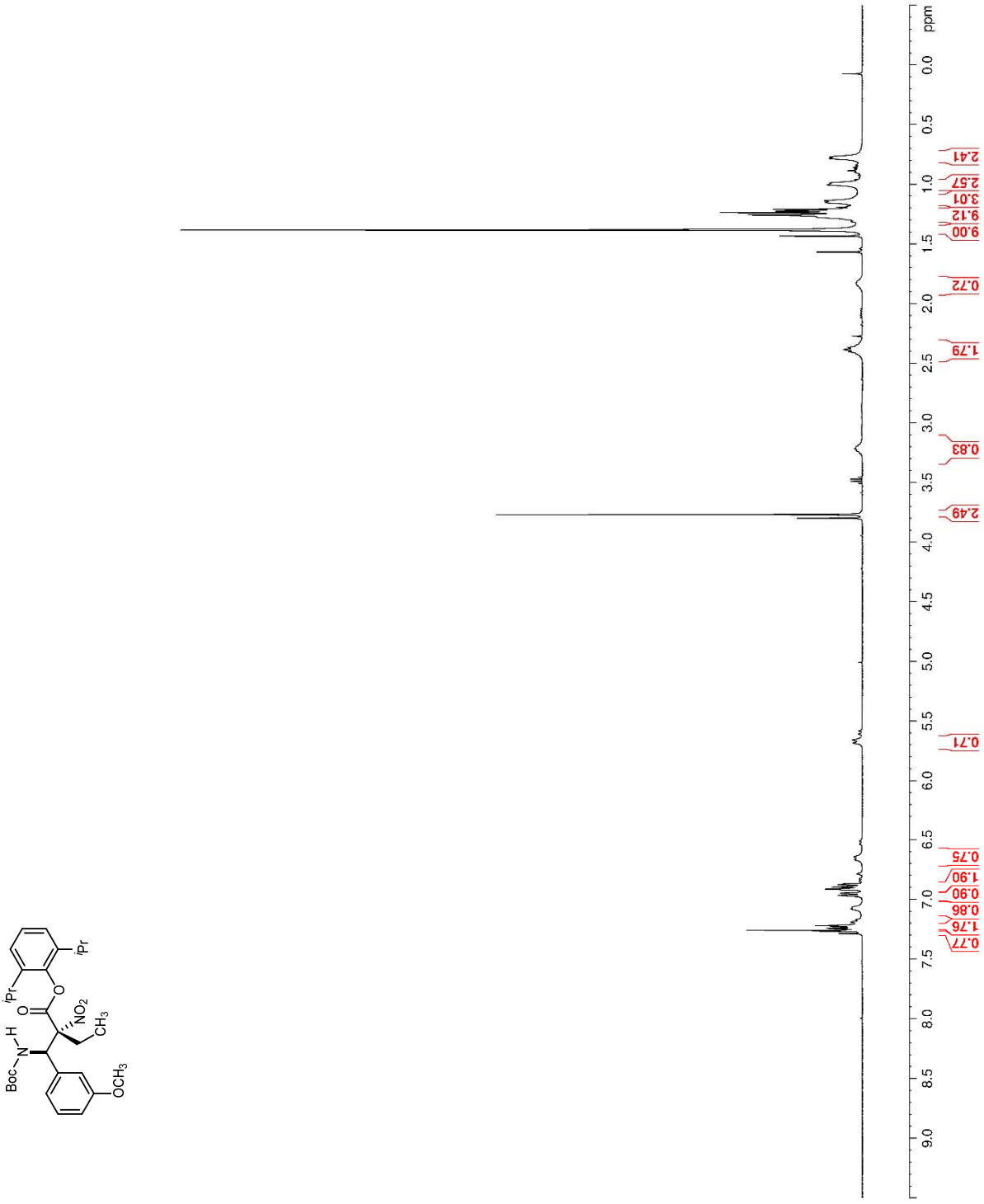


Figure 34. ^{13}C NMR (100 MHz, $CDCl_3$) of **13m**

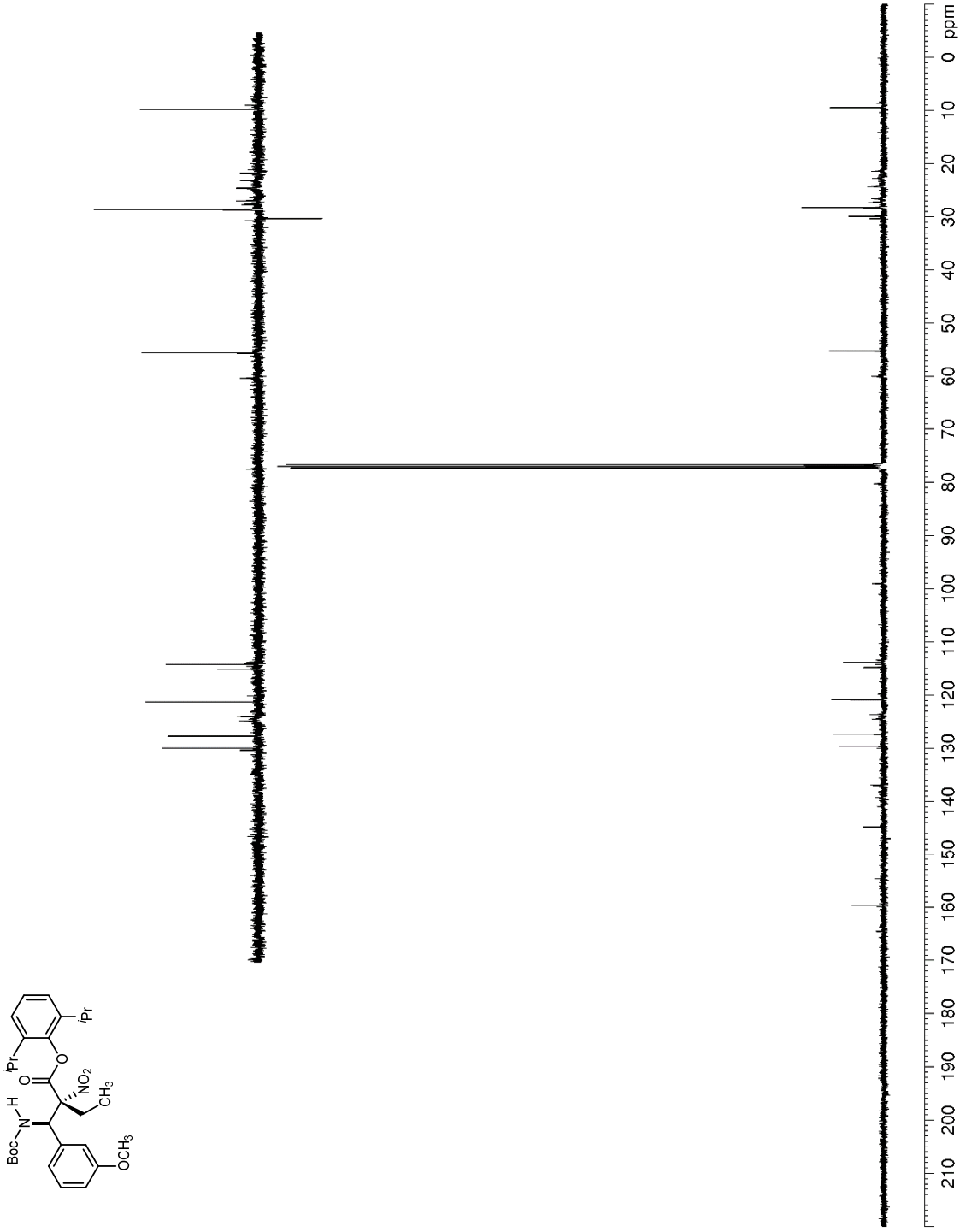


Figure 35. ^{1}H NMR (400 MHz, $CDCl_3$) of **13o**

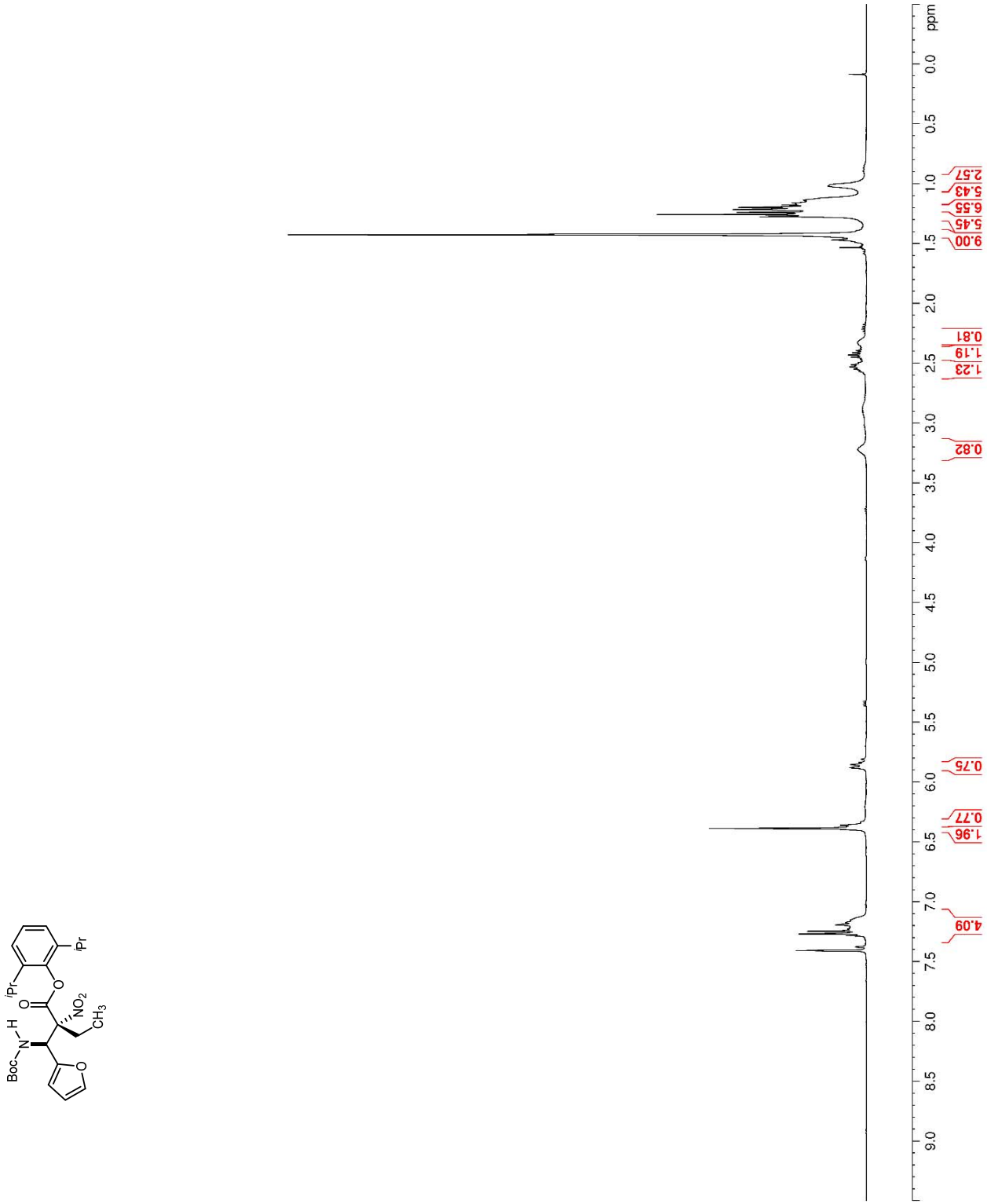


Figure 36. ^{13}C NMR (100 MHz, $CDCl_3$) of **13o**

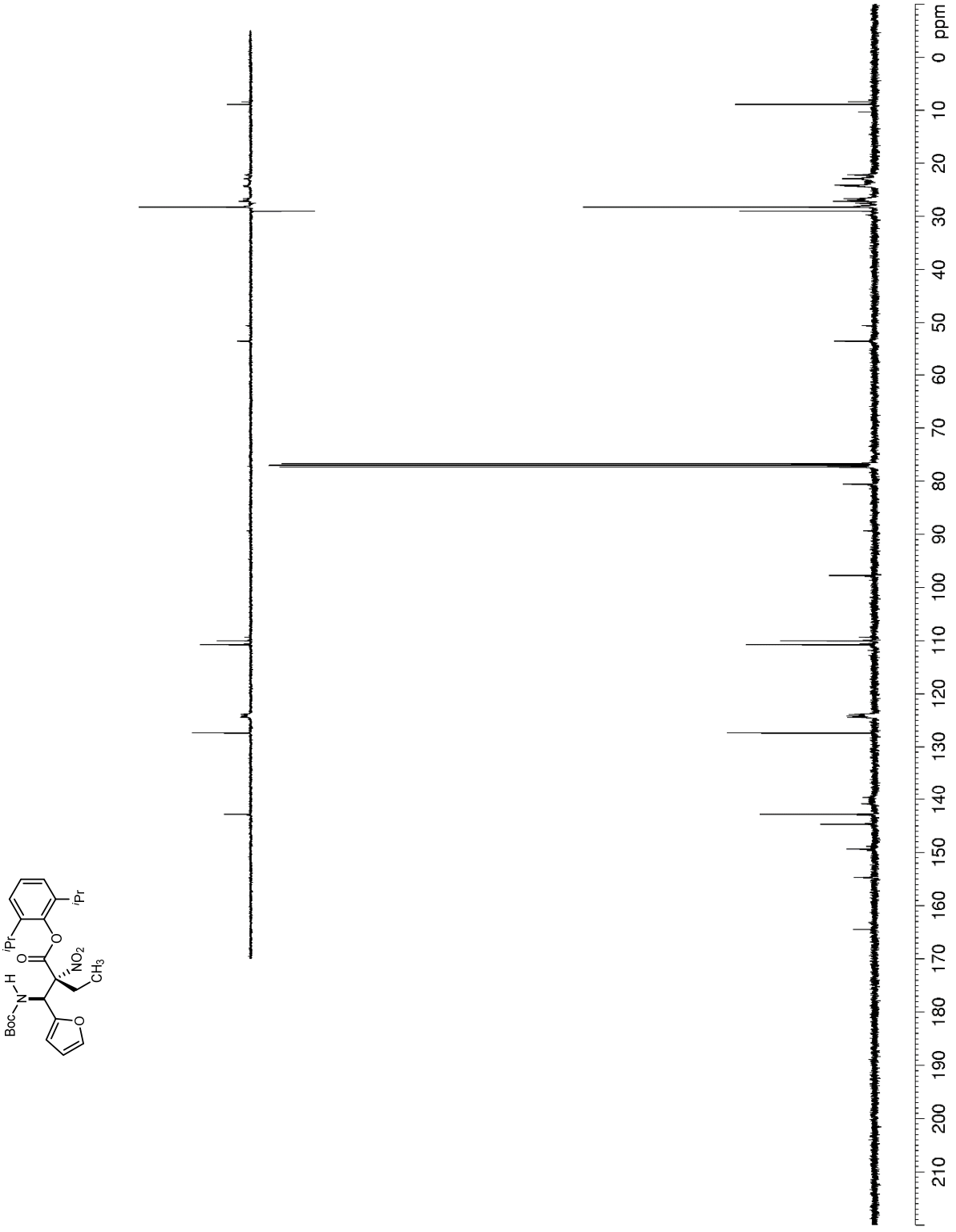


Figure 37. ^{1}H NMR (400 MHz, $CDCl_3$) of **13p**

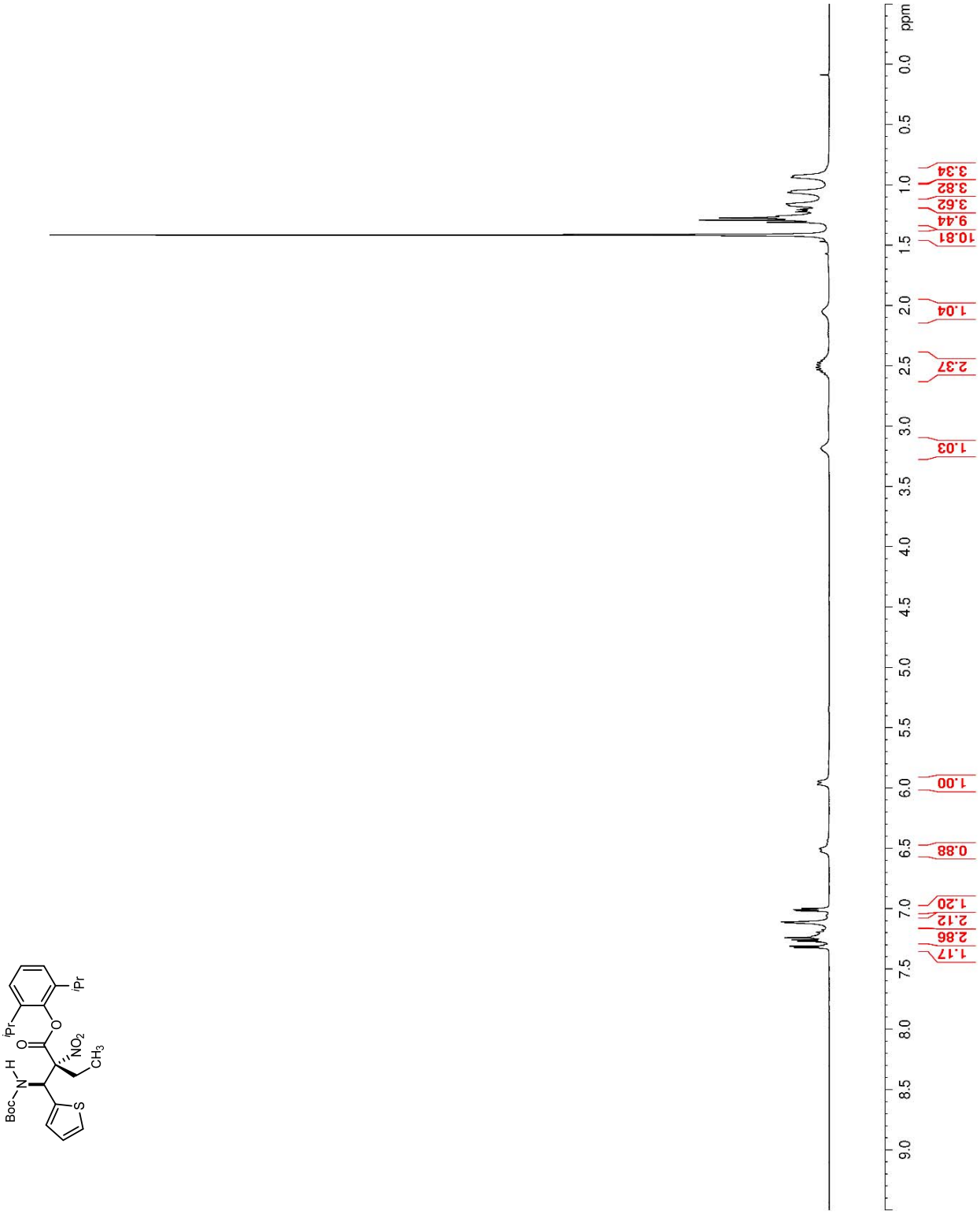


Figure 38. ^{13}C NMR (100 MHz, $CDCl_3$) of **13p**

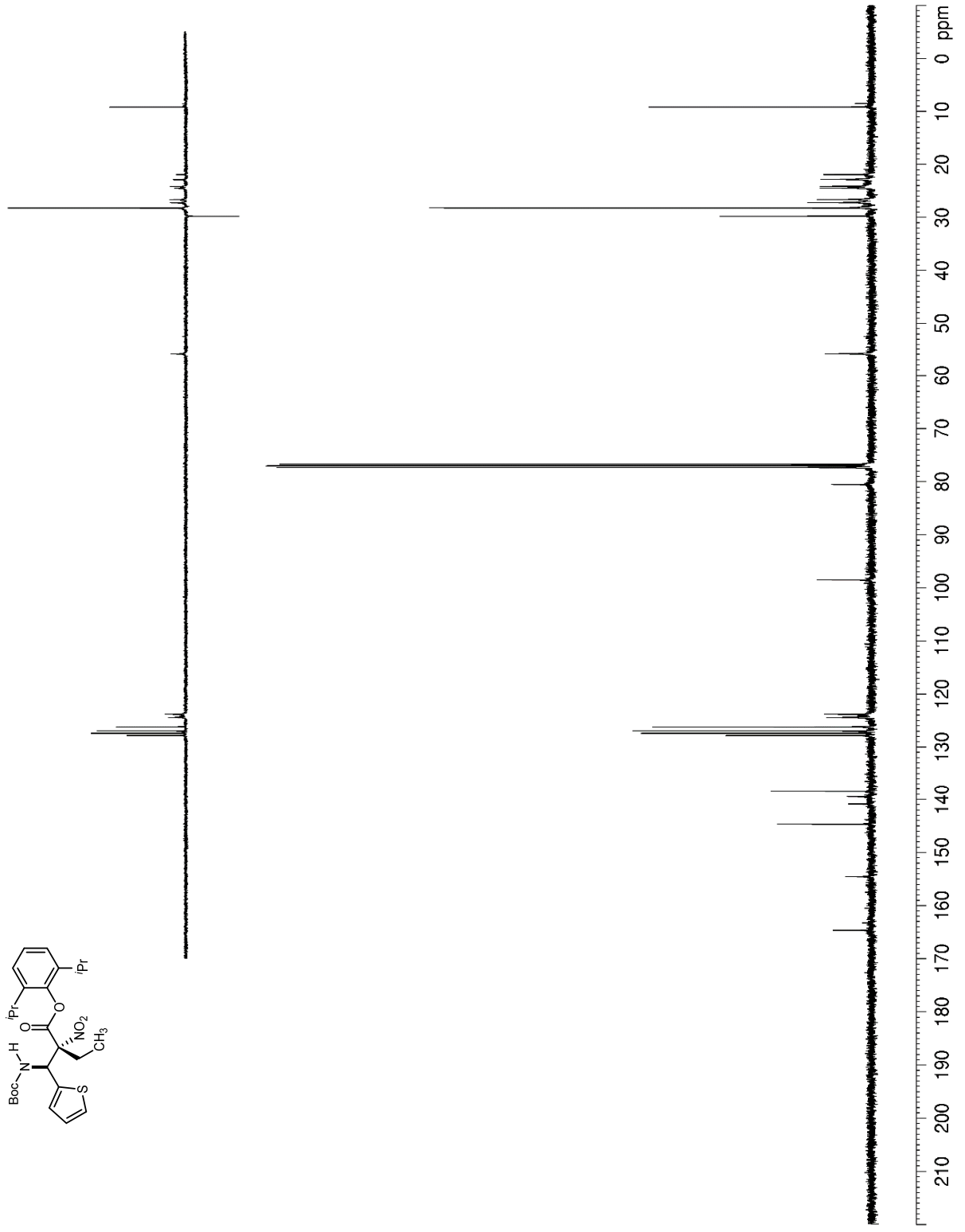


Figure 39. ^{1}H NMR (400 MHz, $CDCl_3$) of **13r**

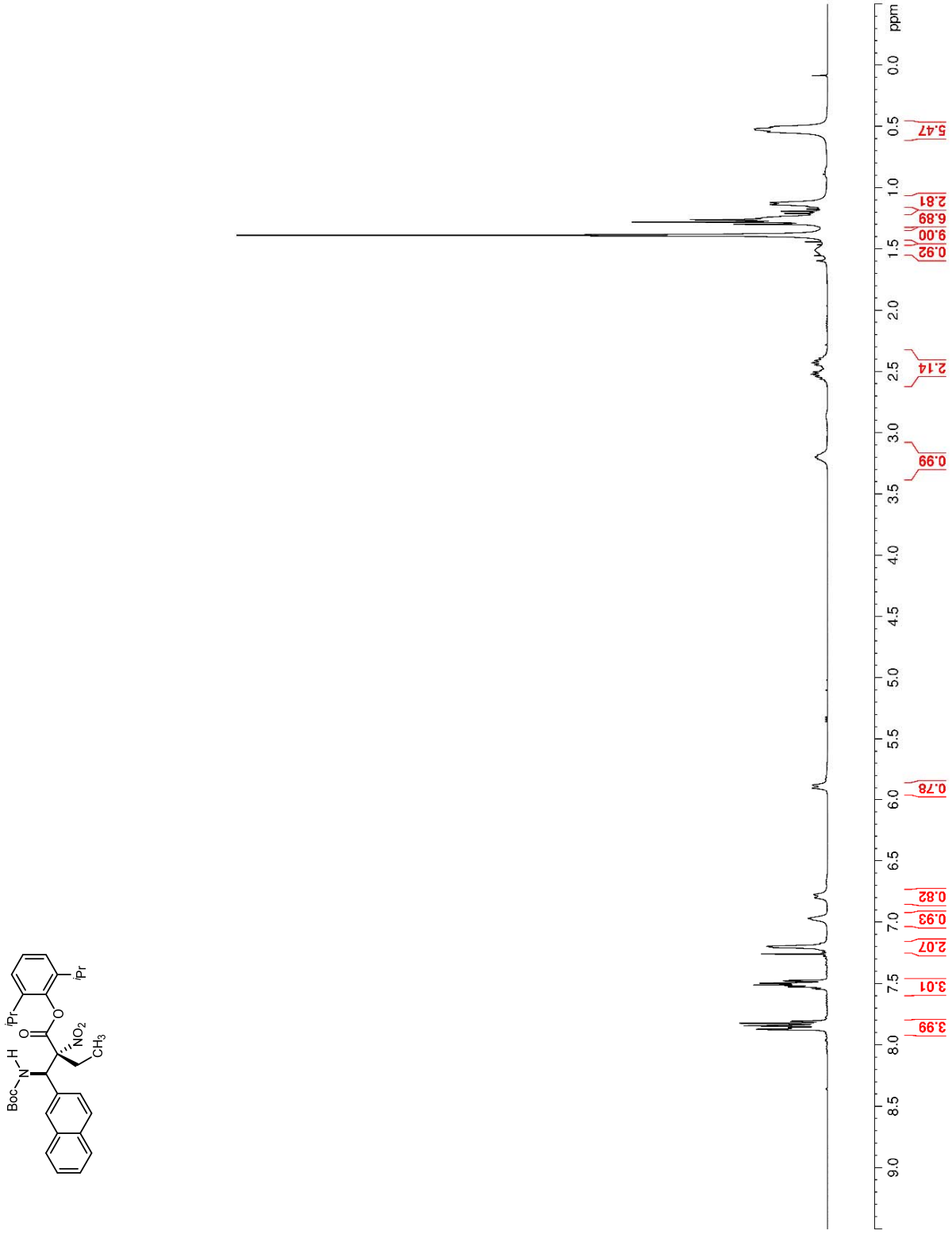


Figure 40. ^{13}C NMR (100 MHz, $CDCl_3$) of **13r**

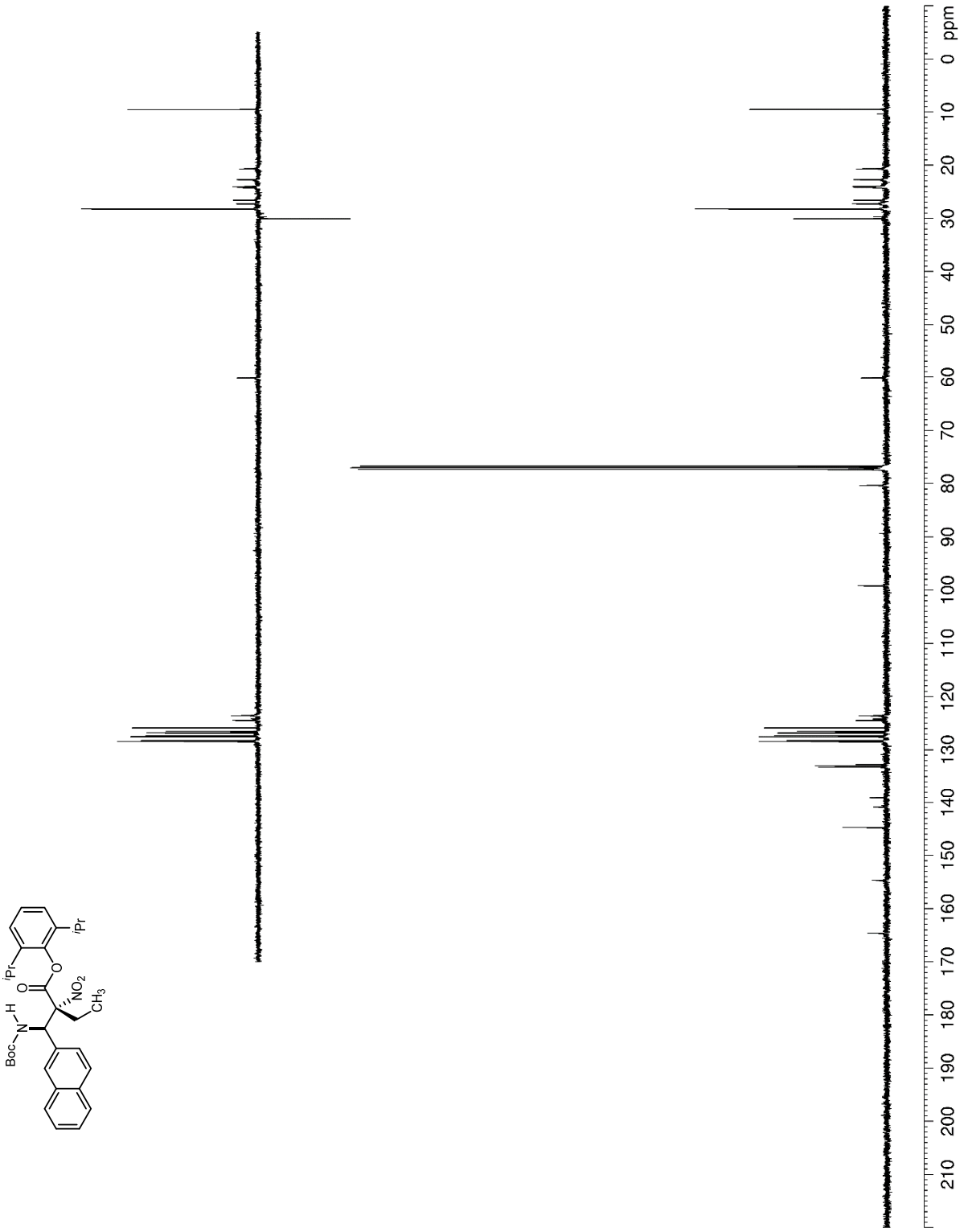


Figure 41. ^{1}H NMR (500 MHz, $CDCl_3$) of **13s**

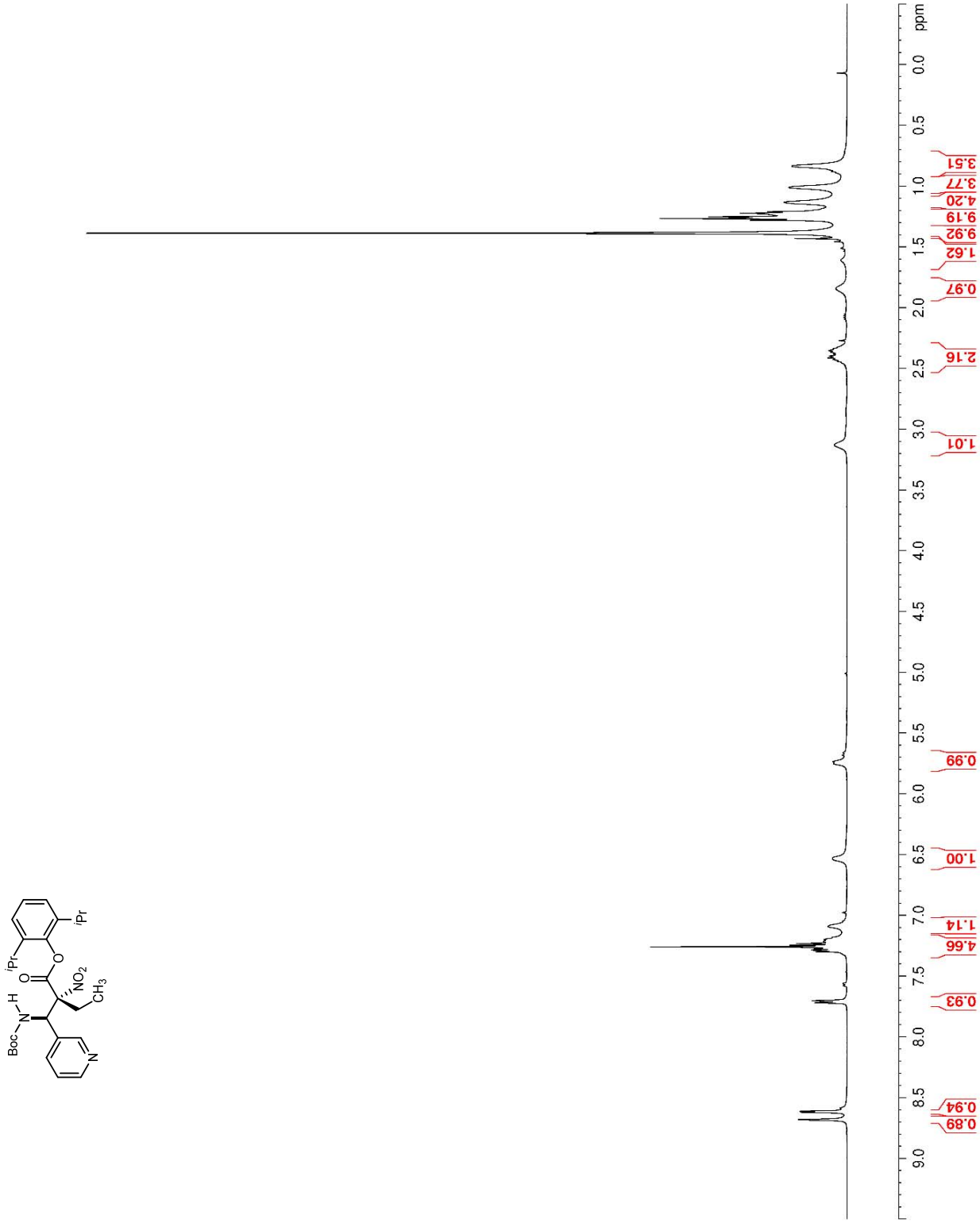


Figure 42. ^{13}C NMR (125 MHz, $CDCl_3$) of **13s**

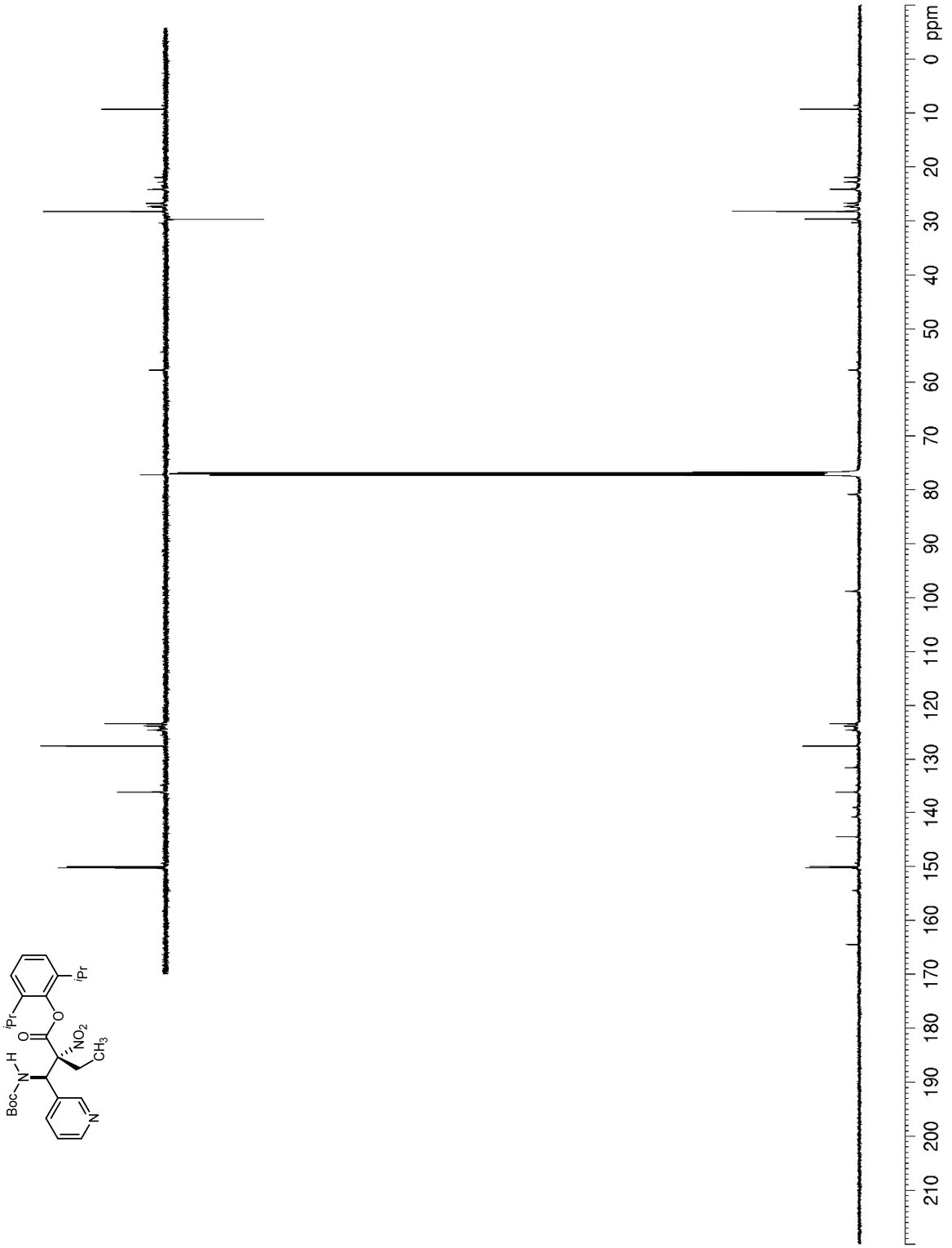


Figure 43. ^{1}H NMR (500 MHz, $CDCl_3$) of **13t**

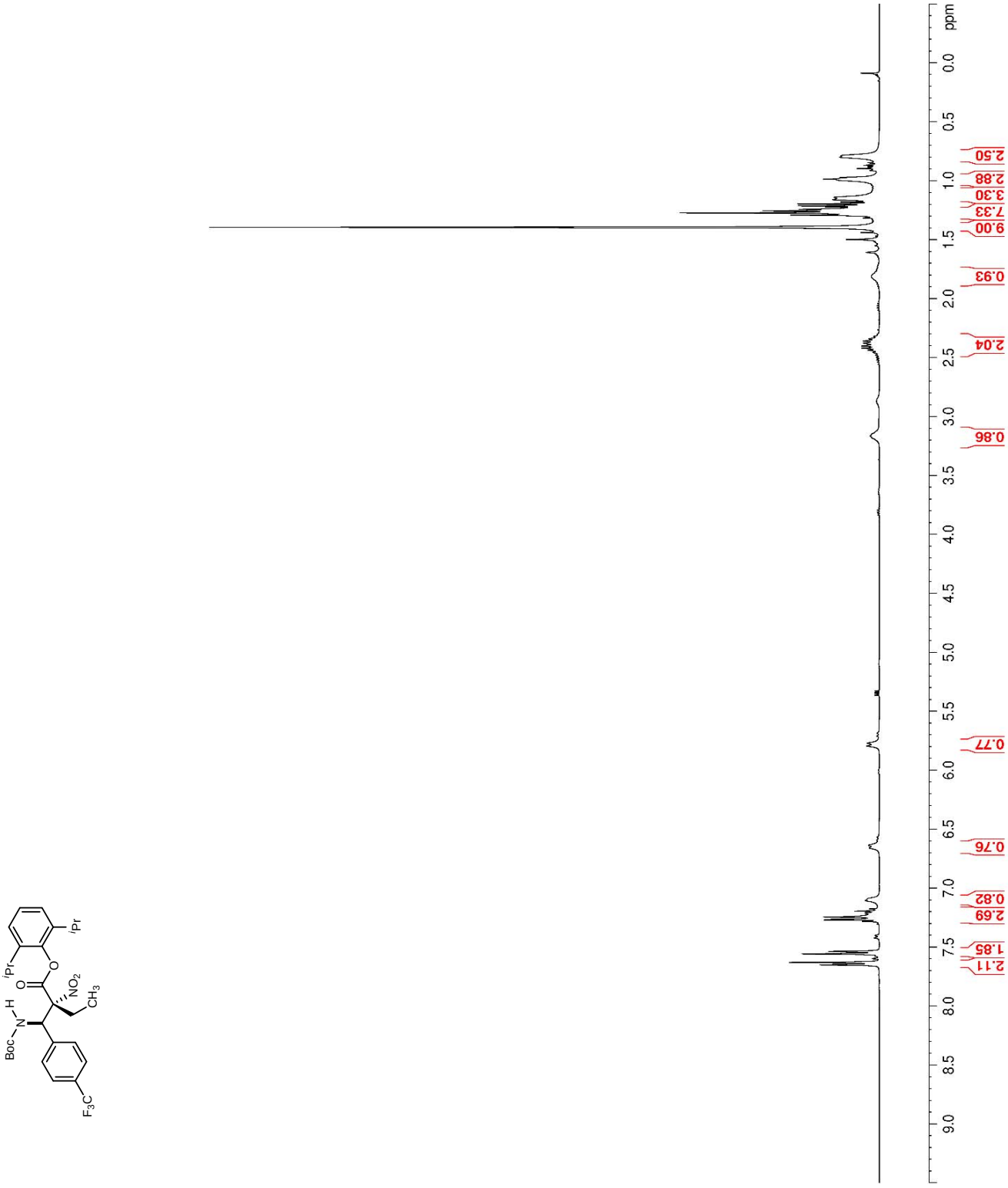


Figure 44. ^{13}C NMR (125 MHz, $CDCl_3$) of **13t**

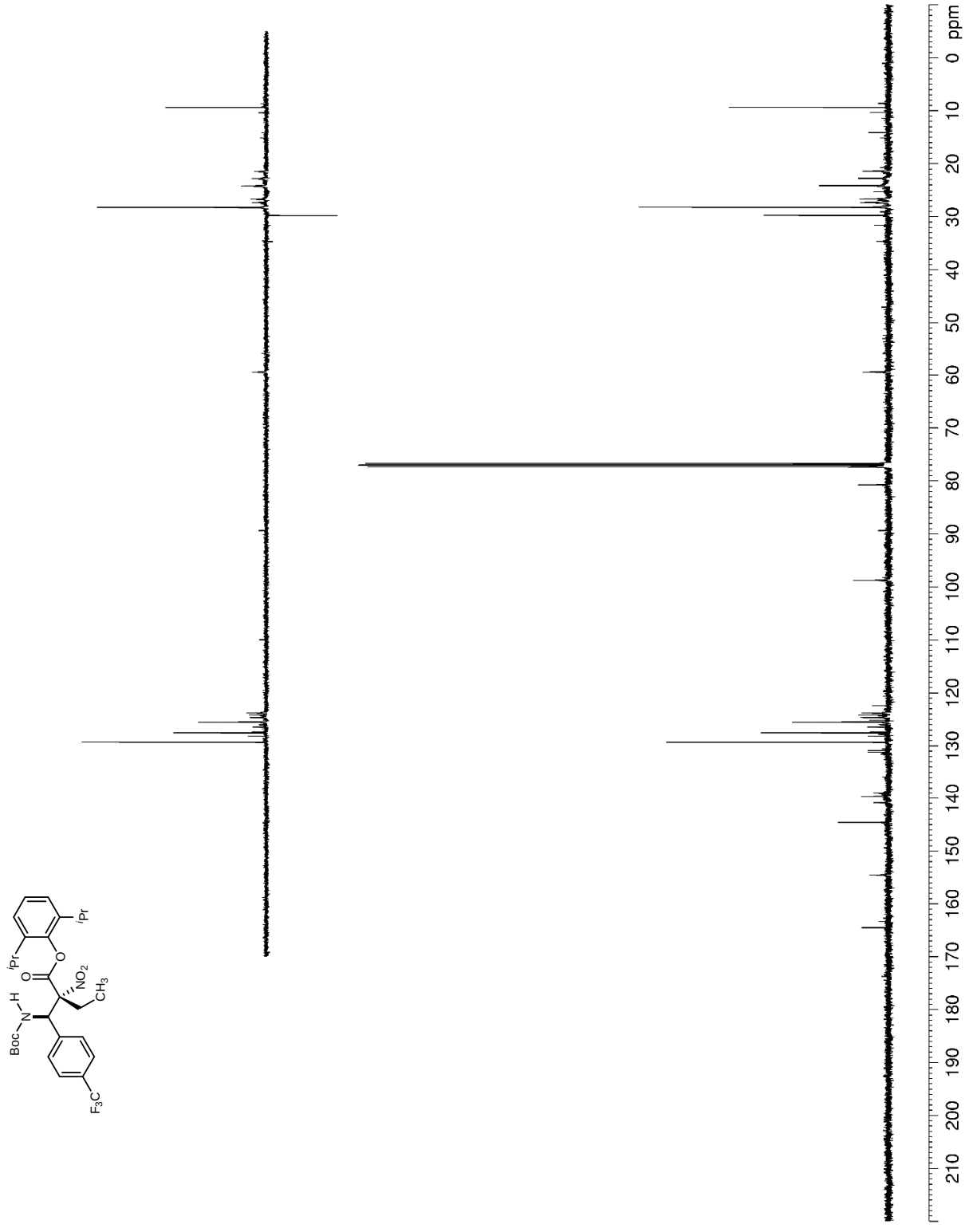


Figure 45. ^{1}H NMR (400 MHz, $CDCl_3$) of **13u**

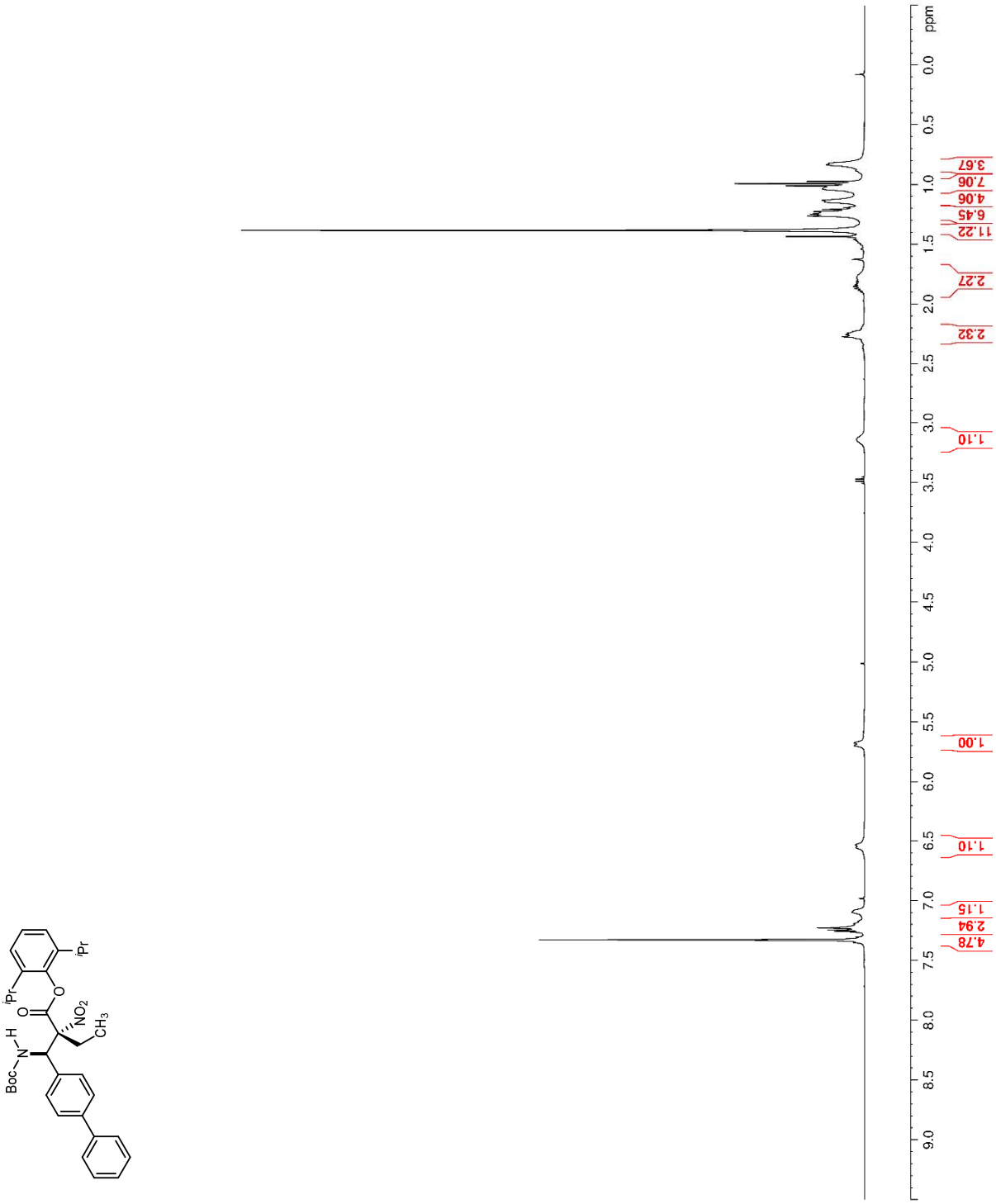


Figure 46. ^{13}C NMR (100 MHz, $CDCl_3$) of **13u**

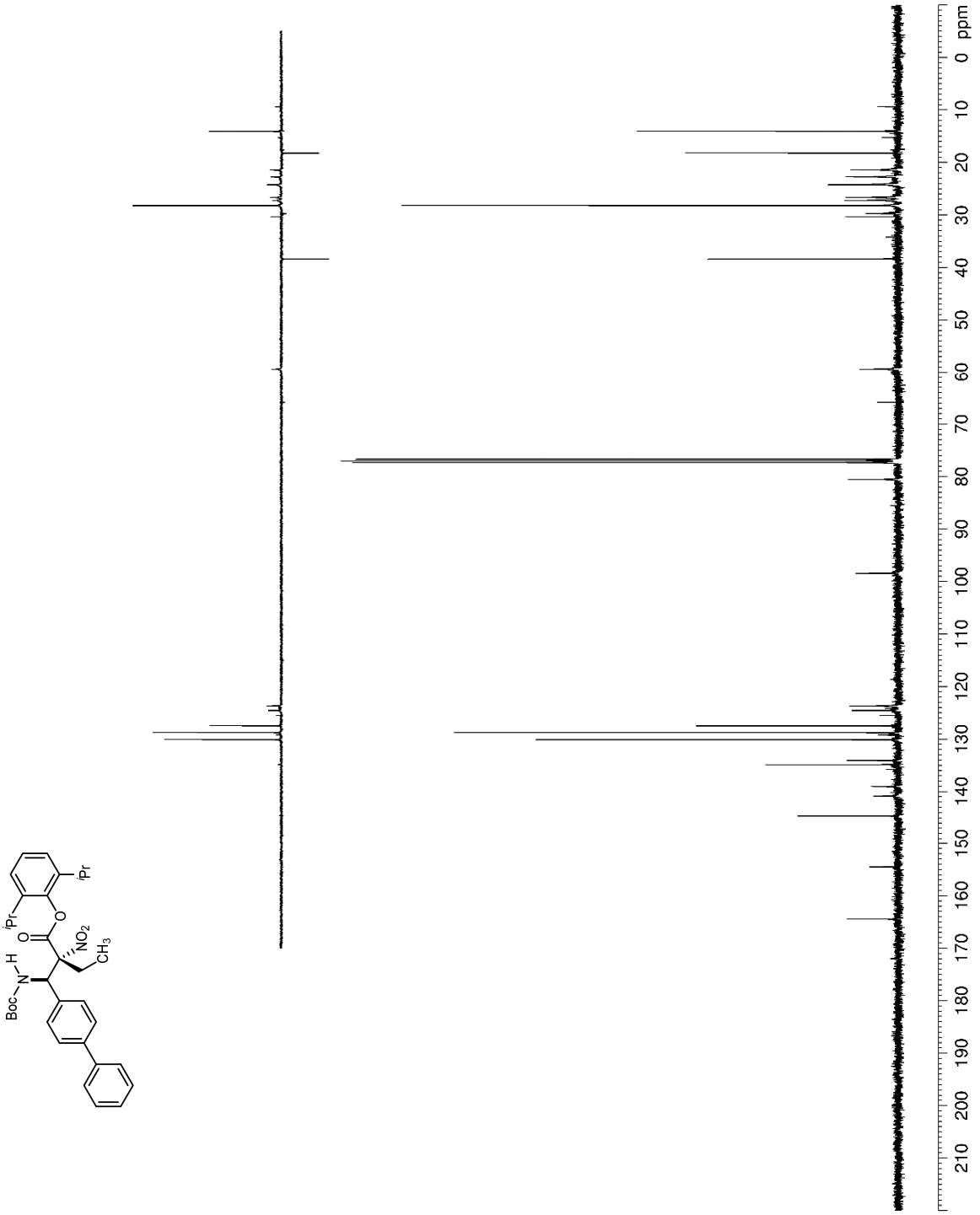


Figure 47. ^{1}H NMR (400 MHz, $CDCl_3$) of **14**

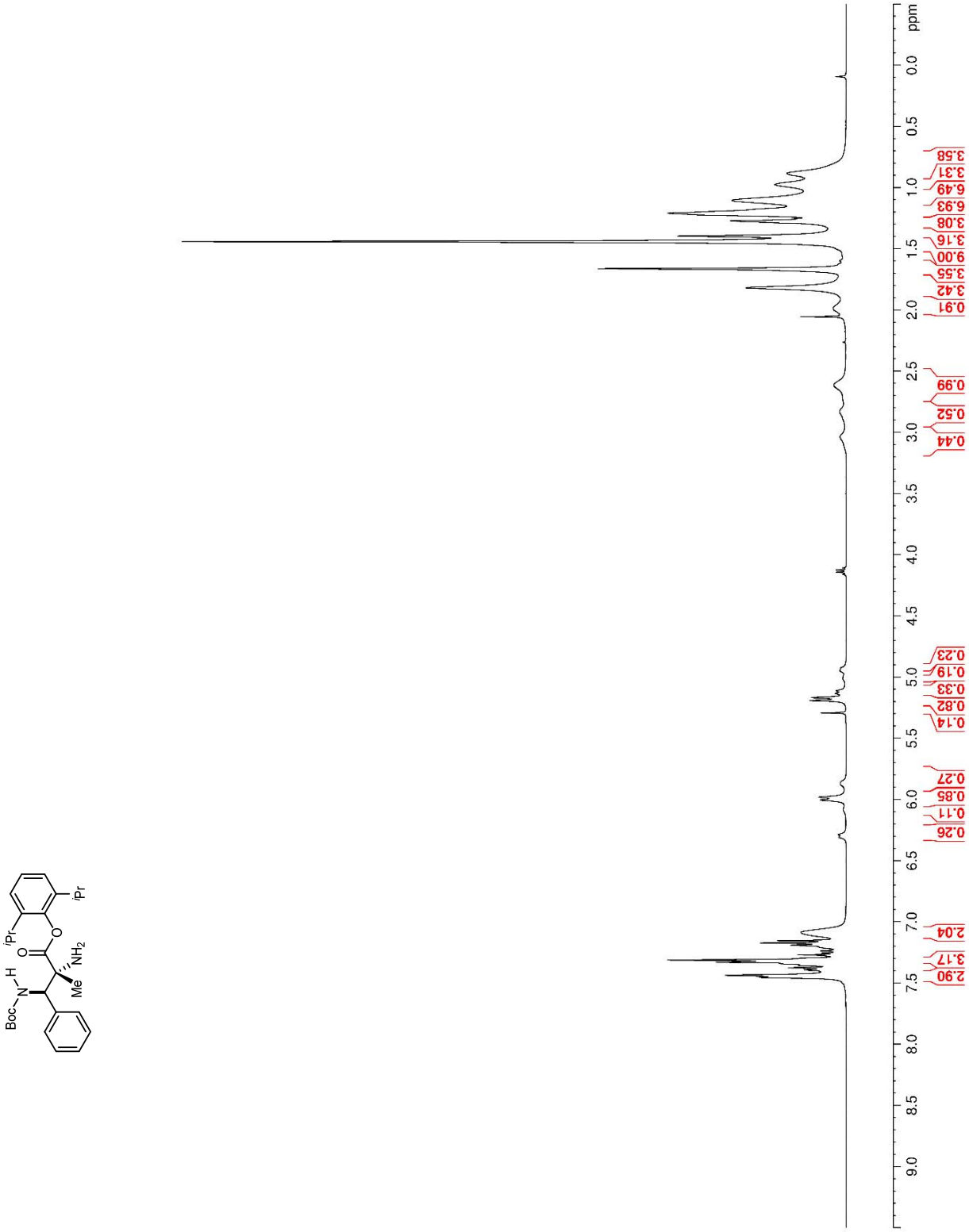


Figure 48. ^{13}C NMR (100 MHz, $CDCl_3$) of **14**

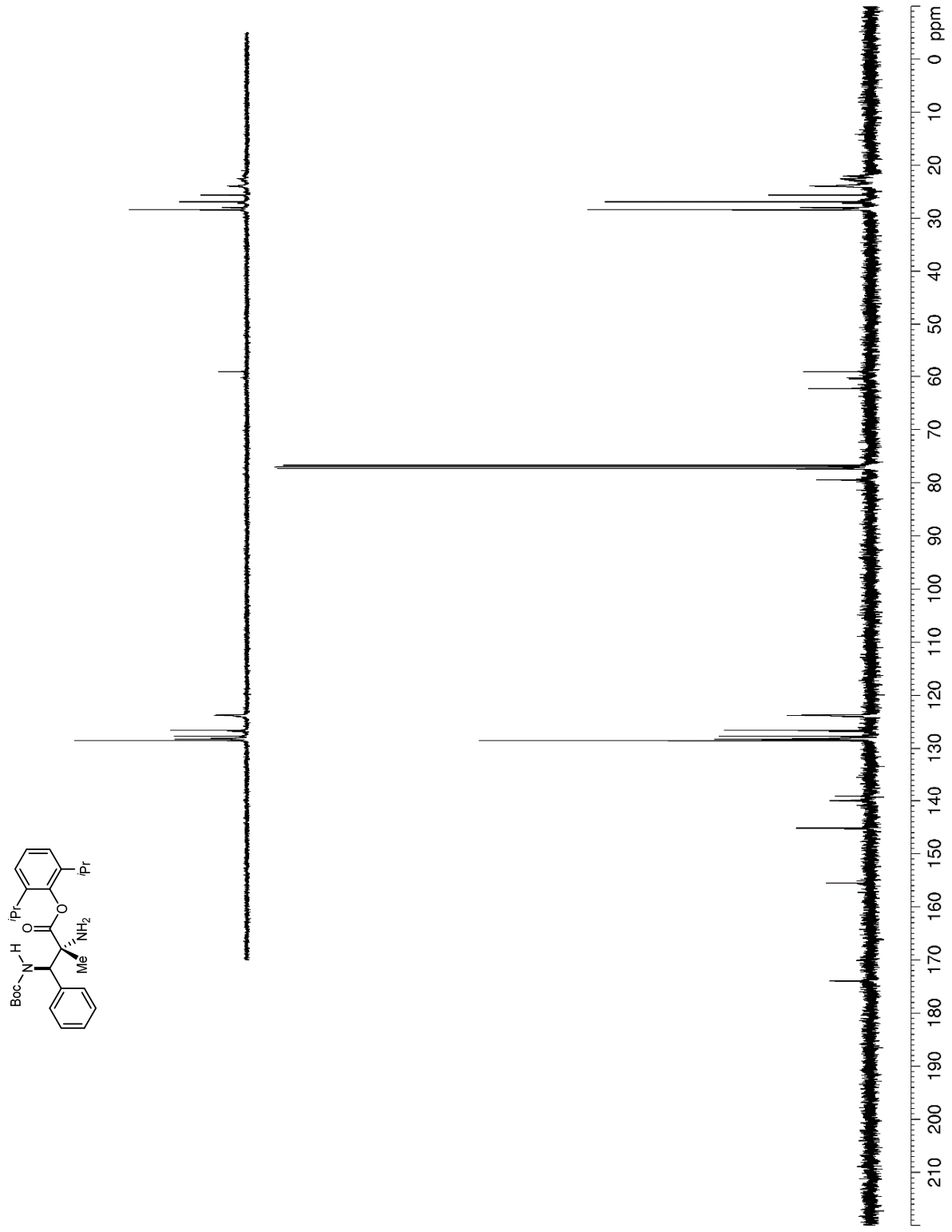


Figure 49. ^{1}H NMR (500 MHz, DMSO-d_6) of **SI-1**

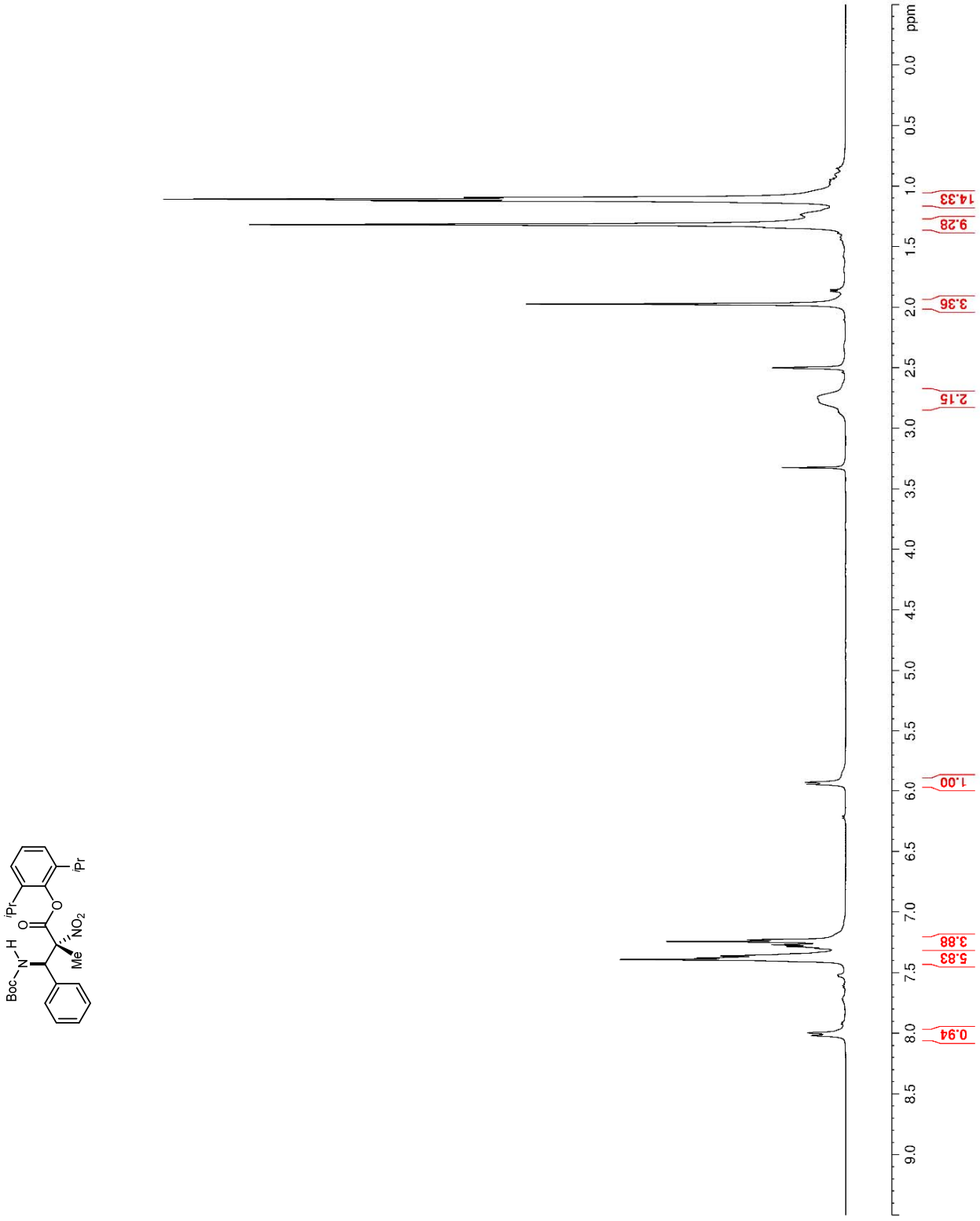


Figure 50. ^{13}C NMR (125 MHz, DMSO-d_6) of **SI-1**

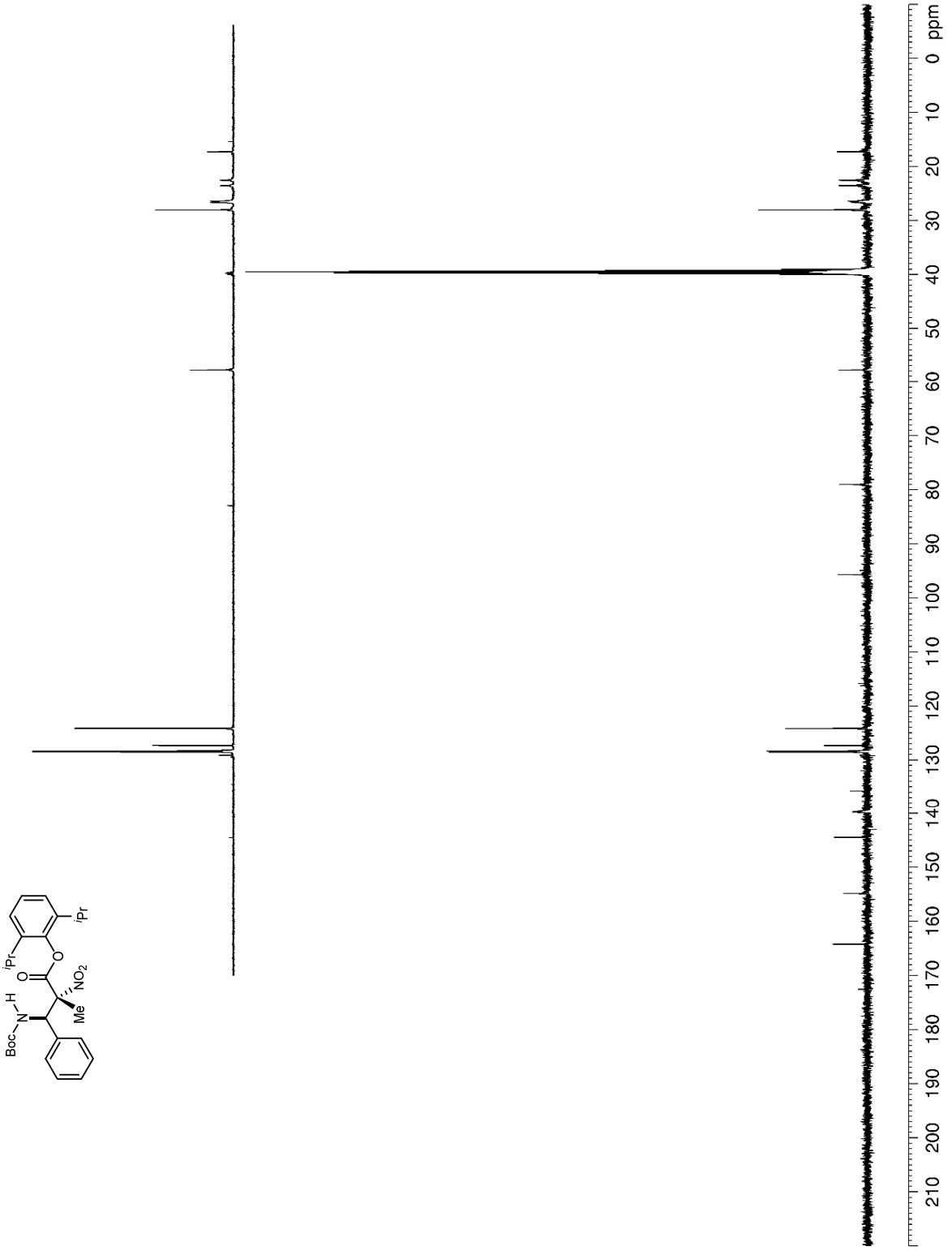
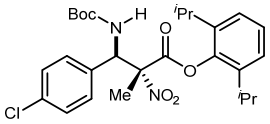
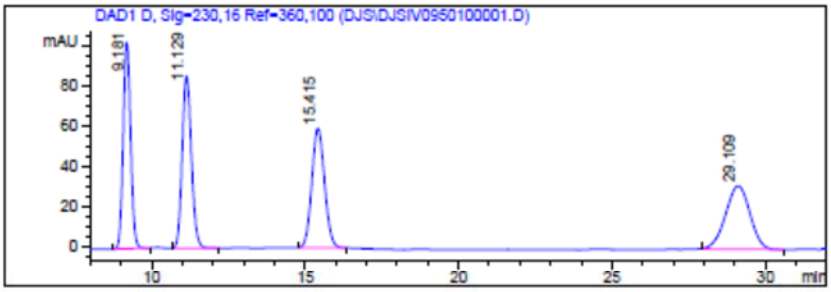


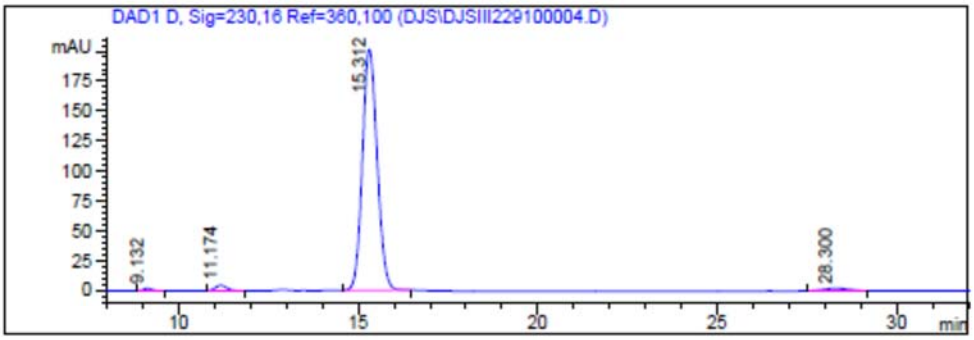
Figure 51. HPLC trace of **13a**





Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	9.181	0.281	1732.558	24.76
2	11.129	0.350	1797.143	25.68
3	15.415	0.483	1719.821	24.58
4	29.109	0.924	1748.465	24.99



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	9.132	0.287	35.665	0.59
2	11.174	0.384	101.297	1.69
3	15.312	0.476	5748.913	95.73
4	28.300	0.881	119.543	1.99

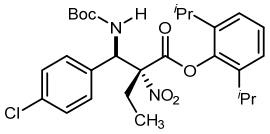
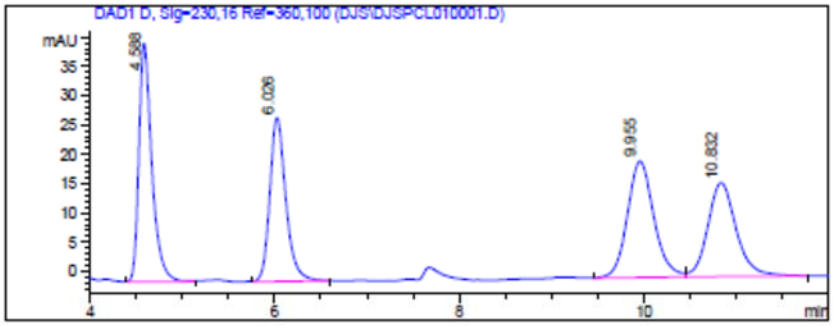
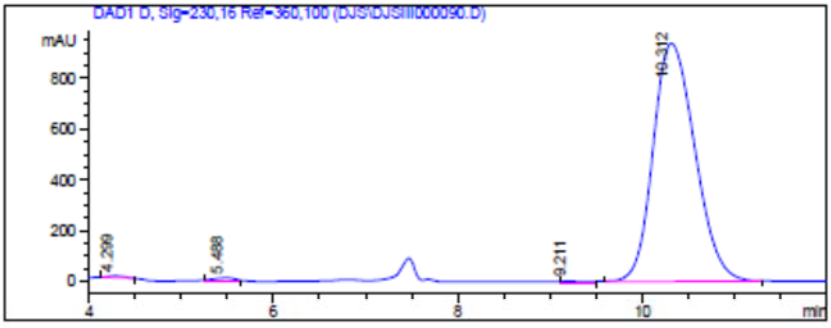


Figure 52. HPLC trace of **13b**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

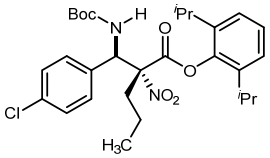
Peak #	RT [min]	Width [min]	Area	Area %
1	4.588	0.162	395.129	26.83
2	6.026	0.201	337.076	22.89
3	9.955	0.332	397.256	26.98
4	10.832	0.355	343.018	23.30

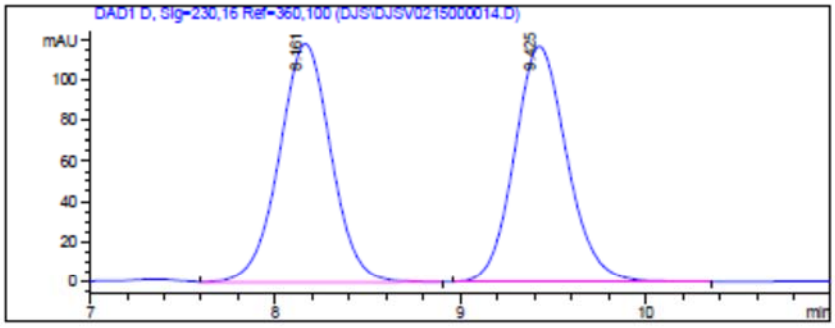


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.299	0.204	81.523	0.27
2	5.488	0.245	158.381	0.53
3	9.211	0.358	54.916	0.18
4	10.312	0.526	29516.441	99.01

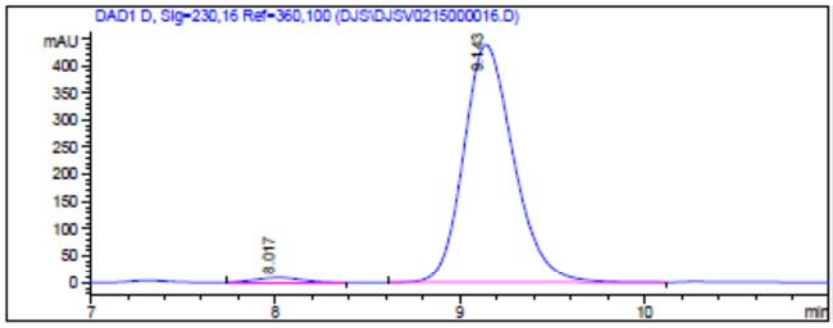
Figure 53. HPLC trace of **13c**





Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	8.161	0.327	2319.935	49.97
2	9.425	0.331	2322.924	50.03



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	8.017	0.276	138.022	1.64
2	9.143	0.315	8275.297	98.36

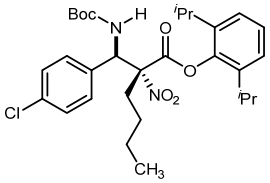
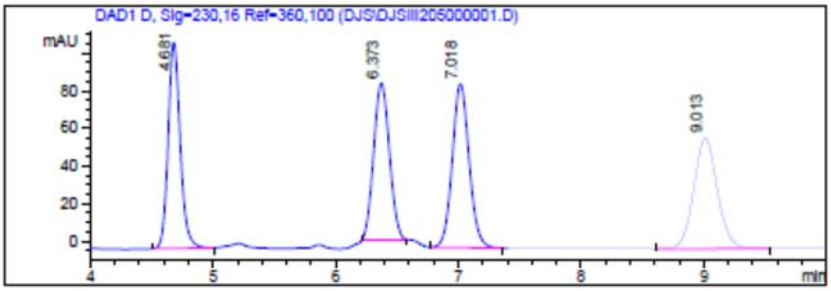
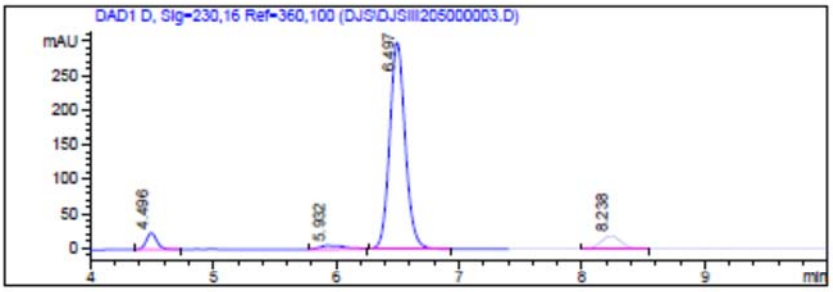


Figure 54. HPLC trace of **13d**



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.681	0.114	748.867	23.96
2	6.373	0.149	750.449	24.01
3	7.018	0.159	834.238	26.69
4	9.013	0.223	792.462	25.35



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.496	0.098	141.020	4.57
2	5.932	0.244	79.387	2.57
3	6.497	0.147	2635.708	85.49
4	8.238	0.195	227.084	7.37

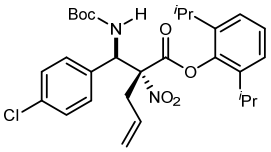
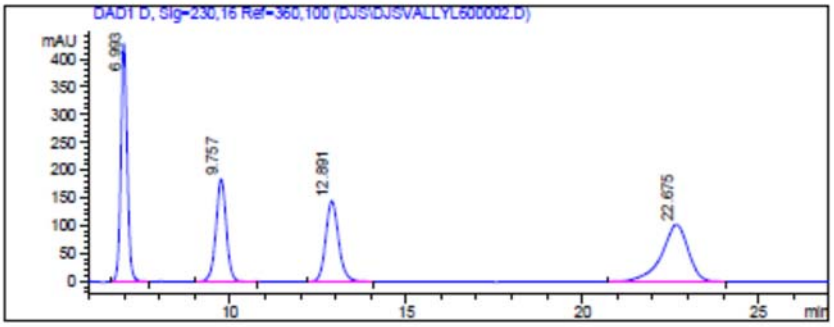
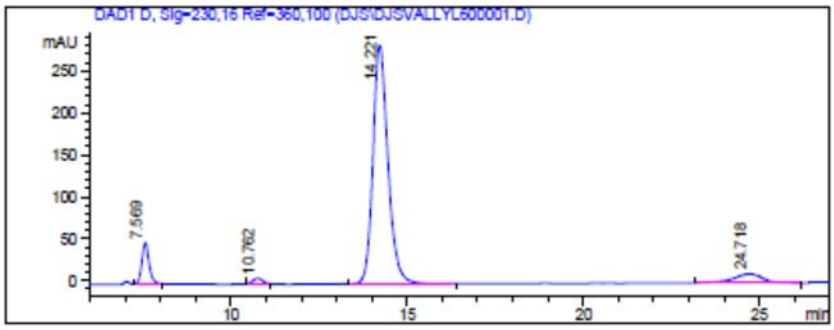


Figure 55. HPLC trace of **13e**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	6.993	0.209	5376.496	29.02
2	9.757	0.343	3800.438	20.51
3	12.891	0.434	3809.733	20.56
4	22.675	0.896	5542.191	29.91



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	7.569	0.239	702.016	7.12
2	10.762	0.332	130.307	1.32
3	14.221	0.494	8446.417	85.62
4	24.718	0.907	586.605	5.95

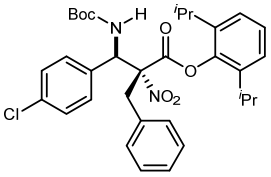
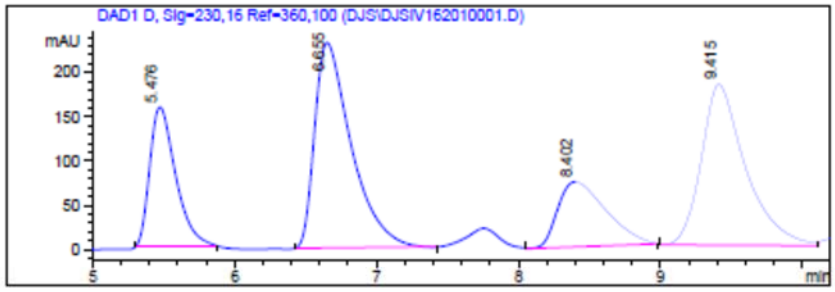
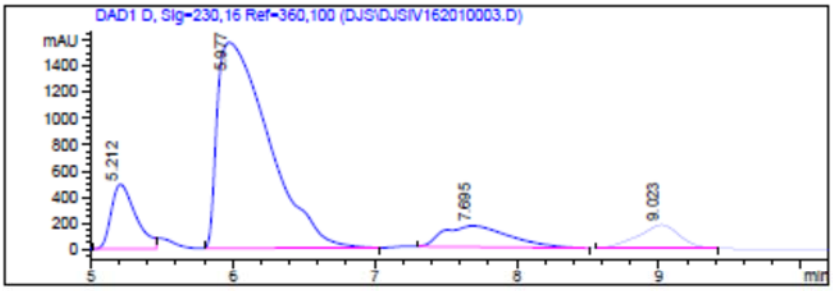


Figure 56. HPLC trace of **13f**[1]



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	5.476	0.209	1962.621	16.65
2	6.655	0.299	4154.844	35.24
3	8.402	0.391	1727.450	14.65
4	9.415	0.362	3944.966	33.46

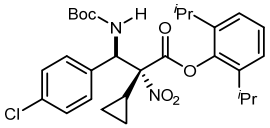


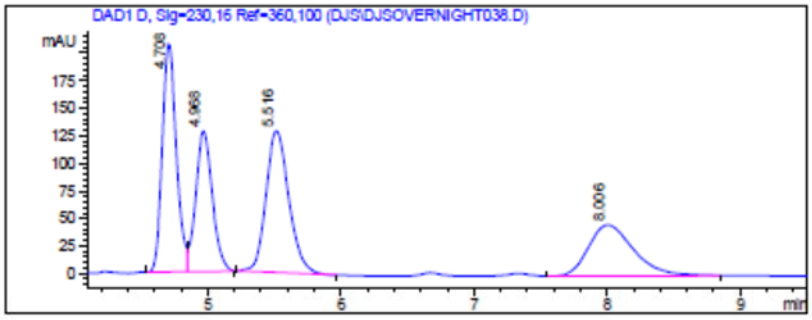
Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	5.212	0.201	5970.524	10.97
2	5.977	0.420	39633.594	72.81
3	7.695	0.536	5205.801	9.56
4	9.023	0.338	3622.799	6.66

[1] Product was unable to be separated from starting material impurity by column chromatography, however, all 4 peaks of the product are unaffected and visible in the HPLC chromatogram, allowing for determination of selectivity from the reaction (the *anti* peaks are peaks 2 and 4 in the spectrum).

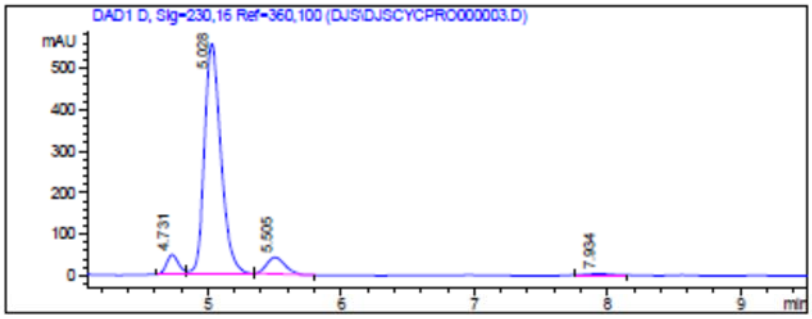
Figure 57. HPLC trace of **13g**





Signal 1: DAD1 D, Sig=230,16 Ref=360,100

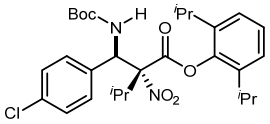
Peak #	RT [min]	Width [min]	Area	Area %
1	4.708	0.123	1521.462	29.05
2	4.968	0.144	1101.792	21.04
3	5.516	0.198	1525.785	29.13
4	8.006	0.392	1088.827	20.79

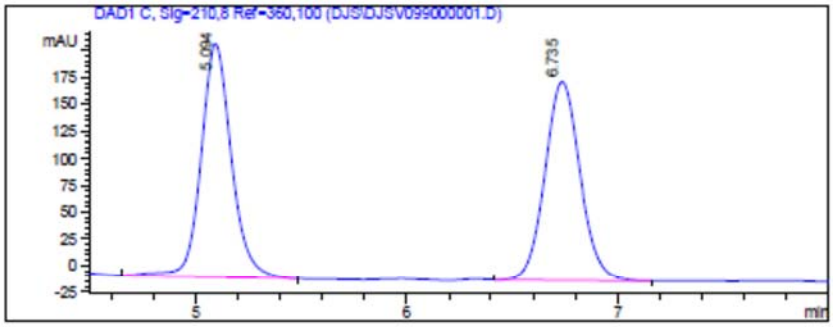


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.731	0.105	301.070	5.43
2	5.028	0.144	4815.134	86.83
3	5.505	0.162	388.966	7.01
4	7.934	0.226	40.401	0.73

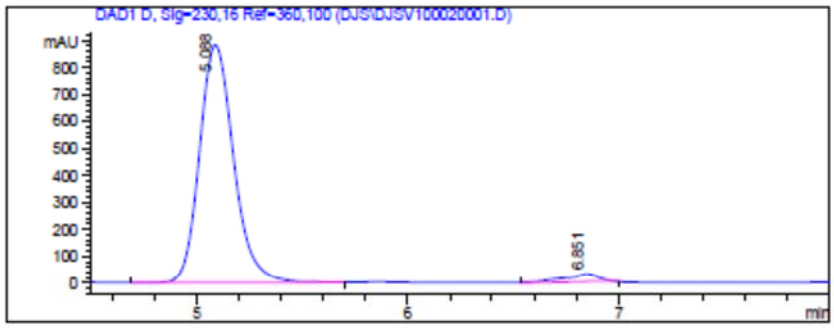
Figure 58. HPLC trace of **13h**





Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	5.094	0.169	2200.285	50.56
2	6.735	0.194	2151.210	49.44



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	5.088	0.190	10103.221	96.73
2	6.851	0.205	341.890	3.27

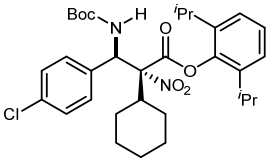
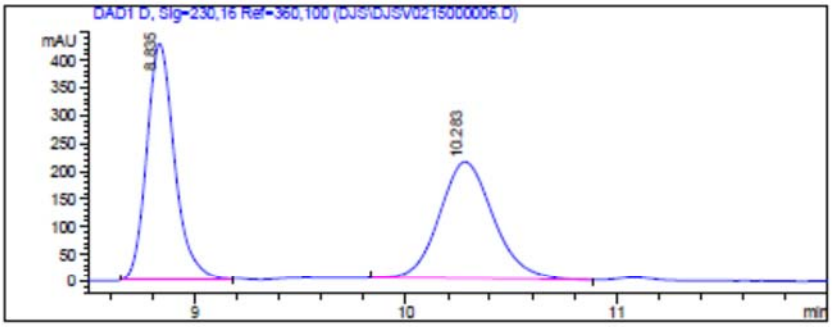
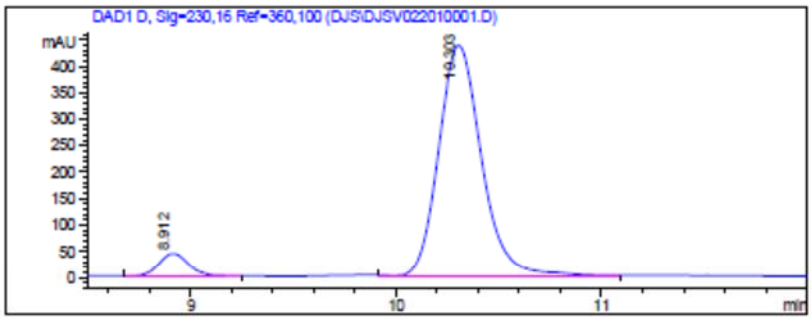


Figure 59. HPLC trace of **13i**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

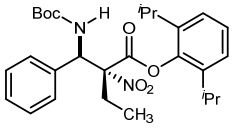
Peak #	RT [min]	Width [min]	Area	Area %
1	8.835	0.152	3883.956	50.58
2	10.283	0.298	3795.124	49.42

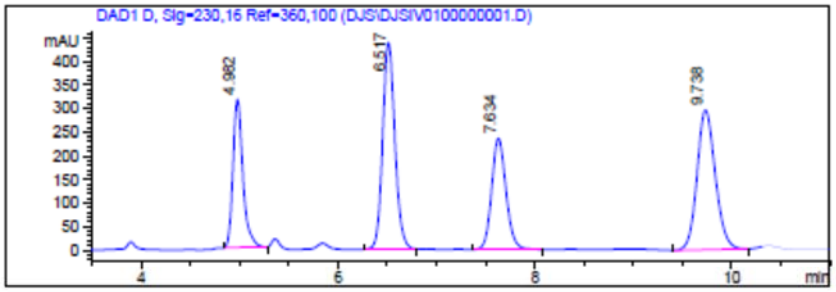


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	8.912	0.168	444.695	6.54
2	10.303	0.242	6352.126	93.46

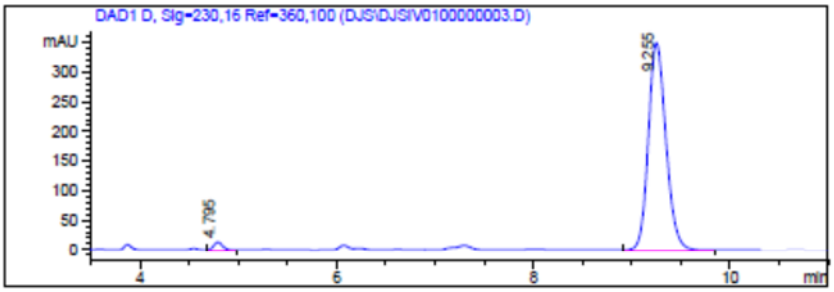
Figure 60. HPLC trace of **13j**





Signal 1: DAD1 D, Sig=230,16 Ref=360,100

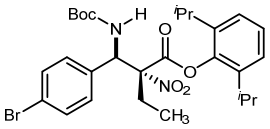
Peak #	RT [min]	Width [min]	Area	Area %
1	4.982	0.117	2200.071	18.03
2	6.517	0.144	3777.581	30.95
3	7.634	0.169	2401.456	19.68
4	9.738	0.215	3825.402	31.34

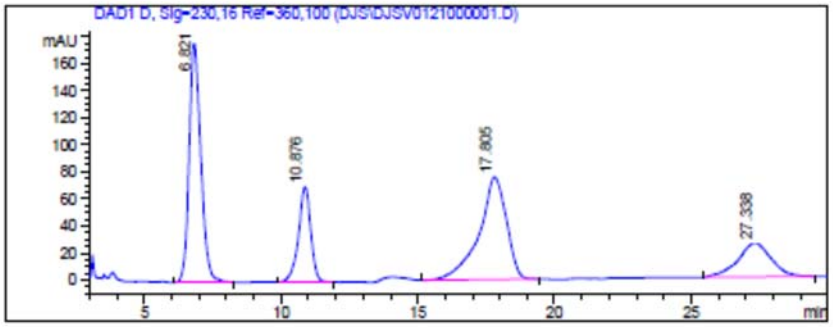


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.795	0.105	86.437	1.94
2	9.255	0.207	4359.929	98.06

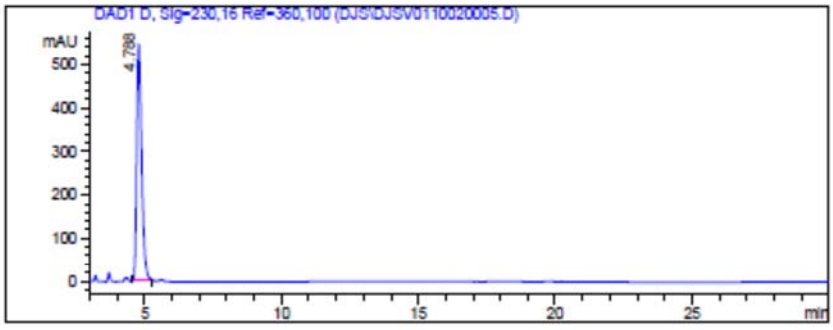
Figure 61. HPLC trace of **13k**





Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	6.821	0.496	5261.827	35.25
2	10.876	0.525	2226.999	14.92
3	17.805	1.169	5321.908	35.65
4	27.338	1.407	2116.072	14.18



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.788	0.213	6961.615	100.00

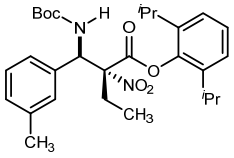
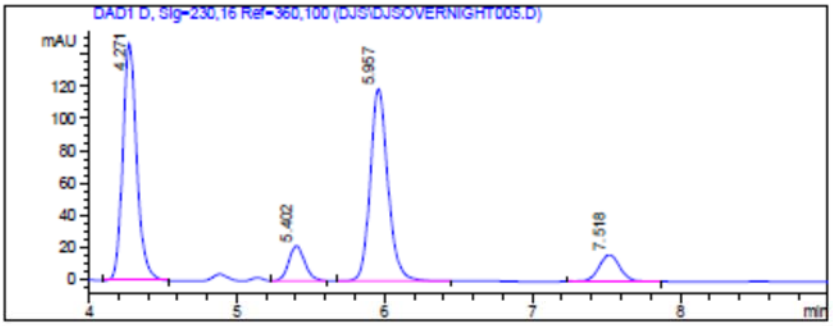
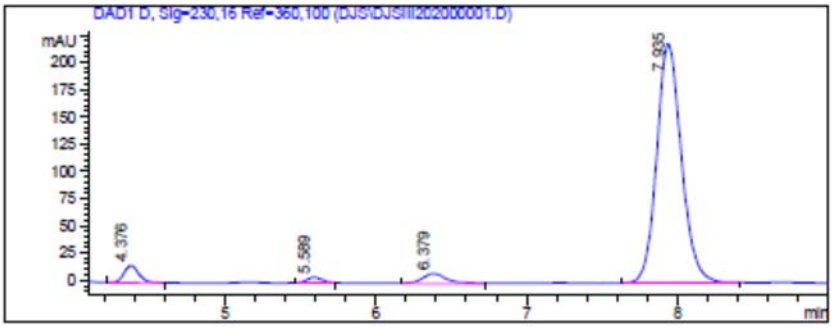


Figure 62. HPLC trace of **13l**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.271	0.110	968.415	42.34
2	5.402	0.125	163.946	7.17
3	5.957	0.139	993.731	43.45
4	7.518	0.161	161.119	7.04



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.376	0.117	112.484	4.10
2	5.589	0.113	33.327	1.21
3	6.379	0.167	102.333	3.73
4	7.935	0.189	2495.709	90.96

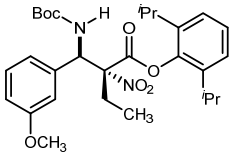
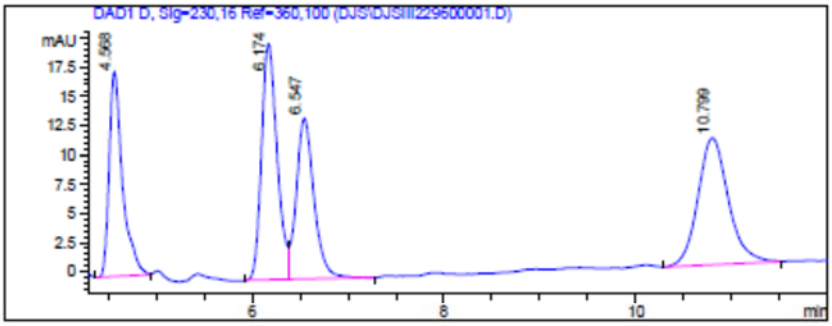
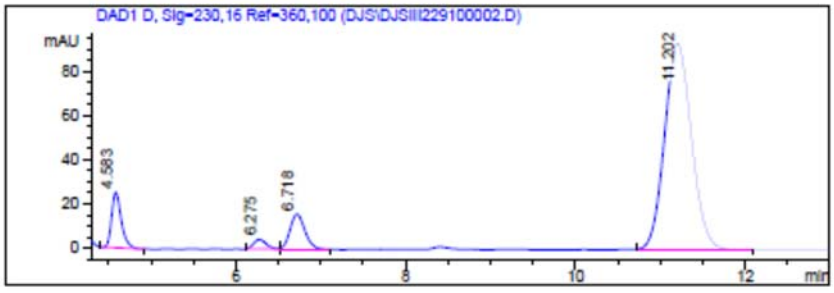


Figure 63. HPLC trace of **13m**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

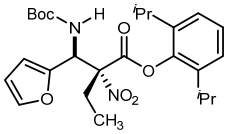
Peak #	RT [min]	Width [min]	Area	Area %
1	4.568	0.161	169.195	20.84
2	6.174	0.188	228.191	28.11
3	6.547	0.213	175.896	21.67
4	10.799	0.367	238.463	29.38

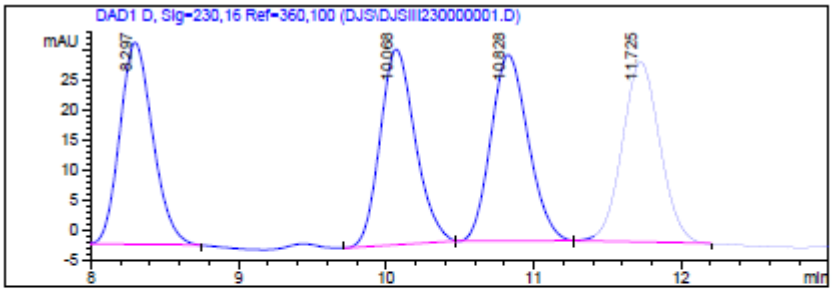


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.583	0.132	198.499	8.02
2	6.275	0.172	42.868	1.73
3	6.718	0.201	190.837	7.71
4	11.202	0.365	2043.087	82.54

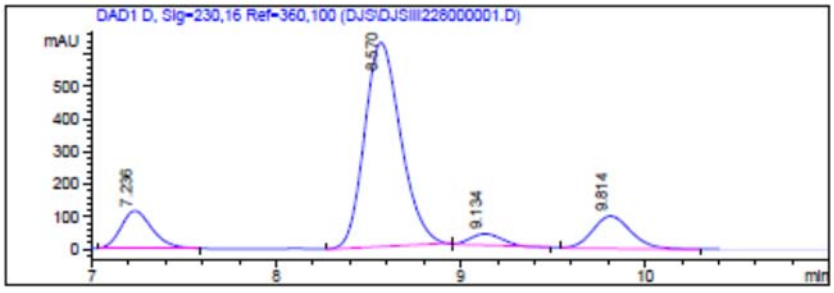
Figure 64. HPLC trace of **13o**





Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	8.297	0.259	524.881	24.45
2	10.068	0.276	541.293	25.21
3	10.828	0.292	546.372	25.45
4	11.725	0.296	534.589	24.90



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	7.236	0.184	1230.795	10.52
2	8.570	0.227	8585.271	73.42
3	9.134	0.194	405.434	3.47
4	9.814	0.244	1472.593	12.59

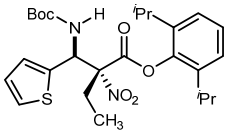
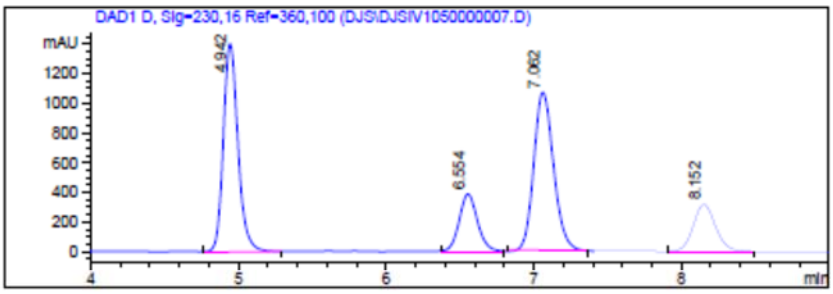
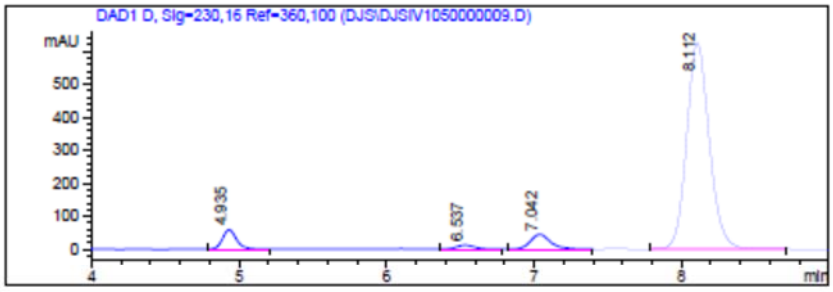


Figure 65. HPLC trace of **13p**



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.942	0.115	9739.674	37.01
2	6.554	0.144	3361.386	12.77
3	7.062	0.154	9859.396	37.47
4	8.152	0.176	3355.291	12.75



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.935	0.109	388.537	5.12
2	6.537	0.141	102.983	1.36
3	7.042	0.158	422.848	5.57
4	8.112	0.178	6673.846	87.95

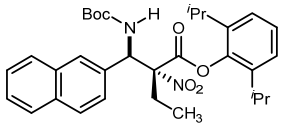
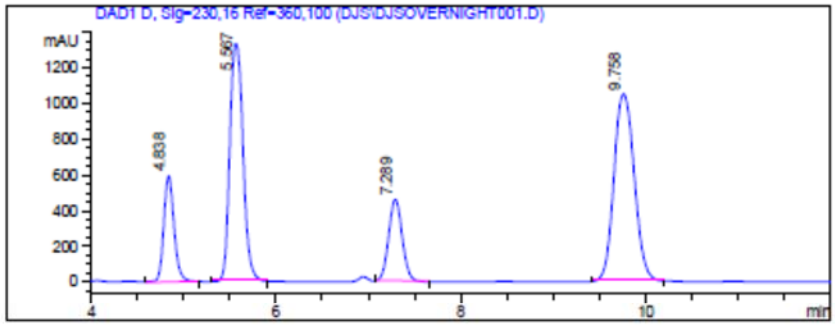
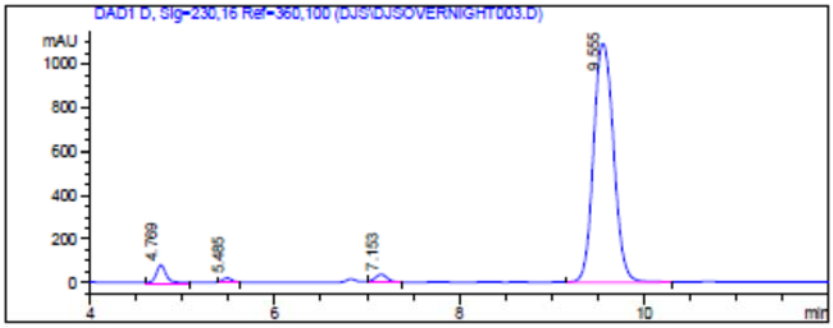


Figure 66. HPLC trace of **13r**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.838	0.129	4629.875	12.16
2	5.567	0.164	13068.275	34.32
3	7.289	0.167	4587.058	12.05
4	9.758	0.252	15791.271	41.47



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.769	0.131	665.205	3.74
2	5.485	0.111	127.301	0.72
3	7.153	0.156	330.658	1.86
4	9.555	0.254	16655.787	93.68

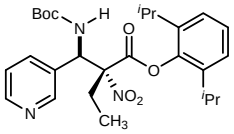
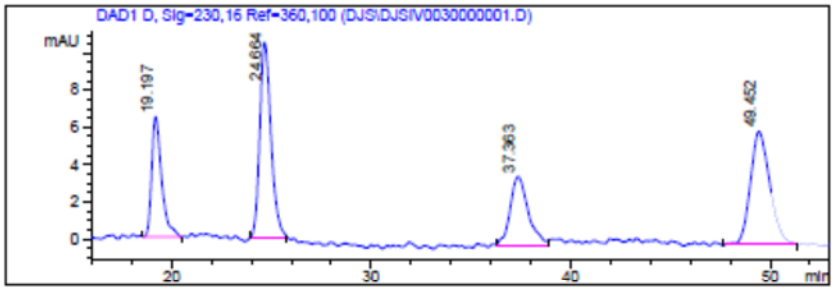
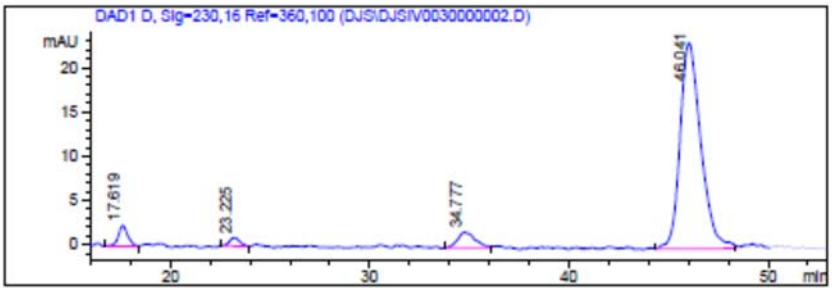


Figure 67. HPLC trace of **13s**



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

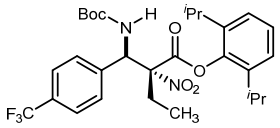
Peak #	RT [min]	Width [min]	Area	Area %
1	19.197	0.579	224.281	17.49
2	24.664	0.655	413.658	32.26
3	37.363	1.042	231.462	18.05
4	49.452	1.131	412.803	32.19

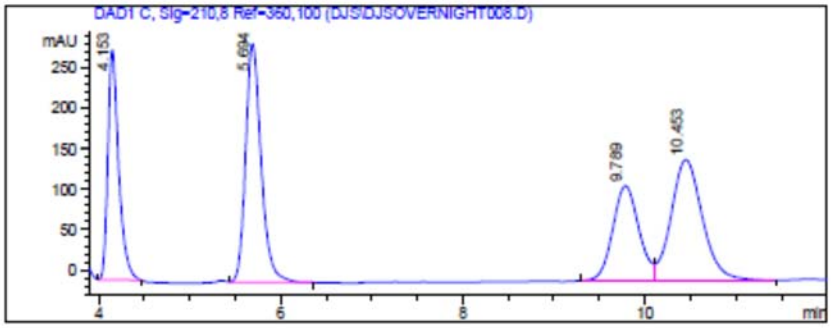


Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	17.619	0.526	73.799	3.86
2	23.225	0.620	34.850	1.82
3	34.777	1.028	107.879	5.65
4	46.041	1.214	1693.910	88.67

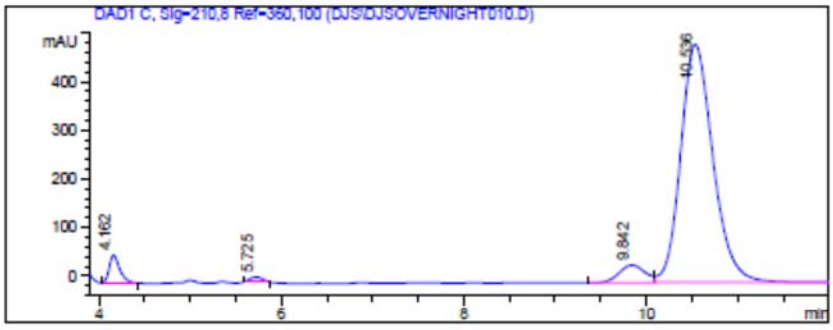
Figure 68. HPLC trace of **13t**





Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.153	0.138	2345.768	19.89
2	5.694	0.198	3497.544	29.65
3	9.789	0.332	2347.997	19.91
4	10.453	0.400	3604.464	30.56



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	4.162	0.131	451.034	3.40
2	5.725	0.148	82.500	0.62
3	9.842	0.325	702.720	5.29
4	10.536	0.410	12035.822	90.69

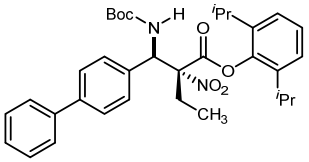
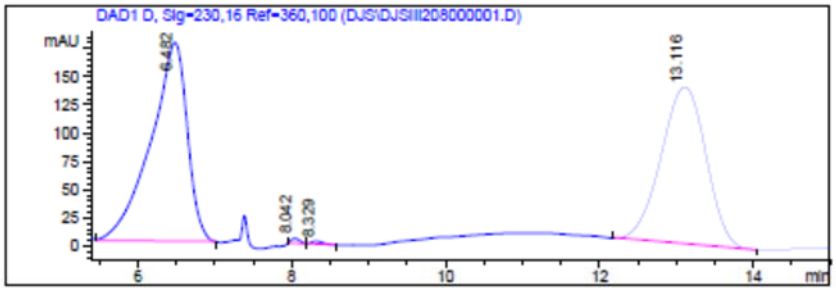
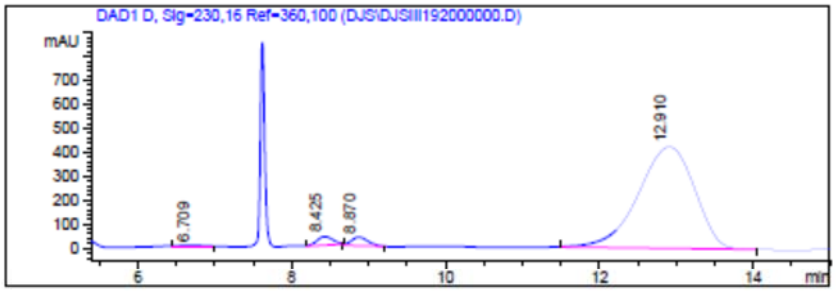


Figure 69. HPLC trace of **13u**[1]



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

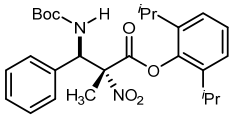
Peak #	RT [min]	Width [min]	Area	Area %
1	6.482	0.552	5814.730	50.68
2	8.042	0.126	33.470	0.29
3	8.329	0.166	23.753	0.21
4	13.116	0.675	5602.249	48.82

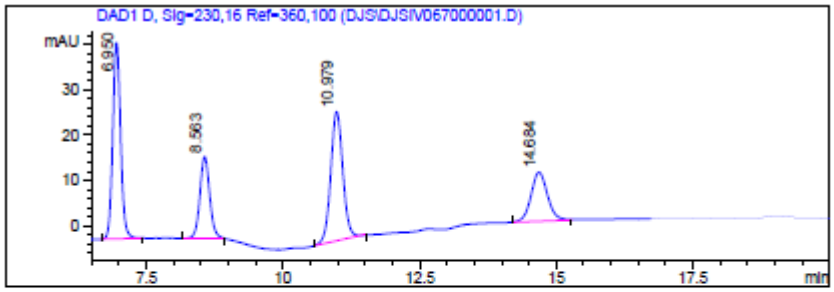


Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	6.709	0.347	97.340	0.43
2	8.425	0.245	539.446	2.37
3	8.870	0.251	539.384	2.37
4	12.910	0.848	21578.768	94.83

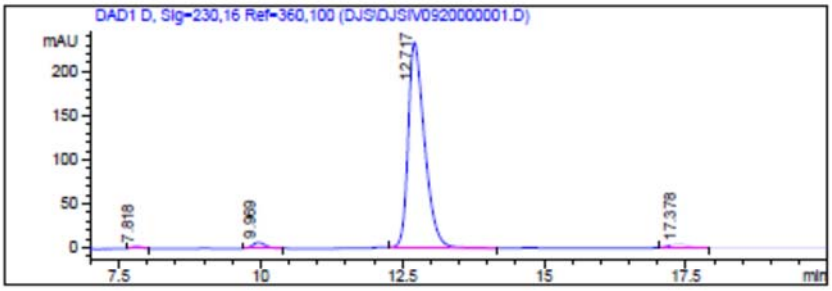
Figure 70. HPLC trace of **SI-1**





Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	6.950	0.167	432.810	32.75
2	8.563	0.209	226.393	17.13
3	10.979	0.255	435.921	32.99
4	14.684	0.350	226.234	17.12



Signal 1: DAD1 D, Sig-230,16 Ref-360,100

Peak #	RT [min]	Width [min]	Area	Area %
1	7.818	0.196	29.793	0.60
2	9.969	0.259	103.128	2.09
3	12.717	0.336	4694.535	95.31
4	17.378	0.388	97.836	1.99