Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

Molybdenum Catalysts based on Salan Ligands for the Deoxydehydration Reaction

Nathan J. Wagner,[1] Wei-Chien Tang,[1] Jonathan K. Wagner,[1] Binh T. Nguyen,[1] Jamie Y. Lam,[1] Skyler K. Gibbons-Stovall,[1] Andrea C. Matias,[1] Stephenie E. Martinez,[1] Tristhan Trieu-Tran,[1] Garrit M. Clabaugh,[1] Christine A. Navarro,[1] Ibrahim Abboud,[1] Francis X. Flores,[1] Kenneth M. Nicholas,[2] and Alex John[1]*

[1]Chemistry and Biochemistry Department

California State Polytechnic University, Pomona

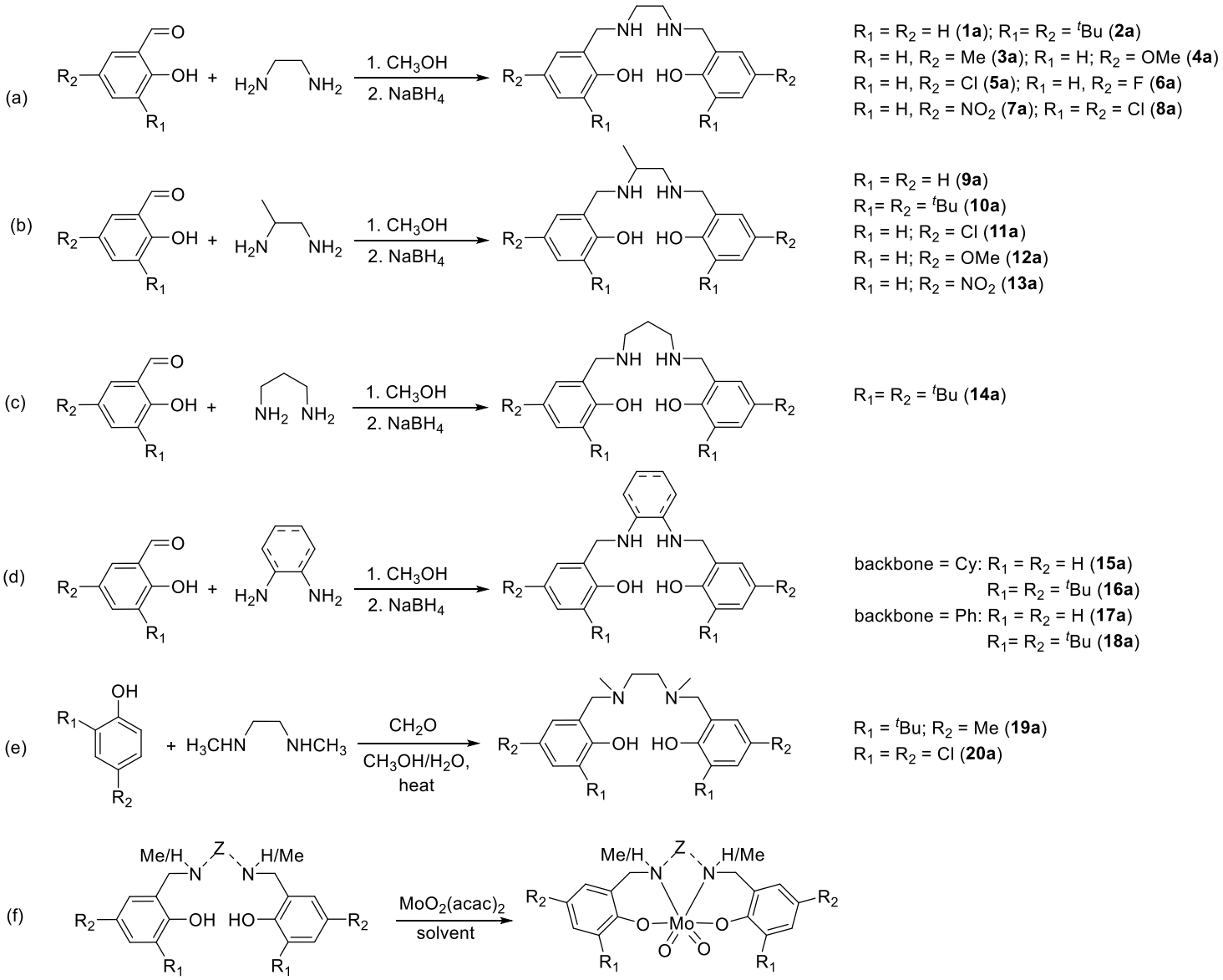
3801 West Temple Ave., Pomona CA 91768.

[2]Department of Chemistry and Biochemistry

Stephenson Life Sciences Research Center, 101 Stephenson Parkway

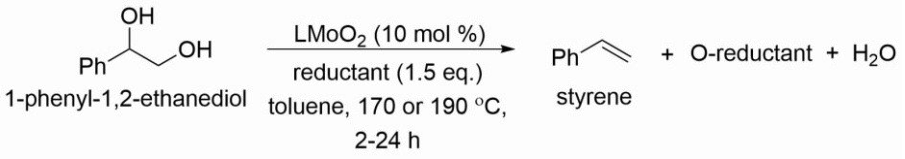
University of Oklahoma, Norman, OK 73019.

Email:ajohn@cpp.edu



Scheme S1. Synthesis of salan ligands (a-e) and molybdenum complexes (f).

Table S1. Deoxydehydration of styrene glycol catalyzed by molybdenum catalysts.[a]



			Yield[b]	
entry	backbone	catalyst	PPh_3	Na_2SO_3
1.		$^{H,H}L_2MoO_2$	46 (52)	34
2.		$^{t\text{Bu},t\text{Bu}}L_2MoO_2$	48 (54)	40
3.		$^{H,OMe}L_2MoO_2$	38 (51)	
4.		$^{H,Cl}L_2MoO_2$	39 (56)	
5.		$^{H,NO_2}L_2MoO_2$	10 (26)	4

[a]Reaction conditions: Styrene glycol (0.500 mmol), catalyst (10 mol %) and reductant (1.5 equiv.) in toluene (*ca*. 2.5 mL) at 170 °C for 24 hours. [b]Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]Yield in parentheses refers to a reaction carried out at 190 °C.

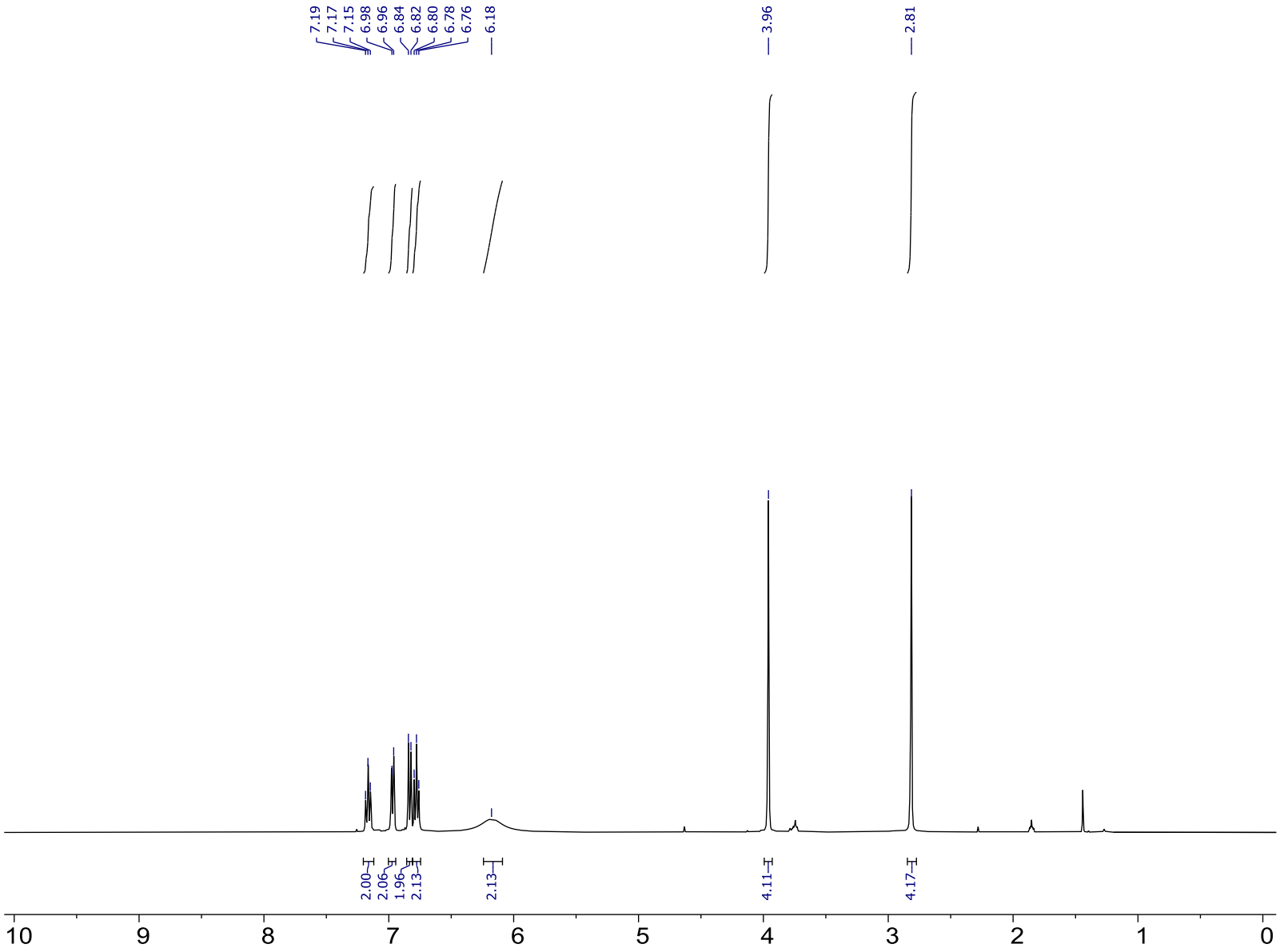


Figure S1. ^{1}H NMR spectrum of $^{H,H}L_1$ (**1a**) in $CDCl_3$.

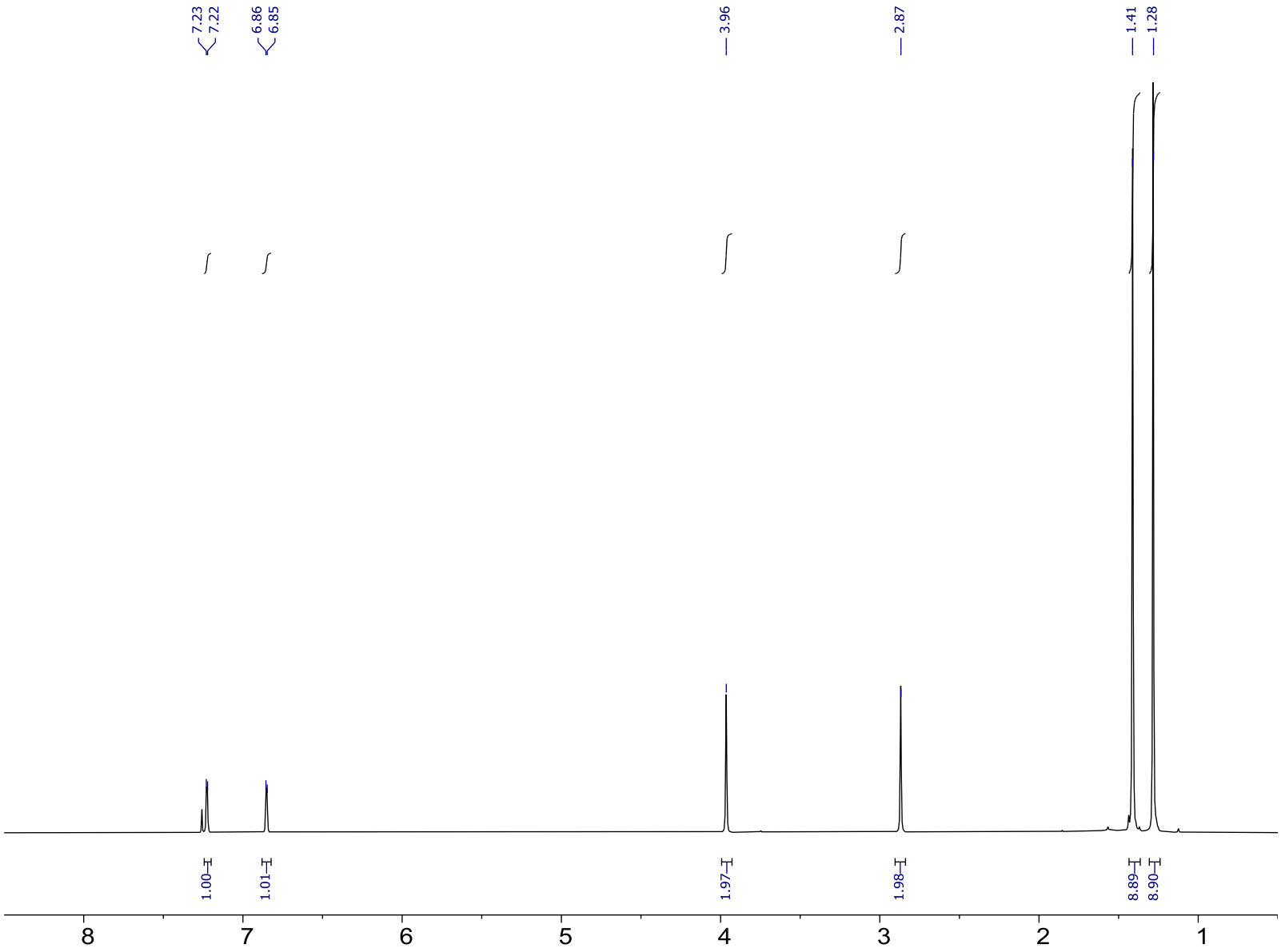


Figure S2. ^{1}H NMR spectrum of $^{tBu,tBu}L_1$ (**2a**) in $CDCl_3$.

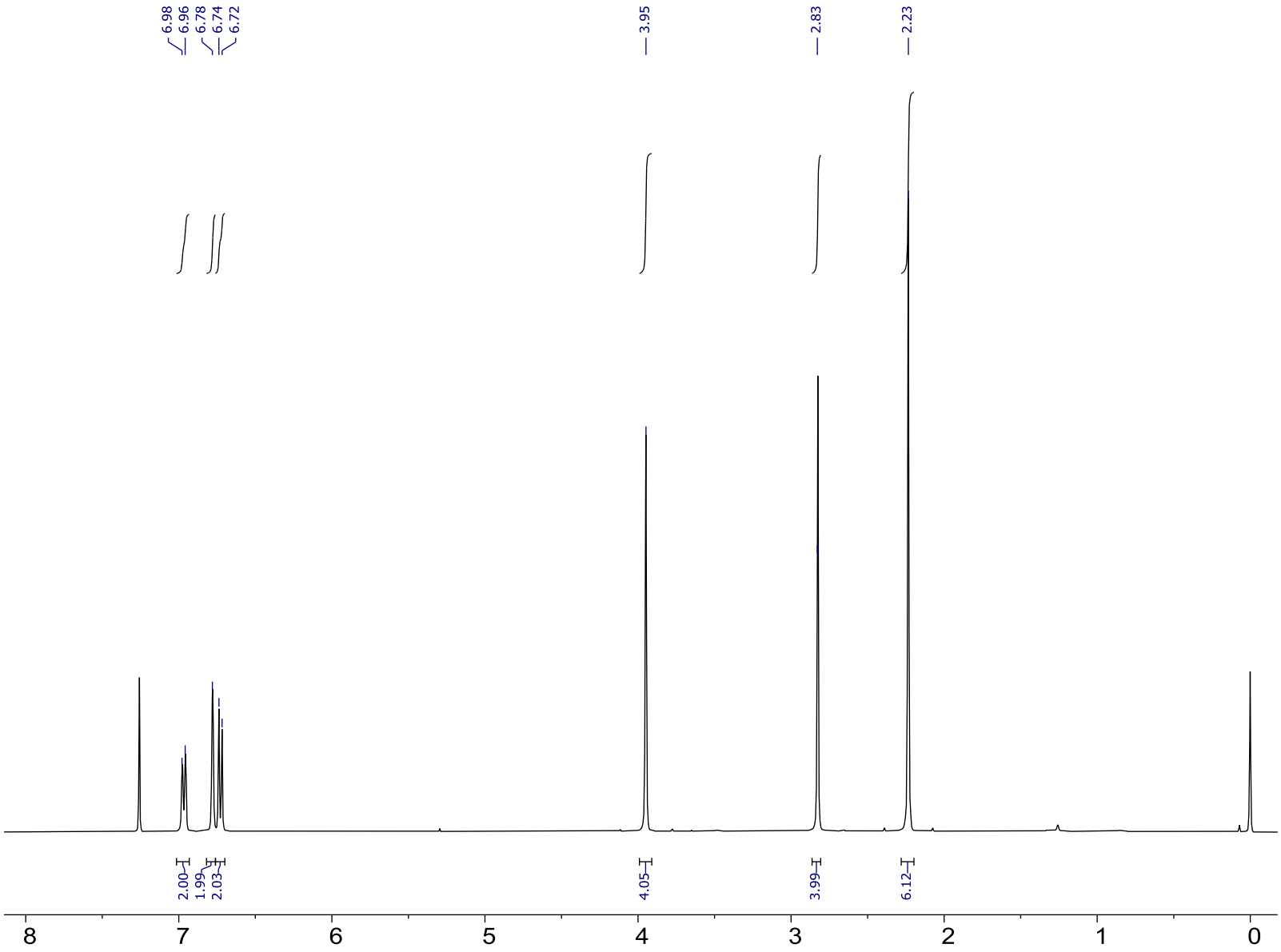


Figure S3. ^{1}H NMR spectrum of $^{H,Me}L_1$ (**3a**) in $CDCl_3$.

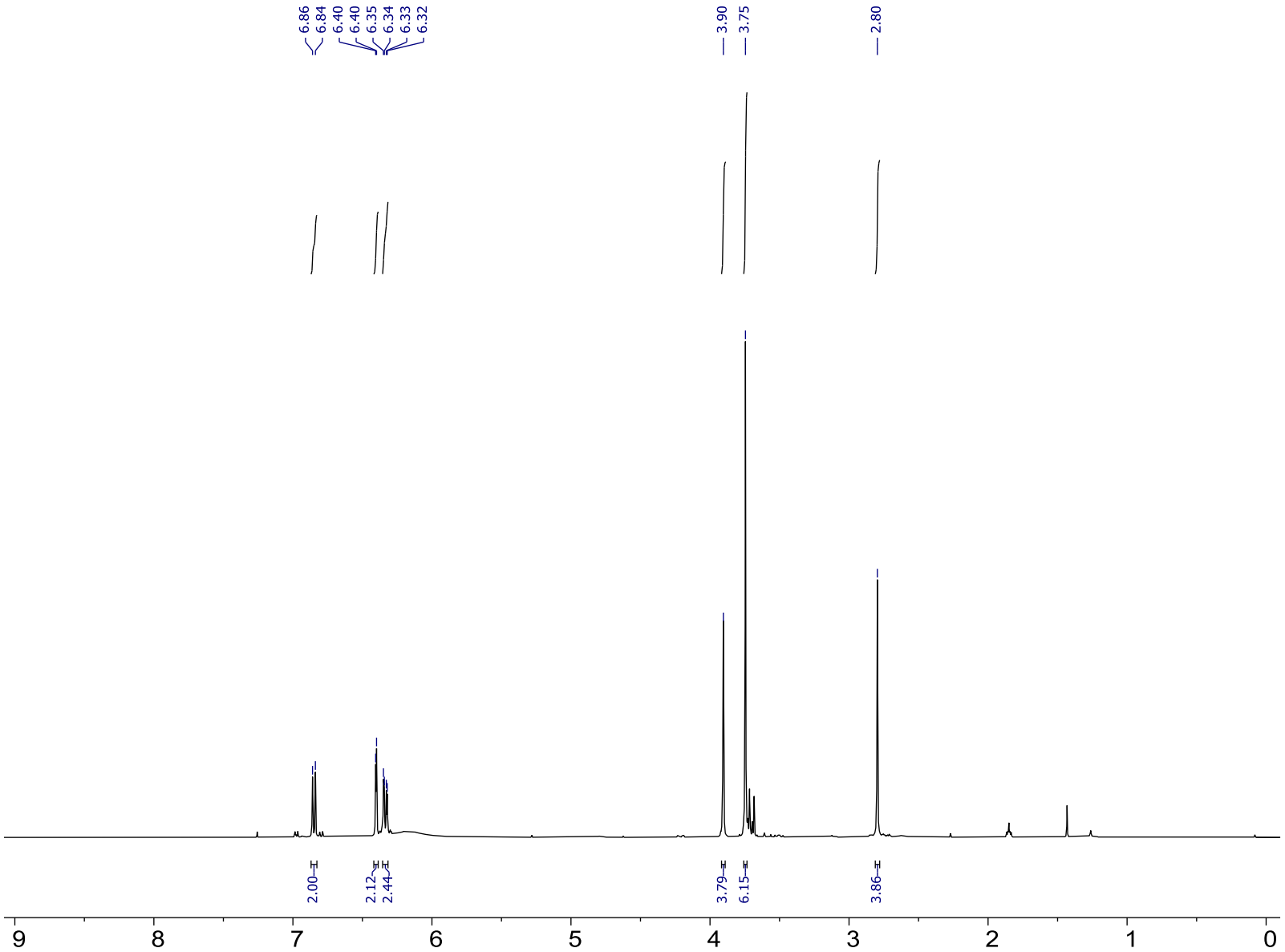


Figure S4. ^{1}H NMR spectrum of $^{H,OMe}L_1$ (**4a**) in $CDCl_3$.

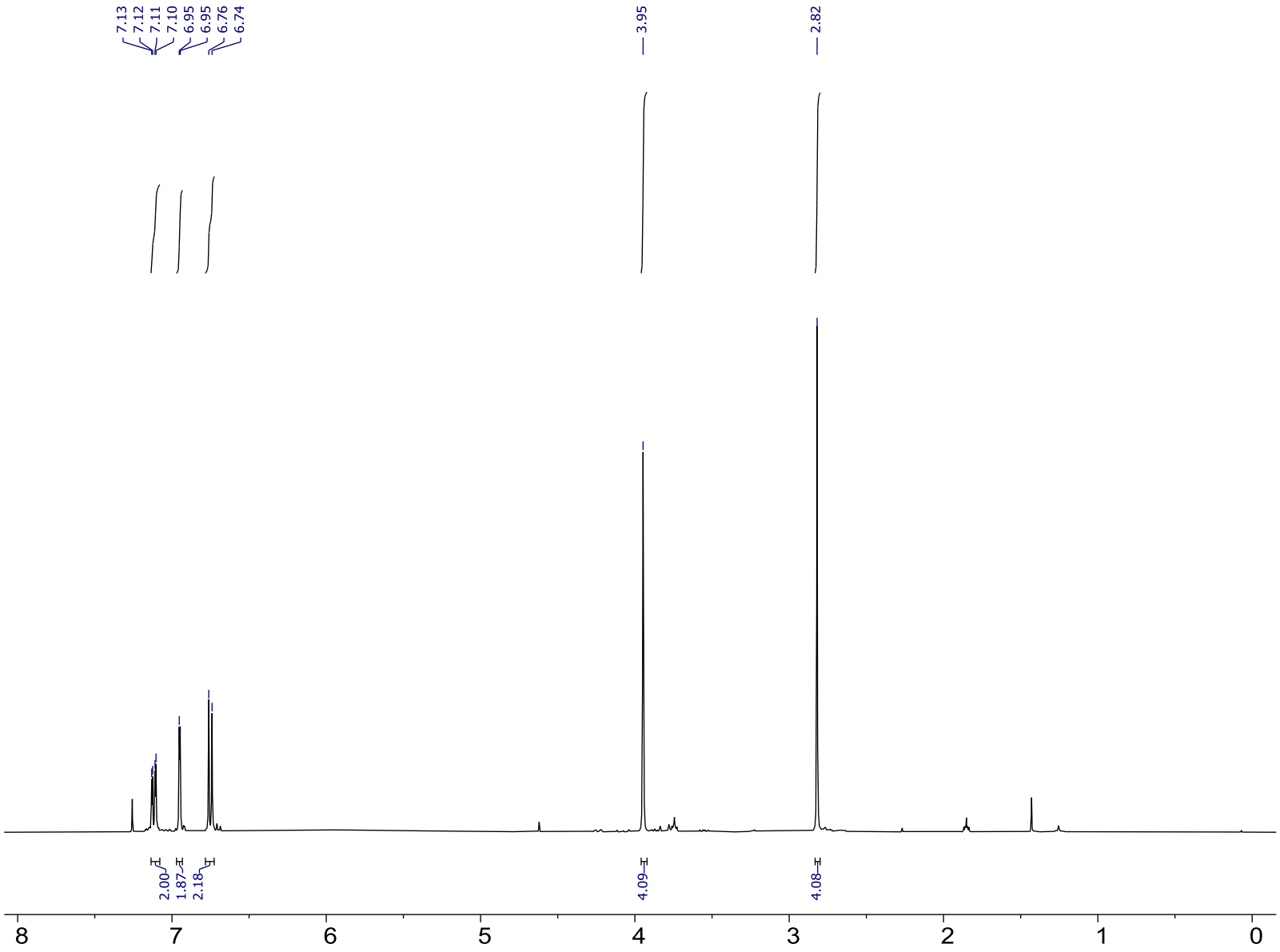


Figure S5. ^{1}H NMR spectrum of $^{H,Cl}L_1$ (**5a**) in $CDCl_3$.

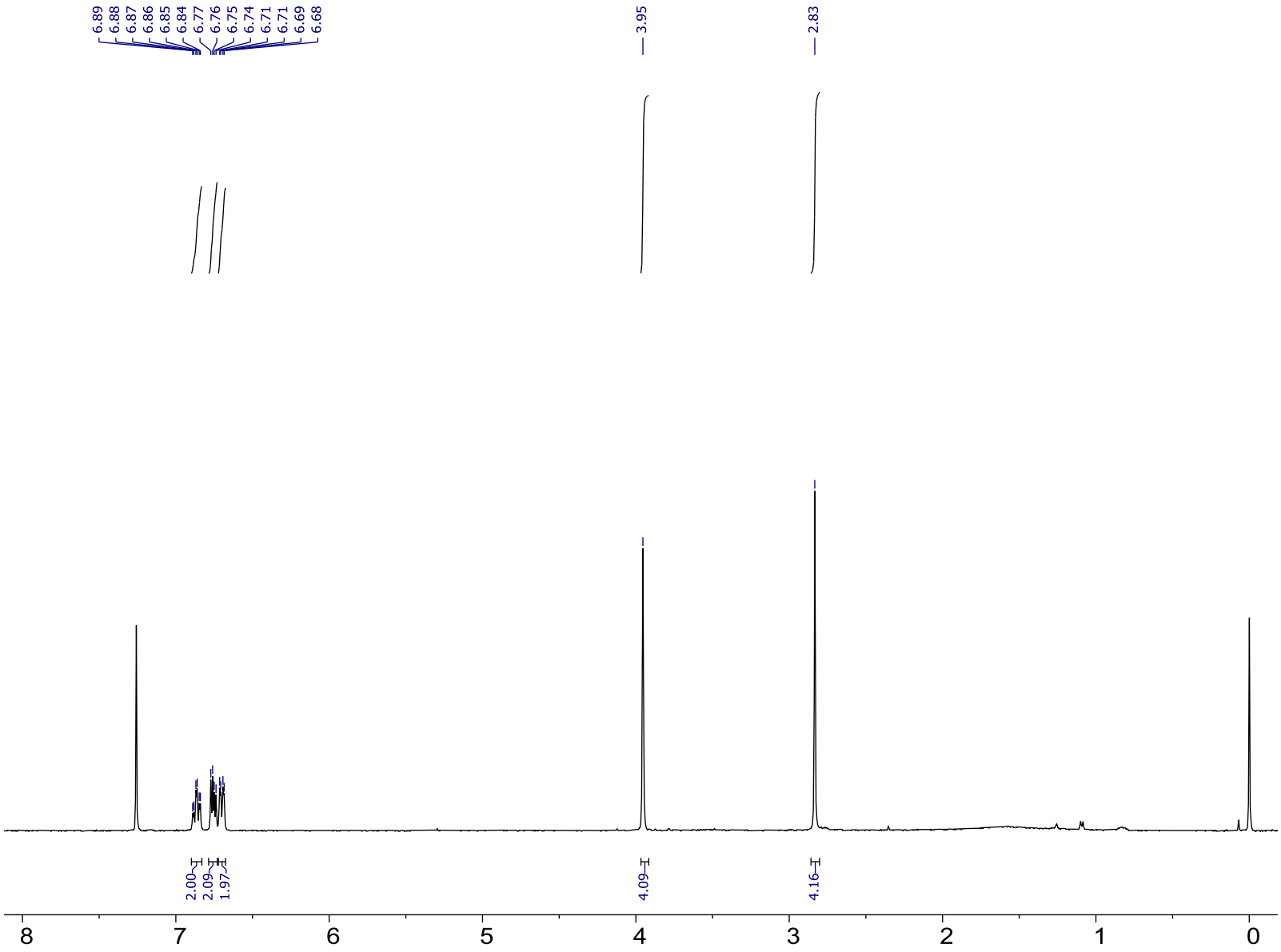


Figure S6. ^{1}H NMR spectrum of $^{H,F}L_1$ (**6a**) in $CDCl_3$.

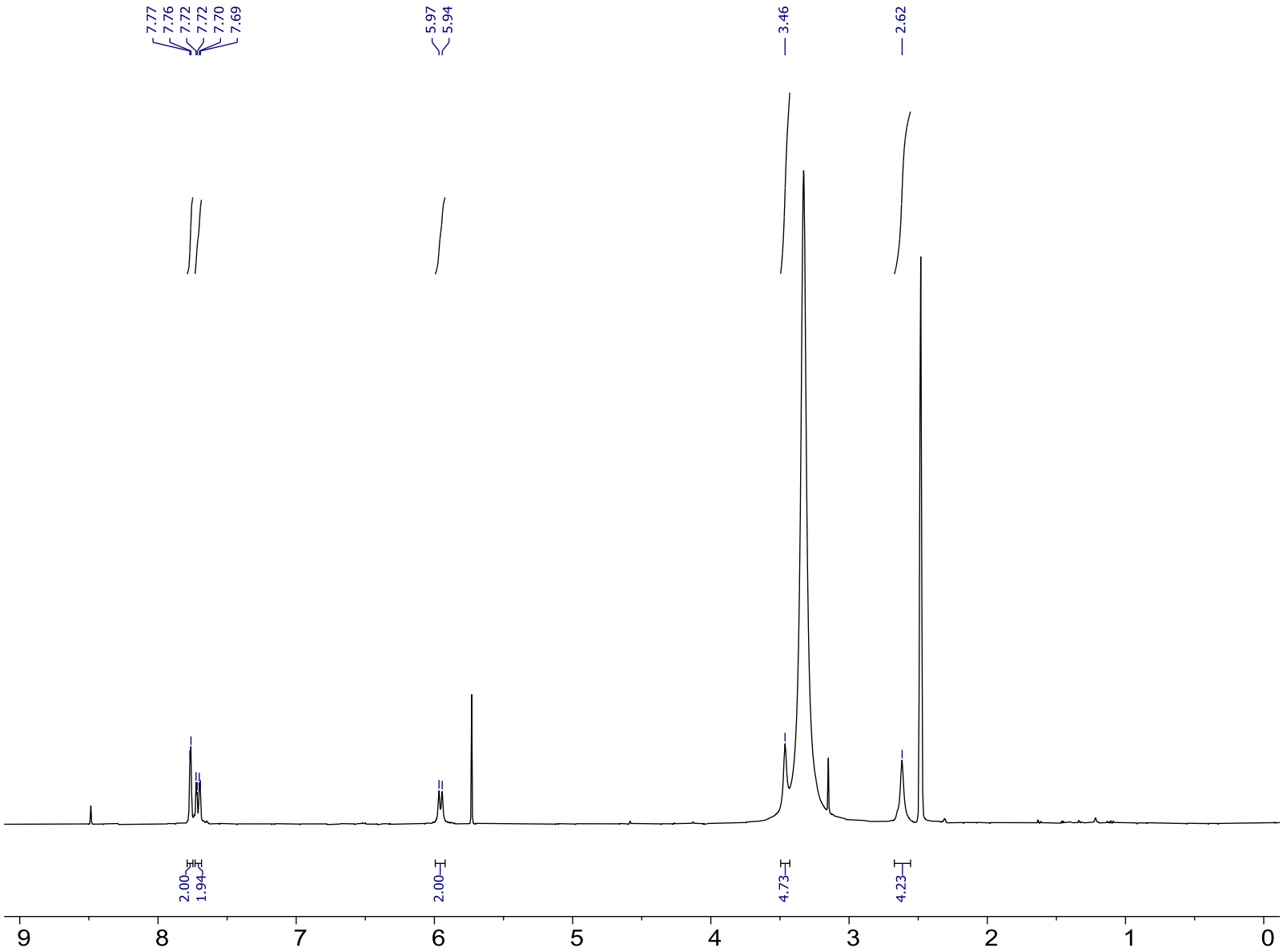


Figure S7. ^{1}H NMR spectrum of $^{H,NO2}L_1$ (**7a**) in DMSO-d_6.

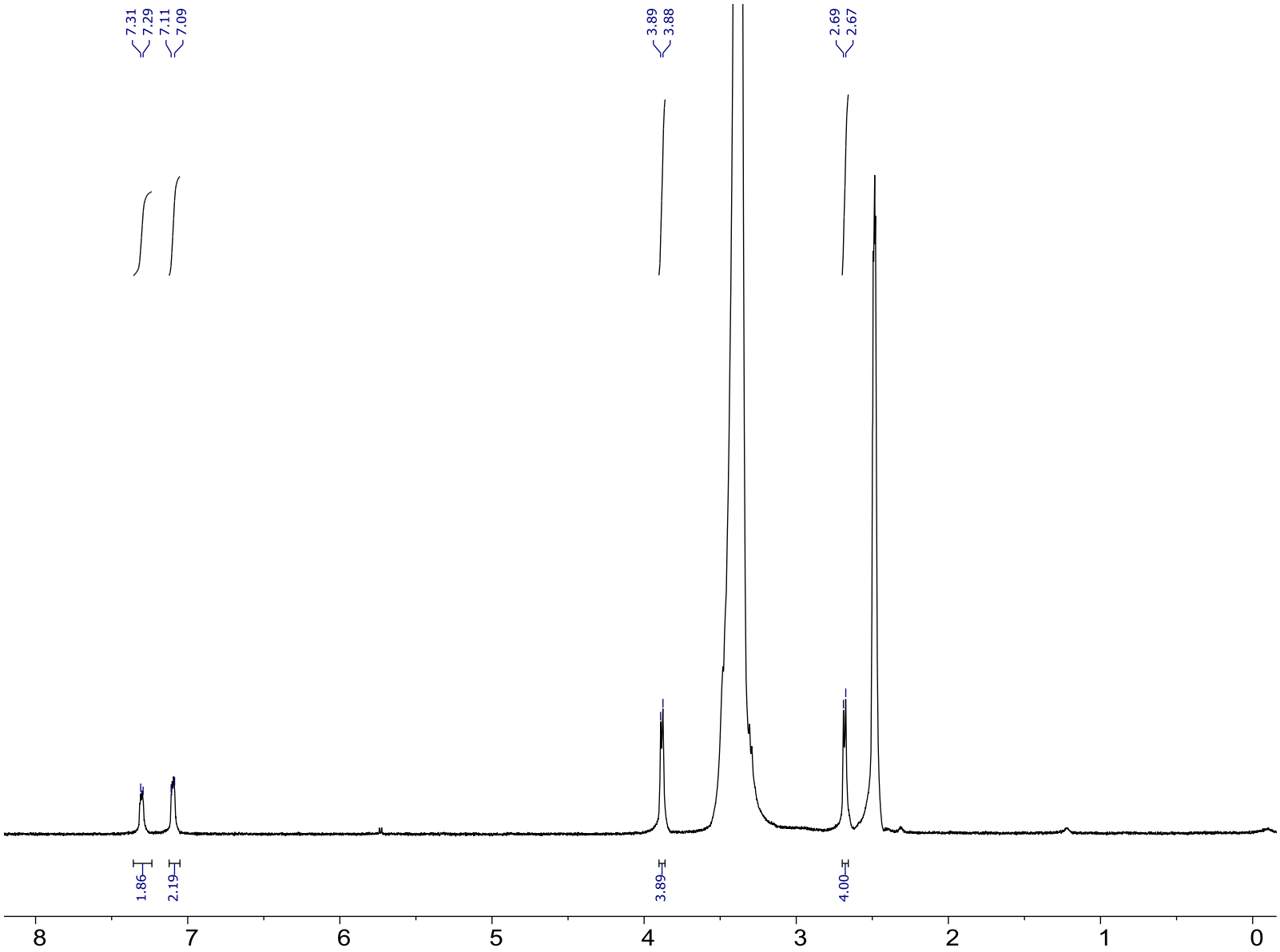


Figure S8. ^{1}H NMR spectrum of $^{Cl,Cl}L_1$ (**8a**) in DMSO-d_6.

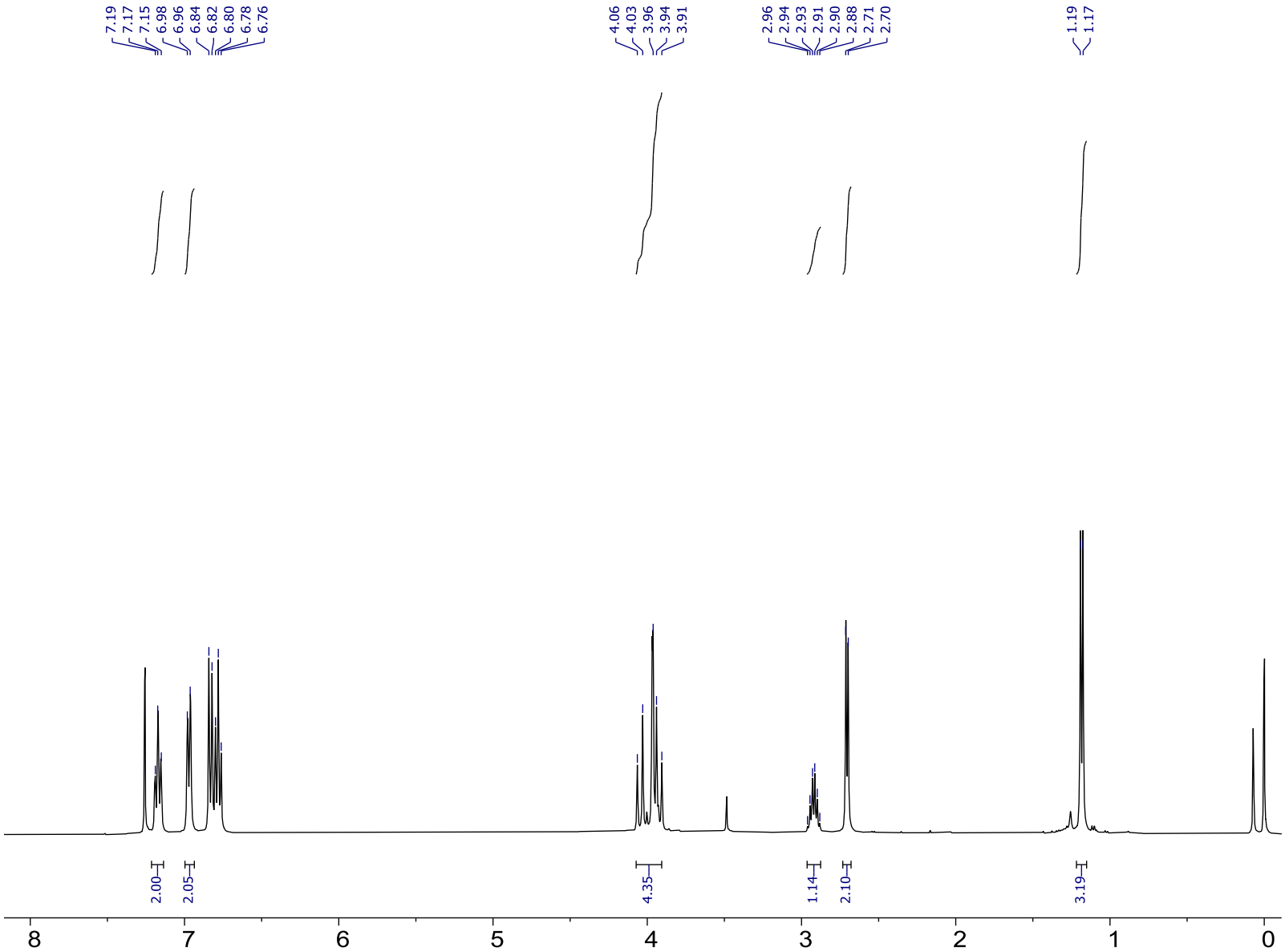


Figure S9. ^{1}H NMR spectrum of $^{H,H}L_2$ (**9a**) in $CDCl_3$.

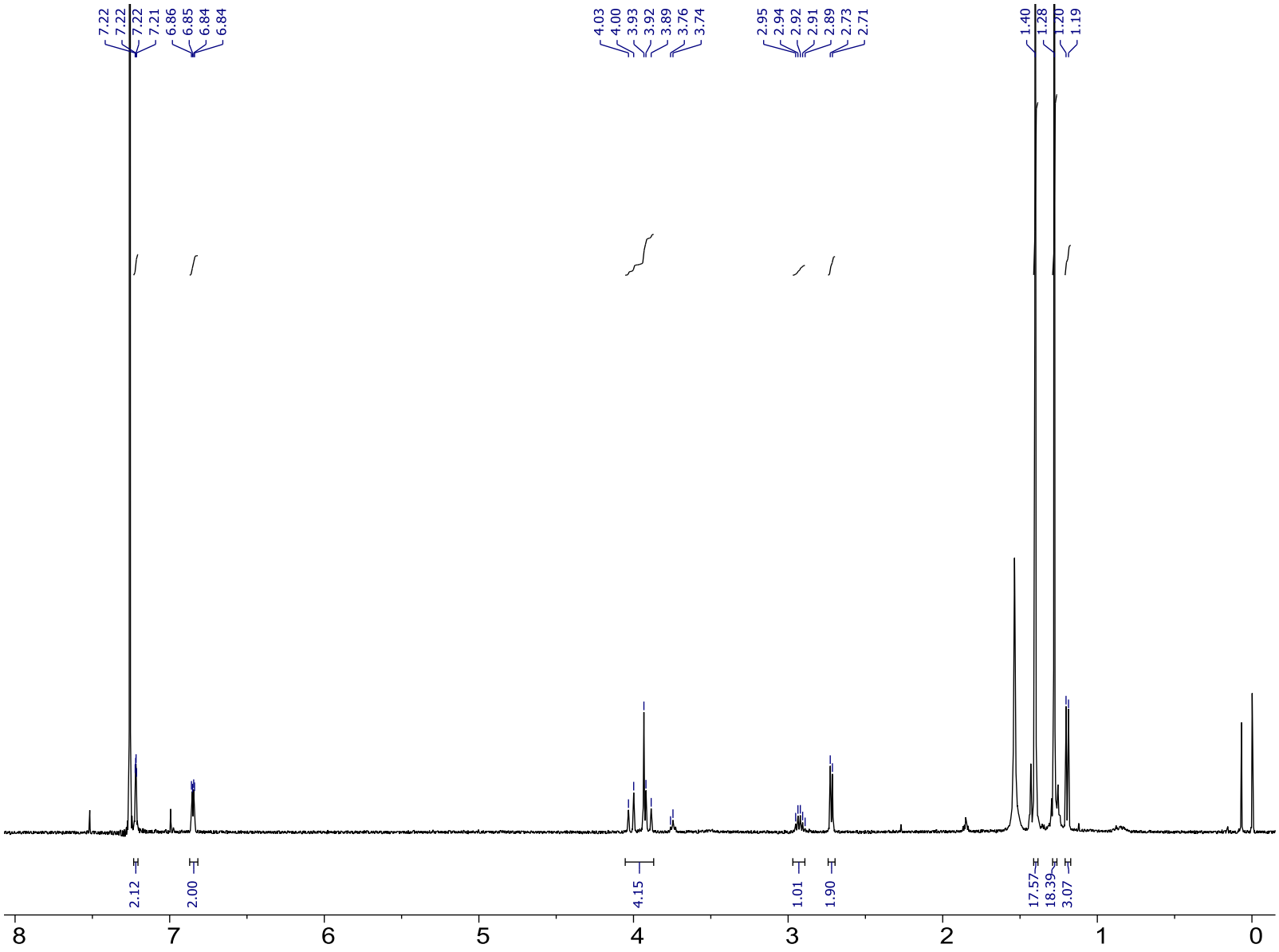


Figure S10. ^{1}H NMR spectrum of $^{tBu,tBu}L_2$ (**10a**) in $CDCl_3$.

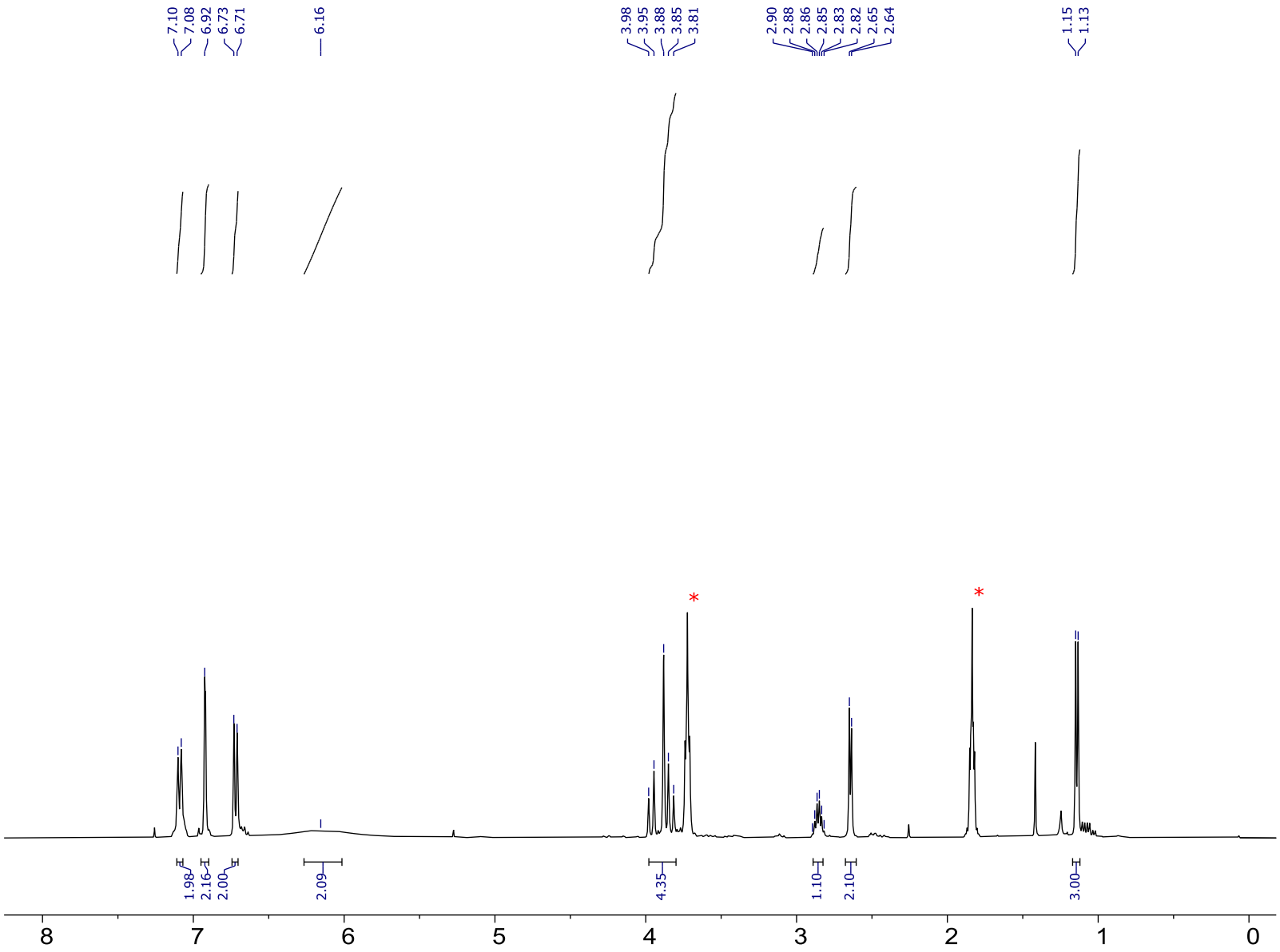


Figure S11. ^{1}H NMR spectrum of $^{H,Cl}L_2$ (**11a**) in $CDCl_3$ (*tetrahydrofuran).

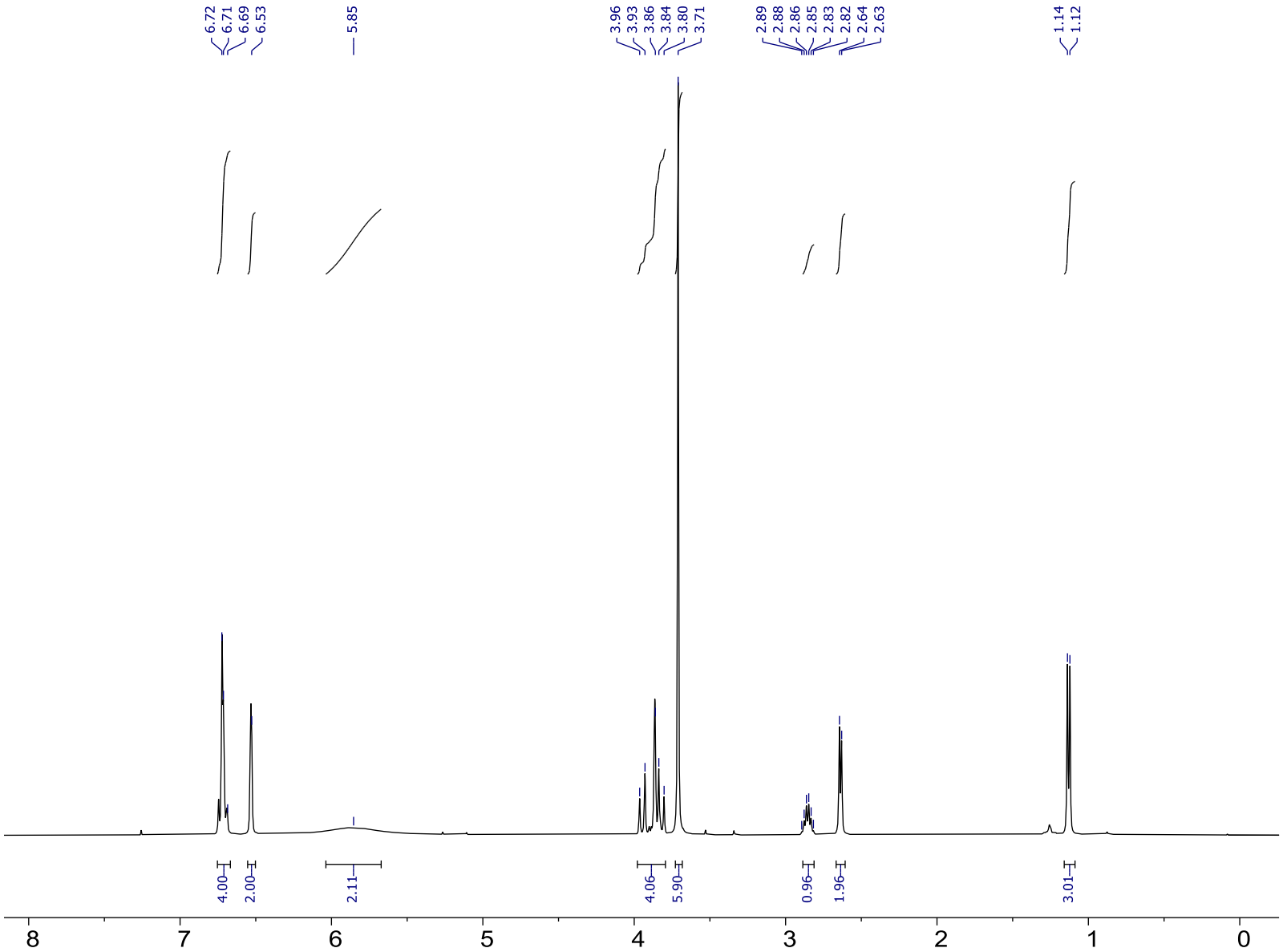


Figure S12. ^{1}H NMR spectrum of $^{H,OMe}L_2$ (**12a**) in $CDCl_3$.

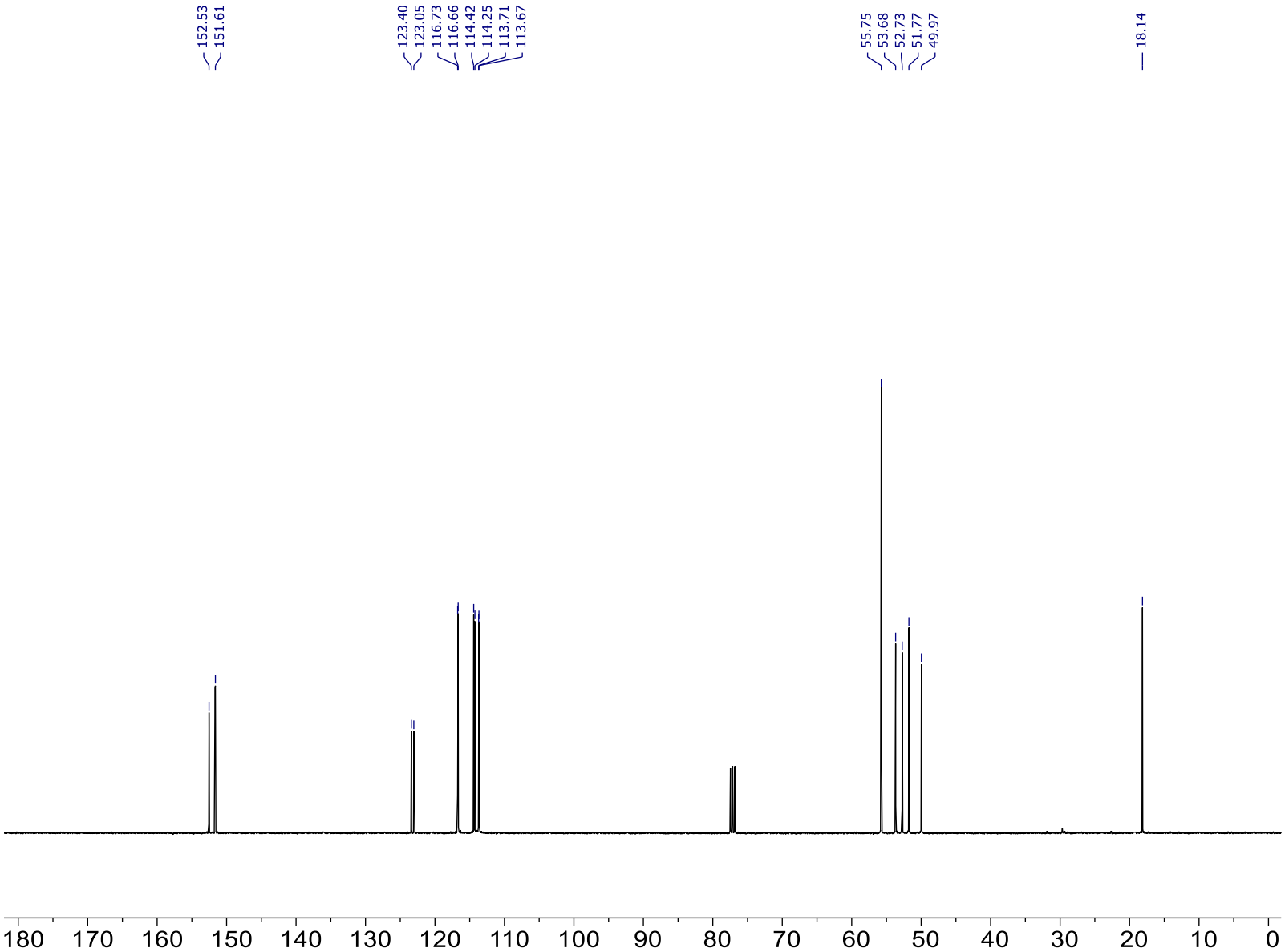


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,OMe}L_2$ (**12a**) in $CDCl_3$.

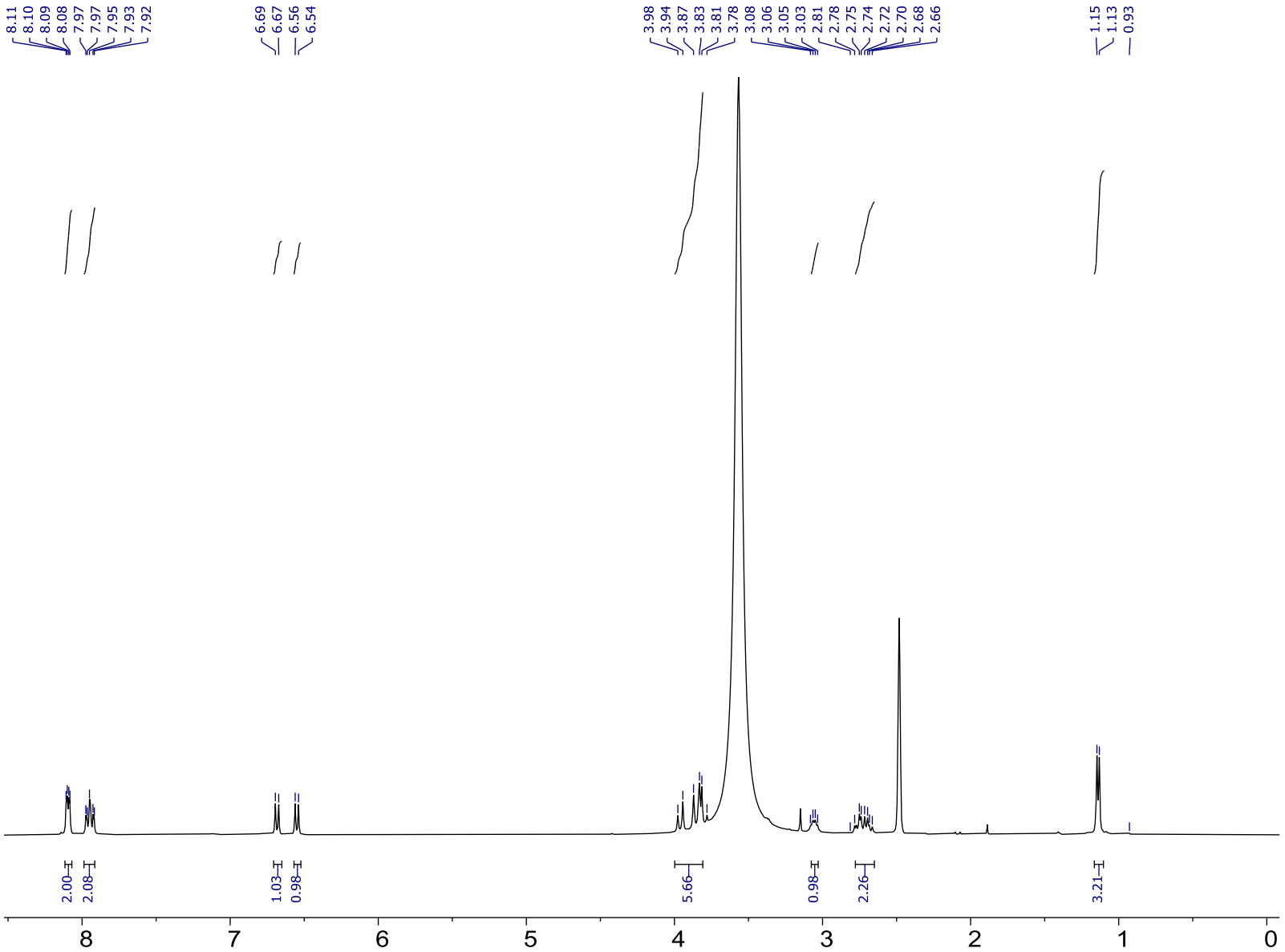


Figure S14. ^{1}H NMR spectrum of $^{H,NO2}L_2$ (**13a**) in $CDCl_3$.

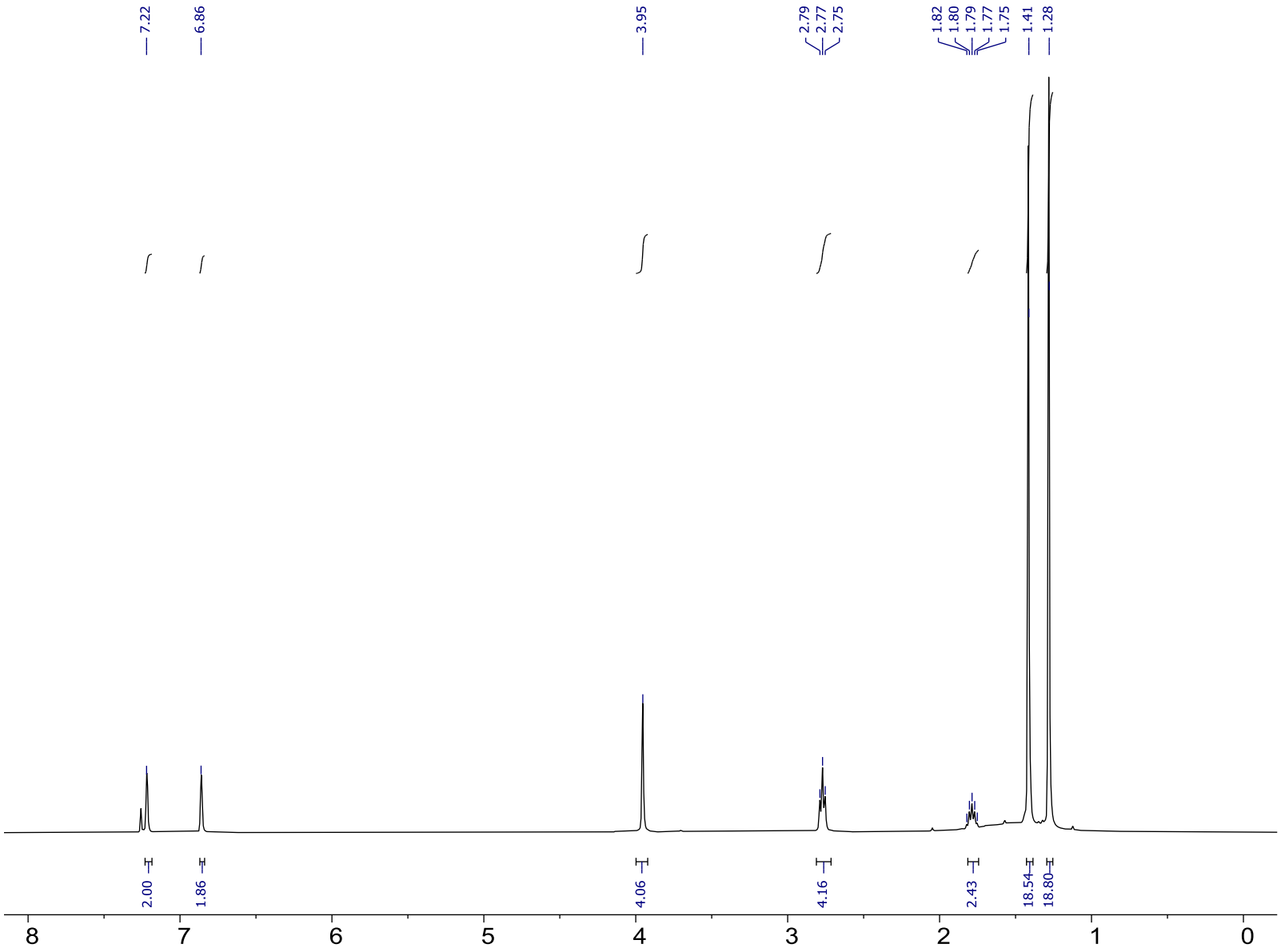


Figure S15. ^{1}H NMR spectrum of $^{tBu,tBu}L_3$ (**14a**) in $CDCl_3$.

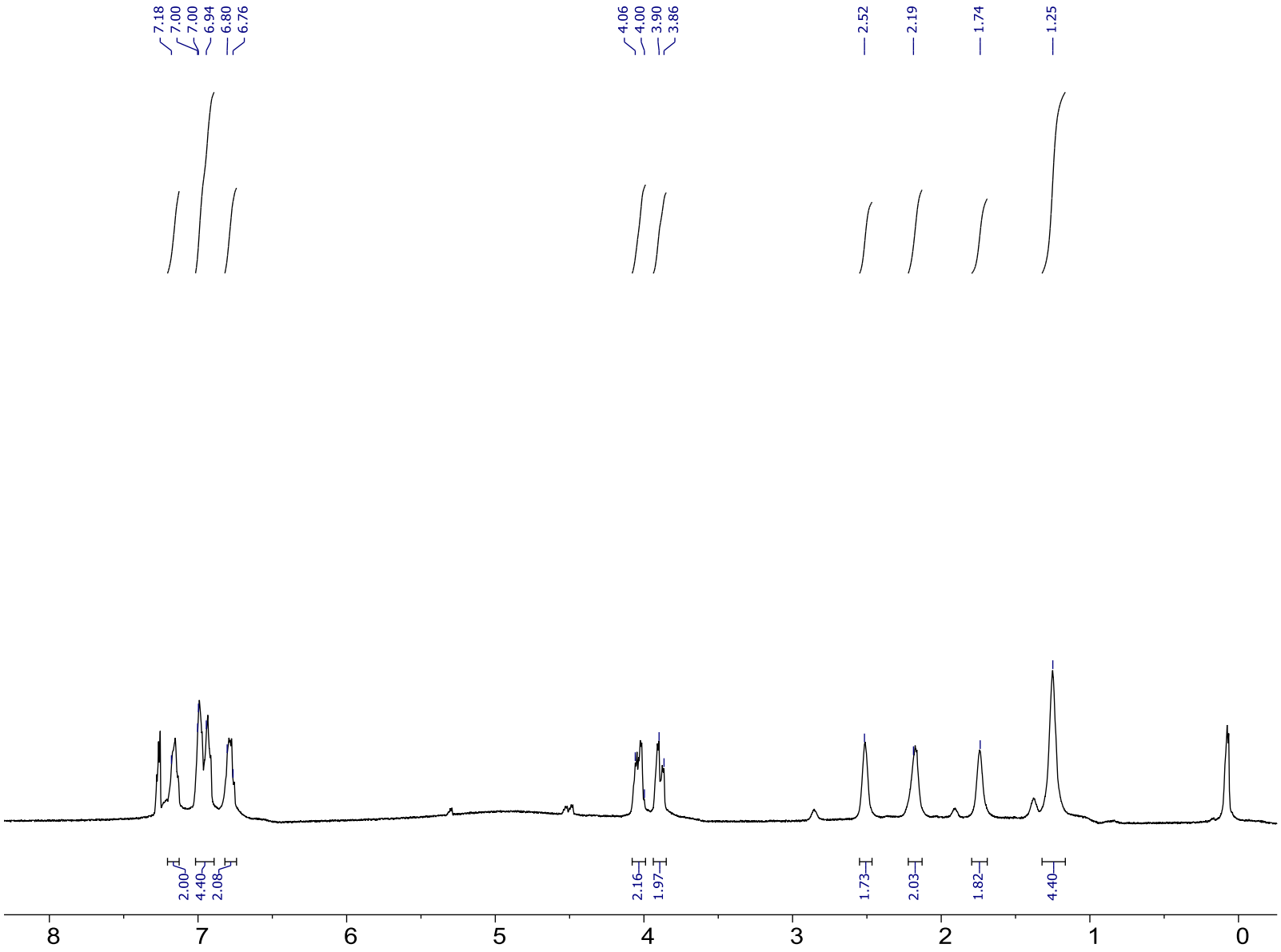


Figure S16. ^{1}H NMR spectrum of $^{H,H}L_4$ (**15a**) in $CDCl_3$.

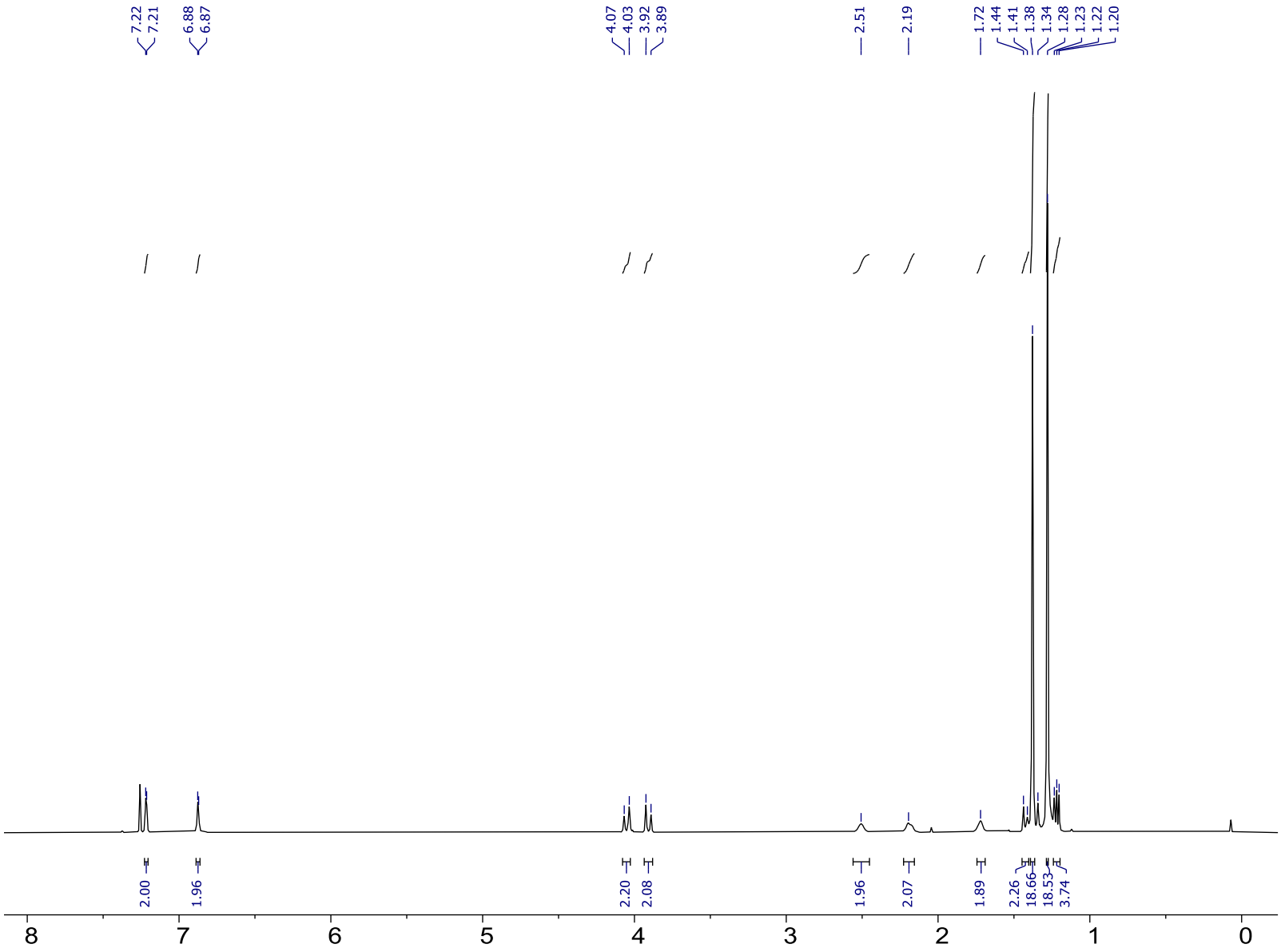


Figure S17. ^{1}H NMR spectrum of $^{tBu,tBu}L_4$ (**16a**) in $CDCl_3$.

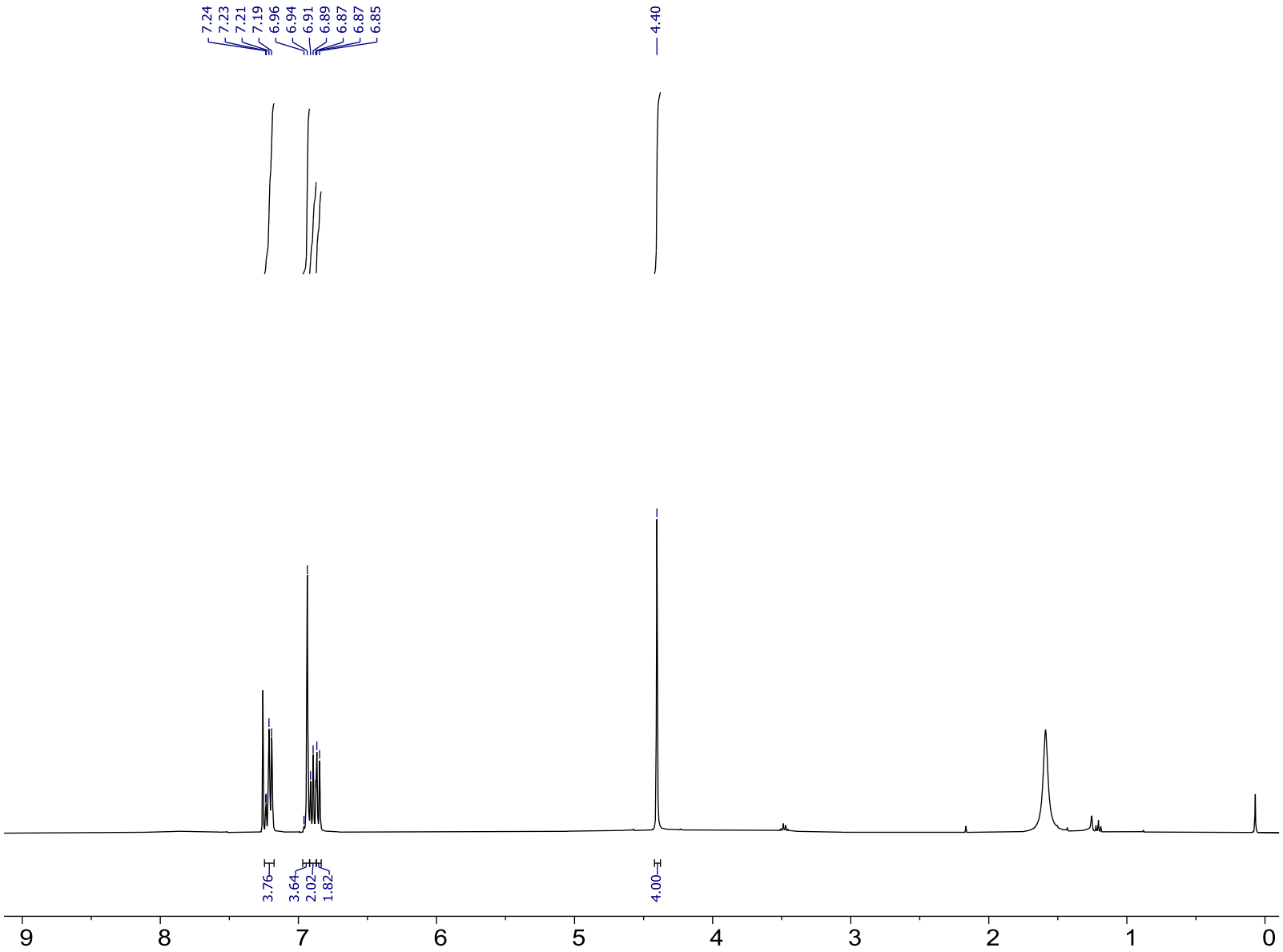


Figure S18. ^{1}H NMR spectrum of $^{H,H}L_5$ (**17a**) in $CDCl_3$.

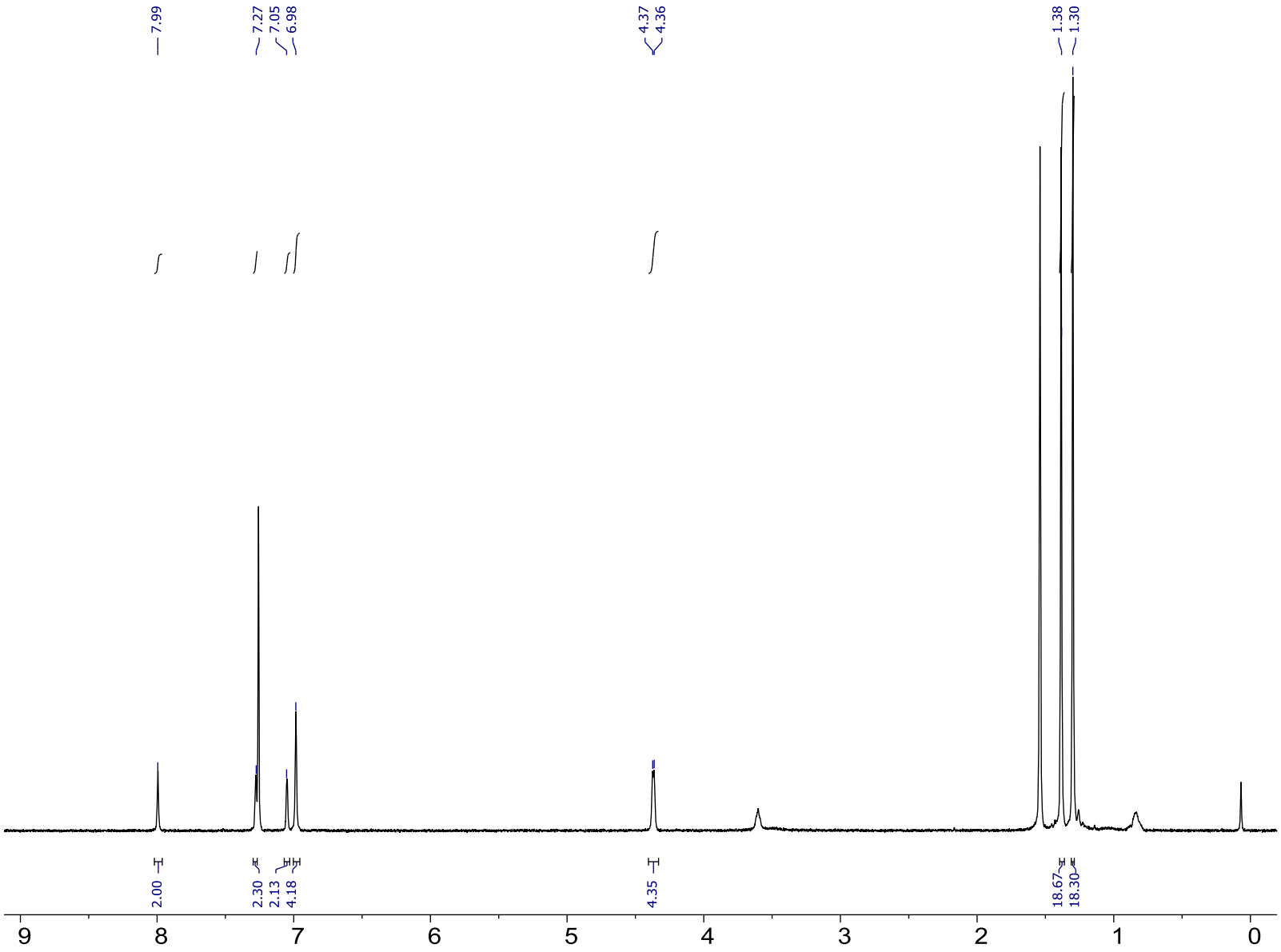


Figure S19. ^{1}H NMR spectrum of $^{tBu,tBu}L_5$ (**18a**) in $CDCl_3$.

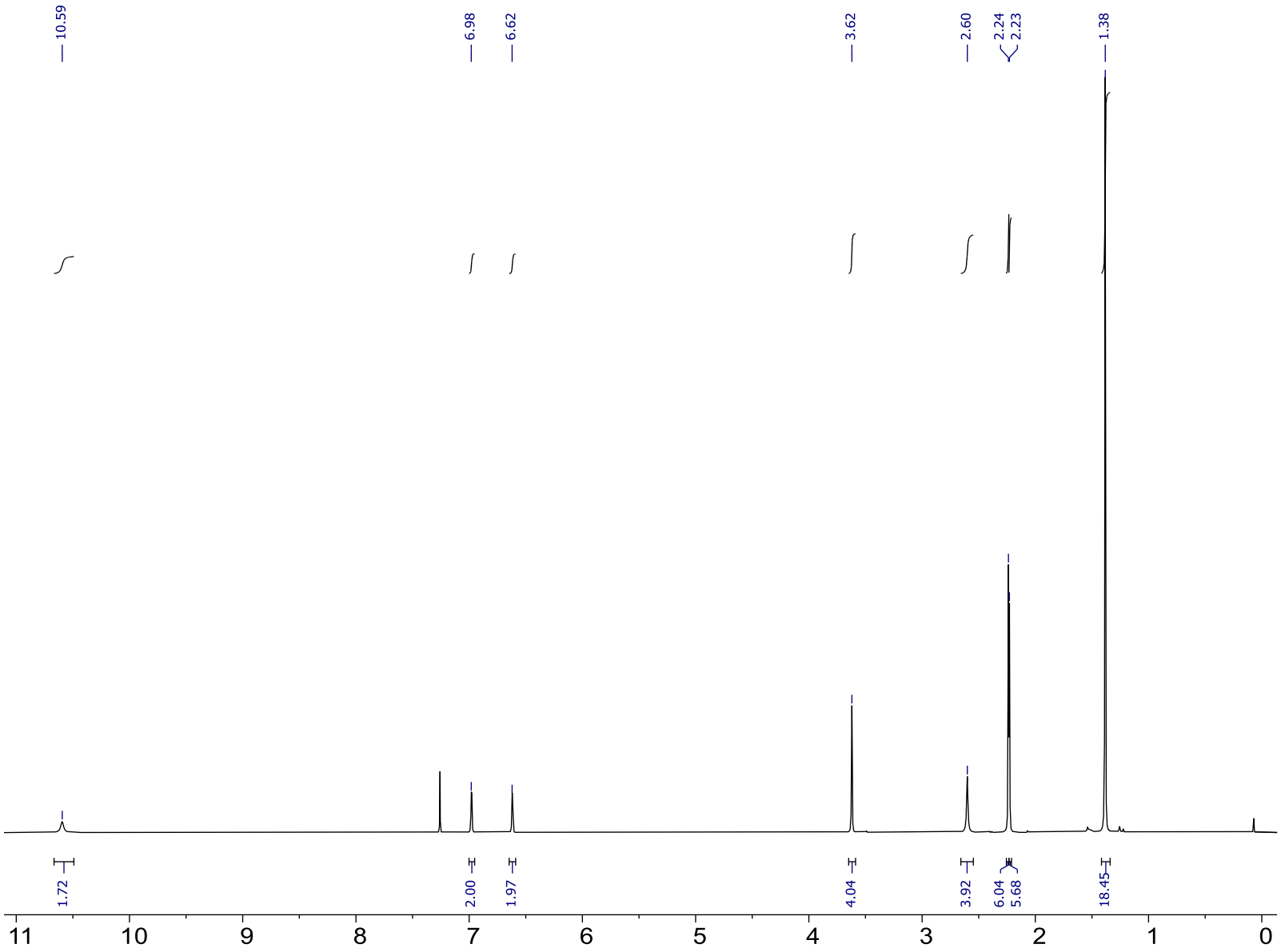


Figure S20. ^{1}H NMR spectrum of $^{tBu,tBu}L_6$ (**19a**) in $CDCl_3$.

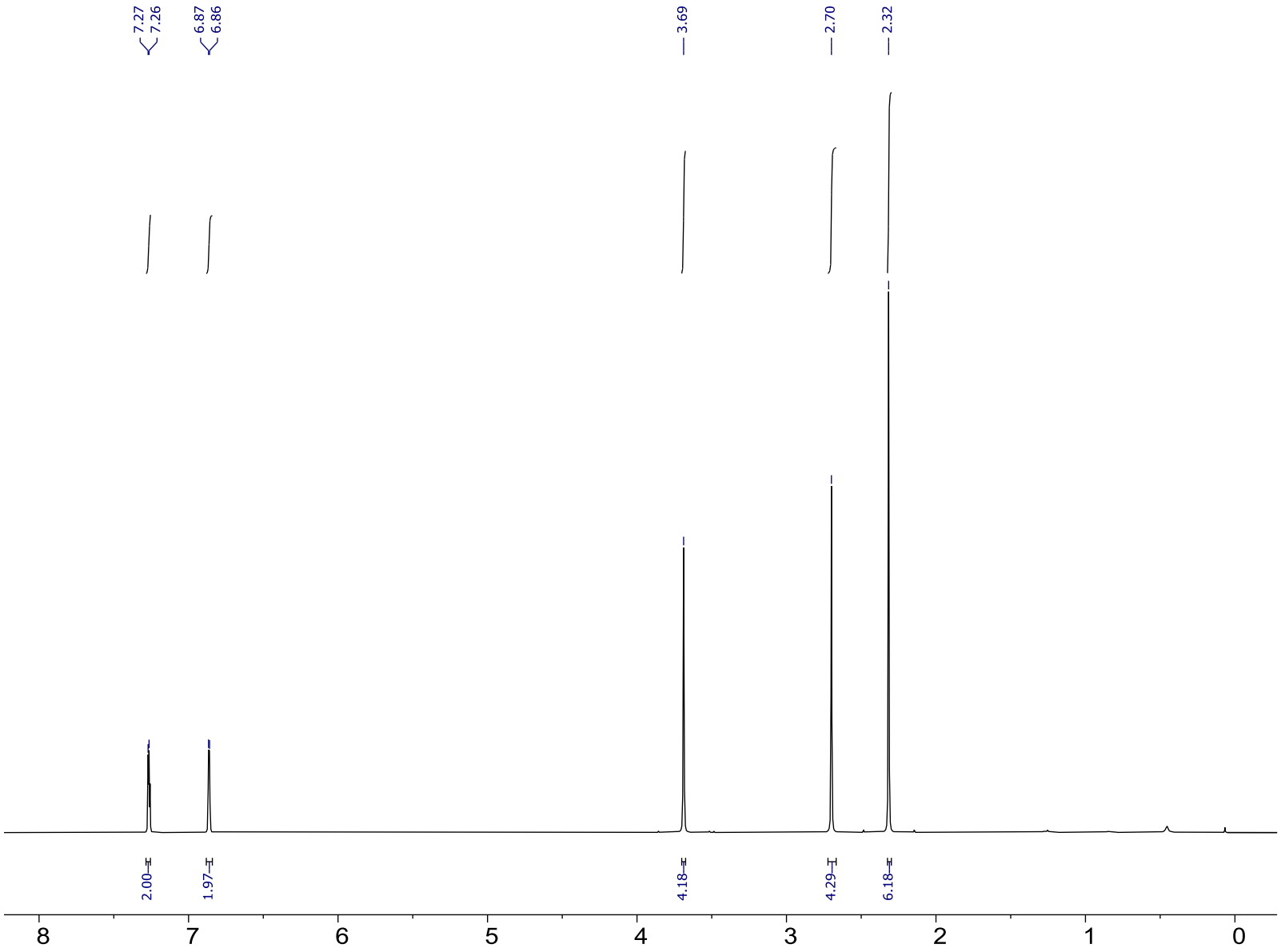


Figure S21. ^{1}H NMR spectrum of $^{Cl,Cl}L_6$ (**20a**) in $CDCl_3$.

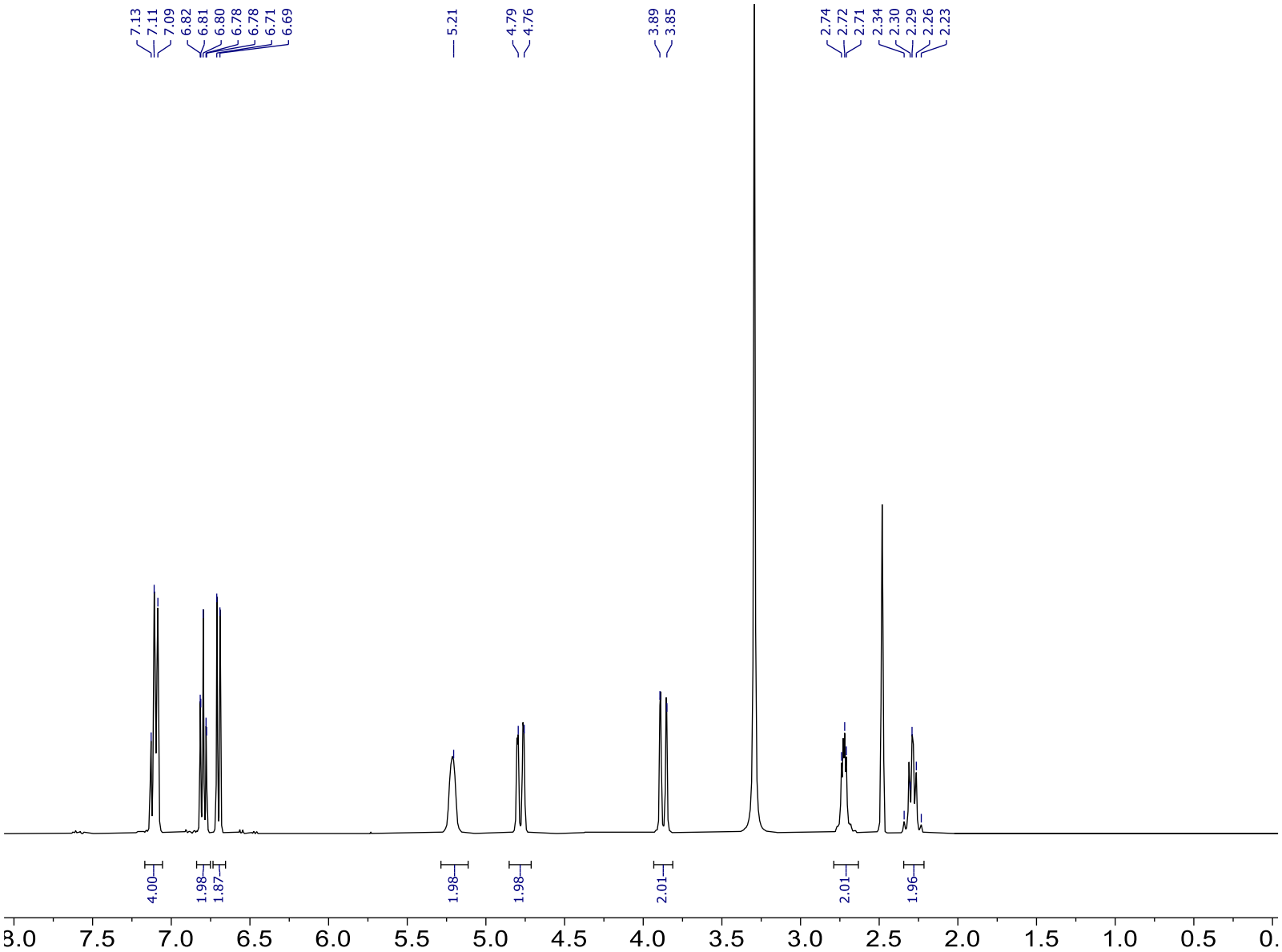


Figure S22. ^{1}H NMR spectrum of $^{H,H}L_1MoO_2$ (**1b**) in DMSO-d_6.

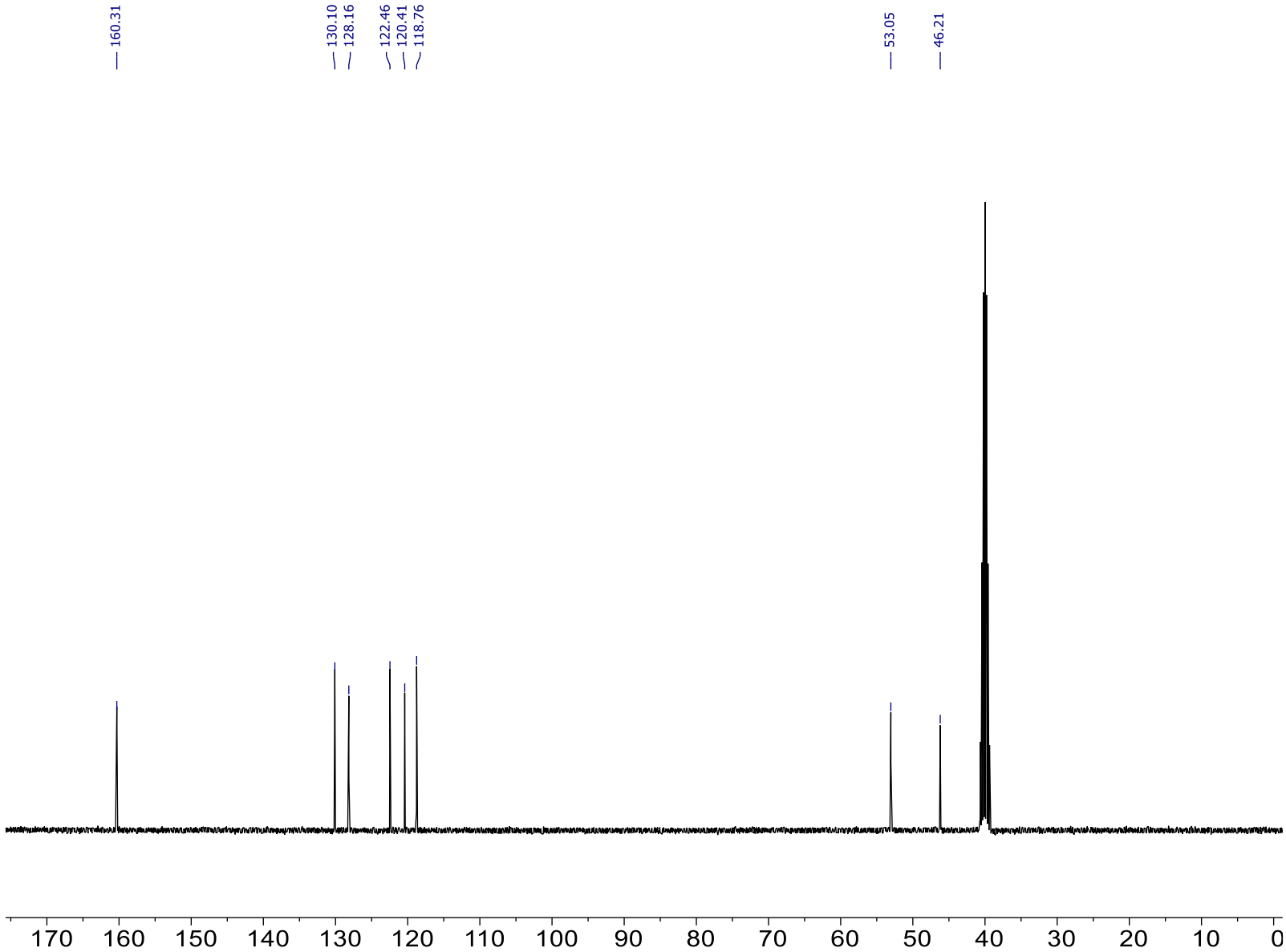


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,H}L_1MoO_2$ (**1b**) in $CDCl_3$.

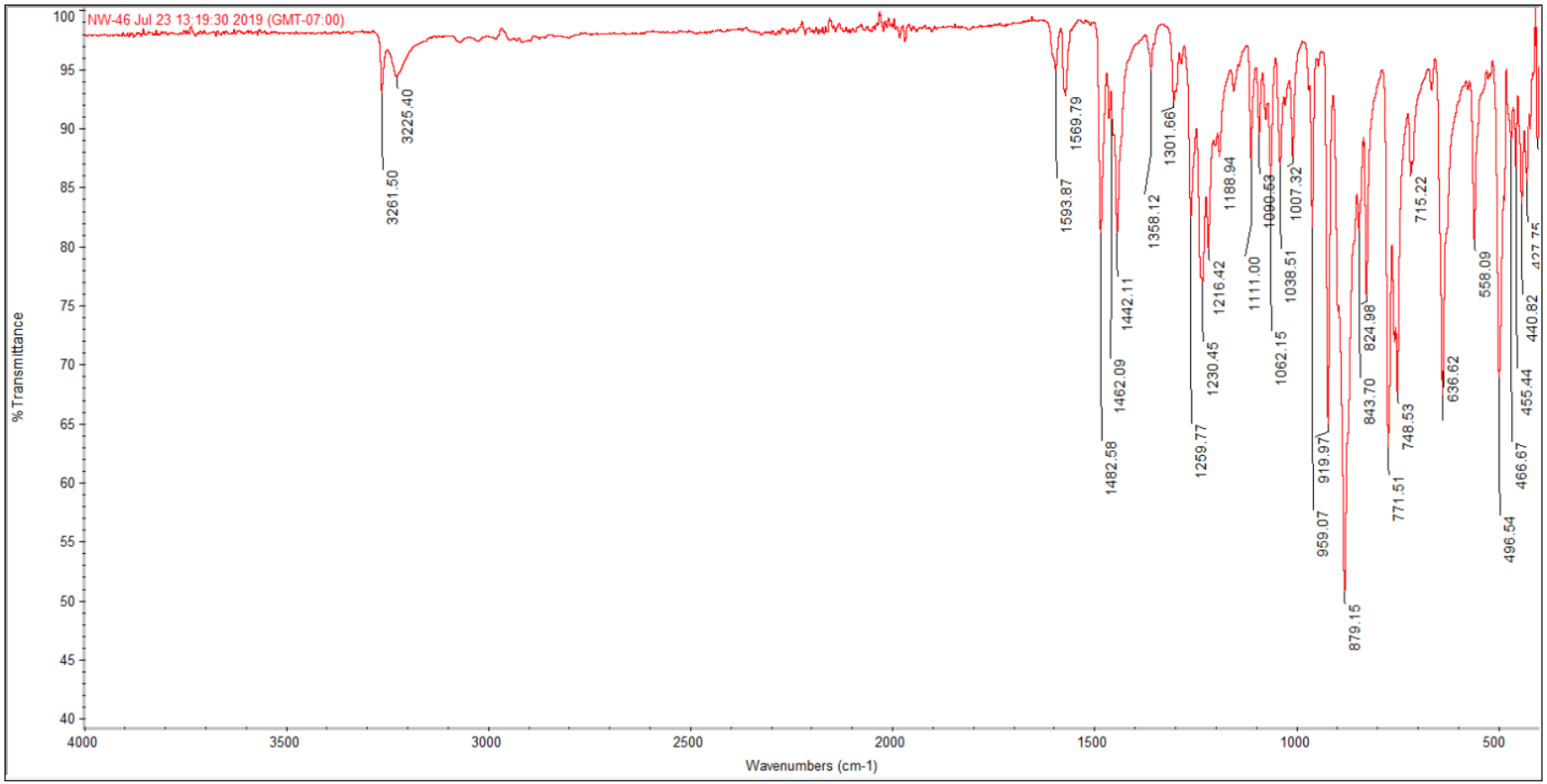


Figure S24. IR spectrum of $^{H,H}L_1MoO_2$ (**1b**).

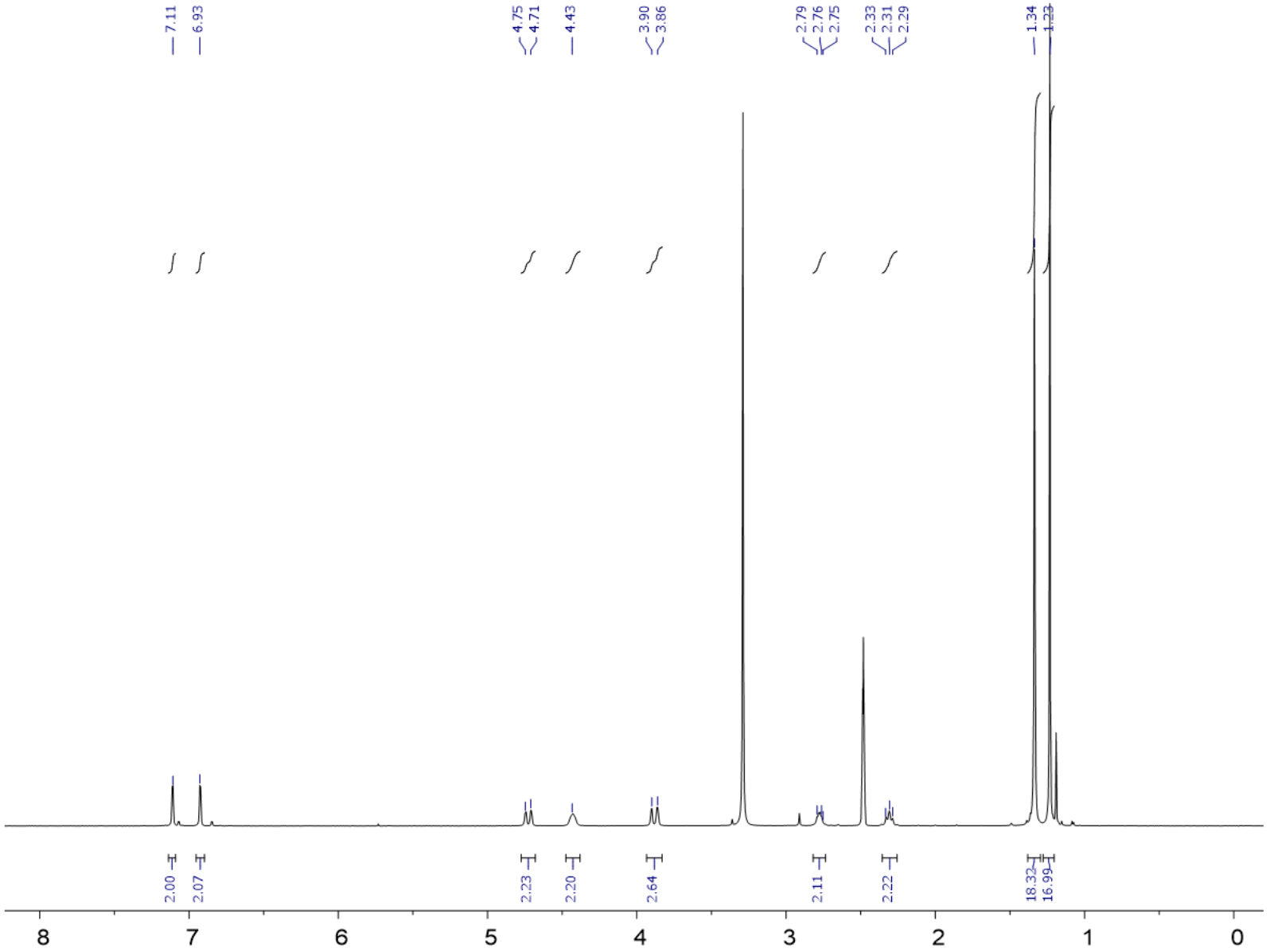


Figure S25. ^{1}H NMR spectrum of $^{tBu,tBu}L_1MoO_2$ (**2b**) in DMSO-d_6.

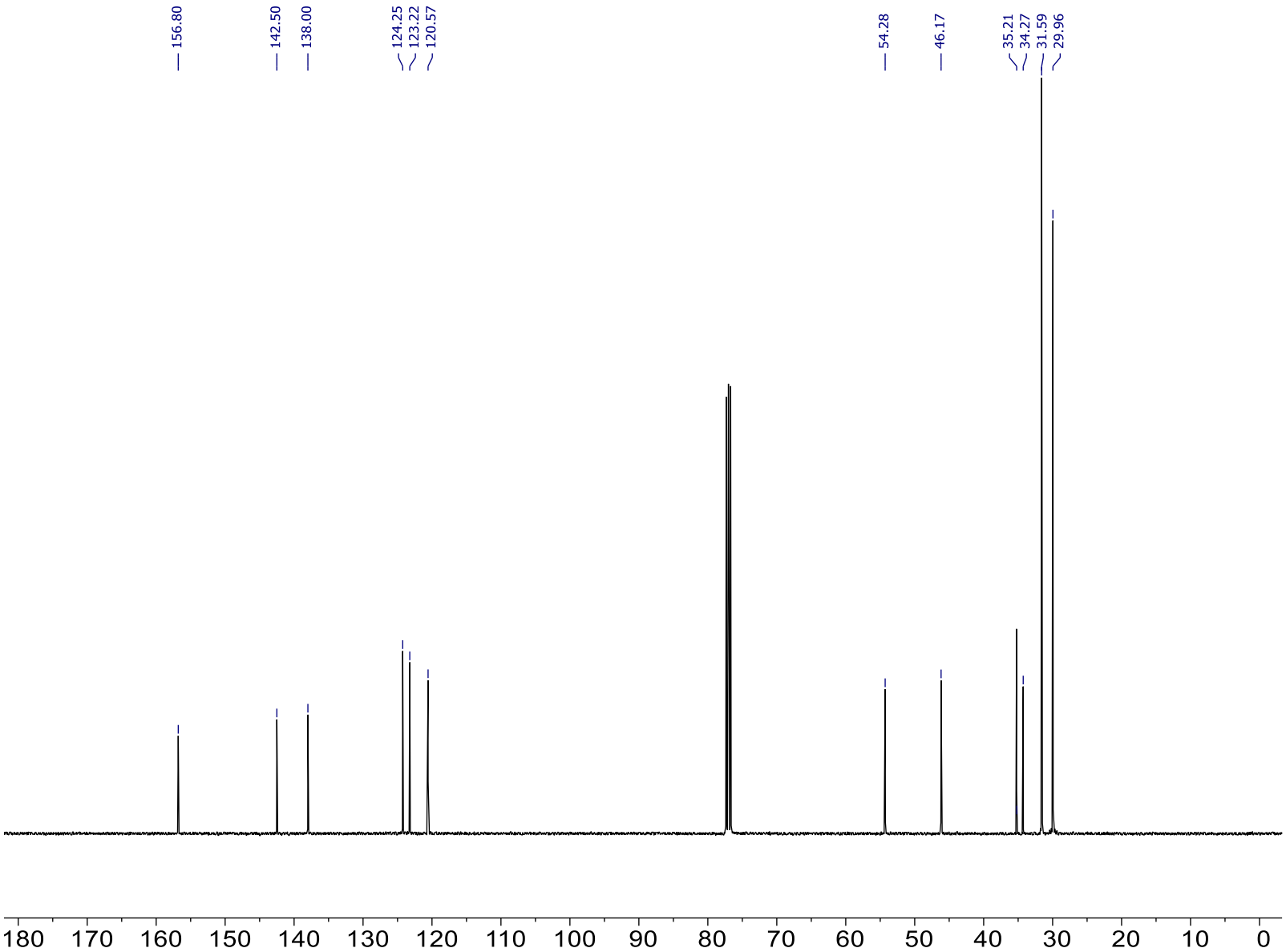


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of $^{tBu,tBu}L_1MoO_2$ (**2b**) in $CDCl_3$.

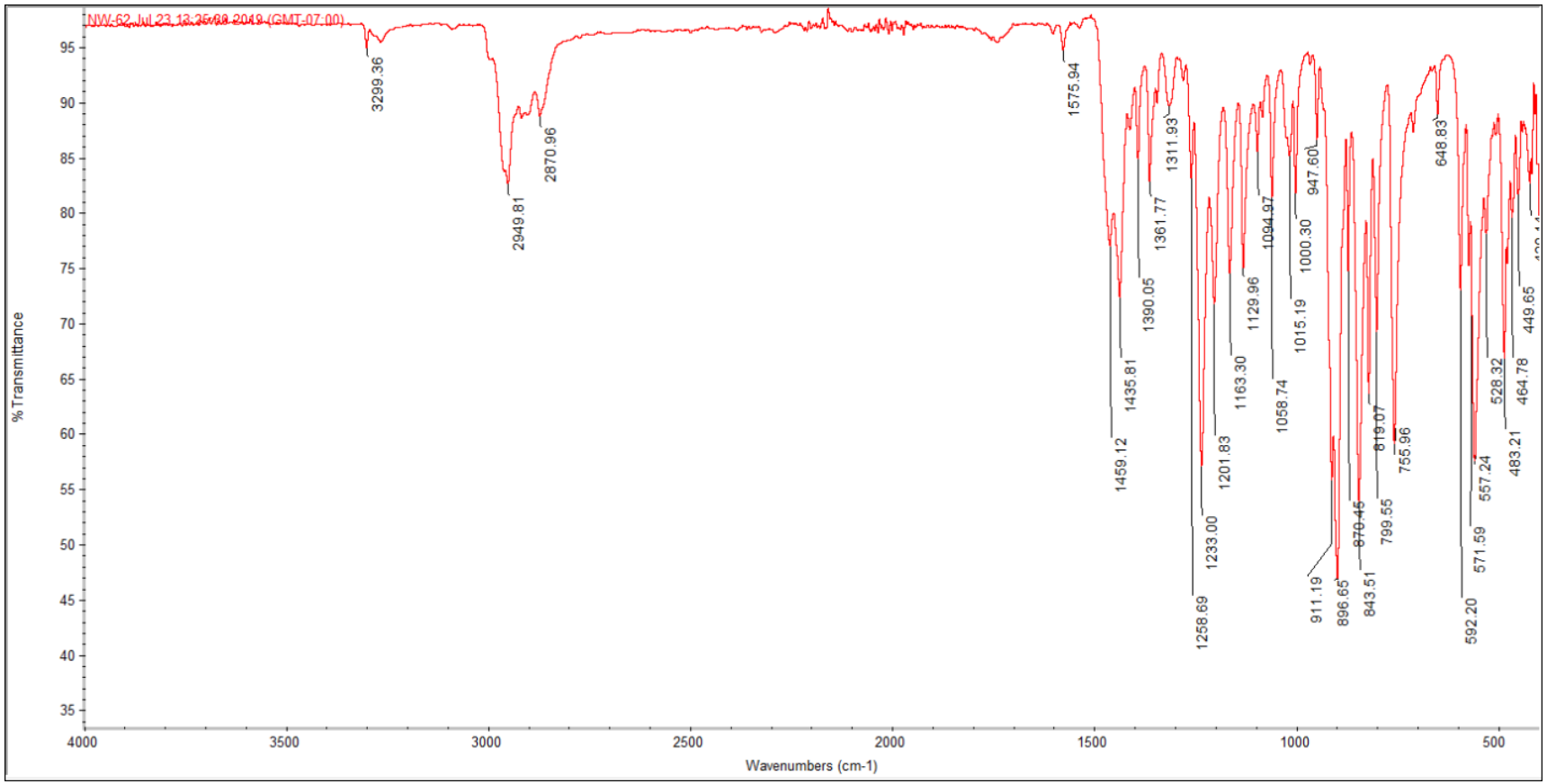


Figure S27.IR spectrum of $^{tBu,tBu}L_1MoO_2$ (**2b**).

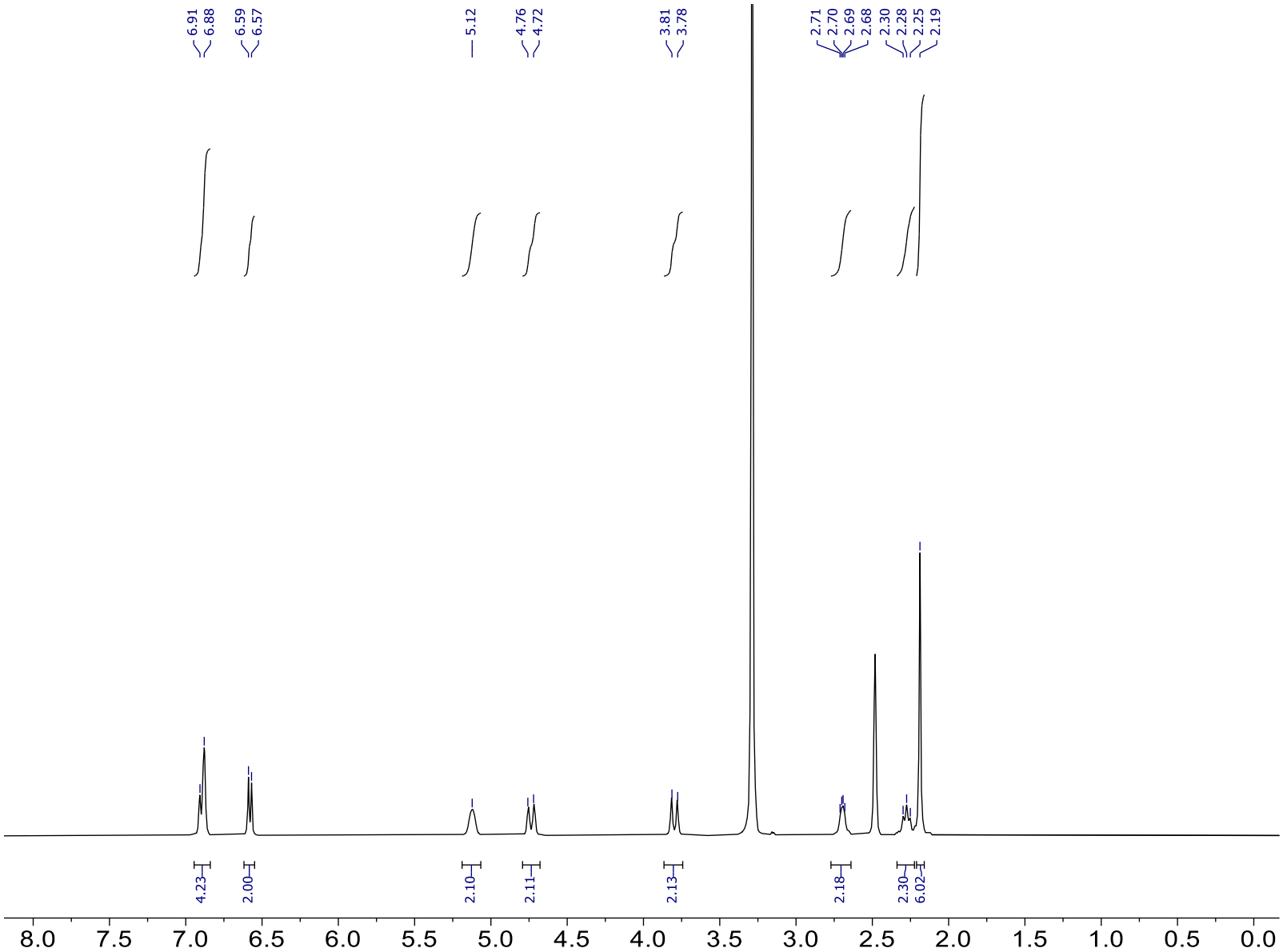


Figure S28. ^{1}H NMR spectrum of $^{H,Me}L_1MoO_2$ (**3b**) in DMSO-d_6.

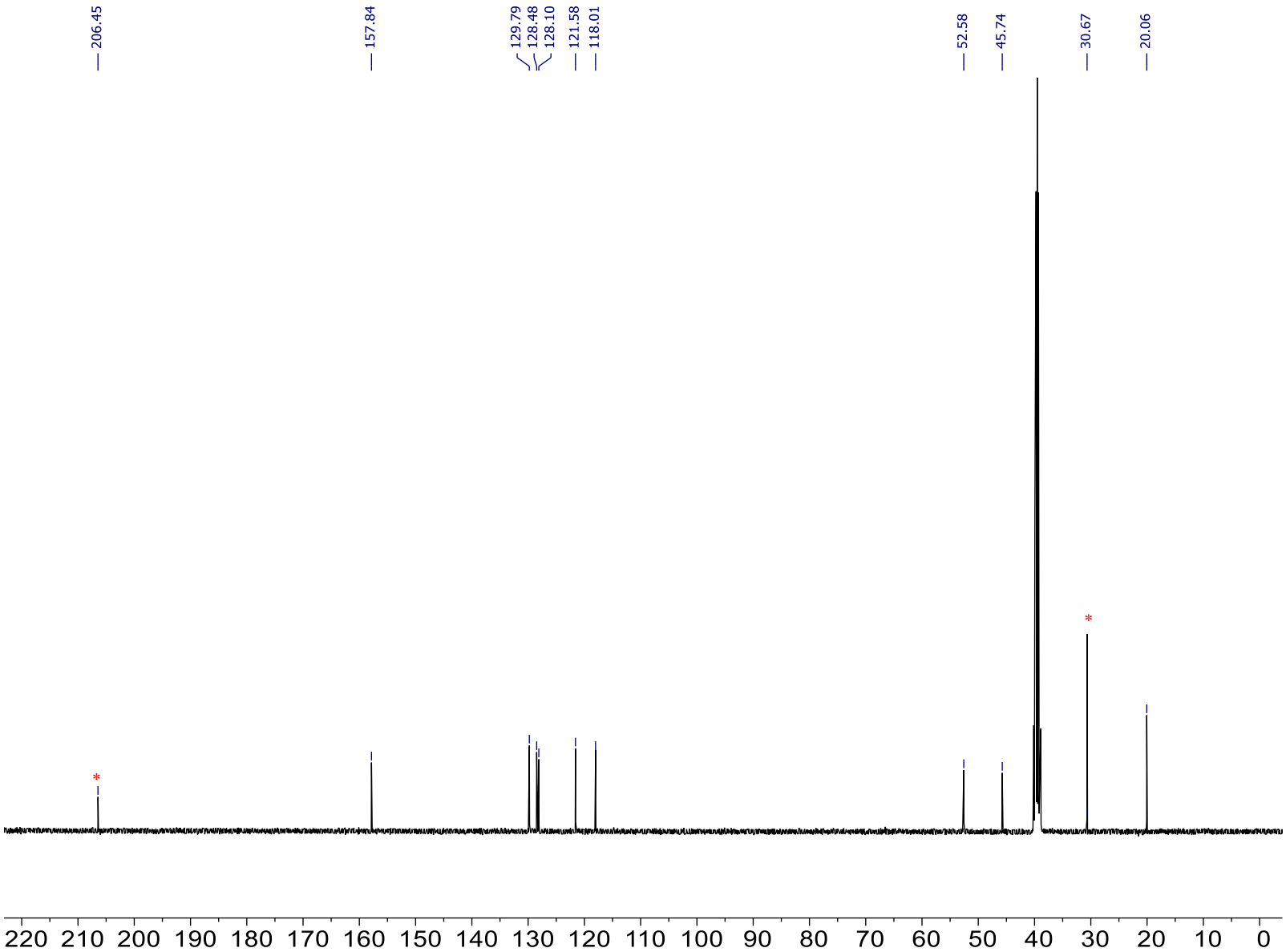


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,Me}L_1MoO_2$ (**3b**) in DMSO-d_6(*acetone).

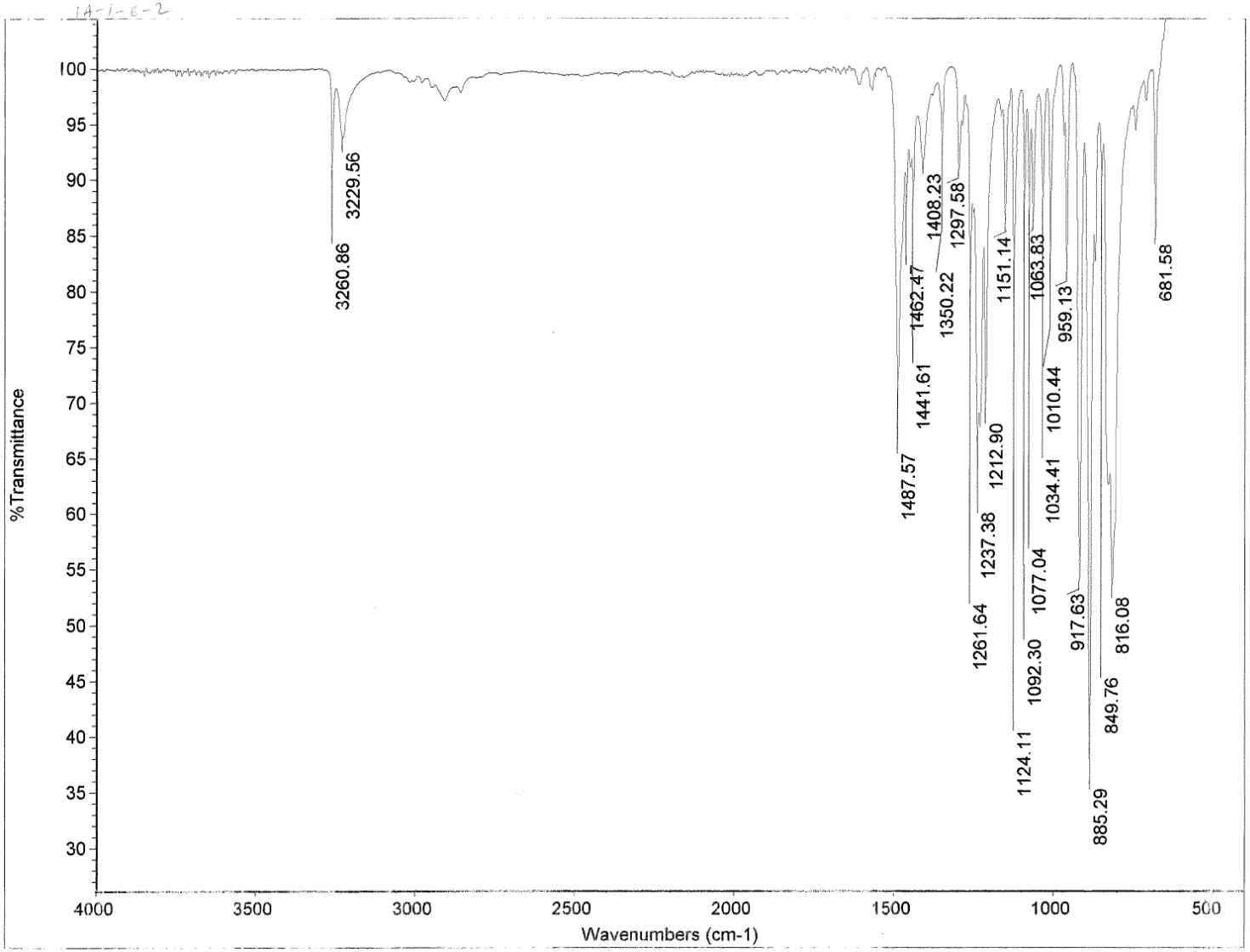


Figure S30. IR spectrum of $^{H,Me}L_1MoO_2$ (**3b**).

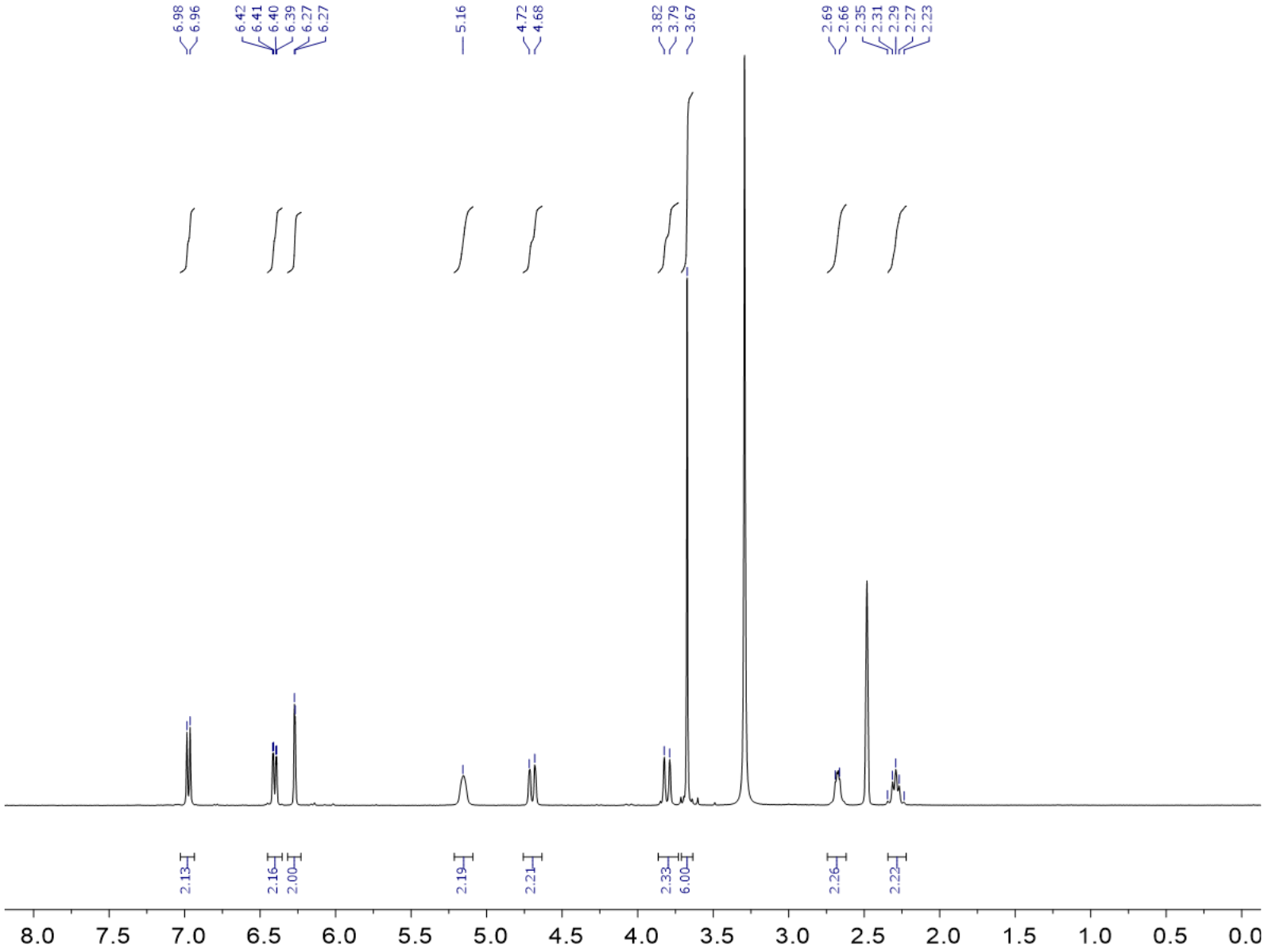


Figure S31. ^{1}H NMR spectrum of $^{H,OMe}L_1MoO_2$ (**4b**) in DMSO-d_6.

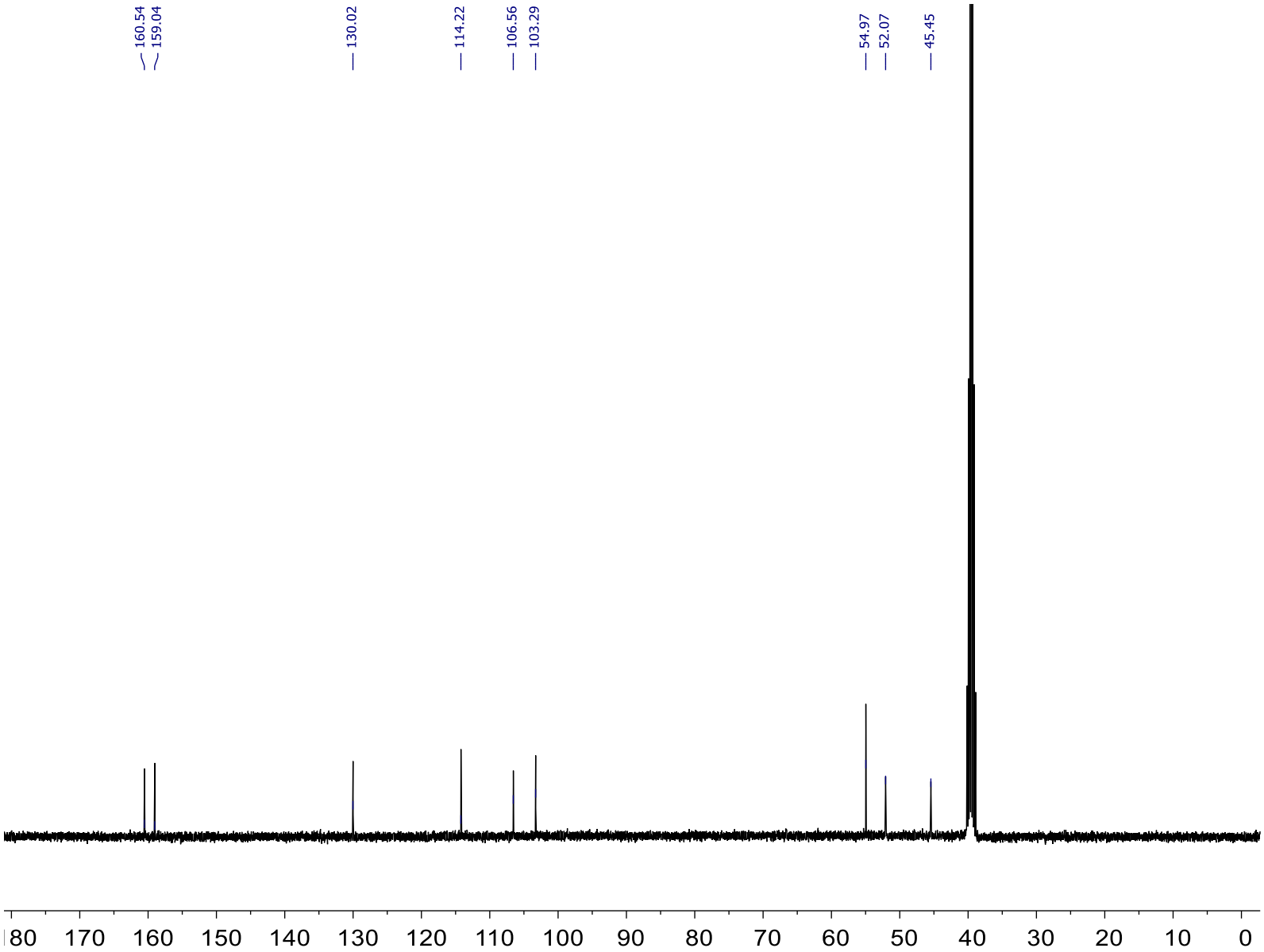


Figure S32. $^{13}C\{^{1}H\}$NMR spectrum of $^{H,OMe}L_1MoO_2$ (**4b**) in DMSO-d_6.

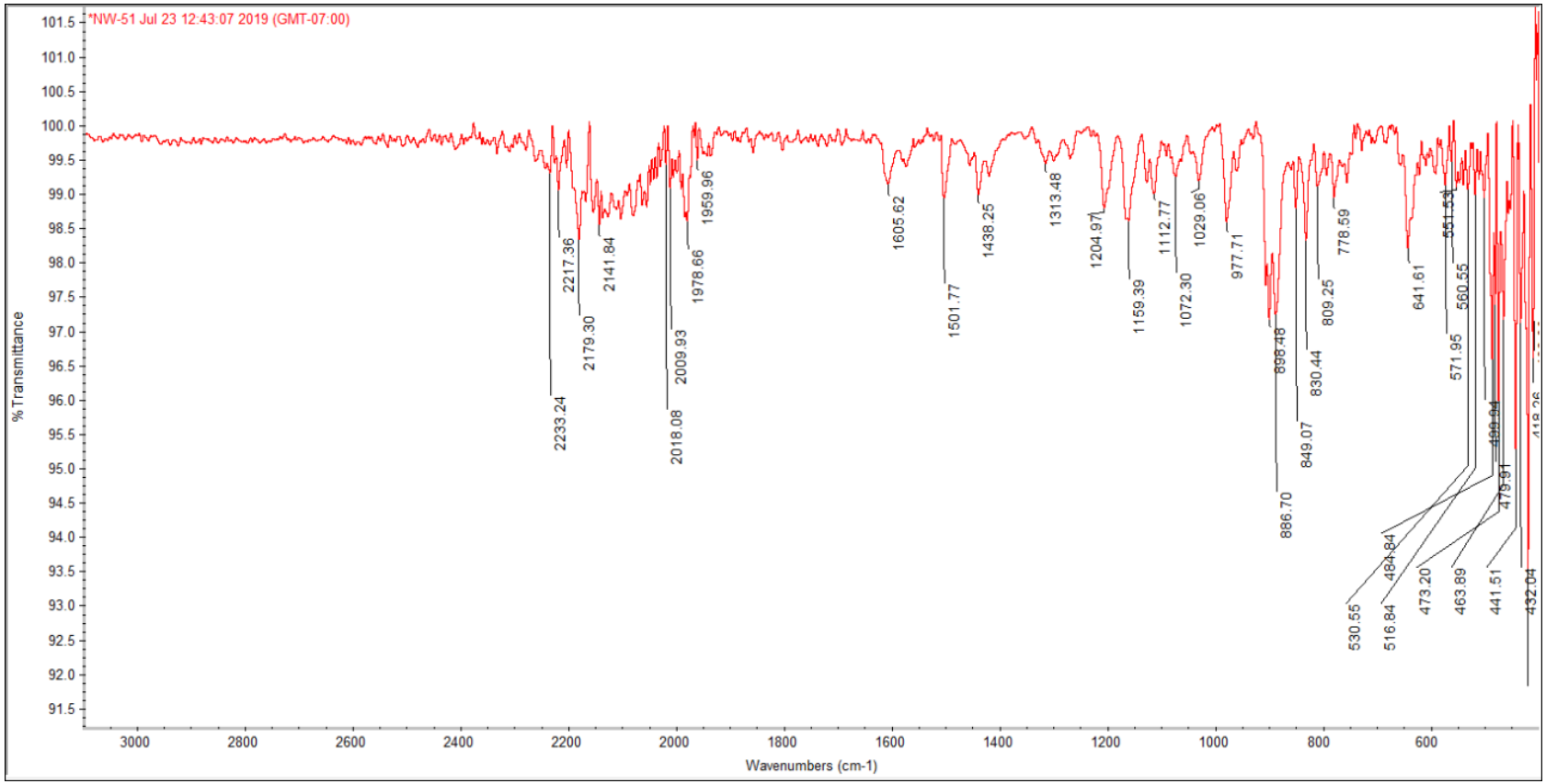


Figure S33. IR spectrum of $^{H,OMe}L_1MoO_2$ (**4b**).

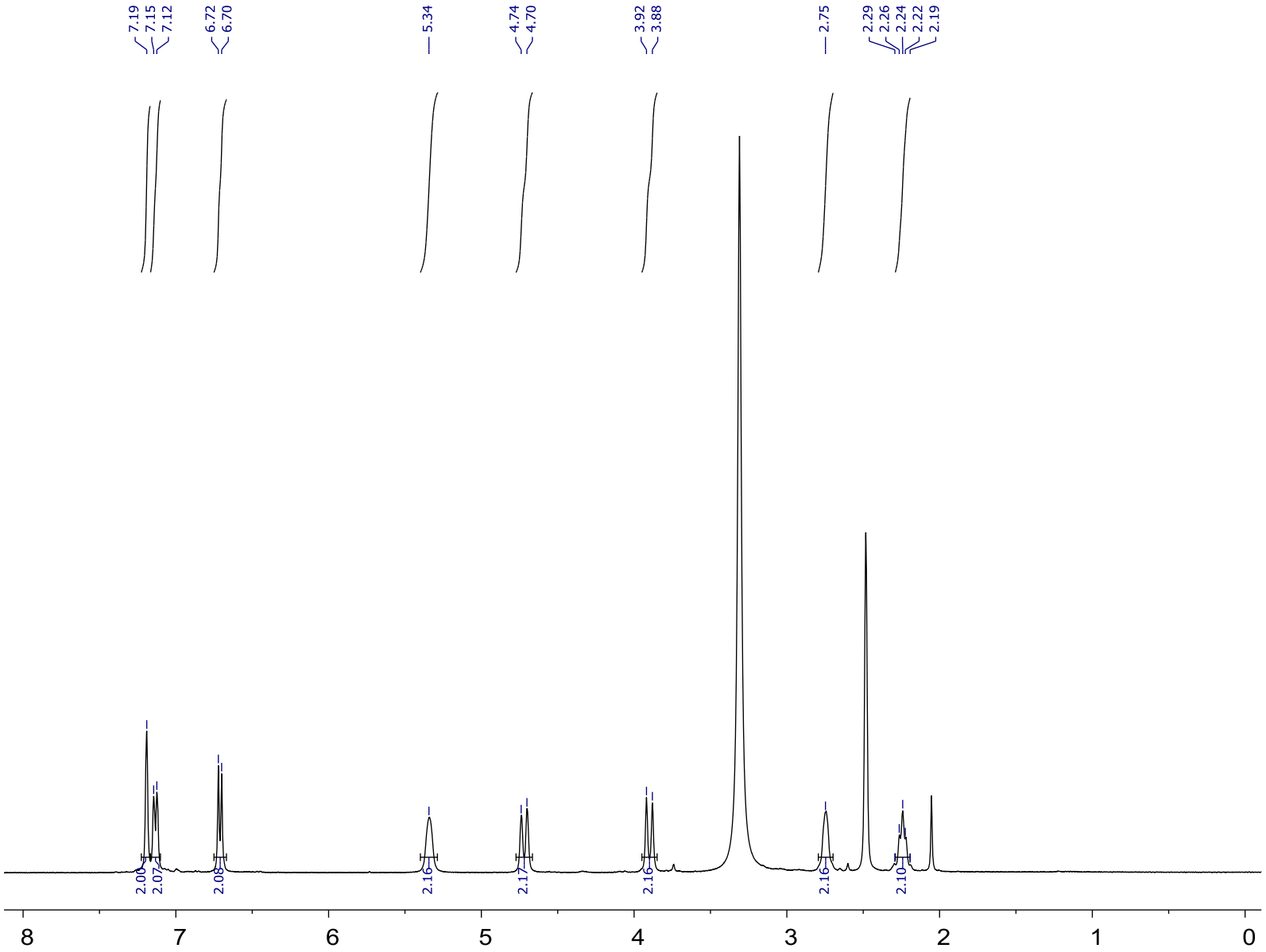


Figure S34. ^{1}H NMR spectrum of $^{H,Cl}L_1MoO_2$ (**5b**) in DMSO-d_6.

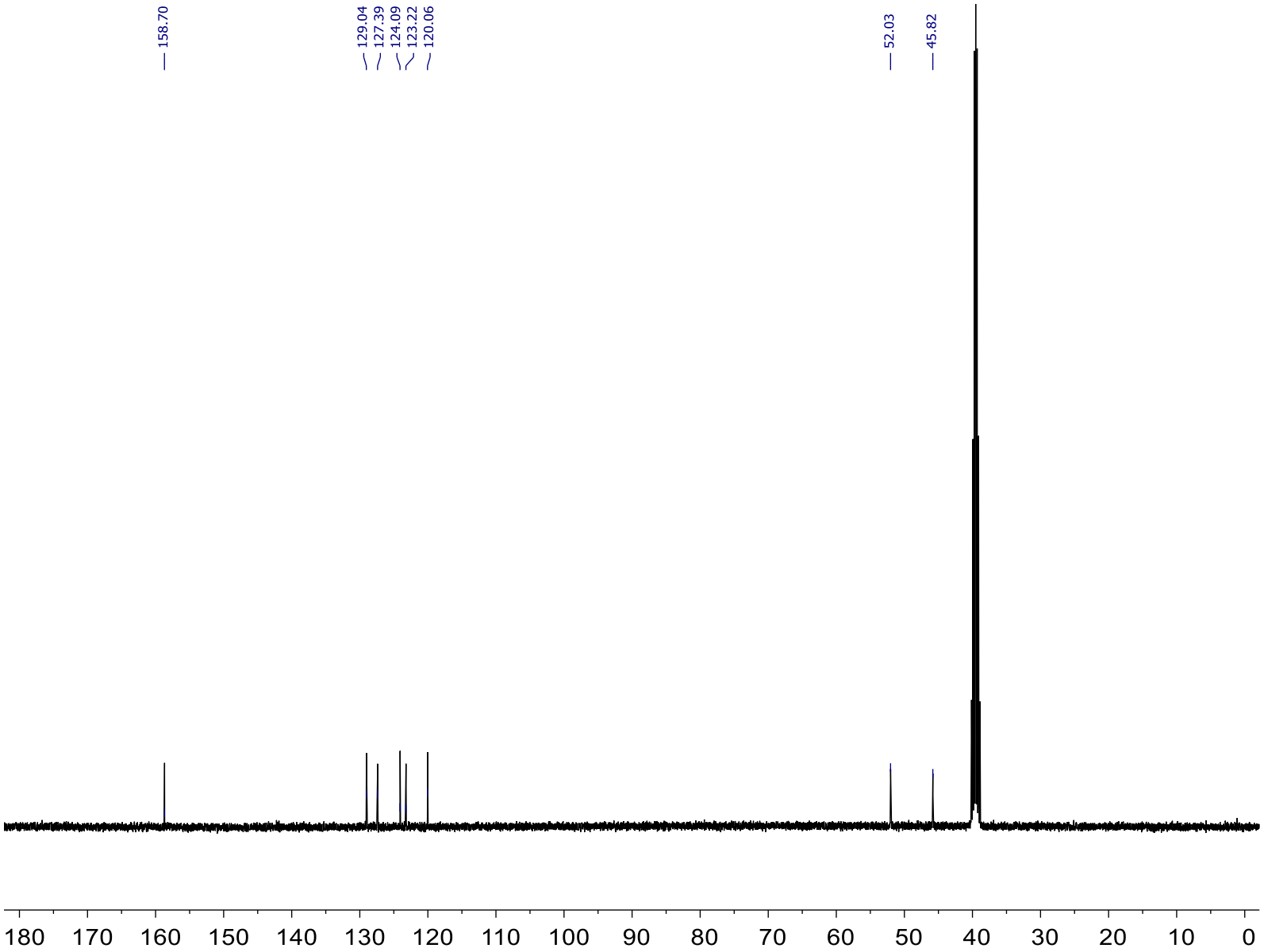


Figure S35. $^{13}C\{^{1}H\}$NMR spectrum of $^{H,Cl}L_1MoO_2$ (**5b**) in DMSO-d_6.

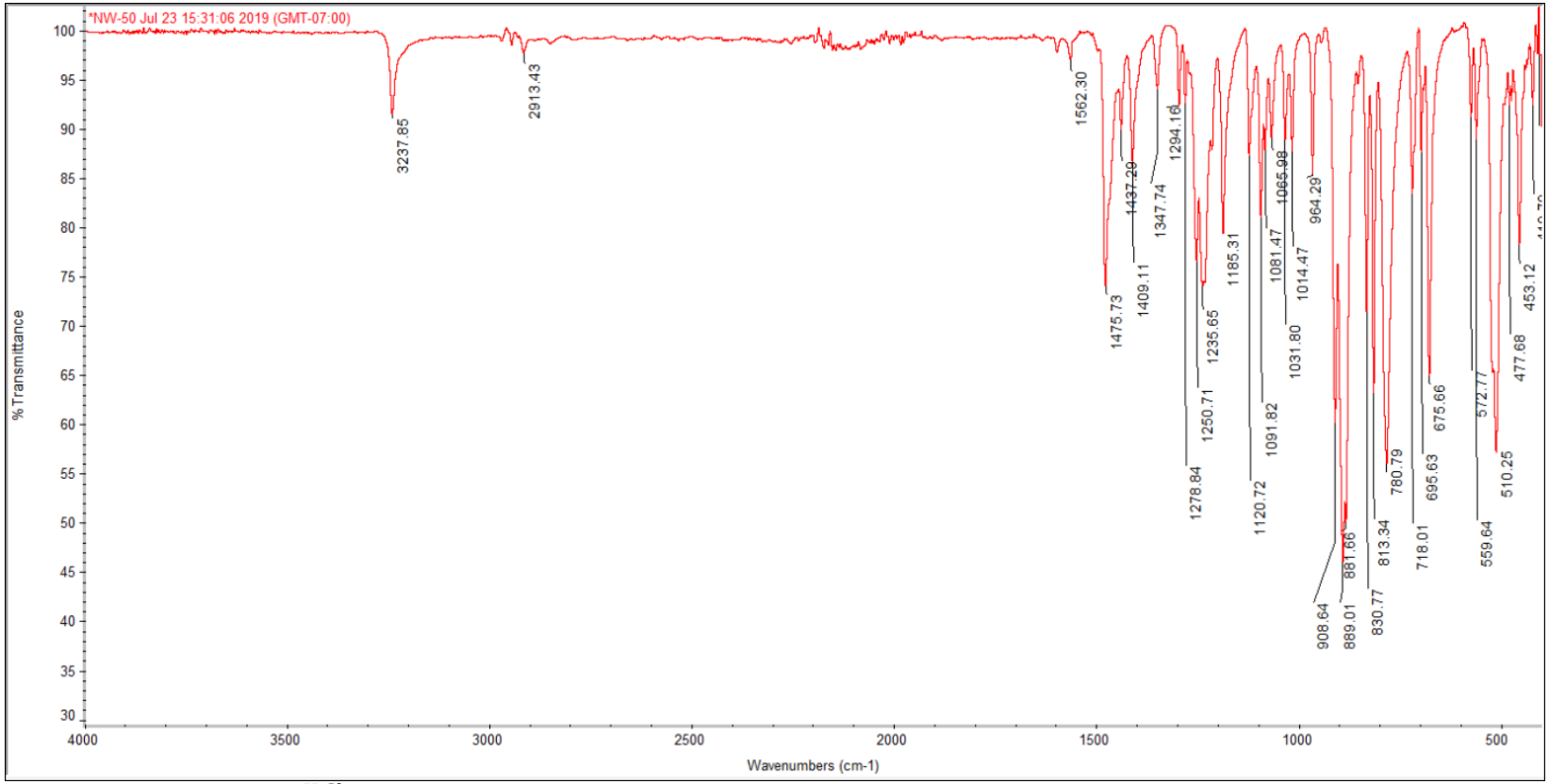


Figure S36. IR spectrum of $^{H,Cl}L_1MoO_2$ (**5b**).

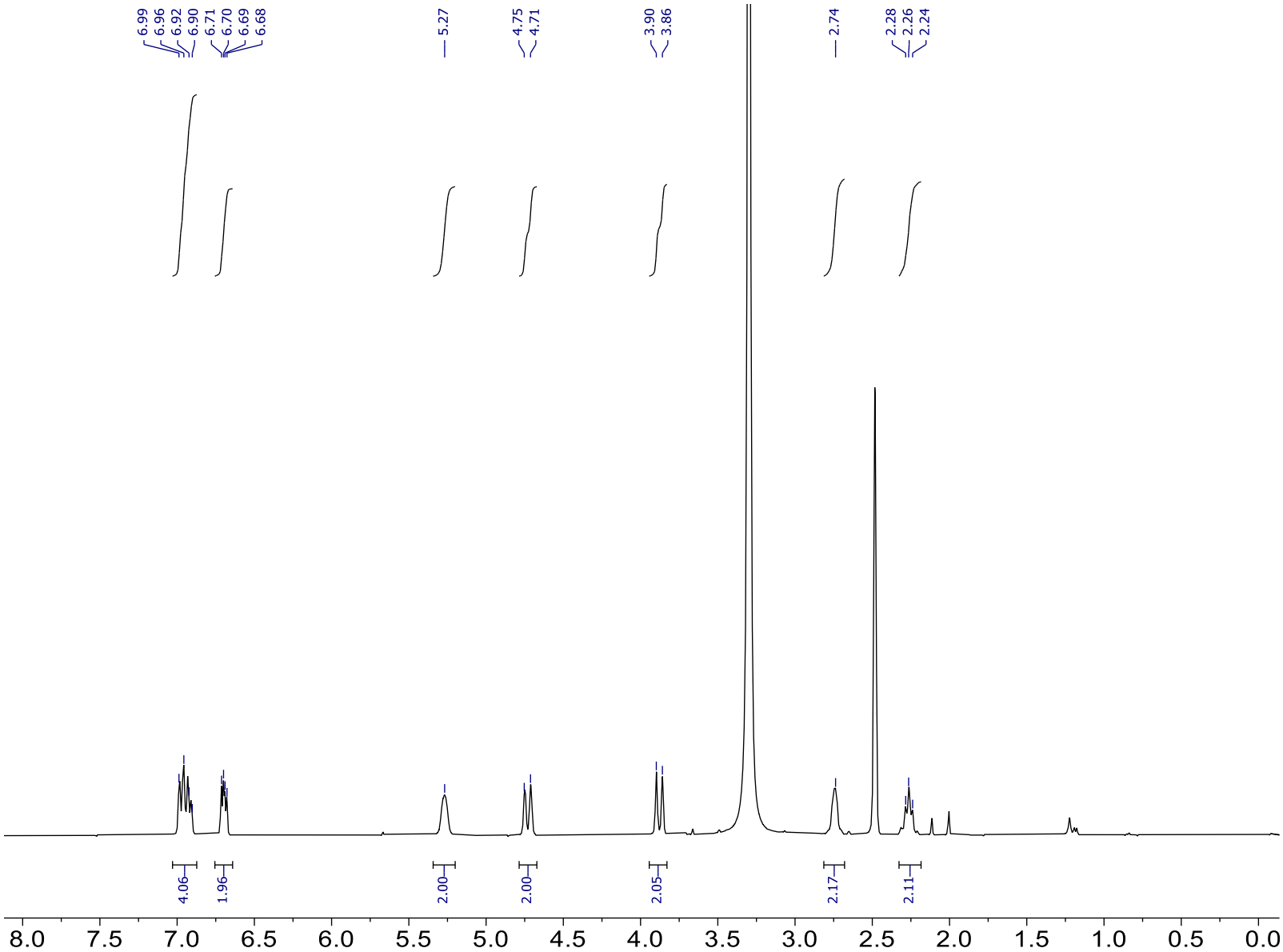


Figure S37. ^{1}H NMR spectrum of $^{H,F}L_1MoO_2$ (**6b**) in DMSO-d_6.

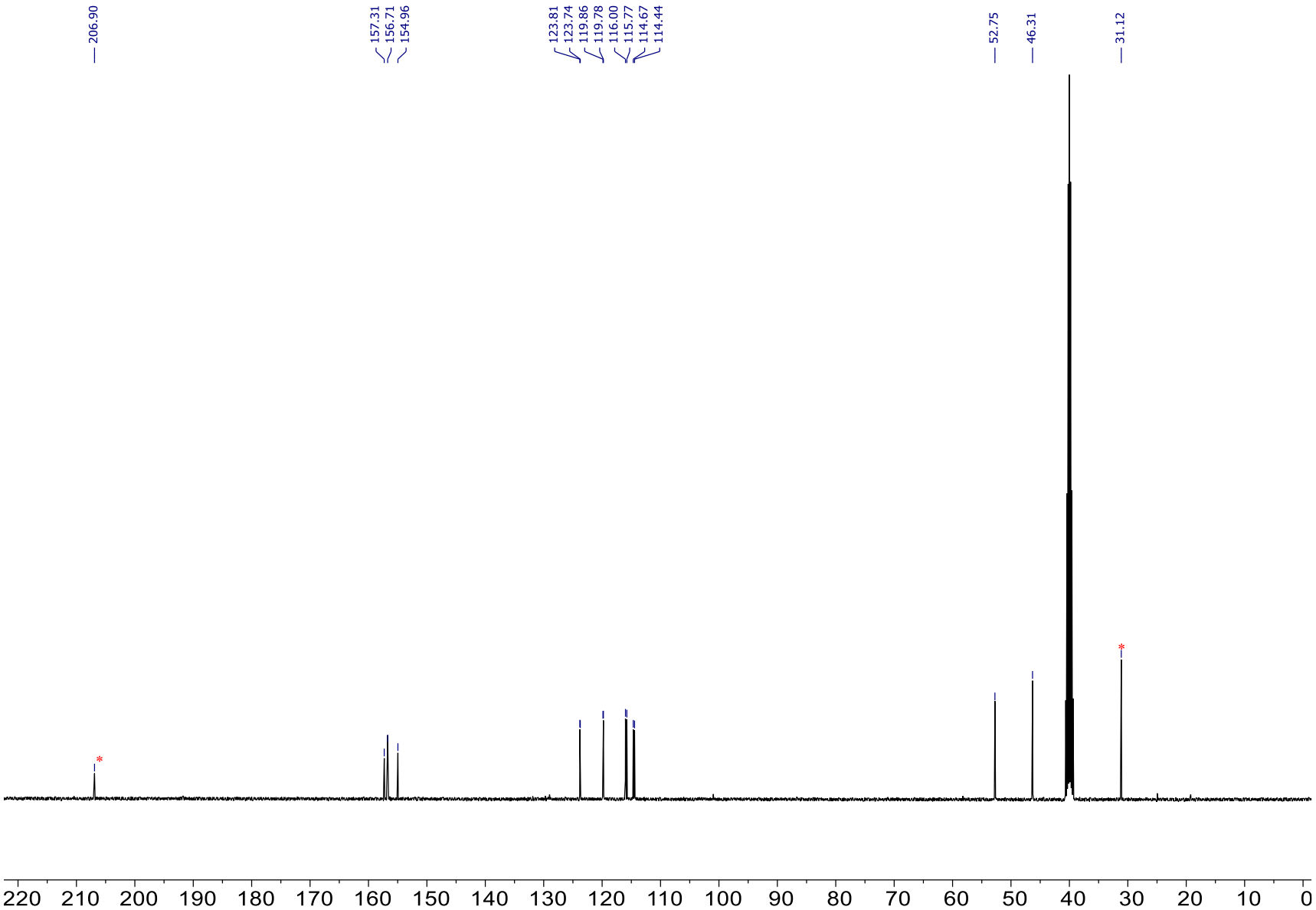


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,F}L_1MoO_2$ (**6b**) in DMSO-d_6(*acetone).

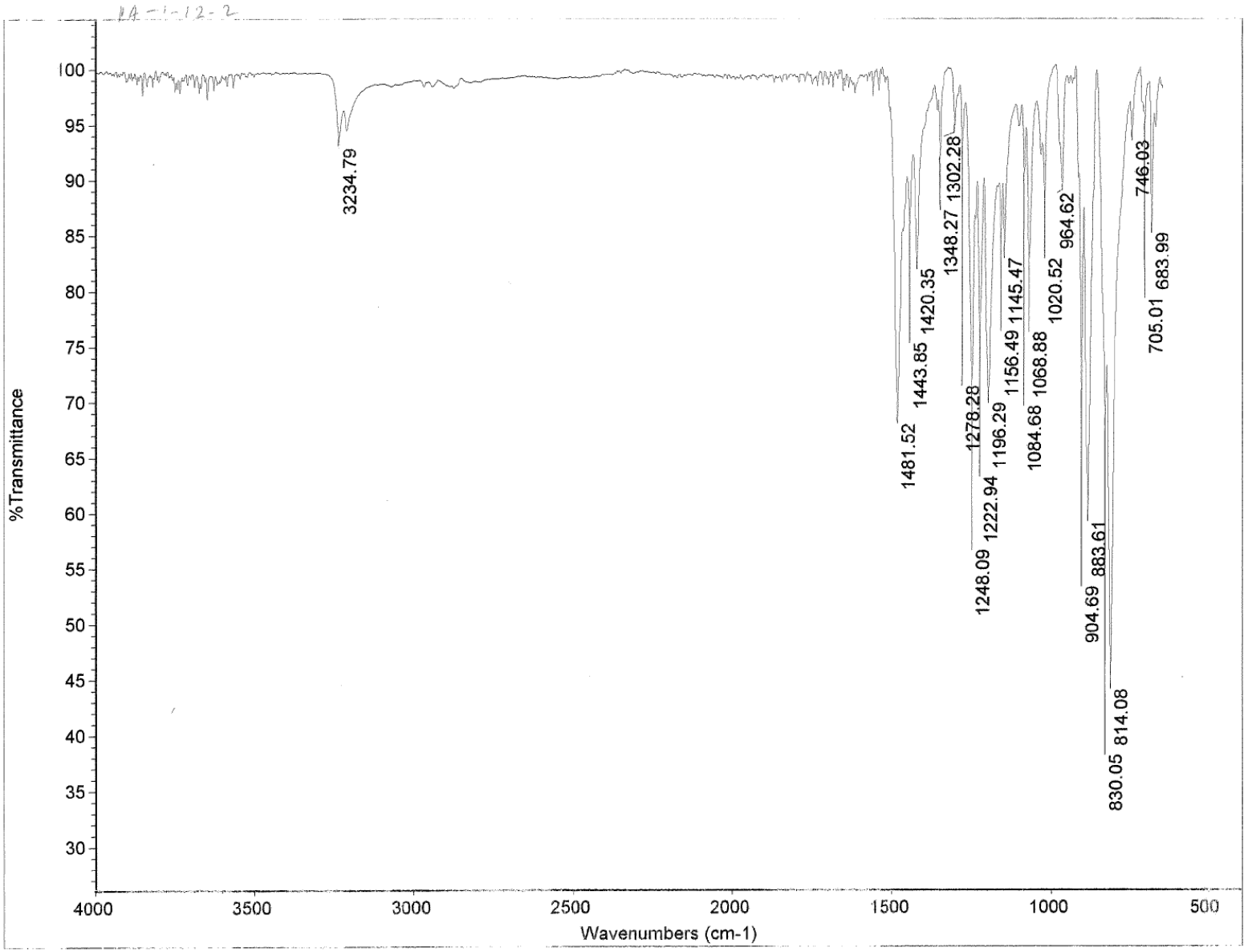


Figure S39. IR spectrum of $^{H,F}L_1MoO_2$ (**6b**).

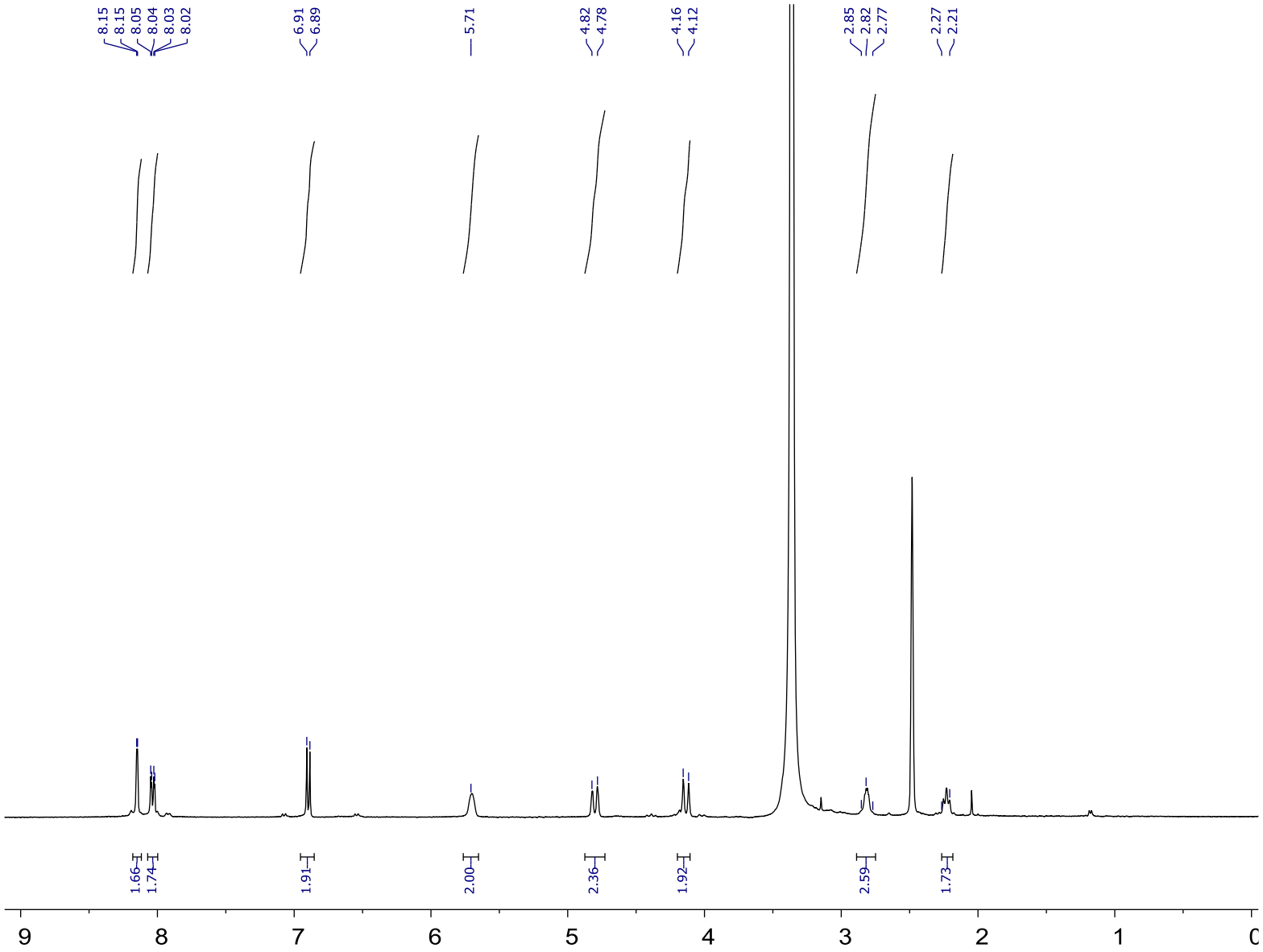


Figure S40. ^{1}H NMR spectrum of $^{H,NO2}L_1MoO_2$ (**7b**) in DMSO-d_6.

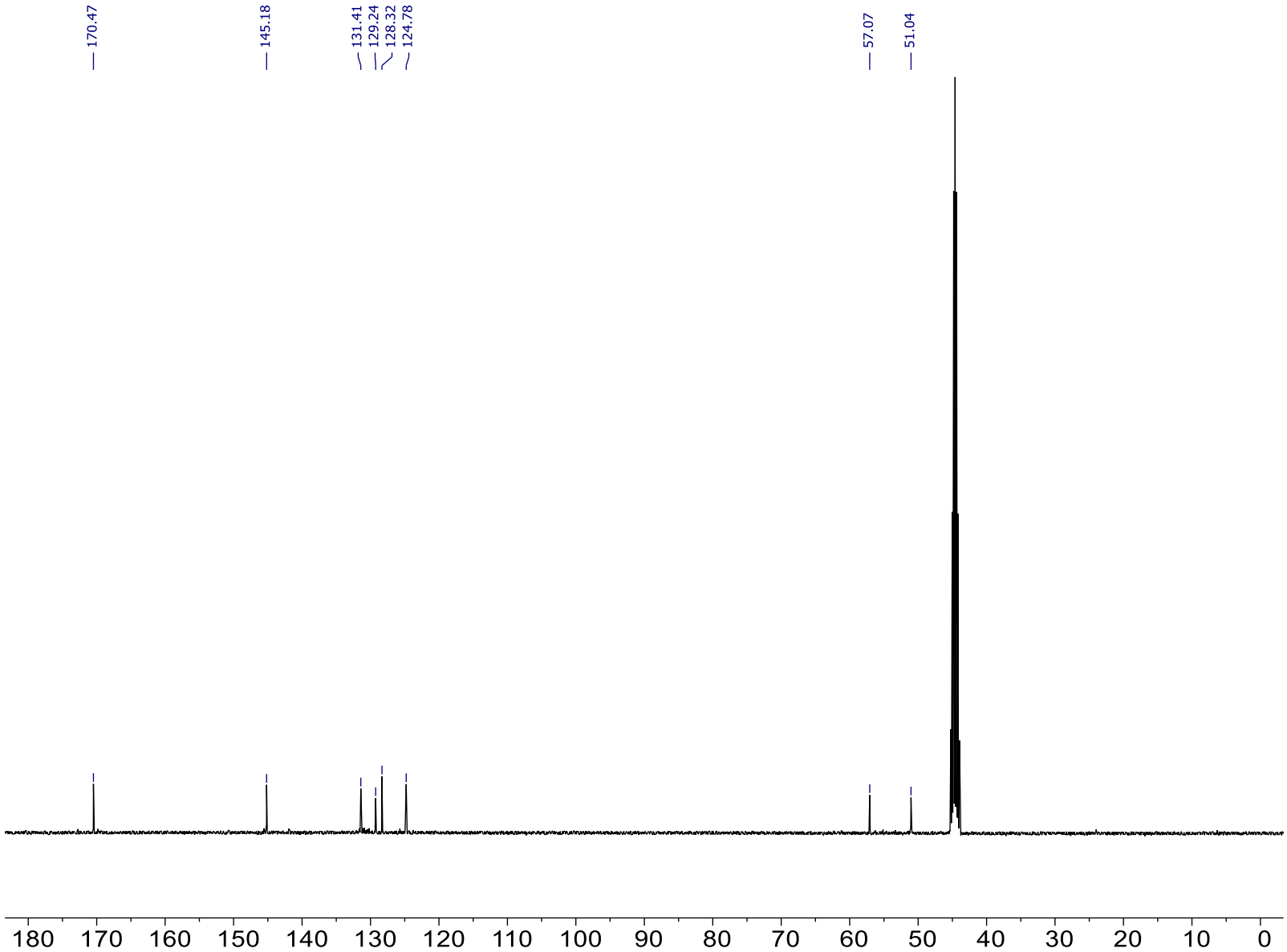


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,NO2}L_1MoO_2$ (**7b**) in DMSO-d_6.

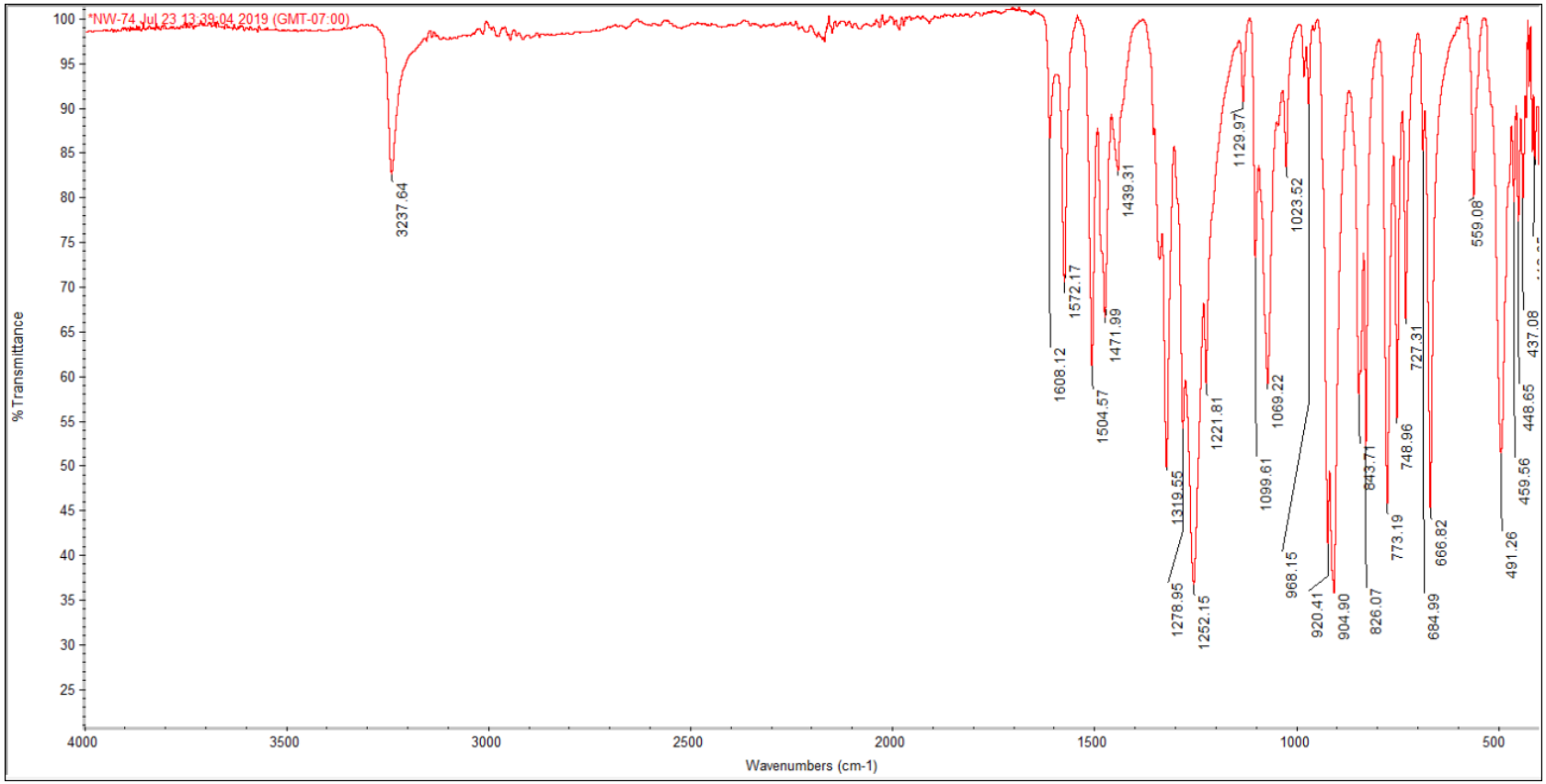


Figure S42. IR spectrum of $^{H,NO2}L_1MoO_2$ (**7b**).

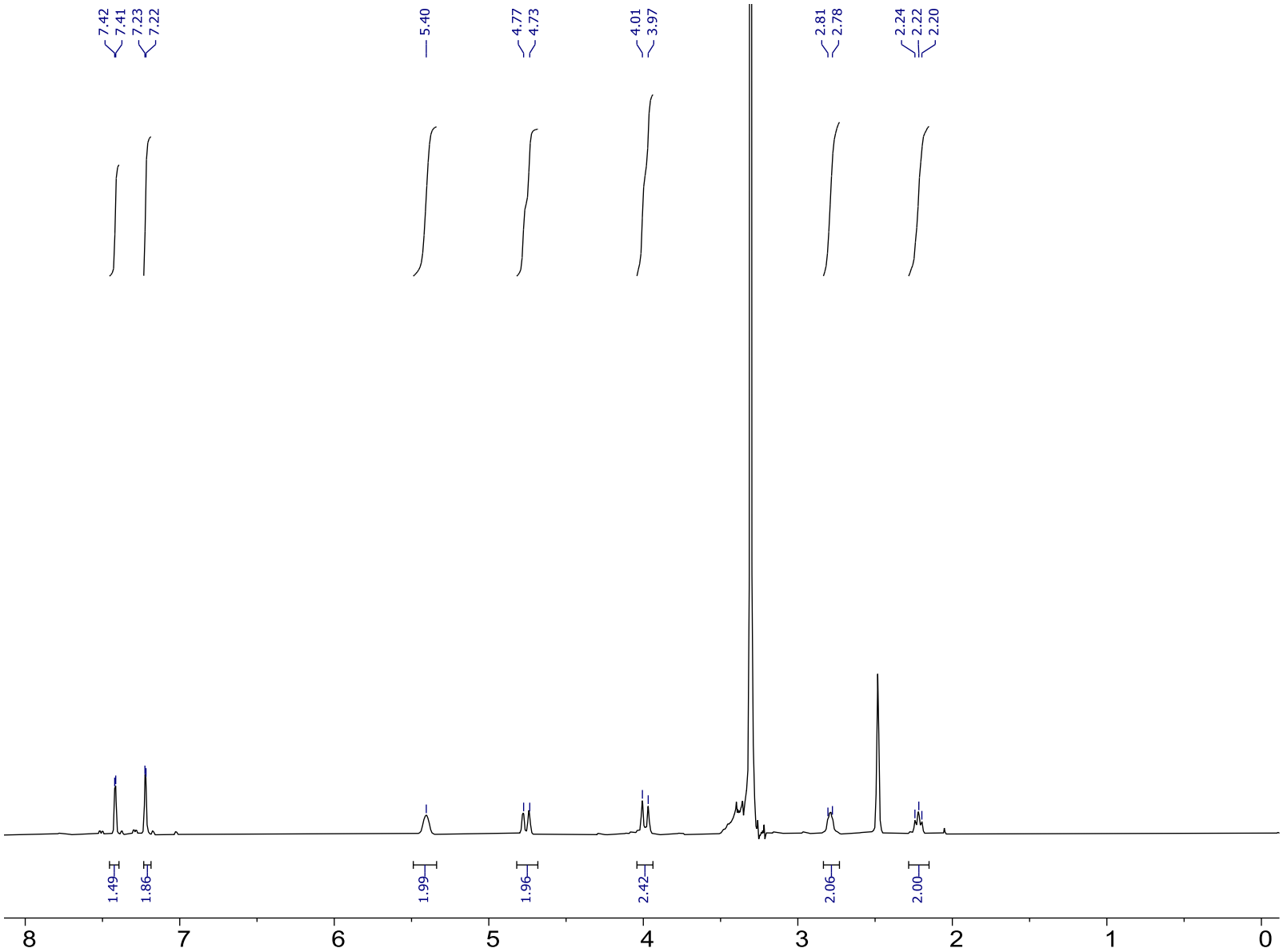


Figure S43. ^{1}H NMR spectrum of $^{Cl,Cl}L_1MoO_2$ (**8b**) in DMSO-d_6.

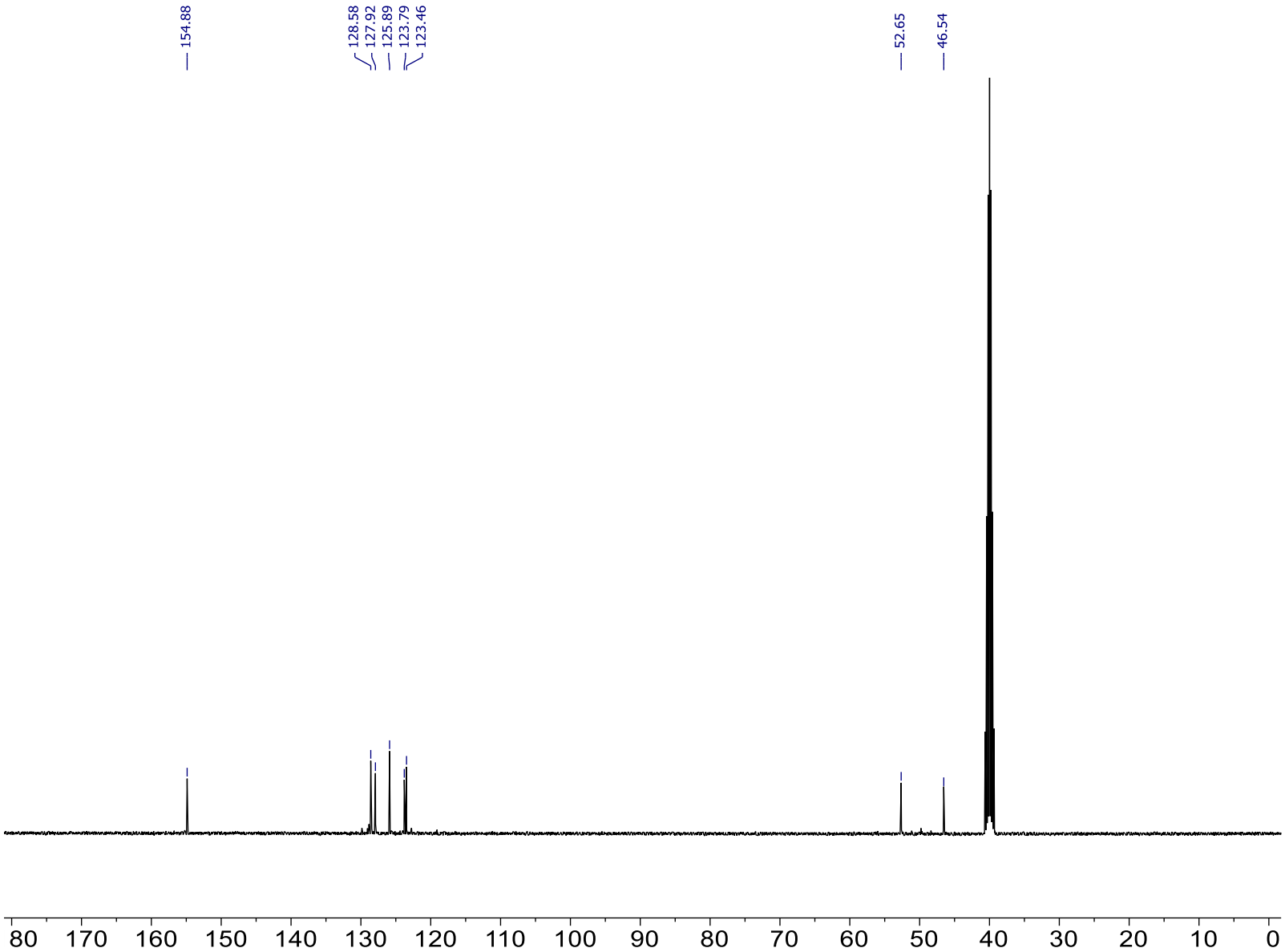


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of $^{Cl,Cl}L_1MoO_2$ (**8b**) in DMSO-d_6.

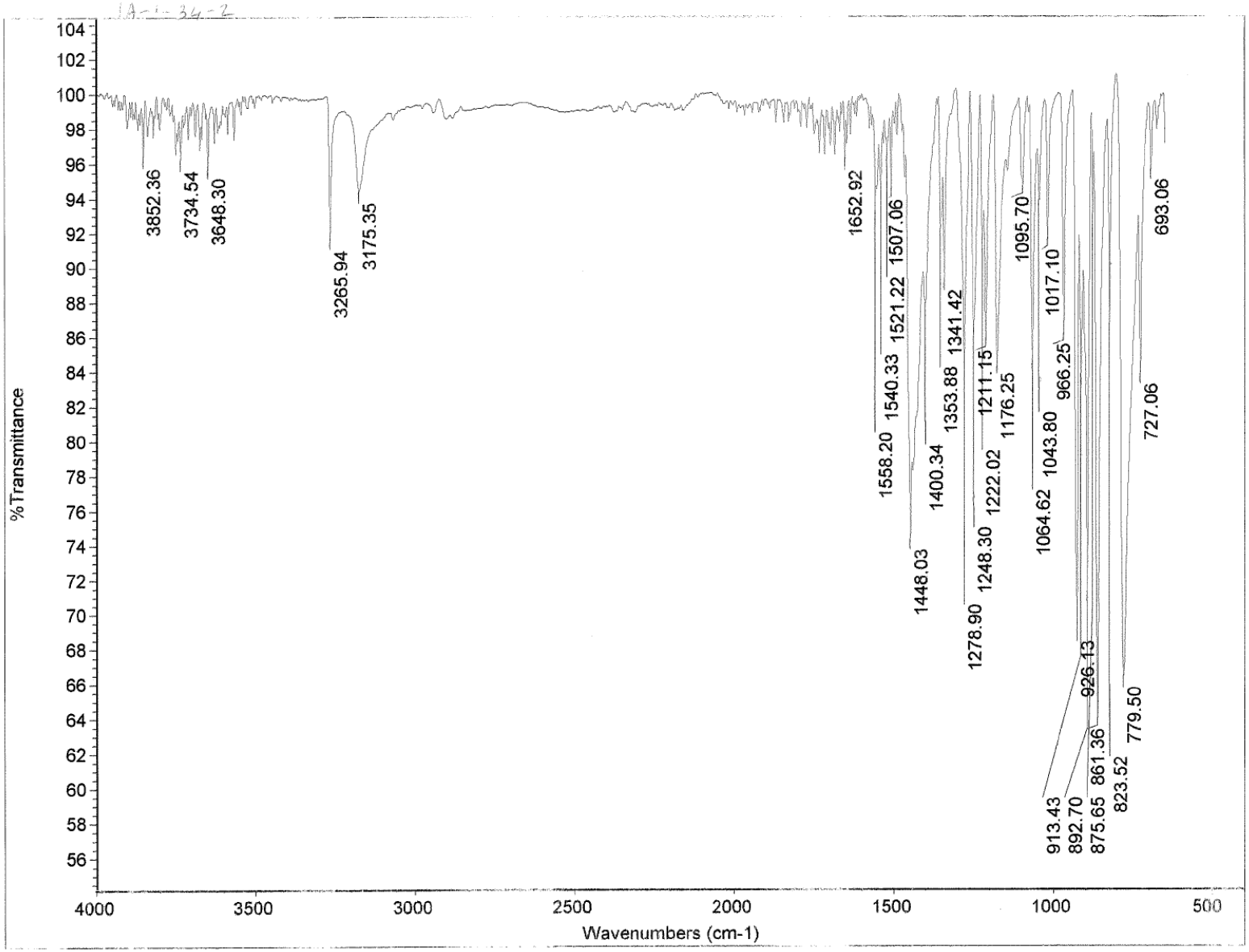


Figure S45. IR spectrum of $^{Cl,Cl}L_1MoO_2$ (**8b**).

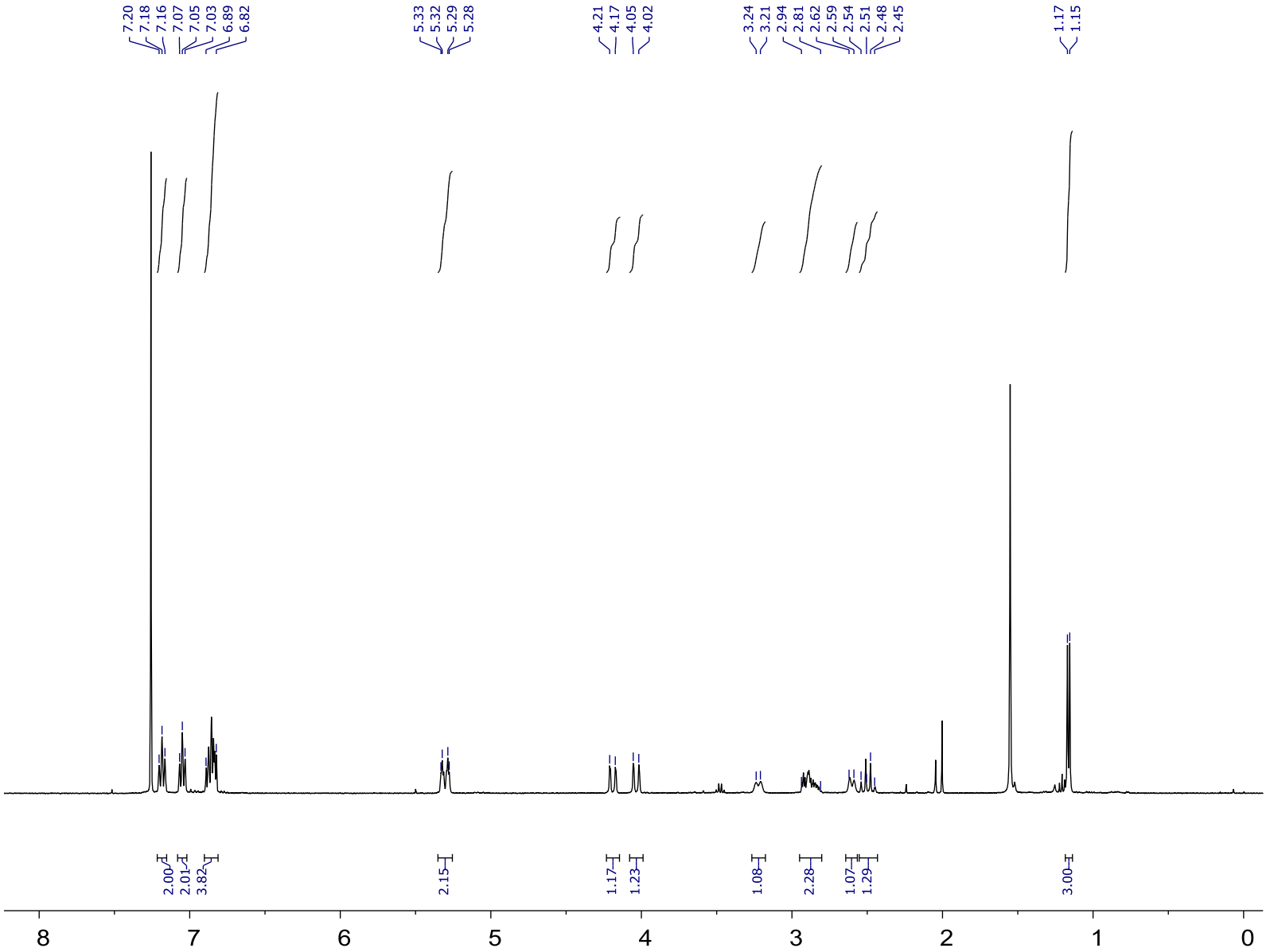


Figure S46. ^{1}H NMR spectrum of $^{H,H}L_2MoO_2$ (**9b**) in $CDCl_3$.

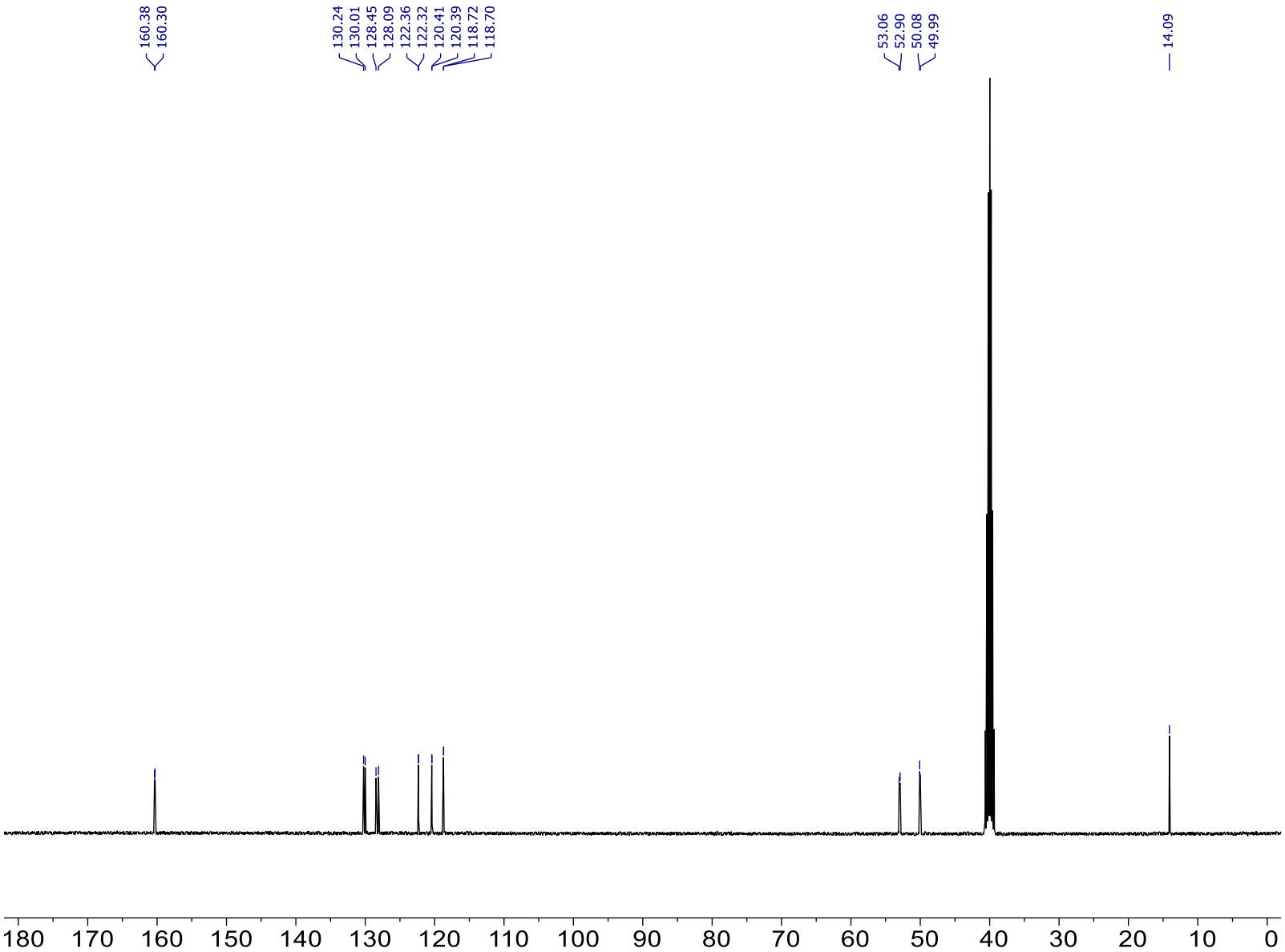


Figure S47. $^{13}C\{^{1}H\}$ NMR of $^{H,H}L_2MoO_2$ (**9b**) in DMSO-d_6.

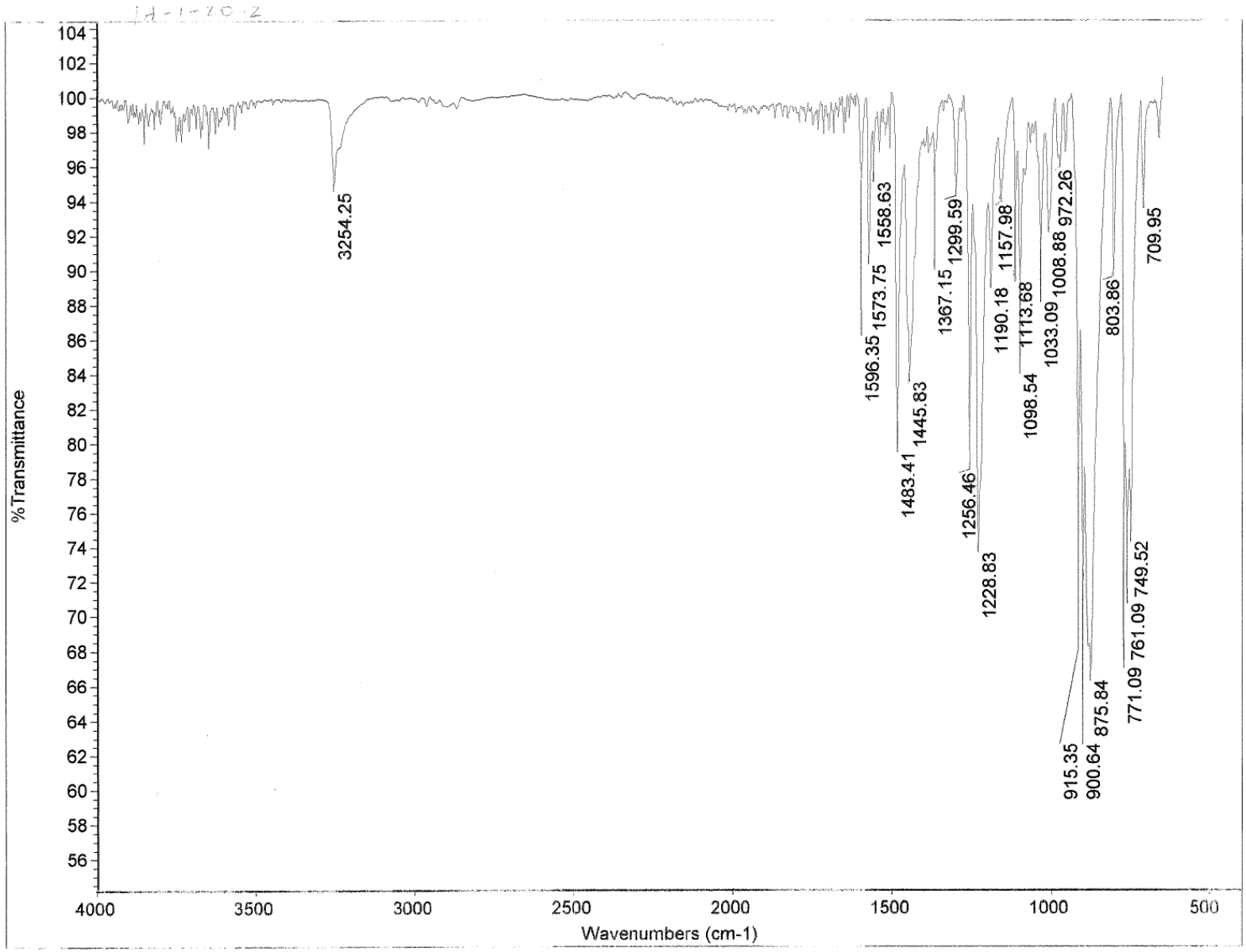


Figure S48. IR of $^{H,H}L_2MoO_2$ (**9b**).

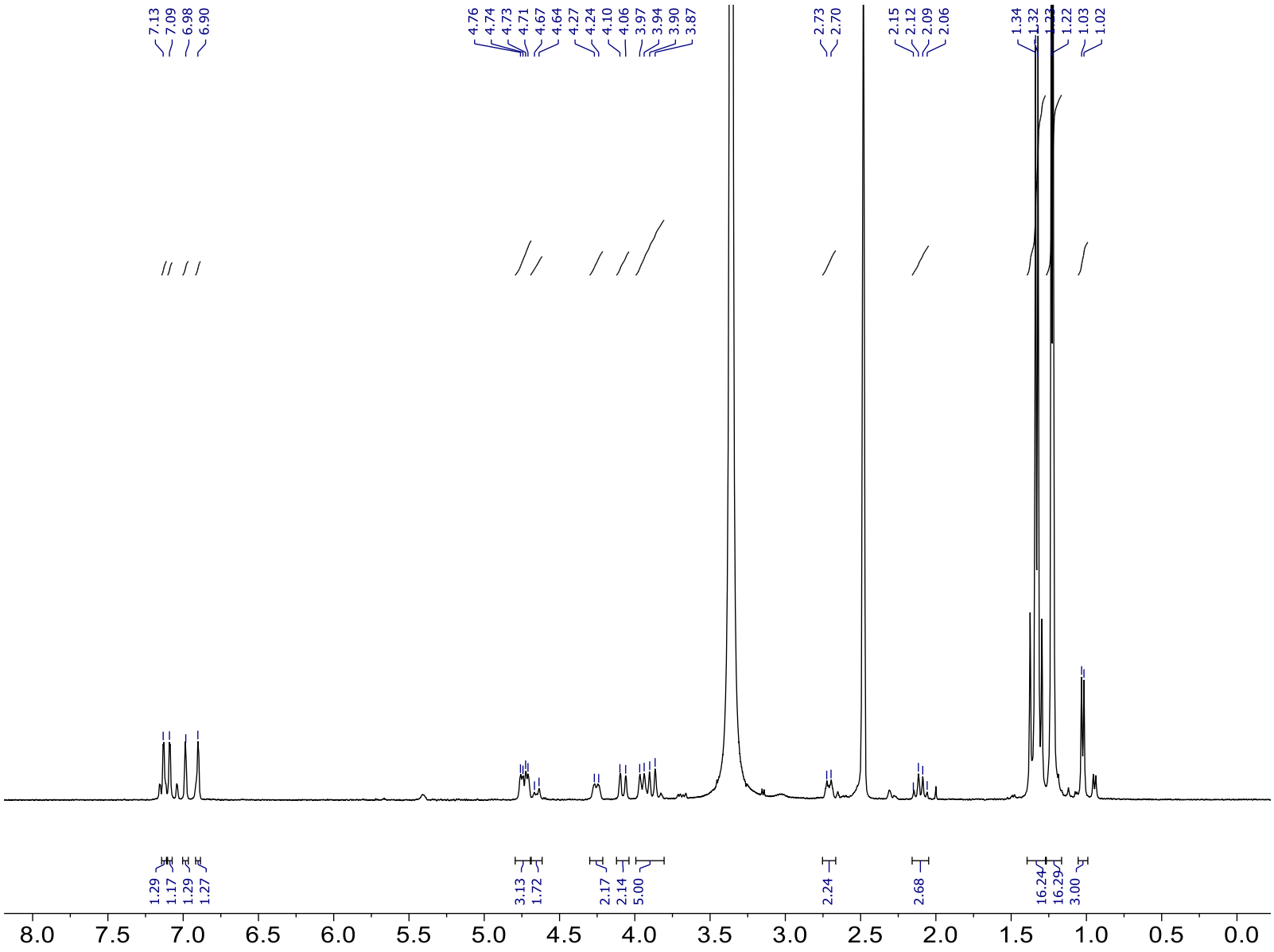

7.13
7.09
6.98
6.90
4.76
4.74
4.73
4.71
4.67
4.64
4.27
4.24
4.10
4.06
3.97
3.94
3.90
3.87
2.73
2.70
2.15
2.12
2.09
2.06
1.34
1.32
1.22
1.03
1.02
1.29
1.17
1.29
1.27
3.13
1.72
2.17
2.14
5.00
2.24
2.68
16.24
16.29
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

Figure S49. ^{1}H NMR spectrum of $^{tBu,tBu}L_2MoO_2$ (**10b**) in DMSO-d_6.

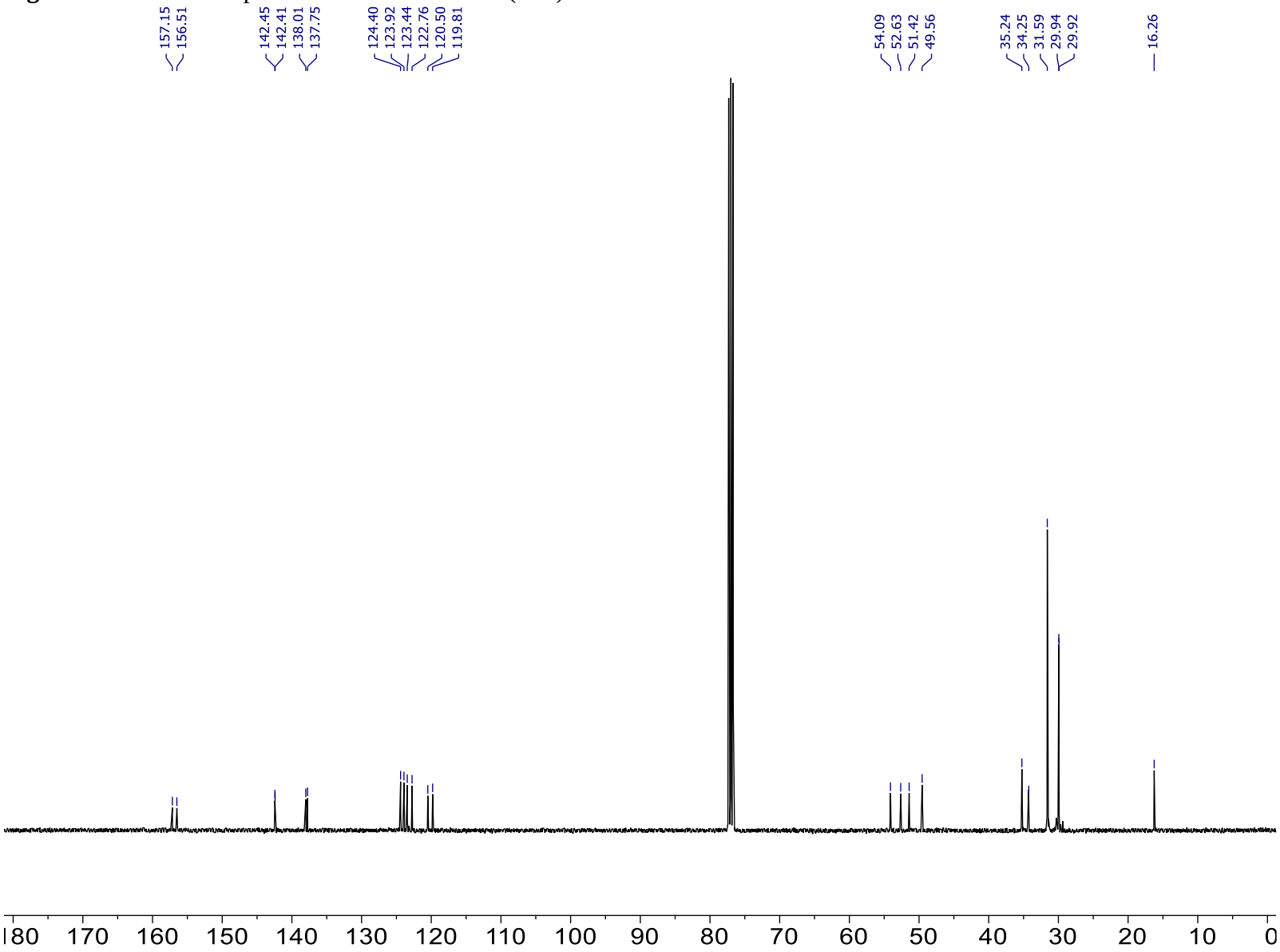


Figure S50. $^{13}C\{^{1}H\}$ NMR of $^{tBu,tBu}L_2MoO_2$ (**10b**) in $CDCl_3$.

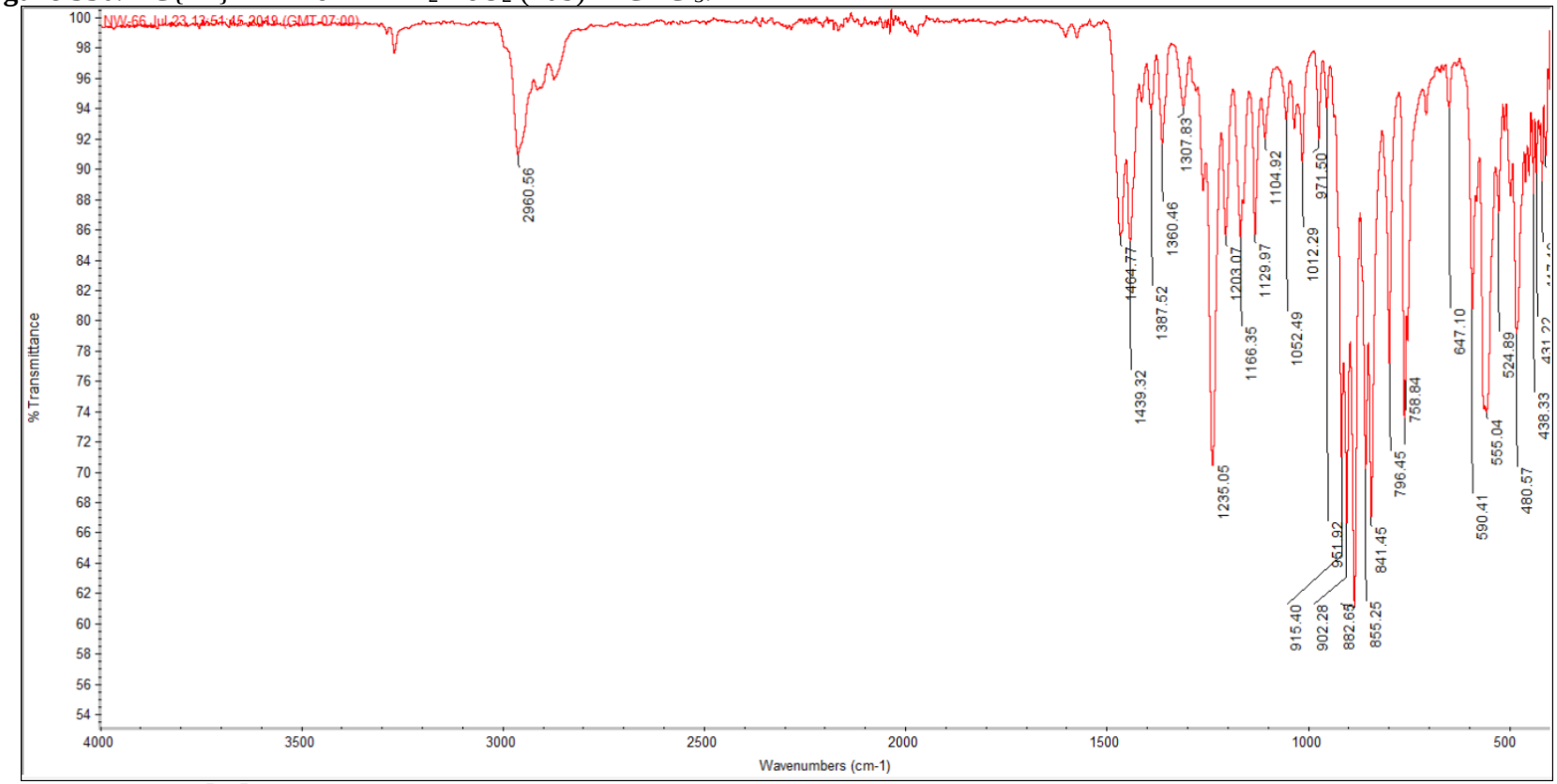


Figure S51. IR of $^{tBu,tBu}L_2MoO_2$ (**10b**).

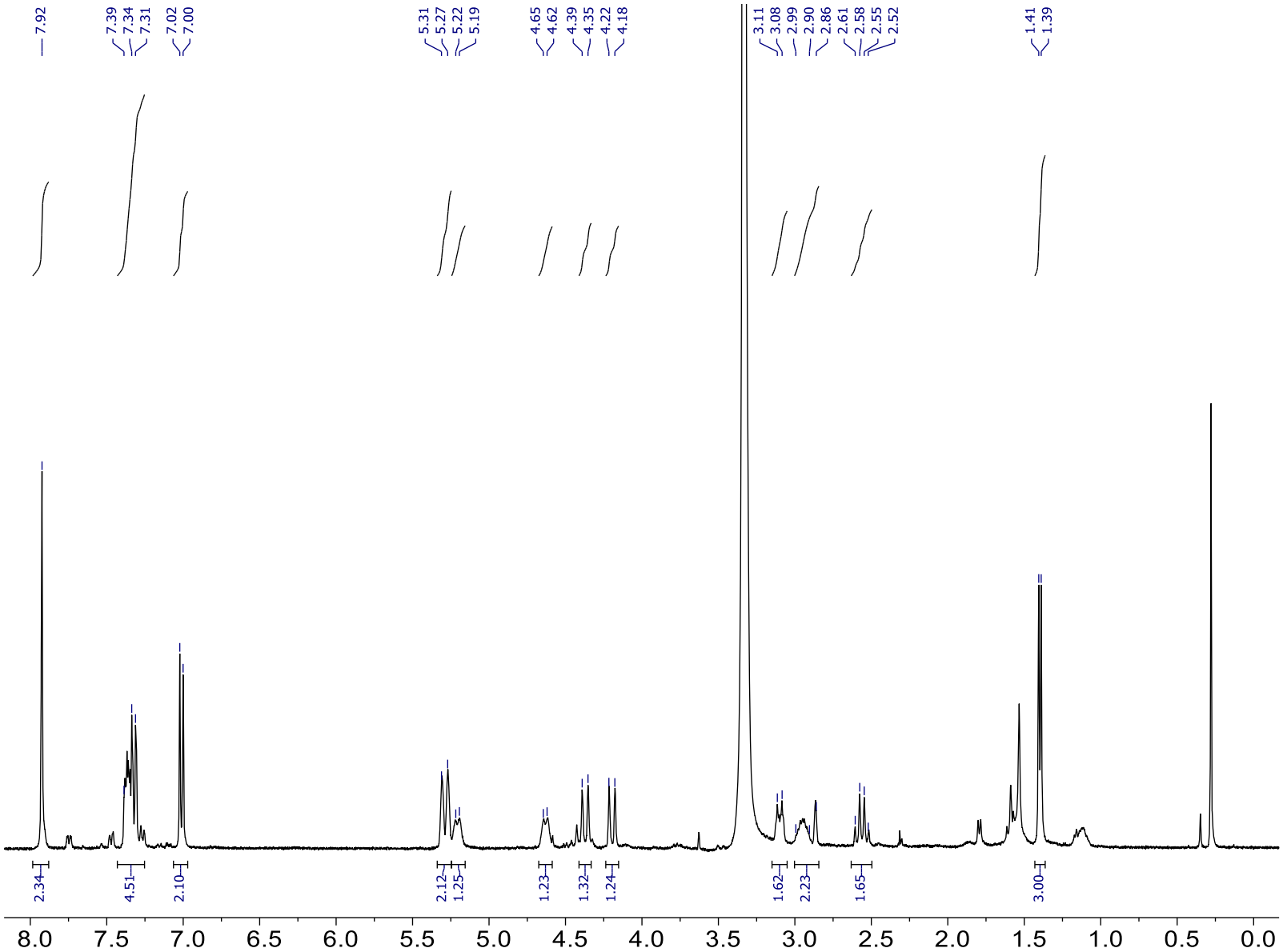


Figure S52. ^{1}H NMR spectrum of $^{H,Cl}L_2MoO_2$ (**11b**) in DMSO-d_6.

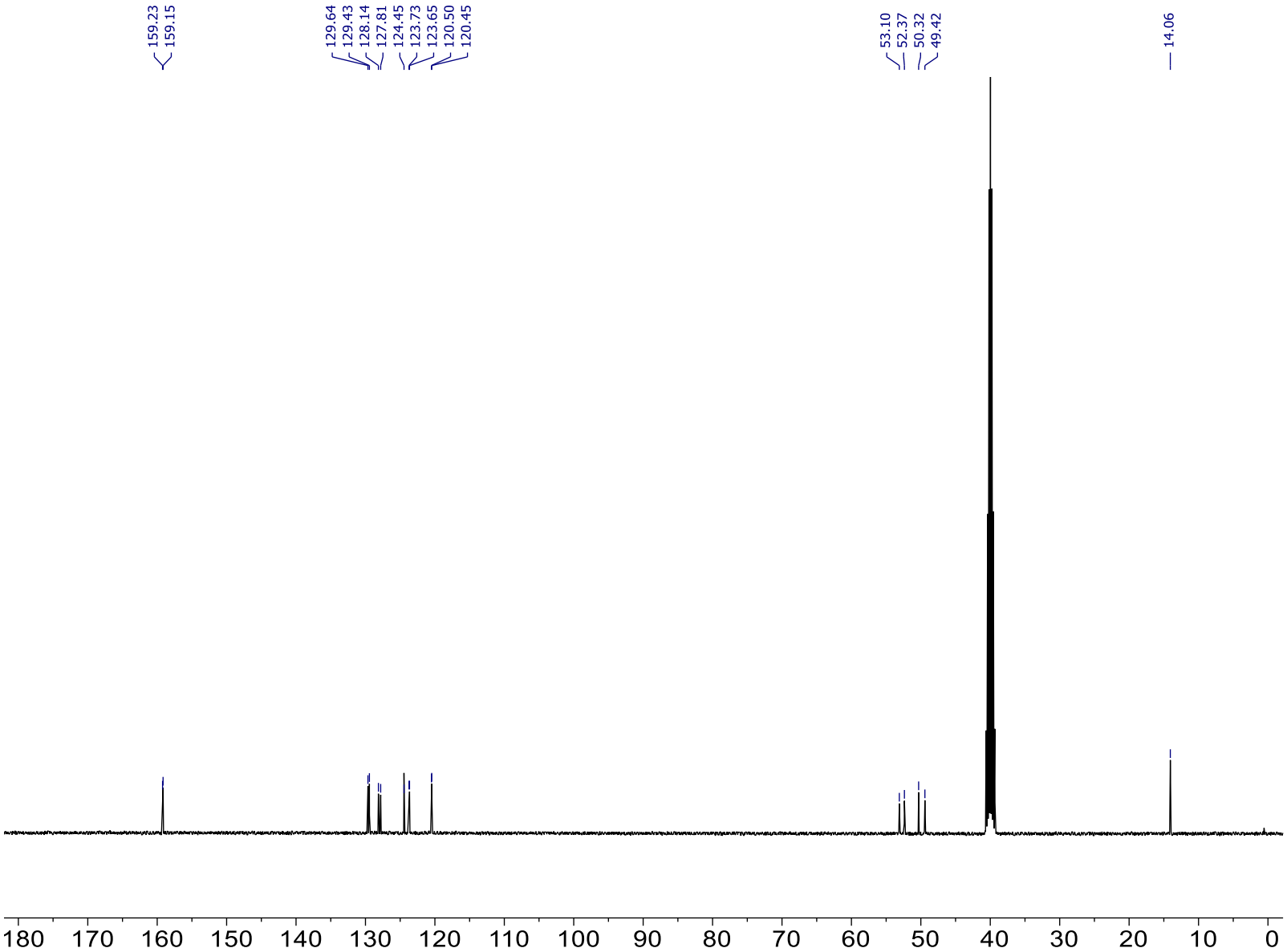


Figure S53. $^{13}C\{^{1}H\}$ NMR of $^{H,Cl}L_2MoO_2$ (**11b**) in DMSO-d_6.

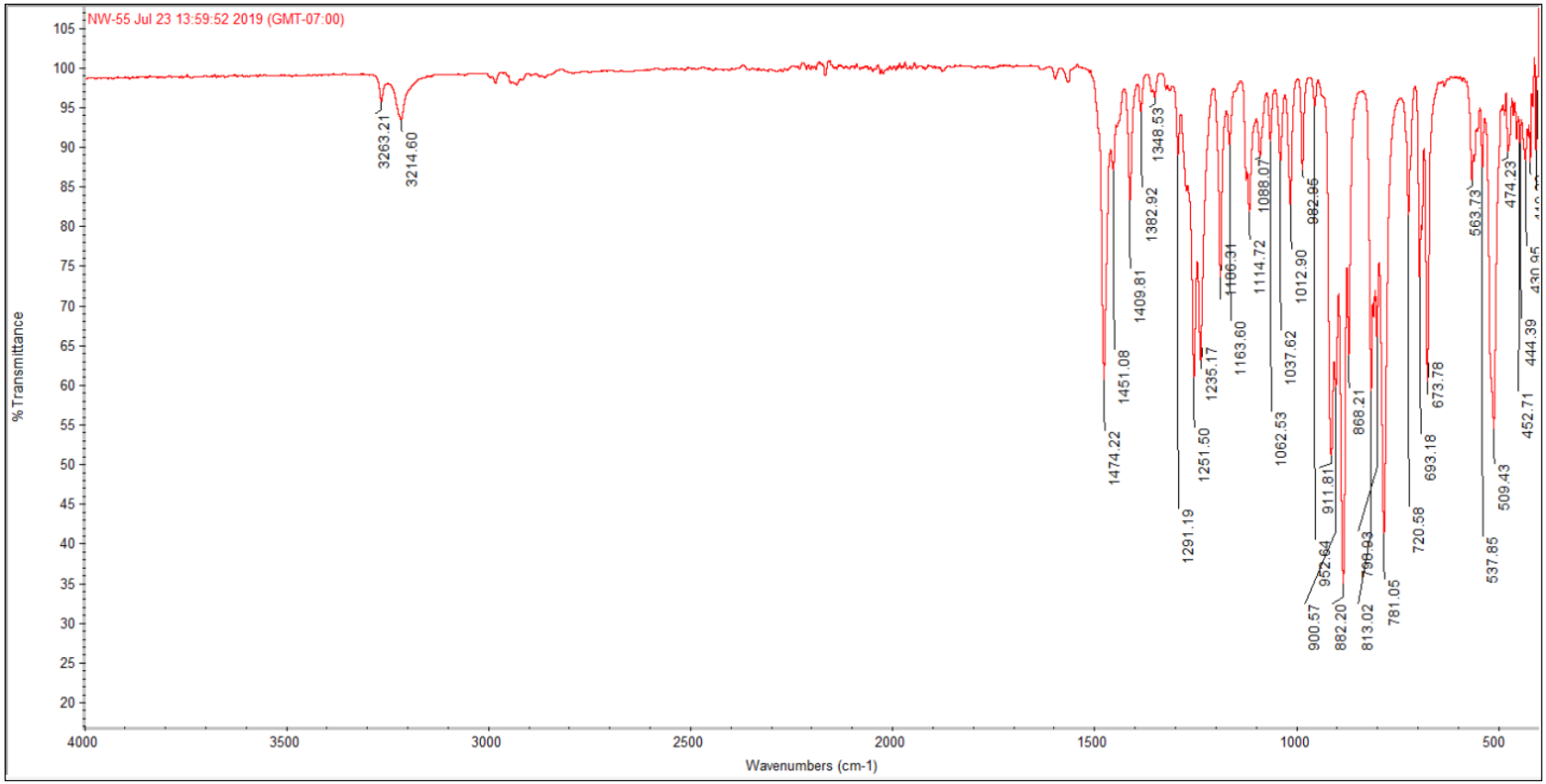


Figure S53. IR of $^{H,Cl}L_2MoO_2$ (**11b**).

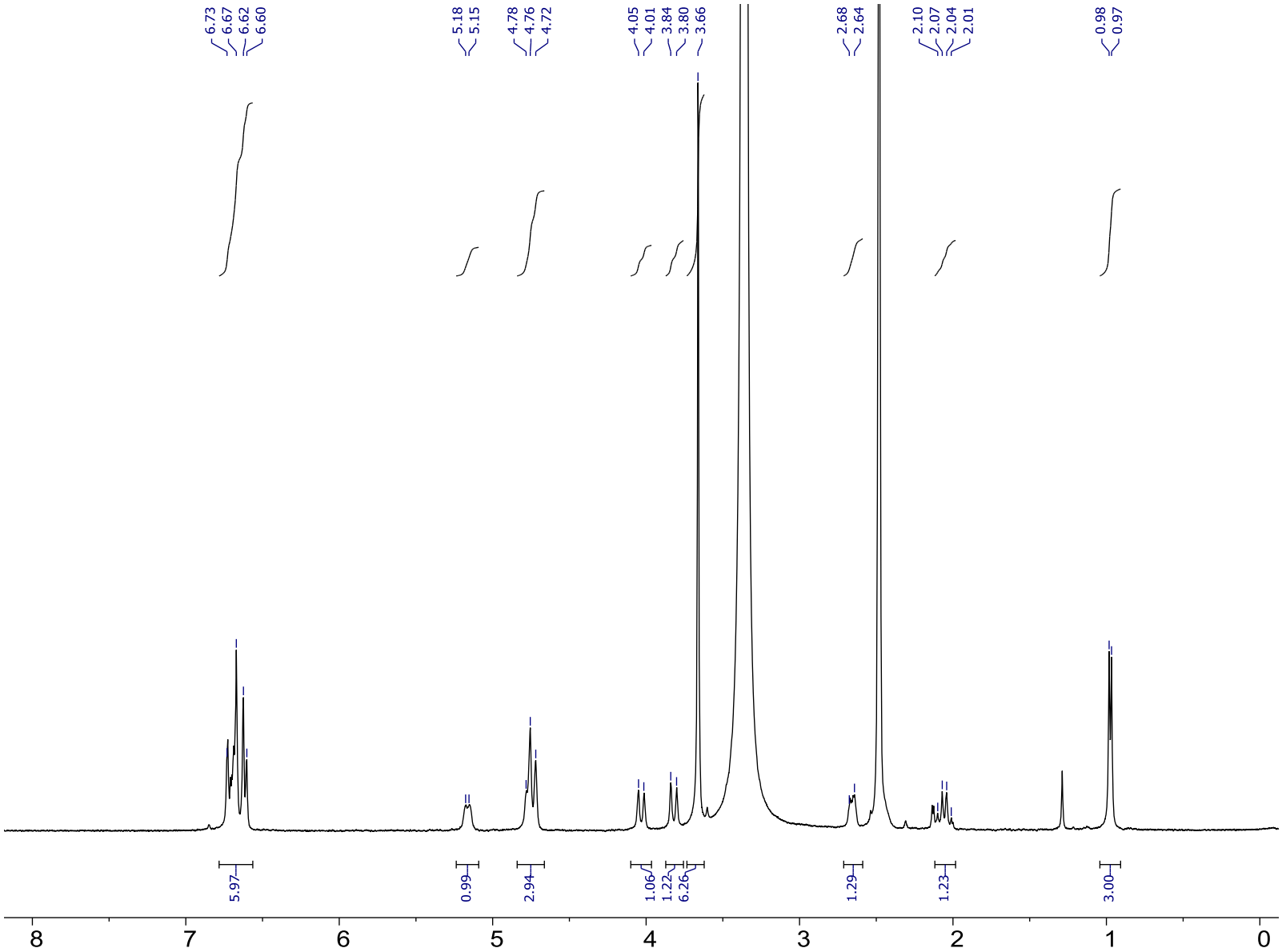


Figure S54. ^{1}H NMR spectrum of $^{H,OMe}L_2MoO_2$ (**12b**) in DMSO-d_6.

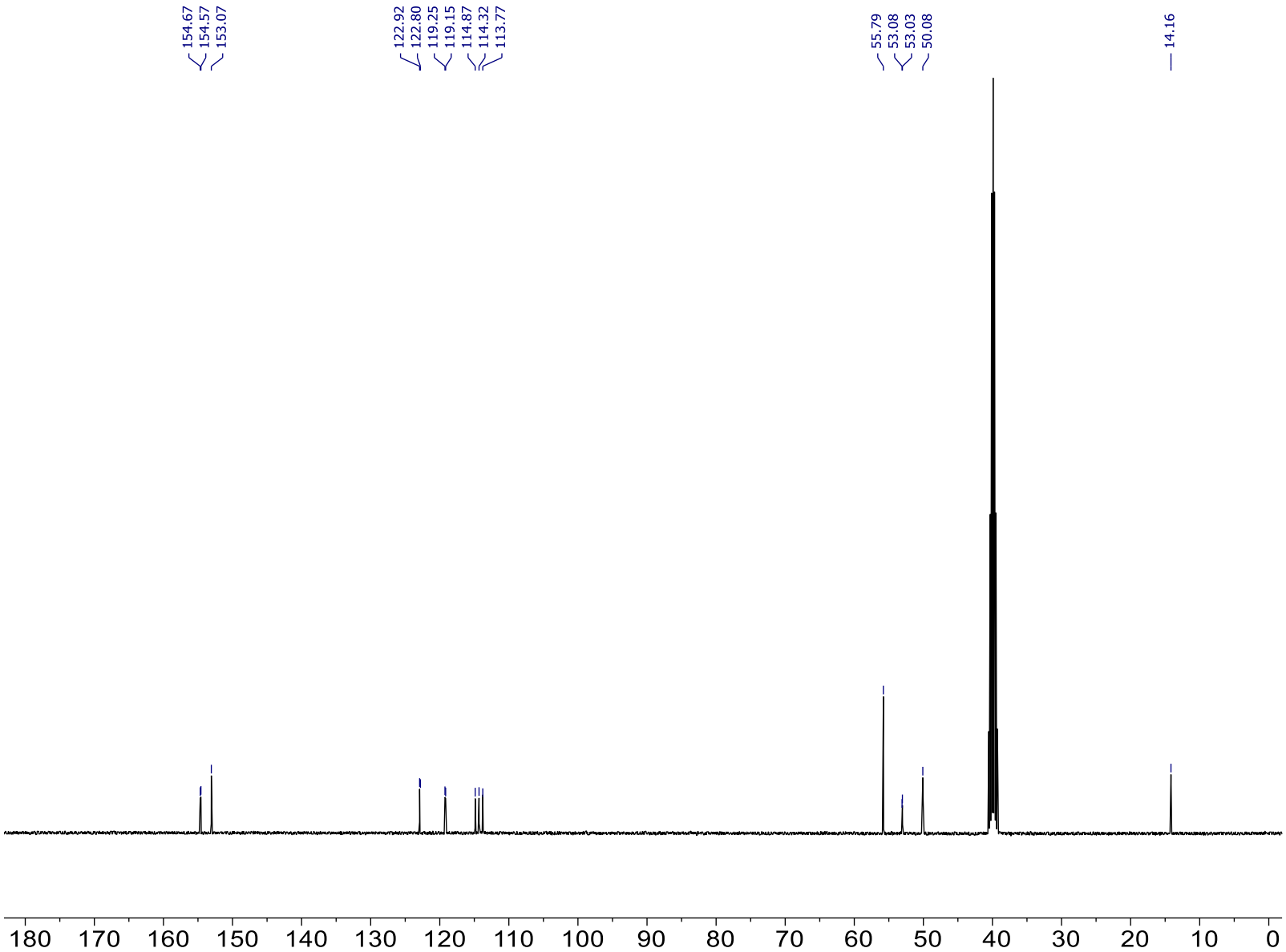


Figure S55. $^{13}C\{^{1}H\}$ NMR of $^{H,OMe}L_2MoO_2$ (**12b**) in DMSO-d_6.

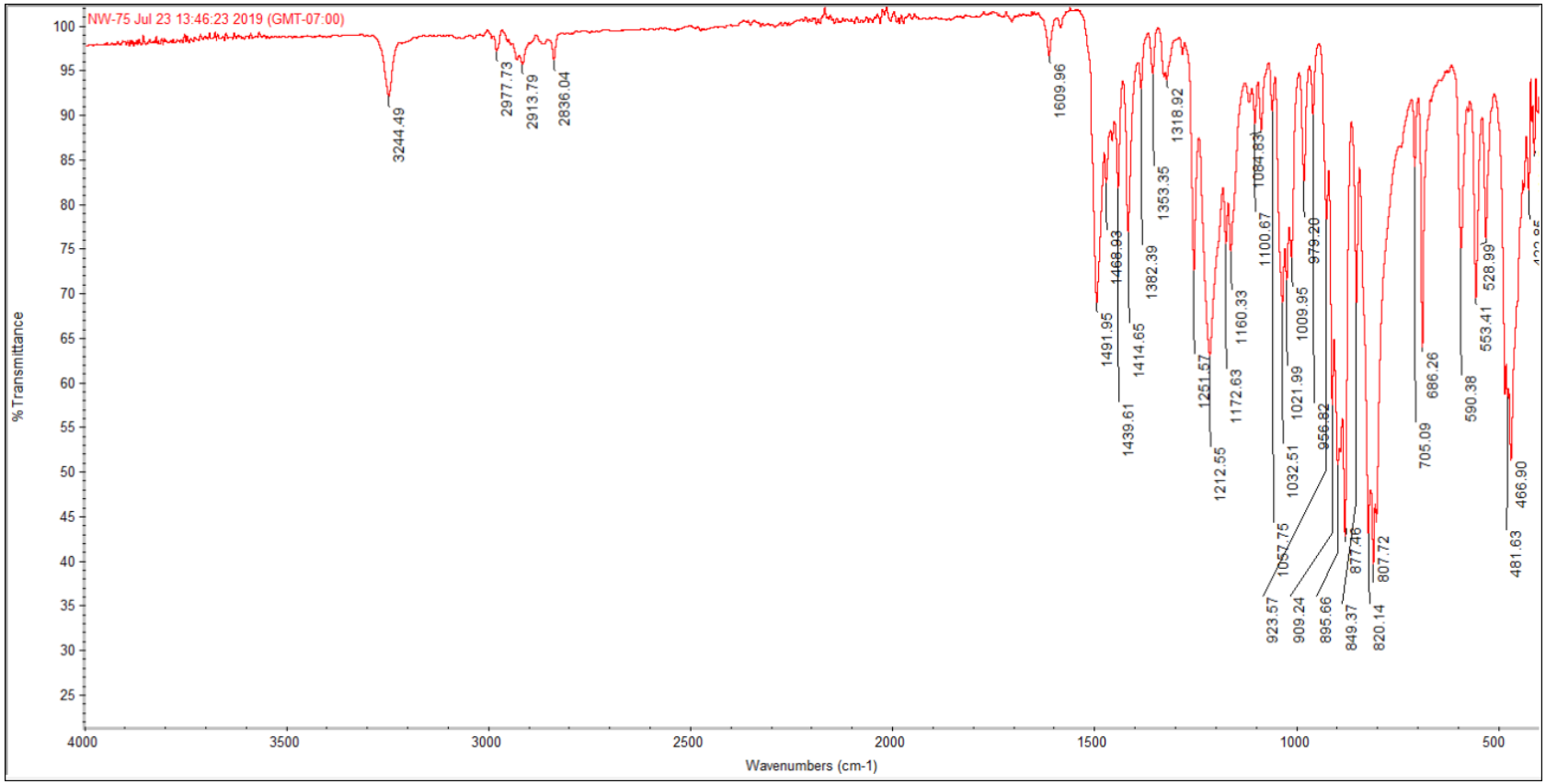


Figure S56. IR of $^{H,OMe}L_2MoO_2$ (**12b**).

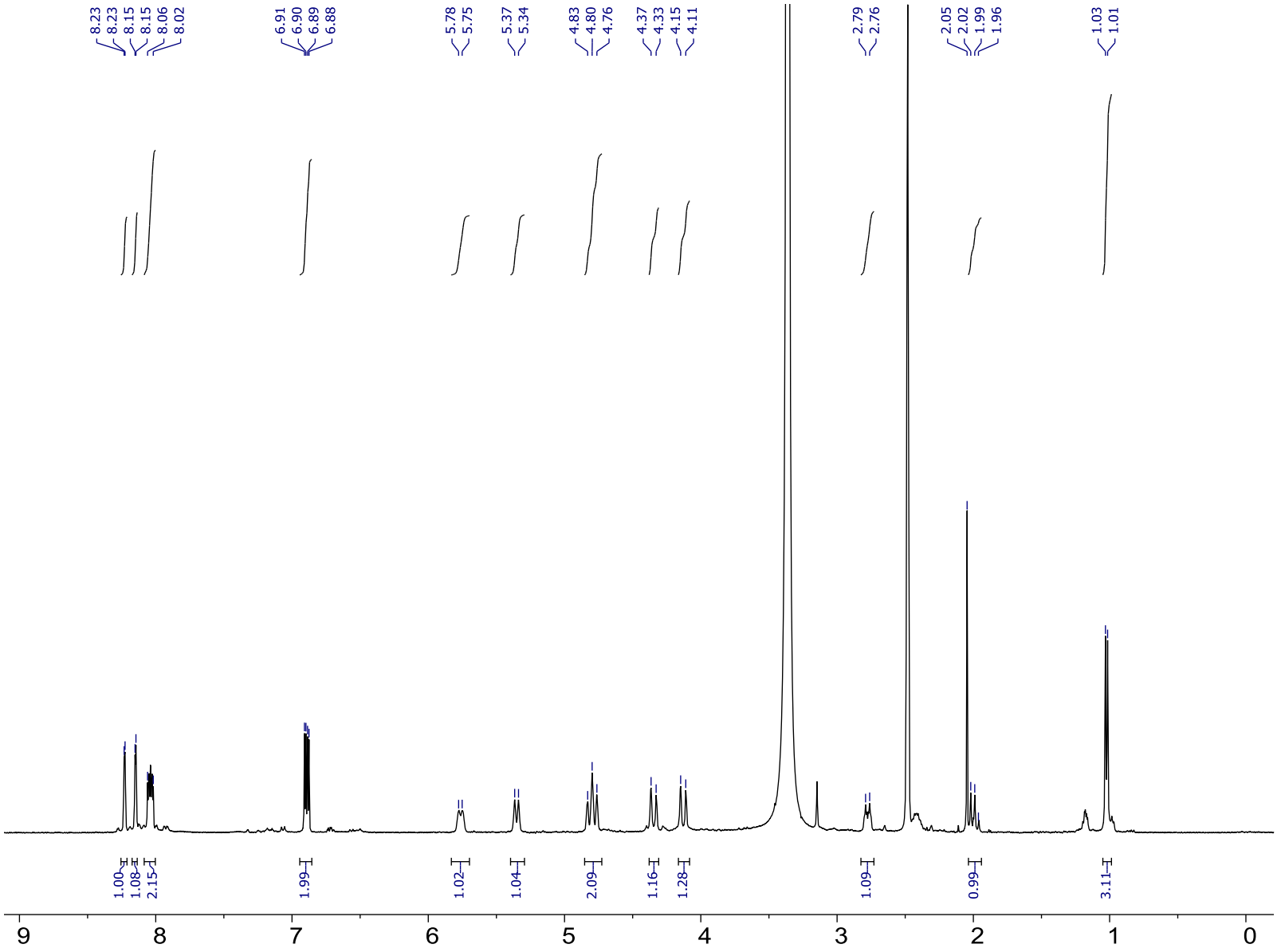


Figure S57. ^{1}H NMR spectrum of $^{H,NO2}L_2MoO_2$ (**13b**) in DMSO-d_6.

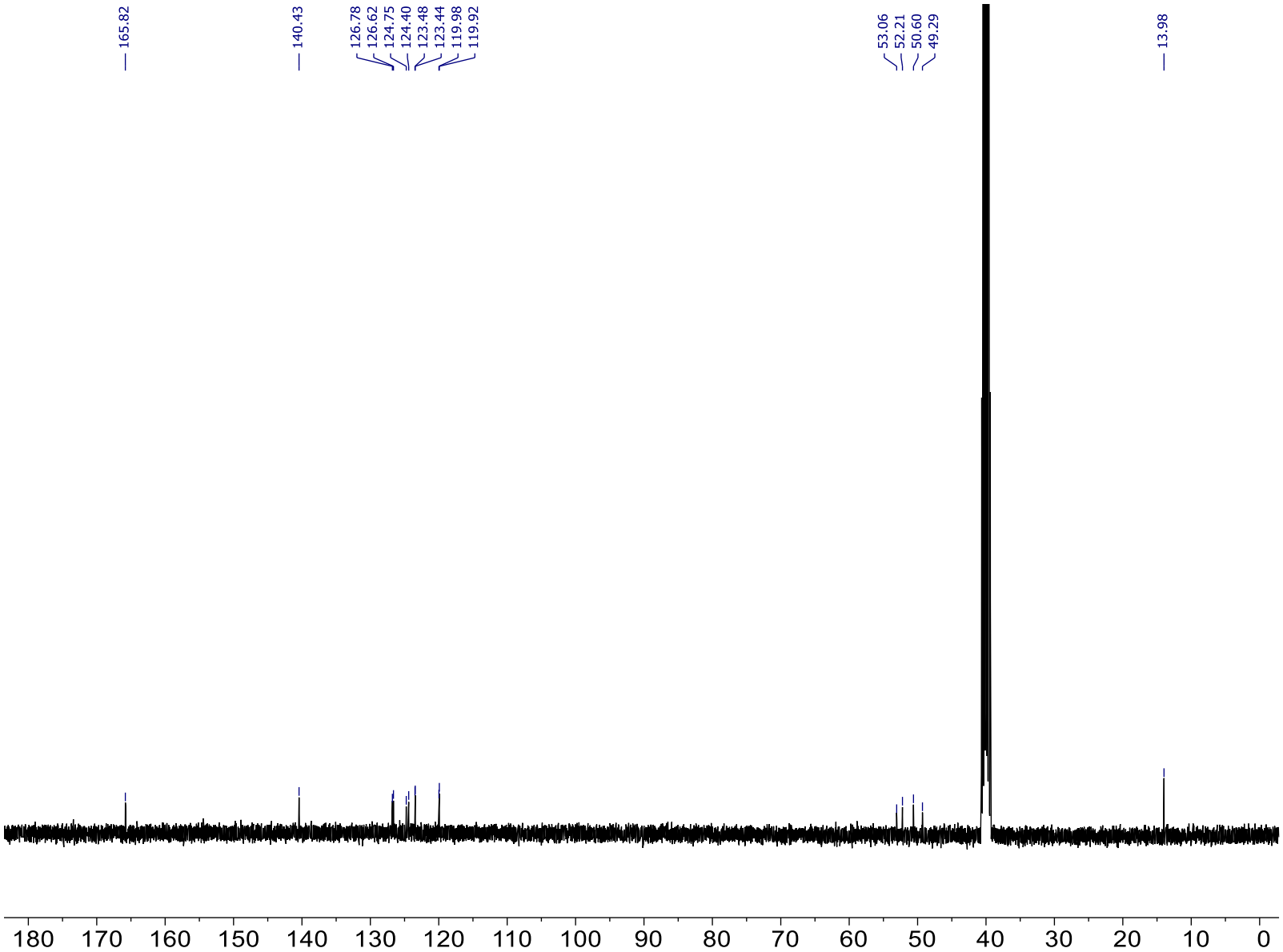


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,NO2}L_2MoO_2$ (**13b**) in DMSO-d_6.

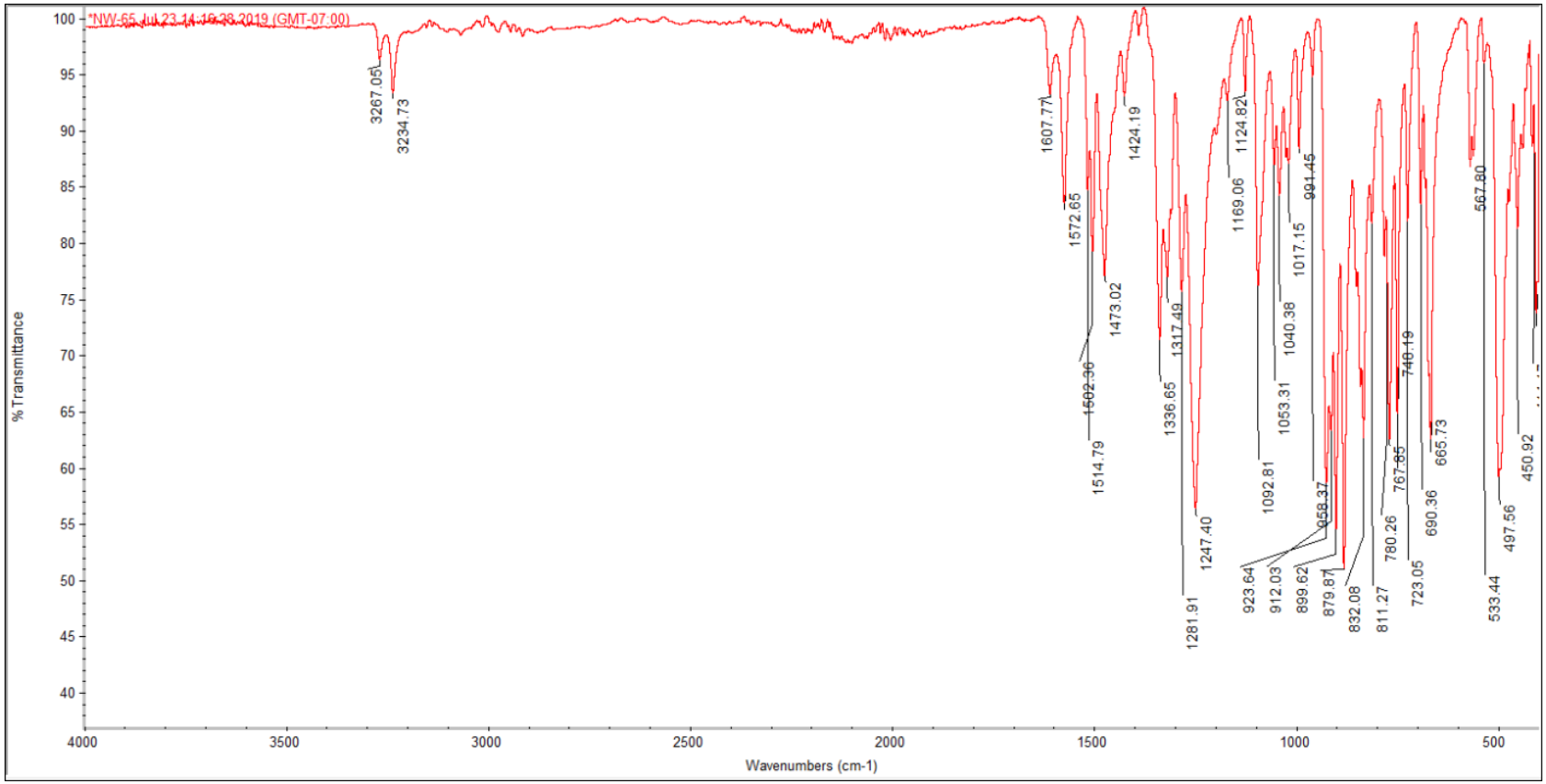


Figure S59. IR spectrum of $^{H,NO2}L_2MoO_2$ (**13b**).

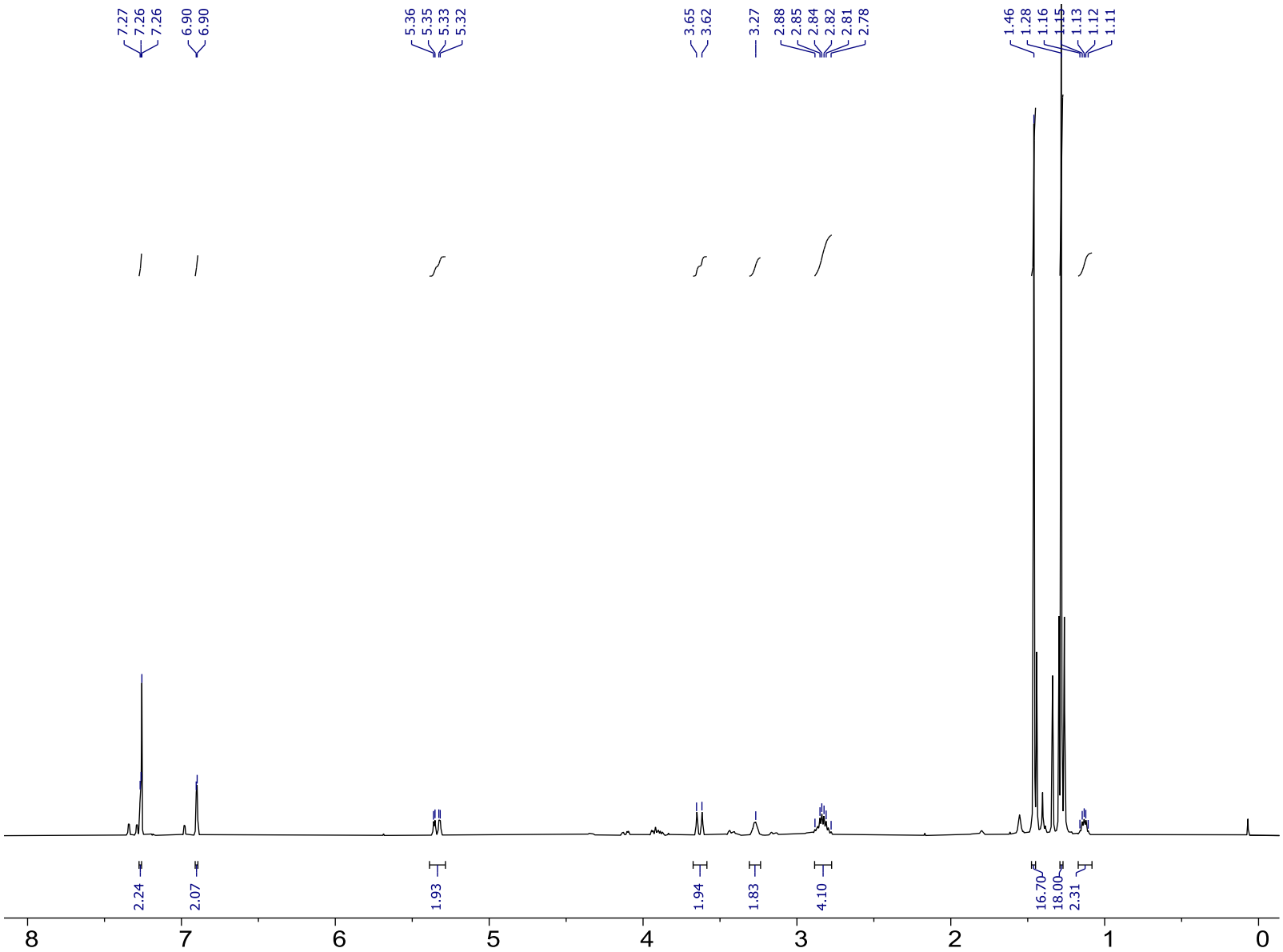


Figure S60. ^{1}H NMR spectrum of $^{tBu,tBu}L_3MoO_2$ (**14b**) in $CDCl_3$.

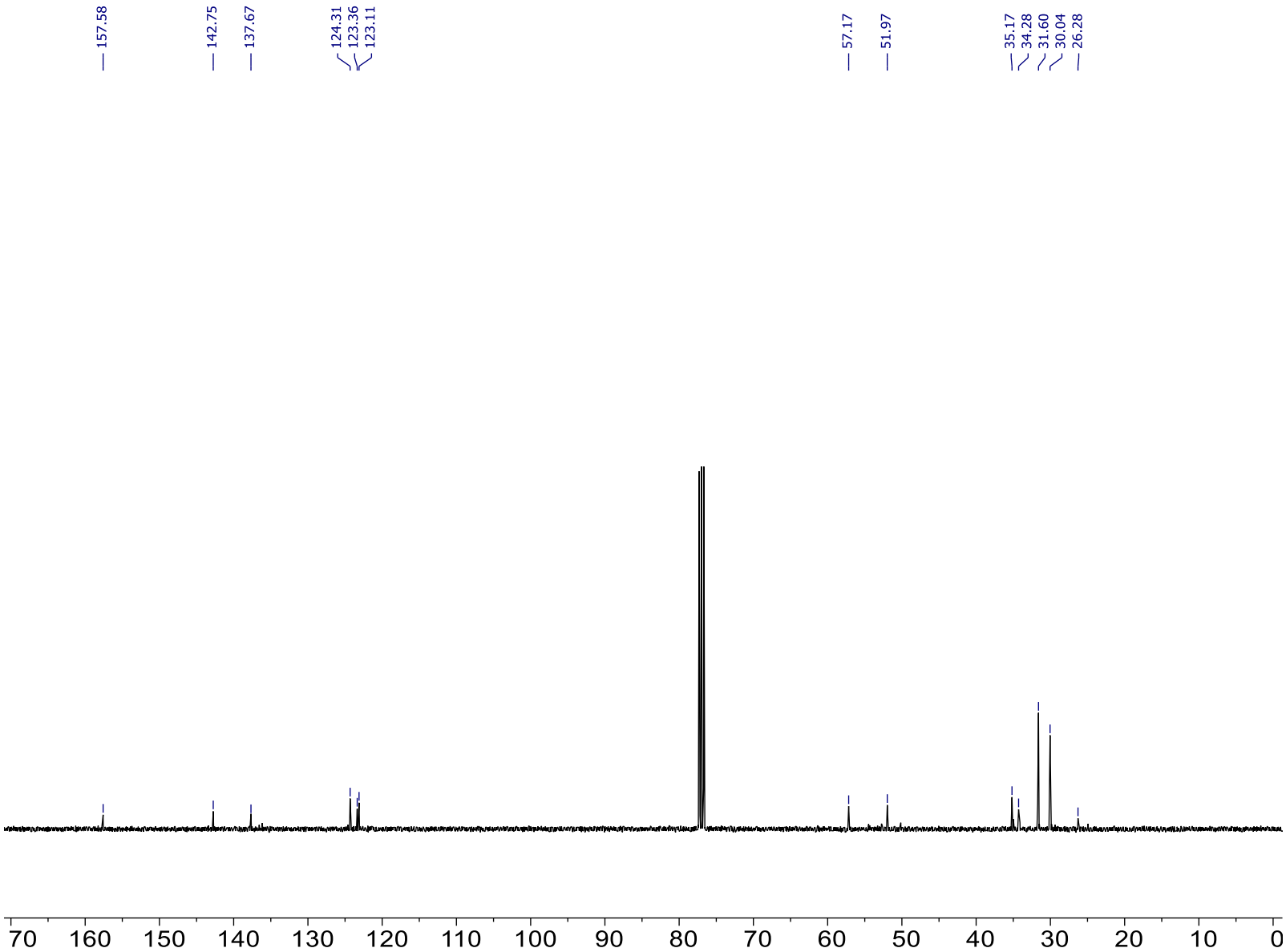


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of $^{tBu,tBu}L_3MoO_2$ (**14b**) in $CDCl_3$.

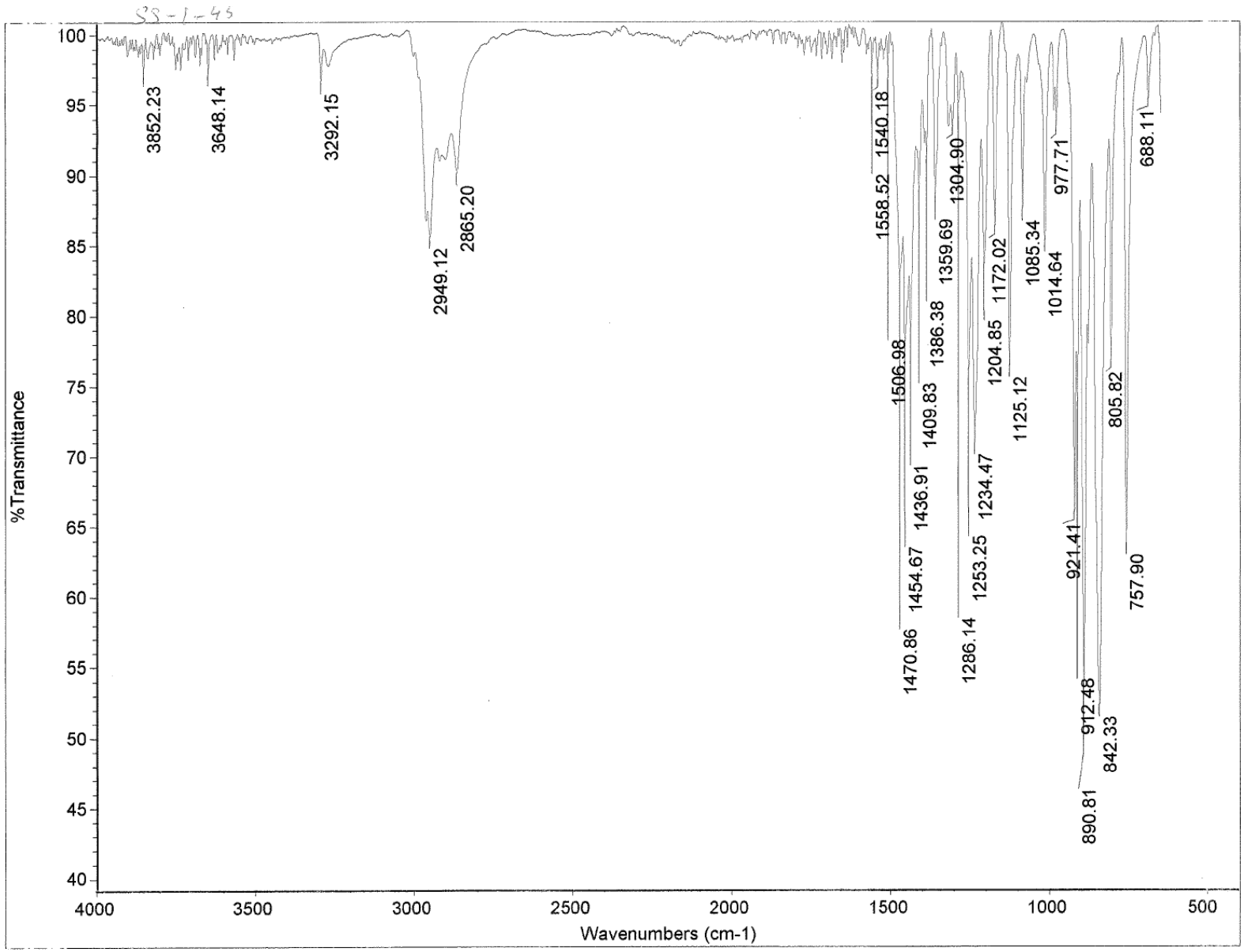


Figure S62. IR spectrum of $^{tBu,tBu}L_3MoO_2$ (**14b**).

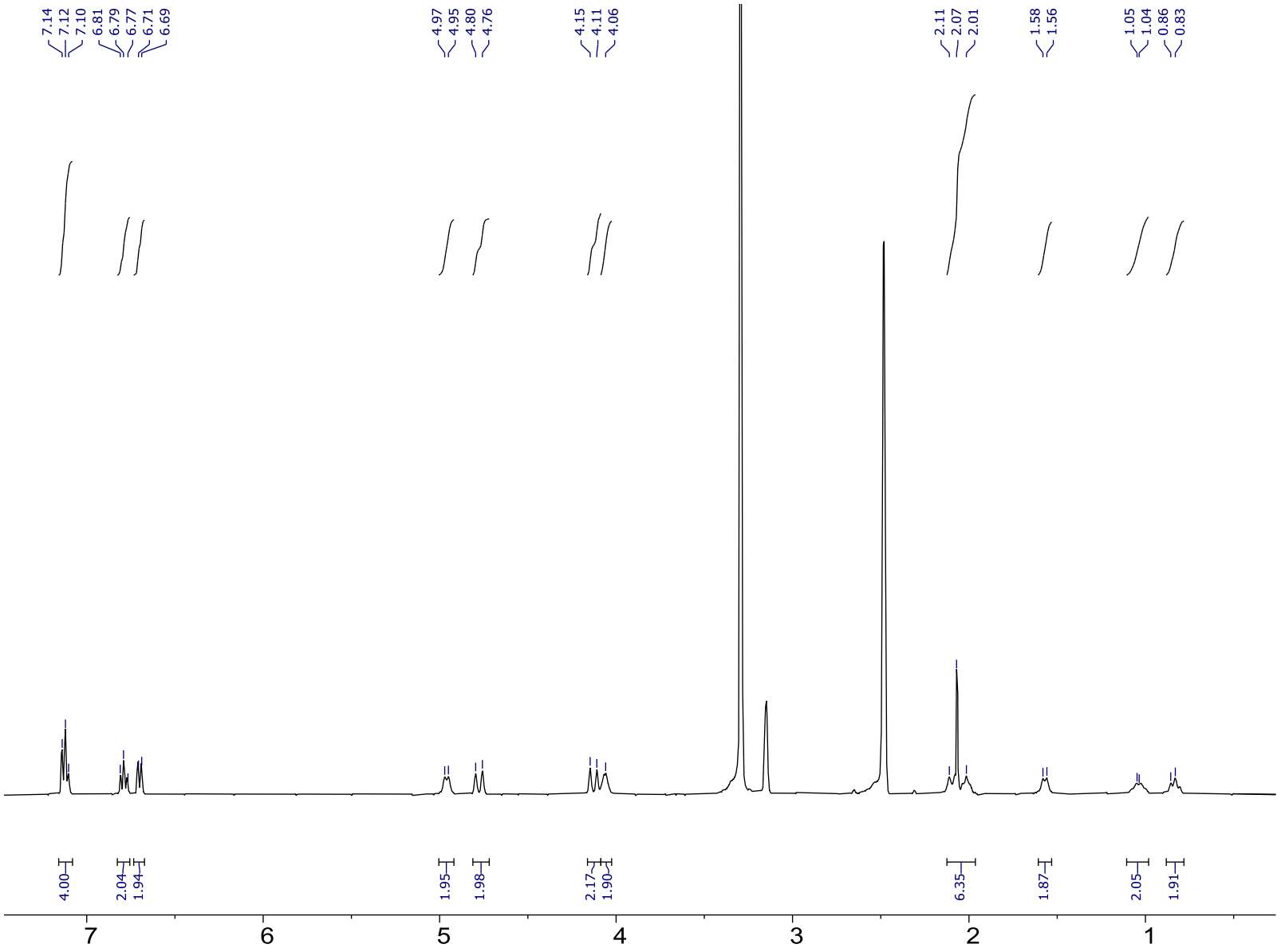


Figure S63. ^{1}H NMR spectrum of $^{H,H}L_4MoO_2$ (**15b**) in DMSO-d_6.

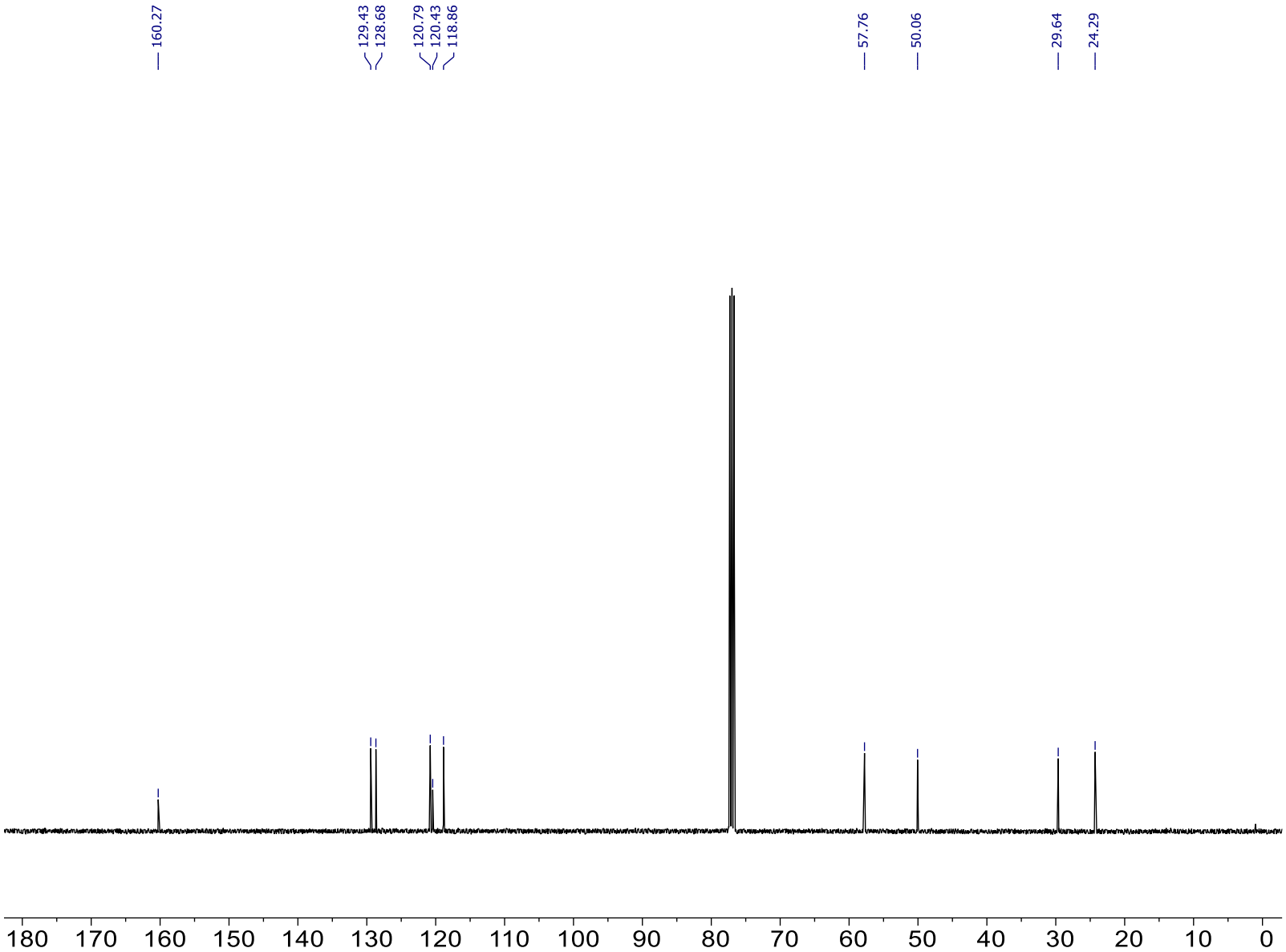


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,H}L_4MoO_2$ (**15b**) in $CDCl_3$.

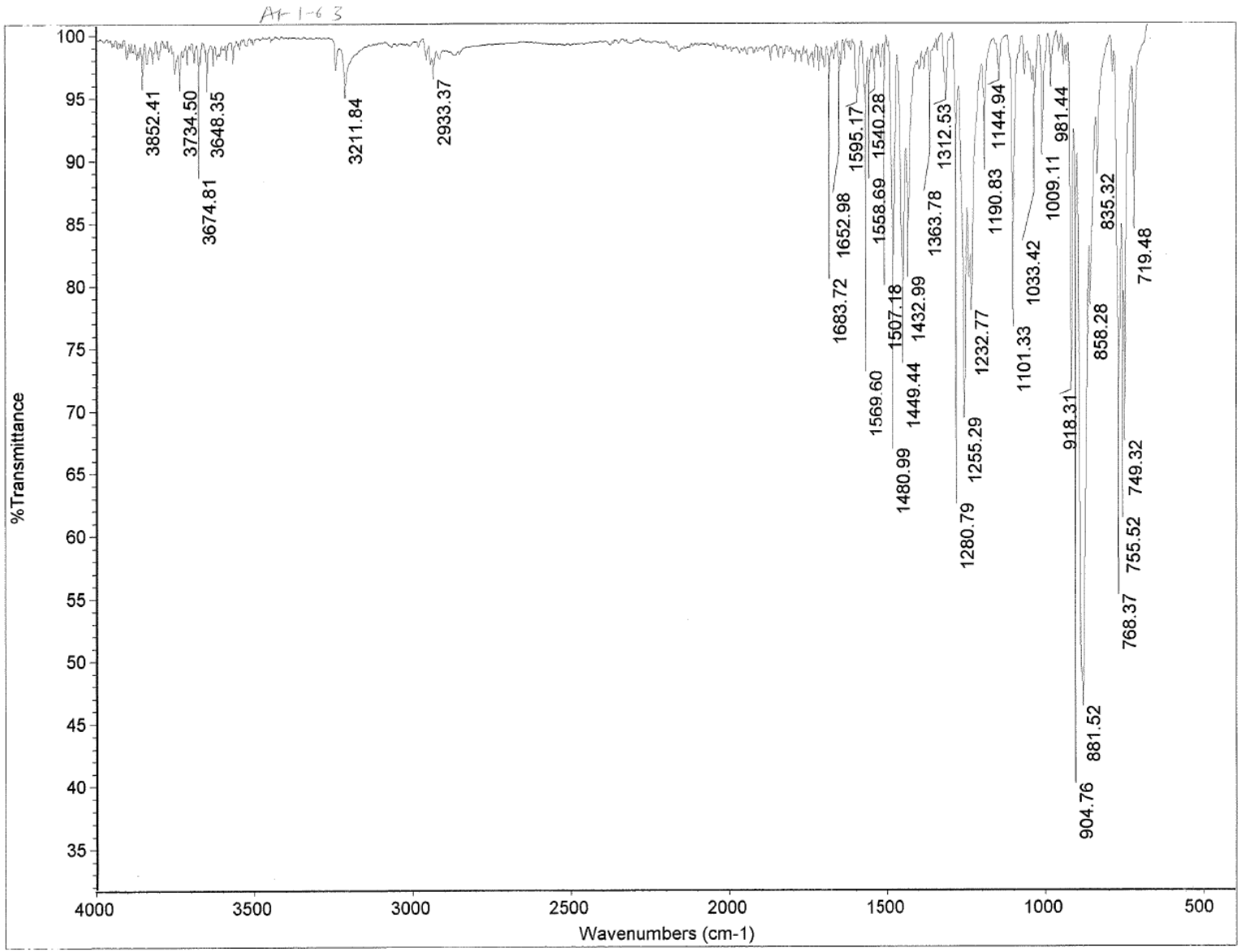


Figure S65. IR spectrum of $^{H,H}L_4MoO_2$ (**15b**).

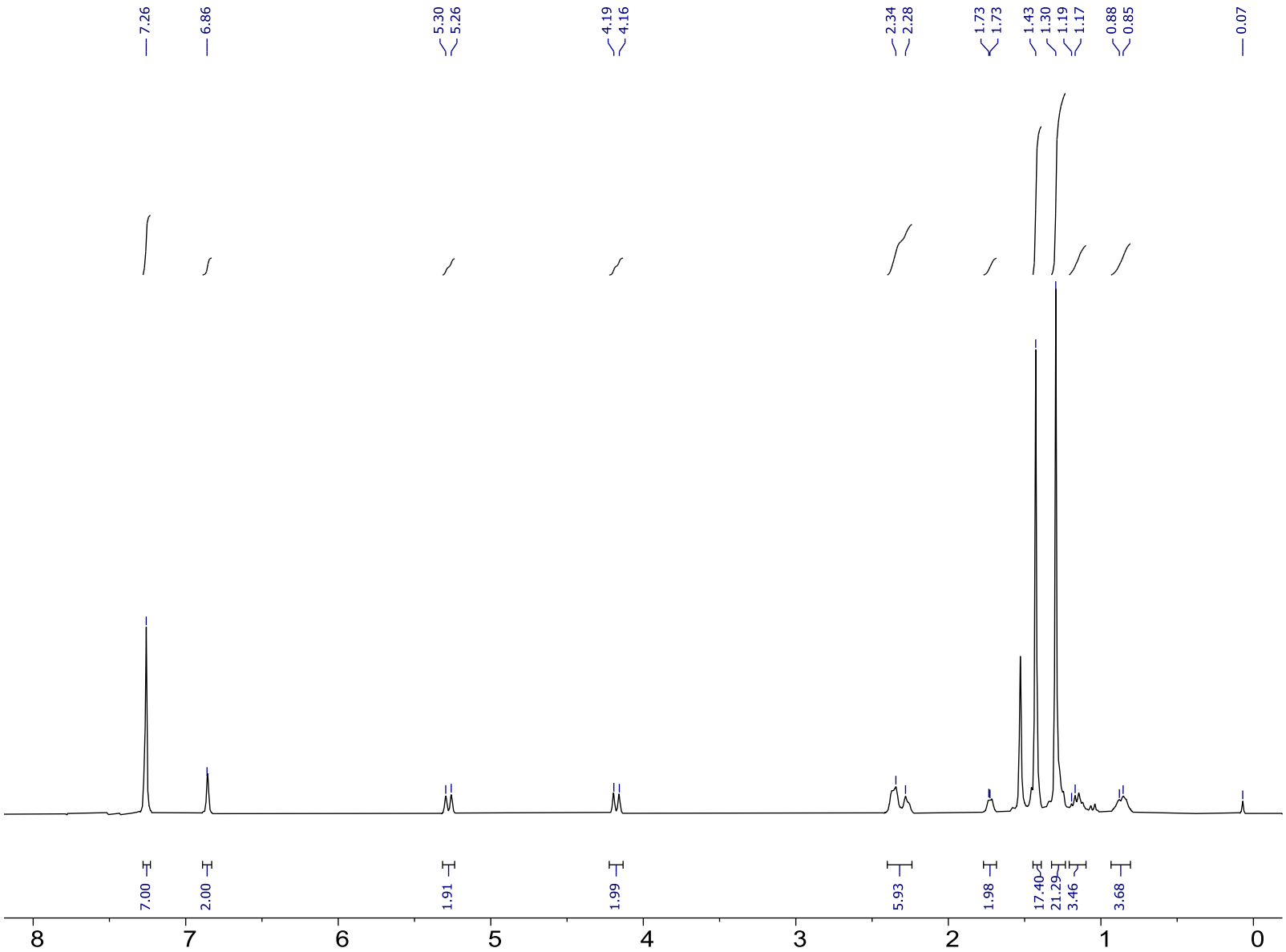


Figure S66. ^{1}H NMR spectrum of $^{tBu,tBu}L_4MoO_2$ (**16b**) in $CDCl_3$.

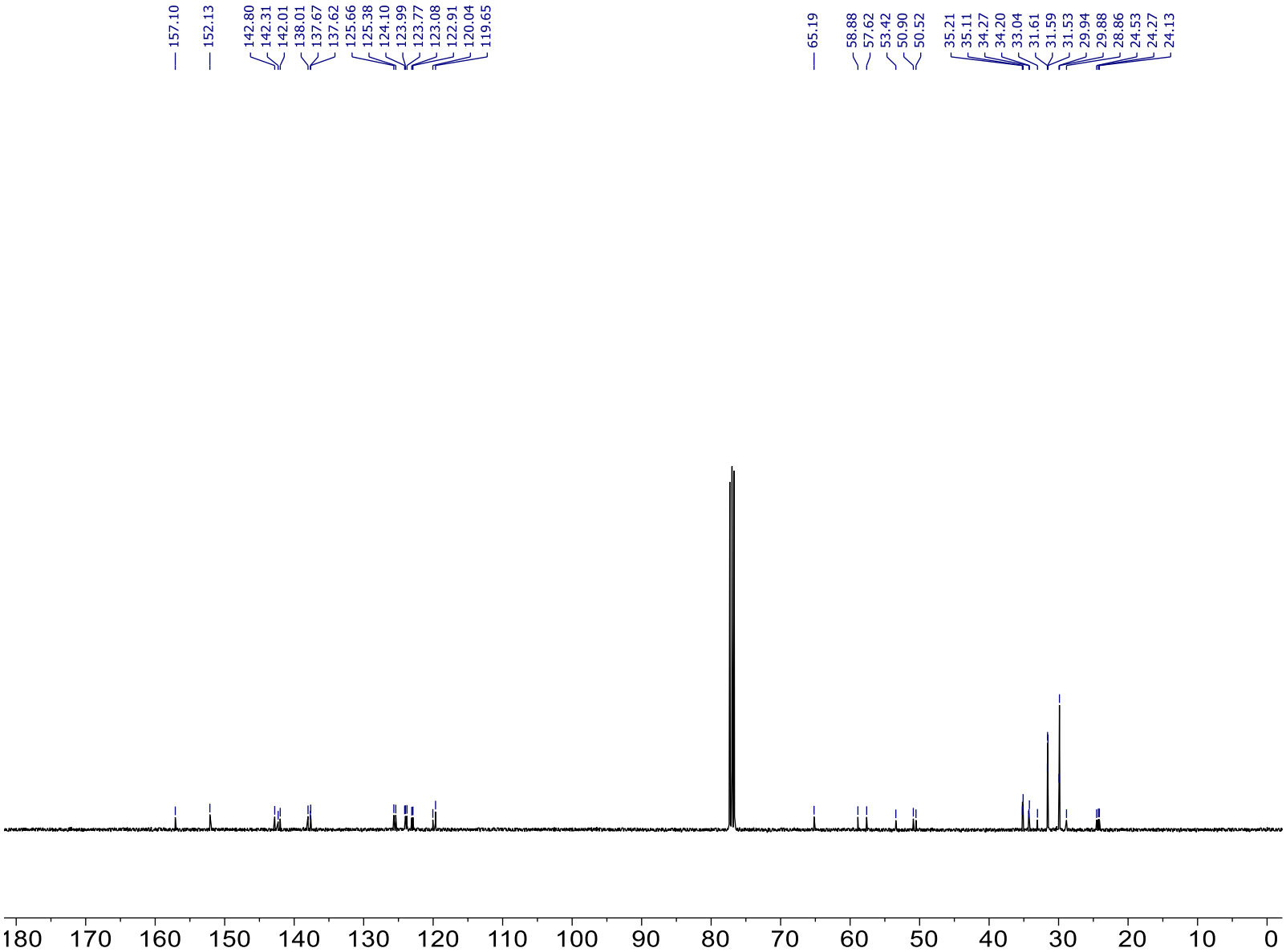


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of $^{tBu,tBu}L_4MoO_2$ (**16b**) in $CDCl_3$.

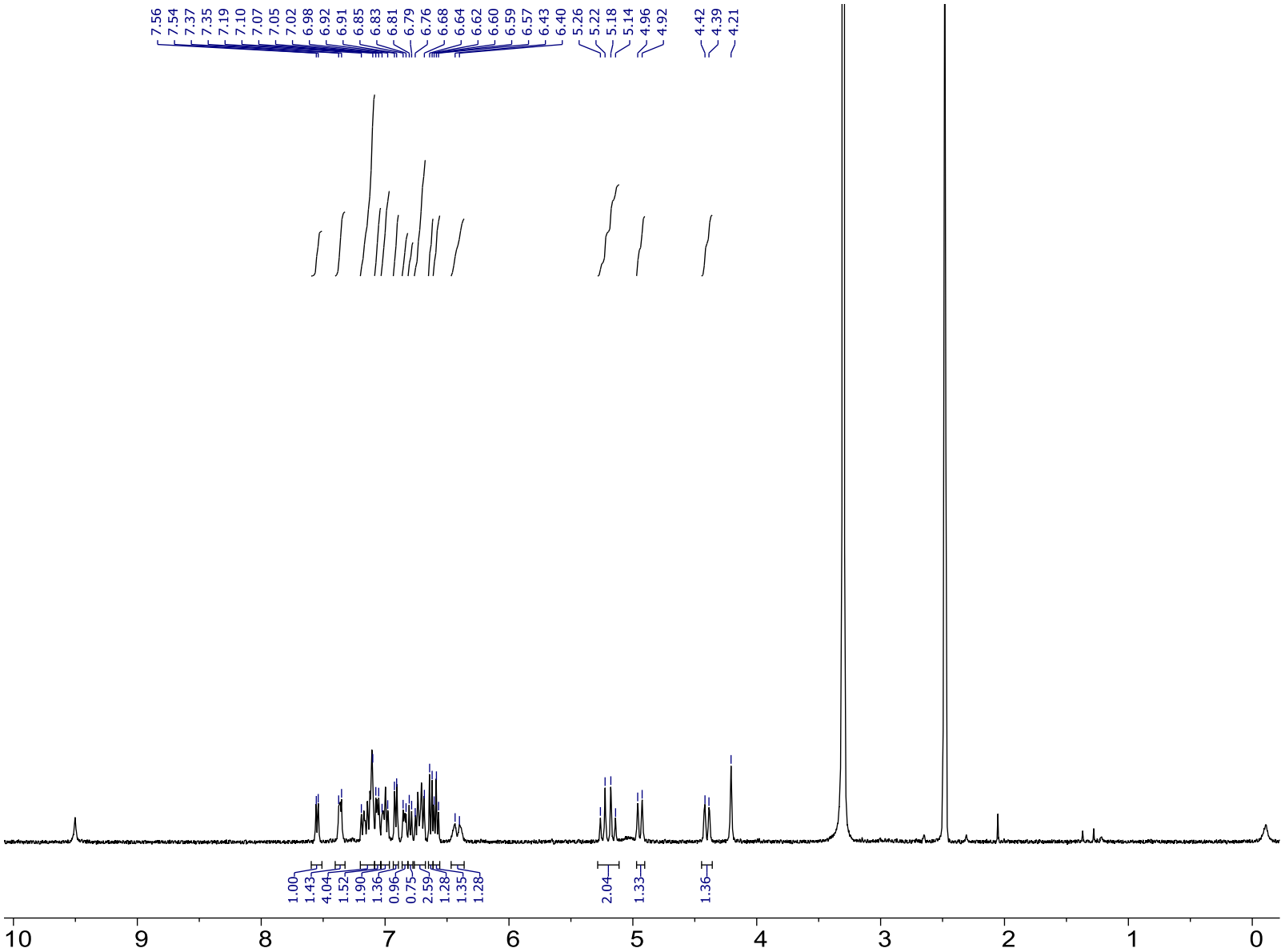


Figure S69. ^{1}H NMR spectrum of $^{H,H}L_5MoO_2$ (**17b**) in DMSO-d_6.

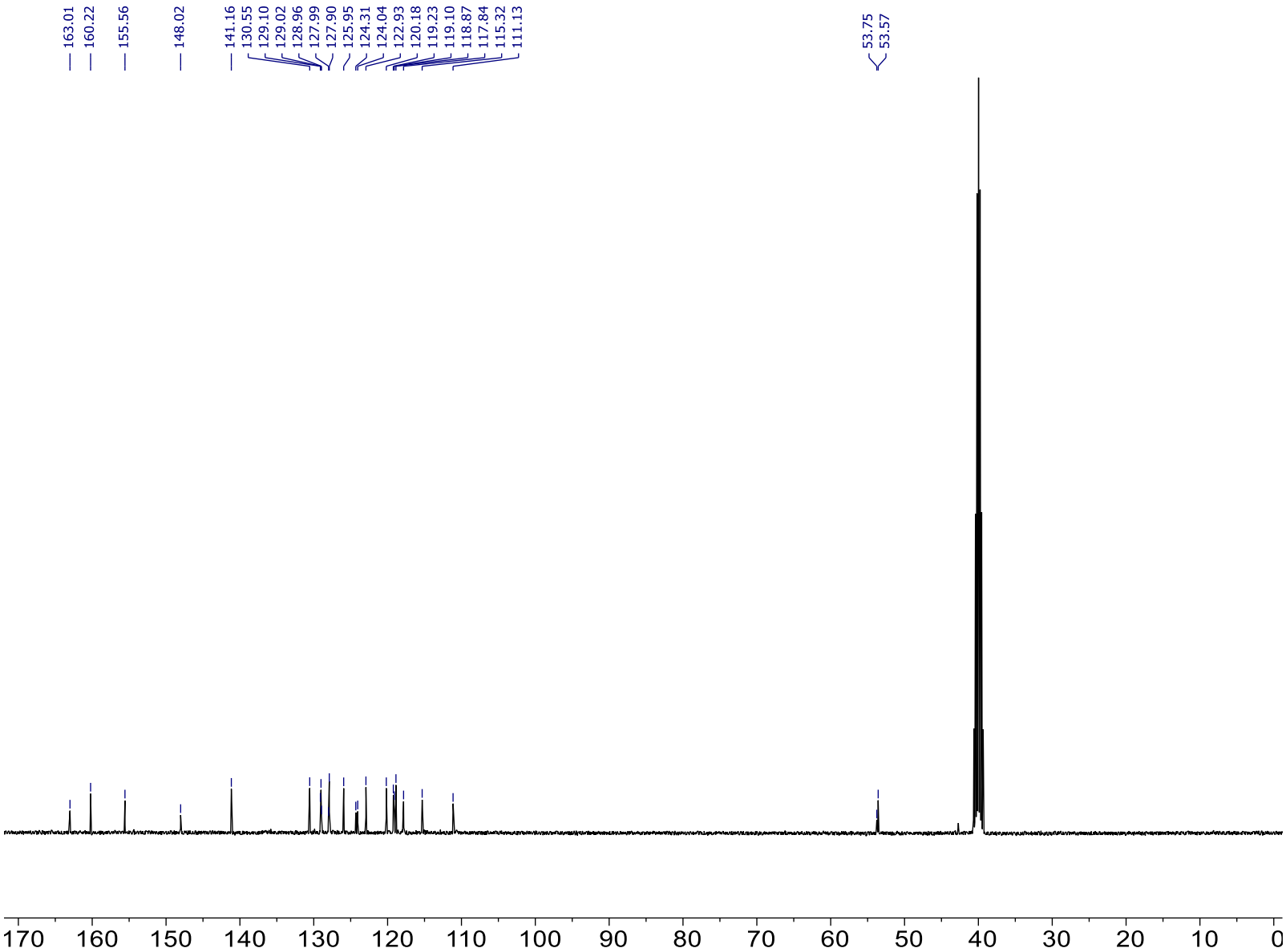


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of $^{H,H}L_5MoO_2$ (**17b**) in DMSO-d_6.

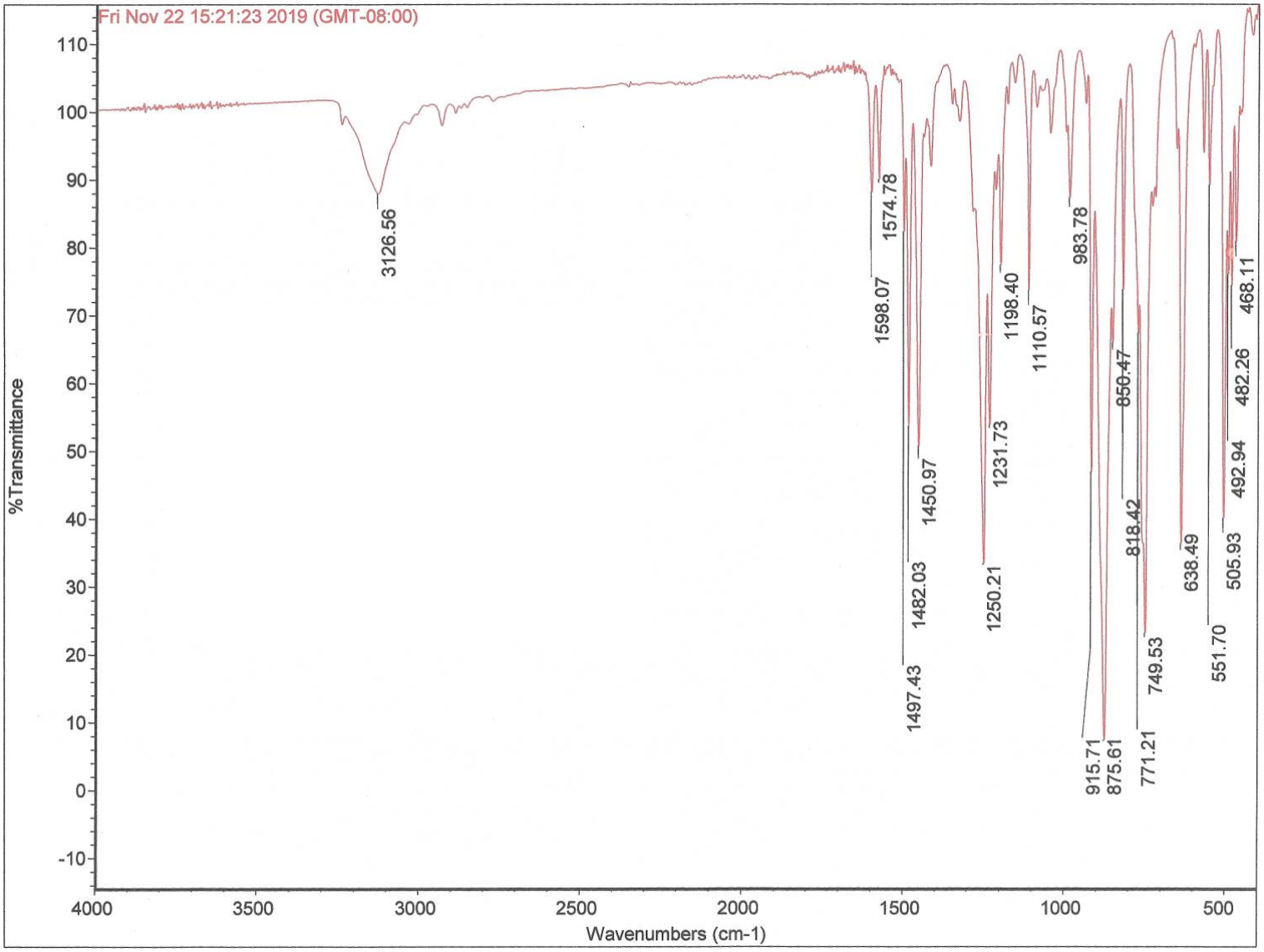


Figure S71. IR spectrum of $^{H,H}L_5MoO_2$ (**17b**).

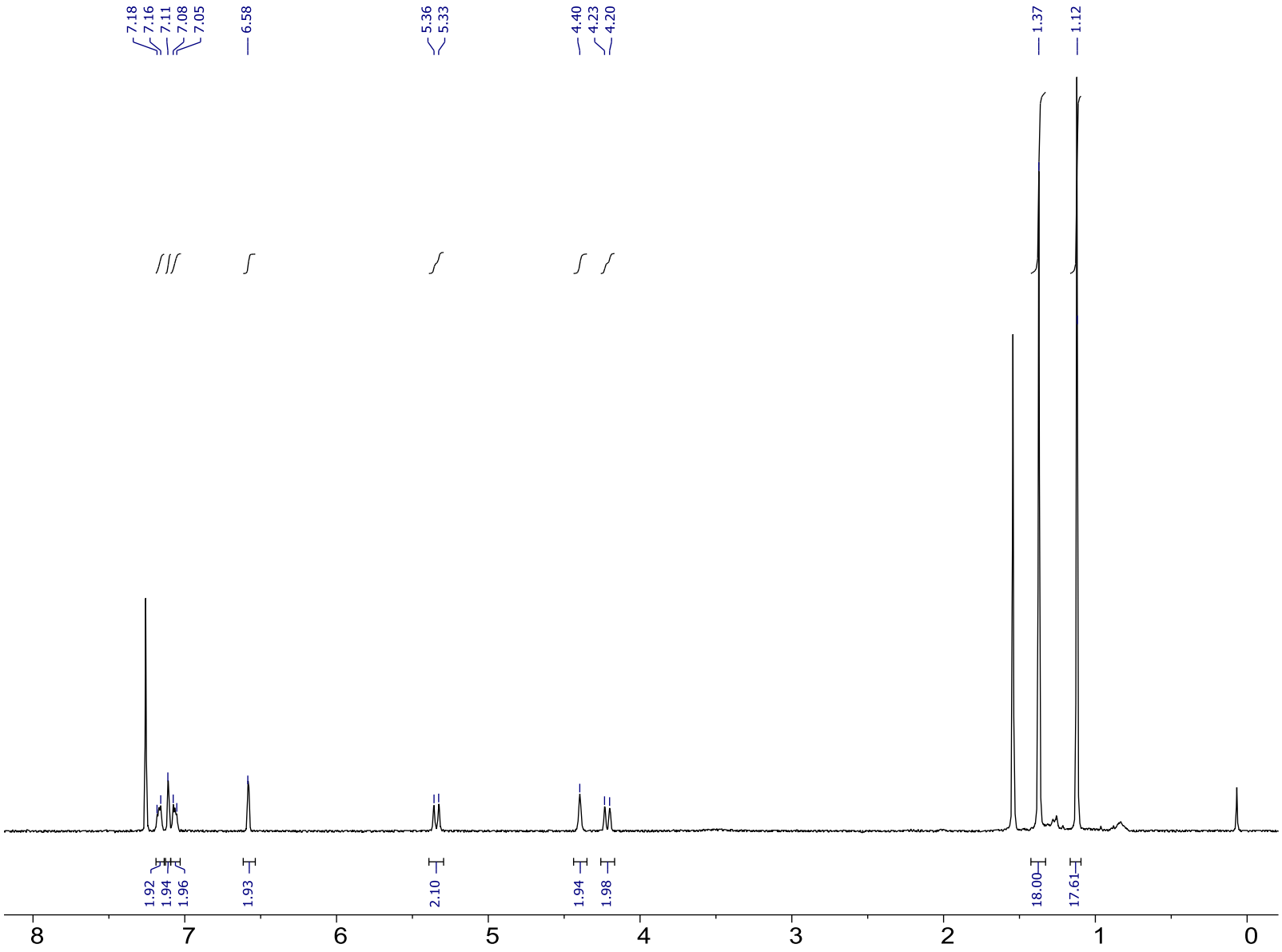


Figure S72. ^{1}H NMR spectrum of $^{tBu,tBu}L_5MoO_2$ (**18b**) in $CDCl_3$.

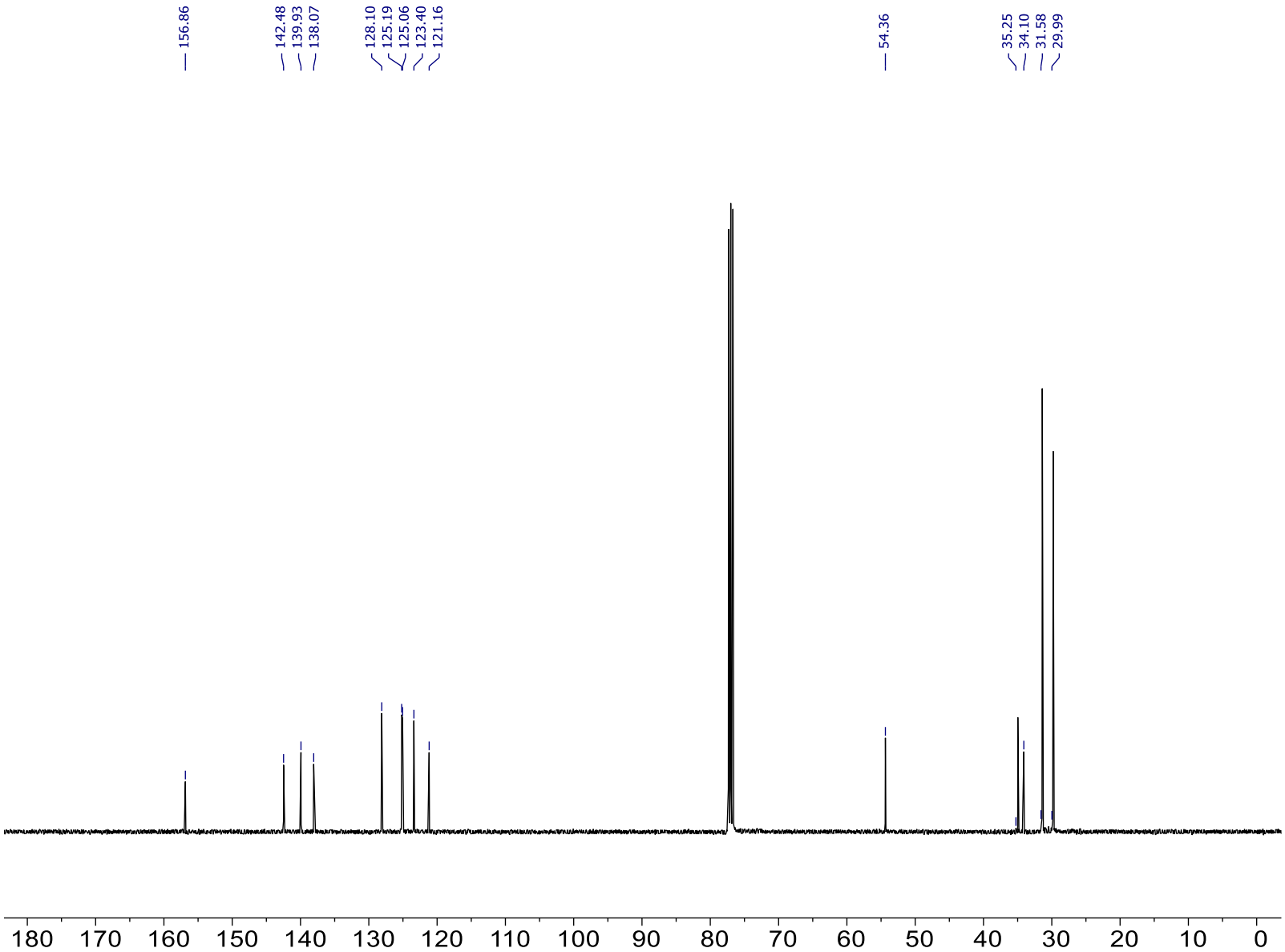


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of $^{tBu,tBu}L_5MoO_2$ (**18b**) in $CDCl_3$.

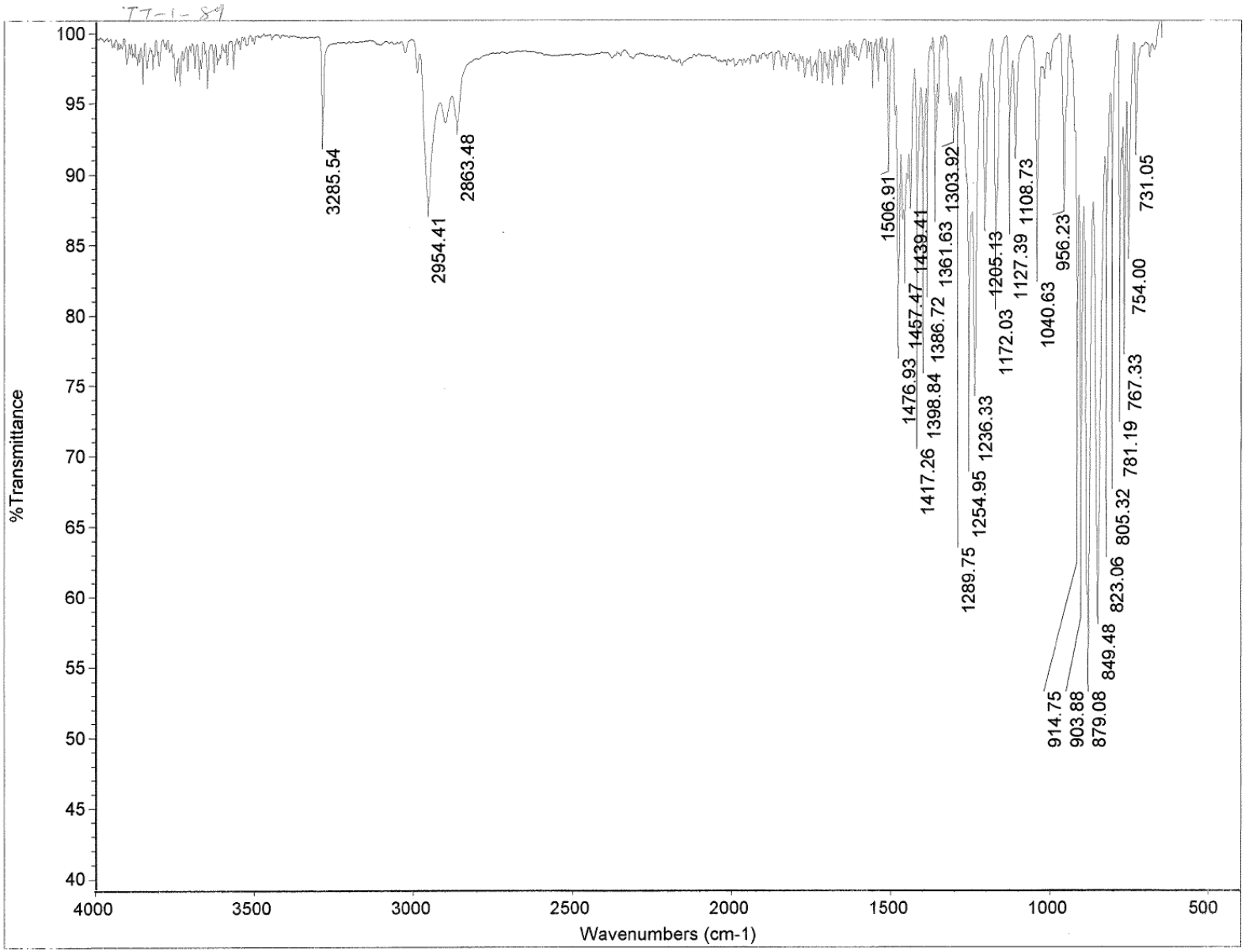


Figure S74. IR spectrum of $^{tBu,tBu}L_5MoO_2$ (**18b**).

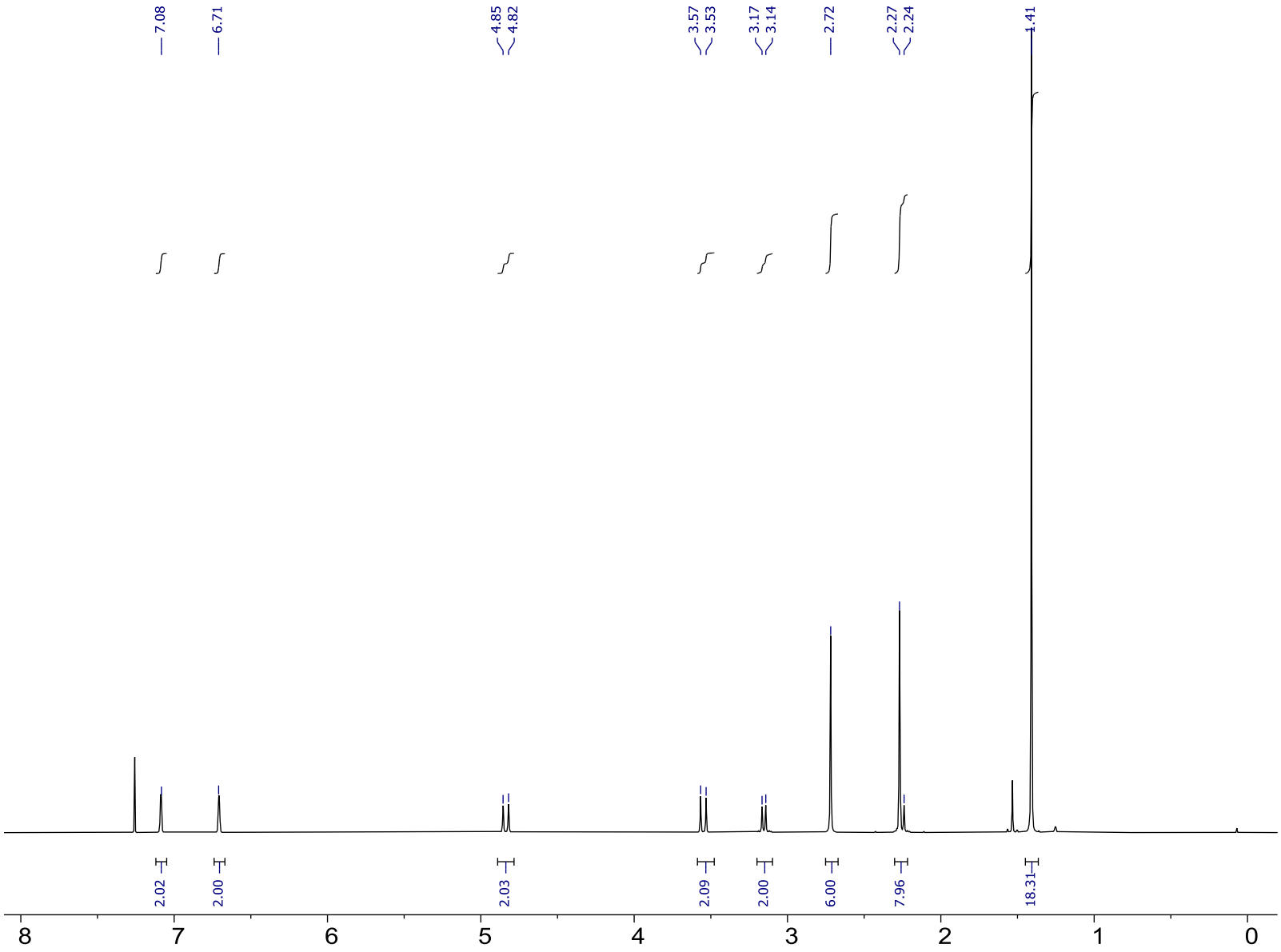


Figure S75. ^{1}H NMR spectrum of $^{tBu,Me}L_6MoO_2$ (**19b**) in $CDCl_3$.

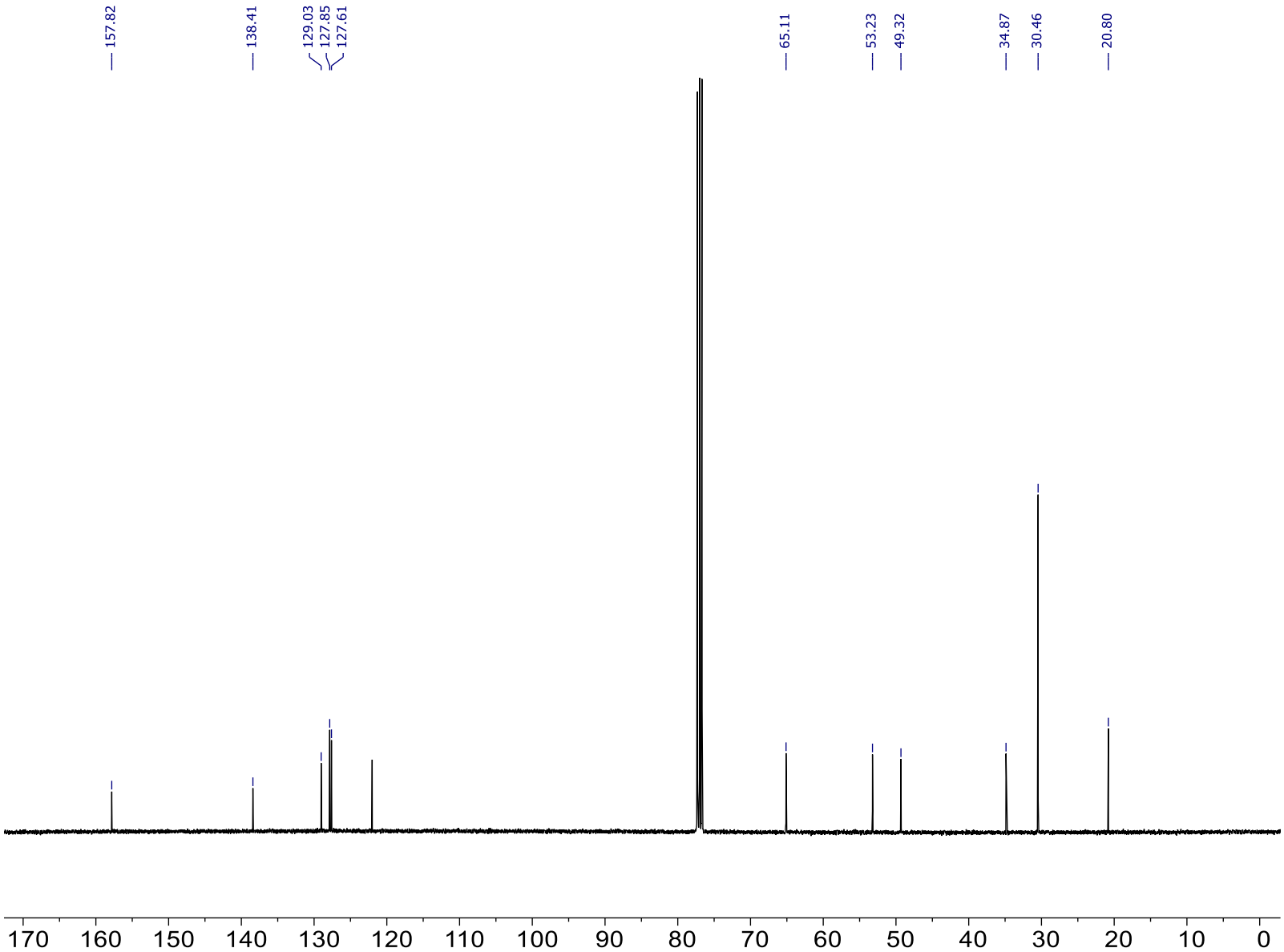


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of $^{tBu,Me}L_6MoO_2$ (**19b**) in $CDCl_3$.

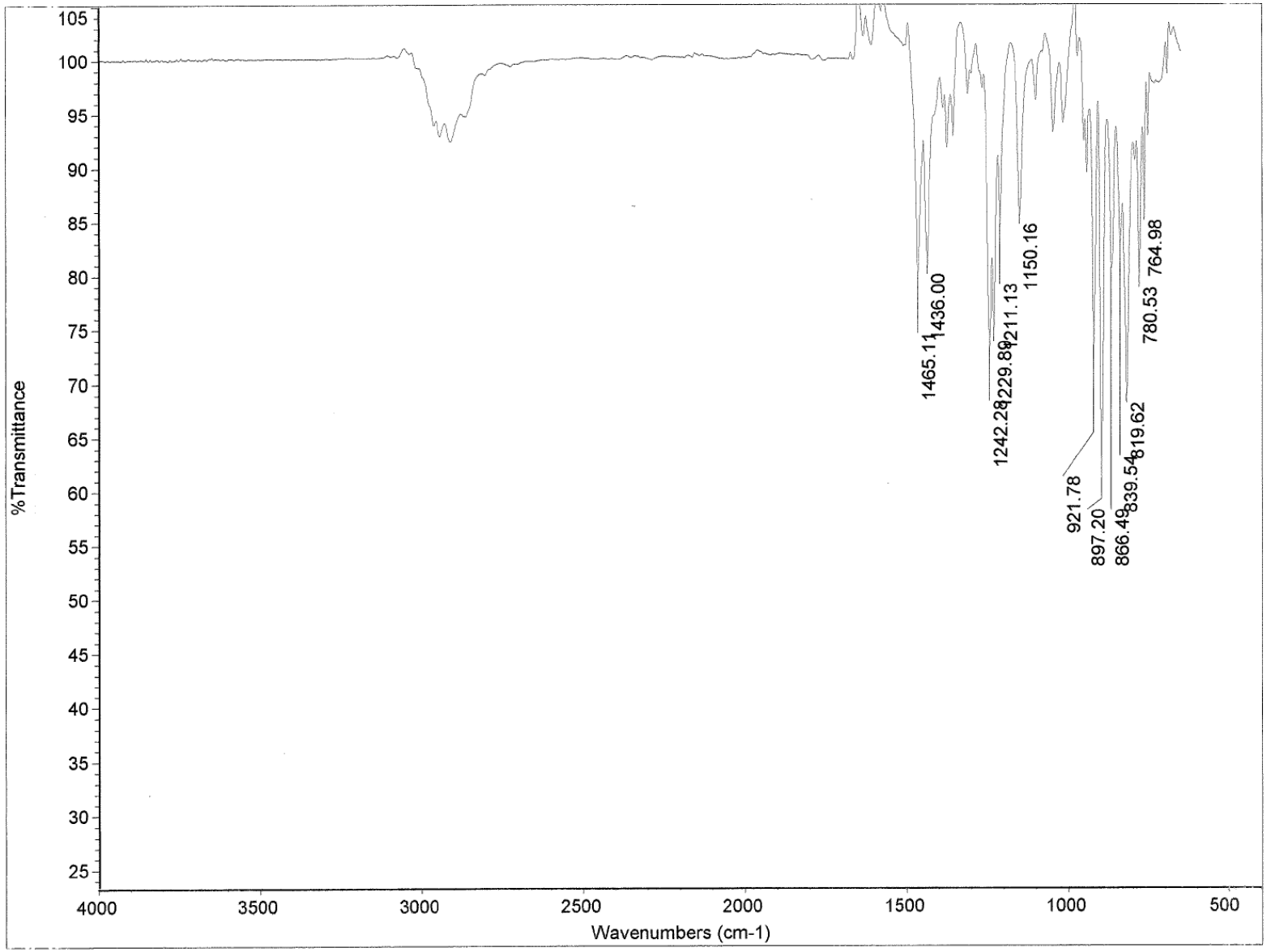


Figure S77. IR spectrum of $^{tBu,Me}L_5MoO_2$ (**19b**).

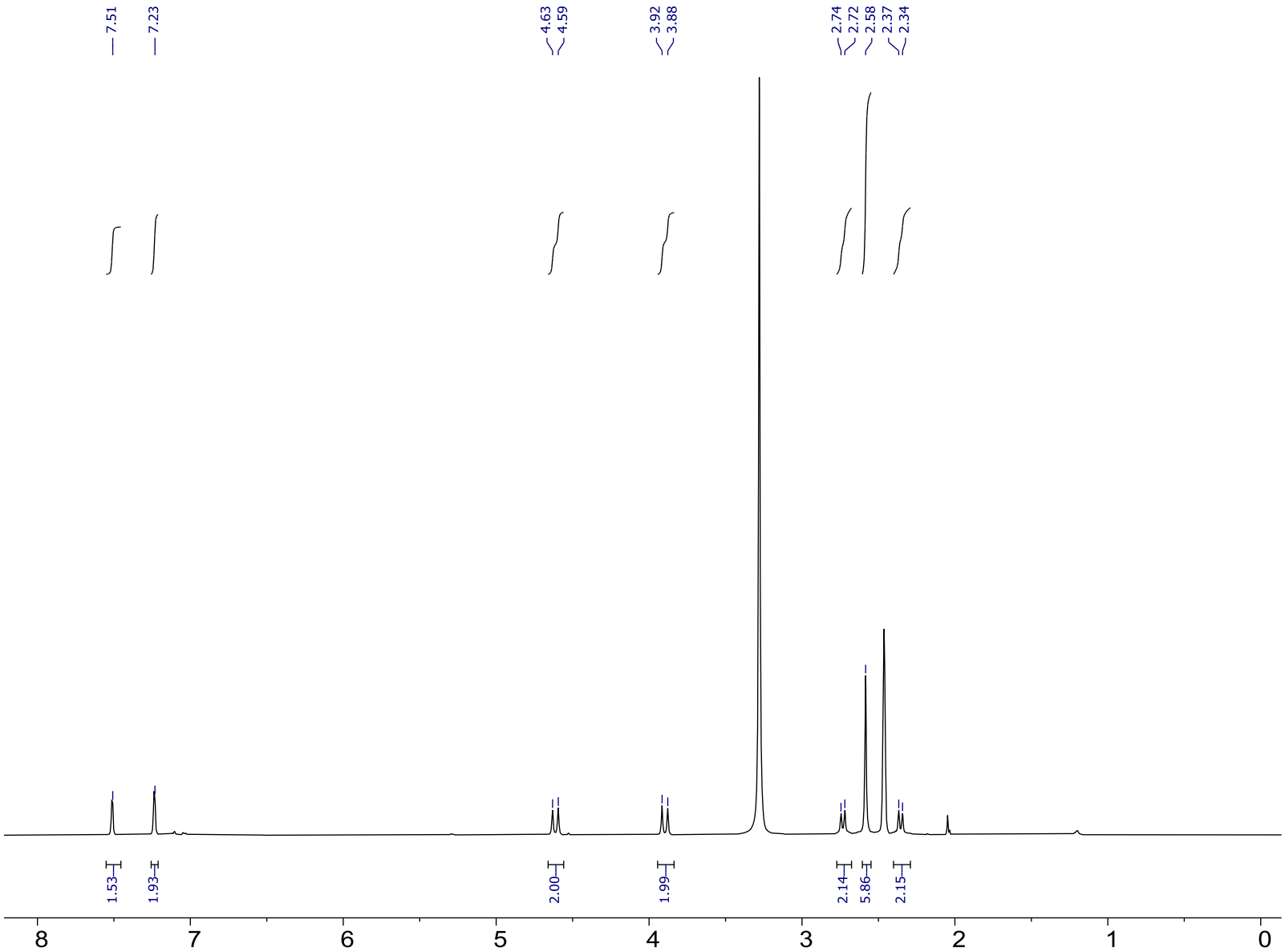


Figure S78. ^{1}H NMR spectrum of $^{Cl,Cl}L_6MoO_2$ (**20b**) in $CDCl_3$.

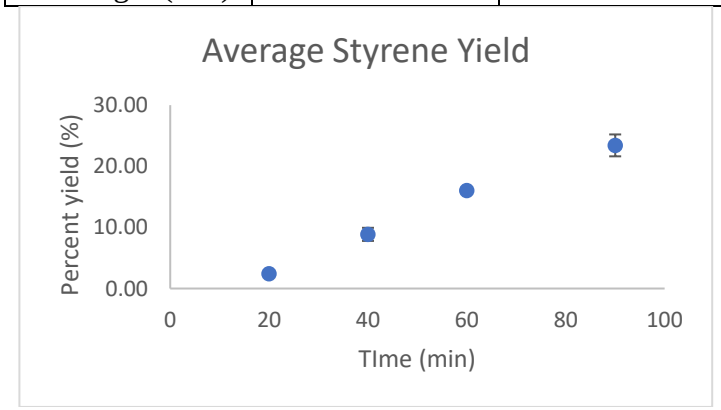
Data from Time-Dependence Study

Catalyst: **1b** – styrene yield {= (integration of peak @5.75ppm)*moles of internal standard)/theoretical yield}

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene yield (trial 1)	Styrene yield (trial 2)	Average styrene yield (%)	Standard Deviation
20	0.17	0.21	2.15	2.66	2.41	0.36
40	0.64	0.76	8.10	9.62	8.86	1.07
60	1.28	1.25	16.20	15.82	16.01	0.27
90	1.95	1.75	24.69	22.15	23.42	1.79
Overnight (16h)	3.17	3.24	40.13	41.02	40.57	0.63

Catalyst: **1b** – styrene glycol remaining

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene glycol (trial 1)	Styrene glycol (trial 2)	Average styrene glycol remaining (%)	Standard Deviation
20	6.51	6.9	82.41	87.35	84.88	0.36
40	5.09	4.76	64.44	60.26	62.35	1.07
60	3.54	3.46	44.81	43.80	44.31	0.27
90	1.61	2.26	20.38	28.61	24.50	1.79
Overnight (16h)	0	0	0.00	0.00	0.00	0



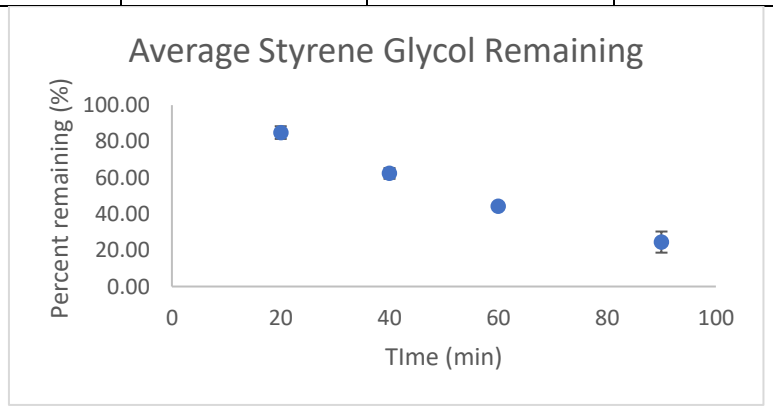


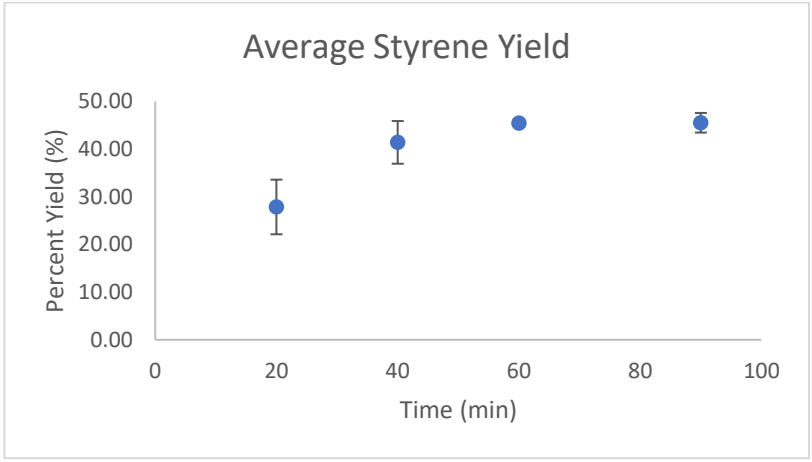
Figure S79. Time-dependence data for conversion of styrene glycol to styrene using **1b** (10 mol%) at 170 °C.

Catalyst: **2b** – styrene yield

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene yield (trial 1)	Styrene yield (trial 2)	Average styrene yield (%)	Standard Deviation
20	1.88	2.52	23.80	31.90	27.85	5.73
40	3.02	3.52	38.23	44.56	41.40	4.48
60	3.58	3.6	45.32	45.57	45.45	0.18
90	3.48	3.71	44.06	46.97	45.51	2.06
Overnight (16h)	3.55	3.87	44.94	48.99	46.97	2.86

Catalyst: **2b** – styrene glycol remaining

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene glycol (trial 1)	Styrene glycol (trial 2)	Average styrene glycol remaining (%)	Standard Deviation
20	4.69	3.14	59.37	39.75	49.56	13.88
40	1.58	0.93	20.00	11.52	15.89	5.82
60	0	0	0.00	0.00	0.00	0.00
90	0	0	0.00	0.00	0.00	0.00
Overnight (16h)	0	0	0.00	0.00	0.00	0.00



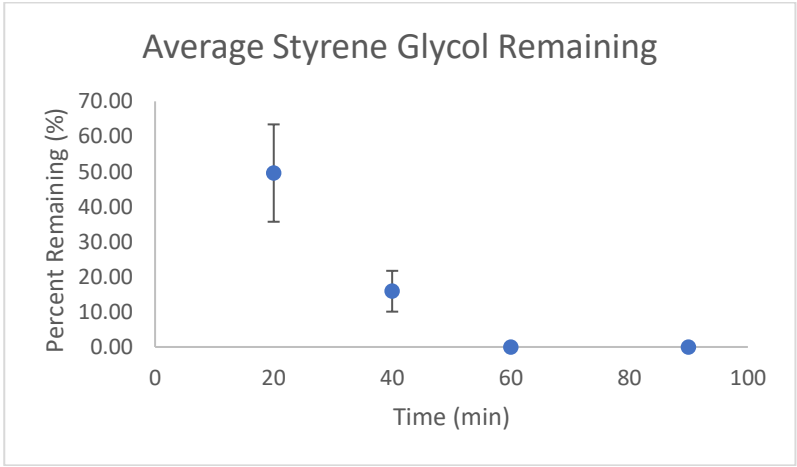


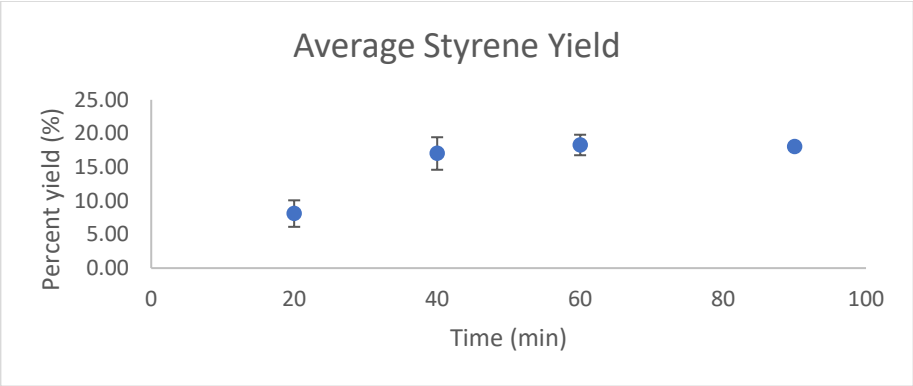
Figure S80. Time-dependence data for conversion of styrene glycol to styrene using **2b** (10 mol%) at 170 °C.

Catalyst: **6b** – styrene yield

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene yield (trial 1)	Styrene yield (trial 2)	Average styrene yield (%)	Standard Deviation
20	.53	.75	6.71	9.49	8.10	1.97
40	1.48	1.21	18.74	15.32	17.03	2.42
60	1.53	1.36	19.37	17.22	18.29	1.52
90	1.41	1.44	17.85	18.23	18.04	.26
Overnight (16h)	3.21	3	40.64	37.98	39.31	1.88

Catalyst: **6b** – styrene glycol remaining

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene glycol (trial 1)	Styrene glycol (trial 2)	Average styrene glycol remaining (%)	Standard Deviation
20	6.91	7.05	87.48	89.25	88.36	1.25
40	5.81	4.51	73.55	57.09	65.32	11.64
60	4.89	4.30	61.91	54.44	58.17	5.28
90	2.97	3.53	37.60	44.69	41.14	5.01
Overnight (16h)	0	0	0	0	0	0



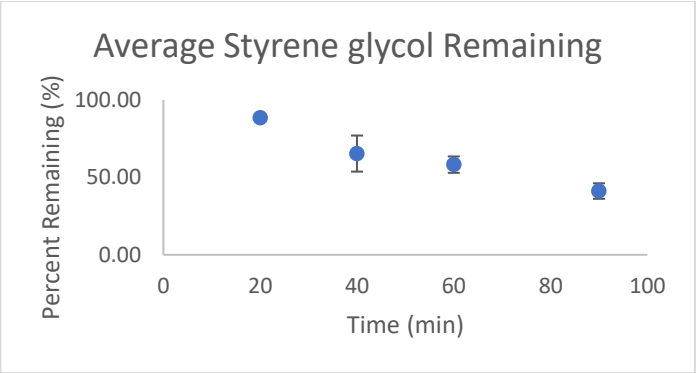


Figure S81. Time-dependence data for conversion of styrene glycol to styrene using **6b** (10 mol%) at 170 °C.

Catalyst: **17b –** styrene yield

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene yield (trial 1)	Styrene yield (trial 2)	Average styrene yield (%)	Standard Deviation
20	0.23	0.19	2.91	2.41	2.66	0.36
40	0.37	0.35	4.68	4.43	4.56	0.18
60	0.49	0.39	6.2	4.94	5.57	0.9
90	0.61	0.54	7.72	6.84	7.28	0.63
Overnight (16h)	1.98	2.02	25.07	25.57	25.32	0.36

Catalyst: **17b** – styrene glycol remaining

Time (min)	NMR integration (Trial 1)	NMR integration (Trial 2)	Styrene glycol (trial 1)	Styrene glycol (trial 2)	Average styrene glycol remaining (%)	Standard Deviation
20	6.40	6.62	81.02	83.81	82.41	0.36
40	5.57	5.92	70.51	74.94	72.73	0.18
60	4.93	5.32	62.41	67.35	64.88	0.9
90	3.88	4.56	49.12	57.73	53.42	0.63
Overnight (16h)	0	0	0	0	0	0

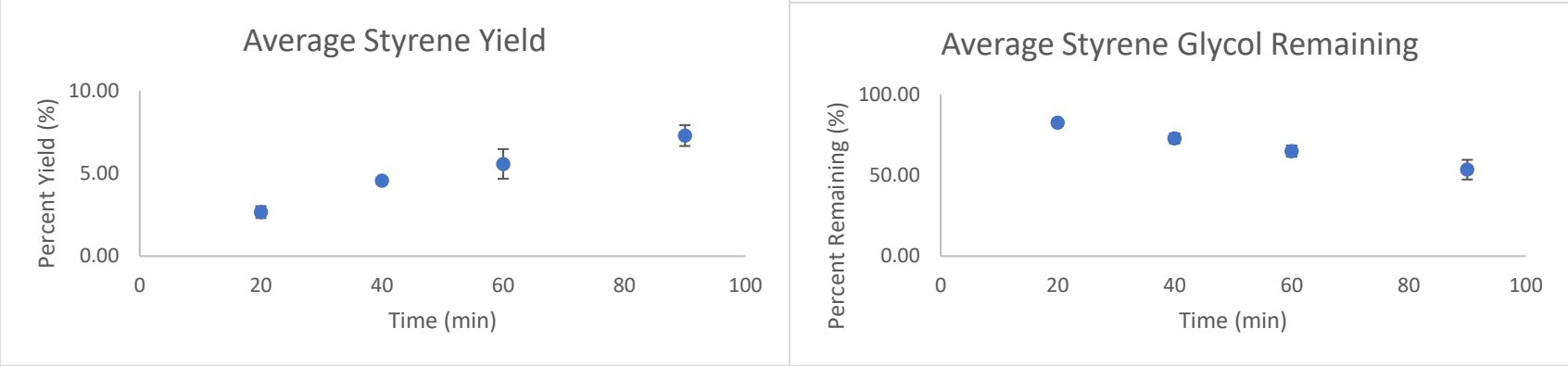


Figure S82. Time-dependence data for conversion of styrene glycol to styrene using **17b** (10 mol%) at 170 °C.

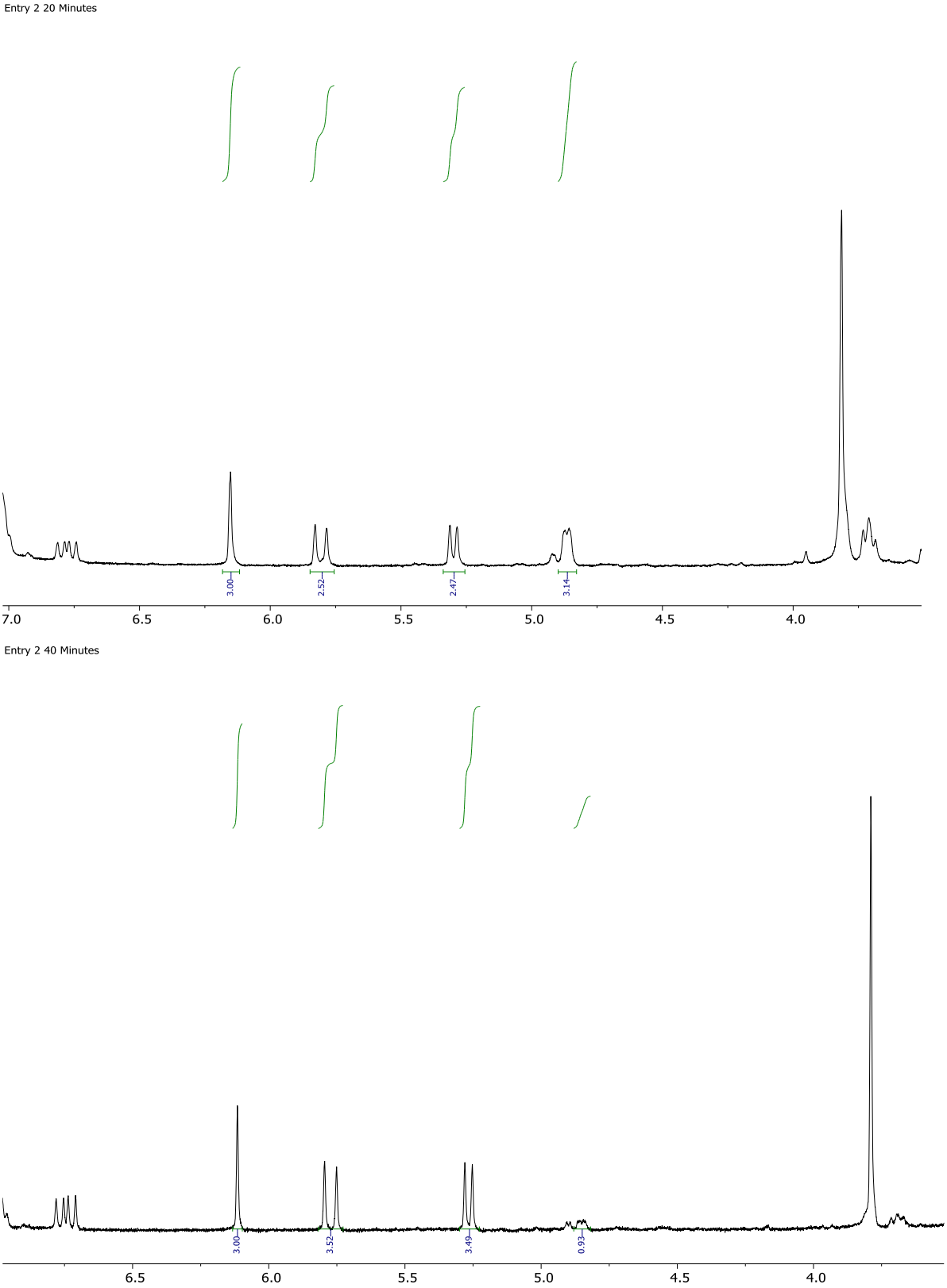


Figure S83. Representative NMR data for DODH of styrene glycol using **2b** at 20 and 40 mins.

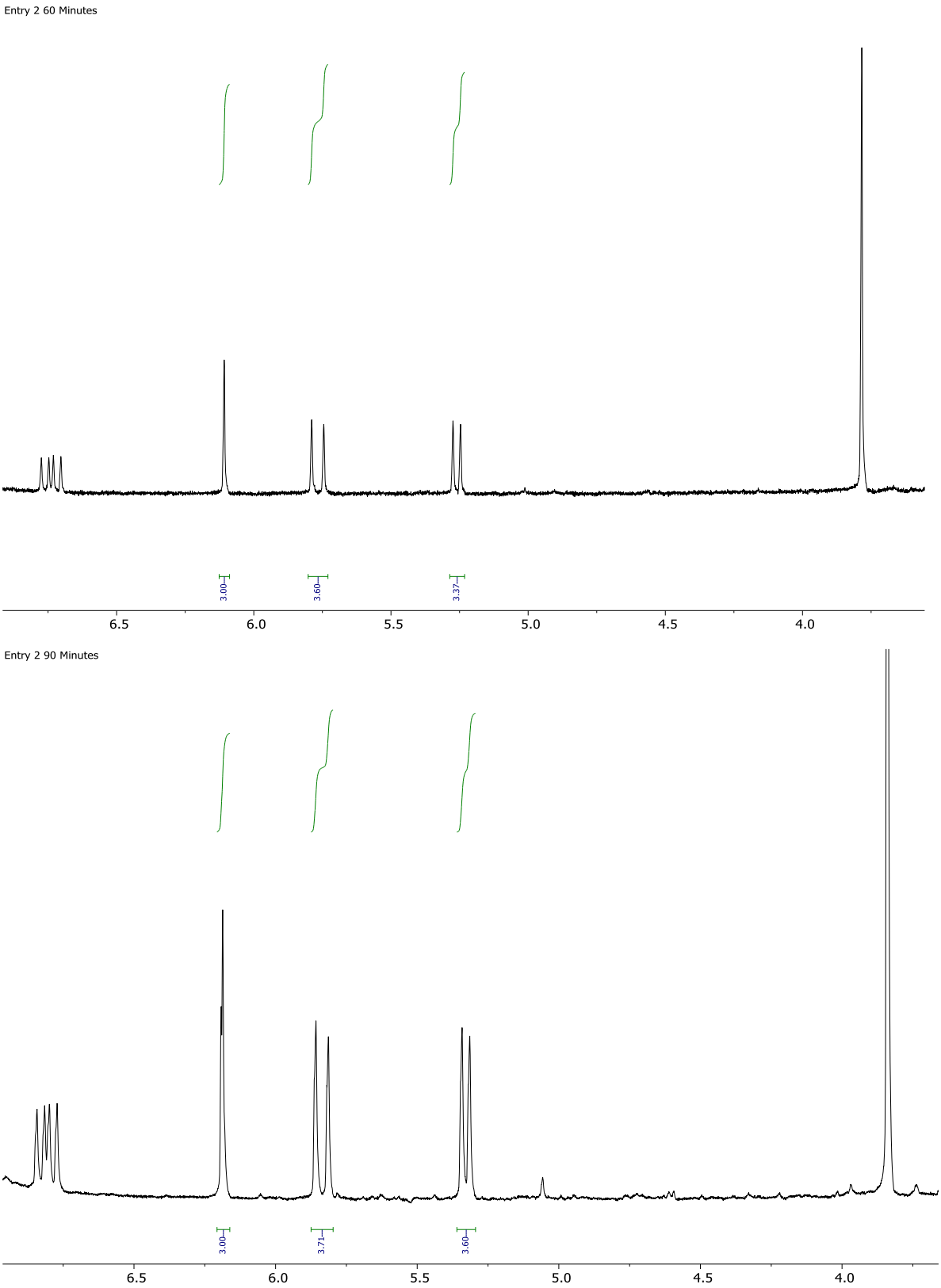


Figure S84. Representative NMR data for DODH of styrene glycol using **2b** at 60 and 90 mins.

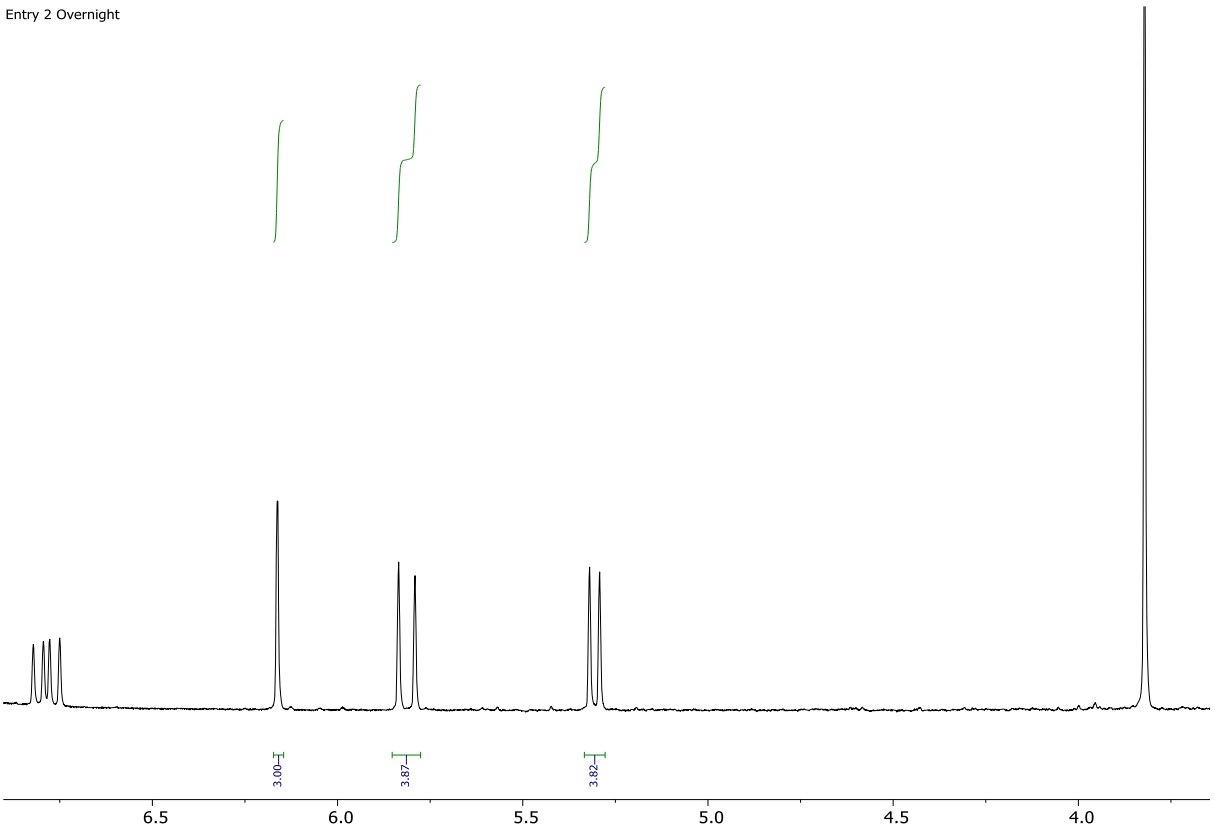


Figure S85. Representative NMR data for DODH of styrene glycol using **2b** after overnight run.