

Supporting Information for

**Influence of the Pendant Arm in Deoxydehydration Catalyzed by
Dioxomolybdenum Complexes Supported by Amine Bisphenolate Ligands**

Timothy C. Siu,[†] Israel Silva Jr.,[†] Maiko J. Lunn, and Alex John*

Chemistry and Biochemistry Department
California State Polytechnic University, Pomona
3801 West Temple Ave., Pomona CA 91768.

Email: ajohn@cpp.edu

Experimental Section

General Procedures:

All air and water sensitive manipulations were carried out under a nitrogen atmosphere by using standard Schlenk line techniques or using an MBraun Labstar pro glovebox. All ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{31}P NMR spectra were collected on a Varian 400-MR spectrometer. Chemical shifts (δ) for ^1H NMR spectra were referenced to the residual protons on deuterated chloroform (7.26 ppm) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to the residual chloroform (77.1 ppm). Infra-red spectra were recorded on a Thermo Scientific NICOLET iS10 Spectrophotometer equipped with a SMART iTR. Gas Chromatography-Mass Spectrometric (GC-MS) analysis was performed on an Agilent 6850 series GC system connected to an Agilent 5973N Mass Selective Detector equipped with a HP-5MS column (30m \times 0.25mm \times 0.25 μm). Elemental analysis was performed at Robertson Microlit Laboratories (New Jersey, USA). Precursors for ligand and complex synthesis were used as received. CDCl_3 was used as received from Sigma. Solvents (methanol, toluene, and hexanes) were purchased from Fisher Scientific and used as received. All starting materials were procured from commercial sources and used without further purification. The ligands (**1a-5a**) and complex **5b** used in this study were synthesized by modifications of literature protocols.^{1,2}

Synthesis of aminebisphenolate ligands

Synthesis of **1a**: To a round bottom flask was added 2-tert-butyl-4-methylphenol (1.00 g, 6.09 mmol), 2-aminomethylpyridine (0.321g, 2.97 mmol) and 37% aqueous formaldehyde (0.366 g, 12.2 mmol) in methanol (*ca.* 5 mL). The mixture was refluxed for 24 hours at the end of which it was cooled to room temperature. The reaction mixture was then filtered to collect the product as a white powder (0.393 g, 28 %): ^1H NMR (CDCl_3 , 400MHz, 28 $^\circ\text{C}$) δ 10.5 (s, 2H), 8.70 (d, 1H,

$^3J_{\text{HH}} = 8 \text{ Hz}$), 7.70 (t, 1H, $^3J_{\text{HH}} = 8 \text{ Hz}$), 7.30 (t, 1H, $^3J_{\text{HH}} = 8 \text{ Hz}$), 7.11 (d, 1H, $^3J_{\text{HH}} = 8 \text{ Hz}$), 7.00 (s, 2H), 6.74 (s, 2H), 3.81 (s, 2H), 3.75 (s, 4H), 2.23 (s, 6H), 1.39 (18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 26 °C, 100 MHz) δ 156.1, 154.0, 148.2, 137.4, 137.2, 129.0, 127.2, 127.1, 123.7, 122.6, 122.1, 56.3, 55.3, 34.8, 29.7, 20.8.

Synthesis of 2a: To a round bottom flask was added *N,N* dimethylethyldiamine (0.205 g, 2.33 mmol), 2-tert-butyl-4-methylphenol (0.767g, 4.66 mmol), 37% aqueous formaldehyde (0.212g, 7.07 mmol) and water (*ca.* 10 mL). The resulting mixture was refluxed for 24 hours before gravity filtered and methanol washed to receive a white precipitate (0.434 g, 43%). ^1H NMR (CDCl_3 , 400 MHz, 28°C) δ , 9.61 (s, 2H), 6.97 (s, 2H), 6.69 (s, 2H), 3.54, (s, 4H), 2.55 (s, 4H), 2.28 (s, 6H), 2.22, (s, 6H), 1.37 (s, 18H).

Synthesis of 3a: To a stirred mixture of 2-tert-butyl-4-methylphenol (5.00 g, 30.4 mmol), water (*ca.* 13mL), and 37% formaldehyde (2.26 mL, 0.123 mol), 2-methoxyethylamine (1.14 g, 15.2 mmol) was added drop wise. The mixture was refluxed for 24 hours before triturating with cold methanol to form a white precipitate. The beige precipitate was gravity filtered and washed with methanol and the product was obtained after drying (5.46 g, 84 %) ^1H NMR (CDCl_3 , 28 °C, 400 MHz) δ 8.37 (s,2H), 6.99 (s, 2H), 6.70 (s, 2H), 3.69 (s, 4H), 3.50 (t, 2H, $^3J_{\text{HH}} = 8 \text{ Hz}$), 3.45 (s, 3H), 3.50 (t, 2H, $^3J_{\text{HH}} = 8 \text{ Hz}$), 2.22 (s, 3H), 1.39 (s, 18H).

Synthesis of 4a: To a stirred mixture of 2-tert-butyl-4-methylphenol (10.0 g, 60.9 mmol) water (*ca.* 32 mL), and 37% formaldehyde (4.53 mL, 0.061 mol), benzylamine (3.26 g, 30.4 mmol) was added dropwise. The mixture was refluxed for 24 hours before triturating with cold methanol to form a white precipitate. The white precipitate was gravity filtered and washed with methanol and the product was obtained after drying (11.9 g, 85 %). ^1H NMR (CDCl_3 , 28 °C, 400 MHz) δ 7.39-7.30 (m, 5H), 6.99 (s, 2H), 6.74 (s, 2H), 3.59 (s, 4H), 3.53 (s, 2H), 2.23 (s, 6H), 1.38 (s, 18H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 26 °C, 100 MHz) δ 152.3, 137.6, 136.8, 129.6, 129.1, 129.0, 128.1, 128.0, 127.5, 122.1, 58.5, 56.6, 34.7, 29.6, 20.8.

Synthesis of **5a**: To a round bottom flask was added 2-picolyamine (0.500 g, 4.62 mmol) and 3,5 di-*tert*-butyl-2-hydroxybenzylbenzaldehyde (1.08 g, 4.62 mmol) in methanol (*ca.* 15 mL). The mixture was stirred at room temperature for 2 hours before addition of NaBH_4 (0.175 g, 4.62 mmol). After addition of NaBH_4 , the mixture was then further stirred at room temperature for 2 hours. The mixture was then extracted with dichloromethane and washed with water. After extraction, the solvent was evaporated to dryness and ethyl acetate (*ca.* 2 mL) was added. The resulting solution was concentrated on the rotary evaporator to produce a white precipitate (0.491g, 32%). ^1H NMR (CDCl_3 , 400 MHz, 28°C) δ , 8.58 (d, 1H, $^3J_{\text{HH}} = 8$ Hz), 7.66 (t, 1H, $^3J_{\text{HH}} = 8$ Hz), 7.26–7.19 (m, 4H), 6.85 (s, 1H), 3.99 (s, 2H), 3.95 (s, 2H), 1.43 (s, 9H), 1.29 (s, 9H).

Representative procedure for deoxydehydration reactions.

A pressure tube reactor was charged with diol (.500 mmol), reductant (.750 mmol), molybdenum complex (.050 mmol) and 2.5 mL of solvent. The reactor tube was sealed and the reaction mixture was stirred at 170 °C for 24 hours. The reactions were cooled to room temperature before adding the internal standard for analysis. 1,3,5-trimethoxybenzene (.010 g, .059 mmol) was added after the 24 hours in heat as an internal standard. An aliquot of the sample of the reaction mixture was analyzed by ^1H NMR in CDCl_3 . The integration of peaks corresponding to the internal standard to diol and alkene product was used to determine yield of alkene product and carbonyl compound.

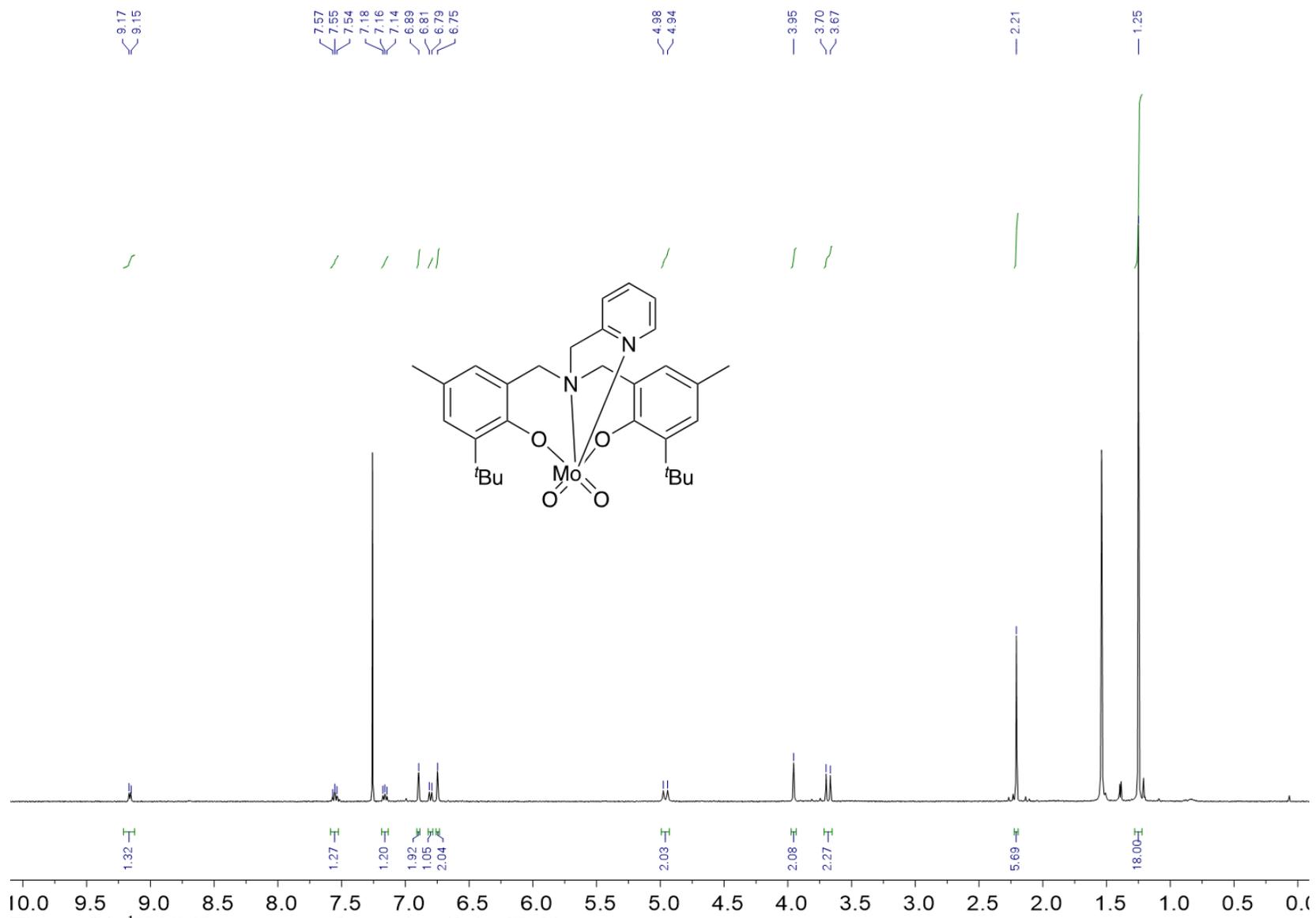
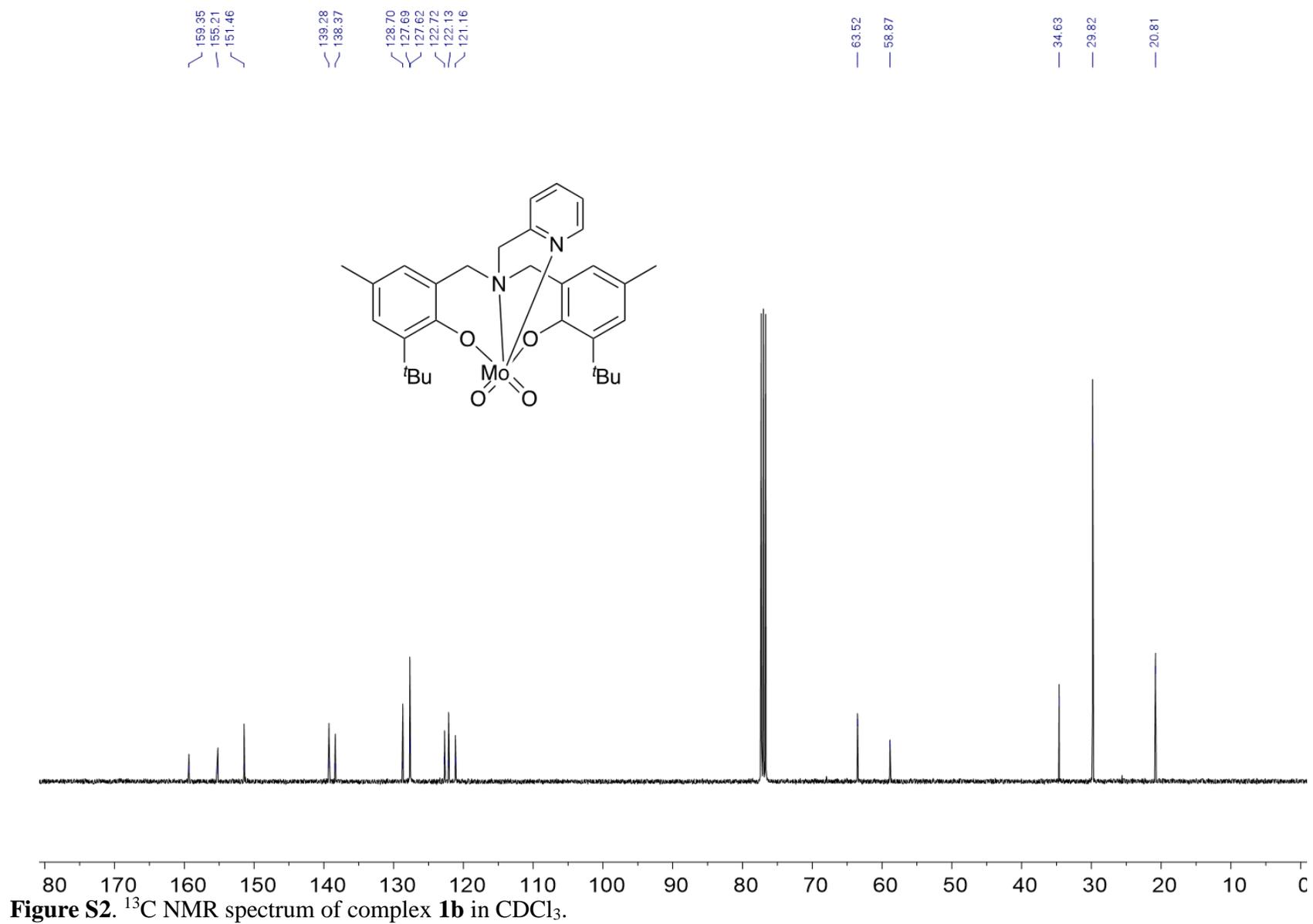
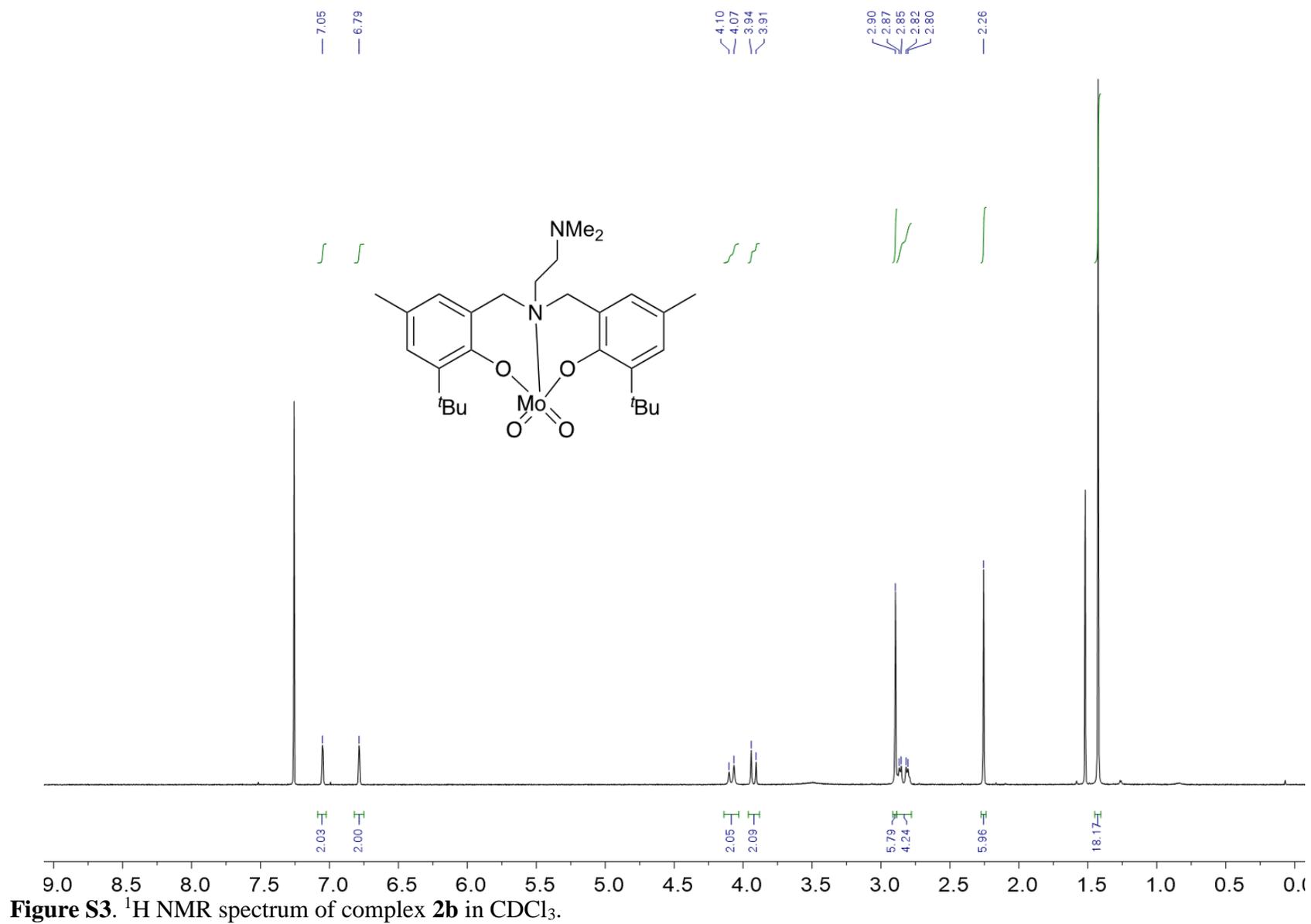


Figure S1. ¹H NMR spectrum of complex **1b** in CDCl₃.





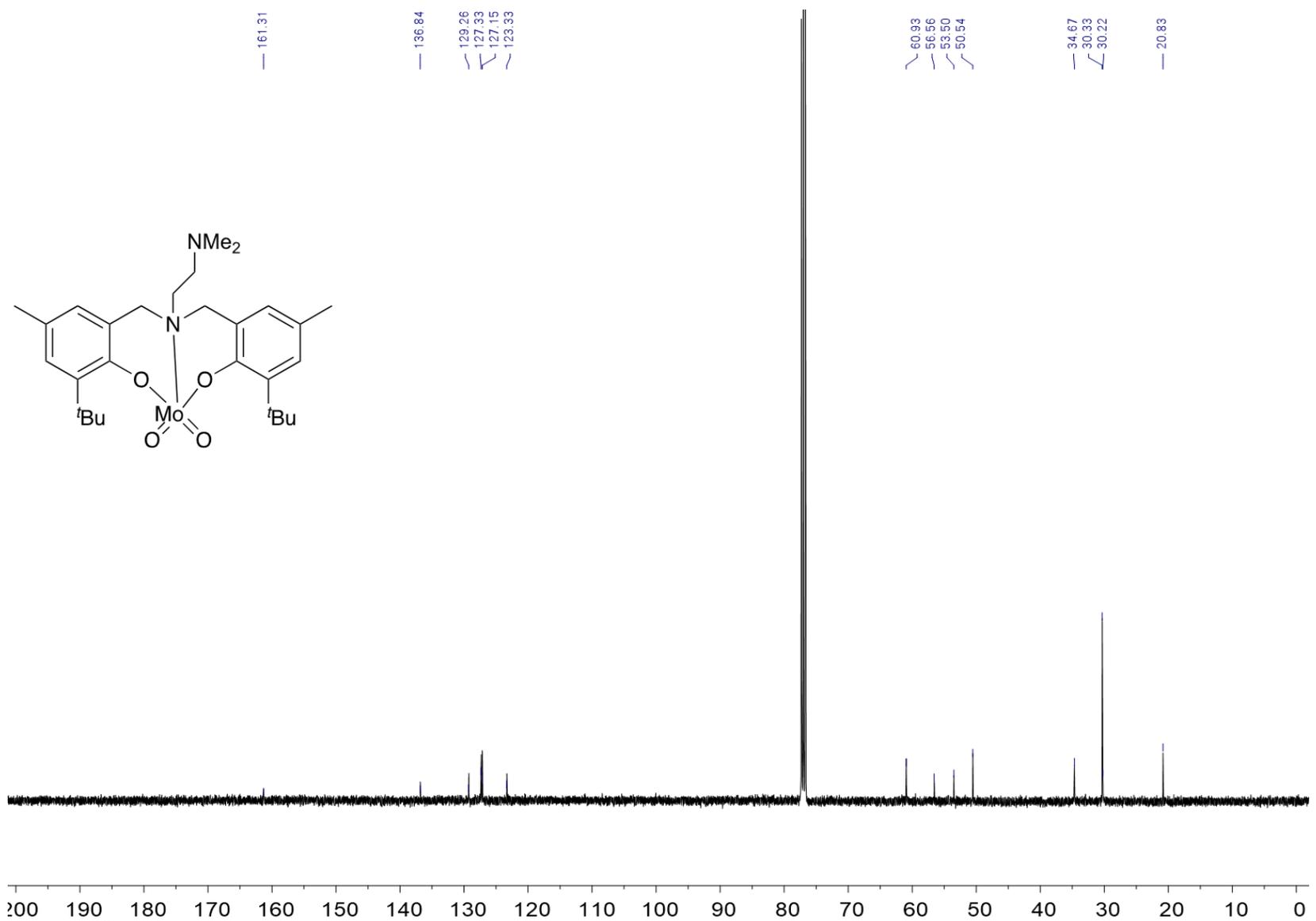
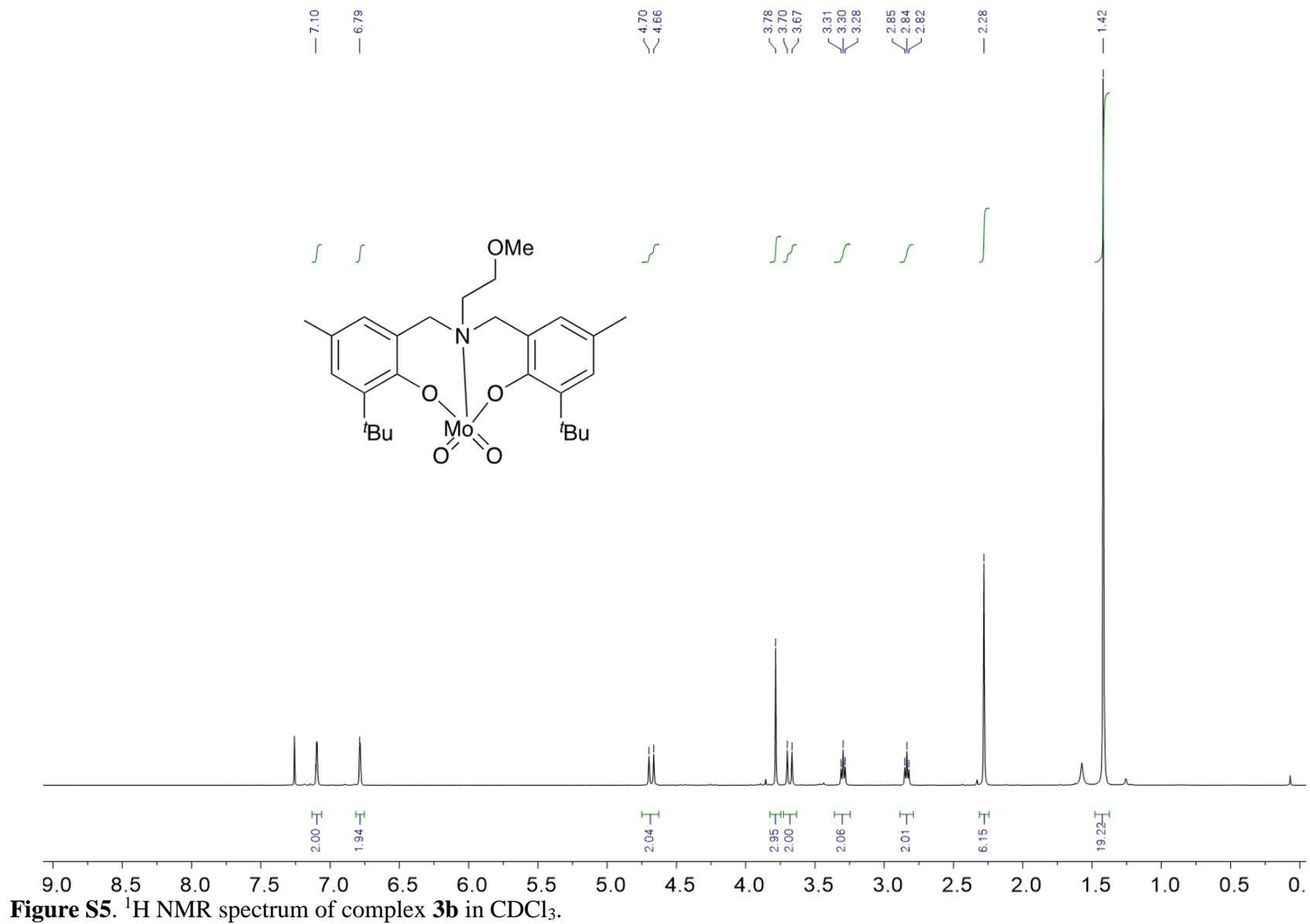


Figure S4. ¹³C NMR spectrum of complex **2b** in CDCl₃.



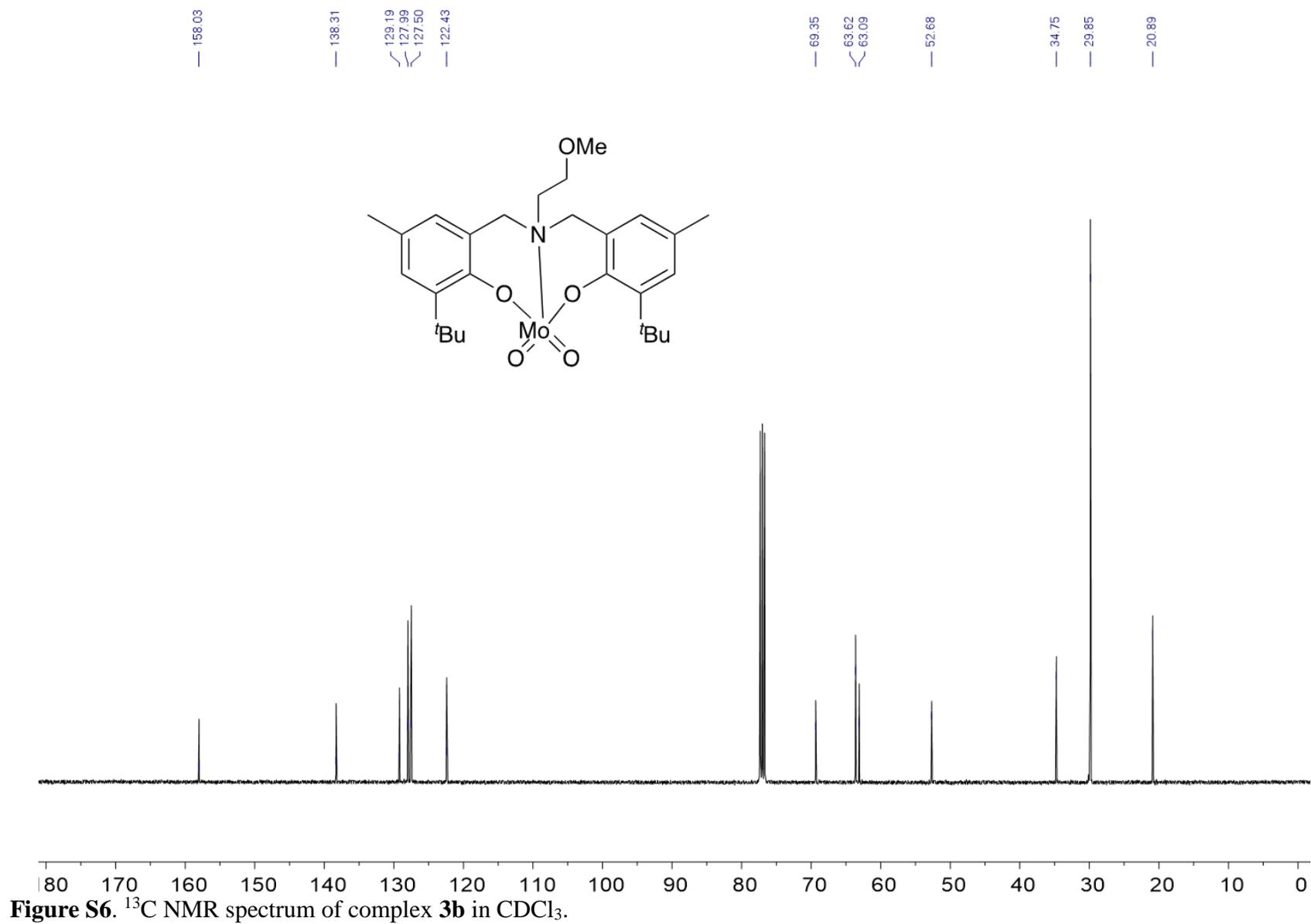


Figure S6. ^{13}C NMR spectrum of complex **3b** in CDCl_3 .

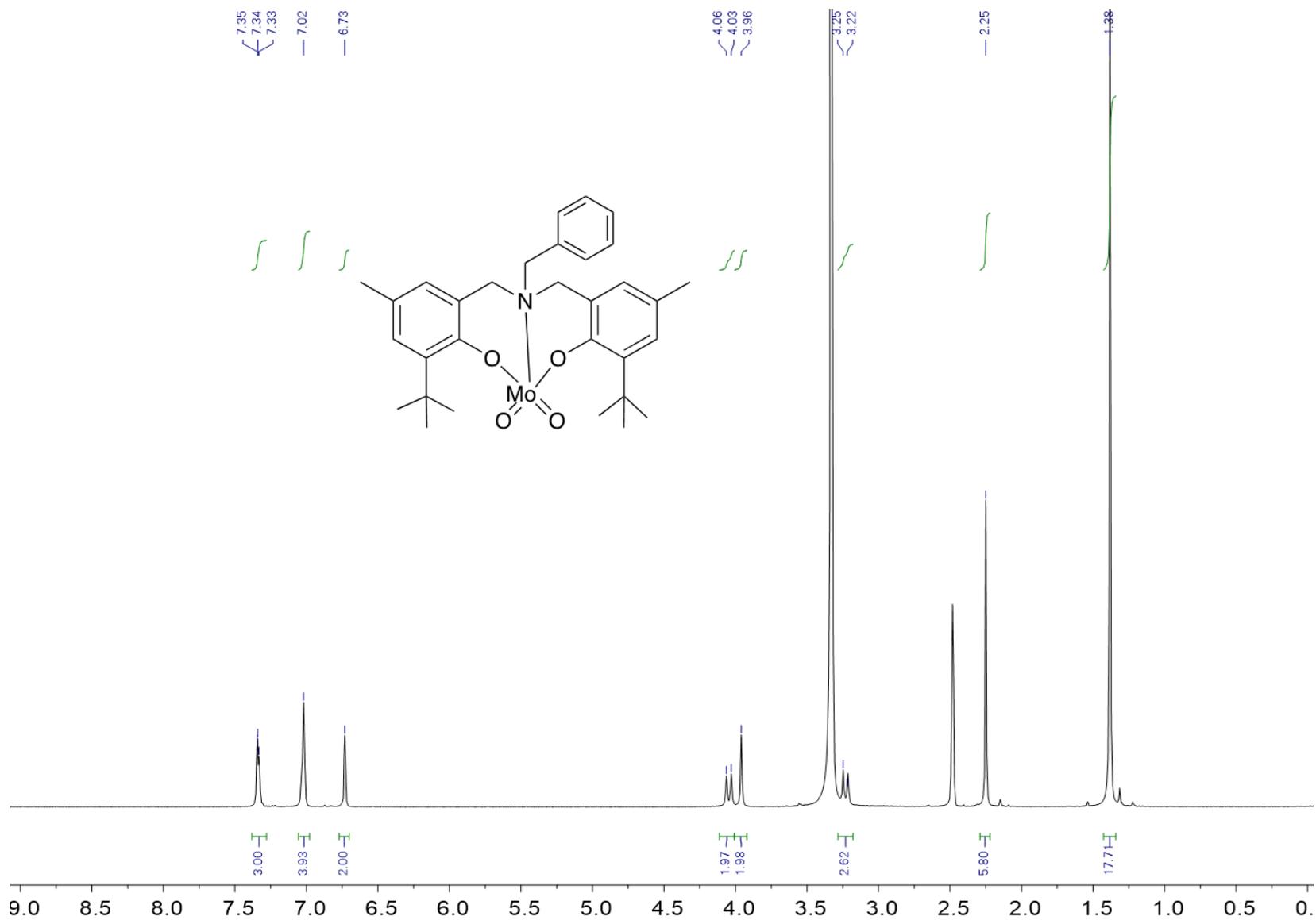


Figure S7. ¹H NMR spectrum of complex **4b** in DMSO-*d*₆.

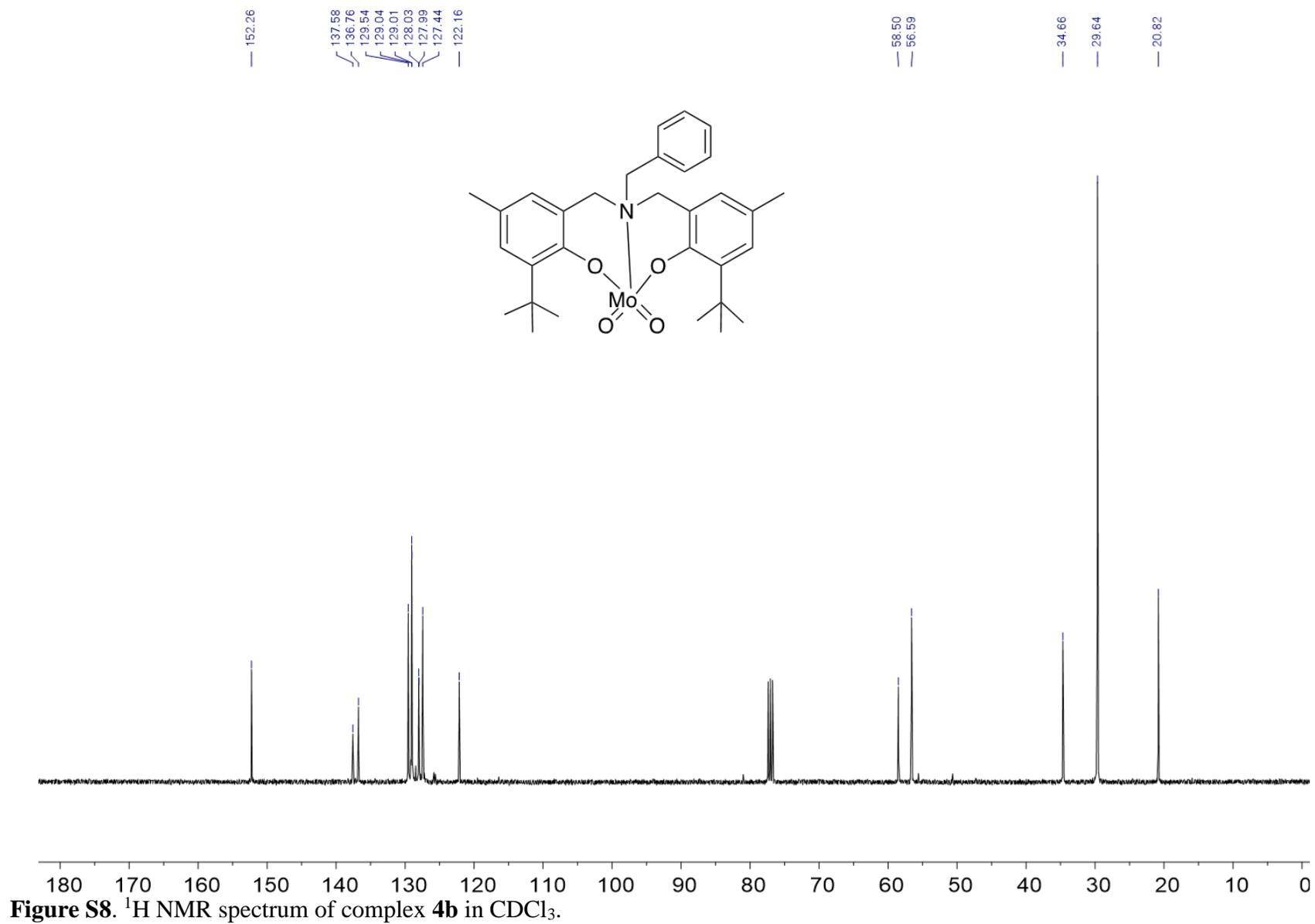


Figure S8. ¹H NMR spectrum of complex **4b** in CDCl₃.



Figure S9. ¹H NMR spectrum of complex **5b** in CDCl₃.

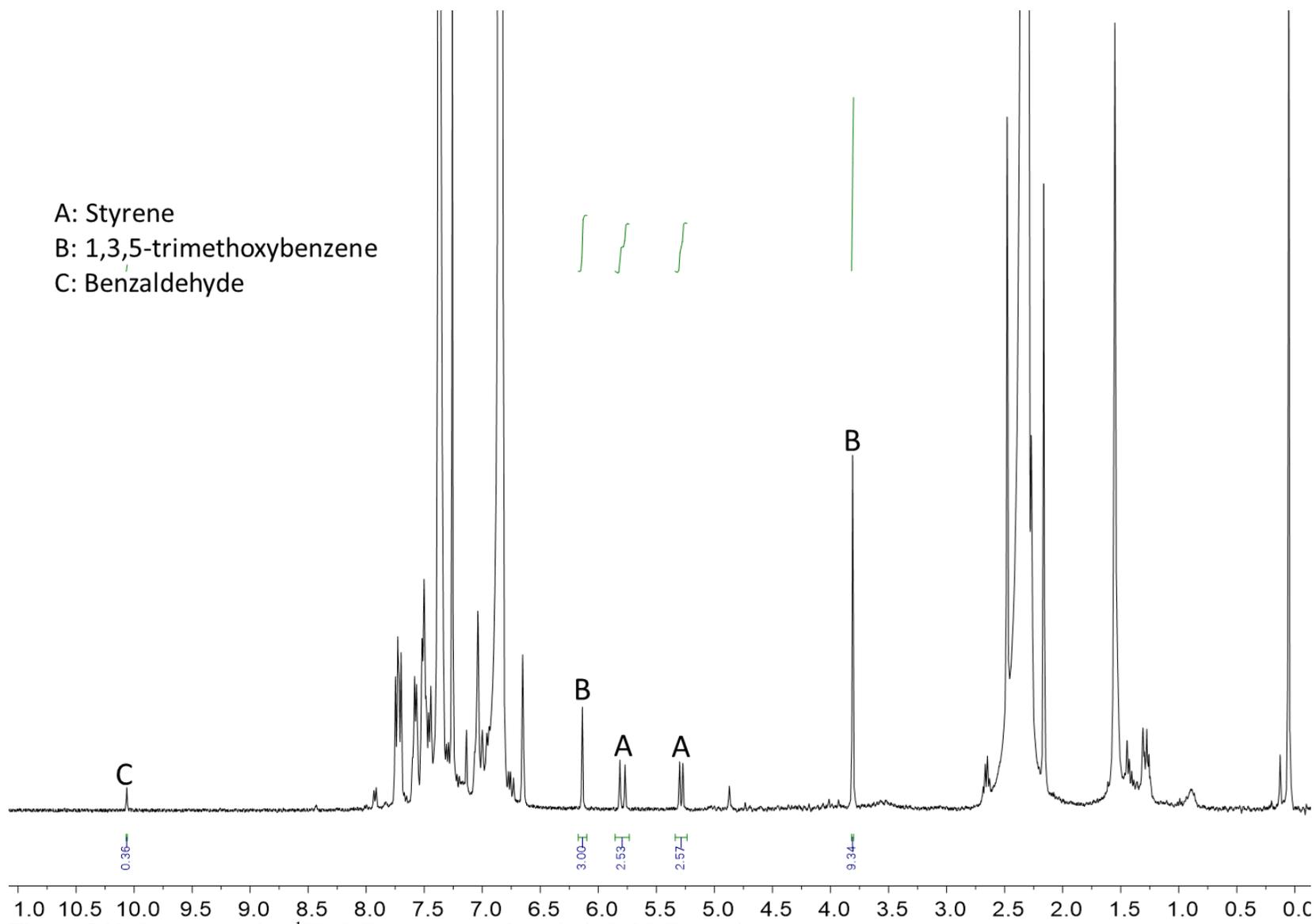


Figure S10. Representative ^1H NMR spectrum of catalytic DODH reaction.

A: Styrene
B: 1,3,5-trimethoxybenzene
C: Catalyst 4b
D: Benzaldehyde

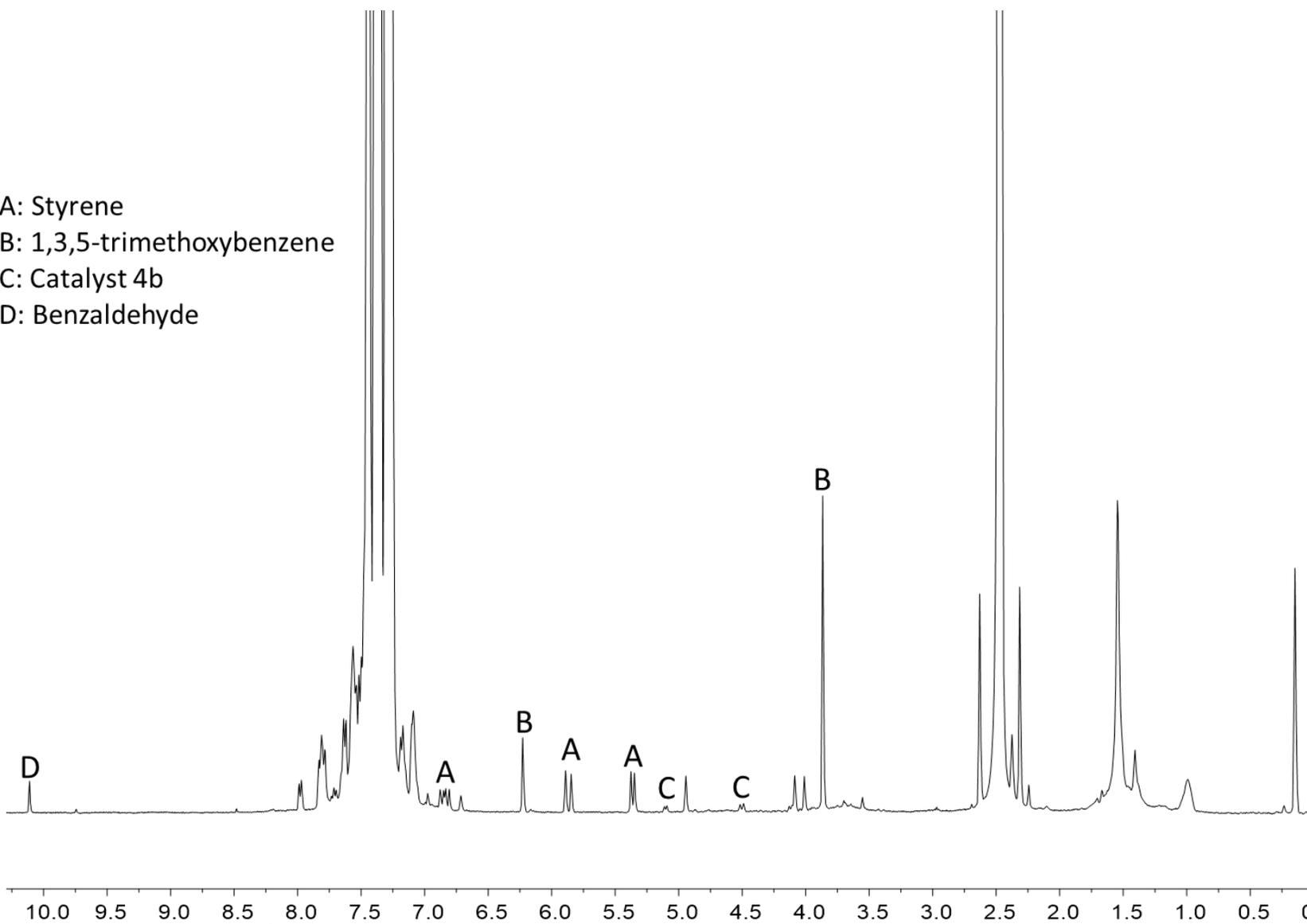


Figure S11. Representative ¹H NMR spectrum of catalytic DODH reaction (catalyst resonances shown).

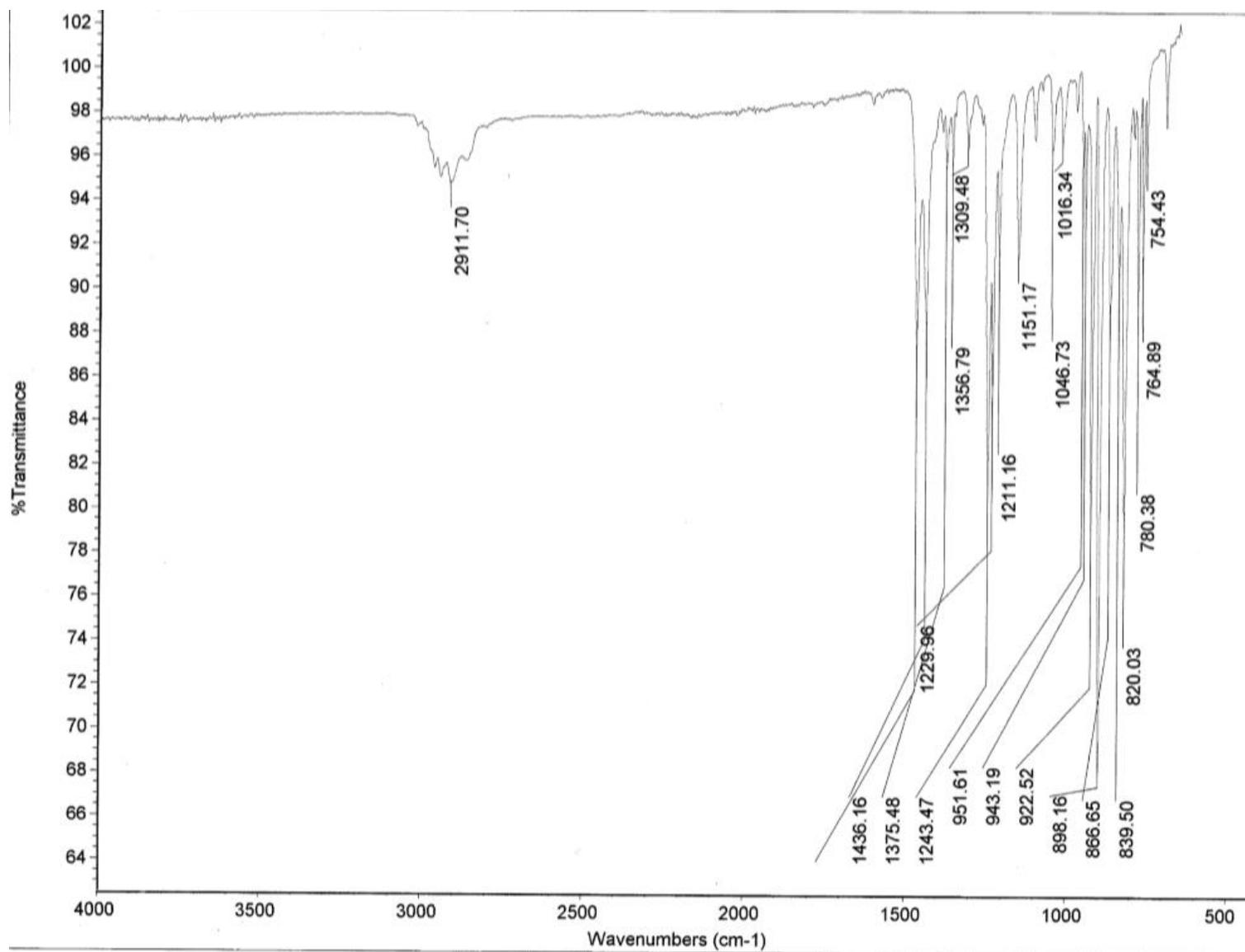


Figure S12. IR Spectra for complex 1b.

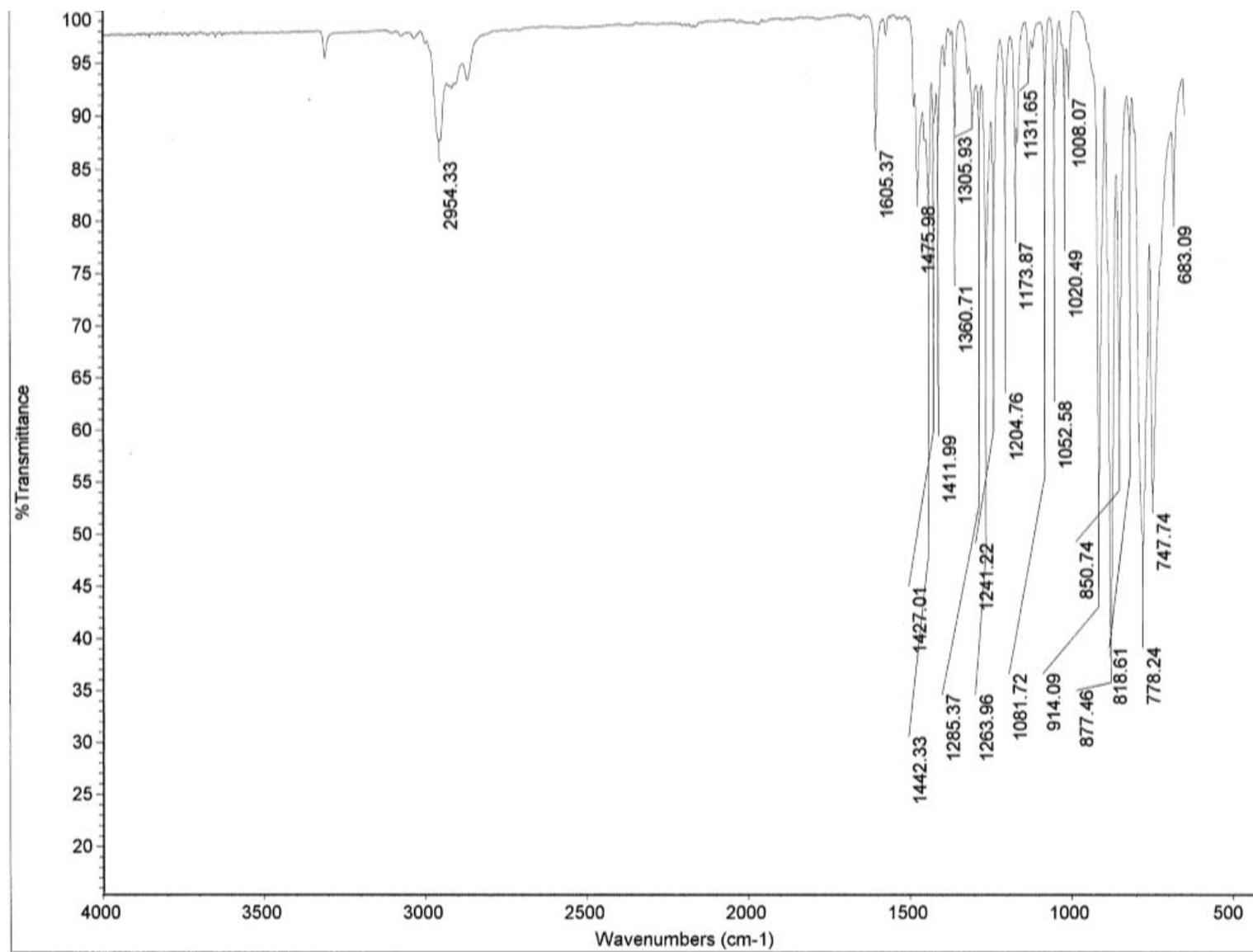


Figure S13. IR Spectra for 2b.

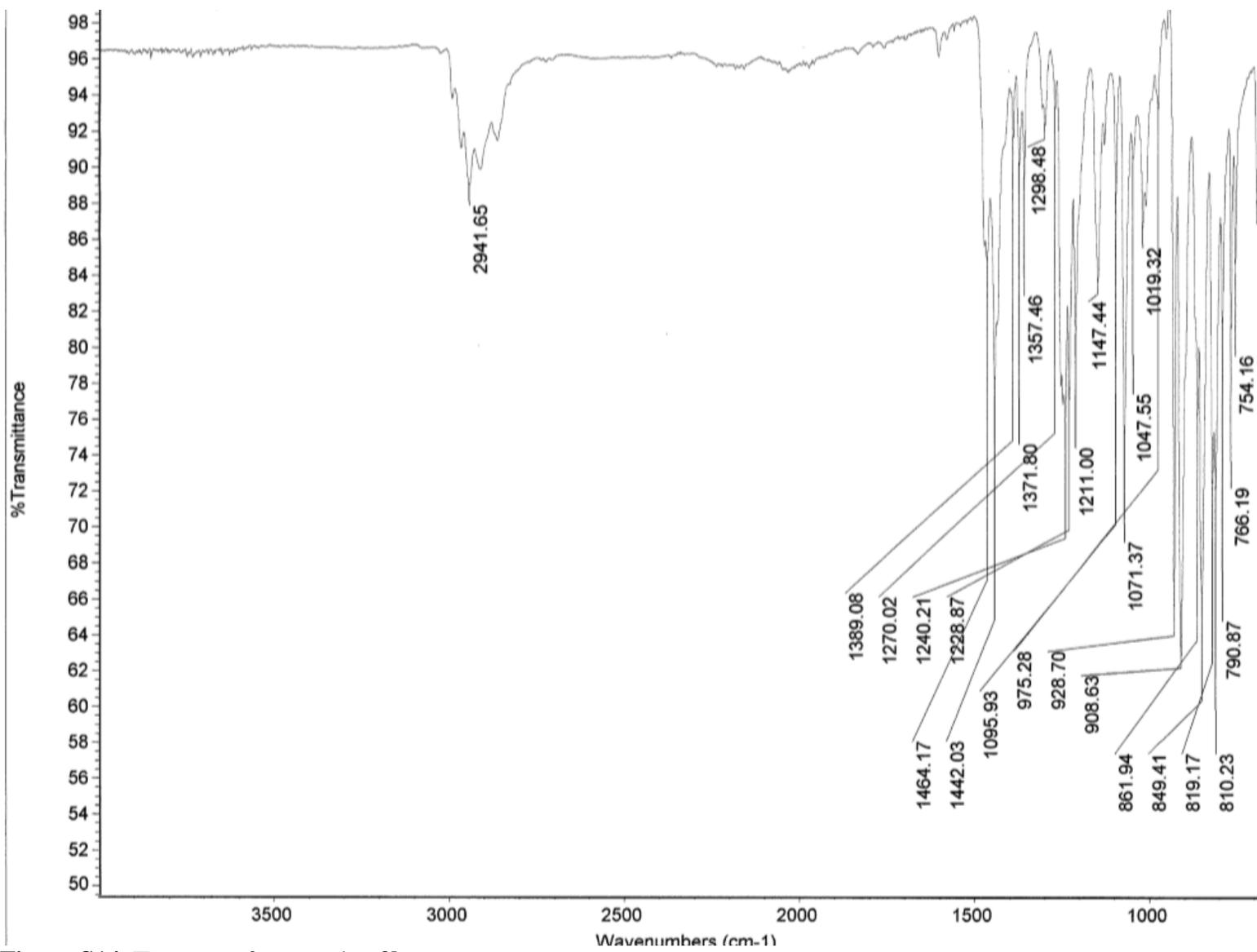


Figure S14. IR spectra for complex 3b.

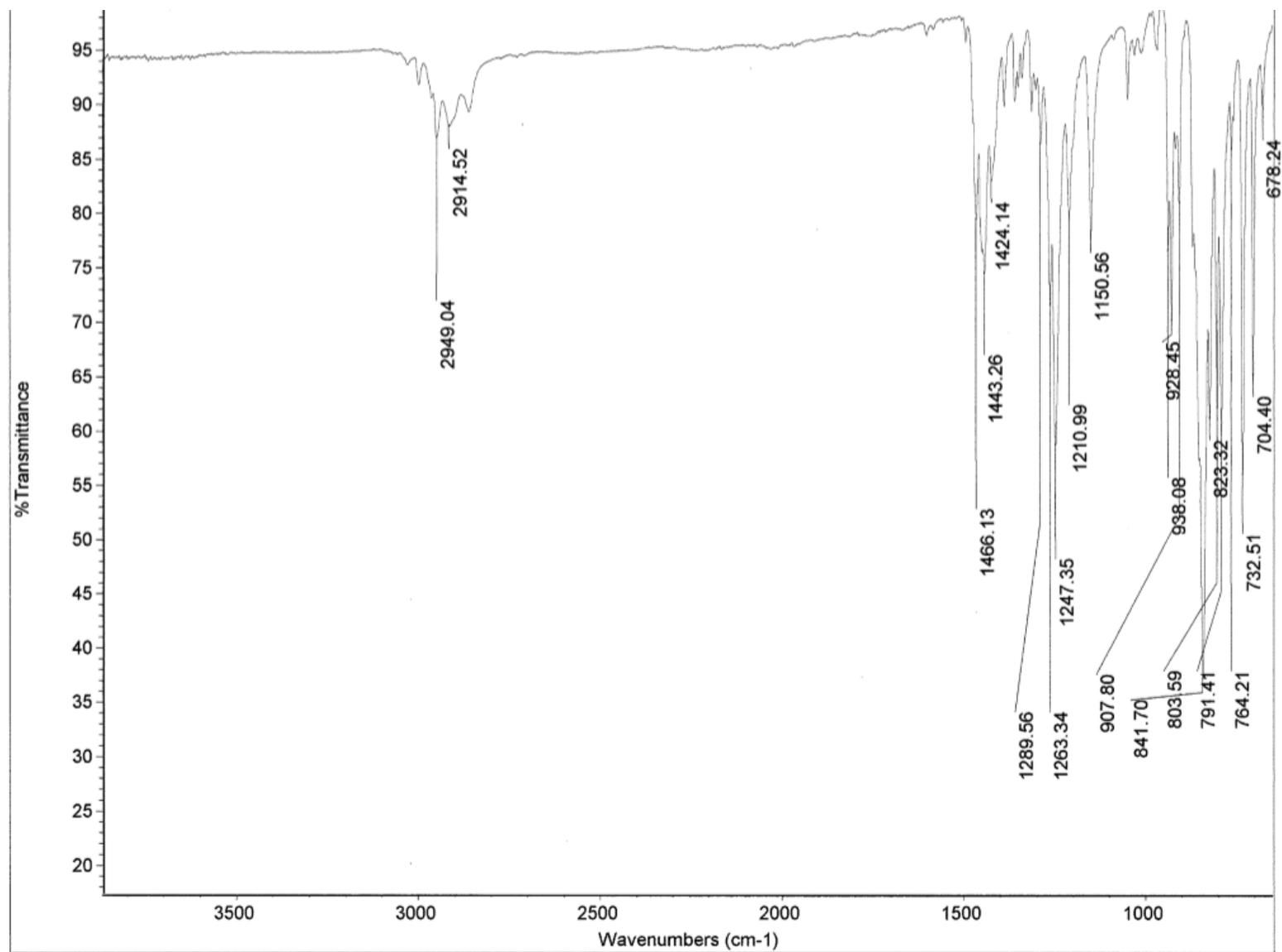


Figure S15. IR Spectra for complex 4b.

Table S1. Deoxydehydration of styrene glycol catalyzed by reported dioxomolybdenum complexes.

entry	Mo complex	conditions	Reductant (eq.)	yield (%)	Ref.
1.	(acylpyrazolonate) ₂ MoO ₂	Mo (2 mol %), toluene (15 mL), 110 °C, 18h	PPh ₃ (1.1)	10-13	9a
2.	(acac) ₂ MoO ₂ /β-diketone (4 eq.)	Mo (10 mol %), mesitylene (2 mL), 150 °C, 2h	PPh ₃ (1.5)	51	9f
3.	(Pincer-ONO)MoO ₂	Mo (10 mol %), toluene (10 mL), 150 °C, 48h.	PPh ₃ (1) carbon (1) zinc (1) Na ₂ SO ₃ (1)	31 46 30 27	10
4.	(Pincer-ONO)MoO ₂ (OPPh ₃)	Mo (10 mol %), toluene (10 mL), 150 °C, 48h.	PPh ₃ (1) carbon (1) zinc (1) Na ₂ SO ₃ (1)	31 37 36 29	10
5.	4b	Mo (10 mol %), toluene (2.5 mL), 150 °C, 24h.	PPh ₃ (1.5) carbon (1.5) zinc (1.5) Na ₂ SO ₃ (1.5)	34 31 31 37	<i>this work</i>

References

- (a) A. John, M. M. Shaikh and P. Ghosh, "Structural and functional mimic of galactose oxidase by a copper complex of a sterically demanding [N₂O₂] ligand" *Dalton Trans.* 2008, 2815-2824.

(b) Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, "Titanium, zinc and alkaline-earth metal complexes supported by bulky O,N,N,O-multidentate ligands: syntheses, characterisation and activity in cyclic ester polymerisation" *Dalton Trans.* 2006, 340-350.

(c) K. Hasan, L. N. Dawe and C. M. Kozak, "Synthesis, Structure, and C–C Cross-Coupling Activity of (Amine)bis(phenolato)iron(acac) Complexes" *Eur. J. Inorg. Chem.* 2011, 4610-4621.

(d) X. Qian, L. N. Dawe and C. M. Kozak, "Catalytic alkylation of aryl Grignard reagents by iron(III) amine-bis(phenolate) complexes" *Dalton Trans.* 2011, **40**, 933-943.
- J. M. Mitchell and N. S. Finney, "New Molybdenum Catalysts for Alkyl Olefin Epoxidation. Their Implications for the Mechanism of Oxygen Atom Transfer". *J. Am. Chem. Soc.* 2001, **123**, 862.