

Supporting Information

Utilization of CS₂ as a Source of C₁ Chemistry for the Generation of Methyldithioformate

Thirumanavelan Gandhi, Munirathinam Nethaji, and Balaji R. Jagirdar*

Department of Inorganic & Physical Chemistry, Indian Institute of

Science, Bangalore 560 012, India

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Experimental Section

General Procedures.

All reactions were carried out under N_2 or Ar atmosphere at room temperature using standard Schlenk¹ and inert-atmosphere techniques unless otherwise noted. Solvents were dried and distilled before use. The NMR spectra were obtained using an AMX Bruker or Avance Bruker 400 MHz spectrometer. The shift of the residual protons of the deuterated solvent was used as an internal reference. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured relative to 85% H_3PO_4 (aqueous solution) as an external standard. Elemental analyses were carried out using a Heraeus CHNO Rapid elemental analyzer; samples containing fluorine atoms were characterized by mass spectral analysis (Electrospray MS). The *trans*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{SC}(\text{S})\text{H})]$ **1** complex was synthesized by a reported procedure.²

Preparation of *trans*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{SC}(\text{SCH}_3)\text{H})][\text{OTf}]$ (**2**).

A solution of *trans*-[(dppe)₂Ru(H)(SC(S)H)] (1.00 g, 1 mmol) in CH₂Cl₂ (30 mL) was treated with 4 equiv of MeOTf (0.46 mL, 4 mmol). An immediate color change from yellow to orange was observed. The resulting solution was stirred for 15 min and then the volume was reduced to ca. 5 mL. The product *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] **2** was precipitated by adding excess Et₂O and the precipitate was washed with more Et₂O (3 x 10 mL) and dried in vacuo. Yield 1.00 g (86.0 %). Characterization data for **2** are as follows. ¹H NMR (CDCl₃): δ -12.74 (qnt, 1H, Ru-H, *J*(H,P) = 20.0 Hz); 2.29 and 2.82 (br s, 8H, PCH₂CH₂P); 2.48 (s, 3H, SCH₃); 6.62-7.59 (m, 40H, Ph₂PCH₂CH₂PPh₂); 8.00 (s, 1H, HC(S)). ³¹P{¹H} NMR (CDCl₃): δ 63.1 (s, 4P, Ph₂PCH₂CH₂PPh₂). ¹³C{¹H} NMR (CDCl₃): δ 17.79 (s, SCH₃); 33.29 (qnt, Ph₂PCH₂CH₂PPh₂, *J*(C,P) = 12 Hz); 128.01-133.30 (m, Ph₂PCH₂CH₂PPh₂); 135.76 (unres br s, CF₃SO₃); 213.48 (s, HC(S)). MS (ESMS) *m/z*: 991 (P⁺ of cation); 913 (P⁺-HC(S)SH).

Reaction of *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] with H₂

The *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] complex (20 mg, 0.017 mmol) was dissolved in CDCl₃ (0.7 mL) in a 5 mm NMR tube and then H₂ gas was purged through the solution for ca. 5 min. The resulting solution was analyzed using NMR spectroscopy which indicated the partial formation of a hydride dihydrogen complex *trans*-[(dppe)₂Ru(H)(η²-H₂)][OTf]³ **3** and some free methyldithioformate.

Reaction of *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] with CH₃CN

A CH₂Cl₂ solution (10 mL) of *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] (0.05 g, 0.043 mmol) was treated with 4 equiv of CH₃CN (9 μL, 0.17 mmol) and the resulting solution was stirred for 1 h at room temperature. During this time, the color of the solution turned from orange to yellow. The volume of the solution was reduced and the

product of *trans*-[(dppe)₂Ru(H)(CH₃CN)][OTf] **4** was precipitated by the addition of excess Et₂O. The solid was vacuum dried. Yield 0.03 g (63 %). Characterization data for **4** are as follows. ¹H NMR (CDCl₃): δ -15.96 (qnt, 1H, Ru-*H*, *J*(H,P) = 18.0 Hz); 1.80 (s, 3H, CH₃CN); 2.06 and 2.64 (br s, 8H, PCH₂CH₂P); 6.61-7.41 (m, 40H, Ph₂PCH₂CH₂PPh₂). ³¹P{¹H} NMR (CDCl₃): δ 65.1 (s, 4P, Ph₂PCH₂CH₂PPh₂). ¹³C{¹H} NMR (CDCl₃): δ 3.65 (s, CH₃CN); 32.37 (qnt, Ph₂PCH₂CH₂PPh₂, *J*(C,P) = 12 Hz); 123.68 (s, CH₃CN); 134.45 (unres br s, CF₃SO₃). MS (ESMS) *m/z*: 913 (P⁺-HCN); 897 (P⁺-(HCN+CH₄)).

Isolation of free MeSC(S)H

A reaction of *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] (0.70 g, 0.61 mmol) with 7 equiv of CH₃CN (0.22 mL) was carried as described above. Upon ensuring that the reaction was complete (color change from orange to pale yellow), the volatiles were fractionally distilled and the fractions boiling at 45-46 °C, 55-56 °C, and 65-66 °C were collected separately. The fraction collected at 55-56 °C contained considerable amount of free methyldithioformate. The NMR spectral details of this fraction matched those obtained in the NMR scale experiments.

Reaction of *trans*-[(dppe)₂Ru(H)(SC(S)H)] with MeI

To a CH₂Cl₂ solution (5 mL) of *trans*-[(dppe)₂Ru(H)(SC(S)H)] (0.100 g, 0.1 mmol) was added 5 equiv of MeI (32 μL, 0.5 mmol) and the resulting solution was stirred for 2 h. The yellow solution turned red. Then the volume of the solution was reduced to ca. 2 mL and excess Et₂O was added to cause complete precipitation of a product of *trans*-[(dppe)₂Ru(H)I] **5** that was dried in vacuo. Yield 0.080 g (76 %). Characterization data for **5** are as follows. ¹H NMR (CDCl₃): δ -16.24 (qnt, 1H, Ru-*H*,

$J(\text{H,P}) = 20.0 \text{ Hz}$; 2.14 and 2.77 (br s, 8H, $\text{PCH}_2\text{CH}_2\text{P}$); 6.95-7.25 (m, 40H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 59.97 (s, 4P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). MS (ESMS) m/z : 997 ($\text{P-C}_2\text{H}_4$).

Reaction of *trans*-[(dppe)₂Ru(H)I] with excess NaBH₄

The *trans*-[(dppe)₂Ru(H)I] (0.10 g, 0.097 mmol) was dissolved in a mixture of THF (10 mL) and methanol (5 mL). Under nitrogen pressure, excess NaBH₄ (0.46 g, 12.12 mmol) was added all at once with vigorous stirring. The solution turned color from brown to pale yellow in ca. an hour after which time, the volatiles were removed in vacuo and the residual solid was washed several times with methanol. The solid that was left behind was dried in vacuo and identified using NMR spectroscopy as *cis*-[(dppe)₂RuH₂]. Yield 0.042 g (48 %). Anal. Calcd. for C₅₂H₅₀P₄Ru: C, 69.43; H, 5.56. Found: C, 68.91; H, 5.24.

Reaction of *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] with excess NaBH₄

The *trans*-[(dppe)₂Ru(H)(SC(SCH₃)H)][OTf] (0.05 g, 0.043 mmol) was dissolved in a mixture of THF (20 mL) and methanol (10 mL). Under N₂ pressure, excess NaBH₄ (0.20 g, 125 equiv, 5.3 mmol) was added with vigorous stirring. After 1 h of stirring, the solution turned color from orange to pale yellow. The solvents were removed in vacuo and the residual solid was washed several times with methanol. The product was identified as *cis*-[(dppe)₂RuH₂] by comparing its ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data with that of an authentic sample and from the literature.³ Yield 0.026 g (68 %). Anal. Calcd. for C₅₂H₅₀P₄Ru: C, 69.43; H, 5.56. Found: C, 68.89; H, 5.09.

References

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3. *trans*-[(dppe)₂Ru(H)(η^2 -H₂)] [BF₄]: Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, 113, 4876-4887.

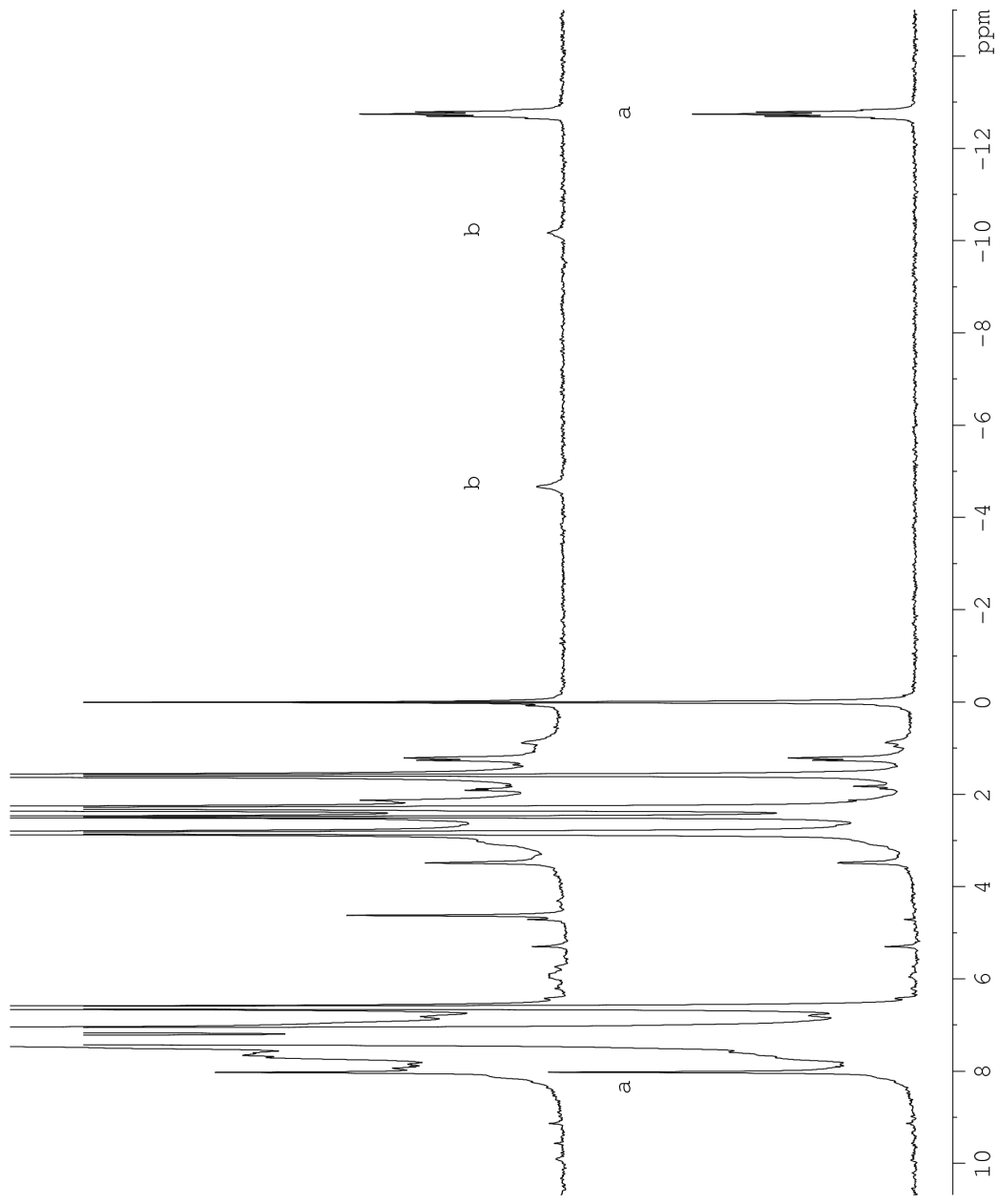


FIG. S1

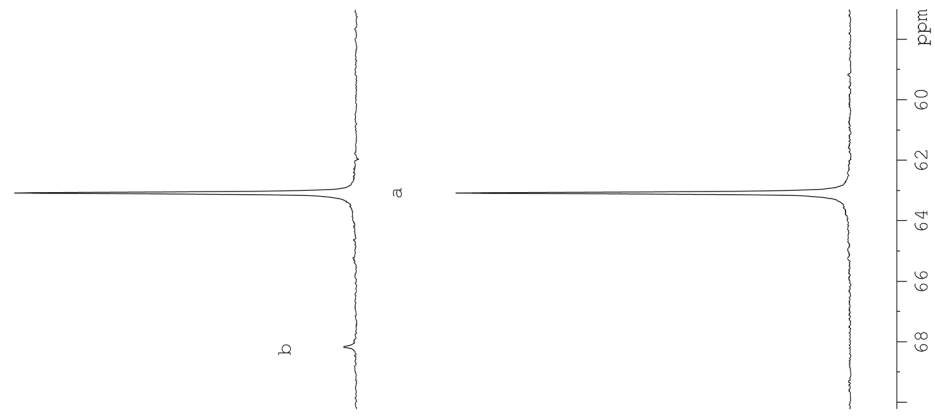


FIG. S2

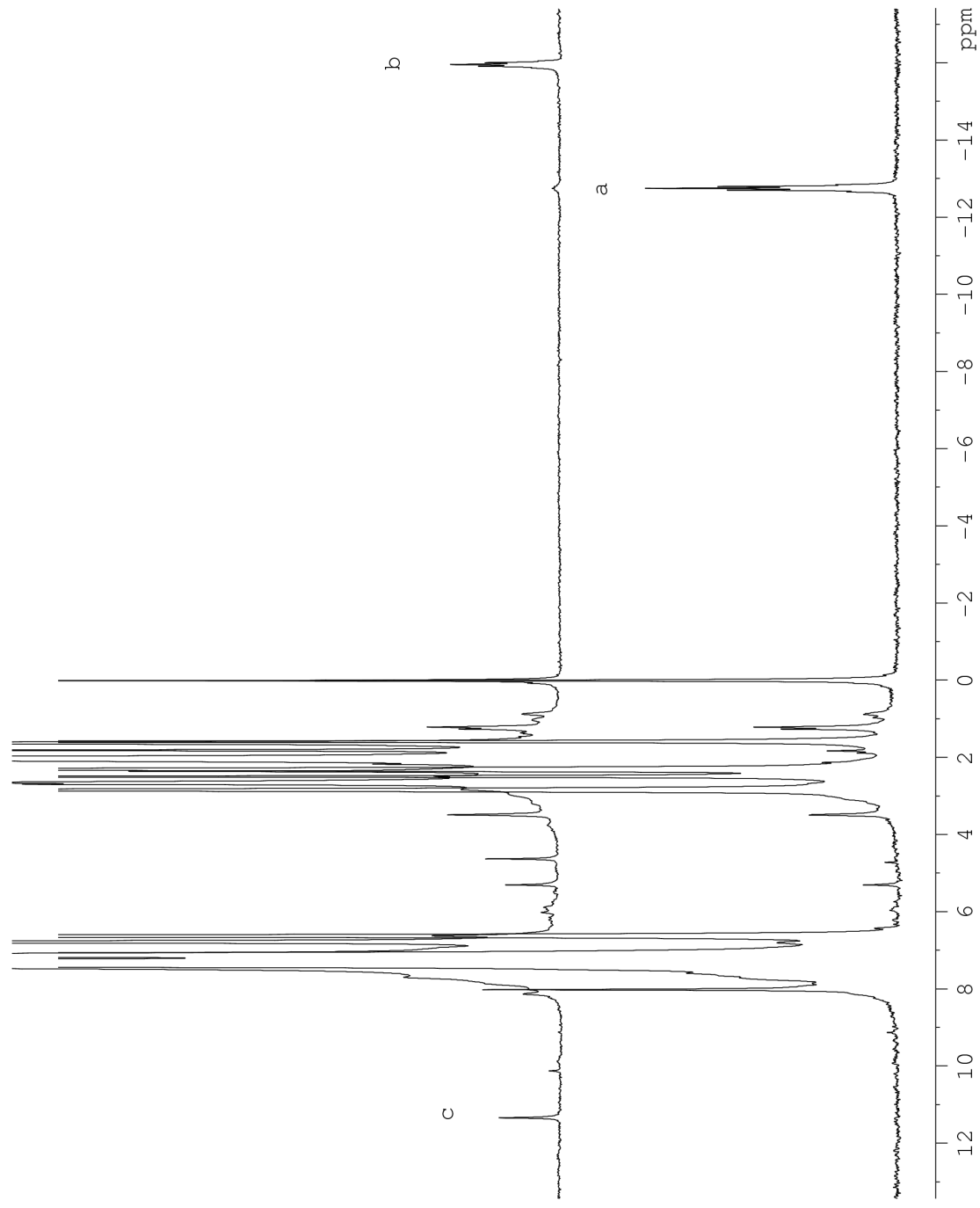


FIG. S3

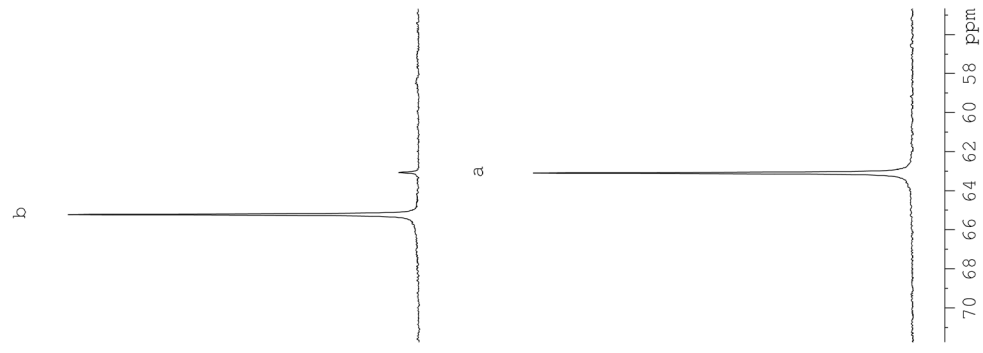


FIG. S4

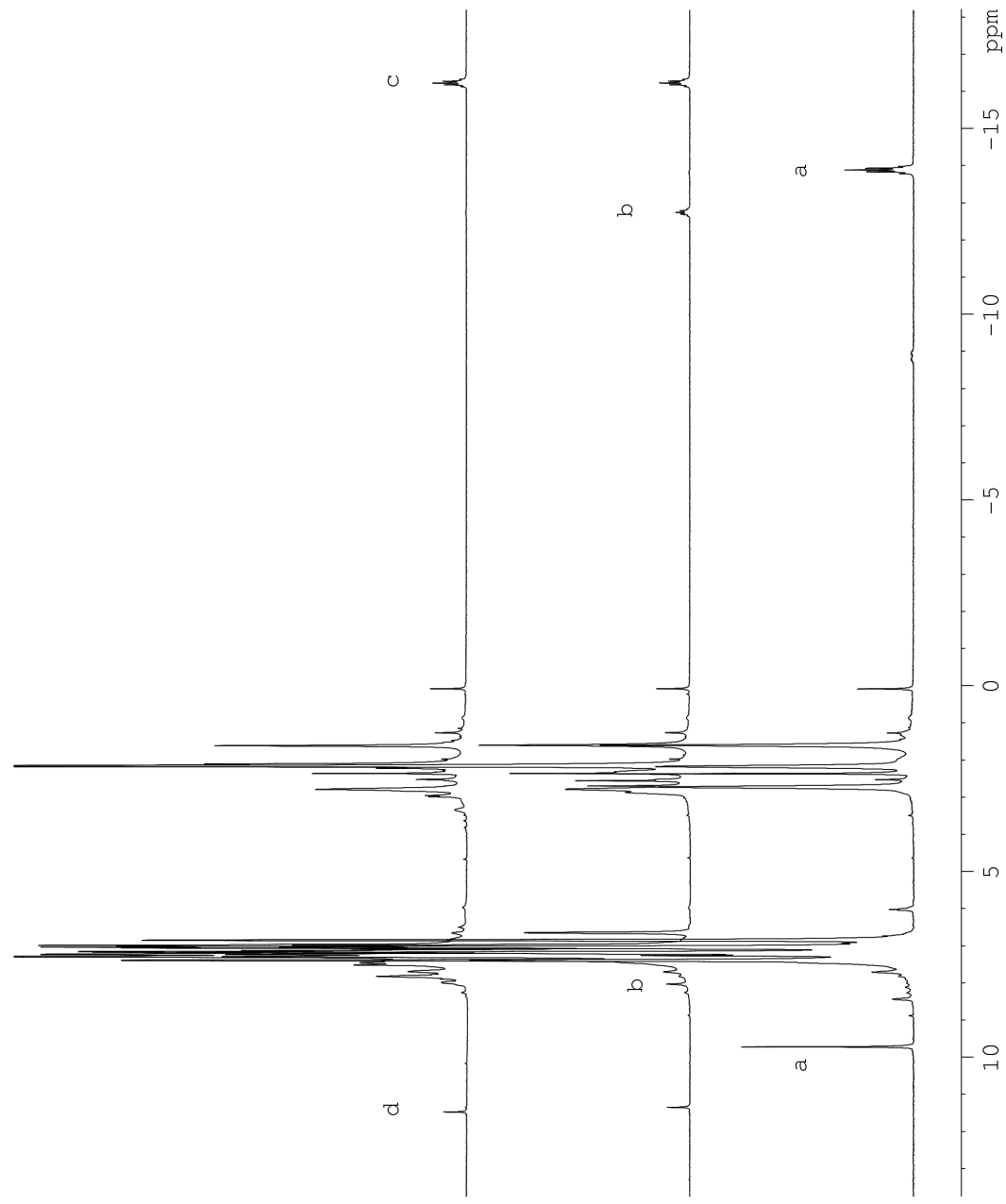


FIG. S5

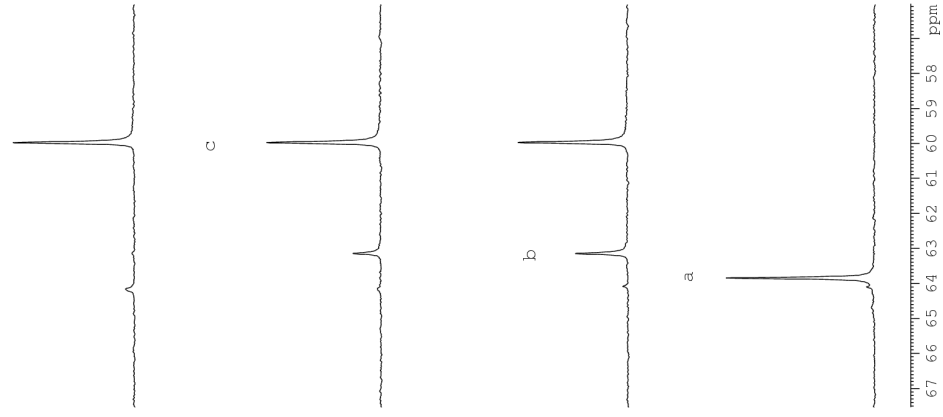


FIG. S6

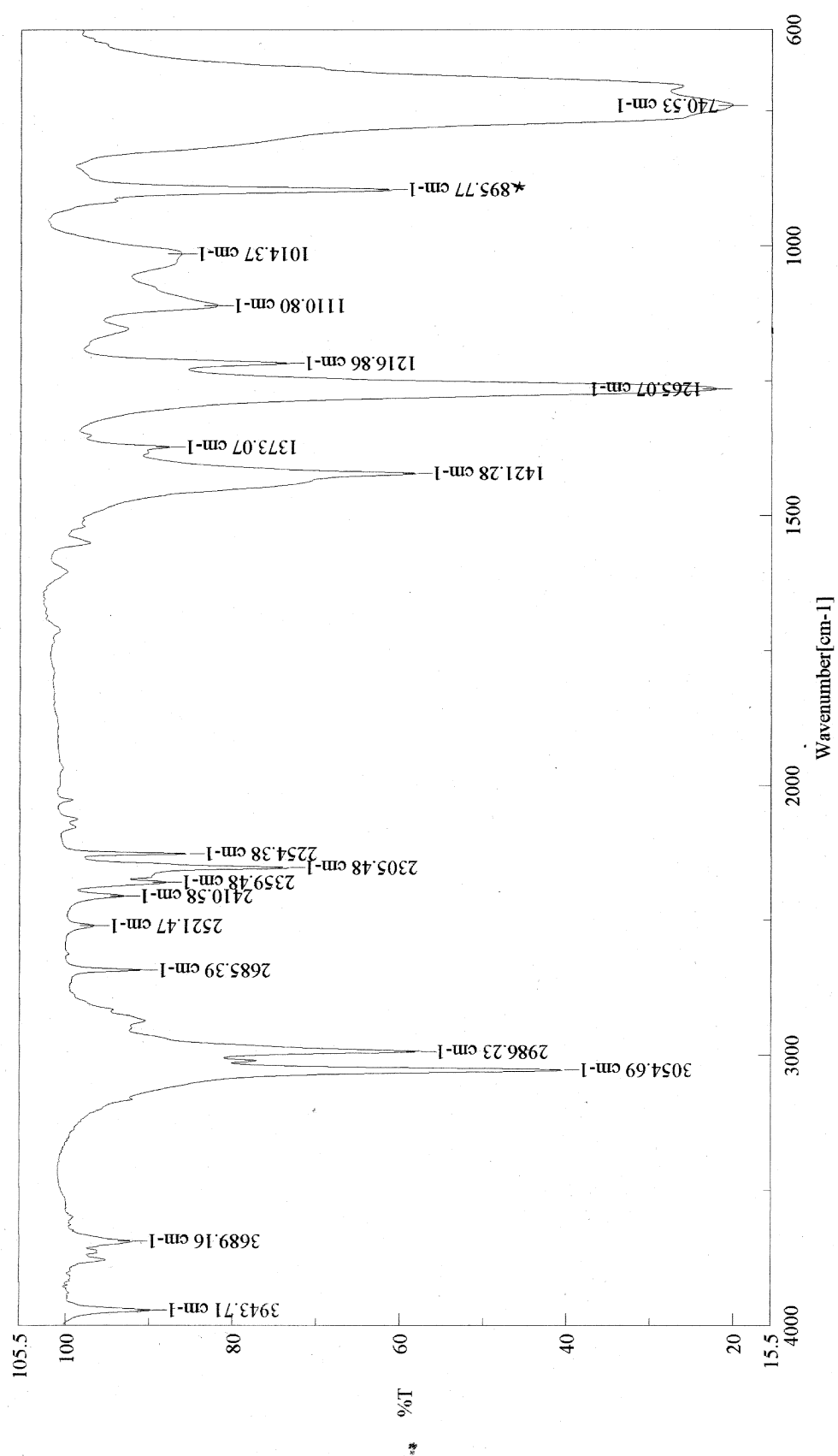


FIG. S7

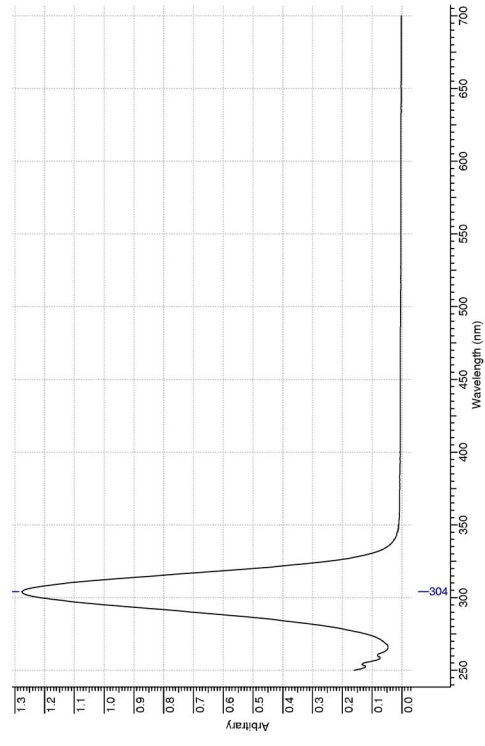


FIG. S8