

Electronic Supplementary Information

Transfer Hydrogenation of Carbon Dioxide via Bicarbonate Promoted by Bifunctional C–N Chelating Cp*Ir(III) Complexes

Yasuhiro Sato,^{†,‡} Yoshihito Kayaki,^{*,†} and Takao Ikariya[†]

[†]Department of Chemical Science and Engineering, School of Materials and Chemical
Technology, Tokyo Institute of Technology, O-okayama2-12-1-E4-1, Meguro-ku
Tokyo 152-8552, Japan

[‡]Hazardous Materials Laboratory, Research and Development Division, National
Research Institute of Fire and Disaster, Jindaiji-higashimachi 4-35-3, Chofu, Tokyo
182-8508, Japan

Contents

1. General Information	S2
2. Supplementary Experiments	S5
3. References	S7
4. NMR Spectra	S8
5. FTIR Spectrum	S14

1. General Information

All experiments were conducted under an argon atmosphere using Schlenk techniques or dry box techniques unless otherwise noted. All deuterated NMR solvents and ^{13}C -labelled methanol were dried and degassed by appropriate methods. Solvents were distilled under argon after refluxing over CaH_2 (methanol, ethanol, 2-propanol, *tert*-butyl alcohol). Water was deionised by using a Merck-Millipore Direct-Q 3 UV system and degassed by bubbling argon. The starting Ir, Rh and Ru complexes, $[\text{Cp}^*\text{IrCl}_2]_2$,^{S1} $\text{Cp}^*\text{IrCl}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2-2-\text{C}_6\text{H}_4\}]$ (**1a**),^{S2} $\text{Cp}^*\text{IrCl}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{CH}_3)_2-2-\text{C}_6\text{H}_4\}]$ (**1b**),^{S2} $\text{Cp}^*\text{RhCl}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2-2-\text{C}_6\text{H}_4\}]$ (**2a**),^{S3} $\text{Cp}^*\text{RhCl}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{CH}_3)_2-2-\text{C}_6\text{H}_4\}]$ (**2b**),^{S3} $\text{RuCl}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2-2-\text{C}_6\text{H}_4\}]$ (**3a**),^{S3} $\text{RuCl}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{CH}_3)_2-2-\text{C}_6\text{H}_4\}]$ (**3b**),^{S3} $\text{Cp}^*\text{IrCl}(\text{PMSdpn})$ (**4**),^{S4} $\text{Cp}^*\text{Ir}[\kappa^2(\text{N},\text{C})-\{\text{NHC}(\text{C}_6\text{H}_5)_2-2-\text{C}_6\text{H}_4\}]$ (**5a**),^{S2} $\text{Cp}^*\text{Ir}[\kappa^2(\text{N},\text{C})-\{\text{NHC}(\text{CH}_3)_2-2-\text{C}_6\text{H}_4\}]$ (**5b**),^{S2} $\text{Cp}^*\text{IrH}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2-2-\text{C}_6\text{H}_4\}]$ (**6a**)^{S2} and $\text{Cp}^*\text{IrH}[\kappa^2(\text{N},\text{C})-\{\text{NH}_2\text{C}(\text{CH}_3)_2-2-\text{C}_6\text{H}_4\}]$ (**6b**),^{S2} were prepared according to the procedures described in the literature with modifications. Other reagents were purchased from Tokyo Chemical Industry Co. Ltd., Sigma-Aldrich Co. LLC., Kanto Chemical Co. Inc., Nacalai Tesque Ltd., and ISOTEC used as delivered. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on JNM-ECX400 spectrometers and referenced to an external tetramethylsilane signal (0.0 ppm) by using the signals of residual proton impurities in the deuterated solvents. IR spectra were recorded on a JASCO FT/IR-610 spectrometer.

General Procedure of the Transfer Hydrogenation of Carbon Dioxide Using KO^tBu in 2-Propanol (Table 1): A 20-mL Schlenk flask was charged with an appropriate catalyst (0.50 μmol), KO^tBu (0.56 g, 5.0 mmol) and 2-propanol (5.0 mL) under an argon atmosphere. The solution was degassed via freeze-pump-thaw cycles by using liquid nitrogen. After the Schlenk flask was then filled with CO_2 (1 atm) at room temperature, the reaction mixture was stirred at 80 $^\circ\text{C}$ for 5 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in D_2O . The yield of HCOOK was determined by ^1H NMR spectroscopy using sodium acetate (41 mg, 0.50 mmol) as an internal standard.

General Procedure of the Transfer Hydrogenation of Carbon Dioxide Using KOH in 2-Propanol and H_2O Catalysed by Amido- and Hydrido-iridium Complexes (Scheme 2): A 20-mL Schlenk flask was charged with an appropriate catalyst (0.50 μmol) and KOH (0.28 g, 5.0 mmol), followed by addition of H_2O (5.0 mL) and 2-propanol (5.0 mL) under argon atmosphere. The solution was degassed via freeze-pump-thaw cycles with liquid nitrogen. After the Schlenk flask was then filled with CO_2 (1 atm) at room temperature, the reaction mixture was stirred at 80 $^\circ\text{C}$ for 5 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in D_2O . The yield of HCOOK was determined by ^1H NMR spectroscopy using sodium acetate (41 mg, 0.50 mmol) as an internal standard.

mmol) as an internal standard.

General Procedure for the Transfer Hydrogenation of Bicarbonate or Carbonate Salt in 2-Propanol and H₂O in the Presence or Absence of CO₂ Catalysed by 5a (Table 2): A 20-mL Schlenk flask was charged with **5a** (0.23 mg, 0.39 μmol) and bicarbonate or carbonate salt (3.9 mmol), followed by addition of H₂O (3.9 mL) and 2-propanol (3.9 mL) under argon atmosphere. The solution was degassed via freeze-pump-thaw cycles with liquid nitrogen, and the Schlenk flask was then filled with CO₂ (1 atm) at room temperature, if required. The reaction mixture was stirred at 80 °C for 5 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in D₂O. The yield of HCOOK was determined by ¹H NMR spectroscopy using sodium acetate (32 mg, 0.39 mmol) as an internal standard.

General Procedure of ¹³C-Labeling Experiments for the Transfer Hydrogenation of Potassium Bicarbonate in 2-Propanol and H₂O under CO₂ Catalysed by 5a (Scheme 3 and Figure 1): A 20-mL Schlenk flask was charged with **5a** (0.20 mg, 0.34 μmol) and KHCO₃ or KH¹³CO₃ (0.69 g, 6.9 mmol), followed by addition of H₂O (6.9 mL) and 2-propanol (6.9 mL) under an argon atmosphere. The solution was degassed via freeze-pump-thaw cycles with liquid nitrogen. After the Schlenk flask was then filled with ¹³C-labelled- or -unlabelled CO₂ (1 atm) at room temperature, the reaction mixture was stirred at 80 °C for 1 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in D₂O. The yields of HCOOK and H¹³COOK were determined by ¹H NMR spectroscopy using sodium acetate (28 mg, 0.34 mmol) as an internal standard.

General Procedure of the Transfer Hydrogenation of Bicarbonate Salts in 2-Propanol and H₂O Catalysed by 5a (Table 3): A 20-mL Schlenk flask was charged with **5a** (0.29 mg, 0.10 μmol), bicarbonate salts (0.50 g, 1.0 mmol), and an appropriate additive (1.0 mmol), followed by addition of H₂O (1.0 mL) and 2-propanol (1.0–8.0 mL) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 5 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in D₂O. The yield of HCOOK was determined by ¹H NMR spectroscopy using sodium acetate (41 mg, 0.50 mmol) as an internal standard.

Synthesis of Cp*IrH[κ²(N,C)-{N(CH₃)₂CH₂-2-C₆H₄}] (7).

A mixture of Cp*IrCl[κ²(N,C)-{N(CH₃)₂CH₂-2-C₆H₄}]^{S5} (0.16 g, 0.32 mmol) and dry KO^tBu (0.057 g, 0.51 mmol) in 2-propanol (10 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and washed with hexane. After the residue was dissolved in diethyl ether, insoluble material was removed by filtration. Evaporation of the filtrate to dryness

gave the pale yellow product (0.063 g, 0.14 mmol). Isolated yield: 44%. ^1H NMR (399.8 MHz, CD_2Cl_2 , rt): δ -13.92 (s, 1H; IrH), 1.81 (s, 15H; C(CH₃)₅), 2.64, 3.13 (each s, 3H; N(CH₃)₂), 3.44, 3.73 (each d, $^2J_{\text{HH}} = 12.2$ Hz, 1H; CH₂), 6.70-7.39 (m, 4H; C₆H₄); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , rt): δ 9.9 (C₅(CH₃)₅), 54.5, 59.3 (N(CH₃)₂), 79.2 (CH₂), 87.5 (C₅(CH₃)₅), 119.1, 120.6, 125.5, 134.4, 147.7, 151.5 (C₆H₄). Anal. Calcd for C₁₉H₂₈IrN: C, 49.33; H, 6.10; N 3.03. Found: C, 49.27; H, 5.91; N, 3.14.

2. Supplementary Experiments

Time Course of the Transfer Hydrogenation of Carbon Dioxide Using KOH in 2-Propanol and H₂O Catalysed by 5a (Figure S1): A 20-mL Schlenk flask was charged with **5a** (0.50 μmol) and KOH (0.28 g, 5.0 mmol), followed by addition of H₂O (5.0 mL) and 2-propanol (10.0 mL) under argon atmosphere. The solution was degassed via freeze-pump-thaw cycles with liquid nitrogen. After the Schlenk flask was then filled with CO₂ (1 atm) at room temperature, the reaction mixture was stirred at 80 °C for the appropriate time. The solvent was evaporated under reduced pressure, and the residue was dissolved in D₂O. The yield of HCOOK was determined by ¹H NMR spectroscopy using sodium acetate (41 mg, 0.50 mmol) as an internal standard.

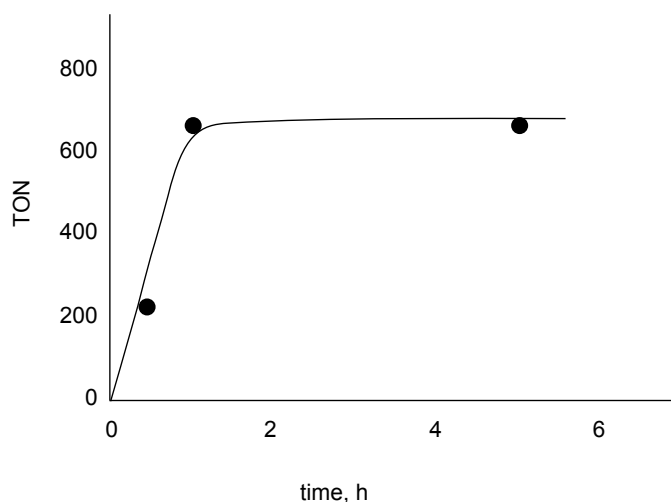
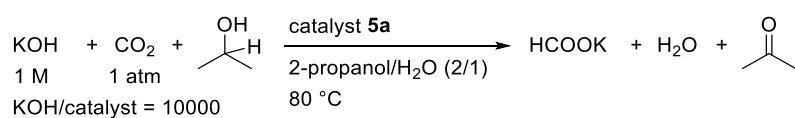
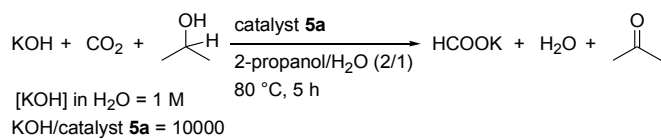


Figure S1. Time Course of the Transfer Hydrogenation of Carbon Dioxide Using KOH in 2-Propanol and H₂O Catalysed by **5a**.

General Procedure of Transfer Hydrogenation of Carbon Dioxide Using KOH in 2-Propanol and H₂O Catalysed by 5a under Pressurised CO₂ (Table S1): A 50-mL stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer was loaded with the amidoiridium catalyst **5a** (0.29 mg, 0.50 μmol) under argon atmosphere. After addition of 2-propanol (10.0 mL) and KOH (0.28 mg, 5.0 mmol) in H₂O (5.0 mL), the autoclave was flushed with CO₂ and then pressurised to appropriate pressure. The reaction mixture was stirred in oil bath at 80 °C for 5 h. After carefully venting CO₂, the solvent was evaporated under reduced pressure, and the residue was dissolved in D₂O. The yield of HCOOK was determined by ¹H NMR spectroscopy using sodium acetate (41 mg, 0.50 mmol) as an internal standard.

Table S1. Pressure effect on the transfer hydrogenation of CO₂.

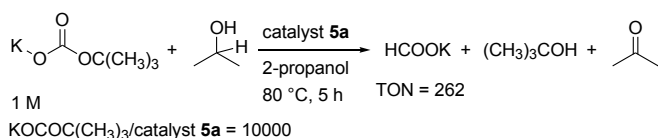


Entry	CO ₂ , atm	TON
1	1	672
2	5	550
3	10	270
4	20	131

[a] Determined by ¹H NMR spectrum using NaOAc as an internal standard. The repeatability error was within 5%.

With increasing the CO₂ pressure, the yields of formate are reduced, possibly due to deactivation of the catalytically active amidoiridium species.

Transfer Hydrogenation of KOCO₂^tBu in 2-Propanol and H₂O Catalysed by 5a: The progress of transfer hydrogenation of CO₂ in 2-propanol may be caused by formation of transient bicarbonate-like species even without water. By treatment of KO^tBu with CO₂ without catalyst and solvent, a half-carbonate ester salt, KOCO₂^tBu, was confirmed by IR spectrum displaying a C=O stretching band at 1646 cm⁻¹. When the transfer hydrogenation of KOCO₂^tBu in the absence of CO₂ in dehydrated 2-propanol was performed (Scheme S1), potassium formate was successfully obtained, along with KOCO₂CH(CH₃)₂ and KOCH(CH₃)₂ produced by exchange with 2-propanol. Reaction procedure: a 20-mL Schlenk flask was charged with **5a** (0.26 mg, 0.44 μmol), KOCO₂^tBu (0.62 g, 0.44 mmol), and 2-propanol (4.4 mL) were introduced to the reactor under argon atmosphere. The reaction mixture was stirred at 80 °C for 5 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in D₂O. The yield of HCOOK was determined by ¹H NMR spectroscopy using sodium acetate (36 mg, 0.44 mmol) as an internal standard.



Scheme S1. Transfer hydrogenation of KOCO₂^tBu in 2-propanol catalysed by **5a**.

3. References

- S1) C. White, A. Yates, P. M. Maitlis and D. M. Heinekey, *Inorg. Synth.*, 1992, **29**, 228.
- S2) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Organometallics*, 2008, **27**, 2795.
- S3) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Angew. Chem., Int. Ed.*, 2008, **47**, 2447.
- S4) B. Villa-Marcos, C. Li, K. R. Mulholland, P. J. Hogan and J. Xiao, *Molecules*, 2010, **15**, 2453.
- S5) D. L. Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S. T. Hilton and D. R. Russell, *Dalton Trans.*, 2003, 4132.

4. NMR Spectra

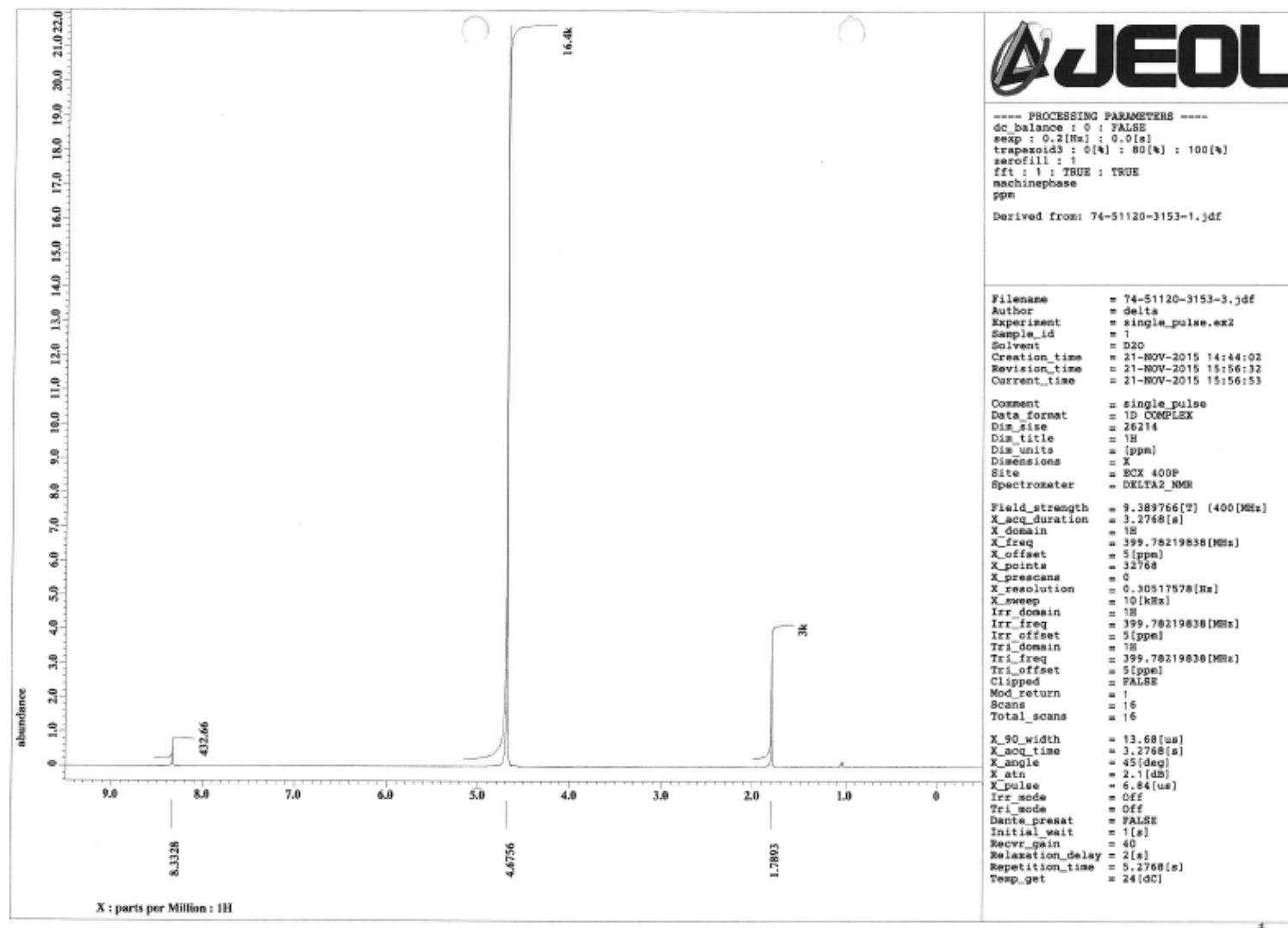


Figure S2: ¹H NMR spectrum (399.78 MHz, CD₂Cl₂, RT) of the transfer hydrogenation product from CO₂ catalysed by **1a** (Table 1, entry 12).

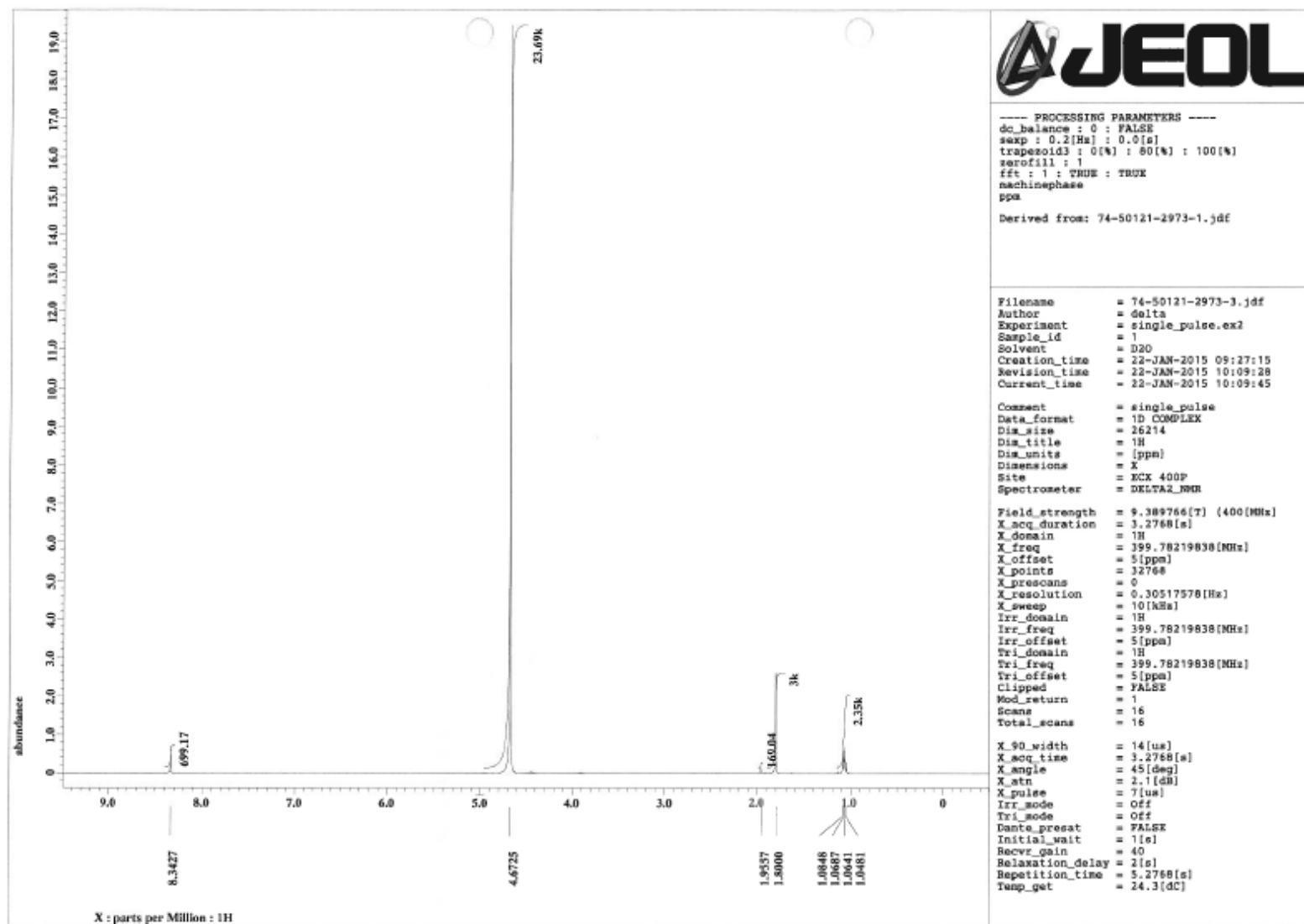


Figure S3: ^1H NMR spectrum (399.78 MHz, CD_2Cl_2 , RT) of the transfer hydrogenation product from CO_2 catalysed by **6a** in Scheme 2.

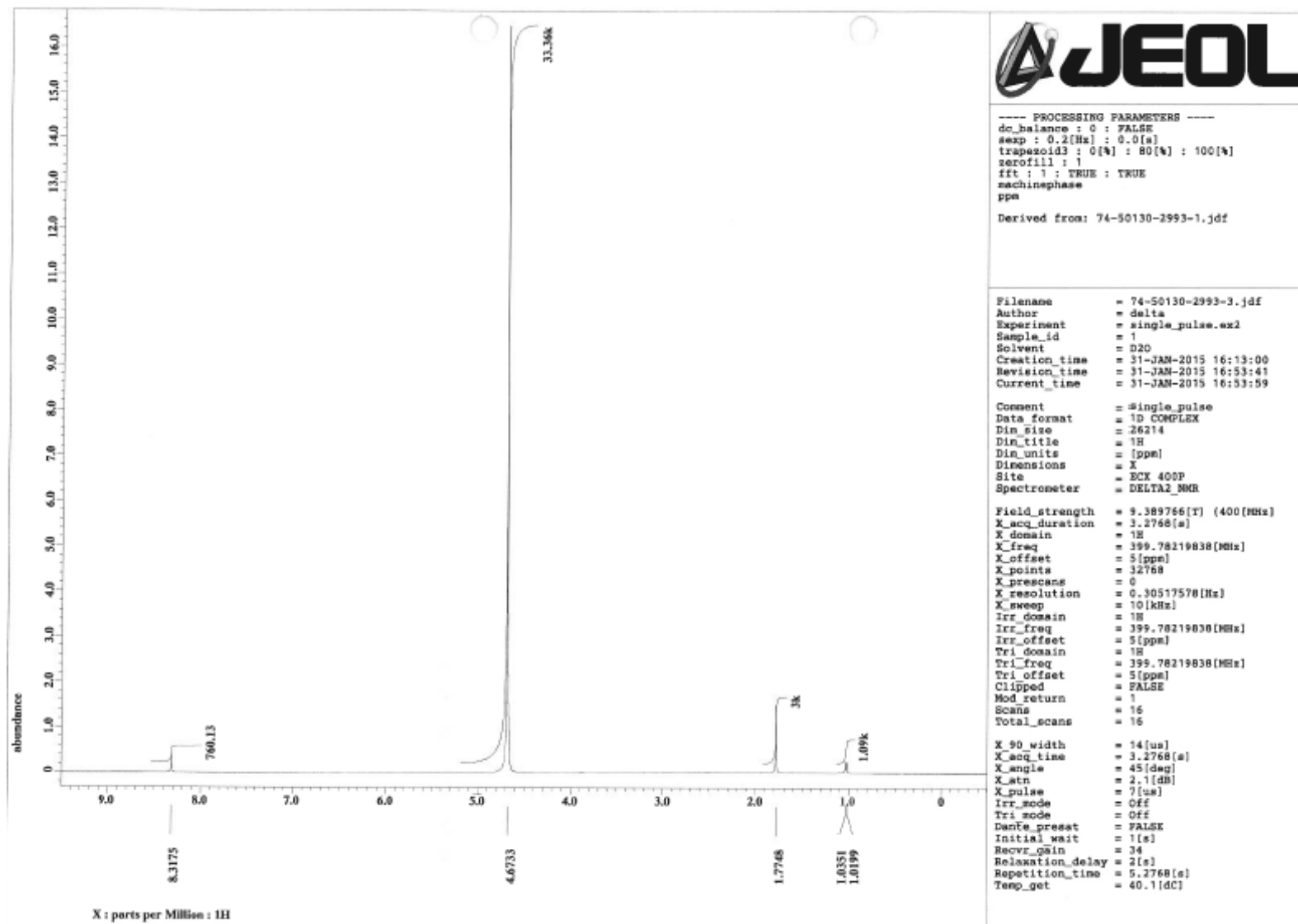


Figure S4: ^1H NMR spectrum (399.78 MHz, CD_2Cl_2 , RT) of the transfer hydrogenation product from KHCO_3 catalysed by **5** (Table 2, entry 3).

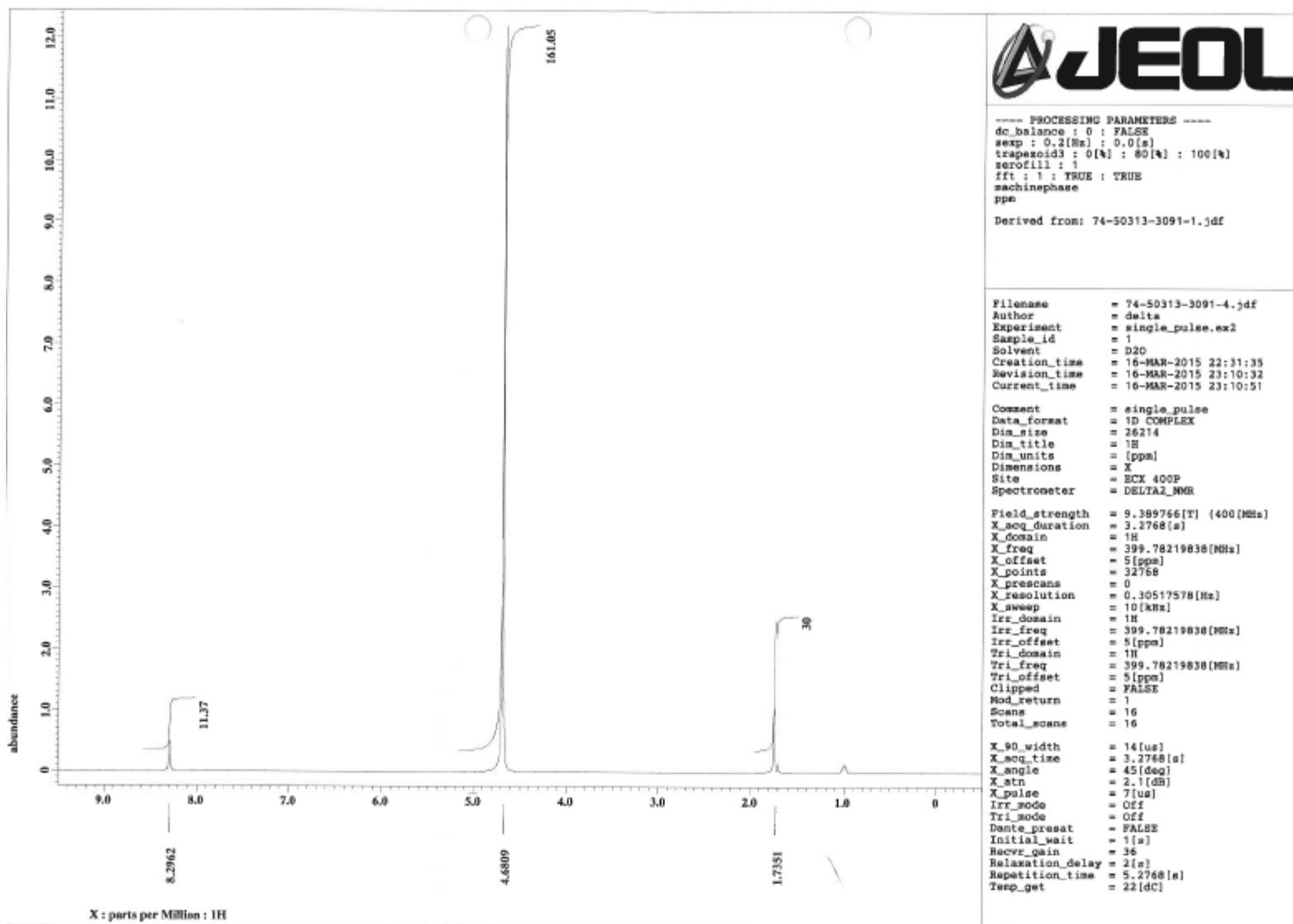


Figure S5: ^1H NMR spectrum (399.78 MHz, CD_2Cl_2 , RT) of the transfer hydrogenation product from CsHCO_3 catalysed by **5** (Table 3, entry 5).

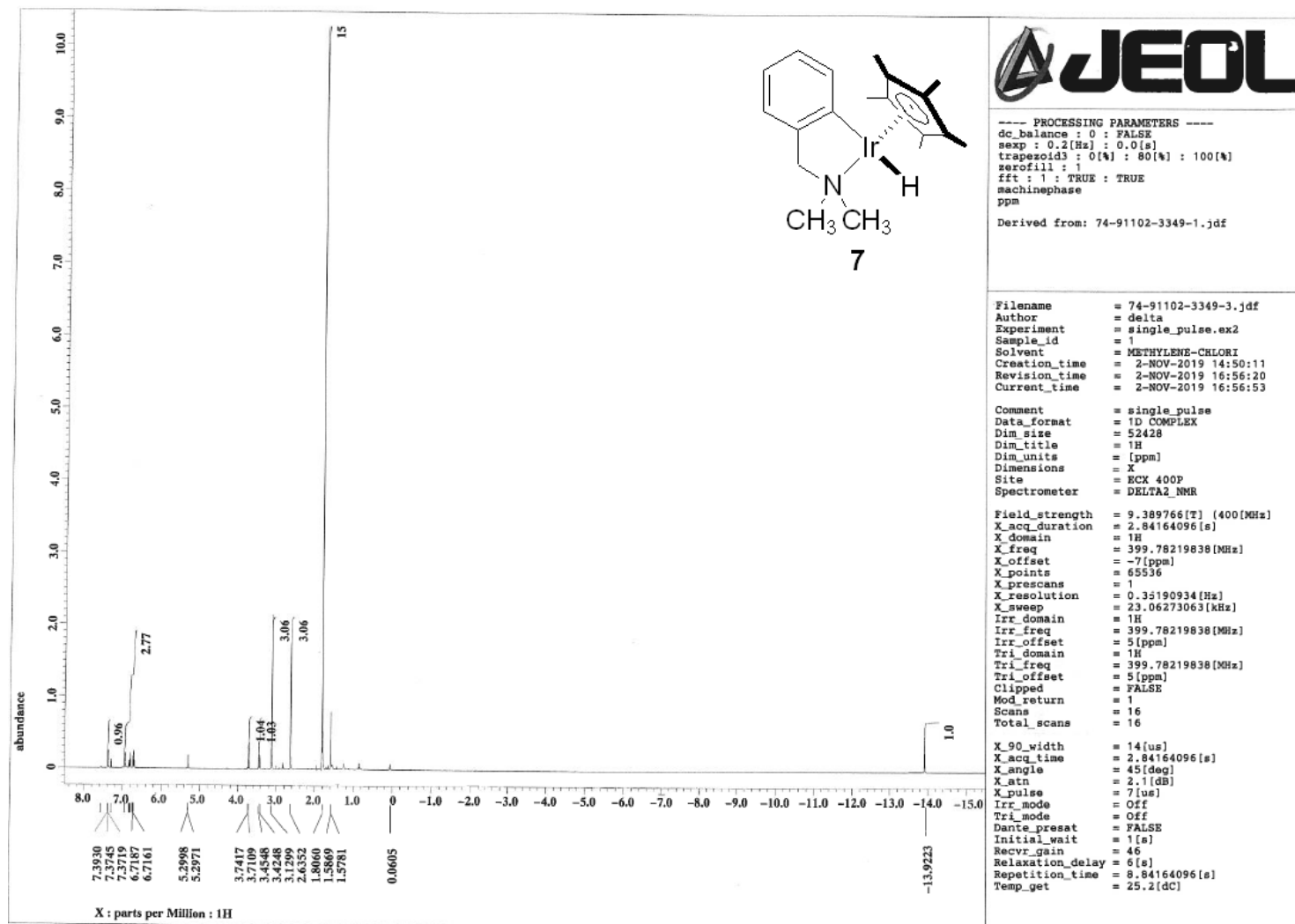


Figure S6: ¹H NMR spectrum (399.78 MHz, CD₂Cl₂, RT) of 7.

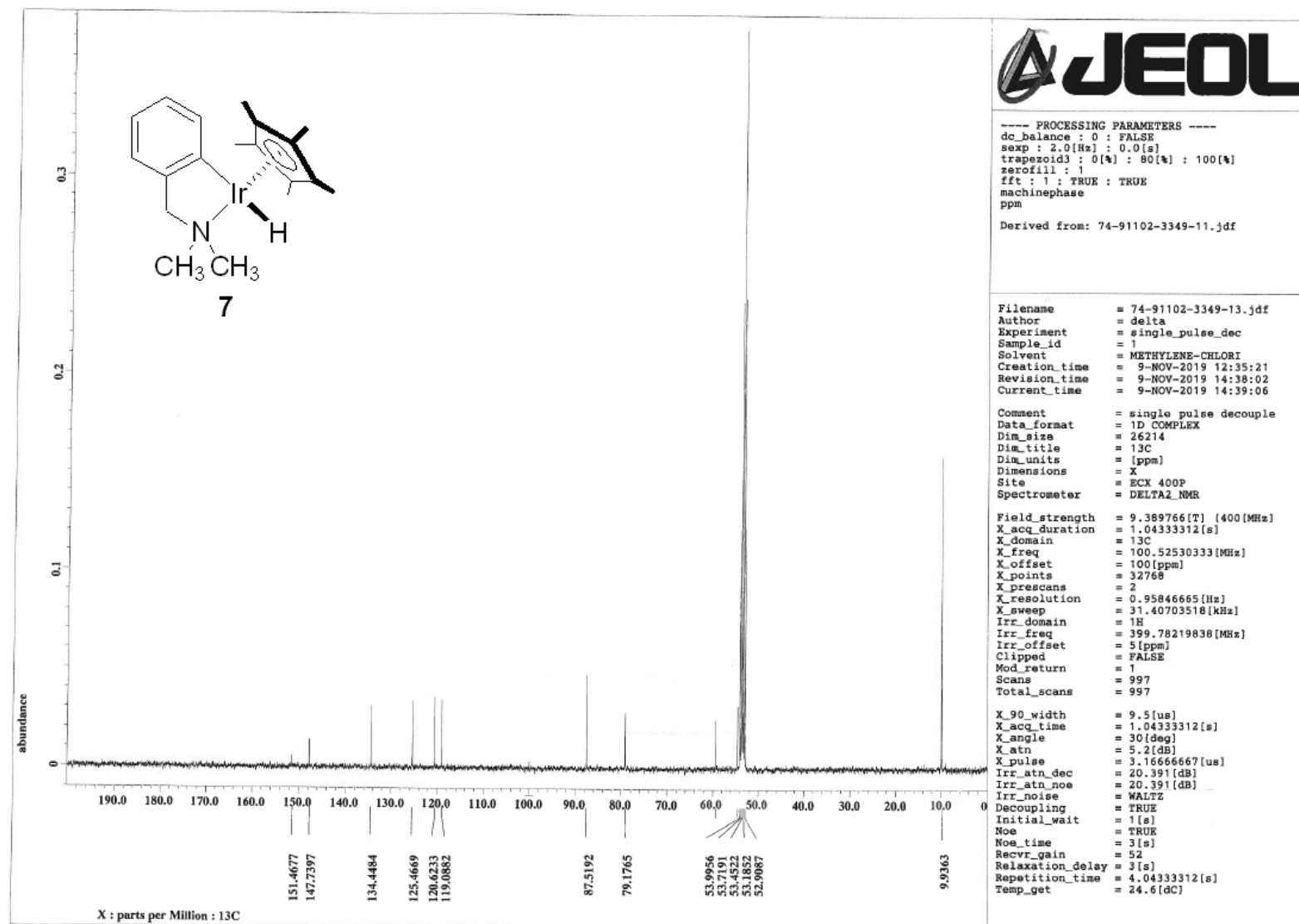
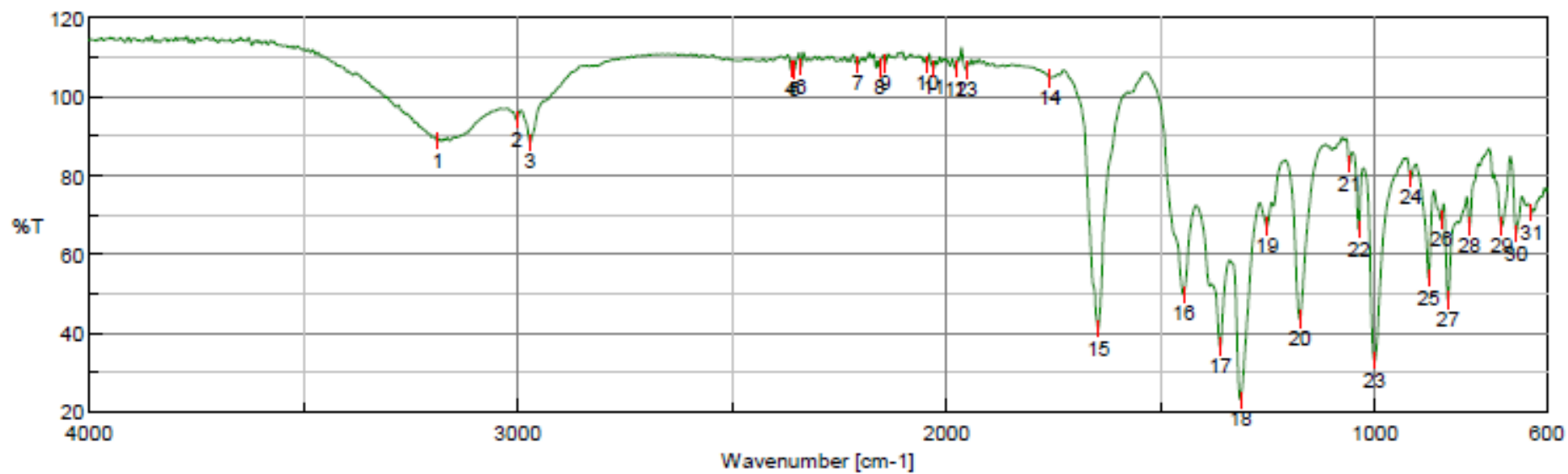


Figure S7: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.53MHz, CD_2Cl_2 , RT) of 7.

5. FTIR Spectrum



No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3186.79	88.6099	2	3002.62	94.1412	3	2970.8	88.3973	4	2362.37	106.905
5	2354.66	106.809	6	2339.23	107.481	7	2206.17	108.206	8	2156.03	107.389
9	2142.53	108.433	10	2045.14	108.291	11	2029.71	107.135	12	1978.61	107.08
13	1954.5	106.865	14	1758.76	104.679	15	1645.95	40.9305	16	1447.31	49.653
17	1361.5	36.3875	18	1314.25	22.9492	19	1252.54	67.0744	20	1176.36	43.4258
21	1059.69	82.7372	22	1038.48	66.2669	23	1001.84	32.7582	24	916.986	79.2572
25	875.524	53.9124	26	846.597	68.5918	27	830.205	48.2354	28	780.065	67.0198
29	704.855	67.0148	30	671.106	65.1662	31	635.43	70.3422			

Figure S8: FTIR Spectrum of $\text{KOCO}_2\text{C}(\text{CH}_3)_3$.