

Supporting Information

Cyclometalated Ir(III)-NHC complex as recyclable catalyst for acceptorless dehydrogenation of alcohols to carboxylic acids

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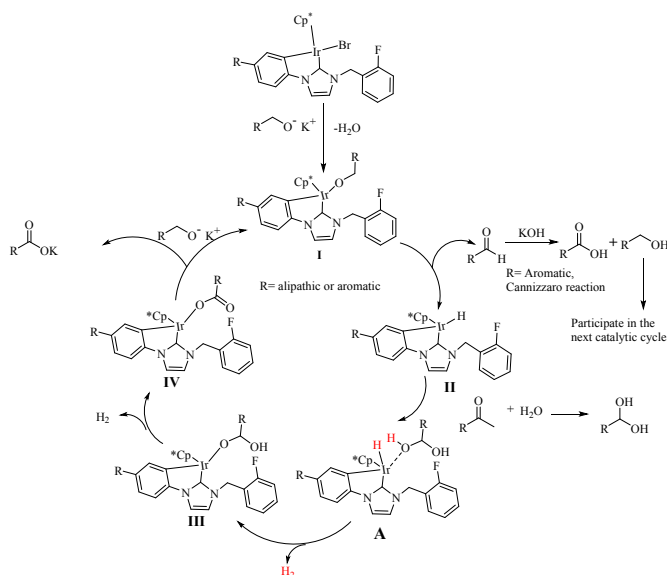
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Table S1: Crystallographic data

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1. Proposed reaction mechanism

The first step of the reaction would involve generation of an alkoxy-iridium species I by the reaction of complex **1a** with benzyl alcohol in presence of base KOH. Notably, formation of similar iridium-alkoxide species was also observed by Williams et. al.¹ Thereafter, the alkoxy-iridium species I would undergo a β -hydrogen elimination leads to the formation of hydrido-iridium species II with concomitant release of an aldehyde molecule. Next, the hydrido-intermediate II would possibly react with an aldehyde and water release a hydrogen molecule and generate intermediate III (through intermediate A) which subsequently would release another molecule of H₂ to give intermediate IV. The potassium salt of the acid would finally be produced by the reaction of IV with benzyl alcohol and KOH and thus the cycle continues. The existence of possible species I and IV was evidenced by the *in situ* ESI/MS spectra of the catalytic system with *m/z* 716.67 and 730.42 (See supporting information Fig S64) respectively and hydrido intermediate I was detected through *in situ* ¹H NMR spectroscopy. Although, the existence of the intermediary species III could not be traced, literature evidence suggests this is the most likely species involved in the process.^{2,3}



References

1. V. Cherepakhin, T. J. Williams, *ACS Catal.*, 2018, **8**, 3754–3763.
2. D. Gong, B. Hu and D. Chen, *Dalton Trans.*, 2019, **48**, 8826.

3. A. Sarbajna, I. Dutta, P. Daw, S. Dinda, W. S. M. Rahaman, A. Sarkar, J. K. Bera, *ACS Catal.*, 2017, 7, 4, 2786–2790.

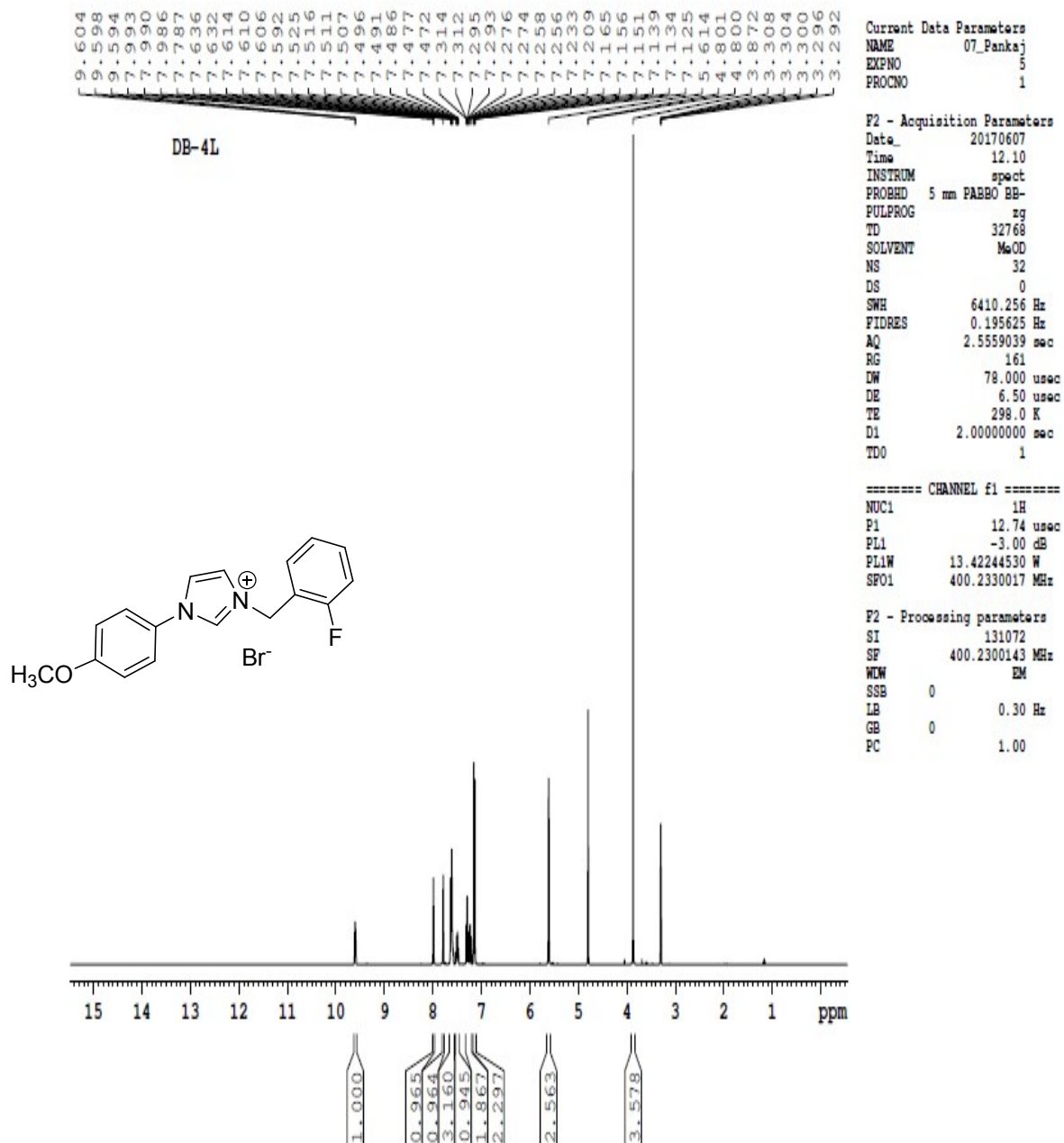
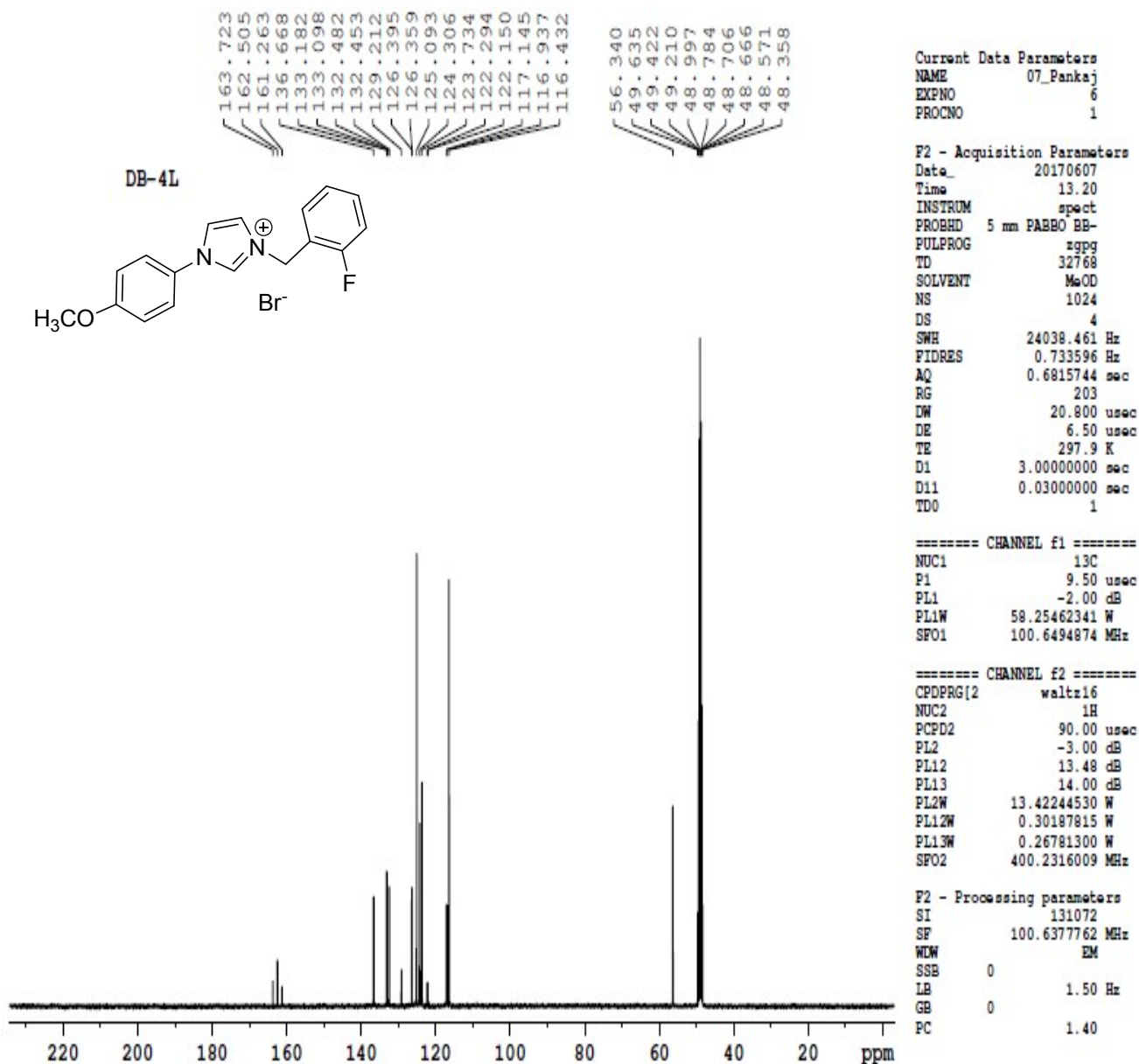


Figure S1. ^1H NMR of Ligand Precursor L_1 in CD_3OD

Figure S2. ^{13}C NMR of Ligand Precursor L_1 in CD_3OD

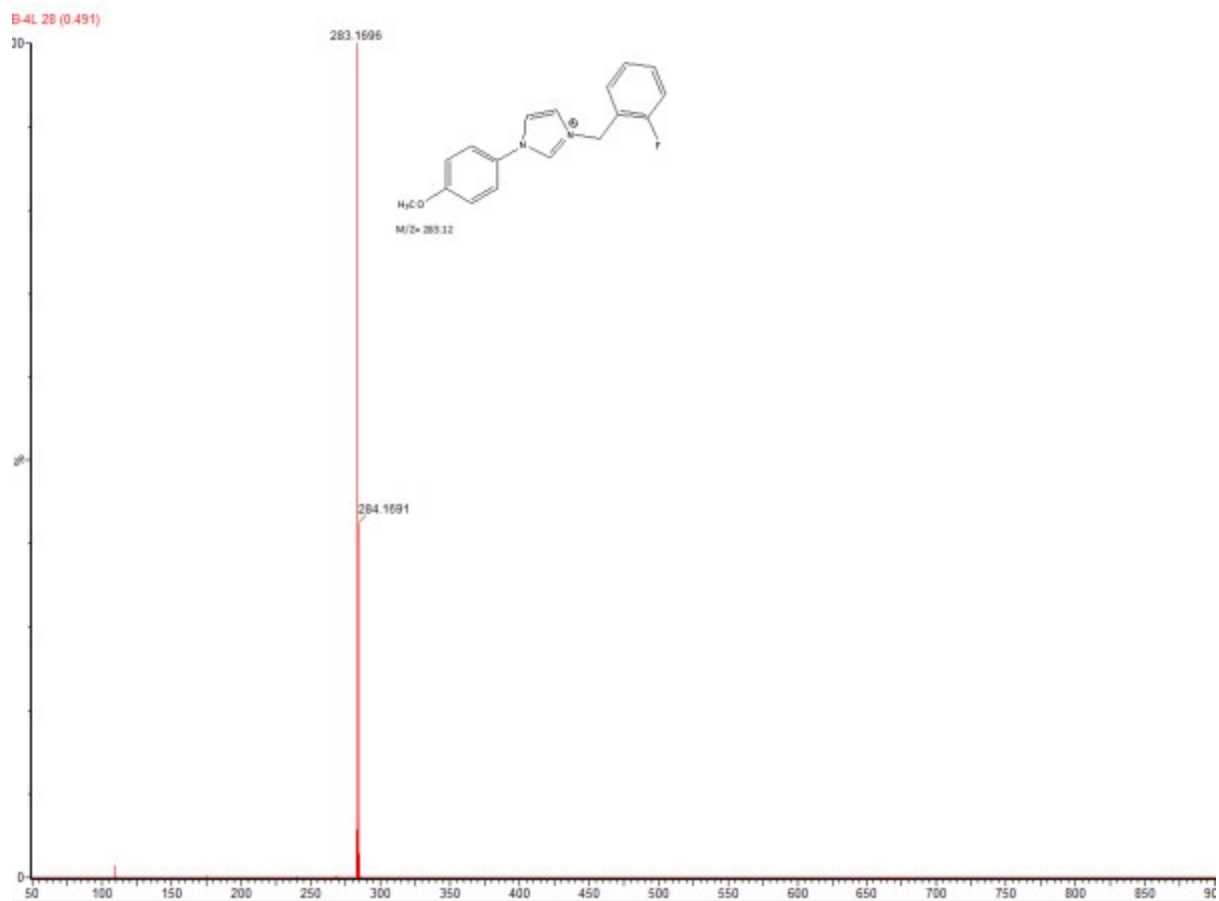
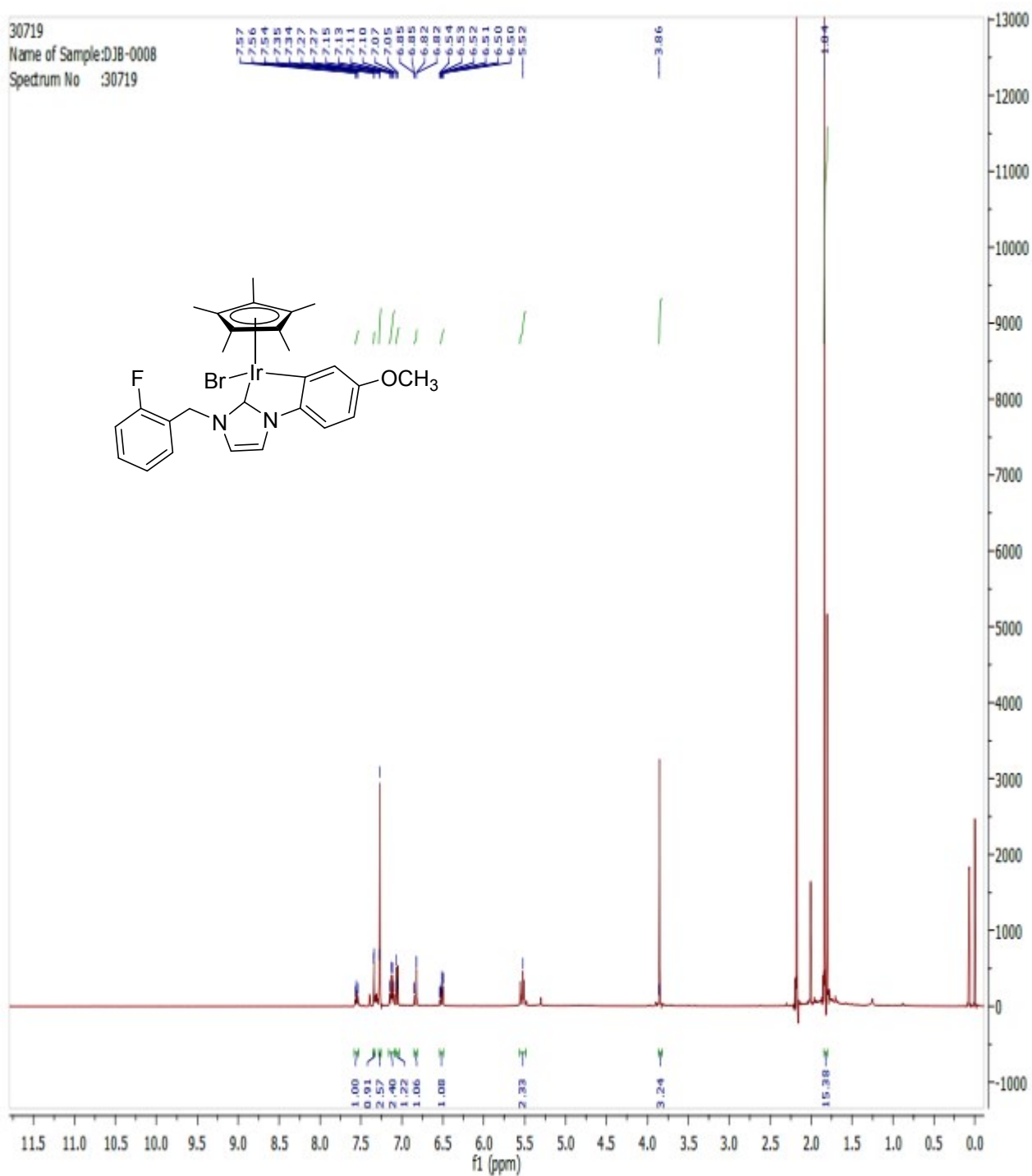


Figure S3. HRMS of Ligand Precursor L₁

Figure S4. ^1H NMR of Complex **1a** in CDCl_3

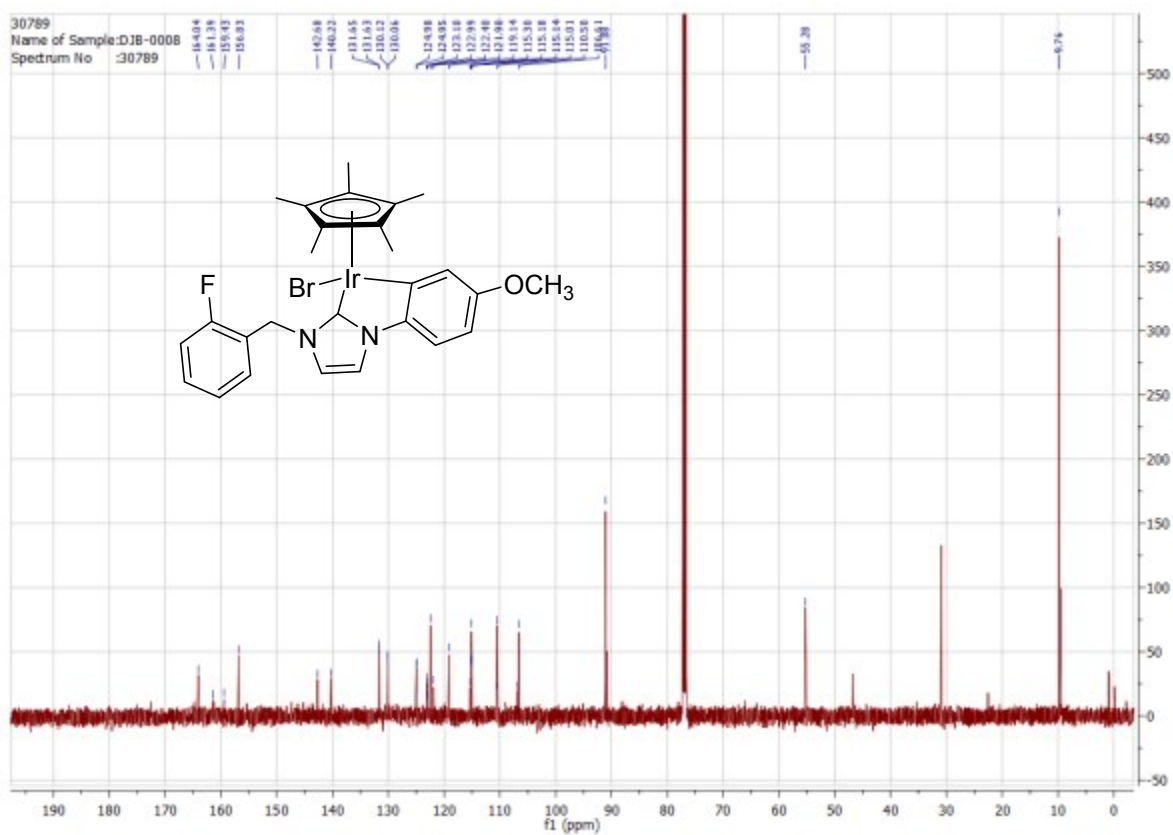


Figure S5. ^{13}C NMR of Complex **1a** in CDCl_3

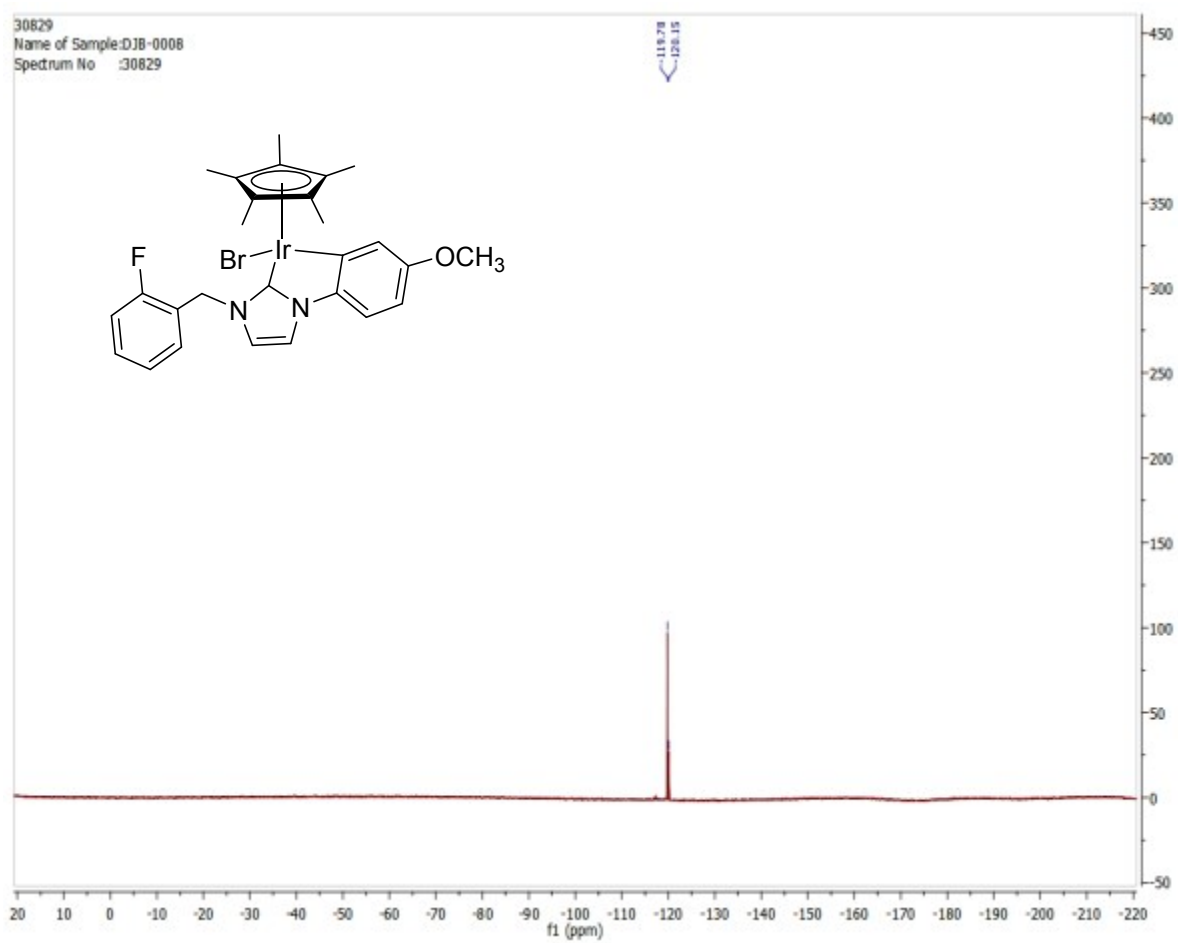


Figure S6. ^{19}F NMR of Complex **1a** in CDCl_3

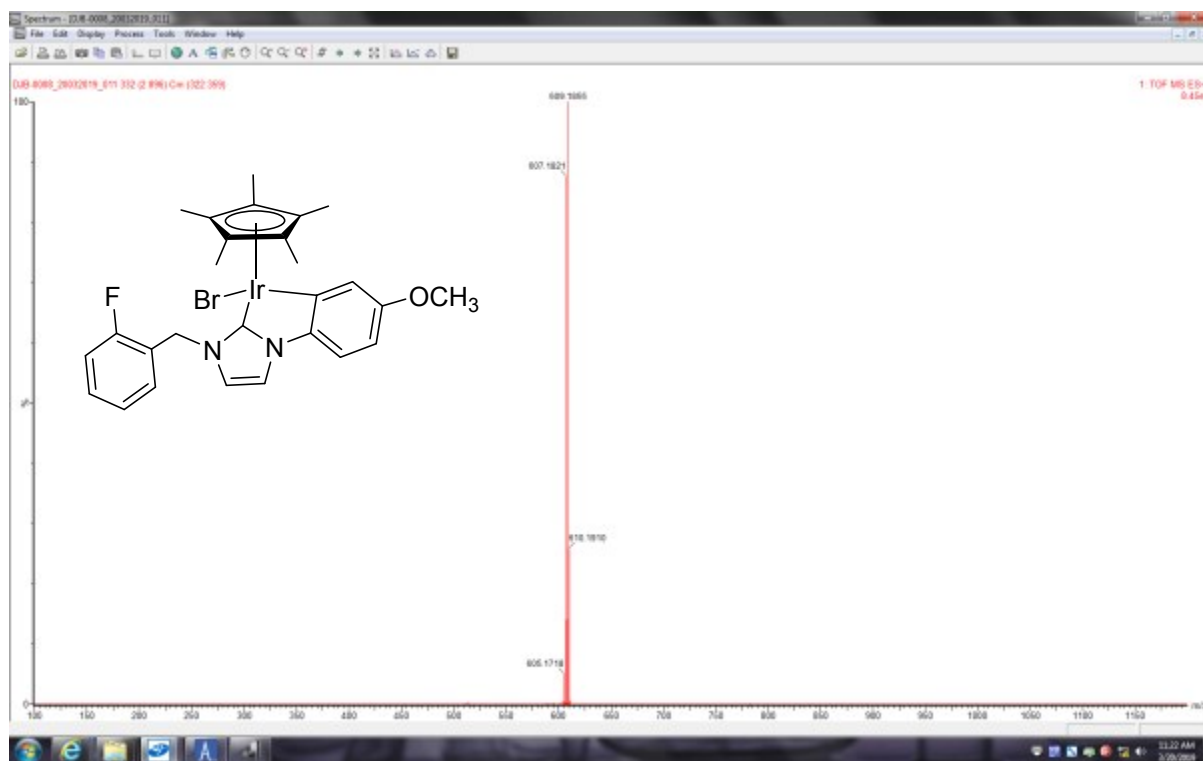


Figure S7. HRMS of Complex 1a

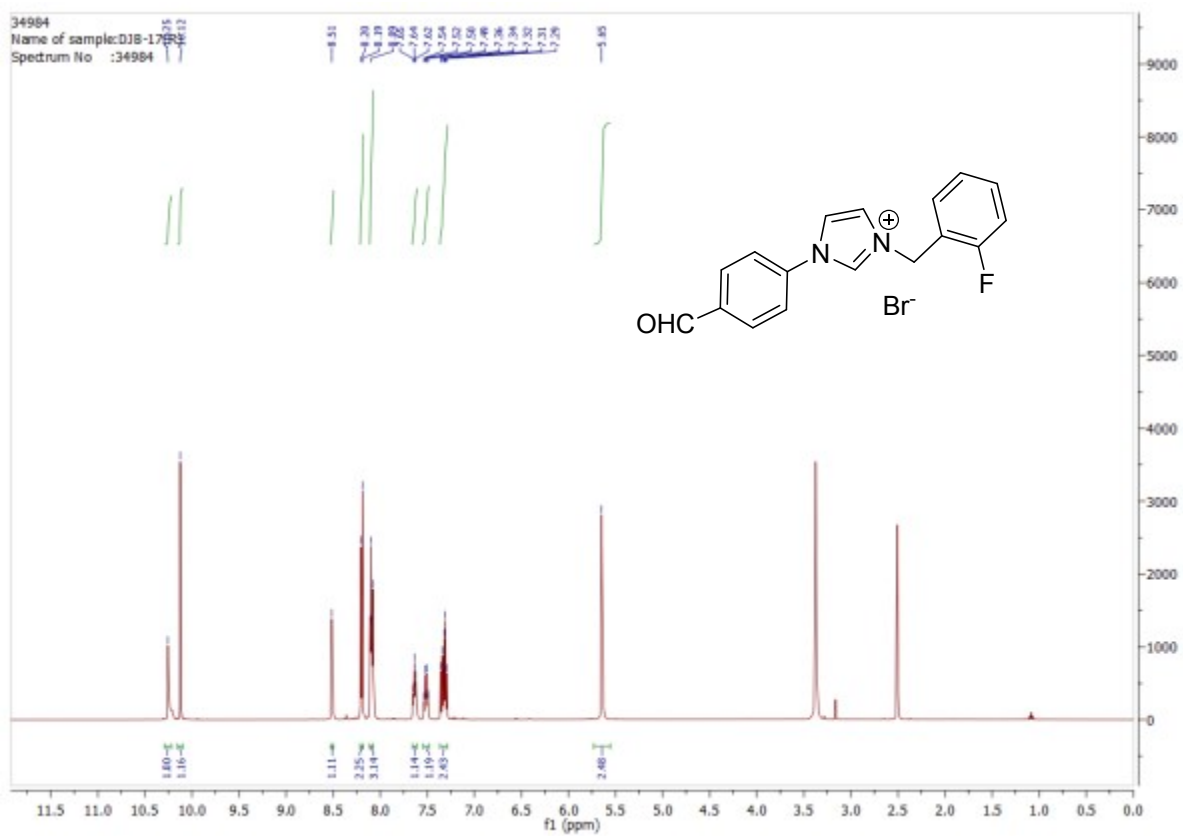


Figure S8. ^1H NMR of Ligand Precursor L₂ in DMSO-d₆

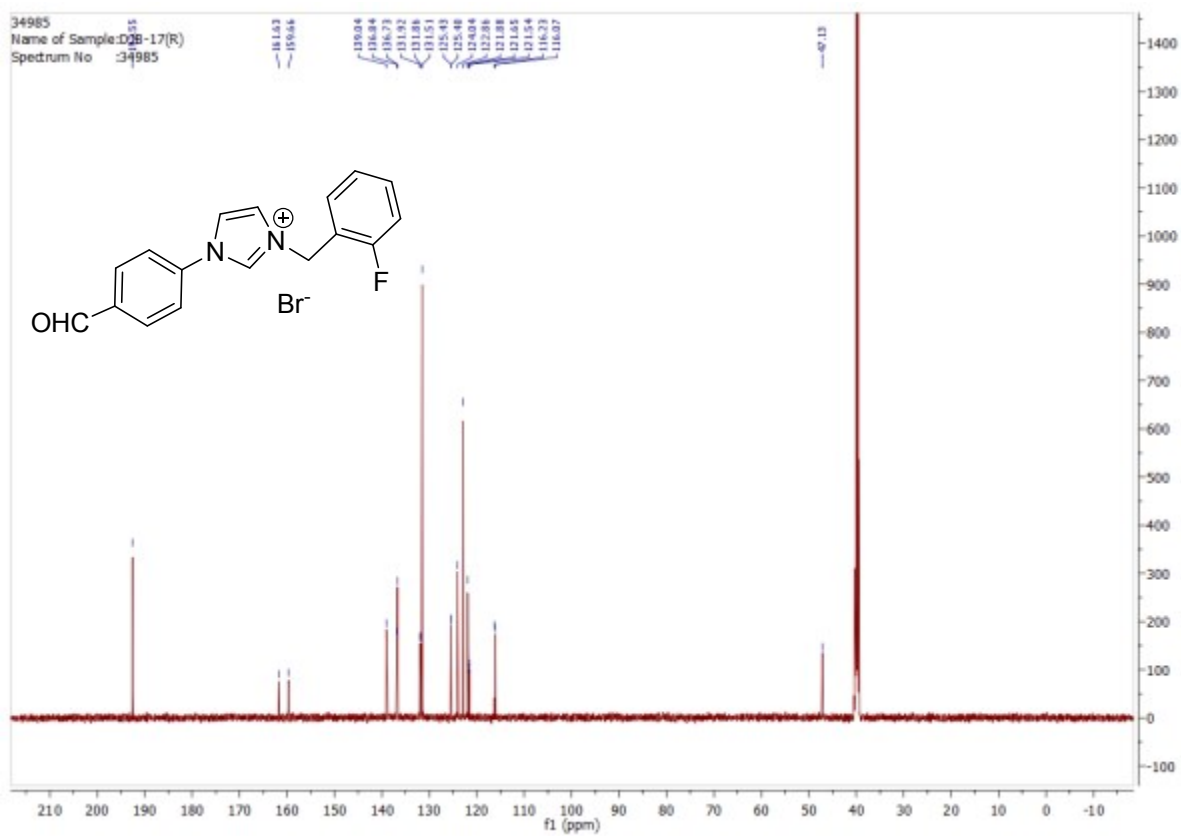


Figure S9. ¹³C NMR of Ligand Precursor L₂ in DMSO-d₆

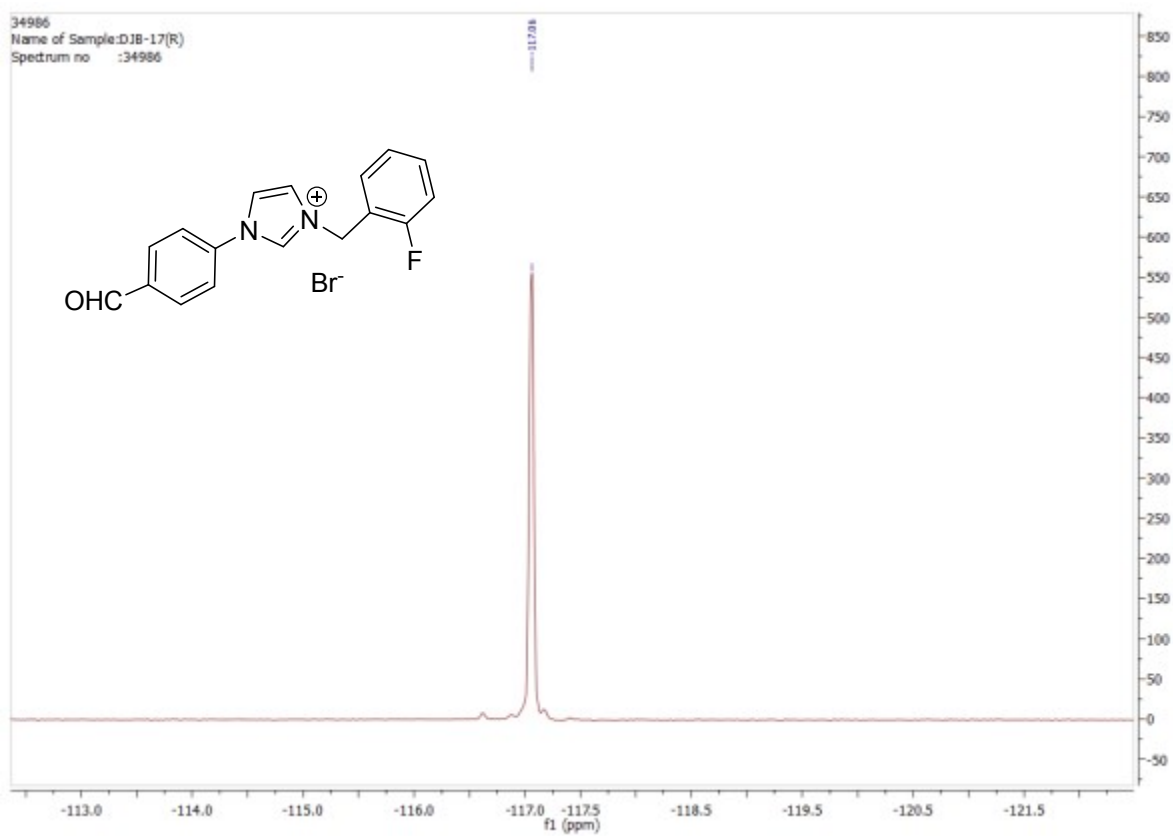
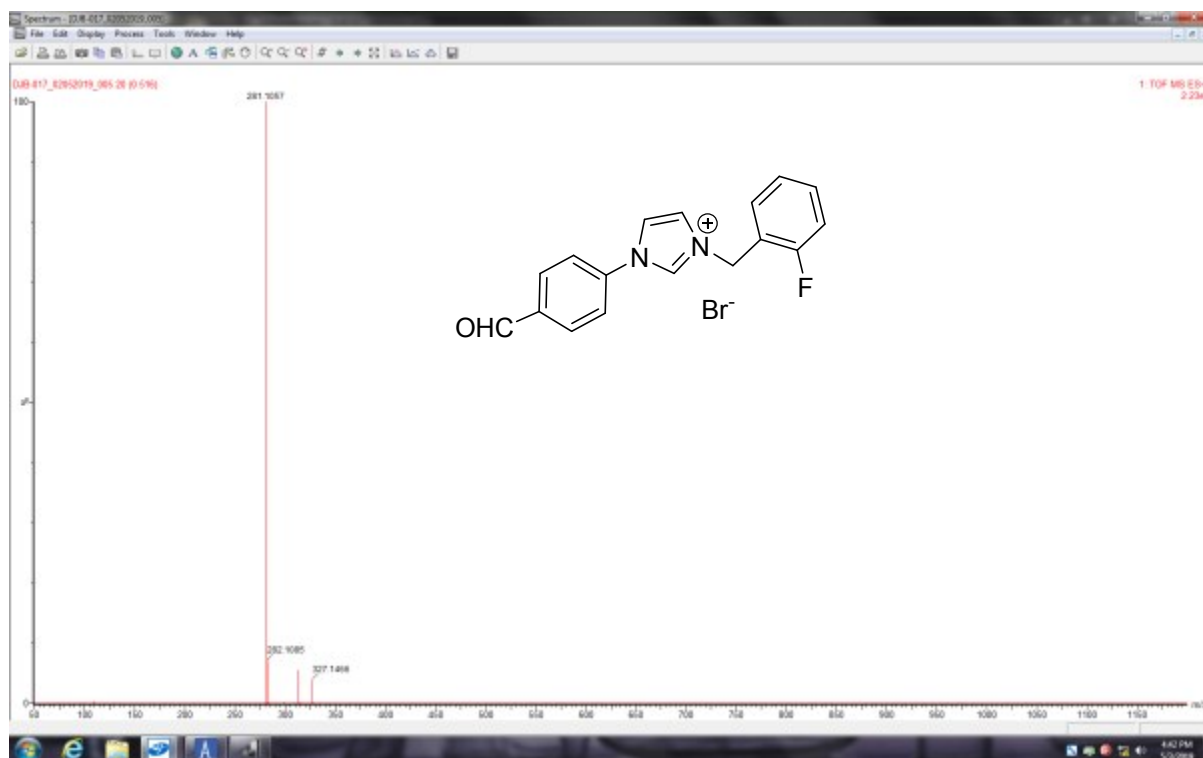


Figure S10. ¹⁹F NMR of Ligand Precursor L₂ in DMSO-d₆

Figure S11. HRMS of Ligand Precursor L₂

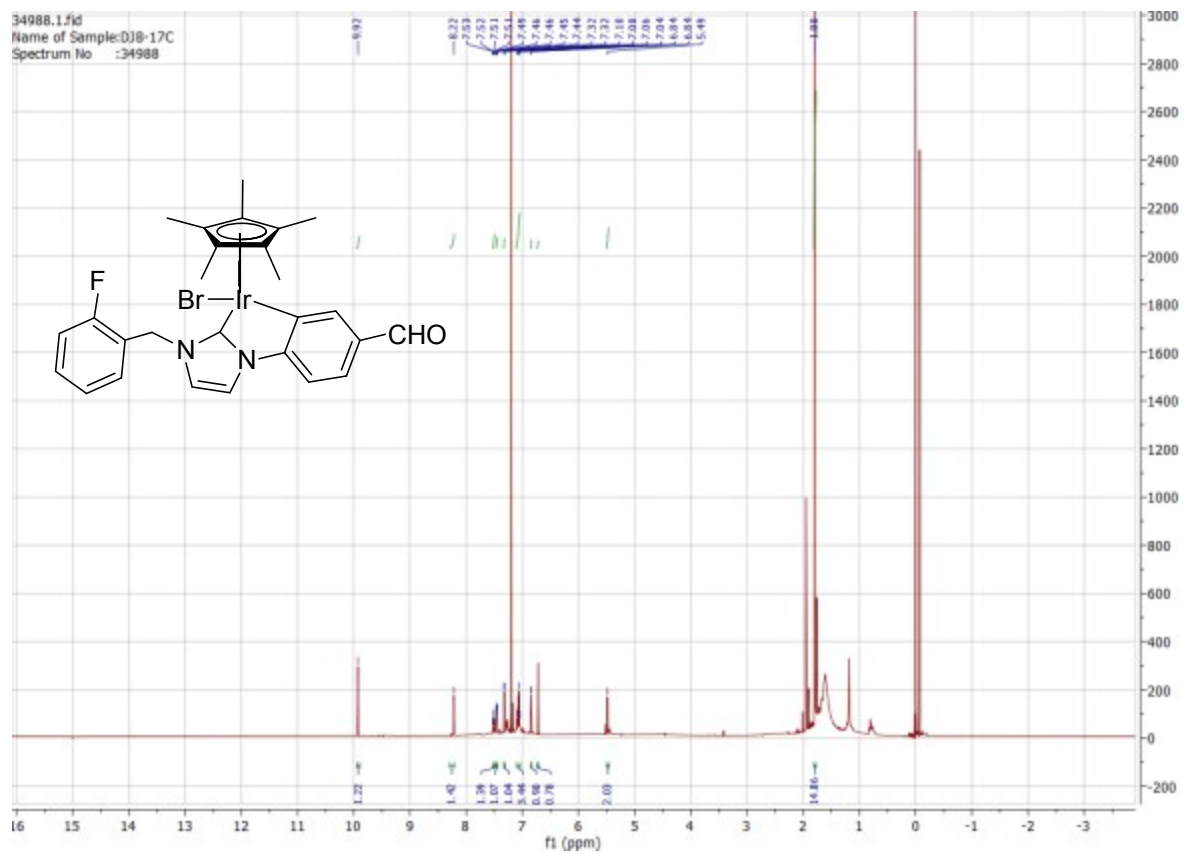


Figure S12. $^1\text{H NMR}$ of Complex **1b** in CDCl_3

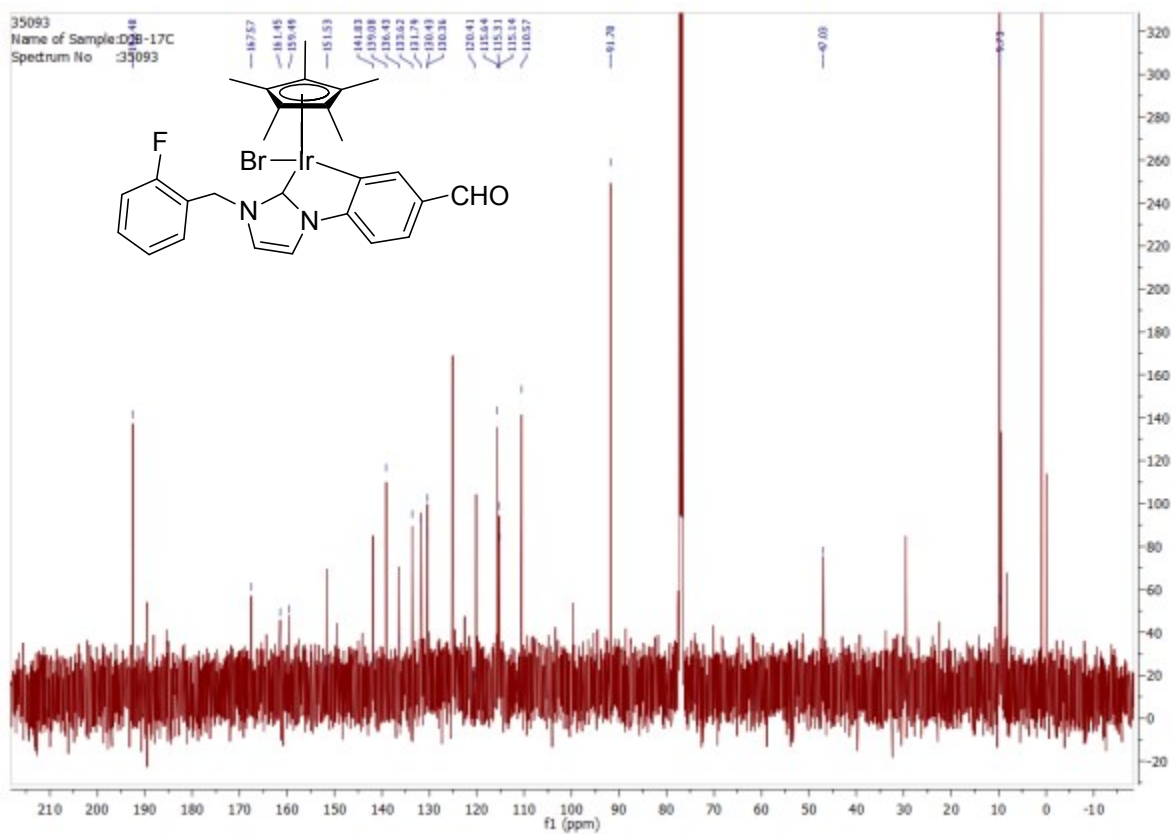


Figure S13. ^{13}C NMR of Complex **1b** in CDCl_3

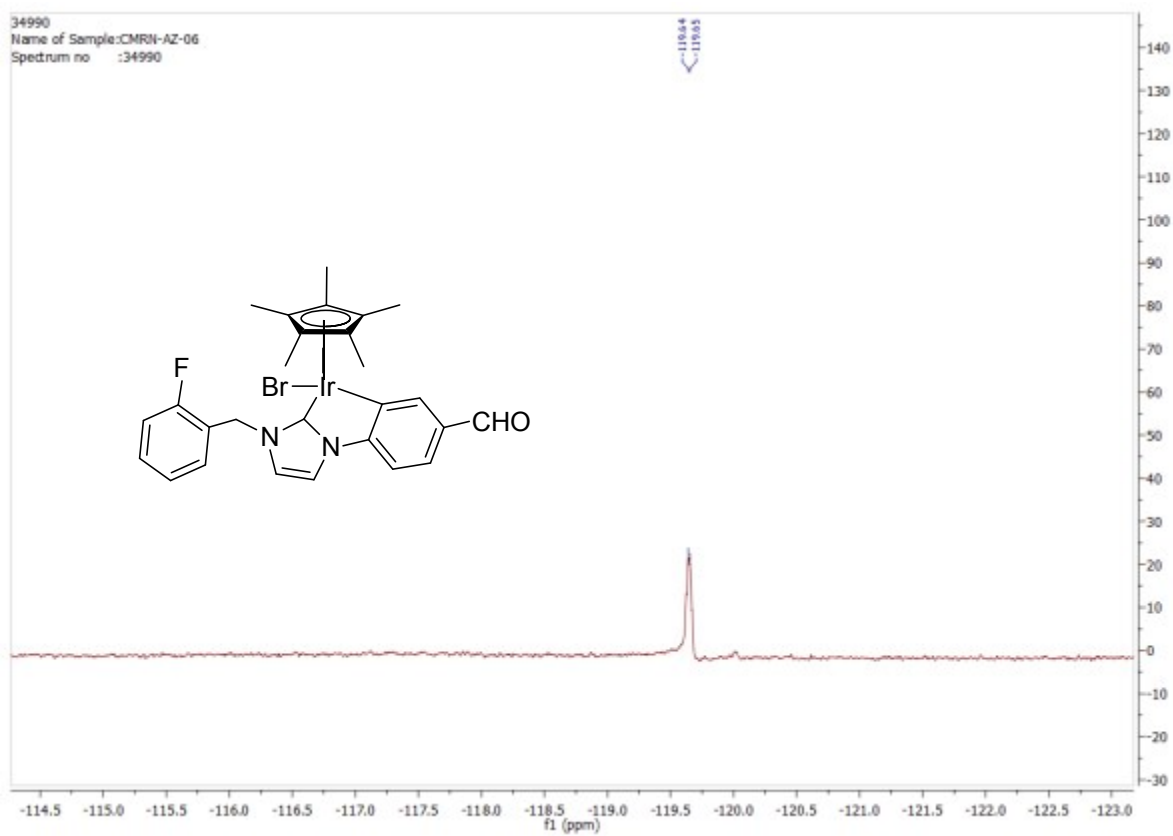
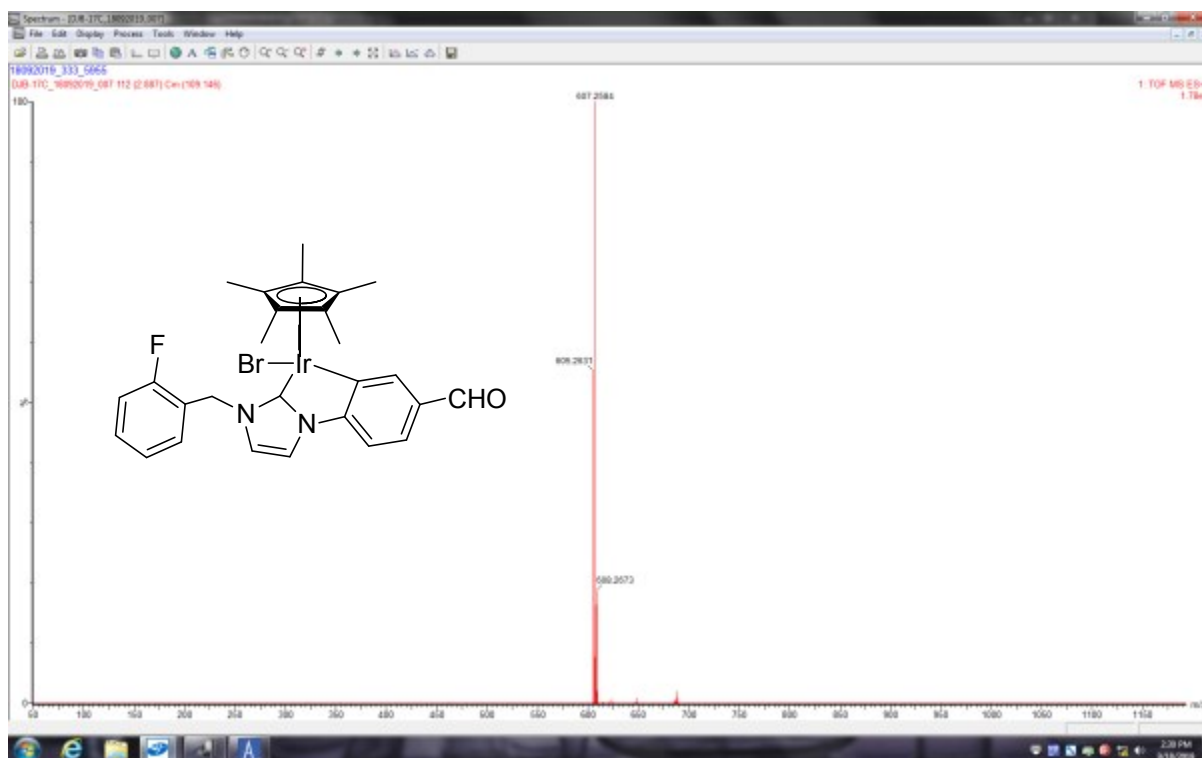


Figure S14. ^{19}F NMR of Complex **1b** in CDCl_3

Figure S15. HRMS Spectrum of Complex **1b**

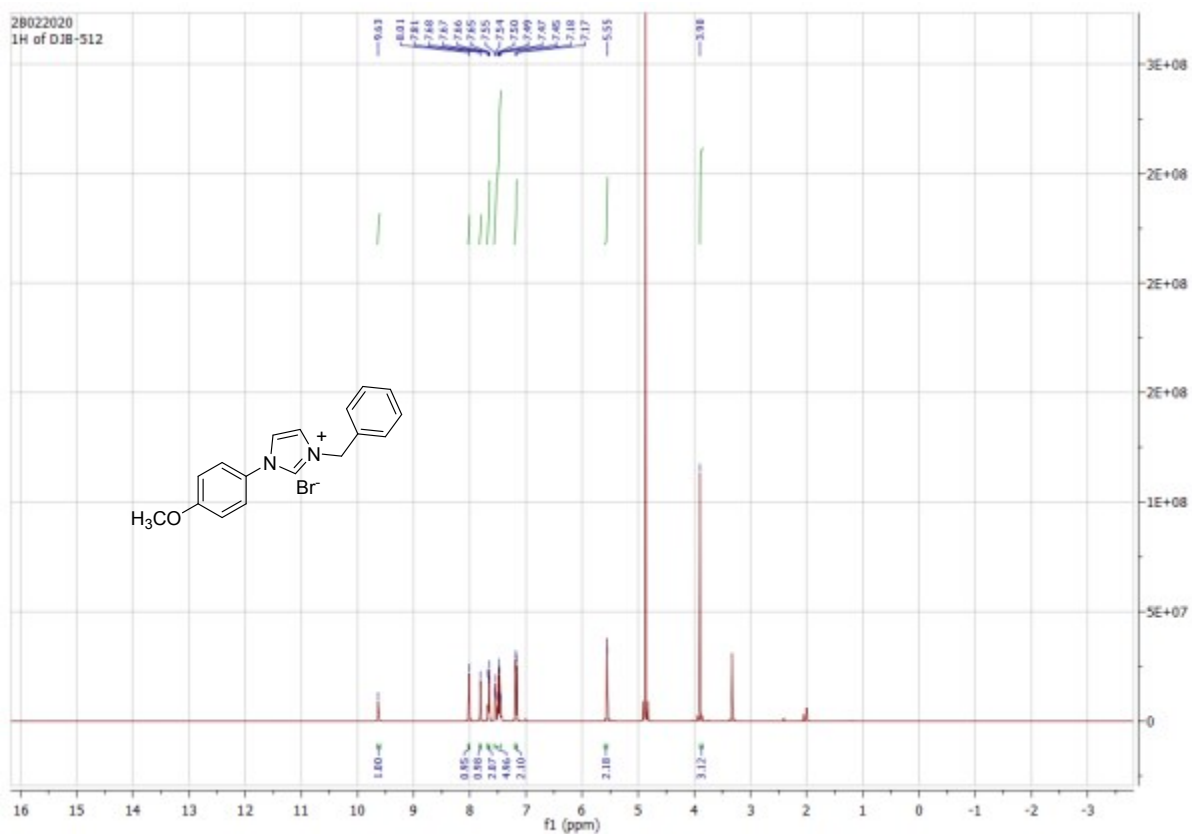


Figure S16. ^1H NMR of Ligand Precursor L_3 in $\text{CD}_3\text{OD-d}_3$

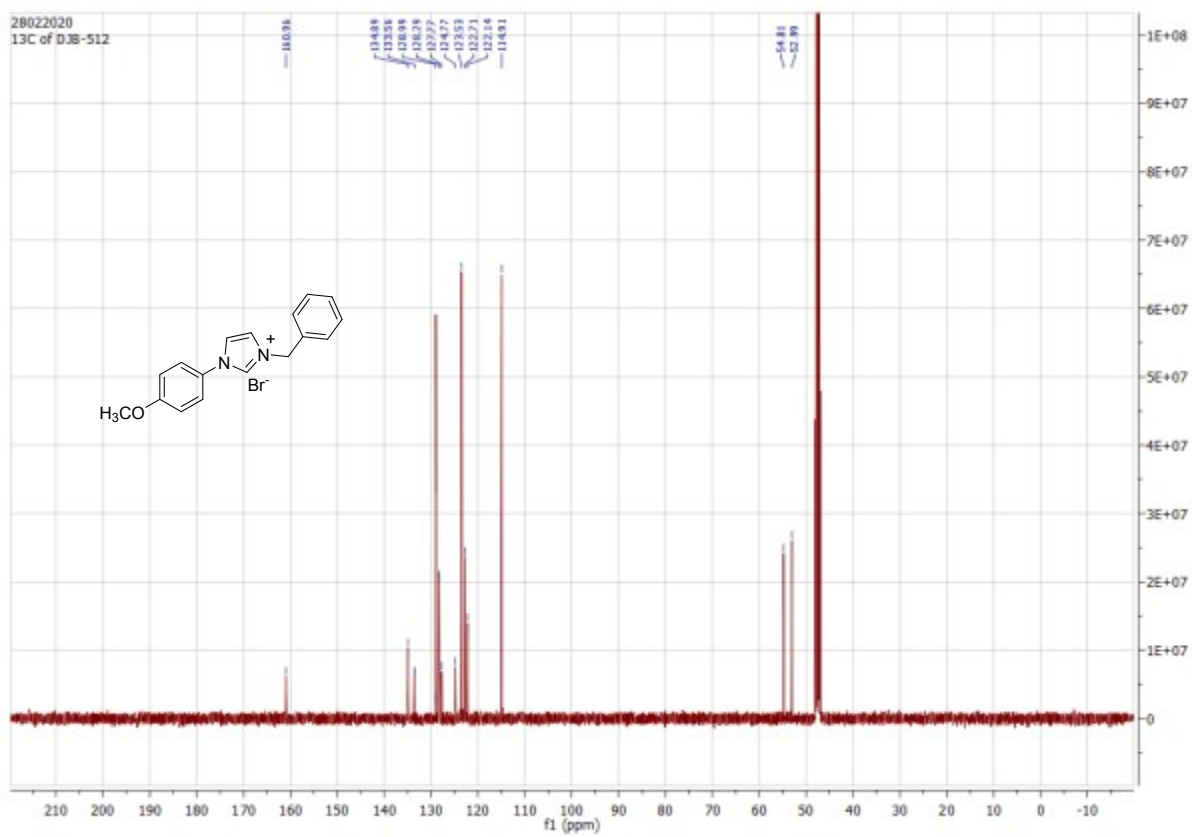


Figure S17. ¹³C NMR of Ligand Precursor L₃ in CD₃OD-d₃

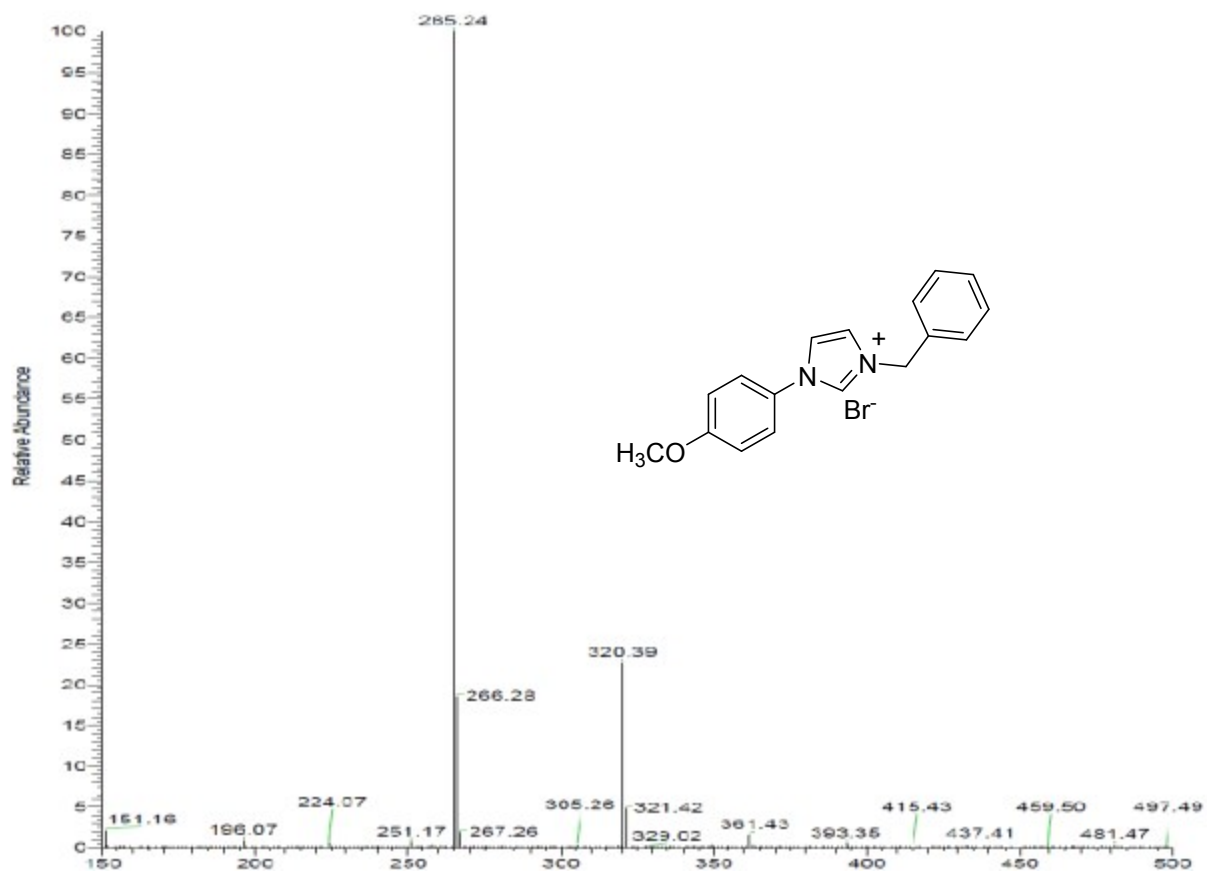
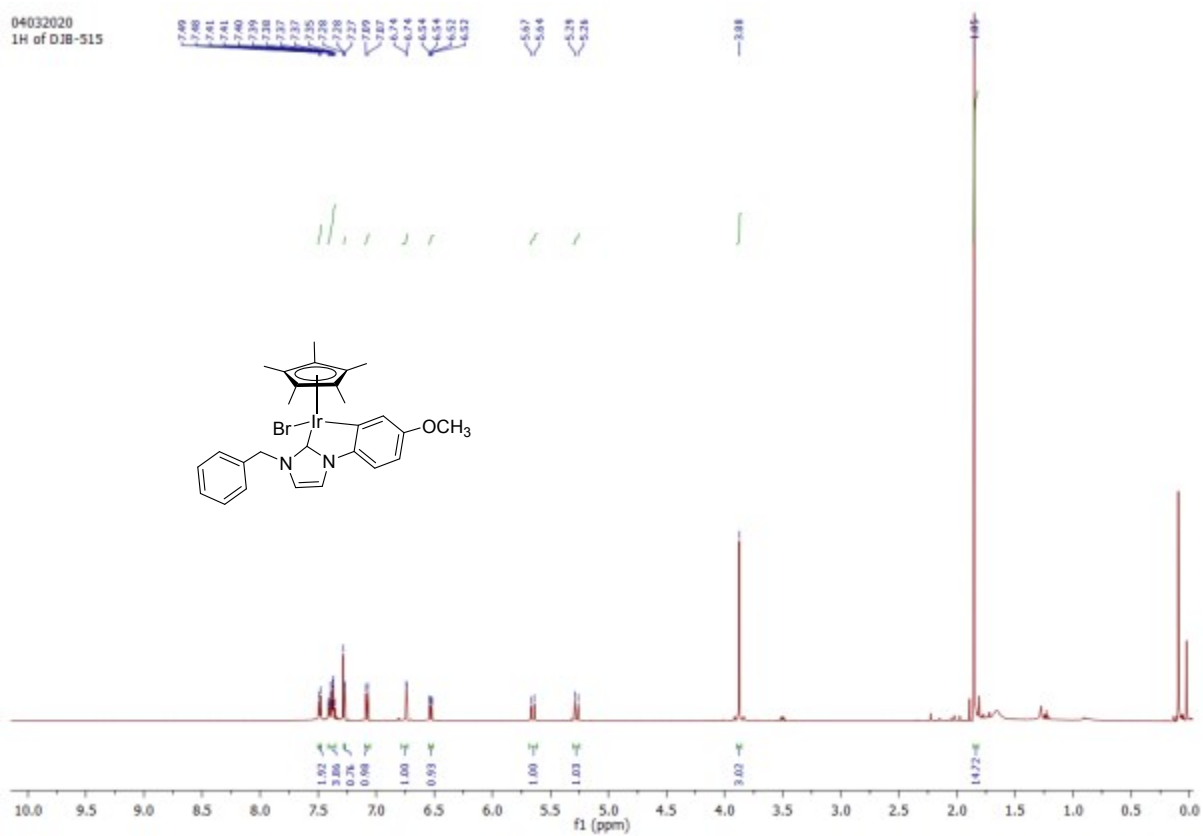


Figure S18. LC-MS spectrum of Ligand Precursor L₃ .

Figure S19. ^1H NMR of Complex 1c in $\text{CDCl}_3\text{-d}_1$

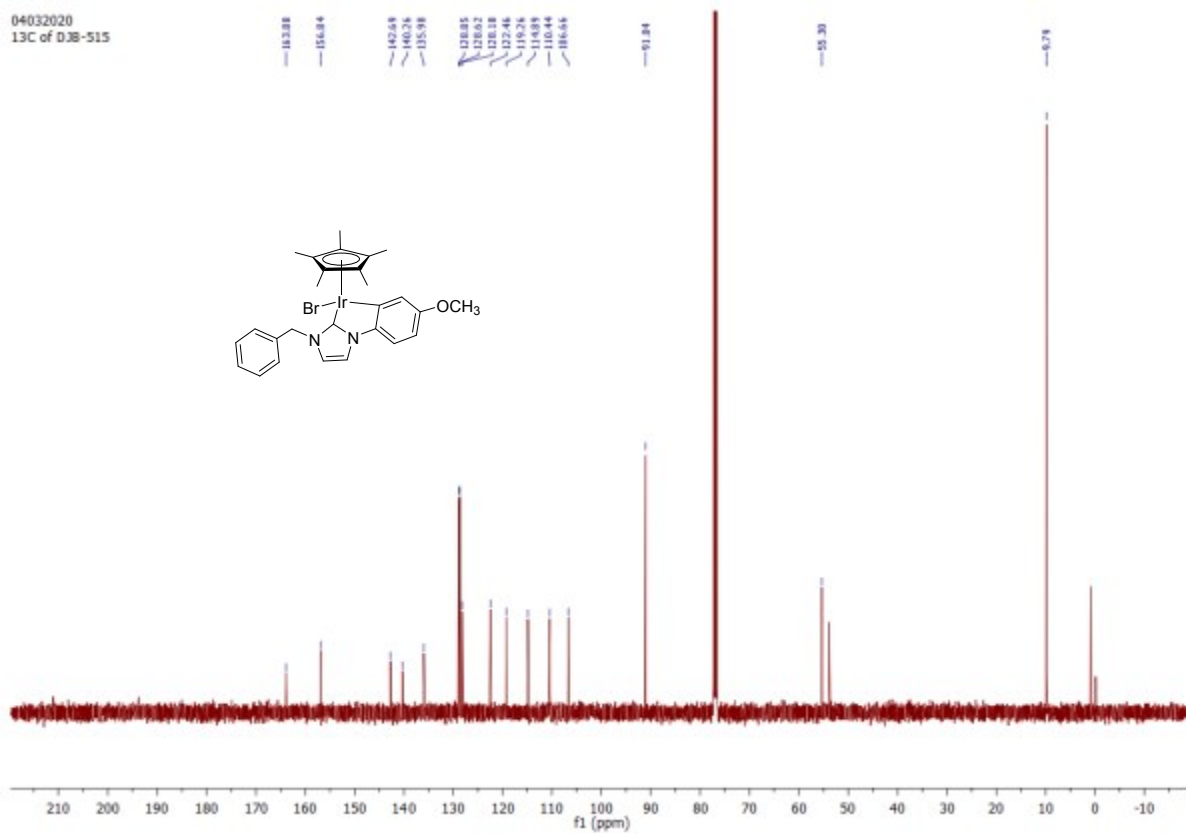


Figure S20. ^{13}C NMR of Complex 1c in $\text{CDCl}_3\text{-d}_1$

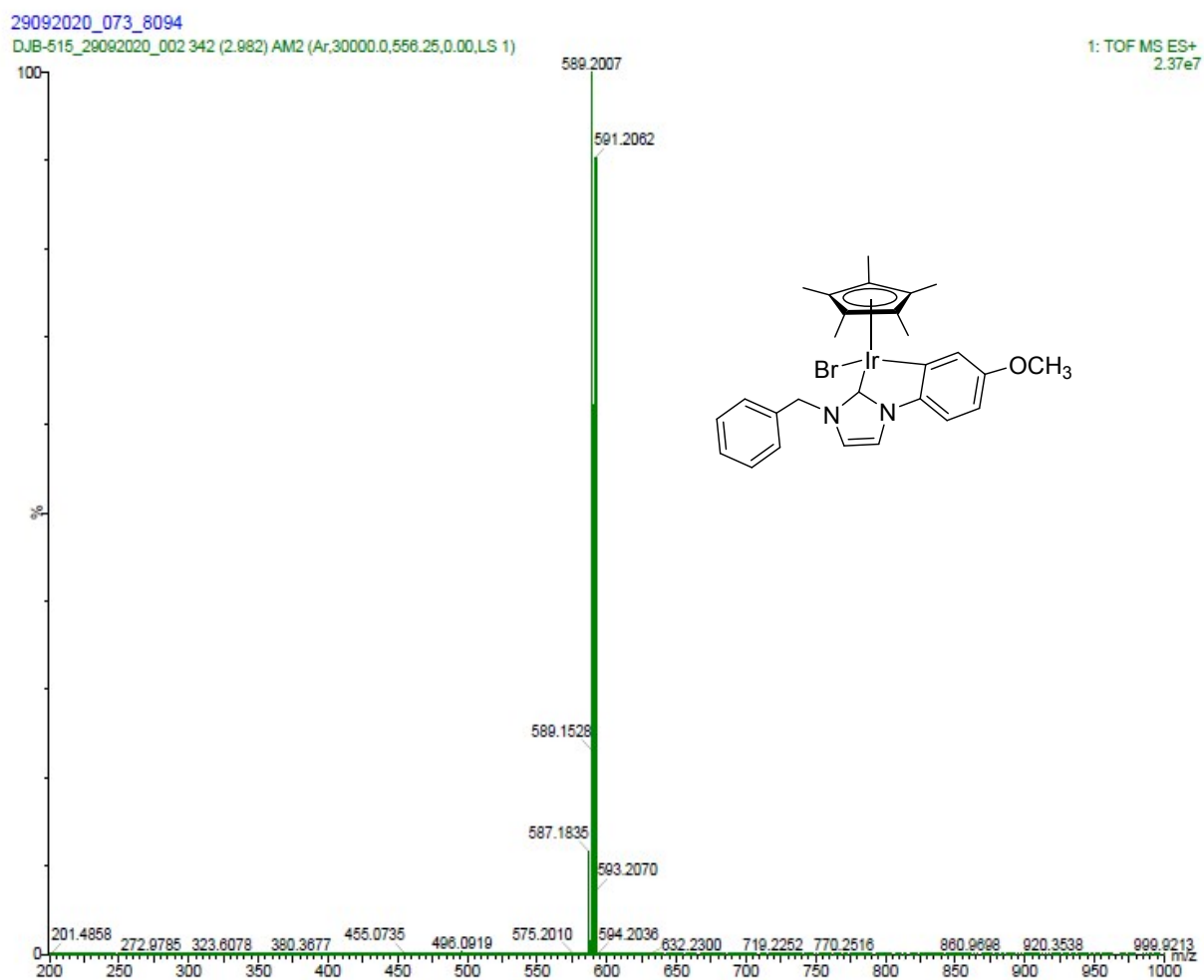


Figure S21. HR-MS spectra of Complex 1c .

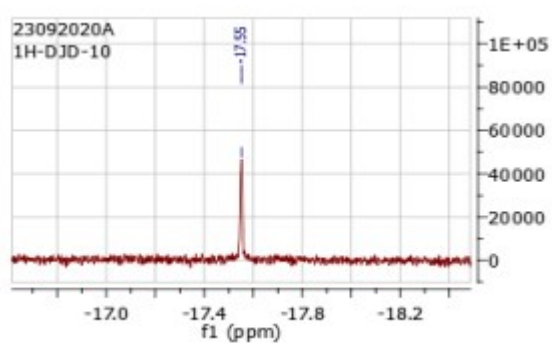
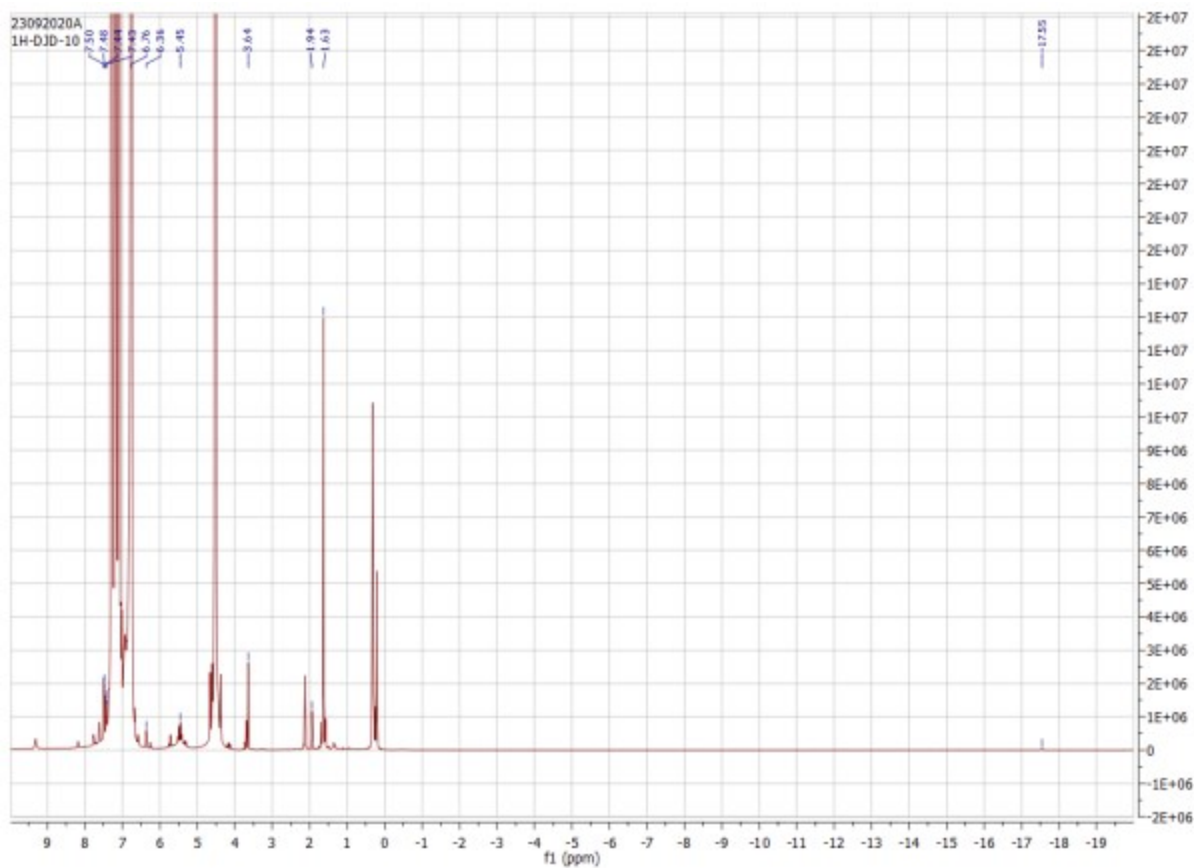


Figure S22 : ^1H NMR spectrum of *in situ* generated Ir-H from the complex **1a** at 50°C in toluene d_8 . (heated for 10 minutes)

(The assigned signals are for the complex)

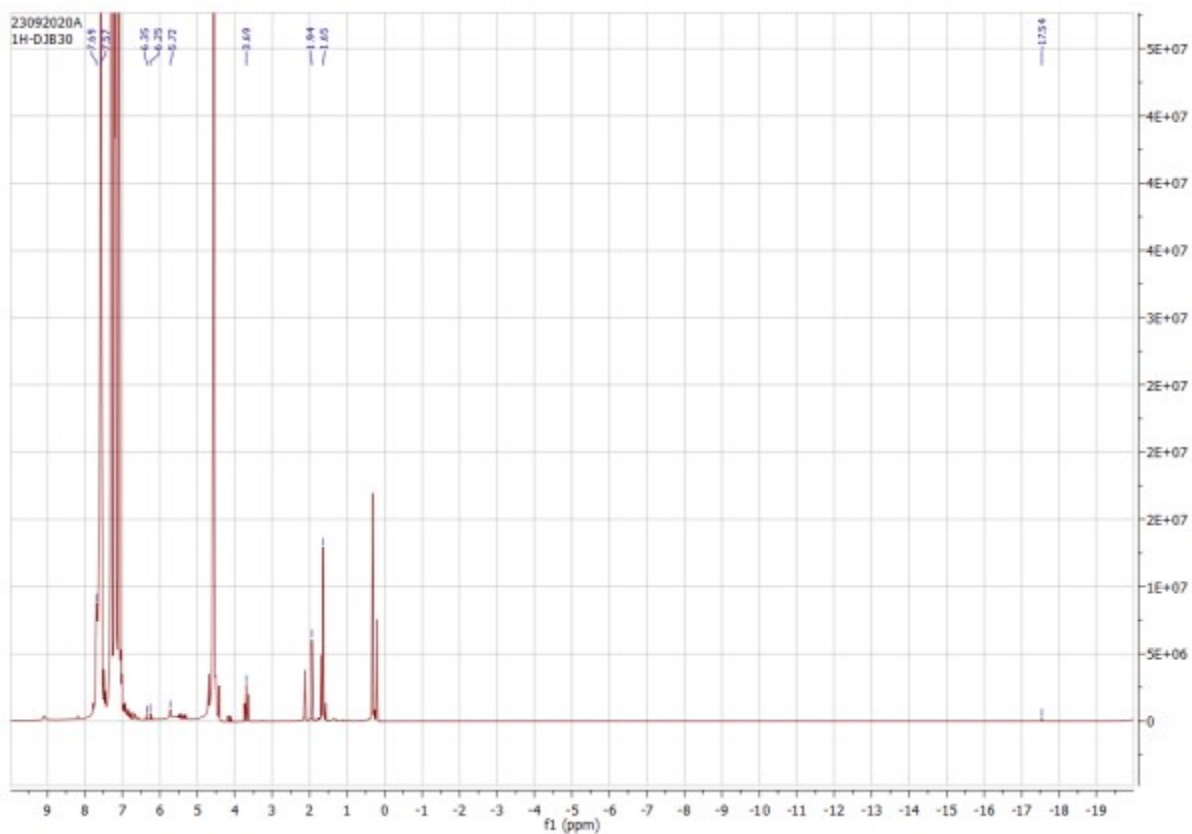


Figure S23 : ^1H NMR spectrum of *in situ* generated Ir-H from the complex **1a** in **toluene-d8**. (under standard reaction conditions, heated for 20 minutes)

(The assigned signals are for the complex)

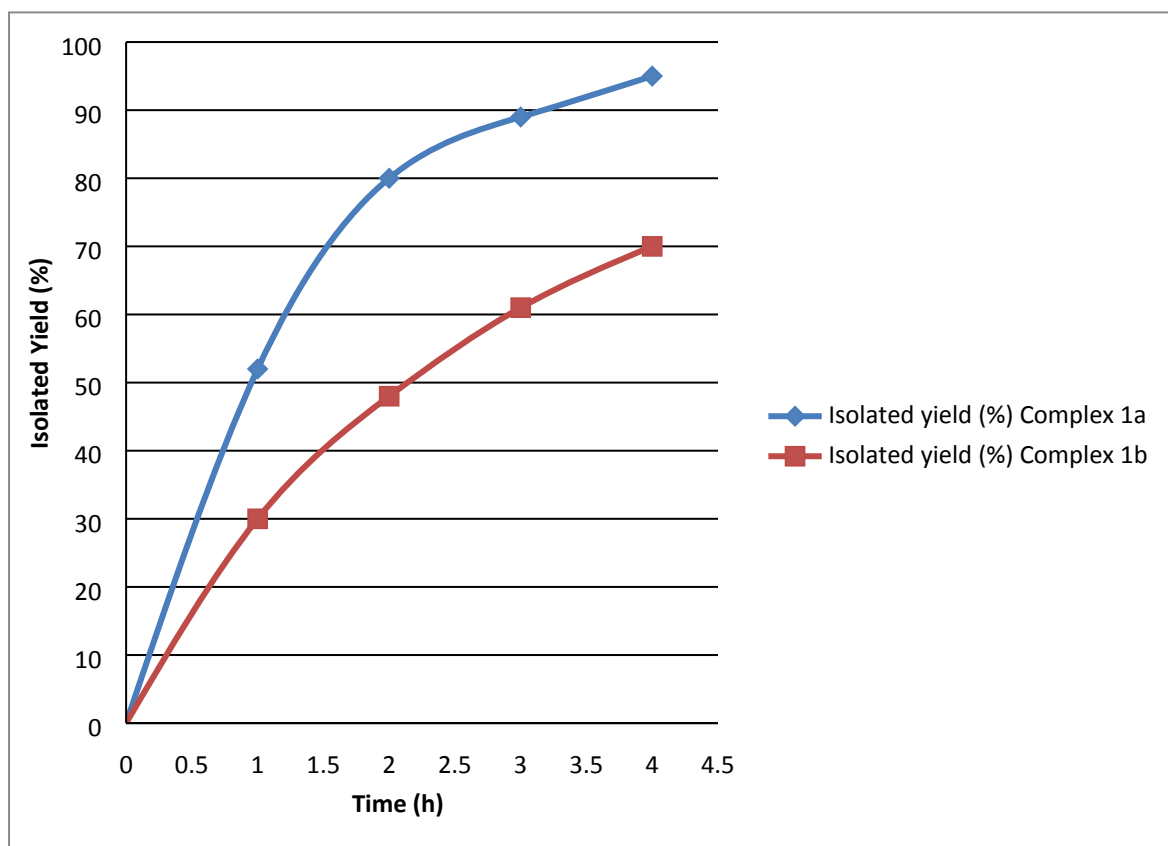


Figure S24: Time course of the catalytic acceptorless dehydrogenation of benzyl alcohol.

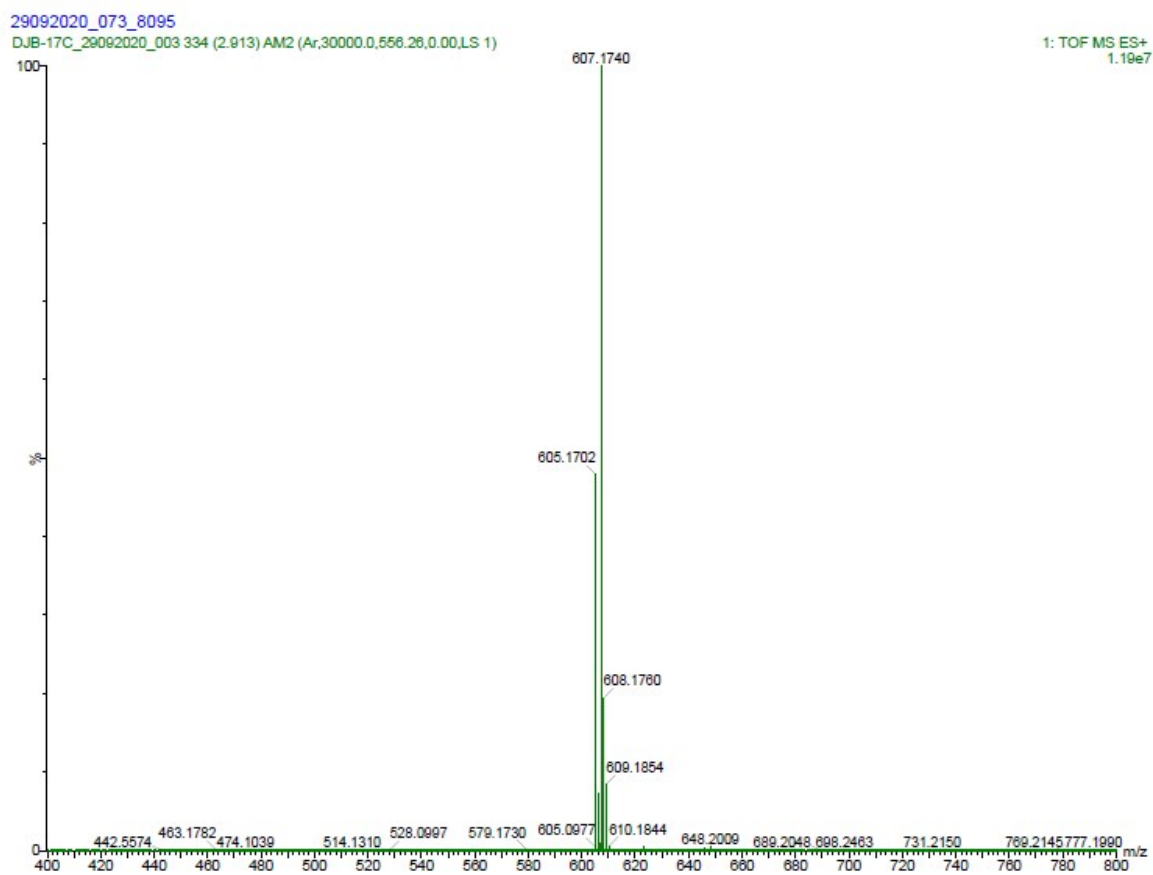


Figure S25: HR-MS spectrum of the reaction mixture of **1b** and KOH in toluene.

Condition : Complex **1b** (0.1 mmol), KOH (1.1 mmol), Toluene (10 mL), Temperature 120°C, Time 24 h

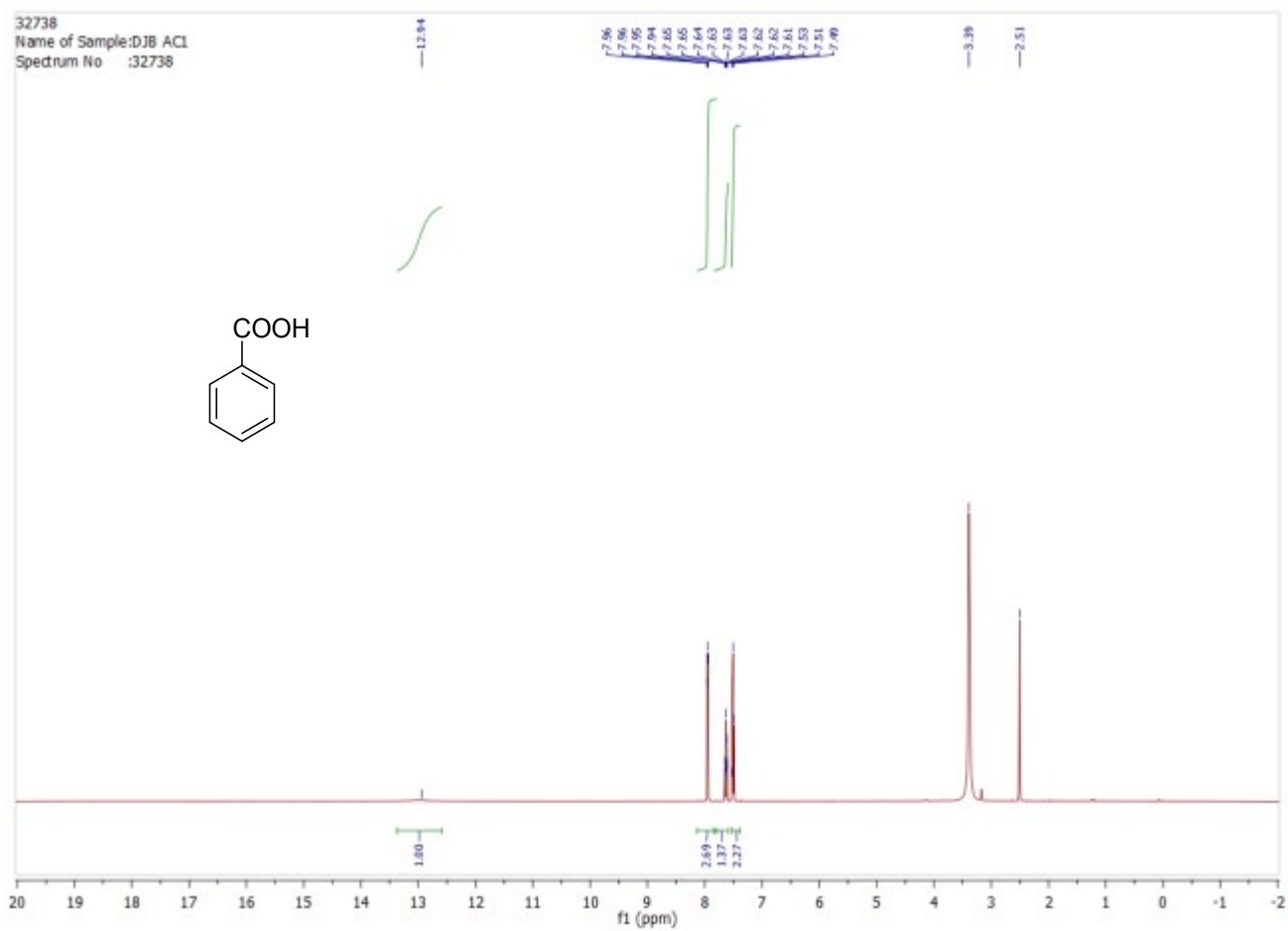


Figure S26. ^1H NMR of Acid **1** in DMSO-d_6 (Table 2, Entry 1)

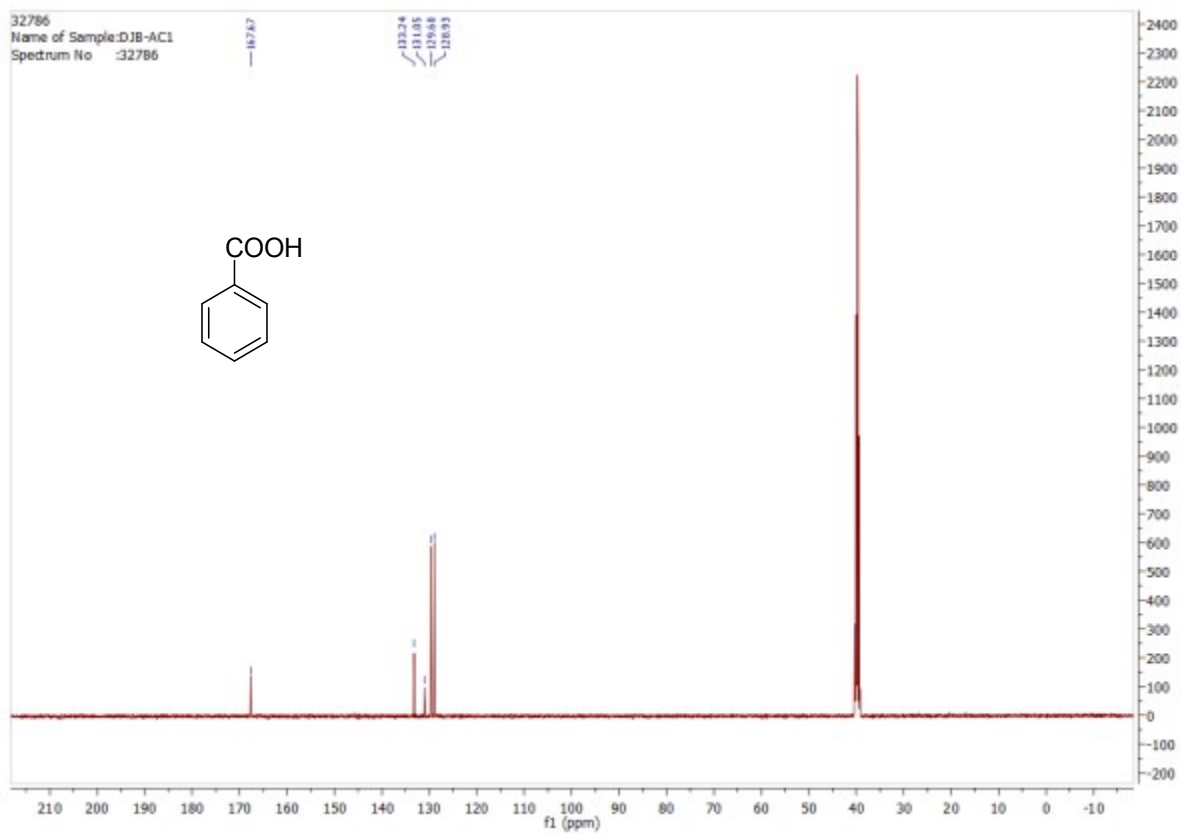


Figure S27. ^{13}C NMR of Acid 1 in DMSO-d_6 (Table 2, Entry 1)

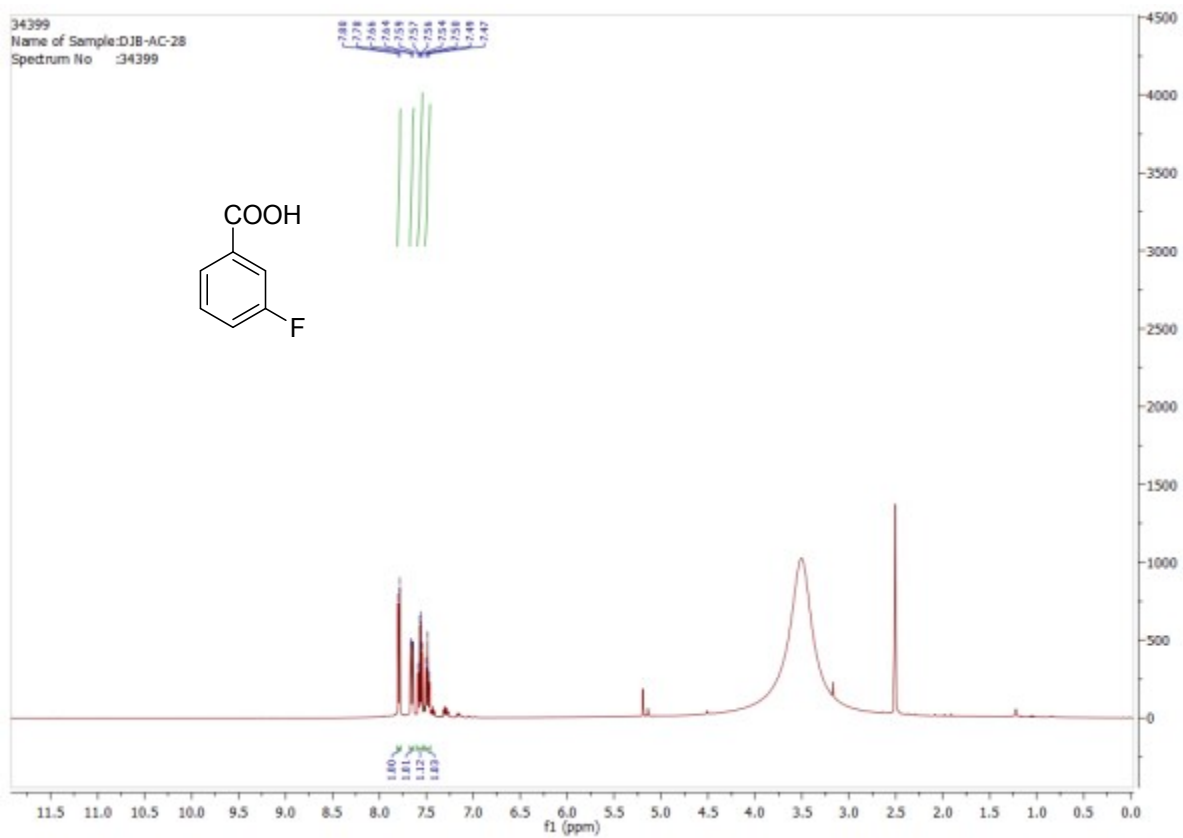


Figure S28. ^1H NMR of Acid **2** in DMSO-d_6 (Table 2, Entry 2)

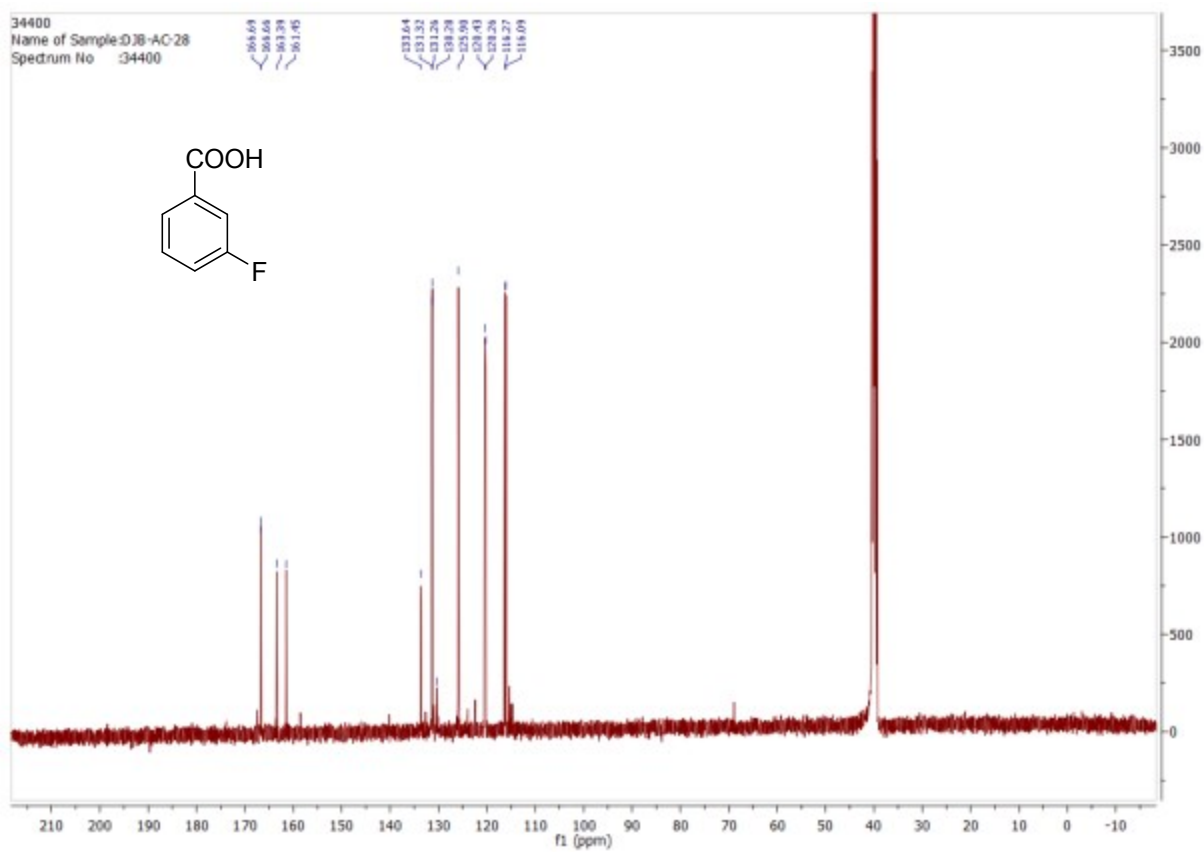


Figure S29. ^{13}C NMR of Acid 2 in DMSO-d_6 (Table 2, Entry 2)

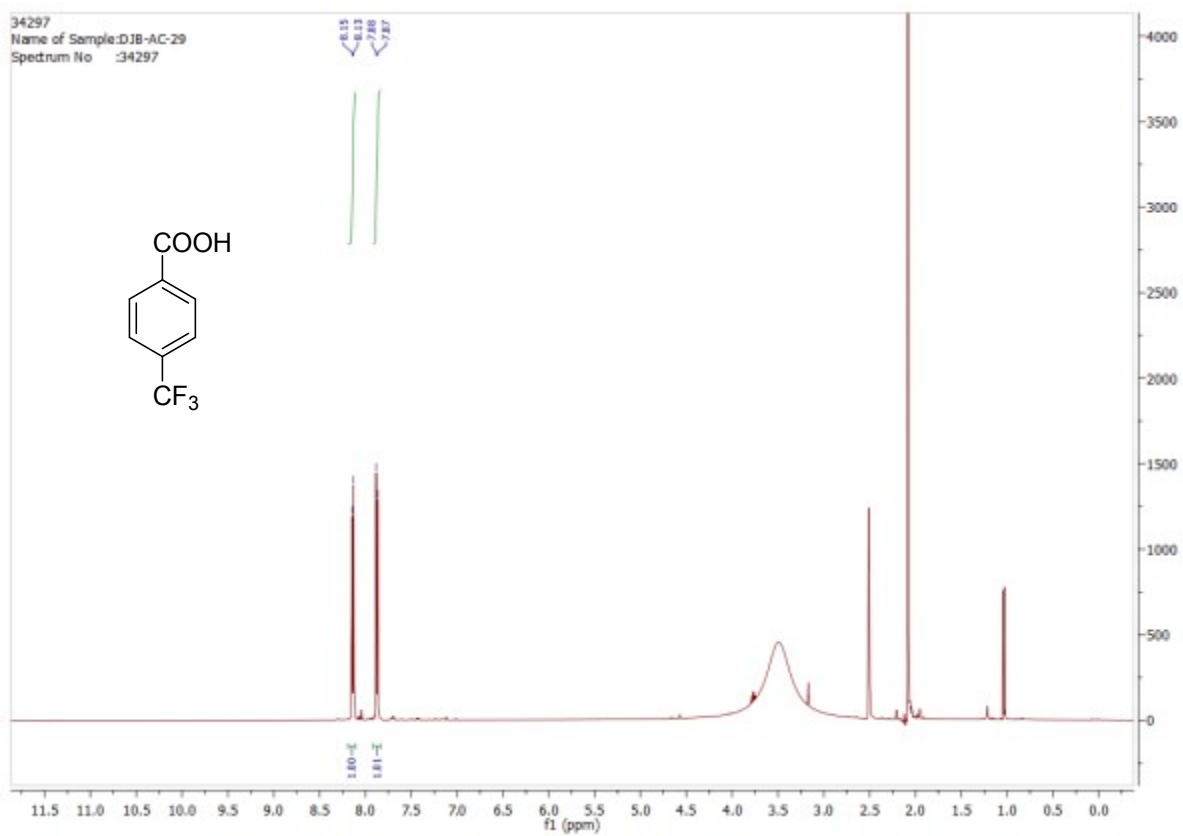


Figure S30. ^1H NMR of Acid **3** in DMSO-d_6 (Table 2, Entry 3)

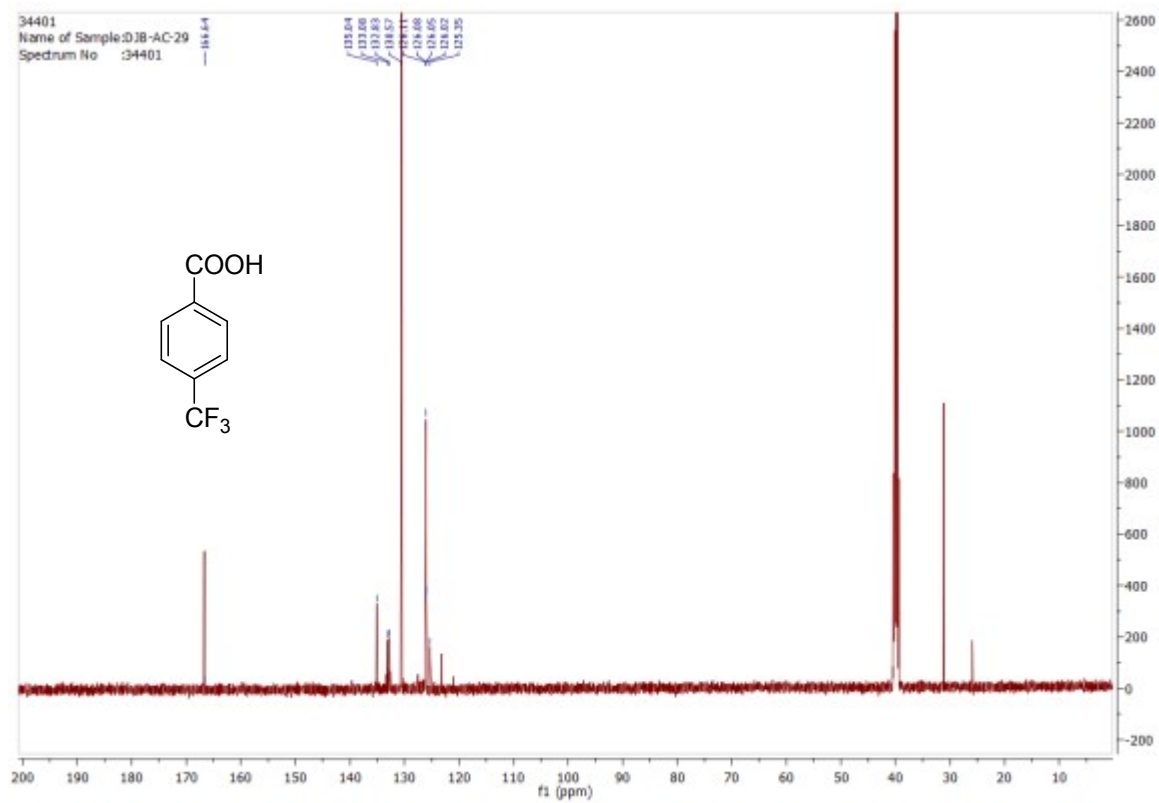


Figure S31. ^{13}C NMR of Acid **3** in DMSO-d_6 (Table 2, Entry 3)

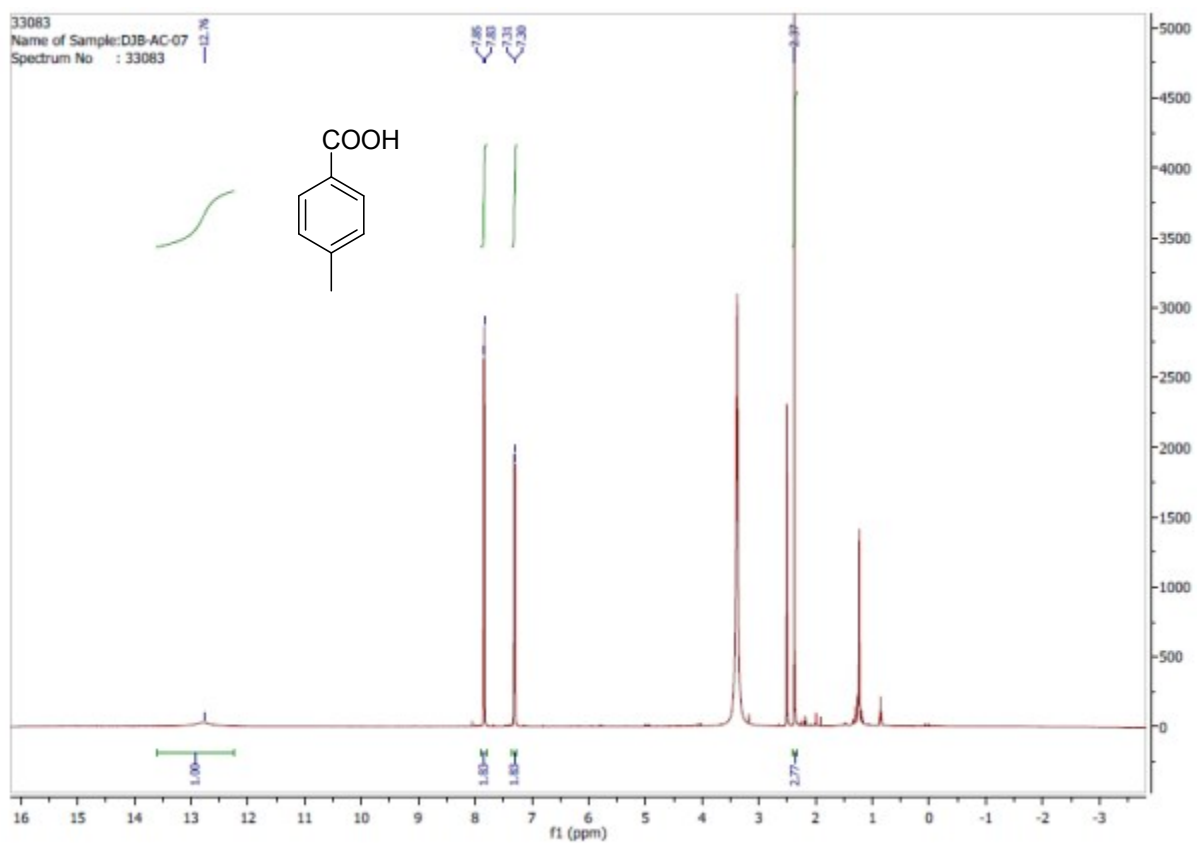


Figure S32. ^1H NMR of Acid 4 in DMSO-d_6 (Table 2, Entry 4)

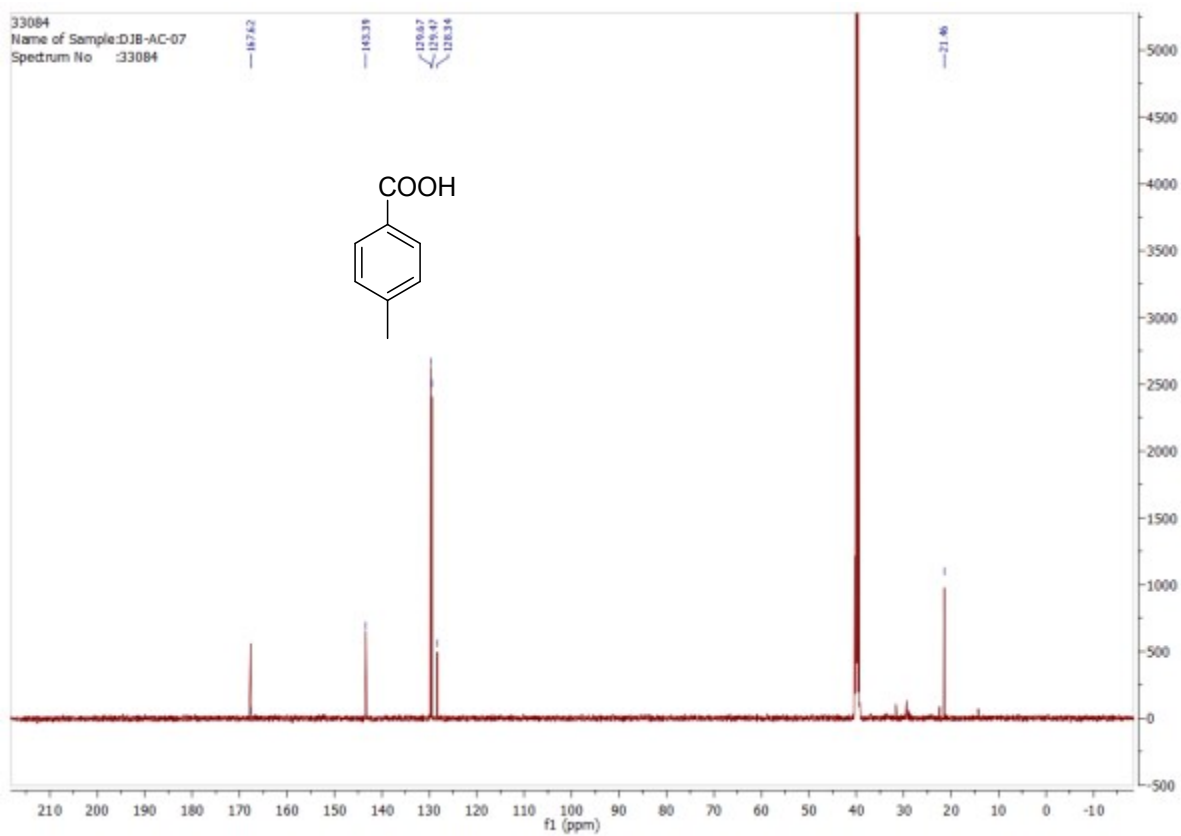


Figure S33. ^{13}C NMR of Acid 4 in DMSO-d_6 (Table 2, Entry 4)

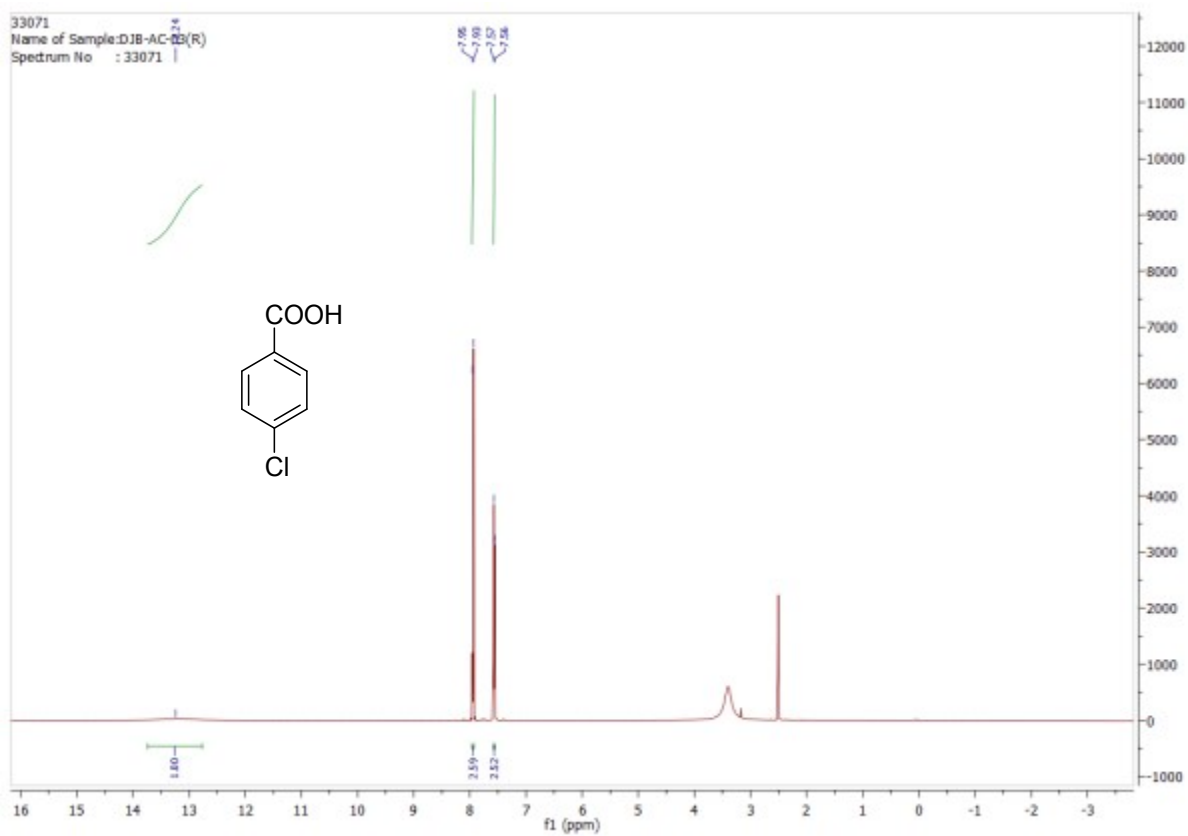


Figure S34. ^1H NMR of Acid **5** in DMSO-d_6 (Table 2, Entry 5)

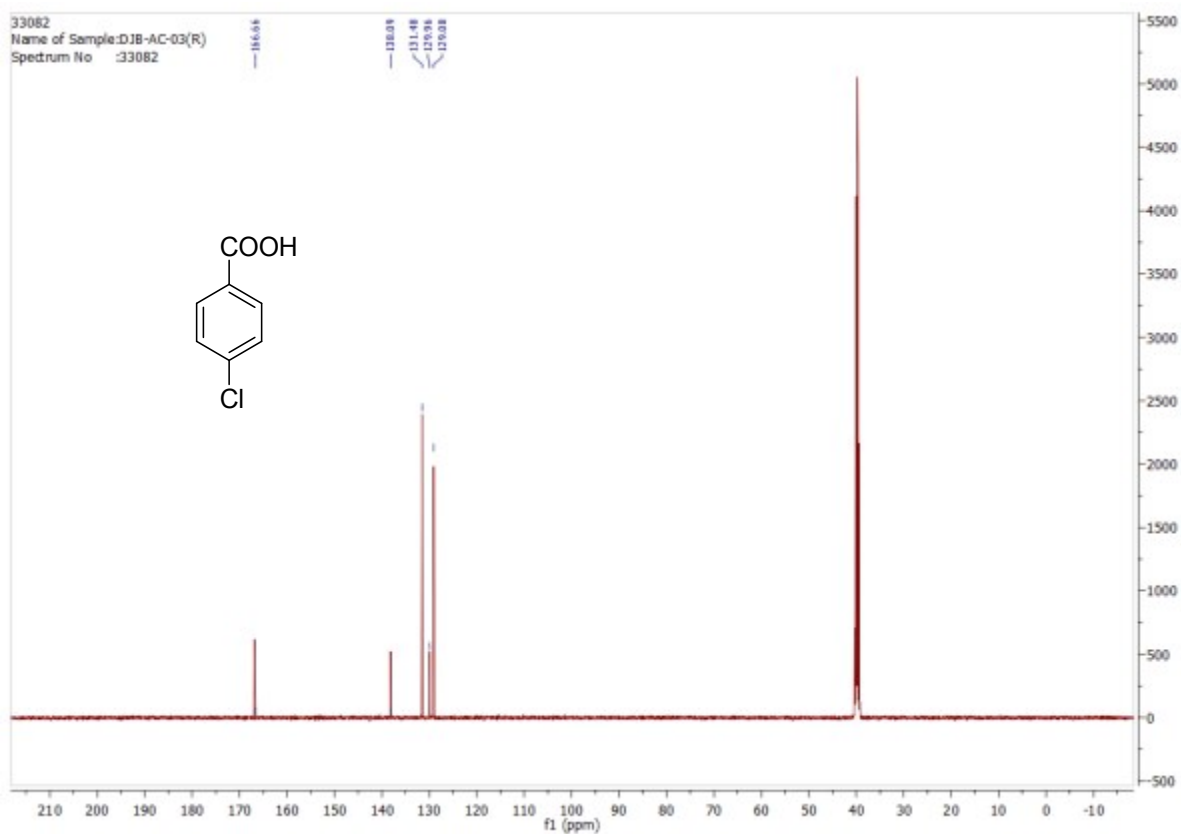


Figure S35. ^{13}C NMR of Acid 5 in DMSO-d_6 (Table 2, Entry 5)

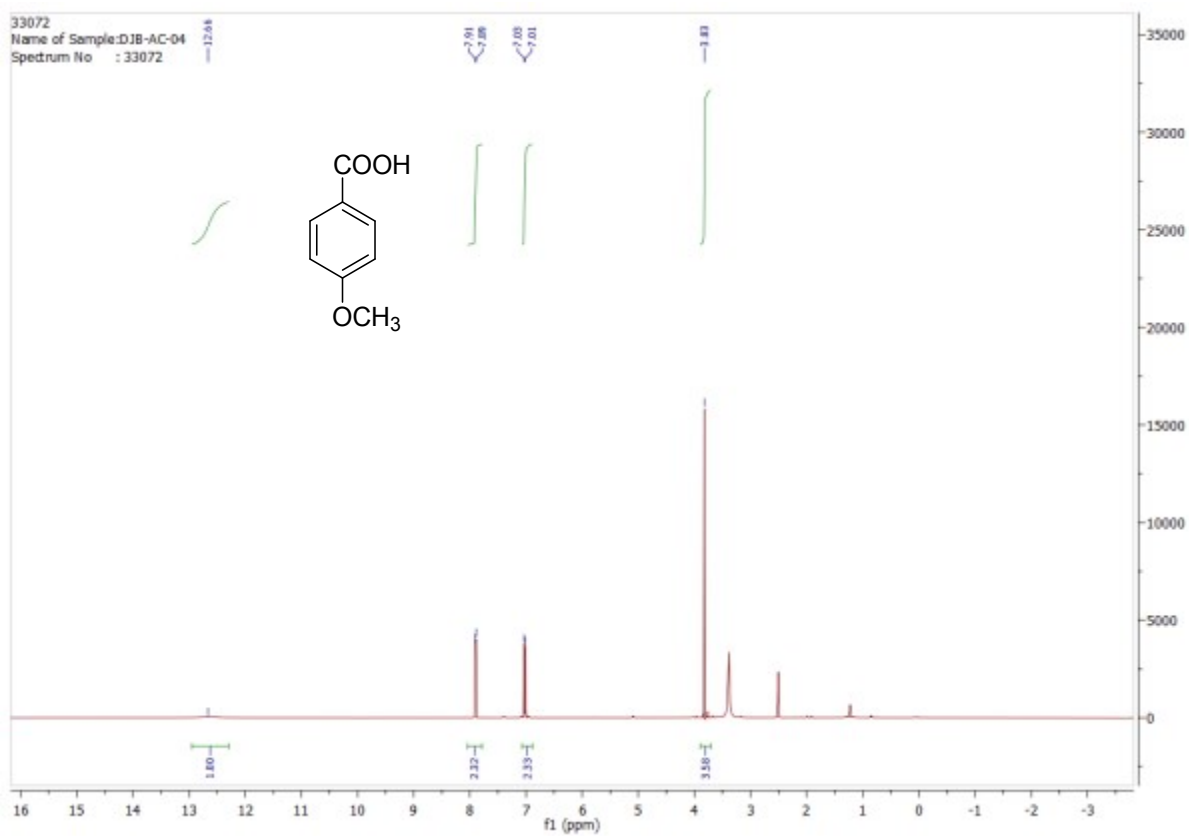


Figure S36. ¹H NMR of Acid **6** in DMSO-d₆ (Table 2, Entry 6)

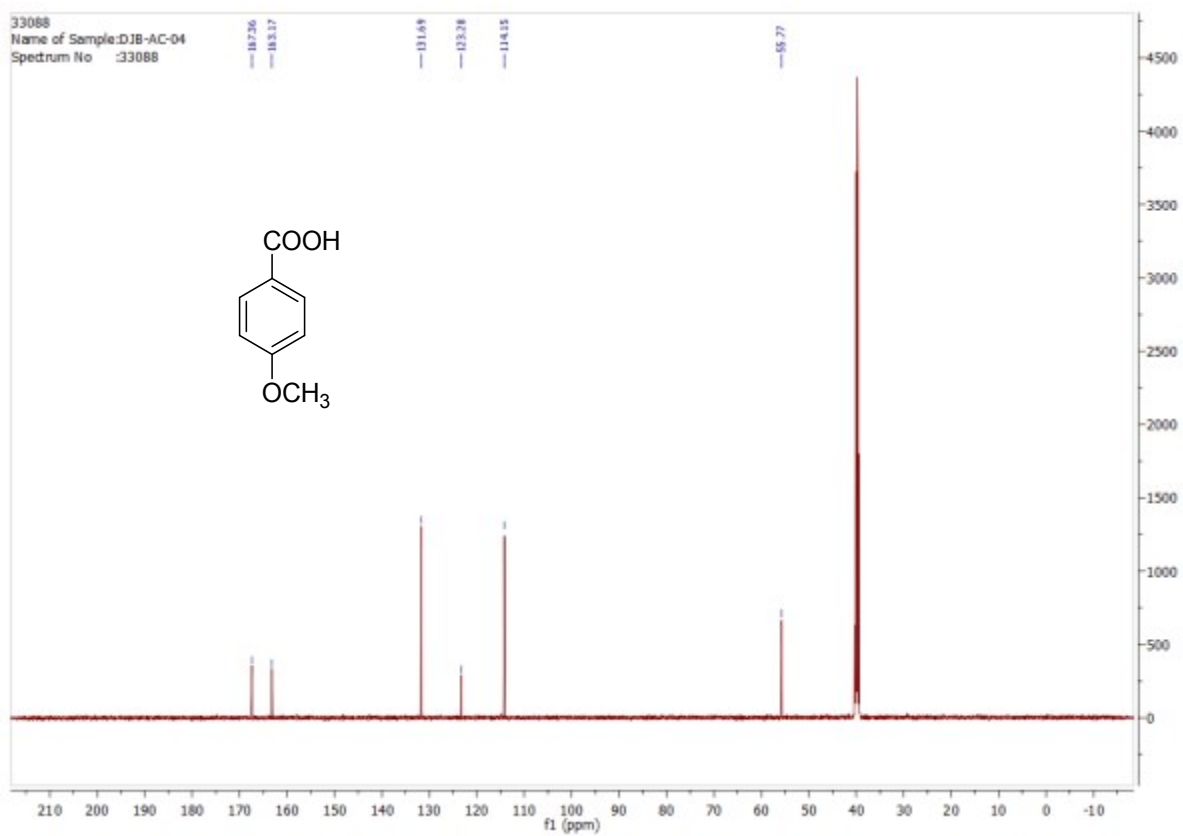


Figure S37. ^{13}C NMR of Acid 6 in DMSO-d_6 (Table 2, Entry 6)

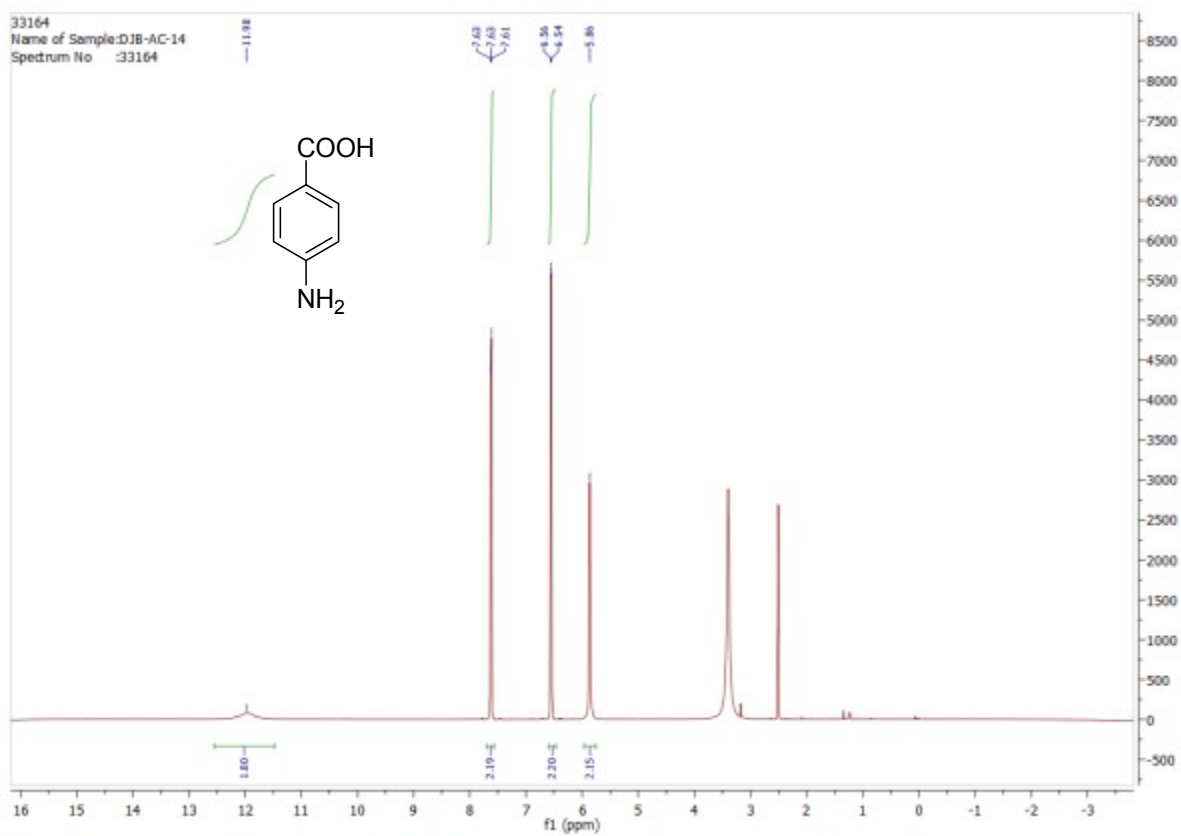


Figure S38. ¹H NMR Spectra of Acid 7 in DMSO-d₆ (Table 2, Entry 7)

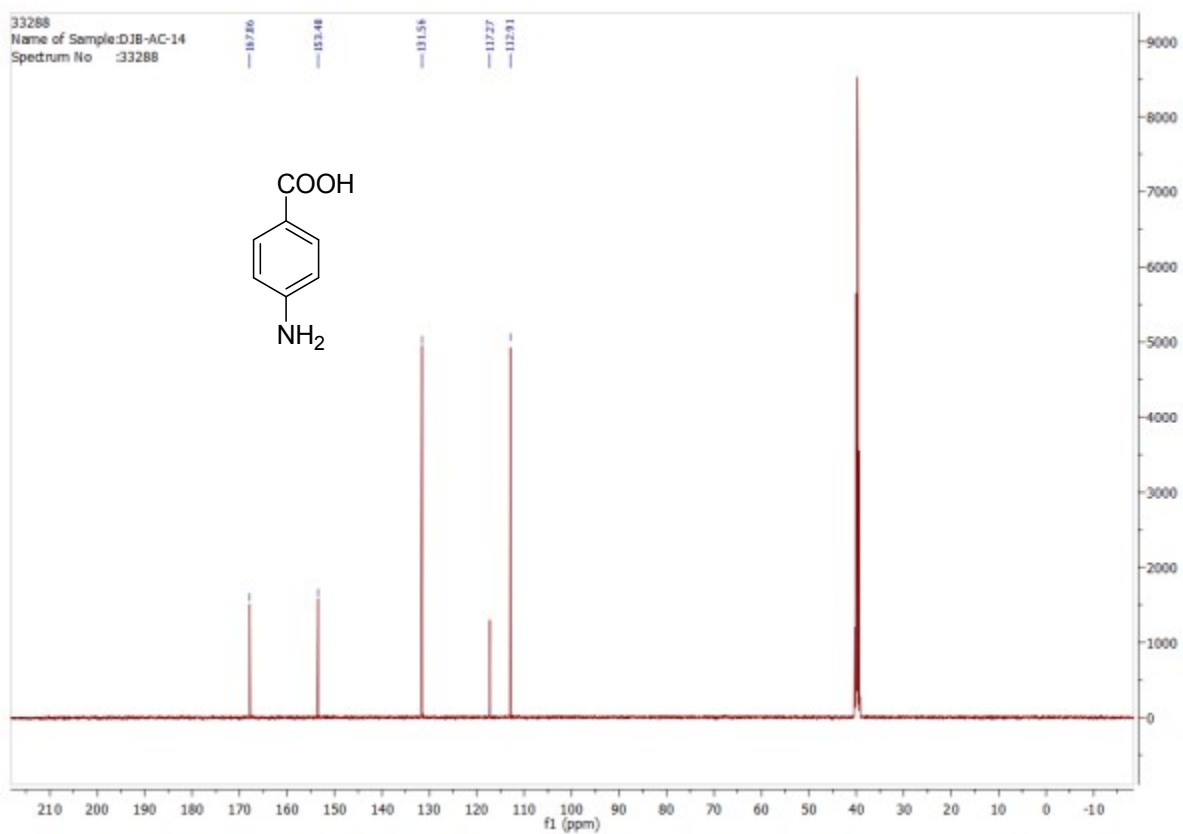


Figure S39. ^{13}C NMR of Acid 7 in DMSO-d_6 (Table 2, Entry 7)

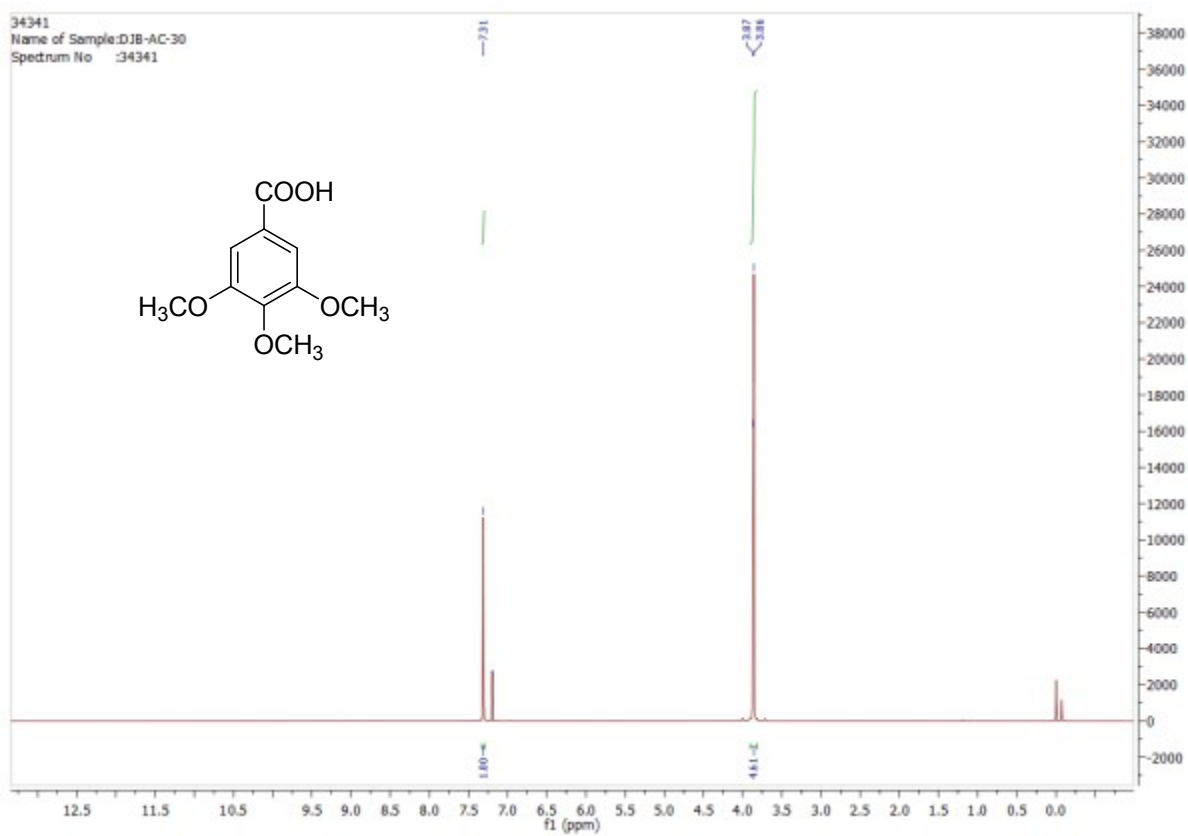


Figure S40. ^1H NMR of Acid **8** in DMSO-d_6 (Table 2, Entry 8)

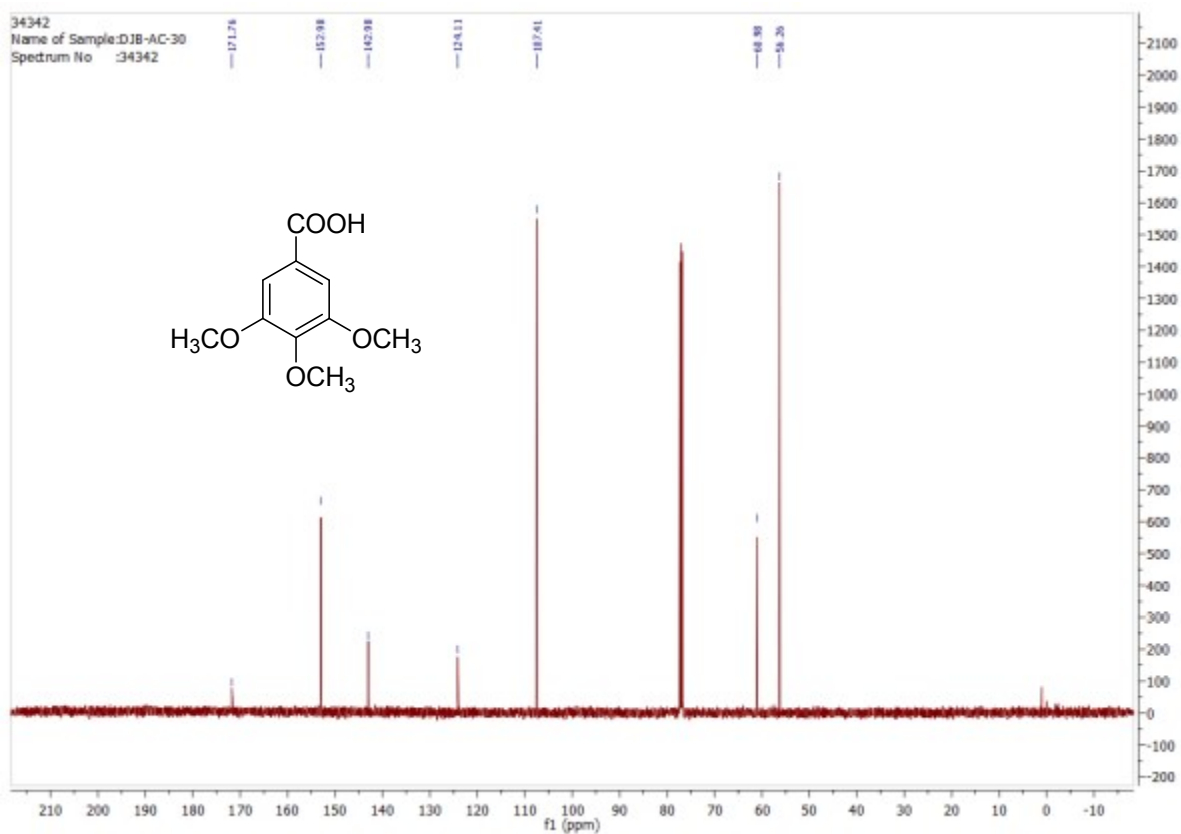


Figure S41. ^{13}C NMR of Acid **8** in DMSO-d_6 (Table 2, Entry 8)

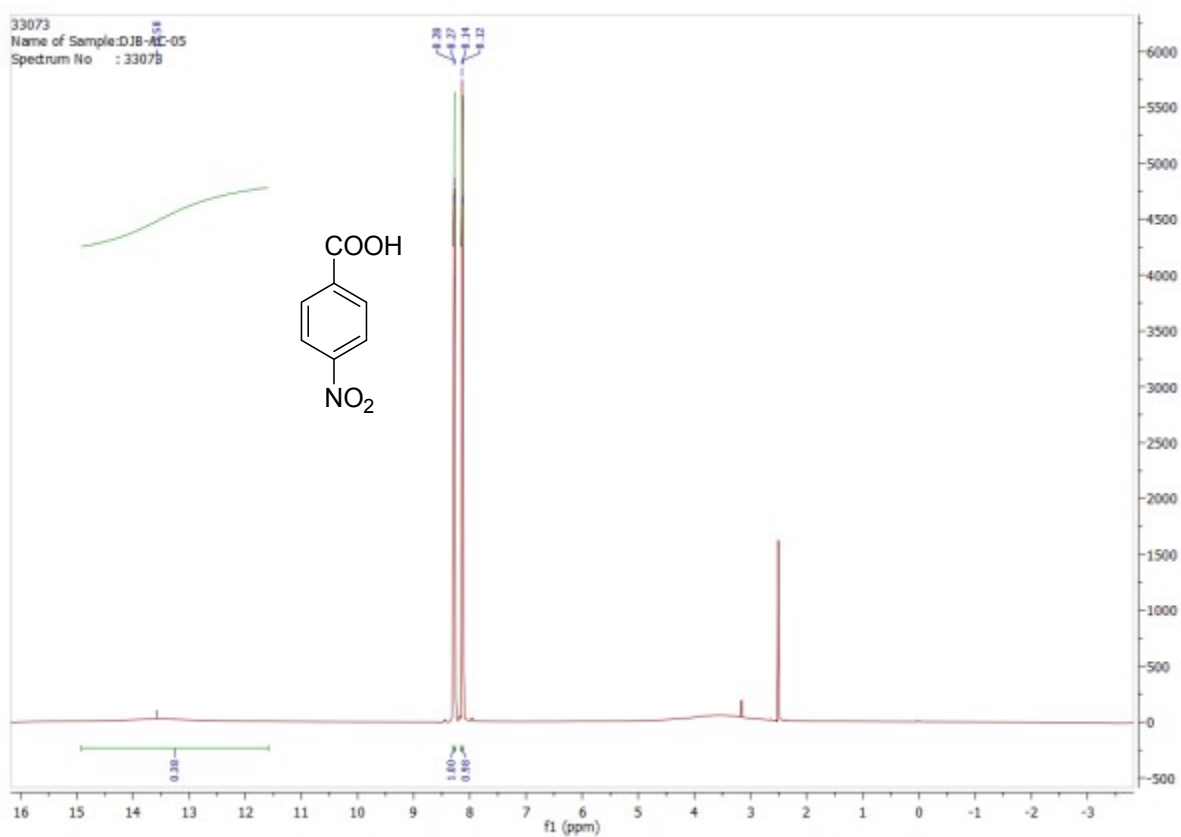


Figure S42. ¹H NMR of Acid **9** in DMSO-d₆ (Table 2, Entry 9)

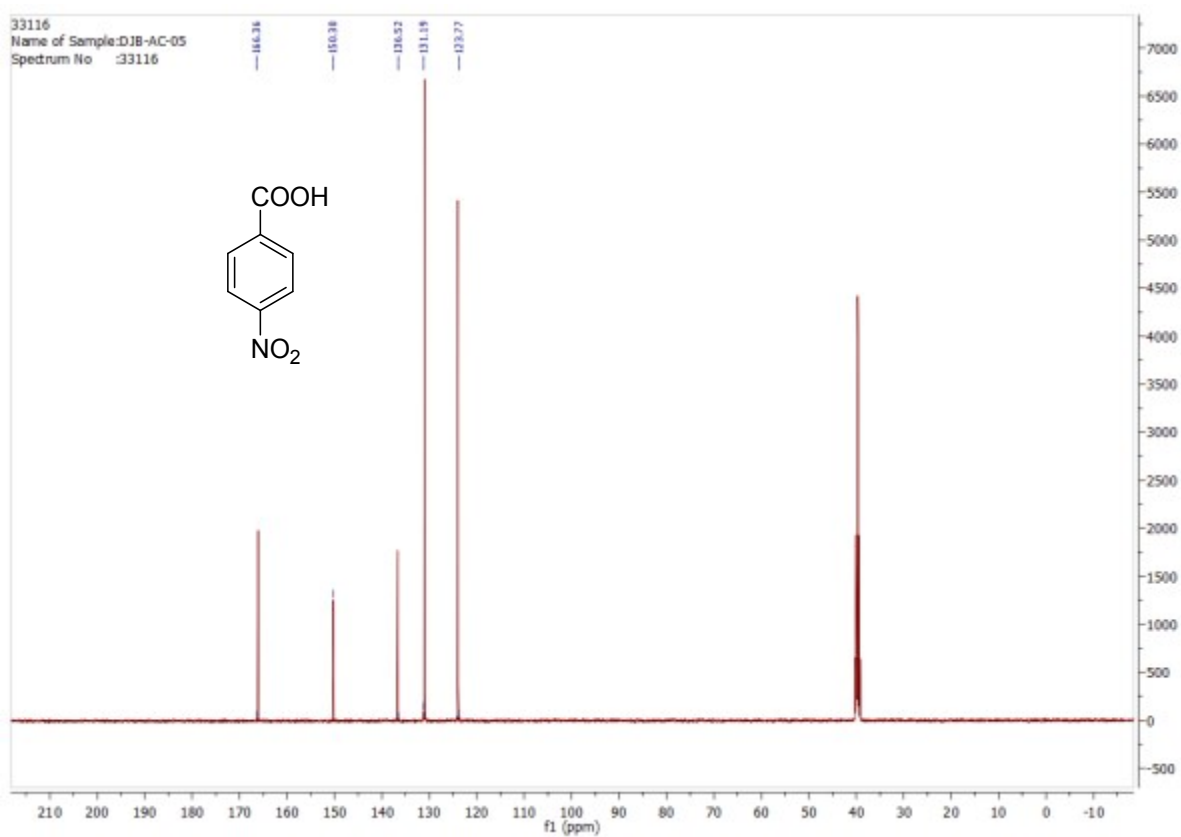


Figure S43. ^{13}C NMR of Acid 9 in DMSO-d_6 (Table 2, Entry 9)

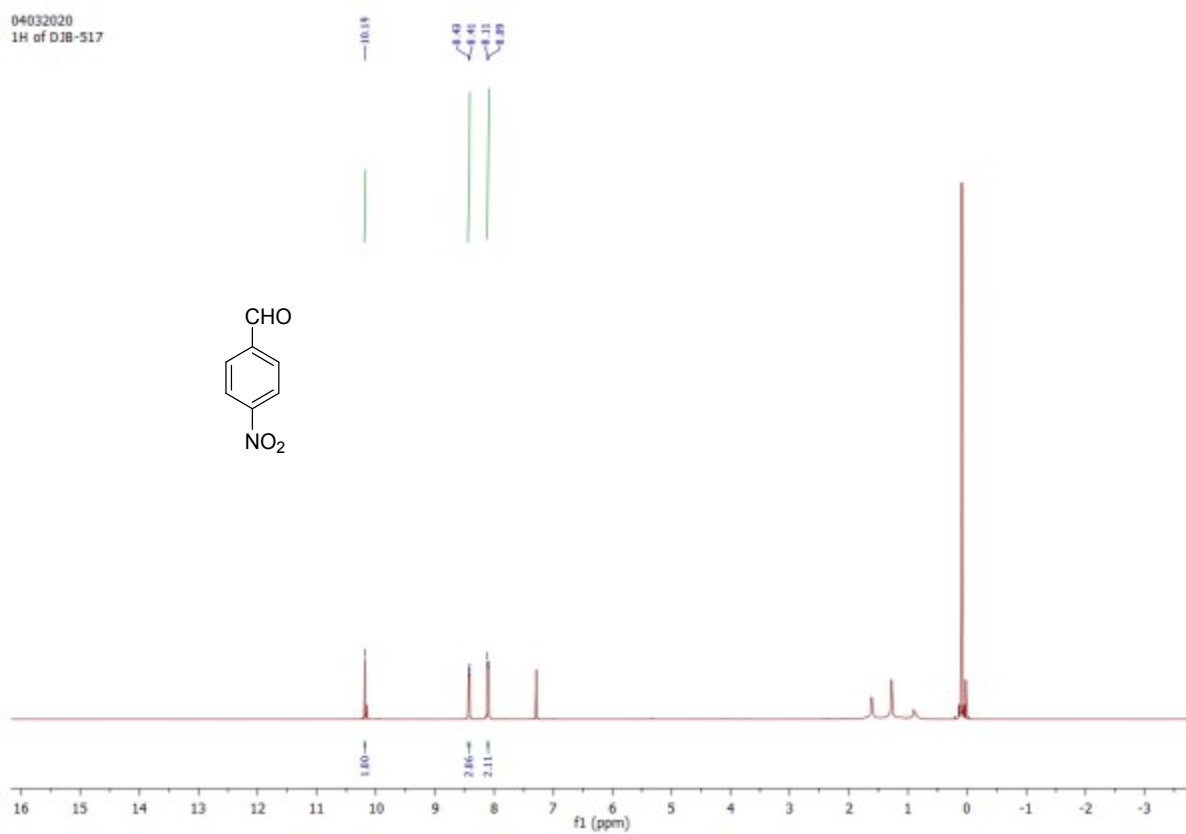


Figure S44. ^1H NMR of 4-Nitrobenzaldehyde (9a) in $\text{CDCl}_3\text{-d}_1$.

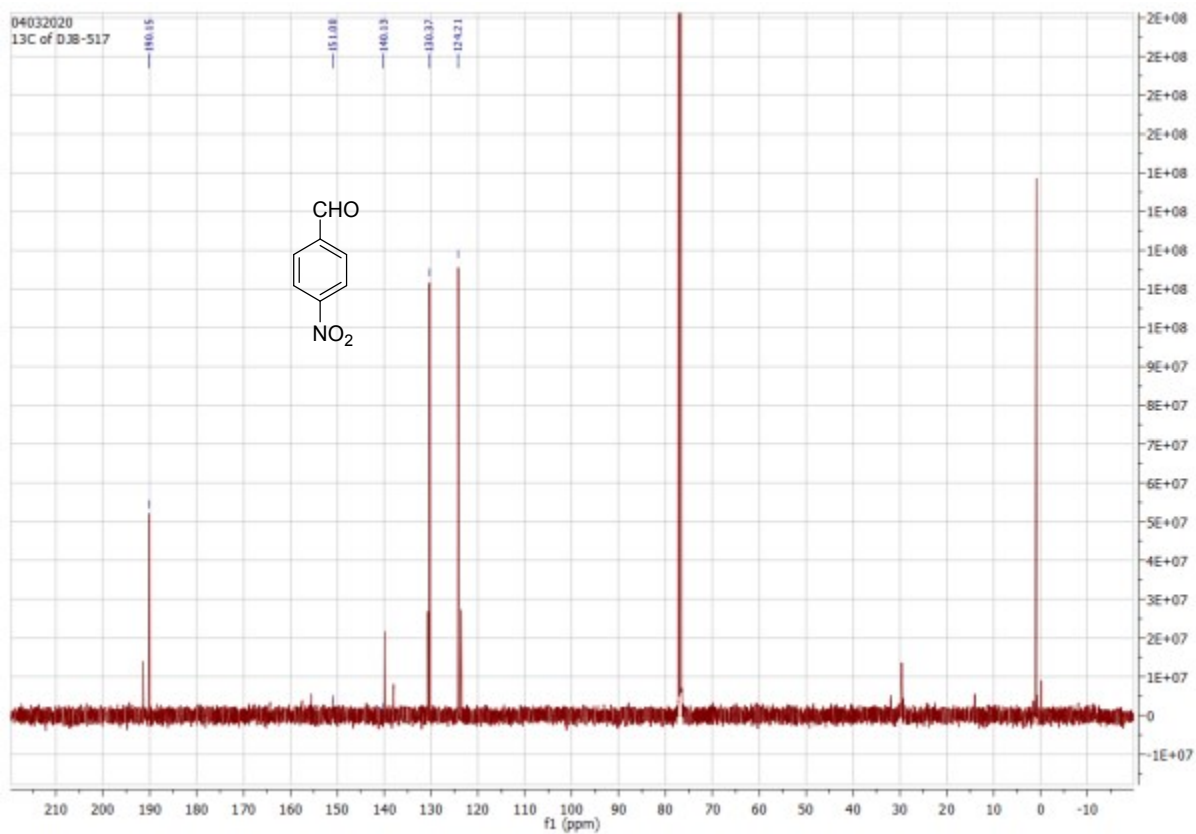


Figure S45. ^{13}C NMR of of 4-Nitrobenzaldehyde (9a) in $\text{CDCl}_3\text{-d}_1$

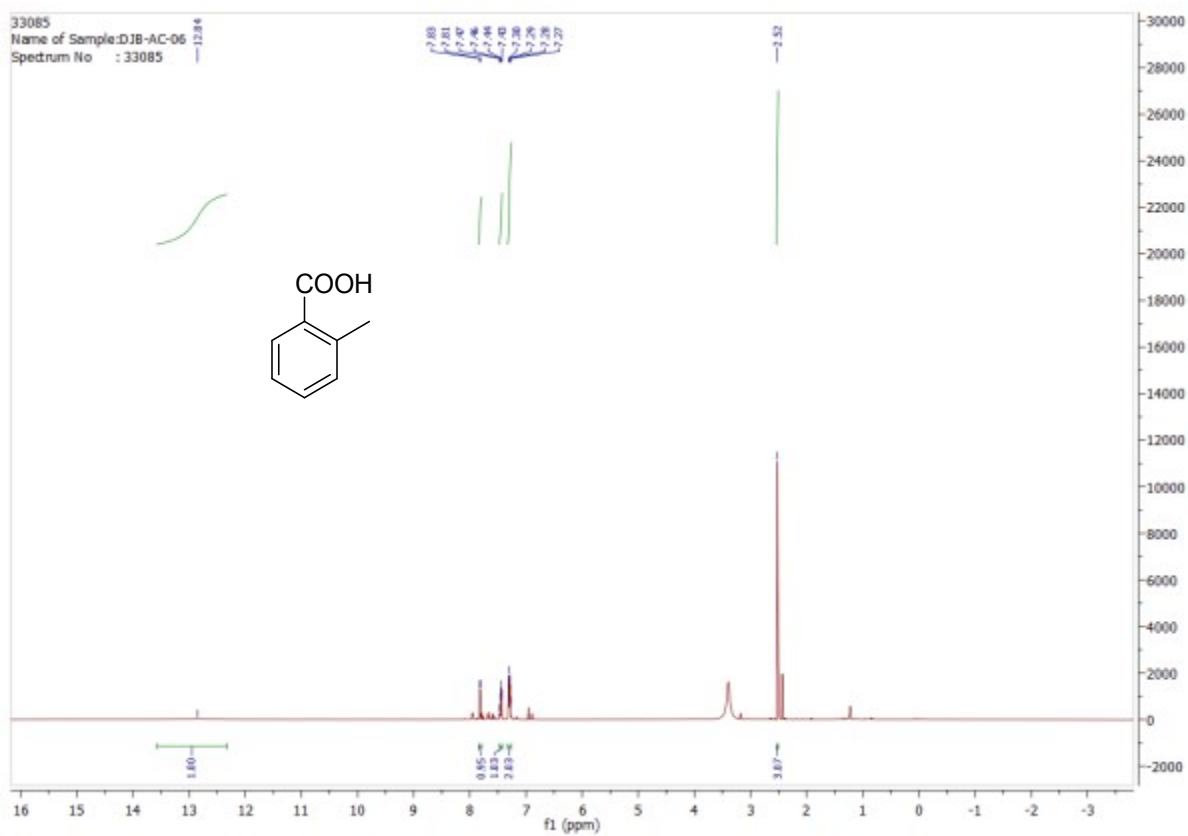


Figure S46. ^1H NMR of Acid **10** in DMSO-d_6 (Table 2, Entry 10)

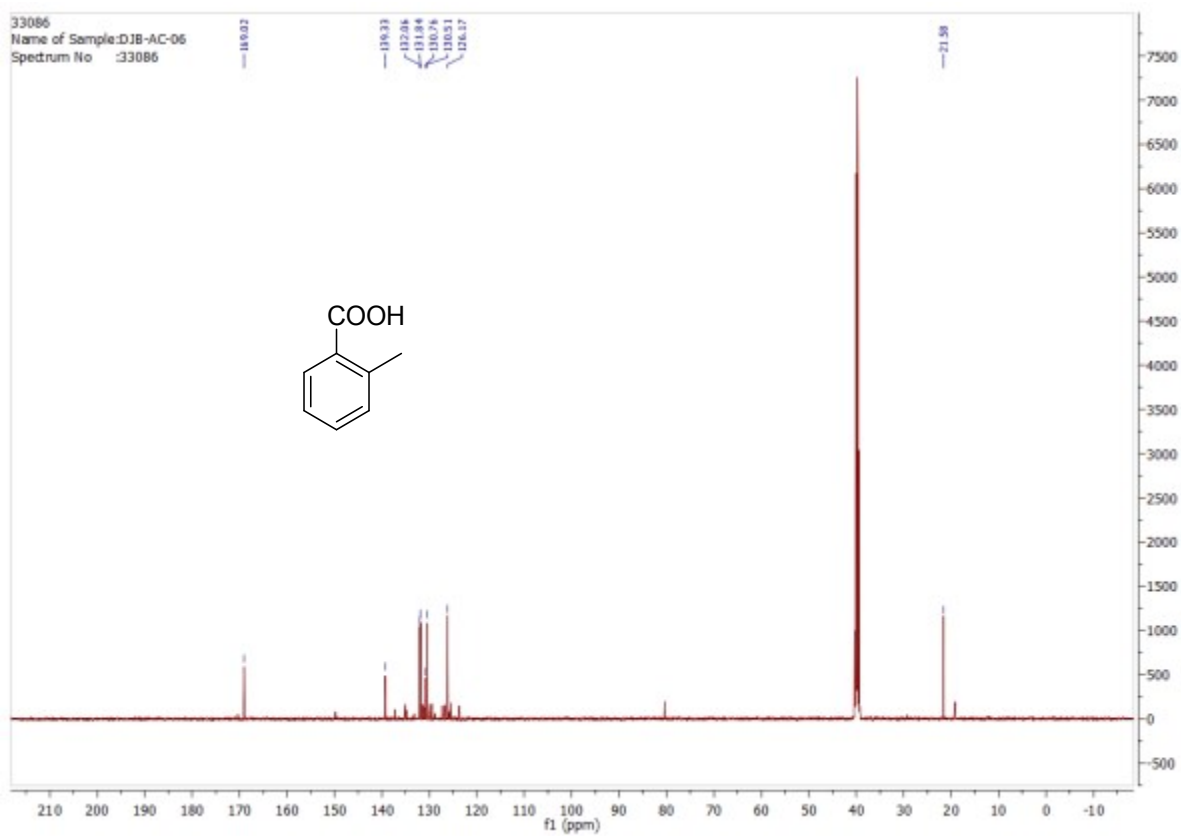


Figure S47. ^{13}C NMR of Acid **10** in DMSO-d_6 (Table 2, Entry 10)

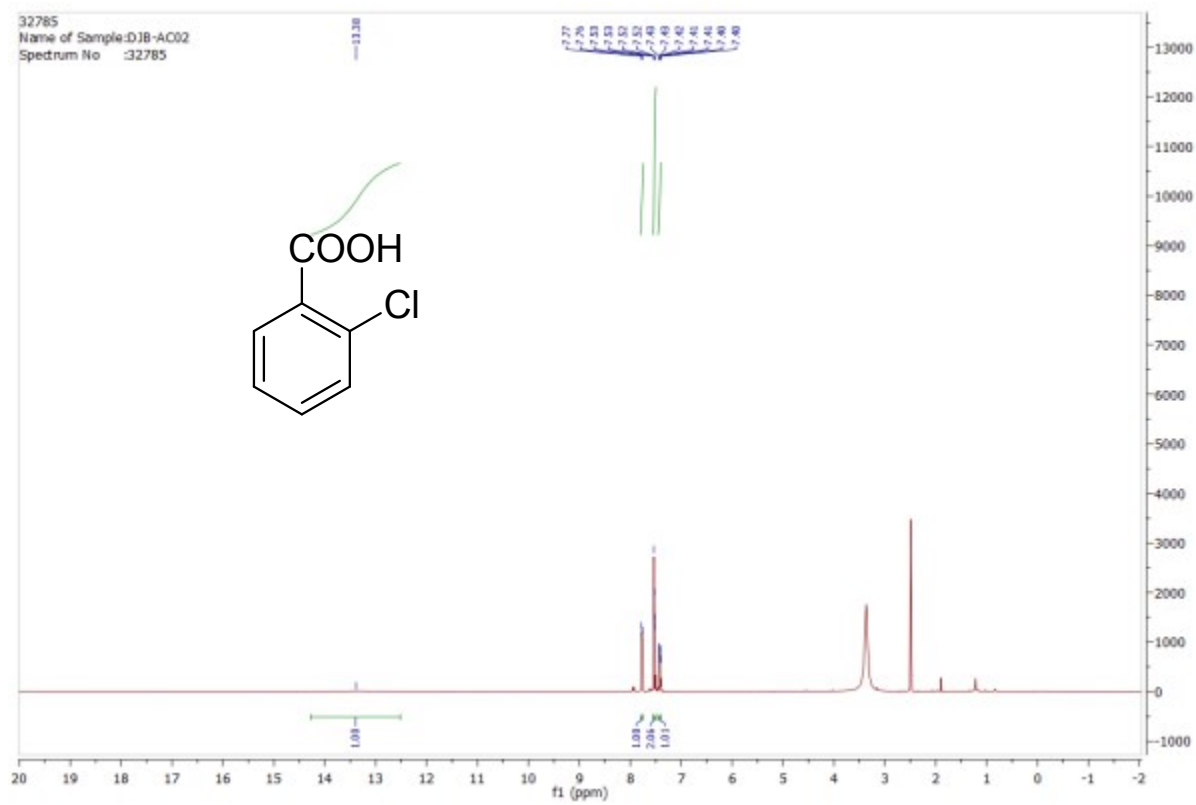


Figure S48. ^1H NMR of Acid **11** in DMSO-d_6 (Table 2, Entry 11)

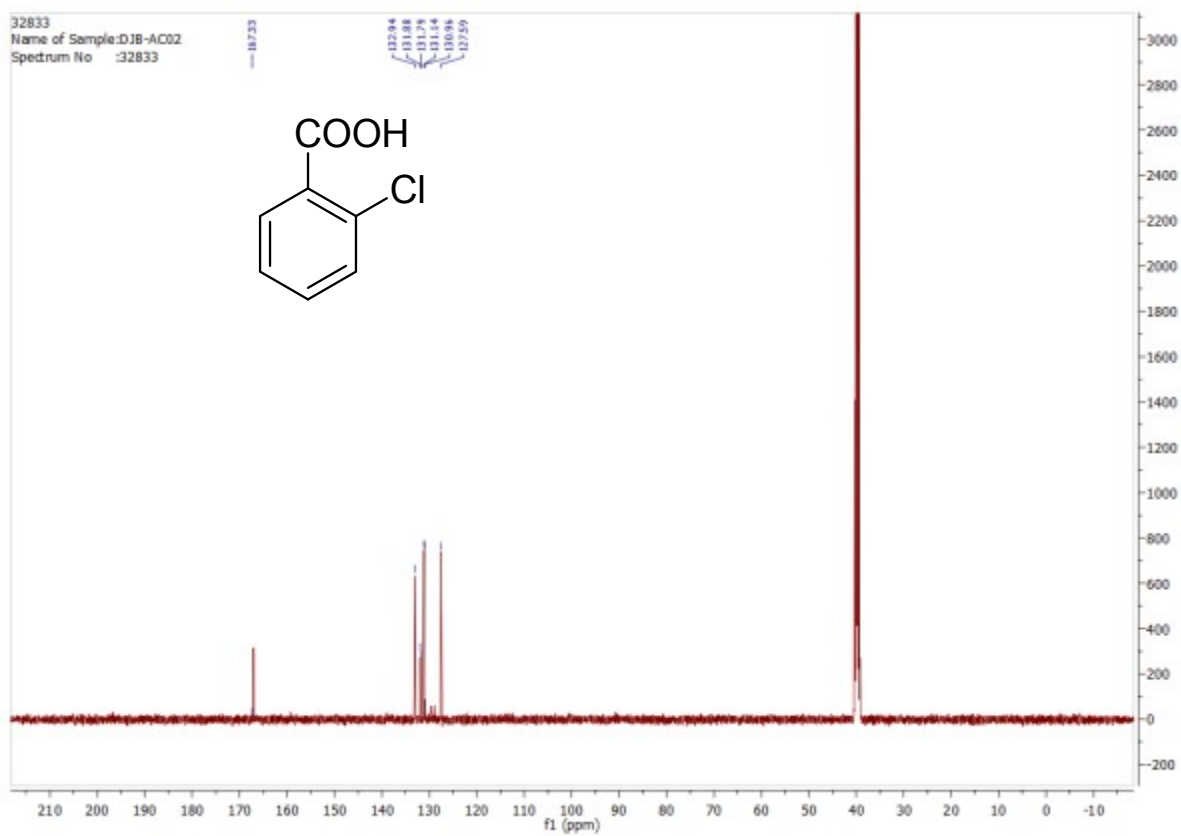


Figure S49. ^{13}C NMR of Acid **11** in DMSO-d_6 (Table 2, Entry 11)

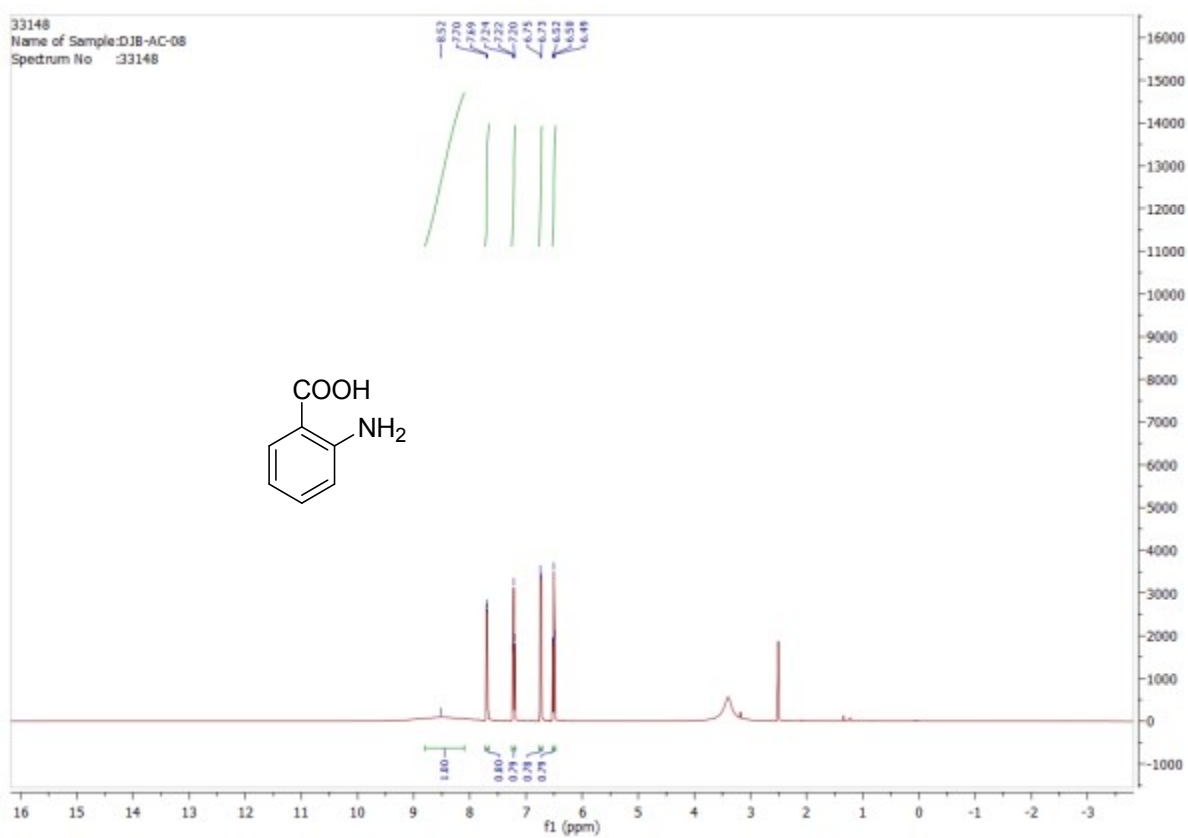


Figure S50. ^1H NMR of Acid **12** in DMSO-d_6 (Table 2, Entry 12)

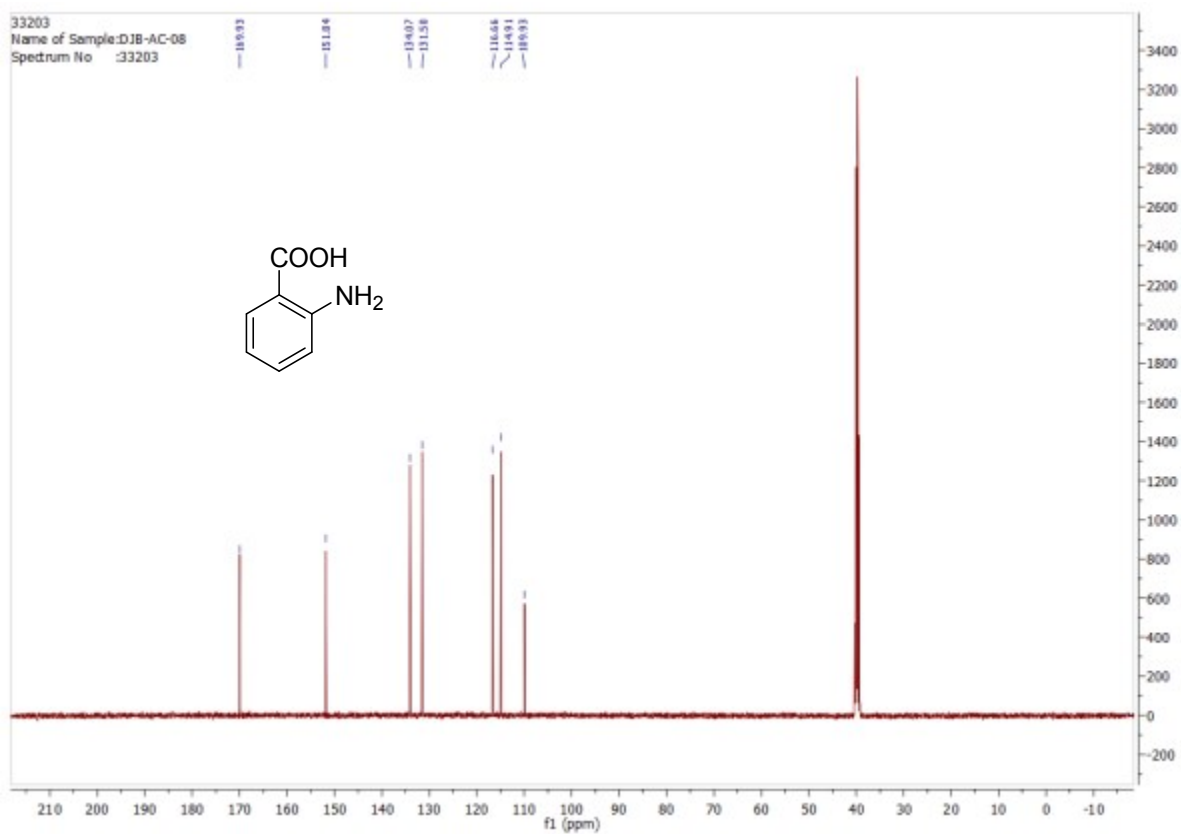


Figure S51. ^{13}C NMR of Acid 12 in DMSO-d_6 (Table 2, Entry 12)

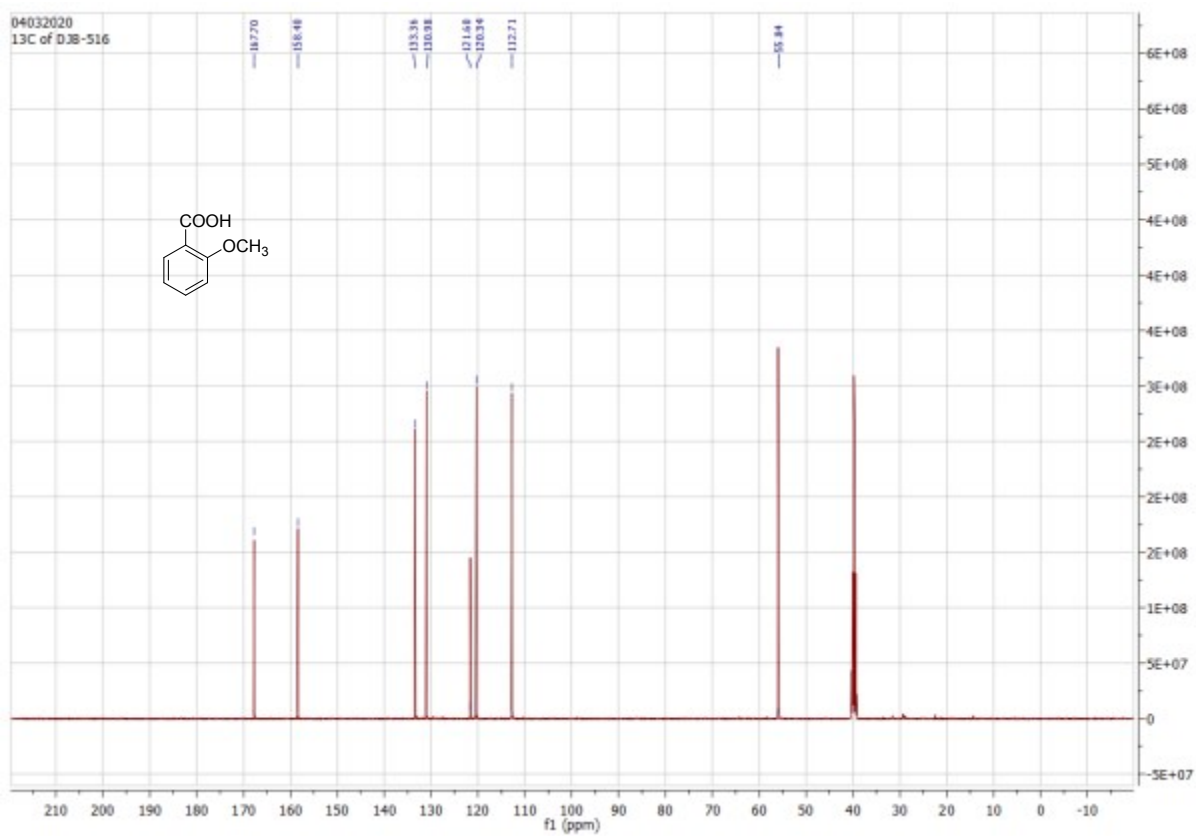


Figure S53. ^{13}C NMR of Acid **13** in DMSO-d_6 (Table 2, Entry 13)

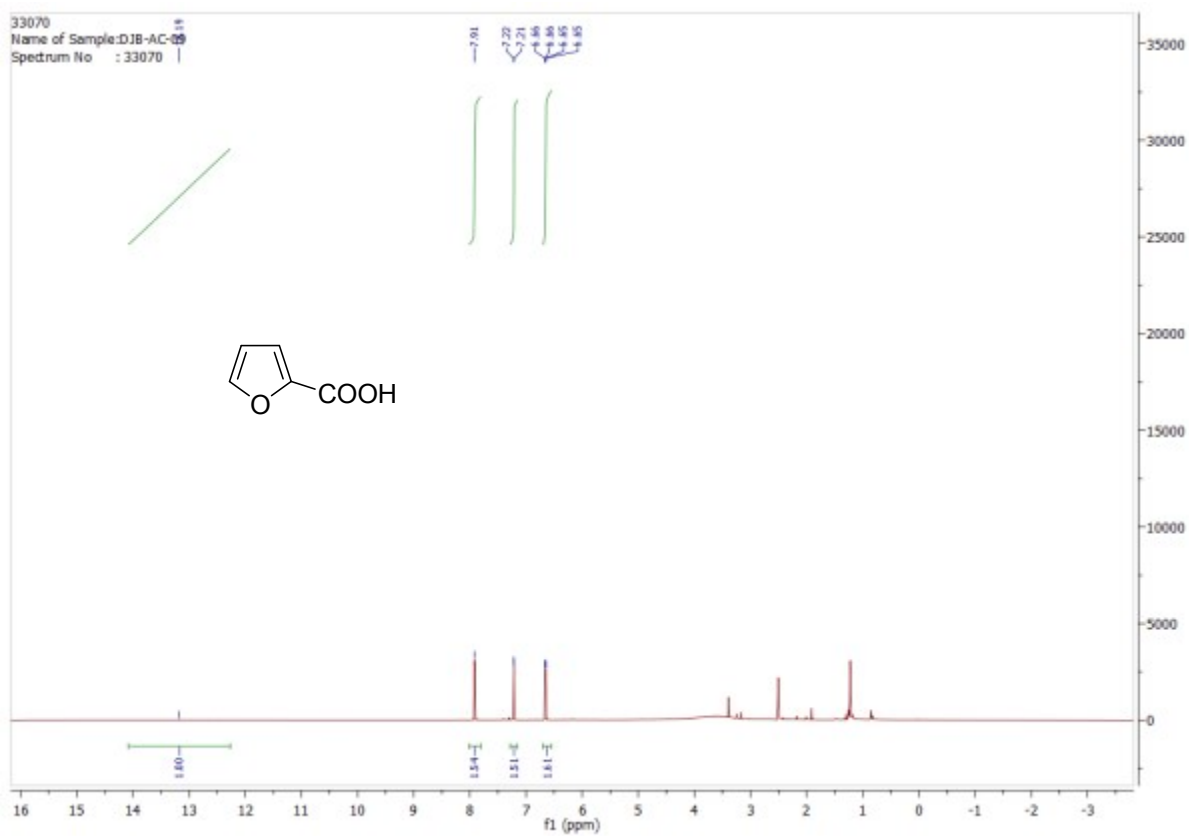


Figure S54. ¹H NMR of Acid **14** in DMSO-d₆ (Table 2, Entry 14)

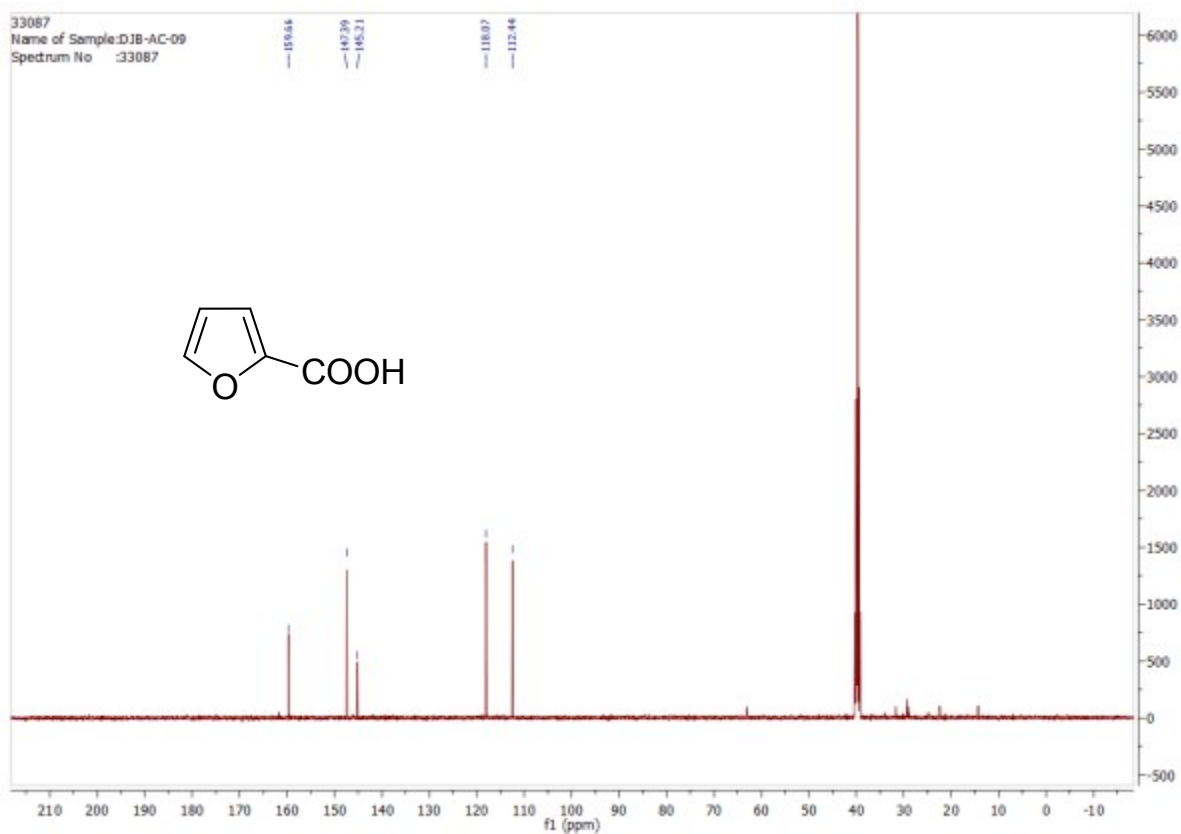


Figure S55. ^{13}C NMR of Acid **14** in DMSO-d_6 (Table 2, Entry 14)

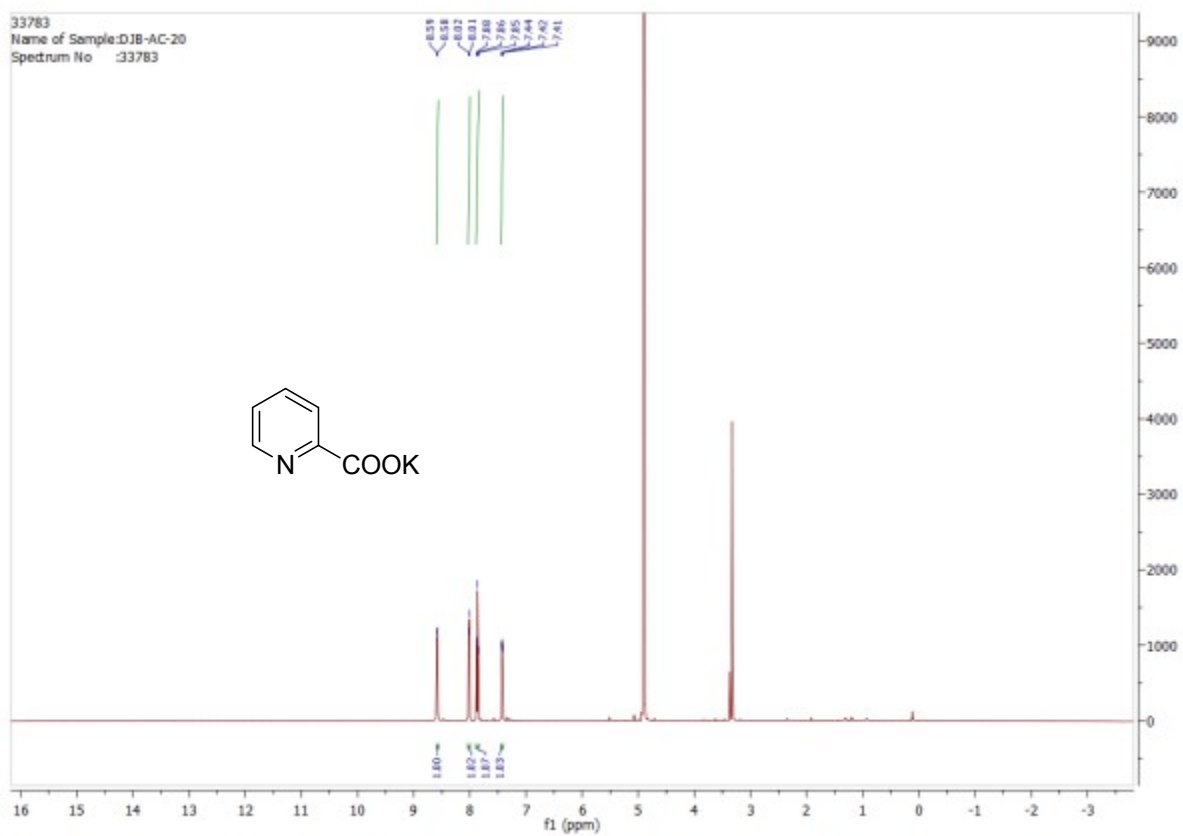


Figure S56. ^1H NMR of Acid salt **15** in DMSO-d_6 (Table 2, Entry 15)

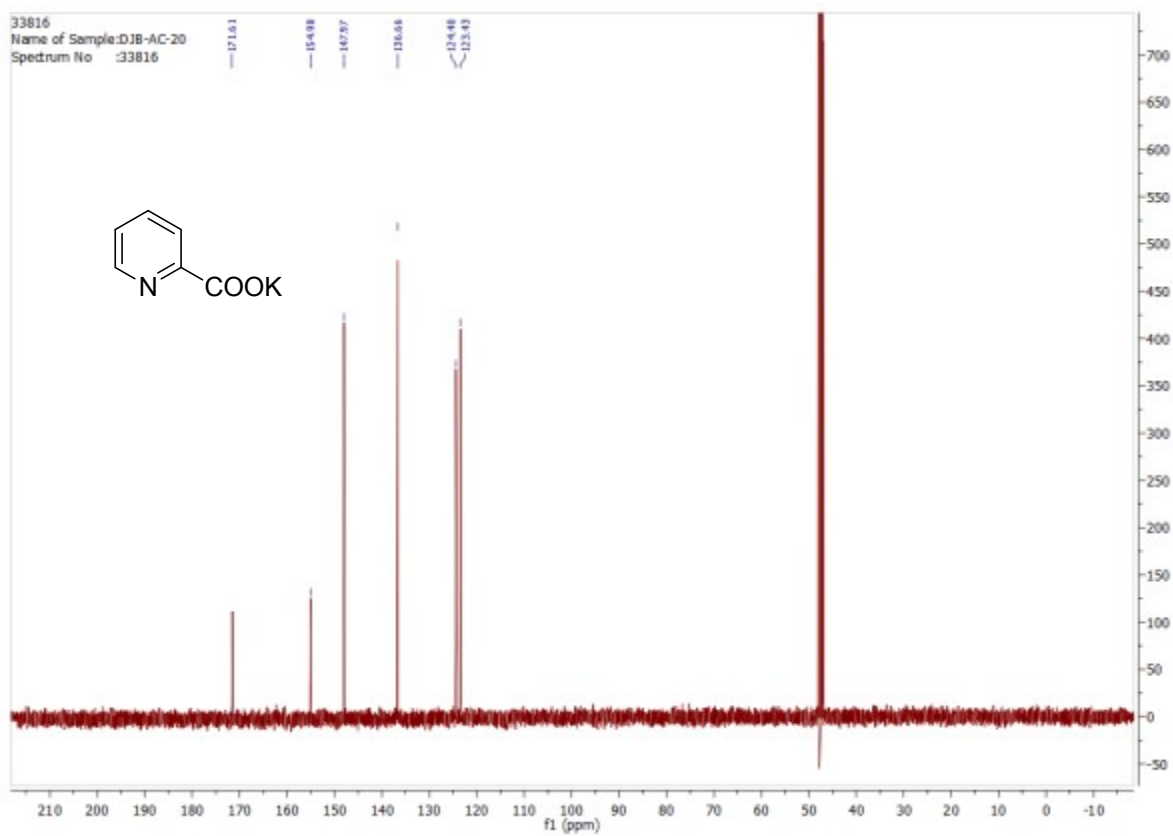


Figure S57. ^{13}C NMR of Acid salt **15** in DMSO-d_6 (Table 2, Entry 15)

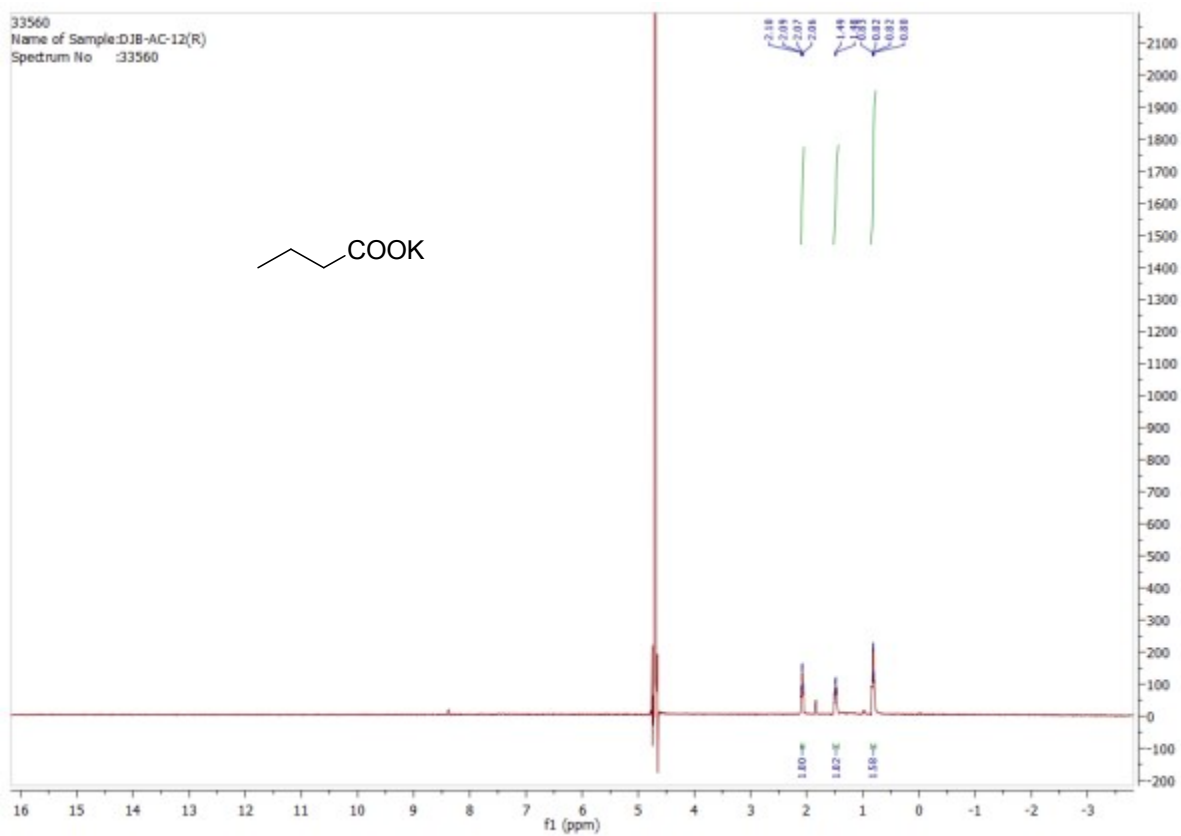


Figure S58. ^1H NMR of Acid Salt **16** in DMSO-d_6 (Table 2, Entry 16)

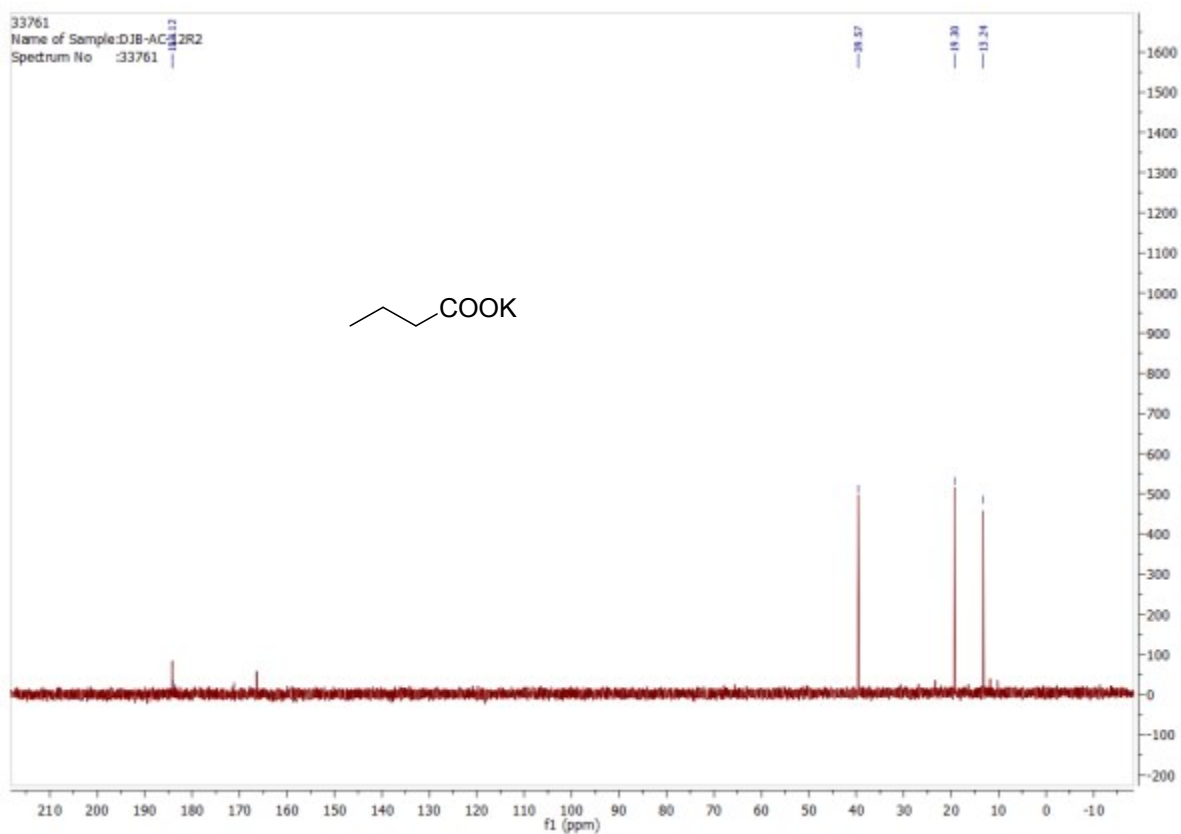


Figure S59. ^{13}C NMR Spectra of Acid Salt **16** in DMSO-d_6 (Table 2, Entry 16)

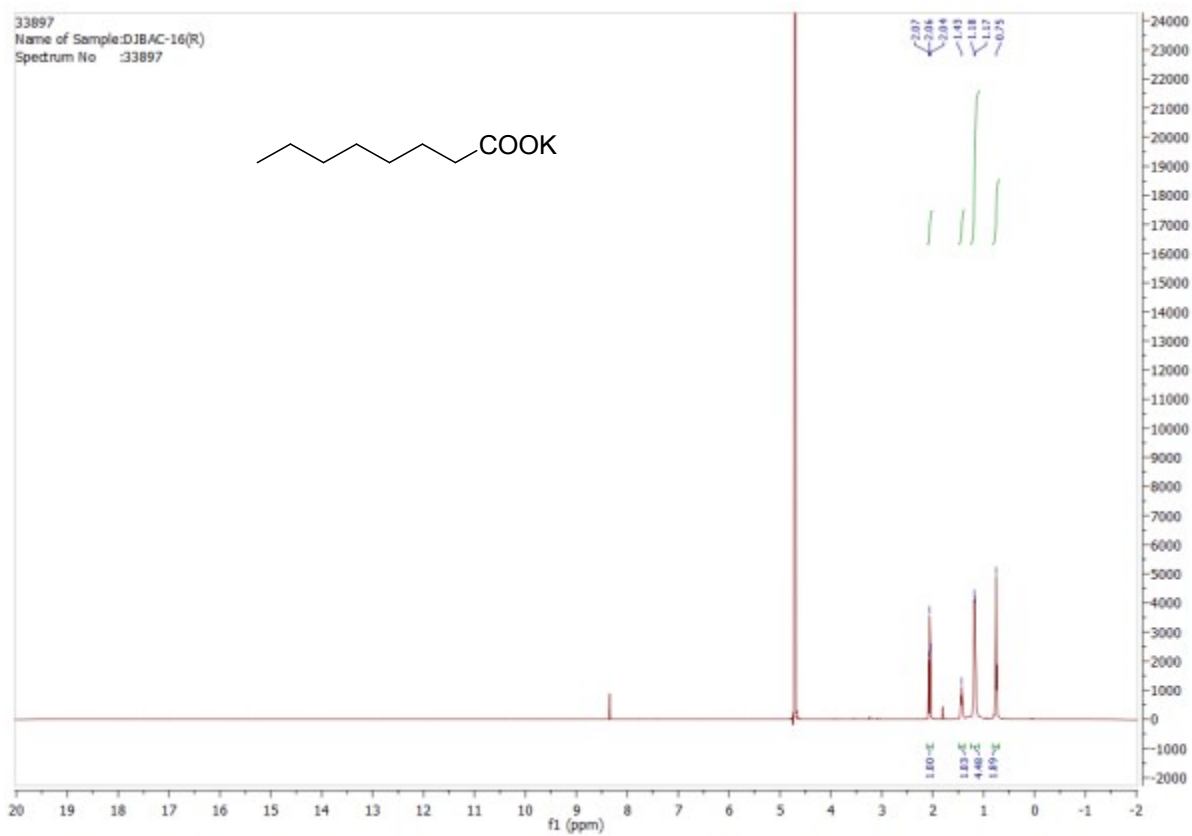


Figure S60. ^1H NMR of Acid Salt **17** in DMSO-d_6 (Table 2, Entry 17)

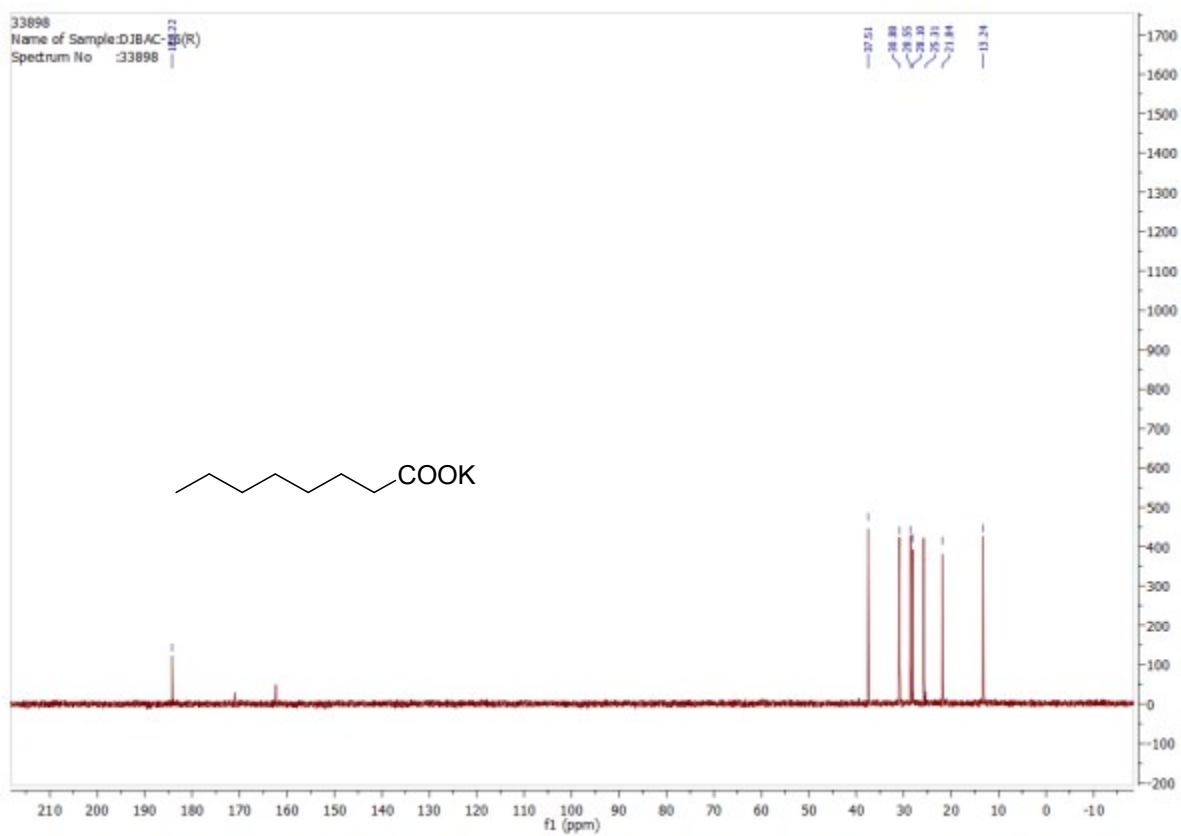


Figure S61. ^{13}C NMR of Acid Salt 17 in DMSO-d_6 (Table 2, Entry 17)

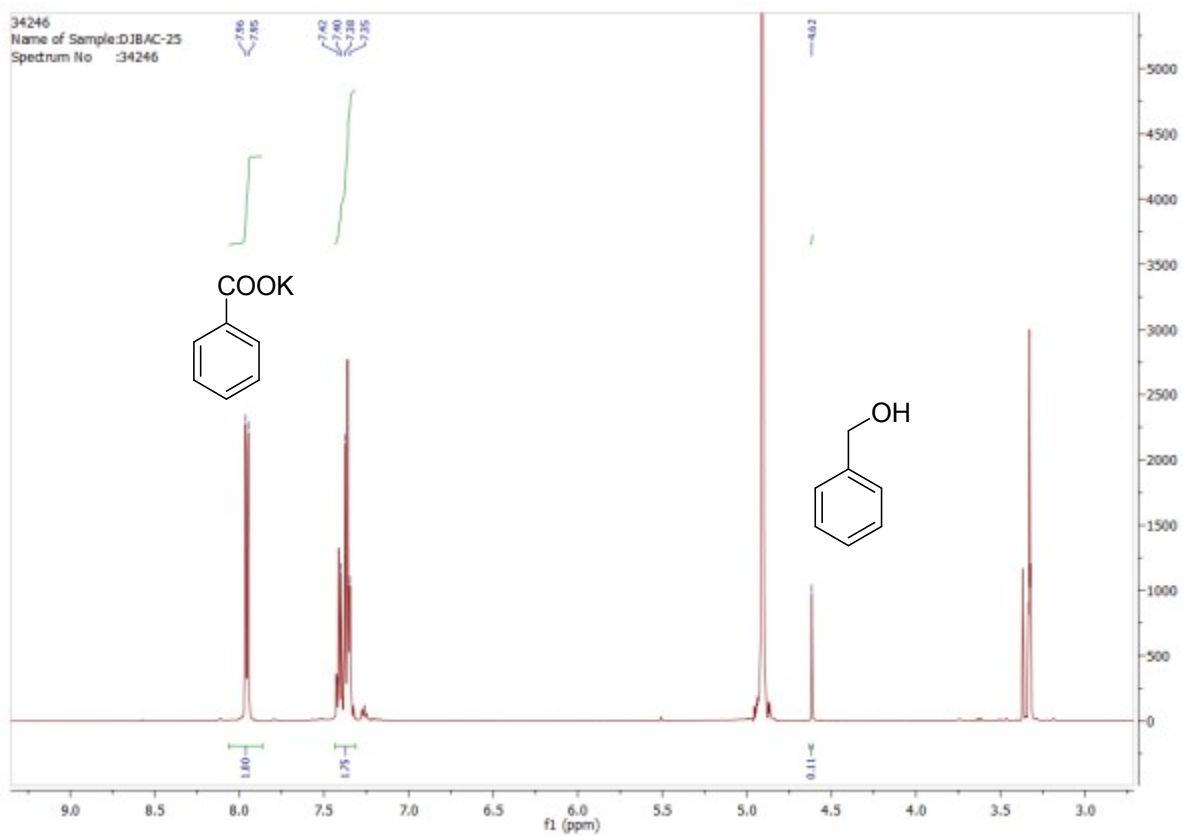


Figure S62. ^1H NMR of reaction products (dehydrogenation of benzaldehyde) in CD_3OD .

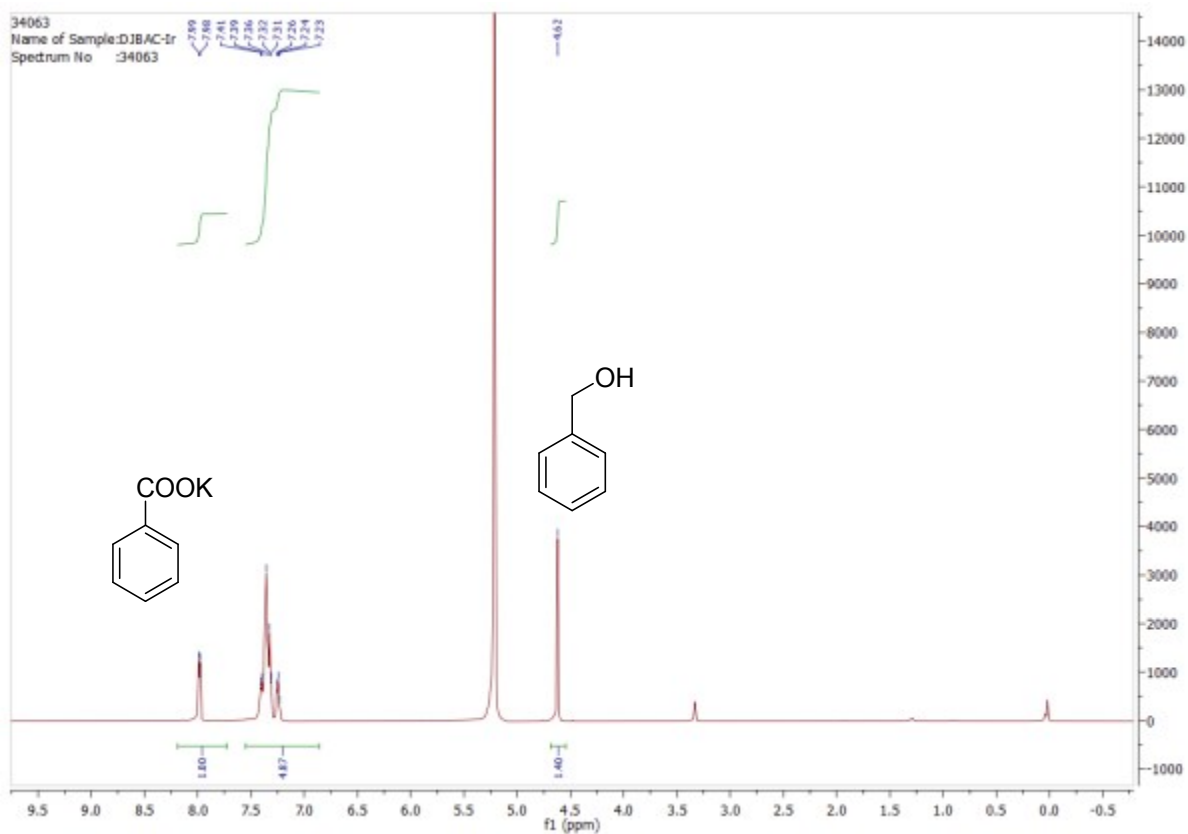


Figure S63. ¹H NMR of reaction products (dehydrogenation of benzyl alcohol) in CD₃OD catalysed by [Ir(Cp*)Cl₂]₂.

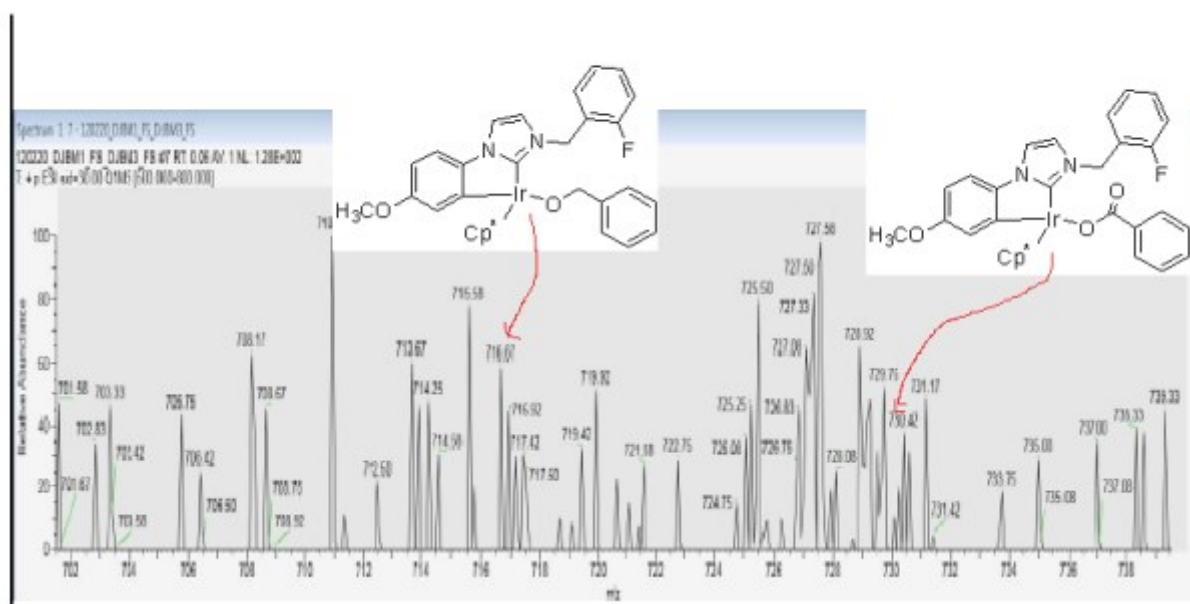


Figure S64. ESI-MS spectrum of the catalytic reaction mixture. Catalyst **1a** (0.1 mol%), KOH (1.1 mmol), benzyl alcohol (1 mmol), Toluene (10 mL), Refluxing conditions. The spectrum was recorded after 30 minutes of the reaction time.

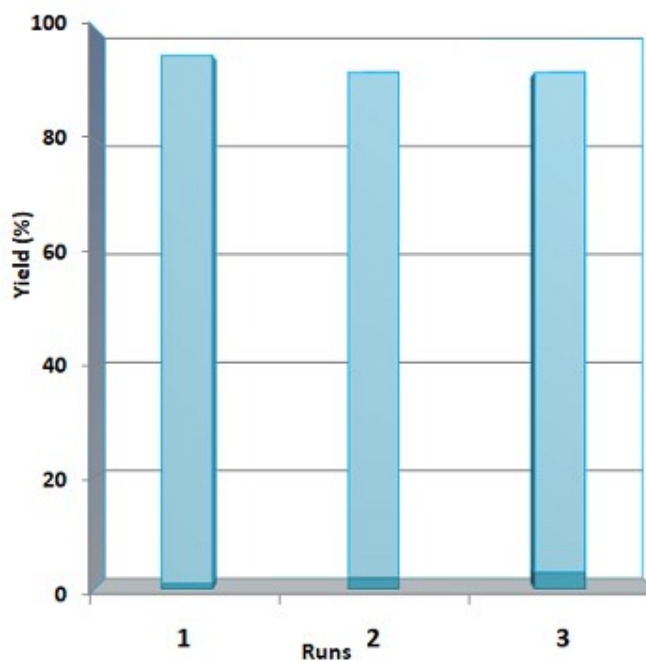


Figure S65. Reusability of catalyst **1a** for dehydrogenation reactions of benzyl alcohol to benzoic acid under standard conditions.

Crystal Data	1a
Formula unit	C ₂₇ H ₂₉ BrFIrN ₂ O
Formula wt.	688.63
Crystal system	monoclinic
T [K]	100
<i>a</i> [Å]	11.135(6)
<i>b</i> [Å]	16.187(9)
<i>c</i> [Å]	14.755(8)
α [°]	90
β [°]	107.165(8)
γ [°]	90
Volume [Å ³]	2541(2)
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4
<i>D</i> _{calc} [g cm ⁻³]	1.800
μ /mm ⁻¹	6.856
Reflns. Collected	38113
Unique reflns.	6584
Observed reflns.	3549
<i>R</i> ₁ [<i>I</i> >2 σ (<i>I</i>)], <i>wR</i> ₂	0.0676, 0.1571
GOF	0.999
Instrument	Bruker APEX-II CCD
X-ray	MoK α
CCDC Reference No.	1973746

Table S1: Crystallographic data



BB.cif