Bidentate Ru(II)-NC complexes as catalysts for the dehydrogenative reaction from primary alcohols to carboxylic acids

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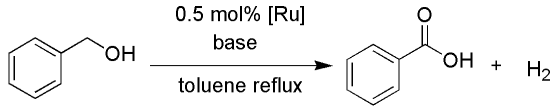
Control Experiment

Table S1. Intermediates **6**-**8** as catalysts for catalytic reaction in different time.



Entry	[Ru]	time	Conversion (%)[a]
1	**1**	1h	29
2	**1**	2h	51
3	**1**	4h	80
4	**1**	6h	91
5	**6**	1h	30
6	**6**	2h	53
7	**6**	4h	80
8	**6**	6h	91
9	**7**	1h	29
10	**7**	2h	52
11	**7**	4h	80
12	**7**	6h	90
13	**8**	1h	20
14	**8**	2h	35
15	**8**	4h	52
16	**8**	6h	65

Reaction conditions: benzyl alcohol (2 mmol), base (3 mmol), toluene (6 mL), N_2, catalyst (0.5 mol%), 120 ^oC, the conversion was calculated by GC using dodecane (1 mmol) as the internal standard.

Crystallographic Details

3: A total of 18755 reflections ($-14 \leq h \leq 15$, $-15 \leq k \leq 16$, $-23 \leq l \leq 22$) were collected at T = 120(2) K in the range of 5.818 to 58.142^{o} of which 10223 were unique (R_{int} = 0.0316); Mo_K radiation (λ = 0.71073 Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.44 and -0.52 eA^{-3}, respectively. The least squares refinement converged normally with residuals of $R(F)$ = 0.0525, $wR(F^2)$ = 0.0987 and a GOF = 0.980 ($I>2\sigma(I)$). $C_{51}H_{40}ClNOP_2Ru$, Mw = 881.30, space group Pnma, Orthorhombic, a = 11.5301(6), b = 12.0841(8), c = 17.3369(12) Å, V = 2261.7(3) Å^3, Z = 2, ρ_{calcd} = 1.294 Mg/m^3. CCDC-1890662 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7: A total of 58791 reflections ($-14 \leq h \leq 14$, $-32 \leq k \leq 57$, $-26 \leq l \leq 27$) were collected at T = 120(10) K in the range of 5.612^{o} to 58.104^{o} of which 29481 were unique (R_{int} = 0.0534); Mo_K radiation (λ = 0.71073 Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.666 and -0.591 eA^{-3}, respectively. The least squares refinement converged normally with residuals of $R(F)$ = 0.0709, $wR(F^2)$ = 0.0956 and a GOF = 1.038 ($I>2\sigma(I)$). $C_{117}H_{94}Cl_8N_2O_6P_4Ru_2$, Mw = 1949.96, space group $P2_1$, Orthorhombic, a = 10.7582(2), b = 43.2244(8), c = 19.8552(3) Å, V = 9231.8(2) Å^3, Z = 4, ρ_{calcd} = 1.403 Mg/m^3. CCDC-1890663 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

IR Spectra

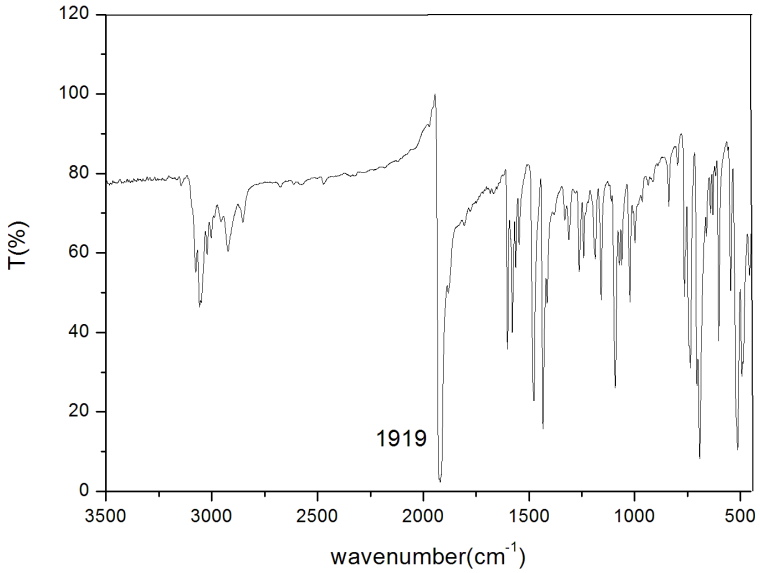


Figure S1. IR spectrum of **1**

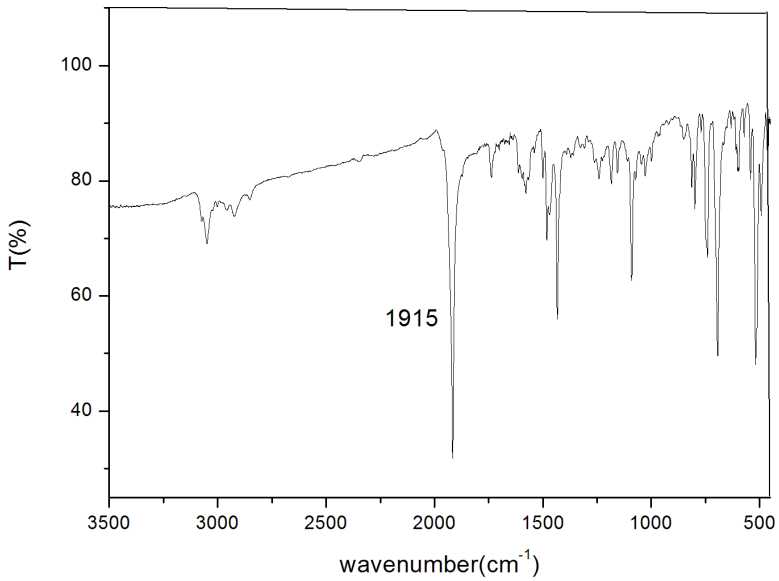


Figure S2. IR spectrum of **2**

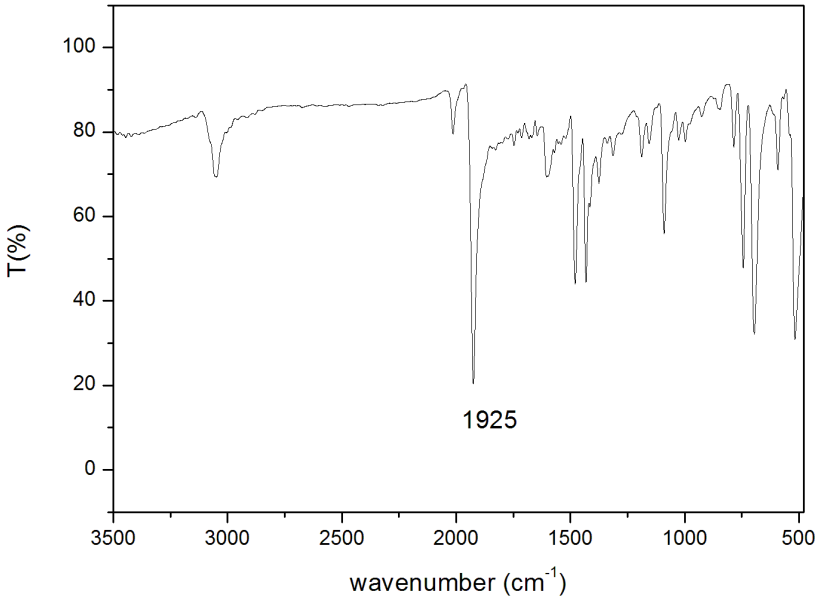


Figure S3. IR spectrum of **3**

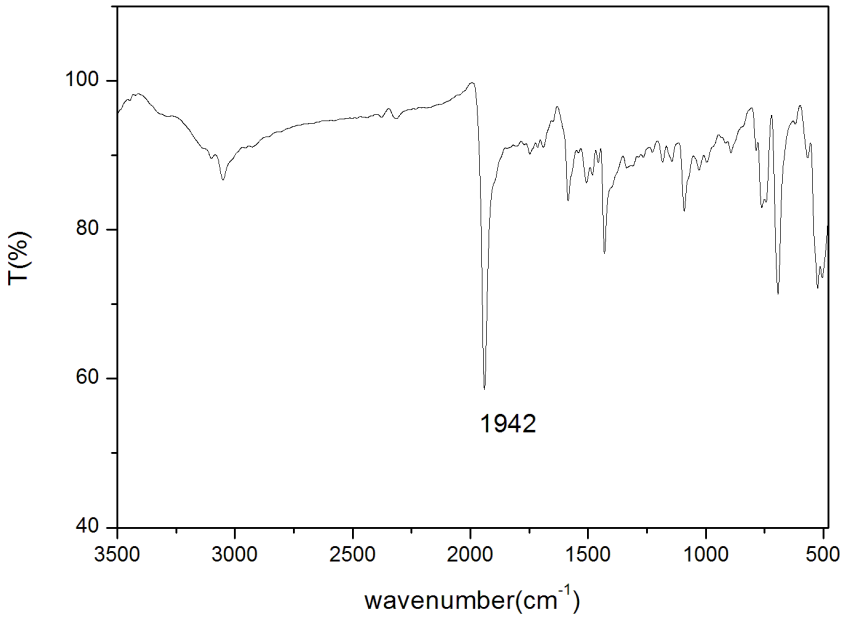


Figure S4. IR spectrum of **4**

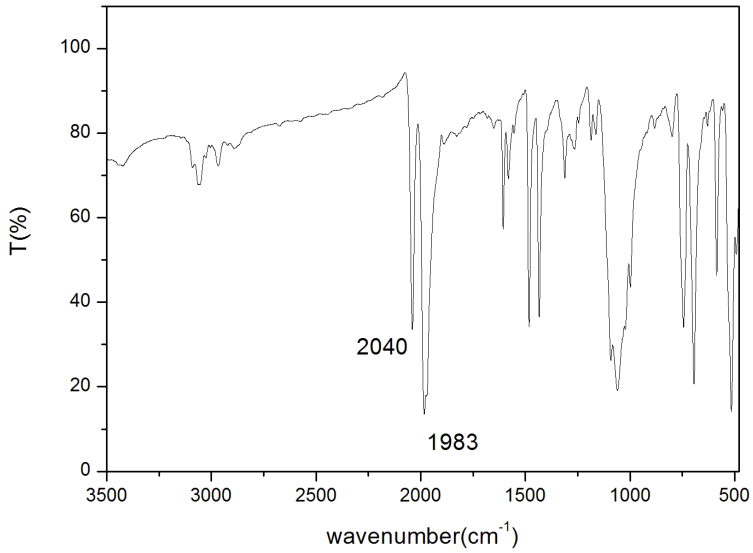


Figure S5. IR spectrum of **5**

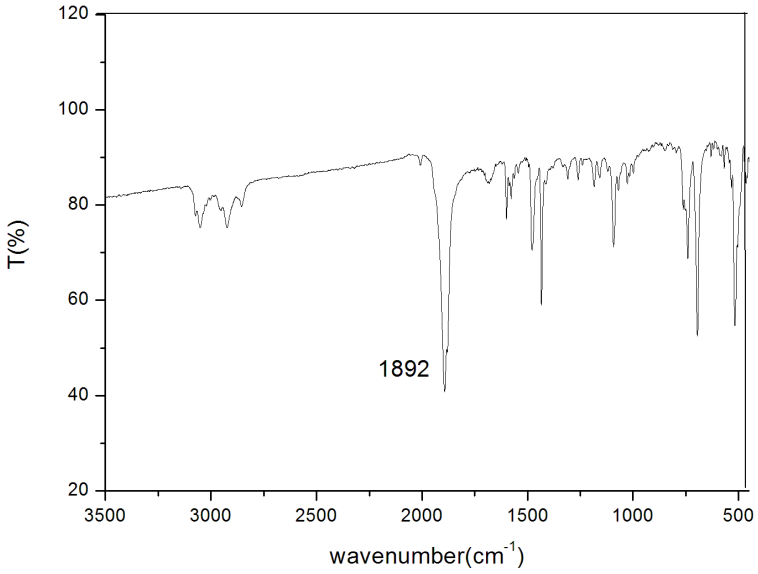


Figure S6. IR spectrum of **6**

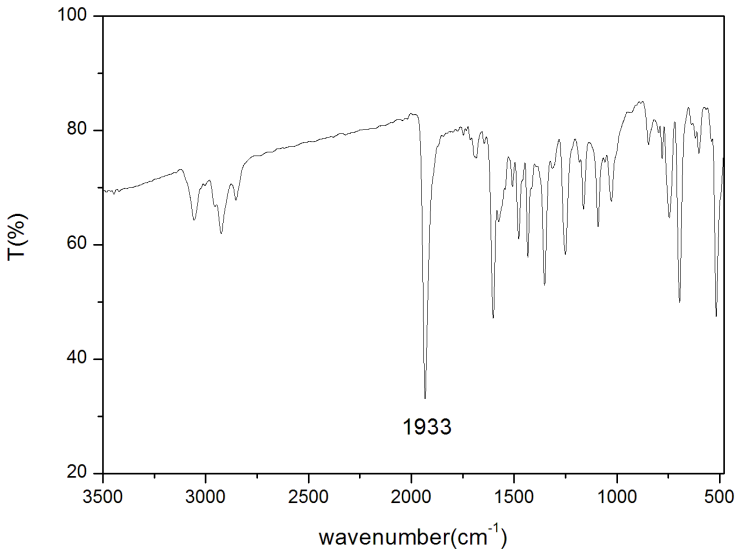


Figure S7. IR spectrum of **7**

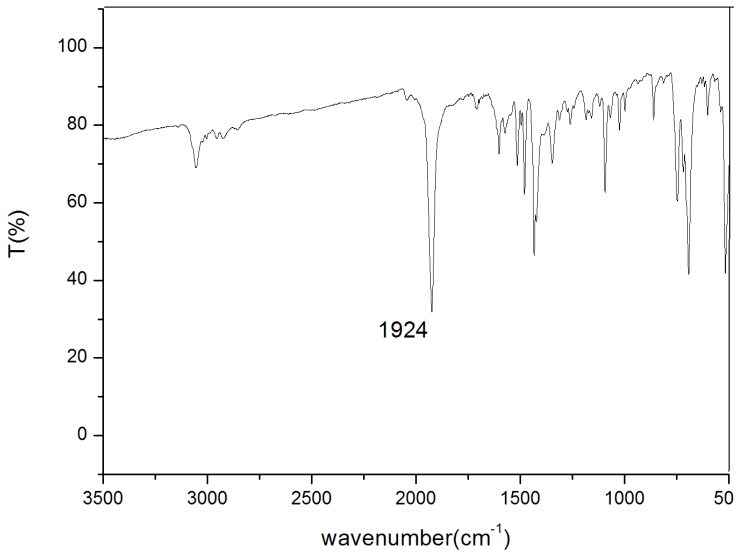


Figure S8. IR spectrum of **8**

NMR Spectra of the Orgaonometallic Complexes

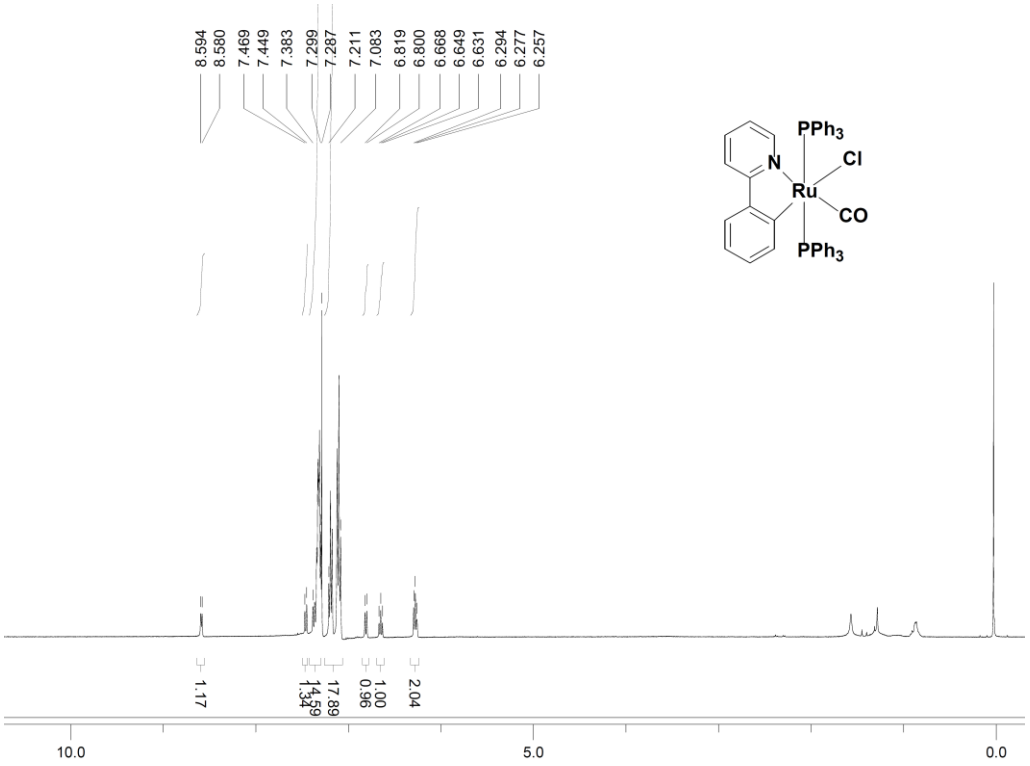


Figure S9. ^{1}H NMR spectrum of **1** in $CDCl_3$

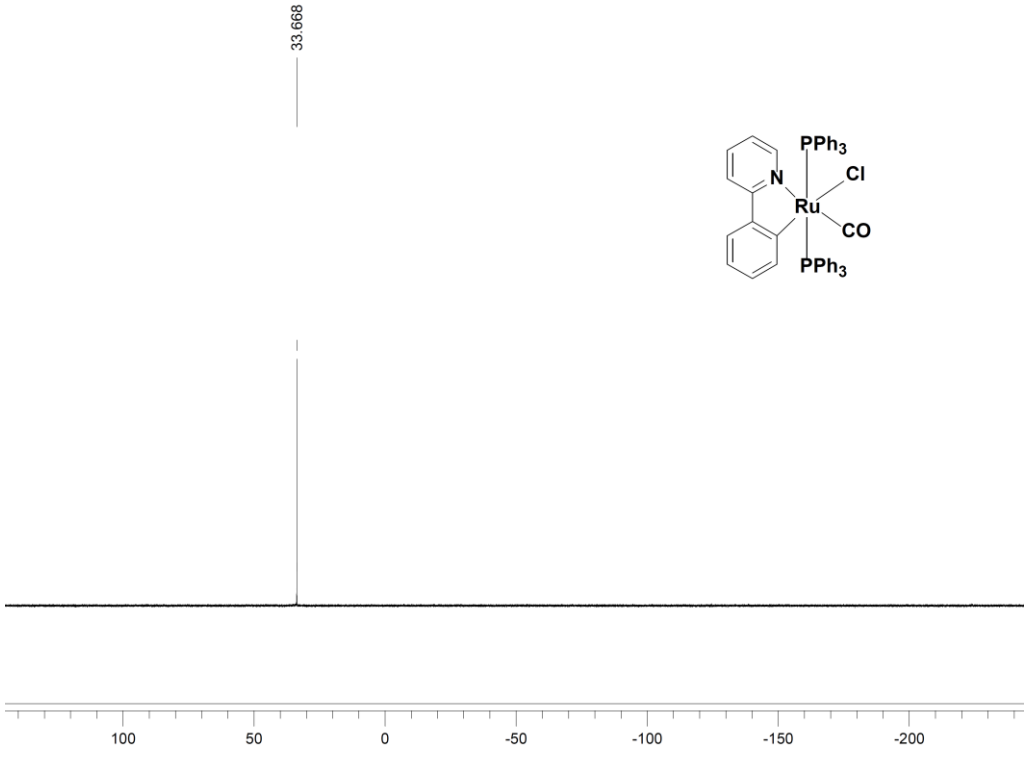


Figure S10. ^{31}P NMR spectrum of **1** in $CDCl_3$.

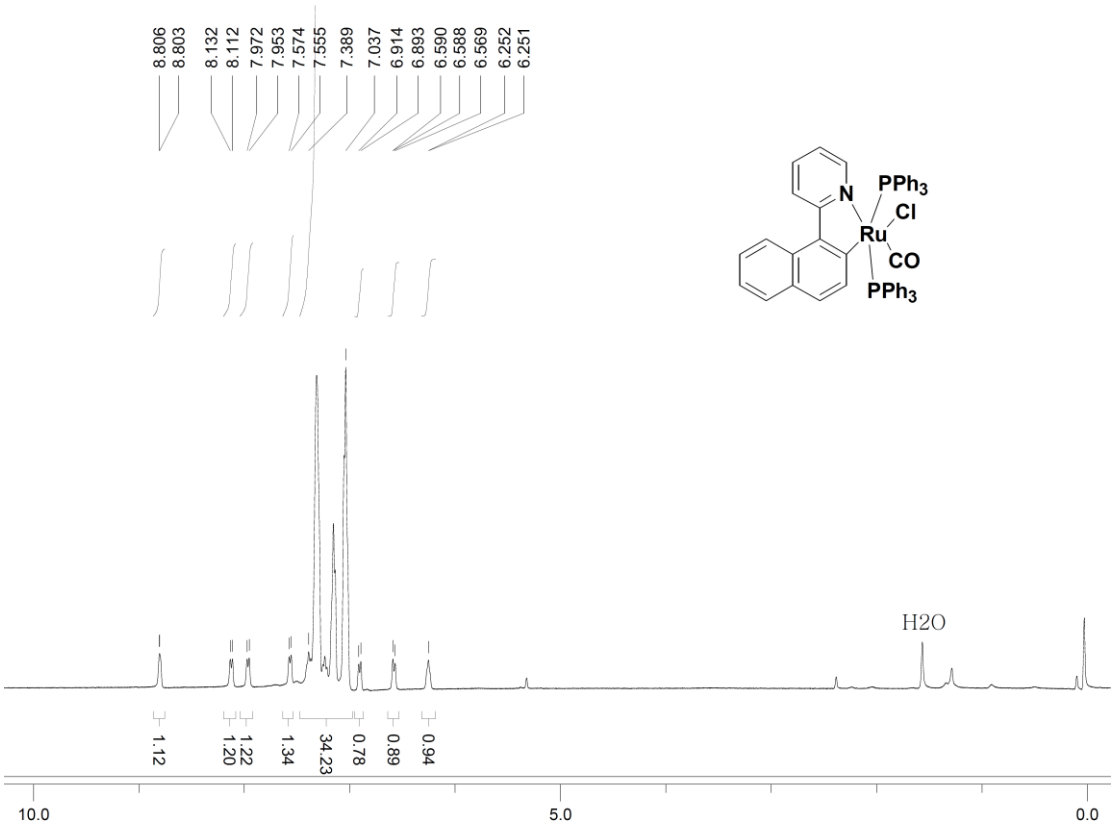


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$

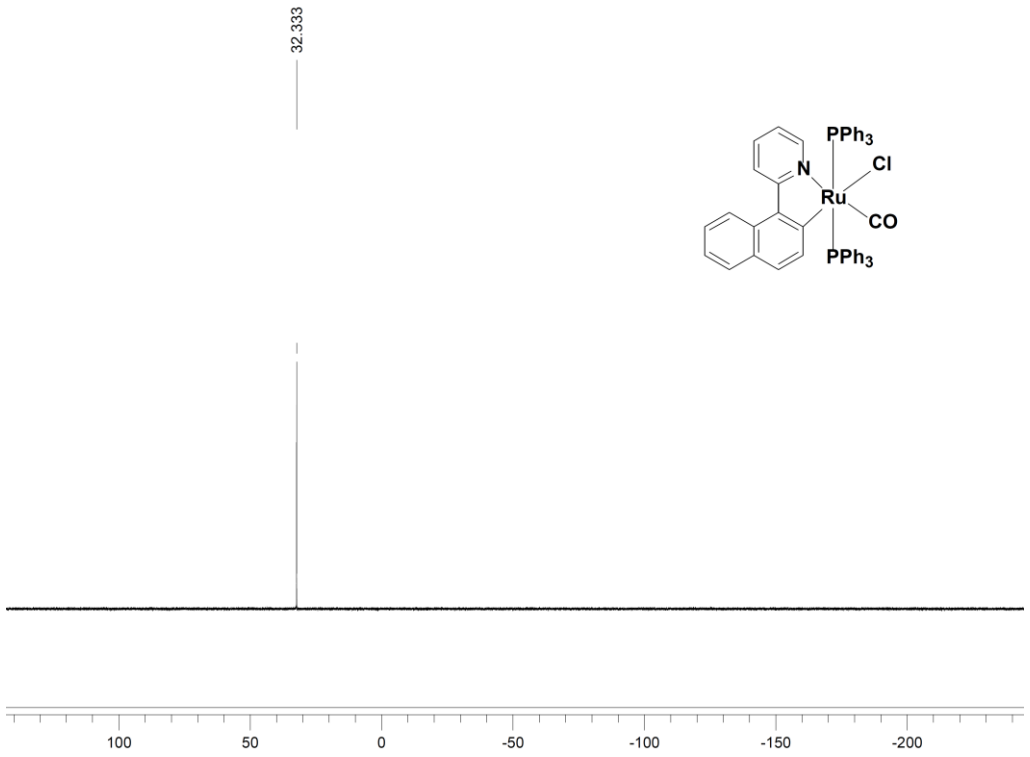


Figure S12. ^{31}P NMR spectrum of **2** in $CDCl_3$.

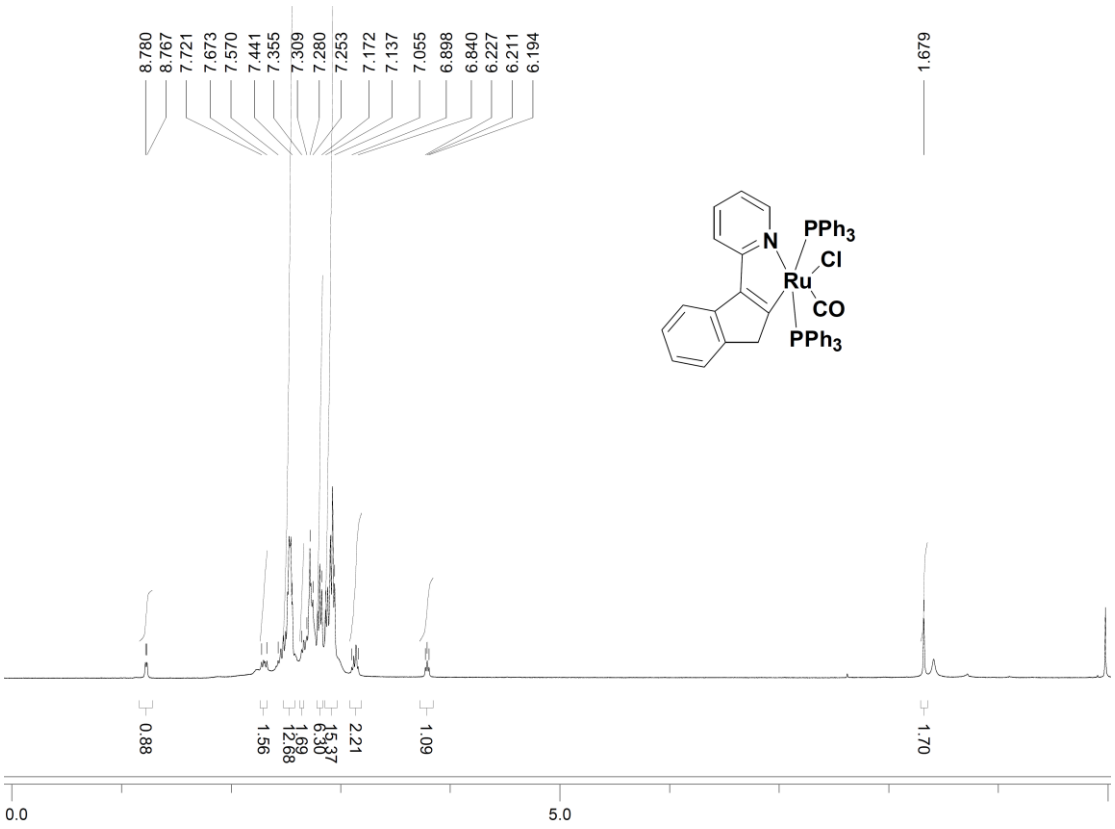


Figure S13. ^{1}H NMR spectrum of **3** in $CDCl_3$

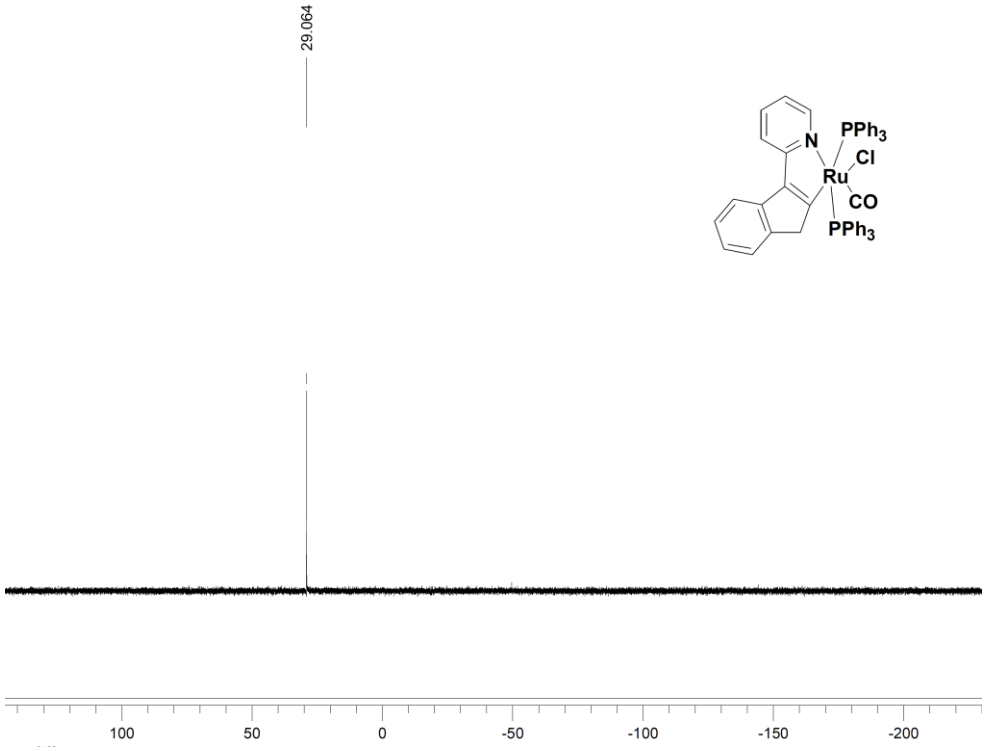


Figure S14. ^{31}P NMR spectrum of **3** in $CDCl_3$.

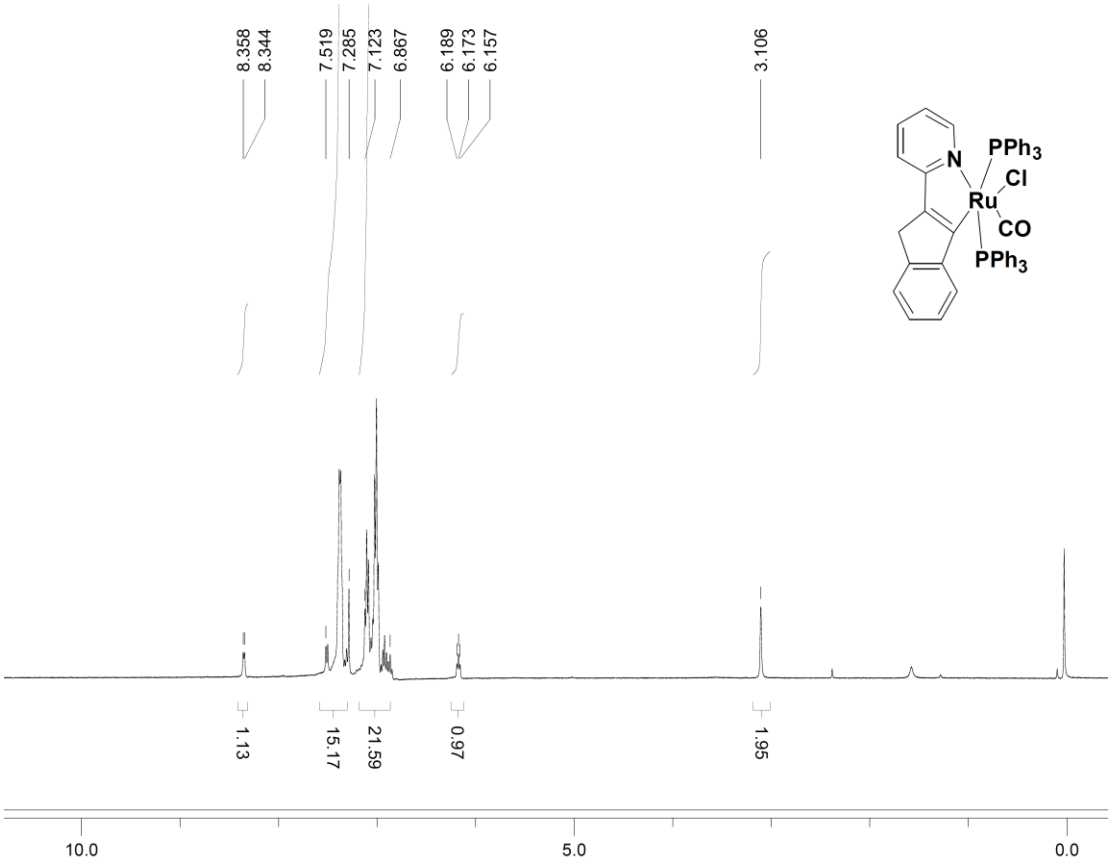


Figure S15. ^{1}H NMR spectrum of **4** in $CDCl_3$

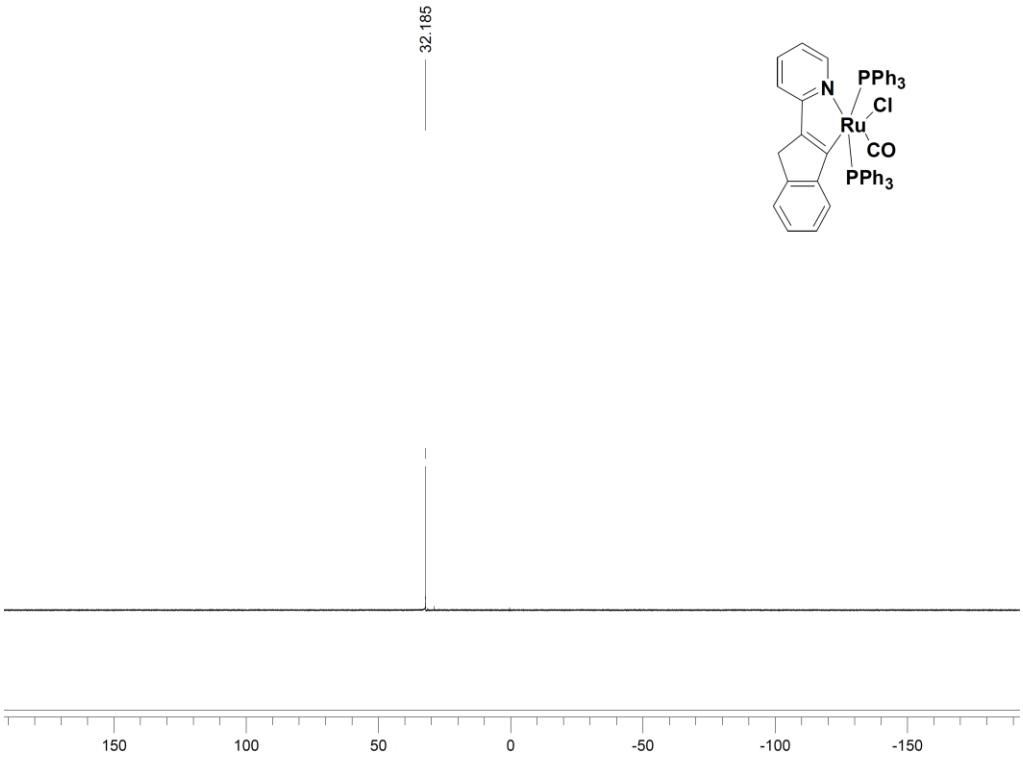


Figure S16. ^{31}P{1H} NMR spectrum of **4** in $CDCl_3$.

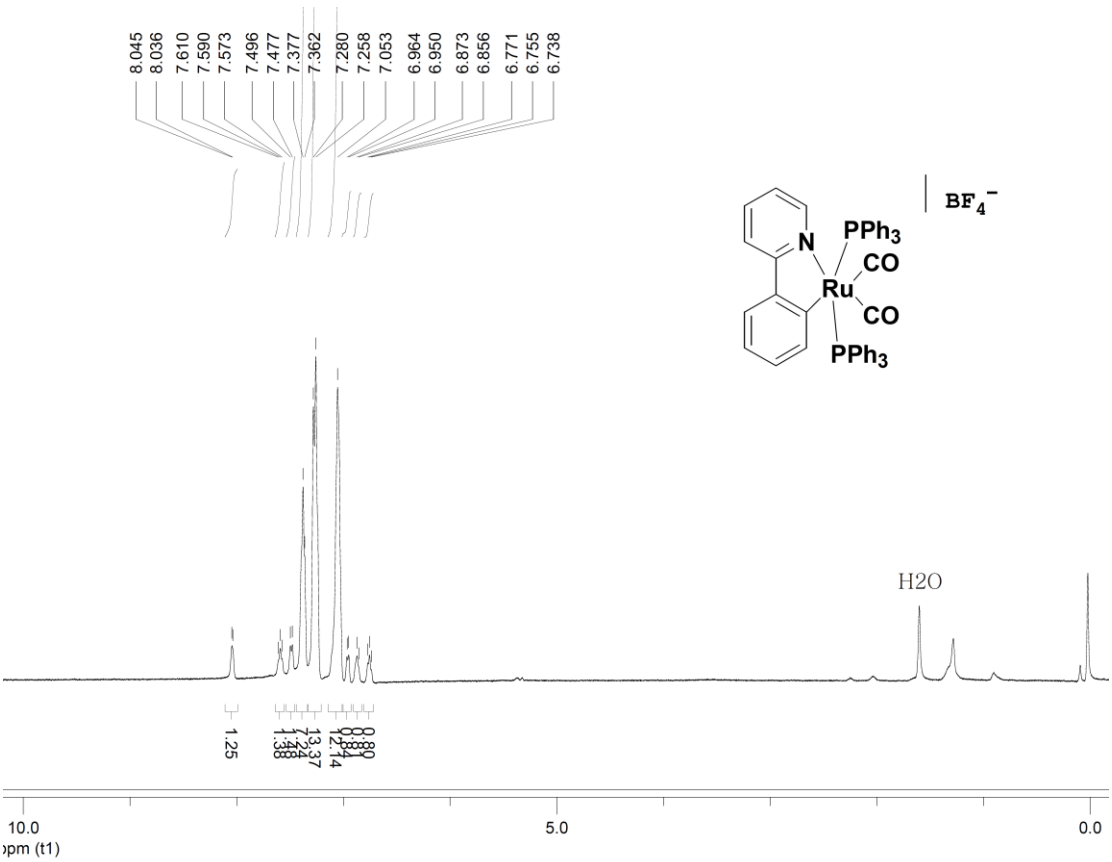


Figure S17. ^{1}H NMR spectrum of **5** in $CDCl_3$

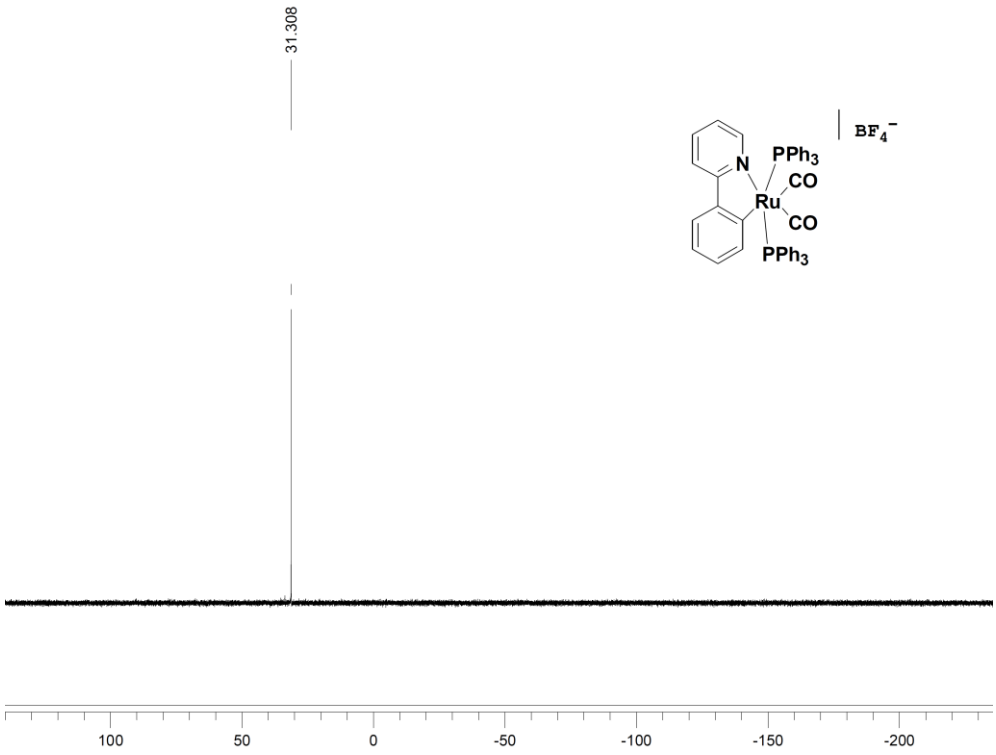


Figure S18. ^{31}P{1H} NMR spectrum of **5** in $CDCl_3$.

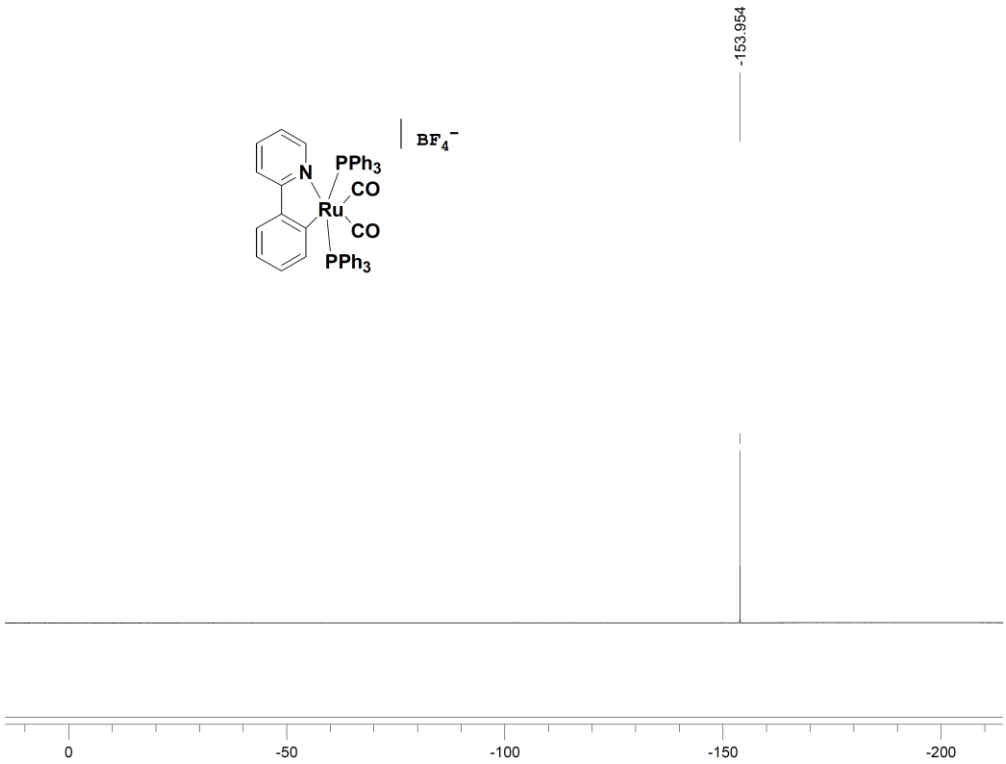


Figure S19. ^{19}F NMR spectrum of **5** in $CDCl_3$.

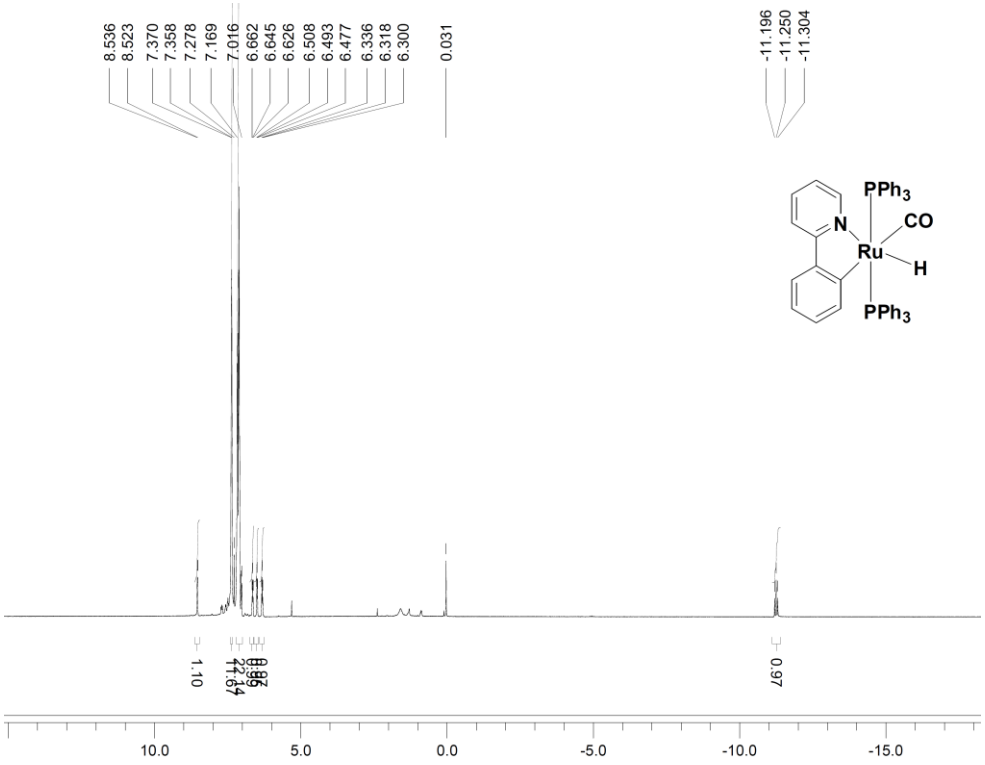


Figure S20-1. ^{1}H NMR spectrum of **6** in $CDCl_3$ (full region).

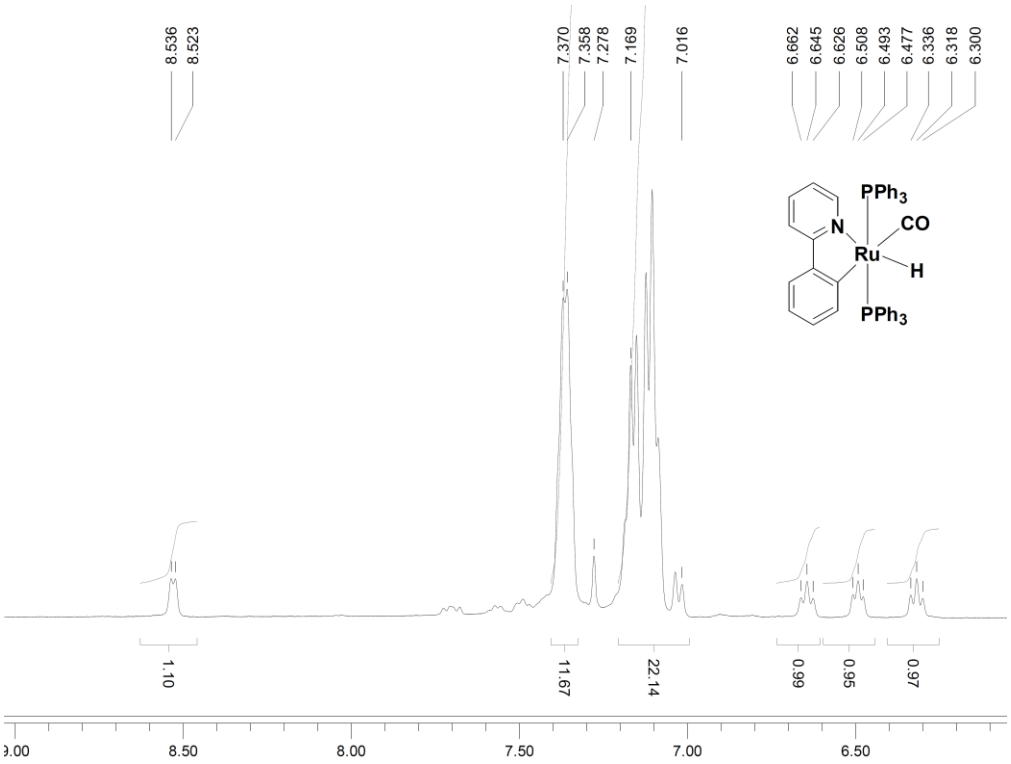


Figure S20-2. ^{1}H NMR spectrum of **6** in $CDCl_3$ (the region without Ru-H).

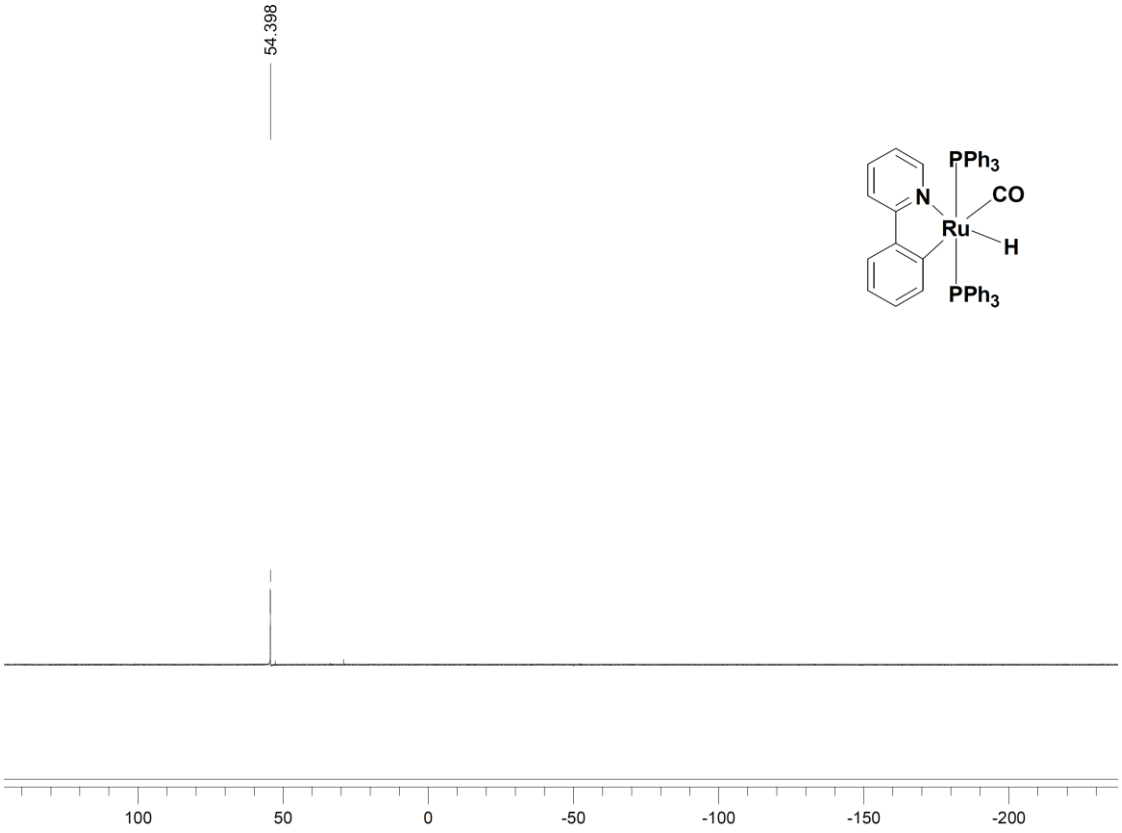


Figure S21. ^{31}P{1H} NMR spectrum of **6** in $CDCl_3$.

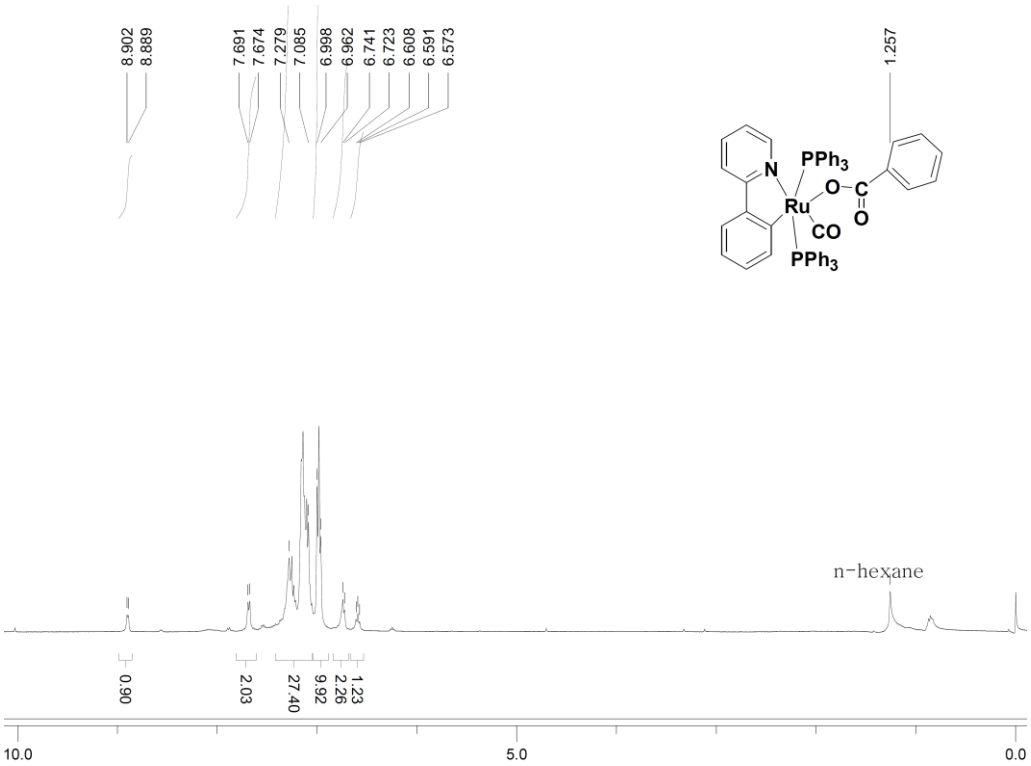


Figure S22. ^{1}H NMR spectrum of **7** in $CDCl_3$

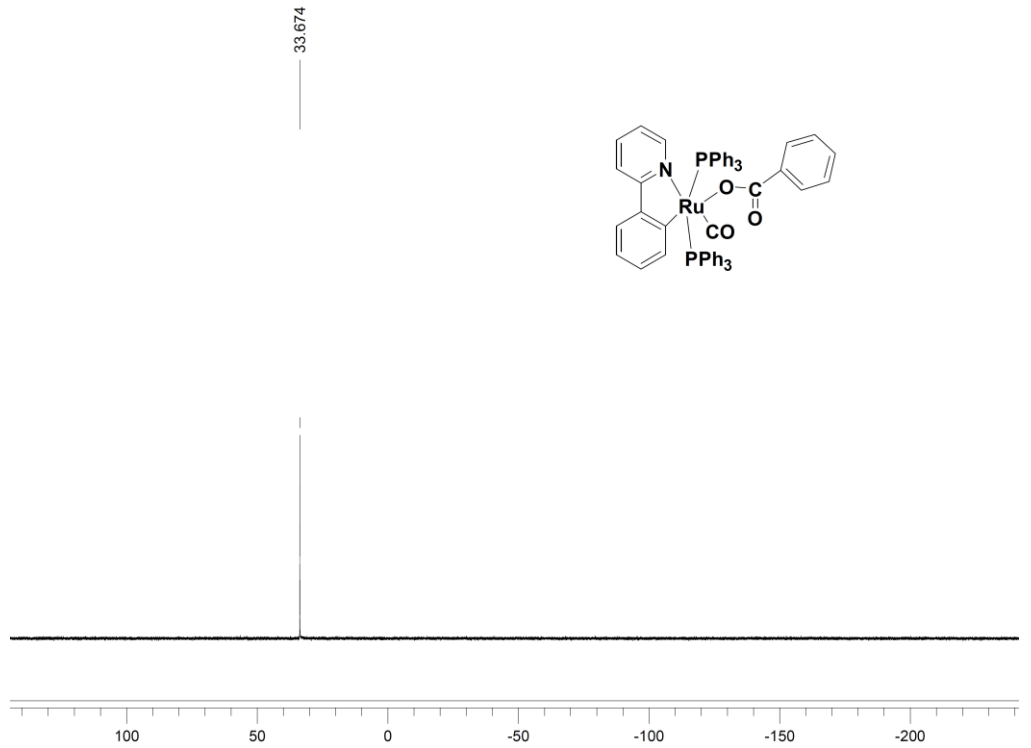


Figure S23. ^{31}P{1H} NMR spectrum of **7** in $CDCl_3$.

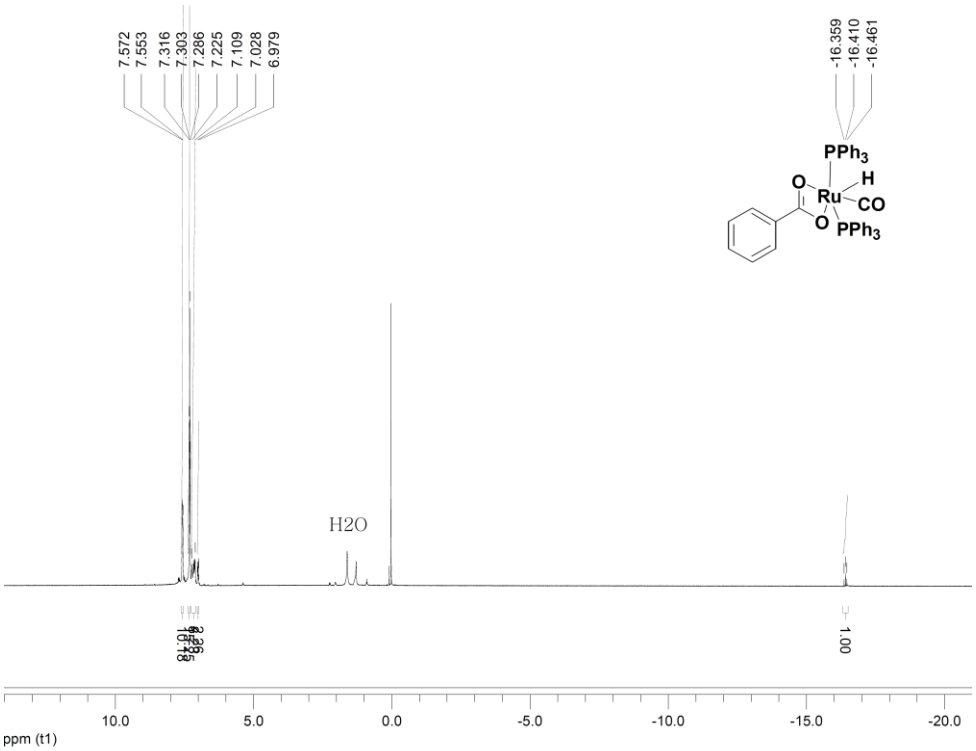


Figure S24-1. ^{1}H NMR spectrum of **8** in $CDCl_3$ (full region).

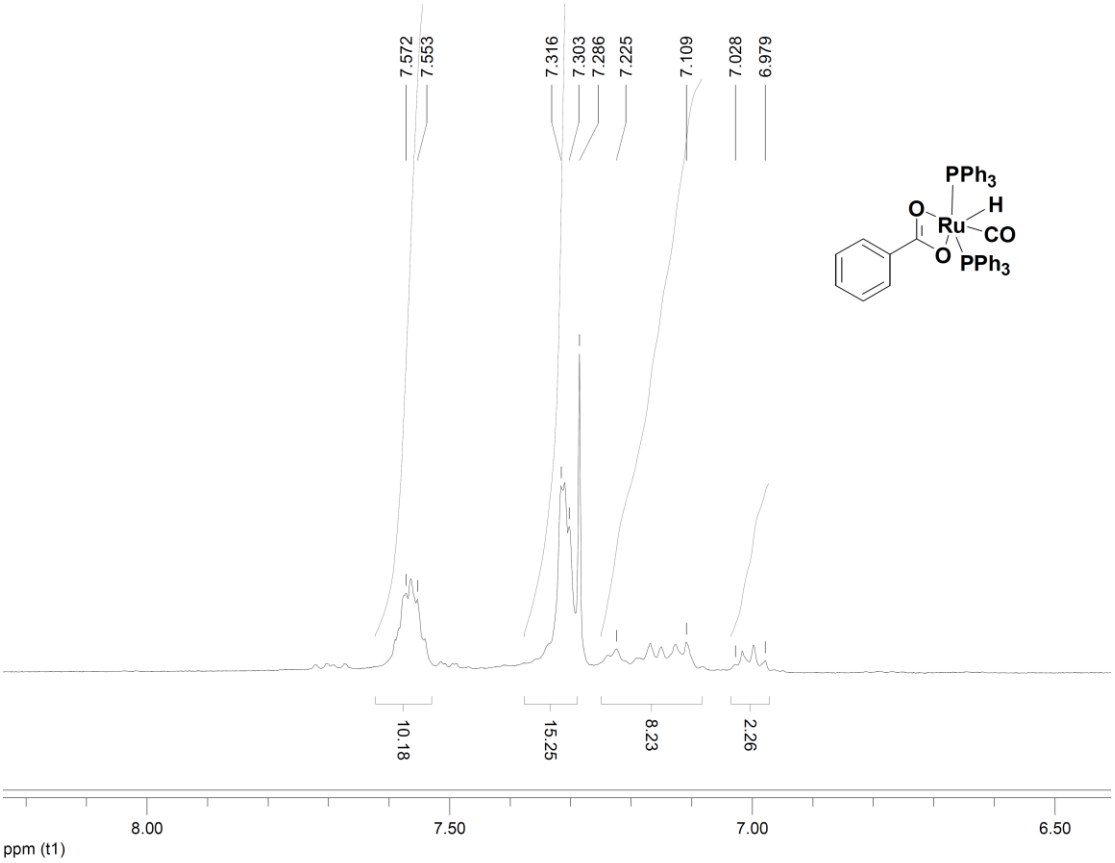


Figure S24-2. ^{1}H NMR spectrum of **8** in $CDCl_3$. (the region without Ru-H).

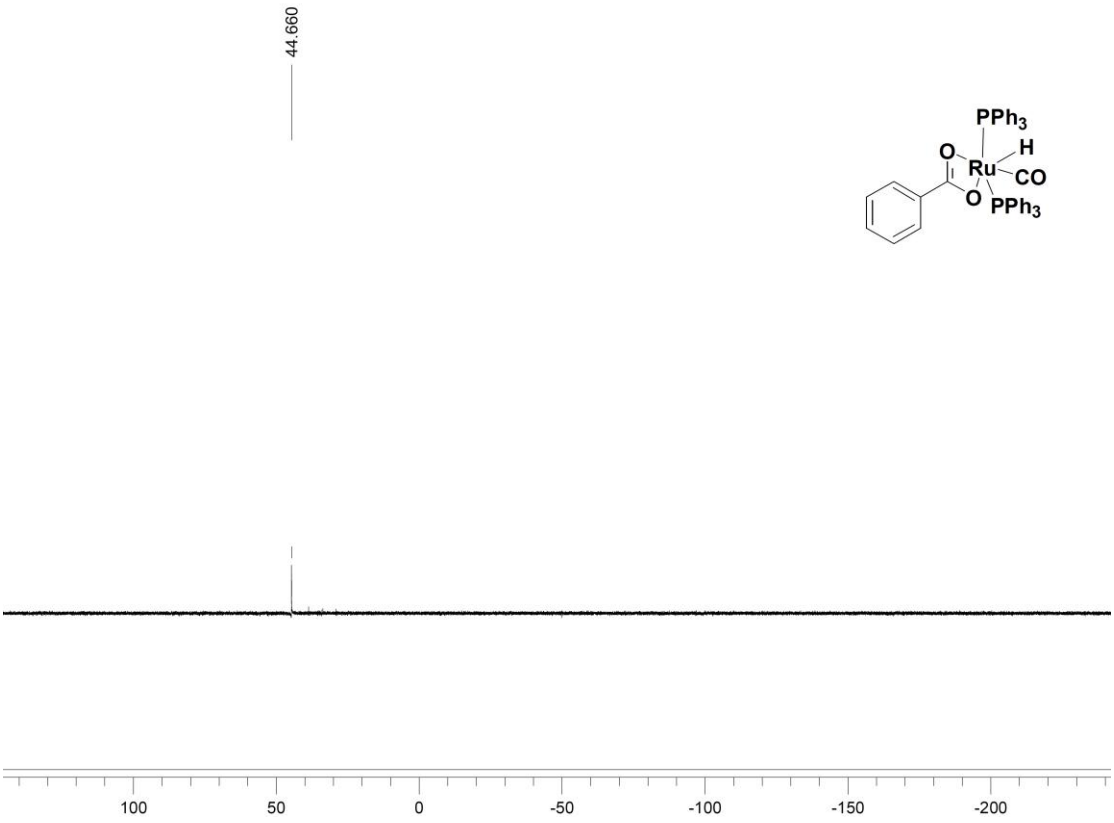


Figure S25. $^{31}P\{1H\}$ NMR spectrum of **8** in $CDCl_3$.

^{1}H NMR Spectra of the Carboxylic Acids

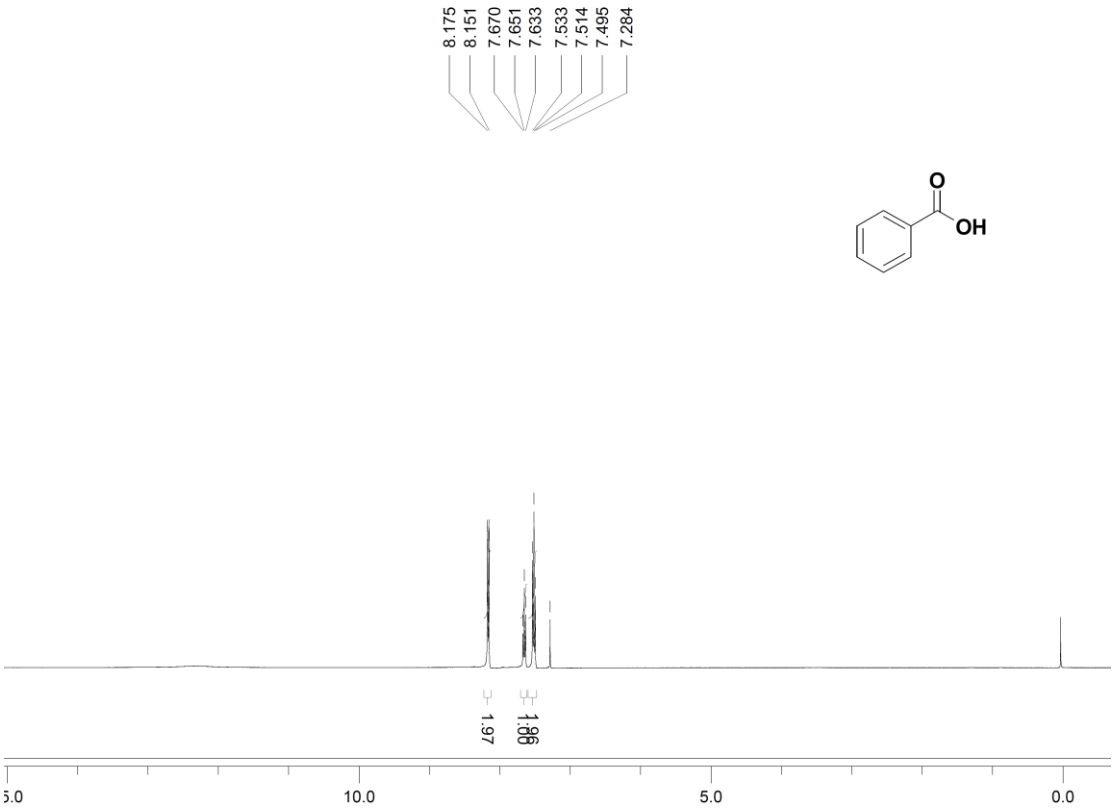


Figure S26. ^{1}H NMR spectrum of benzoic acid in $CDCl_3$

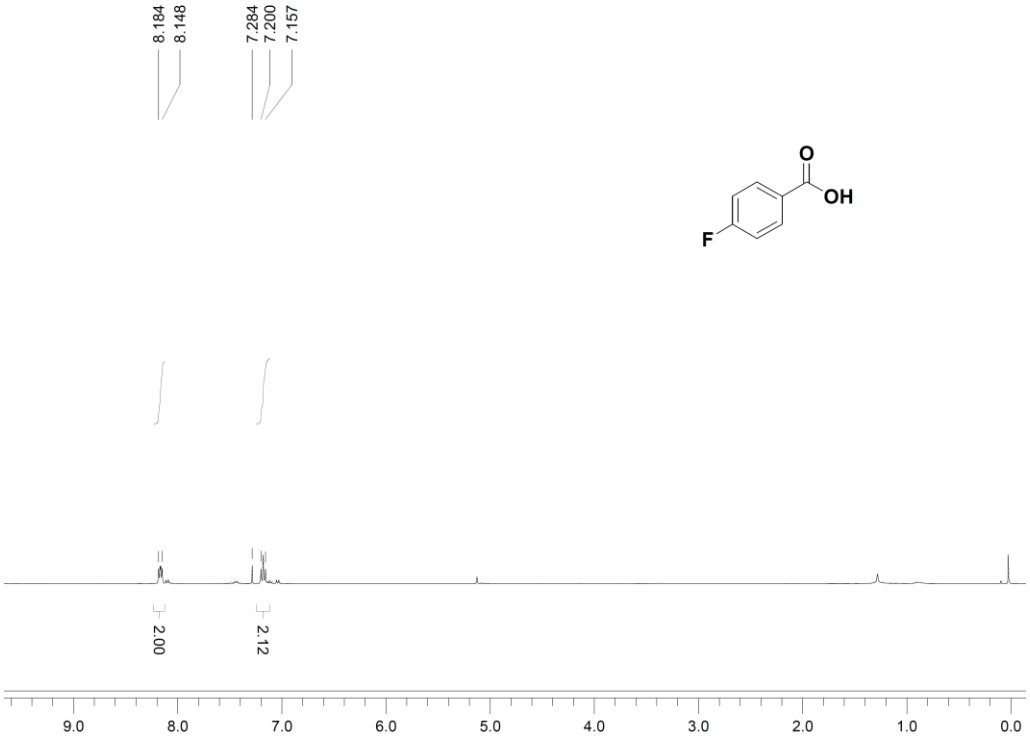


Figure S27. ^{1}H NMR spectrum of 4-fluorobenzoic acid in $CDCl_3$

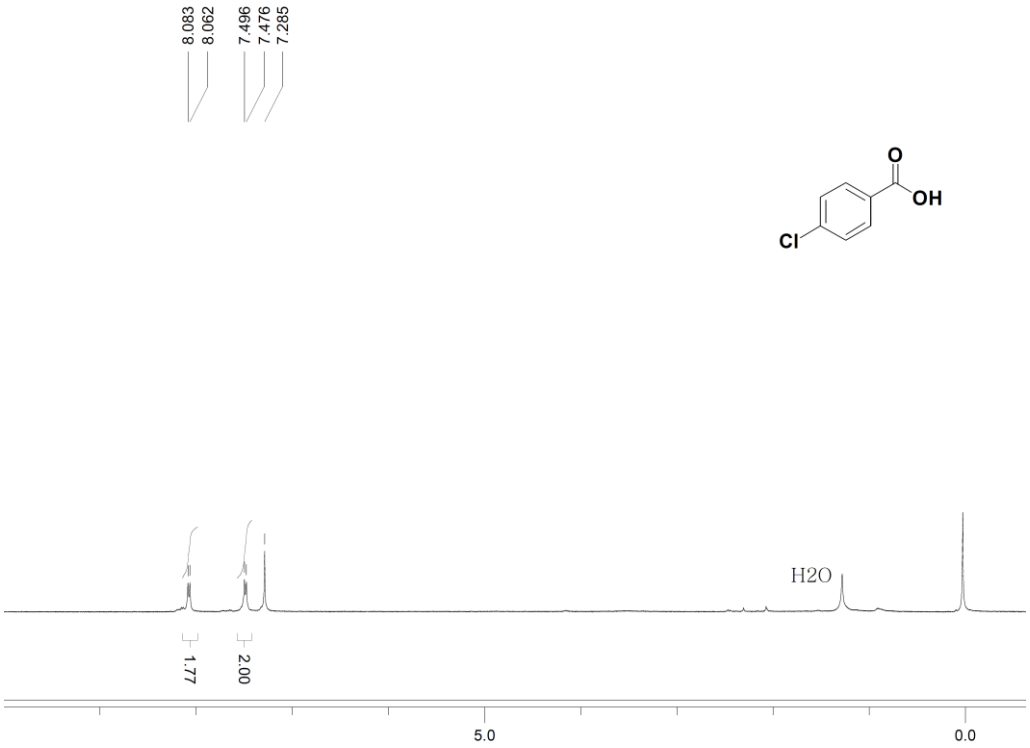


Figure S28. ^{1}H NMR spectrum of 4-chlorobenzoic acid in $CDCl_3$

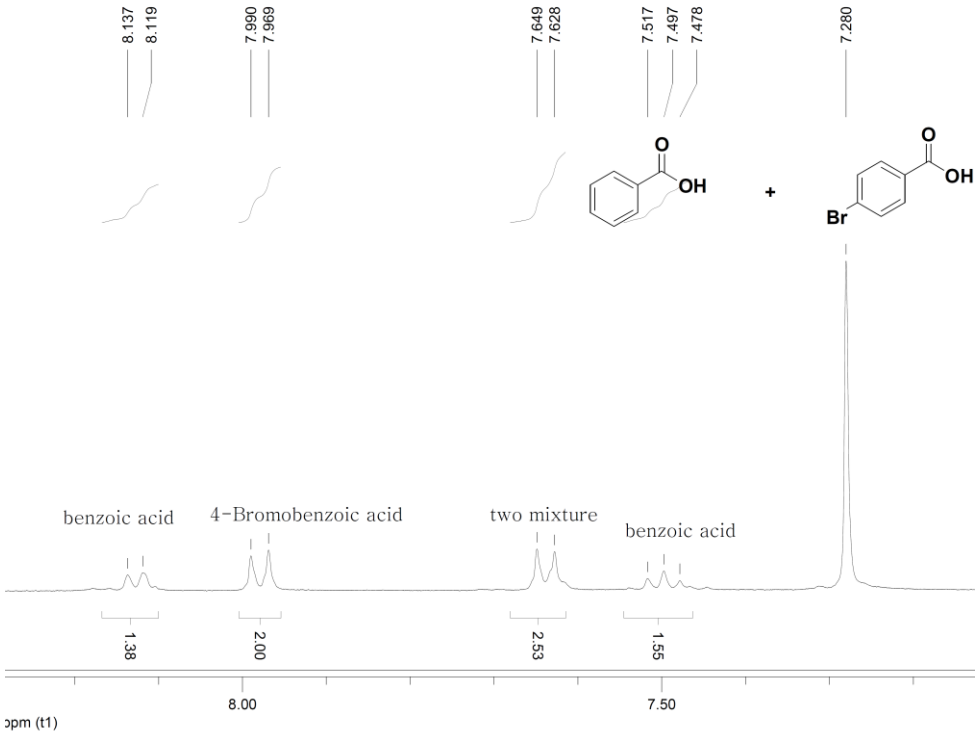


Figure S29. ^{1}H NMR spectrum of 4-bromobenzoic acid in $CDCl_3$

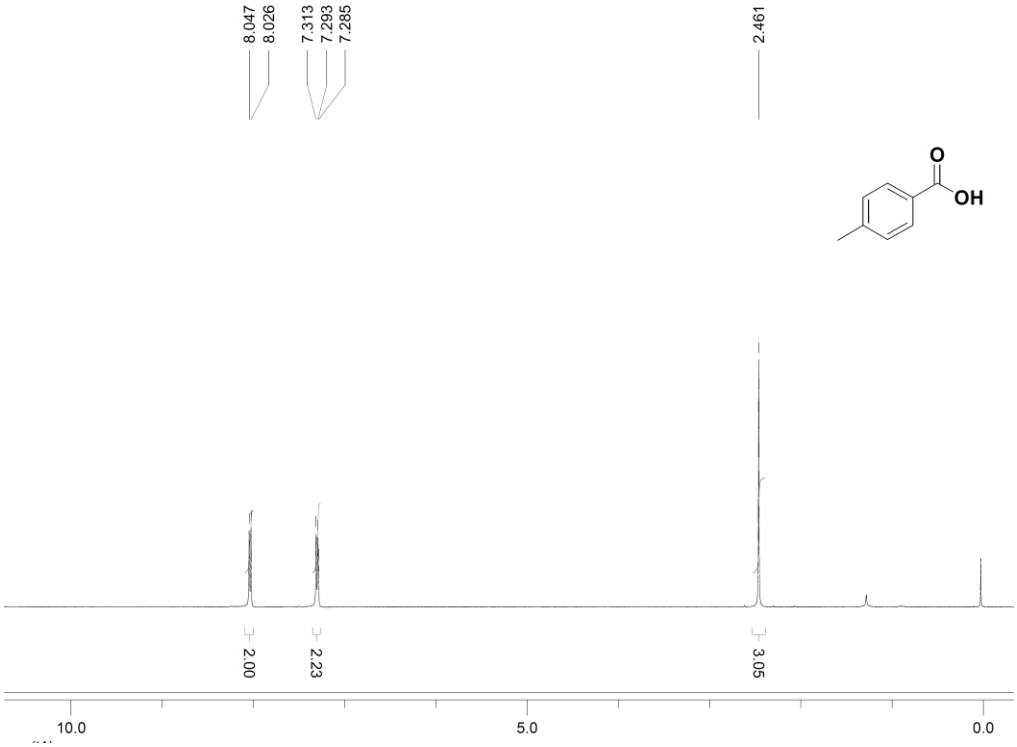


Figure S30. ^{1}H NMR spectrum of 4-methylbenzoic acid in $CDCl_3$

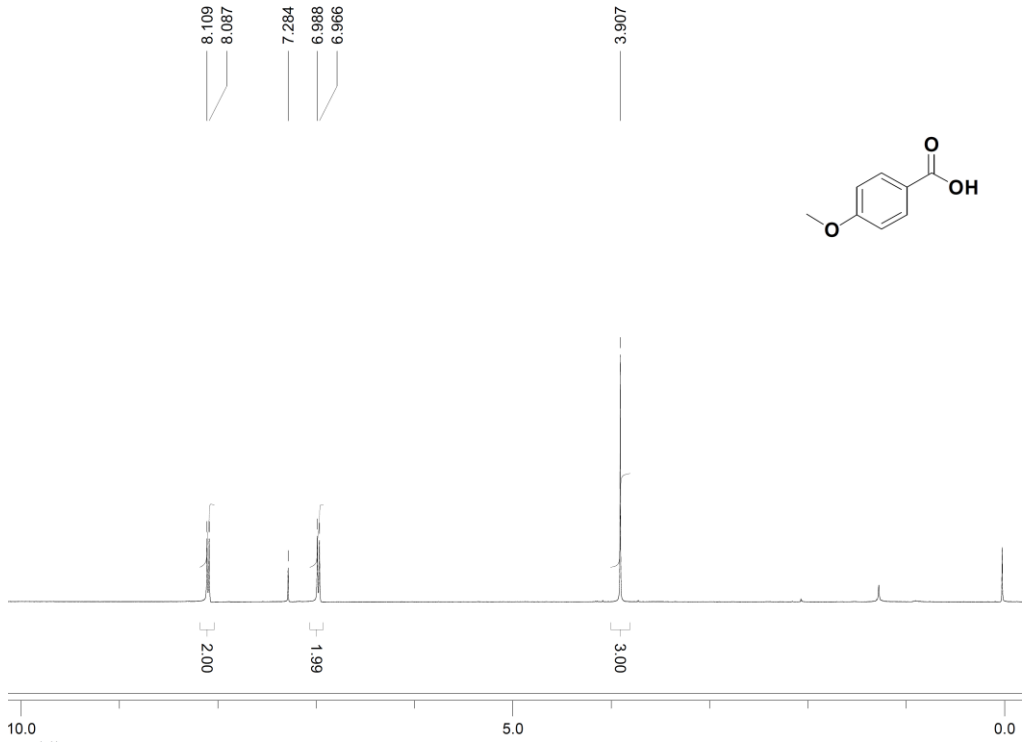


Figure S31. ^{1}H NMR spectrum of 4-methoxybenzoic acid in $CDCl_3$

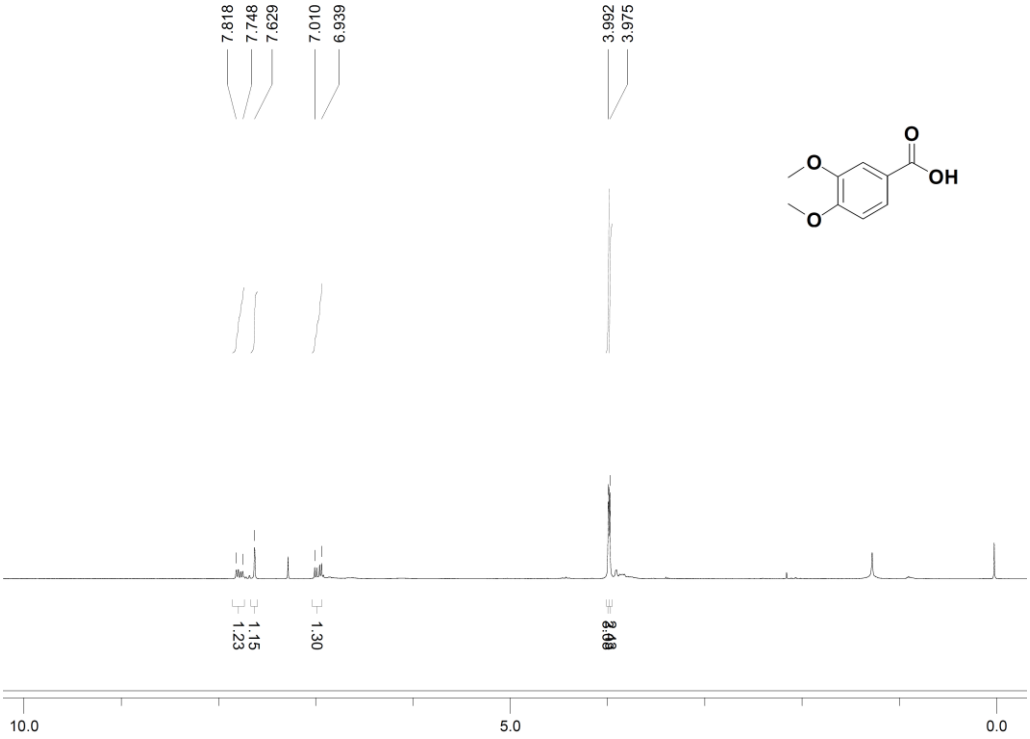


Figure S32. ^{1}H NMR spectrum of 3,4-Dimethoxybenzoic acid in $CDCl_3$

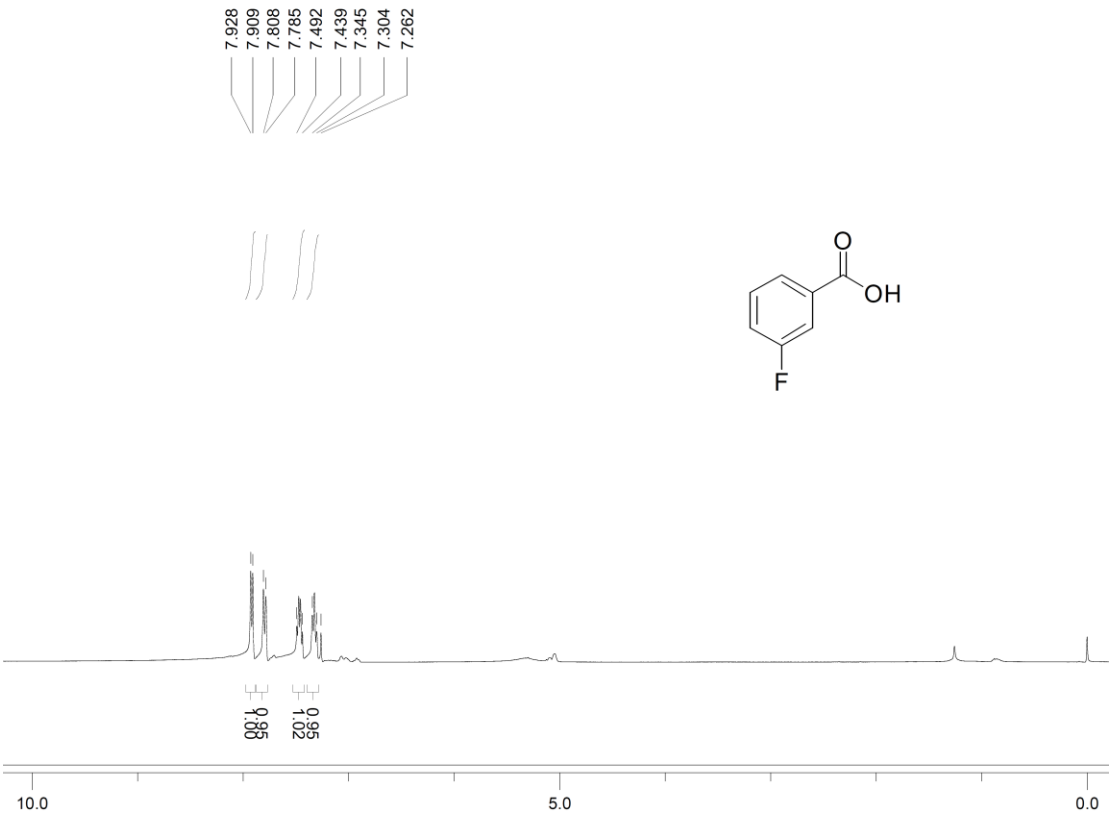


Figure S33. ^{1}H NMR spectrum of 3-fluorobenzoic acid in $CDCl_3$

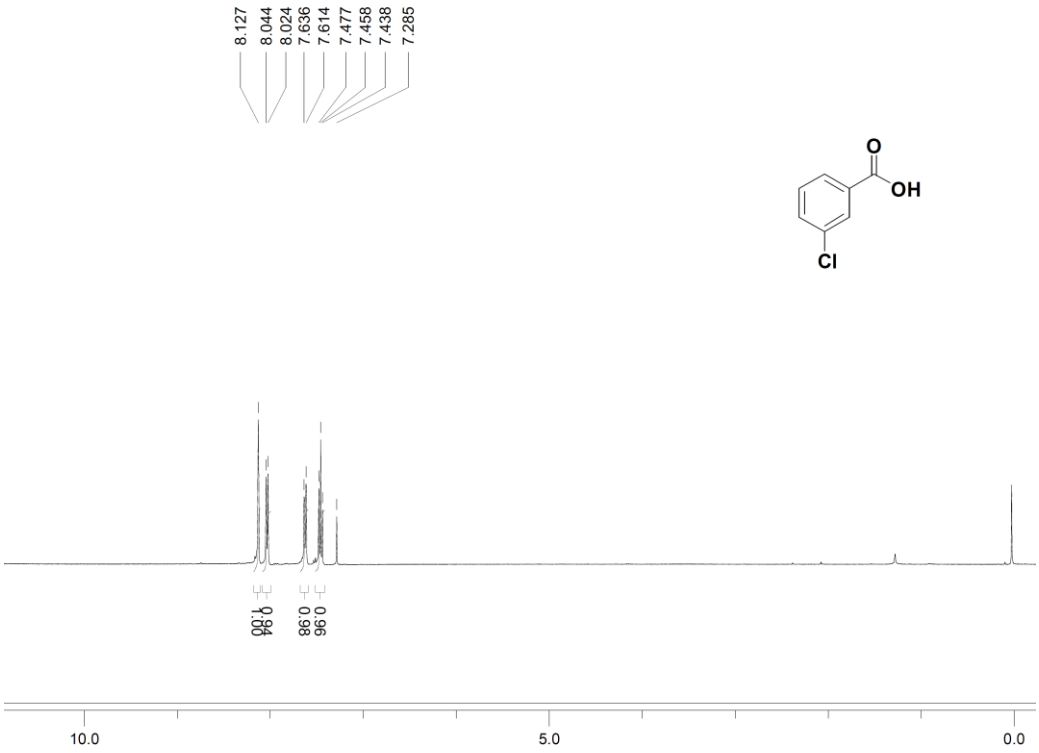


Figure S34. ^{1}H NMR spectrum of 3-chlorobenzoic acid in $CDCl_3$

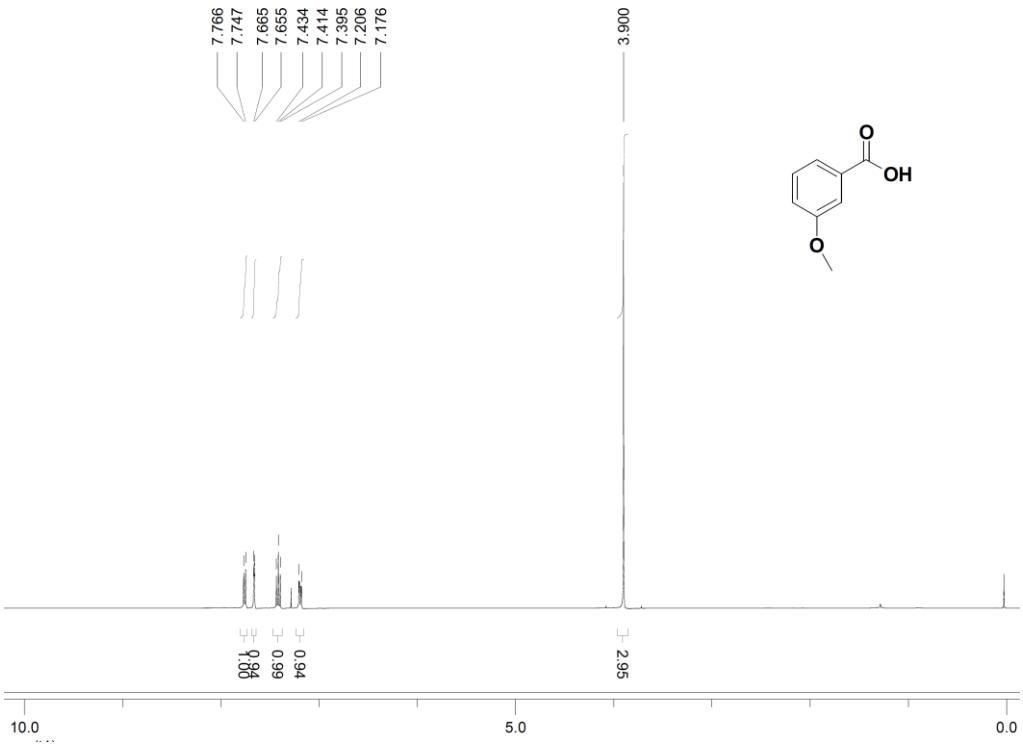


Figure S35. ^{1}H NMR spectrum of 3-methoxybenzoic acid in $CDCl_3$

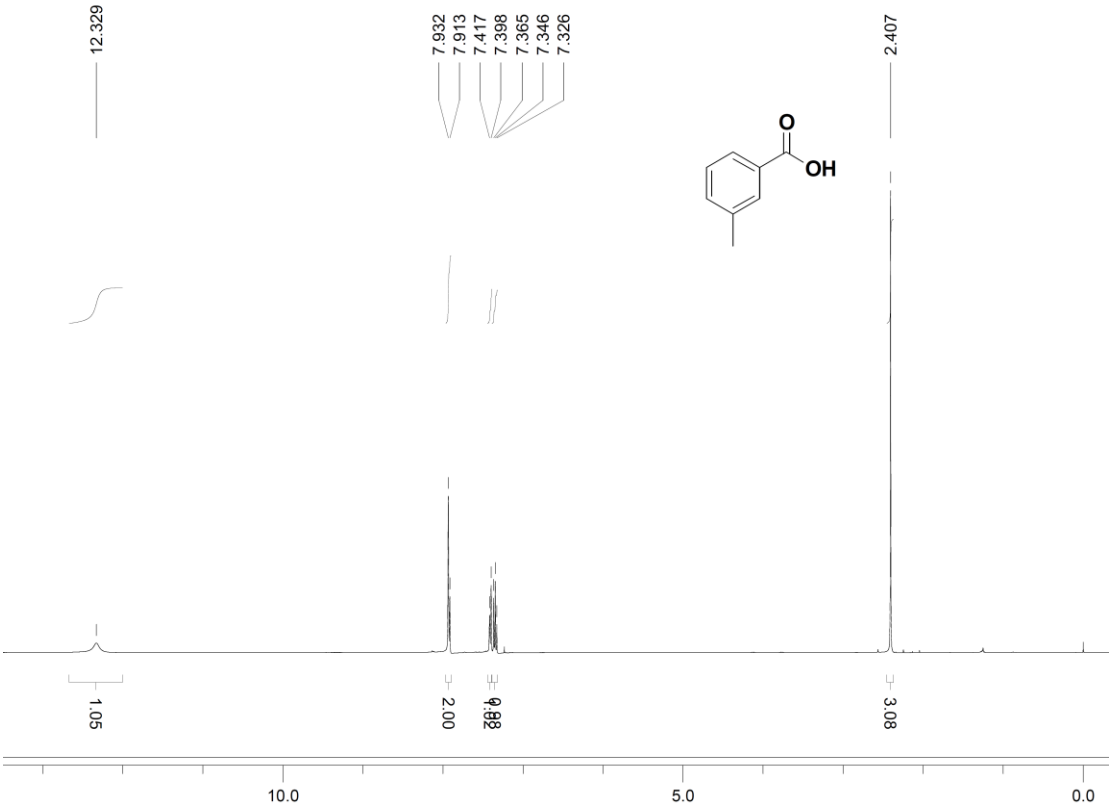


Figure S36. ^{1}H NMR spectrum of 3-methylbenzoic acid in $CDCl_3$

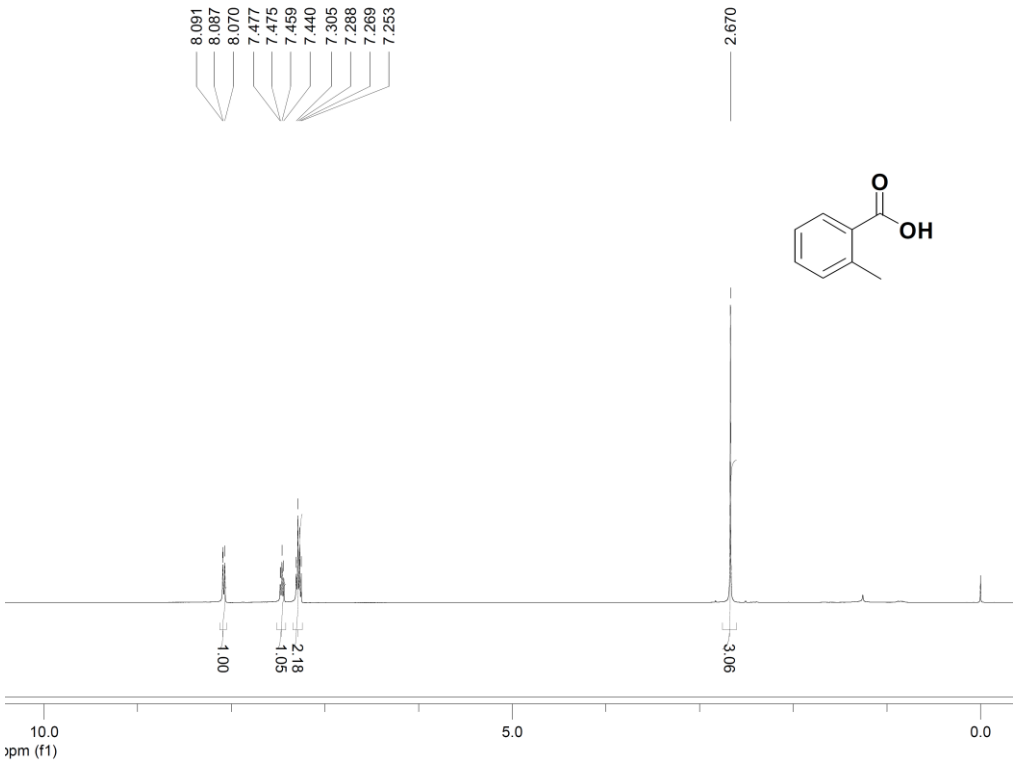


Figure S37. ^{1}H NMR spectrum of 2-methylbenzoic acid in $CDCl_3$

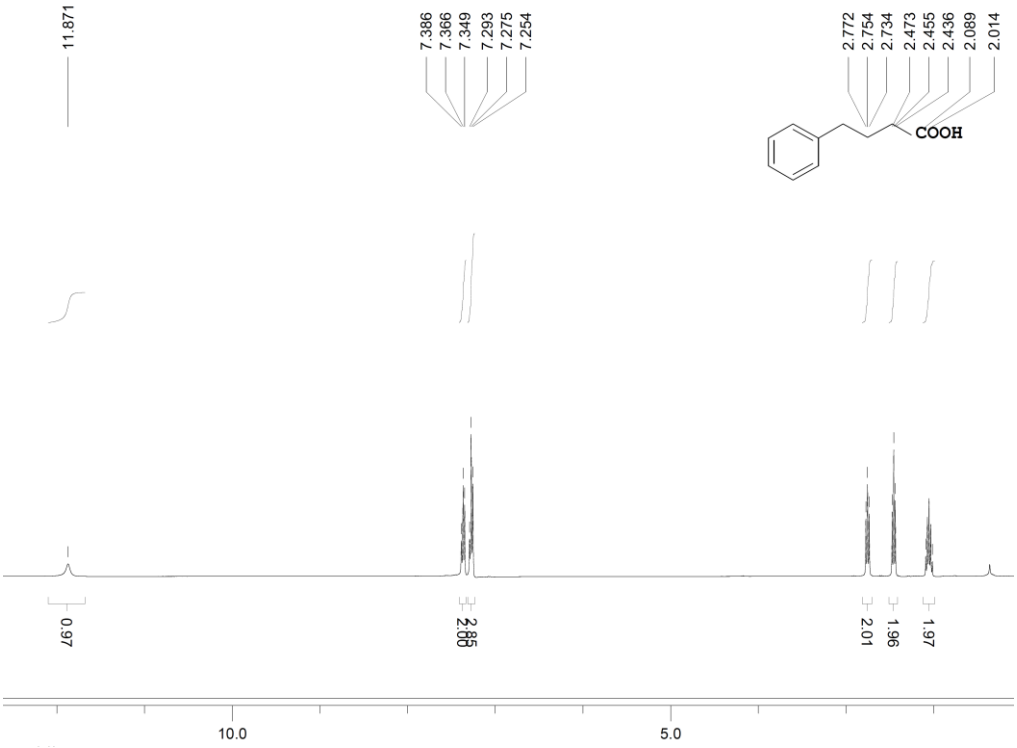


Figure S38. ^{1}H NMR spectrum of 4-phenylbutyric acid in $CDCl_3$

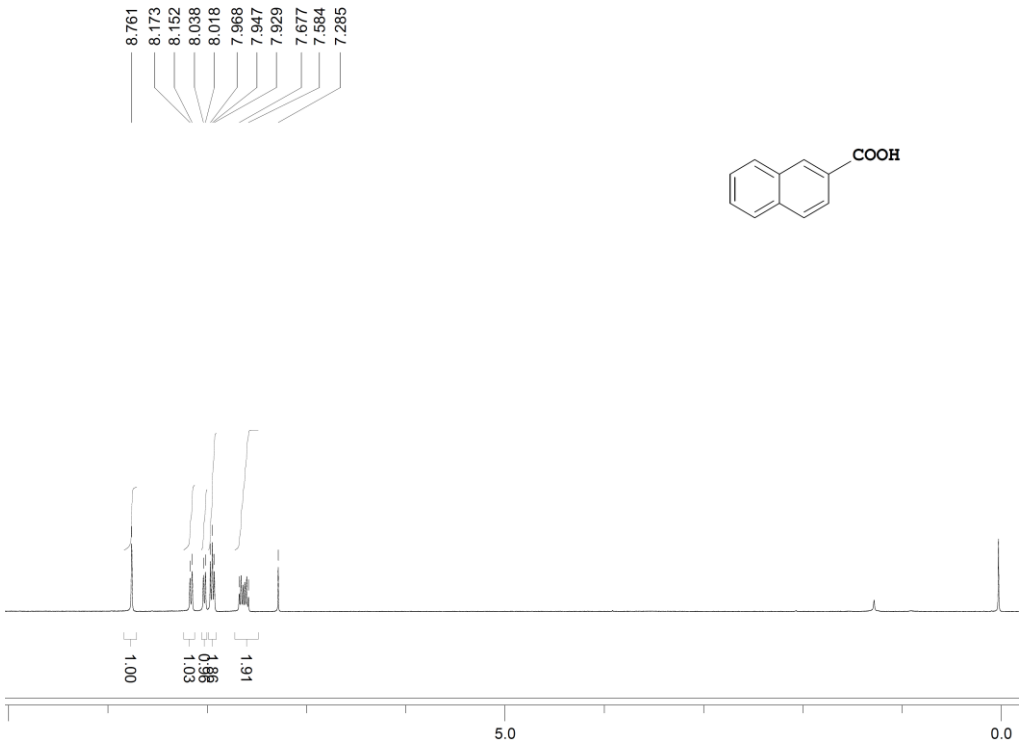


Figure S39. ^{1}H NMR spectrum of naphthalene-2-carboxylic acid in $CDCl_3$

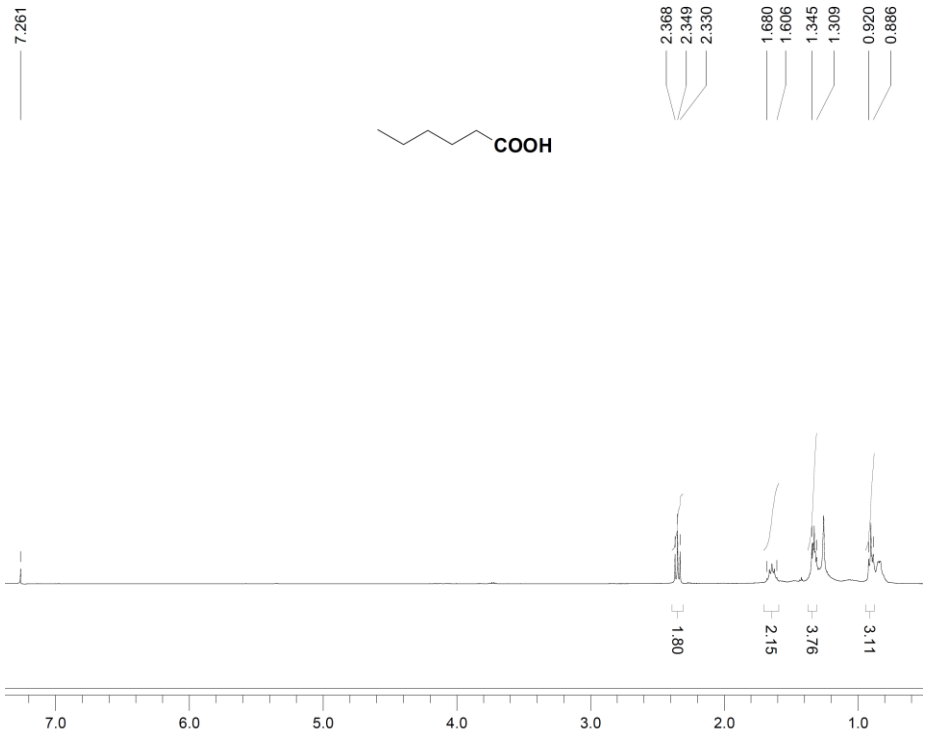


Figure S40. ^{1}H NMR spectrum of n-hexanoic acid in $CDCl_3$

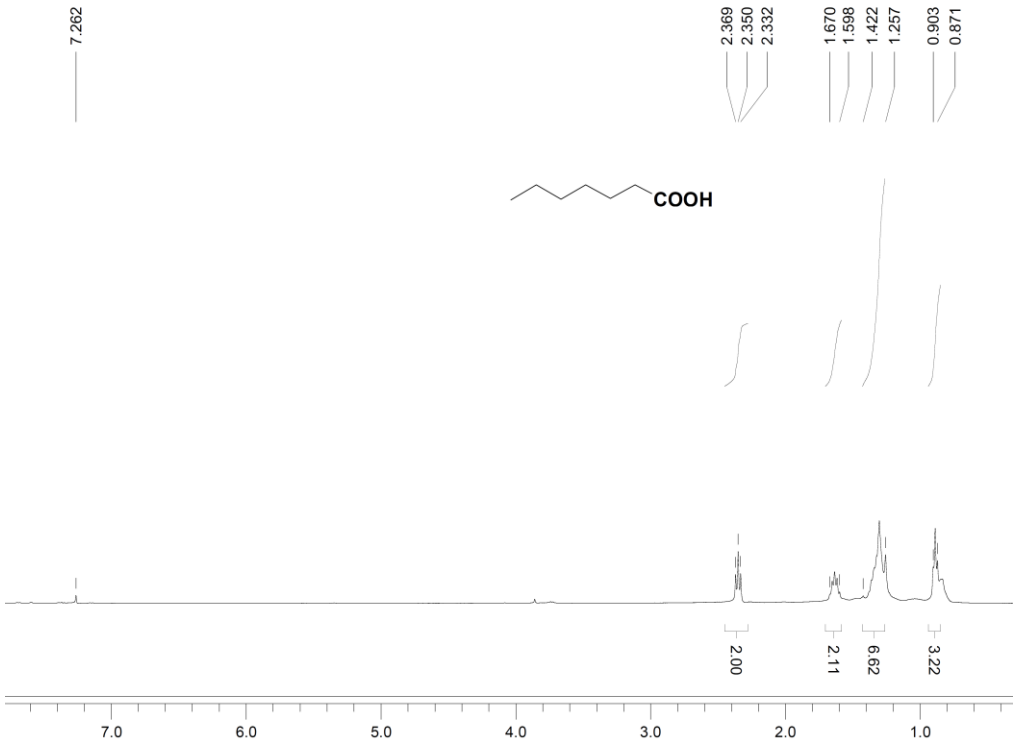


Figure S41. ^{1}H NMR spectrum of n-hepanoic acid in $CDCl_3$