Supporting Information

Molybdenum Catalyzed Hydrogenation of Carbon dioxide, Bicarbonate, and Inorganic Carbonates to Formate

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1. ^{1}H NMR spectra of catalytic runs for CO_2 hydrogenation:

Figure S1. Conditions: **C-1**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 1).

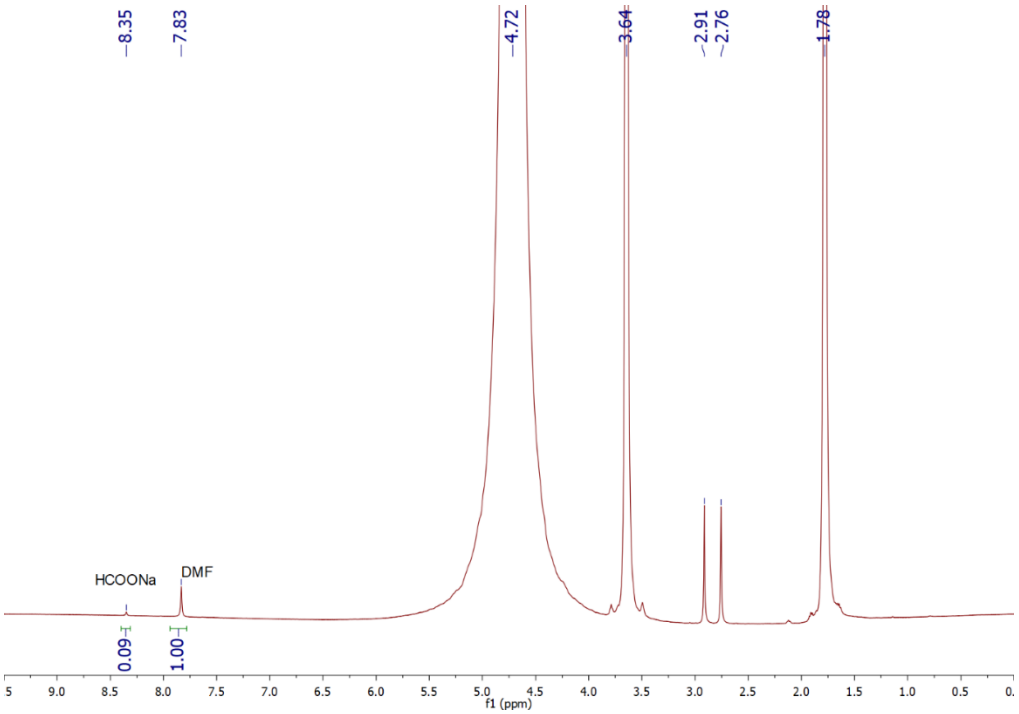


Figure S2. Conditions: **C-2**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 2).

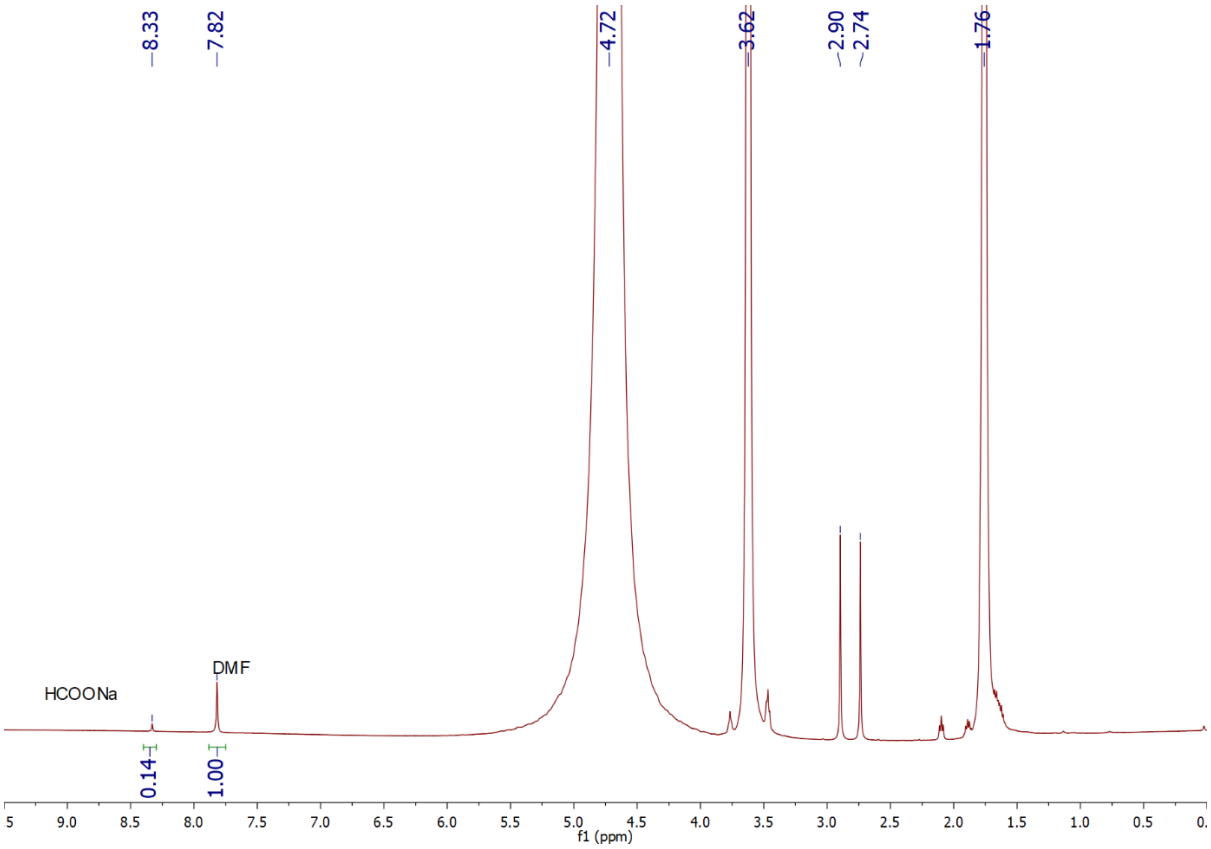


Figure S3. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 3).

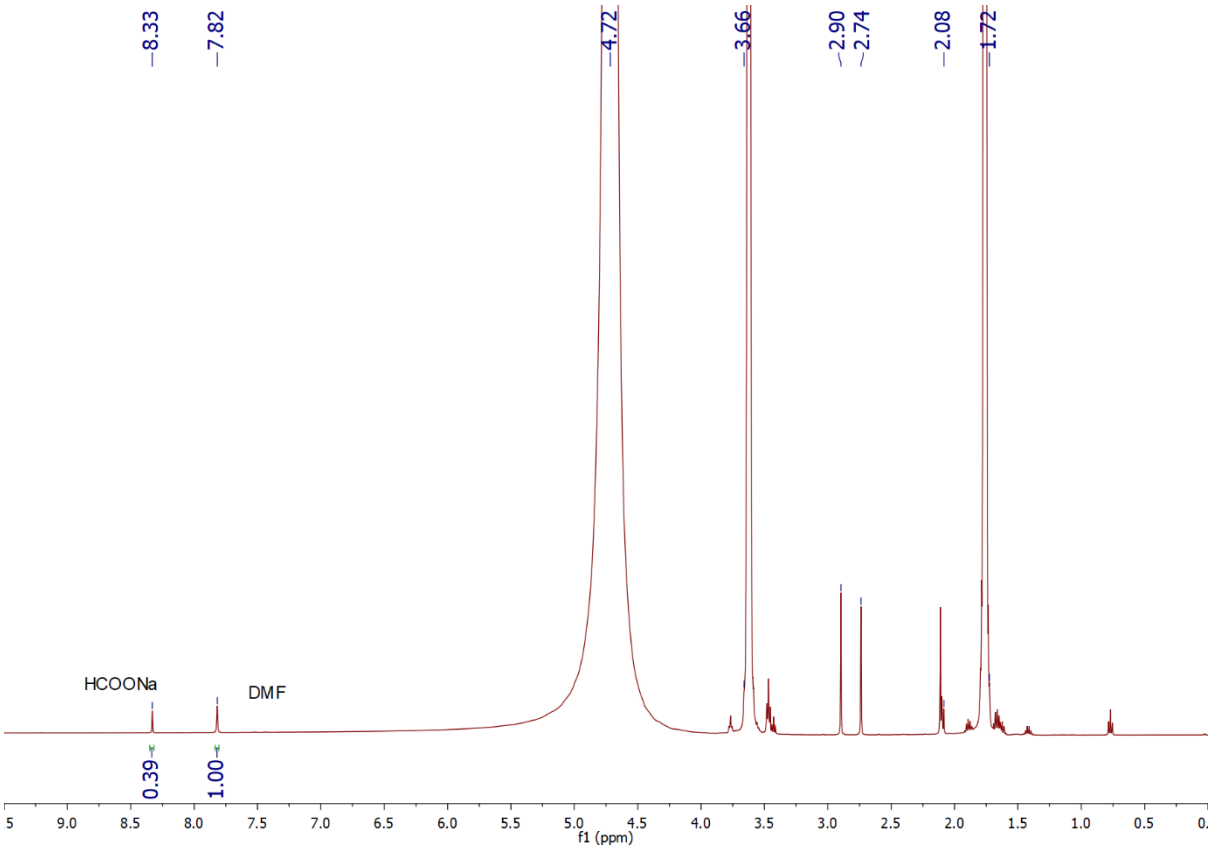


Figure S4. Conditions: **C-4**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 4).

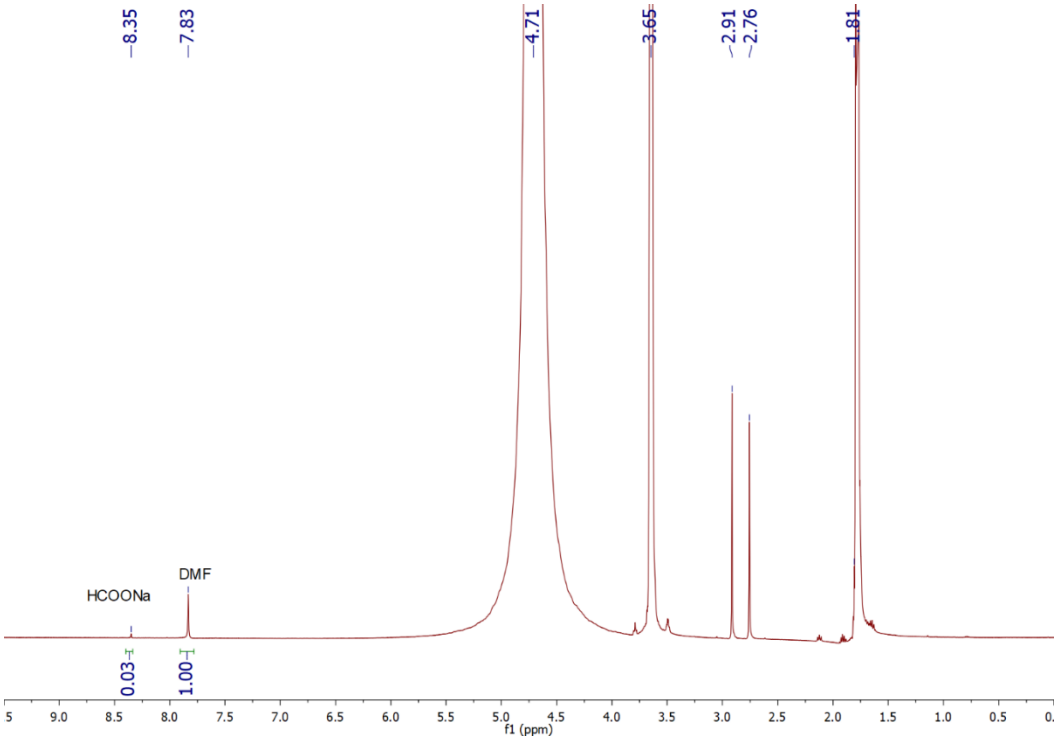


Figure S5. Conditions: **C-5**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 5).

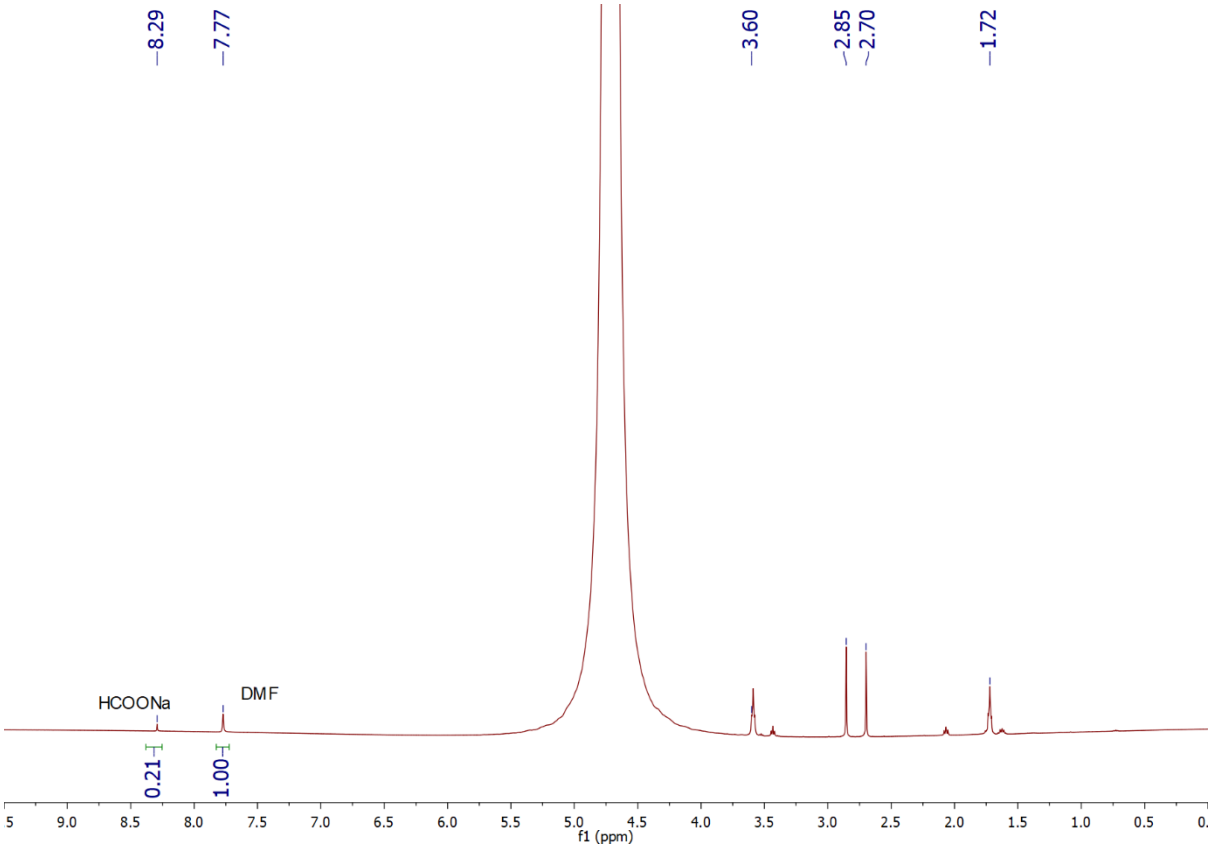


Figure S6. Conditions: **C-6**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 6).

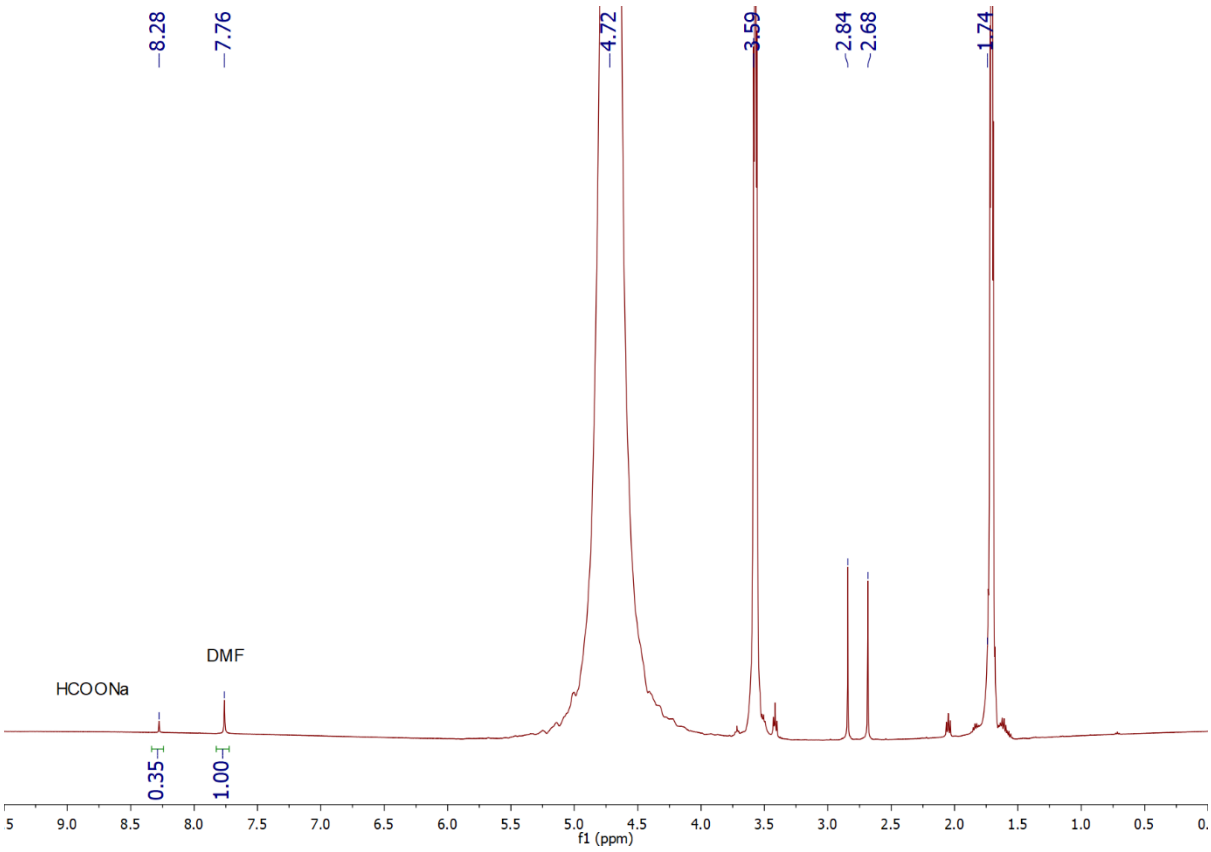


Figure S7. Conditions: NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 7).

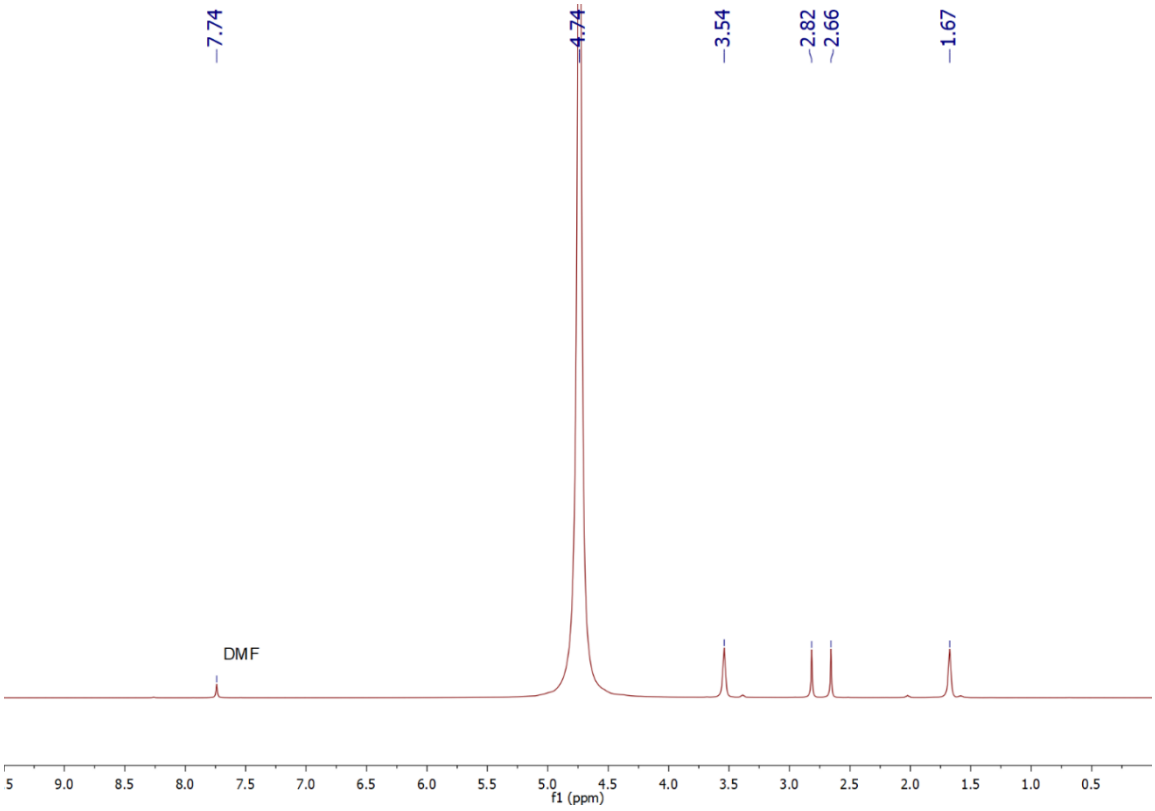


Figure S8. Conditions: **C-7**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 8).

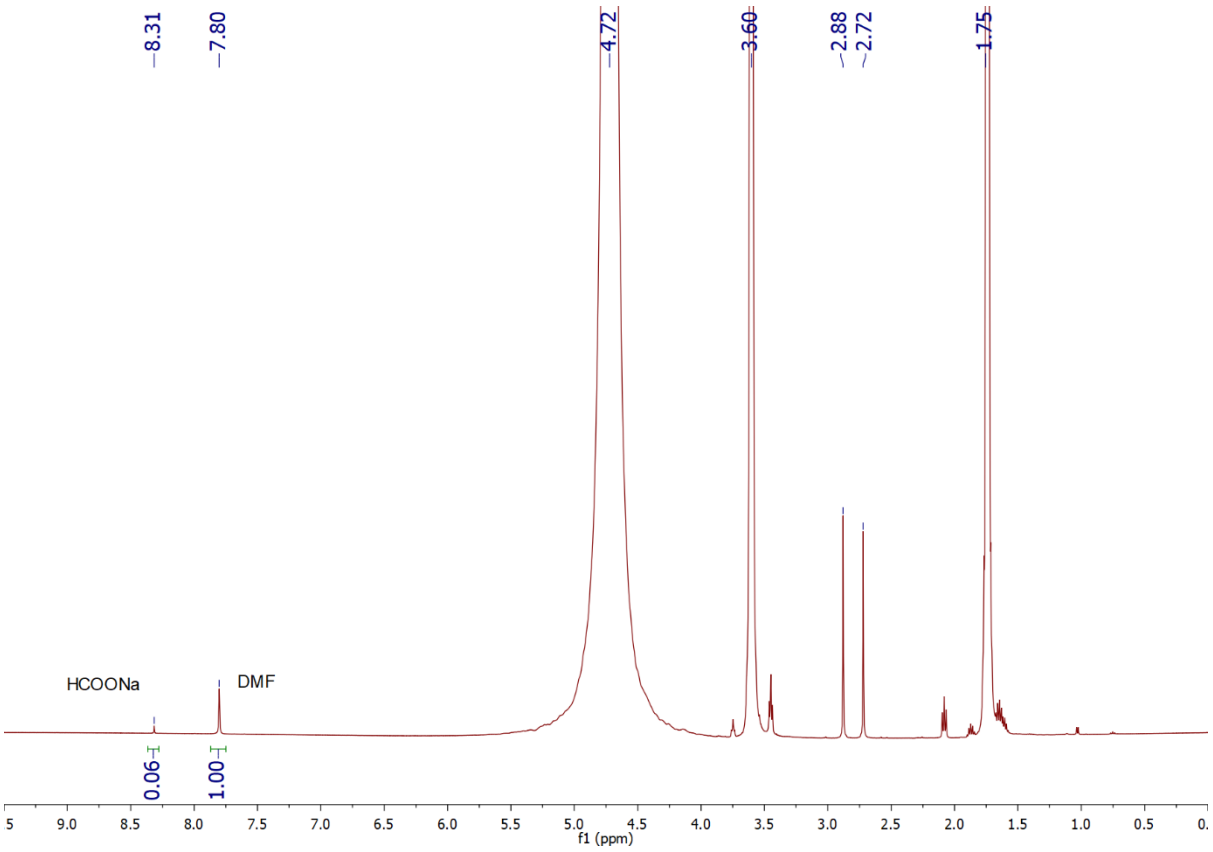


Figure S9. Conditions: **C-8**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 9).

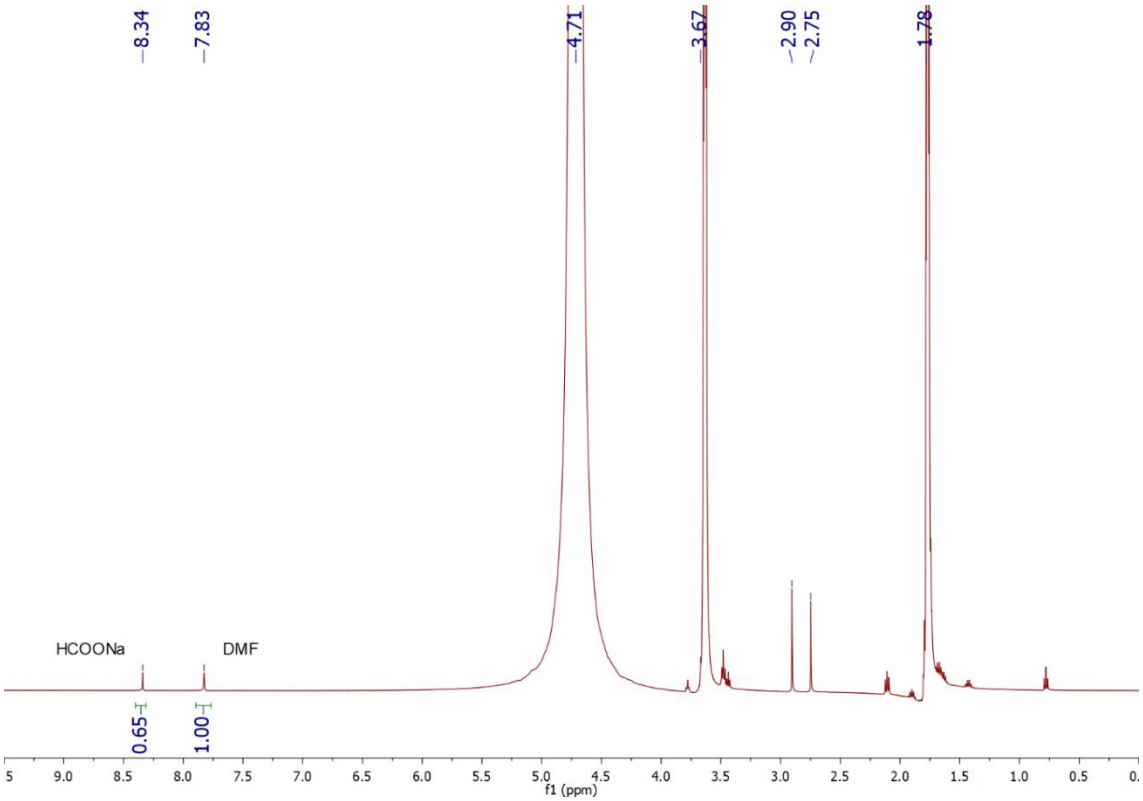


Figure S10. Conditions: **C-3**, DBU, NaOH (0.1 mmol), pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 10).

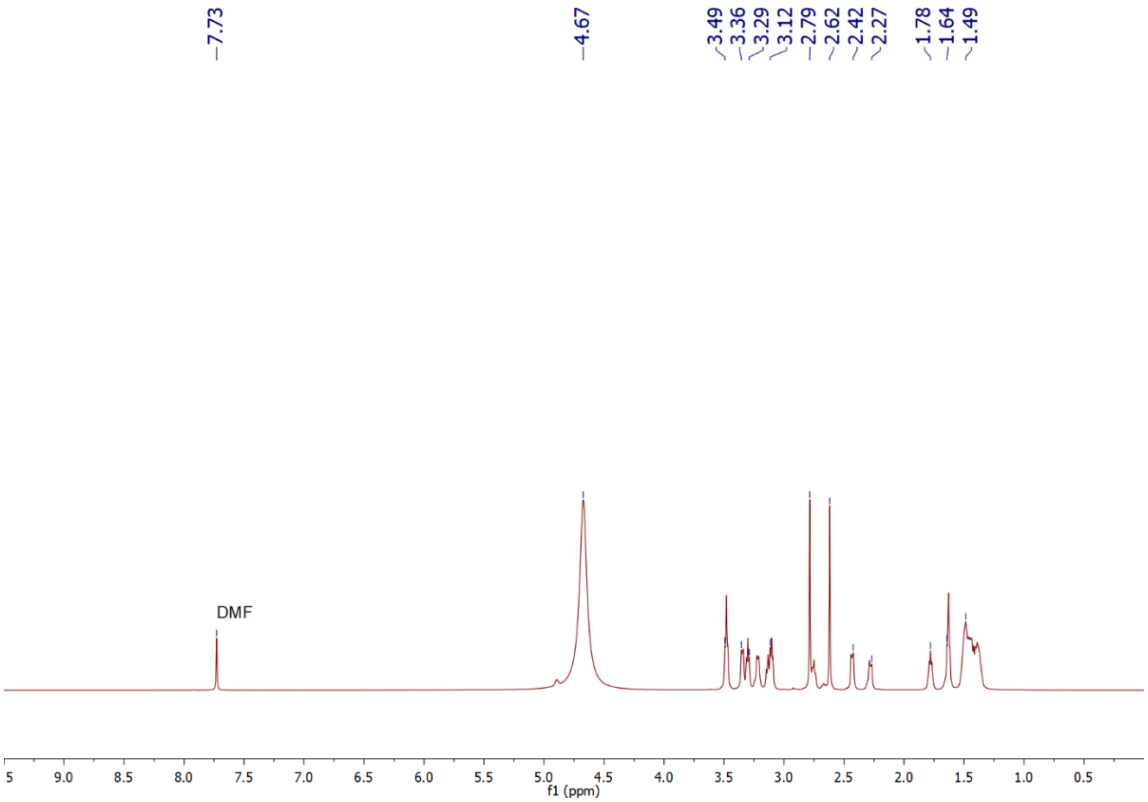


Figure S11. Conditions: **C-3**, Et_3N, NaOH (0.1 mmol), pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 11).

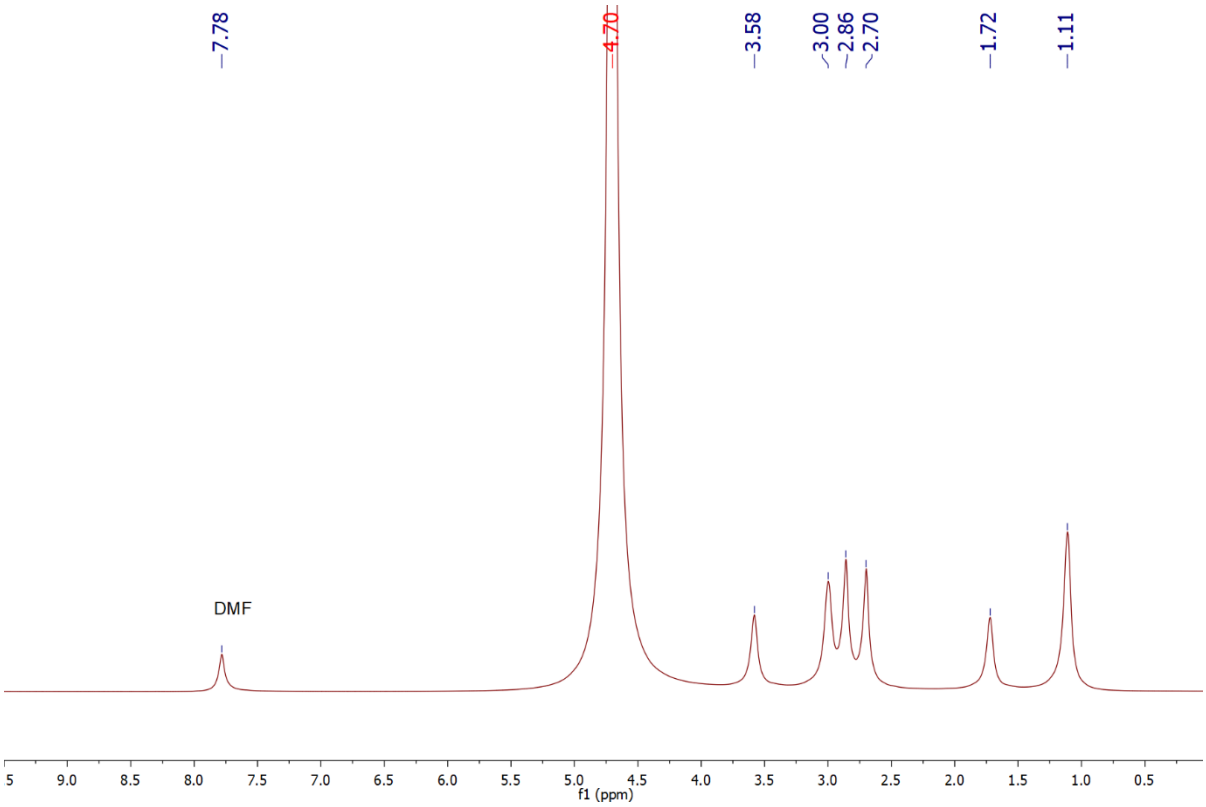


Figure S12. Conditions: **C-3**, K_3PO_4, NaOH (0.1 mmol), pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 12).

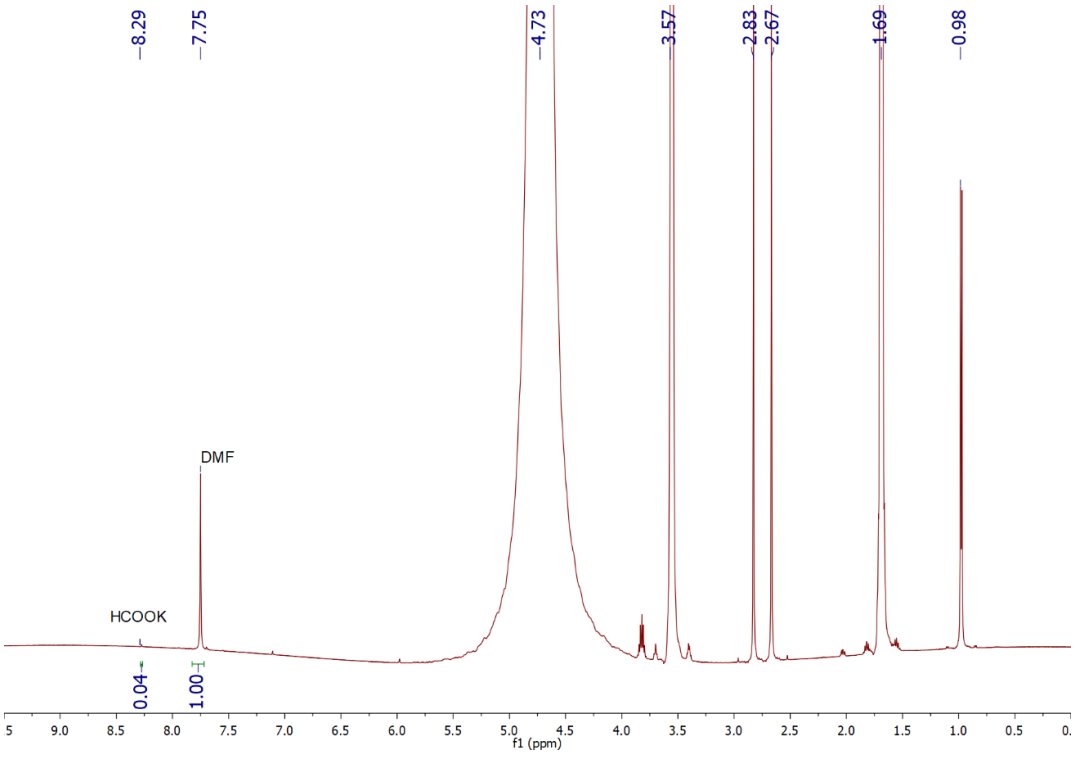


Figure S13. Conditions: **C-3**, KOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 13).

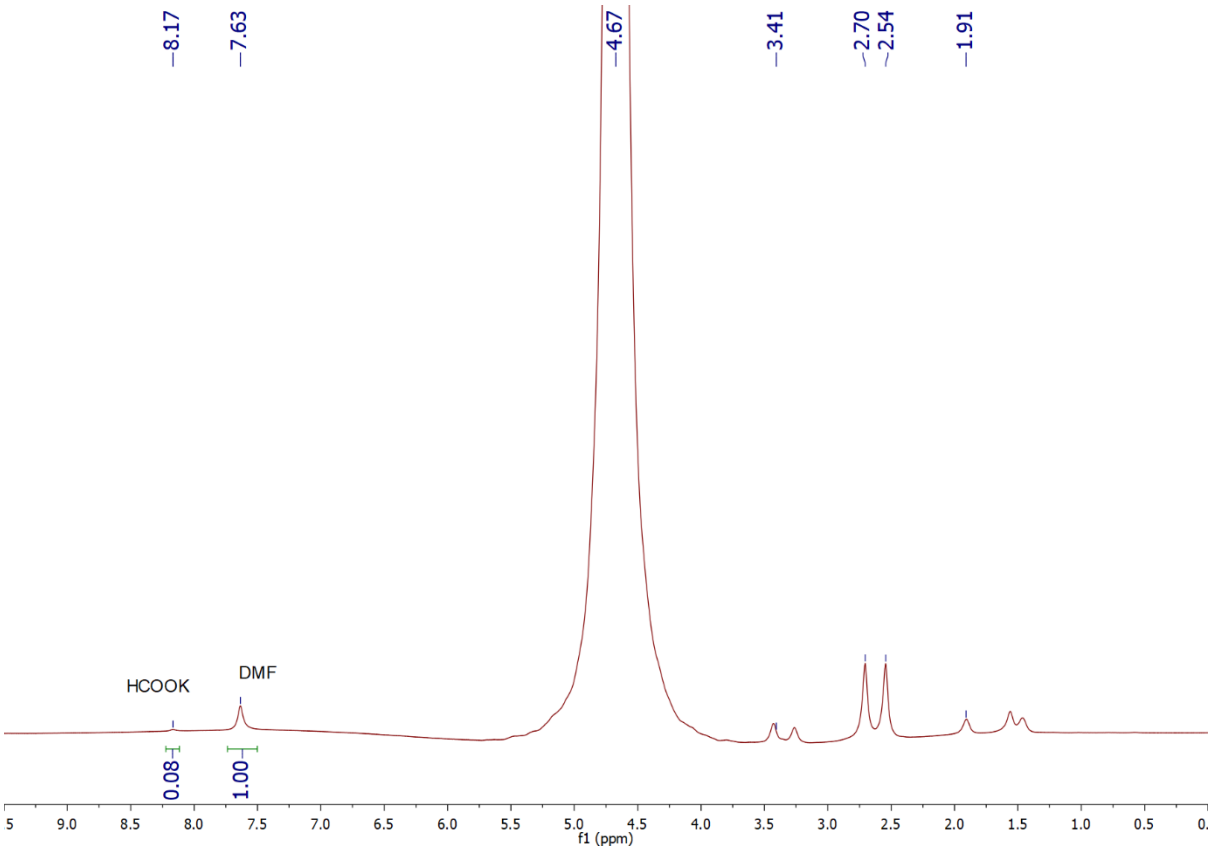


Figure S14. Conditions: **C-3**, LiOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 14).

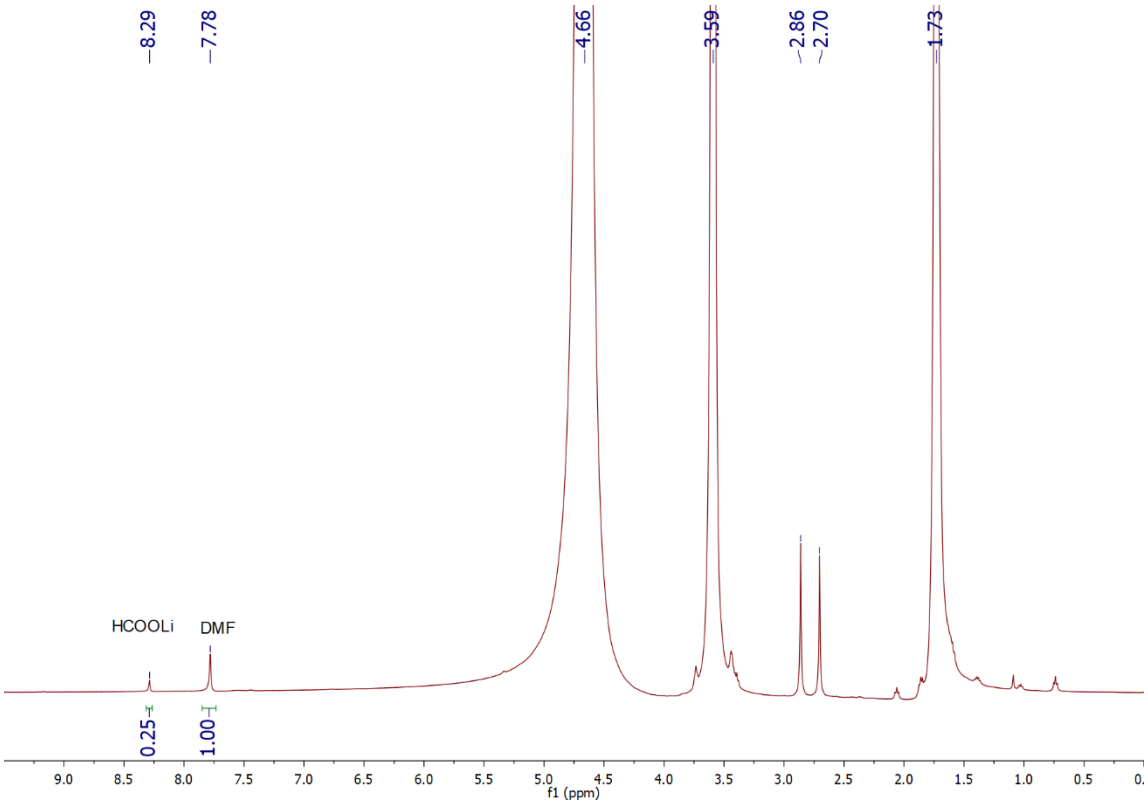


Figure S15. Conditions: **C-3**, $Ca(OH)_2$, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 15).

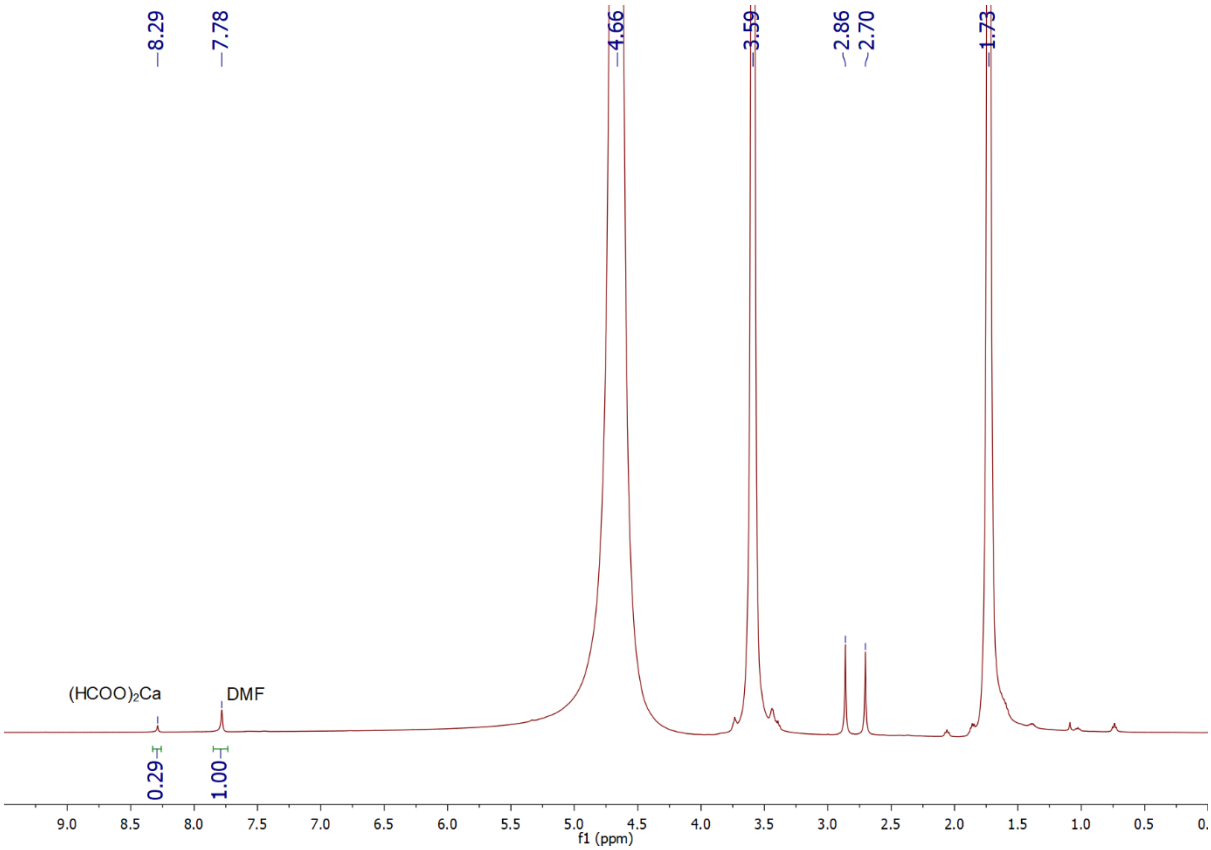


Figure S16. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 12 h (Table 1, entry 16).

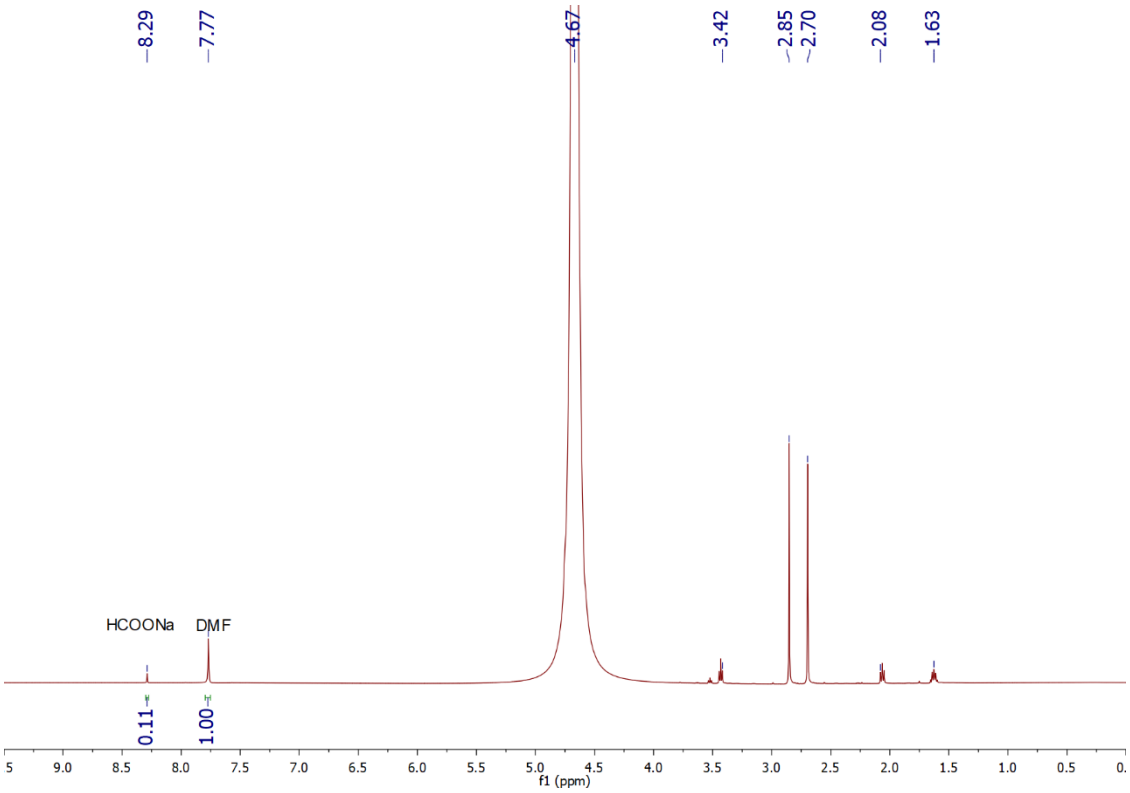


Figure S17. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 48 h (Table 1, entry 17).

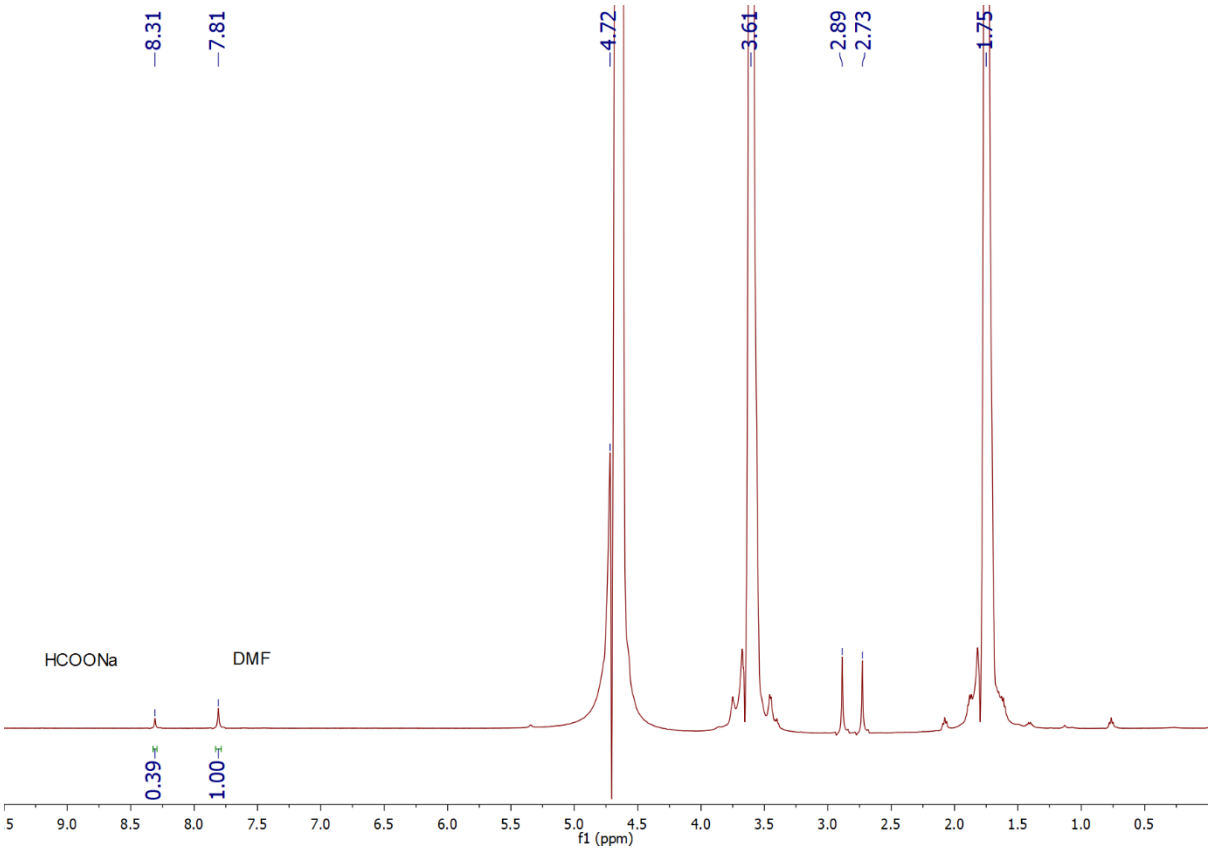


Figure S18. Conditions: **C-3**, NaOH, 0.1 mmol TMNO, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 18).

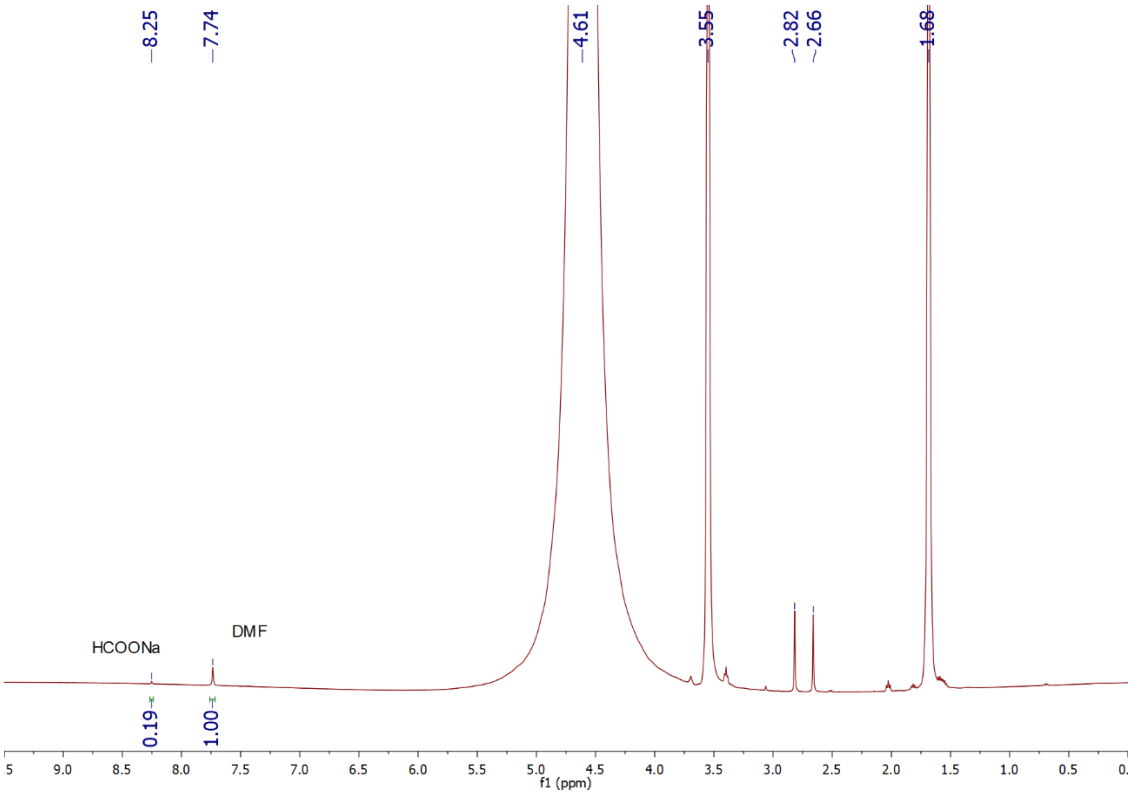


Figure S19. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h (Table 1, entry 19).

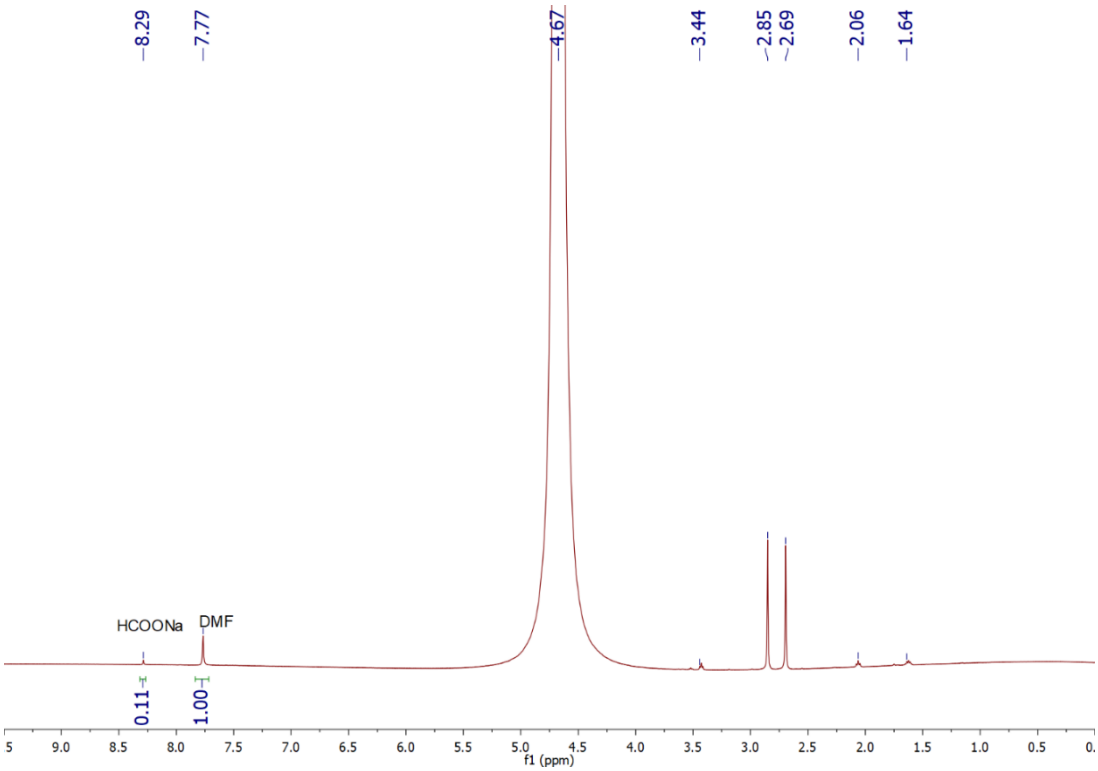


Figure S20. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h only water (Table 1, entry 20).

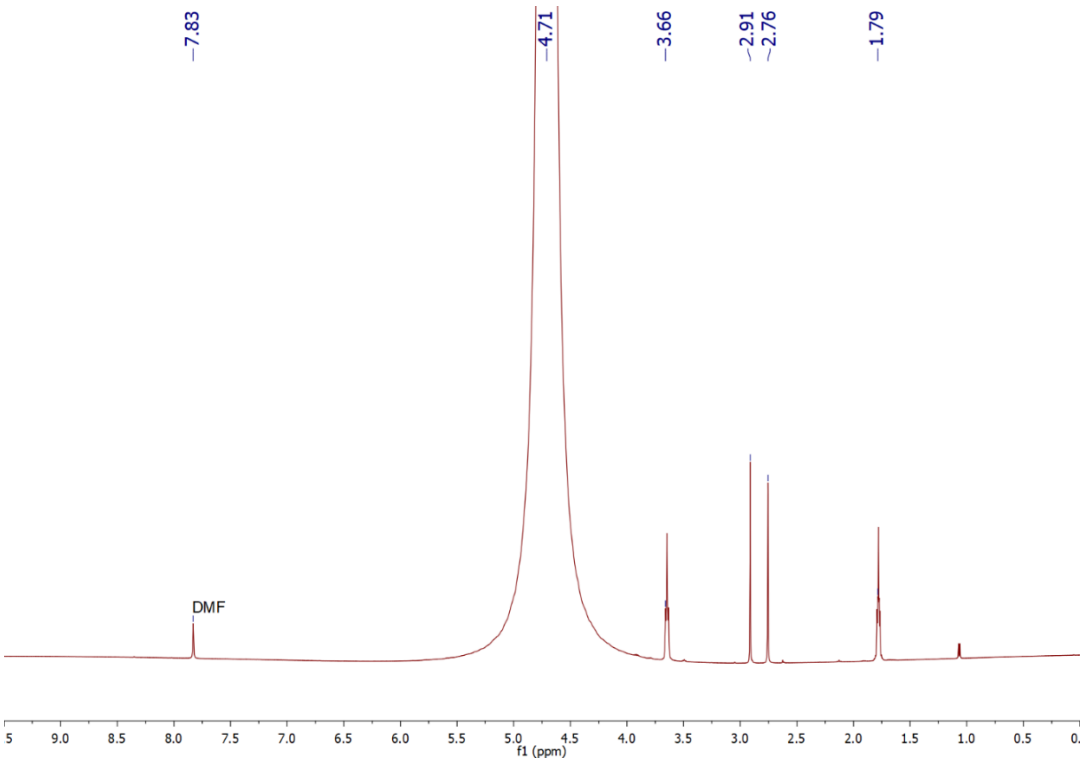


Figure S21. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h only THF (Table 1, entry 21).

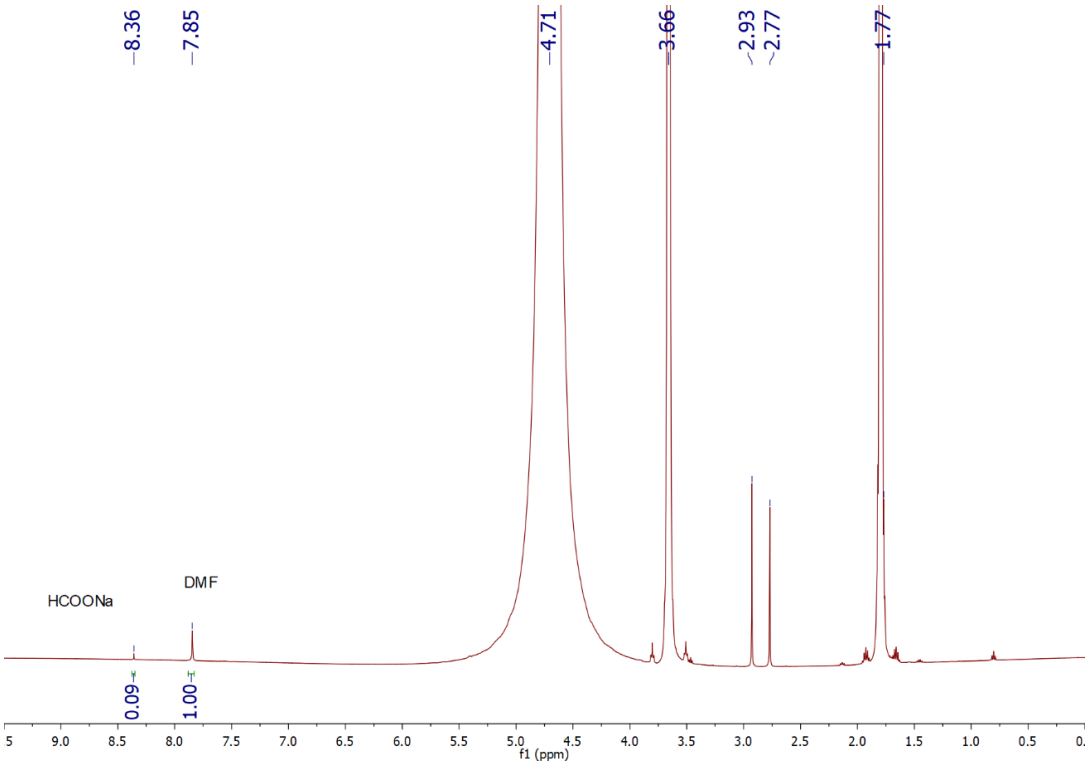


Figure S22. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 10/10, 130 °C, 24 h, (Table 1, entry 22).

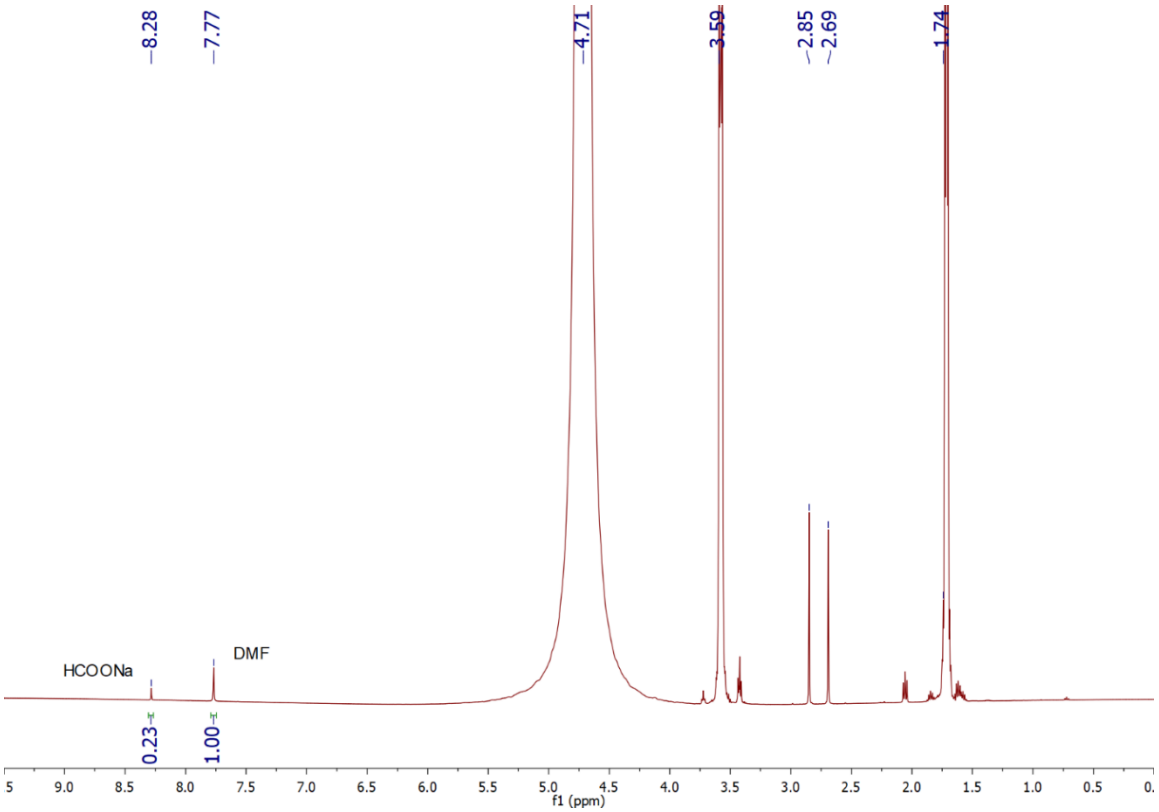
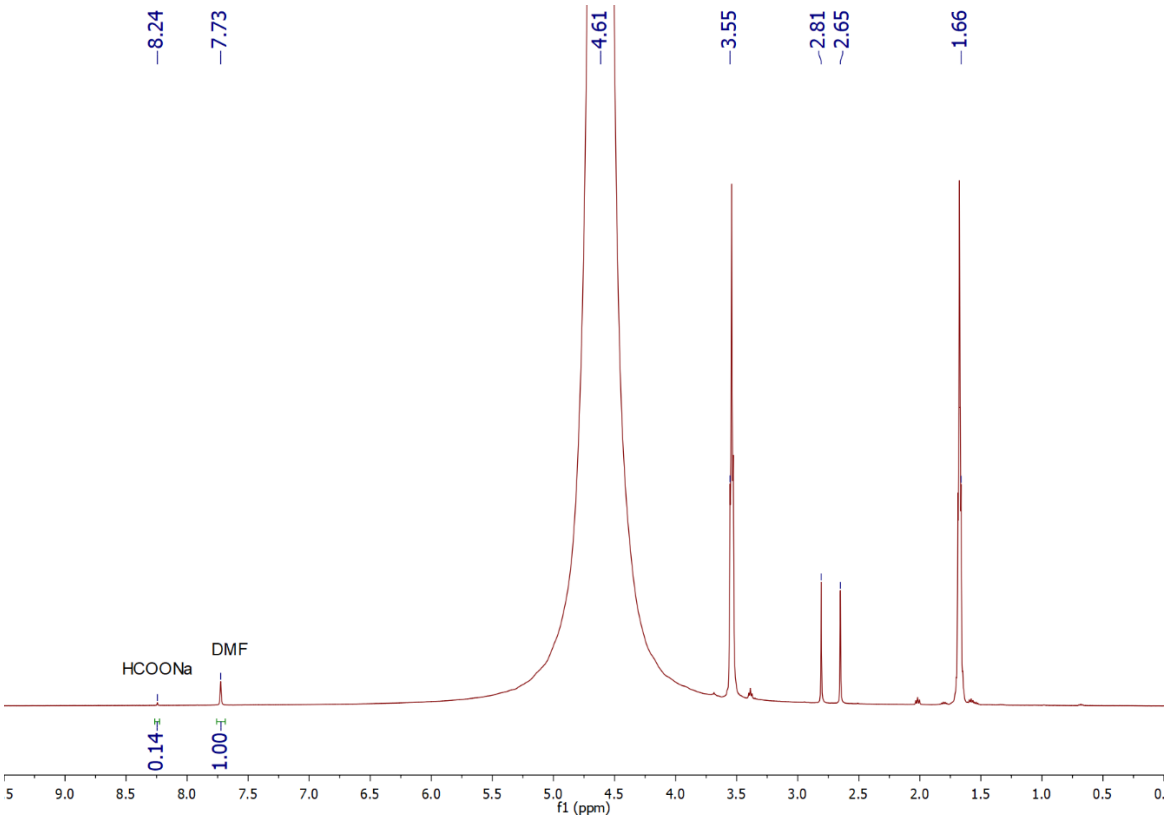


Figure S23. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 5/15, 130 °C, 24 h, (Table 1, entry 23).



2. ^{1}H NMR spectra of catalytic runs for sodium bicarbonate hydrogenation:

Figure S24. Conditions: **C-3**, $NaHCO_3$ (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 2, entry 1).

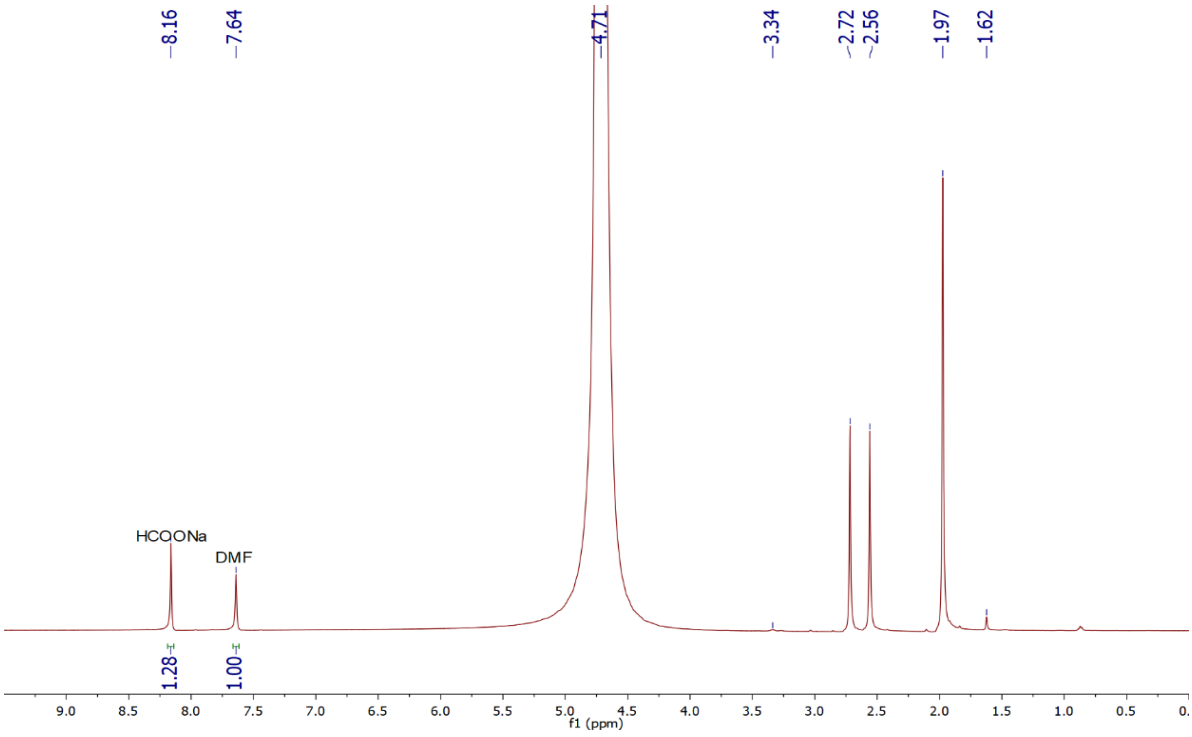


Figure S25. Conditions: **C-3**, $NaHCO_3$ (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 20, 80 °C, 24 h (Table 2, entry 2).

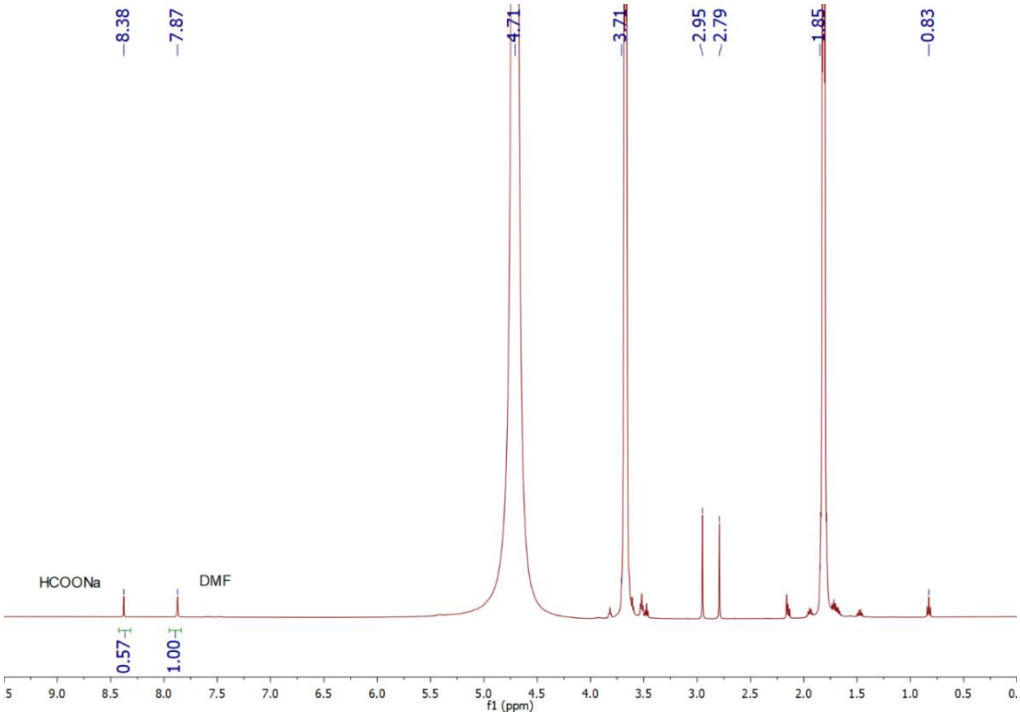


Figure S26. Conditions: **C-3**, $NaHCO_3$ (0.5 mmol), ^{t}BuOK (0.05 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 2, entry 3).

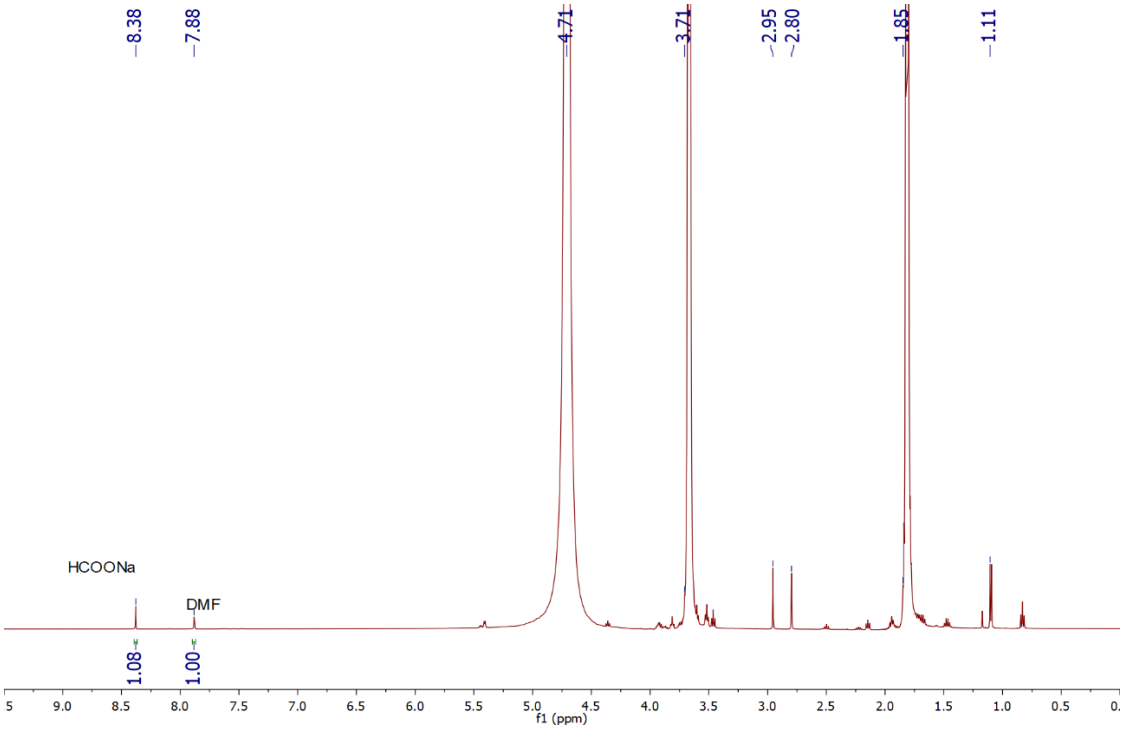


Figure S27. Conditions: **C-3**, $NaHCO_3$ (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 40, 130 °C, 24 h (Table 2, entry 4).

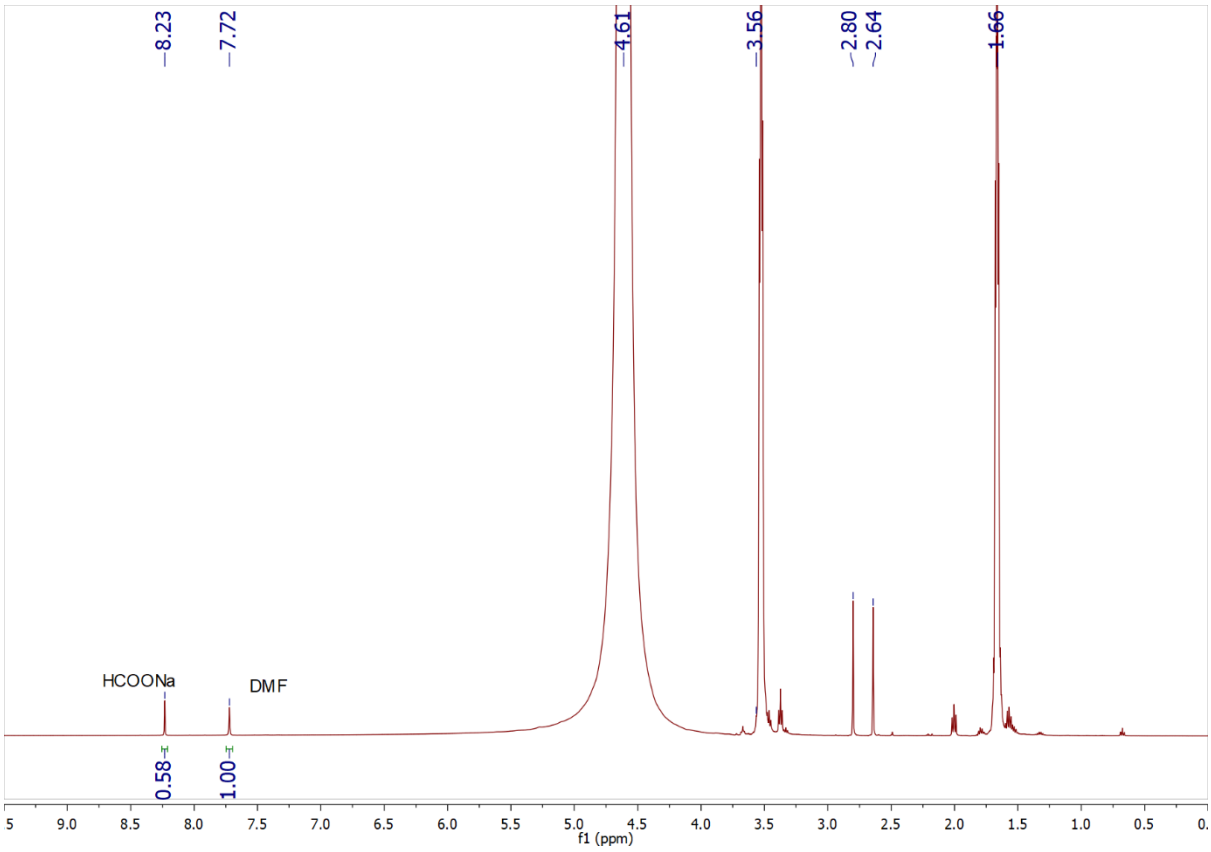


Figure S28. Conditions: $NaHCO_3$ (0.5 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 2, entry 5).

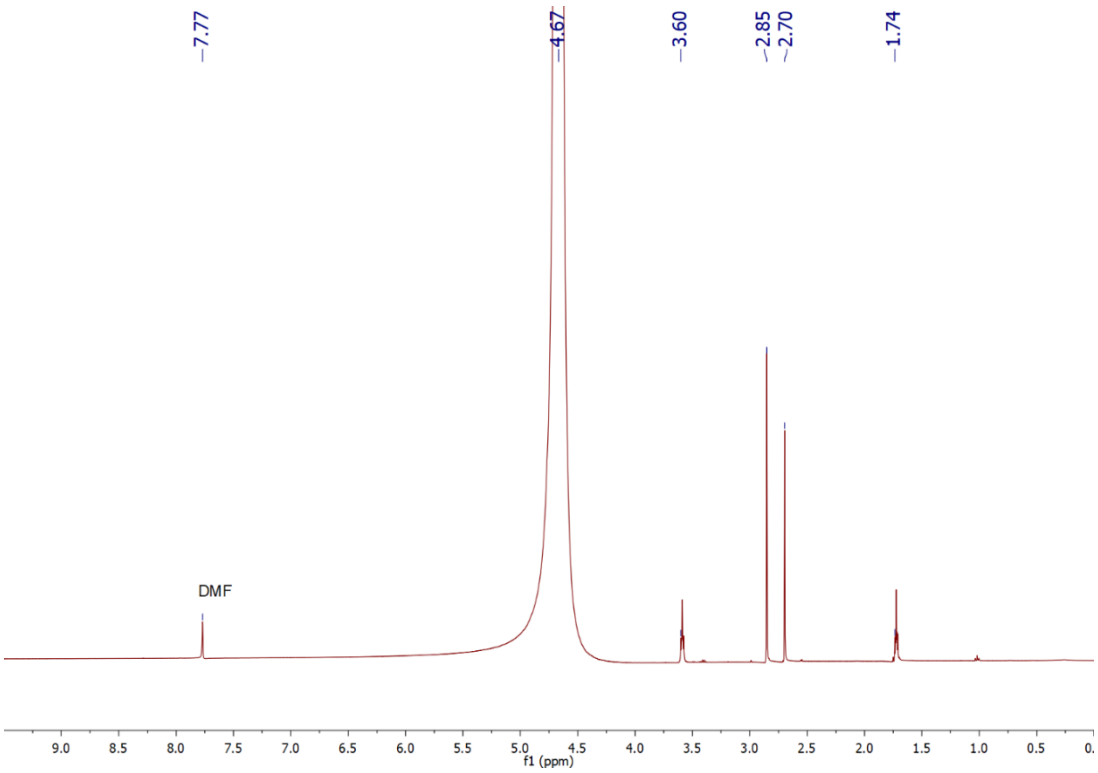
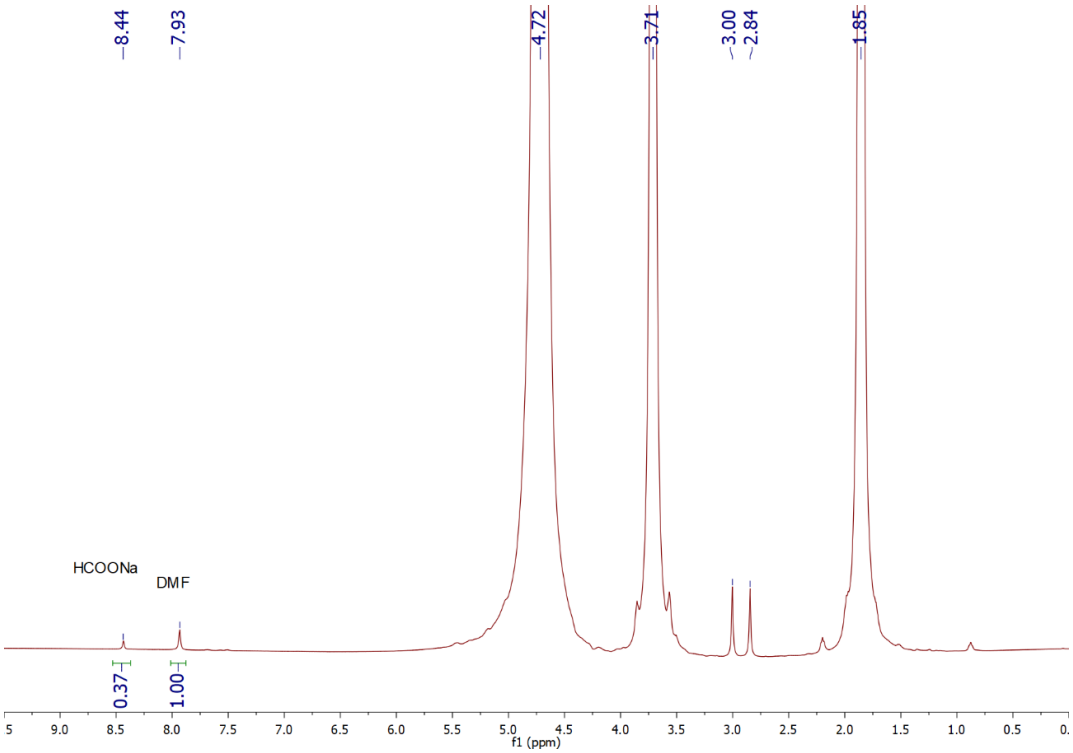


Figure S29. Conditions: **C-3**, $NaHCO_3$ (0.5 mmol), pH_2 (bar) = 20, 80 °C, 24 h (Table 2, entry 6).



3. ^{1}H NMR spectra of catalytic runs for inorganic carbonate hydrogenation:

Figure S30. Conditions: **C-3**, Li_2CO_3 (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 3, entry 1).

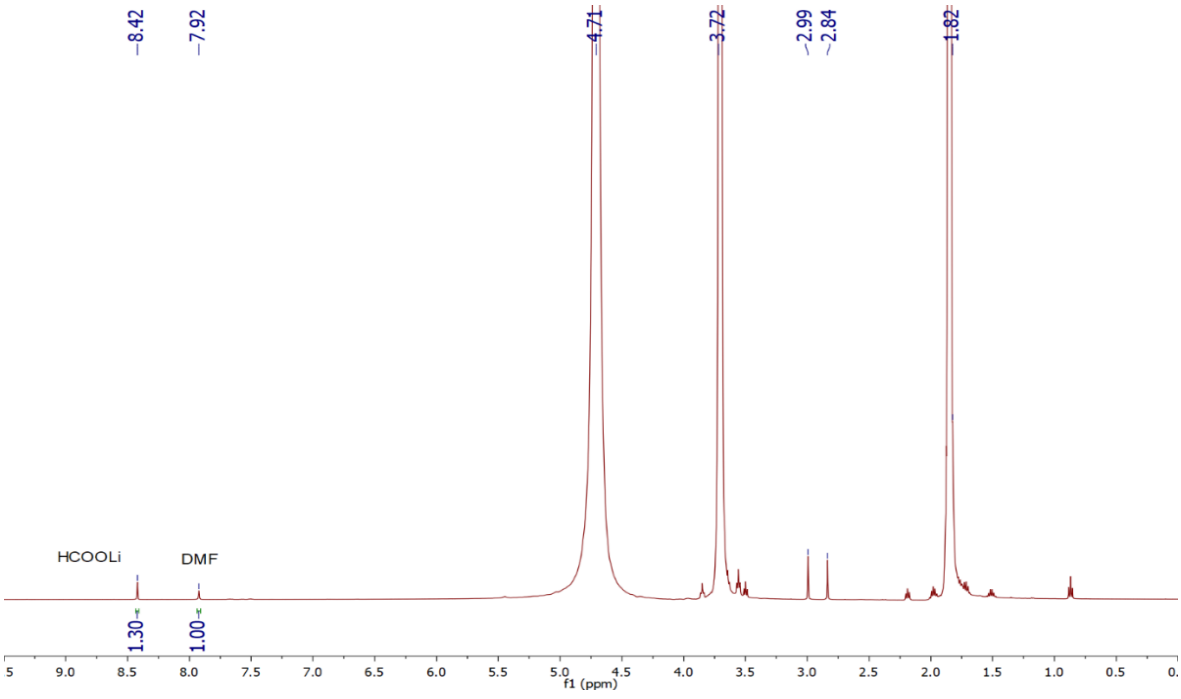


Figure S31. Conditions: **C-3**, Na_2CO_3 (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 3, entry 2).

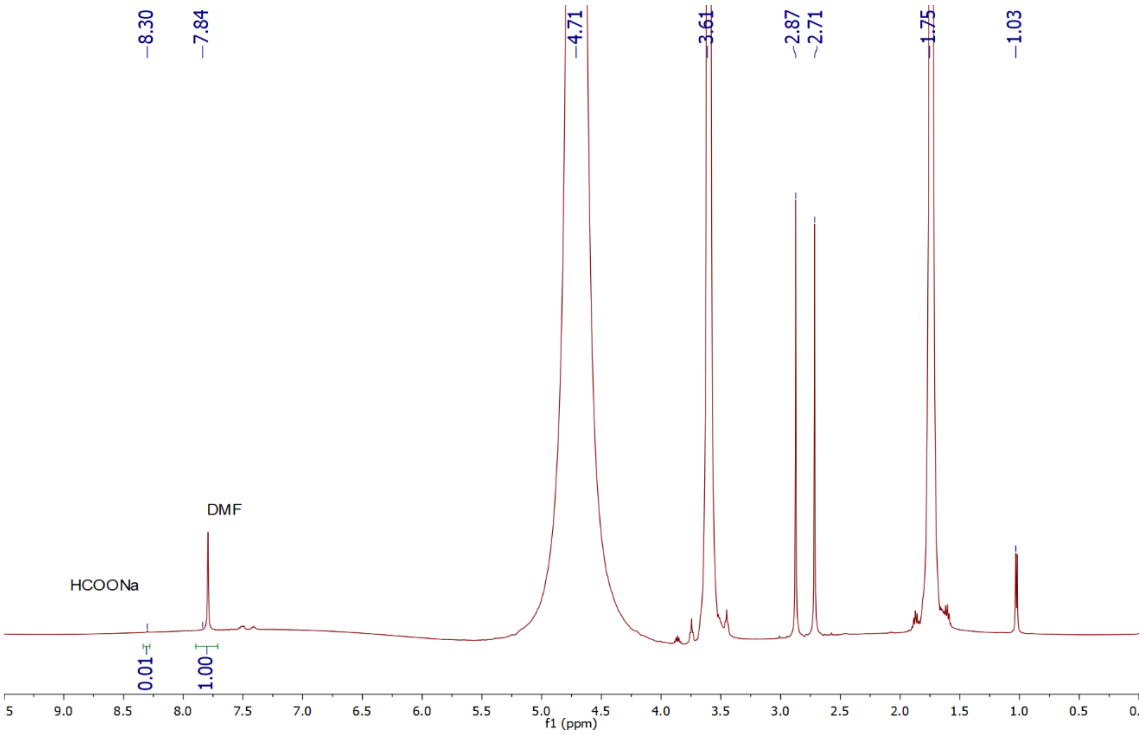


Figure S32. Conditions: **C-3**, K_2CO_3 (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 3, entry 3).

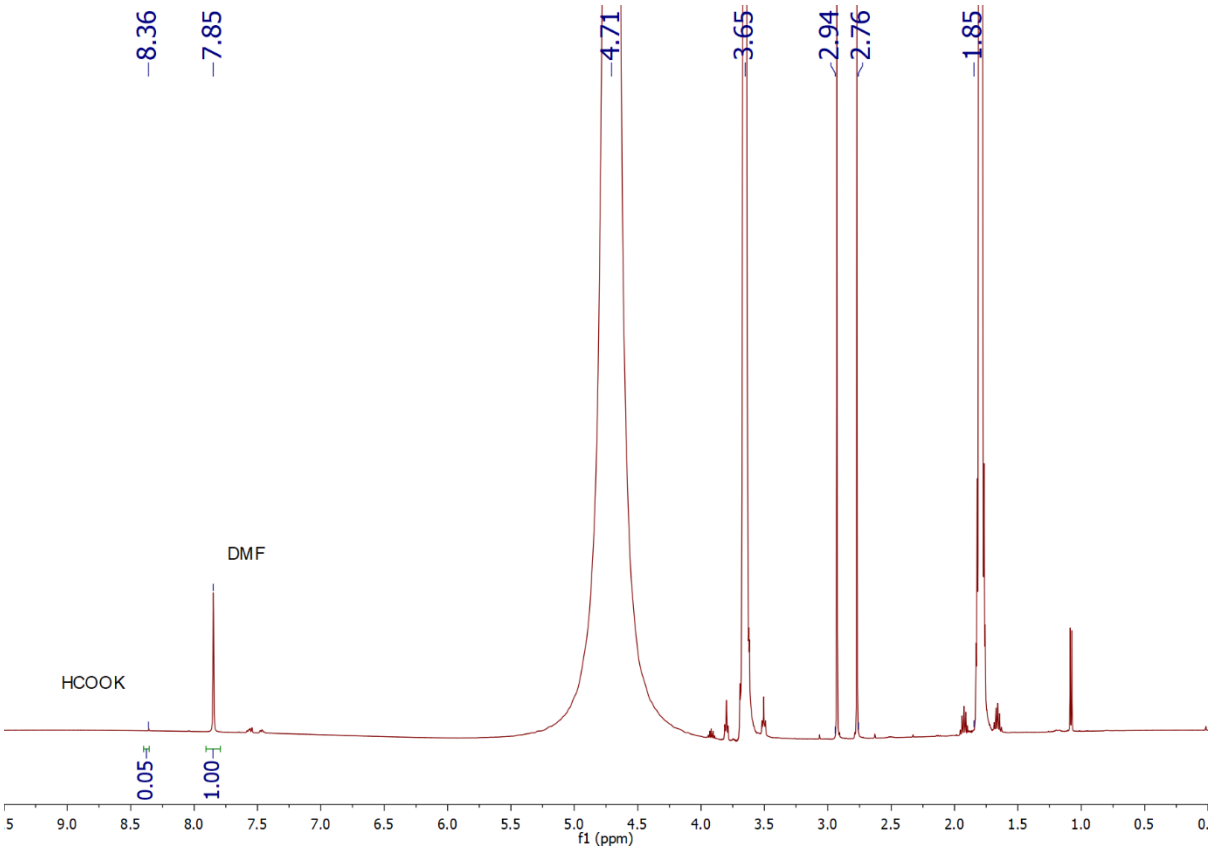


Figure S33. Conditions: **C-3**, Cs_2CO_3 (0.5 mmol), NaOH (0.05 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 3, entry 4).

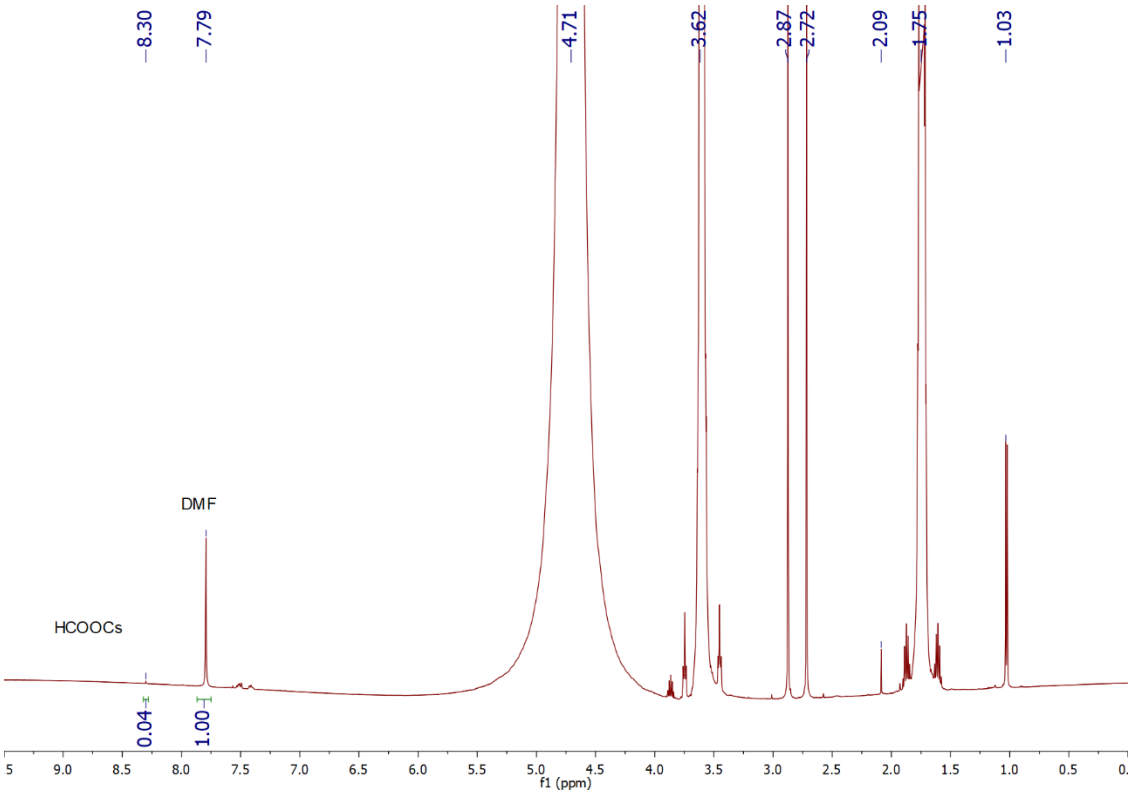
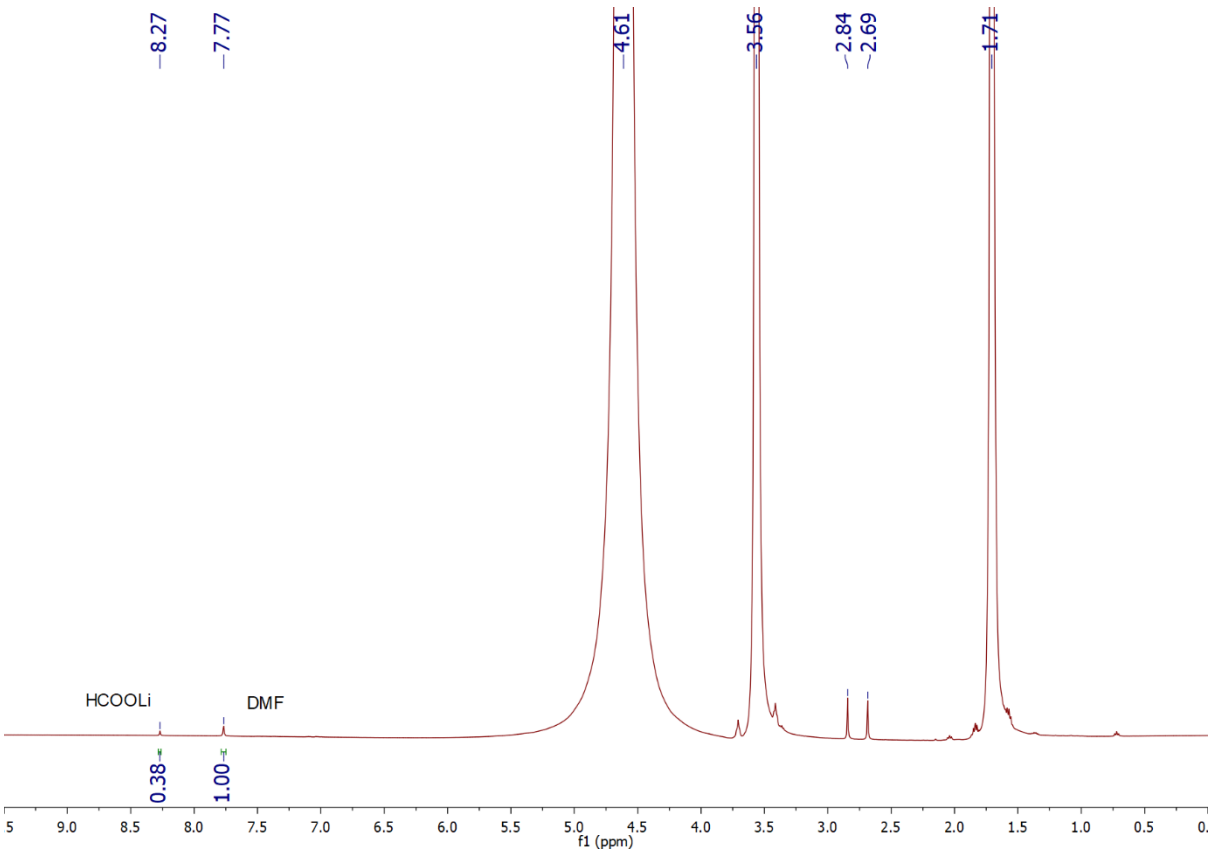
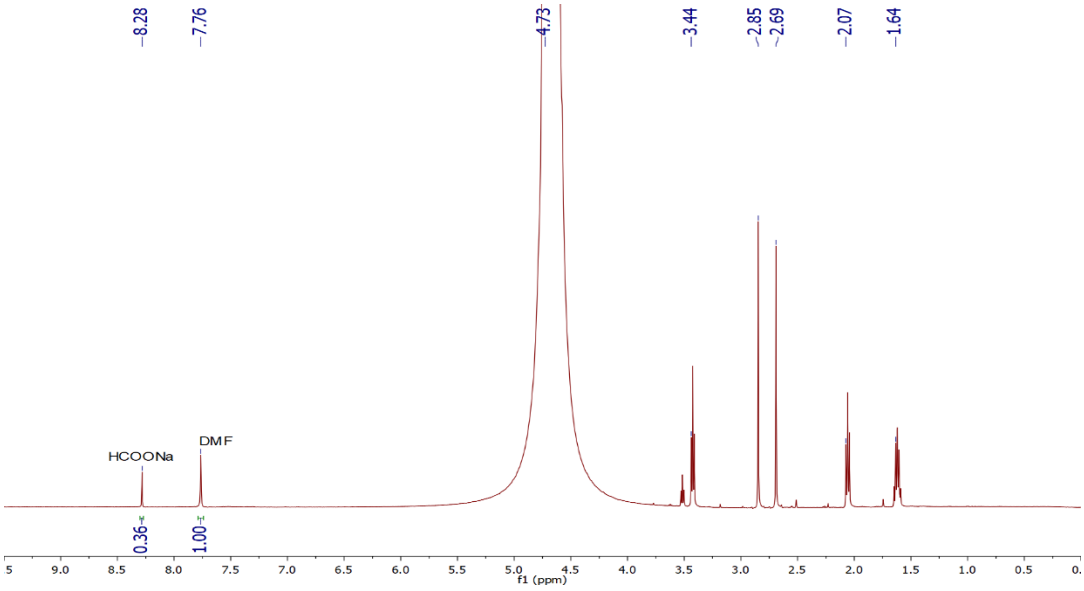


Figure S34. Conditions: **C-3**, Li_2CO_3 (0.5 mmol), pH_2 (bar) = 40, 80 °C, 24 h (Table 3, entry 5).



4. Homogeneity Test: A drop of mercury was added to the reaction mixture and benchmark reaction was performed under optimized conditions of CO_2 hydrogenation. The TON remained almost unaffected (TON= 900), which confirmed the homogeneous nature of reaction.

Figure S35. Conditions: **C-3**, NaOH, pH_2/pCO_2 (bar) = 30/10, 130 °C, 24 h, mercury one drop.



5. Mechanistic experiments:

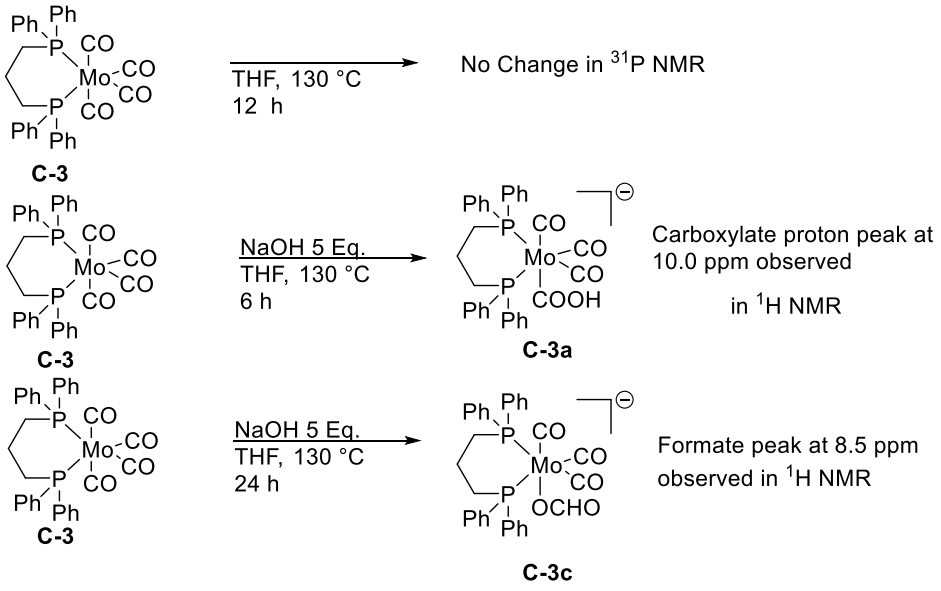


Figure S36. Scheme for mechanistic experiments.

Figure S37. $^{31}P\{^{1}H\}$ NMR of **C-3**.

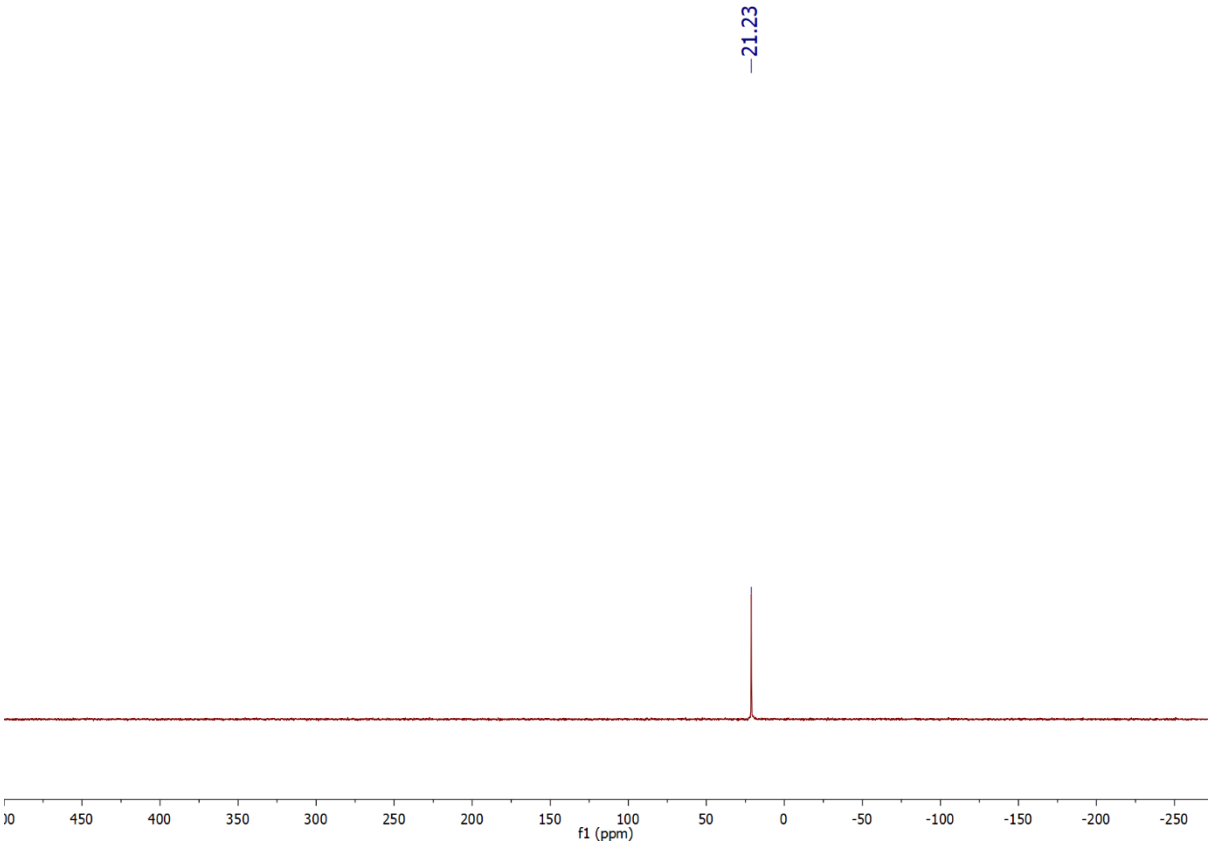


Figure S38. ^{1}H NMR for **C-3a** after 6-hour reaction time.

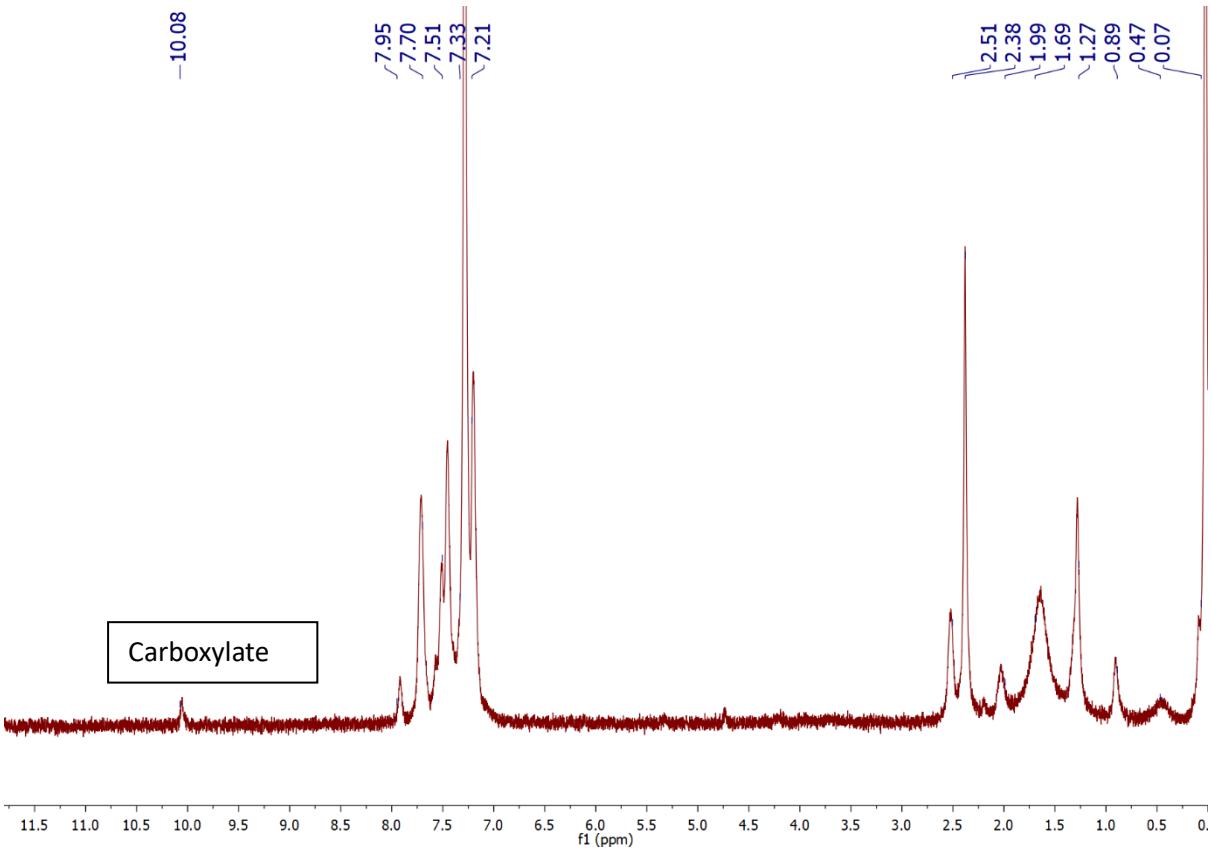


Figure S39. $^{31}P\{^{1}H\}$ NMR taken (in $CDCl_3$) after 6-hour reaction time.

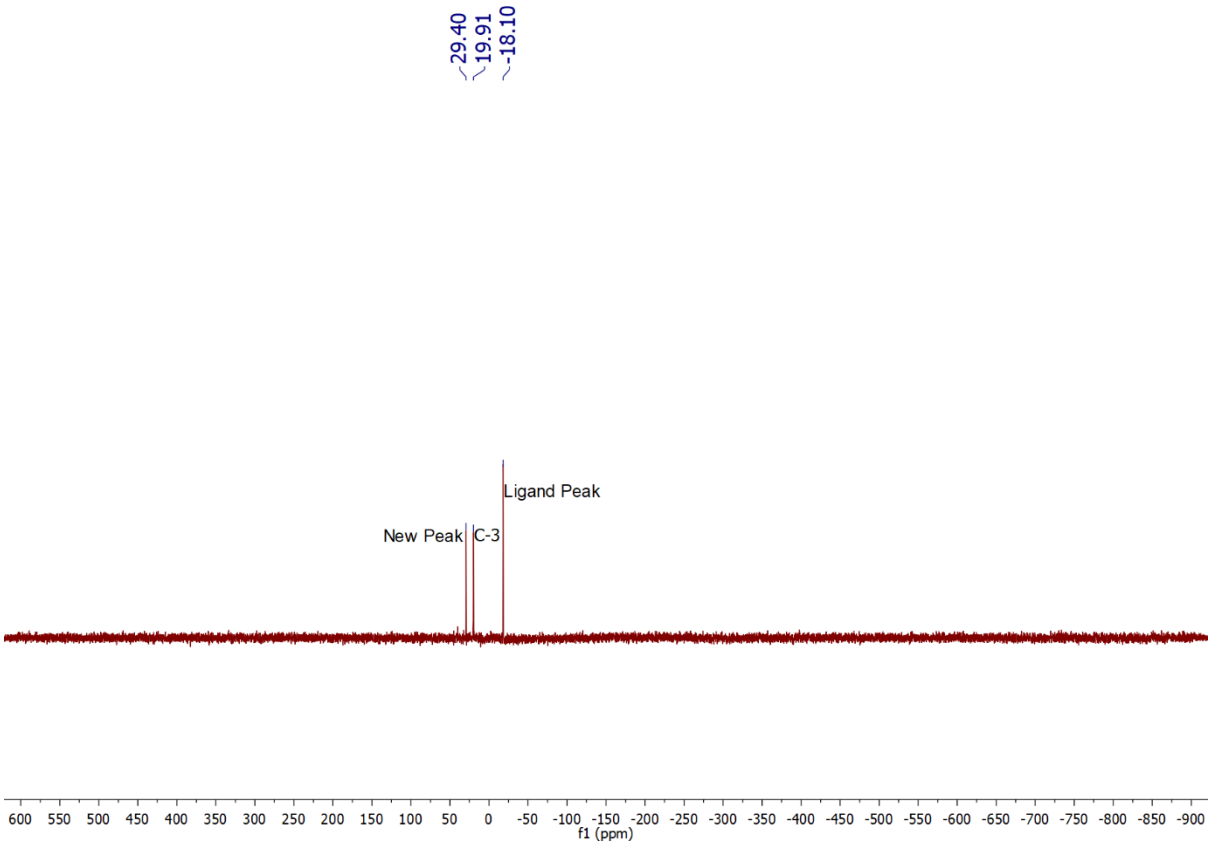


Figure S40. ^{1}H NMR (taken in DMSO d-6) after 24 h reaction time.

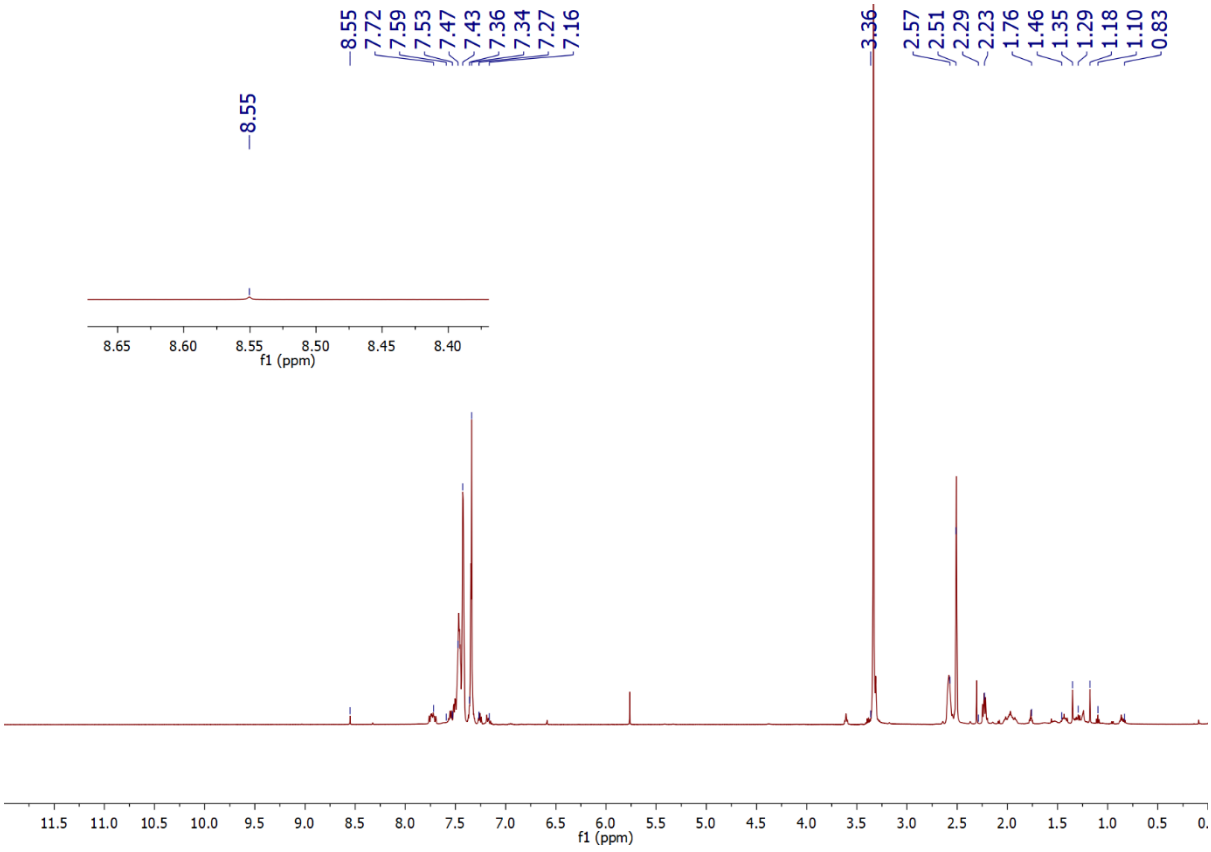


Figure S41. $^{31}P\{^{1}H\}$ NMR taken (taken in DMSO d-6) after 24-hour reaction time.

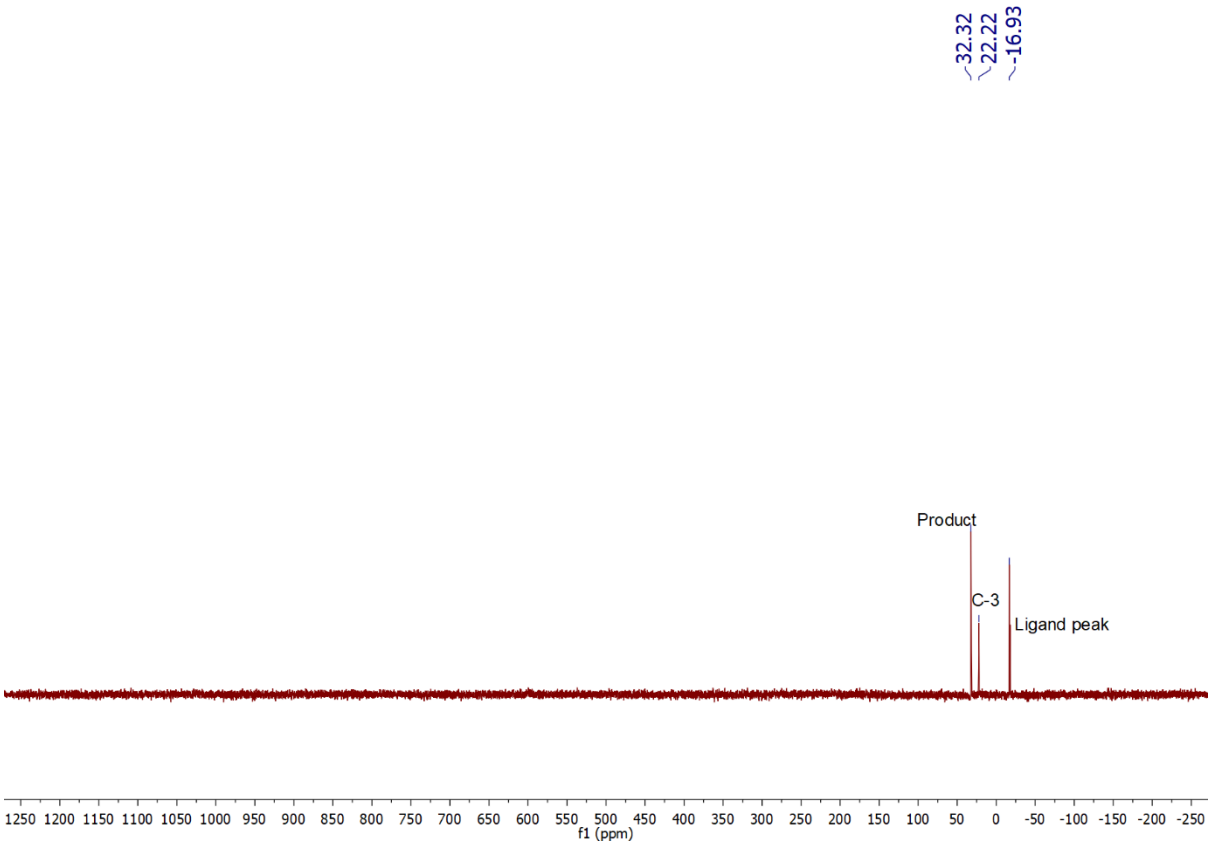


Figure S42. Experimental IR Data for carboxylate intermediate complex **C-3a**.

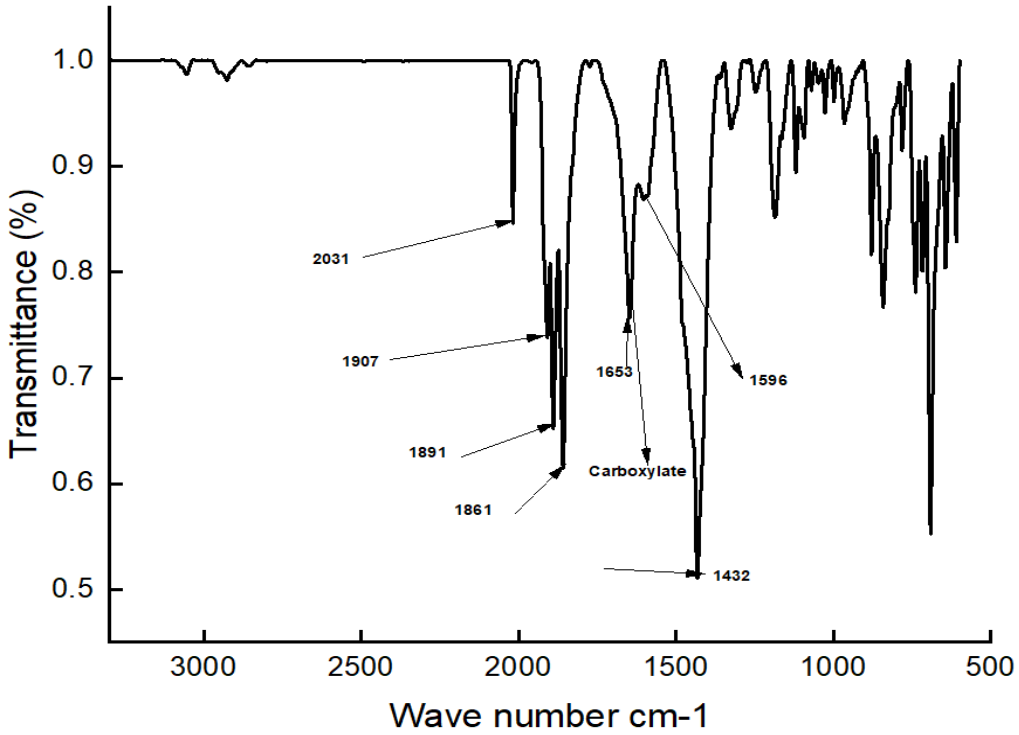


Figure S43. HRMS Data for metal formate fragment.

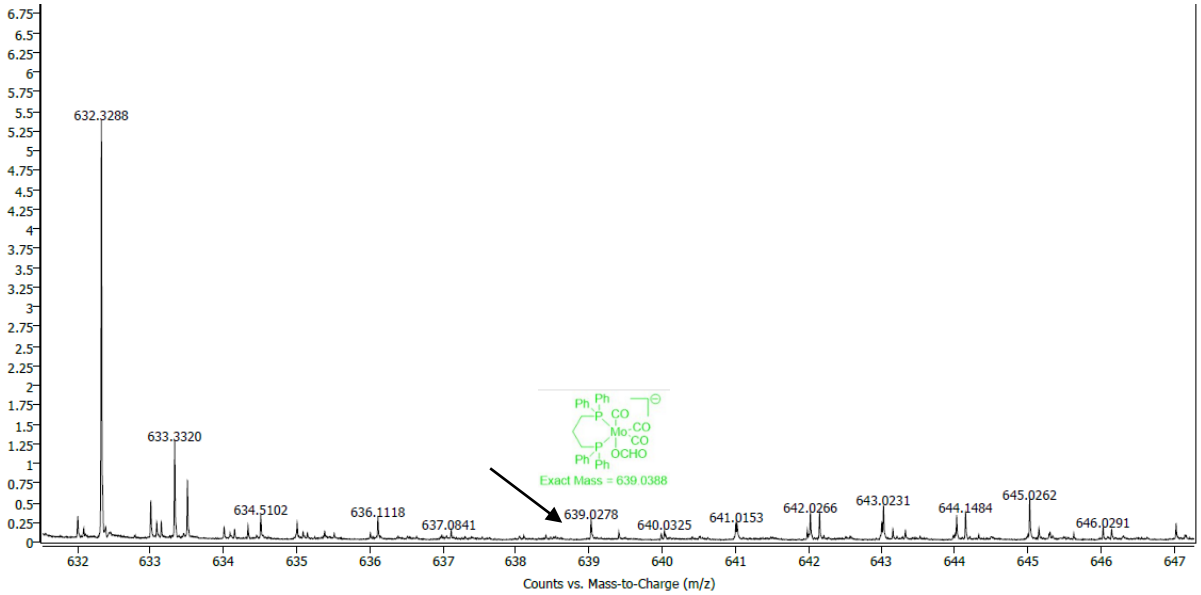
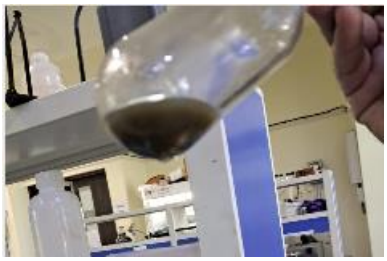


Figure S44. Colour before heating the reaction mixture of complex **C-3** and NaOH.

Figure S45. Colour after heating the reaction mixture of complex **C-3** and NaOH for 6 h.



6. Characterization data for molybdenum complexes.

(a) Characterization data of **C-1**.

$Mo(DPPM)(CO)_4$ (**C-1**)
^1H NMR (500 MHz, $CDCl_3$) δ 7.53-7.26 (m, Ar), 4.45(t).
$^{31}P\{^1H\}$-NMR (203.0 MHz, $CDCl_3$) δ 2.3 (s, 2P).
FT-IR (**cm^{-1}**) ν_{CO} = 2016, 1912, 1857.
HRMS of $C_{29}H_{22}MoO_4P_2$: Calculated 594.0047. Found 594.1570.

Figure S46. ^1H NMR for **C-1**.

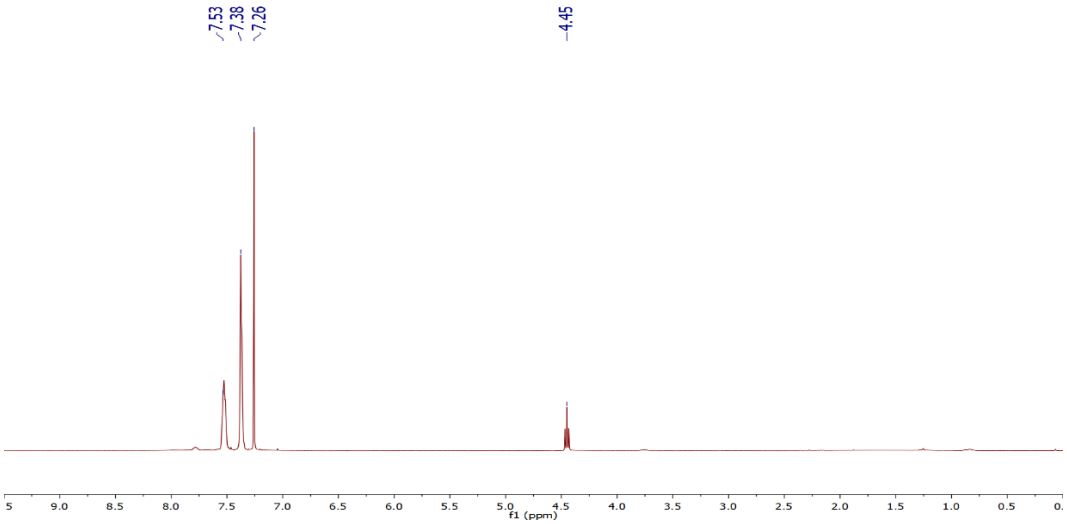


Figure S47. $^{31}P\{^1H\}$ NMR for **C-1**.

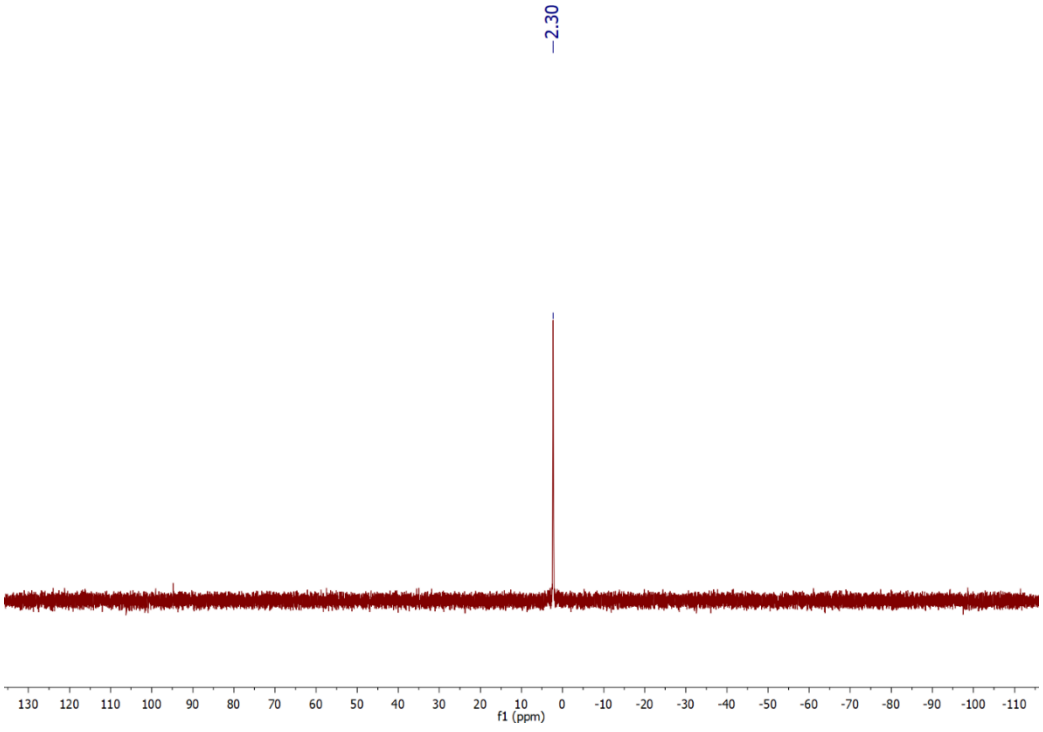


Figure S48. IR data for **C-1**.

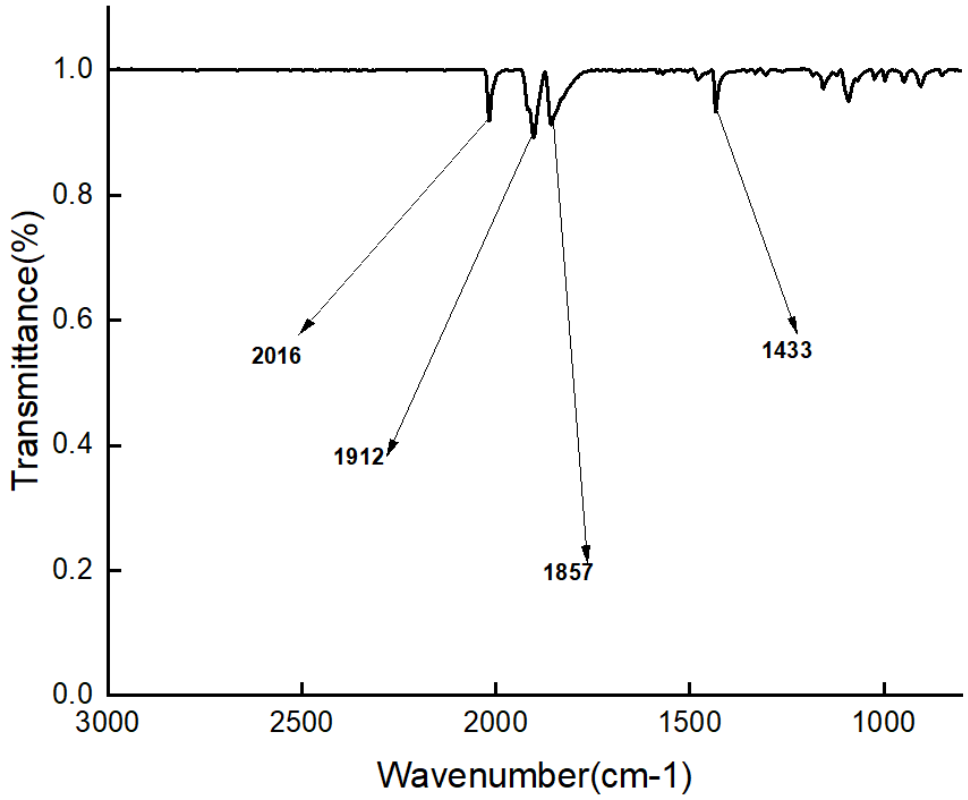
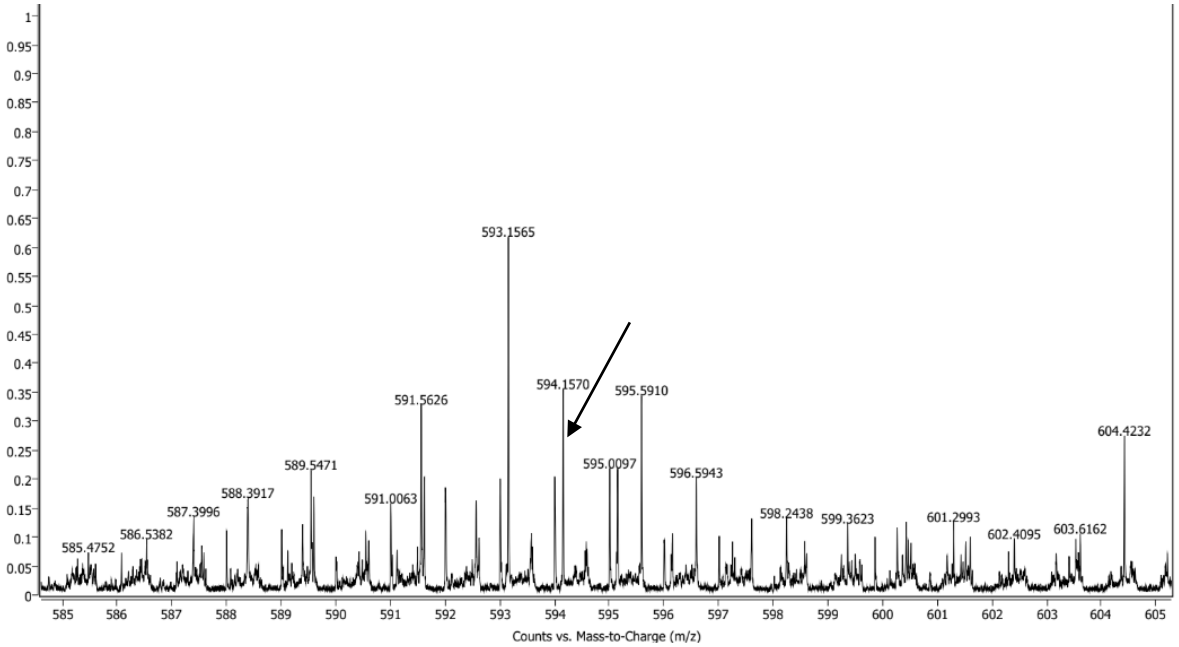


Figure S49. HRMS data for **C-1** (Exact mass = 594.0047).



6(b) Characterization data of C-2.

$Mo(DPPE)(CO)_4$ (**C-2**)
^1H NMR (500 MHz, $CDCl_3$) δ 7.64-7.31 (m, Ar), 2.48 (m, 2H), 2.45 (m, 2H).
$^{31}P\{^1H\}$-NMR (203.0 MHz, $CDCl_3$) δ 55.2 (2P).
FT-IR (cm^{-1}) ν(CO) = 2013, 1902, 1869.

HRMS of $C_{30}H_{24}MoO_4P_2$: Calculated 608.0204. Found 608.6085.

Figure S50. ^{1}H NMR for **C-2**.

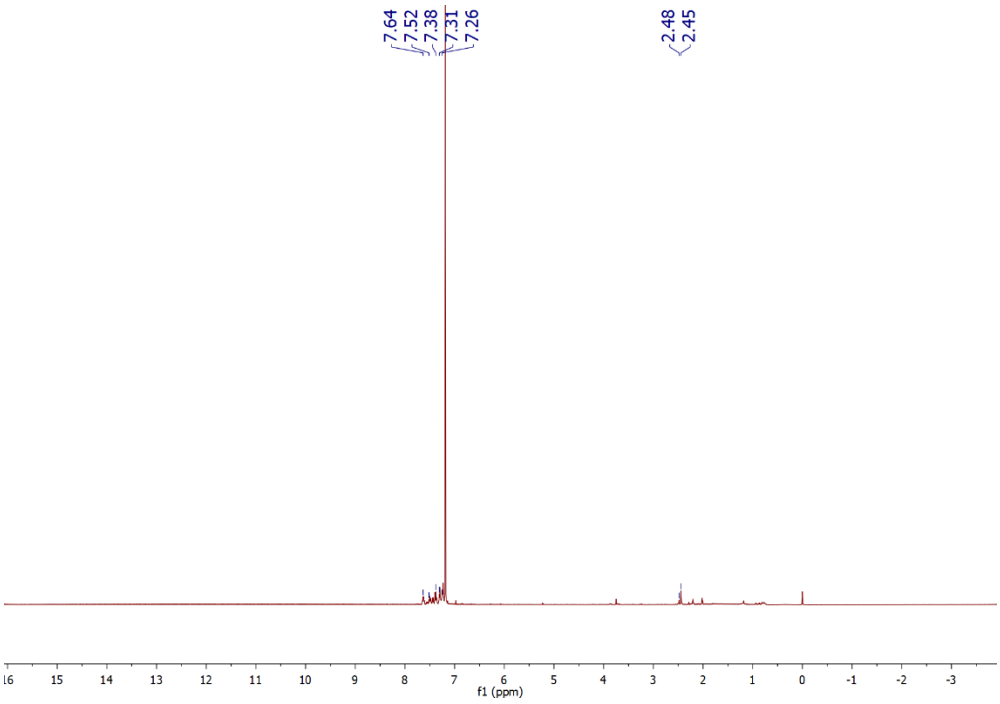


Figure S51. $^{31}P\{^{1}H\}$ NMR for **C-2**.

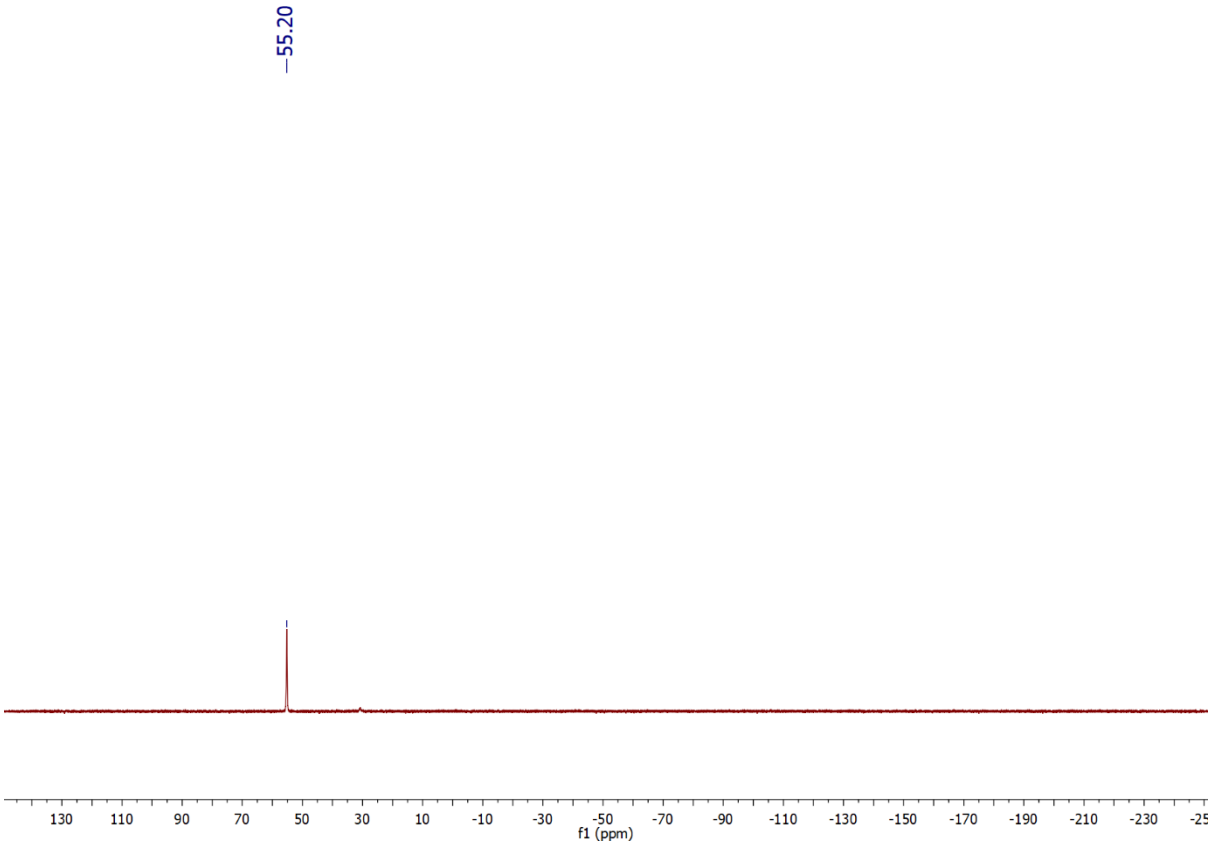


Figure S52. IR data for **C-2**.

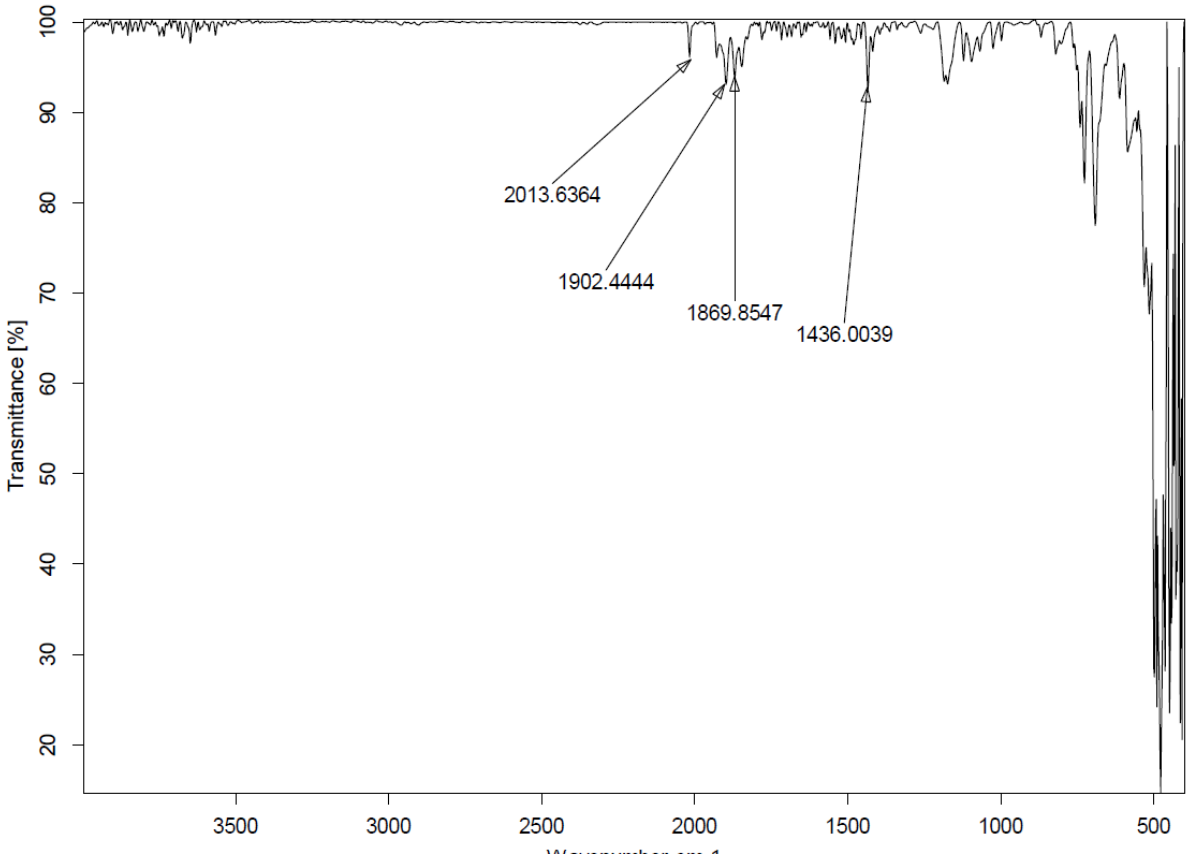
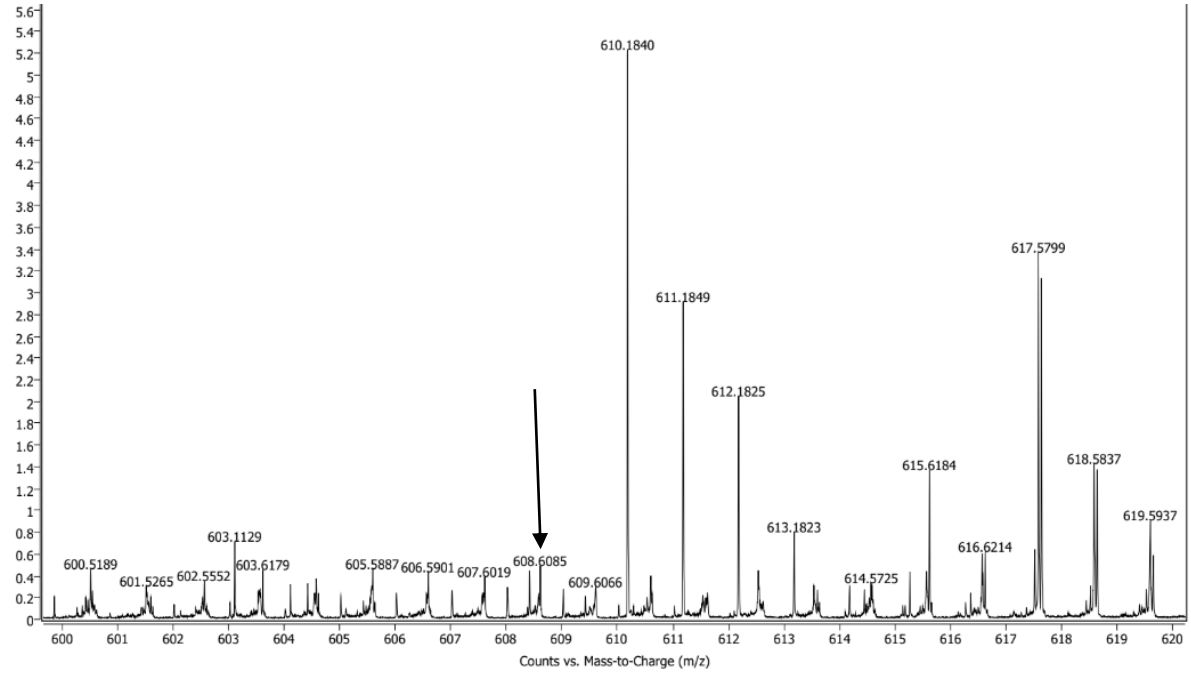


Figure S53. HRMS data for **C-2** (Exact mass = 608.0204).



6 (c) Characterization data of C-3.

$Mo(DPPP)(CO)_4$ (**C-3**)
^1H NMR (500 MHz, $CDCl_3$) δ 7.39-7.19 (m, Ar), 2.38 (m, 4H), 1.90 (2H).

$^{31}P\{^{1}H\}$-NMR (203.0 MHz, $CDCl_3$) δ 21.23 (2P).
FT-IR (cm^{-1}) ν(CO) = 2016, 1905, 1856.
HRMS of $C_{31}H_{26}MoO_4P_2$: Calculated 622.0360. Found 622.0264.

Figure S54. ^{1}H NMR for **C-3**.

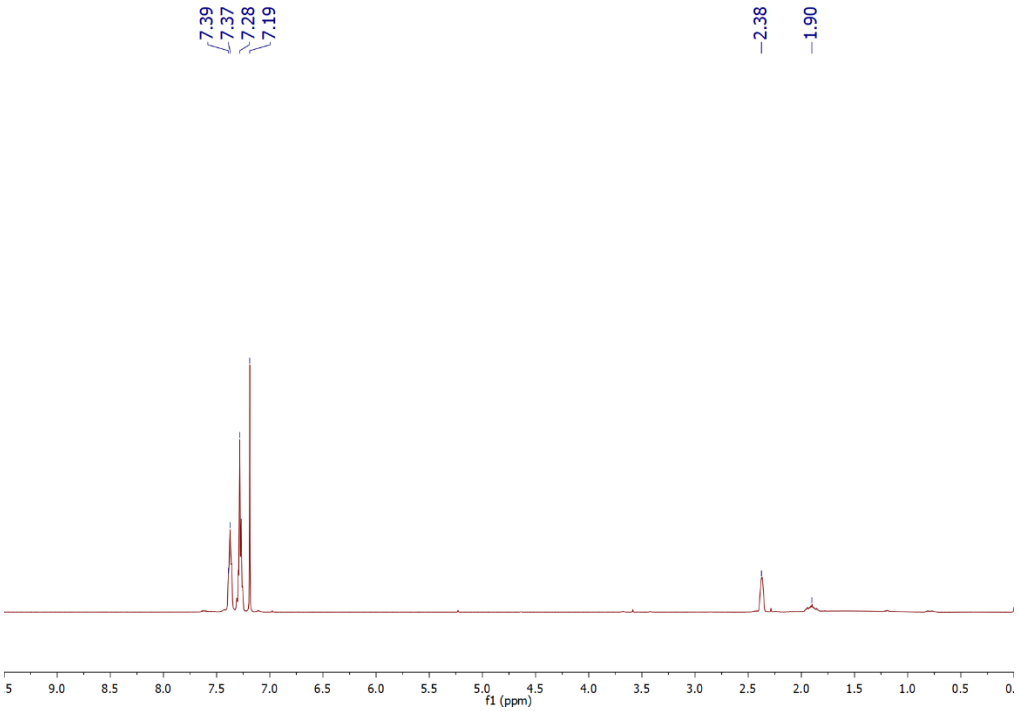


Figure S55. $^{31}P\{^{1}H\}$ NMR for **C-3**.

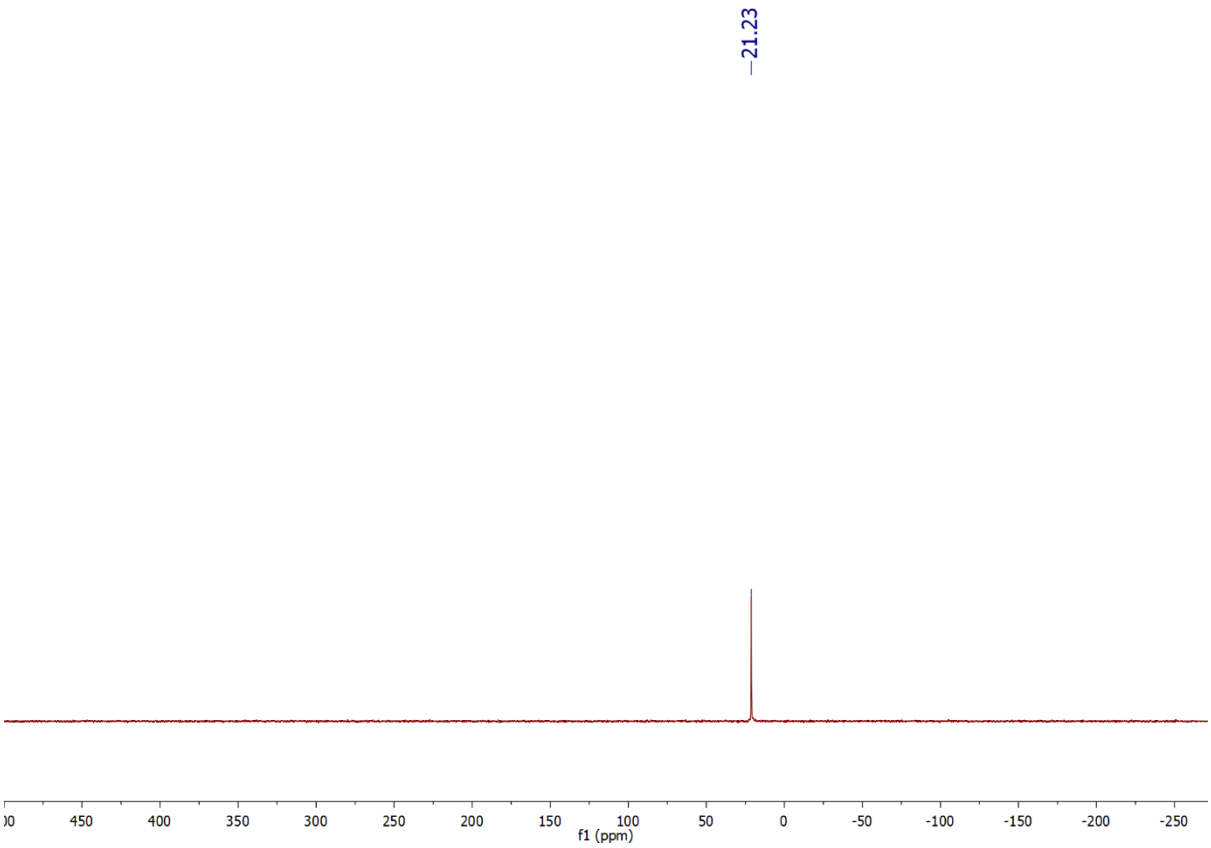


Figure S56. IR data for **C-3**.

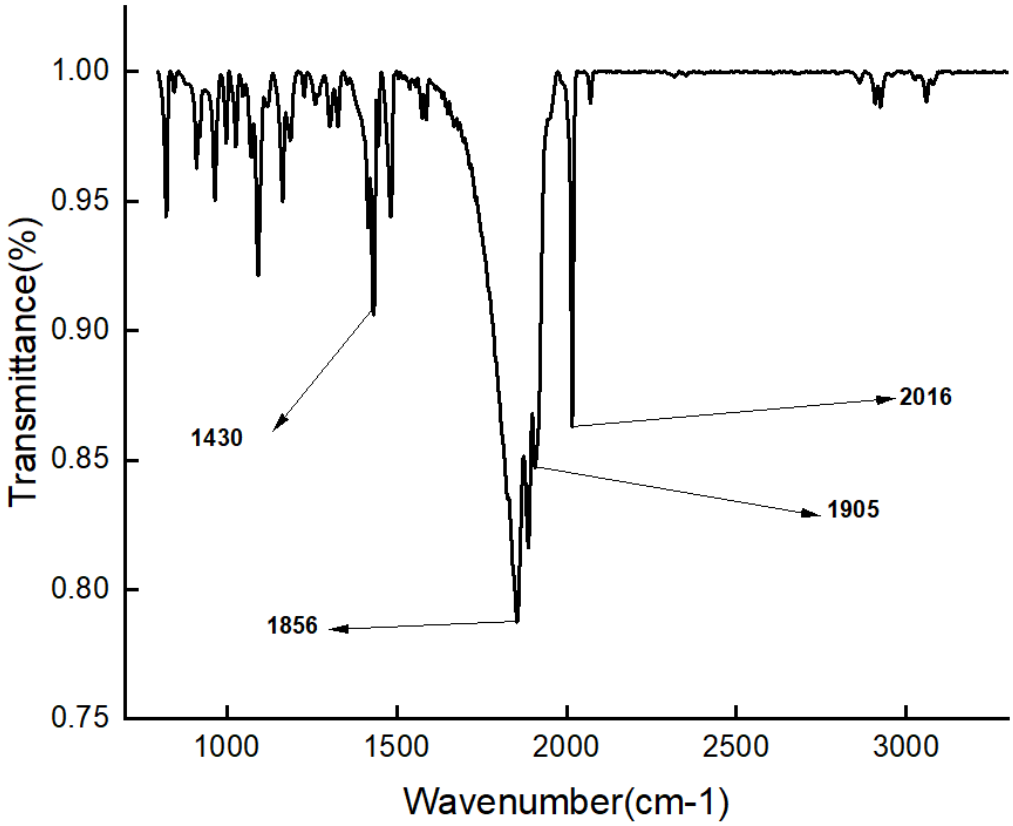
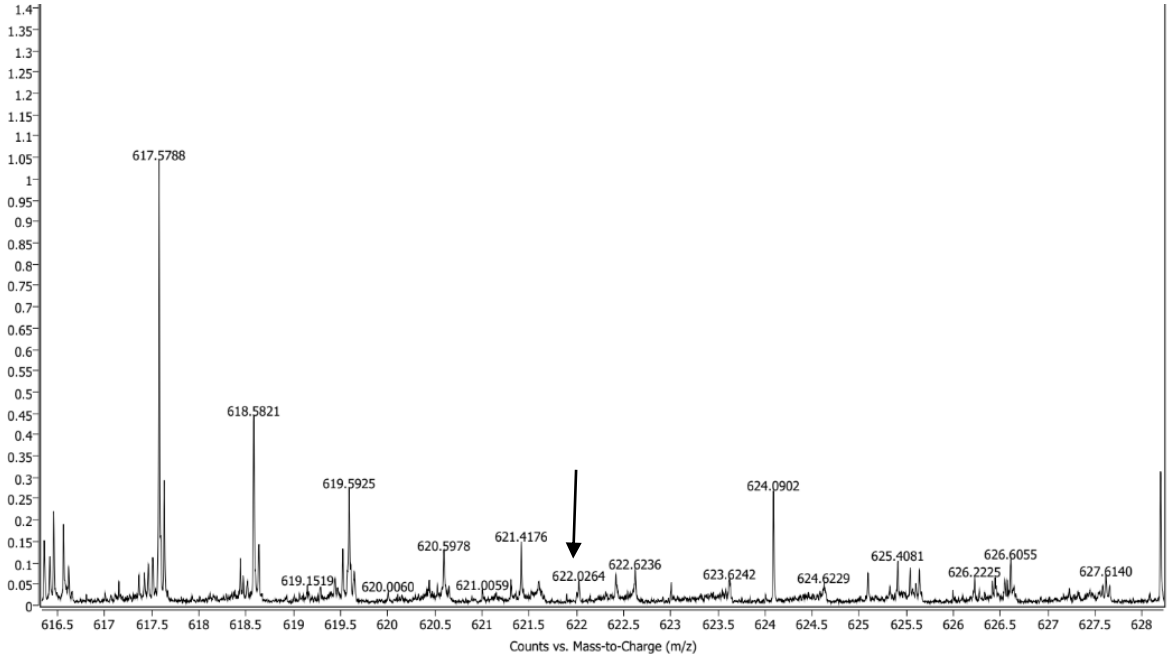


Figure S57. HRMS data for **C-3** (Exact mass = 622.0360).



6(d) Characterization data of C-4.

Mo(DPPF)$(CO)_4$ (**C-4**)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.60 (m, Ar), 4.25 (m, 8H).
$^{31}P\{^1H\}$-NMR (203.0 MHz, $CDCl_3$) δ 33.24 (2P).
FT-IR (cm^{-1}) ν(CO) = 2020, 1891, 1878.
HRMS of $C_{40}H_{34}FeMoO_4P_2$: Calculated 794.0330. Found 794.8298.

Figure S58. ^{1}H NMR for **C-4**.

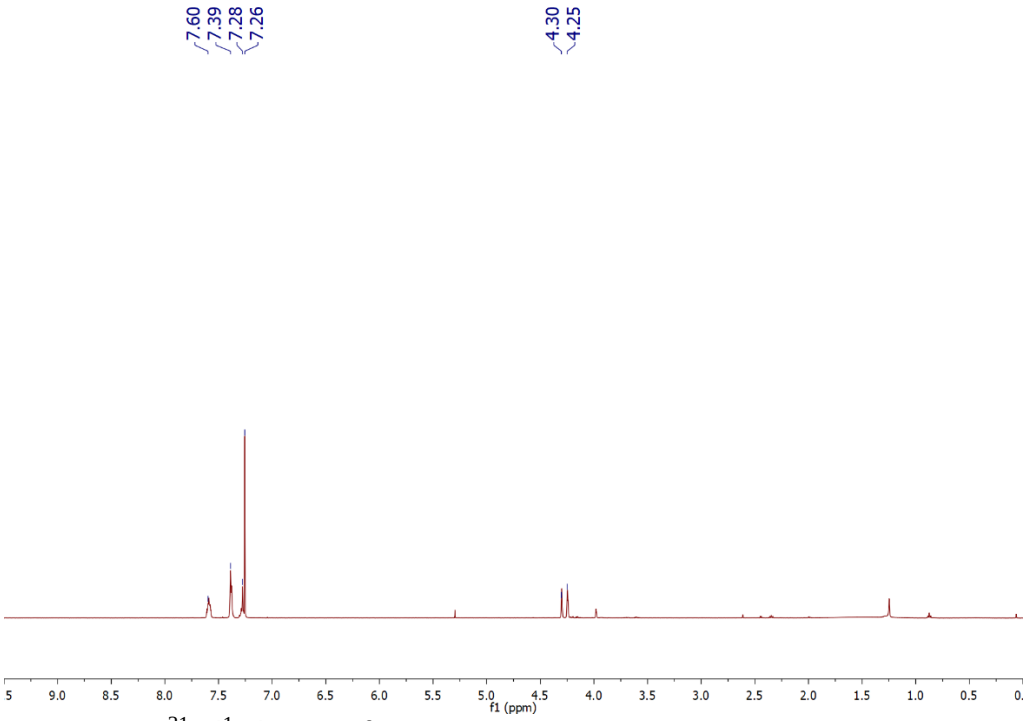


Figure S59. $^{31}P\{^1H\}$ NMR for **C-4**.

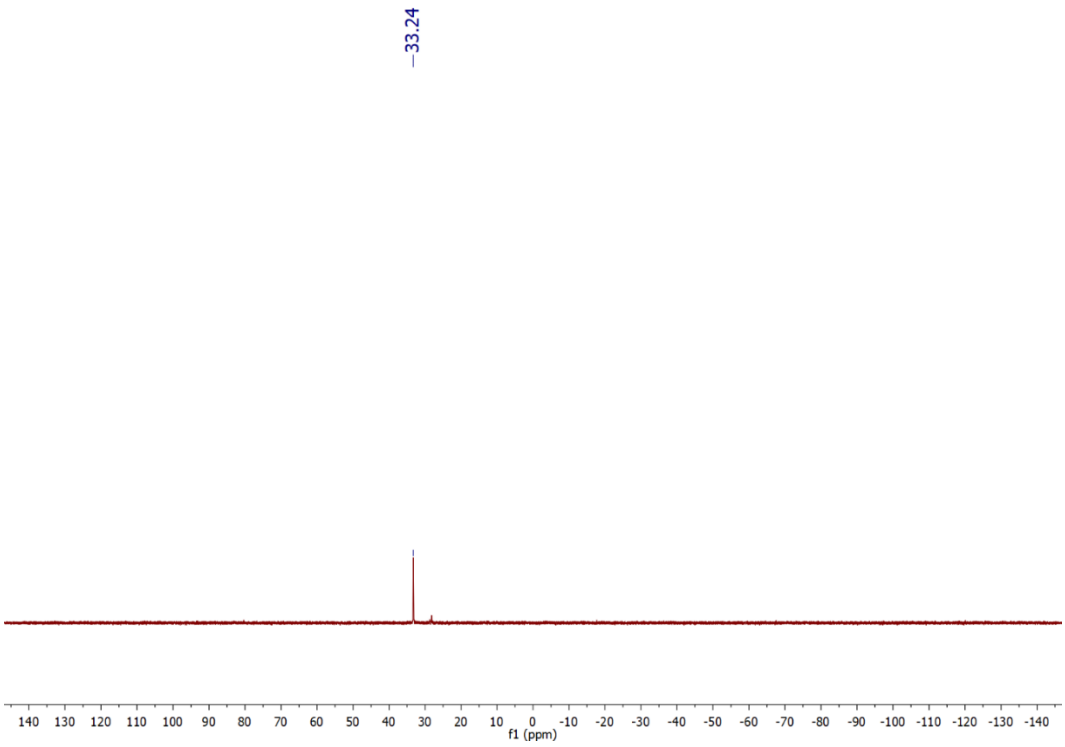


Figure S60. IR data for **C-4**.

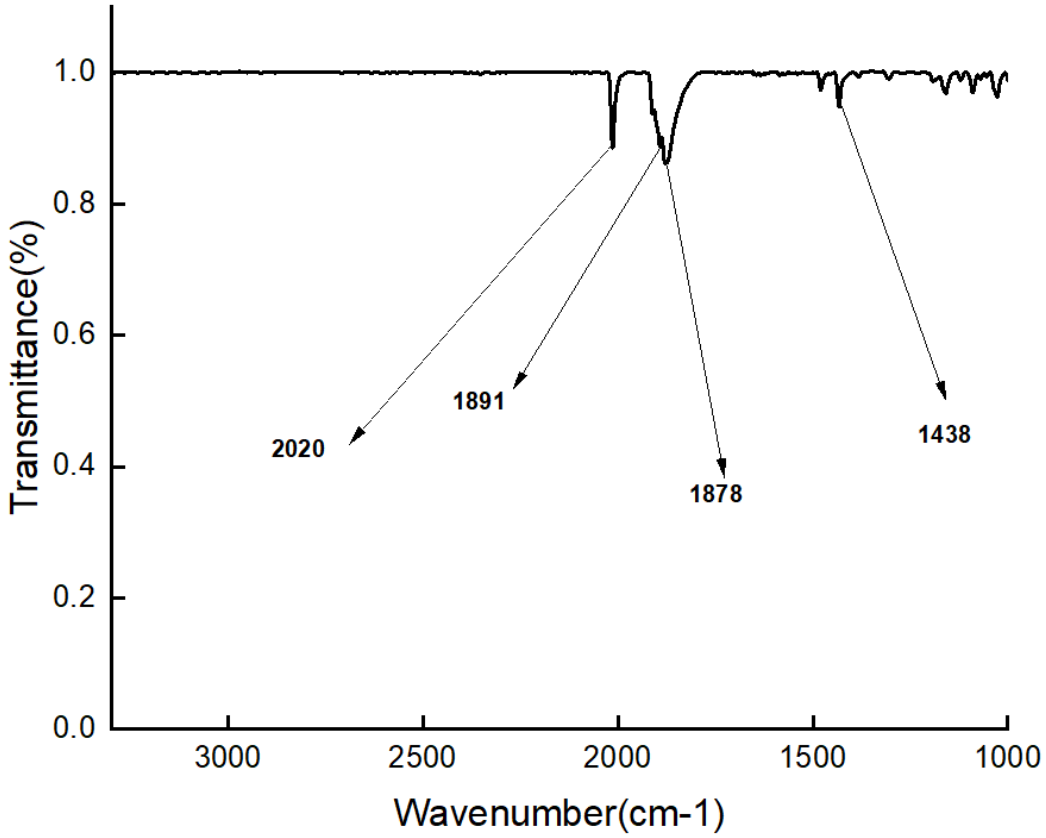
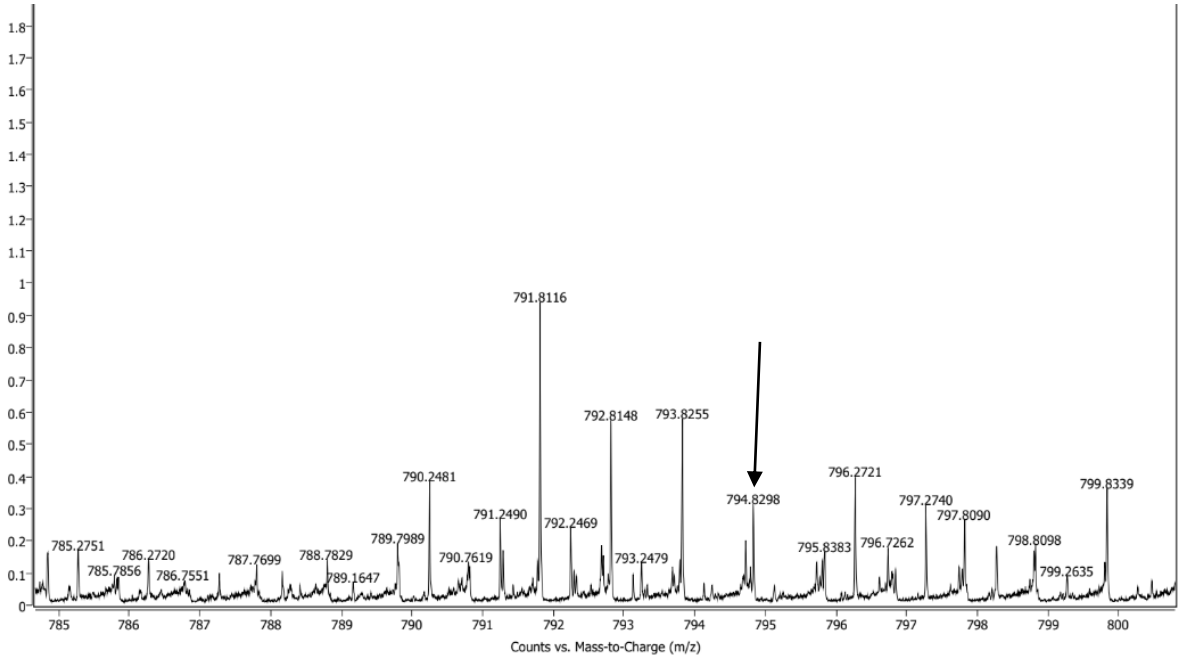


Figure S61. HRMS data for **C-4** (Exact mass = 794.0330).



6 (e) Characterization data of C-5.

Mo(DpePhos)$(CO)_4$ (**C-5**)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-6.87 m (22H), 6.50 t(2H).
$^{31}P\{^1H\}$-NMR (203.0 MHz, $CDCl_3$) δ 26.97 (2P).
FT-IR cm^{-1} ν(CO) 2024, 1922, 1867.
HRMS $C_{40}H_{28}MoO_5P_2$ Calculated 748.0466. Found 748.5423.

Figure S62. ^{1}H NMR for **C-5**.

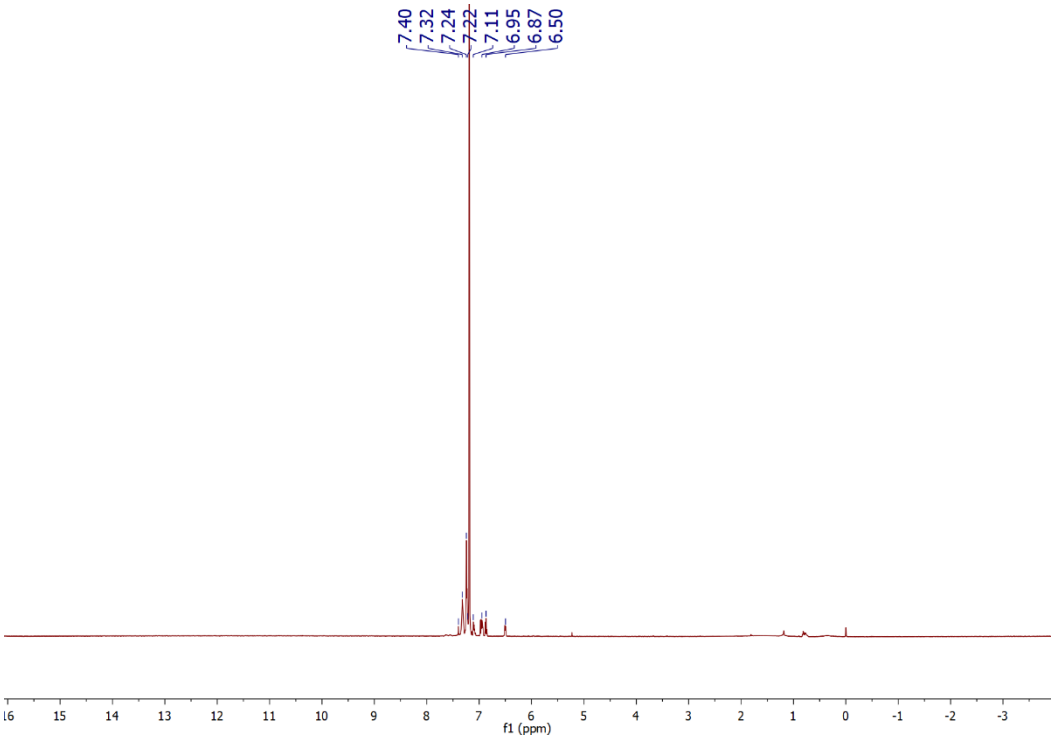


Figure S63. $^{31}P\{^1H\}$ NMR for **C-5**.

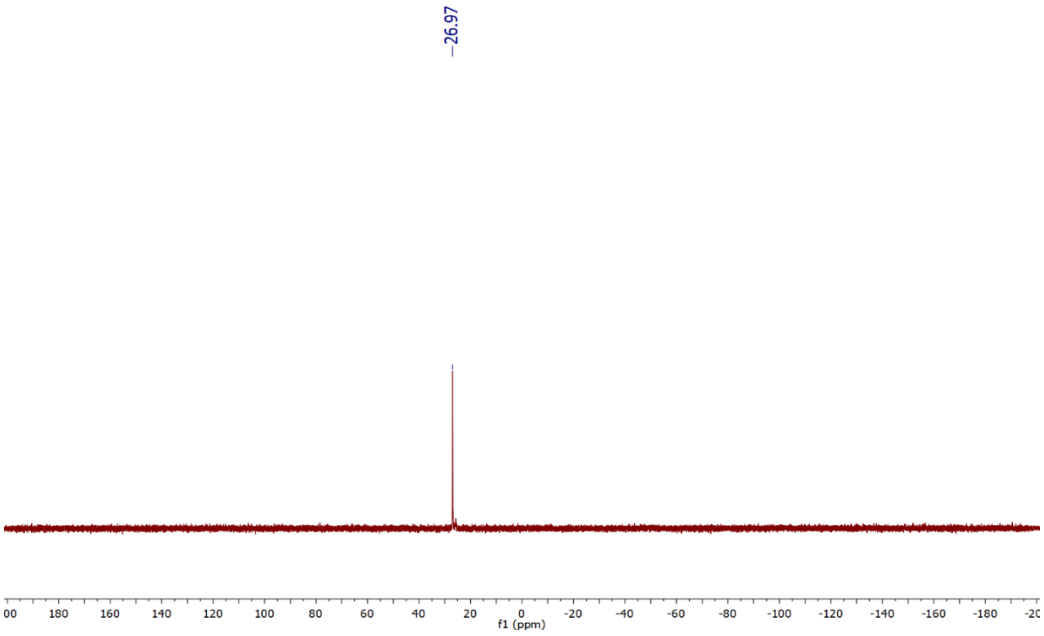


Figure S64. IR data for **C-5**.

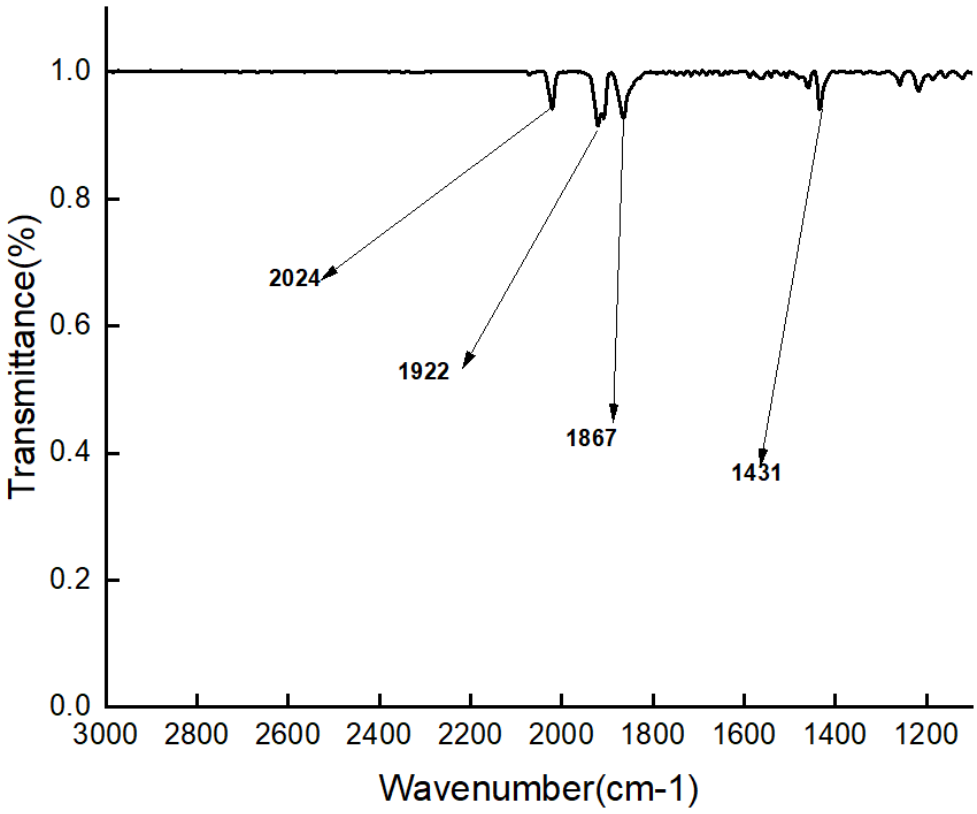
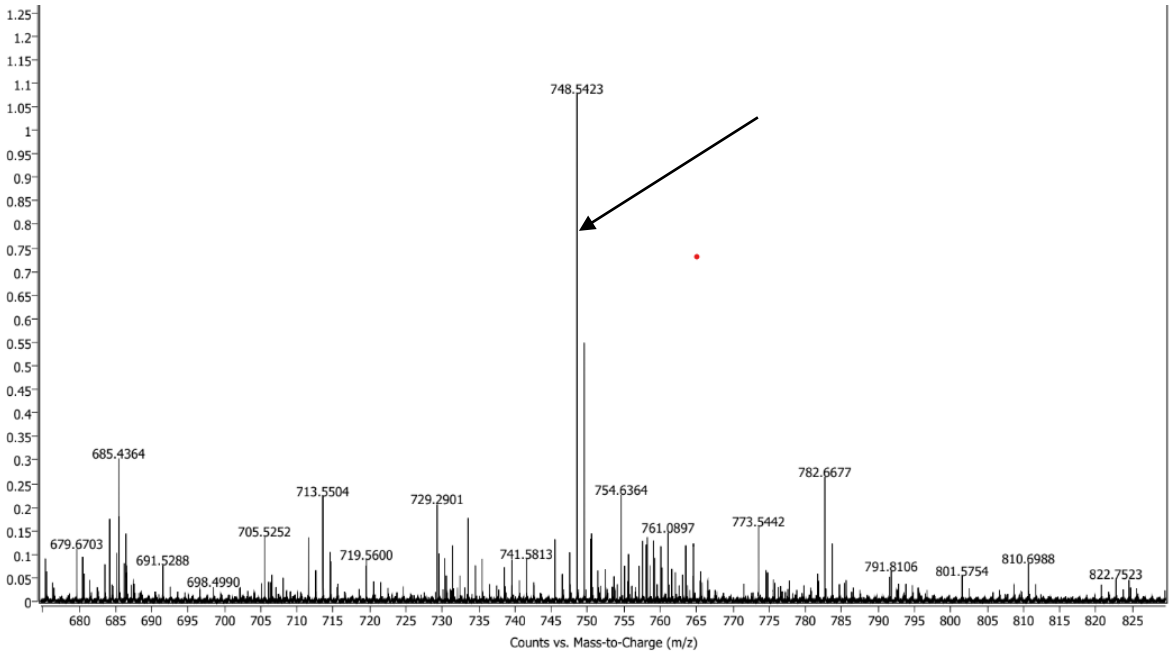


Figure S65. HRMS data for **C-5** (Exact mass = 748.0466).



6(f) Characterization data of C-6.

Mo(Xanthphos)$(CO)_4$ (**C-6**)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-6.97 (m, 22H), 6.54 (t, 2H), 1.56 (t, 6H).
^{31}P{^{1}H}-NMR (203.0 MHz, $CDCl_3$) δ 20.71 (2P).

FT-IR (cm^{-1}) ν(CO) = 2013, 1913, 1862.
HRMS data of $C_{43}H_{32}MoO_5P_2$: Calculated 788.0779. Found 788.0768.

Figure S66. ^{1}H NMR for **C-6**.

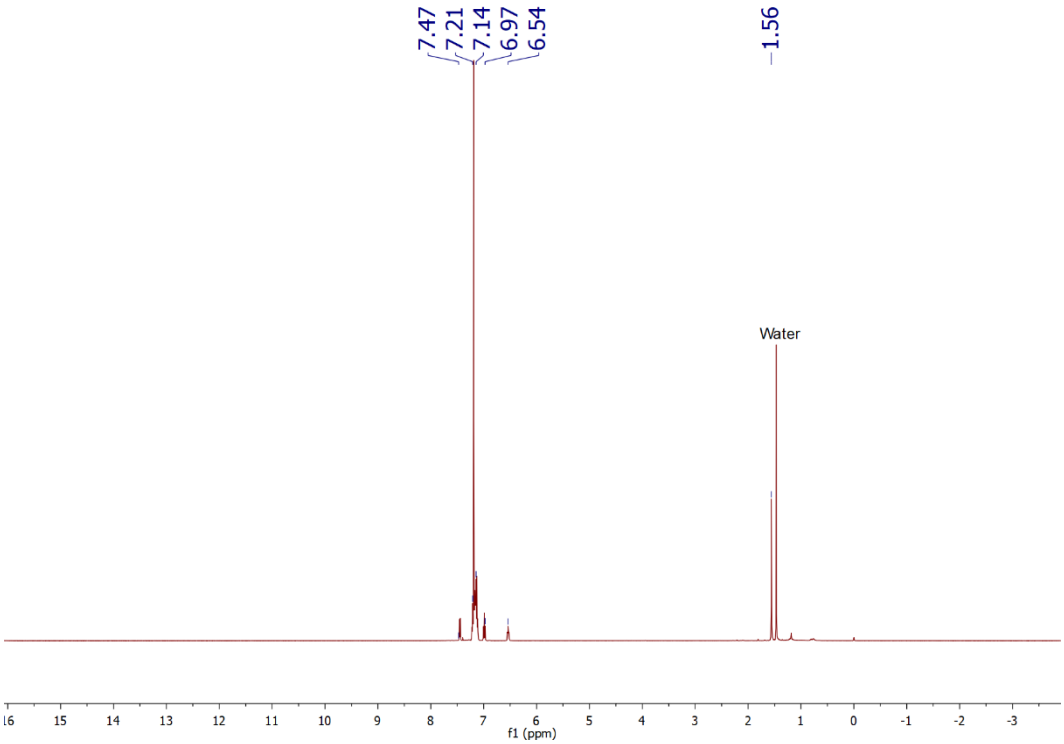


Figure S67. $^{31}P\{^{1}H\}$ NMR for **C-6**.

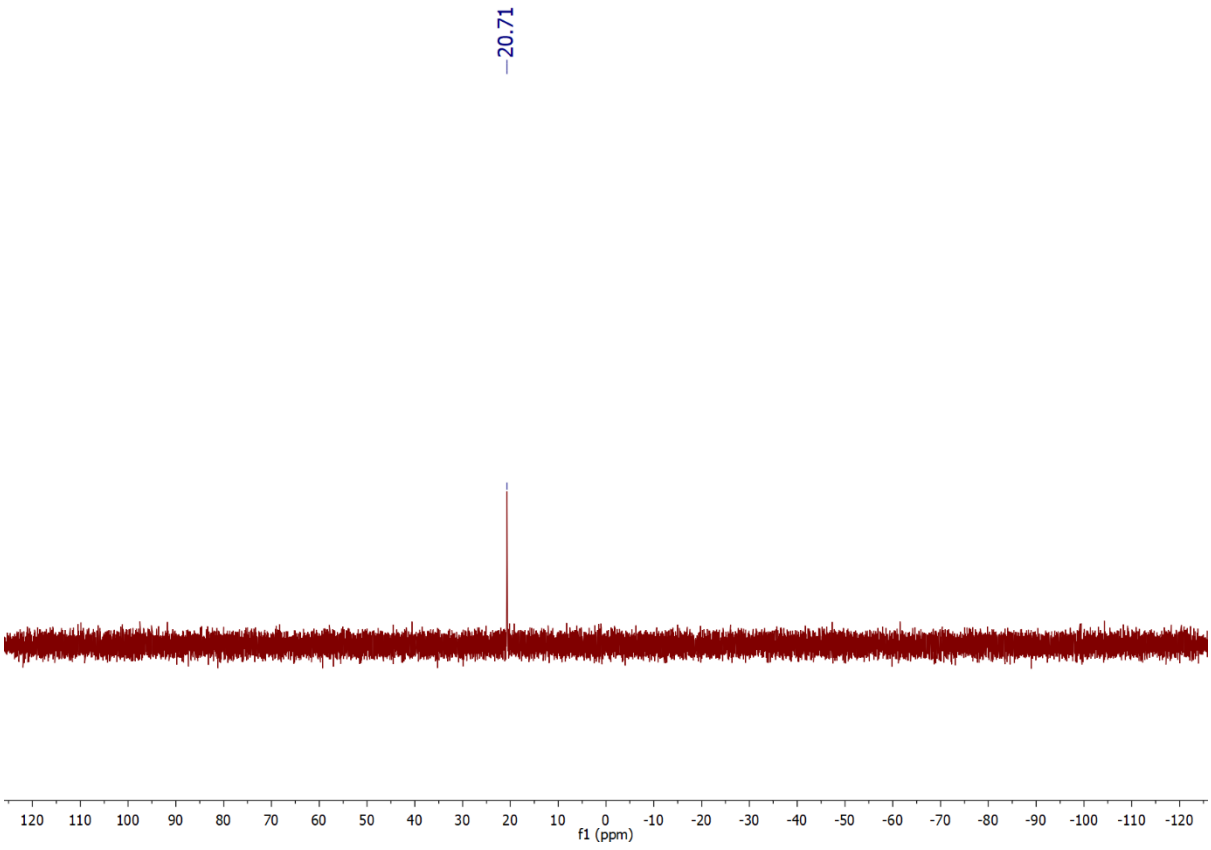


Figure S68. IR data for **C-6**.

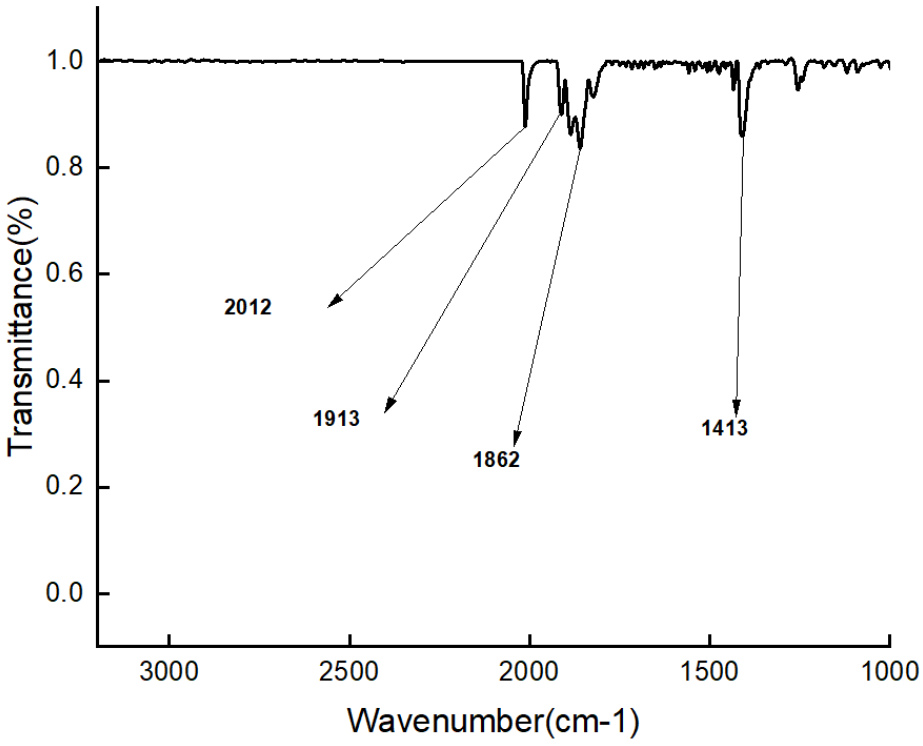
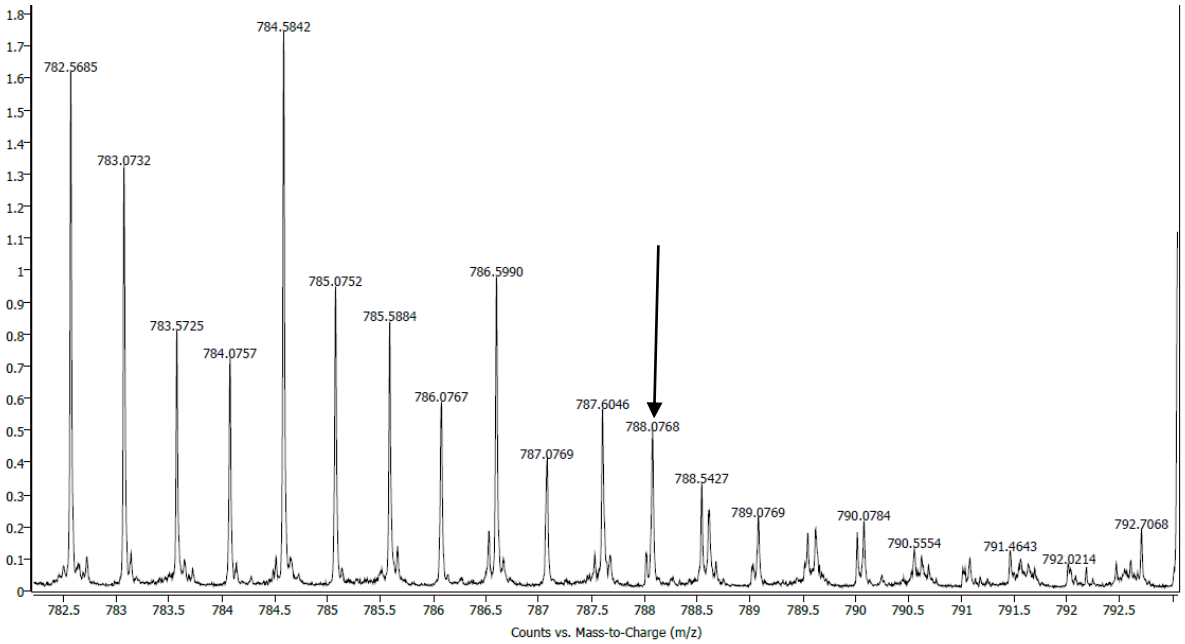


Figure S69. HRMS data for **C-6** (Exact mass = 788.0779).



6(g) Characterization data of C-7.

$Mo(DiPPF)(CO)_4$ (**C-7**)
^1H NMR (500 MHz, $CDCl_3$) δ 4.31 (4H), 4.16 (4H), 2.24 (m, 4H), 1.93-1.24 (m, 24H).
$^{31}P\{^1H\}$-NMR (203.0 MHz, $CDCl_3$) δ 41.25 (2P).

FT-IR (cm^{-1}) ν(CO) = 2010, 1885, 1845.
HRMS of $C_{26}H_{36}FeMoO_4P_2$: Calculated 628.0480. Found 628.0483.

Figure S70. ^{1}H NMR for **C-7**.

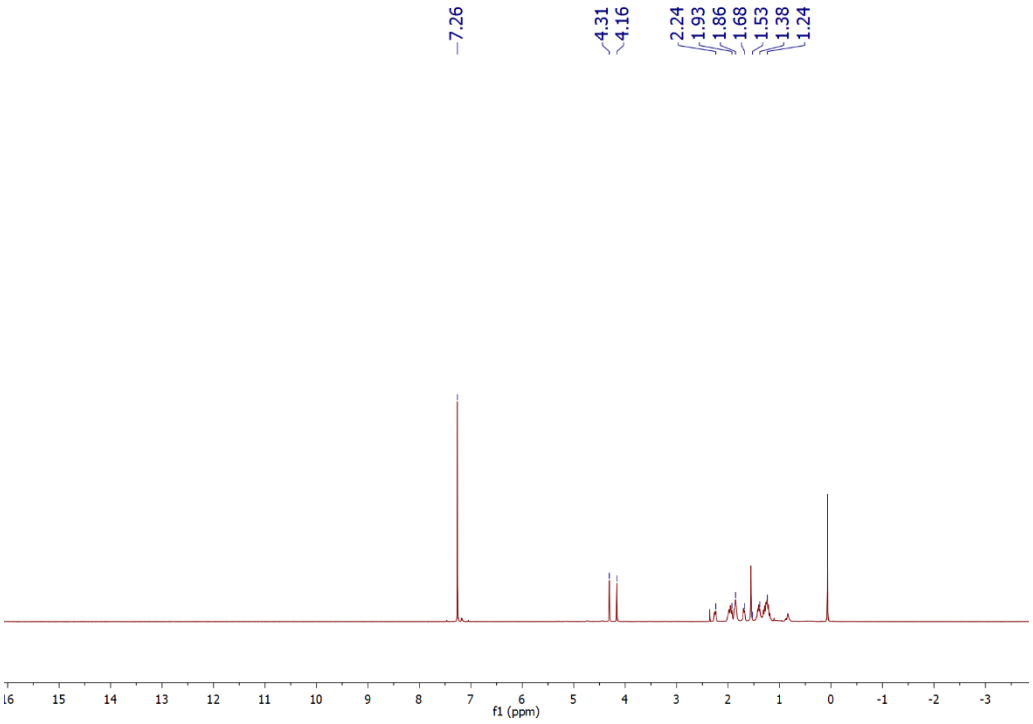


Figure S71. $^{31}P\{^{1}H\}$ NMR for **C-7**.

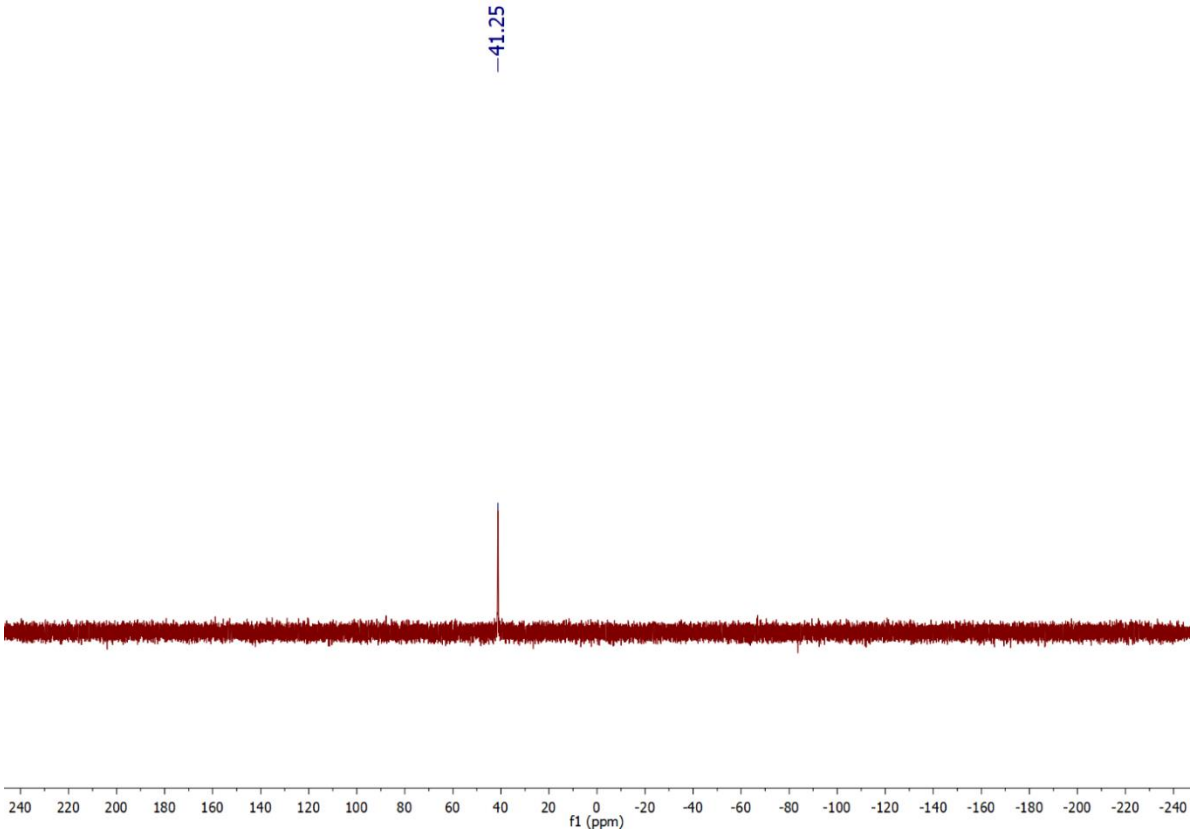


Figure S72. IR data for **C-7**.

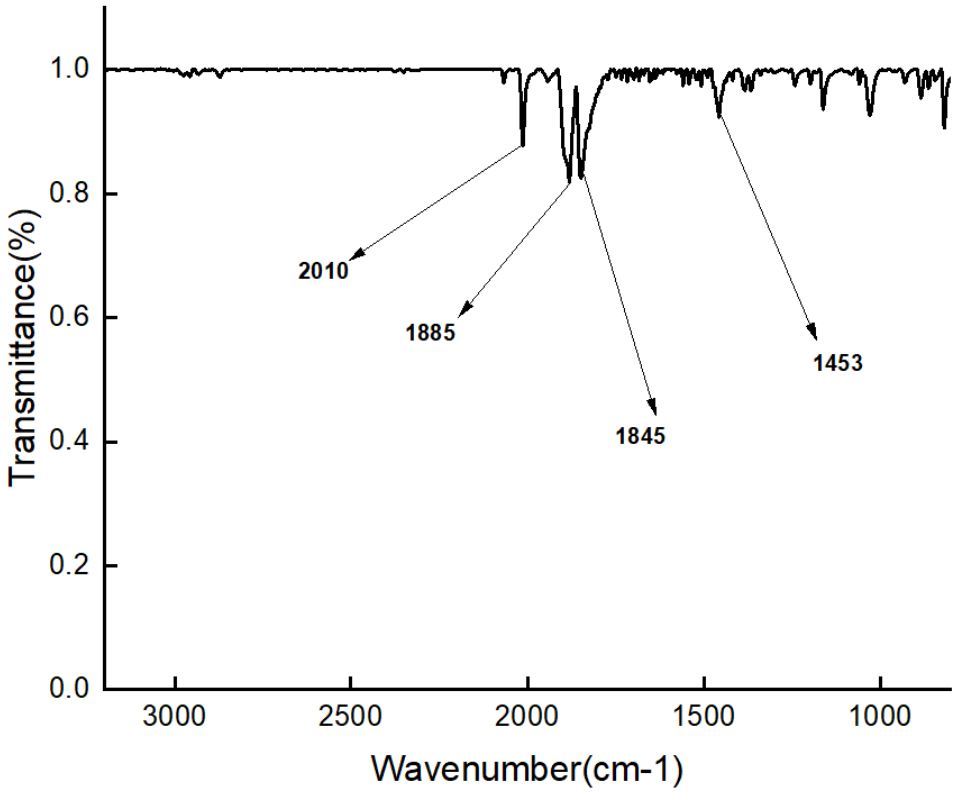
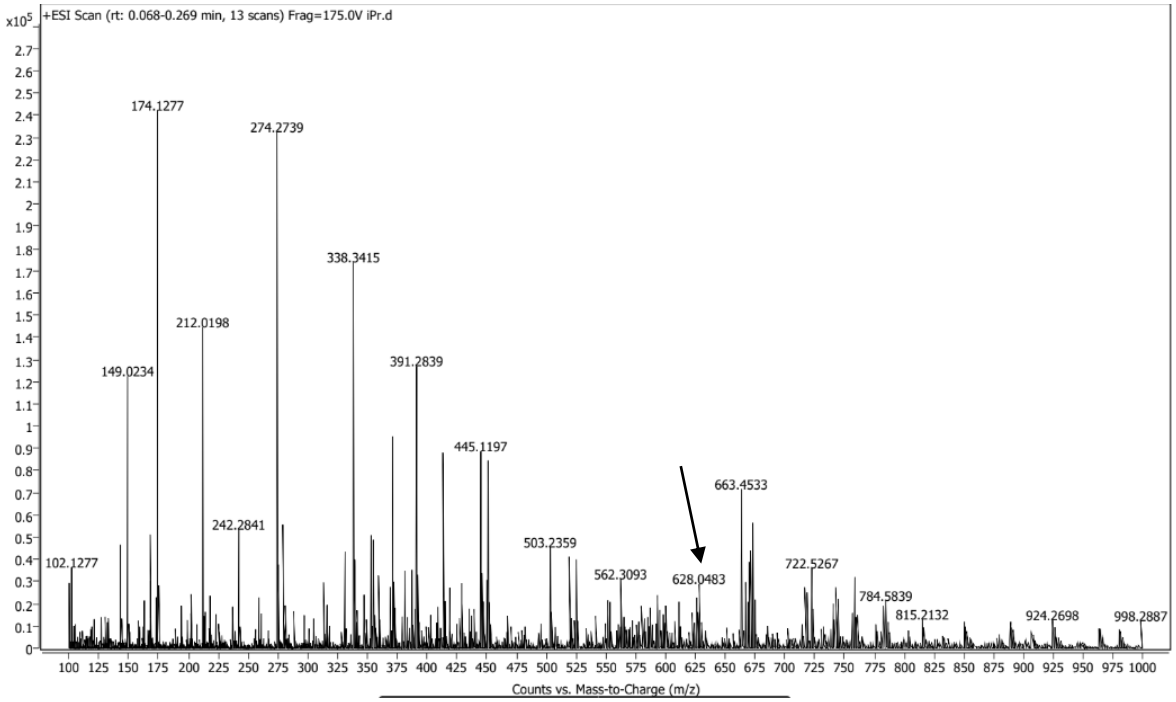


Figure S73. HRMS data for **C-7** (Exact mass = 628.0480).



6(h) Characterization data of C-8. $Mo(DCPF)(CO)_4$ (**C-8**)

^1H NMR (500 MHz, $CDCl_3$) δ 4.34 (4H), 4.24 (4H), 2.31 (4H), 1.55 (4H), 1.30 (m, 20H), 1.20 (m, 16H).

$^{31}P\{^{1}H\}$-NMR (203.0 MHz, $CDCl_3$) δ 33.61 (2P).
FT-IR (cm^{-1}) ν(CO) = 2012, 1857.
HRMS: $C_{38}H_{52}FeMoO_4P_2$ Calculated 788.1738. Found 788.1741.

Figure S74. ^{1}H NMR for **C-8**.

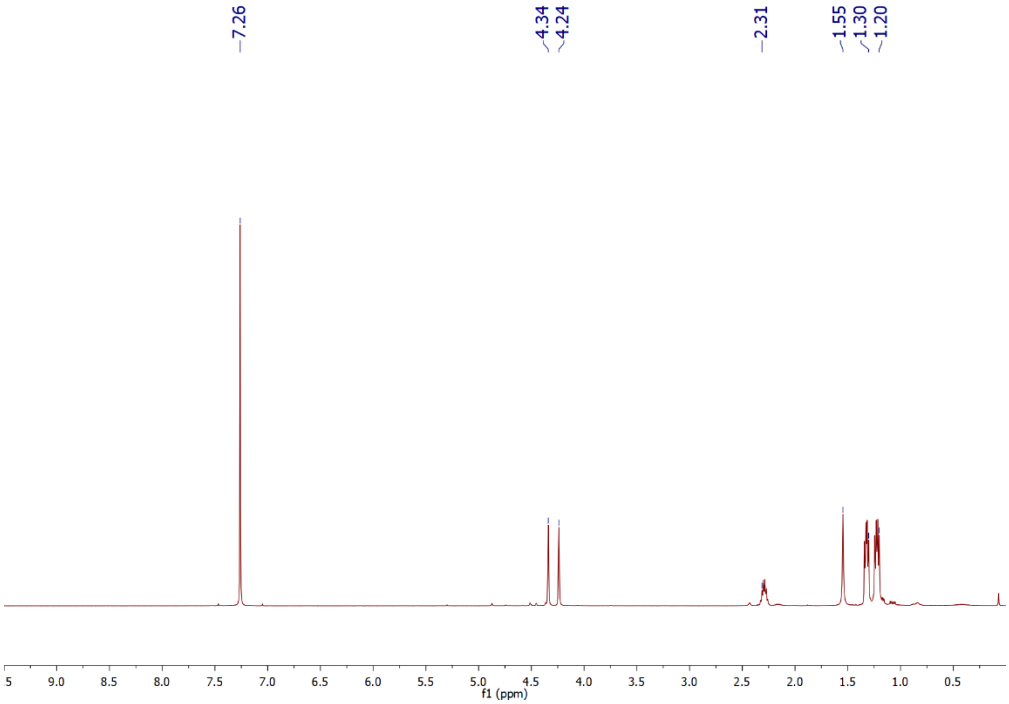


Figure S75. $^{31}P\{^{1}H\}$ NMR for **C-8**.

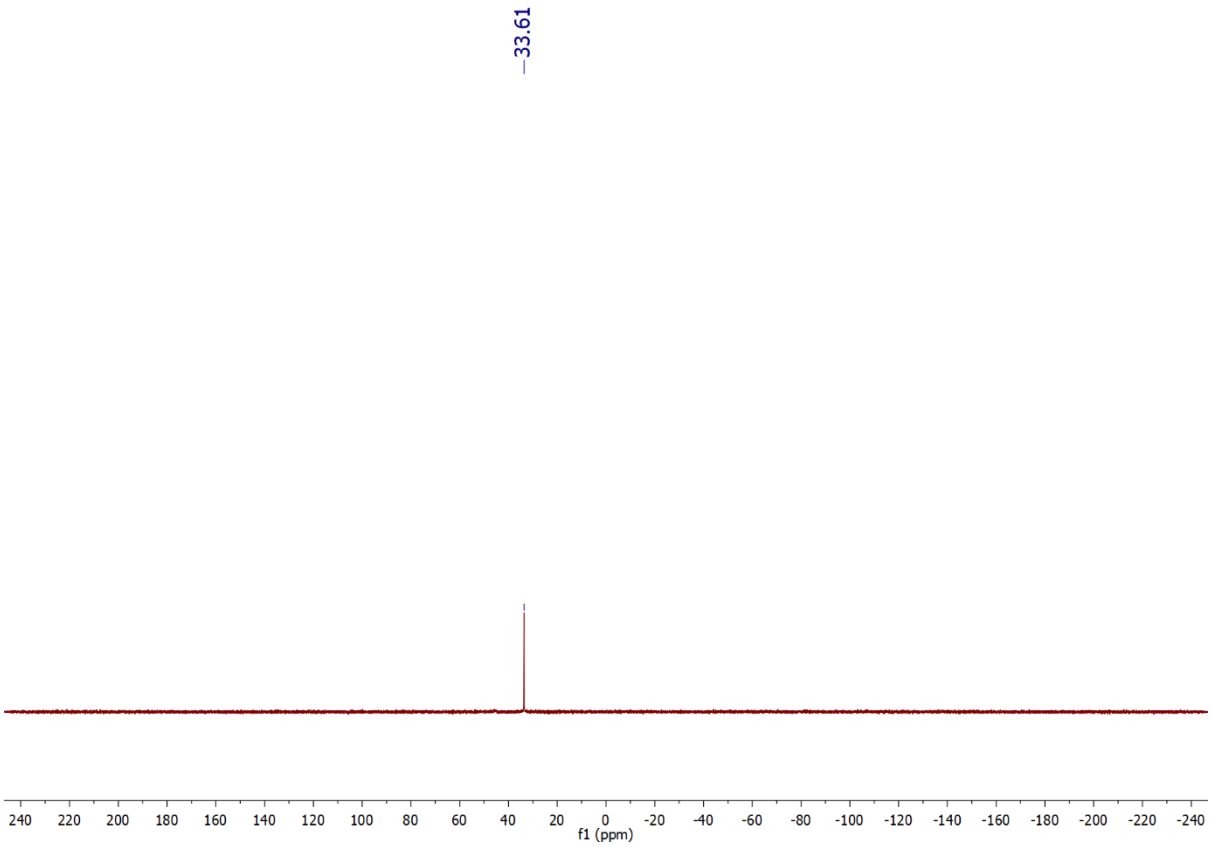


Figure S76. IR data for **C-8.**

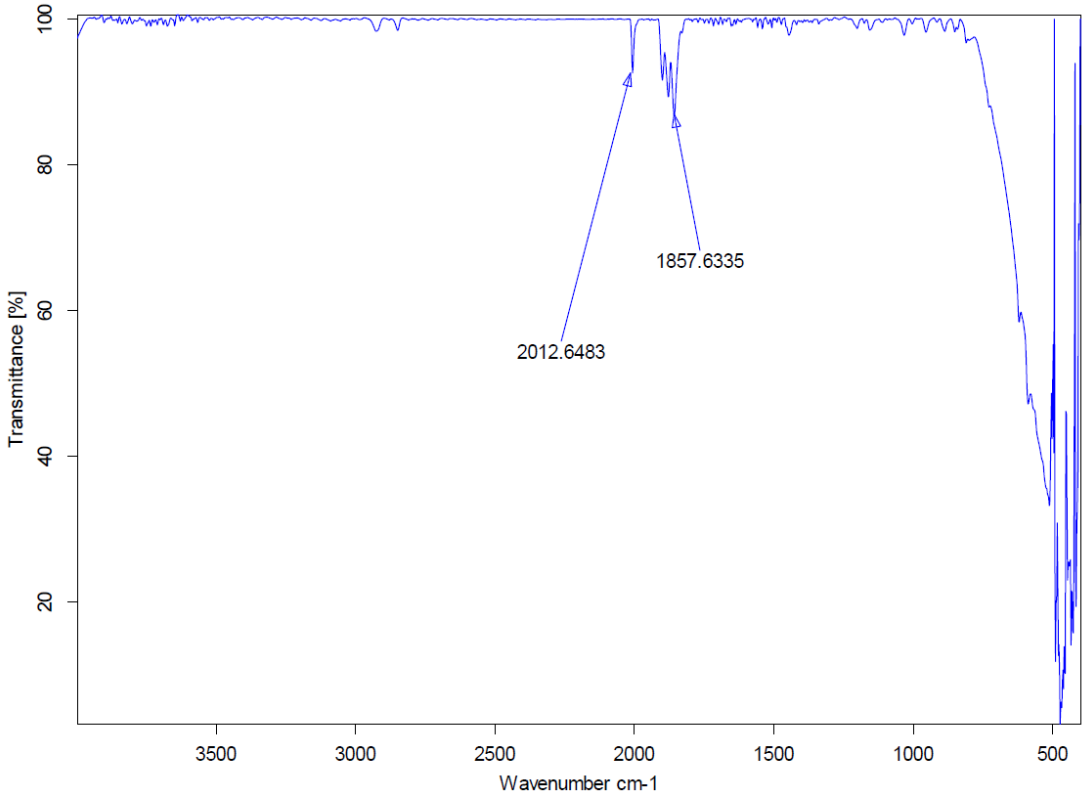
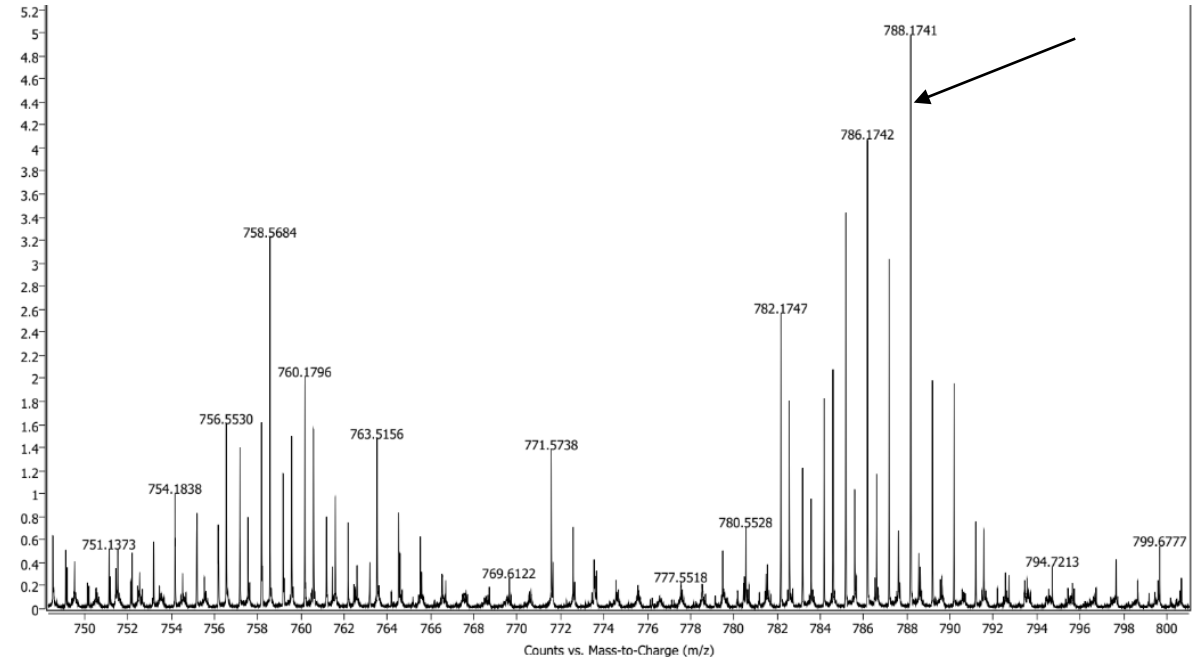


Figure S77. HRMS data for **C-8** (Exact mass = 788.1738)



7. Crystal Data

Mo(DPPM)(CO)$_4$

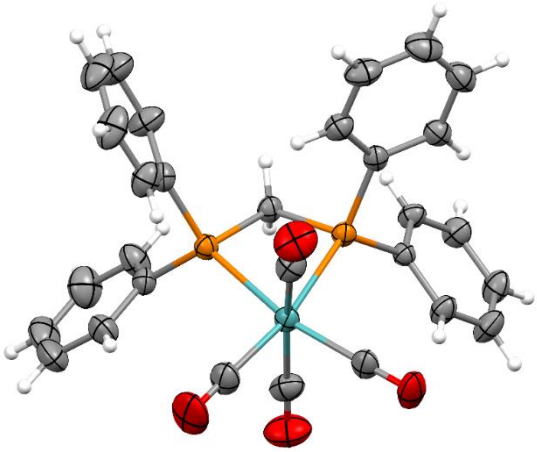


Figure S78. ORTEP drawing of **C-1**.

Table S1: Crystal data and structure refinement for C-1.	
Ccdc no.	2241306
Empirical formula	$C_{29}H_{22}MoO_4P_2$
Formula weight	592.34
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.405(3)
b/Å	9.5092(14)
c/Å	18.135(3)
α/°	90
β/°	103.336(6)
γ/°	90
Volume/Å^3	2752.8(8)
Z	4
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	0.624
F(000)	1200.0
Crystal size/mm^3	0.231 × 0.098 × 0.078
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.616 to 49.996
Index ranges	$-19 \leq h \leq 19$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$
Reflections collected	50748

Independent reflections	4836 [R_{int} = 0.1448, R_{sigma} = 0.0658]
Data/restraints/parameters	4836/0/325
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.0714
Final R indexes [all data]	R_1 = 0.0932, wR_2 = 0.0923
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.58

$Mo(DPPE)(CO)_4$

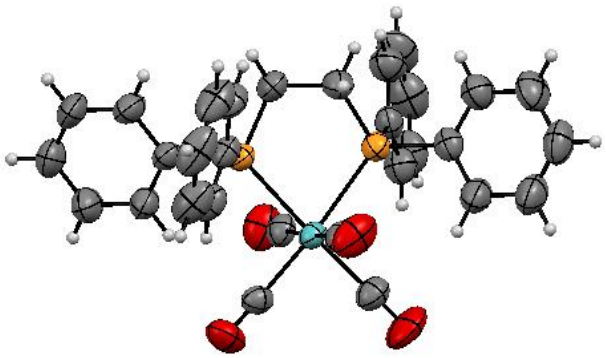


Figure S79. ORTEP drawing of **C-2**.

Table S2: Crystal data and structure refinement for C-2	
Ccdc no.	2241303
Empirical formula	$C_{30}H_{24}MoO_4P_2$
Formula weight	606.37
Temperature/K	298
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.8125(14)
b/Å	14.6185(12)
c/Å	22.679(2)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	5573.9(8)
Z	8
$\rho_{calc}g/cm^3$	1.445

μ/mm^{-1}	0.619
F(000)	2464.0
Crystal size/mm^3	0.145 × 0.125 × 0.086
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.152 to 52.824
Index ranges	-21 ≤ h ≤ 21, -17 ≤ k ≤ 18, -28 ≤ l ≤ 28
Reflections collected	96953
Independent reflections	5714 [R_{int} = 0.1140, R_{sigma} = 0.0401]
Data/restraints/parameters	5714/0/335
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0835
Final R indexes [all data]	R_1 = 0.0698, wR_2 = 0.1042
Largest diff. peak/hole / e Å^{-3}	0.53/-0.56

Mo(DPPF)(CO)$_4$

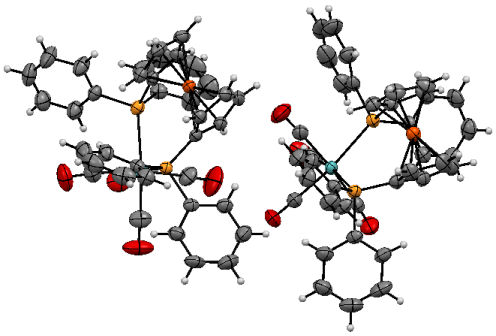


Figure S80. ORTEP drawing of **C-4**.

Table S3: Crystal data and structure refinement for C-4	
Ccdc no.	2241308
Empirical formula	$C_{38}H_{28}FeMoO_4P_2$
Formula weight	762.33
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.3770(7)
b/Å	34.898(3)
c/Å	20.4468(16)
α/°	90
β/°	92.627(3)
γ/°	90
Volume/Å^3	6684.0(9)
Z	8
ρ_{calc}g/cm^3	1.515

μ/mm^{-1}	0.945
F(000)	3088.0
Crystal size/mm^3	0.236 × 0.156 × 0.123
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.502 to 50.892
Index ranges	$-11 \leq h \leq 11$, $-42 \leq k \leq 42$, $-24 \leq l \leq 24$
Reflections collected	87639
Independent reflections	12259 [R_{int} = 0.0926, R_{sigma} = 0.0515]
Data/restraints/parameters	12259/0/829
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0689
Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.0776
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.35

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1. J. Becica, O. D. Glaze, D. I. Wozniak and G. E. Dobereiner, *Organometallics*, 2018, **37**, 482–490.

2. J. Berstler, A. Lopez, D. Ménard, W. G. Dougherty, W. S. Kassel, A. Hansen, A. Daryaei, P. Ashitey, M. J. Shaw, N. Fey and C. Nataro, *J. of Organomet Chem.*, 2012, **712**, 37–45.

3. K. R. Birdwhistell, B. E. Schulz and P. M. Dizon, *Inorg. Chem. Commun*, 2012, **26**, 69–71.