Experimental Supporting Information

Mn(I) Organometallics Containing the $^{i}Pr_2P(CH_2)_2P^{i}Pr_2$ Ligand for the Catalytic Hydration of Aromatic Nitriles

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Characterization of *fac*-[(CO)$_3$Mn(dippe)(Br)] (1)

1 (146.2 mg, 84%). ^{1}H NMR (300 MHz, THF-d_8, δ/ ppm) 3.58 (s, THF), 2.90-2.69 (m, 1H), 2.38-2.22 (m, 1H), 2.18-1.88 (m, 2H), 1.73 (s, THF), 1.47-1.16 (m, 12H). ^{31}P{^{1}H} NMR (121 MHz, THF-d_8, δ/ ppm) 80.45 (s). FTIR (ATR) $\nu_{C\text{-}H}$ (cm^{-1}) 2960.77 m, 2934.09 w, 2898.91 w, 2874.40 w; $\nu_{C\text{-}O}$ (cm^{-1}) 2001.29 s, 1921.98 s, 1885.76 s. Anal. Calcd for **1**, $C_{17}H_{32}BrMnO_3P_2$: C, 42.43; H, 6.70. Found: C, 42.46; H, 6.83.

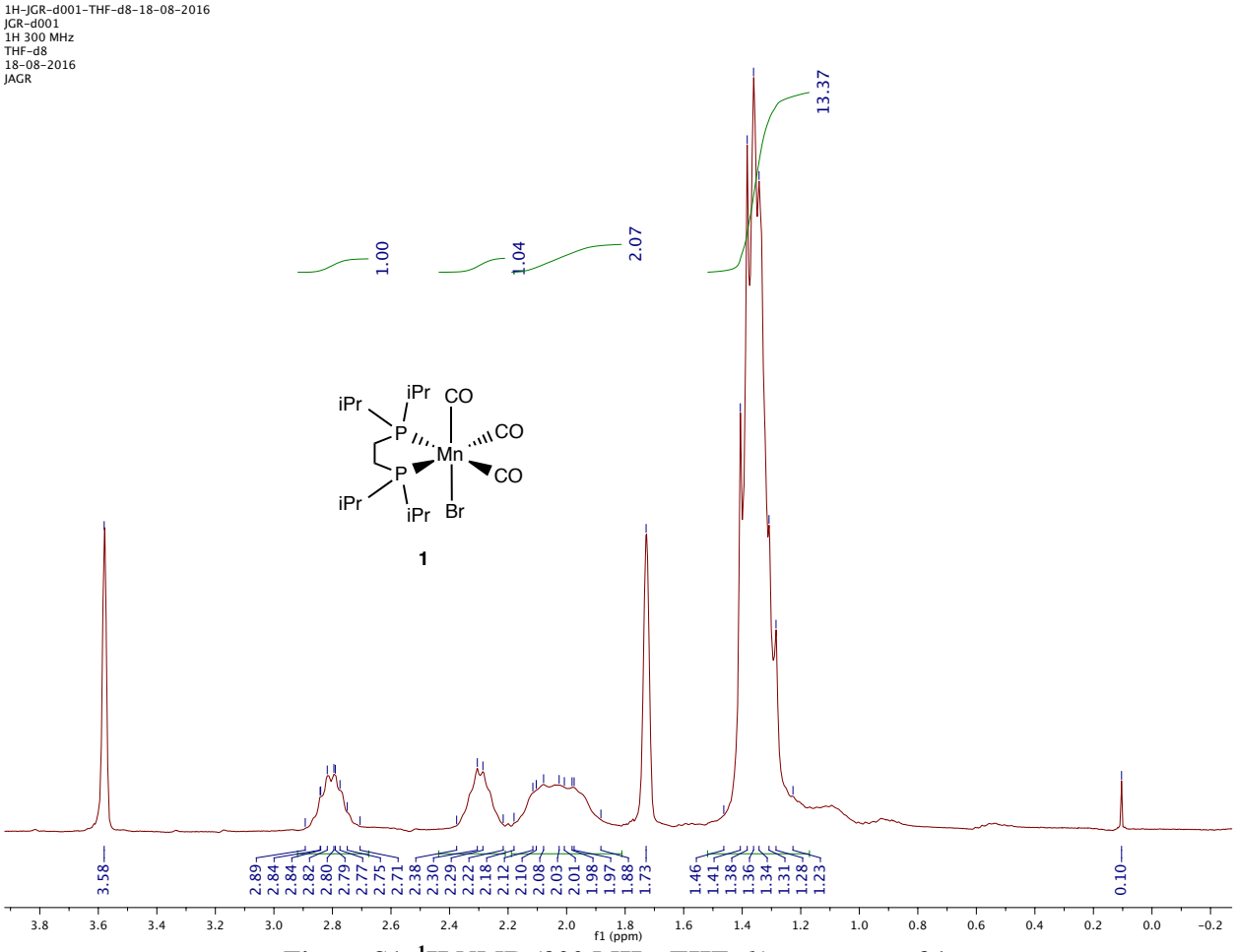

Figure S1. ^{1}H NMR (300 MHz, THF-d_8) spectrum of 1.

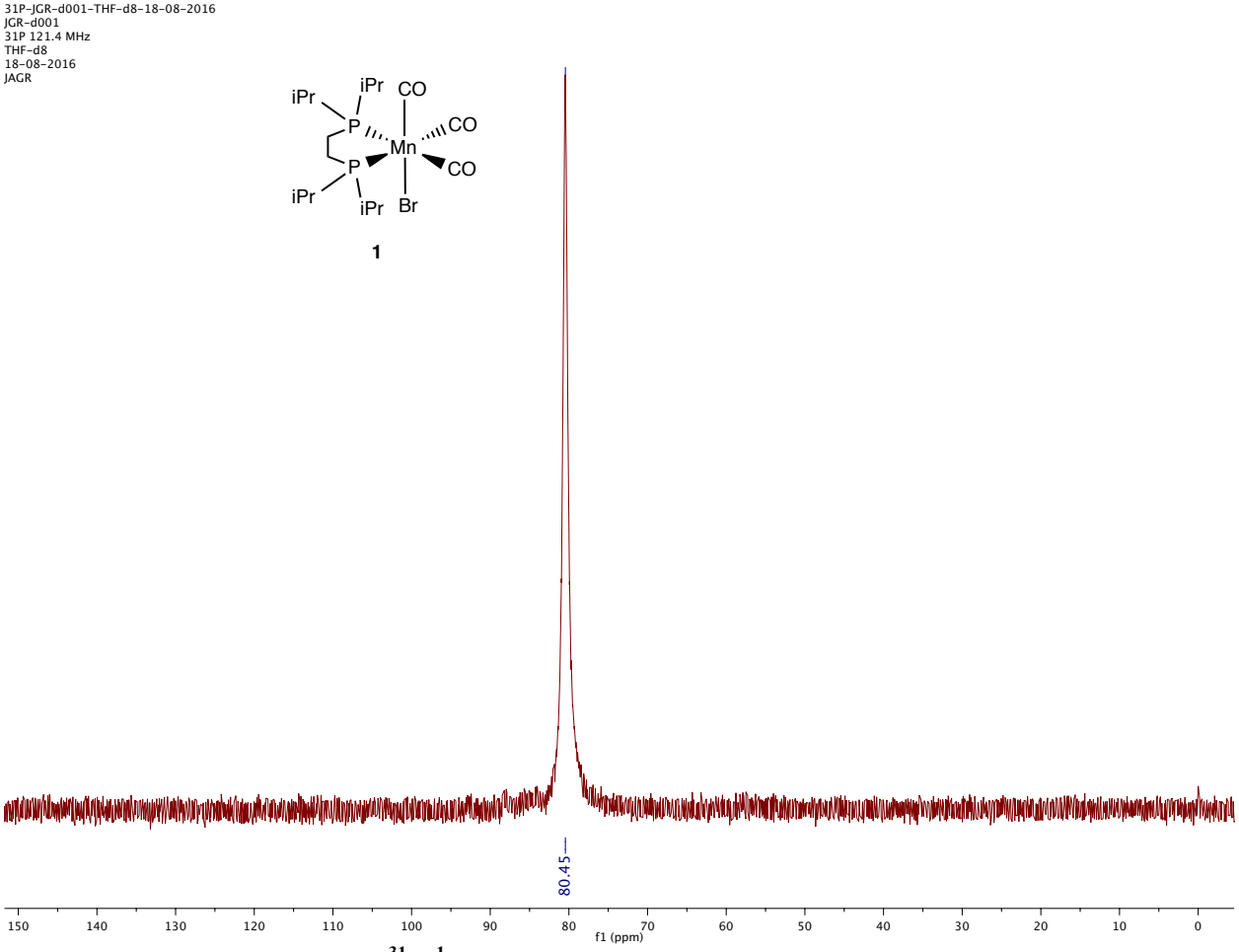

Figure S2. $^{31}P\{^{1}H\}$ NMR (121 MHz, THF-d_8) spectrum of 1.

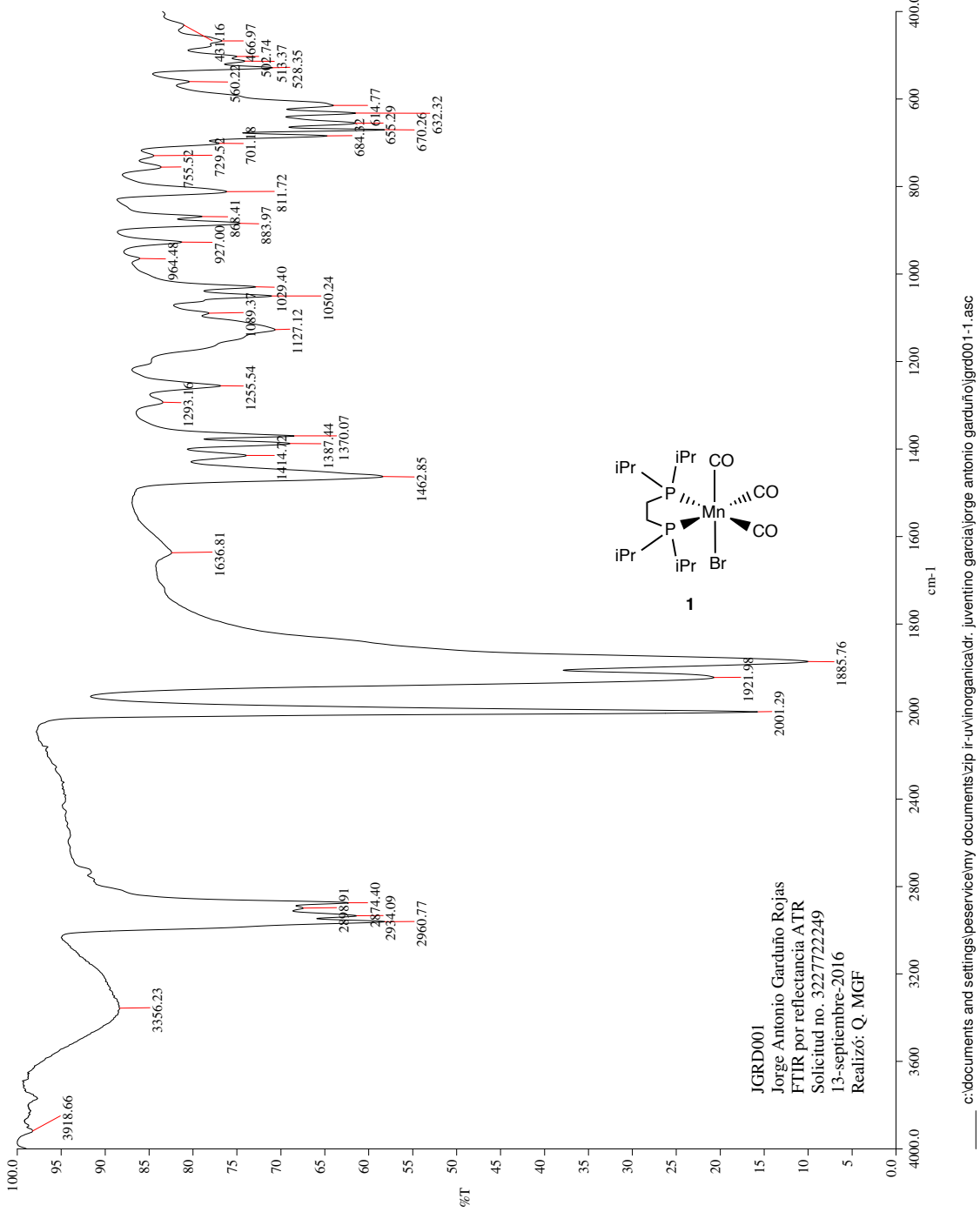

Figure S3. FTIR (ATR) spectrum of 1.

Procedure S1. Assays of air-stability for 1

1 (5 mg) was exposed to air in the solid state, dissolved in $CDCl_3$ (0.5 mL) and placed into an NMR tube. This solution was monitored both after 20 min and one week. Recorded spectra are as follows:

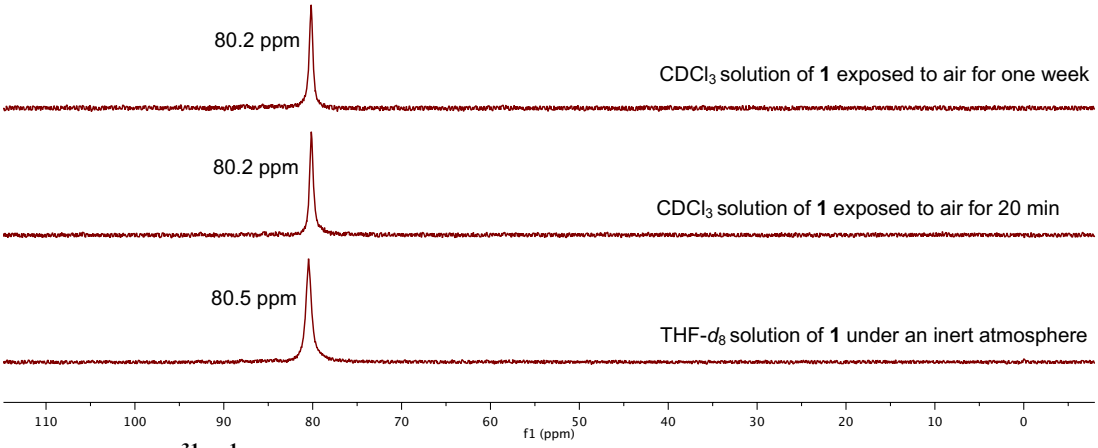

Figure S4. $^{31}P\{^1H\}$ NMR (121 MHz) analysis of a $CDCl_3$ solution of 1 exposed to air.

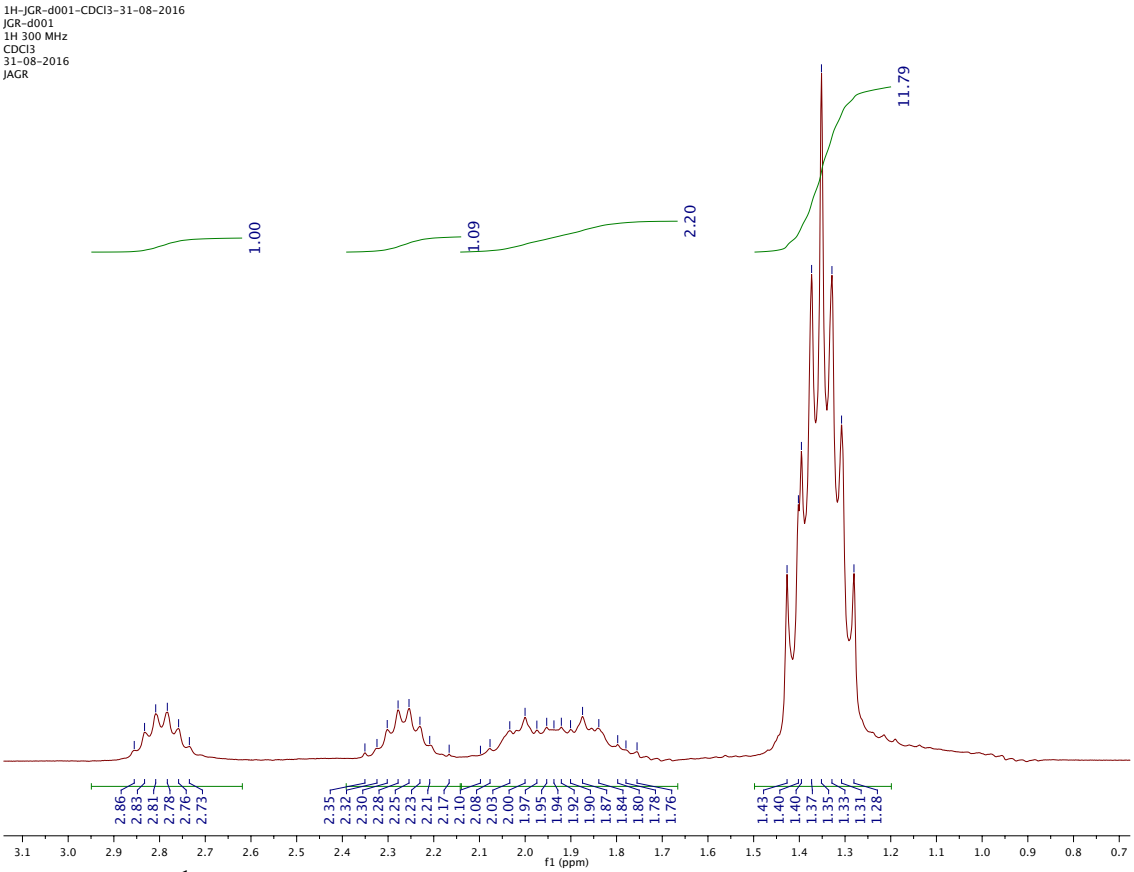

Figure S5. ^1H NMR (300 MHz) of a $CDCl_3$ solution of 1 exposed to air for one week.

Characterization of for *fac*-[$(CO)_3Mn(dippe)(OSO_2CF_3)$] (2)

2 (43.4 mg, 75%). ^{1}H NMR (300 MHz, THF-d_8, δ/ ppm) 2.53-2.27 (m, 1H), 2.18-2.00 (m, 1H), 1.47-1.30 (m, 6H). $^{31}P\{^{1}H\}$ NMR (121 MHz, THF-d_8, δ/ ppm) 85.74 (s). ^{19}F NMR (282 MHz, THF-d_8, δ/ ppm) -78.19 (s). FTIR (ATR) ν_{C-H} (cm^{-1}) 2968.39 m, 2941.35 w, 2881.54 w; ν_{C-O} (cm^{-1}) 2021.57 s, 1957.71 s, 1895.22 s. Anal. Calcd for **2**, $C_{18}H_{32}F_3MnO_6P_2S$: C, 39.28; H, 5.86; S, 5.82. Found: C, 38.44; H, 5.88; S, 5.75.

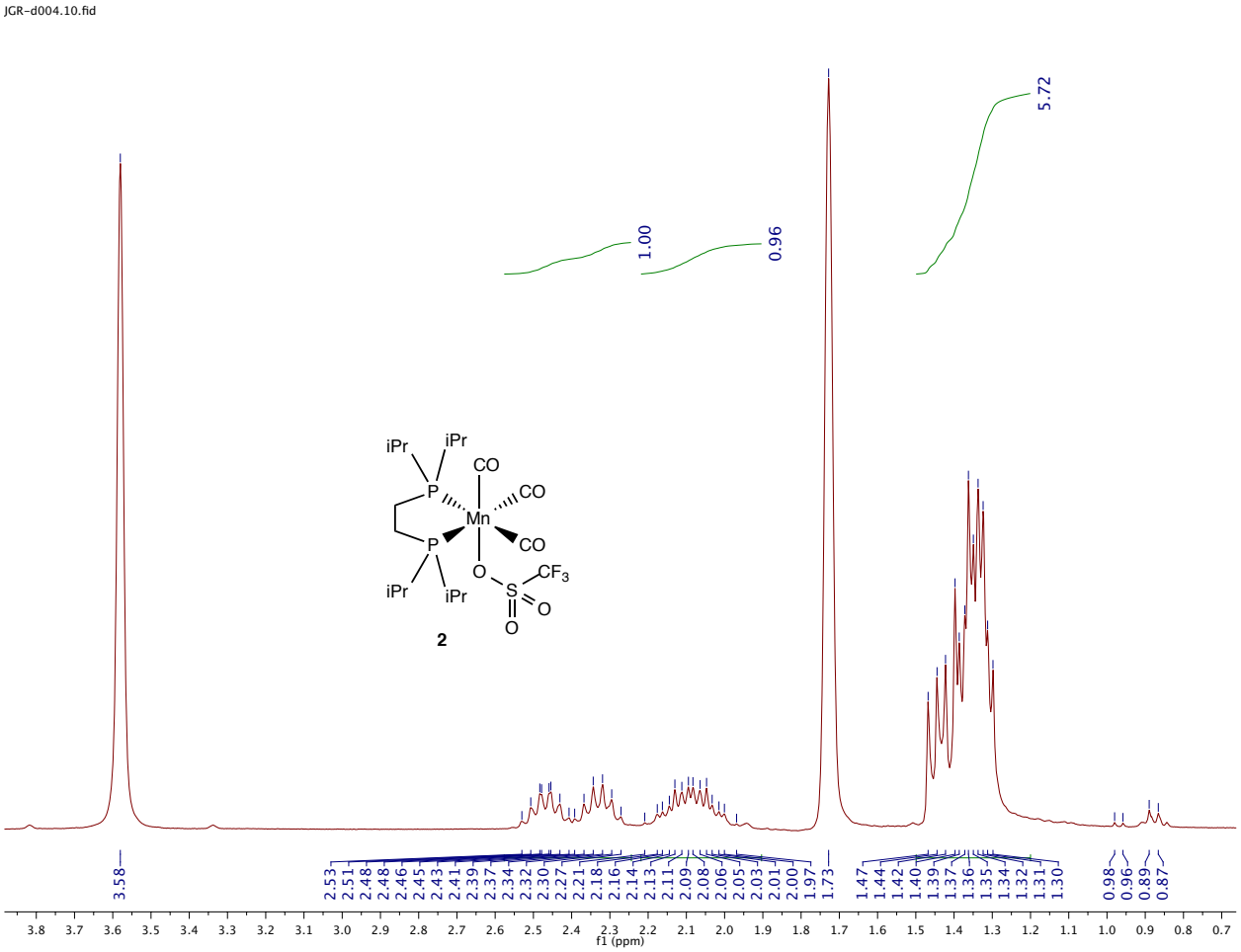

Figure S6. ^{1}H NMR (300 MHz, THF-d_8) spectrum of 2

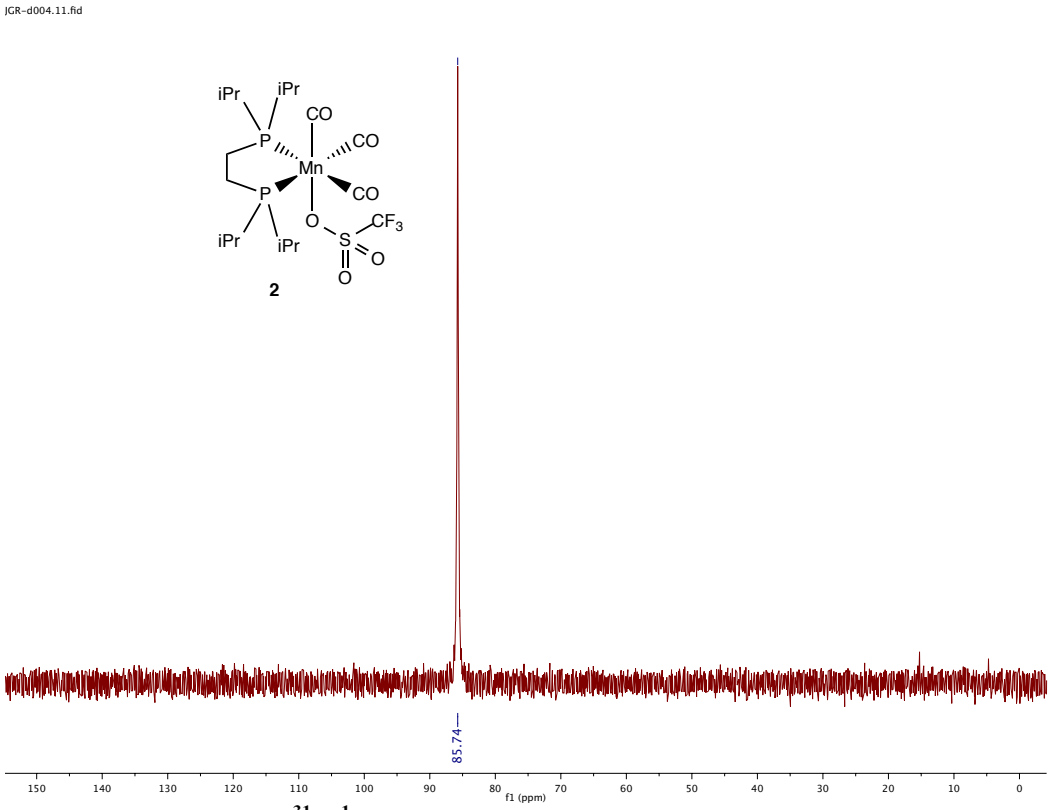

Figure S7. $^{31}P\{^{1}H\}$ NMR (121 MHz, THF-d_8) spectrum of 2.

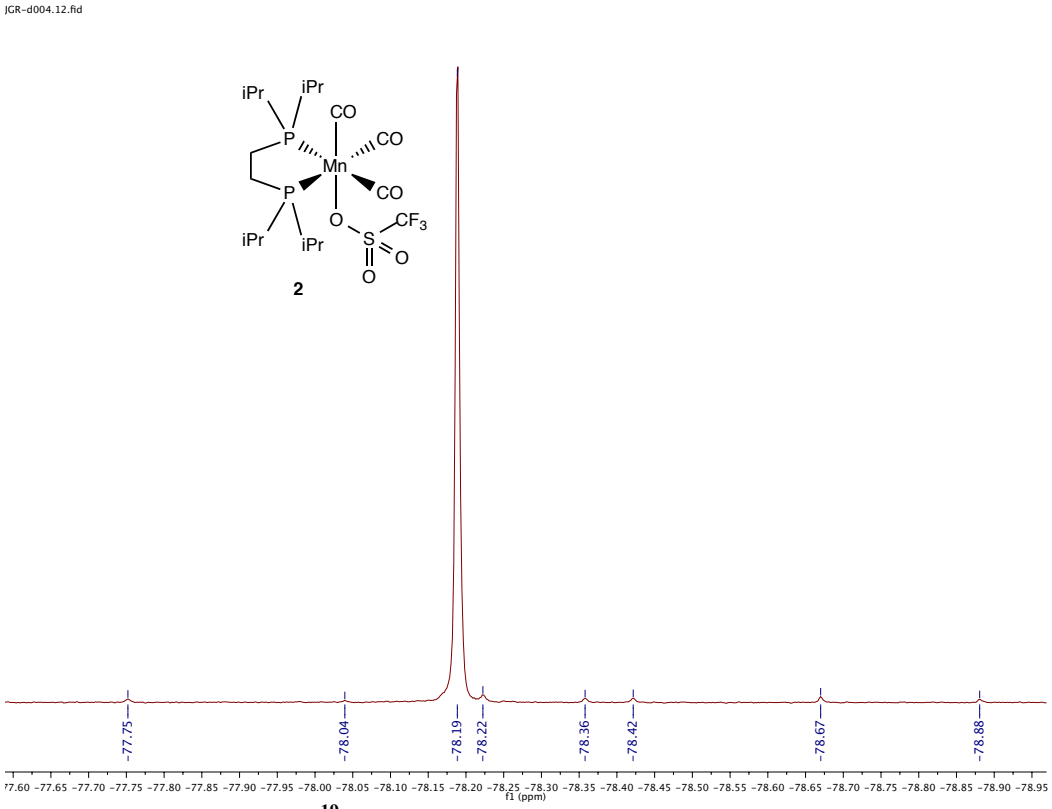

Figure S8. ^{19}F NMR (282 MHz, THF-d_8) spectrum of 2.

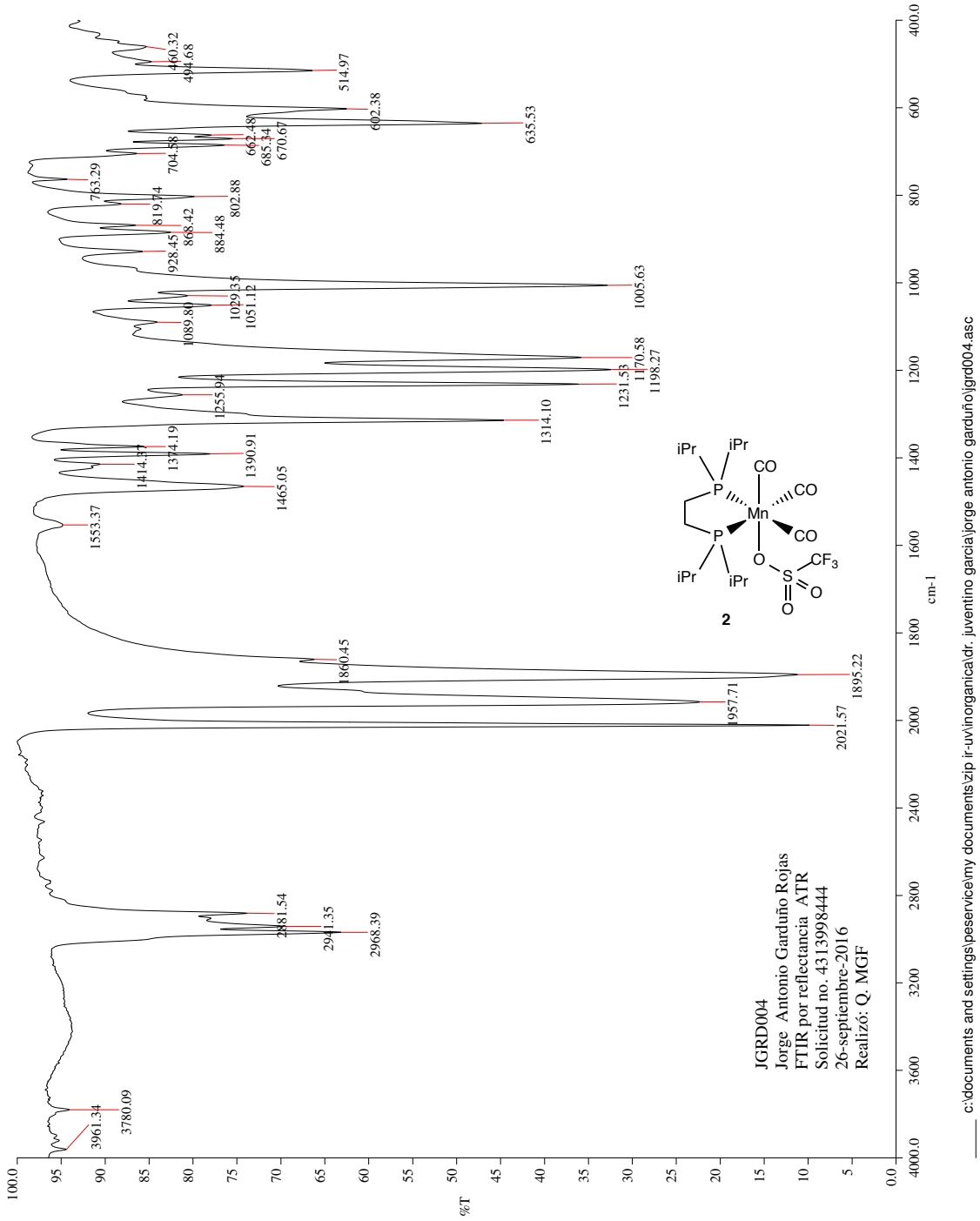

Figure S9. FTIR (ATR) spectrum of 2.

Characterization of *fac*-[(CO)$_3$Mn(dippe)(κ^1-PhCN)](OSO$_2$CF$_3$) (3)

3 (30.9 mg, 85%). ^{1}H NMR (300 MHz, THF-d_8, δ/ ppm) 8.06-7.49 (m, 5H), 3.58 (s, THF), 2.78-1.94 (m, 8H), 1.73 (s, THF), 1.53-1.23 (m, 24 H). ^{31}P{^{1}H} NMR (121 MHz, THF-d_8, δ/ ppm) **3**, 87.03 (s); **2**, 85.74 (s). ^{19}F NMR (282 MHz, THF-d_8, δ/ ppm) -78.17. FTIR (ATR) $\nu_{C\text{-}H}$ (cm^{-1}) 2965.79 w, 2939.65 w, 2878.40 w, 2903.02 w; $\nu_{C\text{-}N}$ (cm^{-1}) 2250.91 vw; $\nu_{C\text{-}O}$ (cm^{-1}) 2021.53 s, 1937.65 s, 1921.16 s. Anal. Calcd for **3**, $C_{25}H_{37}F_3MnNO_6P_2S$: C, 45.95; H, 5.71; N, 2.14; S, 4.91. Found: C, 44.06; H, 5.77; N, 2.00; S, 5.03.

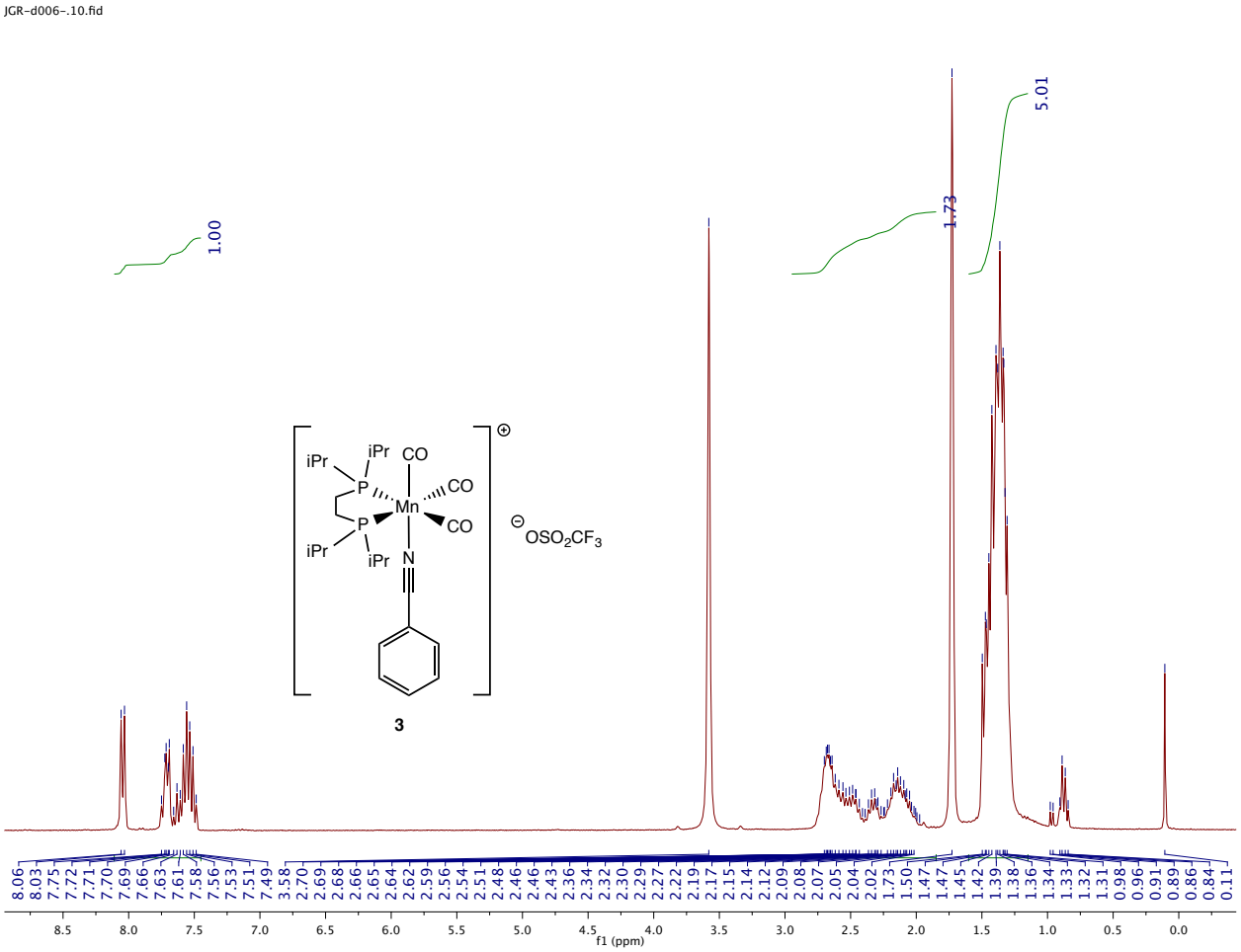

Figure S10. ^{1}H NMR (300 MHz, THF-d_8) spectrum of 3.

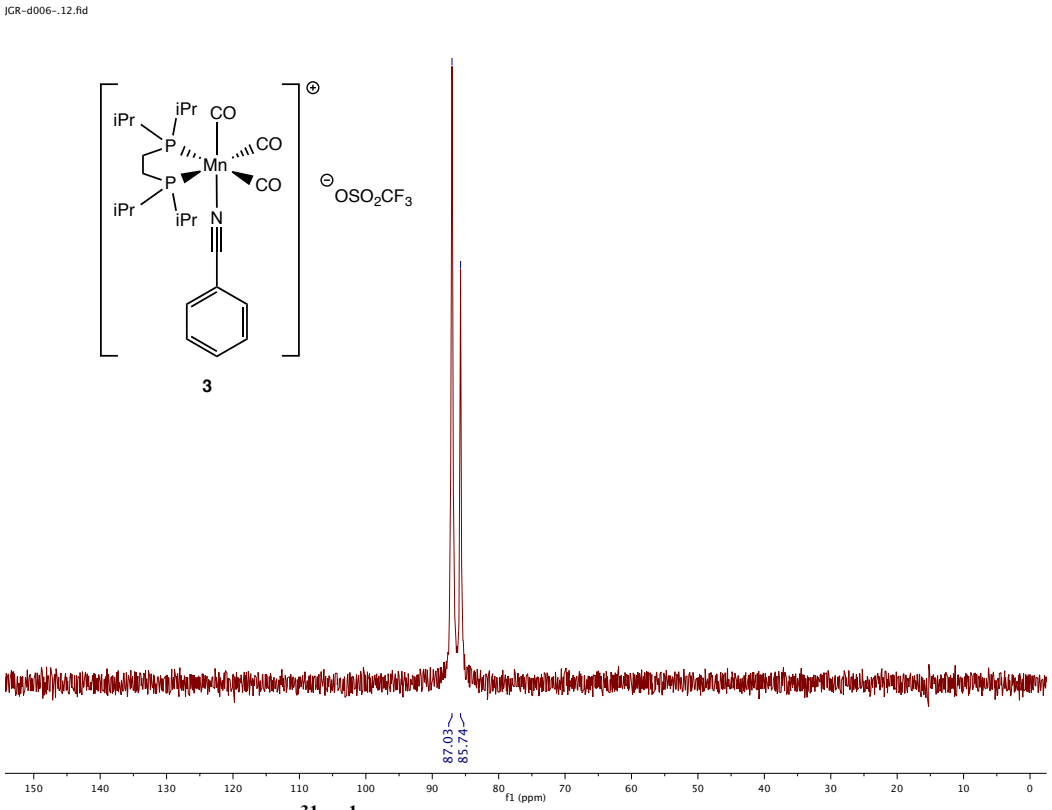

Figure S11. $^{31}P\{^{1}H\}$ NMR (121 MHz, THF-d_8) spectrum of 3.

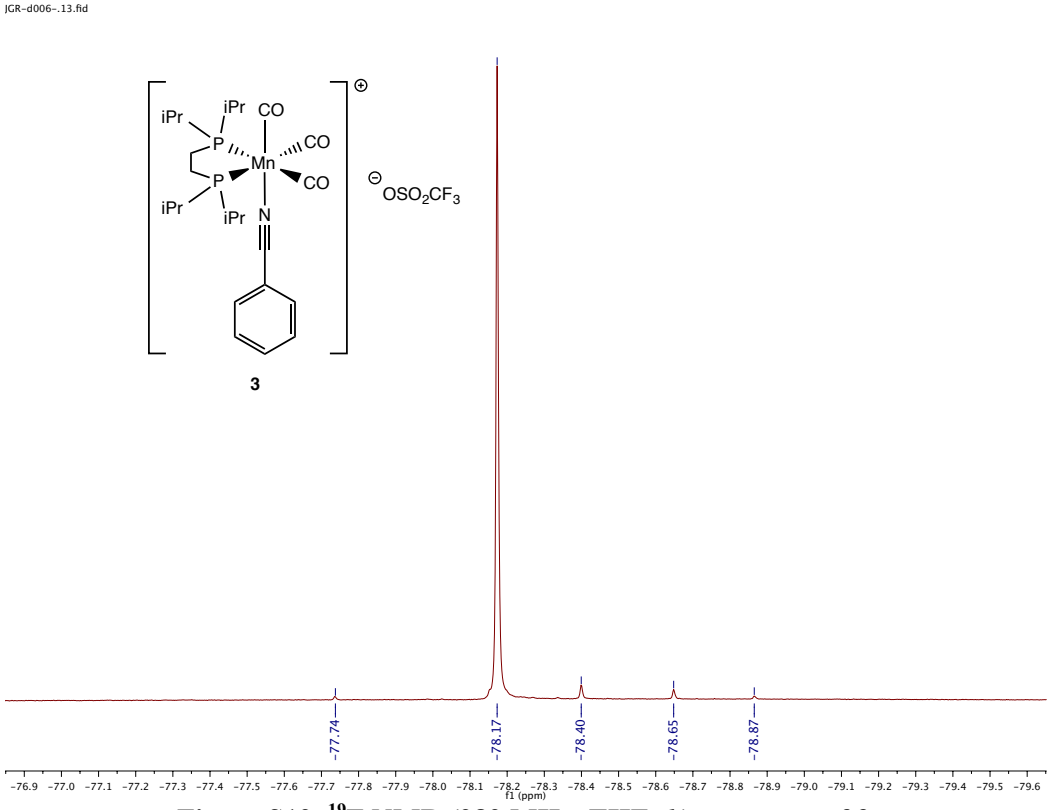

Figure S12. ^{19}F NMR (282 MHz, THF-d_8) spectrum of 3.

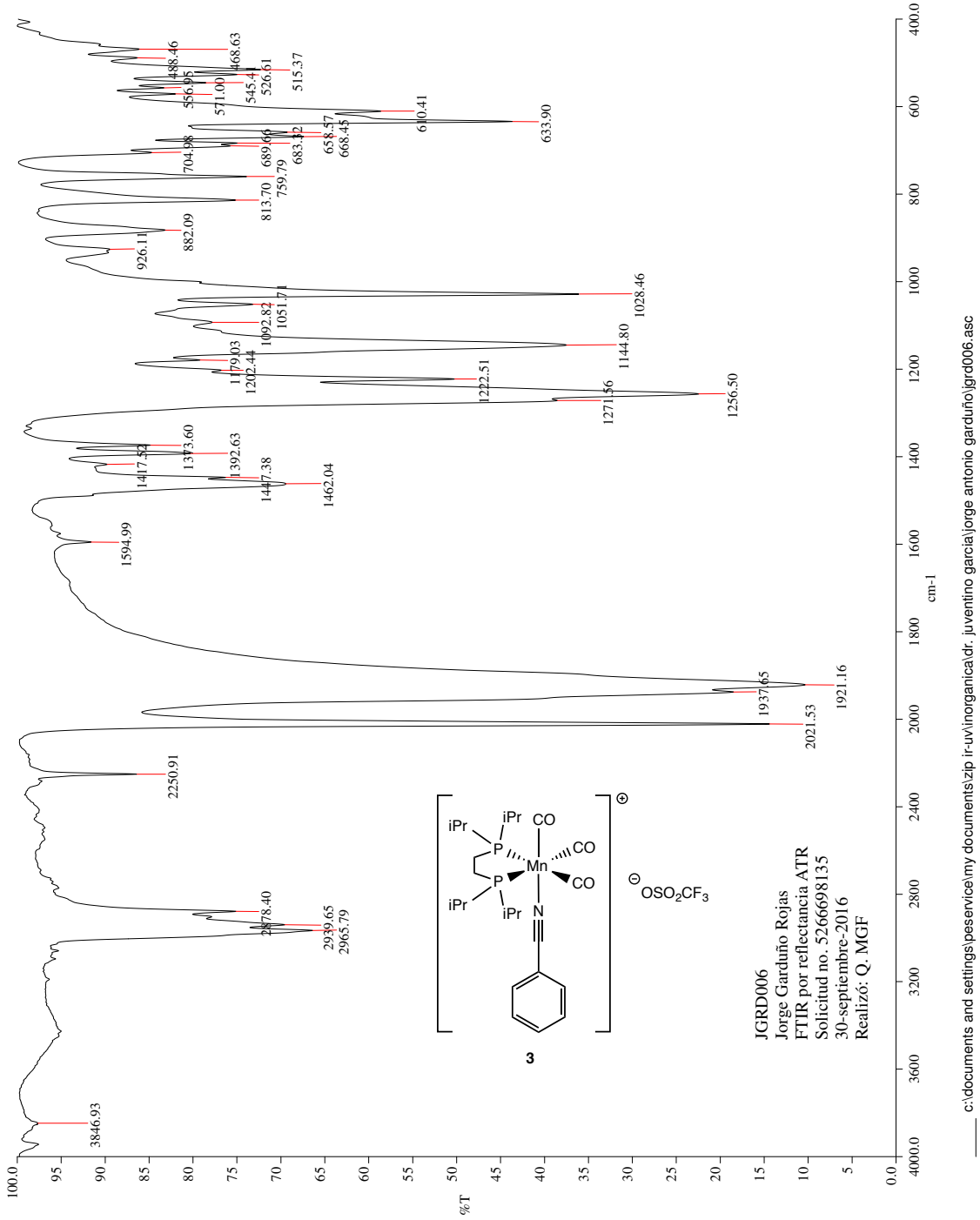

Figure S13. FTIR (ATR) spectrum of 3.

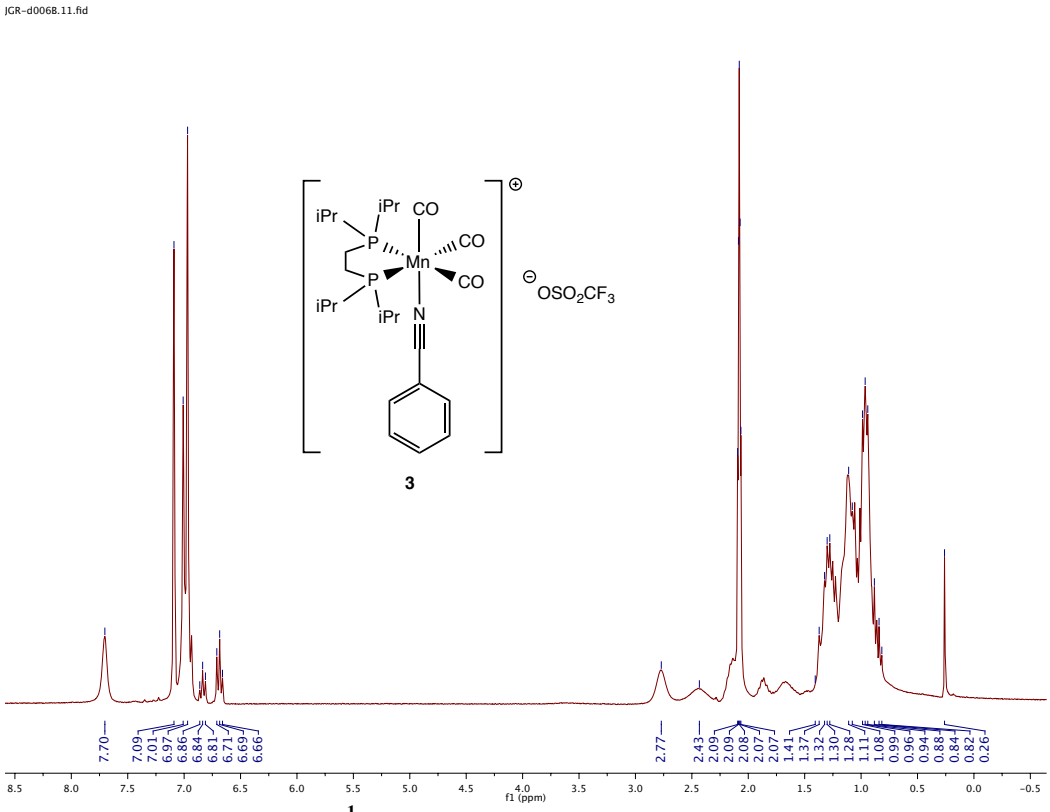

Figure S14. ^{1}H NMR (300 MHz, C_7D_8) spectrum of 3.

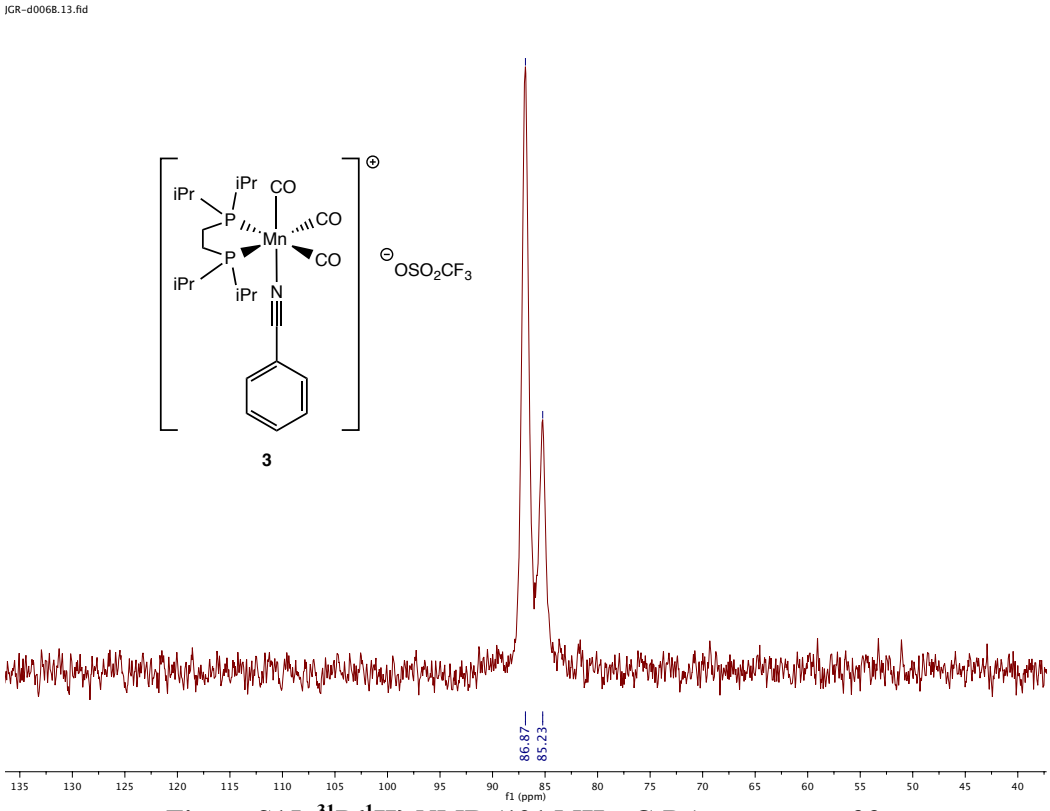

Figure S15. ^{31}P{^{1}H} NMR (121 MHz, C_7D_8) spectrum of 3.

Procedure S2. Competence for a vacant site in the "*fac*-[(CO)$_3$Mn(dippe)]" core

In the glovebox, **3** (11 mg, 0.017 mmol) was dissolved in the minimal amount of THF-d_8. To this pale-yellow solution was added a colorless THF-d_8 solution of benzonitrile (5.3 mg, 0.051 mmol) to form a yellow solution, which was placed in a Wilmad NMR tube equipped with a J. Young valve and stirred for 20 minutes. An NMR analysis of this solution was performed. After that, in the glovebox, benzonitrile (29.8 mg, 0.29 mmol) was added to the same mixture and the almost colorless solution formed was stirred inside the same NMR tube for 20 minutes. A new NMR analysis of the solution was performed. Recorded spectra are as follows:

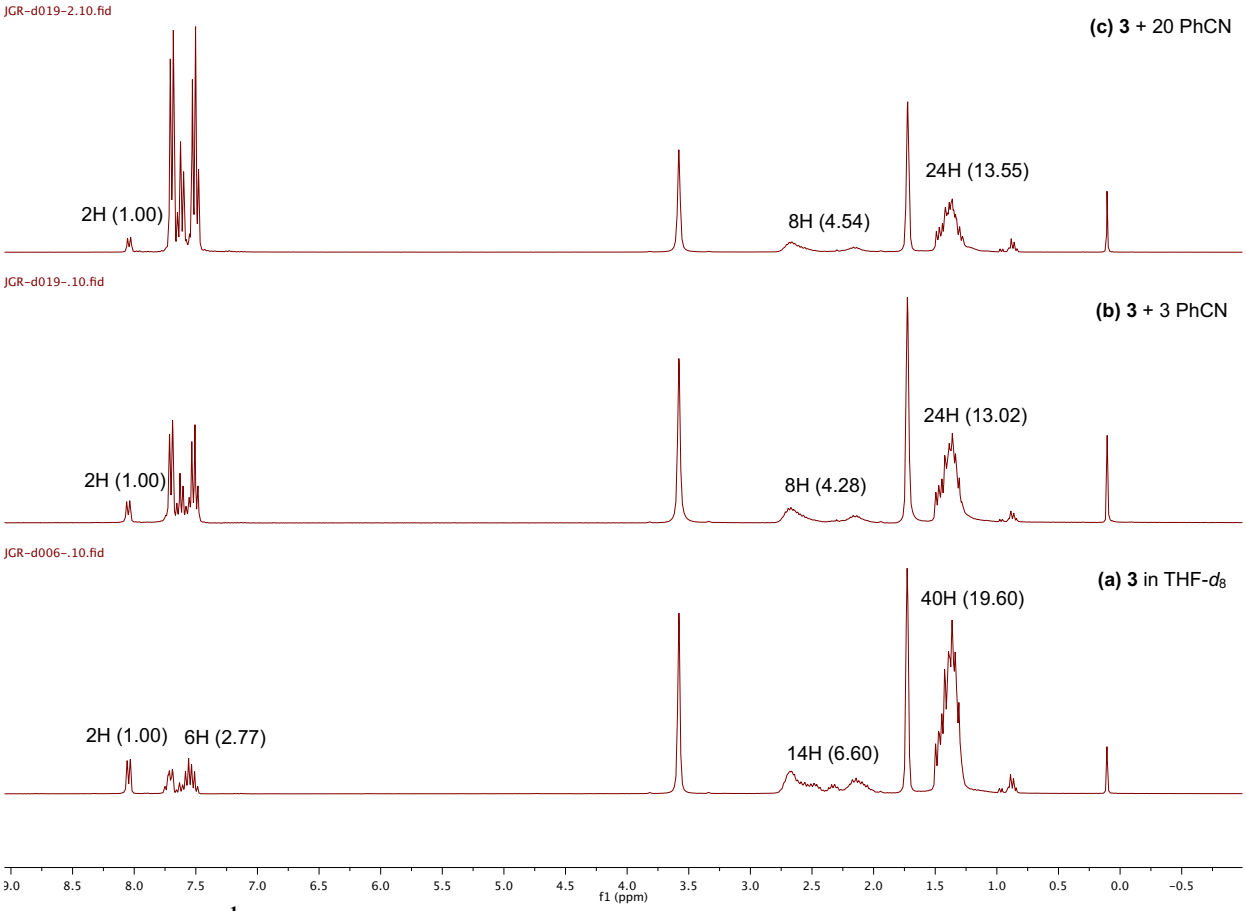

Figure S16. ^{1}H NMR (300 MHz) spectra for 3 in THF-d_8 solution and with added PhCN.

NOTE: In the figure above: **(a) 3** as synthesized and purified in THF-d_8 solution with no extra PhCN added; **(b) 3** in THF-d_8 solution with 3 equivalents of PhCN added; and **(c) 3** in THF-d_8 solution with 20 equivalents of PhCN added. Above each assigned signal are shown values for the integrals. In parentheses are shown the actual integral values as extracted from the spectra. From the integrals on trace **(a)** it is inferred some PhCN dissociates when 3 is in solution. In traces **(b)** and **(c)** the values in parentheses approximate to the expected integral values for **3**, so in the presence of an excess PhCN, species **3** becomes predominant in solution.

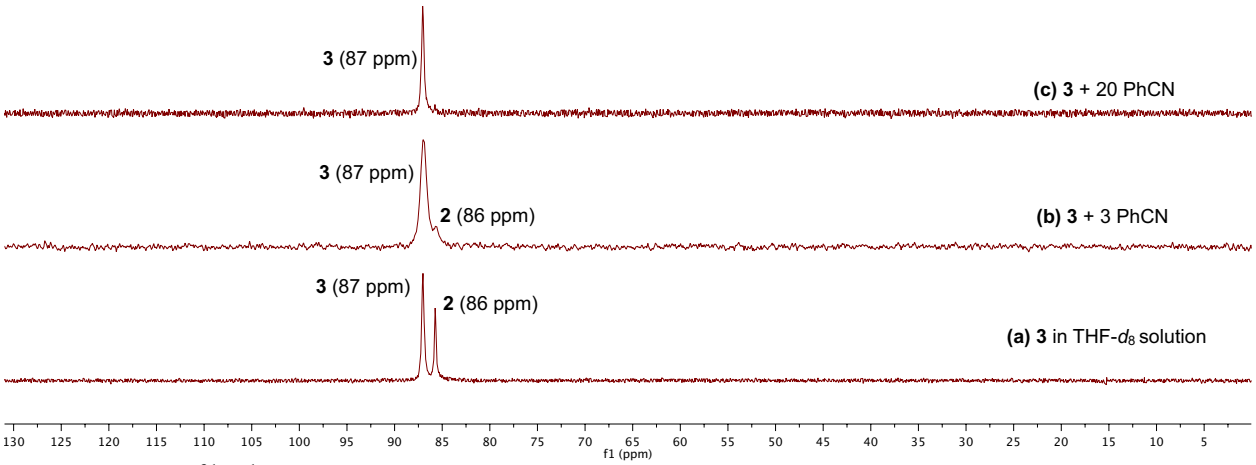

Figure S17. $^{31}P\{^{1}H\}$ NMR (121 MHz) spectra for 3 in THF-d_8 solution and with PhCN added.

NOTE: In Figure S17: **(a) 3** as synthesized and purified in THF-d_8 solution with no extra PhCN added; **(b) 3** in THF-d_8 solution with 3 equivalents of PhCN added; and **(c) 3** in THF-d_8 solution with 20 equivalents of PhCN added. Signals are assigned to species **2** (86 ppm) and **3** (87 ppm) coexisting in solution in trace **(a)**. On increasing the concentration of PhCN [traces **(b)** and **(c)]**, species **3** becomes predominant.

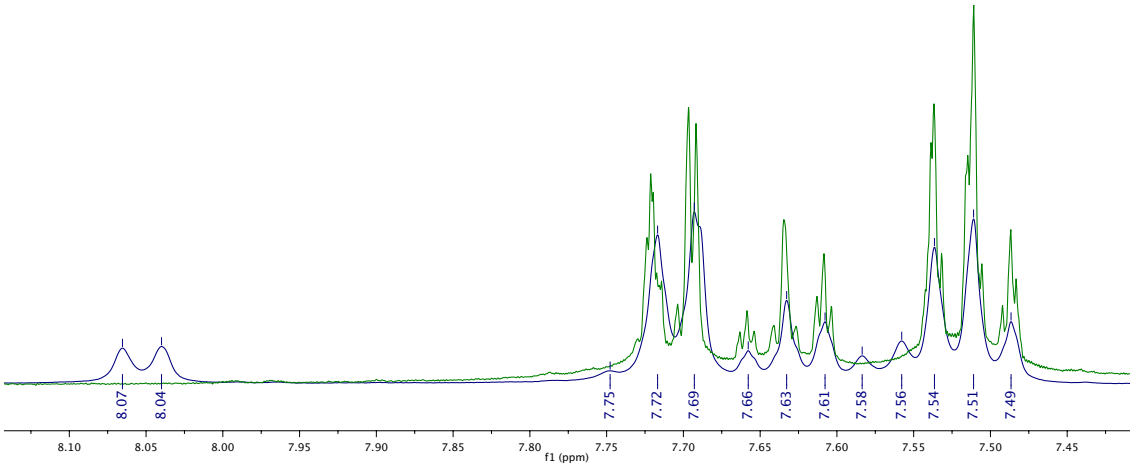

Figure S18. ^{1}H NMR (300 MHz, THF-d_8) of free and coordinated benzonitrile.

NOTE: In Figure S18: the green trace displays the signals for free benzonitrile and the blue trace corresponds to a mixture of free and coordinated benzonitrile in complex **3**. Blue trace was taken from the aromatic region of trace b in Figure S16.

Procedure S3. Thermolysis of 4 in a 1:2 *v*/*v* mixture of THF-d_8/H_2O

In a Wilmad NMR tube equipped with a J. Young valve, **2** (5 mg, 0.0092 mmol) was dissolved in THF-d_8 (0.5 mL) and then H_2O (1 mL, 0.055 mmol) was added. The readily formed yellow solution was heated in an oil bath at 100 ºC for 6 h and then for 12 h to complete a total heating time of 18 h. $^{31}P\{^1H\}$ NMR analysis of the mixture at t = 0, 6 h, and 18 h, were performed at room temperature. Recorded spectra are as follows:

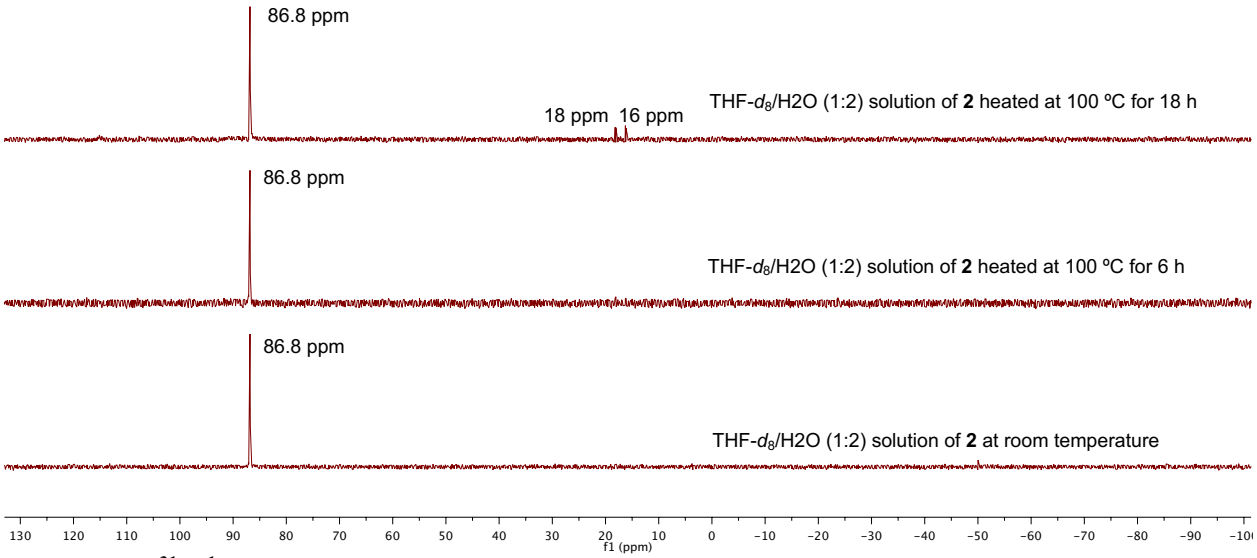

Figure S19. $^{31}P\{^1H\}$ NMR (121 MHz) monitoring of a THF-d_8/H_2O (1:2 v/v) solution of 2 at variable temperature.

NOTE: Upon the addition of excess water to a THF-d_8 solution of **2**, the corresponding chemical shift changes from δ_P 85.7 ppm (See Figure S7) to δ_P 86.8. On the basis of the observed phenomena when increasing the amount of a neutral donor molecule in the medium, namely benzonitrile (See Figure S17), the new signal at 86.8 ppm is proposed to stem from species *fac*-[$(CO)_3$Mn(dippe)(OH_2)](OTf) **(4)**.

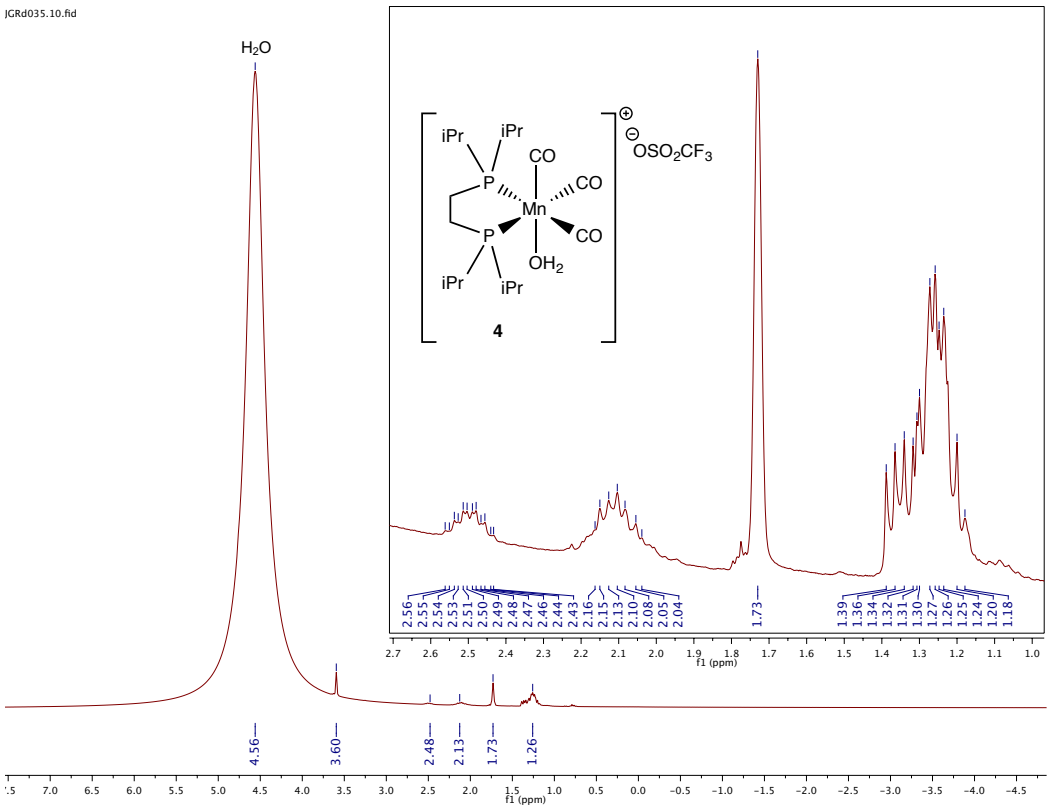

Figure S20. ^{1}H (300 MHz) spectrum of a THF-d_8/H_2O (1:2 v/v) solution of 2 at room temperature.

Procedure S4. $^{31}P\{^{1}H\}$ NMR analysis of the binding of benzamide to the "*fac*-[$(CO)_3$Mn(dippe)]$^{+}$" core

In the glovebox, **2** (15 mg, 0.027 mmol) was dissolved in the minimal amount of THF-d_8. To this yellow solution was added a colorless THF-d_8 solution of benzamide (3.3 mg, 0.027 mmol) to form a yellow solution, which was placed in a Wilmad NMR tube equipped with a J. Young valve and stirred for 20 minutes. An NMR analysis of this solution was performed. After that, in the glovebox, to the same mixture was added benzamide (29 mg, 0.24 mmol) and the yellow solution formed was stirred inside the same NMR tube for 20 minutes. A new NMR analysis of the solution was performed. Recorded spectra are as follows:

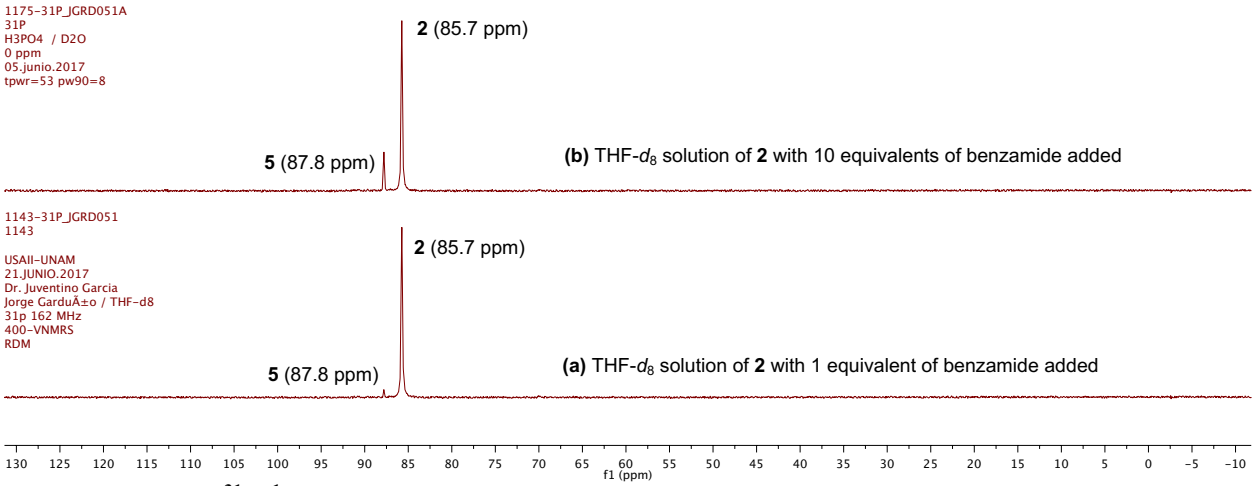

Figure S21. $^{31}P\{^{1}H\}$ NMR spectra for the addition of benzamide to a THF-d_8 solution of 2

NOTE: Upon the addition of excess benzamide to a THF-d_8 solution of **2**, a new signal is observed at δ_P 87.8. On the basis of the observed phenomena when increasing the amount of a neutral donor molecule in the medium, namely benzonitrile (See Figure S17), new signal at 87.8 ppm is proposed to stem from species *fac*-[$(CO)_3$Mn(dippe)(PhC(O)NH_2)](OTf) **(5)**.

Procedure S5. $^{31}P\{^{1}H\}$ NMR analysis of the model reaction crude.

In the glovebox, a colorless THF solution of benzonitrile (47.3 mg, 0.46 mmol) was added dropwise to a yellow THF solution of **2** (5 mg, 0.0092 mmol). The readily formed yellow solution was transferred to a 25 mL Schlenk tube (Synthware Glass) (1 mL THF total volume), to which water (2 mL, 111 mmol) was added to form a pale-yellow emulsion. The reaction mixture was stirred into an oil bath at 100 ºC during 18 h. After that, the solvent and volatiles were removed under reduced pressure in the inert gas/ vacuum double manifold and the residue was dried under vacuum for 4 h. Taking care to not expose the remaining mixture to the air, this was dissolved in THF-d_8 inside the glovebox and transferred to a Wilmad NMR tube equipped with a J. Young valve to perform the corresponding analysis of the readily formed yellow solution.

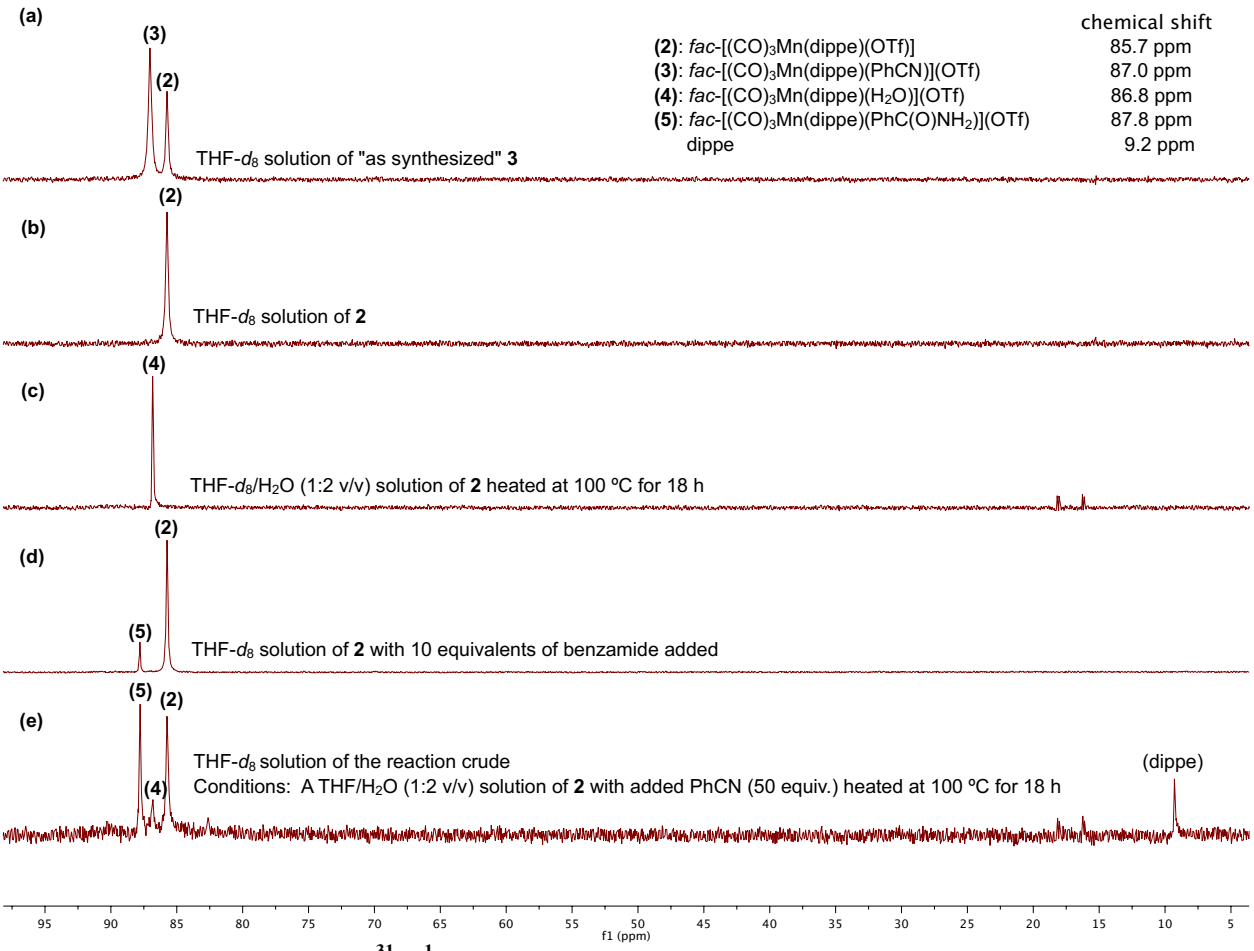

Figure S22. $^{31}P\{^1H\}$ NMR spectrum of the model reaction crude.

NOTE: In the (e) trace is displayed the spectrum recorded after performing the experiment described in **Procedure** S5. The (a) to (d) upper traces are included for comparative purposes.

Procedure S6. NMR analysis of the addition of water to a mixture of 2 and excess benzonitrile.

In the glovebox, **2** (20.4 mg, 0.037 mmol) was dissolved in the minimal amount of THF-d_8. To this yellow solution was added a colorless THF-d_8 solution of benzonitrile (192 mg, 1.86 mmol) to form a yellow solution, which was placed in a Wilmad NMR tube equipped with a J. Young valve and stirred for 20 minutes to finally yield a pale-yellow solution. An NMR analysis of this solution was performed. After that, in the glovebox, to the same mixture was added water (1 μL, 0.056 mmol) and the yellow solution formed was stirred inside the same NMR tube for 20 minutes. A new NMR analysis of the solution was performed. Finally, in the glovebox, to the same mixture was added water (32 μL, 1.78 mmol) and the yellow solution formed was stirred inside the same NMR tube for 20 minutes. A final NMR analysis of the solution was performed. Recorded spectra are as follows:

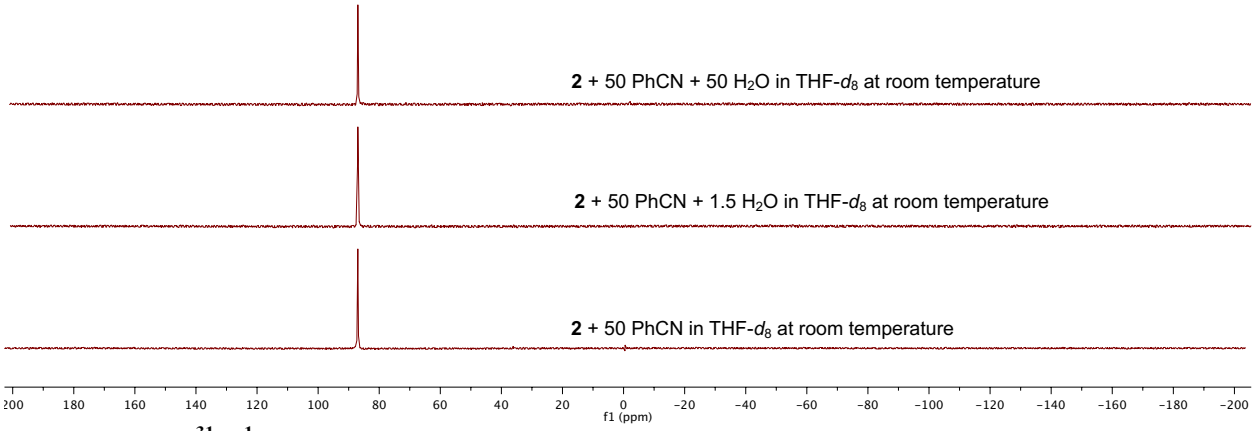

Figure S23. $^{31}P\{^{1}H\}$ (162 MHz) spectra for the addition of water to a THF-d_8 solution of 2 and excess benzonitrile.

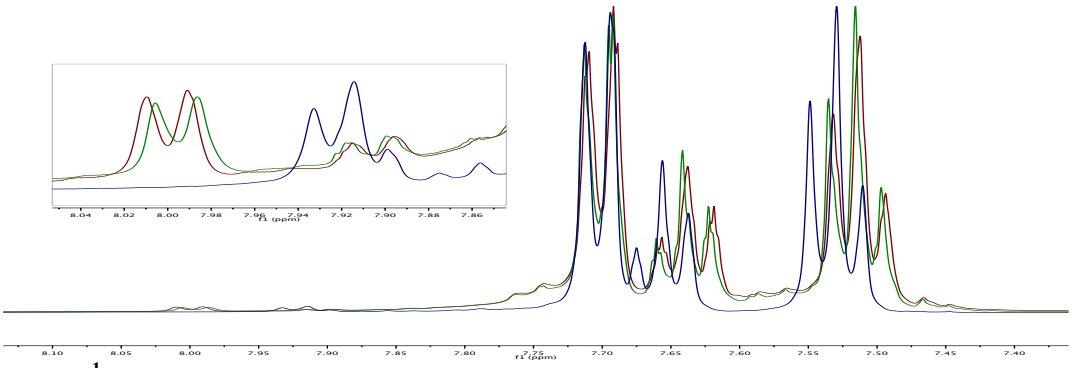

Figure S24. ^{1}H (400 MHz) spectra for the addition of water to a THF-d_8 solution of 2 and excess benzonitrile.

NOTE: In the ^{1}H NMR spectra, upon the addition of water [0 equiv (red trace), 1.5 equiv (green trace), and 50 equiv (blue trace)] to a THF-d_8 solution of **2** and 50 equiv of benzonitrile, the signature signal for coordinated benzonitrile shown in the inset is still observed (to compare see Figure S18). Additionally, in the $^{31}P\{^{1}H\}$ spectra only one signal is observed, corresponding to complex **3**, indicating that under these conditions water does not substitute benzonitrile at the [Mn] core.

Procedure S7. NMR monitoring of the actual model reaction mixture.

In the glovebox, a THF-d_8 colorless solution of benzonitrile (47.3 mg, 0.46 mmol) was added dropwise to a yellow THF-d_8 solution of **2** (5 mg, 0.0092 mmol). The readily formed yellow solution was transferred to a Wilmad NMR tube equipped with a J. Young valve (0.6 mL THF total volume), to which water (1 mL, 56 mmol) was added to form a pale-yellow emulsion. An NMR analysis of the as prepared mixture (aqueous layer) was performed at room temperature. Then, the reaction mixture was heated into an oil bath at 100 ºC for 3 h during which a pale-yellow solution was observed inside the NMR tube. After that, acquisition of NMR spectra was performed at room temperature. Finally, the reaction mixture was heated

into an oil bath at 100 ºC during 6 h (accumulated time of 9 h) and new NMR spectra were recorded at room temperature.

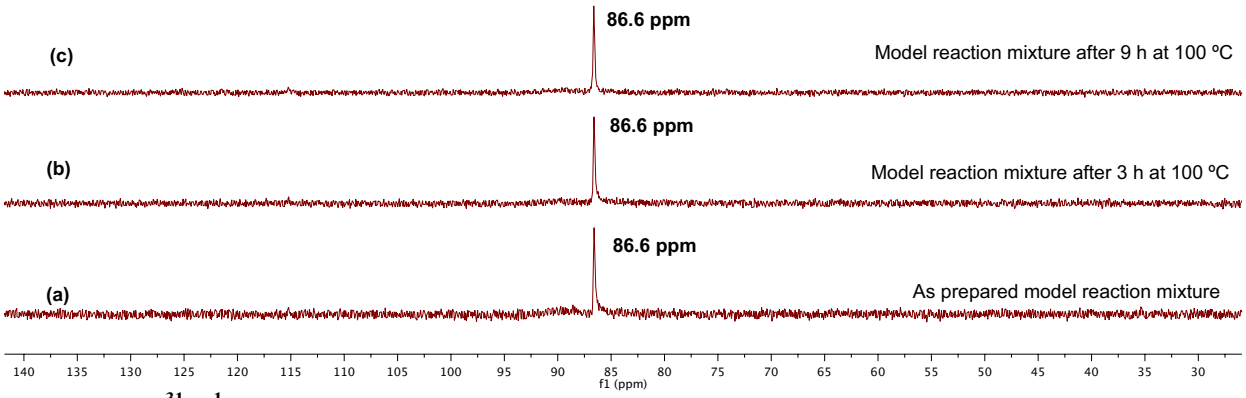

Figure S25. $^{31}P\{^{1}H\}$ NMR (121 MHz, THF-d_8) monitoring of the reaction between benzonitrile and water catalyzed by 2.

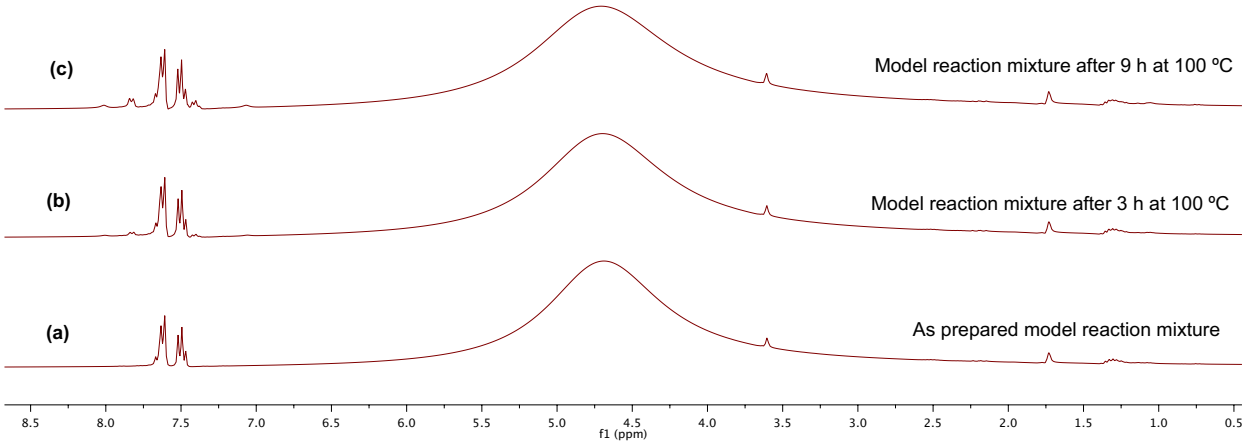

Figure S26. ^{1}H NMR (300 MHz, THF-d_8) monitoring of the reaction between benzonitrile and water catalyzed by 2.

Procedure S8. Single crystal X-Ray Diffraction for 2

In the glovebox, a freshly synthesized batch of **2** (20 mg, 0.036 mmol) was dissolved in toluene (about 1 mL). The yellow solution was stored at -30 ºC for 48 h under an argon atmosphere, after which yellow crystals were obtained. Before analysis, the solid was protected with Fluorolube®.

Table S1. Crystal data and structure refinement for **2**.

Identification code	**2**
Empirical formula	$C_{18}\ H_{32}\ F_3\ Mn\ O_6\ P_2\ S$
Formula weight	550.37
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P\ 2_1\ 2_1\ 2_1$
Unit cell dimensions	a = 8.6949(6) Å b = 13.9549(9) Å c = 19.9508(15) Å
Volume	2420.8(3) $Å^3$
Z	4
Density (calculated)	1.510 Mg/m^3
Absorption coefficient	0.818 mm^{-1}
F(000)	1144
Crystal size	0.400 x 0.130 x 0.030 mm^3
Theta range for data collection	3.394 to 25.347°.
Index ranges	-6<=h<=10, -14<=k<=16, -24<=l<=16
Reflections collected	6815
Independent reflections	4087 [R(int) = 0.1015]
Completeness to theta = 25.347°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4087 / 3 / 277
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0766, wR2 = 0.1661
R indices (all data)	R1 = 0.1202, wR2 = 0.1970
Absolute structure parameter	0.03(4)
Largest diff. peak and hole	0.769 and -0.549 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

x	x	y	z	U(eq)	
C(1)	3651(13)	5646(10)	6474(7)	40(3)	
C(2)	3487(16)	5518(11)	5757(8)	63(4)	
C(3)	4850(20)	4921(12)	4492(9)	75(3)	
C(4)	5077(18)	5826(12)	4132(7)	70(4)	
C(6)	5040(20)	3671(12)	5702(9)	75(3)	
C(9)	5891(14)	5534(8)	7506(6)	36(3)	
C(10)	7459(15)	5787(9)	7817(6)	45(3)	
C(11)	4598(16)	5688(10)	8003(6)	50(3)	
C(12)	5174(15)	7399(7)	6881(6)	36(3)	
C(13)	6649(15)	7980(9)	6965(7)	49(4)	
C(14)	4131(16)	7876(9)	6365(6)	45(3)	
C(15)	8923(17)	6372(9)	6206(6)	38(3)	
C(16)	6870(14)	6760(10)	5372(7)	43(3)	
C(17)	8454(15)	5320(8)	5120(6)	35(3)	
C(18)	8930(17)	3053(10)	6998(8)	50(4)	
F(1)	7809(11)	2530(6)	6743(6)	92(3)	
F(2)	10145(10)	2511(5)	7067(4)	68(3)	
F(3)	8502(12)	3341(7)	7585(5)	84(3)	
Mn(1)	7299(2)	5720(1)	5830(1)	30(1)	
O(6)	9120(12)	5135(7)	4653(5)	56(3)	
O(1)	9961(10)	6820(6)	6377(4)	44(2)	
O(2)	6706(11)	7483(6)	5092(5)	49(2)	
O(3)	7815(9)	4497(5)	6404(4)	33(2)	
O(4)	9857(13)	3663(7)	5858(5)	68(3)	
O(5)	10440(11)	4614(6)	6842(5)	59(3)	
P(1)	5165(4)	4897(2)	5393(2)	34(1)	
P(2)	5562(4)	6123(2)	6686(2)	31(1)	
S(1)	9350(4)	4064(2)	6454(2)	36(1)	
C(5)	3420(20)	4412(17)	4268(12)	75(3)	
C(7)	6120(50)	3080(20)	5240(20)	75(3)	
C(8)	3500(30)	3263(18)	5859(15)	75(3)	
C(5P)	2890(50)	5100(60)	4560(40)	75(3)	
C(7P)	5890(90)	2930(40)	5350(40)	75(3)	
C(8P)	4400(60)	3430(40)	6340(20)	75(3)	

Table S3. Bond lengths [Å] and angles [°] for **2**.

C(1)-C(2)	1.447(19)	Mn(1)-P(2)	2.348(4)
C(1)-P(2)	1.840(12)	Mn(1)-P(1)	2.350(4)
C(1)-H(1A)	1.0078	O(3)-S(1)	1.468(8)
C(1)-H(1B)	0.9900	O(4)-S(1)	1.385(10)
C(2)-P(1)	1.846(15)	O(5)-S(1)	1.445(9)
C(2)-H(2A)	0.9105	C(5)-H(5A)	0.9800
C(2)-H(2B)	0.9734	C(5)-H(5B)	0.9800
C(3)-C(4)	1.47(2)	C(5)-H(5C)	0.9800
C(3)-C(5)	1.50(2)	C(7)-H(7A)	0.9800
C(3)-C(5P)	1.73(4)	C(7)-H(7B)	0.9800
C(3)-P(1)	1.817(18)	C(7)-H(7C)	0.9800
C(3)-H(3)	1.0000	C(8)-H(8A)	0.9800
C(4)-H(4A)	0.9800	C(8)-H(8B)	0.9800
C(4)-H(4B)	0.9800	C(8)-H(8C)	0.9800
C(4)-H(4C)	0.9800	C(5P)-H(5PA)	0.9800
C(6)-C(8P)	1.43(4)	C(5P)-H(5PB)	0.9800
C(6)-C(7P)	1.46(5)	C(5P)-H(5PC)	0.9800
C(6)-C(8)	1.49(3)	C(7P)-H(7PA)	0.9800
C(6)-C(7)	1.55(4)	C(7P)-H(7PB)	0.9800
C(6)-P(1)	1.822(17)	C(7P)-H(7PC)	0.9800
C(6)-H(6)	1.0134	C(8P)-H(8PA)	1.0473
C(9)-C(11)	1.514(16)	C(8P)-H(8PB)	0.9800
C(9)-C(10)	1.539(17)	C(8P)-H(8PC)	0.9801
C(9)-P(2)	1.854(11)		
C(9)-H(9)	1.0000	C(2)-C(1)-P(2)	111.2(9)
C(10)-H(10A)	0.9800	C(2)-C(1)-H(1A)	133.4
C(10)-H(10B)	0.9800	P(2)-C(1)-H(1A)	99.1
C(10)-H(10C)	0.9800	C(2)-C(1)-H(1B)	109.3
C(11)-H(11A)	0.9800	P(2)-C(1)-H(1B)	109.3
C(11)-H(11B)	0.9800	H(1A)-C(1)-H(1B)	91.9
C(11)-H(11C)	0.9800	C(1)-C(2)-P(1)	111.6(10)
C(12)-C(14)	1.525(16)	C(1)-C(2)-H(2A)	96.6
C(12)-C(13)	1.527(17)	P(1)-C(2)-H(2A)	113.6
C(12)-P(2)	1.853(11)	C(1)-C(2)-H(2B)	97.9
C(12)-H(12)	1.0000	P(1)-C(2)-H(2B)	114.5
C(13)-H(13A)	0.9800	H(2A)-C(2)-H(2B)	119.3
C(13)-H(13B)	0.9800	C(4)-C(3)-C(5)	111.9(16)
C(13)-H(13C)	0.9800	C(4)-C(3)-C(5P)	93(3)
C(14)-H(14A)	0.9800	C(4)-C(3)-P(1)	118.7(12)
C(14)-H(14B)	0.9800	C(5)-C(3)-P(1)	114.2(14)
C(14)-H(14C)	0.9800	C(5P)-C(3)-P(1)	94(3)
C(15)-O(1)	1.150(15)	C(4)-C(3)-H(3)	103.1
C(15)-Mn(1)	1.840(15)	C(5)-C(3)-H(3)	103.2
C(16)-O(2)	1.163(15)	C(5P)-C(3)-H(3)	146.5
C(16)-Mn(1)	1.756(14)	P(1)-C(3)-H(3)	103.3
C(17)-O(6)	1.125(14)	C(3)-C(4)-H(4A)	109.5
C(17)-Mn(1)	1.825(13)	C(3)-C(4)-H(4B)	109.5
C(18)-F(3)	1.293(17)	H(4A)-C(4)-H(4B)	109.5
C(18)-F(2)	1.306(15)	C(3)-C(4)-H(4C)	109.5
C(18)-F(1)	1.320(16)	H(4A)-C(4)-H(4C)	109.5
C(18)-S(1)	1.817(14)	H(4B)-C(4)-H(4C)	109.5
Mn(1)-O(3)	2.103(7)	C(8P)-C(6)-C(7P)	117(3)

C(8)-C(6)-C(7)	118(2)
C(8P)-C(6)-P(1)	123(2)
C(7P)-C(6)-P(1)	118(3)
C(8)-C(6)-P(1)	118.9(15)
C(7)-C(6)-P(1)	105.2(15)
C(8P)-C(6)-H(6)	85.3
C(7P)-C(6)-H(6)	92.6
C(8)-C(6)-H(6)	136.4
C(7)-C(6)-H(6)	88.3
P(1)-C(6)-H(6)	82.2
C(11)-C(9)-C(10)	111.2(10)
C(11)-C(9)-P(2)	113.6(8)
C(10)-C(9)-P(2)	113.0(8)
C(11)-C(9)-H(9)	106.1
C(10)-C(9)-H(9)	106.1
P(2)-C(9)-H(9)	106.1
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(14)-C(12)-C(13)	110.0(10)
C(14)-C(12)-P(2)	112.7(8)
C(13)-C(12)-P(2)	112.4(8)
C(14)-C(12)-H(12)	107.1
C(13)-C(12)-H(12)	107.1
P(2)-C(12)-H(12)	107.1
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(1)-C(15)-Mn(1)	173.0(11)
O(2)-C(16)-Mn(1)	173.8(11)
O(6)-C(17)-Mn(1)	174.4(11)
F(3)-C(18)-F(2)	108.5(12)
F(3)-C(18)-F(1)	108.0(14)
F(2)-C(18)-F(1)	108.5(12)
F(3)-C(18)-S(1)	111.0(10)
F(2)-C(18)-S(1)	110.5(11)
F(1)-C(18)-S(1)	110.3(10)
C(16)-Mn(1)-C(17)	88.0(5)
C(16)-Mn(1)-C(15)	88.1(5)
C(17)-Mn(1)-C(15)	92.6(6)
C(16)-Mn(1)-O(3)	178.4(5)
C(17)-Mn(1)-O(3)	93.3(4)
C(15)-Mn(1)-O(3)	90.9(4)
C(16)-Mn(1)-P(2)	92.5(4)
C(17)-Mn(1)-P(2)	172.9(4)
C(15)-Mn(1)-P(2)	94.5(4)
O(3)-Mn(1)-P(2)	86.3(2)
C(16)-Mn(1)-P(1)	92.4(4)
C(17)-Mn(1)-P(1)	89.8(4)
C(15)-Mn(1)-P(1)	177.5(4)
O(3)-Mn(1)-P(1)	88.5(2)
P(2)-Mn(1)-P(1)	83.07(12)
S(1)-O(3)-Mn(1)	124.4(5)
C(3)-P(1)-C(6)	110.1(8)
C(3)-P(1)-C(2)	105.2(8)
C(6)-P(1)-C(2)	105.1(8)
C(3)-P(1)-Mn(1)	118.4(5)
C(6)-P(1)-Mn(1)	112.4(6)
C(2)-P(1)-Mn(1)	104.4(5)
C(1)-P(2)-C(12)	103.4(6)
C(1)-P(2)-C(9)	100.5(6)
C(12)-P(2)-C(9)	105.6(6)
C(1)-P(2)-Mn(1)	109.1(4)
C(12)-P(2)-Mn(1)	120.0(4)
C(9)-P(2)-Mn(1)	115.9(4)
O(4)-S(1)-O(5)	117.7(7)
O(4)-S(1)-O(3)	113.4(6)
O(5)-S(1)-O(3)	114.4(5)
O(4)-S(1)-C(18)	105.3(7)
O(5)-S(1)-C(18)	103.0(6)
O(3)-S(1)-C(18)	100.2(6)
C(3)-C(5)-H(5A)	109.5
C(3)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(3)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(3)-C(5P)-H(5PA)	109.5
C(3)-C(5P)-H(5PB)	109.5

H(5PA)-C(5P)-H(5PB)	109.5
C(3)-C(5P)-H(5PC)	109.5
H(5PA)-C(5P)-H(5PC)	109.5
H(5PB)-C(5P)-H(5PC)	109.5
C(6)-C(7P)-H(7PA)	109.5
C(6)-C(7P)-H(7PB)	109.5
H(7PA)-C(7P)-H(7PB)	109.5
C(6)-C(7P)-H(7PC)	109.5
H(7PA)-C(7P)-H(7PC)	109.5
H(7PB)-C(7P)-H(7PC)	109.5
C(6)-C(8P)-H(8PA)	123.3
C(6)-C(8P)-H(8PB)	108.0
H(8PA)-C(8P)-H(8PB)	105.6
C(6)-C(8P)-H(8PC)	109.3
H(8PA)-C(8P)-H(8PC)	100.5
H(8PB)-C(8P)-H(8PC)	109.5

Table S4. Torsion angles [°] for **2**.

P(2)-C(1)-C(2)-P(1)	47.4(12)	C(2)-C(1)-P(2)-C(9)	-146.7(10)
C(4)-C(3)-P(1)-C(6)	-173.2(14)	C(2)-C(1)-P(2)-Mn(1)	-24.5(11)
C(5)-C(3)-P(1)-C(6)	51.4(16)	C(14)-C(12)-P(2)-C(1)	-45.9(10)
C(5P)-C(3)-P(1)-C(6)	91(3)	C(13)-C(12)-P(2)-C(1)	-170.9(10)
C(4)-C(3)-P(1)-C(2)	74.1(14)	C(14)-C(12)-P(2)-C(9)	-151.0(9)
C(5)-C(3)-P(1)-C(2)	-61.3(16)	C(13)-C(12)-P(2)-C(9)	84.0(10)
C(5P)-C(3)-P(1)-C(2)	-21(3)	C(14)-C(12)-P(2)-Mn(1)	75.8(10)
C(4)-C(3)-P(1)-Mn(1)	-42.0(16)	C(13)-C(12)-P(2)-Mn(1)	-49.3(10)
C(5)-C(3)-P(1)-Mn(1)	-177.4(12)	C(11)-C(9)-P(2)-C(1)	-53.1(10)
C(5P)-C(3)-P(1)-Mn(1)	-137(3)	C(10)-C(9)-P(2)-C(1)	179.0(9)
C(8P)-C(6)-P(1)-C(3)	-144(3)	C(11)-C(9)-P(2)-C(12)	54.2(11)
C(7P)-C(6)-P(1)-C(3)	48(4)	C(10)-C(9)-P(2)-C(12)	-73.7(10)
C(8)-C(6)-P(1)-C(3)	-84.0(19)	C(11)-C(9)-P(2)-Mn(1)	-170.4(8)
C(7)-C(6)-P(1)-C(3)	50(2)	C(10)-C(9)-P(2)-Mn(1)	61.7(9)
C(8P)-C(6)-P(1)-C(2)	-31(3)	Mn(1)-O(3)-S(1)-O(4)	-67.0(8)
C(7P)-C(6)-P(1)-C(2)	161(4)	Mn(1)-O(3)-S(1)-O(5)	71.9(8)
C(8)-C(6)-P(1)-C(2)	29(2)	Mn(1)-O(3)-S(1)-C(18)	-178.7(6)
C(7)-C(6)-P(1)-C(2)	163(2)	F(3)-C(18)-S(1)-O(4)	177.3(10)
C(8P)-C(6)-P(1)-Mn(1)	81(3)	F(2)-C(18)-S(1)-O(4)	57.0(12)
C(7P)-C(6)-P(1)-Mn(1)	-87(4)	F(1)-C(18)-S(1)-O(4)	-63.0(12)
C(8)-C(6)-P(1)-Mn(1)	141.8(17)	F(3)-C(18)-S(1)-O(5)	53.4(12)
C(7)-C(6)-P(1)-Mn(1)	-84(2)	F(2)-C(18)-S(1)-O(5)	-66.9(12)
C(1)-C(2)-P(1)-C(3)	-173.9(10)	F(1)-C(18)-S(1)-O(5)	173.1(11)
C(1)-C(2)-P(1)-C(6)	69.9(12)	F(3)-C(18)-S(1)-O(3)	-64.8(11)
C(1)-C(2)-P(1)-Mn(1)	-48.5(10)	F(2)-C(18)-S(1)-O(3)	174.9(10)
C(2)-C(1)-P(2)-C(12)	104.3(11)	F(1)-C(18)-S(1)-O(3)	54.9(12)

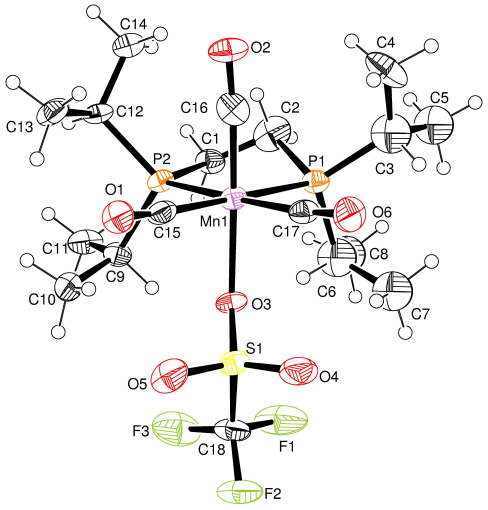

Figure S27. ORTEP plot (50% probability, 130 K) for complex 2

Procedure S9. General procedure for the catalytic hydration of nitriles with complex 2

In the glovebox, a THF solution of the corresponding nitrile (0.46 mmol) was added dropwise to a yellow THF solution of **2** (5 mg, 0.0092 mmol, or 10 mg, 0.0184 mmol). The formed solution was transferred to a 25 mL Schlenk tube (Synthware Glass) (1 mL THF total volume), to which water (2 mL, 111 mmol) was added to form an emulsion, which evolved to a solution upon heating. The reaction mixture was stirred into an oil bath at 100 ºC during 18 h. After that, the solvent and volatiles were removed under reduced pressure in the inert gas/ vacuum double manifold and the residue was chromatographed on a silica gel column with hexanes/ethyl acetate mixtures as the eluent. The solvents of the collected fractions were evaporated under vacuum, the remaining solids were recrystallized from acetone and finally washed with fresh hexanes.

Characterization of amides 2a-j.

2a (50 mg, 90%); m.p. 126-128 ºC (lit.[1] m.p. 126-127 ºC). ^{1}H (400 MHz, DMSO-d_6) 7.97 (bs, 1H), 7.87 (dt, $^{3}J_{HH}$ = 7 Hz, $^{4}J_{HH}$ = 2 Hz, 2H), 7.51 (tt, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 2 Hz, 1H), 7.44 (tdd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 2 Hz, $^{5}J_{HH}$ = 1 Hz, 2H), 7.35 (bs, 1H). ^{13}C{^{1}H} (100 MHz) 167.9, 134.3, 131.2, 128.2, 127.4. MS (EI) m/z 121 [M^{+} (100)], 122 [M+1 (9 ± 0.5)], 123 [M+2 (<1)].

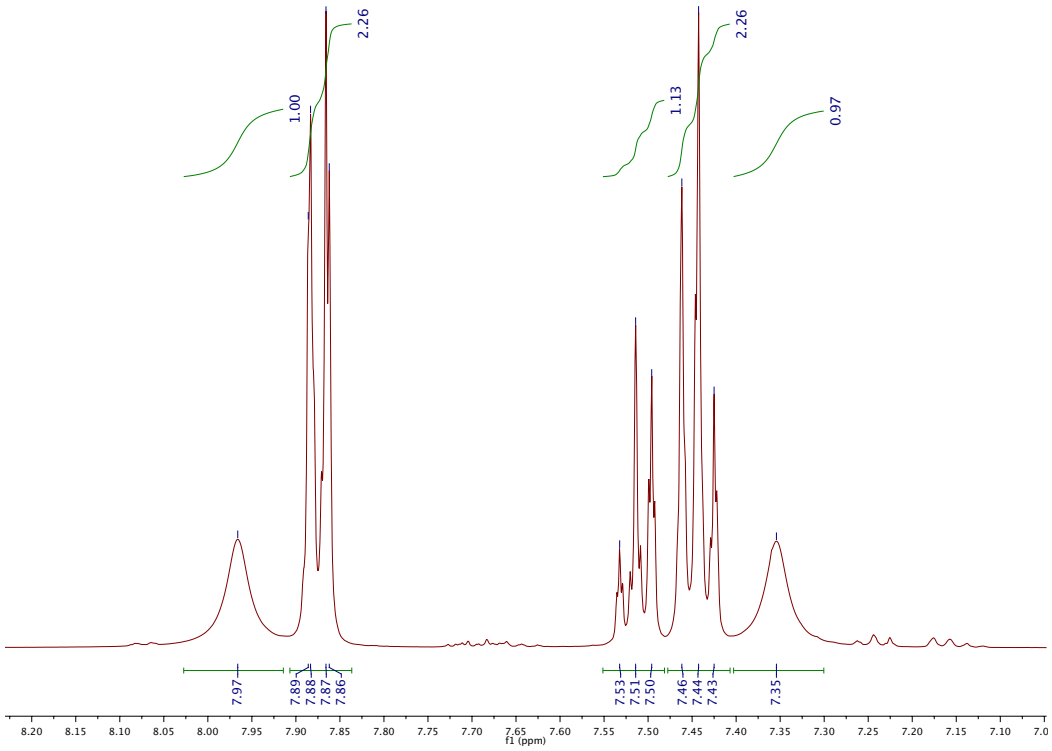

Figure S28. ^{1}H NMR (400 MHz, DMSO-d_6) aromatic region of the spectrum of isolated benzamide from optimized model reaction

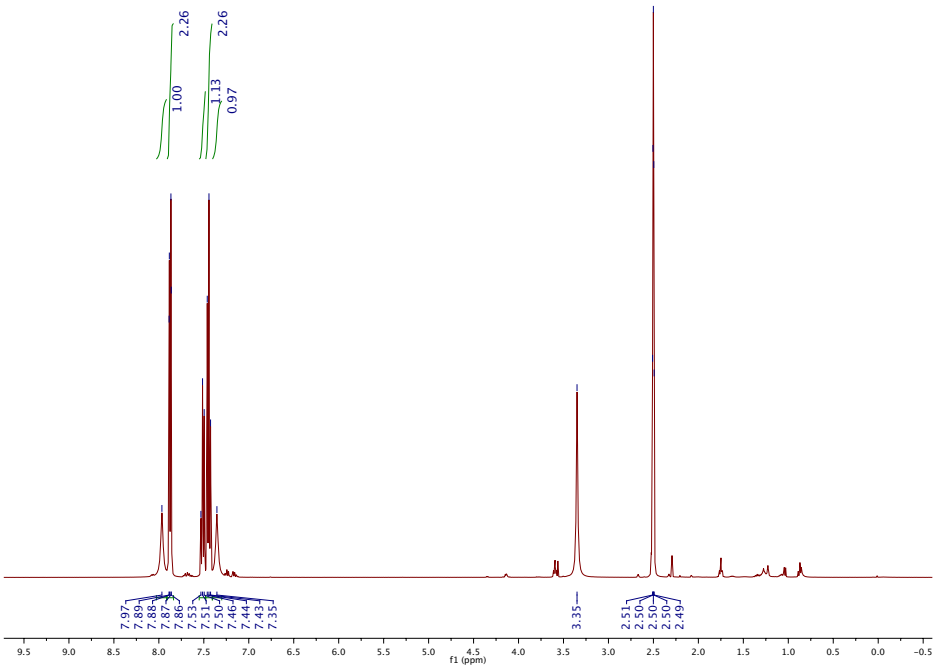

Figure S29. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of isolated benzamide from optimized model reaction

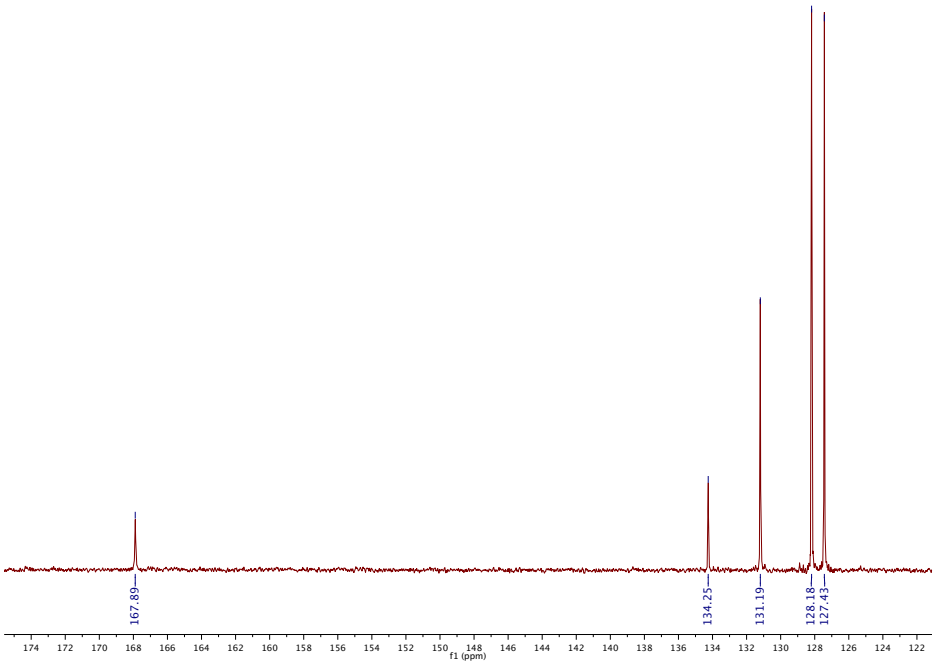

Figure S30. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of isolated benzamide from optimized model reaction

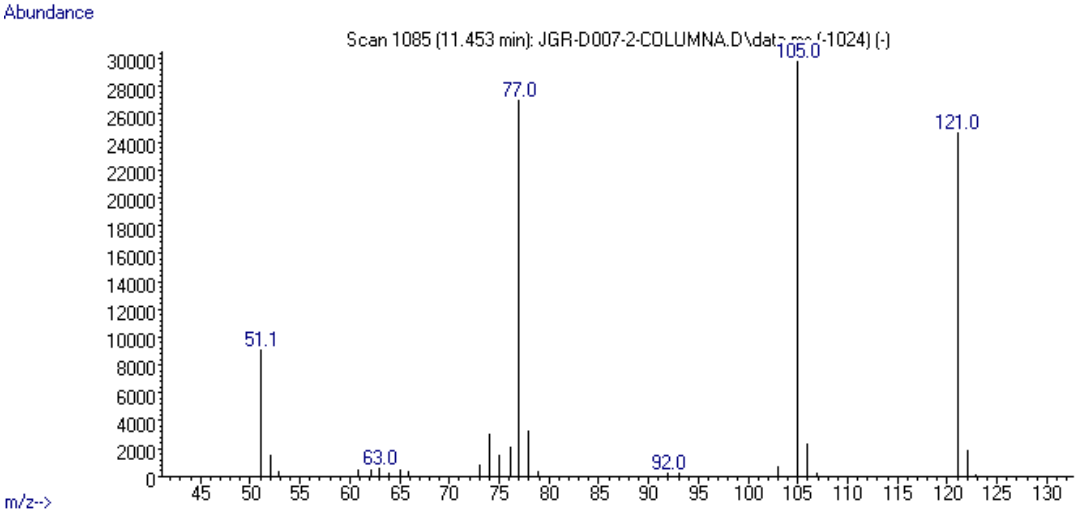

Figure S31. MS(EI) of isolated benzamide from optimized model reaction

2b (77 mg, 88%); m.p. 184-185 ºC (lit.[2] m.p. 182-183 ºC). ^{1}H (400 MHz, $CDCl_3$/DMSO-d_6) 8.04 (bs, 1H), 8.01 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.25 (bs, 1H). ^{13}C{^{1}H} (100 MHz) 167.3, 137.5, 131.8 (q, $^{1}J_{CF}$ = 32.2 Hz), 128.1, 124.8 (q, $^{3}J_{CF}$ = 3.7 Hz), 122.2. ^{19}F (376 MHz) -60.3 (s). MS (EI) m/z 189 (M^{+}).

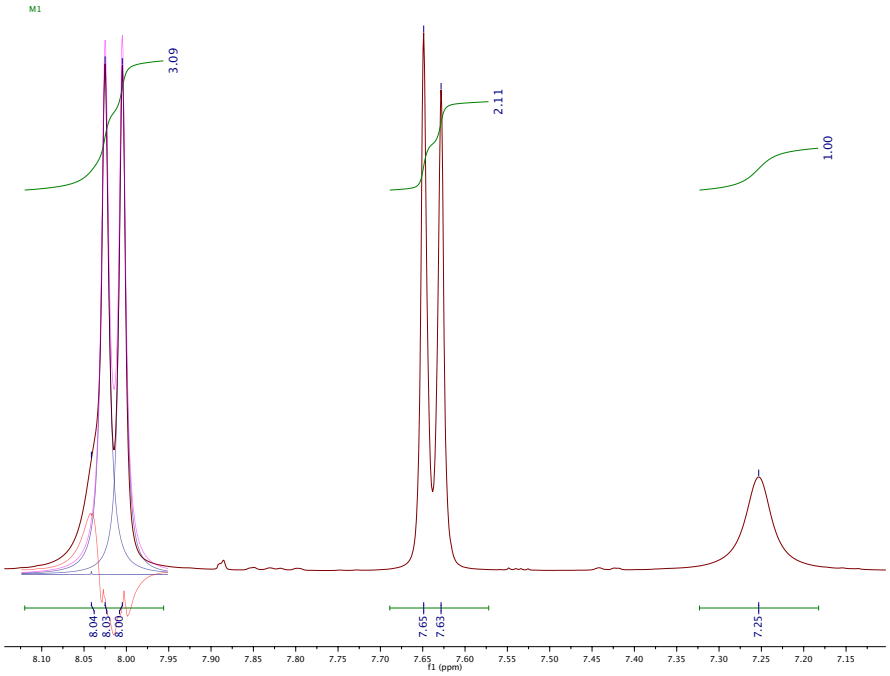

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-trifluoromethylbenzamide

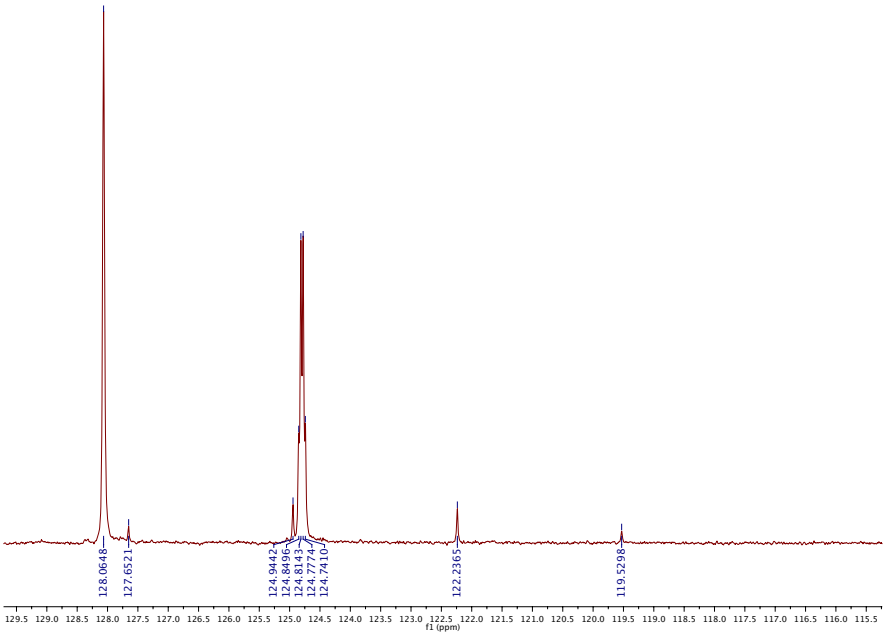

Figure S33. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-trifluoromethylbenzamide

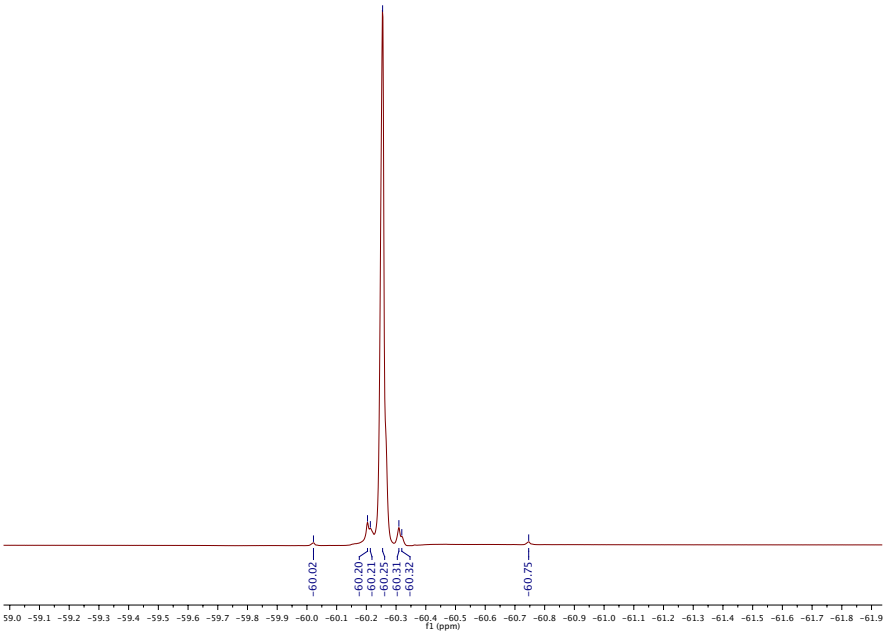

Figure S34. ^{19}F NMR (376 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-trifluoromethylbenzamide

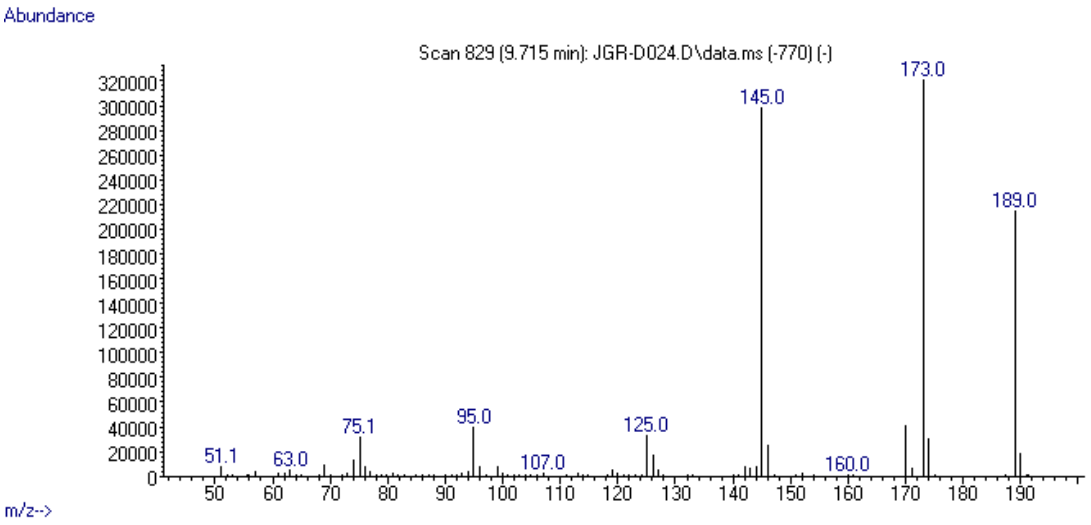

Figure S35. MS(EI) of *p*-trifluoromethylbenzamide

2c (57 mg, 89%); m.p. 154-156 ºC (lit.[3] m.p. 153-154 ºC). ^{1}H (400 MHz, $CDCl_3$/DMSO-d_6) 7.92 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HF}$ = 5.6 Hz, 2H), 7.89 (bs, 1H), 7.22 (bs, 1H), 7.14 (t, $^{3}J_{HH}$ = $^{3}J_{HF}$ = 8.7 Hz, 2H). ^{13}C{^{1}H} (100 MHz) 165.1, 162.6, 130.4, 129.9 (d, $^{3}J_{CF}$ = 8.9 Hz), 114.7 (d, $^{1}J_{CF}$ = 21.5 Hz). ^{19}F (376 MHz) -107.5 (tt, $^{3}J_{FH}$ = 8.6 Hz, $^{4}J_{FH}$ = 5.5 Hz). MS (EI) m/z 139 (M^{+}).

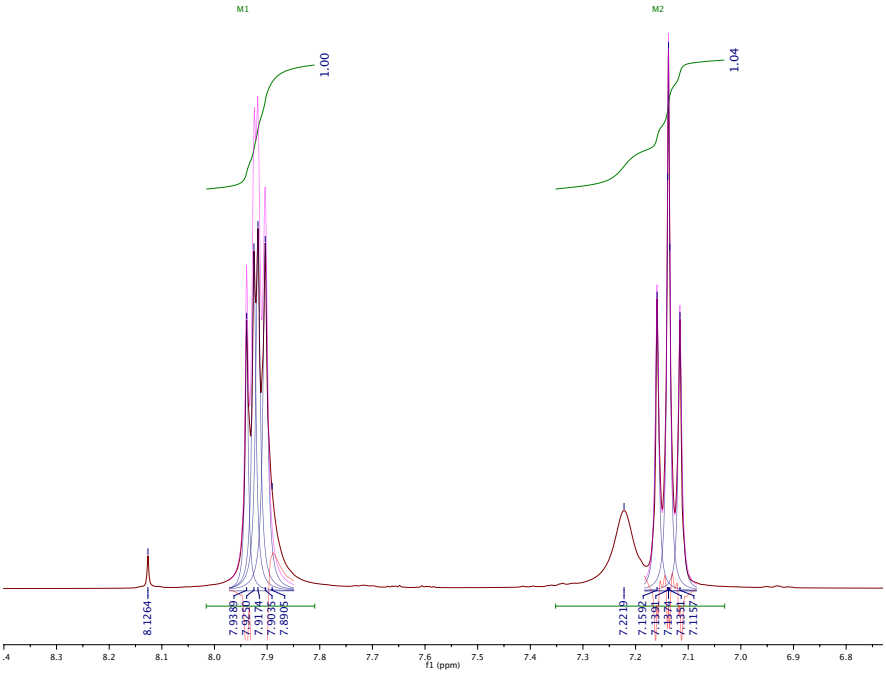

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-fluorobenzamide

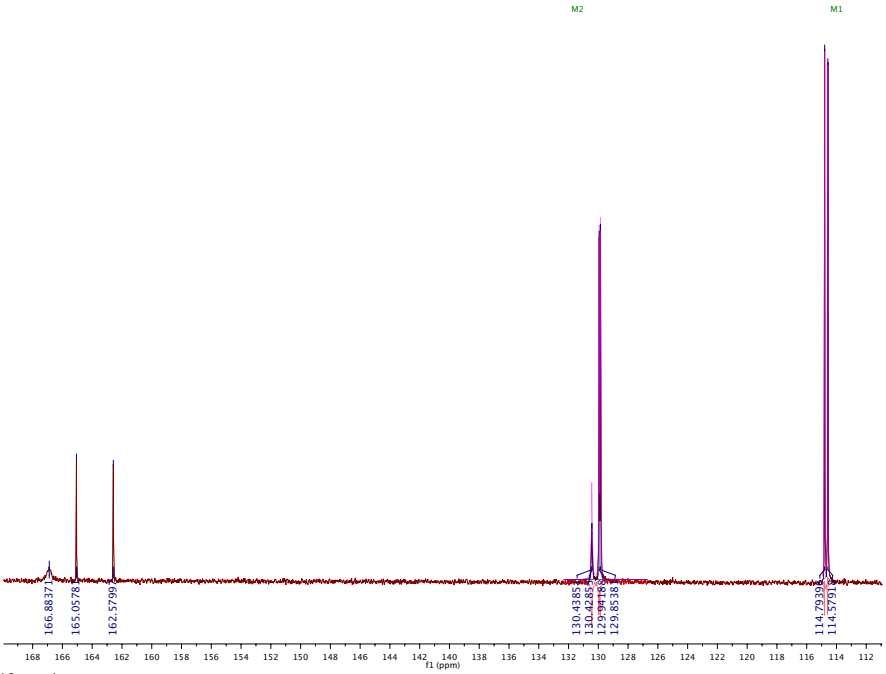

Figure S37. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-fluorobenzamide

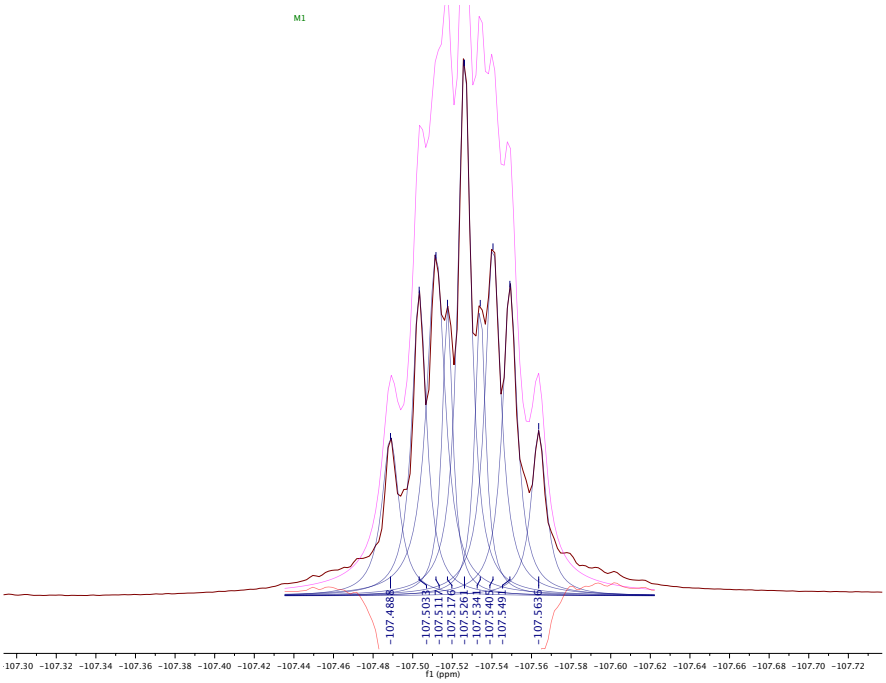

Figure S38. ^{19}F NMR (376 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-fluorobenzamide

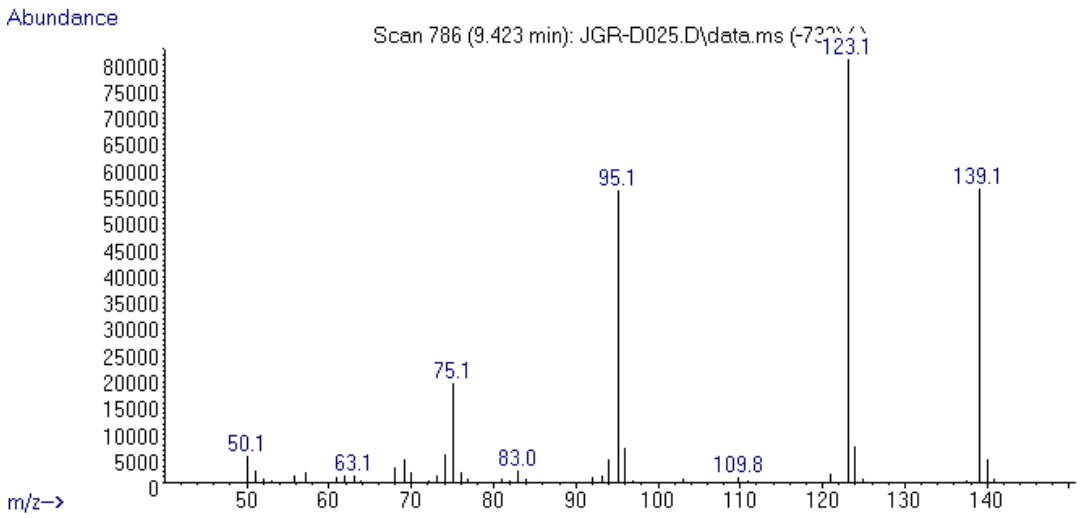

Figure S39. MS(EI) of *p*-fluorobenzamide

2d (91 mg, 94%); m.p. 152-153 ºC (lit.[4] m.p. 150 ºC). ^{1}H (400 MHz, $CDCl_3$/DMSO-d_6) 8.05 (bs, 1H), 7.84 (bs, 1H). $^{13}C\{^{1}H\}$ (100 MHz) 158.5, 144.4-144.0 (m), 142.3-141.6 (m), 139.7-139.4 (m), 138.2-137.7 (m), 135.7-135.2 (m), 113.0-112.4 (m). ^{19}F (376 MHz) -139.3 (dtd, $^{3}J_{FF}$ = 22 Hz, $^{4}J_{FF}$ = 6.2 Hz, $^{5}J_{FF}$ = 2.5 Hz), -151.7 (t, $^{3}J_{FF}$ = 21.2 Hz), -159.5 (tdd, $^{3}J_{FF}$ = 21.4 Hz, $^{4}J_{FF}$ = 6.6, $^{5}J_{FF}$ = 2.7 Hz). MS (EI) m/z 211 (M^{+}).

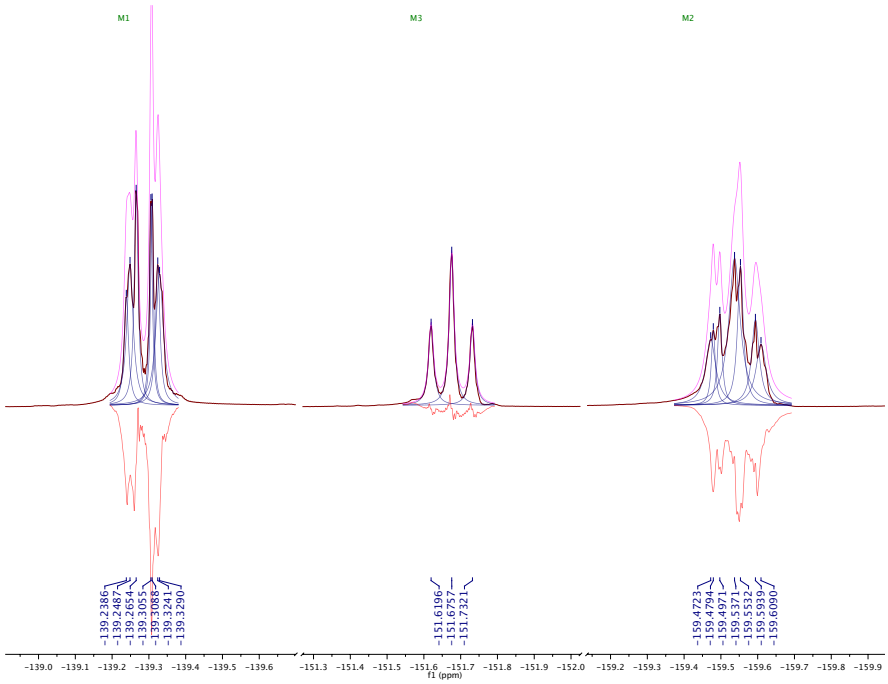

Figure S40. ^{19}F NMR (376 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated 2,3,4,5,6-pentafluorobenzamide

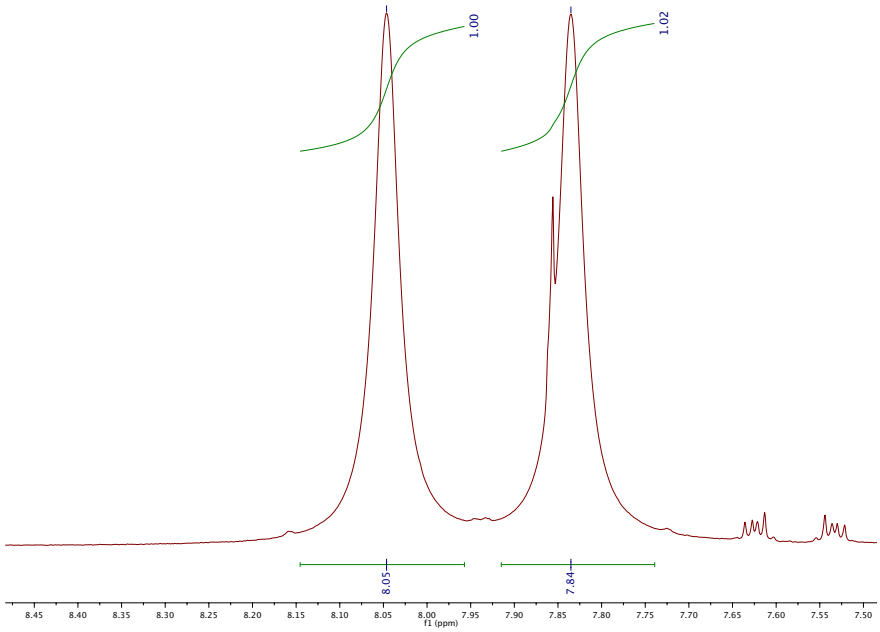

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated 2,3,4,5,6-pentafluorobenzamide

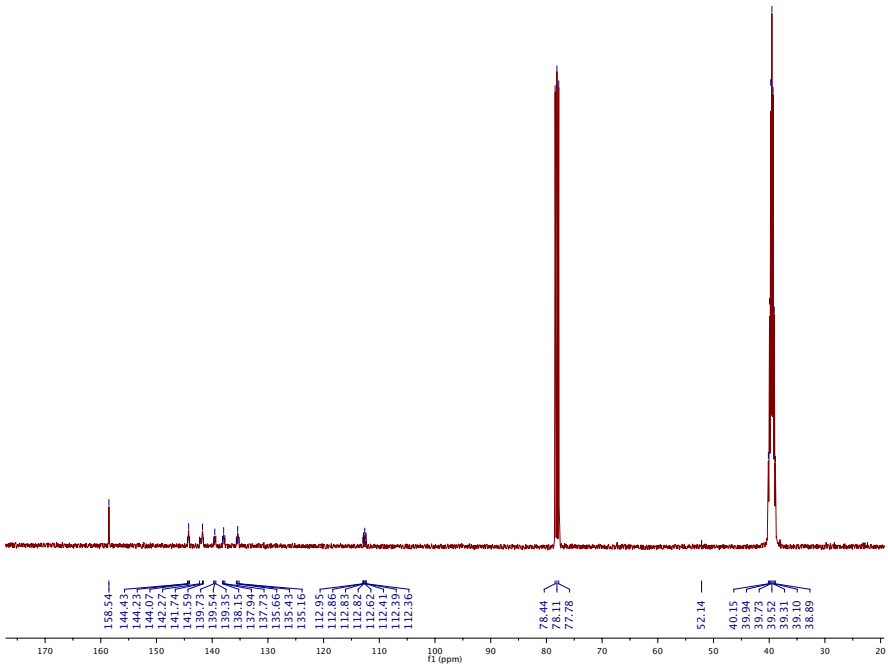

Figure S42. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated 2,3,4,5,6-pentafluorobenzamide

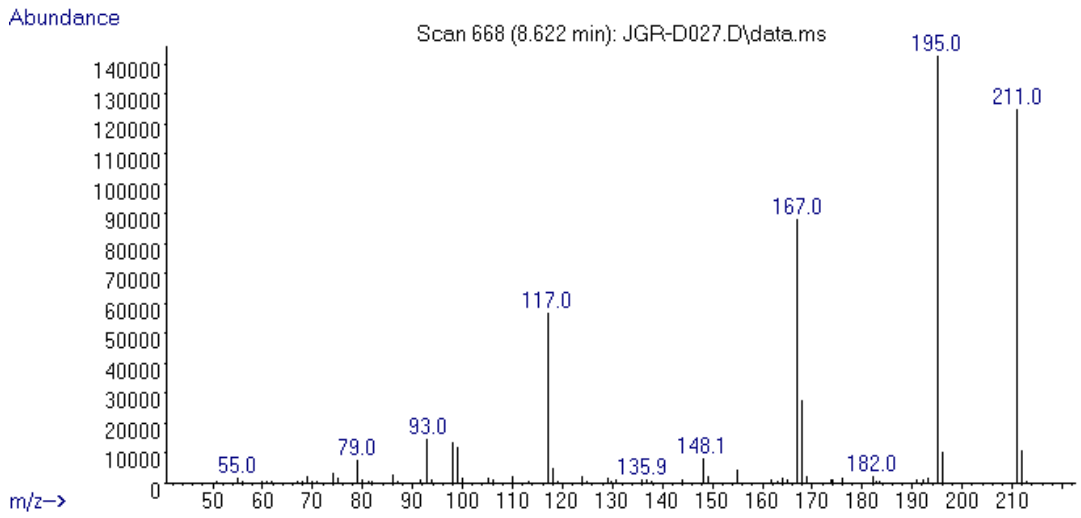

Figure S43. MS(EI) of 2,3,4,5,6-pentafluorobenzamide

2e (50 mg, 90%); m.p. 154-156 ºC (lit.[5] m.p. 158 ºC). MS (EI) m/z 122 (M^+).

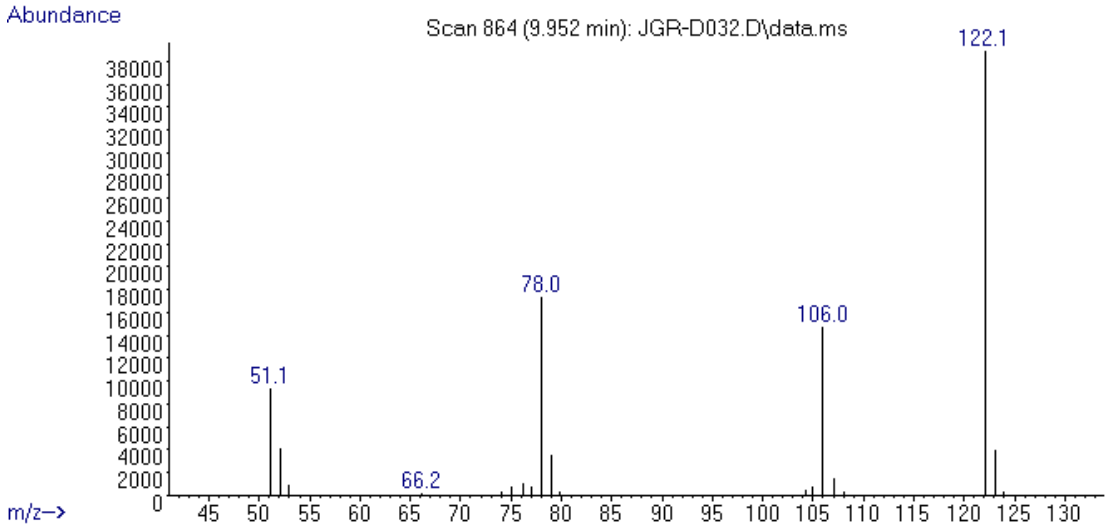

Figure S44. MS(EI) of isonicotinamide

2f (51 mg, 91%); m.p. 130-132 ºC (lit.[6] m.p. 129-131 ºC). MS (EI) m/z 122 (M^+).

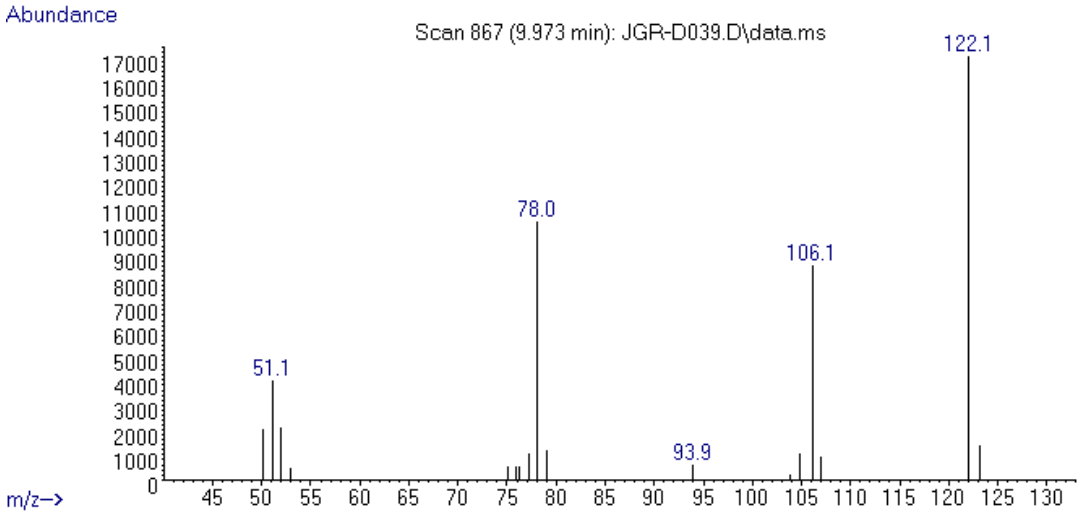

Figure S45. MS(EI) of nicotinamide

2g (39 mg, 70%); m.p. 106-108 ºC (lit.[7] m.p. 105-106 ºC). ^{1}H (400 MHz, DMSO-d_6) 8.62 (d, J = 4.4 Hz, 1H), 8.11 (bs, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.97 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.64 (bs, 1H), 7.58 (ddd, J = 7.4 Hz, 4.7 Hz, 1.3 Hz, 1H) ^{13}C{^{1}H} (100 MHz) 166.0, 150.3, 148.4, 137.6, 126.4, 121.9. MS (EI) m/z 122 (M^+).

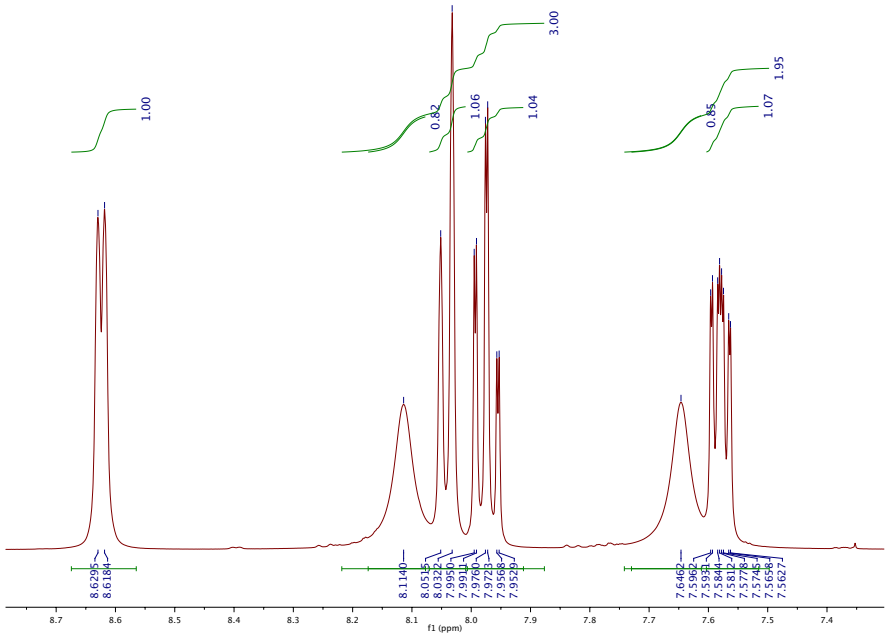

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated picolinamide

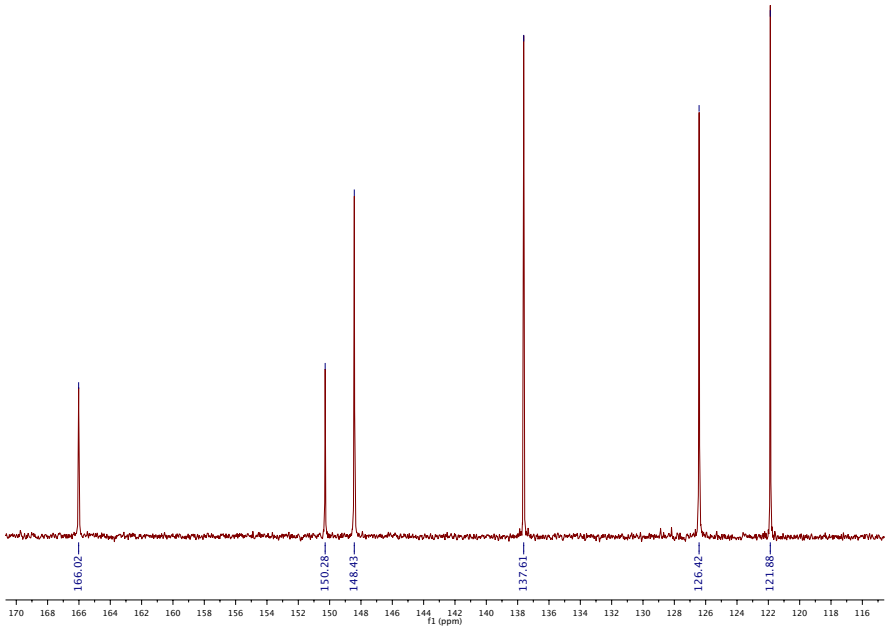

Figure S47. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated picolinamide

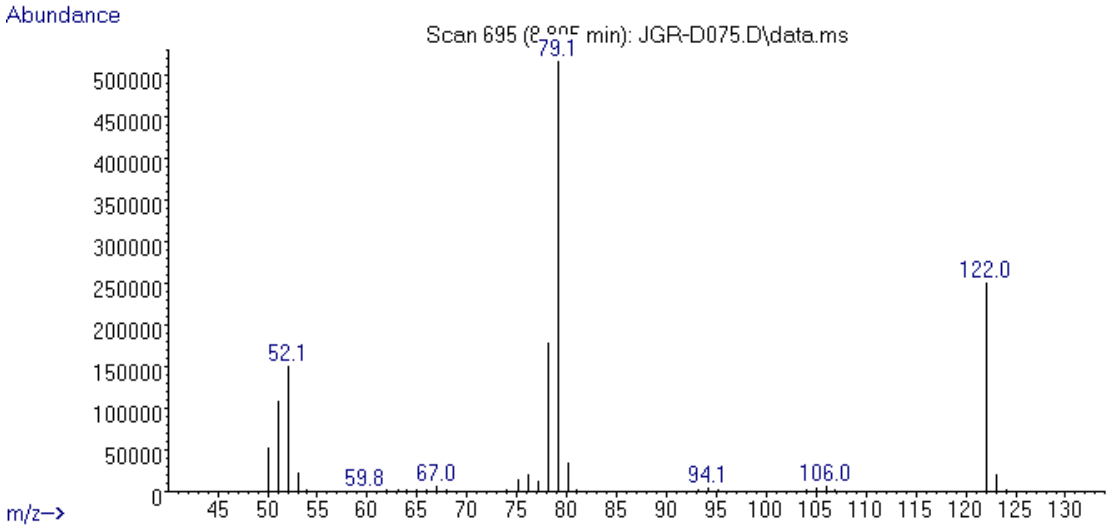

Figure S48. MS(EI) of picolinamide

2h (65 mg, 93%); m.p. 166-168 ºC (lit.[8] m.p. 166 ºC). ^{1}H (400 MHz, $CDCl_3$/DMSO-d_6) 7.83 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 3.6 Hz, $^{5}J_{HH}$ = 1.6 Hz, 2H), 7.70 (bs, 1H), 6.93 (bs, 1H), 6.87 (ddd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 3.6 Hz, $^{5}J_{HH}$ = 1.6 Hz, 2H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$ (100 MHz) 167.8, 161.5, 129.2, 126.2, 112.9, 54.9. MS (EI) m/z 151 (M^{+}).

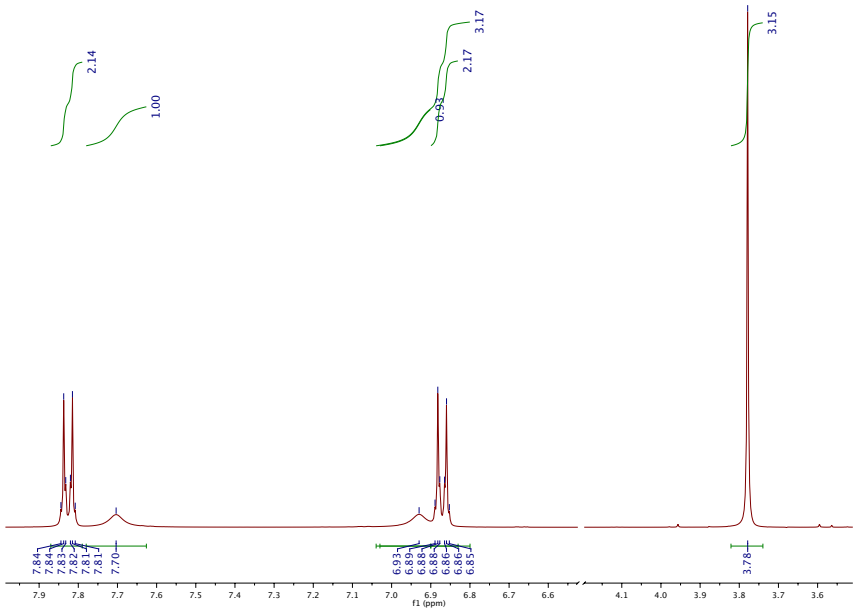

Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-methoxybenzamide

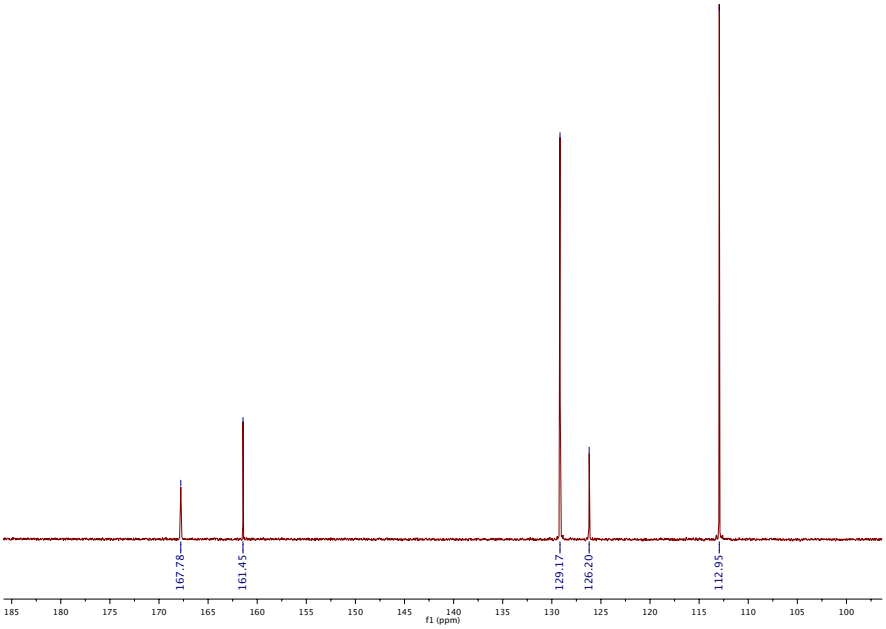

Figure S50. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-d_6) spectrum of isolated *p*-methoxybenzamide

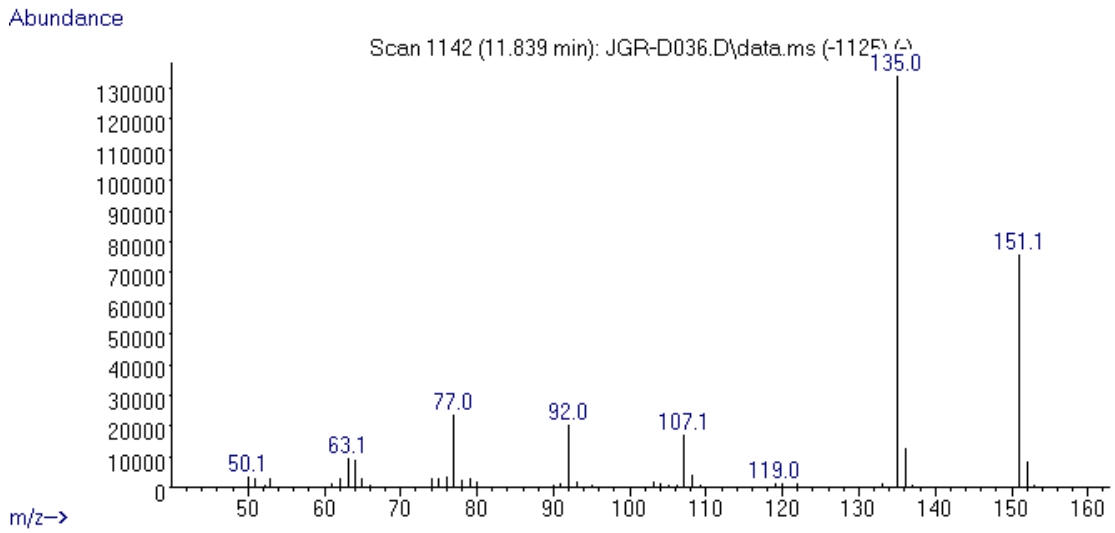

Figure S51. MS(EI) of *p*-methoxybenzamide

2i (56 mg, 90%); m.p. 160-162 ºC (lit.[9] m.p. 162-163 ºC). MS (EI) m/z 135 (M^+).

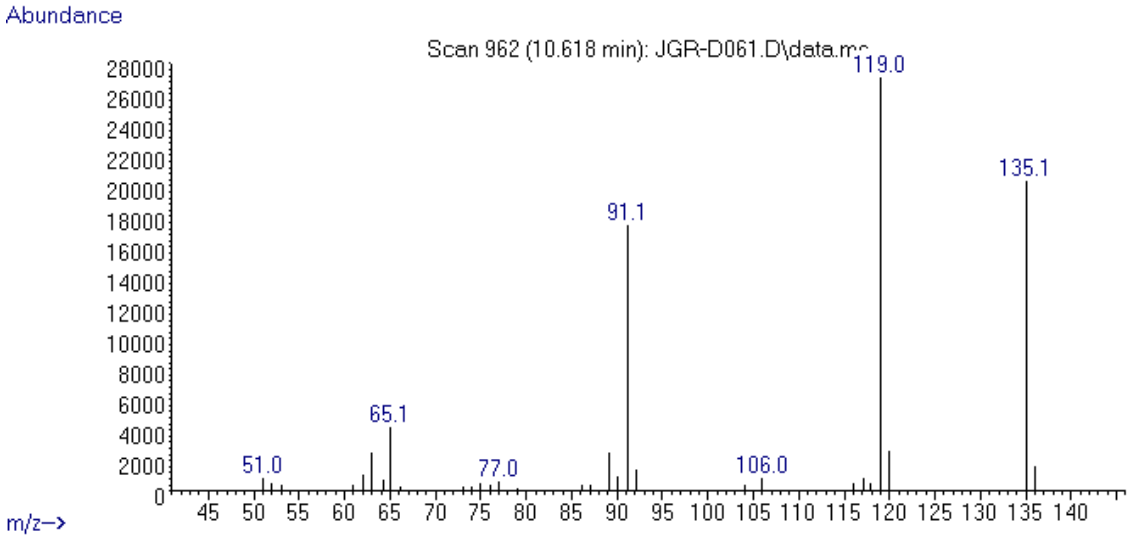

Figure S52. MS(EI) of *p*-toluamide

2j (47 mg, 93%); m.p. 136-138 ºC (lit.[10] m.p. 141-142 ºC). ^{1}H (400 MHz, DMSO-d_6) 7.78 (s, 1H), 7.75 (bs, 1H), 7.36 (bs, 1H), 7.09 (s, 1H), 6.58 (s, 1H). ^{13}C{^{1}H} (100 MHz) 159.4, 147.9, 144.9, 113.5, 111.7. MS (EI) m/z 111 (M^{+}).

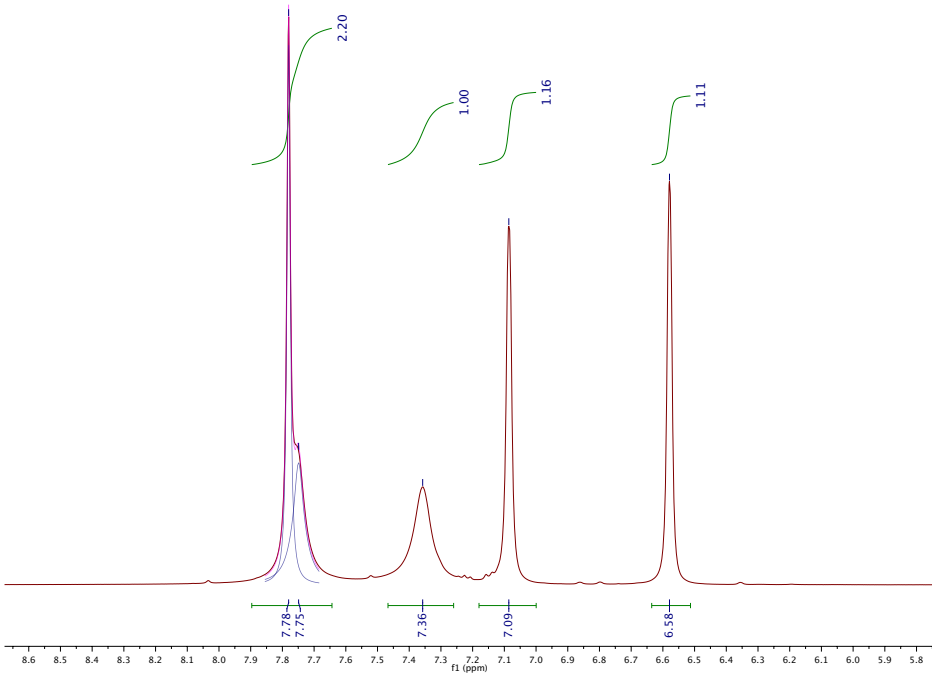

Figure S53. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of isolated furan-2-carbamide

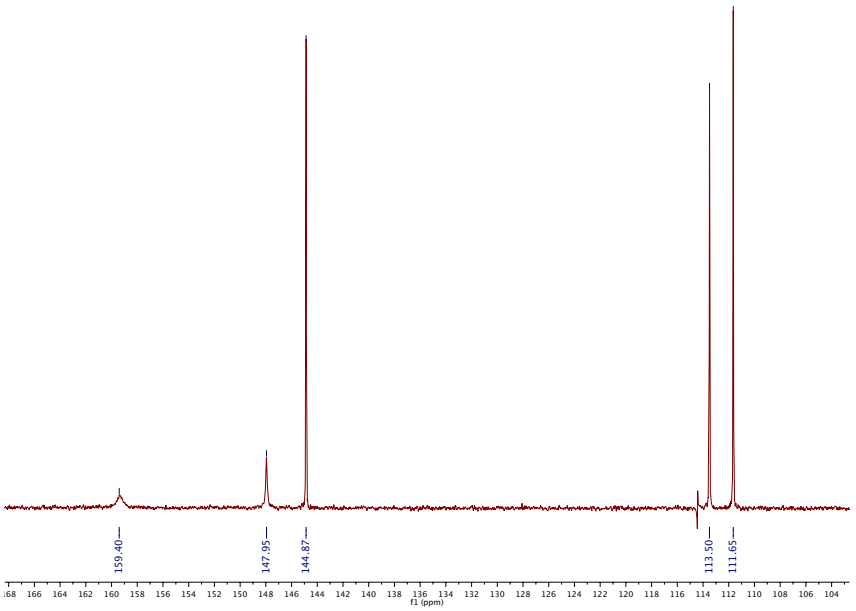

Figure S54. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of isolated furan-2-carbamide

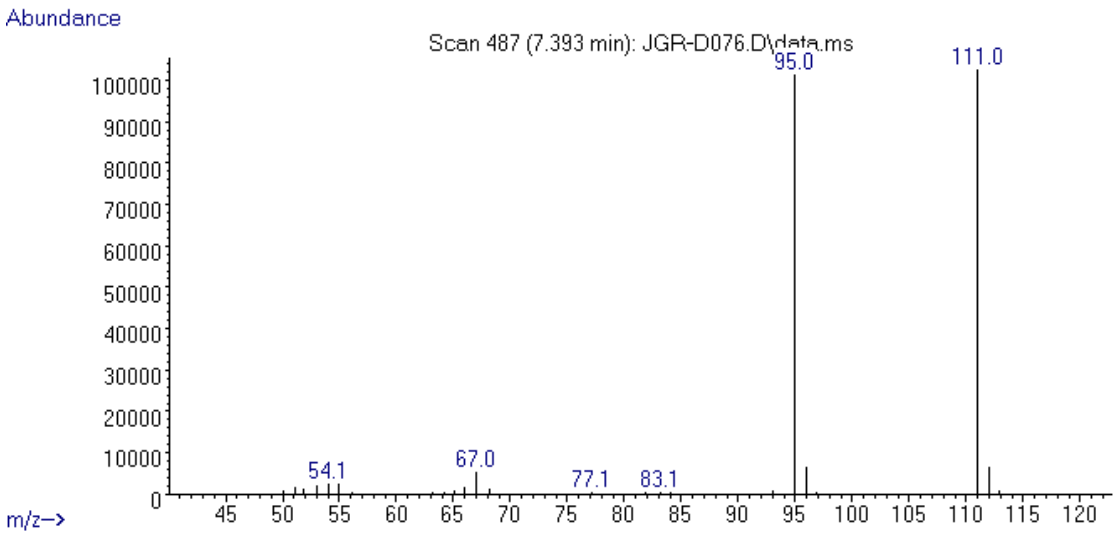

Figure S55. MS(EI) of furan-2-carbamide

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