Supporting Information to

Hydration of Nitriles using a Metal-Ligand Cooperative Ruthenium Pincer Catalyst

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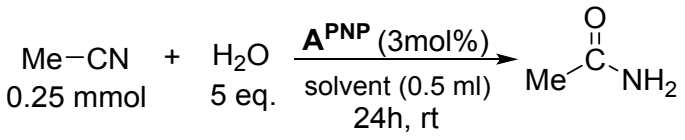
General considerations

The chemicals 2,6-bis(di-tert-butylphosphinomethyl)pyridine (Strem Chemicals, 99%), carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (Strem Chemicals, 99%), [2-(di-tert-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine]ruthenium(II) chlorocarbonyl hydride (**precat^{PNN}**, Sigma-Aldrich, 99%), potassium *tert*-butoxide (Sigma-Aldrich, ≥98%), 2-fluorobiphenyl (Sigma-Aldrich, 96%), 4-fluorobenzonitrile (**1b**, Sigma-Aldrich, 99%), 4-chlorobenzonitrile (**1c**, Sigma-Aldrich, 99%), bromobenzonitrile (**1d-f**, Sigma-Aldrich, 99%), 4-(trifluoromethyl)benzonitrile (**1g**, Sigma-Aldrich, 99%), 4-formylbenzonitrile (**1h**, TCI, >98%), *tert*-butyl 4-cyanobenzoate (**1i**, Enamine Ltd, 95%), 1-naphthonitrile (**1j**, TCI, >95%), 2-naphthonitrile (**1k**, TCI, >98%), 4-methylbenzonitrile (**1l**, Sigma-Aldrich, 98%), 4-methoxybenzonitrile (**1m**, Sigma-Aldrich, 99%), 4-(dimethylamino)benzonitrile (**1n**, TCI, >98%), 4-aminobenzonitrile (**1o**, Sigma-Aldrich, 98%), pyridinecarbonitrile (**1p-r**, Sigma-Aldrich, 98%), 2-furonitrile (**1v**,TCI, >98%), 3-furonitrile (**1w**, Sigma-Aldrich, >97%), terephthalonitrile (**1ag**, Sigma-Aldrich, 98%), 4-acetoxybenzonitrile (Fisher Scientific, 97%), 4-nitrobenzonitrile (Sigma-Aldrich, 97%), 4-hydroxybenzonitrile (Fluka, 98%) and ethyl 4-cyanobenzoate (TCI, >98%) were obtained commercially and used without further purification. The substrates benzonitrile (**1a**, Sigma-Aldrich, 99%), pyrazinecarbonitrile (**1s**, Sigma-Aldrich, 99%), 2-thiophenecarbonitrile (**1t**, Sigma-Aldrich, 99%), 3-thiophenecarbonitrile (**1u**, TCI, >98%), benzyl cyanide (**1x**, Sigma-Aldrich, 98%), 2-phenylpropanitrile (**1y**, Sigma-Aldrich, 96%), 3-phenylpropanitrile (**1z**, Sigma-Aldrich, 99%), cinnamonitrile (**1aa**, Sigma-Aldrich, 97%), n-pentanenitrile (**1ac**, Sigma-Aldrich, 99.5%), cyclohexanecarbonitrile (**1ad**, Sigma-Aldrich, 98%), pivalonitrile (**1ae**, Sigma-Aldrich, 98%), adiponitrile (**1af**, TCI, >98%), were obtained commercially, degassed and passed over columns of Al_2O_3 prior to use. The complex [2,6-Bis(di-tert-butylphosphinomethyl)pyridine]ruthenium(II) chlorocarbonyl hydride (**precat^{PNP}**) was prepared according to a literature procedure.[1][2] Toluene was passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al_2O_3 (Fluka). *Tert* butanol (Boom, >99%), isopropanol (Boom, >99%), 1,4-dioxane (Boom, >99%) and acetonitrile (**1ab**, Boom, >99%) were dried with calcium hydride and distilled under N_2 atmosphere prior to use. Doubly distilled water was obtained from the Microanalytical Department of the University of Groningen and degassed prior to use. *d8*-THF and *d8*-toluene (Aldrich) were vacuum transferred from Na/K alloy and stored in the glovebox. NMR spectra were recorded on Varian 400, Agilent 400 or Varian Inova 500 spectrometers and referenced using the residual solvent resonance. Gas chromatography measurements were performed on HP6890 series equipped with a Rxi-5Sil column for GC/MS and HP5890 series II equipped with Rtx-1701 column for GC-MS/FID. Enantiomeric excess (ee) was determined by chiral HPLC analysis using a Shimadzu LC-20AD HPLC equipped with a Shimadzu SPD-M20A diode array detector. Elemental analysis and high resolution mass spectra (HRMS) were performed at the Microanalytical Department of the University of Groningen.

Optimization of reaction conditions

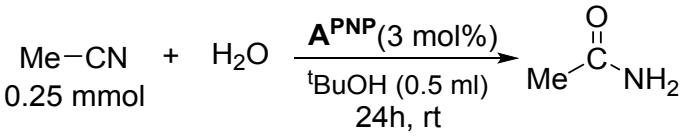
Table S1: Solvent screening for hydration of acetonitrile. Conditions: 3 mol% of catalyst **A^{PNP}** at room temperature in the presence of 5 equiv. of water.



entry	solvent	conversion (%)[a]
1	toluene	-
2	THF	37
3	Isopropanol	<10
4	dioxane	-
5	^{t}BuOH	63(82[b])

a) Conversions were detected by ^{1}H NMR. b) Reaction for 2.5 days.

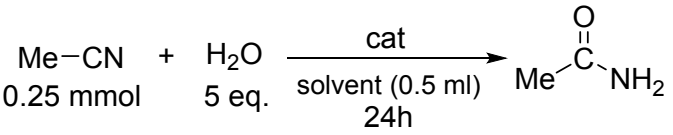
Table S2: Effect of the amount of added water on the hydration of acetonitrile



entry	water (eq.)	conversion (%)[a]
5	5	63(82[b])
6	1	25
7	2	44
8	3	56
9	8	42
10	20	4

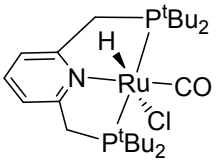
a) Conversions were detected by ^{1}H NMR. b) Reaction for 2.5 days.

Table S3: Influence of catalyst structure and reaction temperature on the hydration of acetonitrile

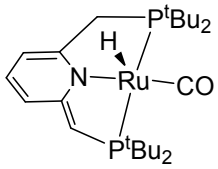


entry	solvent	cat (mol%)	temperature	conversion (%)[a]
5	^{t}BuOH	**A^{PNP}** (3)	rt	63(82[b])
11	^{t}BuOH	**A^{PNN}** (3)	rt	56
12	^{t}BuOH	**A^{PNP}** (3)	50 ^{o}C	>99
13	^{t}BuOH	**precat^{PNP}** (3)	rt	0
14	^{t}BuOH	^{t}BuOK (3)	rt	0

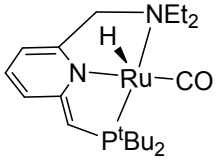
a) Conversions were determined by ^{1}H NMR.



precat^{PNP}



A^{PNP}



A^{PNN}

Synthetic procedures

Preparation of stock solutions of catalysts and reagents

A^{PNP} catalyst (stock solution 1): In the glovebox, the catalyst precursor (PNP)Ru(Cl)(H)(CO)[2][1] (**$precat^{PNP}$**, 28.0 mg, 0.050 mmol) was dissolved in 5 mL of toluene in a 20 ml vial, and then cooled in the freezer to -32 °C. Subsequently, ^{t}BuOK (5.6 mg, 0.050 mmol, 1 eq.) was added and the vial was stored at -32 °C for 1 hour, after which it was allowed to warm to room temperature and stirred for another 3 hours. The solution was filtered and toluene was added to achieve a total volume of 10 mL. This stock solution (0.0050 mol/L) was stored at -32 °C for later use.

A^{PNP} catalyst (stock solution 2, used for reactions on larger scale): In the glovebox, the catalyst precursor (PNP)Ru(Cl)(H)(CO)[2][1] (**$precat^{PNP}$**, 0.375 mmol, 213.0 mg) was dissolved in 25 mL of toluene in a 25 ml vial, and then cooled in the freezer to -32 °C. Subsequently, ^{t}BuOK (42.0 mg, 0.375 mmol, 1 eq.) was added and the vial was stored at -32 °C for 1 hour, after which it was allowed to warm to room temperature and stirred for another 3 hours. The solution was filtered and the filtrate was dried under vacuum for 1 hours. Then the green solid was dissolved in 25 ml ^{t}BuOH and the stock solution (0.0150 mol/L) was used immediately.

A^{PNN} catalyst stock solution: In the glovebox, the catalyst precursor (PNN)Ru(Cl)(H)(CO) (**$precat^{PNN}$**, 14.7 mg, 0.030 mmol) was dissolved in 4 mL of toluene in a 20 ml vial, and then cooled in the freezer to -32 °C. Subsequently, ^{t}BuOK (3.4 mg, 0.030 mmol, 1 eq.) was added and the vial was stored at -32 °C for 1 hour, after which it was allowed to warm to room temperature and stirred for another 3 hours. This stock solution (0.0075 mol/L) was stored at -32 °C for later use.

4-fluorobenzonitrile stock solution: A stock solution (0.30 mol/L) was prepared by dissolving 18.2 mg of 4-fluorobenzonitrile in 0.5 ml *d8*-THF.

4-fluorobenzamide stock solution: A stock solution (0.24 mol/L) was prepared by dissolving 16.7 mg of 4-fluorobenzamide in 0. 5ml *d8*-THF.

Water stock solution: A stock solution (1.70 mol/L) was prepared by dissolving 9.2 µl of H_2O in 300 µl of anhydrous *d8*-THF.

General procedure for catalytic nitrile hydration experiments

In the glovebox, 1.5 mL of a 0.0050 mol/L stock solution of $\mathbf{A}^{\mathbf{PNP}}$ catalyst (0.0075 mmol) was added to a 20 mL vial. After removal of all volatiles under vacuum, 0.5 ml ^{t}BuOH was added to dissolve catalyst again. After ca. 2 min, water (22.5 µl, 1.25 mmol) was added to the catalyst solution, and then the mixture was transferred into a 2 mL GC vial (equipped with a Teflon-lined screw cap and additionally sealed with parafilm) containing the nitrile (0.25 mmol). The reaction mixture was taken out of glovebox and stirred for 16 h to 1 day at rt or 50/80^{o}C. After this time, the reaction mixture was exposed to air to deactivate the catalyst. The procedure for subsequent workup depended on the nature of the reaction mixture:

Procedure a) If precipitated solid product was precipitated during the reaction, 3 mL of ether was added into the vial and the solid product was isolated by filtration and washed with ether. The filtrate was concentrated under vacuum to a viscous oil, then washed with ether/pentane (5:1, 3x2 ml) precipitating the second portion; collecting all the white solid and drying under vacuum gave >99% yield;

Procedure b) If no solid was precipitated during the reaction, the solvent was removed under vacuum to give a viscous oil and the residue was washed with ether/pentane (5:1 or 10:1) to precipitate a solid product; collecting all the white solid and drying under vacuum gave 90-99% yields.

Reactions performed on larger scale

Catalytic hydration reactions for a series of representative nitriles were performed on 2.5 mmol scale. For nitriles **1a**, **1b**, **1i** and **1ad**, 5 mL of a 0.0150 M stock solution of $\mathbf{A}^{\mathbf{PNP}}$ catalyst (0.0750 mmol, 3 mol%) was added to a 20 mL vial containing the nitrile. For nitrile **1r**, 0.8 mL of a 0.0150 M stock solution of $\mathbf{A}^{\mathbf{PNP}}$ catalyst (0.0120 mmol, 0.5 mol%) was diluted with 4.2 mL of ^{t}BuOH and added to a 20 mL vial containing the nitrile. Water (225 µl, 5 equiv relative to nitrile) was added to each of the vials and the mixtures were stirred at 50^{o}C (**1ad**) or rt (**1a**, **1b**, **1i** and **1r**) inside the glovebox. To monitor reaction progress, samples for GC analysis were taken at regular time intervals from each of these reaction mixtures. After the reaction went to completion, workup was carried out as described above.

benzonitrile (**1a**): 257.5 mg (2.5 mmol) of **1a** afforded 287.4 mg (2.38 mmol, 95%) of benzamide (**2a**). Elemental analysis for C_7H_7NO: Calculated: C, 69.41; H, 5.82; N, 11.56; Found: C, 69.44; H, 5.75; N, 11.42.

4-fluorobenzonitrile (**1b**): 302.5 mg (2.5 mmol) of **1b** afforded 336 mg (2.42 mmol, 97%) of 4-fluorobenzamide (**2b**). Elemental analysis for C_7H_6FNO: Calculated: C, 60.43; H, 4.35; N, 10.07; Found: C, 60.64; H, 4.44; N, 9.97.

4-methylbenzonitrile (**1i**): 292.5 mg (2.5 mmol) of **1i** afforded 335.8 mg (2.49 mmol, 99%) of 4-methylbenzamide (**2i**). Elemental Analysis for C_8H_9NO: Calculated: C, 71.09; H, 6.71; N, 10.36; Found: C, 71.26; H, 6.67; N, 10.24.

Cyclohexanecarbonitrile (**1ad**): 272.5 mg (2.5 mmol) of **1ad** afforded 305.0 mg (2.40 mmol, 96%) of cyclohexanecarboxamide (**2ad**). Elemental Analysis for $C_7H_{13}NO$: Calculated: C, 66.11; H, 10.30; N, 11.01; Found: C, 66.09; H, 10.18; N, 10.83.

4-pyridinecarbonitrile (**1r**): 260.0 mg (2.5 mmol) of **1r** afforded 304.0 mg (2.49 mmol, 99%) of 4-pyridinecarboxamide (**2r**). Elemental Analysis for $C_6H_6N_2O$: Calculated: C, 59.01; H, 4.95; N, 22.94; Found: C, 58.87; H, 4.84; N, 22.93.

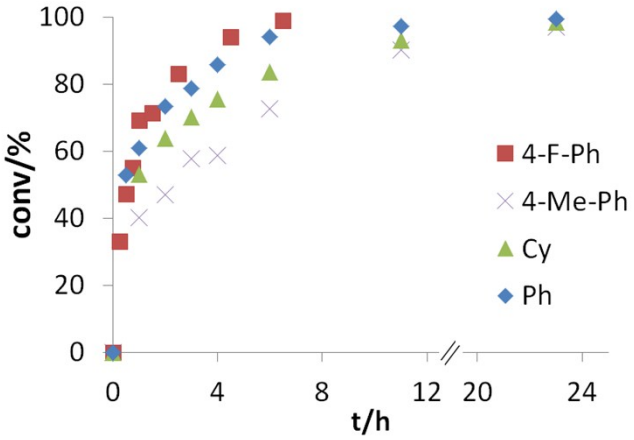
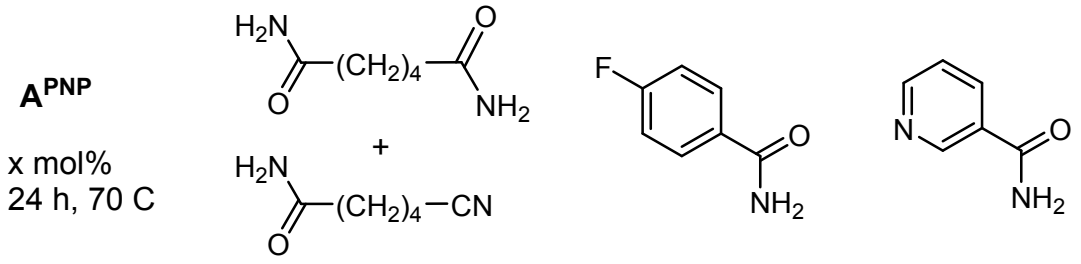


Figure S1. Conversion vs. time plot for hydrdation of nitriles using $\mathbf{A}^{\mathbf{PNP}}$ as catalyst in ^{t}BuOH (3 mol%, 5 eq of H_2O). Reaction progress monitored at room temperature, except for cyclohexane carbonitrile (Cy), which was monitored at 50 ^{o}C.

Reactions performed at 70 °C

Reactions were carried out using the standard procedure described above, but the reaction mixture was heated to 70 °C for 24 h.



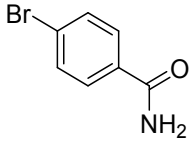
x	0.5 mol%	0.5 mol%	0.1 mol%
conversion	> 99%	98%	> 99%
TON	307	196	1000

Characterization of amide products

All isolated amide products were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as high-resolution mass spectrometry. For the following compounds, these data are in agreement with the literature: **2a-2c**[3], **2e**[3], **2f** [4], **2g**[3], **2h**[3], **2i**[4], **2j**[3], **2k**[3], **2l**[3], **2m**[3], **2n**[3], **2o**[5], **2p-2r**[7], **2s**[8], **2t**[3], **2u**[9], **2v**[3], **2x**[3], **2y**[10], **2z**[11], **2aa**[12], **2ac**[3], **2ad**[13], **2ae**c, **2af**[15], **2ag**[3].

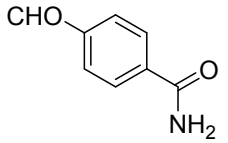
Spectral assignment of amide products for which no NMR data in DMSO-d_6 has been reported in the literature are provided below.

*4-bromobenzamide (**2d**)* [4]



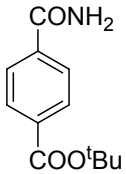
^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.04 (s, 1H, N**H**), 7.81 (d, *J* = 8.2 Hz, 2H, Ph), 7.66 (d, *J* = 8.2 Hz, 2H, Ph), 7.45 (s, 1H, N**H**); ^{13}C NMR (101 MHz, DMSO-*d*6) δ 166.9(**C**ONH$_2$), 133.4 (1-Ph), 131.2 and 129.6 (*o*, *m*-Ph), 125.0 (*p*-Ph). HRMS (ESI) calcd. for C_7H_6BrNO [M+H$^+$] 199.97055, found 199.97005.

*4-formylbenzamide (**2h**)* [16]



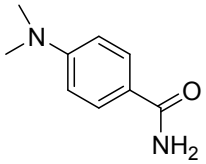
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (s, 1H, C**H**O), 8.17 (s, 1H, N**H**), 8.05 (d, *J* = 8.0 Hz, 2H, Ph), 7.98 (d, *J* = 8.0 Hz, 2H, Ph), 7.60 (s, 1H, N**H**).^{13}C NMR (101 MHz, DMSO-d_6) δ 192.9 (**C**HO), 167.1 (**C**ONH$_2$), 139.3 and 137.8 (Ph, quaternary C), 129.4 and 128.2 (*o*, *m*-Ph). HRMS (ESI) calcd. for $C_8H_7NO_2$ [M+H$^+$] 150.05496, found 150.05477.

*tert-butyl 4-cyanobenzoate (**2i**)*



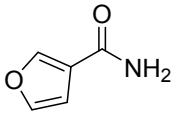
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (s, 1H, N**H**), 7.97(d, *J* = 9.1 Hz, 2H, Ph), 7.95(d, *J* = 9.1 Hz, 2H, Ph), 7.55 (s, 1H, N**H**), 1.55 (s, 9H, *t*Bu); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.1(**C**ONH$_2$), 164.4(**C**OO*t*Bu), 138.0 and 133.5 (Ph, quaternary C), 128.9 and 127.7 (*o*, *m*-Ph), 81.2 (**C**(CH$_3$)$_3$), 27.7 (C(**C**H$_3$)$_3$). HRMS (ESI) calcd. for $C_{12}H_{15}NO_3$ [M+H$^+$] 222.11247, found 222.11229.

*4-(dimethylamino)benzamide (**2n**)*[17]



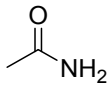
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, *J* = 8.7 Hz, 2H,*o*-Ph), 7.63 (s, 1H, N**H**), 6.93 (s, 1H, N**H**), 6.67 (d, *J* = 8.7 Hz, 2H, *m*-Ph), 2.95 (s, 6H, N(C**H$_3$**)$_2$); ^{13}C NMR (101 MHz, DMSO-*d*6) δ 168.0 (**C**ONH$_2$), 152.1 (*p*-Ph), 128.9 (*o*-Ph), 121.0 (1-Ph), 110.7 (*m*-Ph), 39.7(**C**H$_3$). HRMS (ESI) calcd. for $C_9H_{12}N_2O$ [M+H$^+$] 165.10224, found 165.10172.

*3-furanamide (**2w**)*[5]



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (s, 1H, 1-furan), 7.69 (dd, *J* = 1.7 Hz, 1H, 4-furan), 7.64 (s, 1H, N**H**), 7.18 (s, 1H, N**H**), 6.80 (d, *J* = 1.9 Hz, 1H, 3-furan); ^{13}C NMR (101 MHz, DMSO-*d*6) δ 163.4 (**C**ONH$_2$), 145.3 (1-furan), 143.9 (4-furan), 122.9 (2-furan), 109.3 (3-furan). HRMS (ESI) calcd. for $C_5H_5NO_2$ [M+H$^+$] 112.03930, found 112.03902.

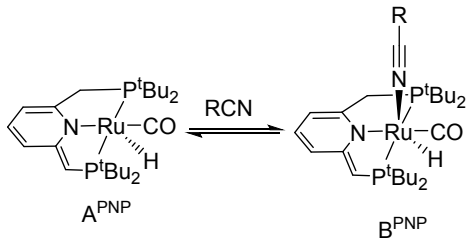
*Acetamide (**2ab**)*[15]



^{1}H NMR (400 MHz, D_2O) δ 2.01 (s, 1H, C**H$_3$**); ^{13}C NMR (101 MHz, D_2O) δ 180.0(**C**O), 23.9(**C**H$_3$).

Stoichiometric NMR scale reactions for **PNP** complexes

Reaction of $\mathbf{A}^{\mathbf{PNP}}$ with 4-fluorobenzonitrile (**1b**)



A solution of $\mathbf{A}^{\mathbf{PNP}}$ was prepared as described above from **precat^{PNP}** (15.6 mg, 0.028 mmol) and ^{t}BuOK (3.1 mg, 0.028 mmol, 1 eq.) in 5 mL of toluene. After the toluene was evaporated, 0.5 mL of THF-d_8 was added to the catalyst, followed by 93 µl of 0.30 mol/L 4-fluorobenzonitrile stock solution (0.028 mmol, 1 eq.), and the solution was transferred into a J. Young NMR tube. Analysis of the NMR spectral data shows the formation of an equilibrium mixture of $\mathbf{B}^{\mathbf{PNP}}$ in rapid exchange with the starting materials $\mathbf{A}^{\mathbf{PNP}}$ + 4-fluorobenzonitrile.[18]

NMR data for the equilibrium mixture [$\mathbf{A}^{\mathbf{PNP}}$ + **1b** ⇄ $\mathbf{B}^{\mathbf{PNP}}$]:

^{19}F NMR (376 MHz, THF-*d8*) δ -102.8;
^{31}P NMR (162 MHz, THF-*d8*) δ 84.8 (d, J = 219.9 Hz), 78.7 (d, J = 219.9 Hz).;
^{1}H NMR (500 MHz, THF-*d8*) δ 7.73 (dd, *J* = 8.8, 5.0 Hz, 2H, *o*-Ph), 7.29 (dd, *J* = 8.3 Hz, 2H, *m*-Ph), 6.23 (t, *J* = 7.7 Hz, 1H, Py-**4H**), 6.01 (d, *J* = 8.8 Hz, 1H, Py-**5H**), 5.39 (d, *J* = 6.4 Hz, 1H, Py-**3H**), 3.43 (d, *J* = 4.0 Hz, 1H, Py-2-C**H**), 3.16 (d, *J* = 8.7 Hz, 2H, Py-5-C**H$_2$**), 1.37 – 1.27 (m, 36H, *t*Bu), -19.06 (s, 1H, Ru**H**).

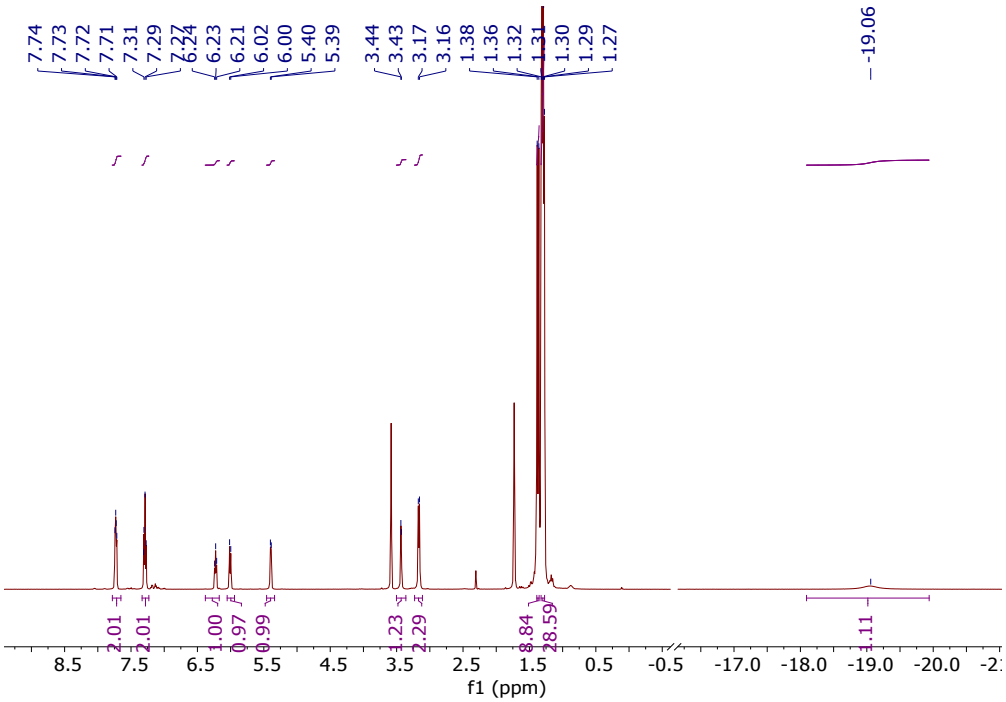


Figure S2A. ^{1}H NMR spectrum of reaction mixture $\mathbf{A}^{\mathbf{PNP}}$ + 4-fluorobenzonitrile (**1b**) in THF-d_8.

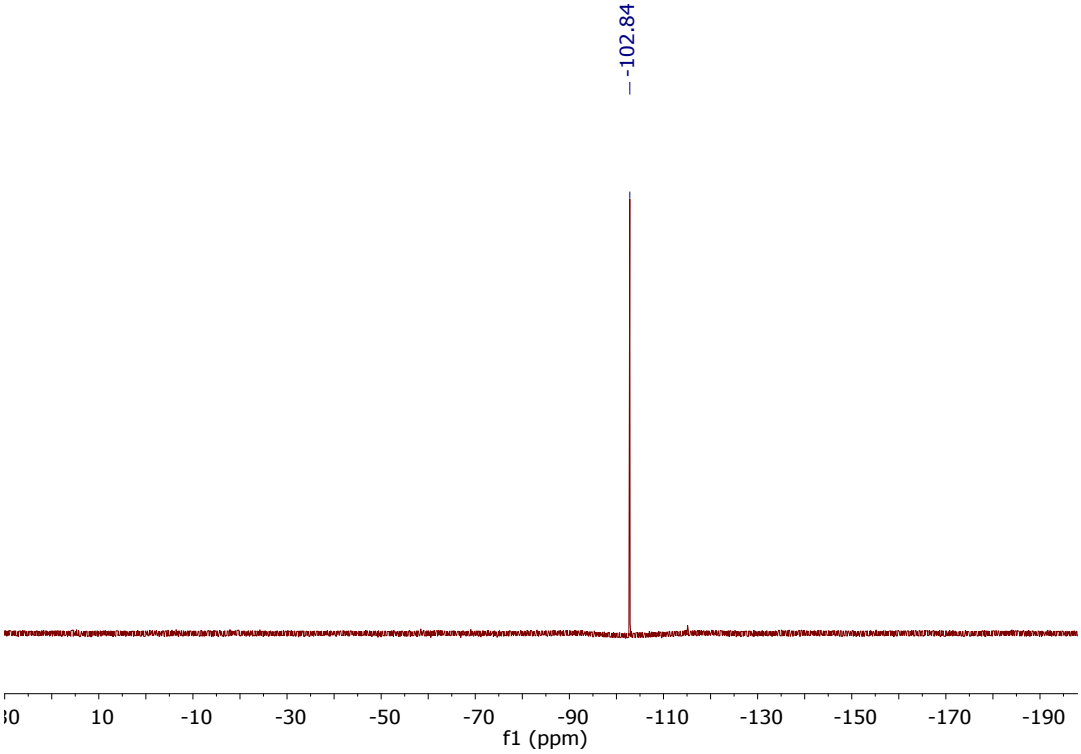


Figure S2B. ^{19}F NMR spectrum of reaction mixture $\mathbf{A}^{\mathbf{PNP}}$ + 4-fluorobenzonitrile (**1b**) in THF-d_8.

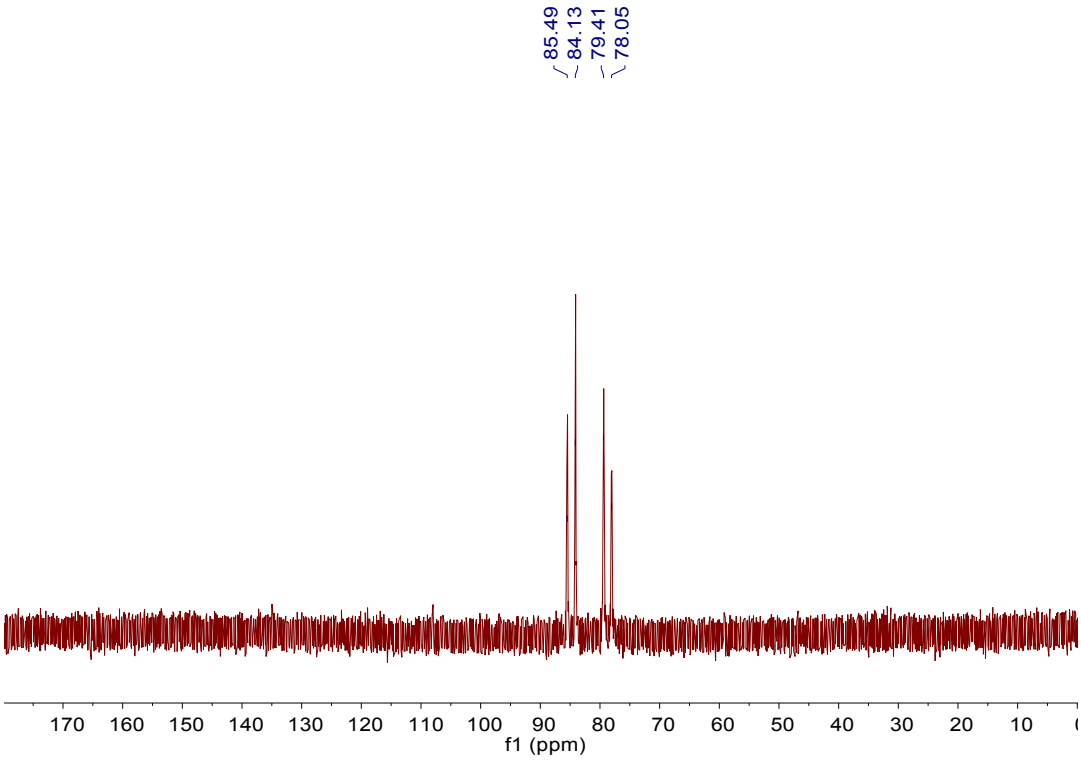
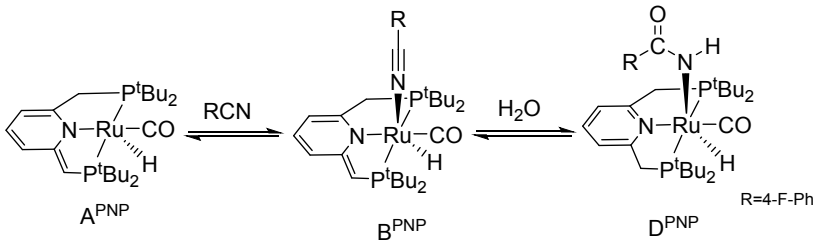


Figure S2C. ^{31}P NMR spectrum of reaction mixture $\mathbf{A}^{\mathbf{PNP}}$ + 4-fluorobenzonitrile (**1b**) in THF-d_8.

Reaction of **A**^{PNP} with 4-fluorobenzonitrile (**1b**) and water



Subsequent addition of 16.4 µl of H_2O stock solution (1.70 mol/L, 0.028 mmol, 1 eq.) to the mixture described above resulted in the slow appearance of a new set of NMR signals that is attributed to the Ru-carboxamide species **D**^{PNP} as the major product.

NMR data for **D**^{PNP}:
^{19}F NMR (376 MHz, THF-*d8*) -118.3 (**D**^{PNP});
^{31}P NMR (162 MHz, THF-*d8*) 82.3(**D**^{PNP});
^{1}H NMR (500 MHz, THF-*d8*) δ -13.05 (t, *J* = 19.8 Hz, 8H, Ru**H** of **D**^{PNP}).

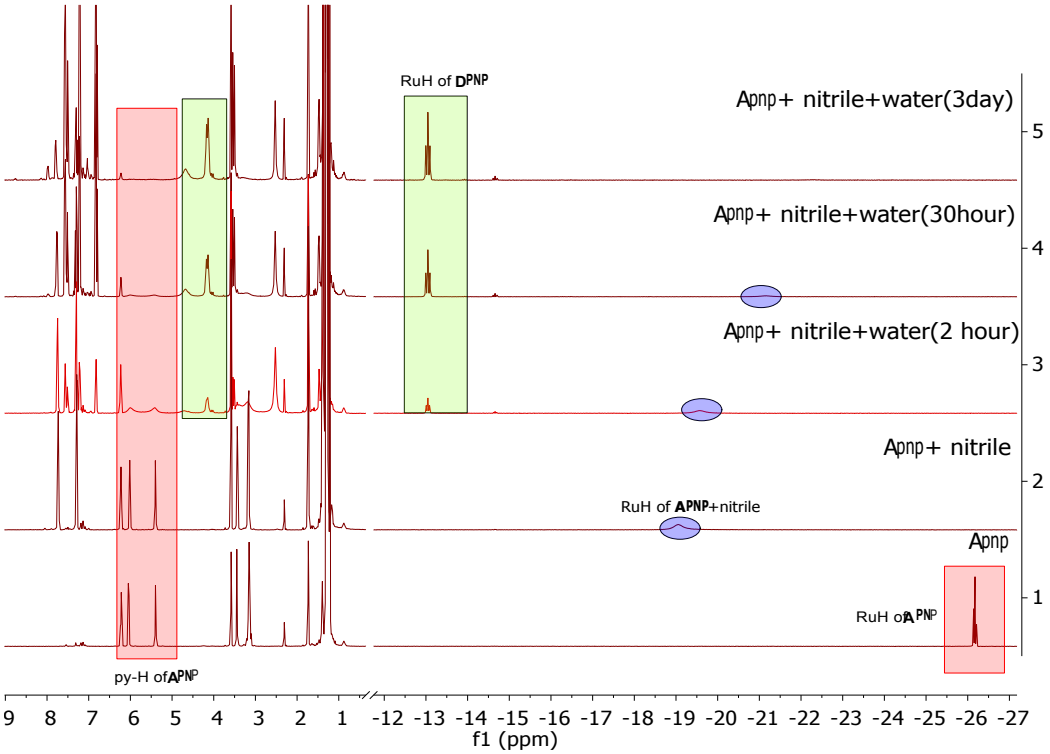


Figure S3A. ^{1}H NMR spectra for the stoichiometric reaction of **A**^{PNP} with 4-fluorobenzonitrile (**1b**) and water

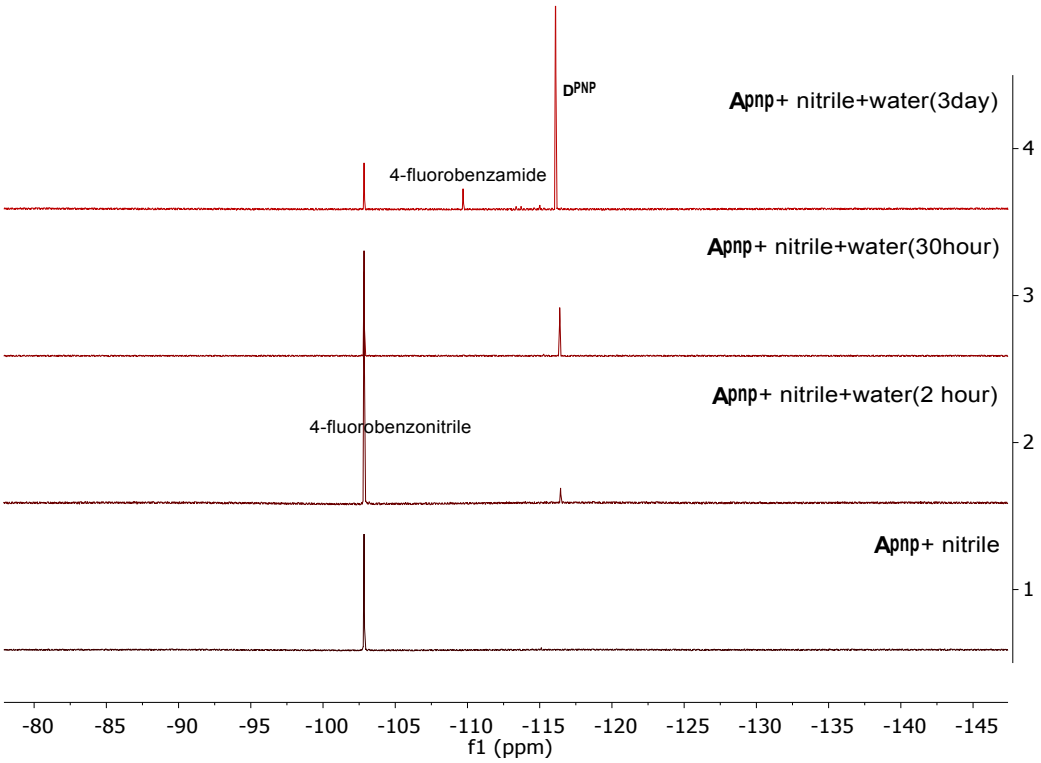


Figure S3B. ^{19}F NMR spectra for the stoichiometric reaction of $\mathbf{A^{PNP}}$ with 4-fluorobenzonitrile (**1b**) and water.

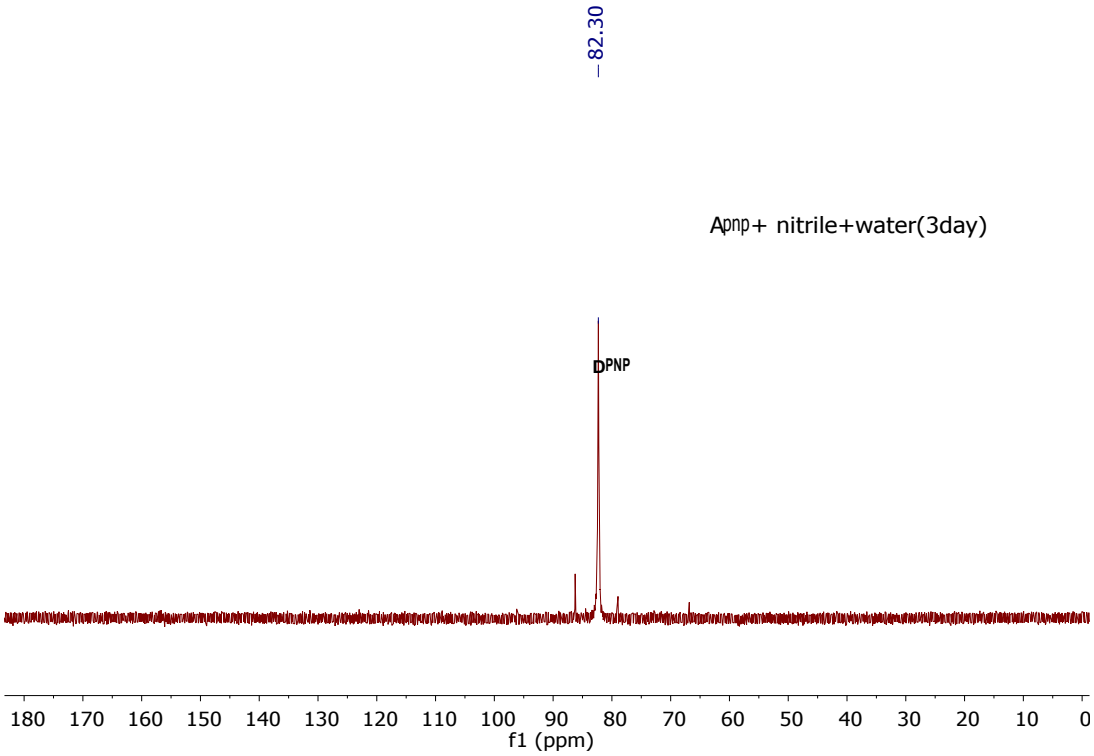
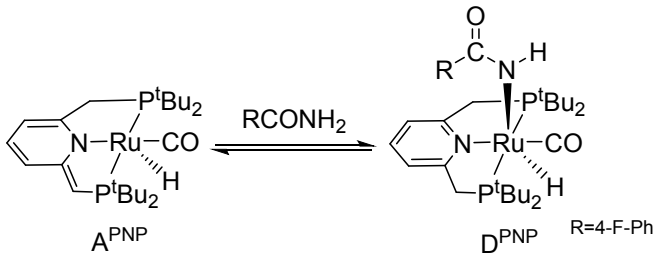


Figure S3C. ^{31}P NMR spectrum for the stoichiometric reaction of $\mathbf{A^{PNP}}$ with 4-fluorobenzonitrile (**1b**) and water, recorded after standing at room temperature for 3 days.

Characterization of $\mathbf{D^{PNP}}$

Assignment of the major product from the above NMR scale reaction ($\mathbf{A^{PNP}}$+ **1b** + H_2O) as compound $\mathbf{D^{PNP}}$ was corroborated by an independent synthesis as described below.



In a glovebox, 1 ml of $\mathbf{A^{PNP}}$ stock solution (0.017 mol/L, 0.017 mmol) was added to a vial. After removal of all volatiles, 0.5 mL of *d8*-THF was added to dissolve the catalyst. Then 70 µl of 4-fluorobenzamide (**2b**) stock solution (0.24 mol/L, 0.017 mmol) was added. The solution was transferred into a J. Young NMR tube and taken out of the glovebox. NMR characterization data are consistent with formation of $\mathbf{D^{PNP}}$ as the major species (> 90%). In addition to compound $\mathbf{D^{PNP}}$, the Ru-H resonance of $\mathbf{A^{PNP}}$ as well as amide **2b** are visible, which shows that these are in equilibrium.

NMR data for $\mathbf{D^{PNP}}$:

^{19}F NMR (376 MHz, THF-*d8*) δ -118.3.
^{31}P NMR (162 MHz, THF-*d8*) δ 82.3.
^{1}H NMR (400 MHz, THF-*d8*) δ 7.56 (dd, *J* = 8.8, 5.9 Hz, 2H, *o*-Ph), 7.51 (t, *J* = 7.7 Hz, 1H, Py-**4H**), 7.21 (d, *J* = 7.7 Hz, 2H, Py-**3,5H**), 6.82 (dd, *J* = 8.8 Hz, 2H, *m*-Ph), 4.66 (s, 1H, N**H**), 4.16 (d, *J* = 16.3 Hz, 2H, py-2,6-C**H$_2$**), 3.52 (dt, *J* = 16.3, 3.9 Hz, 2H, py-2,6-C**H$_2$**), 1.35 (dd, *J* = 6.4 Hz, 18H, P*t*Bu$_2$), 1.29 (t, *J* = 6.4 Hz, 18H, P*t*Bu$_2$), -13.04 (t, *J* = 19.9 Hz, 1H, Ru**H**).
^{13}C NMR (101 MHz, THF-*d8*) δ 209.8 (Ru**C**O), 172.3 (**C**ONH), 165.3 (py-**2,6C**), 163.45 (d, *J* = 243.7 Hz, *p*-F-ph-**4C**), 140.9 (*p*-F-ph-**1C**), 137.7 (py-**4C**), 129.32 (d, *J* = 8.1 Hz, *p*-F-ph-***o*C**), 120.1 (py-**3,5C**), 114.17 (d, *J* = 21.0 Hz, *p*-F-ph-***p*C**), 39.4 (py-2,6-**C**H$_2$), 37.50 (dd, *J* = 5.3 Hz, **C**(CH$_3$)$_3$), 36.56 (dd, *J* = 10.6 Hz, **C**(CH$_3$)$_3$), 30.5 and 30.0 C(**C**H$_3$)$_3$).

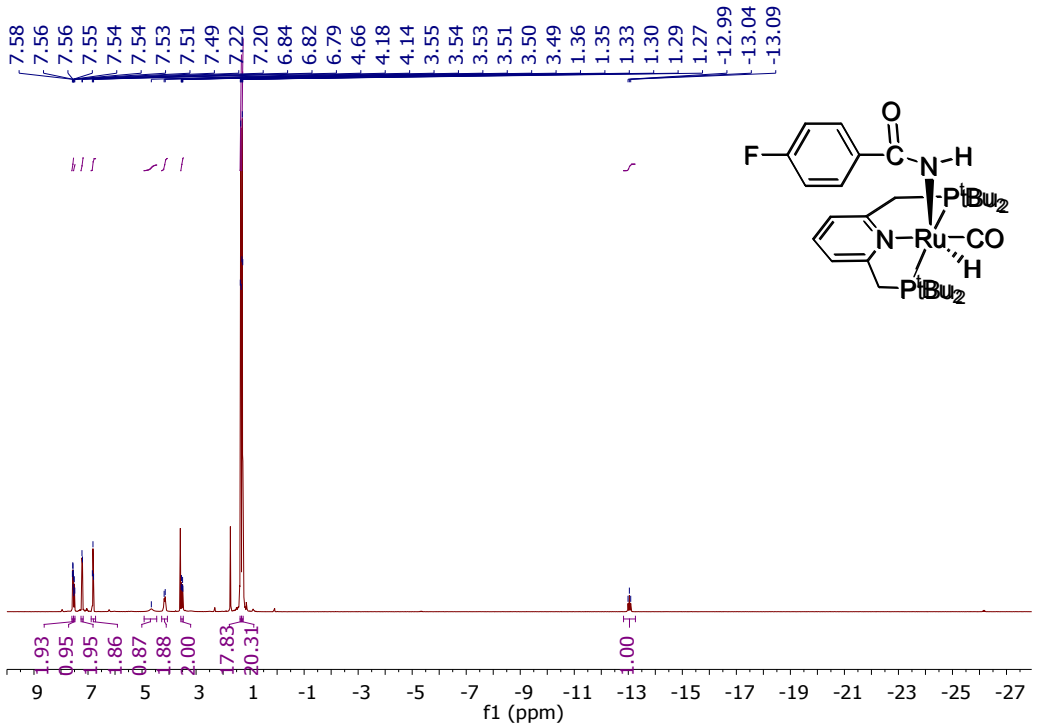


Figure S4A. ^{1}H NMR spectrum of **D^{PNP}** in THF-d_8

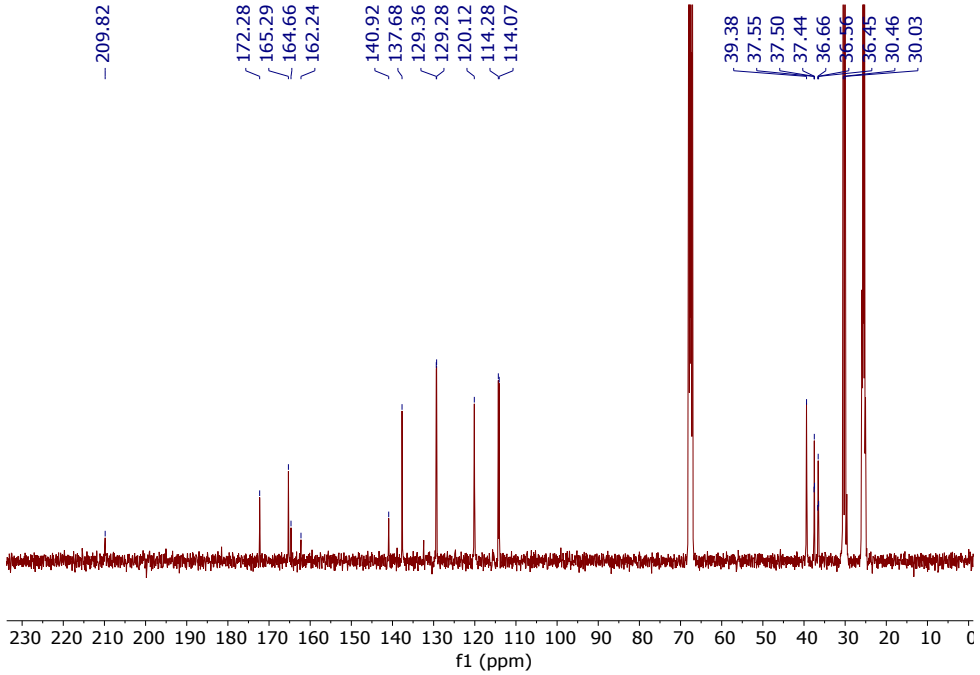


Figure S4B. ^{13}C NMR spectrum of **D^{PNP}** in THF-d_8

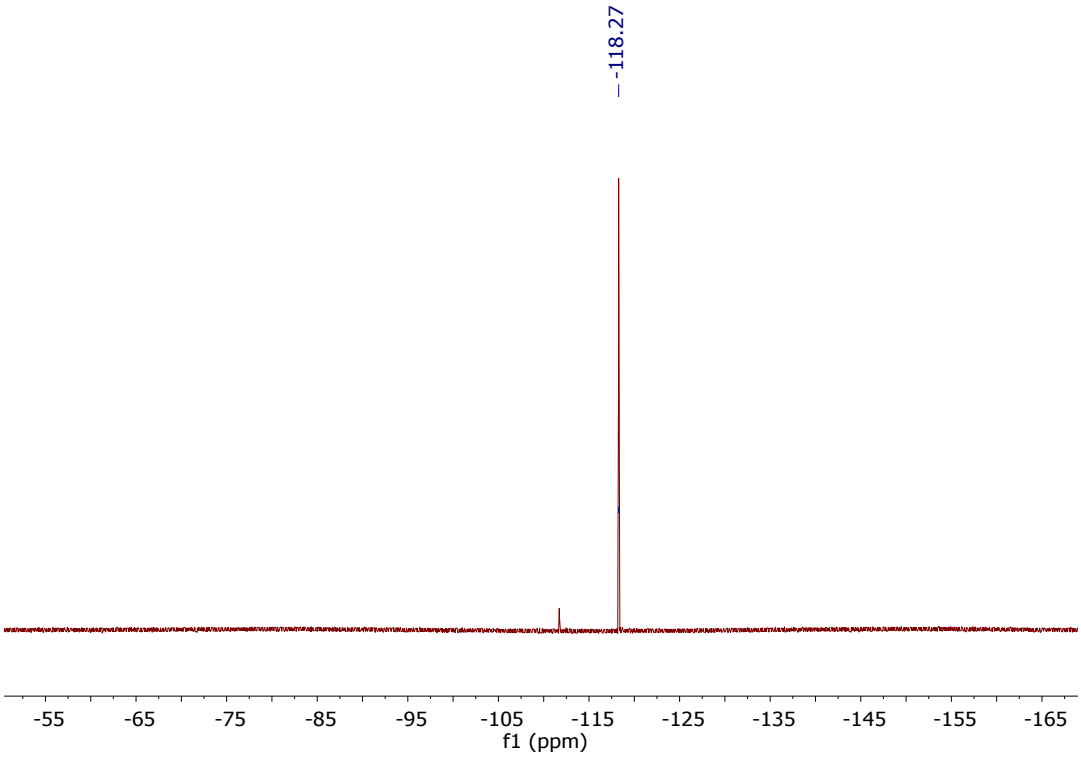


Figure S4C. ^{19}F NMR spectrum of $\mathbf{D^{PNP}}$ in THF-d_8

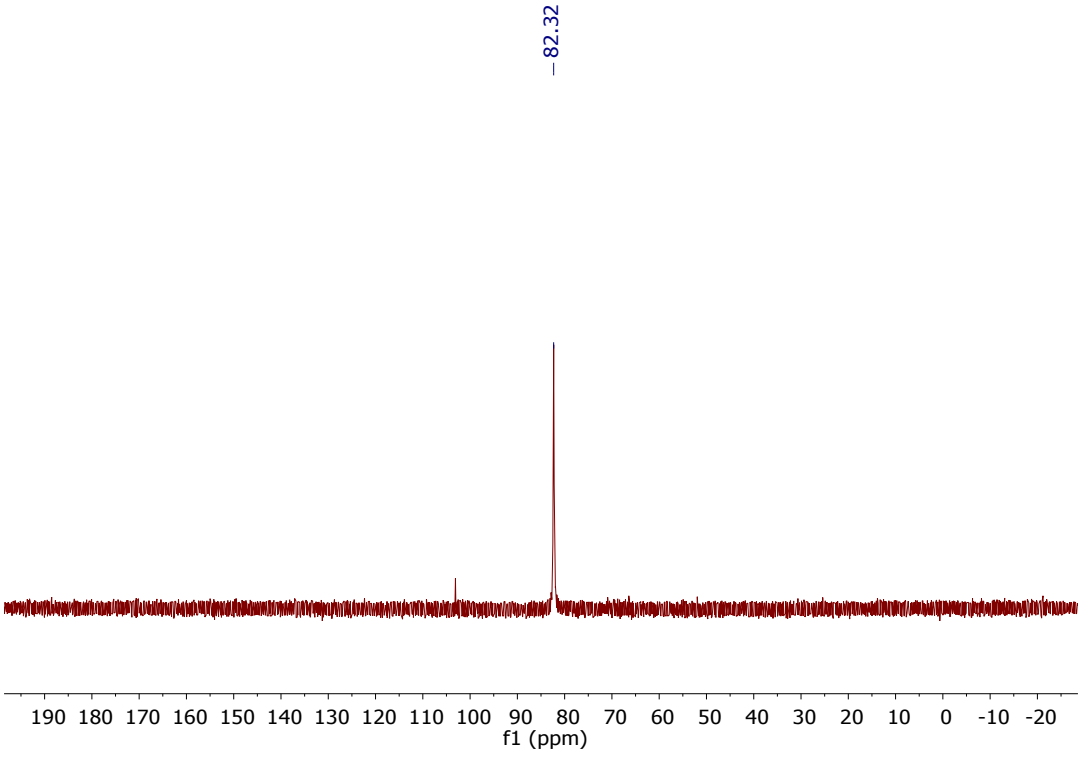
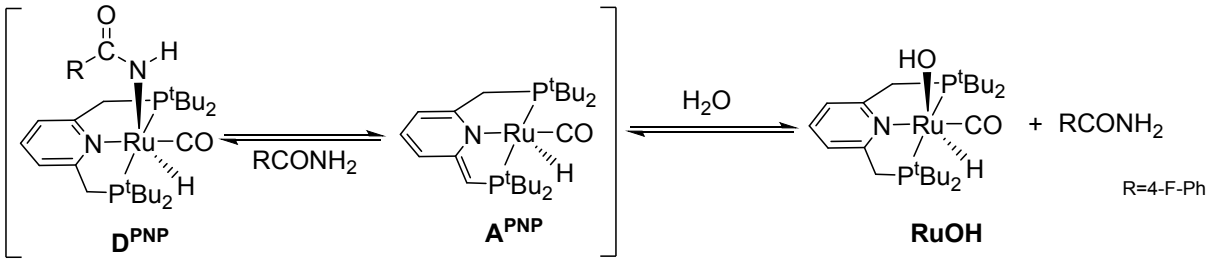


Figure S4D. ^{31}P NMR spectrum of $\mathbf{D^{PNP}}$ in THF-d_8

Reaction of **D^{PNP}** with water



An NMR solution of **D^{PNP}**, prepared as described above, was treated with increasing amounts of water by sequential addition of a 1.70 mol/L stock solution (0.5, 1, 2, 5, 10, 20 eq). After each addition, NMR spectra were recorded.

Before addition of water, the mixture of **A^{PNP}** + amide **2b** shows the formation of **D^{PNP}** as the major product, with a small amount of **A^{PNP}** left in the equilibrium mixture.
Addition of water results in broadening and ultimately disappearance (> 10 equiv H_2O) of the signals due to **A^{PNP}**, with concomitant appearance of a new Ru-H triplet at -14.68 ppm. In the ^{31}P NMR spectrum, a new resonance at 86.3 ppm appears. These signals are attributed to the Ru-hydroxide species shown in the scheme (**RuOH**) by comparison to the literature values reported this compound.[19][20] The changes in the ^{19}F NMR spectrum upon addition of increasing amounts of water show that the amount of free amide **2b** in solution (relative to that bound in **D^{PNP}**) increases ca. twofold upon addition of 20 equiv of water, and the data indicate that the deromatized species **A^{PNP}** is involved in dynamic equilibria with nitrile, amide and water.

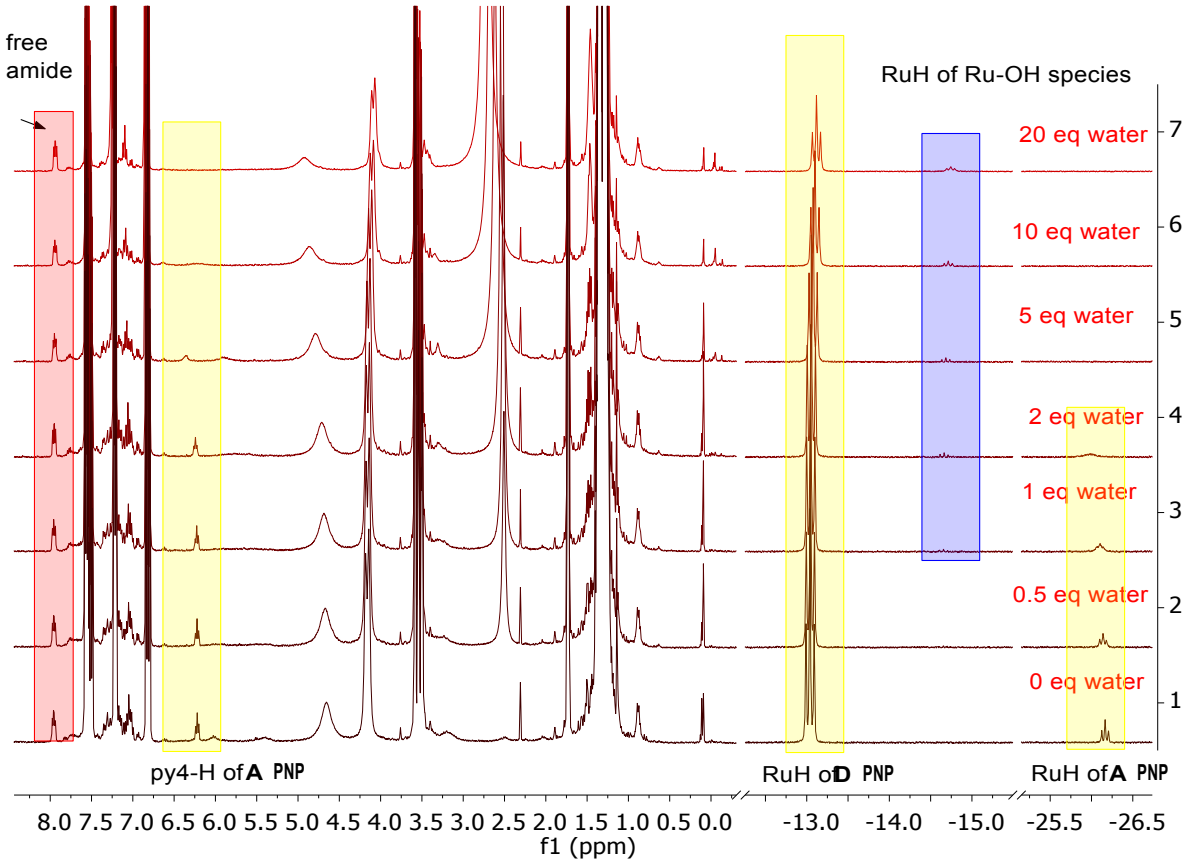


Figure S5A. Effect of water amount on the equilibrium of $\mathbf{D}^{PNP}$ with $\mathbf{A}^{PNP}$ and 4-fluorobenzamide (**2b**) followed by ^{1}H NMR

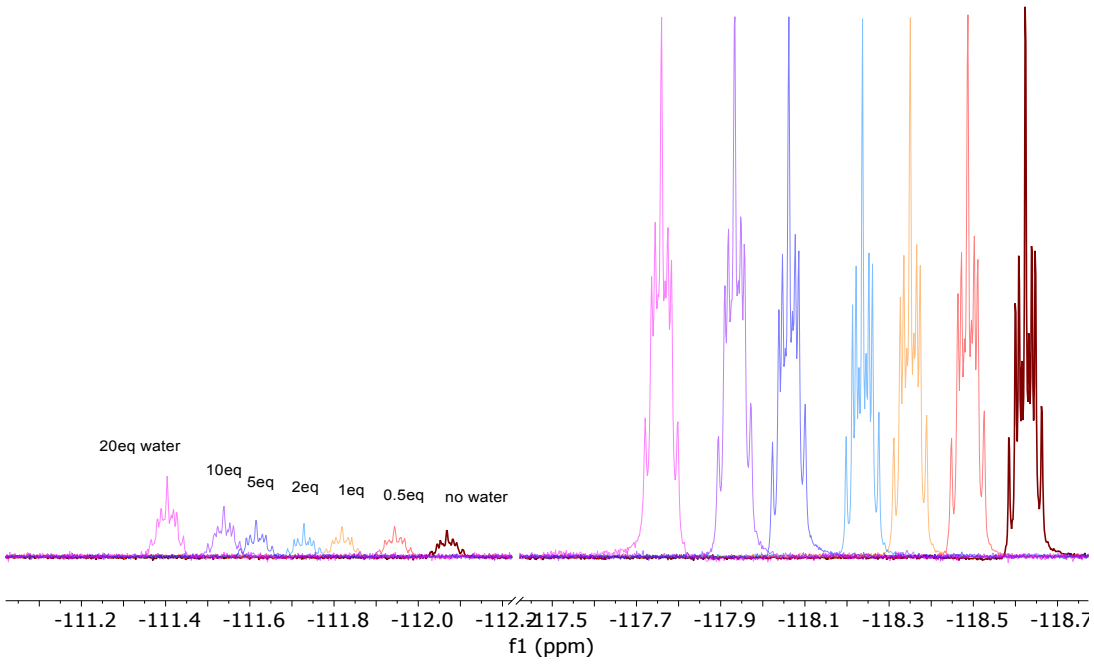


Figure S5B. Effect of water amount on the equilibrium of **D**^{PNP} with **A**^{PNP} and 4-fluorobenzamide (**2b**) followed by ^{19}F NMR

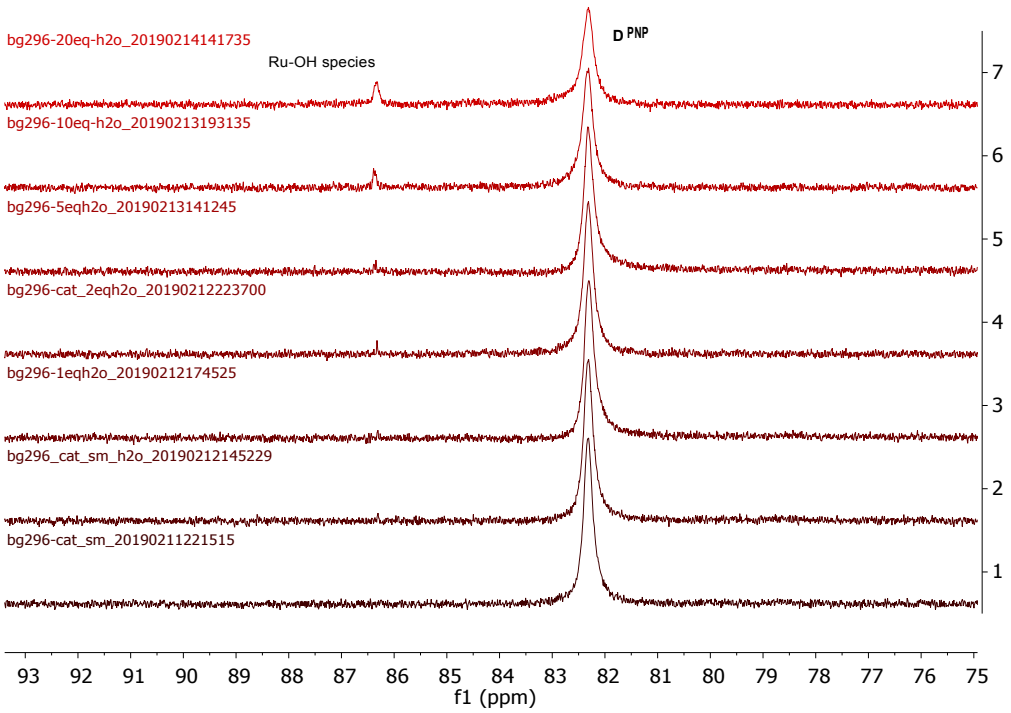
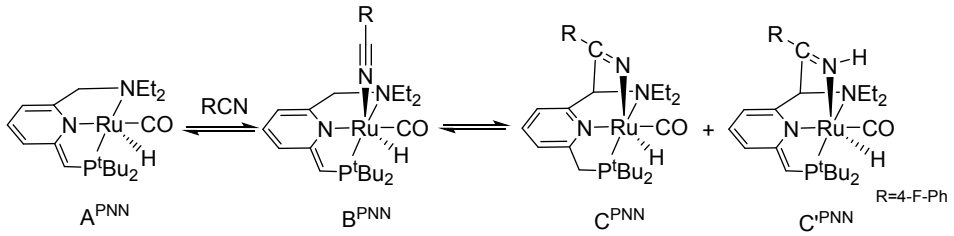


Figure S5C. Effect of water amount on the equilibrium of **D**^{PNP} with **A**^{PNP} and 4-fluorobenzamide (**2b**) followed by ^{31}P NMR

Stoichiometric NMR scale reactions for **PNN** complexes

Reaction of $\mathbf{A^{PNN}}$ with 4-fluorobenzonitrile (**1b**)



A^{PNN} B^{PNN} C^{PNN} C'^{PNN}

In a glovebox, 2 ml of $\mathbf{A^{PNN}}$ stock solution (0.0075 mol/L, 0.015 mmol) was added to a vial. After removal of all volatiles, 0.5 mL of *d8*-THF was added to dissolve the catalyst. Then 50 µl of 4-fluorobenzonitrile stock solution (0.30 mol/L, 0.015 mmol) was added. The solution was transferred into a J. Young NMR tube and taken out of glovebox. NMR characterization data are consistent with formation of an equilibrium mixture of $\mathbf{C^{PNN}}$ and $\mathbf{C'^{PNN}}$ in a ratio of 1 : 3.84. In addition, resonances due to the equilibrium [$\mathbf{A^{PNN}}$ + **1b** ⇄ $\mathbf{B^{PNN}}$] were observed (e.g., Ru-H at -25.24) that account for ca. 7% of the total Ru-H concentration.

selected NMR data for $\mathbf{C^{PNN}}$ and $\mathbf{C'^{PNN}}$:

^{19}F NMR (376 MHz, THF-*d8*) δ -109.6($\mathbf{C'^{PNN}}$), -118.0($\mathbf{C^{PNN}}$).
^{31}P NMR (162 MHz, THF-*d8*) δ 117.6 ($\mathbf{C^{PNN}}$), 102.1 ($\mathbf{C'^{PNN}}$).
^{1}H NMR (500 MHz, THF-*d8*) δ 11.65 (s, 3.2H, N**H** of $\mathbf{C'^{PNN}}$), -10.47 (d, *J* = 25.7 Hz, 1H, Ru**H** of $\mathbf{C^{PNN}}$), -13.75 (d, *J* = 32.8 Hz, 3.8H, Ru**H** of $\mathbf{C'^{PNN}}$).

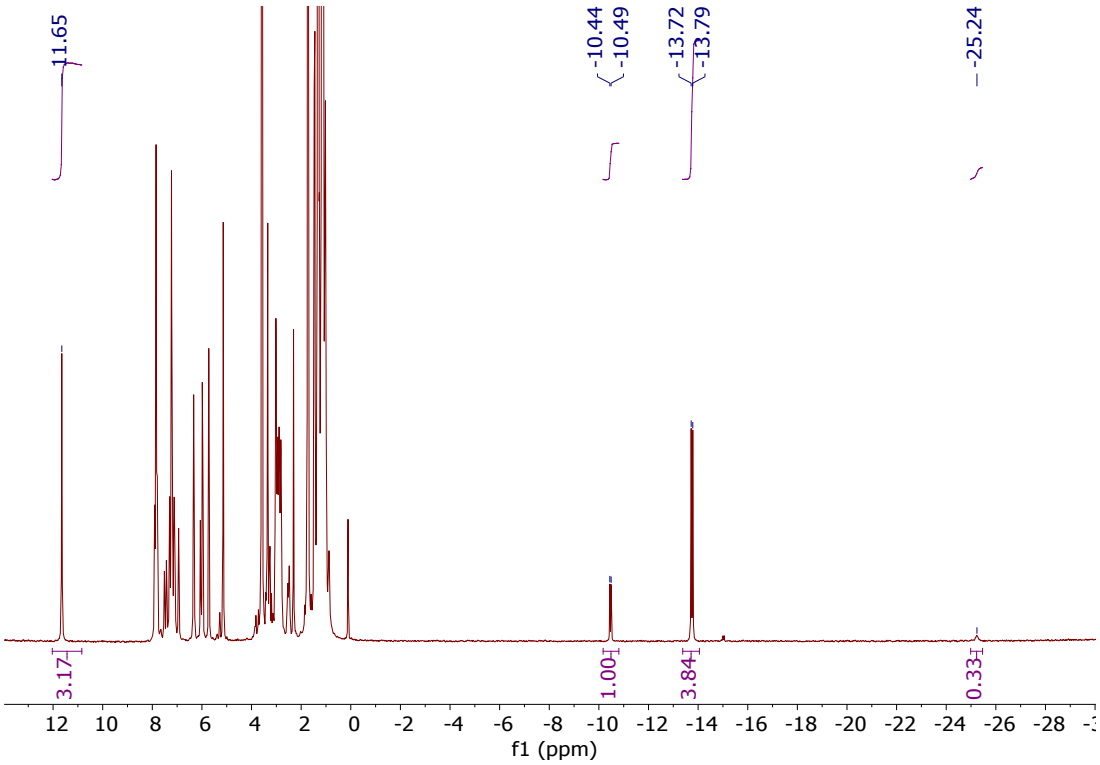


Figure S6A. ^{1}H NMR spectrum of reaction mixture $\mathbf{A}^{\mathbf{PNN}}$ + 4-fluorobenzonitrile (**1b**) in THF-d_8.

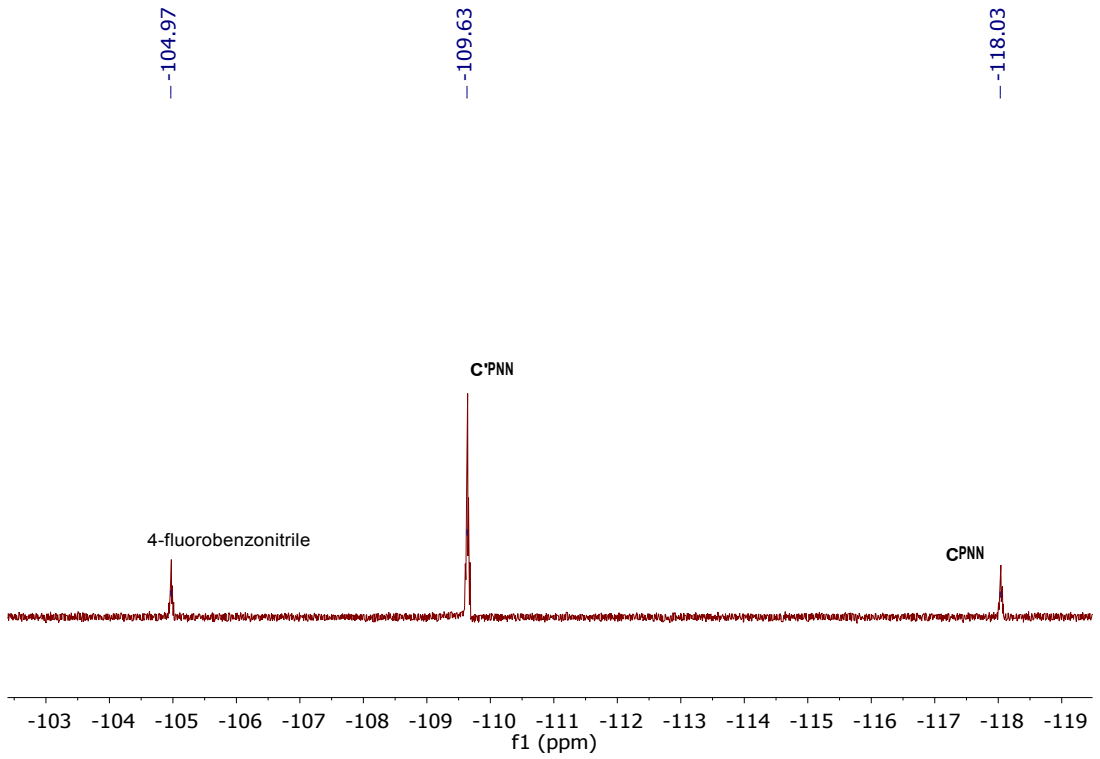


Figure S6B. ^{19}F NMR spectrum of reaction mixture $\mathbf{A}^{\mathbf{PNN}}$ + 4-fluorobenzonitrile (**1b**) in THF-d_8.

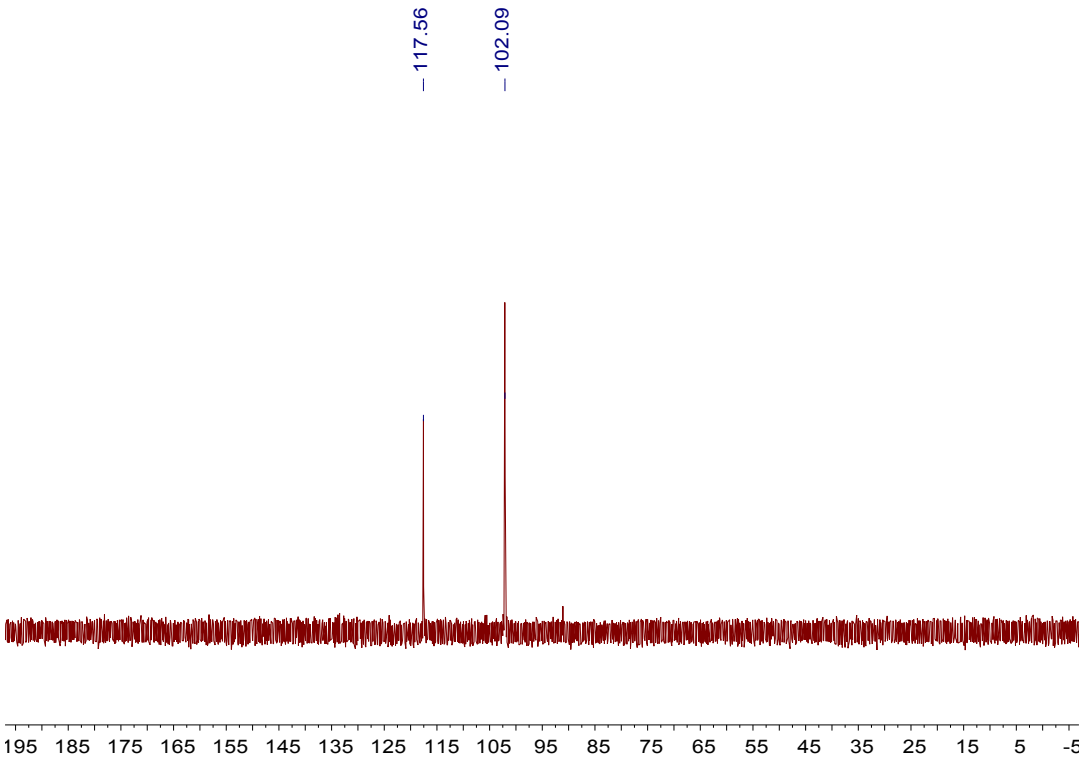
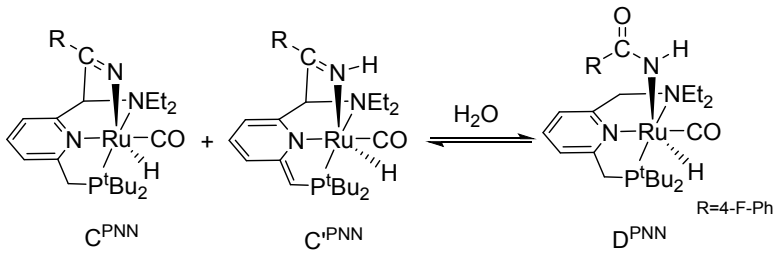


Figure S6C. ^{31}P NMR spectrum of reaction mixture $\mathbf{A}^{\mathbf{PNN}}$ + 4-fluorobenzonitrile (**1b**) in THF-d_8.

Reaction of $\mathbf{A}^{\mathbf{PNN}}$ with 4-fluorobenzonitrile (**1b**) and water



Subsequent addition of 8.8 µl of a H_2O stock solution (1.7 mol/L, 0.015 mmol) to the mixture described above resulted in the slow appearance of a new set of NMR signals that is attributed to the Ru-carboxamide species $\mathbf{D}^{\mathbf{PNN}}$ as the major Ru-containing product.

NMR data for $\mathbf{D}^{\mathbf{PNN}}$:

^{19}F NMR (376 MHz, THF-*d8*) δ -117.7
^{31}P NMR (162 MHz, THF-*d8*) δ 105.3
^{1}H NMR (400 MHz, THF-*d8*) δ -13.06 (d, *J* = 26.9 Hz, Ru**H**)

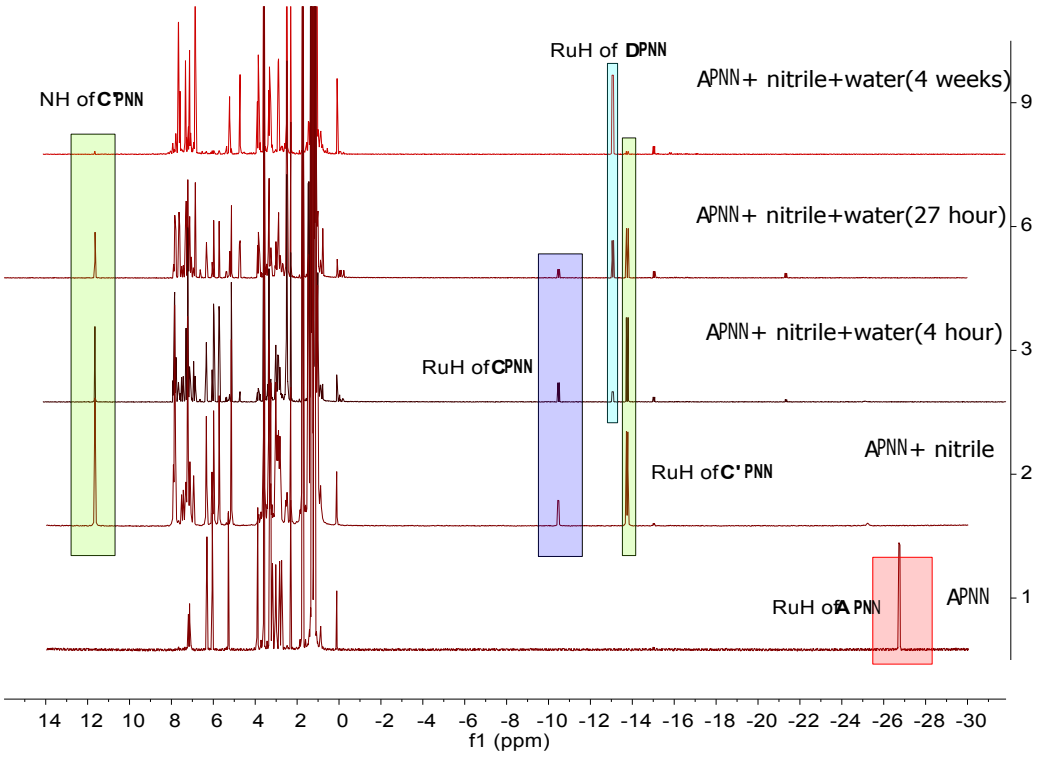


Figure S7A. ^{1}H NMR spectra for the stoichiometric reaction of $\mathbf{A}^{\mathbf{PNN}}$ with 4-fluorobenzonitrile (**1b**) and water.

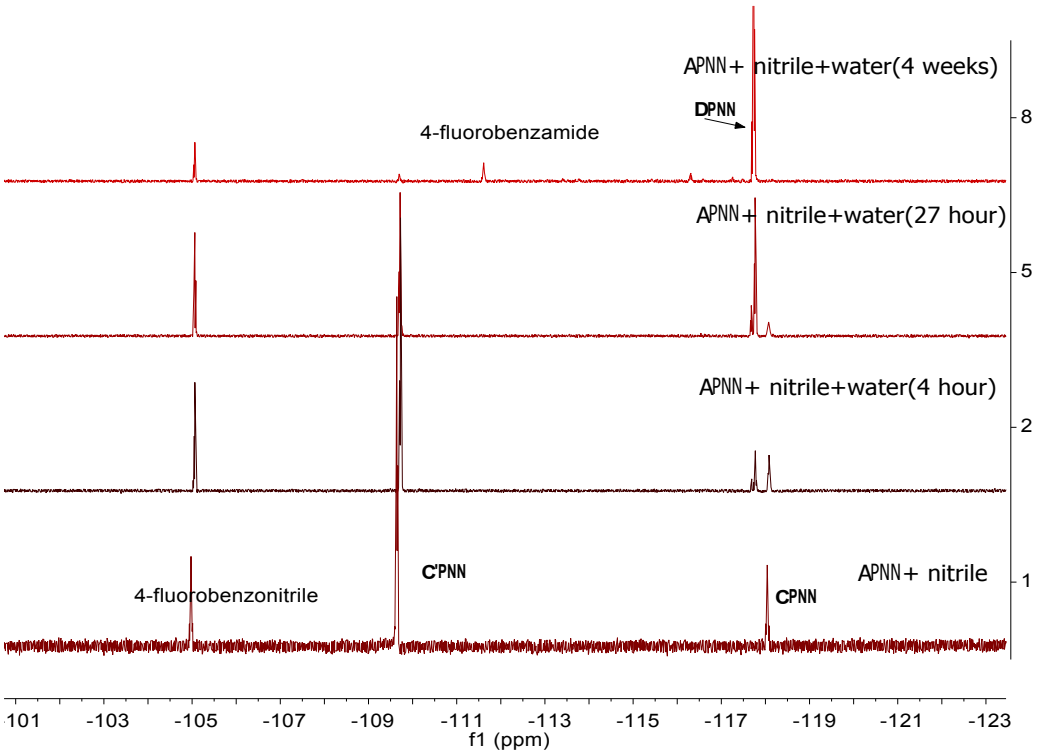


Figure S7B. ^{19}F NMR spectra for the stoichiometric reaction of $\mathbf{A^{PNN}}$ with 4-fluorobenzonitrile (**1b**) and water.

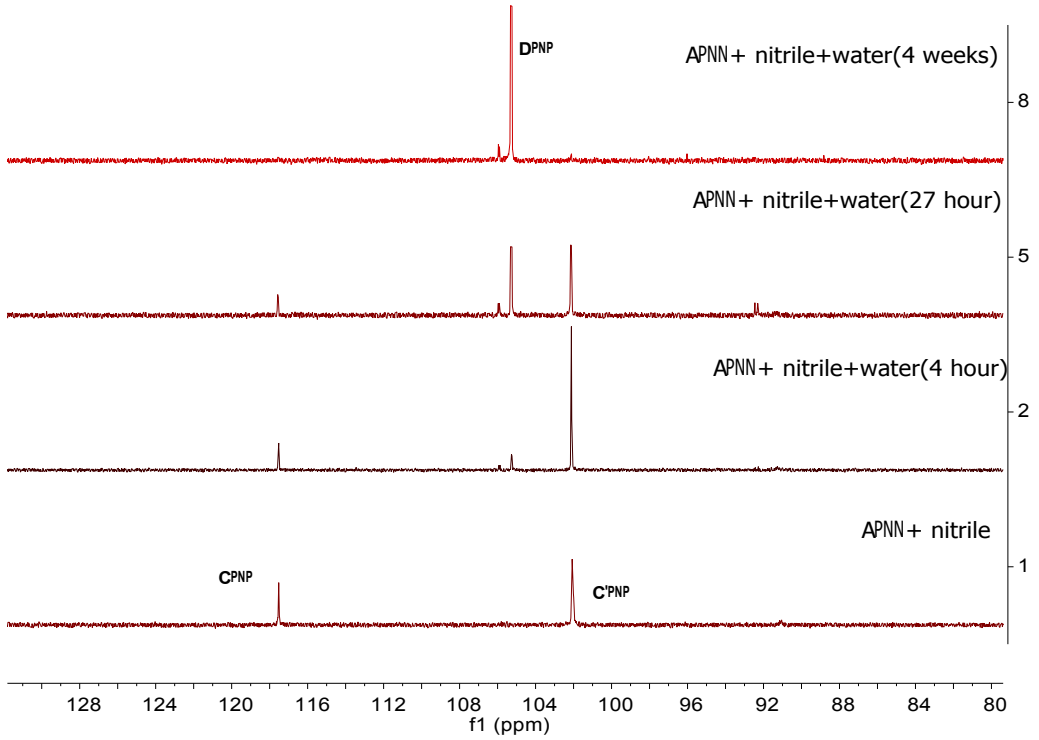
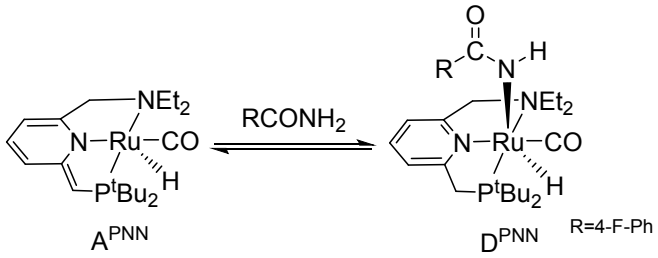


Figure S7C. ^{31}P NMR spectra for the stoichiometric reaction of $\mathbf{A^{PNN}}$ with 4-fluorobenzonitrile (**1b**) and water.

Characterization of $\mathbf{D^{PNN}}$

Assignment of the major product from the above NMR scale reaction ($\mathbf{A^{PNN}}$ + **1b** + H_2O) as compound $\mathbf{D^{PNN}}$ was corroborated by an independent synthesis as described below.



In glovebox, a small vial was added with 2 ml of 0.0075 mol/L $\mathbf{A^{PNN}}$ stock solution (0.0150 mmol, 1 eq.). After under vacuum for 0.5 hour, 0.5 ml *d8*-THF was added to dissolve the catalyst (dark red). Then 63 µl of 0.24 mol/L 4-fluorobenzamide (0.0150 mmol, 1 eq.) was added forming amide adduct $\mathbf{D^{PNN}}$ (light yellow). The solution was then transferred into a J. Young NMR tube and taken out of glovebox to characterize by NMR spectroscopy, which shows full conversion to $\mathbf{D^{PNN}}$.

^{19}F NMR (376 MHz, THF-*d8*) δ -117.7.
^{31}P NMR (162 MHz, THF-*d8*) δ 105.3.
^{1}H NMR (400 MHz, THF-*d8*) δ 7.70 – 7.64 (m, 2H,*p*-F-Ph-***o*H**), 7.61 (t, *J* = 7.7 Hz, 1H,Py-**4H**), 7.32 (d, *J* = 7.8 Hz, 1H, py-**3H**), 7.14 (d, *J* = 7.2 Hz, 1H, py-**5H**), 6.92 – 6.81 (m, 2H, *p*-F-Ph-***m*H**), 5.21 (s, 1H, N**H**), 4.75 (d, *J* = 14.3 Hz, 1H,py-6-C$\mathbf{H_2}$), 3.87 (dd, *J* = 14.4, 2.6 Hz, 1H, py-6-C$\mathbf{H_2}$), 3.81 (dd, *J* = 16.8, 9.5 Hz, 1H, py-2-C$\mathbf{H_2}$), 3.41 – 3.19 (m, 3H, py-2-C$\mathbf{H_2}$ and N(C$\mathbf{H_2}$$CH_3)_2$), 2.96 – 2.85 (m, 2H, N(C$\mathbf{H_2}$$CH_3)_2$), 1.29 (d, *J* = 12.9 Hz, 9H,P*t*Bu_2), 1.28 (t, *J* = 7.0 Hz, 3H, N(CH_2C$\mathbf{H_3}$)$_2$), 1.23 (d, *J* = 12.9 Hz, 9H, P*t*Bu_2), 1.06 (t, *J* = 7.2 Hz, 3H, N(CH_2C$\mathbf{H_3}$)$_2$), -13.06 (d, *J* = 26.9 Hz, 1H, Ru**H**).
^{13}C NMR (101 MHz, THF-*d8*) δ 209.2 (d, *J* = 16.3 Hz, Ru**C**O), 172.3 (**C**ONH), 163.3 (d, *J* = 244.1 Hz, *p*-F-ph-**4C**), 162.4 (d, *J* = 3.9 Hz, py-2**C**), 161.6 (py-6**C**), 140.2 (d, *J* = 2.9 Hz, *p*-F-ph-**1C**), 137.0 (py-4**C**), 129.2 (d, *J* = 8.0 Hz, *p*-F-ph-***o*C**), 120.3 (d, *J* = 9.7 Hz, py-3**C**), 119.1 (py-4**C**), 114.0(d, *J* = 21.1 Hz, *p*-F-ph-***m*C**), 66.5 (py-6-**C**H_2), 55.6 and 50.6 (N(**C**$H_2CH_3)_2$), 38.1 (d, *J* = 20.1 Hz, py-2-**C**H_2), 36.7 (d, *J* = 12.6 Hz, **C**$(CH_3)_3$), 36.4 (d, *J* = 25.5 Hz, **C**$(CH_3)_3$), 29.9 (d, *J* = 3.1 Hz, C(**C**$H_3)_3$), 29.5 (d, *J* = 4.5 Hz, C(**C**$H_3)_3$), 11.6 and 8.6 (N(CH_2**C**$H_3)_2$).

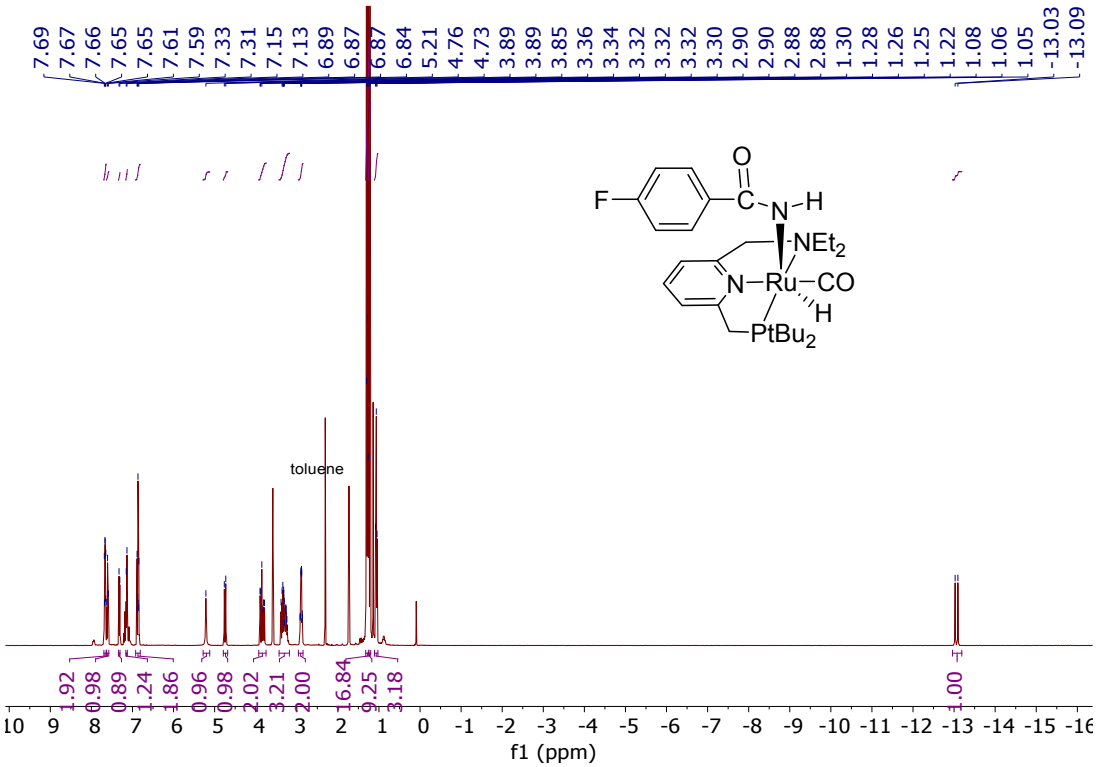


Figure S8A. ^{1}H NMR spectrum of **D^{PNN}**

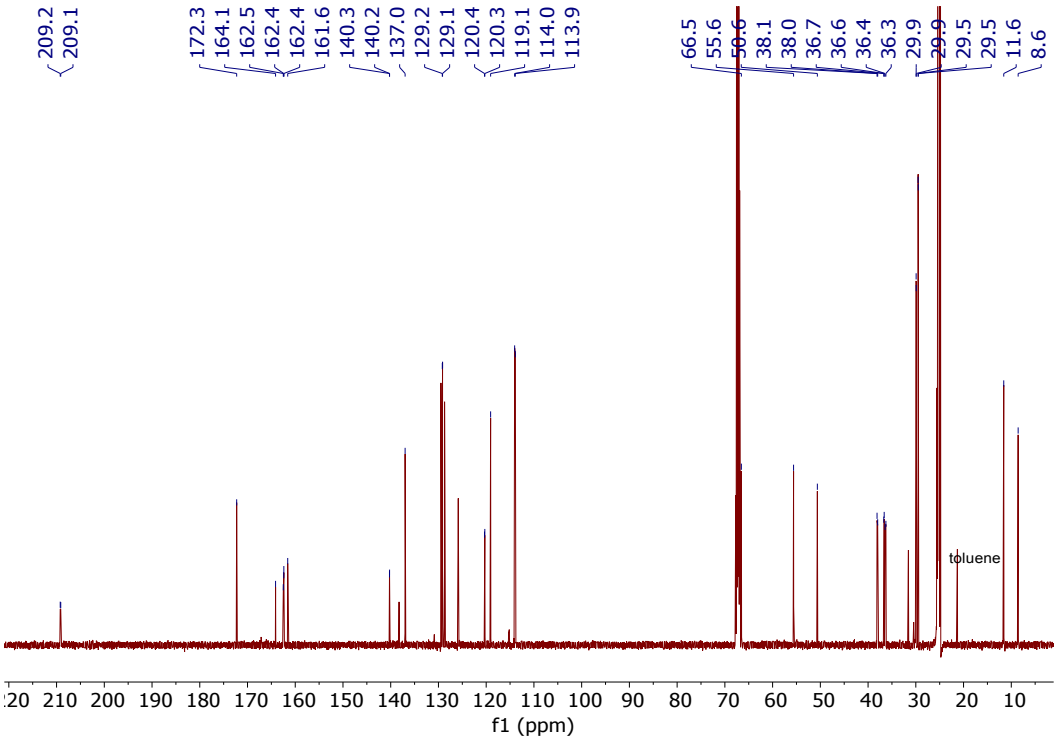


Figure S8B. ^{13}C NMR spectrum of **D^{PNN}**

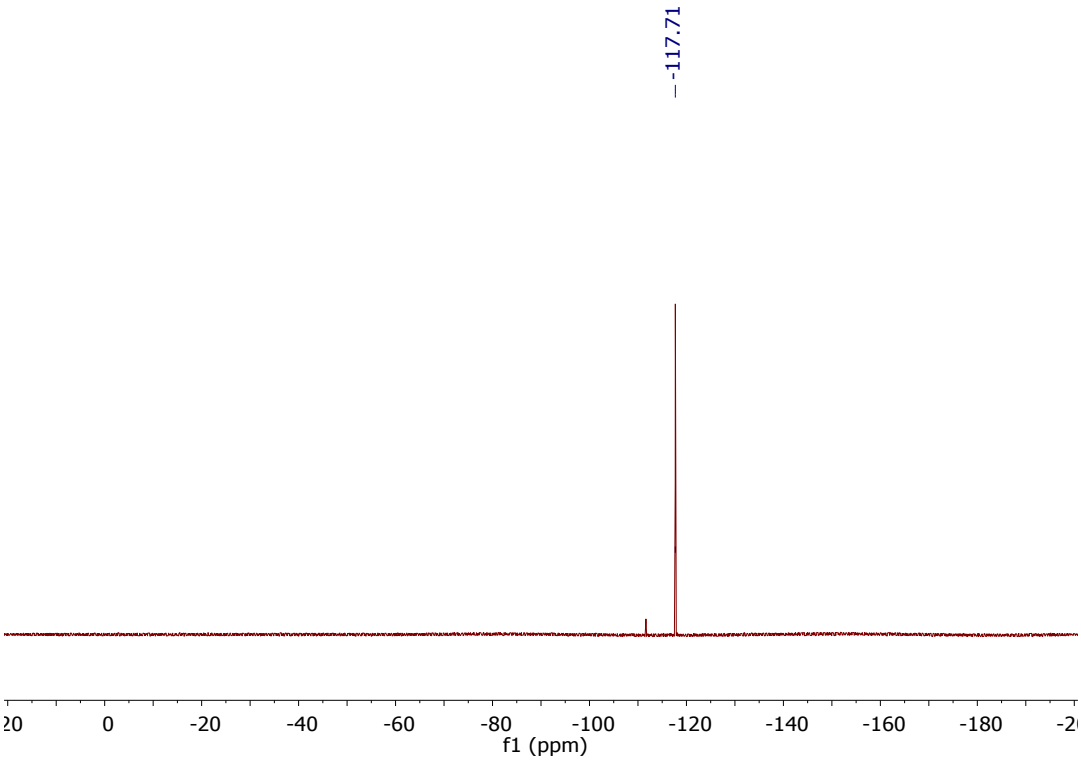


Figure S8C. ^{19}F NMR spectrum of **D^{PNN}** in THF-d_8

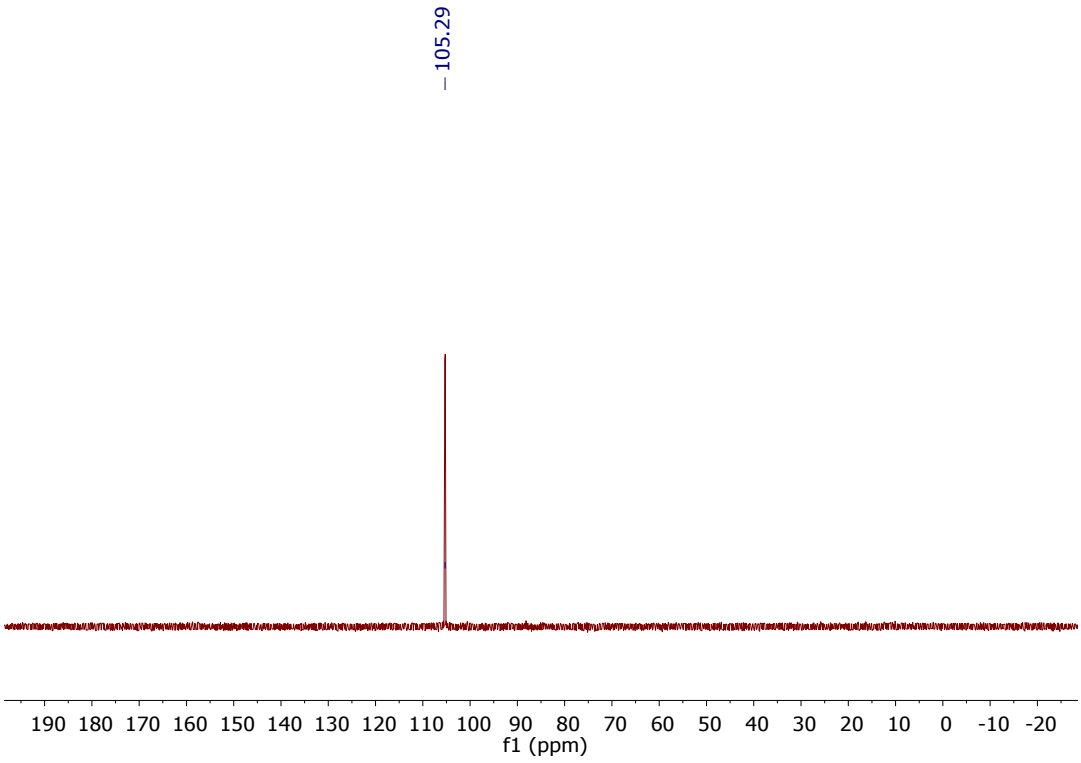
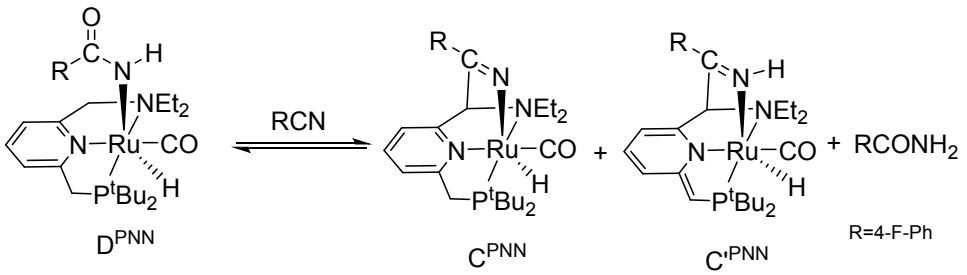


Figure S8D. ^{31}P NMR spectrum of **D^{PNN}** in THF-d_8

Stoichiometric reaction of **D^{PNN}** with 4-fluorobenzonitrile (**1b**)



To a NMR solution of **D^{PNN}**, prepared as described above, was added 50 µl of a 0.30 mol/L stock solution of 4-fluorobenzonitrile (0.015 mmol, 1 eq.), resulting in a color change to light brown. Analysis of the NMR spectral data showed immediate conversion (ca. 13%) of **D^{PNN}** to the C≡N addition products **C^{PNN}** and **C'^{PNN}**. This demonstrates that compounds **C^{PNN}** are kinetically accessible from **D^{PNN}** and nitrile.

^{19}F NMR (376 MHz, THF-*d8*) δ-109.7(**C'^{PNN}**), -117.7(**D^{PNN}**), -118.0(**C^{PNN}**);
^{31}P NMR (162 MHz, THF-*d8*) δ 117.6(**C^{PNN}**), 105.3(**D^{PNN}**), 102.1(**C' ^{PNN}**);
^{1}H NMR (400 MHz, THF-*d8*) δ 11.65 (s, 1H, N**H** of **C'^{PNN}**), -10.47 (d, *J* = 25.8 Hz, 0.22H, Ru**H** of **C^{PNN}**), -13.06 (d, *J* = 26.9 Hz, 8H, Ru**H** of **D^{PNN}**), -13.76 (d, *J* = 32.8 Hz, 1H, Ru**H** of **C'^{PNN}**).

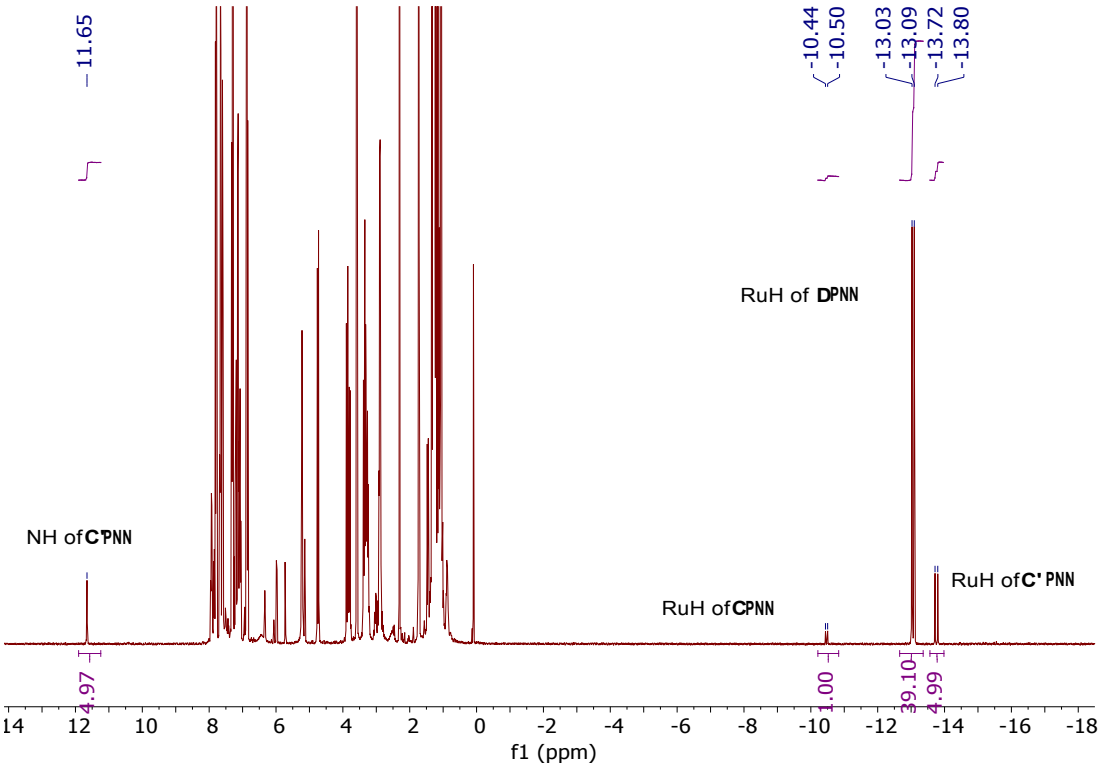


Figure S9A. ^{1}H NMR spectra for the stoichiometric reaction of **D^{PNN}** with 4-fluorobenzonitrile (**2b**).

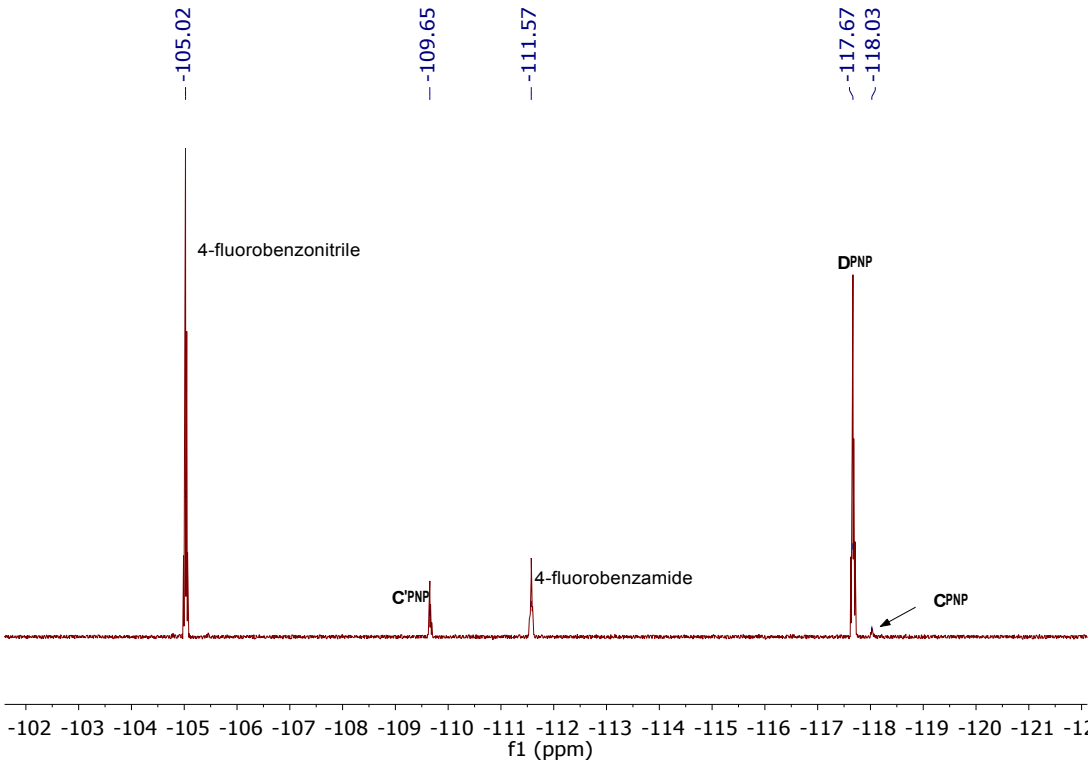


Figure S9B. ^{19}F NMR spectra for the stoichiometric reaction of **D^{PNN}** with 4-fluorobenzonitrile (**2b**).

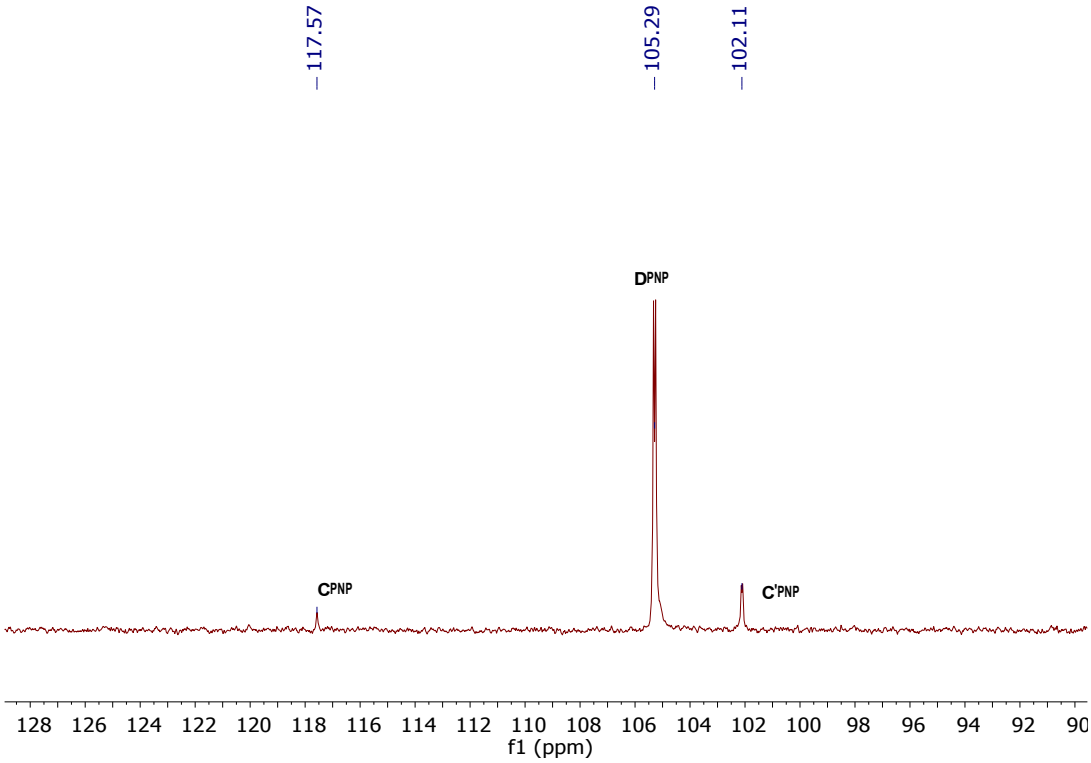


Figure S9C. ^{31}P NMR spectra for the stoichiometric reaction of **D^{PNN}** with 4-fluorobenzonitrile (**2b**).

Catalyst inhibition

a) Hydration of 4-fluorobenzonitrile (**1b**) under standard conditions, with addition of a new batch of substrate after completion

In a glovebox, 0.5 mL of a stock solution of $\mathbf{A}^{\mathbf{PNP}}$ (0.0015 mol/L, 0.0075 mmol, 3 mol%) was added to a vial. After removal of volatiles under vacuum for 0.5 hour, 0.5 mL of ^{t}BuOH and 22.5 ul of water (5 eq.) were added to dissolve the catalyst. The solution was then transferred into another vial containing 4-fluorobenzonitrile (30.3 mg, 121, 0.25 mmol) and an internal standard (2-fluorobiphenyl, 5 mg). The solution was quickly transferred to a J. Young NMR tube and measured by ^{19}F NMR spectroscopy for 10h. After this time, ^{19}F NMR spectroscopy indicated > 98% conversion of nitrile **1b** to the corresponding amide **2b**. The tube was taken into the glovebox and another batch of 4-benzonitrile (30.3 mg, 1 eq.) and water (5.4 ul, 1eq.) were added into the J. Young NMR tube. The reaction was monitored by ^{19}F NMR again for another 15h. Figure S10 shows the conversion vs. time plot of the two sequential nitrile hydration reactions, indicating that a second batch of substrate is converted with a somewhat lower reaction rate.

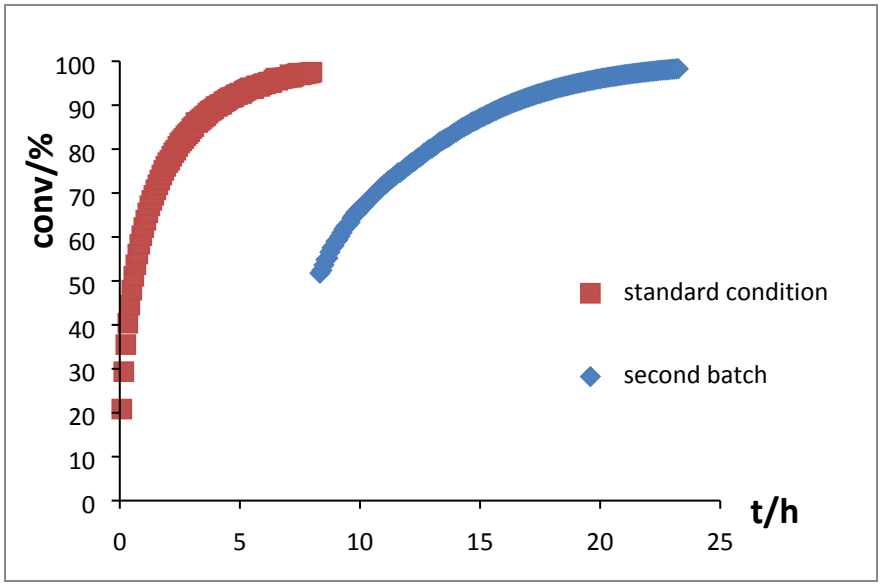


Figure S10. Conversion vs. time plot for hydration of 4-fluorobenzonitrile (3mol% $\mathbf{A}^{\mathbf{PNP}}$ catalyst), followed by addition of a second batch of nitrile substrate.

b) Catalysis with additional amide present from the start.

To test whether the decreased rate in experiment (a) above is due to decomposition of the catalyst, or due to product inhibition, we subsequently carried out a catalytic nitrile hydration reaction under identical conditions, but now with 0.075 mmol amide **2b** present at the start (0.3 equiv. with respect to nitrile **1b**).

The catalyst solution in tBuOH (prepared as described above, 3 mol% $\mathbf{A}^{\mathbf{PNP}}$ + 5 eq. of water) was transferred into a vial containing a mixture of 4-fluorobenzonitrile (30.3 mg, 121, 0.25 mmol), 4-fluorobenzamide (10.4 mg, 139, 0.075 mmol, 0.3 eq.) and internal standard (2-Fluorobiphenyl, 5 mg). The solution was quickly transferred to a J. Young NMR tube and measured by ^{19}F NMR spectroscopy for 10 h. A comparison of the data with and without amide **2b** added at the start (Figure S11) shows that product inhibition takes place.

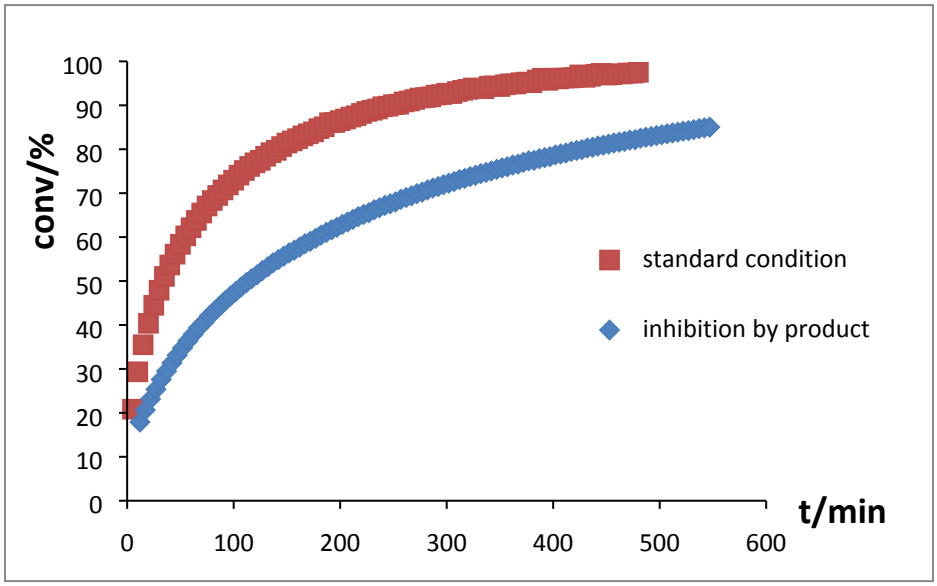


Figure S11. Conversion vs. time plot for hydrdation of 4-fluorobenzonitrile (**1b**) inhibited by 4-fluorobenzamide (**2b**)

c) Effect of nitro group on hydration of nitrile

To test whether the catalyst is deactivated by nitro-groups (as suggested by the lack of catalytic turnover for *p*-nitrobenzonitrile), the hydration of **1b** was carried out in the presence of an equimolar amount of nitrobenzene.

In a glovebox, a small vial was charged with 0.0015 mol/L $\mathbf{A}^{\mathbf{PNP}}$ stock solution (0.5 ml, 0.0075 mmol, 3 mol%). After removal of the volatiles under vacuum for 0.5 hour, 0.5 ml of ^{t}BuOH and 22.5 ul of water (5 eq.,) were added to dissolve the catalyst. The solution was transferred into another vial containing a mixture of 4-fluorobenzonitrile (30.3 mg, 0.25 mmol), nitrobenzene (30.8 mg, 0.25 mmol, 1 eq.) and internal standard (2-Fluorobiphenyl, 5 mg). The solution was quickly transferred to a J. Young NMR tube and measured by ^{19}F NMR spectroscopy for 10 h. A comparison of the data collected in the presence/absence of nitrobenzene is shown in Figure S12, indicating that the catalyst is not deactivated by the -NO_2 functional group.

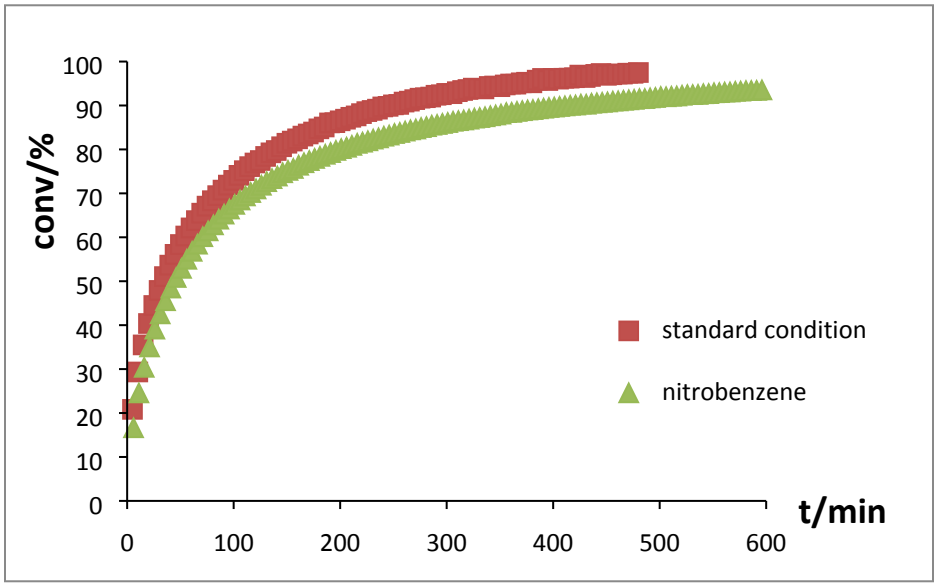
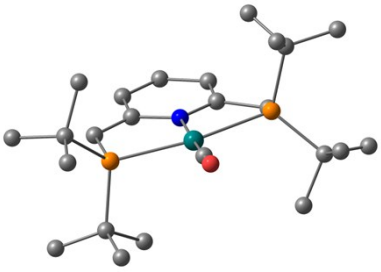


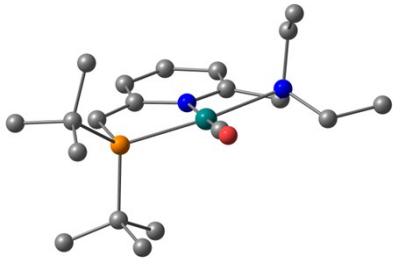
Figure S12. Conversion vs. time plot for hydration of 4-fluorobenzonitrile (**1b**) with additive of nitrobenzene

Preliminary DFT calculations

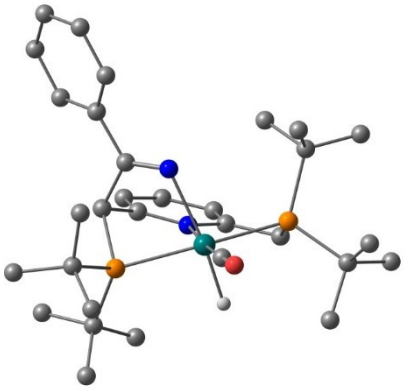
Geometry optimizations were carried out using density functional theory with the TPSSTPSS functional[21] and def2-TZVP basis set[22] on all atoms. The W06 density fitting set was employed. Calculations were carried out with a SMD solvation model[23] with isopropanol, and an empirical dispersion correction using Grimme's D3 damping function.[24] The calculations converged on minima on the potential energy surface, as confirmed by a frequency analysis (no imaginary frequencies). Gibss free energies of the nitrile-MLC activation products **C** (all with PhCN bound) shown below are relative to the dearomatized precursors **A** and PhCN computed at the same level of theory.

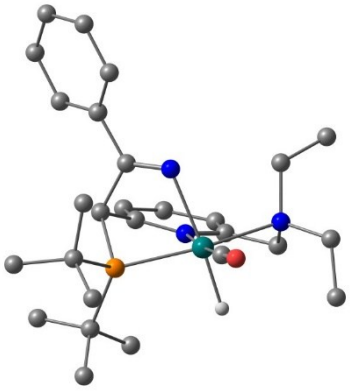


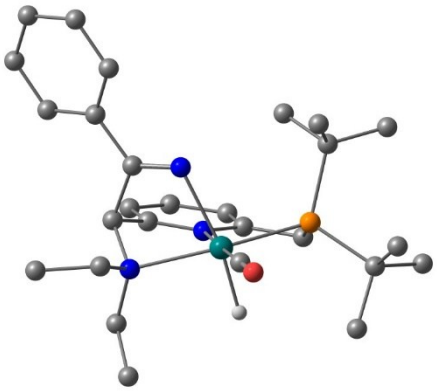
A^{PNP}



A^{PNN}







	C^{PNP}	C^{PNN} (addition to P-arm)	C^{PNN} (addition to N-arm)
ΔG	7.2 kcal/mol	9.4 kcal/mol	-2.7 kcal/mol

Absolute Gibbs free energies and Cartesian coordinates for PhCN and complexes A and C.

PhCN (-324.616336)

C	-0.088550000	-1.221607000	0.000000000
C	0.608429000	0.000062000	0.000026000
C	-0.088621000	1.221638000	-0.000014000
C	-1.480458000	1.212361000	0.000002000
C	-2.175380000	-0.000040000	0.000014000
C	-1.480356000	-1.212426000	-0.000015000
H	0.462143000	-2.156812000	-0.000018000
H	0.461952000	2.156914000	-0.000033000
H	-2.023695000	2.152773000	-0.000005000
H	-3.261895000	-0.000110000	-0.000002000
H	-2.023587000	-2.152842000	-0.000012000
C	2.036220000	0.000058000	0.000003000
N	3.199627000	-0.000029000	-0.000004000

A^{PNP} (-1848.385245)

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O	0.068403000	-3.357532000	-0.623169000
N	-0.014270000	1.723316000	0.247051000
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C	1.186451000	2.437592000	0.082905000
C	1.121488000	3.872758000	0.109014000
H	2.045274000	4.428343000	-0.028002000
C	-0.071467000	4.522451000	0.291403000
H	-0.104599000	5.610073000	0.299874000
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H	-2.212358000	4.267085000	0.658359000
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C	-2.405585000	1.570133000	0.774038000
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C	3.066126000	-0.565910000	1.624970000
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H	2.046397000	1.149360000	2.552516000
H	1.059287000	-0.328371000	2.485238000
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C	3.695810000	-2.101712000	-1.464917000
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H	-2.868053000	2.157990000	-1.839505000
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H	-4.961539000	1.019193000	-0.858243000

A^{PNN} (-1404.493034)

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C	0.271796000	2.367697000	-0.456672000
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H	4.101108000	-2.435066000	-1.595534000
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H	4.828833000	-0.124605000	-2.295903000
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H	1.689553000	0.027123000	-2.932146000
H	2.919446000	-1.180246000	-3.367262000
C	-3.285712000	-0.578037000	-1.265201000
H	-2.792662000	0.183646000	-1.876107000
H	-4.350034000	-0.309559000	-1.201180000
C	-3.135018000	-1.948879000	-1.908565000
H	-3.720791000	-2.715179000	-1.390725000
H	-3.501346000	-1.891739000	-2.939781000
H	-2.087610000	-2.264032000	-1.933243000
C	-3.216439000	-1.492580000	1.058949000
H	-2.898134000	-2.467260000	0.683163000
H	-2.697005000	-1.324076000	2.008356000
C	-4.730113000	-1.479710000	1.279754000
H	-4.980952000	-2.261780000	2.005245000
H	-5.081877000	-0.524763000	1.683219000
H	-5.281190000	-1.692860000	0.358263000
H	2.392979000	2.491243000	-0.757398000

C^{PNP} (-2172.990129)

C	1.674569000	1.126584000	-0.267468000
C	2.029515000	-0.003032000	0.764435000
C	1.059271000	0.214996000	1.881805000
N	-0.244263000	0.033426000	1.528764000
C	-1.241510000	0.344941000	2.393795000
C	-0.948742000	0.801533000	3.676269000
C	0.385237000	0.952929000	4.064081000
C	1.400274000	0.672130000	3.156042000
Ru	-0.634305000	-0.658668000	-0.452907000
C	-1.030108000	-1.140777000	-2.179681000
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C	2.663156000	-1.900012000	-1.580134000
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H	0.626417000	1.301870000	5.064333000
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C	2.617454000	2.278190000	-0.381368000
C	3.531301000	2.618736000	0.630020000
C	2.584415000	3.073291000	-1.541927000
C	4.374679000	3.723867000	0.491239000
H	3.575329000	2.034207000	1.544111000
C	3.432792000	4.167138000	-1.685698000
H	1.880891000	2.808986000	-2.326631000
C	4.332472000	4.501315000	-0.666696000
H	5.065232000	3.976413000	1.292459000
H	3.397836000	4.761302000	-2.595961000
H	4.993576000	5.357140000	-0.777167000
P	1.495804000	-1.589724000	-0.105272000

C	2.724608000	-0.643959000	-2.473825000
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H	2.648411000	-3.111589000	-3.362826000
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H	1.023103000	-2.788720000	-2.734996000
C	0.588260000	-2.942580000	2.230475000
H	0.581148000	-2.048329000	2.857442000
H	-0.380793000	-3.027896000	1.731846000
H	0.715827000	-3.807494000	2.894931000
C	3.060619000	-2.741387000	2.019018000
H	3.164026000	-3.566660000	2.736444000
H	3.953978000	-2.734189000	1.391920000
H	3.031839000	-1.809577000	2.592868000
P	-2.679340000	0.353437000	0.019394000
C	-5.462729000	-0.169927000	0.521765000
H	-5.692834000	0.895567000	0.561111000
H	-6.366056000	-0.691785000	0.178629000
H	-5.251330000	-0.517608000	1.538295000
C	-4.705763000	-0.127042000	-1.887930000
H	-3.884569000	-0.302134000	-2.590879000
H	-5.551864000	-0.754887000	-2.196969000
H	-5.021600000	0.916177000	-1.970982000
C	-1.712450000	2.892759000	0.547971000
H	-0.732006000	2.445022000	0.363994000
H	-1.658948000	3.953718000	0.269210000
H	-1.938291000	2.843410000	1.618675000
C	-2.469910000	2.465720000	-1.791480000
H	-3.228534000	2.059400000	-2.465667000
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H	-1.499831000	2.024084000	-2.041265000

C^{PNN} (addition to P-arm; -1729.094415)

C	-2.087735000	-0.245503000	-0.393910000
C	-2.087676000	0.898333000	0.675429000
C	-1.322277000	0.337637000	1.835936000
N	-0.012815000	0.153817000	1.546331000
C	0.819688000	-0.493347000	2.393620000
C	0.334630000	-0.967750000	3.609782000
C	-1.009597000	-0.760873000	3.938640000
C	-1.854475000	-0.105581000	3.045494000
Ru	0.553566000	0.854590000	-0.338304000
C	1.117951000	1.435636000	-1.986289000
O	1.506005000	1.811155000	-3.034416000
C	2.233836000	-0.650313000	1.911694000
P	2.295377000	-0.570300000	0.039552000
C	2.029928000	-2.373752000	-0.510830000
C	0.794645000	-2.888646000	0.258832000
N	-1.287599000	2.025684000	0.050647000
C	-1.938886000	2.524363000	-1.212962000
C	-3.331432000	3.132911000	-1.047999000

N	-1.000642000	-0.459339000	-1.021576000
C	4.090983000	-0.041382000	-0.302779000
C	4.441545000	-0.320438000	-1.776956000
C	-1.143646000	3.131701000	1.059145000
C	-0.428696000	4.364971000	0.524377000
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C	4.213377000	1.477367000	-0.066727000
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C	1.686470000	-2.370317000	-2.014356000
H	1.480830000	1.990311000	0.415450000
H	-0.582390000	2.713746000	1.898037000
H	-2.142126000	3.401956000	1.430158000
H	5.112002000	-1.823638000	0.519122000
H	4.945035000	-0.487878000	1.673698000
H	6.115570000	-0.379868000	0.354969000
H	2.697804000	-1.552605000	2.321455000
H	2.819594000	0.211988000	2.257698000
H	2.876973000	-4.353347000	-0.494523000
H	3.481270000	-3.340026000	0.824154000
H	4.081147000	-3.106108000	-0.834778000
H	-1.977240000	1.678605000	-1.899806000
H	-1.248785000	3.255512000	-1.638507000
H	3.919161000	1.764831000	0.948159000
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H	5.265732000	1.759490000	-0.207628000
H	4.518504000	-1.390028000	-1.989491000
H	5.416854000	0.132970000	-1.998034000
H	3.706022000	0.120190000	-2.457865000
H	-2.903244000	0.055217000	3.272495000
H	-3.077889000	1.246295000	0.980522000
H	-1.395104000	-1.118249000	4.889384000
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H	0.823684000	-1.725886000	-2.208714000
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H	0.522737000	-3.873591000	-0.143745000
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H	-4.421049000	-0.290276000	1.128534000
C	-4.541124000	-2.711495000	-1.891236000
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C	-5.636595000	-2.617135000	-1.024706000
H	-6.419332000	-1.660632000	0.742014000

H	-4.576592000	-3.390600000	-2.739971000
H	-6.524045000	-3.221648000	-1.193884000

C^{PNN} (addition to N-arm; -1729.113682)

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C	-1.394339000	0.181396000	0.895967000
C	-0.410065000	-0.461007000	1.822333000
N	0.835659000	-0.542231000	1.288305000
C	1.802239000	-1.296484000	1.848668000
C	1.578061000	-1.947369000	3.054978000
C	0.327354000	-1.805383000	3.670478000
C	-0.682253000	-1.075775000	3.046463000
Ru	1.195606000	0.328951000	-0.570172000
C	1.532074000	0.959160000	-2.262712000
O	1.781335000	1.310738000	-3.359893000
C	3.062882000	-1.336183000	1.033344000
C	2.018780000	-2.637356000	-0.797281000
C	-1.703902000	2.480415000	-1.139289000
C	-2.945007000	3.129651000	-0.501248000
N	-0.467881000	-0.955903000	-1.081362000
C	3.963183000	-1.233380000	-1.262674000
C	-0.260125000	2.860925000	1.605159000
C	0.069403000	4.284046000	1.115300000
C	4.748133000	0.066096000	-1.144326000
C	2.807460000	-3.934852000	-0.606239000
H	2.375782000	1.318013000	0.043332000
H	3.688605000	-2.193892000	1.304128000
H	3.629893000	-0.418803000	1.219979000
H	2.141665000	-4.766984000	-0.863252000
H	3.128101000	-4.081616000	0.430495000
H	3.684381000	-4.001713000	-1.256863000
H	5.093693000	0.256876000	-0.123326000
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H	5.636940000	-0.024328000	-1.780684000
H	-1.669936000	-0.992786000	3.487719000
H	-2.349480000	0.394782000	1.377517000
H	0.135044000	-2.291134000	4.623039000
H	0.910041000	4.285044000	0.413060000
H	0.359177000	4.888216000	1.984970000
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C	-4.708310000	-2.700507000	0.504445000
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H	4.624501000	-2.069814000	-1.000170000
H	3.639092000	-1.376094000	-2.298151000
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C	-2.194178000	1.425199000	-2.152078000
H	-1.367844000	0.874299000	-2.608345000
H	-2.883971000	0.707006000	-1.702246000
H	-2.737167000	1.958569000	-2.943633000
C	-0.911217000	3.533311000	-1.946249000
H	-1.557573000	3.897464000	-2.755550000
H	-0.611176000	4.395724000	-1.350472000
H	-0.016701000	3.099165000	-2.401558000
C	0.940459000	2.396119000	2.459146000
H	0.753733000	1.446220000	2.964871000
H	1.853109000	2.302310000	1.865908000
H	1.105940000	3.153898000	3.236622000
C	-1.491206000	2.895844000	2.534392000
H	-1.290674000	3.609969000	3.344484000
H	-2.405248000	3.215088000	2.031318000
H	-1.671169000	1.919459000	2.995655000

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NMR spectra of products (**2a-2ag**)

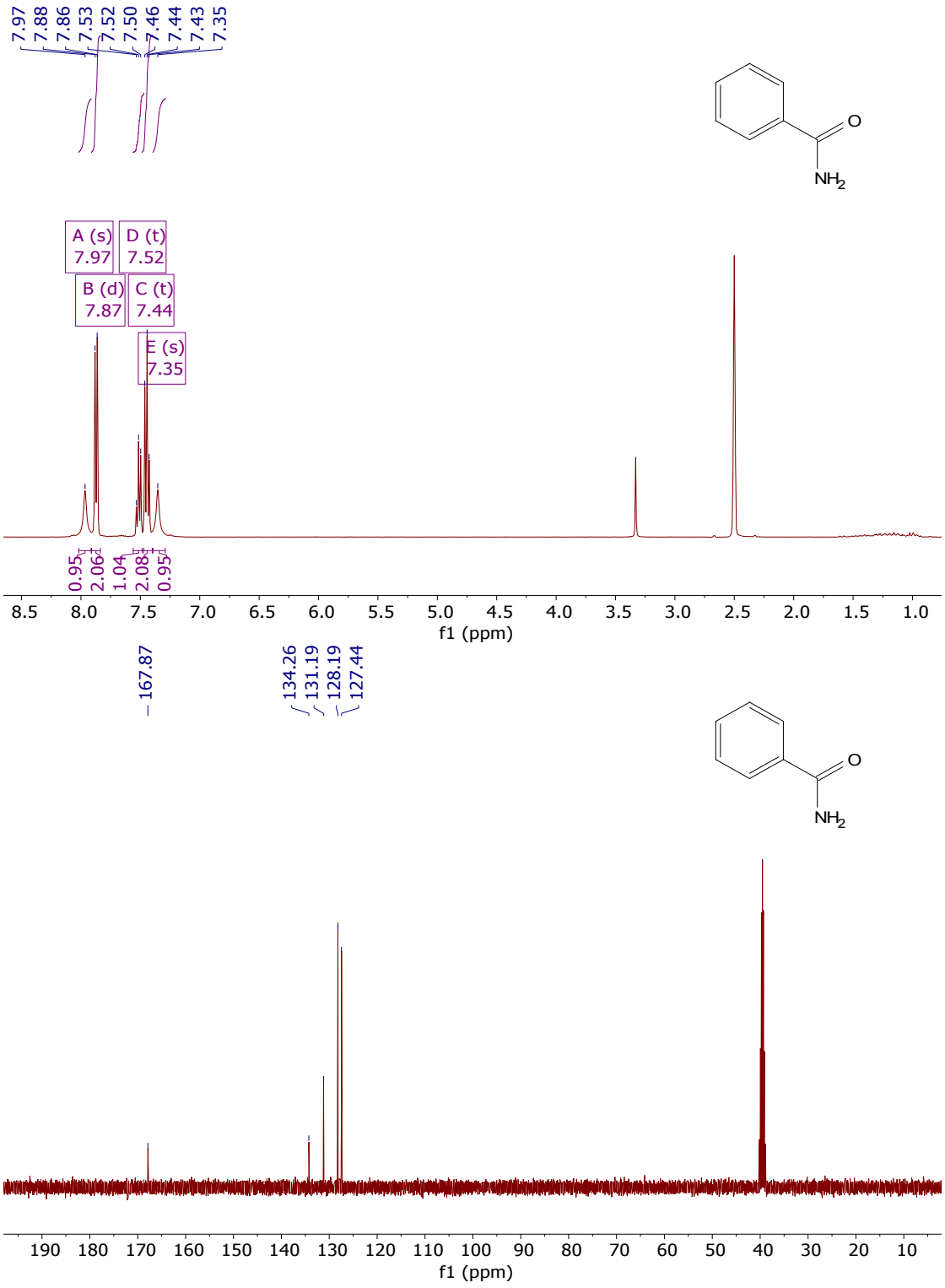
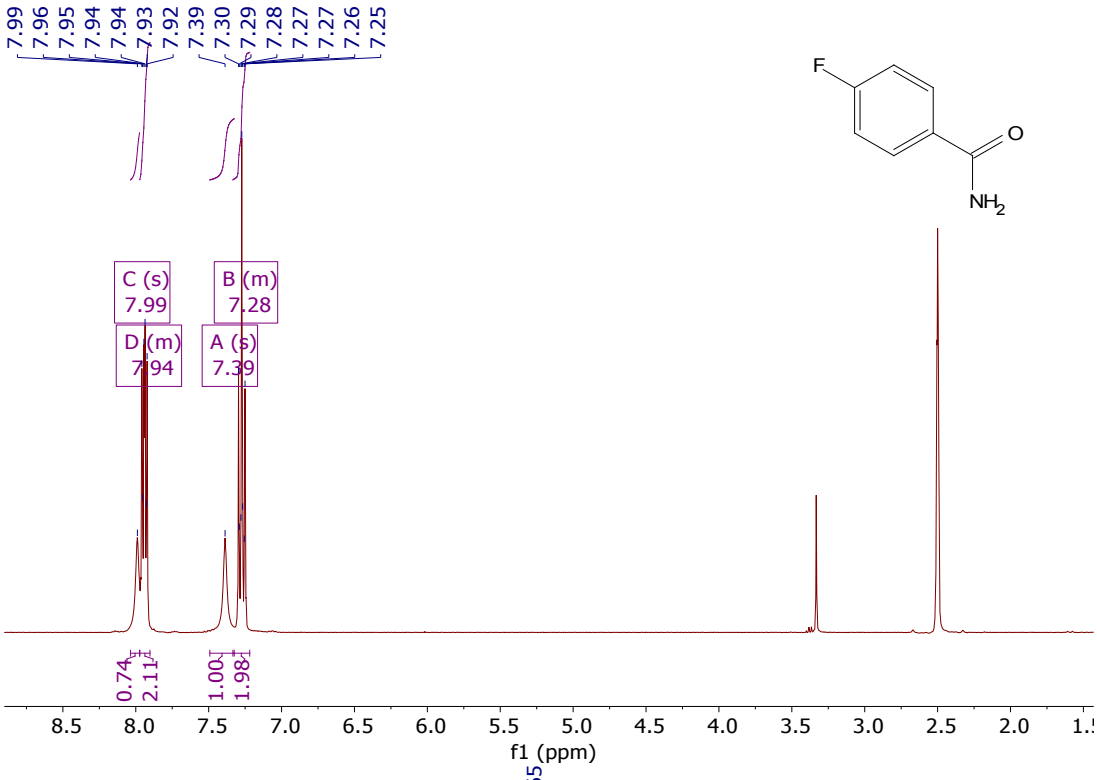
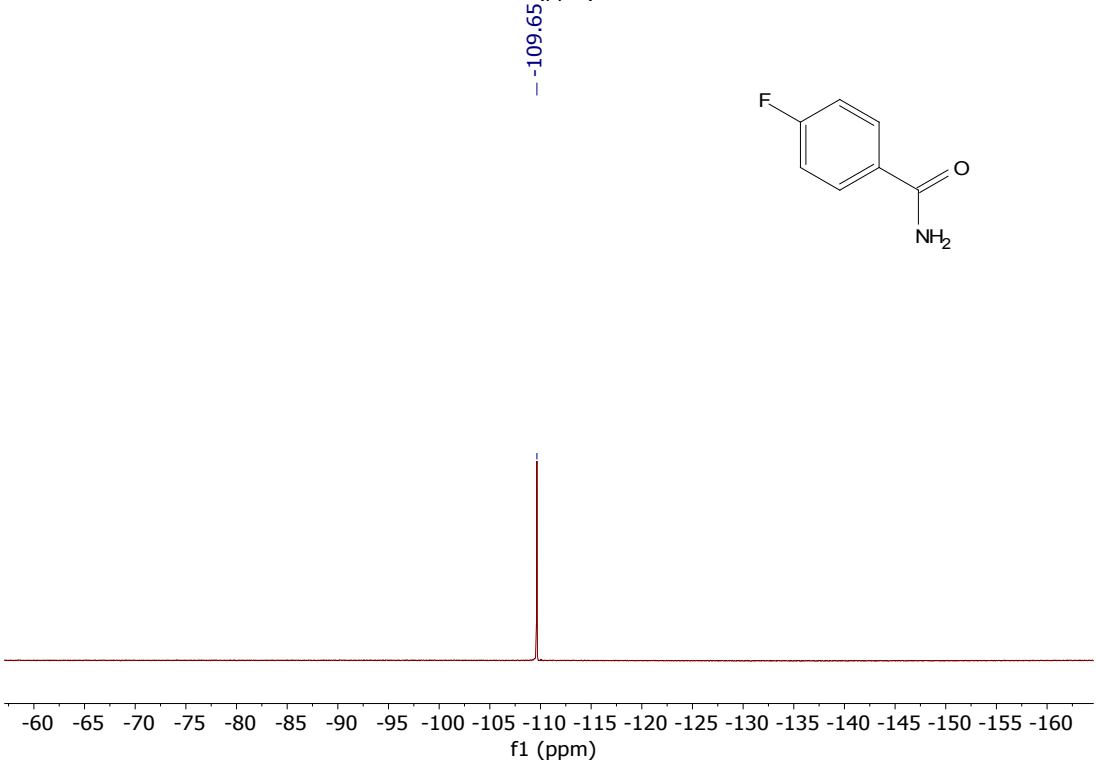


Figure S13. NMR spectra of benzamide (**2a**): ^{1}H NMR(top) and ^{13}C NMR(bottom)


7.99
7.96
7.95
7.94
7.94
7.93
7.92
7.39
7.30
7.29
7.28
7.27
7.27
7.26
7.25
F
O
NH2
C (s)
7.99
B (m)
7.28
D (m)
7.94
A (s)
7.39
0.74
2.11
1.00
1.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


-109.65
F
O
NH2
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
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-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

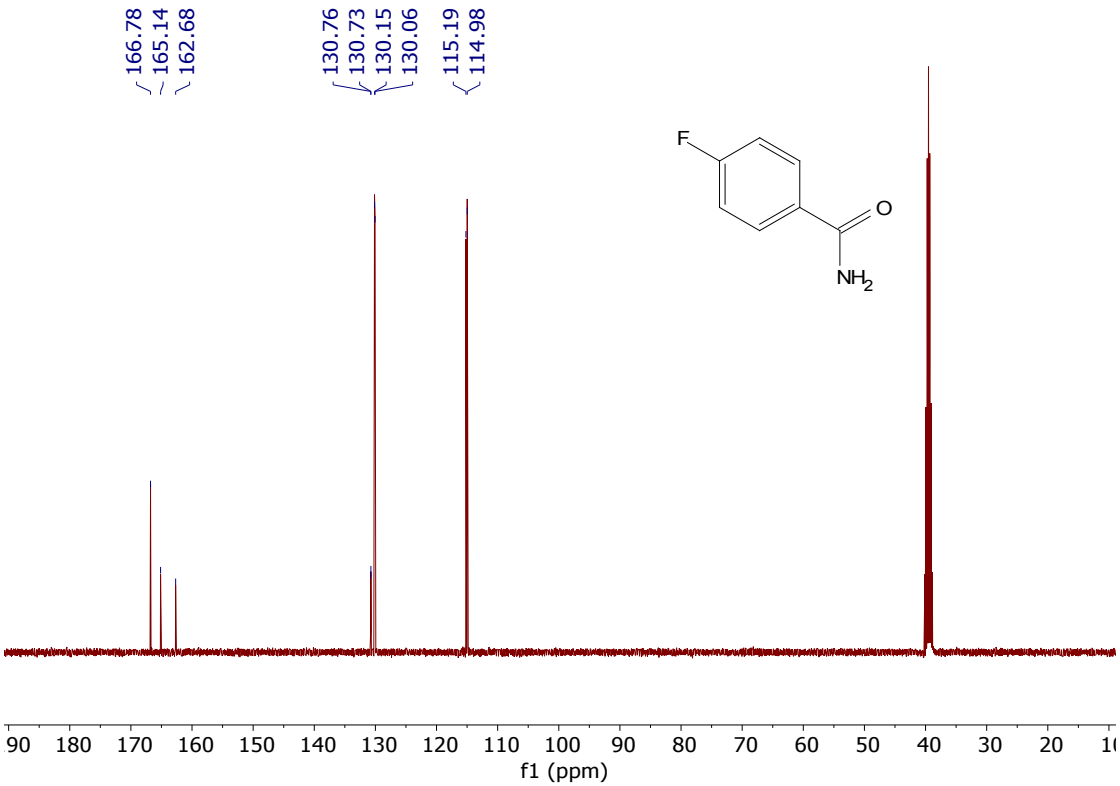


Figure S14. NMR spectra of 4-fluorobenzamide (**2b**): ^{1}H NMR(top), ^{19}F NMR(middle) and ^{13}C NMR(bottom)

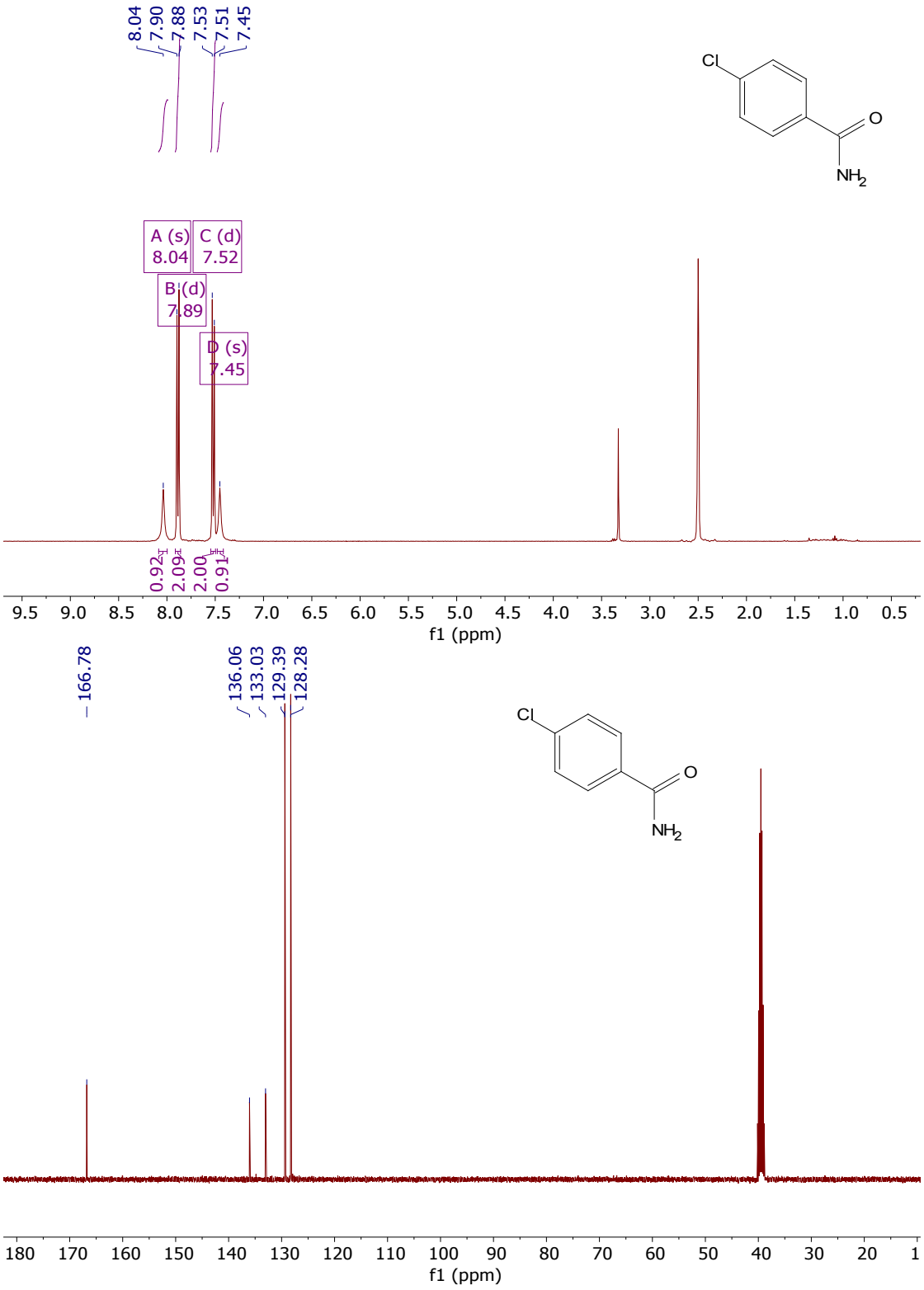


Figure S15. NMR spectra of 4-chlorobenzamide (**2c**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

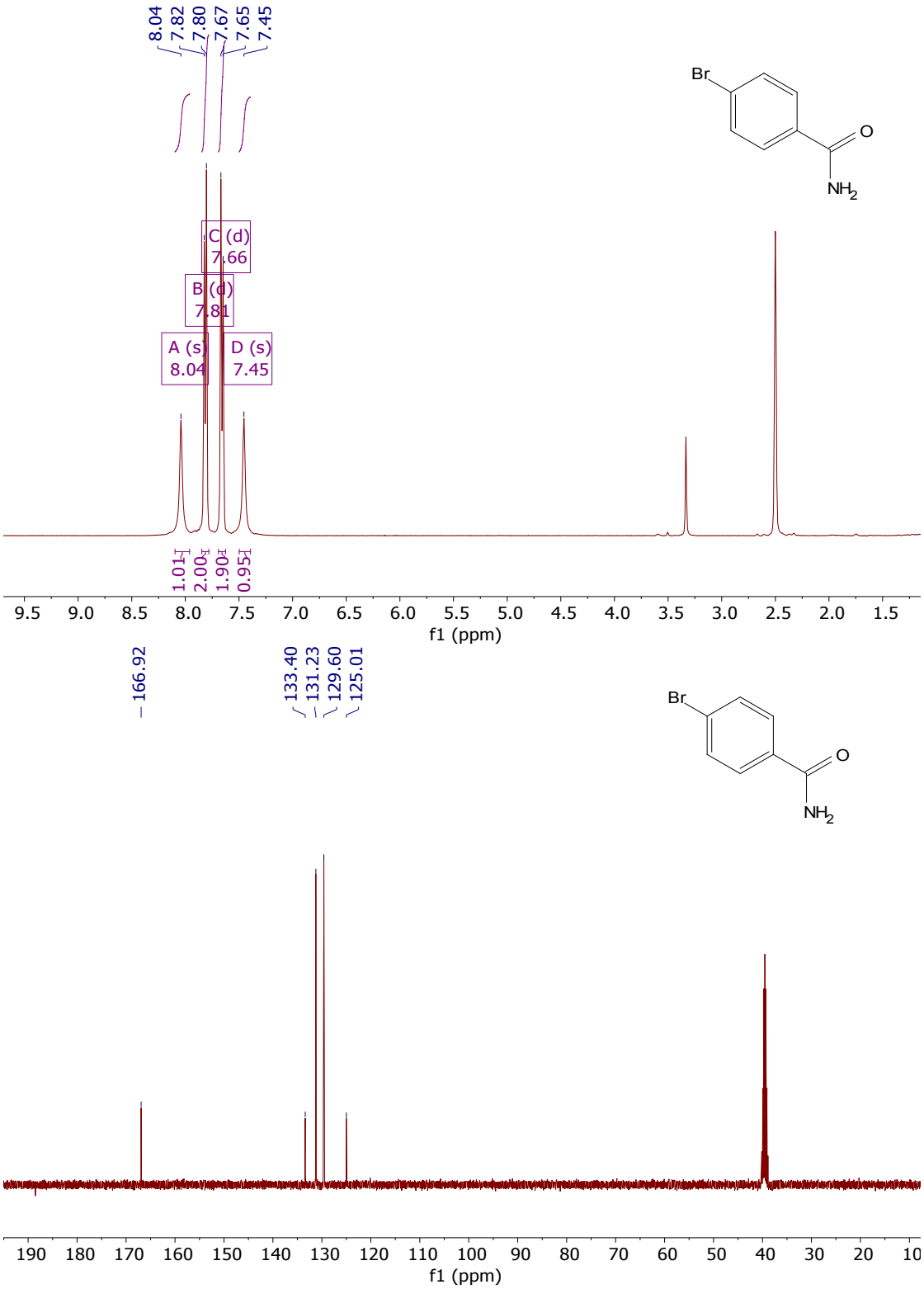


Figure S16. NMR spectra of 4-bromobenzamide (**2d**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

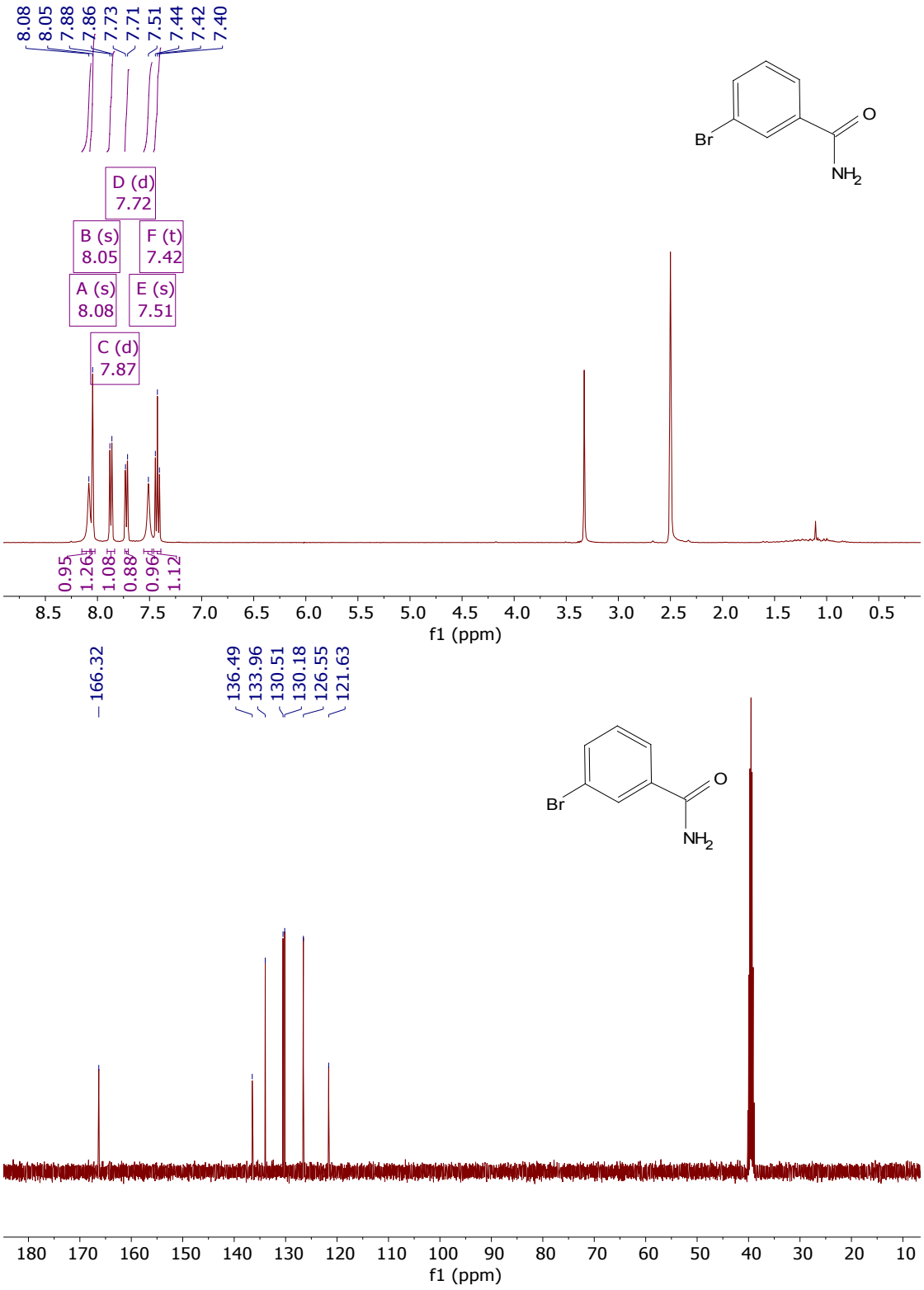


Figure S17. NMR spectra of 3-bromobenzamide (**2e**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

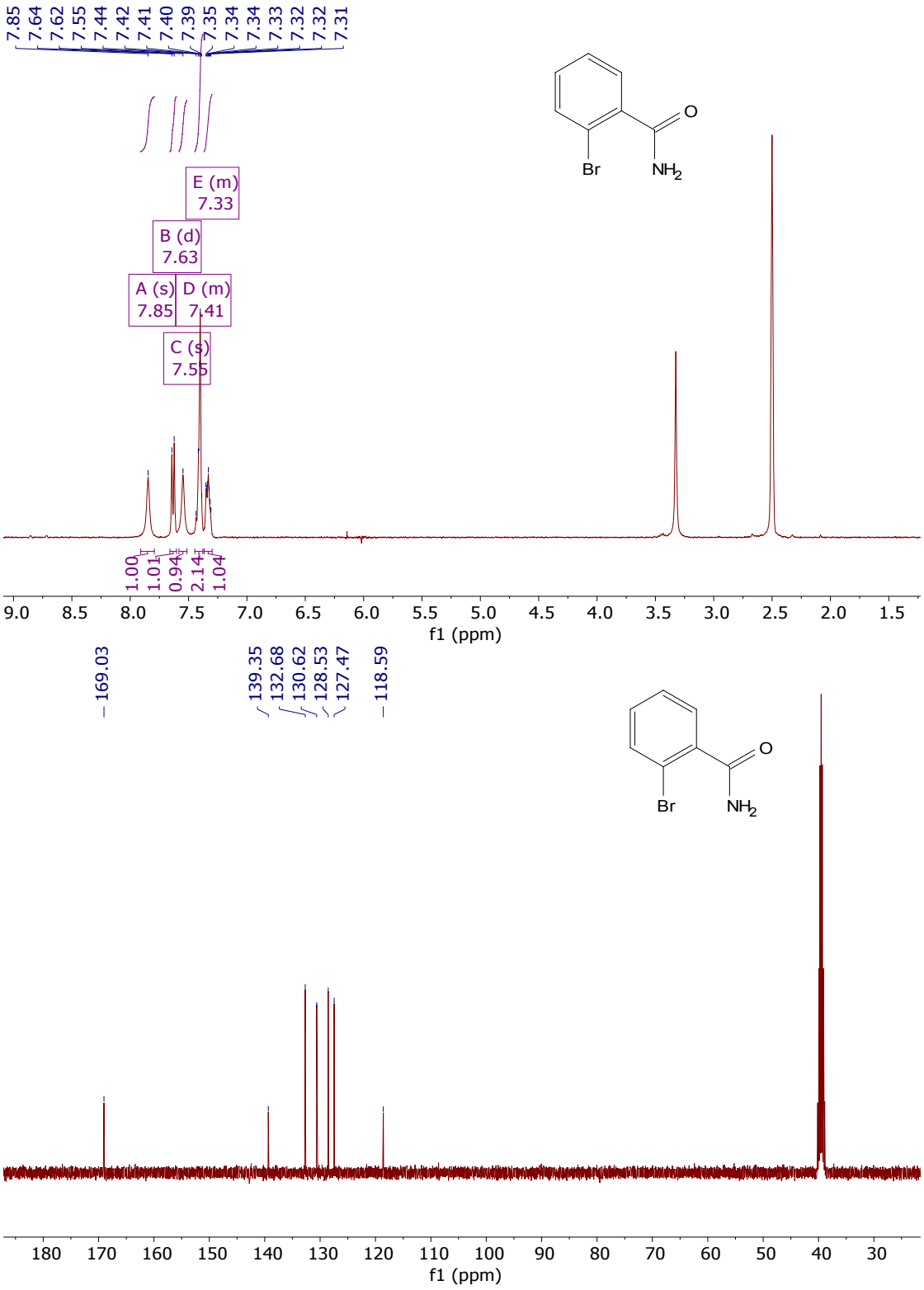
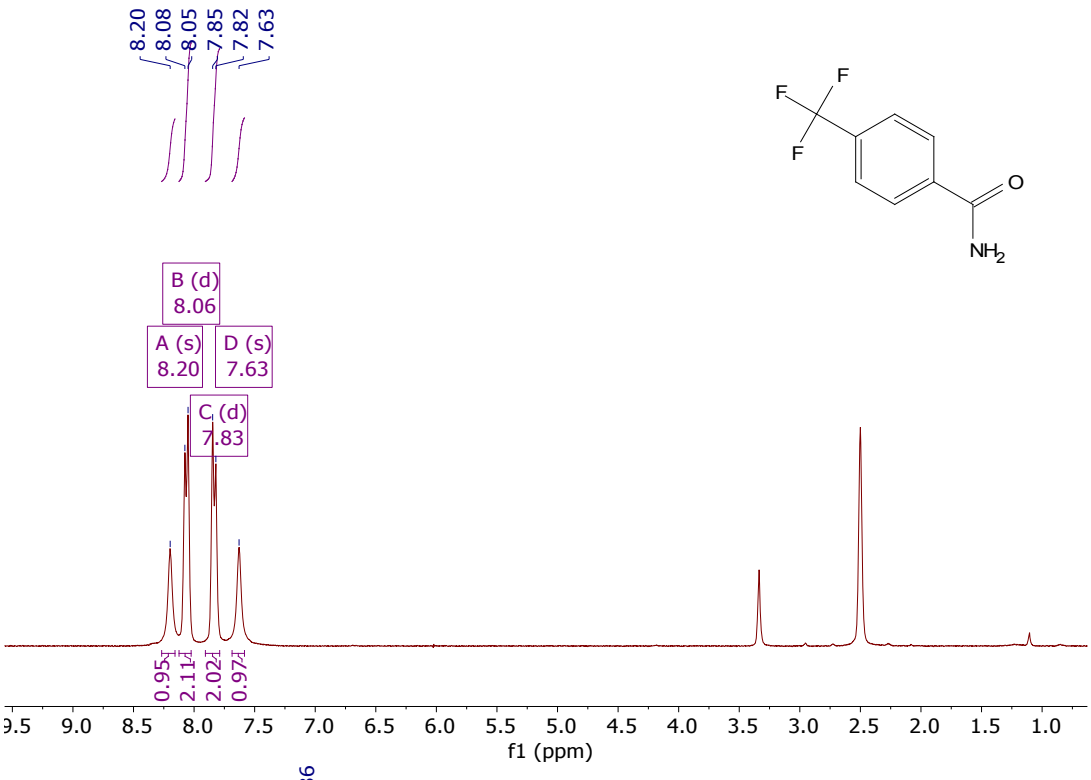


Figure S18. NMR spectra of 2-bromobenzamide (**2f**): ^{1}H NMR(top) and ^{13}C NMR(bottom)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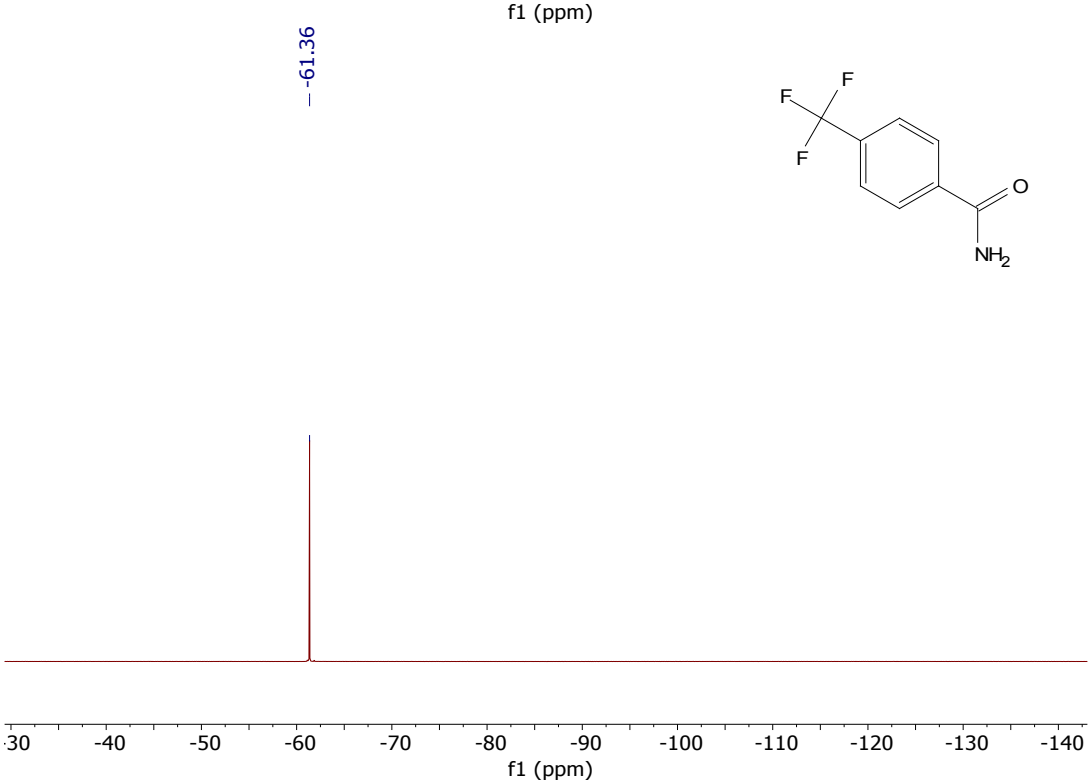
8.08
8.05
7.85
7.82
7.63
B (d)
8.06
A (s)
8.20
D (s)
7.63
C (d)
7.83
0.95
2.11
2.02
0.97
F
F
F
O
NH2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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F
F
F
O
NH2
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

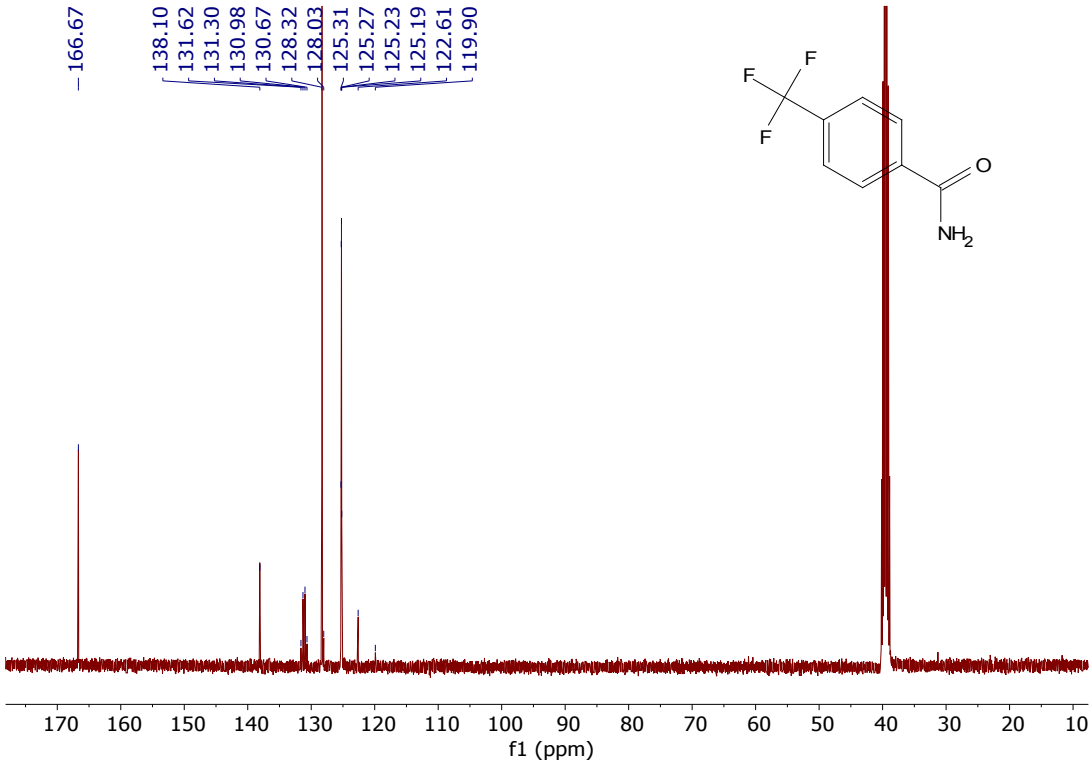

Figure S19. NMR spectra of 4-(trifluoromethyl)benzamide (**2g**): ^{1}H NMR(top), ^{19}F NMR(middle) and ^{13}C NMR(bottom)

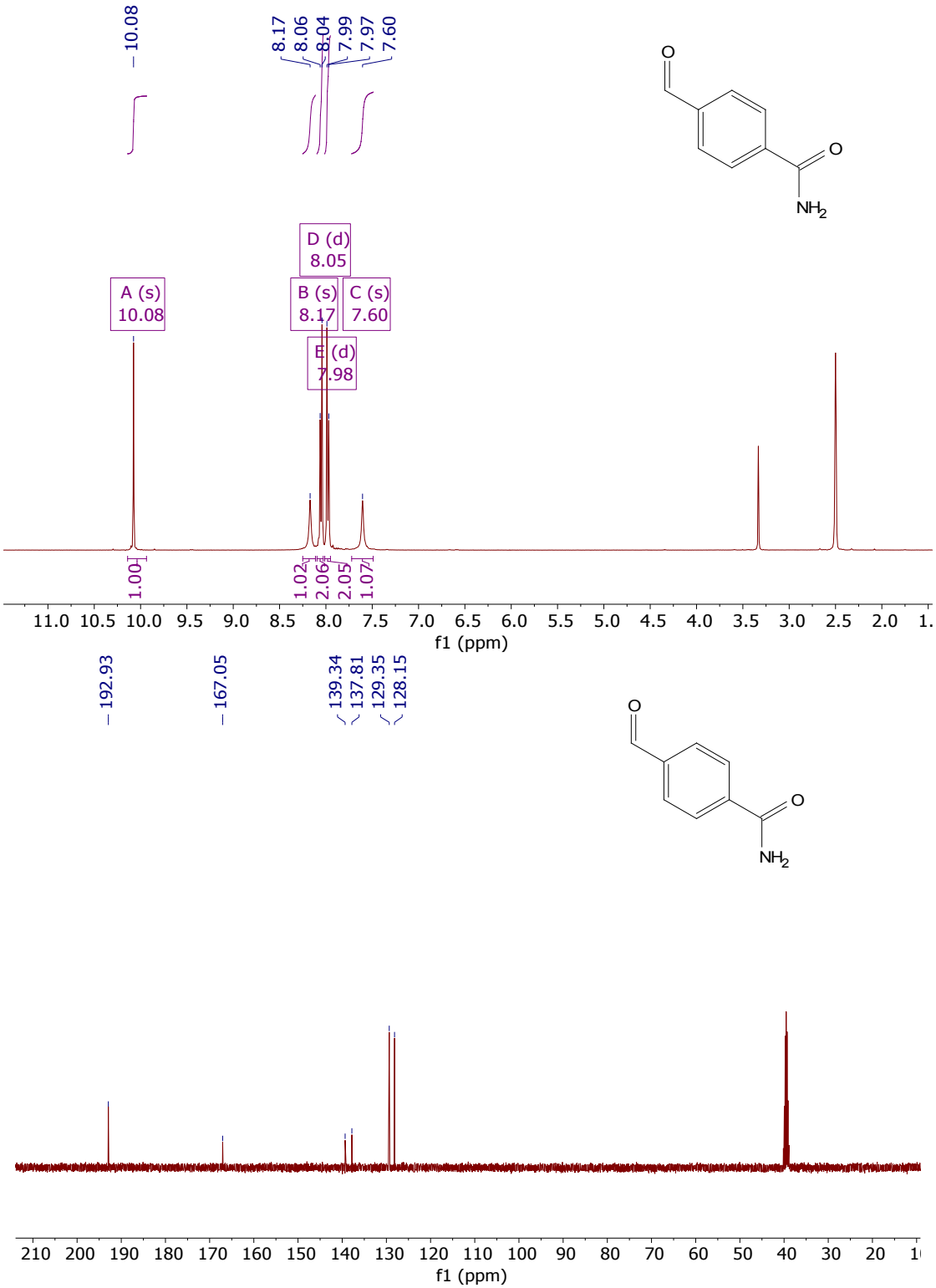

Figure S20. NMR spectra of 4-formylbenzamide (**2h**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

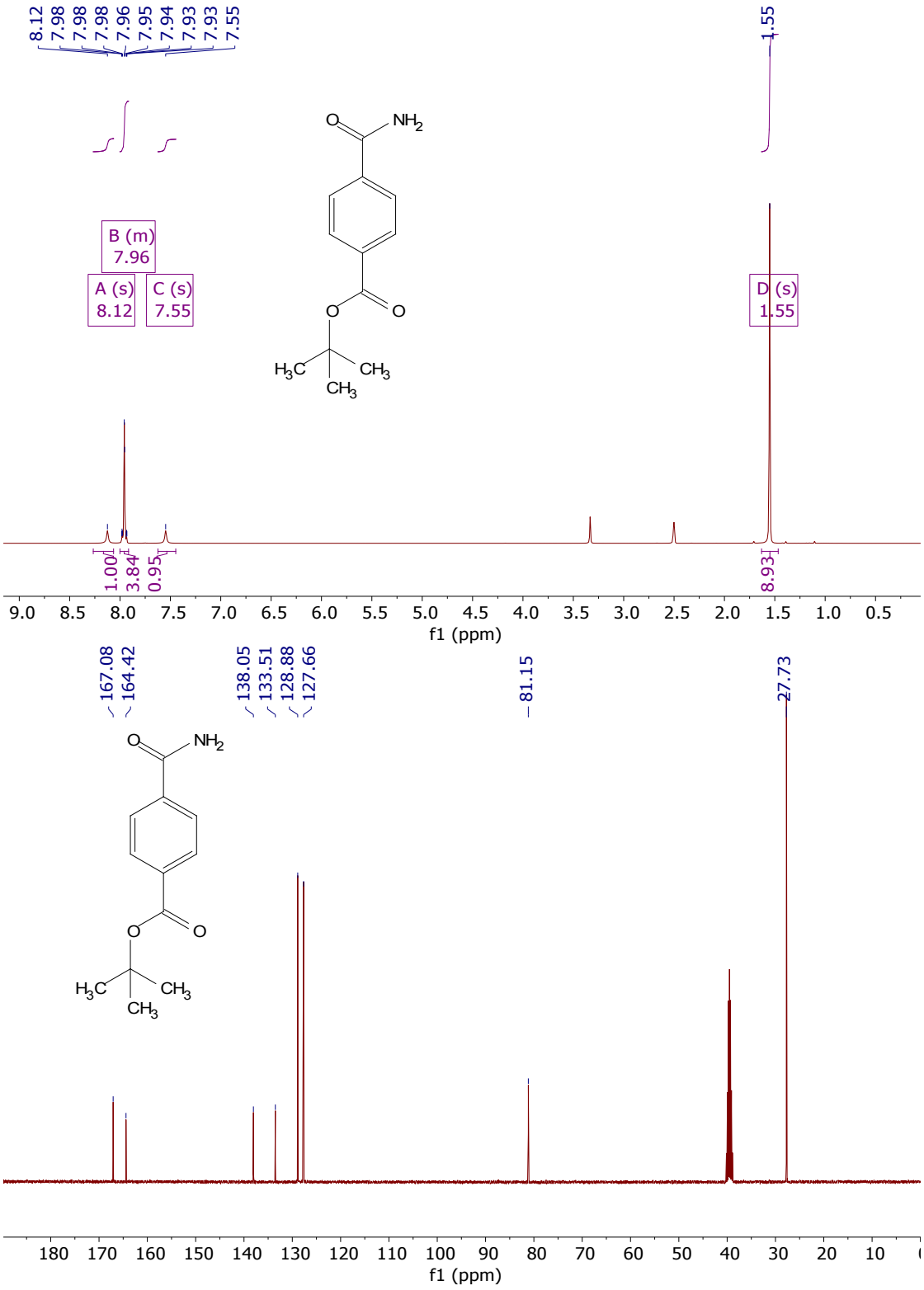

Figure S21. NMR spectra of tert-butyl 4-carbamoylbenzoate (**2i**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

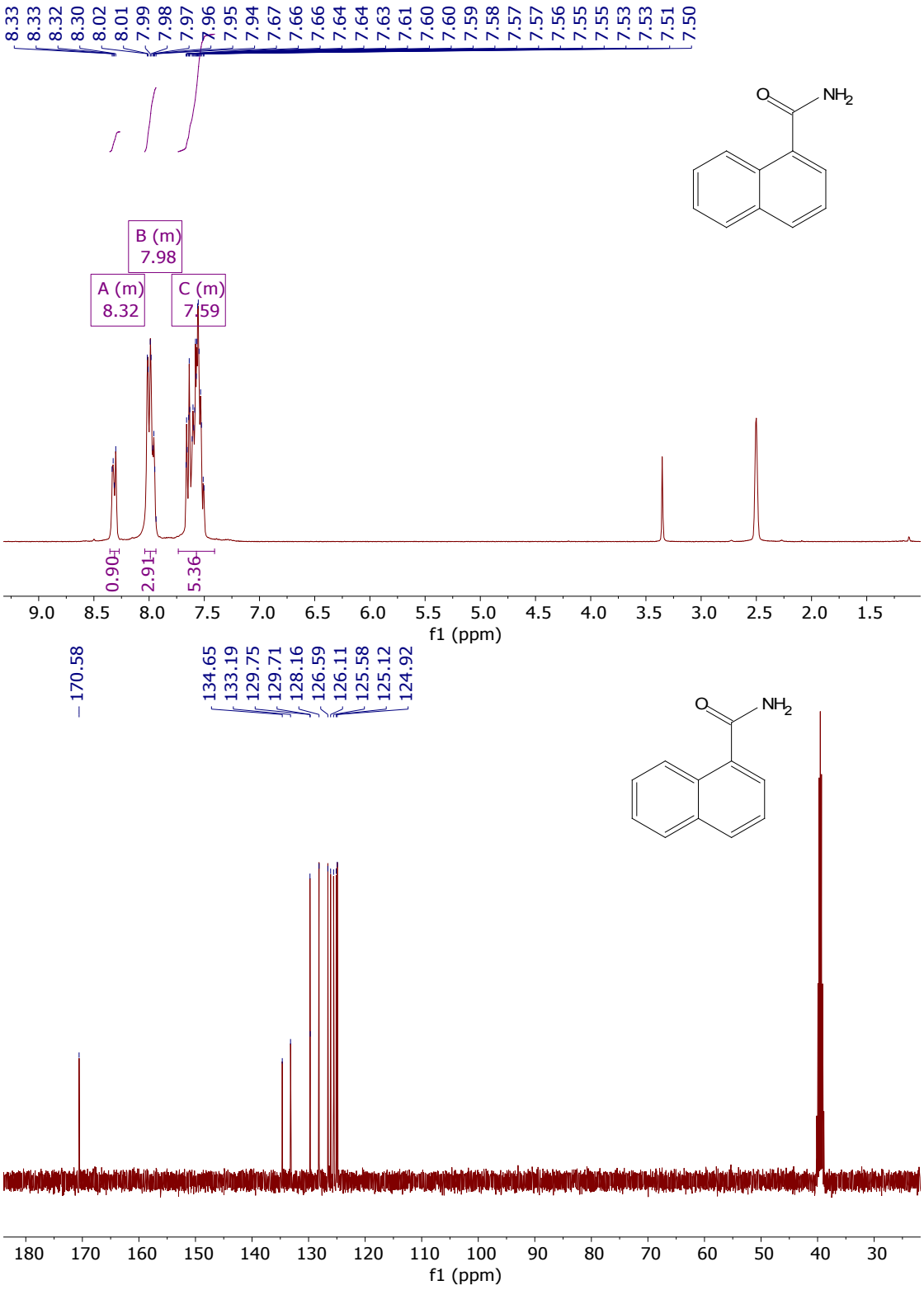

Figure S22. NMR spectra of 1-naphthamide (**2j**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

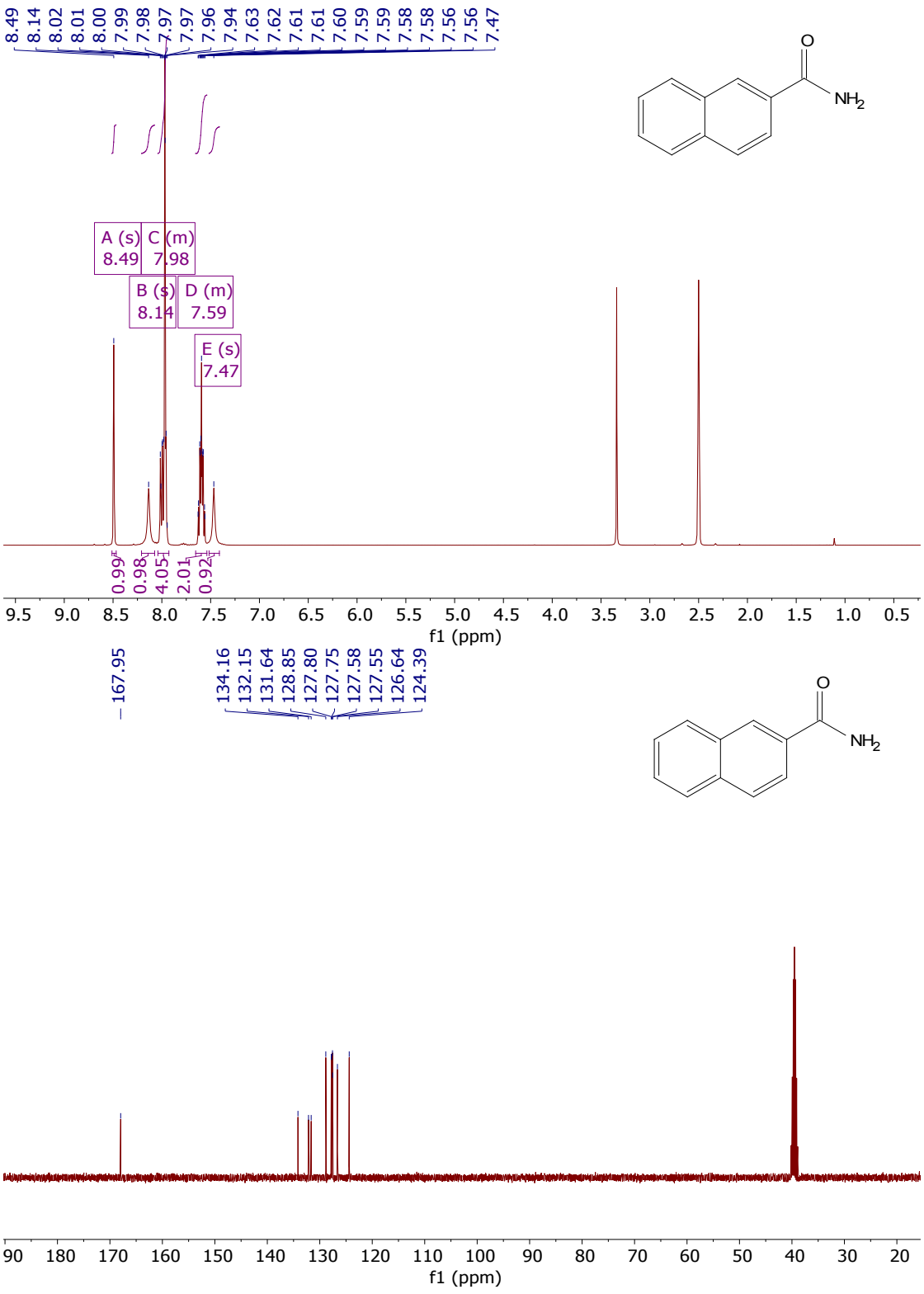

Figure S23. NMR spectra of 2-naphthamide (**2k**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

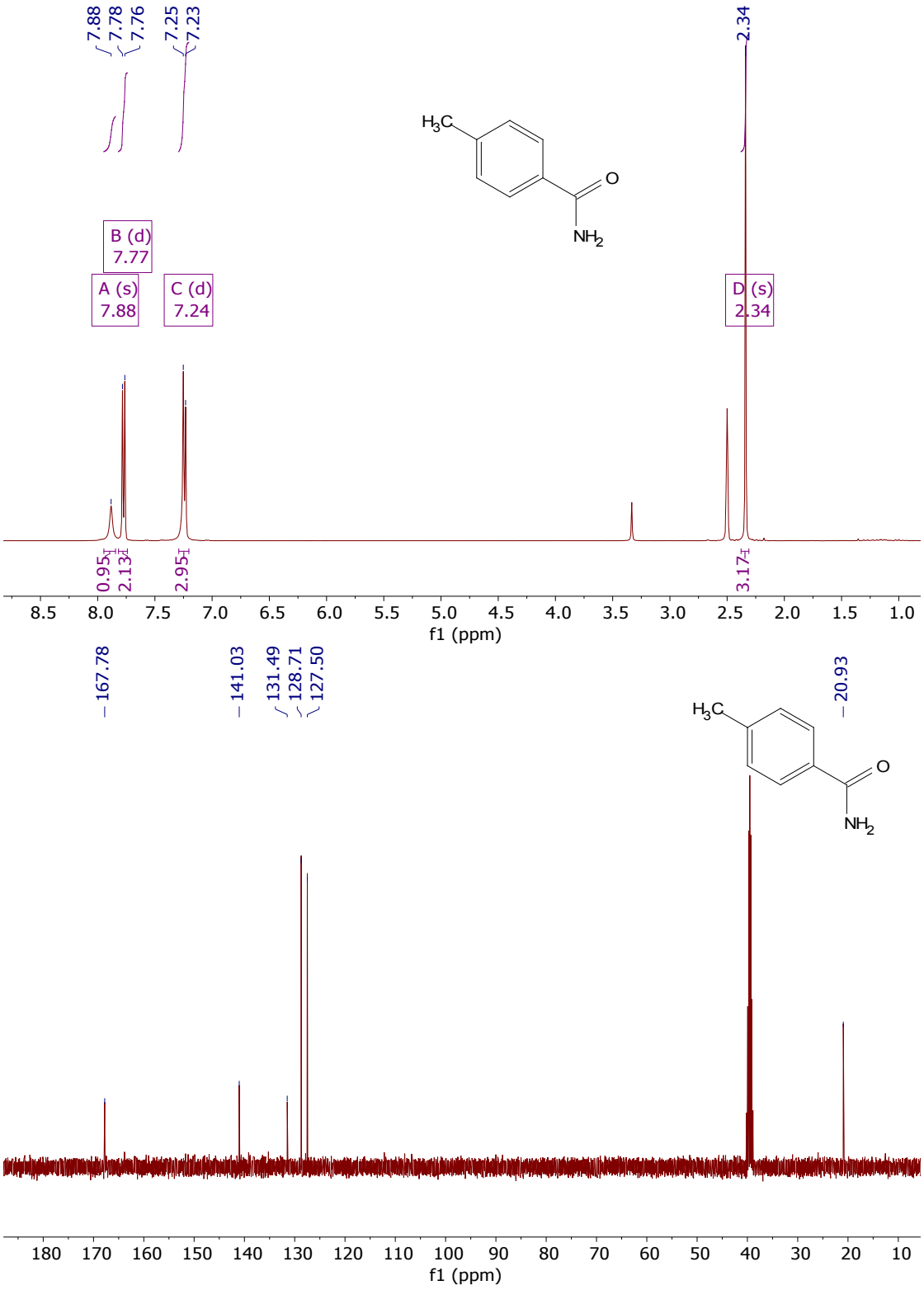

Figure S24. NMR spectra of 4-methylbenzamide (**2l**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

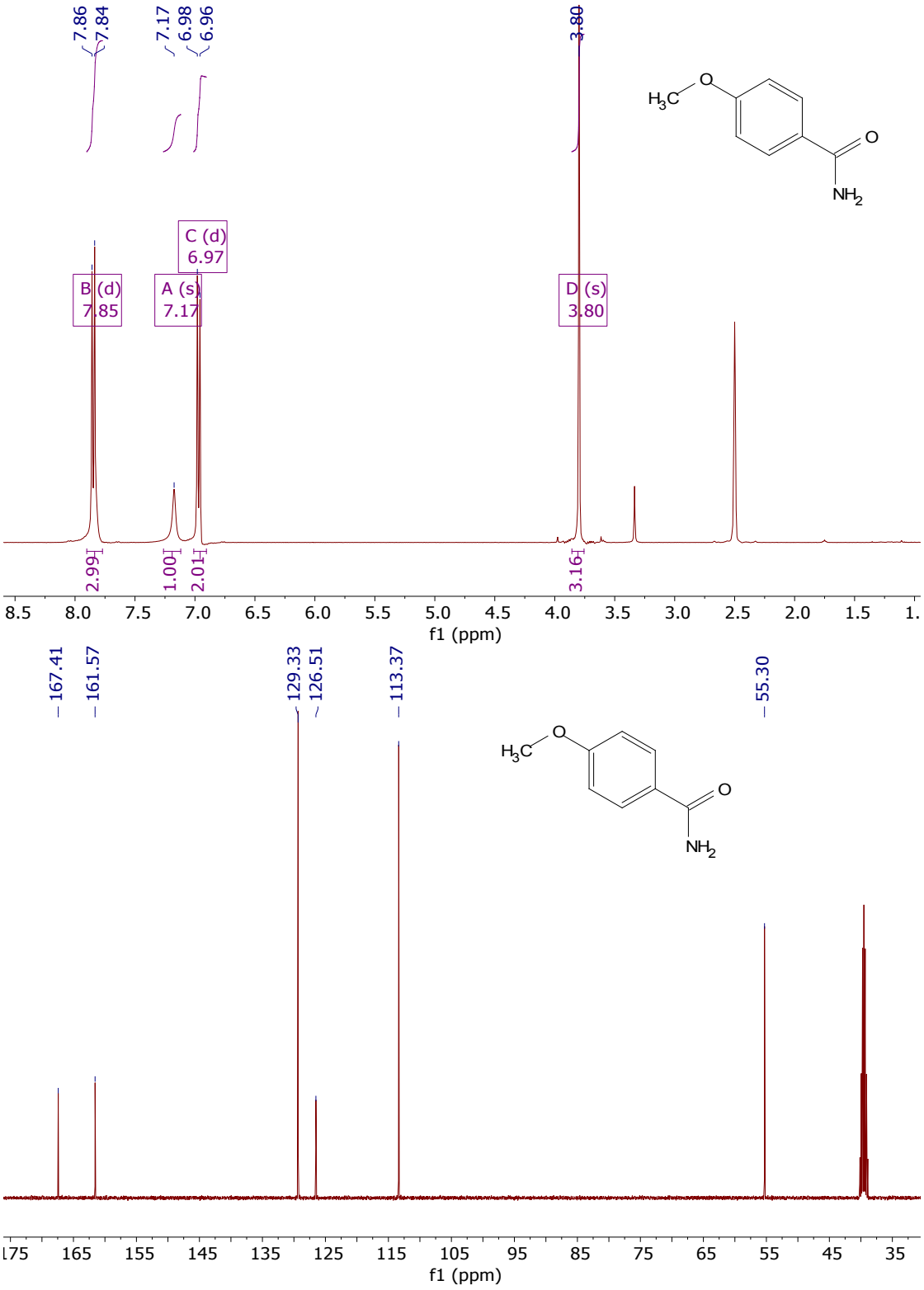

Figure S25. NMR spectra of 4-methoxybenzamide (**2m**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

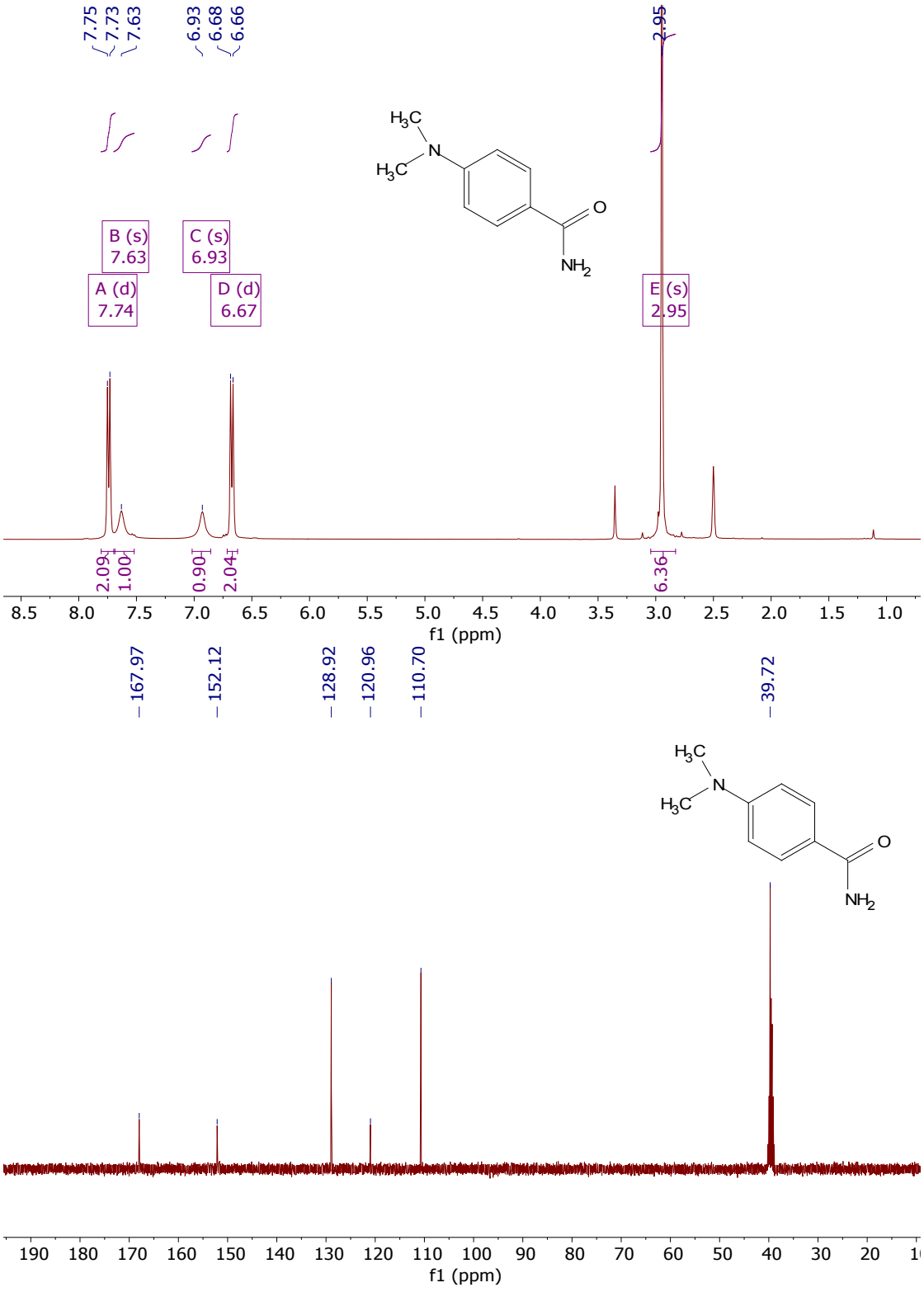

Figure S26. NMR spectra of 4-(dimethylamino)benzamide (**2n**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

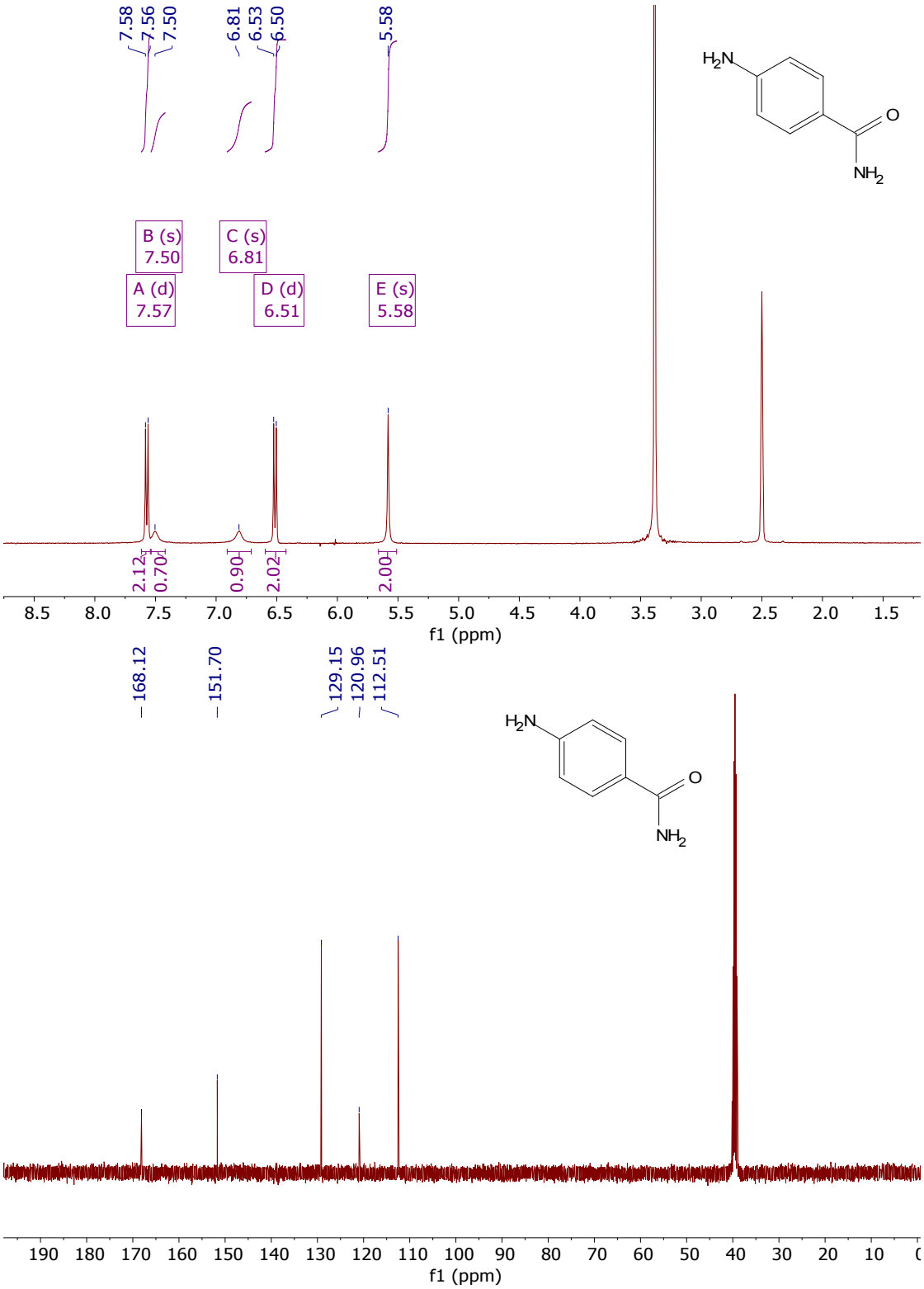

Figure S27. NMR spectra of 4-aminobenzamide (**2o**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

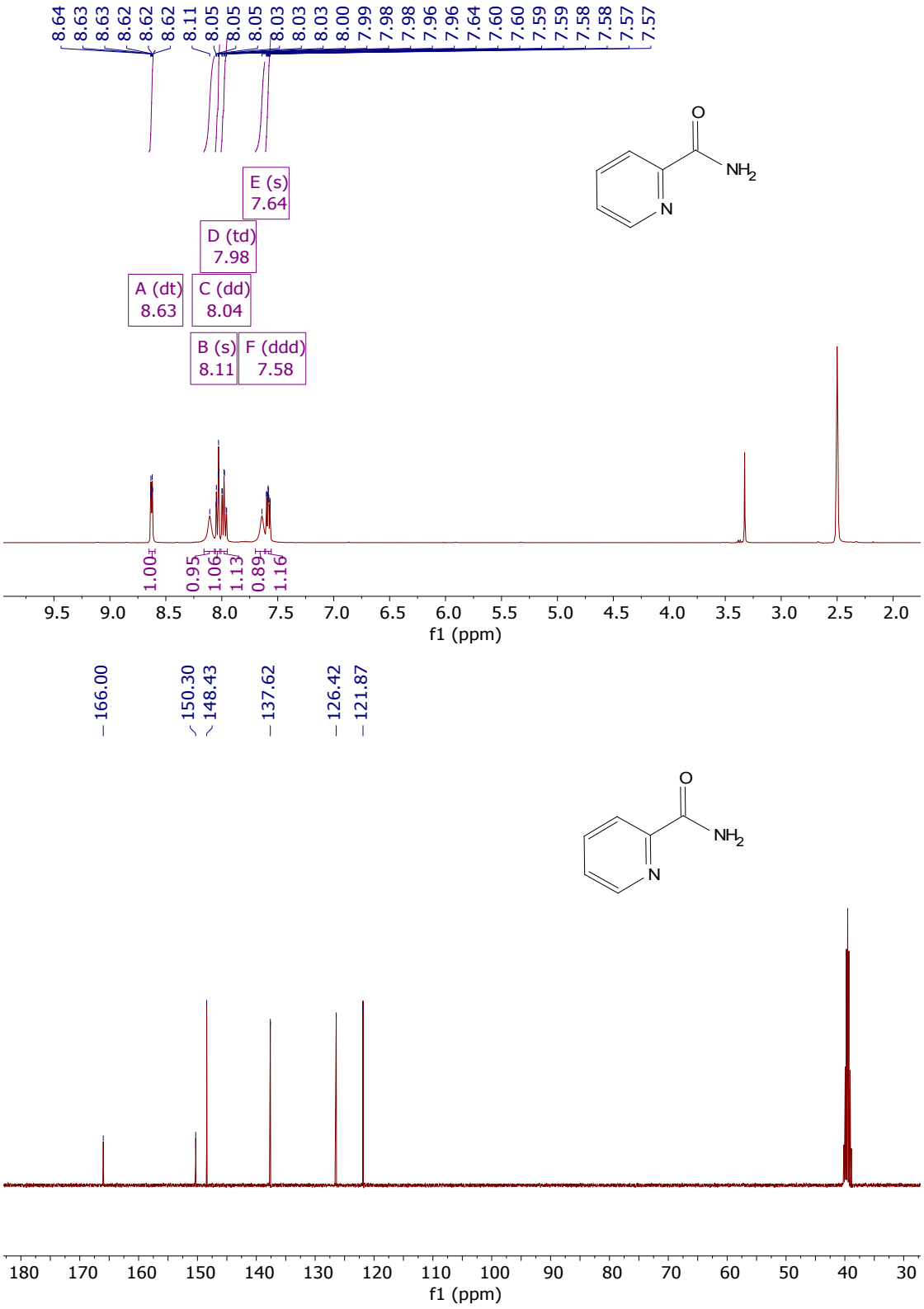

Figure S28. NMR spectra of picolinamide (**2p**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

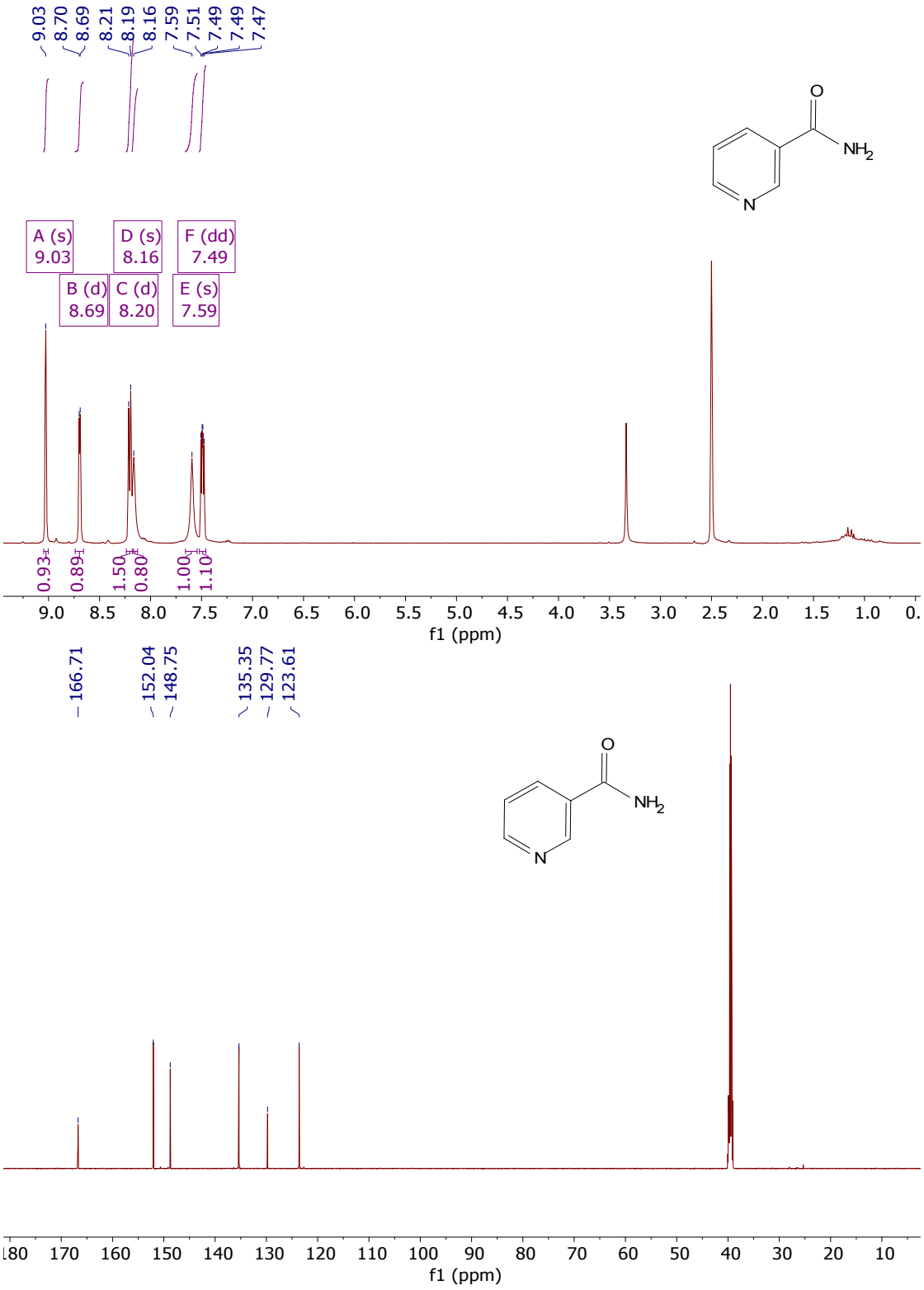

Figure S29. NMR spectra of nicotinamide (**2q**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

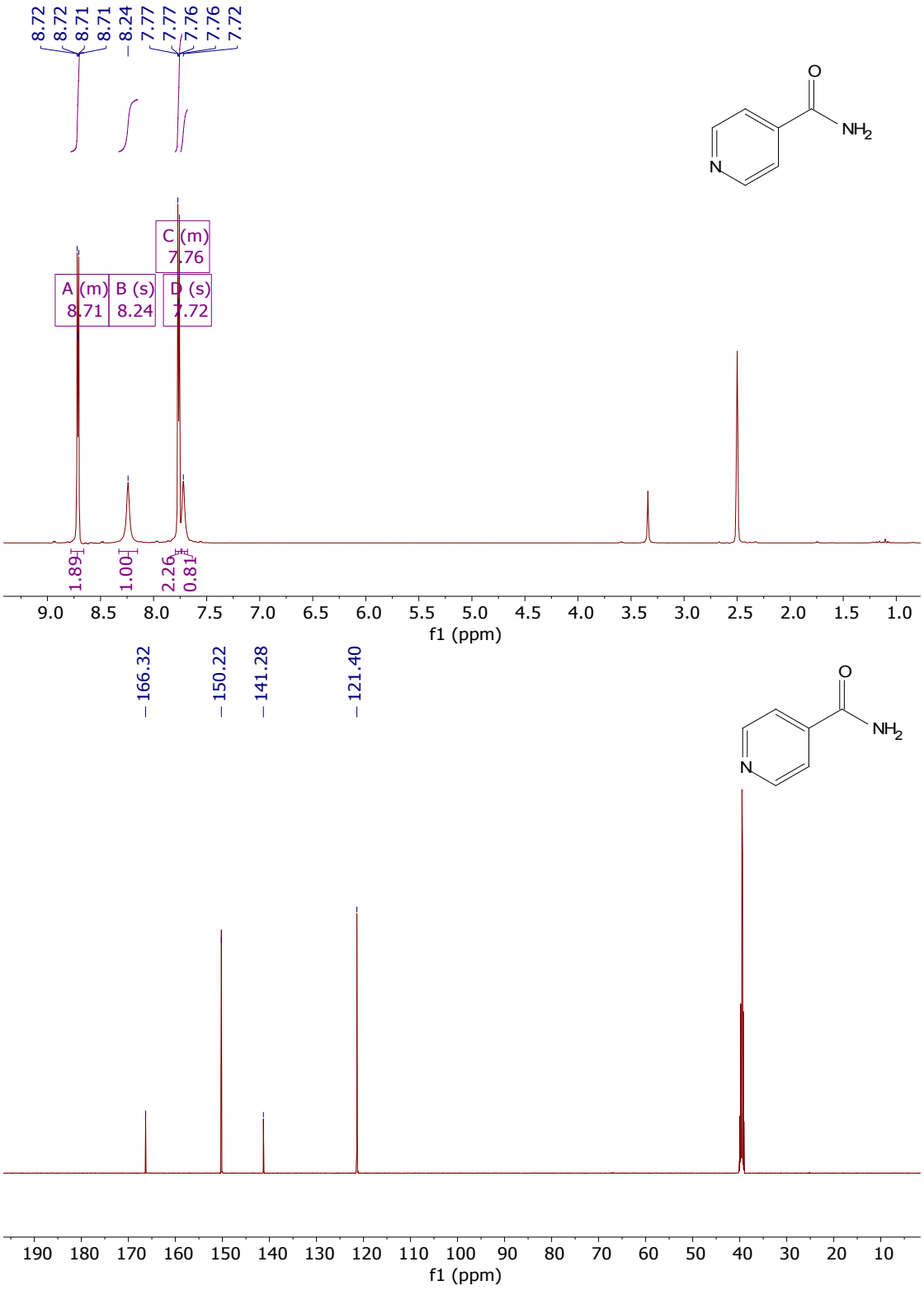

Figure S30. NMR spectra of isonicotinamide (**2r**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

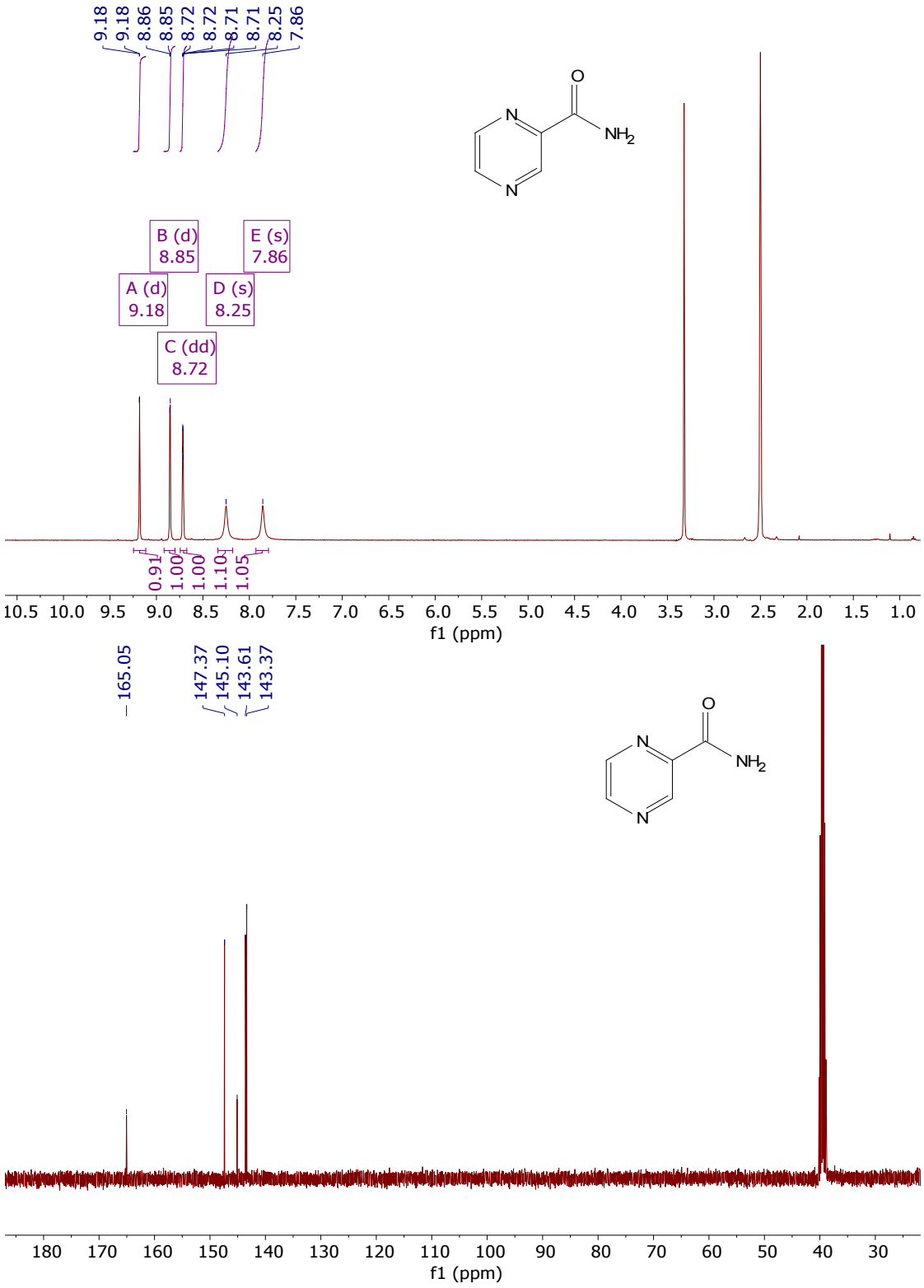

Figure S31. NMR spectra of pyrazine-2-carboxamide (**2s**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

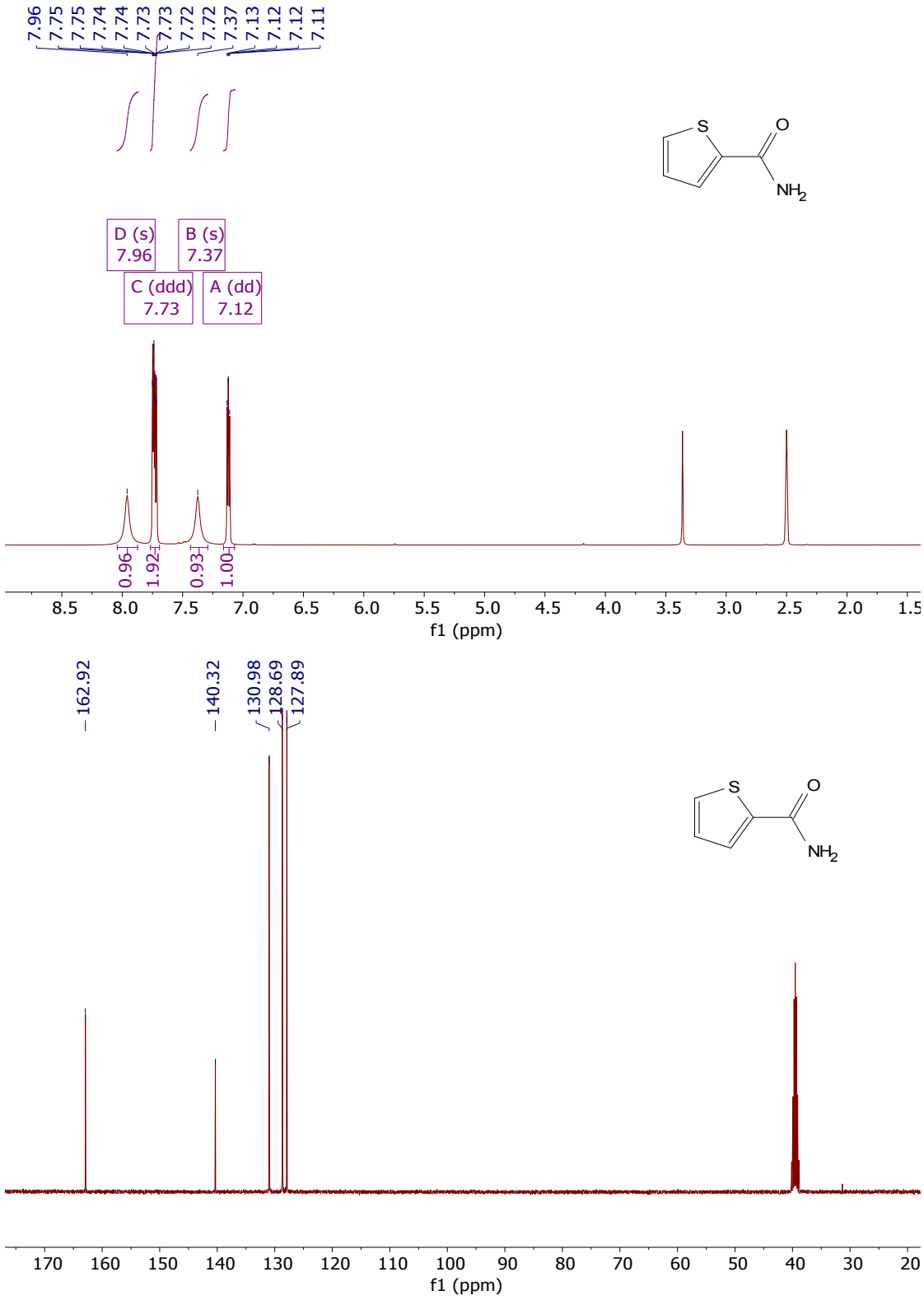

Figure S32. NMR spectra of 2-thiophenecarboxamide (**2t**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

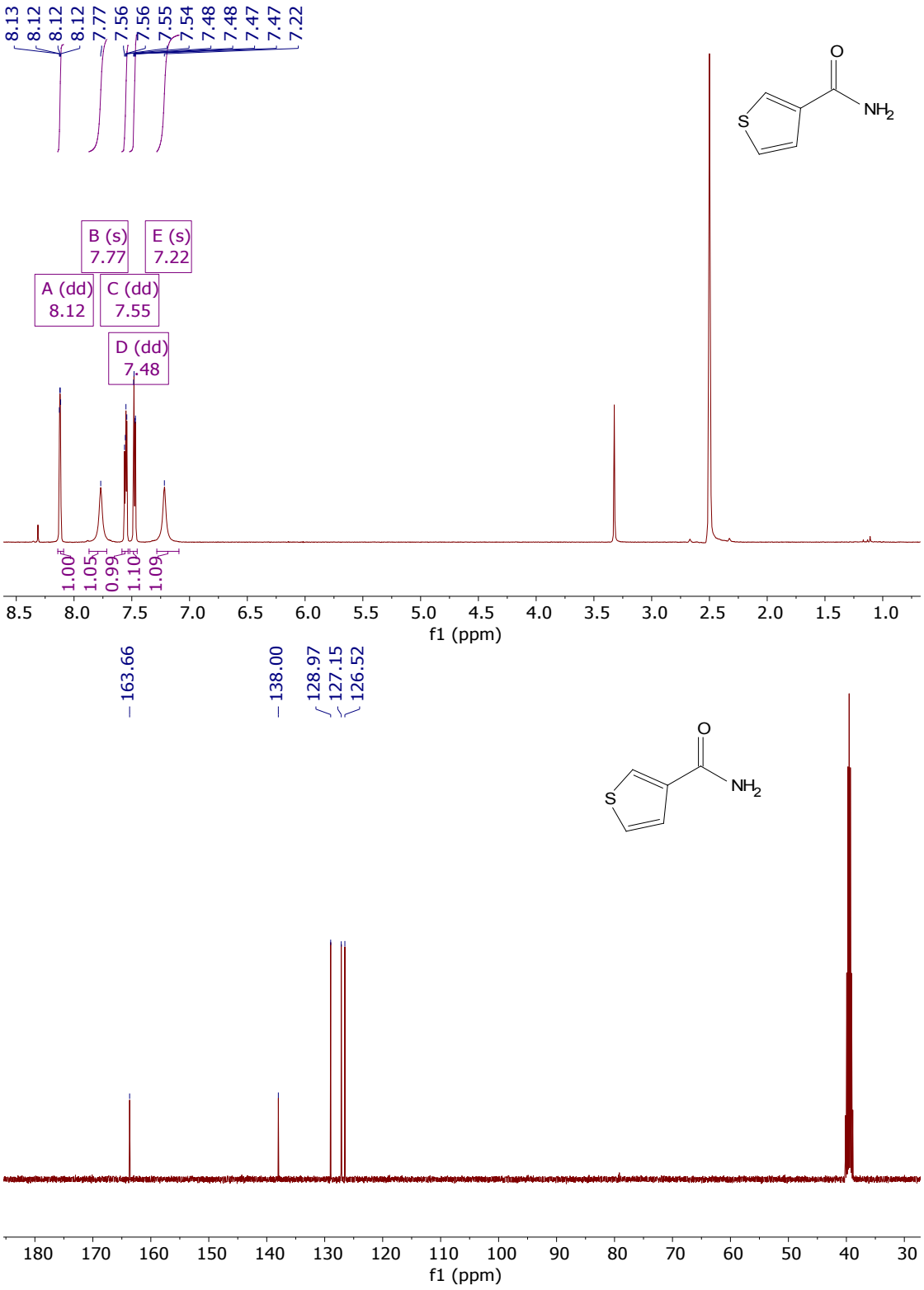

Figure S33. NMR spectra of 3-thiophenecarboxamide (**2u**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

Figure S34. NMR spectra of 2-furamide (**2v**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

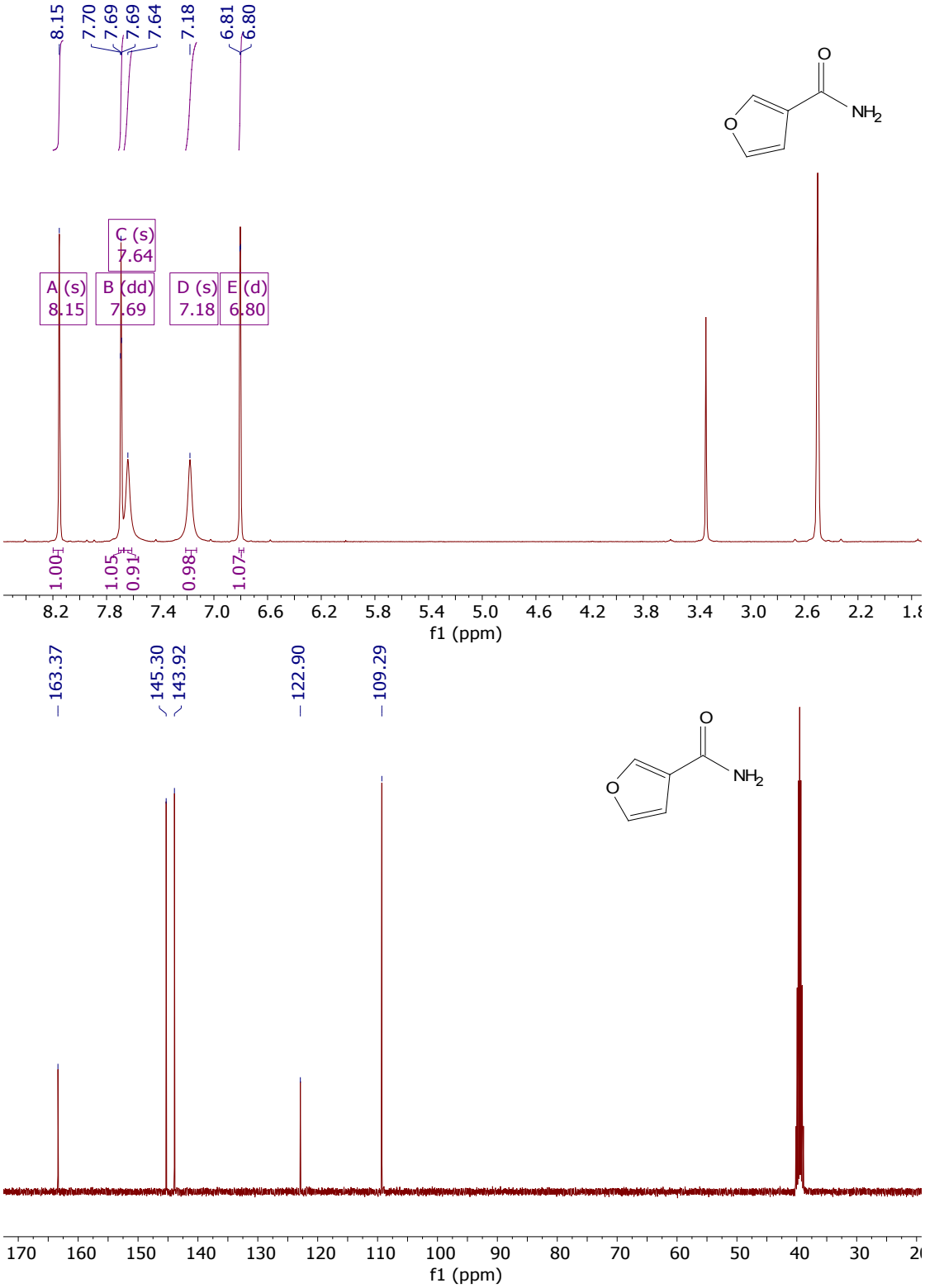

Figure S35. NMR spectra of 3-furamide (**2w**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

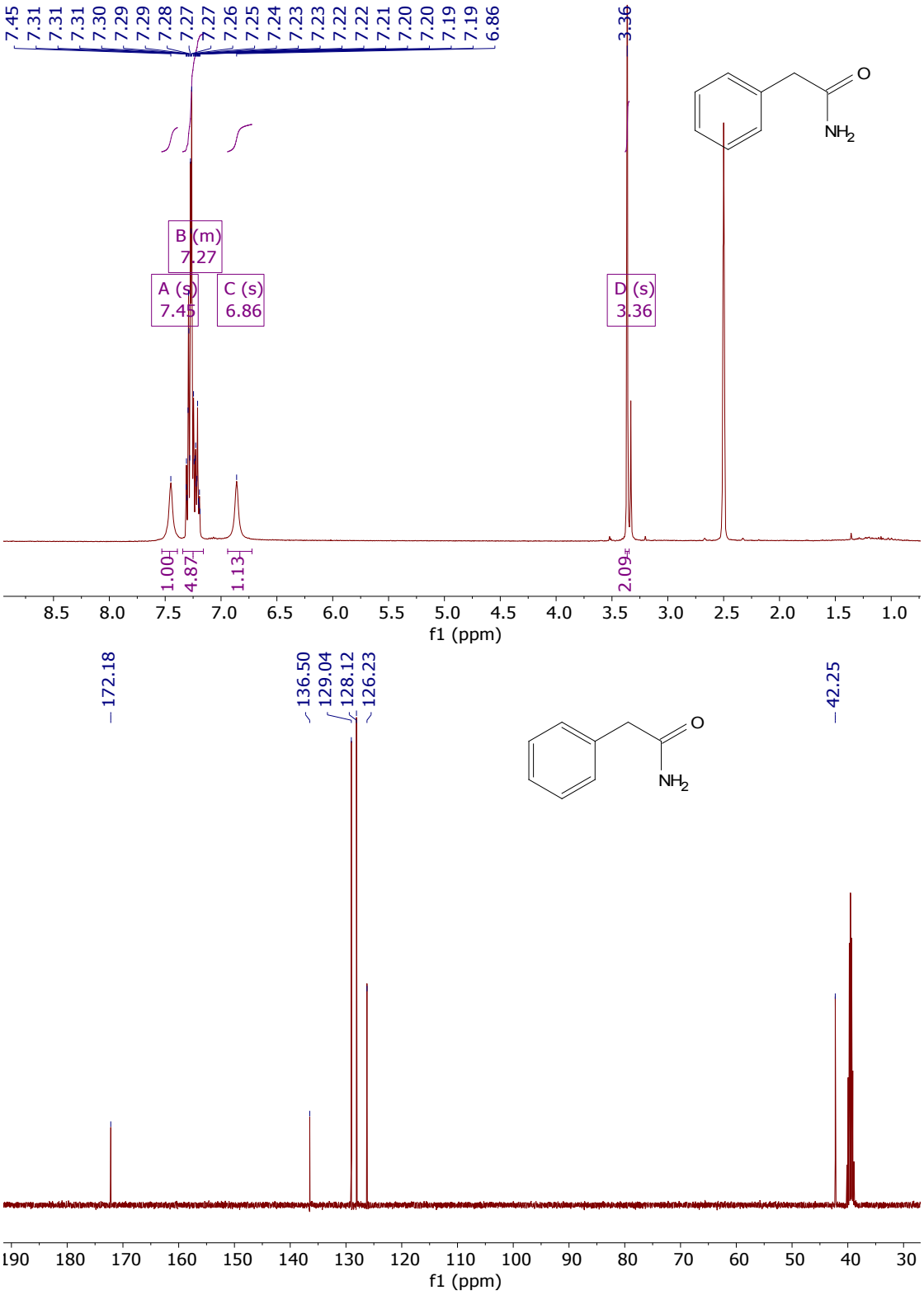

Figure S36. NMR spectra of 2-phenylacetamide (**2x**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

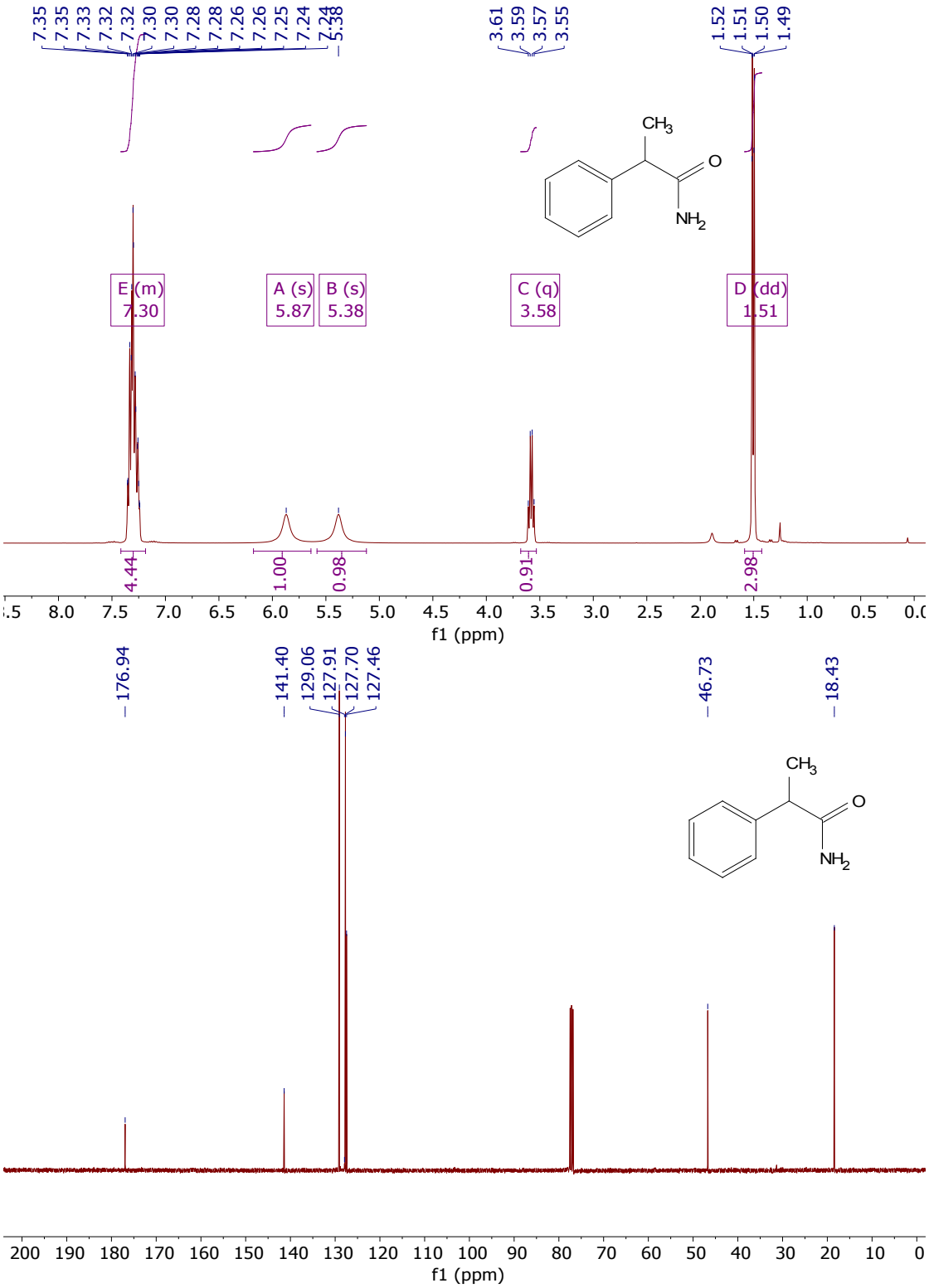

Figure S37. NMR spectra of 2-phenylpropanamide (**2y**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

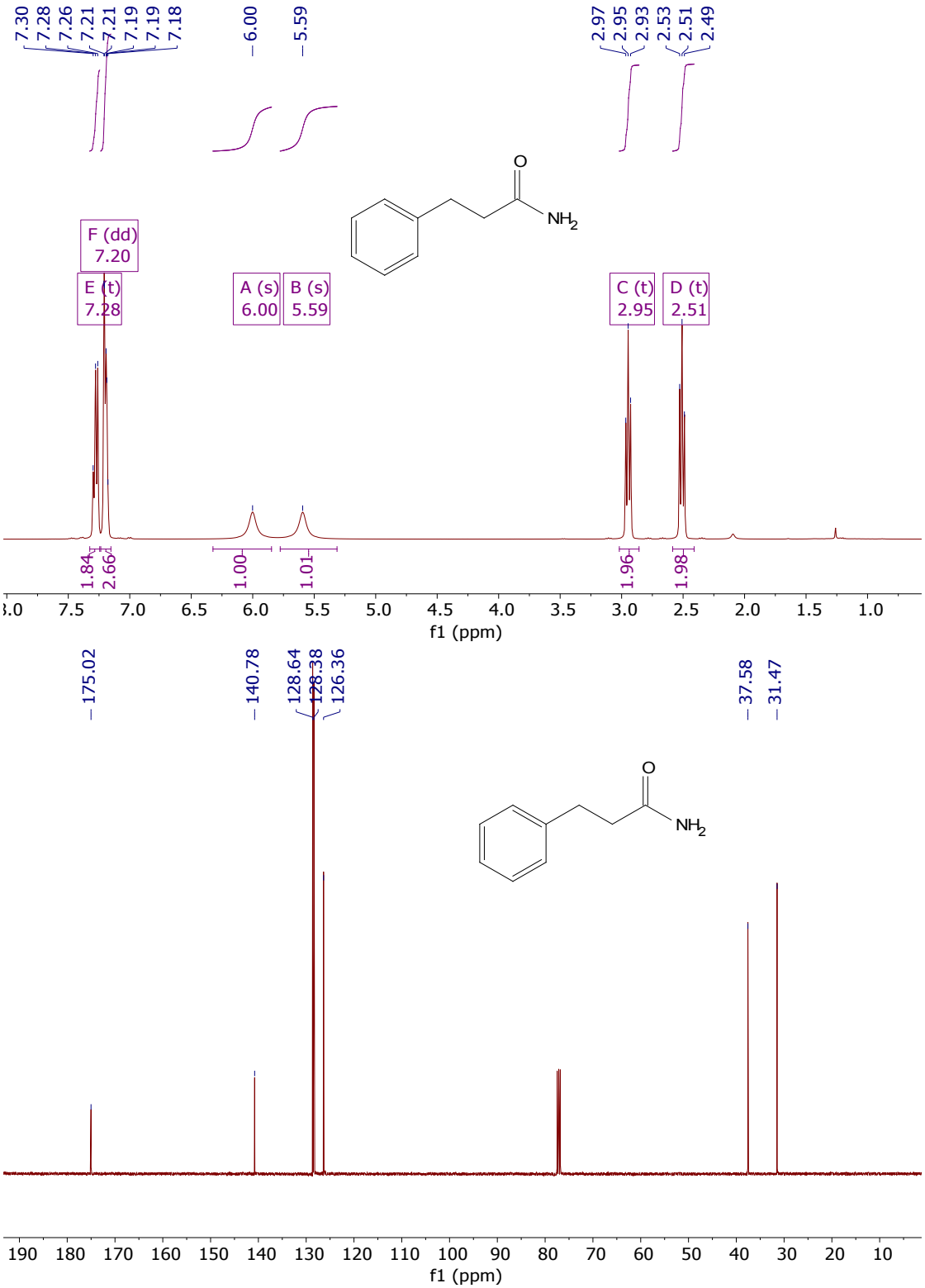

Figure S38. NMR spectra of 3-phenylpropanamide (**2z**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

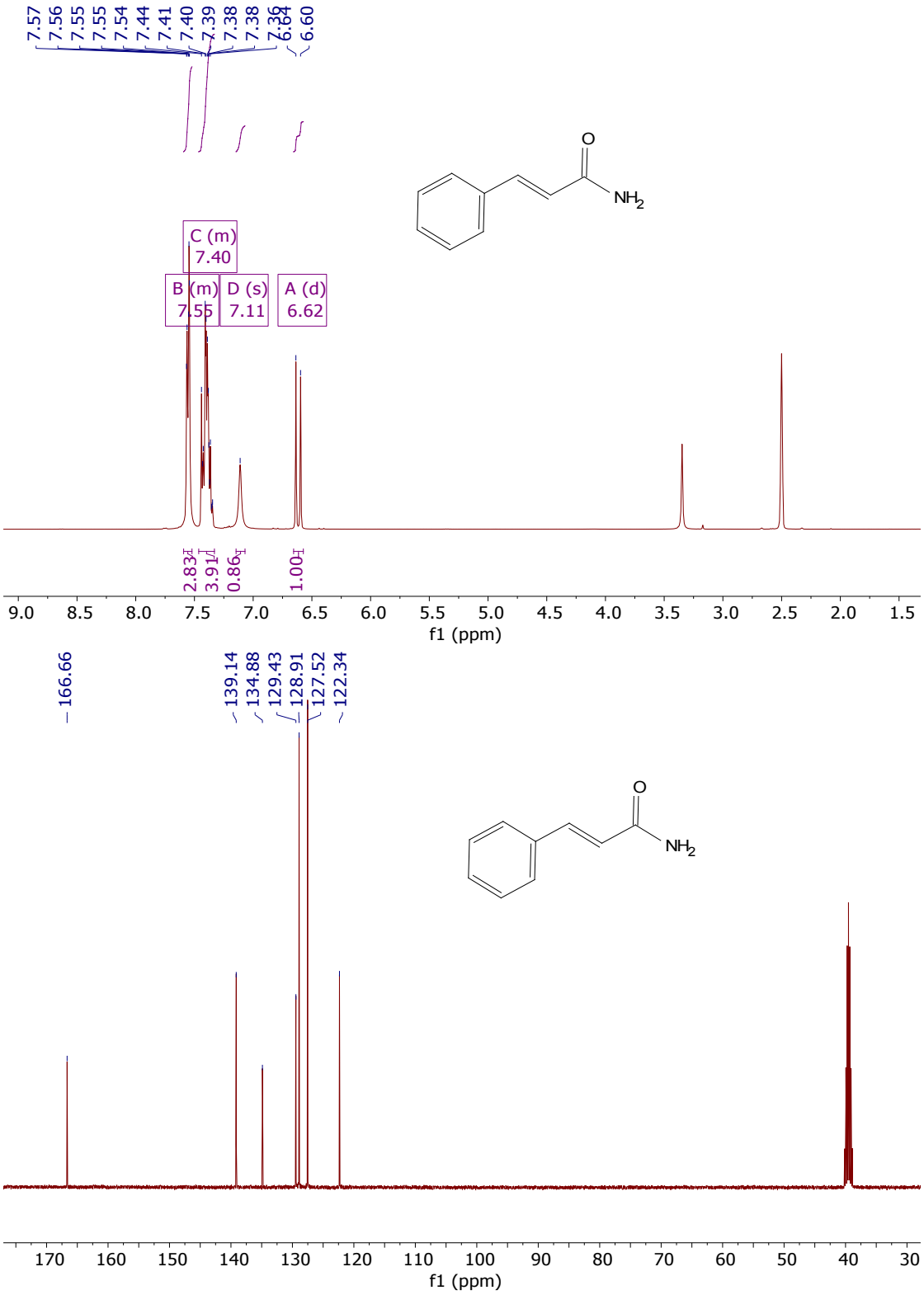

Figure S39. NMR spectra of cinnamamide (**2aa**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

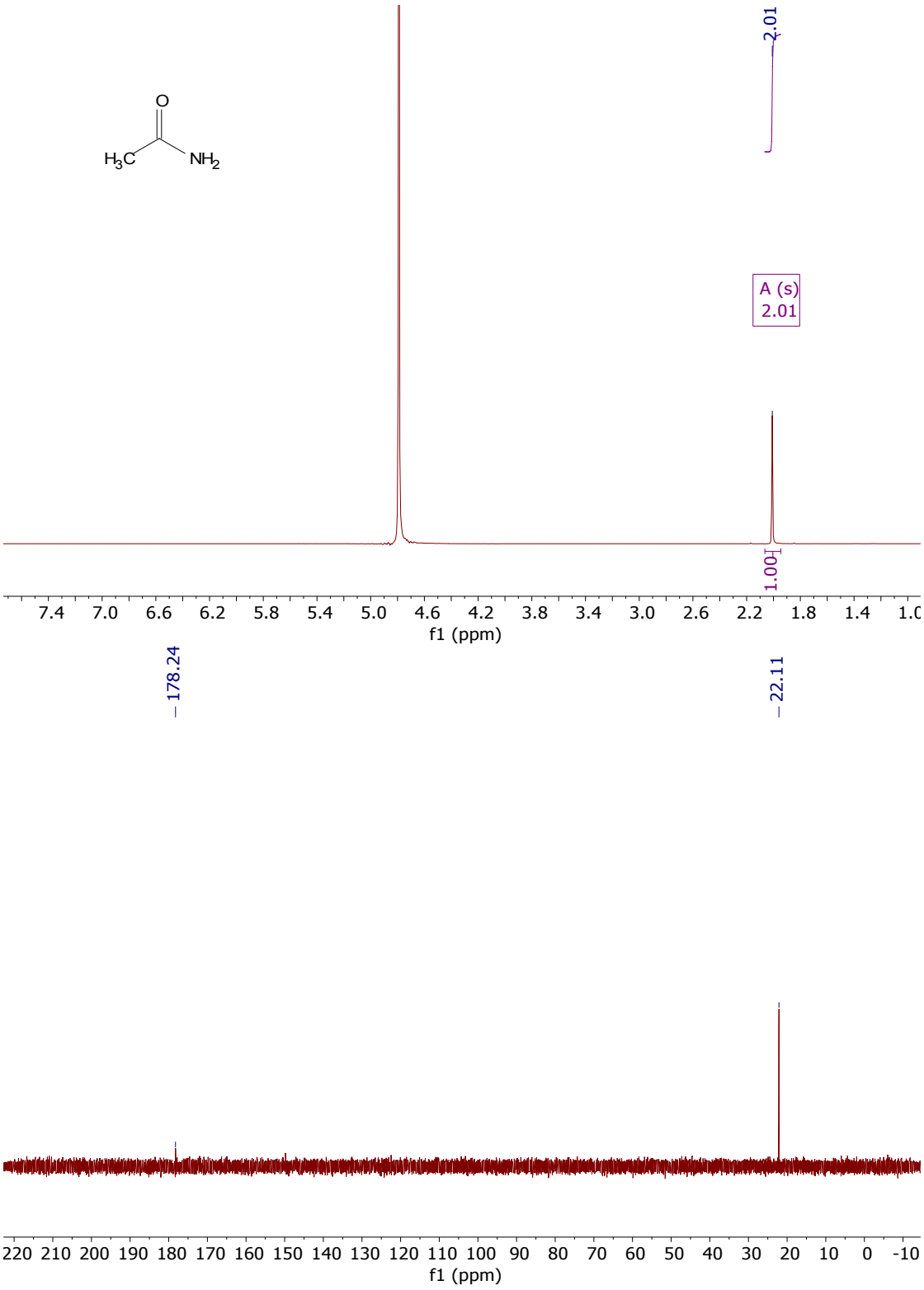

Figure S40. NMR spectra of acetamide (**2ab**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

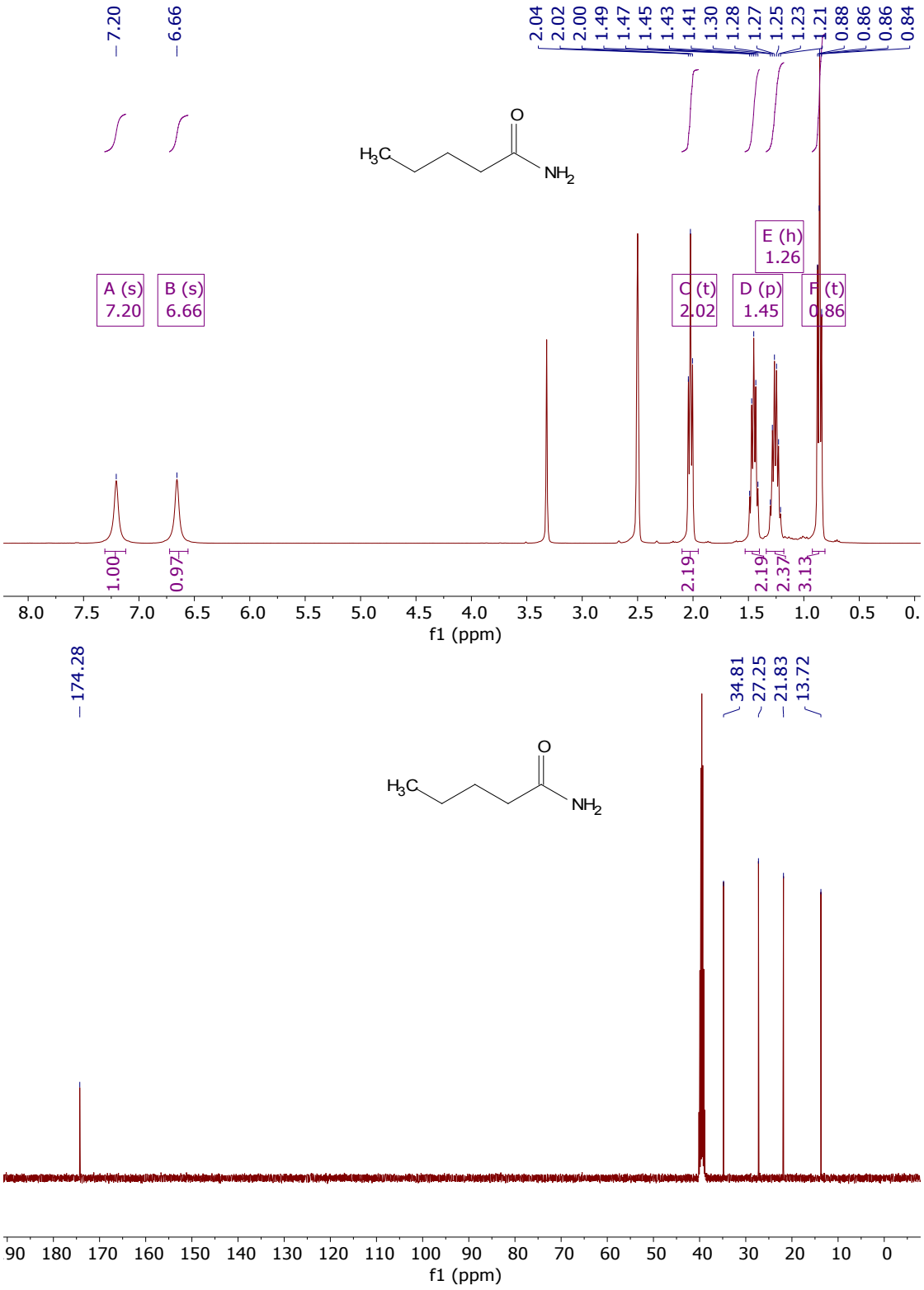

Figure S41. NMR spectra of pentanamide (**2ac**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

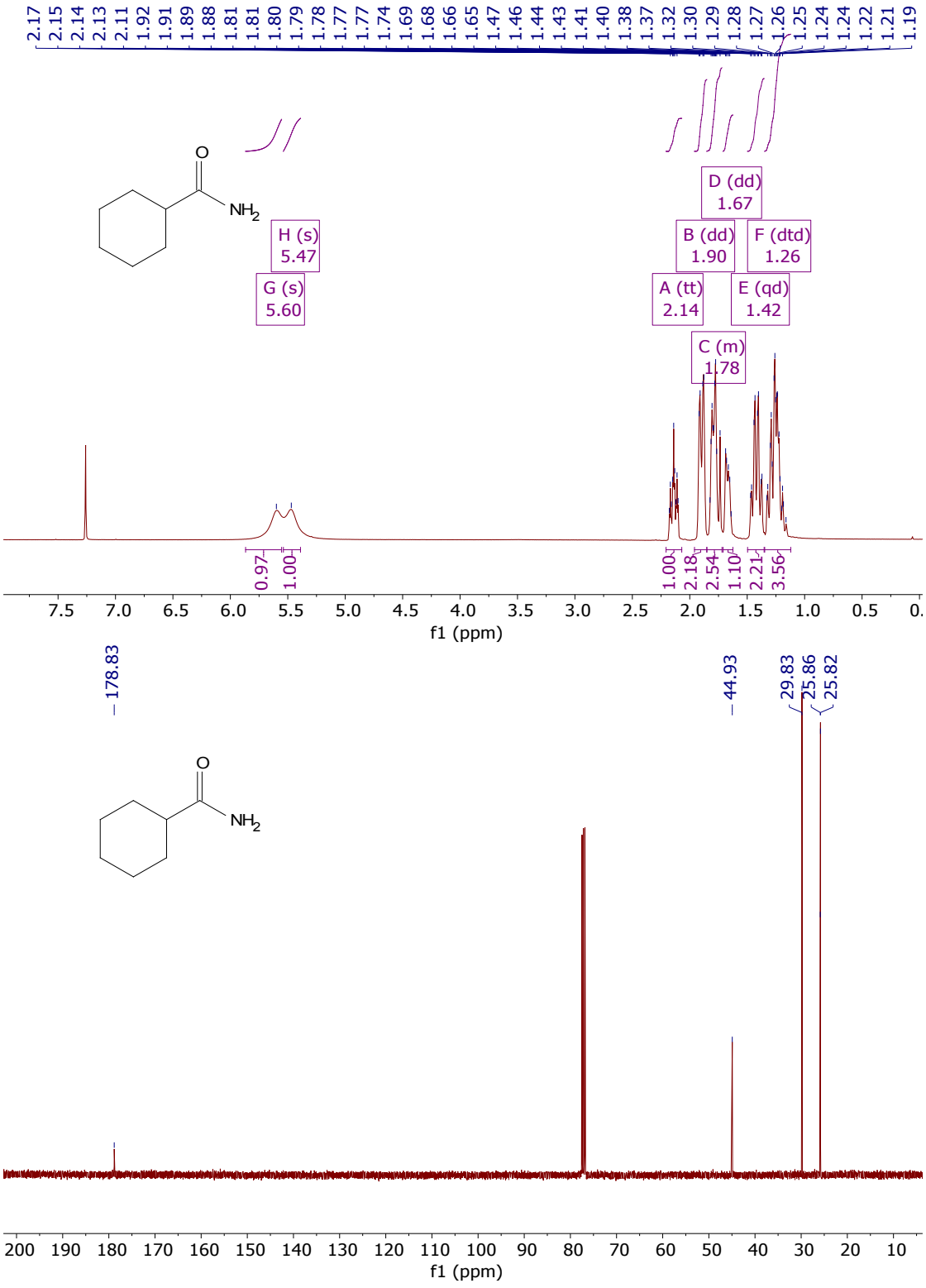

Figure S42. NMR spectra of cyclohexanecarboxamide (**2ad**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

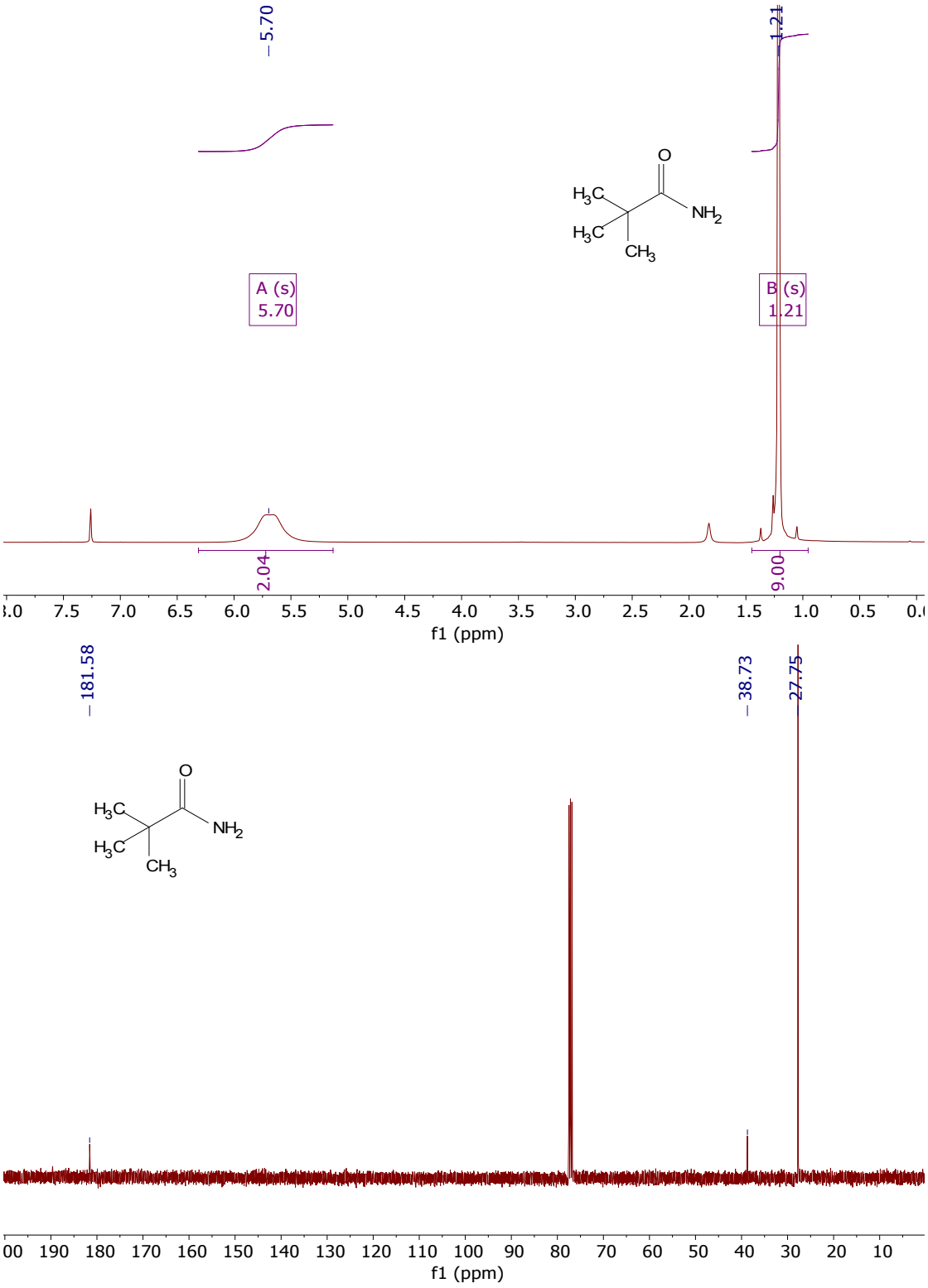

Figure S43. NMR spectra of pivalamide (**2ae**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

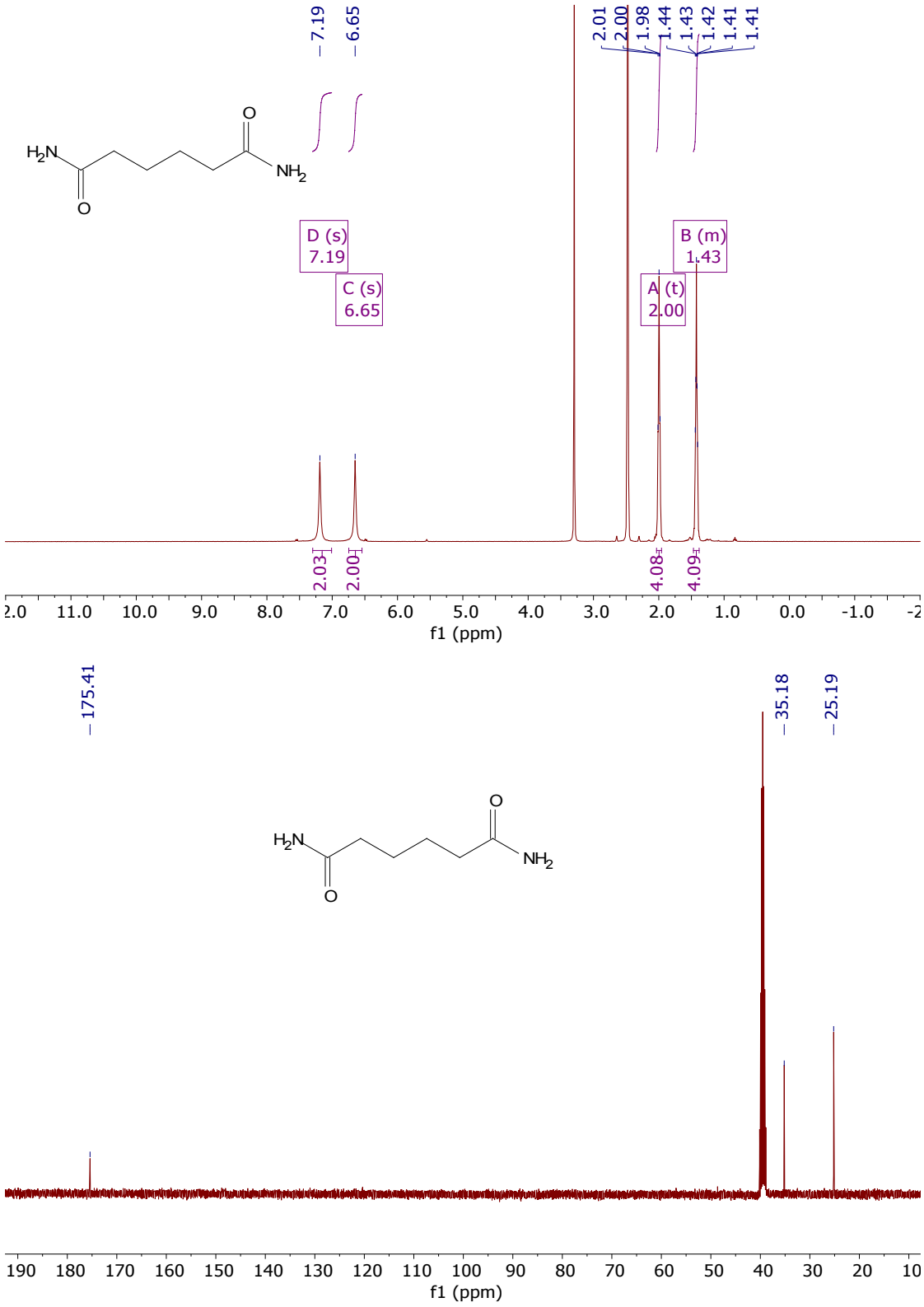

Figure S44. NMR spectra of adipamide (**2af**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

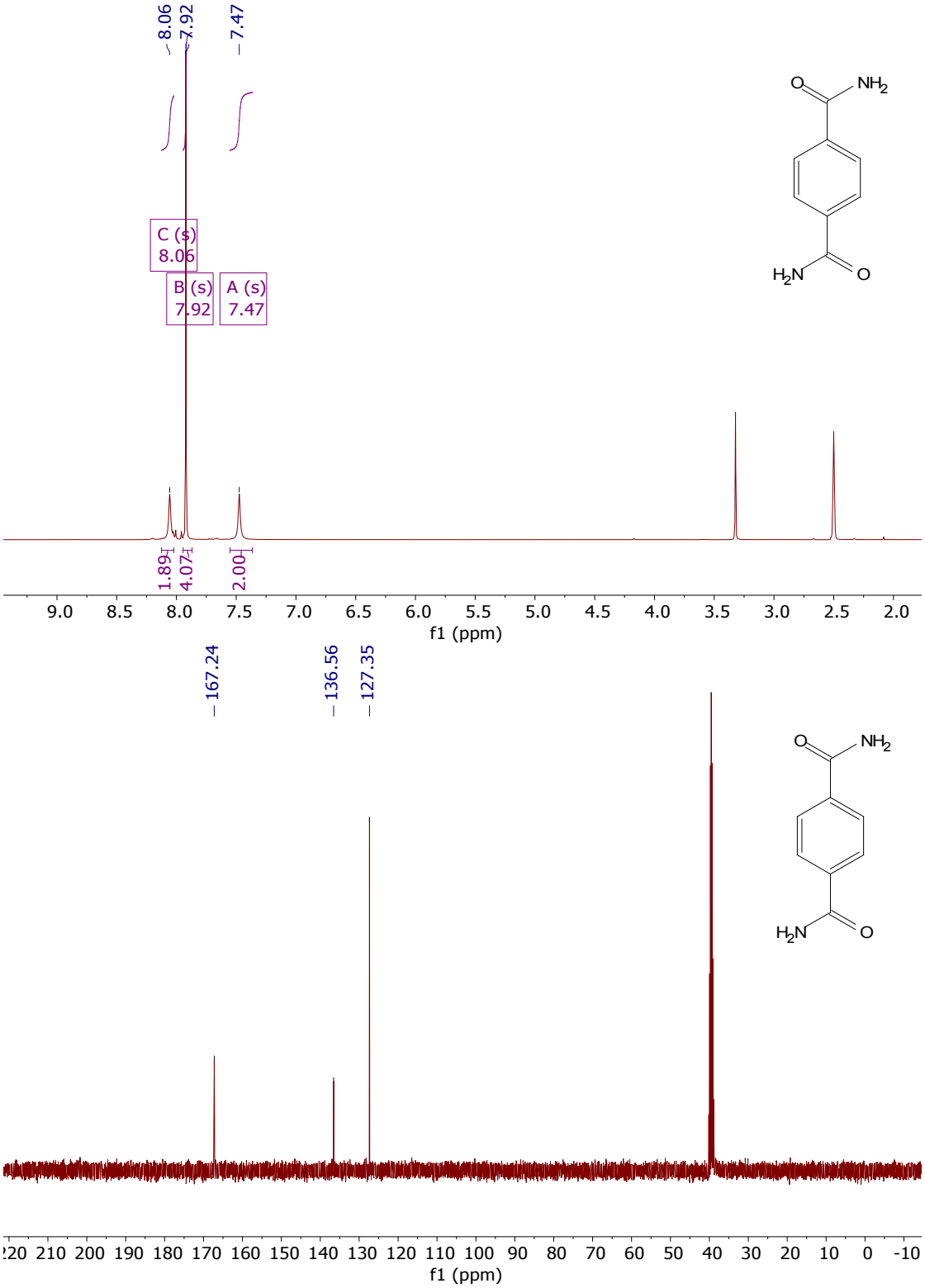

Figure S45. NMR spectra of terephthalamide (**2ag**): ^{1}H NMR(top) and ^{13}C NMR(bottom)

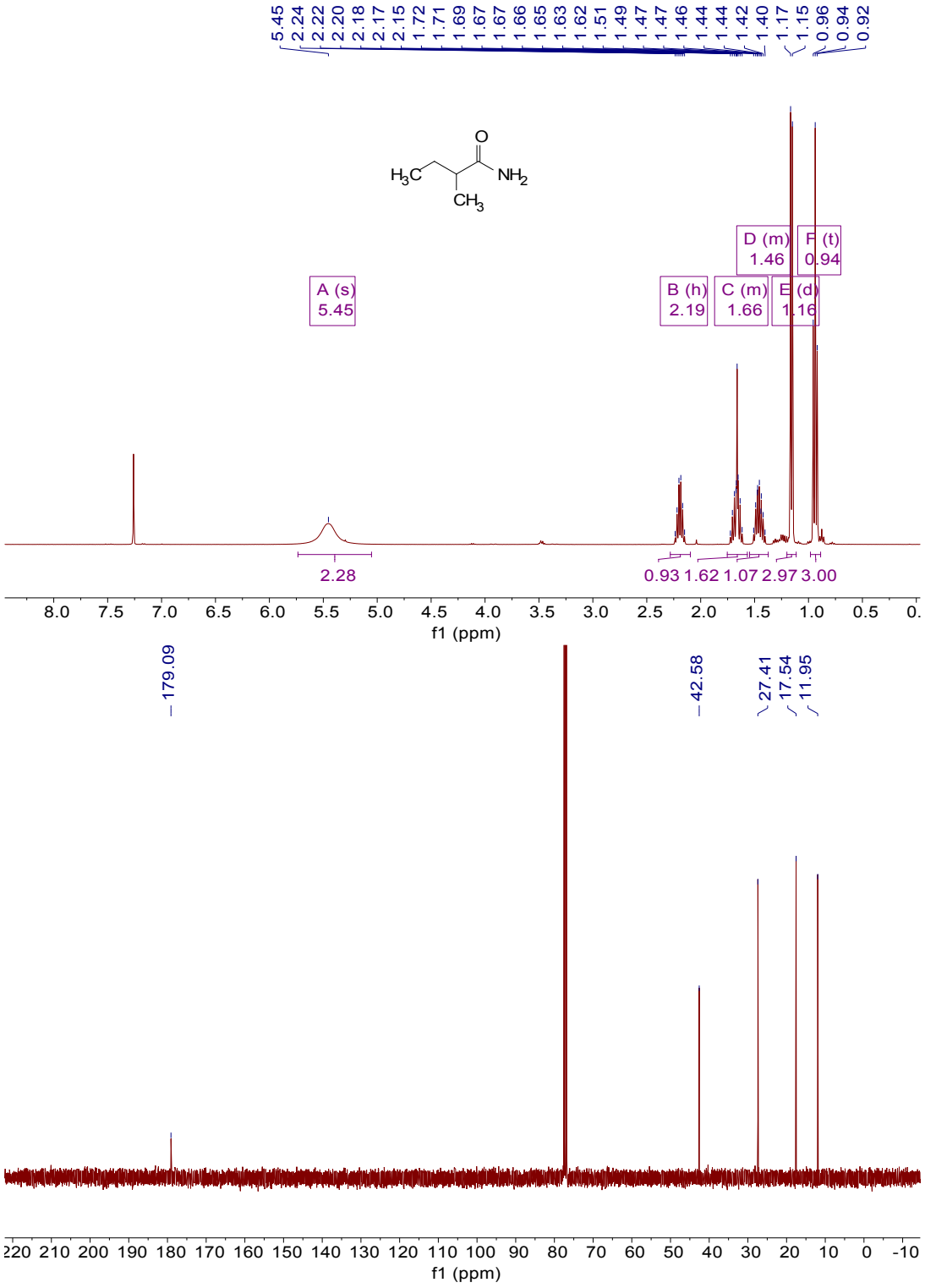

Figure S46. NMR spectra of 2-methylbutanamide: ^{1}H NMR(top) and ^{13}C NMR(bottom)