Supporting Information

Bis(Cyclooctadiene)Nickel(0)-Catalyzed Exhaustive C(sp^2)-X and C(sp^3)-F Hydrodehalogenation and Deuterodefluorination of Pyridines and Arenes with Broad Substrate Scope

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Table of Contents

1. General considerations

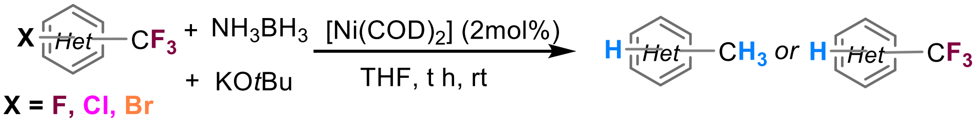
All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (argon) glovebox unless otherwise noted. All glassware was stored in a pre-heated at 200 °C oven prior to use. All glassware were cleaned using base (KOH, *i*PrOH) and acid (HCl (aq)) baths. All reported reaction temperatures correspond to external silicone oil bath temperatures. Room temperature (rt) was approximately 23 °C.

The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[1] HBPin, H_2SiEt_2, $HSiEt_3$, $HSiOEt_3$ and *tert*-butylamine were purchased from Sigma-Aldrich and used as received. $NaHBEt_3$ (1.0 M solution in THF), $NaHBEt_3$ (1.0 M solution in THF), $KHBEt_3$ (1.0 M solution in THF), KO*t*Bu (1.0 M solution in THF), $NaBH_4$, $NHMe_2BH_3$, NH_3BH_3, BH_3.THF, NEt_3BH_3 and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Sigma Aldrich and used as received. NH_3BD_3[2], ND_3BH_3[2] and ND_3BD_3[2] were prepared according to literature procedures. THF-d_8 was distilled from sodium metal under an atmosphere of argon and stored under argon. CD_3CN, DCM-d_2, $CDCl_3$, Benzene-d_6 and DMSO-d_6 were purchased from Thermo Fischer Scientific and used without further purification. D_2O was purchased from Sigma-Aldrich and used without further purification. The pyridines and arenes employed in the substrate scope (**1-43**) were purchased from commercial sources (Thermo Fisher Scientific, AmBeed and Sigma Aldrich), dried over calcium hydride and distilled prior to use. $[Ni(COD)_2]$ was purchased from Strem chemicals.

^1H NMR spectra were recorded on either Varian 400 or 500 spectrophotometers operating at 400 MHz, and 500 MHz, respectively. ^{19}F NMR spectra were recorded on Varian 400 or 500 spectrometers with 376 MHz and 470 MHz frequencies. ^2H NMR spectra were recorded on Varian 400 or 500 spectrometers with 61 MHz and 77 MHz frequencies. All ^1H NMR chemical shifts are reported in ppm relative to $SiMe_4$ using the ^1H (chloroform-*d*: 7.26 ppm; benzene-d_6: 7.16 ppm) and ^{13}C (chloroform-*d*: 77.16 ppm; benzene-d_6: 128 ppm) chemical shifts of the solvent as a standard. ^1H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent, obsc = obscured), coupling constants (Hz), integration, assignment. ^{13}C NMR data for diamagnetic compounds are reported as follows: chemical shift, number of protons attached to carbon (e. g. CH_2), assignment. QC stands for *quaternary carbon*.

2. General catalytic procedures for the C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) hydrodehalogenation (HDH) of pyridines/arenes and perfluoromethylcyclohexane

2.1 General catalytic procedure for the [Ni(COD)$_2$]-catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) HDH of trifluoromethylpyridines/arenes.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3, KO*t*Bu (1.0 M solution in THF), trifluoromethylpyridine/arene substrate (0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.1 mg, 0.004 mmol). The amounts of NH_3BH_3 and KO*t*Bu employed were substrate dependent and are listed in Table S1. The tube was sealed and stirred at room temperature for the times mentioned in Table S1. After that, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F and ^{1}H NMR spectroscopy without additional purification.

Entry	Trifluoromethylpyridine/ arene	Product	t (h)	Amount of NH_3BH_3	Amount of KO*t*Bu
1	2-Trifluoromethylpyridine (**1**)	2-Methylpyridine (**1a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
2	3-Trifluoromethylpyridine (**2**)	3-Methylpyridine (**2a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
3	4-Trifluoromethylpyridine (**3**)	4-Methylpyridine (**3a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
4*	4,4’-Bis(trifluoromethyl)-2,2'-bipyridine (**4**)	4,4'-Dimethyl-2,2'-bipyridyl (**4a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
5	2-Methoxy-6-(trifluoromethyl)pyridine (**5**)	2-Methoxy-6-methylpyridine (**5a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
6	5-Methoxy-2-(trifluoromethyl)pyridine (**6**)	5-Methoxy-2-methylpyridine (**6a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
7	4-Methoxy-2-(trifluoromethyl)pyridine (**7**)	4-Methoxy-2-methylpyridine (**7a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
8**	2-Methoxy-5-(trifluoromethyl)pyridine (**8**)	2-Methoxy-5-methylpyridine (**8a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)

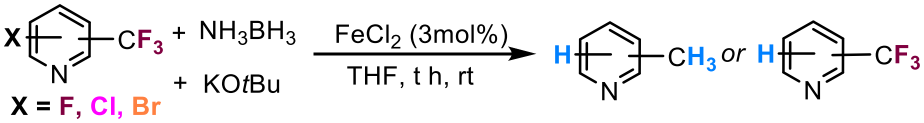
9	2-Amino-6-(trifluoromethyl)pyridine (**9**)	2-Amino-6-methylpyridine (**9a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
10*	2,6-Bis(trifluoromethyl)pyridine (**10**)	2,6-Dimethylpyridine (**10a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
11*	2,6-Bis(trifluoromethyl)pyridine (**10**)	2- Trifluoromethyl-6-methylpyridine (**10a'**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
12	2-Fluoro-6-(trifluoromethyl)pyridine (**15**)	2-Methylpyridine (**1a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
13	2-Chloro-6-(trifluoromethyl)pyridine (**12**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
14	2-Chloro-6-(trifluoromethyl)pyridine (**12a**)	2-Trifluoromethyl pyridine (**1**)	1	6.2 mg (0.200 mmol)	0.2 mL (0.200 mmol)
15	2-Bromo-6-(trifluoromethyl)pyridine (**11**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
16	2-Bromo-6-(trifluoromethyl)pyridine (**11**)	2-Trifluoromethyl pyridine (**1**)	1	6.2 mg (0.200 mmol)	0.2 mL (0.200 mmol)
17	5-Fluoro-2-(trifluoromethyl)pyridine(**16**)	2-Methylpyridine (**1a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
18	5-Bromo-2-(trifluoromethyl)pyridine (**14**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
19	5-Bromo-2-(trifluoromethyl)pyridine (**14**)	2-Trifluoromethyl pyridine (**1**)	1	6.2 mg (0.200 mmol)	0.2 mL (0.200 mmol)
20	4-Bromo-2-(trifluoromethyl)pyridine (**13**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
21	4-Bromo-2-(trifluoromethyl)pyridine (**13**)	2-Trifluoromethyl pyridine (**1**)	1	6.2 mg (0.200 mmol)	0.2 mL (0.200 mmol)
22	3-Fluoro-2-(trifluoromethyl)pyridine (**17**)	2-Methylpyridine (**1a**)	72	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
23	2-Chloro-4-(trifluoromethyl)pyridine (**18**)	4-Methylpyridine (**3a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
24	2-Chloro-4-(trifluoromethyl)pyridine (**18**)	4-Trifluoromethyl pyridine (**3**)	1	6.2 mg (0.200 mmol)	0.2 mL (0.200 mmol)
25*	Benzotrifluoride (**19**)	Toluene (**19a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)

*0.010 mmol (2.8 mg) of [Ni(COD)$_2$] employed

** 0.020 mmol (5.5 mg) of [Ni(COD)$_2$] employed

Table S1: Reaction conditions for [Ni(COD)$_2$] catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) HDH of trifluoromethylpyridines/arenes

2.2 General catalytic procedure for the $FeCl_2$-catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) HDH of trifluoromethylpyridines.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: $FeCl_2$ (0.8 mg, 0.006 mmol), NH_3BH_3, KO*t*Bu (1.0 M solution in THF), trifluoromethylpyridine substrate (0.200 mmol) and THF (0.5 mL). The amounts of NH_3BH_3 and KO*t*Bu used were substrate dependent and are listed in Table S2. The tube was sealed and stirred at rt for the times listed in Table S2. After that, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F and ^{1}H NMR spectroscopy without additional purification.

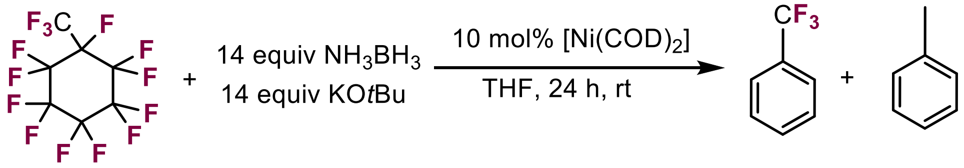
Entry	**Trifluoromethylpyridine**	**Product**	**t (h)**	**Amount of NH_3BH_3**	**Amount of KO*t*Bu**
1	2-trifluoromethylpyridine (**1**)	2-Methylpyridine (**1a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
2	3-trifluoromethylpyridine (**2**)	3-Methylpyridine (**2a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
3	4-trifluoromethylpyridine (**3**)	4-Methylpyridine (**3a**)	24	18.5 mg (0.600 mmol)	0.6 mL(0.600 mmol)
4*	4,4'-Bis(trifluoromethyl)-2,2'-bipyridine (**4**)	4,4'-Dimethyl-2,2'-bipyridyl (**4a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
5	2-Amino-6-(trifluoromethyl)pyridine (**9**)	2-Amino-6-methylpyridine (**9a**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
6*	2,6-Bis(trifluoromethyl)pyridine (**10**)	2,6-Dimethylpyridine (**10a**)	24	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
7	2-Chloro-6-(trifluoromethyl)pyridine (**12**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
8	2-Bromo-6-(trifluoromethyl)pyridine (**11**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)

9	5-Bromo-2-(trifluoromethyl)pyridine (**14**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
10	5-Bromo-2-(trifluoromethyl)pyridine (**14**)	2-Trifluoromethyl pyridine (**1**)	1	6.2 mg (0.200 mmol)	0.2 mL (0.200 mmol)
11	4-Bromo-2-(trifluoromethyl)pyridine (**13**)	2-Methylpyridine (**1a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)
12*	2-Chloro-4-(trifluoromethyl)pyridine (**18**)	4-Methylpyridine (**3a**)	24	24.7 mg (0.800 mmol)	0.8 mL (0.800 mmol)

*0.010 mmol (1.3 mg) of $FeCl_2$ employed

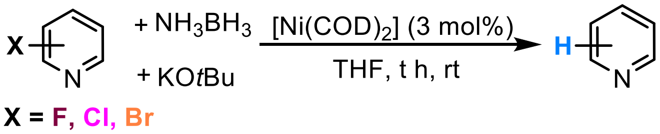
Table S2: Reaction conditions for the $FeCl_2$-catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) HDH of trifluoromethylpyridines

2.3 General catalytic procedure for the [Ni(COD)$_2$]-catalyzed C(sp^3)-F hydrodefluorination (HDF) of perfluoromethylcyclohexane.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (87.4 mg, 2.800 mmol), KO*t*Bu (2.8 mL of a 1.0 M solution in THF, 2.800 mmol), perfluoromethylcyclohexane (40 µL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (5.5 mg, 0.020 mmol). The tube was sealed and stirred at rt for 24 h. After that, the reaction was exposed to air and 1,4 difluorobenzene (10 µL, 0.098 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F and ^{1}H NMR spectroscopy without additional purification.

2.4 General catalytic procedure for HDH of C(sp^2)-X (X = F, Cl, Br) pyridines using [Ni(COD)$_2$] as the catalyst.



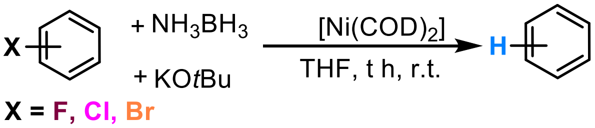
In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3, KO*t*Bu (1.0 M solution in THF), halogenated pyridine (0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.65 mg, 0.006 mmol). The amounts of

NH_3BH_3 and KO*t*Bu used were substrate dependent and are listed in Table S3. The tube was sealed and stirred at rt for the times mentioned in table S3. After that, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification.

Entry	Substrate	t (h)	Amount of NH_3BH_3	Amount of KO*t*Bu
1	2-Fluoropyridine (**20**)	1	18.5 mg (0.600 mmol)	0.4 mL (0.400 mmol)
2	3-Fluoropyridine (**21**)	4	18.5 mg (0.600 mmol)	0.4 mL (0.400 mmol)
3	2-Chloropyridine (**22**)	1	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
4	2-Bromopyridine (**23**)	1	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
5	2,4-Difluoropyridine (**24**)	1	18.5 mg (0.600 mmol)	0.4 mL (0.400 mmol)
6	3,5-Difluoropyridine (**25**)	1	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
7	2,5-Difluoropyridine (**26**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
8	5-Bromo-2-fluoropyridine (**27**)	24	18.5 mg (0.600 mmol)	0.4 mL (0.400 mmol)

Table S3: Reaction conditions for [$Ni(COD)_2$] catalyzed HDH of C(sp^2)-X (X = F, Cl, Br) pyridines

2.5 General catalytic procedure for [$Ni(COD)_2$]-catalyzed HDH of C(sp^2)-X (X = F, Cl, Br) arenes.

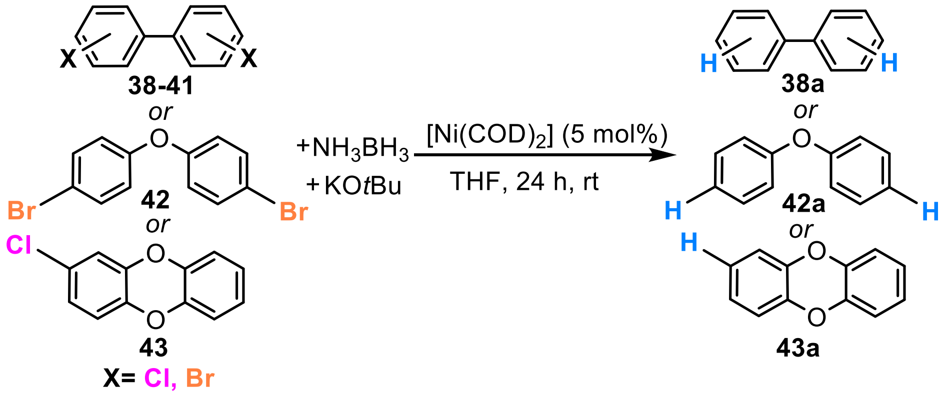


In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3, KO*t*Bu (1.0 M solution in THF), halogenated arene (0.200 mmol) and a THF solution (0.5 mL) of the [$Ni(COD)_2$] catalyst (2.75 mg, 0.010 mmol). The amounts of NH_3BH_3 and KO*t*Bu used were substrate dependent and are listed in Table S4. The tube was sealed and stirred at rt for the times mentioned in table S4. After that, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification.

Entry	Substrate	t (h)	Amount of NH_3BH_3	Amount of KO*t*Bu
1	Fluorobenzene (**28**)	24	12.3 mg (0.400 mmol)	0.4 mL (0.400 mmol)
2	Chlorobenzene (**29**)	24	12.3 mg (0.400 mmol)	0.4 mL (0.400 mmol)
3	Bromobenzene (**30**)	24	12.3 mg (0.400 mmol)	0.4 mL (0.400 mmol)
4	4-Iodotoluene (**31**)	24	12.3 mg (0.400 mmol)	0.4 mL (0.400 mmol)
5	1,2-Difluorobenzene (**32**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
6	1,4-Difluorobenzene (**33**)	48	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
7	1-Chloro-3-fluorobenzene (**34**)	48	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
8	1,2,3-Trifluorobenzene (**35**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
9	1,2,4,5-Tetrafluorobenzene (**36**)	48	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)
10	1,2,4,5-Tetrafluoroanisole (**37**)	48	37.0 mg (1.200 mmol)	1.2 mL (1.200 mmol)

Table S4: Reaction conditions for the [Ni(COD)$_2$]-catalyzed HDH of C(sp^2)-X (X = F, Cl, Br) arenes

2.6. General catalytic procedure for [Ni(COD)$_2$]-catalyzed C(sp^2)-X (X = Cl, Br) HDH of polyhalogenated biphenyls, diphenyl ethers and dibenzo-dioxins.



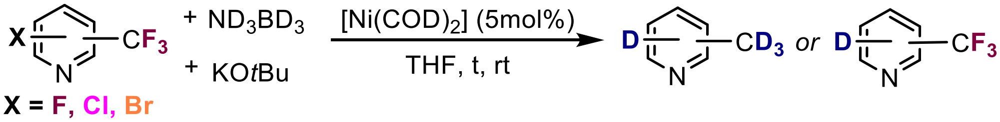
In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 ,KO*t*Bu (1.0 M solution in THF), polyhalogenated arene (0.100 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.4 mg, 0.010 mmol). The amounts of NH_3BH_3 and KO*t*Bu employed were substrate dependent and are listed in Table S5. The tube was sealed and stirred at rt for 24 h. After that, the reaction was exposed to air and mesitylene

(10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification.

Entry	Polyhalogenated arene	Product	Amount of NH_3BH_3	Amount of KO*t*Bu
1	2-Bromobiphenyl (**38**)	Biphenyl (**38a**)	9.3 mg (0.600 mmol)	0.3 mL (0.300 mmol)
2	3-Bromobiphenyl (**39**)	Biphenyl (**38a**)	9.3 mg (0.600 mmol)	0.3 mL (0.300 mmol)
3	2,4’,5-Trichlorobiphenyl (**40**)	Biphenyl (**38a**)	18.5 mg (1.200 mmol)	0.6 mL (1.200 mmol)
4	3,3’,4,4’-Tetrachlorobiphenyl (**41**)	Biphenyl (**38a**)	18.5 mg (1.200 mmol)	0.6 mL (1.200 mmol)
5	Bis(4-bromophenyl) ether (**42**)	Diphenyl ether (**42a**)	9.3 mg (0.600 mmol)	0.3 mL (0.300 mmol)
6	2-Chlorodibenzo-1,4-dioxin (**43**)	Dibenzo-1,4-dioxin (**43a**)	9.3 mg (0.600 mmol)	0.3 mL (0.300 mmol)

Table S5: Reaction conditions for [Ni(COD)$_2$]-catalyzed HDH of polyhalogenated biphenyls, diphenyl ethers and dibenzo-dioxins

3. General catalytic procedure for [Ni(COD)$_2$]-catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) deuterodehalogenation (DDH) of trifluoromethylpyridines.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: ND_3BD_3, KO*t*Bu (1.0 M solution in THF), trifluoromethylpyridine (0.100 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.4 mg, 0.005 mmol). The amounts of all the reagents are mentioned in table S6. The tube was sealed and stirred at rt for the times mentioned in table S13. After that, the sealed flask was moved to the glove box and mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F, ^{1}H and ^{2}H NMR spectroscopy without additional purification.

Entry	Trifluoromethyl-pyridine	Product	t (h)	Amount of ND_3BD_3	Amount of KO*t*Bu
1	2-Trifluoromethyl pyridine (**1**)	2-(Methyl-d_3)pyridine (**1a-d_4**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
2	3-Trifluoromethyl pyridine(**2**)	3-(Methyl-d_3)pyridine-2,5,6-d_3 (**2a-d_6**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
3	4-Trifluoromethyl pyridine(**3**)	4-(Methyl-d_3)pyridine (**3a-d_4**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
4	4,4’-Bis(trifluoromethyl)-2,2'-bipyridine (**4**)	4,4'-(Dimethyl-d_6)-2,2'-bipyridyl (**4a-d_6**)	24	22.0 mg (0.600 mmol)	0.6 mL (0.600 mmol)
5	2-Methoxy-6-(trifluoromethyl)pyridine (**5**)	2-Methoxy-(6-methyl-d_3)pyridine-3,4,5-d_3 (**5a-d_6**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
6	5-Methoxy-2-(trifluoromethyl)pyridine (**6**)	5-Methoxy-(2-methyl-d_3)pyridine-4,6-d_2 (**6a-d_5**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
7	4-Methoxy-2-(trifluoromethyl)pyridine (**7**)	4-Methoxy-(2-methyl-d_3)pyridine-3-*d* (**7a-d_4**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
8*	2-Methoxy-5-(trifluoromethyl)pyridine (**8**)	2-Methoxy-(5-methyl-d_3)pyridine (**8a-d_3**)	24	22.0 mg (0.300 mmol)	0.6 mL (0.300 mmol)
9	2-Amino-6-(trifluoromethyl)pyridine (**9**)	2-Amino-(6-methyl-d_3)pyridine (**9a-d_3**)	24	18.5 mg (0.600 mmol)	0.6 mL (0.600 mmol)
10	2,6-Bis(trifluoromethyl)pyridine (**10**)	2,6-(Dimethyl-d_6)pyridine-3,4,5-d_3 (**10a-d_9**)	24	22.0 mg (0.600 mmol)	0.6 mL (0.600 mmol)
11	2,6-Bis(trifluoromethyl)pyridine (**10**)	2-Trifluoromethyl-6-(methyl-d_3)pyridine-3,4,5-d_3 (**10a’-d_6**)	24	11.0 mg (0.300 mmol)	0.3 mL (0.300 mmol)
12	2-Chloro-6-(trifluoromethyl)pyridine (**12**)	2-Trifluoromethylpyridine-6-*d* (**1-*d***)	1	3.6 mg (0.100 mmol)	0.1 mL (0.100 mmol)
13	2-Chloro-6-(trifluoromethyl)pyridine (**12**)	2-(Methyl-d_3)pyridine-4,5,6-d_3 (**1a-d_6**)	24	14.6 mg (0.400 mmol)	0.4 mL (0.400 mmol)
14	2-Bromo-6-(trifluoromethyl)pyridine (**11**)	2-(Methyl-d_3)pyridine-4,5,6-d_3 (**1a-d_6**)	24	14.6 mg (0.400 mmol)	0.4 mL (0.400 mmol)
15	2-Bromo-6-(trifluoromethyl)pyridine (**11**)	2-Trifluoromethyl-pyridine-6-*d* (**1-*d***)	1	3.6 mg (0.100 mmol)	0.1 mL (0.100 mmol)
16	5-Bromo-2-(trifluoromethyl)pyridine (**14**)	2-Trifluoromethyl pyridine-3,4,5-d_3 (**1-d_3**)	1	3.6 mg (0.100 mmol)	0.1 mL (0.100 mmol)

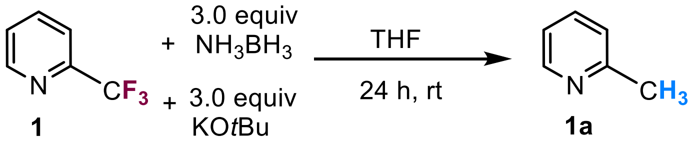
17	4-Bromo-2-(trifluoromethyl)pyridine (**13**)	2-(Methyl-*d*$_3$)pyridine-*3,4,5-d*$_3$ (**1a-*d*$_6$**)	24	14.6 mg (0.400 mmol)	0.4 mL (0.400 mmol)
18	4-Bromo-2-(trifluoromethyl)pyridine (**13**)	2-Trifluoromethyl pyridine-*3,4,5-d*$_3$ (**1-*d*$_3$**)	1	3.6 mg (0.100 mmol)	0.1 mL (0.100 mmol)

*0.010 mmol (2.8 mg) of [Ni(COD)$_2$] employed

Table S6: Reaction conditions for [Ni(COD)$_2$] catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) DDH of trifluoromethylpyridines

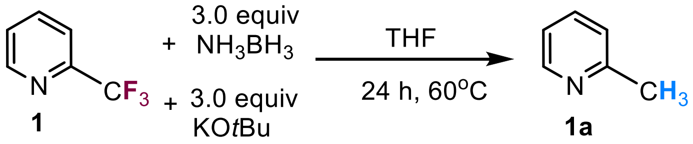
4. Control experiments

4.1 Reaction of 2-trifluoromethylpyridine (1) with NH$_3$BH$_3$ and KO*t*Bu in the absence of [Ni(COD)$_2$] at rt.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH$_3$BH$_3$ (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 μL, 0.200 mmol) and THF (0.5 mL). The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: <5%; Yield **1a**: N.D.

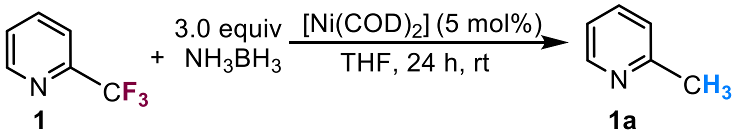
4.2 Reaction of 2-trifluoromethylpyridine (1) with NH$_3$BH$_3$ and KO*t*Bu in the absence of [Ni(COD)$_2$] at 60°C.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH$_3$BH$_3$ (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 μL, 0.200 mmol) and THF (0.5 mL). The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene

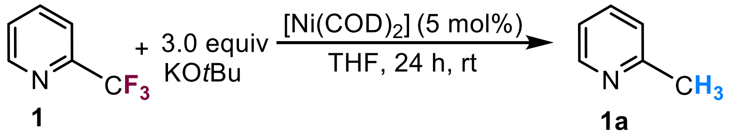
(10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: <5%; Yield **1a**: N.D.

4.3 Reaction of 2-trifluoromethylpyridine (1) with NH_3BH_3 in the absence of KO*t*Bu.



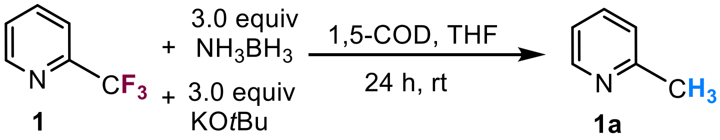
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.5 mg, 0.600 mmol), 2-trifluoromethylpyridine (23 μL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] (2.8 mg, 0.010 mmol). The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: <5%; Yield **1a**: N.D.

4.4 Reaction of 2-trifluoromethylpyridine (1) with KO*t*Bu in the absence of NH_3BH_3.



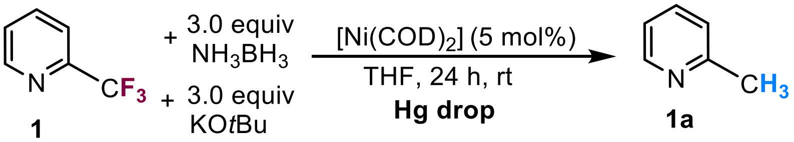
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: THF solution (0.5 mL) of [Ni(COD)$_2$] (2.8 mg, 0.010 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 μL, 0.200 mmol). The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: <5%; Yield **1a**: N.D.

4.5 Reaction of 2-trifluoromethylpyridine (1) with NH_3BH_3 and KO*t*Bu in the presence of 1,5-cyclooctadiene (1,5-COD) as the catalyst.



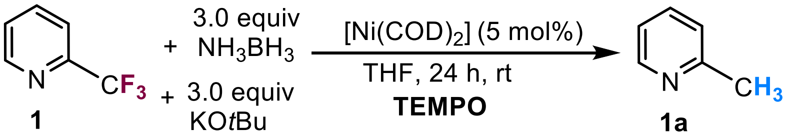
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 1,5-COD (2 µL, 0.010 mmol), 2-trifluoromethylpyridine (23 µL, 0.200 mmol) and THF (0.5 mL). The tube was sealed and stirred at rt for 24 h. After 24 h, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^1H NMR spectroscopy without additional purification. Conversion **1**: <5%; Yield **1a**: <5%.

4.6 Catalytic reaction of 2-trifluoromethylpyridine in the presence of a Hg drop.



In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 µL, 0.200 mmol), a THF solution (0.5 mL) of the [Ni(COD)$_2$] (2.75 mg, 0.010 mmol) and a drop of Hg. The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^1H NMR spectroscopy without additional purification. Conversion **1**: 91%; Yield **1a**: 77%.

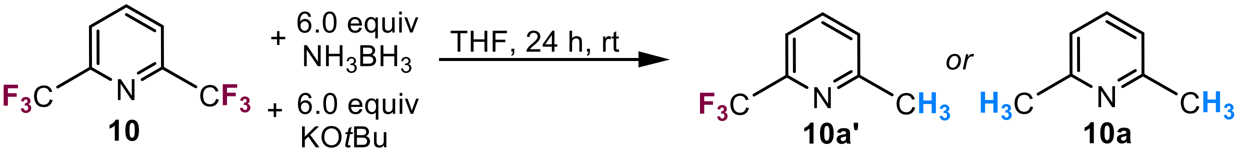
4.7 Catalytic reaction of 2-trifluoromethylpyridine in the presence of TEMPO.



In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 µL, 0.200 mmol), a THF solution (0.5 mL) of the

[Ni(COD)$_2$] (2.75 mg, 0.010 mmol) and TEMPO (31.3 mg, 0.200 mmol). The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: >99%; Yield **1a**: 90%.

4.8 Reaction of 2,6-bis(trifluoromethyl)pyridine (10) with NH$_3$BH$_3$ and KO*t*Bu in the absence of [Ni(COD)$_2$] at rt.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH$_3$BH$_3$ (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2,6-bis(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) and THF (0.5 mL). The tube was sealed and stirred at rt for 24 hours. After 24 h, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Yield **10a**: N.D.; **10a'**: N.D.

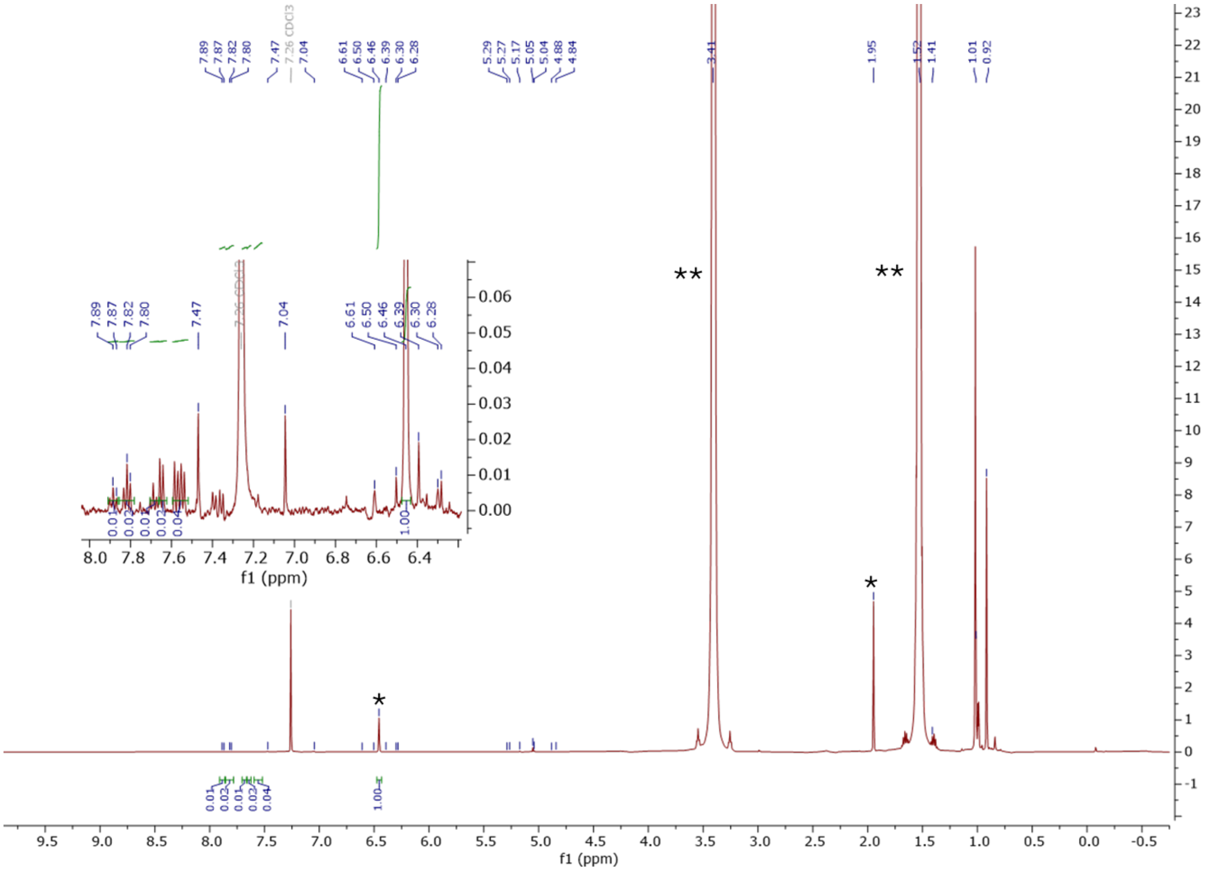


Figure S1: ^{1}H NMR spectrum for the control reaction of **10**.

*= Mesitylene

**= THF

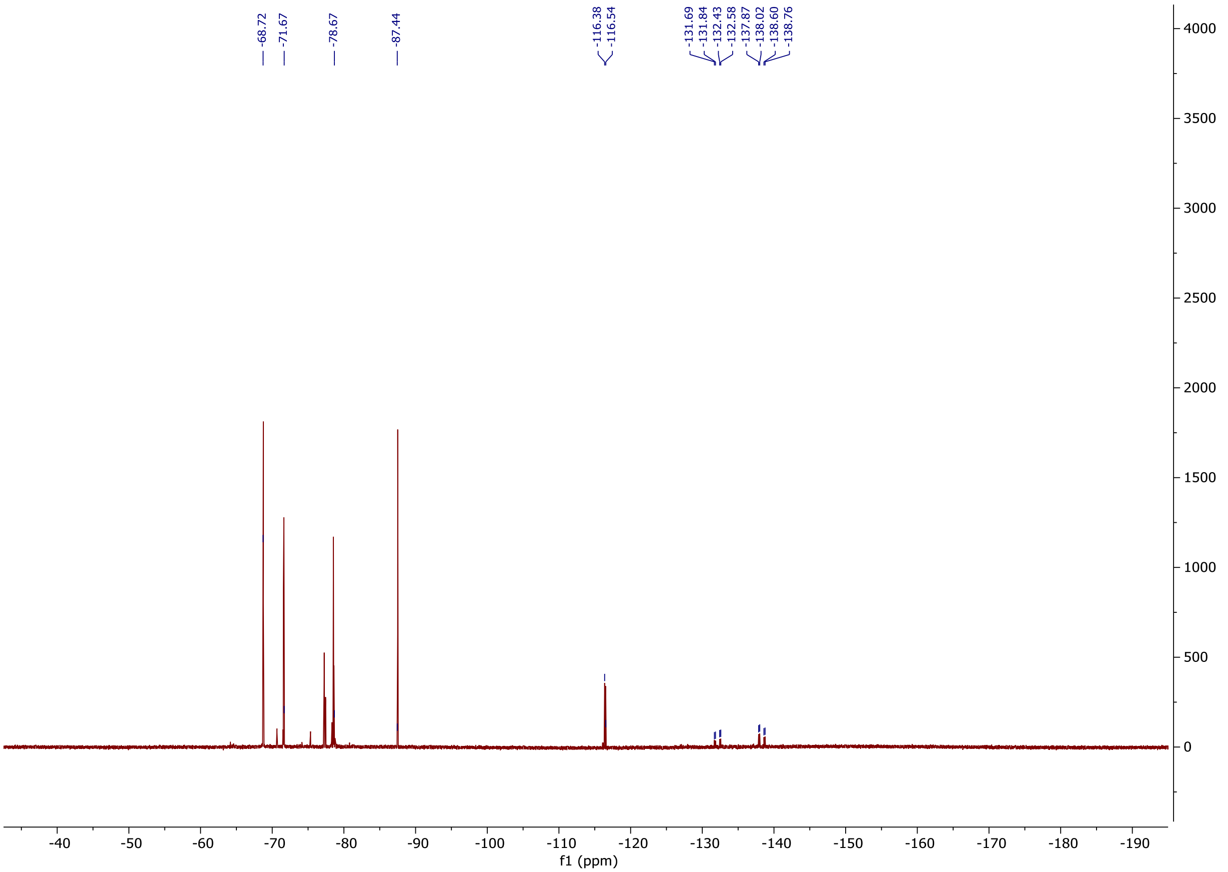
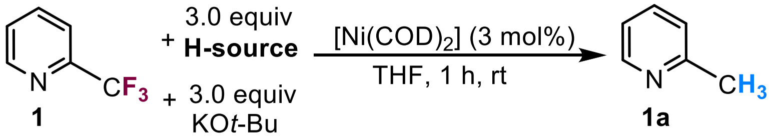


Figure S2: ^{19}F NMR spectrum for the control reaction of **10**.

5. Optimization of the reaction components for the HDH of 2-trifluoromethylpyridine (1).

5.1 Screening of H sources



5.1.1 Procedure for entries 1-15 in Table S5. In an argon-filled glovebox, a J. Young flask was charged with a stir bar and the reagents in the following order: H source, (KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethyl pyridine (23 µL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.65 mg, 0.006 mmol). The amount and identity of the H-source used are mentioned in Table S5. The tube was sealed and stirred at rt for 1 hour. After that, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F and ^{1}H NMR spectroscopy without additional purification. The screening of the H source afforded the % conversion and % yield reported in Table S7.

5.1.2 Procedure for entries 16-20 in Table S5. In an argon-filled glovebox, a J. Young flask was charged with a stir bar and the reagents in the following order: H-source, 2-trifluoromethyl pyridine (23 μL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.65 mg, 0.006 mmol). The amount and identity of the H-source used are mentioned in Table 5. The tube was sealed and stirred at rt for 1 hour. After that, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. The screening of the H source afforded the % conversion and % yield reported in Table S7.

5.1.3 Procedure for entries 21-22 in Table S5. In an argon-filled glovebox a J. Young flask was charged with a stir bar and the reagents in the following order: entry 21, KO*t*Bu (0.6 mL of 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethyl pyridine (23 μL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.65 mg, 0.006 mmol); entry 22, 2-trifluoromethyl pyridine (23 μL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.65 mg, 0.006 mmol). The tube was sealed and brought out of glovebox. The contents of the J. Young flask were frozen and H_2 was passed through the flask. The flask was sealed, thawed and then stirred at rt for 1 hour. After that, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. The screening of the H source afforded the % conversion and % yield reported in Table S7.

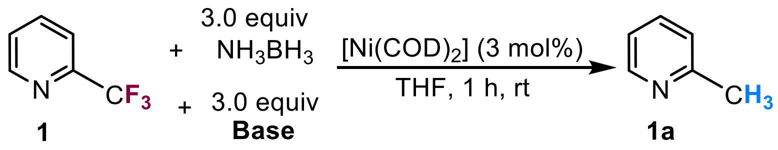
Entry	H source	Amount of H-source	Conv 1 (%)	Yield 1a (%)
1	HBPin	87 µL (0.600 mmol)	68	11
2	HBCat	63 µL (0.600 mmol)	8	N.D.
3	**NH_3BH_3**	18.6 mg (0.600 mmol)	**79**	**63**
4	NMe_2HBH_3	35.4 mg (0.600 mmol)	>99	55
5	NEt_3BH_3	89 µL (0.600 mmol)	<5	N.D.
6	BH_3.THF	0.6 mL of a 1.0 M solution in THF (0.600 mmol)	36	N.D.
7	*t*-$BuNH_2$	63 µL (0.600 mmol)	17	N.D.
8	*t*-$BuNH_2$/ BH_3.THF	63 µL, (0.600 mmol)/ 0.6 mL of a 1.0 M solution in THF (0.600 mmol)	14	13
9*	*t*-$BuNH_2$/ BH_3.THF (stirred before reaction)	63 µL (0.6 mmol)/ 0.6 mL of a 1.0 M solution in THF (0.600 mmol)	41	32
10	H_2SiEt_2	78 µL (0.600 mmol)	80	N.D.
11	$HSiEt_3$	96 µL (0.600 mmol)	3	N.D.
12	$HSiOEt_3$	111 µL (0.600 mmol)	34	N.D.
13	*i*PrOH	46 µL (0.600 mmol)	13	N.D.
14	H_2O	11 µL (0.600 mmol)	8	N.D.
15	$NaBH_4$	22.7 mg (0.600 mmol)	7	N.D.
16	$NaBH_4$ (No KO*t*Bu)	22.7 mg (0.600 mmol)	5	N.D.
17	$NaHBEt_3$ (No KO*t*Bu)	0.6 mL of a 1.0 M solution in THF (0.600 mmol)	46	18

18	$KHBEt_3$ (No KO*t*Bu)	0.6 mL of a 1.0 M solution in THF (0.600 mmol)	52	16
19	$LiHBEt_3$ (No KO*t*Bu)	0.6 mL of a 1.0 M solution in THF (0.600 mmol)	57	8
20	*i*PrOH (No KO*t*Bu)	46 μL (0.600 mmol)	10	N.D.
21	H_2	---	<5	N.D.
22	H_2 (No KO*t*Bu)	---	<5	N.D.

*$(CH_3)_3NH_2$ and BH_3.THF stirred for 5 h before setting up the reaction

Table S7: Screening of H sources

5.2 Screening of bases.



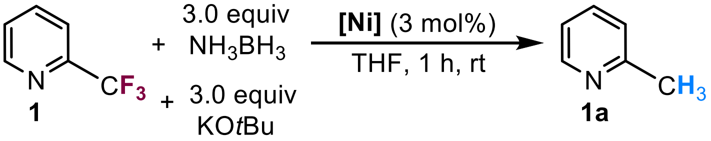
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.6 mg, 0.600 mmol), base, (2-trifluoromethyl pyridine (23 μL, 0.200 mmol) and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.65 mg, 0.006 mmol). The amount and identity of the base used are mentioned in Table 8. The flask was sealed and stirred at rt for 1 hour. After that, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. The screening of the bases afforded the % conversion and % yield reported in table S8.

Entry	Base	Amount of the base	Conv 1 (%)	Yield 1a (%)
1	NaO*t*Bu	0.3 mL of a 2.0 M solution in THF (0.600 mmol)	83	63
2	**KO*t*Bu**	0.6 mL of a 1.0 M solution in THF (0.600 mmol)	**79**	**63**
3	LiO*t*Bu	0.66 mL of a 0.9 M solution in 2 Me-THF (0.600 mmol)	48	27
4	KOPh	79.3 mg (0.600 mmol)	30	10
5	NaOPh	69.6 mg (0.600 mmol)	30	3
6	KOMe	6.0 mL of a 0.1N solution in methanol/toluene (0.600 mmol)	<1	N.D.
7	LiOMe	22.8 mg (0.600 mmol)	4	N.D.
8	NEt_3	84 μL (0.600 mmol)	7	N.D.
9	K_2CO_3	89.2 mg (0.600 mmol)	4	N.D.

10	$KN(SiMe_3)_2$	1.2 mL of a 0.5 M solution in toluene (0.600 mmol)	17	N.D.
11	CsF	91.1 mg (0.600 mmol)	10	N.D.

Table S8: Screening of bases

5.3 Screening of Ni complexes.



1 **1a**

In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.6 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution of THF, 0.600 mmol), 2-trifluoromethylpyridine (23 µL, 0.200 mmol) and a THF solution (0.5 mL) of the Ni complex. For entry 9 and 10, HBPin (87 µL, 0.6 mmol) was employed instead of NH_3BH_3. For entry 10, KO*t*Bu was not added. The amount and identity of the Ni complexes used are mentioned in Table 9. The tube was sealed and stirred at rt for 1 hour. After that, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard**.** The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. The screening of the Ni catalytic system afforded the % conversion and % yield reported in table S9.

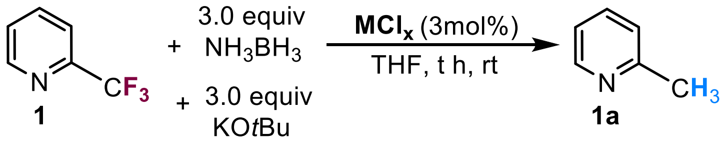
Entry	[Ni]	Amount of [Ni]	Conv 1 (%)	Yield 1a (%)
1	[Ni(COD)(DQ)]	2.0 mg (0.006 mmol)	69	41
2	[$NiCl_2$(DME)]	1.3 mg (0.006 mmol)	57	37
3	**[$Ni(COD)_2$]**	1.65 mg (0.006 mmol)	**79**	**63**
4	[$Ni(COD)_2$] + ^{tBu}bipy	1.65 mg (0.006 mmol) + 1.7 mg (0.006 mmol)	81	62
5	[$Ni(COD)_2$] + ^{iPr}PN	1.65 mg (0.006 mmol) + 1.4 mg (0.006 mmol)	67	59
6	[$Ni(COD)_2$] + PEt_3	1.65 mg (0.006 mmol) + 4 µL (0.024 mmol)	30	3
7	[$Ni(COD)_2$] + dmpe	1.65 mg (0.006 mmol) + 2.0 µL (0.006 mmol)	8	N.D.
8	[Ni(^{iPr}PN)(COD)]	2.3 mg	67	59
9*	[Ni(^{iPr}PN)(COD)]	2.3 mg	68	15
10$^{\#}$	[Ni(^{iPr}PN)(COD)]	2.3 mg	5	N.D.

*HBPin employed instead of NH_3BH_3

$^{\#}$ HBPin employed instead of NH_3BH_3 and KO*t*Bu

Table S9: Screening of Ni complexes

5.4 Screening of transition metal salts as catalysts.



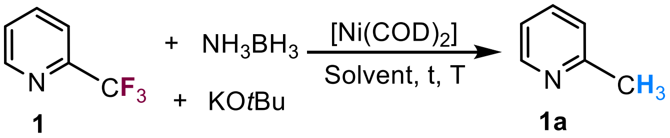
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.6 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 µL, 0.200 mmol) and a THF solution (0.5 mL) of the transition metal salt. The amount and identity of the transition metal salt used are mentioned in Table 6. The tube was sealed and stirred for the times mentioned in table S10. After that, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. The screening of all the catalytic systems afforded the % conversion and % yield reported in table S10.

Entry	MCl_x	Amount of MCl_x	t (h)	Conv 1 (%)	Yield 1a (%)
1	$FeCl_2$	0.8 mg (0.006) mmol)	1	3	N.D.
2	$FeCl_2$	0.8 mg (0.006 mmol)	24	>99	91
3	$FeBr_2$	1.3 mg (0.006 mmol)	24	>99	91
4	$FeCl_3$	1.0 mg (0.006 mmol)	24	>99	90
5	$MnCl_2$	0.8 mg (0.006 mmol)	1	24	N.D.
6	$CoCl_2$	0.8 mg (0.006 mmol)	1	89	80

Table S10: Screening of transition metal catalysts

6. Optimization of reaction conditions for the [Ni(COD)$_2$]-catalyzed HDH

6.1 Optimization of reaction conditions for C(sp^3)-F HDH of 2-trifluoromethylpyridine.



All the catalytic reactions were conducted following the general procedure mentioned in section 2.1 employing 2-trifluoromethylpyridine (23 µL, 0.200 mmol) as the model substrate. The optimization of the reaction conditions afforded the % conversion and % yield reported in table S11.

Entry	[Ni(COD)$_2$] (mol%)	T (h)	T (°C)	Solvent	NH_3BH_3 Equiv	KO*t*Bu Equiv	Conv 1 (%)	Yield 1a (%)
1	5	24	rt	THF	3	3	>99	85
2	5	24	rt	THF	2	2	84	67
3	5	24	rt	THF	1	1	56	40
4	5	24	rt	Neat	3	3	82	54

5	5	24	rt	1,4-Dioxane	3	3	80	75
6	5	24	rt	Benzene	3	3	85	76
7	5	24	rt	Hexane	3	3	46	22
8	5	24	rt	2 Me-THF	3	3	73	47
9	5	24	rt	*i*-PrOH	3	3	39	28
10	5	7	rt	THF	3	3	98	91
11	5	3.5	rt	THF	3	3	81	75
12	5	1	rt	THF	3	3	95	85
13	5	1	60	THF	3	3	>99	84
14	3	1	rt	THF	3	3	79	63
15*	3	1	rt	THF	3	3	63	38
16**	3	1	rt	THF	3	3	65	37
17	3	4	rt	THF	3	3	90	74
18	3	7	rt	THF	3	3	83	74
19	3	16	rt	THF	3	3	>99	91
20	3	24	rt	THF	3	3	>99	86
21	**2**	**24**	**rt**	**THF**	**3**	**3**	**>99**	**93**
22	1	24	rt	THF	3	3	94	83
23	0.5	24	rt	THF	3	3	97	85
24	2	24	rt	THF	3	2	72	48
25	2	24	rt	THF	3	1	45	24
26	2	24	rt	THF	2	3	70	58
27	2	24	rt	THF	1	3	58	15
28***	2	24	rt	THF	3	3	72	26

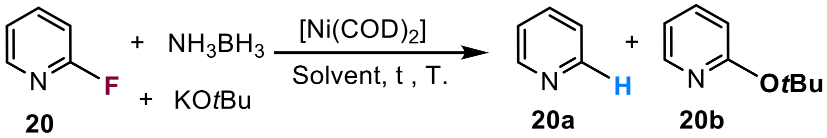
*Reaction conducted under air

**Reaction conducted employing THF as received from commercial source and under air

***Reaction was not stirred

Table S11: Optimization of reaction conditions for the C(sp^3)-F HDH of 2-trifluoromethylpyridine

6.2 Optimization of reaction conditions for C(sp^2)-X (X = F, Cl, Br) HDH of pyridines.

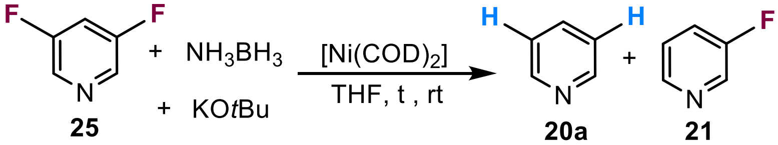


All the catalytic reactions were conducted following the general procedure mentioned in section 2.4 employing 2-fluoropyridine (17 µL, 0.200 mmol). The optimization of the reaction conditions afforded the % conversion and % yield reported in table S12.

Entry	[Ni(COD)$_2$] (mol%)	t (h)	T (°C)	Solvent	NH$_3$BH$_3$ Equiv	KO*t*Bu Equiv	Conv 19 (%)	Yield 19a (%)	Yield 19b (%)
1	5	24	rt	THF	3	3	>99	89	<5
2	3	24	rt	THF	3	3	>99	85	<5
3	2	24	rt	THF	3	3	>99	84	<5
4	1	24	rt	THF	3	3	>99	71	9
5	5	1	rt	THF	3	3	>99	91	9
6	5	30 Min	rt	THF	3	3	>99	90	12
7	5	1	rt	THF	2	2	>99	73	10
8	5	1	rt	THF	3	3	>99	85	6
9	5	1	60	THF	3	3	>99	75	8
10	3	1	rt	THF	3	3	>99	88	11
11	3	30 min	rt	THF	3	3	>99	81	6
12	3	15min	rt	THF	3	3	>99	77	7
13	**3**	**1**	**rt**	**THF**	**3**	**2**	**>99**	**>99**	**<1**
14	2	1	rt	THF	3	2	84	82	--
15	1	1	rt	THF	3	2	86	58	--
16	3	1	rt	THF	2	1	70	46	--
17	3	1	rt	THF	1	0.5	50	38	--

Table S12: Optimization of reaction conditions for the C(sp^2)-F HDF of 2-fluoropyridine

6.3 Optimization of reaction conditions for C(sp^2)-F HDF of 3,5-difluoropyridine.

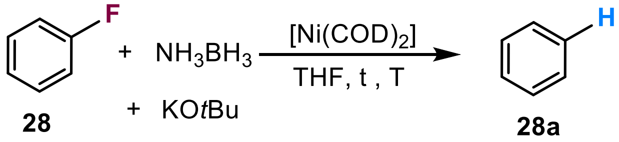


All the catalytic reactions were conducted following the general procedure mentioned in section 2.4 employing 3,5-difluoropyridine (18 µL, 0.200 mmol). The optimization of the reaction conditions afforded the % conversion and % yield reported in table S13.

Entry	[Ni(COD)$_2$] (mol%)	t (h)	Equiv NH_3BH_3	Equiv KOtBu	Conv 24 (%)	Yield 19a (%)	Yield 20 (%)
1	3	1	3	2	>99	43	56
2	5	1	3	2	>99	33	51
3	3	4	3	2	>99	42	38
4	3	1	1	1	51	8	13
5	3	4	3	3	>99	78	--
6	**3**	**1**	**3**	**3**	**>99**	**80**	**--**
7	3	8	3	3	>99	69	--
8	3	16	3	3	>99	78	--
9	3	24	3	3	>99	76	--
10	4	4	3	3	>99	70	--

Table S13: Optimization of reaction conditions for the HDF of 3,5-difluoropyridine

6.4 Optimization of reaction conditions for C(sp^2)-X (X = F, Cl, Br, I) HDH of arenes.

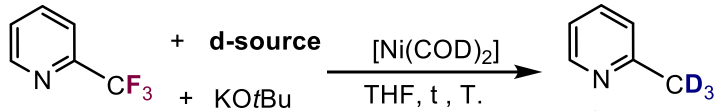


All the catalytic reactions were conducted following the general procedure mentioned in section 2.6 employing fluorobenzene (19 µL, 0.200 mmol). The optimization of the reaction conditions afforded the % conversion and % yield reported in table S14.

Entry	$[Ni(COD)_2]$ (mol%)	t (h)	T (°C)	Solvent	NH_3BH_3 Equiv	KO*t*Bu Equiv	Conv 27 (%)	Yield 27a (%)
1	5	24	rt	THF	3	3	92	82
2	**5**	**24**	**rt**	**THF**	**2**	**2**	**>99**	**98**
3	5	16	rt	THF	2	2	>99	72
4	3	24	rt	THF	2	2	>99	85
5	3	7	rt	THF	3	3	85	80
6	2	24	rt	THF	2	2	85	76
8	1	24	rt	THF	2	2	76	71
9	5	1	rt	THF	3	3	30	30
10	5	1	60	THF	3	3	>99	84

Table S14: Optimization of reaction conditions for the C(sp^2)-F HDF of fluorobenzene

7. Optimization of the reaction conditions for DDH of trifluoromethylpyridines.



1a-*d*$_3$

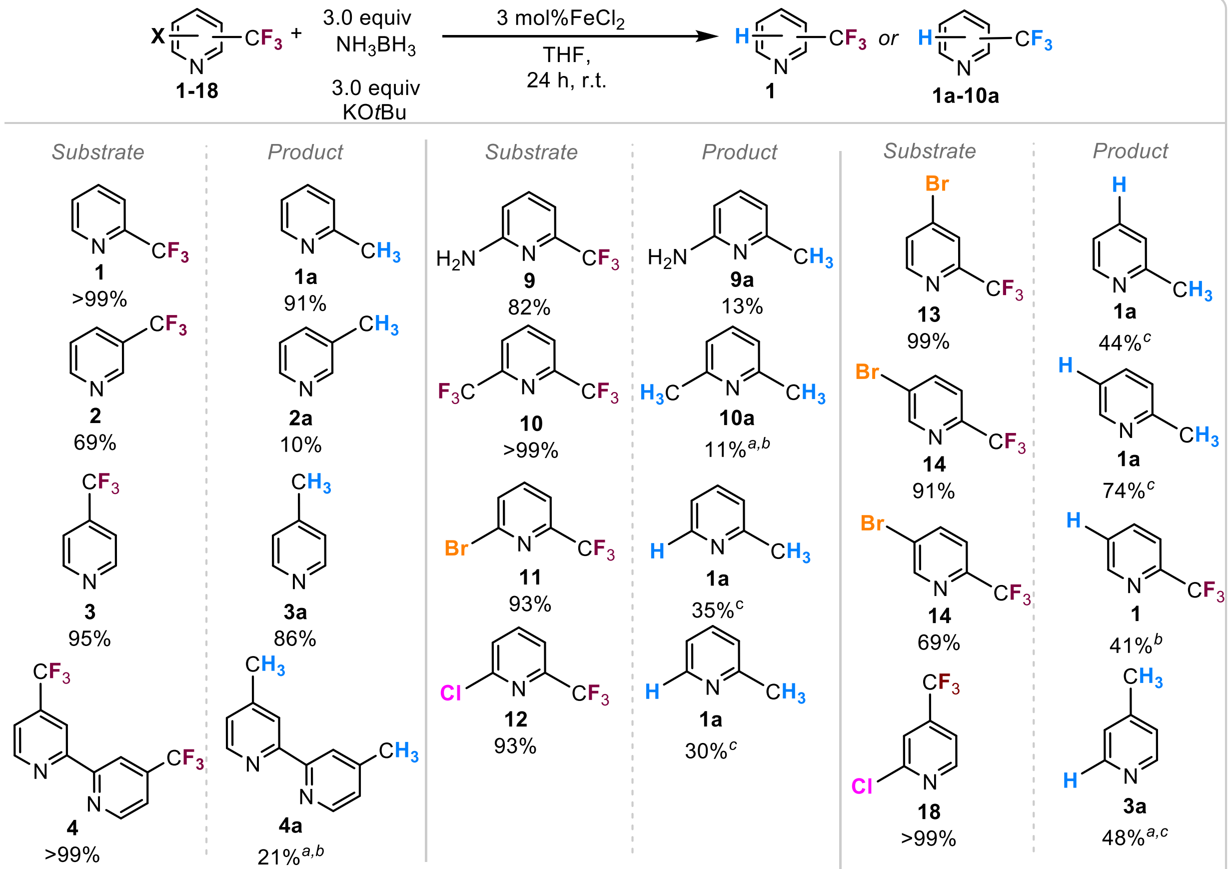
All the catalytic reactions were conducted following the general procedure mentioned in section 3.1 employing 2-trifluoromethylpyridine (12 µL, 0.100 mmol) as the model substrate. The optimization of the reaction conditions afforded the % conversion and % yield reported in table S15.

Entry	$[Ni(COD)_2]$ (mol%)	t (h)	d-source*	d-source Equiv	KO*t*Bu Equiv	Conv 1 (%)	Yield 1a-*d*$_3$ (%)	% d-incorporation in 1a-*d*$_3$
1	2	24	ND_3BH_3	3	3	91	51	98
2	2	24	NH_3BD_3	3	3	43	38	46
3	2	24	ND_3BD_3	3	3	>99	62	>99
4	5	24	ND_3BH_3	3	3	>99	73	84
5	5	48	ND_3BH_3	3	3	>99	73	85
6	5	16	ND_3BH_3	3	3	97	81	88
7	**5**	**24**	**ND_3BD_3**	**3**	**3**	**>99**	**71**	**>99**

*ND_3BH_3, NH_3BD_3 and ND_3BD_3 were obtained with >99%, 90%, and >99% deuterium incorporations respectively.

Table S15: Optimization of reaction conditions for DDH of 2-trifluoromethylpyridine

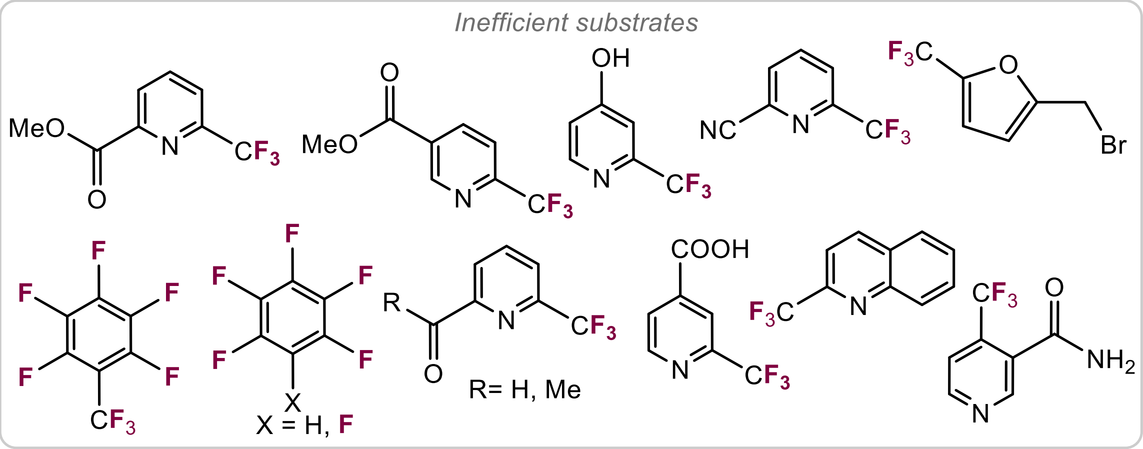
8. Substrate scope for the $FeCl_2$-catalyzed C(sp^3)-F and C(sp^2)-X (X = F, Cl, Br) HDH of trifluoromethylpyridines. The substrate scope (Scheme 1) for the $FeCl_2$-catalyzed HDH was conducted using the general procedure mentioned in section 2.2 affording the conversions and yields reported in Scheme 1.



[a]$FeCl_2$ = 5mol%, [b]6 equivalents of NH_3BH_3 and of KO*t*Bu, [c]4 equivalents of NH_3BH_3 and of KO*t*Bu, [d]1 equivalent of NH_3BH_3 and of KO*t*Bu, Substrate conversion and product yield (given below each structure) are determined by ^{1}H NMR using mesitylene as an internal standard.

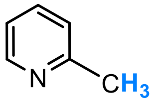
Scheme S1. Substrate scope for the $FeCl_2$-catalyzed HDH of trifluoromethylpyridines

9. Inefficient substrates for the [Ni(COD)$_2$]-catalyzed HDH. All the substrates inefficient for [Ni(COD)$_2$] catalyzed HDH process are shown in Scheme 2. Each reaction was conducted according to the general procedure described in Section 2.1, using the respective substrates listed in Scheme 2.



Scheme S2: Inefficient substrates for the [Ni(COD)$_2$]-catalyzed HDH.

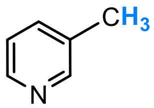
10. Characterization of hydrodehalogenated (HDH) Products



2-Methyl pyridine (1a): Product **1a** was obtained according to the general procedure described in Section 2.1 or 2.2 using 2-trifluoromethylpyridine (23 μL, 0.200 mmol), 2-chloro-6-(trifluoromethyl)pyridine (36.3 mg, 0.200 mmol), 2-bromo-6-(trifluoromethyl)pyridine (45.2 mg, 0.200 mmol), 6-fluoro-2-(trifluoromethyl)pyridine (24 μL, 0.200 mmol), 5-fluoro-2-(trifluoromethyl)pyridine (24 μL, 0.200 mmol), 5-bromo-2-(trifluoromethyl)pyridine (45.2 mg, 0.200 mmol), 4-bromo-2-(trifluoromethyl)pyridine (23 μL, 0.200 mmol) or 3-fluoro-2-(trifluoromethyl)pyridine (24 μL, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.32 (d, 1H), 7.28 (td, 1H), 6.88 (d, 1H), 6.81 (dd, 1H), 2.35 (s, 3H).

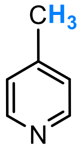
The spectroscopic data matched that previously reported.[3]



3-Methyl pyridine (2a): Product **2a** was obtained according to the general procedure described in Section 2.1 using 3-trifluoromethylpyridine (23 μL, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.36 (d, 1H), 8.32 (d, 1H), 7.09 (d, 1H), 6.83 (dd, 1H), 1.97 (s, 3H).

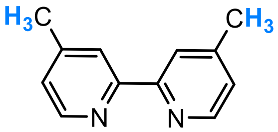
The spectroscopic data matched that previously reported.[3]



4-Methyl pyridine (3a): Product **3a** was obtained according to the general procedure described in Section 2.1 or 2.2 using 4-trifluoromethyl pyridine (23 μL, 0.200 mmol) and 2-chloro-4-(trifluoromethyl)pyridine (26 μL, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.35 (d, 2H), 6.78 (d, 2H), 1.99 (s, 3H).

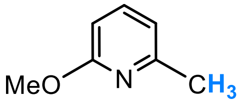
The spectroscopic data matched that previously reported.[3]



4,4'-Dimethyl-2,2'-bipyridyl (4a): Product **4a** was obtained according to the general procedure described in Section 2.1 or 2.2 using 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (58.4 mg, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.46 (s, 2H), 8.42 (d, 2H), 6.77 (d, 2H), 2.06 (s, 6H).

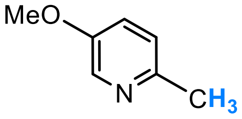
The spectroscopic data matched that previously reported.[4]



2-Methoxy-6-methylpyridine (5a): Product **5a** was obtained according to the general procedure described in Section 2.1 using 2-methoxy-6-(trifluoromethyl)pyridine (28 μL, 0.200 mmol) as the trifluoromethylpyridine.

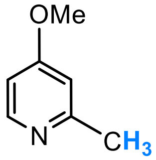
^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 7.15 (t, 1H, obscured by C_6D_6), 6.47 (d, 1H), 6.42 (d, 1H), 3.74 (s, 3H), 2.28 (s, 3H).

The spectroscopic data matched that previously reported.[5]



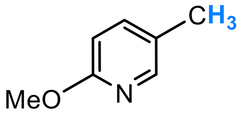
5-Methoxy-2-methylpyridine (6a): Product **6a** was obtained according to the general procedure described in Section 2.1 using 5-methoxy-2-(trifluoromethyl)pyridine (27 µL, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.11 (d, 1H), 6.89 (dd, 1H), 6.82 (d, 1H), 3.52 (s, 3H, obscured by THF), 2.31 (s, 3H).



4-Methoxy-2-methylpyridine (7a): Product **7a** was obtained according to the general procedure described in Section 2.1 using 4-methoxy-2-(trifluoromethyl)pyridine (35.4 mg, 0.200 mmol) as the trifluoromethylpyridine.

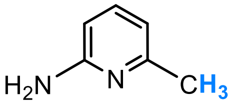
^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ. 8.25 (d, 1H), 6.47 (d, 1H), 6.38 (dd, 1H), 3.34 (s, 3H), 2.37 (s, 3H).



2-Methoxy-5-methylpyridine (8a): Product **8a** was obtained according to the general procedure described in Section 2.1 using 2-methoxy-5-(trifluoromethyl)pyridine (35.4 mg, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ. 7.78 (s, 1H), 7.20 (dd, 1H), 6.46 (dd, 1H), 3.72 (s, 3H, obscured by THF), 2.07 (s, 3H).

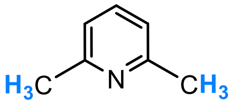
The spectroscopic data matched that previously reported.[6]



2-Amino-6-methylpyridine (9a): Product **9a** was obtained according to the general procedure described in Section 2.1 or 2.2 using 2-amino-6-(trifluoromethyl)pyridine (32.4 mg, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 7.04 (t, 1H), 6.27 (d, 1H), 6.05 (d, 1H), 2.28 (s, 3H).

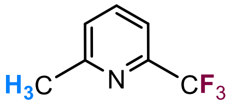
The spectroscopic data matched that previously reported.[7]



2,6-Dimethylpyridine (10a): Product **10a** was obtained according to the general procedure described in Section 2.1 or 2.2 using 2,6-bis(trifluoromethyl)pyridine (43 mg, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, CD_3CN, 25 ºC): δ. 7.47 (t, 1H), 6.97 (d, 2H), 2.42 (s, 6H).

The spectroscopic data matched that previously reported.[8]

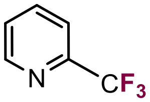


2-Trifluoromethyl-6-methylpyridine (10a'): Product 10a' was obtained according to the general procedure described in Section 2.1 using 2,6-bis(trifluoromethyl)pyridine (43 mg, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, CD_3CN, 25 ºC): δ 7.85 (dd, 1H), 7.56 (d, 1H), 7.45 (d, 1H), 2.57 (s, 3H).

^{19}F NMR (400 MHz, CD_3CN, 25 ºC): δ -68.66 (s).

The spectroscopic data matched that previously reported.[9]

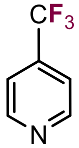


2-Trifluoromethylpyridine (1): Product **1** was obtained according to the general procedure described in Section 2.1 or 2.2 using 2-chloro-6-(trifluoromethyl)pyridine (36.3 mg, 0.200 mmol), 2-bromo-6-(trifluoromethyl)pyridine (43 mg, 0.200 mmol), 5-bromo-2-(trifluoromethyl)pyridine (43 mg, 0.200 mmol) or 4-bromo-2-(trifluoromethyl)pyridine (43 mg, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.40 (d, 2H), 7.32 (m, 2H), 6.95 (t, 1H).

^{19}F NMR (400 MHz, C_6D_6, 25 ºC): δ -68.39 (s).

The spectroscopic data matched that previously reported.[10]

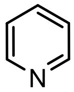


4-Trifluoromethyl pyridine (3): Product **3** was obtained according to the general procedure described in Section 2.1 using 2-chloro-4-(trifluoromethyl)pyridine (26 µL, 0.200 mmol) as the trifluoromethylpyridine.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.50 (d, 2H), 7.09 (d, 2H).

^{19}F NMR (400 MHz, C_6D_6, 25 ºC): δ -65.12 (s).

The spectroscopic data matched that previously reported.[11]



Pyridine (20a): Product **20a** was obtained according to the general procedure described in Section 2.4 using 2-fluoropyridine (17 µL, 0.200 mmol), 3-fluoropyridine (17 µL, 0.200 mmol) , 2-bromopyridine (19 µL, 0.200 mmol), 2-chloropyridine (19 µL, 0.200 mmol), 3,5-difluoropyridine (18 µL, 0.200 mmol), 2,5-difluoropyridine (18 µL, 0.200 mmol) or 5-bromo-2-fluoropyridine (21 µL, 0.200 mmol) as the halogenated pyridines.

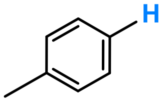
^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.48 (d, 2H), 7.28 (tt, 1H), 6.92 (dd, 2H).

The spectroscopic data matched that previously reported.[12]

Benzene (28a) : Product **28a** was obtained according to the general procedure described in Section 2.5 using fluorobenzene (19 µL, 0.2 mmol), chlorobenzene (20 µL, 0.200 mmol), bromobenzene (21 µL, 0.200 mmol), 1,2-difluorobenzene (20 µL, 0.200 mmol), 1,4-difluorobenzene (21 µL, 0.200 mmol), 3-chloro-1-fluorobenzene (21 µL, 0.200 mmol), 1,2,3-trifluorobenzene (21 µL, 0.200 mmol) or 1,2,4,5-tetrafluorobenzene (22 µL, 0.200 mmol) as the halogenated arenes.

^{1}H NMR (400 MHz, CD_3CN, 25 ºC): δ 7.36 (s, 6H).

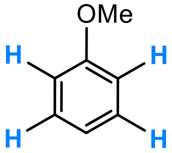
The spectroscopic data matched that previously reported.[12]



Toluene (19a): Product **19a** was obtained according to the general procedure described in section 2.5 using 4-iodotoluene (43.7 mg, 0.200 mmol) or section 2.1 using benzotrifluoride (25 µL, 0.200 mmol) as the halogenated arene.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC): δ 7.17 (m, 2H), 7.11 (m, 2H), 7.07 (m, 2H), 2.29 (s, 3H).

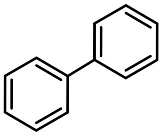
The spectroscopic data matched that previously reported.[12]



Anisole (37a): Product **37a** was obtained according to the general procedure described in Section 2.5 using 1,2,4,5-tetrafluoroanisole (28 µL, 0.200 mmol) as the halogenated arene.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 7.10 (d, 2H), 6.77 (m, 3H), 3.44 (s, 3 H).

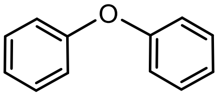
The spectroscopic data matched that previously reported.[13]



Biphenyl (38a): Product **38a** was obtained according to the general procedure described in Section 2.6 using 2-Bromobiphenyl (17 µL, 0.100 mmol), 3-Bromobiphenyl (17 µL, 0.100 mmol), 2,3',5-trichlorobiphenyl (25.6 mg, 0.050 mmol) or 3,3',4,4'-tetrachlorobiphenyl (29.2 mg, 0.050 mmol) as the halogenated arene.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 7.45 (d, 4H), 7.23 (t, 4H), 7.15 (t, 2H).

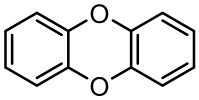
The spectroscopic data matched that previously reported.[14]



Diphenylether (42a): Product **42a** was obtained according to the general procedure described in Section 2.6 using bis(4-bromophenyl) ether (32.8 mg, 0.100 mmol) as the halogenated arene.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 7.12 (t, 4H), 6.86 (m, 6H).

The spectroscopic data matched that previously reported.[1]

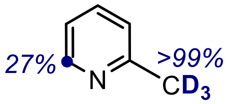


Dibenzo-p-dioxin (43a): Product **43a** was obtained according to the general procedure described in Section 2.6 using 2-chloro dibenzo-1,4-dioxin (21.8 mg, 0.100 mmol) as the halogenated arene.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 6.69-6.72 (m, 4H), 6.62-6.64 (m, 4H).

The spectroscopic data matched that previously reported.[16]

11. Characterization of deuterodehalogenated (DDH) Products

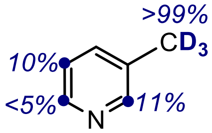


2-(Methyl-*d_3*)pyridine-6-*d* (1a-*d_4*): Product **1a-*d_4*** was obtained according to the general procedure described in Section 3 using 2-trifluoromethylpyridine (12 μL, 0.100 mmol), as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ 8.43 (d, 1H), 7.60 (td, 1H), 7.18 (d, 1H), 7.10 (m, 0.76 H).

^{2}H NMR (500 MHz, C_6D_6, 25 ºC): δ 2.45.

The spectroscopic data matched that previously reported.[17]

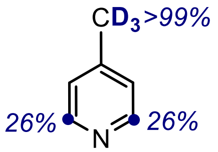


3-(Methyl-*d_3*)pyridine-2,5,6-*d_3* (2a-*d_6*): Product **2a-*d_6*** was obtained according to the general procedure described in Section 3 using 3-trifluoromethylpyridine (12 μL, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ 8.41 (s, 0.98H), 8.35 (d, 0.90H), 7.53 (d, 0.89H), 7.20 (dd, 1H).

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 8.42, 8.41,7.58, 2.28.

The spectroscopic data matched that previously reported.[17]

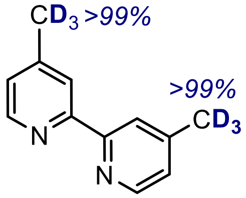


4-(Methyl-*d*$_3$)pyridine-2,6-*d*$_2$ (3a-*d*$_5$): Product **3a-*d*$_5$** was obtained according to the general procedure described in Section 3 using 4-trifluoromethylpyridine (12 µL, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ 8.40 (d, 1.48 H), 7.13 (m, 2H).

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 8.45, 2.30.

The spectroscopic data matched that previously reported.[17]

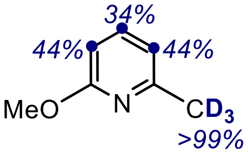


4,4'-(Dimethyl-*d*$_6$)-2,2'-bipyridyl (4a-*d*$_6$): Product **4a-*d*$_6$** was obtained according to the general procedure described in Section 3 using 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (27.2 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 8.48 (d, 2H), 8.29 (d, 2H), 7.17 (dd, 2H).

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 2.38.

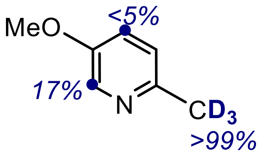
The spectroscopic data matched that previously reported.[18]



2-Methoxy-(6-methyl-*d*$_3$)pyridine-3,4,5-*d*$_3$ (5a-*d*$_6$): Product **5a-*d*$_6$** was obtained according to the general procedure described in Section 3 using 2-methoxy-6-(trifluoromethyl)pyridine (14 µL, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ.7.50 (t, 0.66H), 6.76 (d, 0.56H), 6.53 (d, 0.56H), 3.85 (s, 3H).

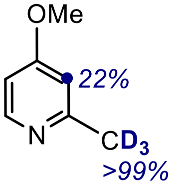
^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 7.55, 6.58, 2.37.



5-Methoxy-(2-methyl-*d₃*)pyridine-4,6-*d₂* (6a-*d₅*): Product **6a-*d₅*** was obtained according to the general procedure described in Section 3 using 5-methoxy-2-(trifluoromethyl)pyridine (14 µL, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 8.14 (d, 0.83H), 7.17 (dd, 0.97H), 7.09 (m, 1H), 3.92 (s, 3H).

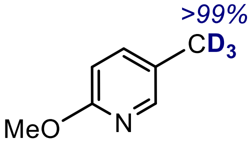
^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 8.18, 7.21, 2.39.



4-Methoxy-(2-methyl-*d₃*)pyridine-3-*d* (7a-*d₄*): Product **7a-*d₄*** was obtained according to the general procedure described in Section 3 using 4-methoxy-2-(trifluoromethyl)pyridine (17.7 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 8.23 (d, 1H), 6.74 (d, 0.78H), 6.68 (dd, 1H), 3.80 (s, 3H).

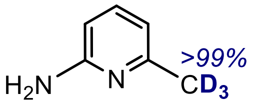
^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 6.80, 2.40.



2-Methoxy-(5-methyl-*d₃*)pyridine (8a-*d₃*): Product **8a-*d₃*** was obtained according to the general procedure described in Section 3 using 2-methoxy-5-(trifluoromethyl)pyridine (17.7 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, C_6D_6, 25 ºC): δ. 7.05 (s, 1H), 7.23 (dd, 1H), 6.50 (dd, 1H), 3.78 (s, 3H, obscured by THF).

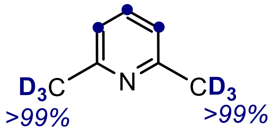
^{2}H NMR (500 MHz, $CDCl_3$, 25 ºC): 2.08.



6-Amino-(2-methyl-*d*$_3$)pyridine (9a-*d*$_3$): Product **9a-*d*$_3$** was obtained according to the general procedure described in Section 3 using 6-amino-2-(trifluoromethyl)pyridine (17.7 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, C_6D_6, 25 ºC): δ. 7.06 (t, 1H), 6.53 (d, 1H), 6.09 (d, 1H).

^{2}H NMR (500 MHz, C_6D_6, 25 ºC): 2.17.

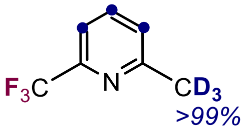


2,6-(Dimethyl-*d*$_6$)pyridine-3,4,5-*d*$_3$ (10a-*d*$_9$): Product **10a-*d*$_9$** was obtained according to the general procedure described in Section 3 using 2,6-bis(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 7.47 (t, <1H), 6.97 (d, <2H). D-incorporation could not be determined as all sites were partially deuterated.

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 7.53, 7.02, 2.40.

The spectroscopic data matched that previously reported.[17]

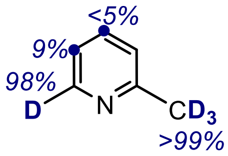


2-trifluoromethyl-6-(methyl-*d*$_3$)pyridine-3,4,5-*d*$_3$ (10a'-*d*$_6$): Product **10a'-*d*$_6$** was obtained according to the general procedure described in Section 3 using 2,6-bis(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 7.84 (t, <1H), 7.57 (d, <1H), 7.47 (d, <1H). D-incorporation could not be determined as all sites were partially deuterated.

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 7.92, 7.64, 7.54, 2.57.

^{19}F NMR (500 MHz, CD_3CN, 25 ºC): -68.66 (s).

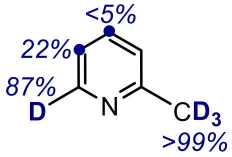


2-(Methyl-*d*$_3$)pyridine-4,5,6-*d*$_3$ (1a-*d*$_6$): Product **1a-*d*$_6$** was obtained according to the general procedure described in Section 3 using 2-bromo-6-(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD$_3$CN, 25 ºC): δ. 8.42 (d, 0.15 H), 7.59 (t, 0.98H), 7.18 (d, 1H), 7.09 (d, 0.91 H).

^{2}H NMR (500 MHz, CD$_3$CN, 25 ºC): δ. 8.47, 7.63, 7.15, 2.45.

The spectroscopic data matched that previously reported.[17]

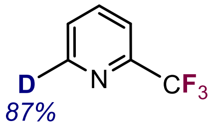


2-(Methyl-*d*$_3$)pyridine-4,5,6-*d*$_3$ (1a-*d*$_6$): Product **1a-*d*$_6$** was obtained according to the general procedure described in Section 3 using 2-chloro-6-(trifluoromethyl)pyridine (18.2 mg, 0.1 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD$_3$CN, 25 ºC): δ. 8.44 (d, 0.13 H), 7.59 (t, 0.98H), 7.18 (d, 1H), 7.09 (d, 0.78 H).

^{2}H NMR (500 MHz, CD$_3$CN, 25 ºC): δ. 8.47, 7.63, 7.15, 2.45.

The spectroscopic data matched that previously reported.[17]

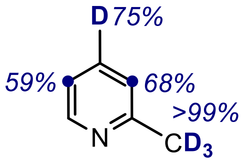


2-Trifluoromethylpyridine-6-*d* (1-*d*): Product **1-*d*** was obtained according to the general procedure described in Section 3 using 2-chloro-6-(trifluoromethyl)pyridine (18.2 mg,0.100 mmol) with 87% D-incorporation or using 2-bromo-6-(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) with 85% D-incorporation.

^{1}H NMR (500 MHz, CD$_3$CN, 25 ºC): δ. 8.72 (d, 0.13 H), 7.98 (t, 1H), 7.77 (d, 1H), 7.60 (d, 1H).

^{2}H NMR (500 MHz, CD$_3$CN, 25 ºC): 8.77.

^{19}F NMR (500 MHz, CD$_3$CN, 25 ºC): δ. -68.71.

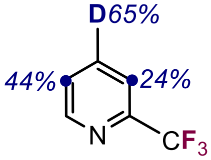


2-(Methyl-d_3)pyridine-*3,4,5*-d_3 (1a-d_6'): Product **1a-d_6'** was obtained according to the general procedure described in Section 3 using 4-bromo-2-(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 8.43 (s, 1H), 7.58 (m, 0.25 H), 7.17 (m, 0.32 H), 7.09 (m, 0.41H).

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 7.63, 7.23, 7.14, 2.45.

The spectroscopic data matched that previously reported.[17]

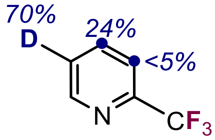


2-trifluoromethylpyridine-*3,4,5*-d_3 (1-d_3): Product **1-d_3** was obtained according to the general procedure described in Section 3 using 4-bromo-2-(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) as the trifluoromethylpyridine.

^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 8.73 (d, 1H), 7.98 (m, 0.35 H), 7.78 (m, 0.56H), 7.60 (m, 0.76H).

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 8.03, 7.83, 7.65.

^{19}F NMR (500 MHz, CD_3CN, 25 ºC): δ. -63.19 (s).



2-Trifluoromethylpyridine-3,*4,5*-d_3 (1-d_3): Product **1-d_3** was obtained according to the general procedure described in Section 3 using 5-bromo-2-(trifluoromethyl)pyridine (21.5 mg, 0.100 mmol) as the trifluoromethylpyridine.

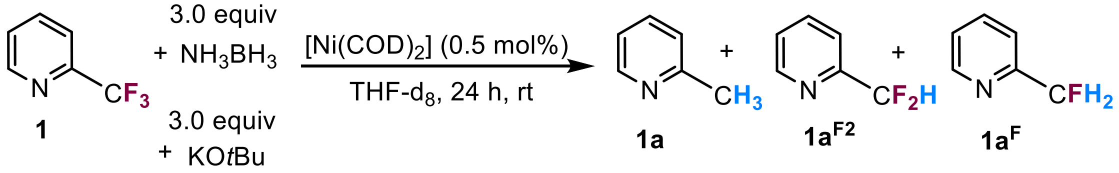
^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ. 8.74 (s, 1H), 7.98 (m, 0.76 H), 7.78 (m, 0.99H), 7.60 (m, 0.30H).

^{2}H NMR (500 MHz, CD_3CN, 25 ºC): 8.06, 7.86, 7.68.

^{19}F NMR (500 MHz, CD_3CN, 25 °C): δ. -63.45 (s).

12. NMR monitoring of the catalytic hydrodefluorination (HDF) of 2-trifluoromethylpyridine (1)

12.1 Qualitative NMR monitoring of the catalytic HDF of 2-trifluoromethylpyridine (1) employing NH_3BH_3 and KO*t*Bu with 0.5 mol% of $[Ni(COD)_2]$.



$[Ni(COD)_2]$ (0.6 mg, 0.002 mmol) and NH_3BH_3 (37.0 mg, 1.200 mmol), were weighed in 20 mL scintillation vials inside the glovebox, which were dissolved in 0.15 mL THF-d_8 separately and transferred into a J. Young NMR tube. The resulting solution was frozen in cold well, then added 2-trifluoromethylpyridine (46 µL, 0.4 mmol), mesitylene (10 µL, 0.070 mmol) followed by KO*t*Bu (134 mg, 1.200 mmol) dissolved in 0.2 mL THF-d_8. The tube was sealed and brought out of the glove box. The reaction was monitored by ^{19}F and ^{1}H NMR spectroscopy at 25°C for 24 hours.

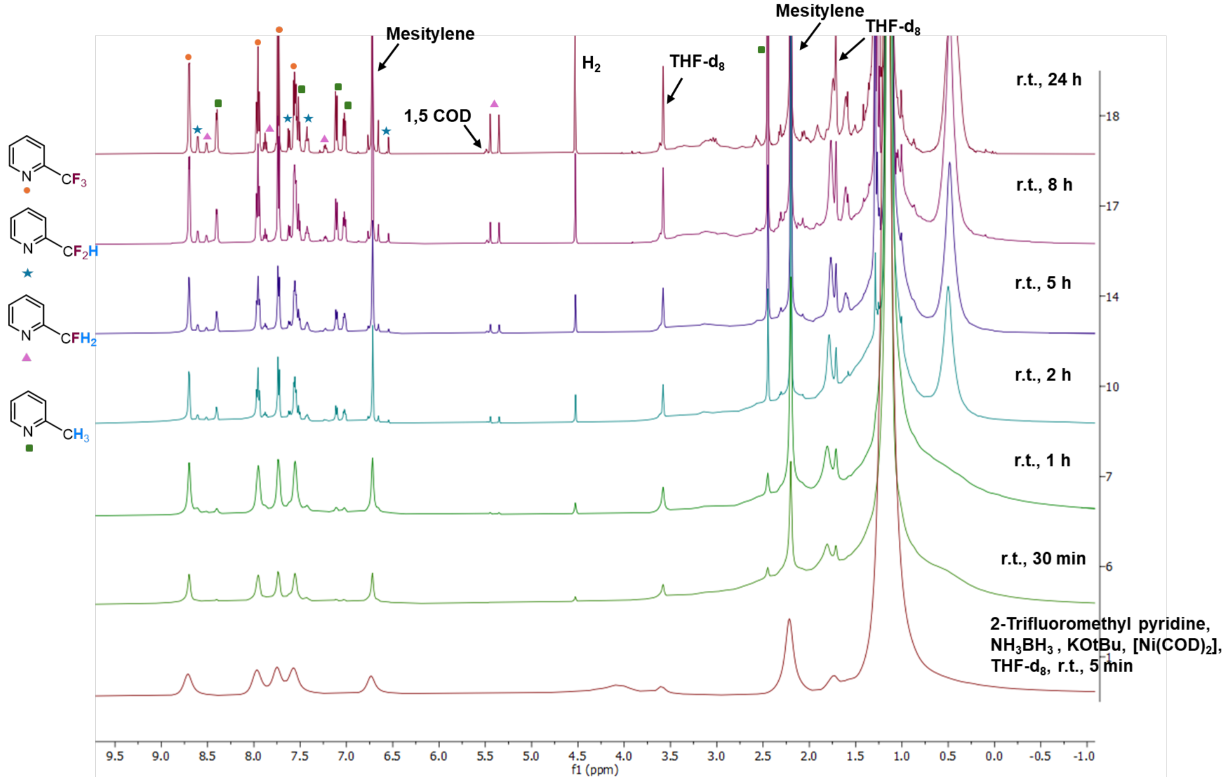


Figure S3: ^{1}H NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 0.5 mol% of $[Ni(COD)_2]$ and mesitylene as internal standard in THF-d_8 at rt.

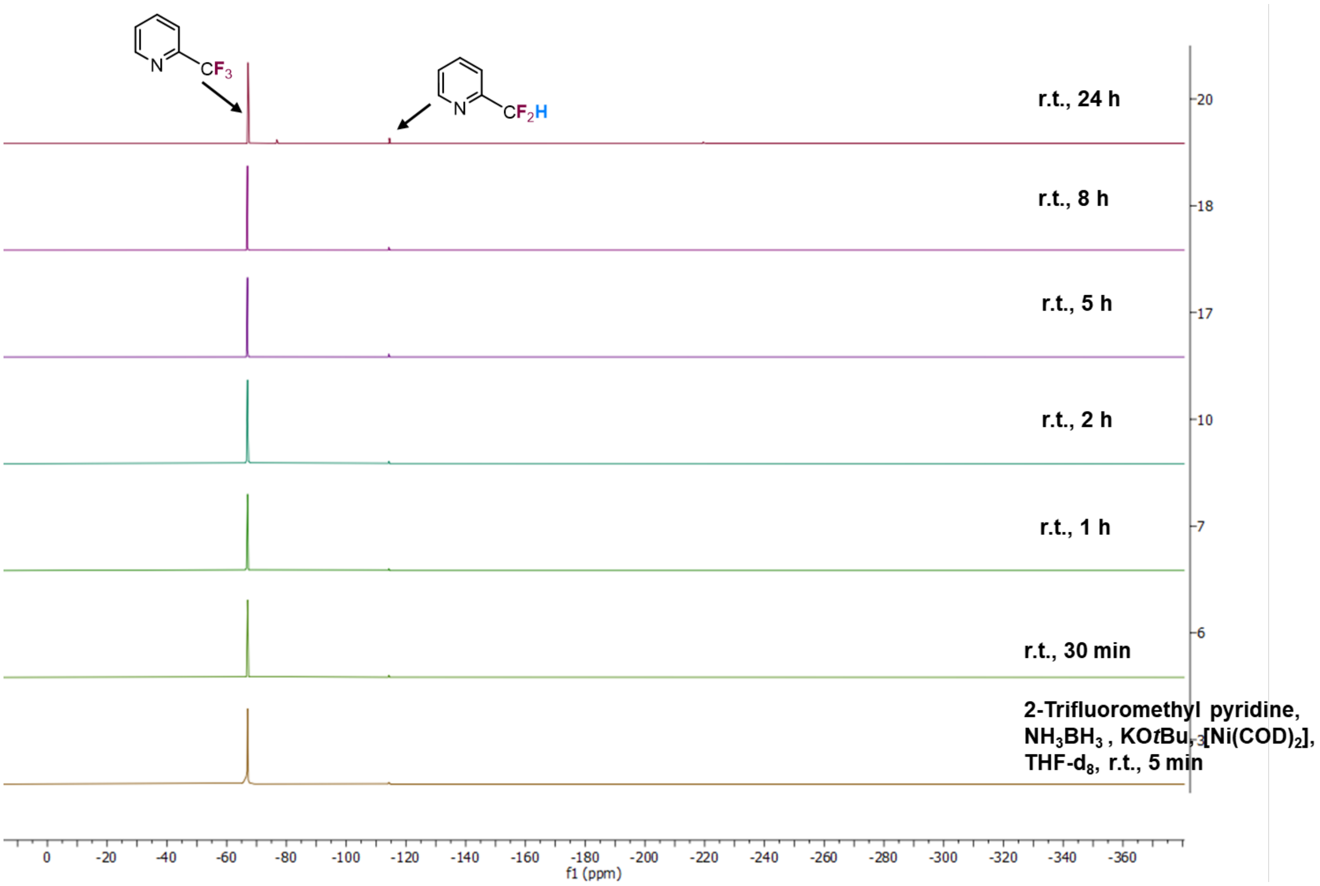


Figure S4: ^{19}F NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 0.5 mol% of $[Ni(COD)_2]$ and mesitylene as internal standard in THF-d_8 at rt.

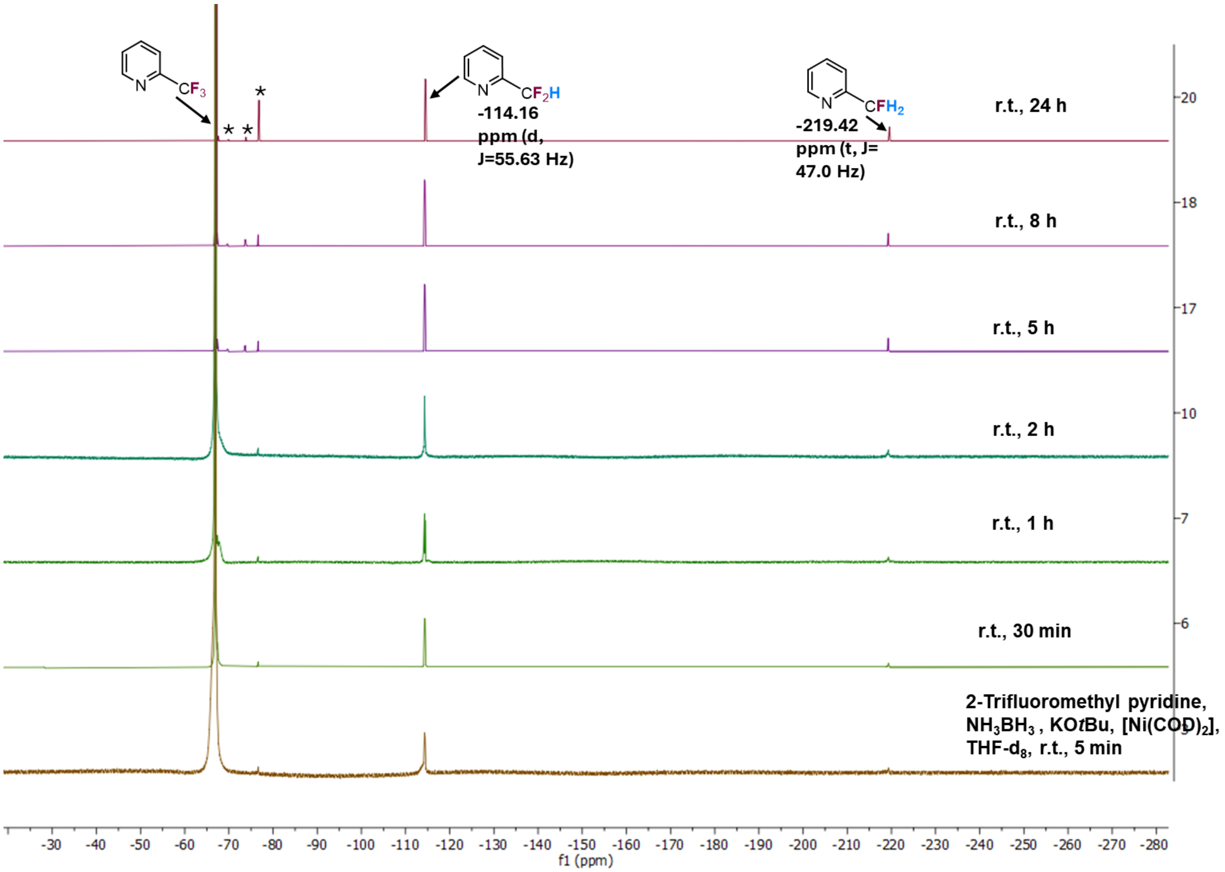
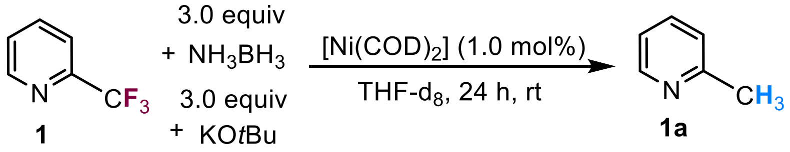


Figure S5: Zoomed in ^{19}F NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 0.5 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d$_8$ at rt. *= Unidentified trace species

12.2 Quantitative NMR monitoring of catalytic HDF of 2-trifluoromethylpyridine (1) employing NH_3BH_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$].



[Ni(COD)$_2$] (0.6 mg, 0.002 mmol) and NH_3BH_3 (18.5 mg, 0.600 mmol), were weighed in 20 mL scintillation vials inside the glovebox, which were dissolved in 0.15 mL THF-d$_8$ separately and transferred into a J. Young NMR tube. The resulting solution was frozen in cold well, then added 2-trifluoromethylpyridine (23 µL, 0.200 mmol), mesitylene (10 µL, 0.070 mmol) followed by KO*t*Bu (67 mg, 0.600 mmol) dissolved in 0.2 mL THF-d$_8$. The tube was sealed and brought out of the glove box. The reaction was monitored by ^{19}F, ^{11}B and ^{1}H NMR spectroscopy at 25°C for 24 hours.

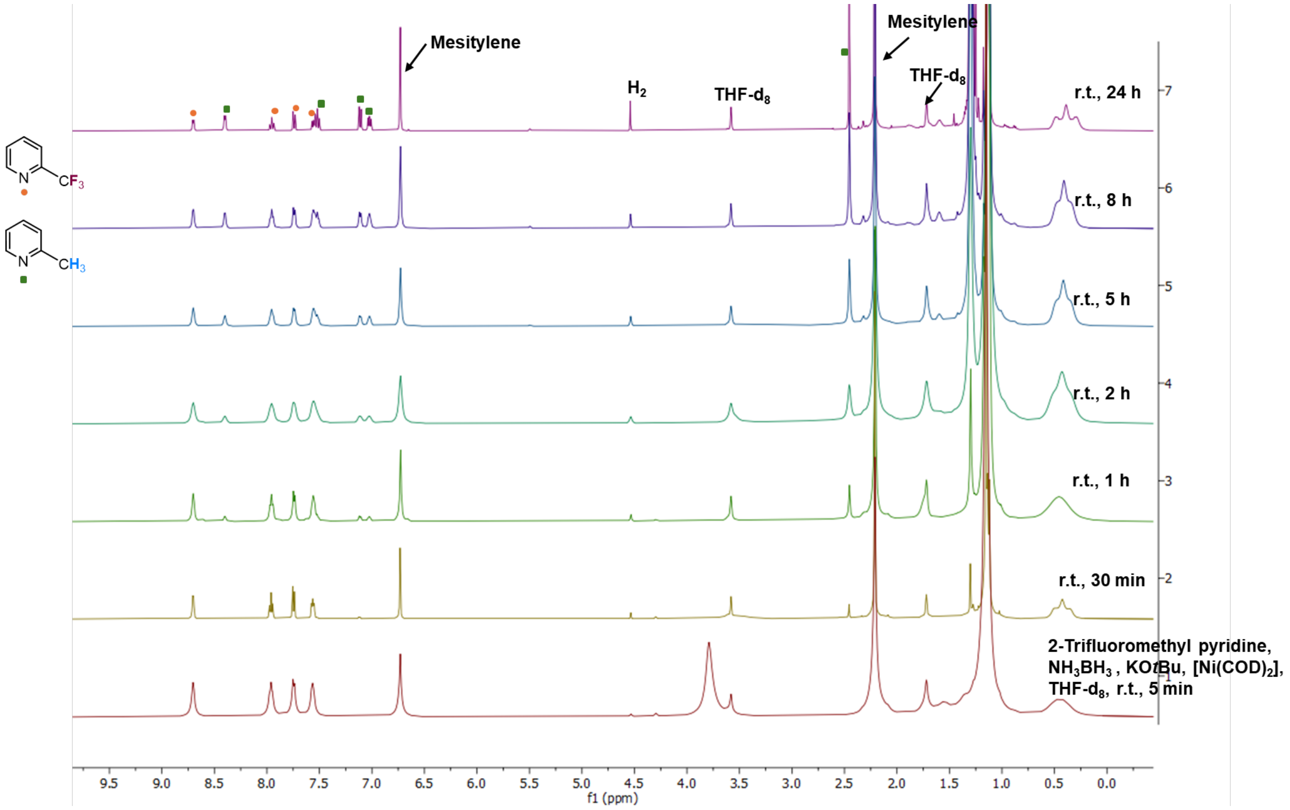


Figure S6: ^{1}H NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d$_8$ at rt.

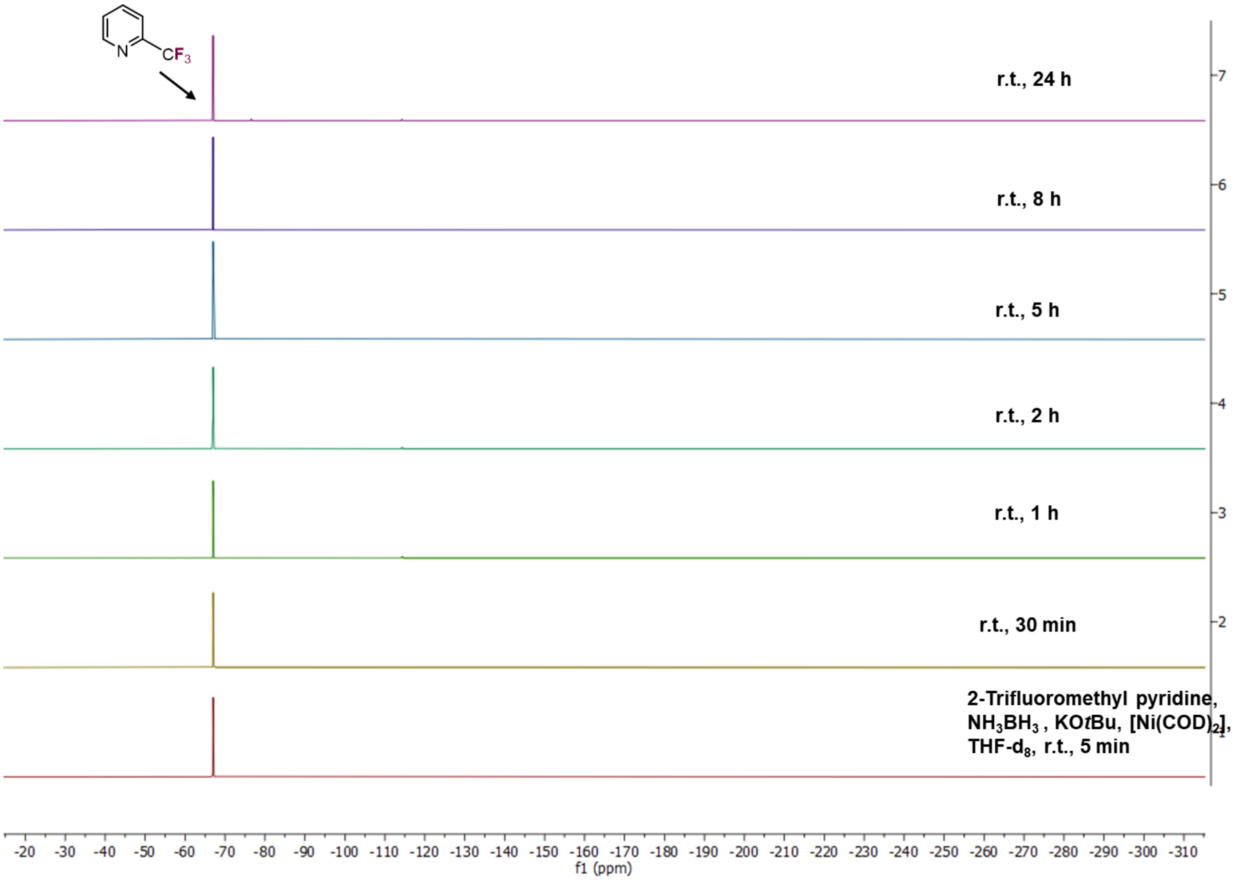


Figure S7: ^{19}F NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 1.0 mol% of $[Ni(COD)_2]$ and mesitylene as internal standard in THF-d_8 at rt.

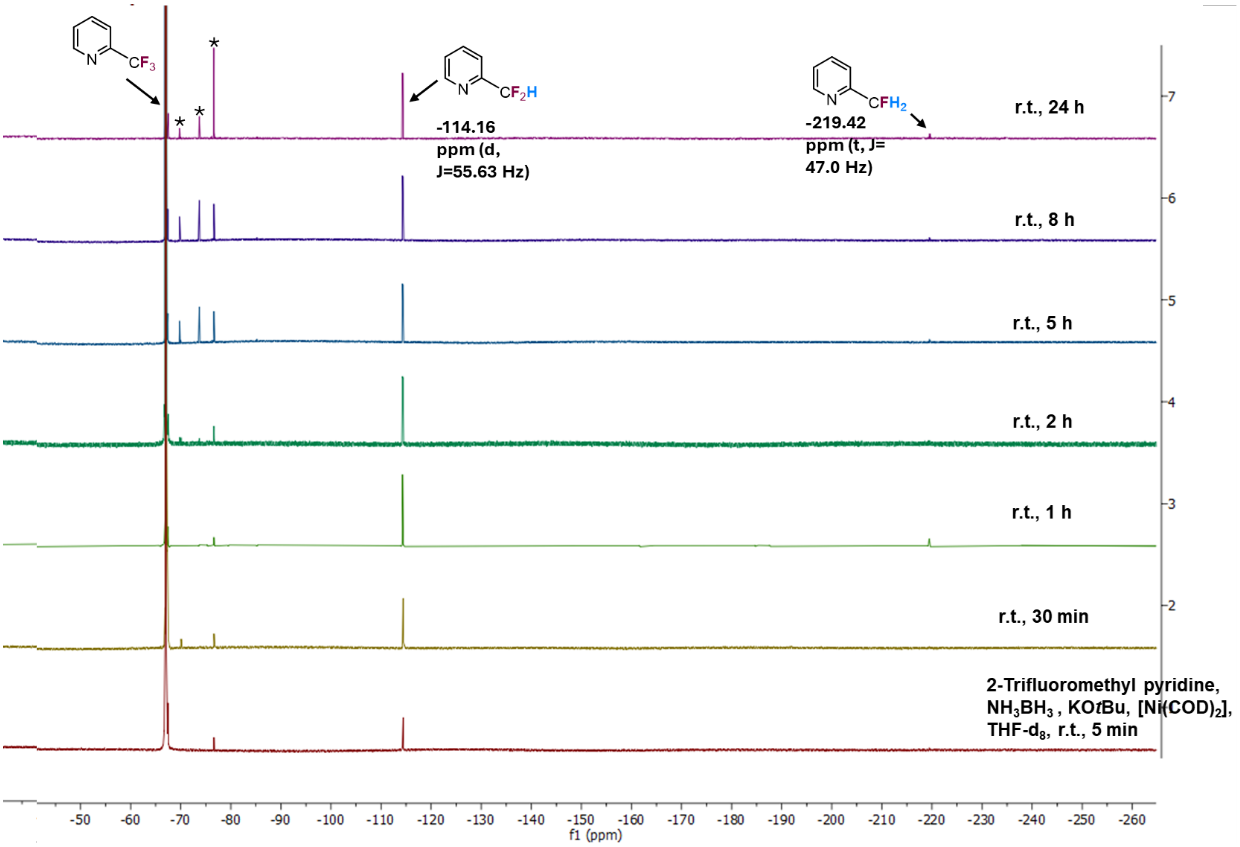


Figure S8: Zoomed in ^{19}F NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d$_8$ at rt. *= Unidentified trace species

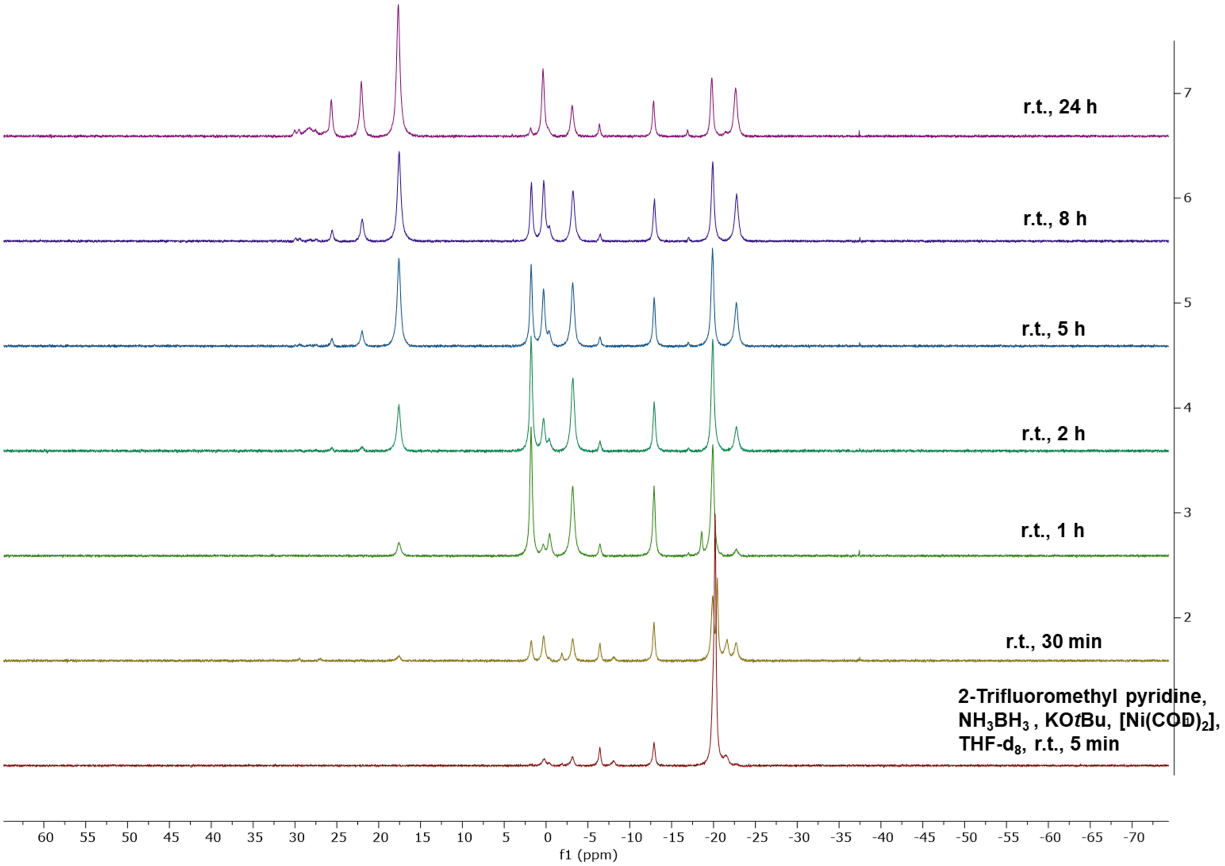


Figure S9: ^{11}B NMR spectra of the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d_8 at rt.

12.3 Reaction profile for the catalytic HDF of 2-trifluoromethylpyridine employing NH_3BH_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$]. The consumption of starting material **1** and formation of product **1a** over 16 hours, following the procedure described in section 12.2, are shown in Figure S7. The amounts of **1** and **1a** were calculated by integrating the signals of **1** (8.70 ppm) and **1a** (8.40 ppm) in the ^{1}H NMR spectra using mesitylene (10 µL, 0.007 mmol) as the internal standard.

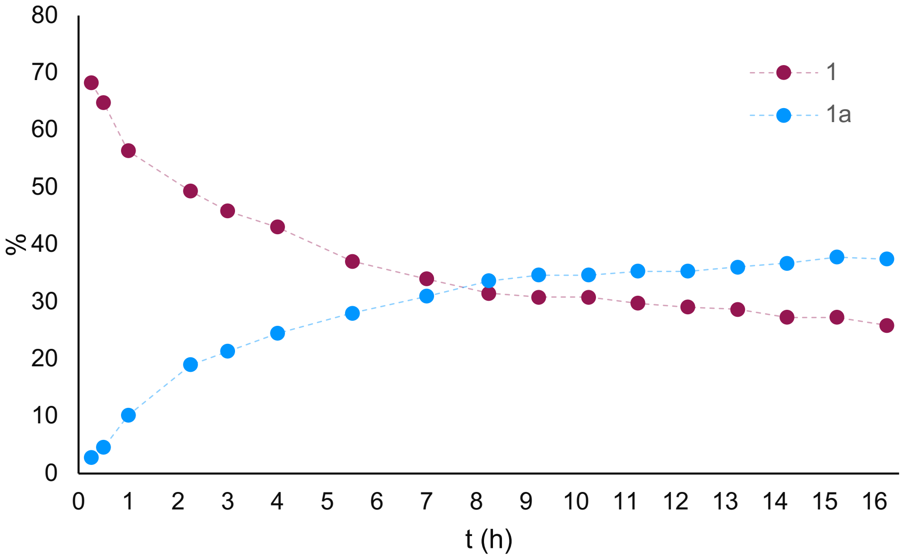
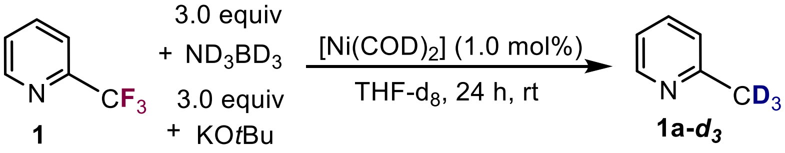


Figure S10. Reaction profile for formation of **1a** at the expense of **1** employing [Ni(COD)$_2$].

13. NMR monitoring of catalytic deuterodefluorination (DDF) of 2-trifluoromethylpyridine (1)

13.1 Quantitative NMR monitoring of catalytic DDF of 2-trifluoromethylpyridine (1) employing ND$_3$BD$_3$ and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$].



[Ni(COD)$_2$] (0.6 mg, 0.002 mmol) and ND$_3$BD$_3$ (21.6 mg, 0.600 mmol), were weighed in 20 mL scintillation vials inside the glovebox, which were dissolved in 0.15 mL THF-d$_8$ separately and transferred into a J. Young NMR tube. The resulting solution was frozen in cold well, then added 2-trifluoromethylpyridine (23 µL, 0.200 mmol), mesitylene (10 µL, 0.070 mmol) followed by KO*t*Bu (67 mg, 0.600 mmol) dissolved in 0.2 mL THF-d$_8$. The tube was sealed and brought out of the glove box. The reaction was monitored by ^{19}F and ^{1}H NMR spectroscopy at 25°C for 24 hours.

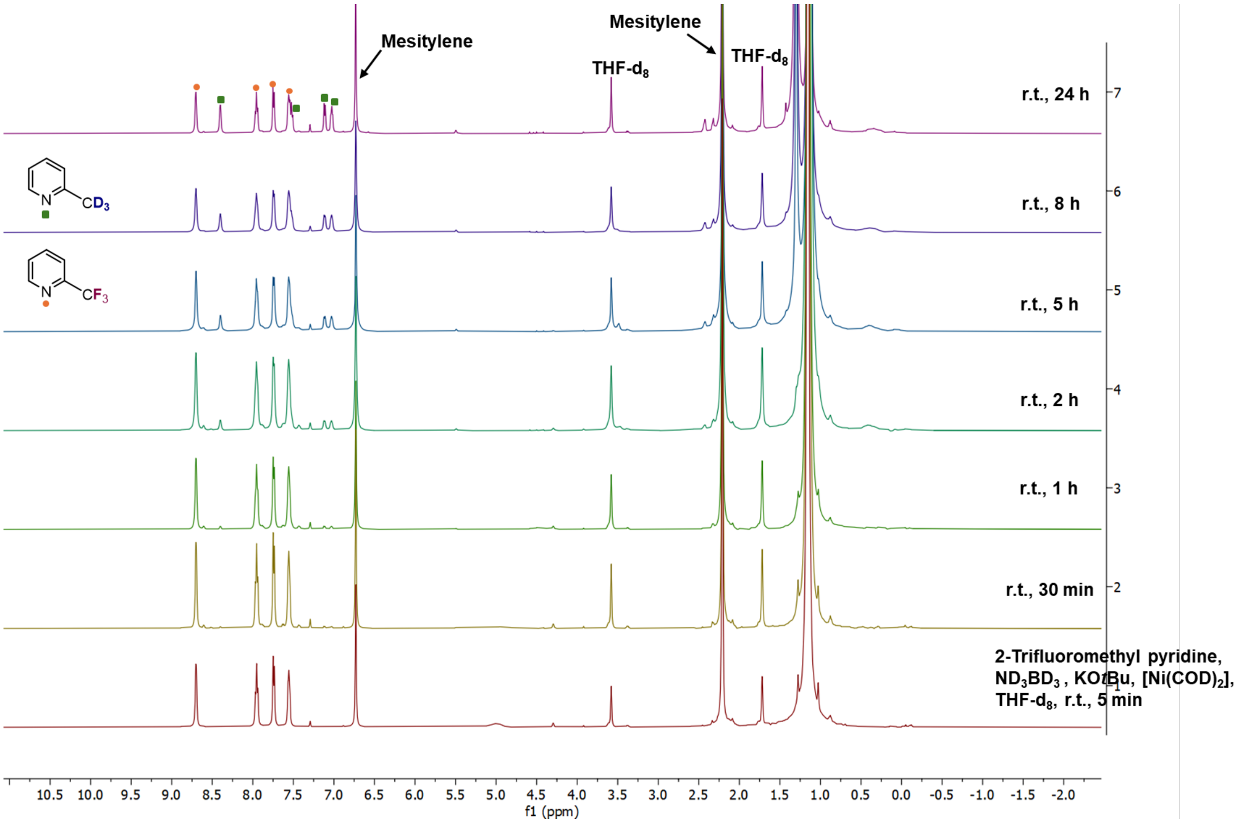


Figure S11: ^{1}H NMR spectra of the catalytic DDF of 2-trifluoromethylpyridine employing ND_3BD_3 and KO*t*Bu with 1.0 mol% of $[Ni(COD)_2]$ and mesitylene as internal standard in THF-d_8 at rt.

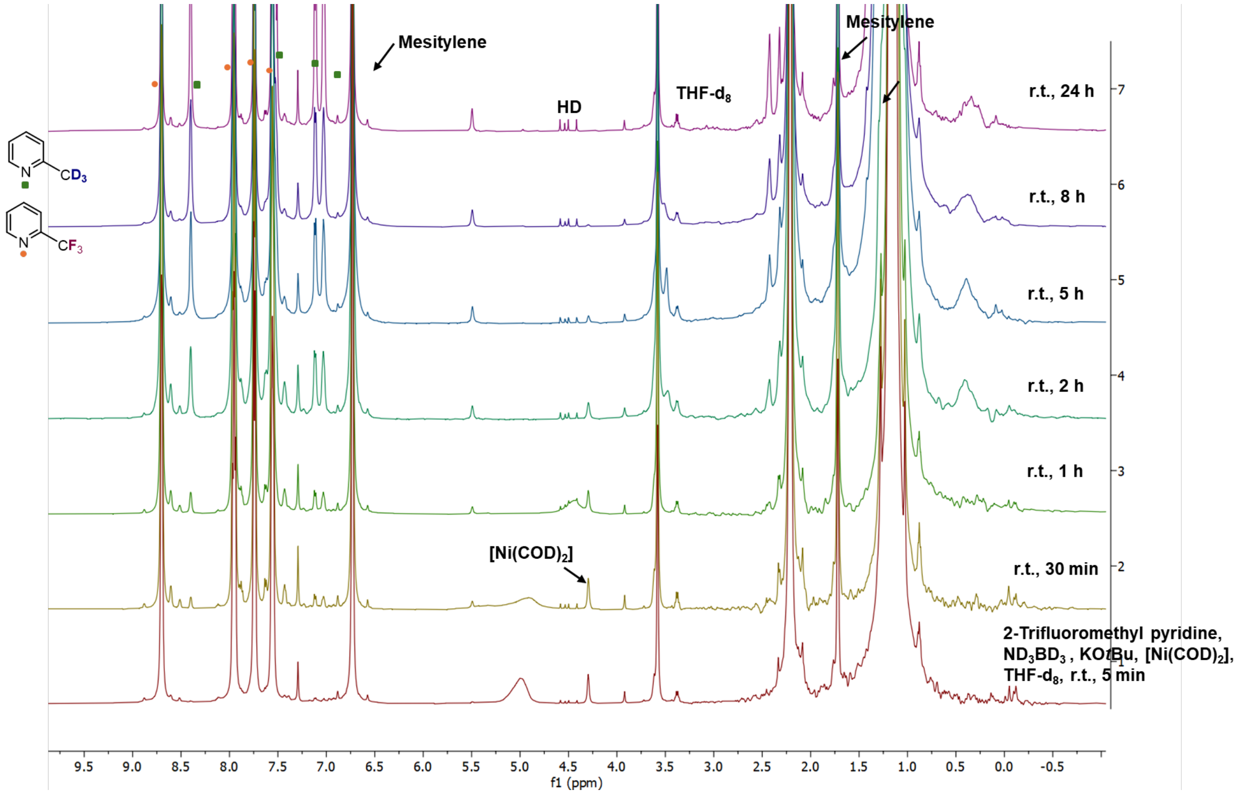


Figure S12: Zoomed in ^{1}H NMR spectra of the catalytic DDF of 2-trifluoromethylpyridine employing ND_3BD_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d_8 at rt.

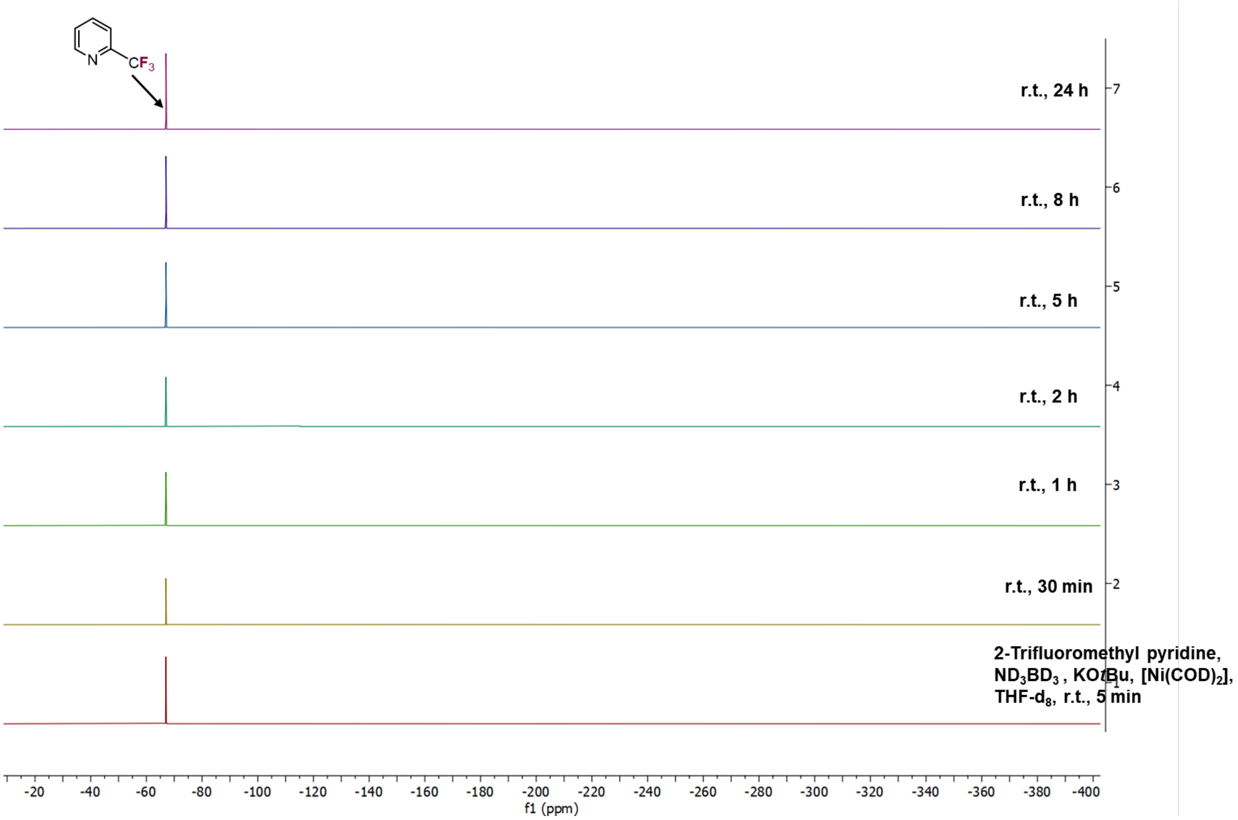


Figure S13: ^{19}F NMR spectra of the catalytic DDF of 2-trifluoromethylpyridine employing ND_3BD_3 and KO*t*Bu with 1.0 mol% of $[Ni(COD)_2]$ and mesitylene as internal standard in THF-d_8 at rt.

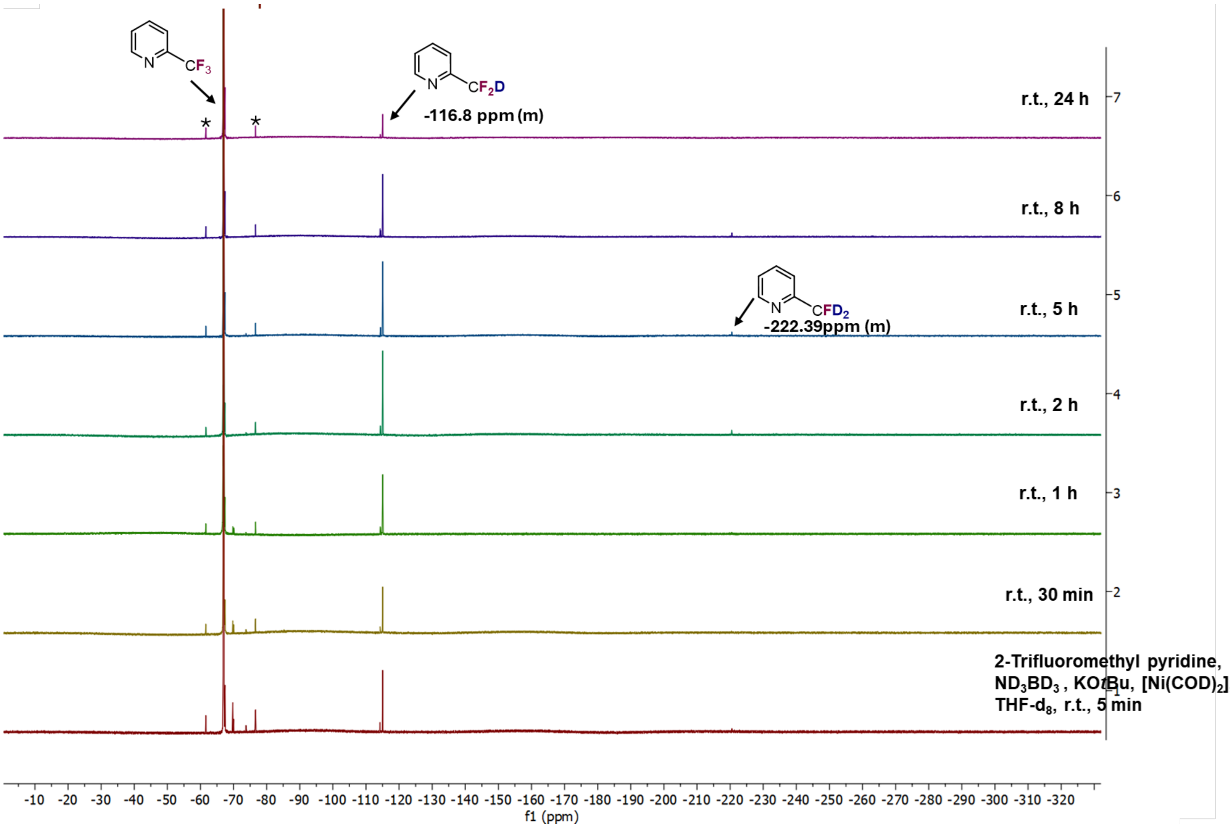


Figure S14: Zoomed in ^{19}F NMR spectra of the catalytic DDF of 2-trifluoromethylpyridine employing ND_3BD_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d_8 at rt. *= Unidentified trace species

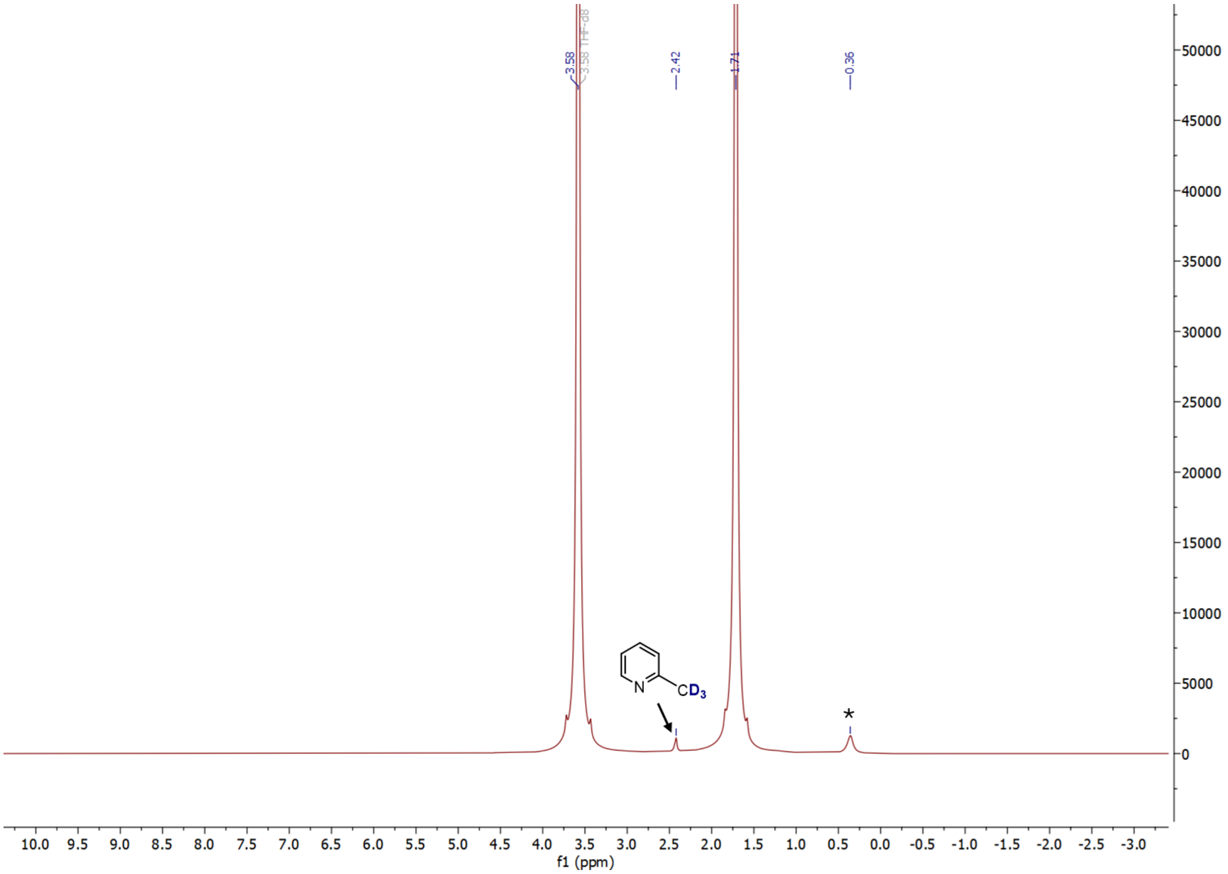


Figure S15: Zoomed in ^{2}H NMR spectra of the catalytic DDF of 2-trifluoromethylpyridine employing ND_3BD_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$] and mesitylene as internal standard in THF-d_8 at rt after 24 h. *= Unidentified trace species

13.2 Reaction profile for the catalytic DDF of 2-trifluoromethylpyridine (1) employing ND_3BD_3 and KO*t*Bu with 1.0 mol% of [Ni(COD)$_2$]. The consumption of starting material **1** and formation of product **1a-*d₃*** over 16 hours, following the procedure described in section 13.1, are shown in Figure S13. The amounts of **1** and **1a-*d₃*** were calculated by integrating the signals of **1** (8.71 ppm) and **1a-*d₃*** (8.41 ppm) in the ^{1}H NMR spectra using mesitylene (10 μL, 0.007 mmol) as the internal standard.

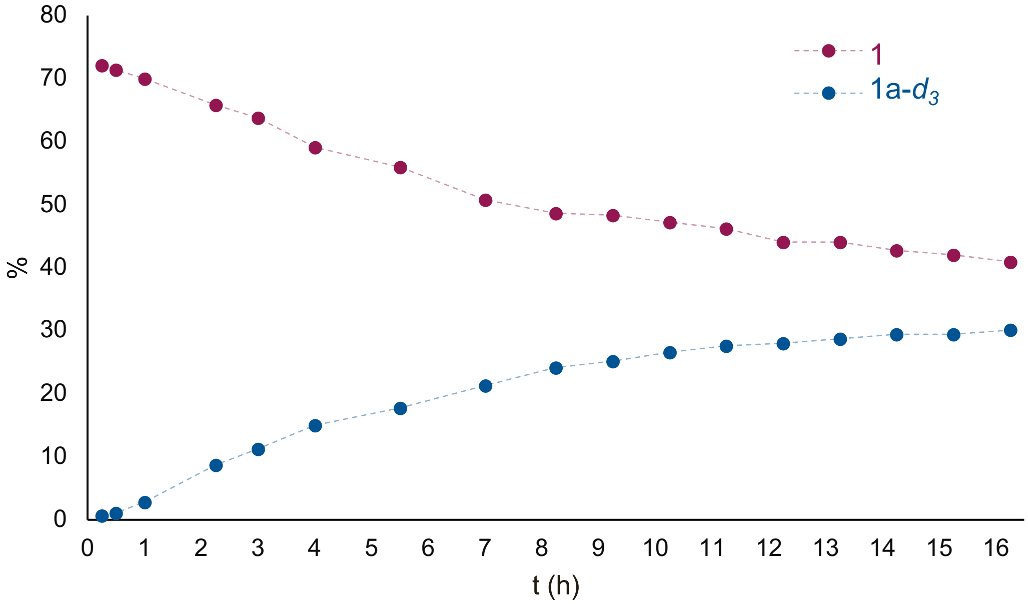


Figure S16. Reaction profile for formation of **1a-*d₃*** at the expense of **1** employing [Ni(COD)$_2$].

14. Kinetic Isotope Effect (KIE) determination. The KIE was calculated by comparing the rate of formation of **1a** from **1** with that of formation of **1a-*d₃*** from **1** in two parallel reactions, the procedures for which are described in sections 12.2 and 13.1 respectively. The reaction progress over the initial 90 minutes is shown in Figure S14. The amounts of **1a** and **1a-*d₃*** were calculated by integrating the signals of **1a** (8.70 ppm) and **1a-*d₃*** (8.71 ppm) in the ^{1}H NMR spectra using mesitylene (10 μL, 0.007 mmol) as the internal standard. Product concentration versus time data were plotted, and the initial rates were used to calculate a KIE value of 3.24.

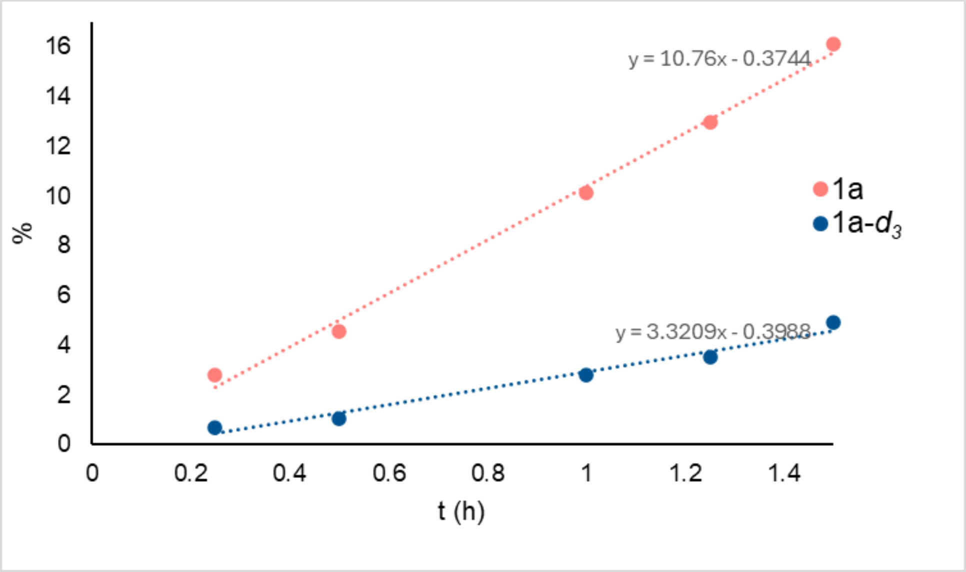
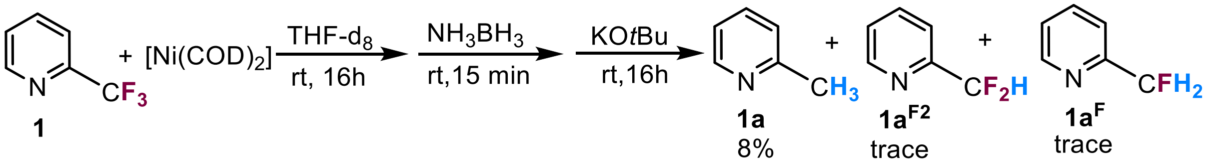


Figure S17: Initial reaction progress for formation of **1a** or **1a-*d*$_3$** from **1** in two parallel reactions

15. NMR monitoring of stoichiometric reactions with 2-trifluoromethylpyridine (1)

15.1 NMR monitoring of the reaction of [Ni(COD)$_2$] with 2-trifluoromethylpyridine (1) followed by the addition of NH$_3$BH$_3$ and KO*t*Bu.



[Ni(COD)$_2$] (27.5 mg, 0.100 mmol) was weighed in a 20 mL scintillation vial inside the glovebox, which was dissolved in 0.3 mL THF-d$_8$. The resulting solution was transferred into a J. Young NMR tube, to which was added 2-trifluoromethylpyridine (12 μL, 0.100 mmol) and internal standard, mesitylene (10 μL, 0.070 mmol). The tube was sealed, shaken vigorously and brought out of the glovebox. The reaction was monitored by ^{19}F and ^{1}H spectroscopy at 25°C for 16 hours. The same J. Young NMR tube was moved to the glove box and NH$_3$BH$_3$ (3.1 mg, 0.100 mmol) dissolved in 0.1 mL THF-d$_8$ was added and its ^{1}H NMR was recorded. After that, KO*t*Bu (11.2 mg, 0.100 mmol) was added to the same J. Young NMR tube, shaken vigorously, sealed and monitored by ^{19}F and ^{1}H NMR spectroscopy at 25°C for 16 hours. Conversion **1**: 40%; Yield **1a**: 8%.

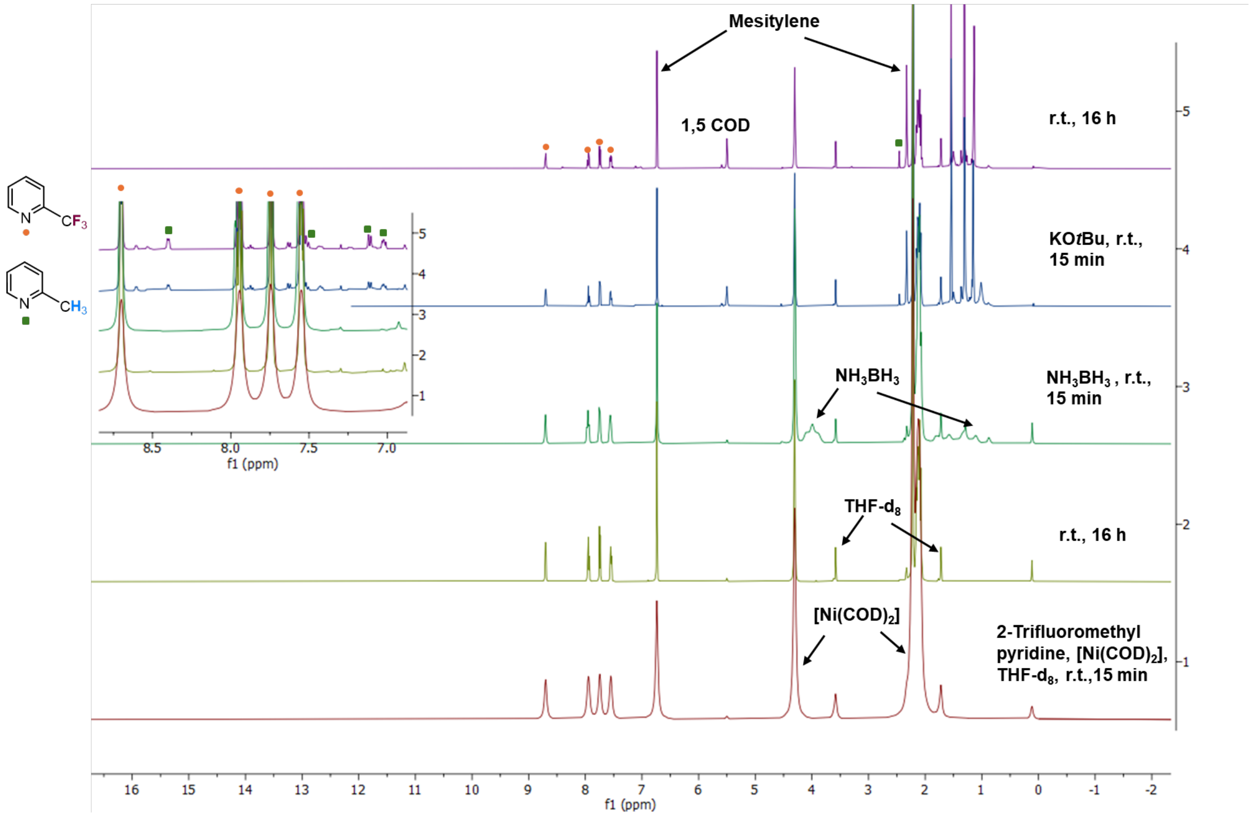


Figure S18: ^{1}H NMR spectra of the stoichiometric reaction of [Ni(COD)$_2$] with 2-trifluoromethylpyridine followed by the addition of NH_3BH_3 and KO*t*Bu in THF-d_8 at rt.

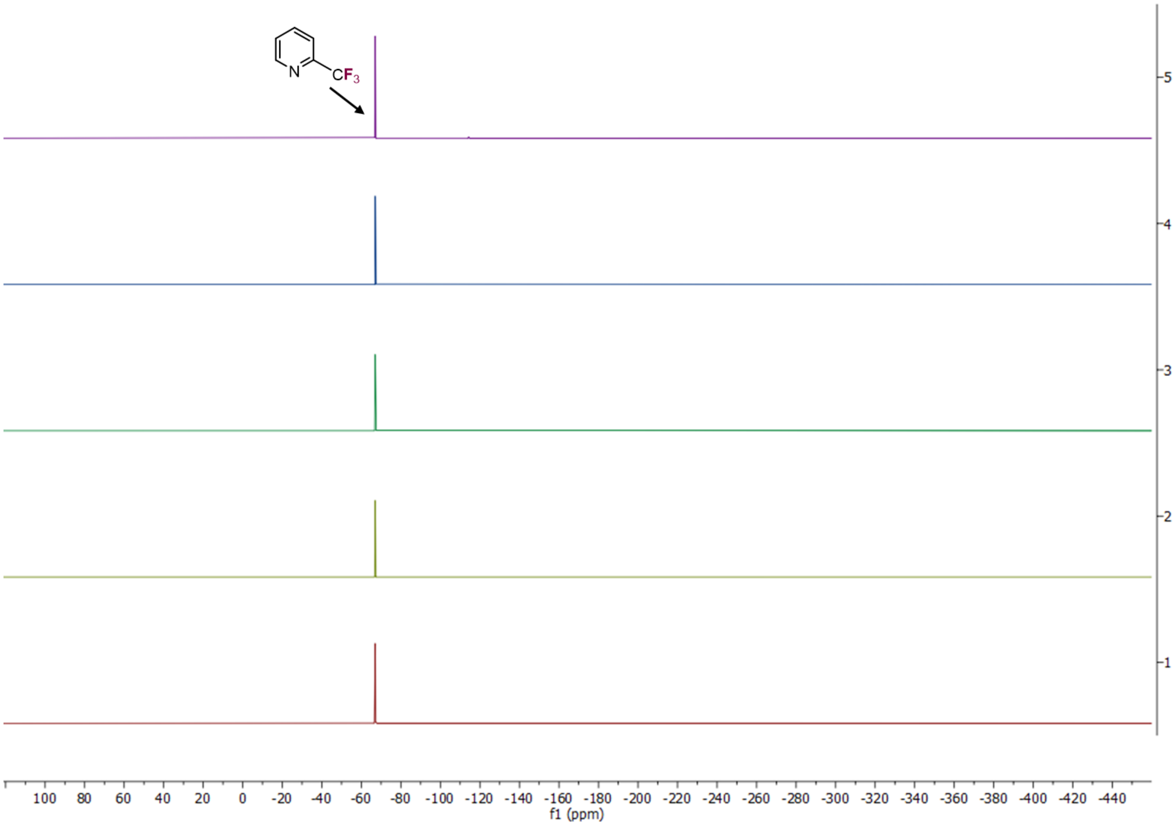


Figure S19: ^{19}F NMR spectra of the stoichiometric reaction of [Ni(COD)$_2$] with 2-trifluoromethylpyridine followed by the addition of NH_3BH_3 and KO*t*Bu in THF-d$_8$ at rt.

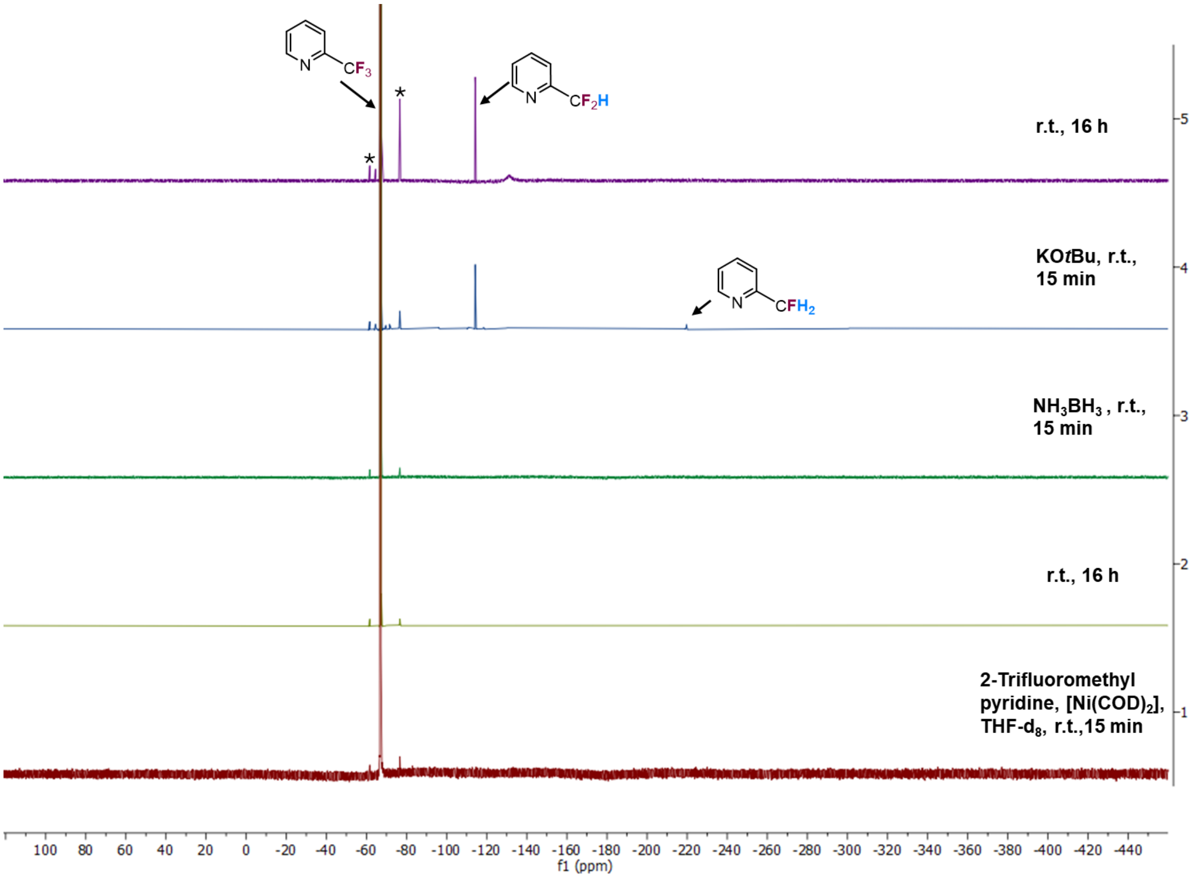
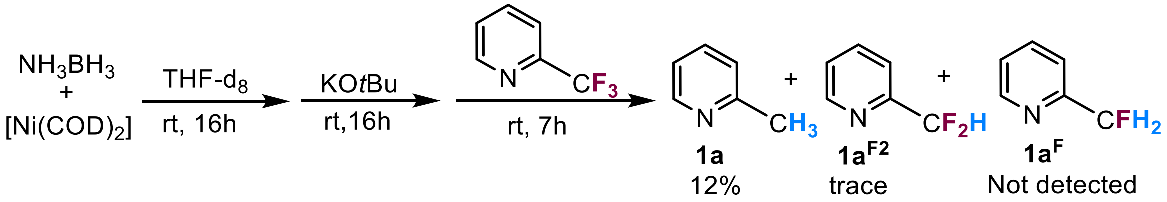


Figure S20: Zoomed in ^{19}F NMR spectra of the stoichiometric reaction of [Ni(COD)$_2$] with 2-trifluoromethylpyridine followed by the addition of NH_3BH_3 and KO*t*Bu in THF-d_8 at rt.

*= Unidentified trace species

15.2 NMR Monitoring of the reaction of [Ni(COD)$_2$] with NH_3BH_3 followed by the addition of KO*t*Bu and 2-trifluoromethylpyridine (1).



[Ni(COD)$_2$] (27.5 mg, 0.1 mmol) and NH_3BH_3 (3.1 mg, 0.100 mmol), were weighed in 20 mL scintillation vials inside the glovebox, which were dissolved in 0.15 mL THF-d_8 separately and transferred into a J. Young NMR tube, to which was added internal standard, mesitylene (10 µL, 0.070 mmol). The J. Young NMR tube was sealed, brought out of the glove box and its ^{1}H NMR was recorded. The same J. Young NMR tube was moved to the glove box and KO*t*Bu (11.2 mg, 0.100 mmol) dissolved in 0.1 mL THF-d_8 was added into it, which was sealed, shaken vigorously and brought out of the glove box. The reaction was monitored by ^1H NMR spectroscopy at 25°C for 16 hours. After that, 2-trifluoromethylpyridine (11.5 μL, 0.100 mmol) was added to the same tube, which was sealed, shaken vigorously and brought out of the glove box and its ^1H NMR was recorded at 25°C. Conversion **1**: 35%; Yield **1a**: 12%.

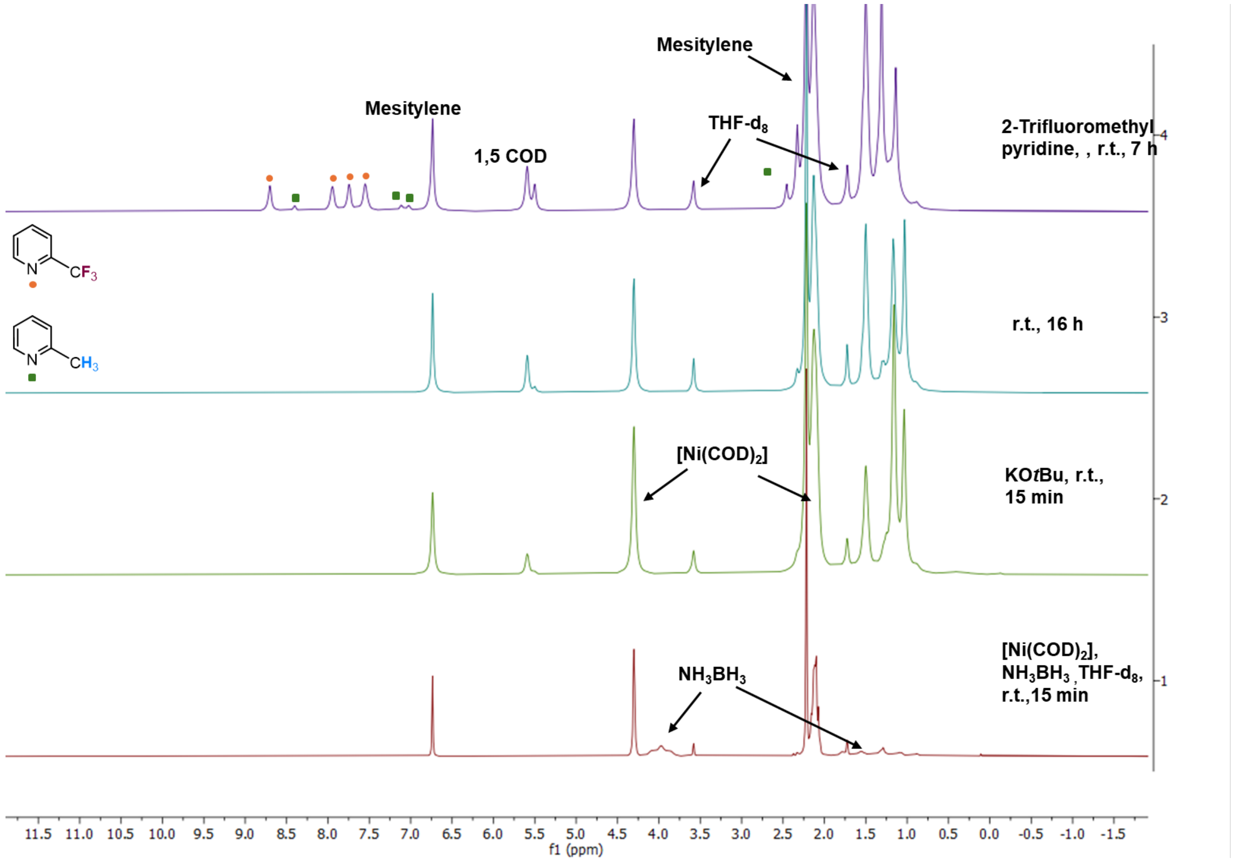
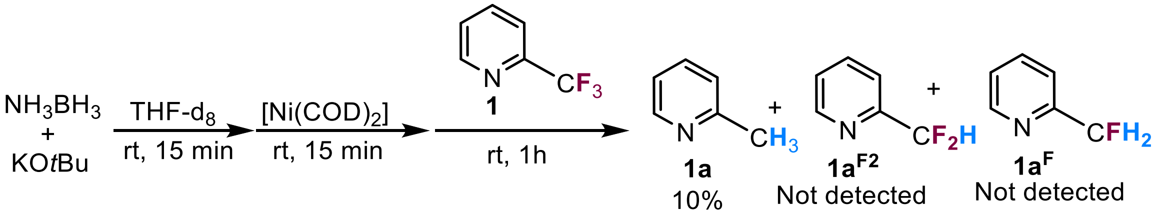


Figure S21: ^1H NMR spectra of the stoichiometric reaction of [Ni(COD)$_2$] with NH_3BH_3 and KO*t*Bu followed by the addition of 2-trifluoromethylpyridine in THF-d_8 at rt.

15.3 NMR Monitoring of the reaction of NH_3BH_3 with KO*t*Bu followed by the addition of [Ni(COD)$_2$] and 2-trifluoromethylpyridine (1).



1a 10%

1a^{F2} Not detected

1a^{F} Not detected

NH_3BH_3 (3.1 mg, 0.100 mmol) and KO*t*Bu (11.2 mg, 0.100 mmol) were weighed in 20 mL scintillation vials inside the glovebox, which were dissolved in 0.15 mL THF-d_8 separately and transferred into a J. Young NMR tube. The J. Young NMR tube was sealed, brought out of the glove box and its ^{1}H NMR was recorded. The same J. Young NMR tube was moved to the glove box and [Ni(COD)$_2$] (27.5 mg, 0.100 mmol) dissolved in 0.2 mL THF-d$_8$ and internal standard, mesitylene (10 µL, 0.070 mmol) were added into it. The tube was sealed, shaken vigorously and brought out of the glove box and its ^{1}H NMR was recorded at 25°C. To the same tube was added 2-trifluoromethylpyridine (12 µL, 0.100 mmol) which was sealed, shaken vigorously and brought out of the glove box and its ^{1}H NMR was recorded at 25°C. Conversion **1**: 12%; Yield **1a**: 10%.

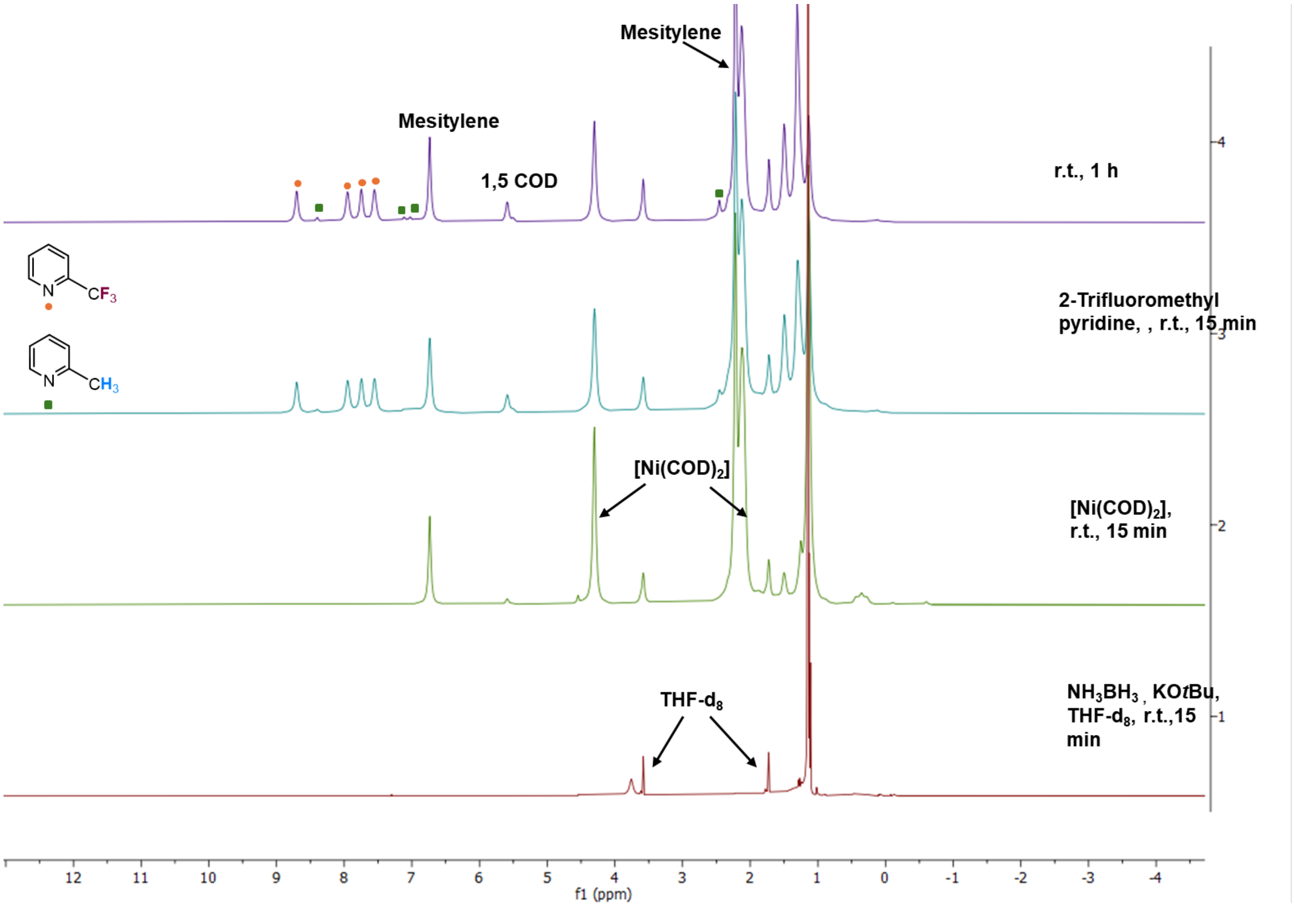


Figure S22: ^{1}H NMR spectra of the stoichiometric reaction of NH_3BH_3 with KO*t*Bu followed by the addition of [Ni(COD)$_2$] and then, 2-trifluoromethylpyridine. in THF-d$_8$ at rt.

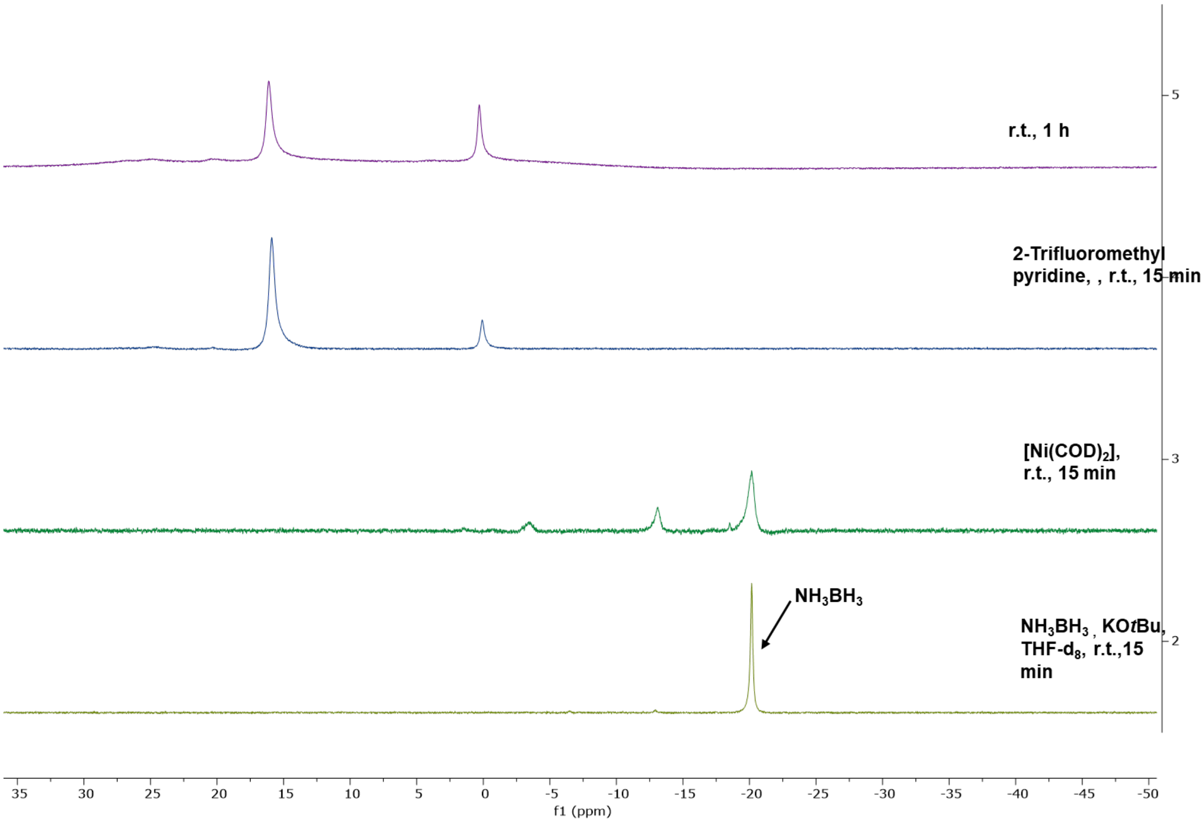
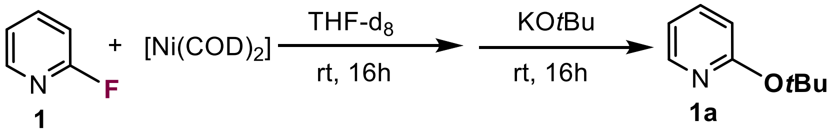


Figure S23: ^{11}B NMR spectra of the stoichiometric reaction of NH_3BH_3 with KO*t*Bu followed by the addition of [Ni(COD)$_2$] and then, 2-trifluoromethylpyridine. in THF-d_8 at rt.

16. NMR Monitoring of stoichiometric reactions with 2-fluoropyridine (20)

16.1 NMR Monitoring of the reaction of [Ni(COD)$_2$] with 2-fluoropyridine (20) followed by the addition of KO*t*Bu.



[Ni(COD)$_2$] (27.5 mg, 0.100 mmol) was weighed in a 20 mL scintillation vial inside the glovebox, which was dissolved in 0.3 mL THF-d_8. The resulting solution was transferred into a J. Young NMR tube, sealed, brought out of the glove box and its ^{1}H NMR was recorded. The same J. Young NMR tube was moved to the glove box and 2-fluoropyridine (9 µL, 0.100 mmol) was added into it, which was sealed, shaken vigorously, and brought out of the glove box. The reaction was monitored by ^{19}F and ^{1}H spectroscopy at 25°C for 16 hours. After that, KO*t*Bu was added to the same J. Young NMR tube, shaken vigorously, sealed, and monitored by ^{19}F and ^{1}H NMR spectroscopy at 25°C for 16 hours.

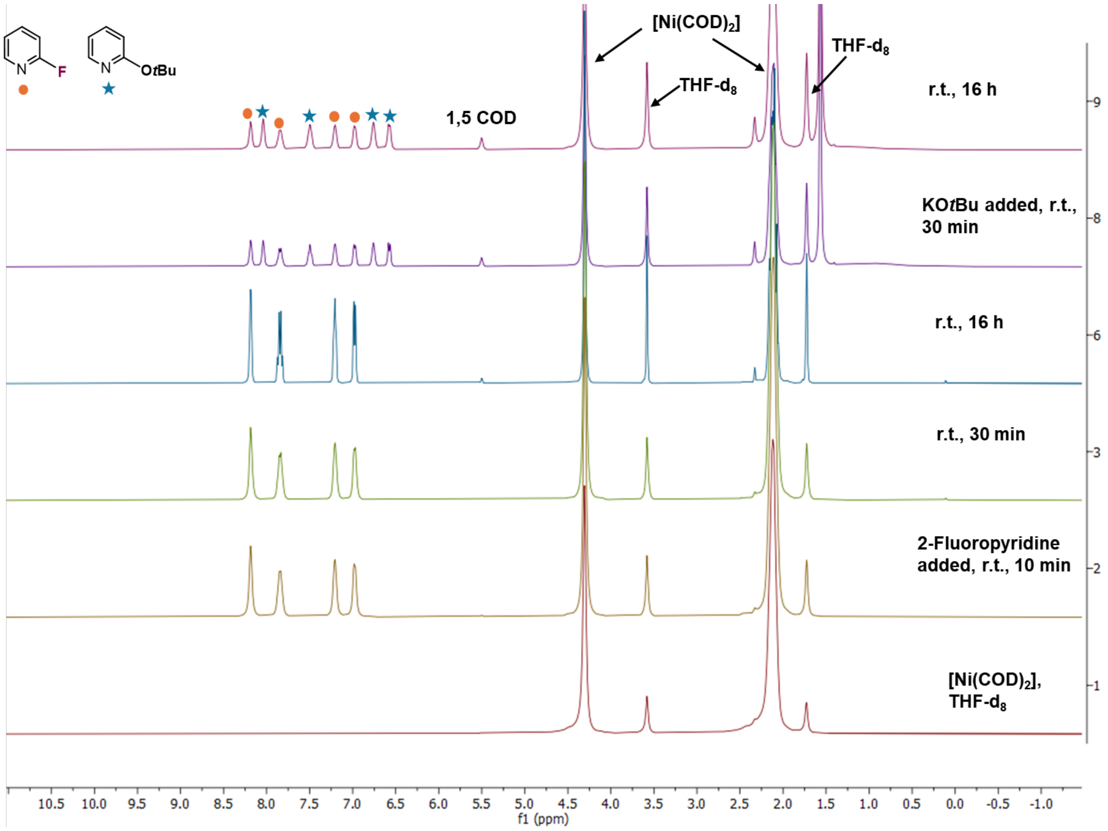
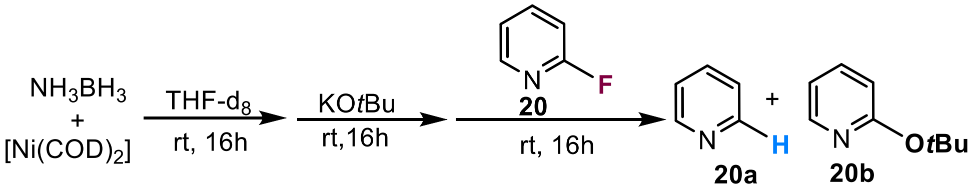


Figure S24: ^{1}H NMR spectra of stoichiometric reaction of [Ni(COD)$_2$] with 2-fluoropyridine followed by the addition of KO*t*Bu in THF-d$_8$ at rt.

16.2 NMR Monitoring of the reaction of [Ni(COD)$_2$] with NH$_3$BH$_3$ followed by the addition of KO*t*Bu and 2-fluoropyridine (20).



[Ni(COD)$_2$] (27.5 mg, 0.100 mmol) and NH$_3$BH$_3$ (3.1 mg, 0.100 mmol), were weighed in 20 mL scintillation vials inside the glovebox, which were dissolved in 0.15 mL THF-d$_8$ separately and transferred into a J. Young NMR tube. The J. Young NMR tube was sealed, brought out of the glovebox and monitored by ^{1}H and ^{11}B NMR spectroscopy at 25°C for 16 hours. The same J. Young NMR tube was moved to the glove box and KO*t*Bu (11.2 mg, 0.100 mmol) dissolved in 0.15 mL THF-d$_8$ was added into it, which was sealed, shaken vigorously, and brought out of the glove box. The reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy at 25°C for 16 hours. After that, 2-fluoropyridine (9 µL, 0.100 mmol) was added to the same J. Young NMR tube, shaken vigorously, sealed and its ^{1}H NMR spectra were recorded at 25°C. Ratios after 5 min of addition of **20; 20a:20b:20 : 1.00:0.30:0.95**

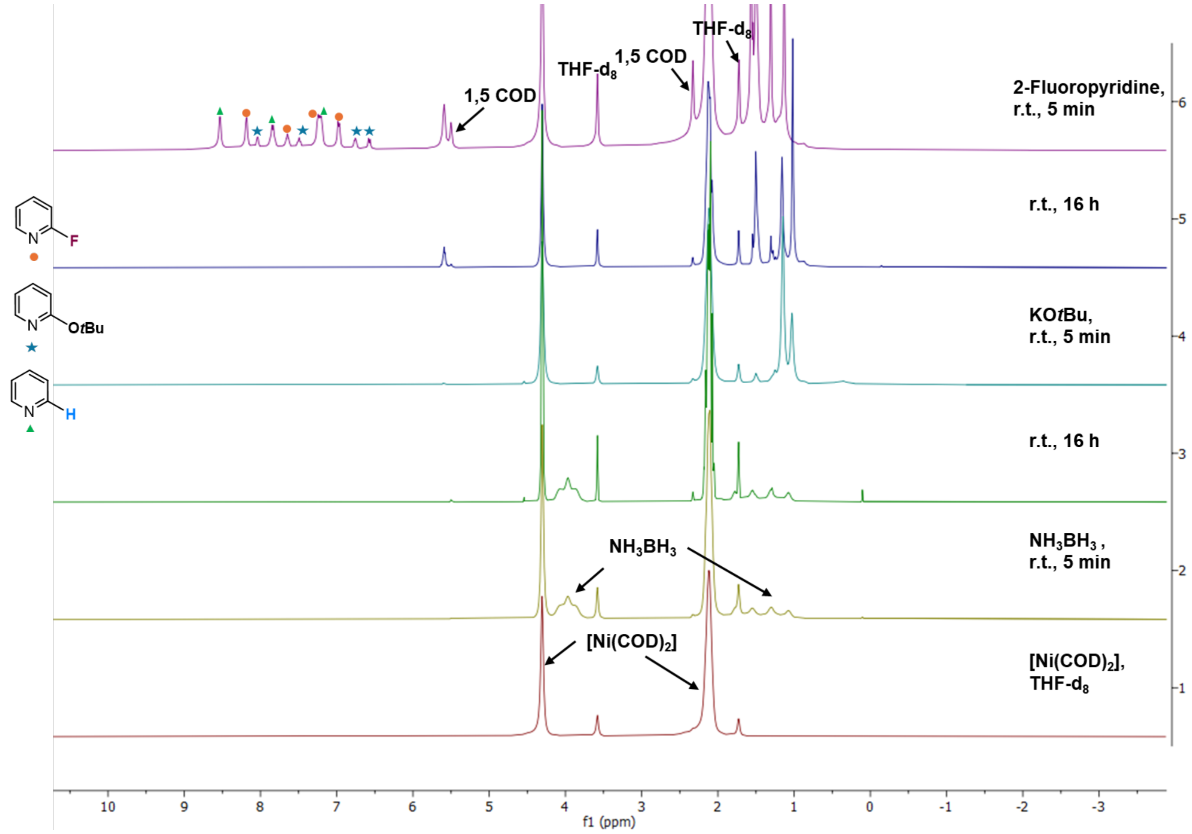
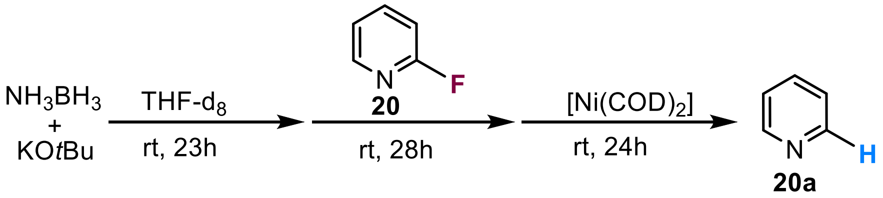


Figure S25: ^{1}H NMR spectra of stoichiometric reaction of [Ni(COD)$_2$] with NH_3BH_3 followed by the addition of KO*t*Bu and 2-fluoropyridine in THF-d_8 at rt.

16.3 NMR Monitoring of the reaction of NH_3BH_3 with KO*t*Bu followed by the addition of 2-fluoropyridine (20) and [Ni(COD)$_2$].



NH_3BH_3 (3.1 mg, 0.100 mmol) was weighed in 20 mL scintillation vial inside the glovebox, which were dissolved in 0.25 mL THF-d_8 and transferred into a J. Young NMR tube. The NMR tube was sealed, brought out of the glove box and its ^{1}H and ^{11}B NMR NMRs were registered at 25°C. The same J. Young NMR tube was moved to the glove box and KO*t*Bu (11.2 mg, 0.100 mmol) dissolved in 0.1 mL THF-d_8 was added into it, which was sealed, shaken vigorously and brought out of the glove box. The reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy at 25°C for 23 hours. After that, 2-fluoropyridine (9 µL, 0.100 mmol) was added to the same J. Young NMR tube, shaken vigorously, sealed and brought out of the glove box. The reaction was monitored by ^{1}H and ^{19}F NMR spectroscopy at 25°C for 23 hours. The same J. Young NMR tube was moved to the glove box and [Ni(COD)$_2$] (27.5 mg, 0.100 mmol) dissolved in 0.15 mL THF-d_8 was added into it, which was sealed, shaken vigorously and brought out of the glove box. The reaction was monitored by ^{1}H NMR spectroscopy at 25°C for 24 hours.

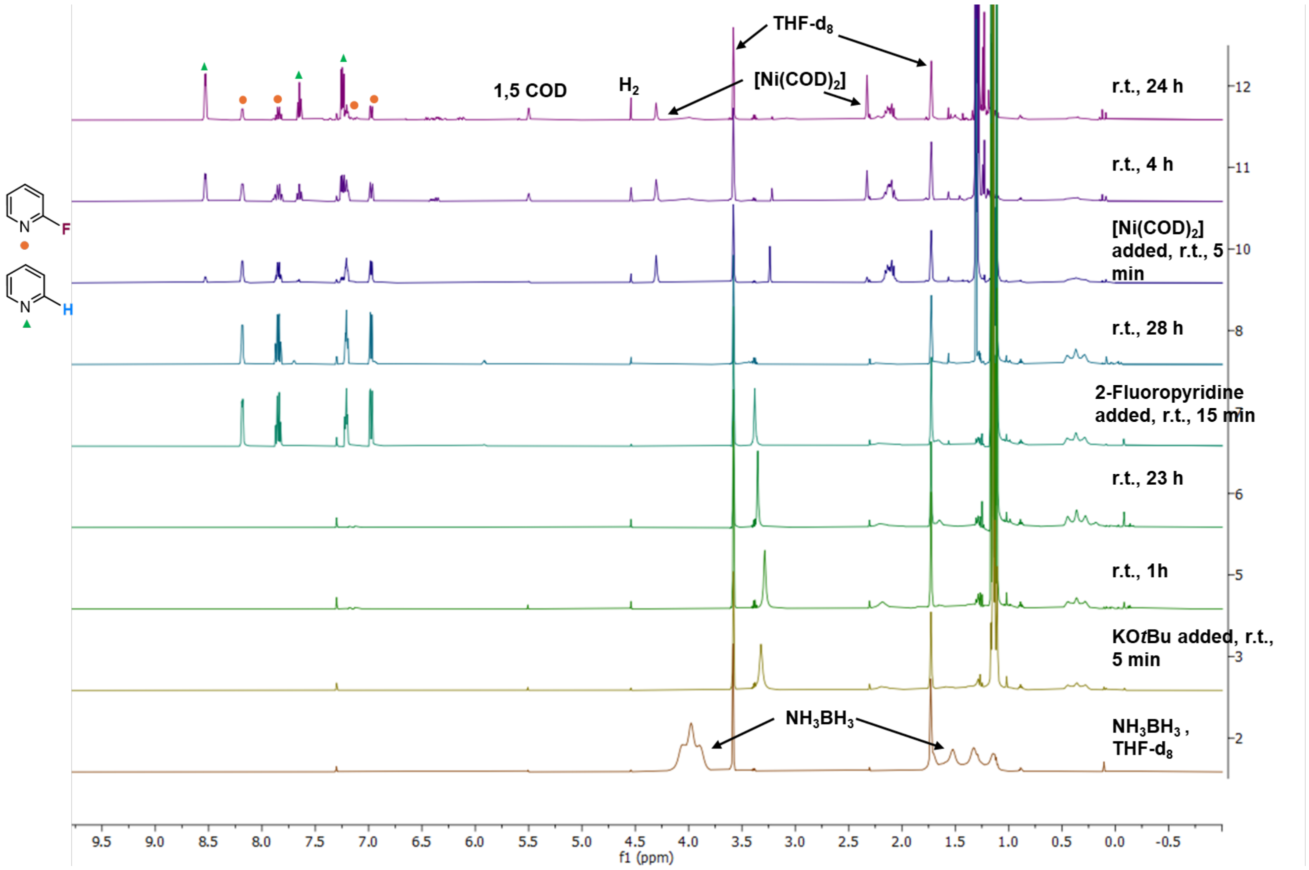
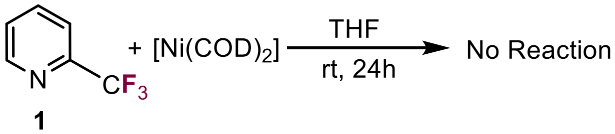


Figure S26: ^{1}H NMR spectra of stoichiometric reaction of NH_3BH_3 and KO*t*Bu followed by the addition of 2-fluoropyridine and then, [Ni(COD)$_2$] in THF-d_8 at r.t.

17. Stoichiometric reactions of $[Ni(COD)_2]$ with different components of the reaction

17.1 Stoichiometric reaction of $[Ni(COD)_2]$ with 2-trifluoromethylpyridine (1).



In an argon filled glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar and $[Ni(COD)_2]$ (27.5 mg, 0.100 mmol), to which was added 0.5 mL THF, then, added 2-trifluoromethylpyridine (12 μL, 0.100 mmol). After 24 h, ^{1}H and ^{19}F NMR were registered in C_6D_6 at 25°C. The spectra indicated the presence of unreacted starting material, with no new signals corresponding to product formation.

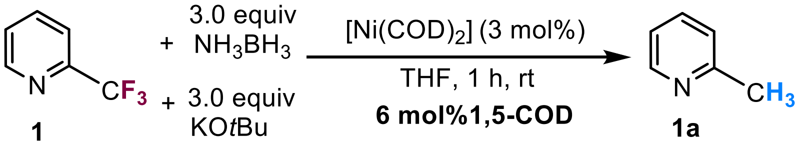
17.2 Stoichiometric reaction of $[Ni(COD)_2]$ with NH_3BH_3 and KO*t*Bu.

$$NH_3BH_3 + KOtBu \xrightarrow[\substack{[Ni(COD)_2]\\ \text{rt, 15 min}}]{\text{THF}} \text{Ni black +Free COD}$$

In an argon filled glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, NH_3BH_3 (3.1 mg, 0.100 mmol) and KO*t*Bu (11.2 mg, 0.100 mmol), which was dissolved in 0.5 mL THF, to which was added $[Ni(COD)_2]$ (27.5 mg, 0.100 mmol). After 24 h, the resulting mixture turned black in color and Ni black started precipitating out. The ^{1}H NMR was registered of the reaction mixture recorded in C_6D_6 at 25°C showed consumption of the starting materials and the appearance of signals corresponding to free 1,5-COD at 2.40 and 5.50 ppm.

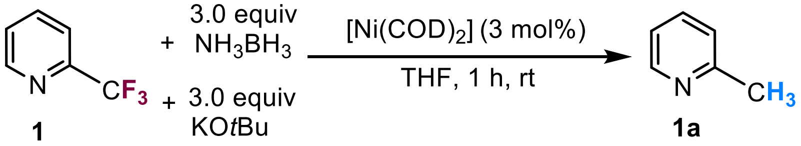
18. Effect of addition of 1,5-COD to the catalytic reaction

18.1 Catalytic reaction in the presence of 1,5-COD.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.5 mg, 0.600 mmol),KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 μL, 0.200 mmol), 1,5-COD (2 μL, 0.012 mmol) and a THF solution (0.5 mL) of the $[Ni(COD)_2]$ catalyst (1.7 mg, 0.006 mmol). The tube was sealed and stirred at rt for 1 h. After that, the reaction was exposed to air and mesitylene (10 μL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: 79%, Yield **1a**: 63%.

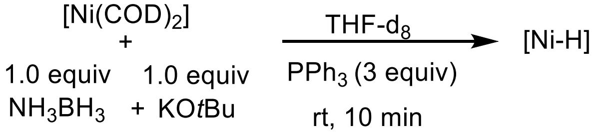
18.2 Catalytic reaction in the absence of 1,5-COD.



In an argon-filled glovebox, a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: NH_3BH_3 (18.5 mg, 0.600 mmol), KO*t*Bu (0.6 mL of a 1.0 M solution in THF, 0.600 mmol), 2-trifluoromethylpyridine (23 µL, 0.200 mmol), and a THF solution (0.5 mL) of the [Ni(COD)$_2$] catalyst (1.7 mg, 0.006 mmol). The tube was sealed and stirred at rt for 1 h. After that, the reaction was exposed to air and mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR and ^{1}H NMR spectroscopy without additional purification. Conversion **1**: 77%, Yield **1a**: 69%.

19. Experiments to trap the *in situ* formed nickel-hydride.

19.1 Reaction of [Ni(COD)$_2$] with NH_3BH_3/KO*t*Bu followed by addition of excess PPh_3.



$$\begin{array}{c}[\mathrm{Ni(COD)_2}]\\ +\\ \begin{array}{cc}1.0\text{ equiv} & 1.0\text{ equiv}\\ \mathrm{NH_3BH_3} & +\ \mathrm{KO}t\mathrm{Bu}\end{array}\end{array} \xrightarrow[\substack{\mathrm{PPh_3}\text{ (3 equiv)}\\ \text{rt, 10 min}}]{\text{THF-}d_8} [\text{Ni-H}]$$

In an argon filled glovebox, a 20 ml scintillation vial was charged with NH_3BH_3 (1.5 mg, 0.050 mmol) and KO*t*Bu (5.6 mg, 0.050 mmol), which were dissolved in 0.2 mL THF-d_8 and transferred into a J. Young NMR tube. To the same tube was added [Ni(COD)$_2$] (13.7 mg, 0.050 mmol) dissolved in 0.15 mL of THF-d_8, and then added PPh_3 (39.3 mg, 0.150 mmol). The resulting mixture turned maroon instantly. The tube was sealed, shaken vigorously and brought out of the glovebox and its ^{1}H and ^{31}P NMR were registered at 25°C.

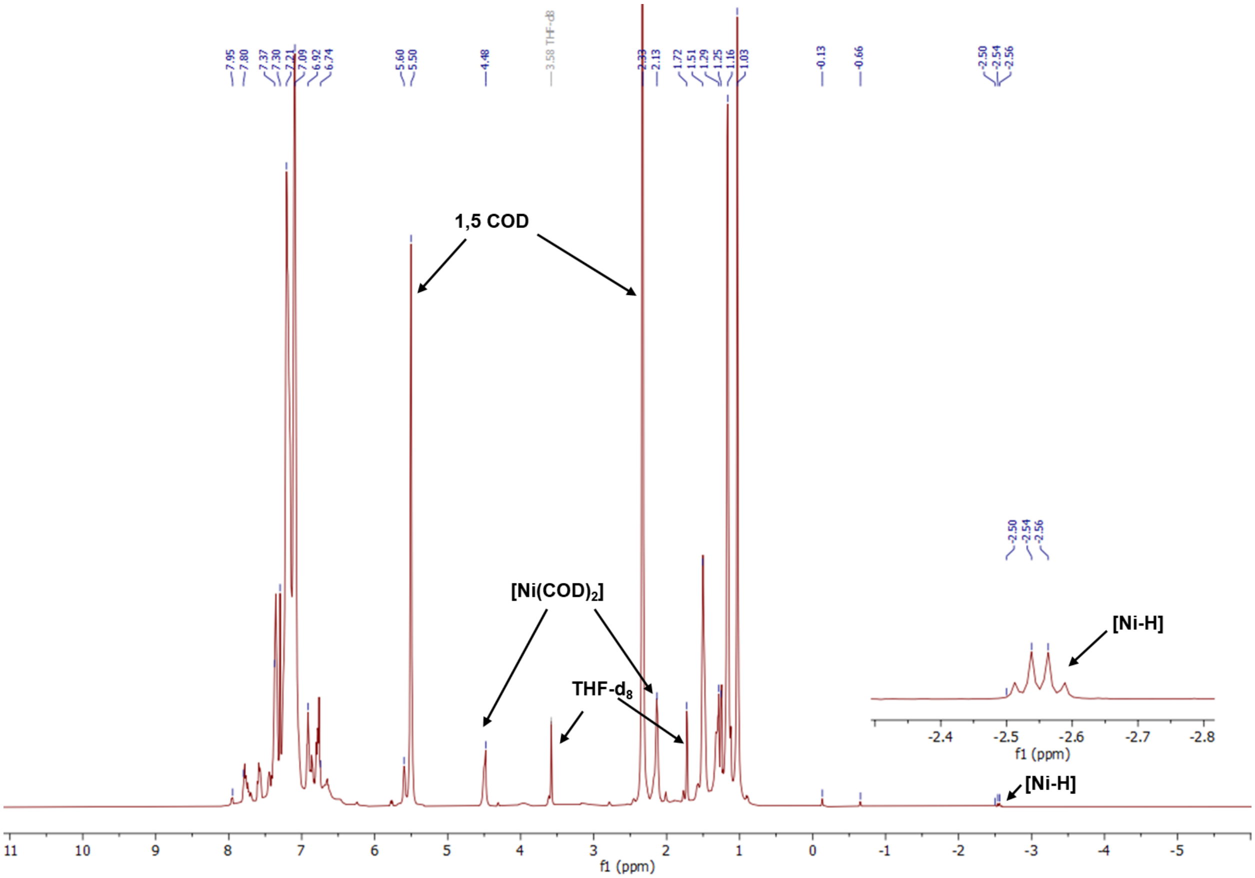


Figure S27: Crude ^{1}H NMR spectrum of [Ni-H] in THF-d_8 at 25°C.

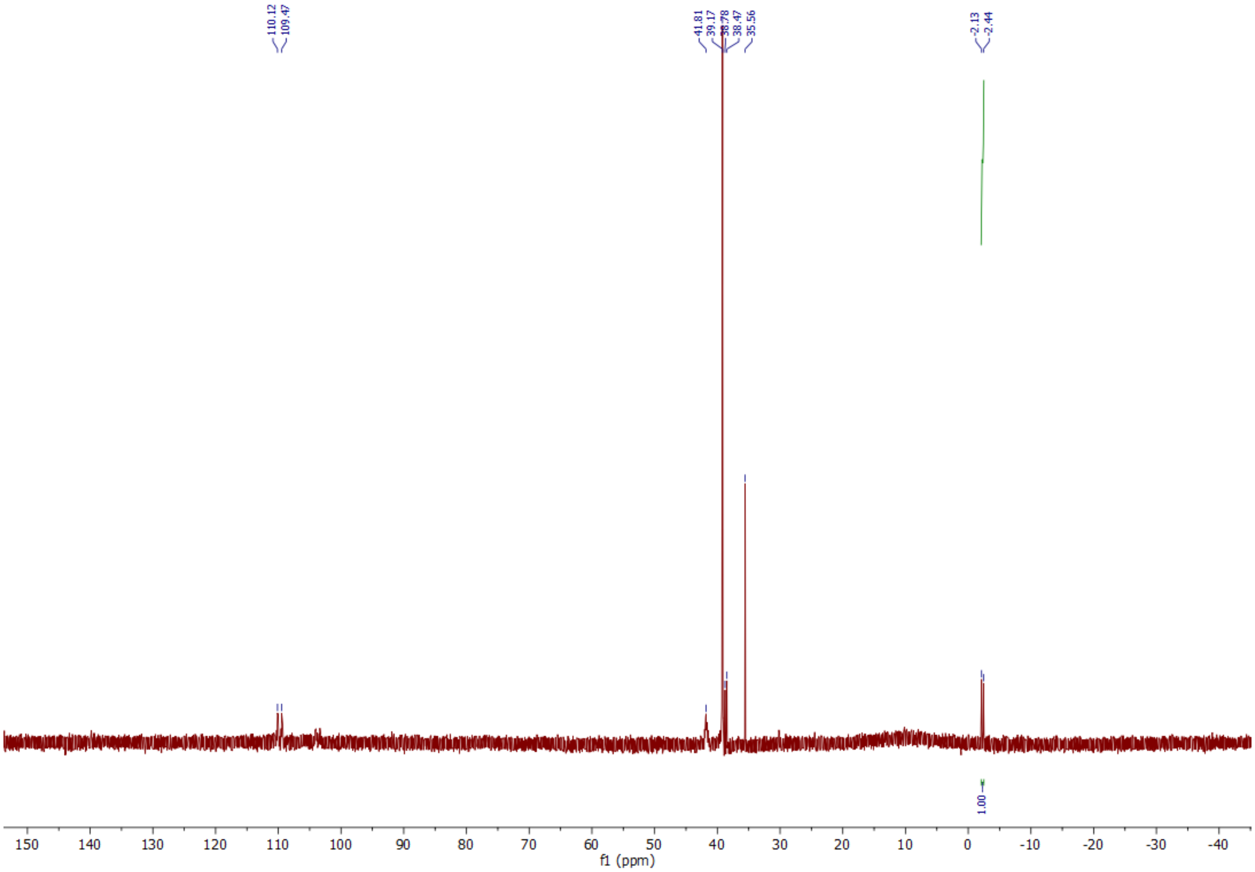


Figure S28: Crude ^{31}P NMR spectrum of [Ni-H] in THF-d_8 at 25°C.

19.2 Reaction of NH_3BH_3/KO*t*Bu with [Ni(COD)$_2$] followed by addition of excess PPh_3.

$$\begin{matrix}\text{1.0 equiv} \\ NH_3BH_3\end{matrix} + \begin{matrix}\text{1.0 equiv} \\ \text{KO}t\text{Bu}\end{matrix} \xrightarrow{\text{THF}} \xrightarrow[\text{rt, 5 min}]{[\text{Ni(COD)}_2]} \xrightarrow[\text{rt, 5 min}]{\begin{matrix}PPh_3 \\ \text{(3 equiv)}\end{matrix}} [\text{Ni-H}]$$

In an argon filled glovebox, a 20 ml scintillation vial was charged with a magnetic stir bar, NH_3BH_3 (1.5 mg, 0.050 mmol) and KO*t*Bu (5.6 mg, 0.050 mmol), which were dissolved in 0.2 mL THF. To this was added, [Ni(COD)$_2$] (13.7 mg, 0.050 mmol) dissolved in 0.15 mL of THF. The contents were stirred for 5 minutes and then added PPh_3 (39.3 mg, 0.100 mmol). The resulting mixture turned maroon instantly, which was stirred for additional 5 minutes. Volatiles were removed under vacuum, and the resulting maroon sticky solid was washed with hexane (5 mL) and diethyl ether (5 mL). After removal of solvents under vacuum, a maroon powder was obtained, which was dissolved in THF-d_8, transferred to a J. Young NMR tube and its ^{1}H and ^{31}P NMR were registered at 25°C.

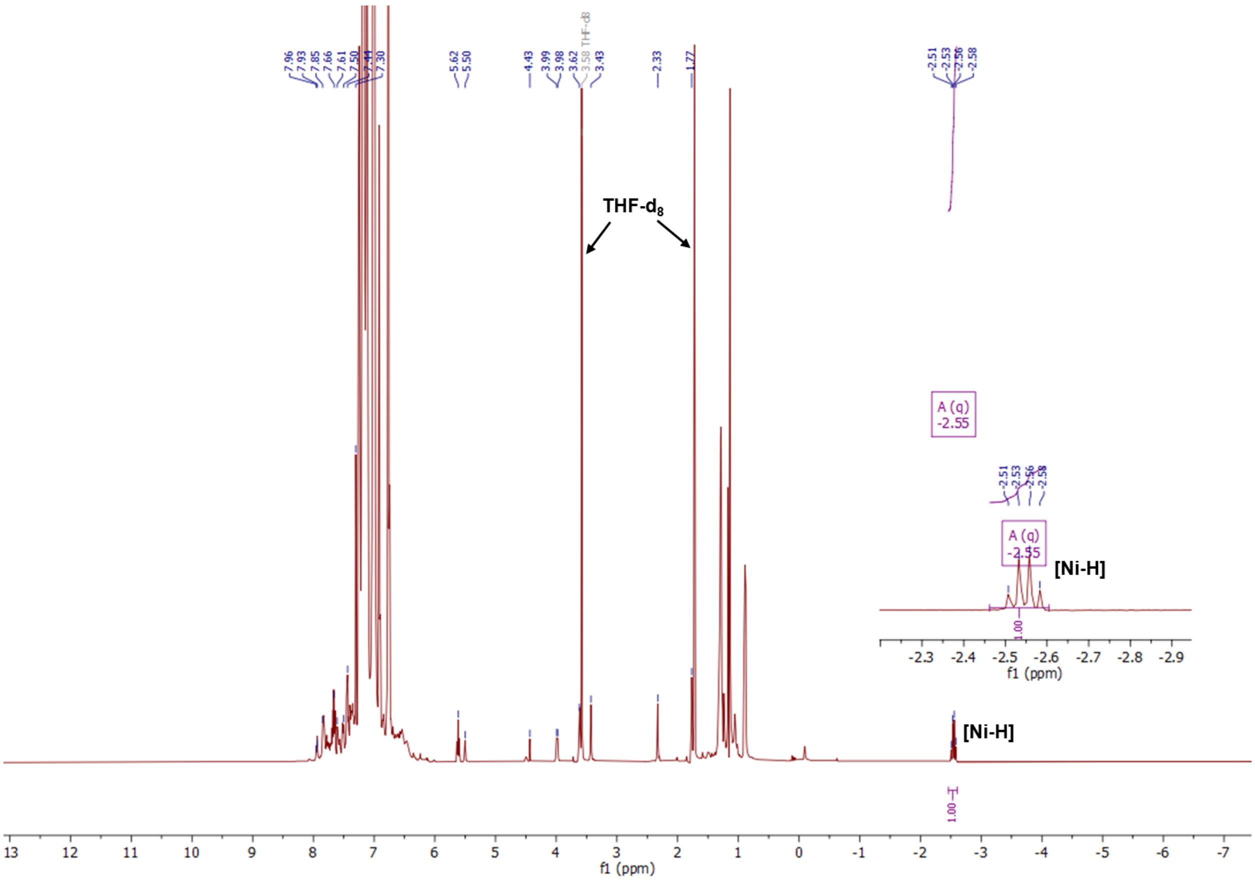


Figure S29: ^{1}H NMR spectrum of [Ni-H] attempted to isolate in THF-d_8 at 25°C.

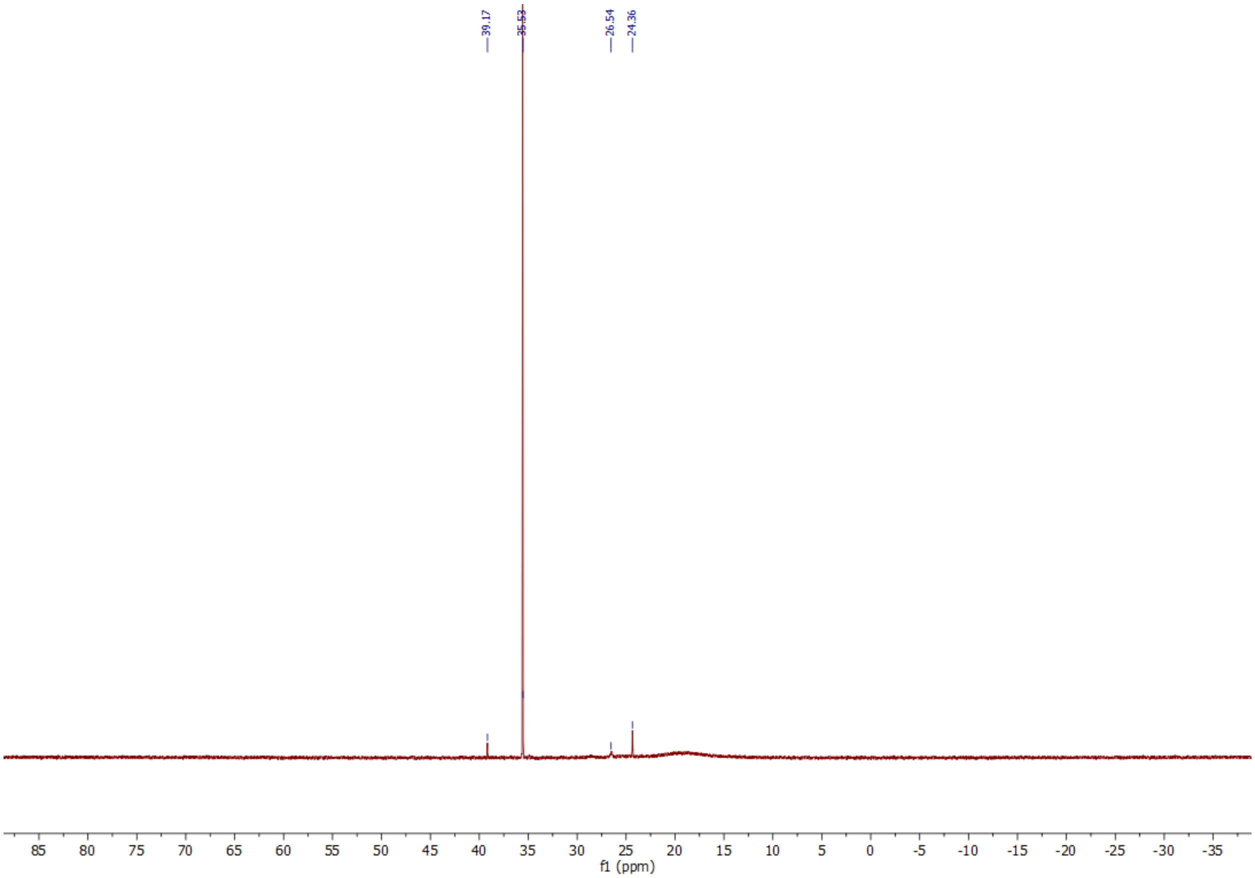
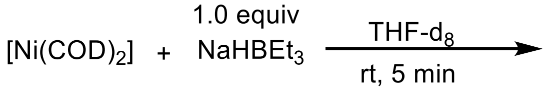


Figure S30: ^{31}P NMR spectrum of [Ni-H] attempted to isolate in THF-d_8 at 25°C.

19.3 Reaction of [Ni(COD)$_2$] with NaHBEt$_3$.



$$[\mathrm{Ni(COD)_2}] + \overset{\text{1.0 equiv}}{\mathrm{NaHBEt_3}} \xrightarrow[\text{rt, 5 min}]{\text{THF-}d_8}$$

In an argon-filled glovebox, a 20 mL scintillation vial was charged with NaHBEt$_3$ (50 μL of a 1.0 M solution in THF, 0.050 mmol). The solvent was removed under vacuum, and the residue was redissolved in 0.2 mL of THF-d_8. This solution was transferred to a J. Young NMR tube containing [Ni(COD)$_2$] (13.7 mg, 0.050 mmol) previously dissolved in 0.2 mL of THF-d_8.The tube was sealed, shaken vigorously and brought out of the glovebox and its ^{1}H and ^{31}P NMR were registered at 25°C.

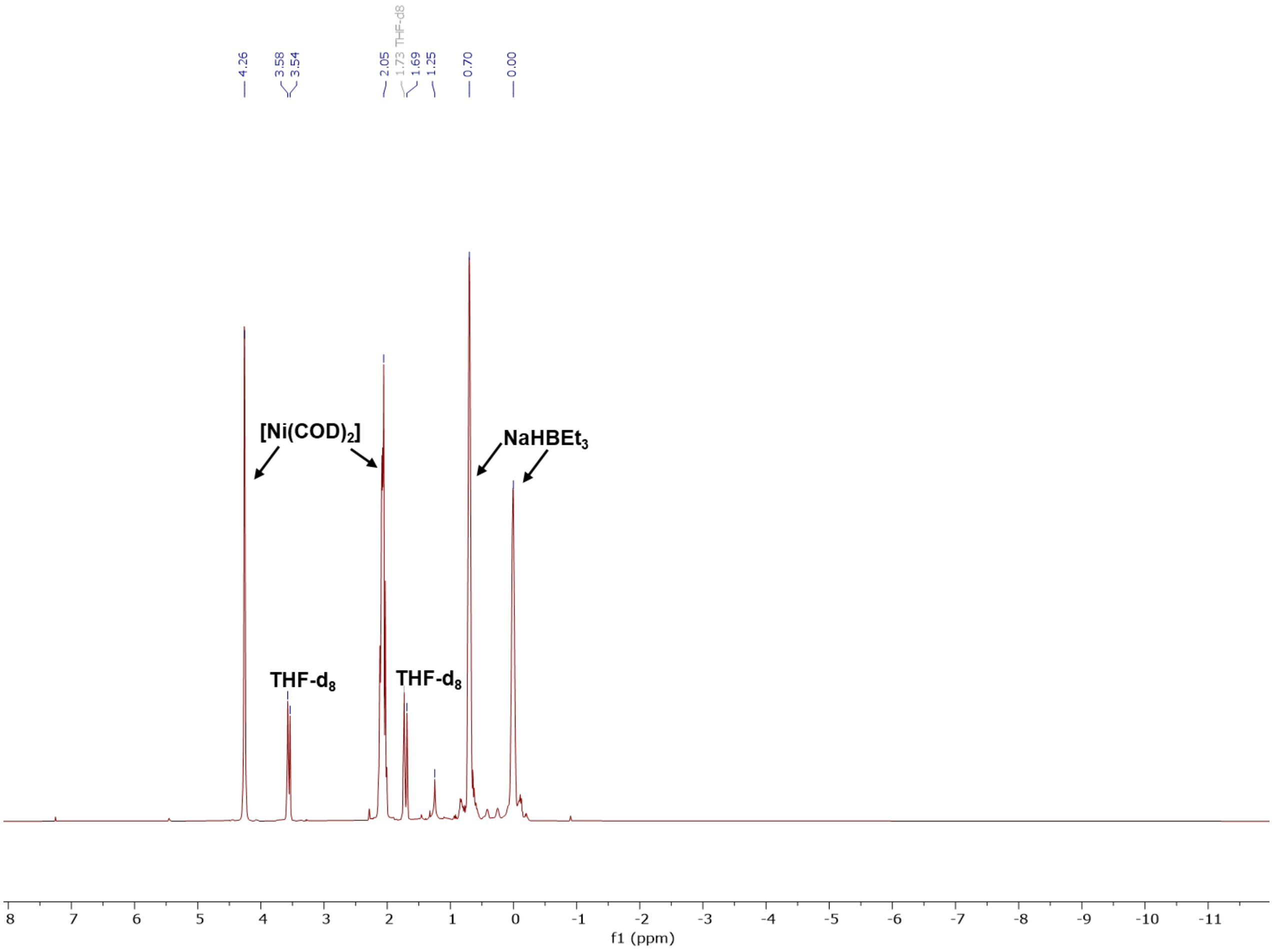


Figure S31: ^{1}H NMR spectrum of the reaction [Ni(COD)$_2$] of NaHBEt$_3$

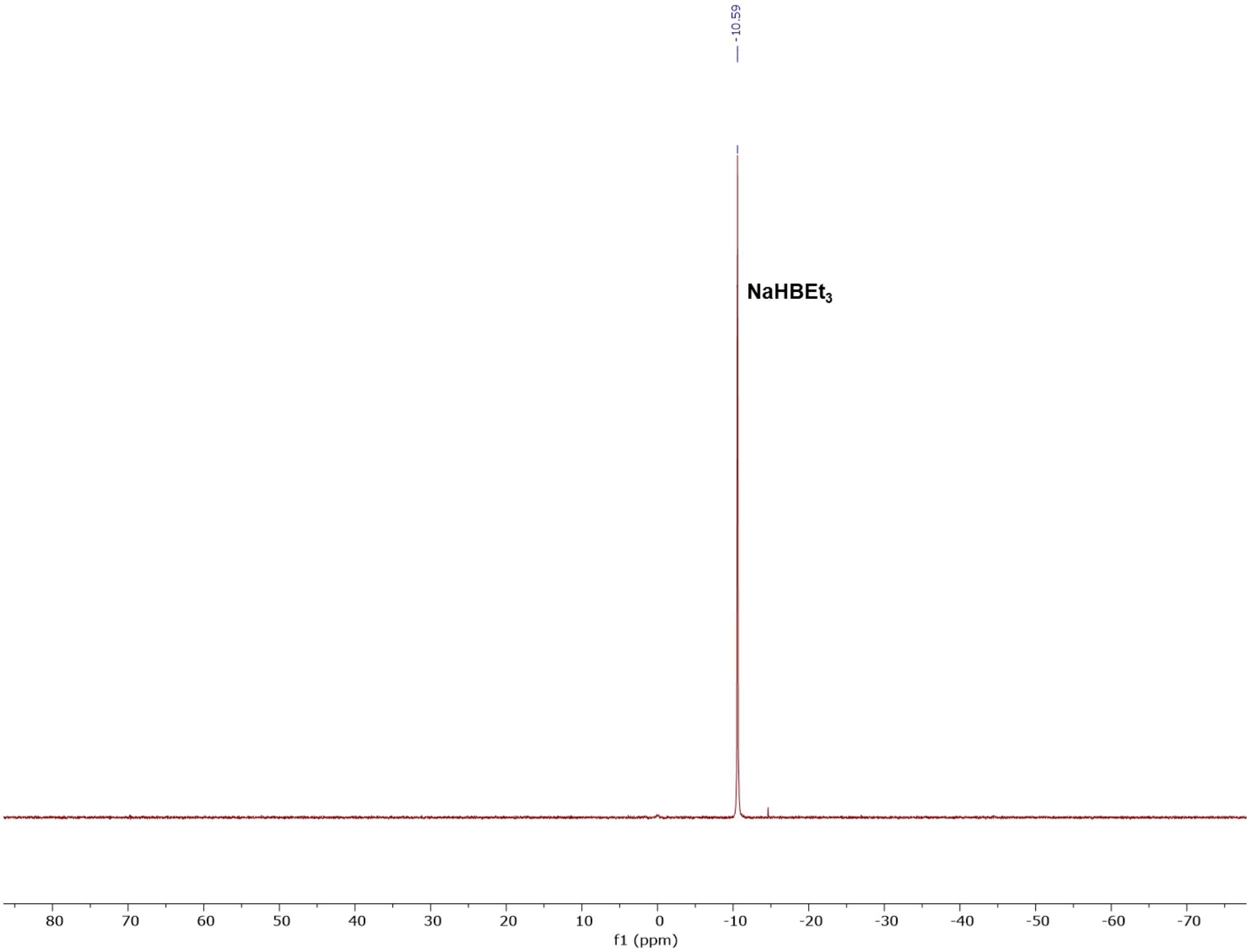


Figure S32: ^{11}B NMR spectrum of the reaction [Ni(COD)$_2$] of NaHBEt$_3$

20. Characterization of the solid formed during the catalytic HDF of 2-trifluoromethylpyridine (1). The catalytic reaction was conducted following the general procedure mentioned in section 2.1 using 2-trifluoromethylpyriidne. The solid formed during the catalytic reaction was filtered out and dissolved in D_2O to register its ^{19}F NMR.

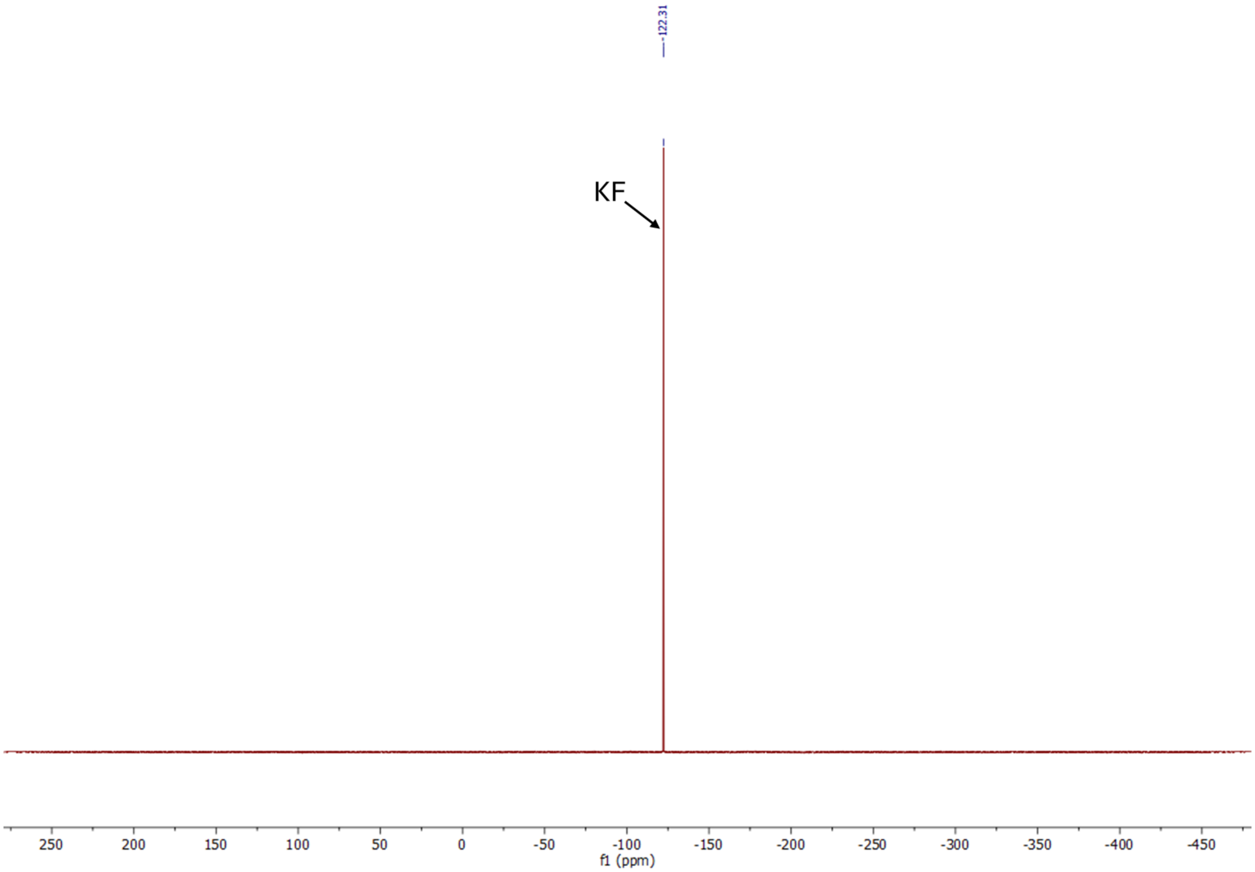
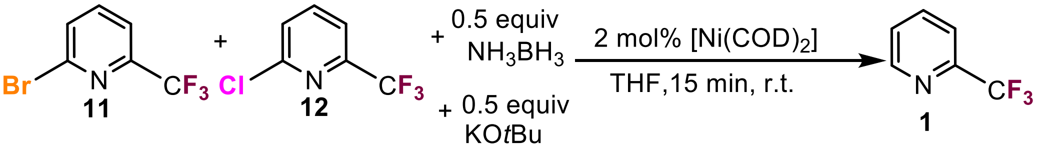


Figure S33: ^{19}F NMR spectrum of the solid formed during the catalytic reaction in D_2O at 25°C.

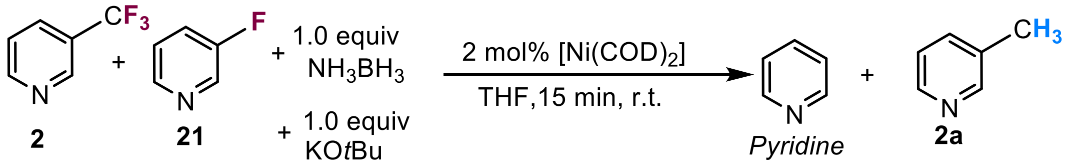
21. Competition experiments:

21.1 Competition experiment employing pyridines with C(sp^2)-Cl or C(sp^2)-Br bonds



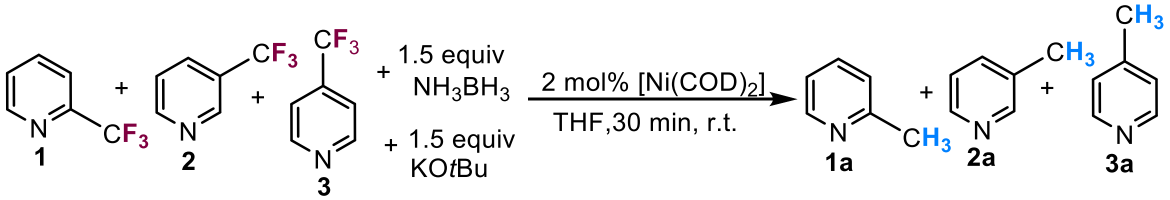
In an argon-filled glovebox, two separate 20 mL scintillation vials were charged with 2-bromo-6-(trifluoromethyl)pyridine (113 mg, 0.50 mmol) and 2-chloro-6-(trifluoromethyl)pyridine (91 mg, 0.50 mmol), each dissolved in 0.6 mL THF. The reaction vial, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with NH_3BH_3 (7.7 mg, 0.25 mmol), KO*t*Bu (0.25 mL of a 1.0 M solution in THF, 0.25 mmol), and [Ni(COD)$_2$] (2.75 mg, 0.010 mmol). The two substrate solutions were then added to the reaction vial. The mixture was stirred at room temperature for 15 minutes, after which mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was analyzed directly by ^{19}F NMR and ^{1}H NMR spectroscopy without further purification. Conversion of **11**: 53%; Conversion of **12**: 13%.

21.2 Competition experiment employing pyridines with C(sp^2)-F or C(sp^3)-F bonds



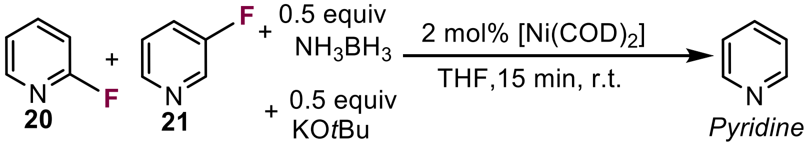
In an argon-filled glovebox, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with NH_3BH_3 (7.7 mg, 0.25 mmol), KO*t*Bu (0.25 mL of a 1.0 M solution in THF, 0.25 mmol), [Ni(COD)$_2$] (2.75 mg, 0.010 mmol), 3-trifluoromethylpyridine (57.7 µL, 0.5 mmol), 3-fluoropyridine (43 µL, 0.5 mmol) and THF (1.25 mL). The mixture was stirred at room temperature for 15 minutes, after which mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was analyzed directly by ^{19}F NMR and ^{1}H NMR spectroscopy without further purification. Conversion of **2**: 10%; Conversion of **21**: 17%.

21.3 Competition employing pyridines with the CF_3 group at different positions of the ring (2 *vs* 3 *vs* 4)



In an argon-filled glovebox, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with NH_3BH_3 (11.6 mg, 0.38 mmol), KO*t*Bu (0.38 mL of a 1.0 M solution in THF, 0.38 mmol), [Ni(COD)$_2$] (2.75 mg, 0.010 mmol), 2-trifluoromethylpyridine (28.8 µL, 0.25 mmol), 3-trifluoromethylpyridine (28.8 µL, 0.25 mmol), 4-trifluoromethylpyridine (28.8 µL, 0.25 mmol), and THF (1.25 mL). The mixture was stirred at room temperature for 30 minutes, after which mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was analyzed directly by ^{19}F NMR and ^{1}H NMR spectroscopy without further purification. Conversion of **1**: 0% ; Conversion of **2**: 13%; Conversion of **3**: 33%.

21.4 Competition experiment employing pyridines with the C(sp^2)-F bond at different positions of the ring (2 *vs* 3).



In an argon-filled glovebox, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with NH_3BH_3 (7.7 mg, 0.25 mmol), KO*t*Bu (0.25 mL of a 1.0 M solution in THF, 0.25 mmol), [Ni(COD)$_2$] (2.75 mg, 0.010 mmol), 2-fluoropyridine (43 µL, 0.5 mmol), 3-fluoropyridine (43 µL, 0.5 mmol) and THF (1.25 mL). The mixture was stirred at room temperature for 15 minutes, after which mesitylene (10 µL, 0.070 mmol) was added as an internal standard. The crude reaction mixture was analyzed directly by ^{19}F NMR and ^{1}H NMR spectroscopy without further purification. Conversion of **20**: 20% ; Conversion of **21**: 20%.

22. Crude NMR spectra of hydrodehalogenated (HDH) products.

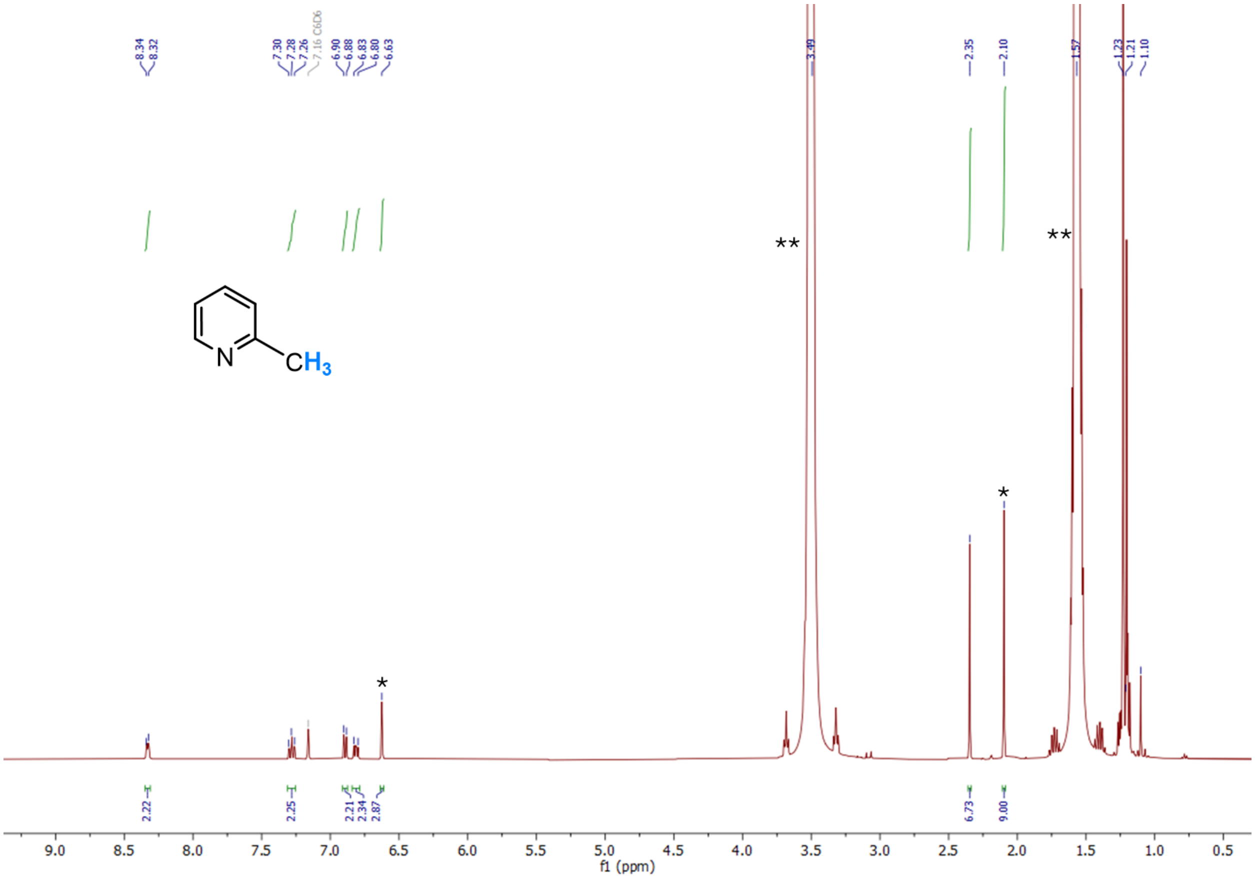


Figure S28: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 2-methylpyridine (**1a**) using 2-trifluoromethylpyridine as the starting material.
*= Internal standard (Mesitylene)
**= THF

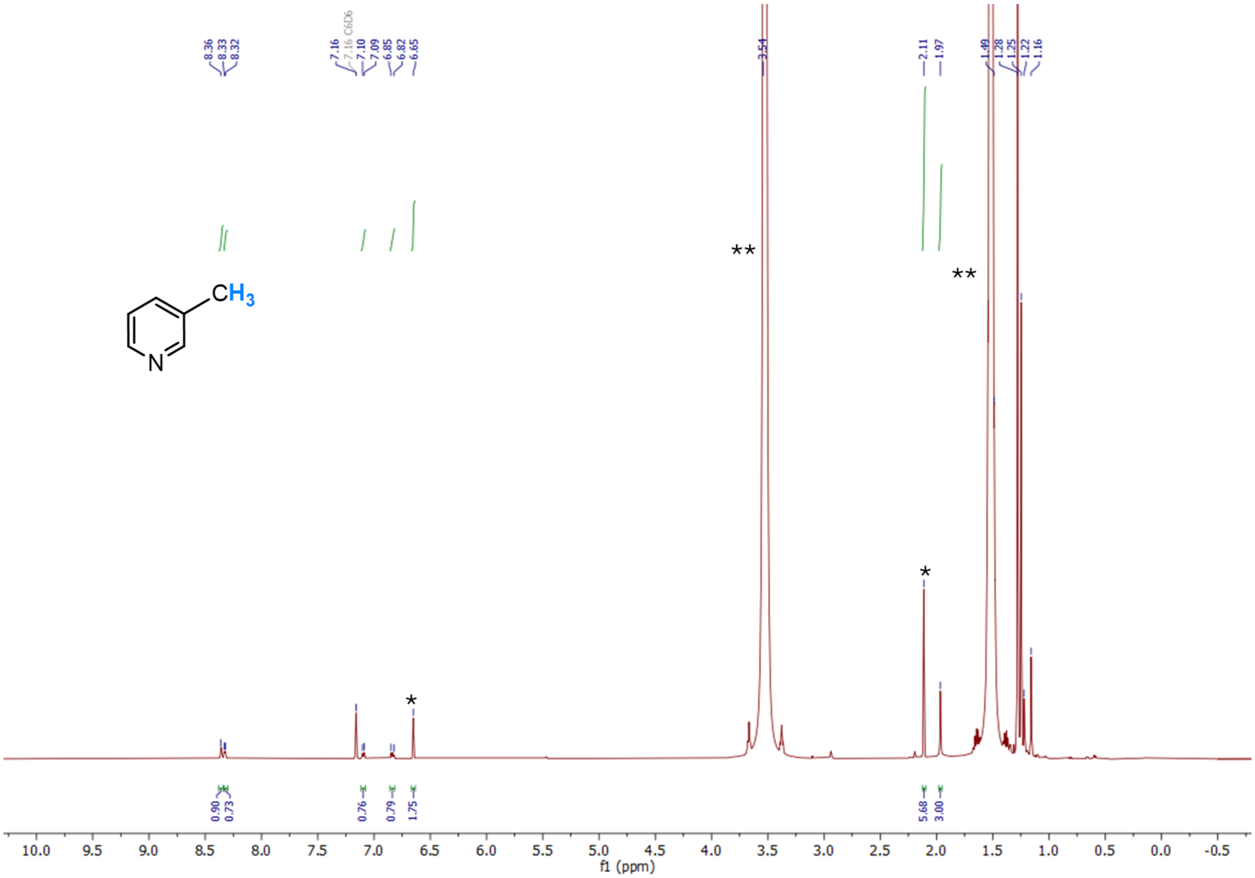


Figure S29: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 3-methylpyridine (**2a**).
*= Internal standard (Mesitylene)
**= THF

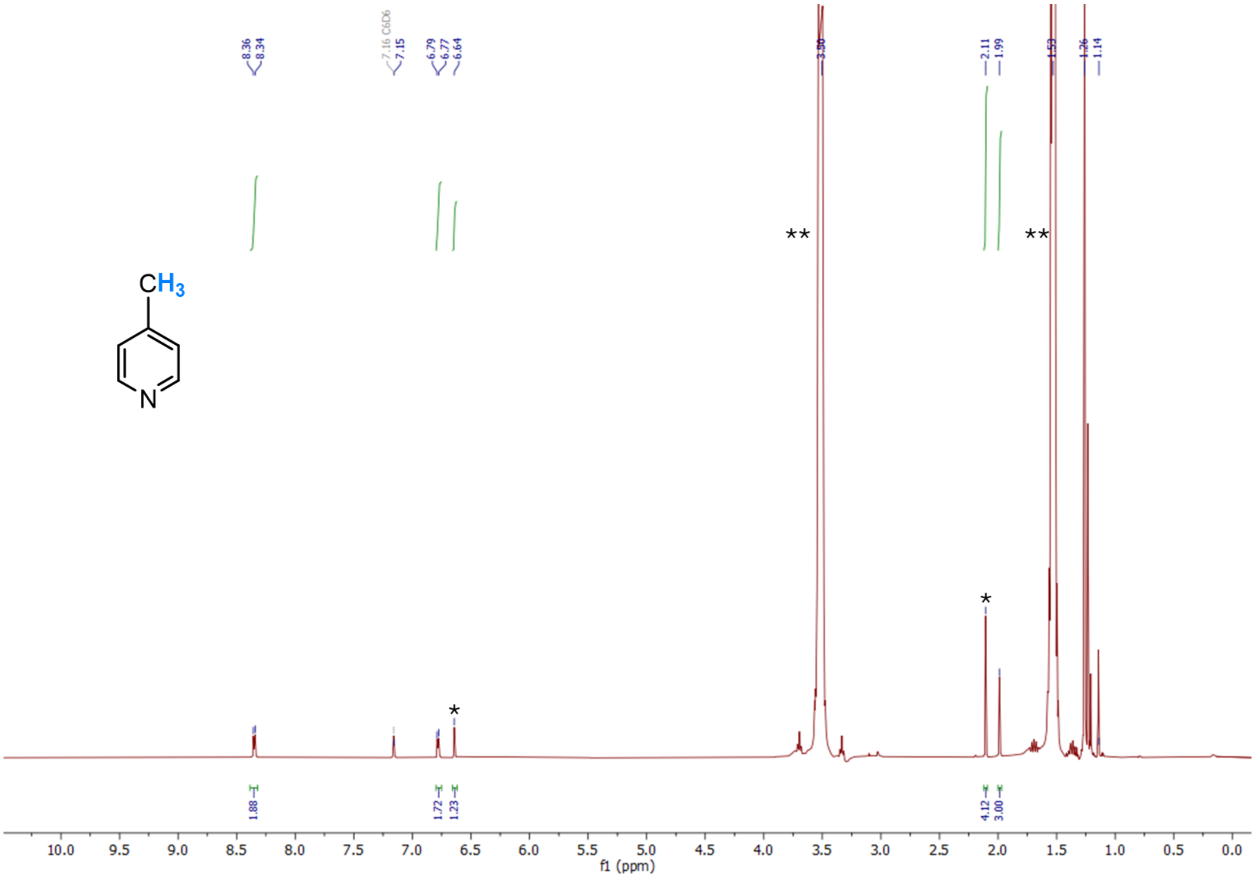


Figure S30: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 4-methylpyridine (**3a**) using 4-trifluoromethylpyridine as the starting material.
*= Internal standard (Mesitylene)
**= THF

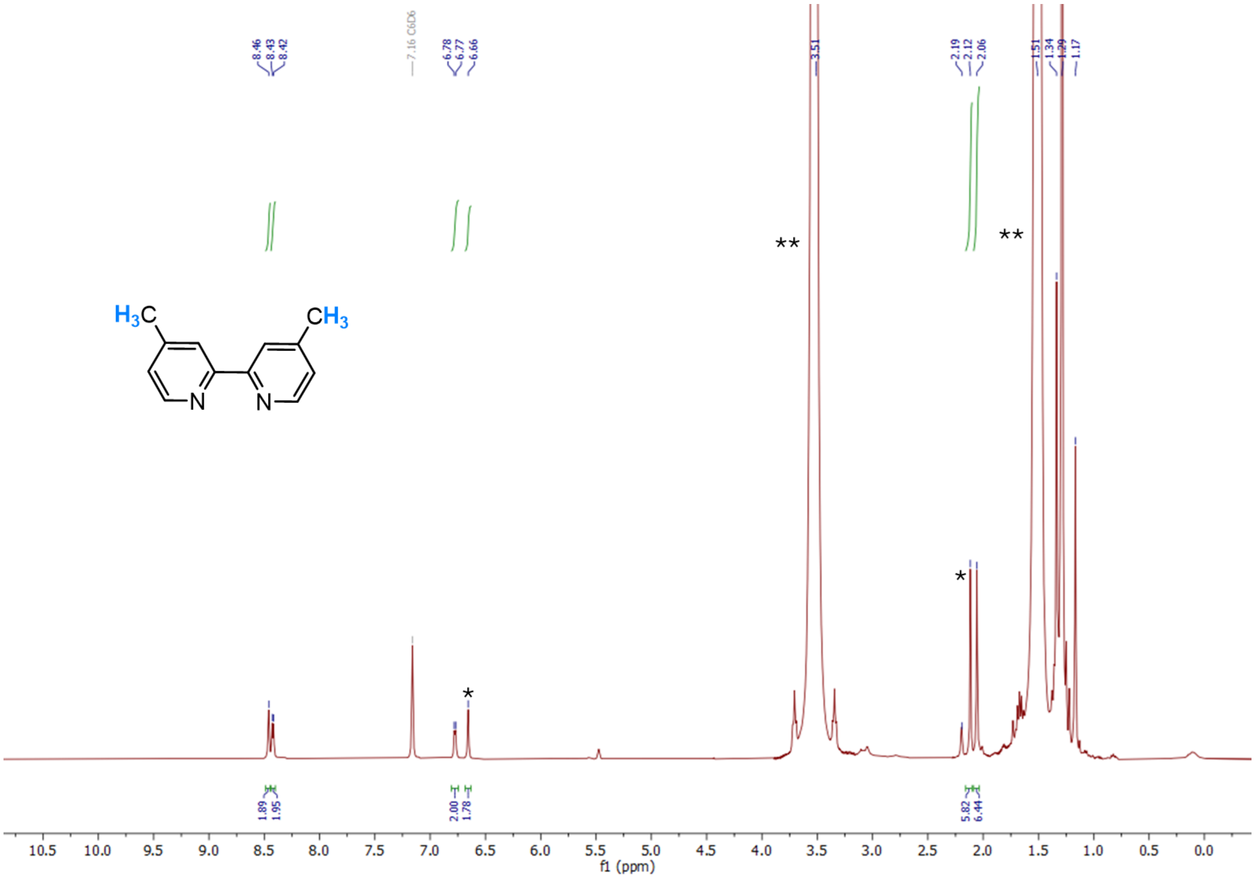


Figure S31: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 4,4'-dimethyl-2,2'-bipyridyl (**4a**).
*= Internal standard (Mesitylene)
**= THF

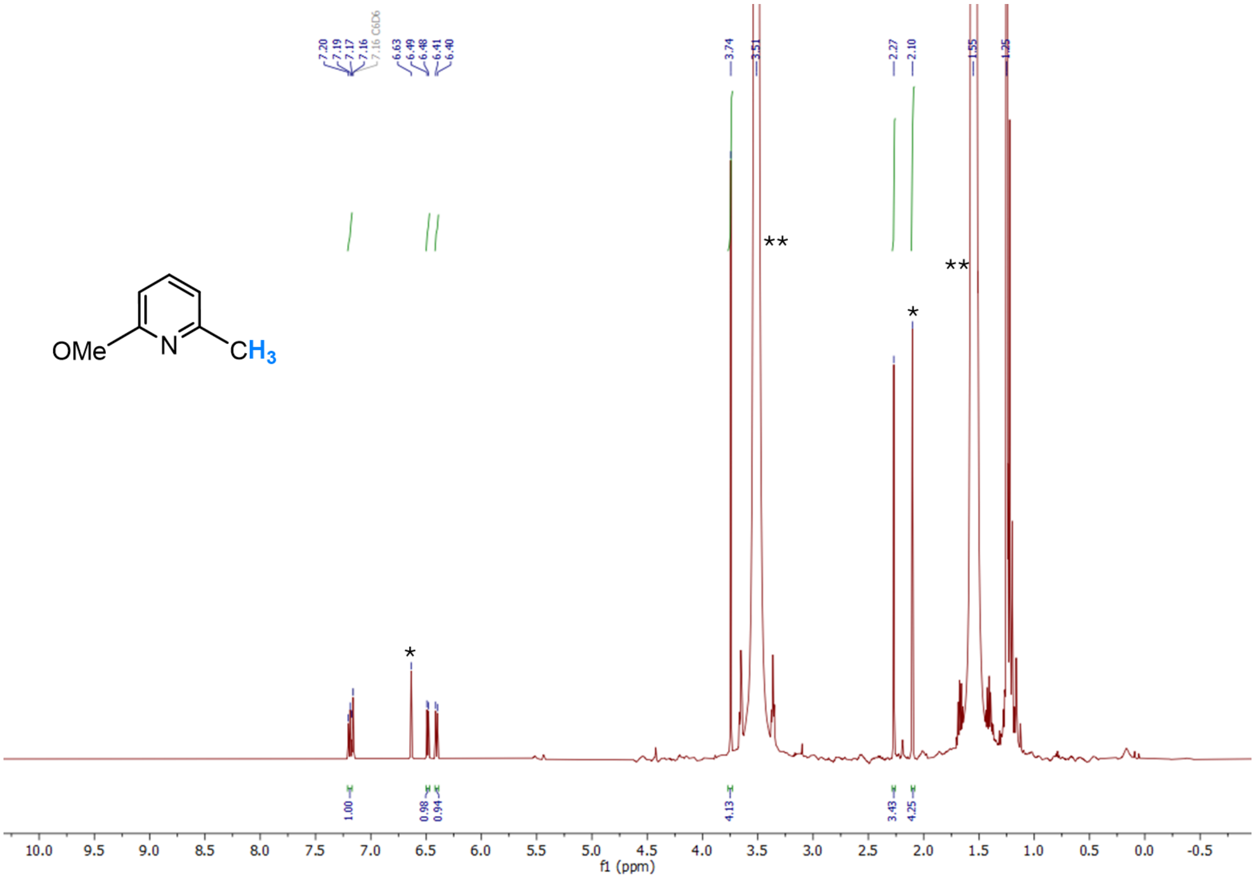


Figure S32: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 2-methoxy-6-methylpyridine (**5a**).
*= Internal standard (Mesitylene)
**= THF

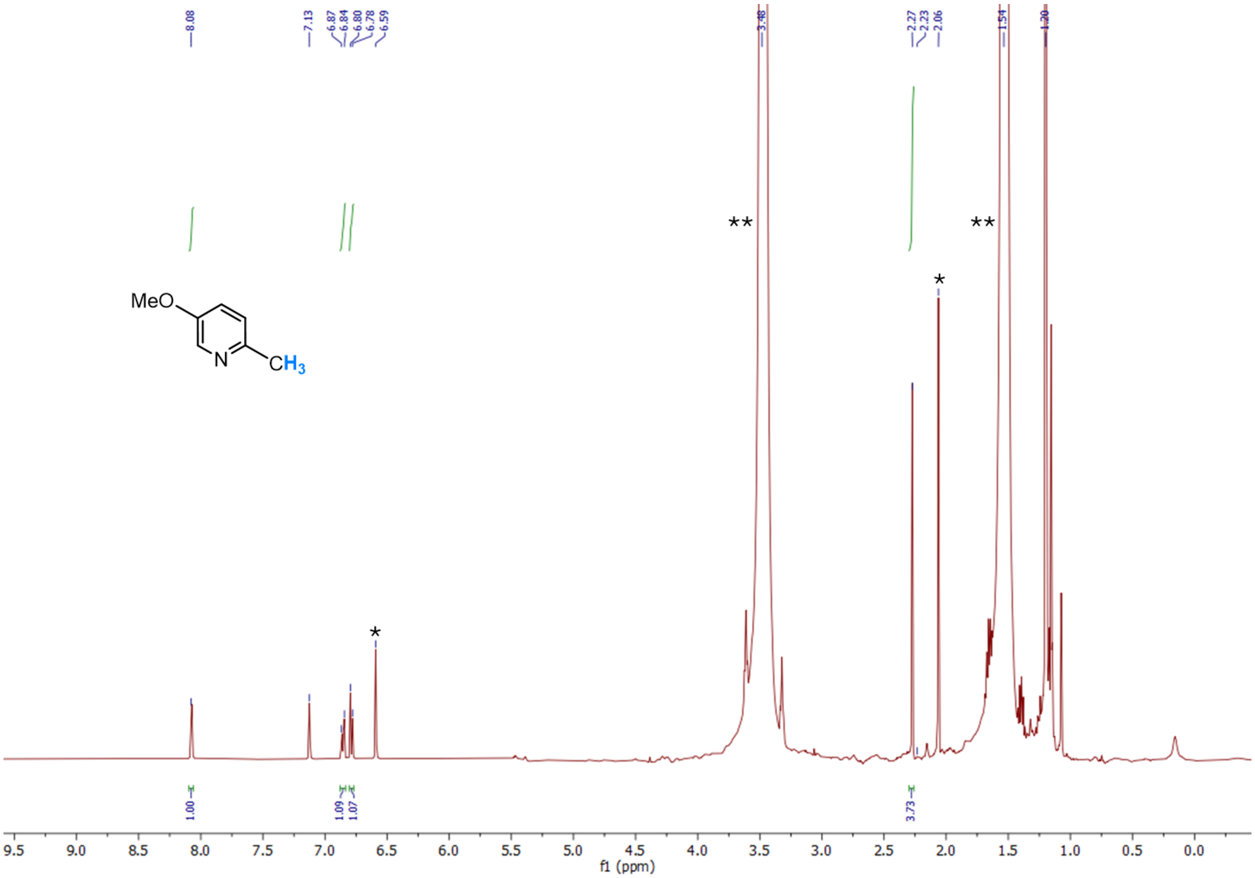


Figure S33: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 5-methoxy-2-methylpyridine (**6a**).
*= Internal standard (Mesitylene)
**= THF

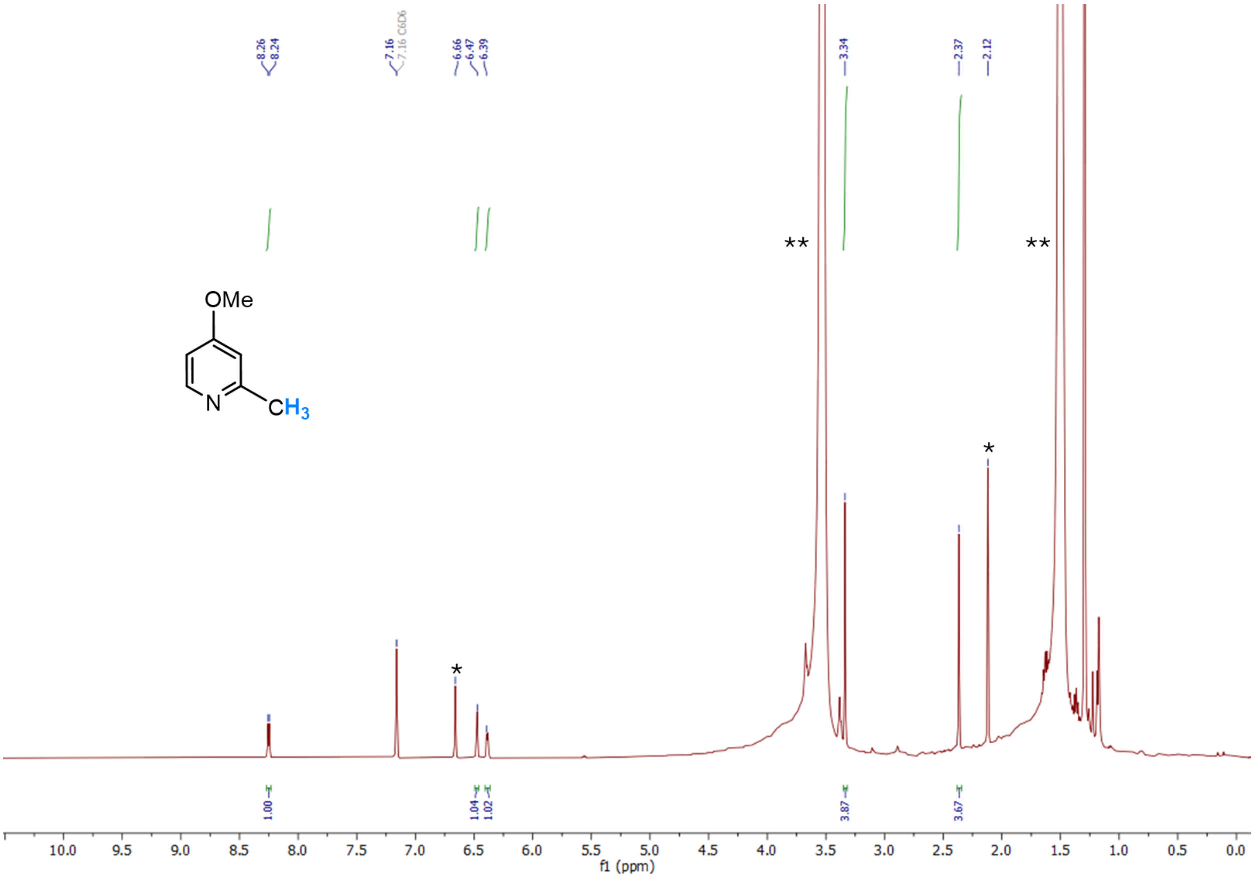


Figure S34: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 4-methoxy-2-methylpyridine (**7a**).
*= Internal standard (Mesitylene)
**= THF

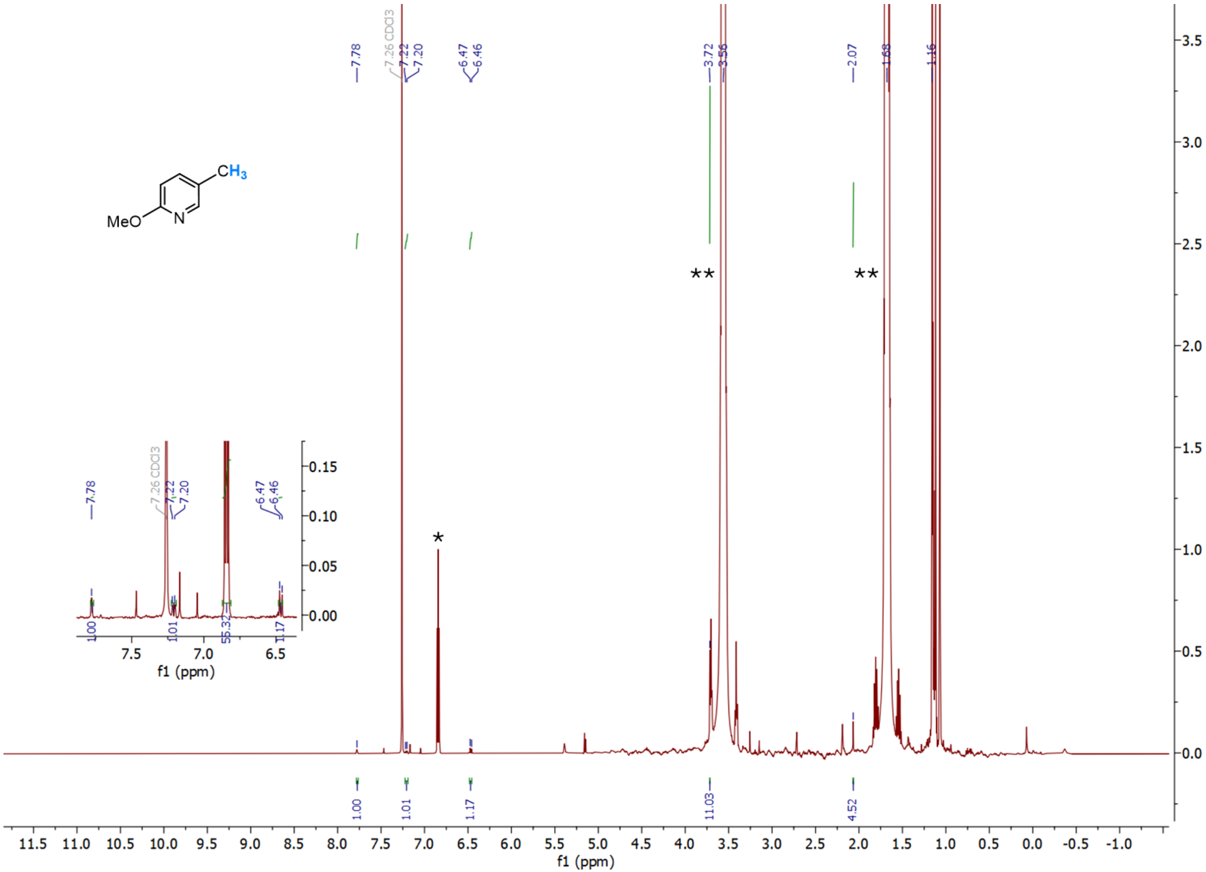


Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of 2-methoxy-5-methylpyridine (**8a**).
*= Internal standard (1,4-difluorobenzene)
**= THF

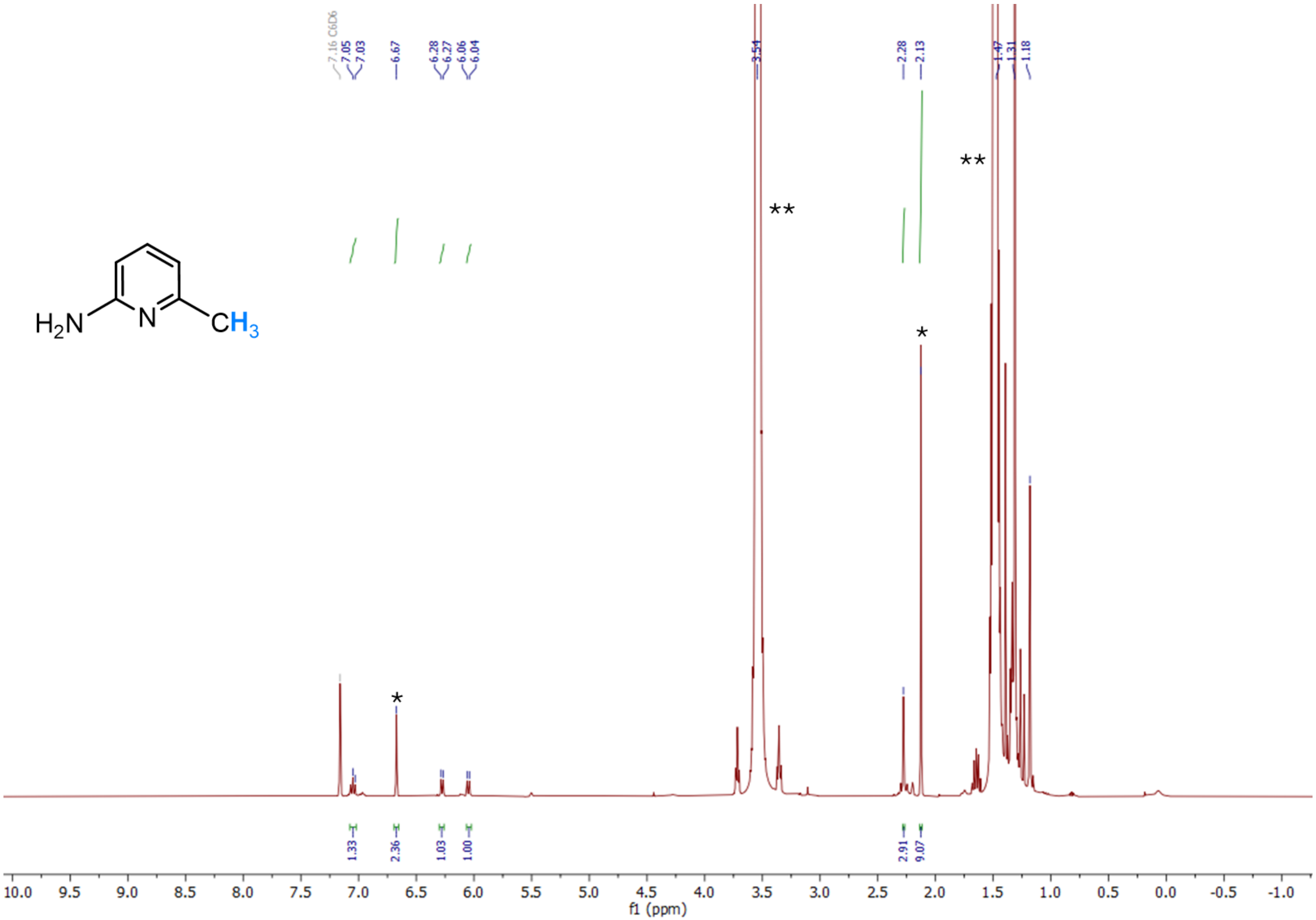


Figure S36: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 2-amino-6-methylpyridine (**9a**).
*= Internal standard (Mesitylene)
**= THF

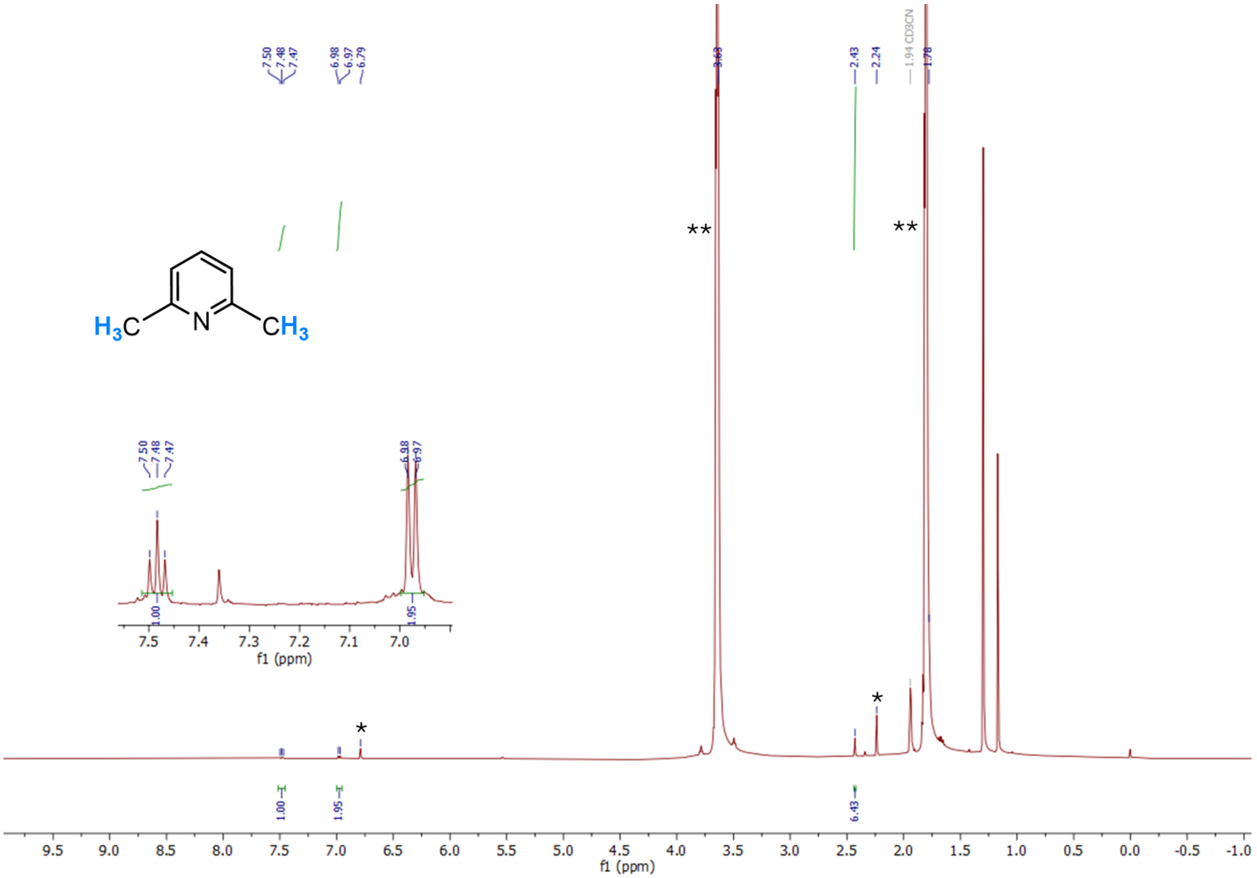


Figure S37: ^{1}H NMR (400 MHz, CD_3CN, 25 ºC) of 2,6-dimethylpyridine (**10a**).
*= Internal standard (Mesitylene)
**= THF

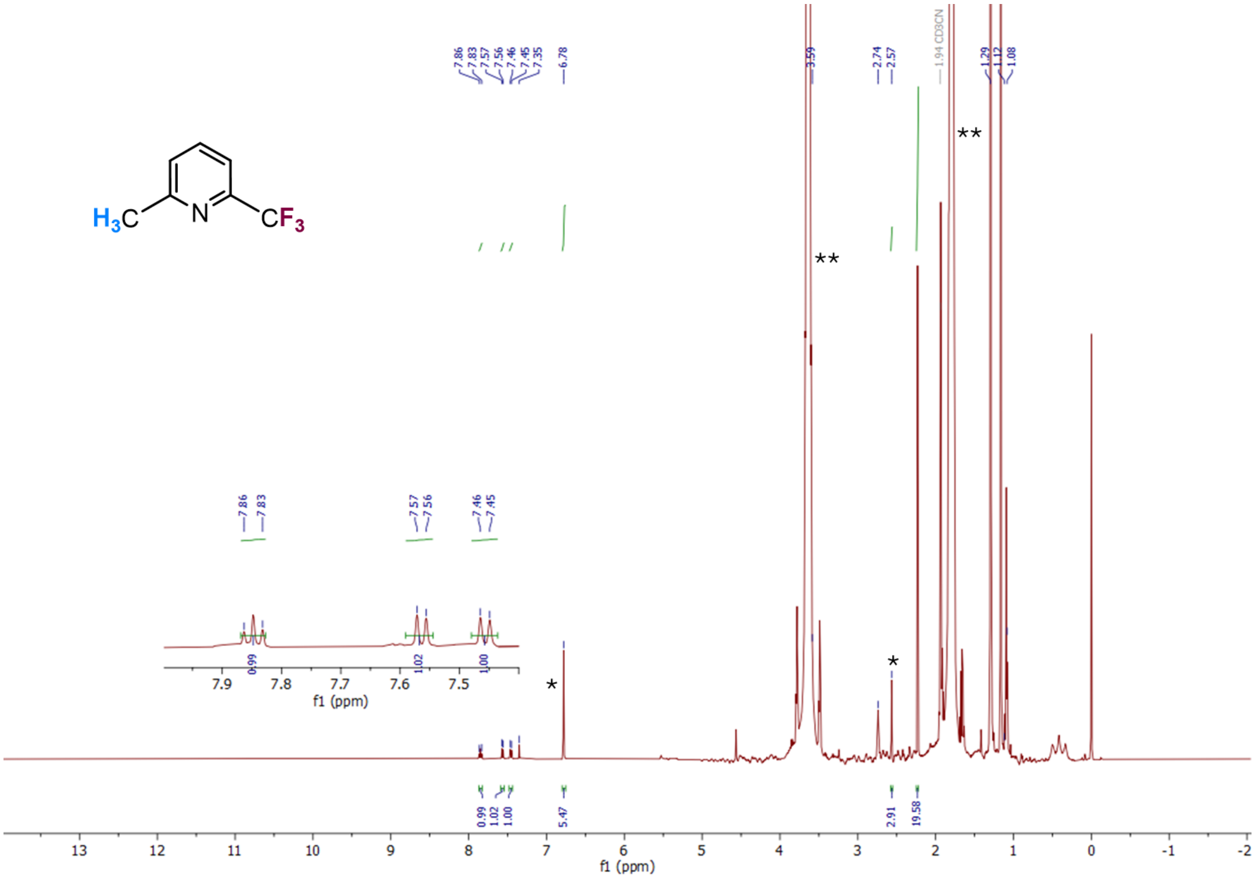


Figure S38: ^{1}H NMR (400 MHz, CD_3CN, 25 ºC) of 2-trifluoromethyl-6-methylpyridine (**10a’**).
*= Internal standard (Mesitylene)
**= THF

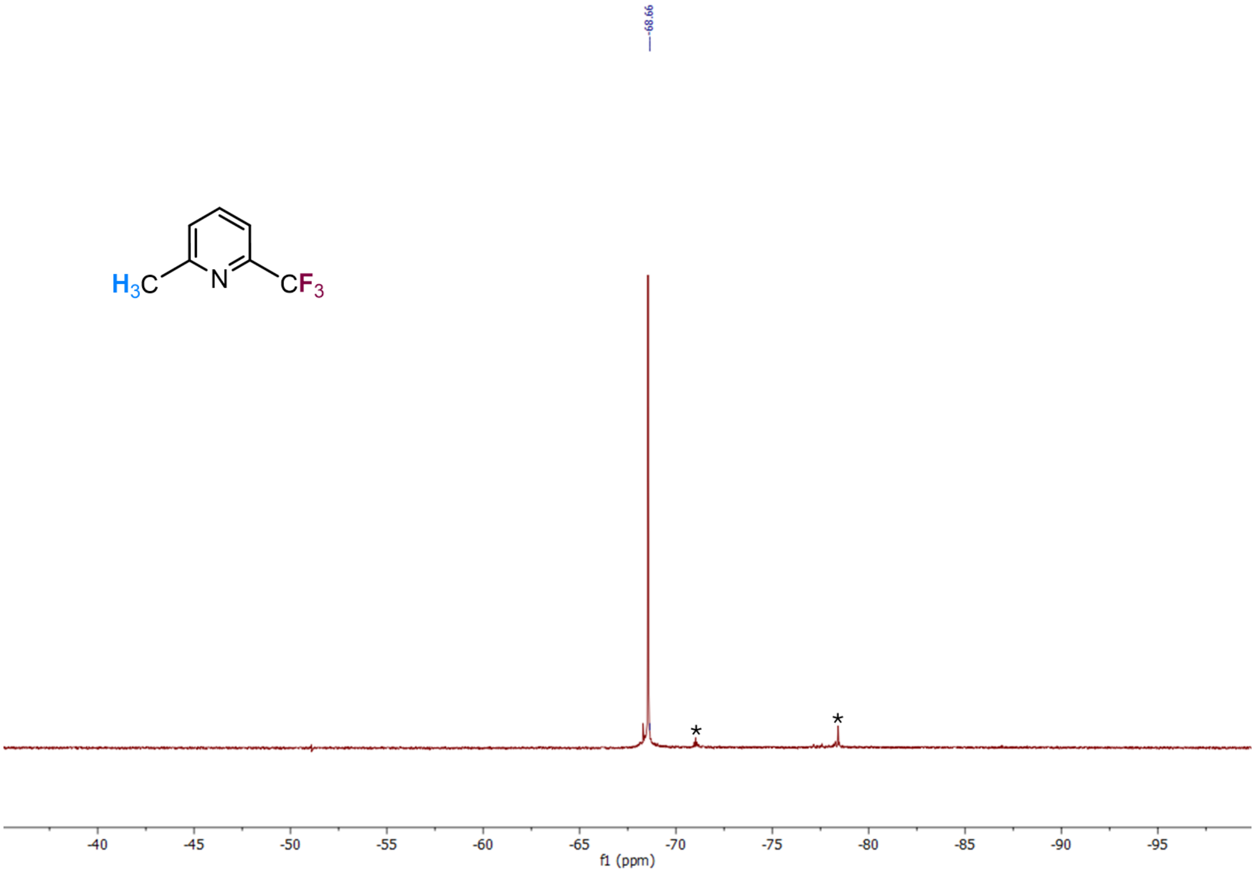


Figure S39: ^{19}F NMR (400 MHz, C_6D_6, 25 ºC) of 2-trifluoromethyl-6-methylpyridine (**10a’**).
*= Unidentified impurities

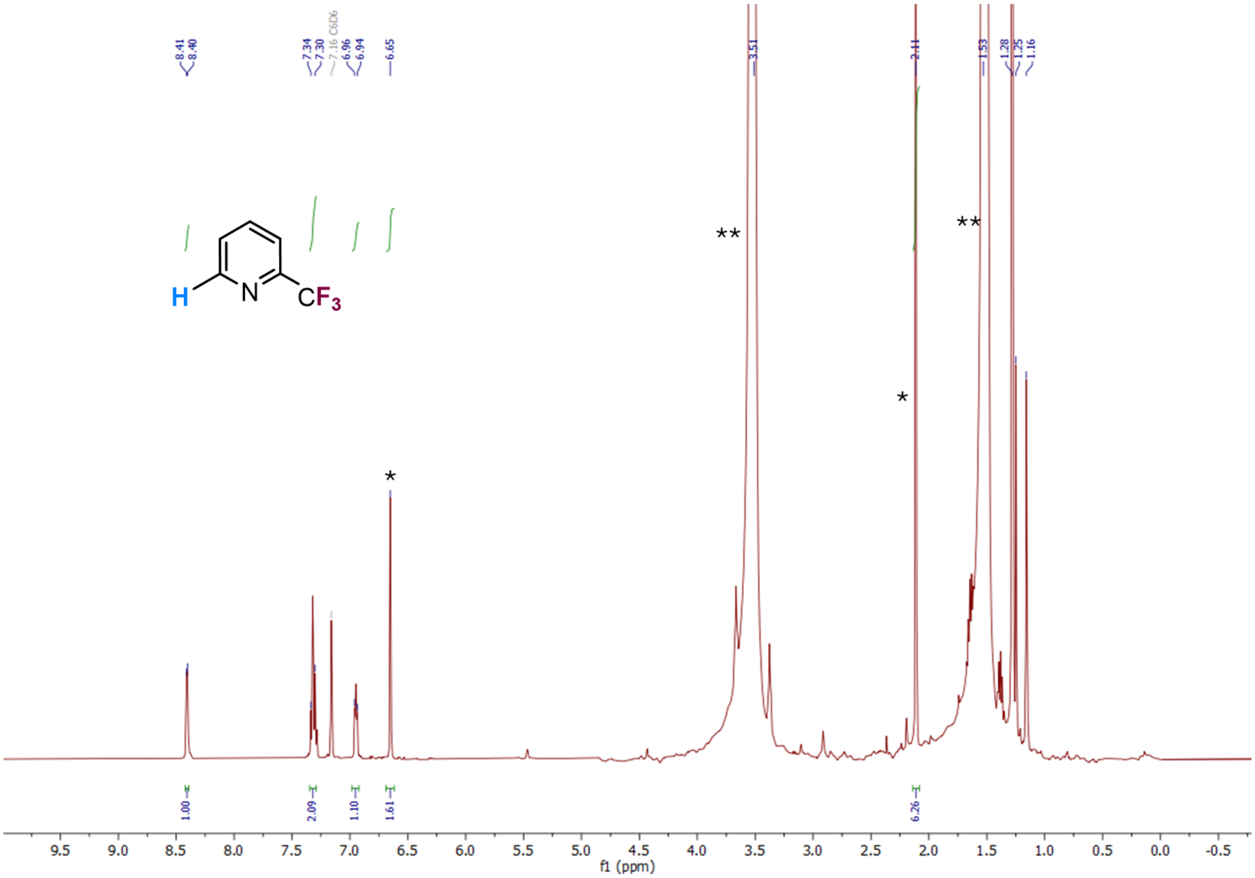


Figure S40: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 2-trifluoromethyl pyridine (**1**) using 2-chloro-6-trifluoromethylpyridine as the starting material.
*= Internal standard (Mesitylene)
**= THF

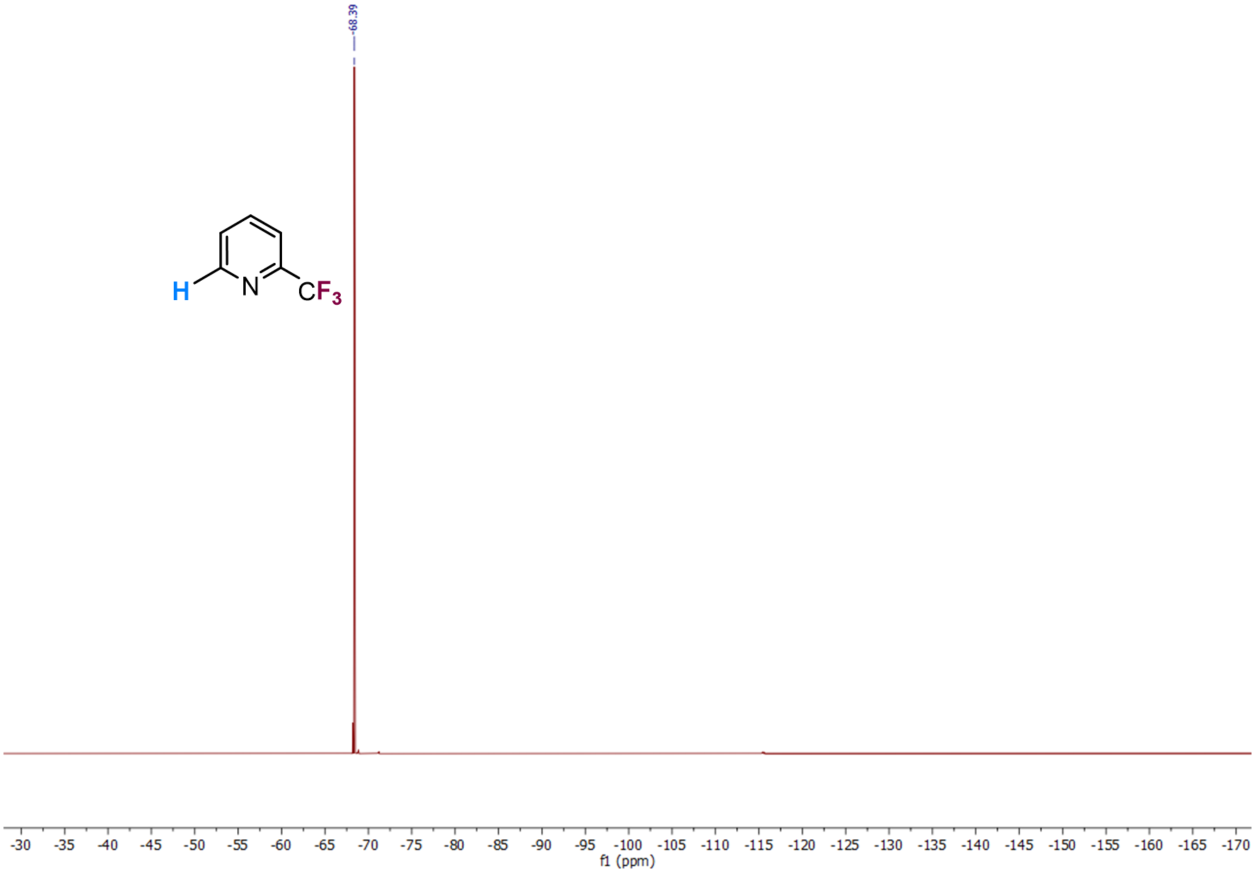


Figure S41: ^{19}F NMR (400 MHz, C_6D_6, 25 ºC) of 2-trifluoromethyl pyridine (**1**) using 2-chloro-6-trifluoromethylpyridine as the starting material.

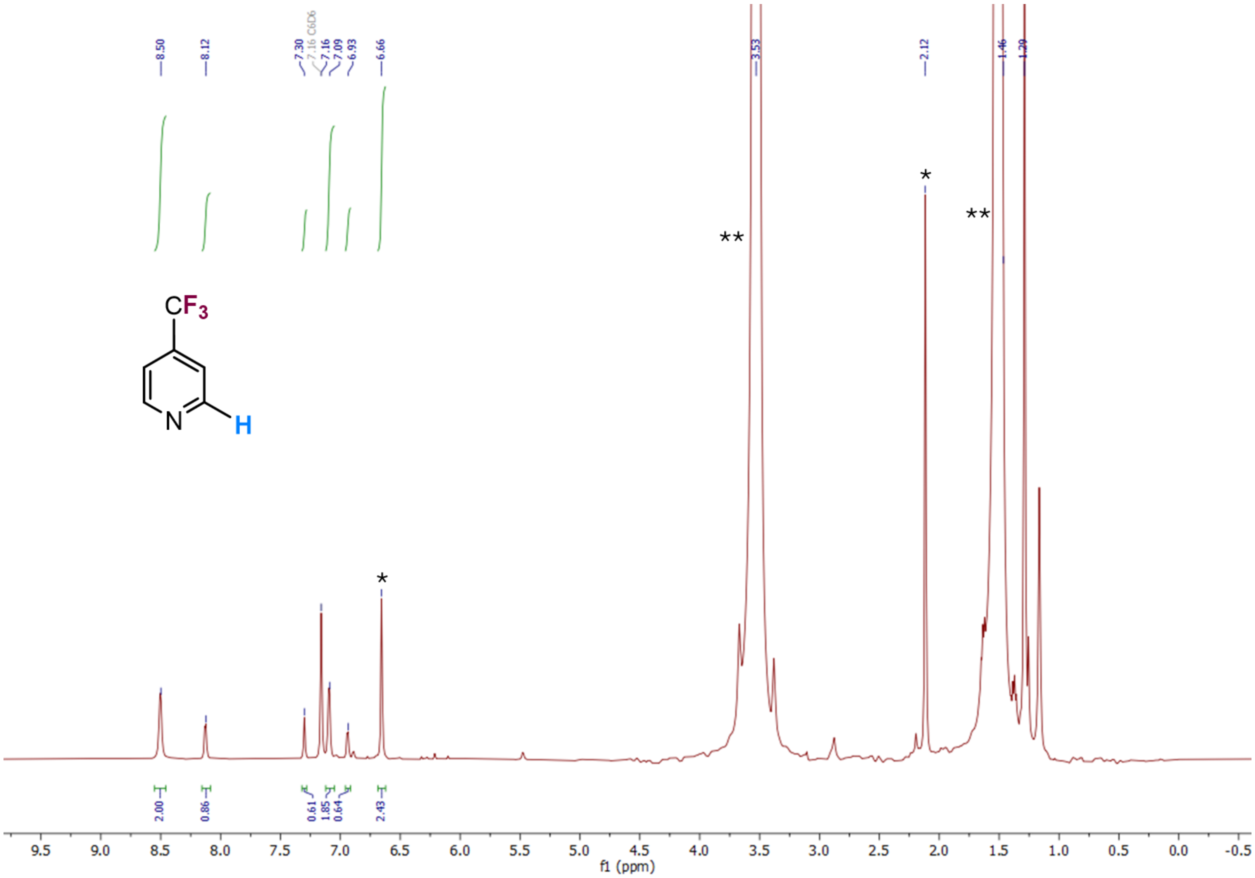


Figure S42: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of 4-trifluoromethyl pyridine (**4**).
*= Internal standard (Mesitylene)
**= THF

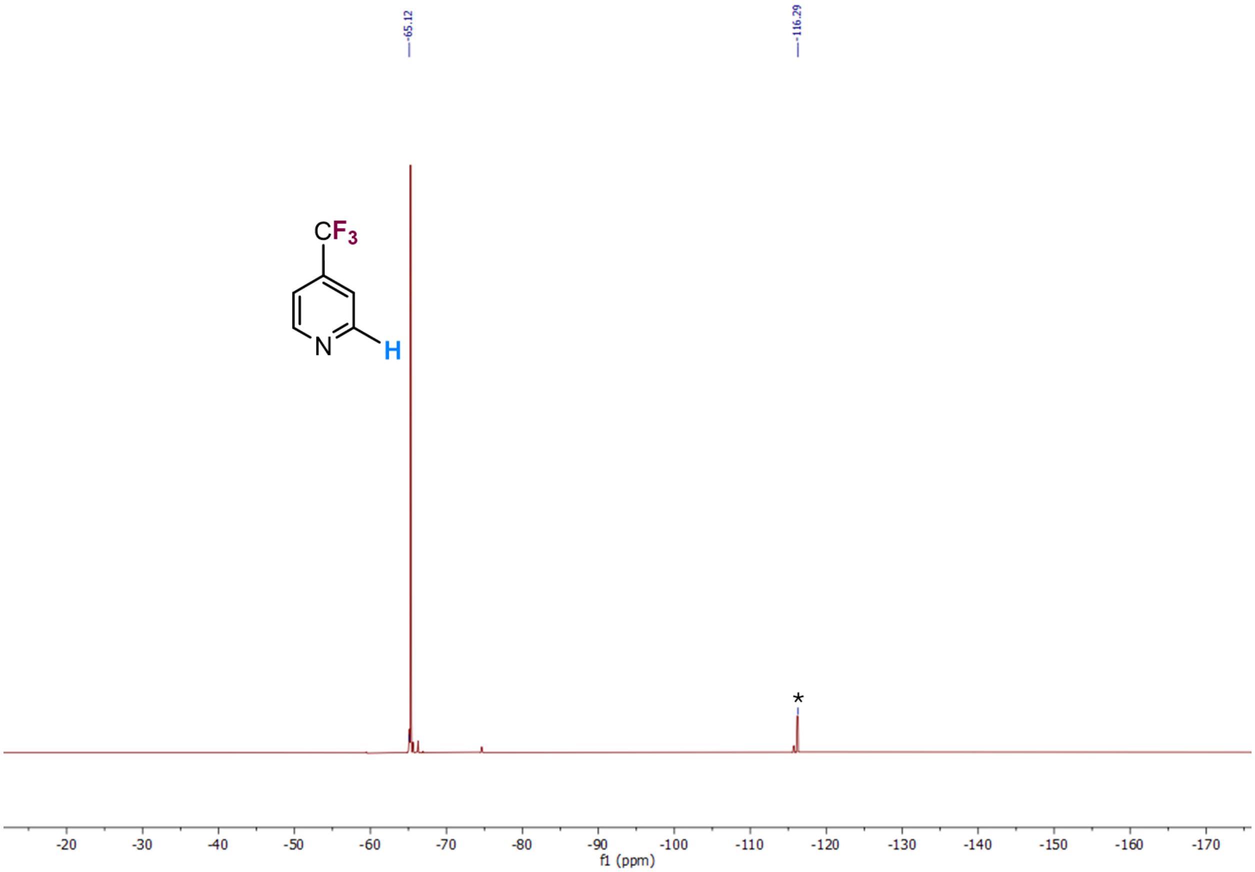


Figure S43: ^{19}F NMR (400 MHz, C_6D_6, 25 ºC) of 4-trifluoromethyl pyridine (**4**).
*= 4-difluoromethylpyridine

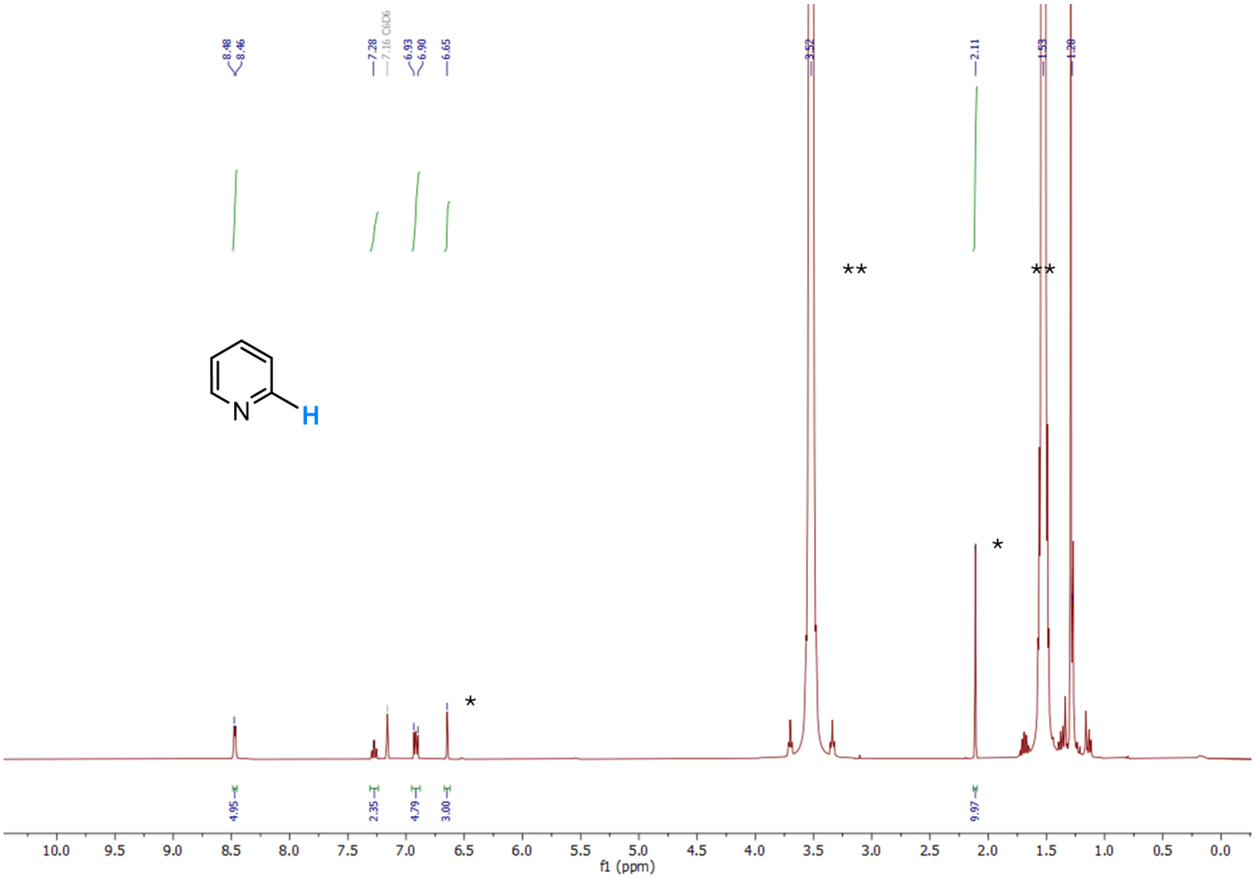


Figure S44: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of pyridine (**20a**) using 2-fluoropyridine as the starting material.

*= Internal standard (Mesitylene)

**= THF

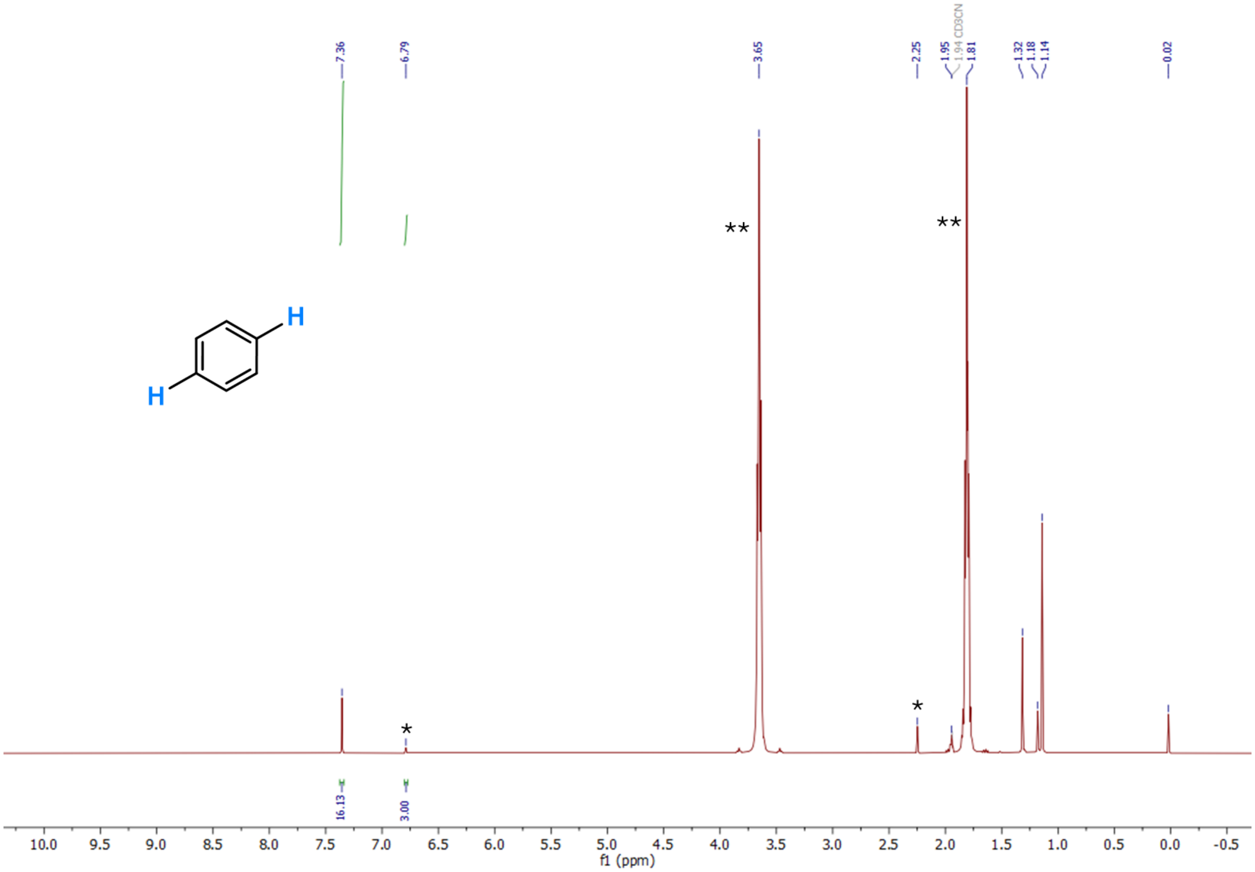


Figure S45: ^{1}H NMR (400 MHz, CD_3CN, 25 ºC) of benzene (**28a**) using 1,2-difluorobenzene as the starting material.
*= Internal standard (Mesitylene)
**= THF

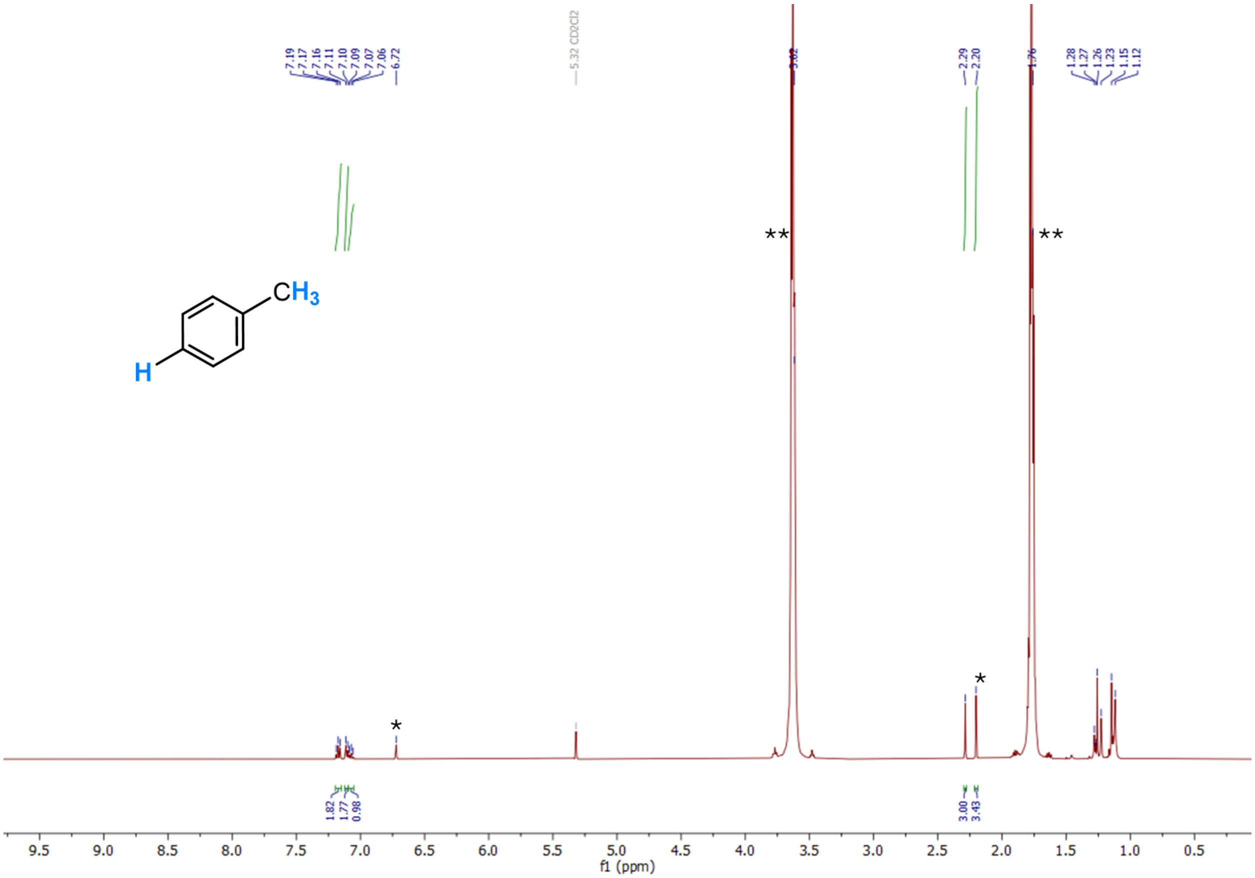


Figure S46: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) of toluene (**19a**) using 4-iodotoluene as the starting material.

*= Internal standard (Mesitylene)

**= THF

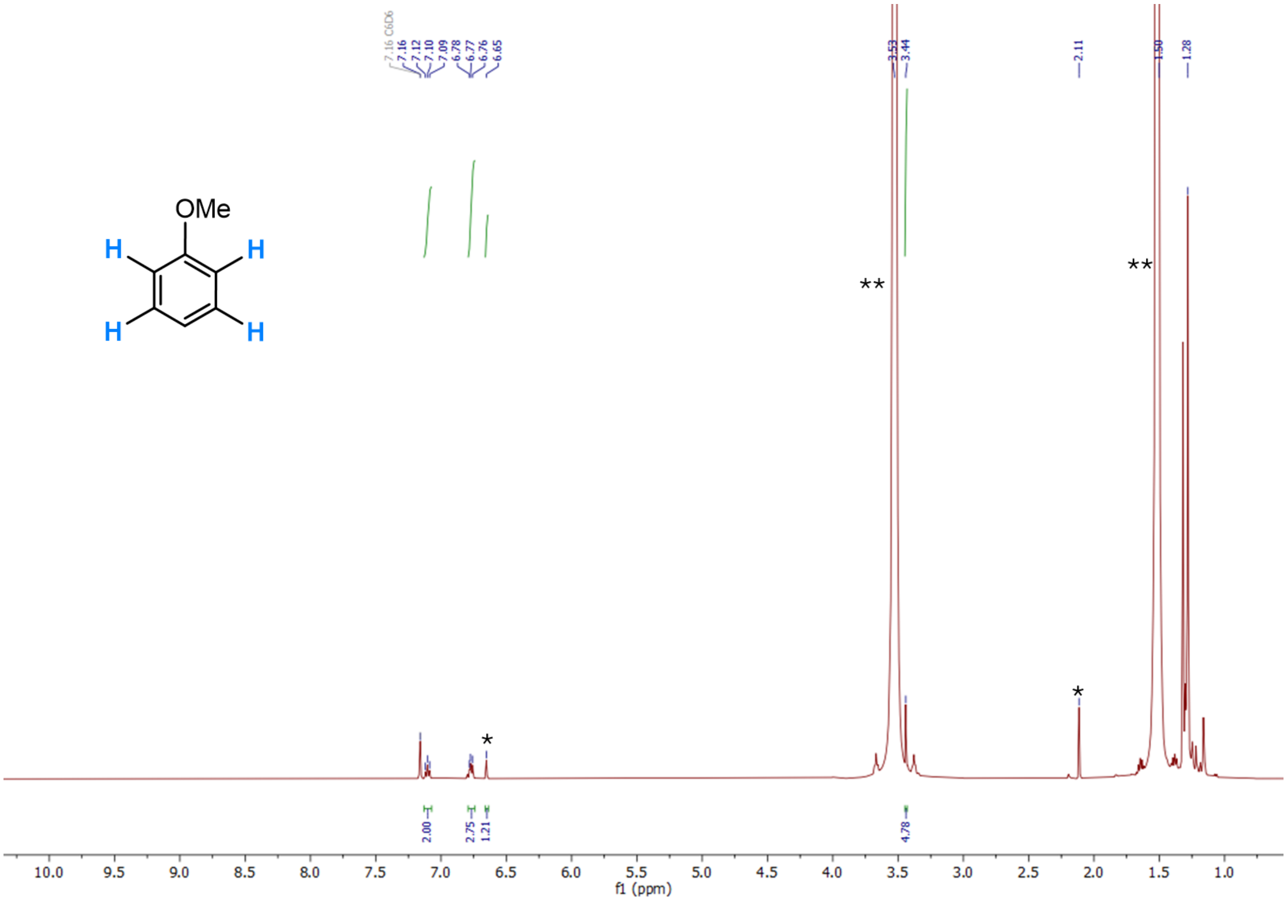


Figure S47: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of anisole (**37a**).
*= Internal standard (Mesitylene)
**= THF

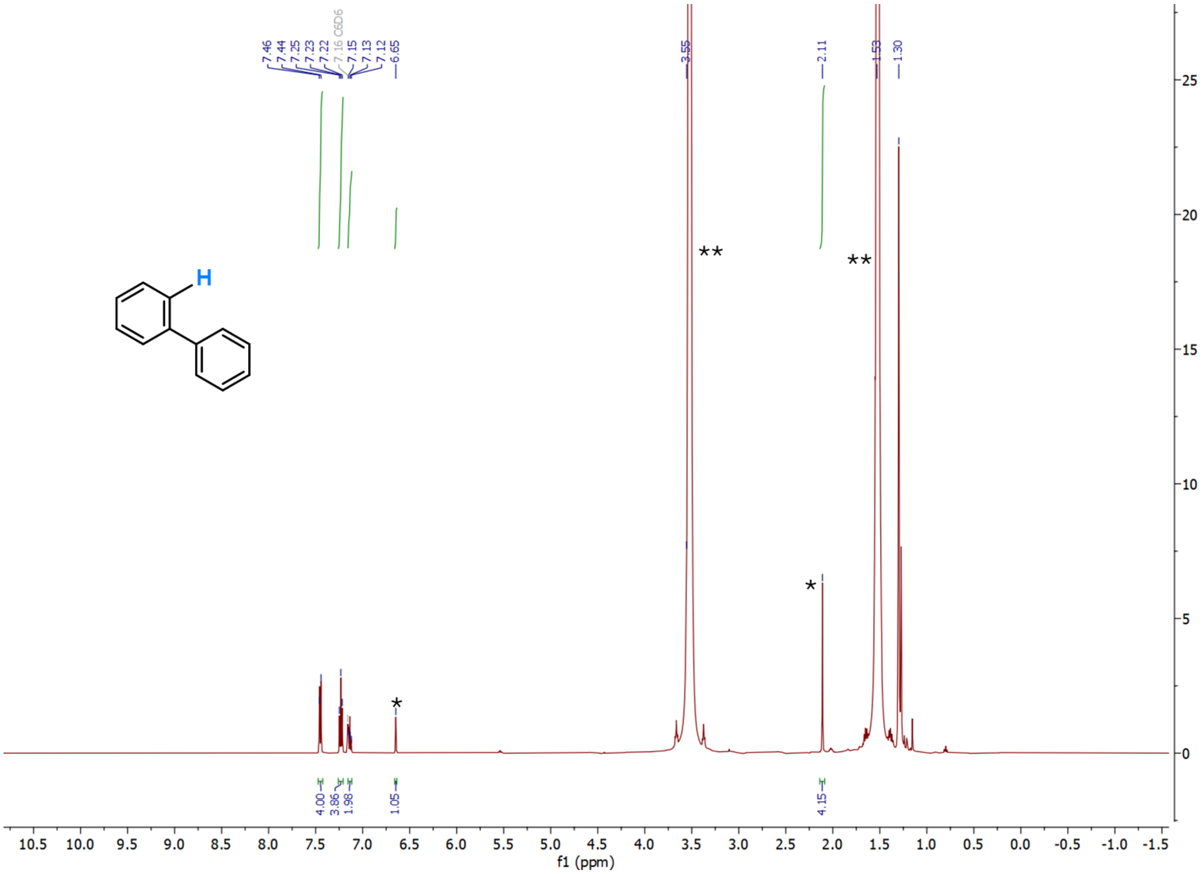


Figure S48: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of biphenyl (**38a**) using 2-bromobiphenyl as the starting material.
*= Internal standard (Mesitylene)
**= THF

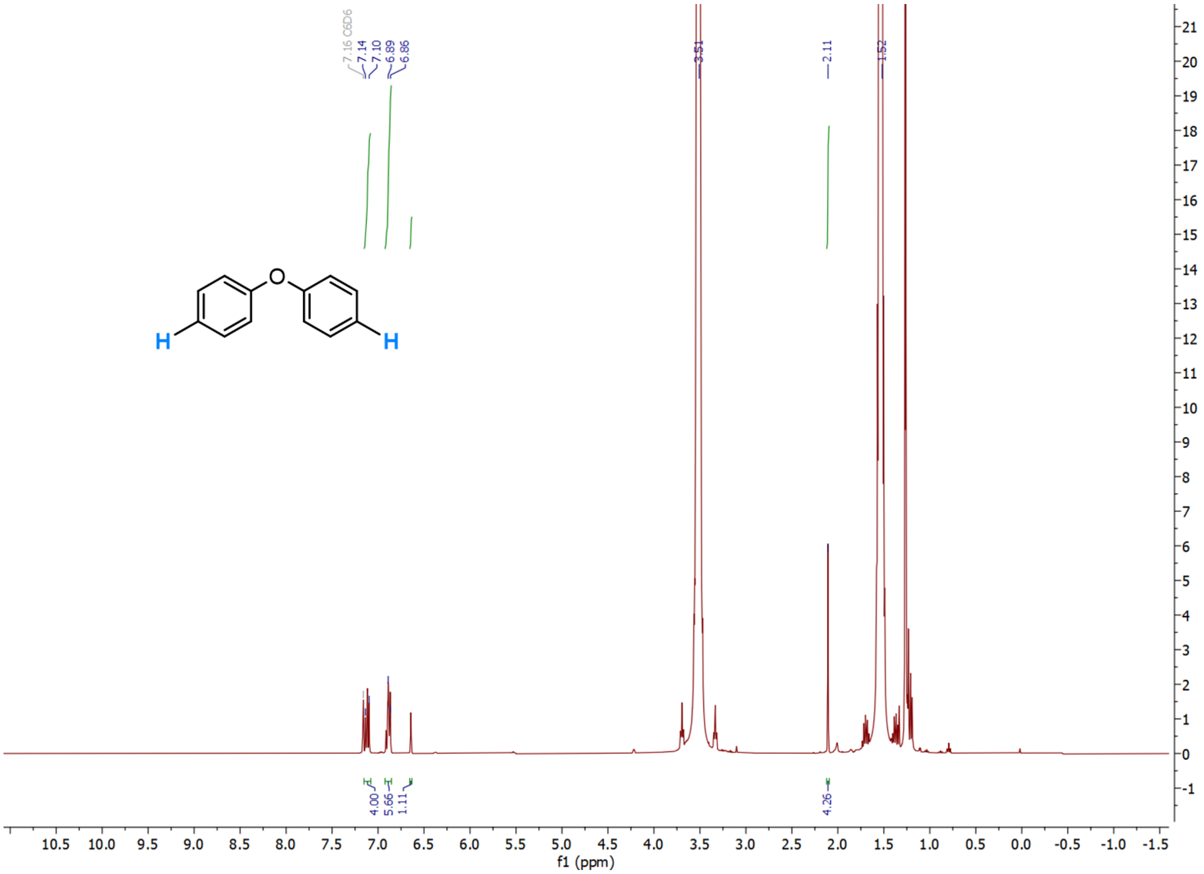


Figure S49: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of diphenyl ether (**42a**).
*= Internal standard (Mesitylene)
**= THF

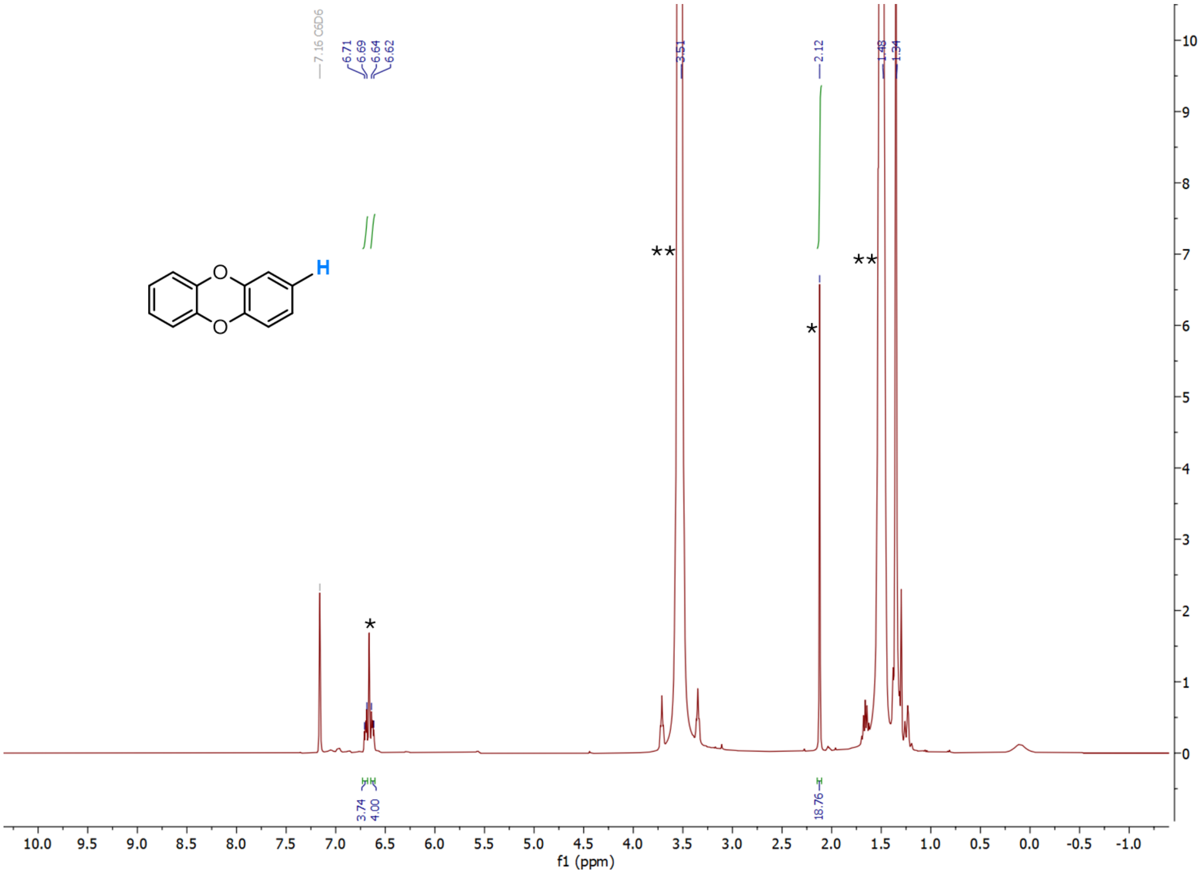


Figure S50: ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) of dibenzo-p-dioxin (**43a**).
*= Internal standard (Mesitylene)
**= THF

23. Crude NMR spectra of deuterodehalogenated (DDH) products.

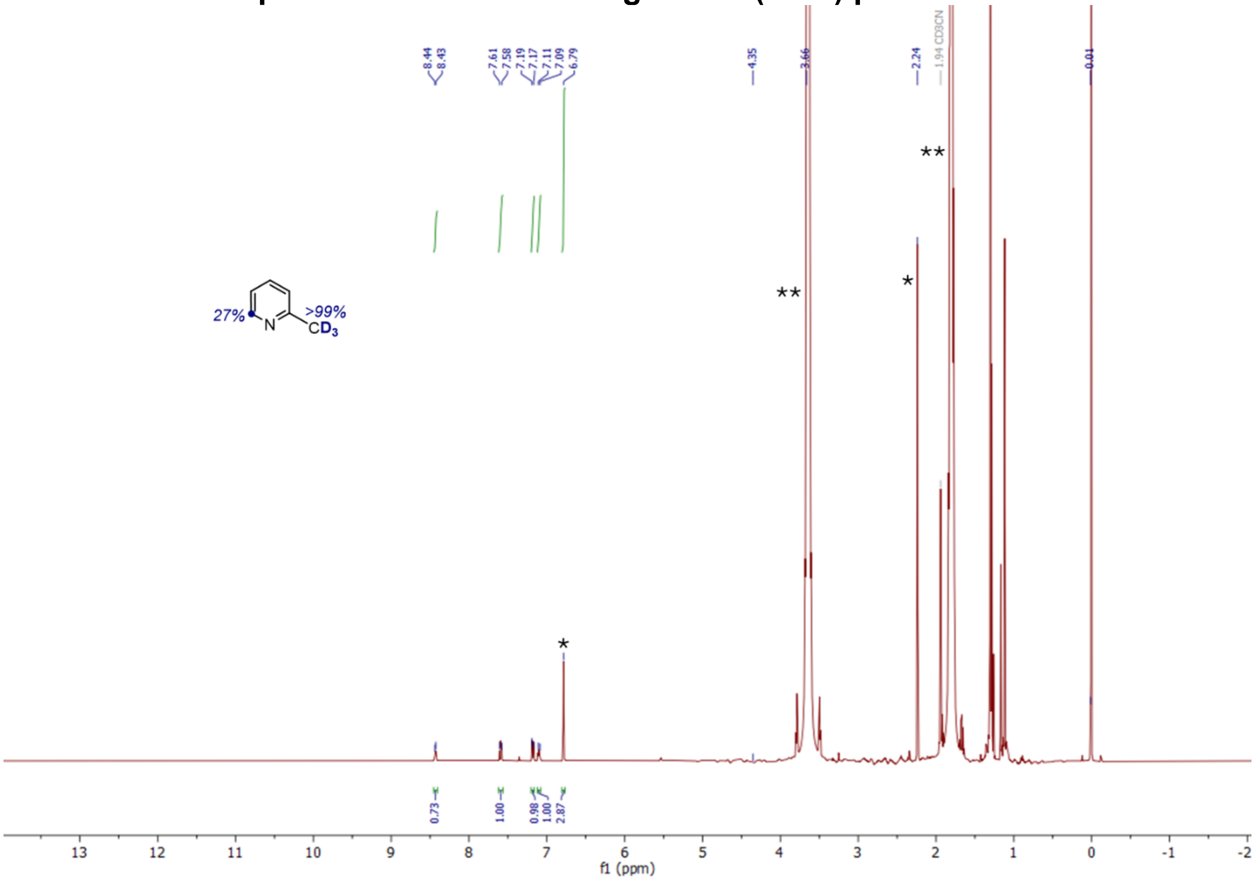


Figure S51: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-(methyl-d_3)pyridine-6-d (**1a-d_4**).

*= Internal standard (Mesitylene)
**= THF

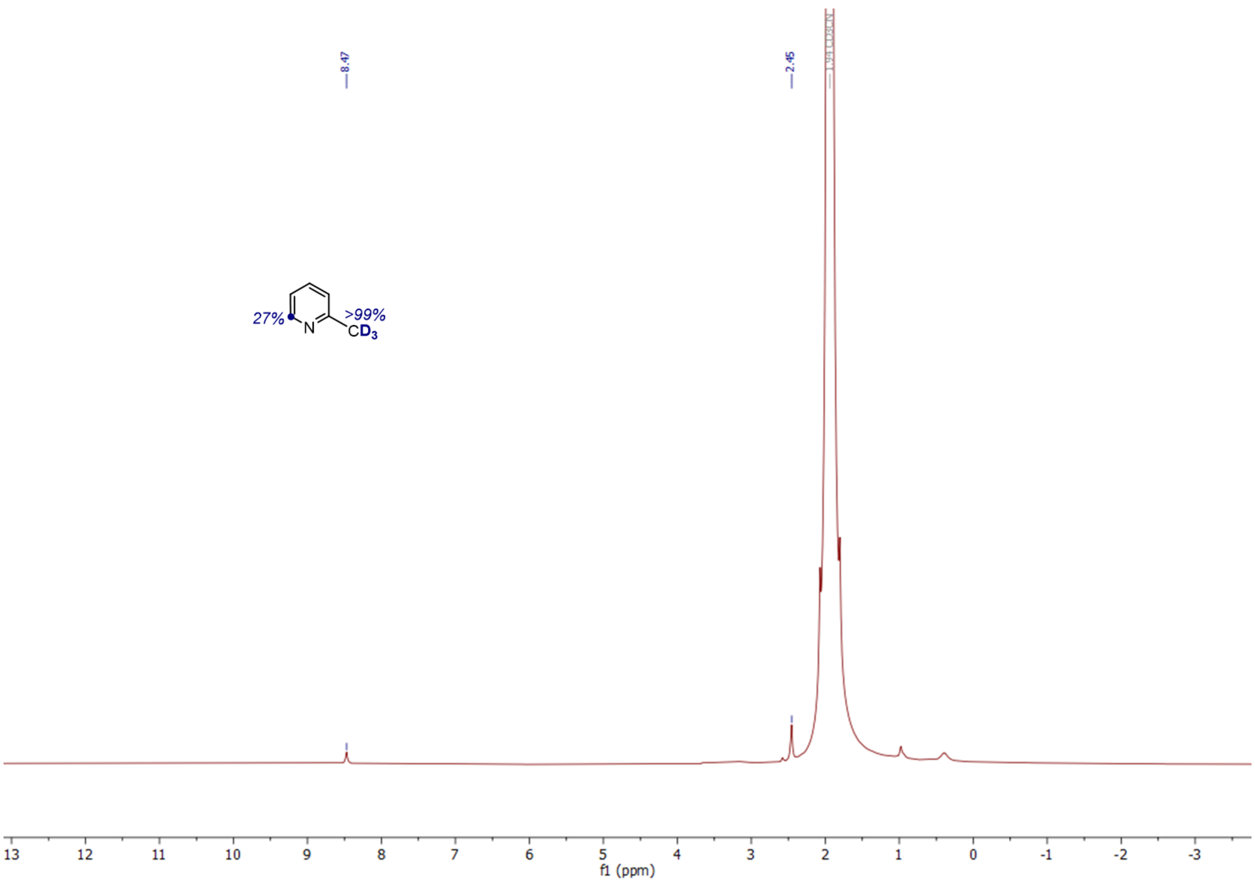


Figure S52: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-(methyl-*d*$_3$)pyridine-6-*d* (**1a-*d*$_4$**).

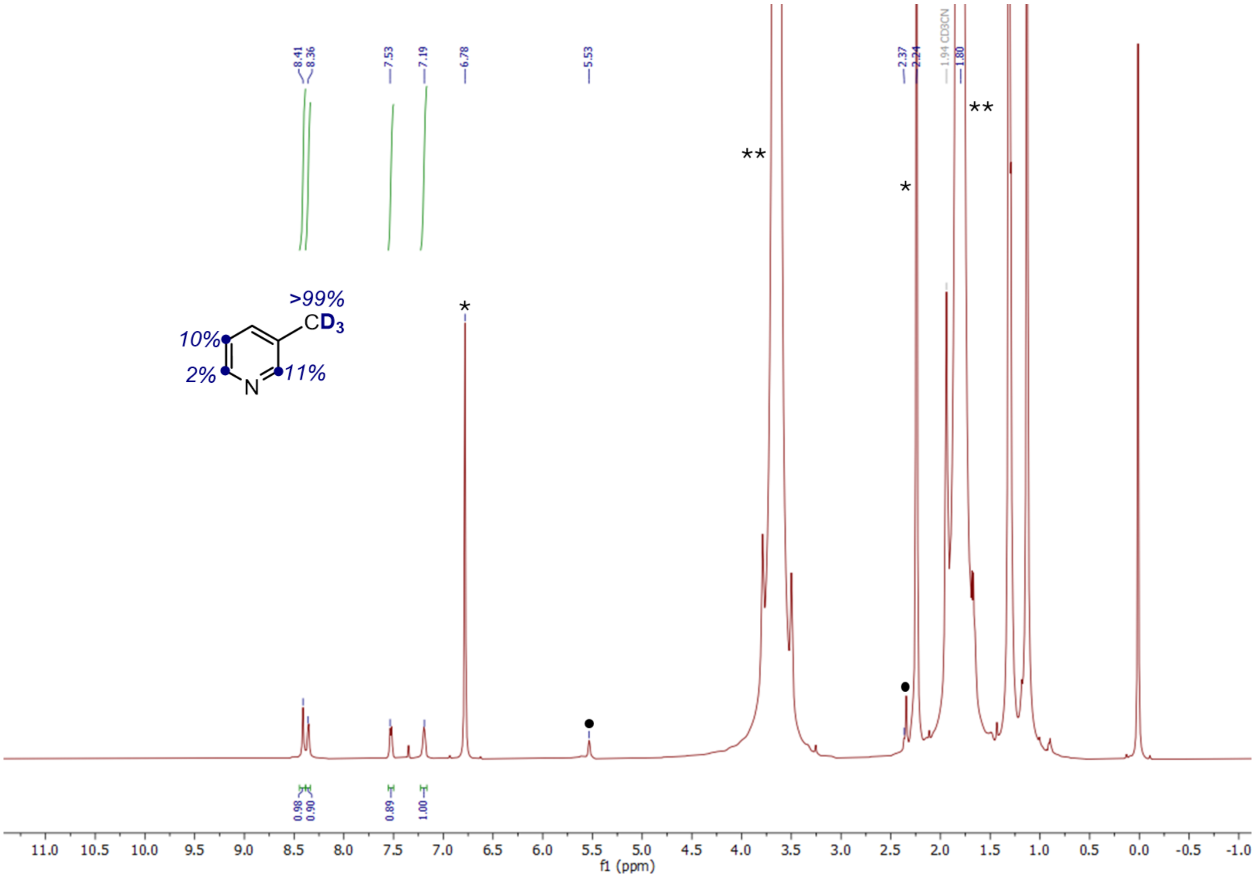


Figure S53: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 3-(methyl-*d_3*)-pyridine-*2,5,6-d_3* (**2a-*d_6***).
*= Internal standard (Mesitylene)
**= THF
●= 1,5 COD

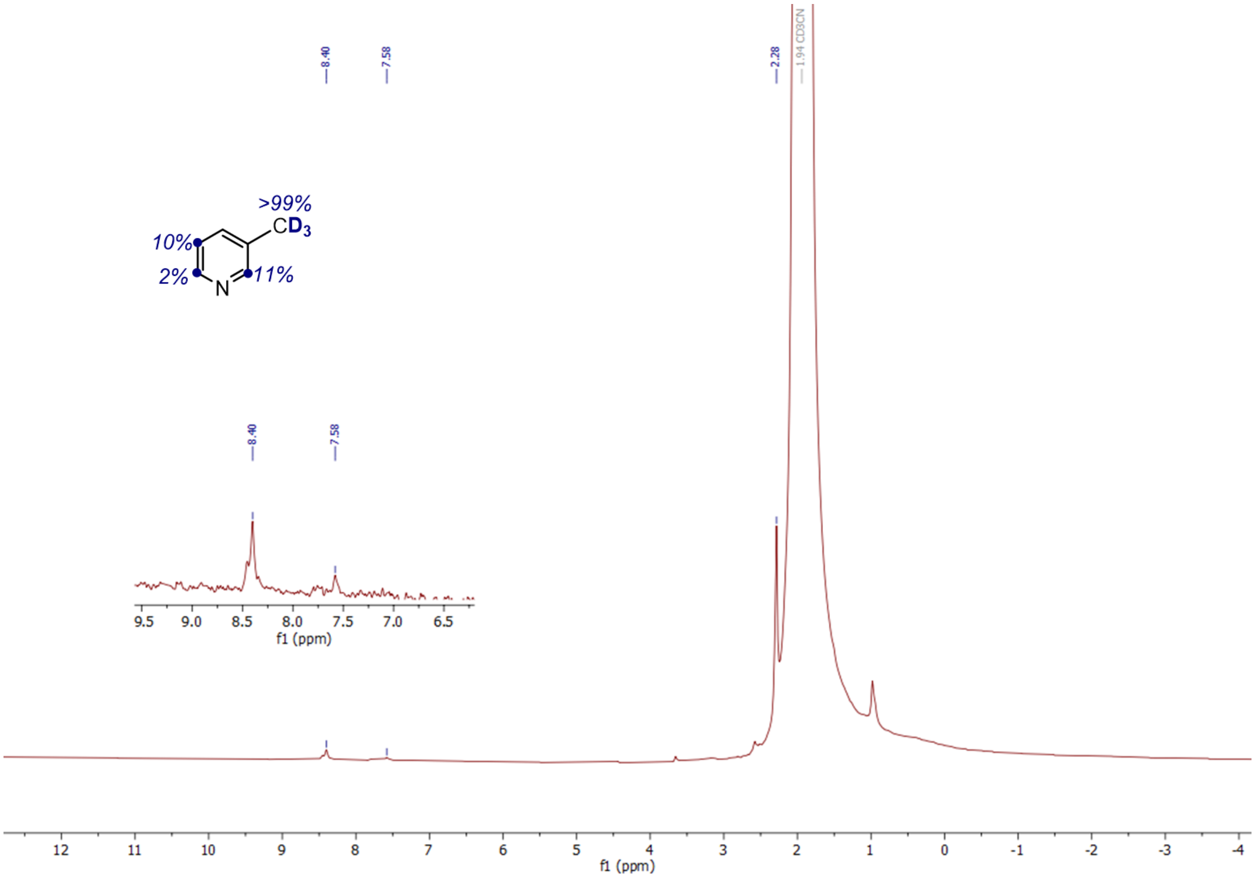


Figure S54: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 3-(methyl-*d_3*)pyridine-2,5,6-*d_3* (**2a-*d_6***).

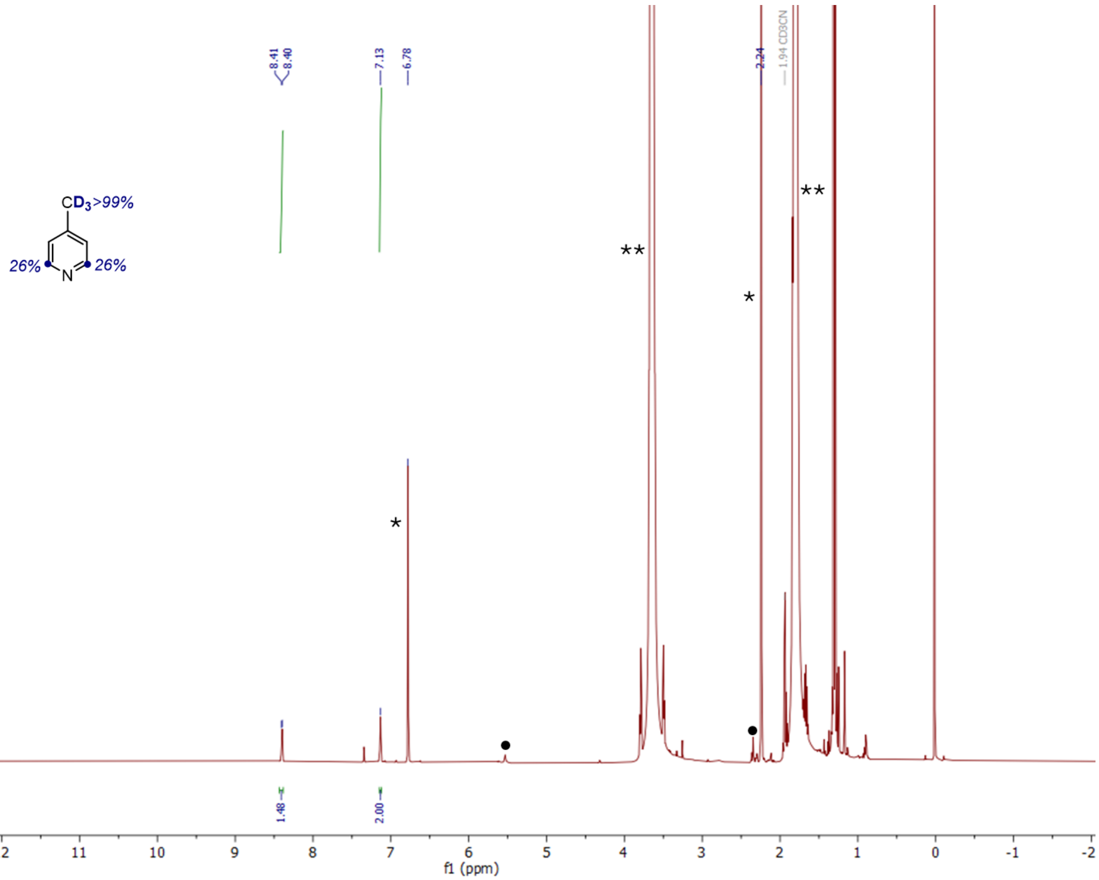


Figure S55: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 4-(methyl-*d*$_3$)pyridine-2,6-*d*$_2$ (**3a-*d*$_5$**).
*= Internal standard (Mesitylene)
**= THF
●= 1,5 COD

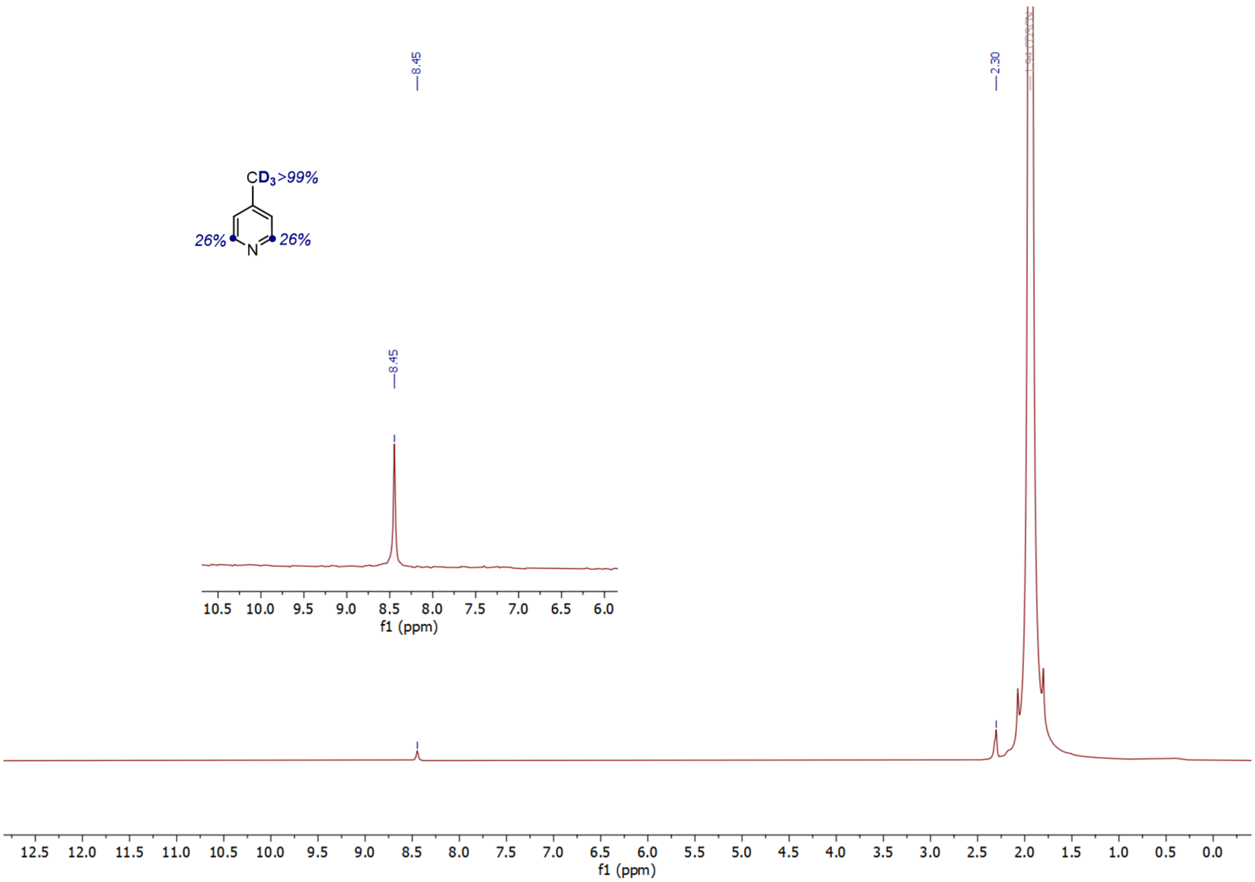


Figure S56: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 4-(methyl-*d*$_3$)pyridine-2,6-*d*$_2$ (**3a-*d*$_5$**).

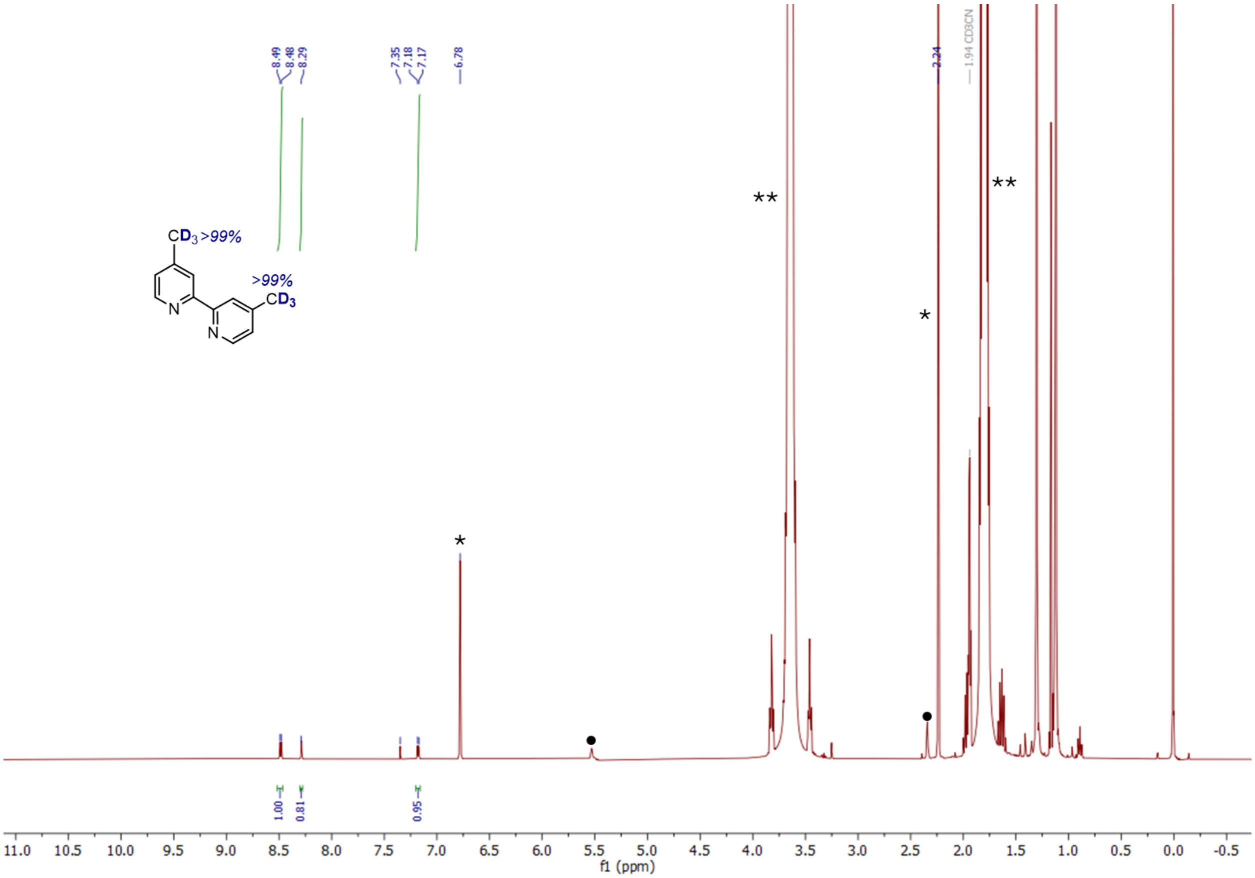


Figure S57: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 4,4'-(dimethyl-*d*$_6$)-2,2'-bipyridyl (**4a-*d*$_6$**).

*= Internal standard (Mesitylene)
**= THF
●= 1,5 COD

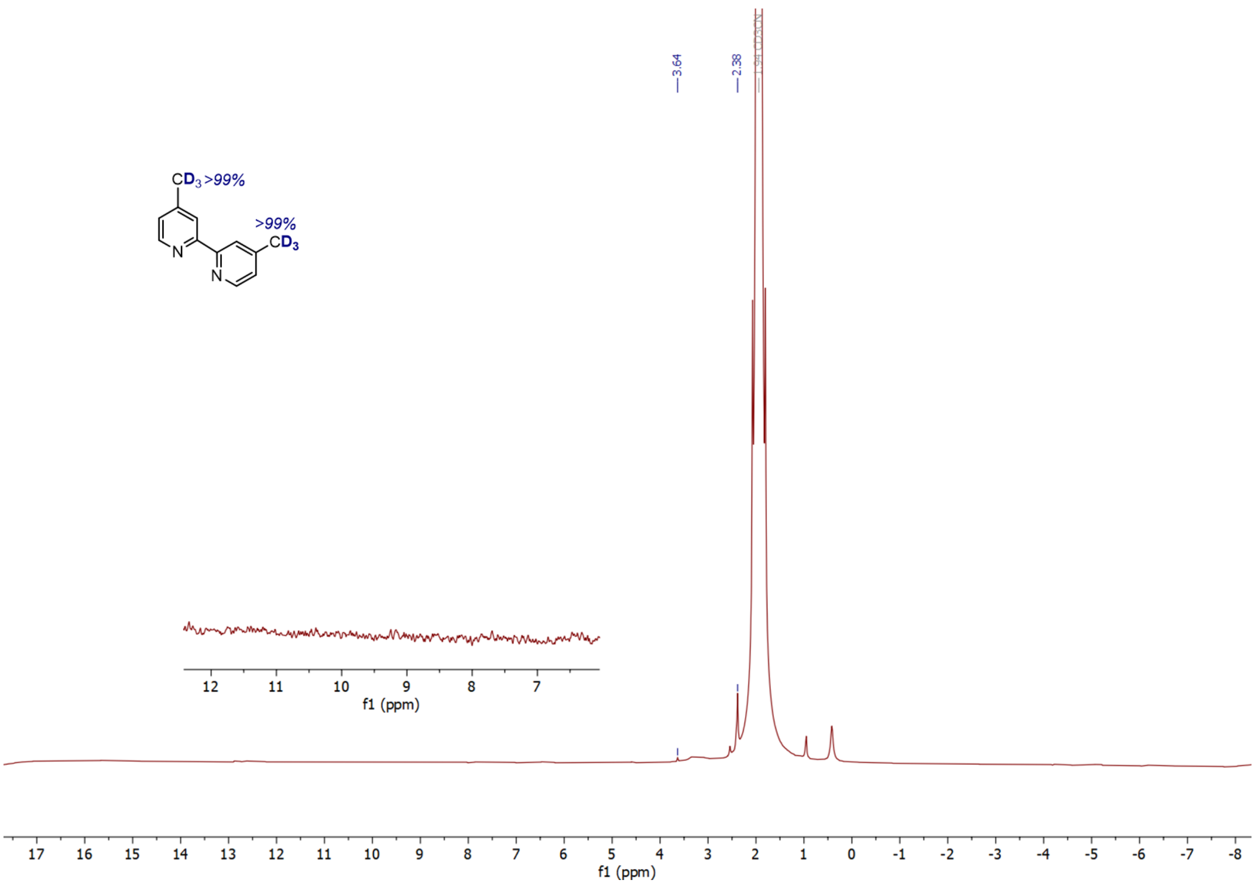


Figure S58: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 4,4'-(dimethyl-*d_6)*-2,2'-bipyridyl (**4a-*d_6***).

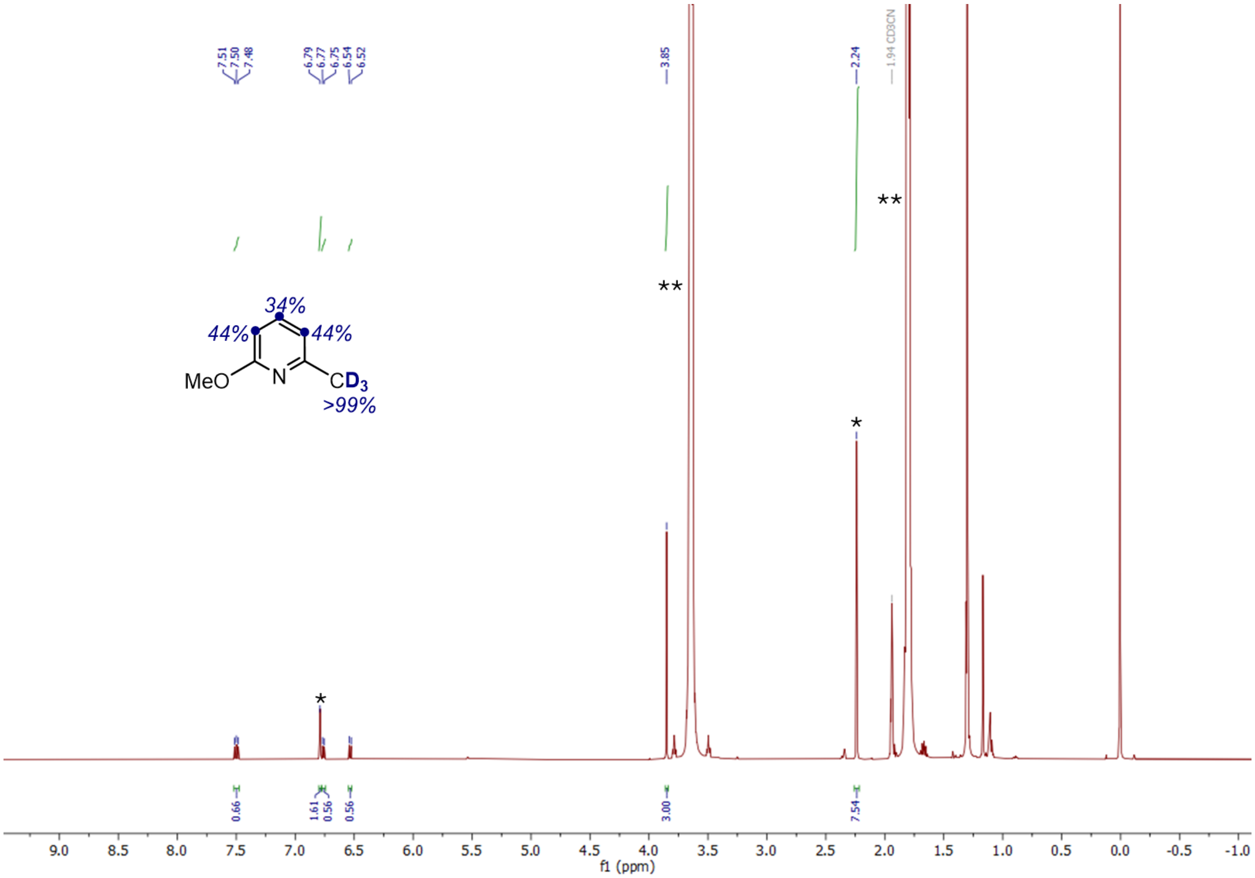


Figure S59: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-methoxy-(6-methyl-*d_3)*pyridine-3,4,5-*d_3* (**5a-*d_6***).

*= Internal standard (Mesitylene)

**= THF

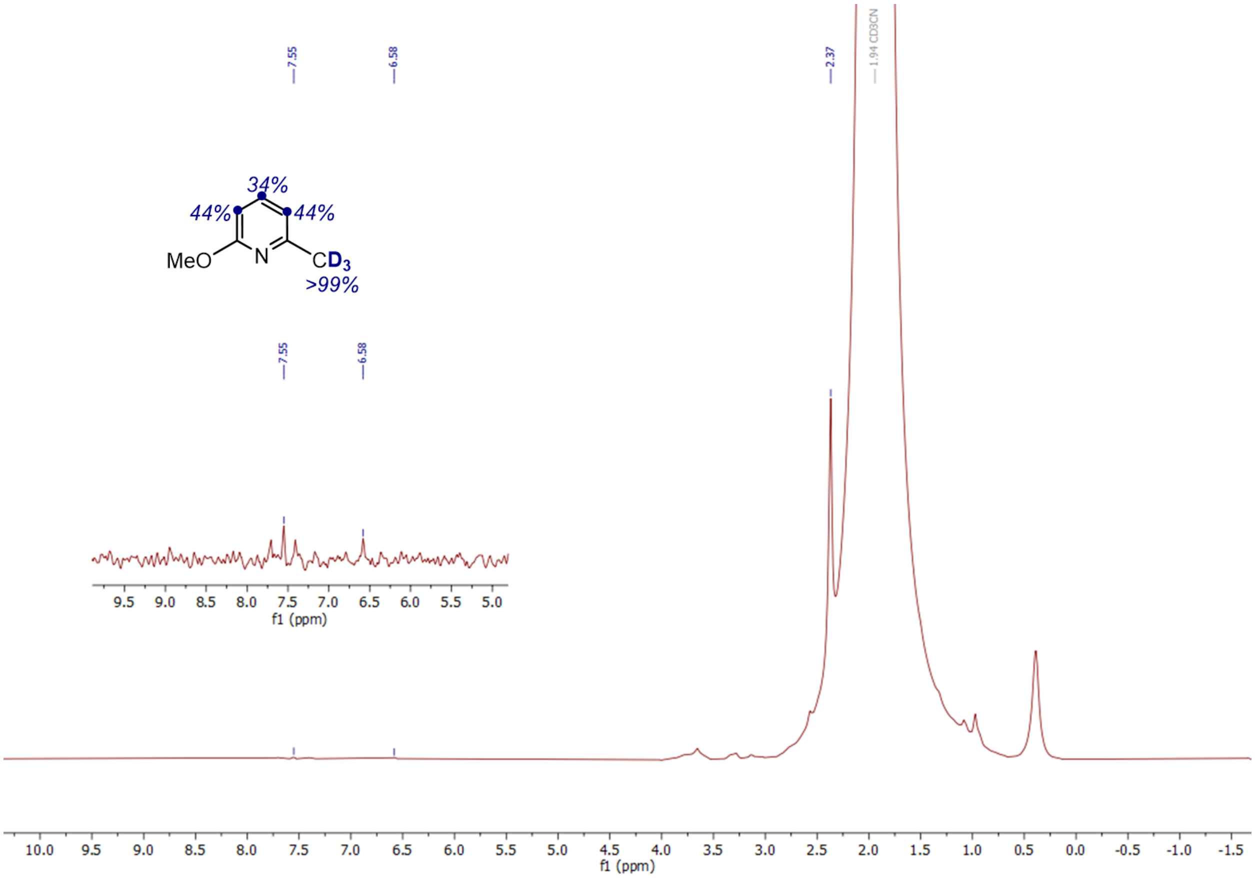


Figure S60: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-methoxy-(6-methyl-*d*$_3$)pyridine-3,4,5-*d*$_3$ (**5a-*d*$_6$**).

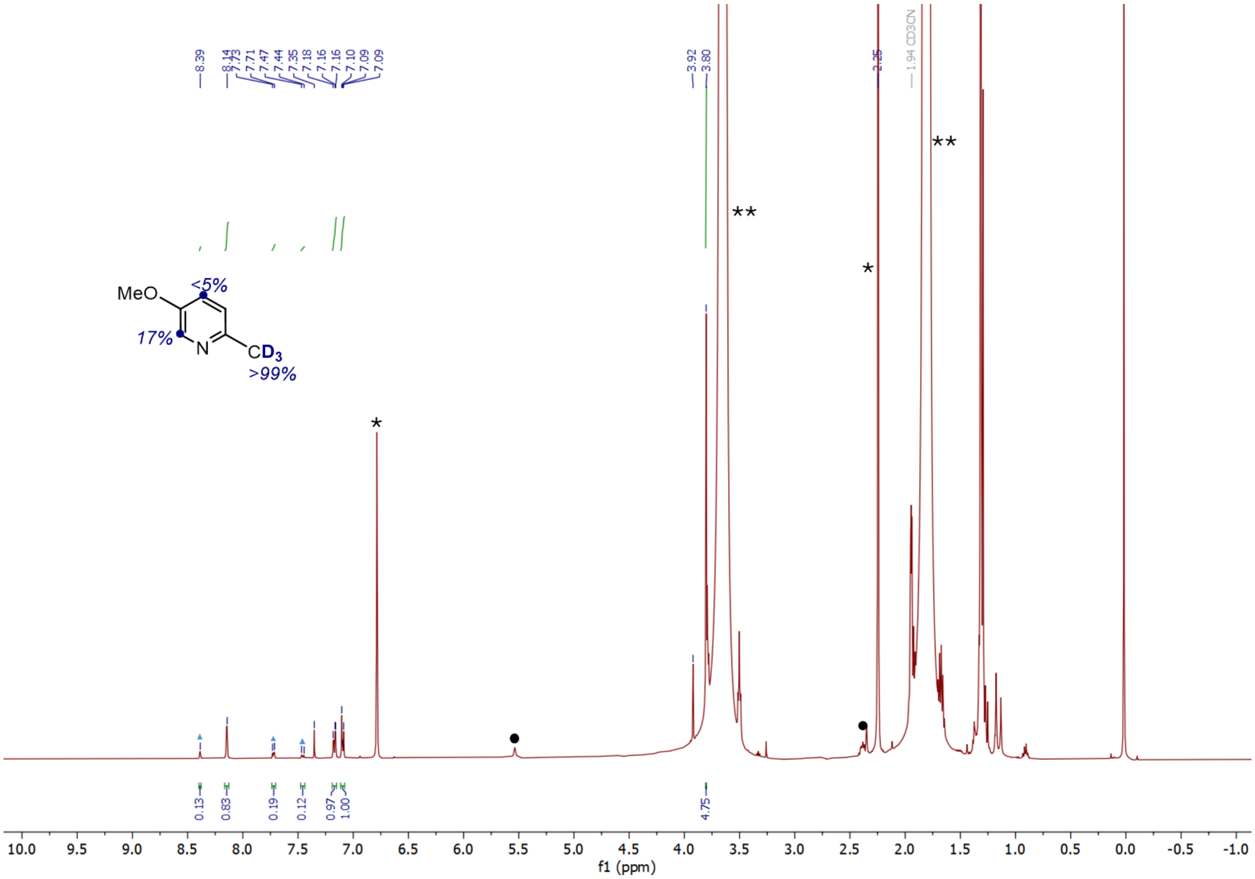


Figure S61: ^{1}H NMR (500 MHz, CD$_3$CN, 25 ºC) of 5-methoxy-(2-methyl-d_3)pyridine-4,6-d_2 (**6a-*d*$_5$**).

*= Internal standard (Mesitylene)

**= THF

▲ = Starting material

● = 1,5-COD

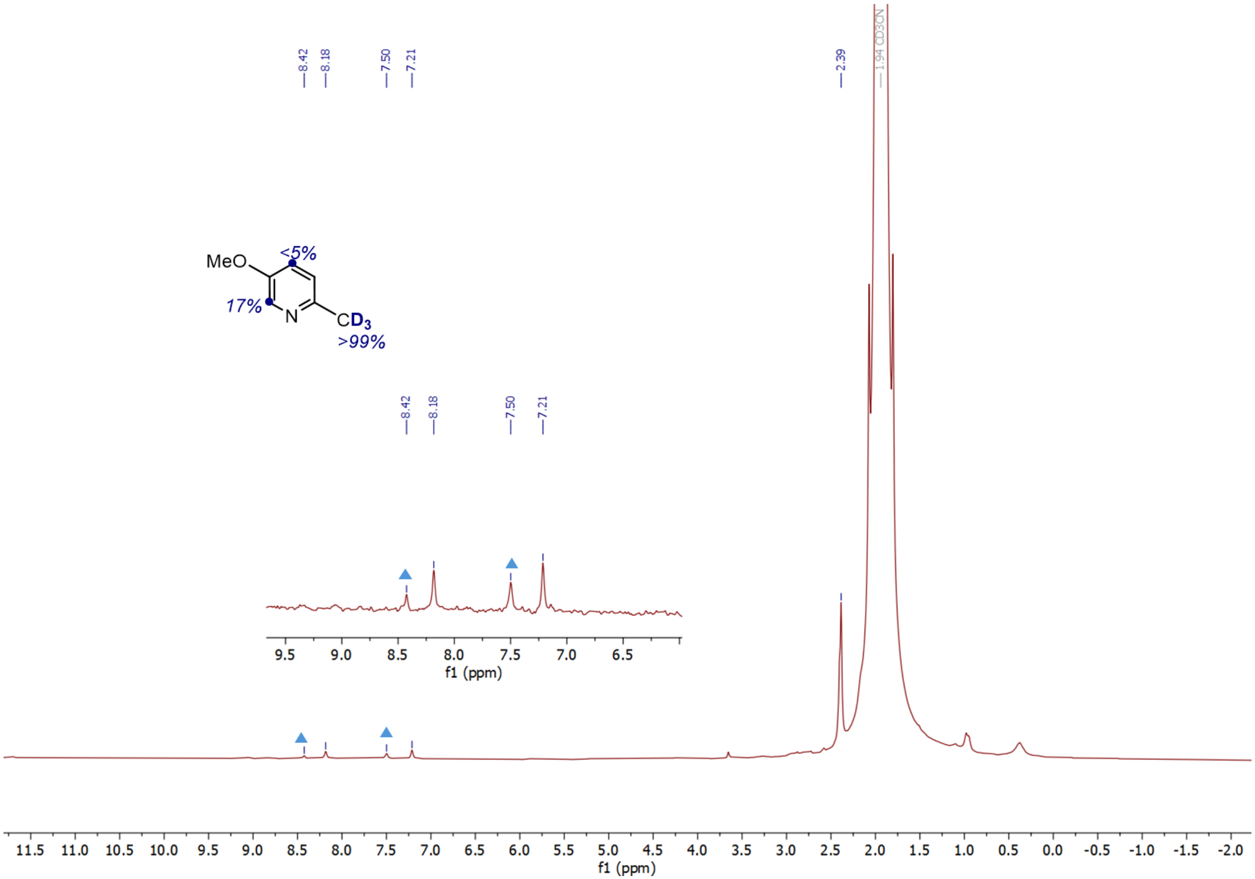


Figure S62: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 5-methoxy-(2-methyl-*d*$_3$)pyridine-4,6-*d*$_2$ (**6a-*d*$_5$**).

▲ = Partially deuterated starting material

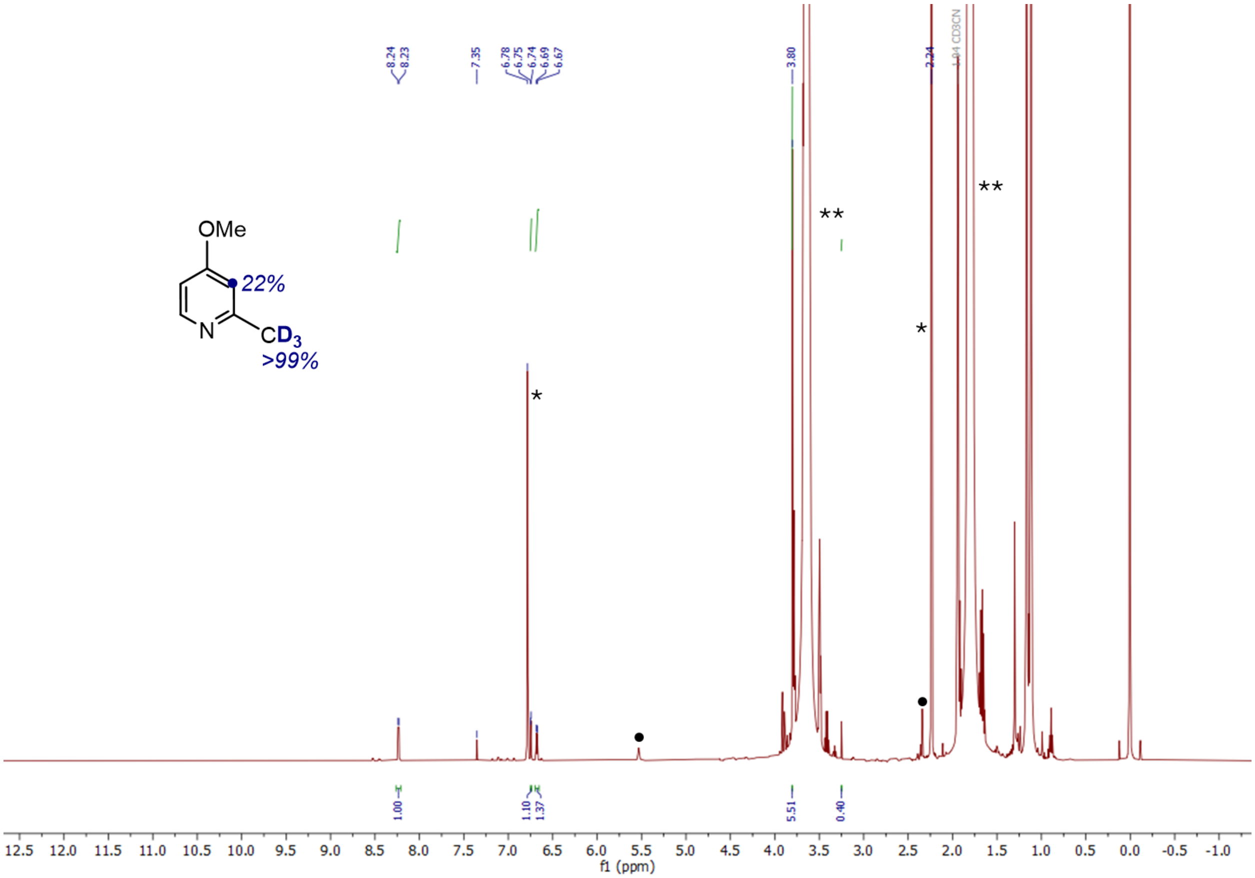


Figure S63: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 4-methoxy-(2-methyl-*d*$_3$)pyridine-4-*d* (**7a-*d*$_4$**).
*= Internal standard (Mesitylene)
**= THF
● =1,5-COD

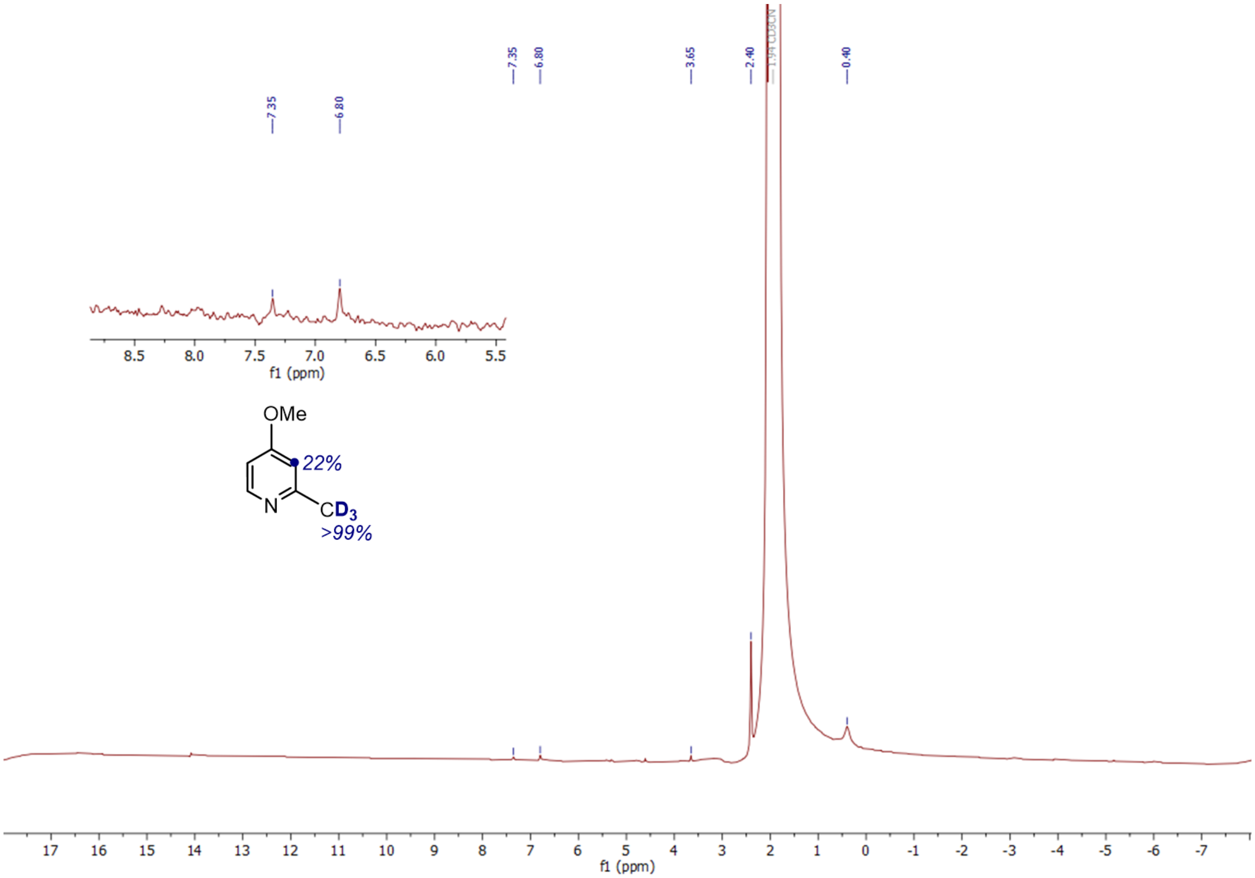


Figure S64: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 4-methoxy-(2-methyl-*d*$_3$)pyridine-3-*d* (**7a-*d*$_4$**).

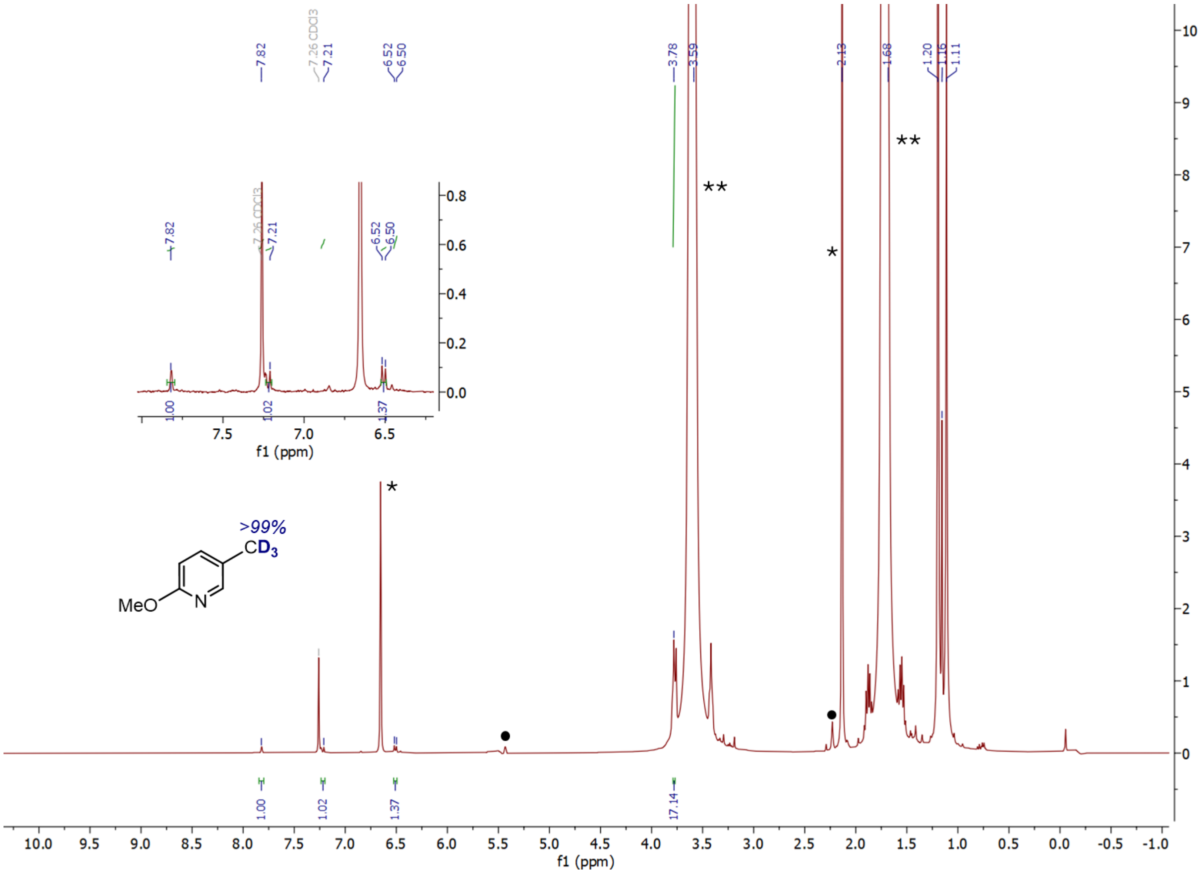


Figure S65: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-methoxy-(5-methyl-*d*$_3$)pyridine (**8a-*d*$_3$**).

*= Internal standard (Mesitylene)

**= THF

●=1,5-COD

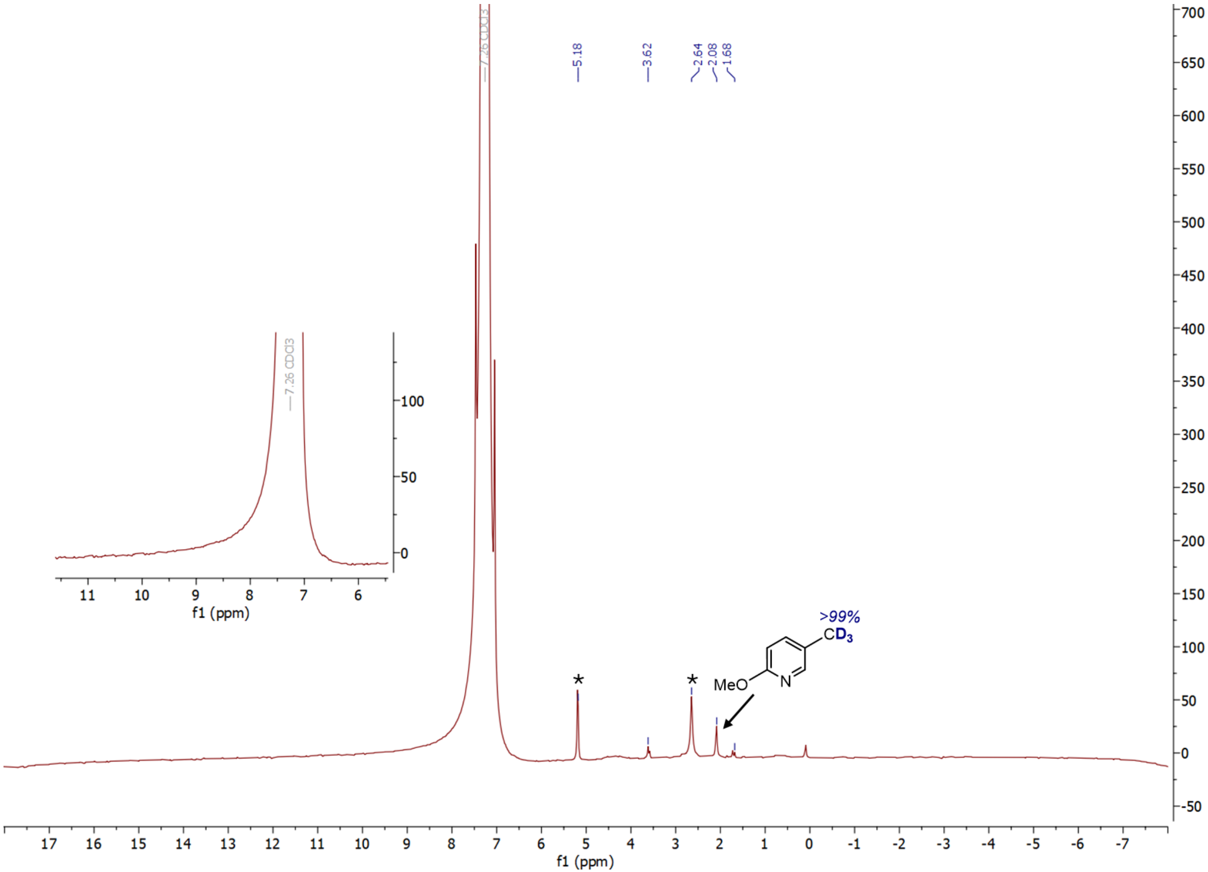


Figure S66: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-methoxy-(5-methyl-*d*$_3$)pyridine (**8a-*d*$_3$**). *= 1,5-COD-*d*$_{12}$

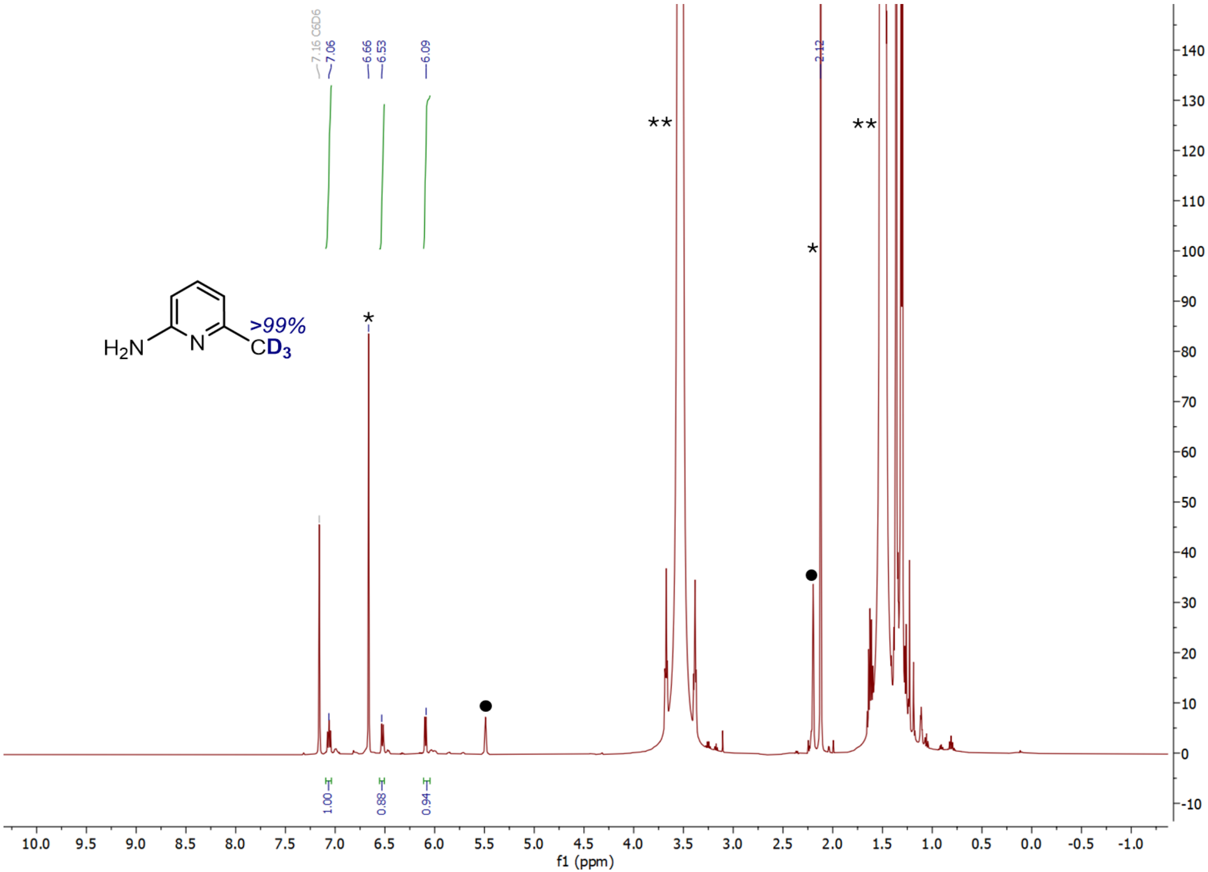


Figure S67: ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) of 2-amino-(6-methyl-*d_3*)pyridine (**9a-*d_3***).
*= Internal standard (Mesitylene)
**= THF
● =1,5-COD

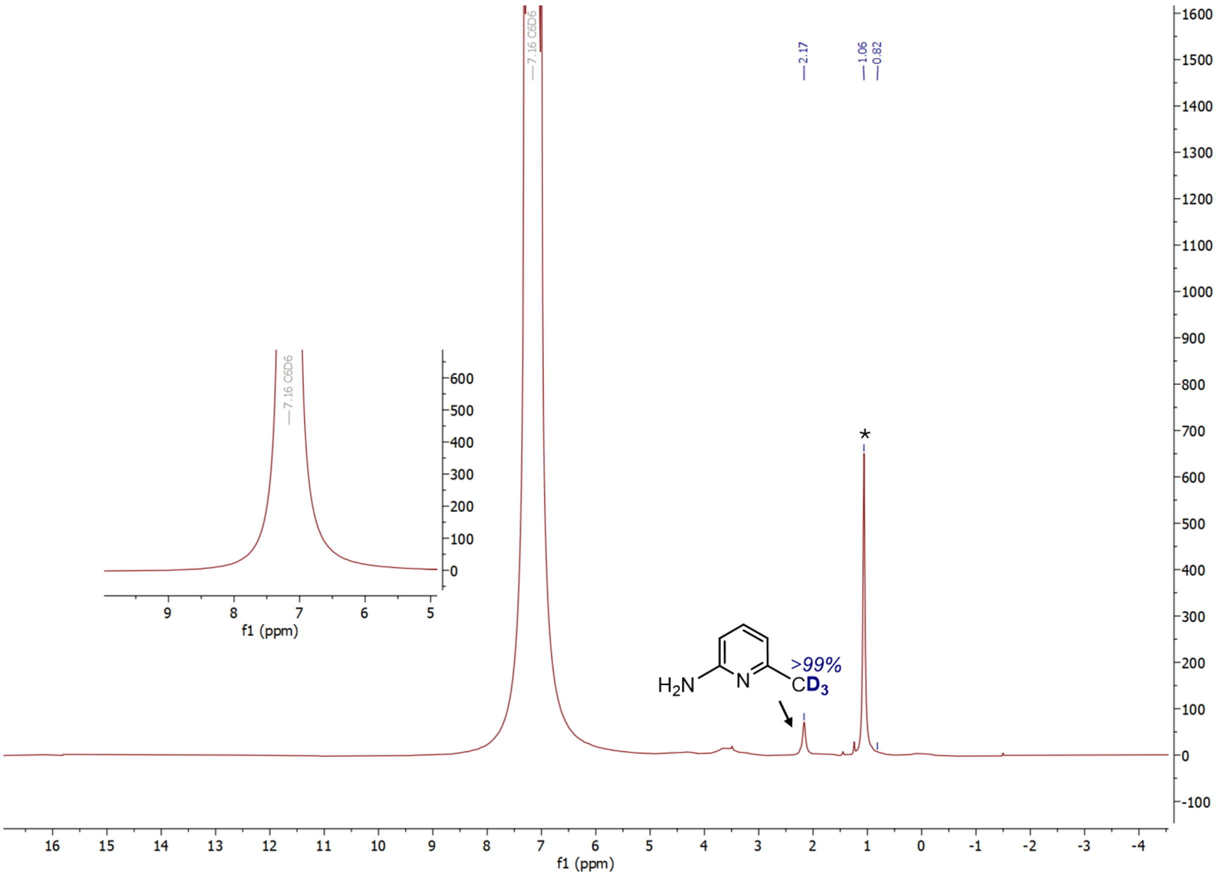


Figure S68: ^{2}H NMR (500 MHz, C_6D_6, 25 ºC) of 2-amino-(6-methyl-d_3)pyridine (**9a-d_3**).
*= Unidentified impurity

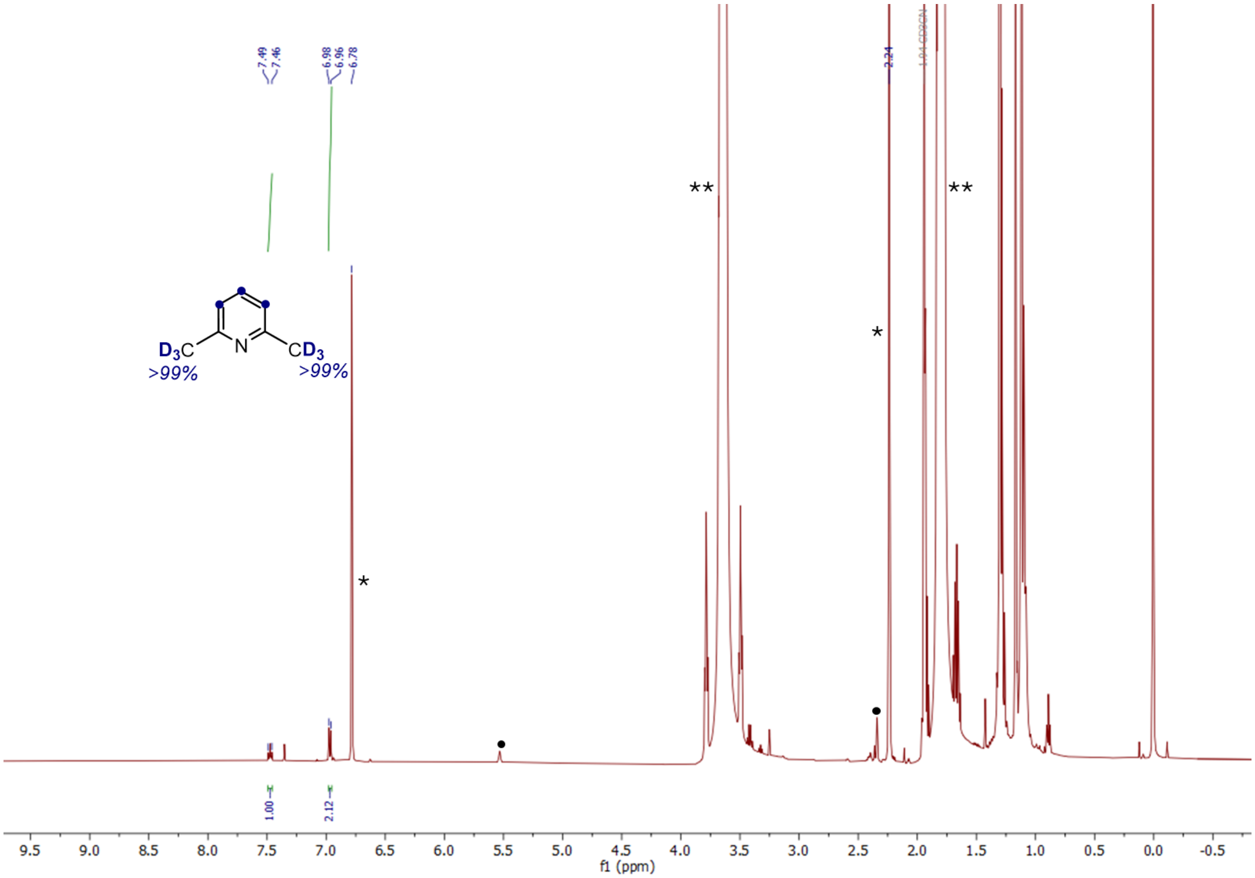


Figure S69: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 2,6-(dimethyl-*d_6)*pyridine-3,4,5-*d_3* (**10a-*d_9***).
*= Internal standard (Mesitylene)
**= THF
● = 1,5-COD

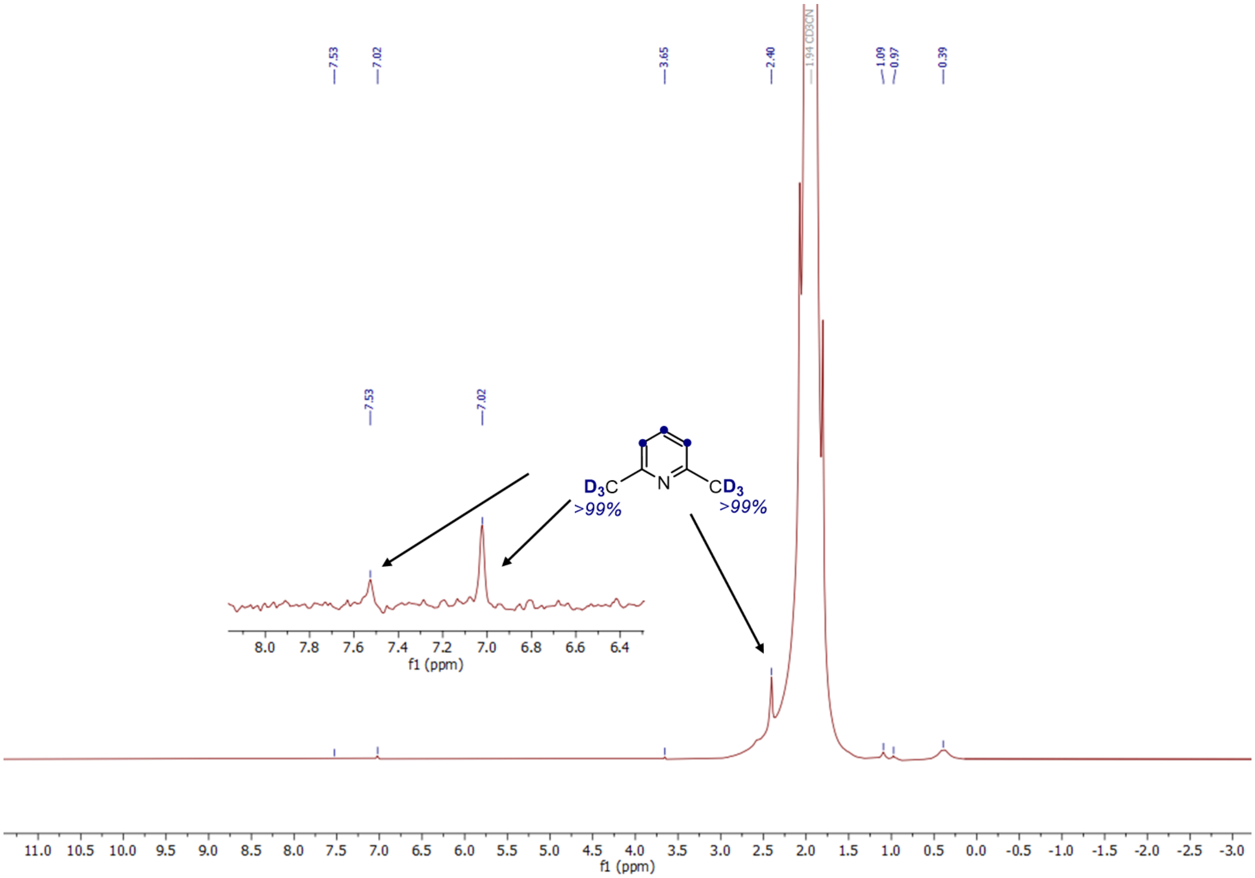


Figure S70: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 2,6-(dimethyl-*d_6*)pyridine-3,4,5-*d_3* (**10a-*d_9***).

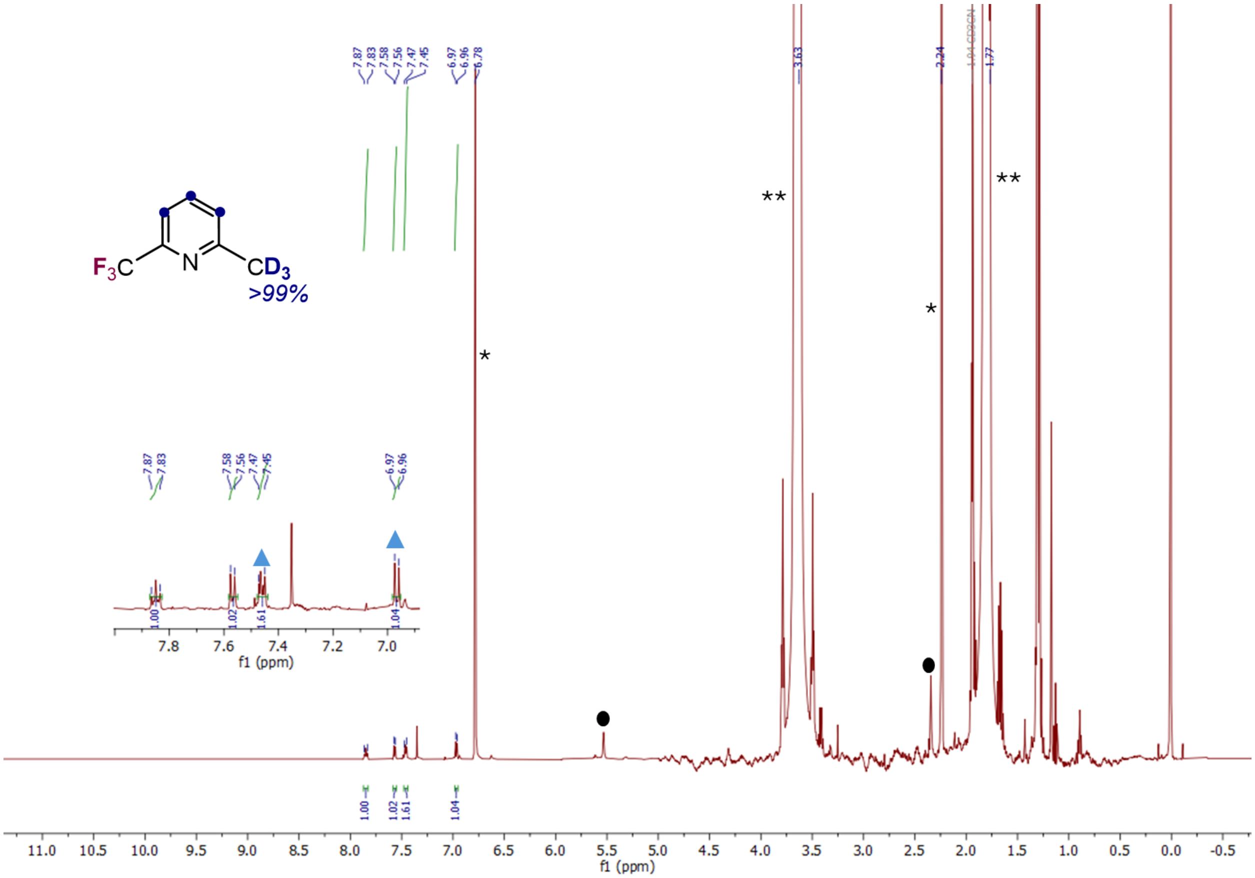


Figure S71: ^{1}H NMR (500 MHz, CD$_3$CN, 25 ºC) of 2-trifluoromethyl-6-(methyl-d_3)pyridine-3,4,5-d_3 (**10a’-d_6**).

*= Internal standard (Mesitylene)

**= THF

●= 1,5-COD

▲= **10a-d_9**

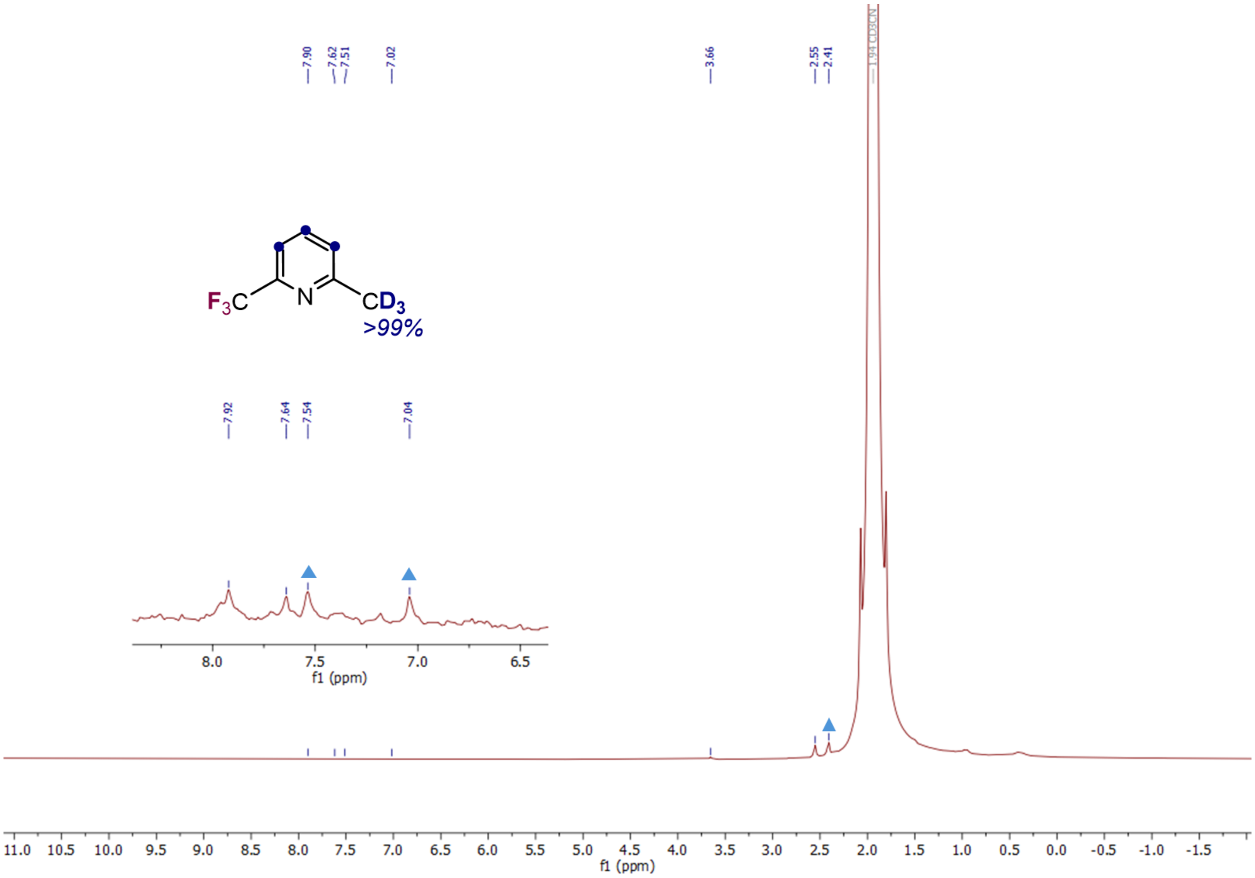


Figure S72: ^{2}H NMR (500 MHz, CD$_3$CN, 25 ºC) of 2-trifluoromethyl-6-(methyl-d_3)pyridine-3,4,5-d_3 (**10a'-*d*$_6$**).

▲= **10a-*d*$_9$**

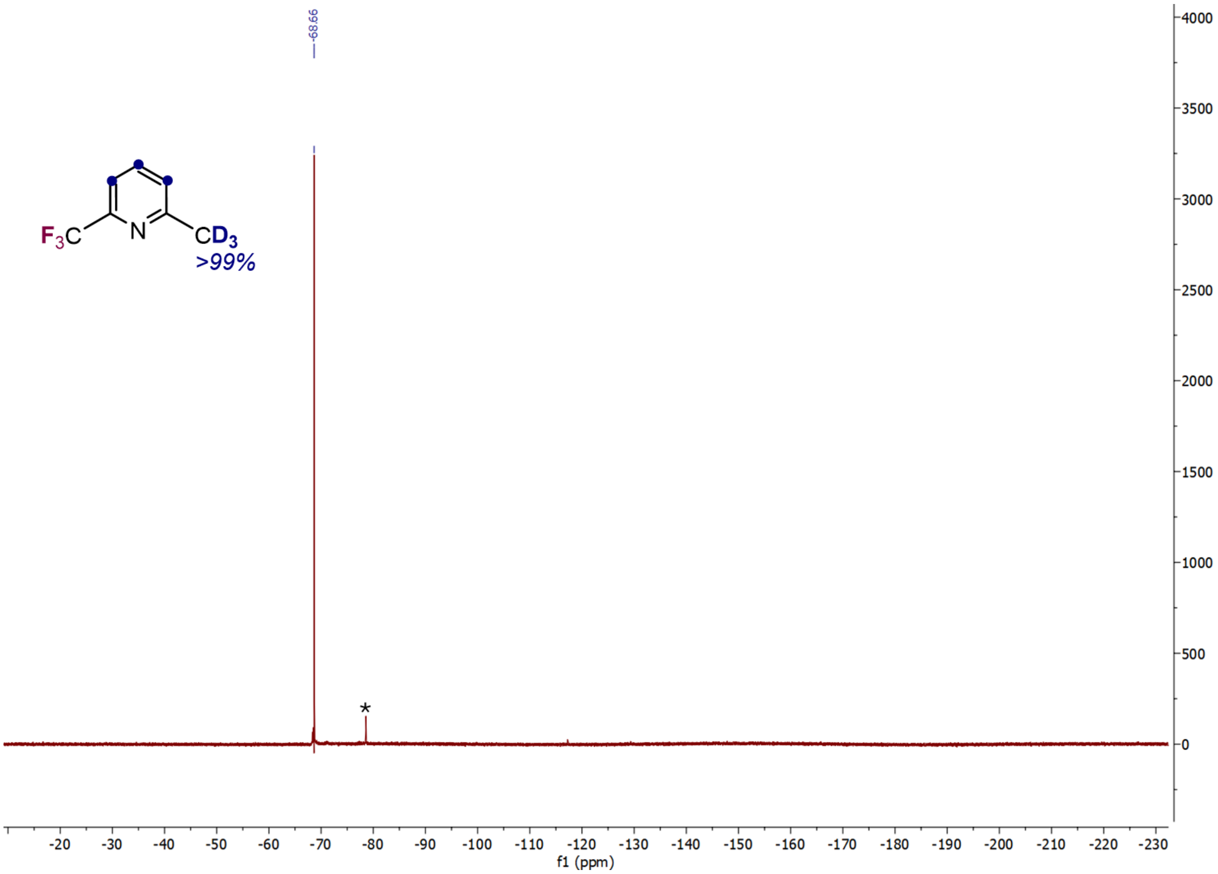


Figure S73: ^{19}F NMR (500 MHz, CD_3CN, 25 ºC) of 2-trifluoromethyl-6-(methyl-*d*$_3$)pyridine-3,4,5-*d*$_3$ (**10a’-*d*$_6$**).
*= Unidentified impurity

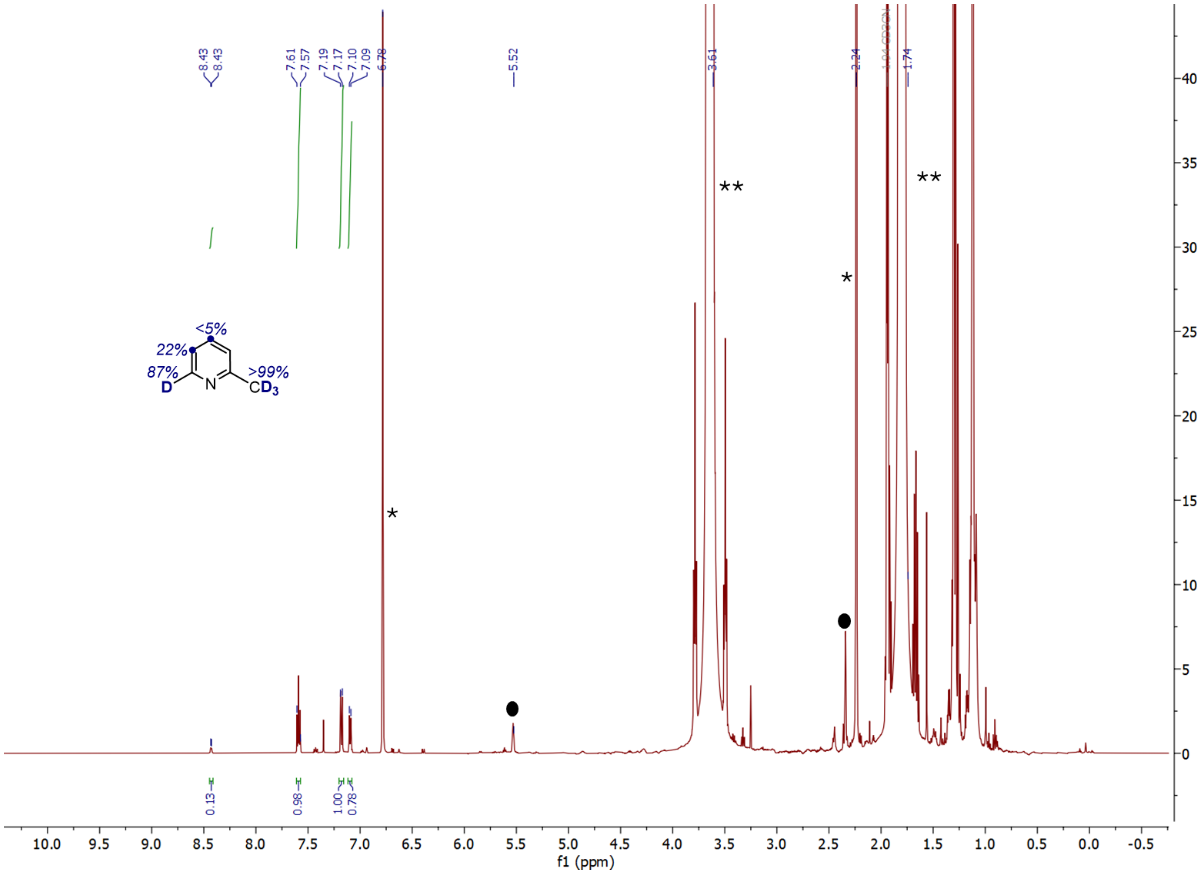


Figure S74: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-(methyl-*d_3*)pyridine-4,5,6-*d_2* (**1a-*d_6***) using 2-chloro-6-trifluoromethyl as the starting material.

*= Internal standard (Mesitylene)

**= THF

●= 1,5-COD

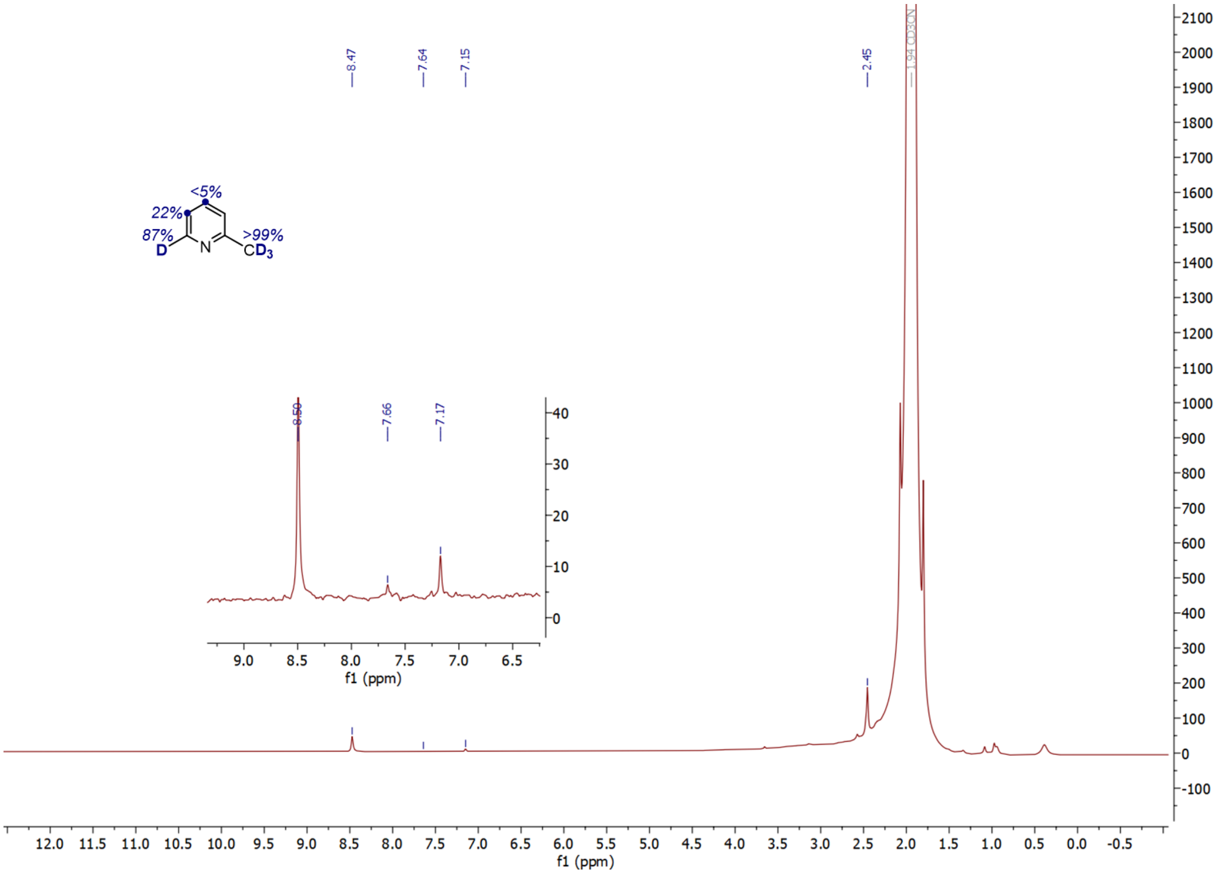


Figure S75: ^{2}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-(methyl-d_3)pyridine-4,5,6-d_3 (**1a-d_6**) using 2-chloro-6-trifluoromethyl as the starting material.

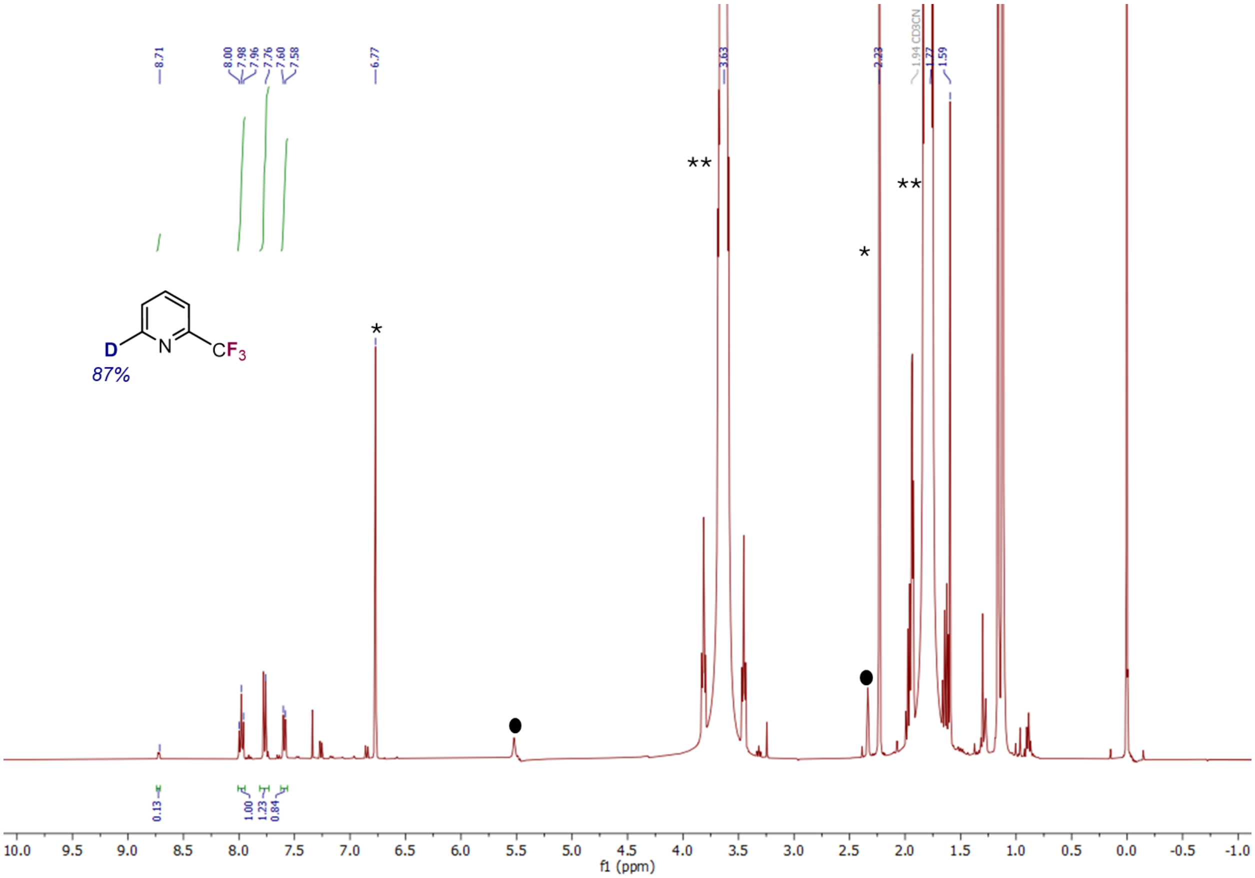


Figure S76: ^{1}H NMR (500 MHz, CD$_3$CN, 25 ºC) of 2-trifluoromethylpyridine-6-*d* (**1-*d***) using 2-chloro-6-trifluoromethyl as the starting material.

*= Internal standard (Mesitylene)

**= THF

●= 1,5-COD

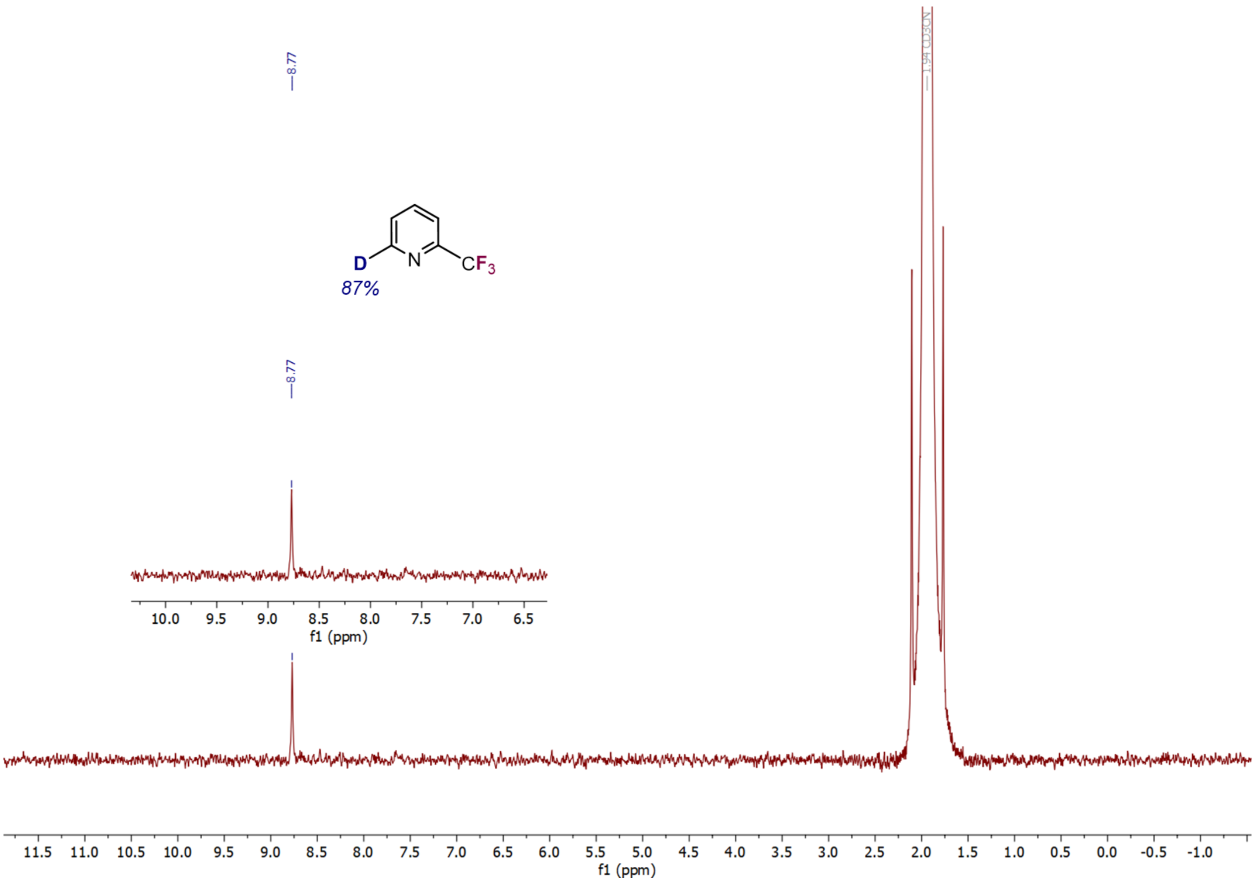


Figure S77: ^{2}H NMR (500 MHz, CD$_3$CN, 25 ºC) of 2-trifluoromethylpyridine-6-*d* (**1-*d***) using 2-chloro-6-trifluoromethyl as the starting material.

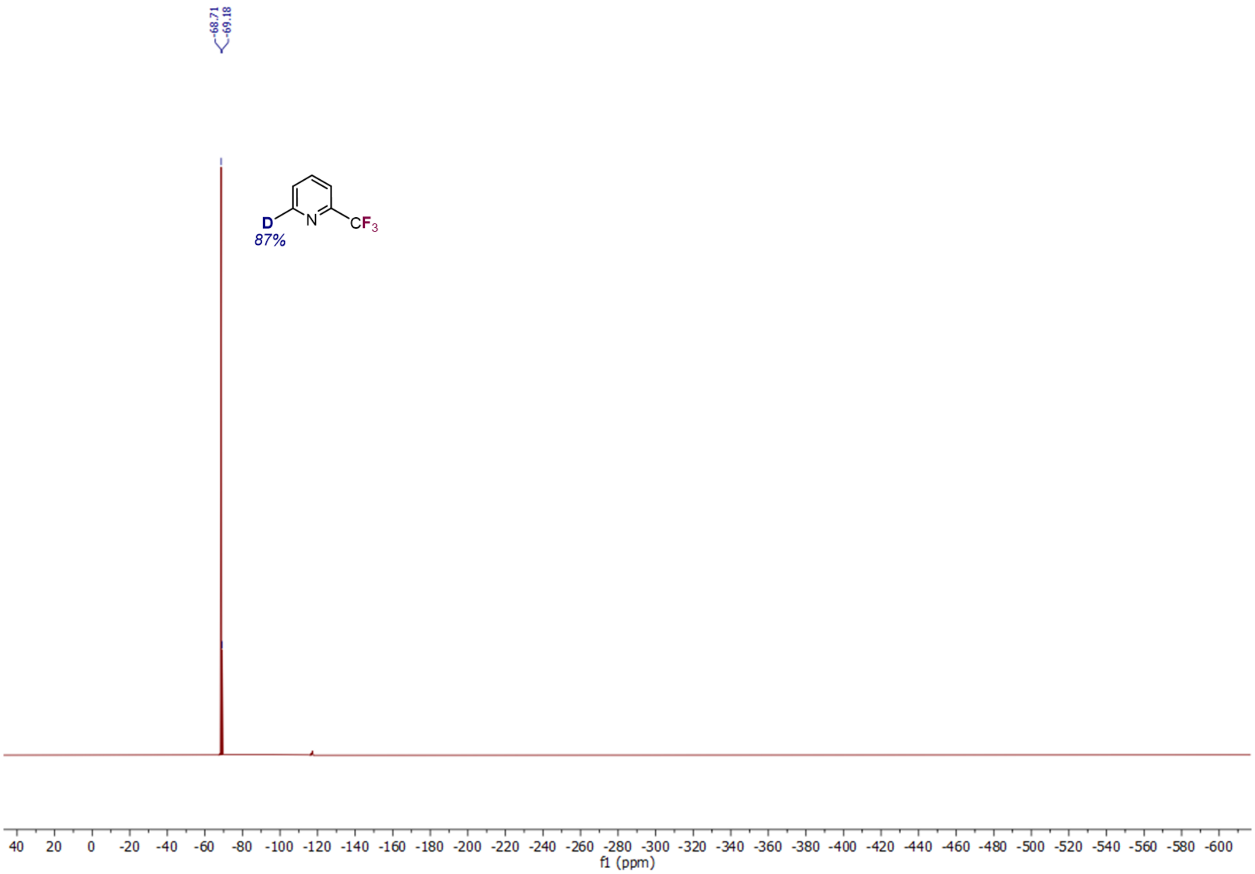


Figure S78: ^{19}F NMR (500 MHz, CD_3CN, 25 ºC) of 2-trifluoromethylpyridine-6-*d* (**1a-*d***) using 2-chloro-6-trifluoromethyl as the starting material.

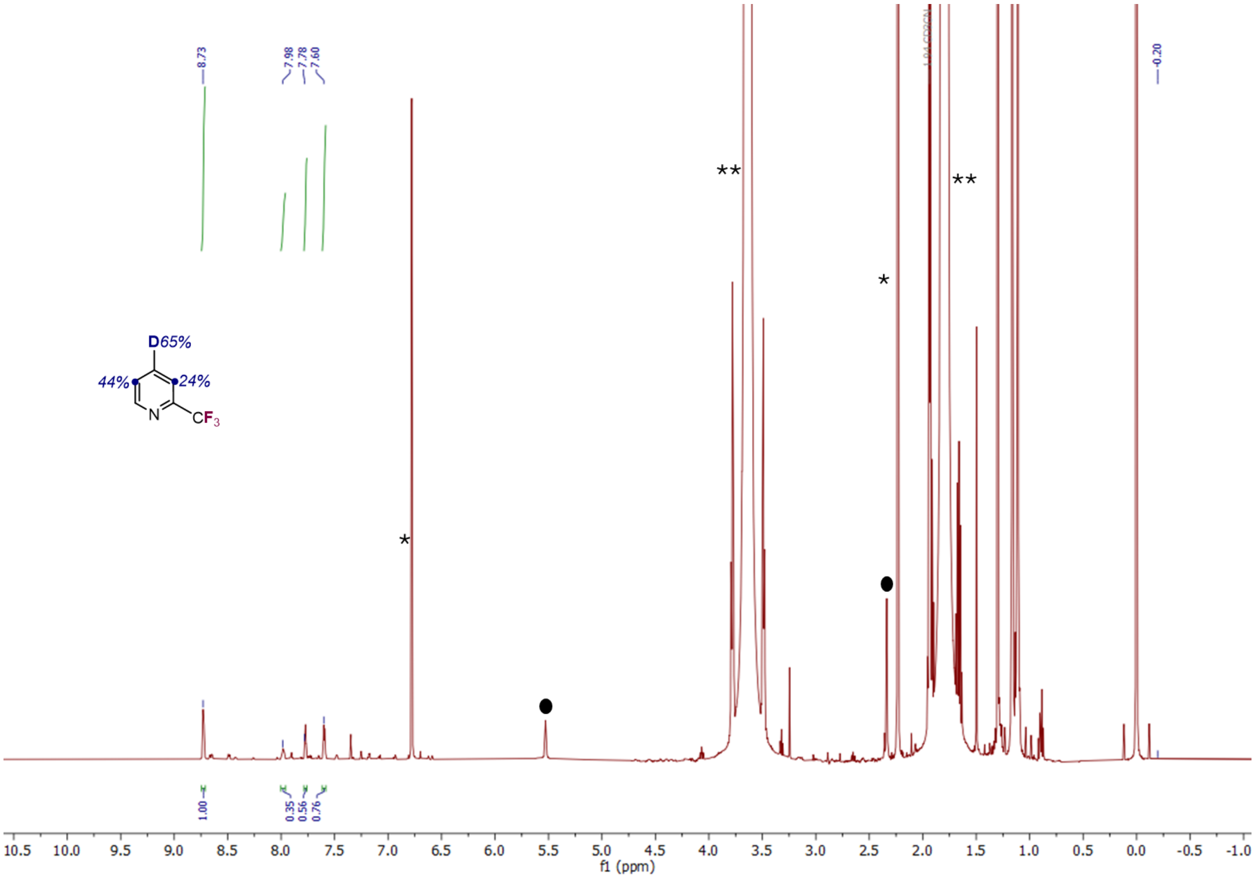


Figure S79: ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) of 2-trifluoromethylpyridine-3,*4,5*-d_3 **(1-d_3)** using 4-bromo-2-trifluoromethylpyridine as the starting material**.**

*= Internal standard (Mesitylene)

**= THF

●= 1,5-COD

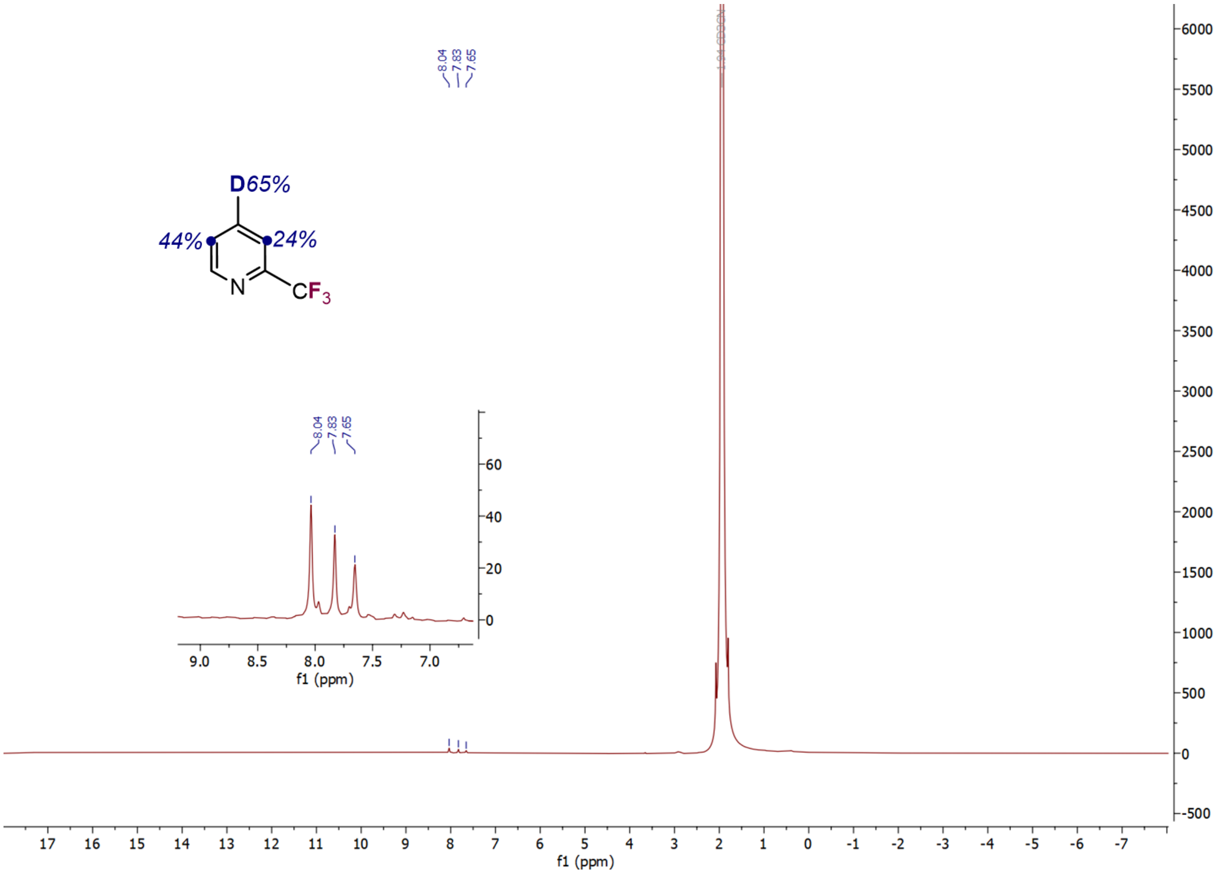


Figure S80: ^{2}H NMR (500 MHz, CD$_3$CN, 25 ºC) of 2-trifluoromethylpyridine-3,*4,5*-*d*$_3$ **(1-*d*$_3$)** using 4-bromo-2-trifluoromethylpyridine as the starting material**.**

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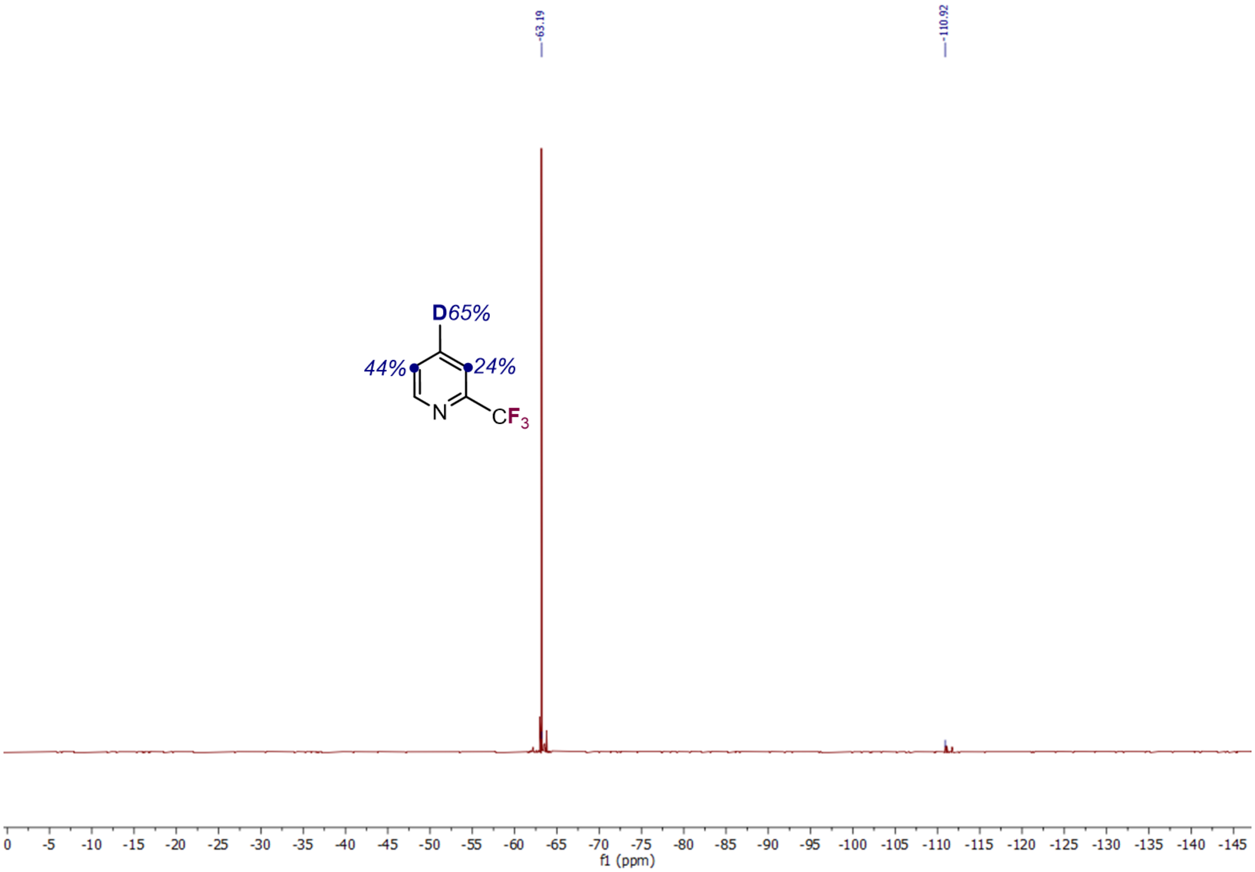

Figure S81: ^{19}F NMR (500 MHz, CD$_3$CN, 25 ºC) of 2-trifluoromethylpyridine-3,*4,5*-*d*$_3$ **(1-*d*$_3$)** using 4-bromo-2-trifluoromethylpyridine as the starting material**.**

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