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Metal-Free Reductive Coupling of Aliphatic Aldehydes/Ketones with 4-Cyanopyridines: Mechanistic Studies and Scope Extension

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1. Computational Investigations

1.1 Computational Details

All DFT calculations were carried out with Gaussian 16 package[1]. Geometry optimizations and vibrational frequencies of all the stationary points were performed by using the B3PW91-D3BJ[2]/6-31G(d,p) method. A "broken-symmetry" guess was used for calculations on open-shell systems. To confirm that each transition state connects the desired reactants and products along the reaction path, we performed intrinsic reaction coordinate (IRC)[3] calculations at the same level. To get more reliable energies, single point energies were computed at the (U)B3PW91-D3BJ/cc-pVTZ level for all the species. The solvent effect was treated with the polarizable continuum model (PCM)[4] with benzene as the solvent. The 3D structures were generated with CYL view package.[5]

Activation free energy barriers here are defined as the free energy difference between the transition state and the lowest-energy stationary point before it in the reaction pathways.

1.2 DFT Calculations on the Bis(pinacolato)diboron Mediated Reductive Coupling Reaction Using Acetone and 4-Cyanopyridine as the Model Substrates.

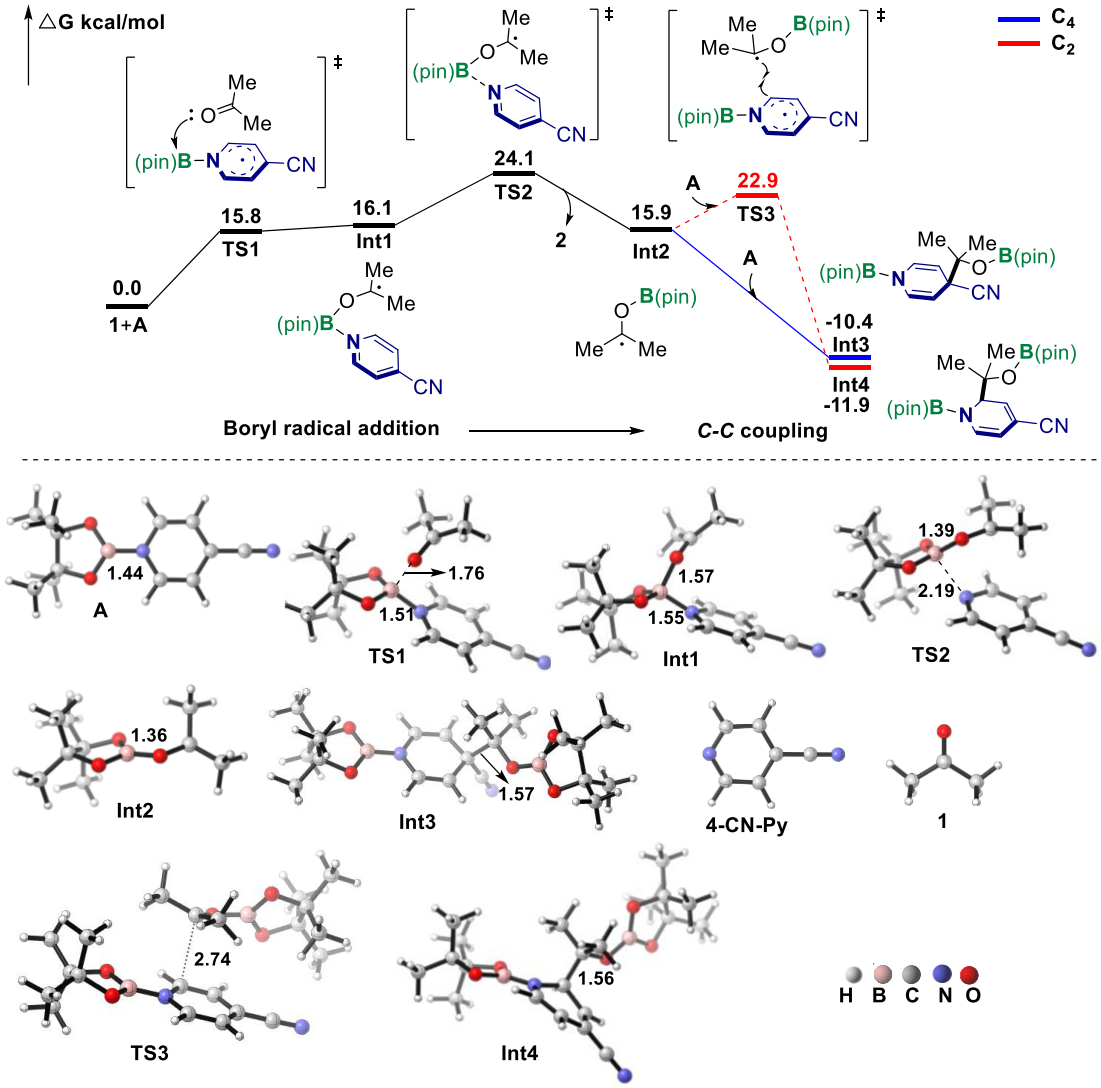


Figure S1. Gibbs free energy profile and 3D structures of the species involved in the bis(pinacolato)diboron (B_2pin_2) mediated reductive coupling of acetone and 4-cyanopyridine. Selected distances were shown in Å.

As shown in Figure S1, our calculations suggested that the in situ generated 4-cyanopyridine-boryl radical (**A**) can coordinate with the carbonyl of acetone (*via* **TS1**, see Figure S2 for IRC analysis) to form the intermediary radical species **Int1**. Subsequent dissociation of 4-cyanopyridine (**2**) affords a ketyl radical **Int2**, which is the rate-determining step in the reaction, and the corresponding barrier is 24.1 kcal/mol (*via* **TS2**, relative to the starting reactants **1a** and **A**). Then, the coupling of **Int2** with C_4 position of 4-cyanopyridine-boryl radical (**A**) afford the key radical-radical coupling

intermediate **Int3**. As shown in Figure S3, the scanning results of C-C bond length indicated that the radical-radical coupling of the active intermediate **Int2** and **A** is a barrierless process and the whole reaction is exothermic by 10.4 kcal/mol. For the formation of C-C_2 cross-coupling intermediate **Int4**, it requires an activation barrier of 22.9 kcal/mol (red line, *via* **TS3**), which is much higher than the C-C_4 pathway. Thus, The C-C_4 coupling reaction is the kinetically more favorable pathway.

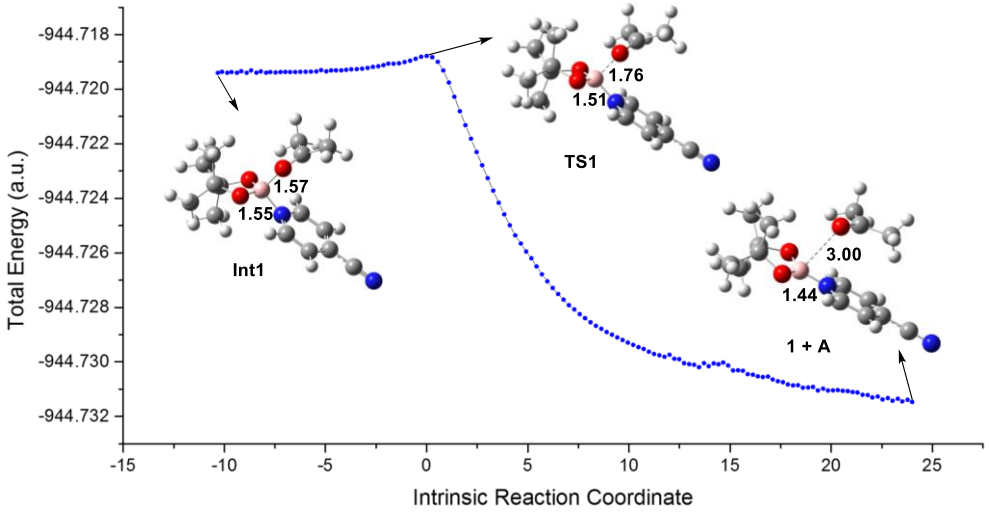


Figure S2. IRC analysis starting from the boryl radical addition transition state (**TS1**) using B3PW91-D3BJ/6-31g(d, p) method.

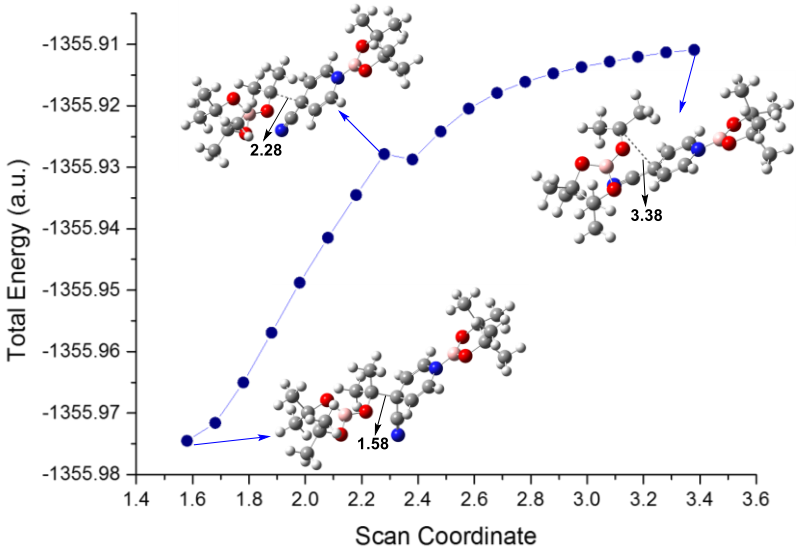


Figure S3. The scan coordinate analysis of C_4-C bond starting from the cross-coupling intermediate **Int3** using B3PW91-D3BJ/6-31g(d, p) method.

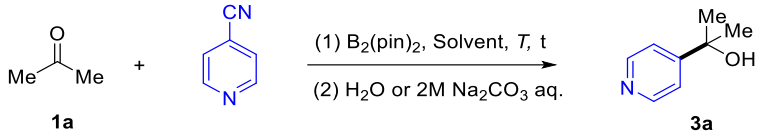
2. Experimental Studies on Substrate Scope

2.1 General Information

Unless otherwise noted, all air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under argon or argon-filled glove-box. Anhydrous methyl tert-butyl ether (MTBE), ethyl acetate (EA), acetonitrile (MeCN), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and 1, 2-dichloroethane (DCE) were purchased from *J&K* used as received. 4-Cyanopyridine and $B_2(pin)_2$ was purchased from TCI. Other commercially available reagents were purchased from Acros, *J&K* and Alfa Aesar Chemical Company. All other commercially available reagents were used without further purification. NMR spectra were recorded on a Bruker AVANCE III–400 spectrometer. Chemical shifts were reported in ppm relative to deuterated solvent for ^1H NMR ($CDCl_3$: 7.26 ppm), ^{13}C NMR ($CDCl_3$: 77.16 ppm). Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using neat thin film technique. High-resolution mass spectra (HRMS) were recorded on Thermo Quest Finnigan LCQDECA system equipped with an ESI ionization source.

2.2 Development of Bis(pinacolato)diboron Mediated Reductive Coupling of Aliphatic Aldehydes/Ketones and 4-Cyano pyridine

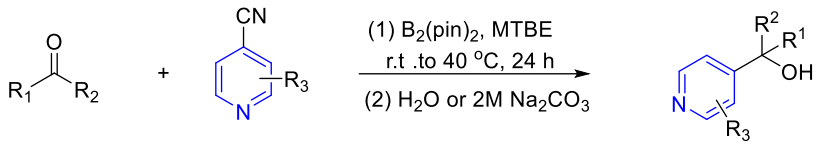
***Table S1*: Optimization of Reaction Conditions.**[a]



Entry	Time (h)	*T*	Solvent	Yield (%)[b]
1	12	r.t.	MeCN	29%
2	12	r.t.	CH_2Cl_2	trace
3	12	r.t.	DCE	16%
4	12	r.t.	EA	58%
5	12	r.t.	$PhCF_3$	61%
6	12	r.t.	THF	68%
7	**12**	**r.t.**	**MTBE**	**81%**
8	**12**	**40** °C	**MTBE**	**85%**
9	12	70°C	MTBE	75%
10	12	90°C	MTBE	62%
11	**24**	**r.t.**	**MTBE**	**92%**
12	**24**	**40** °C	**MTBE**	**96% (92%)**[c]

[a] Reaction conditions: acetone (0.2 mmol), 4-cyanopyridine (0.3 mmol), $B_2(pin)_2$ (0.24 mmol), solvent (1.0 mL). [b] Yields of **3a** were determined by ^1H NMR analysis of the crude reaction mixture with benzyl ether as an internal standard. [c] Isolated yield.

2.3 General procedure for the synthesis of pyridine-functionalized alcohols



General procedure A: In an oven-dried 10 ml Schlenk flask equipped with a magnetic stir bar, 4-cyanopyridines (0.3 mmol, 1.5 equiv), $B_2(pin)_2$ (0.24 mmol, 1.2 equiv), MTBE (1 mL) and the corresponding coupling partner (aldehyde or ketone) were added in turn. Then, the reaction mixture was stirred at 40 °C or room temperature for 24 hours. After cooling to room temperature, the reaction mixture was quenched with 2M Na_2CO_3 aqueous solution (2 mL), and stirred under air for 10 minutes. Then, the reaction mixture extracted with EtOAc (3×5 mL). The combined organic layer was dried over Na_2SO_4, concentrated under vacuum and the residue was purified by preparative TLC or flash chromatography on silca gel to afford the desired product.

Note: The effect of substituents on the pyridine ring was also investigated, 4-cyanopyridines bearing substituents such as F, Cl, and methyl, at C-3 position could afford the corresponding radical-coupling products (**6a**, **6e-6h)** in moderate to high yield. However, 2-position substituted pyridines, including 2-fluoro-4-cyanopyridine, 2-chloro-4-cyanopyridine and 2,4-dicyanopyridine were not tolerated in this reaction (**6b-6d**), presumably due to the fact that these pyridines are not able to activate the B-B bond of $B_2(pin)_2$ to generate the corresponding pyridine-boryl radical for initiating the radical-radical coupling reaction.[6]

3. Experimental Studies on the Reaction Mechanism

Detecting the key Radical Cross-Coupling Intermediate by Spectroscopic Analysis

In order to verify the involvement of the key radical cross-coupling intermediates under the proposed radical addition/coupling addition conditions, NMR, HRMS and XRD analysis was performed to detect the possible intermediates.

(a) Monitoring the radical addition/cross-coupling reaction of acetone-d_6 (1b) by ^{1}H NMR spectroscopy: detection of key radical cross-coupling intermediate.

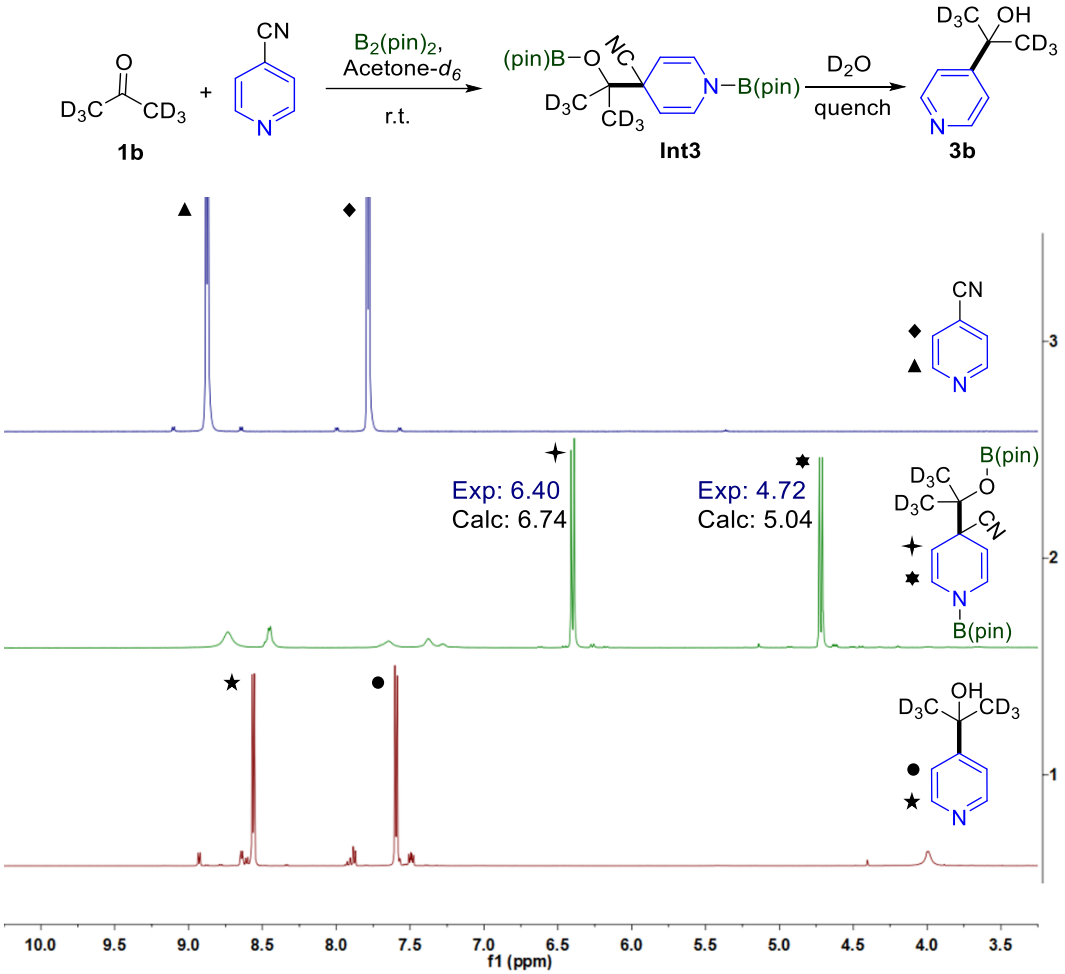
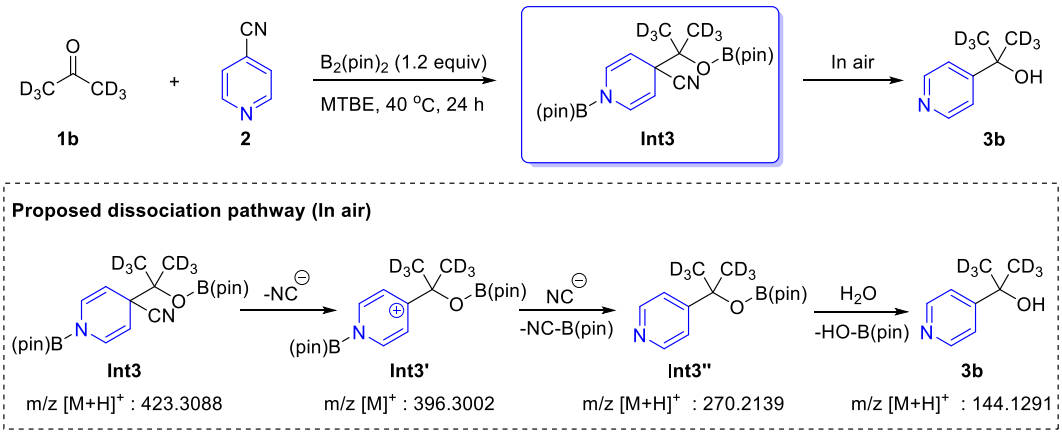


Figure S4. **Top**: ^{1}H NMR spectrum of 4-cyanopyridine in acetone-d_6. **Middle**: ^{1}H NMR spectrum of the reaction mixture of acetone-d_6, 4-cyanopyridine and $B_2(pin)_2$ in acetone-d_6 for 3h. **Bottom**: ^{1}H NMR spectrum of the reaction mixture after add two drops of D_2O for 10 min.

Experimental procedure: B_2pin_2 (30.5 mg, 0.12 mmol) and 4-cyanopyridine (10.4 mg, 0.10 mmol) were mixed in 0.5 mL acetone-d_6 in a NMR tube. The mixture was

stirred at room temperature for 3 h. Then the NMR analysis of the crude reaction mixture was carried out immediately. After which, adding two drops of D_2O into the NMR tube and shaking for 10 min, the ^1H NMR spectrum of the reaction mixture was acquired again.

(b) Detecting the key intermediates by HRMS analysis



Experimental procedure: acetone-d_6 (0.20 mmol), B_2pin_2 (61.0 mg, 0.24 mmol) and 4-cyanopyridine (20.8 mg, 0.20 mmol) were mixed in 1.0 mL MTBE in a Schlenk tube. The mixture was stirred at room temperature for 24h, after which, the ESI-MS analysis of the crude reaction mixture was carried out immediately. The mass for key intermediate (**Int3**) is $C_{21}H_{29}D_6B_2N_2O_5^+$ $[M+H]^+$ calc. 423.3103, found 423.3102 (Figure S3). This result was consistent with the observation from ^1H NMR analysis (See Figure S2). Moreover, the key positive ion (**Int3′**), dissociating from neutral intermediate **Int3**, was also detected by HRMS. Moreover, we were also able to monitor the aromatized intermediate **Int3′′** in the mixture.

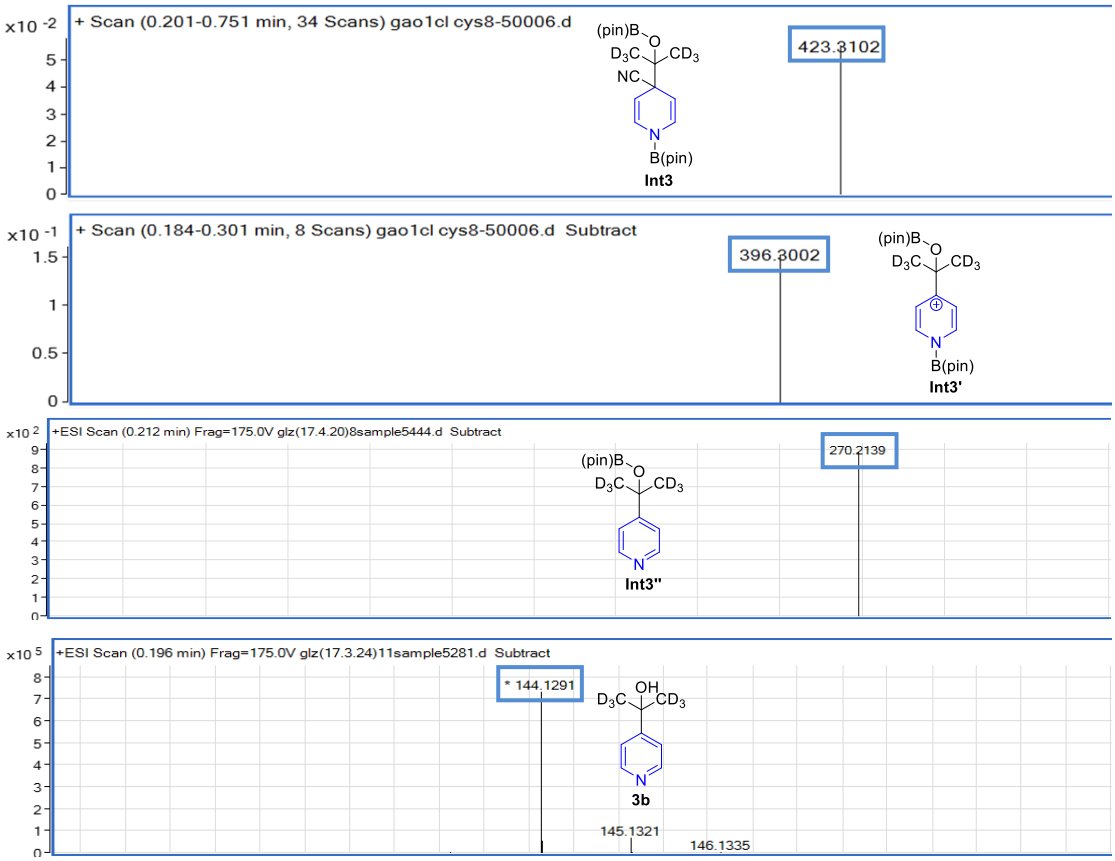


Figure S5. HRMS analysis of the crude reaction mixture of acetone-d_6, $B_2(pin)_2$, 4-cycanopyridine in MTBE.

(c) Structural confirmation of the key intermediate Int3 by single-crystal X-ray diffraction (XRD).

(1) Synthesis of Int3

Experimental procedure: In an oven-dried 10 ml Schlenk tube equipped with a magnetic stir bar, acetone-d_6 (0.2 mmol, 12.8 mg), B_2pin_2 (0.21 mmol, 1.05 equiv, 53.5 mg), 4-cyanopyridine (0.20 mmol, 1.0 equiv, 20.8 mg) and 2.0 mL MTBE was added in turn. Then the reaction mixture was stirred at room temperature for 24h. After which, put this Schlenk tube into a low temperature refrigerator (-30 °C) and the crystals started to precipitate.

(2) X-ray analysis of Int3

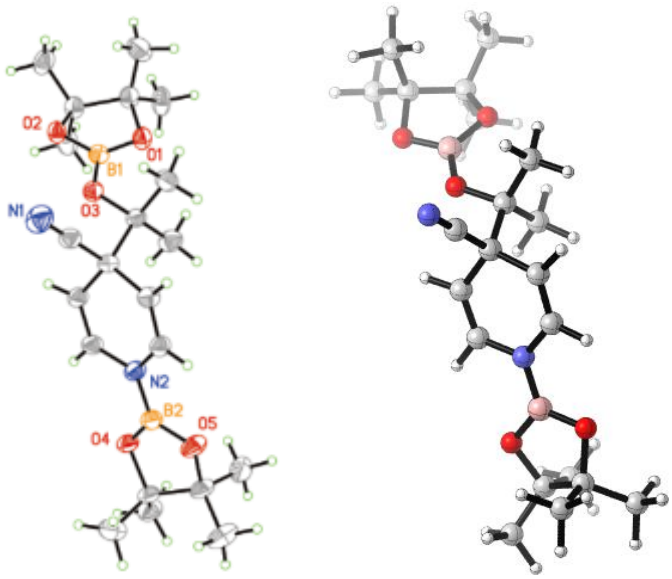


Figure S6. Left: the X-ray structure of **Int3**. Right: the DFT calculation optimized structure of **Int3**.

Table S2. Crystal data and structure refinement for Int3

Molecular Formula	$C_{21}H_{34}B_2N_2O_5$	
Formula mass	416.12	
Crystal system	Monoclinic	
Space group	*P*2(1)/c	
Z	4	
Temp. (K)	120(2)	
Unit cell dimensions	a = 12.4551(6) Å	α = 90°.
	b = 20.4059(10) Å	β = 105.643(2)°.
	c = 12.3794(7) Å	γ = 90°.
Volume	3029.8(3) Å^3	
Density (calculated)	0.912 $g.cm^{-3}$	
Absorption coefficient	0.063 mm^{-1}	
F(000)	896	
Theta range for data collection	1.978° to 25.006°	
Index ranges	-13<=h<=14, -24<=k<=24, -14<=l<=14	
Reflections collected	21721	
Independent reflections	5314 [R(int) = 0.0336]	
Completeness to theta =25.006°	99.4%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5314 / 0 / 281	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.2138	
R indices (all data)	R1 = 0.0582, wR2 = 0.2286	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.985 and -0.590 e.Å^{-3}	

(d) Structural confirmation of the key intermediate Int3 by the NMR analysis

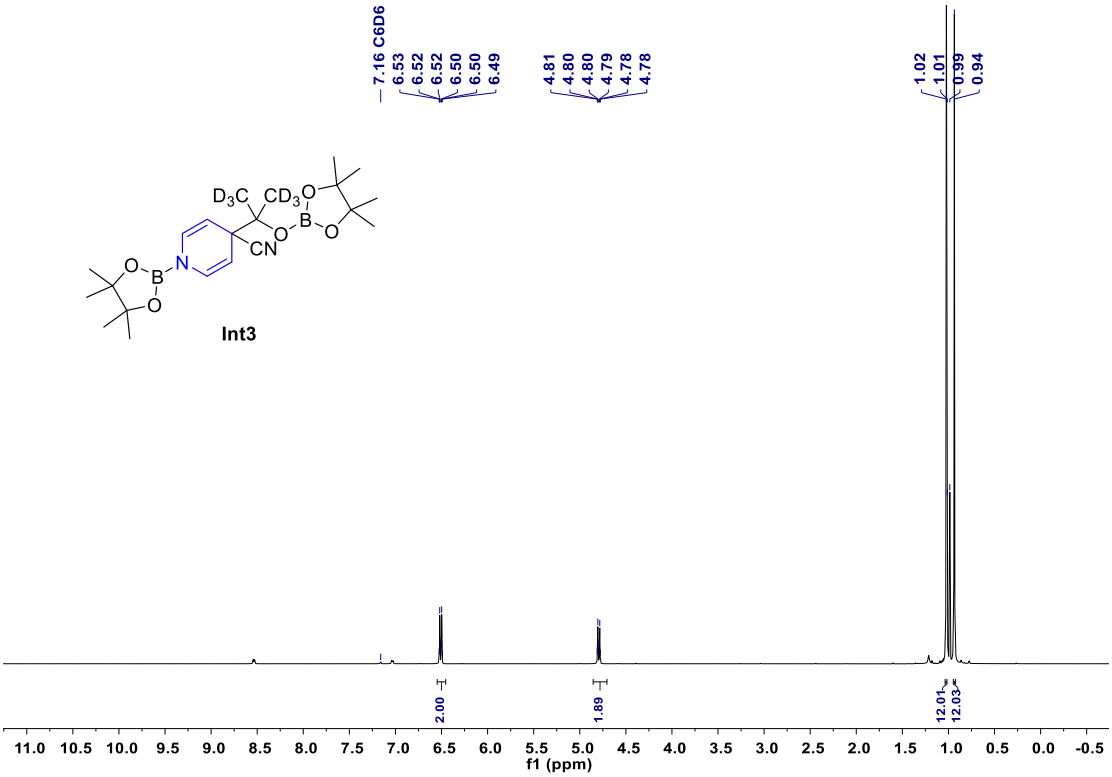


Figure S7. ^{1}H NMR spectra for **Int3** (in benzene-d_6).

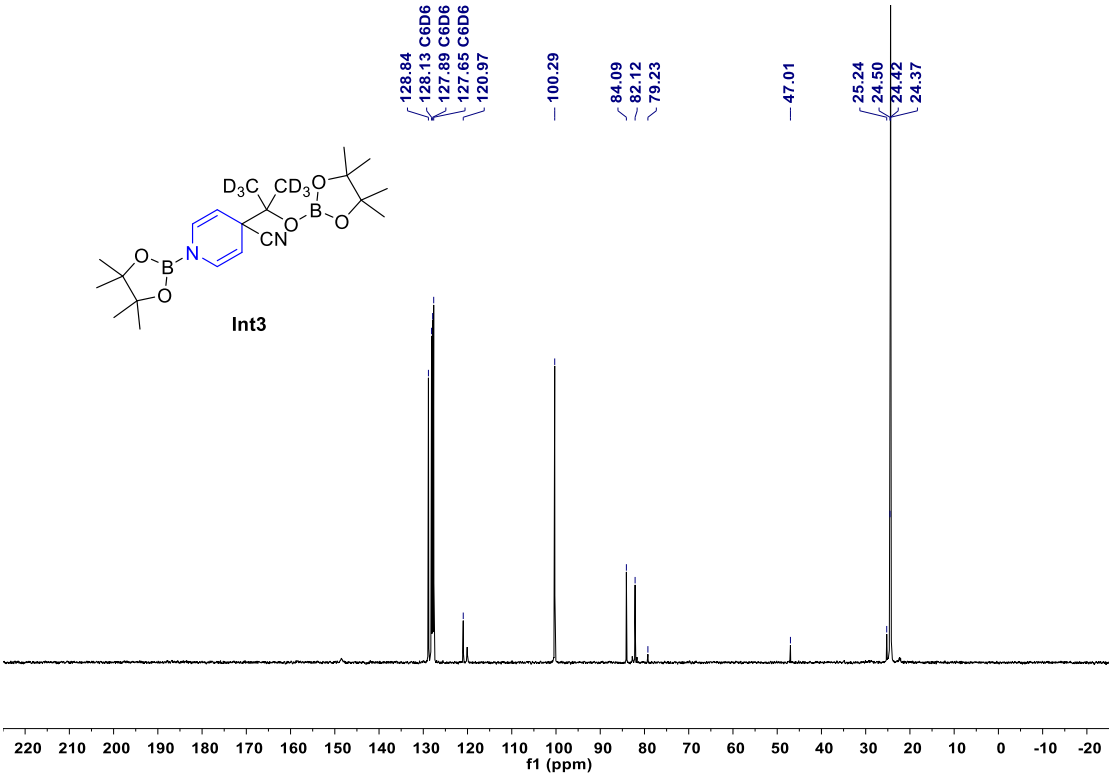


Figure S8. ^{13}C NMR spectra for **Int3** (in benzene-d_6).

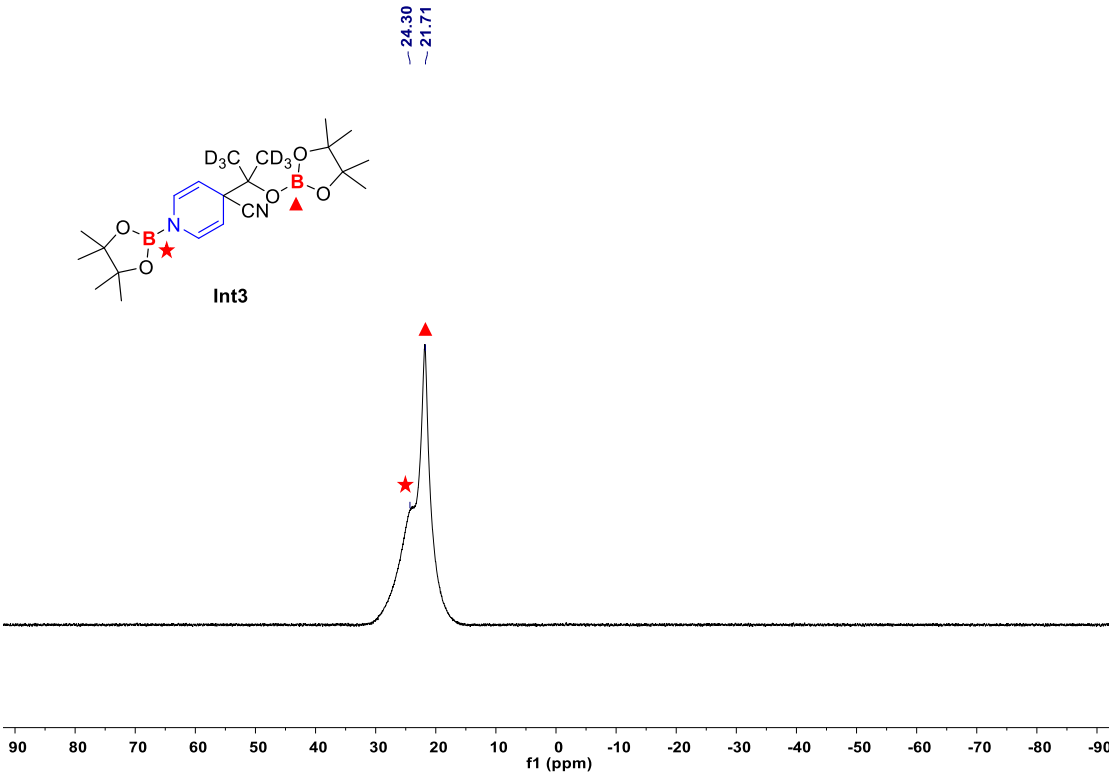
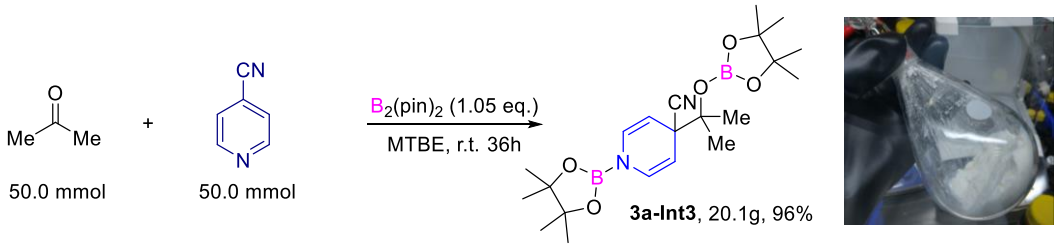


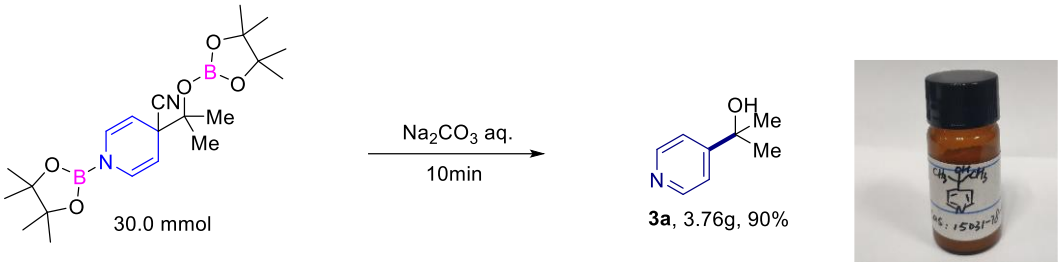
Figure S9. ^{11}B NMR spectra for **Int3** (in benzene-d_6).

4. Synthetic applications

4.1 Gram-scale experiment

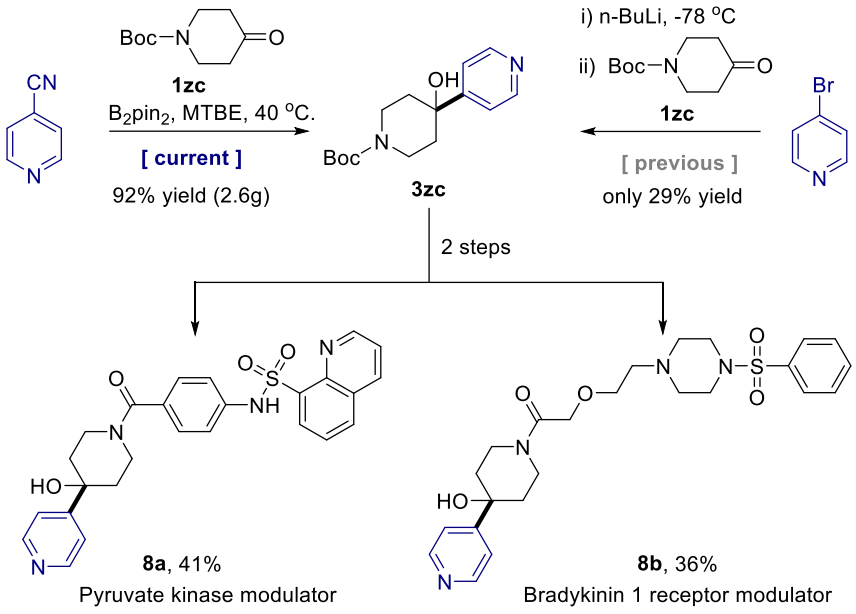


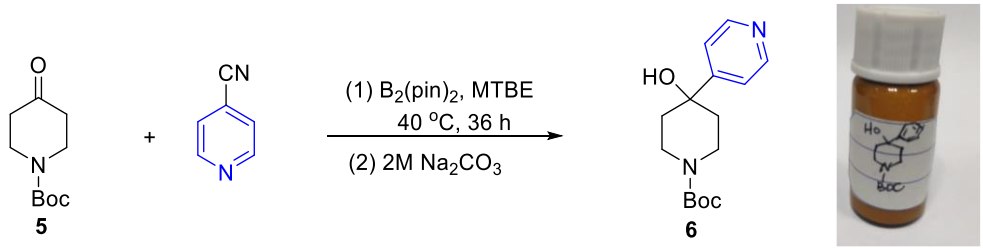
In the glove-box, an oven-dried 250 ml reaction flask equipped with a magnetic stir bar, $B_2(pin)_2$ (13.3 g, 52.5 mmol, 1.05 equiv), MTBE (70.0 mL, super dry), acetone (2.96 g, 50.0 mmol, 1.0 equiv) and 4-cyanopyridine (5.2 g, 50.0 mmol, 1.0 equiv), was added in turn. The reaction mixture was stirred at room temperature for 36 hours. Then the crystallization of the intermediate from the reaction mixture at -35 °C furnished white solid identified as the intermediate compound **Int3** (20.1 g, 96% yield).



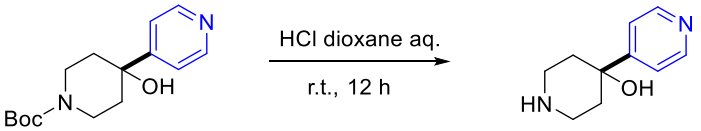
In a 100 ml reaction flask, 30.0 mmol **Int3** (12.5 g) was quenched with 2M Na_2CO_3 aqueous solution (40 mL). The reaction mixture was stirred under air for 10 minutes, and extracted by EtOAc (3 × 50 mL). The combined organic layer was washed with saturated brine (2 × 30 mL) and dried over Na_2SO_4. and then concentrated in vacuo to afford the crude product. This crude material was purified by flash chromatography to afford desired product **3a** in 90% yield (3.76 g scale).

4.2 Applications of the metal-free reductive coupling reaction in pharmaceutical chemistry





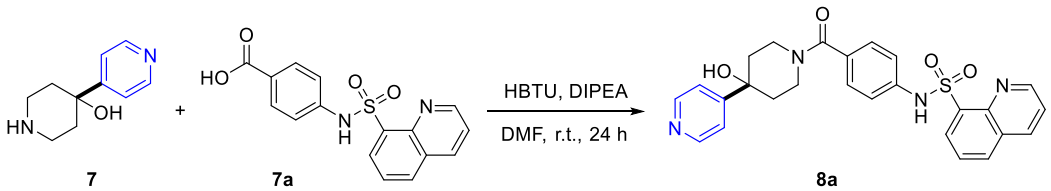
A sealed reaction flask equipped with a magnetic stir bar, 1-Boc-4-piperidone (10.0 mmol, 1.0 equiv), 4-cyanopyridine (15.0 mmol, 1.5 equiv), $B_2(pin)_2$ (12.0 mmol, 1.2 equiv), MTBE (50.0 mL, **Super dry**) was placed in a heated oil bath (40 °C). After 36 hours the reaction was quenched with 2M Na_2CO_3 aqueous solution (20 mL). The reaction mixture was stirred under air for another 10 minutes, and extracted by EtOAc (3 × 50 mL). The combined organic layer was washed with saturated brine (2 × 30 mL) and dried over Na_2SO_4, and then concentrated in vacuo to afford the crude product. This crude material was purified by flash chromatography to afford desired product **3zc** in 92% yield (2.61 g scale).



3zc **7**

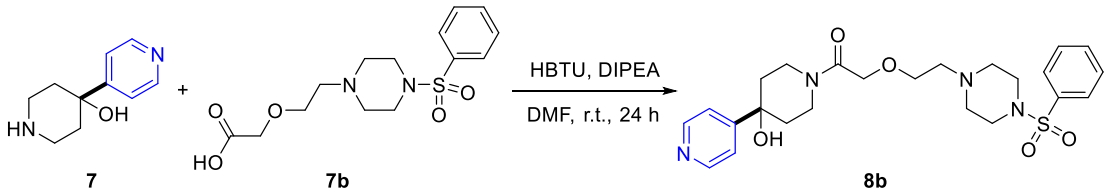
To a solution of **3zc** (1.4 g, 5.0 mmol, 1.0 eq.) in 30.0 mL 1,4-dioxane, was added HCl dioxane aq. (10.0 eq.), the reaction mixture was stirred at room temperature for about 12 hours. Then, the reaction mixture was made alkaline with 2M Na_2CO_3 aq. and concentrated. After which, the crude product was redissolved in 20 mL MeOH/$CHCl_3$ (1:1). The organic layer was anhydrified with Na_2SO_4, and the solvent was removed, to yield the desired product **7** (0.8 g, 90% yield).

The desire products **8a**[7] and **8b**[8] were prepared according to the reported procedure, All synthesized products matched known ^1H and ^{13}C NMR spectra.



7 **7a** **8a**

To a round-bottomed flask was added compound **7** (90.0 mg, 0.5 mmol, 1.0 eq.), DMF (2 mL), DIPEA (3.0 eq.), and **7a** (164.2 mg, 0.5 mmol, 1.0 eq.) sequentially, the reaction mixture was stirred at room temperature for 24 hours. Then, the reaction mixture was diluted with brine, extracted with ethyl acetate, the organic layer was dried with anhydrous Na_2SO_4, filtered, and filtrate was concentrated. The desired product was purified by preparative TLC (100/10, EA/MeOH) to afford **8a** (99.4 mg, 41% yield).

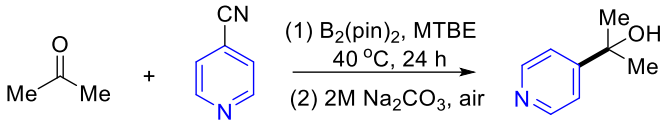


7 **7b** **8b**

To a round-bottomed flask was added compound **7** (90.0 mg, 0.5 mmol, 1.0 eq.), DMF (2 mL), DIPEA (3.0 eq.), and **7b** (164.5 mg, 0.5 mmol, 1.0 eq.) sequentially, the reaction mixture was stirred at room temperature for 24 hours. Then, the reaction mixture was diluted with brine, extracted with ethyl acetate, the organic layer was dried with anhydrous Na_2SO_4, filtered, and filtrate was concentrated. The desired product was purified by preparative TLC (100/10/0.5, DCM/MeOH/NH_3•H_2O) to afford **8b** (88.1 mg, 36% yield).

5. Spectroscopic Characterization of Products

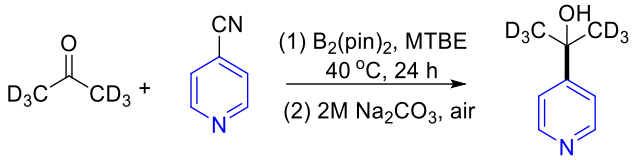
5.1 Using ketones as the coupling partner



1a **3a**

3a: Prepared following *general procedure A* using **1a** (11.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3a** (25.2 mg, 92% yield).

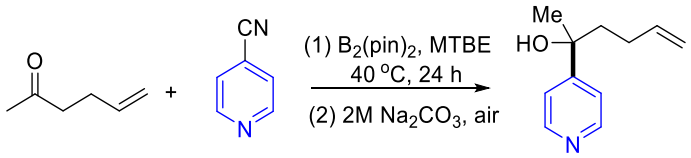
3a: White solid, mp 107-109 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, J = 4.4 Hz, 2H), 7.38 (d, J = 6.2 Hz, 2H), 3.62 (s, 1H), 1.55 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 149.5, 120.0, 71.6, 31.4. **IR** (film): 3196, 2988, 2880, 1605, 1408, 1173, 962, 837 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_8H_{12}NO$ $[M+H]^+$ 138.0913, found 138.0912.



1b **3b**

3b: Prepared following *general procedure A* using **1b** (12.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3b** (26.8 mg, 93% yield).

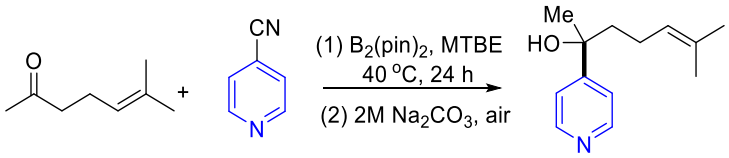
3b: White solid, mp 92-94 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, J = 6.2 Hz, 2H), 7.44 (d, J = 6.4 Hz, 2H), 3.58 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 149.1, 120.5, 71.4, 30.3 (m). **IR** (film): 3201, 2924, 2850, 1605, 1424, 1047, 841 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_8H_6D_6NO$ $[M+H]^+$ 144.1290, found 144.1291.



1c **3c**

3c: Prepared following *general procedure A* using **1c** (19.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3c** (25.4 mg, 72% yield).

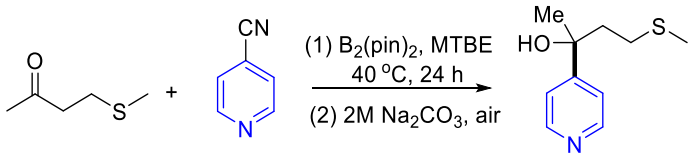
3c: White solid, mp 55-57 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.4 Hz, 2H), 7.36 (d, J = 6.3 Hz, 2H), 5.75 (m, 1H), 4.98-4.86 (m, 2H), 3.33 (s, 1H), 2.13-2.03 (m, 1H), 1.92-1.85 (m, 3H), 1.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 149.4, 138.3, 120.5, 115.0, 73.9, 42.7, 30.1, 28.3. **IR** (film): 3218, 2928, 2853, 1601, 1415, 1163, 910, 826 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226, found 178.1225.



1d **3d**

3d: Prepared following *general procedure A* using **1d** (25.2 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **3d** (37.5 mg, 91% yield).

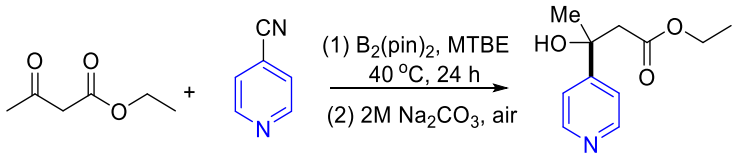
3d: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.3 Hz, 2H), 7.36 (d, J = 6.3 Hz, 2H), 5.06-5.00 (m, 1H), 3.41 (s, 1H), 2.01-1.95 (m, 1H), 1.84-1.77 (m, 3H), 1.61 (s, 3H), 1.51 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 149.3, 132.6, 123.8, 120.6, 74.1, 43.4, 30.2, 25.8, 22.8, 17.7. IR (film): 3217, 2970, 2855, 1714, 1601, 1411, 1201, 826 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1540.



1e **3e**

3e: Prepared following *general procedure A* using **1e** (23.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3e** (34.8 mg, 88% yield).

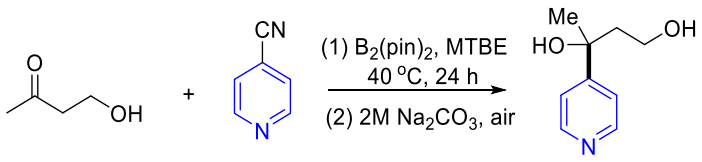
3e: White solid, mp 82-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.0 Hz, 2H), 7.36 (d, J = 6.3 Hz, 2H), 4.18 (s, 1H), 2.48-2.41 (m, 1H), 2.35-2.27 (m, 1H), 2.07 (t, J = 7.7 Hz, 2H), 2.03 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 149.5, 120.5, 74.1, 41.9, 30.4, 28.9, 15.5. **IR** (film): 3212, 2916, 2855, 1601, 1412, 1066, 826 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{16}NOS$ $[M+H]^+$ 198.0947, found 198.0947.



1f **3f**

3f: Prepared following *general procedure A* using **1f** (26.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3f** (18.1 mg, 43% yield).

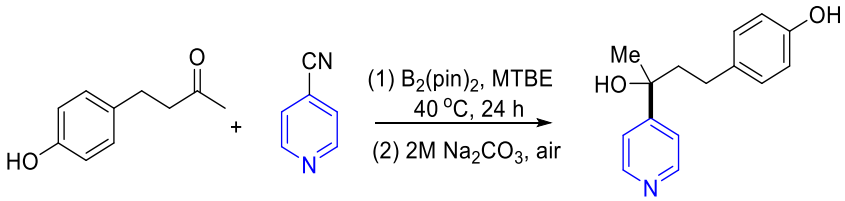
3f: White solid, mp 76-78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, J = 6.4 Hz, 2H), 7.37 (d, J = 6.3 Hz, 2H), 4.58 (s, 1H), 4.11-4.00 (m, 2H), 2.93 (d, J = 16.2 Hz, 1H), 2.79 (d, J = 16.3 Hz, 1H), 1.51 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 156.4, 149.8, 120.1, 72.2, 61.2, 45.7, 30.2, 14.1. **IR** (film): 3188, 2981, 2856, 1736, 1601, 1411, 1201, 826 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{11}H_{16}NO_3$ $[M+H]^+$ 210.1125, found 210.1125.



1g **3g**

3g: Prepared following *general procedure A* using **1g** (17.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (101.6 mg, 0.40 mmol, 2.0 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/2 PE/EtOAc) to afford **3g** (30.1 mg, 90% yield).

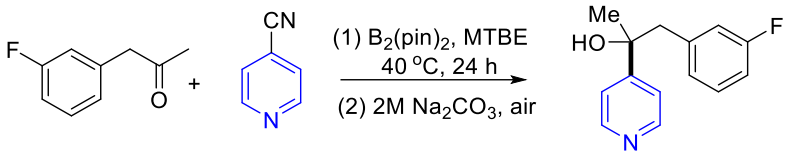
3g: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48-8.40 (m, 2H), 7.37 (d, J = 6.3 Hz, 2H), 5.16 (s, 1H), 4.28 (s, 1H), 3.87-3.69 (m, 1H), 3.59-3.41 (m, 1H), 2.17-1.92 (m, 2H), 151 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 149.1, 120.5, 75.0, 59.6, 42.9, 30.4. **HRMS** (ESI-TOF) calculated for $C_9H_{14}NO_2$ $[M+H]^+$ 168.1019, found 168.1017.



1h **3h**

3h: Prepared following *general procedure A* using **1h** (32.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3h** (19.6 mg, 40% yield).

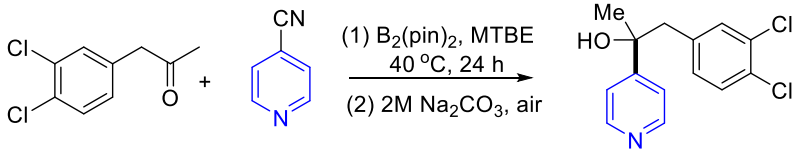
3h: gum. **^{1}H NMR** (400 MHz, CD_3OD) δ 8.54 (d, J = 6.4 Hz, 2H), 7.62 (d, J = 6.4 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 4.93 (s, 2H), 2.65-2.55 (m, 1H), 2.28-2.19 (m, 1H), 2.08-2.03 (m, 2H), 1.58 (s, 3H). **^{13}C NMR** (100 MHz, CD_3OD) δ 162.1, 157.2, 150.5, 135.0, 131.0, 123.3, 116.9, 75.3, 47.9, 31.2, 30.8. **IR** (film): 3193, 2921, 2851, 1604, 1514, 1407, 1244, 825 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{15}H_{18}NO_2$ $[M+H]^+$ 244.1332, found 244.1329.



1i **3i**

3i: Prepared following *general procedure A* using **1i** (30.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3i** (41.6 mg, 90% yield).

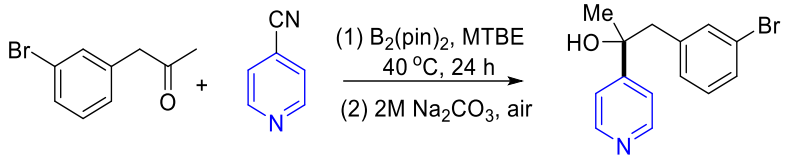
3i: White solid, mp 125-127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, J = 6.2 Hz, 2H), 7.31 (d, J = 6.3 Hz, 2H), 7.19-7.12 (m, 1H), 6.97-6.82 (m, 1H), 6.78-6.73 (m, 2H), 3.06 (s, 1H), 3.04-2.96 (m, 2H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162. 6 (d, $J_{C\text{-}F}$ = 245.8 Hz), 157.0, 149.4, 138.7, 129.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.3, 120.5, 117.5 (d, $J_{C\text{-}F}$ = 21.0 Hz), 113.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 73.8, 49.6, 29.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.3. **IR** (film): 3210, 2926, 2853, 1615, 1423, 1251, 824 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{14}H_{15}FNO$ $[M+H]^+$ 232.1132, found 232.1133.



1j **3j**

3j: Prepared following *general procedure A* using **1j** (40.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3j** (49.5 mg, 88% yield).

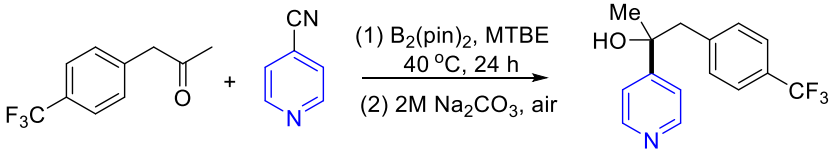
3j: White solid, mp 113-115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, J = 6.4 Hz, 2H), 7.33 (d, J = 6.3 Hz, 2H), 7.23 (d, J = 8.2 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 6.81 (dd, J = 8.2, 2.1 Hz, 1H), 3.46 (s, 1H), 2.95 (s, 2H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 149.2, 136.6, 132.5, 132.0, 131.0, 130.0, 129.9, 120.7, 73.7, 48.9, 28.9. **IR** (film): 3182, 2977, 2926, 2853, 1601, 1471, 1132, 827 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{14}H_{14}Cl_2NO$ $[M+H]^+$ 282.0447, found 282.0446.



1k **3k**

3k: Prepared following *general procedure A* using **1k** (42.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3k** (48.4 mg, 83% yield).

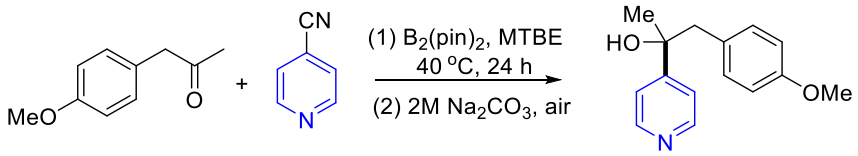
3k: White solid, mp 78-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, J = 6.2 Hz, 2H), 7.33-7.31 (m, 2H), 7.30 (s, 1H), 7.20 (t, J = 1.9 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.92-6.86 (m, 1H), 3.61 (s, 1H), 2.99-2.92 (m, 2H), 1.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 149.1, 138.6, 133.6, 129.9, 129.6, 129.3, 122.2, 120.7, 73.7, 49.5, 28.8. **IR** (film): 3195, 2976, 2852, 1600, 1412, 1136, 998, 823 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{14}H_{15}BrNO$ $[M+H]^+$ 292.0332, found 292.0330.



1l **3l**

3l: Prepared following *general procedure A* using **1l** (40.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **3l** (49.2 mg, 87% yield).

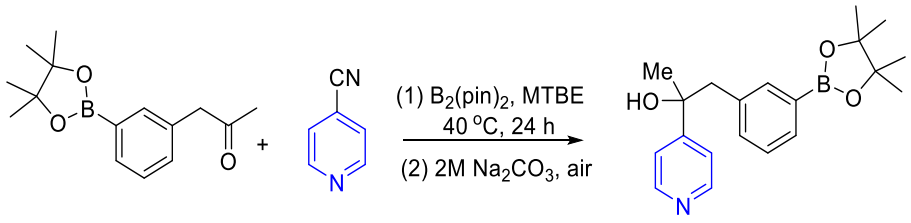
3l: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, J = 6.3 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 6.3 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 3.55 (s, 1H), 3.07 (d, J = 3.4 Hz, 2H), 1.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156. 8, 149.4, 140.5, 131.0, 129.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 125.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $J_{C\text{-}F}$ = 271.9 Hz), 120.5, 73.8, 49.8, 29.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4. **IR** (film): 3212, 2932, 2854, 1613, 1421, 1254, 826 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{15}H_{15}F_3NO$ $[M+H]^+$ 282.1100, found 282.1102.



1m **3m**

3m: Prepared following *general procedure A* using **1m** (32.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **3m** (38.4 mg, 79% yield).

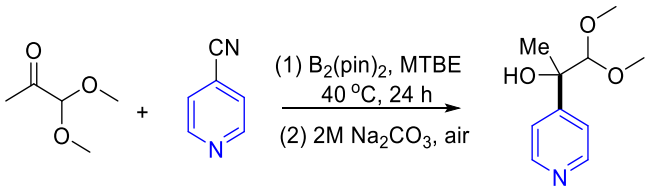
3m: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, J = 6.2 Hz, 2H), 7.29 (d, J = 6.2 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 3.04 (d, J = 13.6 Hz, 1H), 2.95 (d, J = 13.6 Hz, 1H), 2.16 (s, 1H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158. 7, 156.7, 149.5, 131.5, 127.6, 120.4, 113.8, 73.9, 55.2, 48.9, 29.0. **HRMS** (ESI-TOF) calculated for $C_{15}H_{18}NO_2$ $[M+H]^+$ 244.1332, found 244.1330.



1n **3n**

3n: Prepared following *general procedure A* using **1n** (52.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **3n** (52.4 mg, 77% yield).

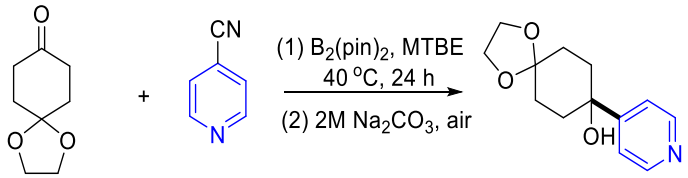
3n: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60-8.49 (m, 2H), 7.70-7.66 (m, 1H), 7.52 (t, J = 1.4 Hz, 1H), 7.38-7.35 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.07-7.03 (m, 1H), 3.04 (q, J = 13.4 Hz, 2H), 2.65 (s, 1H), 1.53 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 149.1, 137.0, 135.0, 133.6, 133.4, 127.9, 121.4, 120.8, 84.0, 73.9, 49.7, 28.9, 25.0, 24.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.1. **IR** (film): 3215, 2978, 1613, 1517, 1410, 1368, 1140, 860 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{20}H_{27}BNO_3$ $[M+H]^+$ 340.2079, found 340.2079.



1o 3o

3o: Prepared following *general procedure A* using **1o** (23.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3o** (29.2 mg, 74% yield).

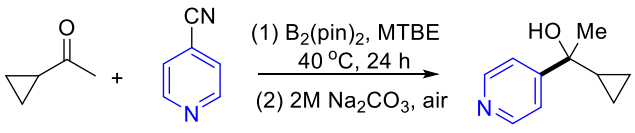
3o: White solid, mp 102-104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, J = 6.2 Hz, 2H), 7.44 (d, J = 6.3 Hz, 2H), 4.18 (s, 1H), 3.47 (s, 3H), 3.38 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 149.3, 121.4, 110.3, 75.5, 58.4, 58.3, 23.6. **IR** (film): 3195, 2935, 2833, 1601, 1454, 1190, 992, 828 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{16}NO_3$ $[M+H]^+$ 198.1225, found 198.1223.



1p 3p

3p: Prepared following *general procedure A* using **1p** (31.2 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3p** (35.8 mg, 76% yield).

3p: White solid, mp 165-167 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, J = 6.3 Hz, 2H), 7.45 (d, J = 6.3 Hz, 2H), 3.96 (t, J = 3.0 Hz, 4H), 2.14-2.04 (m, 4H), 1.76-1.66 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 149.3, 120.4, 108.2, 71.8, 64.5, 64.3, 36.2, 30.6. **IR** (film): 3181, 2926, 2883, 1602, 1427, 1103, 998, 825 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{13}H_{18}NO_3$ $[M+H]^+$ 236.1281, found 236.1280.

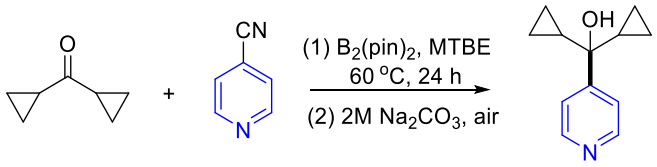


1q 3q

3q: Prepared following *general procedure A* using **1q** (16.8 mg, 0.2 mmol, 1.0 equiv.),

4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3q** (30.1 mg, 92% yield).

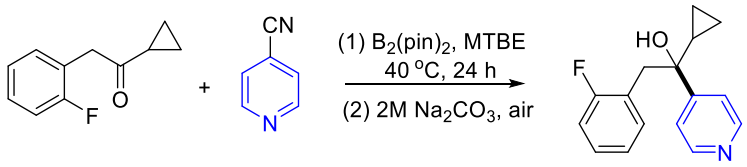
3q: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.4 Hz, 2H), 7.47 (d, J = 6.4 Hz, 2H), 3.25 (s, 1H), 1.45 (s, 3H), 1.21-1.14 (m, 1H), 0.57-0.47 (m, 2H), 0.45-0.34 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 148.0, 119.9, 71.3, 27.0, 21.6, 1.2, 0.1. **IR** (film): 3212, 2977, 1600, 1413, 1049, 901, 825 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1070, found 164.1070.



1r **3r**

3r: Prepared following *general procedure A* using **1r** (22.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 60 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3r** (12.8 mg, 34% yield).

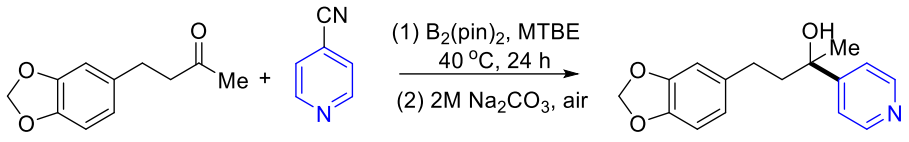
3r: White solid, mp 143-145 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, J = 5.6 Hz, 2H), 7.51 (d, J = 6.3 Hz, 2H), 2.46 (s, 1H), 1.16-1.09 (m, 2H), 0.65-0.60 (m, 2H), 0.59-0.53 (m, 2H), 0.46-0.39 (m, 2H), 0.37-0.30 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 149.0, 121.3, 73.1, 20.2, 2.4, 0.0. **IR** (film): 3205, 3008, 2926, 2853, 1600, 1222, 913, 814 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{12}H_{16}NO$ $[M+H]^+$ 190.1226, found 190.1225.



1s **3s**

3s: Prepared following *general procedure A* using **1s** (35.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3s** (25.6 mg, 50% yield).

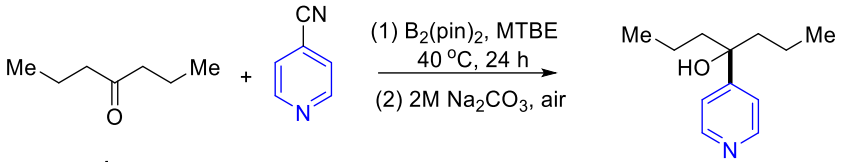
3s: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.0 Hz, 2H), 7.36 (d, *J* = 6.2 Hz, 2H), 7.23-7.09 (m, 1H), 7.04-6.90 (m, 3H), 3.30 (dd, *J* = 13.7 Hz, 1.3 Hz, 1H), 3.09 (dd, *J* = 13.7 Hz, 1.4 Hz, 1H), 2.29 (s, 1H), 1.42-1.34 (m, 1H), 0.52-0.27 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7 (d, J_{C-F} = 244.5 Hz), 155.7, 149.4, 132.7 (d, J_{C-F} = 4.5 Hz), 128.8 (d, J_{C-F} = 8.3 Hz), 123.8 (d, J_{C-F} = 3.5 Hz), 123.1 (d, J_{C-F} = 15.4 Hz), 120.9, 115.3 (d, J_{C-F} = 23.0 Hz), 74.4, 41.5, 20.8, 1.9, 0.4. **^{19}FNMR** (376 MHz, $CDCl_3$) δ -116.1. **HRMS** (ESI-TOF) calculated for $C_{16}H_{17}FNO$ $[M+H]^+$ 258.1289, found 259.1289.



1t **3t**

3t: Prepared following *general procedure A* using **1t** (38.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3t** (46.7 mg, 86% yield).

3t: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.6 Hz, 2H), 7.39 (d, *J* = 6.2 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.57 (s, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.89 (s, 2H), 3.01 (s, 1H), 2.65-2.53 (m, 1H), 2.40-2.24 (m, 1H), 2.12-1.98 (m, 2H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.2, 149.7, 147.7, 145.8, 135.7, 121.0, 120.4, 108.8, 108.3, 100.9, 73.9, 45.9, 30.3, 30.1. **HRMS** (ESI-TOF) calculated for $C_{16}H_{18}NO_3$ $[M+H]^+$ 272.1281, found 272.1281.

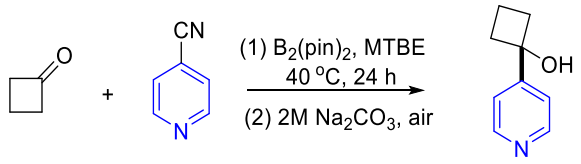


1u **3u**

3u: Prepared following *general procedure A* using **1u** (22.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3u** (20.1 mg, 52% yield).

3u: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.3 Hz, 2H), 7.29 (d, *J* = 6.3 Hz, 2H), 1.97 (s, 1H), 1.91-1.55 (m, 4H), 1.40-1.28 (m, 2H), 1.07-0.94 (m, 2H), 0.85 (t, *J*

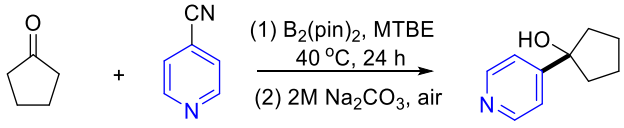
= 7.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.8, 149.5, 120.7, 76.6, 45.0, 16.6, 14.4. **HRMS** (ESI-TOF) calculated for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1539, found 194.1537.



1v **3v**

3v: Prepared following *general procedure A* using **1v** (14.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 70 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3v** (20.1 mg, 67% yield).

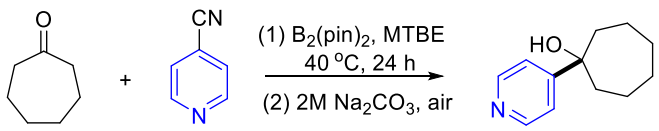
3v: White solid, mp 86-88 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, J = 6.2 Hz, 2H), 7.42 (d, J = 6.2 Hz, 2H), 4.14 (s, 1H), 2.52-2.38 (m, 4H), 2.11-2.03 (m, 1H), 1.82-1.73 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 149.5, 120.1, 75.6, 37.3, 13.1. **IR** (film): 3189, 2932, 2877, 1605, 1411, 813, 738 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_9H_{12}NO$ $[M+H]^+$ 150.0913, found 150.0912.



1w **3w**

3w: Prepared following *general procedure A* using **1w** (16.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3w** (25.1 mg, 76% yield).

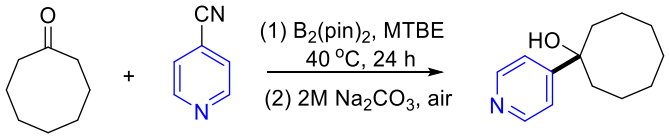
3w: White solid, mp 84-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, J = 6.1 Hz, 2H), 7.38 (d, J = 6.2 Hz, 2H), 3.43 (s, 1H), 2.01-1.93 (m, 6H), 1.87-1.81 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.2, 149.3, 120.5, 82.4, 42.6, 24.3. **IR** (film): 3175, 2964, 2869, 1601, 1405, 829, 751 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1070, found 164.1068.



1x **3x**

3x: Prepared following *general procedure A* using **1x** (22.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3x** (34.8 mg, 91% yield).

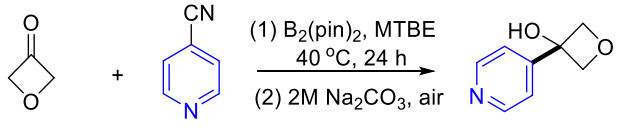
3x: White solid, mp 82-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, J = 6.2 Hz, 2H), 7.40 (d, J = 6.2 Hz, 2H), 3.39 (s, 1H), 1.98-1.90 (m, 2H), 1.87-1.81 (m, 4H), 1.76-1.68 (m, 2H), 1.62-1.54 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 149.3, 120.1, 76.0, 42.8, 28.9, 22.5. **IR** (film): 3212, 2923, 2857, 1614, 1422, 811, 736 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1382.



1y **3y**

3y: Prepared following *general procedure A* using **1y** (25.2 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3y** (36.8 mg, 89% yield).

3y: White solid, mp 73-75 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, J = 6.3 Hz, 2H), 7.41 (d, J = 6.3 Hz, 2H), 3.28 (s, 1H), 1.93-1.91 (m, 4H), 1.80-1.64 (m, 5H), 1.56-1.47 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 149.2, 120.6, 75.8, 37.5, 28.3, 24.3, 21.7. **IR** (film): 3224, 2921, 2851, 1599, 1410, 1001, 845 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1539.

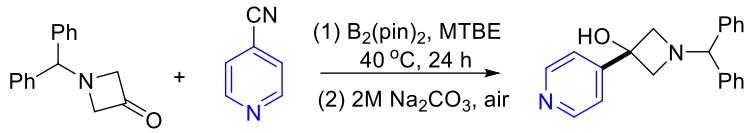


1z **3z**

3z: Prepared following *general procedure A* using **1z** (14.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2

equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3z** (20.9 mg, 65% yield).

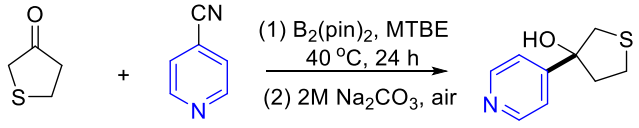
3z: White solid, mp 141-143 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 8.57 (d, *J* = 6.3 Hz, 2H), 7.75 (d, *J* = 6.3 Hz, 2H), 4.92 (s, 1H), 4.90 (d, *J* = 4.7 Hz, 2H), 4.75 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, CD_3OD) δ 155.5, 150.2, 121.3, 86.7, 74.8. **IR** (film): 3359, 2920, 2851, 1602, 1410, 1062, 977, 876 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_8H_{10}NO_2$ $[M+H]^+$ 152.0706, found 152.0701.



1za **3za**

3za: Prepared following *general procedure A* using **1za** (48.9 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3za** (56.1 mg, 87% yield).

3za: White solid, mp 166-168 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 6.2 Hz, 2H), 7.81 (d, *J* = 6.2 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 2H), 5.37 (s, 1H), 4.52 (s, 1H), 3.57 (d, *J* = 8.7 Hz, 2H), 3.41 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6, 149.1, 141.9, 128.7, 127.4, 120.4, 78.1, 69.4, 68.3. Two resonances of C-Ar were overlapped. **IR** (film): 2181, 2939, 2838, 1602, 1451, 1070, 823 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{21}H_{21}N_2O$ $[M+H]^+$ 317.1648, found 317.1648.

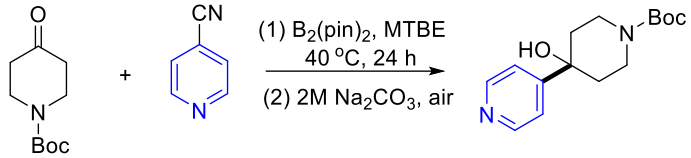


1zb **3zb**

3zb: Prepared following *general procedure A* using **1zb** (20.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3zb** (28.0 mg, 77% yield).

3zb: White solid, mp 123-125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 6.2 Hz,

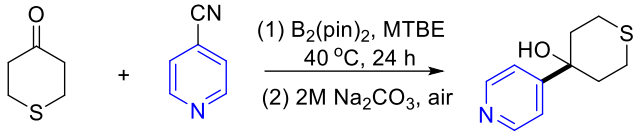
2H), 7.47 (d, J = 6.2 Hz, 2H), 4.45 (s, 1H), 3.23-3.13 (m, 2H), 3.09-2.96 (m, 2H), 2.33-2.18 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 149.6, 120.6, 82.8, 45.4, 44.0, 29.5. **IR** (film): 3160, 2936, 2850, 1601, 1412, 1211, 1043, 820 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_9H_{12}NOS$ $[M+H]^+$ 182.0634, found 182.0632.



1zc **3zc**

3zc: Prepared following *general procedure A* using **1zc** (39.9 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3zc** (49.2 mg, 88% yield).

3zc: White solid, mp 137-139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, J = 5.7 Hz, 2H), 7.38 (d, J = 5.7 Hz, 2H), 4.38 (s, 1H), 4.06-3.84 (m, 2H), 3.21 (s, 2H), 1.91-1.84 (m, 2H), 1.67-1.63 (m, 2H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 154.9, 149.4, 120.2, 79.9, 70.8, 39.9, 37.6, 28.5. **IR** (film): 3212, 2975, 1698, 1600, 1033, 961, 821 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{15}H_{23}N_2O_3$ $[M+H]^+$ 279.1703, found 279.1699.

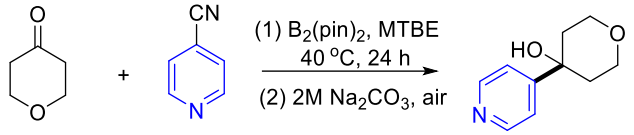


1zd **3zd**

3zd: Prepared following *general procedure A* using **1zd** (23.2 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3zd** (35.5 mg, 90% yield).

3zd: White solid, mp 152-154 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.3 Hz, 2H), 7.39 (d, J = 6.3 Hz, 2H), 3.27-3.19 (m, 2H), 3.10 (s, 1H), 2.46 (d, J = 14.4 Hz, 2H), 2.16-2.08 (m, 2H), 1.97 (d, J = 13.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3, 149.7, 119.9, 71.5, 39.0, 23.9. **IR** (film): 3135, 2946, 2833, 1602, 1422, 1090, 821 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{14}NOS$ $[M+H]^+$ 196.0791, found

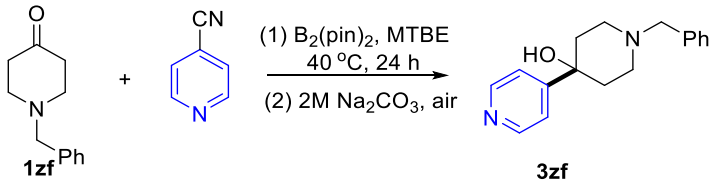
196.0788.



1ze **3ze**

3ze: Prepared following *general procedure A* using **1ze** (20.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/2 PE/EtOAc) to afford **3ze** (26.6 mg, 74% yield).

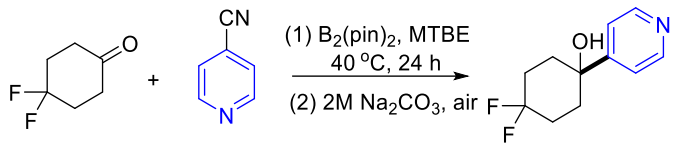
3ze: White solid, mp 204-206 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, J = 6.2 Hz, 2H), 7.41 (d, J = 6.3 Hz, 2H), 3.98-3.84 (m, 4H), 3.60 (s, 1H), 2.15-2.06 (m, 2H), 1.65-1.60 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 149.6, 120.1, 70.2, 63.6, 38.3. **IR** (film): 3147, 2960, 2863, 1603, 1422, 1128, 920, 825 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.1019, found 180.1017.



1zf **3zf**

3zf: Prepared following *general procedure A* using **1zf** (38.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **3zf** (43.4 mg, 81% yield).

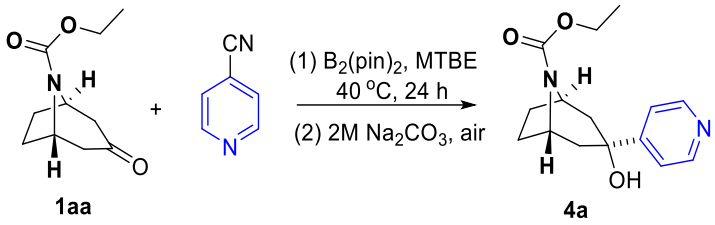
3zf: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, J = 5.1 Hz, 2H), 7.42 (d, J = 6.3 Hz, 2H), 7.37-7.23 (m, 5H), 3.59 (s, 2H), 3.42 (s, 1H), 2.81 (d, J = 11.3 Hz, 2H), 2.50 (td, J = 12.1 Hz, 2.4 Hz, 2H), 2.11 (td, J = 13.2 Hz, 4.4 Hz, 2H), 1.68 (dd, J = 11.8 Hz, 2.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 149.5, 138.1, 129.3, 128.4, 127.3, 120.2, 70.8, 63.2, 49.1, 38.1. **IR** (film): 3218, 2941, 2814, 1703, 1600, 1410, 1046, 938 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{17}H_{21}N_2O$ $[M+H]^+$ 269.1648, found 269.1651.



1zg **3zg**

3zg: Prepared following *general procedure A* using **1zg** (26.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **3zg** (37.2 mg, 87% yield).

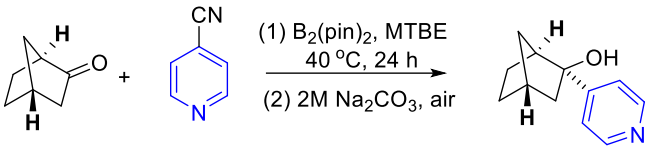
3zg: White solid, mp 126-128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, J = 6.3 Hz, 2H), 7.43 (d, J = 6.3 Hz, 2H), 2.92 (s, 1H), 2.42-2.24 (m, 2H), 2.14-2.04 (m, 4H), 1.87-1.81 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 149.7, 123.0 (dd, $J_{C\text{-}F}$ = 243.1, 238.7 Hz), 120.1, 71.5, 35.1 (d, $J_{C\text{-}F}$ = 10.0 Hz), 29.7 (t, $J_{C\text{-}F}$ = 24.8 Hz). **^{19}F NMR** (376 MHz, CDCl3) δ -93.4 (d, J = 237.6 Hz, 1F), -105.6 (d, J = 237.5 Hz, 1F). **IR** (film): 3129, 2973, 2851, 1617, 1412, 1105, 821 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{11}H_{14}F_2NO$ $[M+H]^+$ 214.1038, found 214.1037.



1aa **4a**

4a: Prepared following *general procedure A* using **1aa** (39.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **4a** (37.5 mg, 68% yield).

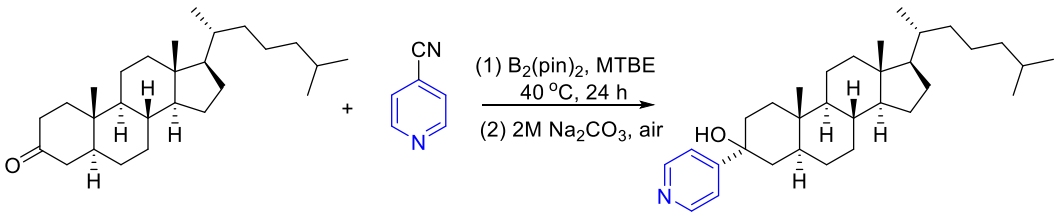
4a: White solid, mp 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, J = 6.3 Hz, 2H), 7.30 (d, J = 6.3 Hz, 2H), 4.35 (s, 2H), 4.18-4.12 (m, 2H), 3.79 (s, 1H), 2.30 (s, 3H), 2.14 (d, J = 11.0 Hz, 1H), 1.98-1.90 (m, 2H), 1.83 (d, J = 14.5 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 154.1, 149.3, 120.2, 72.9, 61.2, 53.3, 44.4, 43.4, 29.8, 28.3, 27.7, 14.9. **IR** (film): 3419, 2978, 2873, 1682, 1599, 1416, 1040, 813 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{15}H_{20}N_2O_3$ $[M+H]^+$ 277.1547, found 277.1547.



1ab **4b**

4b: Prepared following *general procedure A* using **1ab** (22.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **4b** (31.6 mg, 83% yield).

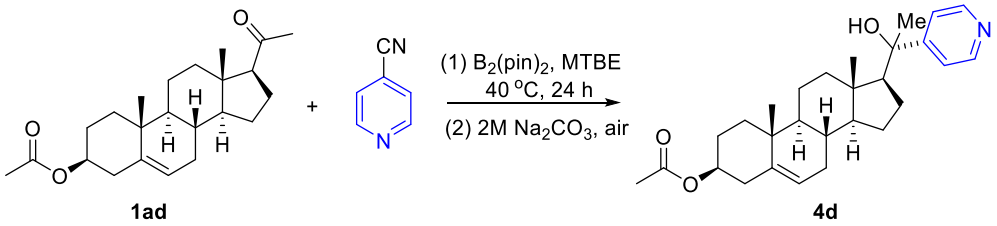
4b: White solid, mp 179-181 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, J = 4.6 Hz, 2H), 7.40 (d, J = 6.3 Hz, 2H), 3.34 (s, 1H), 2.45 (d, J = 3.8 Hz, 1H), 2.32 (t, J = 3.8 Hz, 1H), 2.20-2.09 (m, 2H), 1.69-1.58 (m, 1H), 1.52-1.40 (m, 4H), 1.38-1.32 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 149.2, 121.6, 79.7, 47.5, 46.7, 38.9, 37.6, 28.9, 22.4. **IR** (film): 3027, 2952, 2869, 1601, 1413, 1026, 817 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{12}H_{15}NO$ $[M+H]^+$ 190.1226, found 190.1226.



1ac **4c**

4c: Prepared following *general procedure A* using **1ac** (77.3 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **4c** (83.8 mg, 90% yield).

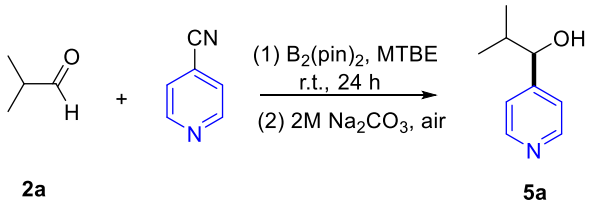
4c: White solid, mp 233-235 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, J = 5.1 Hz, 2H), 7.40 (d, J = 6.2 Hz, 2H), 2.22-0.98 (m, 32H), 0.94-0.81 (m, 12H), 0.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 149.8, 119.9, 73.4, 56.6, 56.4, 54.3, 42.7, 41.6, 41.2, 40.1, 39.7, 36.3, 35.9, 35.7, 34.6, 34.0, 32.1, 28.5, 28.4, 28.2, 24.3, 24.0, 23.0, 22.7, 21.1, 18.8, 12.3, 11.5, 1.2. **IR** (film): 3207, 2932, 2310, 1747, 1507, 1456, 877 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{32}H_{52}NO$ $[M+H]^+$ 466.4043, found 466.4052.



4d: Prepared following *general procedure A* using **1ad** (71.7 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) under the room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **4d** (26.1 mg, 30% yield).

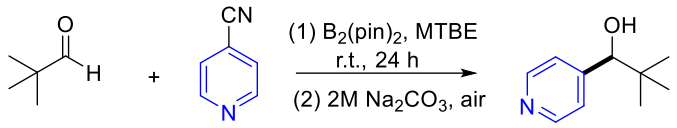
4d: White solid, mp 233-235 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, J = 6.0 Hz, 2H), 7.38 (d, J = 6.3 Hz, 2H), 5.34-5.30 (m, 1H), 4.59-4.48 (m, 1H), 2.30-2.22 (m, 2H), 2.09 (s, 1H), 2.04-1.64 (m, 10H), 1.52-0.88 (m, 15H), 0.75 (s, 3H), 0.62-0.52 (m, 1H), 0.45-0.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 157.6, 149.4, 139.8, 122.4, 120.7, 75.5, 73.9, 59.7, 56.8, 49.9, 42.9, 39.1, 38.2, 36.9, 36.6, 32.0, 31.8, 31.3, 27.8, 23.5, 23.0, 21.5, 20.6, 19.3, 13.6. **HRMS** (ESI-TOF) calculated for $C_{28}H_{40}NO_3$ $[M+H]^+$ 438.3003, found 438.3002.

5.2 Using aldehydes as the coupling partner



5a: Prepared following *general procedure A* using **2a** (14.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **5a** (26.3 mg, 87% yield).

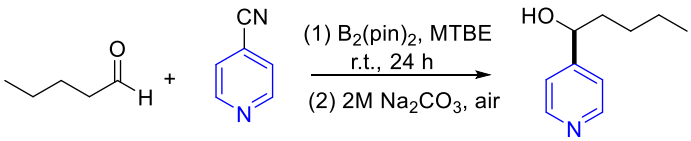
5a: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, J = 6.2 Hz, 2H), 7.23 (d, J = 6.2 Hz, 2H), 4.42 (d, J = 5.7 Hz, 1H), 3.86 (s, 1H), 1.97-1.88 (m, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 149.1, 122.0, 77.8, 35.1, 19.0, 17.4. **IR** (film): 2959, 1935, 1602, 1416, 1002, 836 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_9H_{14}NO$ $[M+H]^+$ 152.1069, found 152.1069.



2b **5b**

5b: Prepared following *general procedure A* using **2b** (17.2 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5b** (27.6 mg, 83% yield).

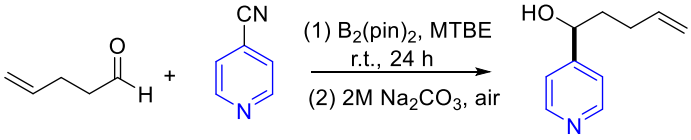
5b: White solid, mp 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, J = 6.3 Hz, 2H), 7.24 (d, J = 6.1 Hz, 2H), 4.35 (s, 1H), 3.61 (s, 1H), 0.90 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 148.6, 123.3, 80.8, 35.7, 25.9. **IR** (film): 3212, 2953, 1602, 1479, 1416, 1063, 823 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1226, found 166.1227.



2c **5c**

5c: Prepared following *general procedure A* using **2c** (17.2 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5c** (31.5 mg, 95% yield).

5c: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, J = 6.1 Hz, 2H), 7.30 (d, J = 6.1 Hz, 2H), 4.68 (dd, J = 7.4, 5.4 Hz, 1H), 3.69 (s, 1H), 1.72-1.62 (m, 2H), 1.38-1.23 (m, 4H), 0.85 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 148.0, 120.6, 71.6, 37.7, 26.7, 21.6, 13.1. **IR** (film): 3200, 2956, 1942, 1602, 1416, 1001, 836 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{16}NO$ $[M+H]^+$ 166.1226, found 166.1226.

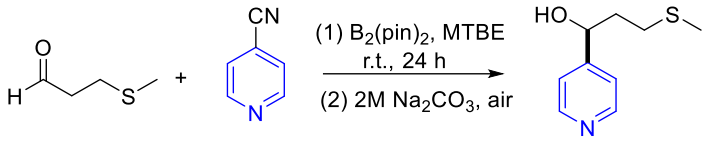


2d **5d**

5d: Prepared following *general procedure A* using **2d** (16.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2

equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5d** (29.8 mg, 93% yield).

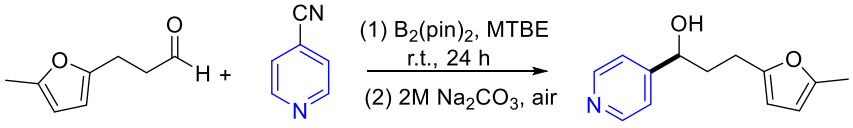
5d: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (m, 2H), 7.31 (d, J = 6.1 Hz, 2H), 5.92-5.68 (m, 1H), 5.09-4.89 (m, 2H), 4.72 (dd, J = 7.7, 5.2 Hz, 1H), 3.87 (s, 1H), 2.16 (q, J = 7.1 Hz, 2H), 1.82-1.72 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 149.1, 137.8, 121.6, 115.6, 71.9, 38.0, 29.8. **IR** (film): 3212, 2921, 2852, 1619, 1416, 1065, 913, 819 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1070, found 164.1068.



2e **5e**

5e: Prepared following *general procedure A* using **2e** (20.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5e** (32.3 mg, 88% yield).

5e: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, J = 6.2 Hz, 2H), 7.28 (d, J = 6.1 Hz, 2H), 4.86 (dd, J = 7.9, 4.7 Hz, 1H), 4.46 (s, 1H), 2.69-2.52 (m, 2H), 2.09 (s, 3H), 2.01-1.93 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.2, 149.5, 121.0, 71.4, 37.7, 30.5, 15.5. **IR** (film): 3207, 2915, 1602, 1416, 1065, 1003, 959, 820 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_9H_{14}NOS$ $[M+H]^+$ 184.0791, found 184.0789.

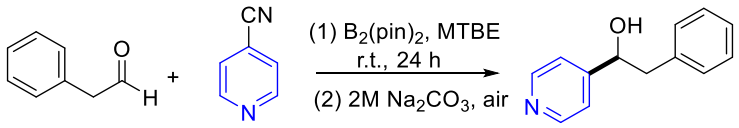


2f **5f**

5f: Prepared following *general procedure A* using **2f** (27.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **5f** (40.1 mg, 92% yield).

5f: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, J = 4.8 Hz, 2H), 7.33 (d, J = 6.4 Hz, 2H), 5.84 (d, J = 3.0 Hz, 1H), 5.81 (d, J = 3.0 Hz, 1H), 4.74 (dd, J = 7.4 Hz, 5.4 Hz, 2H), 3.91 (s, 1H), 2.69 (t, J = 7.6 Hz, 2H), 2.21 (s, 3H), 2.03-1.96 (m, 2H). **^{13}C NMR**

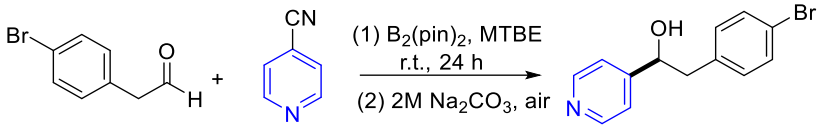
(100 MHz, $CDCl_3$) δ 156.0, 153.1, 150.7, 148.9, 121.7, 106.1, 106.0, 71.6, 37.3, 24.2, 13.6. **IR** (film): 3175, 2921, 1619, 1567, 1416, 1065, 1020, 823 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1176, found 218.1176.



2g **5g**

5g: Prepared following *general procedure A* using **2g** (24.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **5g** (28.6 mg, 72% yield).

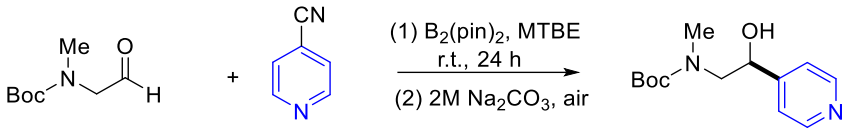
5g: White solid, mp 150-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.1 Hz, 2H), 7.36-7.30 (m, 2H), 7.30-7.25 (m, 3H), 7.19 (d, J = 6.8 Hz, 2H), 4.92 (dd, J = 8.3 Hz, 4.93 Hz, 1H), 3.14 (s, 1H), 3.08-2.94 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 149.7, 137.2, 129.7, 128.8, 127.0, 121.1, 73.8, 45.8. **IR** (film): 3175, 2922, 2852, 1681, 1414, 1054, 820 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1070, found 200.1068.



2h **5h**

5h: Prepared following *general procedure A* using **2h** (39.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5h** (32.1 mg, 58% yield).

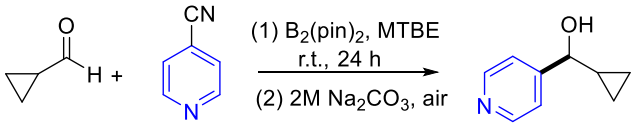
5h: White solid, mp 135-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, J = 6.1 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 6.0 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 4.86 (dd, J = 7.8 Hz, 5.2 Hz, 1H), 3.46 (s, 1H), 2.96-2.88 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 149.5, 136.2, 131.7, 131.4, 121.2, 120.9, 73.5, 45.0. **IR** (film): 3195, 2976, 2852, 1600, 1412, 1136, 998, 823 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{13}H_{13}BrNO$ $[M+H]^+$ 278.0175, found 278.0174.



2i **5i**

5i Prepared following *general procedure A* using **2i** (34.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **5i** (30.4 mg, 60% yield).

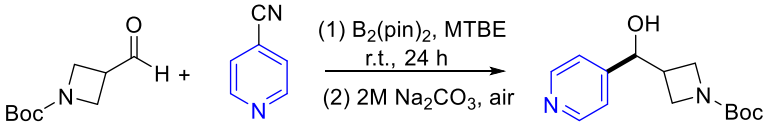
5i: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52-8.40 (m, 2H), 7.41-7.28 (m, 2H), 4.92-4.71 (m, 2H), 3.48-3.26 (m, 2H), 2.96-2.62 (m, 3H), 1.47-1.27 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 153.0, 149.2, 121.5, 80.7 and 80.1, 72.4 and 71.7, 57.0 and 56.7, 36.9 and 36.2, 28.4. **IR** (film): 3400, 2976, 2930, 1697, 1481, 1456, 1393, 1151 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{13}H_{21}N_2O_3$ $[M+H]^+$ 253.1547, found 253.1547.



2j **5j**

5j: Prepared following *general procedure A* using **2j** (14.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5j** (26.9 mg, 90% yield).

5j: White solid, mp 80-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, J = 6.1 Hz, 2H), 7.36 (d, J = 6.1 Hz, 2H), 4.01 (d, J = 8.4 Hz, 1H), 3.76 (s, 1H), 1.18-1.04 (m, 1H), 0.63-0.56 (m, 2H), 0.50-0.40 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 149.4, 121.3, 76.7, 19.2, 3.6, 3.2. **IR** (film): 3207, 2854, 1604, 1415, 1044, 950, 813 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_9H_{12}NO$ $[M+H]^+$ 150.0913, found 150.0912.

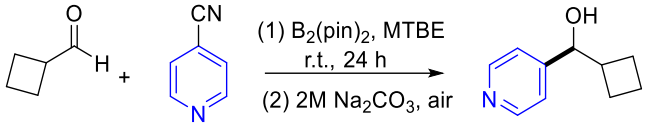


2k **5k**

5k: Prepared following *general procedure A* using **2k** (37.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2

equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5k** (25.4 mg, 48% yield).

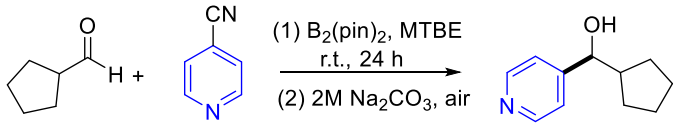
5k: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, J = 5.1 Hz, 2H), 7.28 (d, J = 6.2 Hz, 2H), 4.78 (d, J = 7.0 Hz, 1H), 4.18 (s, 1H), 3.96-3.73 (m, 4H), 2.83-2.74 (m, 1H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 152.2, 149.6, 121.4, 79.8, 73.4, 50.8, 35.3, 28.5. **IR** (film): 3366, 2975, 2886, 1693, 1602, 1416, 1142, 1064 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{14}H_{21}N_2O_3$ $[M+H]^+$ 265.1547, found 265.1546.



2l **5l**

5l: Prepared following *general procedure A* using **2l** (16.8mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **5l** (29.5 mg, 90% yield).

5l: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, J = 5.9 Hz, 2H), 7.25 (d, J = 6.1 Hz, 2H), 4.56 (d, J = 7.4 Hz, 1H), 3.43 (s, 1H), 2.60-2.46 (m, 1H), 2.01-1.93 (m, 2H), 1.88-1.75 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 149.1, 121.6, 76.1, 42.3, 24.3, 17.8. **IR** (film): 3219, 2930, 2849, 1601, 1447, 1419, 1031, 832 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1070, found 164.1070.

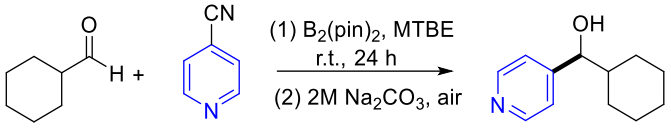


2m **5m**

5m: Prepared following *general procedure A* using **2m** (19.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5m** (24.9 mg, 70% yield).

5m: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, J = 6.1 Hz, 2H), 7.26 (d, J = 6.0 Hz, 2H), 4.46 (d, J = 7.5 Hz, 1H), 3.48 (s, 1H), 2.19-2.09 (m, 1H), 1.80-1.71 (m, 1H), 1.65-1.41 (m, 6H), 1.26-1.20 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 149.4, 121.7, 76.9, 47.5, 29.4, 28.8, 25.6, 25.5. **IR** (film): 3227, 2953, 2867, 1602, 1414, 1035, 819

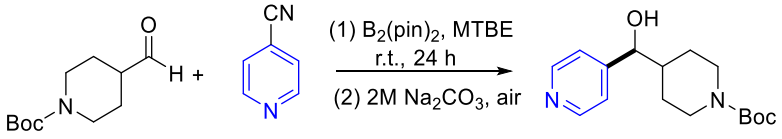
cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226, found 178.1224.



2n **5n**

5n: Prepared following *general procedure A* using **2f** (22.4 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **5n** (32.8 mg, 86% yield).

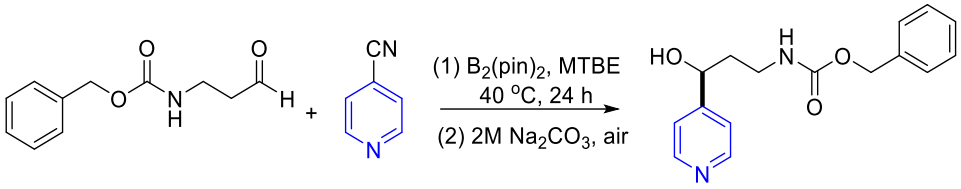
5n: White solid, mp 101-103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, J = 5.9 Hz, 2H), 7.22 (d, J = 6.1 Hz, 2H), 4.41 (d, J = 6.0 Hz, 1H), 3.69 (s, 1H), 1.80-1.66 (m, 3H), 1.65-1.54 (m, 2H), 1.45 (d, J = 13.7 Hz, 1H), 1.22-1.10 (m, 3H), 1.08-0.99 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 149.1, 122.1, 77.4, 44.9, 29.4, 27.9, 26.4, 26.2, 26.1. **IR** (film): 3217, 2924, 2851, 1603, 1450, 1415, 1030, 831 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1382.



2o **5o**

5o: Prepared following *general procedure A* using **2o** (42.6 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **5o** (53.4 mg, 91% yield).

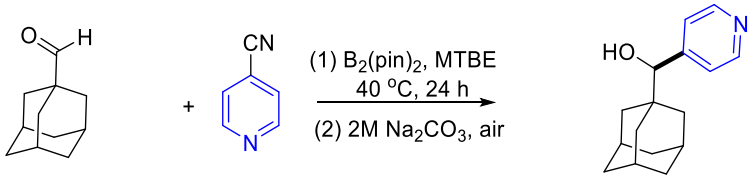
5o: White solid, mp 78-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, J = 6.1 Hz, 2H), 7.20 (d, J = 6.0 Hz, 2H), 4.40 (d, J = 6.3 Hz, 1H), 4.26 (s, 1H), 4.10-4.01 (m, 2H), 2.55 (s, 2H), 1.79-1.61 (m, 2H), 1.38 (s, 9H), 1.33-1.27 (m, 1H), 1.25-1.17 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 153.1, 149.3, 121.9, 79.6, 76.4, 43.3, 28.5, 28.4, 27.4. **IR** (film): 3366, 2975, 2886, 1693, 1602, 1416, 1064, 931 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{16}H_{25}N_2O_3$ $[M+H]^+$ 293.1860, found 293.1859.



2p **5p**

5p: Prepared following *general procedure A* using **2p** (41.5 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **5p** (36.2 mg, 63% yield).

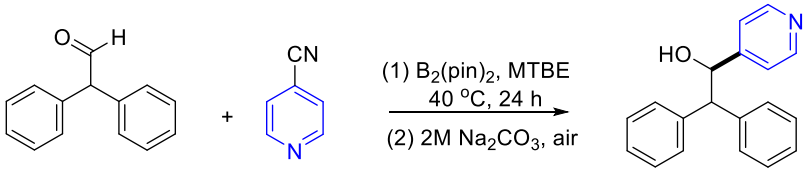
5p: White solid, mp 79-81 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, J = 4.6 Hz, 2H), 7.37-7.32 (m, 5H), 7.25 (d, J = 4.3 Hz, 2H), 5.41 (s, 1H), 5.09 (s, 2H), 4.73 (dd, J = 9.7, 3.4 Hz, 1H), 4.48 (s, 1H), 3.52 (s, 1H), 3.30-3.20 (m, 1H), 1.92-1.71 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 153.8, 149.6, 136.4, 128.7, 128.4, 128.2, 120.9, 69.9, 67.1, 39.1, 37.9. **IR** (film): 3359, 2923, 2853, 1715, 1507, 1456, 1247, 869 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{16}H_{19}N_2O_3$ $[M+H]^+$ 287.1390, found 287.1391.



2q **5q**

5q: Prepared following *general procedure A* using **2q** (32.9 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **5q** (43.0 mg, 88% yield).

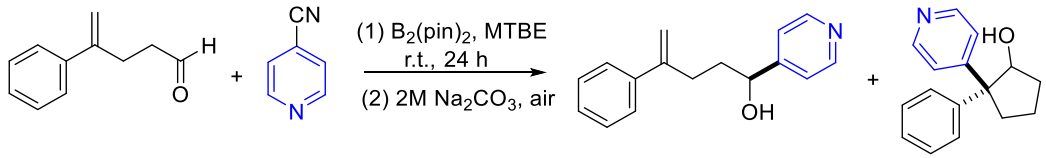
5q: White solid, m.p. 174-176 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, J = 6.1 Hz, 2H), 7.18 (d, J = 6.1 Hz, 2H), 4.18 (s, 1H), 2.46 (s, 1H), 1.98-194 (m, 3H), 1.70-1.65 (m, 3H), 1.62-1.52 (m, 6H), 1.50-1.44 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 148.8, 123.3, 81.6, 38.1, 37.2, 37.0, 28.3. **IR** (film): 3207, 2928, 2851, 1600, 1449, 1145, 828 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{16}H_{22}NO$ $[M+H]^+$ 244.1696, found 244.1696.



2r **5r**

5r Prepared following *general procedure A* using **2r** (34.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **5r** (41.8 mg, 76% yield).

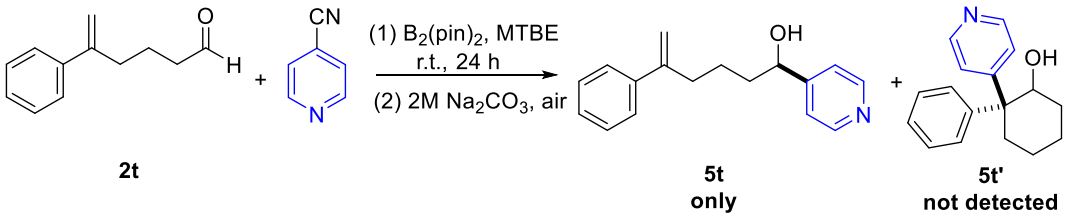
5r: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 6.0 Hz, 2H), 7.38 (d, J = 7.1 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 7.21-7.04 (m, 7H), 5.38 (d, J = 8.3 Hz, 1H), 4.15 (d, J = 8.3 Hz, 1H), 3.68 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 148.7, 140.9, 140.1, 129.0, 128.8, 128.6, 128.4, 127.2, 126.9, 122.4, 75.3, 59.8. **IR** (film): 3060, 2922, 1617, 1601, 1494, 1416, 1064, 1031, 810 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found 276.1383.



2s **5s** only **5s'** not detected

5s: Prepared following *general procedure A* using **2s** (32.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **5s** (45.1 mg, 94% yield).

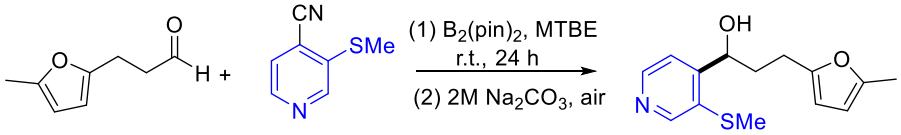
5s: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 6.1 Hz, 2H), 7.34-7.30 (m, 2H), 7.30-7.14 (m, 5H), 5.26 (d, J = 1.4 Hz, 1H), 5.06-5.02 (m, 1H), 4.72-4.66 (m, 1H), 4.35 (s, 1H), 2.69-2.52 (m, 2H), 1.85-1.74 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 148.9, 147.7, 140.8, 128.5, 127.6, 126.2, 121.6, 113.1, 71.8, 37.4, 31.3. **IR** (film): 3200, 3080, 2923, 1619, 1603, 1414, 1220, 1065 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1383, found 240.1387.



2t **5t** only **5t'** not detected

5t: Prepared following *general procedure A* using **2t** (34.8 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at room temperature. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **5t** (44.0 mg, 86% yield).

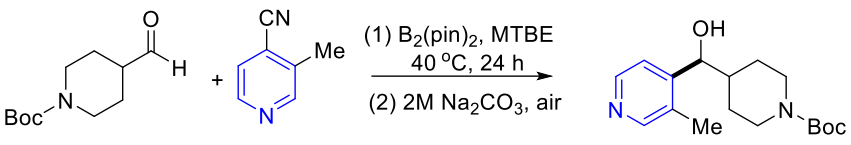
5t: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, J = 6.1 Hz, 2H), 7.37-7.32 (m, 2H), 7.33-7.27 (m, 2H), 7.26-7.24 (m, 1H), 7.22 (d, J = 6.1 Hz, 2H), 5.26 (d, J = 1.4 Hz, 1H), 5.03 (d, J = 1.5 Hz, 1H) 4.65-4.62 (m, 1H), 4.15 (s, 1H), 2.52 (t, J = 7.3 Hz, 2H), 1.79-1.68 (m, 2H), 1.64-1.57 (m, 1H), 1.55-1.44 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 149.1, 148.0, 141.1, 128.4, 127.5, 126.2, 121.3, 112.8, 72.3, 38.4, 35.0, 24.1. **IR** (film): 3200, 3079, 2939, 1621, 1603, 1414, 1212, 1065 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1543.



2f **6a**

6a: Prepared following *general procedure A* using **2f** (27.6 mg, 0.2 mmol, 1.0 equiv.), 3-methylthio-4-cyanopyridine (45.0 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (5/3 PE/EtOAc) to afford **6a** (42.0 mg, 79% yield).

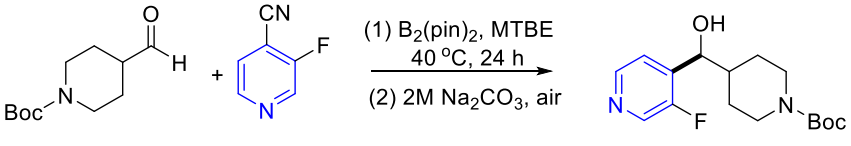
6a: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30-8.26 (m, 2H), 7.44 (d, J = 5.0 Hz, 1H), 5.88 (d, J = 2.9 Hz, 1H), 5.82 (d, J = 2.9 Hz, 1H), 5.05 (dd, J = 8.7, 3.5 Hz, 1H), 3.99 (s, 1H), 2.83-2.73 (m, 2H), 2.45 (d, J = 1.3 Hz, 3H), 2.22 (s, 3H), 2.08-2.01 (m, 1H), 1.95-1.85 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 152.5, 150.6, 146.8, 146.5, 132.1, 120.2, 106.0, 105.9, 69.1, 35.6, 24.5, 16.3, 13.6. **IR** (film): 3212, 2921, 2852, 1681, 1434, 1218, 1020, 948 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{14}H_{18}NO_2S$ $[M+H]^+$ 264.1053, found 264.1053.



2o **6e**

6e: Prepared following *general procedure A* using **2o** (42.7 mg, 0.2 mmol, 1.0 equiv.), 3-methyl-4-cyanopyridine (35.4 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **6e** (49.2 mg, 80% yield).

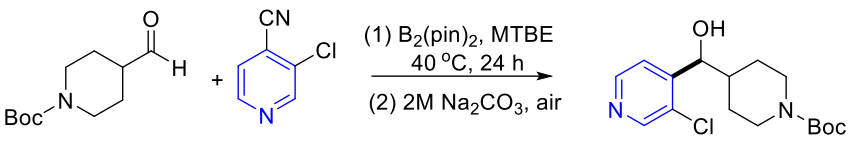
6e: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37-8.20 (m, 2H), 7.35 (d, J = 5.1 Hz, 1H), 4.68-4.62 (m, 1H), 4.16-4.00 (m, 2H), 3.46 (s, 1H), 2.62-2.54 (m, 2H), 2.26 (s, 3H), 1.80-1.66 (m, 2H), 1.42 (s, 9H), 1.36-1.30 (m, 1H), 1.30-1.24 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 151.4, 150.6, 147.5, 130.5, 121.5, 79.6, 72.9, 43.8, 42.6, 28.6, 27.2, 16.4. **IR** (film): 3290, 2922, 1704, 1589, 1402, 1218, 1092, 843 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{17}H_{27}N_2O_3$ $[M+H]^+$ 307.2016, found 307.2013.



2o **6f**

6f: Prepared following *general procedure A* using **2o** (42.7 mg, 0.2 mmol, 1.0 equiv.), 3-fluoro-4-cyanopyridine (36.6 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **6f** (26.7 mg, 43% yield).

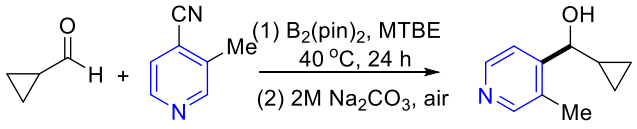
6f: White solid, mp 76-78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36-8.28 (m, 2H), 7.44 (t, J = 5.5 Hz, 1H), 4.83-4.81 (m, 1H), 4.07 (s, 2H), 3.74 (s, 1H), 2.62-2.52 (m, 2H), 1.80-1.68 (m, 2H), 1.39 (s, 9H), 1.37-1.33 (m, 1H), 1.31-1.23 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (d, $J_{C\text{-}F}$ = 254.6 Hz), 154.9, 145.7, 139.6, 137.6 (d, $J_{C\text{-}F}$ = 26.9 Hz), 122.7, 79.7, 70.1, 43.7, 42.7, 28.5, 27.6 (d, $J_{C\text{-}F}$ = 89.7 Hz). **^{19}F NMR** (376 MHz, CDCl3) δ -132.1. **IR** (film): 3420, 2929, 1693, 1417, 1218, 1163, 1092, 844 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{16}H_{24}FN_2O_3$ $[M+H]^+$ 311.1765, found 311.1766.



2o **6g**

6g: Prepared following *general procedure A* using **2o** (42.7 mg, 0.2 mmol, 1.0 equiv.), 3-chloro-4-cyanopyridine (41.6 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (1/1 PE/EtOAc) to afford **6g** (27.1 mg, 41% yield).

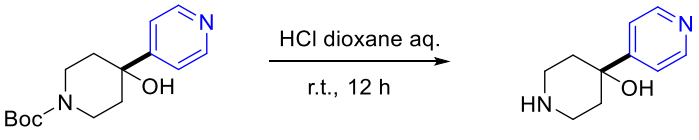
6g: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45-8.38 (m, 2H), 7.46 (d, J = 5.0 Hz, 1H), 4.90 (d, J = 5.2 Hz, 1H), 4.15-4.03 (m, 2H), 3.69 (s, 1H), 2.62-2.50 (m, 2H), 1.80-1.56 (m, 2H), 1.40 (s, 9H), 1.40-1.36 (m, 2H), 1.32-1.28 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 150.2, 149.1, 147.7, 130.1, 122.9, 79.7, 72.5, 43.8, 42.0, 28.5, 26.3. **IR** (film): 3420, 2975, 2927, 2856, 1693, 1428, 1165, 731 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{16}H_{24}ClN_2O_3$ $[M+H]^+$ 327.1470, found 327.1472..



2j **6h**

6h: Prepared following *general procedure A* using **2j** (14.0 mg, 0.2 mmol, 1.0 equiv.), 4-cyanopyridine (31.2 mg, 0.3 mmol, 1.5 equiv.), $B_2(pin)_2$ (61.9 mg, 0.24 mmol, 1.2 equiv) and MTBE (1.0 mL) at 40 °C. After 24 hours, following the described workup procedure, the reaction mixture was purified by preparative TLC (2/1 PE/EtOAc) to afford **6h** (27.4 mg, 84% yield).

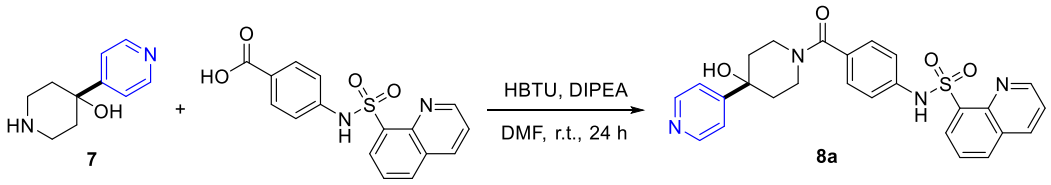
6h: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38-8.22 (m, 2H), 7.42 (d, J = 5.1 Hz, 1H), 4.42 (d, J = 7.4 Hz, 1H), 3.55 (s, 1H), 2.29 (s, 3H), 1.24-1.15 (m, 1H), 0.61-0.49 (m, 2H), 0.40-0.32 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 150.5, 147.3, 130.6, 121.0, 72.5, 17.5, 16.4, 3.1, 2.5. **IR** (film): 3207, 2930, 2854, 1602, 1415, 1044, 966, 816 cm^{-1}. **HRMS** (ESI-TOF) calculated for $C_{10}H_{13}NO$ $[M+H]^+$ 164.1070, found 164.1068.



3zc **7**

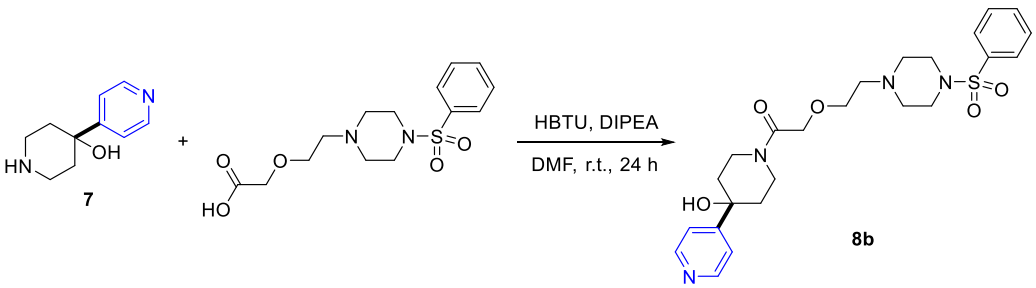
7: To a solution of **3zc** (1.4 g, 5.0 mmol, 1.0 eq.) in 30.0 mL 1,4-dioxane, was added HCl dioxane aq. (10.0 eq.), the reaction mixture was stirred at room temperature for about 12 hours. Then, the reaction mixture was made alkaline with 2M Na_2CO_3 aq. and concentrated. After which, the crude product was redissolved in 20 mL MeOH/$CHCl_3$ (1:1). The organic layer was anhydrified with Na_2SO_4, and the solvent was removed, to yield the desired product **7** (0.8 g, 90% yield).

7: White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 6.2 Hz, 2H), 7.41 (d, *J* = 6.2 Hz, 2H), 3.73 (s, 1H), 3.15-3.07 (m, 2H), 3.02-2.94 (m, 2H), 2.15 (s, 1H), 2.01-1.93 (m, 2H), 1.70-1.64 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 149.9, 119.8, 71.4, 42.1, 38.7. **HRMS** (ESI-TOF) calculated for $C_{10}H_{15}N_2O$ $[M+H]^+$ 179.1179, found 179.1179.



8a

8a: White solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 9.12 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.55-8.45 (m, 3H), 8.41 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.27 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.76-7.68 (m, 2H), 7.52-7.41 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 1H), 4.31 (s, 1H), 4.04 (s, 1H), 3.16-2.98 (m, 2H), 1.88-1.72 (m, 2H), 1.62-1.38 (m, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 168.3, 157.6, 151.5, 149.3, 142.7, 138.9, 136.9, 135.1, 134.4, 132.2, 130.9, 128.4, 127.9, 125.6, 122.6, 120.1, 118.5, 69.9, 38.5, 36.9. **HRMS** (ESI-TOF) calculated for $C_{26}H_{25}N_4O_4S$ $[M+H]^+$ 489.1591, found 489.1591.

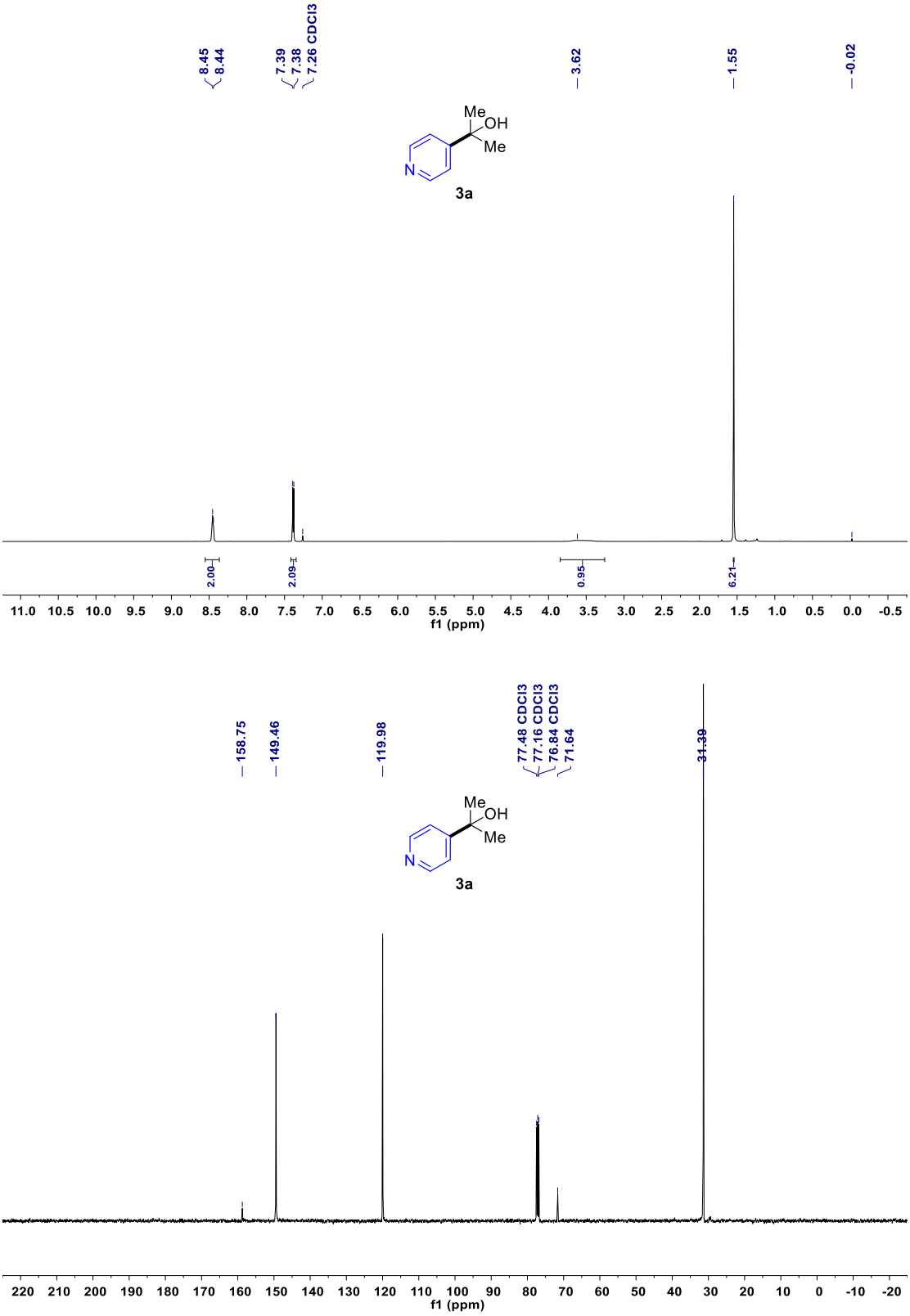


8b

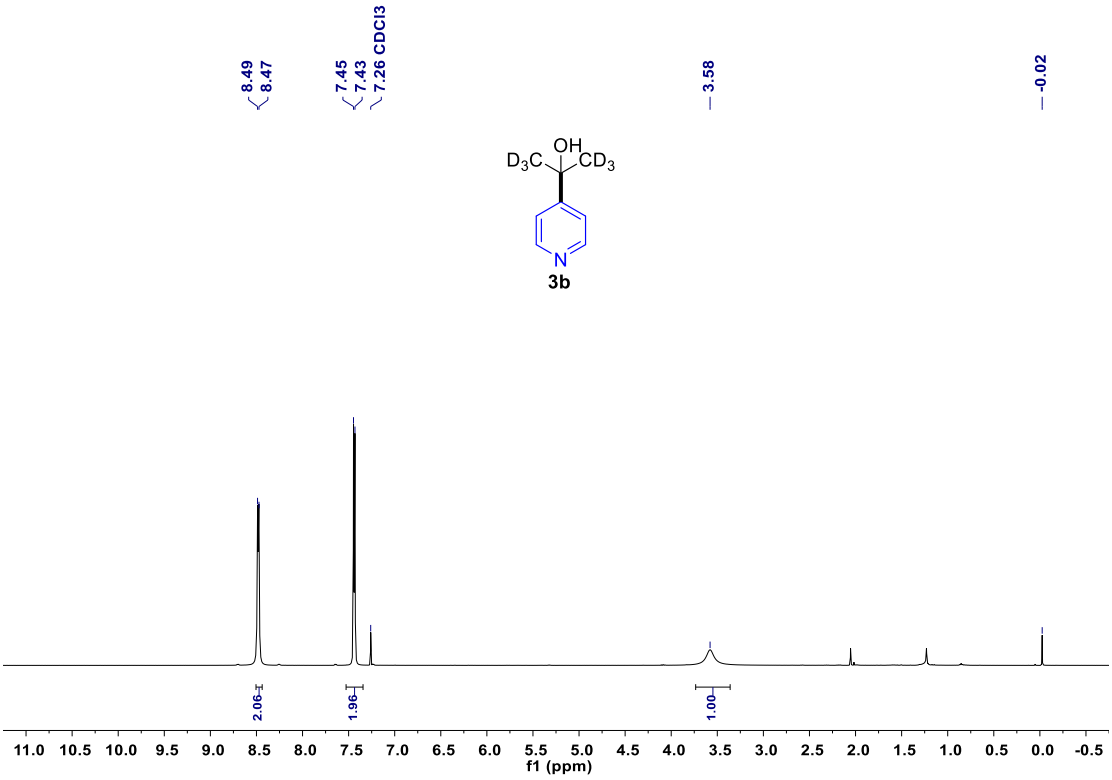
8b: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.1 Hz, 2H), 7.75-7.67 (m, 2H), 7.60-7.55 (m, 1H), 7.52-7.47 (m, 2H), 7.34 (d, *J* = 6.1 Hz, 2H), 4.54-4.40 (m, 1H), 4.20-4.08 (m, 2H), 3.77-3.67 (m, 1H), 3.64-3.58 (m, 2H), 3.55-3.47 (m, 1H), 3.21-2.90 (m,

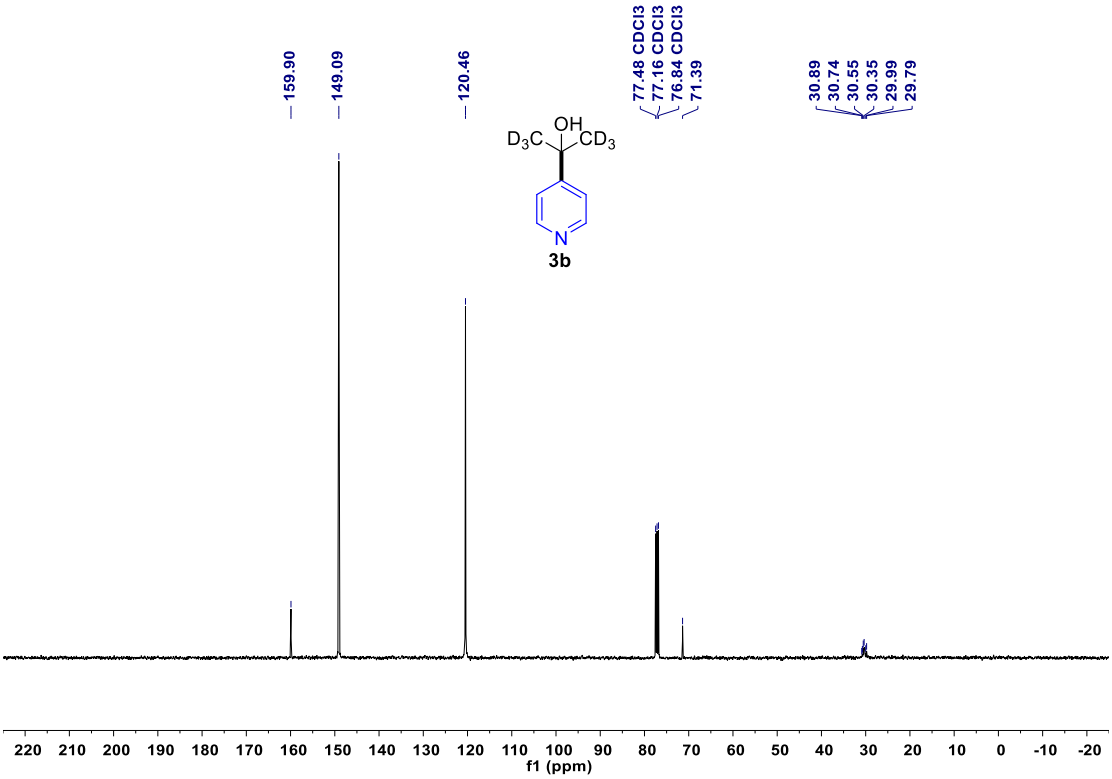
6H), 2.65-2.56 (m, 6H), 1.98-1.78 (m, 2H), 1.77-1.67 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 156.9, 149.9, 135.3, 133.0, 129.2, 127.9, 119.9, 71.0, 70.2, 68.5, 57.4, 52.5, 45.9, 41.0, 38.4, 37.8, 37.3. **HRMS** (ESI-TOF) calculated for $C_{24}H_{33}N_4O_5S$ $[M+H]^+$ 489.2166, found 489.2165.

6. NMR Spectra

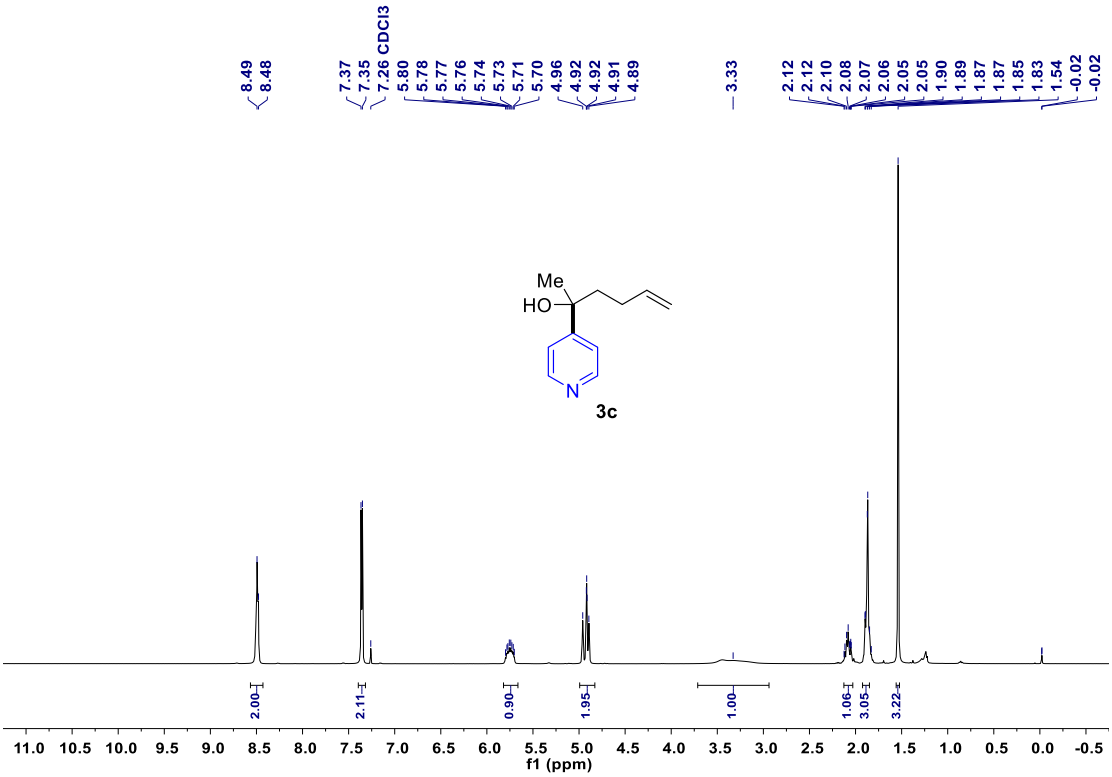


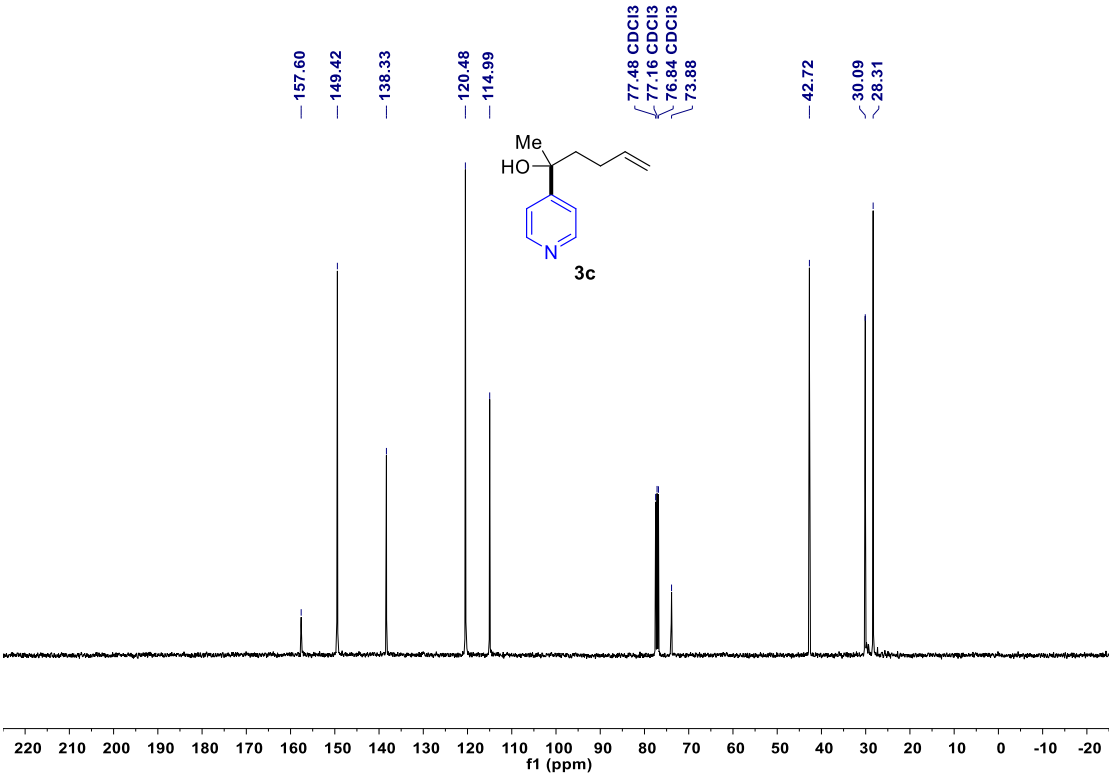
^{1}H and ^{13}C NMR spectra for compound 3a



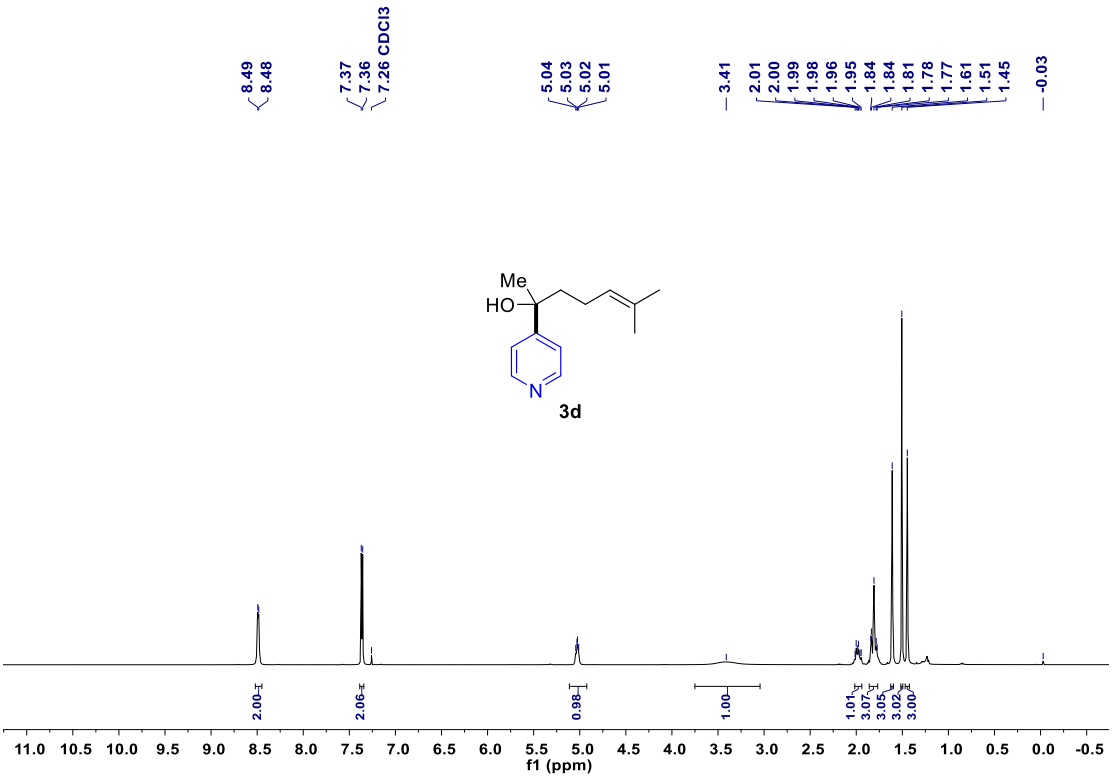


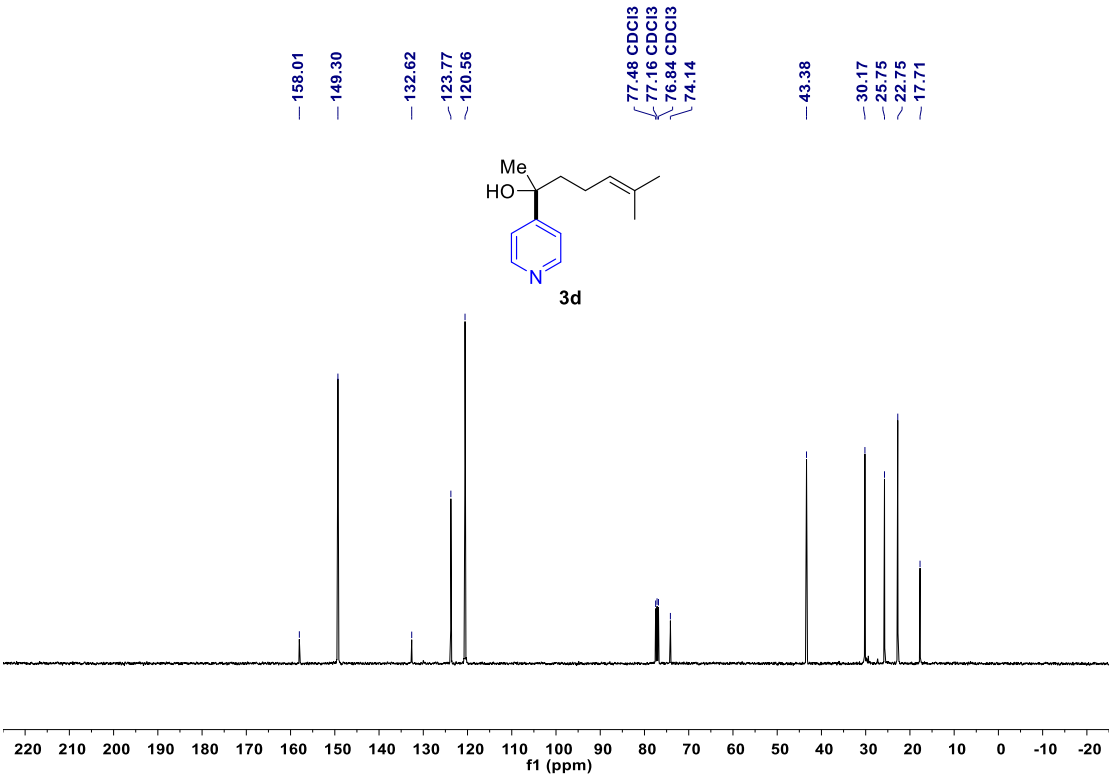
^{1}H and ^{13}C NMR spectra for compound 3b



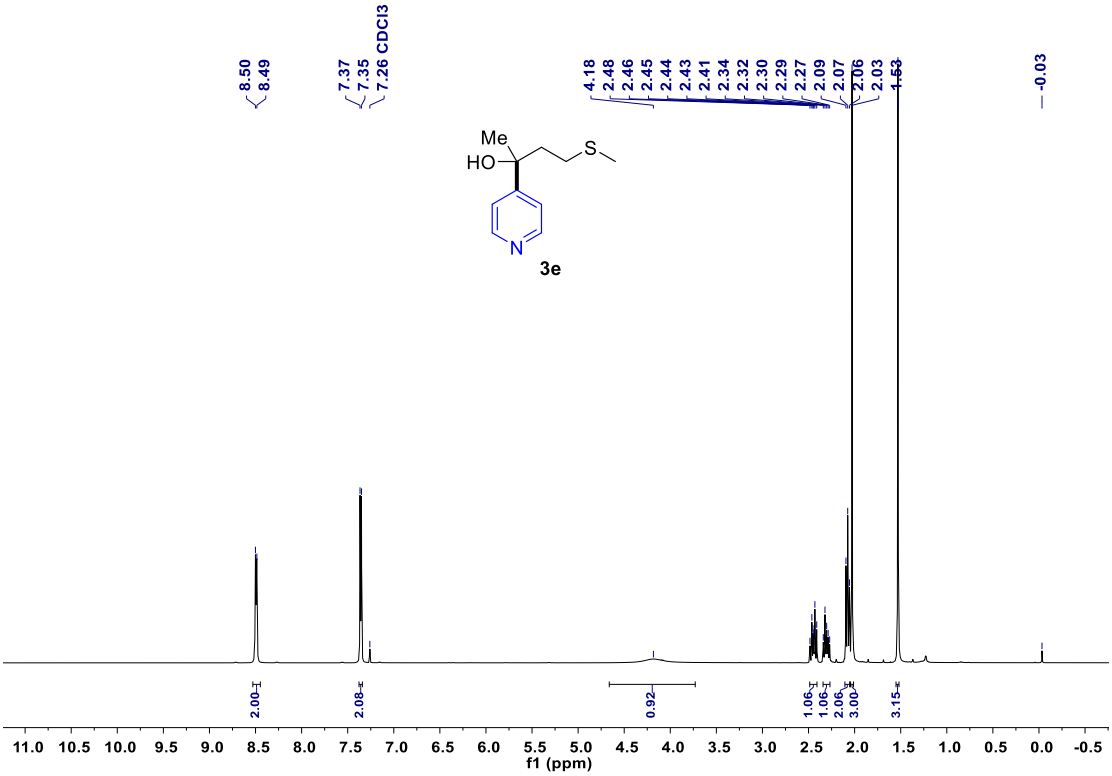


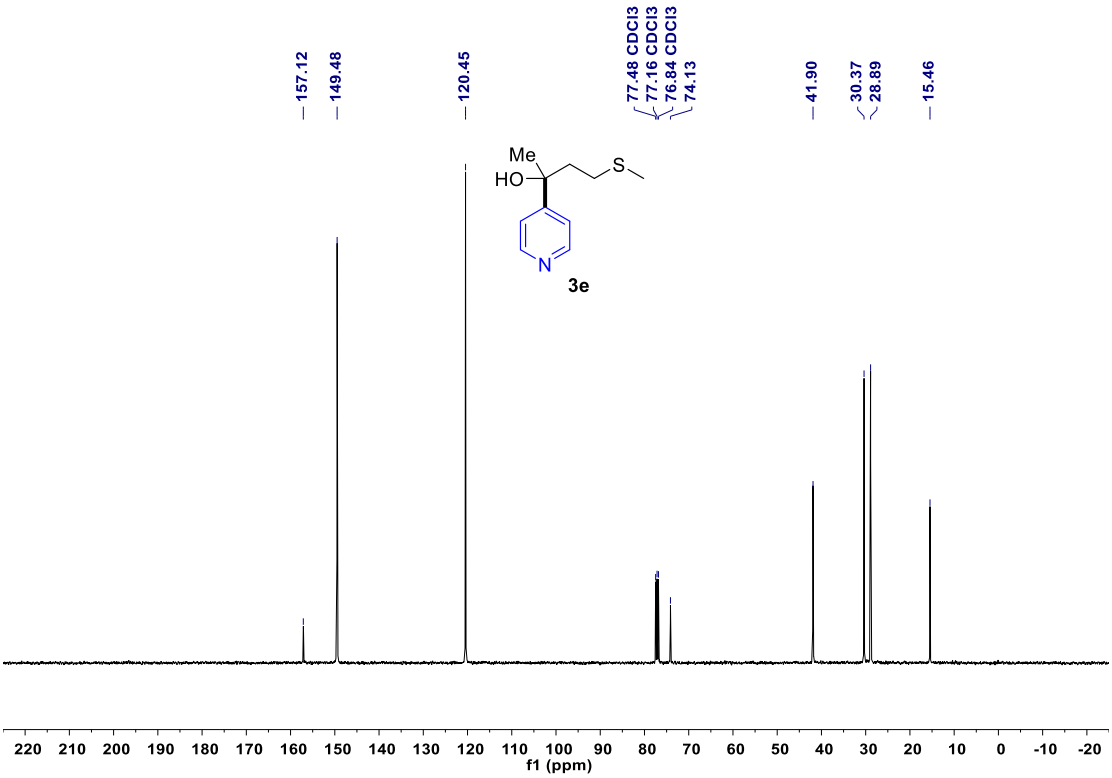
^{1}H and ^{13}C NMR spectra for compound 3c



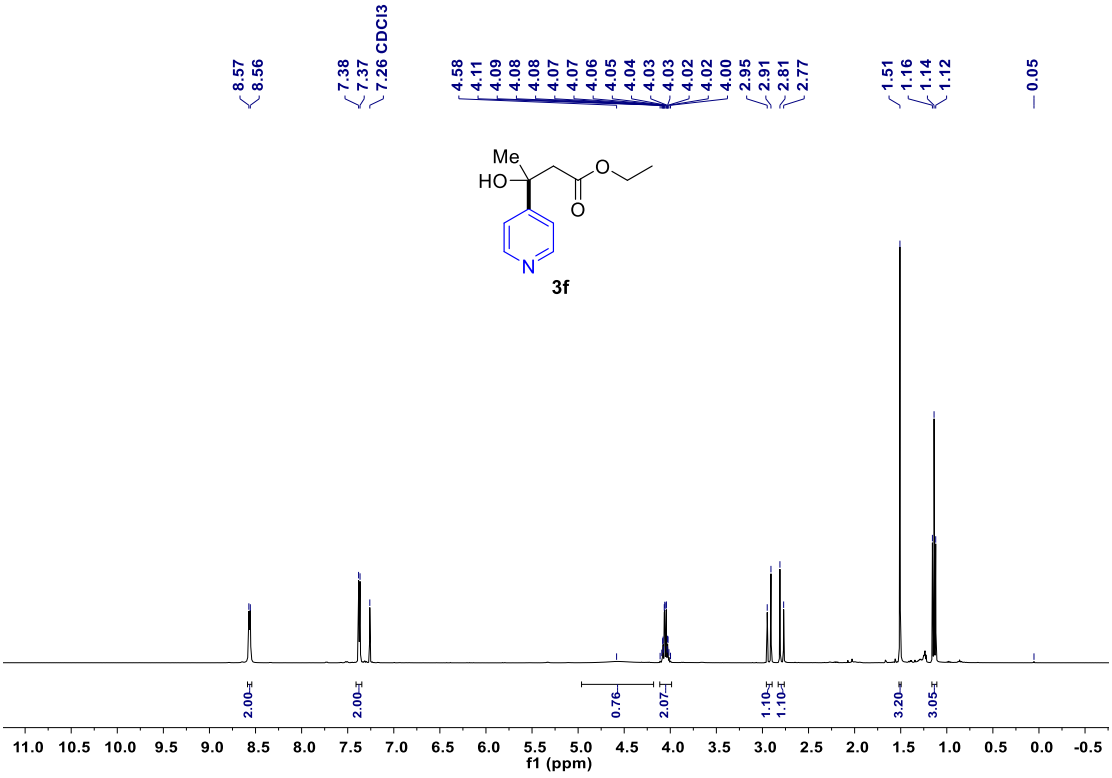


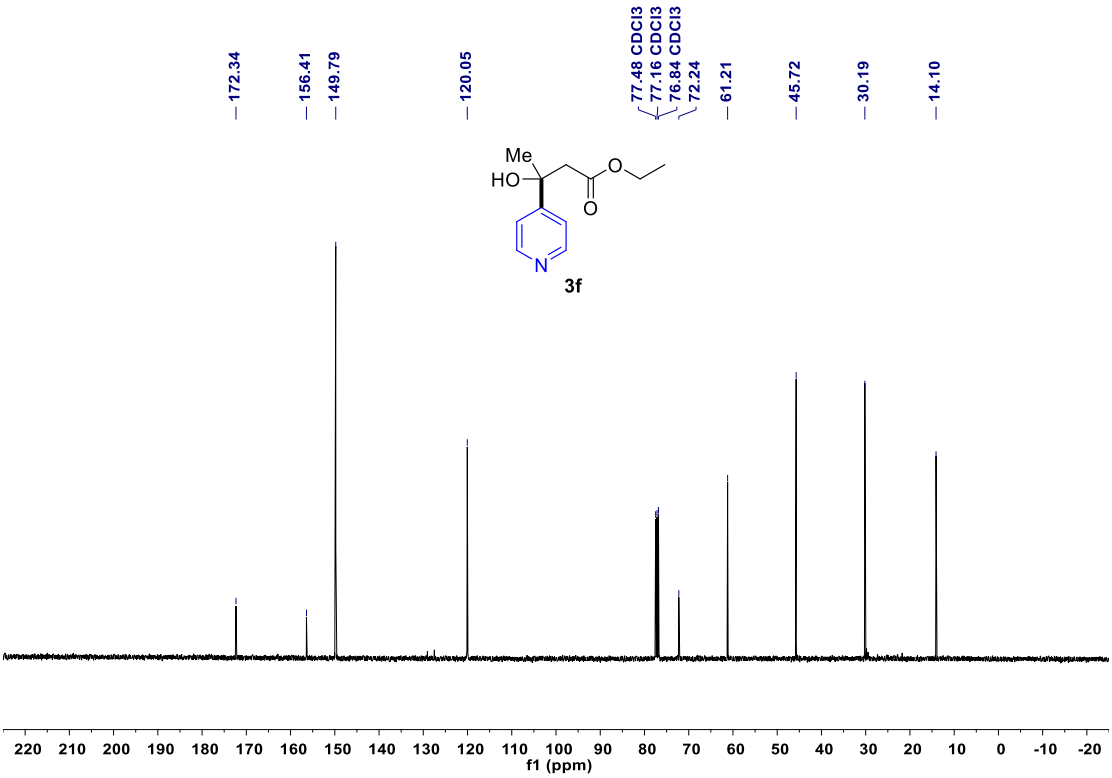
^{1}H and ^{13}C NMR spectra for compound 3d



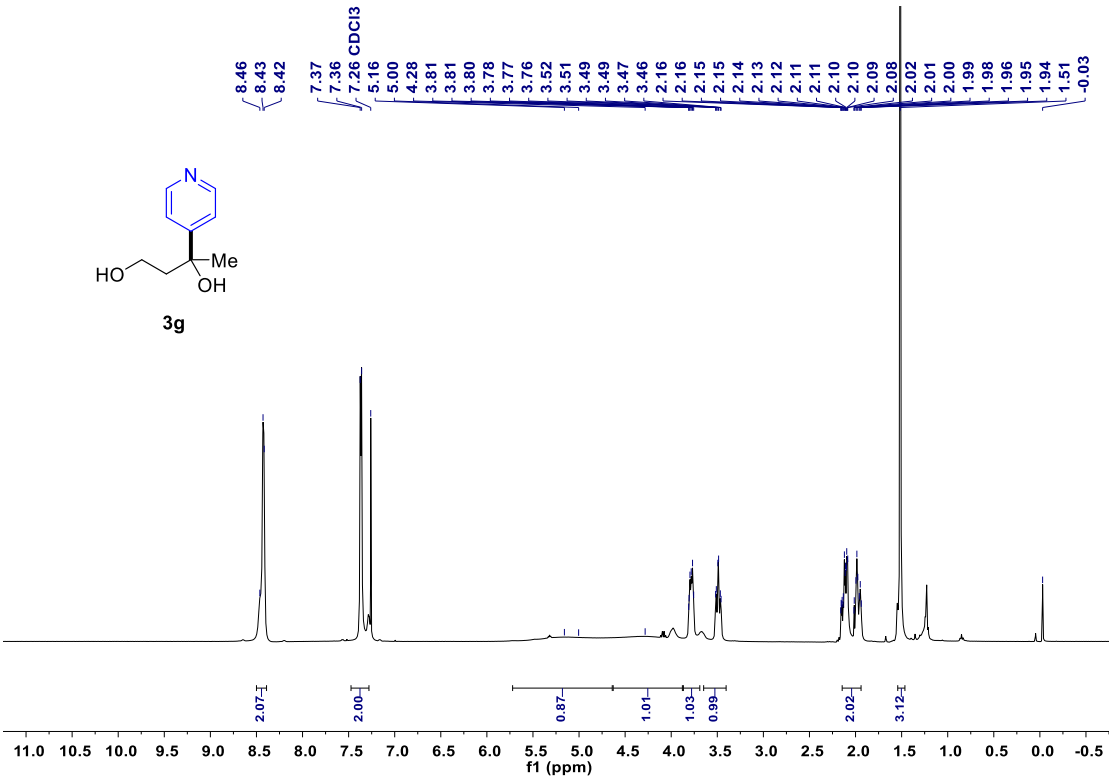


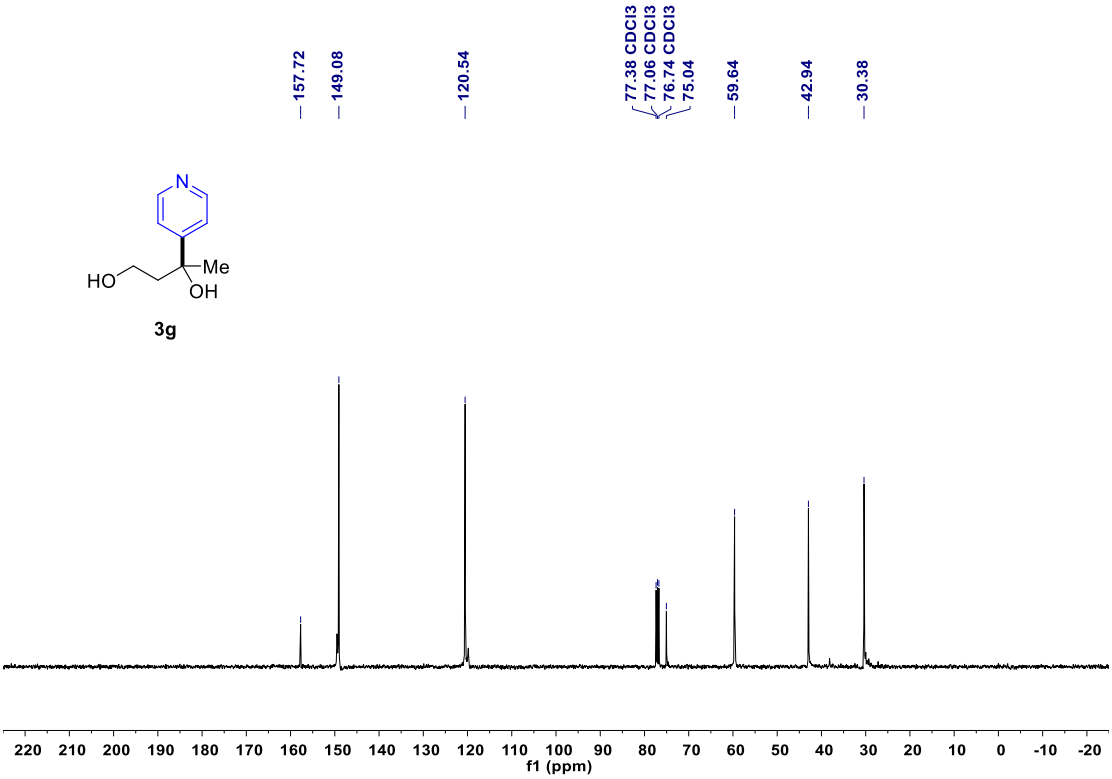
^{1}H and ^{13}C NMR spectra for compound 3e



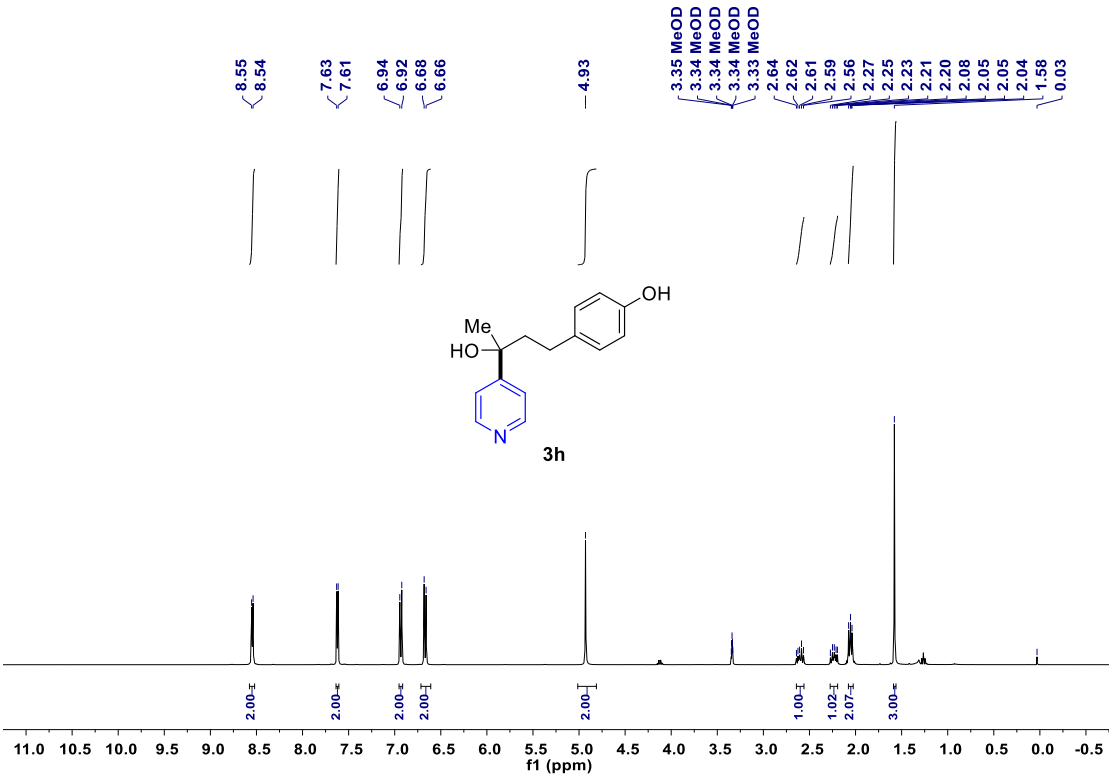


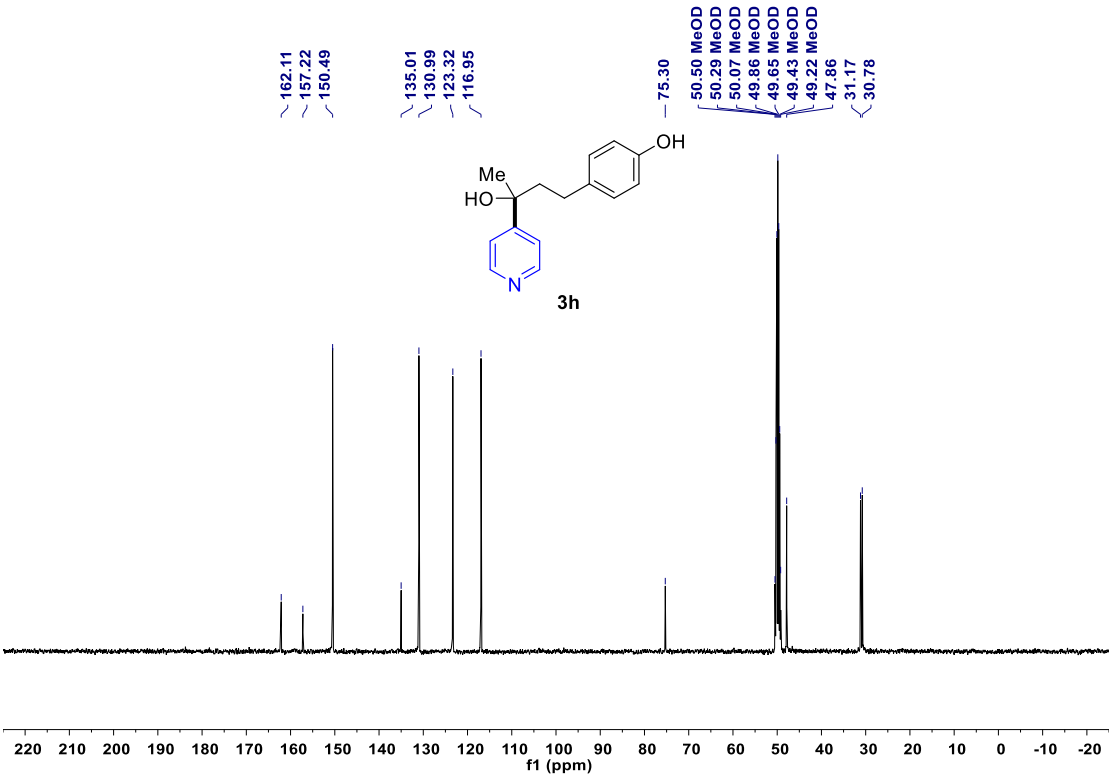
^{1}H and ^{13}C NMR spectra for compound 3f



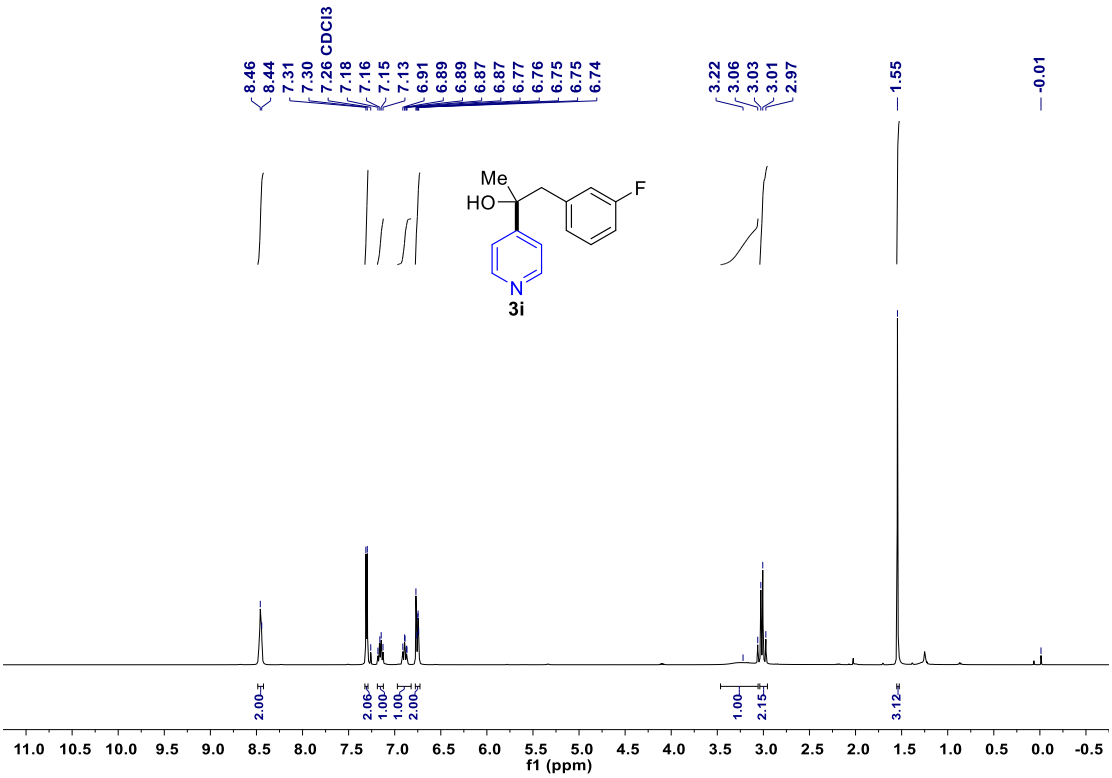


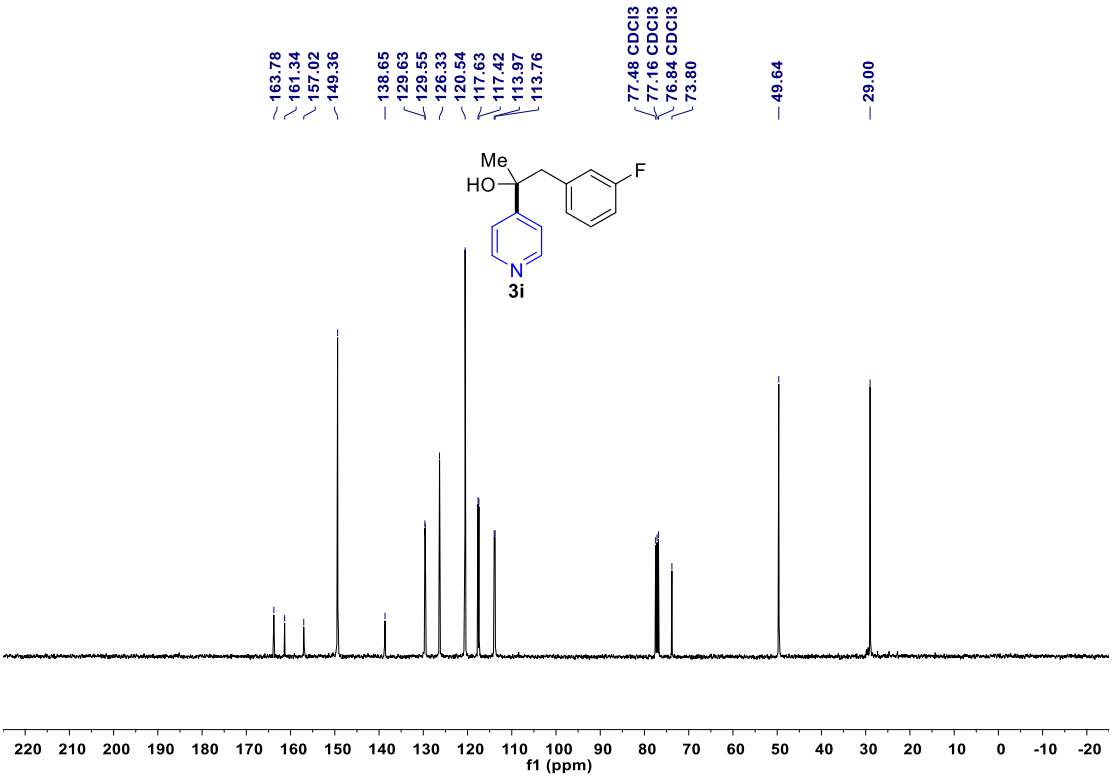
^{1}H and ^{13}C NMR spectra for compound 3g



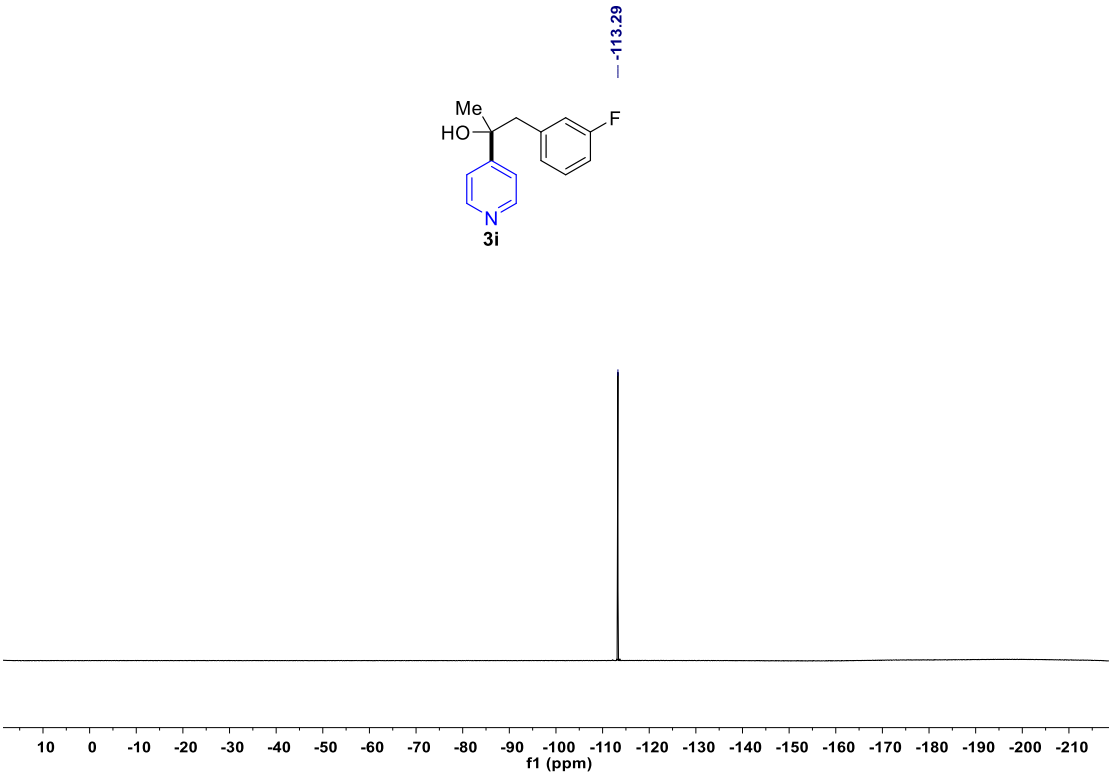


^{1}H and ^{13}C NMR spectra for compound 3h

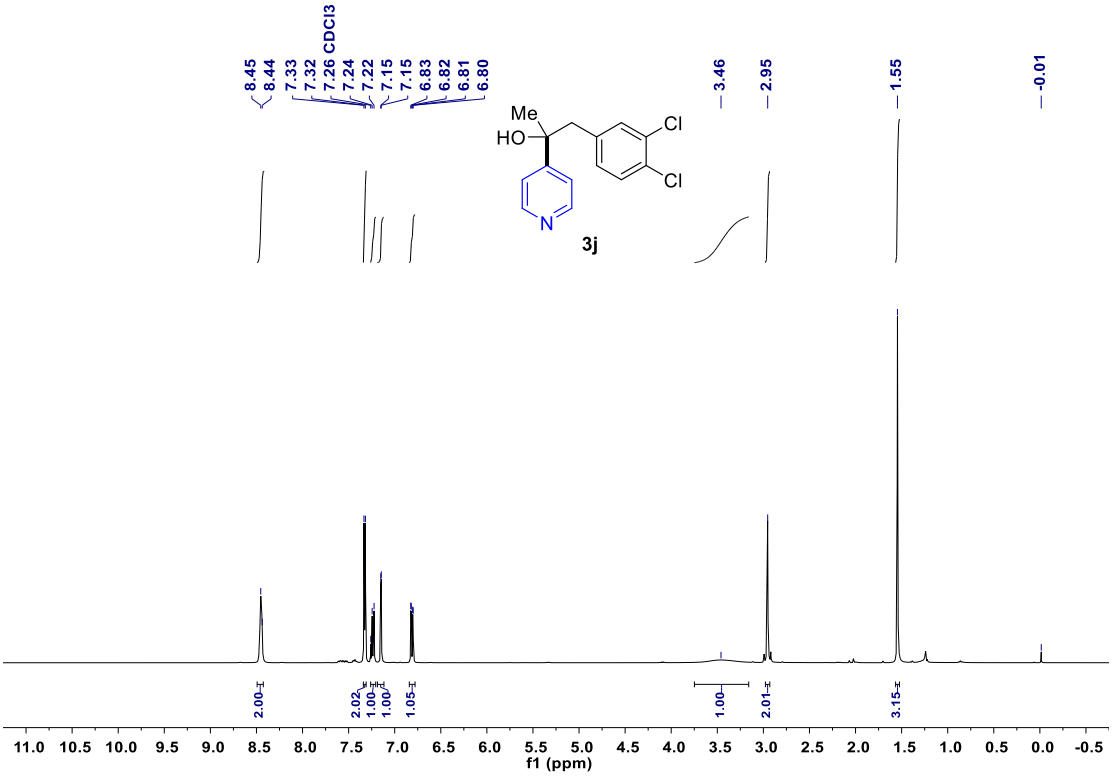


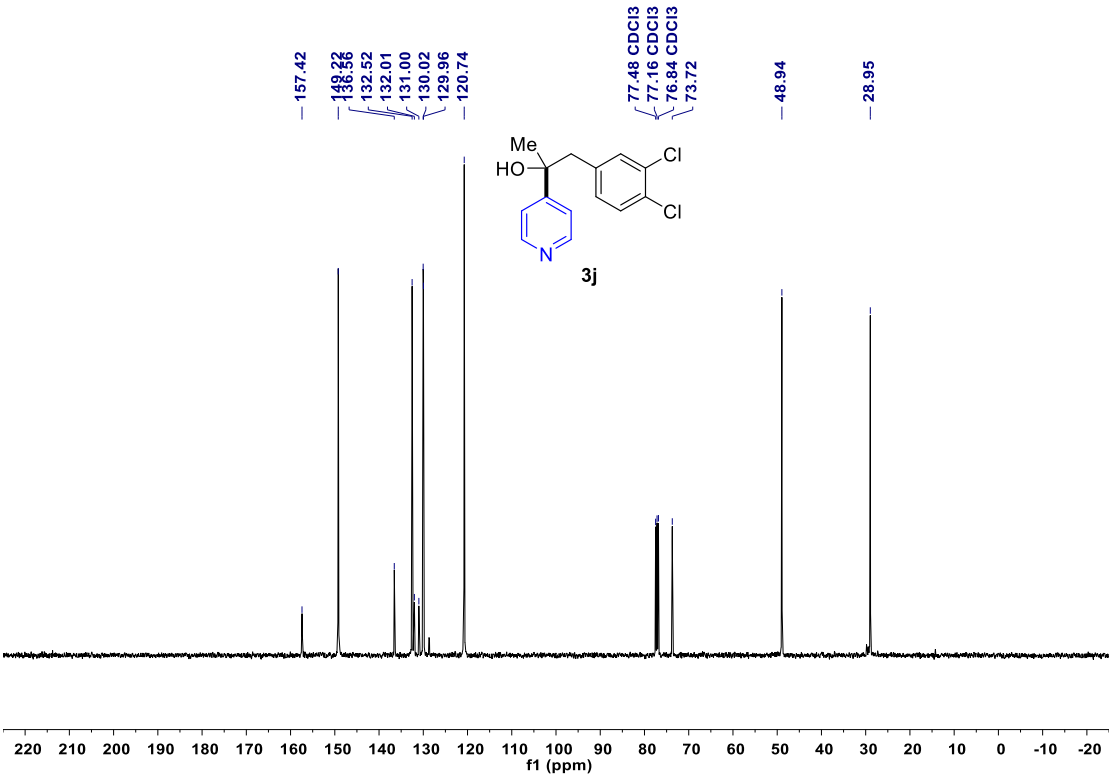


^{1}H and ^{13}C NMR spectra for compound 3i

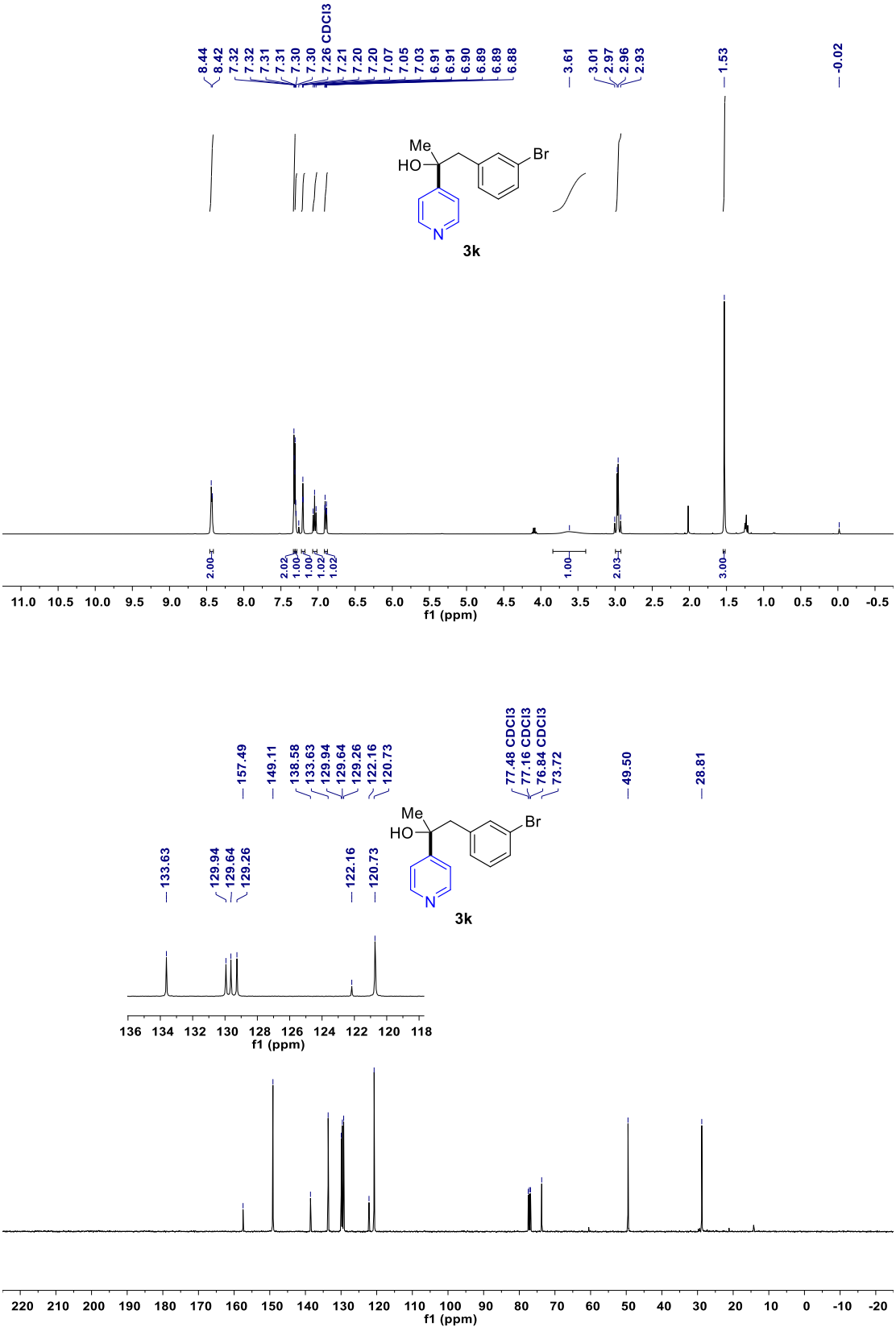


^{19}F NMR spectra for compound 3i

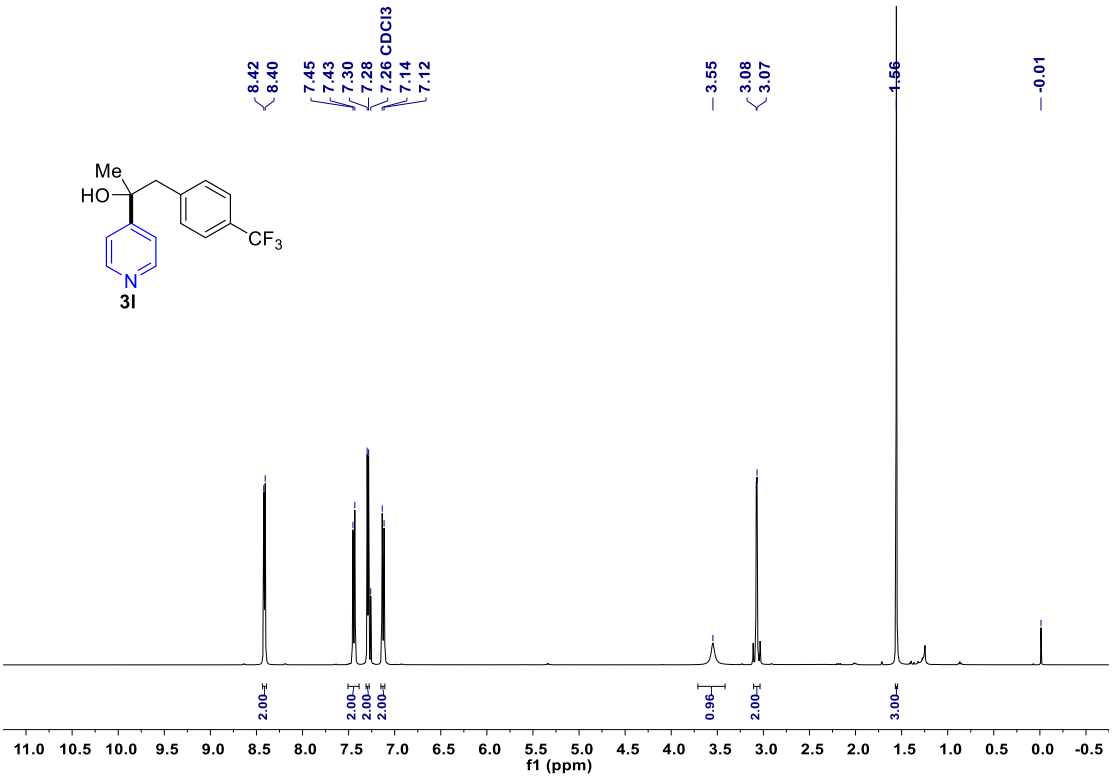


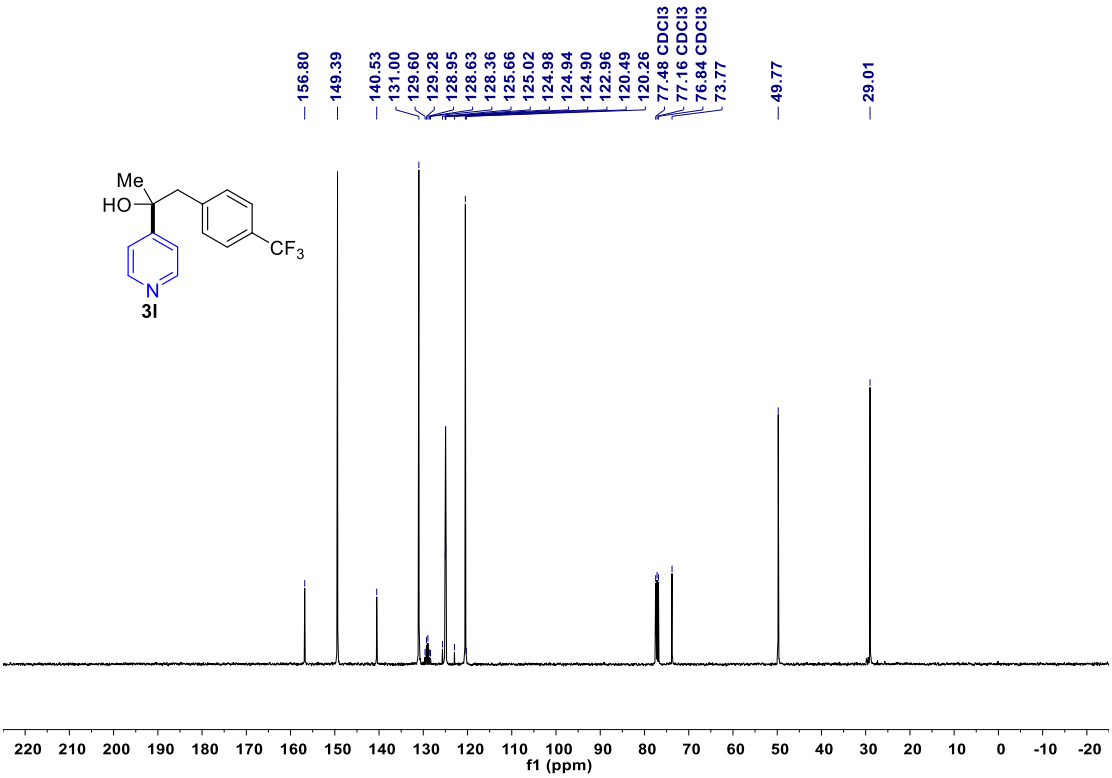


^{1}H and ^{13}C NMR spectra for compound 3j

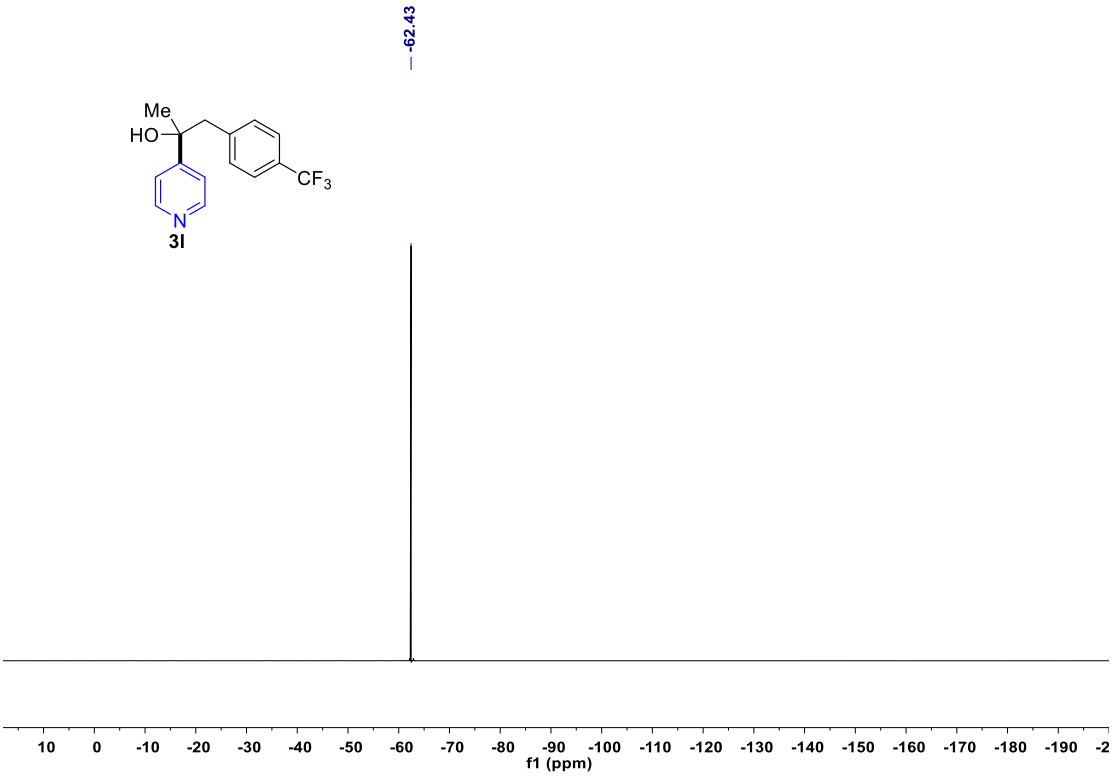


^{1}H and ^{13}C NMR spectra for compound 3k

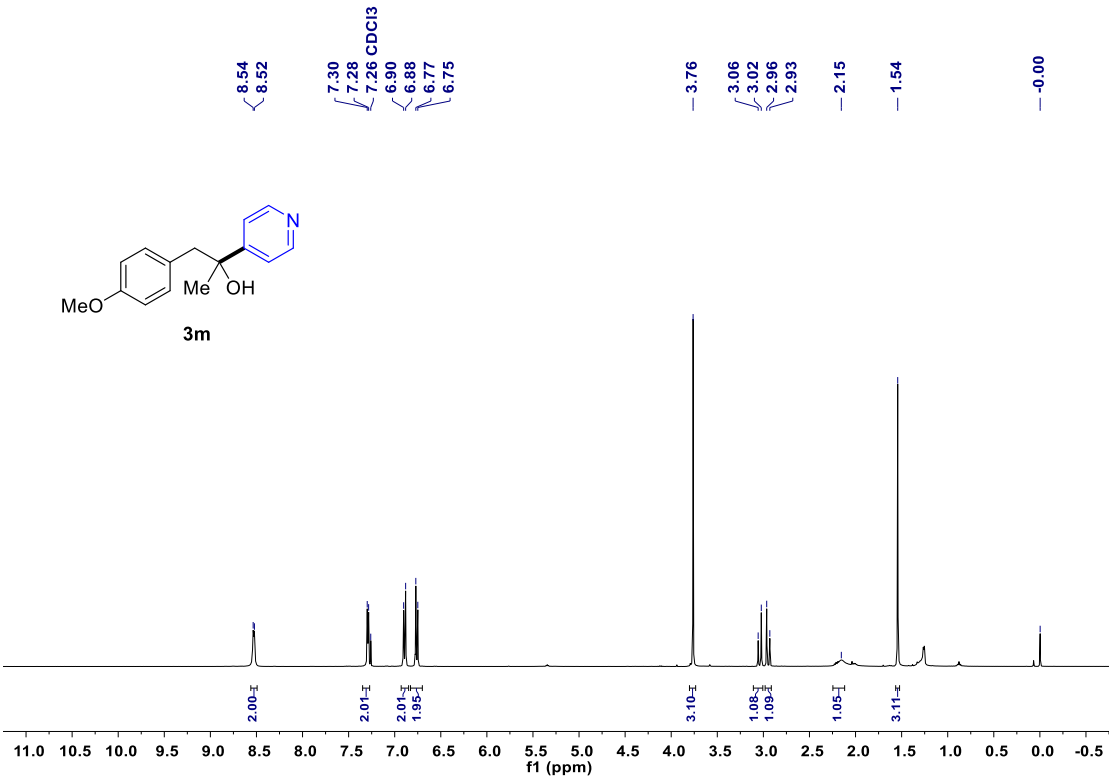


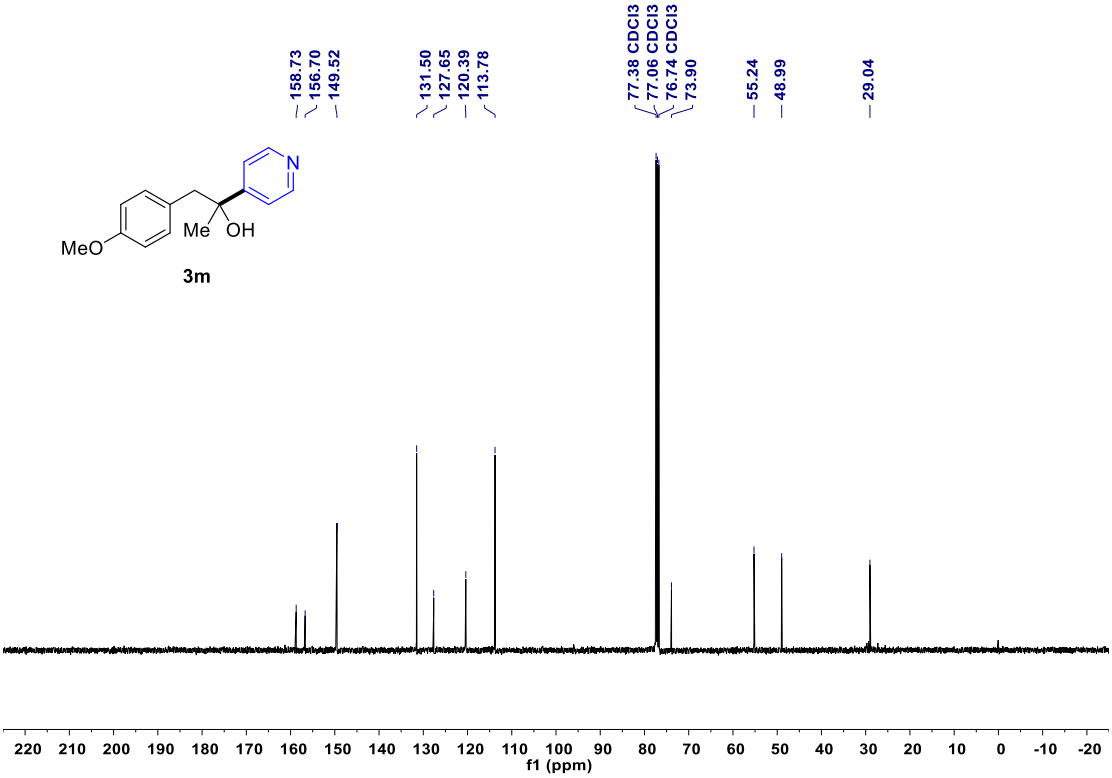


^{1}H and ^{13}C NMR spectra for compound 3l

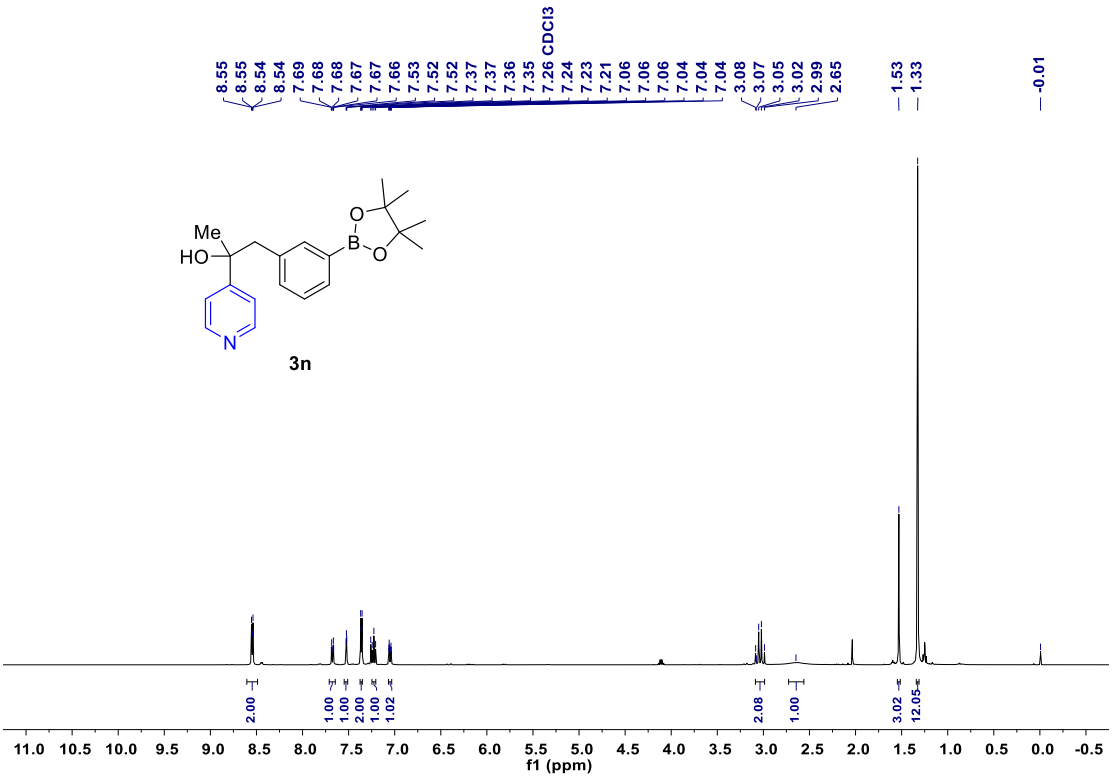


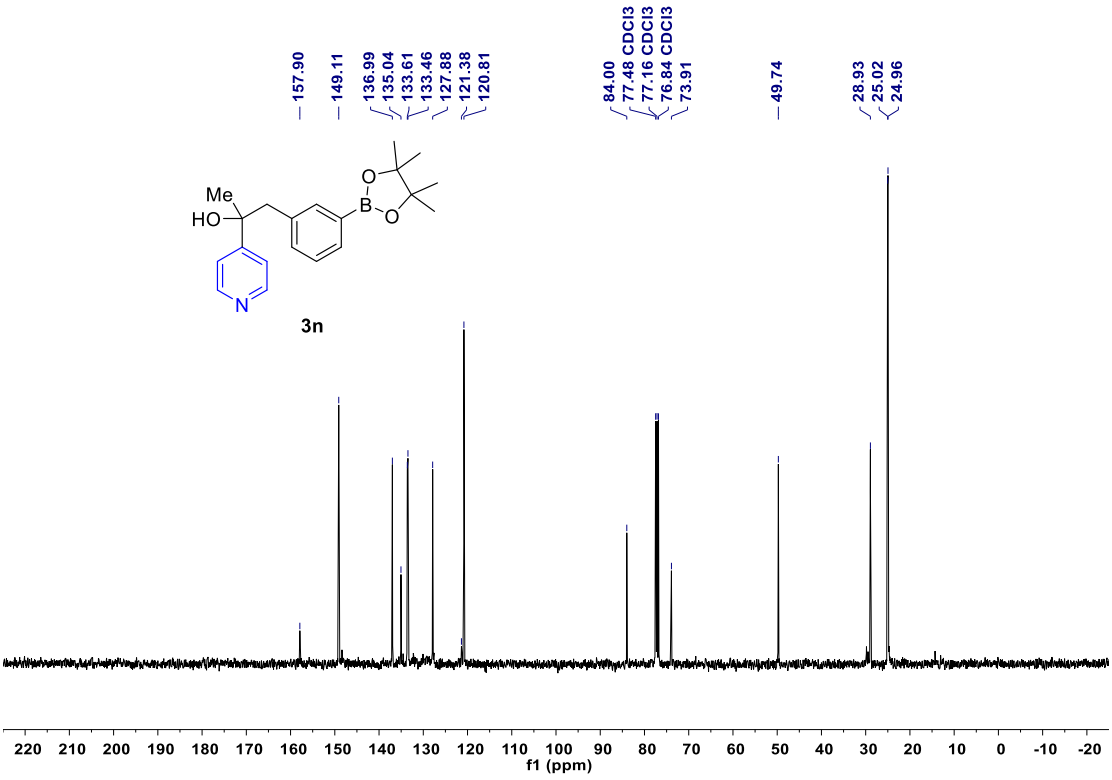
^{19}F NMR spectra for compound 3l



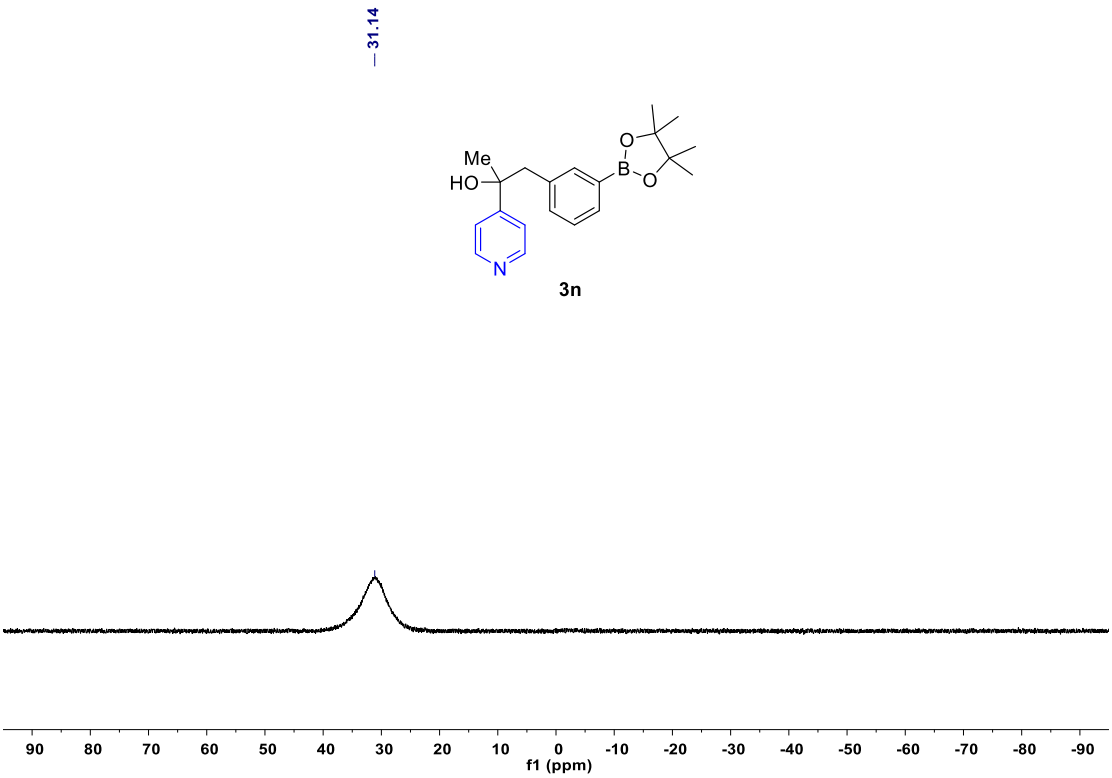


^{1}H and ^{13}C NMR spectra for compound 3m

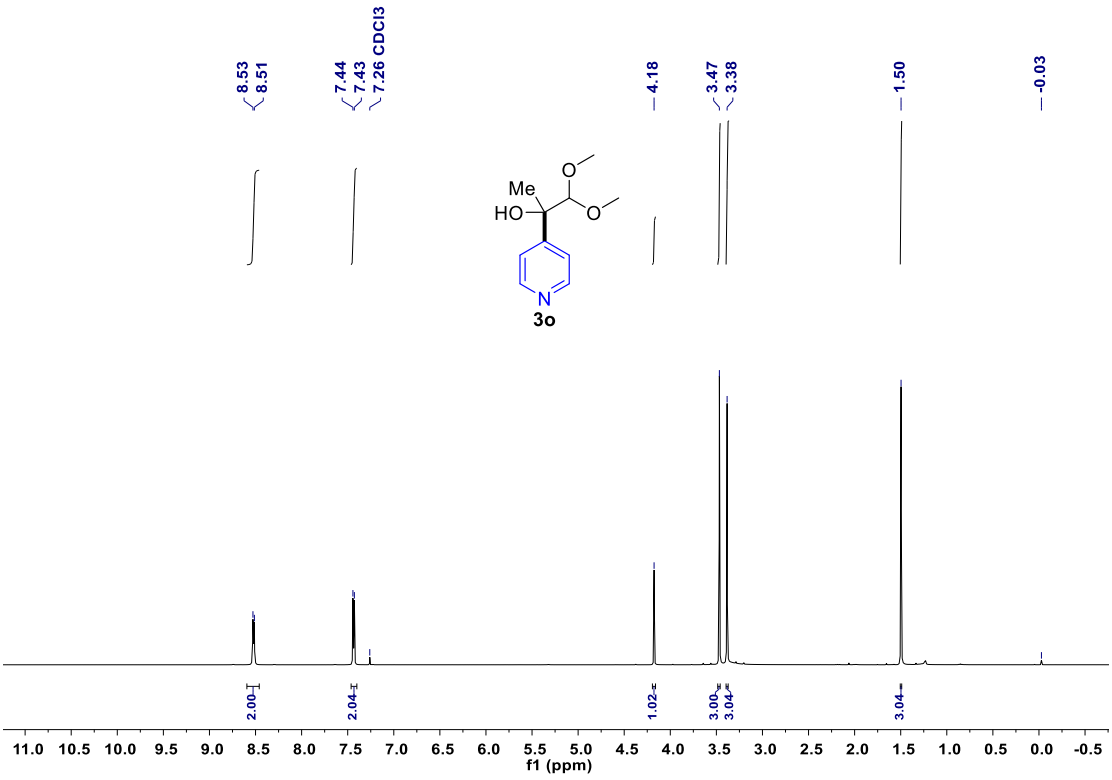


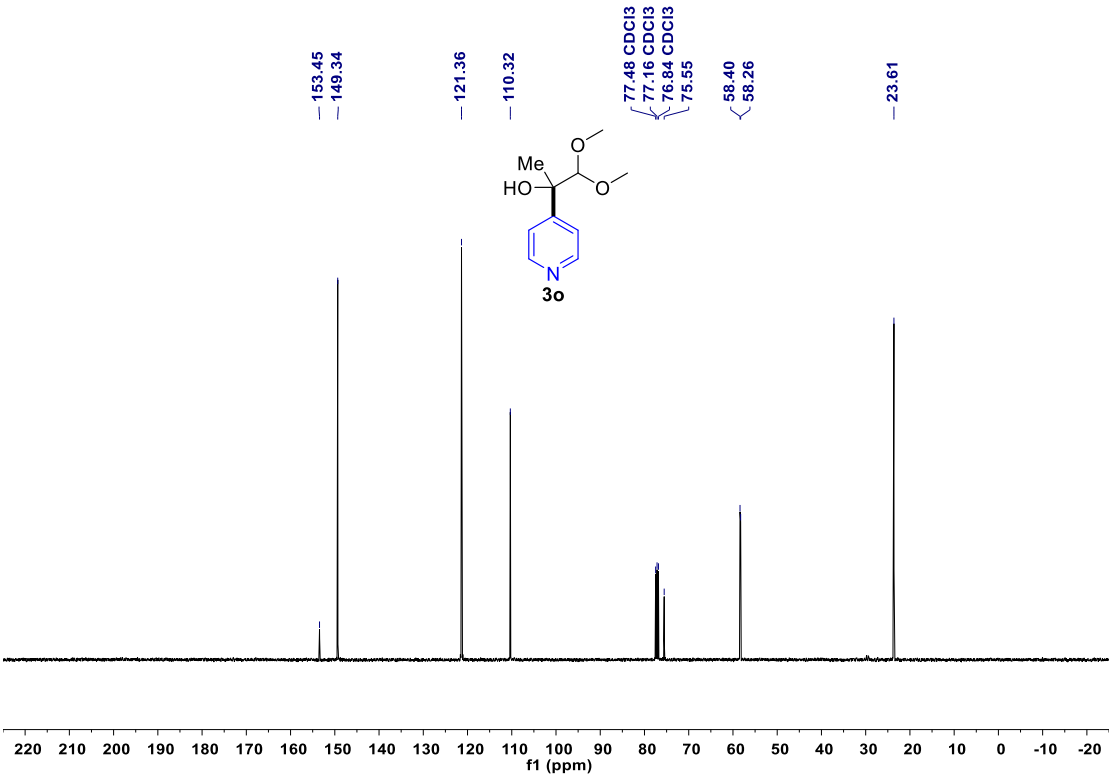


^{1}H and ^{13}C NMR spectra for compound 3n

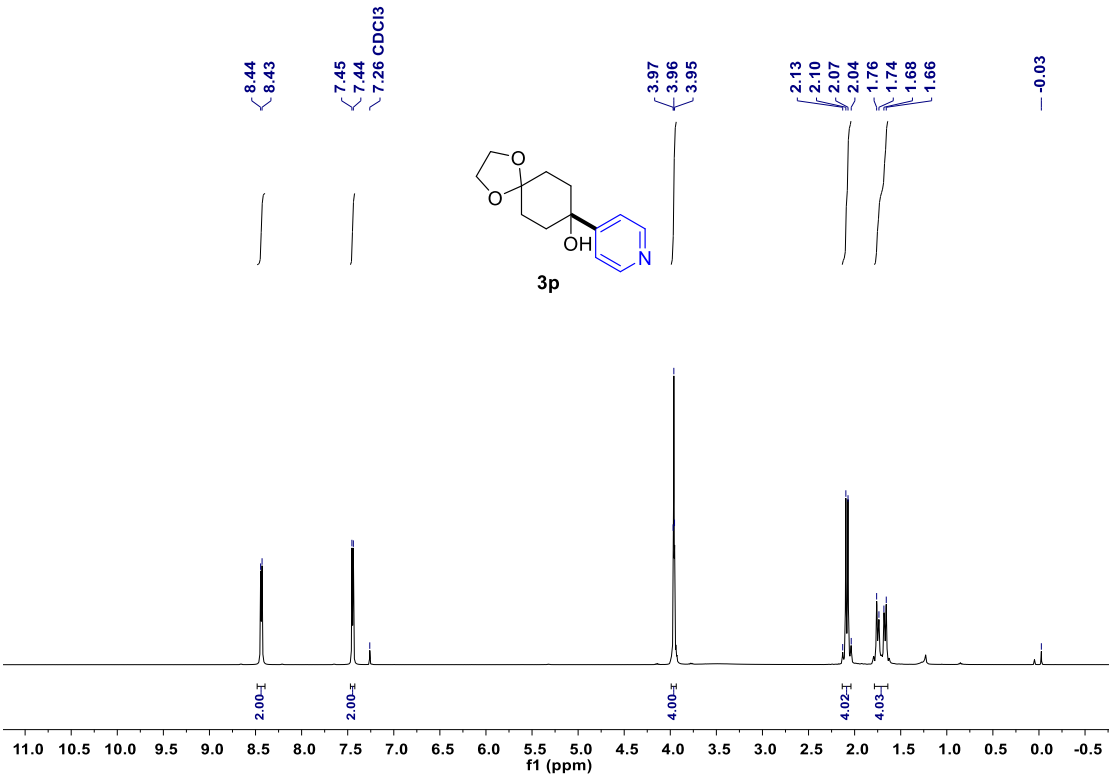


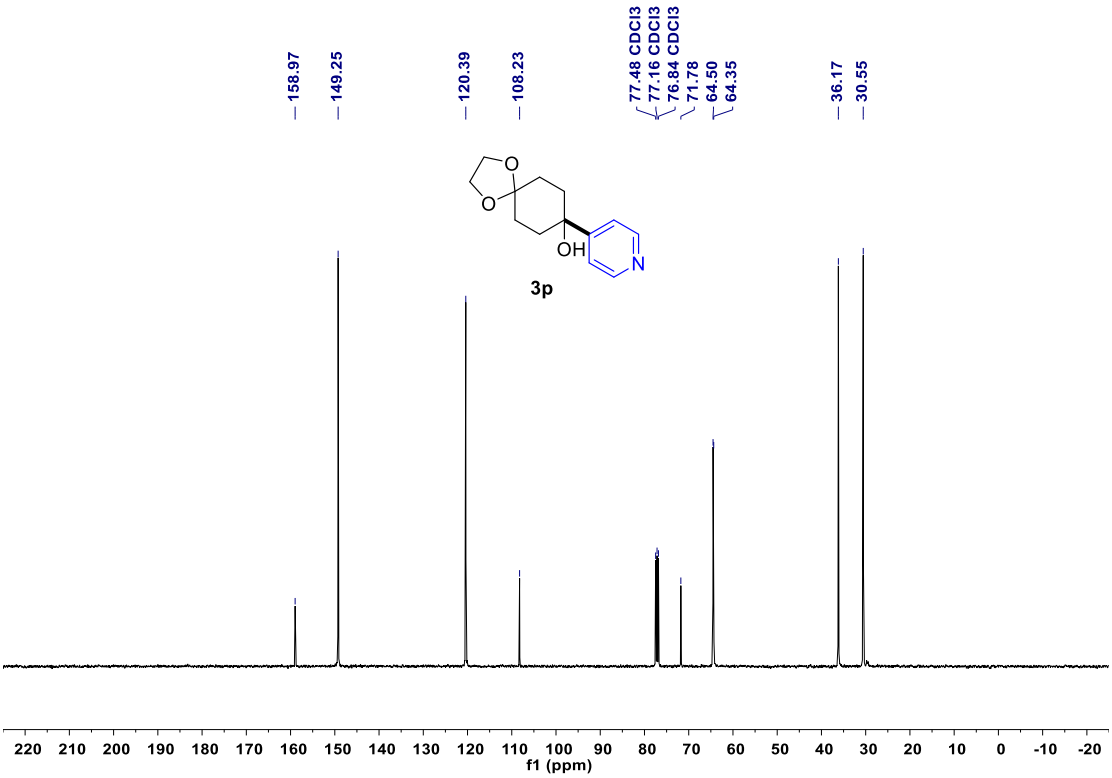
^{11}B NMR spectra for compound 3n



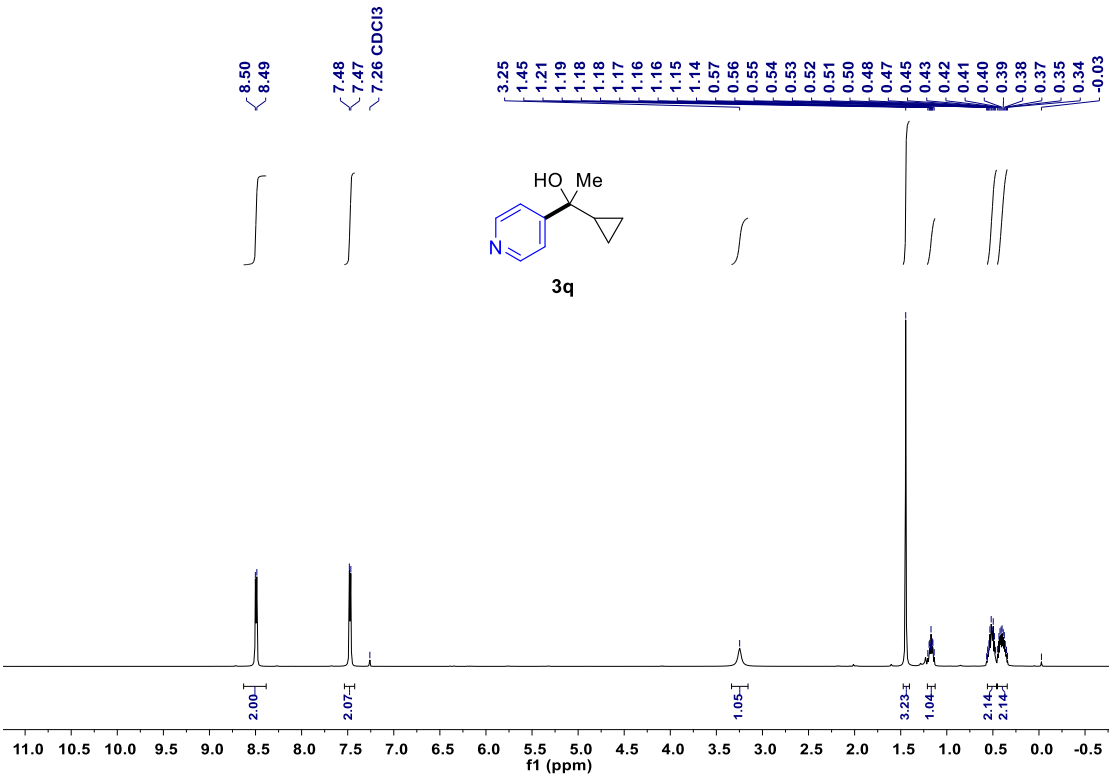


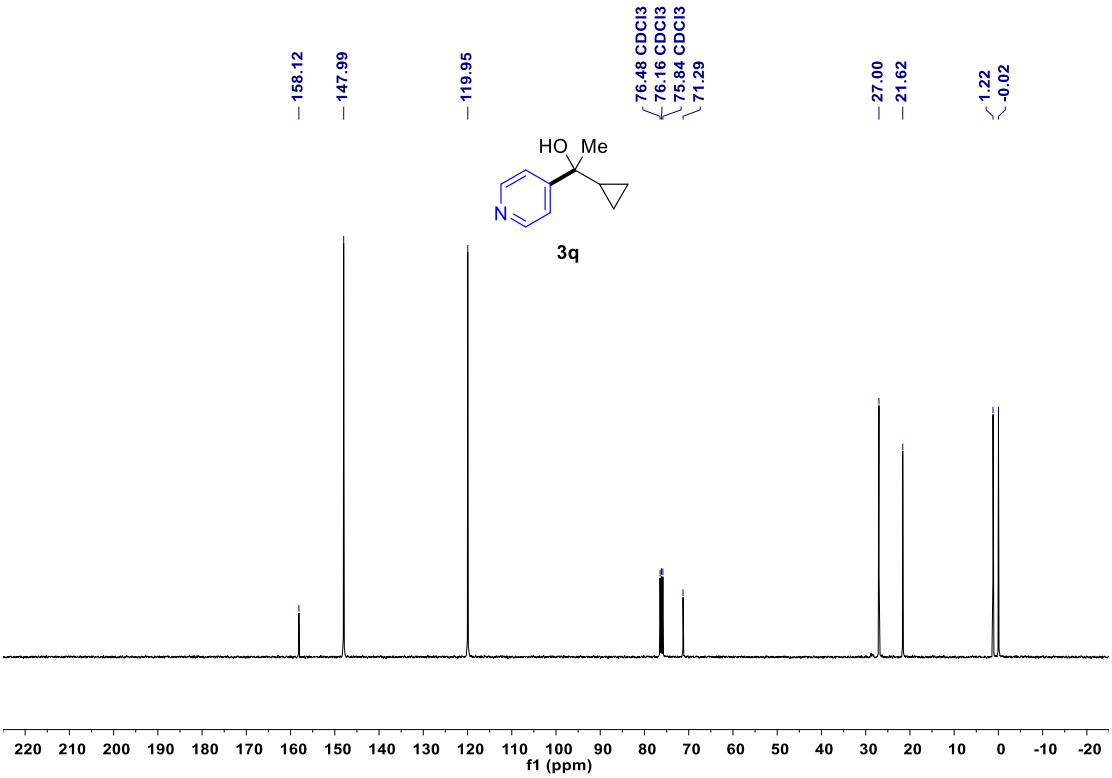
^{1}H and ^{13}C NMR spectra for compound 3o



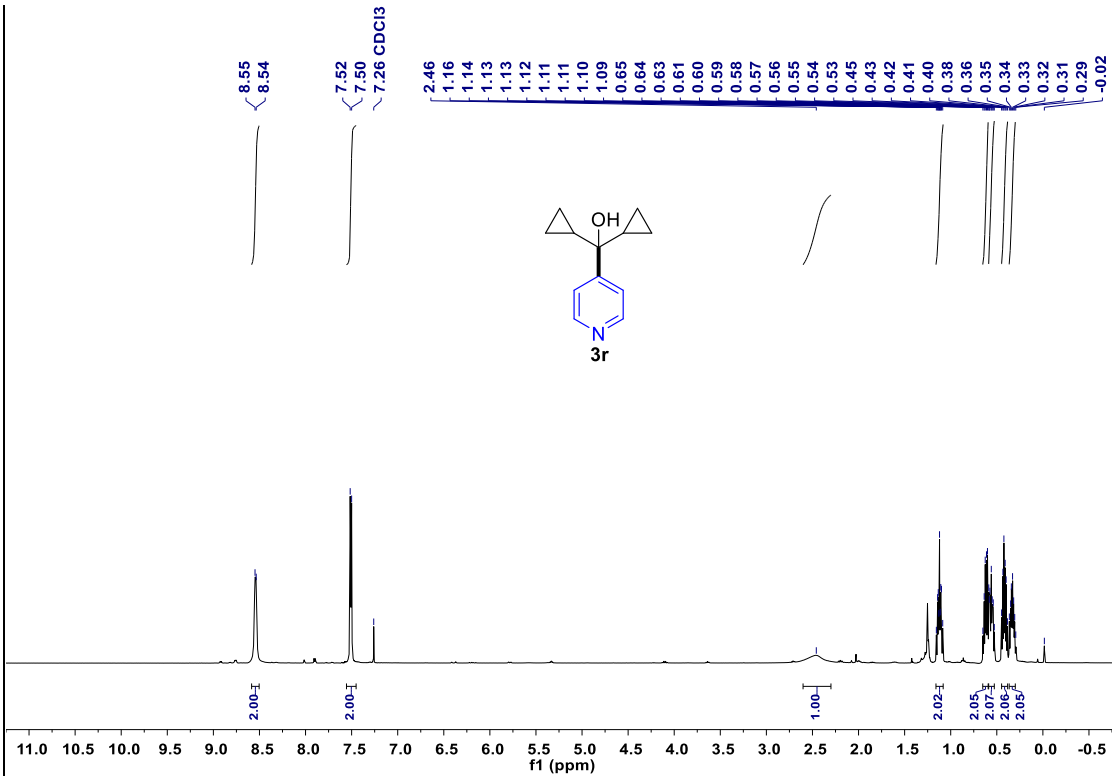


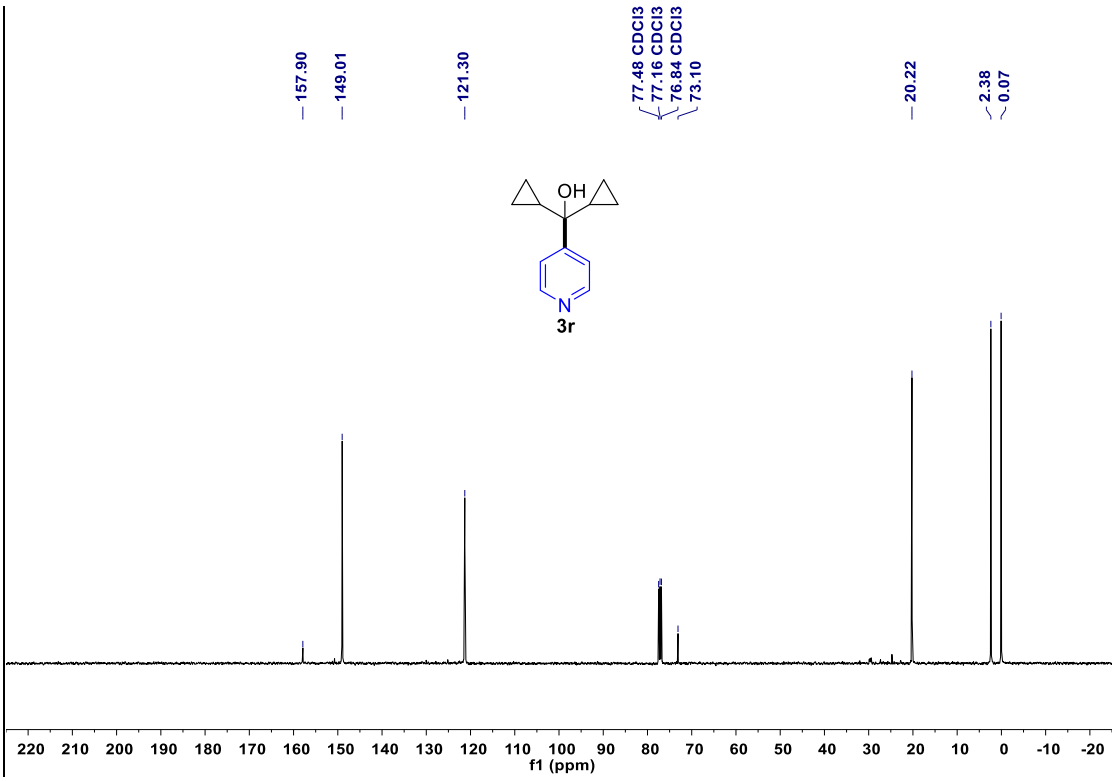
^{1}H and ^{13}C NMR spectra for compound 3p



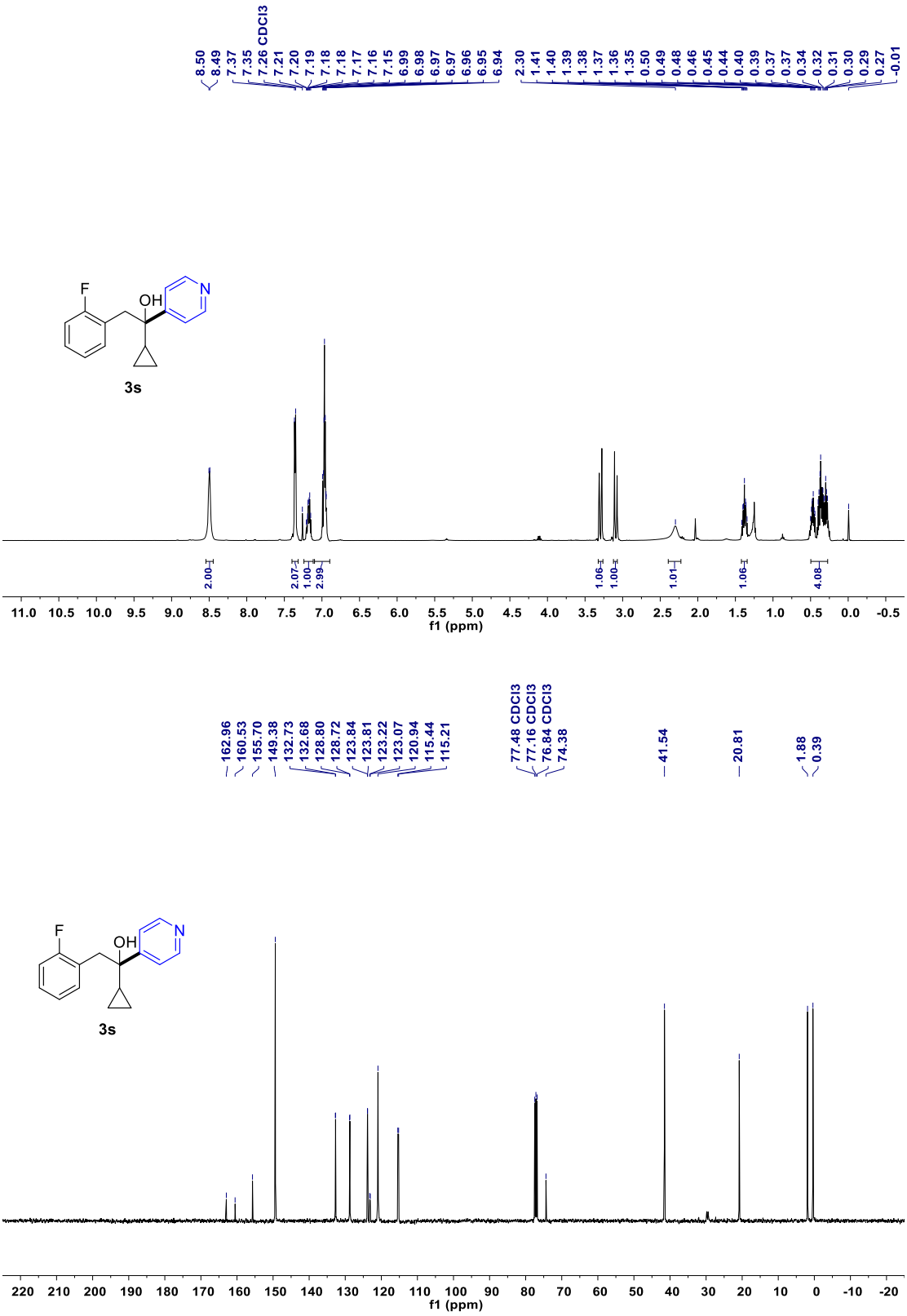


^{1}H and ^{13}C NMR spectra for compound 3q

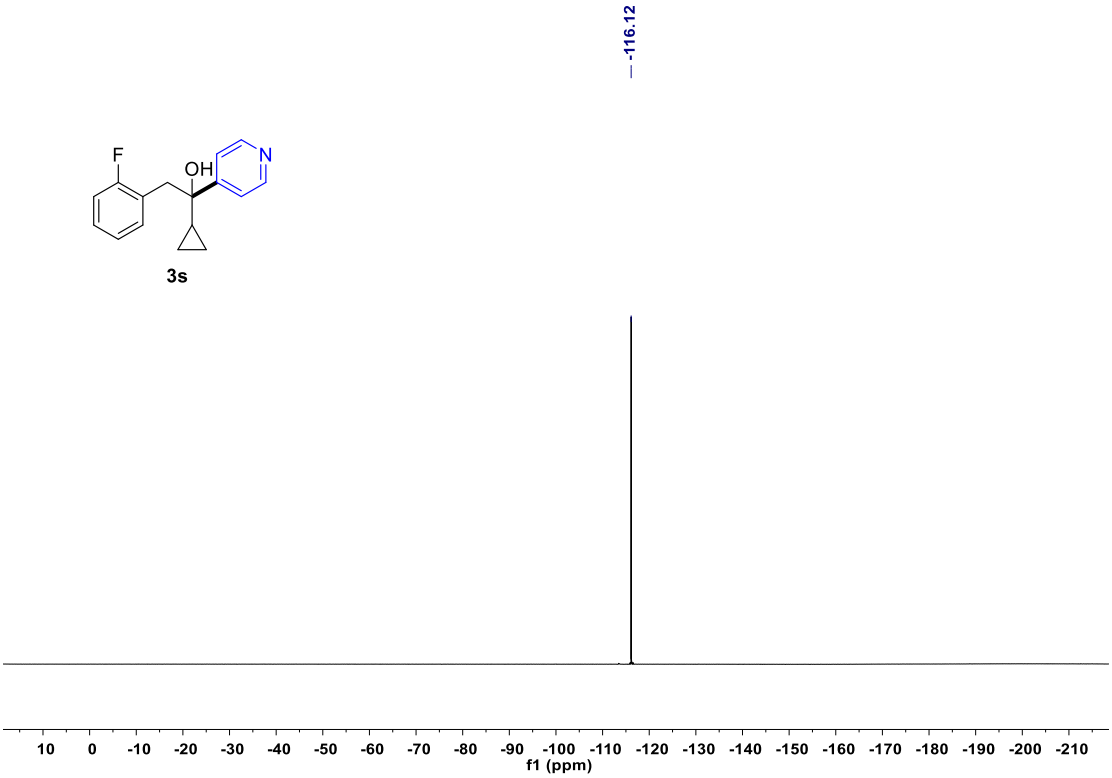




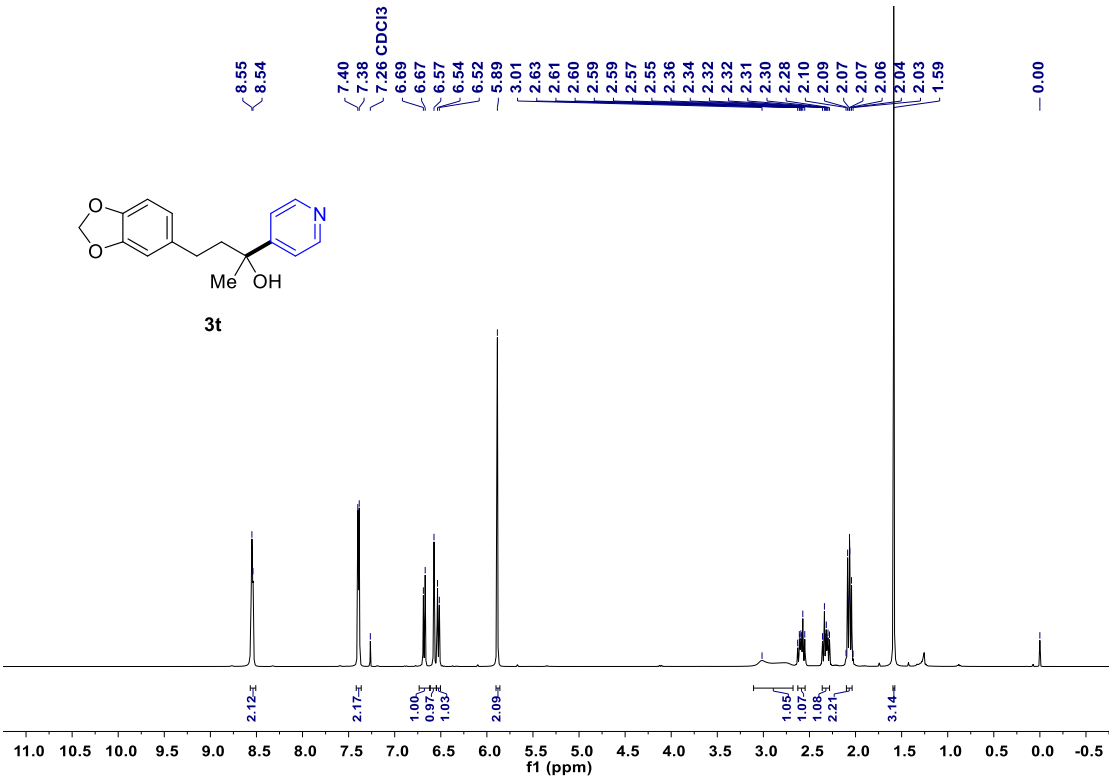
^{1}H and ^{13}C NMR spectra for compound 3r

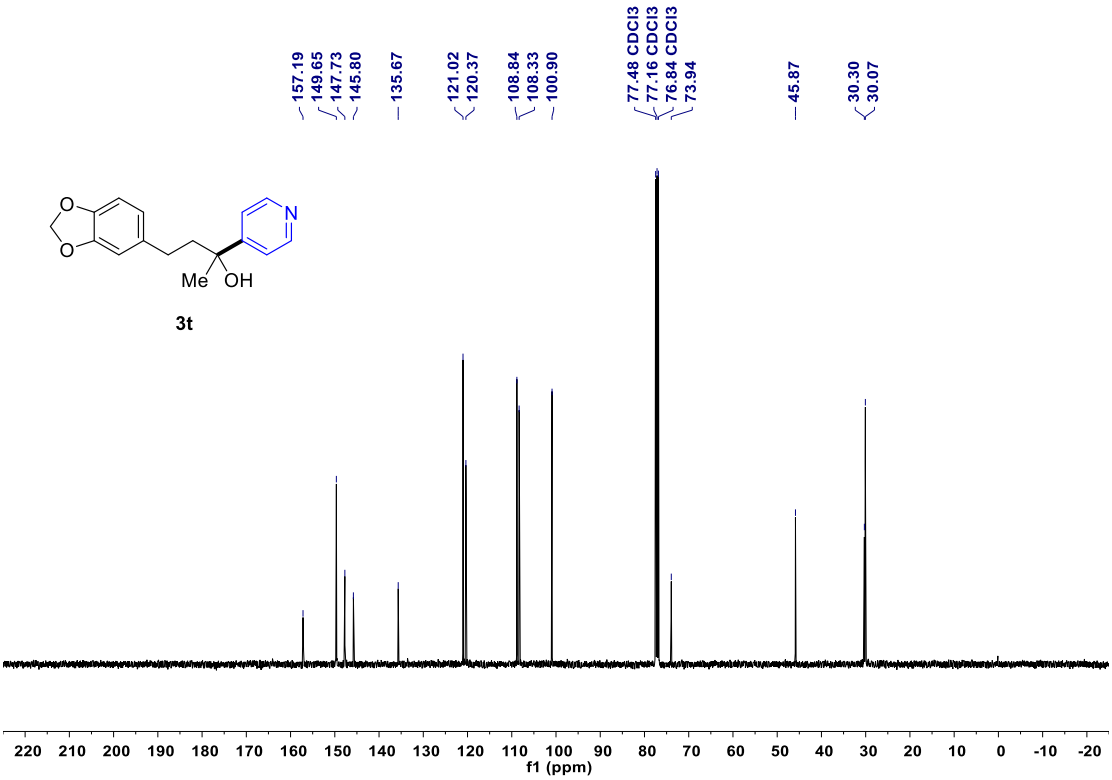


^{1}H and ^{13}C NMR spectra for compound 3s

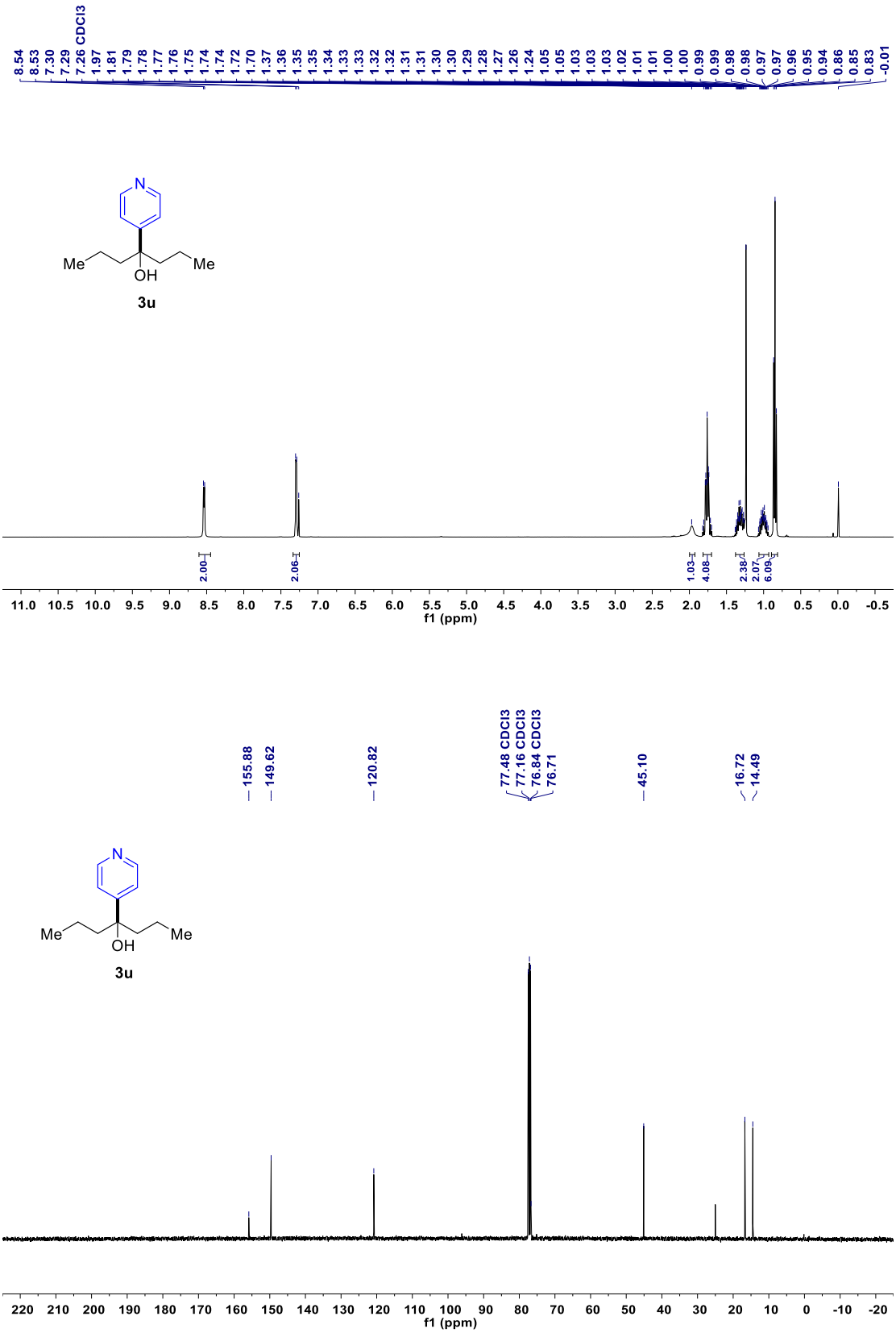


^{19}F NMR spectra for compound 3s

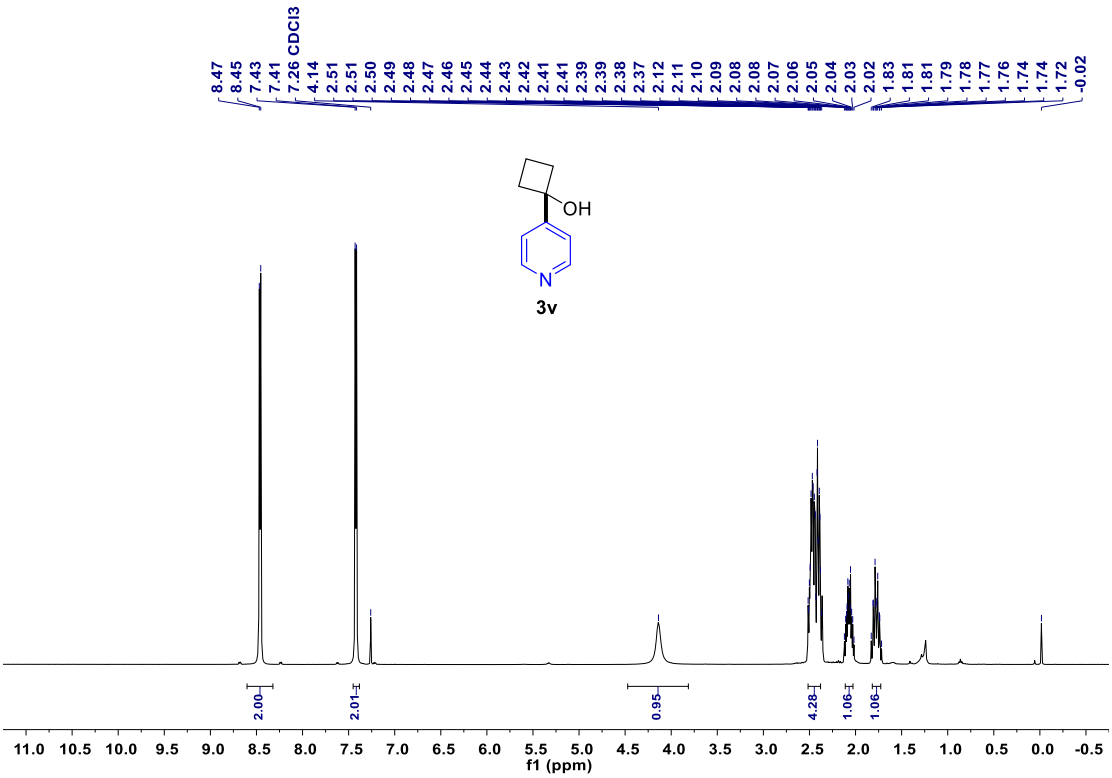


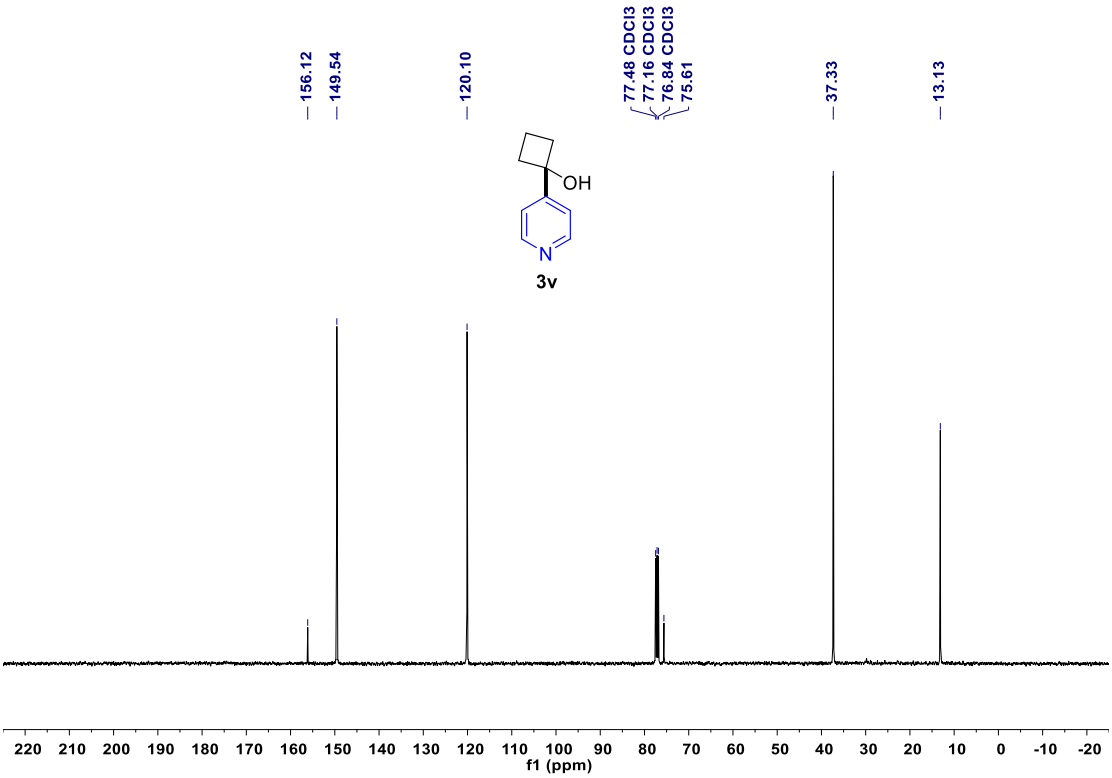


^{1}H and ^{13}C NMR spectra for compound **3t**

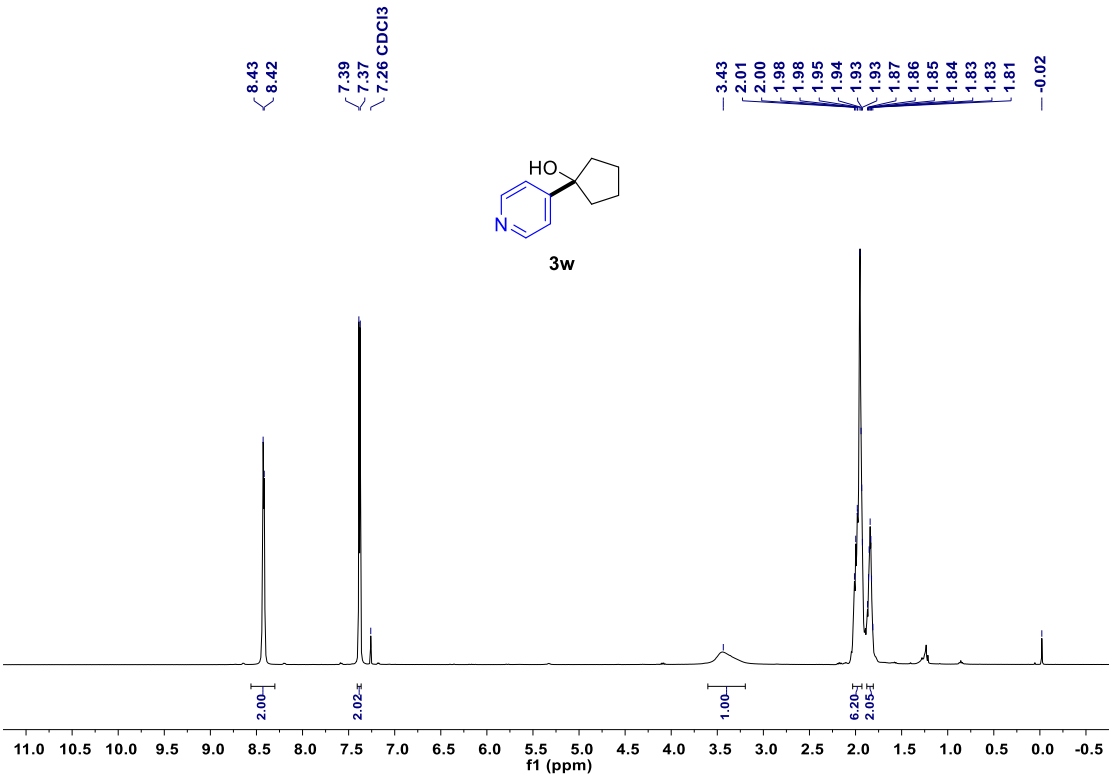


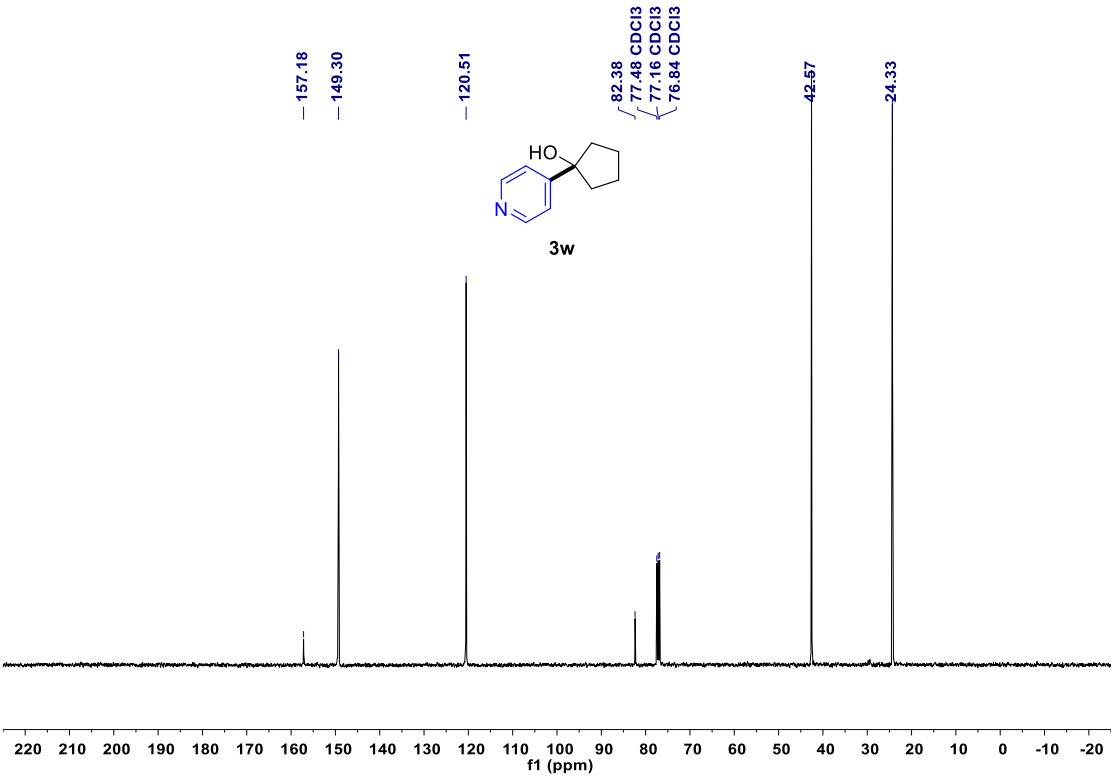
^{1}H and ^{13}C NMR spectra for compound **3u**



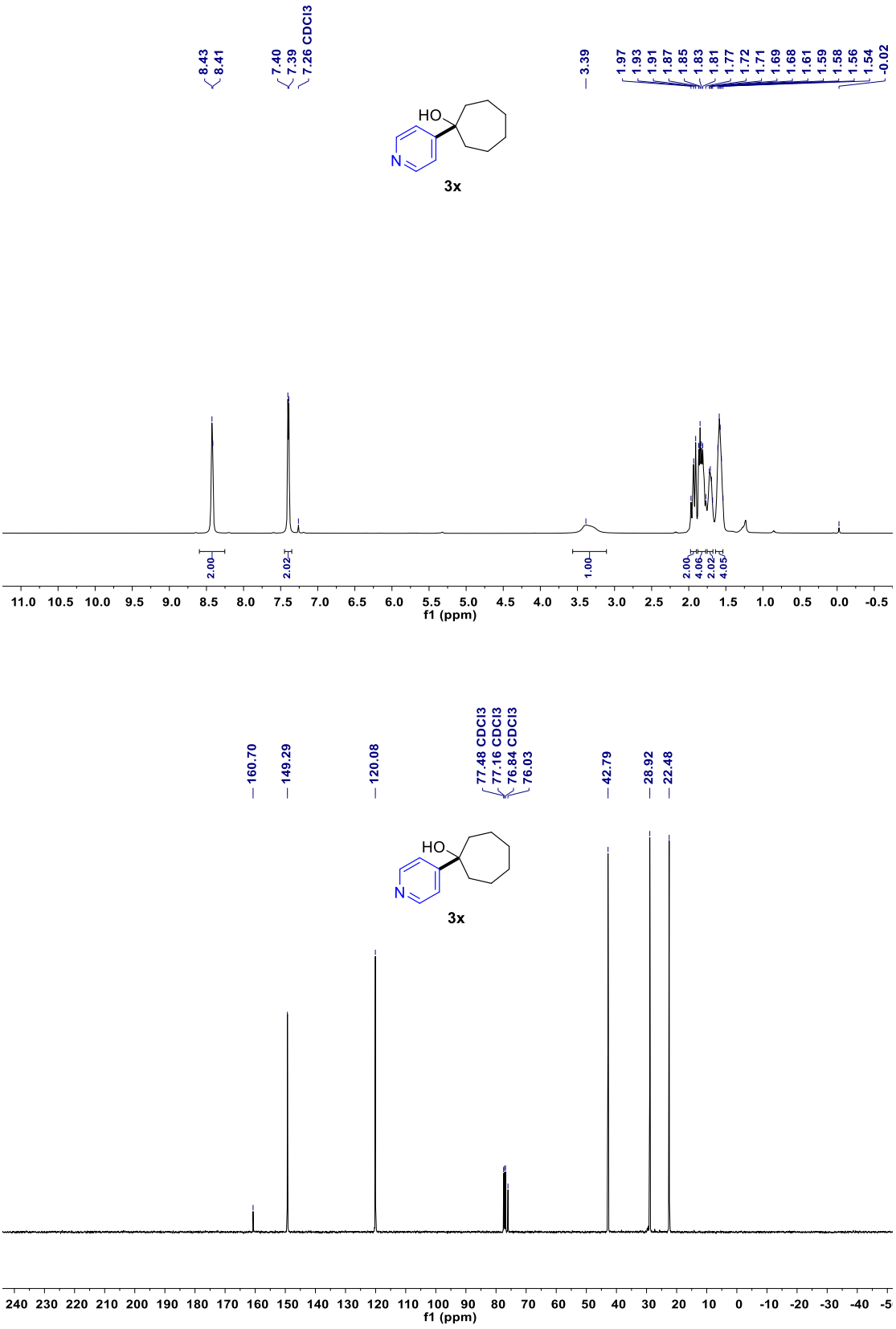


^{1}H and ^{13}C NMR spectra for compound **3v**

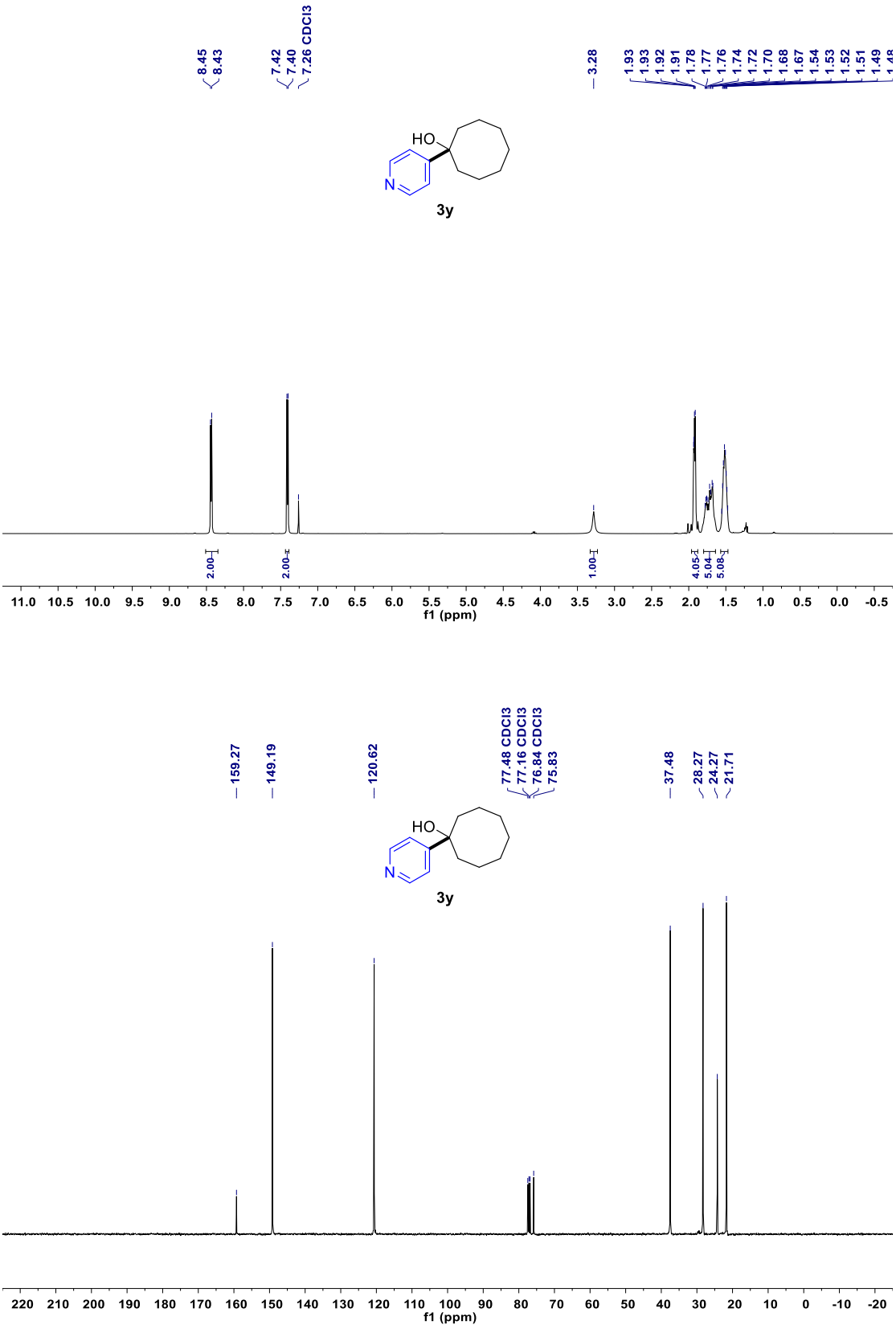




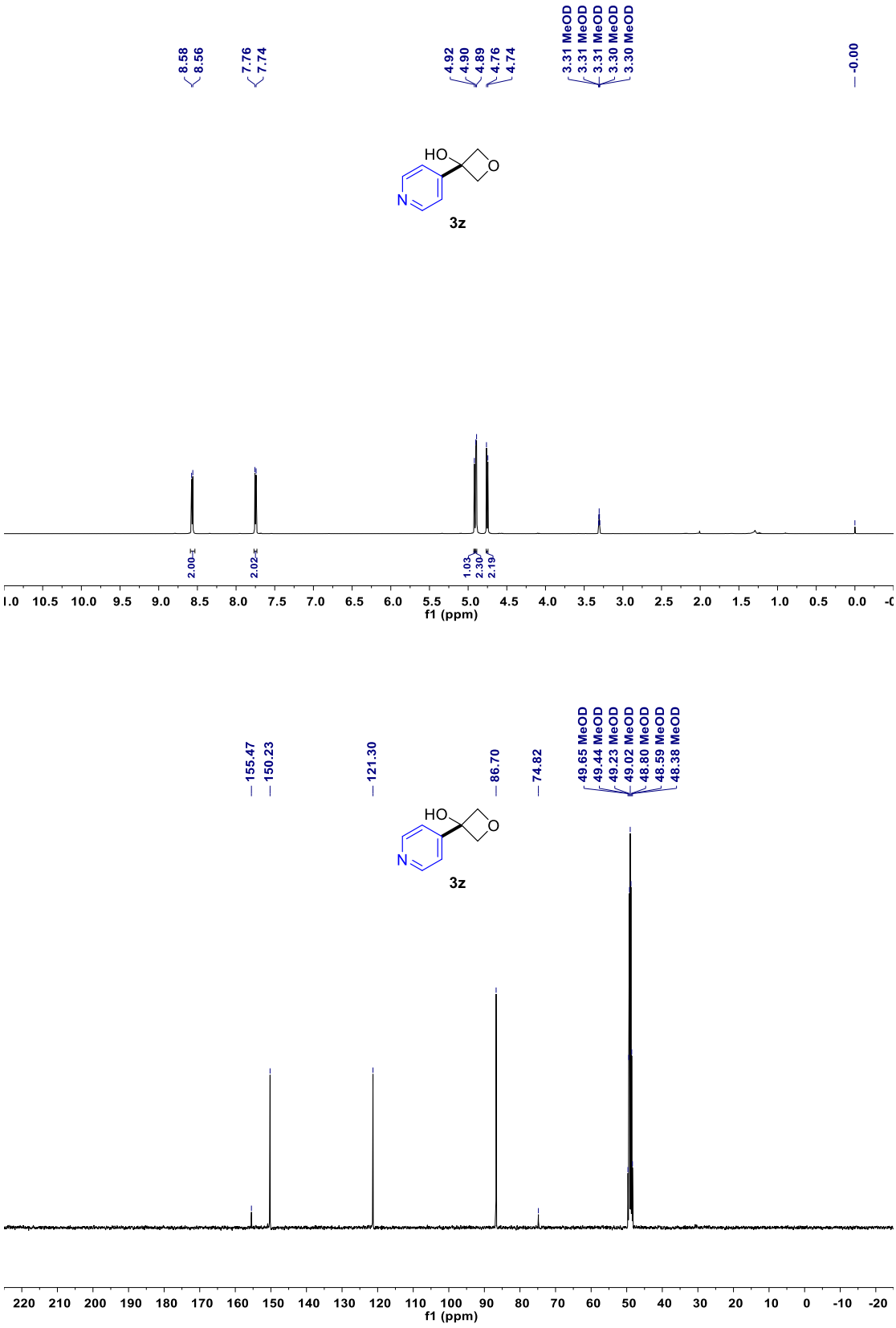
^{1}H and ^{13}C NMR spectra for compound **3w**



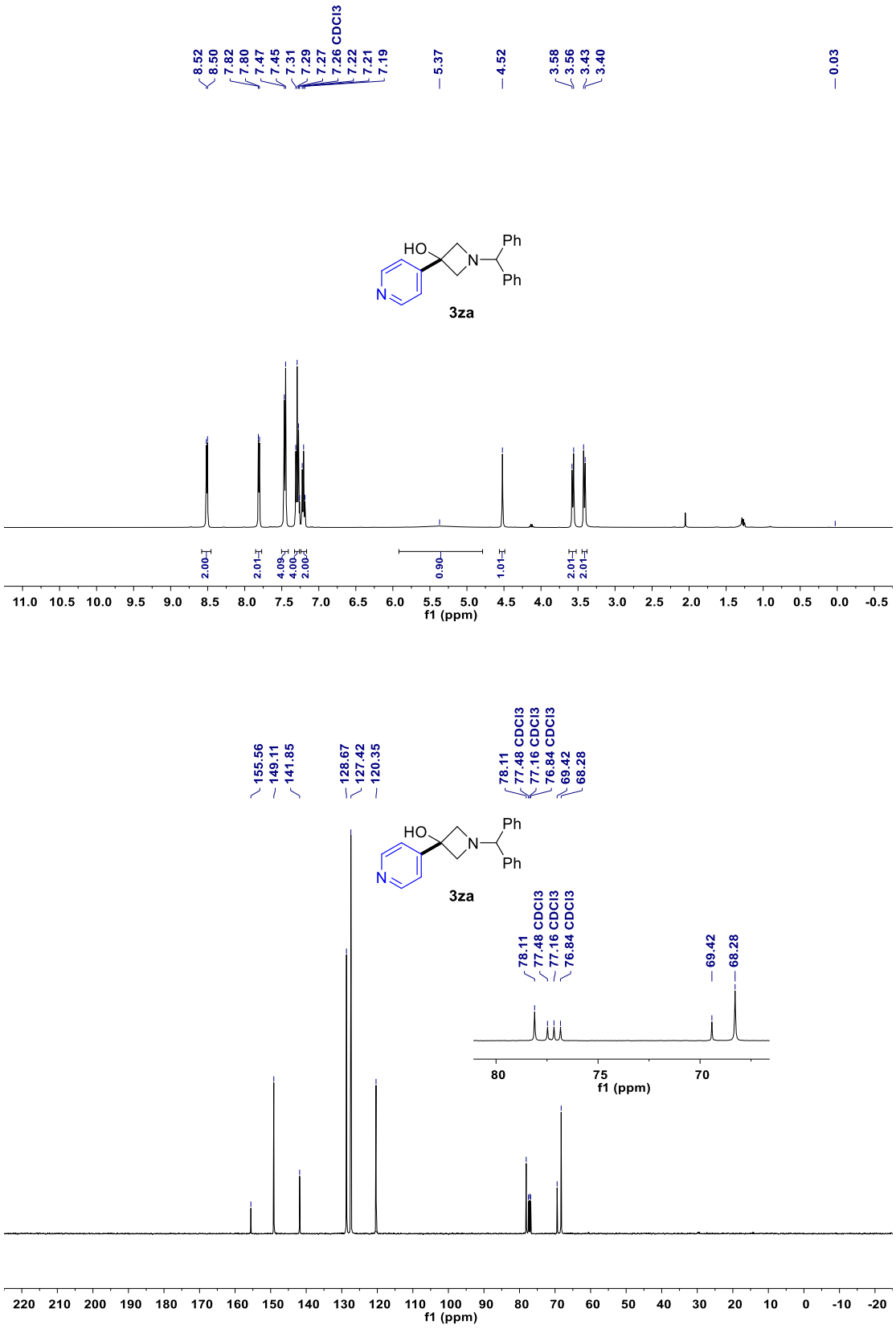
^{1}H and ^{13}C NMR spectra for compound **3x**



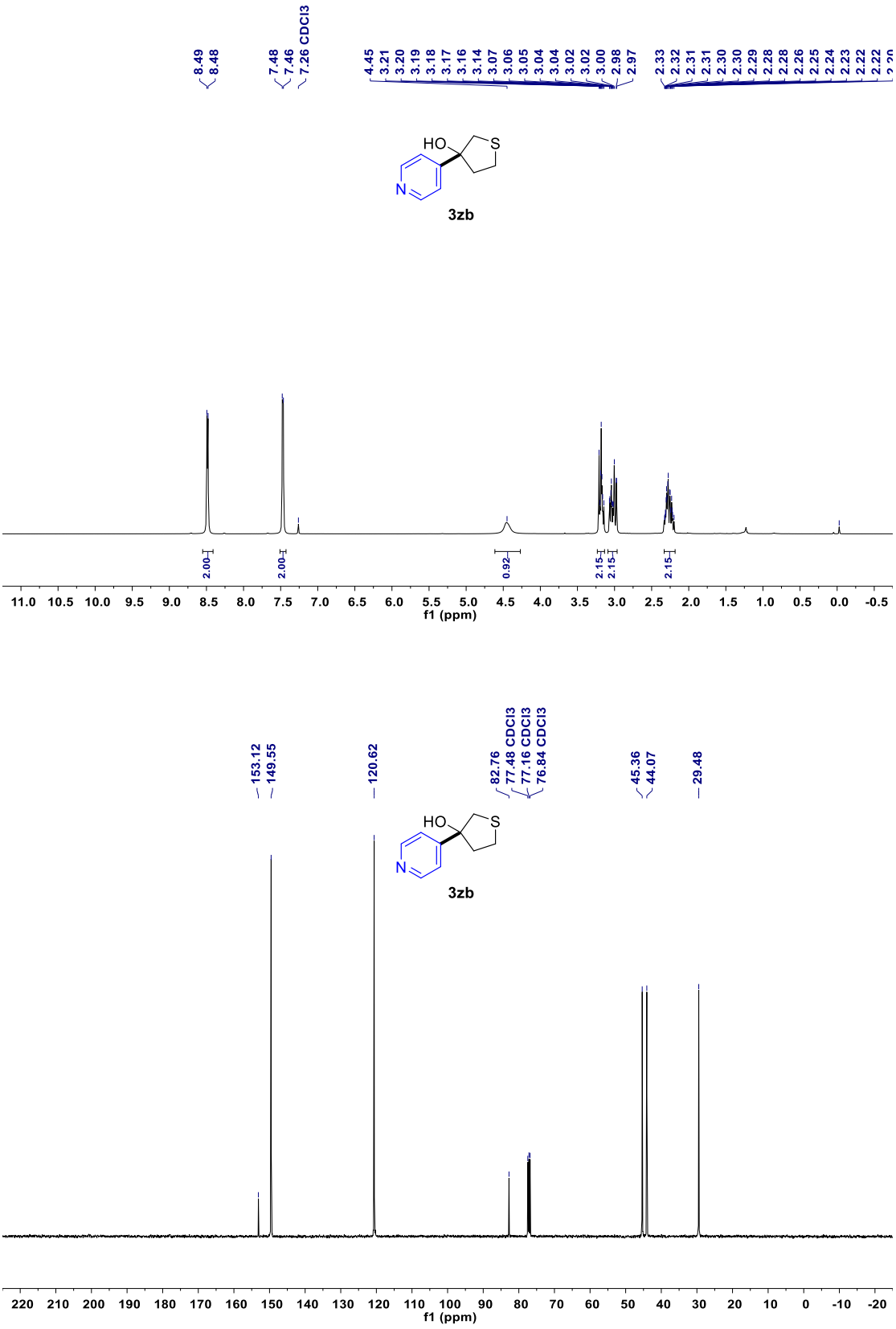
^{1}H and ^{13}C NMR spectra for compound **3y**



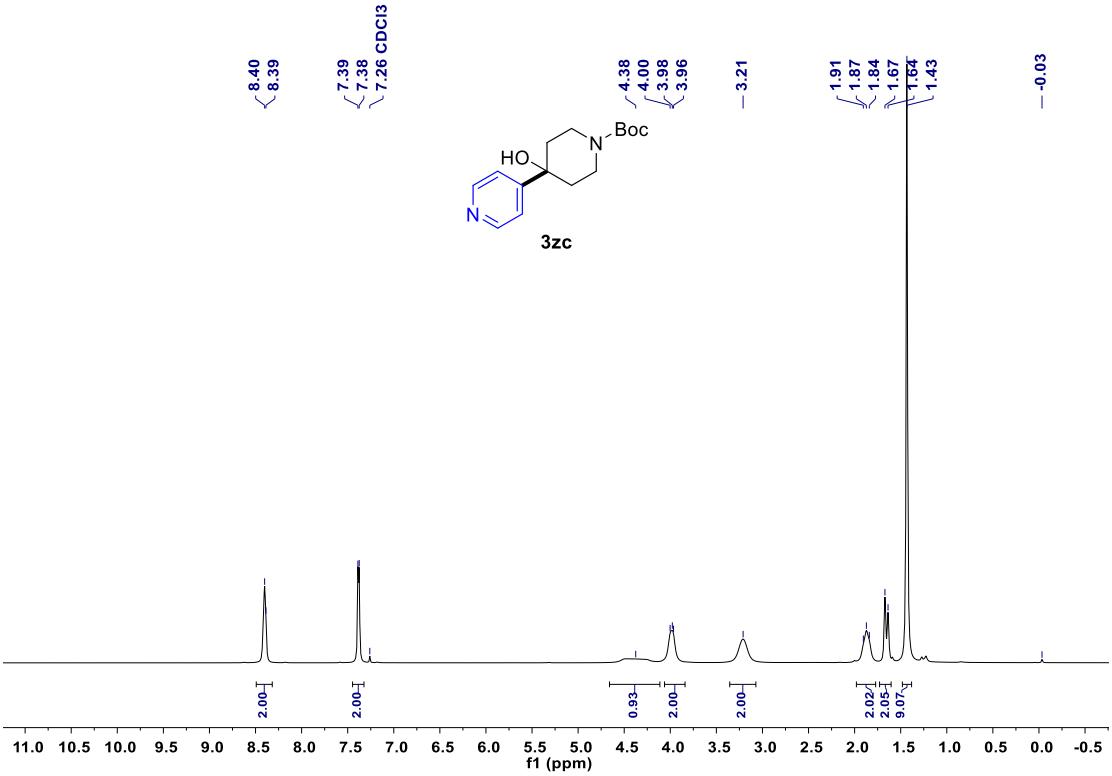
^{1}H and ^{13}C NMR spectra for compound 3z

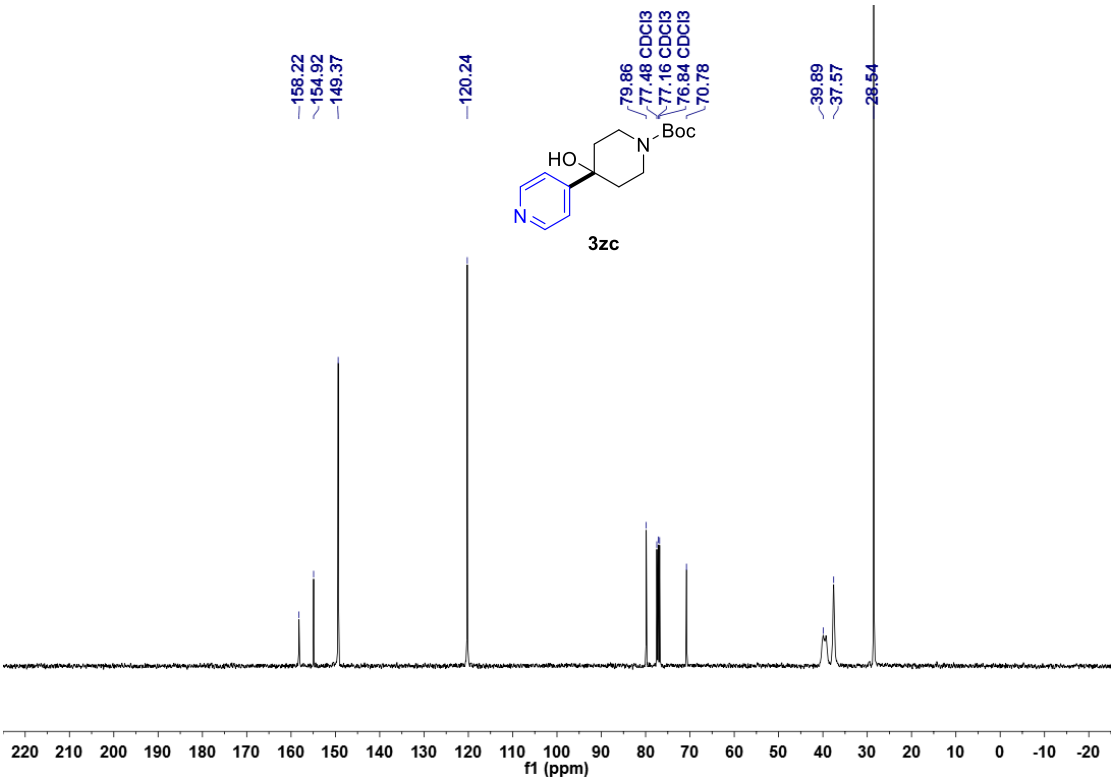


^{1}H and ^{13}C NMR spectra for compound 3za

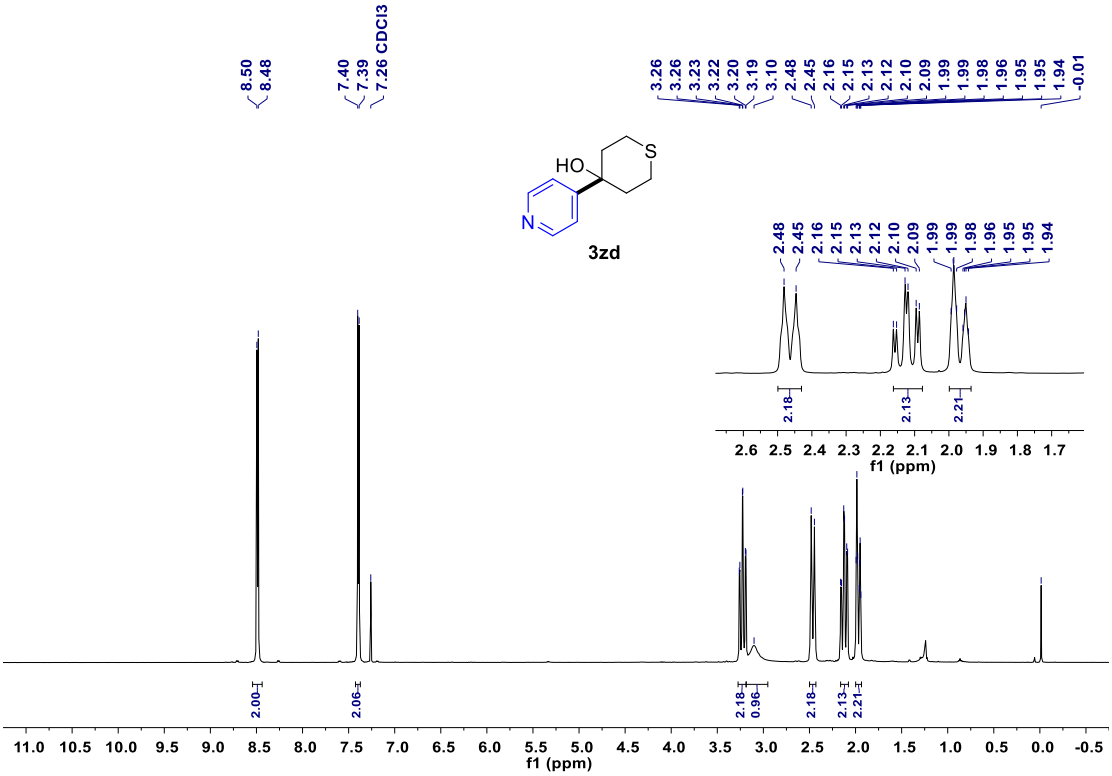


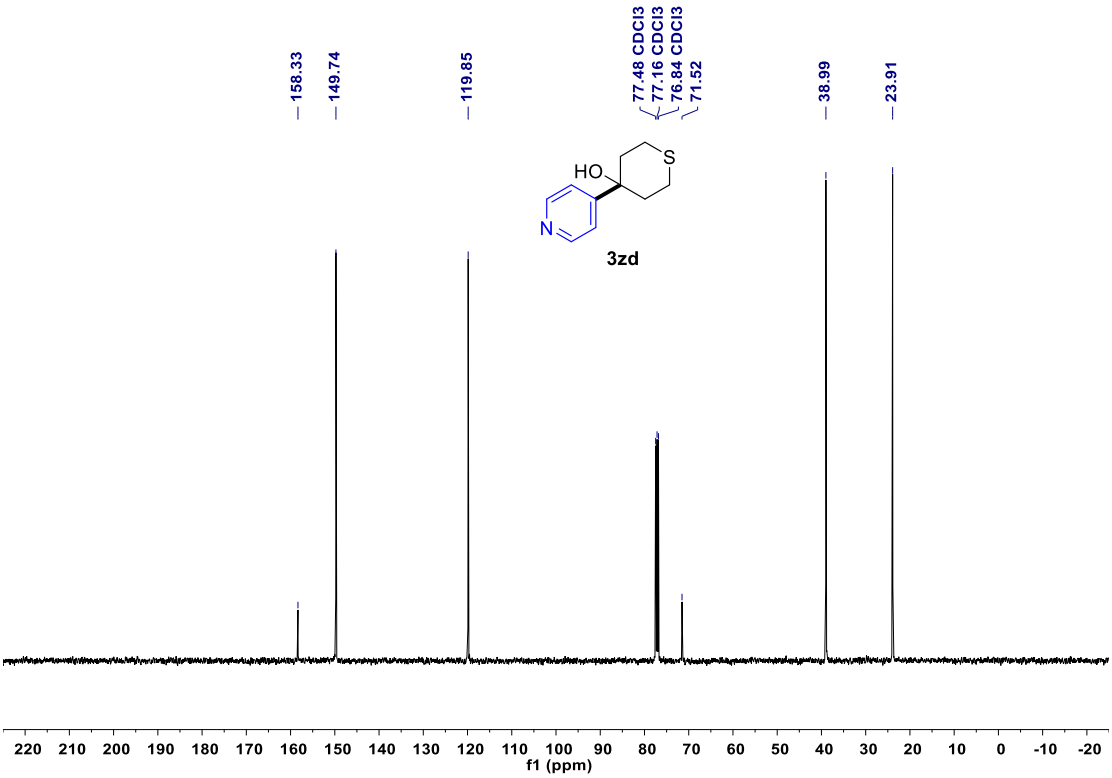
^{1}H and ^{13}C NMR spectra for compound 3zb



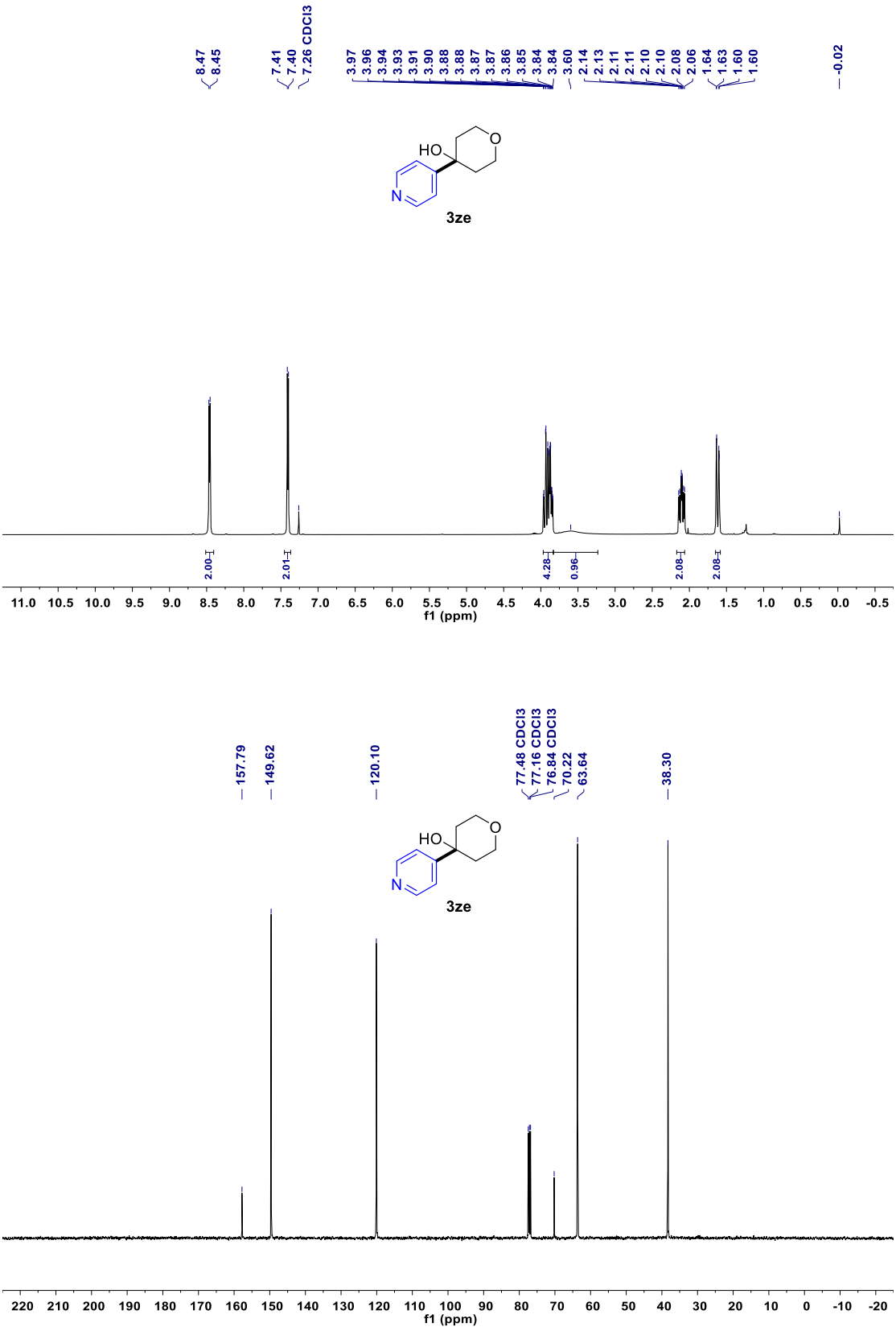


^{1}H and ^{13}C NMR spectra for compound **3zc**

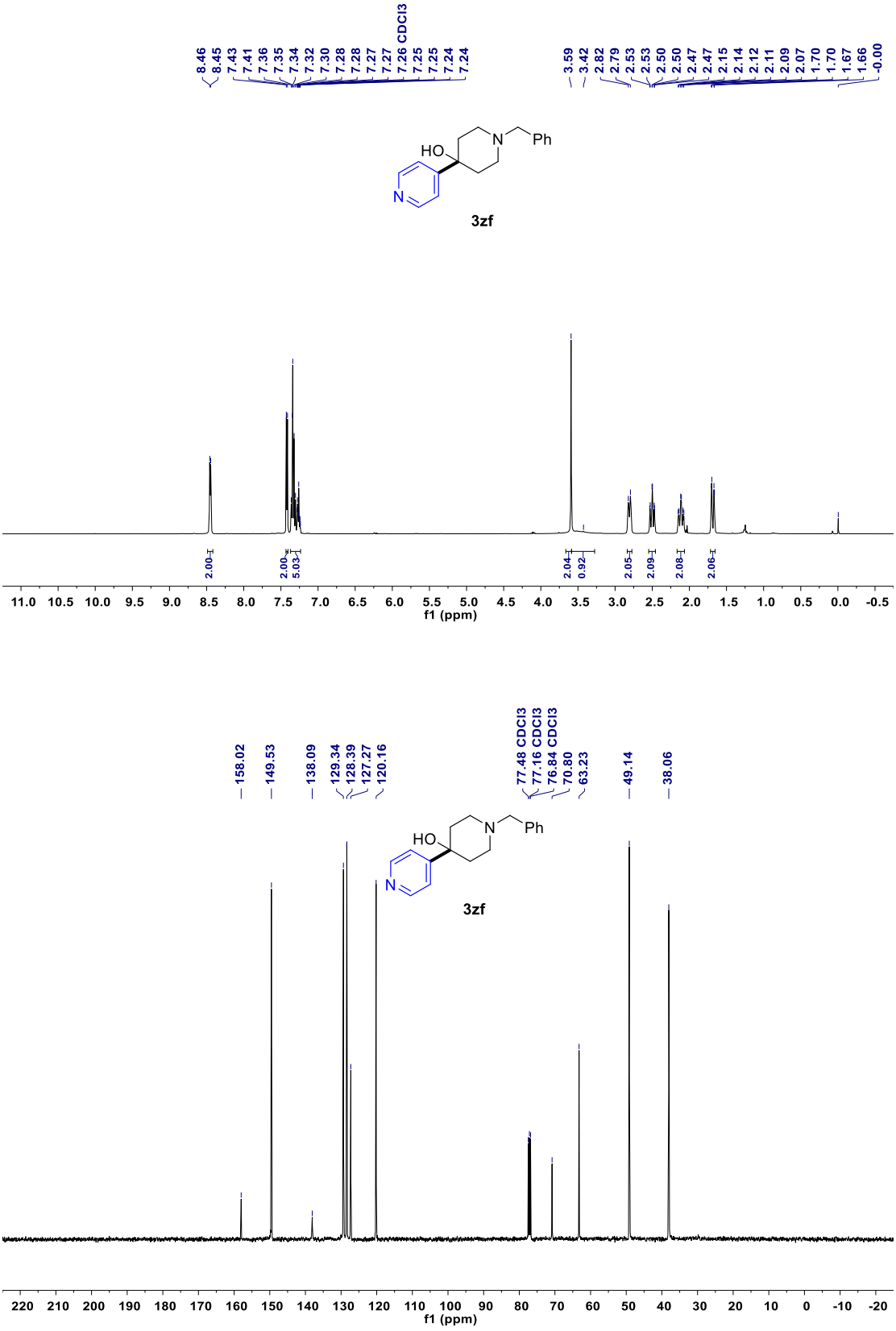




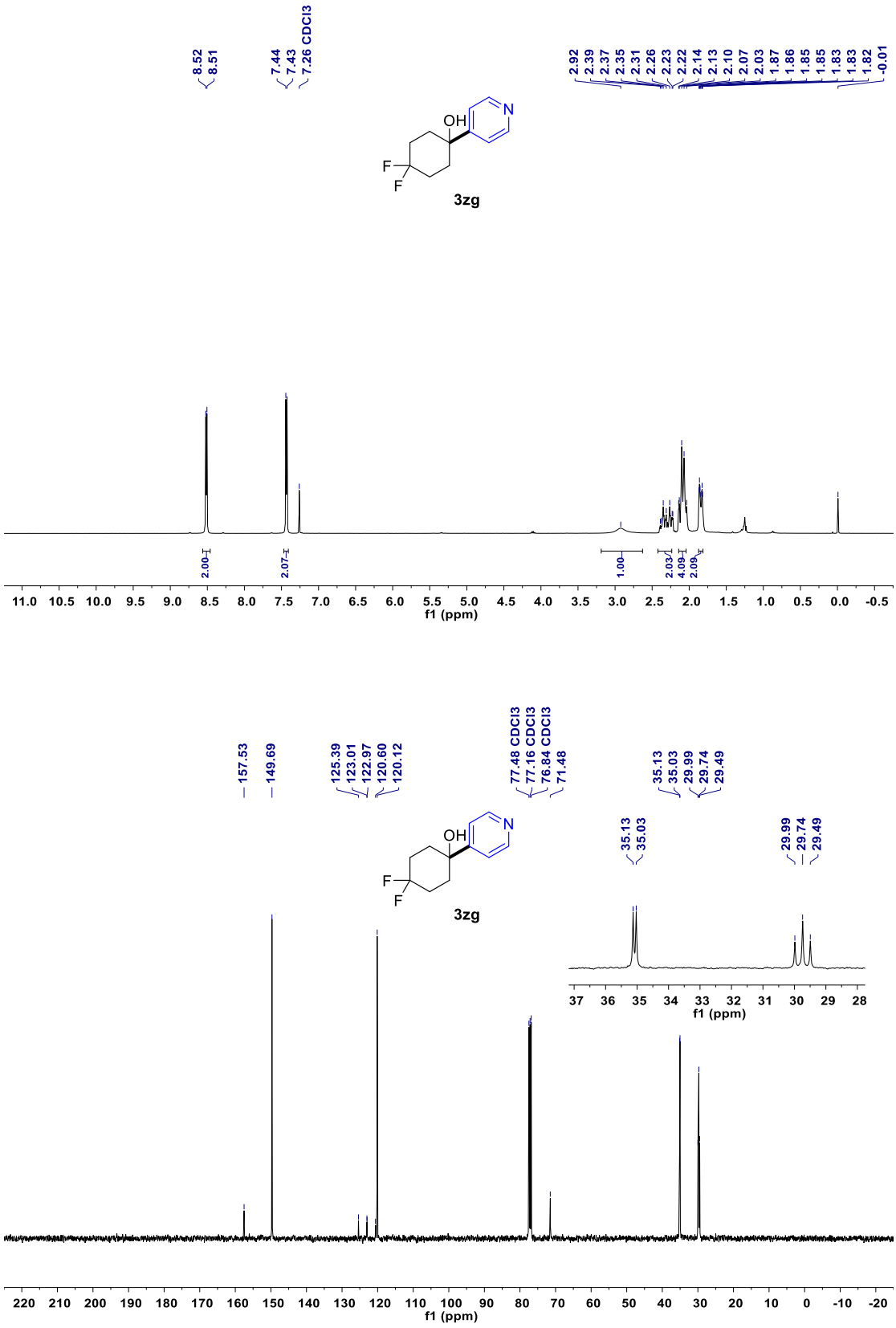
^{1}H and ^{13}C NMR spectra for compound 3zd



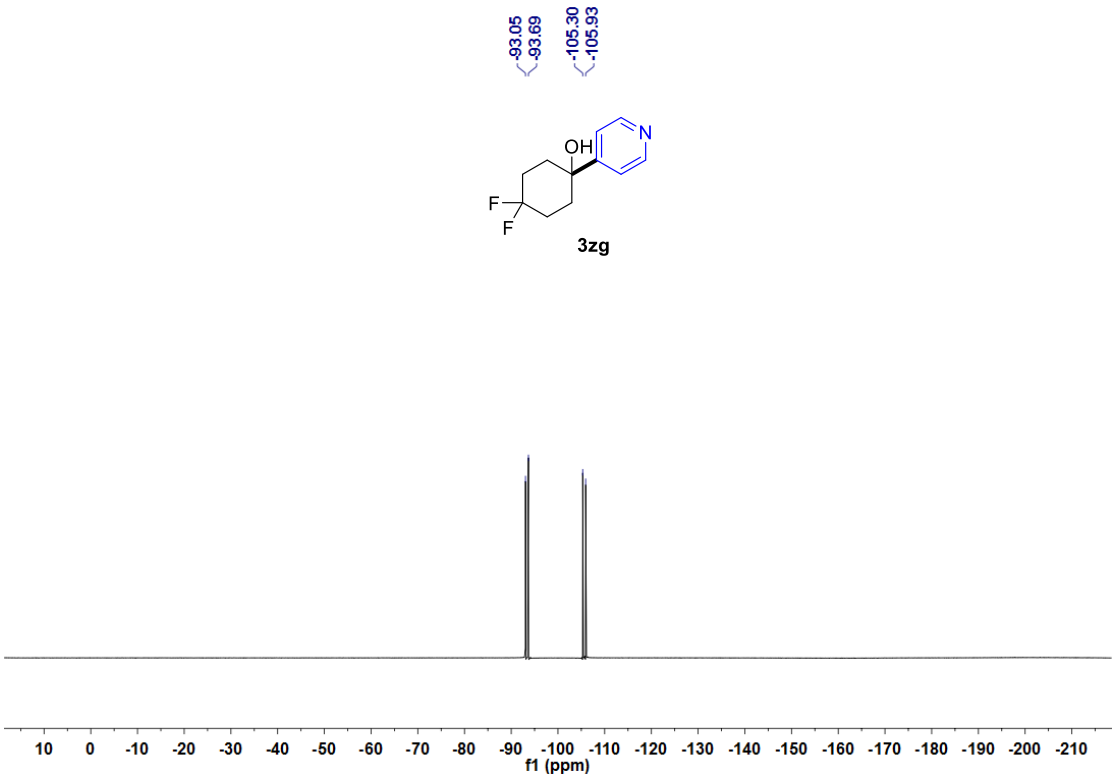
^{1}H and ^{13}C NMR spectra for compound 3ze



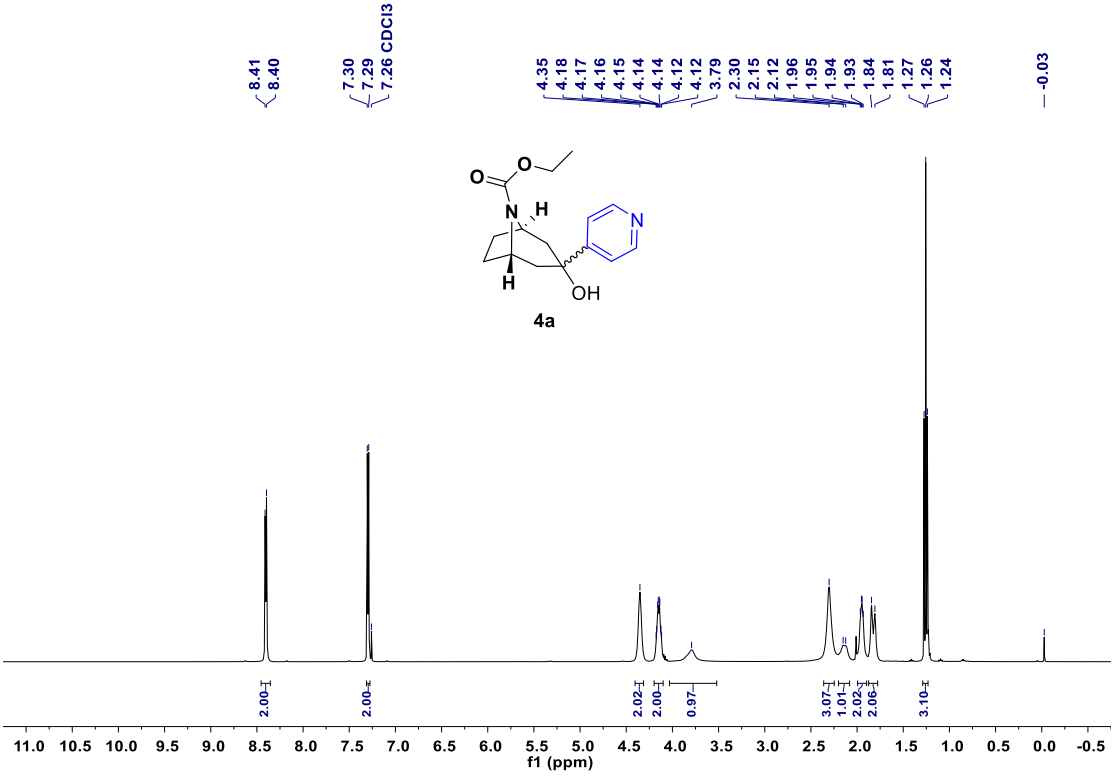
^{1}H and ^{13}C NMR spectra for compound 3zf

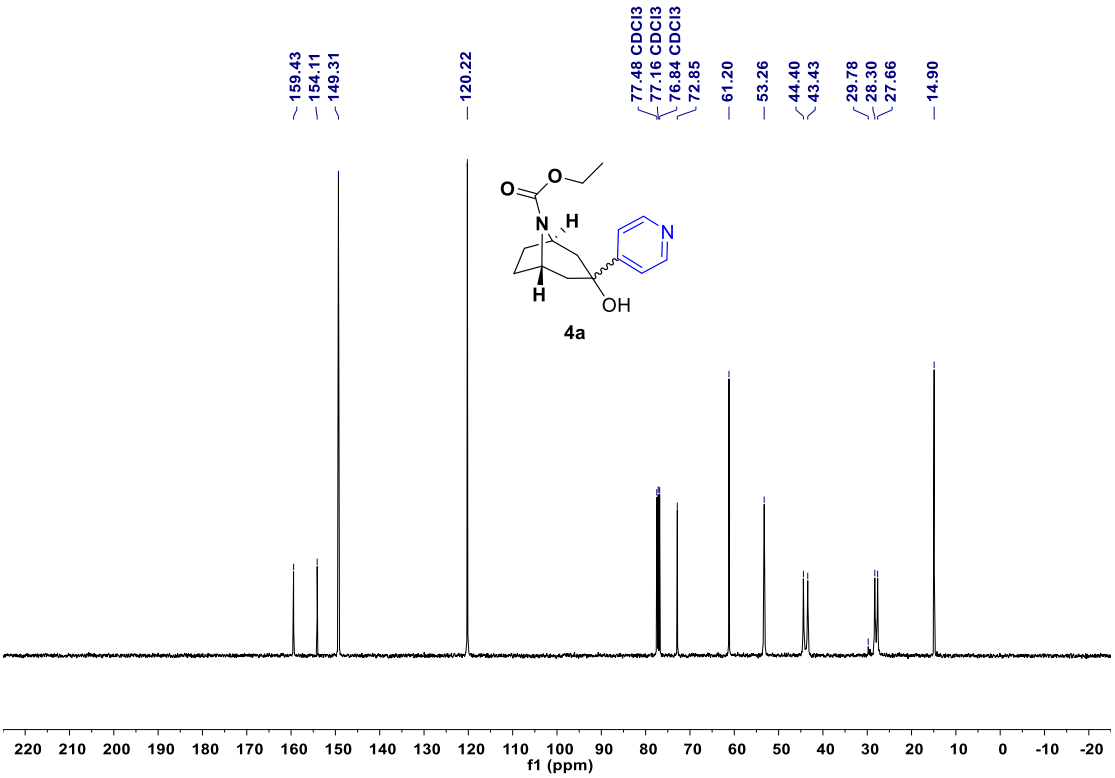


^{1}H and ^{13}C NMR spectra for compound 3zg

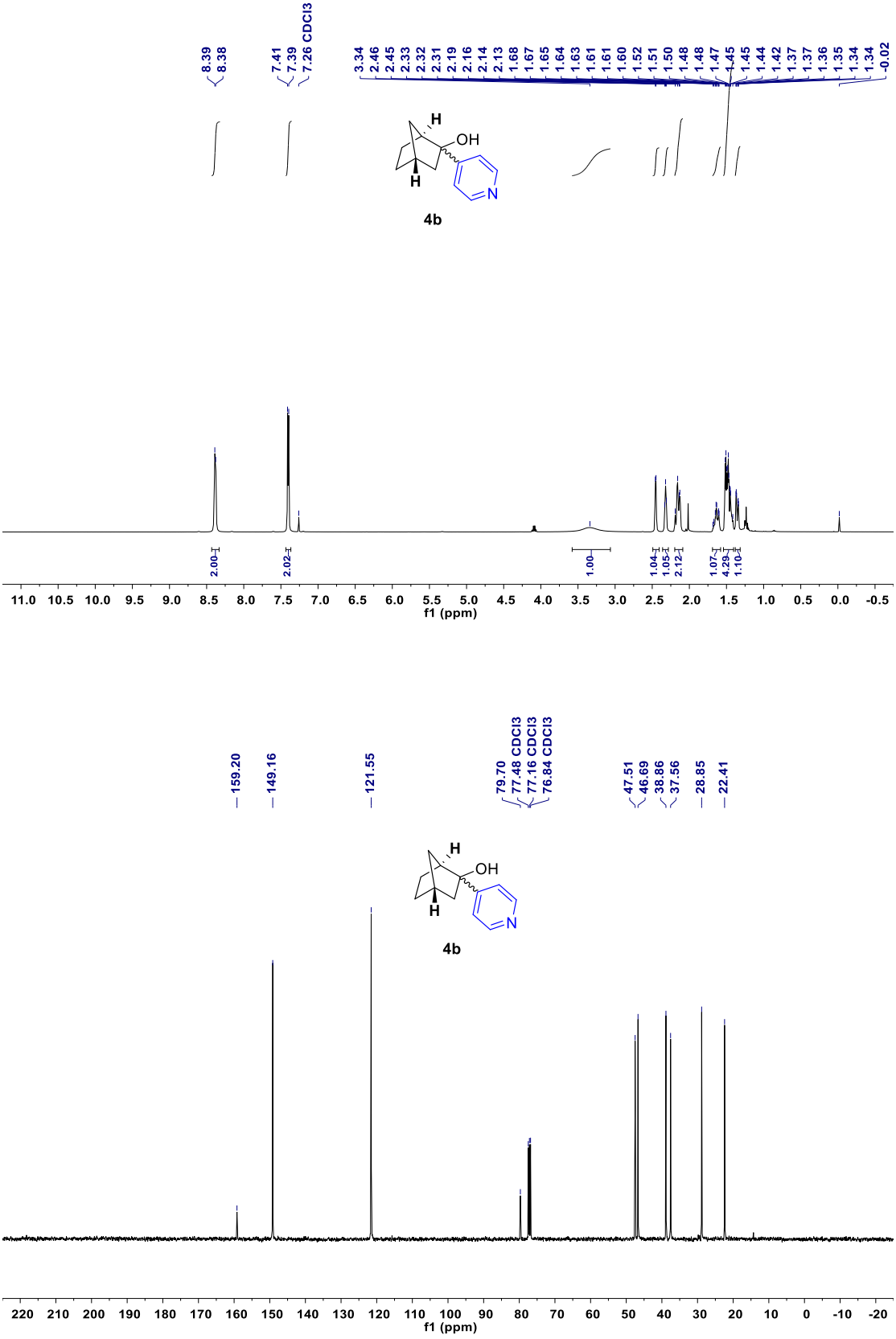


^{19}F NMR spectra for compound 3zg

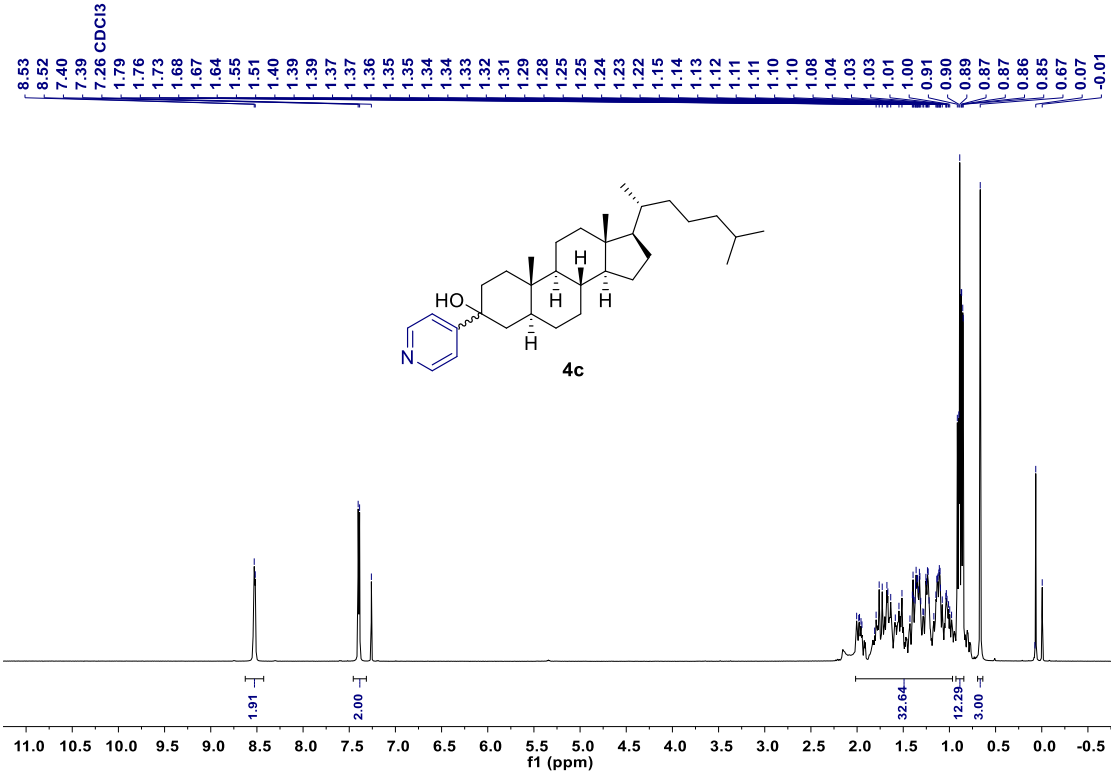


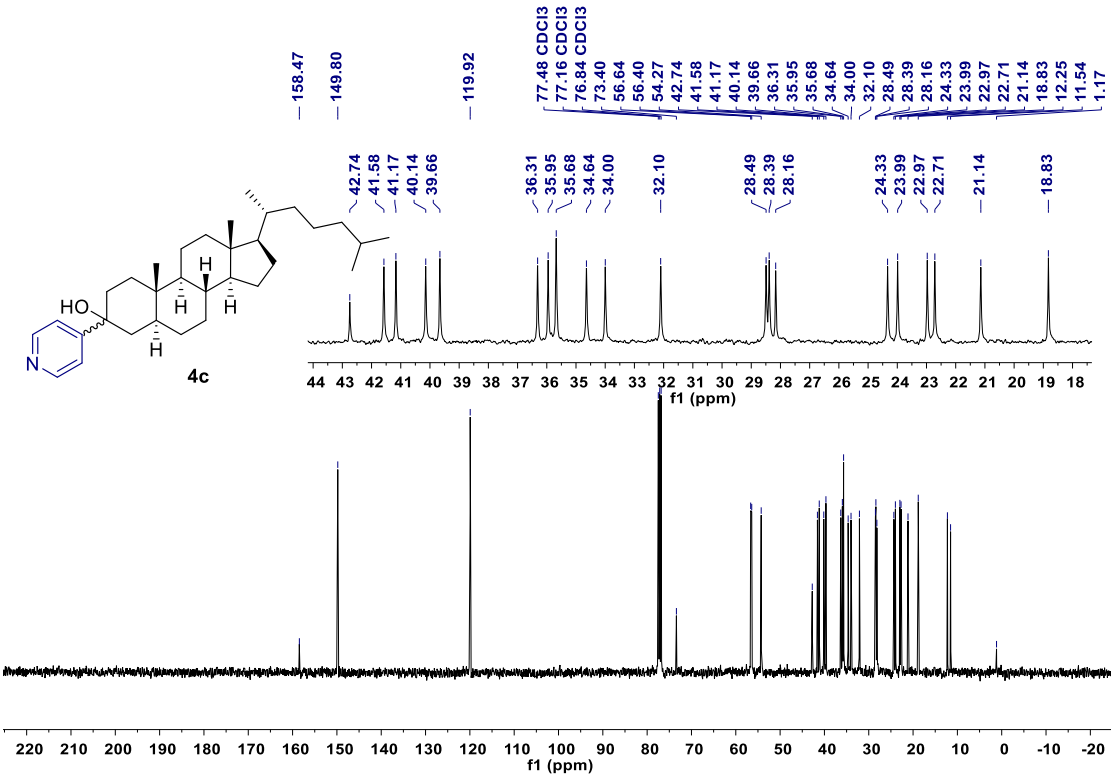


^{1}H and ^{13}C NMR spectra for compound 4a

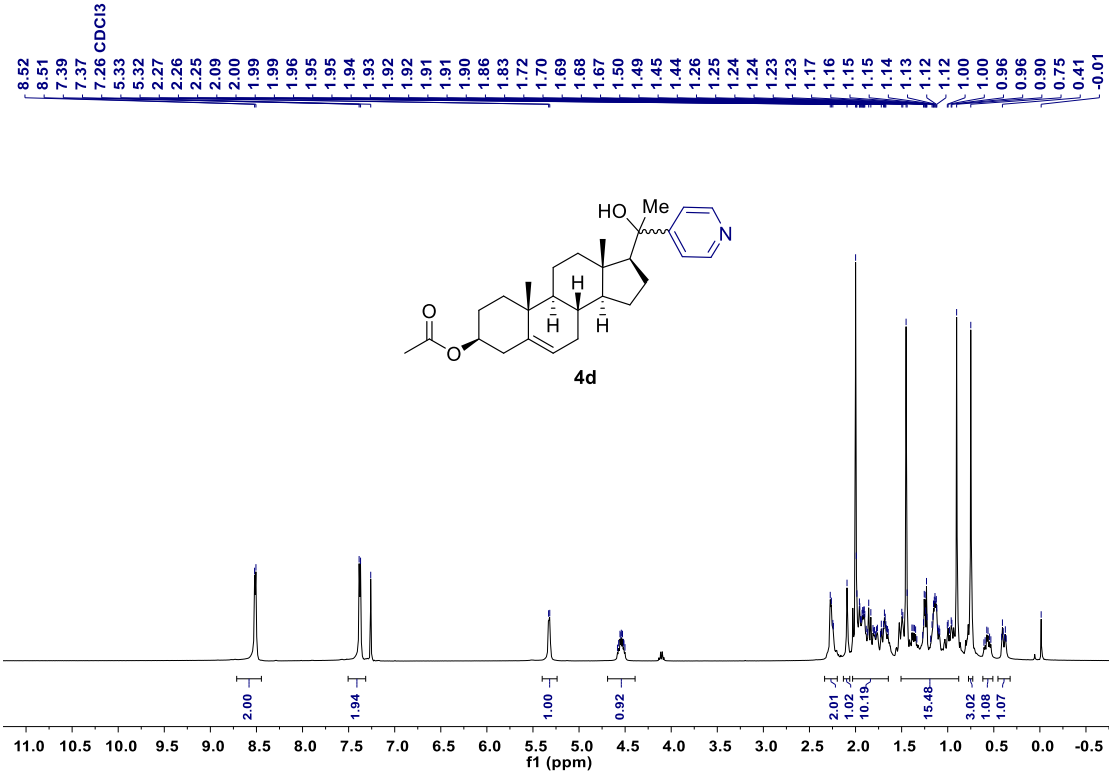


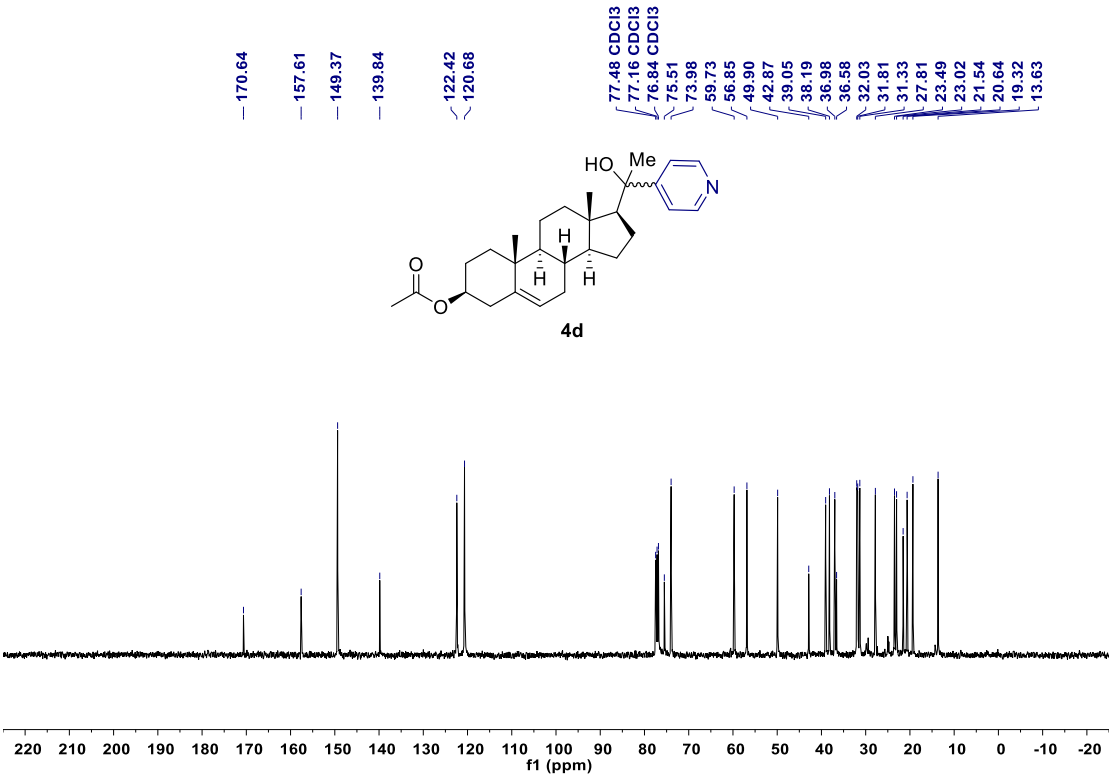
^{1}H and ^{13}C NMR spectra for compound 4b



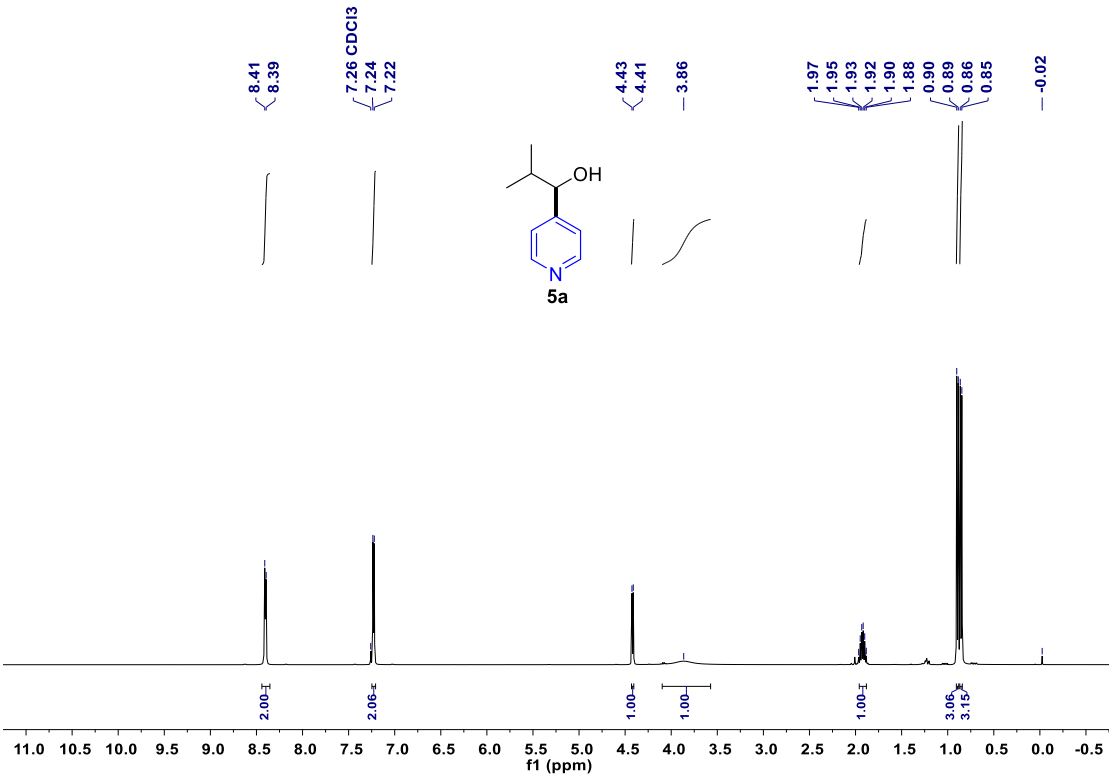


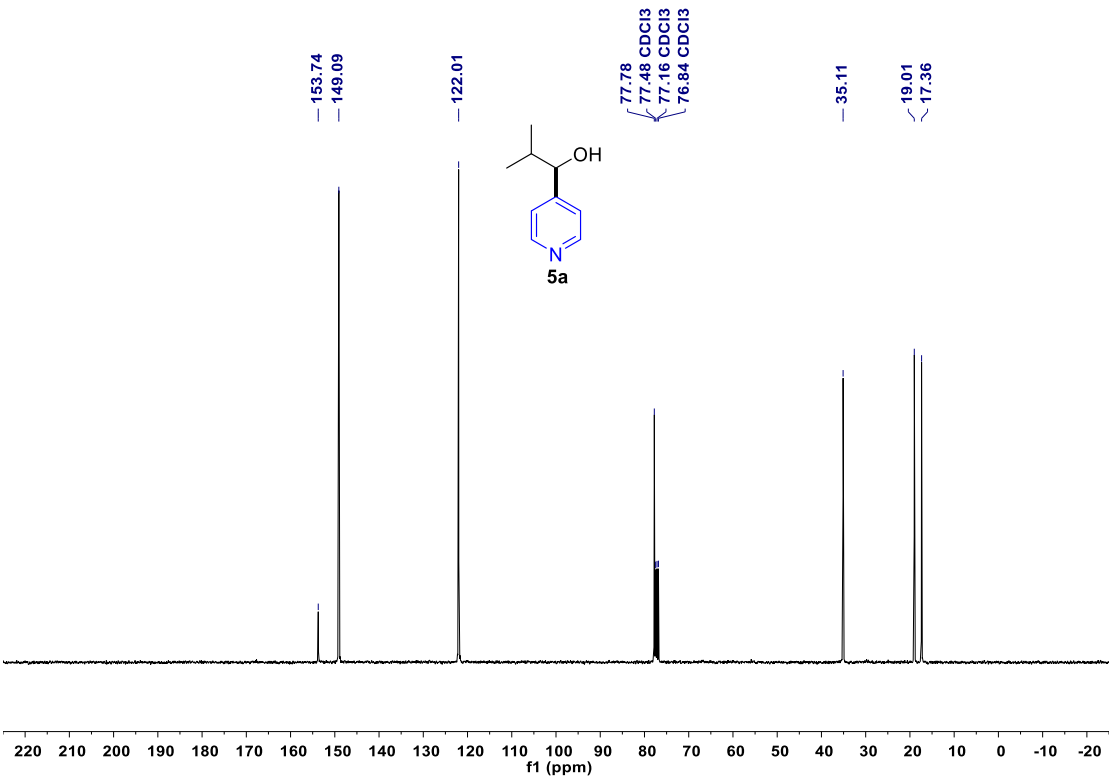
^{1}H and ^{13}C NMR spectra for compound 4c



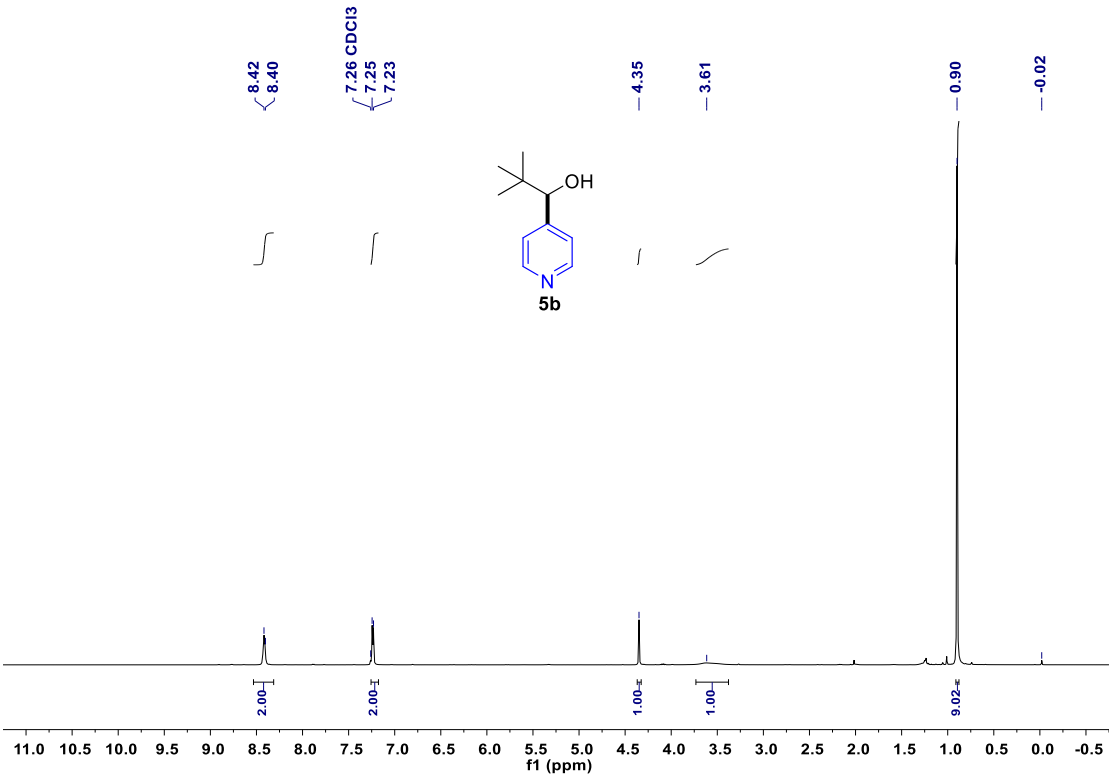


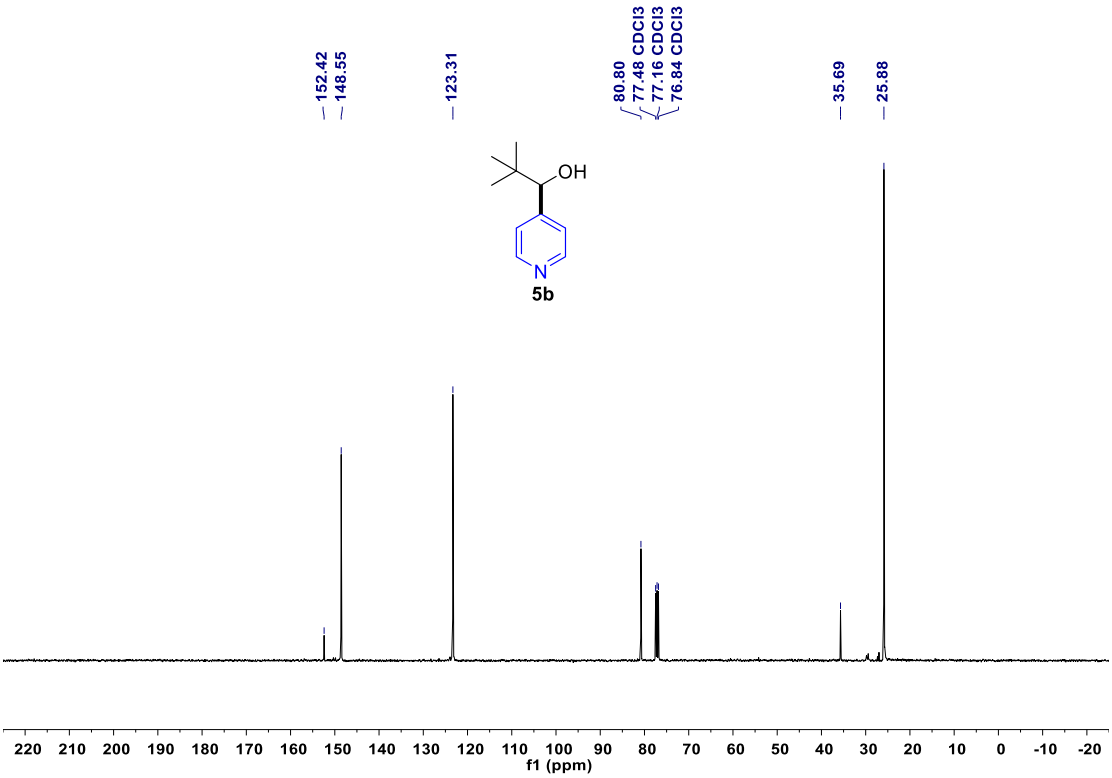
^{1}H and ^{13}C NMR spectra for compound 4d



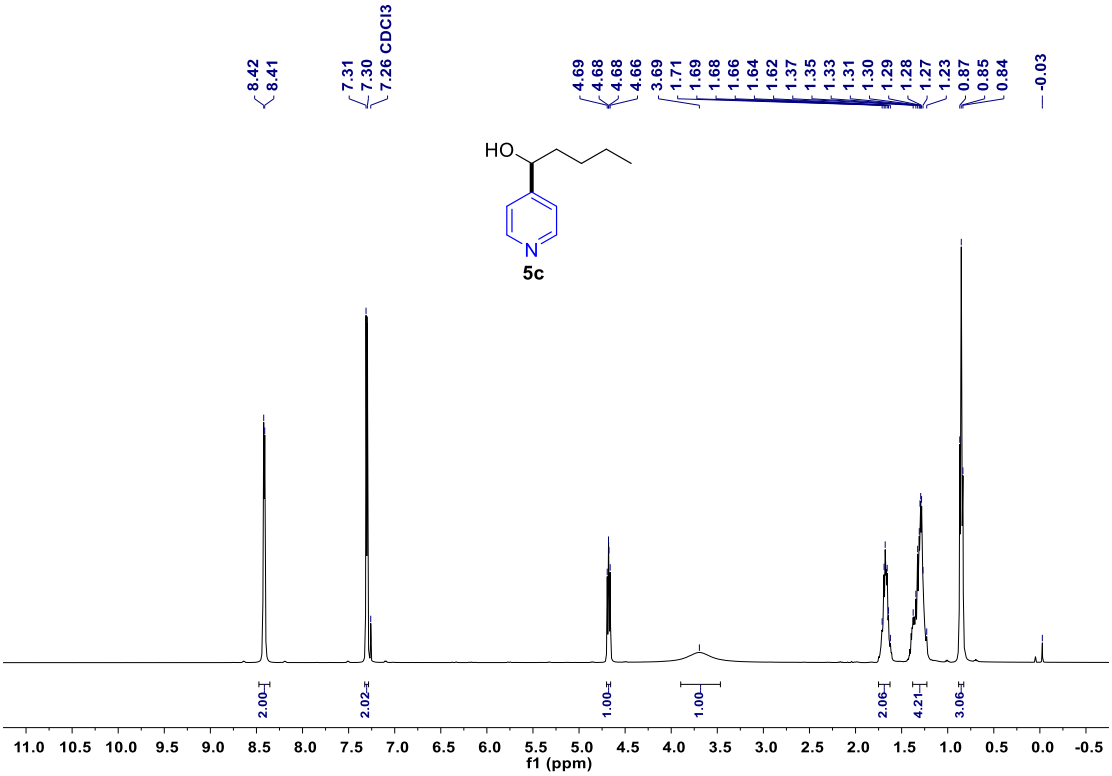


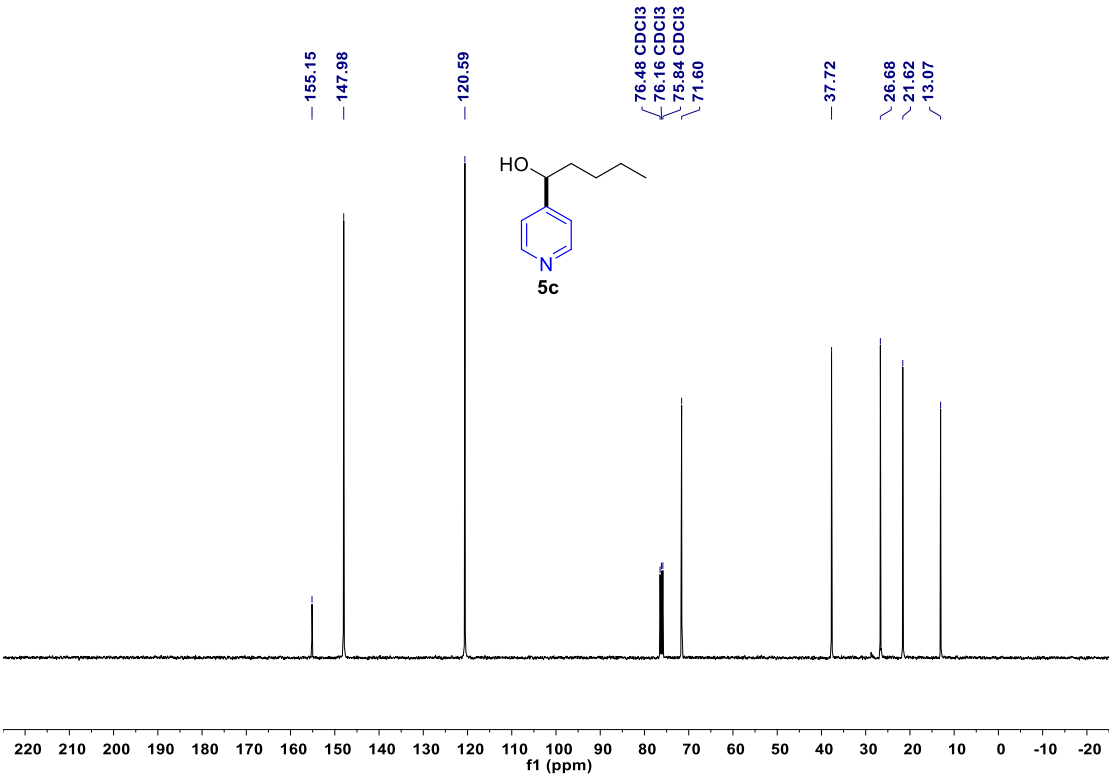
^{1}H and ^{13}C NMR spectra for compound 5a



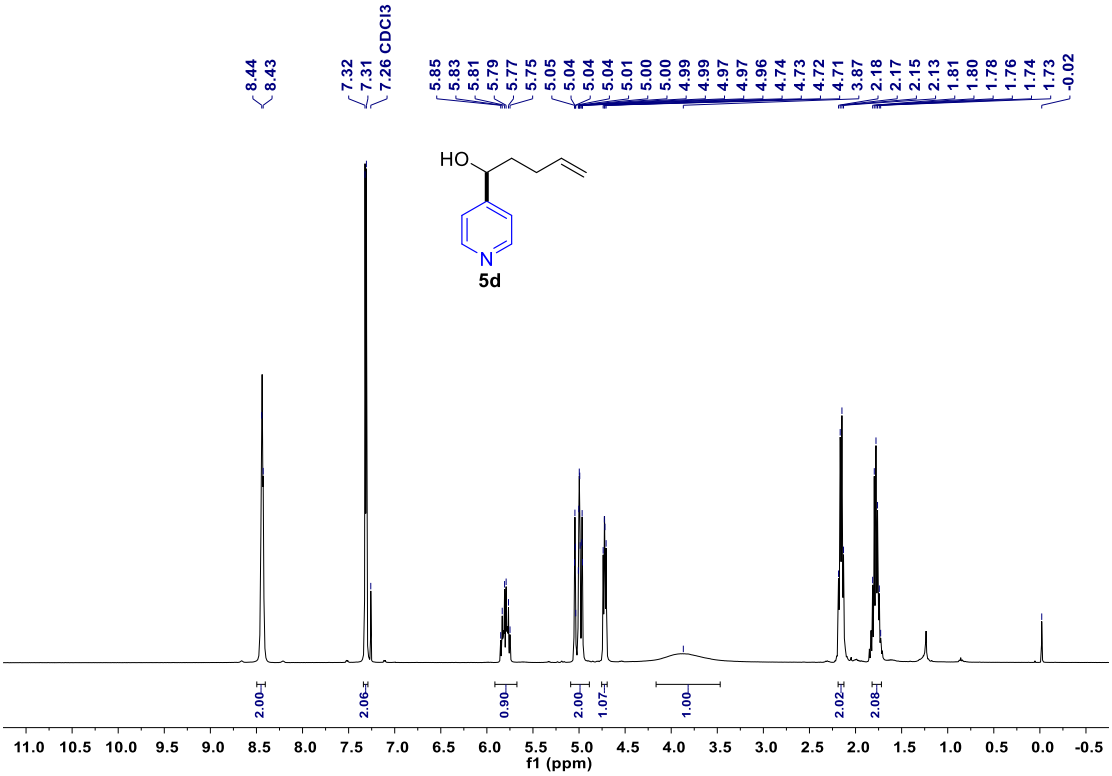


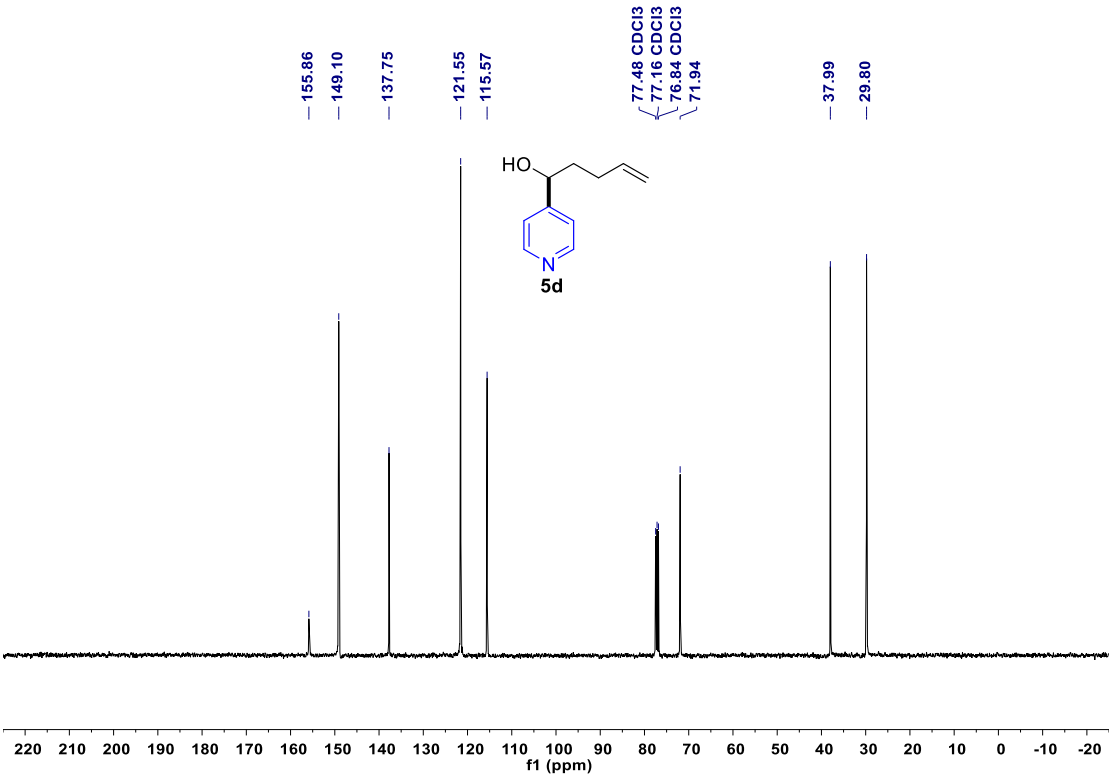
^{1}H and ^{13}C NMR spectra for compound 5b



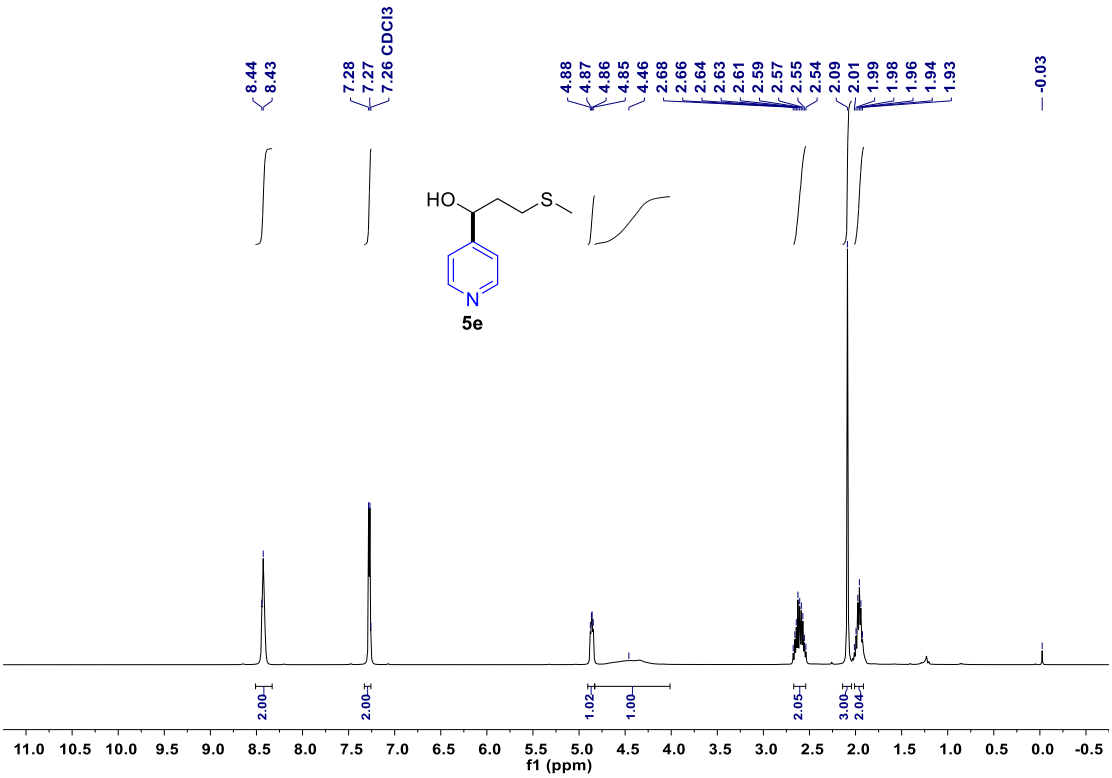


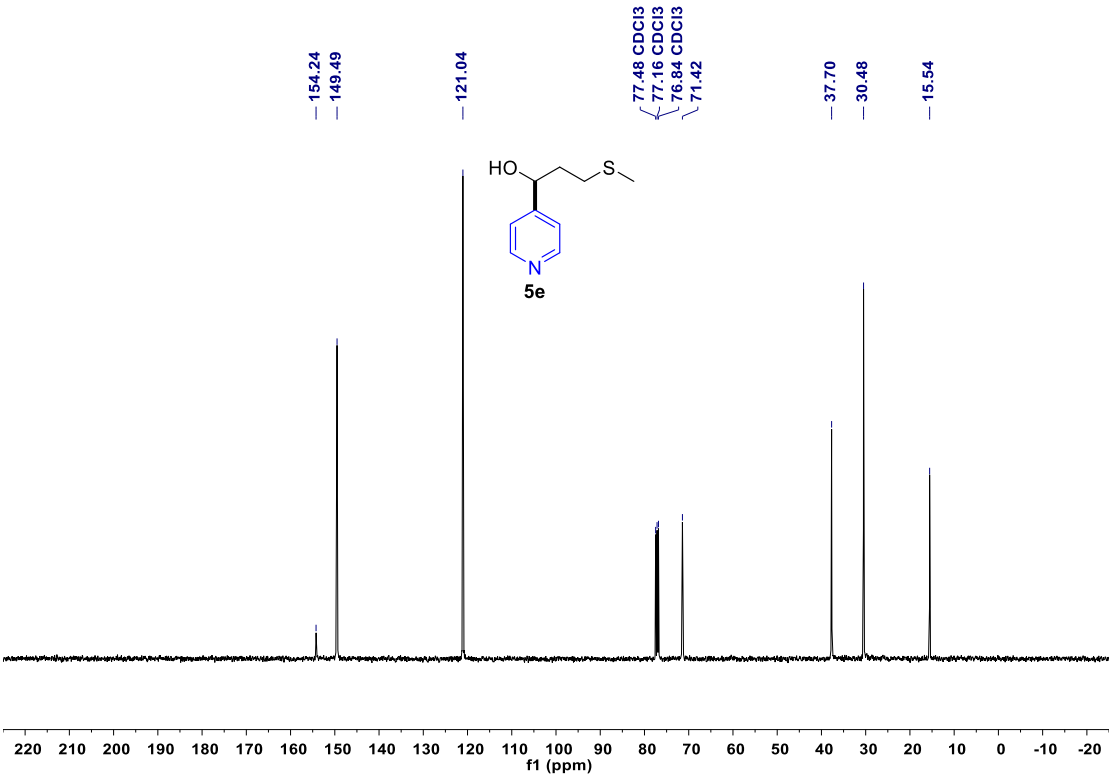
^{1}H and ^{13}C NMR spectra for compound 5c



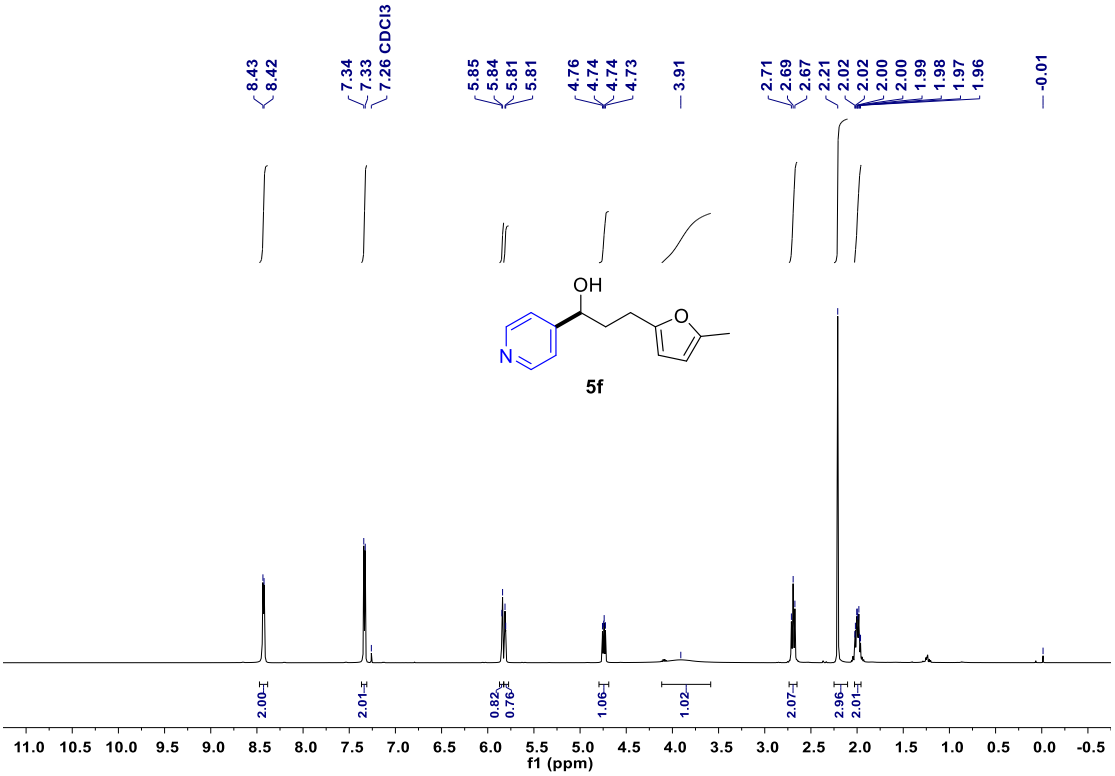


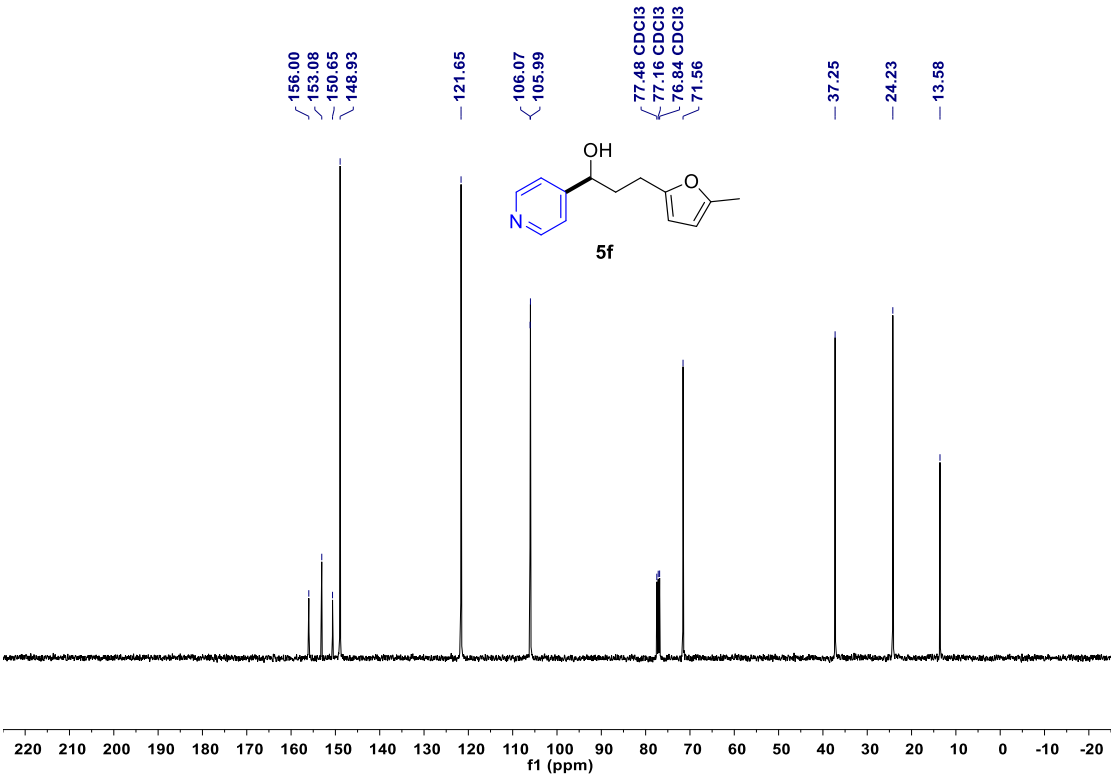
^{1}H and ^{13}C NMR spectra for compound 5d



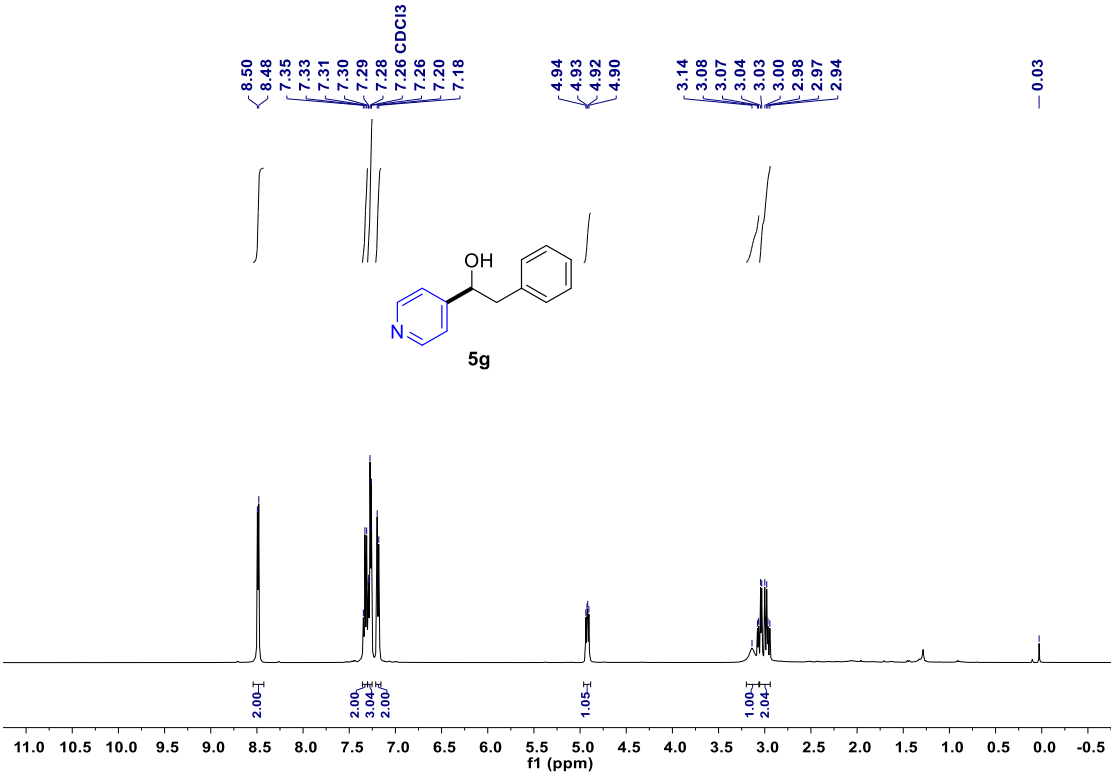


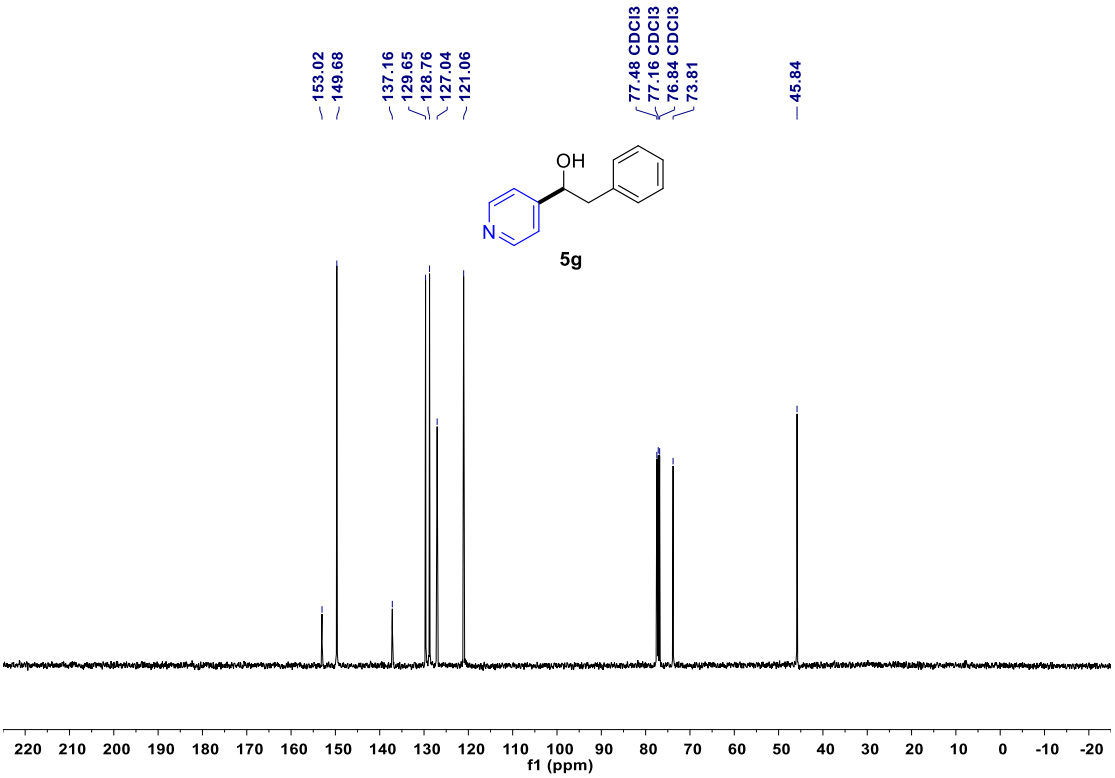
^{1}H and ^{13}C NMR spectra for compound 5e



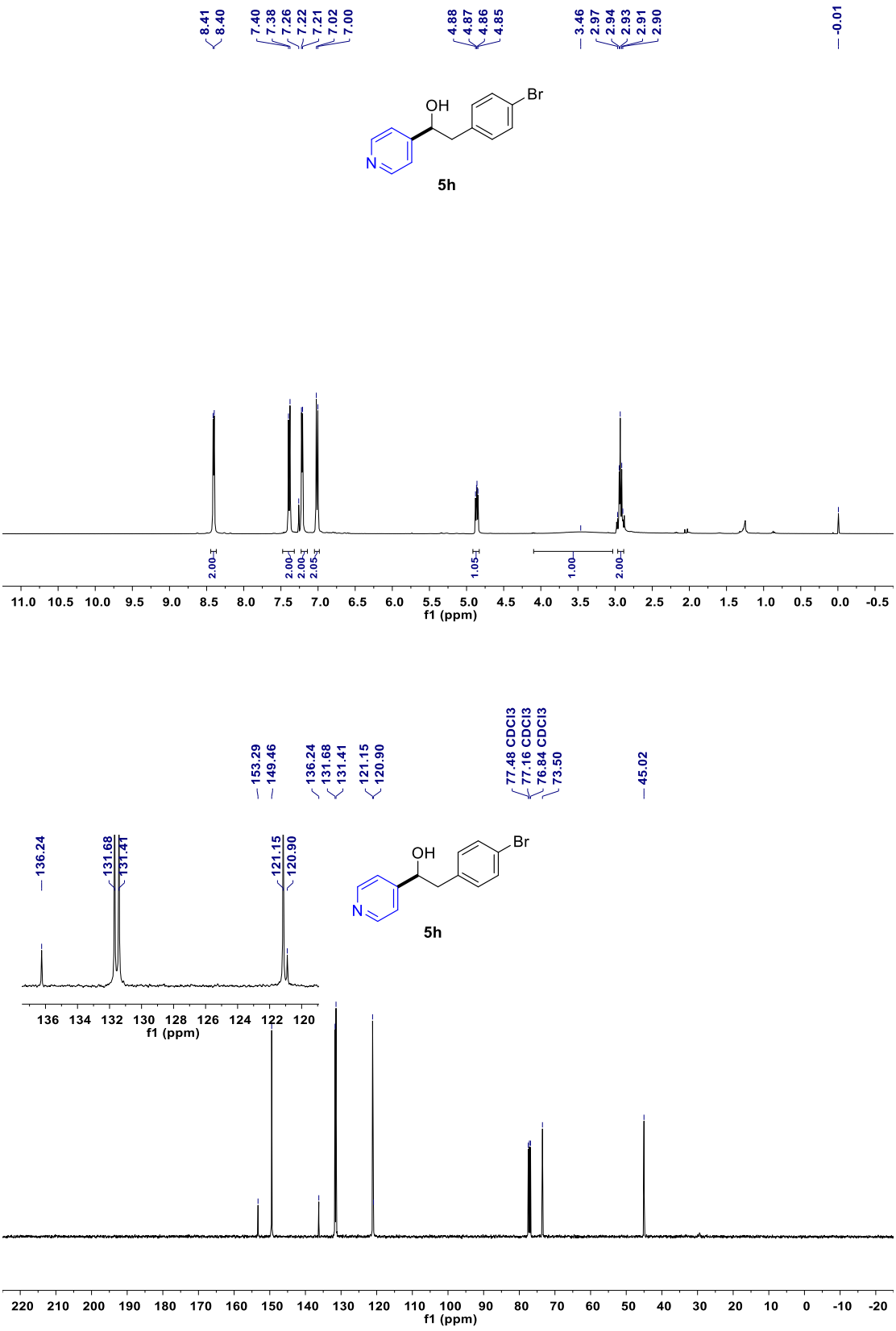


^{1}H and ^{13}C NMR spectra for compound 5f

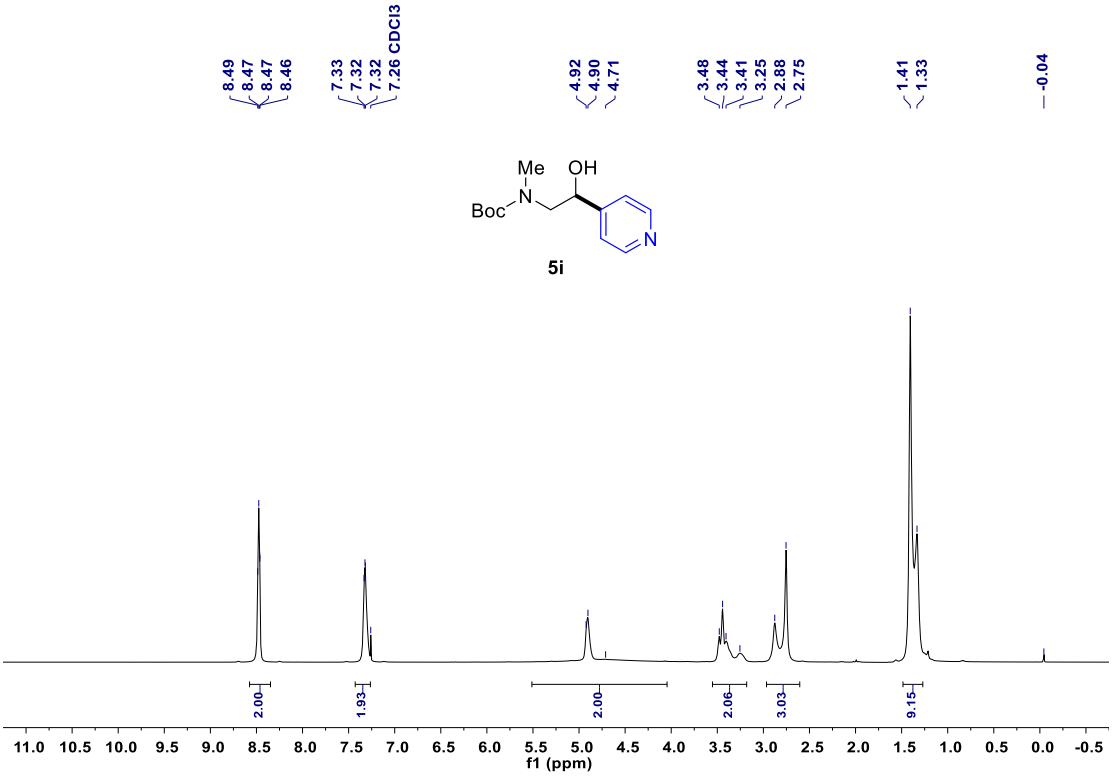


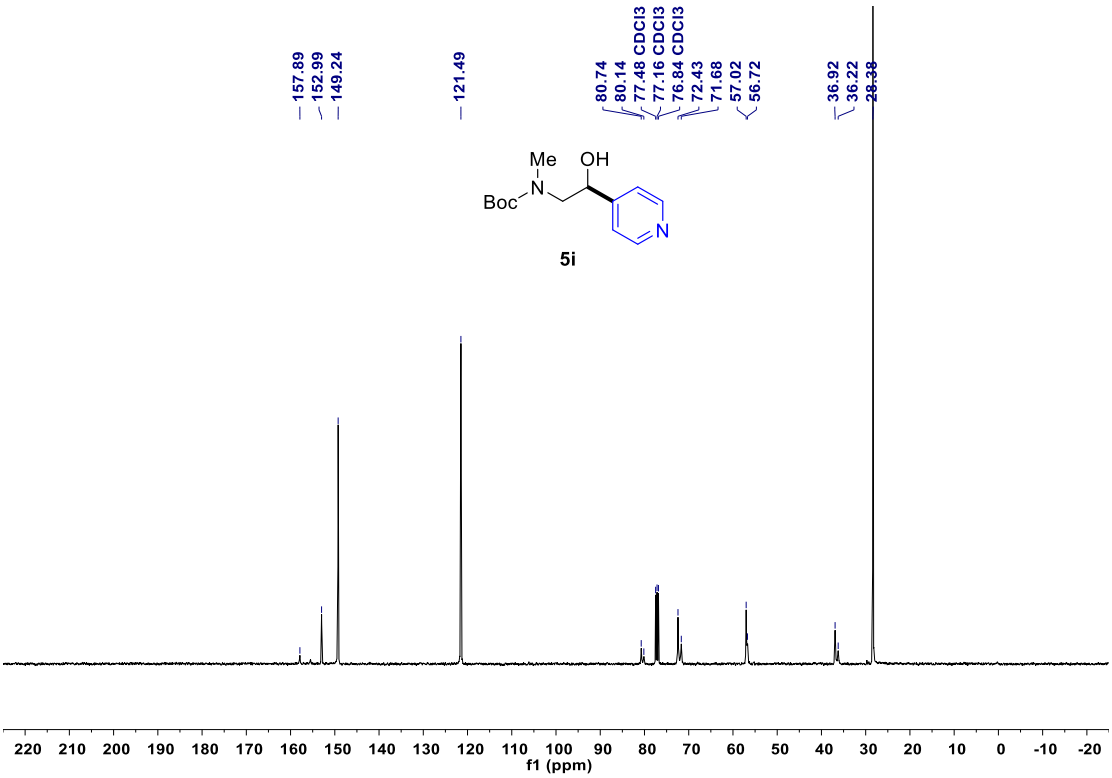


^{1}H and ^{13}C NMR spectra for compound 5g

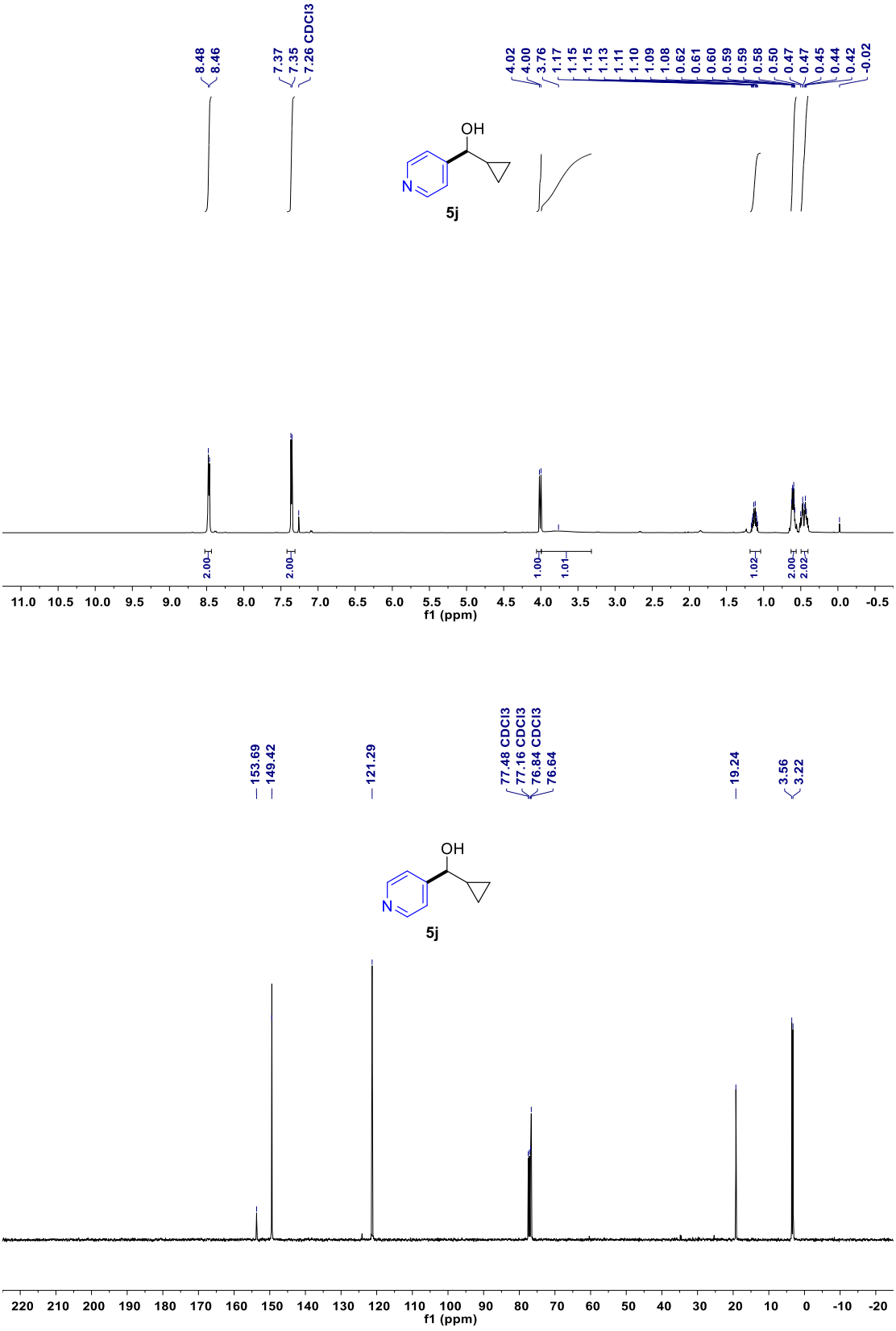


^{1}H and ^{13}C NMR spectra for compound 5h

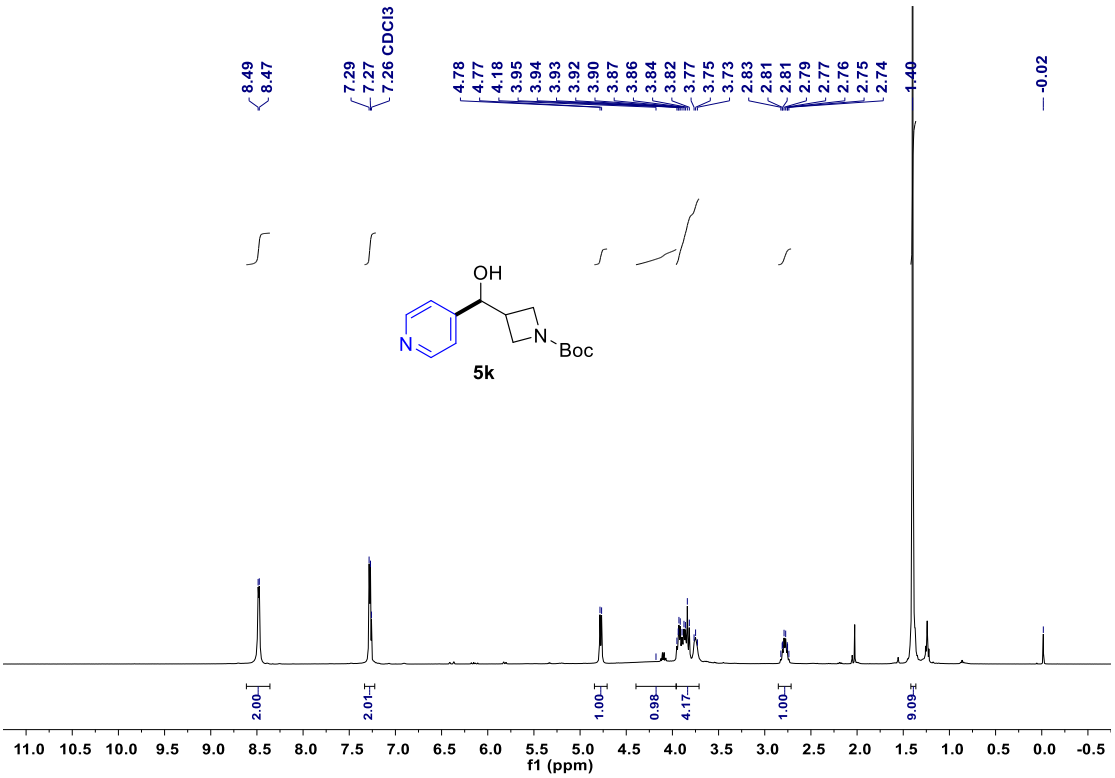


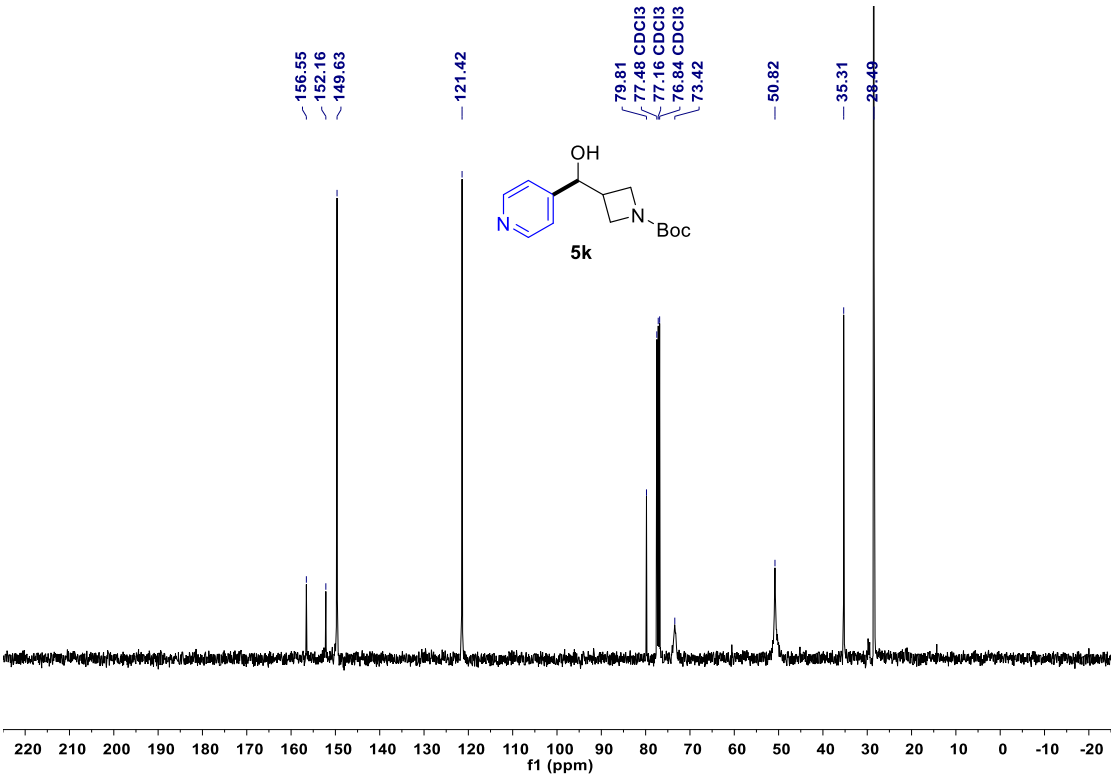


^{1}H and ^{13}C NMR spectra for compound 5i

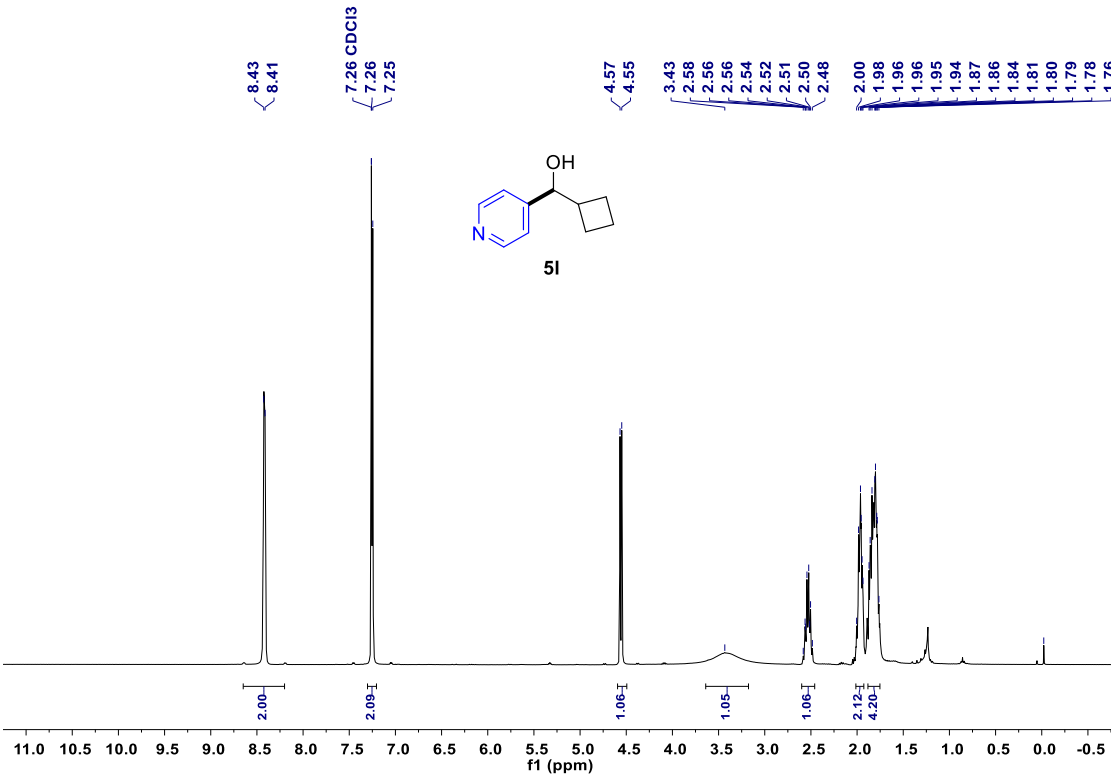


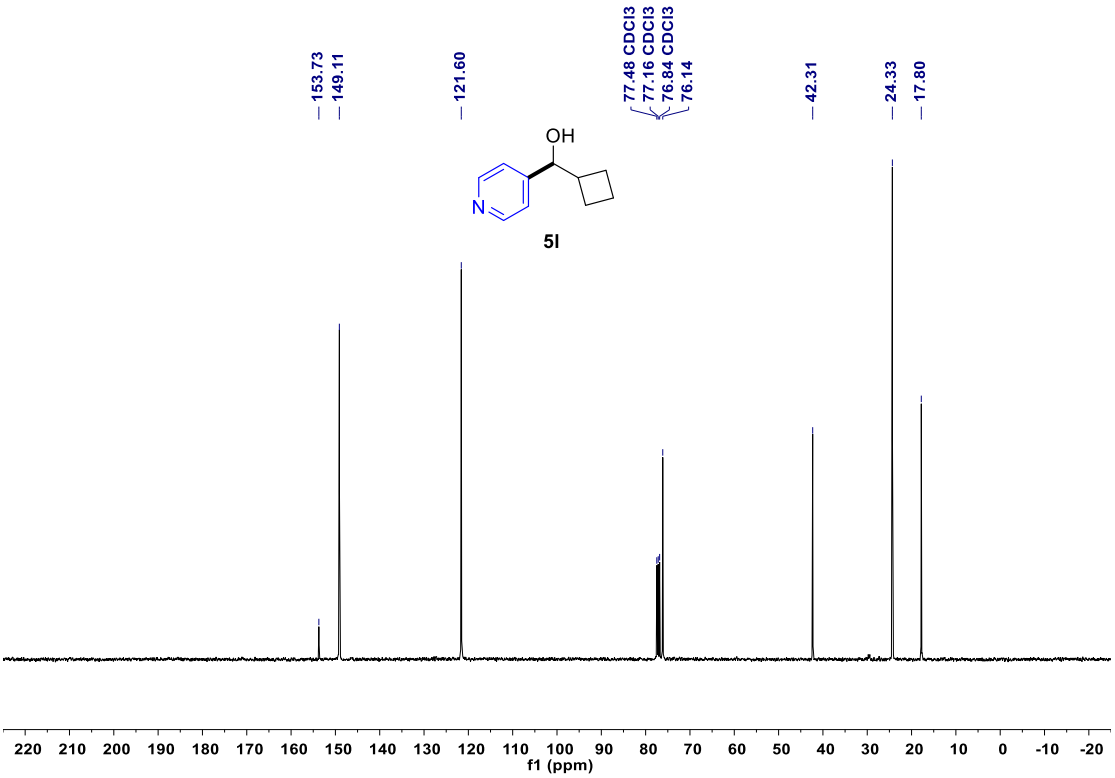
^{1}H and ^{13}C NMR spectra for compound 5j



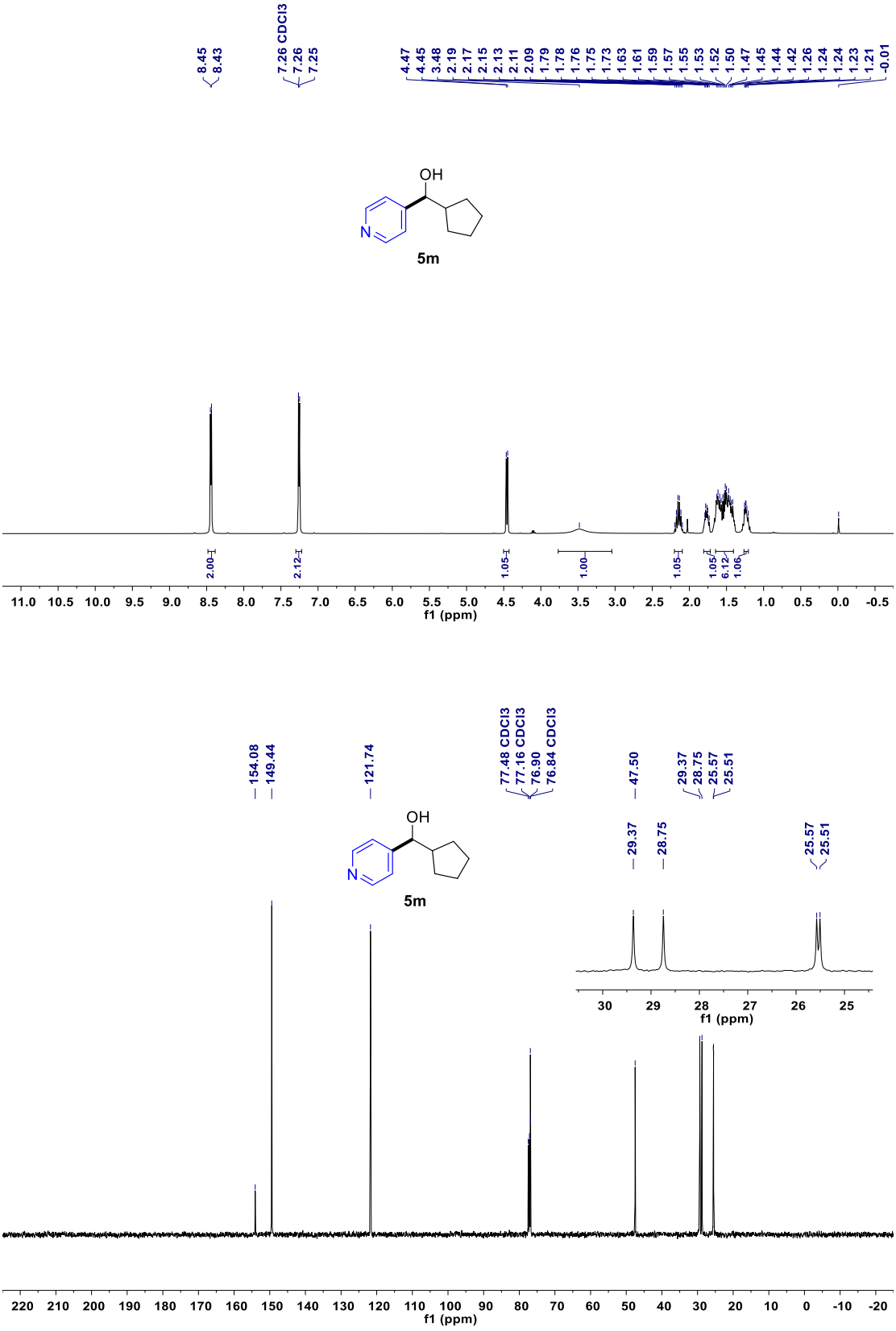


^{1}H and ^{13}C NMR spectra for compound 5k

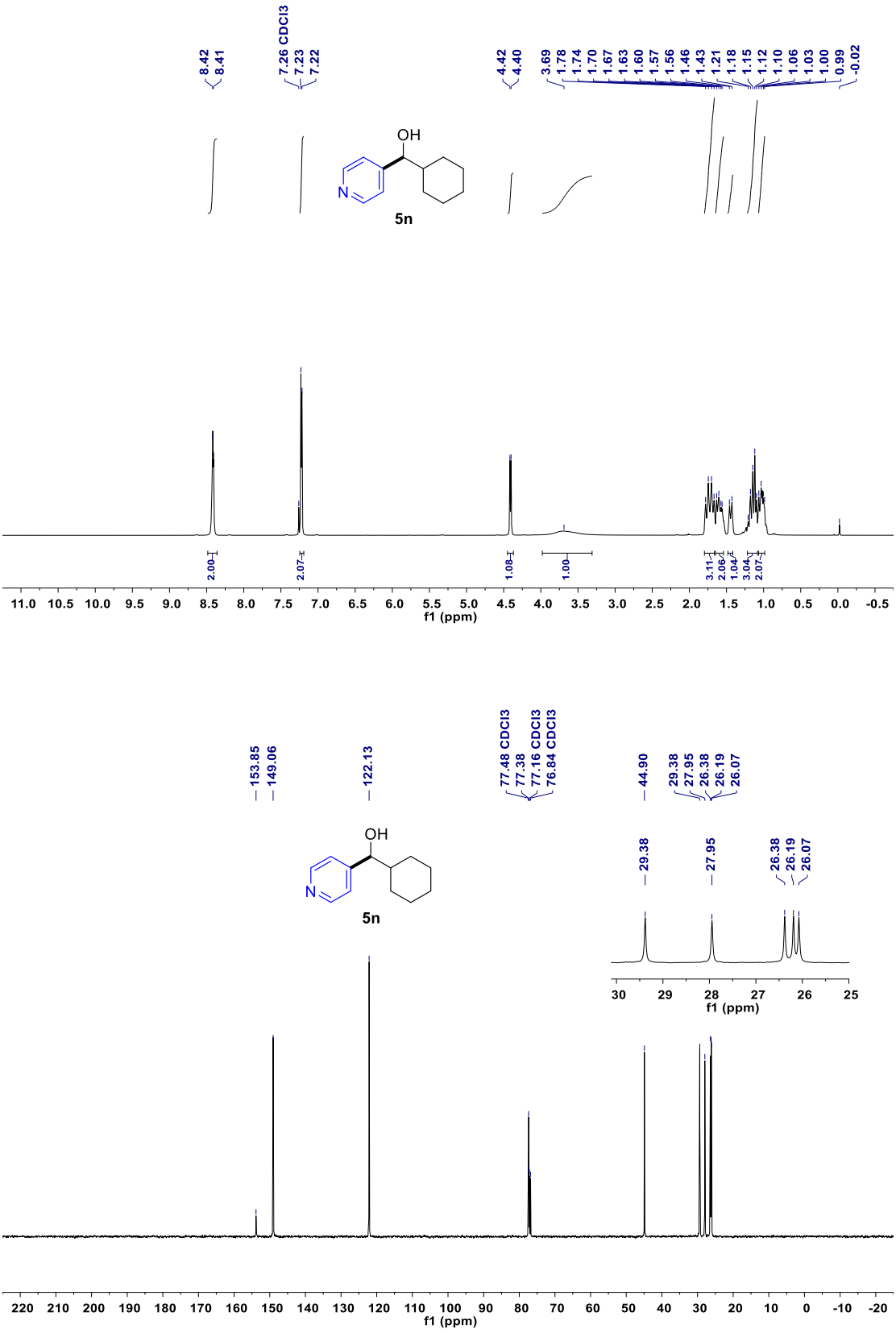




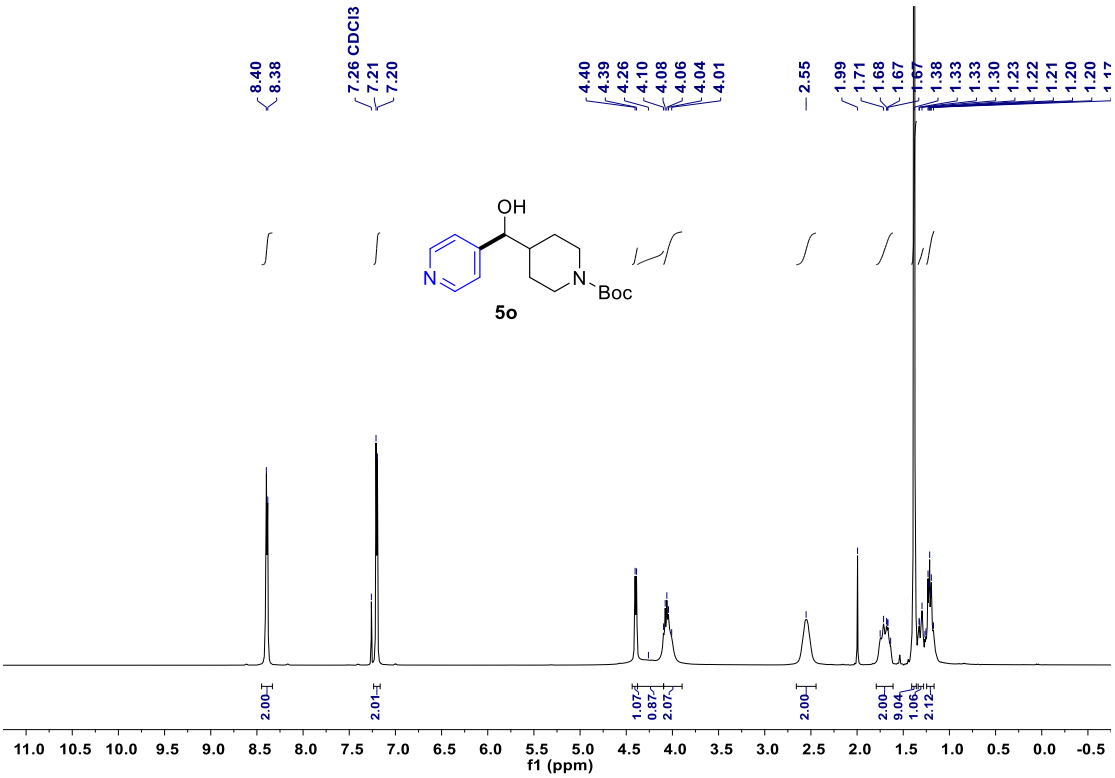
^{1}H and ^{13}C NMR spectra for compound 5l

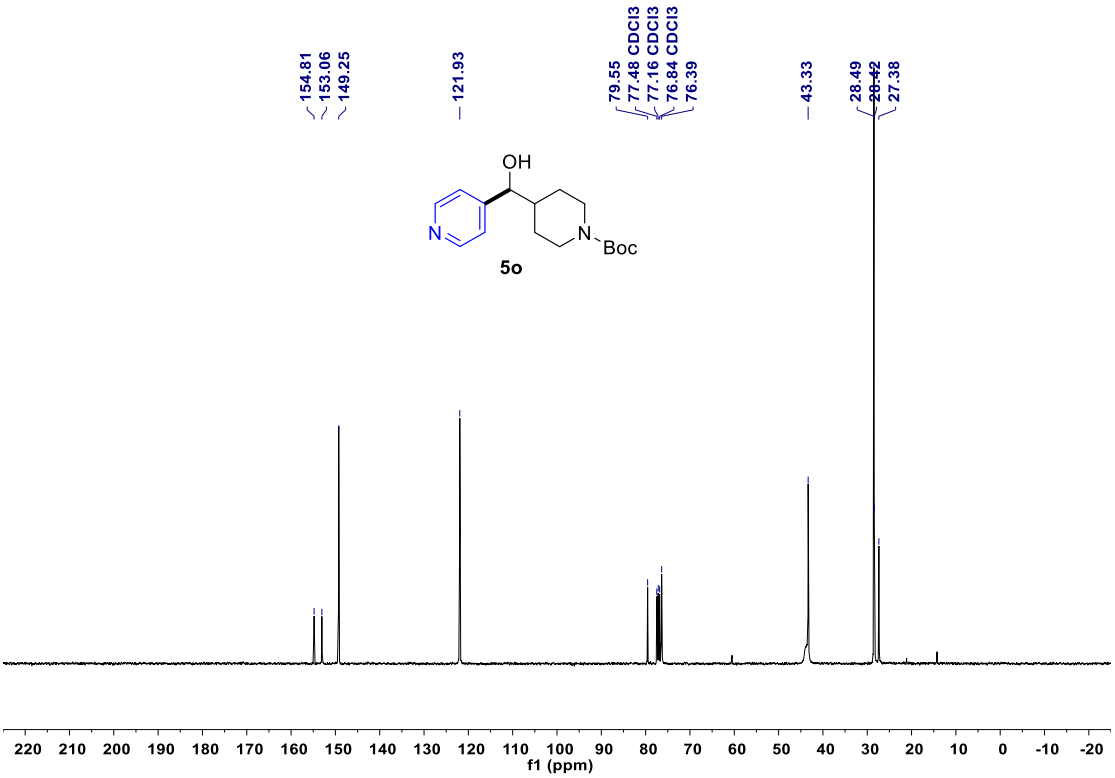


^{1}H and ^{13}C NMR spectra for compound 5m

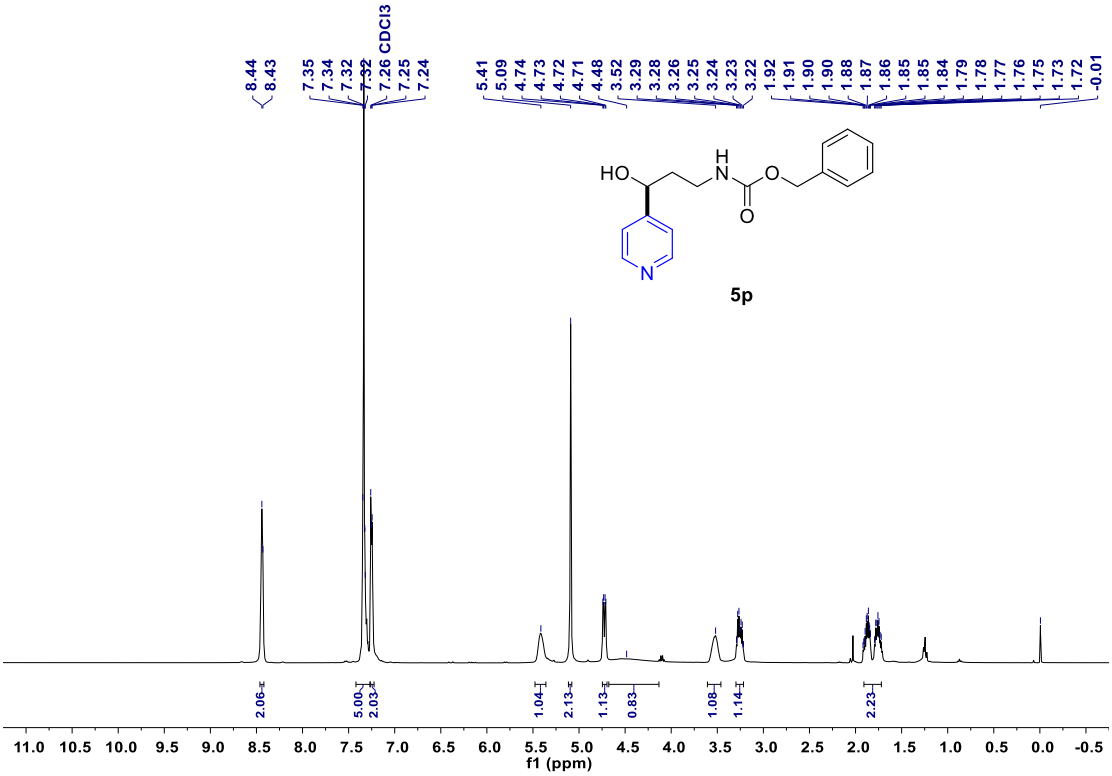


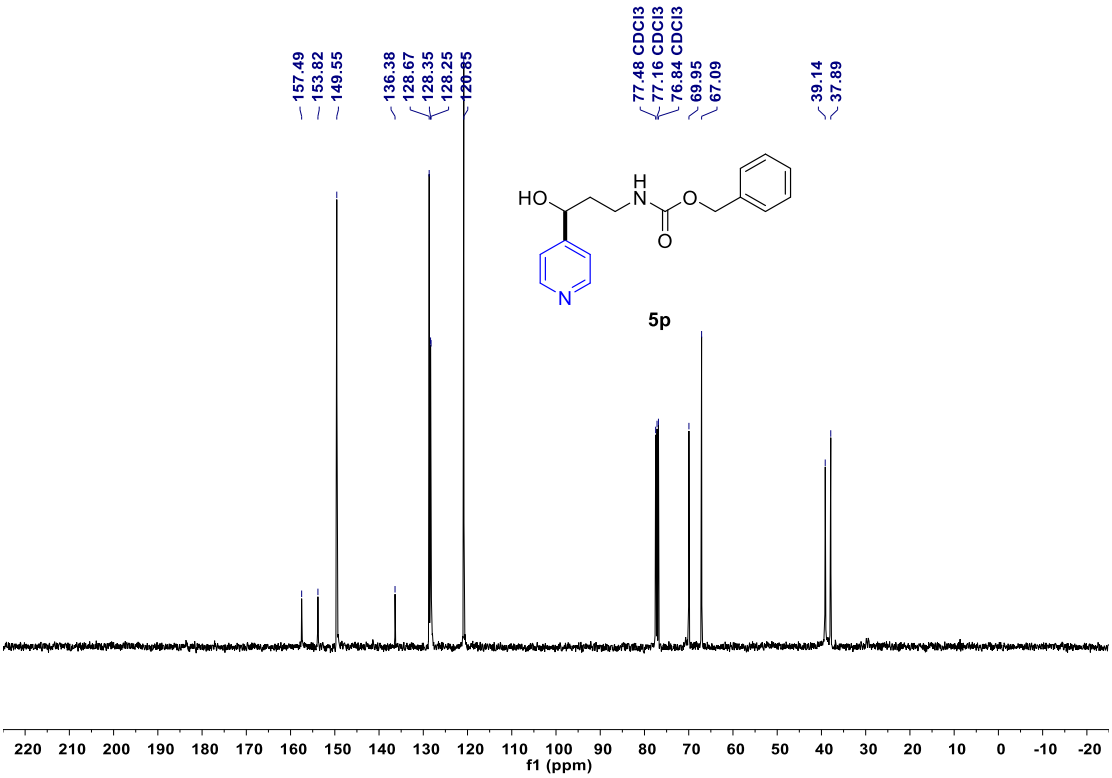
^{1}H and ^{13}C NMR spectra for compound **5n**



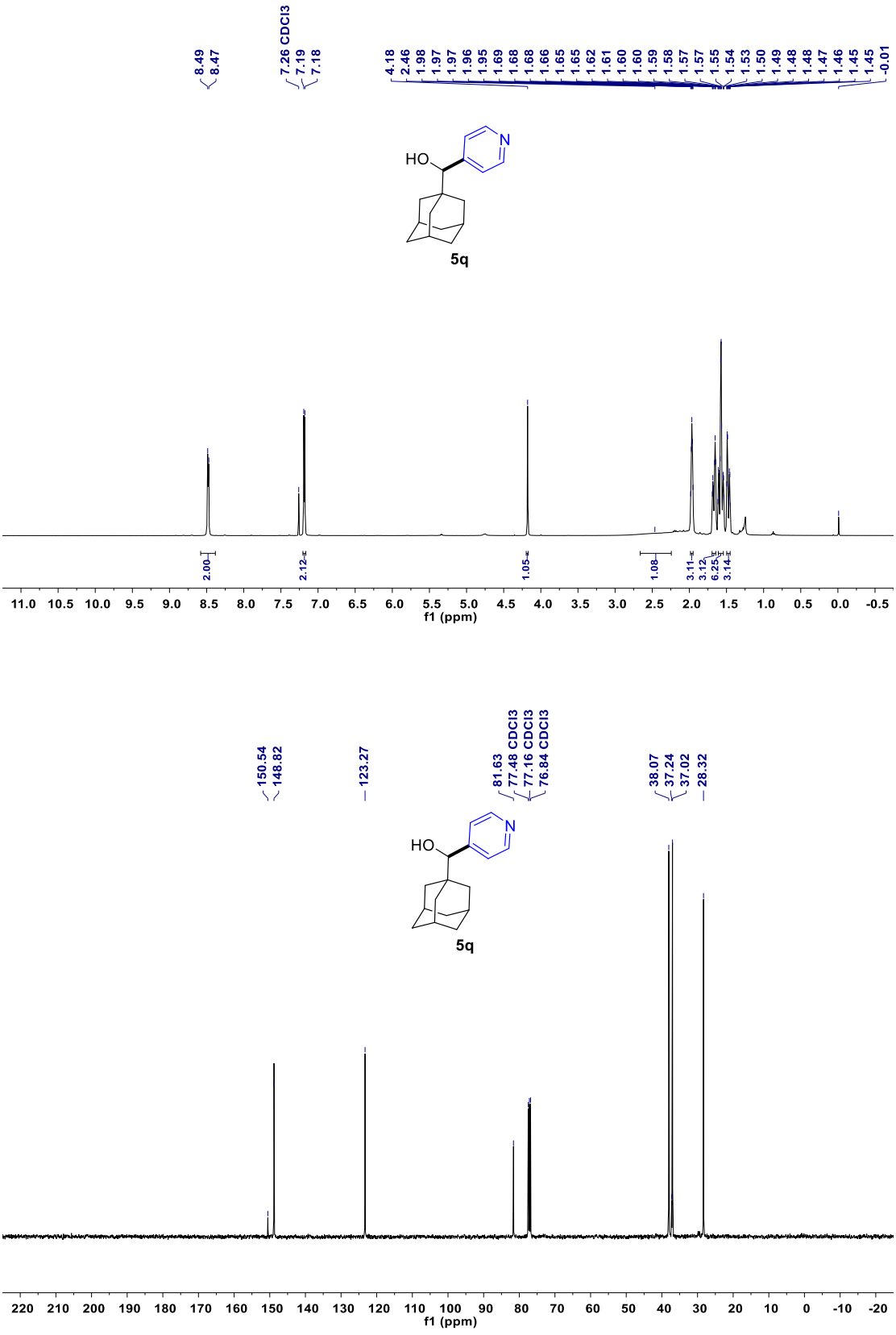


^{1}H and ^{13}C NMR spectra for compound **5o**

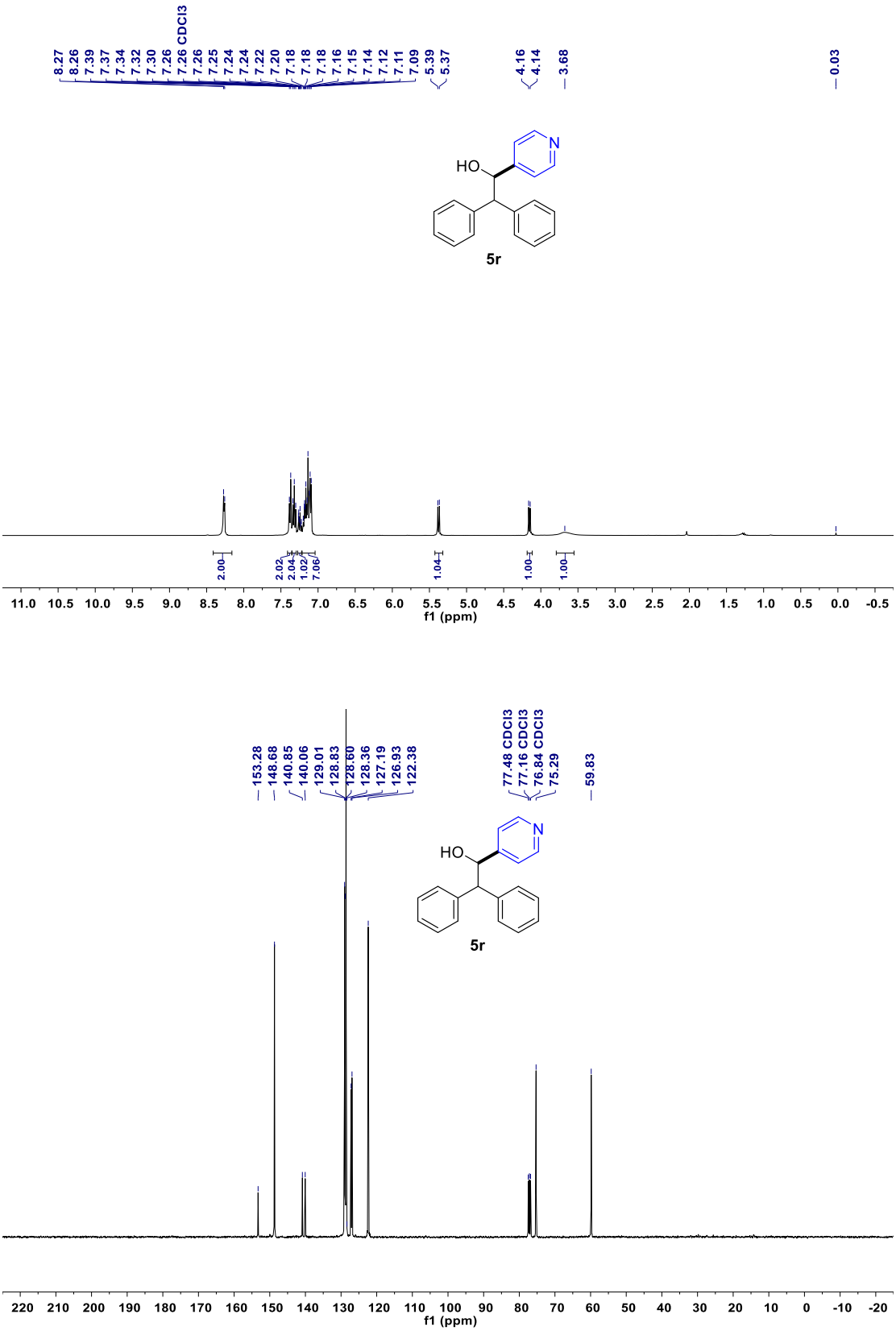




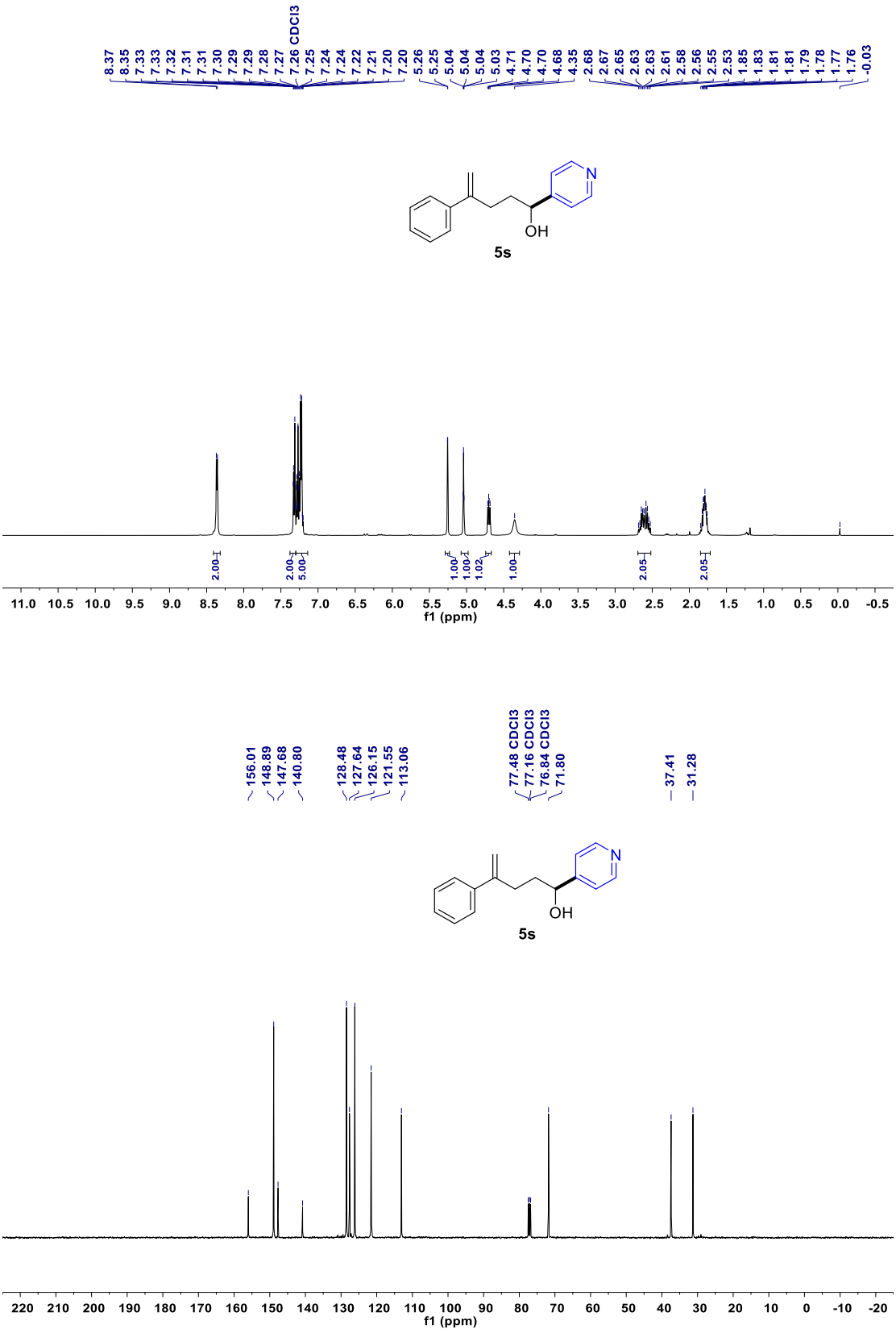
^{1}H and ^{13}C NMR spectra for compound **5p**



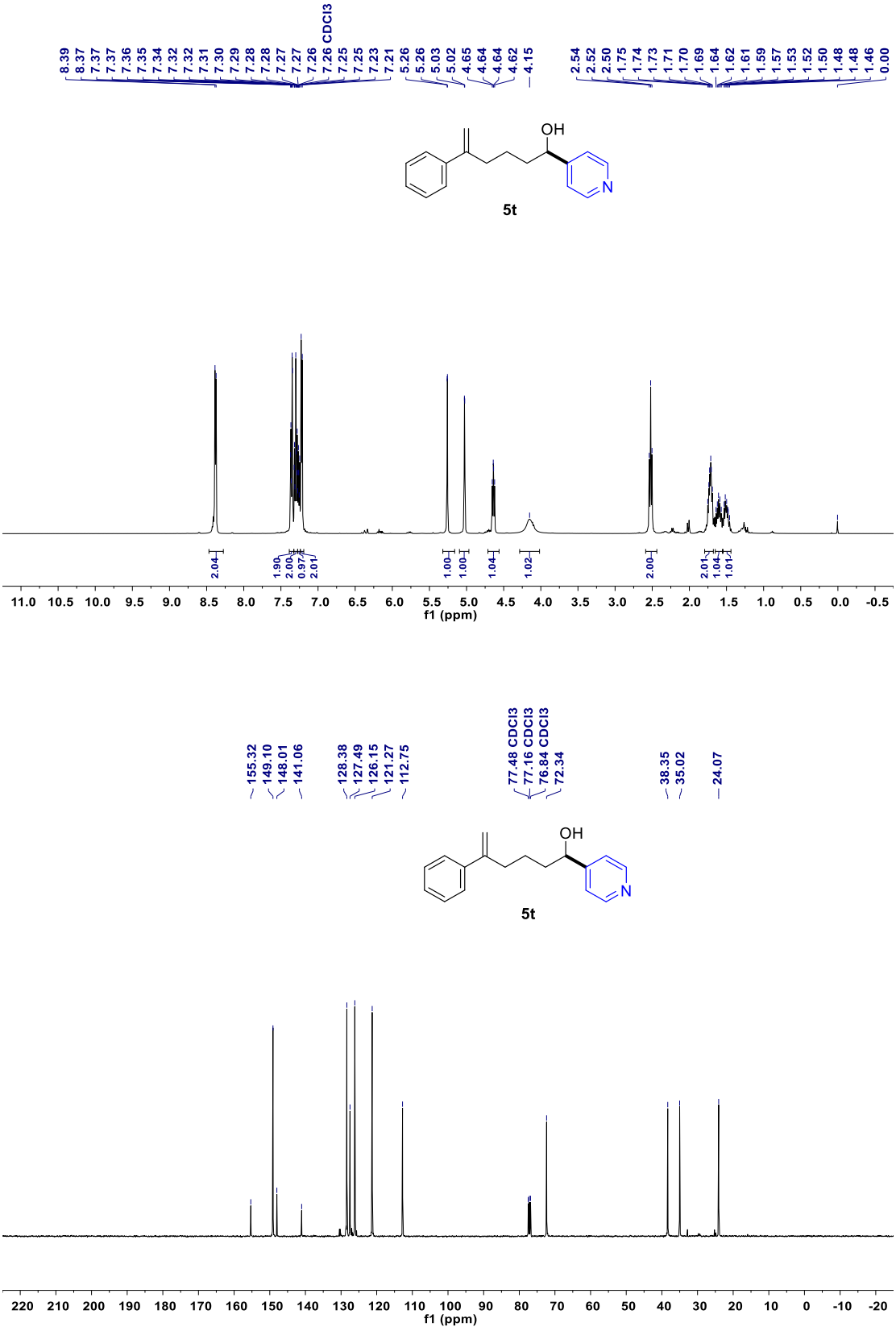
^{1}H and ^{13}C NMR spectra for compound **5q**



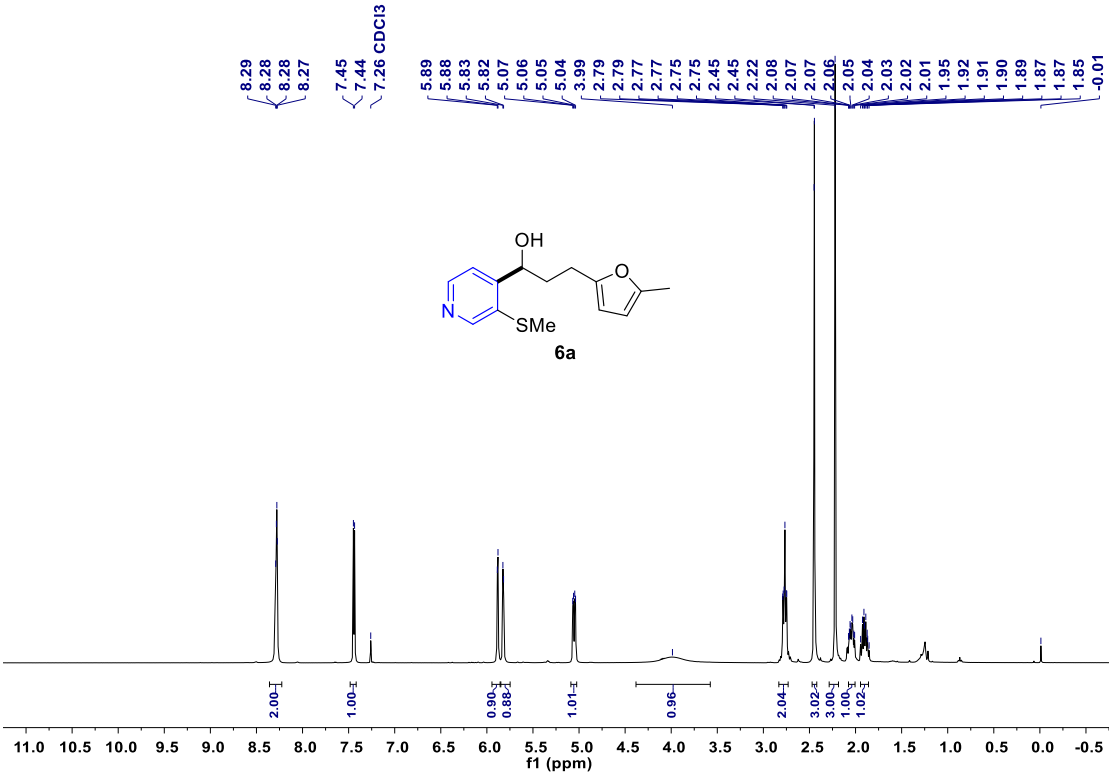
^{1}H and ^{13}C NMR spectra for compound **5r**

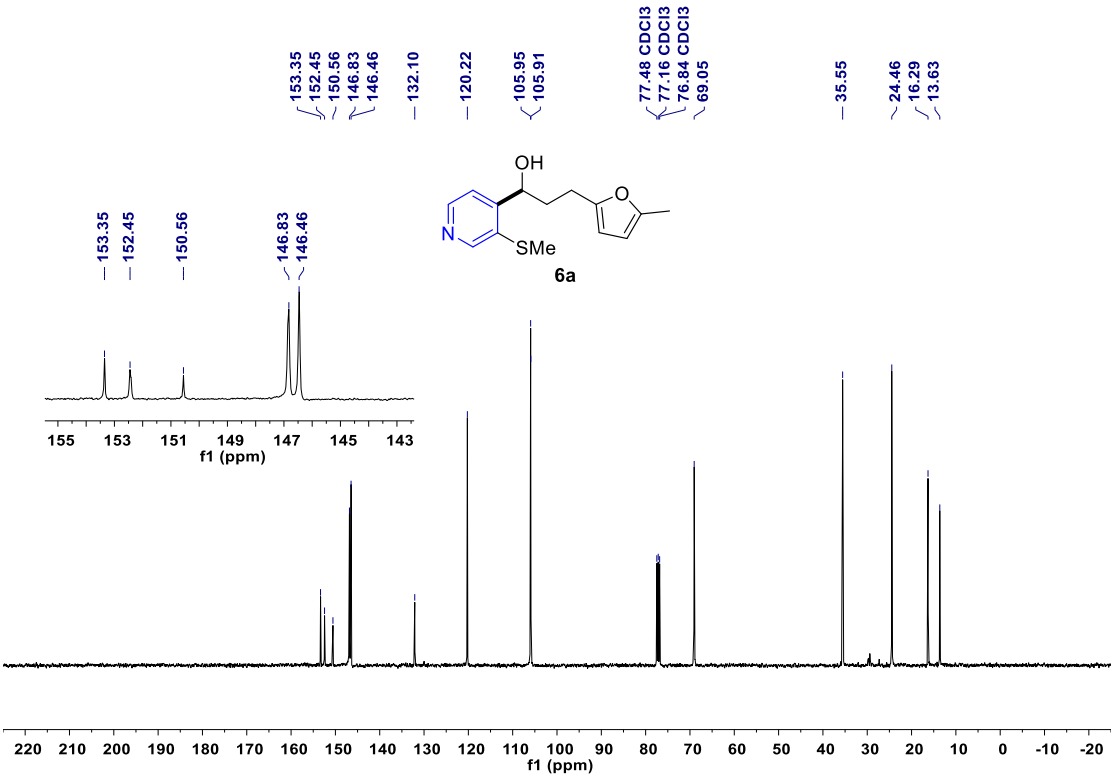


^{1}H and ^{13}C NMR spectra for compound **5s**

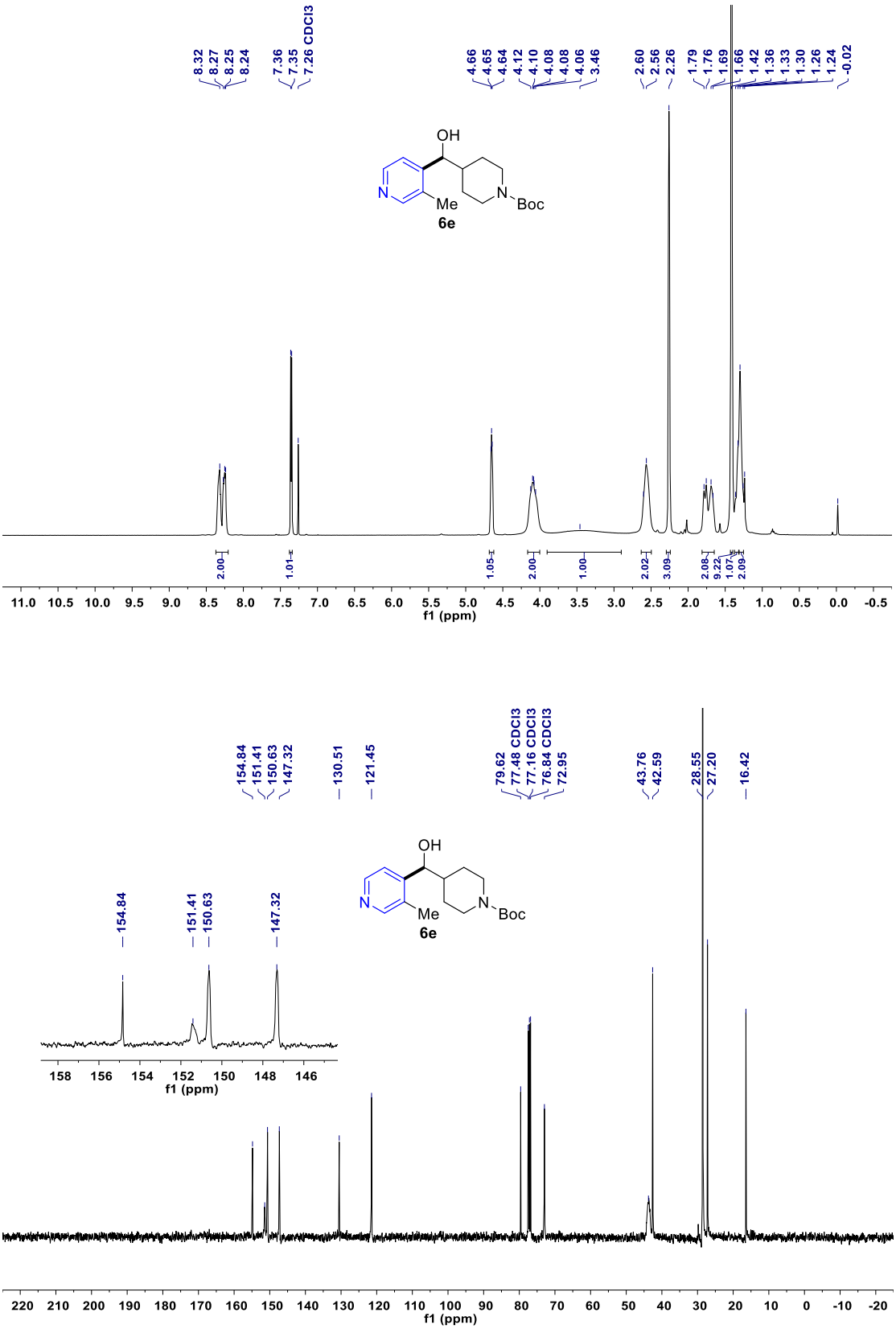


^{1}H and ^{13}C NMR spectra for compound **5t**

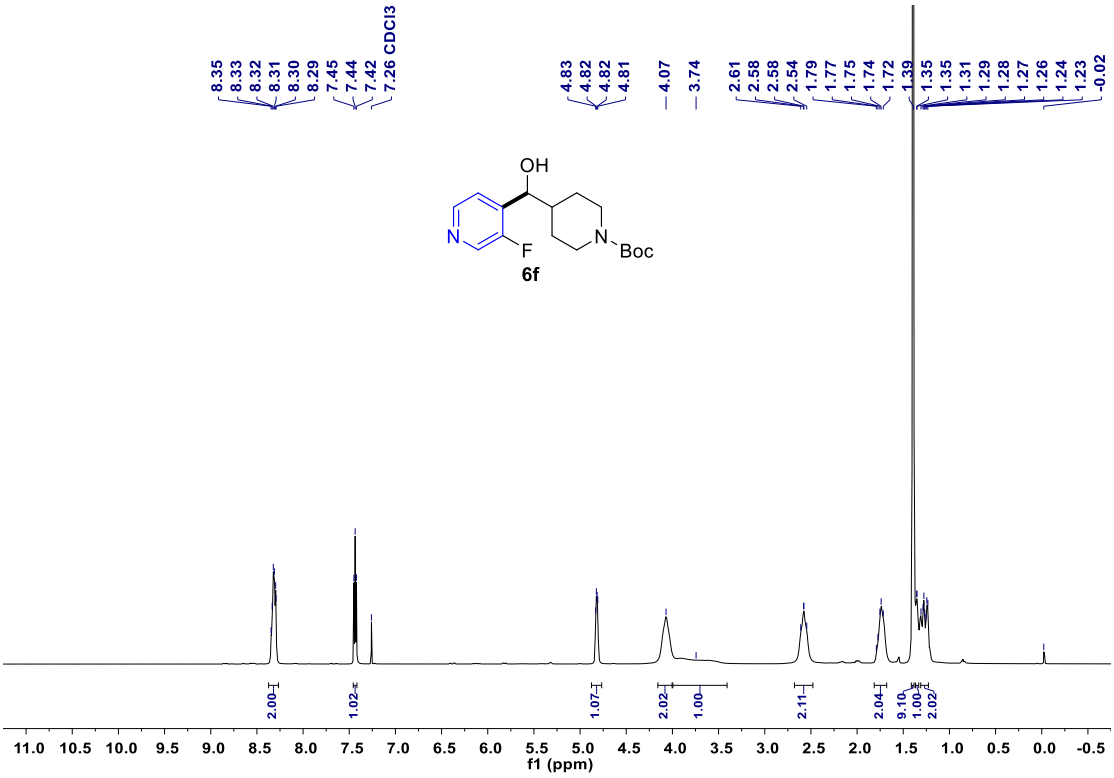


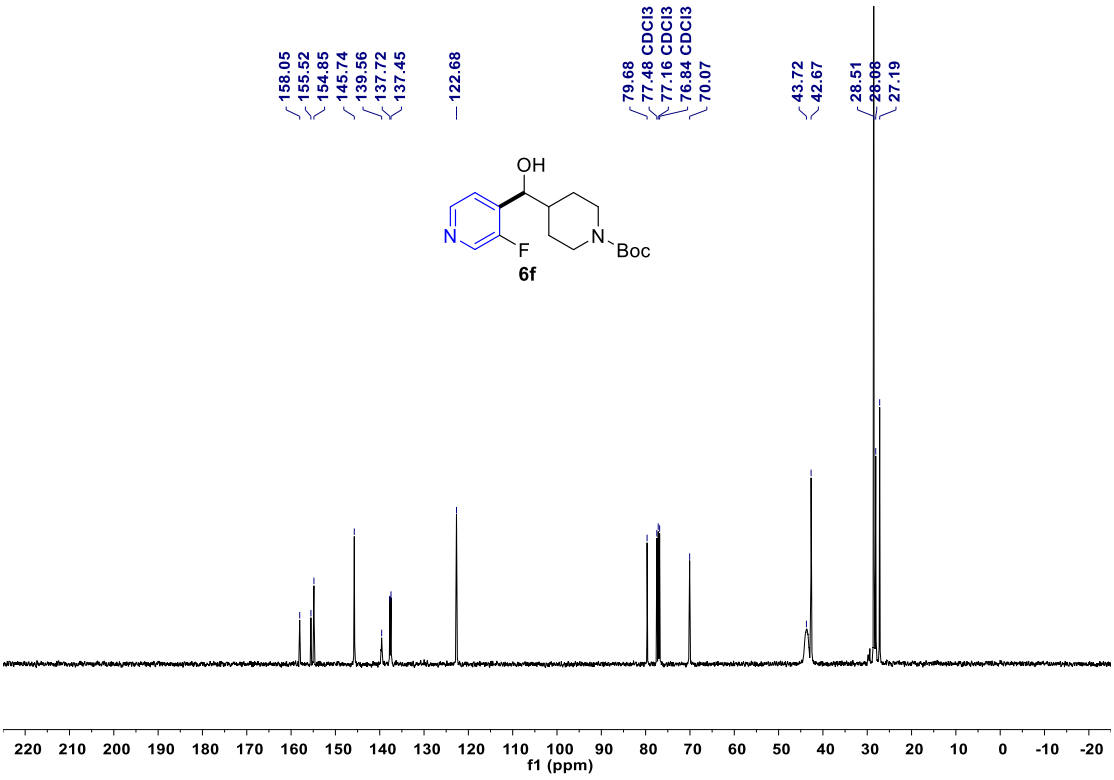


^{1}H and ^{13}C NMR spectra for compound **6a**

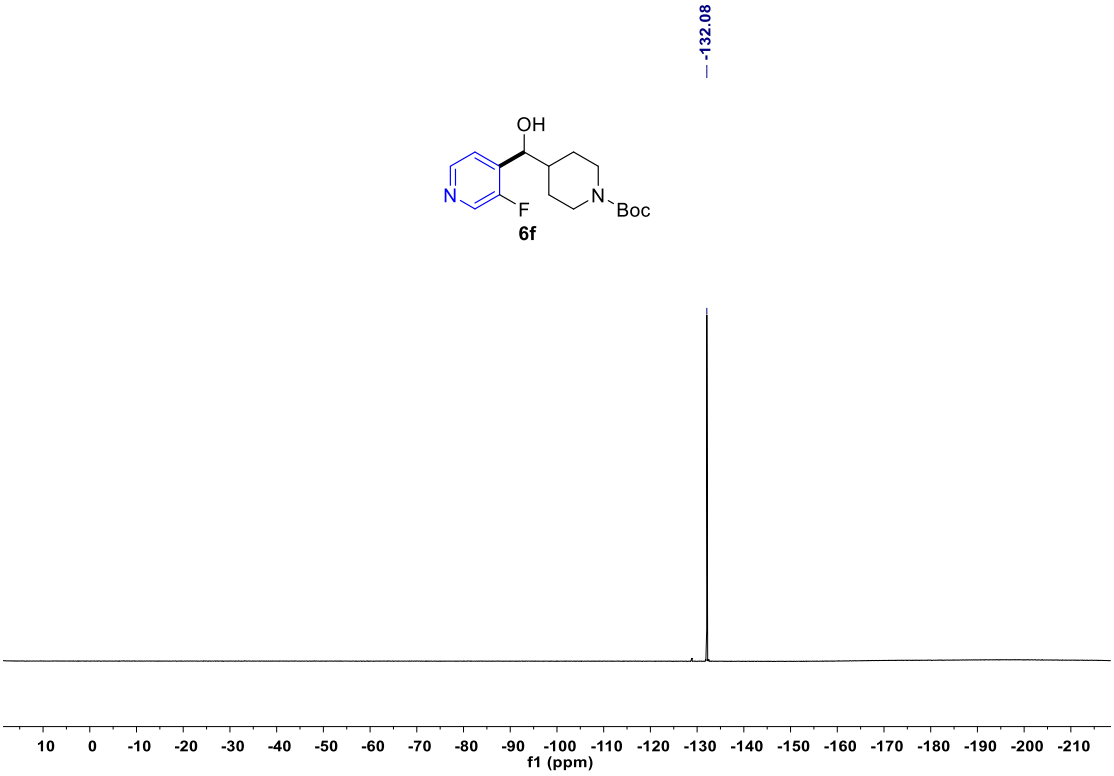


^{1}H and ^{13}C NMR spectra for compound **6e**

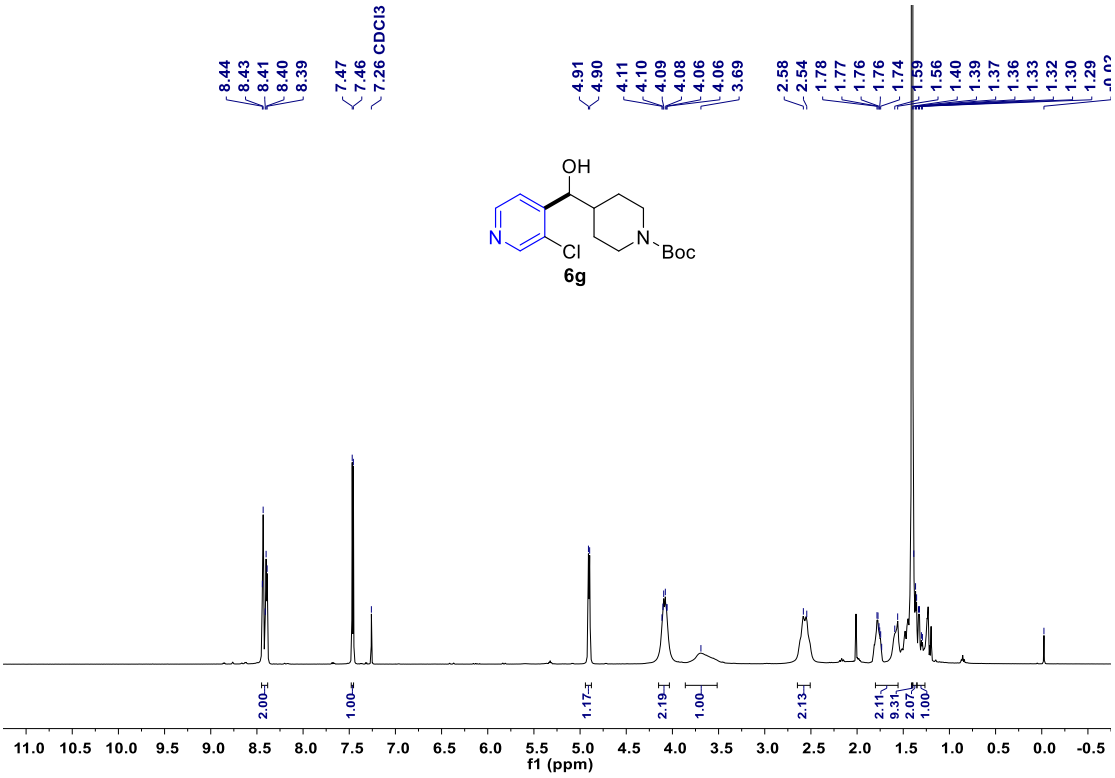


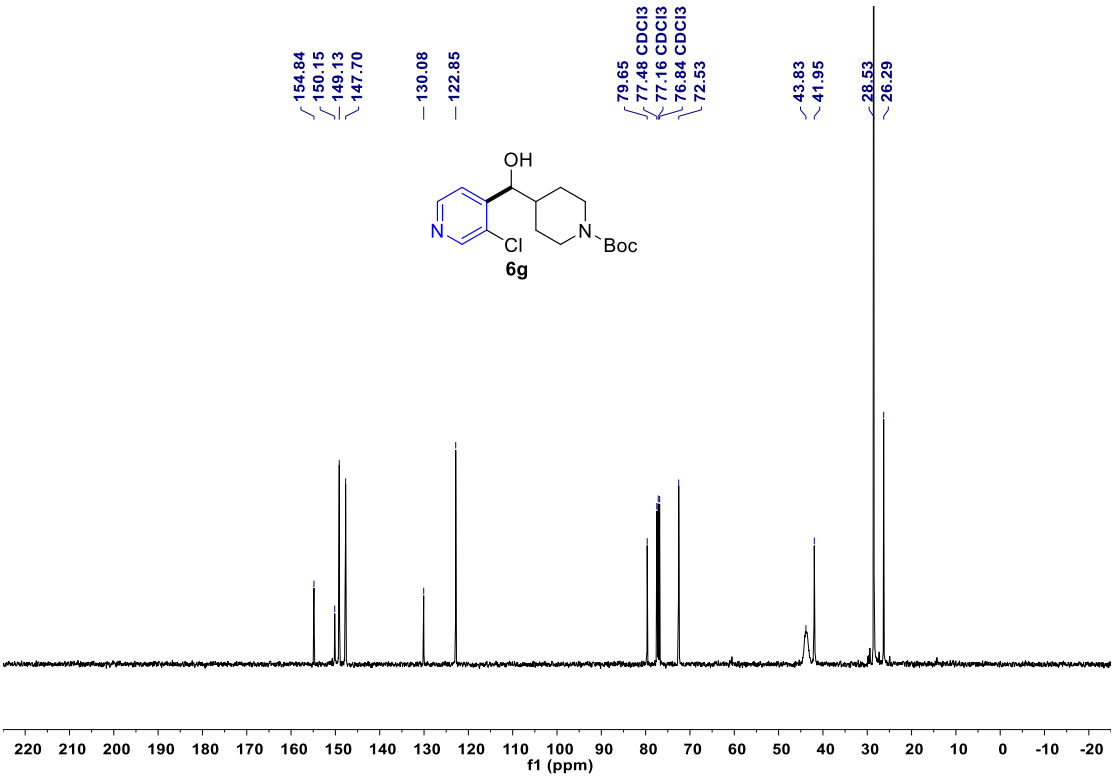


^{1}H and ^{13}C NMR spectra for compound **6f**

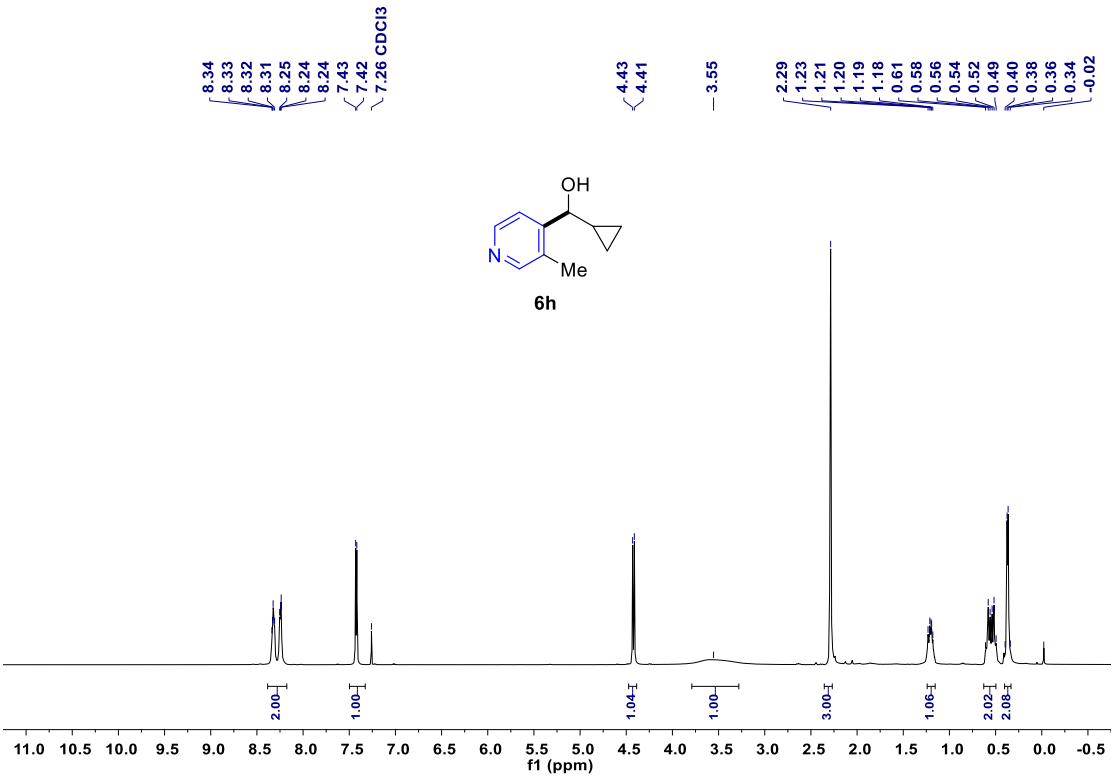


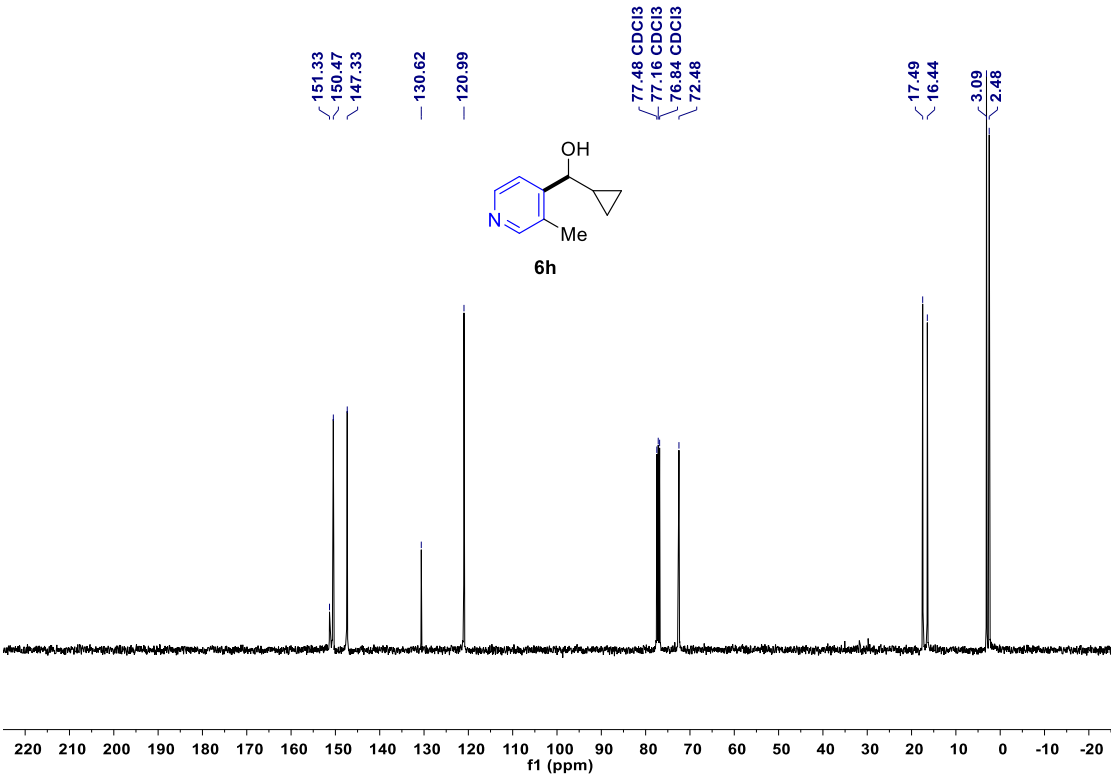
^{19}F NMR spectra for compound **6f**



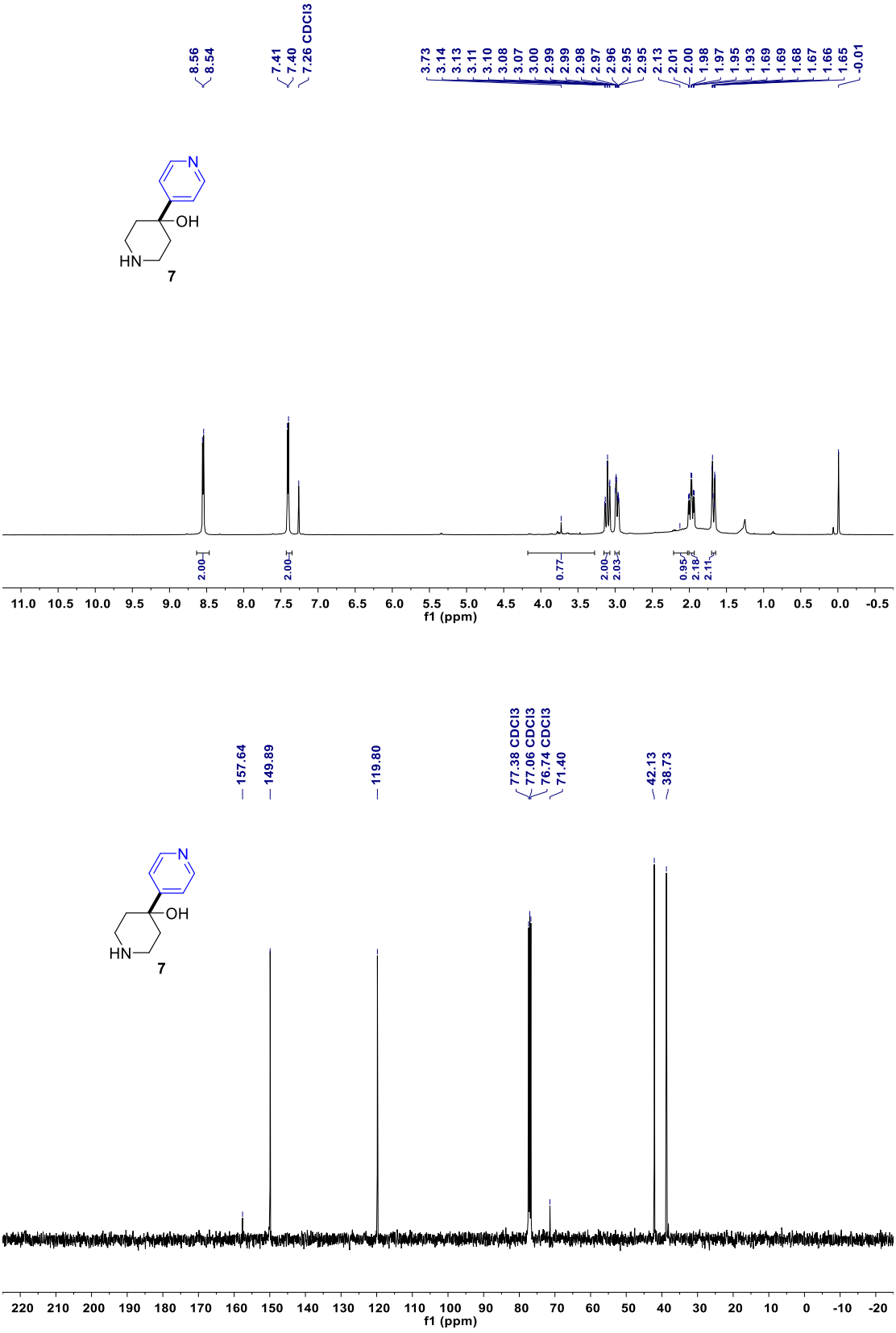


^{1}H and ^{13}C NMR spectra for compound 6g

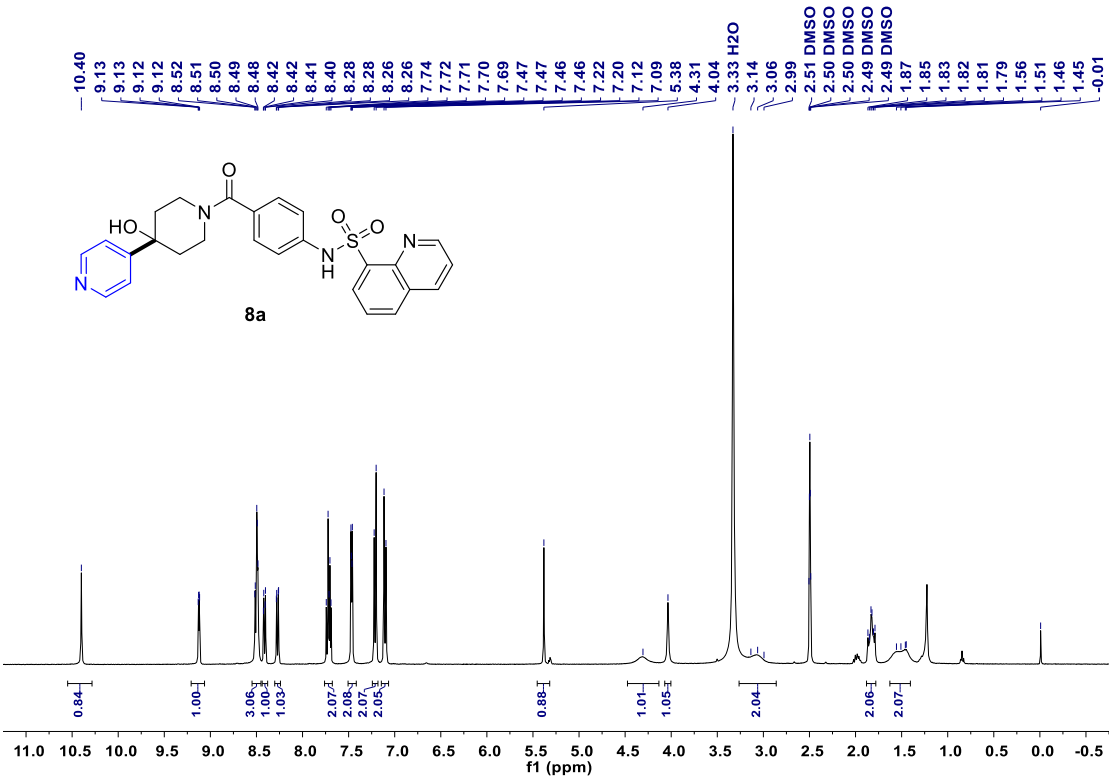


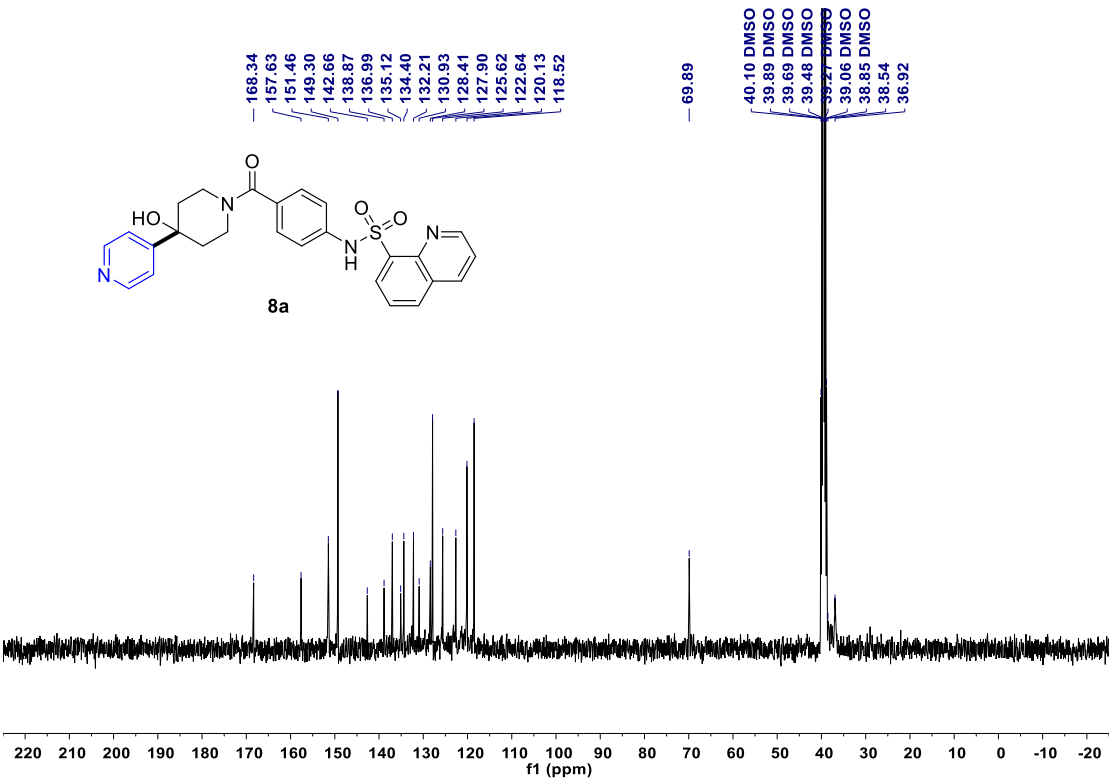


^{1}H and ^{13}C NMR spectra for compound 6h

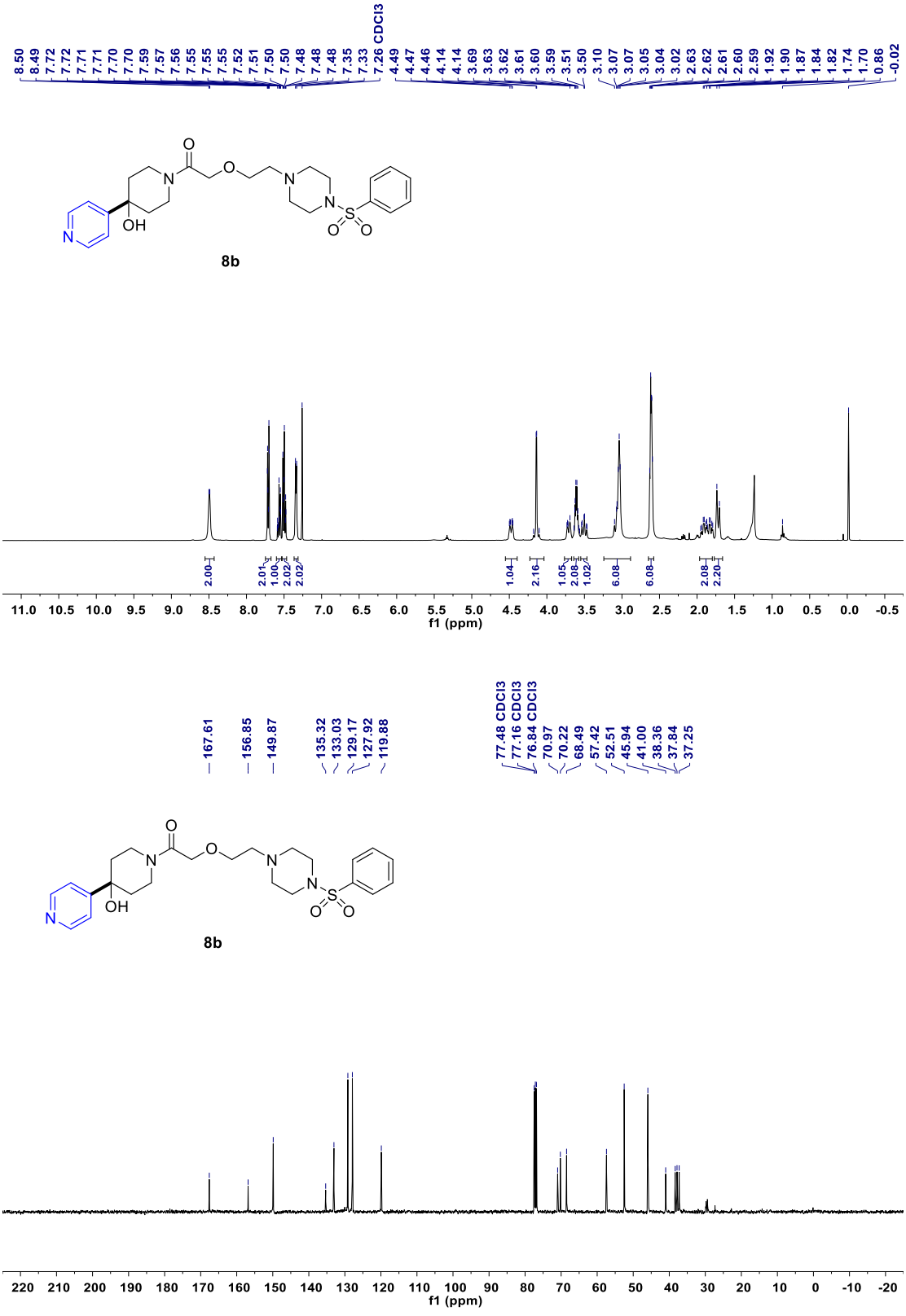


^{1}H and ^{13}C NMR spectra for compound **7**





^{1}H and ^{13}C NMR spectra for compound **8a**.



^{1}H and ^{13}C NMR spectra for compound **8b**.

7. Cartesian Coordinates and Energies of the Optimized Structures

Geometry optimizations and characters of all the stationary points were calculated by using the M06-2X/6-31G(d,p) method. Single point energies (**Esol**, a.u.) are computed by using the M06-2X/cc-PVTZ method in solvent (benzene). The solvent effect was treated with the polarizable continuum model (PCM).

2 (4-cyanopyridine)

Thermal correction to Energy=	0.093717
Thermal correction to Enthalpy=	0.094661
Thermal correction to Gibbs Free Energy=	0.057431
Sum of electronic and zero-point Energies=	-340.327193
Sum of electronic and thermal Energies=	-340.321179
Sum of electronic and thermal Enthalpies=	-340.320235
Sum of electronic and thermal Free Energies=	-340.357464

Esol= -340.5237333

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.501623	1.141229	0.000013
2	6	0	0.111742	1.204296	0.000010
3	6	0	-0.599670	0.000000	0.000000
4	6	0	0.111742	-1.204295	-0.000010
5	6	0	1.501623	-1.141228	-0.000013
6	7	0	2.195794	0.000000	0.000000
7	1	0	2.086228	2.058582	0.000016
8	1	0	-0.407006	2.156103	0.000015
9	1	0	-0.407006	-2.156102	-0.000015
10	1	0	2.086228	-2.058581	-0.000015
11	6	0	-2.031091	0.000000	0.000000
12	7	0	-3.193446	0.000000	0.000000

4-CN-Py-Bpin

Thermal correction to Energy=	0.287707
Thermal correction to Enthalpy=	0.288652
Thermal correction to Gibbs Free Energy=	0.226908
Sum of electronic and zero-point Energies=	-751.343019
Sum of electronic and thermal Energies=	-751.326571
Sum of electronic and thermal Enthalpies=	-751.325627

Sum of electronic and thermal Free Energies= -751.387371

Esol= -751.8516827
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.656372	1.187121	-0.160765
2	6	0	3.012996	1.206199	-0.163801
3	6	0	3.760870	-0.000018	-0.000056
4	6	0	3.012988	-1.206227	0.163712
5	6	0	1.656365	-1.187136	0.160716
6	7	0	0.939273	-0.000004	-0.000013
7	1	0	1.050493	2.075493	-0.280271
8	1	0	3.528811	2.150651	-0.291605
9	1	0	3.528798	-2.150685	0.291500
10	1	0	1.050481	-2.075502	0.280241
11	6	0	5.167592	-0.000025	-0.000077
12	7	0	6.337732	-0.000031	-0.000095
13	5	0	-0.499423	0.000003	0.000008
14	8	0	-1.233722	-1.131120	0.229716
15	8	0	-1.233719	1.131132	-0.229678
16	6	0	-2.602916	-0.777258	-0.102576
17	6	0	-2.602906	0.777282	0.102654
18	6	0	-3.539328	-1.540018	0.815886
19	1	0	-4.575645	-1.232238	0.646093
20	1	0	-3.465209	-2.611184	0.611149
21	1	0	-3.291809	-1.376633	1.865767
22	6	0	-2.822438	-1.183573	-1.556116
23	1	0	-2.594762	-2.246860	-1.664485
24	1	0	-3.857321	-1.017898	-1.867089
25	1	0	-2.163187	-0.623848	-2.225585
26	6	0	-3.539338	1.540050	-0.815782
27	1	0	-4.575653	1.232281	-0.645958
28	1	0	-3.465201	2.611216	-0.611049
29	1	0	-3.291852	1.376661	-1.865670
30	6	0	-2.822384	1.183598	1.556200
31	1	0	-2.594700	2.246884	1.664563
32	1	0	-3.857260	1.017929	1.867201
33	1	0	-2.163119	0.623869	2.225650

Acetone

Thermal correction to Energy= 0.089338
Thermal correction to Enthalpy= 0.090282
Thermal correction to Gibbs Free Energy= 0.055278
Sum of electronic and zero-point Energies= -193.016311
Sum of electronic and thermal Energies= -193.010876
Sum of electronic and thermal Enthalpies= -193.009932
Sum of electronic and thermal Free Energies= -193.044936

Esol= -193.1674538
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.185437	0.644245	-0.605068
2	6	0	1.301232	0.720492	0.045799
3	6	0	-0.050504	1.401936	0.050209
4	8	0	-0.215198	2.495353	0.551552
5	1	0	-2.103341	1.230170	-0.549726
6	1	0	-0.946463	0.429125	-1.652588
7	1	0	2.037014	1.353037	0.543206
8	1	0	1.622652	0.518123	-0.982065
9	1	0	1.241919	-0.248029	0.554962
10	1	0	-1.334042	-0.321948	-0.109820

TS1

Thermal correction to Energy= 0.378322
Thermal correction to Enthalpy= 0.379266
Thermal correction to Gibbs Free Energy= 0.304807
Sum of electronic and zero-point Energies= -944.362520
Sum of electronic and thermal Energies= -944.340473
Sum of electronic and thermal Enthalpies= -944.339528
Sum of electronic and thermal Free Energies= -944.413988

Esol= -945.0166572
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.894186	3.514072	-0.830585
2	6	0	0.386719	2.806939	1.285047
3	6	0	-0.031767	2.518550	-0.121736

4	8	0	0.325334	1.499405	-0.746025
5	1	0	-0.911528	3.305779	-1.900751
6	1	0	-1.917696	3.434077	-0.442628
7	1	0	0.886308	1.946430	1.727920
8	1	0	-0.473924	3.118082	1.885234
9	6	0	2.668541	-0.866999	-0.726426
10	6	0	2.504874	-0.894515	0.829694
11	8	0	1.351726	-0.052725	1.029096
12	5	0	0.601674	-0.135161	-0.160482
13	8	0	1.302520	-0.792061	-1.170050
14	6	0	3.300772	-2.114852	-1.319204
15	6	0	3.399026	0.381305	-1.219513
16	6	0	3.674328	-0.312295	1.604293
17	6	0	2.152524	-2.284237	1.355040
18	1	0	3.375325	-2.009831	-2.405099
19	1	0	4.309712	-2.265912	-0.922210
20	1	0	2.701359	-3.001199	-1.105184
21	1	0	3.267928	0.457983	-2.301806
22	1	0	2.985654	1.284450	-0.764340
23	1	0	4.469999	0.335960	-1.001624
24	1	0	3.465779	-0.355936	2.677048
25	1	0	4.588230	-0.883668	1.413760
26	1	0	3.850876	0.730209	1.333346
27	1	0	3.007230	-2.964909	1.307861
28	1	0	1.836009	-2.197720	2.397821
29	1	0	1.326757	-2.715444	0.783062
30	6	0	-2.935036	-0.898743	-1.162266
31	6	0	-1.574584	-0.910564	-1.135110
32	7	0	-0.860206	-0.475462	-0.039353
33	6	0	-1.557858	-0.035308	1.068030
34	6	0	-2.921510	0.009067	1.091543
35	6	0	-3.673258	-0.410876	-0.039210
36	6	0	-5.080769	-0.354335	-0.045954
37	7	0	-6.249439	-0.301021	-0.051388
38	1	0	-3.456753	-1.261401	-2.039949
39	1	0	-0.969443	-1.253716	-1.964767
40	1	0	-0.945738	0.234392	1.919067
41	1	0	-3.430058	0.348493	1.986921
42	1	0	-0.559388	4.539128	-0.643073
43	1	0	1.080333	3.658835	1.271236

Int1

Thermal correction to Energy= 0.379128

Thermal correction to Enthalpy= 0.380072
Thermal correction to Gibbs Free Energy= 0.304231
Sum of electronic and zero-point Energies= -944.362742
Sum of electronic and thermal Energies= -944.340287
Sum of electronic and thermal Enthalpies= -944.339342
Sum of electronic and thermal Free Energies= -944.415183

Esol= -945.0155274
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.088593	4.042960	-0.406968
2	6	0	2.856344	3.447860	1.977049
3	6	0	1.753227	3.657183	0.993954
4	8	0	0.528423	3.408499	1.248137
5	1	0	1.187411	4.059419	-1.020555
6	1	0	2.555205	5.035646	-0.428301
7	1	0	2.466636	3.281822	2.980506
8	1	0	3.558086	4.288387	1.959961
9	6	0	-1.430882	1.841455	3.463725
10	6	0	-0.441847	2.405997	4.534696
11	8	0	0.478030	3.152434	3.723028
12	5	0	-0.264738	3.597286	2.591994
13	8	0	-1.499878	2.919028	2.520214
14	6	0	-2.830458	1.555445	3.981479
15	6	0	-0.870612	0.614049	2.744416
16	6	0	0.334482	1.352647	5.306824
17	6	0	-1.121622	3.377990	5.498859
18	1	0	-3.451686	1.165170	3.170411
19	1	0	-2.804935	0.806907	4.779967
20	1	0	-3.303098	2.461995	4.363373
21	1	0	-1.484986	0.414981	1.862576
22	1	0	0.154263	0.794538	2.409765
23	1	0	-0.881029	-0.273995	3.383430
24	1	0	1.006078	1.837441	6.021265
25	1	0	-0.344283	0.702355	5.867721
26	1	0	0.936738	0.736791	4.636810
27	1	0	-1.770817	2.858114	6.209414
28	1	0	-0.351147	3.912249	6.061417
29	1	0	-1.717902	4.114020	4.953482
30	6	0	-1.528173	6.990605	1.462278
31	6	0	-1.513356	5.686816	1.870032

32	7	0	-0.439168	5.139392	2.511144
33	6	0	0.654292	5.925188	2.764455
34	6	0	0.708026	7.237576	2.367984
35	6	0	-0.387559	7.813478	1.689691
36	6	0	-0.353642	9.161124	1.261508
37	7	0	-0.323064	10.272645	0.904804
38	1	0	-2.404455	7.393980	0.969517
39	1	0	-2.339386	5.004514	1.710690
40	1	0	1.437705	5.456318	3.345706
41	1	0	1.584266	7.833699	2.596243
42	1	0	2.817016	3.346336	-0.841583
43	1	0	3.432850	2.559904	1.676579

TS2

Thermal correction to Energy= 0.378514
Thermal correction to Enthalpy= 0.379458
Thermal correction to Gibbs Free Energy= 0.304920
Sum of electronic and zero-point Energies= -944.352399
Sum of electronic and thermal Energies= -944.330370
Sum of electronic and thermal Enthalpies= -944.329425
Sum of electronic and thermal Free Energies= -944.403963

Esol= -945.003491
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.489823	2.991664	-0.855418
2	6	0	0.344257	3.084970	0.982046
3	6	0	-0.342412	2.377882	-0.135604
4	8	0	0.358210	1.496383	-0.890852
5	1	0	-2.050724	2.230381	-1.405392
6	1	0	-2.165745	3.493900	-0.157925
7	1	0	1.006722	3.880163	0.600082
8	1	0	0.965023	2.399985	1.563167
9	6	0	2.772982	-1.055282	-0.682284
10	6	0	2.534100	-0.790983	0.847849
11	8	0	1.711734	0.394850	0.829319
12	5	0	1.069797	0.405753	-0.400758
13	8	0	1.591446	-0.506821	-1.297865
14	6	0	2.885680	-2.522580	-1.058946
15	6	0	3.960855	-0.272202	-1.237951

16	6	0	3.795455	-0.485458	1.639158
17	6	0	1.746520	-1.902907	1.536550
18	1	0	3.032940	-2.613425	-2.138591
19	1	0	3.740628	-2.988736	-0.558875
20	1	0	1.981065	-3.071199	-0.791448
21	1	0	3.945614	-0.340359	-2.328658
22	1	0	3.891363	0.784322	-0.964845
23	1	0	4.915491	-0.666318	-0.877952
24	1	0	3.538178	-0.310008	2.687469
25	1	0	4.490763	-1.329736	1.597424
26	1	0	4.299404	0.404800	1.259902
27	1	0	2.349401	-2.808411	1.650440
28	1	0	1.455770	-1.558848	2.533231
29	1	0	0.836862	-2.142580	0.984136
30	6	0	-2.917216	-0.895700	-1.033739
31	6	0	-1.543017	-1.034847	-0.921565
32	7	0	-0.840993	-0.543485	0.104065
33	6	0	-1.483857	0.144647	1.057661
34	6	0	-2.862205	0.345001	1.040322
35	6	0	-3.591669	-0.180964	-0.027045
36	6	0	-5.007371	0.007439	-0.096544
37	7	0	-6.158453	0.162106	-0.154924
38	1	0	-3.458138	-1.315003	-1.873671
39	1	0	-0.959014	-1.541433	-1.685140
40	1	0	-0.870307	0.497509	1.880594
41	1	0	-3.355798	0.900478	1.829291
42	1	0	-1.155128	3.742714	-1.589989
43	1	0	-0.388590	3.562861	1.638872

Acetone-Bpin—Int2

Thermal correction to Energy= 0.283265
Thermal correction to Enthalpy= 0.284209
Thermal correction to Gibbs Free Energy= 0.225523
Sum of electronic and zero-point Energies= -604.011345
Sum of electronic and thermal Energies= -603.996052
Sum of electronic and thermal Enthalpies= -603.995108
Sum of electronic and thermal Free Energies= -604.053794

Esol= -604.470722
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.014605	-1.932990	-0.583818
2	6	0	0.353270	-2.009488	-3.159040
3	6	0	-0.022121	-1.276101	-1.920893
4	8	0	-1.032116	-0.357065	-2.140103
5	1	0	0.024036	-1.194530	0.222483
6	1	0	-0.862625	-2.585115	-0.429590
7	1	0	0.507548	-1.315140	-3.990893
8	1	0	-0.431617	-2.719496	-3.471484
9	6	0	-2.390434	2.471537	-0.491848
10	6	0	-0.938594	2.426574	0.094752
11	8	0	-0.508908	1.090605	-0.256828
12	5	0	-1.255708	0.729690	-1.355549
13	8	0	-2.290782	1.588842	-1.630865
14	6	0	-2.841912	3.840464	-0.968944
15	6	0	-3.426594	1.866453	0.452184
16	6	0	-0.852420	2.588366	1.601778
17	6	0	0.012347	3.395096	-0.602954
18	1	0	-3.856643	3.773789	-1.370214
19	1	0	-2.849835	4.554780	-0.139595
20	1	0	-2.191177	4.222790	-1.756827
21	1	0	-4.362301	1.726713	-0.094683
22	1	0	-3.098739	0.889870	0.819811
23	1	0	-3.618658	2.515903	1.310746
24	1	0	0.192283	2.533663	1.919380
25	1	0	-1.250839	3.560766	1.907395
26	1	0	-1.406557	1.804019	2.119754
27	1	0	-0.195330	4.432834	-0.327765
28	1	0	1.037490	3.156349	-0.308736
29	1	0	-0.060667	3.300819	-1.690094
30	1	0	0.907130	-2.558158	-0.492725
31	1	0	1.272117	-2.582183	-3.005135

Int3

Thermal correction to Energy=	0.577354
Thermal correction to Enthalpy=	0.578298
Thermal correction to Gibbs Free Energy=	0.484131
Sum of electronic and zero-point Energies=	-1355.428798
Sum of electronic and thermal Energies=	-1355.397282
Sum of electronic and thermal Enthalpies=	-1355.396338
Sum of electronic and thermal Free Energies=	-1355.490506

Esol= -1356.3960843

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.080904	-0.200627	-4.468643
2	6	0	-0.382326	1.779499	-2.980067
3	6	0	0.112842	0.339294	-3.046055
4	8	0	-0.672586	-0.490484	-2.183022
5	1	0	0.397748	-1.246414	-4.482809
6	1	0	-0.933253	-0.124343	-4.865442
7	1	0	-0.352632	2.151431	-1.952506
8	1	0	-1.409700	1.829713	-3.344909
9	6	0	-4.066654	-1.383688	-1.736993
10	6	0	-4.088888	-0.788772	-3.185192
11	8	0	-2.827176	-0.083206	-3.241413
12	5	0	-2.001566	-0.700901	-2.322537
13	8	0	-2.656820	-1.597372	-1.513701
14	6	0	-4.794975	-2.707204	-1.583791
15	6	0	-4.541119	-0.386334	-0.683219
16	6	0	-5.212066	0.195497	-3.457103
17	6	0	-4.044770	-1.864768	-4.266722
18	1	0	-4.722073	-3.049369	-0.548167
19	1	0	-5.855061	-2.594628	-1.832213
20	1	0	-4.362799	-3.476538	-2.225704
21	1	0	-4.294329	-0.777204	0.306866
22	1	0	-4.037995	0.577481	-0.801401
23	1	0	-5.621621	-0.225862	-0.735285
24	1	0	-5.141132	0.562876	-4.484562
25	1	0	-6.185925	-0.288886	-3.335887
26	1	0	-5.161231	1.054072	-2.785650
27	1	0	-4.994805	-2.401075	-4.341446
28	1	0	-3.838749	-1.391086	-5.230066
29	1	0	-3.250962	-2.589419	-4.064606
30	6	0	7.018705	-1.480524	-5.606700
31	6	0	6.430545	-2.926332	-5.473106
32	8	0	5.397863	-2.745736	-4.471012
33	5	0	5.041624	-1.424157	-4.541363
34	8	0	5.862337	-0.652188	-5.322889
35	6	0	7.541654	-1.130278	-6.987459
36	6	0	8.061765	-1.165121	-4.538819
37	6	0	7.413471	-3.970317	-4.975793
38	6	0	5.736776	-3.403659	-6.745395
39	1	0	7.924635	-0.106422	-6.988084

40	1	0	8.360360	-1.799674	-7.268805
41	1	0	6.756030	-1.199434	-7.741304
42	1	0	8.265121	-0.091474	-4.549132
43	1	0	7.697664	-1.433337	-3.543057
44	1	0	8.999085	-1.697079	-4.722598
45	1	0	6.916330	-4.941400	-4.906645
46	1	0	8.254480	-4.067412	-5.669384
47	1	0	7.799874	-3.715902	-3.987775
48	1	0	6.459042	-3.637873	-7.532140
49	1	0	5.166279	-4.307878	-6.518981
50	1	0	5.042480	-2.647832	-7.123207
51	6	0	2.578470	1.017035	-3.235968
52	6	0	3.626431	0.472583	-3.863337
53	7	0	3.907769	-0.891229	-3.851503
54	6	0	3.061543	-1.706445	-3.096316
55	6	0	1.996748	-1.248719	-2.432736
56	6	0	1.568845	0.203454	-2.455967
57	6	0	1.539700	0.706678	-1.065190
58	7	0	1.557254	1.121181	0.019481
59	1	0	2.455175	2.093081	-3.260825
60	1	0	4.336759	1.073190	-4.419335
61	1	0	3.341567	-2.753127	-3.082769
62	1	0	1.384171	-1.930250	-1.856741
63	1	0	0.234322	2.428032	-3.607756
64	1	0	0.759554	0.372294	-5.105558

TS3

Thermal correction to Energy= 0.573042
Thermal correction to Enthalpy= 0.573986
Thermal correction to Gibbs Free Energy= 0.476214
Sum of electronic and zero-point Energies= -1355.372076
Sum of electronic and thermal Energies= -1355.339549
Sum of electronic and thermal Enthalpies= -1355.338605
Sum of electronic and thermal Free Energies= -1355.436377
Esol= -1356.3351232
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.003218	-0.984445	-6.908764
2	6	0	4.409659	-0.747976	-7.861821

3	6	0	3.191586	-0.157872	-7.245583
4	8	0	3.022813	1.169457	-7.542960
5	1	0	1.359623	-0.472478	-6.185292
6	1	0	1.381432	-1.211315	-7.787885
7	1	0	5.314240	-0.193707	-7.592524
8	1	0	4.338817	-0.740529	-8.961922
9	6	0	0.333476	3.493771	-7.713928
10	6	0	-0.375461	2.145840	-8.098288
11	8	0	0.746822	1.271594	-8.381373
12	5	0	1.814646	1.790954	-7.697271
13	8	0	1.601876	3.040067	-7.178472
14	6	0	-0.383015	4.302925	-6.648183
15	6	0	0.659282	4.361360	-8.926007
16	6	0	-1.253201	2.221773	-9.334910
17	6	0	-1.139634	1.519911	-6.938266
18	1	0	0.187314	5.210934	-6.433813
19	1	0	-1.375293	4.602505	-7.000171
20	1	0	-0.493664	3.742543	-5.718411
21	1	0	1.325004	5.169139	-8.611817
22	1	0	1.170104	3.781537	-9.700314
23	1	0	-0.242306	4.803863	-9.358352
24	1	0	-1.698547	1.242495	-9.529847
25	1	0	-2.065004	2.939950	-9.184146
26	1	0	-0.681596	2.517090	-10.216276
27	1	0	-2.045920	2.083171	-6.701877
28	1	0	-1.425338	0.501257	-7.213688
29	1	0	-0.529650	1.475775	-6.034381
30	6	0	7.240279	-2.130782	-4.624908
31	6	0	6.397317	-3.407294	-4.293416
32	8	0	5.231577	-2.837894	-3.638037
33	5	0	5.112016	-1.577363	-4.164511
34	8	0	6.204719	-1.143575	-4.868552
35	6	0	8.105630	-2.239392	-5.866902
36	6	0	8.058783	-1.637814	-3.436342
37	6	0	7.060330	-4.392484	-3.352076
38	6	0	5.882985	-4.094351	-5.555868
39	1	0	8.644706	-1.301218	-6.022017
40	1	0	8.842664	-3.040250	-5.753257
41	1	0	7.505847	-2.435963	-6.756661
42	1	0	8.436825	-0.636532	-3.656806
43	1	0	7.444884	-1.580380	-2.533140
44	1	0	8.910801	-2.293732	-3.238073
45	1	0	6.392390	-5.239095	-3.173010
46	1	0	7.986267	-4.776590	-3.790950

47	1	0	7.291654	-3.931870	-2.390374
48	1	0	6.679268	-4.612146	-6.096108
49	1	0	5.110251	-4.817188	-5.284554
50	1	0	5.440893	-3.337821	-6.210007
51	6	0	2.748506	1.269676	-4.484821
52	6	0	3.841215	0.468198	-4.650263
53	7	0	3.931812	-0.777847	-4.018144
54	6	0	2.829704	-1.233392	-3.292313
55	6	0	1.714863	-0.481483	-3.138811
56	6	0	1.630036	0.821373	-3.738070
57	6	0	0.486003	1.627294	-3.591870
58	7	0	-0.467122	2.299512	-3.489047
59	1	0	2.721252	2.232909	-4.979378
60	1	0	4.728911	0.788364	-5.175487
61	1	0	2.942886	-2.219371	-2.860571
62	1	0	0.884220	-0.870840	-2.562431
63	1	0	4.533883	-1.788128	-7.549548
64	1	0	2.329023	-1.929337	-6.465153

Int4

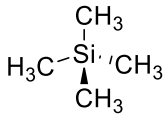
Thermal correction to Energy= 0.577588
Thermal correction to Enthalpy= 0.578532
Thermal correction to Gibbs Free Energy= 0.484547
Sum of electronic and zero-point Energies= -1355.432831
Sum of electronic and thermal Energies= -1355.401348
Sum of electronic and thermal Enthalpies= -1355.400404
Sum of electronic and thermal Free Energies= -1355.494389
Esol= -1356.3989738
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.975524	-0.779981	-5.727502
2	6	0	3.219309	-0.504237	-6.823707
3	6	0	2.313877	-0.054768	-5.683689
4	8	0	2.118805	1.368004	-5.748566
5	1	0	0.309157	-0.405385	-4.947479
6	1	0	0.504393	-0.626614	-6.700162
7	1	0	4.181534	0.010718	-6.780434
8	1	0	2.733926	-0.292938	-7.778913
9	6	0	0.808875	3.758459	-8.006922

10	6	0	0.196625	2.429974	-8.565438
11	8	0	1.014208	1.426475	-7.918907
12	5	0	1.484320	2.007625	-6.757781
13	8	0	1.258916	3.361806	-6.693956
14	6	0	-0.179153	4.902323	-7.862341
15	6	0	2.041798	4.211174	-8.785249
16	6	0	0.306497	2.255553	-10.069241
17	6	0	-1.239026	2.200279	-8.101588
18	1	0	0.332375	5.781916	-7.462741
19	1	0	-0.606557	5.168703	-8.834144
20	1	0	-0.990040	4.643963	-7.179640
21	1	0	2.544236	5.000081	-8.220100
22	1	0	2.746815	3.385238	-8.916514
23	1	0	1.776875	4.604267	-9.770764
24	1	0	-0.134463	1.299221	-10.363323
25	1	0	-0.233299	3.052863	-10.589450
26	1	0	1.347283	2.264808	-10.396723
27	1	0	-1.937432	2.877009	-8.601448
28	1	0	-1.526988	1.172098	-8.335415
29	1	0	-1.328827	2.342636	-7.021036
30	6	0	7.009794	-1.783036	-4.964600
31	6	0	6.570235	-3.285741	-4.950790
32	8	0	5.315311	-3.230857	-4.227681
33	5	0	4.833129	-1.958735	-4.418260
34	8	0	5.735728	-1.092917	-4.984073
35	6	0	7.807299	-1.362476	-6.185524
36	6	0	7.723156	-1.362106	-3.683432
37	6	0	7.515125	-4.219450	-4.217081
38	6	0	6.256213	-3.822208	-6.344327
39	1	0	8.056495	-0.300506	-6.114236
40	1	0	8.742233	-1.927805	-6.247885
41	1	0	7.240695	-1.517144	-7.105000
42	1	0	7.800342	-0.272190	-3.664227
43	1	0	7.163022	-1.679581	-2.799460
44	1	0	8.731180	-1.781916	-3.627643
45	1	0	7.125423	-5.240229	-4.251190
46	1	0	8.502224	-4.216209	-4.689601
47	1	0	7.625300	-3.932981	-3.170160
48	1	0	7.165388	-3.970571	-6.933236
49	1	0	5.746354	-4.783837	-6.246211
50	1	0	5.596908	-3.139814	-6.888434
51	6	0	2.179394	0.281913	-3.178079
52	6	0	3.039718	-0.204825	-4.307460
53	7	0	3.509839	-1.571105	-4.051867

54	6	0	2.697191	-2.453139	-3.355646
55	6	0	1.674984	-2.034101	-2.586450
56	6	0	1.495262	-0.598014	-2.414260
57	6	0	0.620338	-0.129976	-1.383327
58	7	0	-0.103612	0.229692	-0.546668
59	1	0	2.084026	1.350614	-3.033115
60	1	0	3.924585	0.434323	-4.388324
61	1	0	2.983871	-3.496342	-3.430972
62	1	0	1.058624	-2.735334	-2.040723
63	1	0	3.400640	-1.580637	-6.763128
64	1	0	1.120589	-1.851248	-5.571773

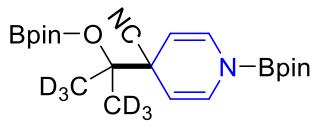
NMR



TMS

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.504440	0.481018	0.000000
2	6	0	0.124746	1.366880	1.536657
3	1	0	-0.223110	2.399899	1.569001
4	1	0	-0.219835	0.873517	2.446090
5	1	0	1.214819	1.384552	1.563284
6	6	0	0.123155	-1.293638	0.000080
7	1	0	-0.223532	-1.836099	0.880295
8	1	0	-0.223465	-1.836158	-0.880124
9	1	0	1.213142	-1.326371	0.000124
10	6	0	-2.386417	0.480313	-0.000072
11	1	0	-2.782925	1.496155	-0.000116
12	1	0	-2.780923	-0.028316	-0.880309
13	1	0	-2.780991	-0.028265	0.880163
14	6	0	0.124860	1.366784	-1.536665
15	1	0	1.214934	1.384461	-1.563211
16	1	0	-0.219649	0.873360	-2.446094
17	1	0	-0.223000	2.399800	-1.569104

Int3



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.571266	-1.676317	-1.604782
2	6	0	-0.519504	-1.405027	-3.868533
3	6	0	-0.474166	-0.986304	-2.406198
4	8	0	-0.597007	0.431242	-2.294258
5	1	0	-1.547831	-1.366829	-0.562018
6	1	0	-2.542172	-1.422501	-2.021984
7	1	0	0.243604	-0.884569	-4.442998
8	1	0	-1.496051	-1.170654	-4.284551
9	6	0	-2.720810	3.137233	-3.139048
10	6	0	-3.712399	1.921973	-3.248110
11	8	0	-2.809590	0.793215	-3.256421
12	5	0	-1.643180	1.206976	-2.653768
13	8	0	-1.604211	2.561204	-2.437594
14	6	0	-3.239683	4.320757	-2.342470
15	6	0	-2.203598	3.610471	-4.494613
16	6	0	-4.550765	1.886125	-4.512612
17	6	0	-4.608261	1.769709	-2.023212
18	1	0	-2.479936	5.099544	-2.314213
19	1	0	-4.133369	4.739648	-2.804471
20	1	0	-3.472385	4.045611	-1.317947
21	1	0	-1.380037	4.302577	-4.331364
22	1	0	-1.829361	2.780125	-5.091257
23	1	0	-2.975136	4.125429	-5.064249
24	1	0	-5.191305	1.005978	-4.502369
25	1	0	-5.190901	2.765547	-4.575509
26	1	0	-3.933542	1.842200	-5.405198
27	1	0	-5.359947	2.555540	-1.977716
28	1	0	-5.121248	0.811345	-2.077160
29	1	0	-4.030258	1.791958	-1.101192
30	6	0	6.477422	-3.118098	-4.789628
31	6	0	5.827022	-4.547746	-4.707061
32	8	0	4.747448	-4.339224	-3.765304
33	5	0	4.454355	-3.003514	-3.795300
34	8	0	5.352500	-2.253376	-4.502820
35	6	0	7.040241	-2.745775	-6.148299

36	6	0	7.518378	-2.868113	-3.704130
37	6	0	6.736033	-5.636572	-4.168633
38	6	0	5.192944	-4.995872	-6.019248
39	1	0	7.447235	-1.737148	-6.110093
40	1	0	7.846341	-3.422148	-6.430348
41	1	0	6.278240	-2.771218	-6.921636
42	1	0	7.773979	-1.810558	-3.698629
43	1	0	7.138139	-3.126896	-2.717593
44	1	0	8.428201	-3.437646	-3.883619
45	1	0	6.194629	-6.580049	-4.133864
46	1	0	7.602071	-5.770215	-4.815878
47	1	0	7.083572	-5.411698	-3.164718
48	1	0	5.947313	-5.240125	-6.764771
49	1	0	4.595605	-5.886548	-5.835168
50	1	0	4.537788	-4.229858	-6.430129
51	6	0	2.033538	-0.501210	-2.519683
52	6	0	3.077622	-1.066787	-3.119258
53	7	0	3.308764	-2.440438	-3.142784
54	6	0	2.390825	-3.231839	-2.464507
55	6	0	1.315437	-2.754410	-1.840361
56	6	0	0.960093	-1.285390	-1.798137
57	6	0	0.949961	-0.856552	-0.384028
58	7	0	0.975481	-0.557824	0.726690
59	1	0	1.936178	0.571938	-2.530484
60	1	0	3.822185	-0.474708	-3.627855
61	1	0	2.614262	-4.287311	-2.466017
62	1	0	0.685307	-3.447040	-1.305016
63	1	0	-0.349424	-2.475252	-3.964994
64	1	0	-1.462492	-2.757869	-1.650500

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