

Rh^{III}-promoted directed C–H *N*-heteroarylation of 2-pyridones

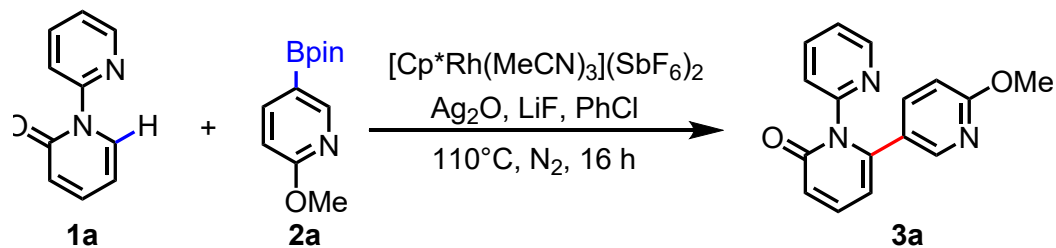
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1. Experiments

Table S1 Control experiments

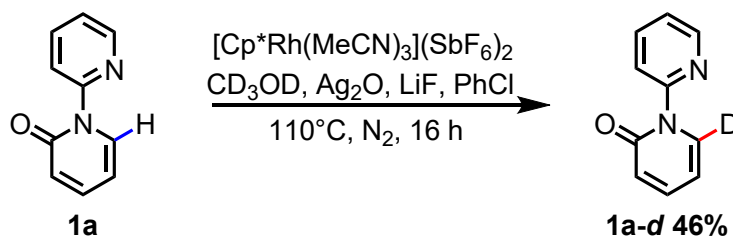


entry	Cat.	oxidant	base	solvent	yield(%) ^a
1	$[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$	Ag_2O	LiF	PhCl	82
2 ^b	—	Ag_2O	LiF	PhCl	nr
3 ^c	$[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$	—	LiF	PhCl	nr
4 ^d	$[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$	Ag_2O	—	PhCl	71

^aConditions: **1a** (17.2 mg, 0.1 mmol), **2a** (47.9 mg, 0.2 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (8.3 mg, 0.01 mmol), Oxidant (0.2 mmol), Base (0.2 mmol) in 2 mL dry PhCl, 110 °C, 16 h, N_2 atmosphere. Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. ^bWithout catalyst. ^cWithout Ag_2O . ^dWithout LiF.

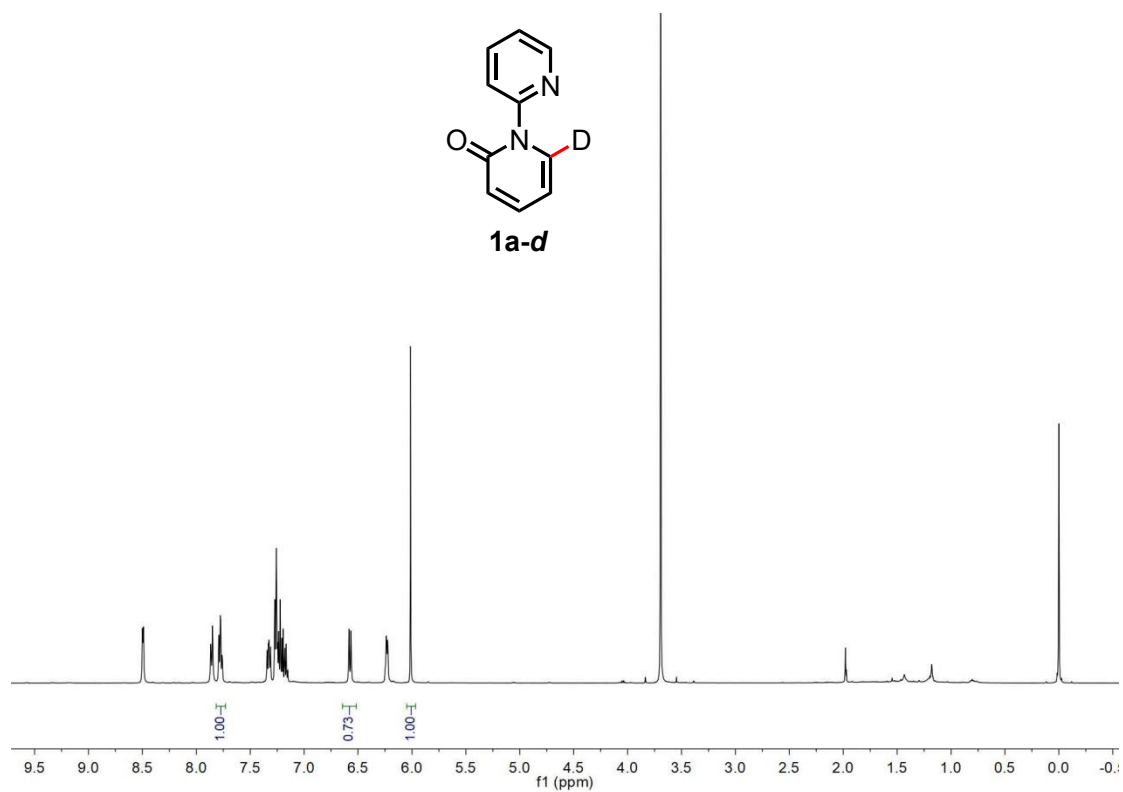
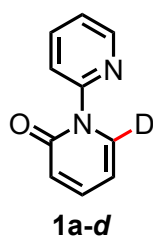
2. Control experiments

2.1 H/D exchange experiment

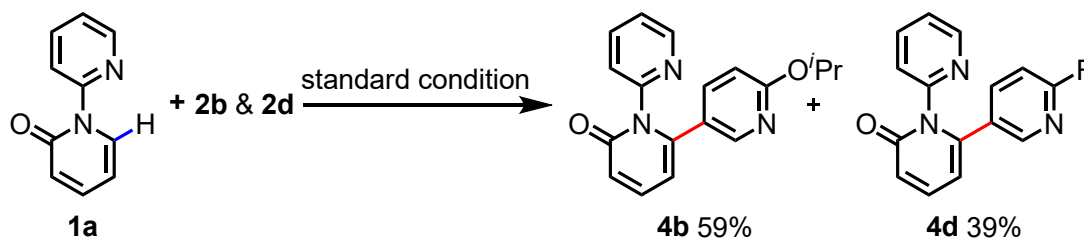


To a 25 mL Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate **1a** (0.1 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (8.3 mg, 0.01 mmol), Ag_2O (46.3 mg, 0.2 mmol), LiF (5.2 mg, 0.2 mmol), CD_3OD (10 equiv.) and dry PhCl (2.0 mL) under N_2 atmosphere. The tube was capped, and subjected to a 110 °C

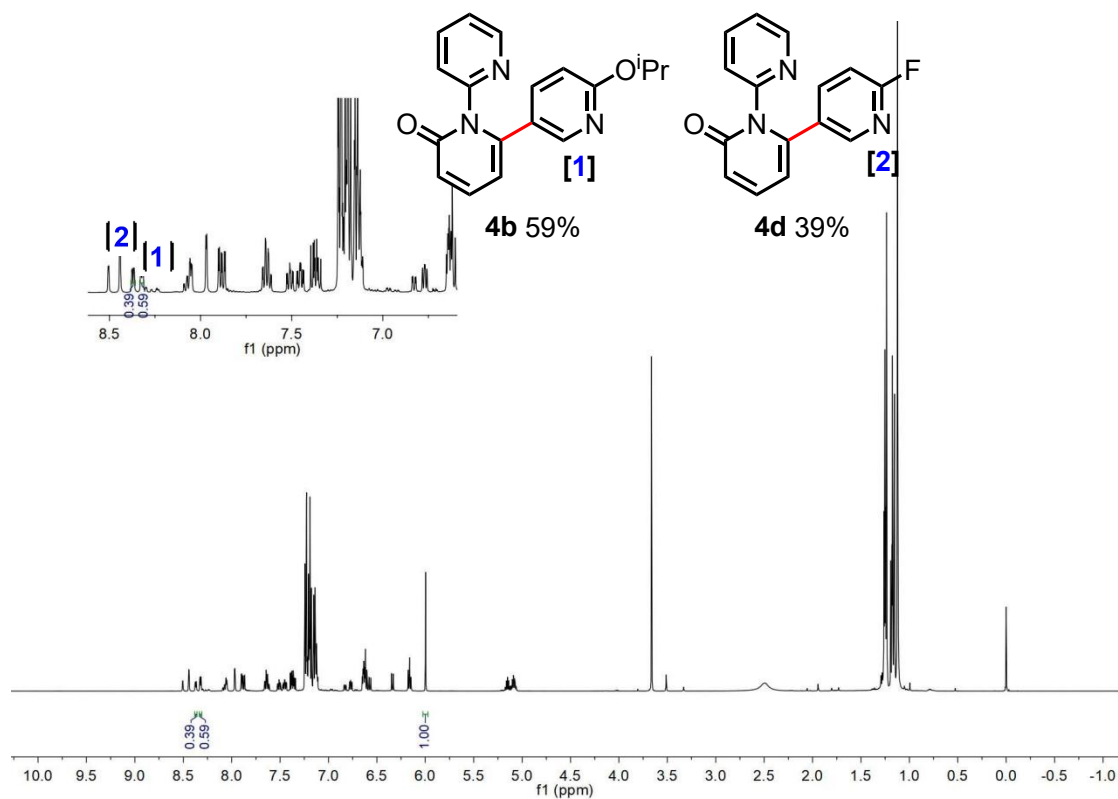
preheated oil bath for 16 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude products. The ratio was identified by ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard.



2.2 Competitive experiments

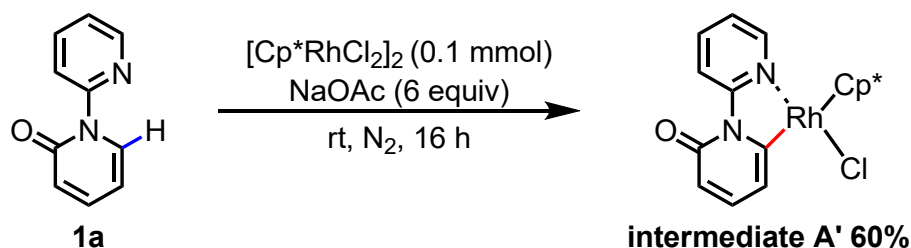


To a 25 mL Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate **1a** (0.1 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (8.3 mg, 0.01 mmol), heteroaryl acid pinacol esters **2b** (0.2 mmol) and **2d** (0.2 mmol), Ag₂O (46.3 mg, 0.2 mmol), LiF (5.2 mg, 0.2 mmol) and dry PhCl (2.0 mL) under N₂ atmosphere. The tube was capped, and subjected to a 110 °C preheated oil bath for 16 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude products. The yields of the products (**4b** 59% and **4d** 39%) was determined by ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard.

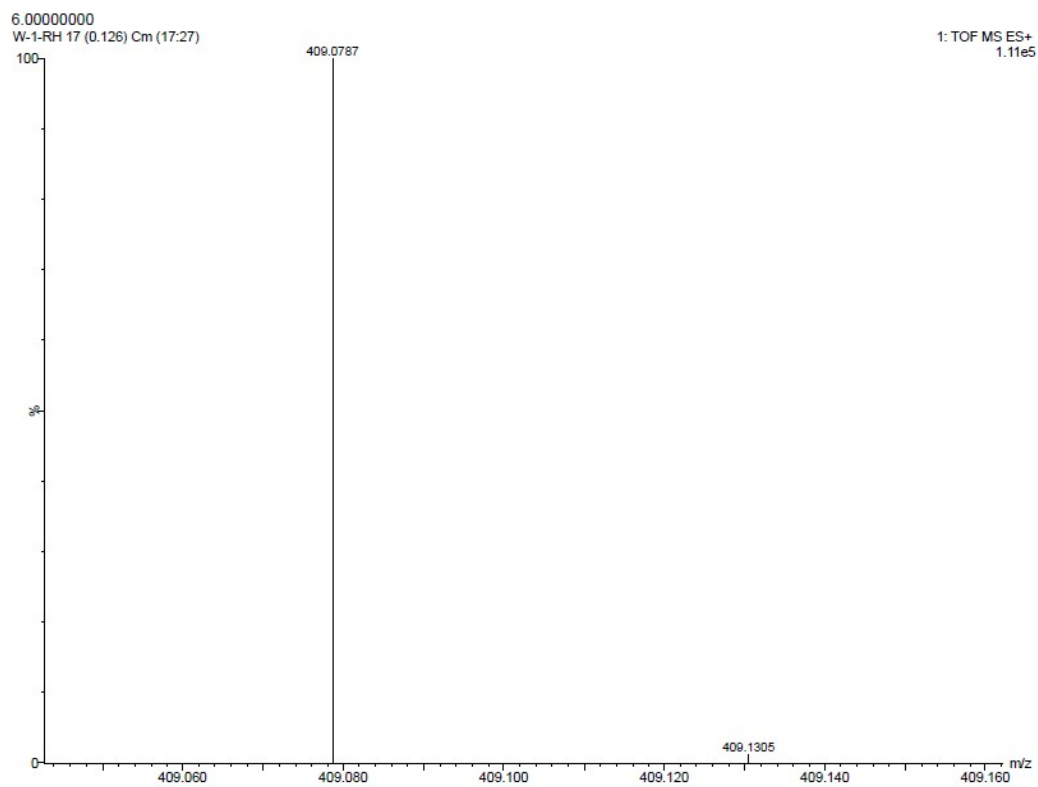
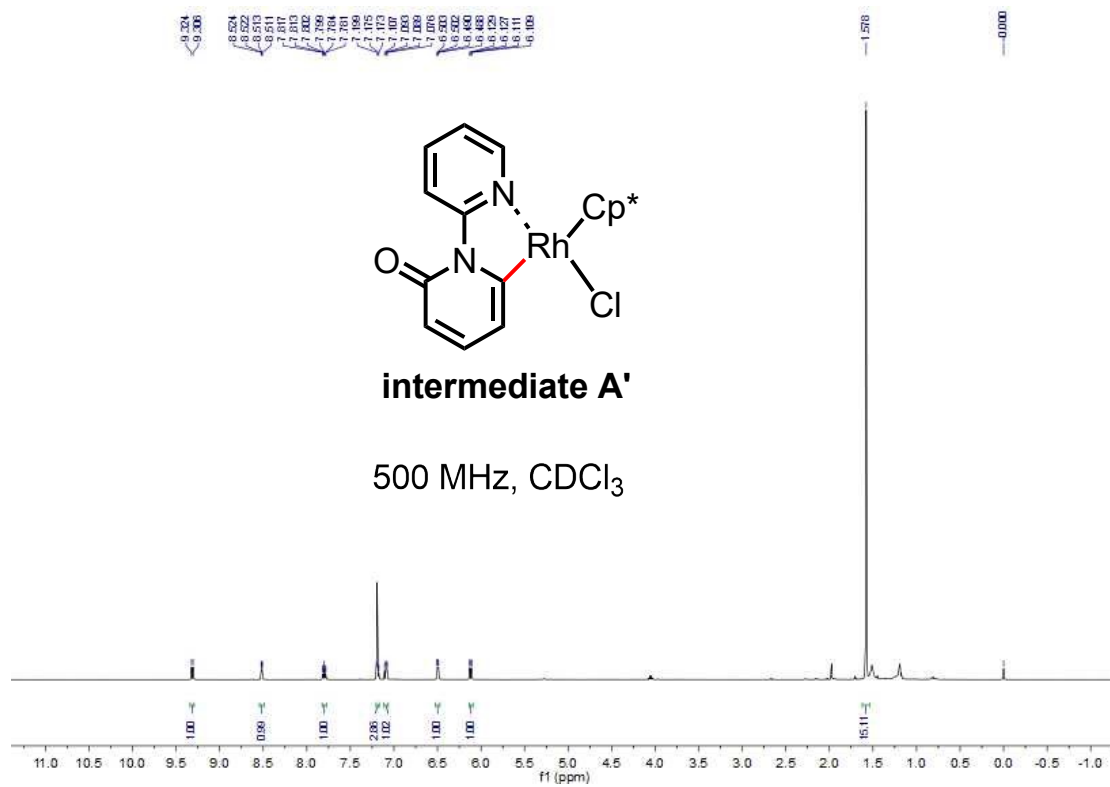


2.3 Catalytic activity of intermediate A'

Preparation and Characterization of Intermediate A'^[1]



An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was sequentially charged with **1a** (36.1 mg, 0.21 mmol), [Cp*RhCl₂]₂ (31.2 mg, 0.1 mmol), NaOAc (49.2 mg, 0.6 mmol) were stirred overnight in CH₂Cl₂ (6 mL) at room temperature. The solvent was then removed under reduced pressure, and the residue was dissolved in CH₂Cl₂, and filtered to remove NaOAc. Column chromatography was performed on silica gel using EA/PE = 4:1 to afford Rhodium(III) Complex **intermediate A'** in 60% yield. ¹H NMR (500 MHz, CDCl₃): δ 9.32 (d, *J* = 9.0 Hz, 1H), 8.52 (dd, *J*₁ = 5.5 Hz, *J*₂ = 1.0 Hz, 1H), 7.82-7.78 (m, 1H), 7.20-7.17 (m, 1H), 7.09 (dd, *J*₁ = 7.0 Hz, *J*₂ = 15.0 Hz, 1H), 6.50 (dd, *J*₁ = 6.5 Hz, *J*₂ = 0.5 Hz, 1H), 6.12 (dd, *J*₁ = 9.0 Hz, *J*₂ = 1.0 Hz, 1H), 1.58 (s, 15H). HRMS (ESI) *m/z*: [M-Cl]⁺ Calcd for C₂₀H₂₂RhN₂O 409.0787; Found 409.0787.



3. X-ray single crystal data for compound **4k**

General Procedure for Crystal Preparation:

Compounds **4k** (around 20 mg) were dissolved in CDCl₃ (1 ml) separately, and the NMR tube was capped with a closed-top cap. The single crystals were grown by slow evaporation of solvents at room temperature.

X-ray structure determination of compounds **4k**:

Single-crystal X-ray data for Cd-CP were collected on a Siemens Smart CCD diffractometer with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The raw data frames were integrated into SHELX-format reflection files and corrected using SAINT program.² The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELX program.³ Displacement parameters were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Basic information pertaining to crystal parameters and structure refinement are summarized in Table S1 and selected bond lengths and angles are listed in Table S2. CCDC 2254051 (**4k**) contains the supplementary crystallographic data for this paper.

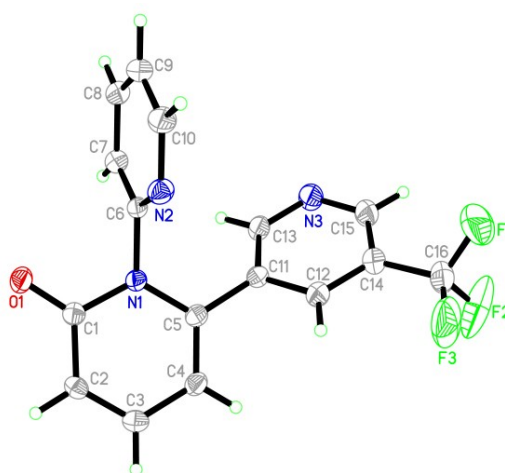


Figure S1. Single crystals of compound **4k**

Table S1. Crystal data and structure refinements for **4k**

Formula	C ₁₆ H ₁₀ F ₃ N ₃ O
Formula weight	317.27
T (K)	298.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a (Å)	14.5478(12)
b (Å)	9.6153(8)
c (Å)	10.2086(9)
α	90
β	101.992(4)
γ	90
V	1396.8(2)
Z	4
Dcalc (g/cm ⁻³)	1.509
F(000)	648.0
2θ for data collection	5.112 to 50.02
Reflections collected	6619
Unique reflections	2463
Goodness-of-fit on F ²	1.101
R ₁ , [I > 2σ]	0.0770
wR ₂ , [I > 2σ]	0.2114

Table S2. Bond lengths [Å] and angles [°] for **4k**

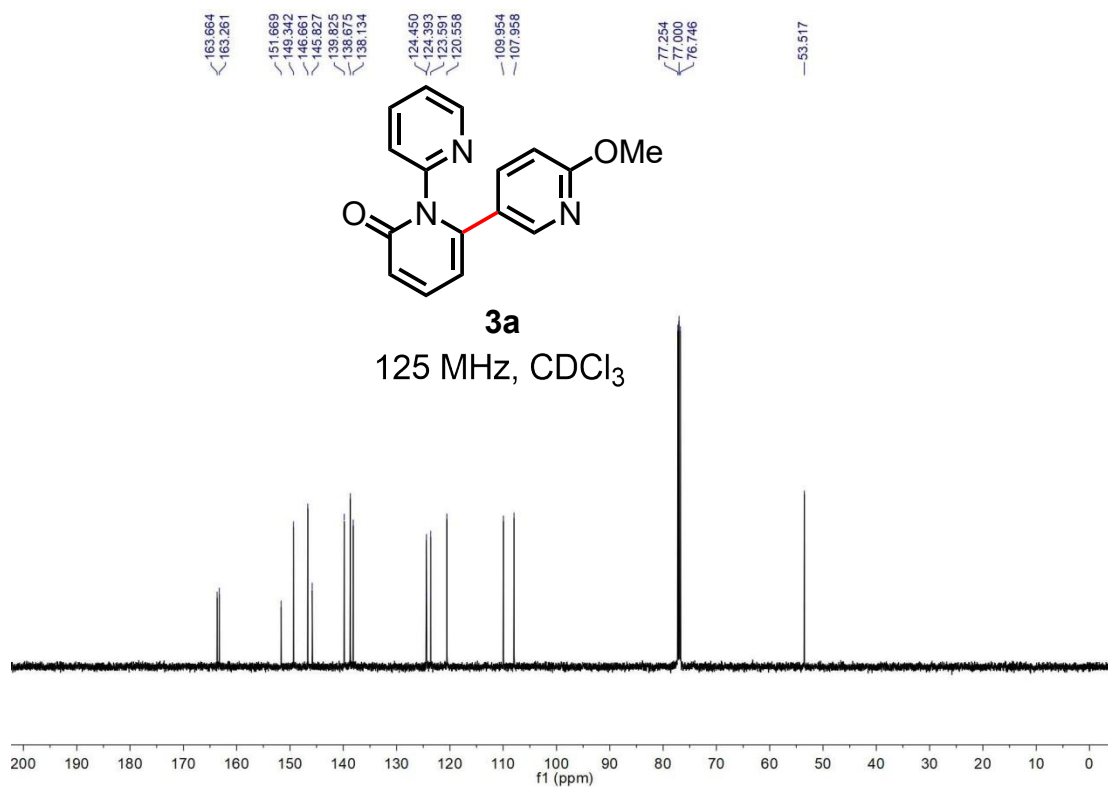
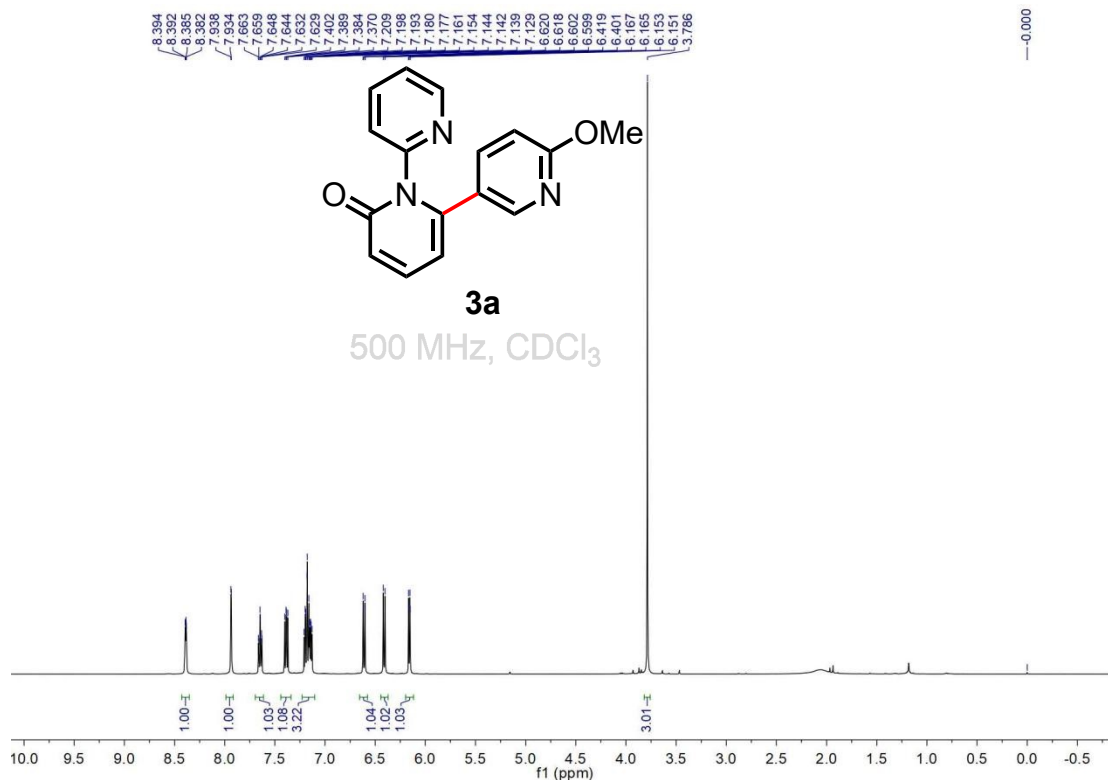
O1-C1	1.223(5)	C3-C4	1.398(6)
N1-C1	1.385(5)	C4-C5	1.328(5)
N1-C5	1.390(5)	C5-C11	1.472(6)
N1-C6	1.440(5)	C6-C7	1.364(6)
N2-C6	1.308(5)	C7-C8	1.370(6)
N2-C10	1.329(5)	C8-C9	1.356(7)
N3-C13	1.324(5)	C9-C10	1.351(7)
N3-C15	1.324(6)	C11-C12	1.374(6)
F1-C16	1.267(6)	C11-C13	1.378(6)
F2-C16	1.272(7)	C12-C14	1.368(6)
F3-C16	1.291(7)	C14-C15	1.364(7)
C1-C2	1.418(5)	C14-C16	1.457(7)
C2-C3	1.341(6)		
C1-N1-C5	122.6(3)	C9-C8-C7	118.9(4)
C1-N1-C6	117.2(3)	C10-C9-C8	119.4(4)
C5-N1-C6	119.1(3)	N2-C10-C9	123.2(4)
C6-N2-C10	116.2(4)	C12-C11-C5	120.1(4)

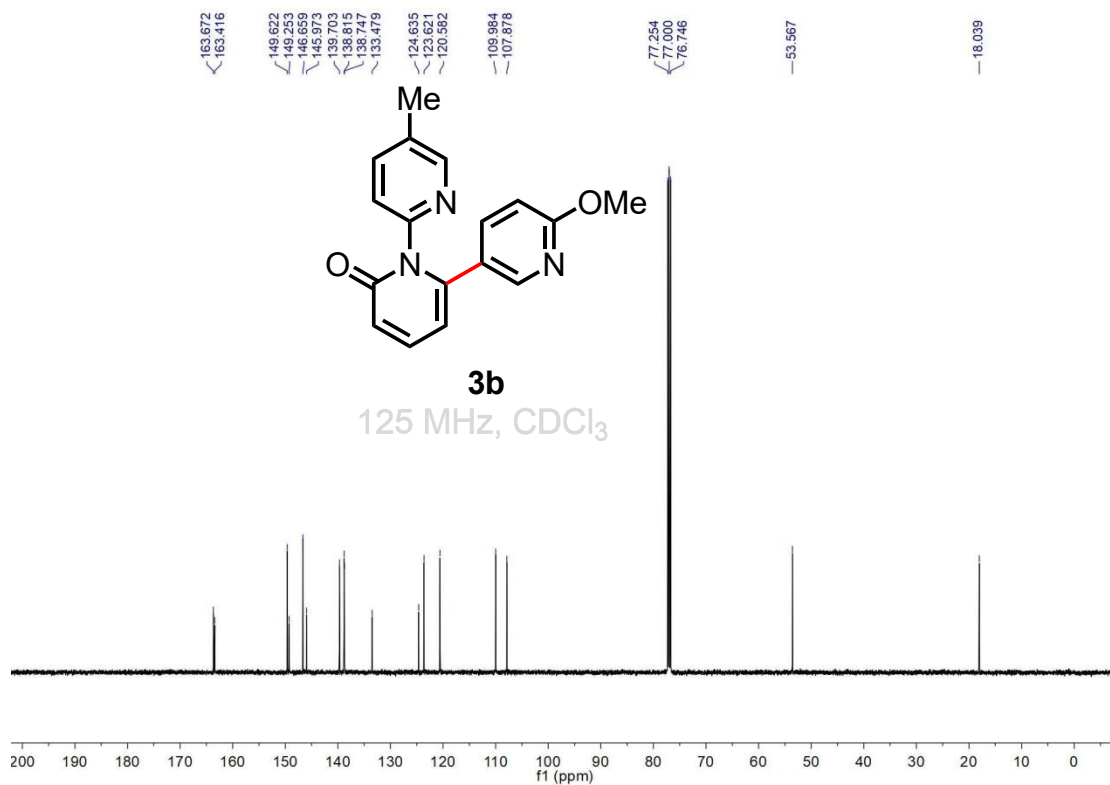
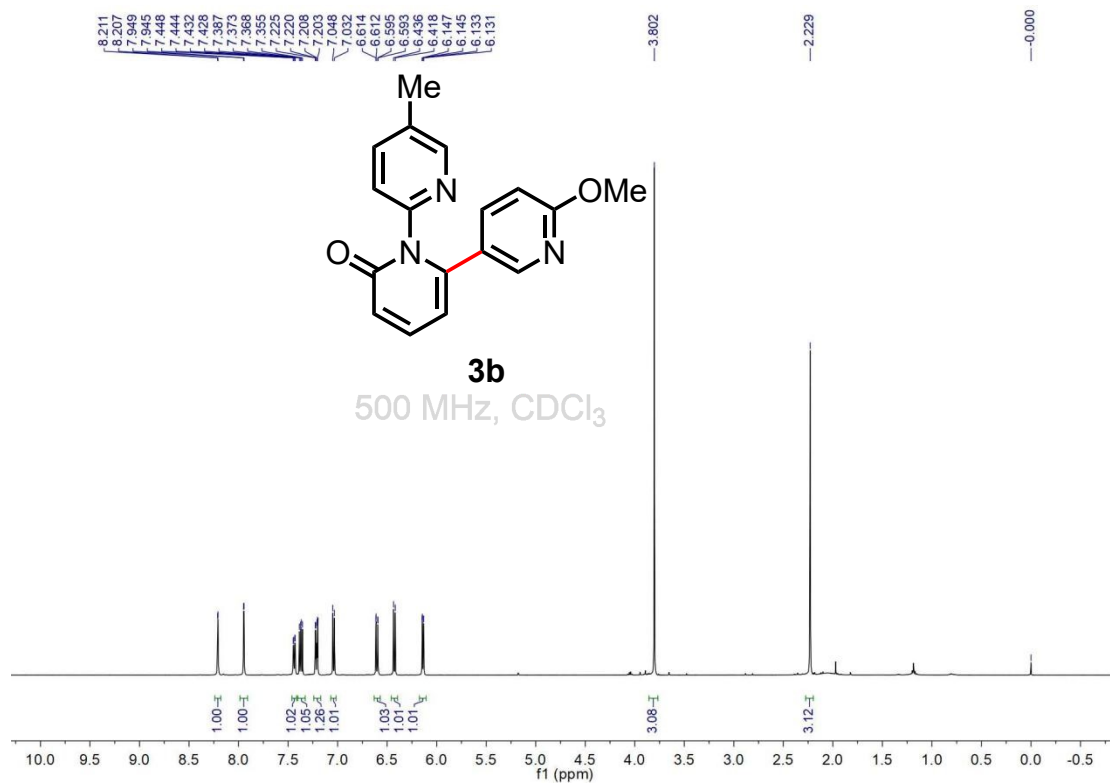
C13-N3-C15	116.9(4)	C12-C11-C13	117.5(4)
O1-C1-N1	120.0(3)	C13-C11-C5	122.1(4)
O1-C1-C2	124.3(4)	C14-C12-C11	119.0(4)
N1-C1-C2	115.7(3)	N3-C13-C11	124.1(4)
C3-C2-C1	121.4(4)	C12-C14-C16	121.5(5)
C2-C3-C4	120.3(4)	C15-C14-C12	119.0(4)
C5-C4-C3	120.6(4)	C15-C14-C16	119.5(4)
N1-C5-C11	119.1(3)	N3-C15-C14	123.4(4)
C4-C5-N1	119.2(4)	F1-C16-F2	105.9(6)
C4-C5-C11	121.6(4)	F1-C16-F3	104.0(6)
N2-C6-N1	114.4(3)	F1-C16-C14	114.7(5)
N2-C6-C7	125.1(4)	F2-C16-F3	101.5(5)
C7-C6-N1	120.5(4)	F2-C16-C14	114.3(5)
C6-C7-C8	117.1(4)	F3-C16-C14	115.0(5)

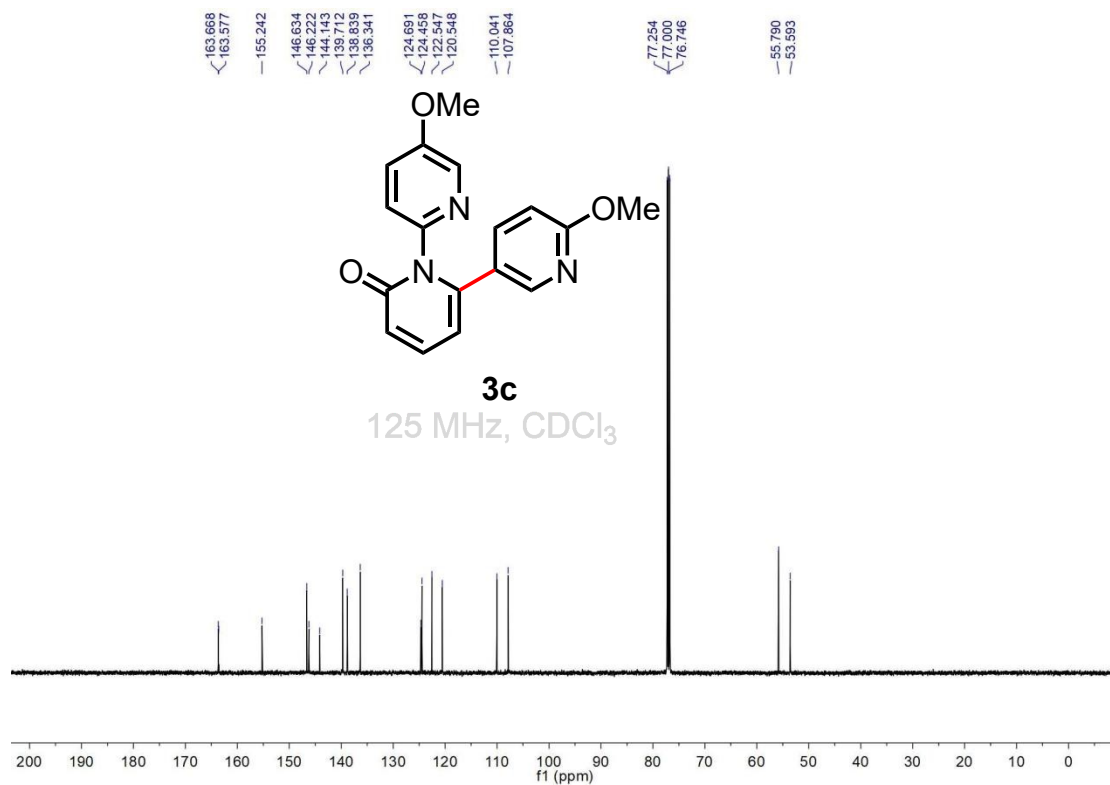
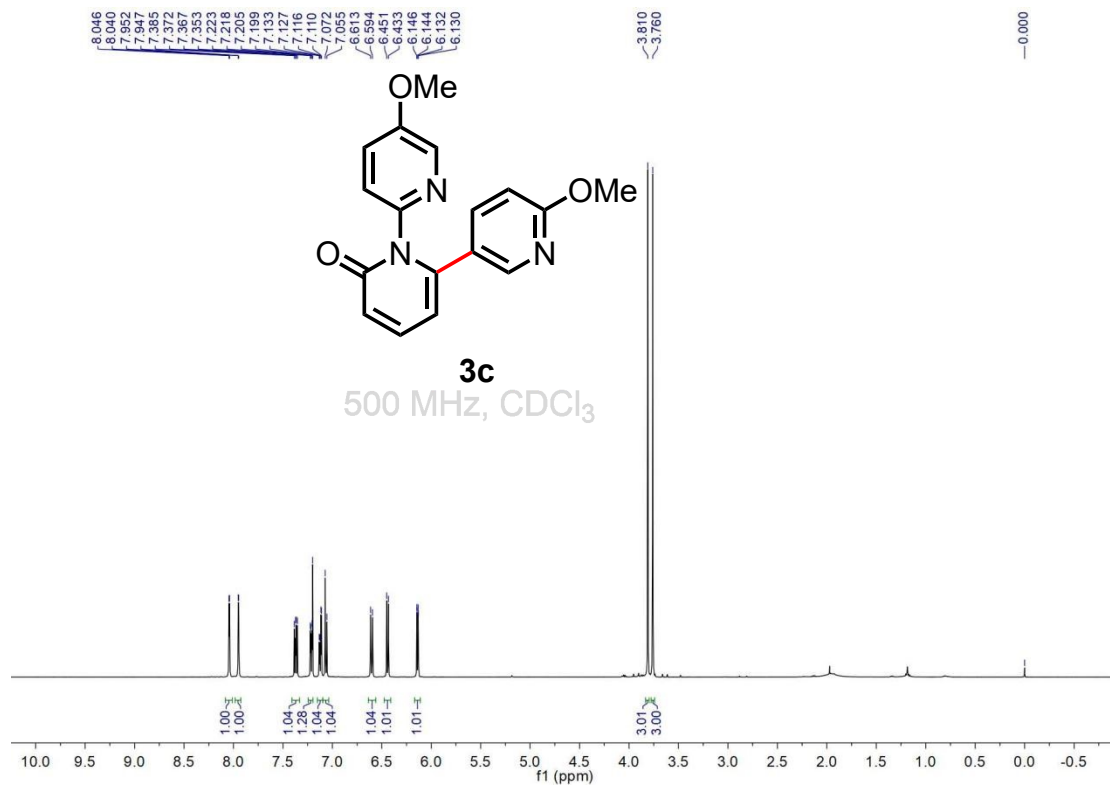
4. References

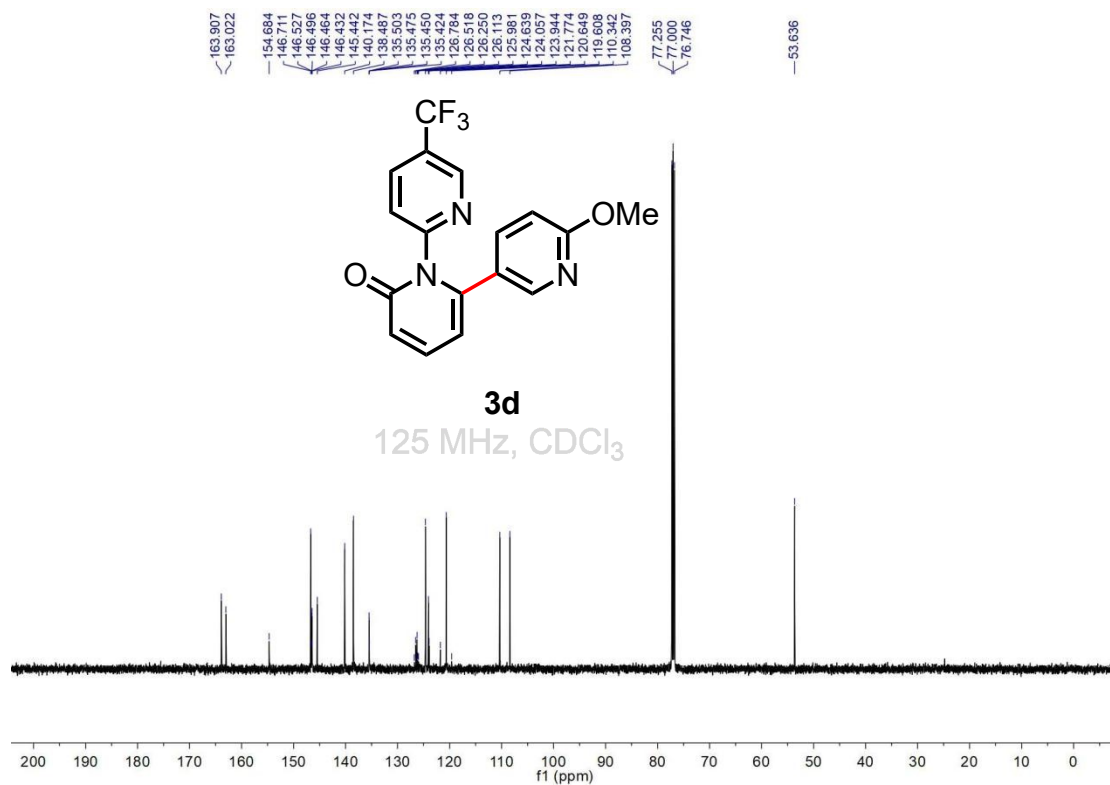
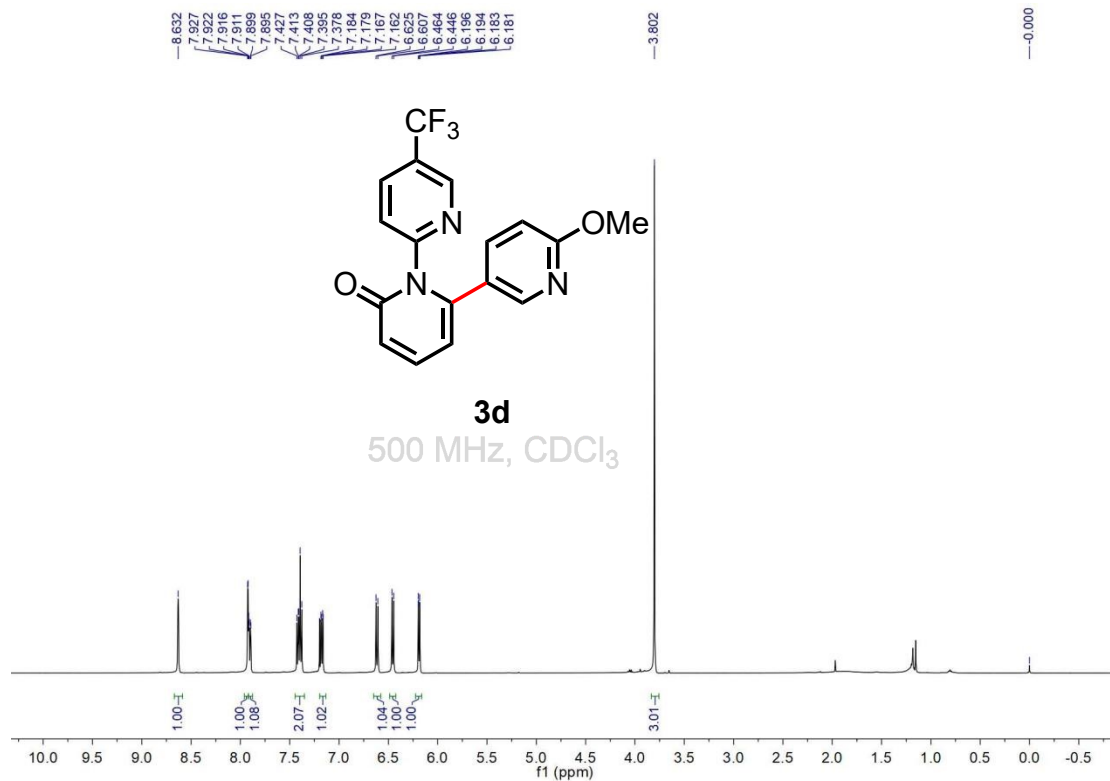
1. Huang, G.; Shan, Y.-J.; Yu, J.-T.; Pan, C.-D. Rh^{III}-Catalyzed C6-Selective Oxidative C–H/C–H Crosscoupling of 2-Pyridones with Thiophenes. *Chem. Eur. J.*, **2021**, *27*, 12294–12299.
2. SAINT, *Version 6.02a*, Bruker AXS Inc, Madison, WI, **2002**.
3. (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*, Göttingen University, Göttingen, Germany, **1997**; (b) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sec. C: Struct. Chem.* **2015**, *71*, 3.

5. NMR Spectra



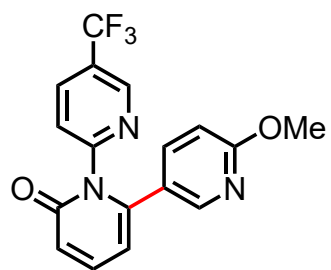






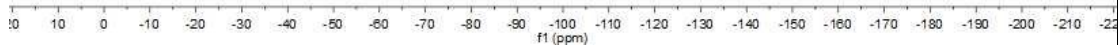
^{19}F NMR spectrum

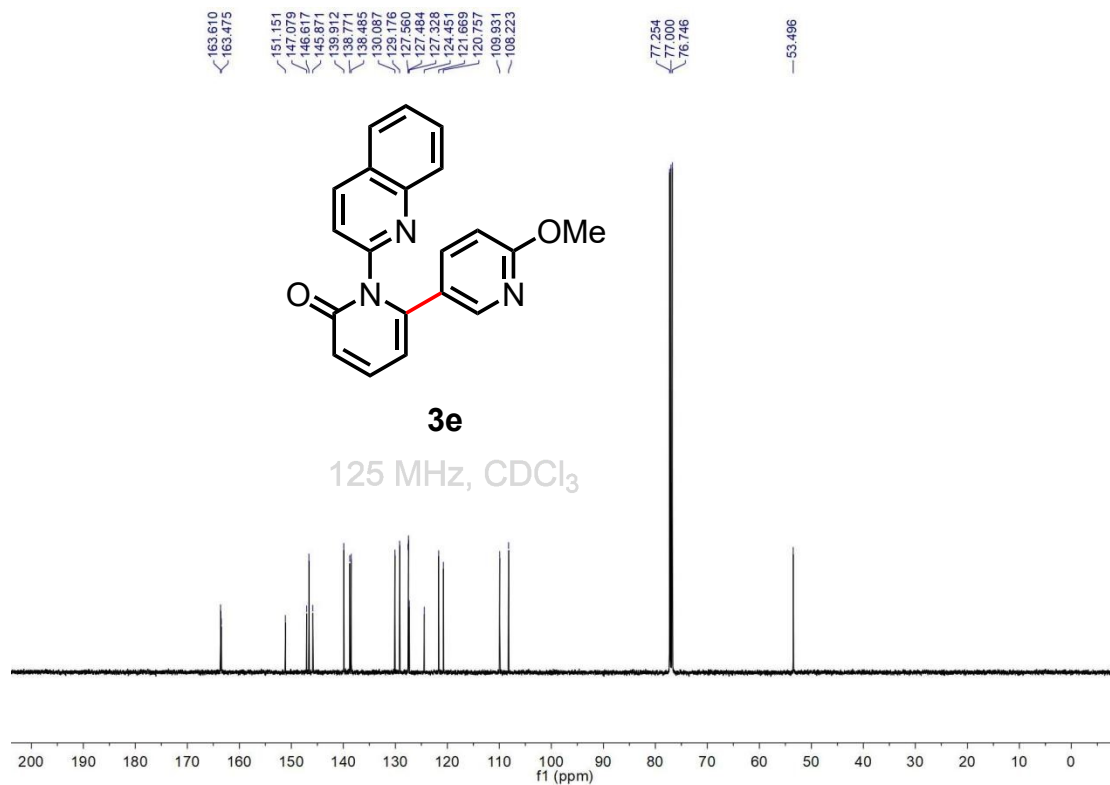
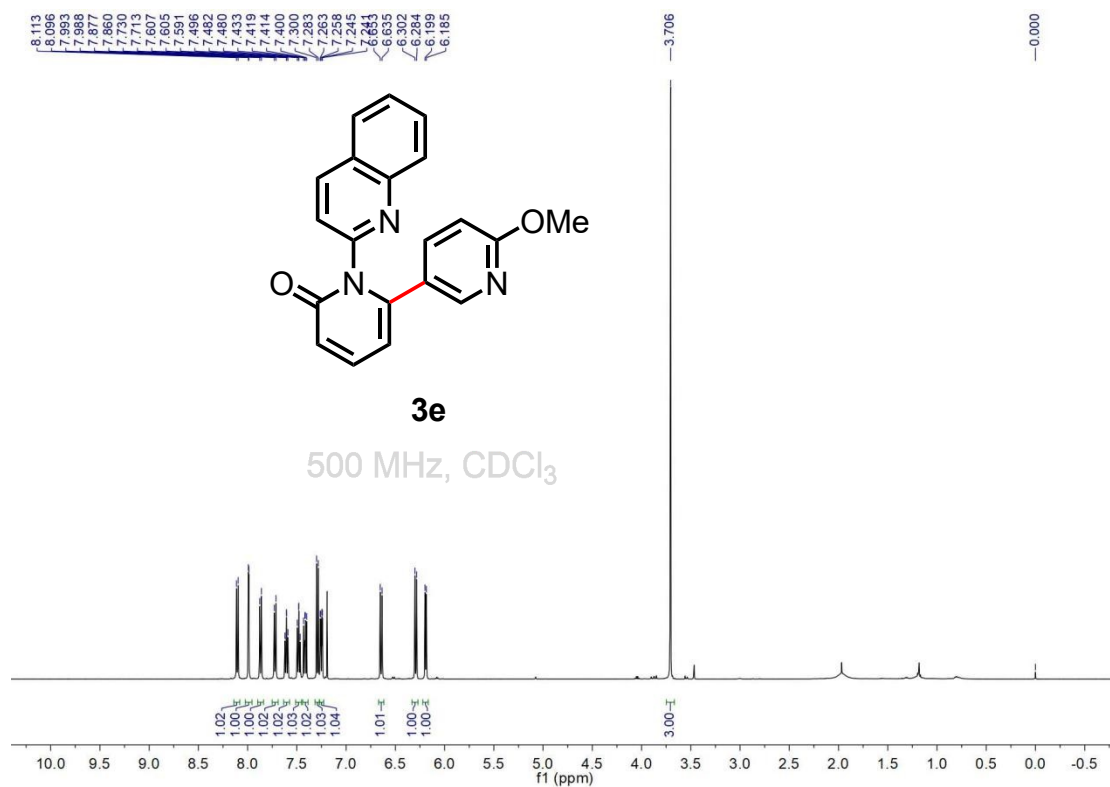
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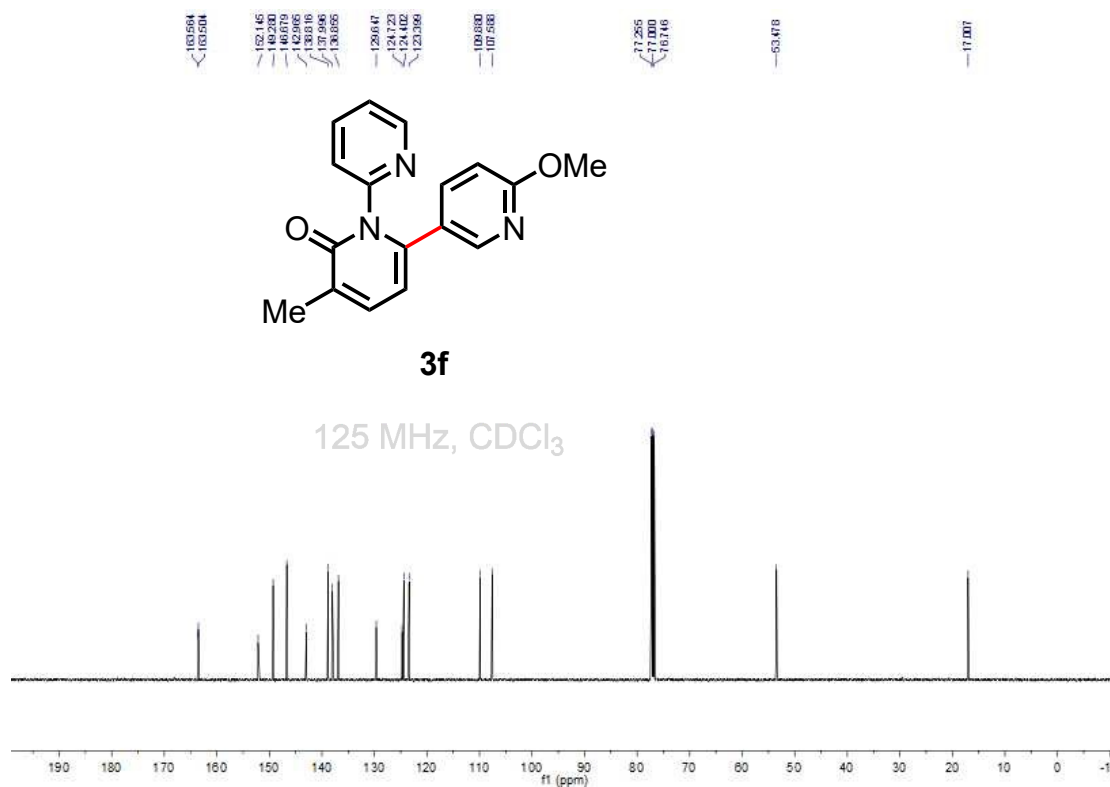
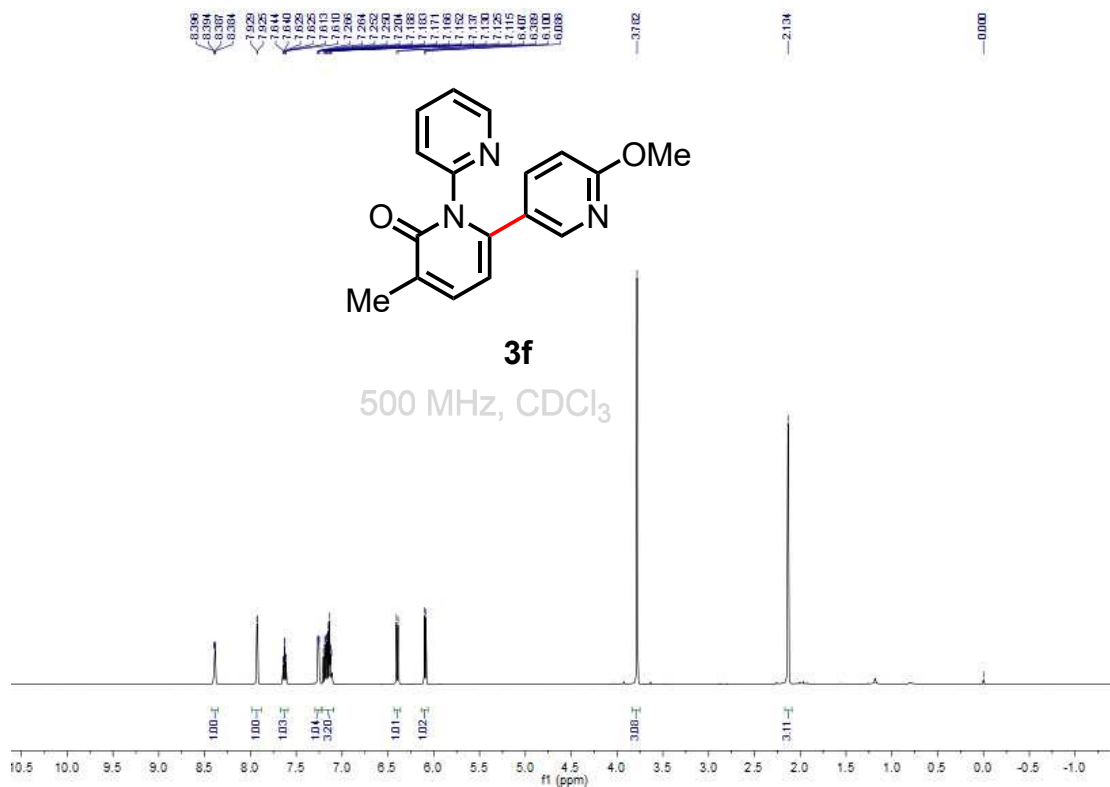


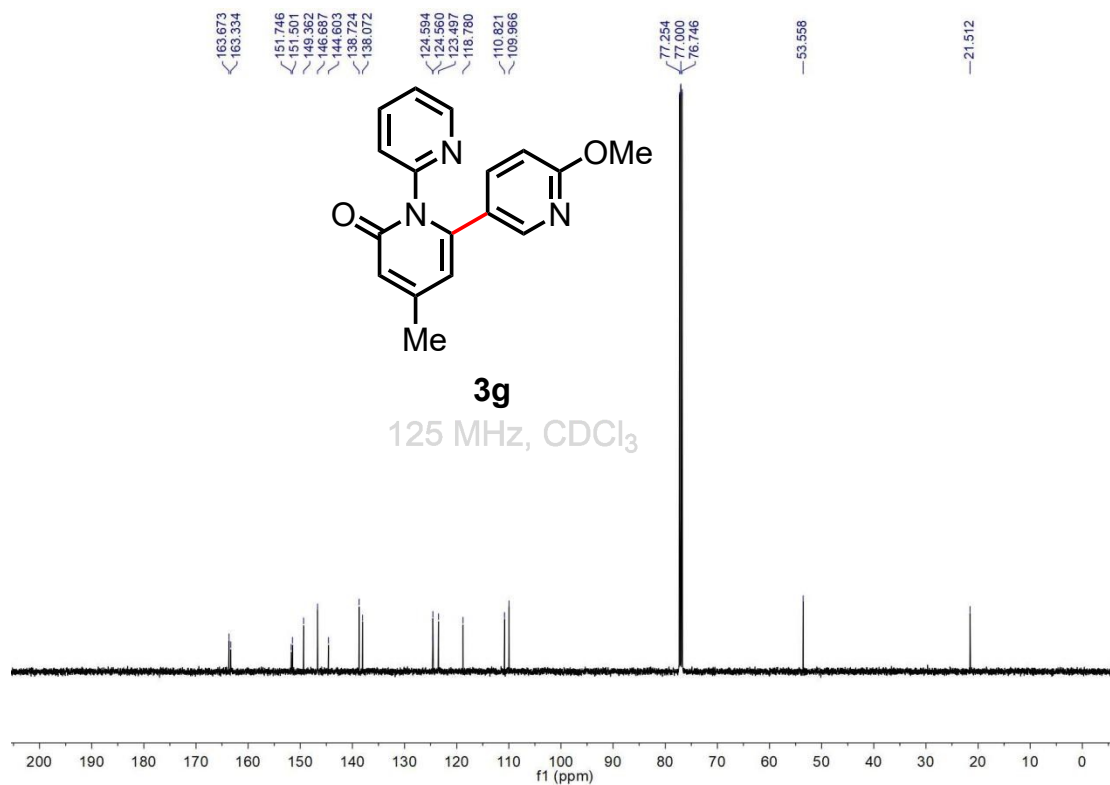
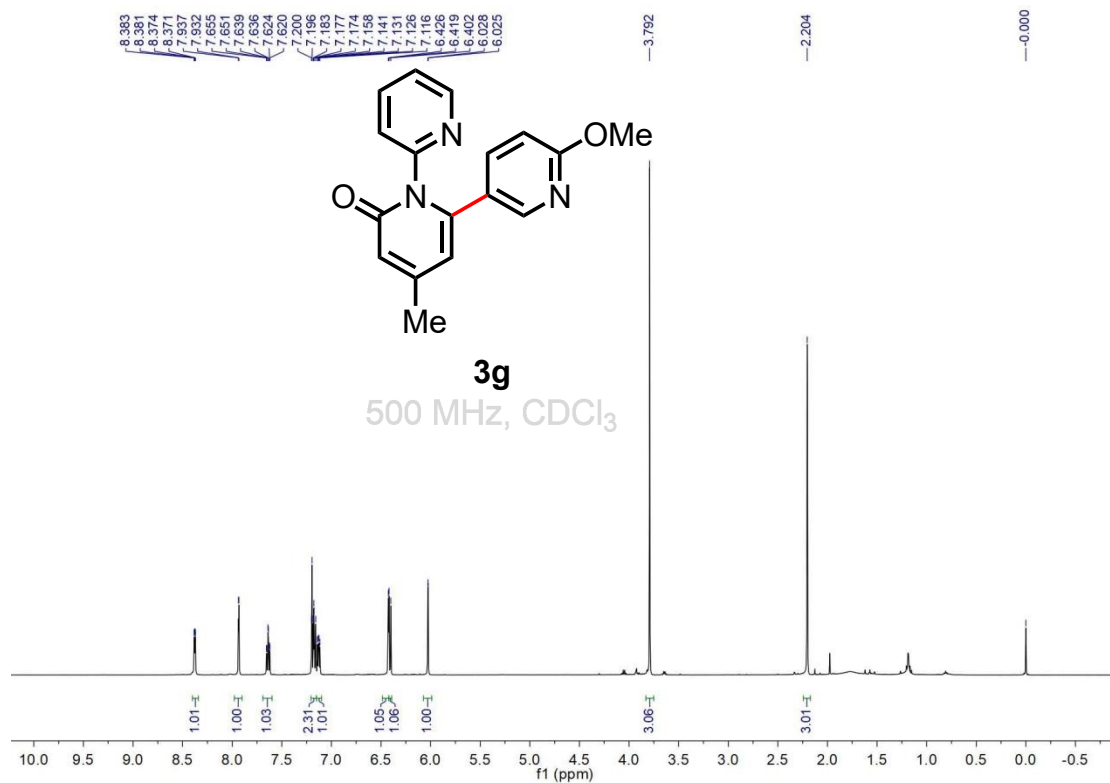
3d

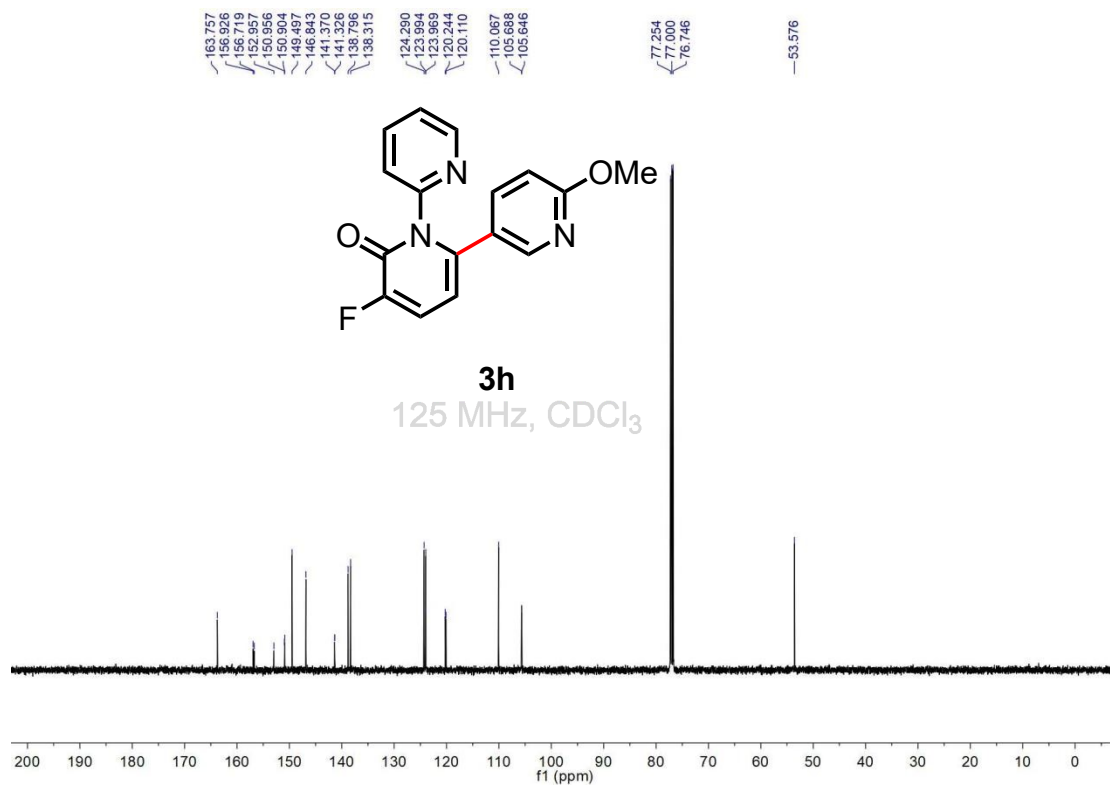
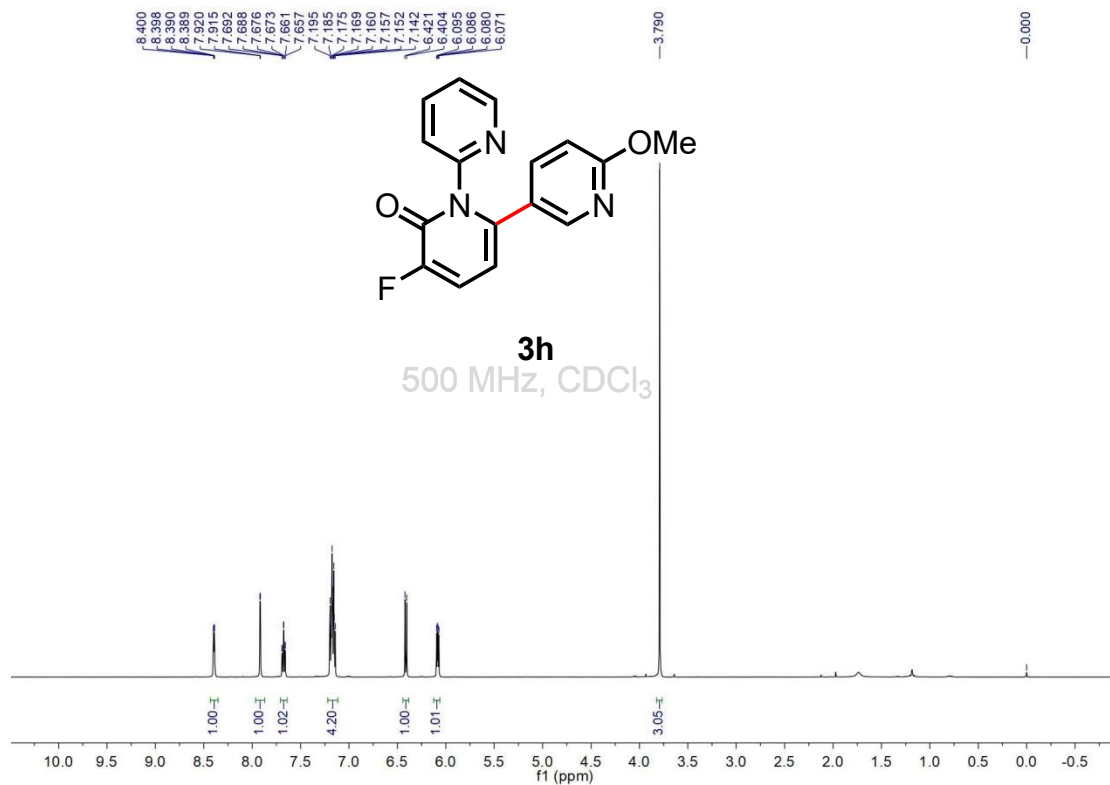
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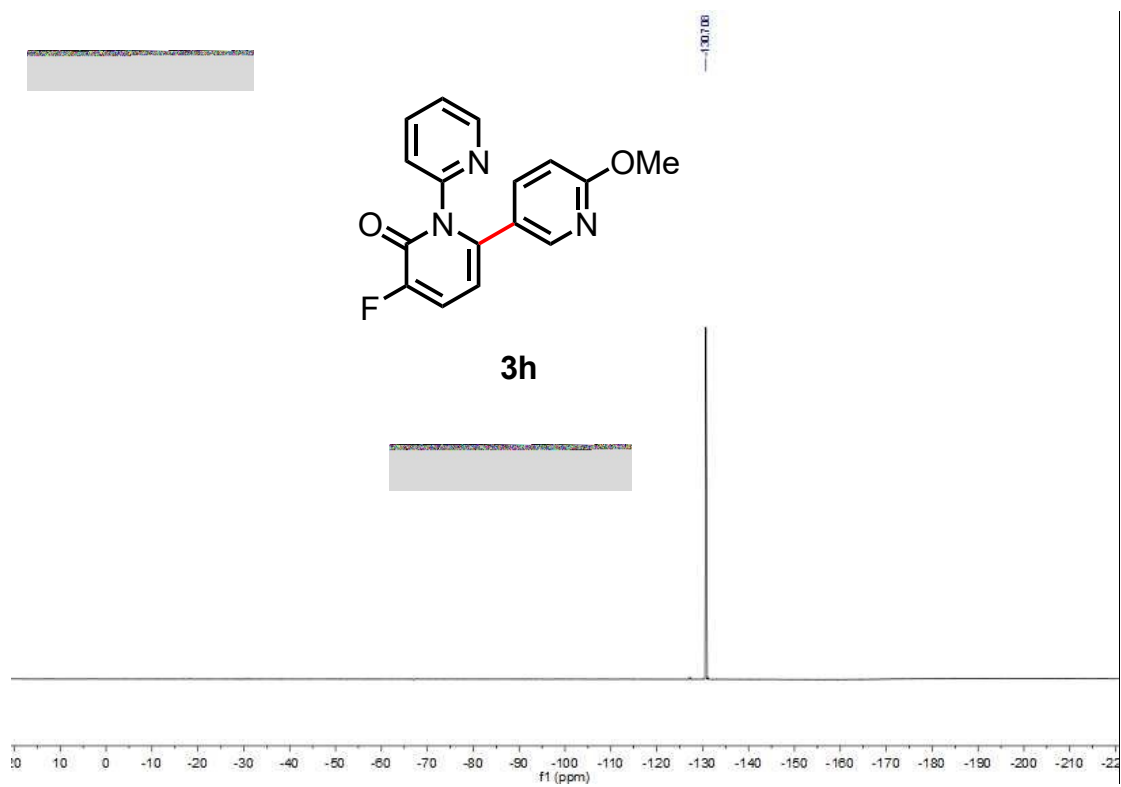


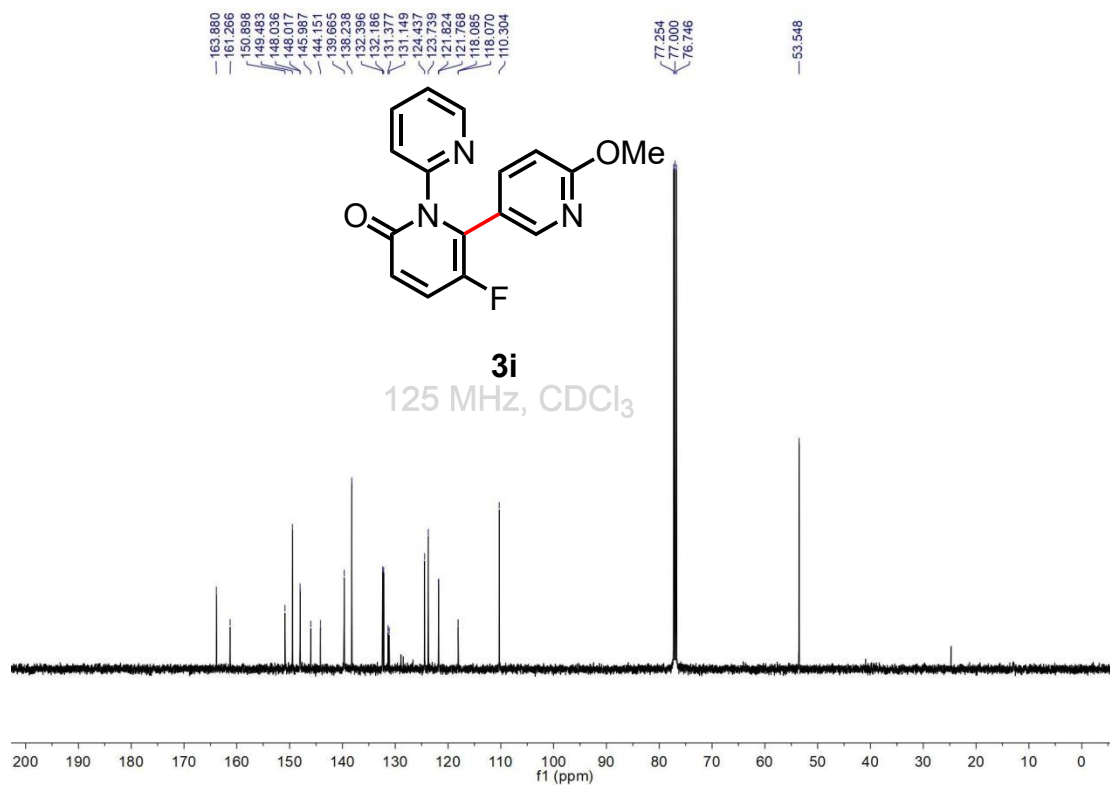
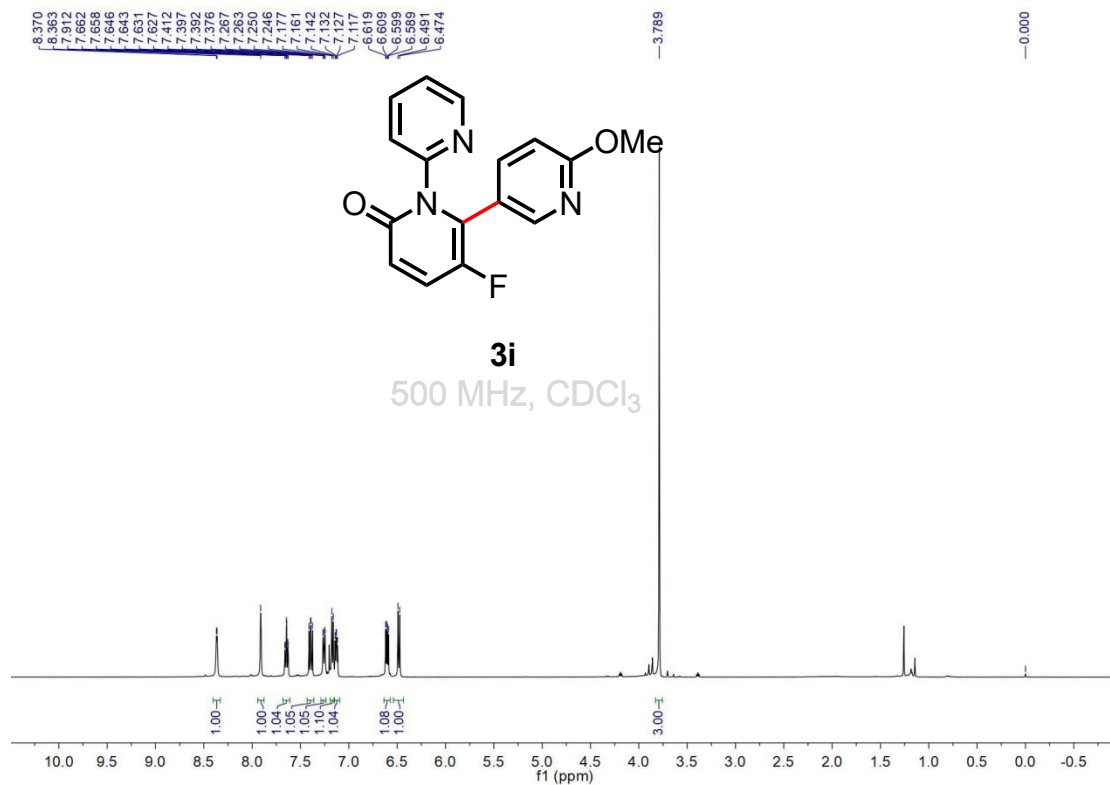


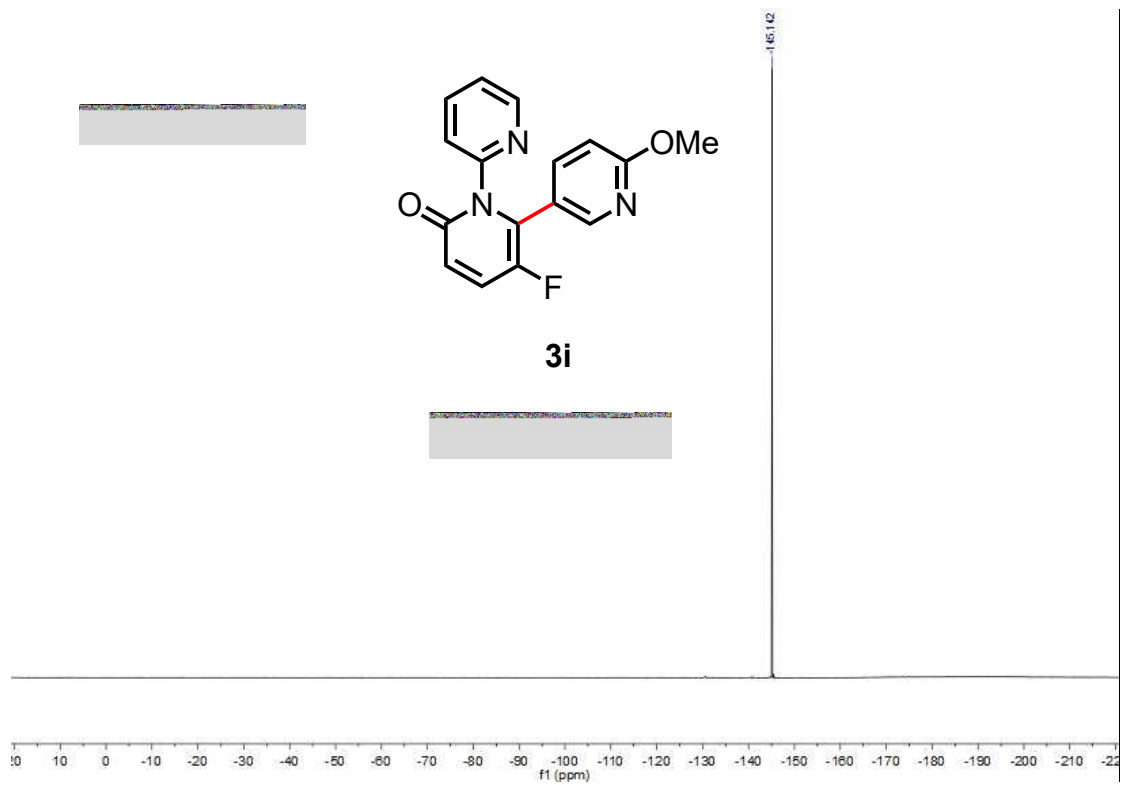


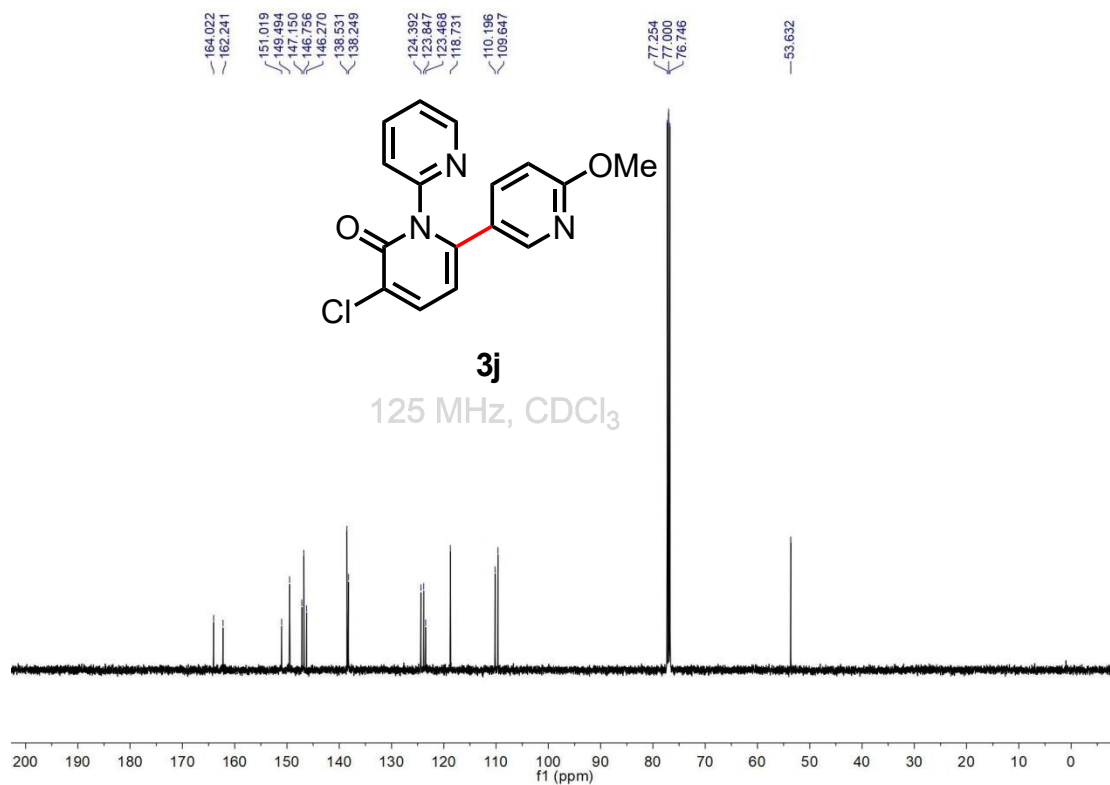
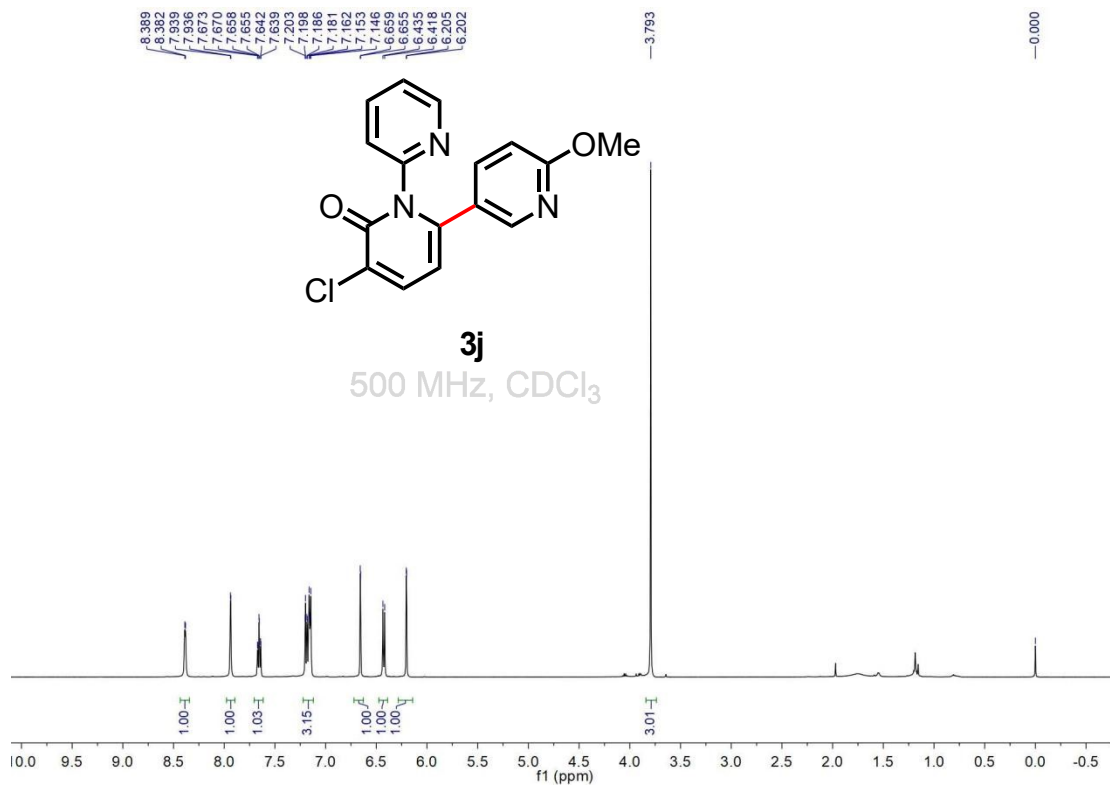


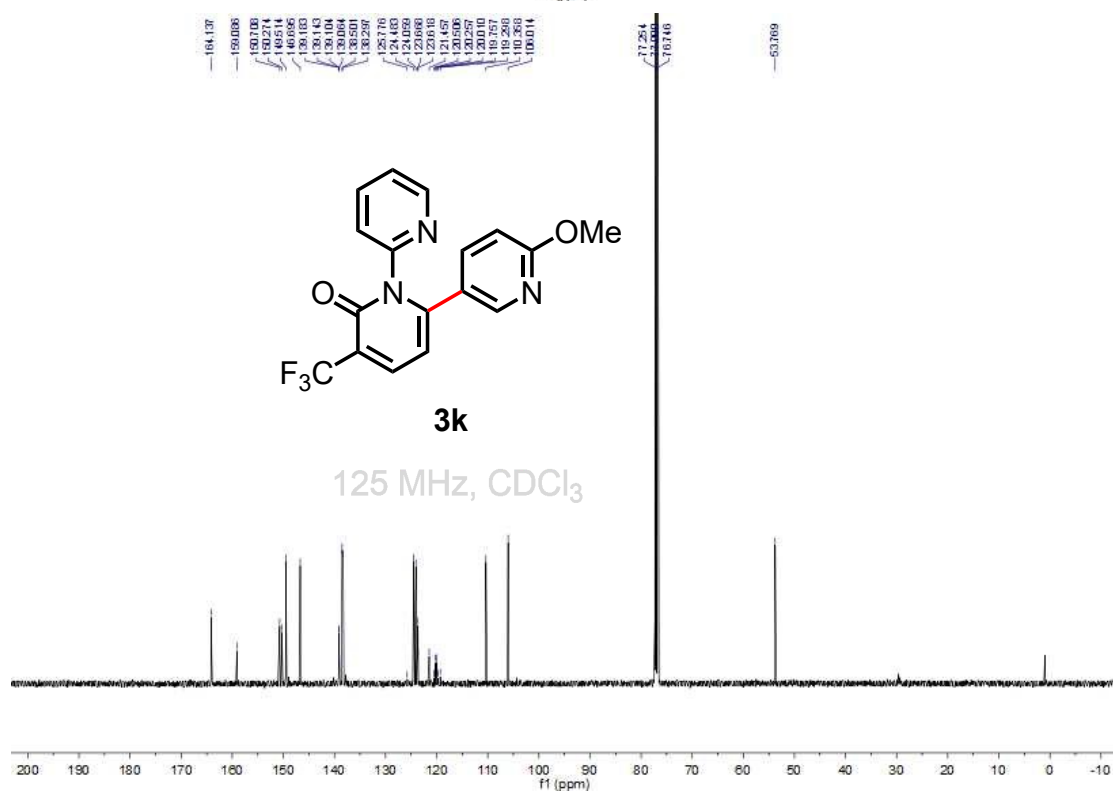
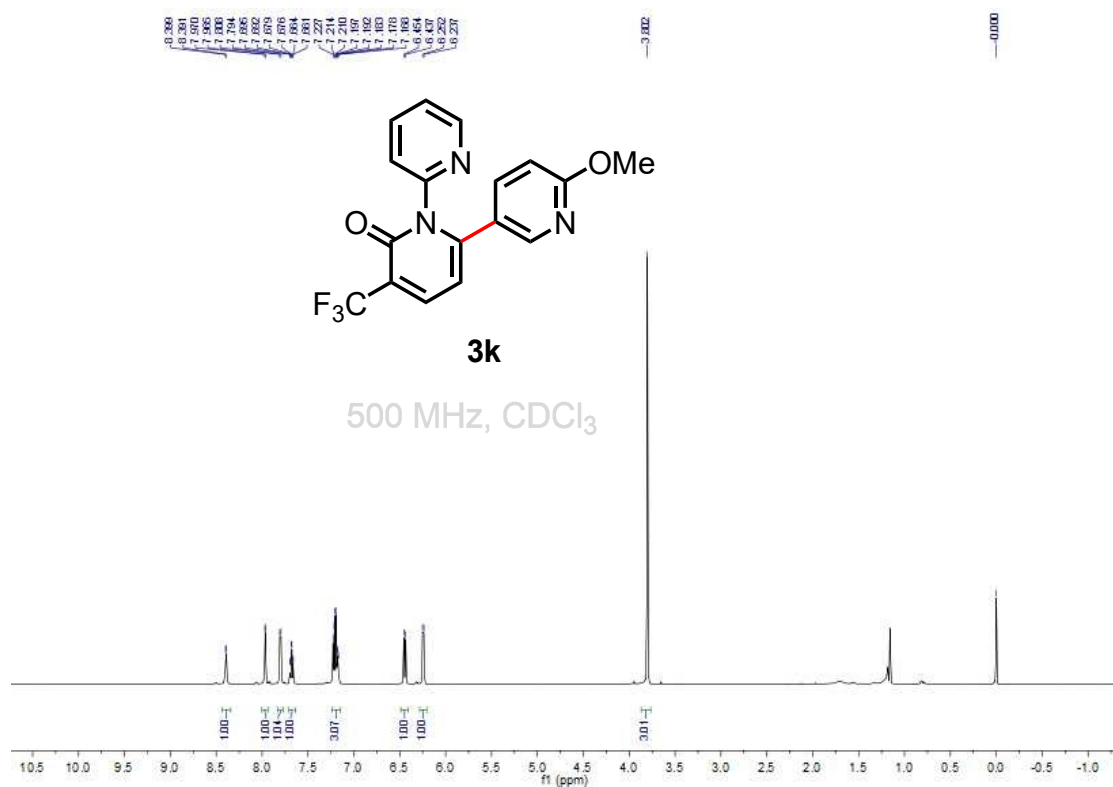


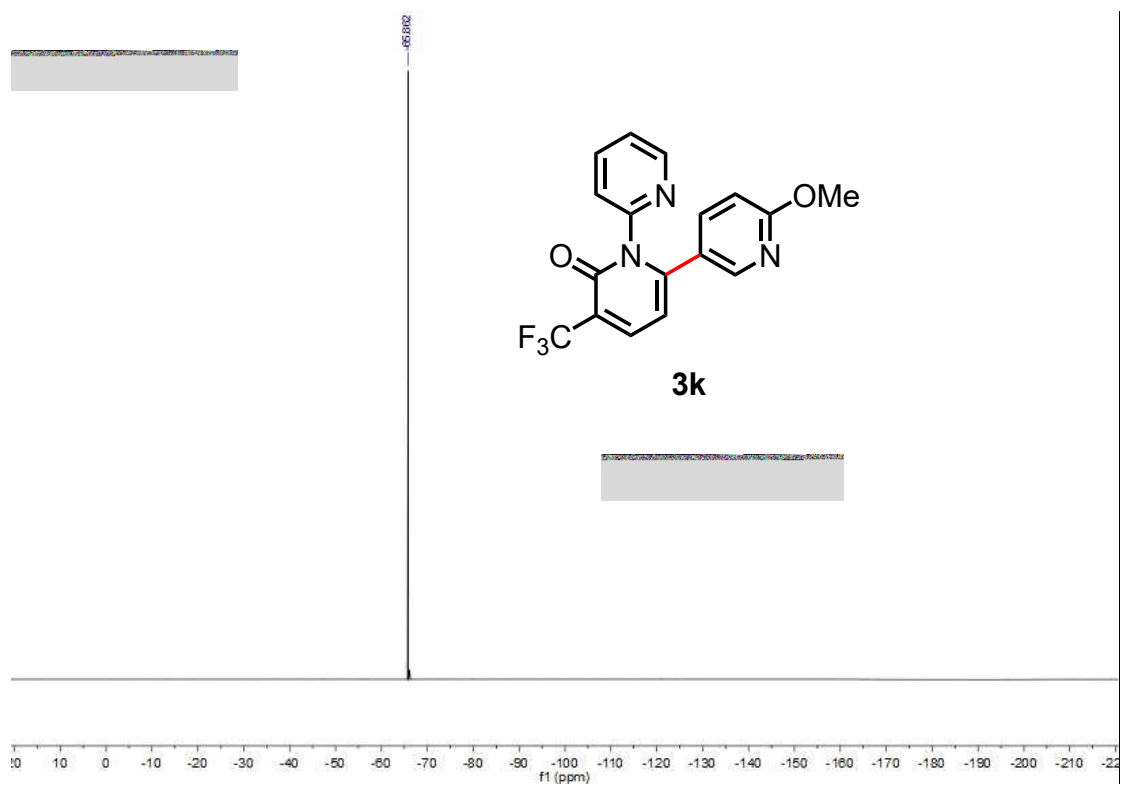


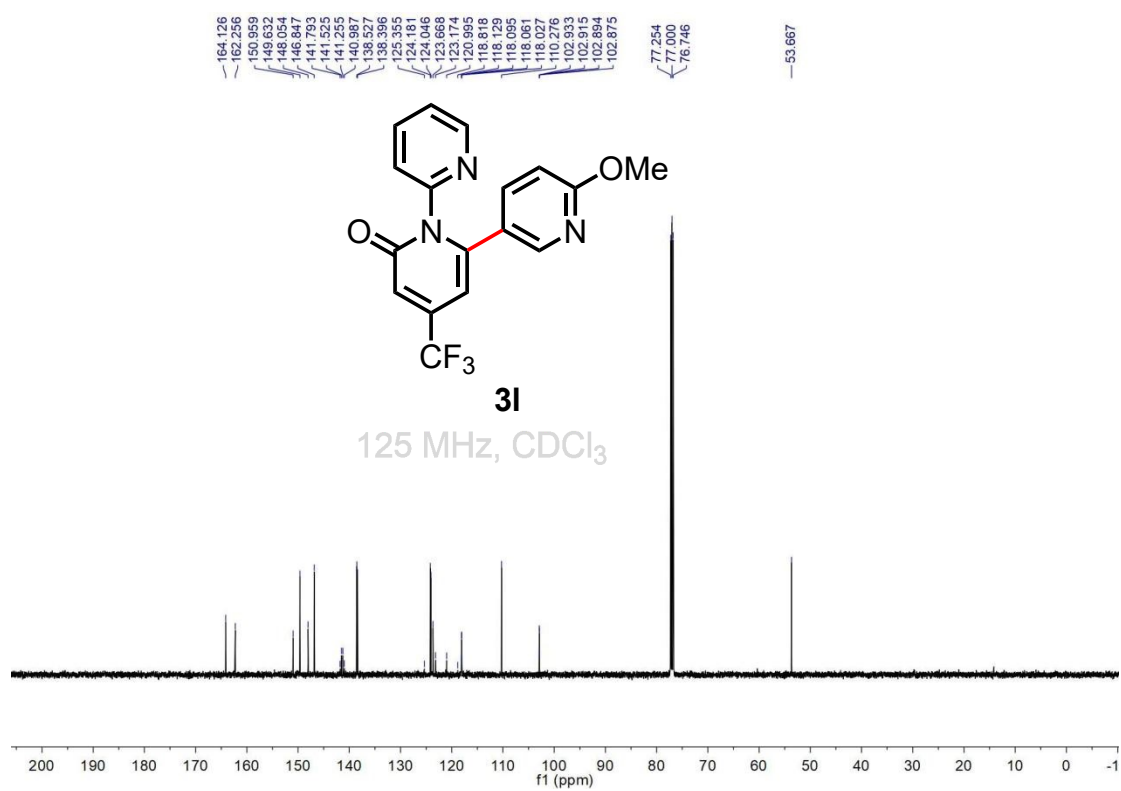
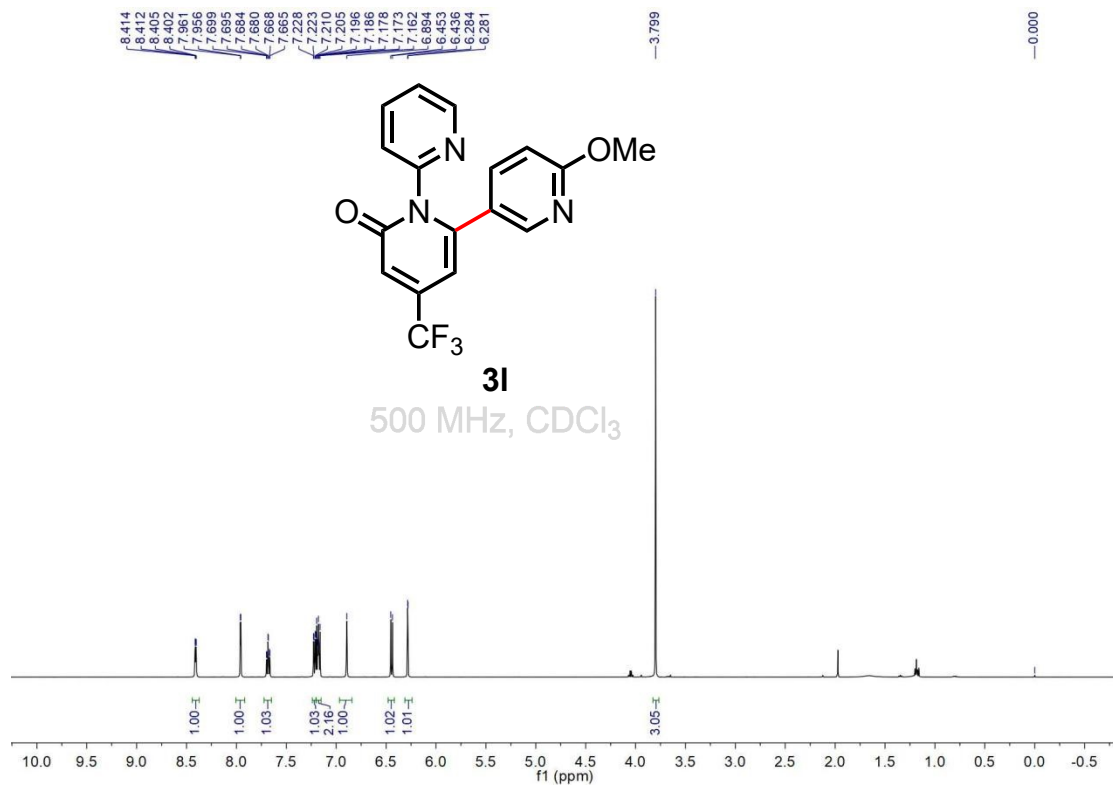


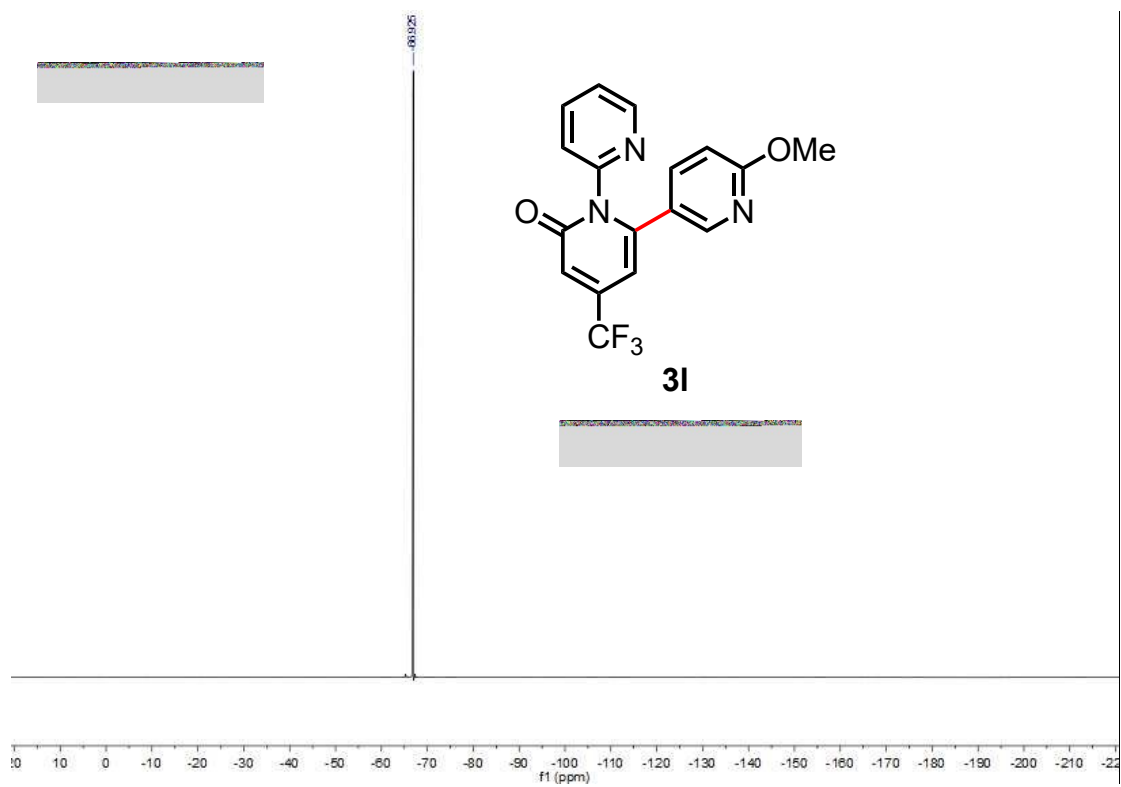


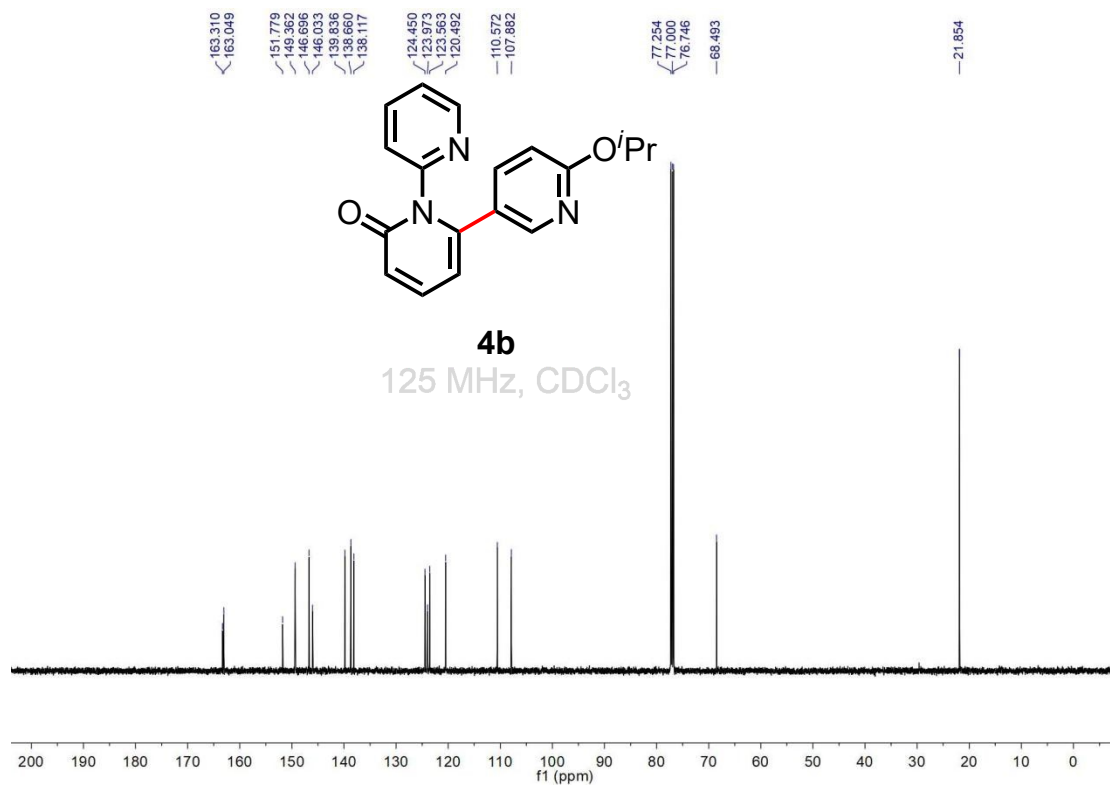
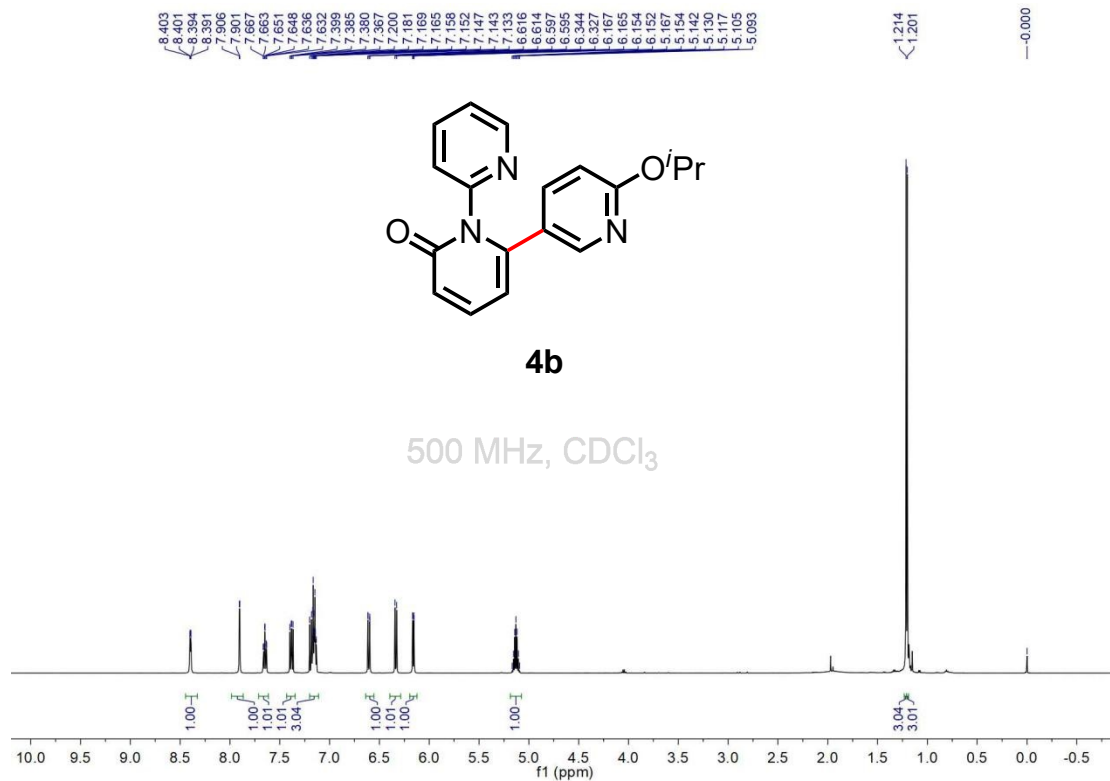


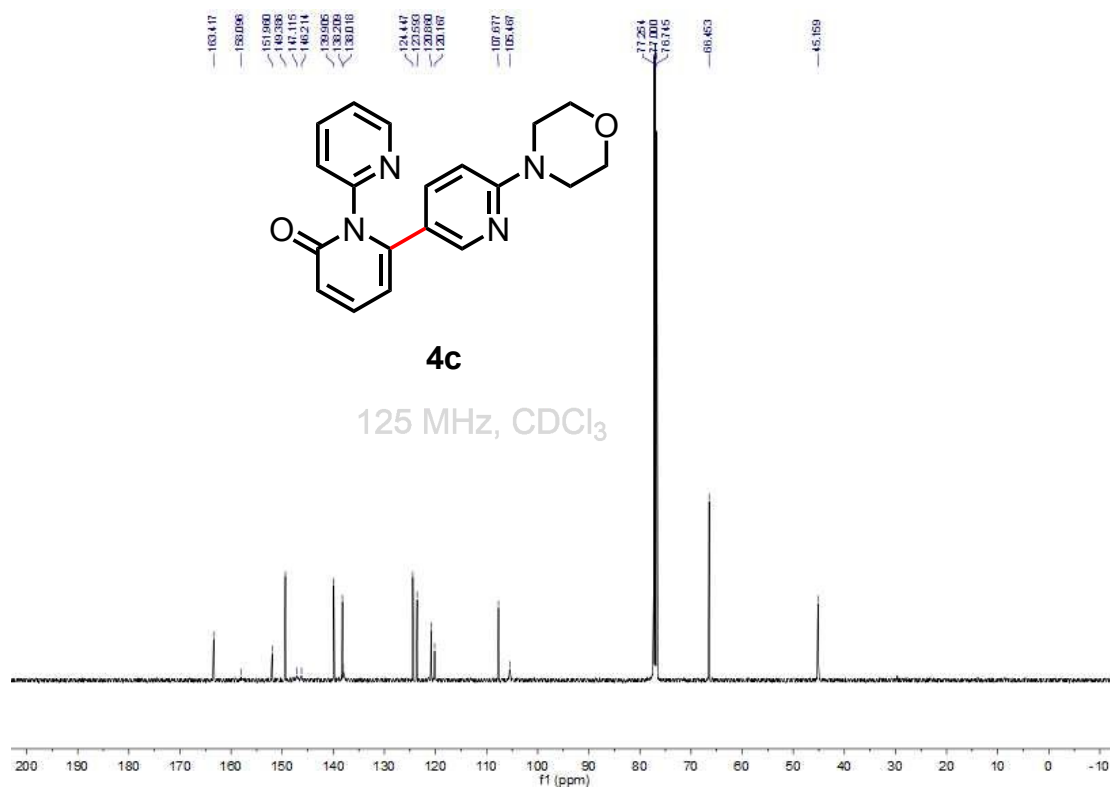
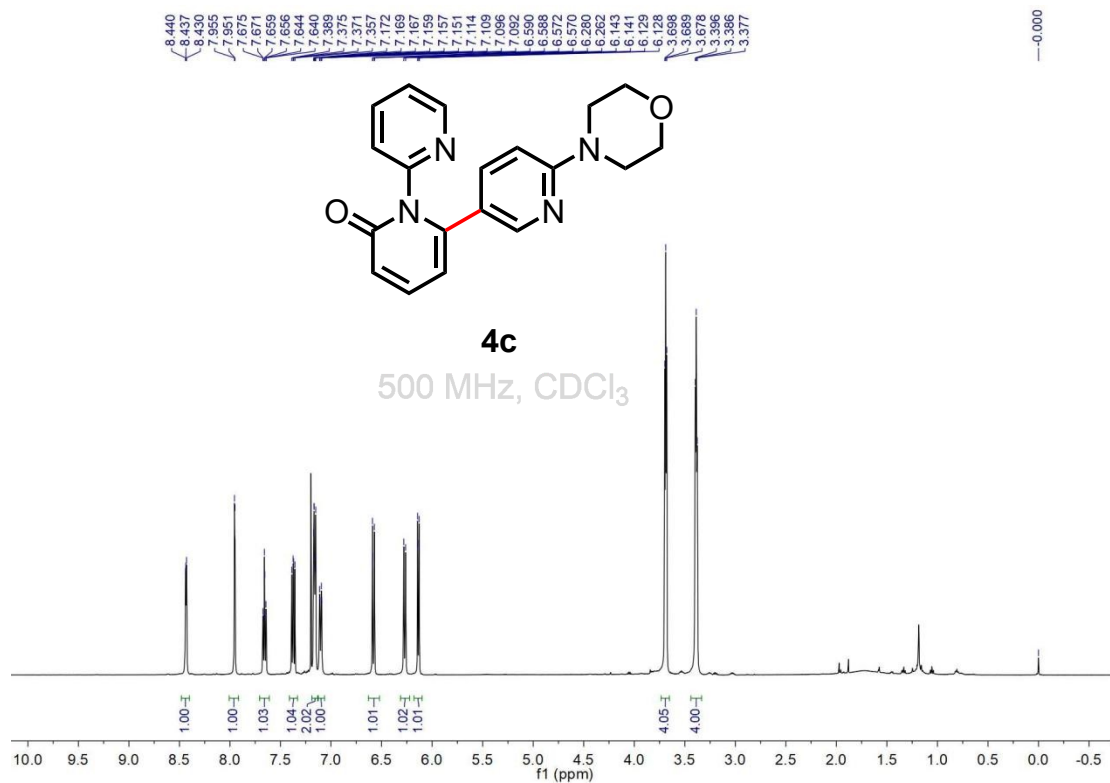






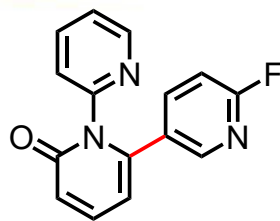






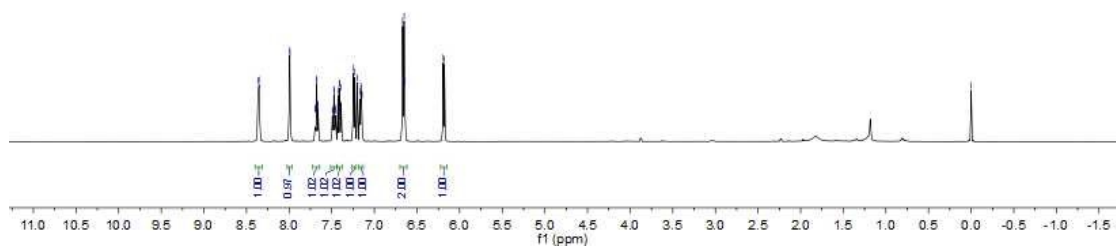
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7.825
7.825
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7.803
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4.679

0.000

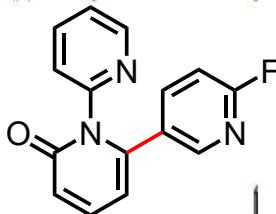


4d

500 MHz, CDCl₃

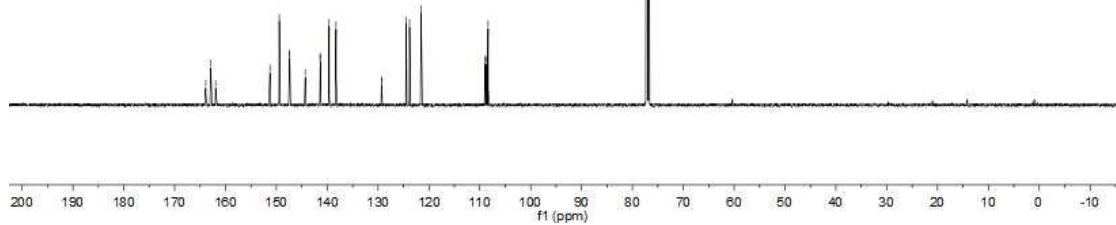


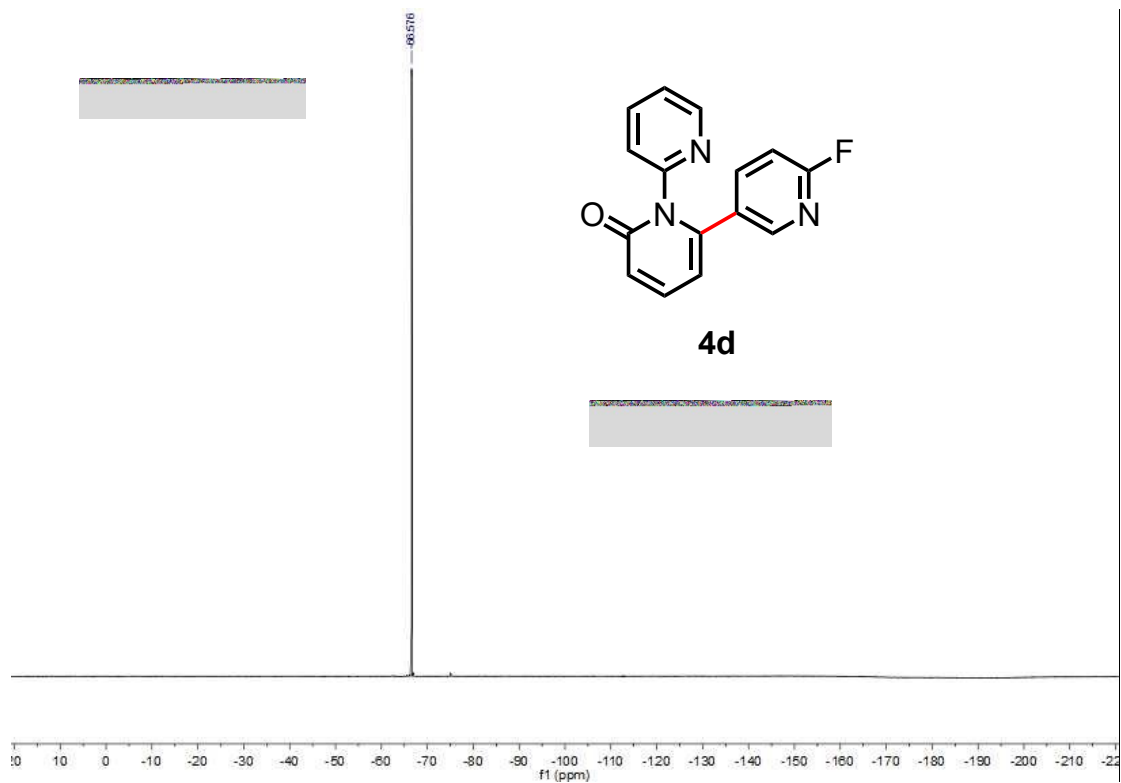
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108.596
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77.000
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4d

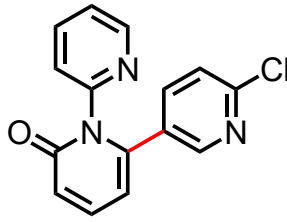
125 MHz, CDCl₃





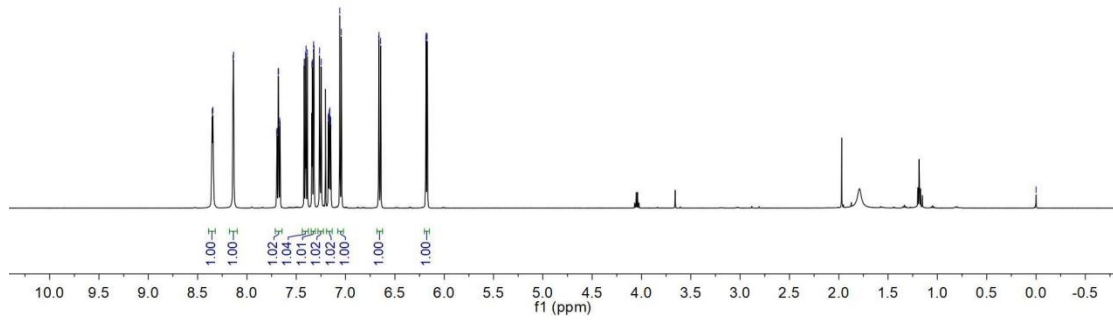
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7.247
7.175
7.163
7.164
7.160
7.158
7.150
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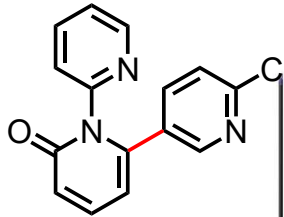


4e

500 MHz, CDCl₃

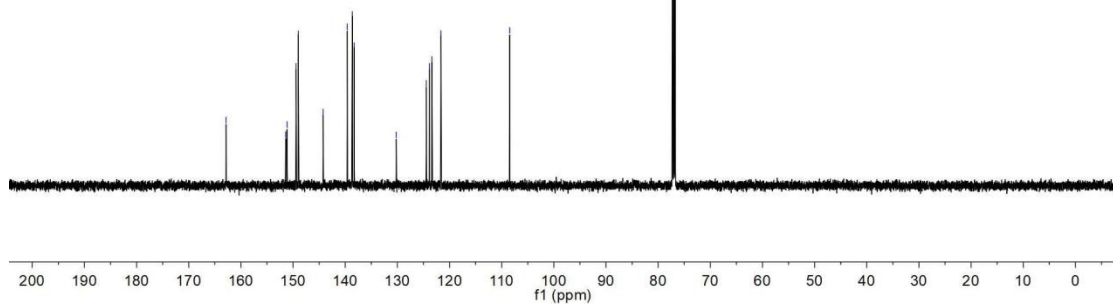


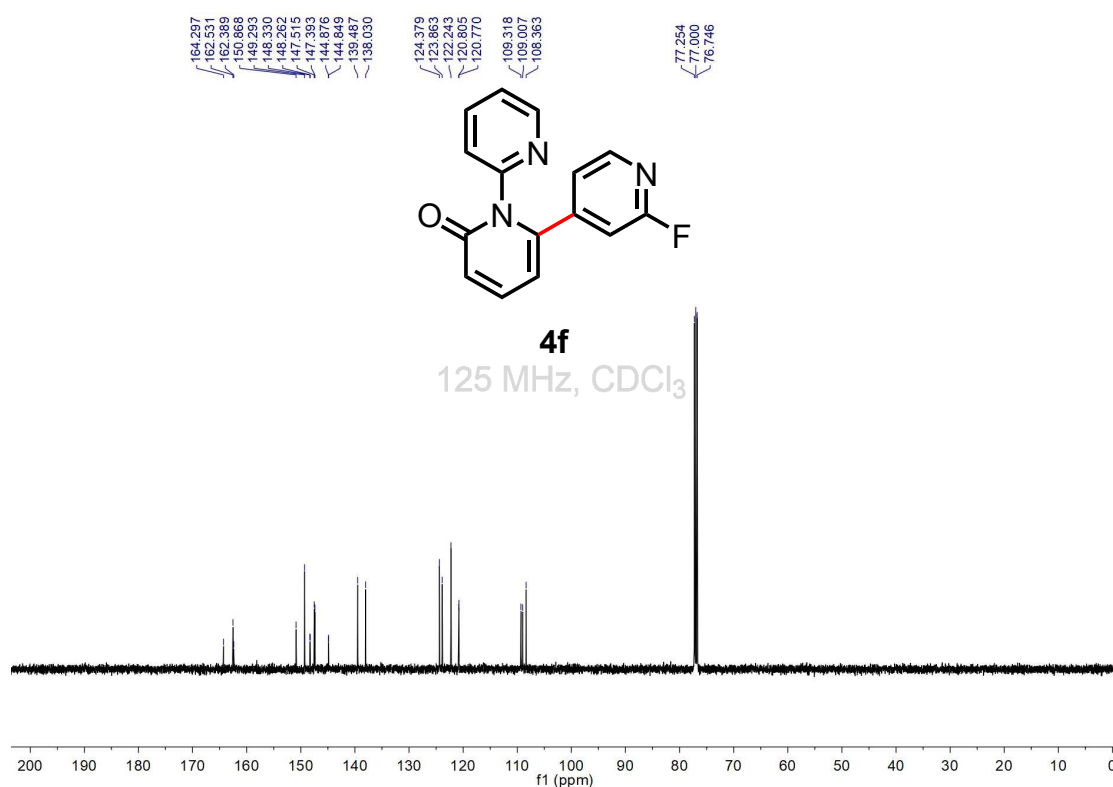
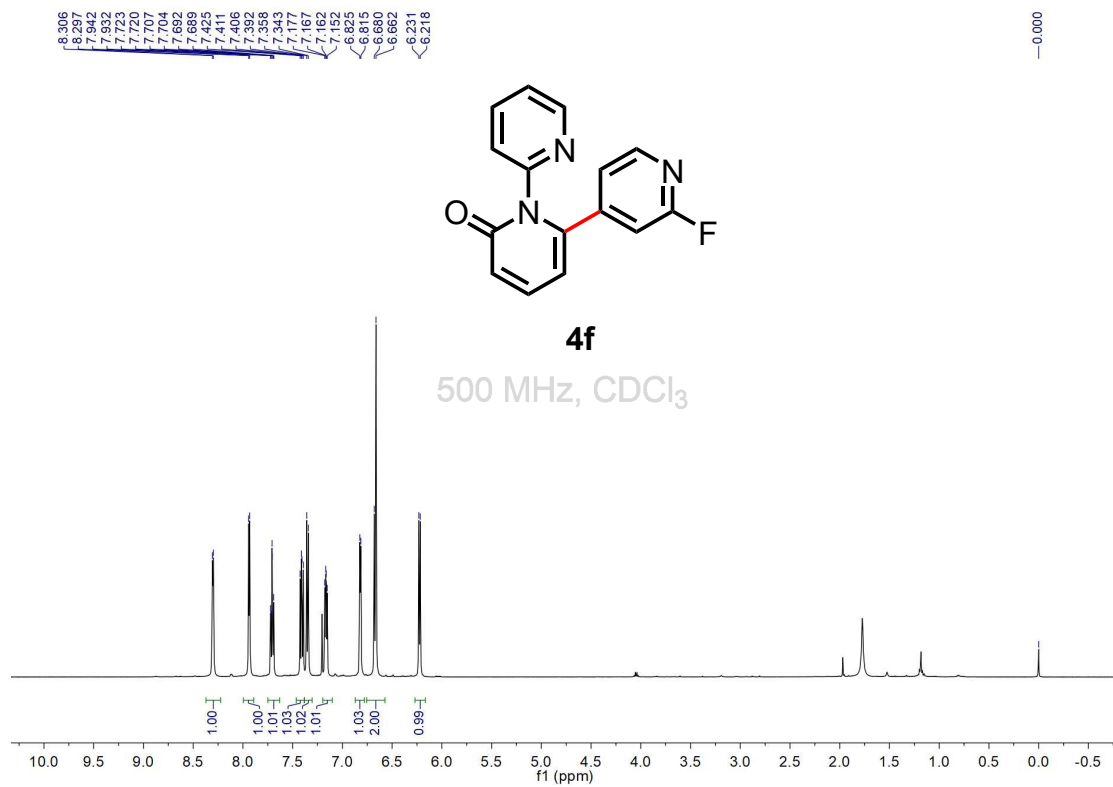
162.846
151.405
151.130
149.424
148.578
146.565
146.565
138.832
138.266
130.216
124.455
123.876
123.385
121.640
108.462
77.254
77.000
76.746

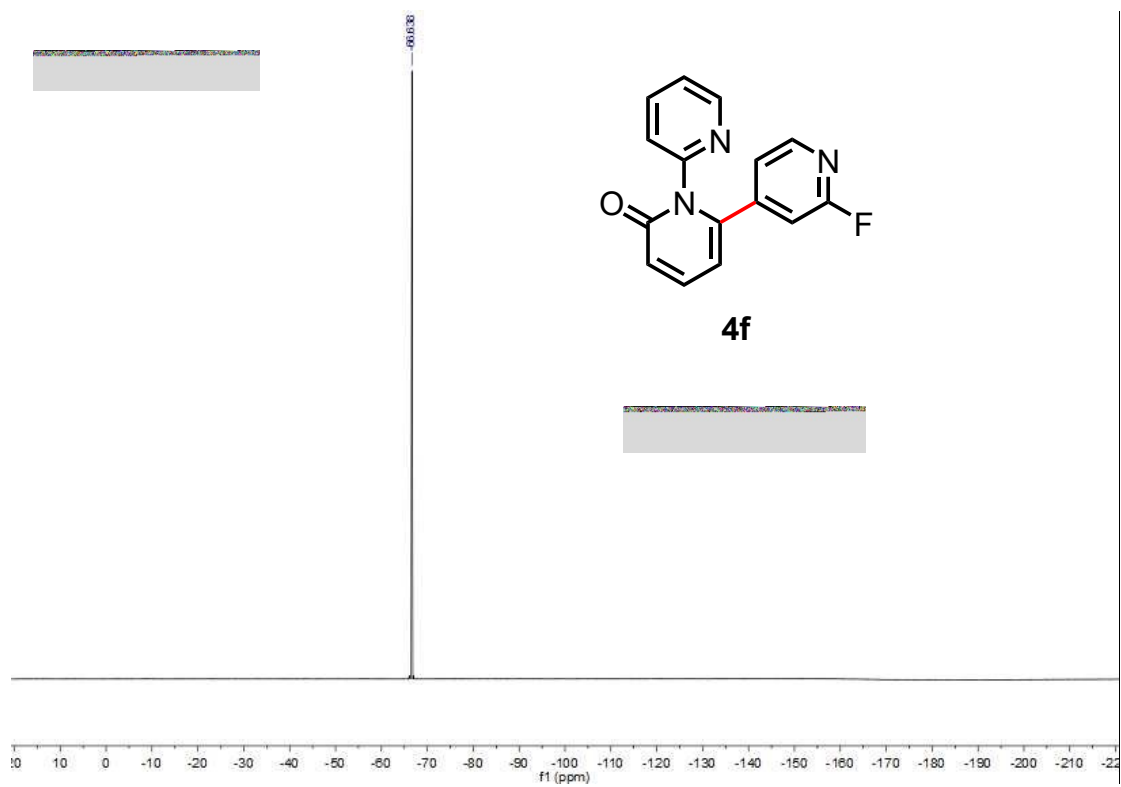


4e

125 MHz, CDCl₃

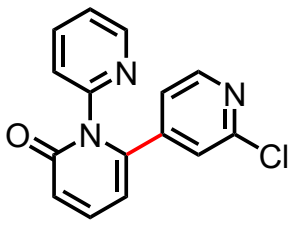






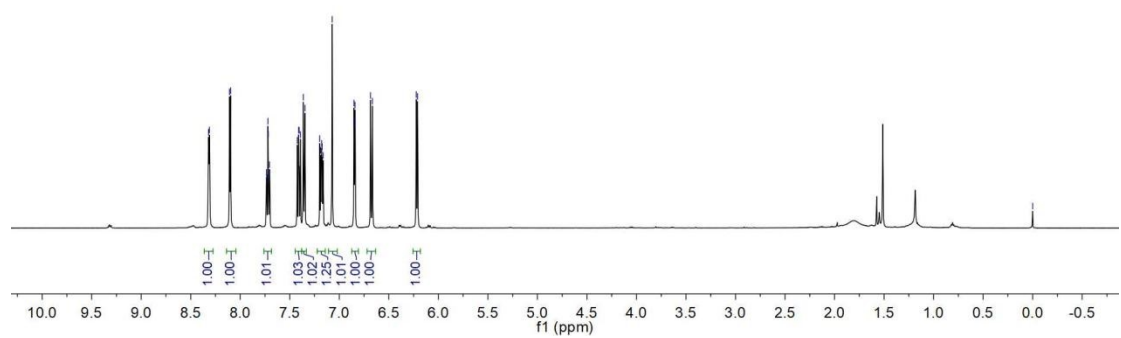
8.320
8.311
8.108
8.098
7.736
7.733
7.720
7.717
7.705
7.702
7.424
7.410
7.405
7.392
7.363
7.347
7.198
7.188
7.178
7.175
7.163
7.072
6.852
6.849
6.841
6.839
6.684
6.686
6.223
6.210

-0.000

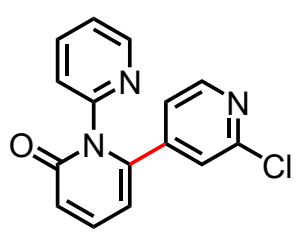


4g

500 MHz, CDCl₃

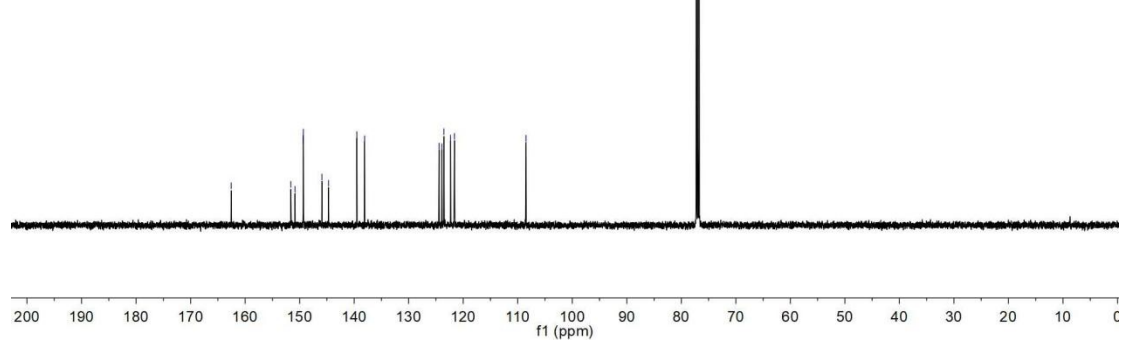


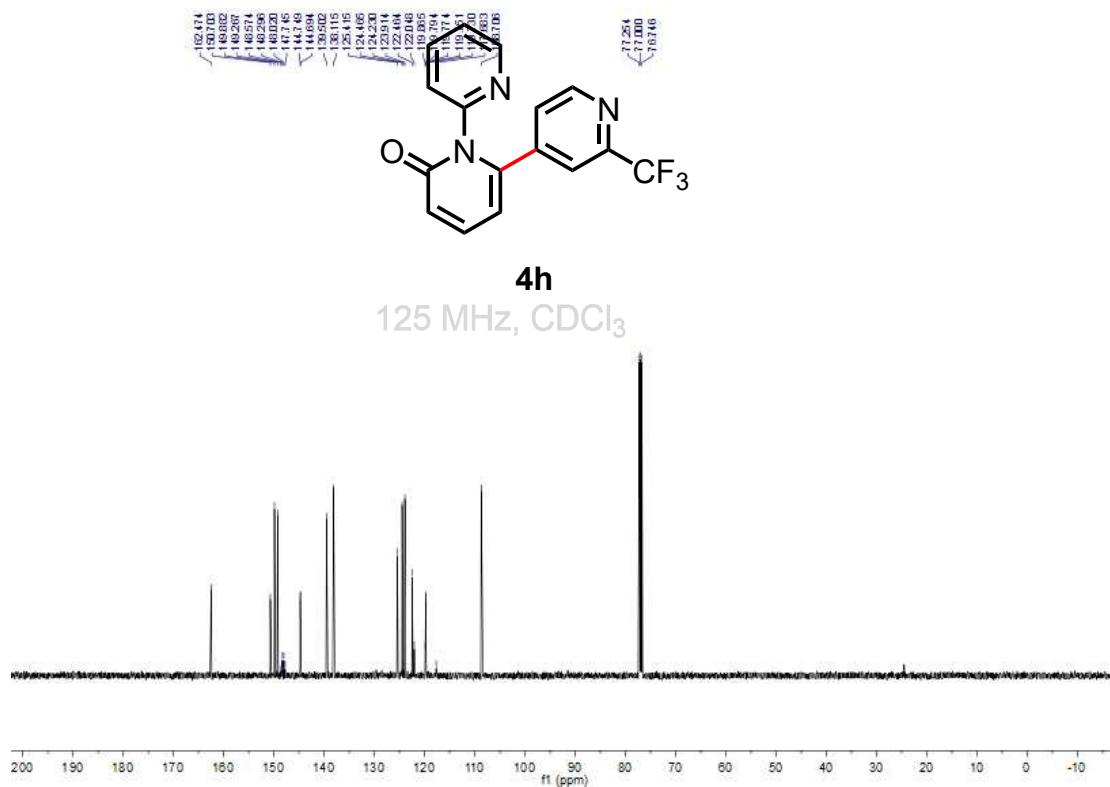
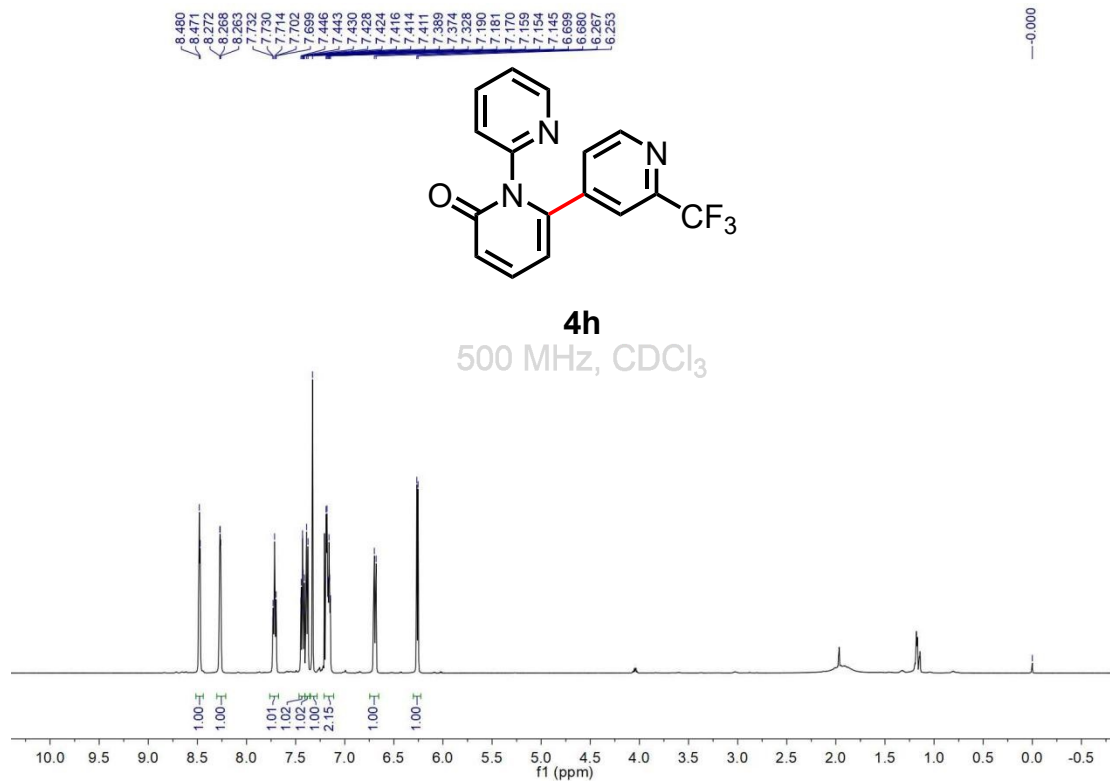
162.548
151.609
150.845
149.349
149.314
145.913
144.714
139.510
138.085
124.433
123.919
123.545
122.307
121.605
108.481
77.254
77.000
76.746

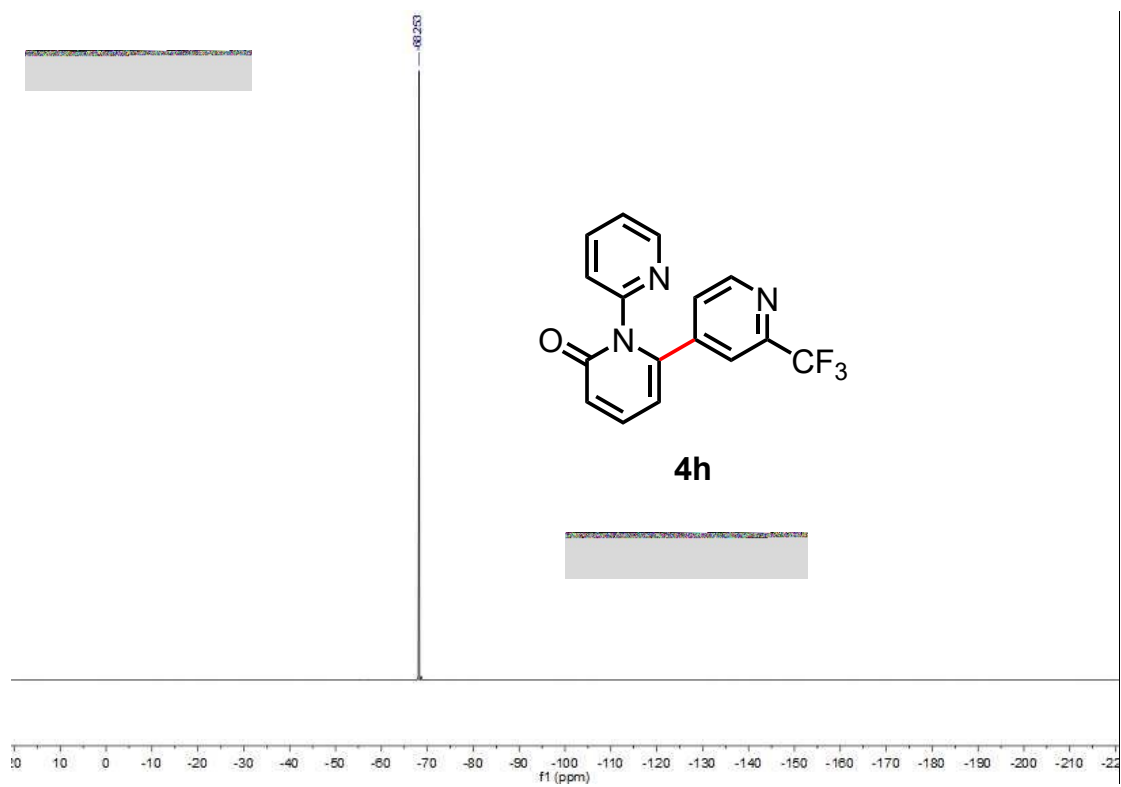


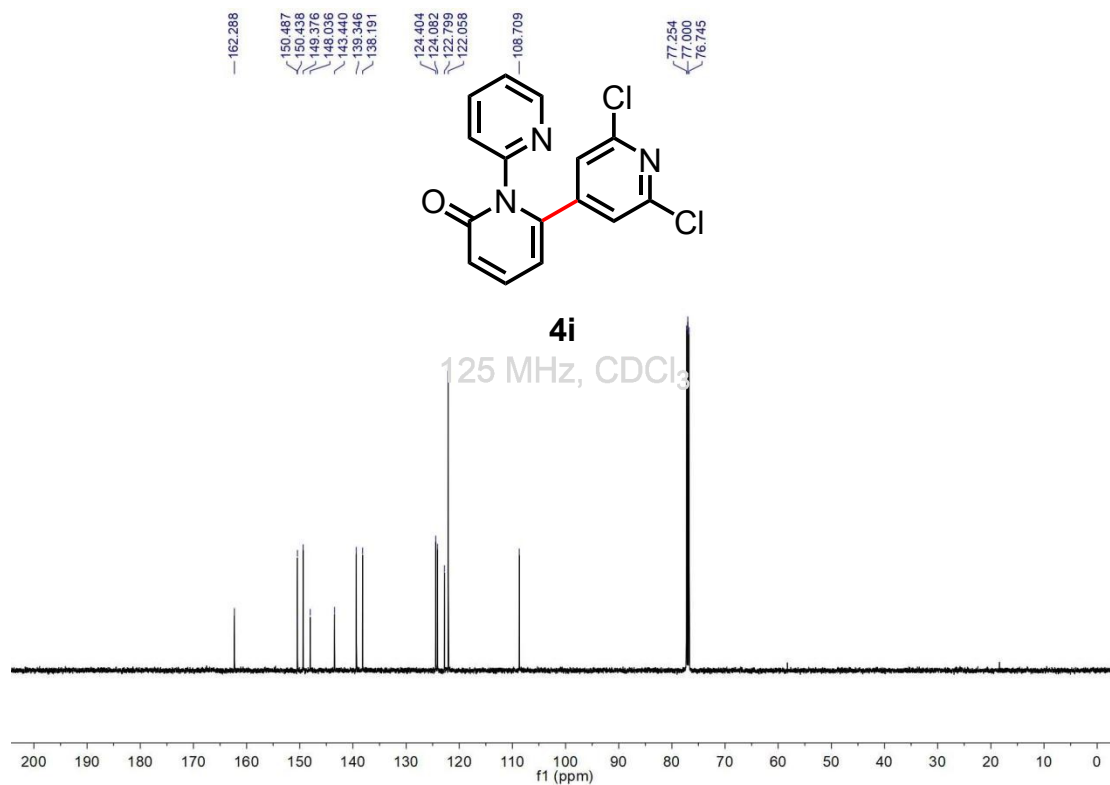
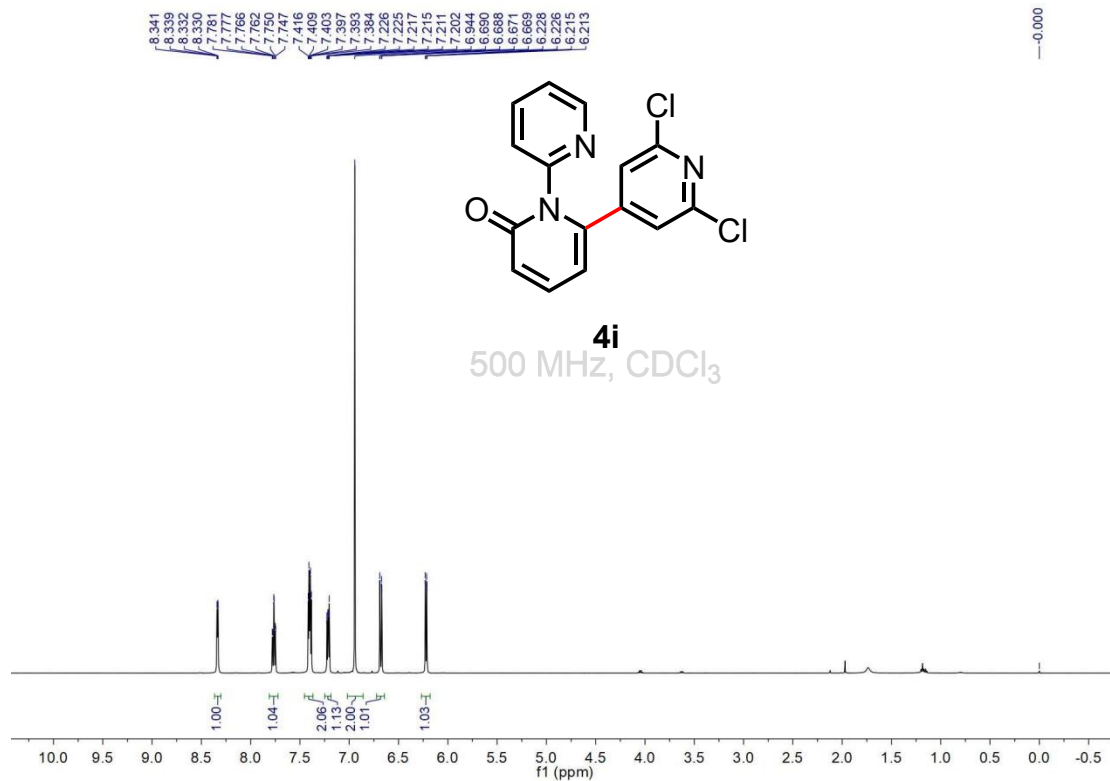
4g

125 MHz, CDCl₃



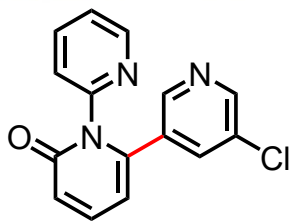






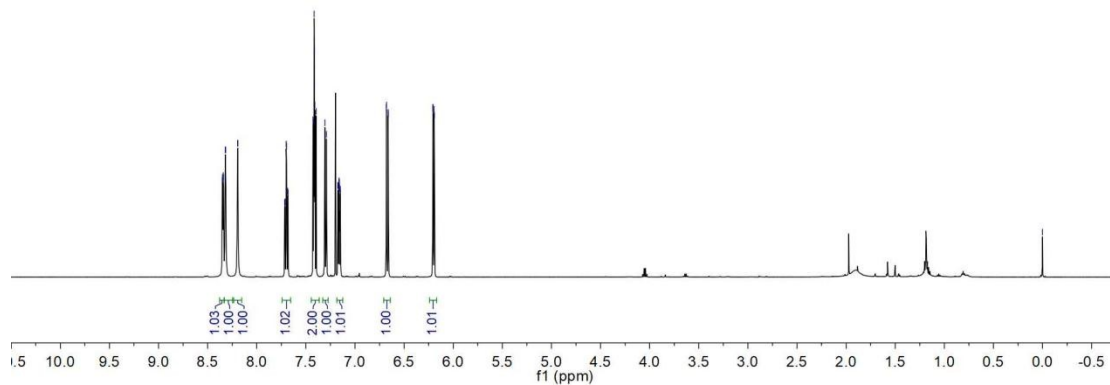
8.951
8.348
8.341
8.339
8.320
8.316
8.195
8.193
7.716
7.712
7.697
7.685
7.681
7.427
7.421
7.416
7.414
7.413
7.409
7.395
7.391
7.291
7.174
7.172
7.165
7.163
7.159
7.157
7.150
7.144
6.878
6.871
6.870
6.663
6.660
6.208
6.205
6.194
6.192

-0.000

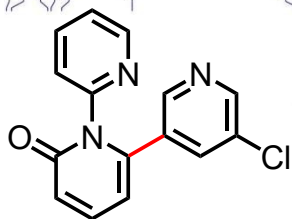


4j

500 MHz, CDCl₃

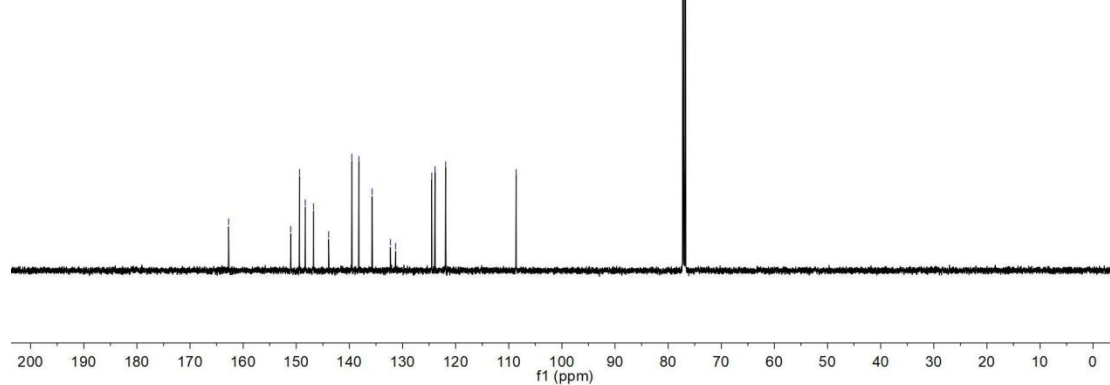


162.748
151.045
149.408
148.311
146.764
143.914
139.557
138.220
135.718
132.267
131.319
124.885
121.885
108.615
77.254
77.000
76.746



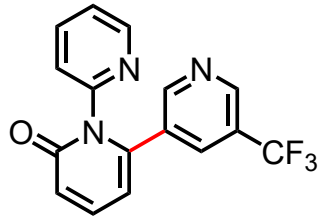
4j

125 MHz, CDCl₃



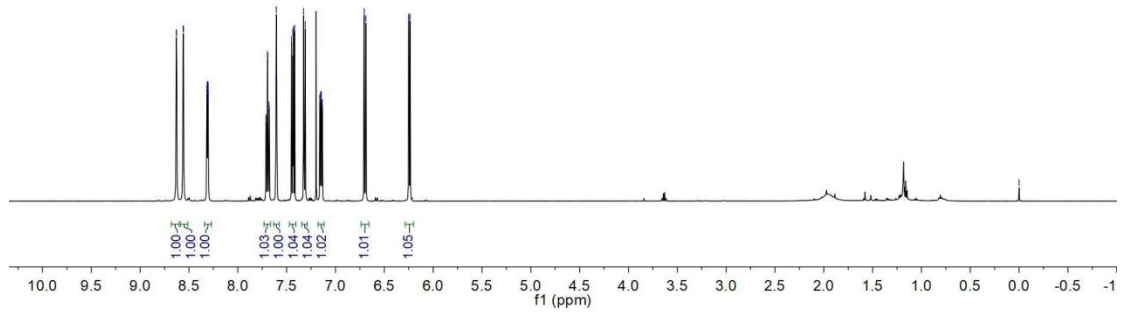
8.629
8.627
8.560
8.556
8.317
8.316
8.314
8.312
8.307
8.306
8.305
8.302
7.712
7.708
7.696
7.693
7.681
7.677
7.608
7.605
7.592
7.492
7.436
7.431
7.418
7.325
7.310
7.161
7.159
7.151
7.149
7.148
7.144
7.136
7.134
6.708
6.706
6.689
6.687
6.249
6.247
6.235

0.000

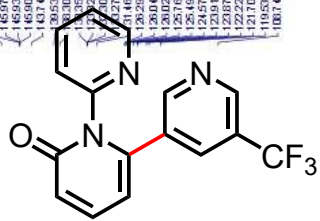


4k

500 MHz, CDCl₃

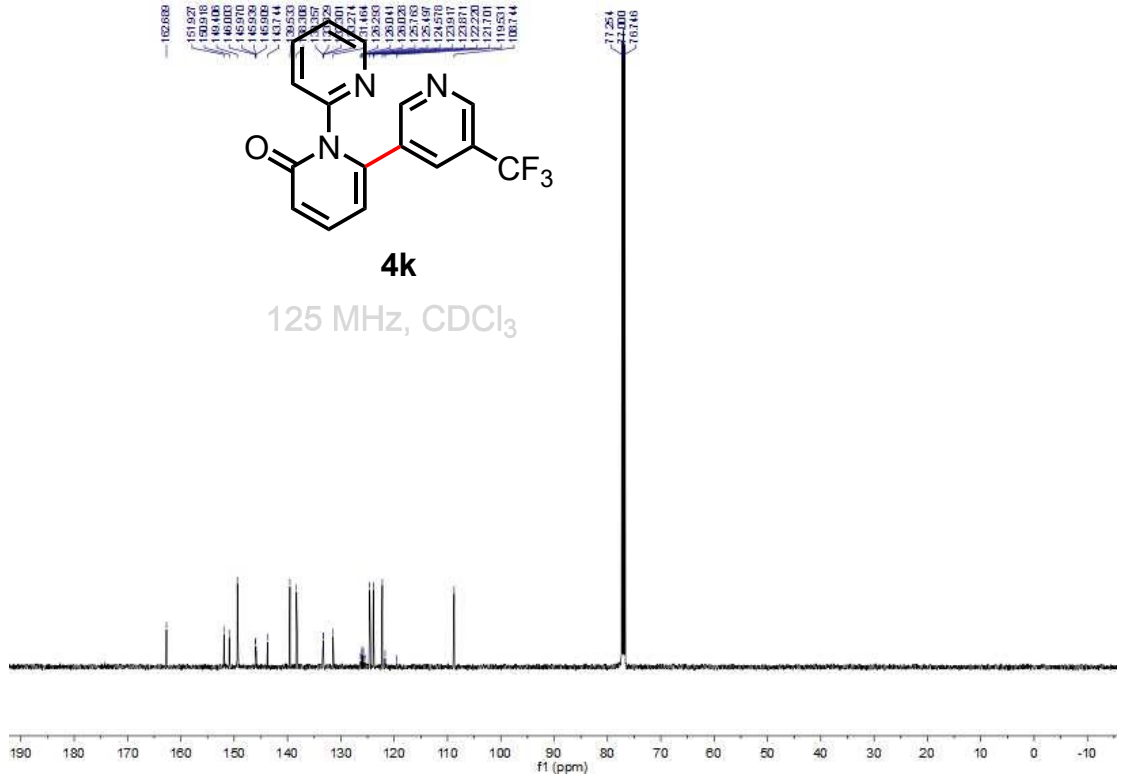


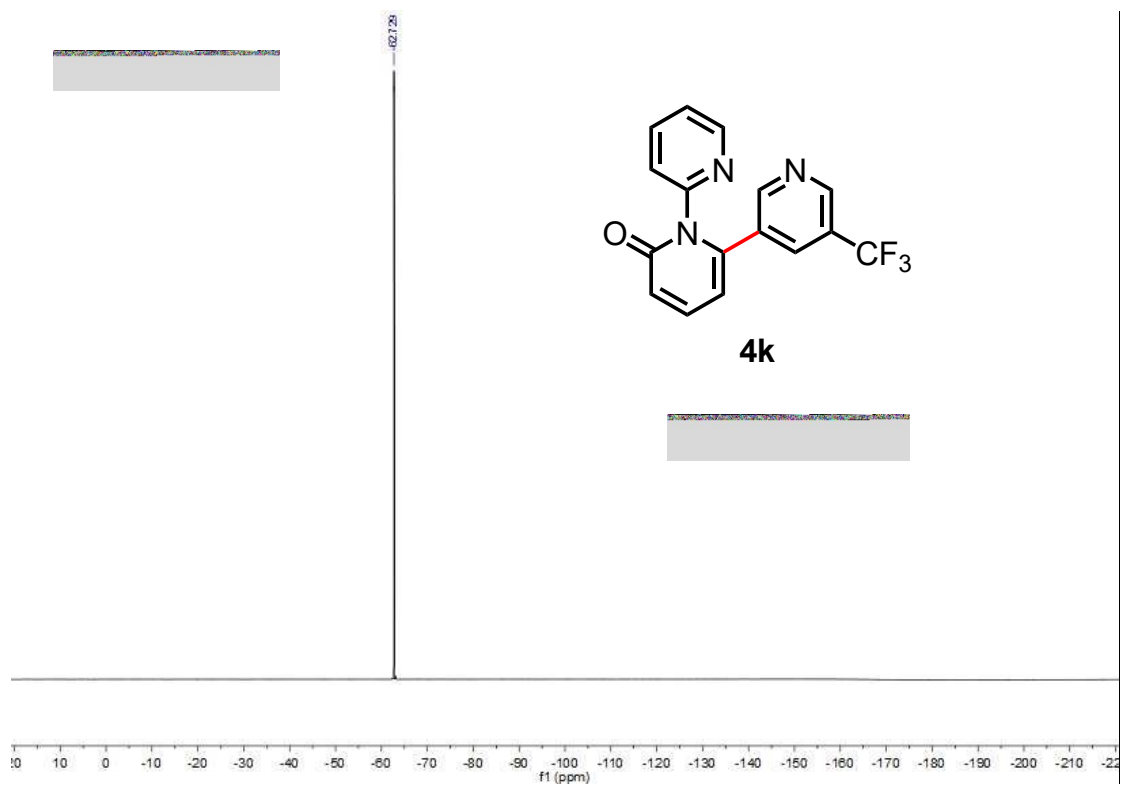
162.083
151.927
150.918
149.910
149.000
145.970
145.939
145.908
139.103
138.103
137.000
135.274
131.464
130.250
129.100
129.020
125.763
125.497
125.467
125.437
123.917
123.671
122.220
121.701
119.574
118.714

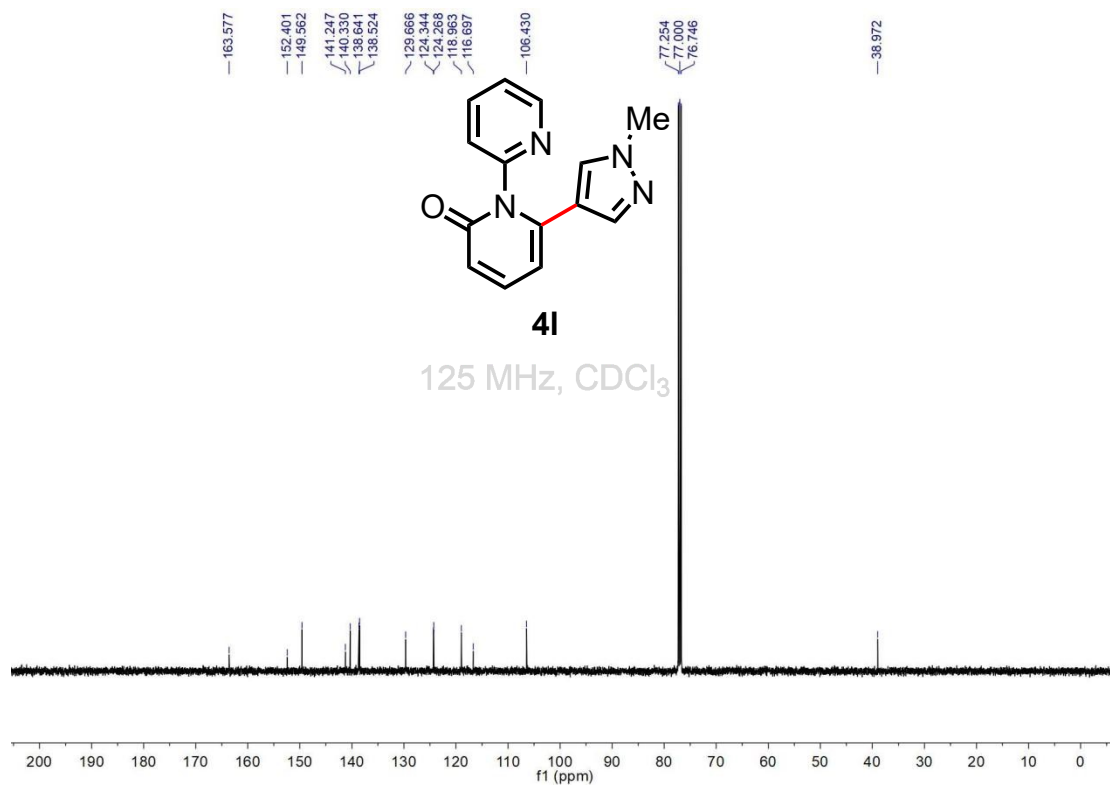
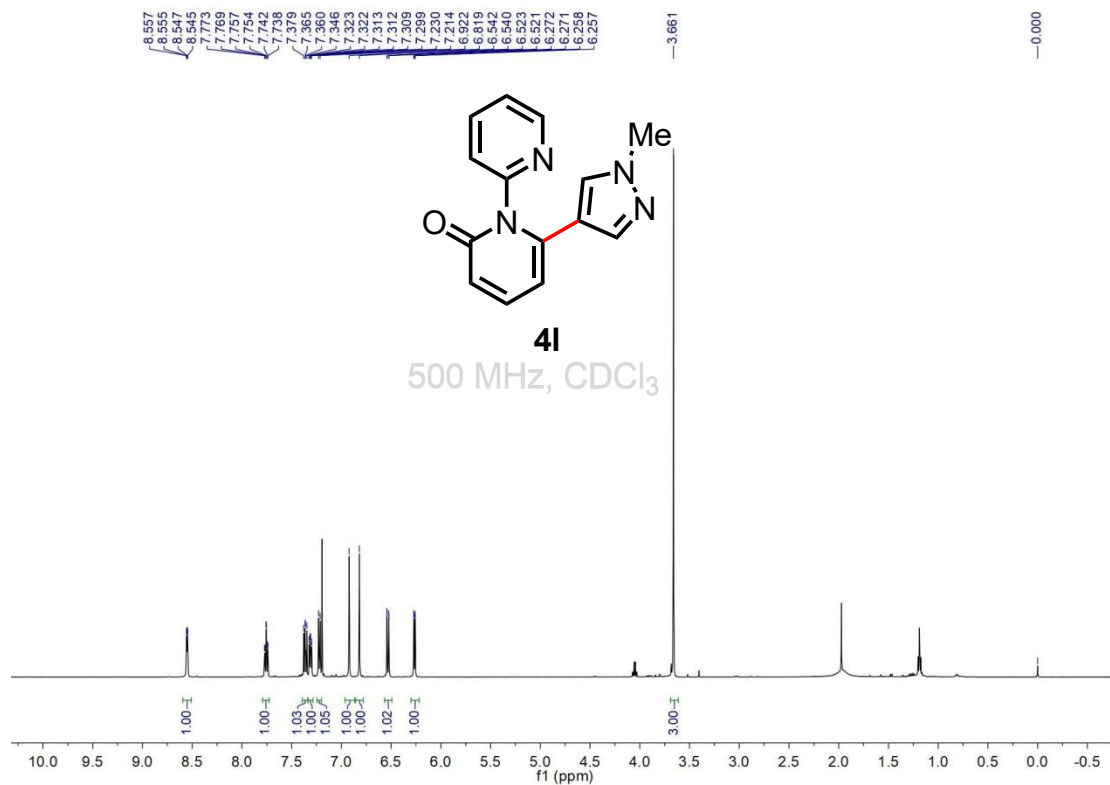


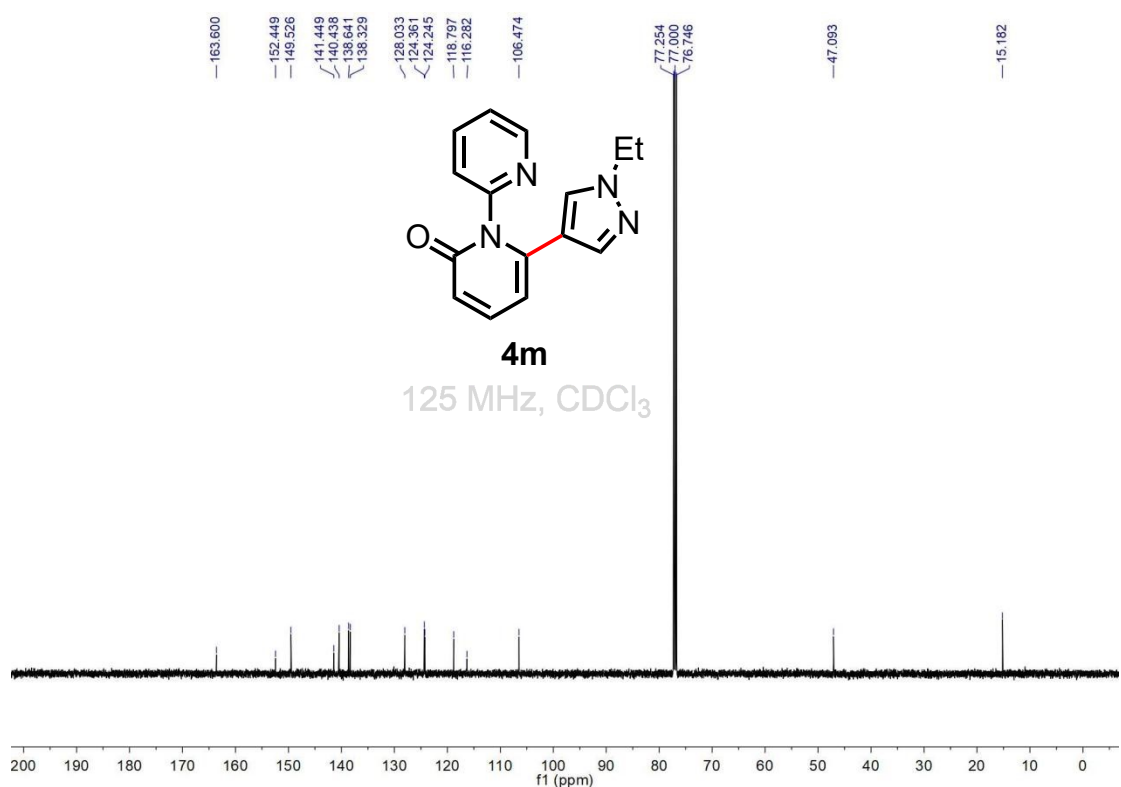
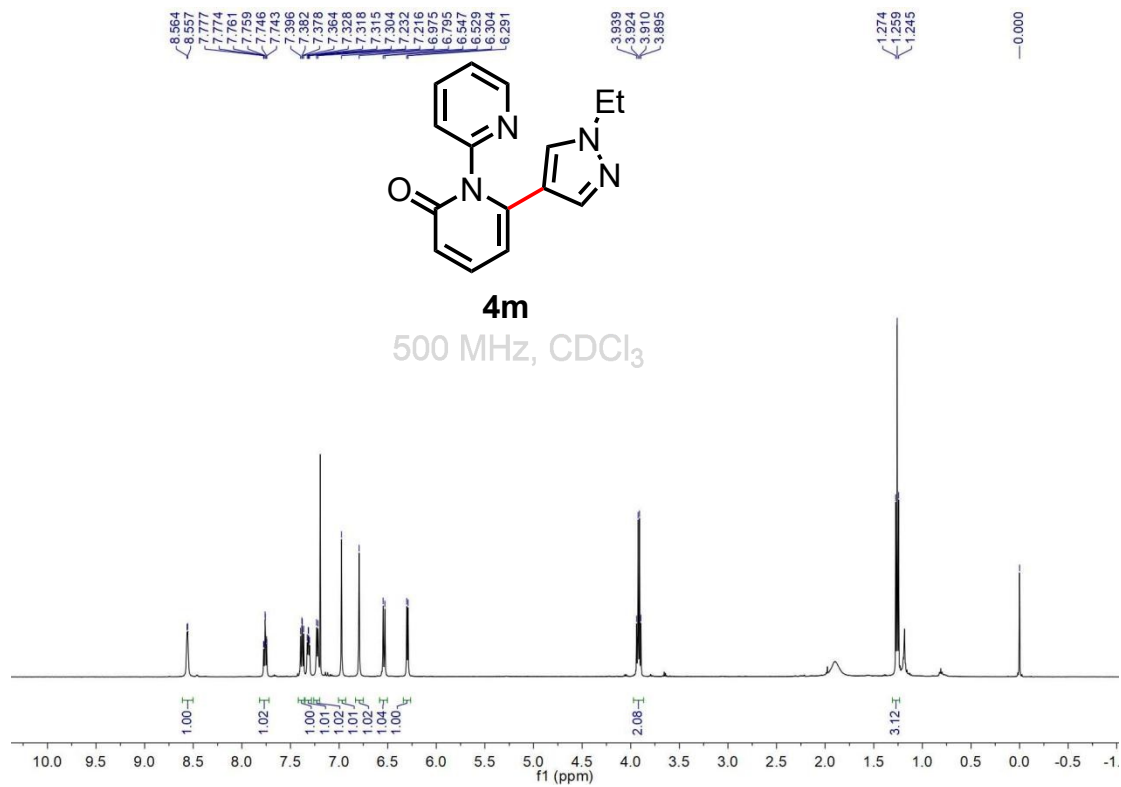
4k

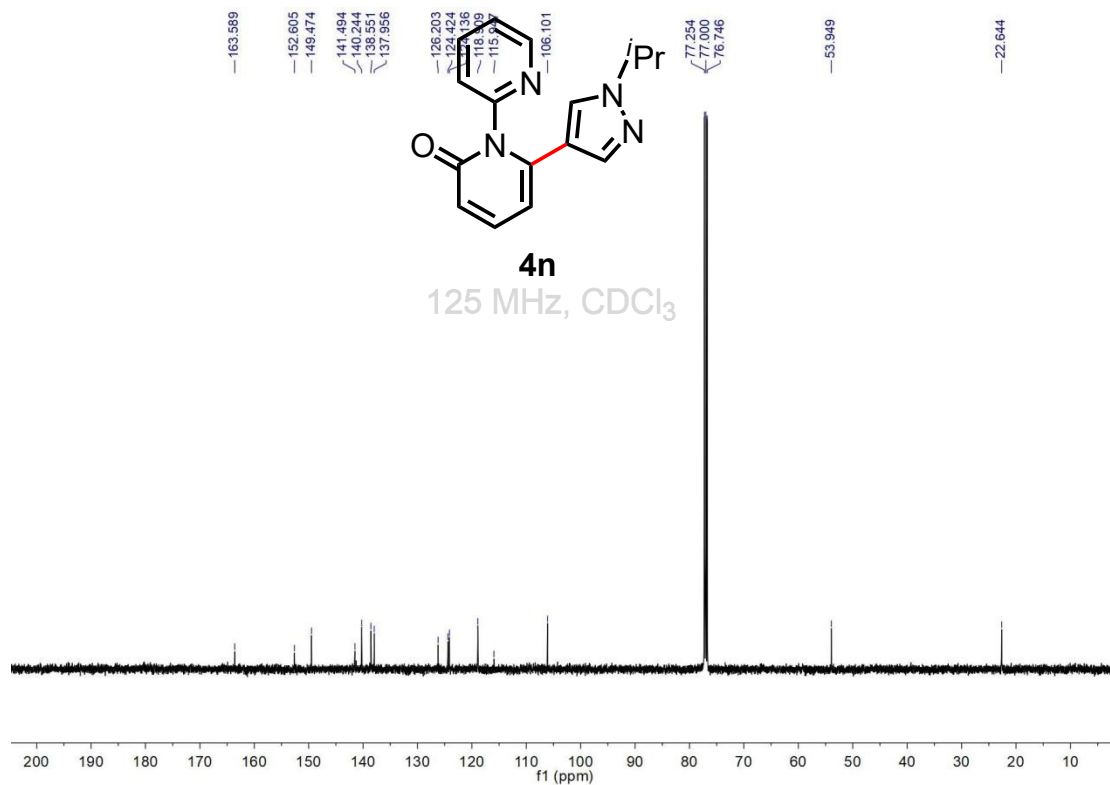
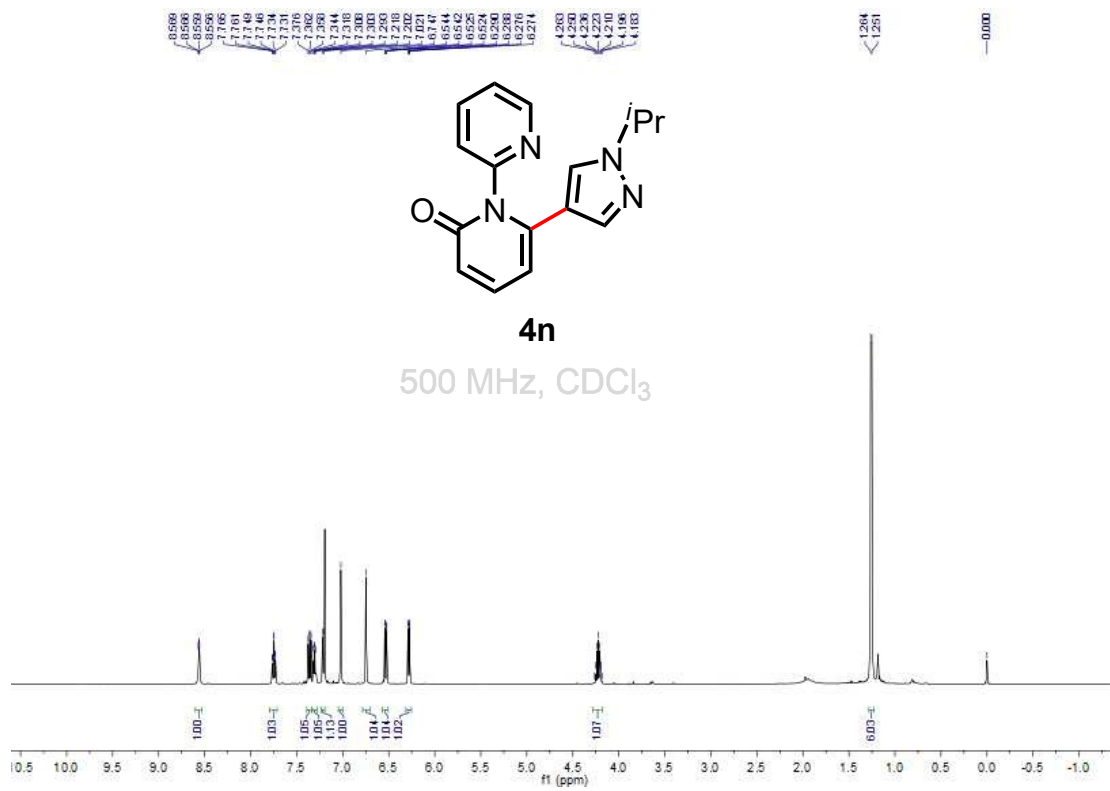
125 MHz, CDCl₃

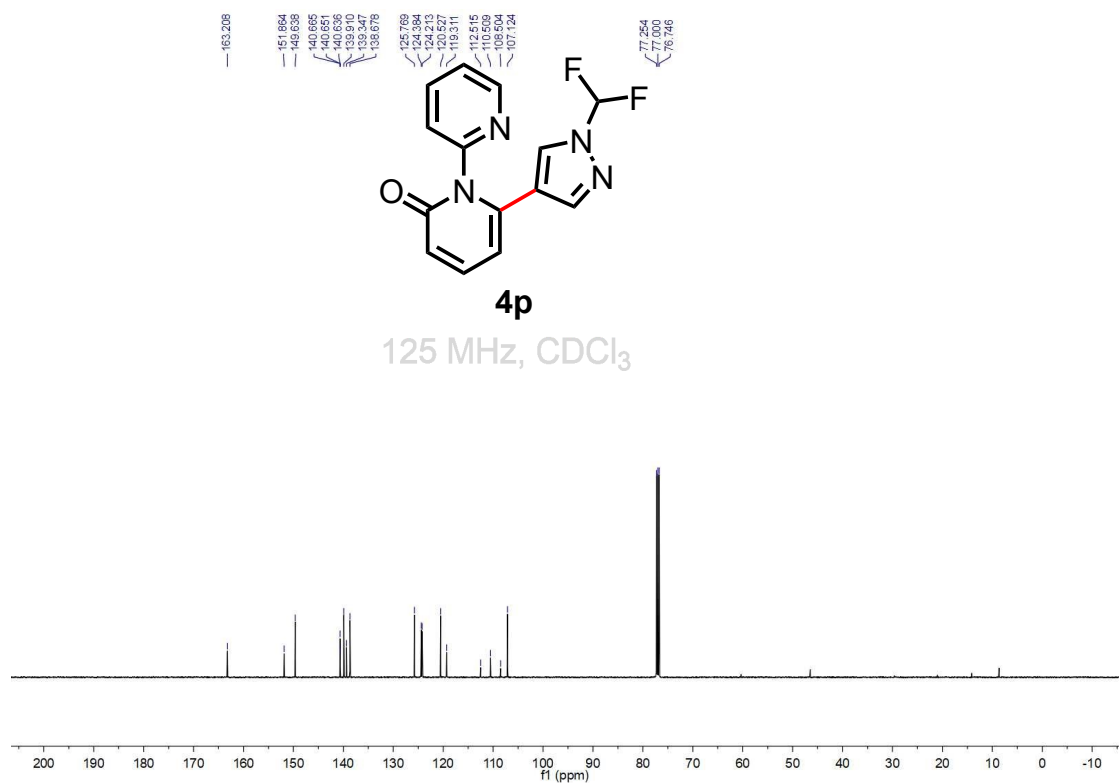
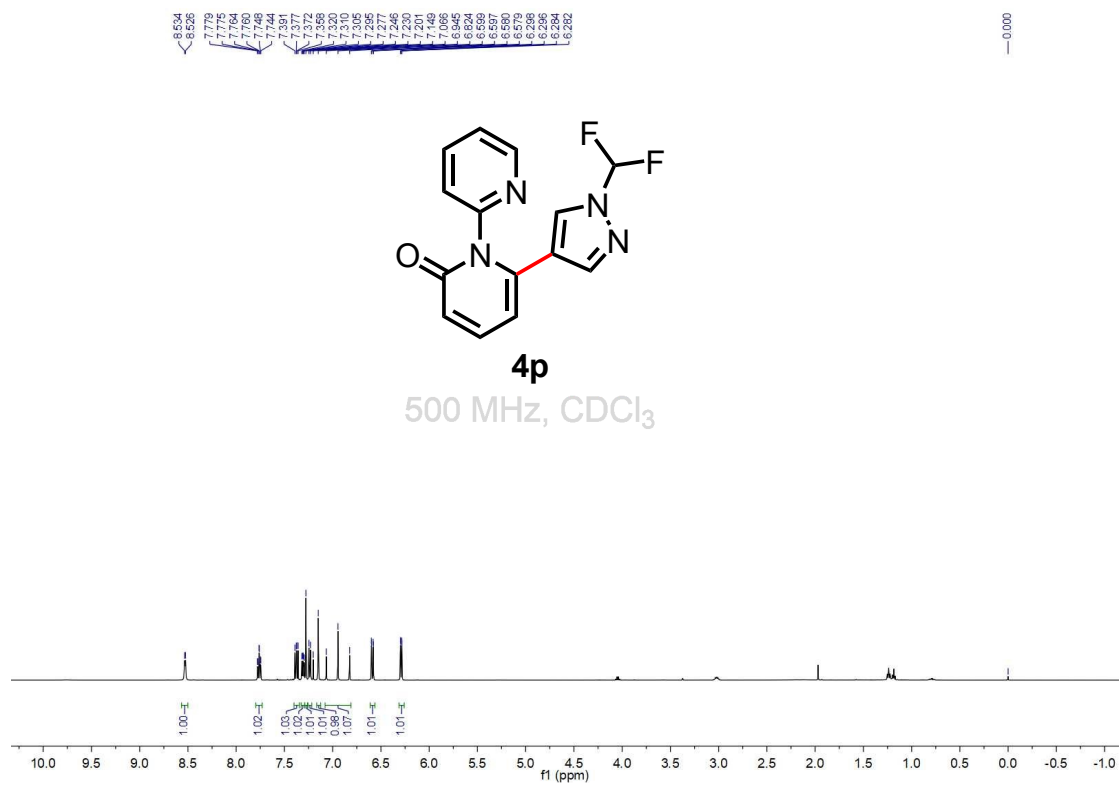


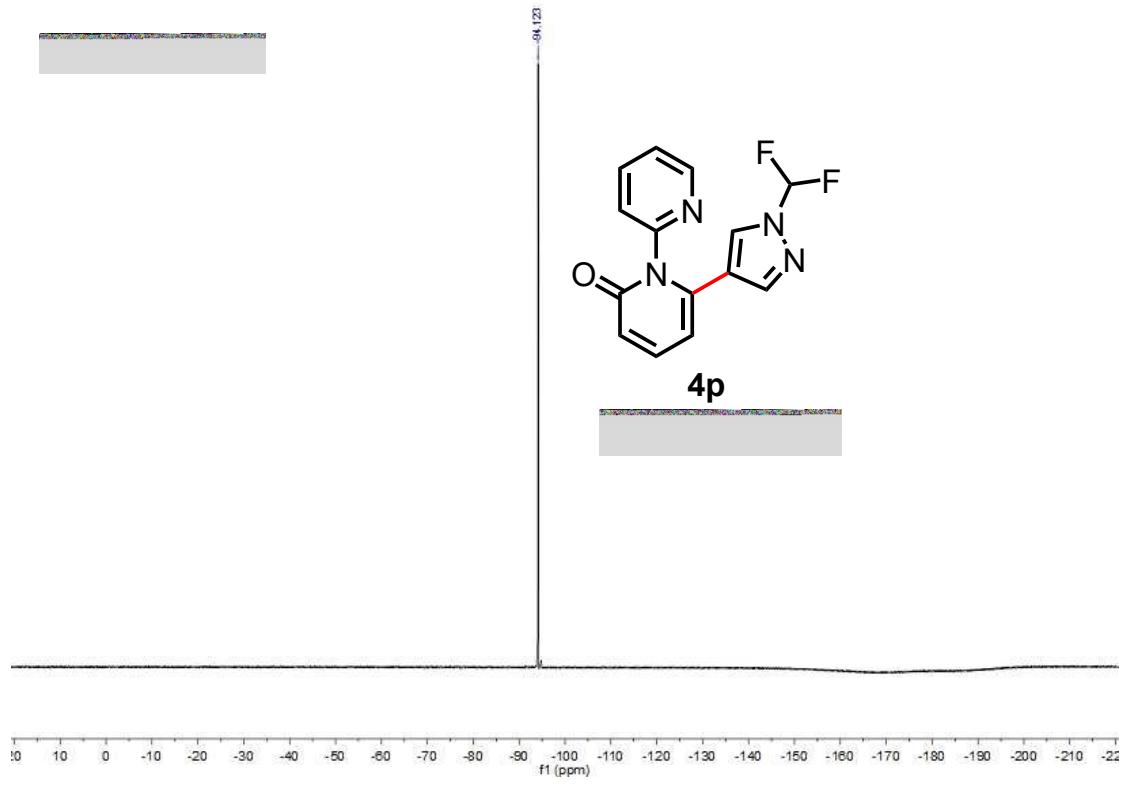


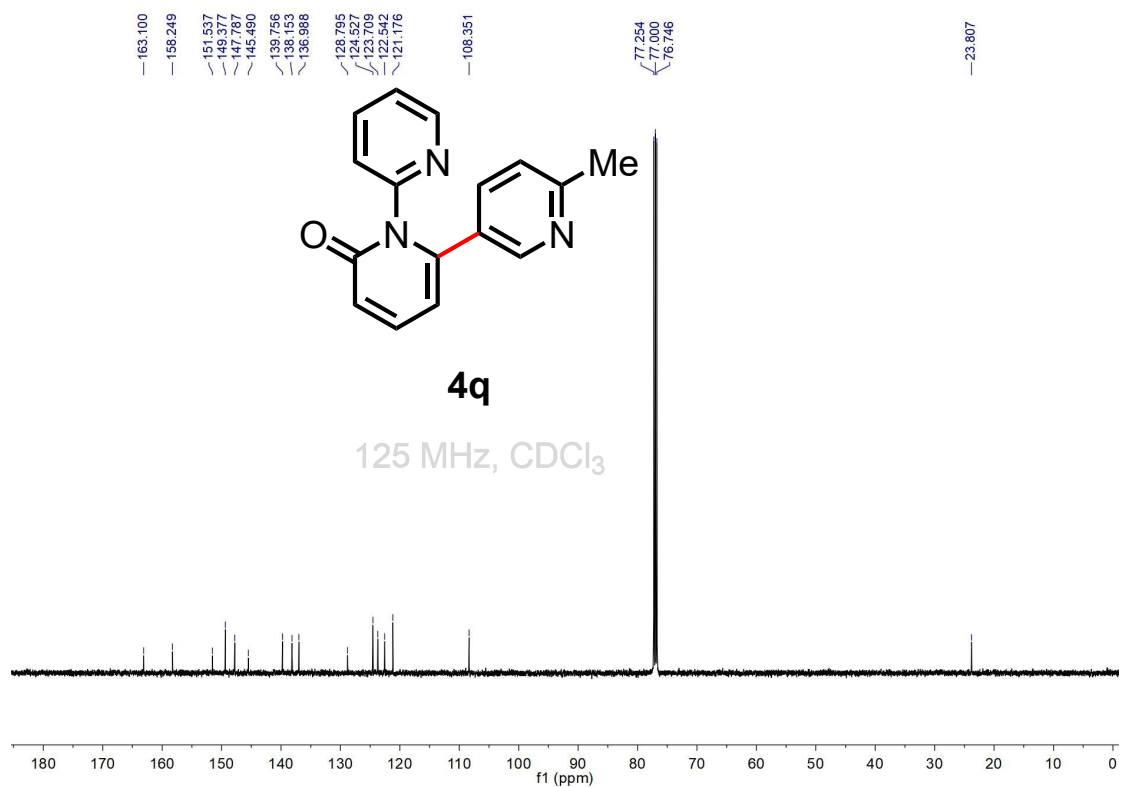
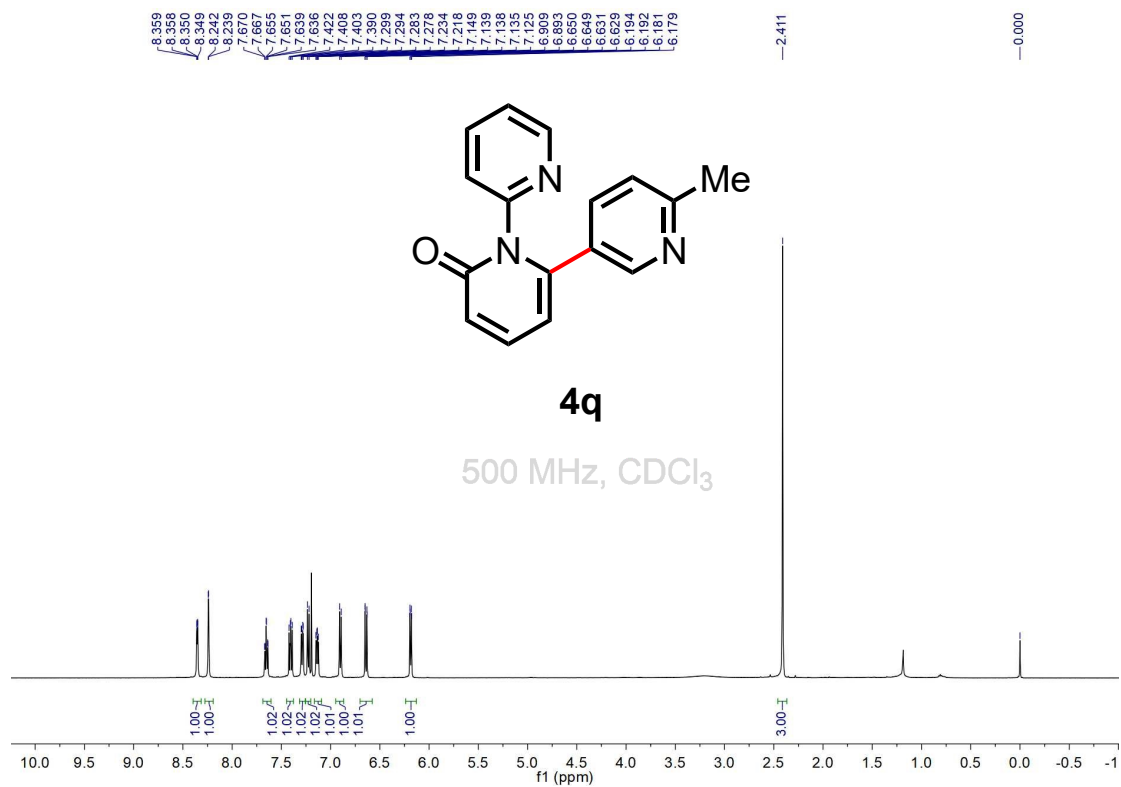


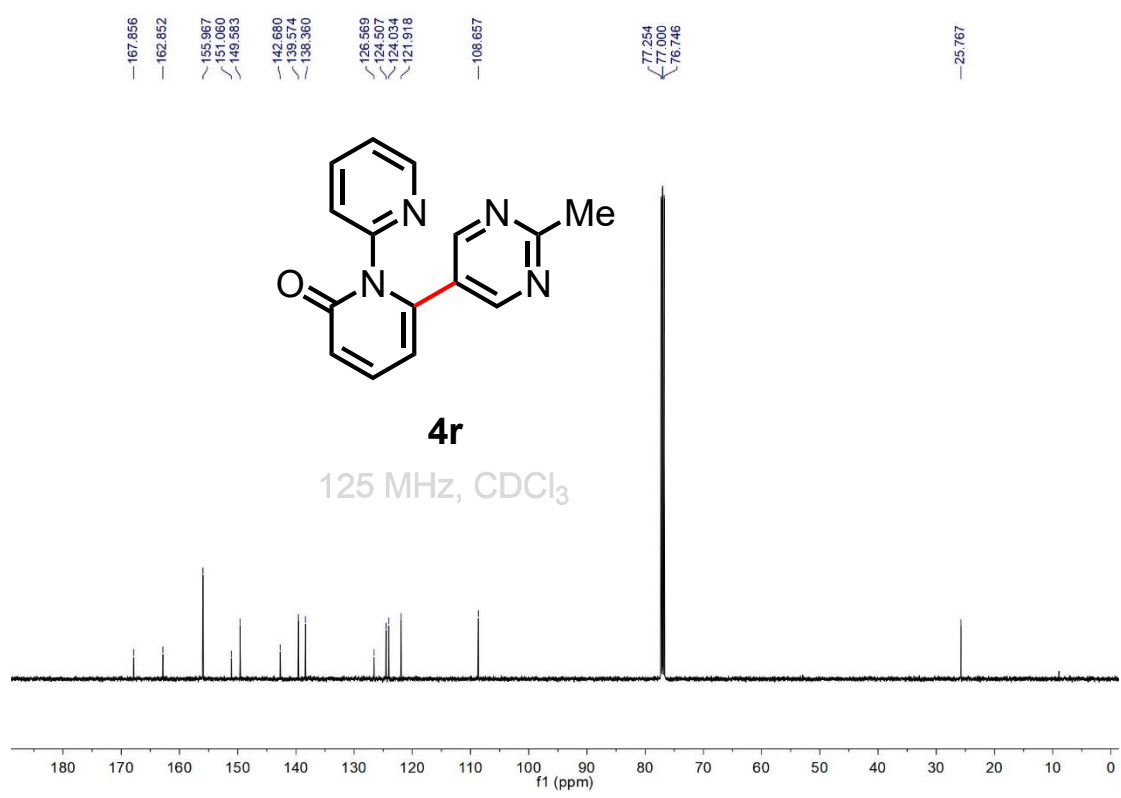
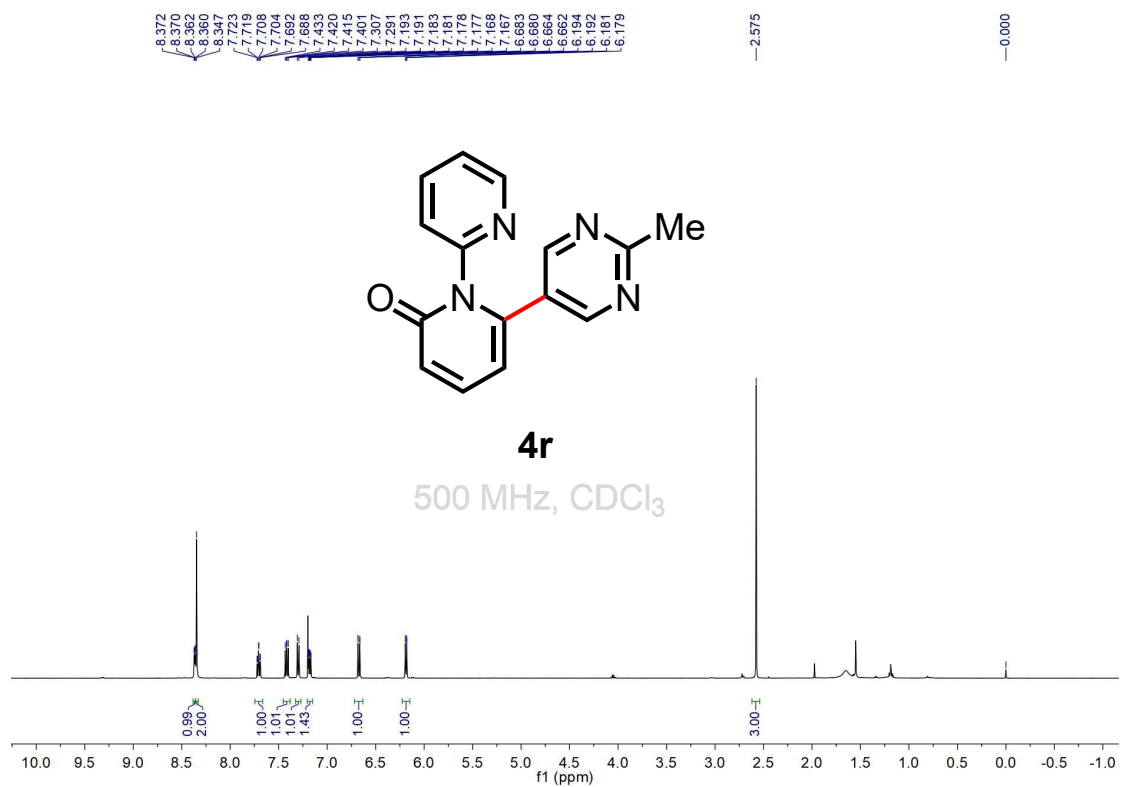






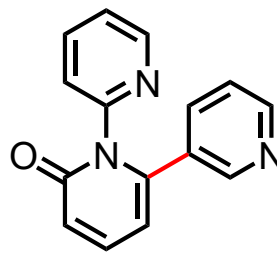






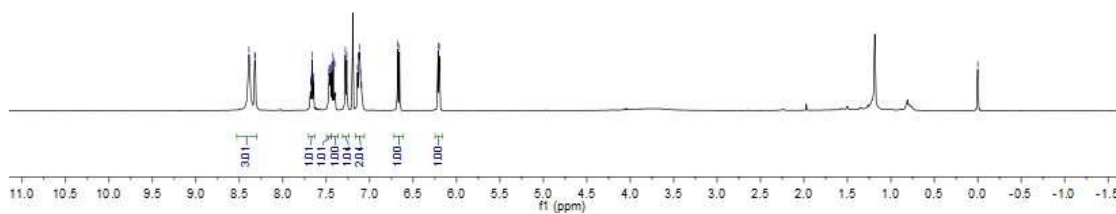
8.390
8.324
8.317
7.877
7.685
7.682
7.646
7.646
7.488
7.485
7.452
7.430
7.421
7.416
7.410
7.294
7.139
7.132
7.115
7.115
7.107
7.090
6.616
6.050
6.210
6.199

0.000



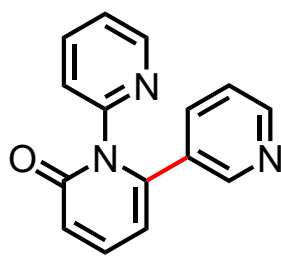
4s

500 MHz, CDCl₃



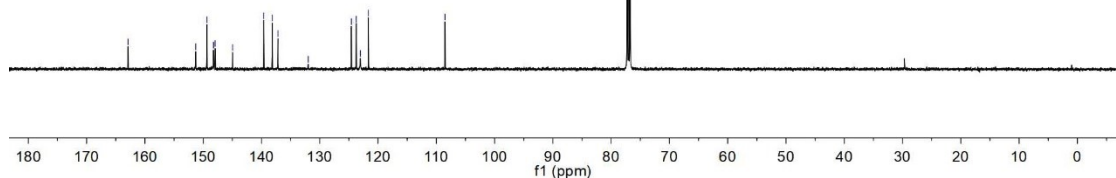
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5

162.881
151.289
149.268
148.233
147.958
144.956
139.615
138.147
137.171
131.982
124.574
123.734
123.037
121.654
106.503
77.254
77.006
76.746



4s

125 MHz, CDCl₃



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

