

Supplementary Materials

Transition-Metal-Catalyzed Transformation of Sulfonates via S–O Bond Cleavage: Synthesis of Alkyl Aryl Ether and Diaryl Ether

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1. General information

Unless otherwise noted, all reactions or reagents were obtained from commercial suppliers and used as received. Unless otherwise noted, All catalytic reactions were set up in an argon atmosphere glovebox (Vigor, SGI800-750TS-F). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox, unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Thin Layer Chromatography analyses were performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV254. For detection of spots, irradiation of UV light at 254 nm or staining reagent using phosphomolybdic acid solution was used. Flash column chromatography was conducted with silica gel 60 (particle size 230–400 mesh, Huanghai) at room temperature and under elevated pressure.

Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2030 instrument equipped with a Rtx-5 column (30 m × 0.25 mm) with dodecane as an internal standard. GC-MS analysis was conducted on a Agilent 5977B GC/MSD instrument equipped with a HP-5MS UI column (30 m × 0.25 mm). ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and at 101 MHz, respectively in CDCl₃ (or (CD₃)₂SO) at room temperature. ¹H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for CDCl₃ (or 2.50 ppm for (CD₃)₂SO) for ¹H NMR. ¹³C NMR spectra (¹H-broadband decoupled) were reported in ppm using the central peak of CDCl₃ (77.16 ppm). High-resolution mass spectrometric measurements were provided by the Department of The State Key Laboratory of Biotherapy, Sichuan University. The molecular ion [M+H]⁺ and [M+Na]⁺ are given in m/z units.

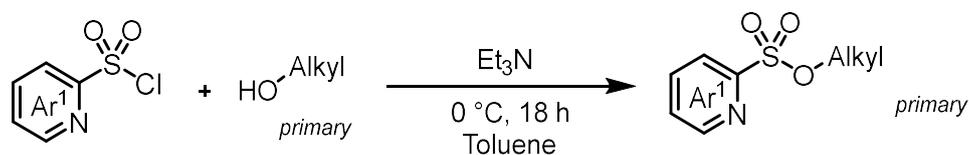
2. General procedure for the synthesis of Pyridylsulfonates.

2.1 General procedure for the synthesis of pyridylsulfonyl chloride

Unless otherwise noted, pyridylsulfonyl chloride were synthesized according to procedures reported in the literature^[1]. To a solution of mercaptopyridine (2.3 g, 20 mmol) in conc. H₂SO₄ (56 ml) was added dropwise a commercially available bleach solution (roughly 5% NaClO, 220 ml) using constant pressure dropping funnel. The resulting mixture was stirred at 0 °C for 15 min before it was extracted with CH₂Cl₂. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated (caution: in a fume hood because of the presence of Cl₂) to afford 2-pyridylsulfonyl chloride as a light yellow liquid. This compound is relatively unstable at room temperature and it was immediately used without further purification.

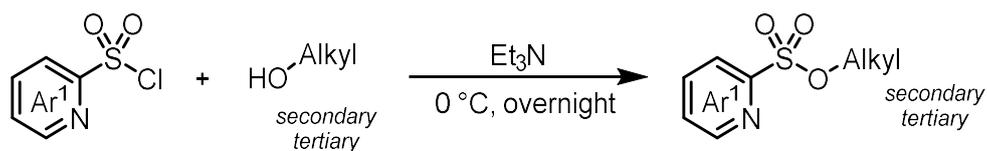
2.2. Synthesis of alkyl sulfonates.

[Method A]^[2]



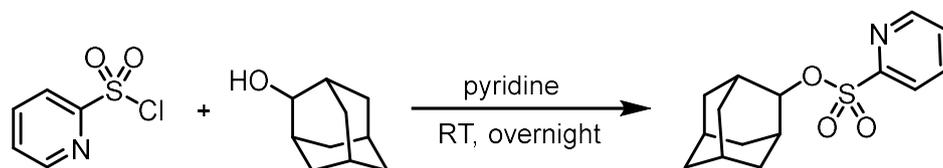
To a round-bottom flask with the anhydrous triethylamine (2.0 equiv, 10 mmol) in 2 ml dry toluene were added primary alkyl alcohol (5 mmol). After the solution was cooled to 0 °C, 6 mmol freshly prepared pyridylsulfonyl chloride was added in one portion. The resulting mixture was kept at 0 °C for 18 h. The reaction was quenched with a few milliliters of cold water and extracted three times with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated under reduced pressure and the residue was purified by flash column chromatography to give the desired product.

[Method B]^[2]



To a round-bottom flask with the anhydrous triethylamine (approximately 2 ml) were added secondary or tertiary alkyl alcohol (5 mmol) .After the solution was cooled to 0 °C , 6 mmol freshly prepared pyridylsulfonyl chloride was added in one portion. The resulting mixture was kept at 0 °C for overnight. The reaction was quenched with a few milliliters of cold water and extracted three times with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated under reduced pressure and the residue was purified by flash column chromatography to give the desired product.

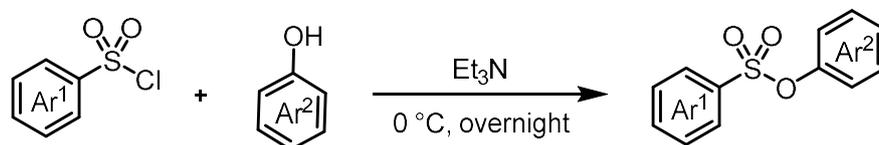
[Method C]



To a round-bottom flask containing a magnetic stirring bar and adamantan-2-ol (2 mmol) and pyridylsulfonyl chloride (1.2 equiv, 2.4 mmol) was dissolved in pyridine (2.0 ml) at 0 °C. the reaction mixture was then left at room temperature overnight. The reaction was quenched

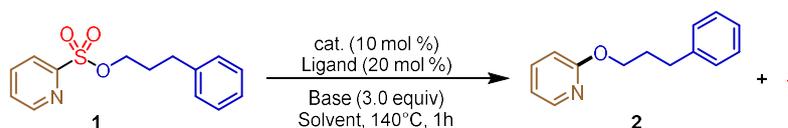
with a few milliliters of cold water and extracted three times with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated under reduced pressure and the residue was purified by flash column chromatography to give the desired product.

2.3. General procedure for synthesis of aryl sulfonates.



To a round-bottom flask with substituted phenol (1.2 equiv, 6 mmol) and triethylamine (4 ml) was added pyridylsulfonyl chloride (1.0 equiv, 5 mmol) dropwise. The resulting mixture was kept at 0 °C for overnight. the reaction was quenched with saturated aq. NaHCO₃ and extracted three times with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated in vacuo. The residue was purified by flash column chromatography.

3. Optimization.



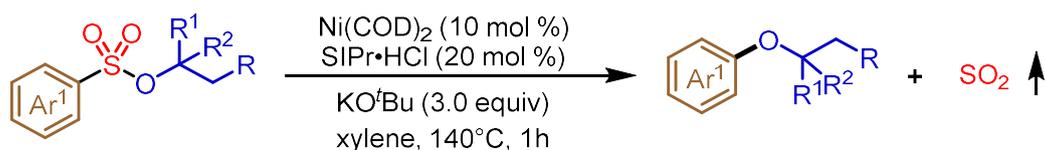
entry	Cat.	Ligand	Base	Solvent	Yield (2) ⁱ
1	Ni(COD) ₂	SIPr·HCl	LiOtBu	Xylene	0
2	Ni(COD) ₂	SIPr·HCl	NaOtBu	Xylene	21%
3	<i>Ni(COD)₂</i>	<i>SIPr·HCl</i>	<i>KOtBu</i>	<i>Xylene</i>	95%
4	Ni(COD) ₂	SIPr·HCl	K ₂ CO ₃	Xylene	0
5	Ni(COD) ₂	SIPr·HCl	K ₃ PO ₄	Xylene	0
6	Ni(COD) ₂	SIPr·HCl	KHMDS	Xylene	7%
7	Ni(COD) ₂	IMes·HCl	KOtBu	Xylene	62%
8	Ni(COD) ₂	SIMes·HCl	KOtBu	Xylene	66%
9	NiCl ₂	SIPr·HCl	KOtBu	Xylene	69%

10	Ni(OTf) ₂	SIPr·HCl	KOtBu	Xylene	70%
11	Ni(COD) ₂	SIPr·HCl	KOtBu	DMF	25%
12	Ni(COD) ₂	SIPr·HCl	KOtBu	DMSO	23%
13	Ni(COD) ₂	SIPr·HCl	KOtBu	Toluene	60%
14	Ni(COD) ₂	SIPr·HCl	KOtBu	Dioxane	73%
15	Ni(COD) ₂	SIPr·HCl	KOtBu	Anisole	72%
16 ^a	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	trace
17 ^b	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	15%
18 ^c	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	34%
19 ^d	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	57%
20 ^e	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	80%
21 ^f	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	52%
22 ^g	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	22%
23	-	SIPr·HCl	KOtBu	Xylene	0
24	Ni(COD) ₂	-	KOtBu	Xylene	0
25	-	-	KOtBu	Xylene	0
26 ^h	Ni(COD) ₂	SIPr·HCl	KOtBu	Xylene	92

^aNi(COD)₂ (1 mol %), SIPr·HCl (2 mol %); ^bNi(COD)₂ (2 mol %), SIPr·HCl (4 mol %); ^cNi(COD)₂ (3 mol %), SIPr·HCl (6 mol %); ^dNi(COD)₂ (5 mol %), SIPr·HCl (10 mol %); ^eNi(COD)₂ (7 mol %), SIPr·HCl (14 mol %); ^f120 °C; ^g100 °C; ^hWith an argon balloon; ⁱYields were determined by GC using dodecane as an internal standard.

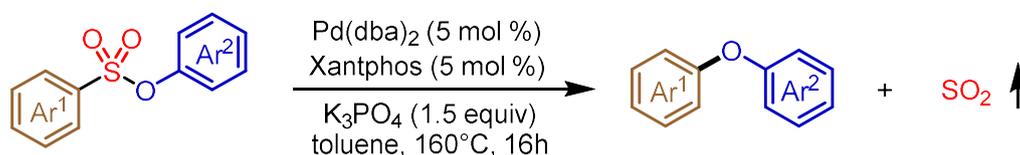
4. Scope of intramolecular desulfative C–O coupling reactions

General Procedure A



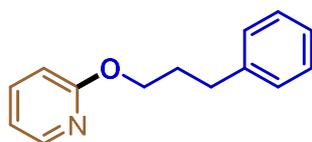
In the glovebox, Ni(COD)_2 (10 mol %, 5.5 mg), $\text{SIPr}\cdot\text{HCl}$ (20 mol %, 17.2 mg), KO^tBu (3.0 equiv, 67.3 mg), and alkyl sulfonates (0.2 M in xylenes, 1 ml) were added into an oven-dried 8 ml vial with a magnetic stirring bar, followed by addition of xylenes (1.5 ml). The vial was sealed and removed out of the glovebox and heated to 140 °C. After 1 h, the vial was cooled to room temperature. The mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired product.

General Procedure B



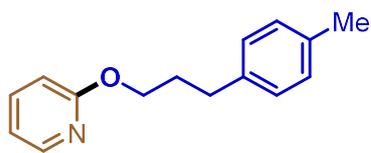
In the glovebox, aryl pyridine sulfonate (0.2 mmol), Pd(dba)_2 (5 mol %, 5.8 mg), Xantphos (5 mol %, 5.8 mg), K_3PO_4 (1.5 equiv, 63.7 mg) were added into an oven-dried 8 ml vial with a magnetic stirring bar, followed by addition of toluene (3 ml). The vial was sealed and removed out of the glovebox and heated to 160 °C for 16 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired product.

2-(3-phenylpropoxy)pyridine (Figure 2, 2)



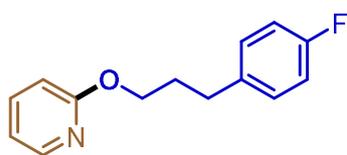
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (40.5 mg, 95%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.15 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.56 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.31–7.26 (m, 2H), 7.24–7.16 (m, 3H), 6.85 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.75 (d, $J = 8.4$ Hz, 1H), 4.33 (t, $J = 6.4$ Hz, 2H), 2.80 (t, $J = 7.6$ Hz, 2H), 2.15–2.08 (m, 2H), $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 163.9, 146.8, 141.7, 138.6, 128.5, 128.4, 125.8, 116.6, 111.1, 65.2, 32.3, 30.8. HRMS m/z calculated for $\text{C}_{14}\text{H}_{15}\text{NO}$ $[\text{M}+\text{H}]^+$: 214.1226, found: 214.1232.

2-(3-(*p*-tolyl) propoxy)pyridine (Figure 2, 3)



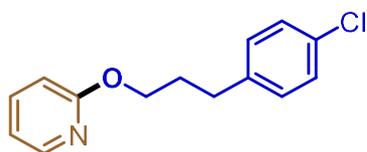
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (30.0 mg, 66%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.56 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 7.16–7.06 (m, 4H), 6.85 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 4.32 (t, *J* = 6.4 Hz, 2H), 2.81–2.72 (m, 2H), 2.32 (s, 3H), 2.16–2.03 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.9, 146.9, 138.6, 138.5, 135.26, 129.0, 128.4, 116.5, 111.0, 65.2, 31.9, 30.8, 21.0. HRMS *m/z* calculated for C₁₅H₁₇NO [M+H]⁺: 228.1383, found: 228.1386.

2-(3-(4-fluorophenyl)propoxy)pyridine (Figure 2, 4)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (30.1 mg, 65%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.19–7.15 (m, 2H), 6.99–6.94 (m, 2H), 6.85 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.11–2.04 (m, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -117.81. ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.9, 161.3 (d, *J* = 244.2 Hz), 146.8, 138.6, 137.3 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 7.8 Hz), 116.6, 115.1 (d, *J* = 21.2 Hz), 111.0, 64.9, 31.5, 30.8. HRMS *m/z* calculated for C₁₄H₁₄FNO [M+H]⁺: 232.1132, found: 232.1131.

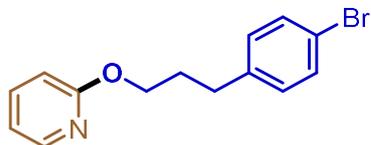
2-(3-(4-chlorophenyl)propoxy)pyridine (Figure 2, 5)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (28.2 mg, 57%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.26–7.23 (m, 2H), 7.16–7.13 (m, 2H), 6.88–6.84 (m, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.79–2.74 (m, 2H), 2.12–2.04 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.8, 146.8, 140.1, 138.6, 131.6, 129.8,

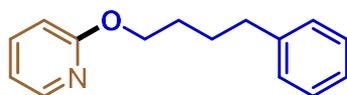
128.4, 116.6, 111.0, 64.9, 31.7, 30.6. HRMS m/z calculated for $C_{14}H_{14}ClNO$ $[M+H]^+$: 248.0837, found: 248.0841.

2-(3-(4-bromophenyl)propoxy)pyridine (Figure 2, 6)



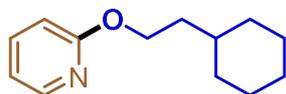
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (29.2 mg, 50%). 1H NMR (400 MHz, Chloroform- d) δ 8.14 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.57 (ddd, $J = 8.8, 7.2, 2.0$ Hz, 1H), 7.41–7.37 (m, 2H), 7.11–7.07 (m, 2H), 6.87–6.83 (m, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 4.30 (t, $J = 6.4$ Hz, 2H), 2.78–2.72 (m, 2H), 2.11–2.04 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.9, 146.9, 140.7, 138.5, 131.4, 119.6, 130.2, 116.6, 111.0, 64.8, 31.8, 30.5. HRMS m/z calculated for $C_{14}H_{14}BrNO$ $[M+H]^+$: 292.0332, found: 292.0333.

2-(4-phenylbutoxy)pyridine (Figure 2, 7)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (34.1 mg, 75%). 1H NMR (400 MHz, DMSO- d_6) δ 8.14 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.67 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.30–7.24 (m, 2H), 7.22–7.13 (m, 3H), 6.94 (dd, $J = 7.2, 5.2$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 4.26 (t, $J = 6.0$ Hz, 2H), 2.63 (t, $J = 7.2$ Hz, 2H), 1.73–1.67 (m, 4H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 163.8, 147.3, 142.5, 139.5, 128.8, 128.7, 126.1, 117.3, 111.1, 65.5, 35.3, 28.6, 28.0. HRMS m/z calculated for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383, found: 228.1391.

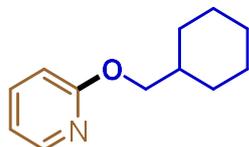
2-(2-cyclohexylethoxy)pyridine (Figure 2, 8)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (100:1) as eluent (33.3 mg, 81%); 1H NMR (400 MHz, DMSO- d_6) δ 8.13 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.69–7.64 (m, 1H), 6.93 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 4.27 (t, $J = 6.8$ Hz, 2H), 1.74–1.57 (m, 8H), 1.23–1.13 (m, 3H), 0.99–0.89 (m, 2H). ^{13}C NMR (101 MHz,

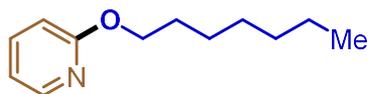
DMSO-*d*₆) δ 163.8, 147.3, 139.5, 117.3, 111.2, 63.7, 36.4, 34.6, 33.2, 26.5, 26.2. HRMS *m/z* calculated for C₁₃H₁₉NO [M+H]⁺: 206.1539, found: 206.1546.

2-(cyclohexylmethoxy)pyridine (Figure 2, 9)



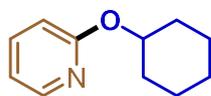
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (100:1) as eluent (30.1 mg, 81%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.13 (d, *J* = 5.2 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 6.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.05 (d, *J* = 6.0 Hz, 2H), 1.80–1.65 (m, 6H), 1.27–1.16 (m, 3H), 1.07–0.98 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 163.9, 147.3, 139.5, 117.2, 111.1, 70.8, 37.3, 29.8, 26.5, 25.7. HRMS *m/z* calculated for C₁₂H₁₇NO [M+H]⁺: 192.1383, found: 192.1390.

2-(heptyloxy)pyridine (Figure 2, 10)



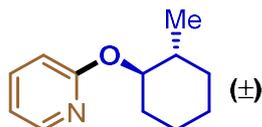
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (50:1) as eluent (25.1 mg, 65%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.57–7.51 (m, 1H), 6.83 (t, *J* = 6.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 1.81–1.73 (m, 2H), 1.47–1.41 (m, 2H), 1.35–1.25 (m, 6H), 0.91–0.87 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 146.9, 138.4, 116.4, 111.1, 66.0, 31.8, 29.1, 29.1, 26.0, 22.6, 14.1. HRMS *m/z* calculated for C₁₂H₁₉NO [M+H]⁺: 194.1539, found: 194.1541.

2-(cyclohexyloxy)pyridine (Figure 2, 11)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (100:1) as eluent (28.7 mg, 81%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.58–7.49 (m, 1H), 6.83–6.78 (m, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.07–4.99 (m, 1H), 2.06–1.97 (m, 2H), 1.84–1.74 (m, 2H), 1.54–1.40 (m, 4H), 1.36–1.24 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.5, 146.8, 138.4, 116.2, 111.6, 73.0, 31.9, 25.7, 24.0. HRMS *m/z* calculated for C₁₁H₁₅NO [M+H]⁺: 178.1226, found: 178.1231.

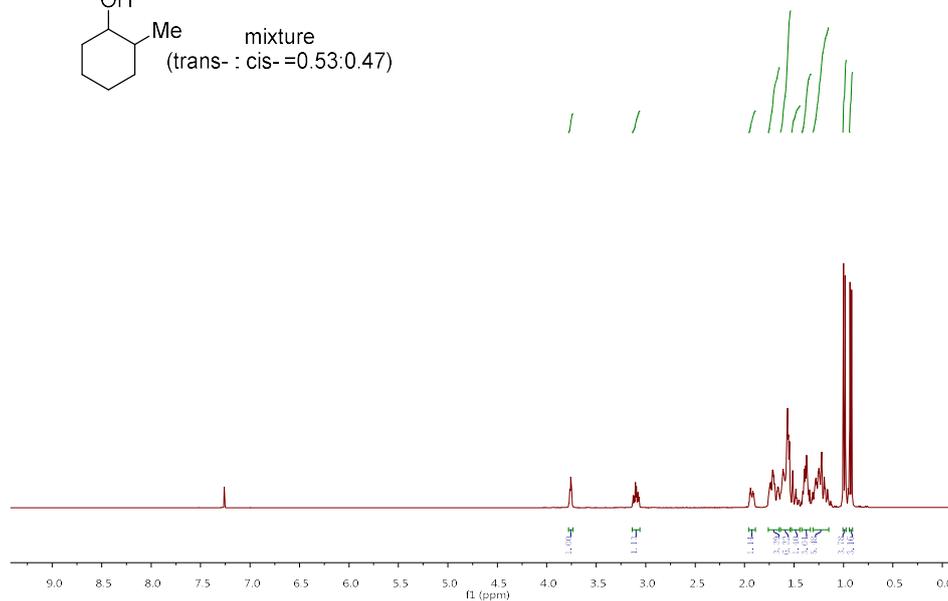
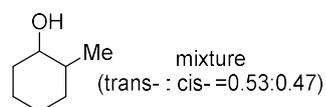
2-((2-methylcyclohexyl)oxy)pyridine (Figure 2, 12)



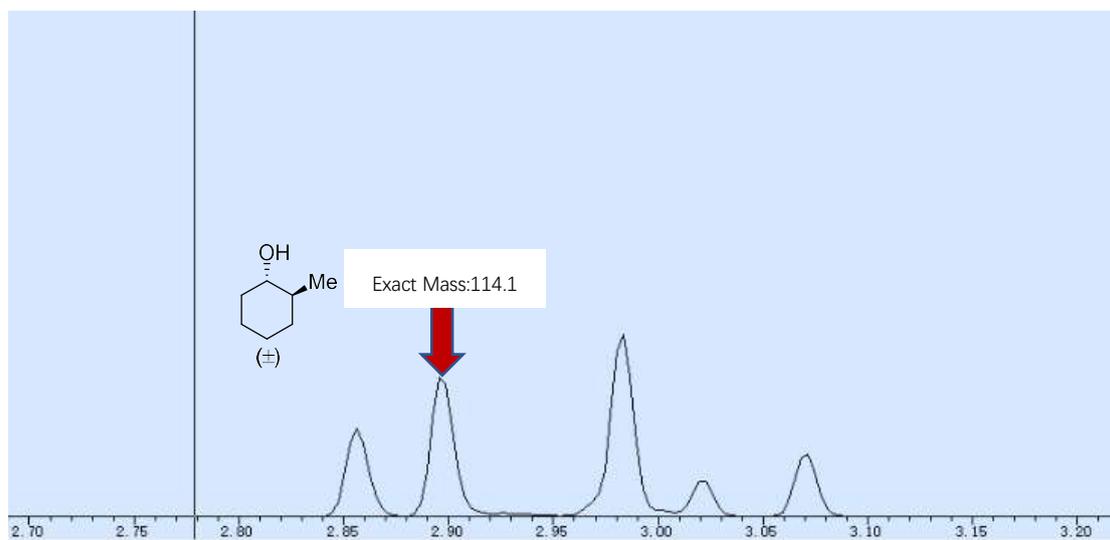
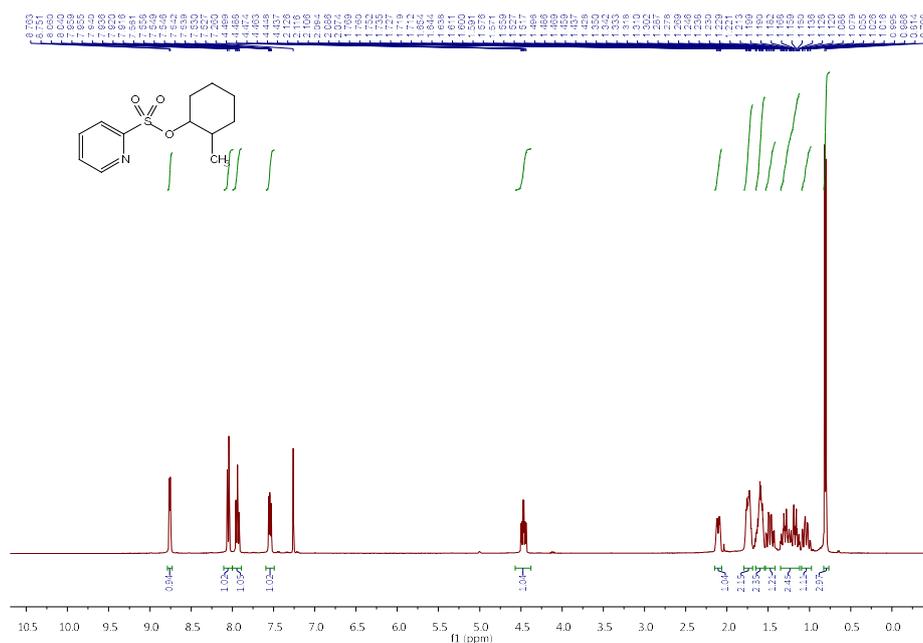
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (100:1) as eluent (29.8 mg, 78%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.11 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.68–7.63 (m, 1H), 6.90 (dd, $J = 7.2, 5.2$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 4.68 (td, $J = 10.0, 4.0$ Hz, 1H), 2.09–2.04 (m, 1H), 1.80–1.68 (m, 2H), 1.65–1.58 (m, 2H), 1.35–1.24 (m, 2H), 1.23–1.08 (m, 2H), 0.89 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 164.1, 146.8, 138.5, 116.1, 111.5, 78.9, 37.9, 33.8, 31.6, 25.6, 24.8, 18.7. HRMS m/z calculated for $\text{C}_{12}\text{H}_{17}\text{NO}$ $[\text{M}+\text{Na}]^+$: 214.1202, found: 214.1208.

Diastereomeric information of Compound **12**.

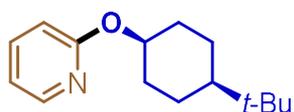
The corresponding sulfonate was synthesized from pyridylsulfonyl chloride and alkyl alcohol. The alkyl alcohol is commercial available. From its ^1H -NMR, we can see it contains isomer mixtures.



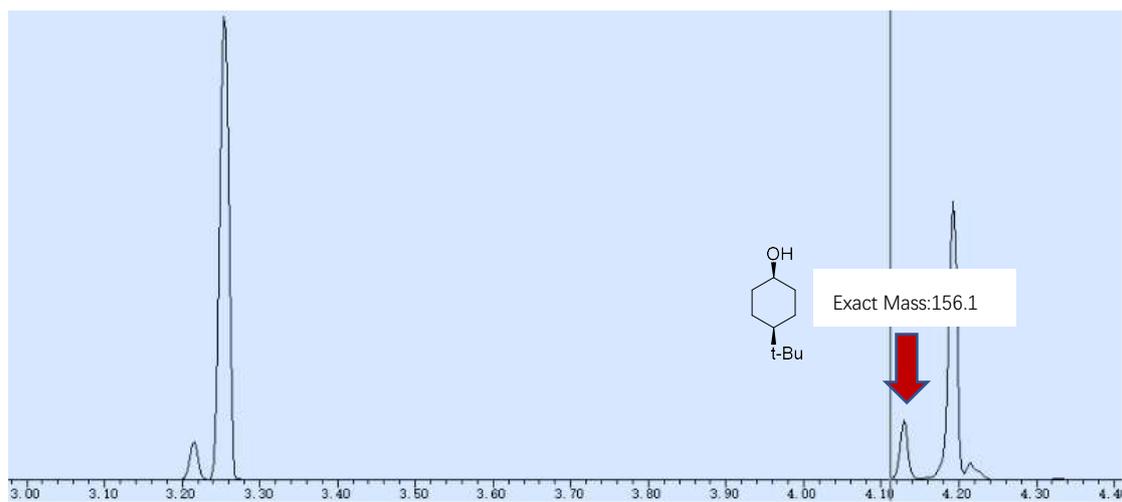
However, we found the sulfonate was diastereospecific. To get the diastereomeric information of sulfonate, the sulfonate was hydrolyzed to alkyl alcohol in acidic conditions. From the GC-MS spectra, the corresponding alcohol was detected.



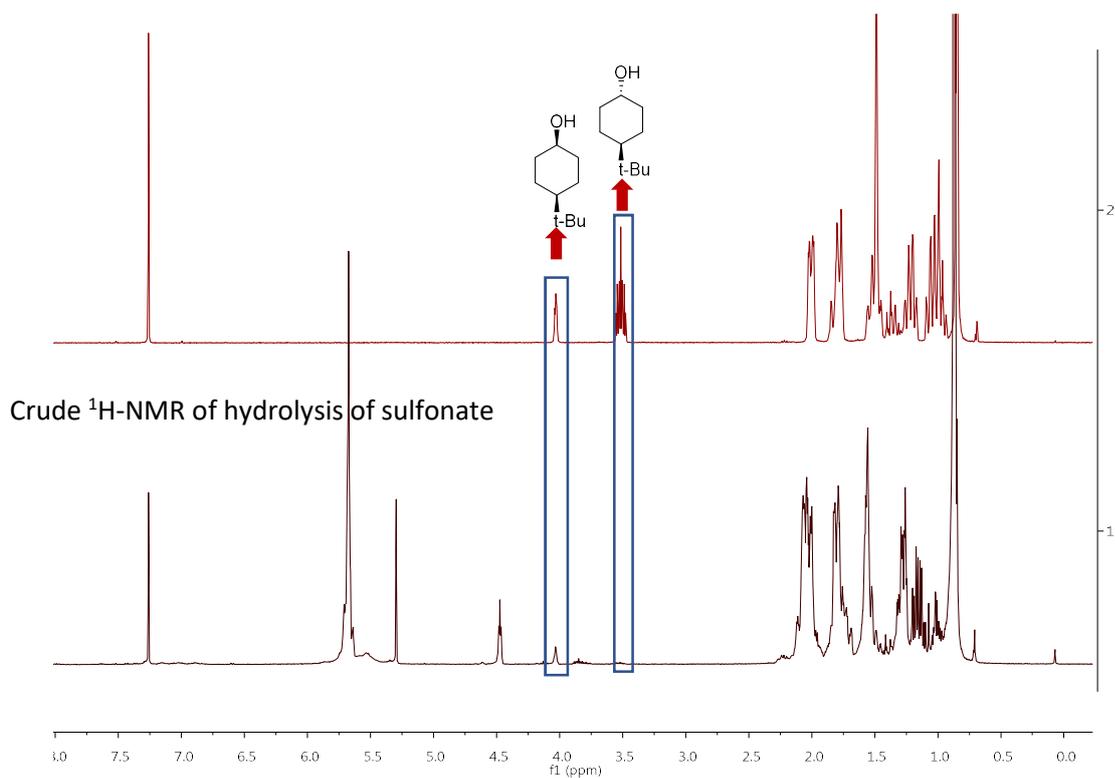
From the crude $^1\text{H-NMR}$, we could know *trans*-isomer of alcohol³ was transformed to sulfonate. Therefore, the diastereomeric information of Compound 12 was determined **2-((4-*tert*-butyl)cyclohexyl)oxy)pyridine (Figure 2, 13)**



Prepared by general procedure A; isolated as a white solid using petroleum ether/ethyl acetate (100:1) as eluent. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.13 (dd, $J = 4.8, 1.2$ Hz, 1H), 7.56–7.50 (m, 1H), 6.80 (ddd, $J = 6.8, 4.8, 0.8$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 4.96–4.87 (m, 1H), 2.23–2.17 (m, 2H), 1.84 (m, 2H), 1.44–1.33 (m, 2H), 1.26–1.18 (m, 2H), 1.10–1.02 (m, 1H), 0.88 (s,



From the crude $^1\text{H-NMR}$, we could know cis-isomer of alcohol⁴ was transformed to sulfonate. Therefore, the diastereomeric information of Compound 13 was determined.

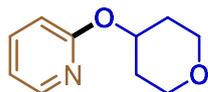


2-(((1*r*,4*r*)-4-methylcyclohexyl)oxy)pyridine (Figure 2, 14)



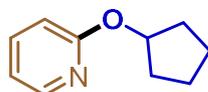
Prepared by general procedure A; isolated as a white solid using petroleum ether/diethyl ether (100:1) as eluent (26.5 mg, 70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 6.80 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 5.25–5.20 (m, 1H), 2.02–1.96 (m, 2H), 1.65–1.49 (m, 5H), 1.44–1.36 (m, 2H), 0.94 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.5, 146.9, 138.4, 116.1, 111.7, 70.0, 31.4, 29.6, 29.5, 22.0. HRMS *m/z* calculated for C₁₂H₁₇NO [M+H]⁺: 192.1383, found: 192.1389.

2-((tetrahydro-2H-pyran-4-yl)oxy)pyridine (Figure 2, 15)



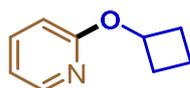
Prepared by general procedure A; isolated as a white solid using petroleum ether/ethyl acetate (10:1) as eluent (23.3 mg, 65%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 6.84 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.28–5.21 (m, 1H), 4.01–3.96 (m, 2H), 3.67–3.56 (m, 2H), 2.10–2.04 (m, 2H), 1.84–1.75 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.0, 146.7, 138.7, 116.6, 111.7, 69.4, 65.6, 32.1. HRMS *m/z* calculated for C₁₀H₁₃NO₂ [M+H]⁺: 180.1019, found: 180.1021.

2-(cyclopentyloxy)pyridine (Figure 2, 16)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (100:1) as eluent (26.1 mg, 80%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.14 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.68–7.62 (m, 1H), 6.92 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.38–5.32 (m, 1H), 1.95–1.88 (m, 2H), 1.68 (m, 4H), 1.58 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.7, 147.0, 138.4, 116.2, 111.5, 77.6, 32.8, 23.9. HRMS *m/z* calculated for C₁₀H₁₃NO [M+Na]⁺: 186.0889, found: 186.0896.

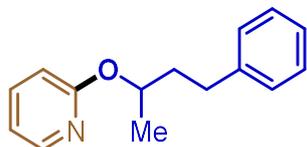
2-cyclobutoxy pyridine (Figure 2, 17)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (20:1) as eluent (18.8 mg, 63%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.47 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 6.76 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 5.15–5.06 (m, 1H), 2.43–2.35 (m, 2H), 2.12–2.02 (m, 2H), 1.80–1.72 (m, 1H), 1.66–

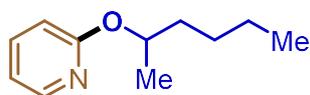
1.57 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 147.0, 138.5, 116.5, 110.9, 69.8, 30.8, 13.5. HRMS m/z calculated for $\text{C}_9\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 150.0913, found: 150.0916.

2-((4-phenylbutan-2-yl)oxy)pyridine (Figure 2, 18)



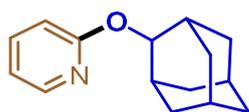
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (80:1) as eluent (43.2mg, 95%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (ddd, $J = 5.2, 2.0, 0.8$ Hz, 1H), 7.55 (ddd, $J = 8.0, 7.2, 2.0$ Hz, 1H), 7.28–7.24 (m, 2H), 7.20–7.15 (m, 3H), 6.82 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 5.29–5.20 (m, 1H), 2.83–2.76 (m, 1H), 2.73–2.65 (m, 1H), 2.13–2.03 (m, 1H), 1.96–1.87 (m, 1H), 1.36 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 146.9, 142.2, 138.5, 128.4, 128.3, 125.7, 116.3, 111.6, 70.8, 38.2, 31.9, 20.0. HRMS m/z calculated for $\text{C}_{15}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$: 228.1383, found: 228.1386.

2-(hexan-2-yloxy)pyridine (Figure 2, 19)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (20:1) as eluent (22.9 mg, 64%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.13 (ddd, $J = 5.2, 2.0, 0.8$ Hz, 1H), 7.53 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 6.80 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.67 (d, $J = 8.4$ Hz, 1H), 5.23–5.14 (m, 1H), 1.79–1.69 (m, 1H), 1.63–1.54 (m, 1H), 1.44–1.32 (m, 4H), 1.31 (d, $J = 6.4$ Hz, 3H), 0.92–0.87 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 146.9, 138.4, 116.2, 111.6, 71.3, 36.1, 27.7, 22.7, 19.9, 14.0. HRMS m/z calculated for $\text{C}_{11}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$: 180.1383, found: 180.1388.

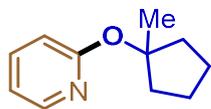
2-(((1*r*, 3*r*, 5*r*, 7*r*)-adamantan-2-yl)oxy)pyridine (Figure 2, 20)



Prepared by general procedure A; isolated as a pale yellow solid using petroleum ether/diethyl ether (60:1) as eluent (16.3 mg, 35%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.54 (ddd, $J = 8.8, 7.2, 2.0$ Hz, 1H), 6.80 (dd, $J = 7.2, 5.2$ Hz, 1H), 6.74 (d, $J = 8.8$ Hz, 1H), 5.17–5.15 (m, 1H), 2.21–2.12 (m, 4H), 1.87 (s, 6H), 1.79–1.73 (m, 2H), 1.58–1.53 (m, 2H). ^{13}C

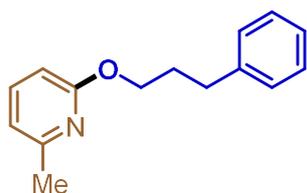
NMR (101 MHz, Chloroform-*d*) δ 163.5, 146.9, 138.5, 116.1, 111.8, 77.3, 37.6, 36.5, 31.8, 31.8, 27.5, 27.3. HRMS *m/z* calculated for C₁₅H₁₉NO [M+H]⁺: 230.1539, found: 230.1539.

2-((1-methylcyclopentyl)oxy)pyridine (Figure 2, 21)



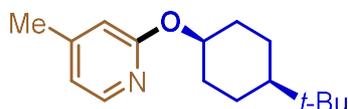
Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/ethyl acetate (100:1) as eluent (11.0 mg, 31%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H), 6.78 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 2.33–2.23 (m, 2H), 1.82–1.71 (m, 4H), 1.69 (s, 3H), 1.67–1.62 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.8, 146.6, 138.1, 116.0, 113.0, 89.1, 39.6, 29.7, 28.7, 24.8, 24.0. HRMS *m/z* calculated for C₁₁H₁₅NO [M+H]⁺: 178.1226, found: 178.1227.

2-methyl-6-(3-(phenylpropoxy)pyridine (Figure 2, 22)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (60:1) as eluent (31.8 mg, 70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.32–7.27 (m, 2H), 7.25–7.17 (m, 3H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.81 (t, *J* = 8.0, 2H), 2.44 (s, 3H), 2.15–2.07 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.5, 156.3, 141.9, 138.7, 128.5, 128.4, 125.8, 115.6, 107.0, 65.0, 32.4, 30.8, 24.2. HRMS *m/z* calculated for C₁₅H₁₇NO [M+H]⁺: 228.1383, found: 228.1386.

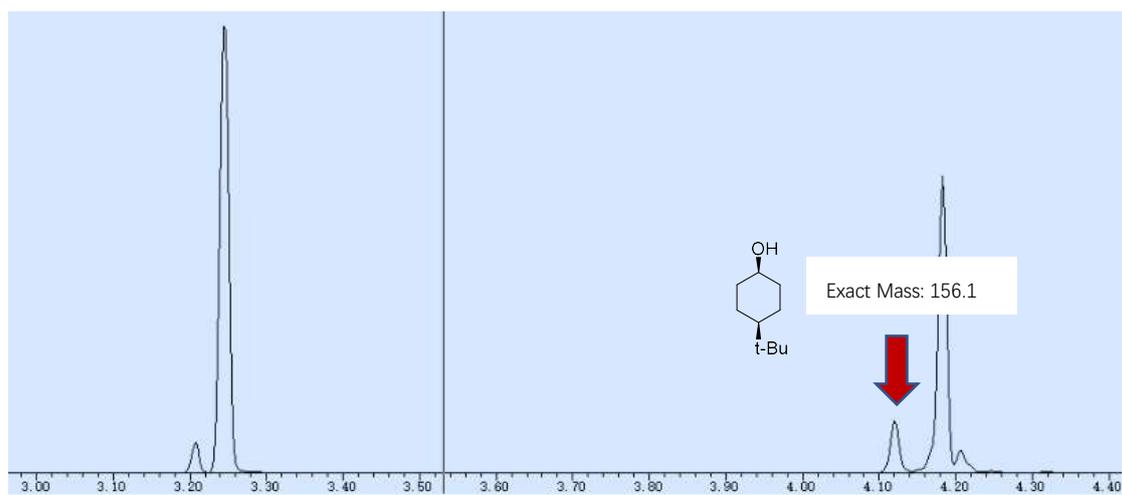
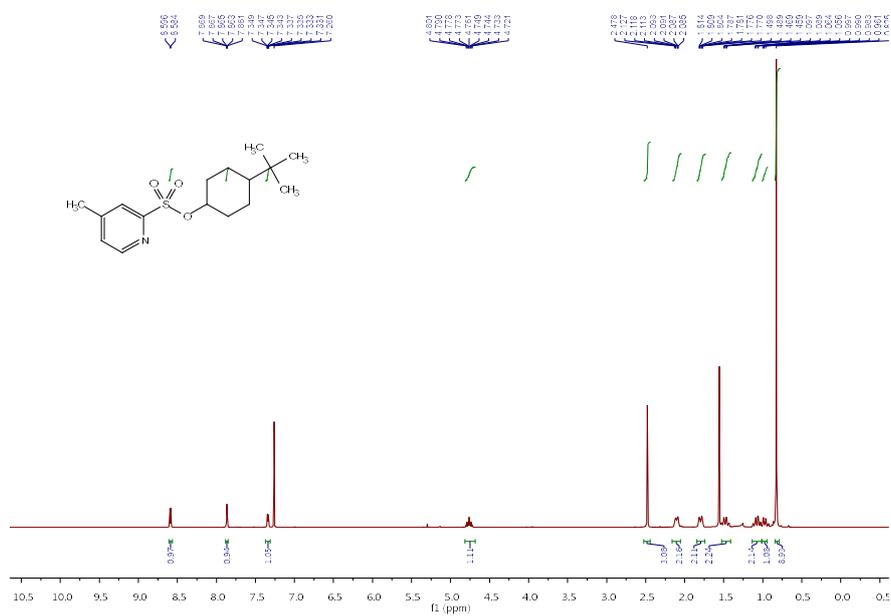
2-((4-(*tert*-butyl)cyclohexyl)oxy)-4-methylpyridine (Figure 2, 23)



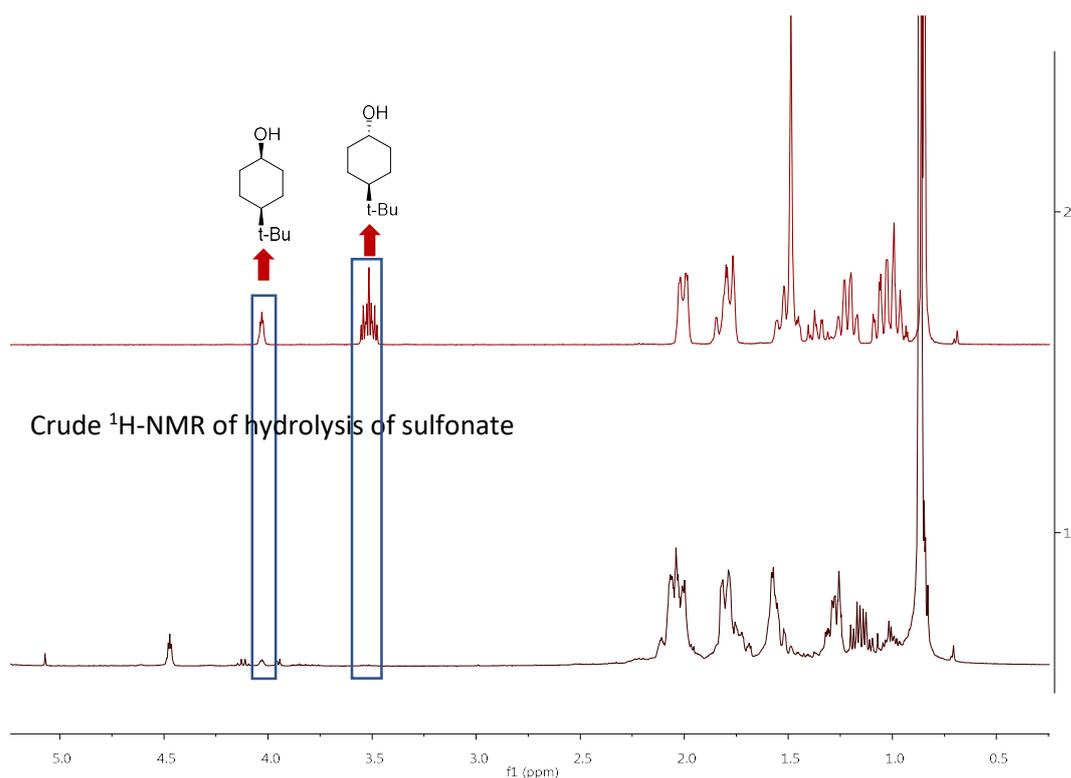
Prepared by general procedure A; isolated as a pale yellow solid using petroleum ether/diethyl ether (60:1) as eluent (36.1 mg, 73%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 5.2 Hz, 1H), 6.65 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.50 (d, *J* = 1.2 Hz, 1H), 4.92–4.85 (m, 1H), 2.27 (s, 3H), 2.21–2.16 (m, 2H), 1.85–1.80 (m, 2H), 1.41–1.33 (m, 2H), 1.24–1.16 (m, 2H), 1.09–1.01 (m, 1H), 0.87 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.8, 149.8, 146.4, 117.8, 111.7, 74.0, 47.3, 32.4, 32.4, 27.6, 25.6, 20.9. HRMS *m/z* calculated for C₁₆H₂₅NO [M+H]⁺: 248.2009, found: 248.2014.

Diastereomeric information of Compound **23**.

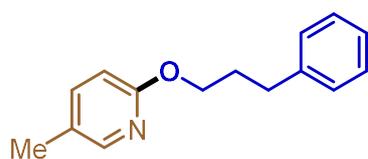
Same procedure with **12**.



From the crude ¹H-NMR, we could know cis-isomer of alcohol⁴ was transformed to sulfonate. Therefore, the diastereomeric information of Compound **23** was determined.

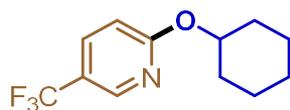


5-methyl-2-(3-phenylpropoxy)pyridine (Figure 2, 24)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (50:1) as eluent (22.8 mg, 51%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.95 (dd, $J = 1.6, 0.8$ Hz, 1H), 7.39 (ddd, $J = 8.4, 2.8, 0.4$ Hz, 1H), 7.31–7.25 (m, 2H), 7.24–7.16 (m, 3H), 6.66 (d, $J = 8.4$ Hz, 1H), 4.28 (t, $J = 6.4$ Hz, 2H), 2.83–2.77 (m, 2H), 2.24 (s, 3H), 2.14–2.05 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 162.2, 146.3, 141.8, 139.6, 128.5, 128.4, 125.8, 125.4, 110.3, 65.1, 32.3, 30.8, 17.4. HRMS m/z calculated for $\text{C}_{15}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$: 228.1383, found: 228.1383.

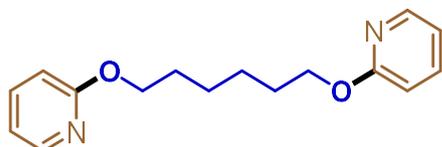
2-(cyclohexyloxy)-5-(trifluoromethyl)pyridine (Figure 2, 25)



Prepared by general procedure A; isolated as a pale yellow liquid using petroleum ether/diethyl ether (160:1) as eluent (28.0 mg, 57%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.42–8.39 (m, 1H), 7.73 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.75 (d, $J = 8.8$ Hz, 1H), 5.14–5.06 (m, 1H), 2.05–

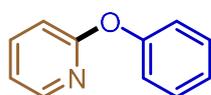
1.96 (m, 2H), 1.83–1.75 (m, 2H), 1.64–1.56 (m, 2H), 1.56–1.48 (m, 2H), 1.46–1.38 (m, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.5. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 144.9 (q, J = 4.3 Hz), 135.5 (q, J = 3.2 Hz), 124.1 (q, J = 271.9 Hz), 119.3 (q, J = 33.2 Hz), 111.7, 74.2, 31.7, 25.6, 23.8. HRMS m/z calculated for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 246.1100, found: 246.1101.

1,6-bis(pyridine-2-yloxy)hexane (Figure 2, 26)



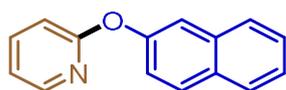
Prepared by general procedure A; isolated as a pale yellow solid using petroleum ether/diethyl ether (6:1) as eluent (20.2 mg, 74%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, J = 5.2, 2.0 Hz, 2H), 7.58–7.52 (m, 2H), 6.83 (ddd, J = 7.2, 5.2, 0.8 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 4.29 (t, J = 6.4 Hz, 4H), 1.84–1.78 (m, 4H), 1.57–1.51 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.0, 146.9, 138.4, 116.4, 111.1, 65.8, 29.0, 25.9. HRMS m/z calculated for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 273.1598, found: 273.1604.

2-phenoxy pyridine (Figure 3, 28)



Prepared by general procedure B; isolated as a white solid using petroleum ether/diethyl ether (15:1) as eluent (30.5 mg, 89%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, J = 5.2, 2.0 Hz, 1H), 7.68 (ddd, J = 8.4, 7.2, 2.0 Hz, 1H), 7.45–7.37 (m, 2H), 7.16–7.23 (m, 1H), 7.17–7.09 (m, 2H), 6.99 (ddd, J = 7.2, 5.2, 0.8 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 154.2, 147.8, 139.4, 129.7, 124.7, 121.2, 118.4, 111.5. HRMS m/z calculated for $\text{C}_{11}\text{H}_9\text{NO}$ $[\text{M}+\text{H}]^+$: 172.0757, found: 172.0764.

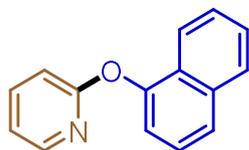
2-(naphthalen-2-yloxy)pyridine (Figure 3, 29)



Prepared by general procedure B; isolated as a yellow solid using petroleum ether/diethyl ether (10:1) as eluent (35.8 mg, 81%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, J = 5.2, 2.0 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.71 (ddd, J = 8.8, 7.2, 2.0 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.51–7.41 (m, 2H), 7.31 (dd, J = 8.8, 2.4 Hz, 1H),

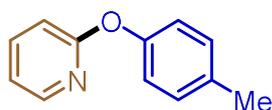
7.02 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.97 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.8, 151.8, 147.8, 139.5, 134.3, 131.0, 129.6, 127.8, 127.5, 126.4, 125.2, 121.4, 118.6, 117.4, 111.6. HRMS m/z calculated for $\text{C}_{15}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 222.0913, found: 222.0919.

2-(naphthalen-1-yloxy)pyridine (Figure 3, 30)



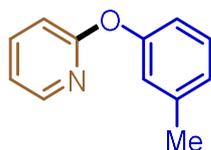
Prepared by general procedure B; isolated as a white solid using petroleum ether/diethyl ether (30:1) as eluent (37.5 mg, 85%). ^1H NMR (400 MHz, Chloroform- d) δ 8.22 (dd, $J = 5.2, 2.0$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.72 (ddd, $J = 8.8, 7.2, 2.0$ Hz, 1H), 7.57–7.43 (m, 3H), 7.28 (d, $J = 4.0$ Hz, 1H), 7.02 (dd, $J = 7.2, 5.2$ Hz, 1H), 6.97 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 164.4, 150.1, 148.0, 139.5, 135.0, 128.0, 127.5, 126.4, 126.1, 125.8, 125.0, 122.1, 118.4, 117.1, 111.0. HRMS m/z calculated for $\text{C}_{15}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 222.0913, found: 222.0916.

2-(*p*-tolylxy)pyridine (Figure 3, 31)



Prepared by general procedure B; isolated as a pale green liquid using petroleum ether/diethyl ether (30:1) as eluent (31.1 mg, 84%). ^1H NMR (400 MHz, Chloroform- d) δ 8.19 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.66 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.22–7.18 (m, 2H), 7.05–7.01 (m, 2H), 6.96 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 164.1, 151.8, 147.7, 139.3, 134.3, 130.2, 121.1, 118.2, 111.3, 20.9. HRMS m/z calculated for $\text{C}_{12}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 186.0913, found: 186.0917.

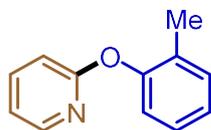
2-(*m*-tolylxy)pyridine (Figure 3, 32)



Prepared by general procedure B; isolated as a yellow-green liquid using petroleum ether/diethyl ether (30:1) as eluent (24.0 mg, 66%). ^1H NMR (400 MHz, Chloroform- d) δ 8.17 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.66–7.60 (m, 1H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.00–6.88 (m, 4H), 6.85 (d, $J = 8.4$ Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.9, 154.2, 147.8, 139.8,

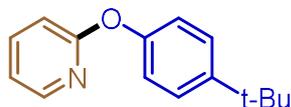
139.4, 129.4, 125.5, 121.8, 118.3, 118.1, 111.5, 21.4. HRMS m/z calculated for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0913, found: 186.0915.

2-(*o*-tolylloxy)pyridine (Figure 3, 33)



Prepared by general procedure B; isolated as a white solid using petroleum ether/ diethyl ether (30:1) as eluent (29.0 mg, 78%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.66 (ddd, $J = 8.8, 7.2, 2.0$ Hz, 1H), 7.29–7.21 (m, 2H), 7.14 (td, $J = 7.6, 1.2$ Hz, 1H), 7.06 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.96 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 152.2, 147.8, 139.4, 131.4, 130.8, 127.1, 125.2, 121.8, 118.0, 110.6, 16.4. HRMS m/z calculated for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0913, found: 186.0918.

2-(4-(*tert*-butyl)phenoxy)pyridine (Figure 3, 34)



Prepared by general procedure B; isolated as a white solid using petroleum ether/diethyl ether (30:1) as eluent (34.0 mg, 75%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.67 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.43–7.38 (m, 2H), 7.09–7.04 (m, 2H), 6.98 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.9, 151.7, 147.7, 147.3, 139.4, 126.6, 120.5, 118.2, 111.4, 34.4, 31.5. HRMS m/z calculated for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383, found: 228.1386.

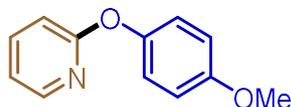
N,N-dimethyl-4-(pyridin-2-yloxy)aniline (Figure 3, 35)



Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (10:1) as eluent (25.0 mg, 58%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.6 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.06–7.01 (m, 2H), 6.93 (ddd, $J = 7.2, 5.2, 2.0$ Hz, 1H), 6.83 (d, $J = 8.4$ Hz, 1H), 6.80–6.74 (m, 2H), 2.95 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-

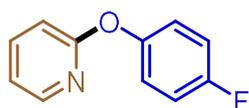
d) δ 164.7, 148.1, 147.8, 144.8, 139.1, 122.0, 117.8, 113.8, 110.8, 41.1. HRMS m/z calculated for $C_{13}H_{14}N_2O$ $[M+H]^+$: 215.1179, found: 215.1184.

2-(4-methoxyphenoxy)pyridine (Figure 3, 36)



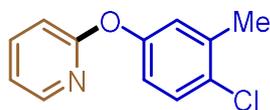
Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (15:1) as eluent (29.0 mg, 73%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.65 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.10–7.05 (m, 2H), 6.98–6.91 (m, 3H), 6.86 (d, $J = 8.4$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 156.6, 147.7, 147.4, 139.3, 122.4, 118.1, 114.8, 111.0, 55.6. HRMS m/z calculated for $C_{12}H_{11}NO_2$ $[M+H]^+$: 202.0863, found: 202.0867.

2-(4-fluorophenoxy)pyridine (Figure 3, 37)



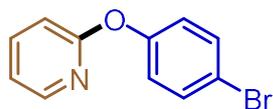
Prepared by general procedure B; isolated as a white solid using petroleum ether/diethyl ether (10:1) as eluent (28.5 mg, 75%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.18 (ddd, $J = 5.2, 2.0, 0.8$ Hz, 1H), 7.69 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.14–7.05 (m, 4H), 6.99 (ddd, $J = 7.2, 5.0, 0.8$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.5. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 159.6 (d, $J = 243.71$ Hz), 147.6, 149.8 (d, $J = 2.6$ Hz), 139.5, 122.7 (d, $J = 8.3$ Hz), 118.5, 116.2 (d, $J = 23.5$ Hz), 111.4. HRMS m/z calculated for $C_{11}H_8FNO$ $[M+H]^+$: 190.0663, found: 190.0662.

2-(4-chloro-3-methylphenoxy)pyridine (Figure 3, 38)



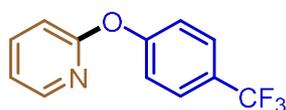
Prepared by general procedure B; isolated as a colorless liquid using petroleum ether/diethyl ether (30:1) as eluent (37.4 mg, 85%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.69 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.34 (d, $J = 8.6$ Hz, 1H), 7.05–6.97 (m, 2H), 6.92 (dd, $J = 8.4, 3.2$ Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5, 152.5, 147.7, 139.5, 137.5, 130.1, 123.0, 123.6, 120.0, 118.6, 111.6, 20.3. HRMS m/z calculated for $C_{12}H_{10}ClNO$ $[M+H]^+$: 220.0524, found: 220.0529.

2-(4-bromophenoxy)pyridine (Figure 3, 39)



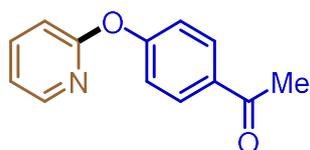
Prepared by general procedure B; isolated as a yellow solid using petroleum ether/ethyl acetate (5:1) as eluent (37.8 mg, 76%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.82 (ddd, $J = 4.8, 1.6, 0.8$ Hz, 1H), 8.00–7.96 (m, 1H), 7.96–7.91 (m, 1H), 7.61 (ddd, $J = 7.2, 4.8, 1.6$ Hz, 1H), 7.46–7.40 (m, 2H), 7.06–7.01 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 150.6, 148.8, 138.2, 132.8, 128.1, 124.3, 124.1, 120.8. HRMS m/z calculated for $\text{C}_{12}\text{H}_8\text{BrNO}$ $[\text{M}+\text{H}]^+$: 249.9862, found: 249.9868.

2-(4-(trifluoromethyl)phenoxy)pyridine (Figure 3, 40)



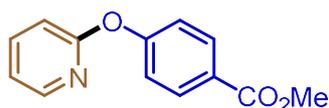
Prepared by general procedure B; isolated as a yellow-green liquid using petroleum ether/diethyl ether (10:1) as eluent (40.6 mg, 85%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (ddd, $J = 5.2, 2.0, 0.8$ Hz, 1H), 7.74 (ddd, $J = 8.0, 7.2, 2.0$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.06 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.0. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.8, 157.0, 147.7, 139.8, 127.0 (q, $J = 3.8$ Hz), 126.5 (q, $J = 32.8$ Hz), 124.1 (q, $J = 272.7$ Hz), 121.1, 119.3, 112.2. HRMS m/z calculated for $\text{C}_{12}\text{H}_8\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 240.0631, found: 240.0647.

1-(4-(pyridin-2-yloxy)phenyl)ethan-1-one (Figure 3, 41)



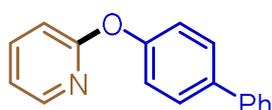
Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (10:1) as eluent (40.0 mg, 94%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, $J = 4.8, 2.0$ Hz, 1H), 8.03–7.99 (m, 2H), 7.74 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.23–7.18 (m, 2H), 7.06 (ddd, $J = 7.2, 4.8, 0.8$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.8, 162.8, 158.4, 147.8, 139.8, 133.4, 130.3, 120.6, 119.4, 112.4, 26.5. HRMS m/z calculated for $\text{C}_{13}\text{H}_{11}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 214.0863, found: 214.0869.

methyl 4-(pyridin-2-yloxy)benzoate (Figure 3, 42)



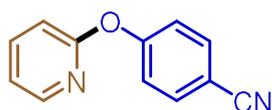
Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (15:1) as eluent (33.0 mg, 71%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, $J = 5.2, 2.0$ Hz, 1H), 8.11–8.05 (m, 2H), 7.73 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.20–7.15 (m, 2H), 7.06 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 3.91 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 162.8, 158.3, 147.8, 139.8, 131.5, 126.2, 120.4, 119.3, 112.4, 52.1. HRMS m/z calculated for $\text{C}_{13}\text{H}_{11}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 230.0812, found: 230.0817.

2-([1,1'-biphenyl]-4-yloxy)pyridine (Figure 3, 43)



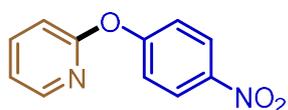
Prepared by general procedure B; isolated as a white solid using petroleum ether/diethyl ether (20:1) as eluent (47.7 mg, 96%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.71 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.64–7.56 (m, 4H), 7.47–7.41 (m, 2H), 7.37–7.31 (m, 1H), 7.24–7.19 (m, 2H), 7.02 (dd, $J = 7.2, 5.2$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 153.6, 147.7, 140.6, 139.6, 137.8, 128.8, 128.4, 127.1, 127.1, 121.4, 118.6, 111.7. HRMS m/z calculated for $\text{C}_{17}\text{H}_{13}\text{NO}$ $[\text{M}+\text{Na}]^+$: 270.0889, found: 270.0900.

4-(pyridin-2-yloxy)benzotrile (Figure 3, 44)



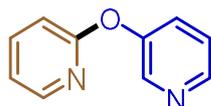
Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (15:1) as eluent (32.7 mg, 83%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.77 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.71–7.65 (m, 2H), 7.25–7.21 (m, 2H), 7.10 (ddd, $J = 7.2, 5.2, 2.0$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.2, 158.0, 147.7, 140.0, 133.9, 121.4, 119.8, 118.7, 112.6, 107.9. HRMS m/z calculated for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 197.0709, found: 197.0713.

2-(4-nitrophenoxy)pyridine (Figure 3, 45)



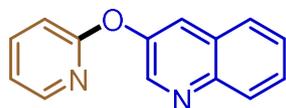
Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (10:1) as eluent (39.0 mg, 90%). ¹H NMR (400 MHz, Chloroform-d) δ 8.30–8.25 (m, 2H), 8.23 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.79 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.29–7.25 (m, 2H), 7.12 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 162.2, 159.6, 147.8, 144.0, 140.1, 125.6, 120.8, 120.0, 112.7. HRMS *m/z* calculated for C₁₁H₈N₂O₃ [M+Na]⁺ : 239.0427, found: 239.0440.

2-(pyridin-3-yloxy)pyridine (Figure 3, 46)



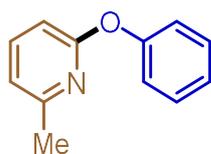
Prepared by general procedure B; isolated as a yellow solid using petroleum ether/ ethyl acetate (4:1) as eluent (25.0 mg, 73%). ¹H NMR (400 MHz, Chloroform-d) δ 8.51 (d, *J* = 2.8 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.16 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.73 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.53 (ddd, *J* = 8.4, 2.8, 1.6 Hz, 1H), 7.34 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.04 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 162.9, 150.6, 147.5, 145.6, 143.5, 139.7, 128.7, 123.9, 119.1, 111.8. HRMS *m/z* calculated for C₁₀H₈N₂O [M+H]⁺:173.0709, found: 173.0712.

3-(pyridin-2-yloxy)quinolone (Figure 3, 47)



Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (15:1) as eluent (37.0 mg, 84%). ¹H NMR (400 MHz, Chloroform-d) δ 8.82 (d, *J* = 2.4 Hz, 1H), 8.17 (dd, *J* = 5.6, 1.6 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.81–7.73 (m, 2H), 7.70–7.64 (m, 1H), 7.58–7.51 (m, 1H), 7.03–7.08 (m, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 163.1, 147.50, 147.46, 146.6, 145.4, 139.8, 129.3, 128.6, 128.4, 127.4, 127.1, 124.8, 119.2, 111.8. HRMS *m/z* calculated for C₁₄H₁₀N₂O [M+Na]⁺ : 245.0685, found: 245.0691.

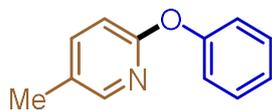
2-methyl-6-phenoxy pyridine (Figure 3, 48)



Prepared by general procedure B; isolated as a yellow-green liquid using petroleum ether/diethyl ether (20:1) as eluent (33.0 mg, 89%). ¹H NMR (400 MHz, Chloroform-d) δ 7.53

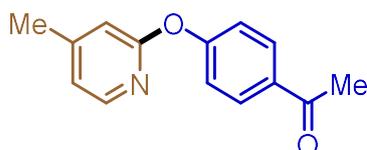
(t, $J = 7.6$ Hz, 1H), 7.40–7.34 (m, 2H), 7.20–7.16 (m, 1H), 7.15–7.11 (m, 2H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 8.0$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.2, 157.6, 154.7, 139.6, 129.6, 124.3, 120.7, 118.0, 107.5, 24.1. HRMS m/z calculated for $\text{C}_{12}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 186.0913, found: 186.0914.

5-methyl-2-phenoxy pyridine (Figure 3, 49)



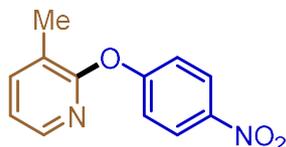
Prepared by general procedure B; isolated as a yellow-green liquid using petroleum ether/ethyl acetate (10:1) as eluent (18.0 mg, 49%). ^1H NMR (400 MHz, Chloroform-d) δ 8.03 (d, $J = 2.4$ Hz, 1H), 7.49 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.42–7.35 (m, 2H), 7.20–7.14 (m, 1H), 7.14–7.08 (m, 2H), 6.81 (d, $J = 8.4$ Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.9, 154.7, 147.4, 140.3, 129.6, 127.8, 124.3, 120.8, 111.1, 17.5. HRMS m/z calculated for $\text{C}_{12}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 186.0913, found: 186.0915.

1-(4-((4-methylpyridin-2-yl)oxy)phenyl)ethan-1-one (Figure 3, 50)



Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (10:1) as eluent (42.3 mg, 93%). ^1H NMR (400 MHz, Chloroform-d) δ 8.07 (d, $J = 5.2$ Hz, 1H), 8.03–7.97 (m, 2H), 7.22–7.14 (m, 2H), 6.89 (d, $J = 5.2$ Hz, 1H), 6.79 (s, 1H), 2.59 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 196.9, 163.0, 158.7, 151.5, 147.3, 133.2, 130.3, 120.8, 120.4, 112.7, 26.5, 21.0. HRMS m/z calculated for $\text{C}_{14}\text{H}_{13}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 228.1019, found: 228.1026.

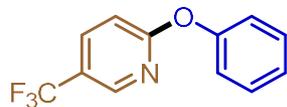
3-methyl-2-(4-nitrophenoxy)pyridine (Figure 3, 51)



Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (15:1) as eluent (37.1 mg, 81%). ^1H NMR (400 MHz, Chloroform-d) δ 8.31–8.22 (m, 2H), 8.04 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.61 (ddd, $J = 7.2, 2.0, 0.8$ Hz, 1H), 7.25–7.21 (m, 2H), 7.04 (dd, $J = 7.2, 4.8$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.4, 160.0, 144.9, 143.8, 140.6,

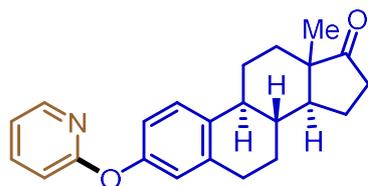
125.5, 122.7, 120.6, 120.3, 15.8. HRMS m/z calculated for $C_{12}H_{10}N_2O_3$ $[M+H]^+$: 231.0764, found: 231.0772.

2-phenoxy-5-(trifluoromethyl)pyridine (Figure 3, 52)



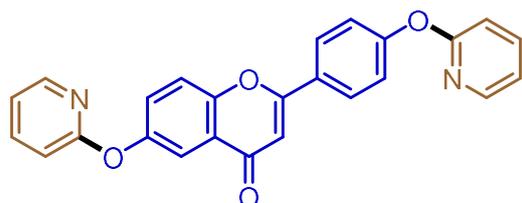
Prepared by general procedure B; isolated as a yellow-green liquid using petroleum ether/diethyl ether (15:1) as eluent (32.7 mg, 68%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.69 (dd, $J = 8.8, 2.8$ Hz, 1H), 7.26–7.19 (m, 2H), 7.09–7.04 (m, 1H), 6.99–6.93 (m, 2H), 6.80 (d, $J = 8.8$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.6. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 153.2, 145.6 (q, $J = 4.3$ Hz), 136.7, 129.8, 125.5, 123.7 (q, $J = 272.0$ Hz), 121.5, 121.3 (q, $J = 33.0$ Hz), 111.2. HRMS m/z calculated for $C_{12}H_8F_3NO$ $[M+H]^+$: 240.0631, found: 240.0630.

(8R,9S,13S,14S)-13-methyl-3-(pyridin-2-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (Figure 3, 53)



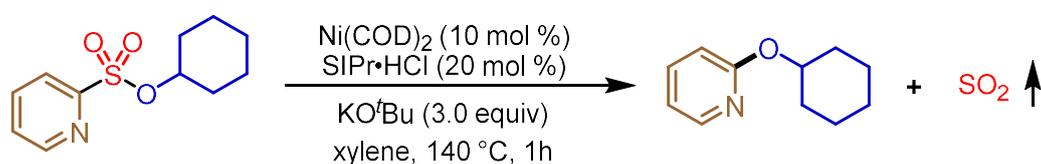
Prepared by general procedure B; isolated as a white solid using petroleum ether/ethyl acetate (15:1) as eluent (55.8 mg, 72%). 1H NMR (400 MHz, Chloroform-*d*) δ 8.20 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.67 (ddd, $J = 8.4, 7.2, 2.0$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 6.97 (ddd, $J = 7.2, 5.2, 0.8$ Hz, 1H), 6.94–6.84 (m, 3H), 2.94–2.87 (m, 2H), 2.58–2.47 (m, 1H), 2.45–2.38 (m, 1H), 2.35–2.26 (m, 1H), 2.21–1.95 (m, 4H), 1.70–1.48 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.8, 163.9, 151.9, 147.7, 139.4, 138.2, 136.2, 126.6, 121.2, 118.6, 118.2, 111.5, 50.5, 48.0, 44.2, 38.1, 35.9, 31.6, 29.5, 26.4, 25.8, 21.6, 13.9. HRMS m/z calculated for $C_{23}H_{25}NO_2$ $[M+H]^+$: 348.1958, found: 348.1961.

6-(pyridin-2-yloxy)-2-(4-(pyridin-2-yloxy)phenyl)-4H-chromen-4-one (Figure 3, 54)

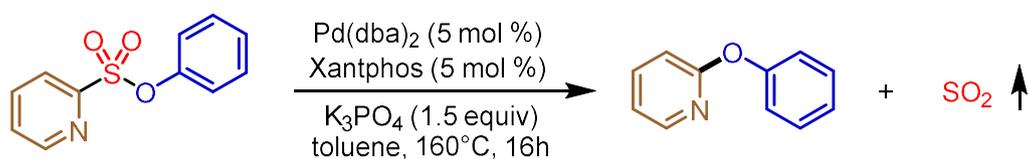


Prepared by general procedure B (0.1 mmol); isolated as a white solid using petroleum ether/ethyl acetate (3:2) as eluent (27.0 mg, 60%). ¹H NMR (400 MHz, Chloroform-d) δ 8.33 (d, *J* = 8.8 Hz, 1H), 8.25 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.22 (dd, *J* = 5.2, 2.0 Hz, 1H), 8.01 (s, 1H), 7.78 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.65–7.59 (m, 2H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.24–7.18 (m, 3H), 7.11 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.01 (ddd, *J* = 7.2, 5.2, 0.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 175.6, 163.6, 162.4, 158.8, 157.2, 154.2, 152.9, 147.8, 147.7, 140.0, 139.5, 130.3, 128.1, 128.0, 124.8, 121.2, 121.1, 119.8, 118.8, 118.6, 112.6, 111.7, 109.0. HRMS *m/z* calculated for C₂₅H₁₆N₂O₄ [M+Na]⁺ : 431.1002, found: 431.1008.

5. Gram scale of the desulfitative cross-coupling reaction

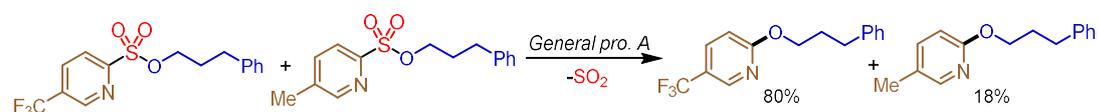


In the glovebox, Ni(COD)₂ (10 mol %, 137.5 mg), SIPr·HCl (20 mol %, 427.1 mg), KO^tBu (3.0 equiv, 1.68 g), cyclohexyl pyridine-2-sulfonate (5 mmol, 1.21 g) were added into an oven-dried two-neck flask with a condenser, followed by addition of xylenes (63 ml). The flask was sealed and removed out of the glovebox and heated with stirring in a pre-heated oil bath at 140 °C for 1 h with an argon balloon. After cooling the reaction mixture to room temperature, the mixture was concentrated and purified by flash column chromatography to afford 658 mg **11**, 77% yield

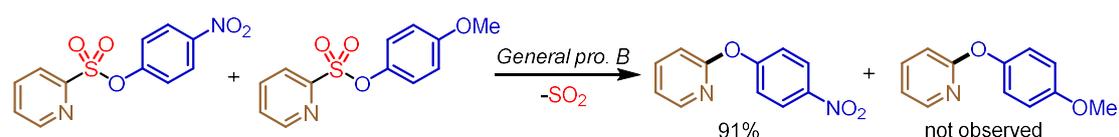


In the glovebox, phenyl pyridine-2-sulfonate (4.25 mmol, 1.0 g), Pd(dba)₂ (5 mol %, 122.2 mg), Xantphos (5 mol %, 122.9 mg), K₃PO₄ (1.5 equiv, 1.35 g) were added into an oven-dried tube with a magnetic stirring bar, followed by addition of toluene (64 ml). The tube was sealed and removed out of the glovebox and heated to 160 °C for 16 h. After cooling the reaction mixture to room temperature, the mixture was concentrated and purified by flash column chromatography to afford 342 mg **28**, 47% yield.

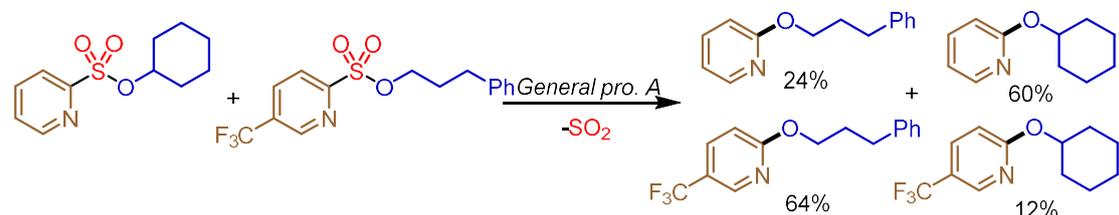
6. Controlled experiments



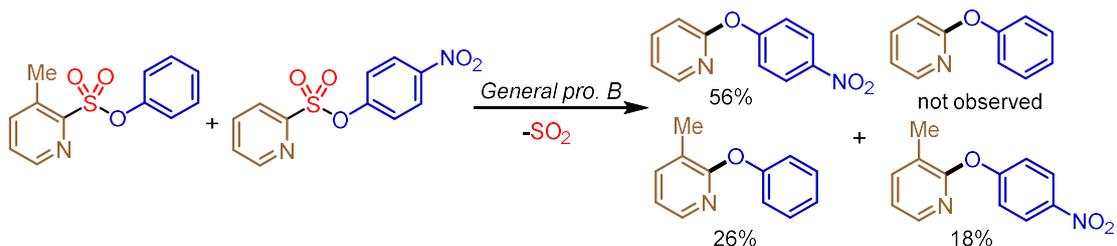
In the glovebox, Ni(COD)₂ (10 mol %, 5.5 mg), SIPr·HCl (20 mol %, 17.2 mg), KO^tBu (3.0 equiv, 67.3 mg), 3-phenylpropyl 5-(trifluoromethyl)pyridine-2-sulfonate (0.2 mmol) and 3-phenylpropyl 5-methylpyridine-2-sulfonate (0.2 mmol) were added into an oven-dried 8 ml vial with a magnetic stirring bar, followed by addition of xylenes (2.5 ml). The vial was sealed and removed out of the glovebox and heated to 140 °C. After 1 h, the vial was cooled to room temperature. The mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired products.



In the glovebox, 4-nitrophenyl pyridine-2-sulfonate (0.2 mmol), 4-methoxyphenyl pyridine-2-sulfonate (0.2 mmol), Pd(dba)₂ (5 mol %, 5.8 mg), Xantphos (5 mol %, 5.8 mg), K₃PO₄ (1.5 equiv, 63.7 mg) were added into an oven-dried 8 ml vial with a magnetic stirring bar, followed by addition of toluene (3 ml). The vial was sealed and removed out of the glovebox and heated to 160 °C for 16 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired products.



In the glovebox, Ni(COD)₂ (10 mol %, 5.5 mg), SIPr·HCl (20 mol %, 17.2 mg), KO^tBu (3.0 equiv, 67.3 mg), cyclohexyl pyridine-2-sulfonate (0.2 mmol) and 3-phenylpropyl 5-(trifluoromethyl)pyridine-2-sulfonate (0.2 mmol) were added into an oven-dried 8 ml vial with a magnetic stirring bar, followed by addition of xylenes (2.5 ml). The vial was sealed and removed out of the glovebox and heated to 140 °C. After 1 h, the vial was cooled to room temperature. The mixture was passed through a short silica gel pad. The filtrate was concentrated and the residue was purified by flash column chromatography to give the products.

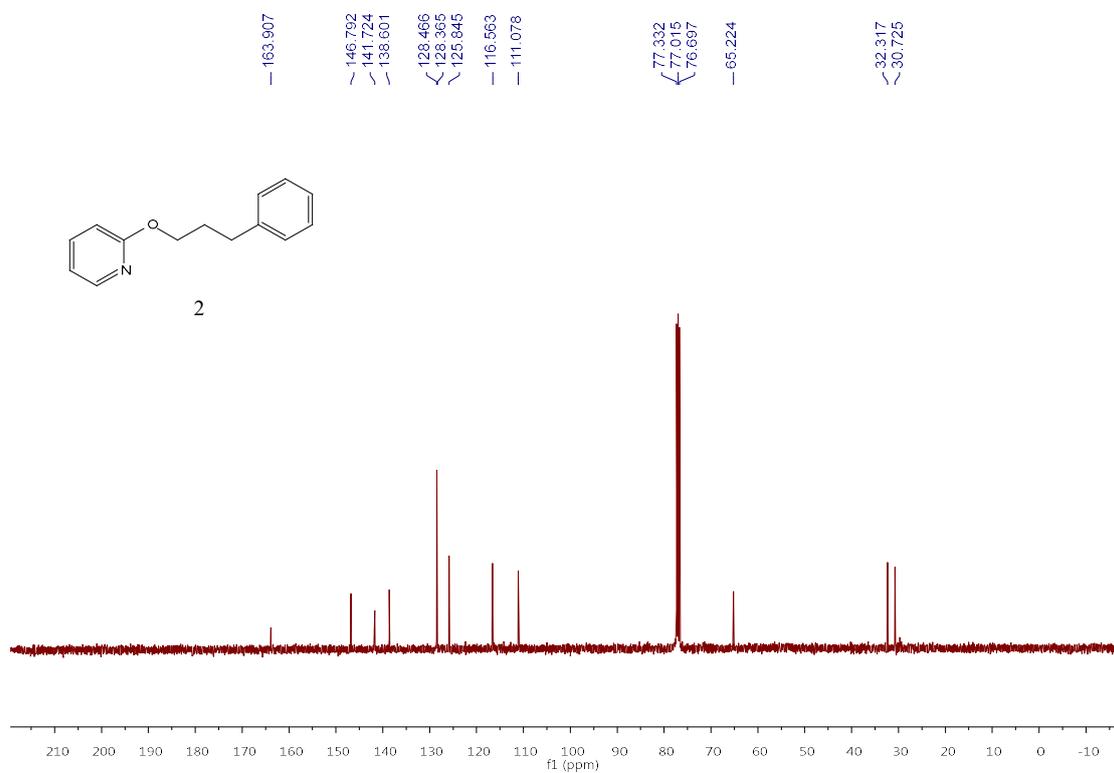
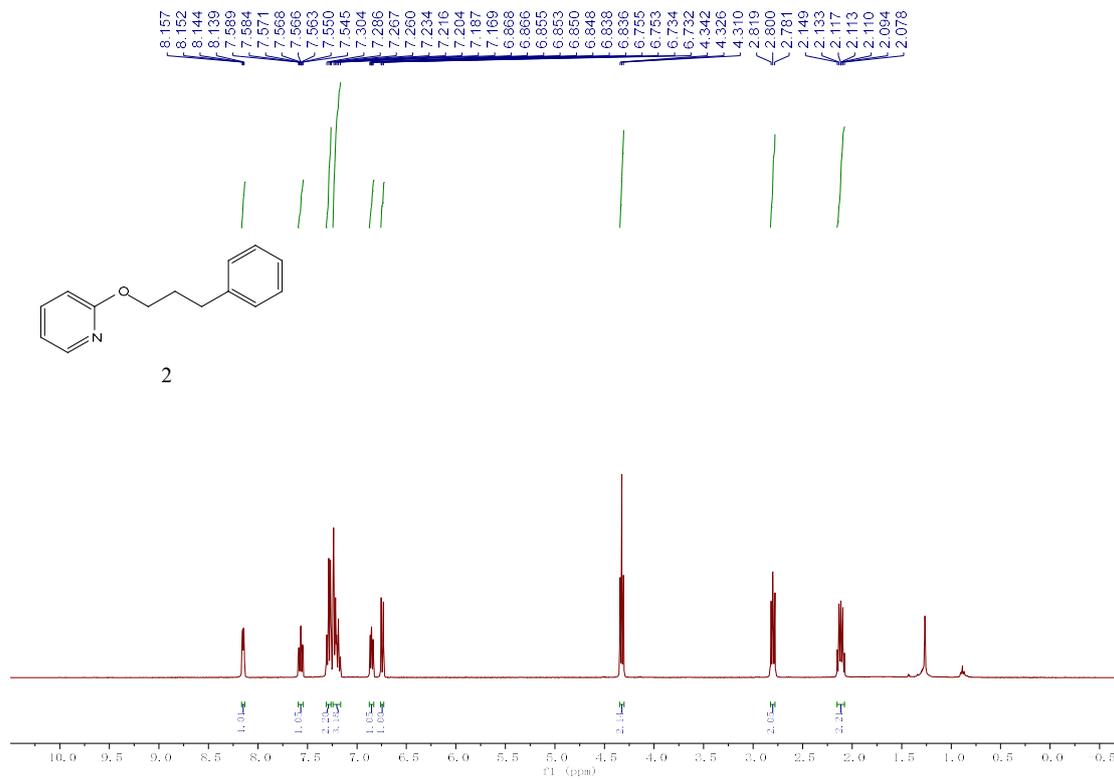


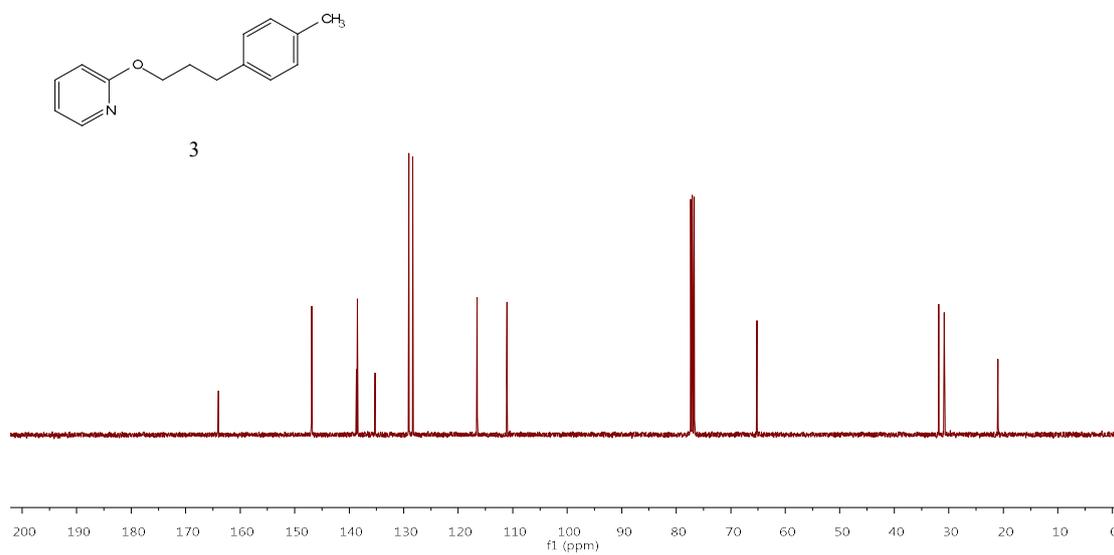
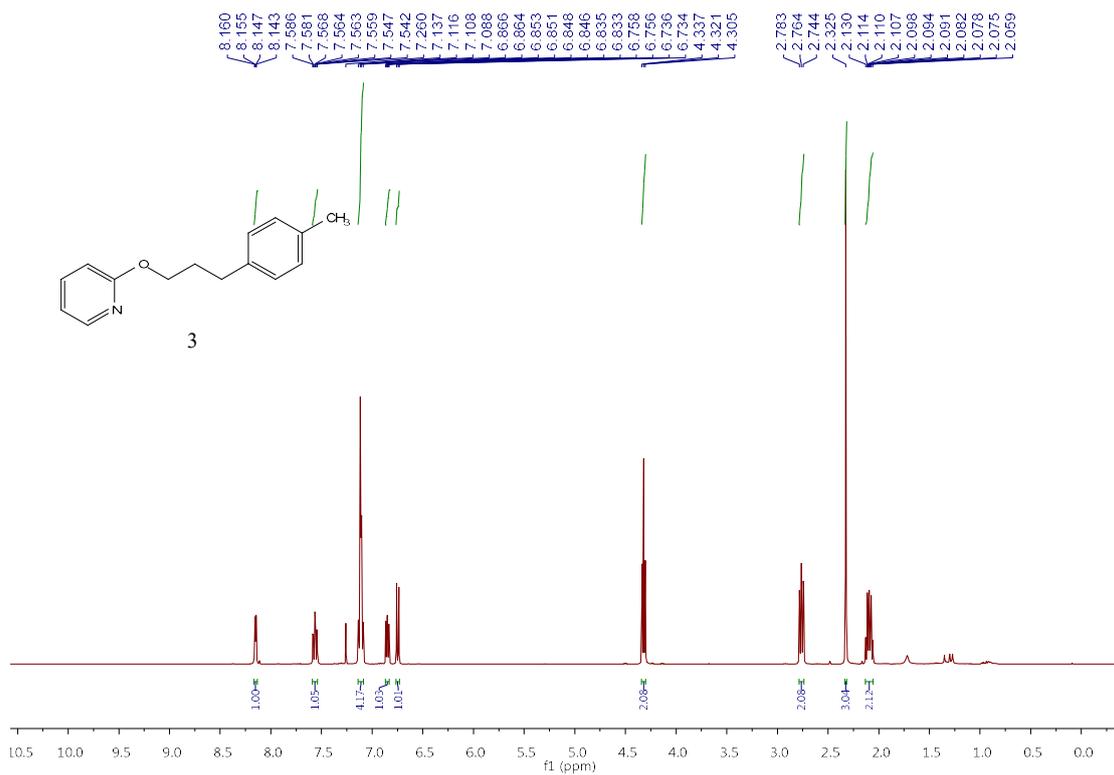
In the glovebox, phenyl 3-methylpyridine-2-sulfonate (0.2 mmol), 4-nitrophenyl pyridine-2-sulfonate (0.2 mmol), Pd(dba)₂ (5 mol %, 5.8 mg), Xantphos (5 mol %, 5.8 mg), K₃PO₄ (1.5 equiv, 63.7 mg) were added into an oven-dried 8 ml vial with a magnetic stirring bar, followed by addition of toluene (3 ml). The vial was sealed and removed out of the glovebox and heated to 160 °C for 16 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired products.

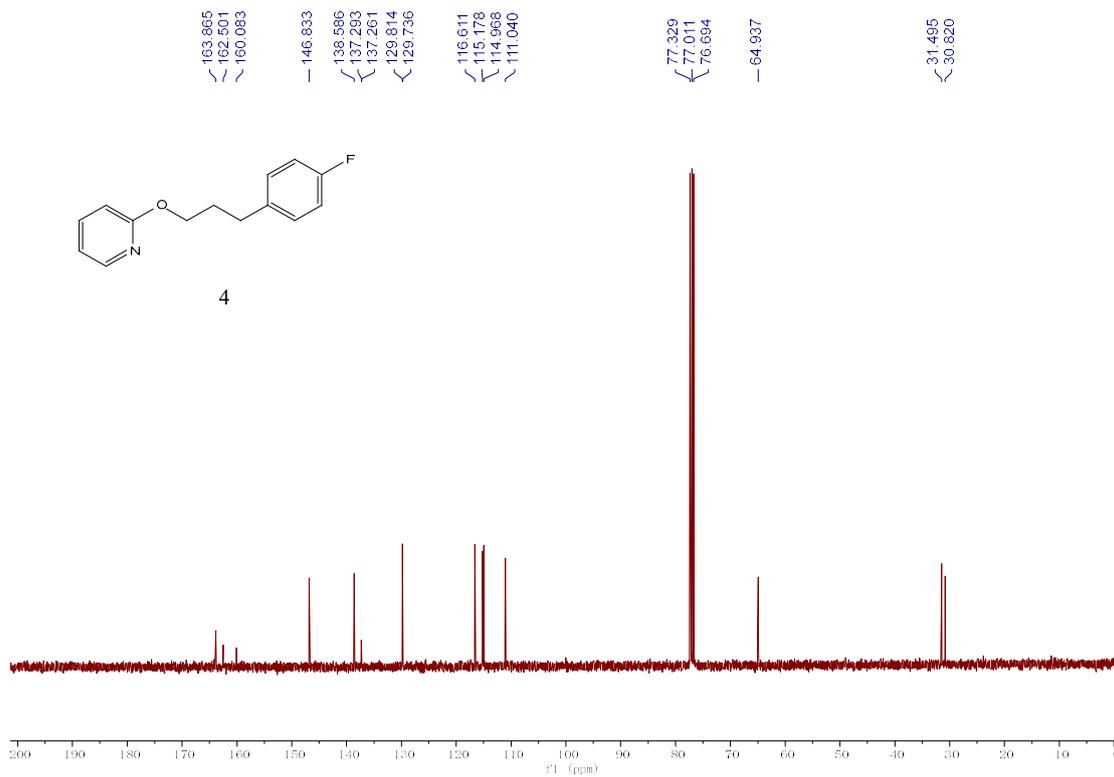
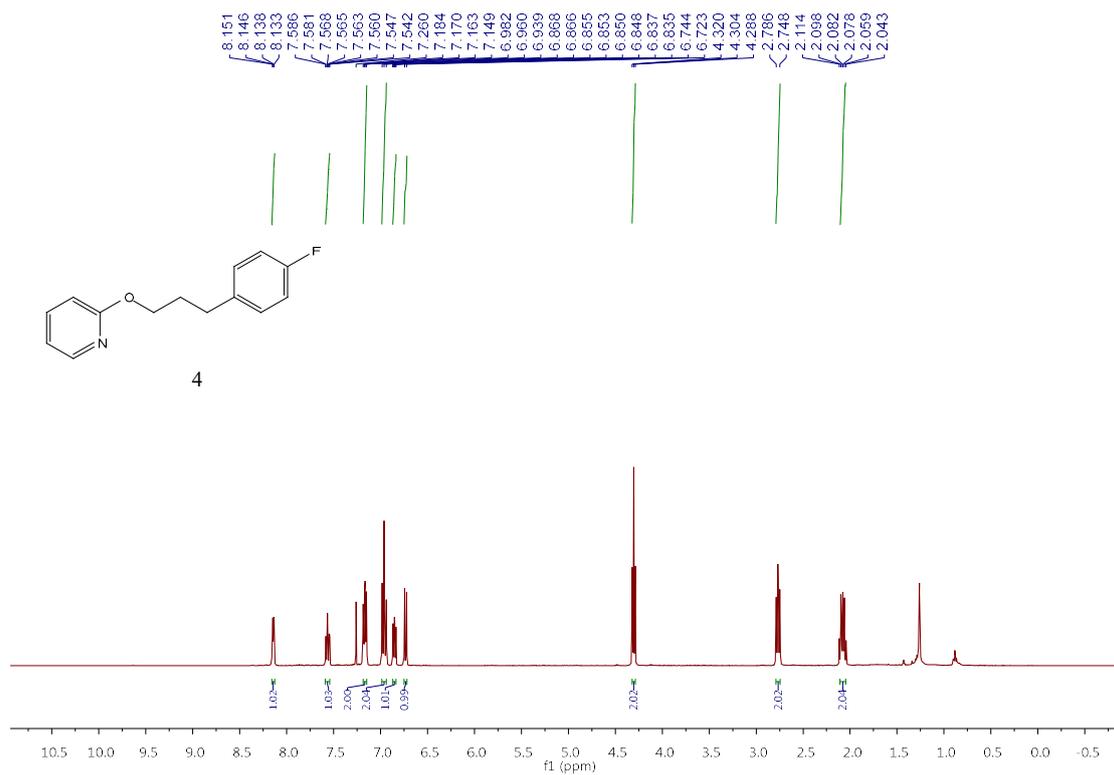
7. References

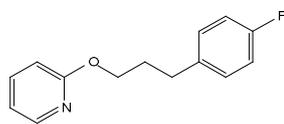
- [1] Garcia-Rubia, A., Urones, B., Arrayas, R. G. & Carretero, J. C. *Angew. Chem. Int. Ed.* **2011**, *50*, 10927-1093.
- [2] Corey, E. J. *et al. J. Org. Chem.* **1989**, *54*, 389-393.
- [3] Ramachandran, P. V.; Drolet, M. P.; Kulkarni, A. S., *Chem. Commun.* **2016**, *52*, 11897-11900.
- [4] Li, H.; Wang, L.; Zhang, Y.; Wang, J. B., *Angew. Chem. Int. Ed.* **2012**, *51*, 2943-2946.

8. NMR spectrum



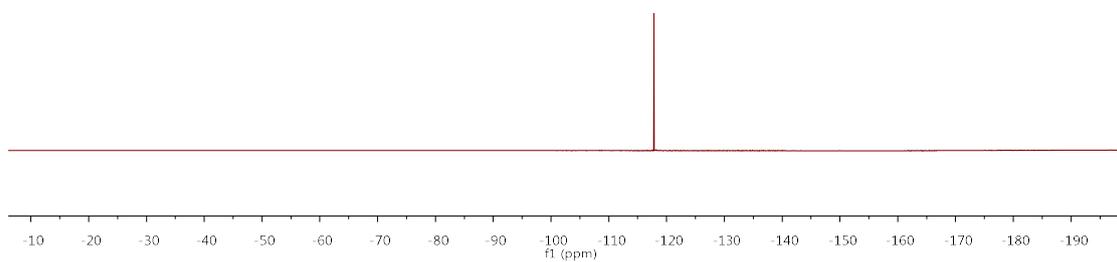


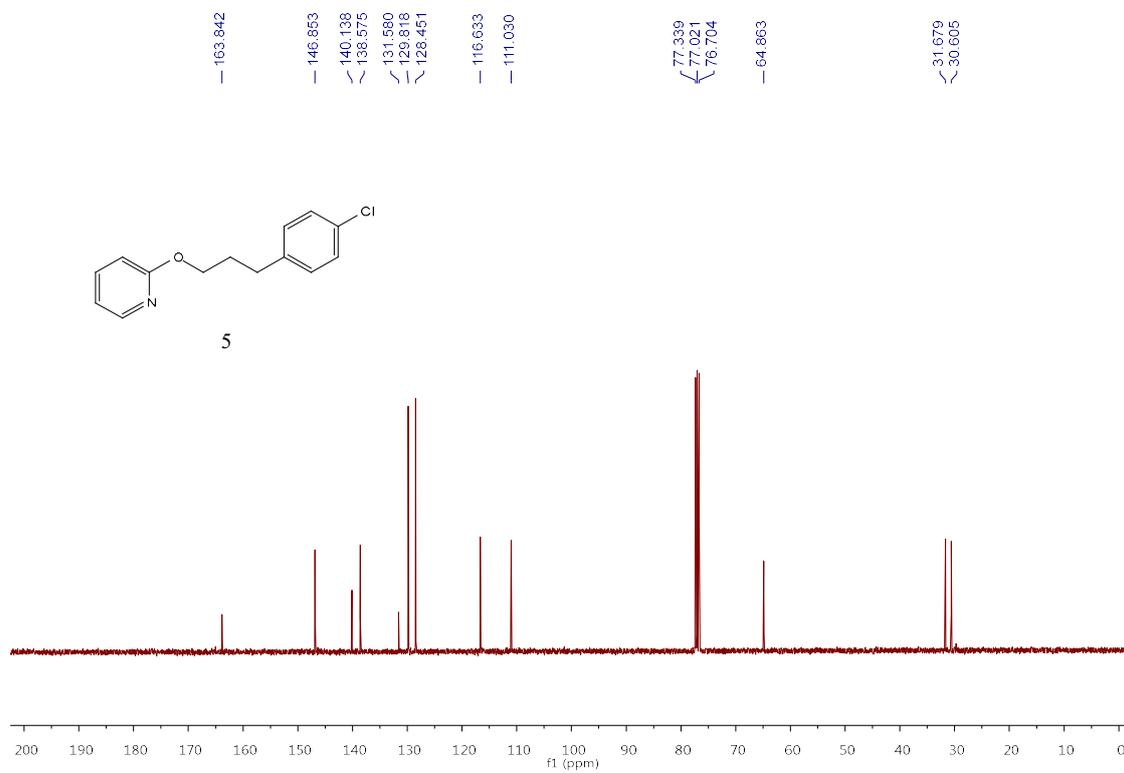
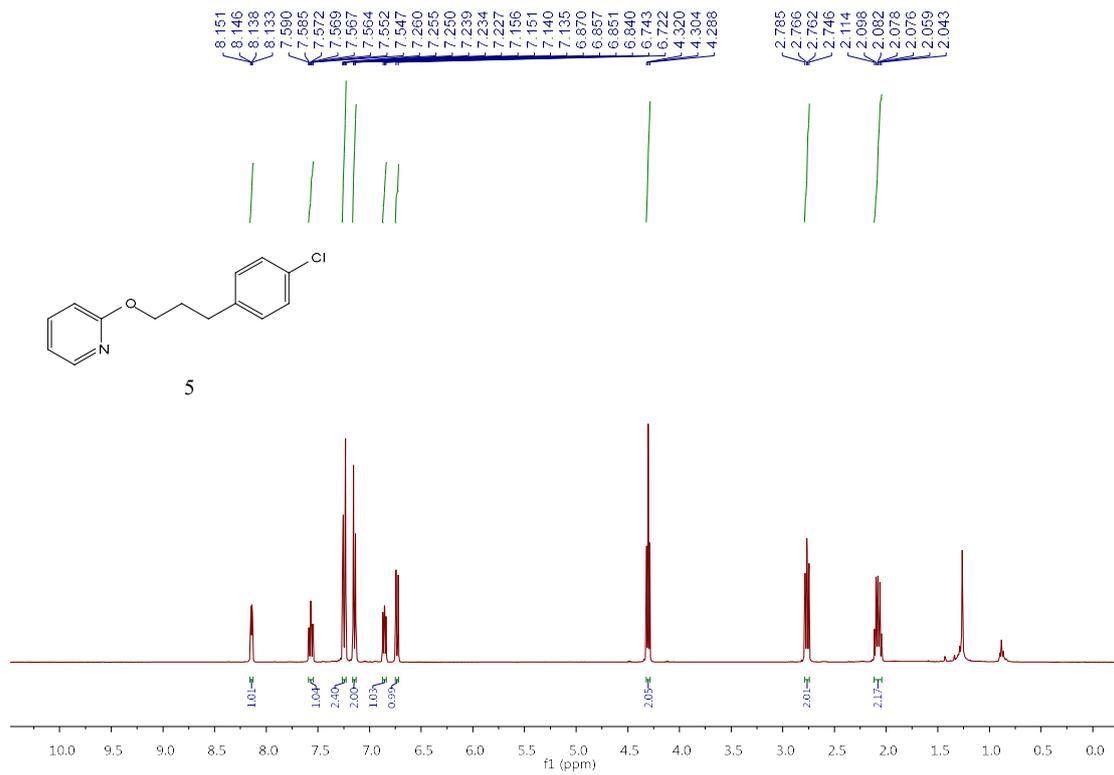


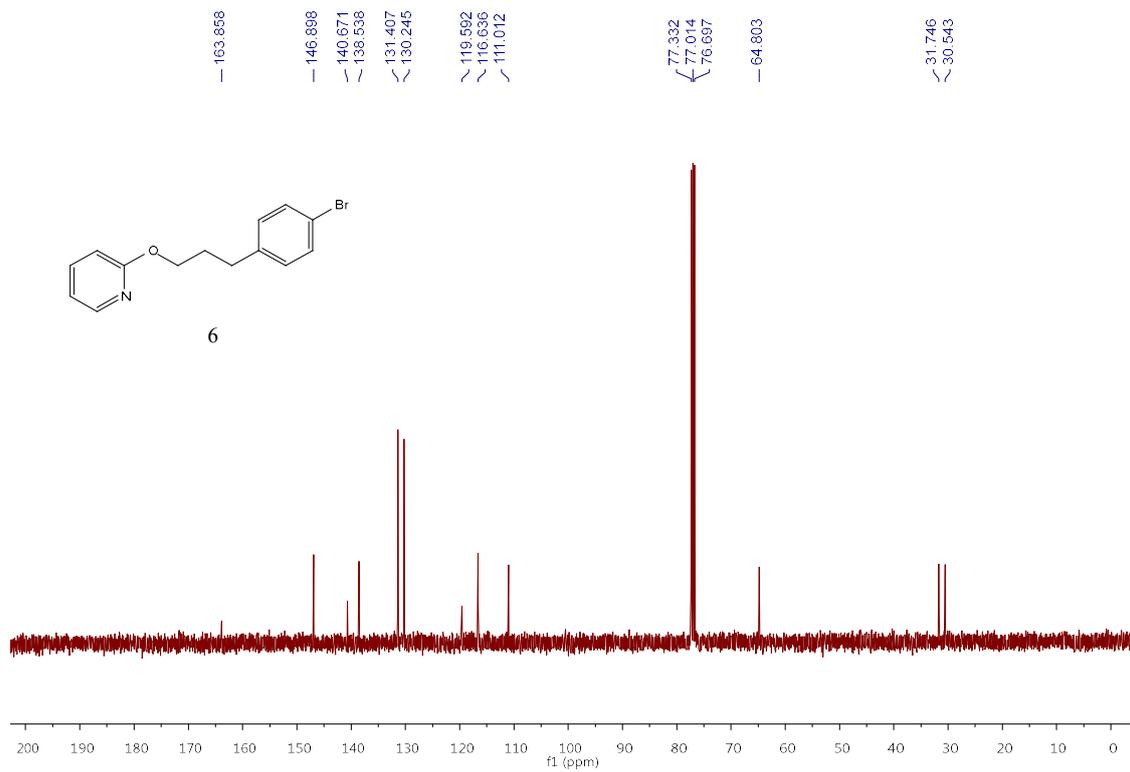
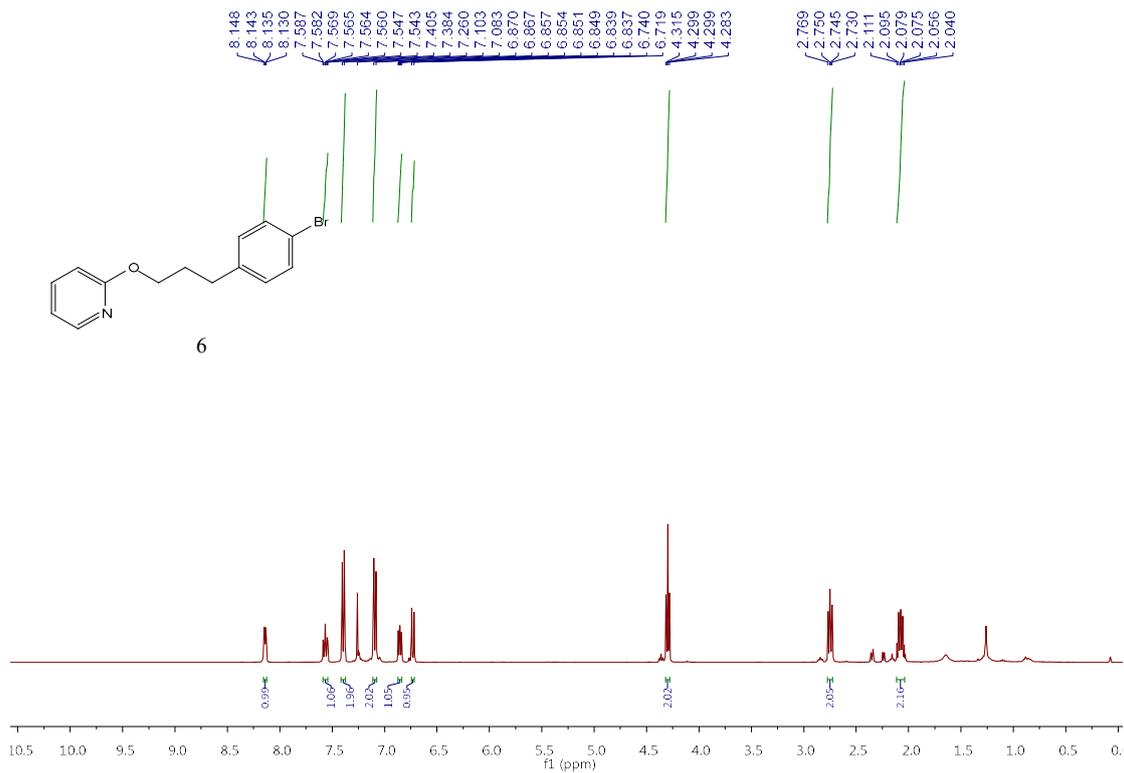


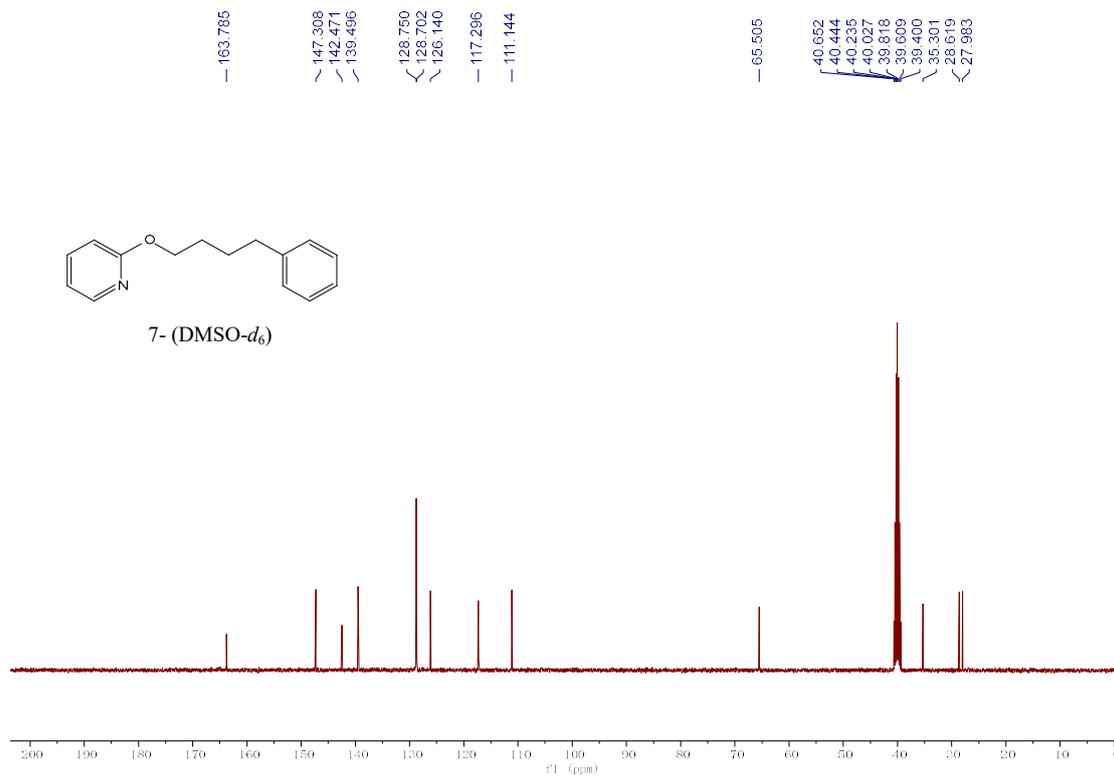
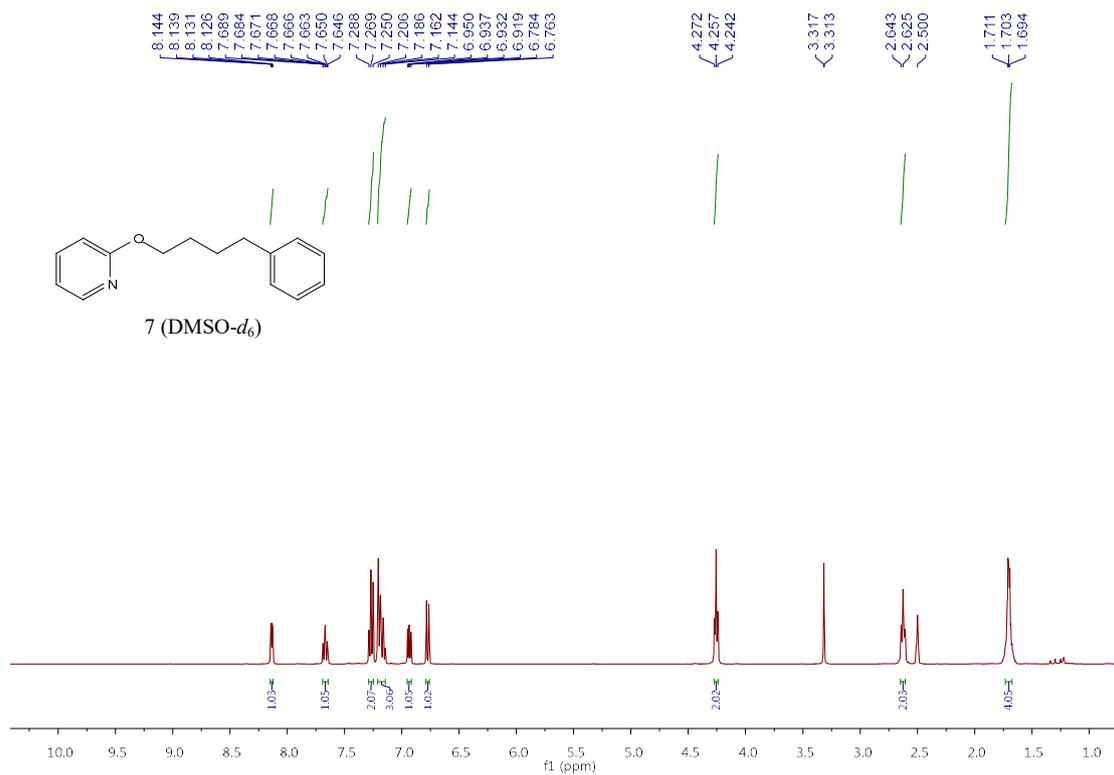
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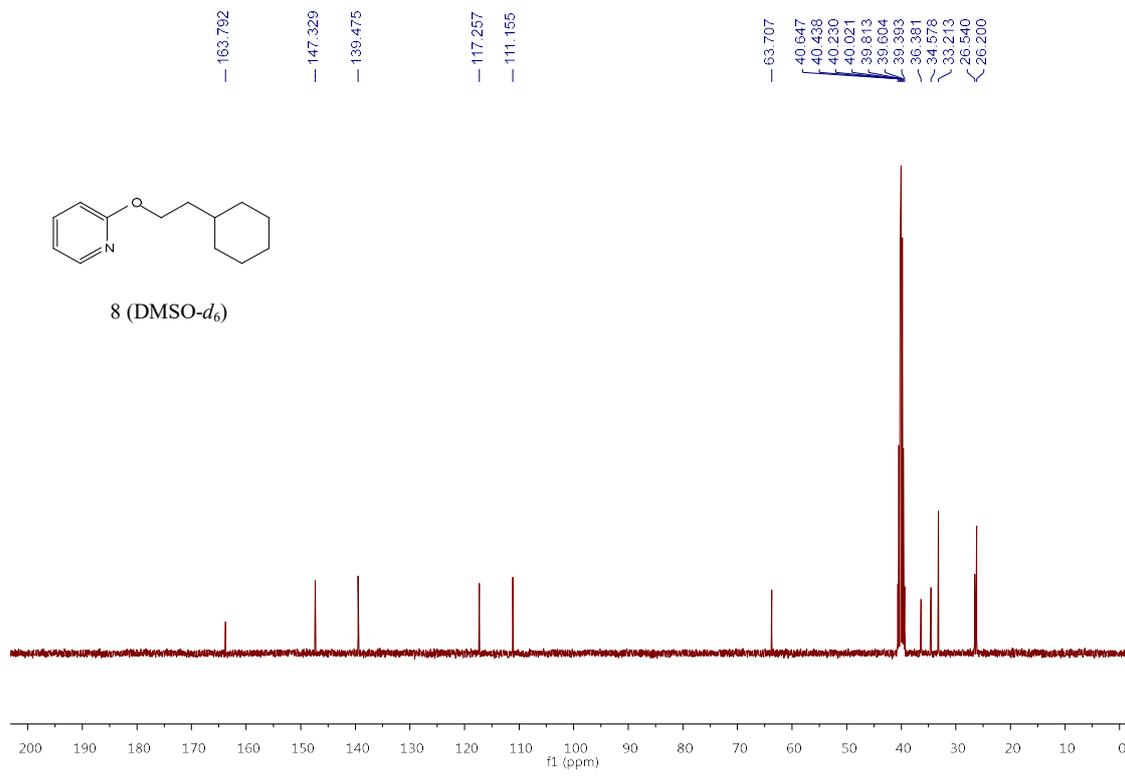
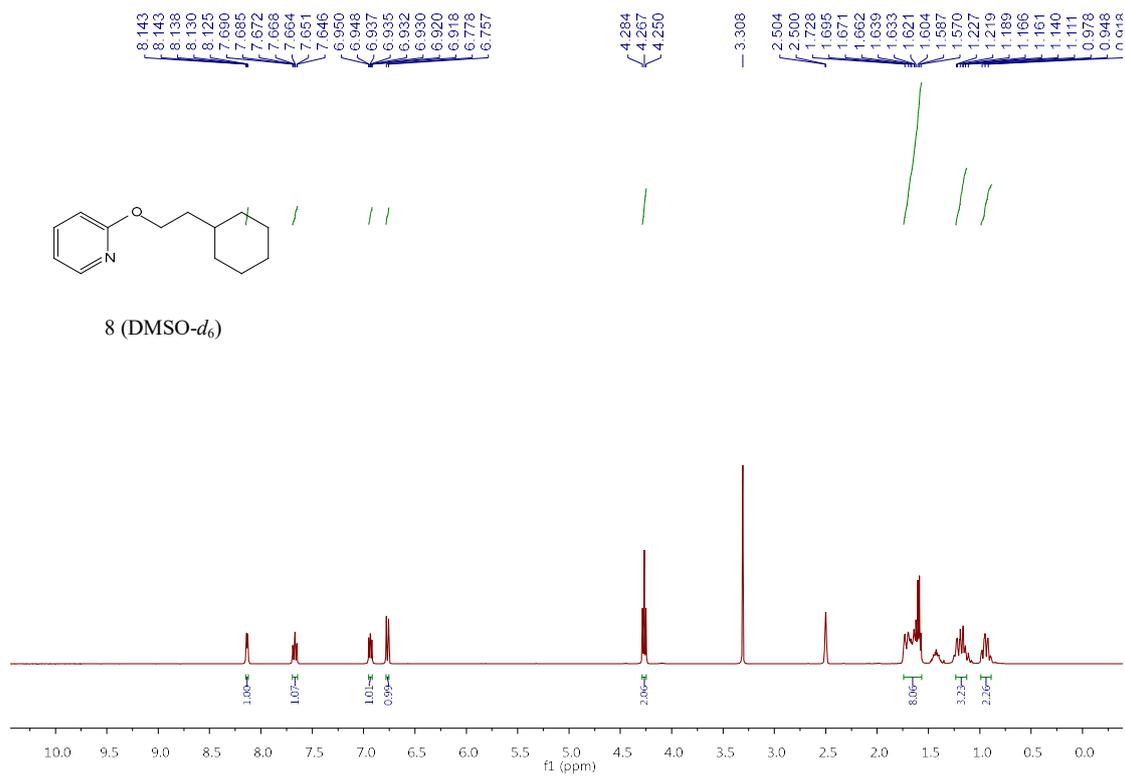
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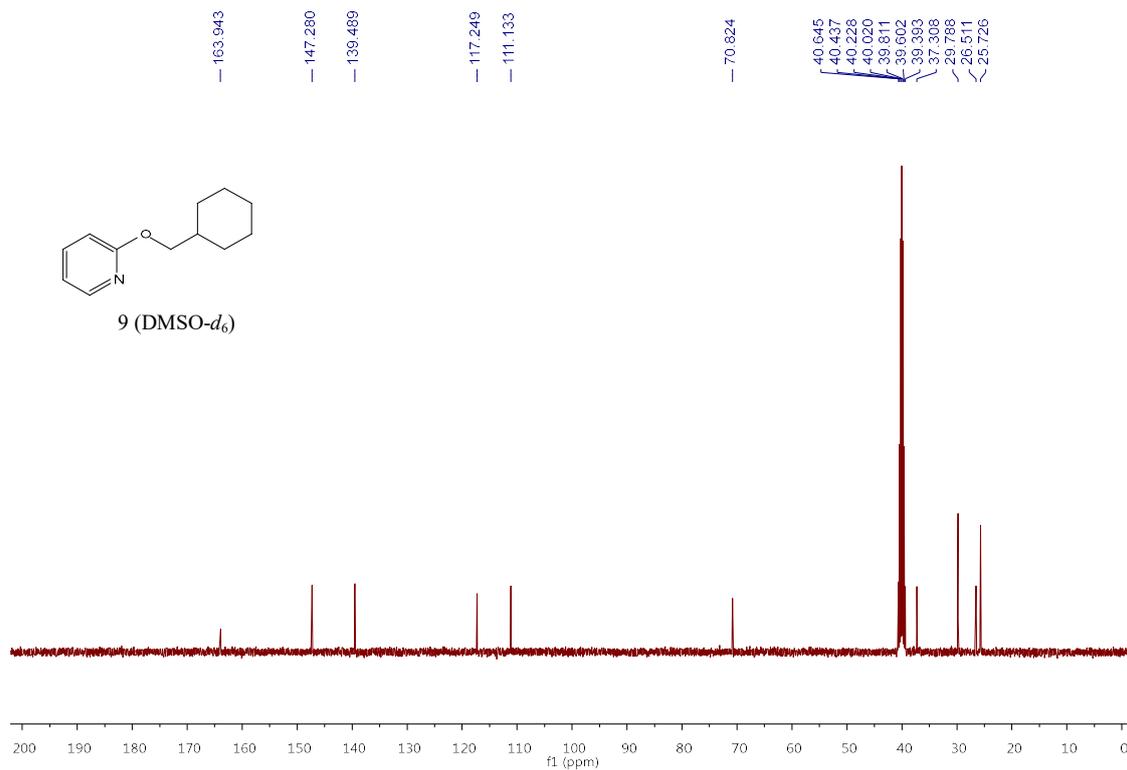
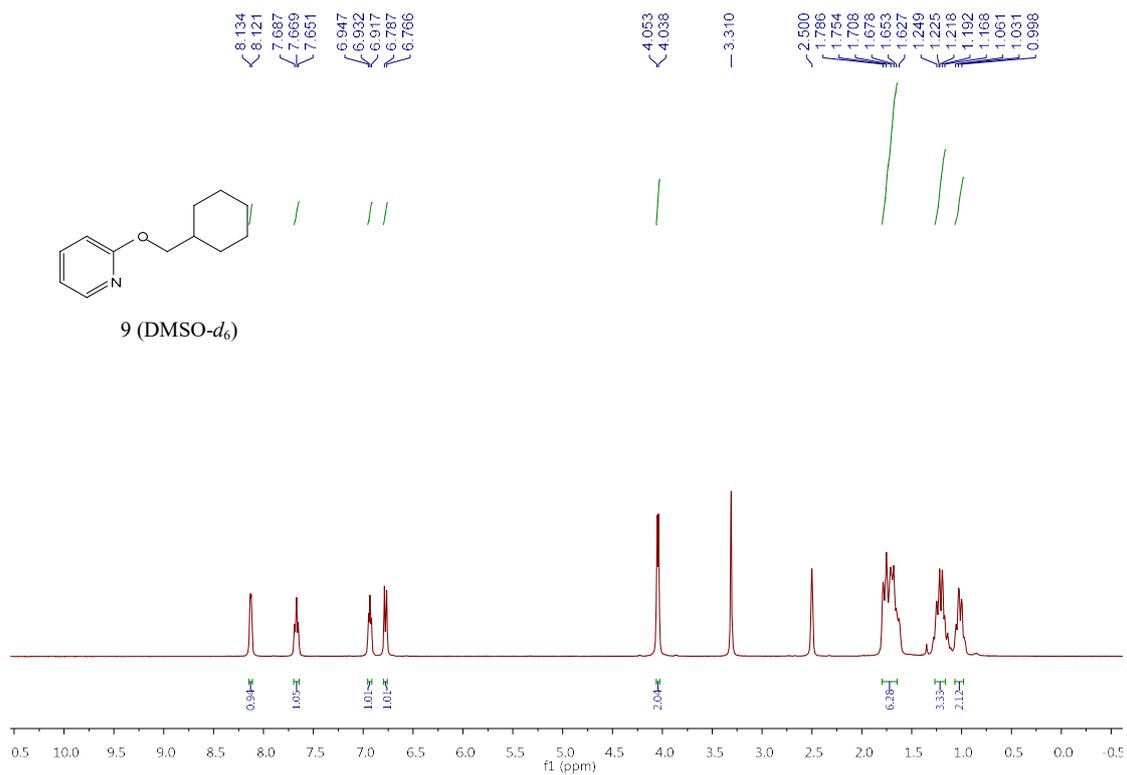


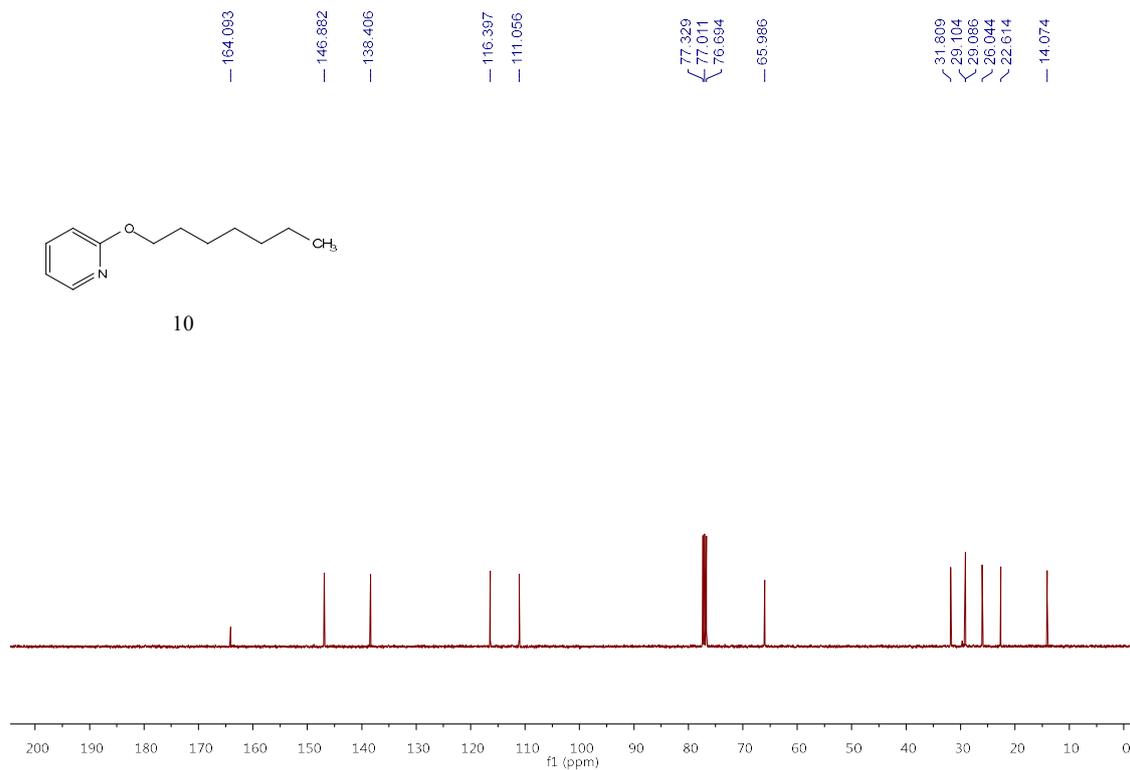
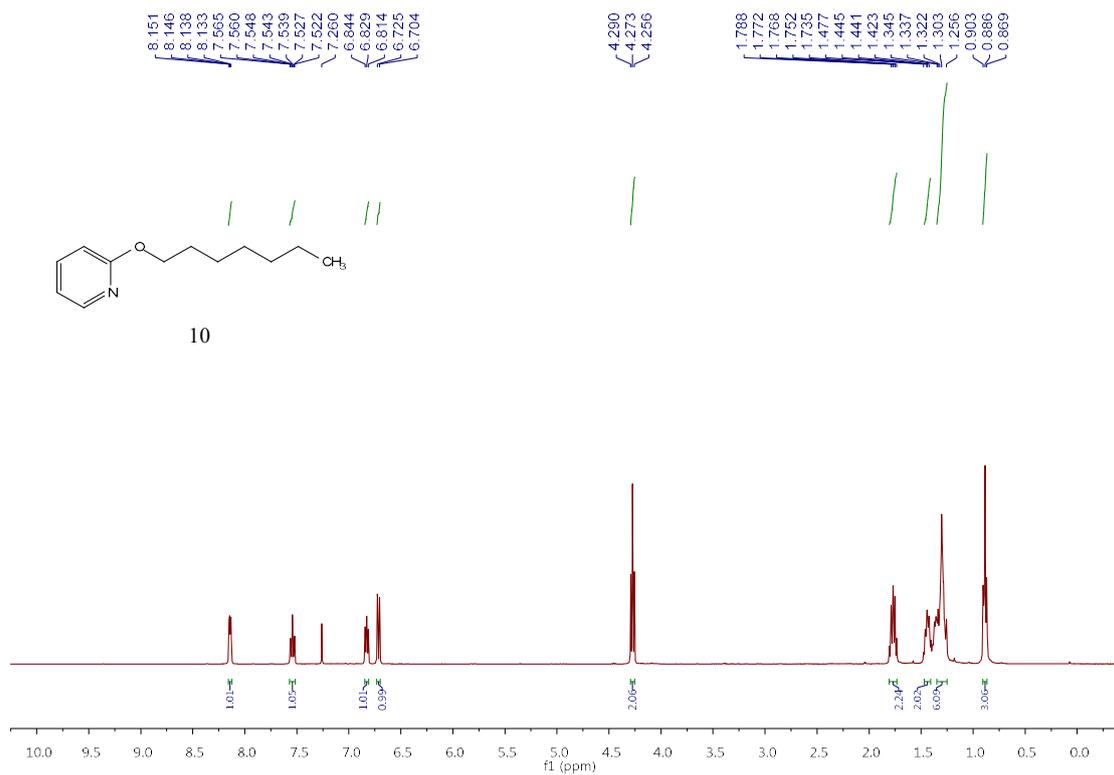


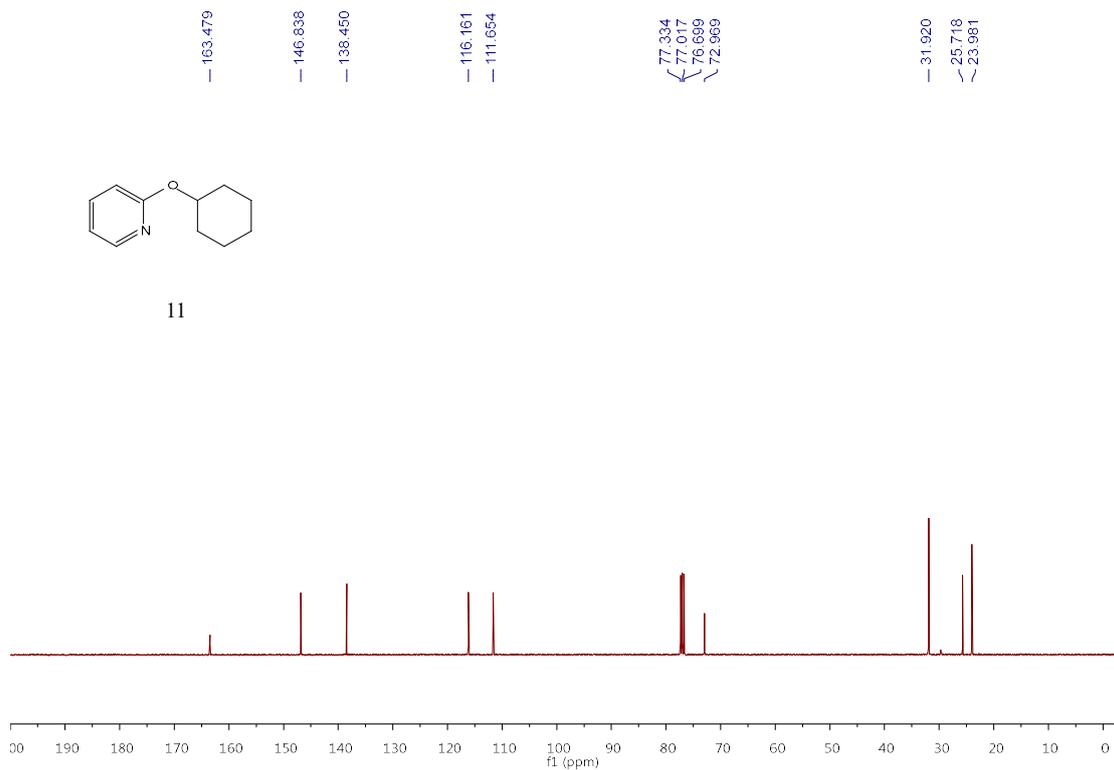
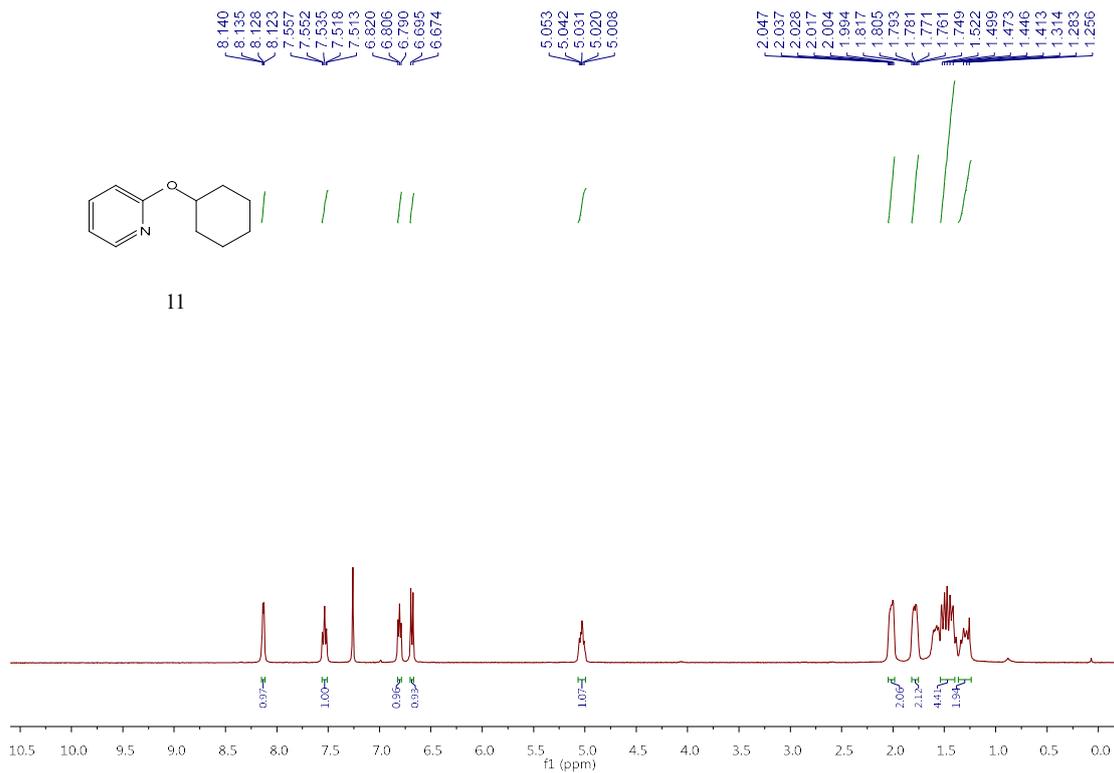


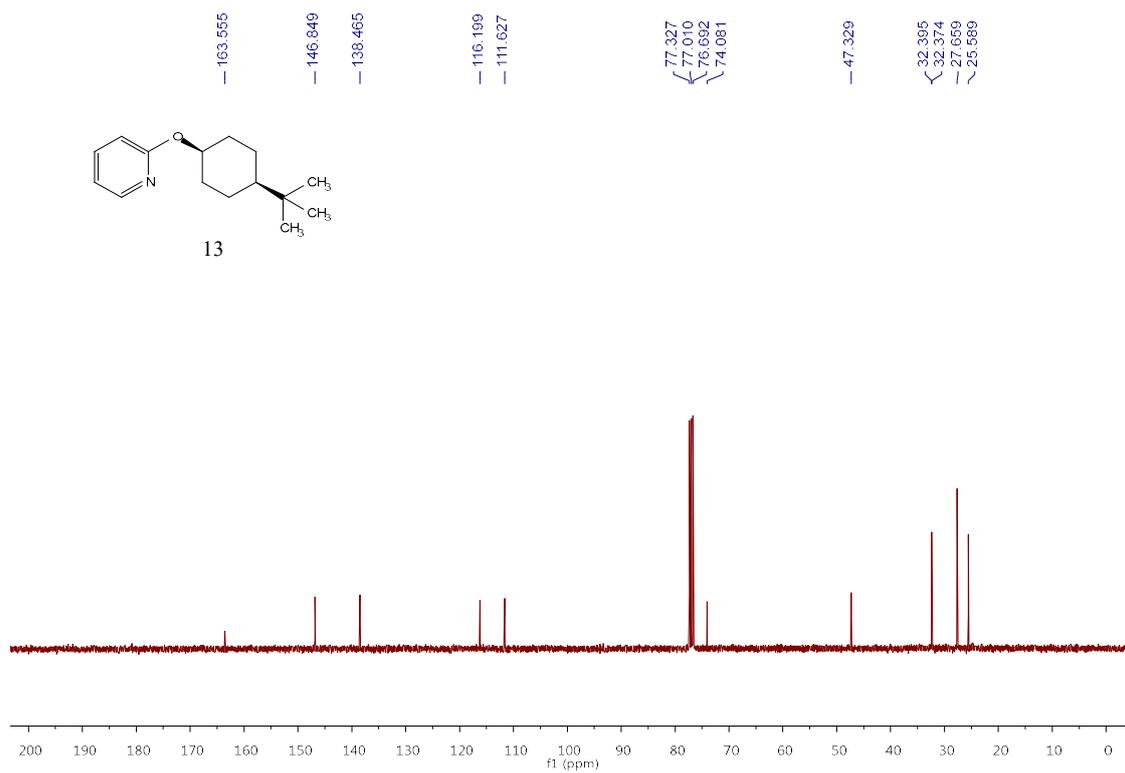
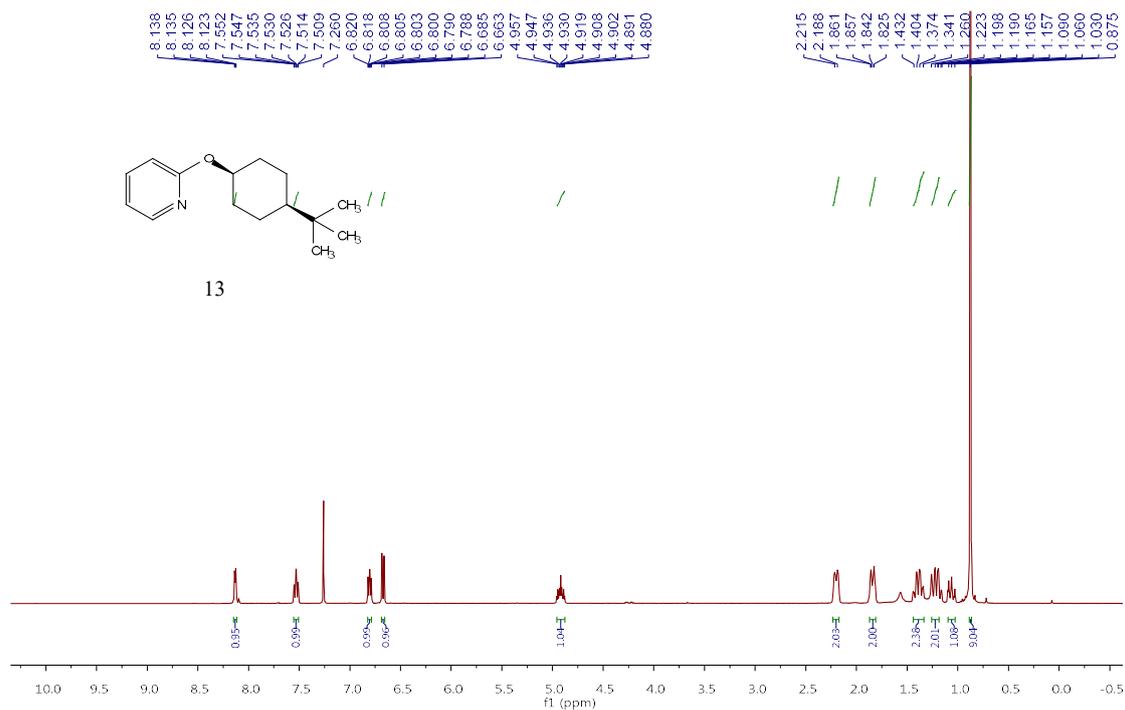


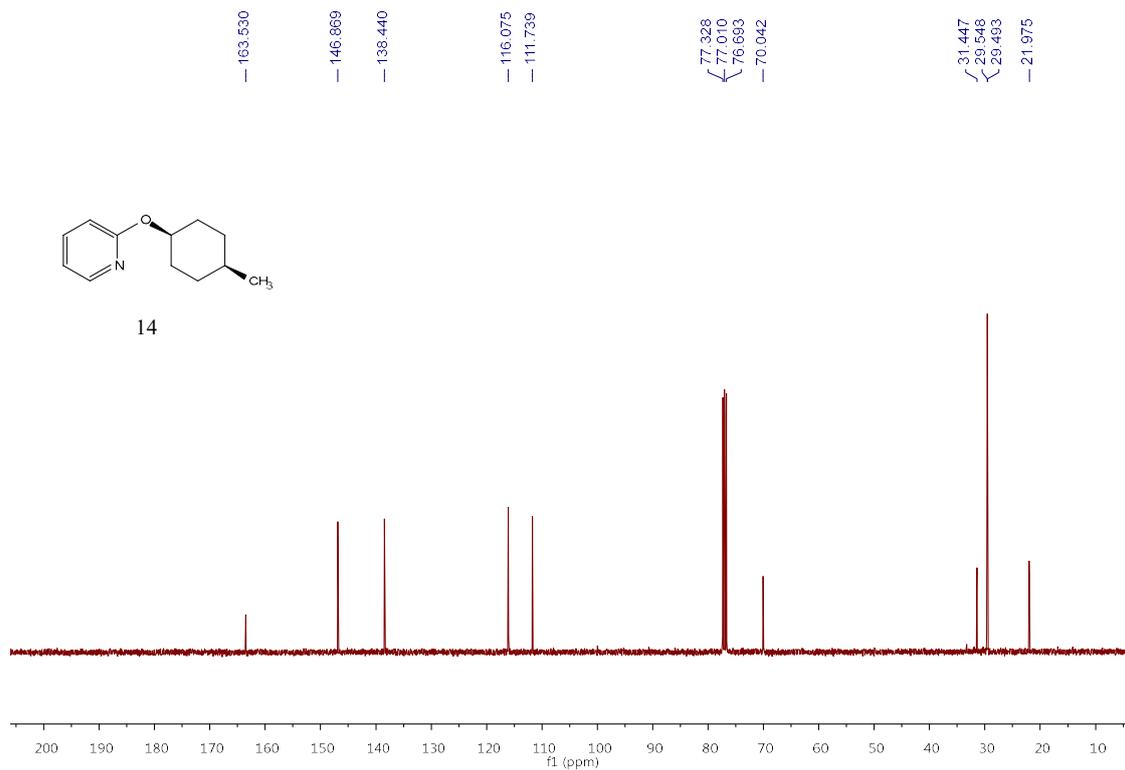
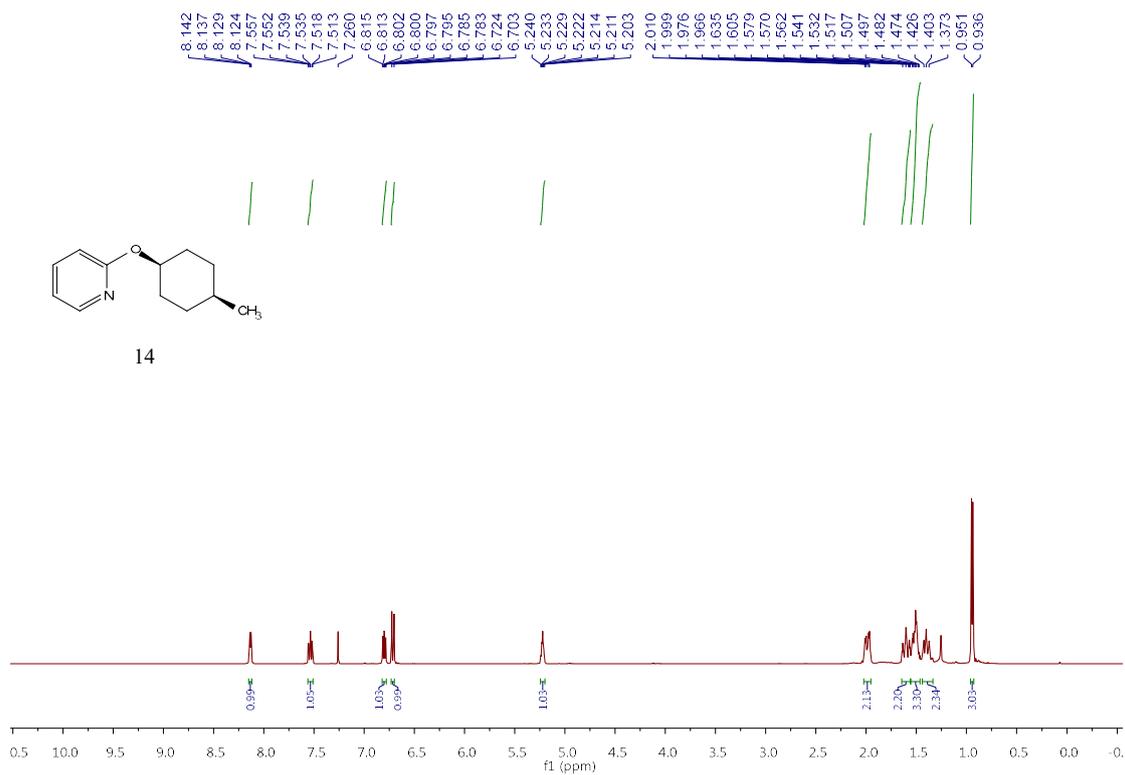


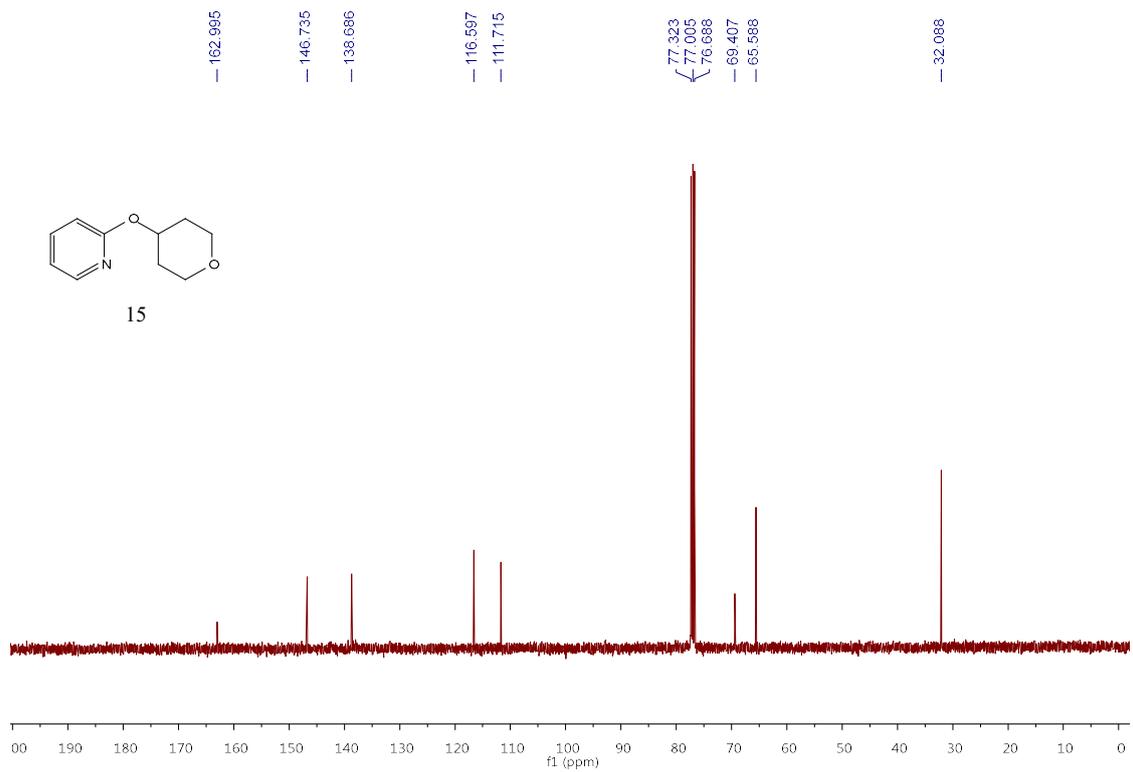
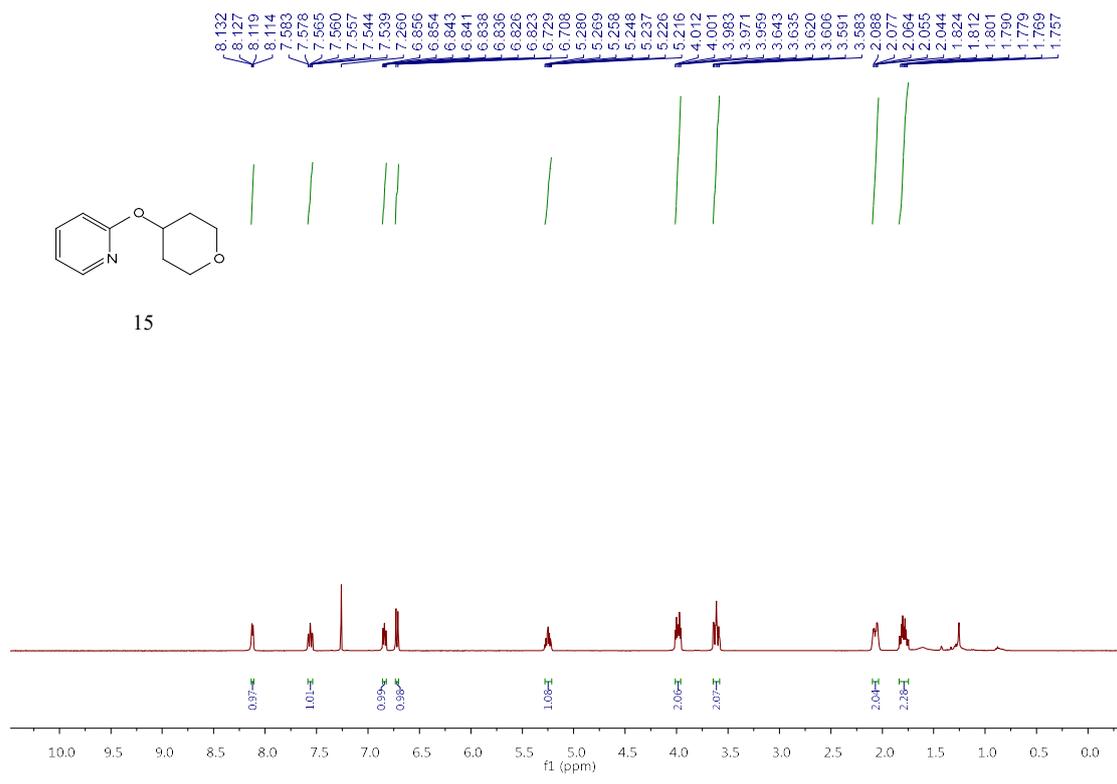


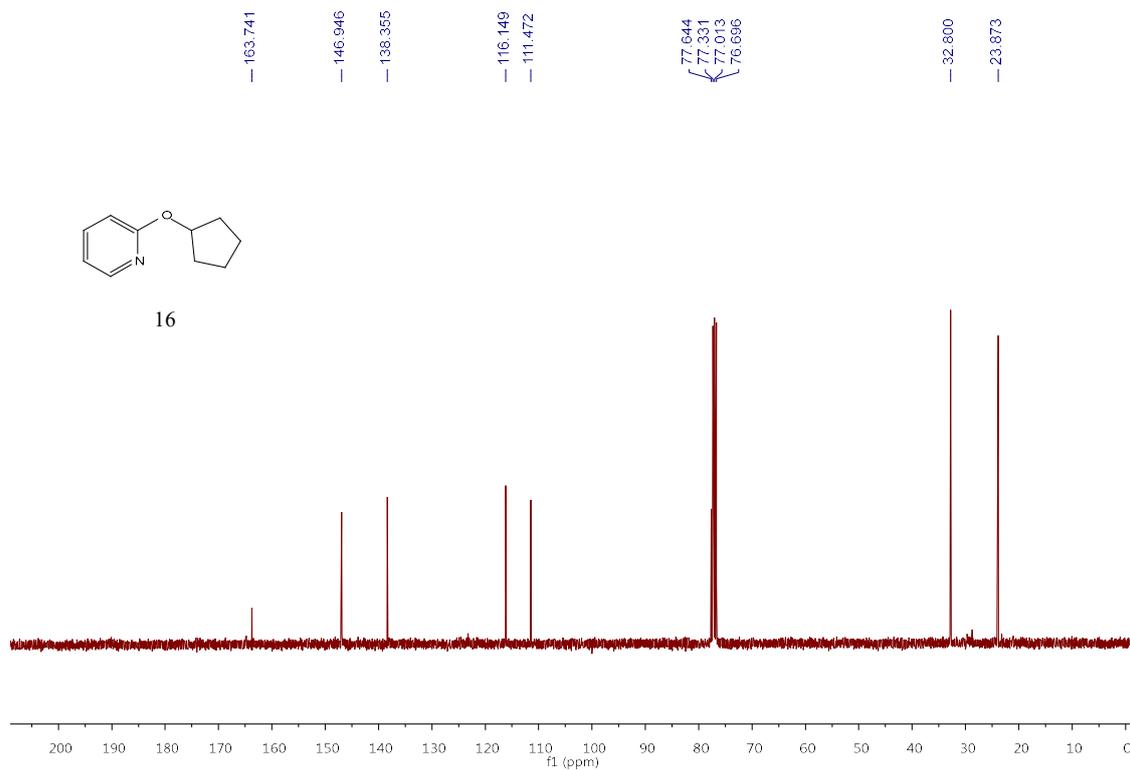
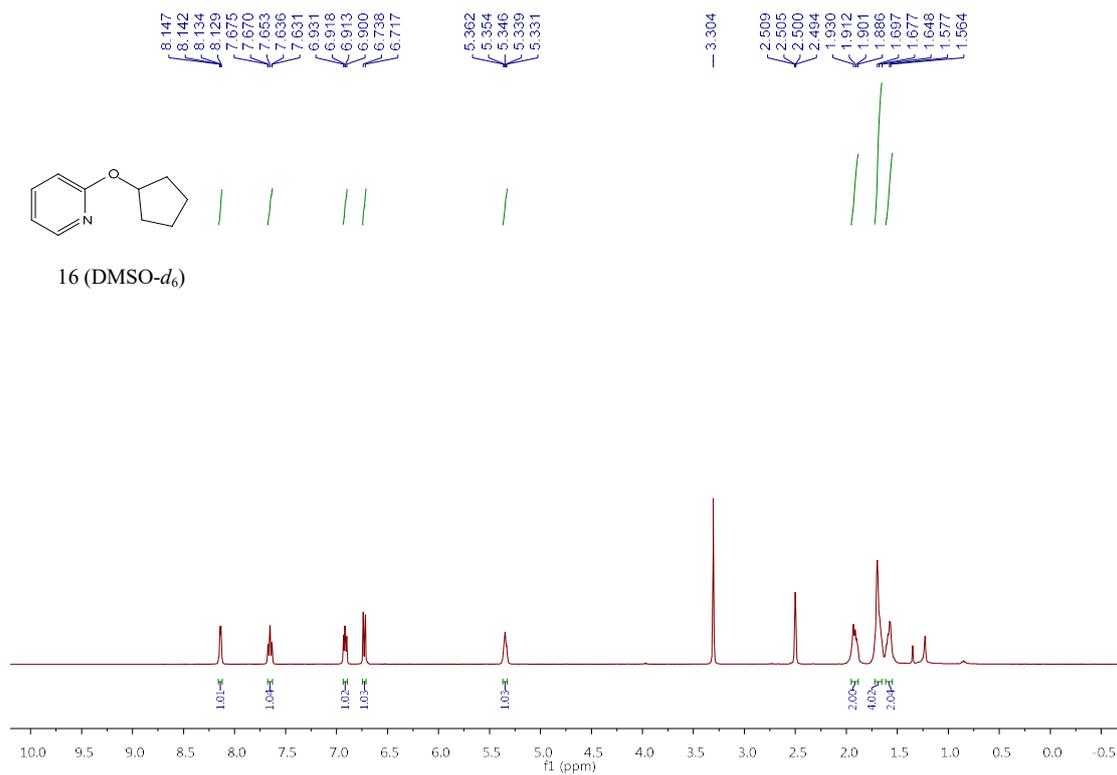


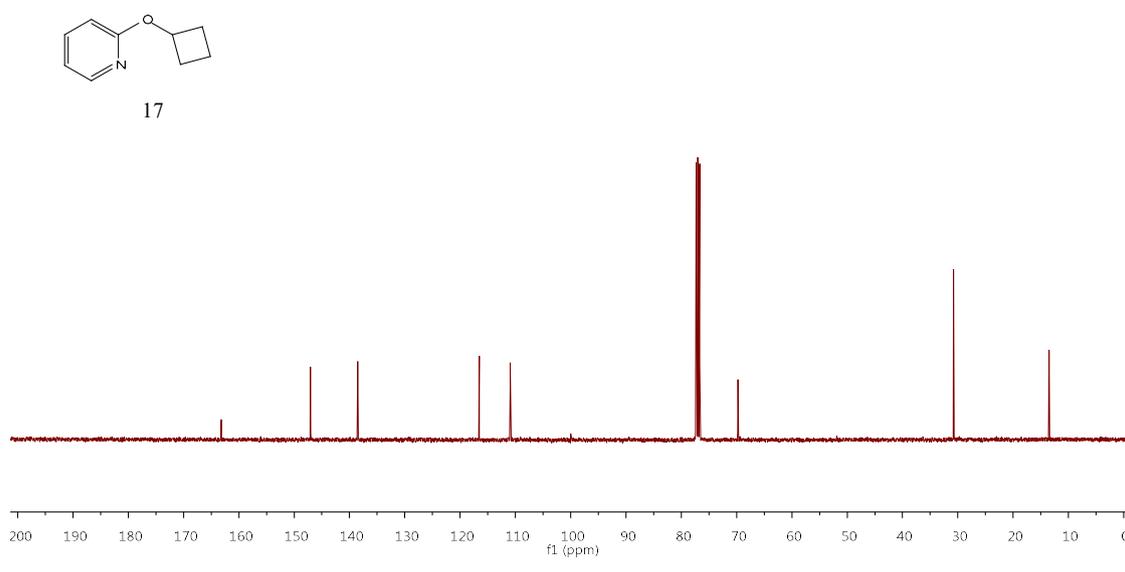
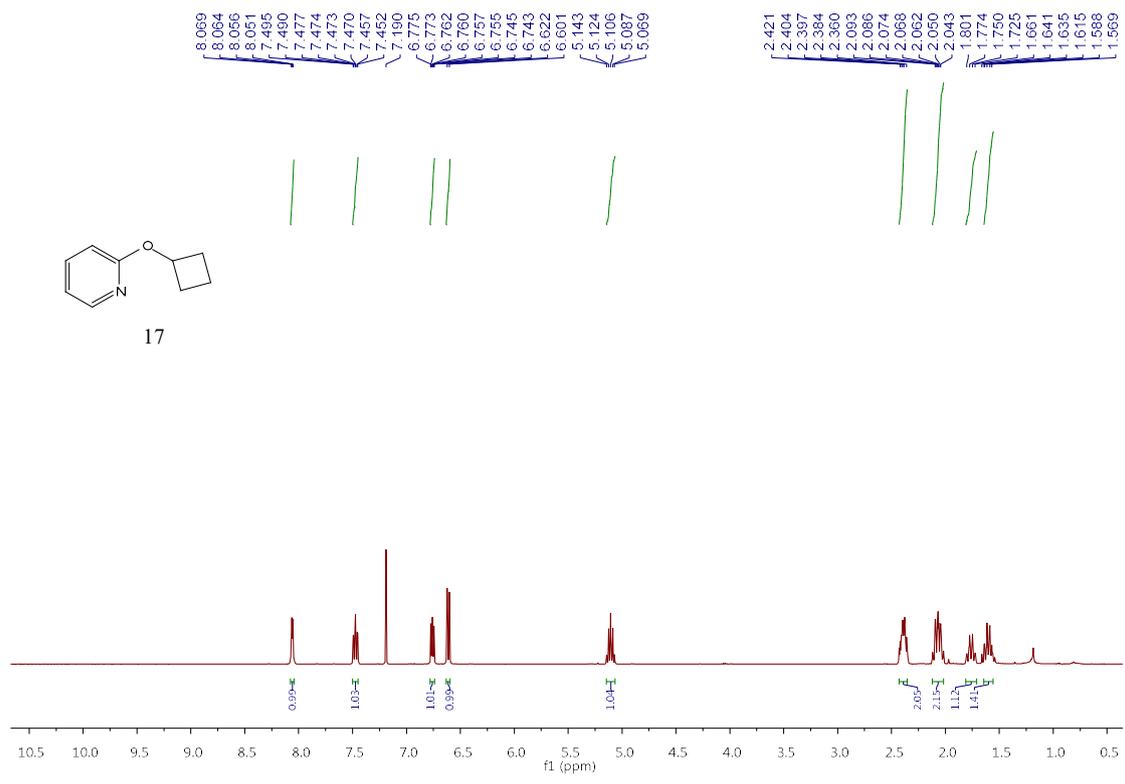


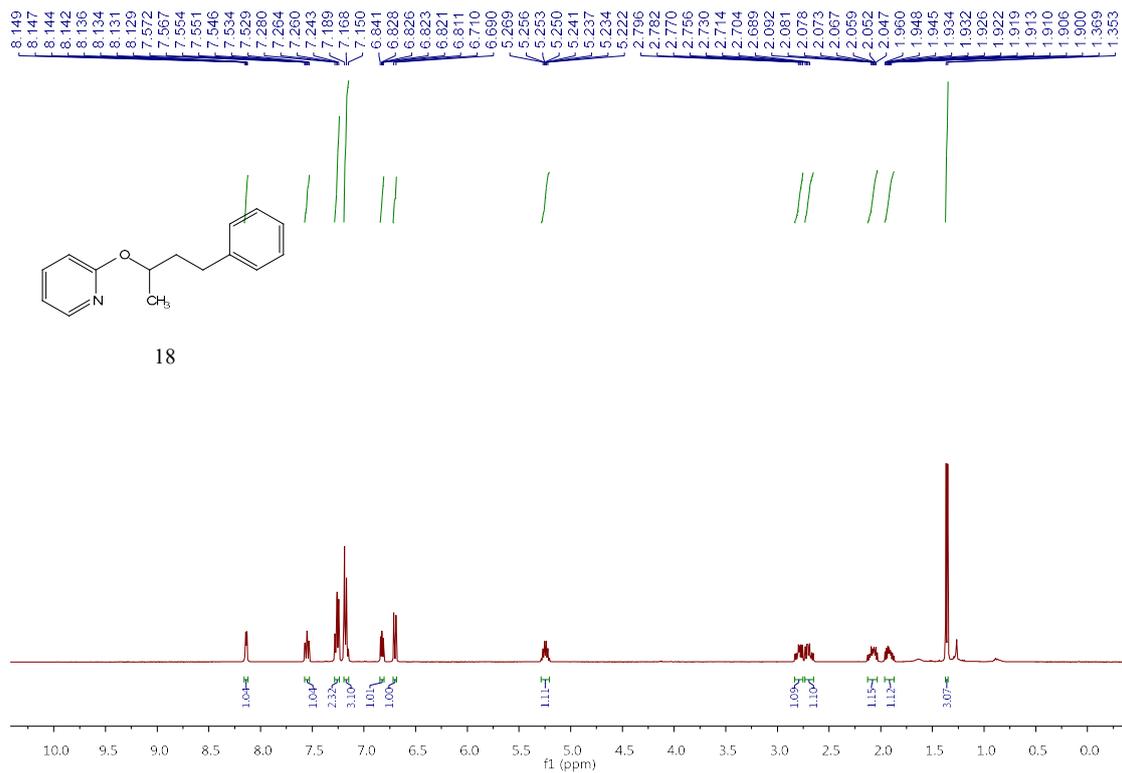




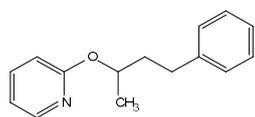




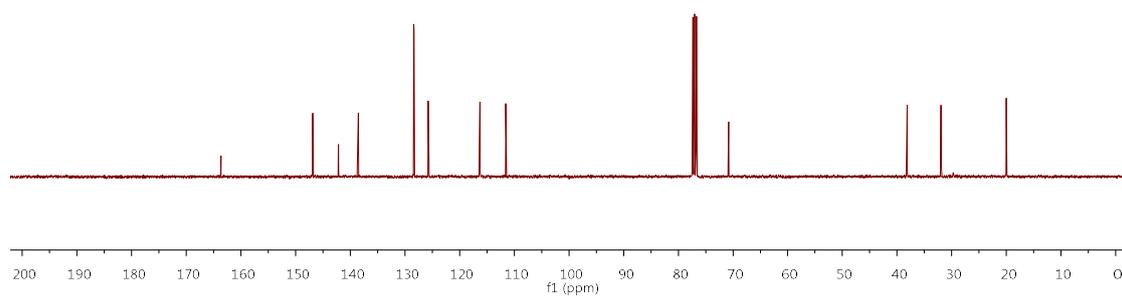


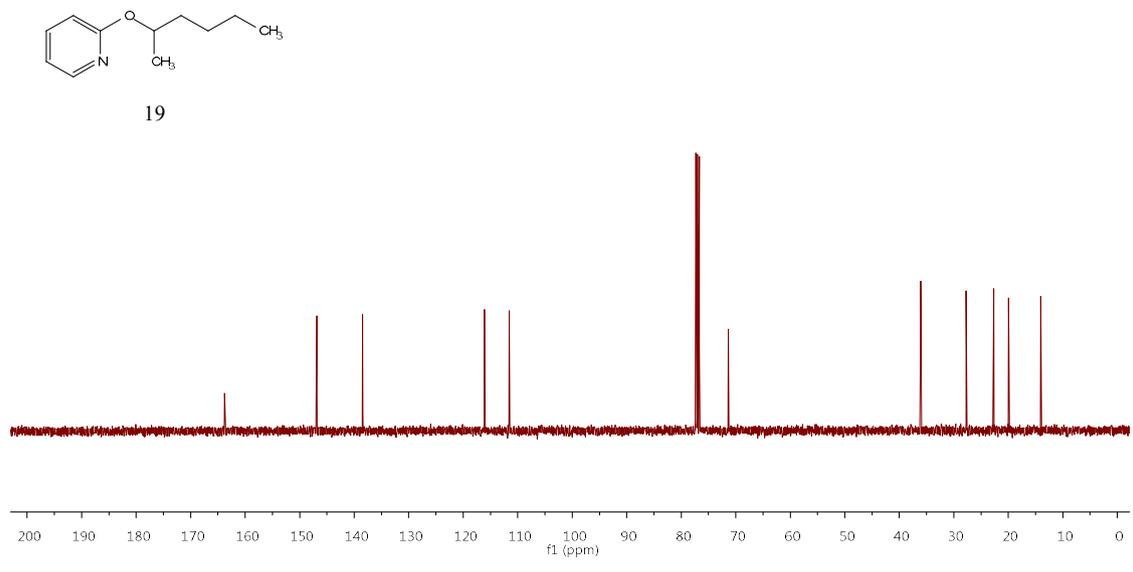
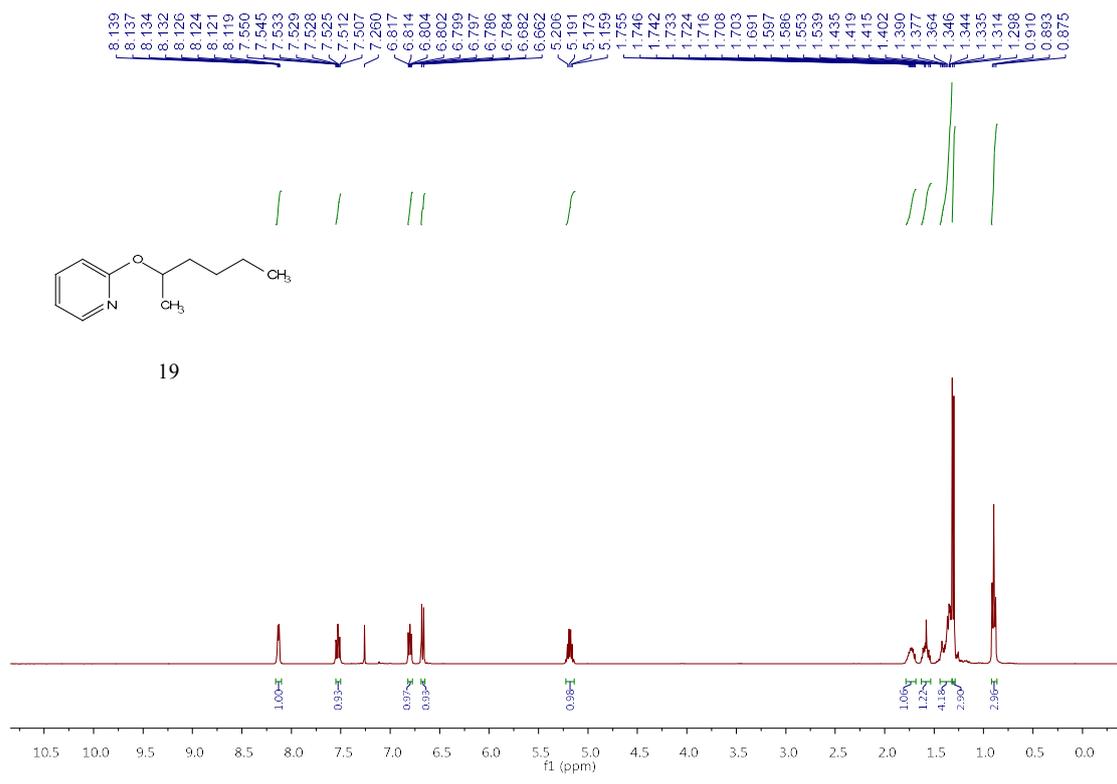


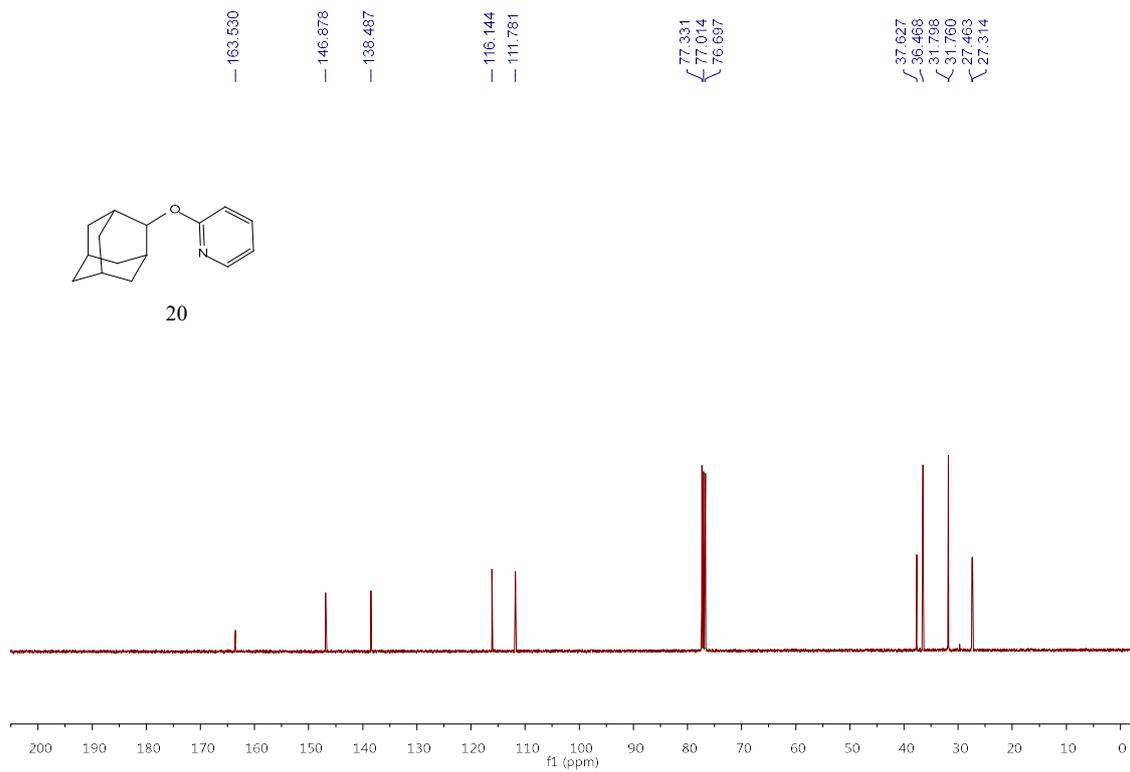
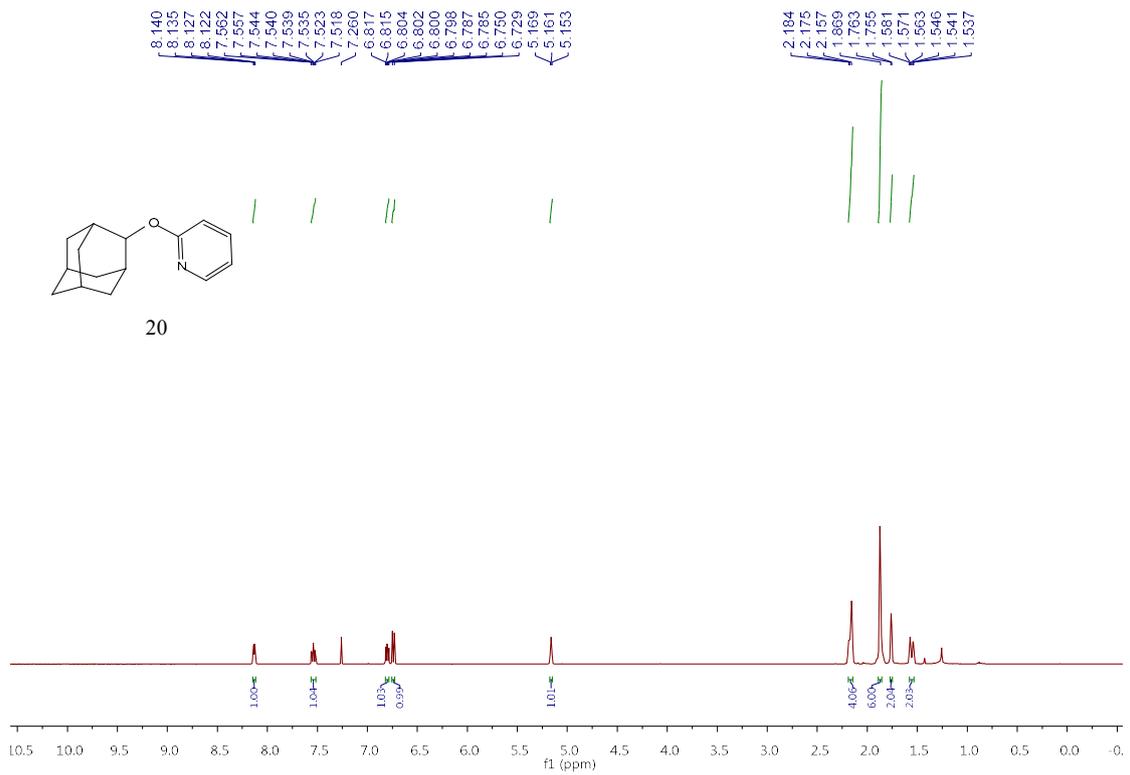
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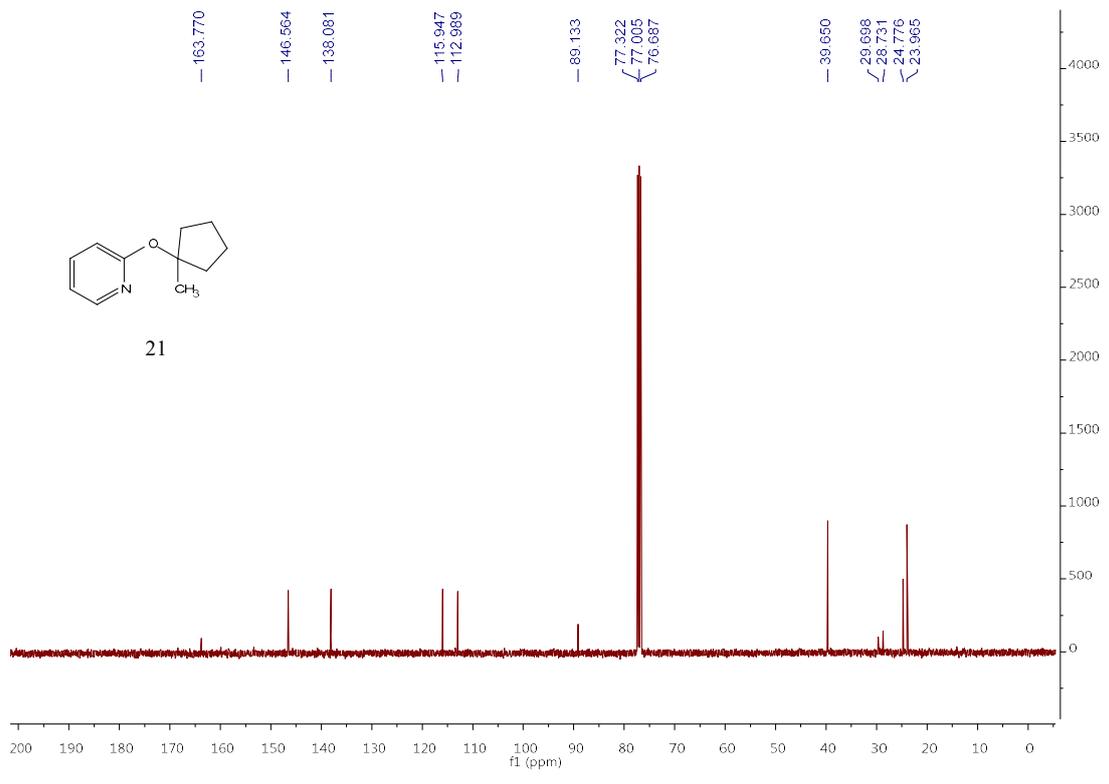
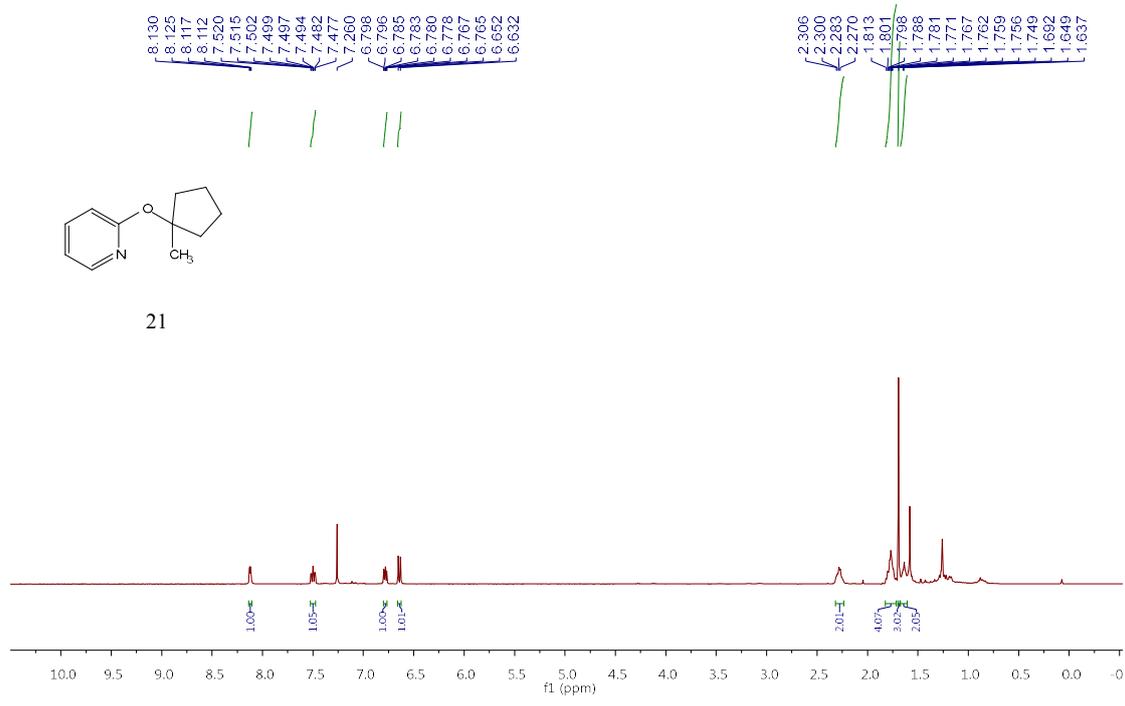


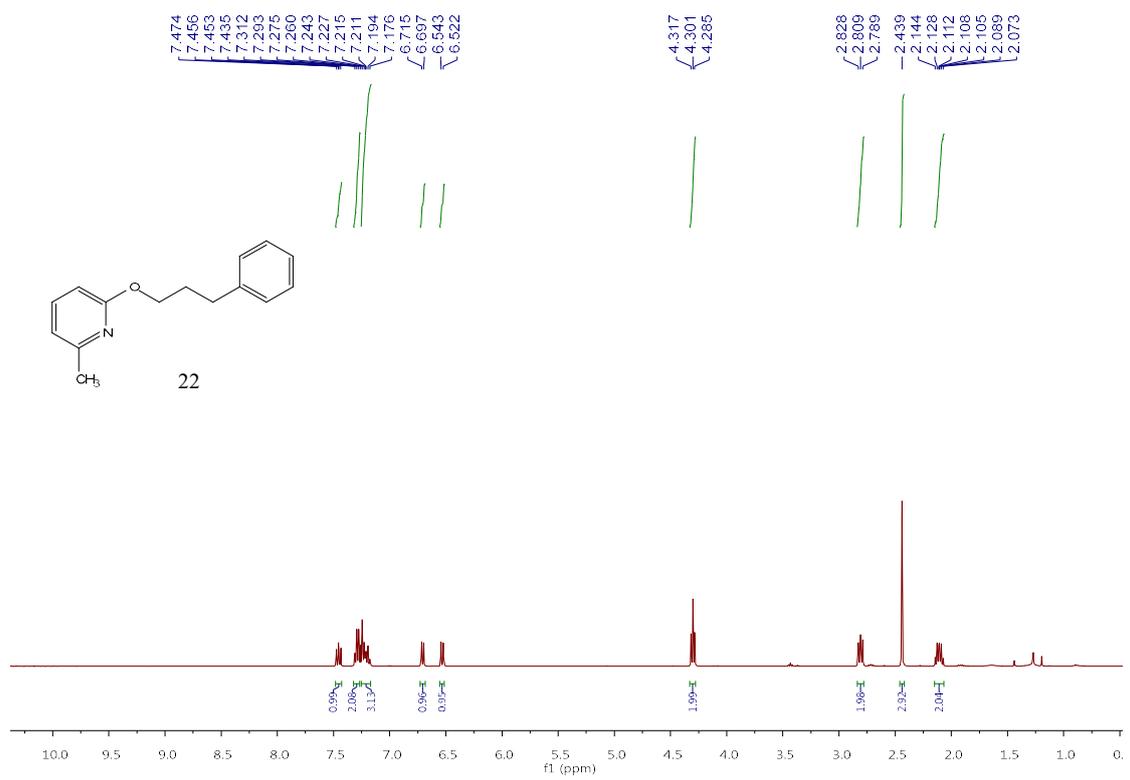
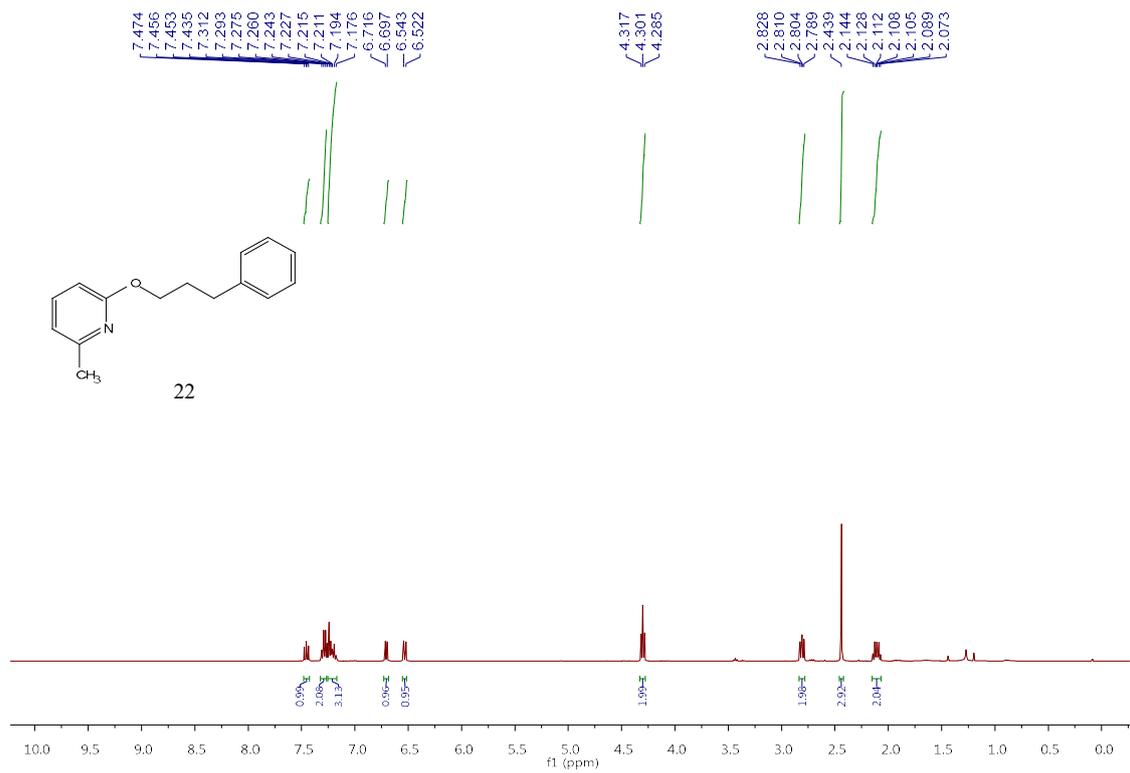
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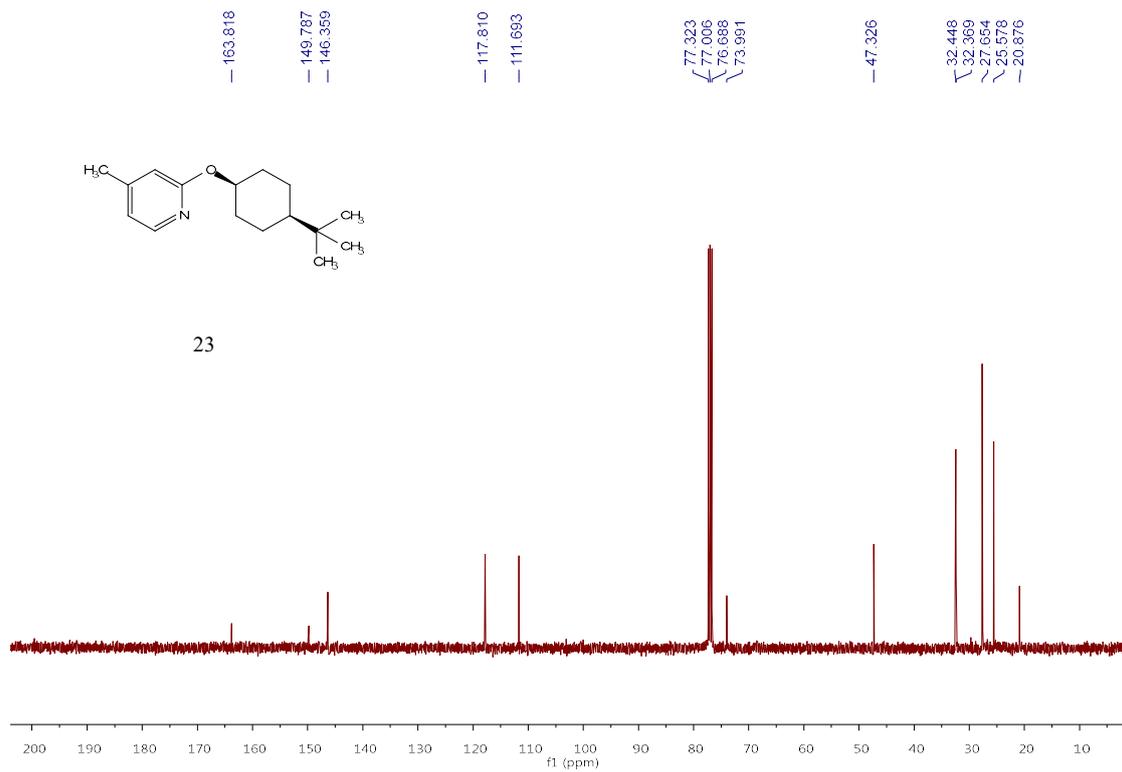
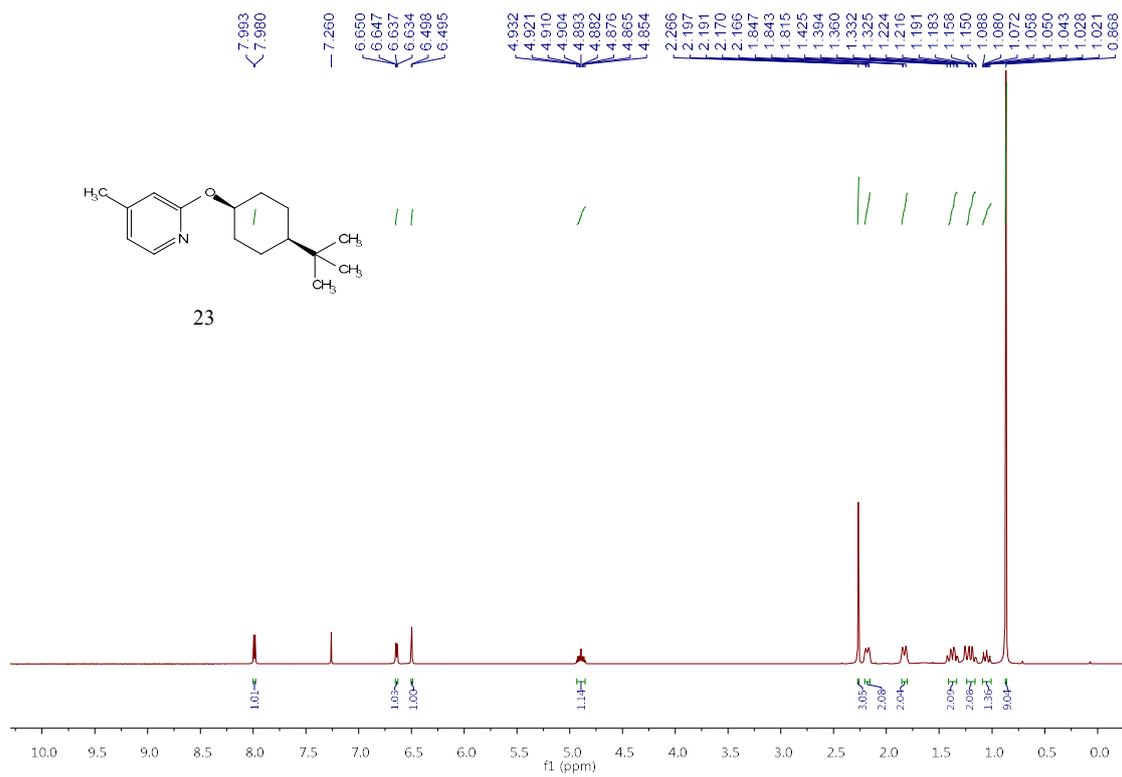


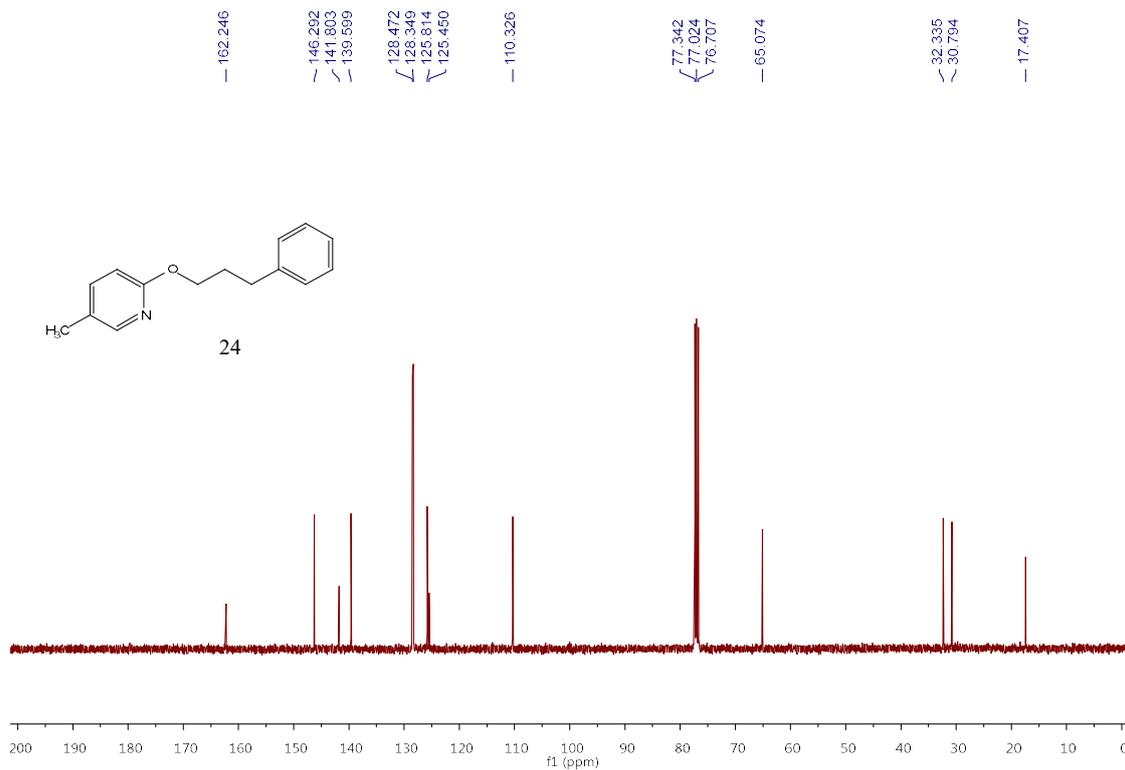
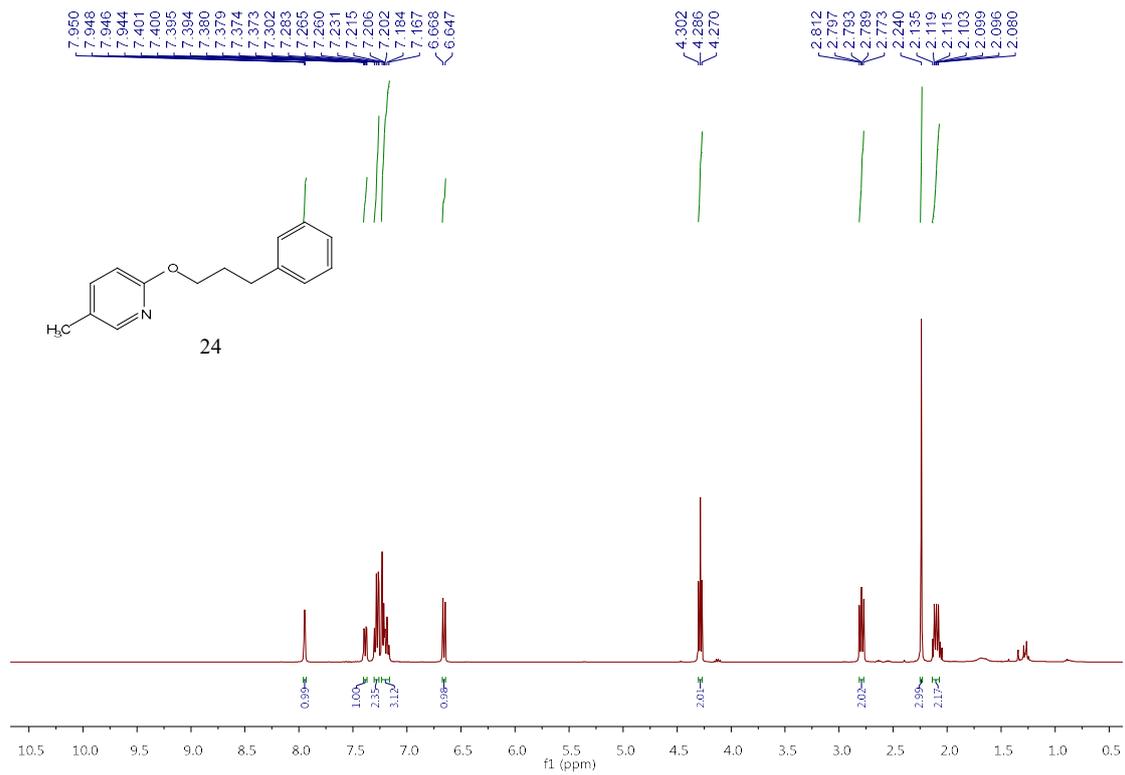


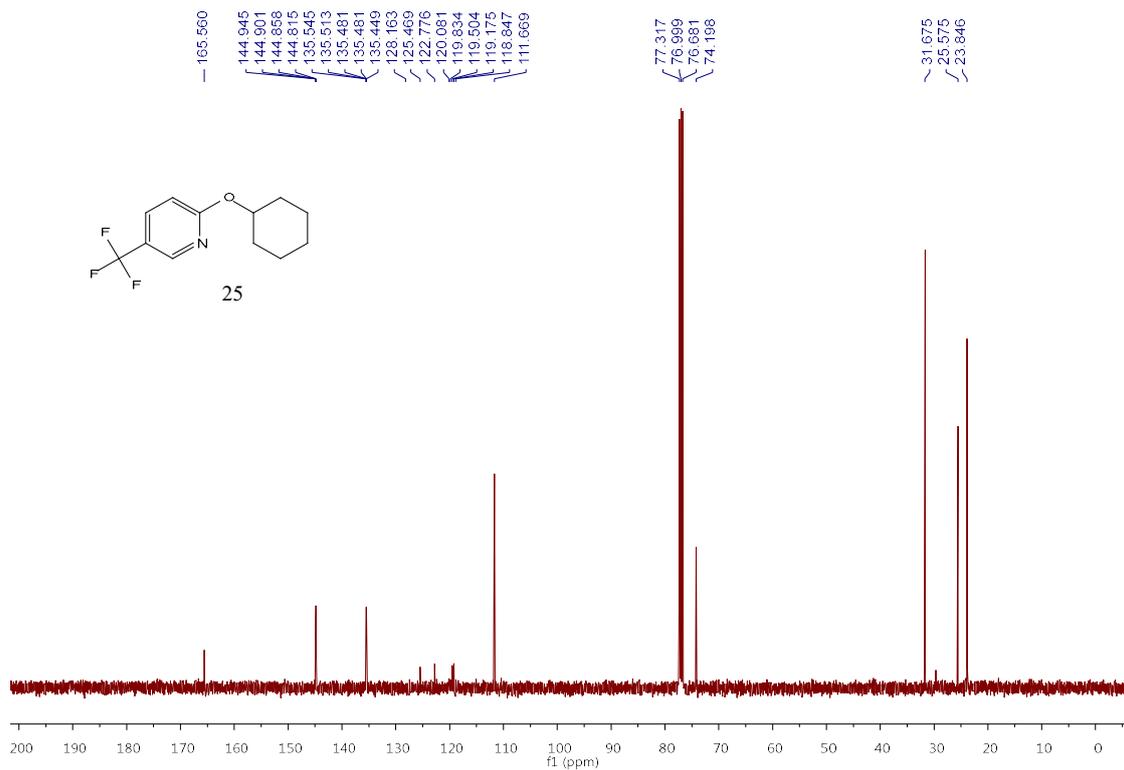
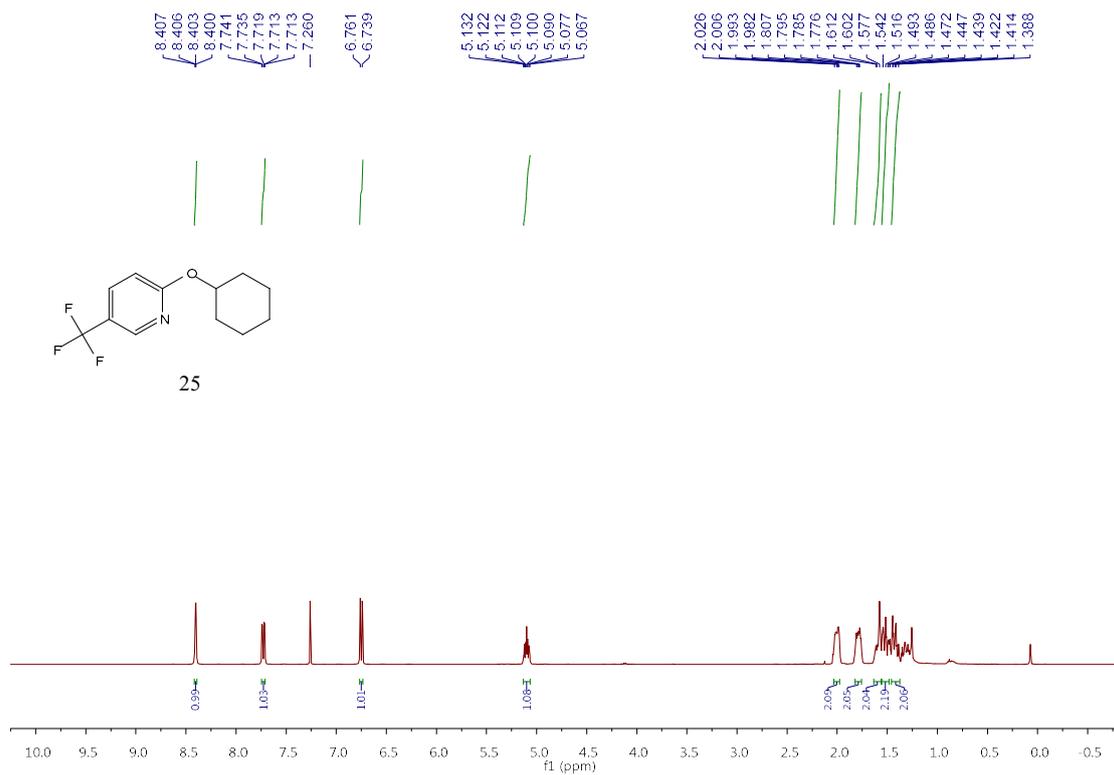


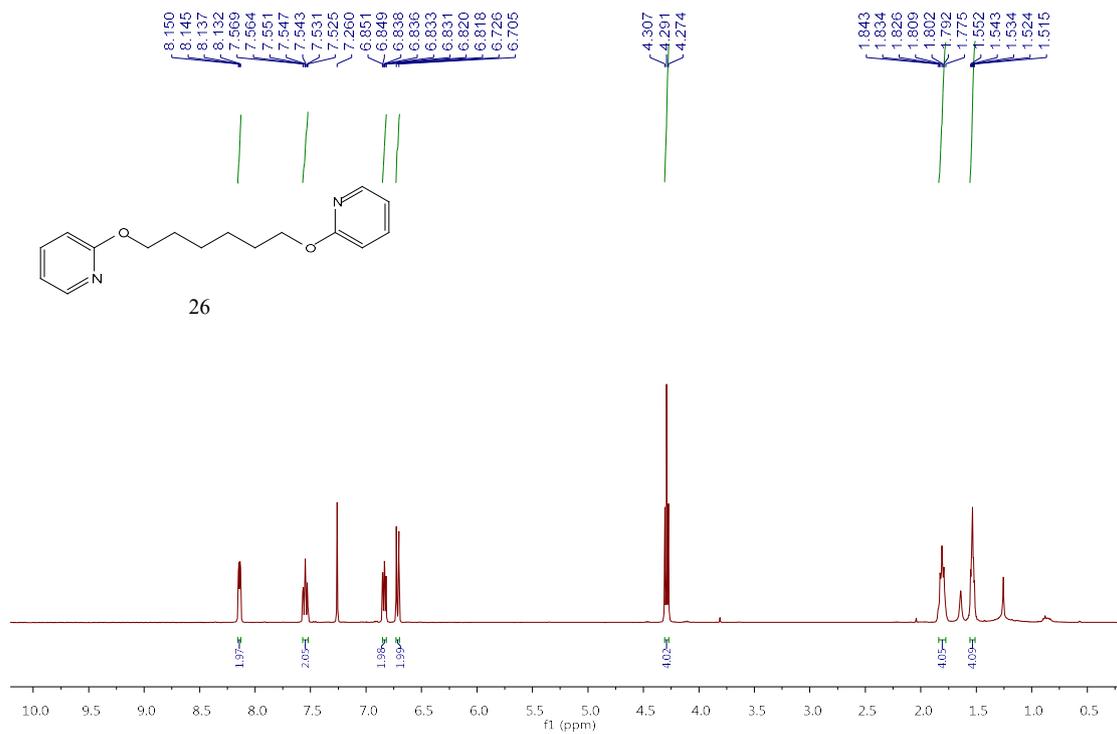
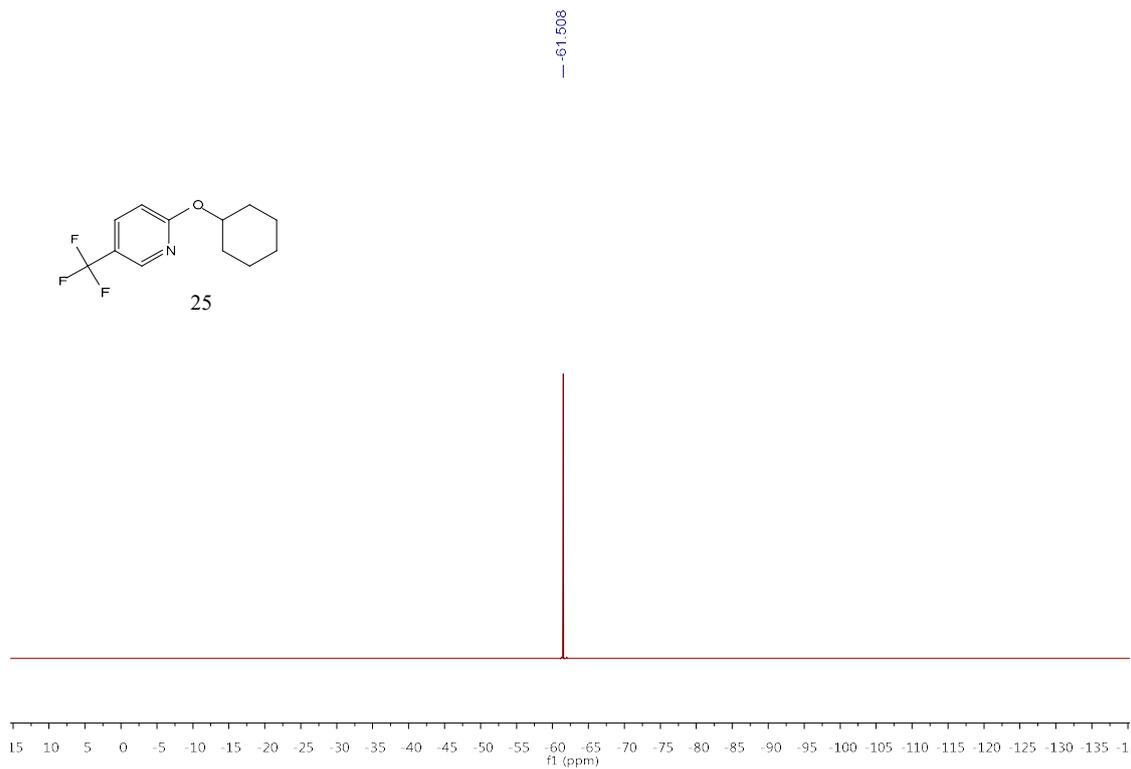


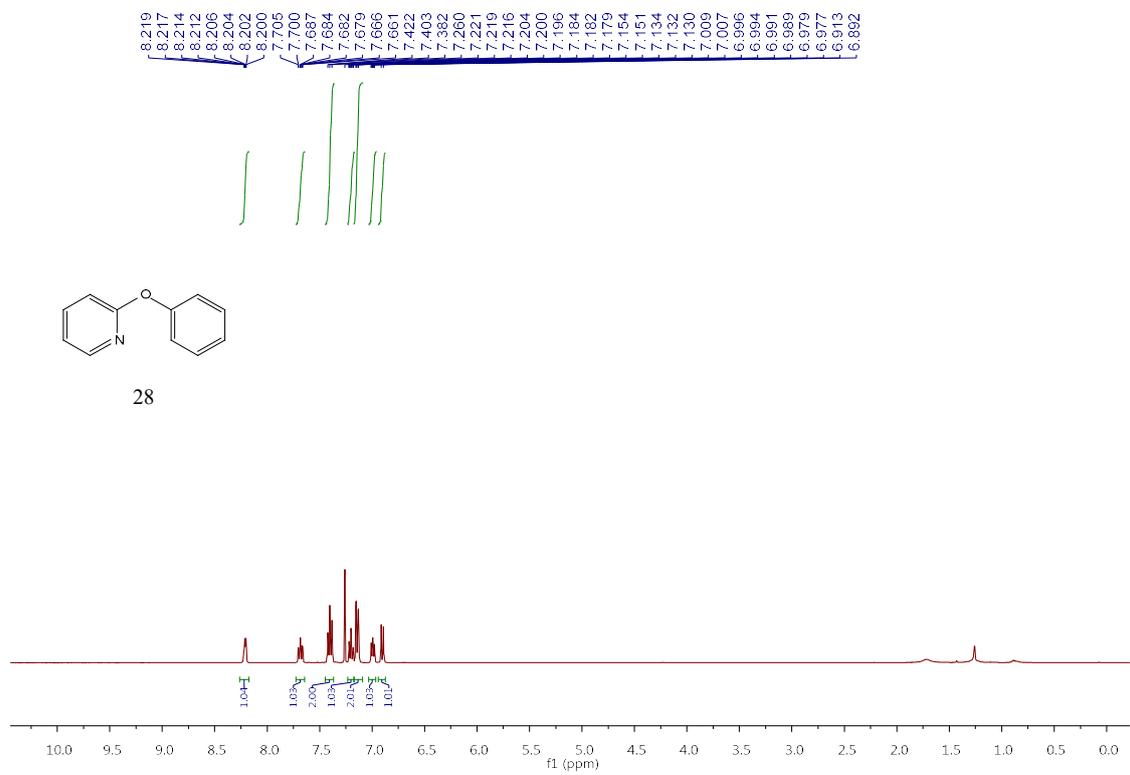
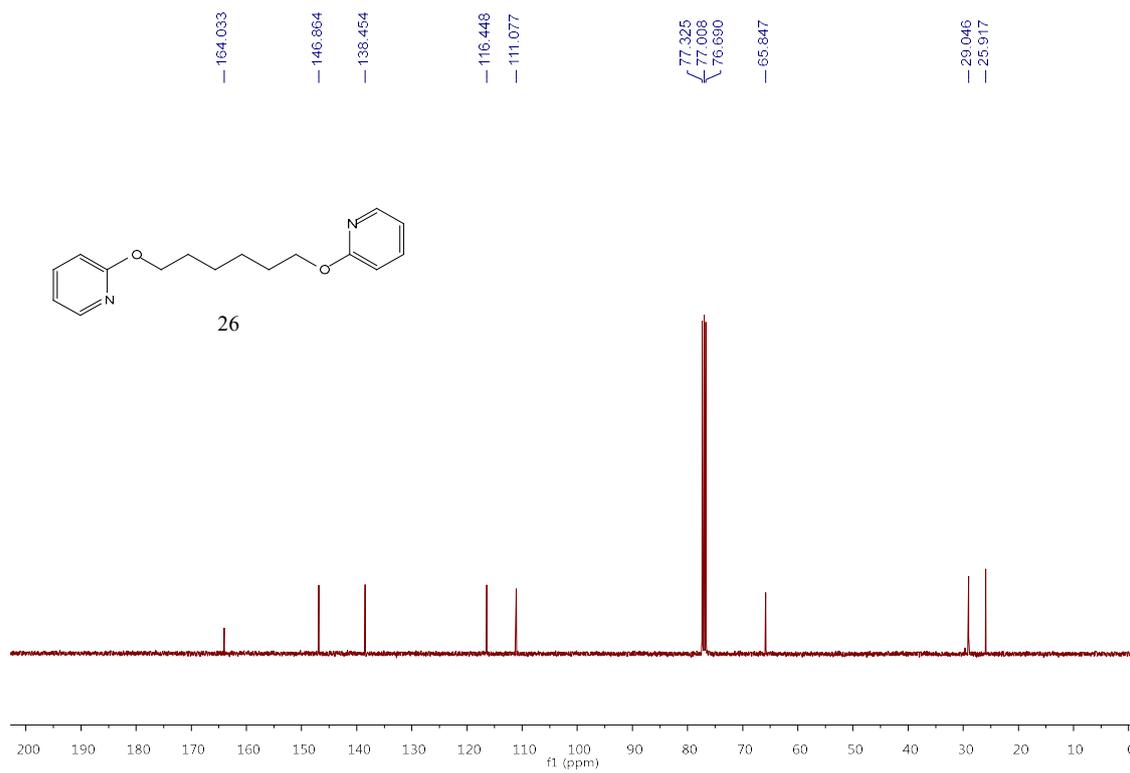


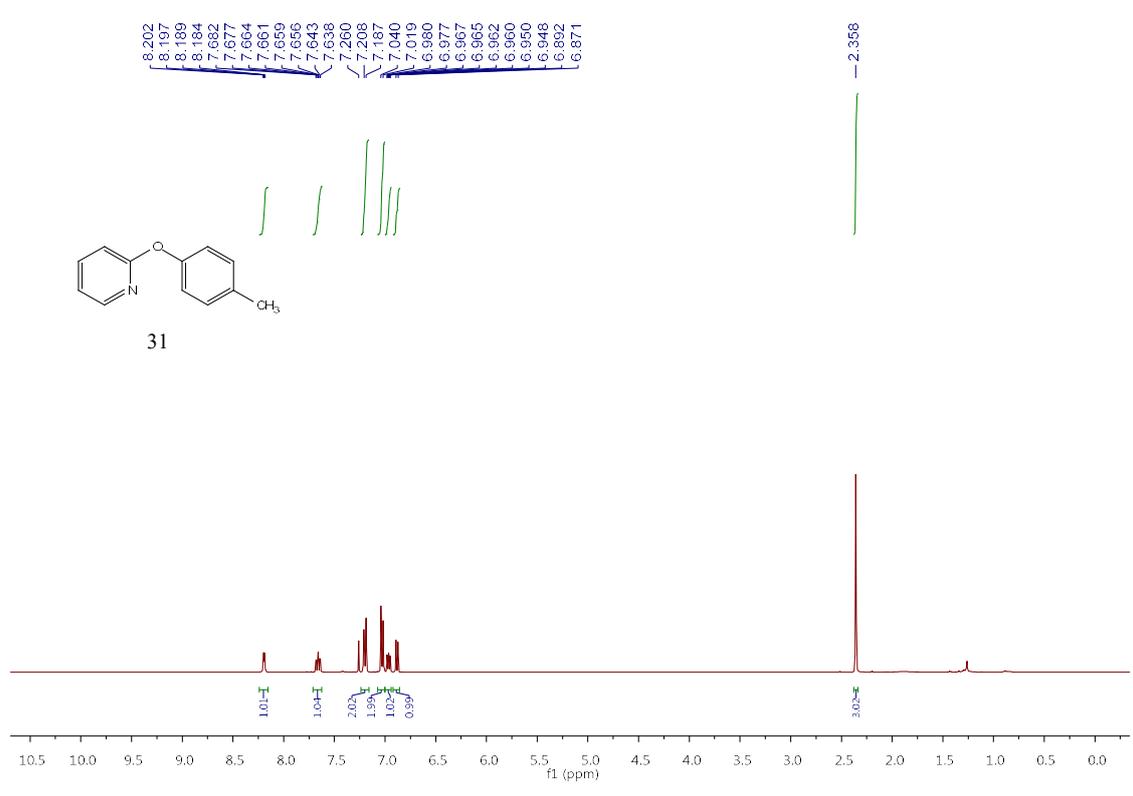
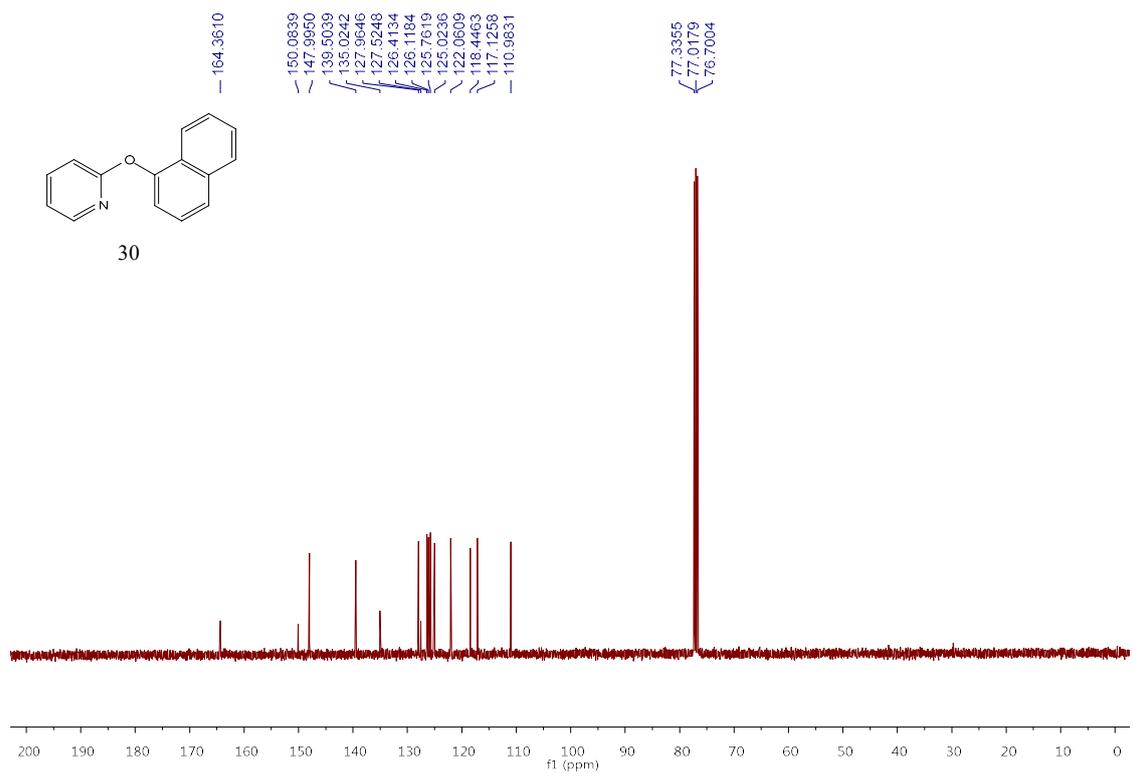


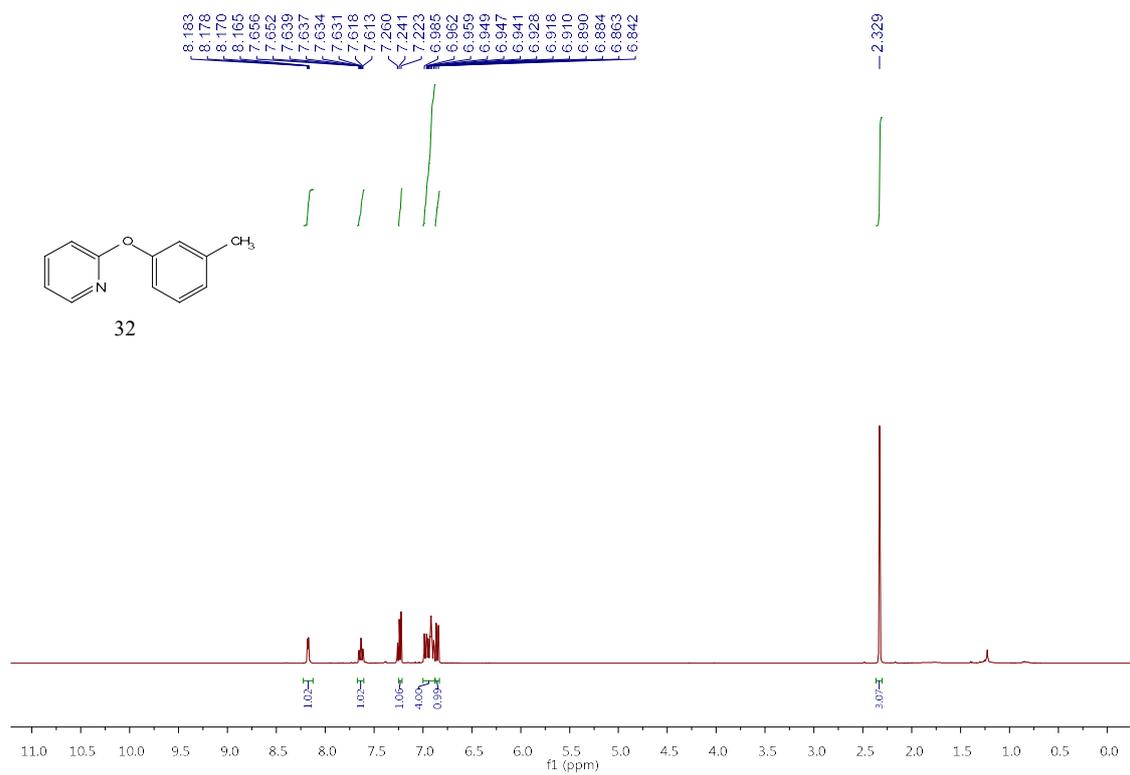
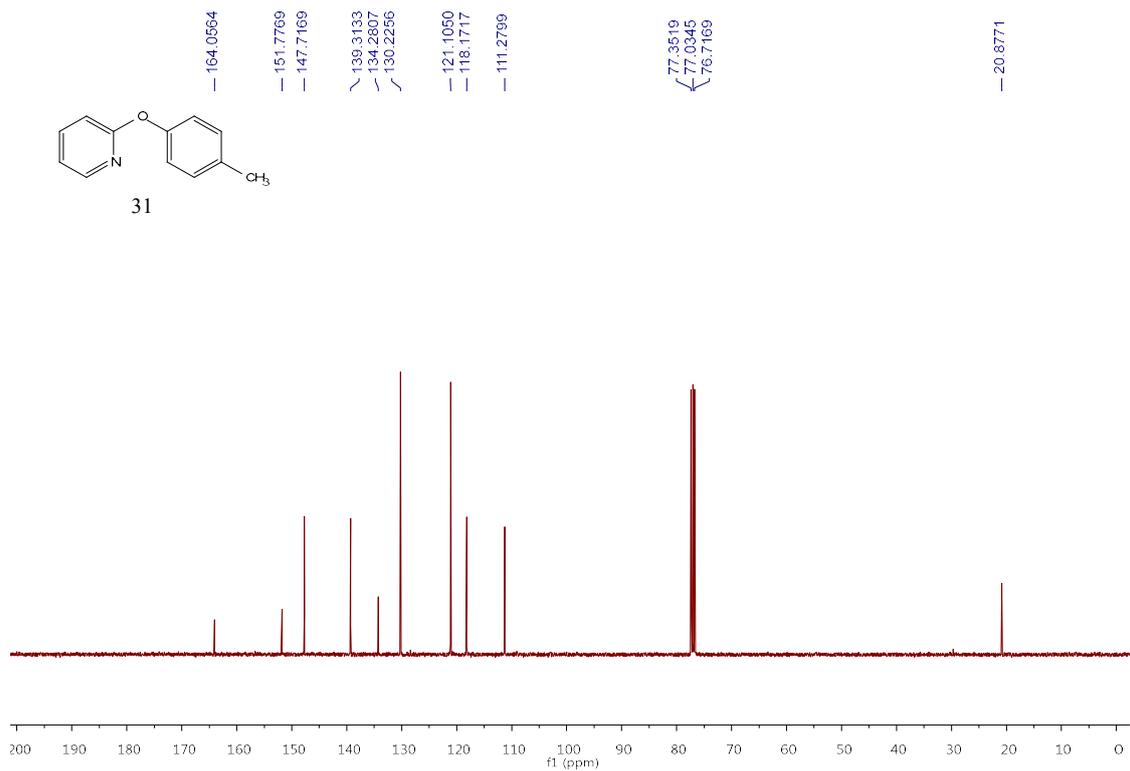


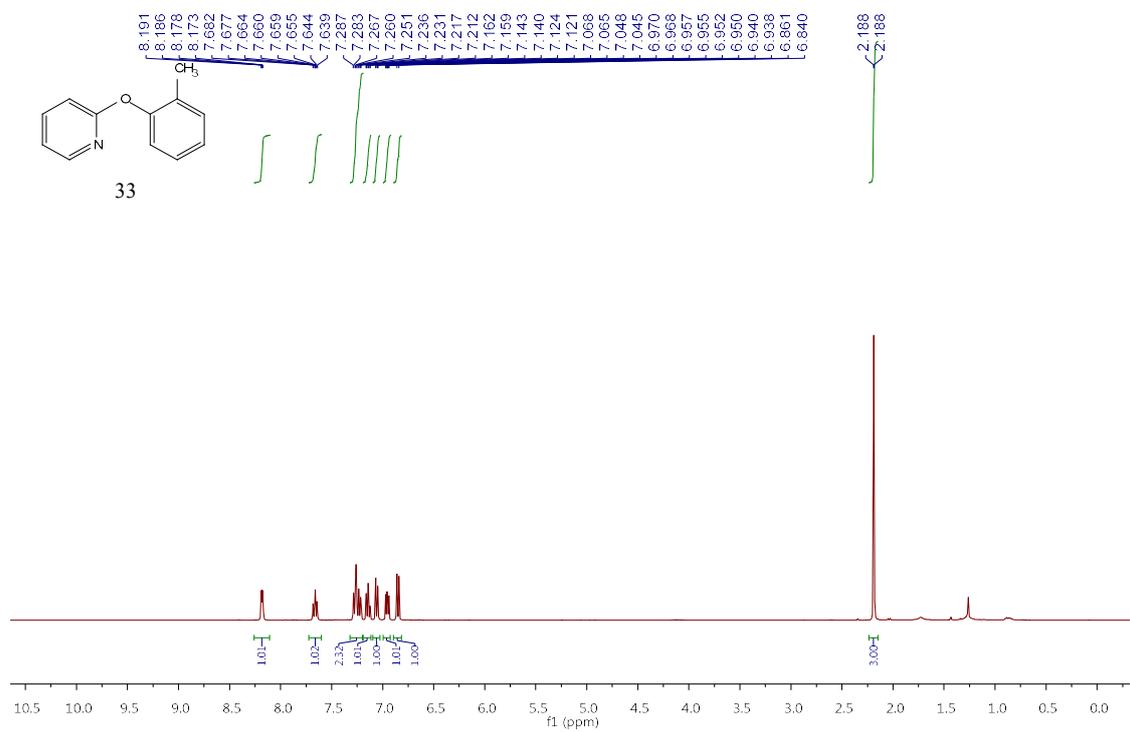
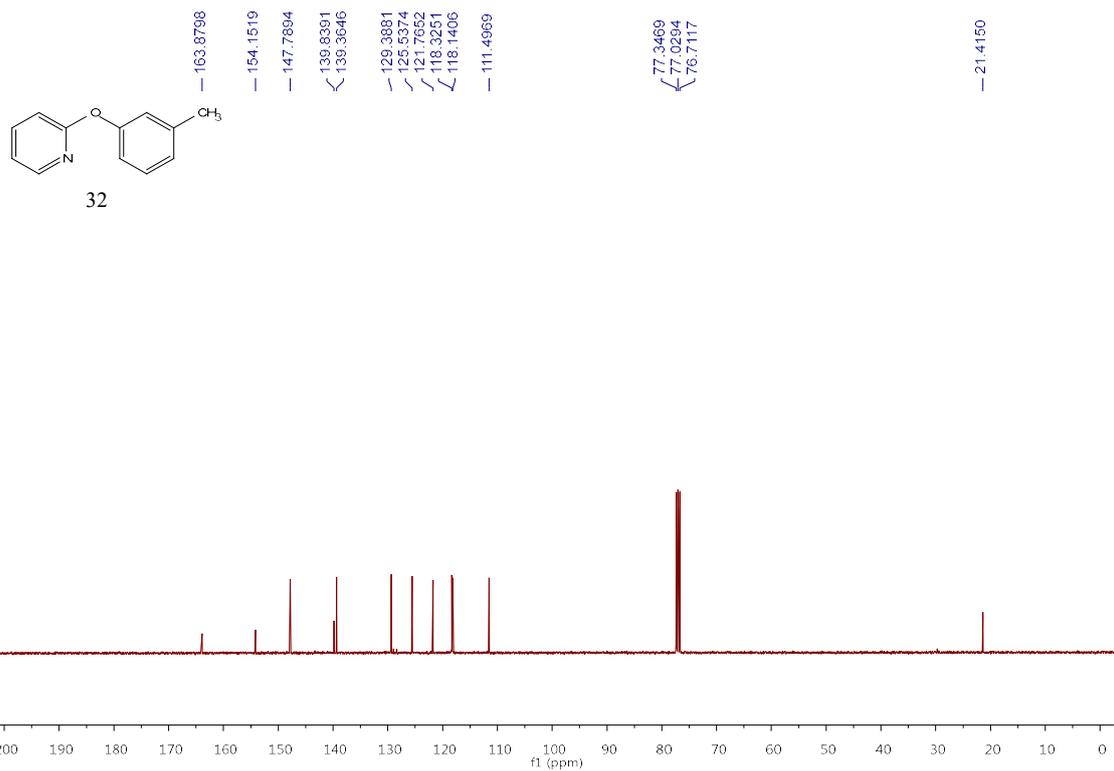


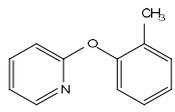










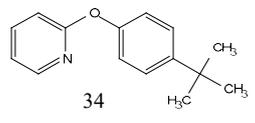
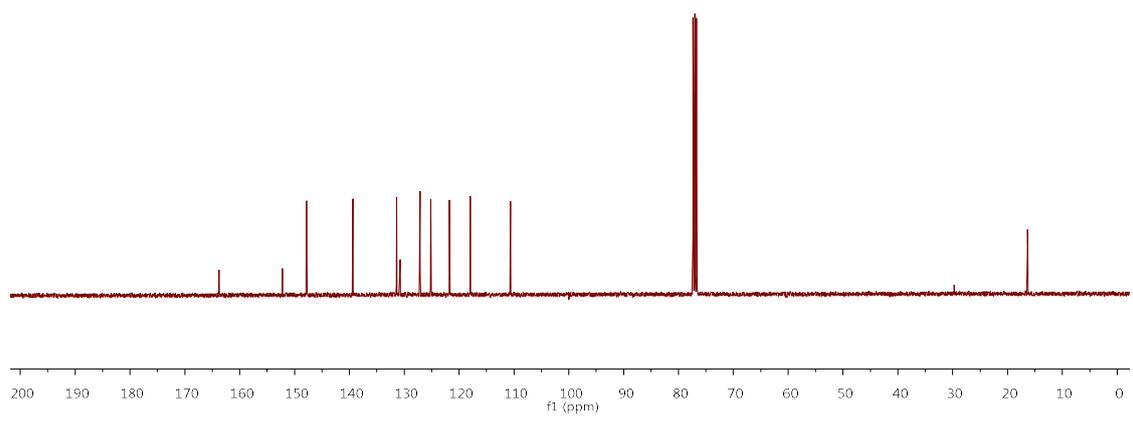


33

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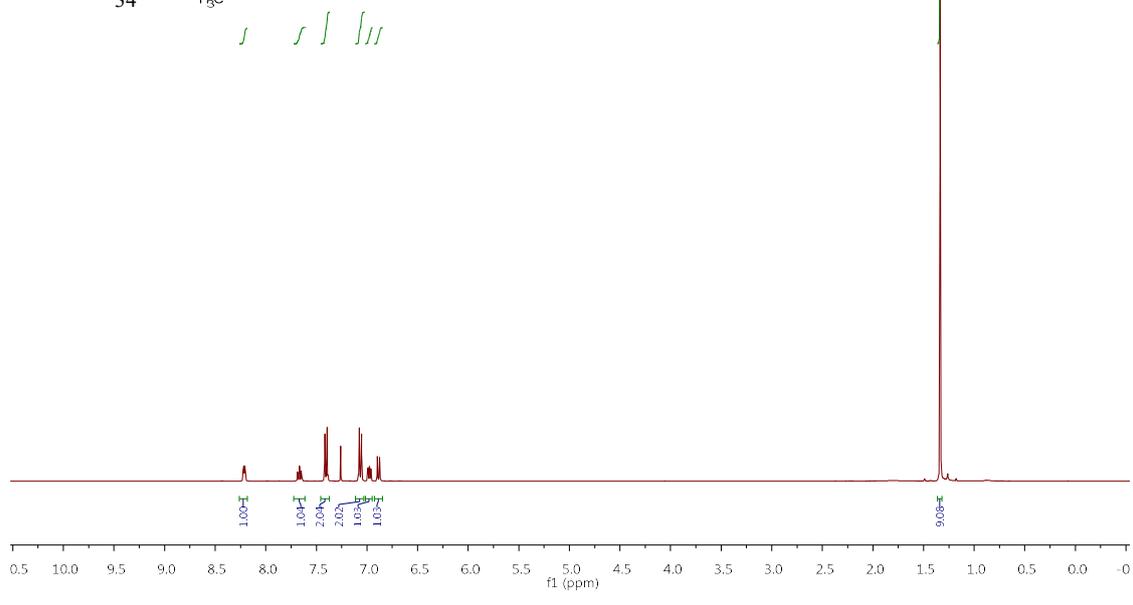
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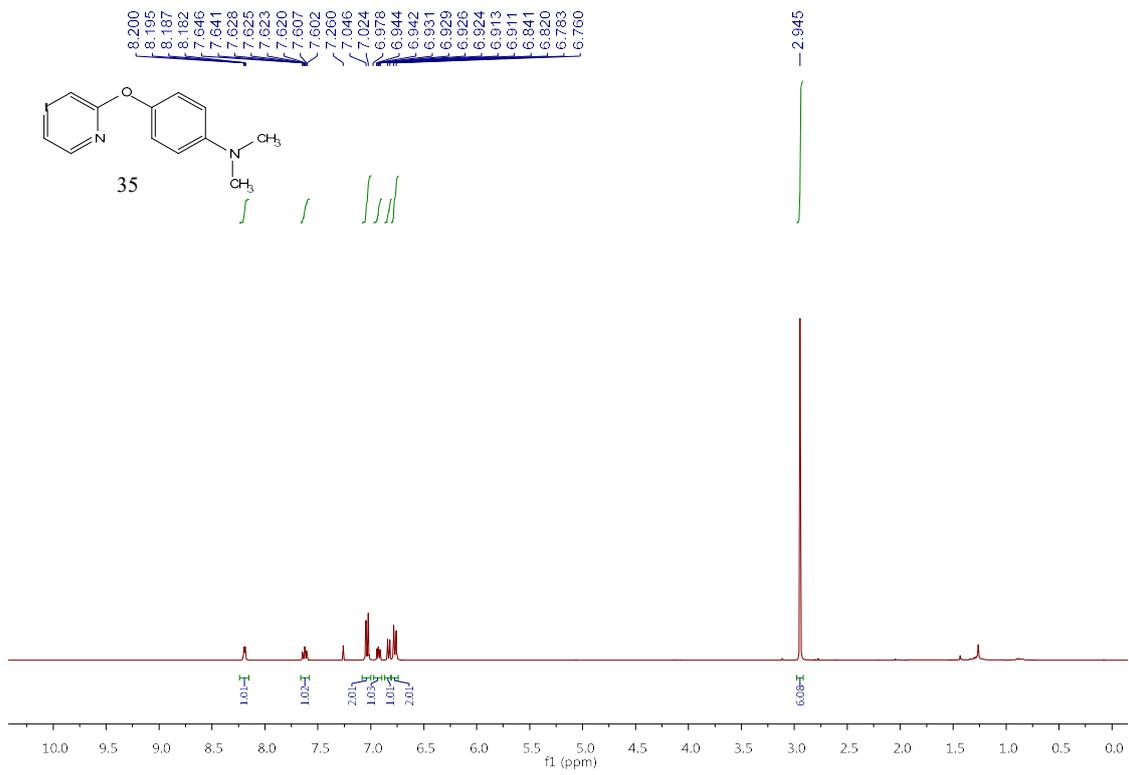
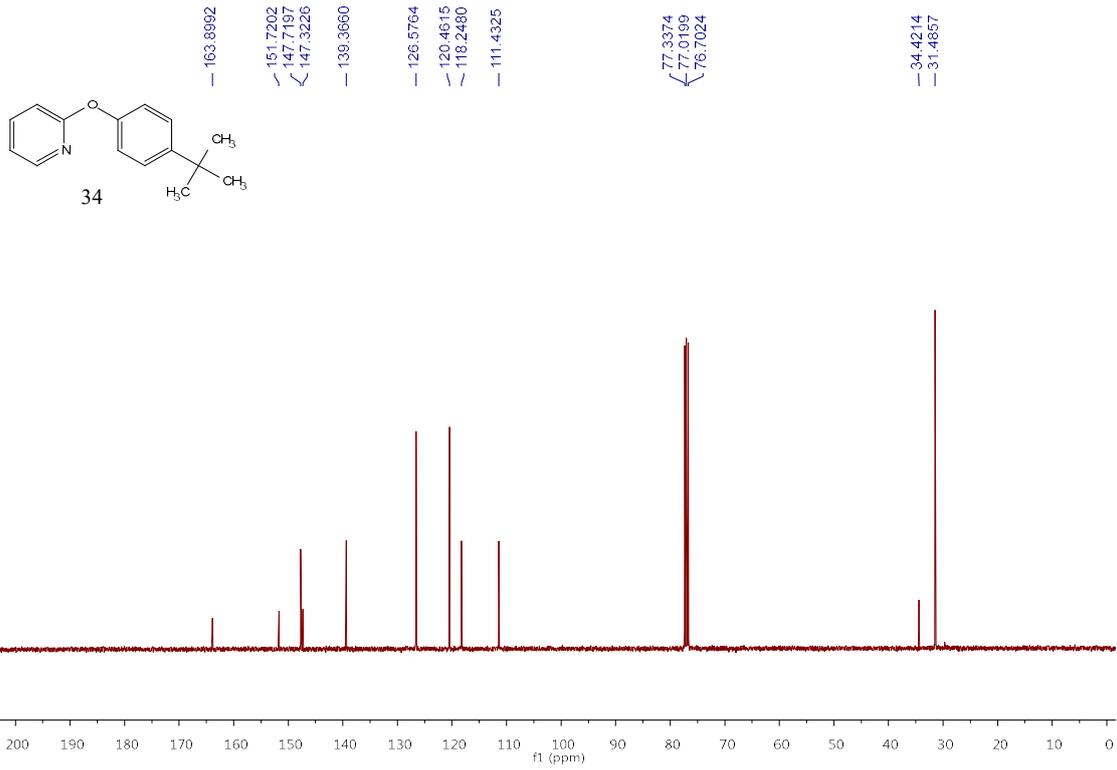


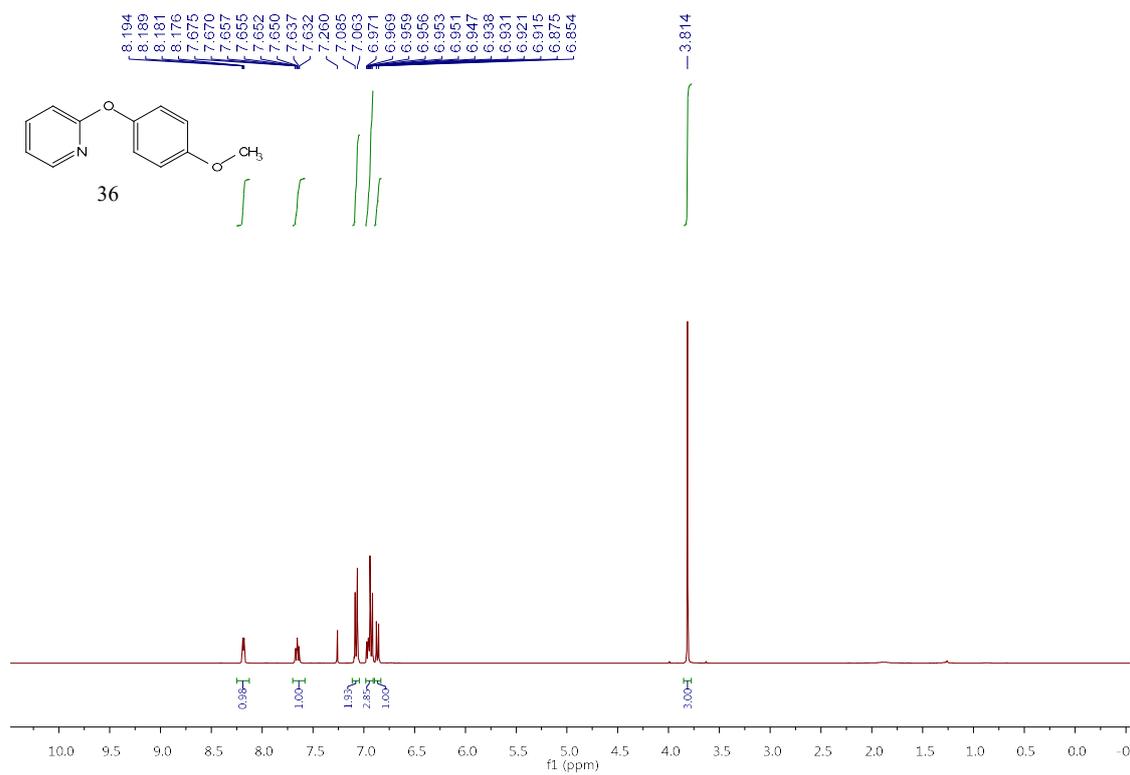
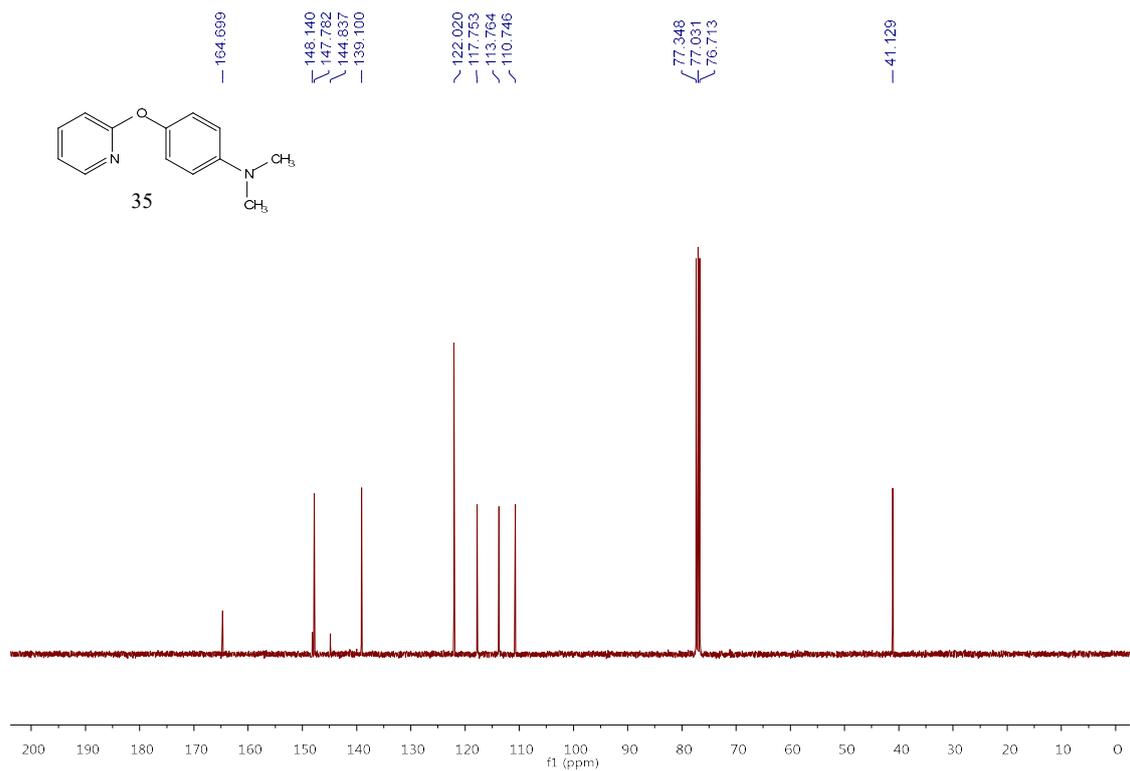
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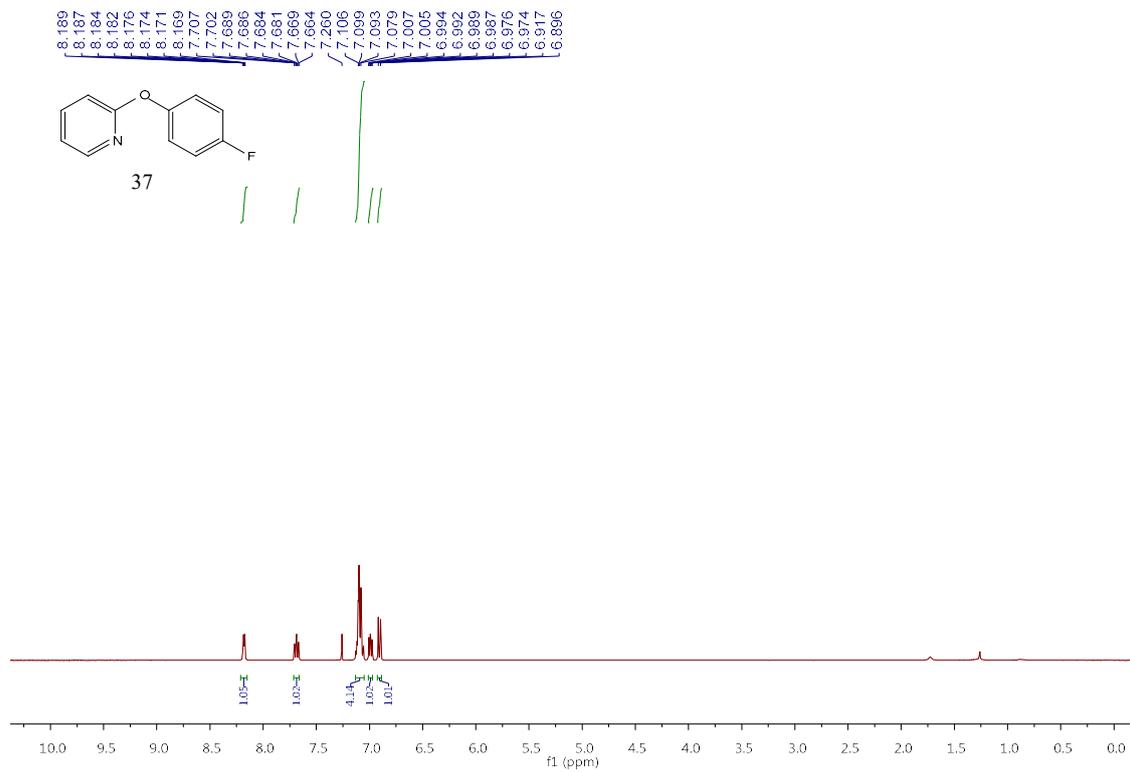
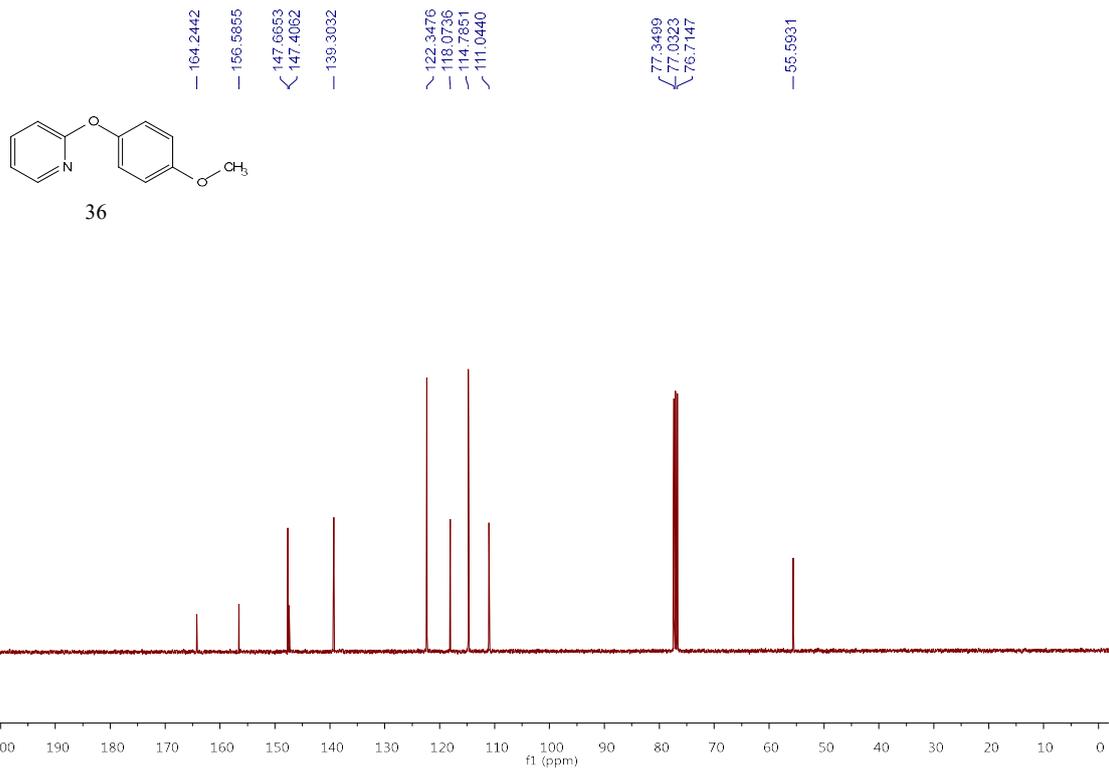
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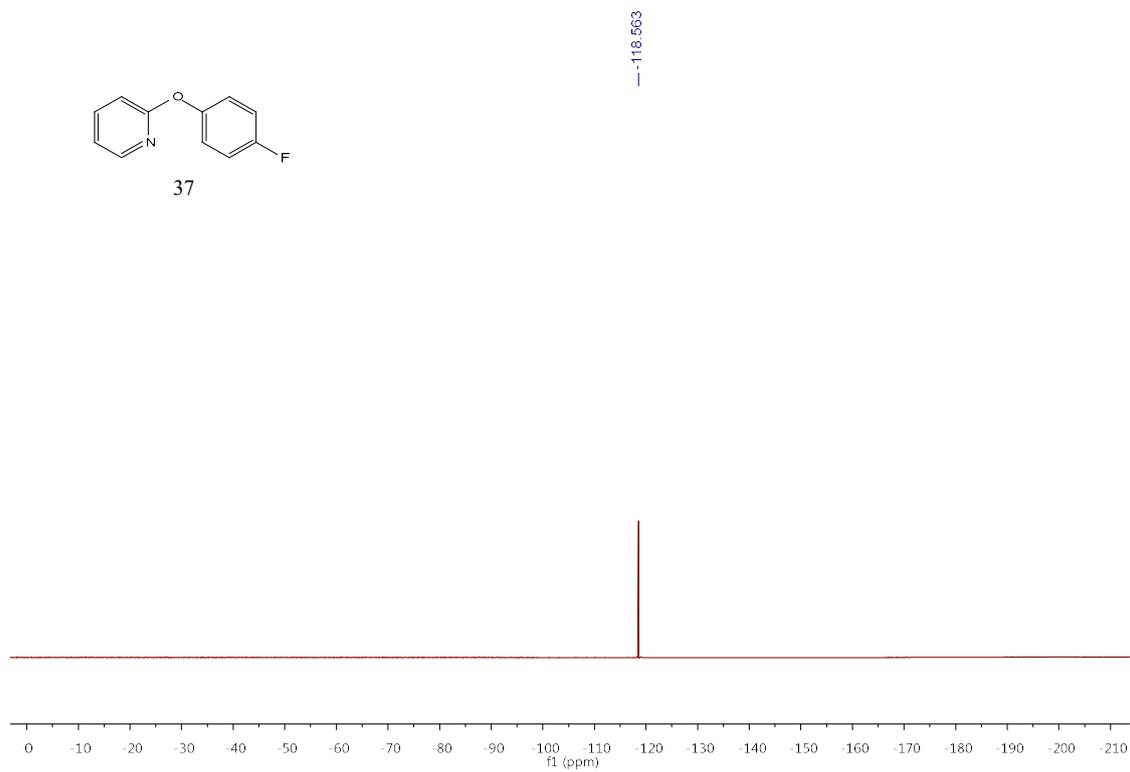
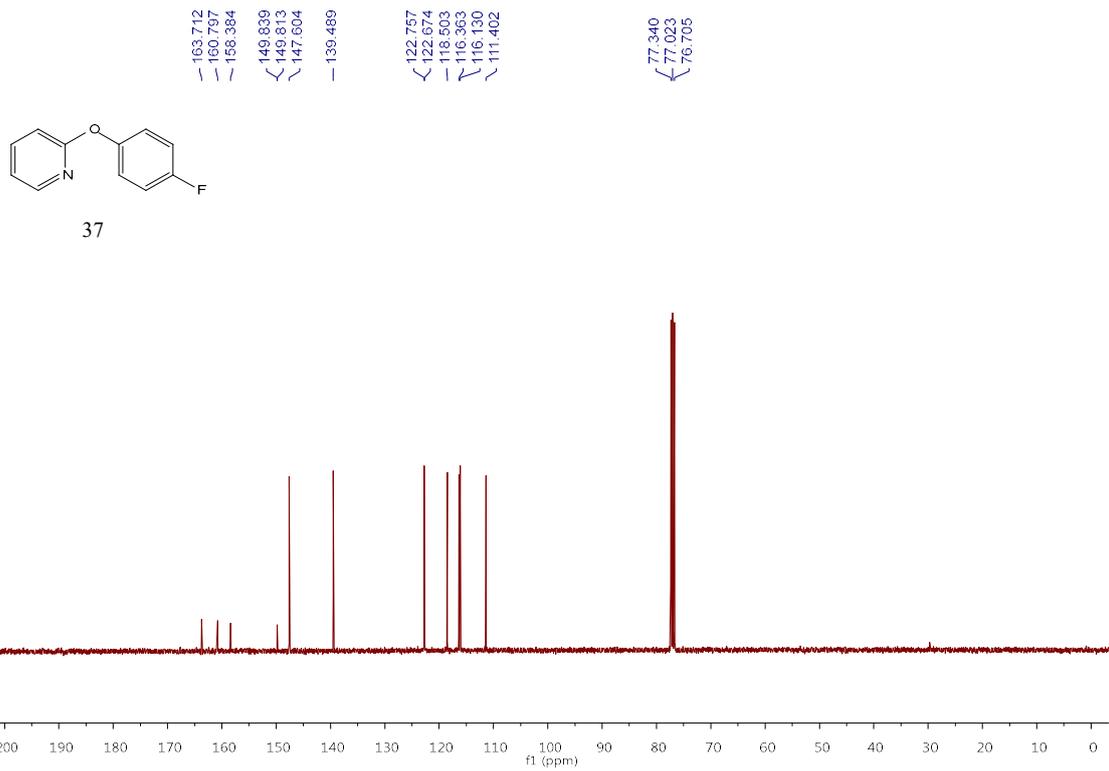
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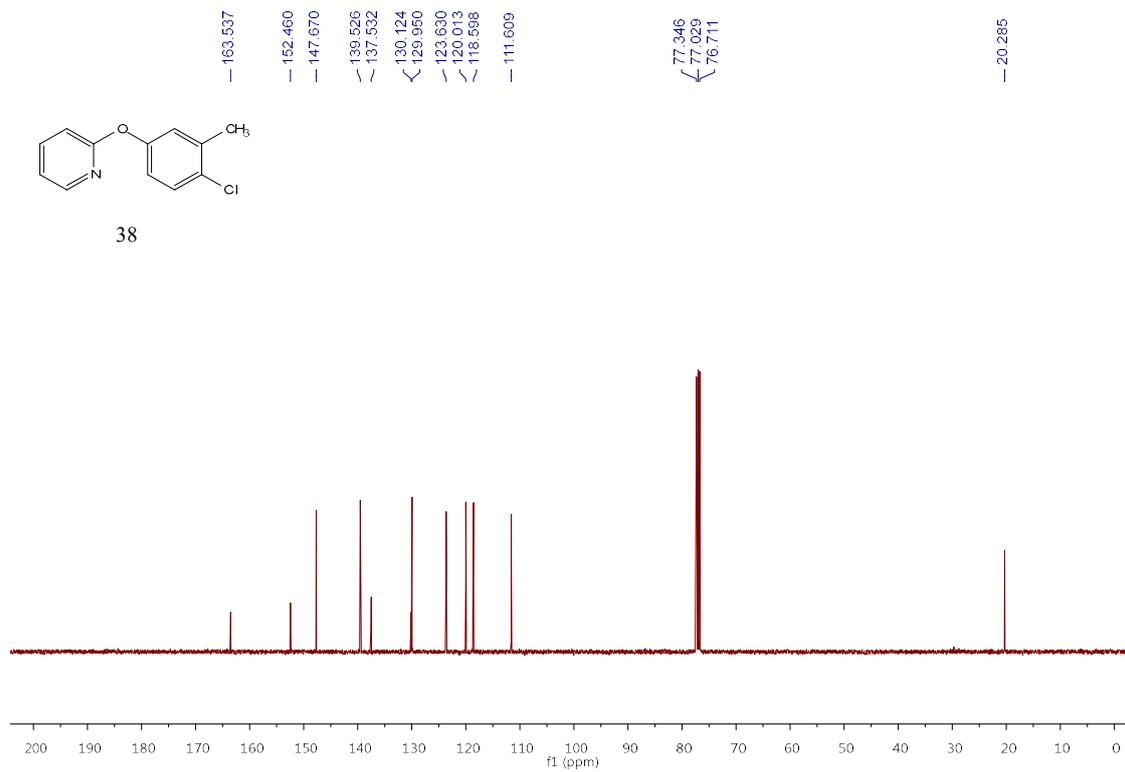
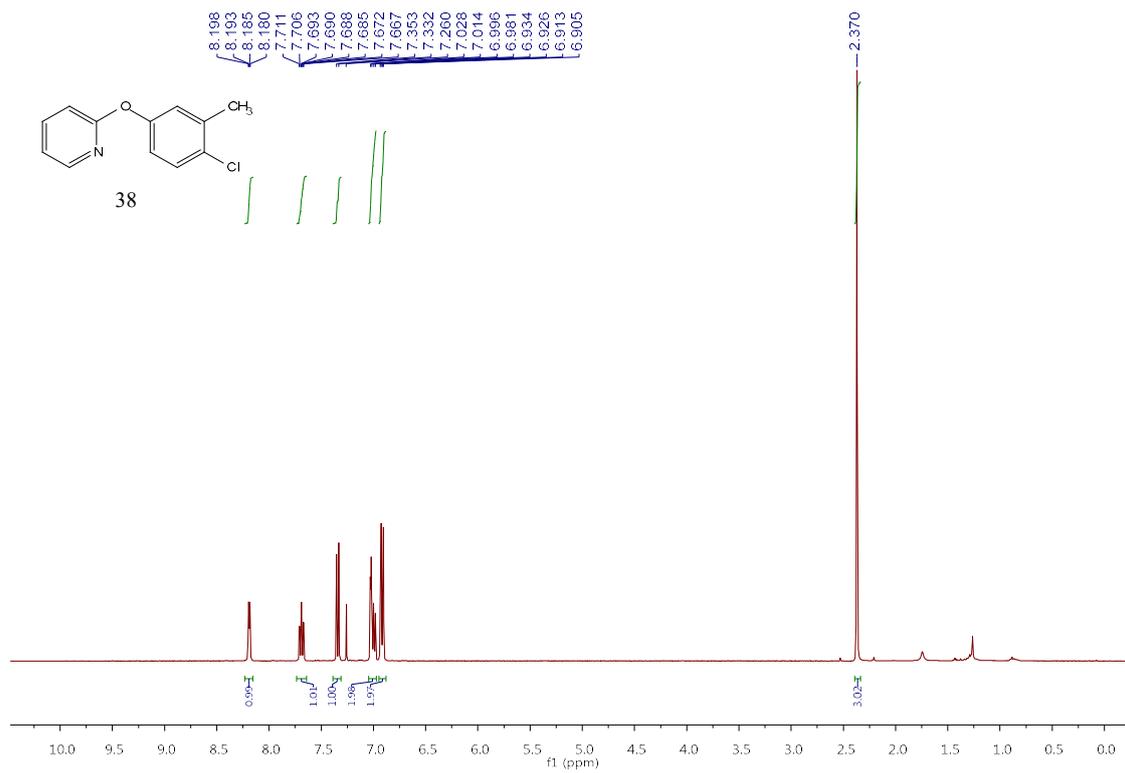


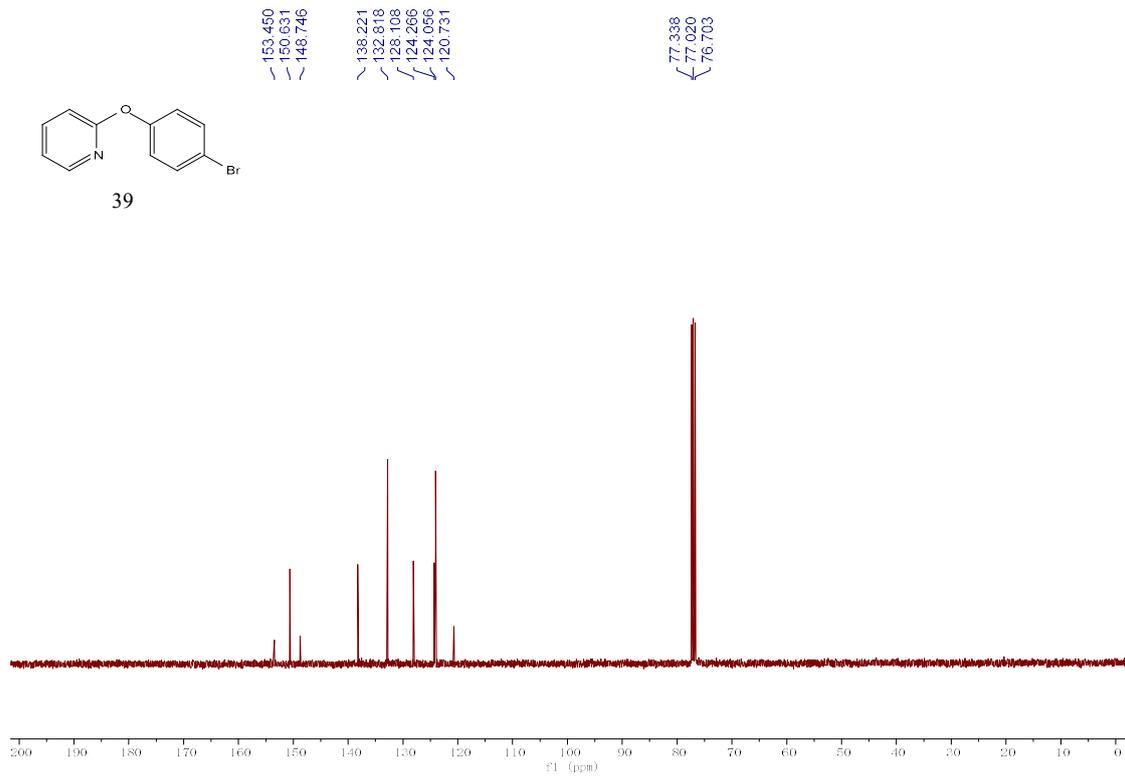
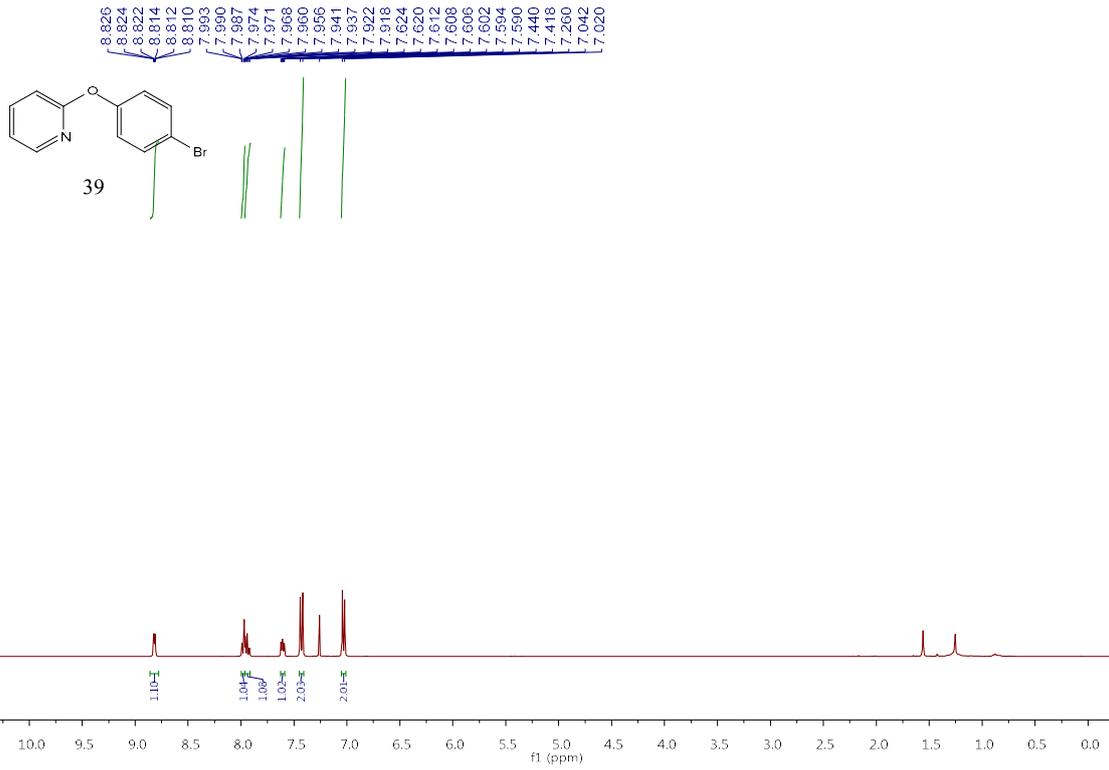


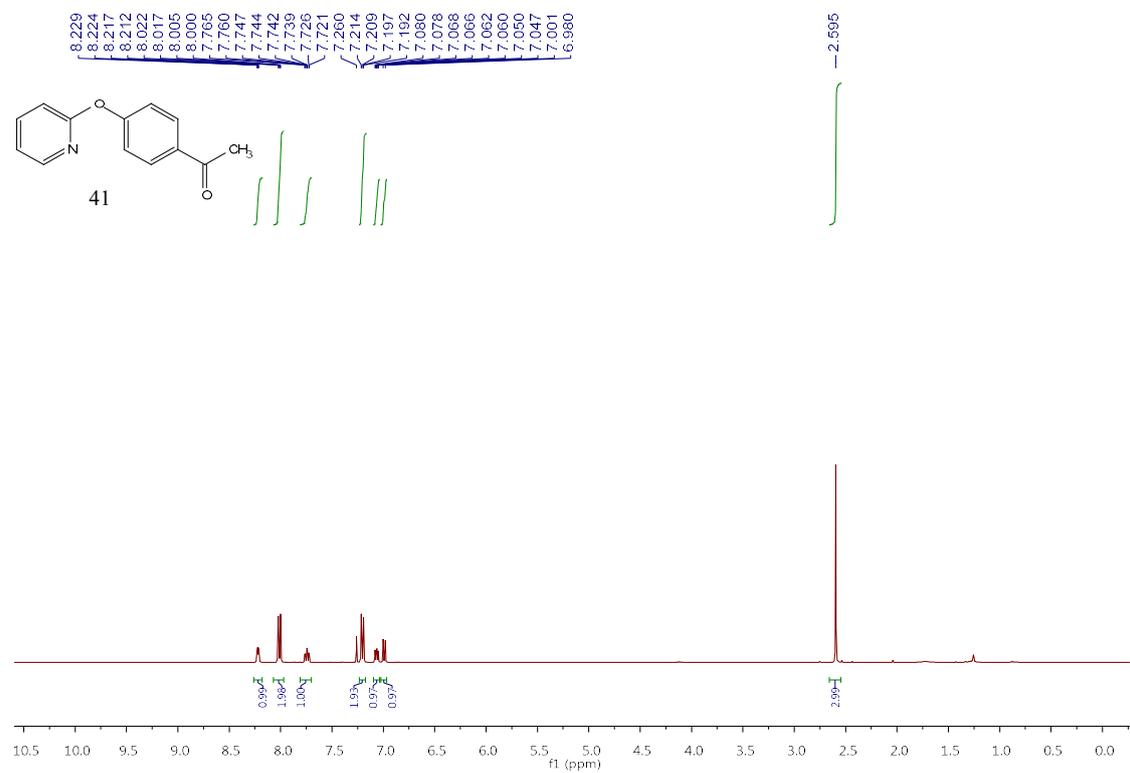
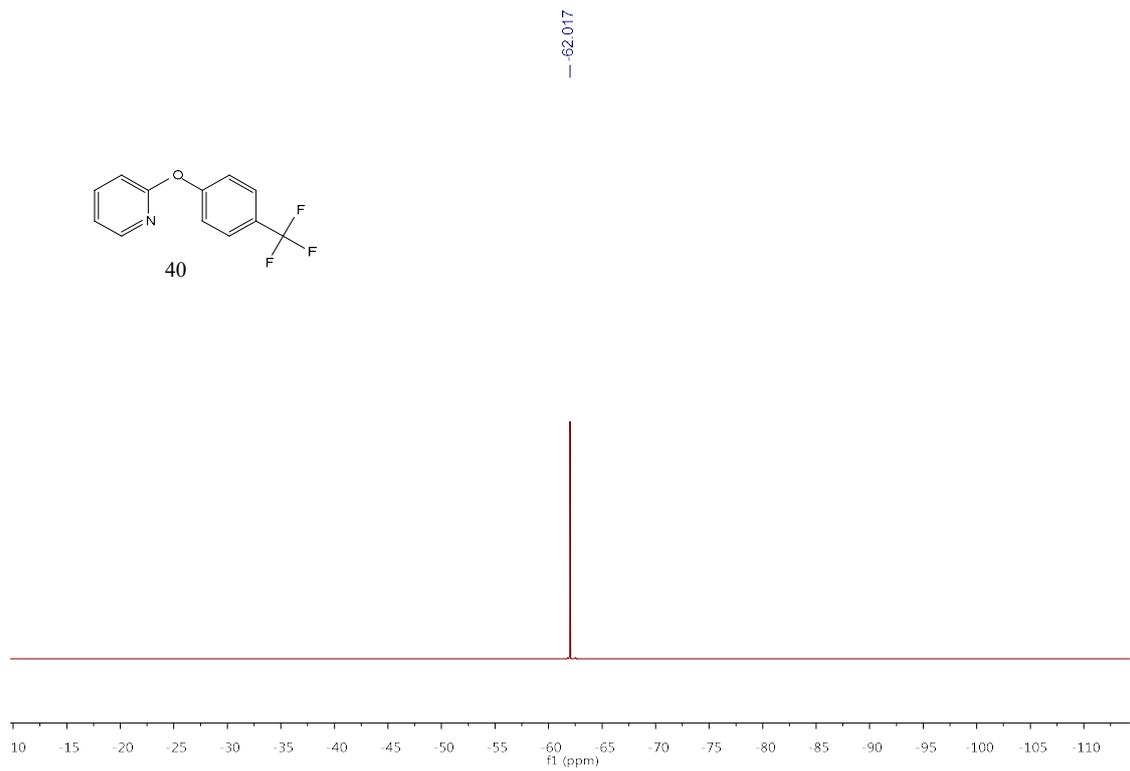


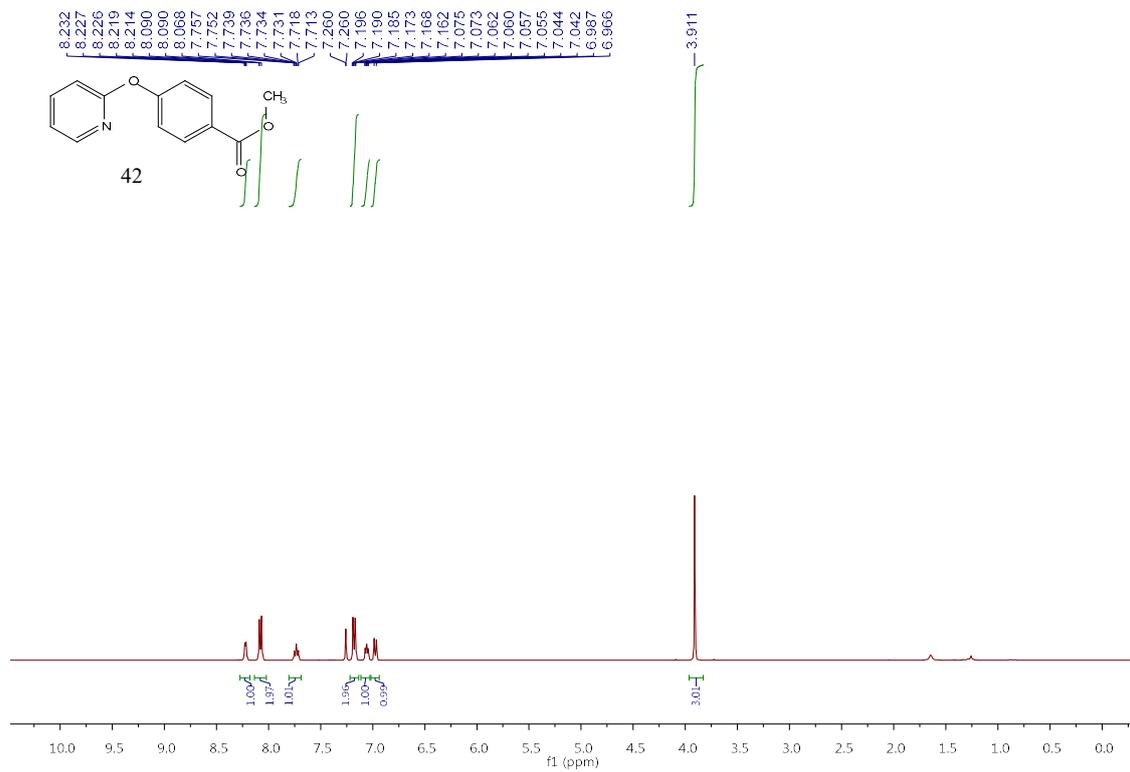
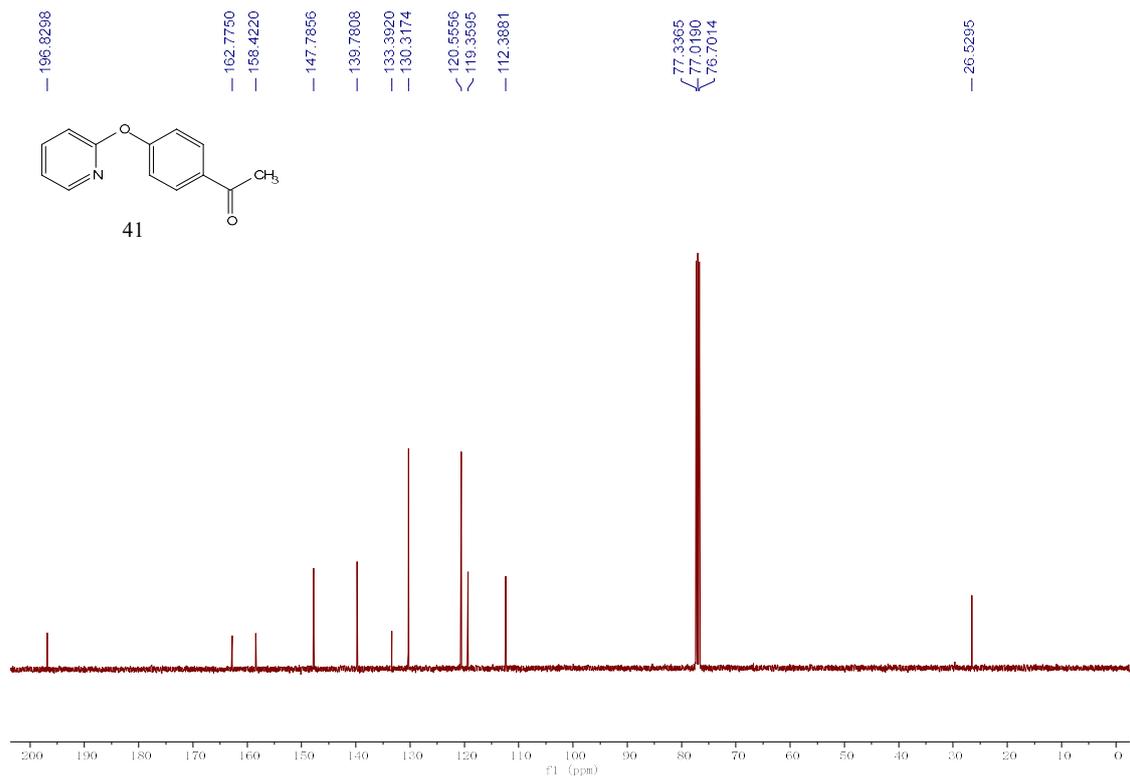


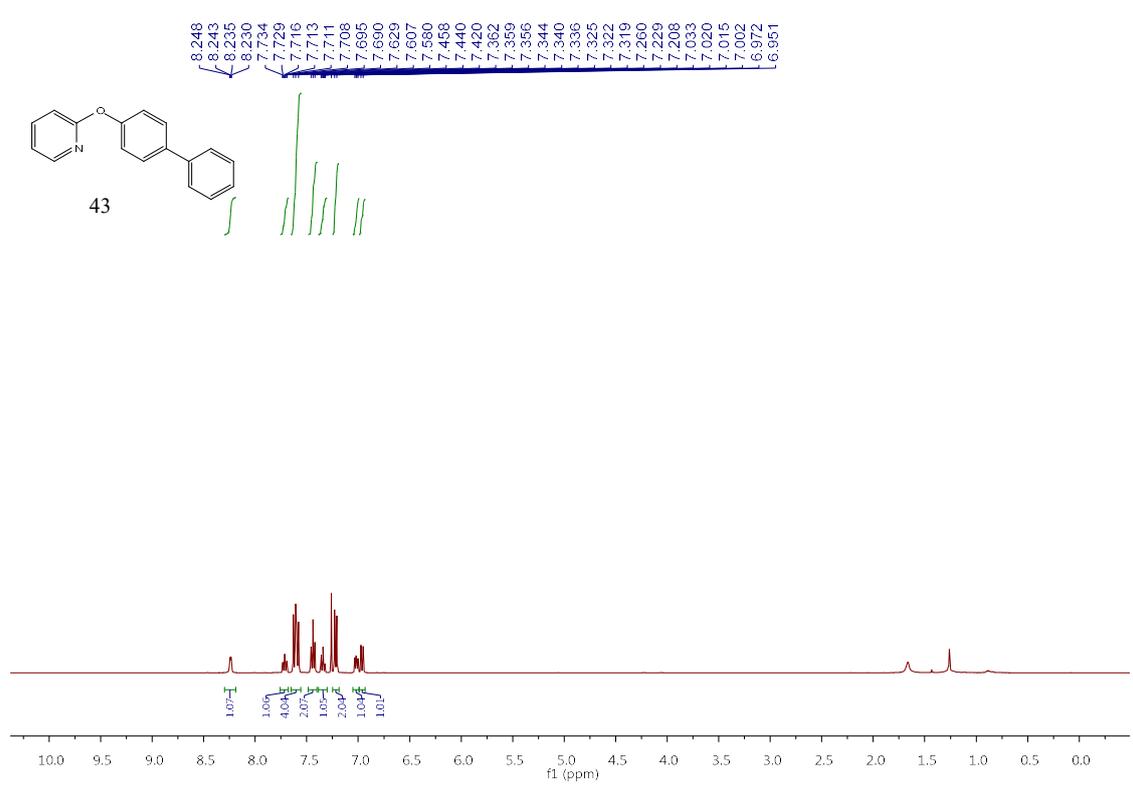
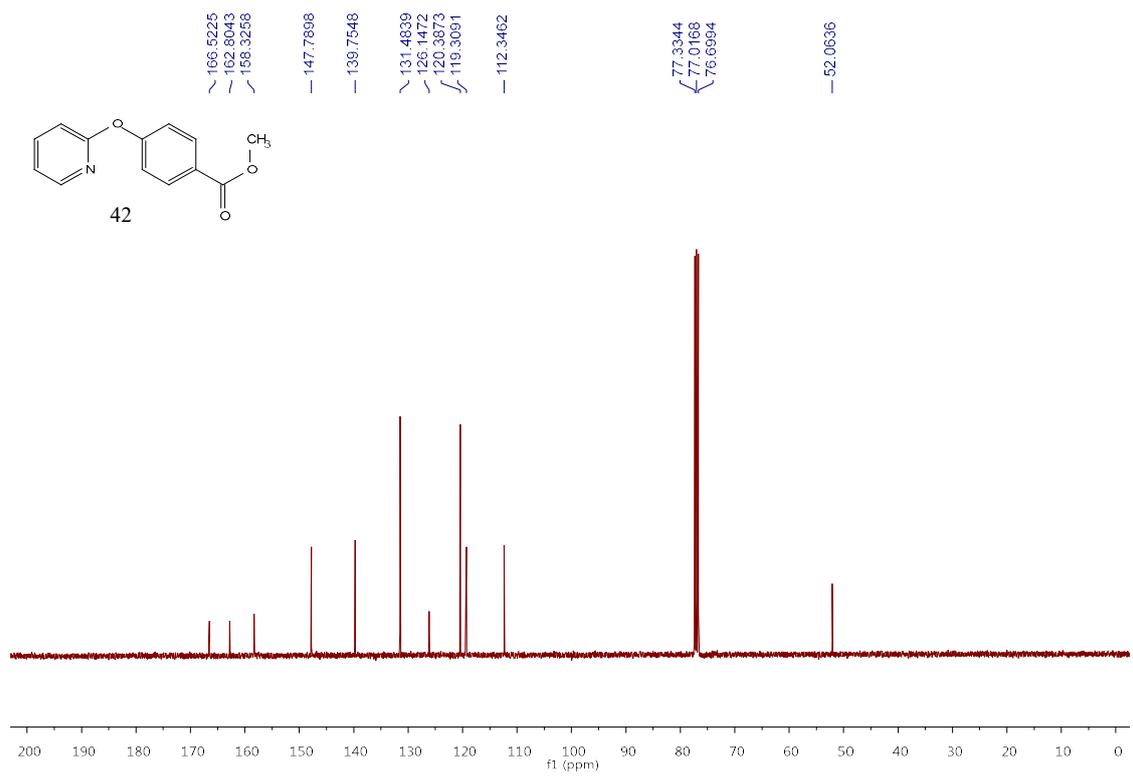


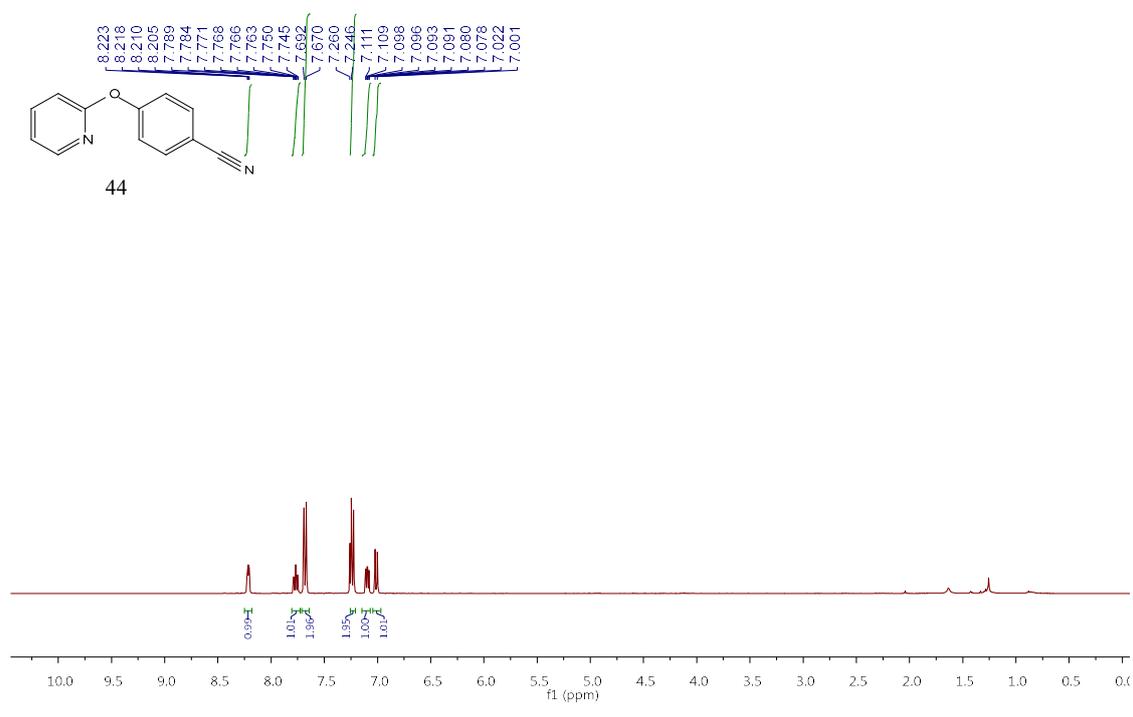
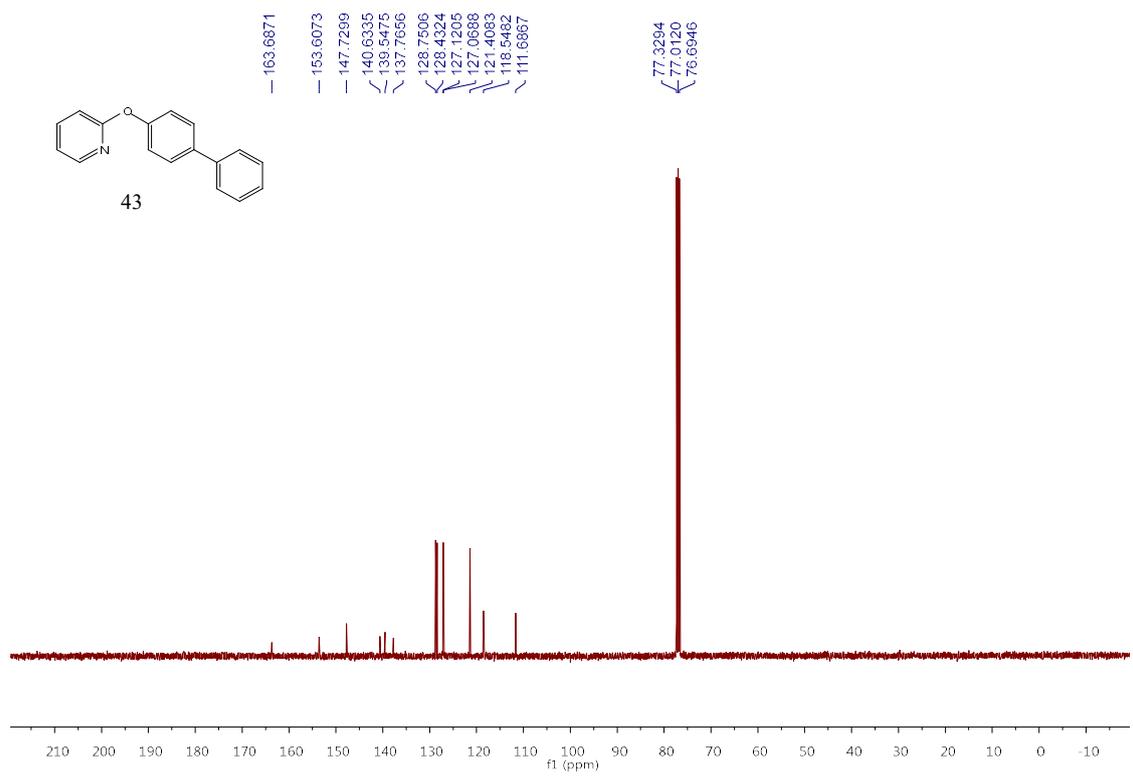


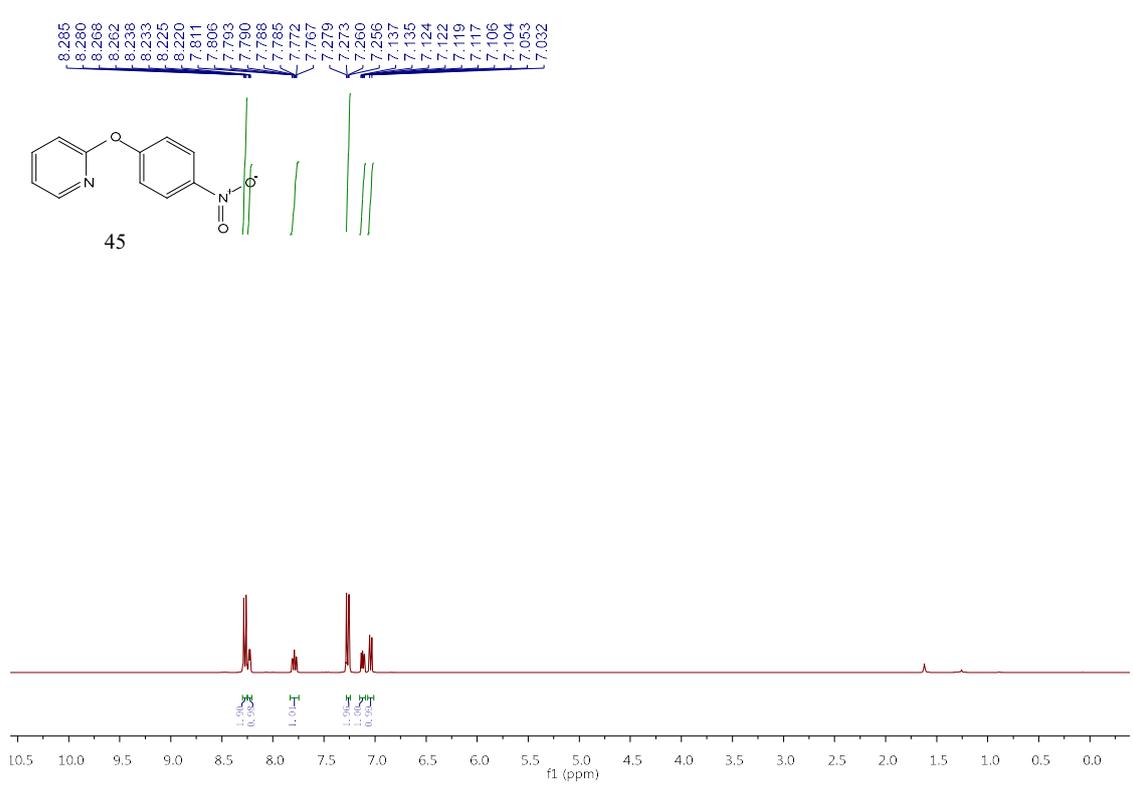
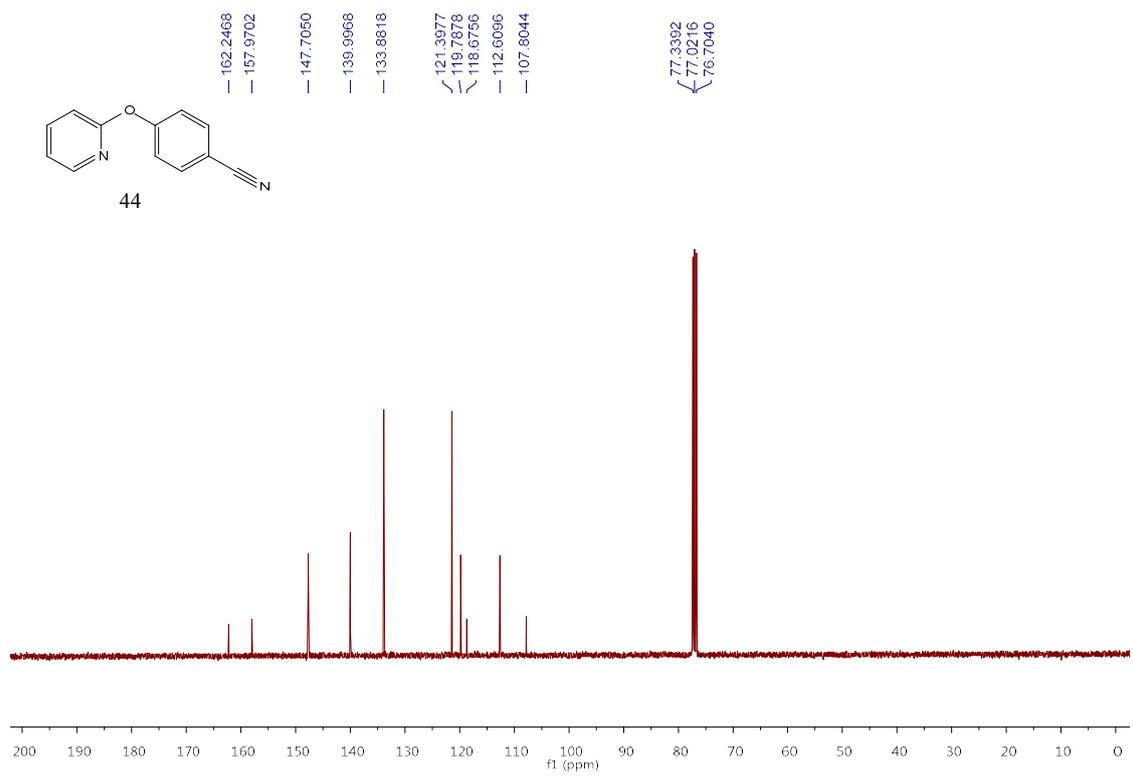


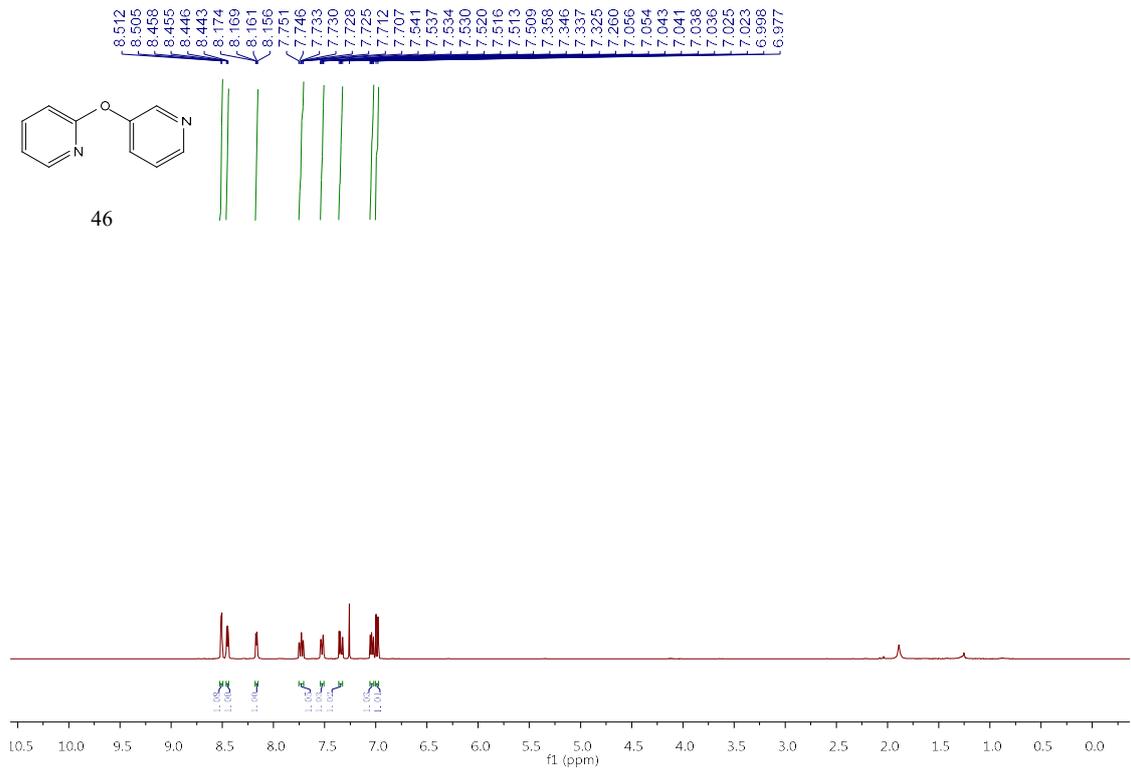
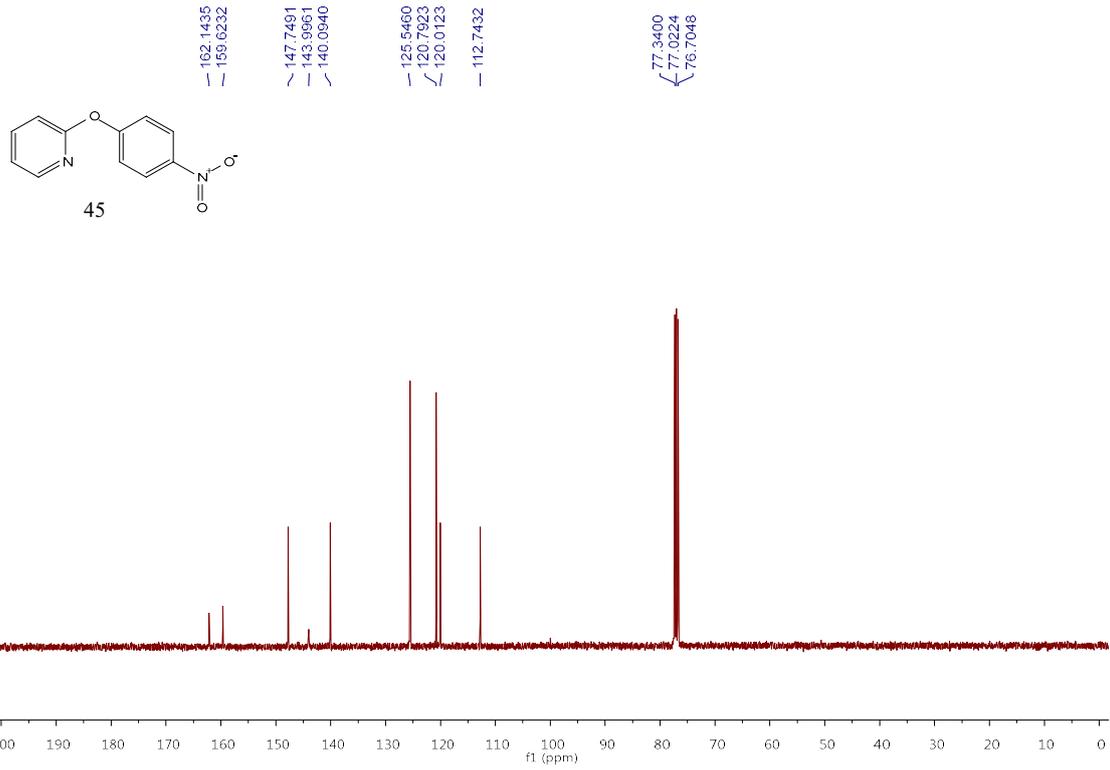


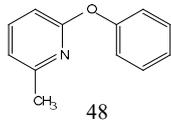












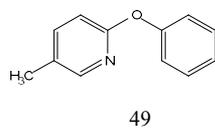
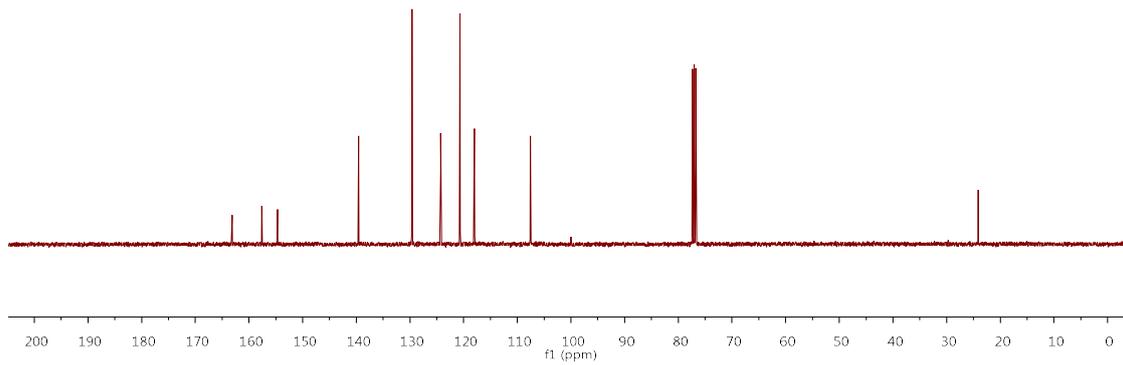
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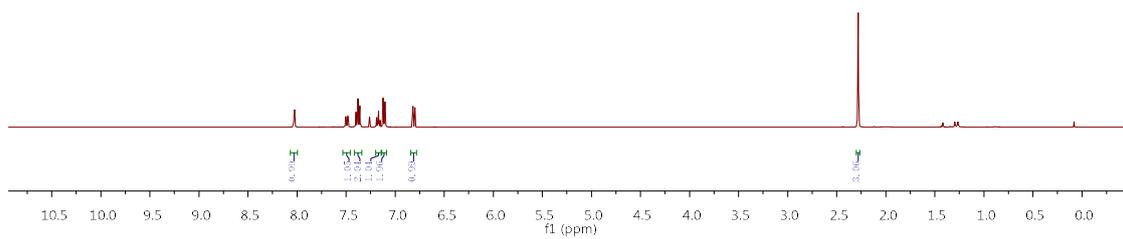
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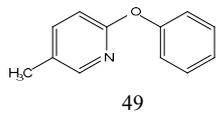
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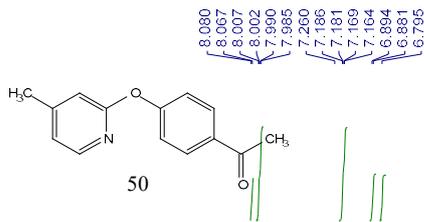
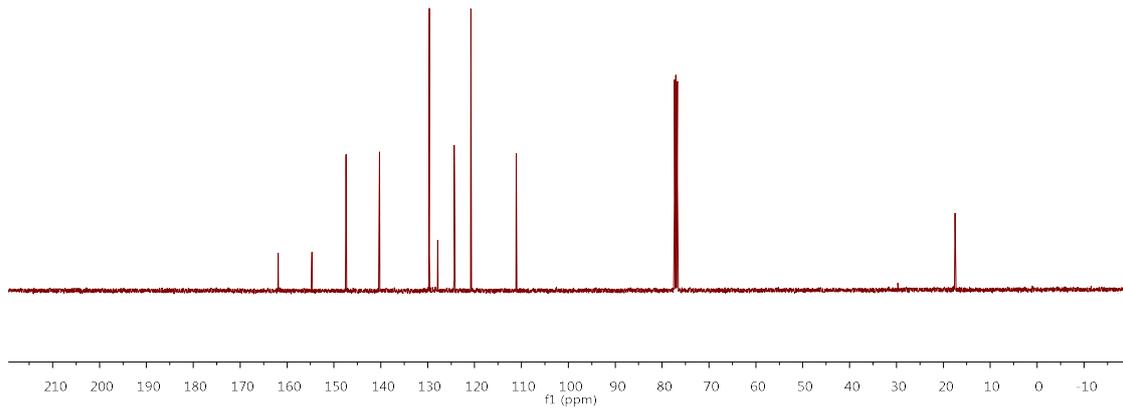




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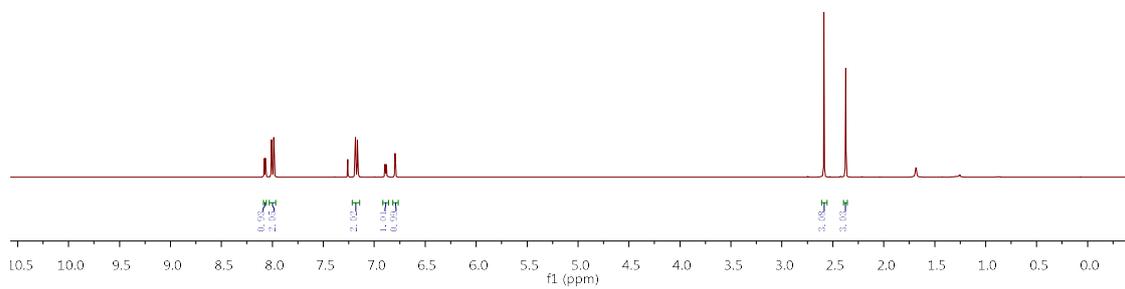
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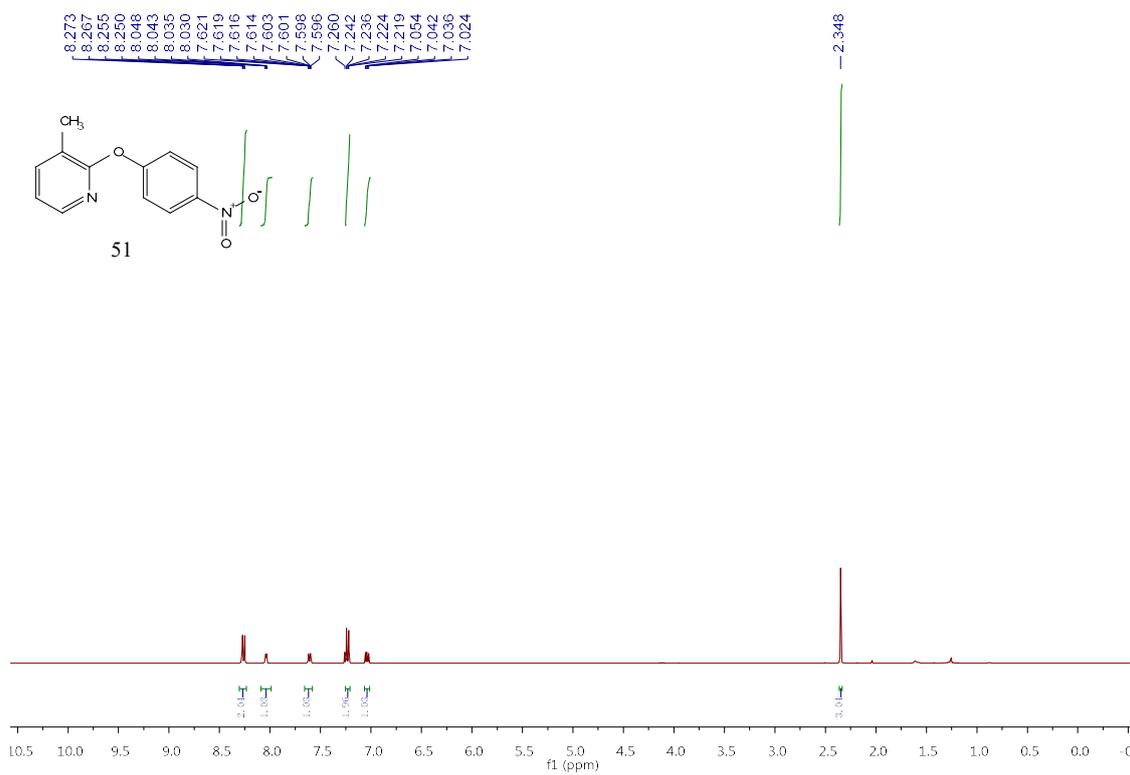
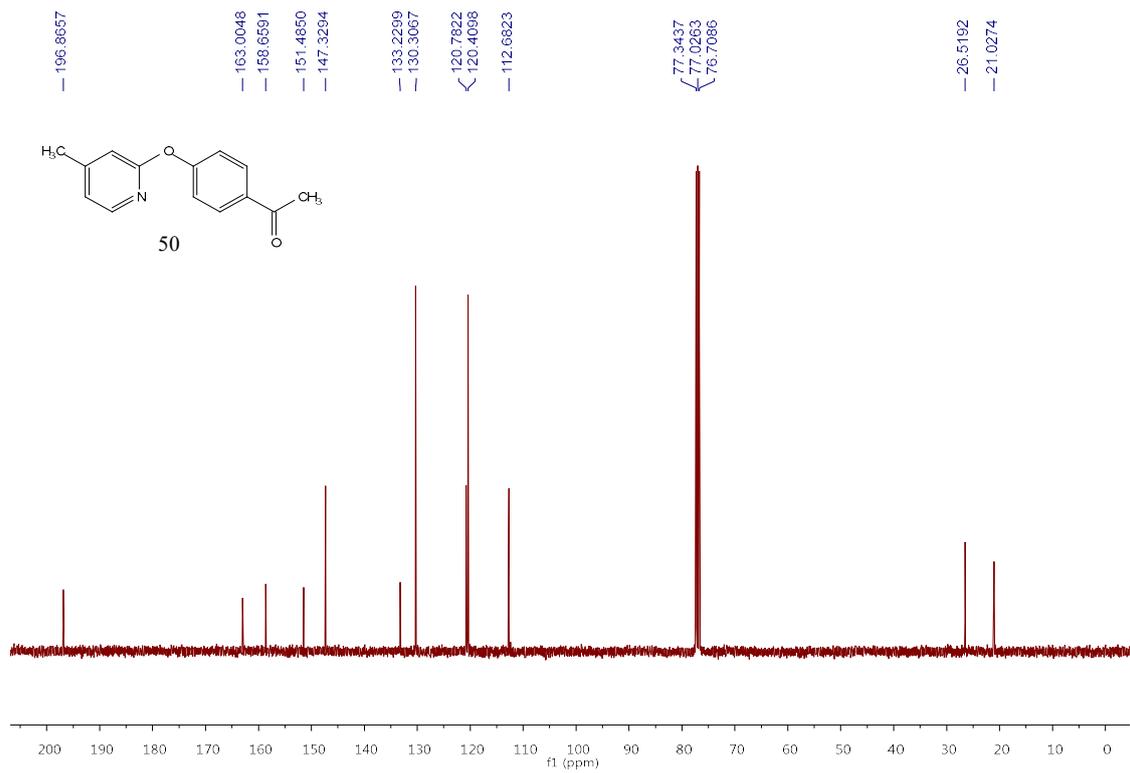
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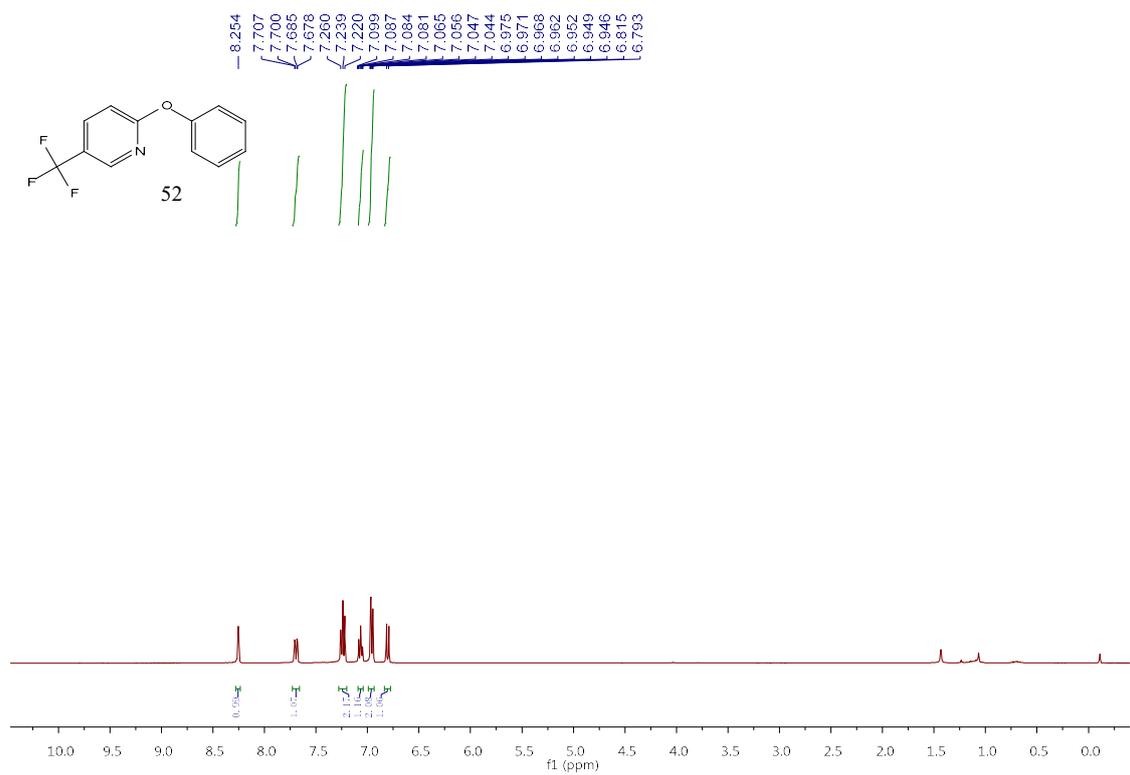
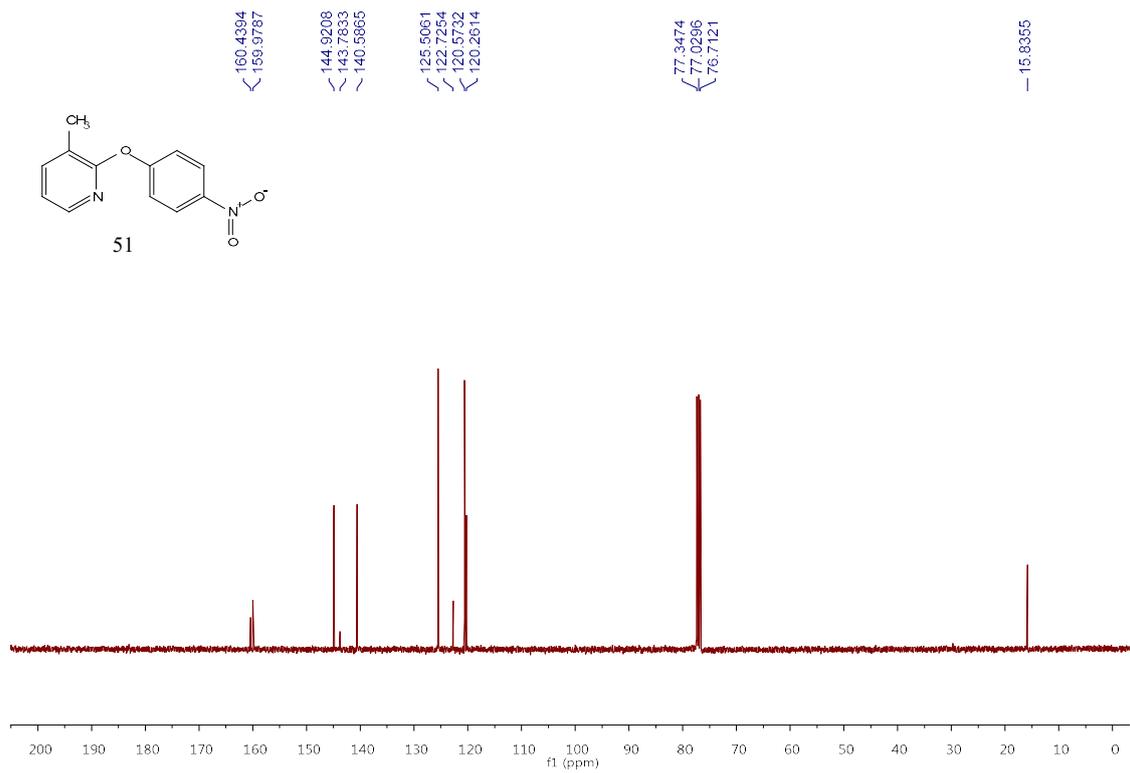


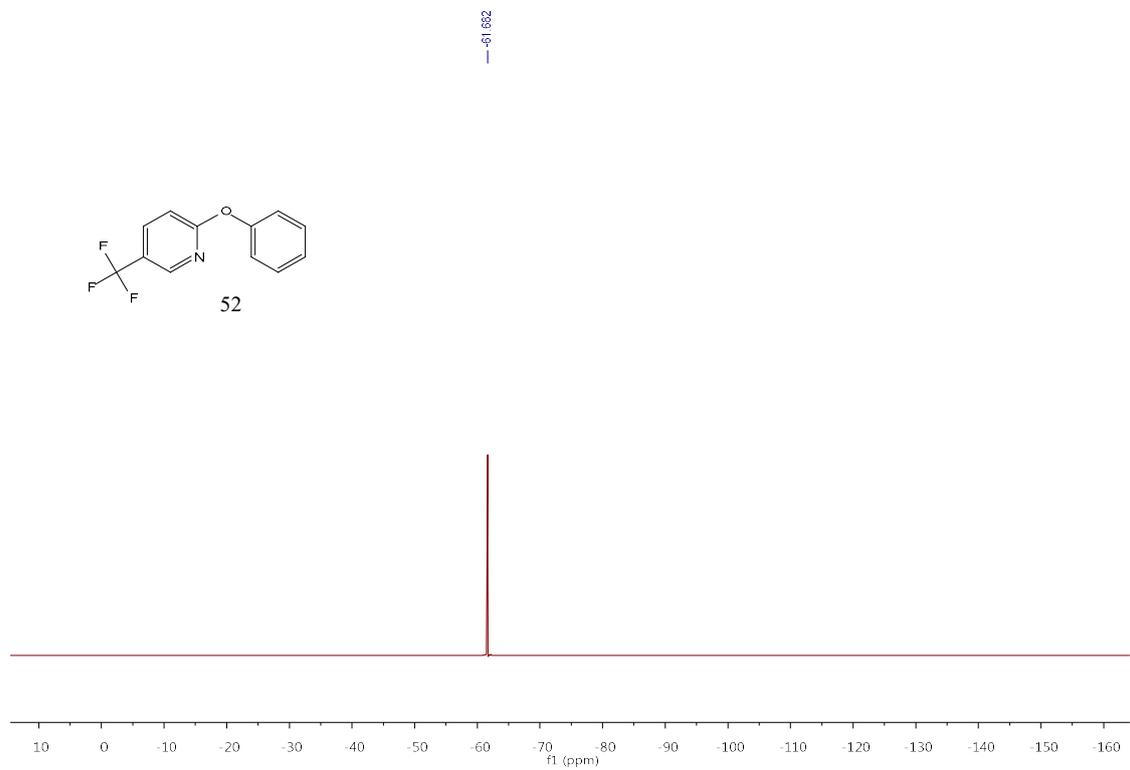
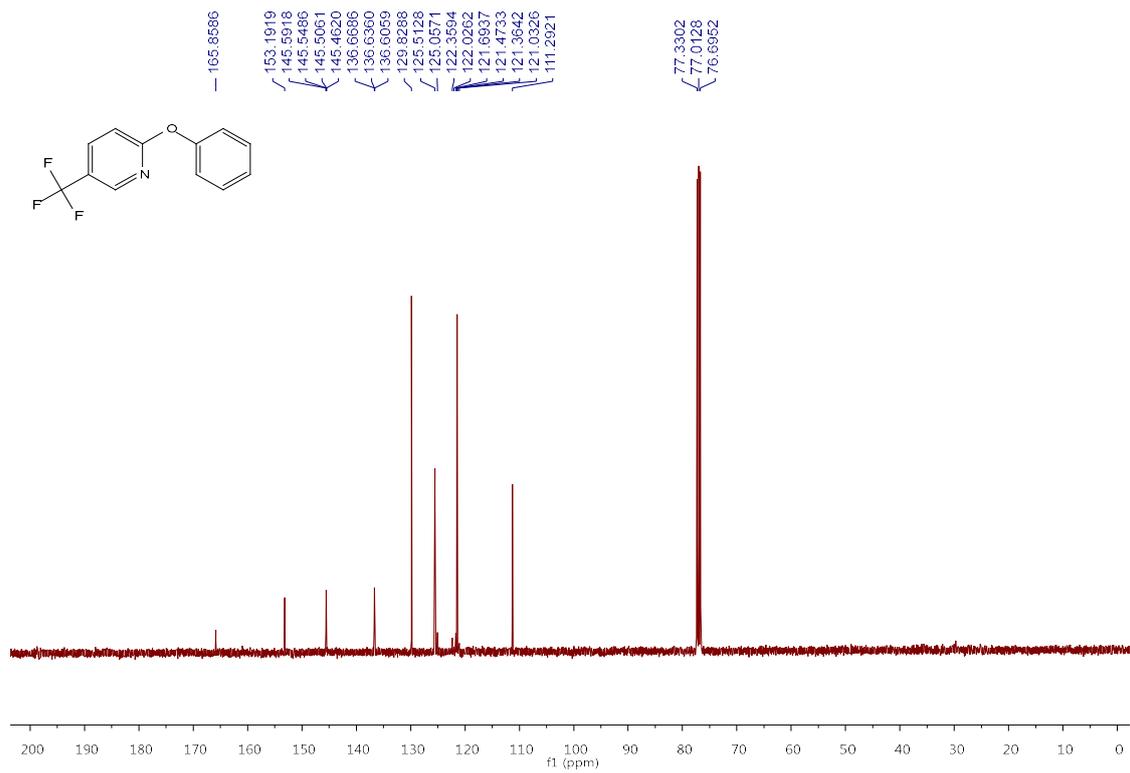
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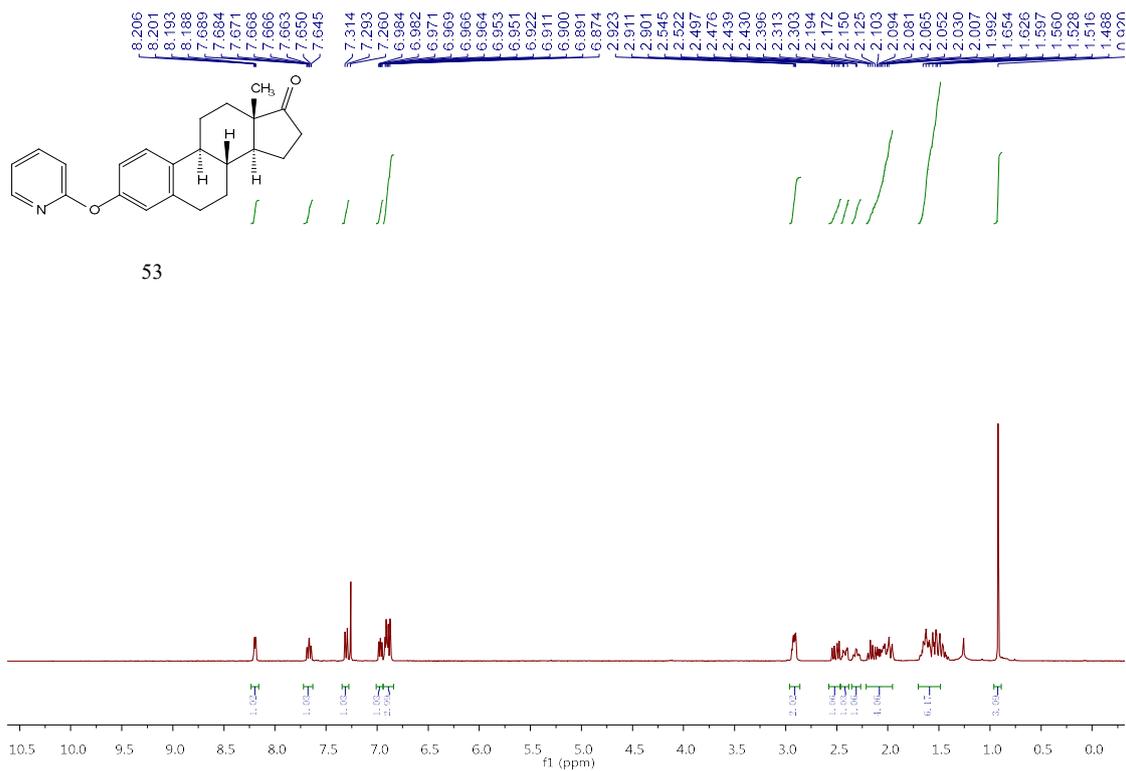
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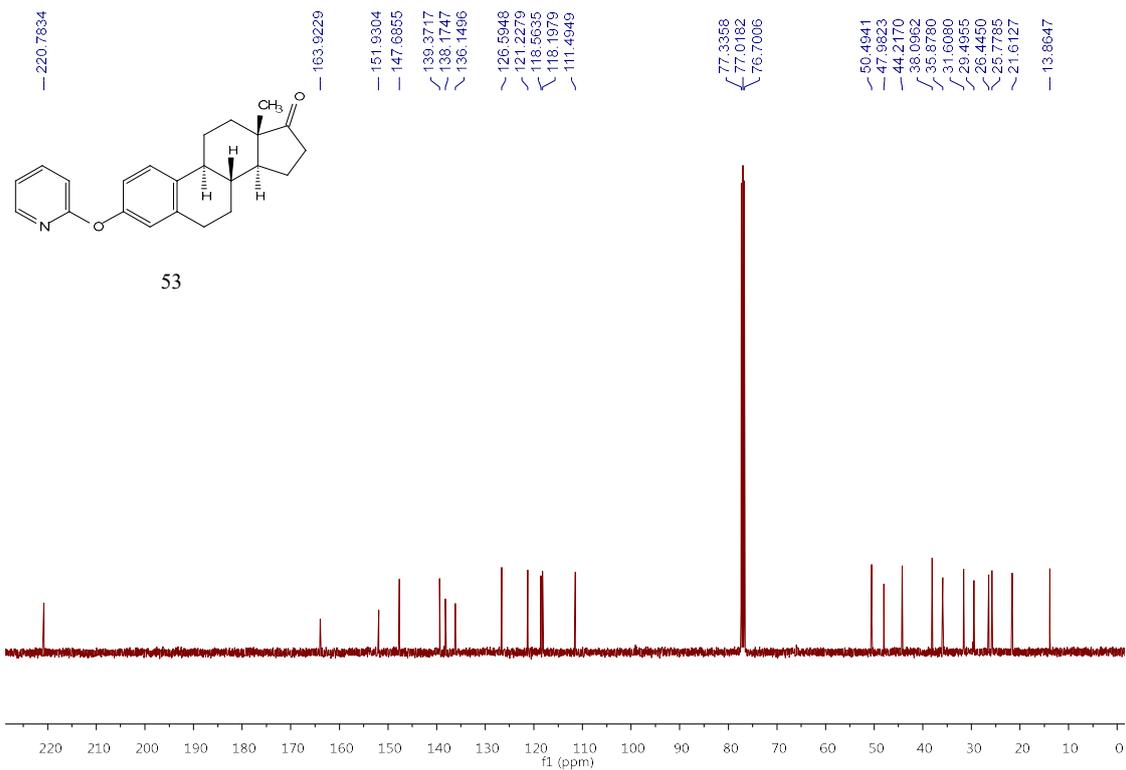








53



53

