Supporting Information

A directing group assisted ruthenium catalyzed approach to access *meta*-nitrated phenol

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1. General Consideration

Reagent Information:

Unless otherwise stated, all the reactions were carried out in screw cap reaction tubes. All the solvents were bought from Aldrich/Alfa Aesar (India)/TCI (India)/Merck in a sure-seal bottle and were used as received.

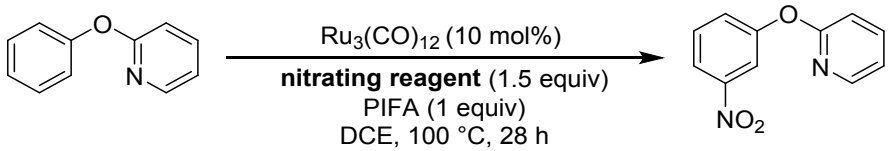
Triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$ was bought from Sigma Aldrich. Copper nitrate trihydrate, Silver trifluoroacetate were obtained from Sigma Aldrich. (Bis(trifluoroacetoxy)iodo)benzene was purchased from Ark Pharma. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254).

Analytical Information:

All isolated compounds are characterized by ^{1}H NMR, ^{13}C NMR spectroscopy. NMR spectra were recorded either on a Bruker 500 or 400 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.23 ppm), All coupling constants were reported in Hertz (Hz) and all were obtained with ^{1}H decoupling. High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer. Single crystals were diffracted in Rigaku X-ray single crystal diffractometer.

2. Optimization Details for *meta*-C–H Nitration of 2-Phenoxypyridine

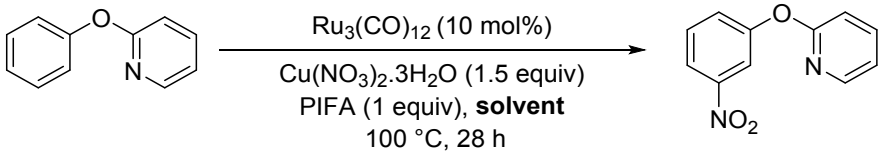
Table 1: Optimization of Nitrating Reagent



Entry	Nitrating reagent	GC yield (%)	Selectivity (*meta*:*others*)
1	$AgNO_3$	12	2:1
2	$NaNO_3$	10	1:1
3	$NaNO_2$	14	1:1
4	$AgNO_2$	10	*ortho*
5	^{t}BuONO	12	2:1

6	$Bi(NO_3)_3.5H_2O$	14	2:1
7	$Ni(NO_3)_2.6H_2O$	18	3:1
8	KNO_3	-	-
9	$La(NO_3)_3.H_2O$	14	2:1
10	**$Cu(NO_3)_2.3H_2O$**	**27**	**3:1**

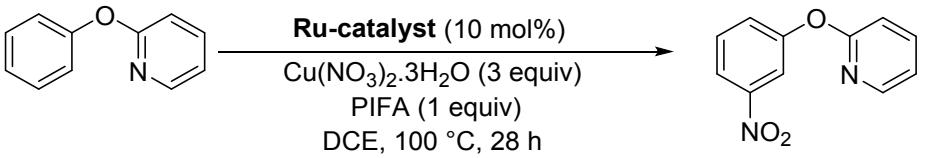
Table 2. Optimization of Solvent



Entry	Solvent	GC Yield (%)	Selectivity (*meta*:*others*)
1	DCM	18	3:1
2	THF	10	1:1
3	1,4 dioxane	-	-
4	Toluene	8	1:2
5	DMF	24	1:1
6	*m*-xylene	21	3:1
7	Acetonitrile	23	1:1
8	DMA	12	3:1
9	**DCE**	**27**	**3:1**
10	Benzene	8	2:1
11	Chlorobenzene	14	1:3
13	DMSO	24	1:1
14	TBME	-	-

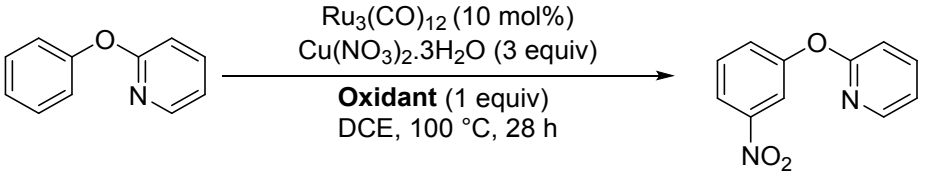
15	2-Me-THF	-	-
16	MeOH	10	1:1
17	HFIP	-	-
18	TFT	26	1:1

Table 3. Optimization of Ru-catalyst



Sr. No.	Ru-catalyst	GC yield (%)	Selectivity (*meta*:*others*)
1	$RuCl_3$	18	2:1
2	**$Ru_3(CO)_{12}$**	**64**	**3:1**
3	$Ru[(p\text{-cymene})Cl_2]_2$	20	2:1
4	$Ru(acac)_3$	-	-

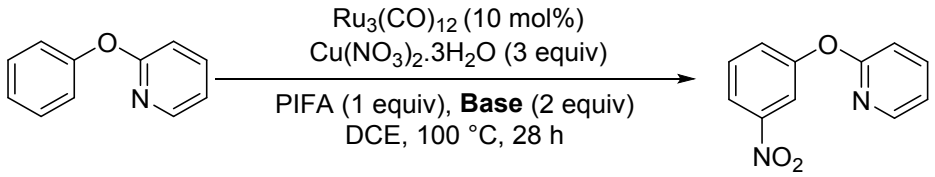
Table 4. Optimization of Oxidant



Sr. No.	Oxidant	GC yield (%)	Selectivity (*meta*:*others*)
1	**PIFA**	**64**	**3:1**
2	$PhI(OAc)_2$	6	1:2
3	$K_2S_2O_8$	54	1:2
4	Oxone	37	1:2
5	$Cu(OAc)_2$	28	1:1
6	BQ	13	1:2

7	TBHP	-	-
8	Selectfluor	30	1:2
9	Ag_2CO_3	20	*ortho*
10	AgTFA	10	1:1
11	CuO	10	1:1

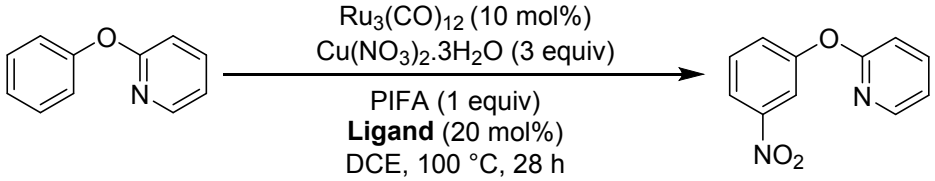
Table 5. Optimization of Base



Sr. No.	Base	GC yield (%)	Selectivity (*meta*:*others*)
1	Na_2CO_3	10	*ortho*
2	K_2CO_3	13	*ortho*
3	Li_2CO_3	8	*ortho*
4	$NaHCO_3$	20	2:1
5	$KHCO_3$	18	2:1
6	NaOAc	20	1:1
7	Cs_2CO_3	13	*ortho*
8	NaTFA	20	*ortho*
9	NaOTf	16	*ortho*
10	KO^tBu	10	*ortho*
11	K_3PO_4	14	*ortho*
12	NaOH	25	*ortho*
13	Na_2HPO_4	20	1:1
14	K_2HPO_4	24	1:1

15	NaOPiv	65	2:1
16	KOAc	45	2:1
17	NaH_2PO_4	55	2:1
18	KH_2PO_4	60	2:1
19	DABCO	-	-
20	DBU	-	-
21	Et_3N	25	2:1

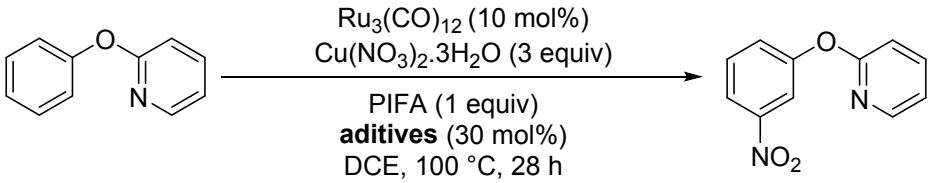
Table 6. Optimization of Ligand



Sr. No.	Ligand	GC yield (%)	Selectivity (*meta*:*others*)
1	DMAP	39	1:1
2	L-proline	44	1:1
3	L-alanine	37	2:1
4	L-valine	40	3:1
5	Boc–Leucine-OH	52	3:1
6	FMOC–L-alanine	24	2:1
7	N–Acetyl L-valine	42	2:1
8	2–L-alanine	40	2:1
9	N–Formyl glycine	56	2:1
10	N–Boc-glycine	40	2:1
11	N–Acetyl glycine	50	3:1
12	(S) – Xyl Phos	50	3:1

13	7-Chloro quinaldine	11	*meta*
14	Tris[2-(diphenyl phosphino)ethyl]phosphine	60	2:1
15	Cyclohexyl JohnPhos	30	3:1
16	DPE Phos	10	*ortho*
17	Me Phos	22	2:1
18	Tris(2,4,6-trimethoxy phenyl) phosphine	42	2:1
19	S-Phos	20	3.5:1

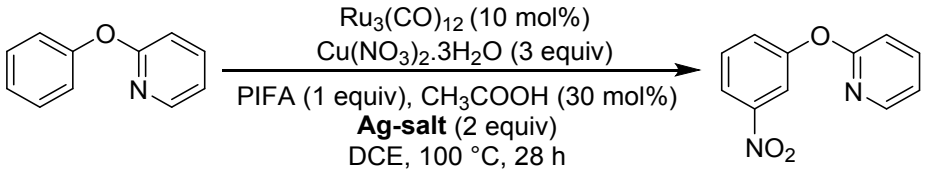
Table 7. Optimization of Additive



Sr. No.	Addidives	GC yield (%)	Selectivity (*meta*: *others*)
1	Piv-OH	48	2:1
2	Ad-COOH	60	2:1
3	Mes-COOH	40	1:1
4	Benzoic acid	37	1:1
5	**Acetic acid**	**70**	**3:1**
6	Trifluoromethyl acetic acid	60	2:1
7	2-Methylbutanoic acid	24	1:2
8	Cyclohexane carboxylic acid	50	2:1
9	2-Ethyl butyric acid	26	1:1
10	2,2-Dimethyl butyric acid	66	2:1
11	Cyclohexane acetic acid	68	2:1

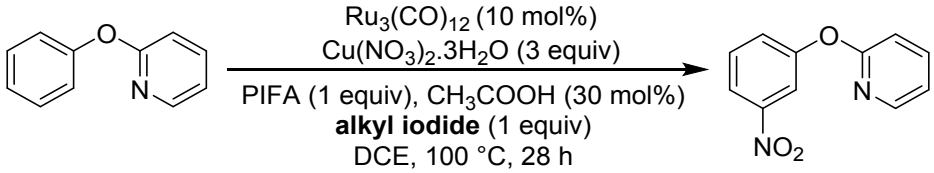
12	Ferrocene	-	-
13	TBACl	26	1:1
14	TBABr	26	1:1
15	TBAF	28	1:1

Table 8. Optimization of Silver Salts



Sr. No.	Silver salt	GC yield (%)	Selectivity (*meta*:*others*)
1	Ag_2CO_3	43	1:2
2	**AgTFA**	**85**	**6:1**
3	AgF	13	1:2
4	AgBr	12	1:3
5	Ag_2O	24	1:3
6	AgI	4	1:1

Table 9. Optimization of Alkyl Iodide



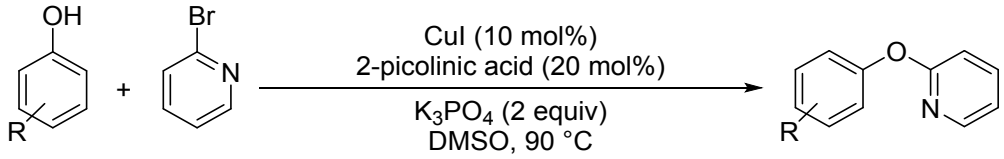
Sr. No.	Alkyl Iodide	GC yield (%)	Selectivity (*meta*:*others*)
1	Iodoethane	72	2:1
2	1-Iodo-3-methyl butane	40	1:1
3	1-Iodobutane	30	1:2

4	1-Iodopropane	20	1:3

This nitration reaction undergoes a radical process and alkyl iodides are known to be radical initiators.[1] Therefore, we thought to examine the presence of various alkyl iodides.

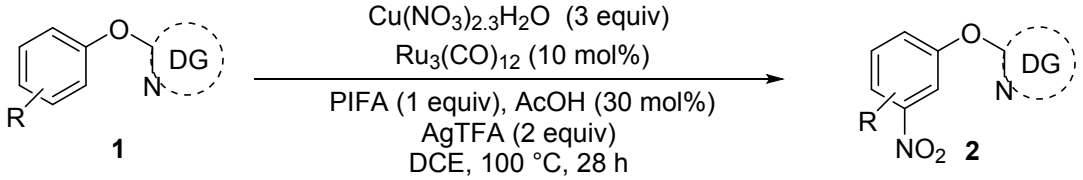
3. Experimental procedures

3.1 General Procedure A to Prepare 2-Phenoxypyridines[2]



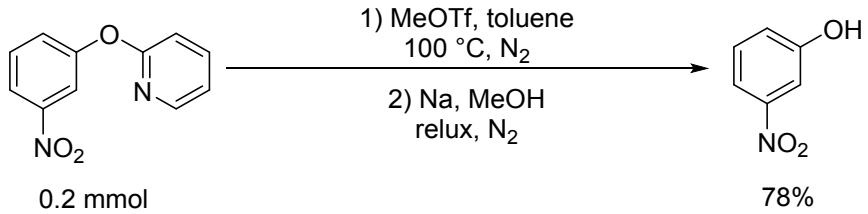
An oven-dried screw-cap test tube containing a stirring bar was charged with CuI (0.31 mmol, 60mg, 10 mol%), 2 picolinic acid (0.62 mol, 77.4 mg, 20 mol%), K_3PO_4 (6.2 mmol, 1.335 g, 2 equiv). Then to this mixture 2-bromo pyridine (3.1 mmol, 1equiv) and phenol derivatives (3.7 mmol, 1.2 equiv) were added, 6 mL DMSO was used as solvent. Then this reaction was put to a pre-heated oil bath at 90 ˚C for 24 h. After cooling this reaction mixture to room temperature it was diluted with ethyl acetate and extracted with water three times. Then organic layer was collected dried with Na_2SO_4 and concentrated. Product was purified on column chromatography with petroleum ether/ethyl acetate as the eluent.

3. 2 General Procedures B for Ru-Catalyzed *meta*-C_{Ar}-H Nitration of Phenol Derivative



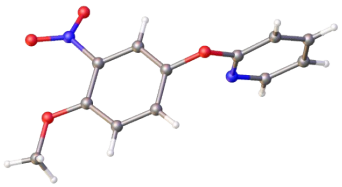
An oven-dried screw-cap test tube containing a stirring bar was charged with phenol derivative, $Ru_3(CO)_{12}$ (10 mol%), $PhI(TFA)_2$ (1 equiv), AgTFA (2 equiv). To this reaction tube $Cu(NO_3)_2.3H_2O$ (3 equiv) was added inside the glove box then CH_3COOH (30 mol%) and DCE was added using syringe. The mixture was stirred at 100 ˚C for 28 h. After cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified on column chromatography with petroleum ether/ethyl acetate as the eluent to afford the nitrated products.

3.3 General Procedure C for the Synthesis of *meta*-Nitrophenol through DG Removal[3]



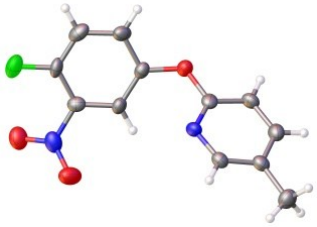
Under an argon atmosphere, to a well-stirred solution of nitrated compound **2** (0.2 mmol) dry toluene (5 mL) was added MeOTf (39.8 μL, 0.36 mmol) at 100 °C for 2 h. After cooling to room temperature, the solution was evaporated under vacuum. Without purification, the crude product was subsequently added into a Na (110.4 mg, 4.8 mmol)/MeOH (5 mL) solution, heated to reflux, and stirred for a further 15 min. After cooling to room temperature, the solvent was evaporated under vacuum and water (15 mL) was added to the residue. The aqueous solution was extracted by ethyl acetate (10 mL × 3), and the organic layers were combined, dried over $MgSO_4$, filtered, and evaporated under vacuum. The residue was further purified by silica gel chromatography using petroleum/ethyl acetate (6/1, V/V) as the eluent to give pure.

4. Crystal data



4.1 Crystal data and structure refinement for C_{12} H_{10} N_2O_4 (ORTEP diagram of 2f)
CCDC Number: 1996668

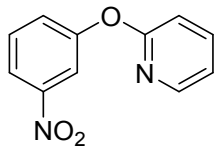
Bond precision:	C–C = 0.0020 A	Wavelength=0.71073
Cell:	a=8.5310(4)	alpha=90
	b=11.1285(5)	beta=110.333(5)
	c=12.0481(6)	gamma=90
Temperature:	150 K	
Volume	1072.55(9)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	0.444(C12 H10 N2 O4)	
Sum formula.	C5 33 H4.44 N0.89 O1.78	
Mr	109.4	
Dx,g cm-3	1.525	
Z	9	
Mu (mm-1)	0.117	
F(000)	512.0	
h,k,lmax	10,13,13	
Nref	1797	
Tmin,Tmax	0.416,1.000	
Data completeness	0.950	
Theta(max)	25.000	
R(reflections)	0.0414(1633)	
wR2(reflections)	0.1143(1797)	
S = 1.065	Npar= 164	



4.2 Crystal data and structure refinement for $C_{12}H_9FN_2O_3$ (ORTEP diagram of 2m)
CCDC Number: 1996667

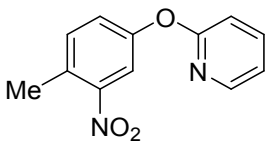
Bond precision:	C–C = 0.0094 A	Wavelength=0.71073
Cell:	a=13.7895(17)	alpha=90
	b=20.620(2)	beta=90
	c=3.8818(7)	gamma=90
Temperature:	150 K	
Volume	1103.8(3)	
Space group	P n a 21	
Hall group	P 2c -2n	
Moiety formula	0.8(C12 H9 F N2 O3)	
Sum formula.	C9.60 H7.20 F0.80 N1.60 O2.40	
Mr	198.57	
Dx,g cm-3	1.494	
Z	5	
Mu (mm-1)	0.120	
F(000)	512.0	
h,k,l_{max}	16,24,4	
N_{ref}	1909	
T_{min},T_{max}	0.532,1.000	
Data completeness	1.68/0.98	
Theta(max)	24.991	
R(reflections)	0.0710(1140)	
wR2(reflections)	0.1654(1909)	
S = 1.069	Npar = 164	

5. Characterization data



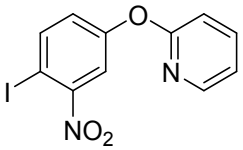
2-(3-nitrophenoxy)pyridine **(Table 2**, **2a):** Following the general procedure B, Compound **2a** was obtained from 2-phenoxypyridine **1a**, isolated by column chromatography (85%, 31.5 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: Yellow solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3091, 2925, 2855, 1589, 1527, 1428, 1466, 1345, 1241. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 4.9, 1.4 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 8.02 (t, J = 2.1 Hz, 1H), 7.76 (td, J = 8.3, 1.9 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.08 (dd, J = 6.8, 5.3 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.7, 154.8, 149.2, 147.8, 140.2, 130.3, 127.7, 119.7, 119.6, 116.7, 112.4. **LRMS** [ESI, (+) ve]: 217.0629.



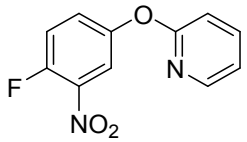
2-(4-methyl-3-nitrophenoxy)pyridine **(Table 2**, **2b):** Following the general procedure B, Compound **2b** was obtained from 2-(4-methyl-phenoxy)pyridine **1b**, isolated by column chromatography (80%, 33.5 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: yellow solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3064, 2926, 2855, 1594, 1573, 1526, 1466, 1428, 1348, 1243, 1143. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (ddd, J = 5.0, 2.0, 0.7 Hz, 1H), 7.82 (d, J = 2.3 Hz, 1H), 7.74 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.32 (dd, J = 8.4, 2.4 Hz, 1H), 7.05 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 6.99 (dt, J = 8.3, 0.8 Hz, 1H), 2.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.0, 152.6, 147.8, 140.0, 133.8, 130.0, 126.5, 119.5, 118.0, 112.2, 77.2, 20.4. **HRMS** [ESI, (+) ve]: calcd. for ($C_{12}H_{11}N_2O_3$) 231.0764, found 231.0765.



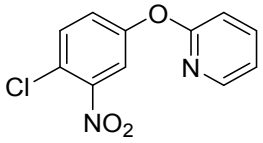
2-(4-iodo-3-nitrophenoxy)pyridine **(Table 2, 2c):** Following the general procedure B, Compound **2c** was obtained from 2-(4-iodo-phenoxy)pyridine **1c**, isolated by column chromatography (70%, 47 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: Brownish solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3091, 2924, 2853, 1590, 1534, 1464, 1429, 1343, 1268, 1238, 777**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 4.8 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.76 (ddd, J = 10.7, 8.5, 2.1 Hz, 2H), 7.14 (dd, J = 8.6, 2.7 Hz, 1H), 7.09 (dd, J = 6.8, 5.4 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 154.8, 147.7, 142.6, 140.3, 135.9, 126.9, 126.6, 120.0, 119.0, 112.5, 112.4. **LRMS** [ESI, (+) ve]: 342.089.



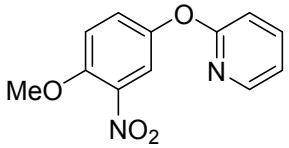
2-(4-fluoro-3-nitrophenoxy)pyridine **(Table 2, 2d):** Following the general procedure B, Compound **2d** was obtained from 2-(4-fluoro-phenoxy)pyridine **1d**, isolated by column chromatography (78%, 36.5 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f: 0.4 (10% EA-PE); Appearance: white solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3068, 2921, 2852, 1602, 1535, 1474, 1378, 1345, 1198, 1128, 1023. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (ddd, J = 5.0, 2.0, 0.7 Hz, 1H), 7.90 (dd, J = 6.2, 2.9 Hz, 1H), 7.76 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.45 (ddd, J = 9.0, 3.6, 3.0 Hz, 1H), 7.31 (dd, J = 10.2, 9.1 Hz, 1H), 7.08 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 7.02 (dt, J = 8.3, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 147.6, 140.2, 129.0 (d, J = 8.2 Hz), 119.8, 119.4, 119.6, 112.2. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_7FN_2O_3$) 235.0442, found 235.0440.



2-(4-chloro-3-nitrophenoxy)pyridine **(Table 2, 2e):** Following the general procedure B, Compound **2e** was obtained from 2-(4-chlorophenoxy)pyridine **1e**, isolated by column chromatography isolated by column chromatography (72%, 36 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: white solid.

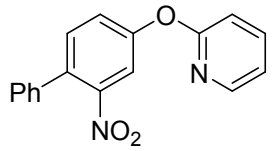
IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3084, 2925, 2853, 1591, 1534, 1464, 1428, 1347, 1267, 1236, 1069, 1142, 851**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (ddd, J = 5.0, 2.0, 0.7 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.75 (dd, J = 3.3, 2.4 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.35 (dd, J = 8.8, 2.8 Hz, 1H), 7.09 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 7.02 (dt, J = 8.3, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 153.0, 147.7, 140.3, 132.7, 126.5, 122.6, 119.9, 118.9, 112.3.



2-(4-methoxy-3-nitrophenoxy)pyridine **(Table 2, 2f):** Following the general procedure B, Compound **2f** was obtained from 2-phenoxypyridine **1f**, isolated by column chromatography (60%, 29.5 mg), Eluent: ethyl acetate/ petroleum ether (4:96 v/v); R_f : 0.5 (10% EA-PE); Appearance: Yellow solid.

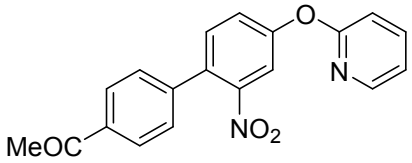
IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3078, 2930, 2852, 1590, 1518, 1528, 1462, 1431, 1345, 1280, 1140, 1080**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (dd, J = 5.0, 1.5 Hz, 1H), 7.74– 7.71(m, 2H), 7.39 (dd, J = 8.8, 2.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.04 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 6.97

(dt, *J* = 8.3, 0.8 Hz, 1H), 3.97 (s, 3H). **HRMS** [ESI, (+) ve]: calcd. for ($C_{12}H_{10}N_2O_4$) 247.0641, found 247.0646.



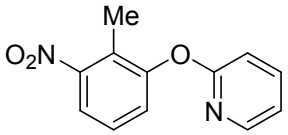
2-(4-phenyl-3-nitrophenoxy)pyridine **(Table 2, 2g):** Following the general procedure B, Compound **2g** was obtained from 2-(4-phenyl-phenoxy)pyridine **1g**, isolated by column chromatography (76%, 44 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f: 0.4 (10% EA-PE); Appearance: pale yellow solid.

IR (thin film, $CHCl_3$): *v* (cm^{-1}) = 3063, 3011, 2928, 2852, 1592, 1531, 1462, 1429, 1350, 1242, 1168. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 3.8 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.36 – 7.31 (m, 2H), 7.13 – 7.08 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 153.7, 149.6, 147.8, 140.3, 137.3, 133.1, 132.6, 128.9, 128.3, 128.2, 125.3, 119.8, 117.2, 112.5. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_7ClN_2O_3$) 293.0921, found 293.0917.



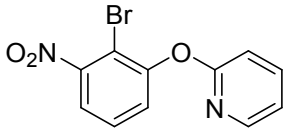
1-(2'-nitro-4'-(pyridine-2-yloxy)-[1,1'-biphenyl]-4-yl)ethane-1-one **(Table 2, 2h):** Following the general procedure B, Compound **2h** was obtained from 1-(4'-(pyridine-2-yloxy)-[1,1'-biphenyl]-4-yl)ethane-1-one **1h**, isolated by column chromatography (75%, 46 mg) Eluent: ethyl acetate/ petroleum ether (6:94 v/v); R_f: 0.4 (20% EA-PE); Appearance: white solid.

IR (thin film, $CHCl_3$): *v* (cm^{-1}) = 3060, 3020, 2925, 2854, 1683, 1595, 1532, 1466, 1429, 1357, 1267, 1238, 829**. ^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 4.9, 1.4 Hz, 1H), 8.04 – 8.00 (m, 2H), 7.81 – 7.79 (m, 1H), 7.78 (d, *J* = 2.2 Hz, 1H), 7.44 (ddd, *J* = 8.4, 7.4, 2.0 Hz, 4H), 7.11 (ddd, *J* = 7.2, 5.0, 0.8 Hz, 1H), 7.06 (t, *J* = 6.0 Hz, 1H), 2.64 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.4, 147.8, 142.3, 140.3, 136.8, 132.9, 131.5, 128.9, 128.6, 125.6, 120.0, 117.6, 112.5. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_7ClN_2O_3$) 335.1026, found 335.1030.



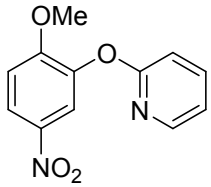
2-(2-methyl-3-nitrophenoxy)pyridine **(Table 2, 2i)**: Following the general procedure B, Compound **2i** was obtained from 2-(2-methyl-phenoxy)pyridine **1i**, isolated by column chromatography (77%, 31mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: yellow solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3060, 2928, 2855, 1574, 1574, 1527, 1467, 1428, 1348, 1230, 1244, 1181, 776**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 7.78 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.03 (ddd, *J* = 7.2, 5.0, 0.8 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.2, 153.5, 147.86, 140.1, 131.8, 127.2, 127.0, 126.9, 121.3, 119.1, 111.4, 12.9. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_7ClN_2O_3$) 231.0764, found 231.0763.



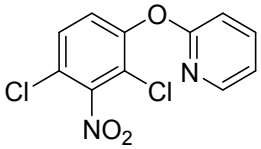
2-(2-bromo-3-nitrophenoxy)pyridine **(Table 2, 2j):** Following the general procedure B, Compound **2j** was obtained from 2-(2-methyl-phenoxy)pyridine **1j**, isolated by column chromatography (65%, 21 mg), Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: yellow solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3082, 2918, 2850, 1596, 1574, 1535, 1453, 1428, 1359, 1266, 1142, 852, 712**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 7.77 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.07 (ddd, *J* = 7.2, 4.6, 1.6 Hz, 2H).



2-(2-methoxy-3-nitrophenoxy)pyridine **(Table 2, 2k):** Following the general procedure B, Compound **2k** was obtained from 2-(2-methyl-phenoxy)pyridine **1k**, isolated by column chromatography Eluent (57%, 28 mg) ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (10% EA-PE); Appearance: yellow solid.

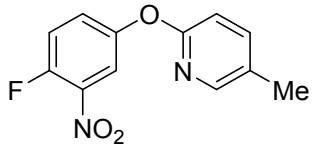
IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3088, 2925, 2851, 1593, 1515, 1528, 1468, 1430, 1344, 1205, 1281, 1237, 1081. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.14 (m, *J* = 9.1, 2.7 Hz, 1H), 8.11 (d, *J* = 3.0 Hz, 1H), 8.06 (d, *J* = 2.7 Hz, 1H), 7.78 – 7.71 (m, *J* = 7.5 Hz, 1H), 7.07 – 7.02 (m, *J* = 12.0, 8.7 Hz, 3H), 3.88 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.9, 157.6, 147.5, 142.4, 141.5, 140.0, 122.5, 119.4, 119.1, 111.8, 111.4, 56.7.



2-(2,4-dichloro-3-nitrophenoxy)pyridine **(Table 2, 2l)**: Following the general procedure B, Compound **2l** was obtained from 2-(2,4-dichloro-phenoxy)pyridine **1l**, isolated by column chromatography (56%, 32 mg), Eluent: ethyl acetate/ petroleum ether (3:98 v/v); R_f : 0.35 (10% EA-PE); Appearance: white solid.

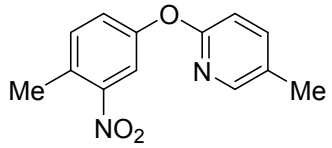
IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3082, 2930, 2856, 1592, 1534, 1464, 1428, 1346, 1236, 1069, 1143, 851, 776**. ^{1}H NMR** (500 MHz, CDCl3) δ 8.13 – 8.10 (m, 1H), 7.80 – 7.74 (m, 1H), 7.46 (d, J = 8.9 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 7.07 (td, J = 5.8, 0.8 Hz, 2H).

.



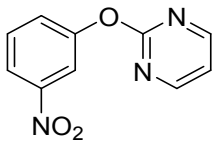
2-(4-fluoro-3-nitrophenoxy)-5-methylpyridine **(Table 2, 2m):** Following the general procedure B, Compound **2m** was obtained from 2-(4-fluoro-phenoxy)-5-methylpyridine **1m**, isolated by column chromatography (80%, 40 mg), Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f: 0.4 (10% EA-PE); Appearance: white solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3062, 2926, 2858, 1602, 1536, 1474, 1378, 1345, 1210, 1234, 1198, 1127**. ^{1}H NMR** (500 MHz, CDCl3) δ 7.97 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.85 (dd, *J* = 6.2, 3.0 Hz, 1H), 7.57 (ddd, *J* = 8.3, 2.4, 0.5 Hz, 1H), 7.42 (ddd, *J* = 9.0, 3.6, 3.0 Hz, 1H), 7.29 (dd, *J* = 10.2, 9.1 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.8, 153.3, 151.3, 150.2 (d, *J* = 3.6 Hz), 147.3, 141.1, 129.3, 128.5 (d, *J* = 8.2 Hz), 119.3, 119.1, 118.6 (d, *J* = 2.5 Hz), 17.7. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_7ClN_2O_3$) 249.0670, found 249.0667.



5-methyl-2-(4-methyl-3nitrophenoxy)pyridine **(Table 2, 2n):** Following the general procedure B, Compound **2n** was obtained from 5-methyl-2-(4-methyl-phenoxy)pyridine **1n**, isolated by column chromatography (70%, 34 mg), Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f: 0.4 (10% EA-PE); Appearance: white solid.

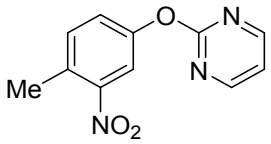
IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3964, 2926, 2855, 1733, 1594, 1573, 1466, 1428, 1348, 1263, 1242, 1190. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 2.59 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 153.1, 147.5, 140.9, 133.8, 130.4, 129.6, 129.0, 126.1, 121.3, 117.4, 111.8, 20.3, 17.7. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_7ClN_2O_3$) 245.0921, found 245.0918.



2-(3-nitrophenoxy)pyrimidine[4] **(Table 2, 2o):** Following the general procedure B, Compound **2o** was obtained from 2-phenoxy pyrimidine **1o**, isolated by column chromatography (60%, 24.5

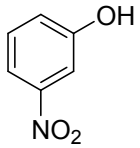
mg),Eluent: ethyl acetate/ petroleum ether (4:96 v/v); R_f: 0.35 (10% EA-PE); Appearance: white solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3095, 2924, 2853, 2078, 2016, 1692, 1571, 1528, 1433, 1403, 1349, 1289, 1218, 1193. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.8 Hz, 2H), 8.16 – 8.10 (m, 2H), 7.64 – 7.54 (m, 2H), 7.13 (dd, J = 7.9, 3.1 Hz, 1H).



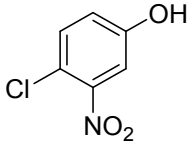
2-(4-methyl-3-nitrophenoxy)pyrimidine **(Table 2, 2p):** Following the general procedure B, Compound **2p** was obtained from 2-(4-methyl-phenoxy)pyrimidine **1p**, isolated by column chromatography (65%, 28.5 mg), Eluent: ethyl acetate/ petroleum ether (4:96 v/v); Rf : 0.35 (10% EA-PE); Appearance: white solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3015, 2929, 2855, 1966, 1574, 1528, 1443, 1403, 1354, 1304, 1218, 1026. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, J = 4.8 Hz, 2H), 7.90 (d, J = 2.3 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.11 (t, J = 4.8 Hz, 1H), 2.63 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4, 152.4, 147.6, 140.3, 134.1, 130.3, 127.6, 121.0, 111.0, 20.9. **HRMS** [ESI, (+) ve]: calcd. for ($C_{11}H_{10}N_3O_3$) 232.0717, found 232.0717.



3-nitrophenol[5] **(Scheme 3, 3a):** Following the general procedure **C** Compound **3a** was obtained from 2-(3-nitrophenoxy)pyridine **2a**, isolated by column chromatography (65%, 21 mg)Eluent: ethyl acetate/ petroleum ether (2:96 v/v); R_f: 0. 5 (10% EA-PE); Appearance: white solid.

IR (thin film, $CHCl_3$): ν (cm^{-1}) = 3481, 3387, 2992, 2953, 2852, 1624, 1519, 1351, 1078, 935. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.2, 1.3 Hz, 1H), 7.72 (t, J = 2.2 Hz, 1H), 7.43 (t, J = 8.2 Hz, 1H), 7.20 (dd, J = 8.1, 2.4 Hz, 1H), 5.94 (s, 1H).



4-chloro-3nitrophenol[6] **(Scheme 3, 3b):** Following the general procedure **C** Compound **3b** was obtained from 4-chloro-(3-nitrophenoxy)pyridine **2e**, isolated by column chromatography Eluent: ethyl acetate/ petroleum ether (2:96 v/v); R_f: 0. 5 (10% EA-PE); Appearance: yellow solid.

6. References

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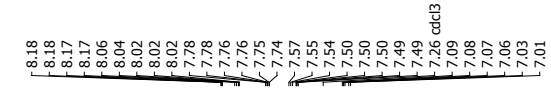
6. R. Calvo, K. Zhang , A. Passera, and D. Katayev *Nat Commun* 2019, **10**, 3410.

Table 2, **2a**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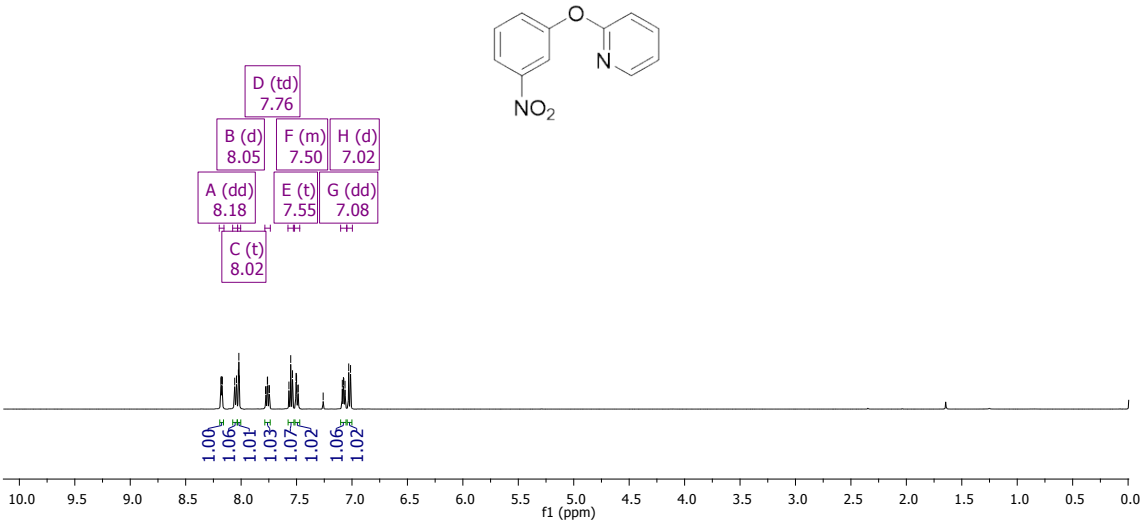
7.01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B (d)
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H (d)
7.02
A (dd)
8.18
E (t)
7.55
G (dd)
7.08
C (t)
8.02
1.00
1.06
1.01
1.03
1.07
1.02
1.06
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.0
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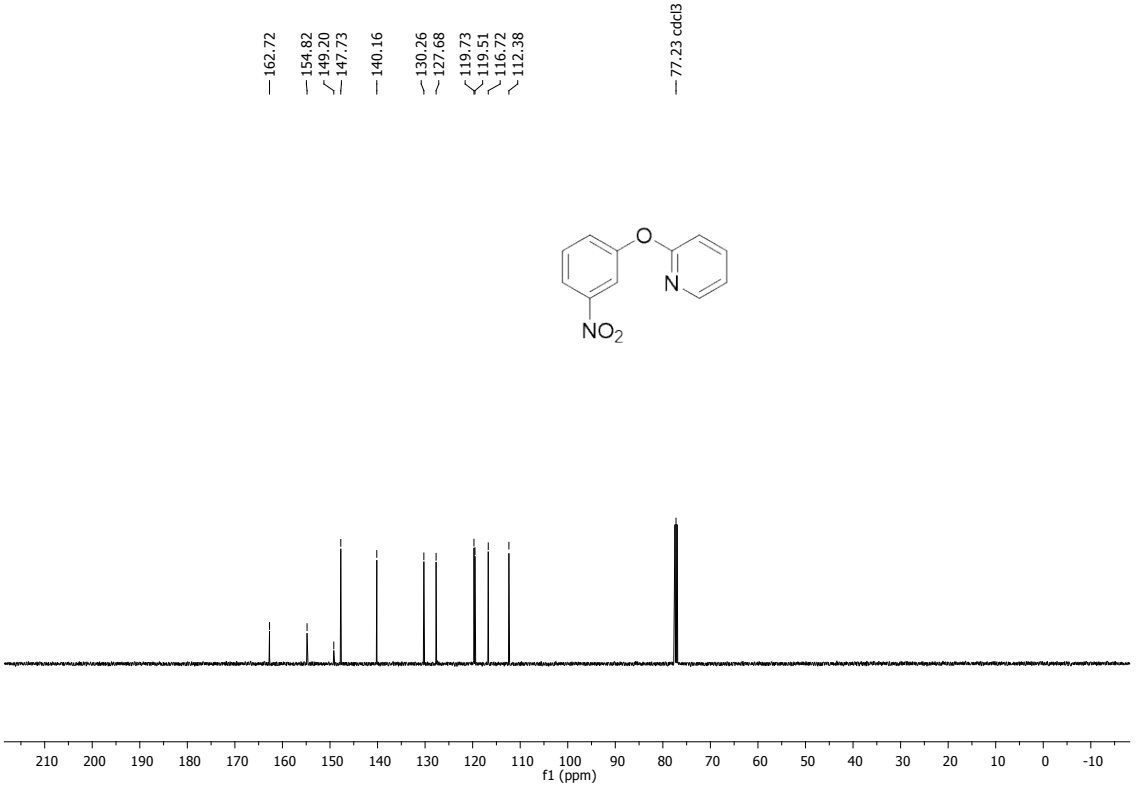
0.0
f1 (ppm)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147.73
140.16
130.26
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119.73
119.51
116.72
112.38
77.23 cdcl3
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N
NO2
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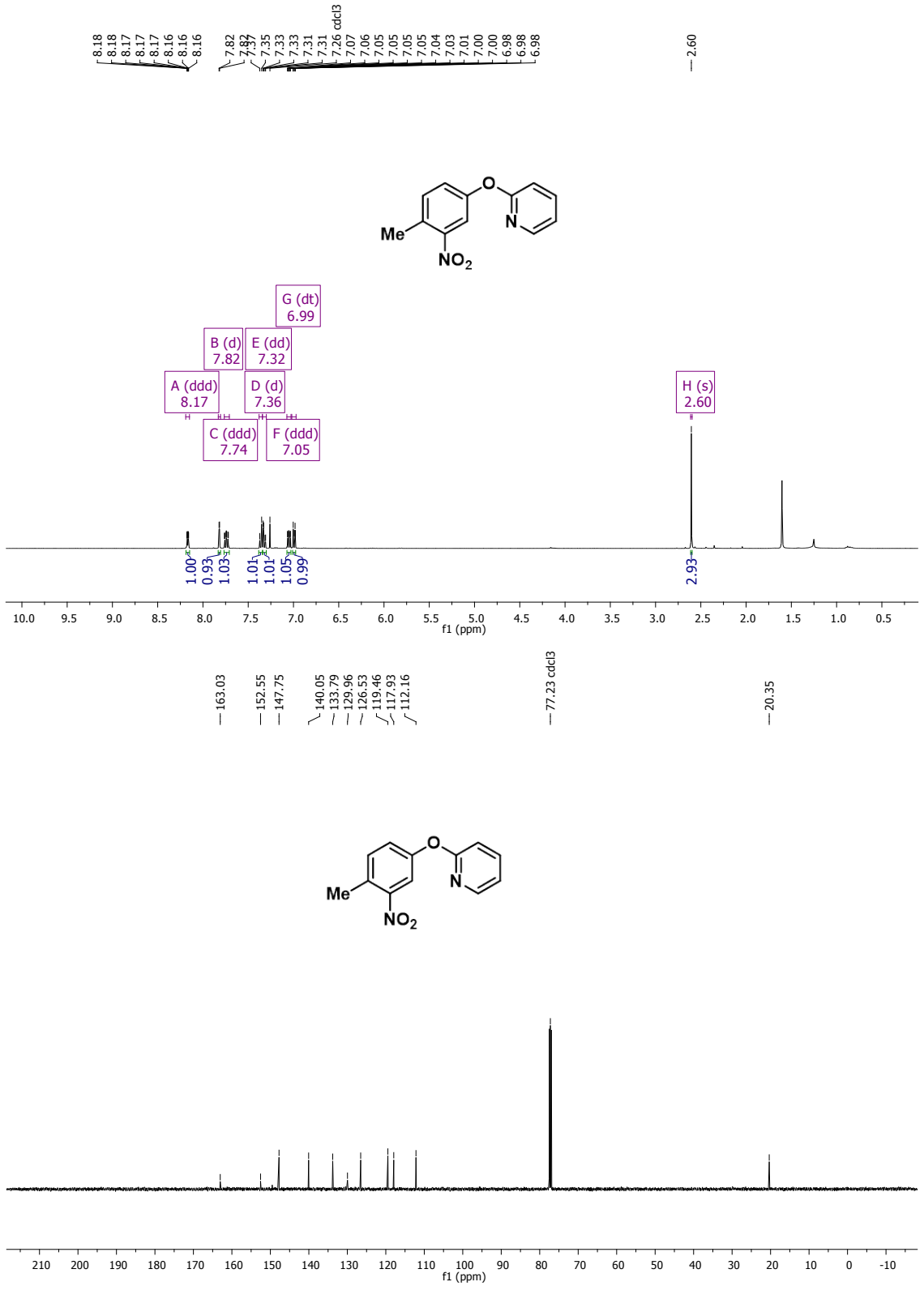
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Table 2, **2b**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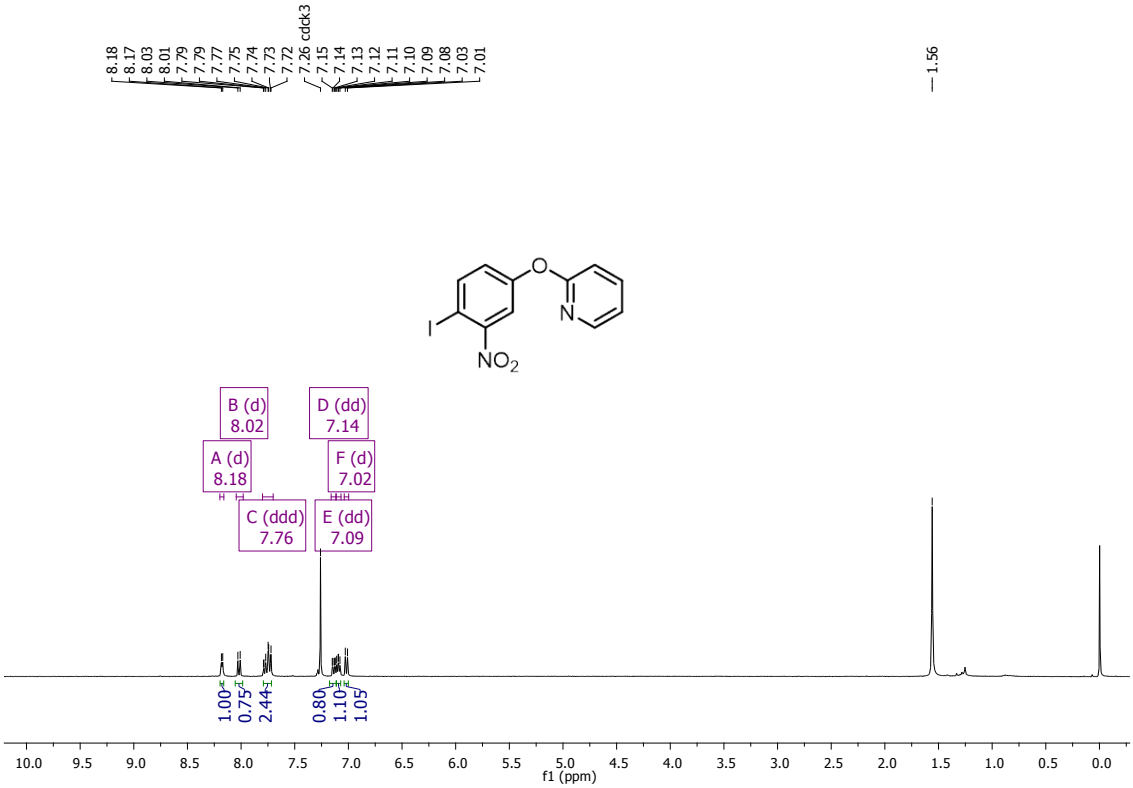
Me
NO2
O
N
G (dt) 6.99
B (d) 7.82
E (dd) 7.32
A (ddd) 8.17
D (d) 7.36
H (s) 2.60
C (ddd) 7.74
F (ddd) 7.05
1.00 0.93 1.03 1.01 1.01 1.05 0.99 2.93
f1 (ppm)
163.03 152.55 147.75 140.05 133.79 129.96 126.53 119.46 117.93 112.16 77.23 cdcl3 20.35
f1 (ppm)

Table 2, 2c


8.18
8.17
8.03
8.01
7.79
7.79
7.77
7.75
7.74
7.73
7.72
7.26 cdck3
7.15
7.14
7.13
7.12
7.11
7.10
7.09
7.08
7.03
7.01
1.56
I
O
N
NO2
B (d) 8.02
D (dd) 7.14
A (d) 8.18
F (d) 7.02
C (ddd) 7.76
E (dd) 7.09
1.00
0.75
2.44
0.80
1.10
1.05
f1 (ppm)

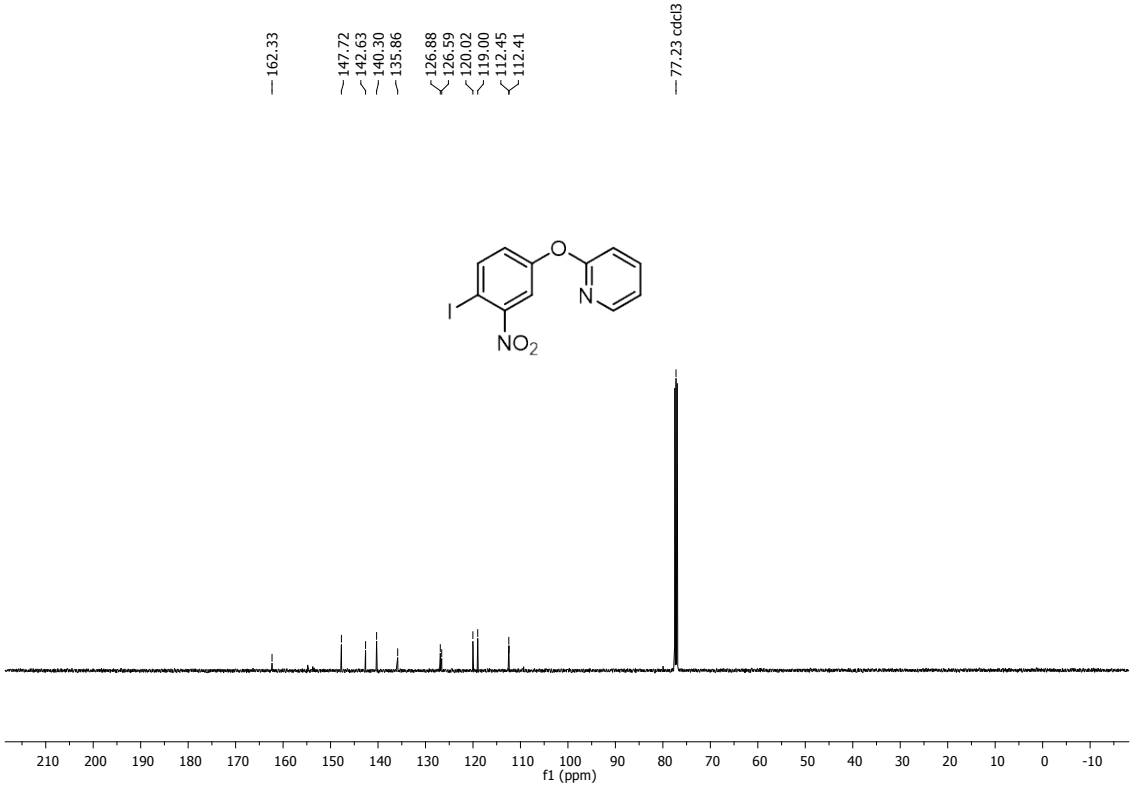
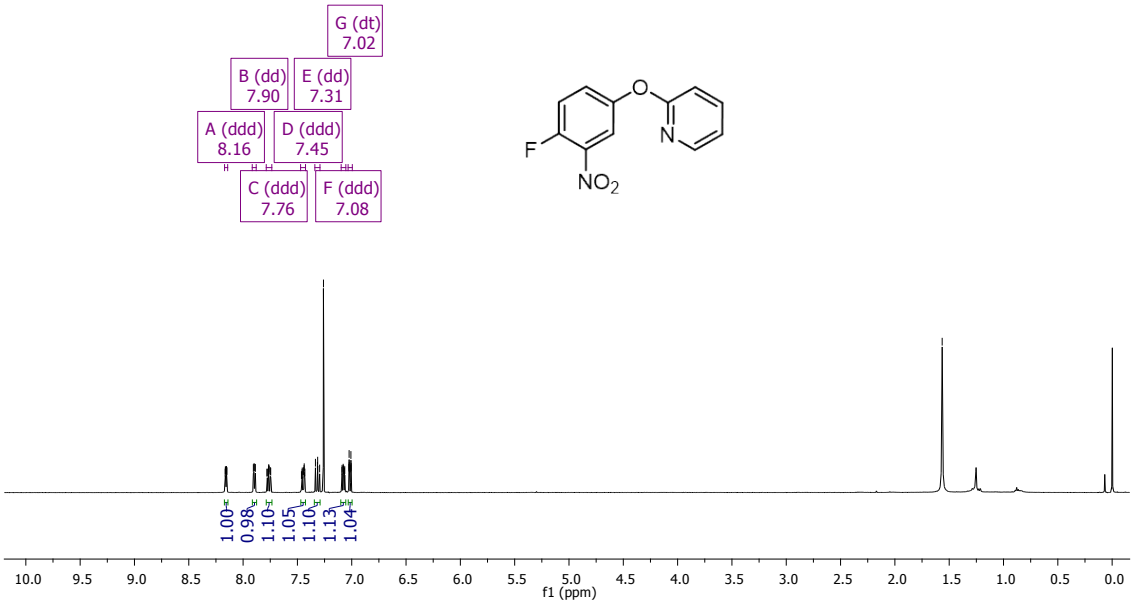

162.33
147.72
142.63
140.30
135.86
126.88
126.59
120.02
119.00
112.45
112.41
77.23 cdcl3
I
O
N
NO2
f1 (ppm)

Table 2, 2d


8.16 8.16 8.16 8.16 8.15 8.15 8.15 8.15 7.91 7.90 7.89 7.89 7.78 7.78 7.77 7.76 7.76 7.76 7.75 7.75 7.46 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.33 7.32 7.31 7.30 7.26 cdcl3 7.09 7.09 7.08 7.08 7.08 7.07 7.07 7.06 7.03 7.02 7.02 7.01 7.01 7.01
1.56


G (dt) 7.02
B (dd) 7.90
E (dd) 7.31
A (ddd) 8.16
D (ddd) 7.45
C (ddd) 7.76
F (ddd) 7.08
O
N
F
NO2
1.00 0.98 1.10 1.05 1.10 1.13 1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

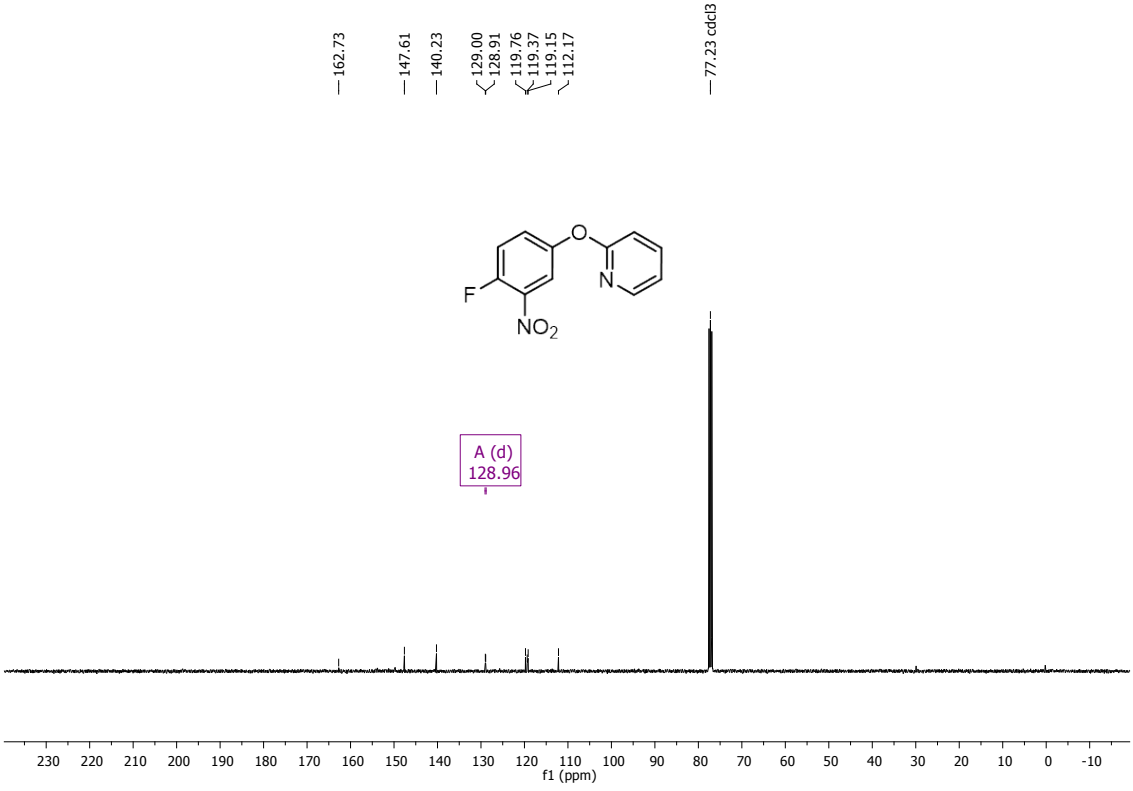

162.73
147.61
140.23
129.00
128.91
119.76
119.37
119.15
112.17
77.23 cdcl3
O
N
F
NO2
A (d) 128.96
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Table 2, 2e

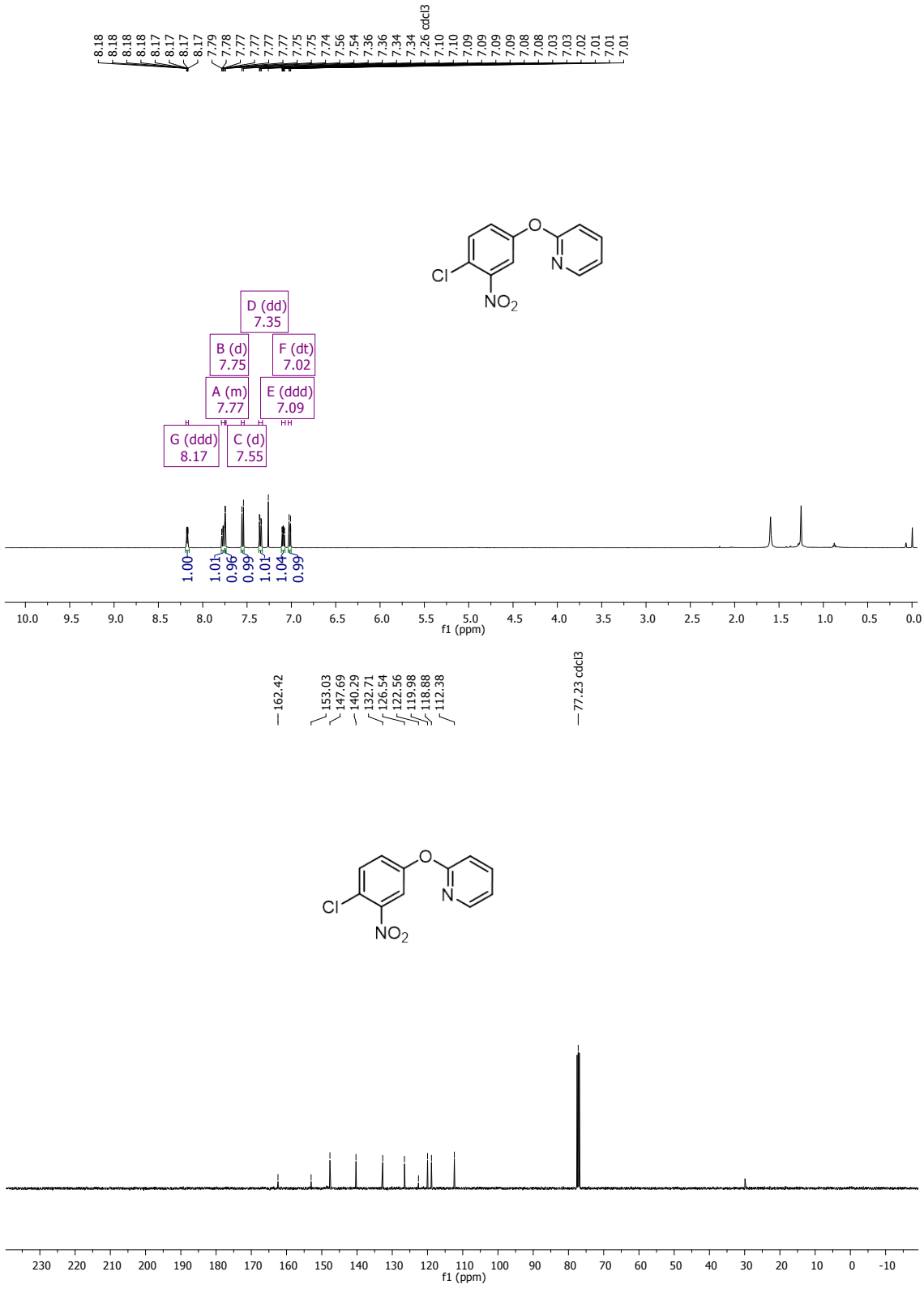

8.18 8.18 8.18 8.17 8.17 8.17 7.79 7.78 7.77 7.77 7.77 7.75 7.75 7.74 7.56 7.54 7.36 7.36 7.34 7.34 7.26 cdcl3 7.10 7.09 7.09 7.09 7.09 7.08 7.08 7.03 7.03 7.02 7.01 7.01 7.01
Cl
O
N
NO2
D (dd) 7.35
B (d) 7.75
F (dt) 7.02
A (m) 7.77
E (ddd) 7.09
G (ddd) 8.17
C (d) 7.55
1.00 1.01 0.96 0.99 1.01 1.04 0.99
f1 (ppm)
162.42
153.03
147.69
140.29
132.71
126.54
122.56
119.98
118.88
112.38
77.23 cdcl3
f1 (ppm)

Table 2, 2f

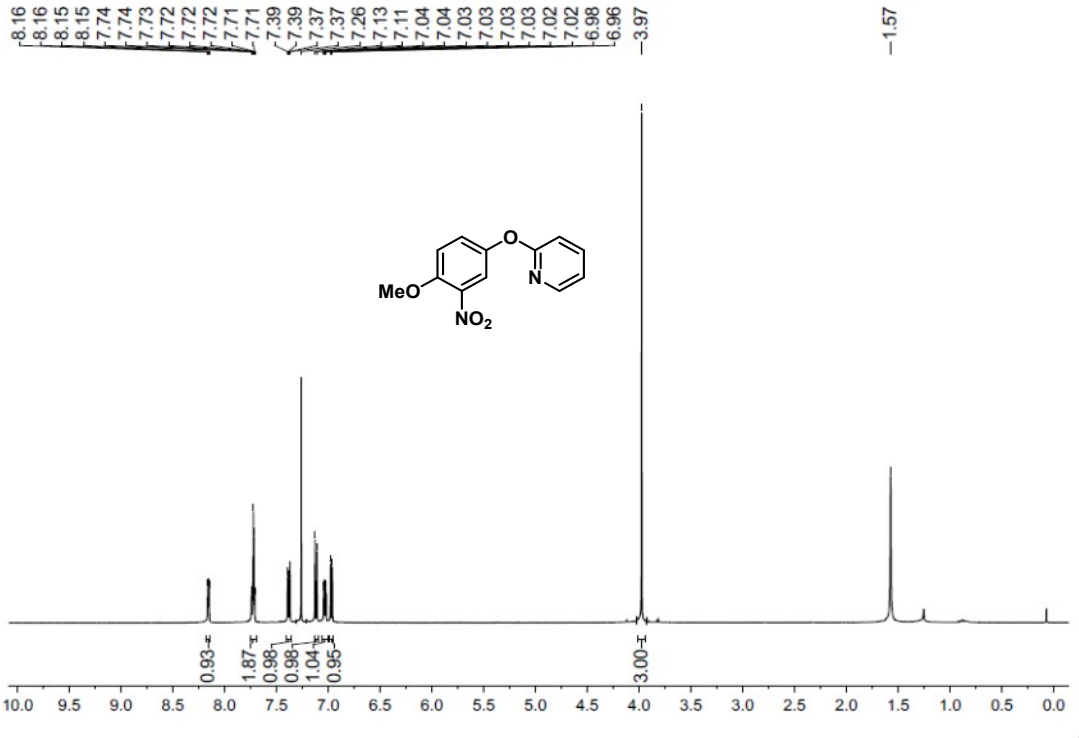
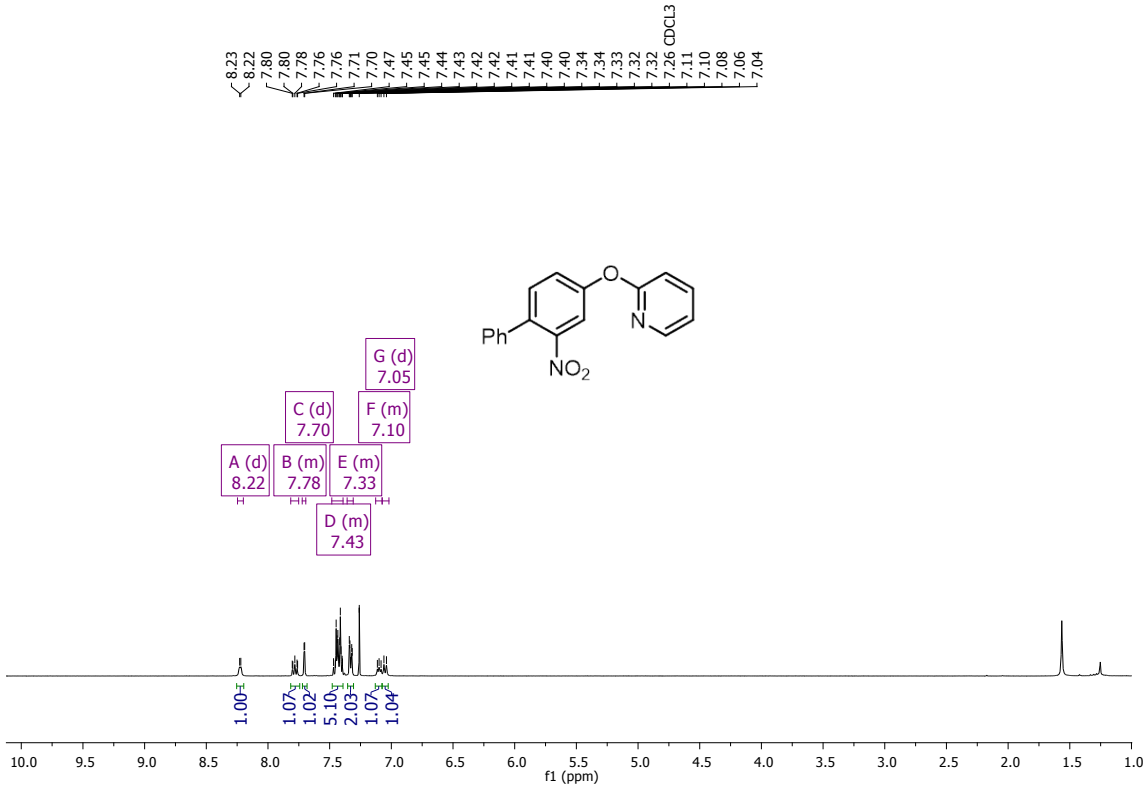


Table 2, 2g



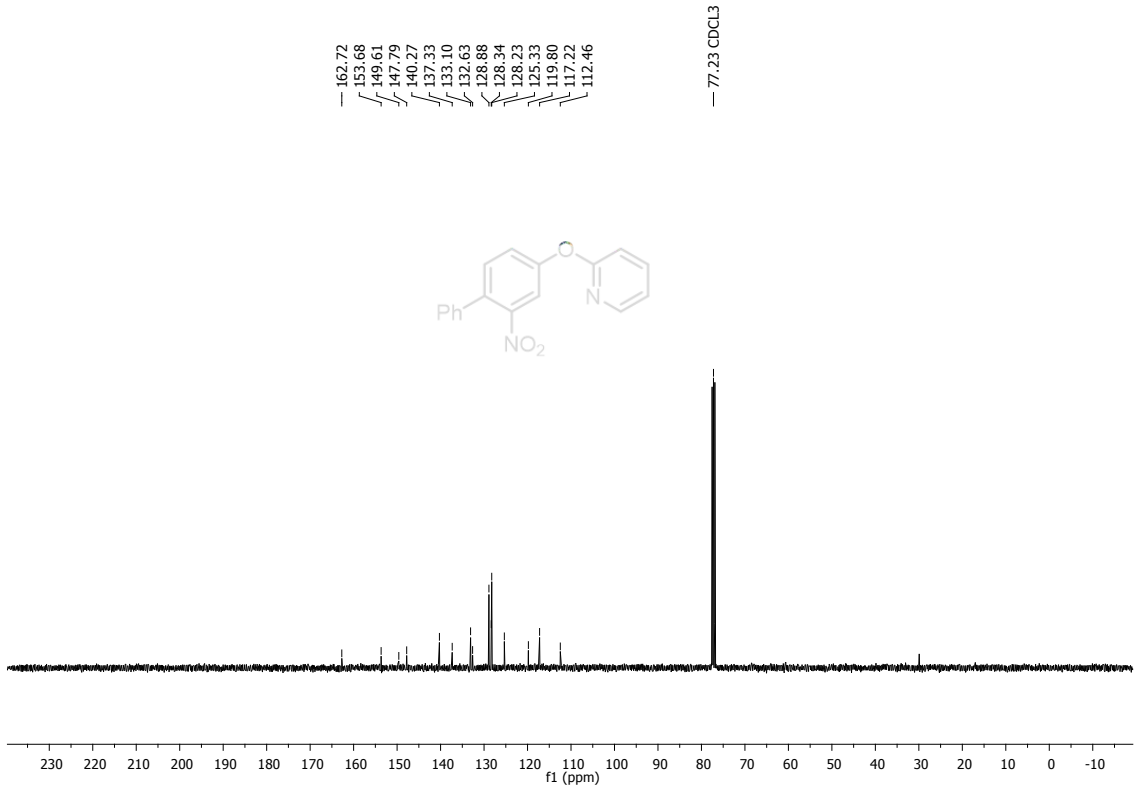
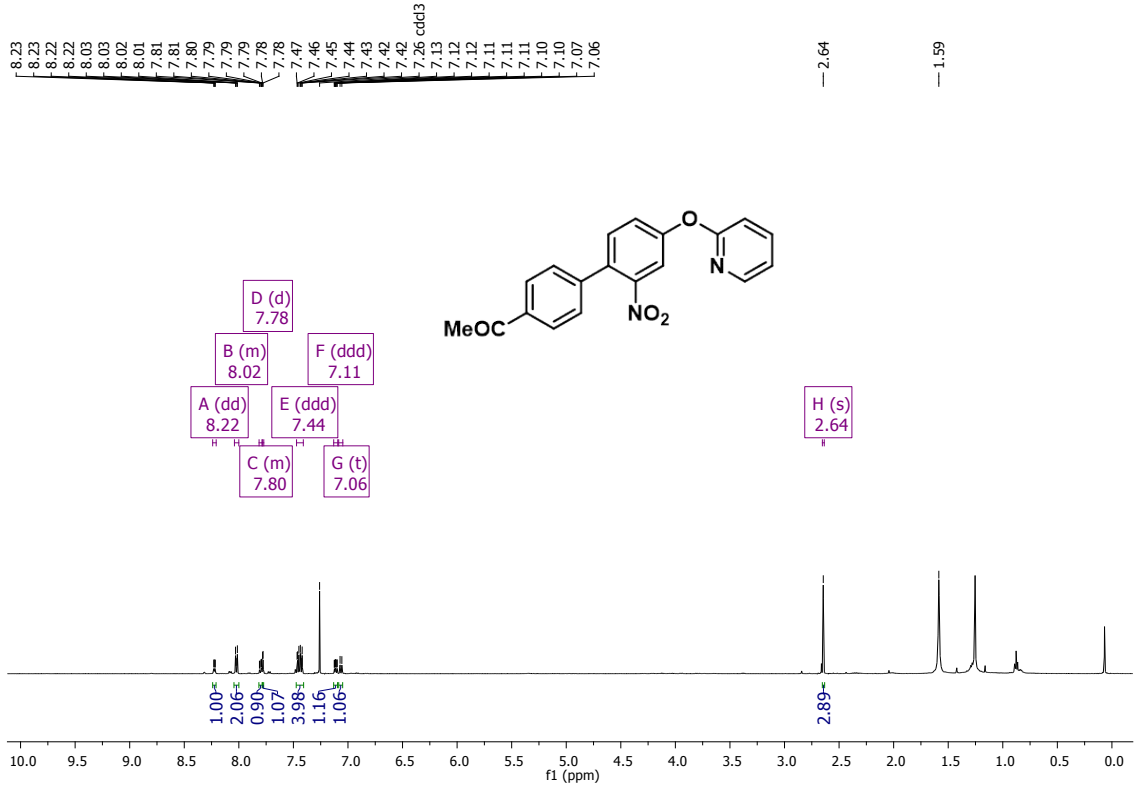

162.72
153.68
149.61
147.79
140.27
137.33
133.10
132.63
128.88
128.34
128.23
125.33
119.80
117.22
112.46
77.23 CDCl3
Ph
NO2
O
N
f1 (ppm)

Table 2, 2h


8.23
8.23
8.22
8.22
8.03
8.03
8.02
8.01
7.81
7.81
7.80
7.79
7.79
7.79
7.78
7.78
7.47
7.46
7.45
7.44
7.43
7.42
7.42
7.26 cdd3
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.07
7.06
2.64
1.59
D (d) 7.78
B (m) 8.02
F (ddd) 7.11
A (dd) 8.22
E (ddd) 7.44
C (m) 7.80
G (t) 7.06
H (s) 2.64
MeOC
NO2
O
N
1.00
2.06
0.90
1.07
3.98
1.16
1.06
2.89
f1 (ppm)

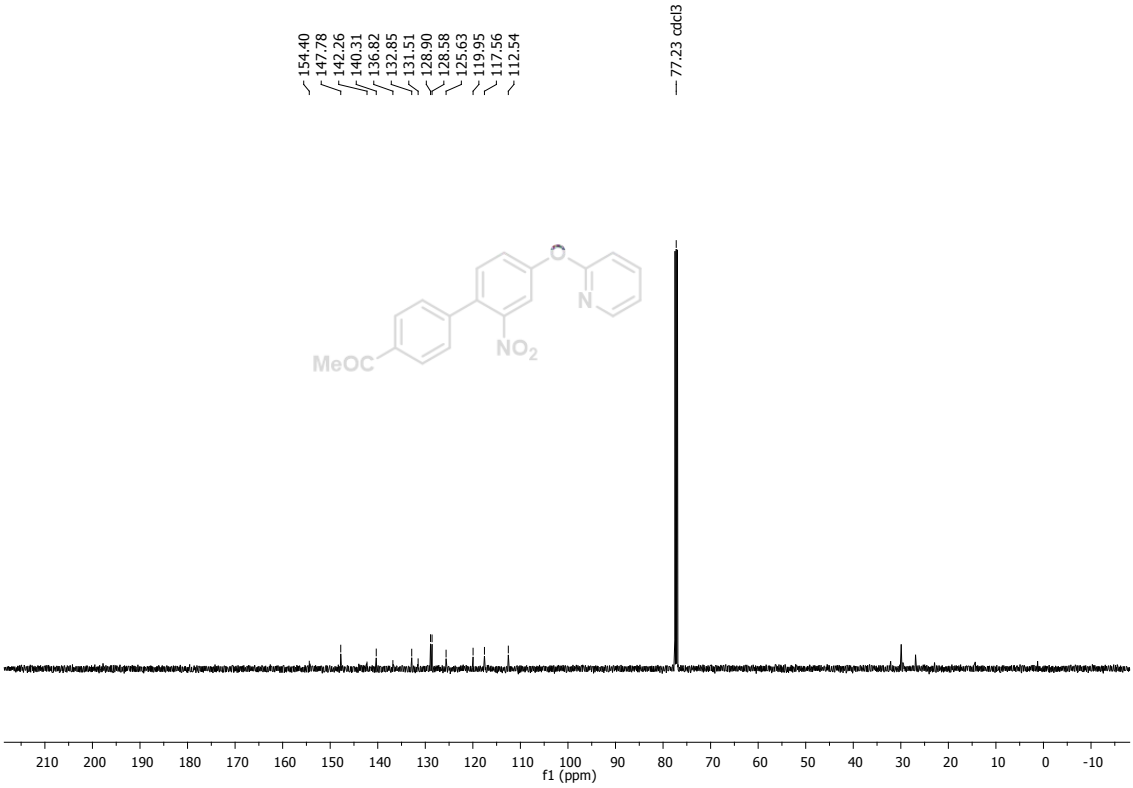
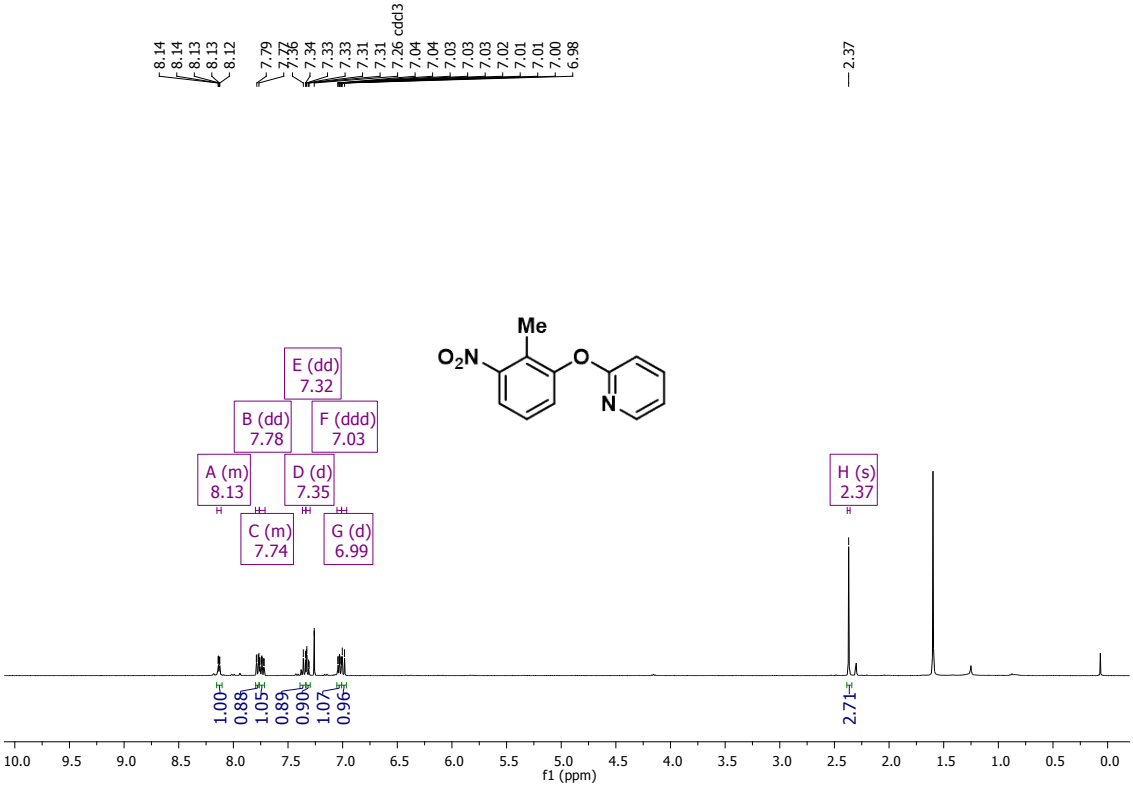

154.40
147.78
142.26
140.31
136.82
132.85
131.51
128.90
128.58
125.63
119.95
117.56
112.54
77.23 cdcl3
MeOC
NO2
O
N
f1 (ppm)

Table 2, 2i


8.14
8.14
8.13
8.13
8.12
7.79
7.77
7.36
7.34
7.33
7.31
7.31
7.26 cdd3
7.04
7.04
7.03
7.03
7.03
7.02
7.01
7.01
7.00
6.98
2.37
Me
O2N
O
N
E (dd) 7.32
B (dd) 7.78
F (ddd) 7.03
A (m) 8.13
D (d) 7.35
C (m) 7.74
G (d) 6.99
H (s) 2.37
1.00
0.88
1.05
0.89
0.90
1.07
0.96
2.71
f1 (ppm)

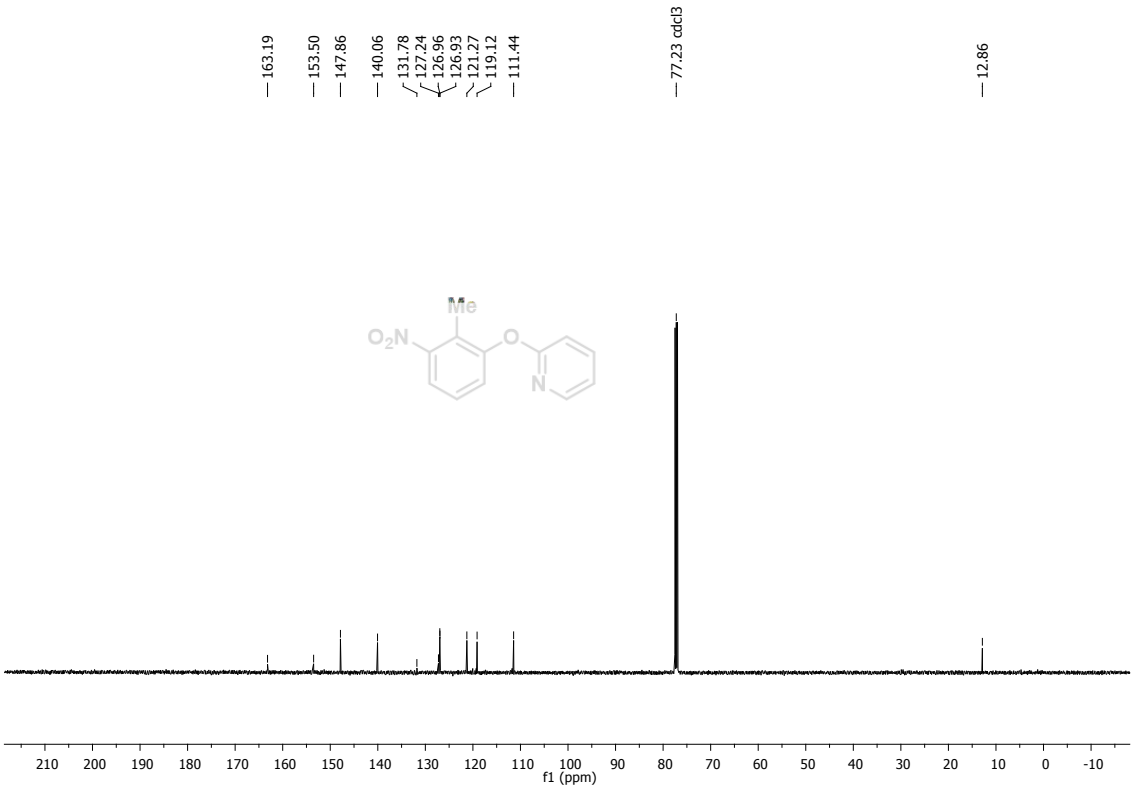

163.19
153.50
147.86
140.06
131.78
127.24
126.96
126.93
121.27
119.12
111.44
77.23 cdcl3
12.86
Me
O2N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Table 2, 2j

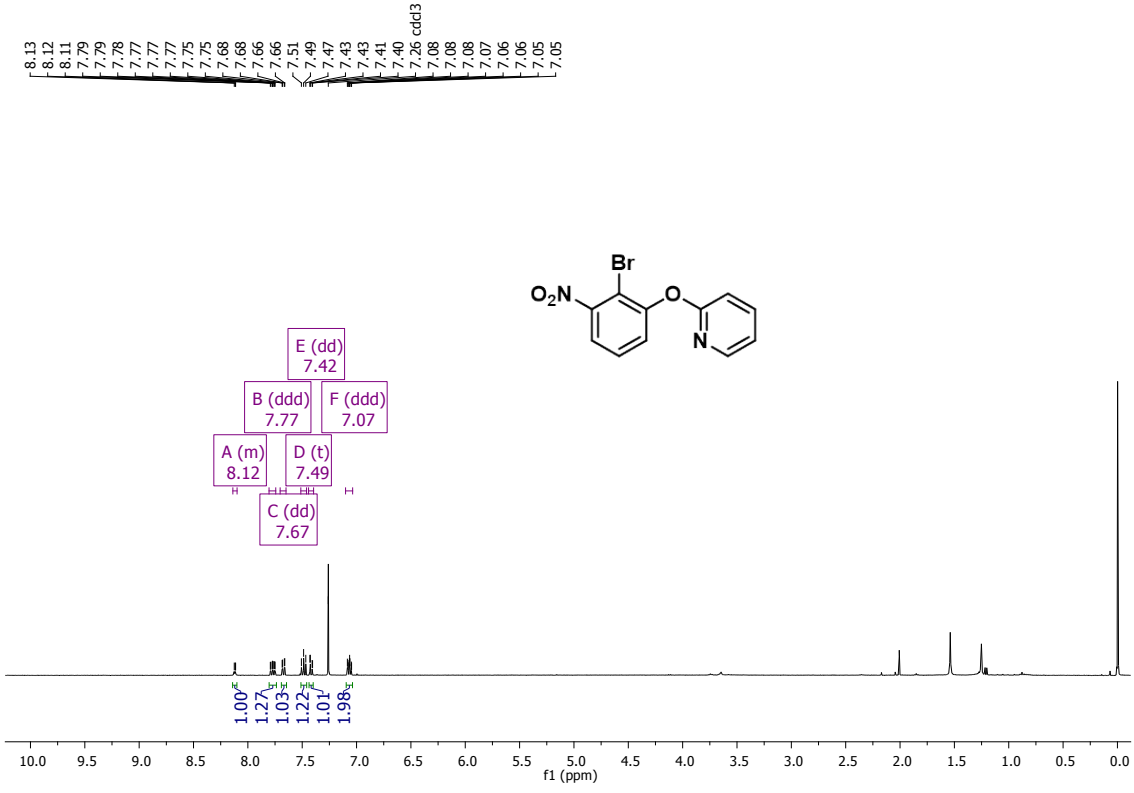
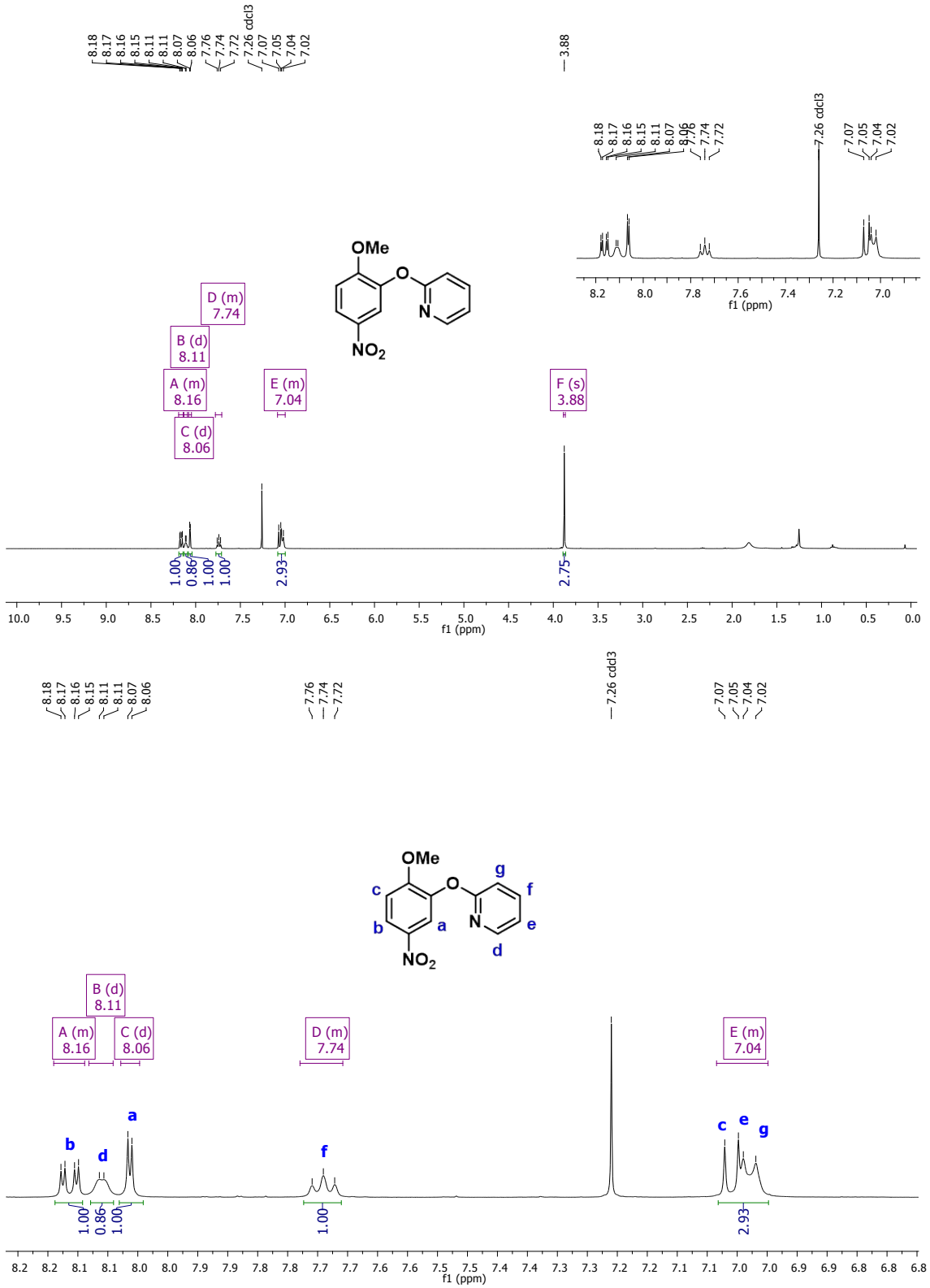
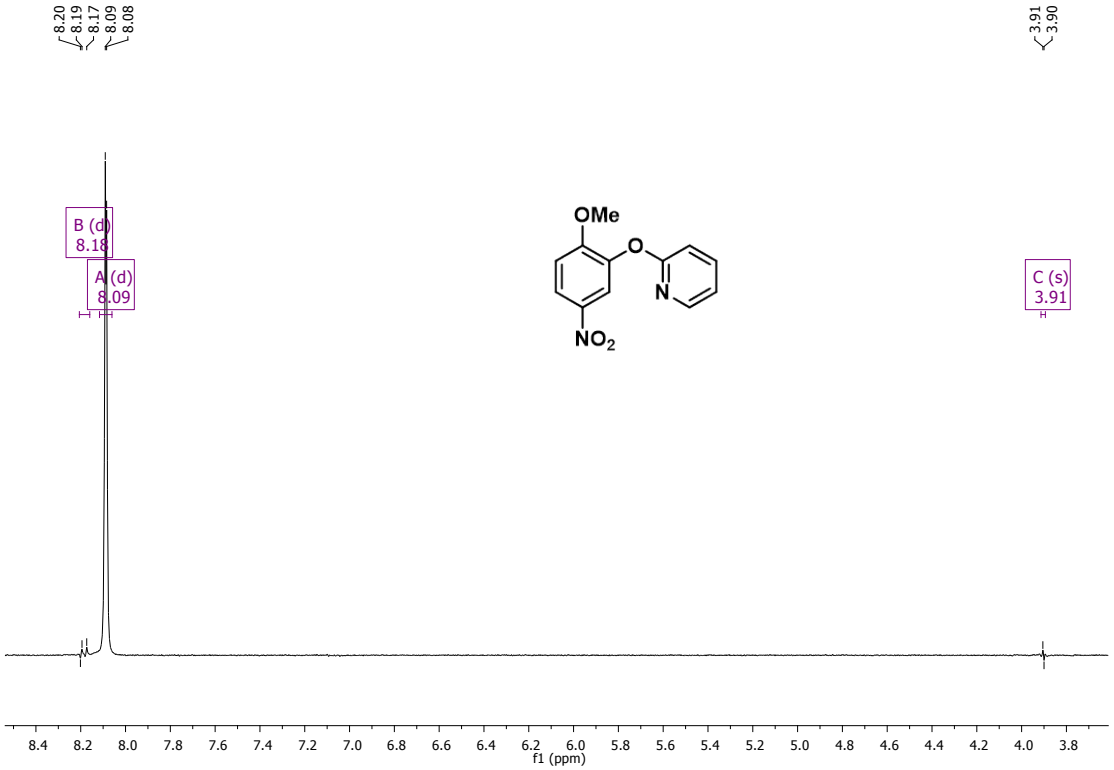
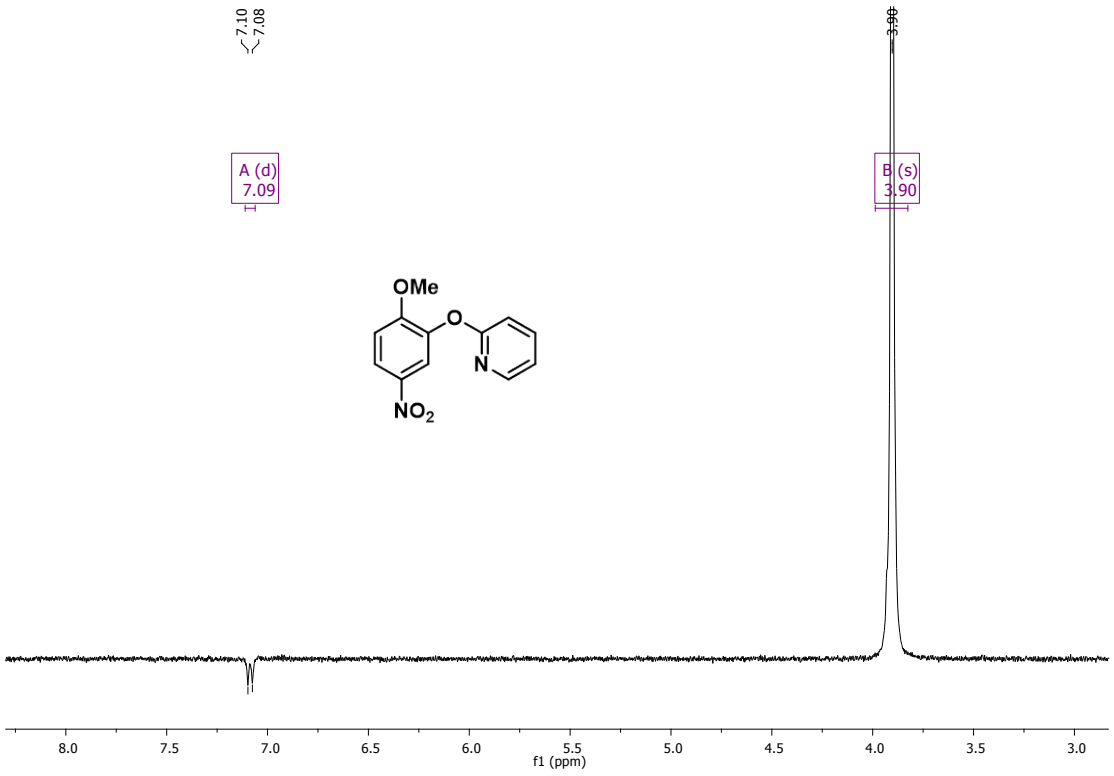

8.13
8.12
8.11
7.79
7.79
7.78
7.77
7.77
7.77
7.75
7.75
7.68
7.68
7.66
7.66
7.51
7.49
7.47
7.43
7.43
7.41
7.40
7.26 cdd3
7.08
7.08
7.08
7.07
7.06
7.06
7.05
7.05
Br
O2N
O
N
E (dd)
7.42
B (ddd)
7.77
F (ddd)
7.07
A (m)
8.12
D (t)
7.49
C (dd)
7.67
1.00
1.27
1.03
1.22
1.01
1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

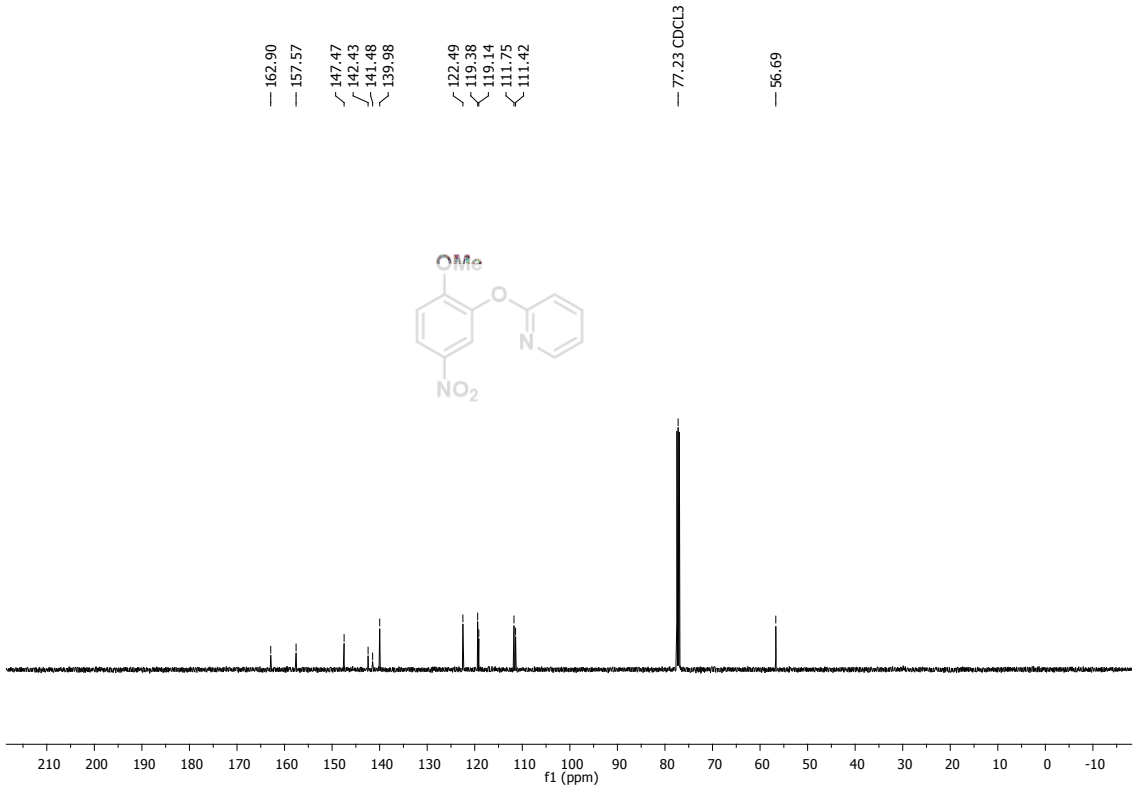
Table 2, 2k


8.18
8.17
8.16
8.15
8.11
8.11
8.07
8.06
7.76
7.74
7.72
7.26 cdcl3
7.07
7.05
7.04
7.02
3.88
OMe
O
N
NO2
D (m)
7.74
B (d)
8.11
A (m)
8.16
C (d)
8.06
E (m)
7.04
F (s)
3.88
1.00
0.86
1.00
1.00
2.93
2.75
f1 (ppm)
a
b
c
d
e
f
g
1.00
0.86
1.00
1.00
2.93

[1]D NOE


8.20
8.19
8.17
8.09
8.08
3.91
3.90
B (d)
8.18
A (d)
8.09
C (s)
3.91
OMe
O
N
NO2
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
f1 (ppm)


7.10
7.08
3.90
A (d)
7.09
B (s)
3.90
OMe
O
N
NO2
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
f1 (ppm)


162.90
157.57
147.47
142.43
141.48
139.98
122.49
119.38
119.14
111.75
111.42
77.23 CDCl3
56.69
OMe
O
N
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Scheme 3, 2l

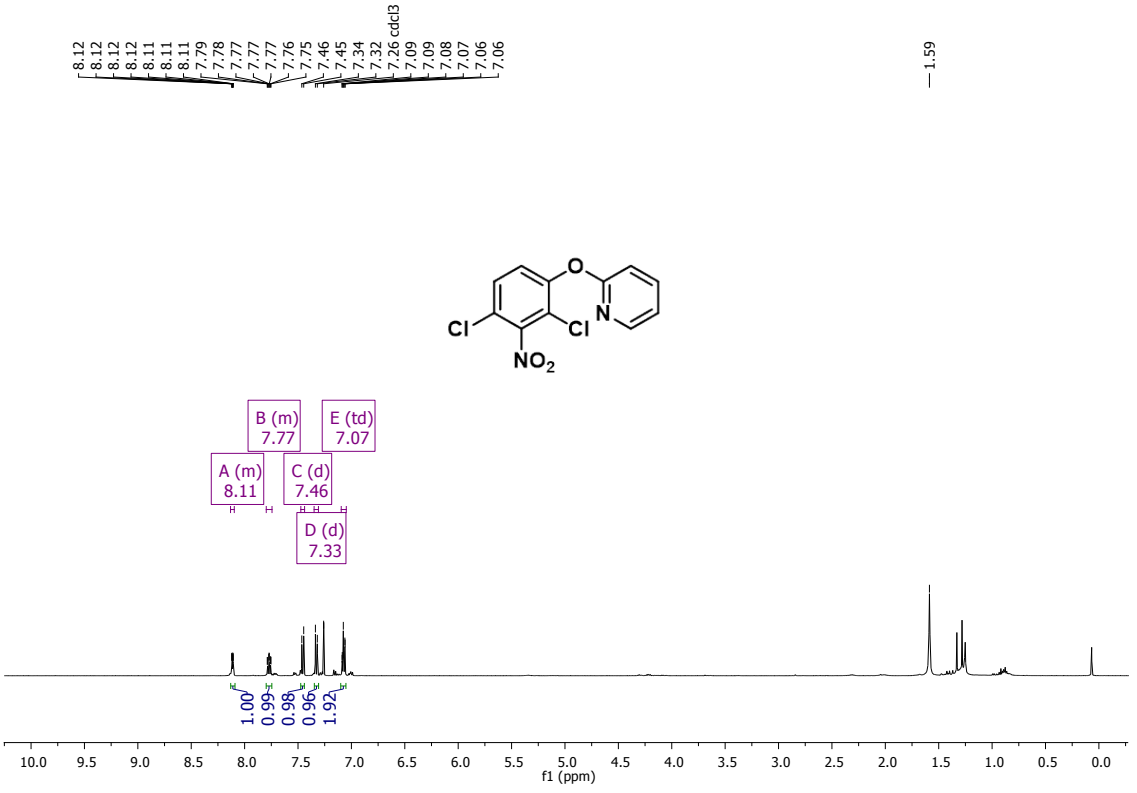

8.12
8.12
8.12
8.12
8.11
8.11
8.11
7.79
7.78
7.77
7.77
7.77
7.76
7.75
7.46
7.45
7.34
7.32
7.26 cdcl3
7.09
7.09
7.08
7.07
7.06
7.06
1.59
O
N
Cl
Cl
NO2
B (m)
7.77
E (td)
7.07
A (m)
8.11
C (d)
7.46
D (d)
7.33
1.00
0.99
0.98
0.96
1.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Table 2, 2m

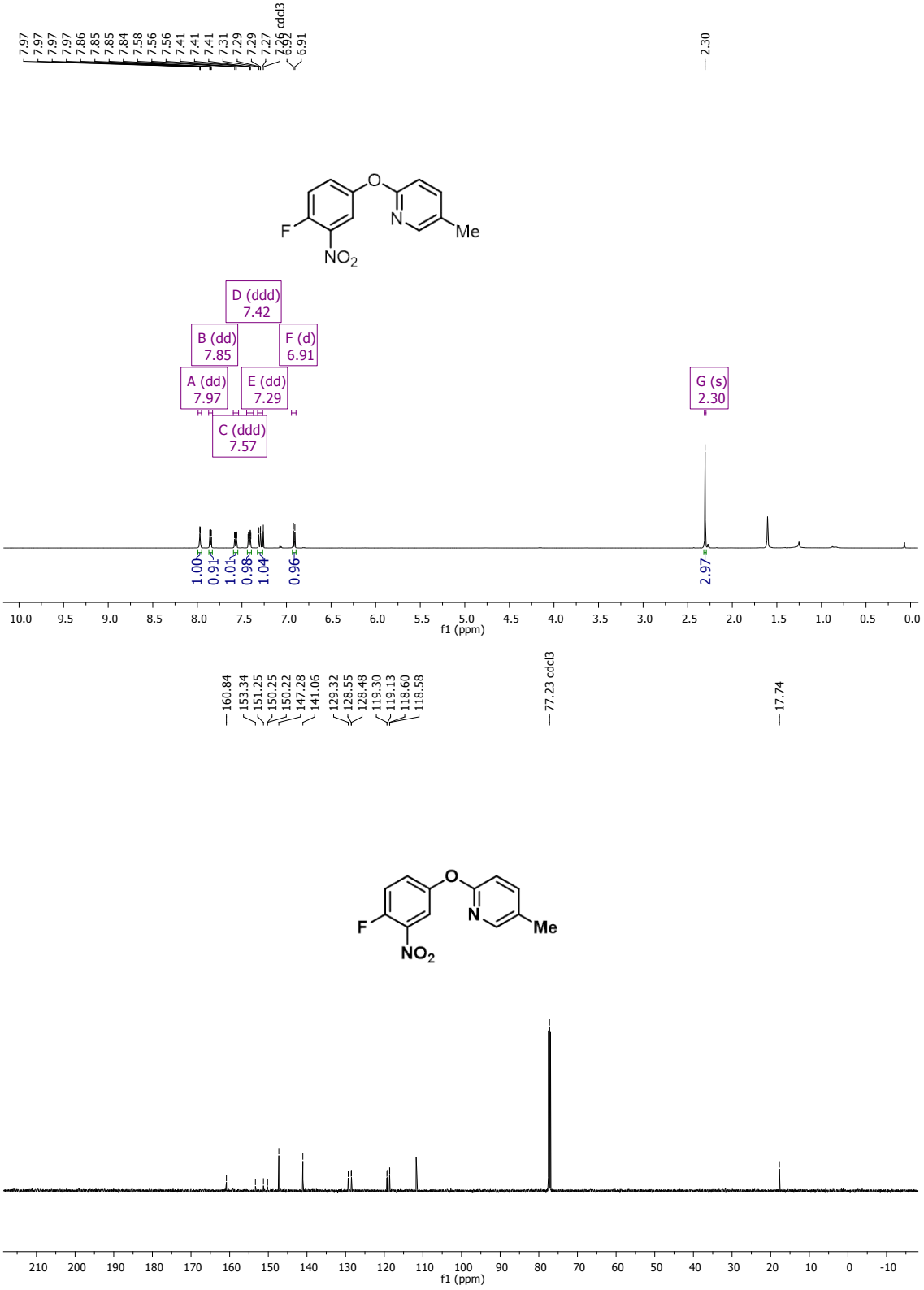

7.97
7.97
7.97
7.97
7.86
7.85
7.85
7.84
7.58
7.56
7.56
7.41
7.41
7.31
7.29
7.29
7.27
7.26 cdcl3
6.92
6.91
2.30
F
O
N
Me
NO2
D (ddd)
7.42
B (dd)
7.85
F (d)
6.91
A (dd)
7.97
E (dd)
7.29
C (ddd)
7.57
G (s)
2.30
1.00
0.91
1.01
0.98
1.04
0.96
2.97
f1 (ppm)
160.84
153.34
151.25
150.25
150.22
147.28
141.06
129.32
128.55
128.48
119.30
119.13
118.60
118.58
77.23 cdcl3
17.74
f1 (ppm)

Table 2, 2n

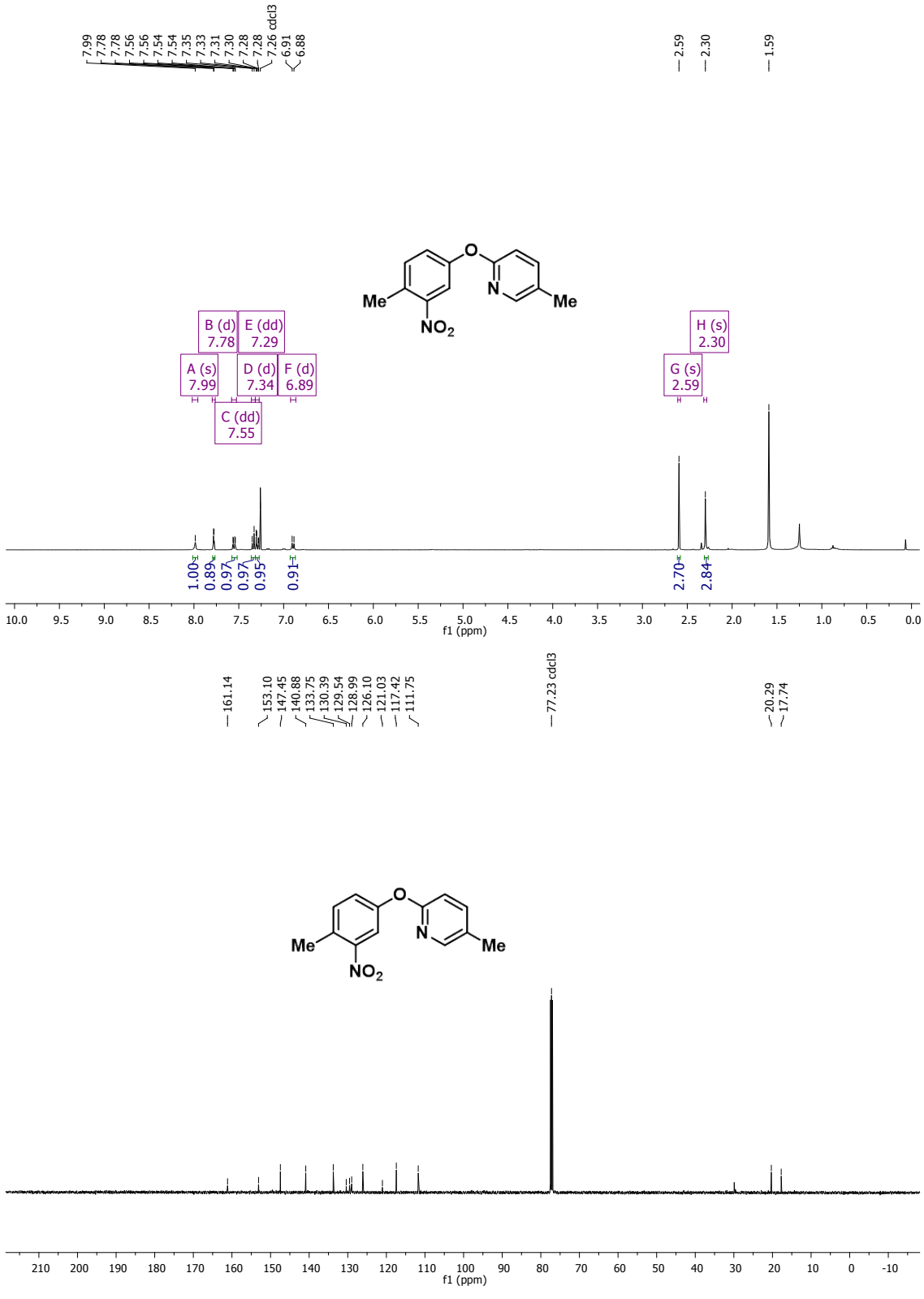

7.99
7.78
7.78
7.56
7.56
7.54
7.54
7.35
7.33
7.31
7.30
7.28
7.28
7.26 cdcl3
6.91
6.88
2.59
2.30
1.59
Me
NO2
N
O
Me
B (d) 7.78
E (dd) 7.29
A (s) 7.99
D (d) 7.34
F (d) 6.89
C (dd) 7.55
H (s) 2.30
G (s) 2.59
1.00
0.89
0.97
0.97
0.95
0.91
2.70
2.84
f1 (ppm)
161.14
153.10
147.45
140.88
133.75
130.39
129.54
128.99
126.10
121.03
117.42
111.75
77.23 cdcl3
20.29
17.74
f1 (ppm)

Table 2, 2o

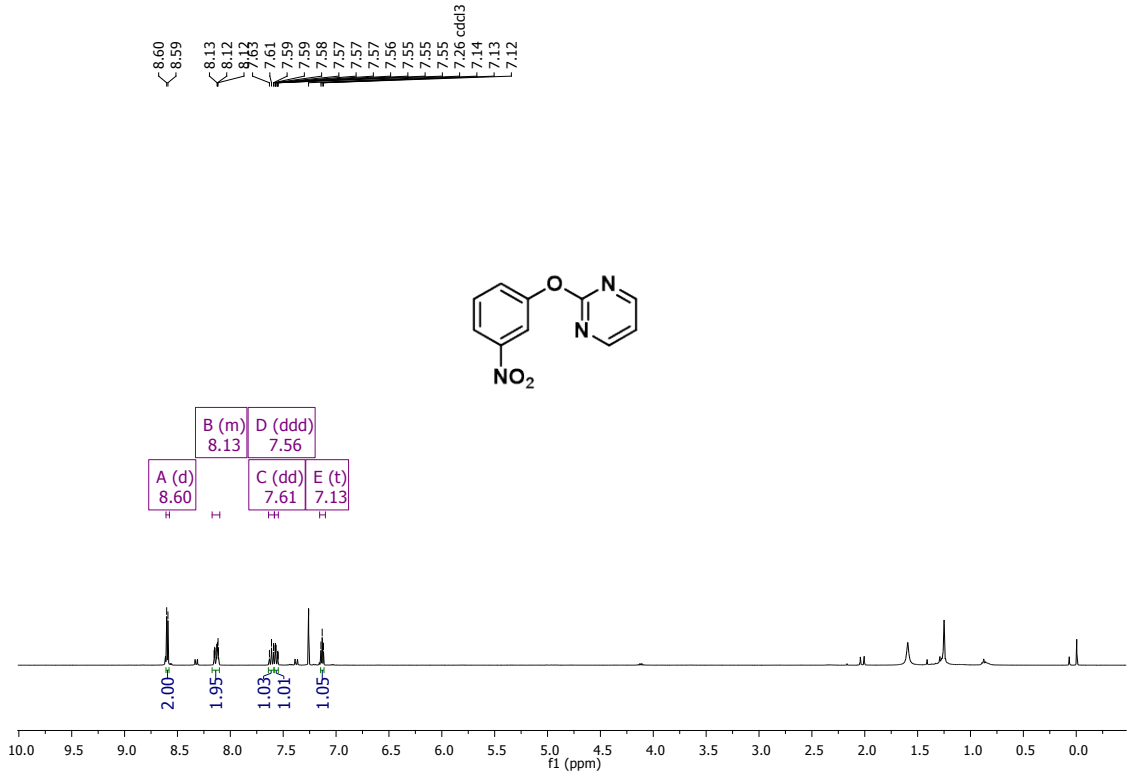
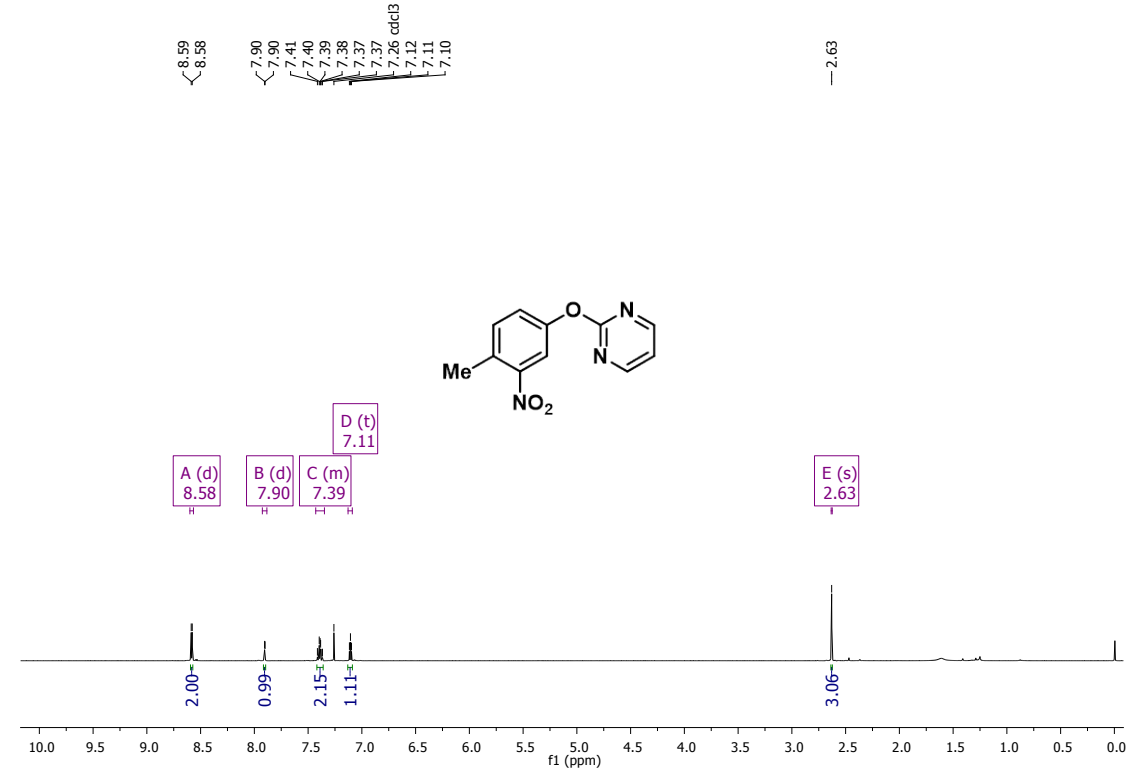
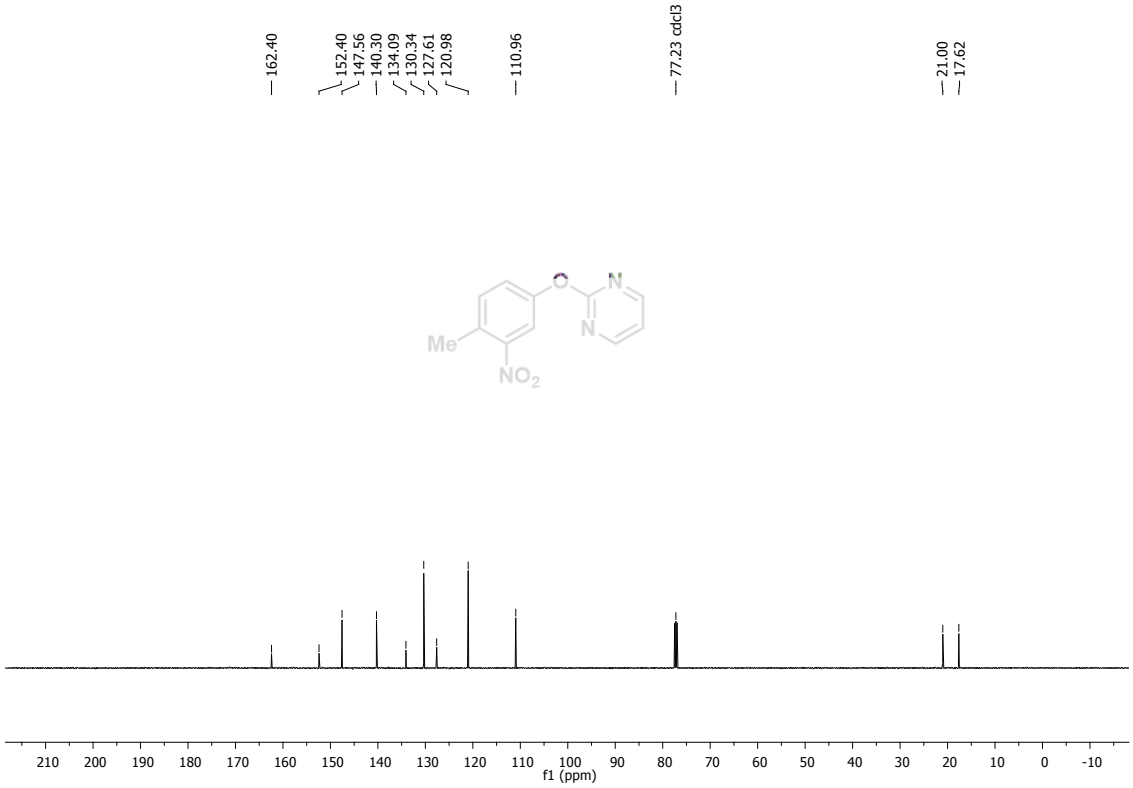
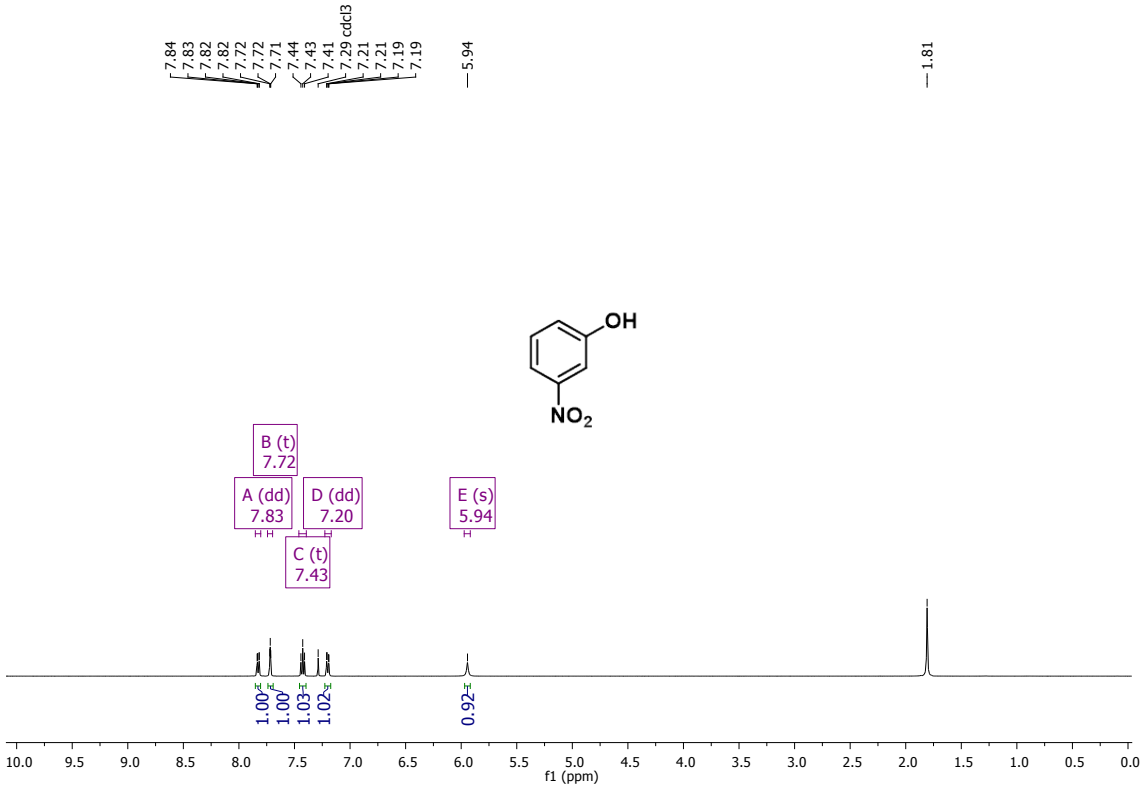


Table 2, 2p




162.40
152.40
147.56
140.30
134.09
130.34
127.61
120.98
110.96
77.23 cdcl3
21.00
17.62
Me
NO2
O
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Scheme 3, 3a


7.84
7.83
7.82
7.82
7.72
7.72
7.71
7.44
7.43
7.41
7.29 cdcl3
7.21
7.21
7.19
7.19
5.94
1.81
OH
NO2
B (t)
7.72
A (dd)
7.83
D (dd)
7.20
C (t)
7.43
E (s)
5.94
1.00
1.00
1.03
1.02
0.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)