Supporting Information

Copper catalyzed oxidative cascade deamination/cyclization of vinyl azide and benzylamine for the synthesis of 2,4,6-triarylpyridines

Rana Chatterjee,*[a] Swadhapriya Bhukta,[a] Kishore Kumar Angajala[b] and Rambabu Dandela*[a]

[a]*Department of Industrial and Engineering Chemistry,*
Institute of Chemical Technology, Indian Oil Odisha Campus, Samantpuri, Bhubaneswar 751013, India

[b]*Department of Humanities and Sciences, Vardhaman College of Engineering, Shamshabad, Hyderabad-501218, Telangana, India.*

Table of contents

1. Experimental Section

1.1. General Information

All starting materials and commercial reagent were purchased from Alfa Aesar, Sigma Aldrich, Avra, Spectrochem, TCI. Thin Layer Chromatography plates were visualizedby exposure to ultraviolet light (UV) with 254 nm of wavelength and then further analyzed byusing iodine chamber. Thin-layer chromatography was performed usingpre-coated plates. Column chromatography was performed in 120 to 200 mesh size silica gel.The reactions were carried out inround bottom flask and sealed tube. and all NMR spectra were recorded by Bruker Avance 400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts for ^{1}H NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Simillarly,^{13}C NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent as the internalstandard ($CDCl_3$: δ 77.0 ppm). The ^{1}H NMRand ^{13}C NMR of the known products were compared with literature reports.

1.2 Synthesis of trisubstituted pyridine (3):

In a 25 mL round bottom flask, vinyl azide (**1**) (290 mg, 2 mmol), iodine (76 mg, 30 mol%) was added in 2 mL DMF solvent at oxygen atmosphere (balloon pressure). The resulting mixture was stirred at 60 ℃ to 70 ℃ for 30 minutes, after that $Cu(OTf)_2$ (36 mg, 10 mol%) and benzyl amine (**2**, 107 mg, 1.0 mmol) was added to the reaction mixture and temperature was raised to 95 ℃ for another 12 h. After the reaction completed, monitoring by TLC, 10mL of cold water was added to the mixture, then extracted with EtOAc three times (3 × 15 mL). The extract was washed with 10% Na_2SO_3 solution (w/w), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to yield the desired product **3** as a pale-yellow solid.

2. Characterization data

2.1. X-ray crystallographic data for 3h:

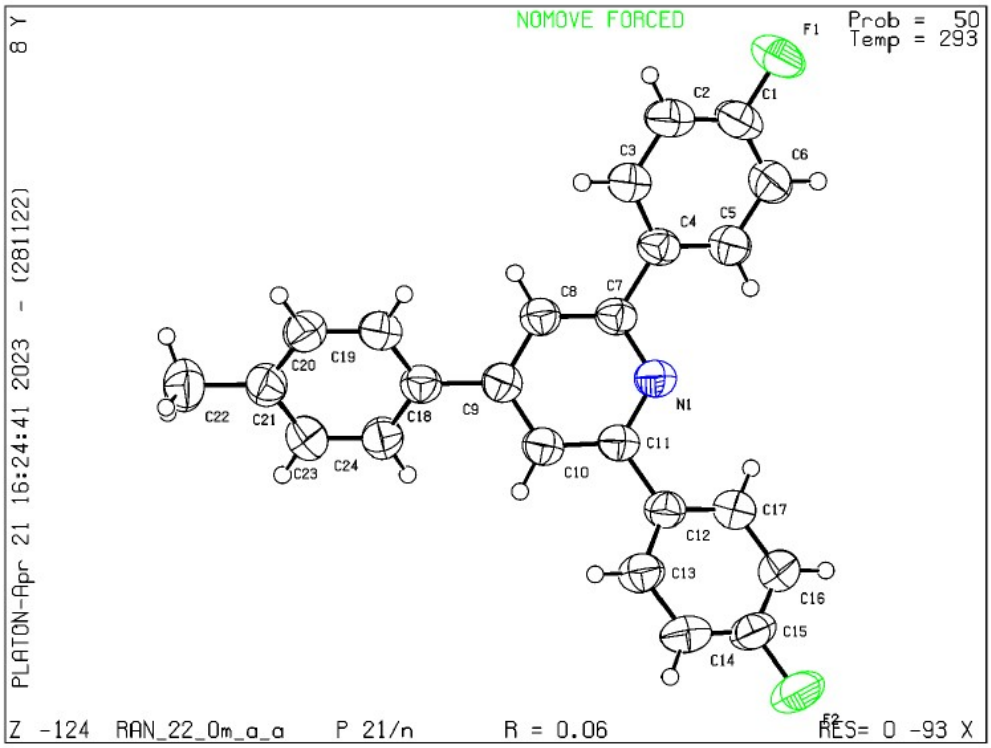


Fig. 1. X-ray crystal structure of **3h** with 50% ellipsoid probability

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with a CCDC reference number CCDC **2258109.**

Data collection and structure solution details:

The quality single crystals suitable for SC-XRD experiments of the compound were obtained from ethyl acetate and *n*-hexane solvent by the slow evaporation method. The single-crystal X-ray diffraction measurements were performed to determine the crystal structure of compounds at 273 K using APEX3 (Bruker, 2016; Bruker D8 Venture photon 100 CMOS detector) diffractometer having graphite-monochromatized (MoKα = 0.71073 Å). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5º steps φ/ω. The data were collected within a time frame of 10 sec for the three components by setting the sample to detector distance fixed at 40 cm. The data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and

SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2018) was used for structure solution and full-matrix least-squares refinement on F. The program(s) used to refine the molecular structures of compounds 1-3 is SHELXL 2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined by the anisotropic method and hydrogen atoms were either refined or placed in calculated positions. All the structural refinements converged to good R-factors, as listed in Table 1, and the intermolecular interactions were computed by using PLATON software. The molecular graphics of ORTEP diagrams were performed by XP software. The crystal symmetry of the three components was cross-checked by running the .cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The single-crystal data the crystal was collected on a Bruker diffractometer. The diffractometer is equipped with an APEX CCD area detector, using graphite-monochromatic Mo.Kα radiation (λ= 0.71073 Å). The data were collected in a φ and ω scan modes at room temperature and in all the cases the process was smooth and the crystals were found to be stable throughout the duration of the experiment. Bruker suite of data processing programme (SAINT) (SAINT; Bruker AXS, I. Analytical X-ray Systems 2000, 5373) has been used to process the intensity data and absorption corrections were applied using SADABS (SADABS; Siemens Industrial Automation, I. 1996). The structure solution for all the complexes has been carried out by direct methods and refinements were performed by full-matrix least-squares on F2 using the SHELXTL-PLUS suite of programs39 All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed using AFIX constraint.

Table 1 Crystal data and structure refinement for 3h.

Identification code	3h
Empirical formula	$C_{24}H_{17}F_2N$
Formula weight	357.38
Temperature/K	293(2)
Crystal shape	block
Crystal colour	colourless
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.748(13)
b/Å	7.359(5)
c/Å	21.472(14)

α/°	90
β/°	94.50(3)
γ/°	90
Volume/Å^3	1851(3)
Z	4
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	0.088
F(000)	744.0
Crystal size/mm^3	0.24 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.854 to 52.568
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -26 ≤ l ≤ 25
Reflections collected	27658
Independent reflections	3738 [R_{int} = 0.0996, R_{sigma} = 0.0590]
Data/restraints/parameters	3738/0/246
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1466
Final R indexes [all data]	R_1 = 0.1056, wR_2 = 0.1909
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3h. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F2	748.6(11)	9065(3)	6640.8(8)	100.5(6)
F1	9480.7(15)	7281(3)	9545.3(7)	104.8(6)
N1	6039.1(15)	7605(2)	7134.7(8)	55.2(5)
C7	7175.0(18)	7310(3)	7152.2(10)	52.8(5)
C4	7798.0(18)	7299(3)	7789.2(10)	54.1(6)
C8	7733.6(19)	7030(3)	6614.7(10)	56.4(6)
C18	7720.4(18)	6839(3)	5447.4(10)	55.8(6)
C12	4198.8(18)	8026(3)	6577.2(10)	56.2(6)
C24	7205(2)	5912(3)	4932.7(10)	64.1(6)
C9	7131.9(18)	7090(3)	6028.9(10)	54.5(5)
C11	5445.8(18)	7665(3)	6568.1(10)	53.1(5)
C21	8868(2)	6314(3)	4347.9(11)	64.6(6)
C13	3584.4(19)	8940(3)	6090.3(11)	66.4(6)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3h. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C10	5965.7(19)	7418(3)	6014.9(11)	57.3(6)
C3	8946(2)	7761(3)	7876.2(11)	65.1(6)
C23	7772(2)	5664(3)	4396.8(11)	68.1(7)
C19	8822(2)	7510(4)	5396.9(11)	66.2(7)
C20	9377(2)	7250(4)	4858.2(12)	70.4(7)
C5	7230(2)	6849(3)	8310.4(10)	62.6(6)
C17	3613(2)	7453(4)	7081.7(11)	68.6(7)
C15	1899.3(19)	8717(4)	6617.4(13)	70.7(7)
C14	2425(2)	9291(4)	6112.5(13)	74.0(7)
C16	2455(2)	7793(4)	7107.3(13)	78.1(8)
C22	9478(2)	6042(5)	3762.9(12)	90.2(9)
C6	7788(2)	6848(4)	8901.3(11)	71.6(7)
C2	9516(2)	7763(4)	8469.0(12)	72.8(7)
C1	8916(2)	7298(4)	8961.8(11)	71.2(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3h. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F2	48.0(8)	134.2(15)	118.2(13)	-20.1(11)	-0.2(8)	11.9(8)
F1	101.8(13)	143.1(17)	64.2(9)	-10.2(9)	-28.0(8)	14.8(11)
N1	51.4(11)	55.2(11)	57.9(11)	-1.9(8)	-2.7(8)	3.0(8)
C7	52.9(12)	47.7(12)	56.5(12)	-1.9(9)	-3.4(9)	3.8(9)
C4	55.1(13)	48.8(12)	56.7(13)	-2.9(9)	-5.5(10)	7.5(10)
C8	52.0(12)	59.6(14)	56.8(13)	-3.0(10)	-0.9(10)	5.9(10)
C18	53.9(13)	57.6(13)	55.4(12)	1.2(10)	0.1(9)	3.9(10)
C12	50.7(12)	60.3(14)	56.5(13)	-5.5(10)	-2.6(9)	0.9(10)
C24	59.3(14)	71.0(16)	62.0(14)	-4.4(11)	5.6(11)	-7.0(12)
C9	56.6(13)	52.1(13)	54.4(12)	-1.3(9)	1.8(10)	2.5(10)
C11	51.1(12)	51.0(12)	55.9(12)	-1.6(9)	-4.3(9)	2.4(10)
C21	66.3(15)	69.0(16)	59.0(14)	10.2(11)	8.3(11)	10.5(12)
C13	55.3(14)	70.8(16)	72.1(15)	8.3(12)	-1.2(11)	1.9(12)
C10	56.0(13)	59.0(14)	55.6(13)	-1.1(10)	-3.4(10)	2.9(10)
C3	58.3(14)	74.0(16)	62.0(14)	1.3(11)	-2.3(11)	-0.1(12)
C23	74.8(16)	70.9(16)	58.4(14)	-4.7(11)	3.4(11)	-0.5(13)
C19	57.6(14)	79.5(17)	60.0(14)	2.6(11)	-3.9(11)	-1.6(12)
C20	55.5(14)	86.7(19)	68.9(15)	9.4(13)	5.0(11)	-1.8(13)
C5	60.3(14)	67.6(15)	59.2(14)	-2.1(11)	-0.5(10)	4.3(11)
C17	58.5(14)	88.2(18)	57.9(14)	-2.0(12)	-2.5(11)	3.3(13)
C15	43.8(13)	84.3(18)	83.0(17)	-18.2(14)	-1.7(12)	3.8(12)
C14	55.5(14)	76.5(17)	87.4(18)	3.1(14)	-10.8(13)	7.9(13)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3h. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	58.7(15)	110(2)	66.1(15)	-10.4(14)	5.7(12)	-1.0(14)
C22	91(2)	112(2)	71.0(17)	9.7(15)	24.4(14)	11.0(17)
C6	74.7(17)	80.3(18)	59.0(14)	-0.3(12)	0.1(12)	7.7(14)
C2	61.2(15)	79.2(18)	75.1(17)	-4.6(13)	-13.5(12)	0.8(13)
C1	78.7(18)	76.3(17)	55.1(14)	-7.6(12)	-16.6(12)	12.4(14)

Table 4 Bond Lengths for 3h.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F2	C15	1.381(3)	C24	C23	1.386(3)
F1	C1	1.371(3)	C9	C10	1.389(3)
N1	C7	1.350(3)	C11	C10	1.390(3)
N1	C11	1.355(3)	C21	C23	1.385(4)
C7	C4	1.500(3)	C21	C20	1.389(4)
C7	C8	1.387(3)	C21	C22	1.507(3)
C4	C3	1.389(3)	C13	C14	1.391(4)
C4	C5	1.387(3)	C3	C2	1.391(3)
C8	C9	1.394(3)	C19	C20	1.385(3)
C18	C24	1.396(3)	C5	C6	1.382(3)
C18	C9	1.485(3)	C17	C16	1.389(4)
C18	C19	1.397(3)	C15	C14	1.356(4)
C12	C11	1.490(3)	C15	C16	1.374(4)
C12	C13	1.396(3)	C6	C1	1.362(4)
C12	C17	1.393(3)	C2	C1	1.361(4)

Table 5 Bond Angles for 3h.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C11	117.92(18)	C23	C21	C20	117.2(2)
N1	C7	C4	115.90(19)	C23	C21	C22	121.5(2)
N1	C7	C8	122.1(2)	C20	C21	C22	121.3(2)
C8	C7	C4	122.0(2)	C14	C13	C12	120.9(2)
C3	C4	C7	121.4(2)	C9	C10	C11	120.2(2)
C5	C4	C7	120.4(2)	C4	C3	C2	121.1(2)
C5	C4	C3	118.2(2)	C21	C23	C24	121.8(2)
C7	C8	C9	120.4(2)	C20	C19	C18	121.0(2)
C24	C18	C9	121.6(2)	C19	C20	C21	121.7(2)
C24	C18	C19	117.3(2)	C6	C5	C4	121.1(2)
C19	C18	C9	121.1(2)	C16	C17	C12	121.4(2)
C13	C12	C11	121.8(2)	C14	C15	F2	118.6(2)
C17	C12	C11	120.2(2)	C14	C15	C16	123.2(2)

Table 5 Bond Angles for 3h.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	C12	C13	118.0(2)	C16	C15	F2	118.2(2)
C23	C24	C18	121.0(2)	C15	C14	C13	118.5(2)
C8	C9	C18	121.2(2)	C15	C16	C17	117.8(2)
C10	C9	C8	117.0(2)	C1	C6	C5	118.4(2)
C10	C9	C18	121.78(19)	C1	C2	C3	118.0(2)
N1	C11	C12	115.54(19)	C6	C1	F1	118.8(2)
N1	C11	C10	122.3(2)	C2	C1	F1	118.0(3)
C10	C11	C12	122.20(19)	C2	C1	C6	123.1(2)

Table 6 Torsion Angles for 3h.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F2	C15	C14	C13	179.9(2)	C9	C18	C24	C23	-179.0(2)
F2	C15	C16	C17	-179.7(2)	C9	C18	C19	C20	178.9(2)
N1	C7	C4	C3	-153.0(2)	C11	N1	C7	C4	178.59(18)
N1	C7	C4	C5	26.1(3)	C11	N1	C7	C8	-1.5(3)
N1	C7	C8	C9	1.5(3)	C11	C12	C13	C14	-178.9(2)
N1	C11	C10	C9	0.2(3)	C11	C12	C17	C16	179.1(2)
C7	N1	C11	C12	-179.04(19)	C13	C12	C11	N1	149.5(2)
C7	N1	C11	C10	0.6(3)	C13	C12	C11	C10	-30.2(3)
C7	C4	C3	C2	179.5(2)	C13	C12	C17	C16	-0.7(4)
C7	C4	C5	C6	-179.4(2)	C3	C4	C5	C6	-0.3(3)
C7	C8	C9	C18	178.5(2)	C3	C2	C1	F1	179.3(2)
C7	C8	C9	C10	-0.7(3)	C3	C2	C1	C6	-0.6(4)
C4	C7	C8	C9	-178.5(2)	C23	C21	C20	C19	0.7(4)
C4	C3	C2	C1	0.1(4)	C19	C18	C24	C23	0.3(4)
C4	C5	C6	C1	-0.2(4)	C19	C18	C9	C8	-35.9(3)
C8	C7	C4	C3	27.1(3)	C19	C18	C9	C10	143.2(2)
C8	C7	C4	C5	-153.8(2)	C20	C21	C23	C24	-0.7(4)
C8	C9	C10	C11	-0.2(3)	C5	C4	C3	C2	0.4(3)
C18	C24	C23	C21	0.2(4)	C5	C6	C1	F1	-179.3(2)
C18	C9	C10	C11	-179.3(2)	C5	C6	C1	C2	0.6(4)
C18	C19	C20	C21	-0.1(4)	C17	C12	C11	N1	-30.2(3)
C12	C11	C10	C9	179.8(2)	C17	C12	C11	C10	150.1(2)
C12	C13	C14	C15	-0.4(4)	C17	C12	C13	C14	0.9(4)
C12	C17	C16	C15	0.0(4)	C14	C15	C16	C17	0.6(4)
C24	C18	C9	C8	143.4(2)	C16	C15	C14	C13	-0.4(4)
C24	C18	C9	C10	-37.5(3)	C22	C21	C23	C24	-179.9(2)
C24	C18	C19	C20	-0.4(4)	C22	C21	C20	C19	179.8(2)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3h.

Atom	*x*	*y*	*z*	U(eq)
H8	8514.56	6801.54	6645.2	68
H24	6470.17	5452.83	4949.68	77
H13	3955.6	9319.1	5746.12	80
H10	5531.45	7472.08	5634.07	69
H3	9339.65	8073.46	7532.58	78
H23	7405.93	5044.6	4060.6	82
H19	9188.4	8141.2	5730.2	79
H20	10109.73	7713.07	4837.61	84
H5	6460.34	6541.54	8261.31	75
H17	4006.46	6830.49	7408.37	82
H14	2018.62	9906.93	5788.43	89
H16	2068.09	7407.57	7445.12	94
H22A	9151.15	5023.27	3534.05	135
H22B	10272.64	5816.51	3873.67	135
H22C	9397.5	7114.39	3508.5	135
H6	7403.35	6548.44	9249.37	86
H2	10284.73	8073.24	8526.74	87

Experimental

Single crystals of $C_{24}H_{17}F_2N$ **3h** were collected by slow evaporation. A suitable crystal was selected on a Bruker D8 quest photon detector diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 3h

Crystal Data for $C_{24}H_{17}F_2N$ (M =357.38 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.748(13) Å, b = 7.359(5) Å, c = 21.472(14) Å, β = 94.50(3)°, V = 1851(3) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.088 mm^{-1}, *Dcalc* = 1.283 g/cm^3, 27658 reflections measured (5.854° ≤ 2Θ ≤ 52.568°), 3738 unique (R_{int} = 0.0996, R_{sigma} = 0.0590) which were used in all calculations. The final R_1 was 0.0571 (I > 2σ(I)) and wR_2 was 0.1909 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C8(H8), C24(H24), C13(H13), C10(H10), C3(H3), C23(H23), C19(H19),
C20(H20),
```

```
 C5(H5), C17(H17), C14(H14), C16(H16), C6(H6), C2(H2)
2.b Idealised Me refined as rotating group:
 C22(H22A,H22B,H22C)
```

2.2. ^{1}H and ^{13}C data of compounds

2,4,6-triphenylpyridine (3a)[1]

(Yield: 90%, 276 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.1 Hz, 4H), 7.80 (s, 2H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.39 (m, 6H), 7.40 – 7.31 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.54, 150.26, 139.59, 139.10, 129.04, 129.08, 129.01, 128.94, 128.73, 127.21, 127.18, 117.16.

4-phenyl-2,6-di-p-tolylpyridine (3b)[1]

(Yield: 84%, 281 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.4 Hz, 4H), 7.88 (s, 2H), 7.78 (d, *J* = 6.8 Hz, 2H), 7.61 – 7.47 (m, 3H), 7.36 (d, *J* = 7.3 Hz, 4H), 2.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.43, 150.05, 139.30, 138.99, 136.92, 129.43, 129.09, 128.89, 127.12 (d, *J* = 18.3 Hz), 116.55, 21.35.

2,6-bis(4-fluorophenyl)-4-phenylpyridine (3c)[1]

(Yield: 85%, 291 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 4H), 7.86 (s, 2H), 7.76 (d, *J* = 7.0 Hz, 2H), 7.55 (dt, *J* = 13.3, 6.5 Hz, 3H), 7.23 (t, *J* = 8.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.92, 162.44, 156.53, 138.88, 129.03 (dd, *J* = 24.0, 6.2 Hz), 127.17, 116.75, 115.75, 115.54.

2,6-bis(4-chlorophenyl)-4-phenylpyridine (3d)[1]

(Yield: 87%, 326 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 4H), 7.79 (s, 2H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.39, 150.67, 138.71, 137.75, 135.35, 129.20, 128.94, 128.40, 127.17, 117.16.

2,6-bis(2-methoxyphenyl)-4-phenylpyridine (3e)[2]

(Yield: 67%, 245 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 4H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.36 (d, *J* = 6.9 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.17, 155.95, 147.82, 139.49, 131.62, 129.81, 129.27 (d, *J* = 61.0 Hz), 128.89 – 128.87 (m), 128.58, 127.38, 121.46, 121.11, 111.52, 77.36, 77.04, 76.72, 55.79.

2,6-diphenyl-4-(p-tolyl)pyridine (3f)[1]

(Yield: 86%, 276 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 4H), 7.77 (s, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 4H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50, 150.12, 139.70, 139.12, 136.12, 129.87, 129.03, 128.72, 127.12 (d, *J* = 15.5 Hz), 116.94, 21.28.

2,4,6-tri-p-tolylpyridine (3g)[3]

(Yield: 79%, 275 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 4H), 7.70 (s, 2H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 6H), 2.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.40, 149.93, 138.95 (d, *J* = 4.4 Hz), 137.04, 136.34, 129.83, 129.43, 127.06 (d, *J* = 2.2 Hz), 116.34, 21.32 (d, *J* = 7.5 Hz).

2,6-bis(4-fluorophenyl)-4-(p-tolyl)pyridine (3h)[3]

(Yield: 84%, 299 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.6 Hz), 7.69, 7.52 (d, *J* = 7.5 Hz), 7.23 (d, *J* = 7.4 Hz), 7.09 (t, *J* = 8.3 Hz), 2.34. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.89, 162.42, 156.44, 150.34, 139.28, 135.96 – 135.55 (m), 129.89, 128.91 (d, *J* = 8.2 Hz), 126.98, 116.47, 115.71, 115.50, 21.26.

2,6-bis(4-chlorophenyl)-4-(p-tolyl)pyridine (3i)[4]

(Yield: 81%, 315 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 4H), 7.84 (s, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 4H), 7.36 (d, *J* = 7.3 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.26, 150.37, 139.37, 137.87, 135.69, 135.24, 129.91, 128.89, 128.35, 126.97, 116.81, 21.29.

4-(4-methoxyphenyl)-2,6-diphenylpyridine (3j)[2]

(Yield: 78%, 262 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 4H), 7.77 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 4H), 7.36 (d, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.53, 157.47, 149.70, 139.71, 131.31, 129.00, 128.70, 128.35, 127.17, 116.64, 114.58, 55.44.

4-(4-methoxyphenyl)-2,6-di-p-tolylpyridine (3k)[2]

(Yield: 71%, 259 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 4H), 7.72 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.42, 157.37, 149.47, 138.87, 137.06, 131.56, 129.39, 128.32, 127.00, 116.03, 114.52, 55.43, 21.31.

2,6-bis(4-fluorophenyl)-4-(4-methoxyphenyl)pyridine (3l)[2]

(Yield: 79%, 294 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 4.7 Hz, 4H), 7.69 (s, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 8.1 Hz, 4H), 6.96 (d, *J* = 7.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.87, 162.40, 160.63, 156.44, 149.93, 135.70 (d, *J* = 3.1 Hz), 131.05, 128.90 (d, *J* = 8.3 Hz), 128.32, 116.19, 115.70, 115.49, 114.61, 55.44.

2,6-bis(4-chlorophenyl)-4-(4-methoxyphenyl)pyridine (3m)[2]

(Yield: 74%, 299 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.5 Hz, 4H), 7.84 (s, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 4H), 7.29 (s, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.67, 156.31, 150.02, 137.94, 135.22, 130.90, 128.89, 128.34 (d, *J* = 3.5 Hz), 116.56, 114.63, 55.46.

4-(4-fluorophenyl)-2,6-diphenylpyridine (3n)[1]

(Yield: 82%, 266 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.1 Hz, 4H), 7.77 (s, 2H), 7.66 (d, *J* = 4.7 Hz, 2H), 7.48 – 7.38 (m, 6H), 7.19 – 7.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.59, 149.30, 139.32, 135.14, 129.34 – 128.65 (m), 127.20, 117.01, 116.27, 116.05, 109.92.

4-(4-fluorophenyl)-2,6-di-p-tolylpyridine (3o)[2]

(Yield: 77%, 271 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 4H), 7.70 (s, 2H), 7.64 (d, *J* = 4.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 4H), 7.13 (t, *J* = 8.4 Hz, 2H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.63, 162.15, 157.49, 149.07, 139.12, 136.68, 129.43, 128.93 (d, *J* = 8.3 Hz), 127.04, 116.27 (d, *J* = 17.4 Hz), 115.96, 21.32.

2,4,6-tris(4-fluorophenyl)pyridine (3p)[3]

(Yield: 79%, 285 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.4 Hz, 2H), 7.80 (s, 1H), 7.74 (d, *J* = 4.4 Hz, 1H), 7.24 (dd, *J* = 17.8, 8.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.95, 162.47, 156.61, 149.44, 135.50, 134.95, 129.07 – 128.76 (m), 116.50, 116.30, 116.08, 115.77, 115.56.

2,6-bis(4-chlorophenyl)-4-(4-fluorophenyl)pyridine (3q)[5]

(Yield: 76%, 298 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.73 (s, 1H), 7.64 (d, *J* = 4.2 Hz, 1H), 7.44 (dd, *J* = 19.1, 7.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.98, 163.72, 156.46, 149.88, 137.56, 135.47, 130.58 (d, *J* = 8.6 Hz), 129.29 (d, *J* = 15.5 Hz), 128.97, 128.47 (d, *J* = 14.2 Hz), 116.96, 116.36, 116.14, 115.55, 115.34.

4-(4-fluorophenyl)-2,6-bis(2-methoxyphenyl)pyridine (3r)

White solid (Yield: 64%, 246 mg, m.p: 124-127 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 4.6 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 8.3 Hz, 1H), 7.00 (t, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.48, 162.01, 157.16, 156.09, 146.70, 135.59 (d, *J* = 3.2 Hz), 131.61, 129.87, 129.53, 129.05 (d, *J* = 8.2 Hz), 121.18 (d, *J* = 8.5 Hz), 116.05, 115.84, 111.52, 55.77; HRMS (ESI-MS) calcd for $C_{25}H_{20}FNO_2$ $[M+H]^+$: 386.1551, found: 386.1558.

4-(4-fluorophenyl)-2,6-bis(4-methoxyphenyl)pyridine (3s)[6]

(Yield: 70%, 269 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 2H), 7.09 (t, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.58, 162.11, 160.61, 157.04, 148.95, 135.45 (d, *J* = 3.3 Hz), 132.22, 128.90 (d, *J* = 8.3 Hz), 128.39, 116.14, 115.92, 115.45, 114.08, 55.38.

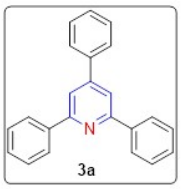
2.3 References:

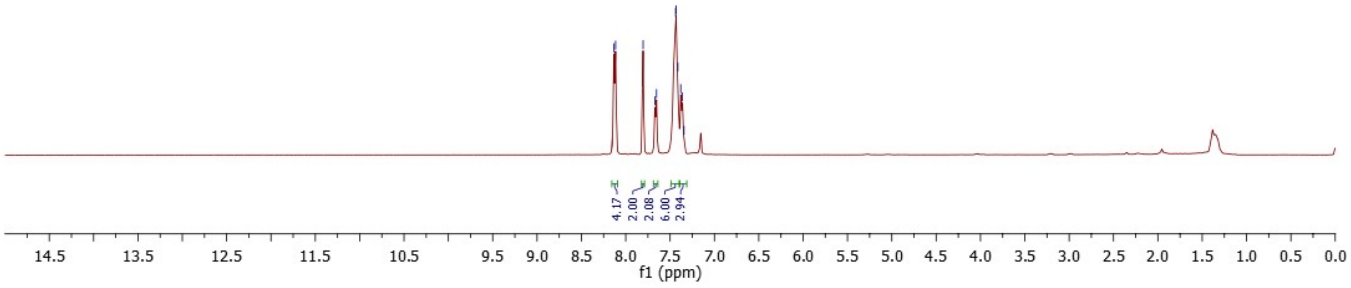
1. Q. Yang, Y. Zhang, W. Zeng, Z. C. Duan, X. Sang and D. Wang, *Green Chem*., 2019, **21**, 5683.
2. R. S. Rohokale, B. Koenig and D. D. Dhavale, *J. Org. Chem*., 2016, **81**, 7121.
3. X. Zhang, Z. Wang, K. Xu, Y. Feng, W. Zhao, X. Xu, Y. Yan and W. Yi, *Green Chem*., 2016, **18**, 2313.
4. M. Adib, N. Ayashi and P. Mirzaei, *Synlett*, 2016, **27**, 417.
5. M. Roozifar, N. Hazeri, and H. F. Niya, *J. Heterocyclic. Chem*., 2021, **58**, 1117.
6. F. Ling, L. Shen, Z. Pan, L. Fang, D. Song, Z. Xie and W. Zhong, *Tetrahedron Lett*., 2018, **59**, 3678.

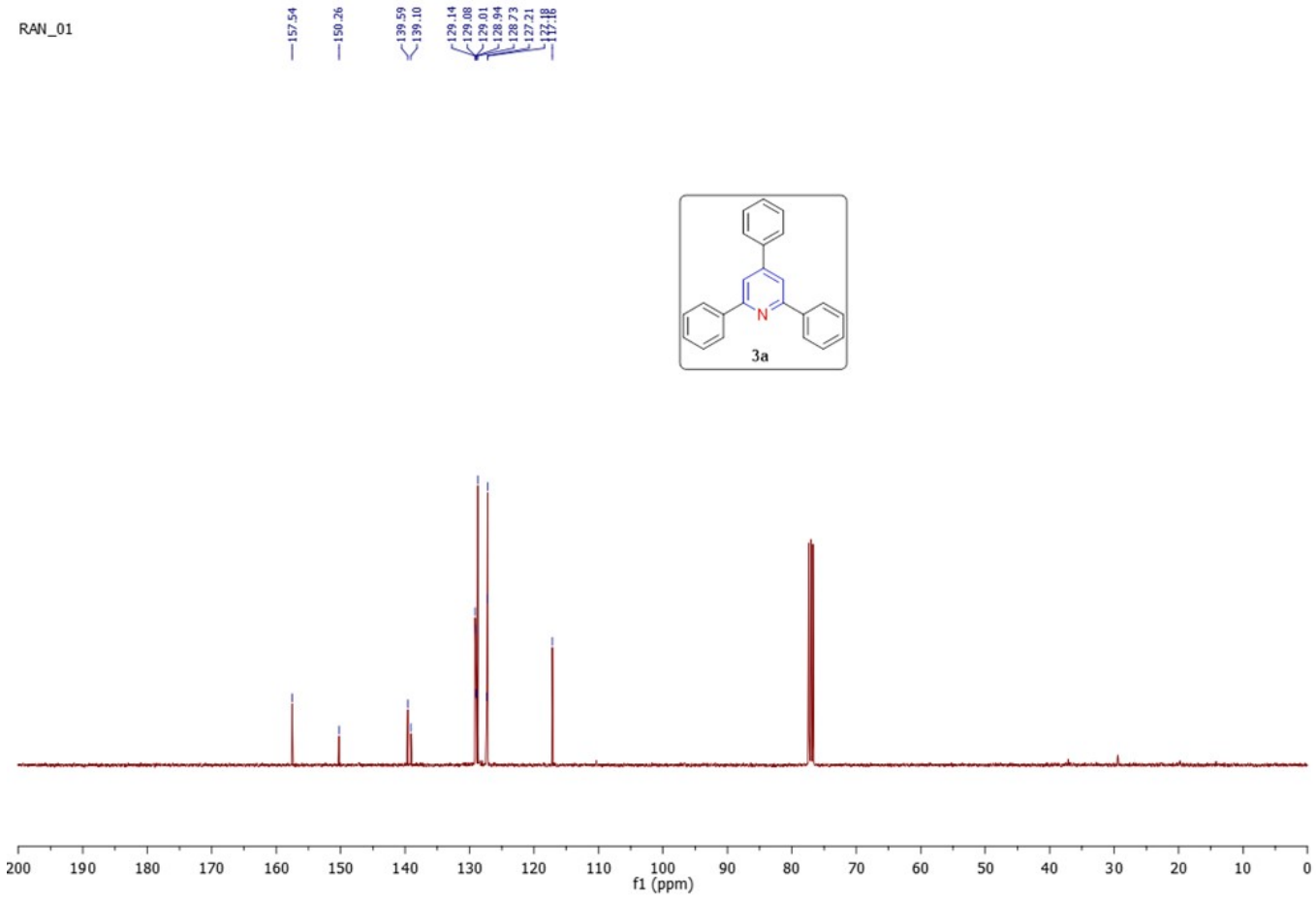
^{1}H and ^{13}C NMR Spectra of Compounds

RAN_01

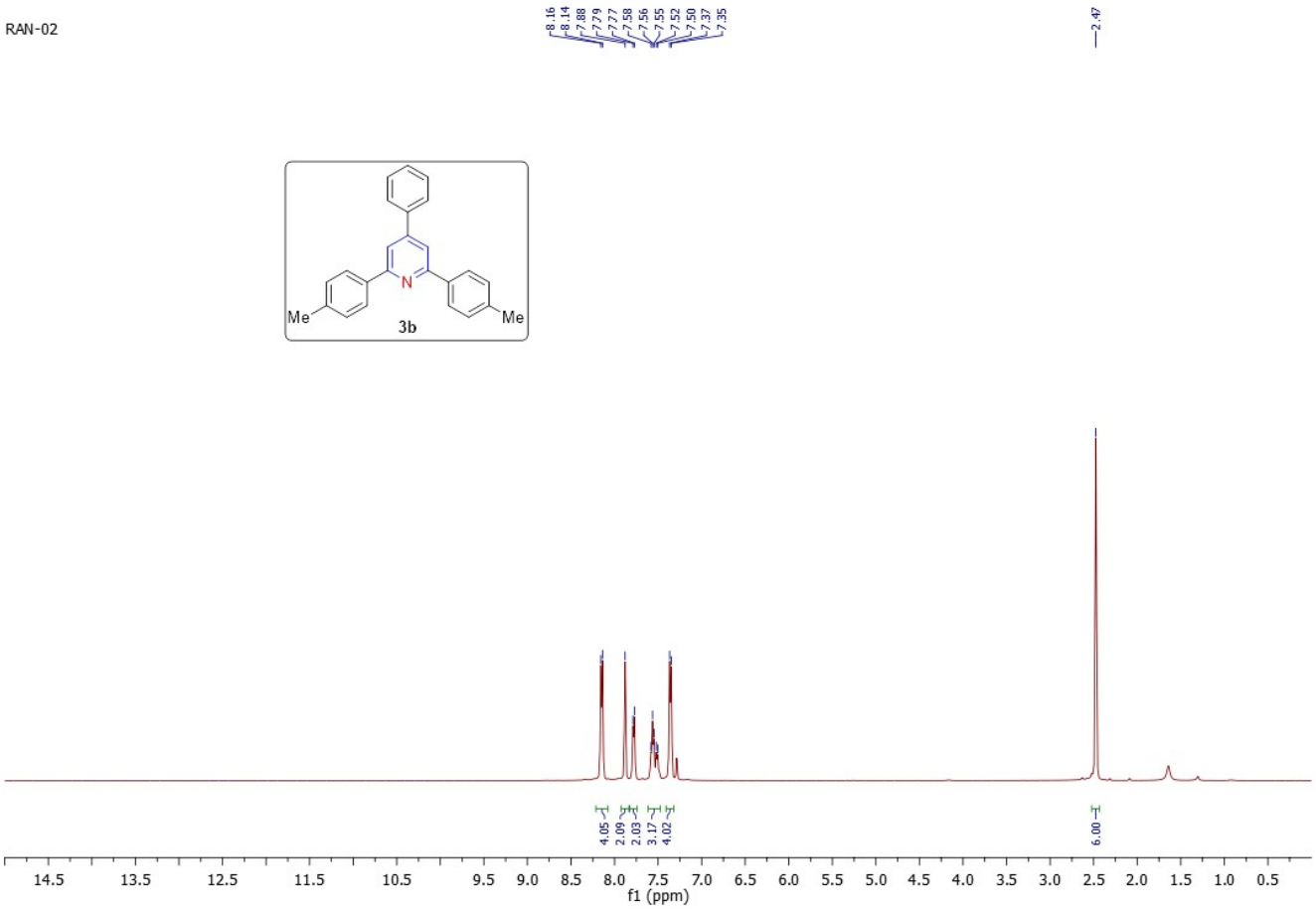

8.13
8.11
7.80
7.67
7.65
7.44
7.43
7.41
7.38
7.36
7.34


N
3a


4.17
2.00
2.08
6.00
2.94
14.5
13.5
12.5
11.5
10.5
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)

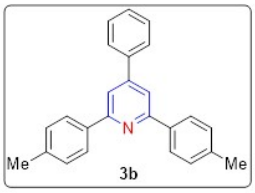

RAN_01
157.54
150.26
139.59
139.10
129.14
129.08
129.01
128.94
128.73
127.21
117.18
N
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

RAN-02

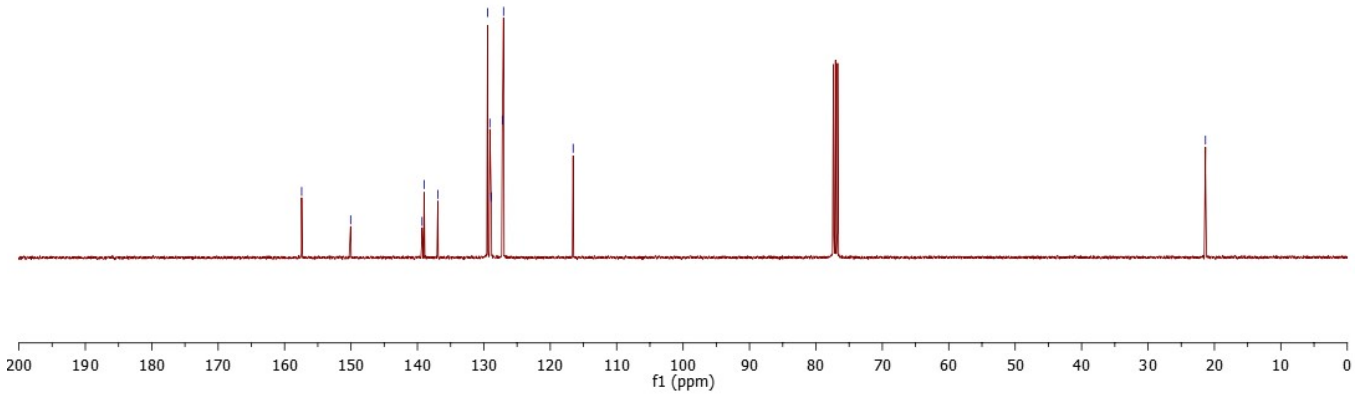

8.16
8.14
7.88
7.79
7.77
7.58
7.56
7.55
7.52
7.50
7.37
7.35
2.47
Me
N
Me
3b
4.05
2.09
2.03
3.17
4.02
6.00
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

RAN-02

157.43
150.05
139.30
138.99
136.92
129.43
129.09
128.89
127.21
127.03
116.55
21.35

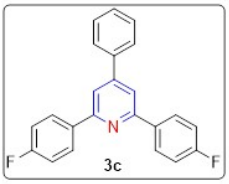


3b

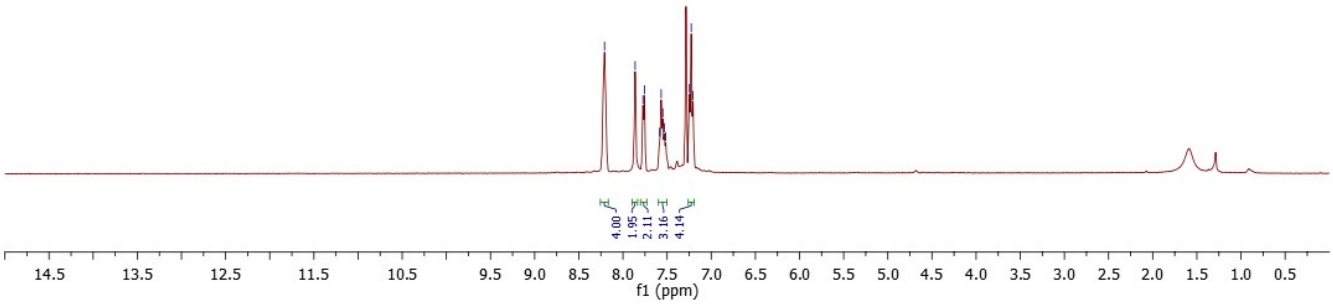


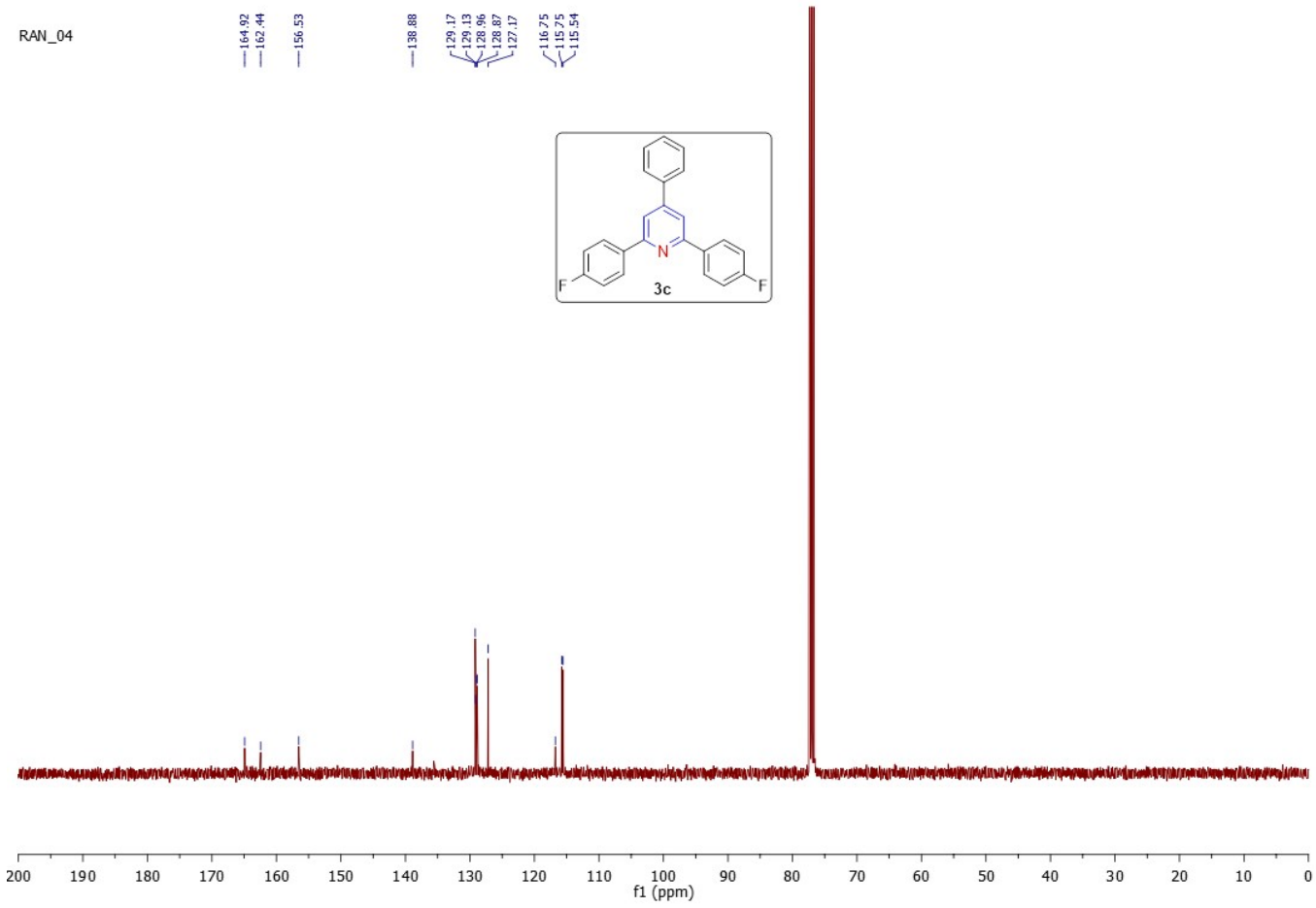
RAN_04


8.21
7.86
7.77
7.76
7.58
7.57
7.55
7.53
7.52
7.25
7.23
7.21

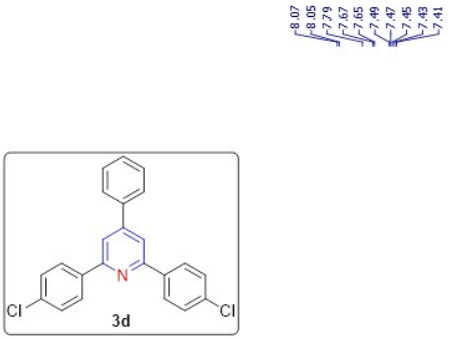

N
F
F

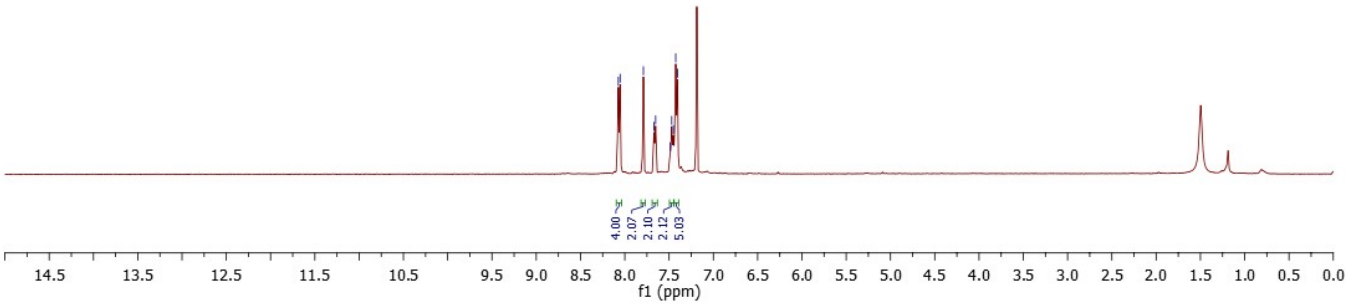
3c

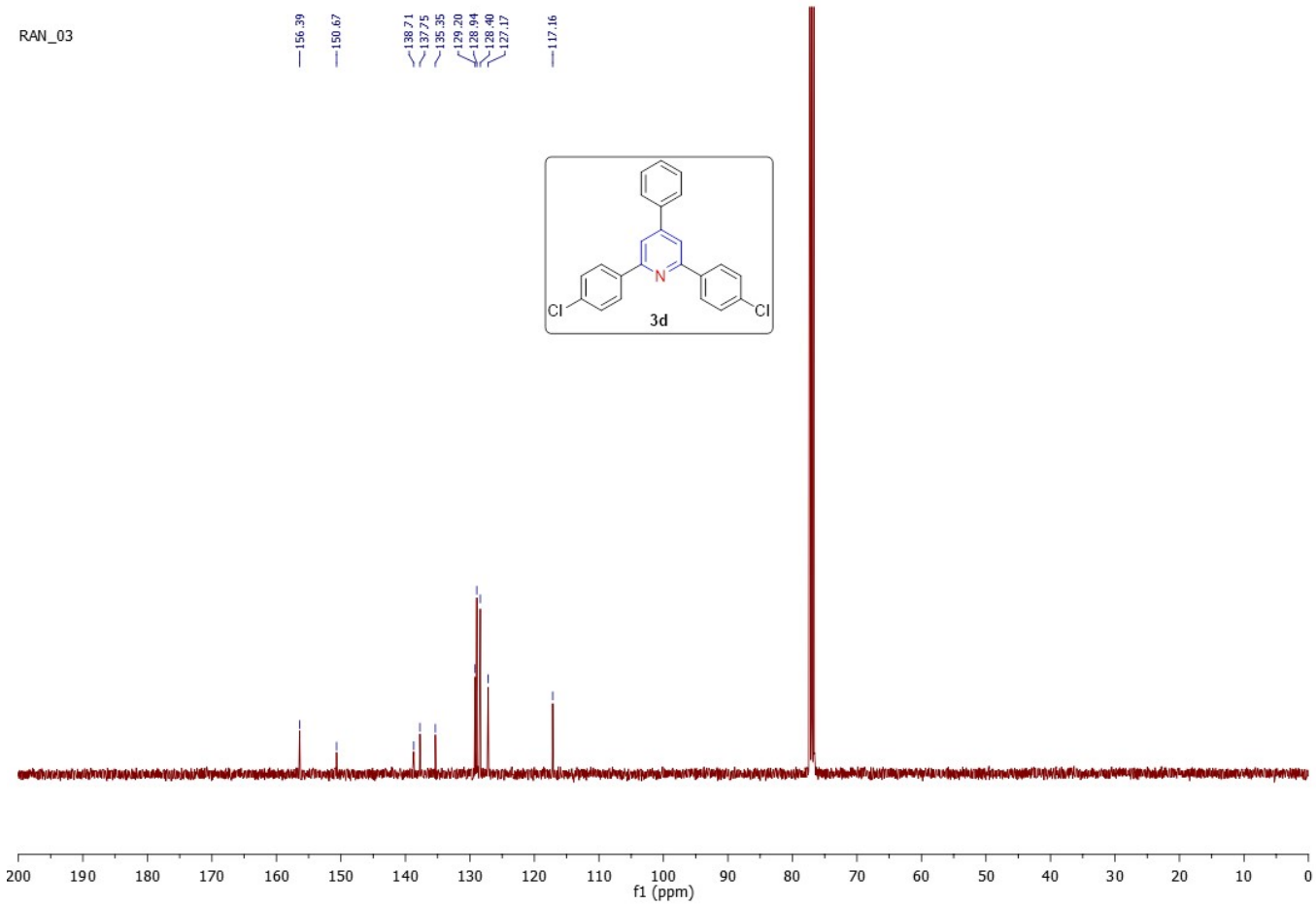

4.00
1.95
2.11
3.16
4.14
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


RAN_04
164.92
162.44
156.53
138.88
129.17
129.13
128.96
128.87
127.17
116.75
115.75
115.54
N
F
F
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

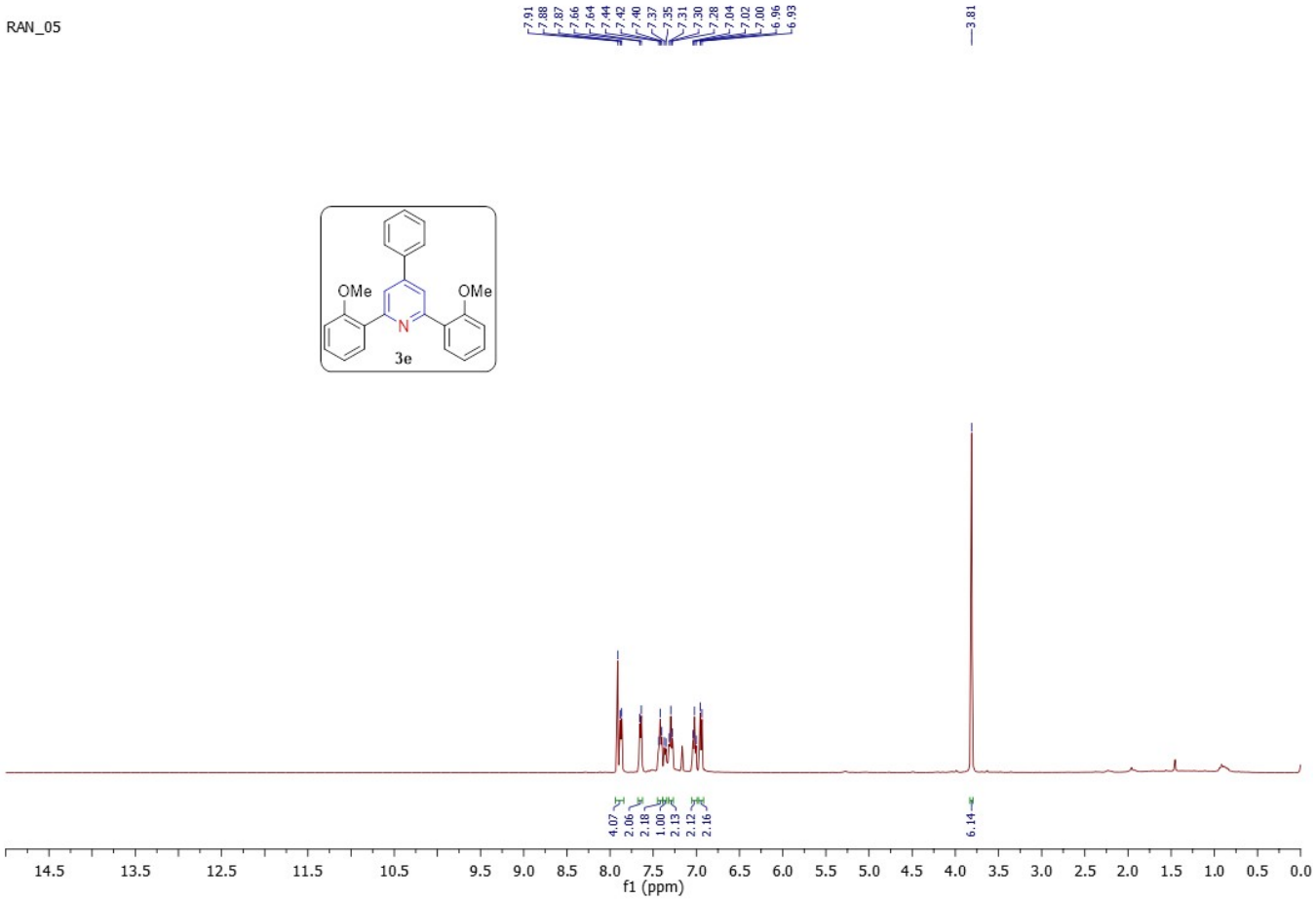
RAN_03

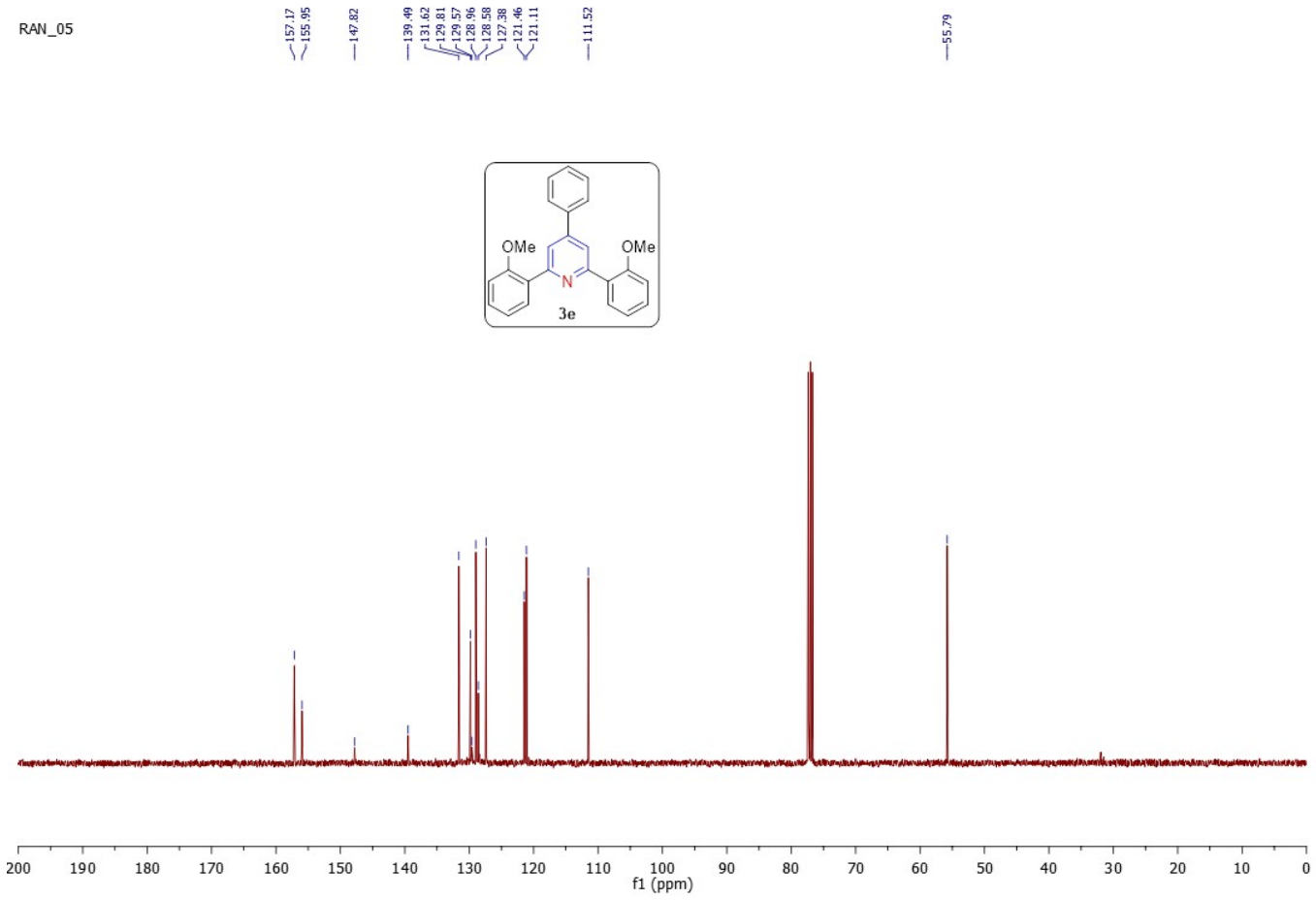

8.07
8.05
7.79
7.67
7.65
7.49
7.47
7.45
7.43
7.41
N
Cl
Cl
3d


4.00
2.07
2.10
2.12
5.03
14.5
13.5
12.5
11.5
10.5
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)

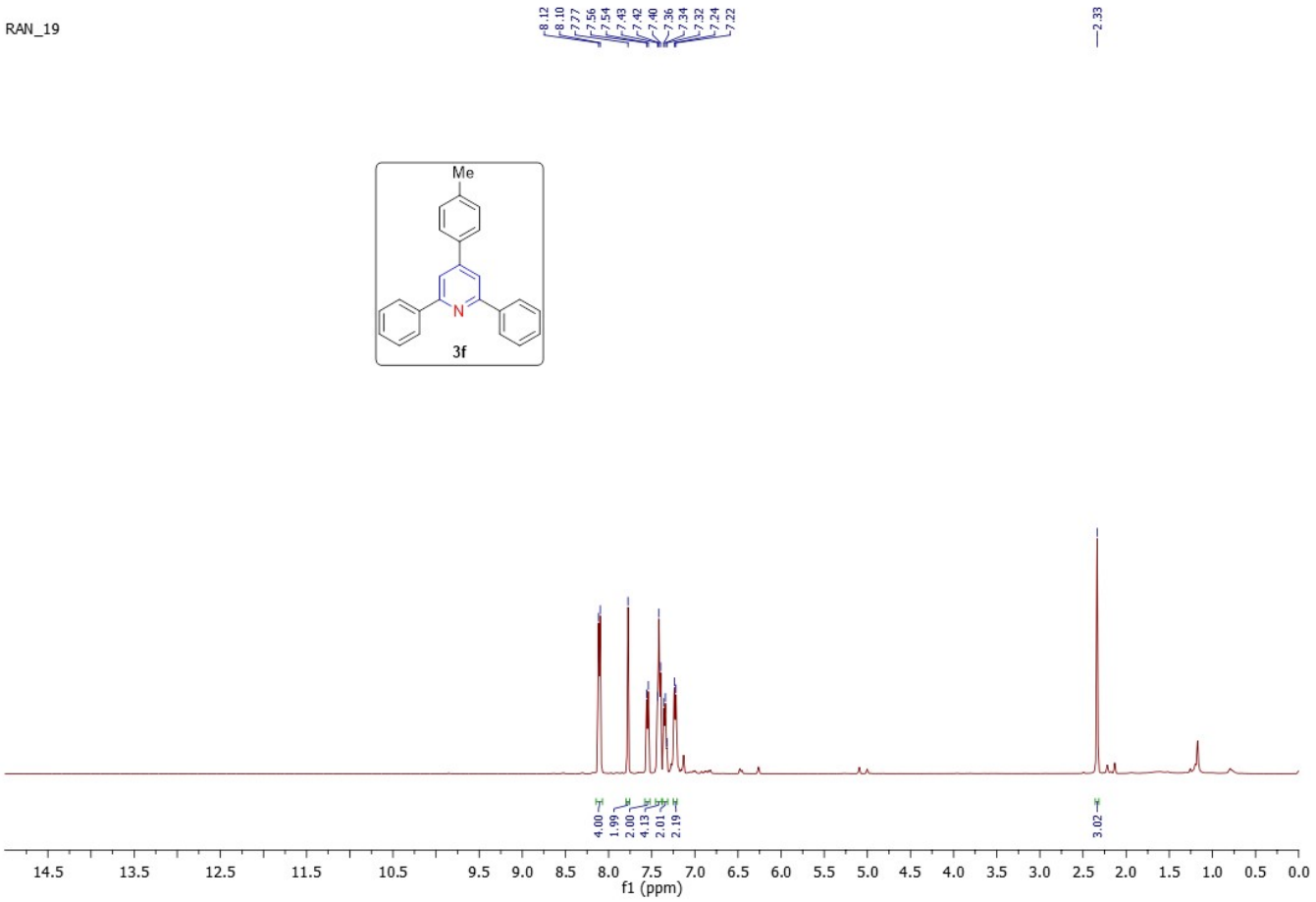

RAN_03
156.39
150.67
138.71
137.75
135.35
129.20
128.94
128.40
127.17
117.16
Cl
N
Cl
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

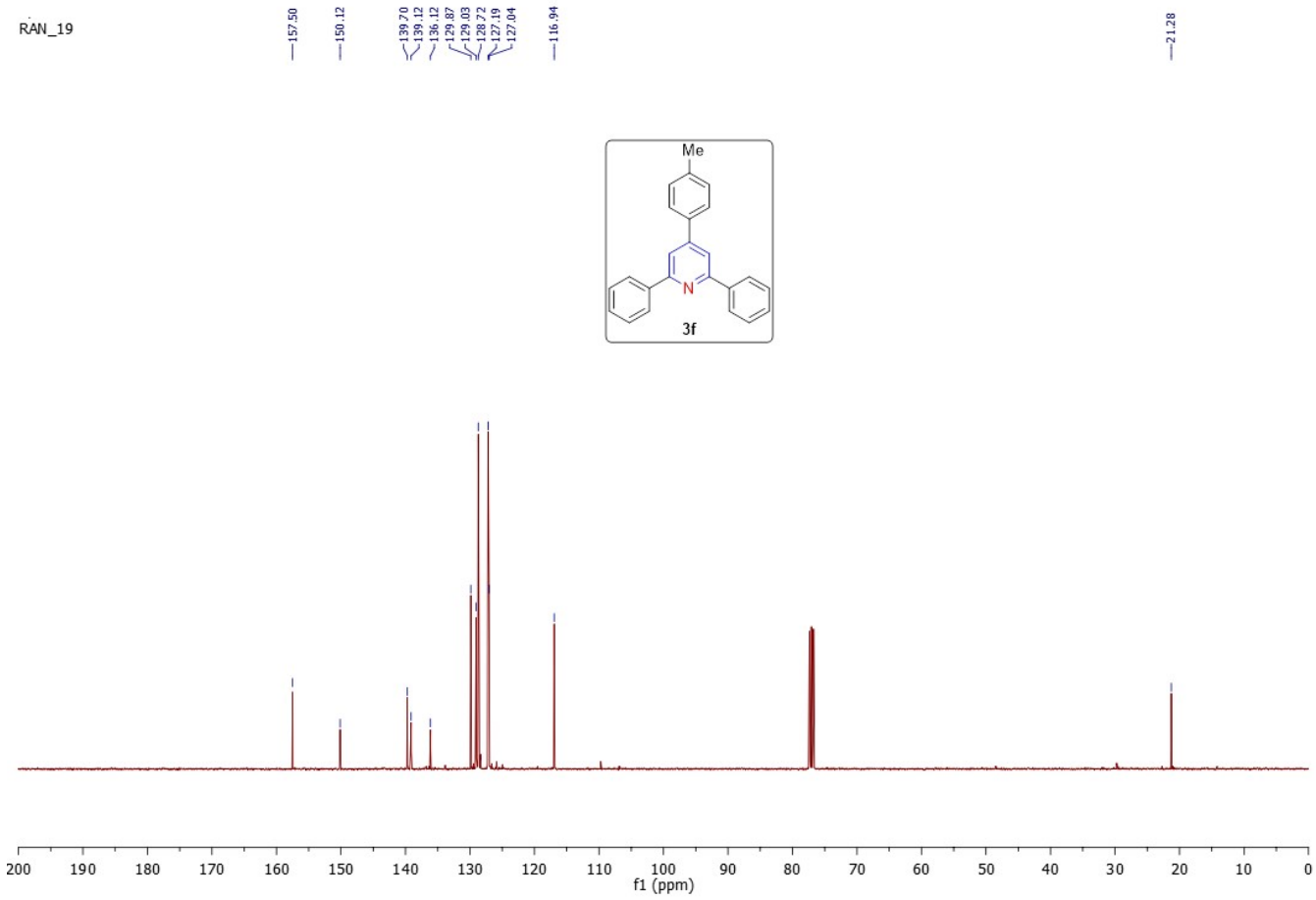
RAN_05

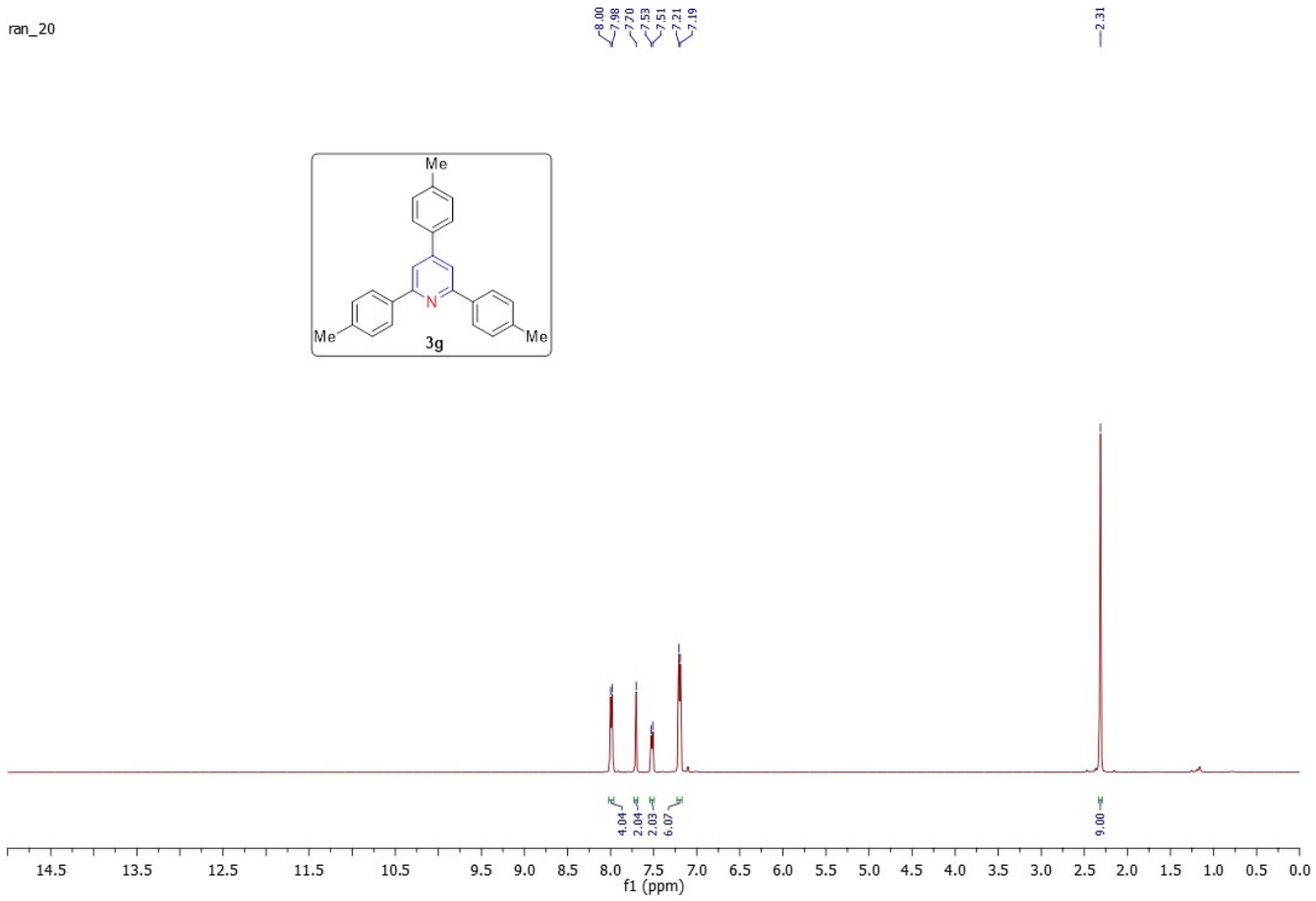

7.91
7.88
7.87
7.66
7.64
7.44
7.42
7.40
7.37
7.35
7.31
7.30
7.28
7.04
7.02
7.00
6.96
6.93
3.81
OMe
OMe
N
3e
4.07
2.06
2.18
1.00
2.13
2.12
2.16
6.14
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

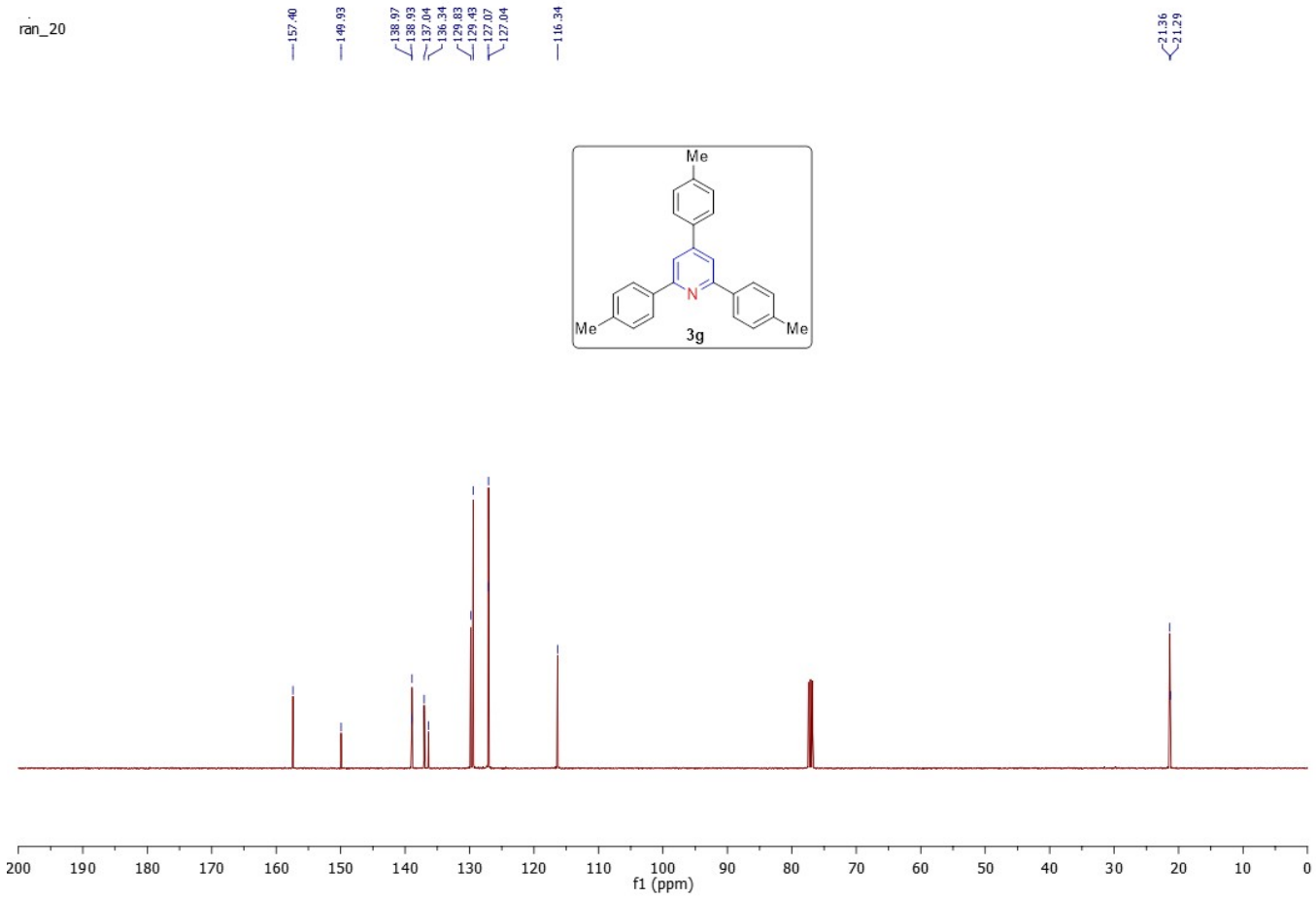

RAN_05
157.17
155.95
147.82
139.49
131.62
129.81
129.57
128.96
128.58
127.38
121.46
121.11
111.52
55.79
OMe
OMe
N
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

RAN_19

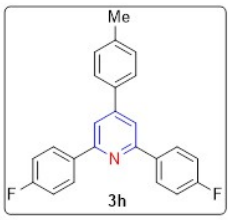

8.12
8.10
7.77
7.56
7.54
7.43
7.42
7.40
7.36
7.34
7.32
7.24
7.22
2.33
Me
N
3f
4.00
1.99
2.00
4.13
2.01
2.19
3.02
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

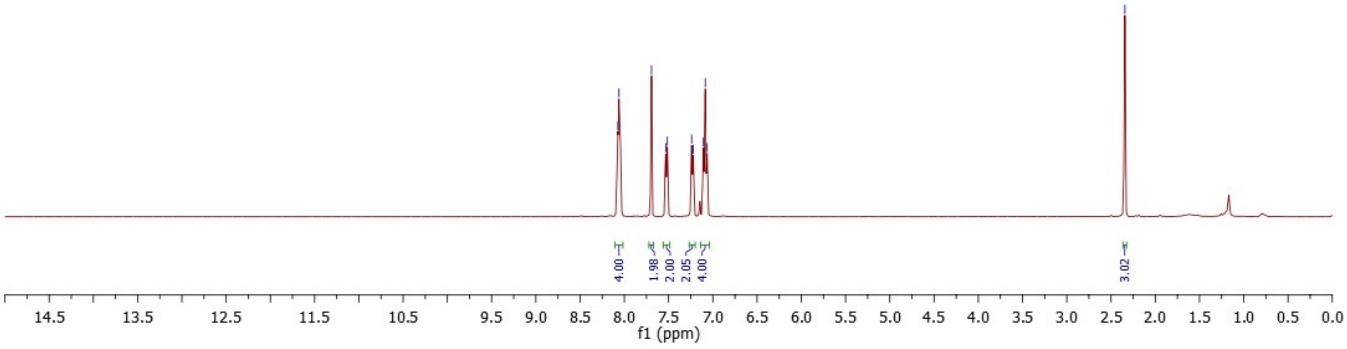

RAN_19
157.50
150.12
139.70
139.12
136.12
129.87
129.03
128.72
127.19
127.04
116.94
21.28
Me
N
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ran_20
8.00
7.98
7.70
7.53
7.51
7.21
7.19
2.31
Me
N
Me
Me
3g
4.04
2.04
2.03
6.07
9.00
14.5
13.5
12.5
11.5
10.5
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)


ran_20
157.40
149.93
138.97
138.93
137.04
136.34
129.83
129.43
127.07
127.04
116.34
21.36
21.29
Me
N
Me
Me
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

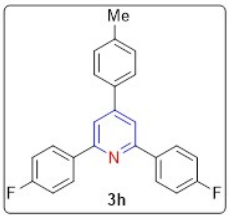
RAN_22


Me
N
F
F
3h

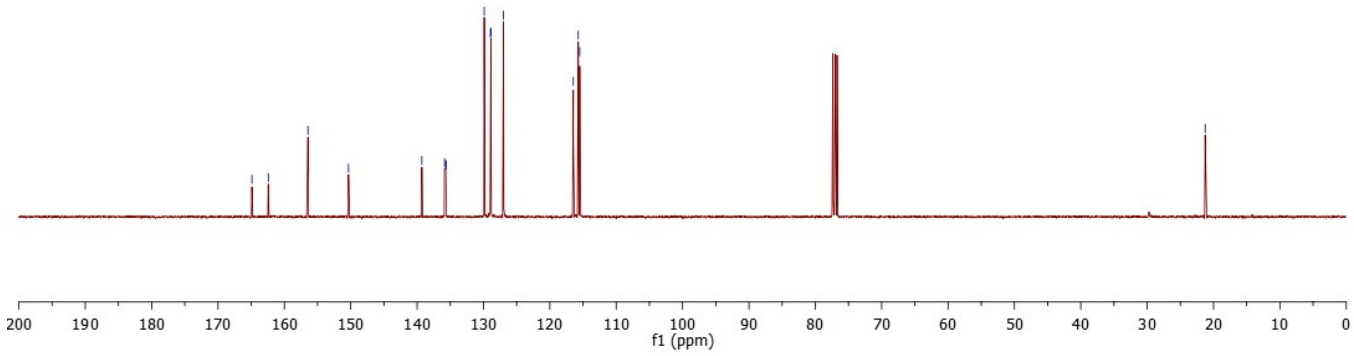

8.07
8.06
7.69
7.53
7.51
7.24
7.22
7.11
7.09
7.06
2.34
4.00
1.98
2.00
2.05
4.00
3.02
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

RAN_22

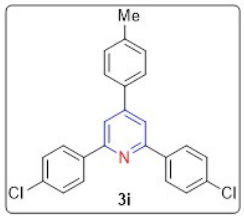
164.89
162.42
156.44
150.34
139.28
135.86
135.68
135.65
129.89
128.95
128.87
126.98
116.47
115.71
115.50
21.26

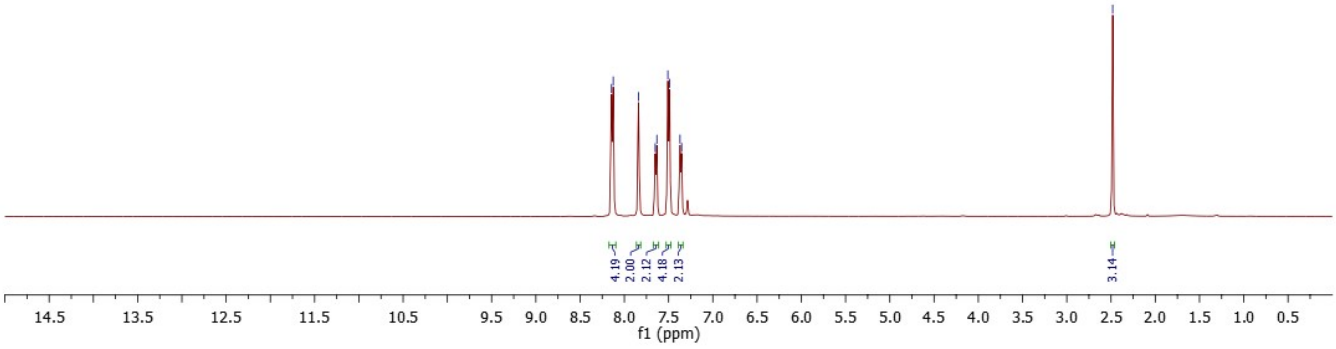


3h



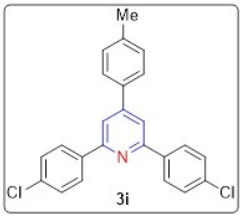
RAN_21


Me
N
Cl
Cl
3i

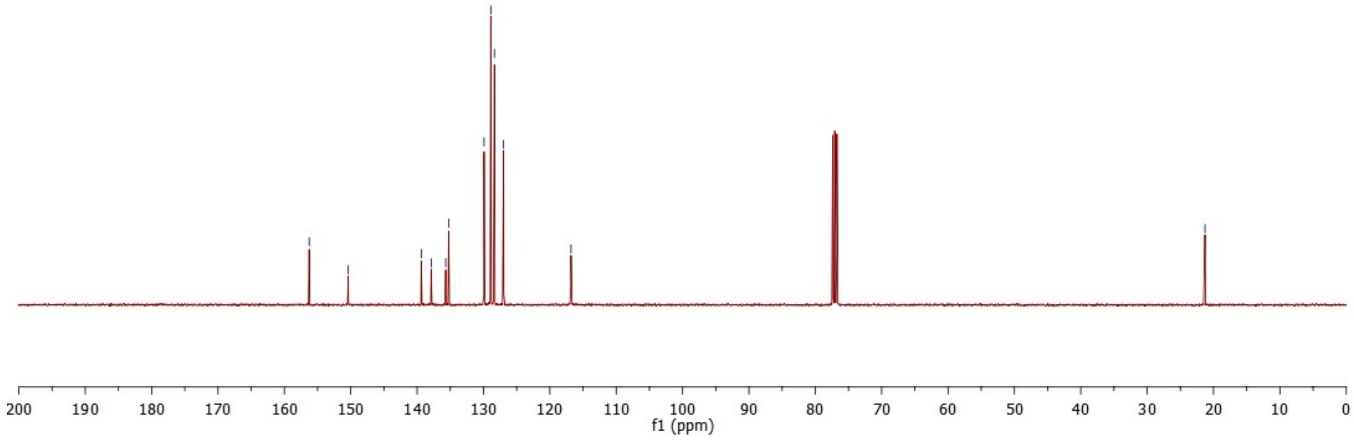

8.14
8.13
7.84
7.65
7.63
7.51
7.49
7.37
7.35
2.48
4.19
2.00
2.12
4.18
2.13
3.14
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

RAN_21

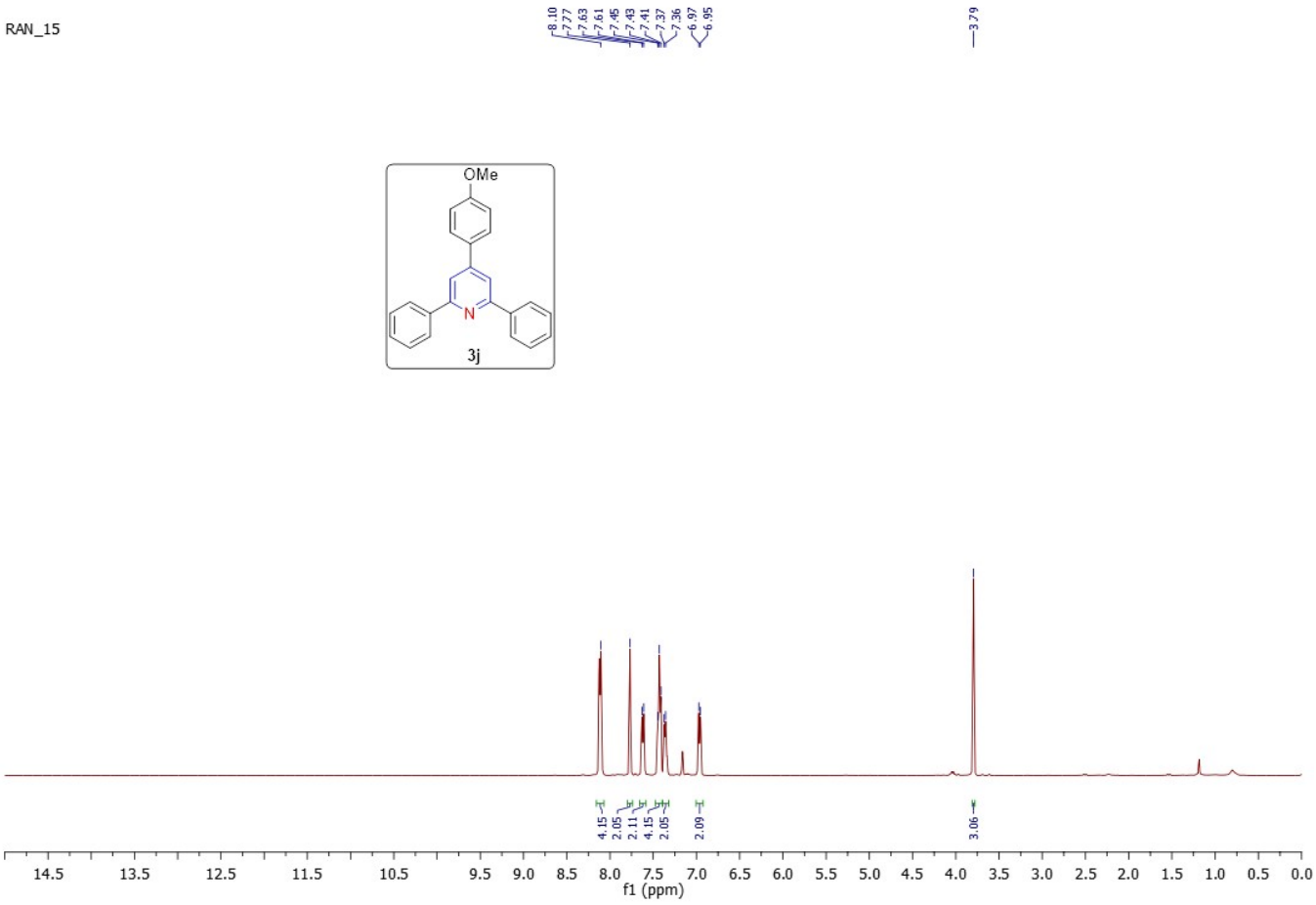
156.26
150.37
139.37
137.87
135.69
135.24
129.91
128.89
128.35
126.97
116.81
21.29

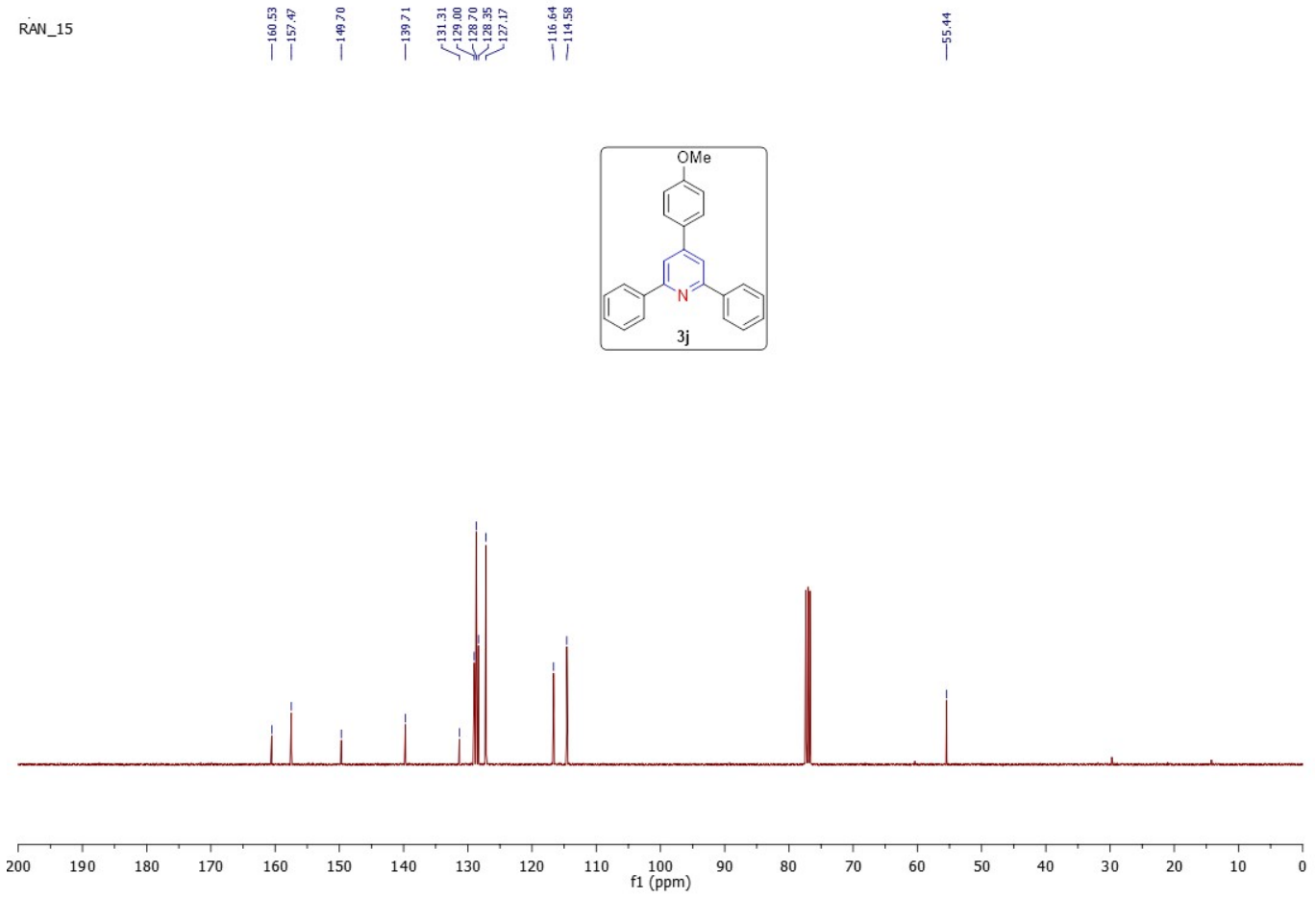


3i

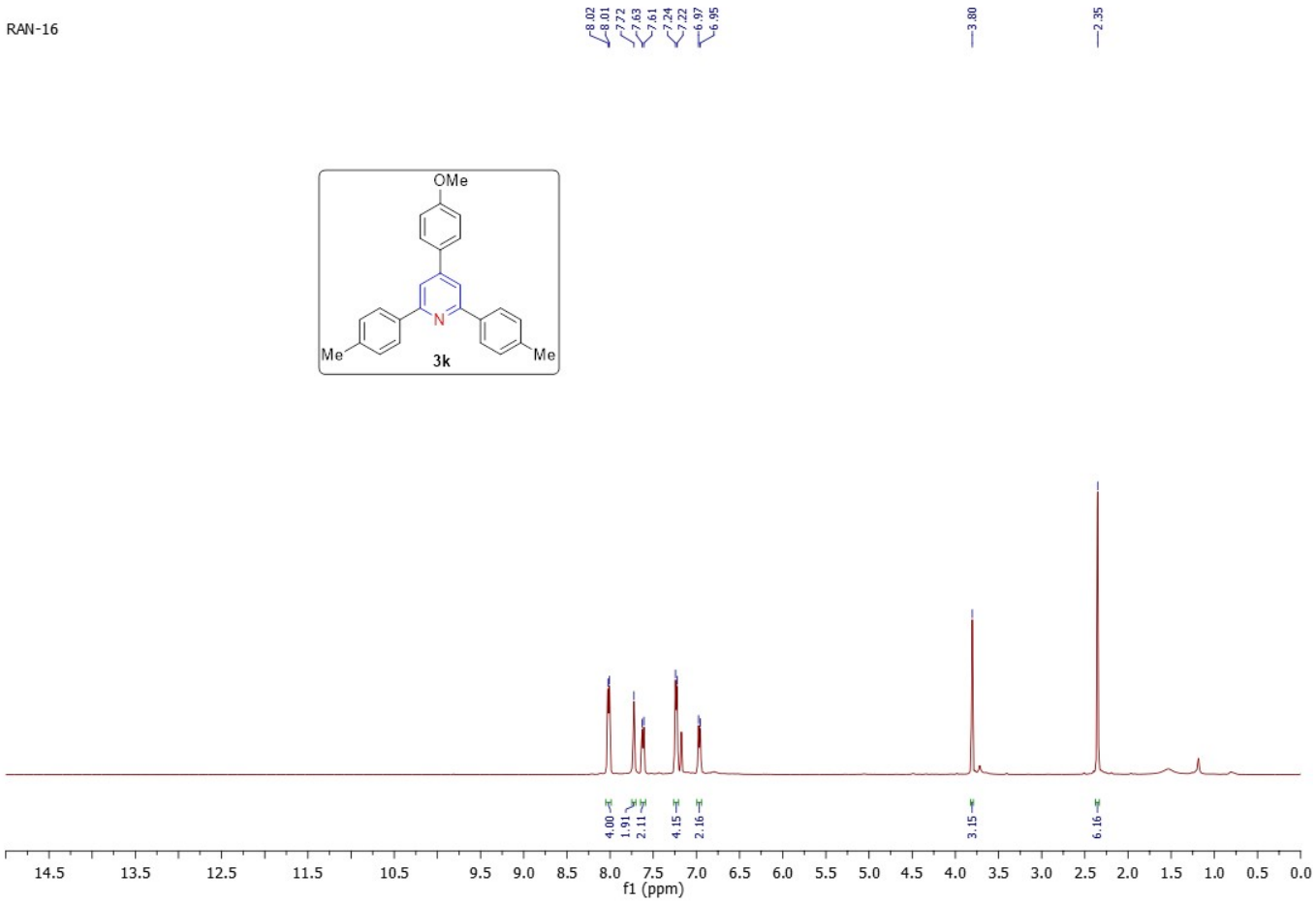


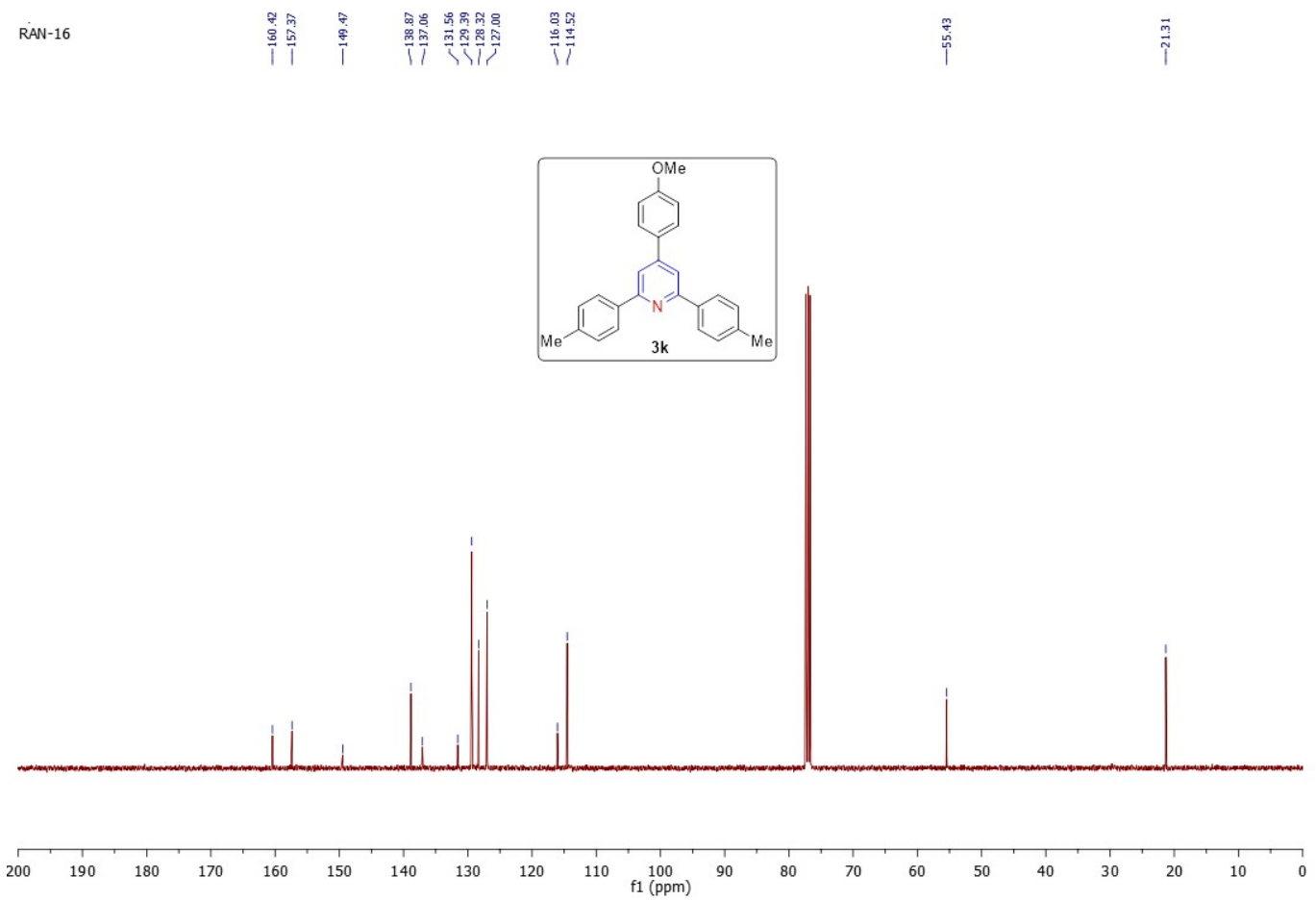
RAN_15


8.10
7.77
7.63
7.61
7.45
7.43
7.41
7.37
7.36
6.97
6.95
3.79
OMe
N
3j
4.15
2.05
2.11
4.15
2.05
2.09
3.06
14.5
13.5
12.5
11.5
10.5
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)

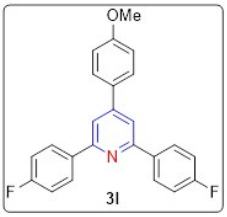

RAN_15
160.53
157.47
149.70
139.71
131.31
129.00
128.70
128.35
127.17
116.64
114.58
55.44
OMe
N
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

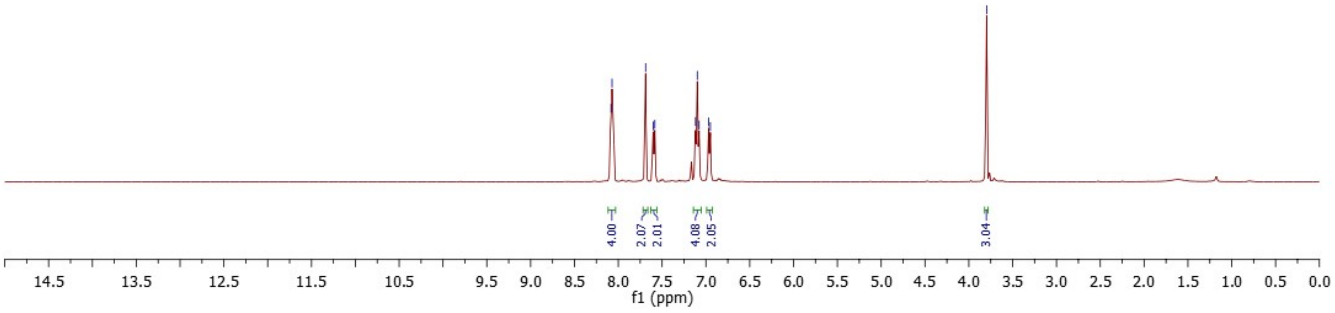
RAN-16


8.02
8.01
7.72
7.63
7.61
7.24
7.22
6.97
6.95
3.80
2.35
OMe
N
Me
Me
3k
4.00
1.91
2.11
4.15
2.16
3.15
6.16
14.5 13.5 12.5 11.5 10.5 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)

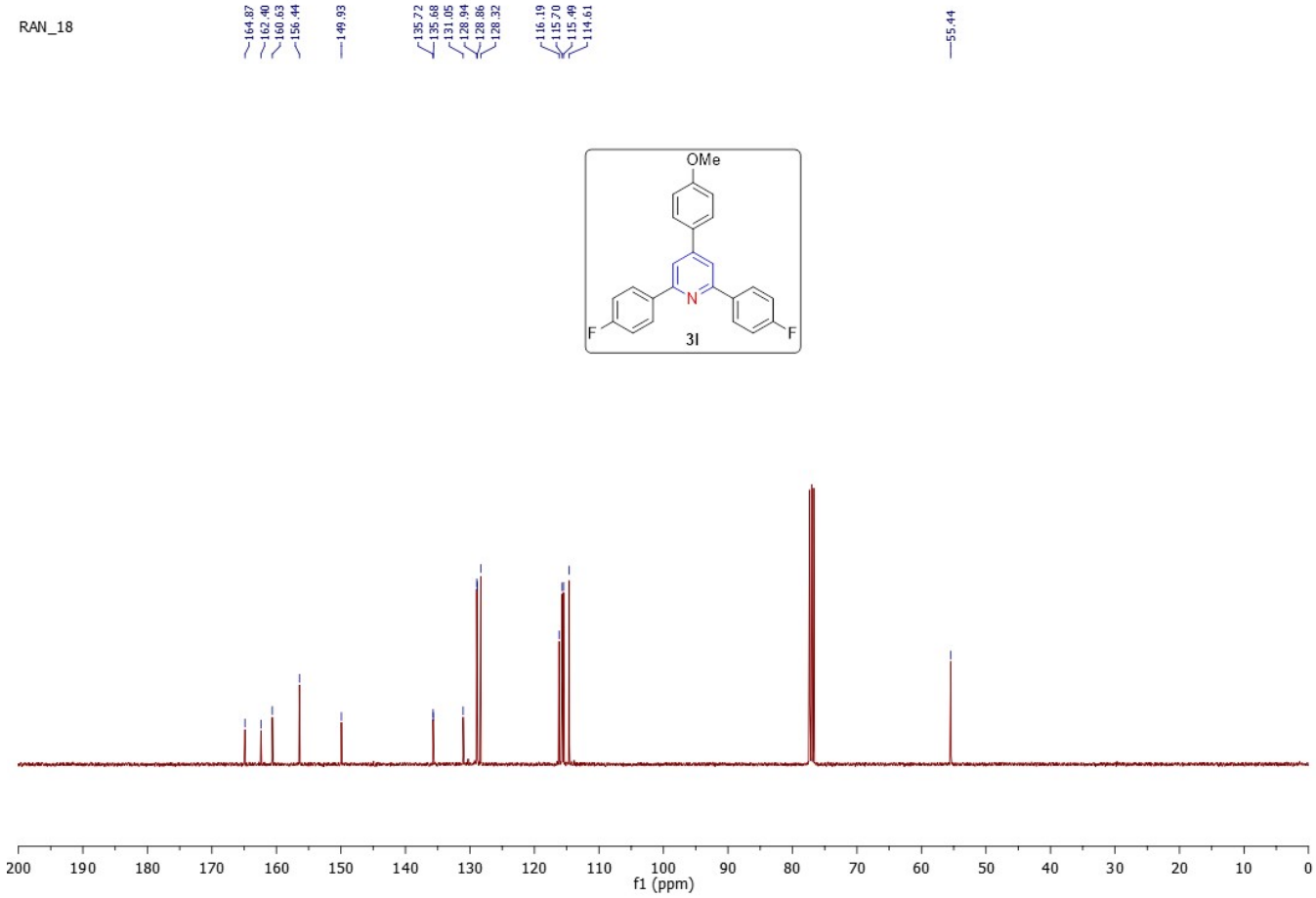

RAN-16
160.42
157.37
149.47
138.87
137.06
131.56
129.39
128.32
127.00
116.03
114.52
55.43
21.31
OMe
N
Me
Me
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

RAN_18

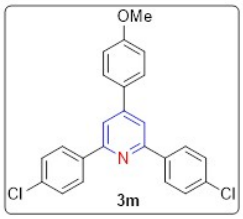

OMe
N
F
F
3l

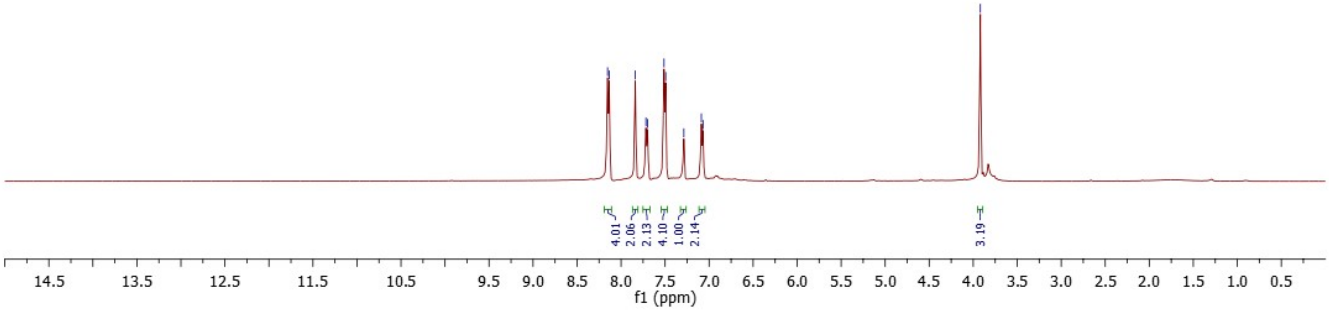

8.08
8.07
7.69
7.60
7.58
7.12
7.10
7.08
6.97
6.95
3.80
4.00
2.07
2.01
4.08
2.05
3.04
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

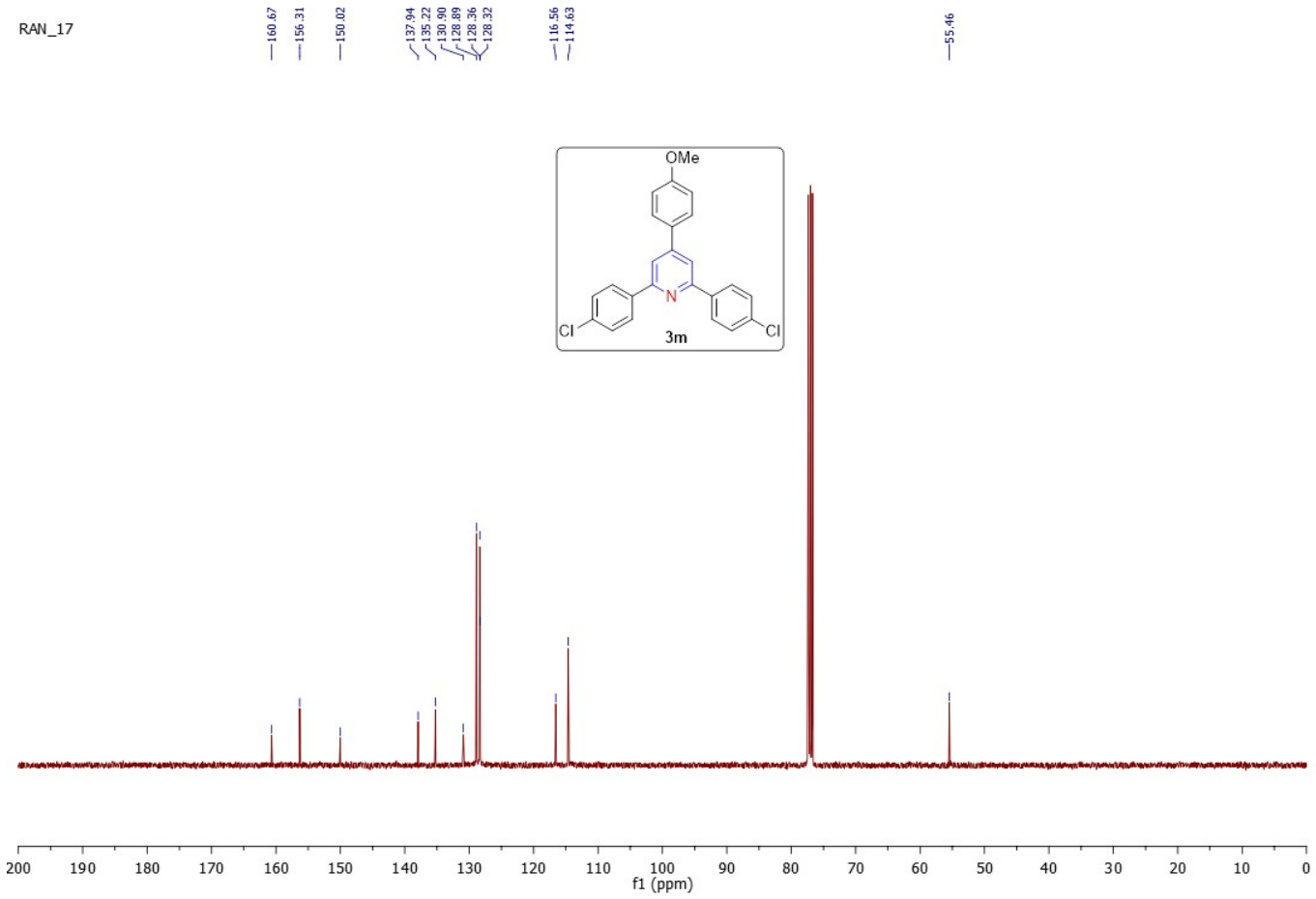
RAN_18


164.87
162.40
160.63
156.44
149.93
135.72
135.68
131.05
128.94
128.86
128.32
116.19
115.70
115.49
114.61
55.44
OMe
N
F
F
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

RAN_17

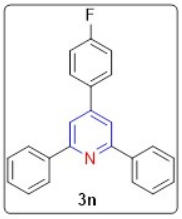

OMe
N
Cl
Cl
3m


8.15
8.13
7.84
7.72
7.70
7.51
7.49
7.29
7.09
7.07
3.92
4.01
2.06
2.13
4.10
1.00
2.14
3.19
14.5 13.5 12.5 11.5 10.5 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
f1 (ppm)

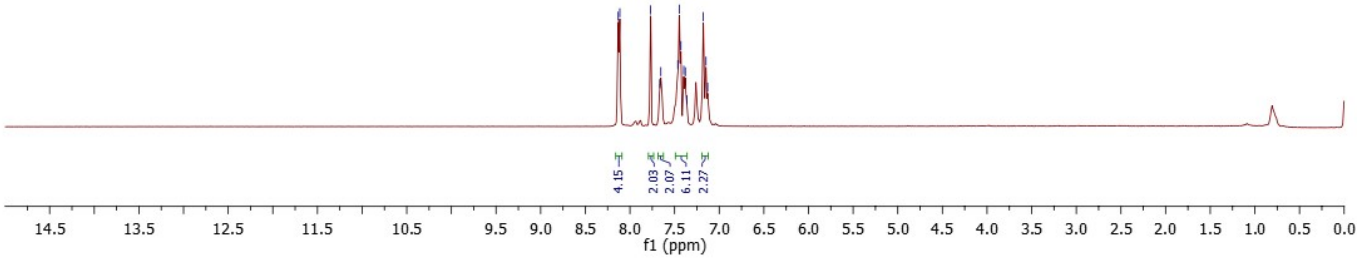

RAN_17
160.67
156.31
150.02
137.94
135.22
130.90
128.89
128.36
128.32
116.56
114.63
55.46
OMe
N
Cl
Cl
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

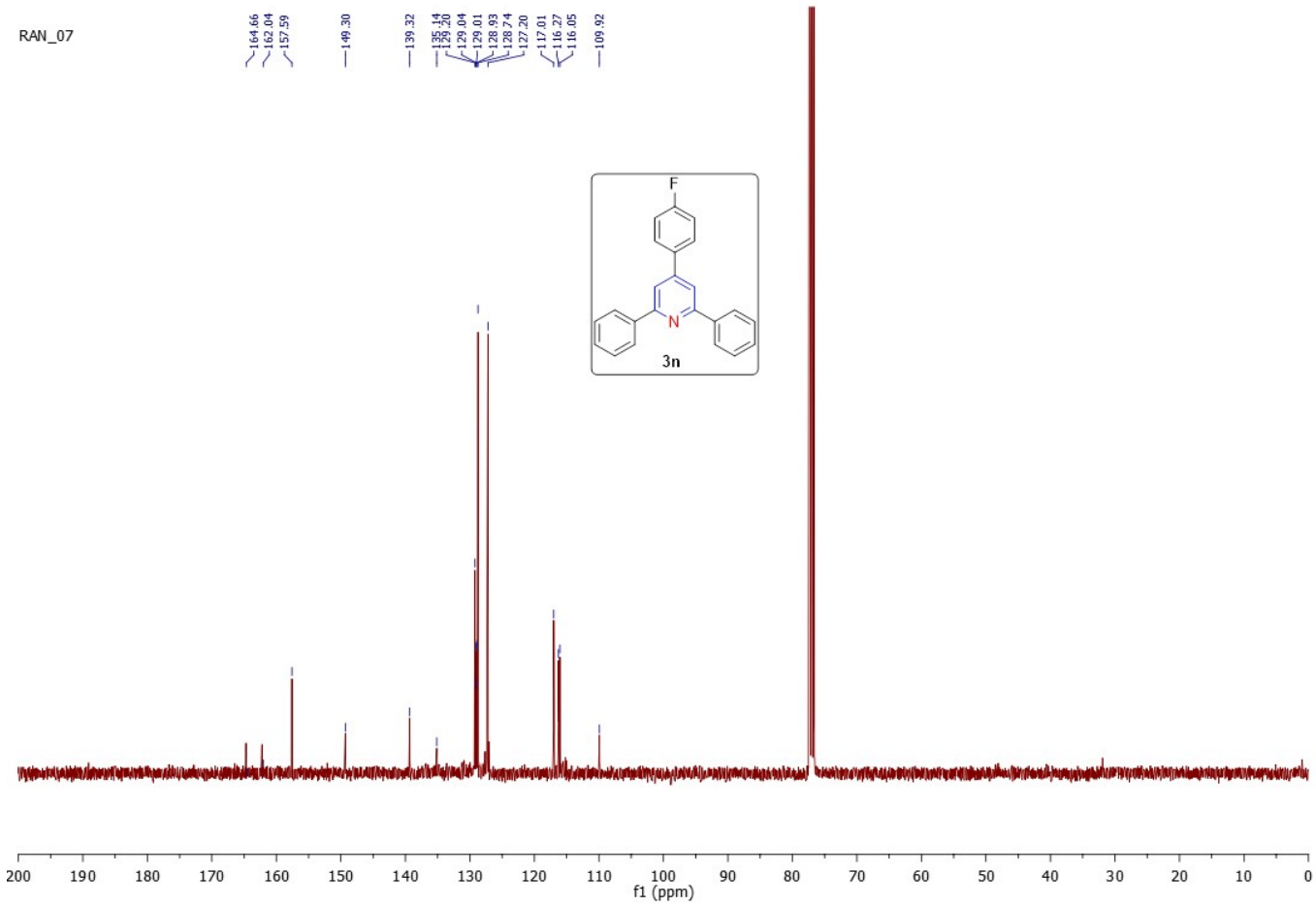
RAN_07


8.13
8.11
7.77
7.67
7.65
7.46
7.45
7.43
7.40
7.38
7.36
7.18
7.15
7.13

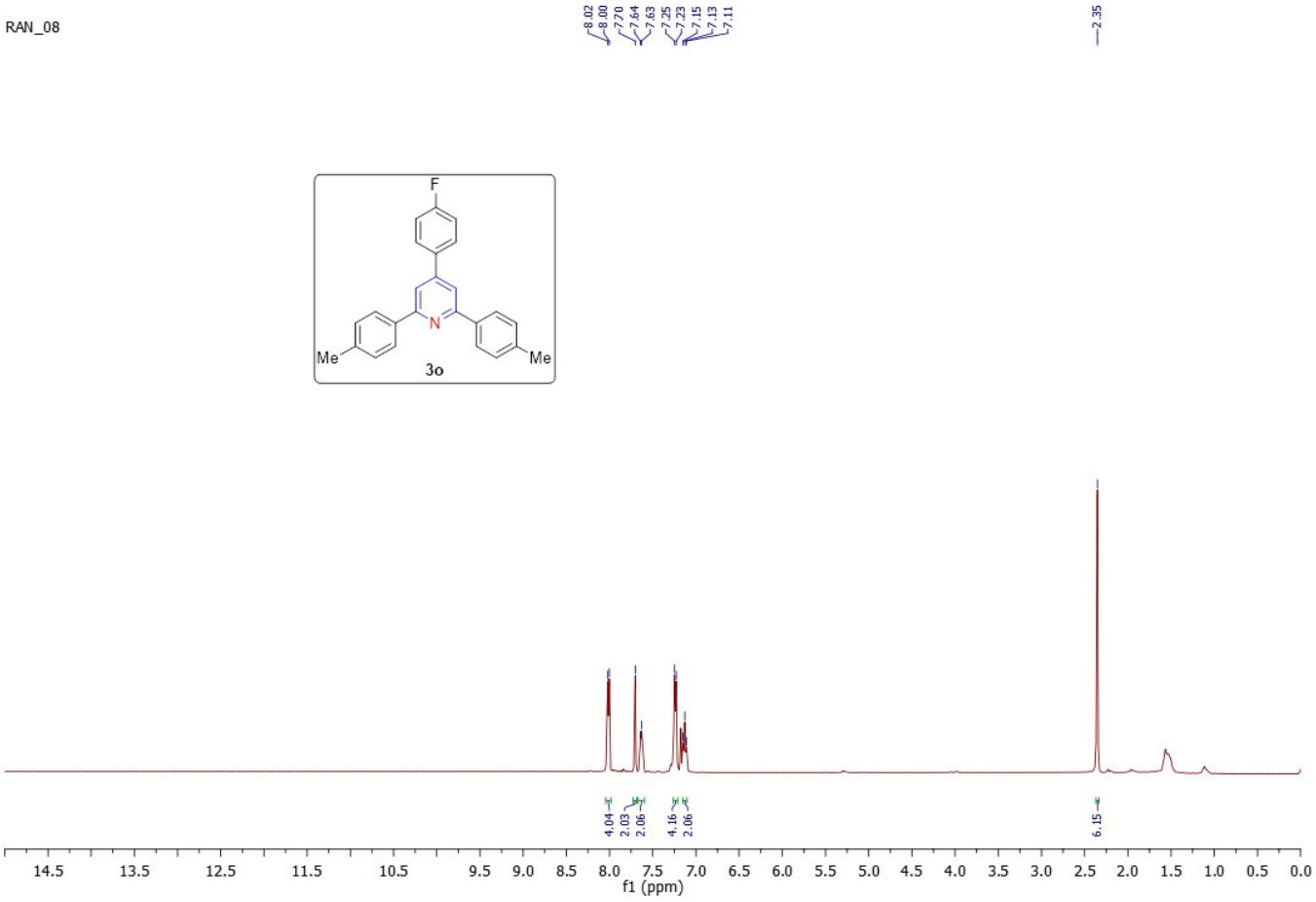

F
N

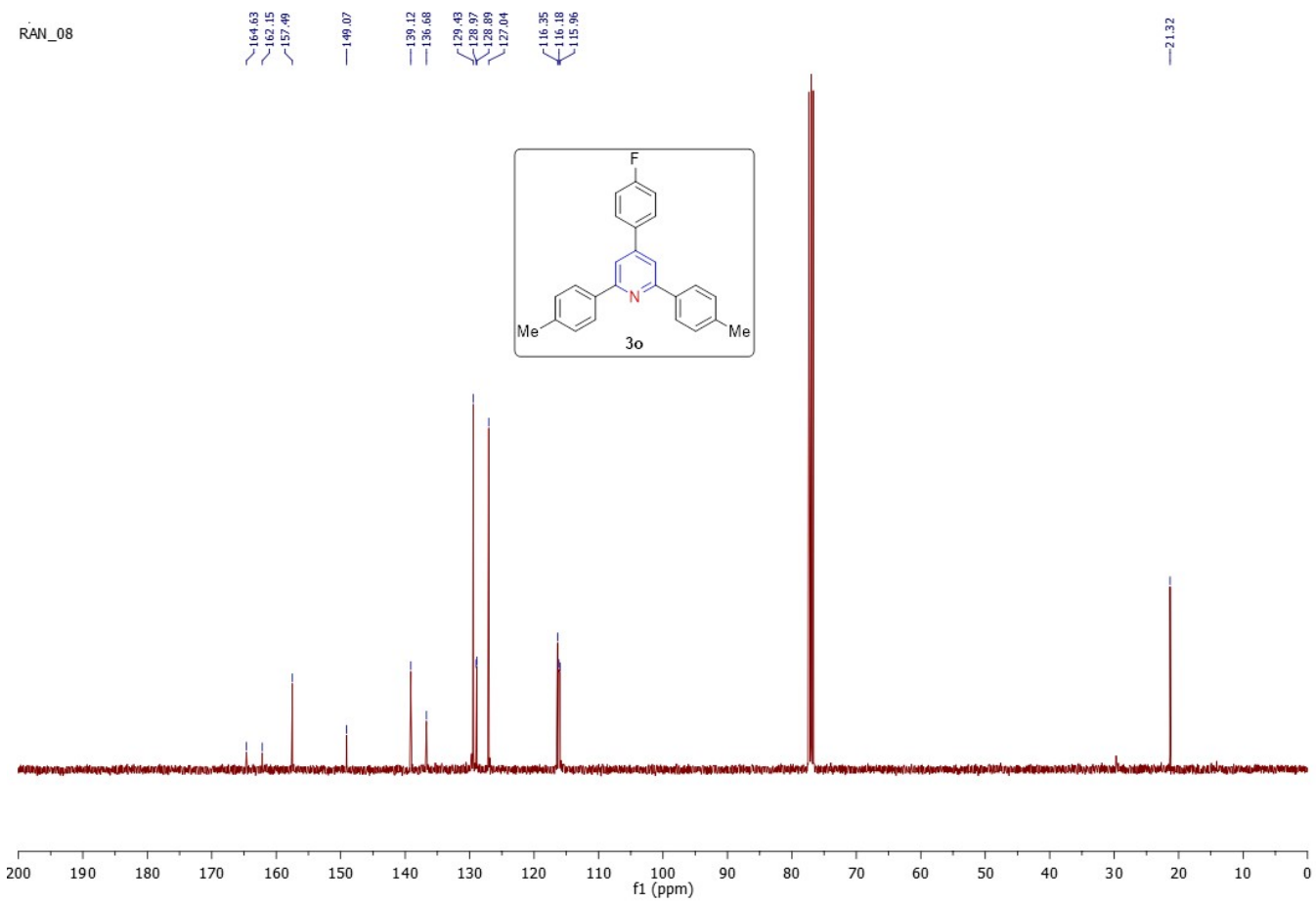
3n


4.15
2.03
2.07
6.11
2.27
14.5
13.5
12.5
11.5
10.5
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)

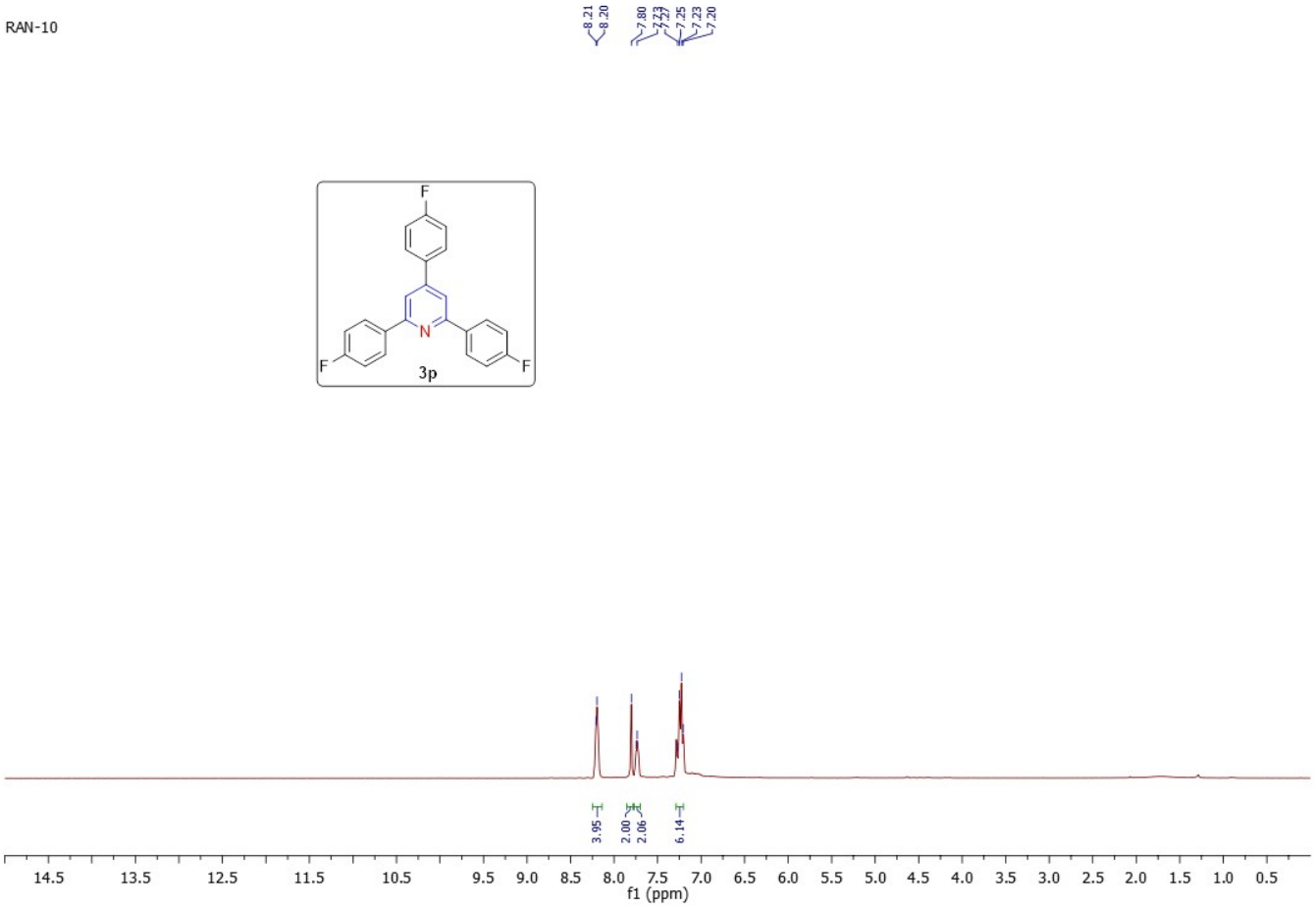

RAN_07
164.66
162.04
157.59
149.30
139.32
135.14
129.20
129.04
129.01
128.93
128.74
127.20
117.01
116.27
116.05
109.92
F
N
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

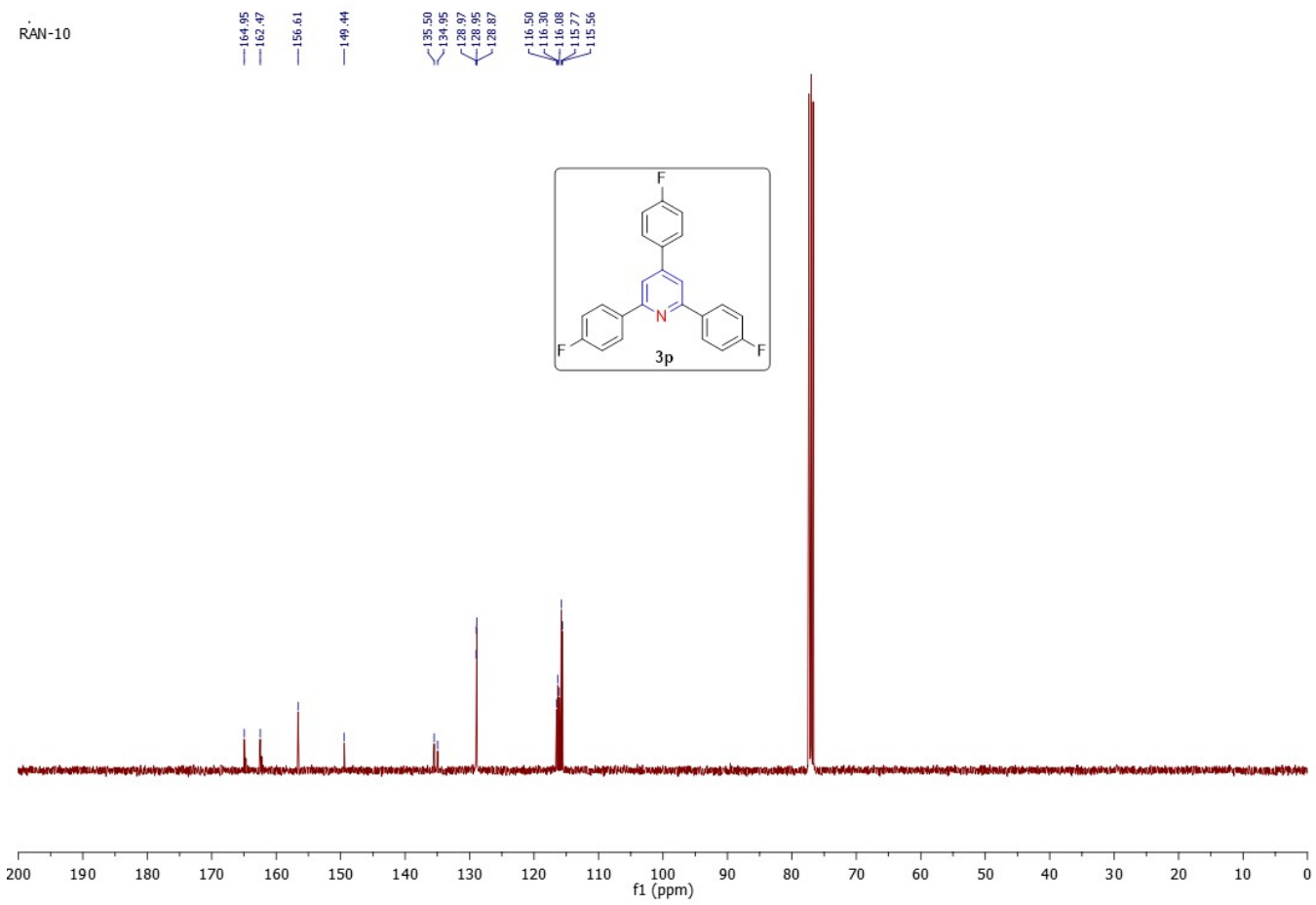
RAN_08


8.02
8.00
7.70
7.64
7.63
7.25
7.23
7.15
7.13
7.11
2.35
F
N
Me
Me
3o
4.04
2.03
2.06
4.16
2.06
6.15
14.5
13.5
12.5
11.5
10.5
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)

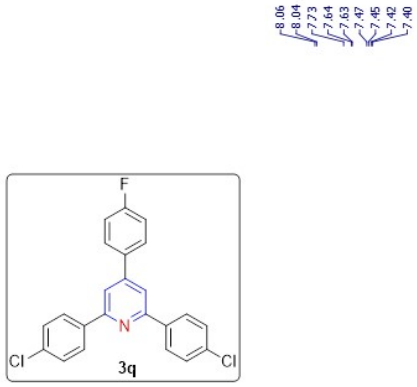

RAN_08
164.63
162.15
157.49
149.07
139.12
136.68
129.43
128.97
128.89
127.04
116.35
116.18
115.96
21.32
F
N
Me
Me
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

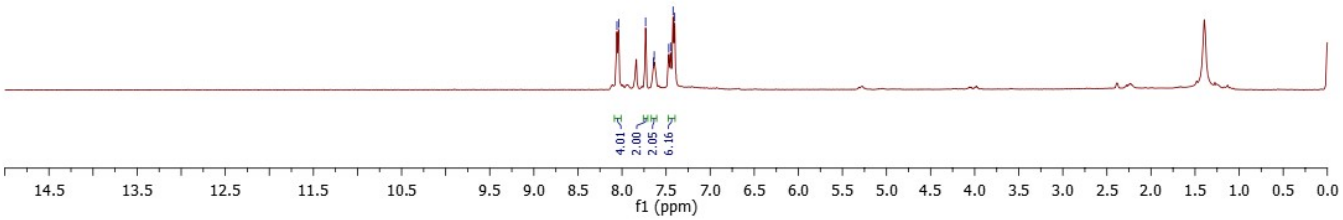
RAN-10

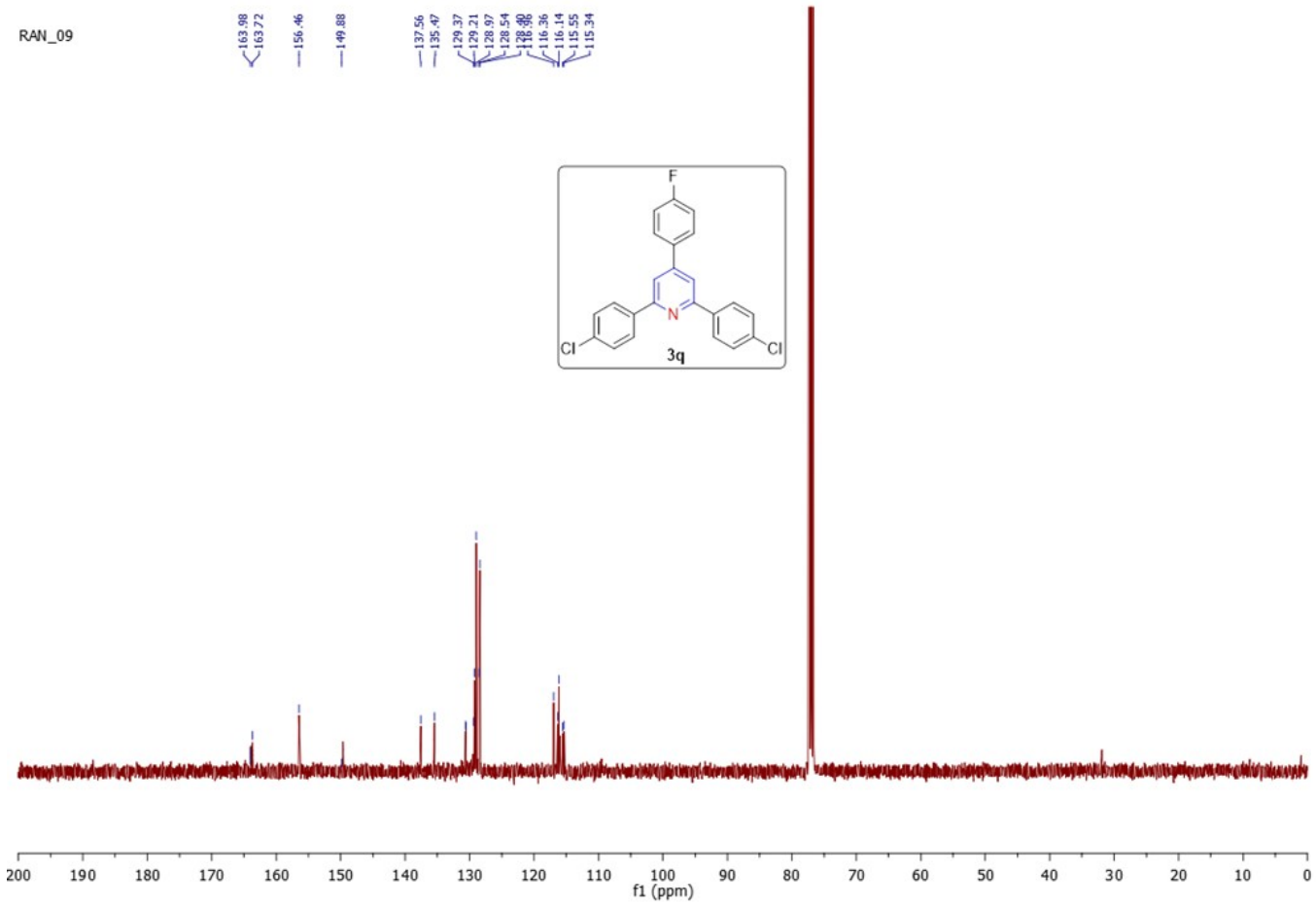

8.21
8.20
7.80
7.73
7.27
7.25
7.23
7.20
F
N
F
F
3p
3.95
2.00
2.06
6.14
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


RAN-10
164.95
162.47
156.61
149.44
135.50
134.95
128.97
128.95
128.87
116.50
116.30
116.08
115.77
115.56
F
N
F
F
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

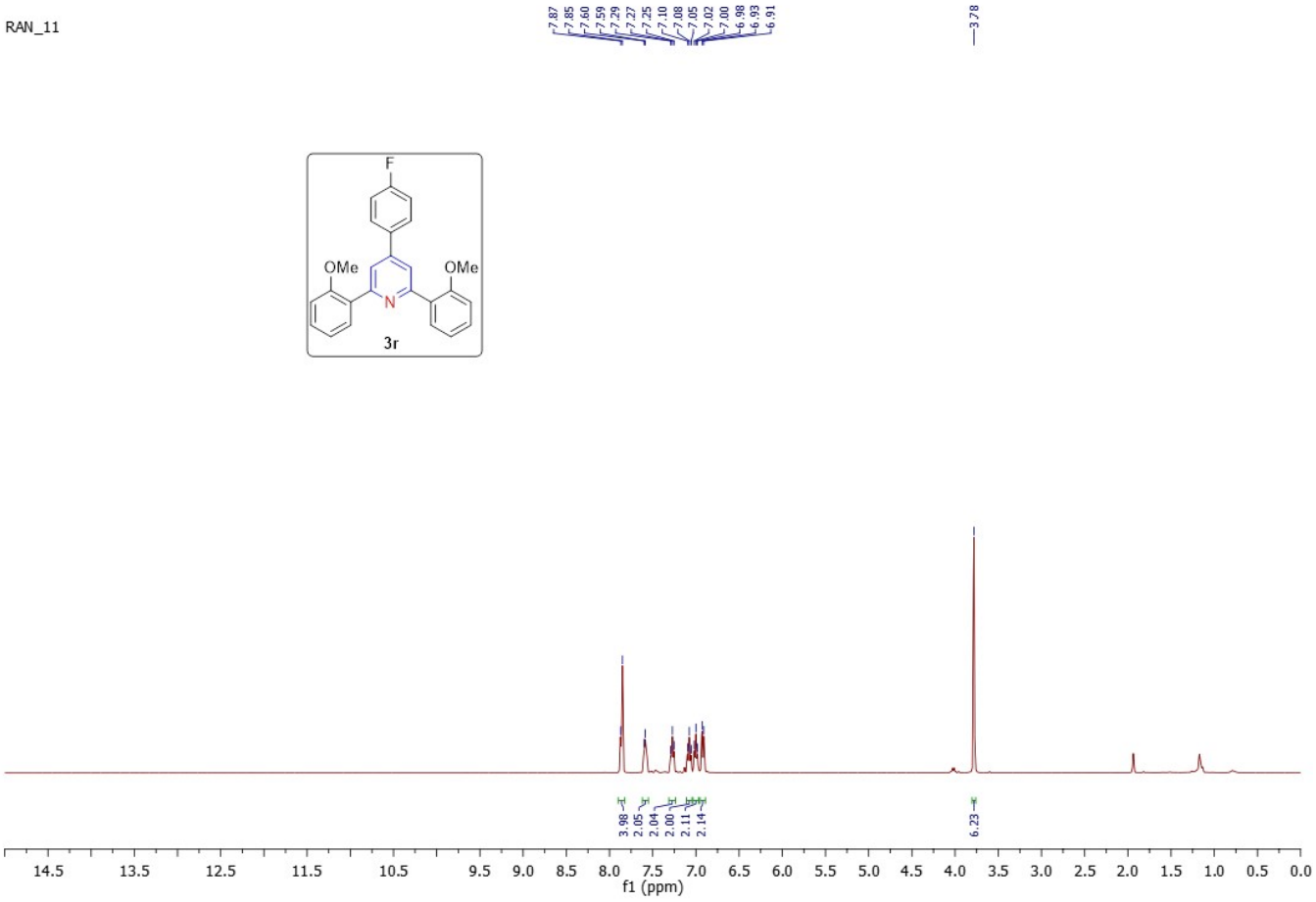
RAN_09


8.06
8.04
7.73
7.64
7.63
7.47
7.45
7.42
7.40
F
N
Cl
Cl
3q


4.01
2.00
2.05
6.16
14.5
13.5
12.5
11.5
10.5
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)

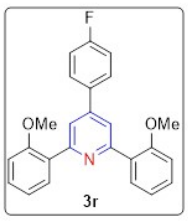

RAN_09
163.98
163.72
156.46
149.88
137.56
135.47
129.37
129.21
128.97
128.54
116.36
116.14
115.55
115.34
F
N
Cl
Cl
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

RAN_11

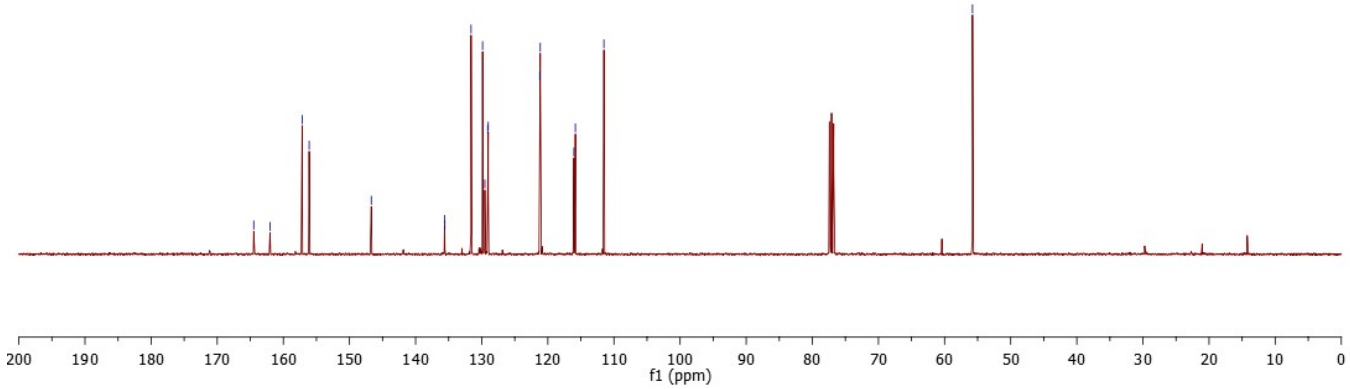

7.87
7.85
7.60
7.59
7.29
7.27
7.25
7.10
7.08
7.05
7.02
7.00
6.98
6.93
6.91
3.78
F
OMe
OMe
N
3r
3.98
2.05
2.04
2.00
2.11
2.14
6.23
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

RAN_11

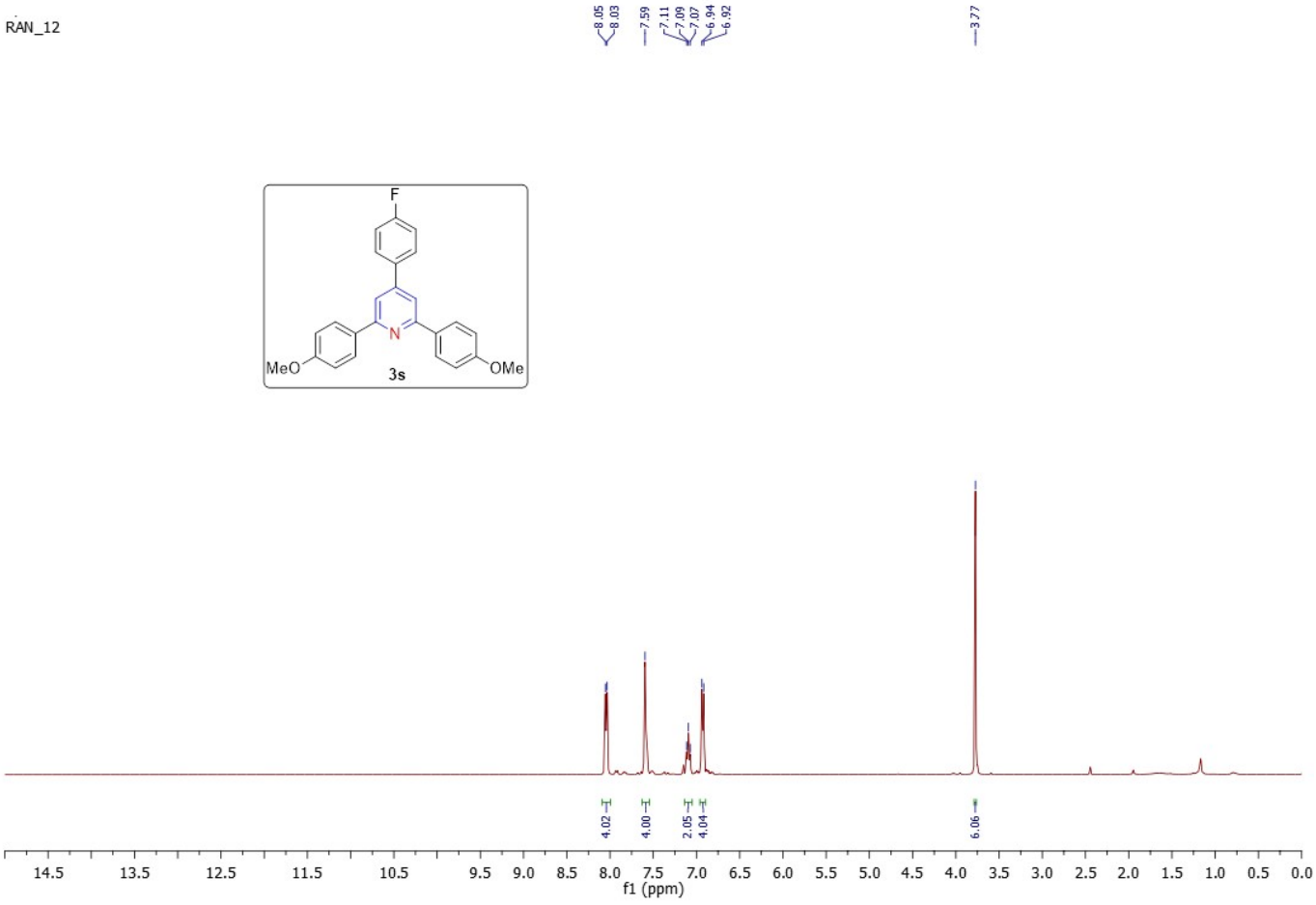
164.48
162.01
157.16
156.09
146.70
135.61
135.58
131.61
129.87
129.53
129.09
129.01
121.23
121.14
116.05
115.84
111.52
55.77

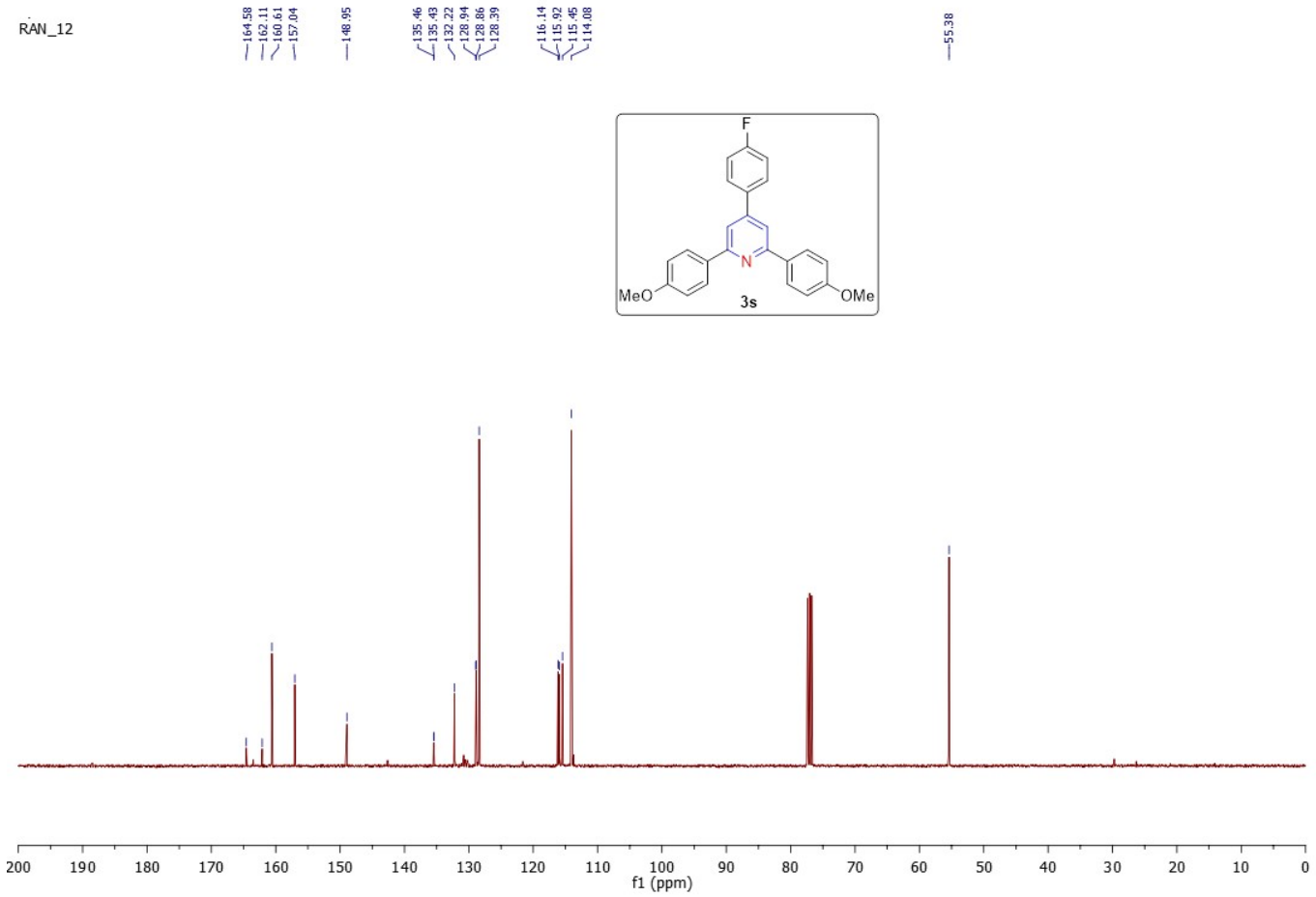


3r



RAN_12


8.05
8.03
7.59
7.11
7.09
7.07
6.94
6.92
3.77
F
N
MeO
OMe
3s
4.02
4.00
2.05
4.04
6.06
14.5
13.5
12.5
11.5
10.5
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)


RAN_12
164.58
162.11
160.61
157.04
148.95
135.46
135.43
132.22
128.94
128.86
128.39
116.14
115.92
115.45
114.08
55.38
F
N
MeO
OMe
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)