Electronic Supplementary Information

Copper-Catalyzed [3+3] Annulation of Ketones with Oxime Acetates for the Synthesis of Pyridines

Yilin Li,[a] Kai Yang,*[, b] and Liang Cao*[, c]

[a] Guangzhou Darui Bio-technology Co. Ltd., China.
[b] College of pharmacy, Gannan Medical University, Ganzhou 341000, P. R. China.
[c] Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China.

✉Correspondence: kai_yangyang@126.com, caol@sustech.edu.cn.

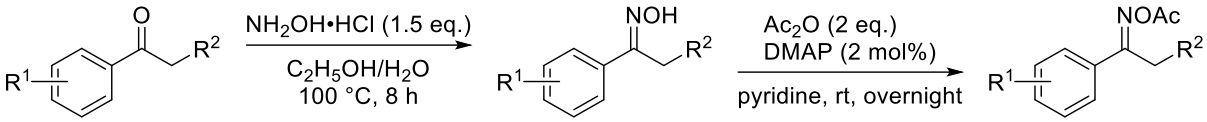
Table of Contents

General information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR, ^{13}C-NMR spectra were obtained on Bruker-500 or 400; Mass spectra were recorded on Trace DSQ GC/MS，High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was affected at 254 nm; All the reagents were purchased from commercial sources, and used without further purification.

Known compounds have been marked with CAS numbers, which can be compared with related references.[1-5]

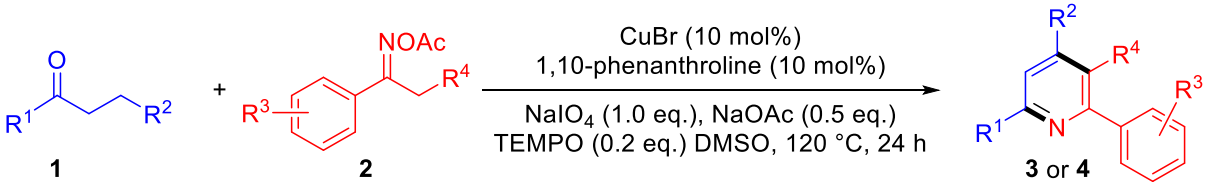
Typical procedure for the synthesis of oxime acetates[1-3]



Ketone (5.0 mmol), hydroxylamine hydrochloride (1.5 eq) in C_2H_5OH/H_2O (10 mL, v/v=1:1) were stirred at 100 °C for 8 h. After completion of the reaction, the solvent was removed under reduced pressure. The mixture was diluted with H_2O (20 mL) and extracted with EtOAc (3 ×15 mL). The organic layer was washed with 1 M HCl, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure. All the obtained products were used for the next step without further purification.

The ketoxime, DMAP (2 mol%) and Ac_2O (2 eq.) were dissolved in pyridine (3 mL). After completion of the reaction, the reaction mixture was extracted three times with EA. The combined organic layers were washed with 1 M HCl and dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue was purified by a flash column chromatography on a silica gel eluting with petroleum ether and ethyl acetate to afford the corresponding oxime esters.

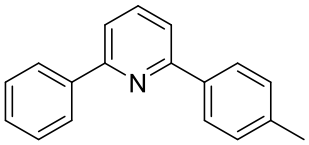
Typical procedure for the synthesis of pyridines



Under N_2 atmosphere, CuBr (10 mol%), 1,10-phenanthroline (10 mol%), **1** (0.5 mmol), **2** (0.25 mmol), $NaIO_4$ (1.0 eq.), $NaIO_4$ (0.5 eq.), TEMPO (0.2 eq.) and DMSO (1.0 mL) were introduced in a Schlenk tube (25 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 120 °C (oil bath temperature) for 24 h. After cooling down to room temperature, quenched with water, extracted with ethyl acetate (3×5 mL), and dried over anhydrous Na_2SO_4. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 °C) and ethyl acetate to give the desired product Pyridines **3** or **4**.

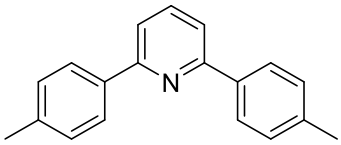
Analytical data of the obtained compounds

(1) 2-phenyl-6-(*p*-tolyl)pyridine (3a).[1] CAS: 1286679-11-5.



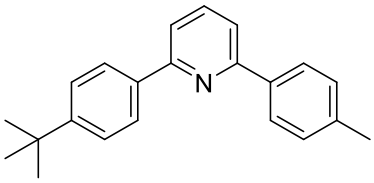
White solid (32 mg, 65%), m.p.:83.2-84.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 156.8, 139.6, 139.0, 137.4, 136.8, 129.4, 128.9, 128.7, 127.0, 126.9, 118.3, 21.3; MS (EI, m/z): 245.11 $[M]^+$.

(2) 2,6-*di*-*p*-tolylpyridine (3b).[2] CAS: 14435-88-2.



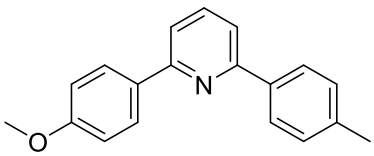
White solid (36 mg, 69%), m.p.: 87.0-88.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 4H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 4H), 2.35 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 137.8, 136.3, 135.8, 128.4, 125.8, 117.0, 20.3; MS (EI, m/z): 259.15 $[M]^+$.

(3) 2-(4-(*tert*-butyl)phenyl)-6-(*p*-tolyl)pyridine (3c).



White solid (60 mg, 64%), m.p.: 98.4-99.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (t, *J* = 8.8 Hz, 4H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 155.7, 151.0, 137.8, 136.3, 135.9, 135.8, 128.3, 125.8, 125.7, 124.6, 117.1, 117.0, 33.7, 30.3, 20.3; HRMS (ESI): Calcd. for $C_{22}H_{24}N$: 302.1904; found: 302.1902.

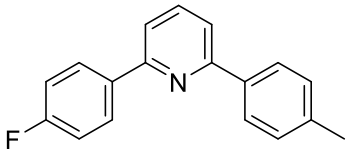
(4) 2-(4-methoxyphenyl)-6-(*p*-tolyl)pyridine (3d).[3] CAS: 959042-66-1.



White solid (33 mg, 60%), m.p.: 135.5-136.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 3.2 Hz, 1H), 7.59 (d, *J* = 3.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ

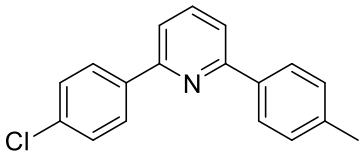
160.4, 156.7, 156.4, 138.9, 137.3, 136.9, 132.3, 129.4, 128.3, 126.8, 117.6, 117.6, 114.0, 55.4, 21.3; MS (EI, m/z): 275.15 $[M]^+$.

(5) 2-(4-fluorophenyl)-6-(*p*-tolyl)pyridine (3e).[3] CAS: 2244167-04-0.



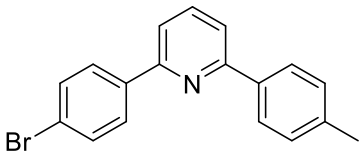
White solid (27 mg, 52%), m.p.: 116.2-117.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.03 (m, 2H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 8.7 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (d, *J* = 252 Hz), 156.9, 155.7, 139.1, 137.5, 136.6, 135.7 (d, *J* = 12.6 Hz), 129.5, 128.8, 128.7, 126.9, 118.1 (d, *J* = 38 Hz), 115.6, 115.5, 21.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.32; MS (EI, m/z): 263.10 $[M]^+$.

(6) 2-(4-chlorophenyl)-6-(*p*-tolyl)pyridine (3f).[3] CAS: 2411884-84-7.



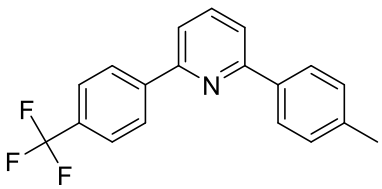
White solid (31 mg, 55%), m.p.: 112.7-113.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 154.5, 138.1, 137.0, 136.5, 135.5, 134.0, 128.4, 127.8, 127.2, 125.8, 117.6, 117.0, 20.3; MS (EI, m/z): 279.07 $[M]^+$.

(7) 2-(4-bromophenyl)-6-(*p*-tolyl)pyridine (3g).[3] CAS: 351333-79-4.



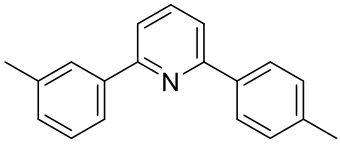
White solid (37 mg, 57%), m.p.:123.7-124.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 4H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56-7.52 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 155.6, 139.1, 138.5, 137.5, 136.5, 131.8, 129.5, 128.6, 126.9, 123.4, 118.7, 118.1, 21.3; MS (EI, m/z): 323.01 $[M]^+$.

(8) 2-(*p*-tolyl)-6-(4-(trifluoromethyl)phenyl)pyridine (3h).[3] CAS: 959070-72-5.



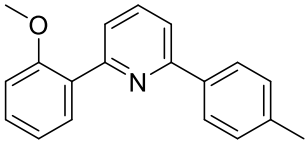
White solid (25 mg, 40%), m.p.: 115.2-116.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 9.3 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 154.2, 138.2, 136.6, 135.4, 128.5, 126.2, 125.8, 124.6 (q, *J* = 7.6 Hz), 118.1, 117.6, 20.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.54; MS (EI, m/z): 313.10 $[M]^+$.

(9) 2-(*m*-tolyl)-6-(*p*-tolyl)pyridine (3i).[4] CAS: 1476744-98-5.



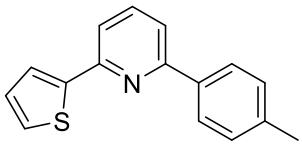
White solid (25 mg, 48%), m.p.: 85.7-86.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.97 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 155.9, 138.5, 137.9, 137.2, 136.3, 135.8, 128.6, 128.4, 127.5, 126.7, 125.9, 123.1, 117.4, 117.3, 20.6, 20.3; MS (EI, m/z): 259.16 $[M]^+$.

(10) 2-(2-methoxyphenyl)-6-(*p*-tolyl)pyridine (3j).



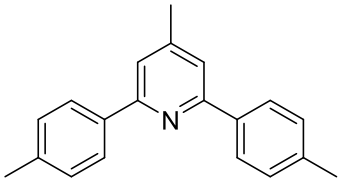
White solid (25 mg, 45%), m.p.: 129.4-129.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 3H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 156.8, 155.4, 138.7, 137.0, 136.3, 131.5, 129.8, 129.4, 129.4, 126.9, 123.2, 121.1, 118.0, 111.5, 55.7, 21.3; HRMS (ESI): Calcd. for $C_{19}H_{18}NO$: 276.1383; found: 276.1381.

(11) 2-(thiophen-2-yl)-6-(*p*-tolyl)pyridine (3l).



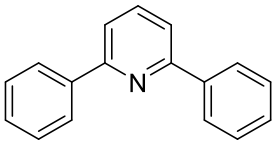
White solid (47 mg, 45%), m.p.: 75.4-76.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 4.6 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 5.9 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16-7.14 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 152.2, 145.6, 139.1, 137.3, 136.2, 129.4, 127.9, 127.5, 126.8, 124.4, 118.0, 116.7, 21.3; HRMS (ESI): Calcd. for $C_{16}H_{14}NS$: 252.0841; found: 252.0839.

(12) 4-methyl-2,6-*di*-*p*-tolylpyridine (3m).[5] CAS: 787623-31-8.



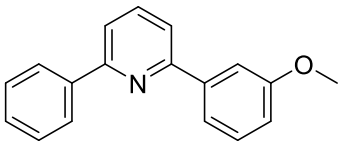
White solid (47 mg, 45%), m.p.: 94.3-95.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 4H), 7.48 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 3H), 2.42 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 148.1, 138.7, 137.0, 129.3, 126.9, 119.1, 21.5, 21.3. MS (EI, m/z): 273.15 $[M]^+$.

(13) 2,6-diphenylpyridine (4a).[1] CAS: 3558-69-8.



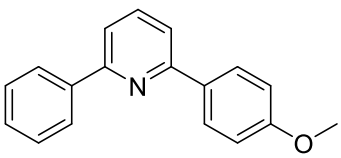
White solid (32 mg, 70%), m.p.: 78.4-79.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 4H), 7.63-7.59 (m, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.29 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 138.4, 136.4, 127.9, 127.6, 125.9, 117.5. MS (EI, m/z): 231.10 $[M]^+$.

(14) 2-(3-methoxyphenyl)-6-phenylpyridine (4b).[1] CAS: 2244166-96-7.



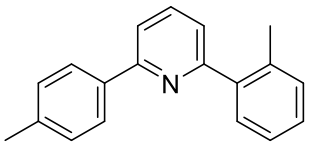
White solid (32 mg, 61%), m.p.: 125.5-126.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 2H), 7.78-7.75 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 6.4 Hz, 1H), 6.97 (d, *J* = 9.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 156.8, 156.6, 141.1, 139.5, 137.5, 129.7, 129.0, 128.7, 127.0, 119.5, 118.8, 114.6, 112.6, 55.4; MS (EI, m/z): 245.11 $[M]^+$.

(15) 2-(4-methoxyphenyl)-6-phenylpyridine (4c).[1] CAS: 33777-95-6.



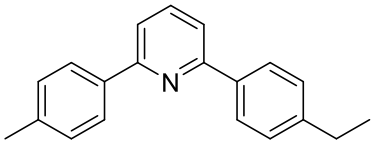
White solid (35 mg, 64%), m.p.: 131.5-132.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.11 (m, 4H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.66-7.63 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 156.7, 156.5, 139.6, 137.4, 132.2, 128.9, 128.7, 128.3, 127.0, 118.0, 117.9, 114.0, 55.4; MS (EI, m/z): 261.12 $[M]^+$.

(16) 2-(*o*-tolyl)-6-(*p*-tolyl)pyridine (4d).



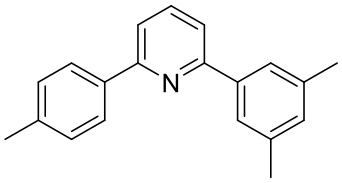
White solid (34 mg, 65%), m.p.: 80.1-81.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 6.5 Hz, 1H), 7.24-7.22 (m, 3H), 7.21-7.17 (m, 3H), 2.41 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 155.5, 139.6, 137.8, 135.9, 135.7, 135.1, 129.8, 128.8, 128.4, 127.2, 125.9, 124.8, 121.1, 116.9, 20.3, 19.7; HRMS (ESI): Calcd. for $C_{19}H_{18}N$: 260.1434; found: 260.1432.

(17) 2-(4-ethylphenyl)-6-(*p*-tolyl)pyridine (4e).



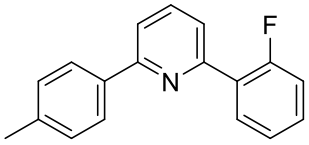
White solid (36 mg, 66%), m.p.:94.2-94.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (t, *J* = 8.0 Hz, 4H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 156.8, 145.2, 138.9, 137.3, 137.1, 136.8, 129.4, 128.2, 127.0, 126.9, 118.1, 118.0, 28.7, 21.3, 15.6; HRMS (ESI): Calcd. for $C_{20}H_{20}N$: 274.1591; found: 274.1590.

(18) 2-(3,5-dimethylphenyl)-6-(*p*-tolyl)pyridine (4f).[3] CAS: 2226087-23-4.



White solid (34 mg, 62%), m.p.: 93.4-93.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.67-7.64 (m, 3H), 7.53 (d, *J* = 7.7 Hz, 2H), 6.97 (s, 1H), 2.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 156.9, 139.6, 138.9, 138.2, 137.3, 136.9, 130.6, 129.4, 127.0, 124.9, 118.5, 118.3, 21.5, 21.3; MS (EI, m/z): 273.17 $[M]^+$.

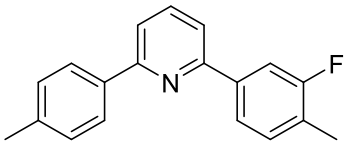
(19) 2-(2-fluorophenyl)-6-(*p*-tolyl)pyridine (4g).



Colorless oil (24 mg, 46%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (t, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.75-7.73 (m, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.40-7.36 (m, 1H), 7.31-7.27 (m, 3H), 7.18-7.14 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8 (d, *J* = 250 Hz), 157.1, 152.7, 139.0, 137.1, 136.6, 131.3, 130.3 (d, *J* = 8.8 Hz), 129.4, 126.8, 124.5, 122.6, 122.5, 118.7, 116.2 (d, *J* = 24

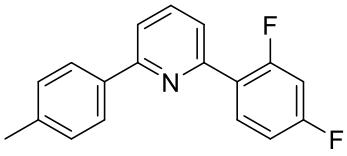
Hz), 21.30; ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.79; HRMS (ESI): Calcd. for $C_{18}H_{15}FN$: 264.1184; found: 264.1180.

(20) 2-(3-fluoro-4-methylphenyl)-6-(*p*-tolyl)pyridine (4h).



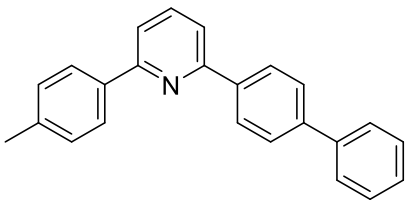
White solid (36 mg, 65%), m.p.:92.5-93.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 11.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.27-7.22 (m, 1H), 2.41 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244 Hz), 156.9, 155.4, 139.3, 139.1, 137.5, 136.6, 131.6 (d, *J* = 5.0 Hz), 129.5, 126.9, 125.5, 122.1, 122.0, 118.5, 118.0, 113.5 (d, *J* = 24.0 Hz), 21.3, 14.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.49; HRMS (ESI): Calcd. for $C_{19}H_{17}FN$: 278.1340; found: 278.1338.

(21) 2-(2,4-difluorophenyl)-6-(*p*-tolyl)pyridine (4i).



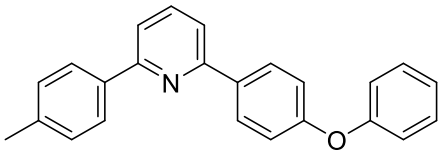
Colorless oil (28 mg, 50%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26-8.20 (m, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.70-7.66 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.05-7.00 (m, 1H), 6.94-6.89 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 252 Hz), 162.1 (d, *J* = 252 Hz), 156.1, 150.8, 150.8, 138.1, 136.2, 135.5, 131.4 (d, *J* = 10 Hz), 131.3 (d, *J* = 10 Hz), 128.4, 125.8, 121.2, 121.1, 117.7, 110.8 (d, *J* = 21.4 Hz), 110.7 (d, *J* = 20.2 Hz), 103.5, 103.3, 103.0, 20.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.65, -112.33; HRMS (ESI): Calcd. for $C_{18}H_{14}F_2N$: 282.1089; found: 282.1085.

(22) 2-([1,1'-biphenyl]-4-yl)-6-(*p*-tolyl)pyridine (4j).



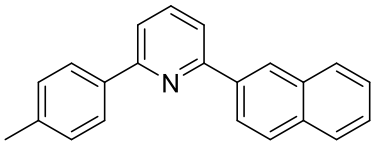
White solid (35 mg, 55%), m.p.: 129.5-130.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 155.3, 140.6, 139.7, 138.0, 137.5, 136.4, 135.7, 128.4, 127.8, 126.4, 126.4, 126.3, 126.1, 125.9, 117.3, 117.2, 20.3; HRMS (ESI): Calcd. for $C_{24}H_{20}N$: 322.1591; found: 322.1588.

(23) 2-(4-phenoxyphenyl)-6-(*p*-tolyl)pyridine (4k).



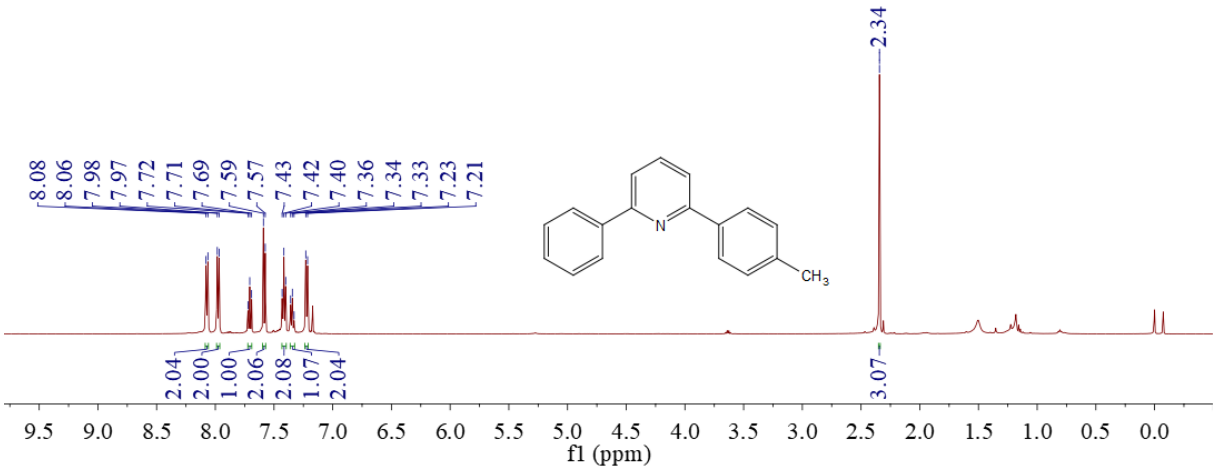
White solid (35 mg, 52%), m.p.: 138.2-139.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.15-7.10 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 156.0, 155.8, 155.1, 137.9, 136.4, 135.7, 133.7, 128.8, 128.4, 127.5, 125.8, 122.5, 118.1, 117.8, 117.0, 116.9, 20.3; HRMS (ESI): Calcd. for $C_{24}H_{20}NO$: 338.1540; found: 338.1538.

(24) 2-(naphthalen-2-yl)-6-(*p*-tolyl)pyridine (4l).

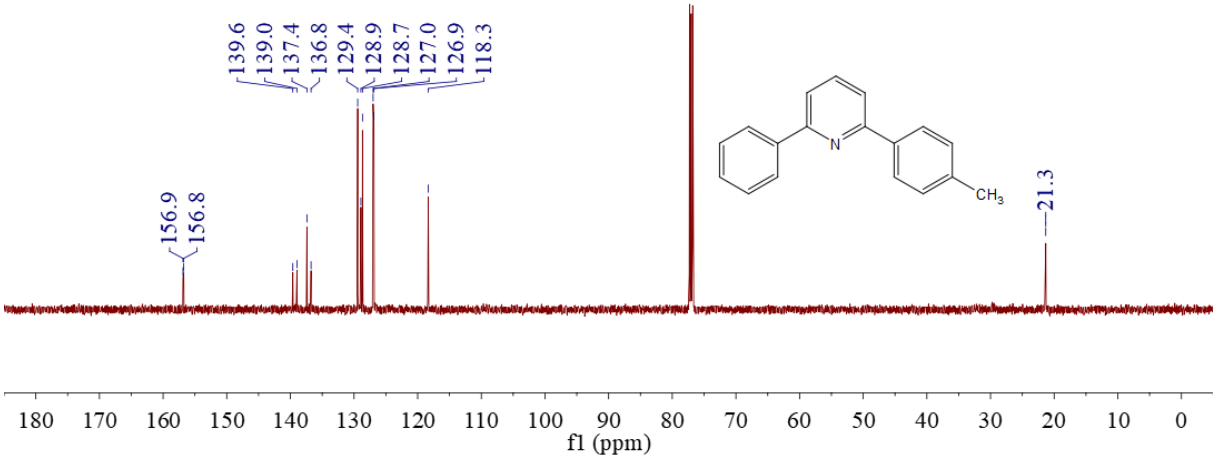


Colorless oil (30 mg, 50%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.99-7.95 (m, 2H), 7.89-7.87 (m, 1H), 7.84-7.80 (m, 2H), 7.69 (d, *J* = 6.8 Hz, 1H), 7.53-7.50 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 156.7, 139.0, 137.5, 137.0, 136.8, 133.7, 133.6, 129.5, 128.8, 128.3, 127.7, 126.9, 126.4, 126.3, 126.2, 124.8, 118.6, 118.5, 21.3; HRMS (ESI): Calcd. for $C_{22}H_{18}N$: 296.1434; found: 296.1432.

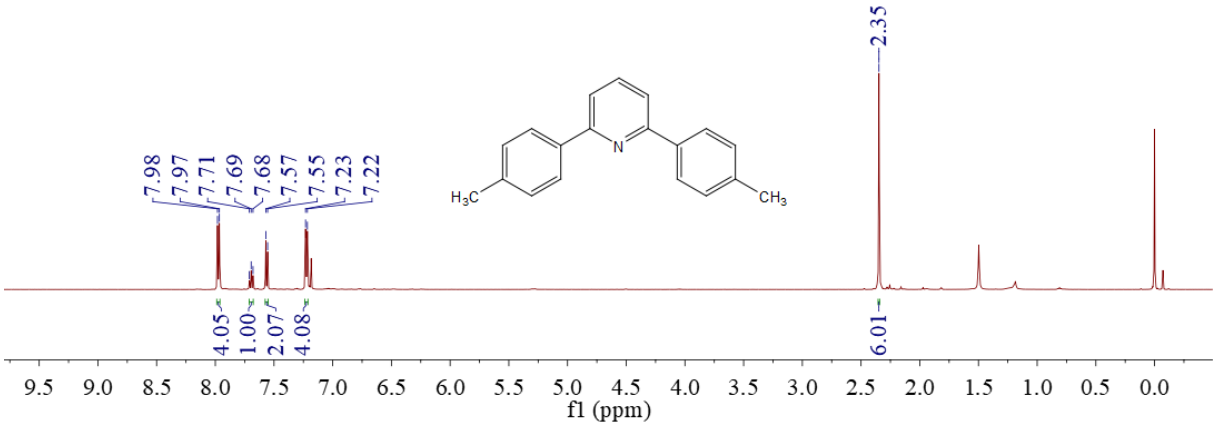
NMR spectra of the obtained compounds



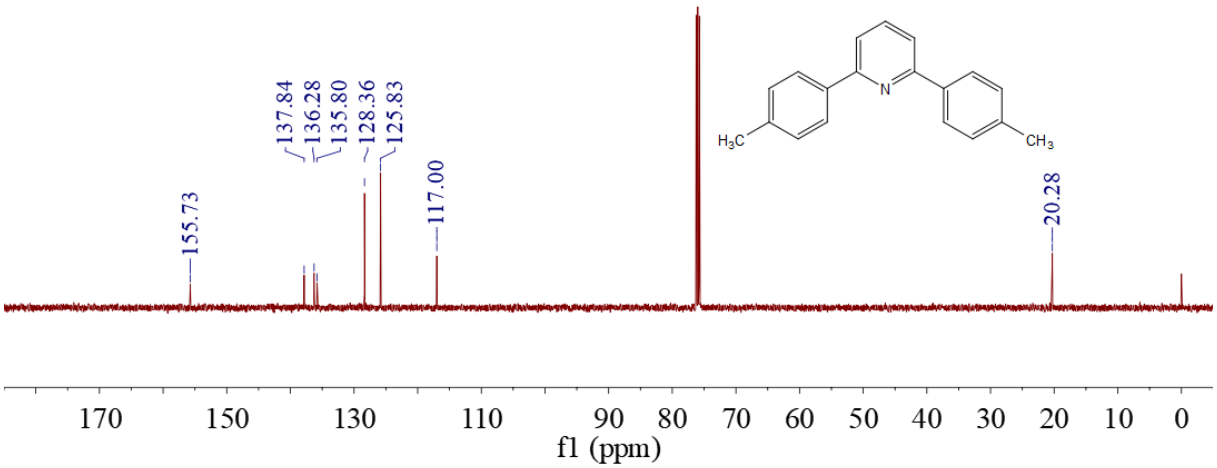
(1) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3a



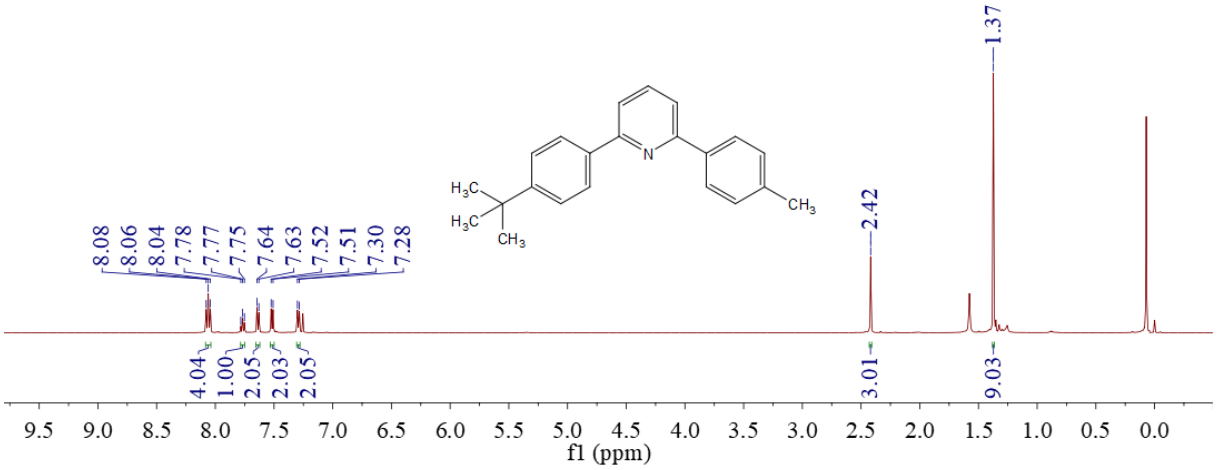
(1) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3a



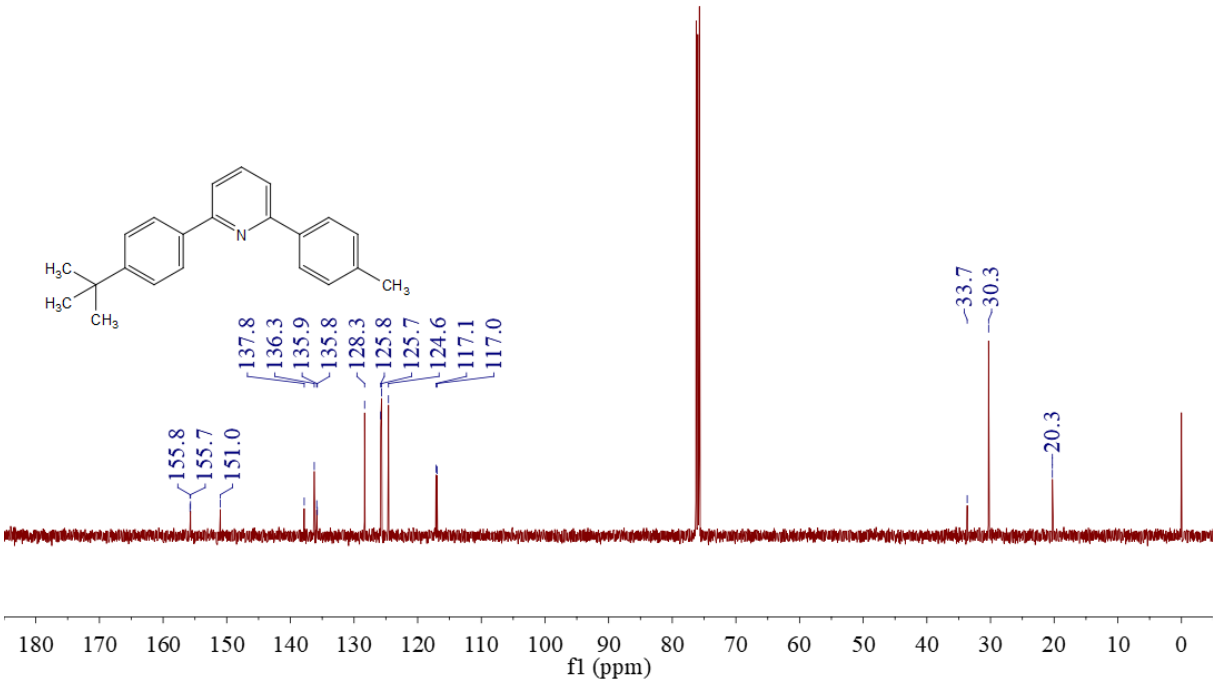
(2) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3b



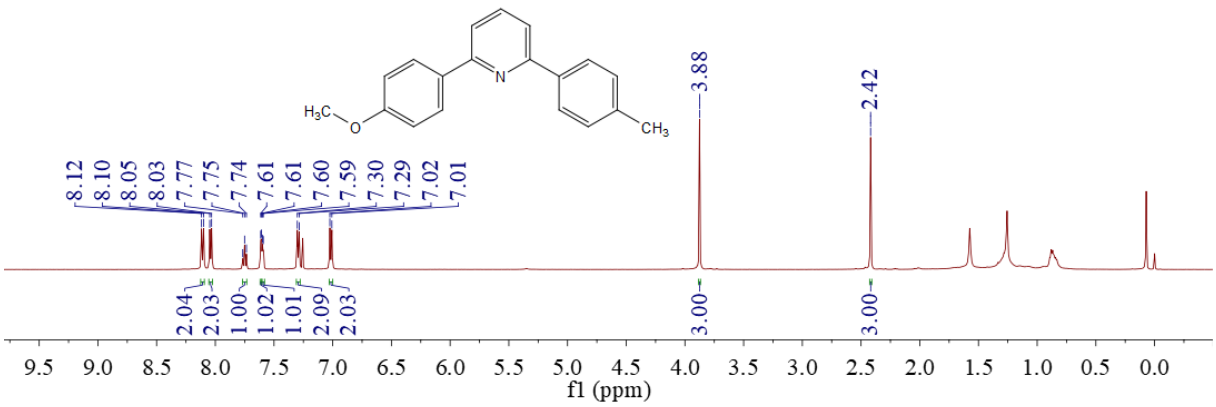
(2) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3b



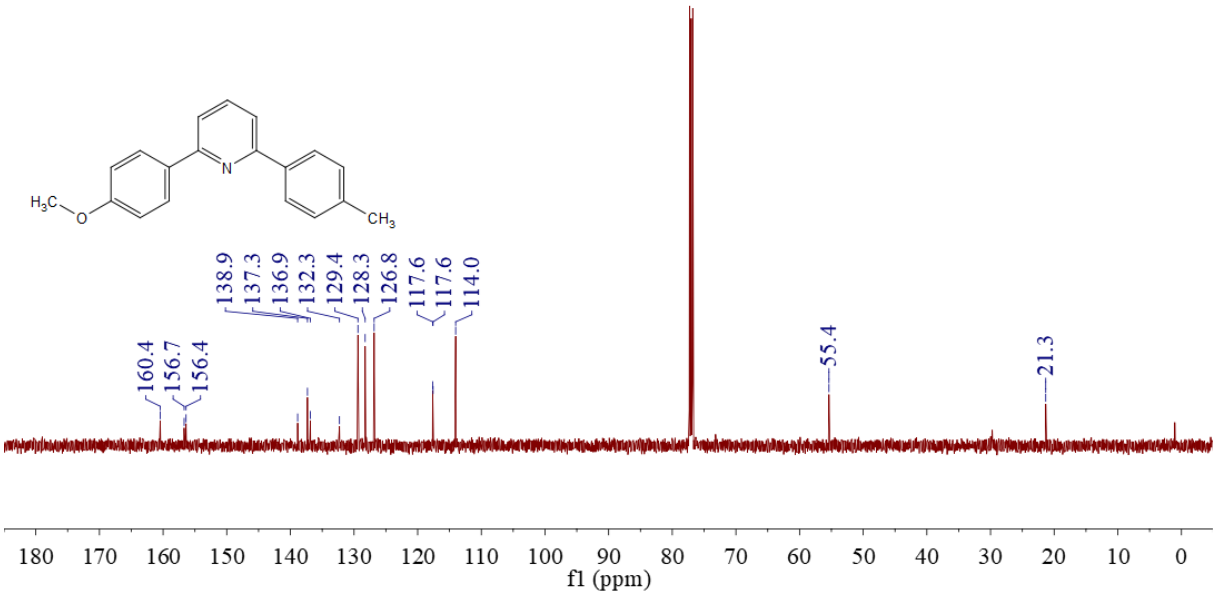
(3) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3c



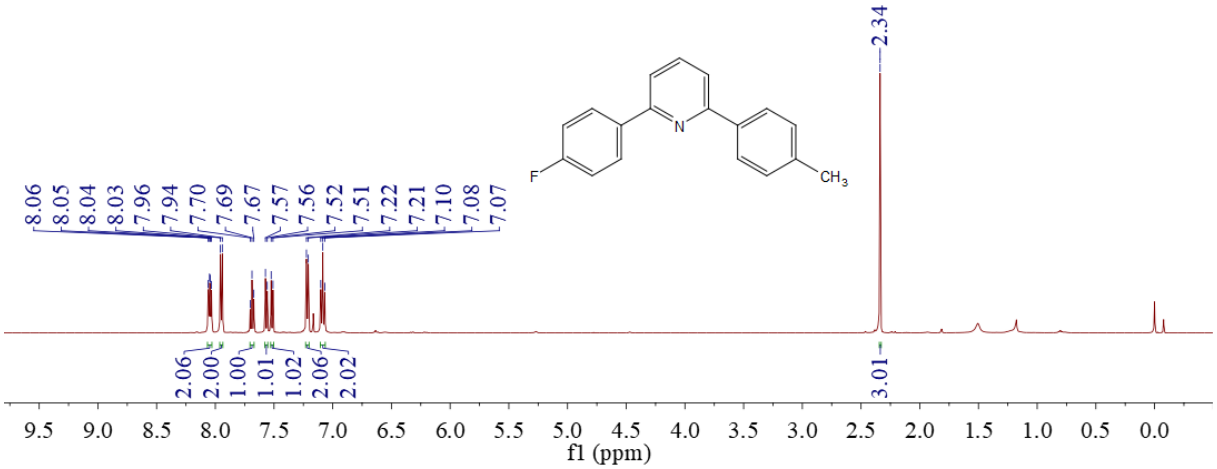
(3) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3c



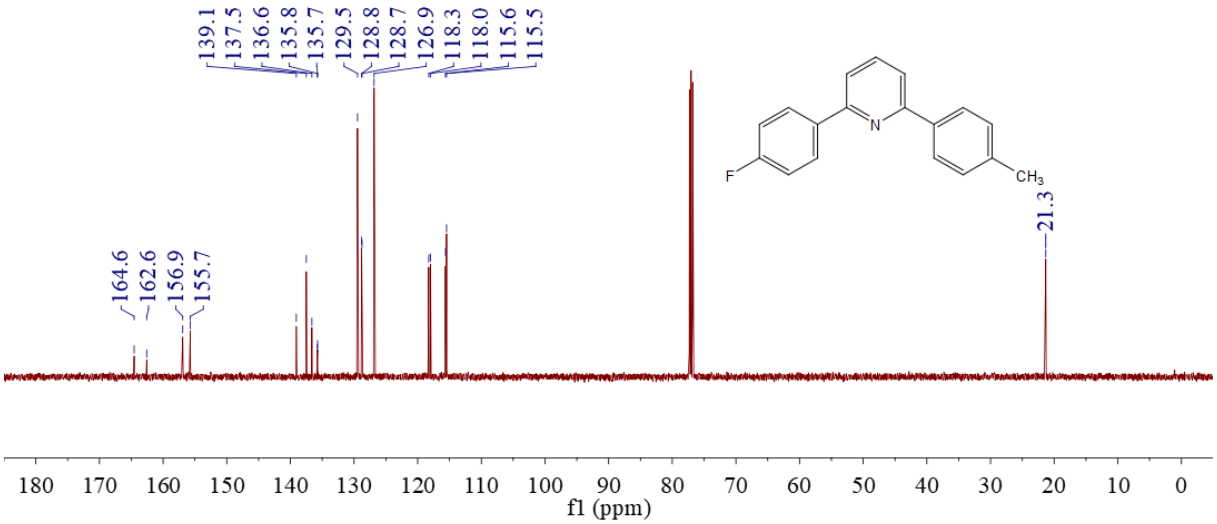
(4) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3d



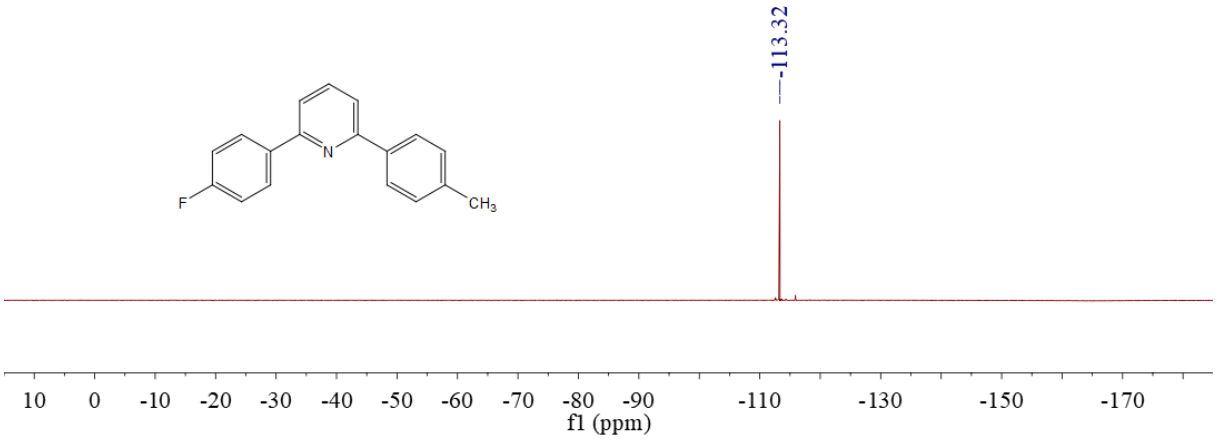
(4) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3d



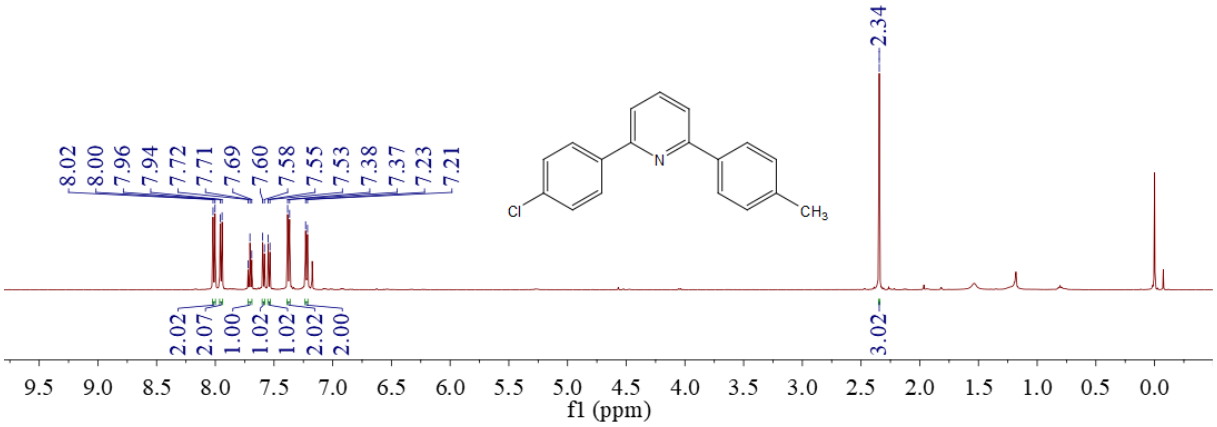
(5) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3e



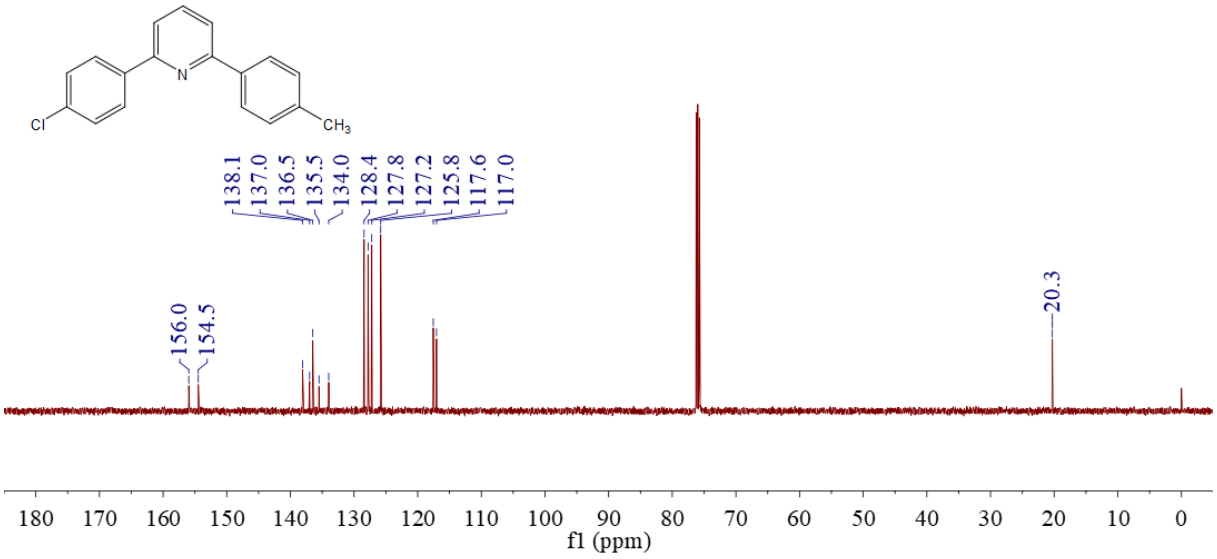
(5) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3e



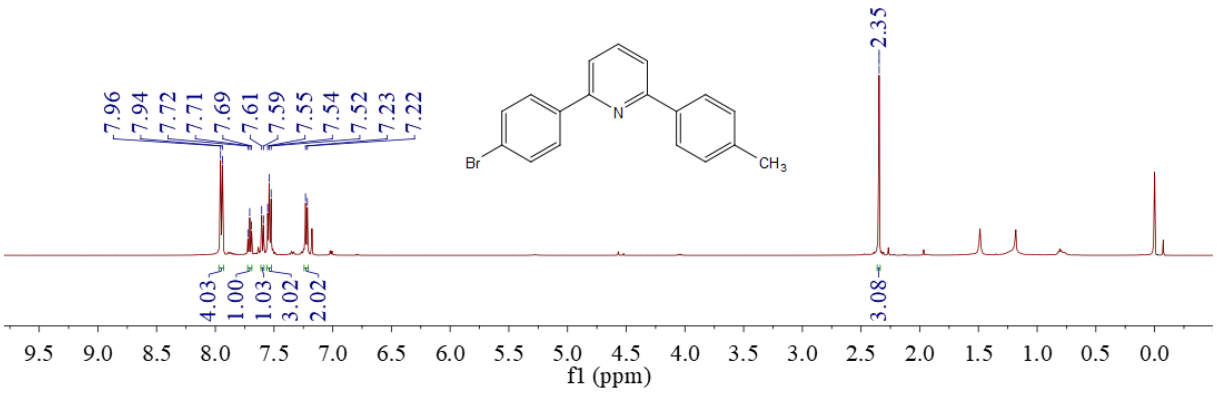
(5) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of 3e



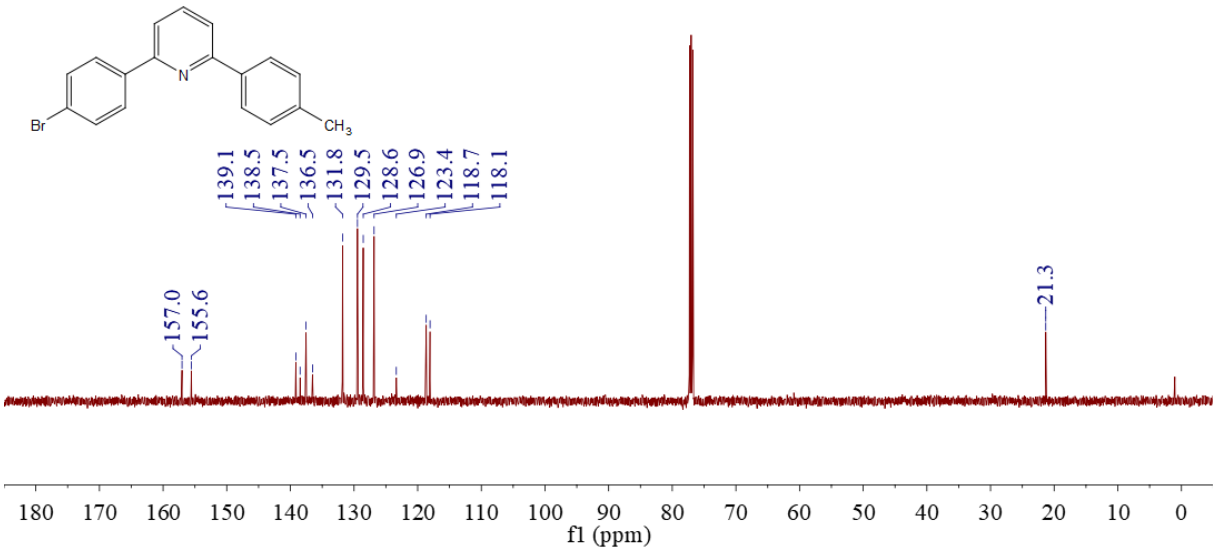
(6) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3f



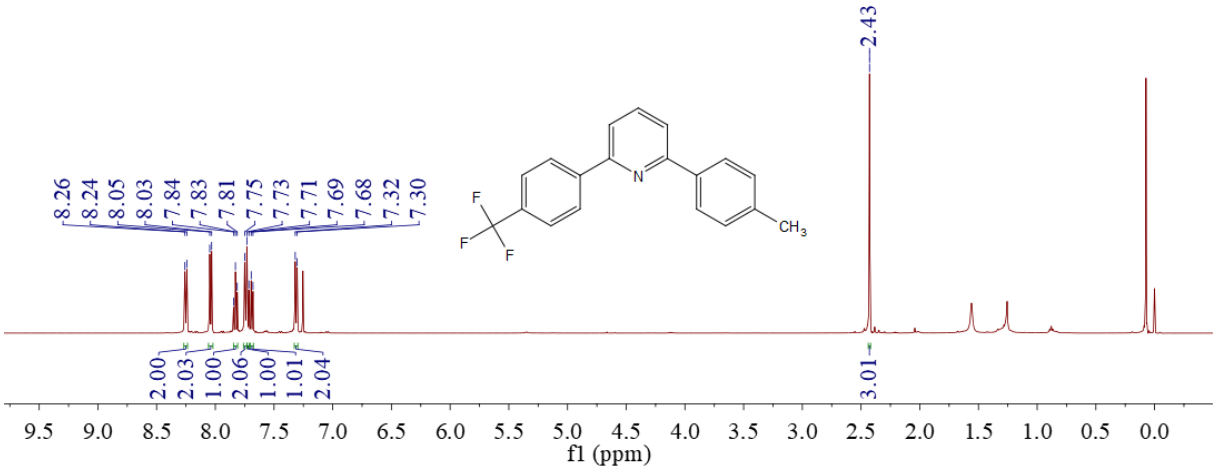
(6) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3f



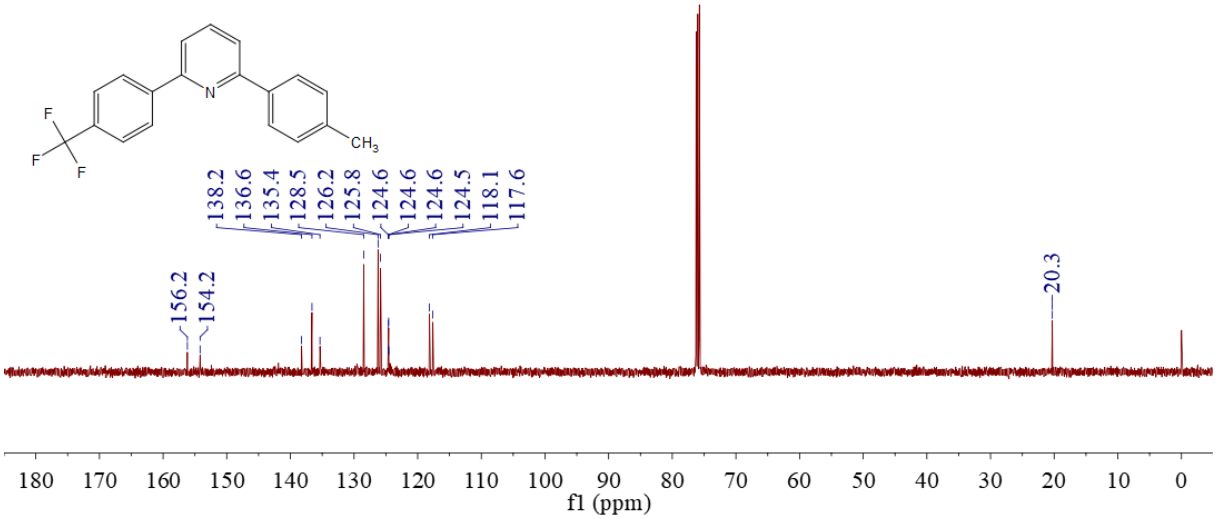
(7) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3g



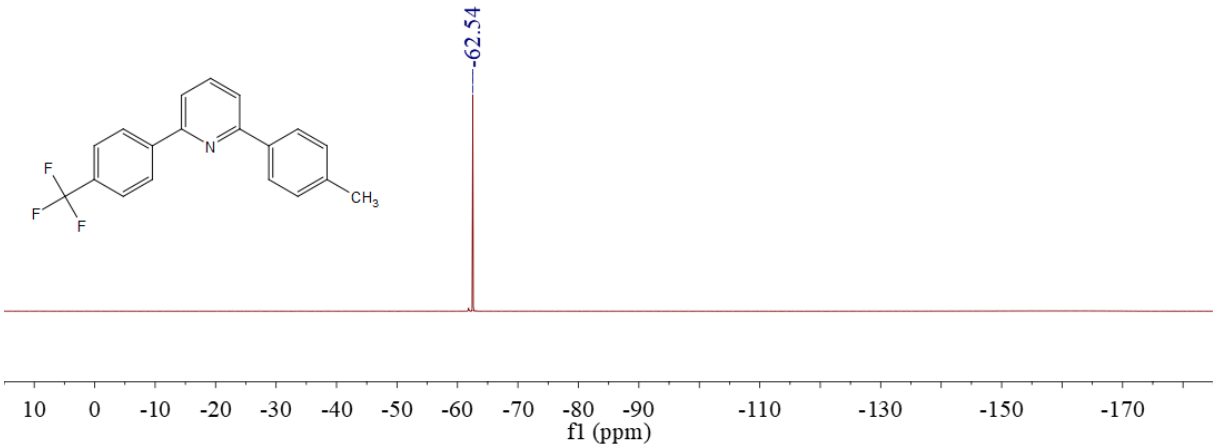
(7) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3g



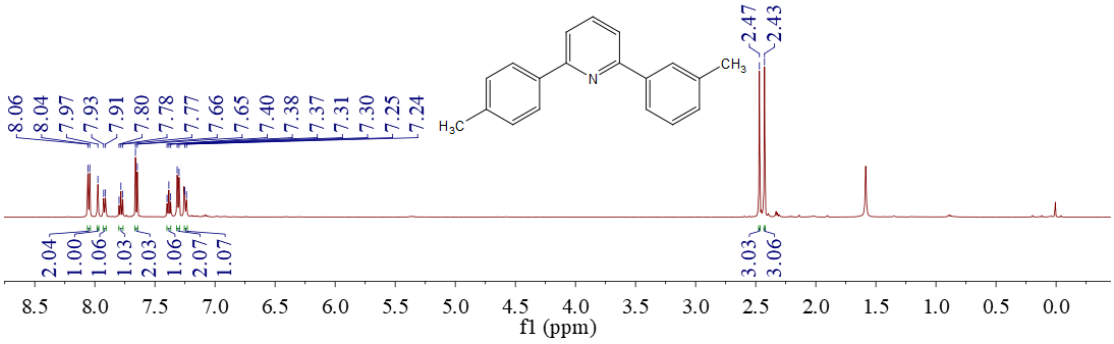
(8) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3h



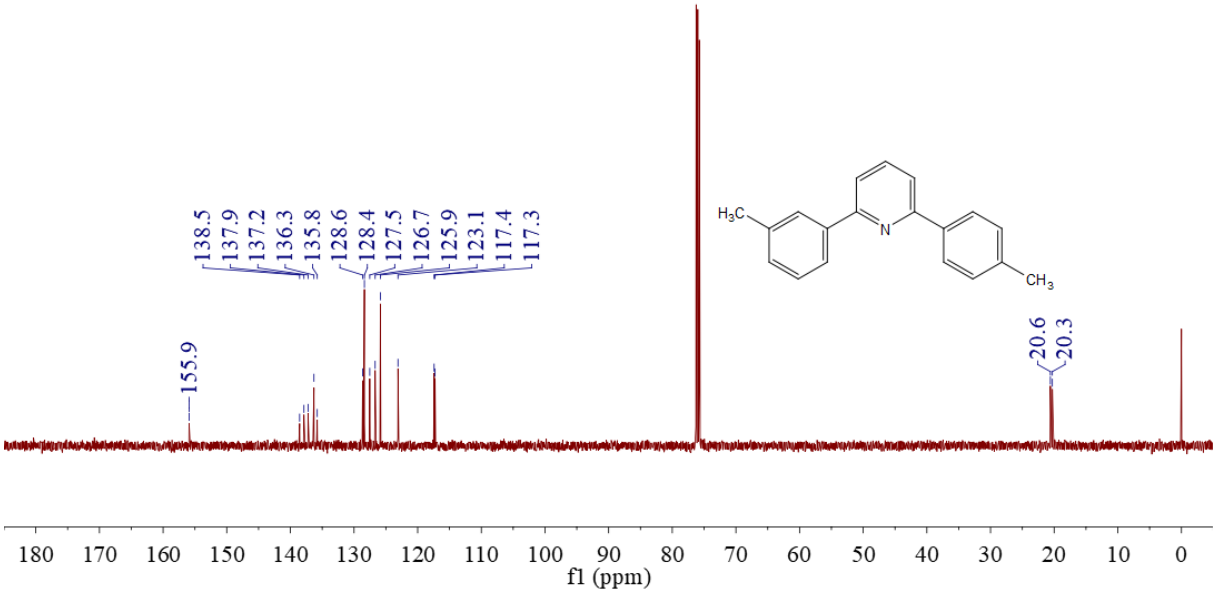
(8) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3h



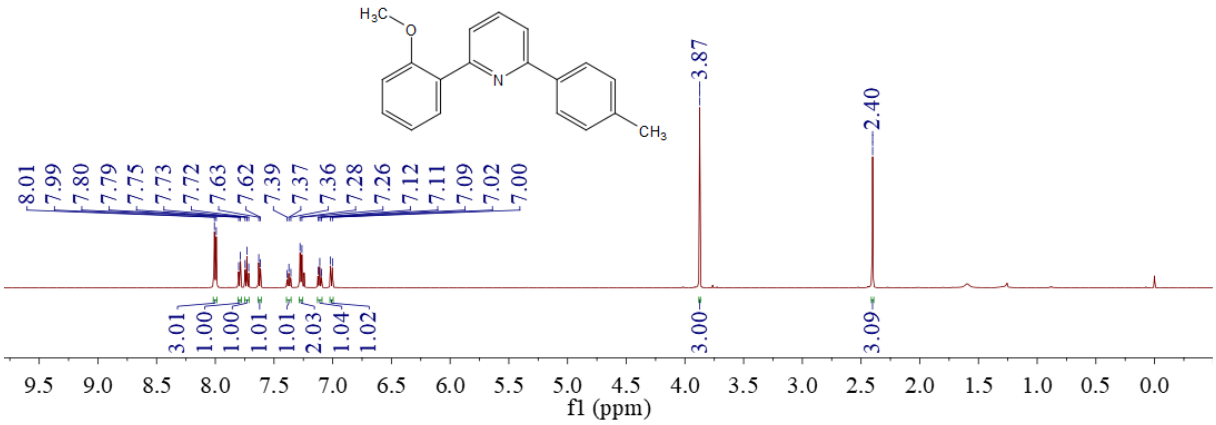
(8) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of 3h



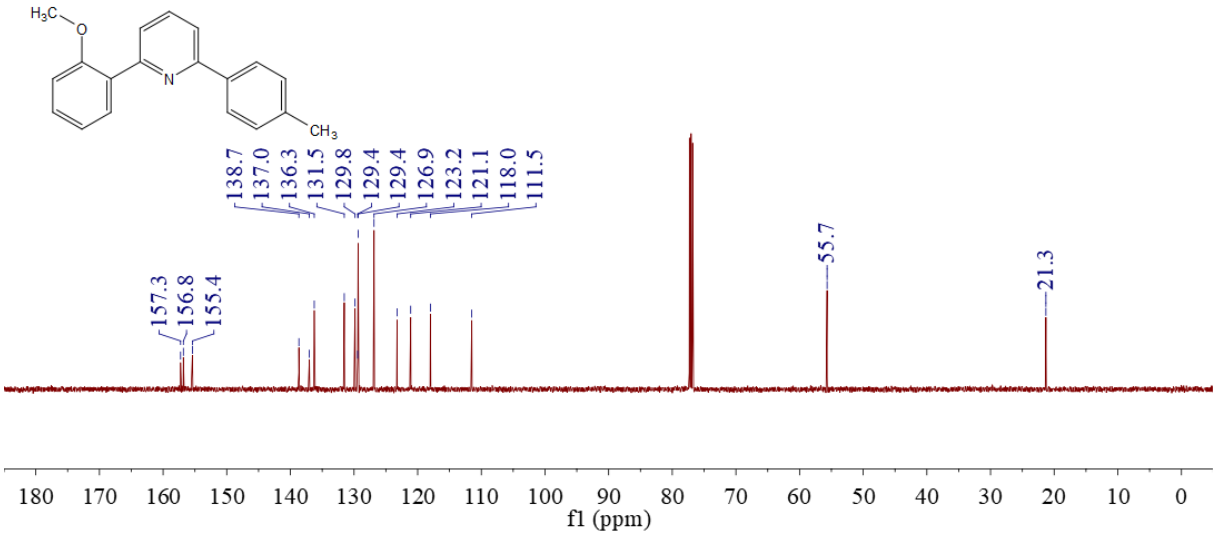
(9) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3i



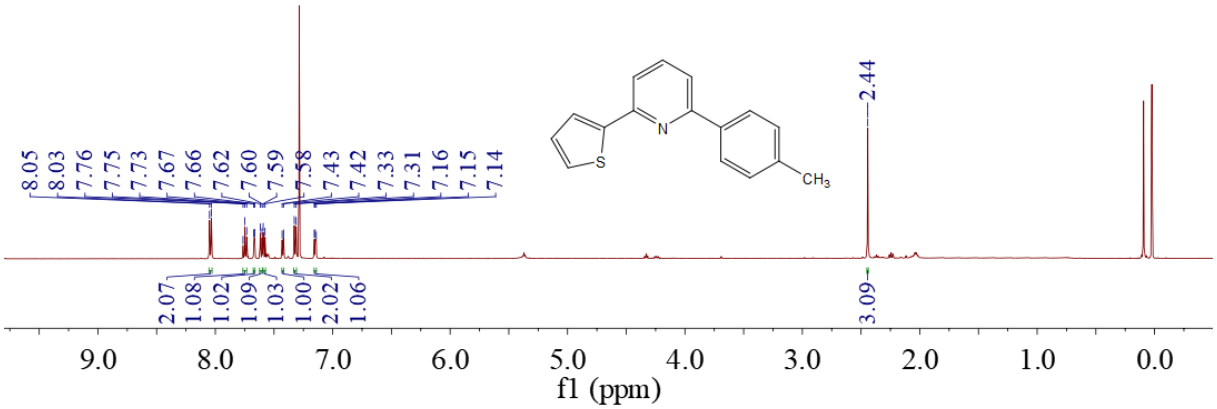
(9) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3i



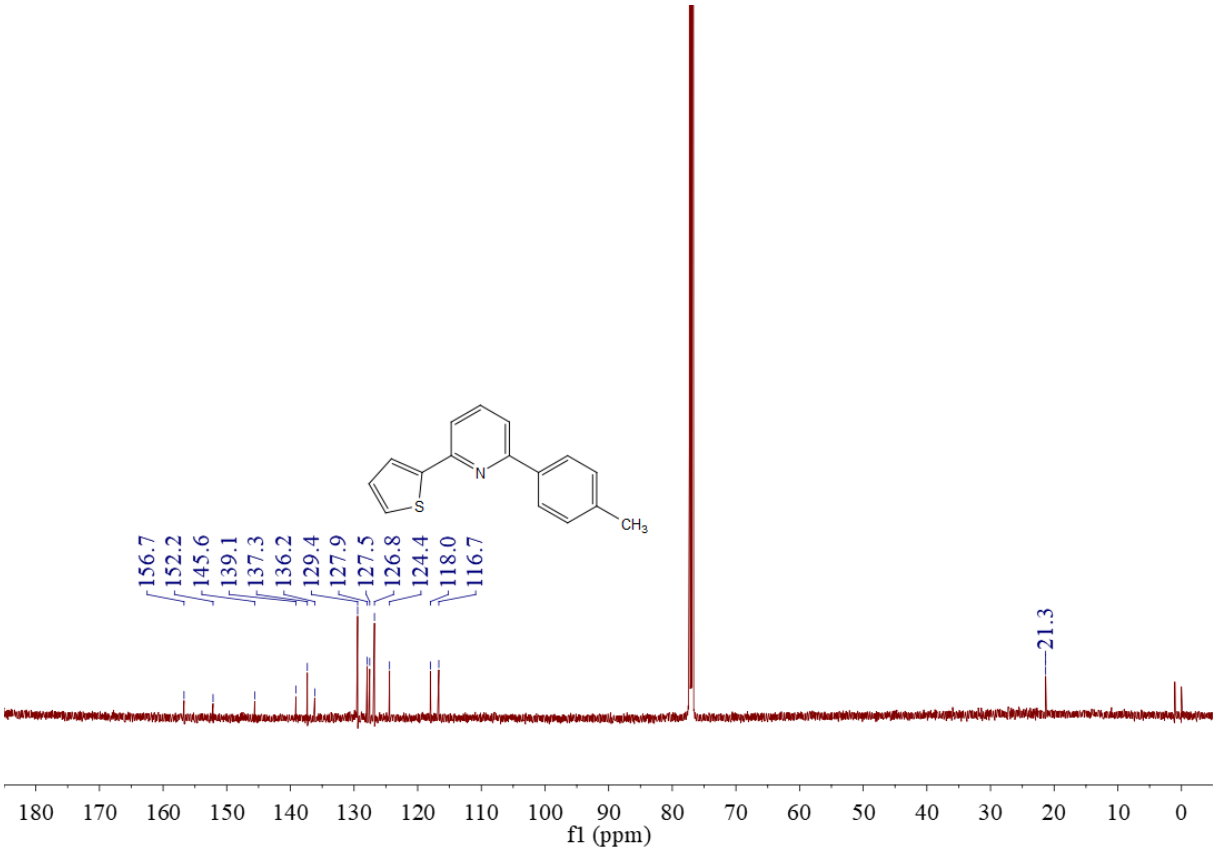
(10) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3j



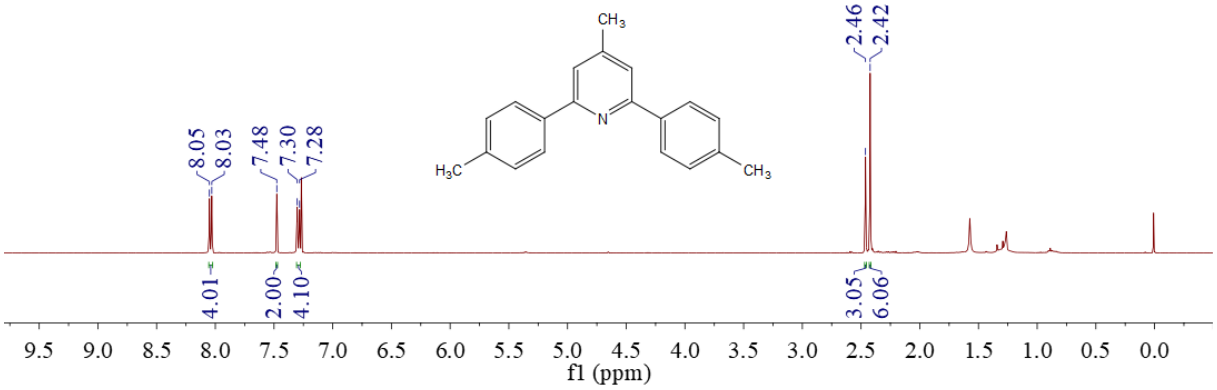
(10) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3j



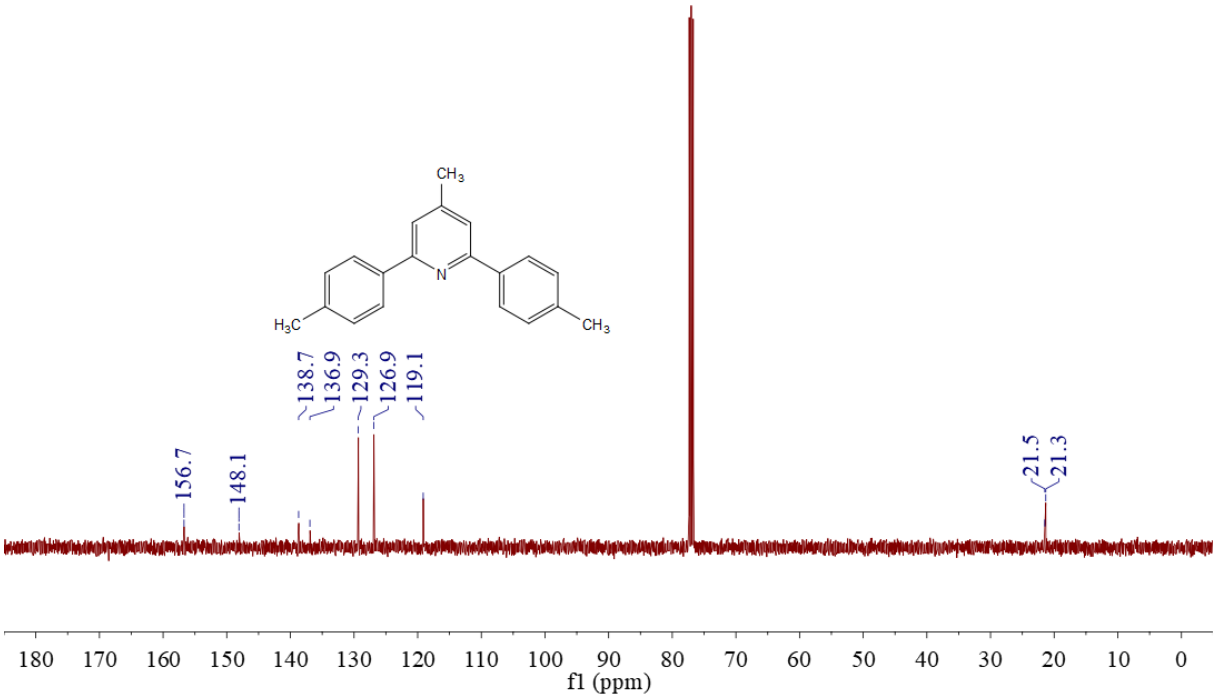
(11) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3l



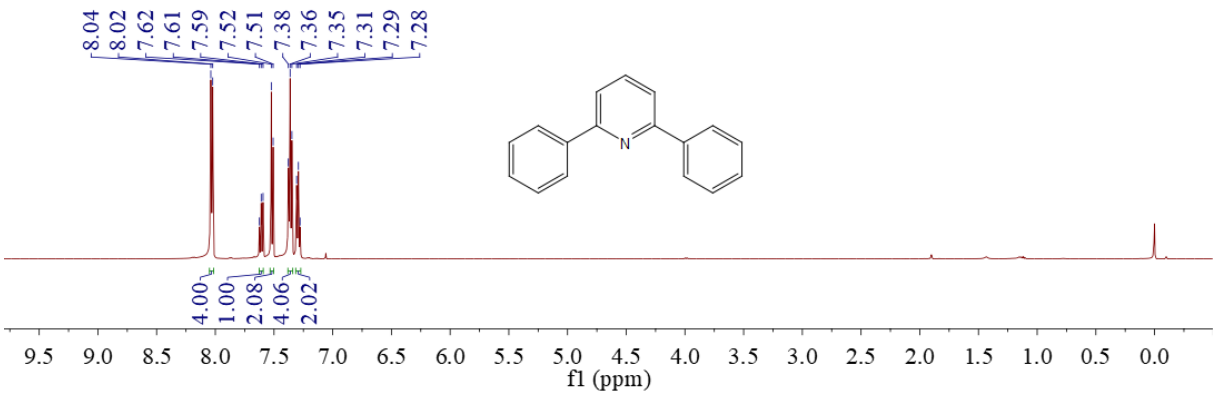
(11) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3l



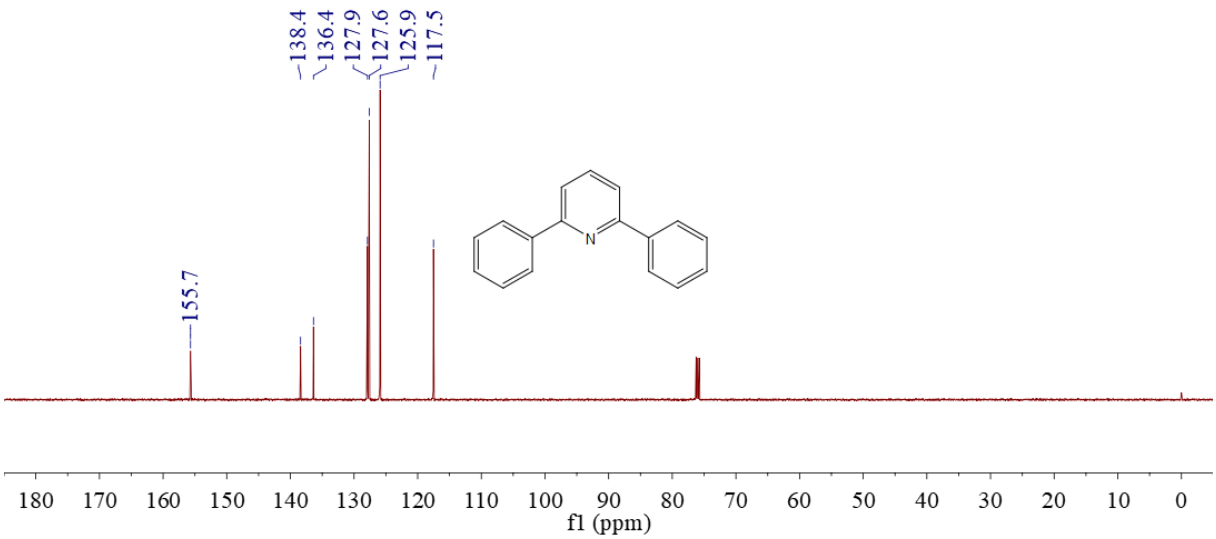
(12) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3m



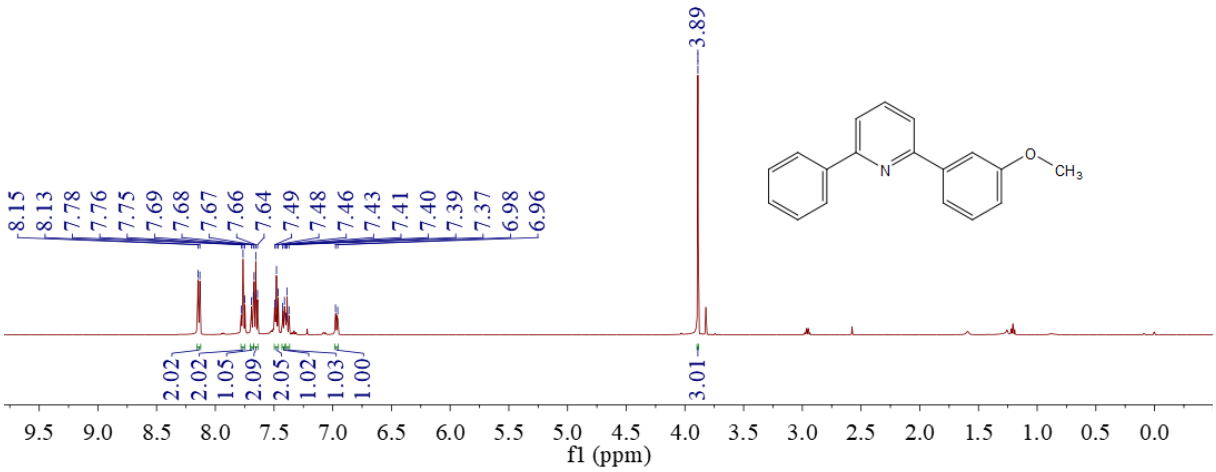
(12) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3m



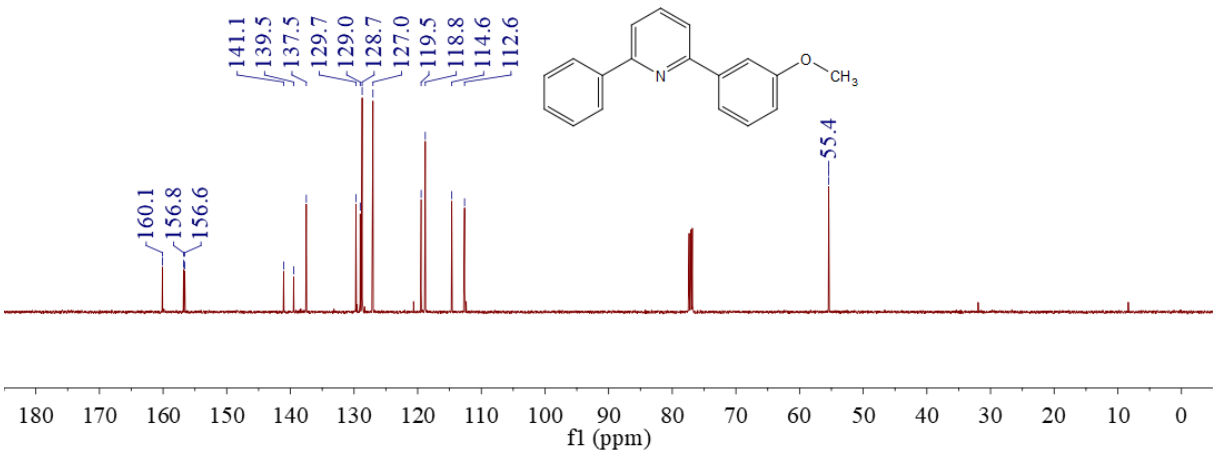
(13) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4a



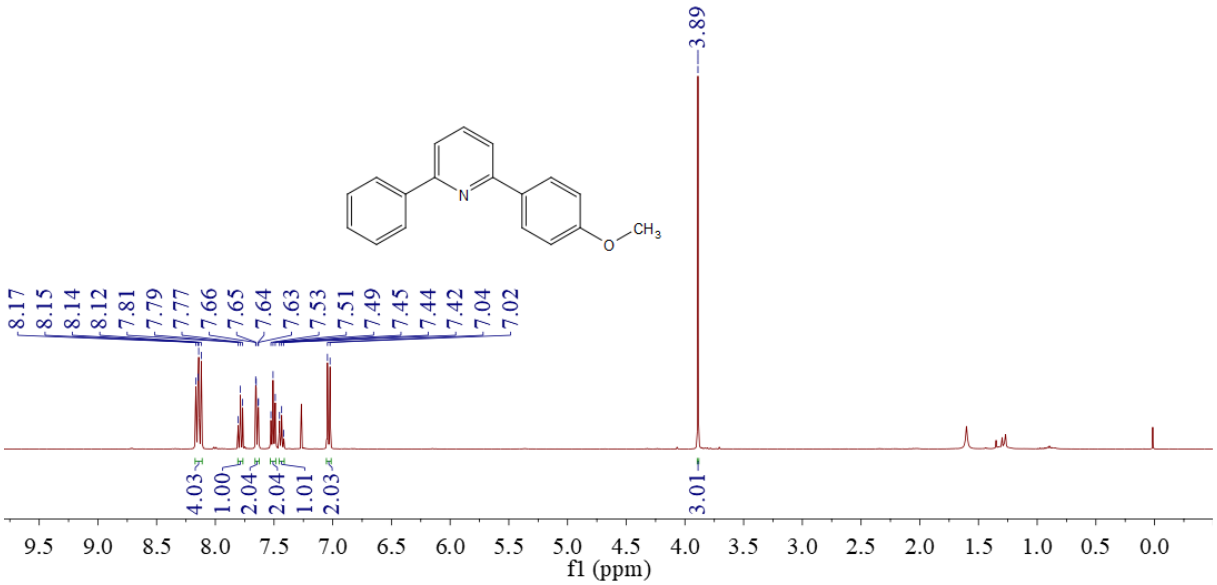
(13) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4a



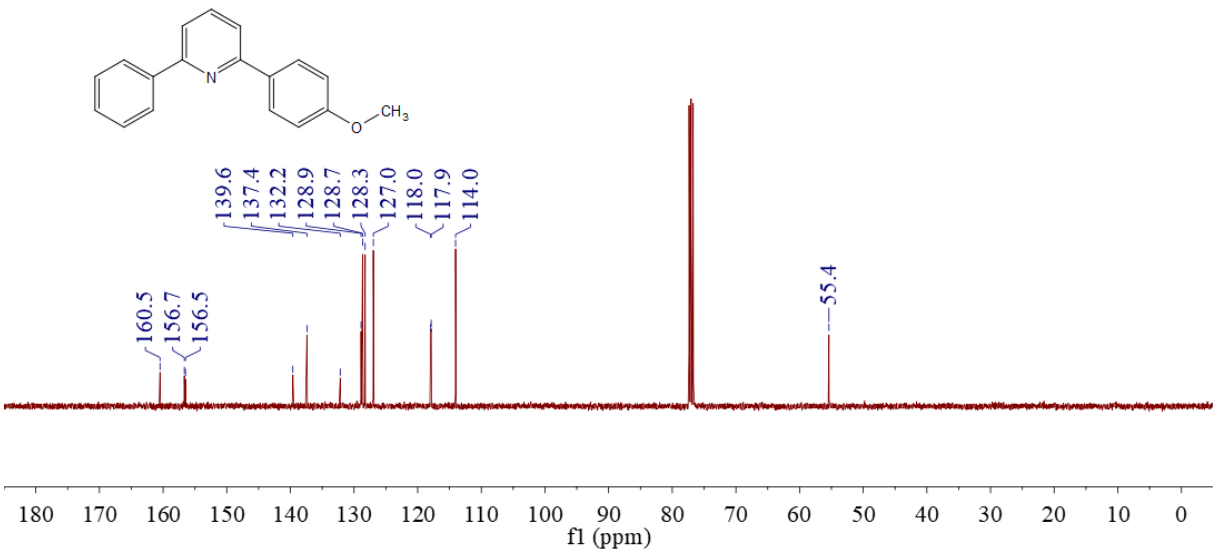
(14) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4b



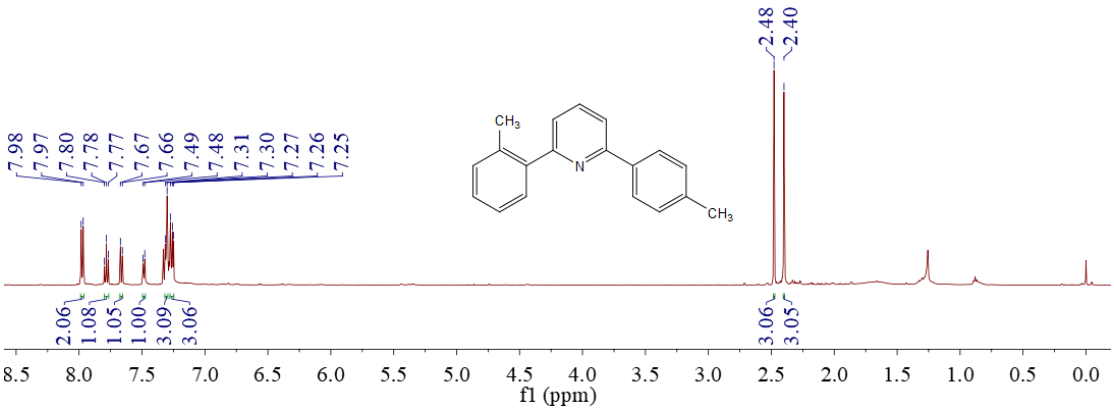
(14) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4b



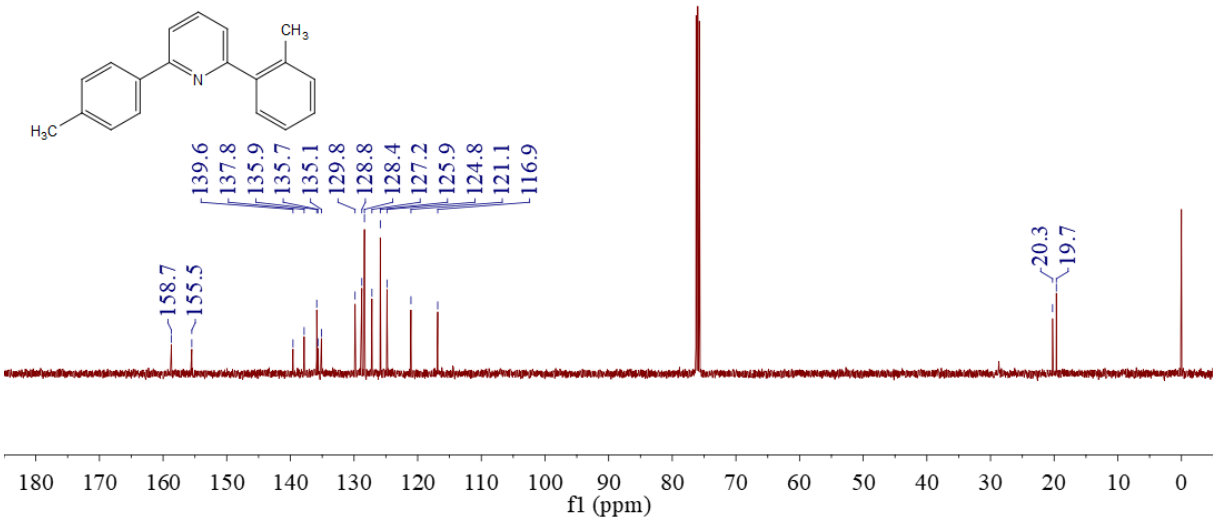
(15) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 4c



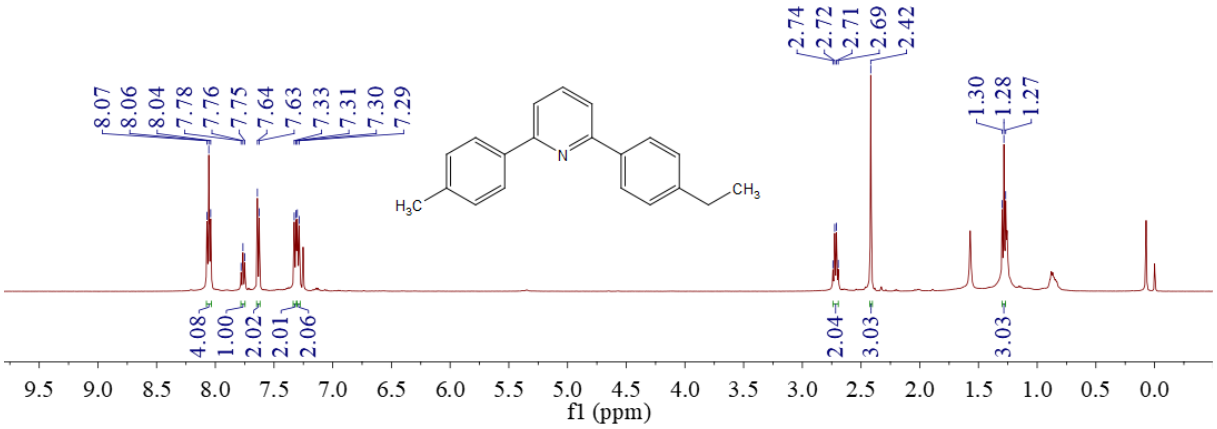
(15) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 4c



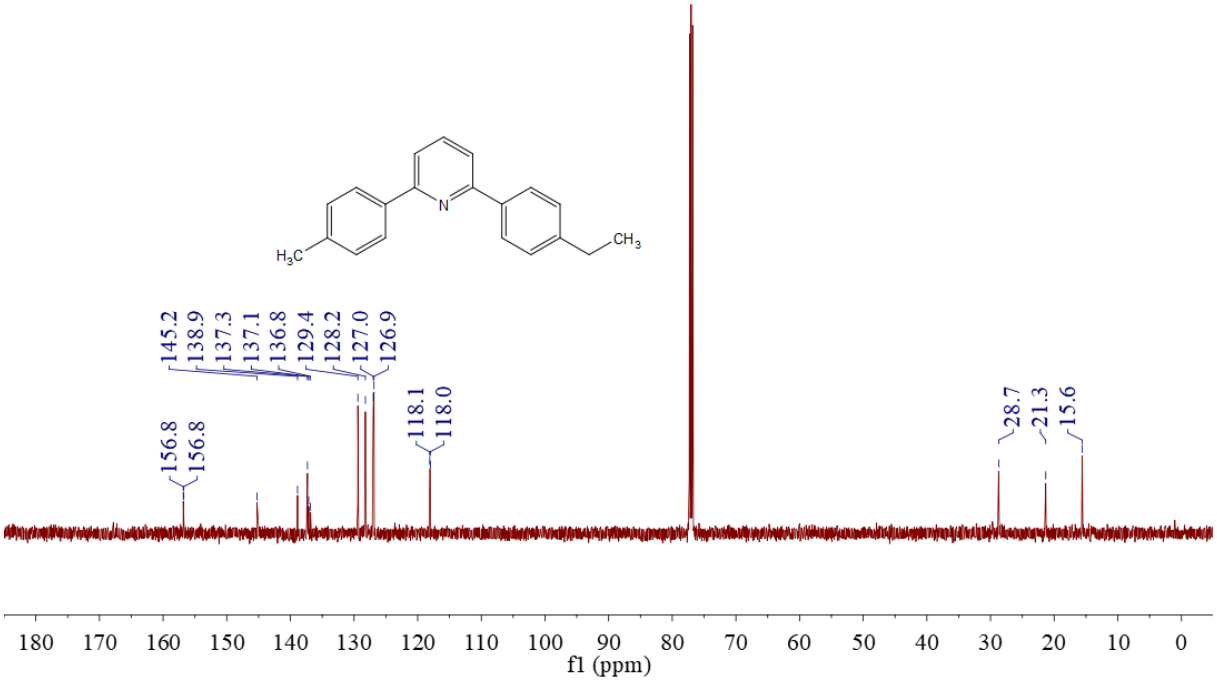
(16) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4d



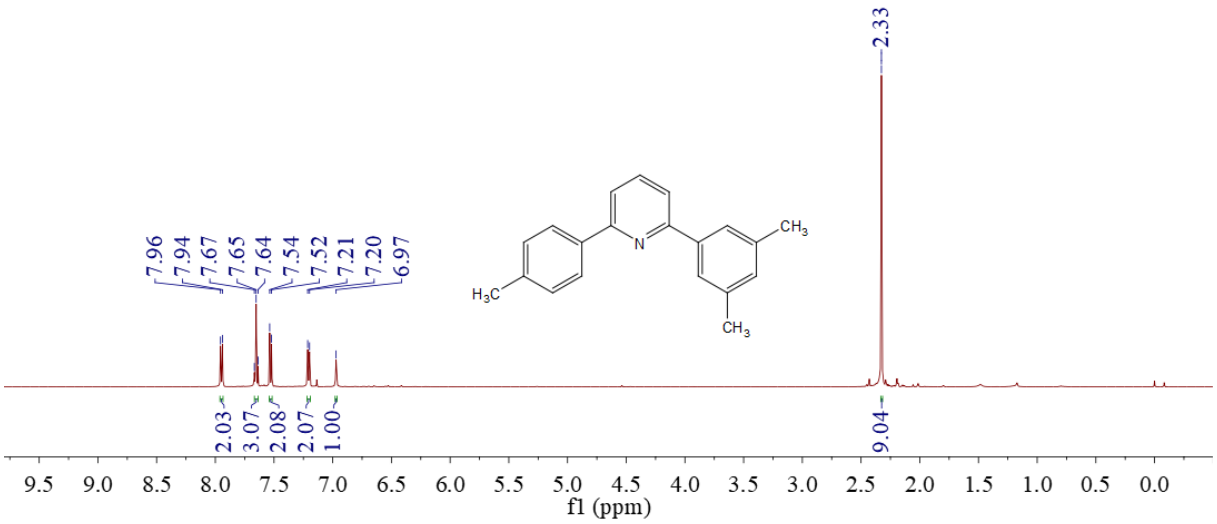
(16) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4d



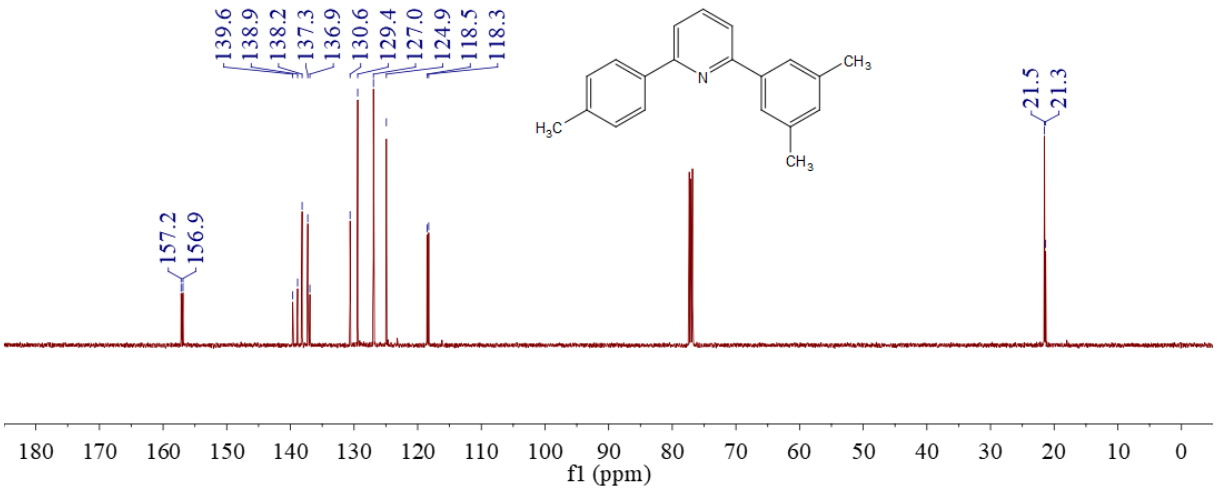
(17) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4e



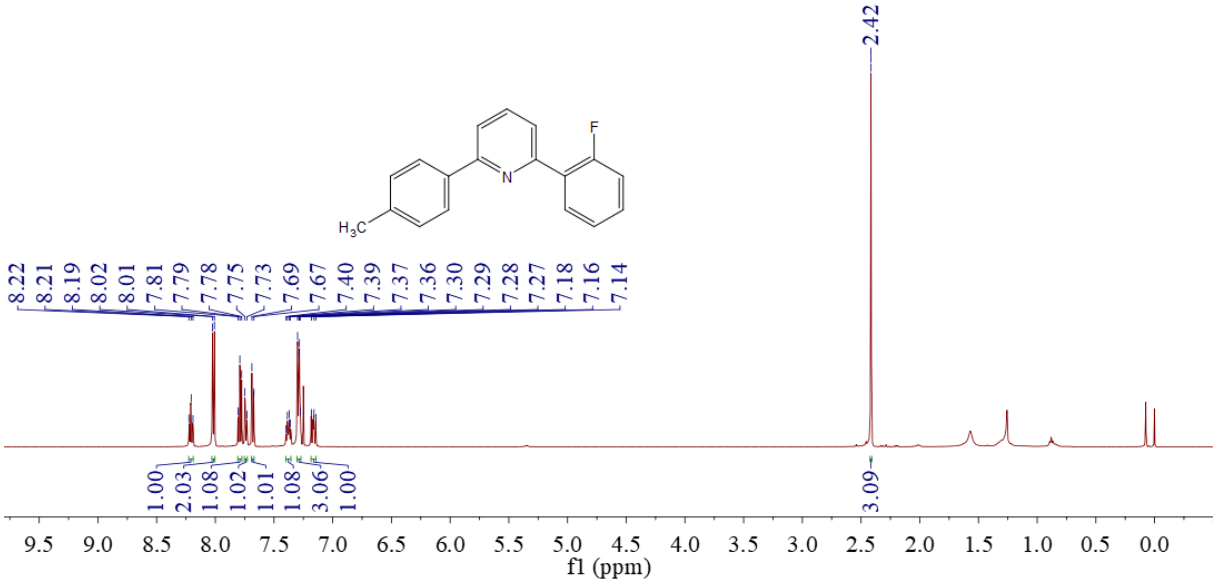
(17) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4e



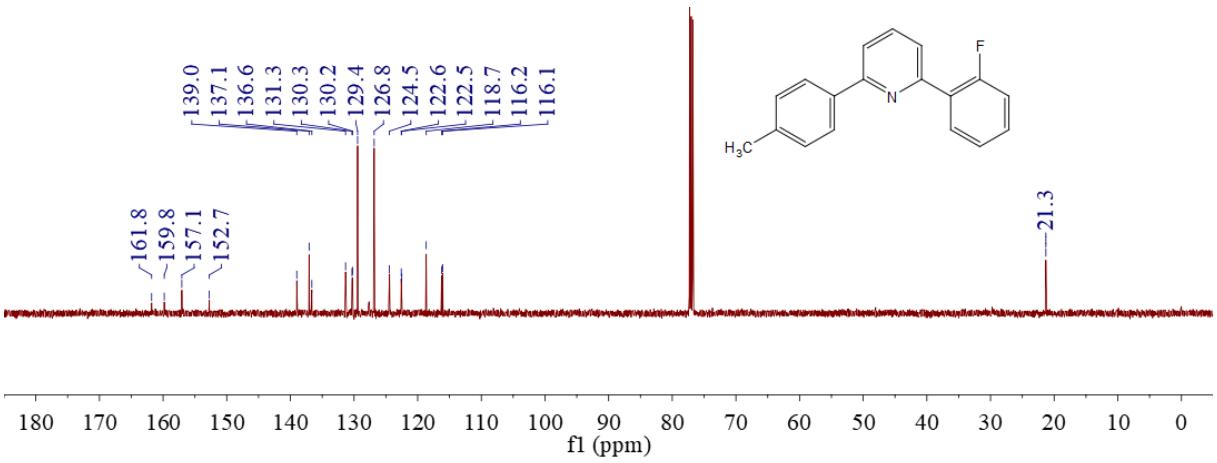
(18) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4f



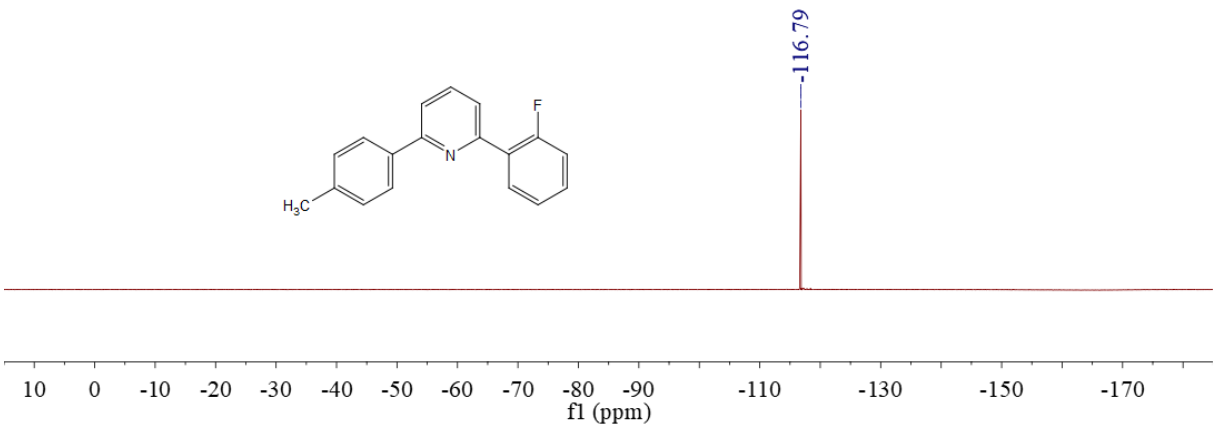
(18) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4f



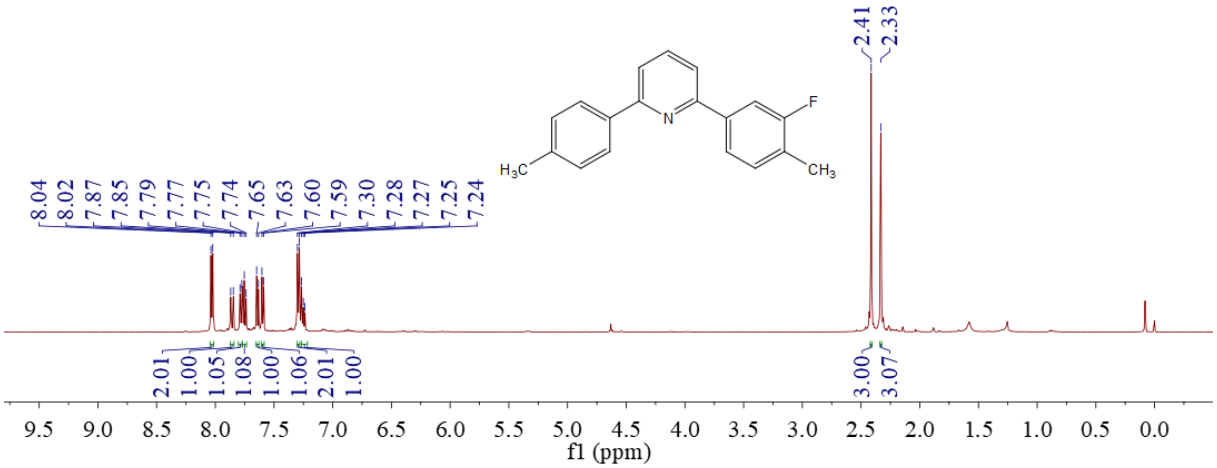
(19) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4g



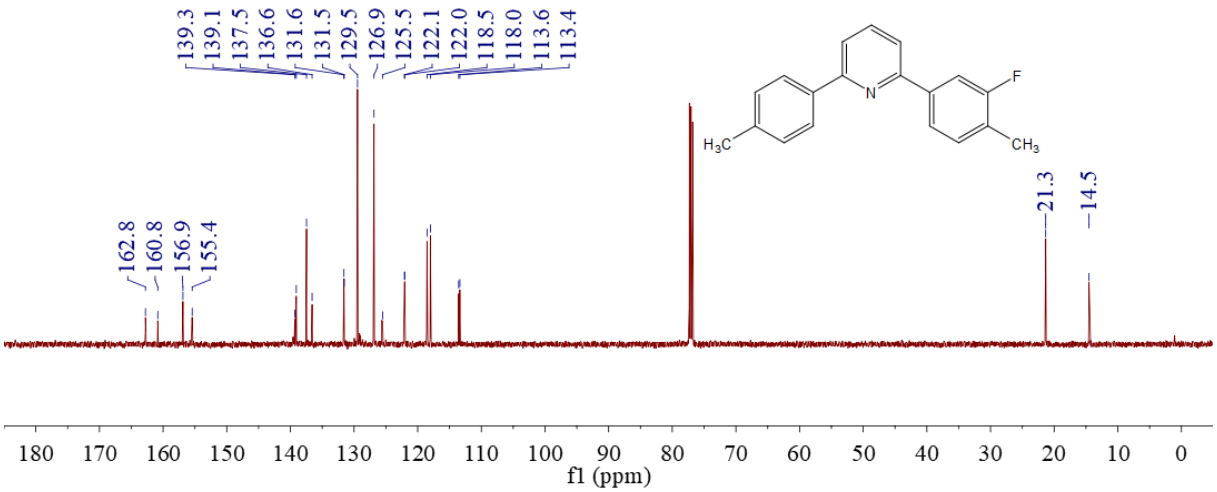
(19) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4g



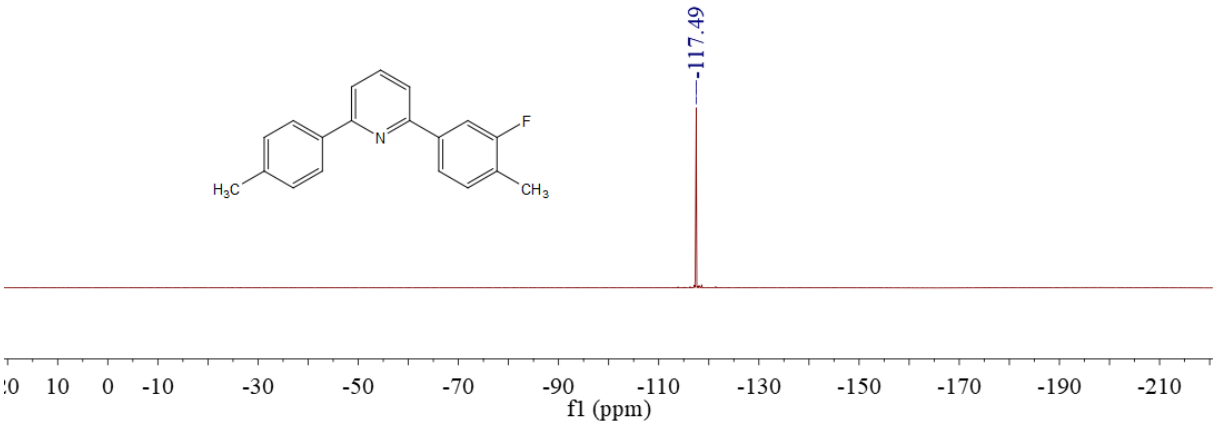
(19) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of 4g



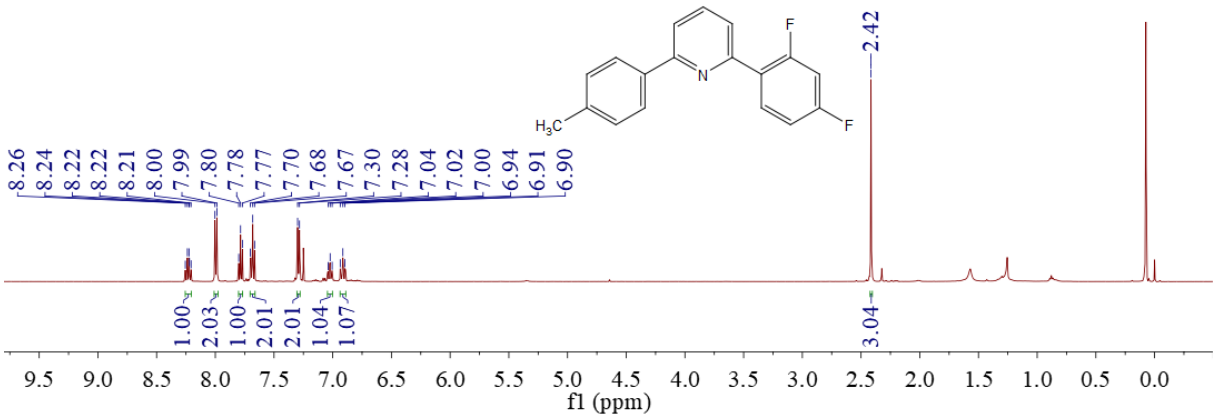
(20) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4h



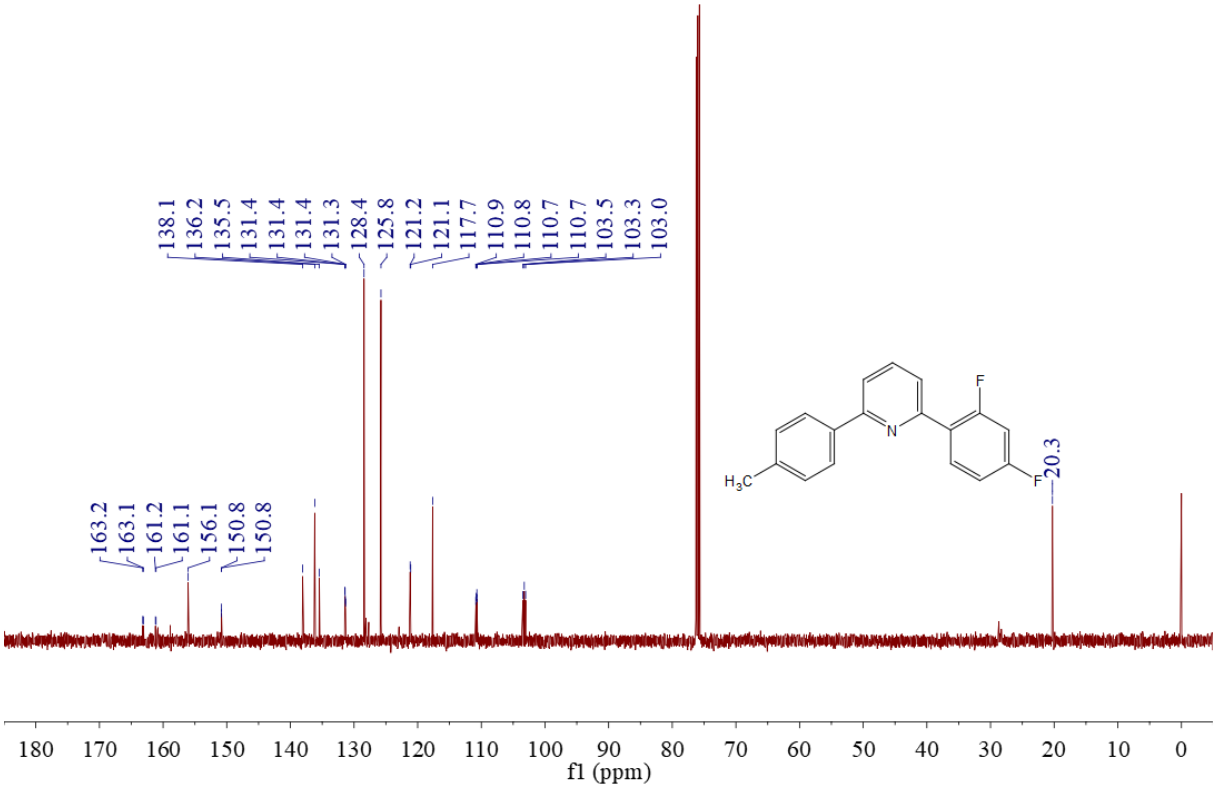
(20) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4h



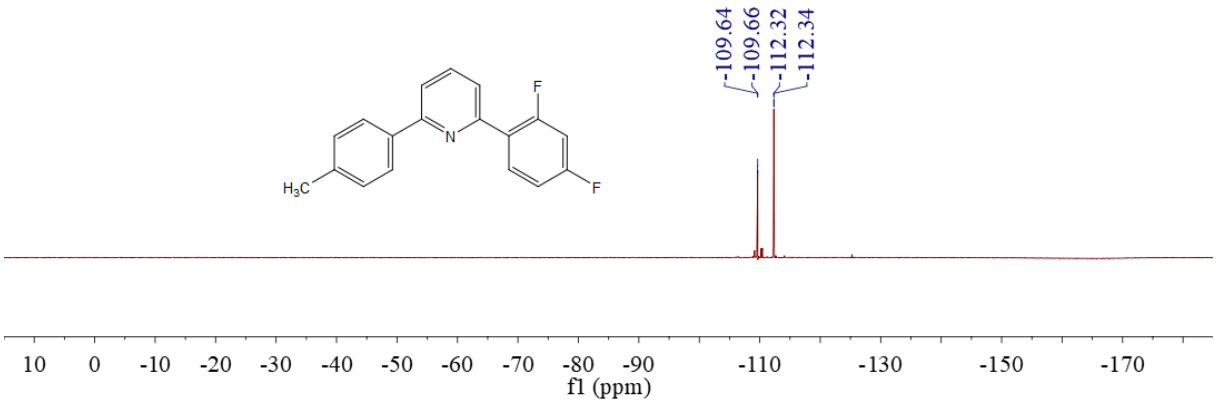
(20) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of 4h



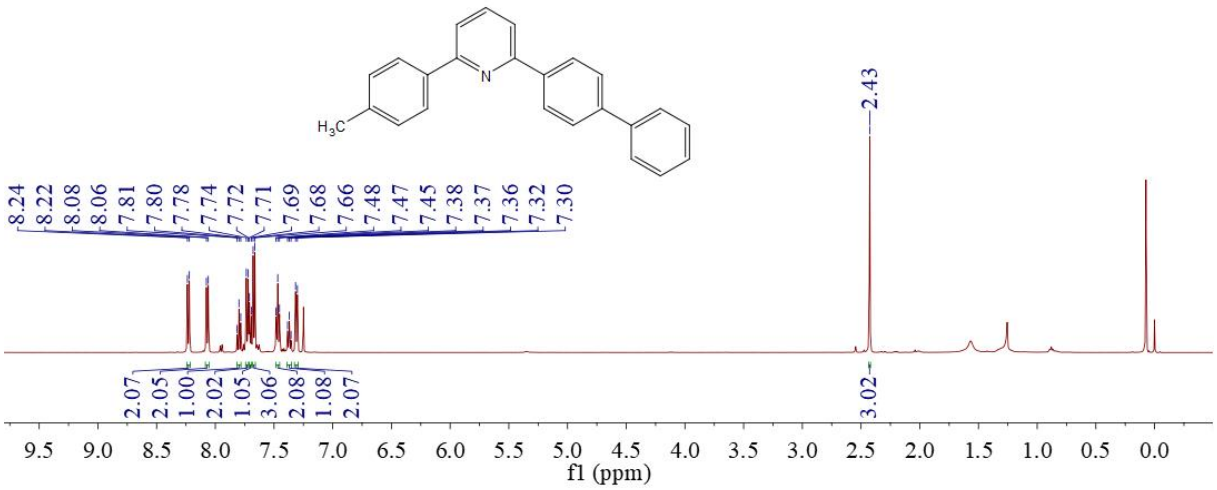
(21) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4i



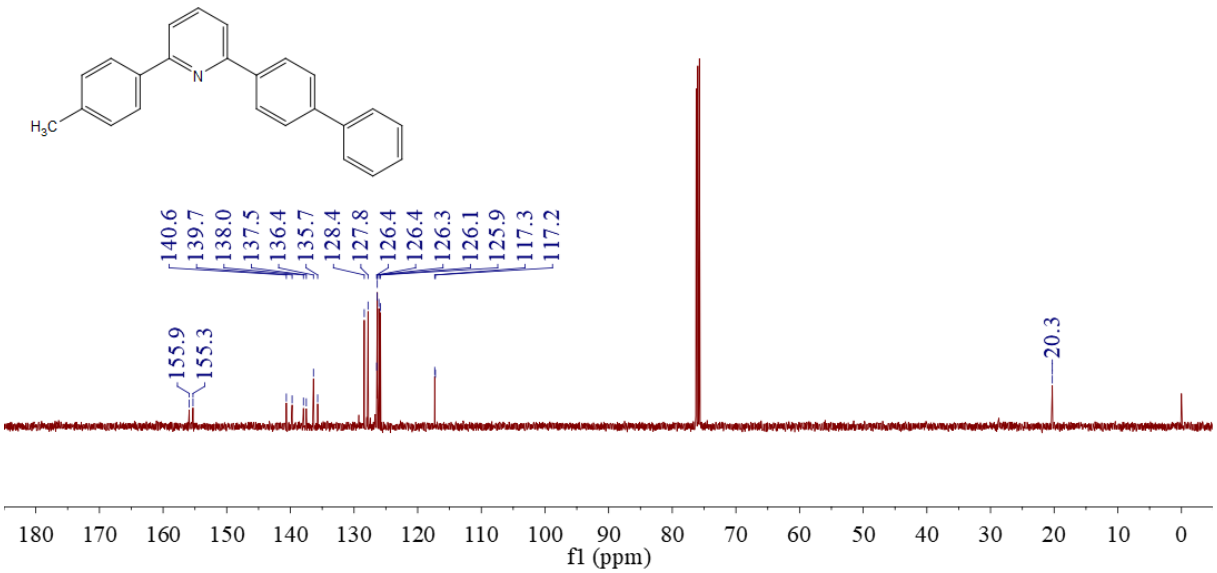
(21) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4i



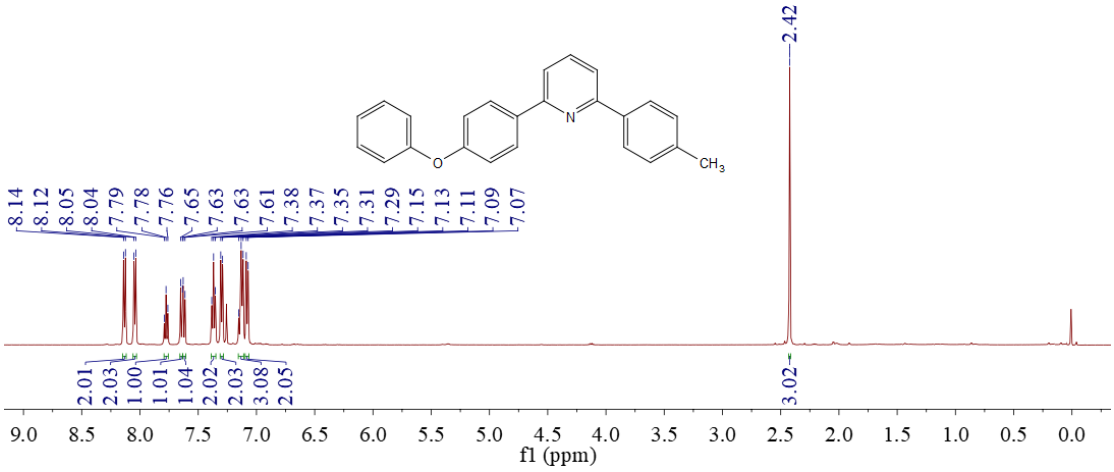
(21) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of 4i



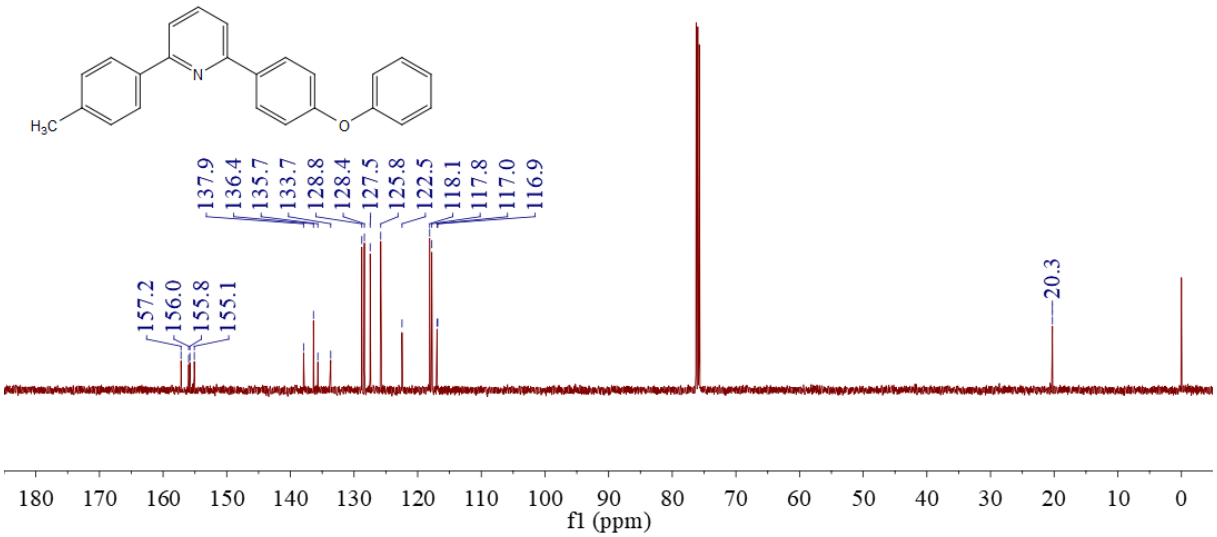
(22) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4j



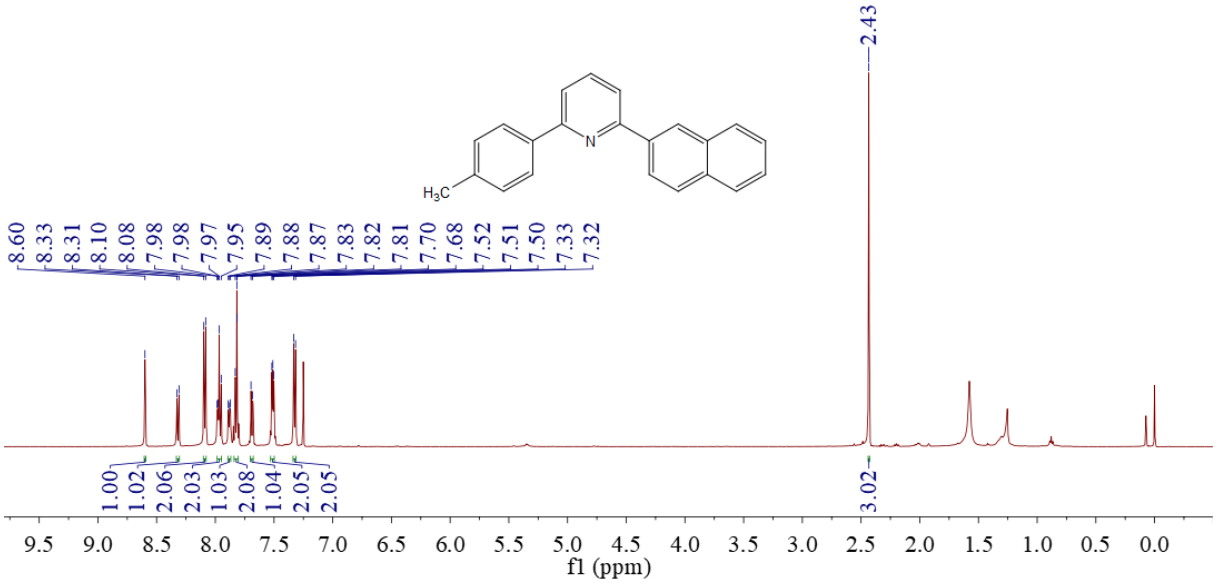
(22) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4j



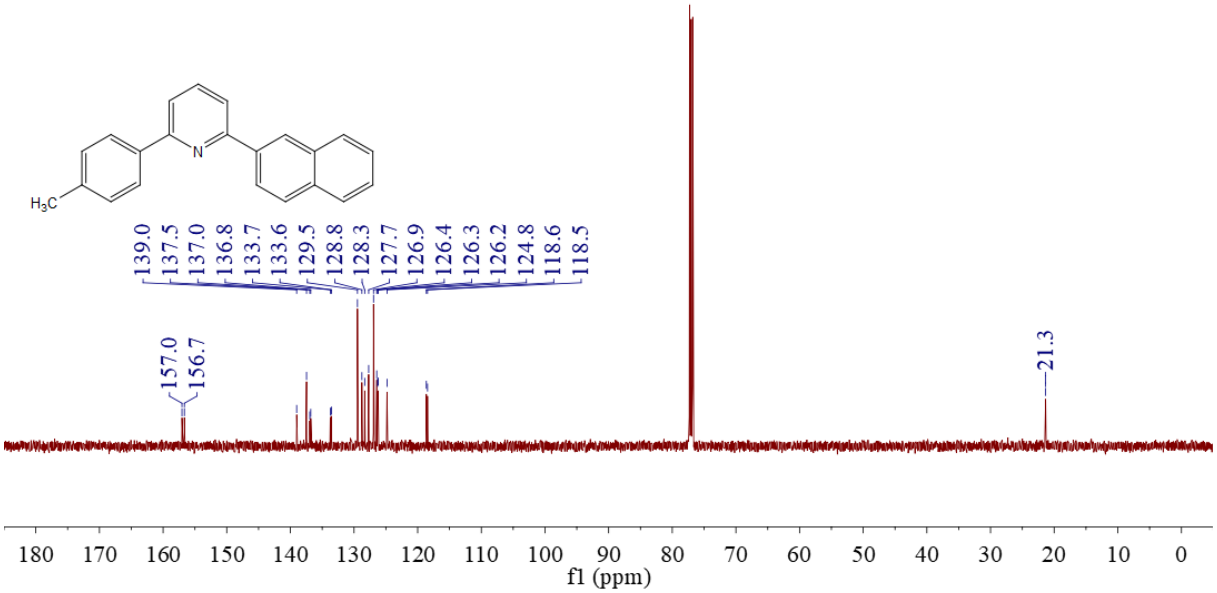
(23) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4k



(23) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4k



(24) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4l



(24) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 4l

References

1. J. L. Zhan, M. W. Wu, D. Wei, B. Y. Wei, Y. Jiang, W. Yu and B. Han, *ACS Catal.*, **2019**, *9*, 4179.
2. L. J. Qi, R. H. Li, X. R. Yao, Q. Q. Zhen, P. Q. Ye, Y. L. Shao and J. X. Chen, *J. Org. Chem.*, **2020**, *85*, 1097.
3. X. R. Yao, L. J. Qi, R. H. Li, Q. Q. Zhen, J. C. Liu, Z. W. Zhao, Y. L. Shao, M. L. Hu and J. X. Chen, *ACS Comb. Sci.*, **2020**, *22*, 114.
4. F. Sha, H. Shen and X. Y. Wu, *Eur. J. Org. Chem.*, **2013**, 2537.
5. W. W. Tan, Y. J. Ong and N. Yoshikai, *Angew. Chem. Int. Ed.*, **2017**, *56*, 8240.