Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


*Supporting Information*

# Copper-catalyzed Regioselective Dimerization of Vinyl Azides by *gem*-Difluoromethylene for trisubstituted Pyridines

Zhenhua Liu†, Guangyu Zhu†, Wen Gao*, Lin Yang, Huimin Ji, Lili Tong and Bo Tang*

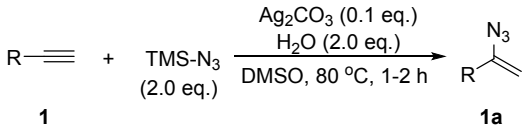
College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan, 250014, P. R. China.
E-mail: gaowen@sdnu.edu.cn and E-mail: tangb@sdnu.edu.cn

## Contents

## I. General information

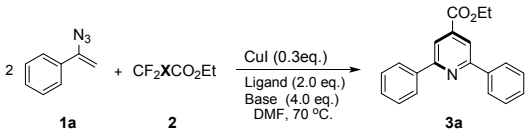
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. 1HNMR and 13C NMR spectra were recorded at 25 ºC on a Varian 400 MHz and 101 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

### II. The synthesis of vinyl azides 1a-1x.




**Typical synthetic procedure** (with **1a** as an example): To a solution of phenylacetylene (**1**) (0.051 mL, 0.5 mmol), TMS-$N_3$ (0.132 mL, 1.0 mmol) and $H_2O$ (0.018 mL, 1.0 mmol) in DMSO (2 mL) at 80 °C, $Ag_2CO_3$ (13.8 mg, 0.05 mmol) was added. The mixture was then stirred for 0.5-1.0 h until substrate **1** was consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3 × 15 mL). The organic layer was washed with brine (3 × 40 mL), dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromat- ography (silica gel; petroleum ether) and concentrated *in vacuo* to afford **1a** in 75% yield as an oil (*Org. Lett.,* 2014, **16**, 3668; *Angew. Chem., Int. Ed.,* 2014, **53**, 5305).

### III. Optimization of experiment conditions for 3a [a]

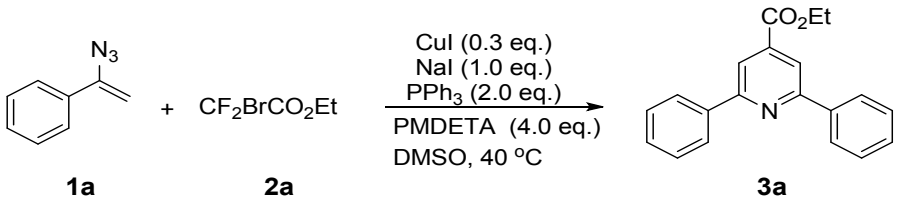



| Entry | Cat. | X | Ligand | Base | Yield/% |
|---|---|---|---|---|---|
| 1 | CuI | Br | $PPh_3$ | TMEDA | trace |
| 2 | CuI | Br | $PPh_3$ | $(Et)_3N$ | 0 |
| 3 | CuI | Br | $PPh_3$ | $(i\text{-}Pr)_2NH$ | 0 |

| | | | | | |
|---|---|---|---|---|---|
| 4 | CuI | Br | $PPh_3$ | DBU | 0 |
| 5 | CuI | Br | $PPh_3$ | $Na_2CO_3$ | 0 |
| 6 | CuI | Br | $PPh_3$ | $K_2CO_3$ | 0 |
| 7 | CuI | Br | $PPh_3$ | $K_3PO_4$ | 0 |
| 8 | CuI | Br | $PPh_3$ | KF | 0 |
| 9 | CuI | Br | 1,10-phen | PMDETA | trace |
| 10 | CuI | I | $PPh_3$ | PMDETA | 91 |
| 11 | CuI | Cl | $PPh_3$ | PMDETA | 0 |
| 12 | CuI | F | $PPh_3$ | PMDETA | 0 |

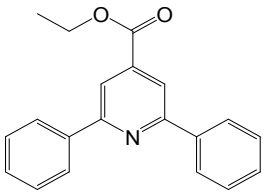
[a]Conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), CuI (0.075 mmol),Ligand (0.5 mmol), Base (1.0 mmol) in DMF (1 mL) at 40 °C under air for 3 h; Yields of isolated products; Yields of isolated products. TMEDA=N,N,N',N'-tetramethylethylenediamine, DBU=1,8-diazabicyclo[5.4.0]undec-7-ene, 1,10-phen=1,10-phenanthroline, DMF = N,N-dimethyl formamide.

## IV. Synthesis and analytical data of compounds 3 and 4.



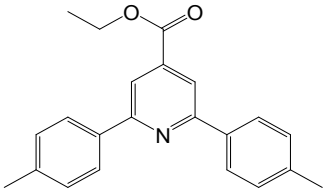

**1a** **2a** **3a**

**Typical synthetic procedure** (with **3a** as an example): To a solution of (1-azidovinyl)benzene (**1a**) (0.072 g, 0.5 mmol), ethyl 2-bromo-2,2-difluoroacetate (**2a**) (0.128 mL, 0.5 mmol), pentamethyldiethylenetriamine (PMDETA) (0.208 mL, 1.0 mmol), $PPh_3$ (0.130 g, 0.5 mmol) and NaI (0.0376 g, 0.25 mmol) in DMSO (1 mL) at 40 ℃, CuI (0.014 g, 0.075 mmol) was added. The reaction mixture was then stirred for 2 h when TLC conformed that substrate **1a** had been consumed. The resulting reaction mixture was cooled to room temperature and taken up by dichloromethane (3 × 15 mL). The organic layer was washed with brine (3 × 40 mL), dried over $MgSO_4$ and concentrated. Purification of the crude product via flash column chromatography (silica gel; petroleum ether/ethyl acetate (60 : 1) ) and concentratinon in vacuo afforded **3a** in 90% yield.



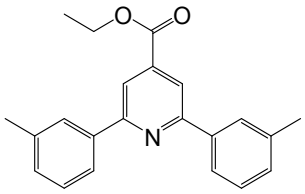
**(3a) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 2H), 8.16−8.10 (m, 4H), 7.44 (t, *J* = 7.3 Hz, 4H), 7.41−7.35 (m, 2H), 4.45−4.36 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.52, 156.79, 138.45, 137.70, 128.41, 127.76, 126.07, 116.78, 60.84, 13.29; **HRMS** (ESI) m/z calculated for $C_{20}H_{17}NO_2$ $[M+H]^+$ : 304.1338, found: 304.1349.

---



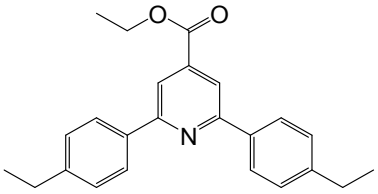
**(3b) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 8.02 (d, *J* = 8.0 Hz, 4H), 7.23 (d, *J* = 7.9 Hz, 4H), 4.43−4.34 (m, 2H), 2.35 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.67, 156.67, 138.40, 138.26, 135.03, 128.45, 125.93, 116.12, 60.75, 20.30, 13.29; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}NO_2$ $[M+H]^+$ : 332.1651, found: 332.1657.

---



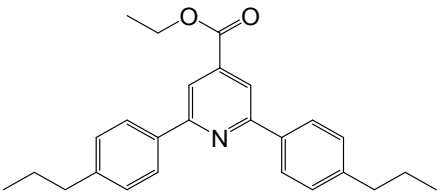
**(3c) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 8.06−7.94 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 4.53−4.43 (m, 2H), 2.48 (s, 6H), 1.47 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.64, 158.04, 139.34, 138.79, 138.43, 130.19, 128.70, 127.79,124.31, 117.86, 61.86, 21.62, 14.35; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}NO_2$ $[M+H]^+$ : 332.1651, found: 332.1669.

---



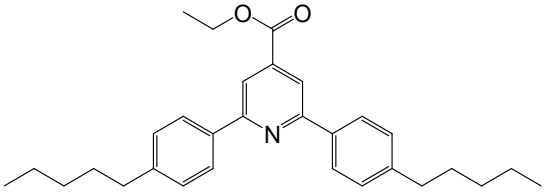
**(3d) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.12 (d, *J* = 8.0 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 4H), 4.51−4.43 (m, 2H), 2.78−2.68 (m, 4H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.6 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.72, 157.77, 145.78, 139.28, 136.35, 128.31, 127.08, 117.22, 61.79, 28.74, 15.56, 14.34; **HRMS** (ESI) m/z calculated for $C_{24}H_{25}NO_2$ $[M+H]^+$ : 360.1964, found: 360.1988.

---



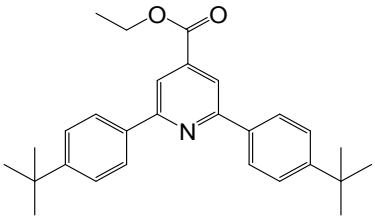
**(3e) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.11 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 4.51−4.42 (m, 2H), 2.66 (t, *J* = 7.6 Hz, 4H), 1.77−1.60 (m, 4H), 1.46 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.74, 157.81, 144.24, 139.29, 136.36, 128.93, 127.00, 117.24, 61.79, 37.87, 24.51, 14.33, 13.84; **HRMS** (ESI) m/z calculated for $C_{26}H_{29}NO_2$ $[M+H]^+$ : 388.2277, found: 388.2278.

---



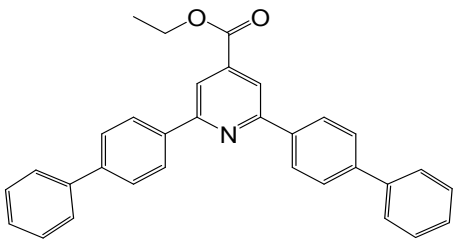
**(3f) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.11 (d, *J* = 8.2 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 4.52−4.43 (m, 2H), 2.68 (t, *J* = 7.7 Hz, 4H), 1.73−1.60 (m, 4H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.41−1.29 (m, 8H), 0.95−0.86 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.72, 157.80, 144.49, 139.27, 136.30, 128.86, 126.99, 117.22, 61.78, 35.75, 31.49, 31.09, 22.57, 14.33, 14.05; **HRMS** (ESI) m/z calculated for $C_{30}H_{37}NO_2$ $[M+H]^+$ : 444.2903, found: 444.2918.

---



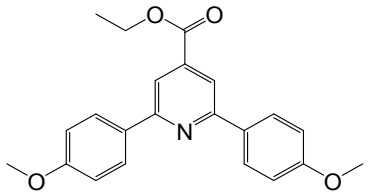
**(3g) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 2H), 8.05 (d, *J* = 8.6 Hz, 4H), 7.45 (d, *J* = 8.6 Hz, 4H), 4.43−4.34 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.30 (s, 18H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.75, 157.78, 152.61, 139.27, 136.13, 126.86, 125.74, 117.31, 61.80, 34.77, 31.34, 14.34; **HRMS** (ESI) m/z calculated for $C_{28}H_{33}NO_2$ $[M+H]^+$ : 416.2590, found: 416.2600.

---



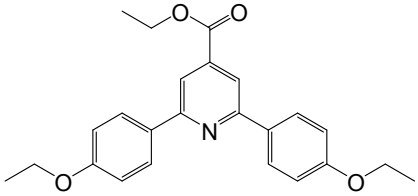
**(3h) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.22−8.16 (m, 6H), 7.69−7.62 (m, 4H), 7.61−7.54 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 4H), 7.32−7.25 (m, 2H), 4.43−4.35 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.54, 157.38, 142.19, 140.57, 139.47, 137.61, 128.93, 127.67, 127.54, 127.51, 127.16, 117.71, 61.94, 14.41; **HRMS** (ESI) m/z calculated for $C_{32}H_{25}NO_2$ $[M+H]^+$ : 456.1964, found: 456.1957.

---



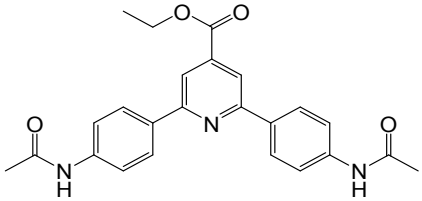
**(3i) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.20−8.14 (m, 4H), 8.12 (s, 2H), 7.08−6.98 (m, 4H), 4.52−4.42 (m, 2H), 3.89 (s, 6H), 1.46 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.80, 160.80, 157.29, 139.26, 131.54, 128.40, 116.30, 114.13, 61.78, 55.40, 14.33; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}NO_4$ $[M+H]^+$ : 364.1550, found: 364.1552.

---



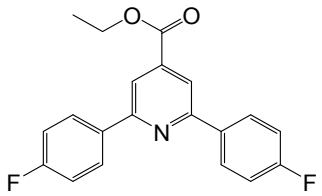
**(3j) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.18−8.13 (m, 4H), 8.11 (s, 2H), 7.08−6.96 (m, 4H), 4.52−4.42 (m, 2H), 4.16−4.07 (m, 4H), 1.46 (t, *J* = 6.5 Hz, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.81, 160.17, 157.30, 139.21, 131.36, 128.36, 116.21, 114.64, 63.57, 61.74, 29.71, 14.84, 14.33; **HRMS** (ESI) m/z calculated for $C_{24}H_{25}NO_4$ $[M+H]^+$ : 392.1863, found: 392.1882.

---



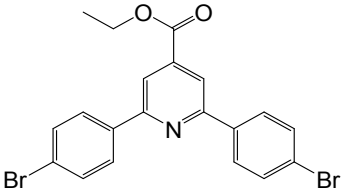
**(3k) $^{1}$H NMR** (400 MHz, DMSO-d6) δ 10.15 (s, 2H), 8.35 (s, 2H), 8.19 (s, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 2H), 4.50−4.40 (m, 2H), 2.10 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, DMSO-d6) δ 169.04, 165.13, 157.40, 140.46, 140.14, 138.74, 129.87, 121.99, 120.74, 117.87, 117.72, 62.32, 24.54, 14.57; **HRMS** (ESI) m/z calculated for $C_{24}H_{23}N_3O_4$ $[M+H]^+$ : 418.1768, found: 418.1770.

---



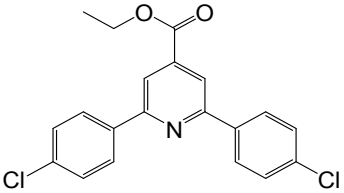
**(3l) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.25−8.11 (m, 6H), 7.24−7.16 (m, 4H), 4.53−4.44 (m, 2H), 1.47 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.36, 165.12, 162.64, 156.83, 139.69, 134.77, 134.74, 128.99, 128.91, 117.40, 115.88, 115.67, 61.99, 14.32; **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -112.13; **HRMS** (ESI) m/z calculated for $C_{20}H_{15}F_2NO_2$ $[M+H]^+$ : 340.1150, found: 340.1164.

---



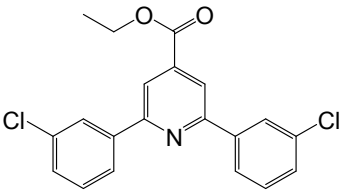
**(3m) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 2H), 7.98 (d, *J* = 8.5 Hz, 4H), 7.57 (d, *J* = 8.3 Hz, 4H), 4.47−4.36 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.18, 156.79, 139.81, 137.36, 132.00, 128.62, 124.15, 117.86, 62.07, 14.33; **HRMS** (ESI) m/z calculated for $C_{20}H_{15}Br_2NO_2$ $[M+H]^+$ : 461.9528, found: 461.9555.

---



**(3n) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.15−8.07 (m, 4H), 7.51−7.44 (m, 4H), 4.52−4.43 (m, 2H), 1.47 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.19, 156.65, 139.74, 136.89, 135.75, 129.02, 128.32, 117.79, 62.05, 14.33; **HRMS** (ESI) m/z calculated for $C_{20}H_{15}Cl_2NO_2$ $[M+H]^+$ : 372.0559, found: 372.0557.

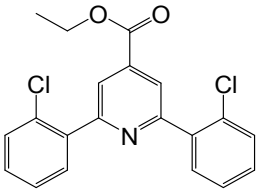
---



**(3o) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.24 (s, 2H), 8.18 (s, 2H), 8.10−8.01 (m, 2H), 7.50−7.39 (m, 4H), 4.55−4.44 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.09, 156.58,

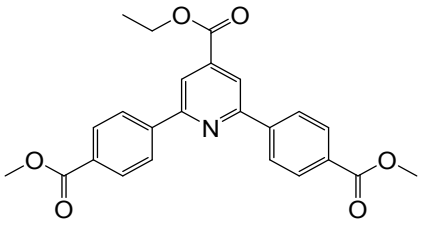
140.23, 139.89, 135.00, 130.10, 129.60, 127.24, 125.21, 118.48, 77.22, 62.12, 14.34; **HRMS** (ESI) m/z calculated for $C_{20}H_{15}Cl_2NO_2$ $[M+H]^+$ : 372.0559, found: 372.0562.

---



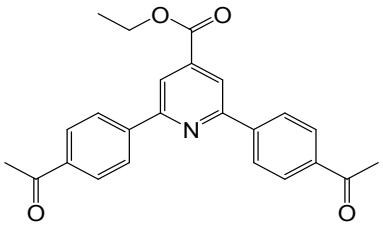
**(3p)** $^1$**H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.65−7.58 (m, 2H), 7.46−7.40 (m, 2H), 7.35−7.24 (m, 4H), 4.43−4.34 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); $^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 165.10, 157.66, 138.53, 138.05, 132.37, 131.76, 130.23, 129.99, 127.12, 122.70, 61.97, 14.26; **HRMS** (ESI) m/z calculated for $C_{20}H_{15}Cl_2NO_2$ $[M+H]^+$ : 372.0559, found: 372.0573.

---



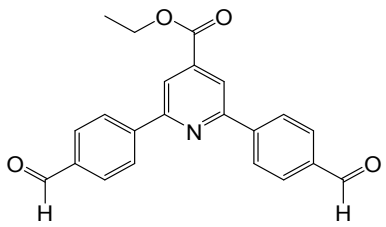
**(3q)** $^1$**H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 8.16 (d, *J* = 8.5 Hz, 4H), 8.08 (d, *J* = 8.5 Hz, 4H), 4.45−4.36 (m, 2H), 3.88 (s, 6H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 166.75, 164.99, 156.76, 142.39, 139.83, 130.93, 130.09, 126.99, 118.96, 62.13, 52.25, 14.32; **HRMS** (ESI) m/z calculated for $C_{24}H_{21}NO_6$ $[M+H]^+$ : 420.1448, found: 420.1468.

---



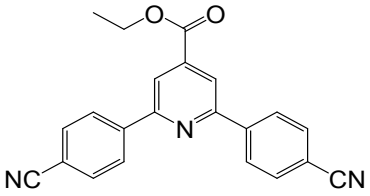
**(3r)** $^1$**H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 8.29 (d, *J* = 8.1 Hz, 4H), 8.11 (d, *J* = 8.1 Hz, 4H), 4.55−4.47 (m, 2H), 2.67 (s, 6H), 1.49 (t, *J* = 7.1 Hz, 3H); $^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 197.68, 165.00, 156.78, 142.51, 139.93, 137.69, 128.88, 127.25, 119.08, 62.18, 26.78, 14.32; **HRMS** (ESI) m/z calculated for $C_{24}H_{21}NO_4$ $[M+H]^+$ : 388.1550, found: 388.1566.

---



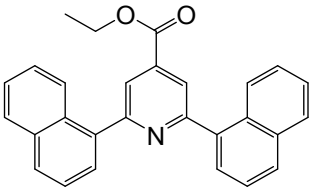
**(3s) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 2H), 8.51−8.31 (m, 6H), 8.06 (d, *J* = 8.1 Hz, 4H), 4.57−4.47 (m, 2H), 1.49 (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 191.88, 164.90, 156.75, 143.77, 140.12, 136.96, 130.26, 127.73, 119.52, 62.28, 14.34; **HRMS** (ESI) m/z calculated for $C_{22}H_{17}NO_4$ $[M+H]^+$ : 360.1237, found: 360.1232.

---



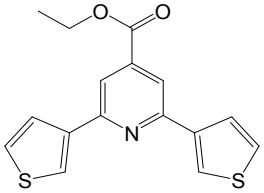
**(3t) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 2H), 8.31 (d, *J* = 8.4 Hz, 4H), 7.85 (d, *J* = 8.5 Hz, 4H), 4.56−4.47 (m, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.32, 165.11, 162.63, 156.79, 139.67, 134.75, 134.72, 131.96, 128.97, 128.89, 128.60, 117.36, 115.86, 115.64, 61.97, 14.32; **HRMS** (ESI) m/z calculated for $C_{22}H_{15}N_3O_2$ $[M+H]^+$ : 354.1243, found: 354.1252.

---



**(3u) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.23−8.15 (m, 4H), 7.97−7.88 (m, 4H), 7.77−7.71 (m, 2H), 7.61−7.55 (m, 2H), 7.54−7.47 (m, 4H), 4.51−4.42 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.39, 160.15, 138.76, 137.95, 133.97, 131.18, 129.29, 128.47, 127.95, 126.66, 125.98, 125.47, 125.37, 122.62, 61.97, 14.28; **HRMS** (ESI) m/z calculated for $C_{28}H_{21}NO_2$ $[M+H]^+$ : 404.1651, found: 404.1667.

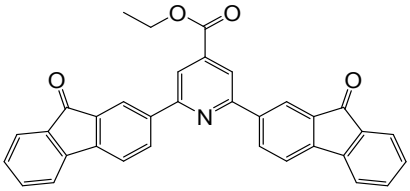
---



**(3v) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.01−7.97 (m, 2H), 7.95 (s, 2H), 7.73 (d, *J* = 5.1 Hz, 2H), 7.38−7.31 (m, 2H), 4.45−4.33 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ

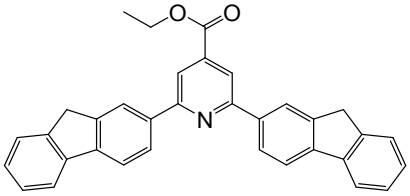
164.42, 152.99, 140.74, 138.28, 125.36, 125.33, 123.35, 116.27, 60.85, 13.28; **HRMS** (ESI) m/z calculated for $C_{16}H_{13}NO_2S_2$ $[M+H]^+$ : 316.0467, found: 316.0468.

---



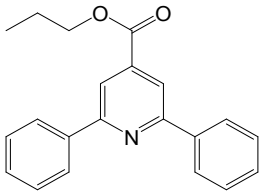
**(3w)** $^1$**H NMR** (400 MHz, $CDCl_3$) δ 8.48−8.42 (m, 2H), 8.40 (s, 2H), 8.28 (s, 2H), 7.72−7.66 (m, 4H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.56−7.50 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 4.55−4.47 (m, 2H), 1.51 (t, *J* = 7.2 Hz, 3H); $^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 193.56, 165.07, 156.43, 145.36, 143.99, 139.91, 139.40, 134.89, 134.80, 134.66, 133.65, 129.42, 124.50, 122.68, 120.79, 120.77, 118.07, 62.17, 14.41; **HRMS** (ESI) m/z calculated for $C_{34}H_{21}NO_4$ $[M+H]^+$ : 508.1550, found: 508.1530.

---



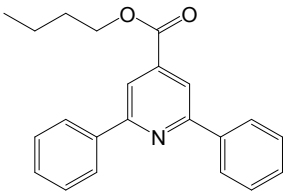
**(3x)** $^1$**H NMR** (400 MHz, $CDCl_3$) δ 8.45−8.40 (m, 2H), 8.28 (s, 2H), 8.26−8.21 (m, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.38−7.31 (m, 2H), 4.55−4.45 (m, 2H), 4.03 (s, 4H), 1.49 (t, *J* = 7.1 Hz, 3H); $^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 165.69, 158.07, 143.97, 143.90, 143.03, 141.27, 139.41, 137.40, 127.14, 126.91, 126.08, 125.17, 123.76, 120.32, 120.12, 117.65, 61.90, 37.11, 14.39; **HRMS** (ESI) m/z calculated for $C_{34}H_{25}NO_2$ $[M+H]^+$ : 480.1964, found: 480.1967.

---



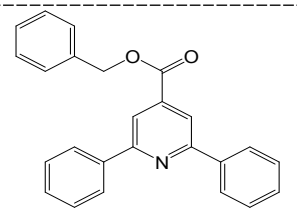
**(4a)** $^1$**H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 2H), 8.23−8.18 (m, 4H), 7.56−7.49 (m, 4H), 7.49−7.43 (m, 2H), 4.39 (t, *J* = 6.7 Hz, 2H), 1.93−1.80 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); $^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 165.61, 157.84, 139.51, 138.74, 129.45, 128.80, 127.10, 117.81, 67.41, 22.09, 10.52; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}NO_2$ $[M+H]^+$ : 318.1495, found: 318.1499.

---



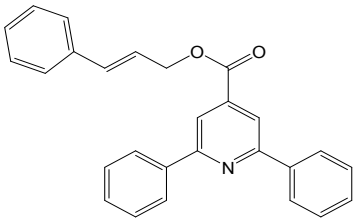
**(4b) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 2H), 8.23−8.18 (m, 4H), 7.57−7.43 (m, 6H), 4.43 (t, *J* = 6.7 Hz, 2H), 1.89−1.77 (m, 2H), 1.56−1.47 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.62, 157.84, 139.51, 138.74, 129.45, 128.80, 127.11, 117.81, 65.76, 30.72, 19.27, 13.78; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}NO_2$ $[M+H]^+$ : 332.1651, found: 332.1657.

---



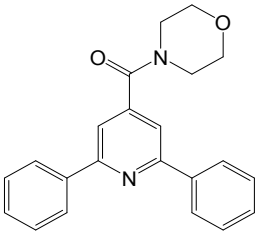
**(4c) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 2H), 8.22−8.16 (m, 4H), 7.55−7.35 (m, 11H), 5.46 (s, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.45, 157.91, 139.15, 138.66, 135.41, 129.48, 128.80, 128.76, 128.60, 128.47, 127.11, 117.87, 67.56; **HRMS** (ESI) m/z calculated for $C_{25}H_{19}NO_2$ $[M+H]^+$ : 366,1495, found: 1505.

---



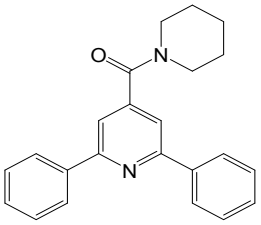
**(4d) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 2H), 8.24−8.18 (m, 4H), 7.56−7.49 (m, 4H), 7.49−7.42 (m, 4H), 7.38−7.33 (m, 2H), 7.32−7.27 (m, 1H), 6.84−6.76 (m, 1H), 6.50−6.40 (m, 1H), 5.11−5.05 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.41, 157.91, 139.24, 138.68, 136.01, 135.35, 129.49, 128.81, 128.70, 128.35, 127.12, 126.76, 122.53, 117.8, 66.49; **HRMS** (ESI) m/z calculated for $C_{27}H_{21}NO_2$ $[M+H]^+$ : 392.1651, found: 392.1661.

---



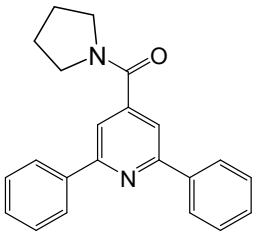
**(4e) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.18−8.12 (m, 4H), 7.66 (s, 2H), 7.55−7.43 (m, 6H), 3.94−3.74 (m, 4H), 3.65 (s, 2H), 3.48 (s, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 168.47, 157.70, 144.74, 138.66, 129.58, 128.85, 127.08, 115.97, 66.85, 48.02, 42.47; **HRMS** (ESI) m/z calculated for $C_{22}H_{20}N_2O_2$ $[M+H]^+$: 345.1604, found: 345.1625.

---



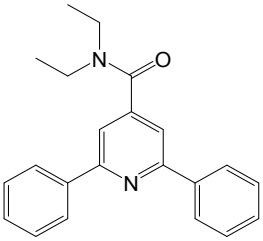
**(4f) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19−8.12 (m, 4H), 7.65 (s, 2H), 7.55−7.41 (m, 6H), 3.78 (s, 2H), 3.44−3.32 (m, 2H), 1.72 (s, 4H), 1.59 (s, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 168.25, 157.46, 145.85, 138.86, 129.40, 128.78, 127.07, 115.87, 48.65, 43.09, 26.66, 25.58, 24.49; **HRMS** (ESI) m/z calculated for $C_{23}H_{22}N_2O$ $[M+H]^+$ : 343.1811, found: 343.1823.

---



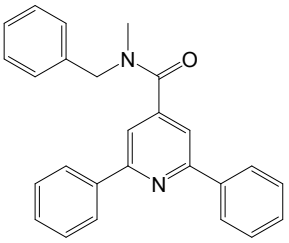
**(4g) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.20−8.13 (m, 4H), 7.76 (s, 2H), 7.55−7.40 (m, 6H), 3.71 (t, *J* = 6.9 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.06−1.97 (m, 2H), 1.98−1.89 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.86, 157.44, 146.35, 138.90, 129.37, 128.77, 127.06, 116.11, 49.42, 46.26, 26.36, 24.45; **HRMS** (ESI) m/z calculated for $C_{22}H_{20}N_2O$ $[M+H]^+$ : 329.1655, found: 329.1663.

---



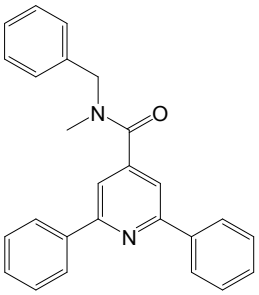
**(4h) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19−8.13 (m, 4H), 7.65 (s, 2H), 7.55−7.40 (m, 6H), 3.67−3.54 (m, 2H), 3.36−3.23 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.31, 157.43, 146.45, 138.88, 129.42, 128.80, 127.08, 115.56, 43.31, 39.44, 14.43, 12.97; **HRMS** (ESI) m/z calculated for $C_{22}H_{22}N_2O$ $[M+H]^+$ : 331.1811, found: 331.1832.

---



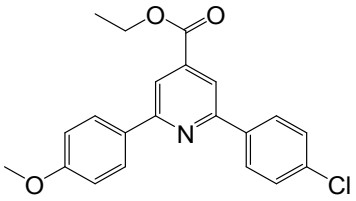
**(4i) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.3 Hz, 2H), 8.02 (d, *J* = 7.0 Hz, 2H), 7.70 (s, 2H), 7.55−7.30 (m, 10H), 7.20 (d, *J* = 7.4 Hz, 1H), 4.55 (s, 2H), 2.91 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.69, 157.43, 145.30, 138.71, 136.28, 129.41, 129.12, 128.89, 128.75, 128.38, 127.87, 127.02, 126.55, 115.89, 50.80, 33.64; **HRMS** (ESI) m/z calculated for $C_{26}H_{22}N_2O$ $[M+H]^+$ : 379.1811, found: 379.1820.

---



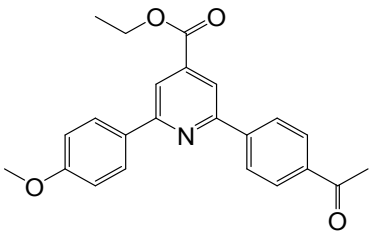
**(4i') $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.3 Hz, 2H), 8.02 (d, *J* = 7.0 Hz, 2H), 7.70 (s, 2H), 7.55−7.30 (m, 10H), 7.20 (d, *J* = 7.4 Hz, 1H), 4.80 (s, 2H), 3.15 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 170.39, 157.54, 145.66, 138.80, 136.49, 129.46, 129.12, 128.89, 128.80, 128.38, 127.87, 127.10, 126.55, 116.00, 55.06, 36.73; **HRMS** (ESI) m/z calculated for $C_{26}H_{22}N_2O$ $[M+H]^+$ : 379.1811, found: 379.1820.

---



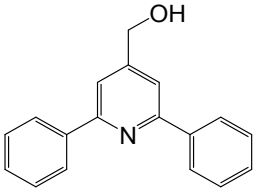
**(3in) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.20−8.17 (m, 1H), 8.17−8.10 (m, 5H), 7.50−7.44 (m, 2H), 7.06−7.01 (m, 2H), 4.51−4.43 (m, 2H), 3.89 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.50, 160.97, 157.59, 156.37, 139.50, 137.27, 135.50, 131.16, 128.95, 128.43, 128.34, 117.32, 116.77, 114.20, 61.91, 55.41, 14.33; **HRMS** (ESI) m/z calculated for $C_{21}H_{18}ClNO_3$ $[M+H]^+$ : 368.1054, found: 368.1019.

---



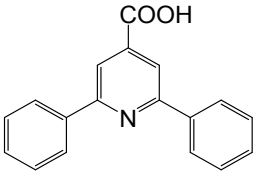
**(3ir) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.33−8.27 (m, 2H), 8.26−8.21 (m, 2H), 8.20−8.13 (m, 2H), 8.14−8.07 (m, 2H), 7.09−7.00 (m, 2H), 4.54−4.45 (m, 2H), 3.90 (s, 3H), 2.67 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.83, 165.42, 161.05, 157.81, 156.29, 143.06, 139.58, 137.47, 131.05, 128.83, 128.47, 127.22, 117.92, 117.52, 114.25, 61.98, 55.43, 26.80, 14.33; **HRMS** (ESI) m/z calculated for $C_{23}H_{21}NO_4$ $[M+H]^+$ : 376.1550, found: 376.1519.

---



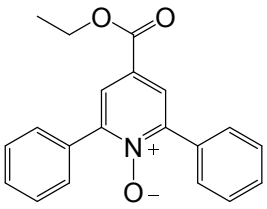
**(5a) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19−8.13 (m, 4H), 7.69 (s, 2H), 7.53−7.47 (m, 4H), 7.47−7.40 (m, 2H), 4.88−4.83 (m, 2H), 2.00−1.90 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.16, 151.20, 139.39, 129.04, 128.68, 127.05, 116.16, 64.12; **HRMS** (ESI) m/z calculated for $C_{18}H_{15}NO$ $[M+H]^+$ : 262.1233, found: 262.1219.

---



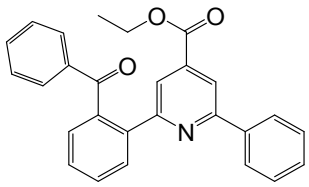
**(5b) $^{1}$H NMR**(400 MHz, DMSO-d6) δ 8.31−8.21 (m, 6H), 7.62−7.45 (m, 7H); **$^{13}$C NMR**(101 MHz, DMSO-d6) δ 166.75, 157.31, 141.22, 138.41, 130.10, 129.40, 127.26, 118.11; **HRMS** (ESI) m/z calculated for $C_{18}H_{13}NO_2$ $[M+H]^+$ : 276.1025, found: 276.1008.

---



**(5c) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.88−7.77 (m, 4H), 7.53−7.42 (m, 6H), 4.46−4.38 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 150.24, 132.62, 129.77, 129.51, 128.26, 126.00, 125.87, 61.91, 14.31; **HRMS** (ESI) m/z calculated for $C_{20}H_{17}NO_3$ $[M+H]^+$ : 320.1287, found: 320.1273.

---




**(5d) $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.08−7.98 (m, 2H), 7.86−7.79 (m, 1H), 7.66−7.53 (m, 5H), 7.53−7.46 (m, 2H), 7.35−7.19 (m, 4H), 7.18−7.11 (m, 2H), 4.41−4.30 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.88, 164.19, 156.35, 156.31, 139.04, 138.41, 138.13, 136.65, 136.57, 131.40, 128.99, 128.48, 128.31, 127.92, 127.85, 127.67, 127.48, 127.00, 125.88, 118.48, 116.47, 60.87, 13.25; **HRMS** (ESI) m/z calculated for $C_{27}H_{21}NO_3$ $[M+H]^+$ : 408.1600, found: 408.1621 .

---

**V. Crystallography of compound 3m**

Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.1 Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. 1 (a) G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Gottingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen, Germany, 1997.

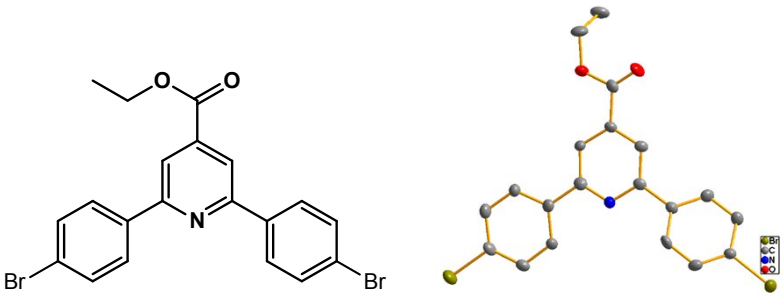
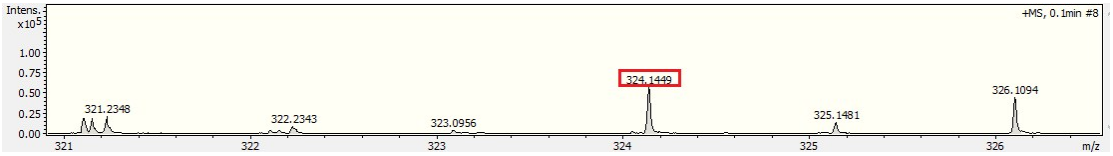


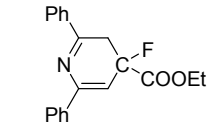

**Table 1**. Crystal data and structure refinement.

| | |
|---|---|
| Empirical formula | $C_{20}H_{15}NO_2Br_2$ |
| Temperature | 150.00(10)K |
| Wavelength | 1.54178 Å |
| Unit cell dimensions | a = 7.0667(3) Å α = 90.00 deg.<br>b = 23.0878(10) Å β = 90.00 deg.<br>c = 21.9663(7) Å γ = 90.00 deg. |
| Volume | 3583.9(2) $Å^3$ |
| Z | 8 |
| Calculated density | 1.709 $Mg/m^3$ |
| Absorption coefficient | 5.846 $mm^{-1}$ |
| F(000) | 1824.0 |
| Crystal size | 0.21 × 0.06 × 0.02 mm |
| Theta range for data collection | 7.66 to 134.14 deg. |
| Reflections collected / unique | 7839 / 5011 [$R_{int}$ = 0.0323, $R_{sigma}$ = 0.0507] |
| Data / restraints / parameters | 5011/1/453 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0415, $wR_2$ = 0.1039 |
| R indices (all data) | $R_1$ = 0.0480, $wR_2$ = 0.1129 |

## VI. Analytical data of Mass spectrum

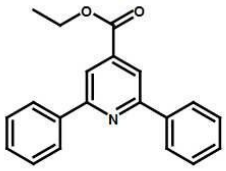


**H**

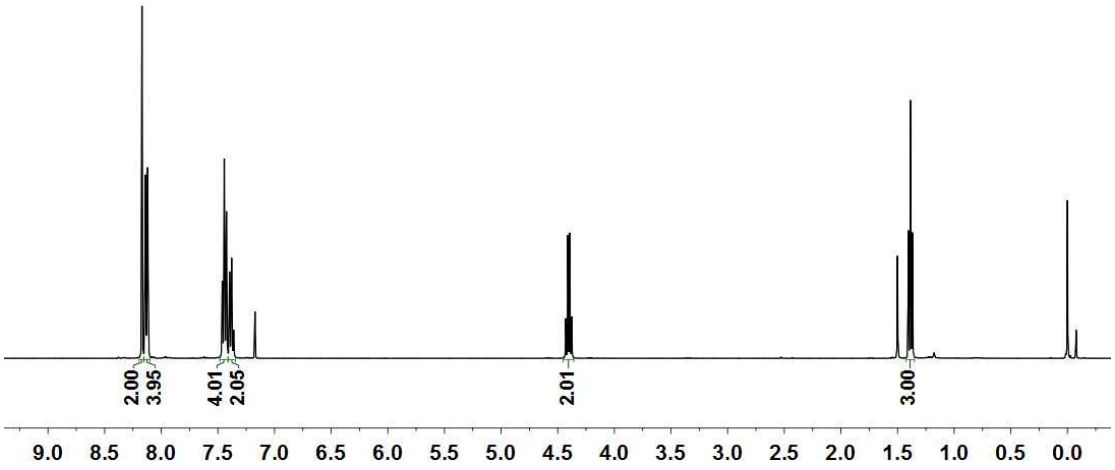


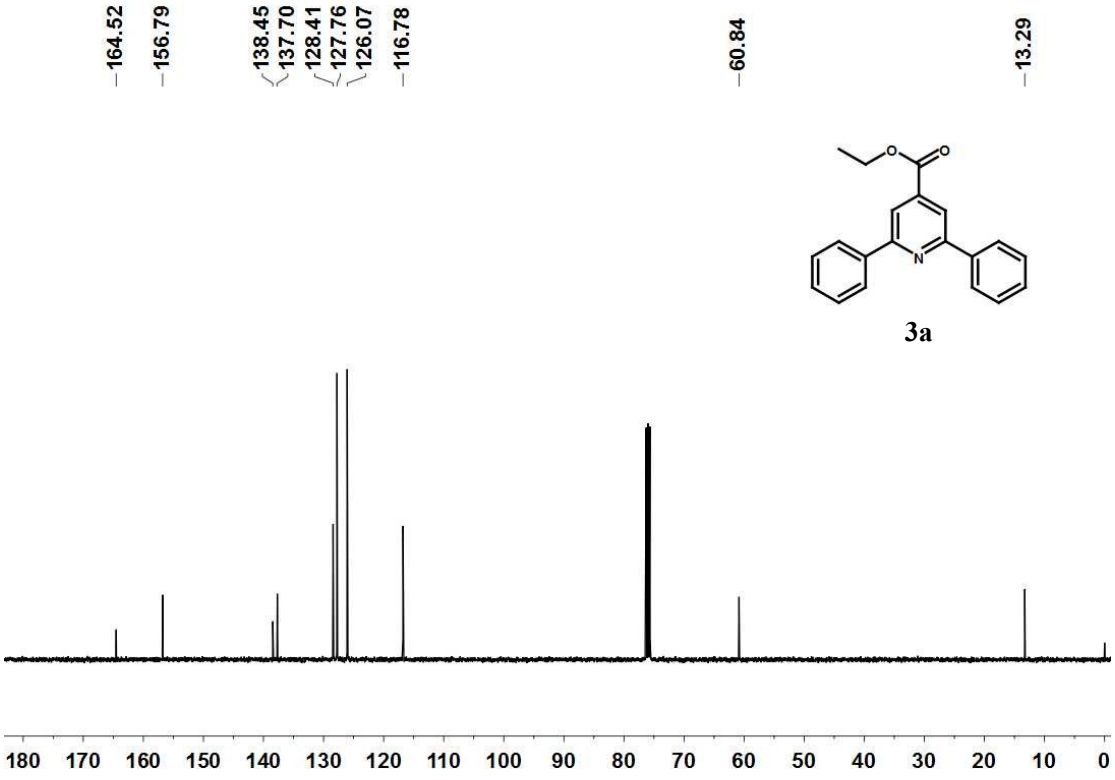

Proposed intermediate **H**, HRMS (ESI) m/z calculated for $C_{20}H_{19}FNO_2$ $[M+H]^+$: 324.1400, found: 324.1449.

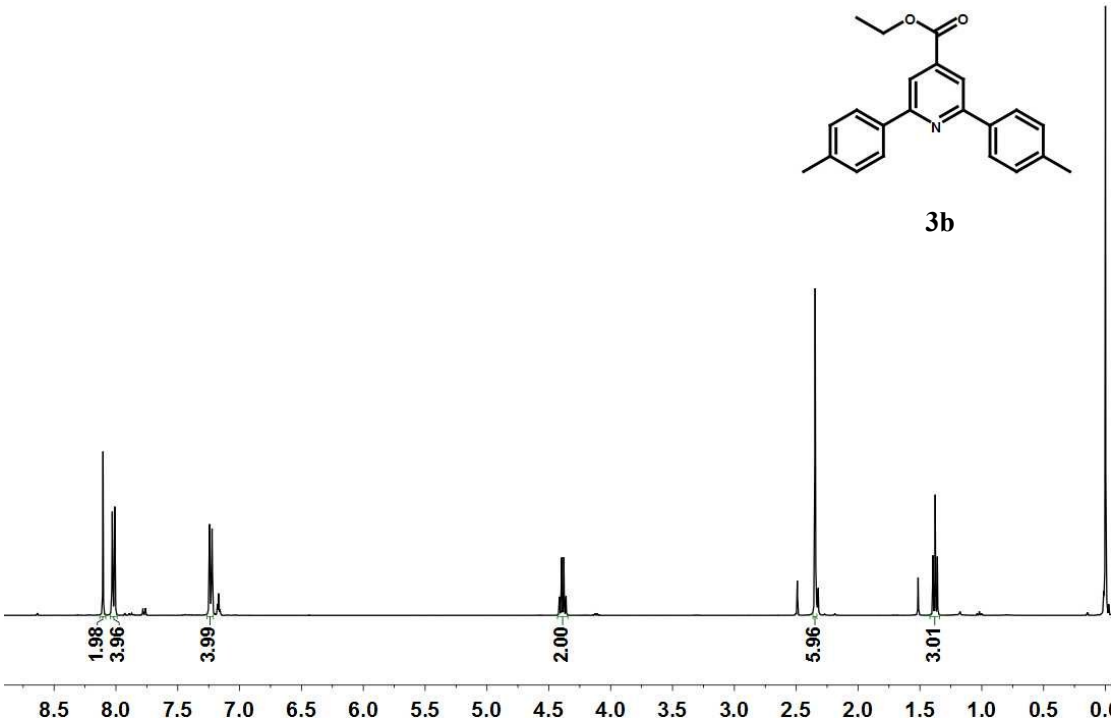
## VII. NMR spectra copies

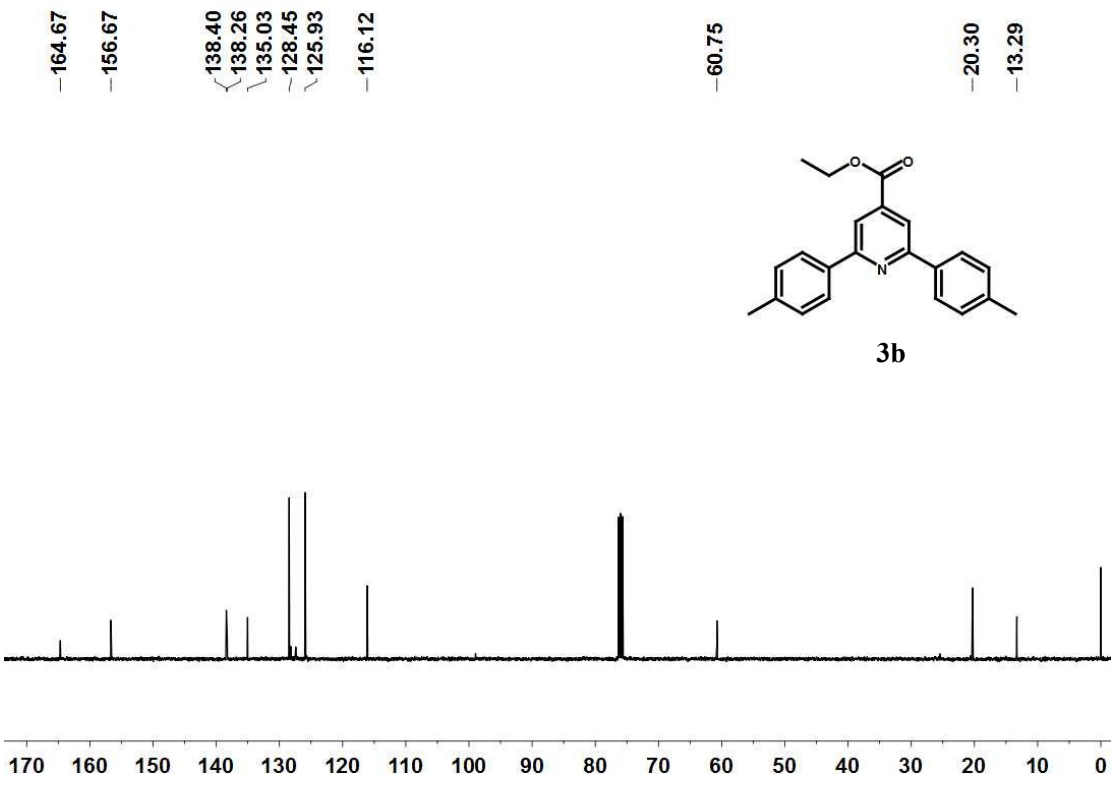



**3a**

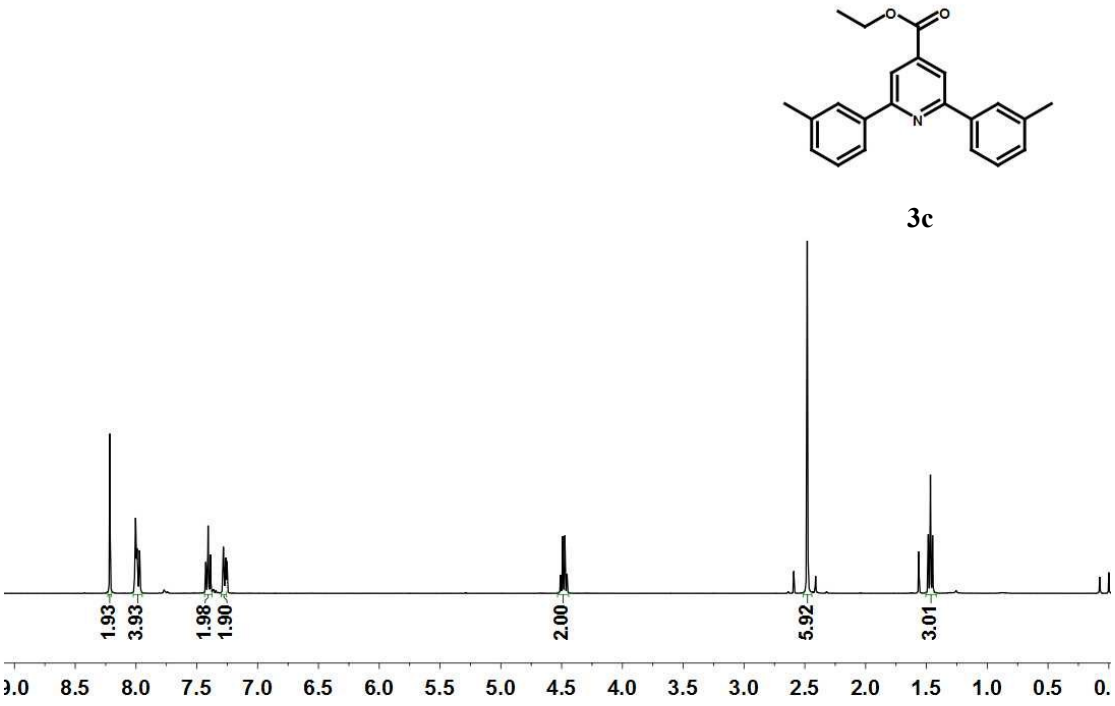



164.52
156.79
138.45
137.70
128.41
127.76
126.07
116.78
60.84
13.29
3a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

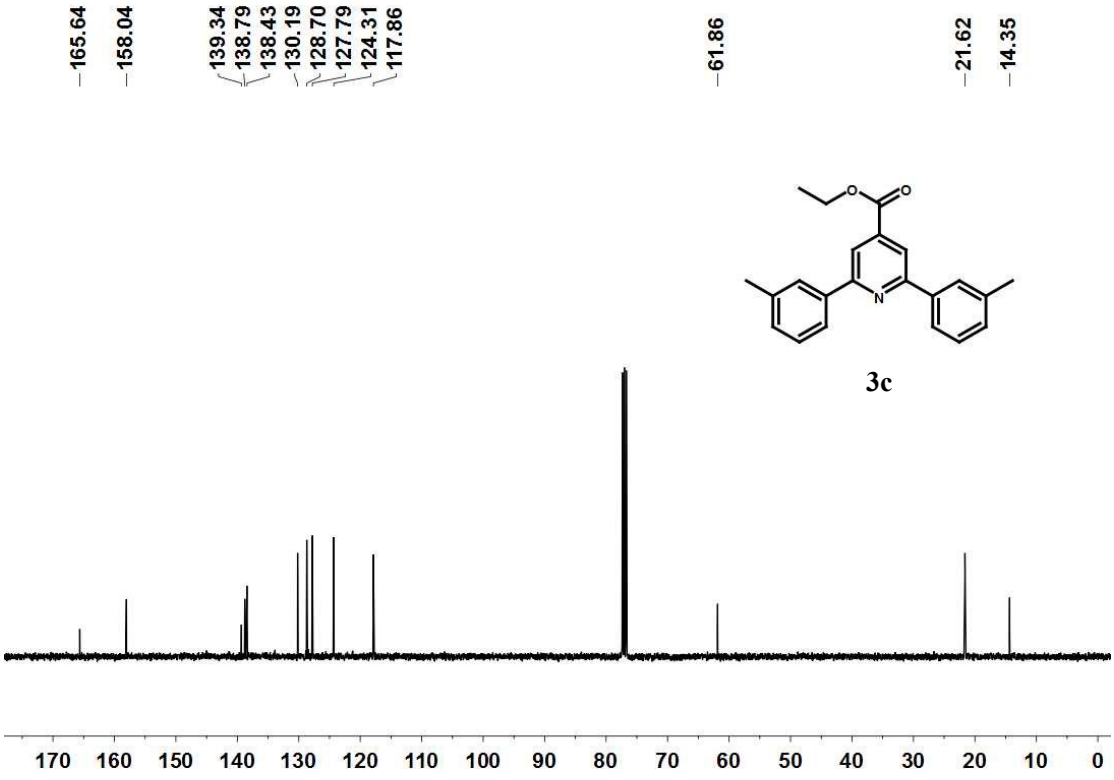

3b
1.98
3.96
3.99
2.00
5.96
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


164.67
156.67
138.40
138.26
135.03
128.45
125.93
116.12
60.75
20.30
13.29
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

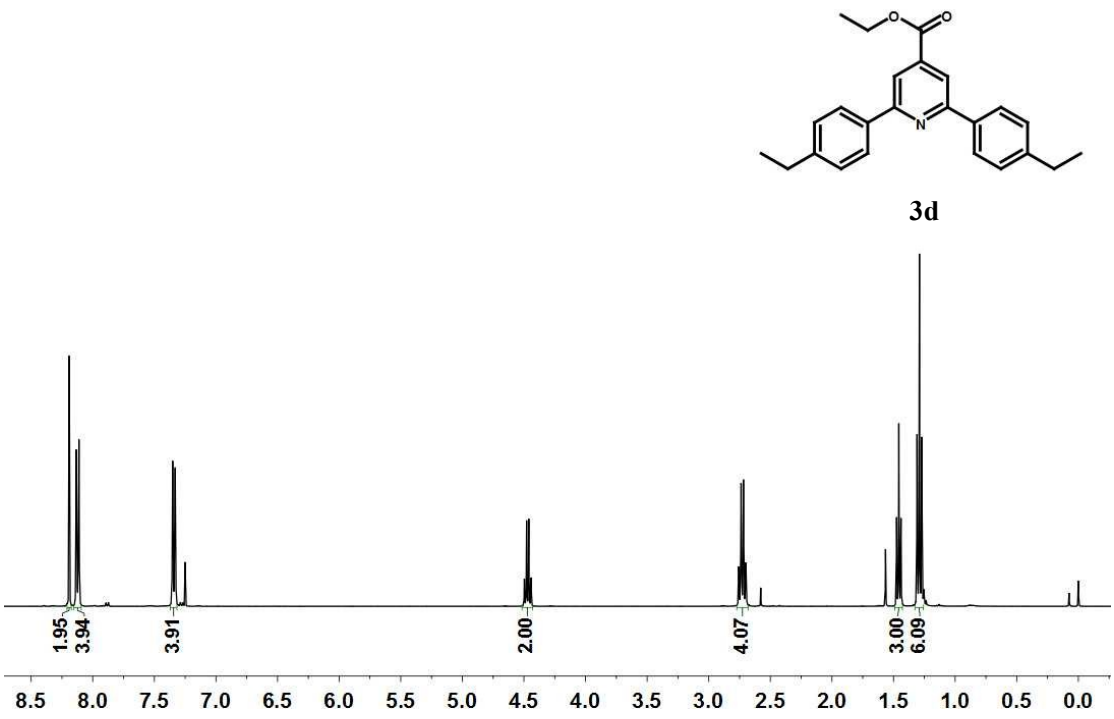
**3b**


O
O
N
1.93
3.93
1.98
1.90
2.00
5.92
3.01
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.

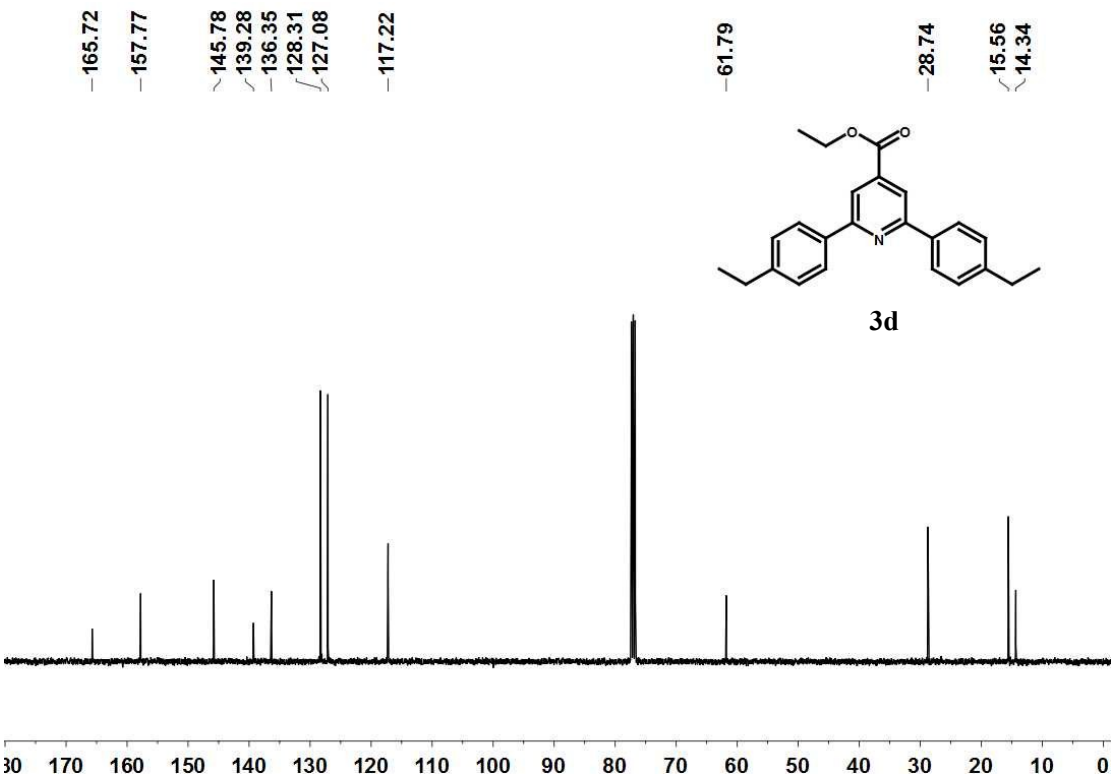
**3c**


165.64
158.04
139.34
138.79
138.43
130.19
128.70
127.79
124.31
117.86
61.86
21.62
14.35
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

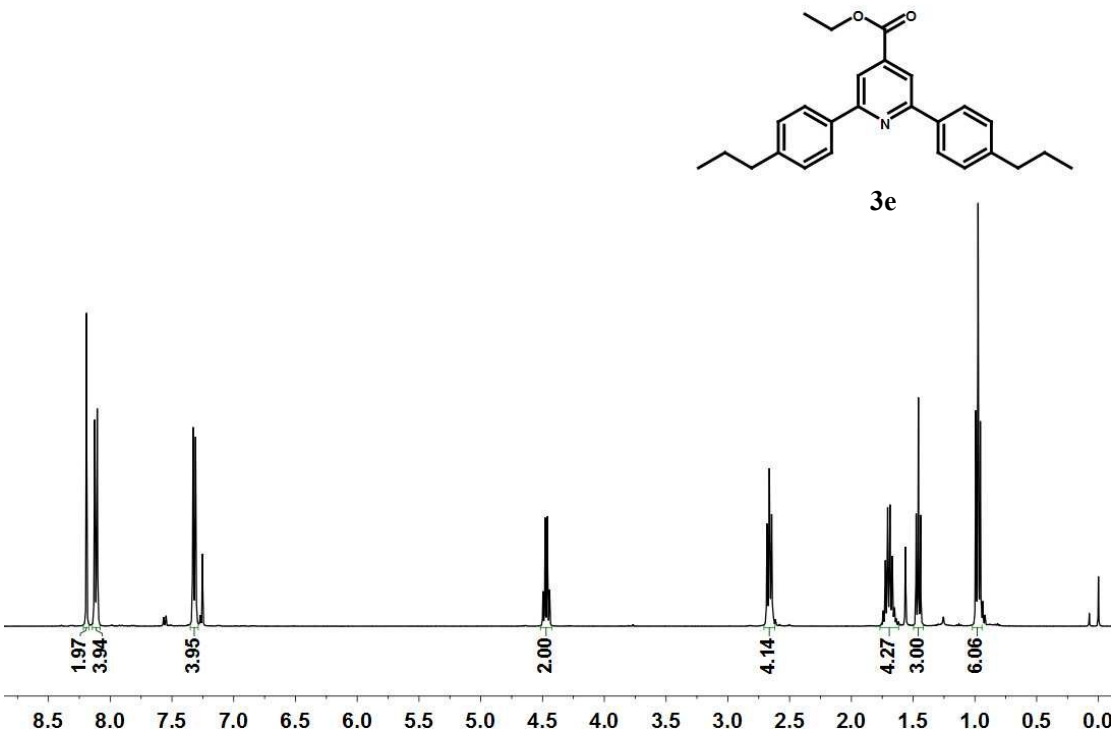
3c


1.95
3.94
3.91
2.00
4.07
3.00
6.09
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

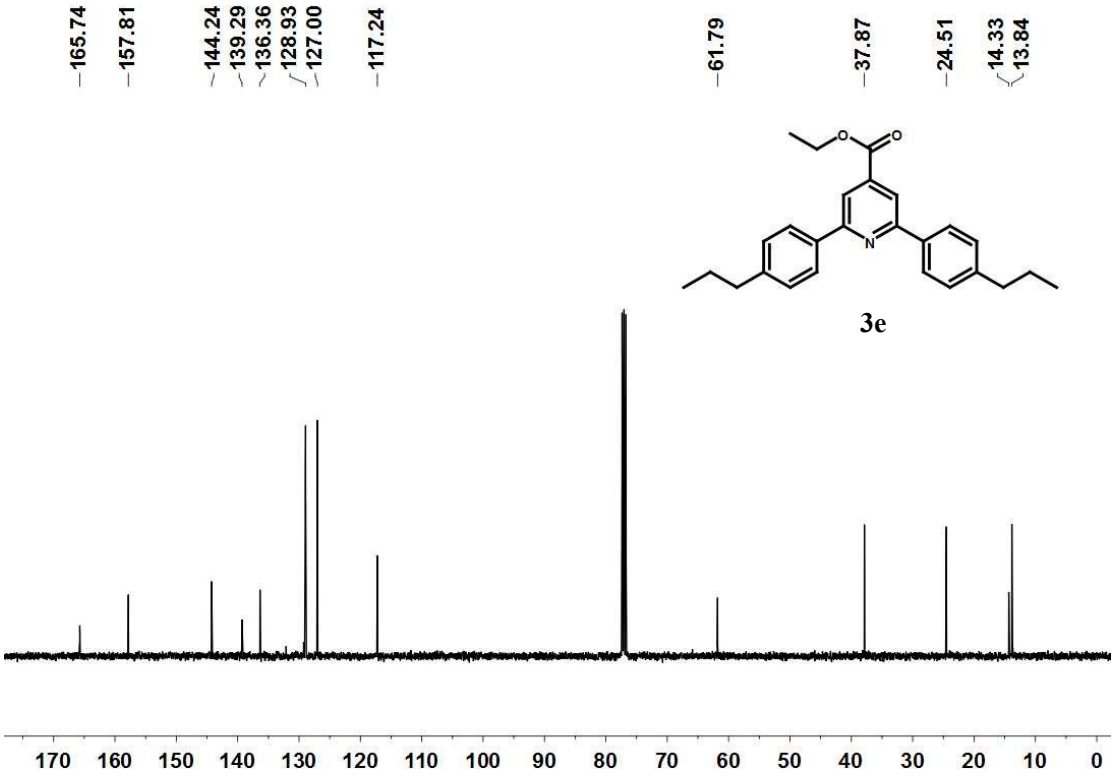
3d


165.72
157.77
145.78
139.28
136.35
128.31
127.08
117.22
61.79
28.74
15.56
14.34
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

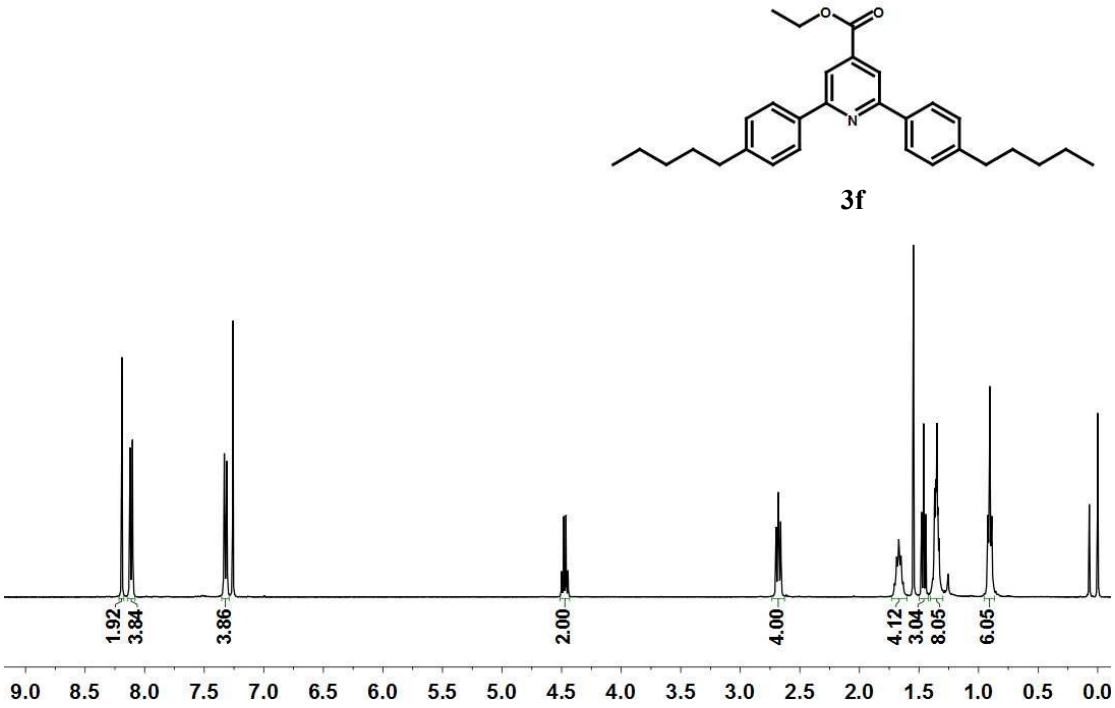
**3d**


O
O
N
1.97
3.94
3.95
2.00
4.14
4.27
3.00
6.06
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

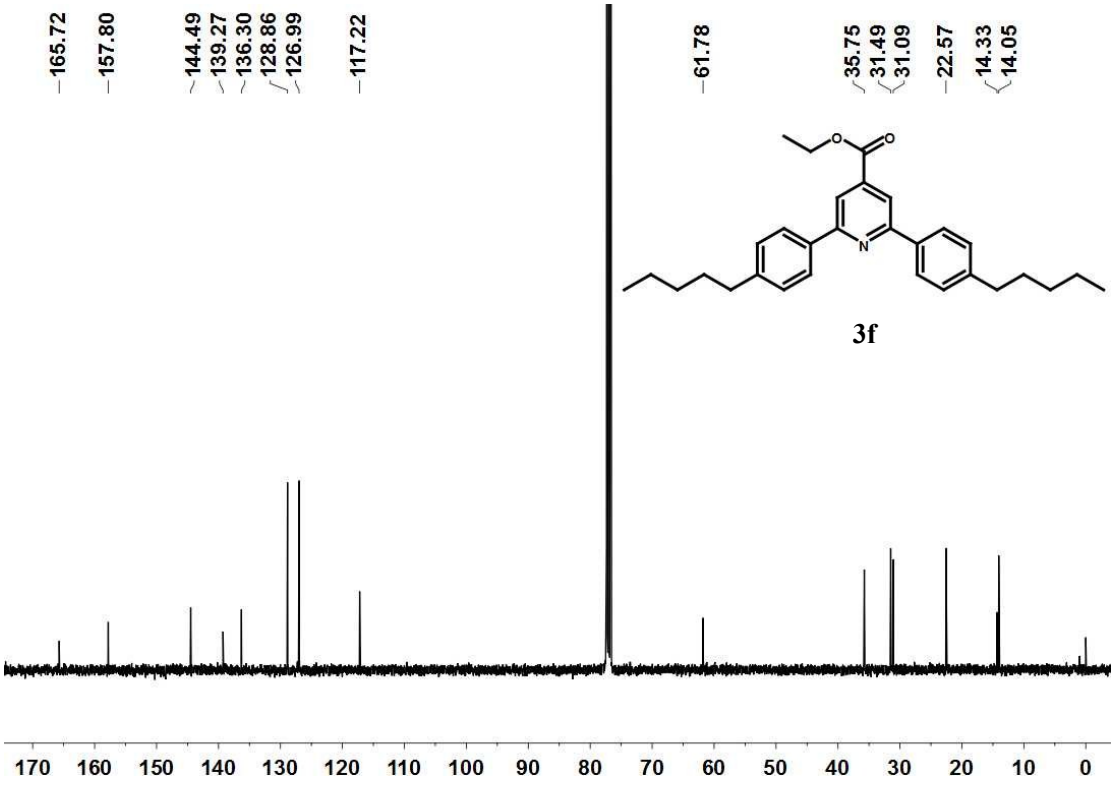
**3e**


165.74
157.81
144.24
139.29
136.36
128.93
127.00
117.24
61.79
37.87
24.51
14.33
13.84
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

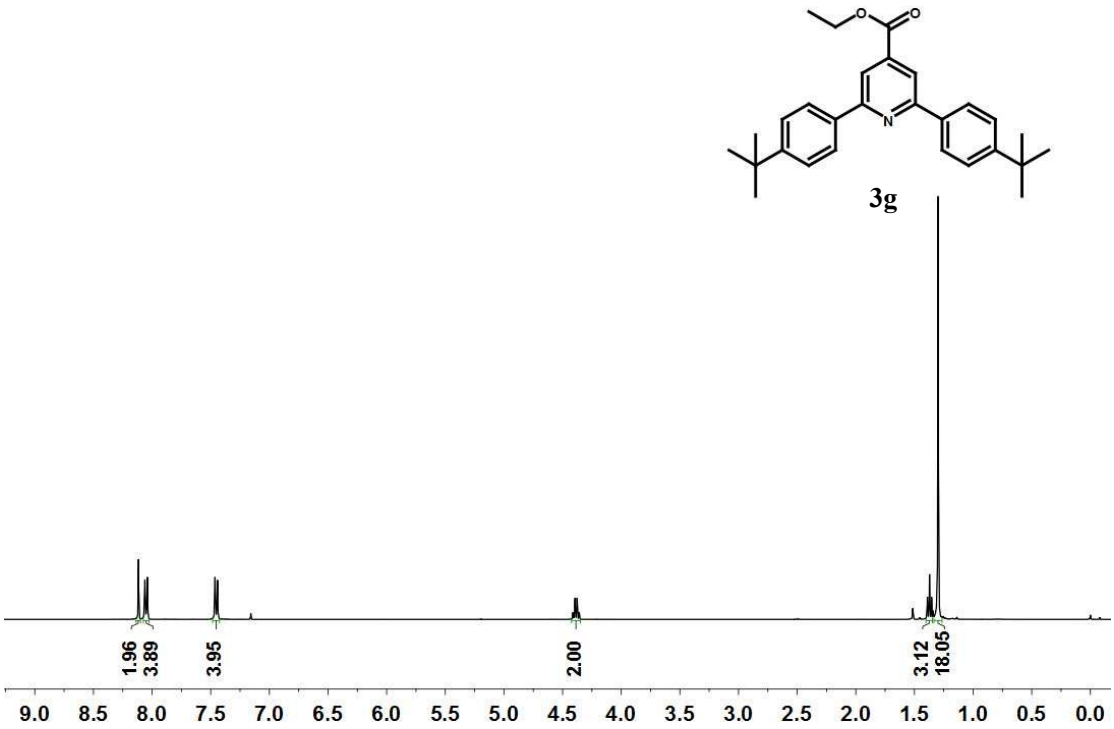
**3e**


O
O
N
1.92
3.84
3.86
2.00
4.00
4.12
3.04
8.05
6.05
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

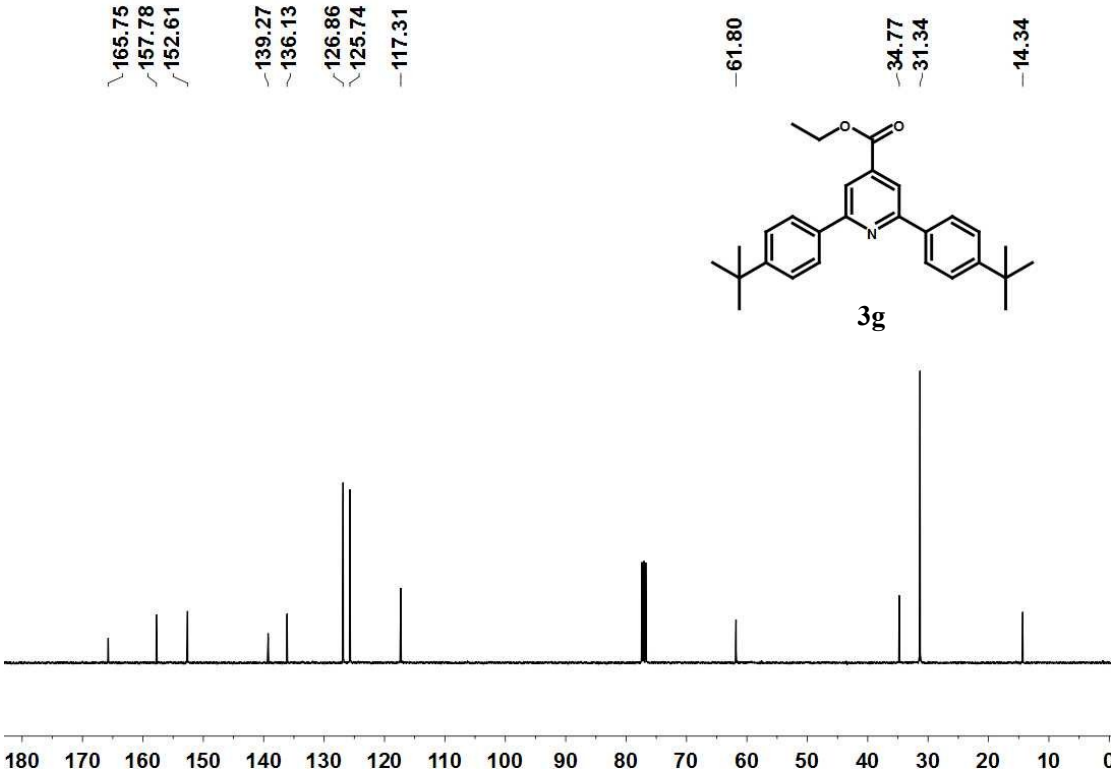
**3f**

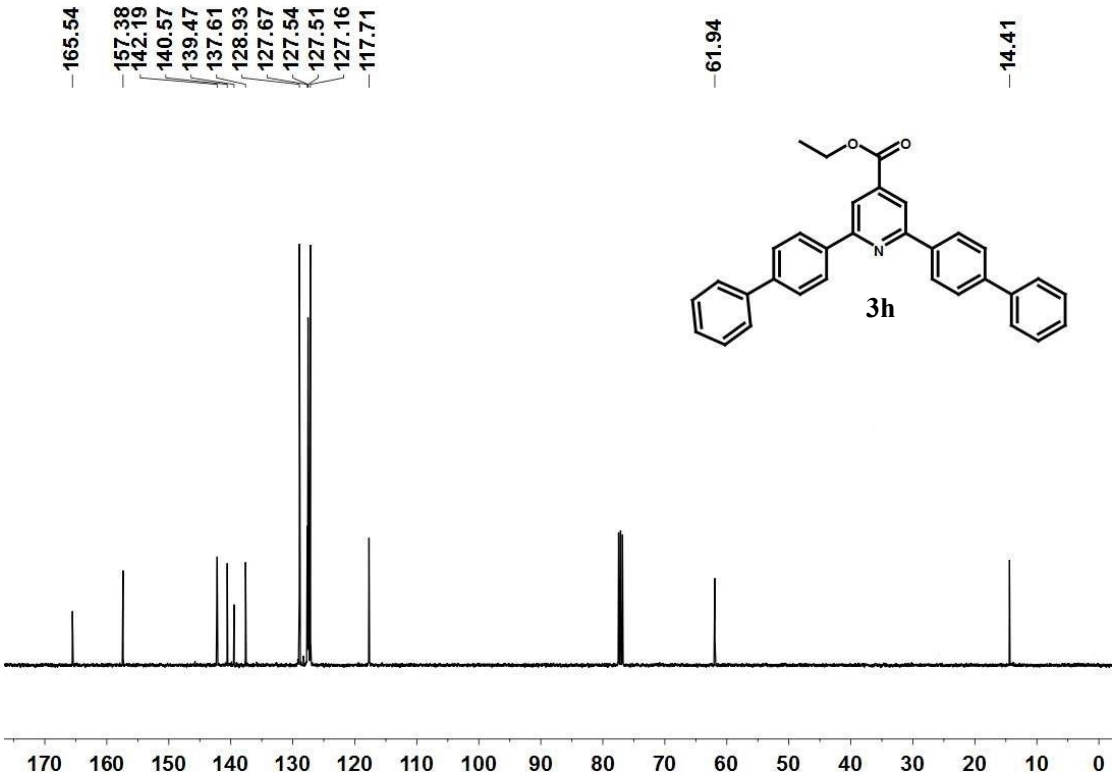

165.72
157.80
144.49
139.27
136.30
128.86
126.99
117.22
61.78
35.75
31.49
31.09
22.57
14.33
14.05
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

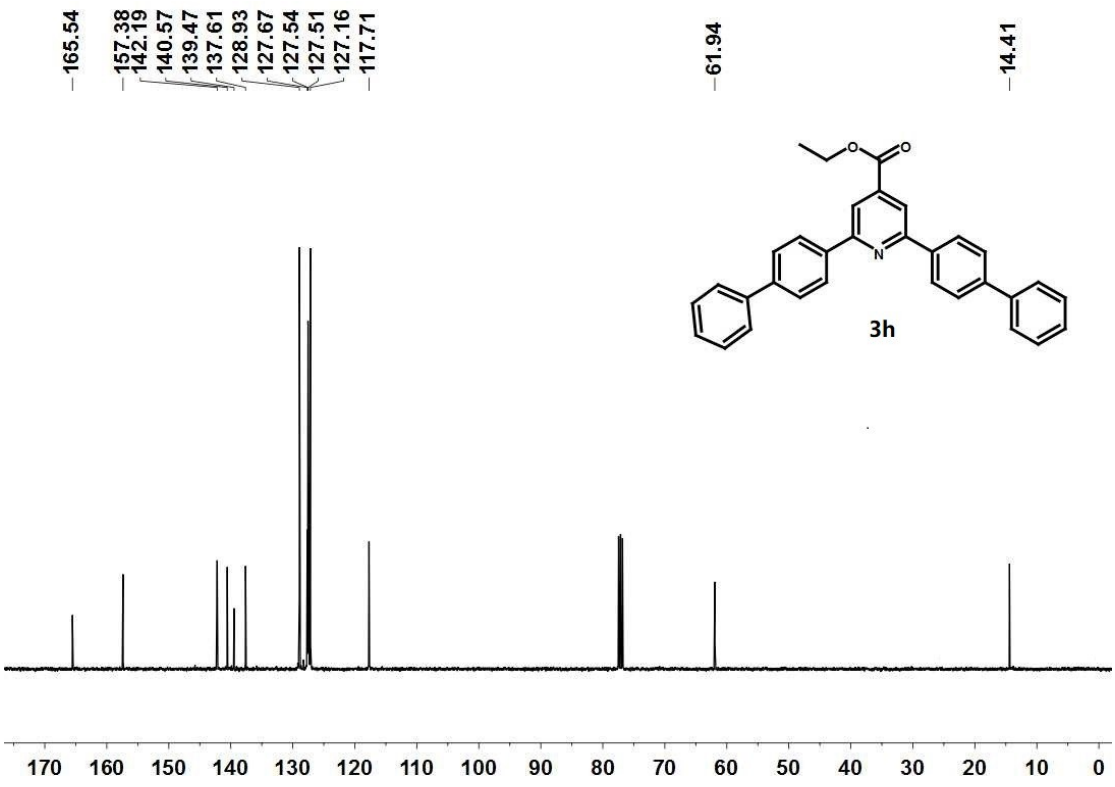
**3f**

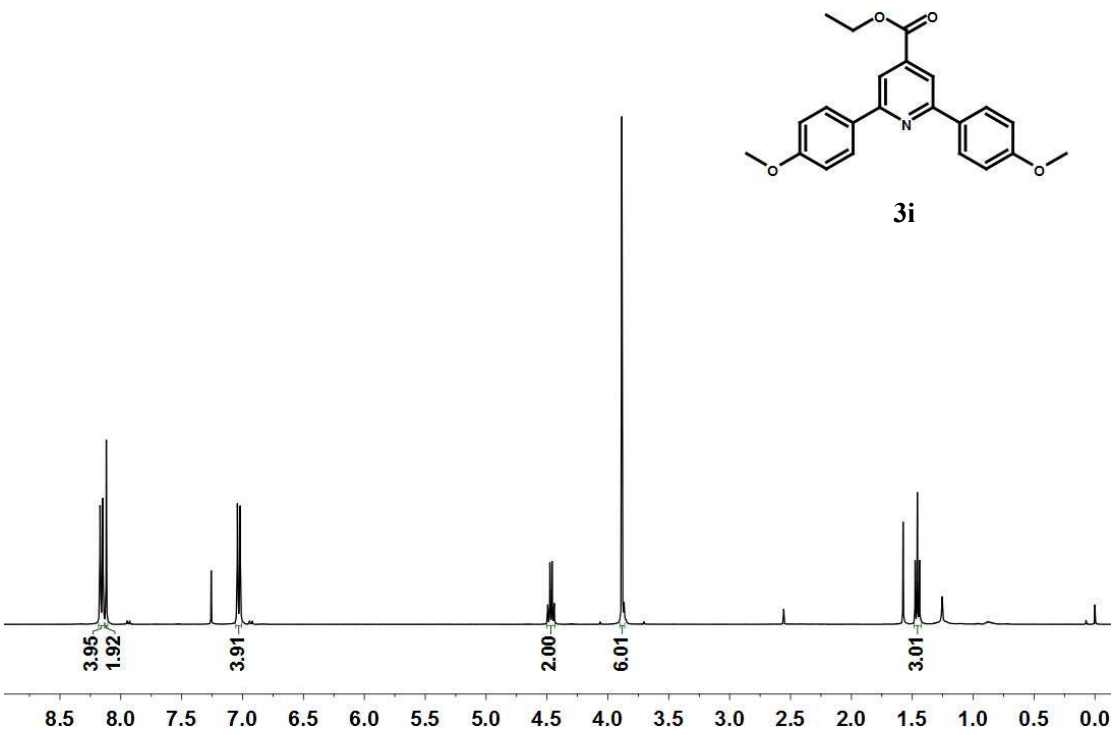

O
O
N
1.96
3.89
3.95
2.00
3.12
18.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

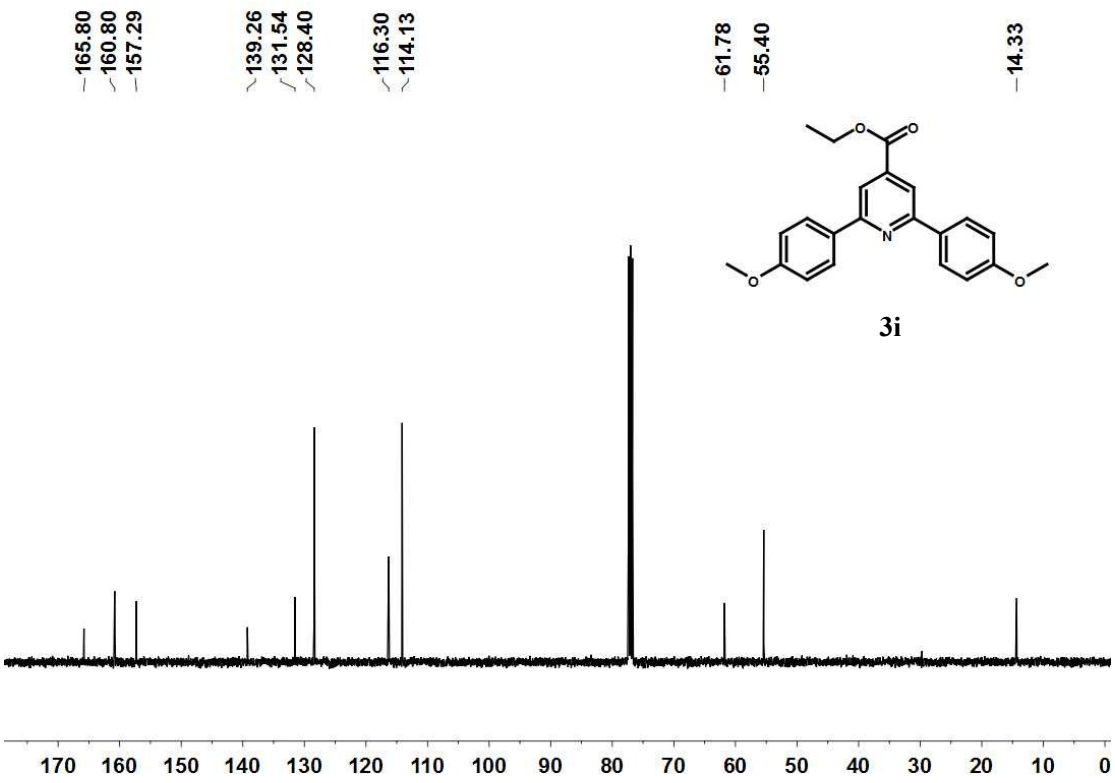
**3g**


165.75
157.78
152.61
139.27
136.13
126.86
125.74
117.31
61.80
34.77
31.34
14.34
3g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

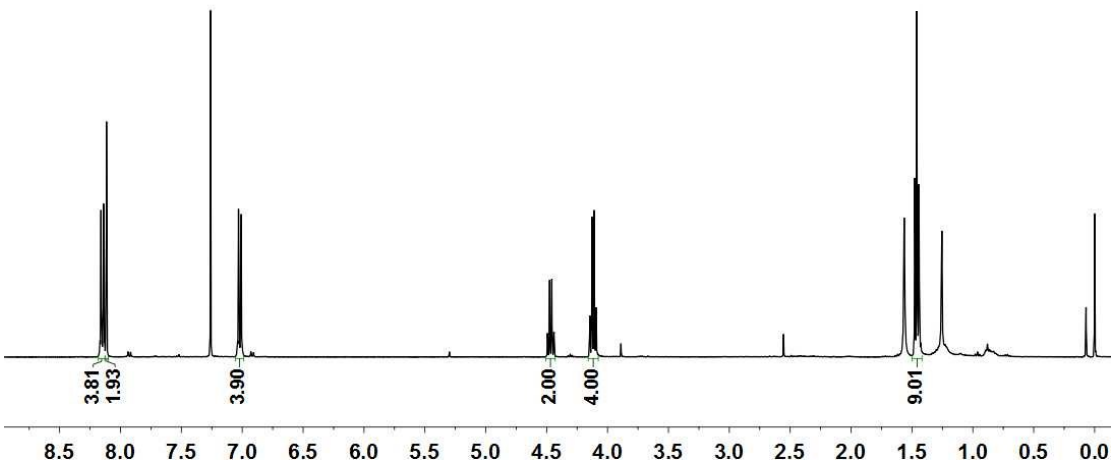

165.54
157.38
142.19
140.57
139.47
137.61
128.93
127.67
127.54
127.51
127.16
117.71
61.94
14.41
3h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


165.54
157.38
142.19
140.57
139.47
137.61
128.93
127.67
127.54
127.51
127.16
117.71
61.94
14.41
3h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

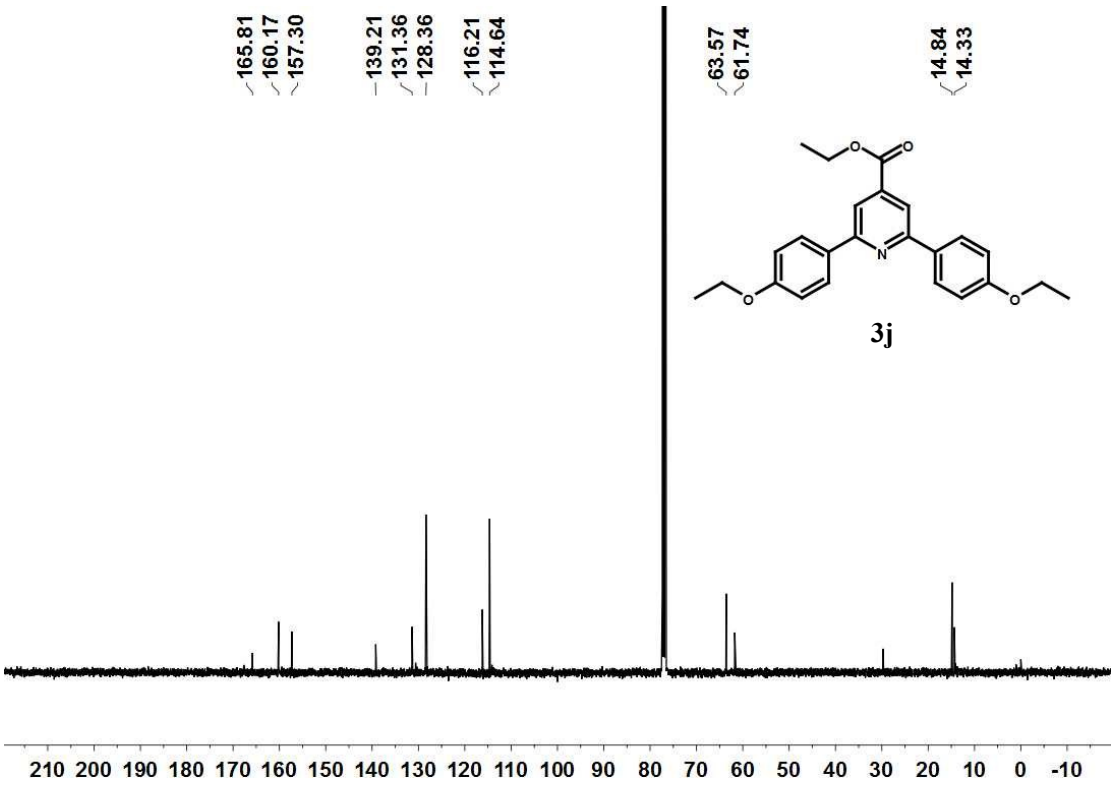

3i
3.95
1.92
3.91
2.00
6.01
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


165.80
160.80
157.29
139.26
131.54
128.40
116.30
114.13
61.78
55.40
14.33
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

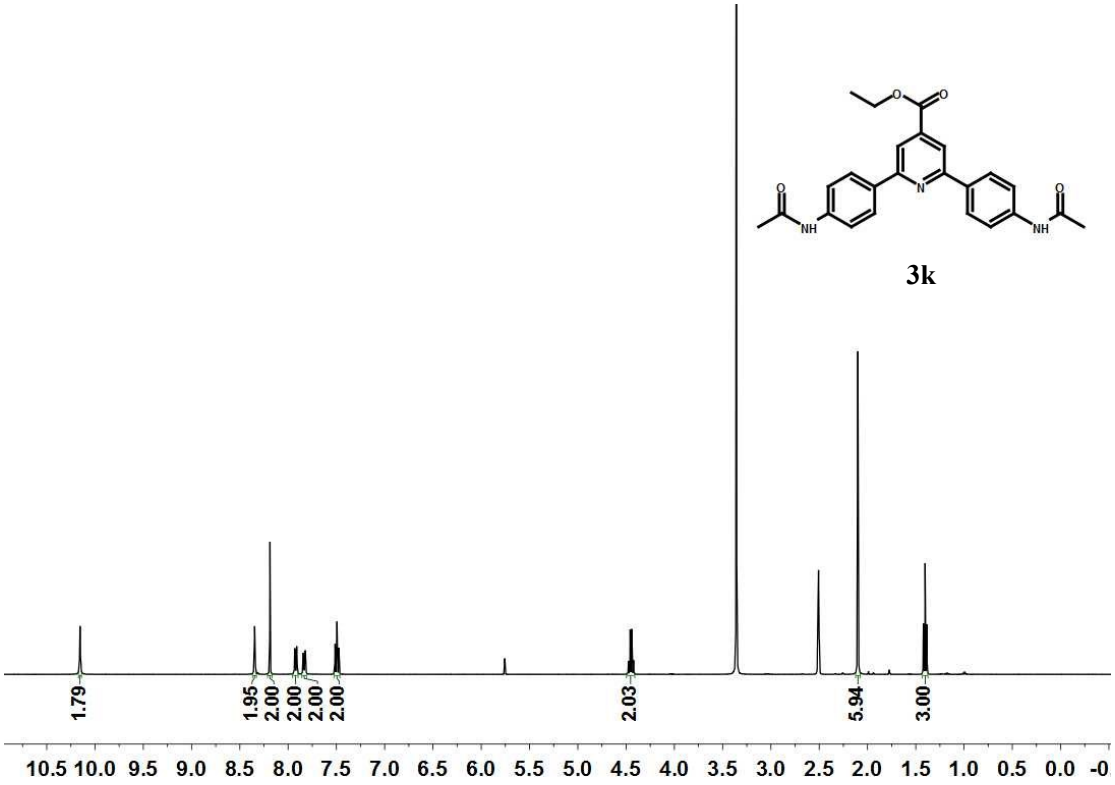
3i


3.81
1.93
3.90
2.00
4.00
9.01
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

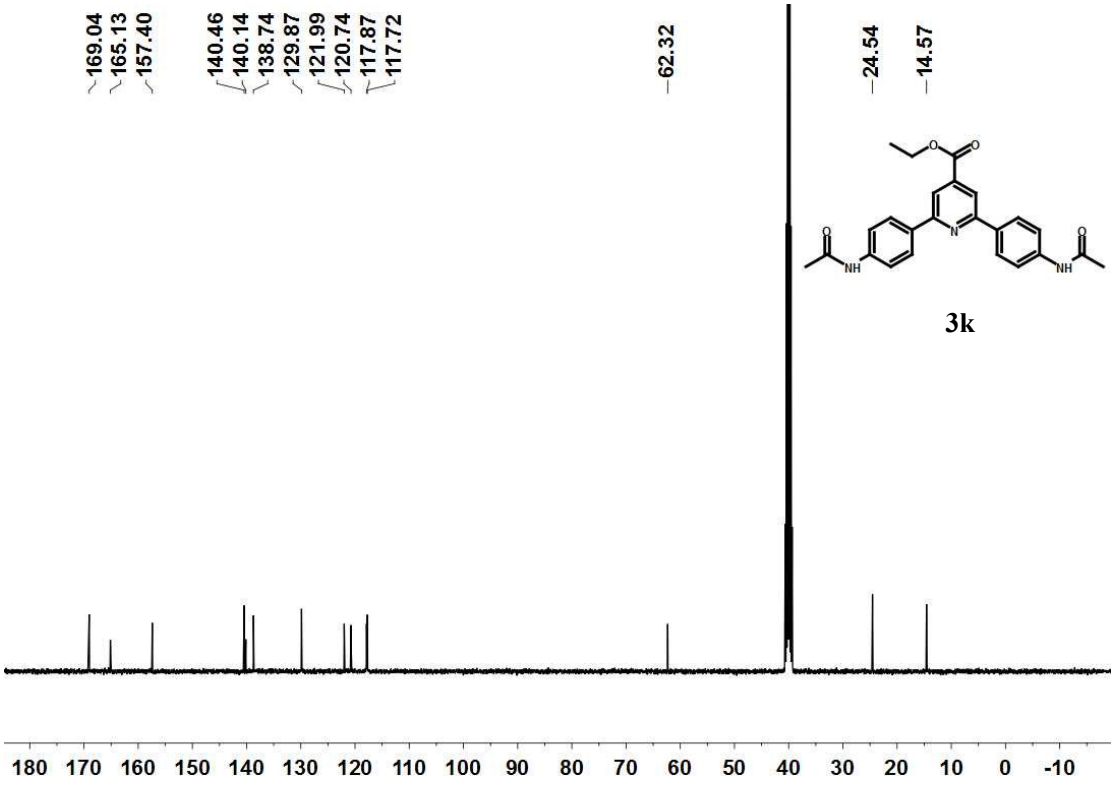
3j


165.81
160.17
157.30
139.21
131.36
128.36
116.21
114.64
63.57
61.74
14.84
14.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

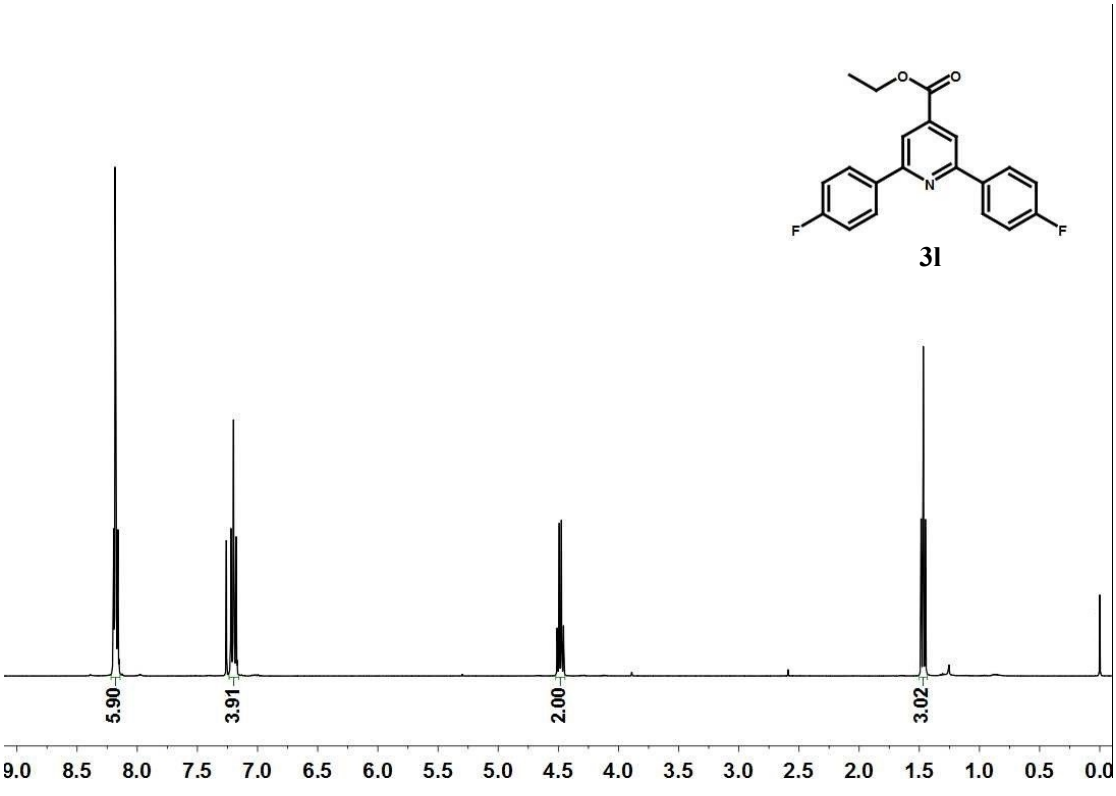
3j


1.79
1.95
2.00
2.00
2.00
2.03
5.94
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

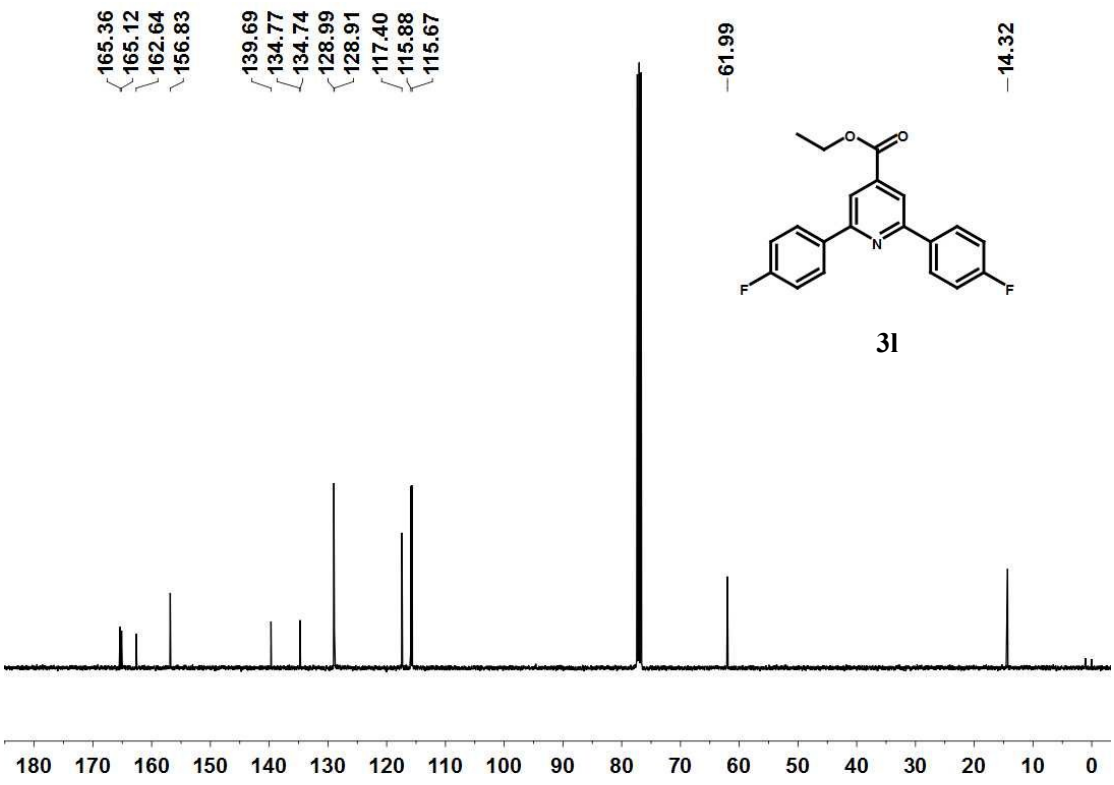
3k


169.04
165.13
157.40
140.46
140.14
138.74
129.87
121.99
120.74
117.87
117.72
62.32
24.54
14.57
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

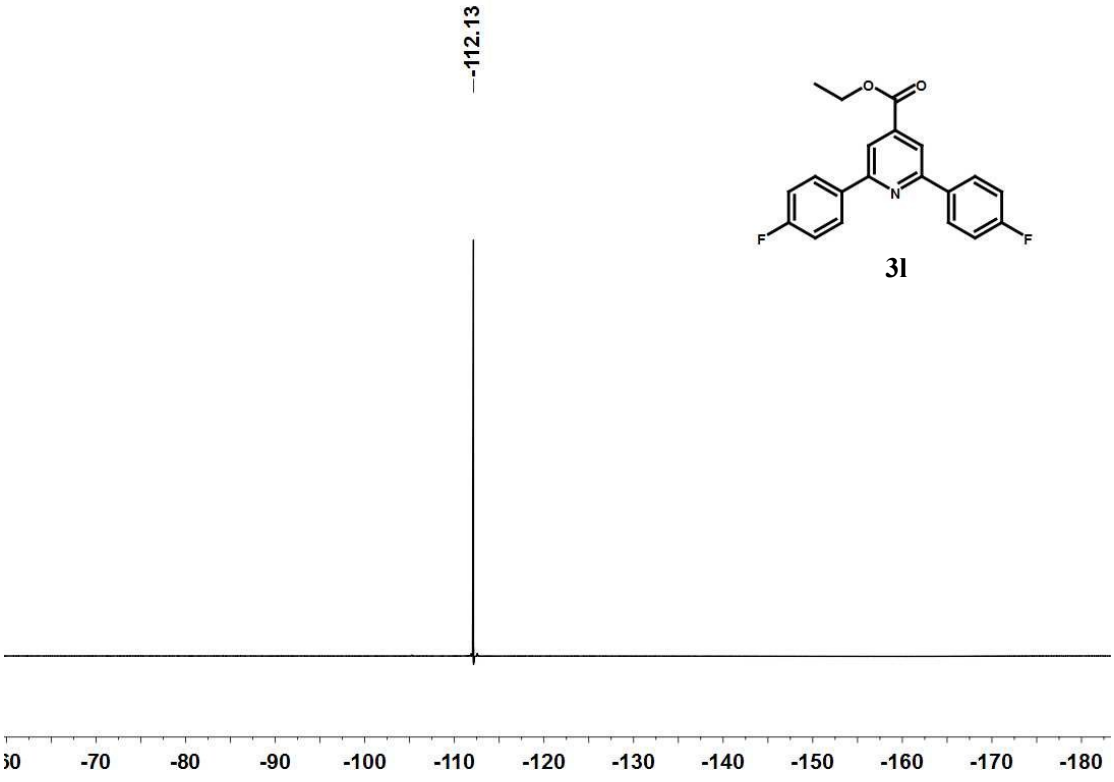
3k


5.90
3.91
2.00
3.02
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

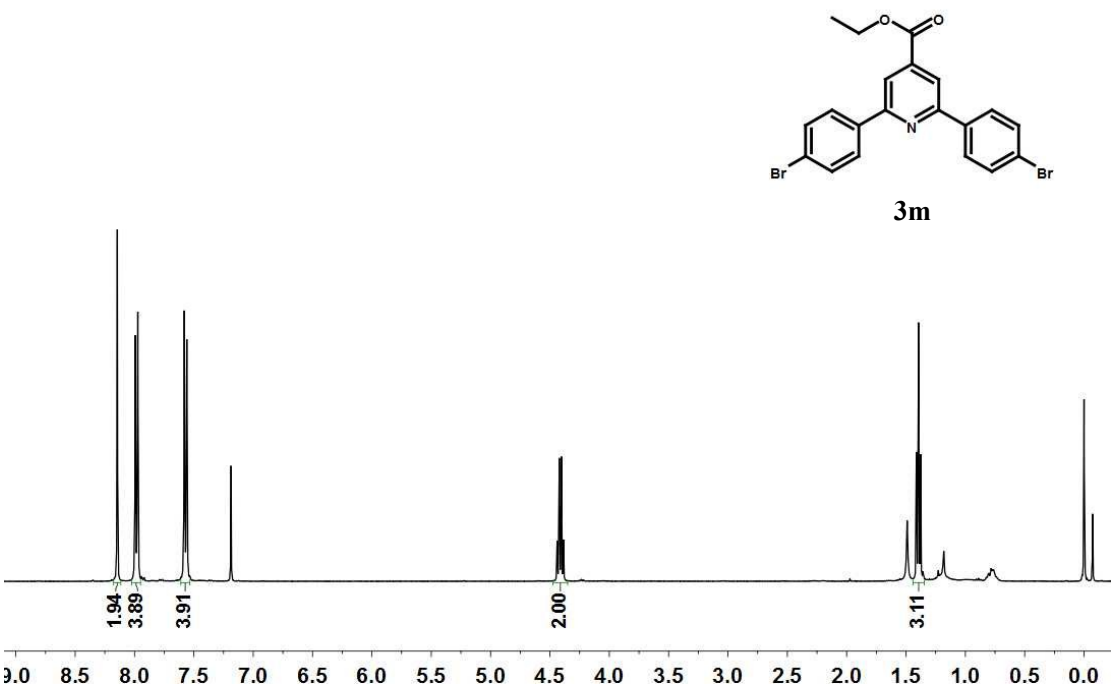
3l


165.36
165.12
162.64
156.83
139.69
134.77
134.74
128.99
128.91
117.40
115.88
115.67
61.99
14.32
O
O
N
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

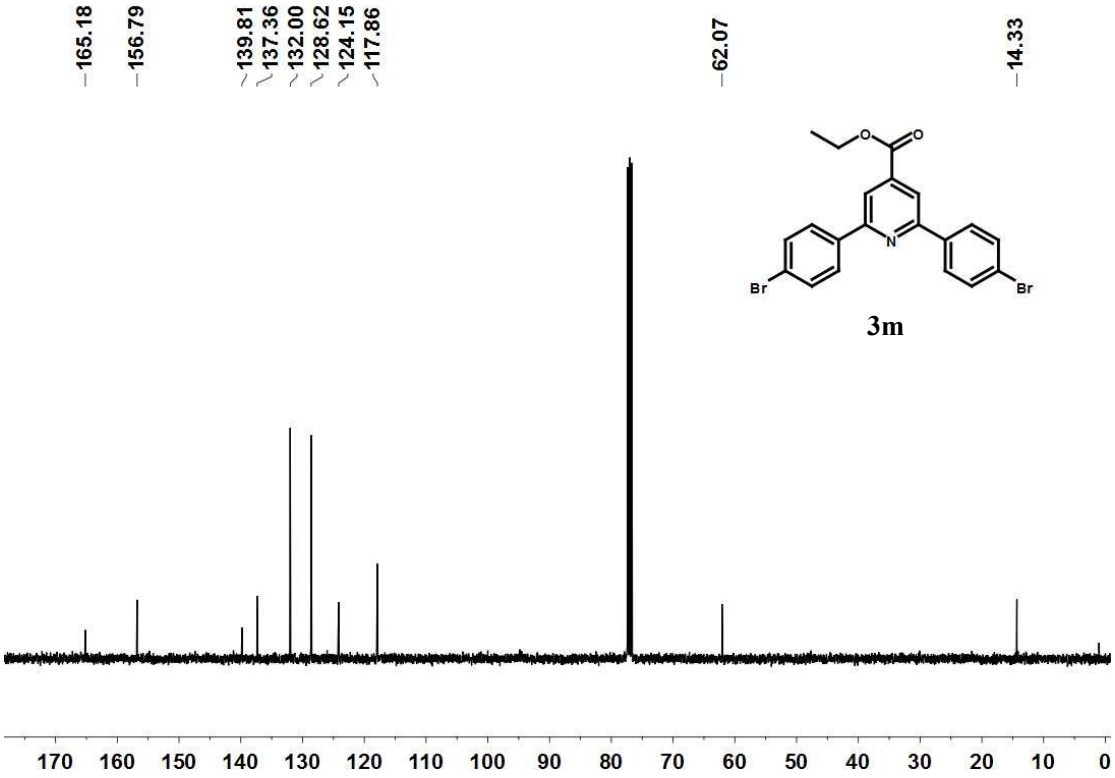
3l


-112.13
O
O
N
F
F
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180

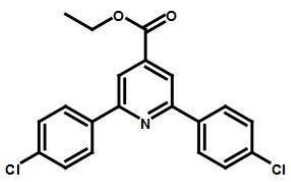
3l


Br
Br
1.94
3.89
3.91
2.00
3.11
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

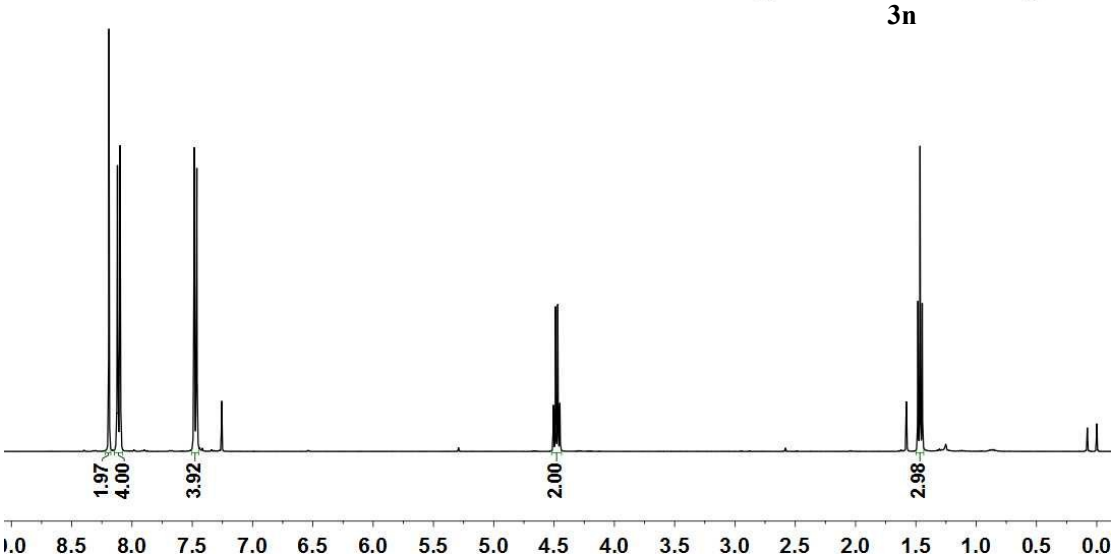
**3m**

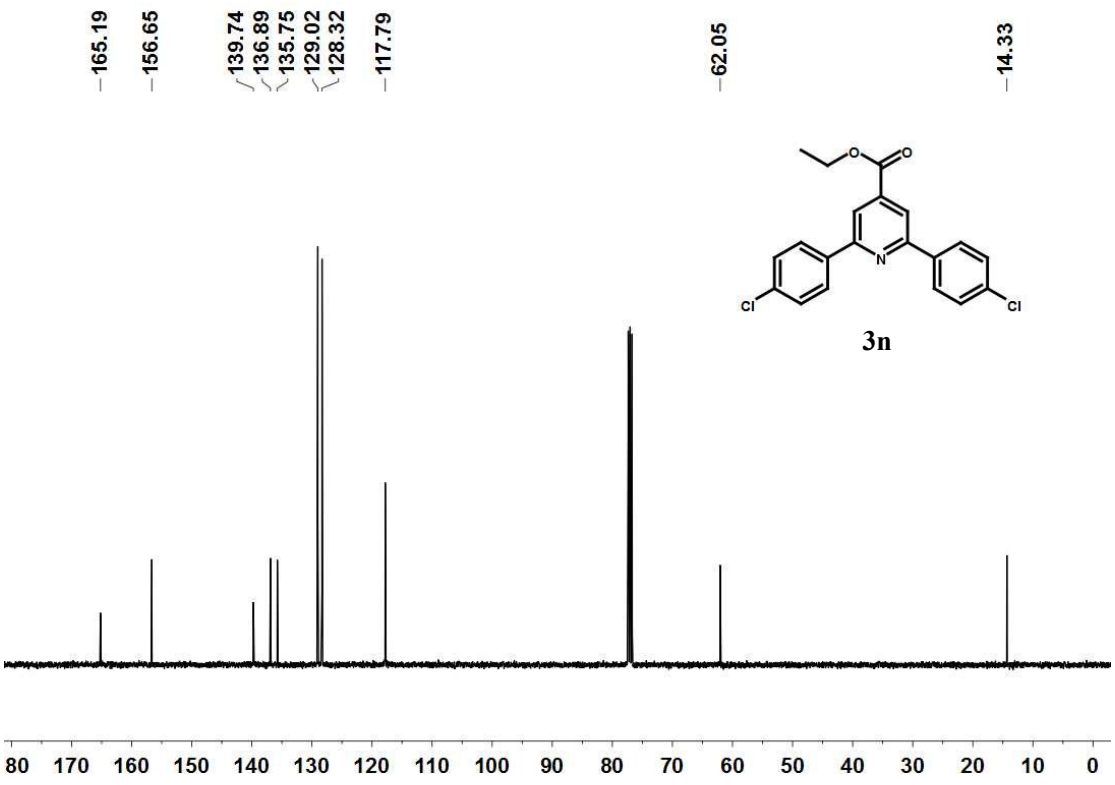

165.18
156.79
139.81
137.36
132.00
128.62
124.15
117.86
62.07
14.33
Br
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**3m**

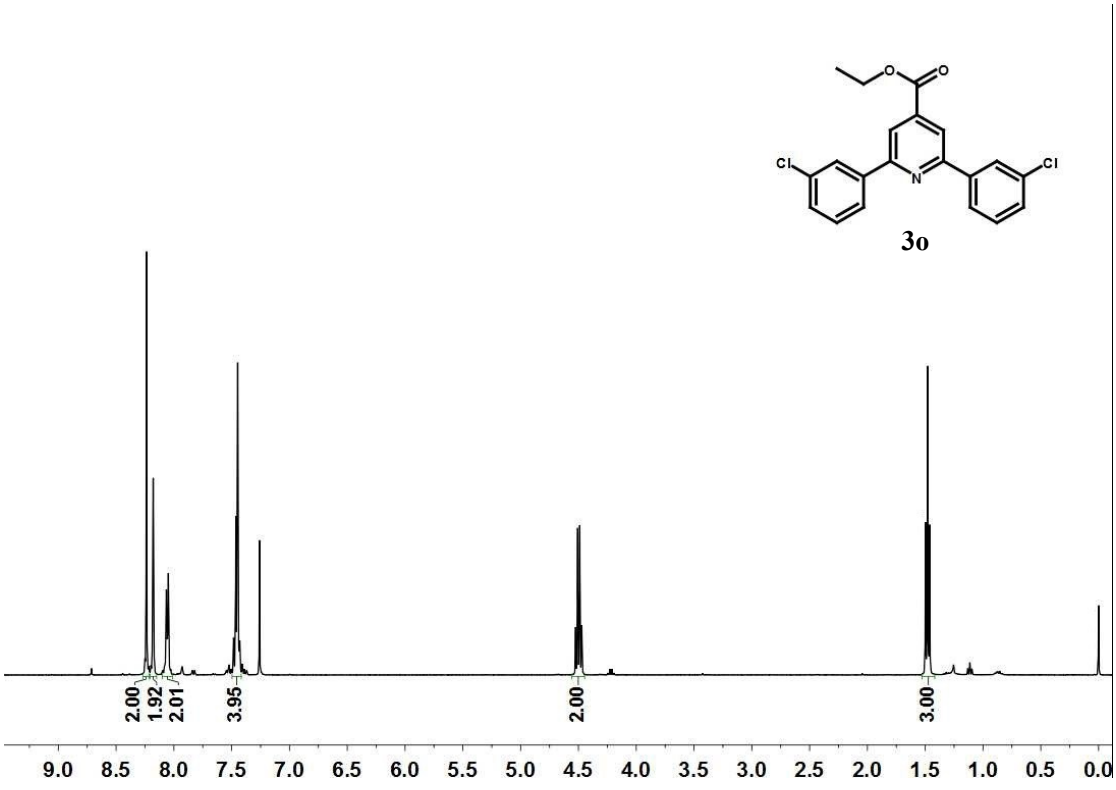

O
O
N
Cl
Cl

**3n**

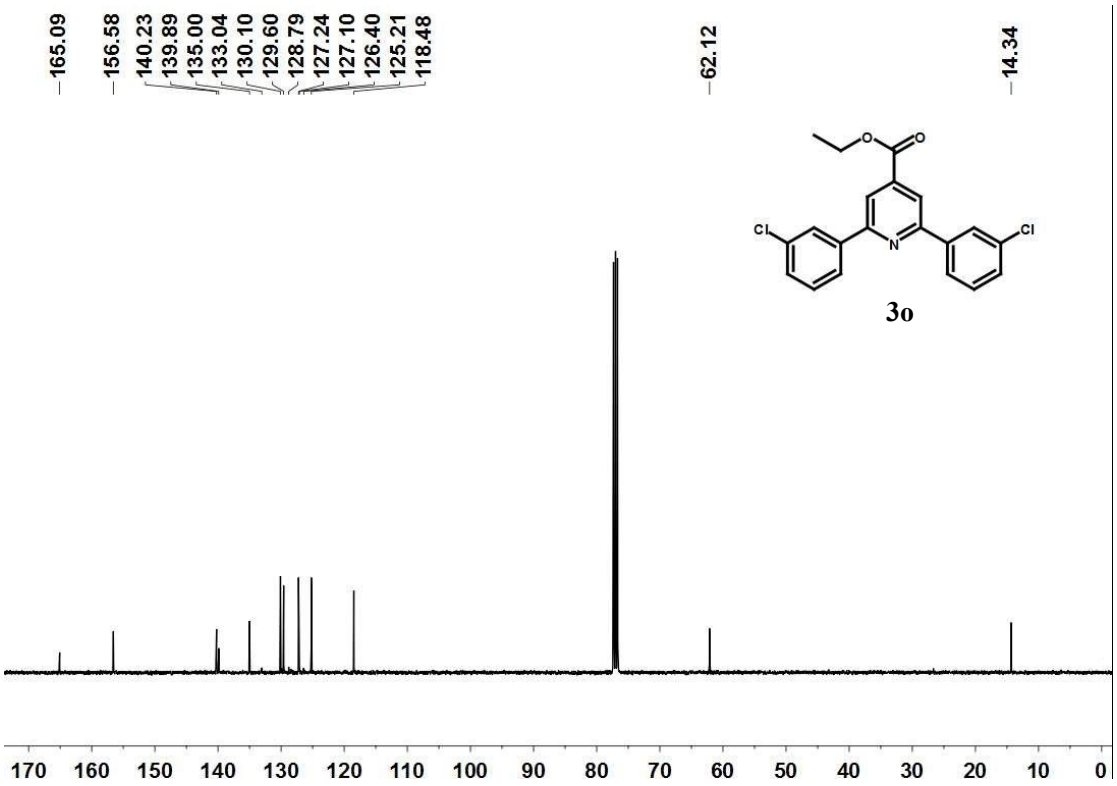

1.97
4.00
3.92
2.00
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


165.19
156.65
139.74
136.89
135.75
129.02
128.32
117.79
62.05
14.33
O
O
N
Cl
Cl
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

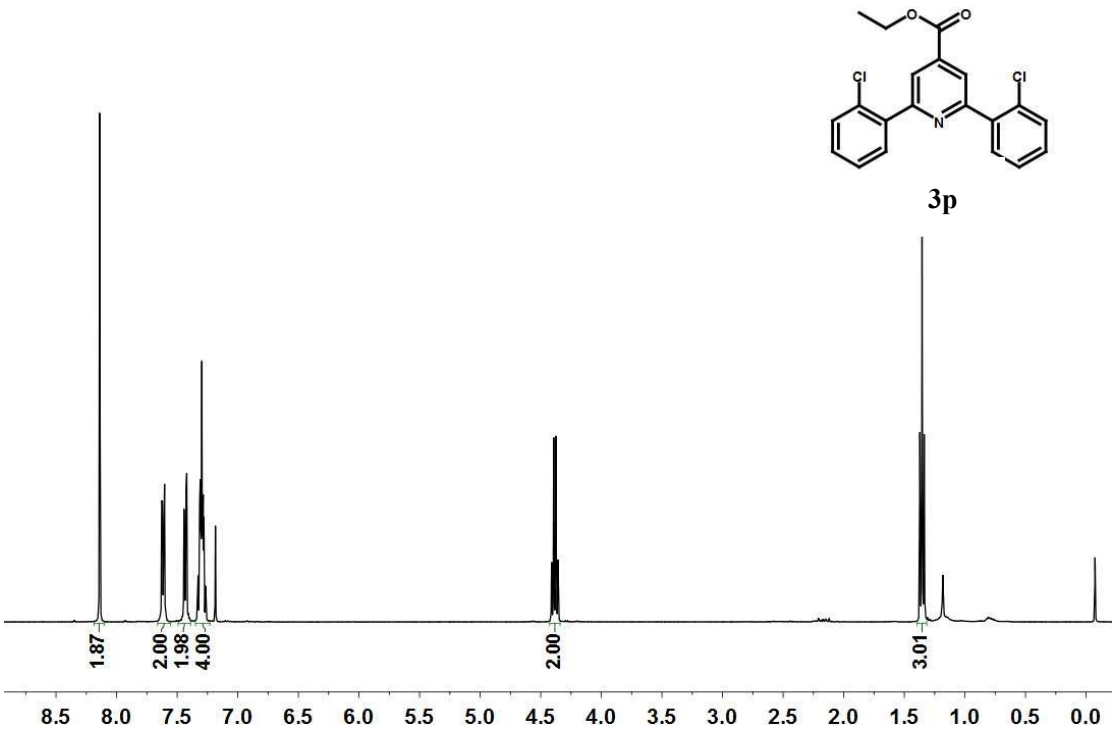
3n


O
O
N
Cl
Cl
2.00
1.92
2.01
3.95
2.00
3.00
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

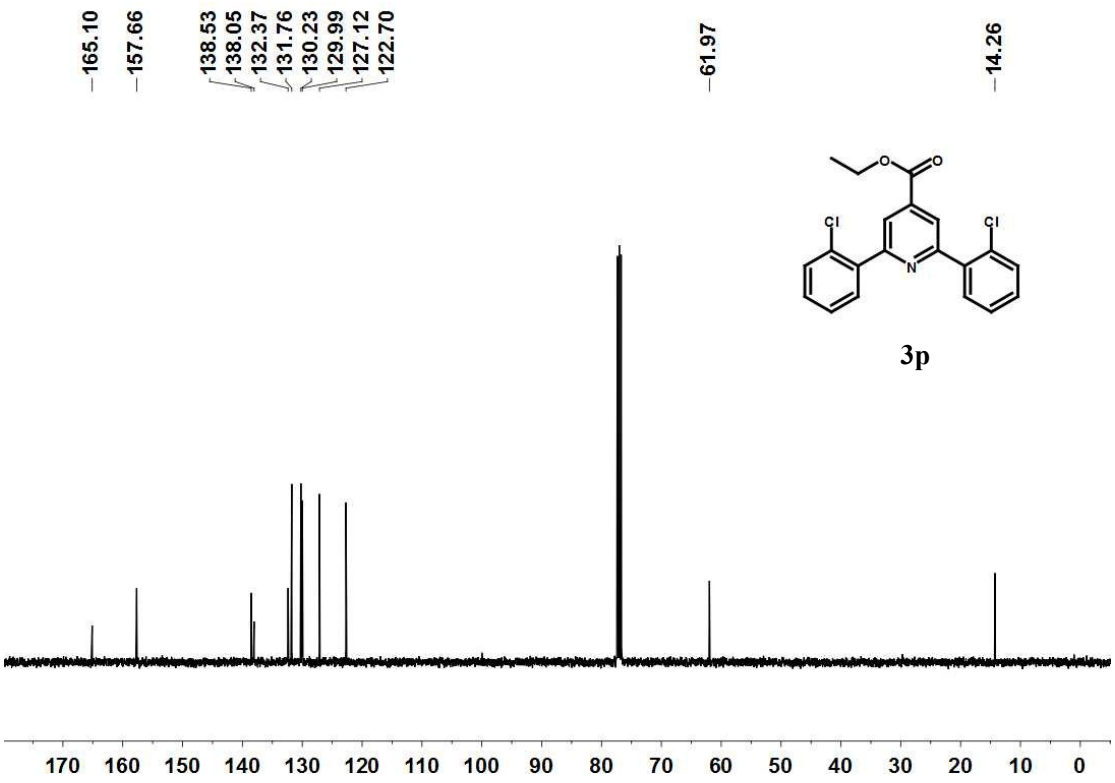
3o


165.09
156.58
140.23
139.89
135.00
133.04
130.10
129.60
128.79
127.24
127.10
126.40
125.21
118.48
62.12
14.34
Cl
N
Cl
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

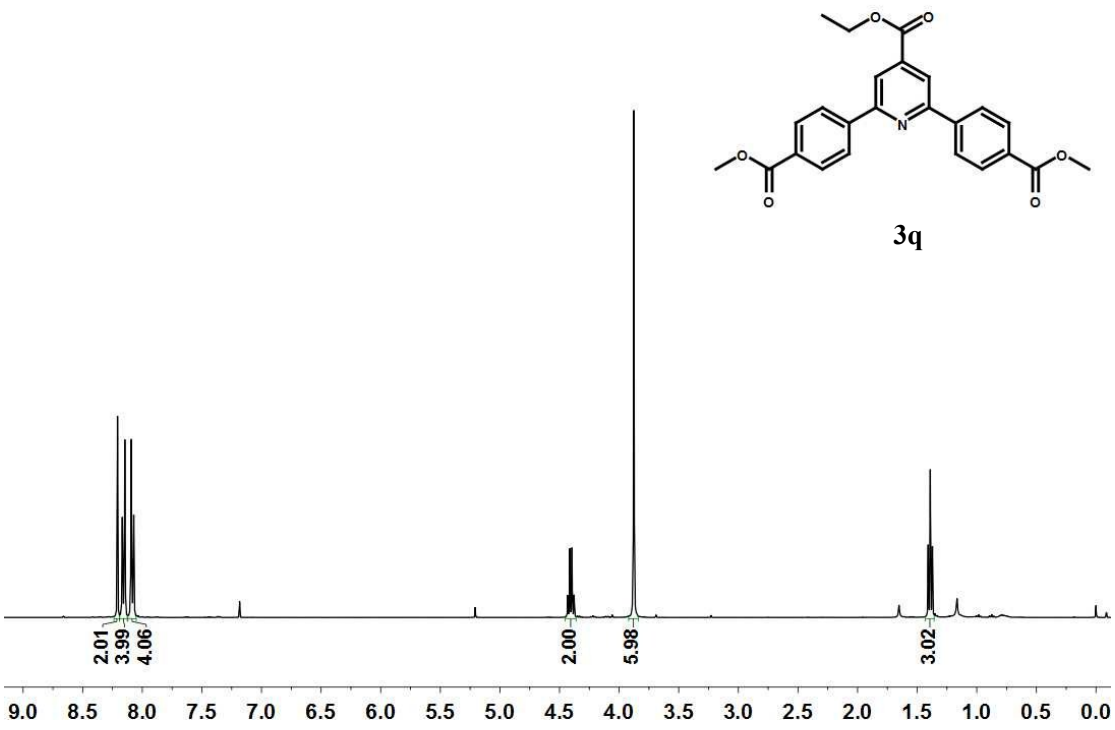
**3o**


Cl
N
Cl
O
O
1.87
2.00
1.98
4.00
2.00
3.01
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

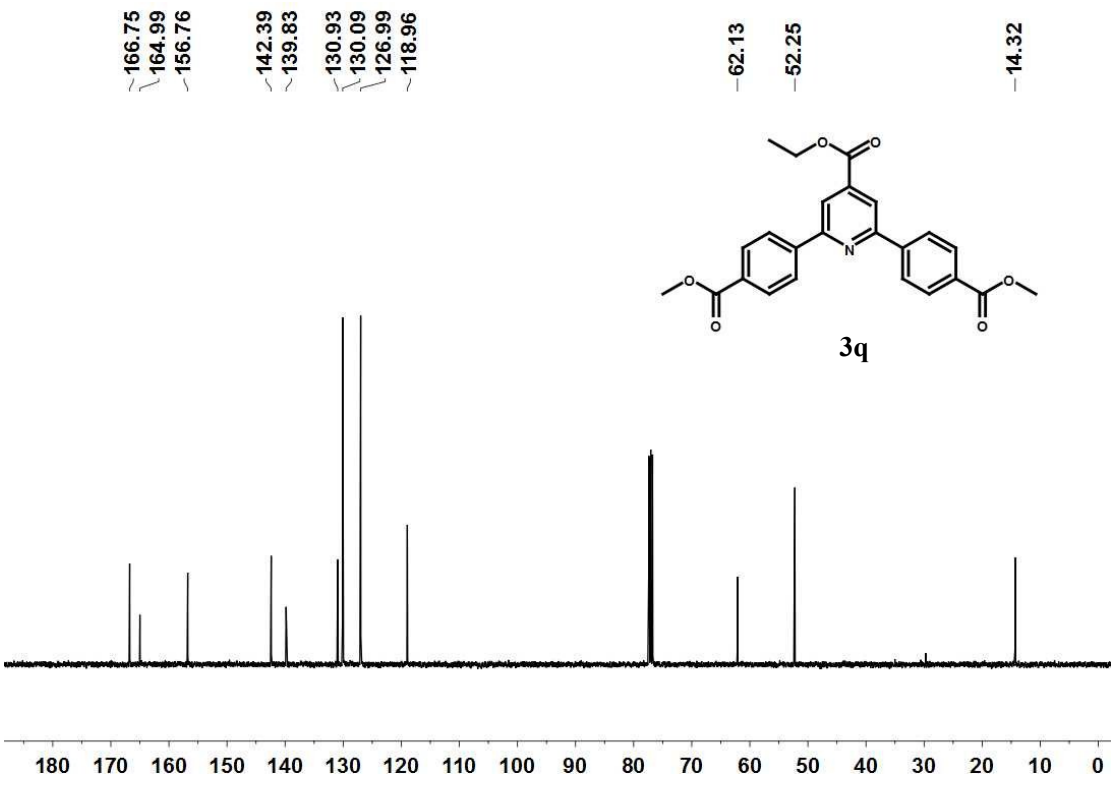
**3p**


165.10
157.66
138.53
138.05
132.37
131.76
130.23
129.99
127.12
122.70
61.97
14.26
Cl
Cl
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

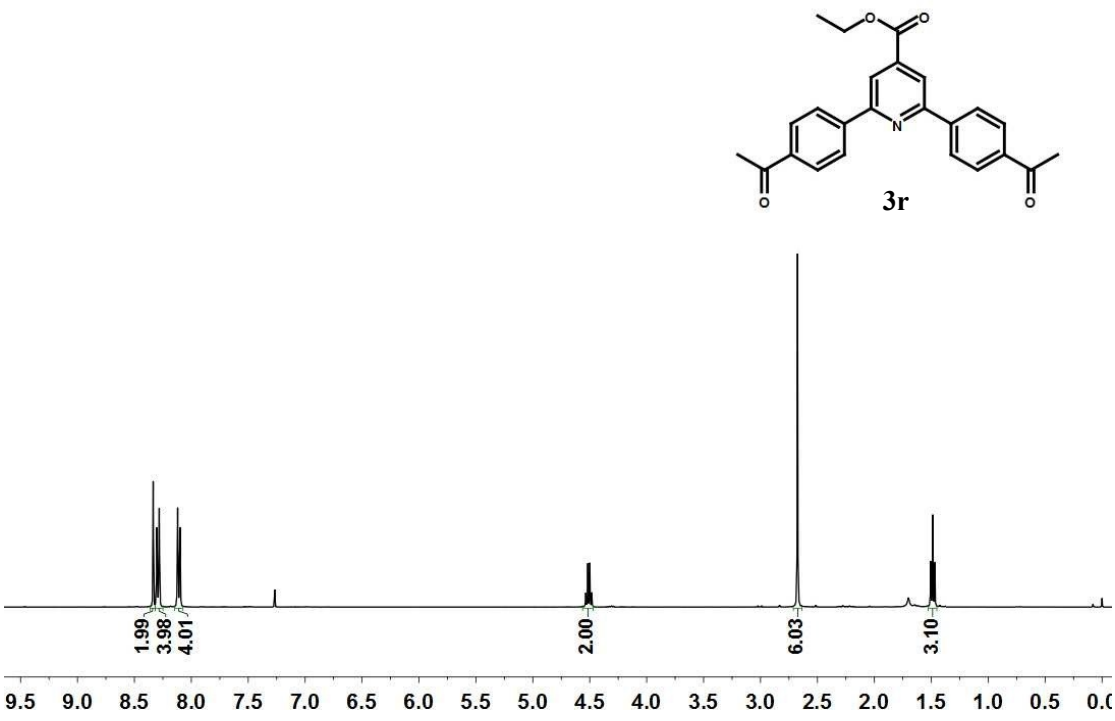
**3p**


N
2.01
3.99
4.06
2.00
5.98
3.02
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

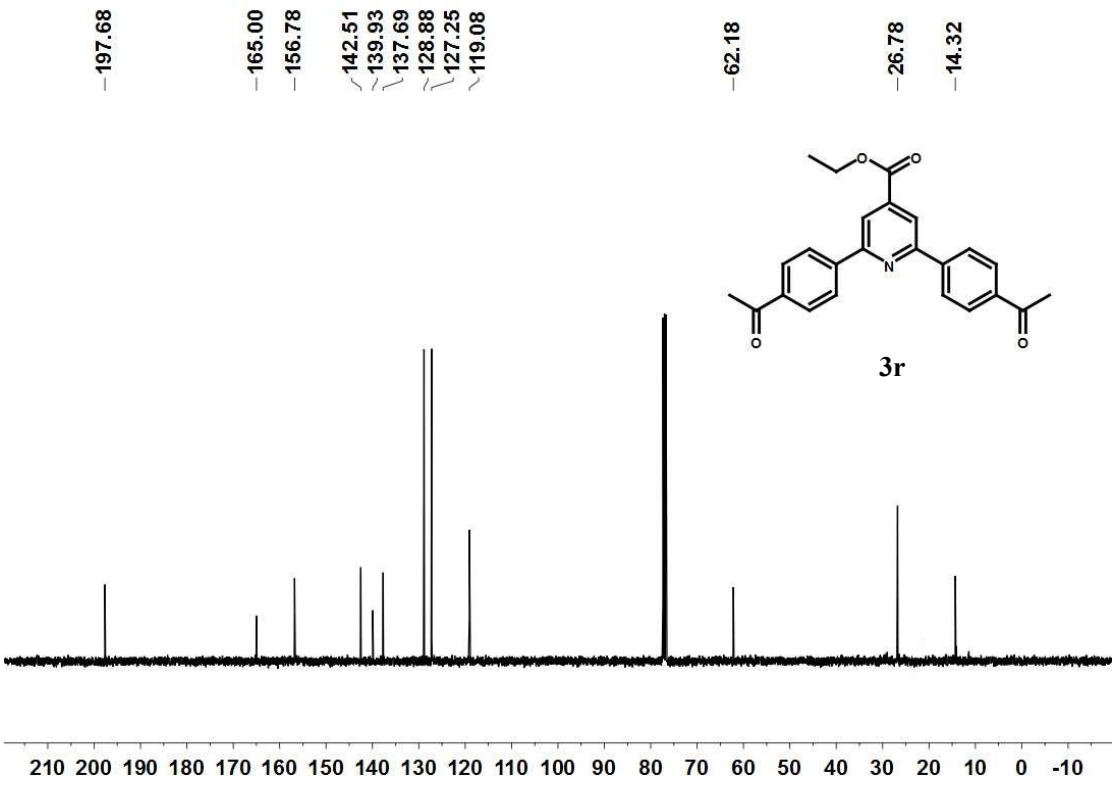
**3q**


166.75
164.99
156.76
142.39
139.83
130.93
130.09
126.99
118.96
62.13
52.25
14.32
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

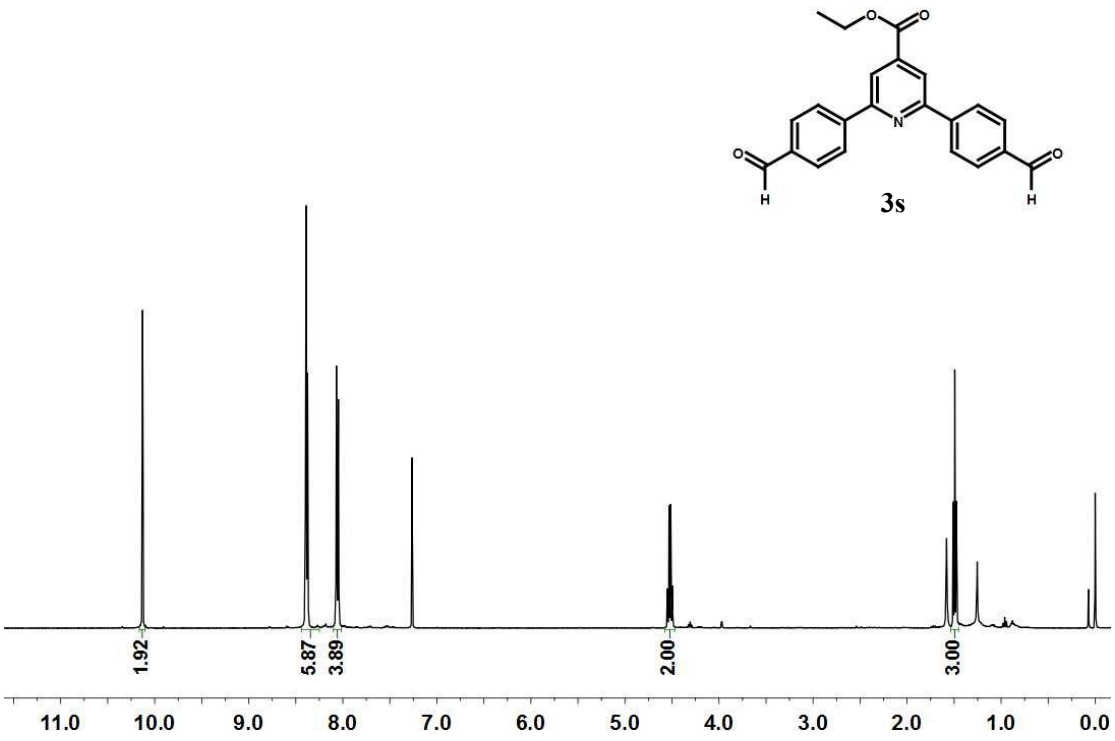
3q


1.99
3.98
4.01
2.00
6.03
3.10
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

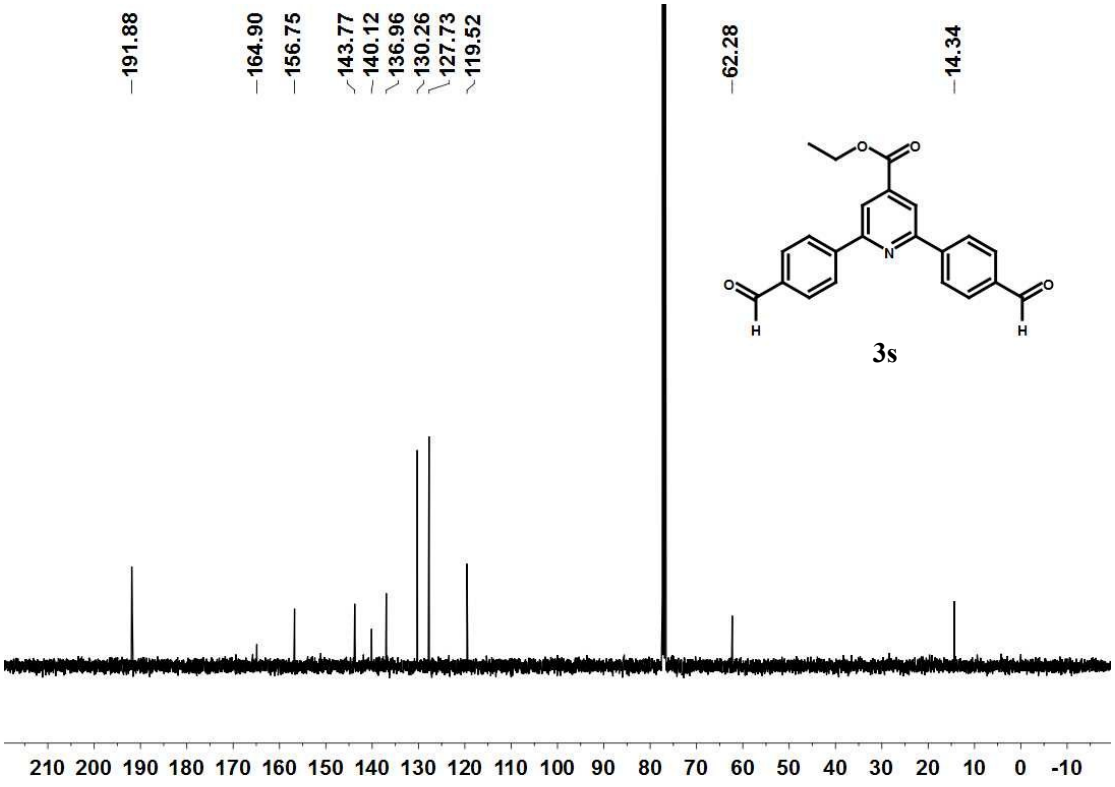
3r


197.68
165.00
156.78
142.51
139.93
137.69
128.88
127.25
119.08
62.18
26.78
14.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3r

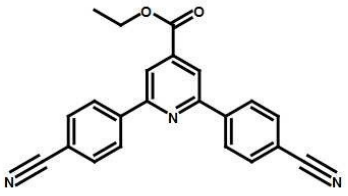

1.92
5.87
3.89
2.00
3.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

3s

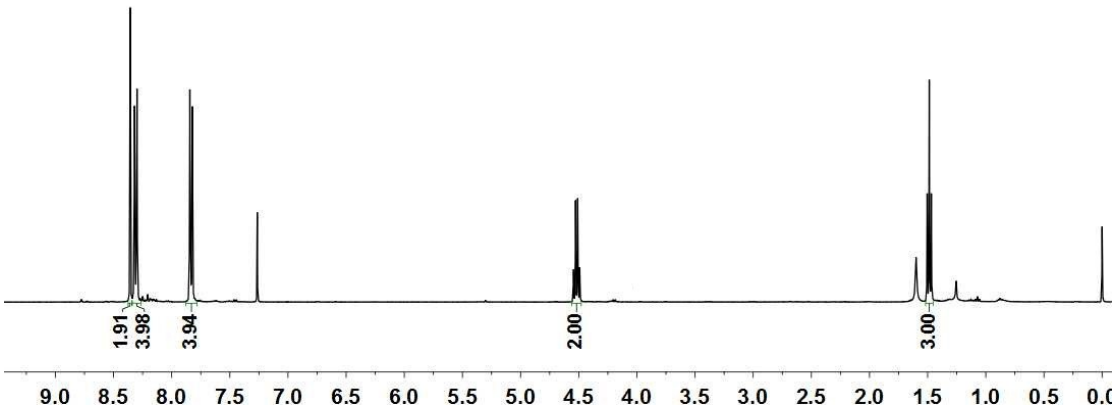

191.88
164.90
156.75
143.77
140.12
136.96
130.26
127.73
119.52
62.28
14.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

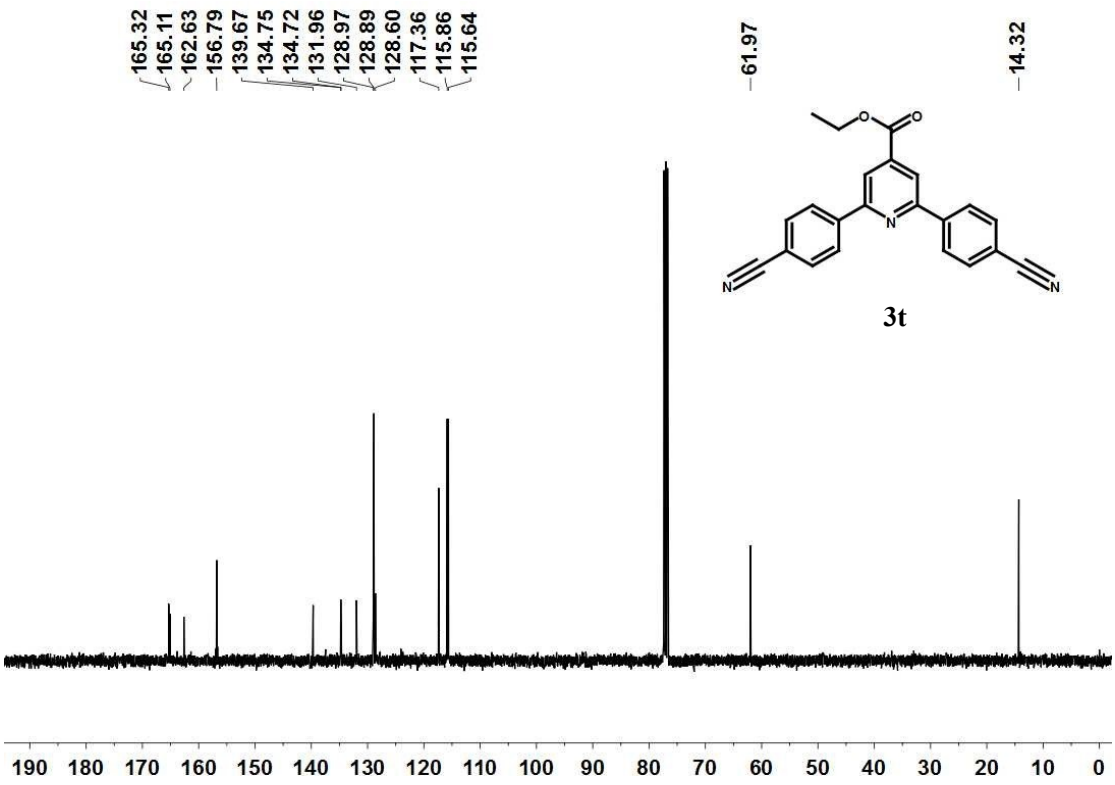


3s

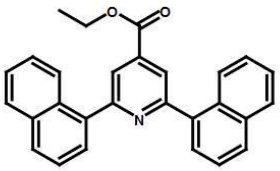


3t

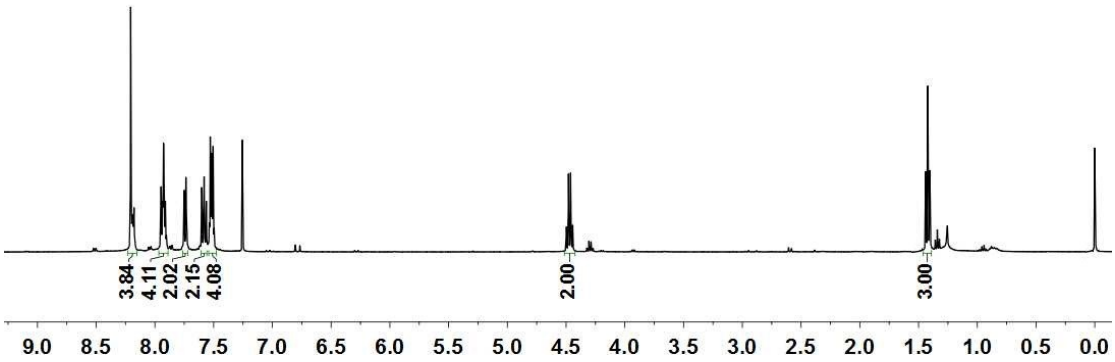

1.91
3.98
3.94
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

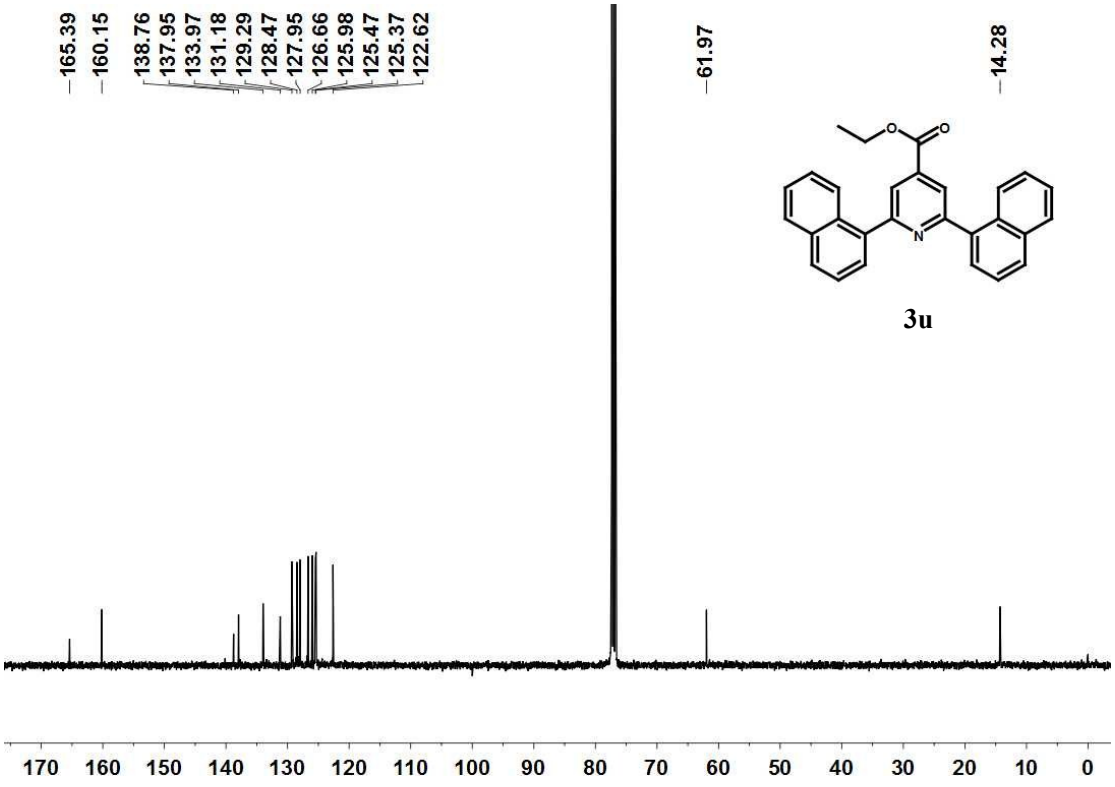

165.32
165.11
162.63
156.79
139.67
134.75
134.72
131.96
128.97
128.89
128.60
117.36
115.86
115.64
61.97
14.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**3t**

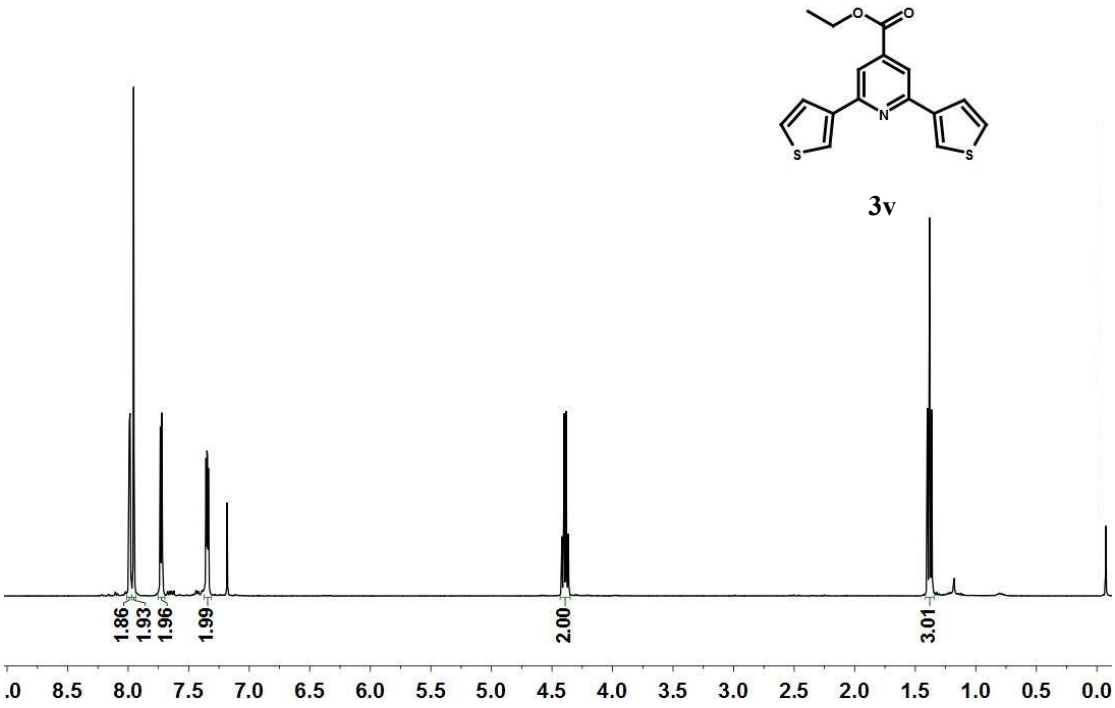


**3u**

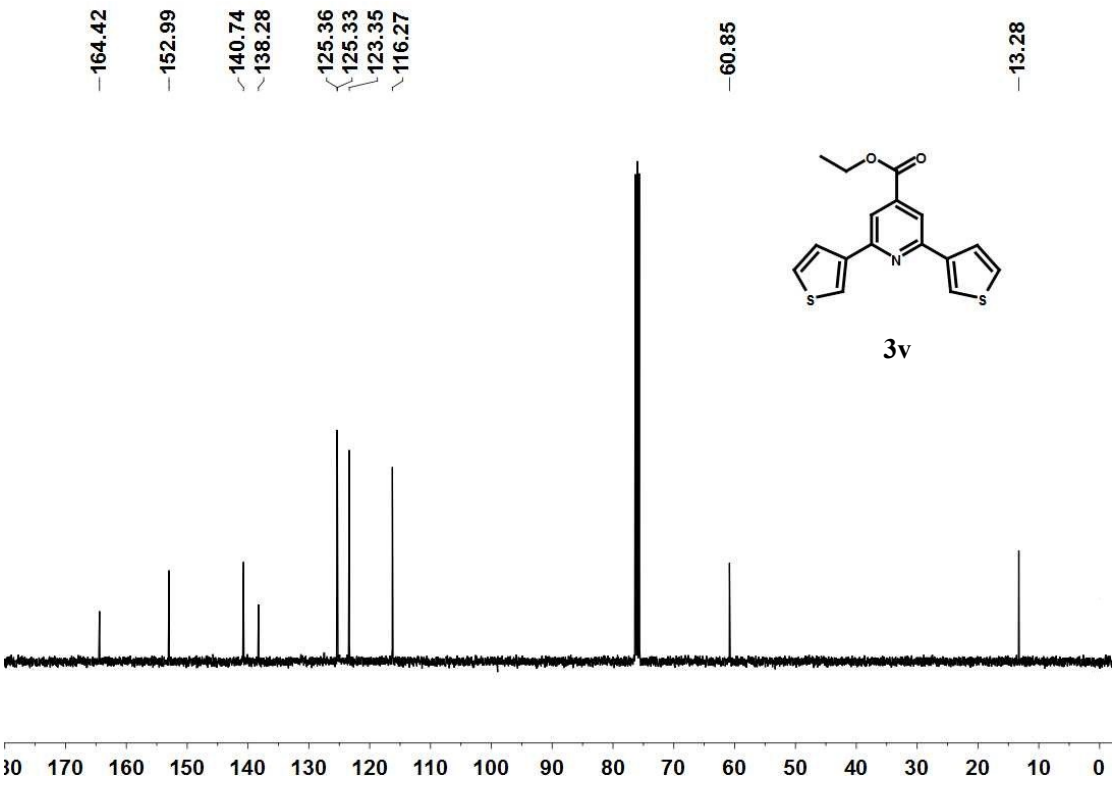

3.84
4.11
2.02
2.15
4.08
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


165.39
160.15
138.76
137.95
133.97
131.18
129.29
128.47
127.95
126.66
125.98
125.47
125.37
122.62
61.97
14.28
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

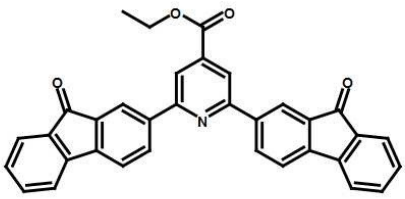
**3u**


O
O
N
S
S
1.86
1.93
1.96
1.99
2.00
3.01
.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

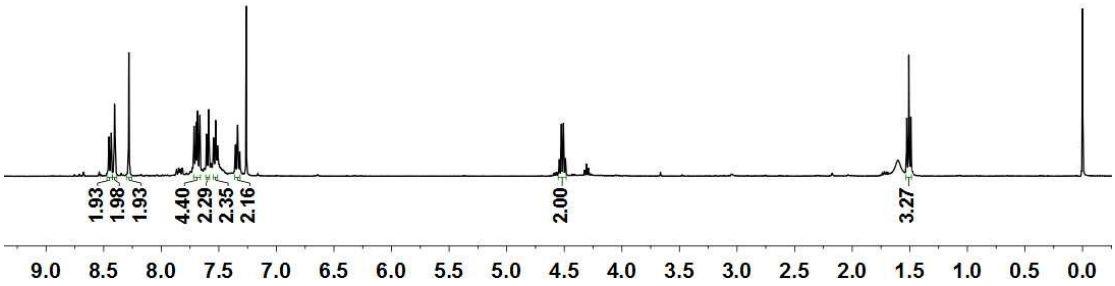
**3v**

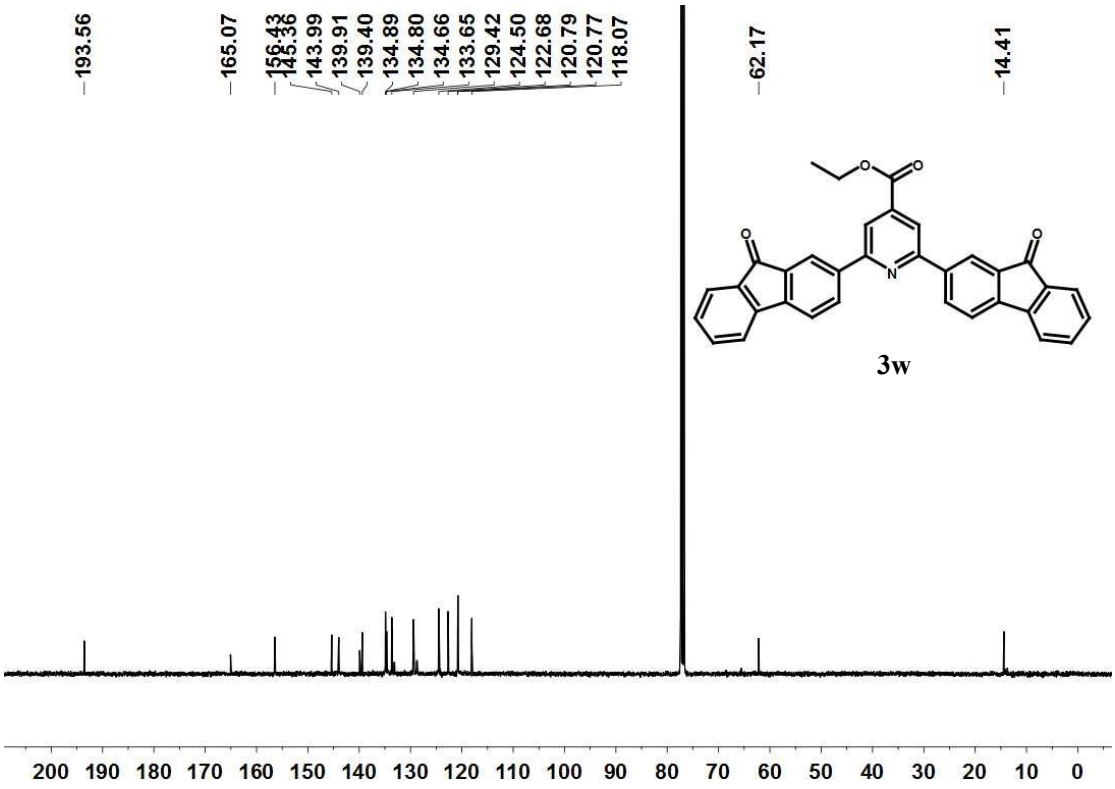

164.42
152.99
140.74
138.28
125.36
125.33
123.35
116.27
60.85
13.28
O
O
O
N
S
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**3v**

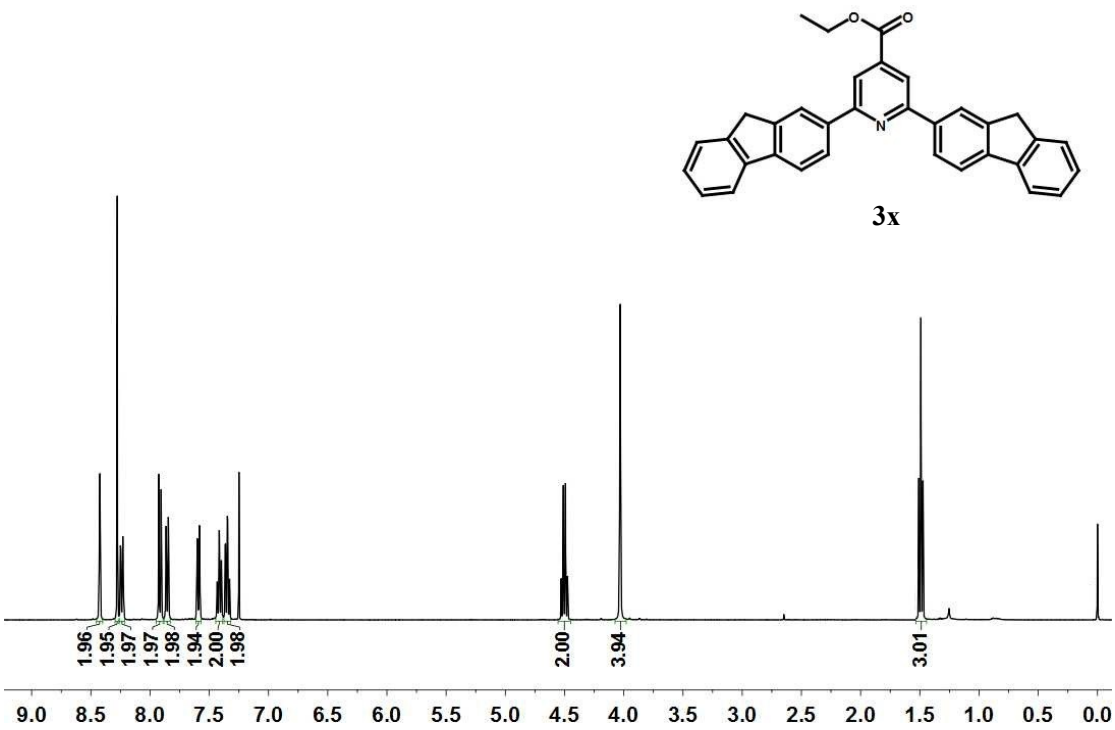

O
O
O
N
O
O

**3w**

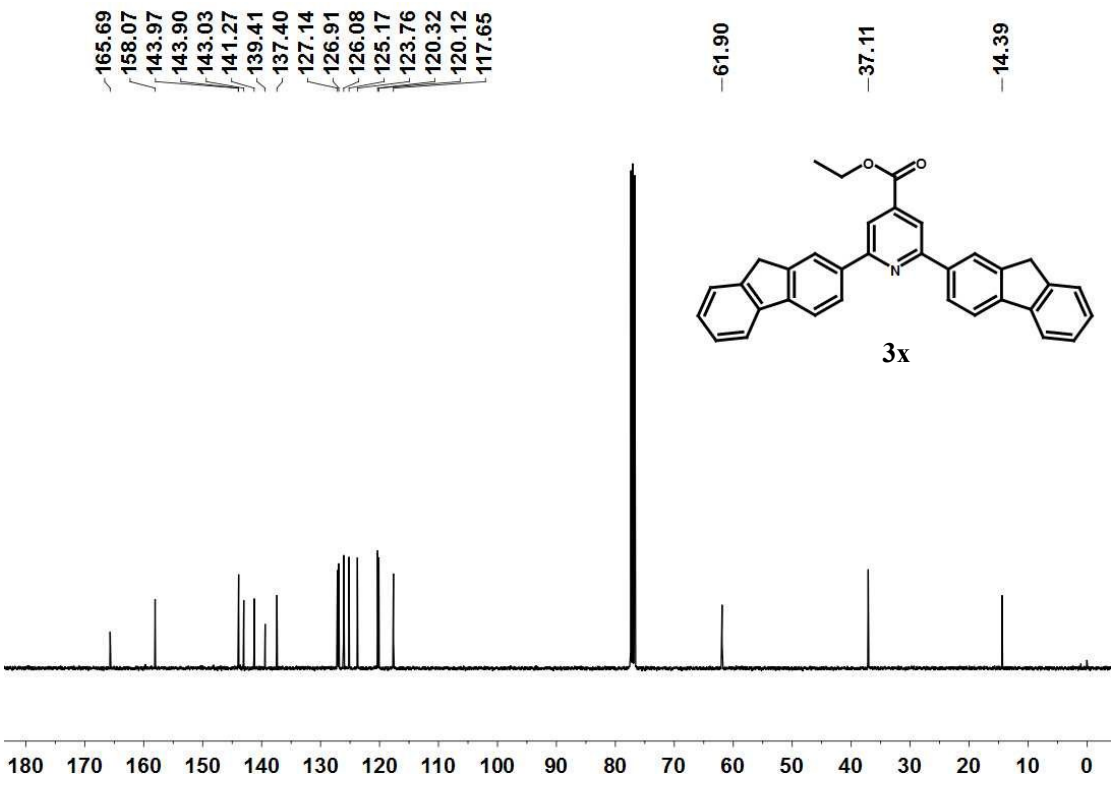

1.93
1.98
1.93
4.40
2.29
2.35
2.16
2.00
3.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


193.56
165.07
156.43
145.36
143.99
139.91
139.40
134.89
134.80
134.66
133.65
129.42
124.50
122.68
120.79
120.77
118.07
62.17
14.41
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3w

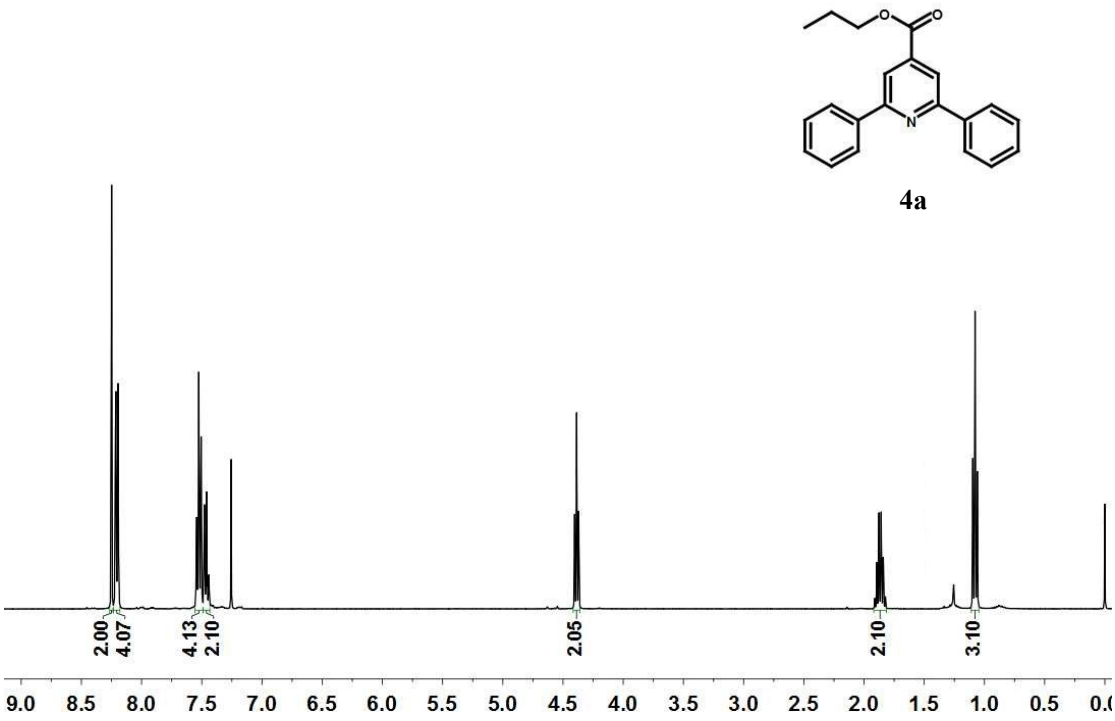

1.96
1.95
1.97
1.97
1.98
1.94
2.00
1.98
2.00
3.94
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3x


165.69
158.07
143.97
143.90
143.03
141.27
139.41
137.40
127.14
126.91
126.08
125.17
123.76
120.32
120.12
117.65
61.90
37.11
14.39
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

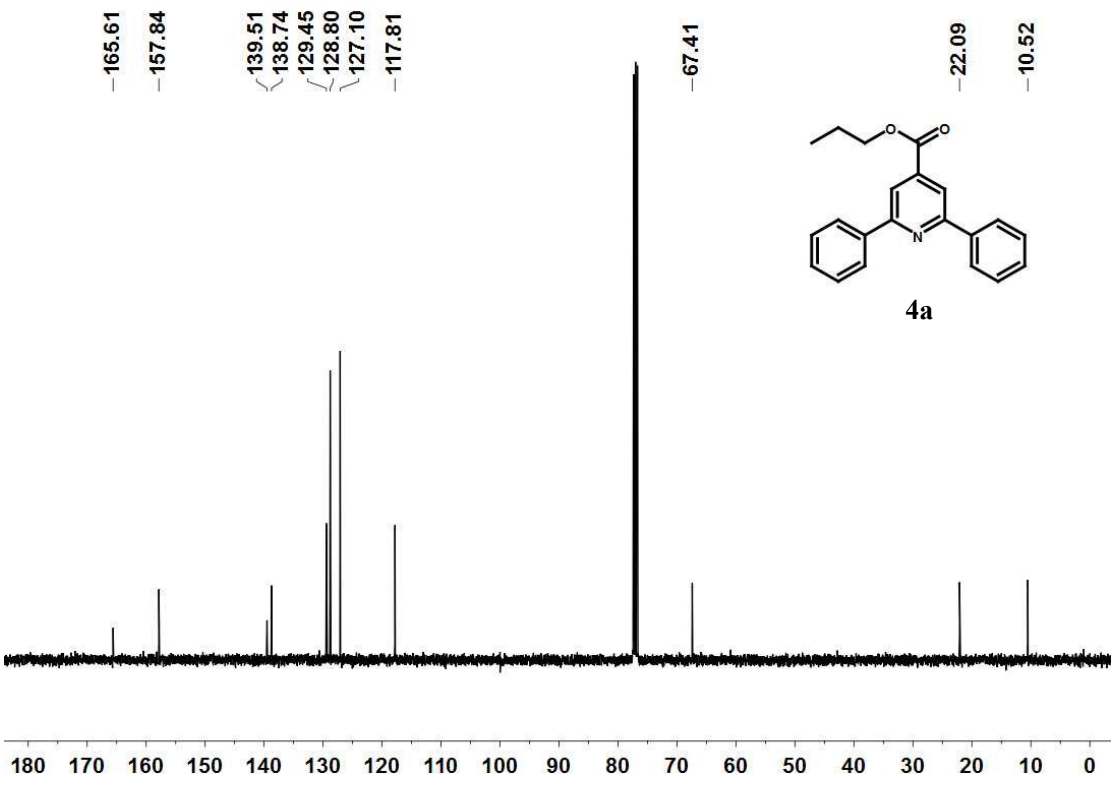


**3x**


2.00
4.07
4.13
2.10
2.05
2.10
3.10
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

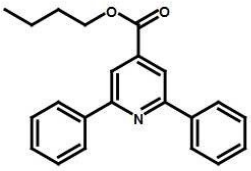


**4a**

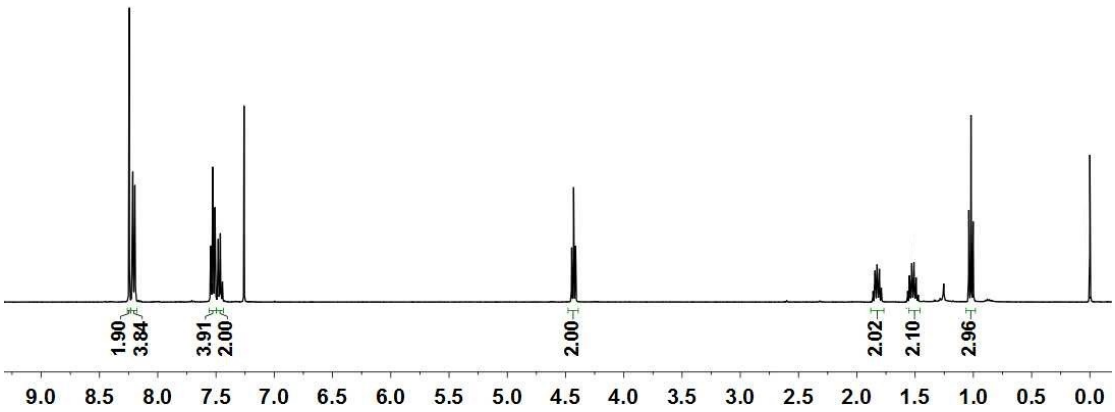

165.61
157.84
139.51
138.74
129.45
128.80
127.10
117.81
67.41
22.09
10.52
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

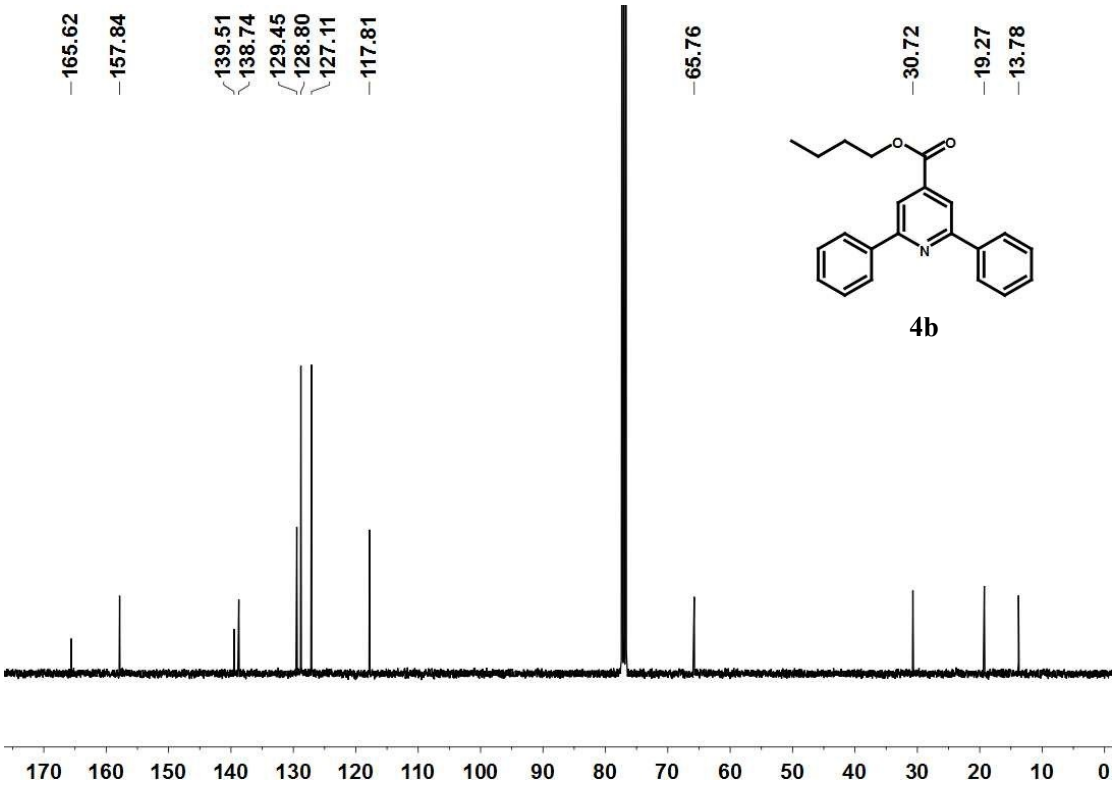


**4a**

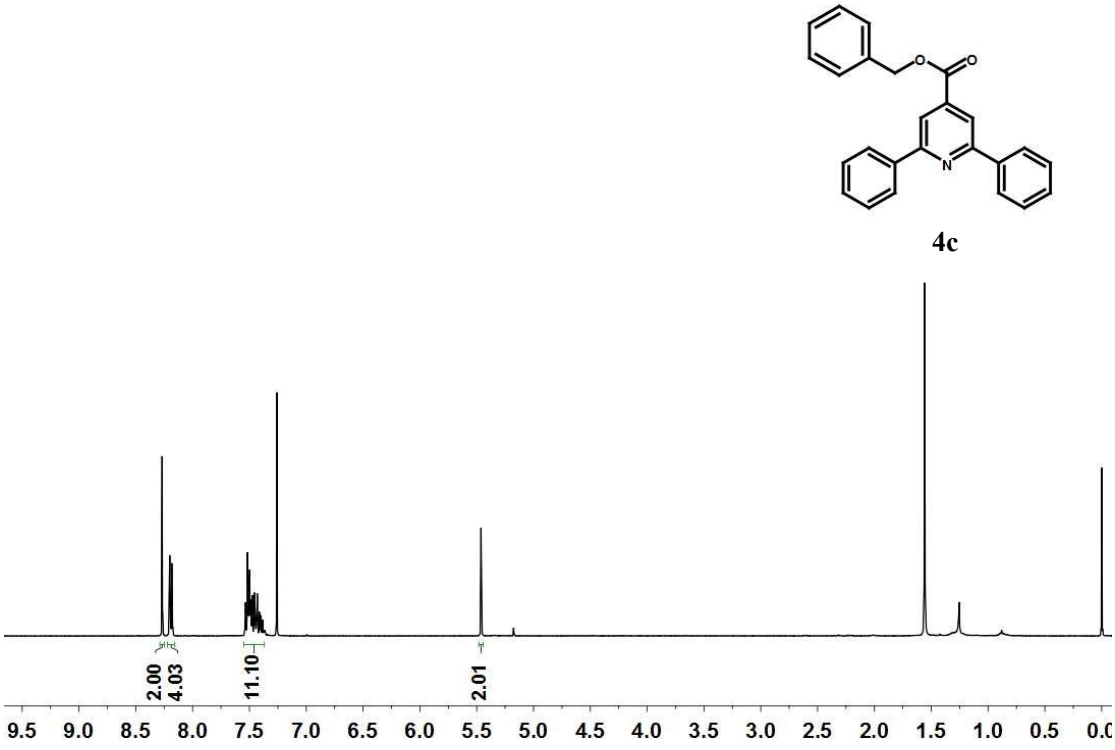


**4b**

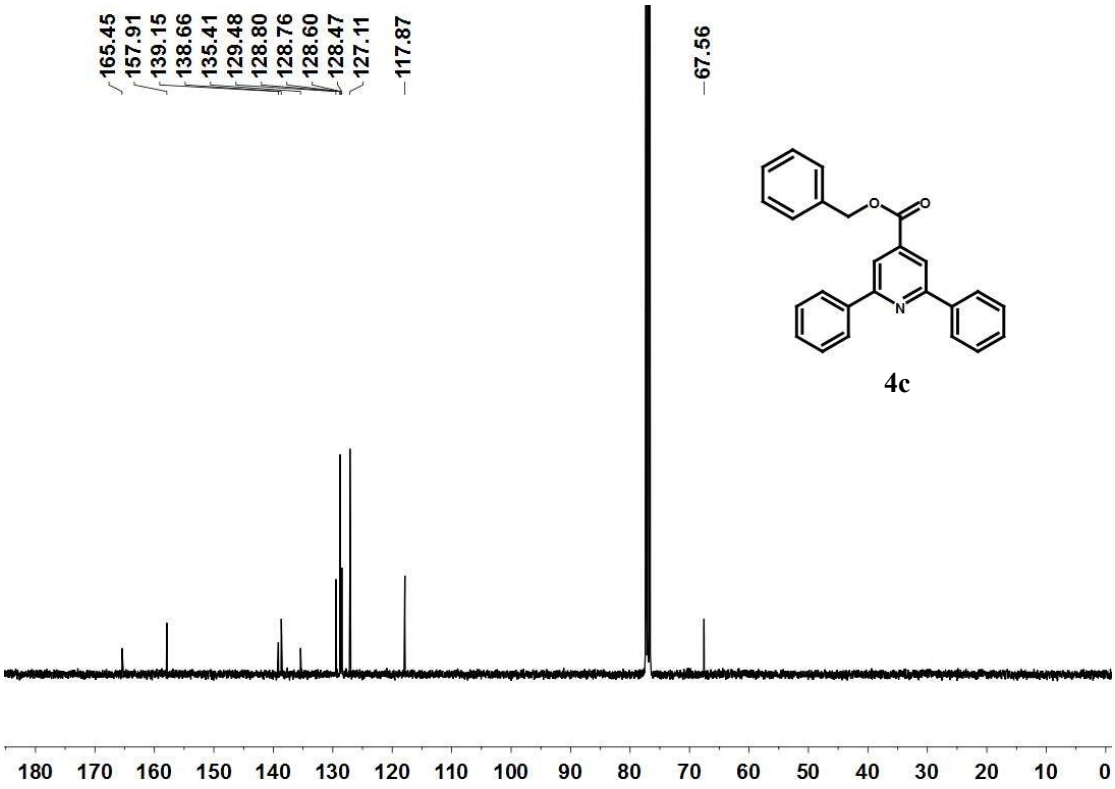

1.90
3.84
3.91
2.00
2.00
2.02
2.10
2.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


165.62
157.84
139.51
138.74
129.45
128.80
127.11
117.81
65.76
30.72
19.27
13.78
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

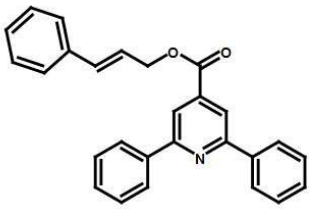
4b


O
O
N
2.00
4.03
11.10
2.01
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

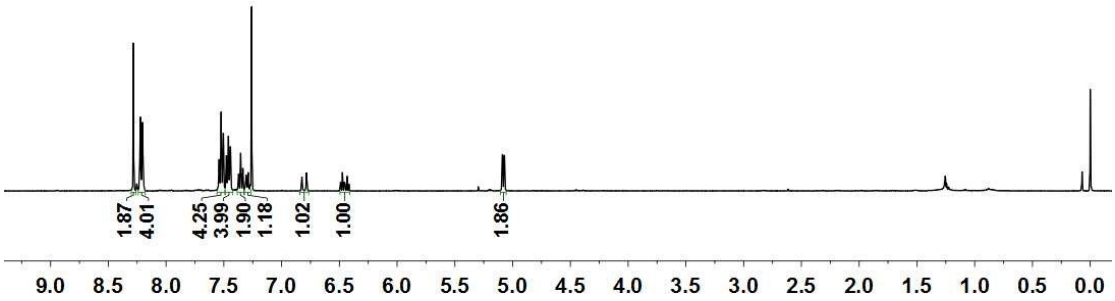
4c

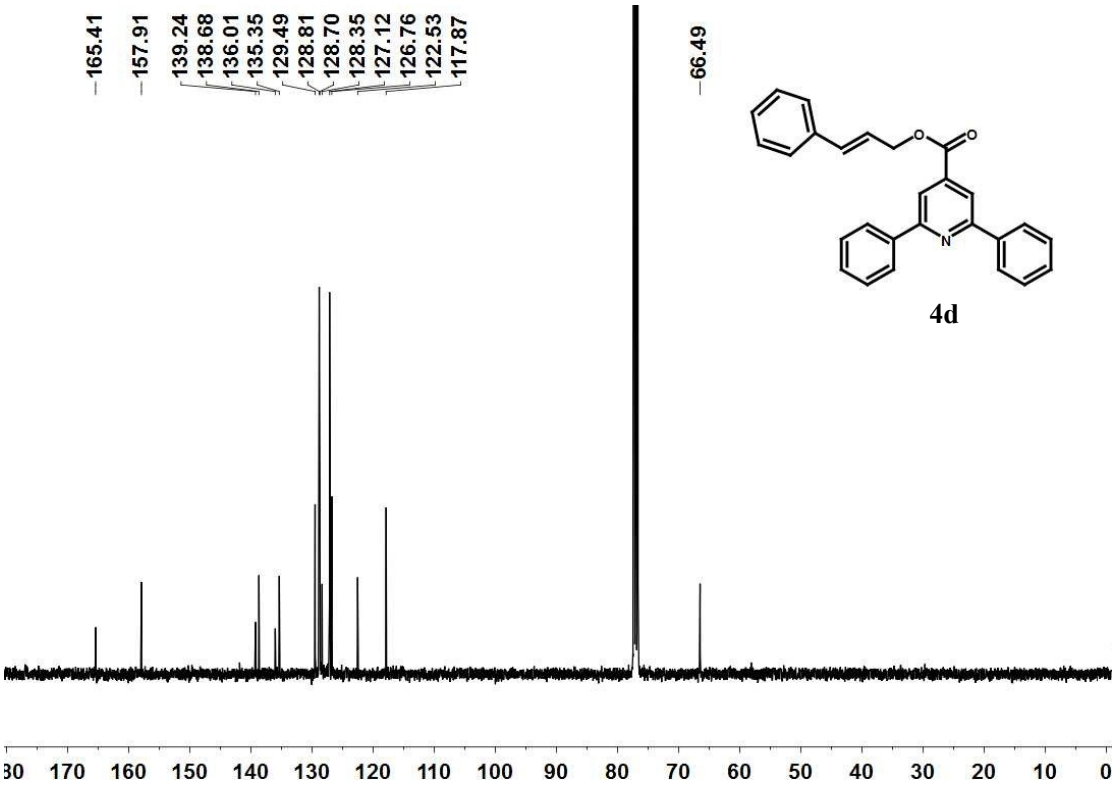

165.45
157.91
139.15
138.66
135.41
129.48
128.80
128.76
128.60
128.47
127.11
117.87
67.56
O
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**4c**

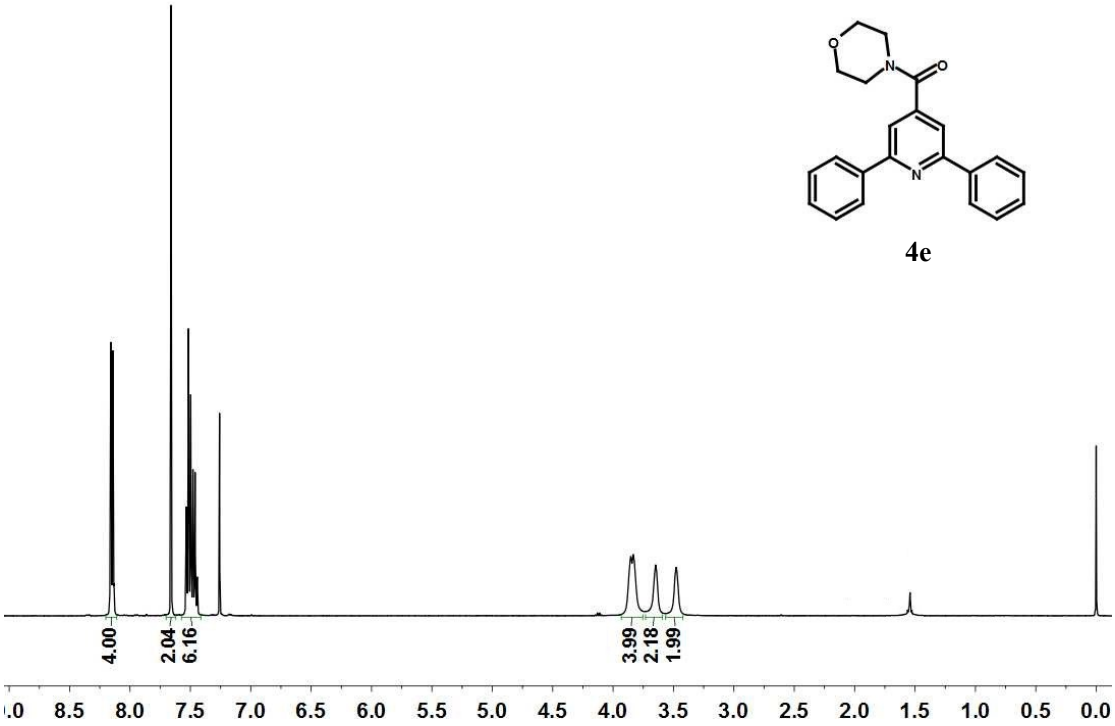

O
O
N

**4d**

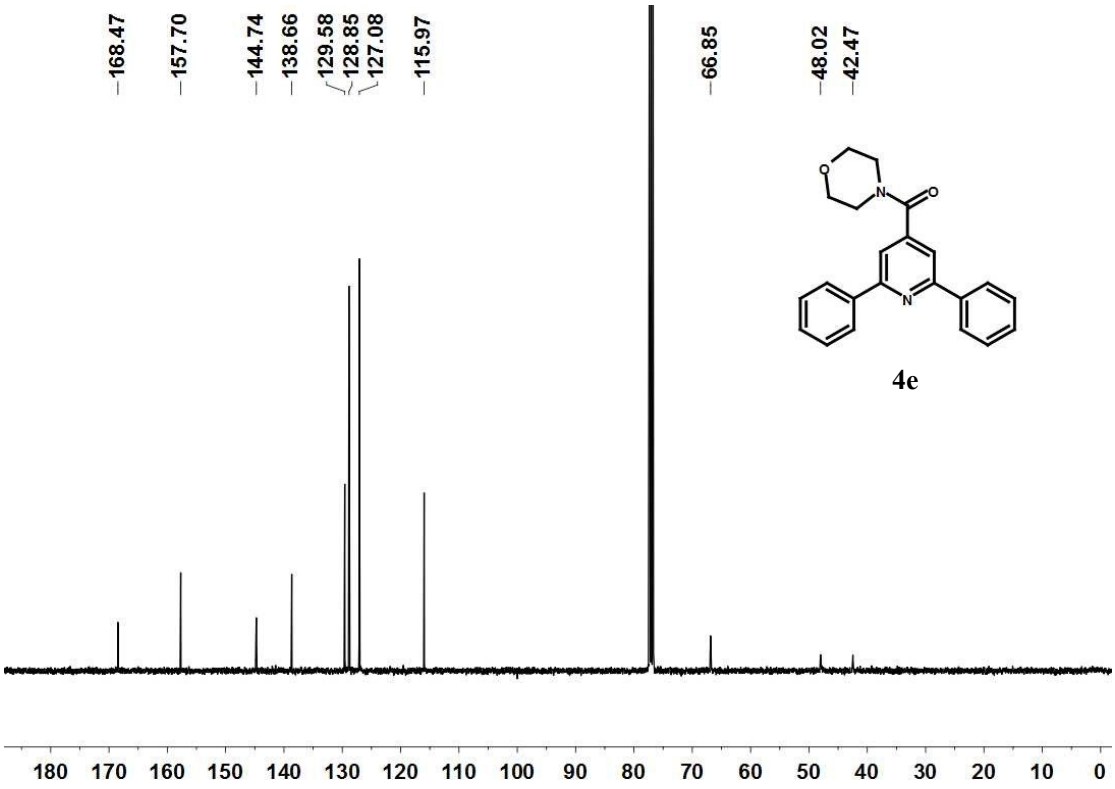

1.87
4.01
4.25
3.99
1.90
1.18
1.02
1.00
1.86
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


165.41
157.91
139.24
138.68
136.01
135.35
129.49
128.81
128.70
128.35
127.12
126.76
122.53
117.87
66.49
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

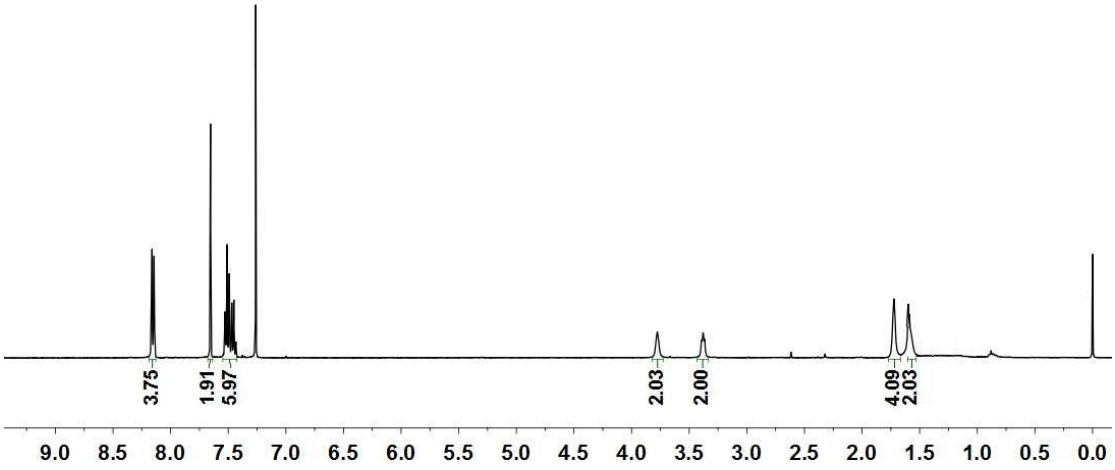
**4d**


O
N
O
N
4.00
2.04
6.16
3.99
2.18
1.99
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

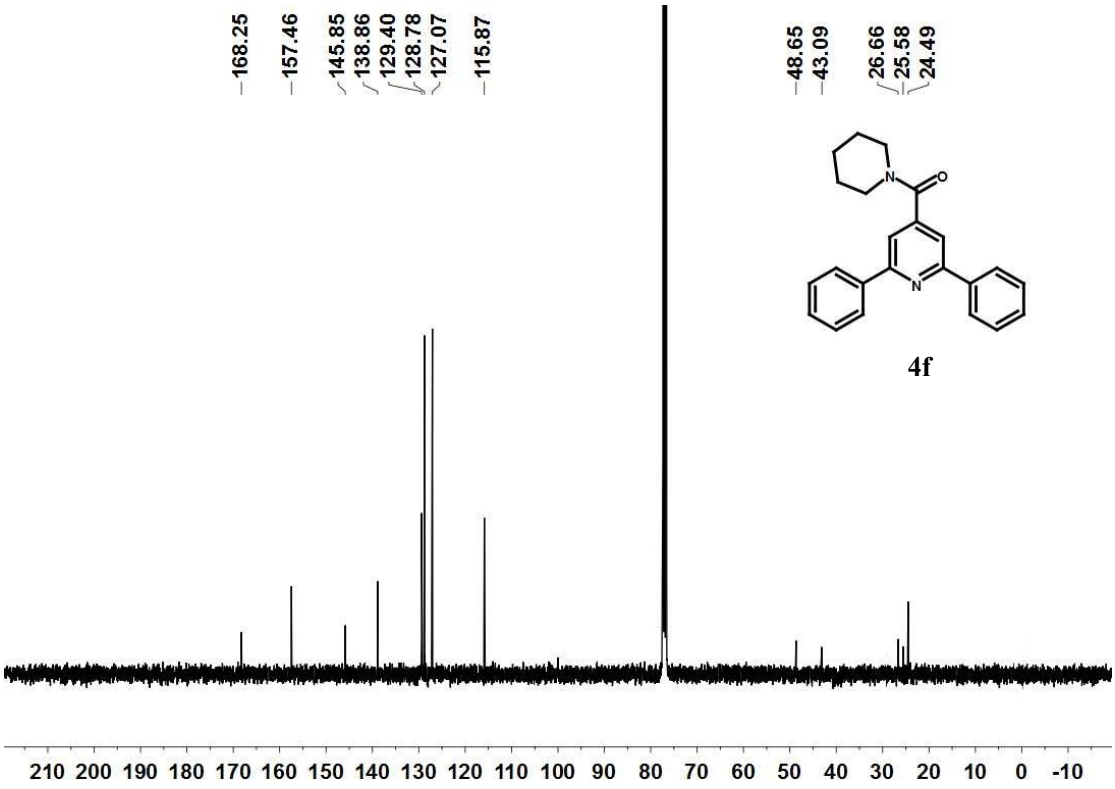
**4e**


168.47
157.70
144.74
138.66
129.58
128.85
127.08
115.97
66.85
48.02
42.47
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

4e

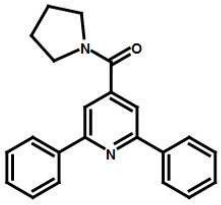

3.75
1.91
5.97
2.03
2.00
4.09
2.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

4f

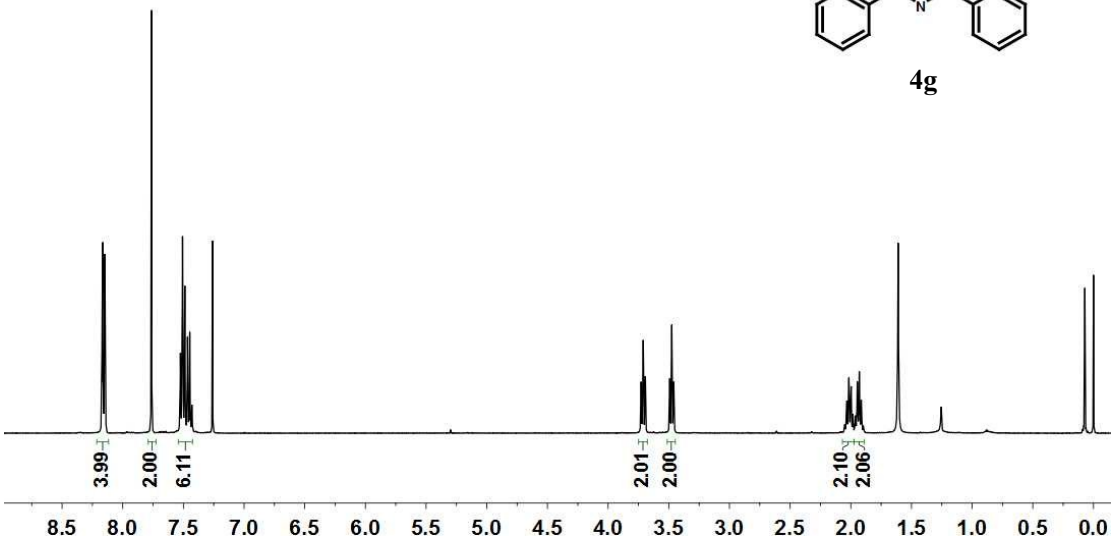

168.25
157.46
145.85
138.86
129.40
128.78
127.07
115.87
48.65
43.09
26.66
25.58
24.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

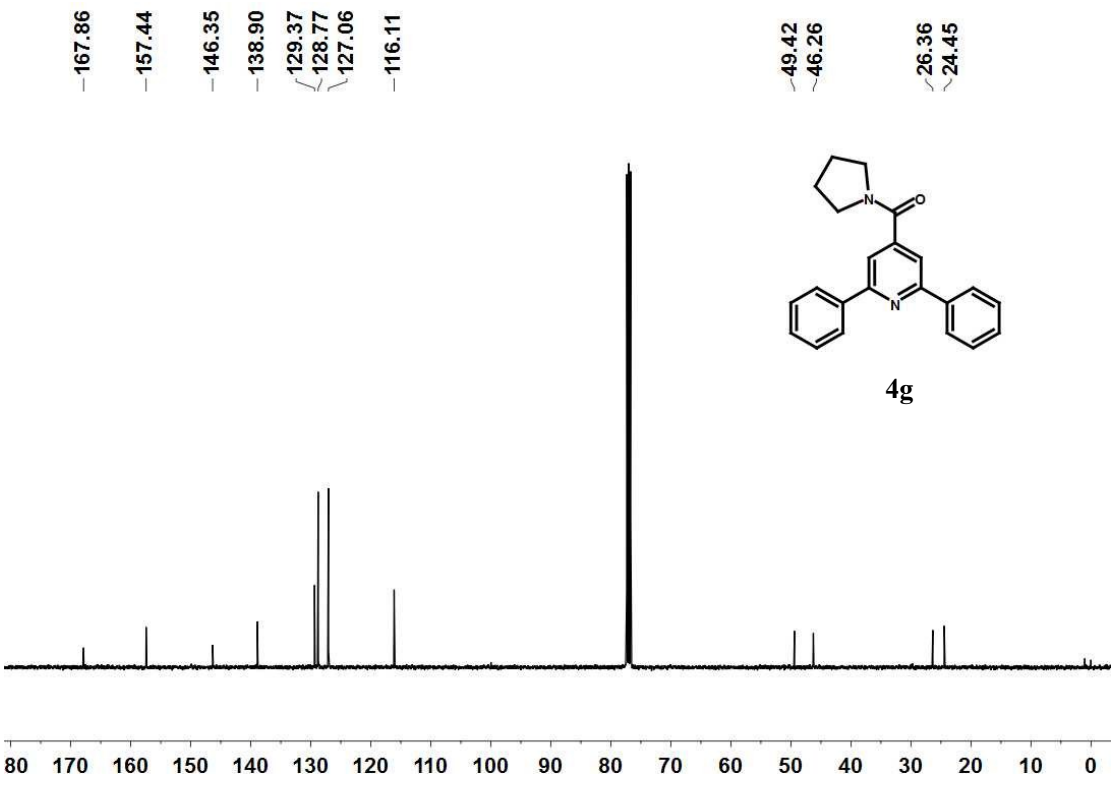


**4f**



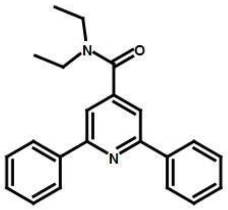
**4g**


3.99
2.00
6.11
2.01
2.00
2.10
2.06
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

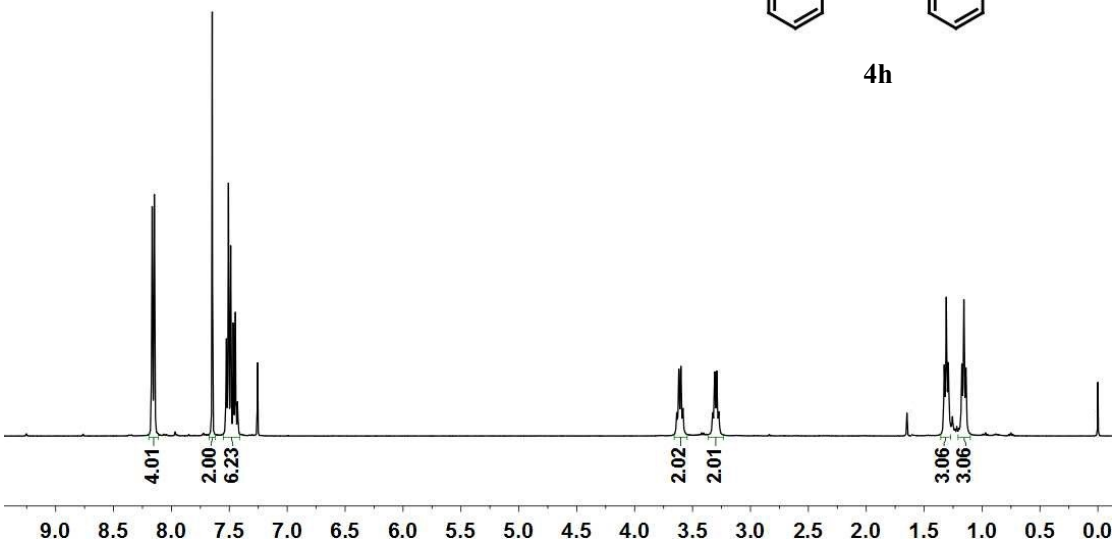

167.86
157.44
146.35
138.90
129.37
128.77
127.06
116.11
49.42
46.26
26.36
24.45
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

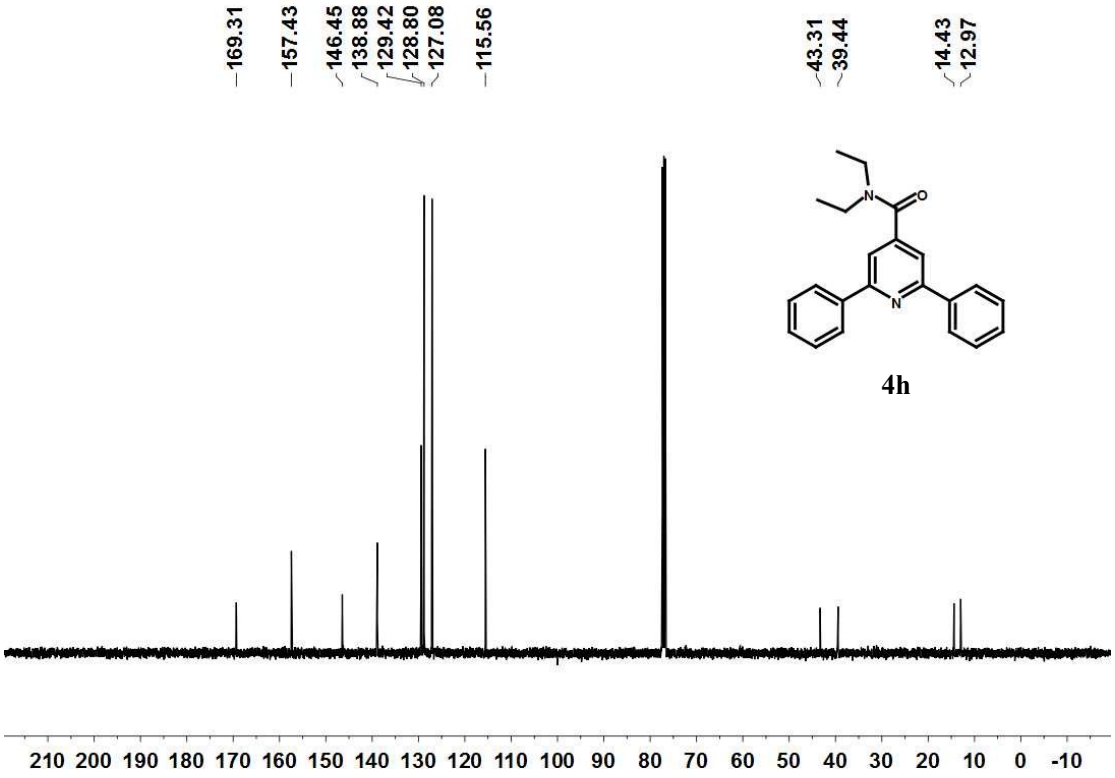


**4g**

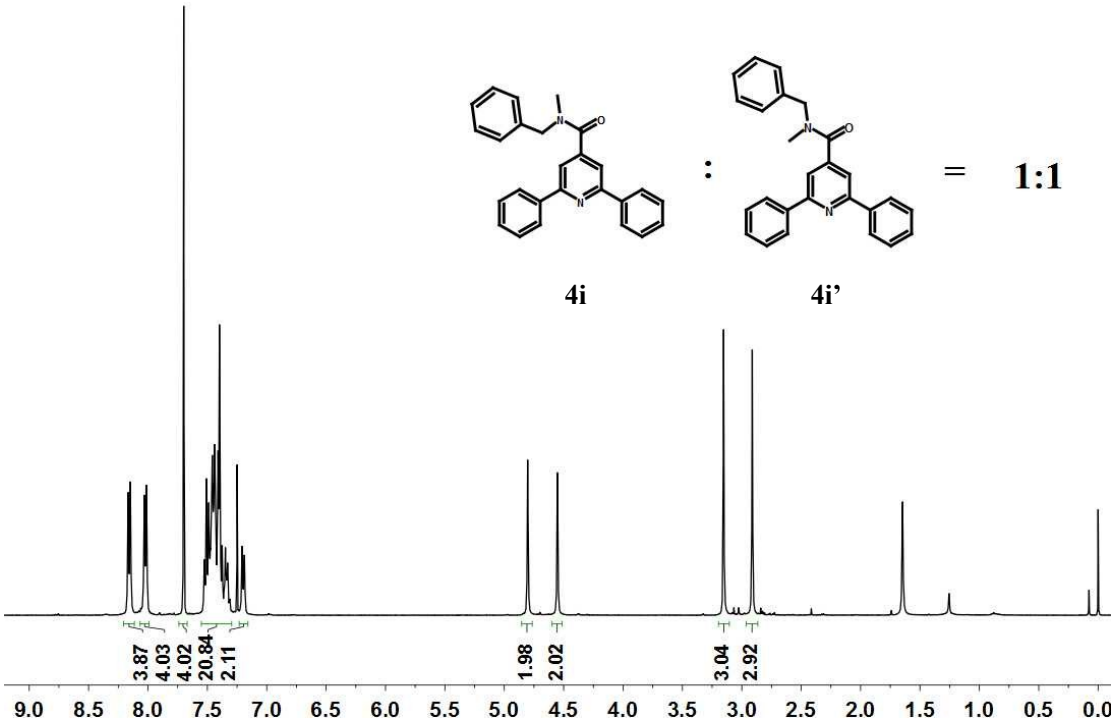


**4h**

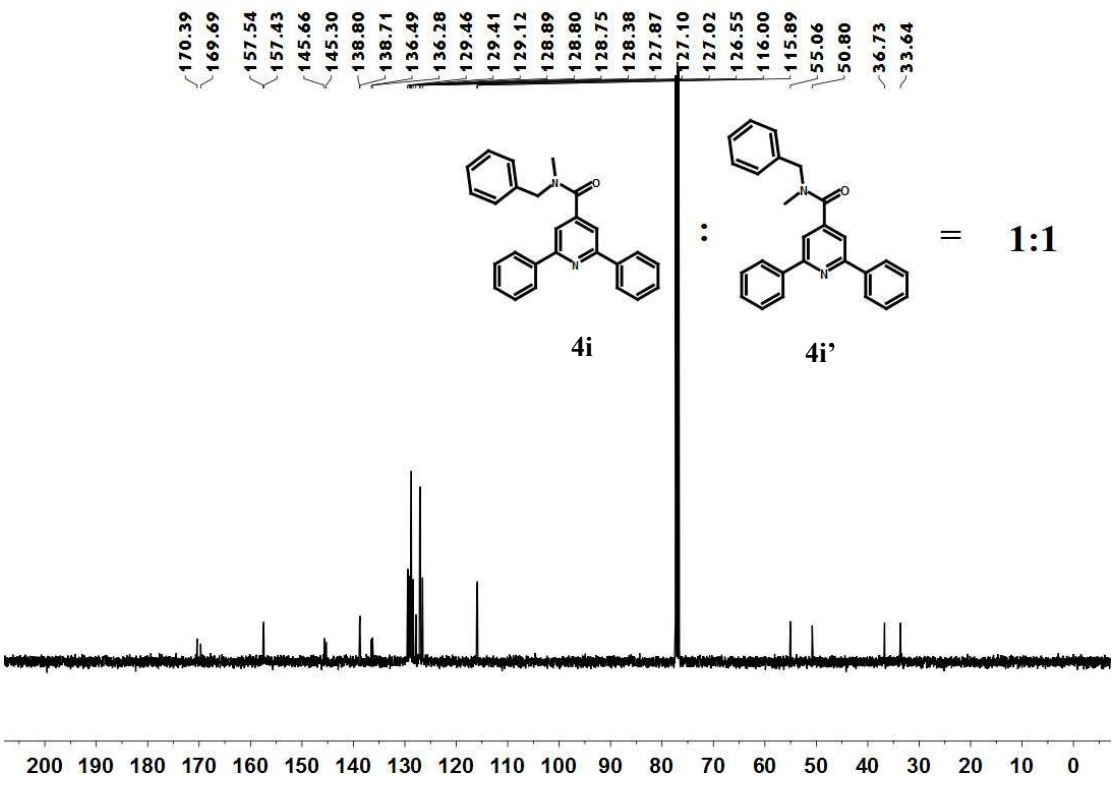

4.01
2.00
6.23
2.02
2.01
3.06
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


169.31
157.43
146.45
138.88
129.42
128.80
127.08
115.56
43.31
39.44
14.43
12.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

4h


3.87
4.03
4.02
20.84
2.11
1.98
2.02
3.04
2.92
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

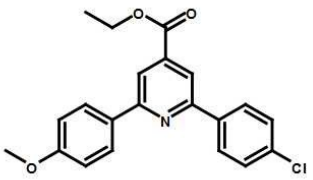
4i : 4i' = 1:1



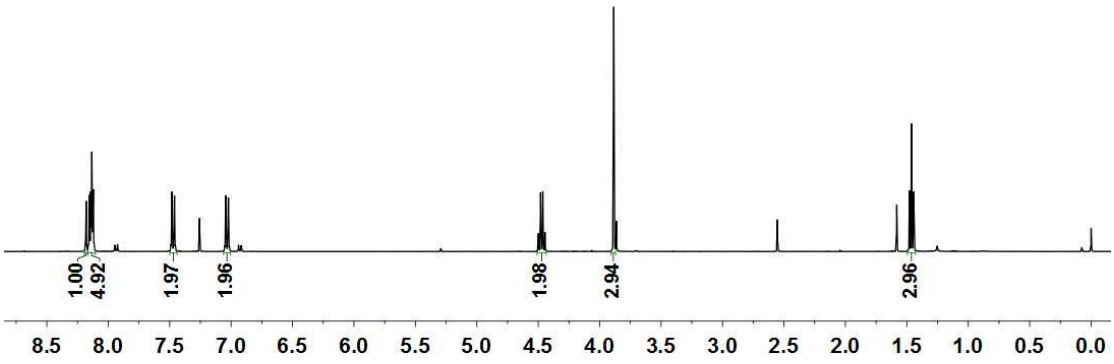

4i : 4i' = 1:1

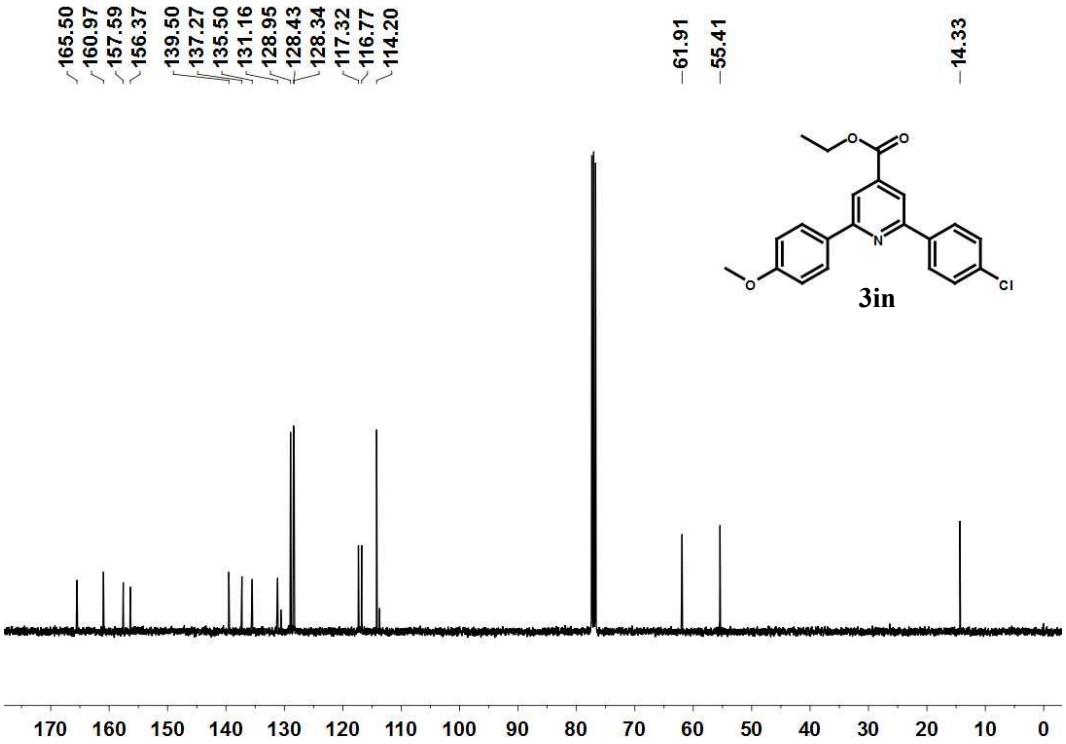
4i

4i'

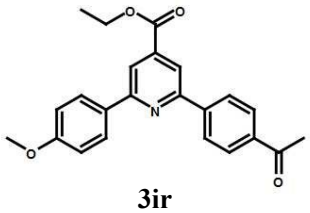


3in

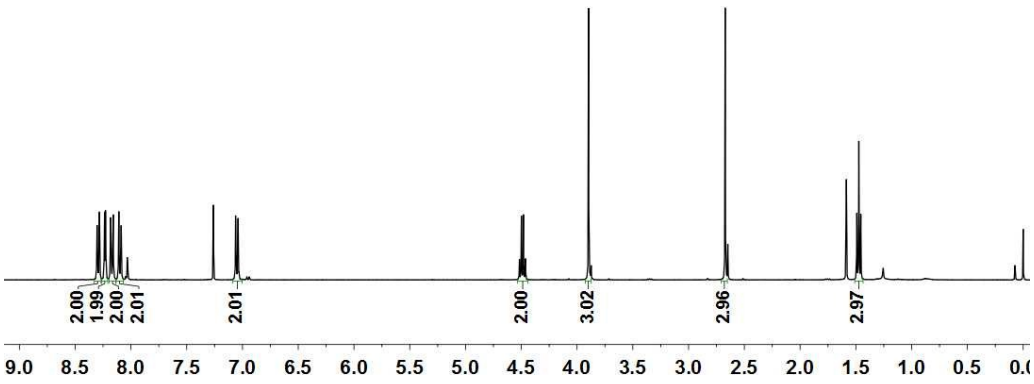


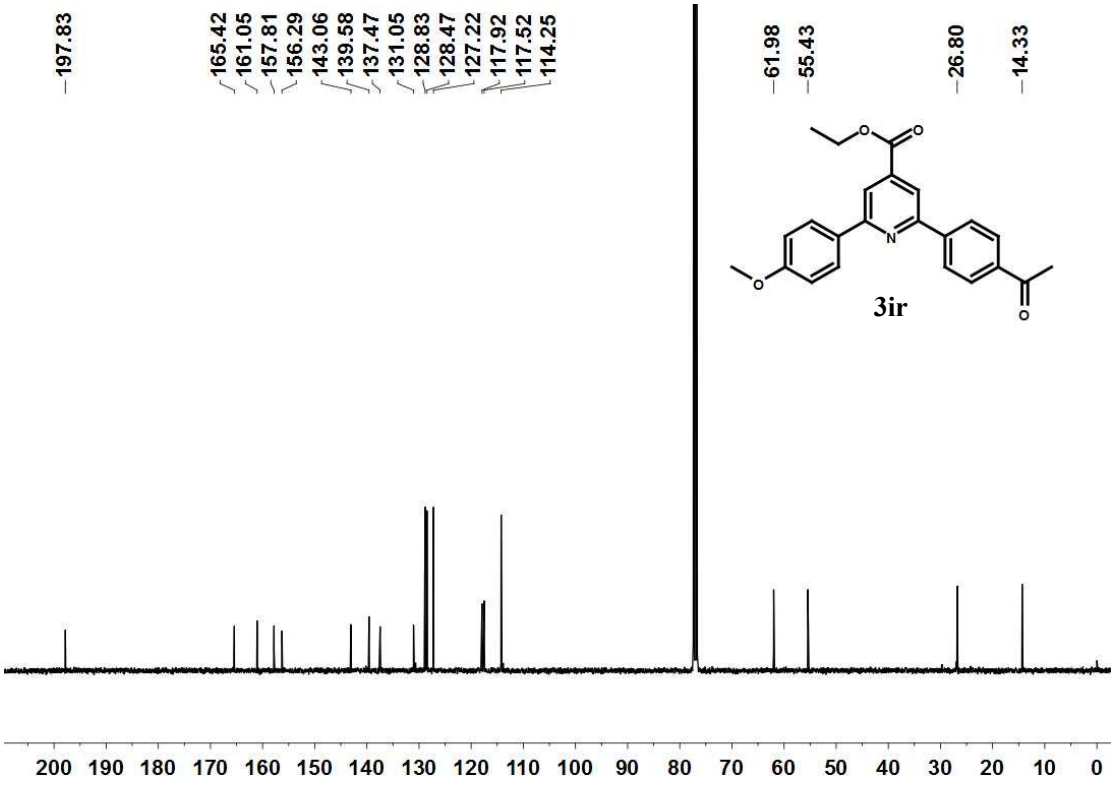

165.50
160.97
157.59
156.37
139.50
137.27
135.50
131.16
128.95
128.43
128.34
117.32
116.77
114.20
61.91
55.41
14.33
O
O
N
O
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**3in**

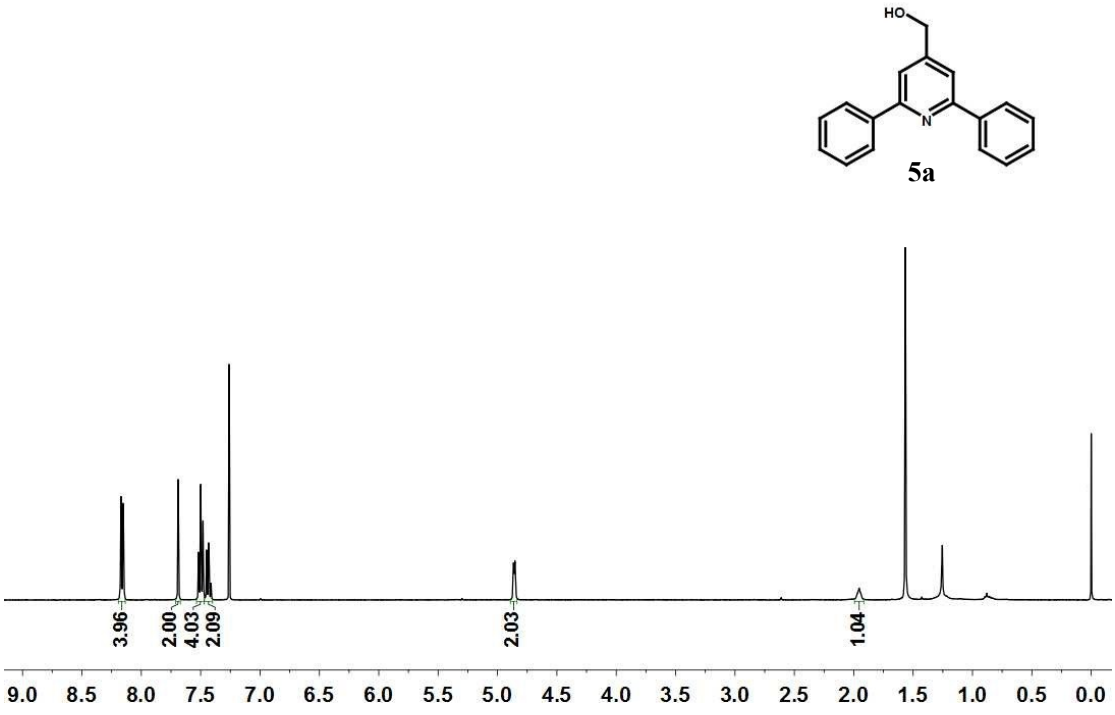

O
O
N
O
O

**3ir**

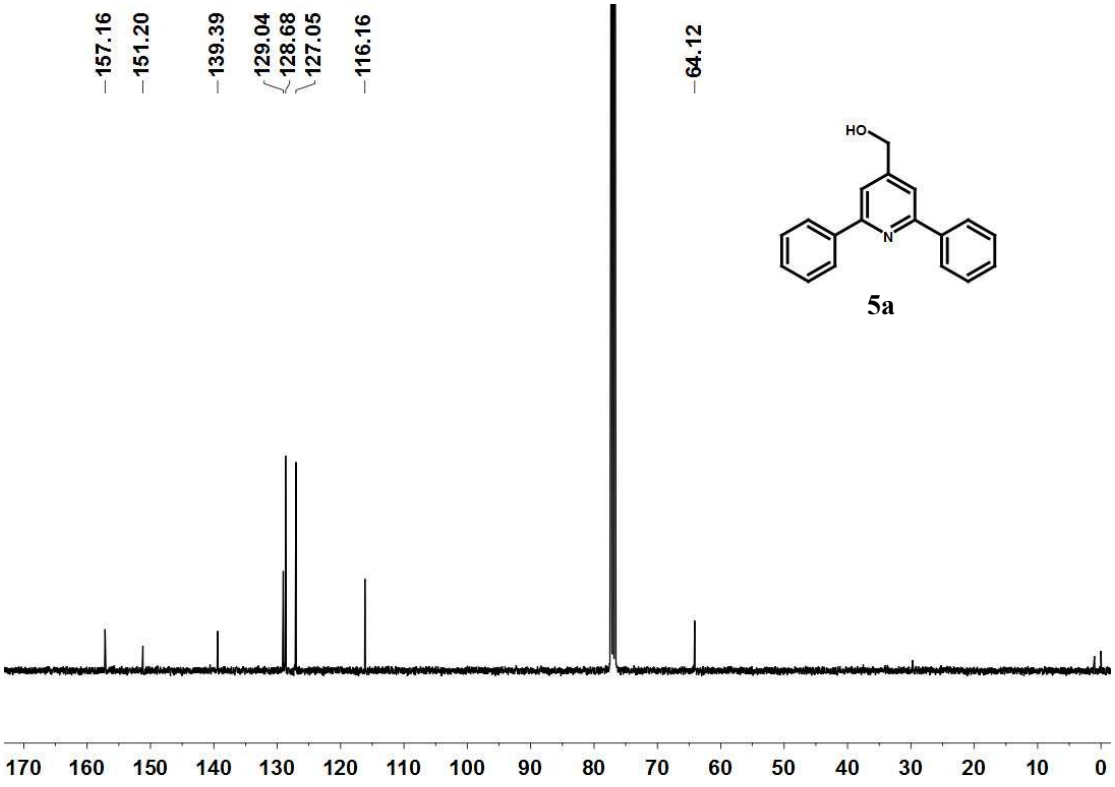

2.00
1.99
2.00
2.01
2.01
2.00
3.02
2.96
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


197.83
165.42
161.05
157.81
156.29
143.06
139.58
137.47
131.05
128.83
128.47
127.22
117.92
117.52
114.25
61.98
55.43
26.80
14.33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

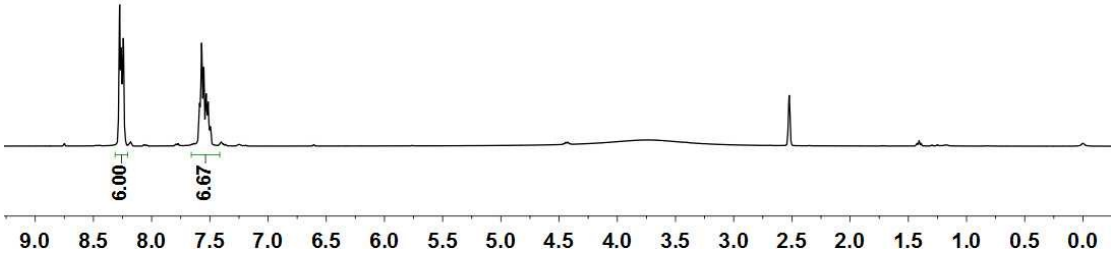
3ir

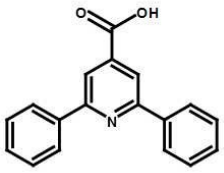

3.96
2.00
4.03
2.09
2.03
1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5a

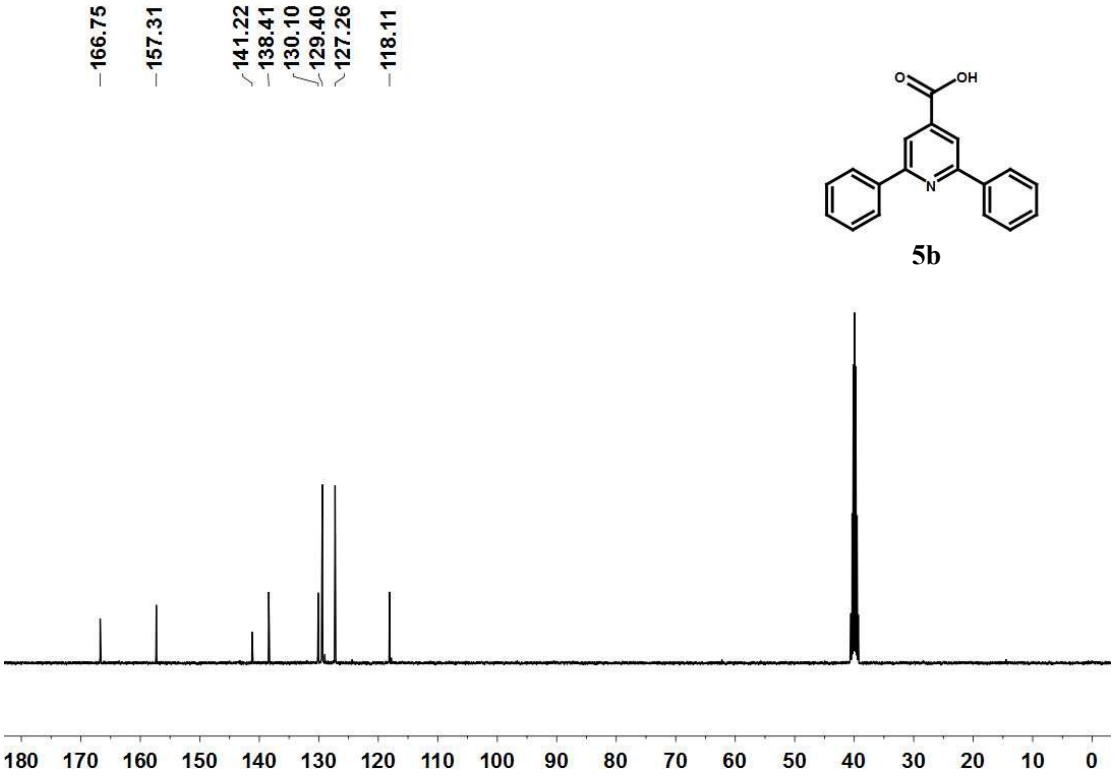

157.16
151.20
139.39
129.04
128.68
127.05
116.16
64.12
HO
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**5a**

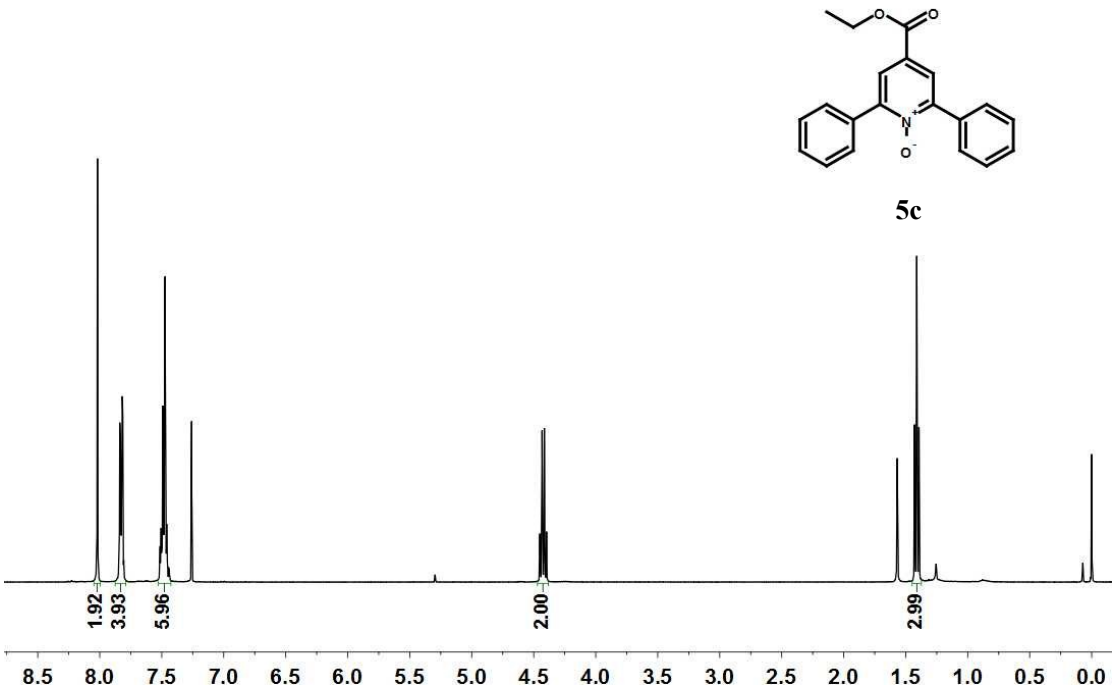

6.00
6.67
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


O
OH
N

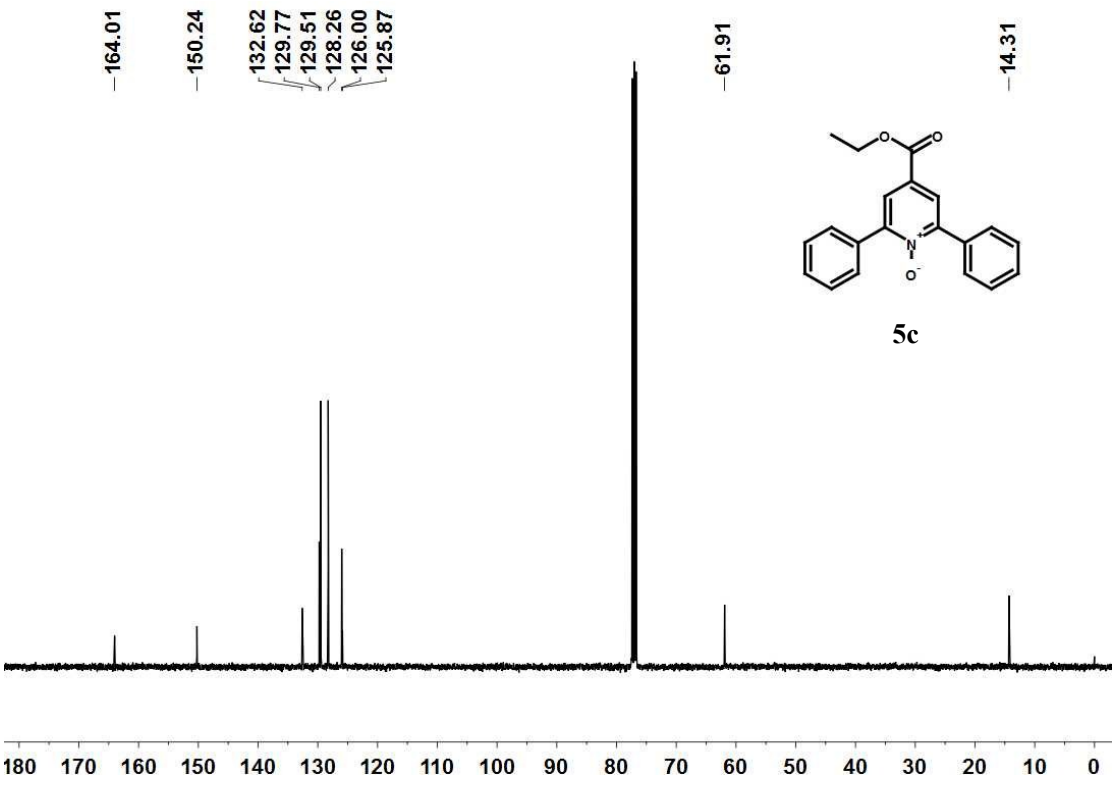
**5b**


166.75
157.31
141.22
138.41
130.10
129.40
127.26
118.11
O
OH
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

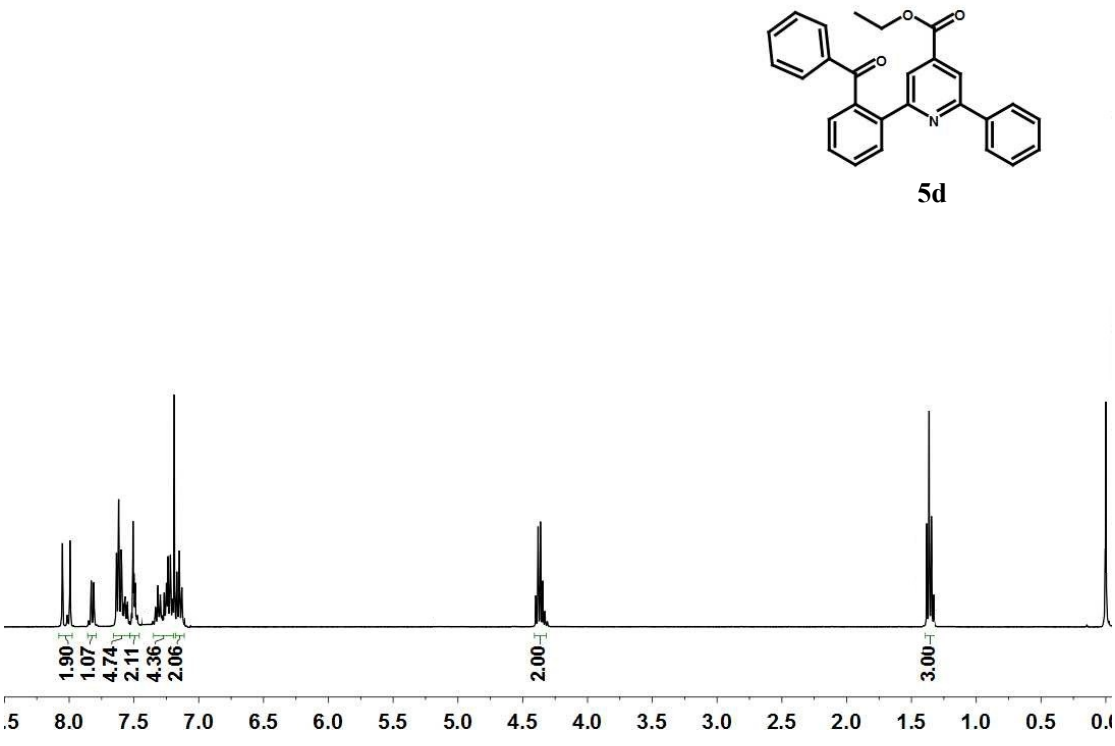
**5b**


O
O
N+
O-
1.92
3.93
5.96
2.00
2.99
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

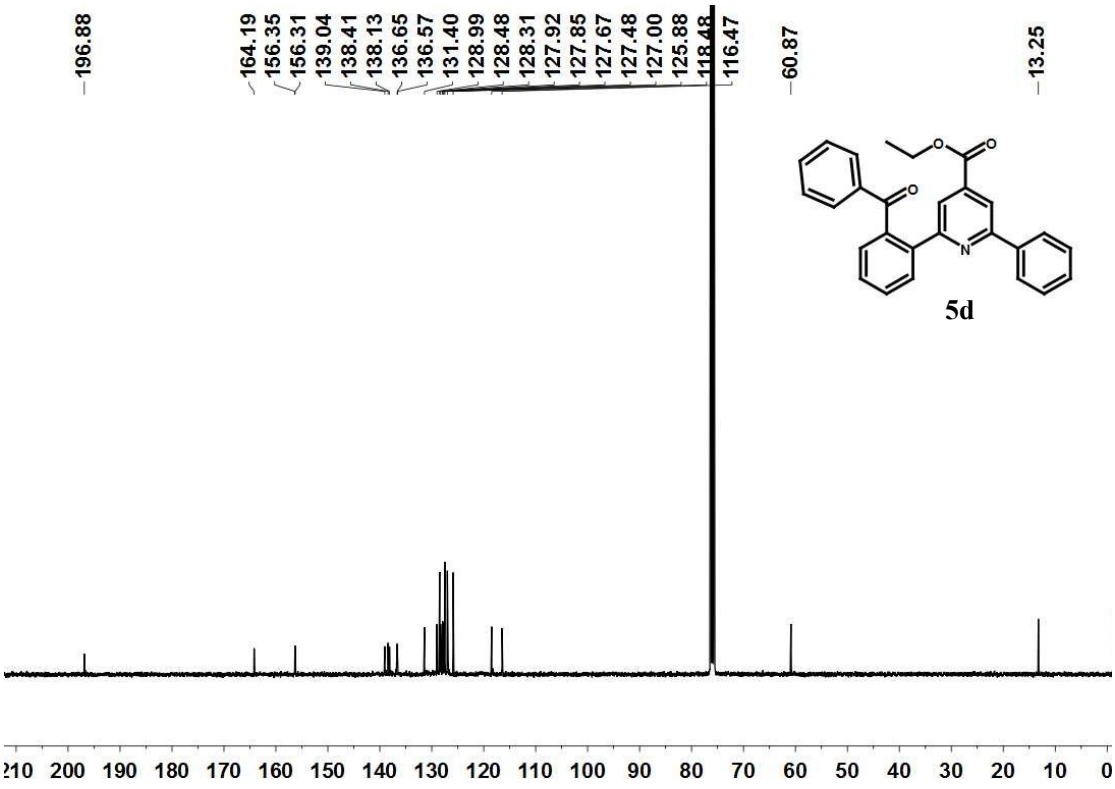
**5c**


164.01
150.24
132.62
129.77
129.51
128.26
126.00
125.87
61.91
14.31
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

5c


1.90
1.07
4.74
2.11
4.36
2.06
2.00
3.00
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

5d


196.88
164.19
156.35
156.31
139.04
138.41
138.13
136.65
136.57
131.40
128.99
128.48
128.31
127.92
127.85
127.67
127.48
127.00
125.88
118.48
116.47
60.87
13.25
O
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**5d**