

Supporting Information

Sulfonyl radical-induced regioselective cyclization of 3-Aza-1,5-enynes with sulfonyl chlorides to produce 1,2-dihydropyridines by copper catalysis

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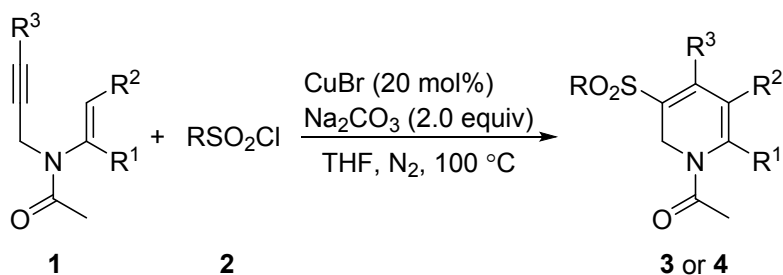
Table of Contents

| | |
|--|----|
| 1. General information | 2 |
| 2. Procedure for the synthesis of compound 3a – 3t, 4a – 4j | 3 |
| 3. Procedures for the formation of 5a - 5e | 4 |
| 4. Characterization Data of 3a – 3t, 4a – 4j, 5a - 5e | 4 |
| 5. X-ray diffraction analysis of compound 3n | 18 |
| 6. NMR spectra for the products | 19 |

1. General information

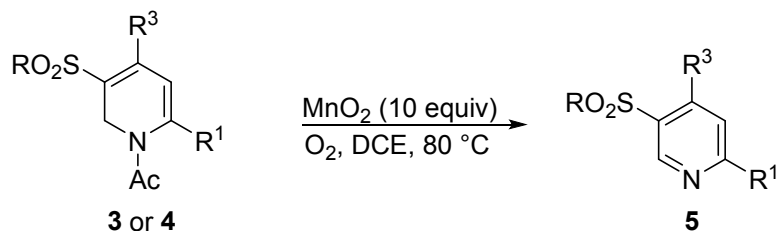
Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^1H -NMR and ^{13}C -NMR spectra were recorded at 25 °C on Bruker Advance 600M NMR spectrometers (CDCl_3 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of SiMe_4 (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and *etc.* Coupling constants are reported as a J value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on WaterXEVOG2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

2. Procedure for the synthesis of compound 3a – 3t, 4a – 4j.



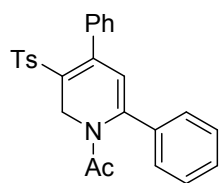
A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with *N*-propargyl enamides (0.1 mmol), Sulfonyl chlorides (0.2 mmol), CuBr (20 mol%), Na₂CO₃ (2.0 equiv), THF (1mL), Then the mixture was charged with N₂ and heated at 100 °C oil bath. After finishing, the reaction mixture was concentrated on a rotary evaporator and the residue was directly subjected to flash column chromatography on silica gel with (10-30% EtOAc/Petroleum ether) as eluate to furnish the desired product.

3. Procedures for the formation of compound 5a-5e.



(10 equiv) MnO₂ was added to the mixture of **3** or **4** (0.2 mmol) and DCE (8 mL) under O₂ atmosphere at 80 °C. After the reaction finished as indicated by TLC, the reaction mixture was diluted with water and extracted with 10 mL CH₂Cl₂ for 3 times. The combined organic layers were washed with water, saturated brine, dried over MgSO₄, concentrated in vacuo and purified by chromatography on silica gel with (30% EtOAc/Petroleum ether) as eluate to furnish the desired product.

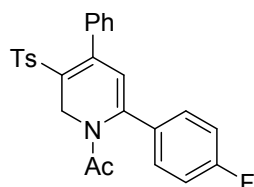
1-(4,6-diphenyl-3-tosylpyridin-1(2H)-yl)ethanone (3a)



Yellow solid; mp 63.2-64.0 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.48 – 7.29 (m, 10H), 7.16 (dd, $J = 13.3, 7.5$ Hz, 4H), 6.09 (s, 1H), 5.00 (s, 2H), 2.36 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.06, 145.12, 144.28, 143.97, 138.51, 136.08, 135.94, 129.94, 129.41, 129.13, 128.51, 128.43, 127.92, 127.57, 127.54, 127.10, 119.05, 43.83, 23.97, 21.56.

HRMS (ESI, m/z): Calcd. For $\text{C}_{26}\text{H}_{23}\text{NSO}_3\text{H}$ $[\text{M}+\text{H}]^+$ 430.1471, found: 430.1474.

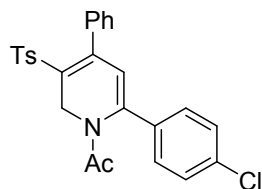
1-(6-(4-fluorophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3b)



Yellow solid; mp 80.4-81.2 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.46 – 7.37 (m, 4H), 7.34 (dt, $J = 14.7, 7.3$ Hz, 3H), 7.15 (t, $J = 7.2$ Hz, 4H), 7.07 (t, $J = 8.1$ Hz, 2H), 6.05 (s, 1H), 4.96 (s, 2H), 2.37 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.93, 163.58 ($J = 252$ Hz), 145.09, 144.02, 143.34, 138.39, 135.80, 132.21, 131.66, 129.40, 128.92, 128.57, 128.42, 127.94, 127.57, 118.90, 116.24 ($J = 21$ Hz), 44.30, 23.91, 21.55.

HRMS (ESI, m/z): Calcd. For $\text{C}_{26}\text{H}_{22}\text{FNSO}_3\text{H}$ $[\text{M}+\text{H}]^+$ 448.1377, found: 448.1379.

1-(6-(4-chlorophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3c)

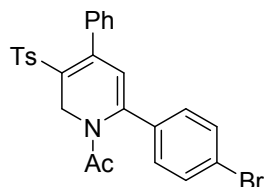


Yellow solid; mp 84.8-85.9 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 4.5$ Hz, 2H), 7.38 – 7.28 (m, 7H), 7.15 (t, $J = 6.5$ Hz, 4H), 6.08 (s, 1H), 4.95 (s, 2H), 2.36 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.86, 144.97, 144.08, 143.18,

138.31, 135.83, 135.70, 134.46, 129.42, 129.33, 128.61, 128.43, 128.21, 127.96, 127.57, 127.56, 119.35, 44.21, 23.79, 21.56.

HRMS (ESI, m/z): Calcd. For $C_{26}H_{22}NSO_3ClH$ $[M+H]^+$ 464.1082, found: 464.1085.

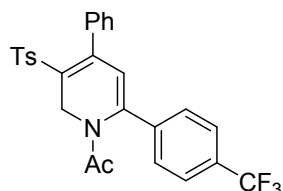
1-(6-(4-bromophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3d)



Yellow solid; mp 80.1-81.5 °C; 1H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 5.5$ Hz, 2H), 7.34 (dt, $J = 7.2$ Hz, 3H), 7.29 – 7.25 (m, 2H), 7.14 (t, $J = 6.3$ Hz, 4H), 6.09 (s, 1H), 4.95 (s, 2H), 2.36 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.86, 151.72, 144.96, 144.09, 143.24, 138.28, 135.67, 134.91, 132.29, 129.43, 128.62, 128.43, 128.43, 127.97, 127.58, 124.11, 119.38, 44.01, 23.79, 21.57.

HRMS (ESI, m/z): Calcd. For $C_{26}H_{22}NSO_3BrH$ $[M+H]^+$ 508.0577, found: 508.0579.

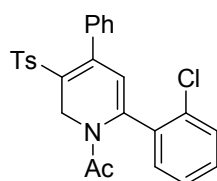
1-(4-phenyl-3-tosyl-6-(4-(trifluoromethyl)phenyl)pyridin-1(2H)-yl)ethanone (3e)



Yellow solid; mp 45-46.2 °C; 1H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, $J = 7.4$ Hz, 2H), 7.52 (d, $J = 7.9$ Hz, 2H), 7.48 – 7.29 (m, 5H), 7.15 (dd, $J = 8.9, 7.8$ Hz, 4H), 6.17 (s, 1H), 4.96 (s, 2H), 2.37 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.71, 144.74, 144.24, 142.88, 139.32, 138.09, 135.49, 131.62, 129.47, 128.72, 128.44, 128.03, 127.61, 127.17, 125.98, 123.76 ($J = 272$ Hz), 120.68, 44.40, 23.49, 21.55.

HRMS (ESI, m/z): Calcd. For $C_{27}H_{22}NSO_3F_3H$ $[M+H]^+$ 498.1345, found: 498.1349.

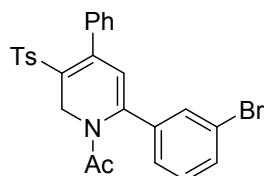
1-(6-(2-chlorophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3f)



Yellow solid; mp 106.1-107.5 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.45 (s, 2H), 7.41 – 7.27 (m, 7H), 7.17 (dd, *J* = 7.6 Hz, 4H), 5.88 (s, 1H), 4.93 (s, 2H), 2.37 (s, 3H), 1.64 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 169.47, 144.66, 144.10, 141.32, 138.26, 135.70, 135.27, 135.25, 131.82, 130.63, 130.63, 130.20, 129.49, 128.59, 128.46, 127.93, 127.60, 127.37, 121.45, 43.19, 23.14, 21.57.

HRMS (ESI, *m/z*): Calcd. For C₂₆H₂₂NSO₃ClH [M+H]⁺ 464.1082, found: 464.1085.

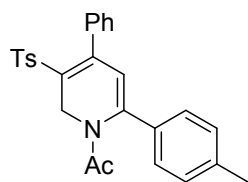
1-(6-(3-bromophenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3g)



Yellow solid; mp 71.3-72.3 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.54 (s, 1H), 7.49 (d, *J* = 6.4 Hz, 1H), 7.42 (d, *J* = 4.7 Hz, 2H), 7.35 (dd, *J* = 7.3 Hz, 4H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 6.9 Hz, 4H), 6.10 (s, 1H), 4.96 (s, 2H), 2.37 (s, 3H), 1.70 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.80, 144.83, 144.12, 142.75, 138.23, 138.02, 135.60, 132.70, 130.55, 129.70, 129.44, 128.64, 128.42, 127.99, 127.59, 127.58, 125.63, 123.19, 119.99, 44.12, 23.79, 21.57.

HRMS (ESI, *m/z*): Calcd. For C₂₆H₂₂NSO₃BrH [M+H]⁺ 508.0577, found: 508.0579.

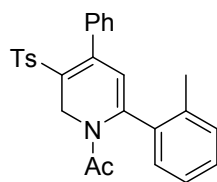
1-(4-phenyl-6-p-tolyl-3-tosylpyridin-1(2H)-yl)ethanone (3h)



Yellow solid; mp 59-60.8 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.27 (m, 5H), 7.20 – 7.10 (m, 6H), 6.05 (s, 1H), 4.98 (s, 2H), 2.36 (s, 3H), 2.36 (s, 3H), 1.69 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.16, 145.32, 144.39, 143.88, 140.33, 138.62, 136.07, 133.28, 129.84, 129.38, 128.45, 128.44, 128.44, 127.89, 127.55, 127.06, 118.25, 43.78, 24.06, 21.56, 21.32.

HRMS (ESI, *m/z*): Calcd. For C₂₇H₂₅NSO₃H [M+H]⁺ 444.1628, found: 444.1632.

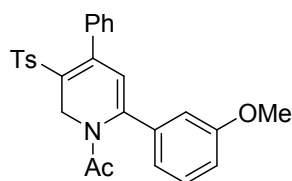
1-(4-phenyl-6-o-tolyl-3-tosylpyridin-1(2H)-yl)ethanone (3i)



Yellow solid; mp 54-55.8 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.34 (dt, *J* = 7.3 Hz, 3H), 7.27 (dd, *J* = 13.5, 6.1 Hz, 2H), 7.19 (dd, *J* = 16.0, 8.0 Hz, 6H), 5.80 (s, 1H), 5.59 – 4.39 (m, 2H), 2.37 (s, 3H), 2.29 (s, 3H), 1.62 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.22, 144.87, 143.96, 143.86, 138.50, 136.23, 136.00, 135.45, 131.04, 129.69, 129.47, 129.47, 129.44, 128.48, 128.37, 127.91, 127.60, 126.58, 120.30, 42.98, 23.85, 21.58, 20.16.

HRMS (ESI, m/z): Calcd. For C₂₇H₂₅NSO₃H [M+H]⁺ 444.1628, found: 444.1632.

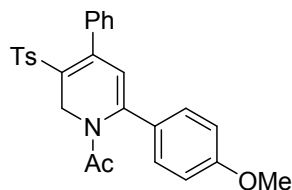
1-(6-(3-methoxyphenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3j)



Yellow solid; mp 63.5-65.0 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.26 (m, 4H), 7.16 (t, *J* = 8.5 Hz, 4H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 6.6 Hz, 2H), 6.08 (s, 1H), 4.99 (s, 2H), 3.78 (d, *J* = 1.9 Hz, 3H), 2.37 (s, 3H), 1.72 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.12, 160.18, 144.99, 144.16, 143.97, 138.49, 137.51, 135.93, 130.21, 129.41, 128.50, 128.42, 127.92, 127.57, 119.64, 119.10, 115.44, 112.60, 112.57, 55.44, 43.80, 23.88, 21.56.

HRMS (ESI, m/z): Calcd. For C₂₇H₂₅NSO₄H [M+H]⁺ 460.1577, found: 460.1579.

1-(6-(4-methoxyphenyl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3k)

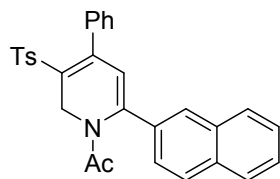


Yellow solid; mp 69.1-70.5 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.15 (dd, *J* = 11.5, 8.1 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 2H),

6.01 (s, 1H), 4.97 (s, 2H), 3.82 (s, 3H), 2.36 (s, 3H), 1.71 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.26, 161.13, 145.54, 144.20, 143.83, 138.72, 136.16, 129.36, 128.62, 128.44, 128.44, 128.44, 127.87, 127.52, 127.49, 117.38, 114.59, 55.43, 43.85, 24.07, 21.55.

HRMS (ESI, m/z): Calcd. For C₂₇H₂₅NSO₄H [M+H]⁺ 460.1577, found: 460.1579.

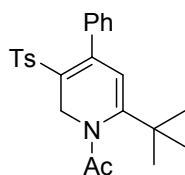
1-(6-(naphthalen-2-yl)-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3l)



Yellow solid; mp 82.6-83.6 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 9.1 Hz, 1H), 7.87 (dd, *J* = 8.6, 3.6 Hz, 2H), 7.55 – 7.49 (m, 5H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.26 – 7.22 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.03 (s, 1H), 5.17 (s, 2H), 2.38 (s, 3H), 1.50 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.36, 144.98, 144.01, 142.73, 138.50, 135.99, 134.19, 133.73, 130.43, 130.32, 129.50, 129.31, 128.95, 128.51, 128.39, 127.96, 127.84, 127.64, 127.59, 126.51, 125.34, 123.87, 121.15, 43.42, 23.82, 21.58.

HRMS (ESI, m/z): Calcd. For C₂₇H₂₅NSO₄H [M+H]⁺ 480.1628, found: 480.1630.

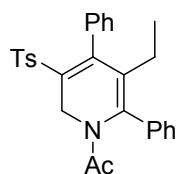
1-(6-tert-butyl-4-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3m)



Amorphous solid; ¹H NMR (600 MHz, CDCl₃) δ 7.31 (d, *J* = 8.0 Hz, 3H), 7.27 – 7.23 (m, 2H), 7.08 (t, *J* = 6.7 Hz, 4H), 5.98 (s, 1H), 4.48 (s, 2H), 2.34 (s, 3H), 2.24 (s, 3H), 1.24 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 172.65, 160.30, 145.91, 143.93, 138.21, 135.95, 129.35, 128.54, 128.41, 127.78, 127.44, 127.41, 120.11, 46.98, 37.59, 31.02, 22.39, 21.50.

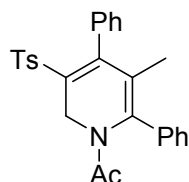
HRMS (ESI, m/z): Calcd. For C₂₄H₂₇NSO₃H [M+H]⁺ 410.1784, found: 410.1789.

1-(5-ethyl-4,6-diphenyl-3-tosylpyridin-1(2H)-yl)ethanone (3n)



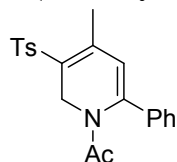
Yellow solid; mp 48.6-50.2 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (dd, $J = 7.4$ Hz, 6H), 7.32 – 7.21 (m, 4H), 7.15 – 6.99 (m, 4H), 4.98 (s, 2H), 2.34 (s, 3H), 2.06 (q, $J = 7.3$ Hz, 2H), 1.53 (s, 3H), 0.58 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.87, 147.58, 143.71, 139.81, 138.91, 138.54, 135.97, 134.26, 131.07, 130.08, 129.64, 129.23, 128.98, 128.61, 128.27, 127.54, 127.43, 43.63, 23.68, 21.53, 14.60. HRMS (ESI, m/z): Calcd. For $\text{C}_{28}\text{H}_{27}\text{NSO}_3\text{H}$ $[\text{M}+\text{H}]^+$ 450.1784, found: 450.1786.

1-(5-methyl-4,6-diphenyl-3-tosylpyridin-1(2H)-yl)ethan-1-one (3o)



Yellow solid; mp 167.5-169.5 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.42 – 7.28 (m, 10H), 7.11 (d, $J = 7.8$ Hz, 2H), 7.04 (d, $J = 7.3$ Hz, 2H), 5.00 (s, 2H), 2.36 (s, 3H), 1.56 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.04, 147.63, 143.85, 138.74, 136.14, 134.58, 129.95, 129.31, 129.21, 128.98, 128.98, 128.61, 128.22, 127.76, 127.50, 123.68, 42.63, 23.91, 21.60, 16.45. HRMS (ESI, m/z): Calcd. For $\text{C}_{27}\text{H}_{25}\text{NSO}_3\text{H}$ $[\text{M}+\text{H}]^+$ 444.1628, found: 444.1632.

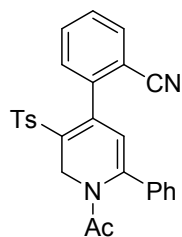
1-(4-methyl-6-phenyl-3-tosylpyridin-1(2H)-yl)ethanone (3p)



Yellow solid; mp 173.4-174.1 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 7.3$ Hz, 2H), 7.39 (s, 5H), 7.33 (d, $J = 7.5$ Hz, 2H), 6.00 (s, 1H), 4.79 (s, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.97, 144.41, 144.23, 142.21, 139.00, 136.16, 129.88, 129.37, 129.14, 127.16, 127.13, 127.03, 119.66, 43.44, 23.96, 21.61, 17.59.

HRMS (ESI, m/z): Calcd. For C₂₁H₂₁NSO₃H [M+H]⁺ 368.1315, found: 368.1316.

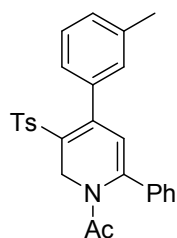
2-(1-acetyl-6-phenyl-3-tosyl-1,2-dihydropyridin-4-yl)benzonitrile (3q)



Yellow solid; mp 44-45.2 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.70 – 7.64 (m, 1H), 7.61 (dt, *J* = 20.5, 10.3 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.45 (dd, *J* = 14.0, 8.0 Hz, 2H), 7.39 (dd, *J* = 10.9, 4.1 Hz, 3H), 7.23 (dd, *J* = 8.0, 2.7 Hz, 2H), 6.05 (s, 1H), 5.39 (s, 1H), 4.58 (d, *J* = 15.7 Hz, 1H), 2.39 (d, *J* = 3.7 Hz, 3H), 1.64 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.60, 145.50, 144.64, 141.13, 139.88, 137.40, 135.86, 132.31, 132.24, 130.87, 130.83, 130.37, 129.71, 129.23, 128.89, 127.63, 127.52, 116.95, 116.73, 111.42, 43.25, 24.07, 21.63.

HRMS (ESI, m/z): Calcd. For C₂₇H₂₂N₂SO₃H [M+H]⁺ 455.1424, found: 455.1426.

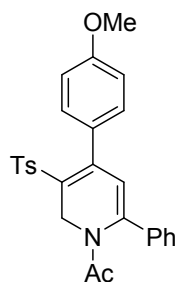
1-(6-phenyl-4-m-tolyl-3-tosylpyridin-1(2H)-yl)ethanone (3r)



Yellow solid; mp 54.6-55.2 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.47 – 7.33 (m, 7H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 6.5 Hz, 3H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 6.09 (s, 1H), 5.01 (s, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.78 (d, *J* = 117.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.09, 145.28, 144.22, 143.86, 143.85, 138.66, 137.55, 136.13, 135.84, 129.88, 129.31, 129.19, 129.11, 128.78, 127.89, 127.61, 127.08, 125.55, 119.11, 43.85, 23.96, 21.54, 21.32.

HRMS (ESI, m/z): Calcd. For C₂₇H₂₅NSO₃H [M+H]⁺ 444.1628, found: 444.1630.

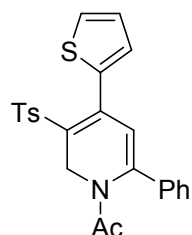
1-(4-(4-methoxyphenyl)-6-phenyl-3-tosylpyridin-1(2H)-yl)ethanone(3s)



Yellow solid; mp 42-43.2 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 5.7 Hz, 2H), 7.39 (d, *J* = 15.6 Hz, 5H), 7.14 (t, *J* = 8.4 Hz, 4H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.08 (s, 1H), 4.97 (s, 2H), 3.84 (dd, *J* = 4.8, 2.5 Hz, 3H), 2.36 (d, *J* = 2.3 Hz, 3H), 1.67 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.03, 160.03, 144.99, 144.28, 143.87, 138.65, 136.11, 130.72, 130.05, 129.88, 129.34, 129.10, 127.97, 127.50, 127.07, 119.30, 113.37, 55.34, 43.93, 23.94, 21.56.

HRMS (ESI, *m/z*): Calcd. For C₂₇H₂₅NSO₄H [M+H]⁺ 460.1577, found: 460.1579.

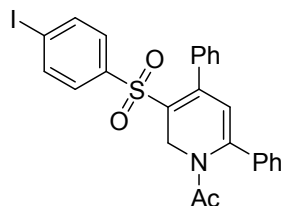
1-(6-phenyl-4-(thiophen-2-yl)-3-tosylpyridin-1(2H)-yl)ethanone (3t)



Yellow solid; mp 114.3-115.7 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.47 (d, *J* = 6.5 Hz, 2H), 7.44 – 7.36 (m, 7H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.05 (s, 1H), 6.15 (s, 1H), 5.04 (s, 2H), 2.36 (s, 3H), 1.67 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.09, 144.71, 144.01, 138.15, 137.94, 135.81, 135.42, 131.45, 130.11, 129.34, 129.16, 127.90, 127.42, 127.21, 127.15, 127.15, 118.82, 44.05, 24.14, 21.61.

HRMS (ESI, *m/z*): Calcd. For C₂₄H₂₁NS₂O₃H [M+H]⁺ 436.1036, found: 436.1039.

1-(3-(4-iodophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4a)

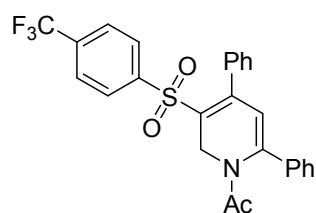


Yellow solid; mp 170.2-171.3 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.08 (s, 1H), 5.04 (s, 2H), 1.72 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.13, 146.03, 144.88, 141.20, 137.94, 135.96, 135.63, 131.96, 130.15, 129.20, 128.81, 128.75, 128.44, 128.05, 127.20, 118.83, 100.78, 43.49, 24.12.

HRMS (ESI, *m/z*): Calcd. For C₂₅H₂₀NISO₃H [M+H]⁺ 542.0281, found: 542.0281.

1-(4,6-diphenyl-3-(4-(trifluoromethyl)phenylsulfonyl)pyridin-1(2H)-yl)ethanone

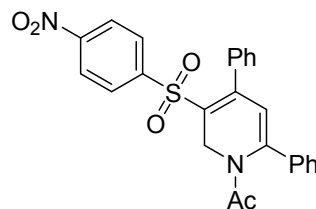
(4b)



Yellow solid; mp 138.9-139.8 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.59 (dd, *J* = 25.4, 7.8 Hz, 4H), 7.46 – 7.35 (m, 6H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.09 (s, 1H), 5.09 (s, 2H), 1.72 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.15, 146.73, 145.31, 145.02, 135.89, 135.46, 134.45 (*J* = 6 Hz), 130.28, 129.24, 128.87, 128.50, 128.10, 127.99, 127.27, 125.72 (*J* = 4.5 Hz), 123.21 (*J* = 272 Hz), 118.64, 43.51, 24.08. ¹⁹F NMR (565 MHz, CDCl₃) δ -63.20.

HRMS (ESI, *m/z*): Calcd. For C₂₆H₂₀F₃NSO₃H [M+H]⁺ 484.1189, found: 484.1190.

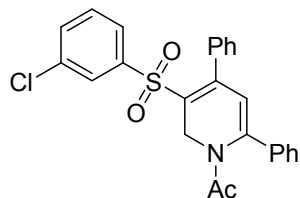
1-(3-(4-nitrophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4c)



Yellow solid; mp 166.2-167.3 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.36 (m, 6H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.11 (s, 1H), 5.10 (s, 2H), 1.71 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.19, 150.16, 147.42, 147.14, 145.67, 135.77, 135.28, 130.45, 129.30, 129.10, 128.73, 128.54, 128.17, 127.33, 126.78, 123.77, 118.58, 43.39, 24.11.

HRMS (ESI, m/z): Calcd. For $C_{25}H_{20}N_2SO_5H$ $[M+H]^+$ 461.1166, found:466.1166.

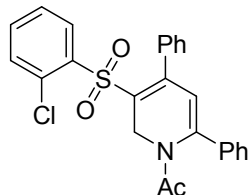
1-(3-(3-chlorophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4d)



Yellow solid; mp 51.2-52.2 °C; 1H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 9H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 2H), 6.10 (s, 1H), 5.05 (s, 2H), 1.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.12, 146.38, 145.02, 143.12, 135.93, 135.37, 134.83, 133.06, 130.17, 130.03, 130.01, 129.20, 128.93, 128.43, 128.06, 127.70, 127.21, 125.51, 118.69, 43.57, 24.05.

HRMS (ESI, m/z): Calcd. For $C_{25}H_{20}NCISO_3H$ $[M+H]^+$ 450.0925, found: 450.0927.

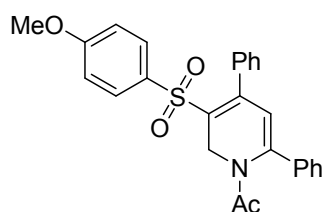
1-(3-(2-chlorophenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4e)



Yellow solid; mp 80.4-81.2 °C; 1H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, $J = 27.5$ Hz, 6H), 7.34 – 7.27 (m, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.11 (t, $J = 7.4$ Hz, 2H), 7.04 (d, $J = 7.3$ Hz, 2H), 6.97 (t, $J = 6.6$ Hz, 1H), 6.09 (s, 1H), 5.14 (s, 2H), 1.66 (d, $J = 63.8$ Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.30, 145.15, 138.01, 136.17, 135.08, 135.04, 133.54, 133.48, 132.29, 131.08, 130.91, 129.98, 129.15, 128.53, 128.29, 127.84, 127.14, 126.52, 118.22, 42.94, 24.39.

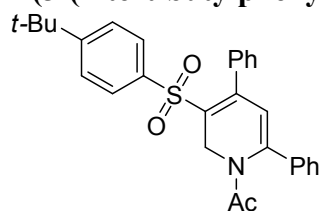
HRMS (ESI, m/z): Calcd. For $C_{25}H_{20}NCISO_3H$ $[M+H]^+$ 450.0925, found: 450.0927.

1-(3-(4-methoxyphenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4f)



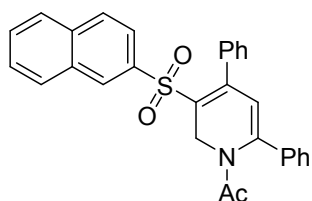
Yellow solid; mp 47.6-48.9 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.31 (m, 8H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 5.00 (s, 2H), 3.82 (d, *J* = 3.3 Hz, 3H), 1.68 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.09, 163.32, 144.62, 144.09, 136.11, 136.02, 133.04, 129.90, 129.75, 129.13, 128.49, 128.45, 127.96, 127.09, 119.09, 114.03, 114.01, 55.63, 43.75, 24.01.
HRMS (ESI, m/z): Calcd. For C₂₆H₂₃NSO₄H [M+H]⁺ 446.1421, found: 446.1420.

1-(3-(4-tert-butylphenylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4g)



Yellow solid; mp 52.1-53 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.32 (m, 8H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.12 (m, 2H), 6.08 (s, 1H), 5.01 (s, 2H), 2.01 – 1.41 (m, 3H), 1.29 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 171.04, 156.85, 145.03, 144.36, 138.26, 136.09, 135.93, 129.88, 129.09, 129.00, 128.45, 127.93, 127.39, 127.06, 125.71, 125.58, 118.96, 43.86, 35.13, 31.03, 23.92.
HRMS (ESI, m/z): Calcd. For C₂₉H₂₉NSO₃H [M+H]⁺ 472.1941, found: 472.1940.

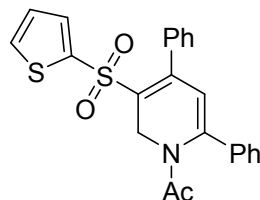
1-(3-(naphthalen-2-ylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4h)



Yellow solid; mp 103-104.5 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.97 (s, 1H), 7.81 (t, *J* = 9.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.41 – 7.34 (m, 5H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.07 (s, 1H), 5.10 (s, 2H), 1.67 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.10, 145.76, 144.58, 138.13, 136.01, 135.67, 134.90, 131.88, 129.98, 129.45, 129.41, 129.11, 129.08, 128.96, 128.64, 128.44, 127.85, 127.77, 127.34, 127.11, 127.11, 122.21, 118.90, 43.88, 23.99.

HRMS (ESI, m/z): Calcd. For C₂₉H₂₄NSO₃H [M+H]⁺ 466.1471, found: 466.1473

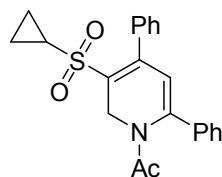
1-(4,6-diphenyl-3-(thiophen-2-ylsulfonyl)pyridin-1(2H)-yl)ethan-1-one (4i)



Yellow solid; mp 172.2-173.8 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 4.8 Hz, 1H), 7.34 (dd, *J* = 12.6, 9.4 Hz, 9H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.91 (s, 1H), 6.05 (s, 1H), 4.93 (s, 2H), 1.61 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.05, 144.32, 143.63, 141.45, 134.94, 134.77, 132.78, 132.58, 129.03, 128.13, 127.65, 127.26, 127.00, 126.45, 126.11, 117.98, 42.33, 23.06.

HRMS (ESI, m/z): Calcd. For C₂₃H₁₉NS₂O₃H [M+H]⁺ 422.0879, found: 422.0885.

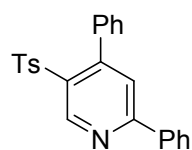
1-(3-(cyclopropylsulfonyl)-4,6-diphenylpyridin-1(2H)-yl)ethanone (4j)



White solid; mp 155.9-160.9 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.47 (s, 2H), 7.41 (s, 7H), 6.20 (s, 1H), 5.01 (s, 2H), 2.28 (s, 1H), 1.76 (s, 3H), 1.11 (s, 2H), 0.87 (s, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 171.36, 144.41, 136.20, 136.06, 130.06, 129.22, 128.81, 128.81, 128.52, 128.13, 127.19, 118.95, 43.78, 32.04, 24.10, 5.50.

HRMS (ESI, m/z): Calcd. For C₂₂H₂₁NSO₃H [M+H]⁺ 380.1315, found: 380.1315.

2,4-diphenyl-5-tosylpyridine (5a)

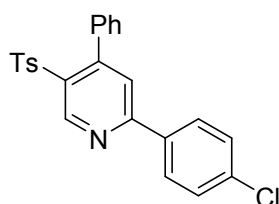


White solid; mp 147.5-148.6 °C; ¹H NMR (600 MHz, CDCl₃) δ 9.54 (s, 1H), 8.09 – 8.00 (m, 2H), 7.55 (s, 1H), 7.46 (d, *J* = 4.9 Hz, 3H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J*

= 7.6 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.5 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 160.98, 150.84, 149.63, 144.04, 137.67, 137.41, 136.27, 134.37, 130.44, 129.28, 129.20, 128.98, 128.65, 127.98, 127.69, 127.49, 122.97, 77.29, 77.07, 76.86, 21.55.

HRMS (ESI, m/z): Calcd. For $\text{C}_{24}\text{H}_{19}\text{NSO}_2\text{H}$ $[\text{M}+\text{H}]^+$ 386.1209, found: 386.1207.

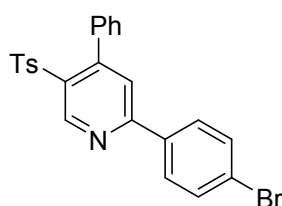
2-(4-chlorophenyl)-4-phenyl-5-tosylpyridine (5b)



White solid; mp 186.5-187.6 °C; ^1H NMR (600 MHz, CDCl_3) δ 9.52 (s, 1H), 7.94 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 7.53 (s, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.72, 151.03, 149.68, 144.13, 137.45, 136.25, 136.06, 134.66, 132.20, 129.24, 129.22, 128.98, 128.75, 127.99, 127.73, 125.23, 122.72, 21.59.

HRMS (ESI, m/z): Calcd. For $\text{C}_{24}\text{H}_{18}\text{NCISO}_2\text{H}$ $[\text{M}+\text{H}]^+$ 420.0820, found: 420.0826.

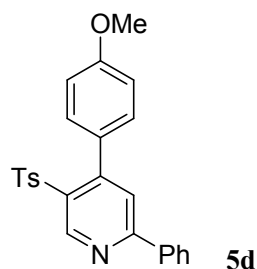
2-(4-bromophenyl)-4-phenyl-5-tosylpyridine (5c)



White solid; mp 182.2-184.3 °C; ^1H NMR (600 MHz, CDCl_3) δ 9.52 (s, 1H), 8.01 (d, J = 8.1 Hz, 2H), 7.53 (s, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.66, 151.01, 149.67, 144.12, 137.46, 136.78, 136.08, 135.80, 134.60, 129.23, 129.22, 128.74, 127.99, 127.73, 122.75, 21.58.

HRMS (ESI, m/z): Calcd. For $\text{C}_{24}\text{H}_{18}\text{NBrSO}_2\text{H}$ $[\text{M}+\text{H}]^+$ 464.0314, found: 464.0317.

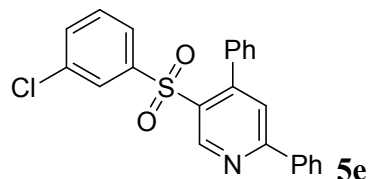
4-(4-methoxyphenyl)-2-phenyl-5-tosylpyridine (5d)



White solid; mp 137.2-139.5 °C; ^1H NMR (600 MHz, CDCl_3) δ 9.50 (s, 1H), 8.04 (d, $J = 7.5$ Hz, 2H), 7.54 (s, 1H), 7.48 (d, $J = 6.1$ Hz, 3H), 7.23 (d, $J = 7.8$ Hz, 2H), 7.05 (dd, $J = 8.0, 3.7$ Hz, 4H), 6.84 (d, $J = 8.2$ Hz, 2H), 3.88 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 160.92, 160.08, 150.77, 149.73, 144.02, 137.65, 137.48, 134.58, 130.73, 130.39, 129.16, 128.98, 128.57, 127.97, 127.47, 123.33, 113.16, 55.45, 21.58.

HRMS (ESI, m/z): Calcd. For $\text{C}_{25}\text{H}_{21}\text{NSO}_3\text{H}$ $[\text{M}+\text{H}]^+$ 416.1315, found: 416.1319.

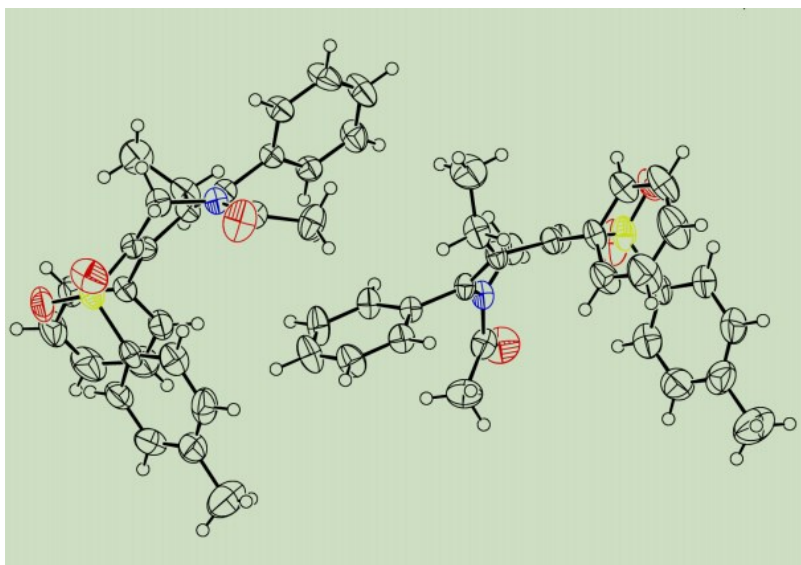
5-((3-chlorophenyl)sulfonyl)-2,4-diphenylpyridine (5e)



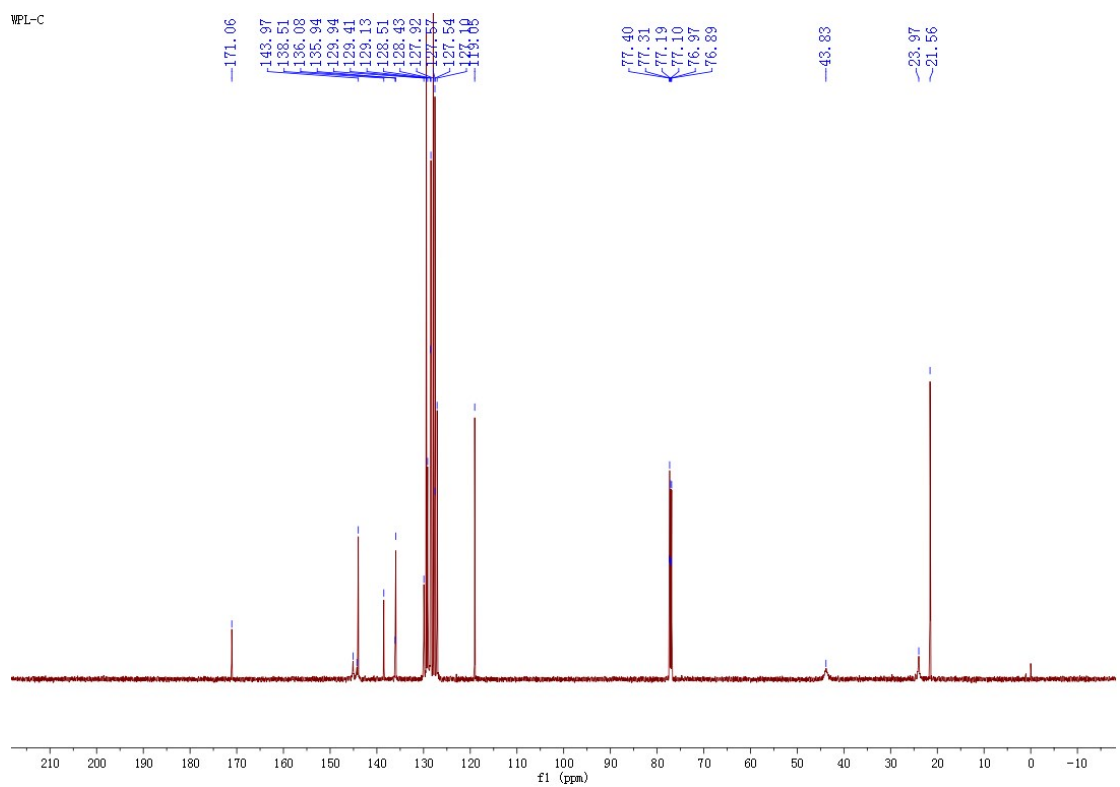
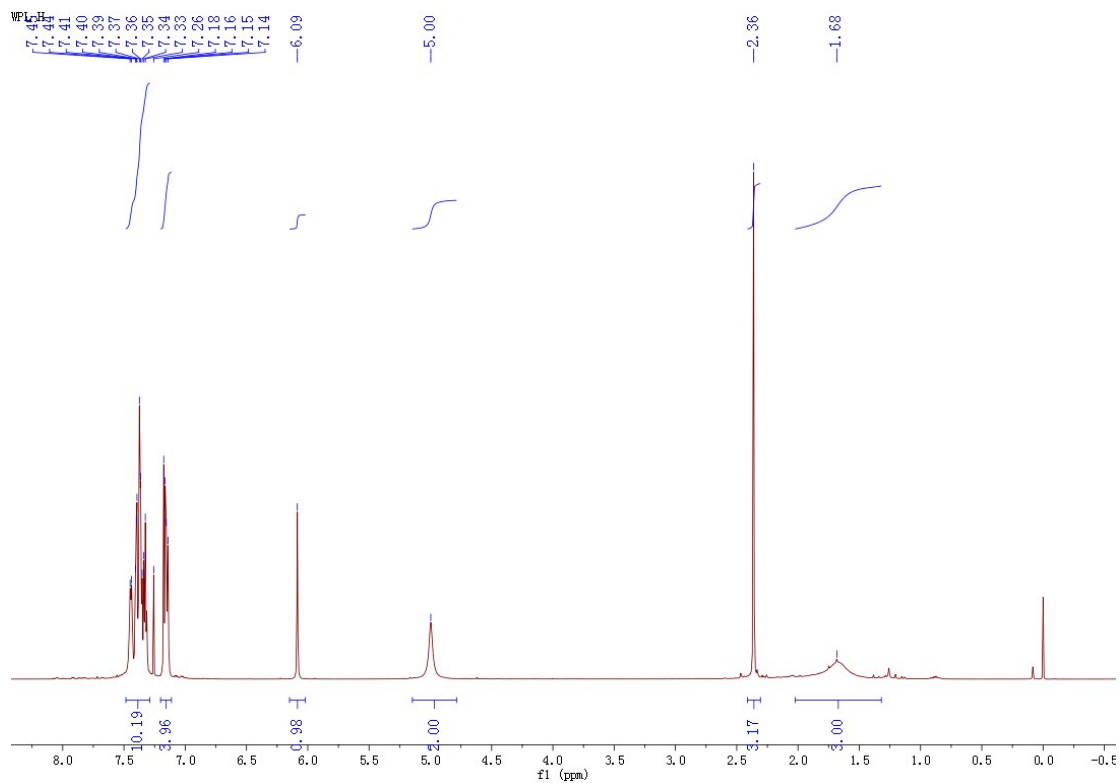
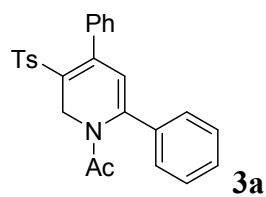
White solid; mp 172.7-173.4 °C; ^1H NMR (600 MHz, CDCl_3) δ 9.54 (d, $J = 24.0$ Hz, 1H), 8.05 (dd, $J = 20.3, 15.5$ Hz, 2H), 7.59 (s, 1H), 7.49 (d, $J = 5.0$ Hz, 3H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.40 (d, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 7.16 (s, 1H), 7.07 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.52, 150.93, 149.60, 142.07, 137.22, 135.64, 134.78, 133.56, 133.22, 130.65, 129.89, 129.23, 129.07, 129.05, 128.24, 127.86, 127.55, 125.99, 122.93.

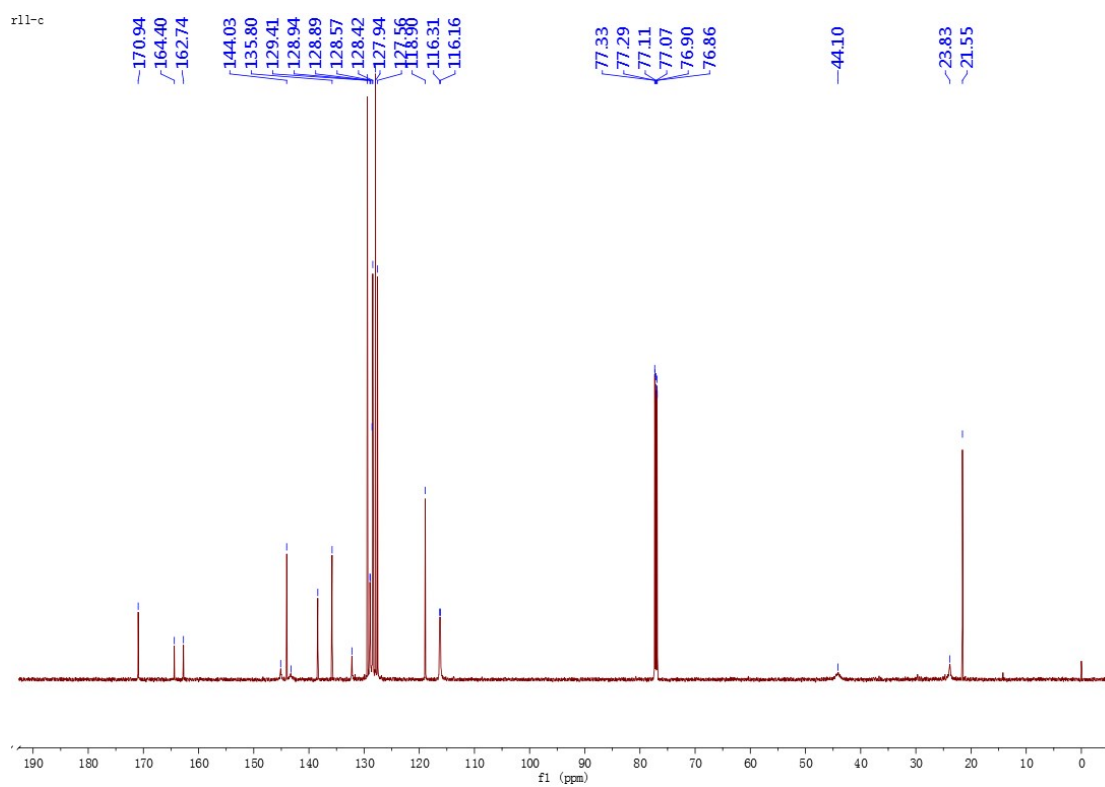
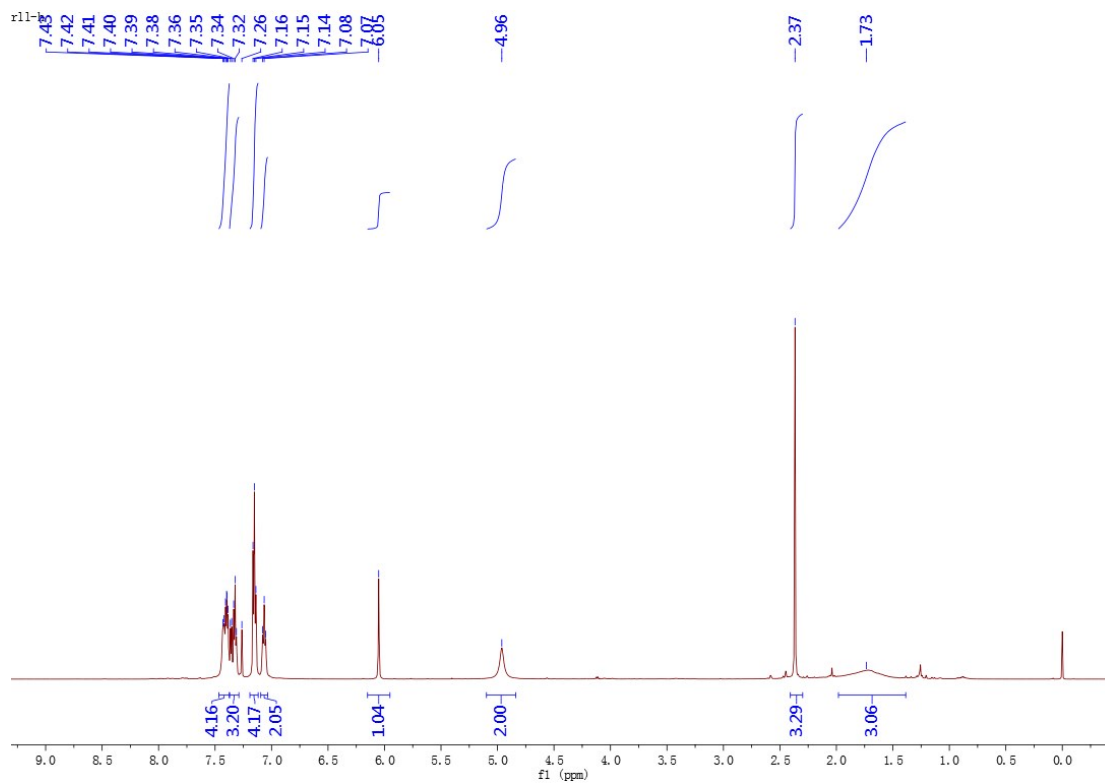
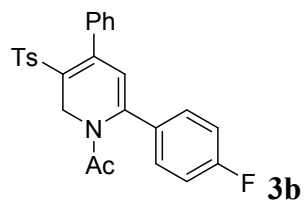
HRMS (ESI, m/z): Calcd. For $\text{C}_{23}\text{H}_{16}\text{NClSO}_2\text{H}$ $[\text{M}+\text{H}]^+$ 406.0663, found: 406.0668.

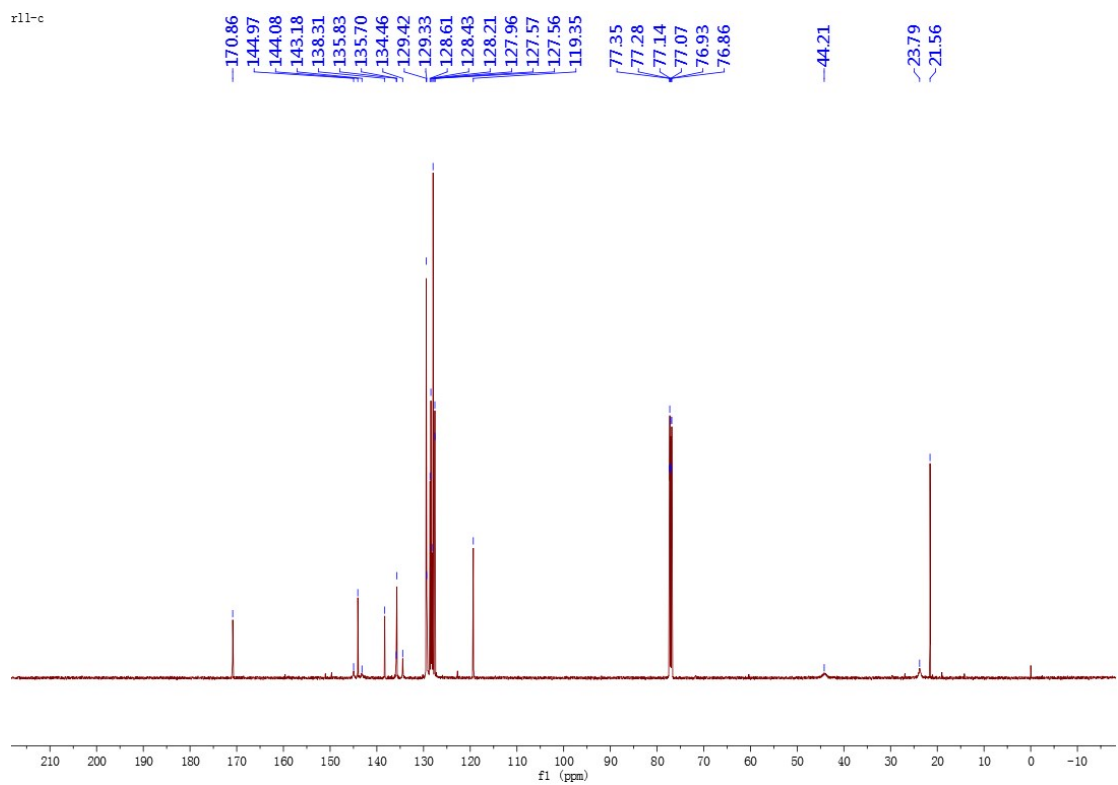
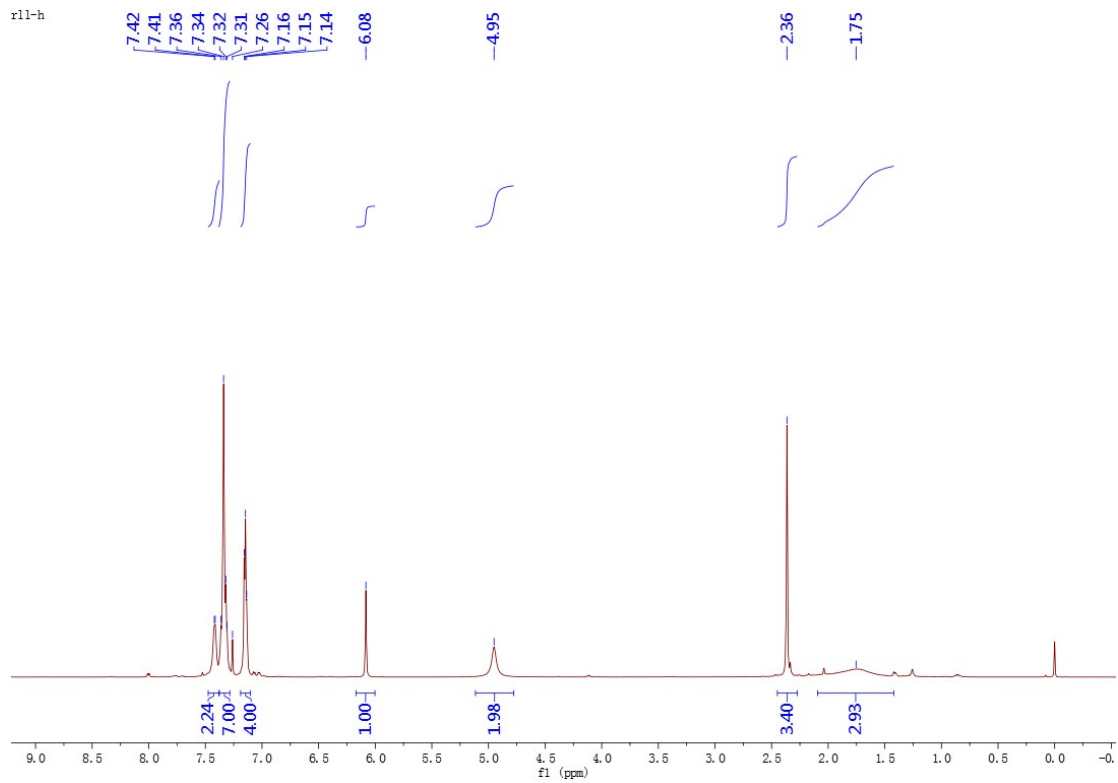
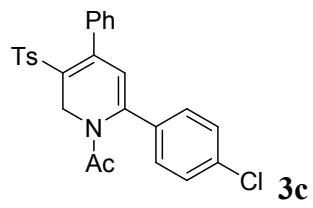
X-ray diffraction analysis of compound **3n**

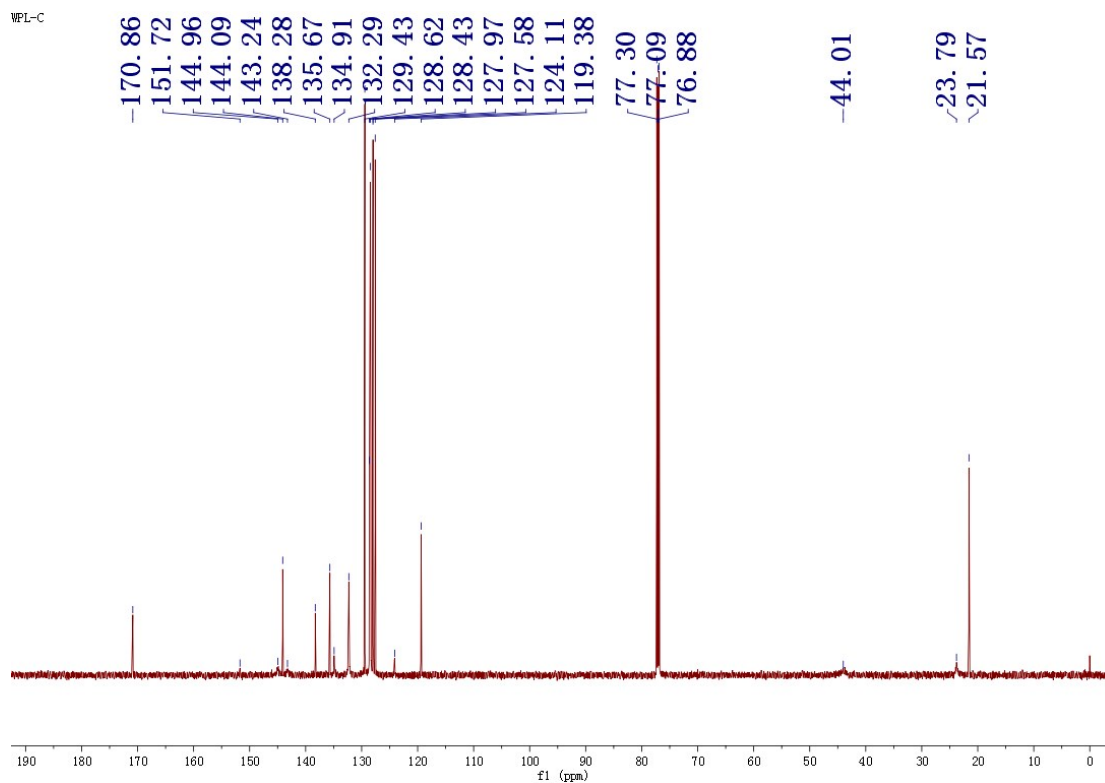
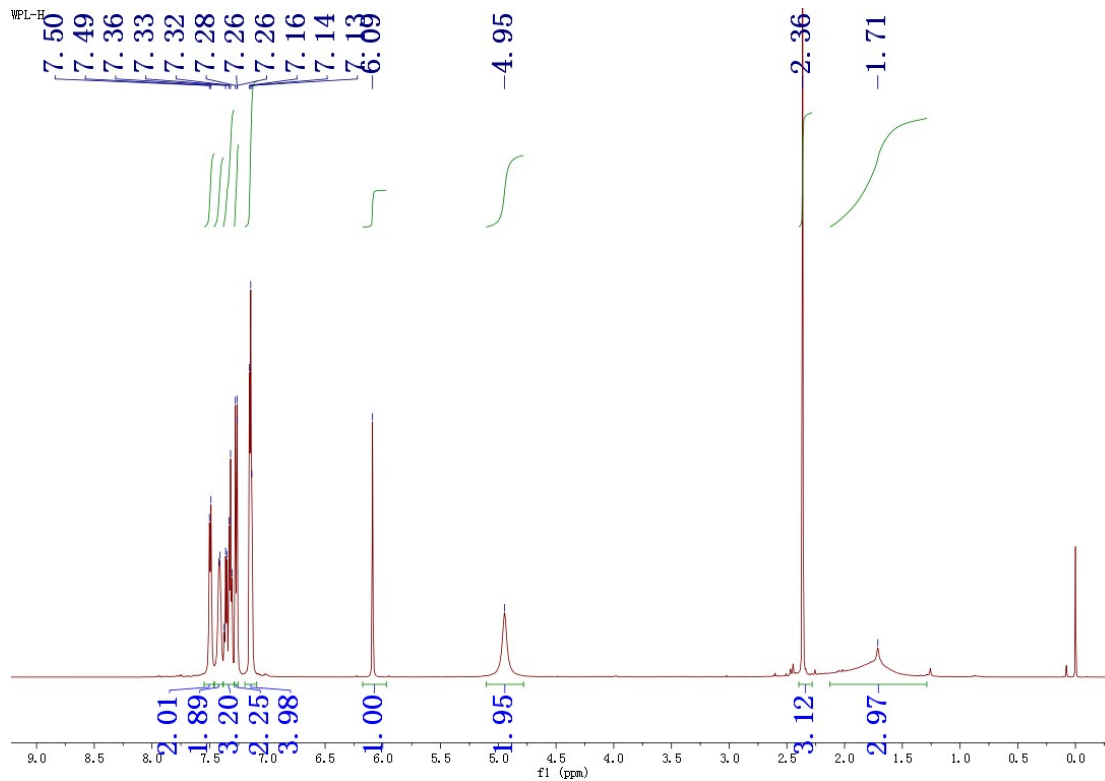
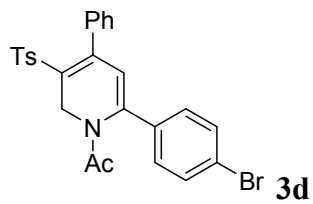


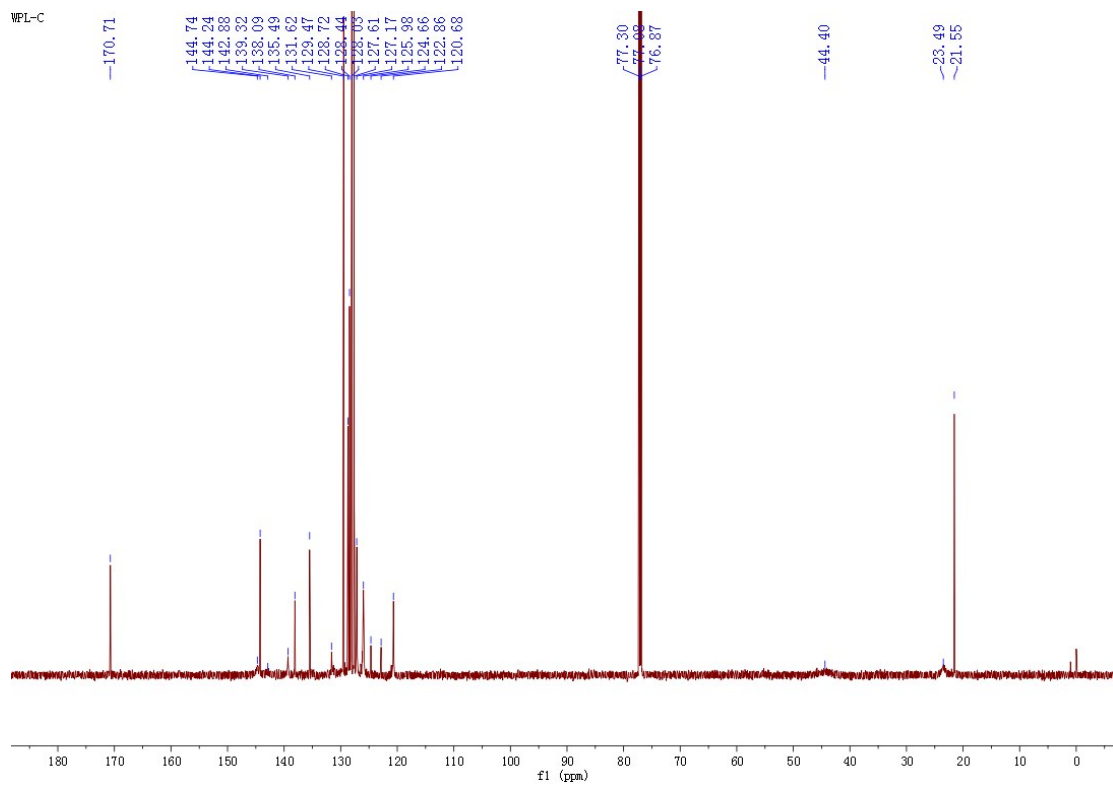
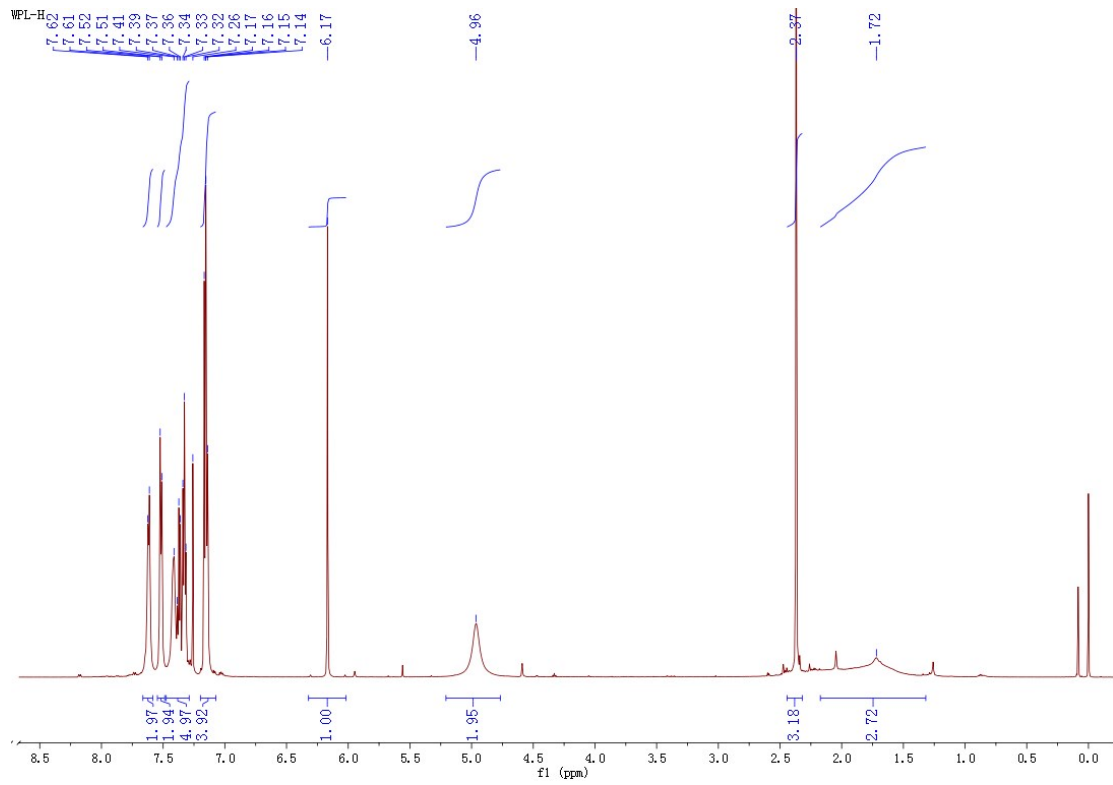
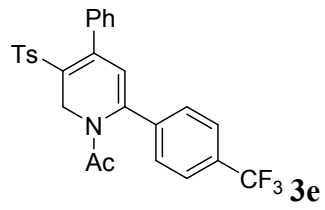
Bond precision: C-C = 0.0045 Å Wavelength=0.71073
Cell: a=9.9944(11) b=16.6828(18) c=16.8624(18)
alpha=117.285(3) beta=92.754(4) gamma=90.642(4)
Temperature: 293 K
Calculated Reported
Volume 2494.1(5) 2494.1(5)
Space group P -1 P -1
Hall group -P 1 -P 1
Moiety formula C₂₈ H₂₇ N O₃ S C₂₈ H₂₇ N O₃ S
Sum formula C₂₈ H₂₇ N O₃ S C₂₈ H₂₇ N O₃ S
Mr 457.57 457.56
D_x,g cm⁻³ 1.219 1.219
Z 4 4
Mu (mm⁻¹) 0.158 0.158
F₀₀₀ 968.0 968.0
F₀₀₀' 968.90
h,k,lmax 13,21,21 12,21,21
N_{ref} 11506 11419
T_{min},T_{max} 0.961,0.980 0.681,0.746
T_{min}' 0.961
Correction method= # Reported T Limits: T_{min}=0.681 T_{max}=0.746
AbsCorr = MULTI-SCAN
Data completeness= 0.992 Theta(max)= 27.564
R(reflections)= 0.0743(7315) wR2(reflections)= 0.2195(11419)
S = 1.024 N_{par}= 601

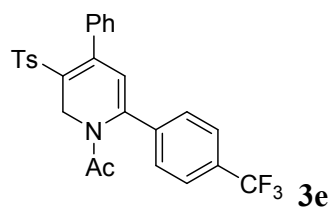




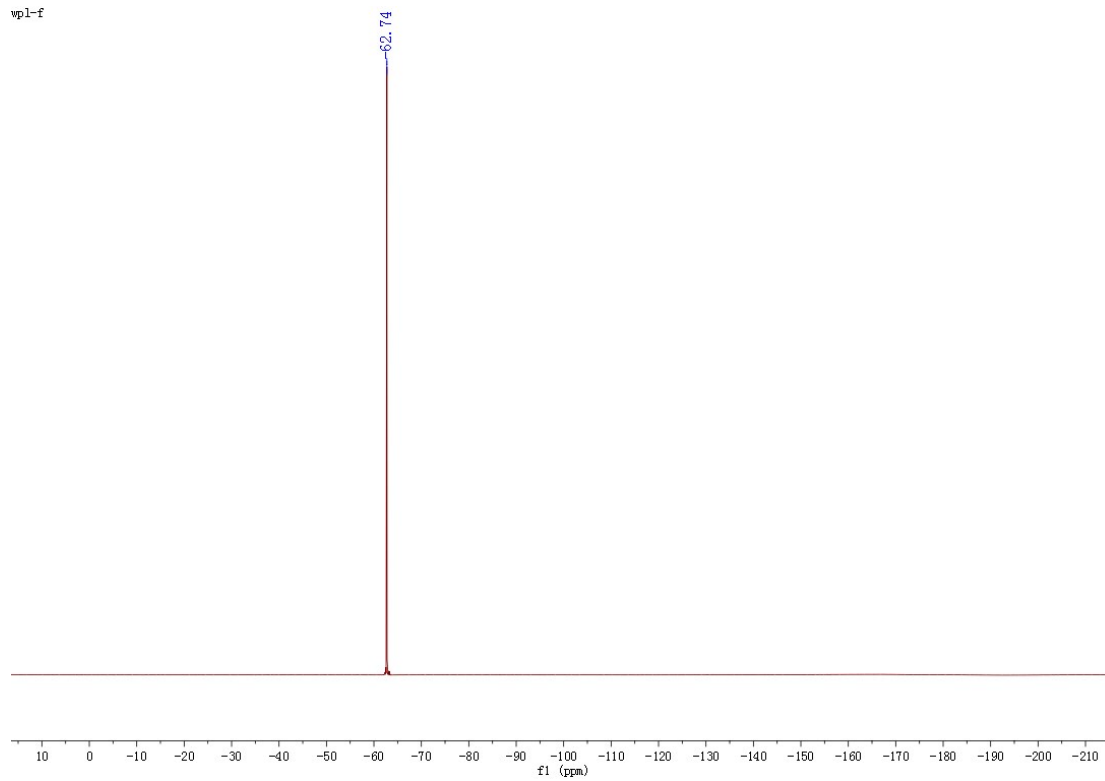


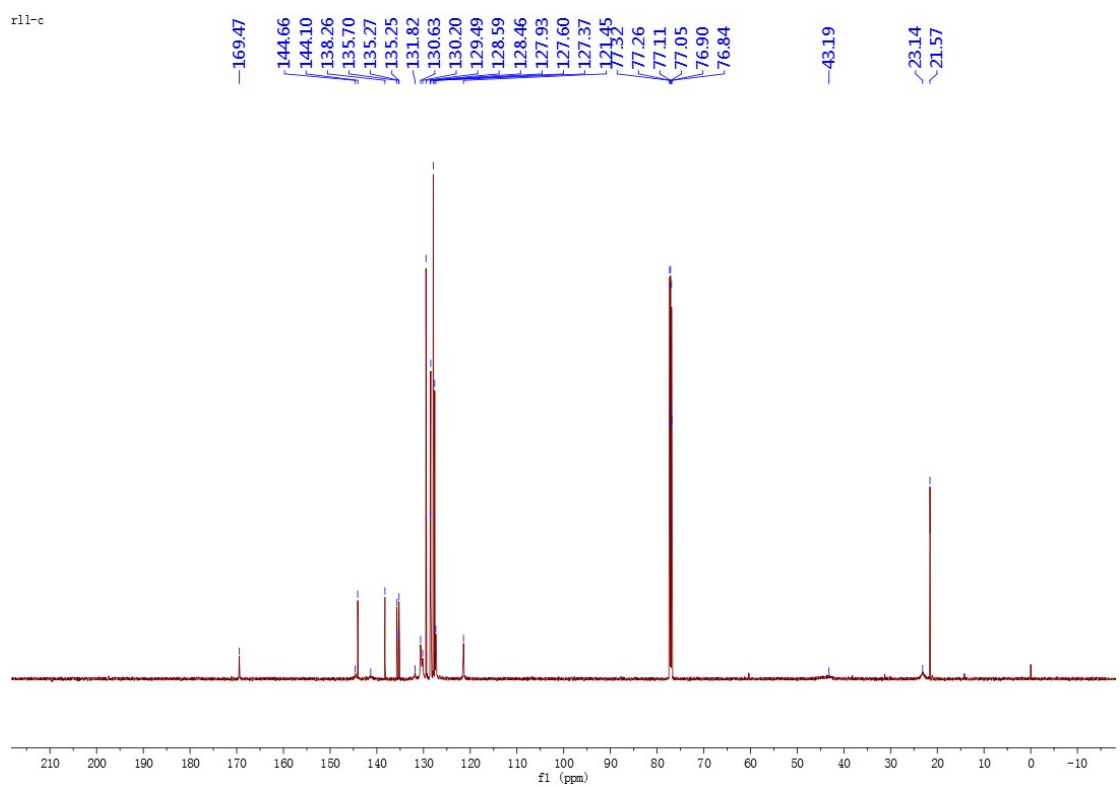
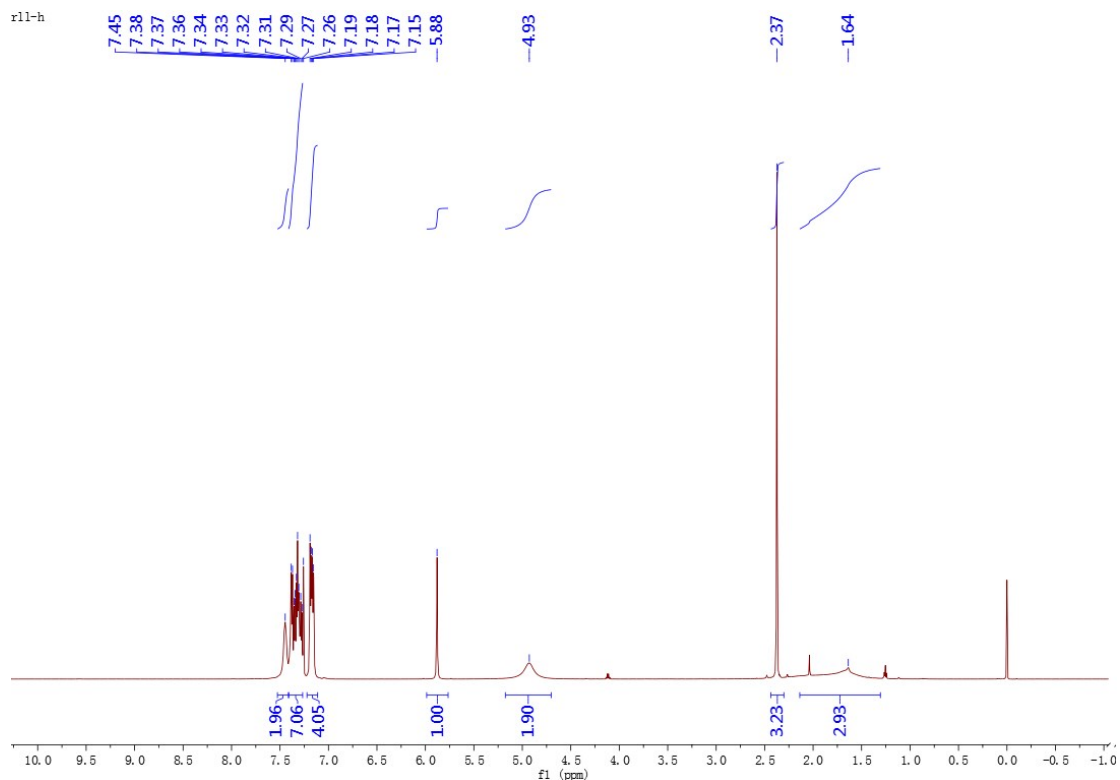
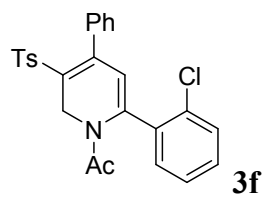


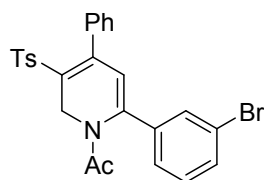




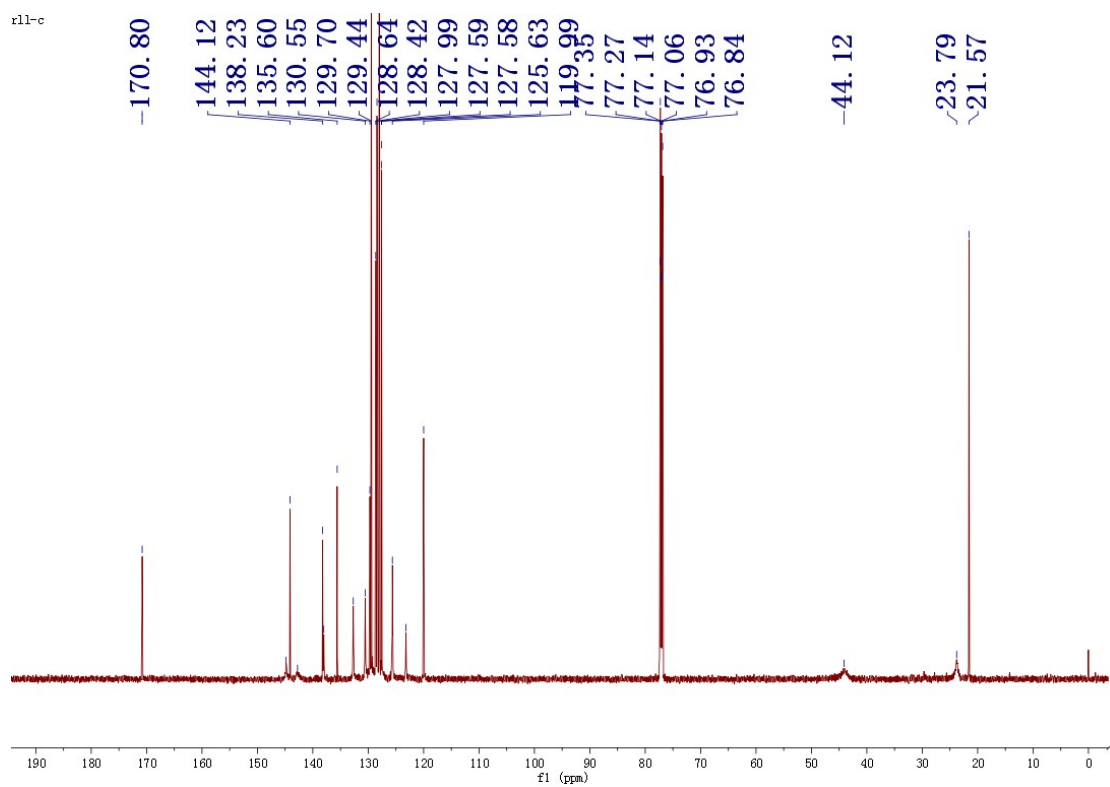
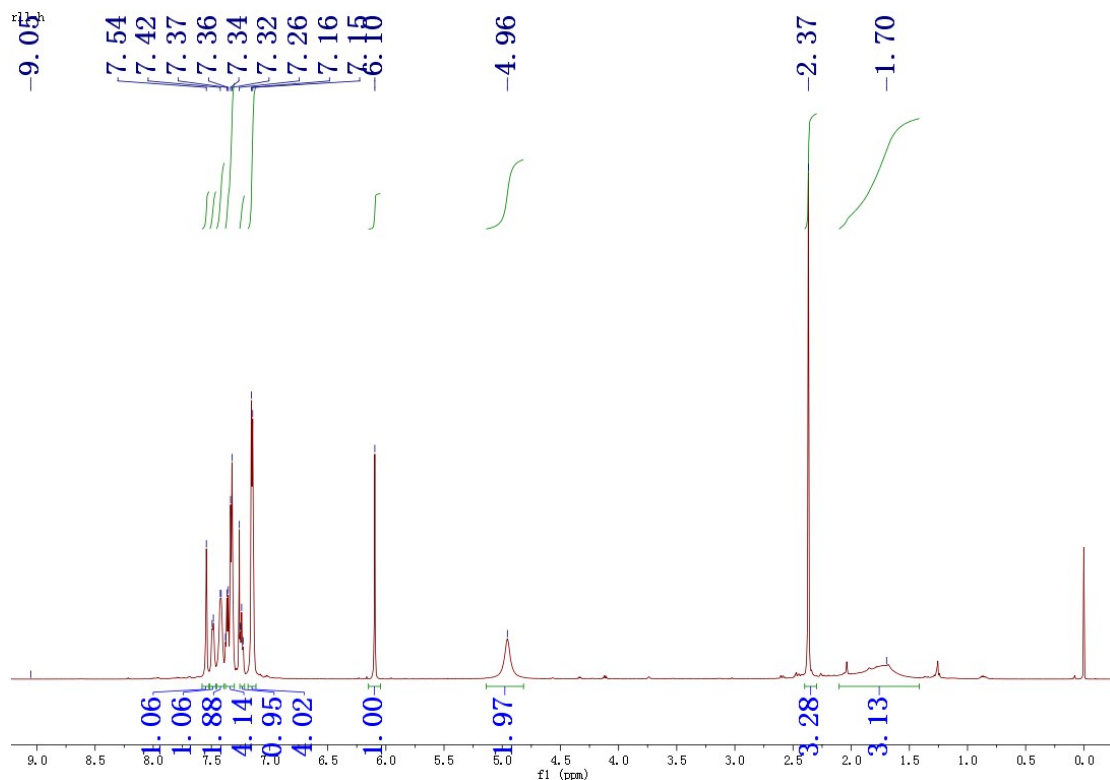
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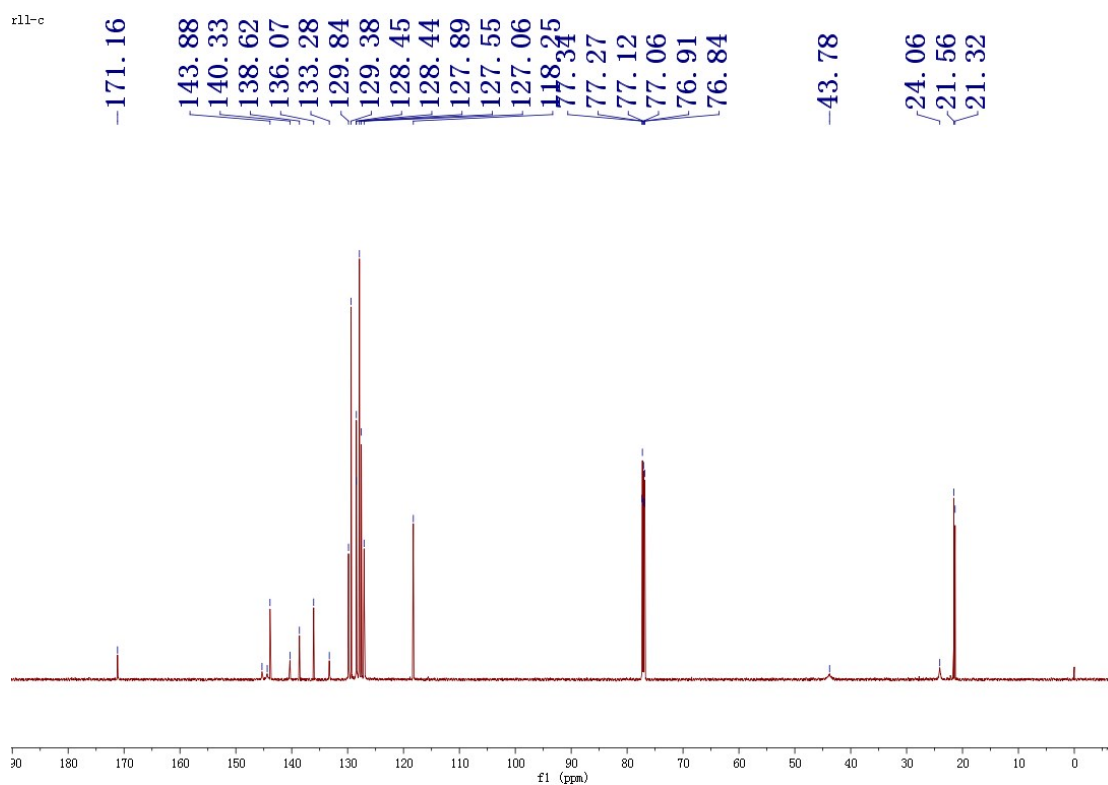
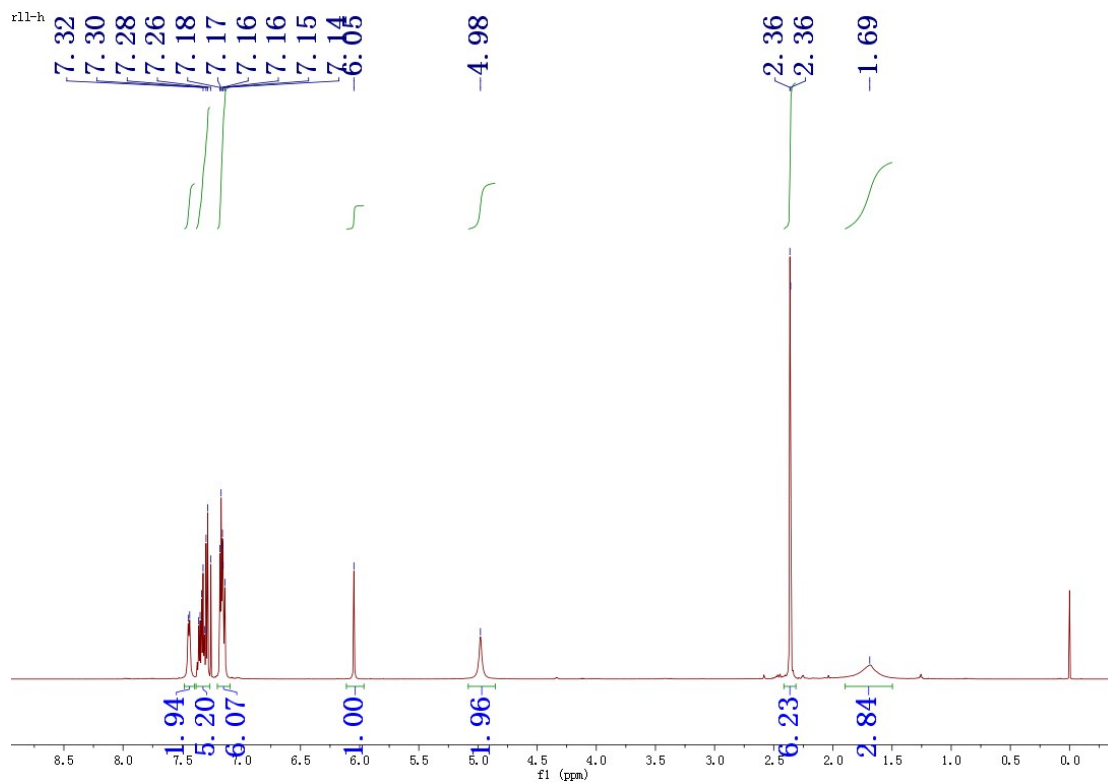
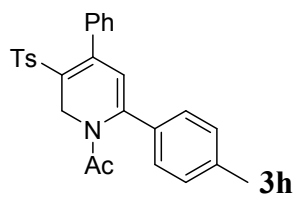


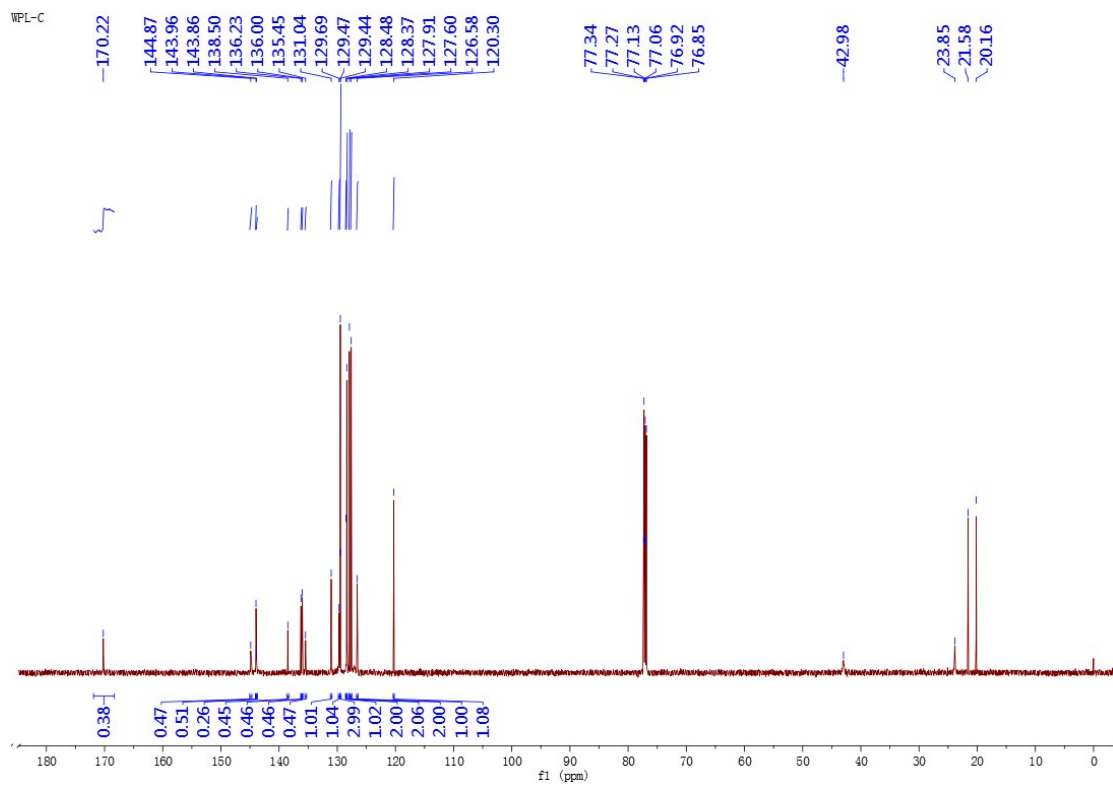
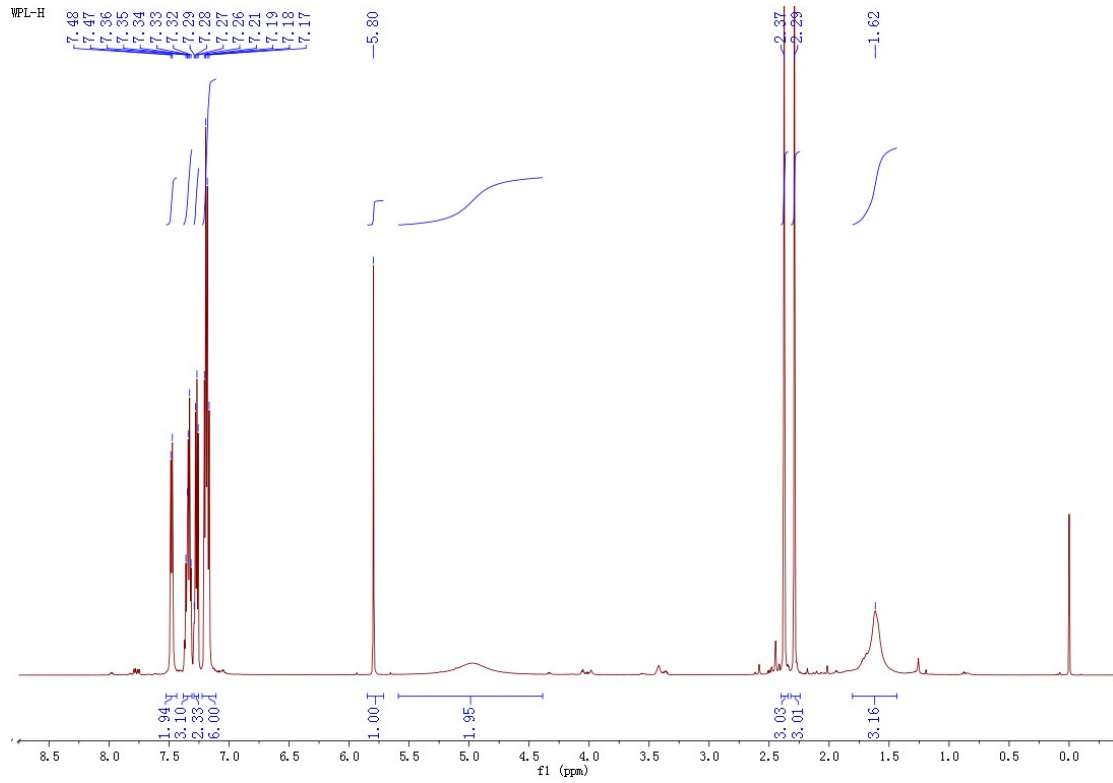
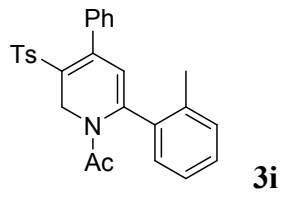


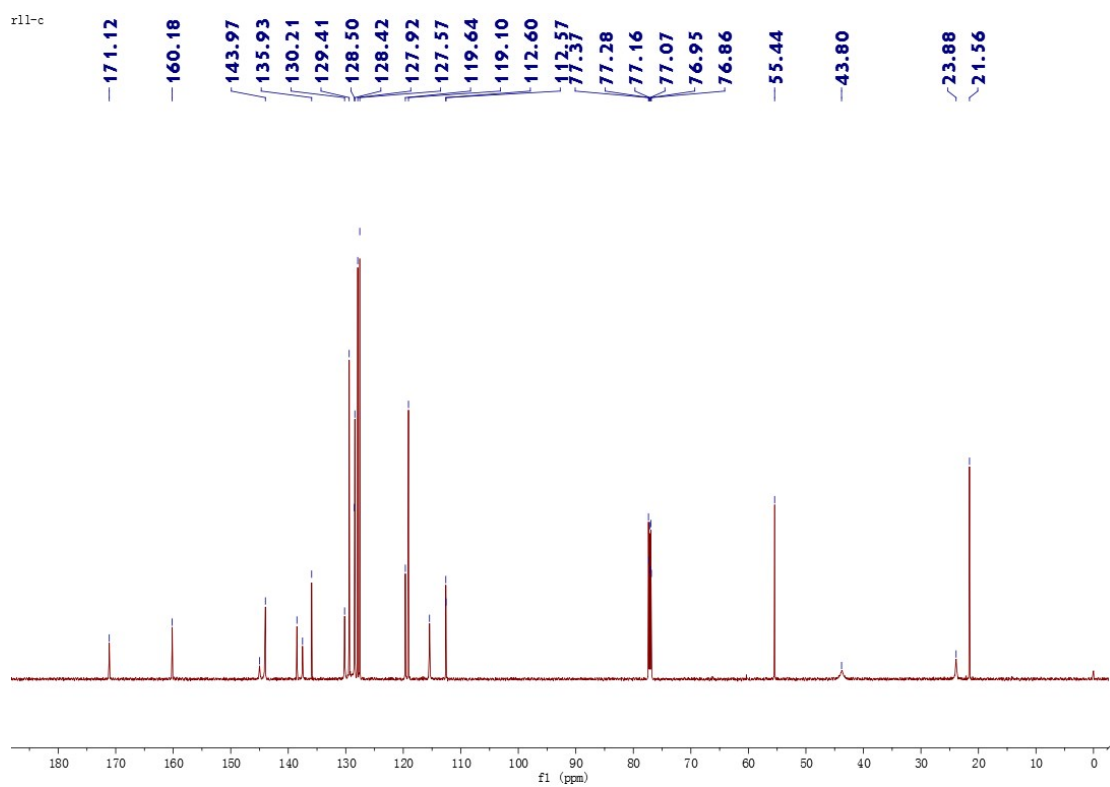
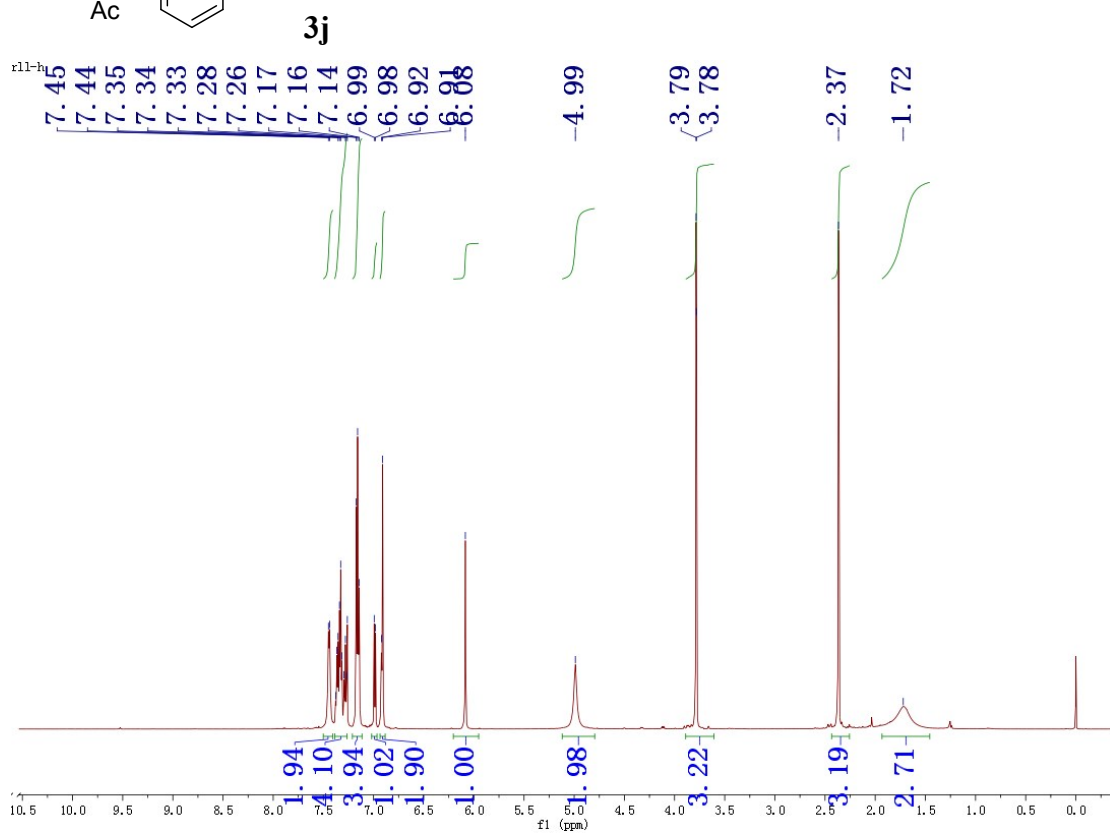
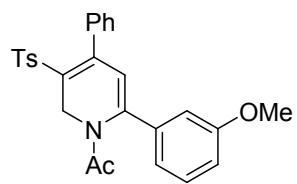


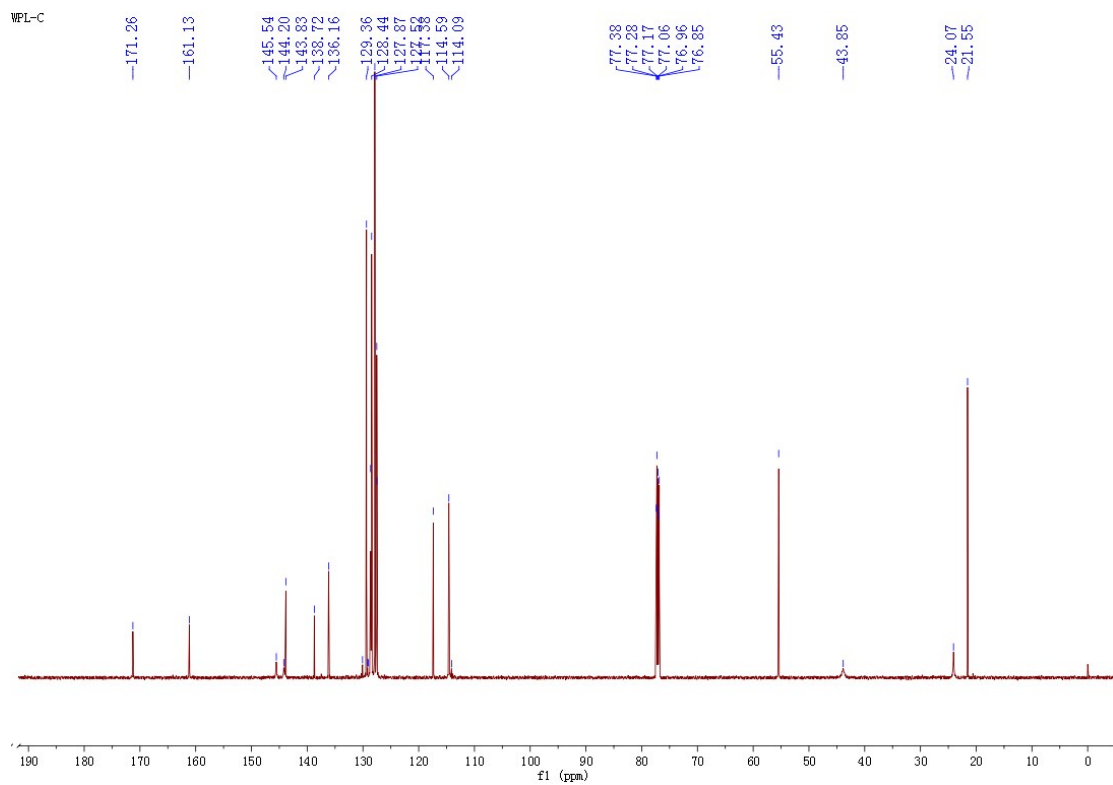
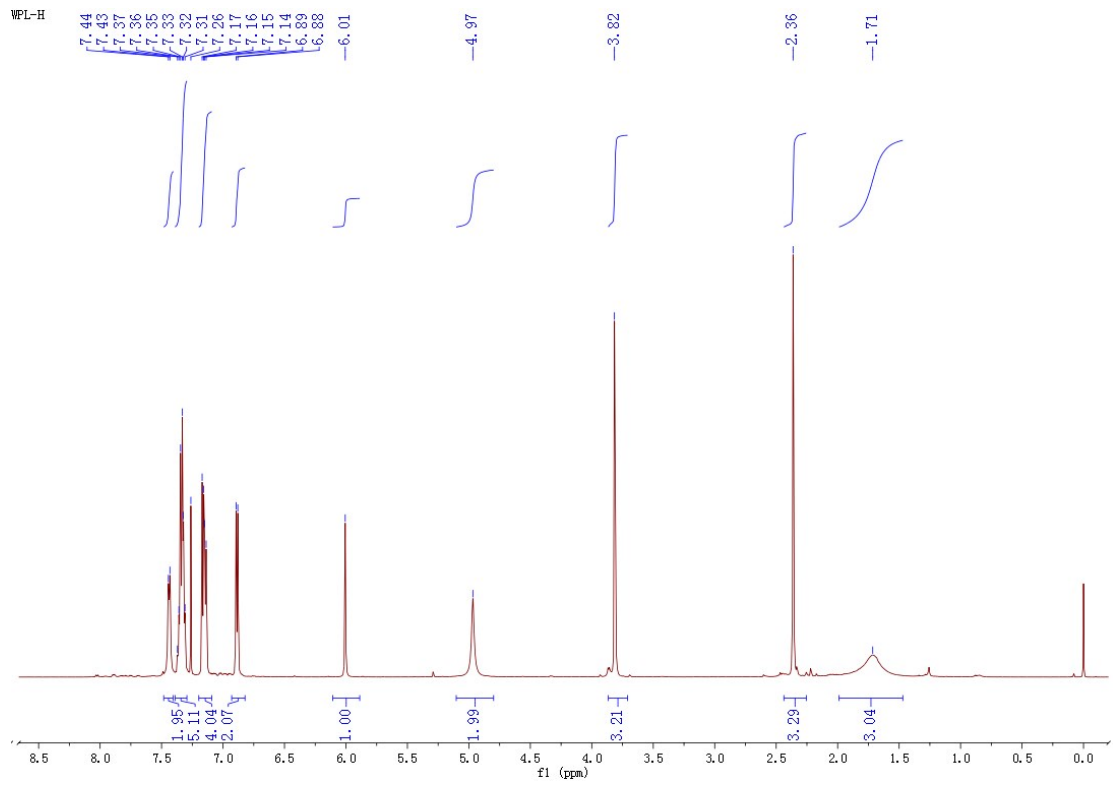
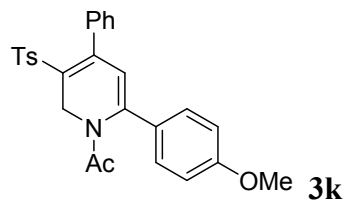
3g

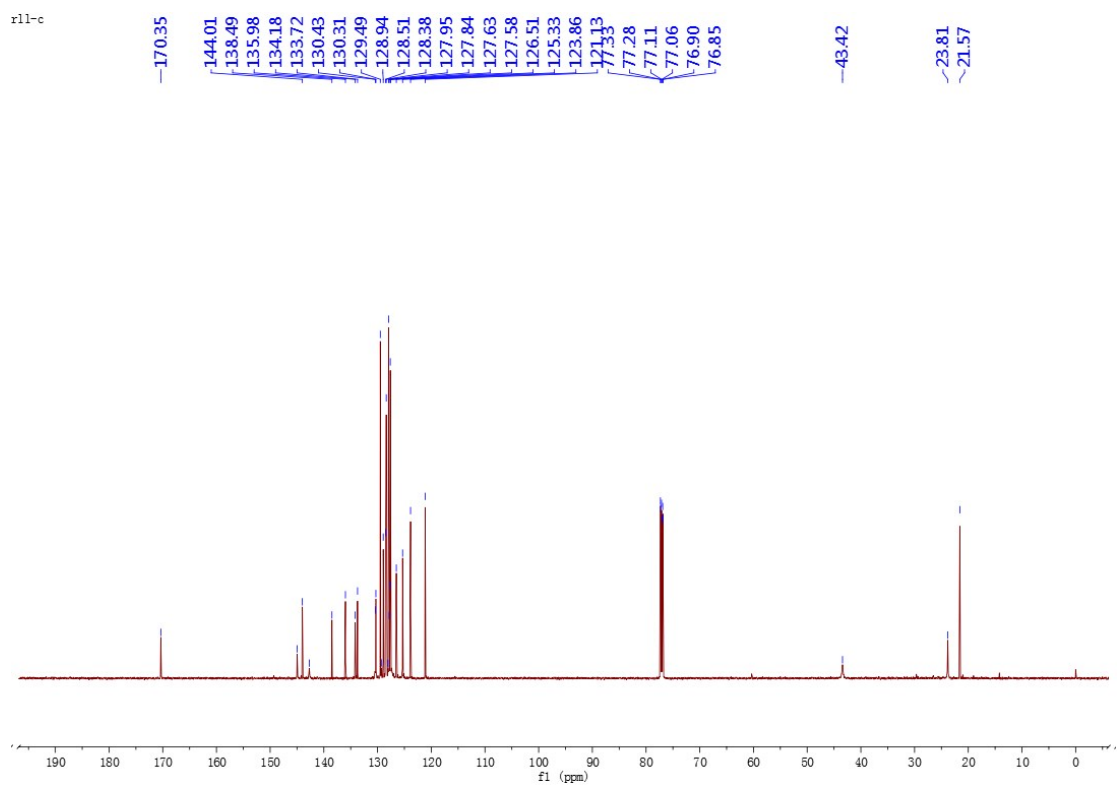
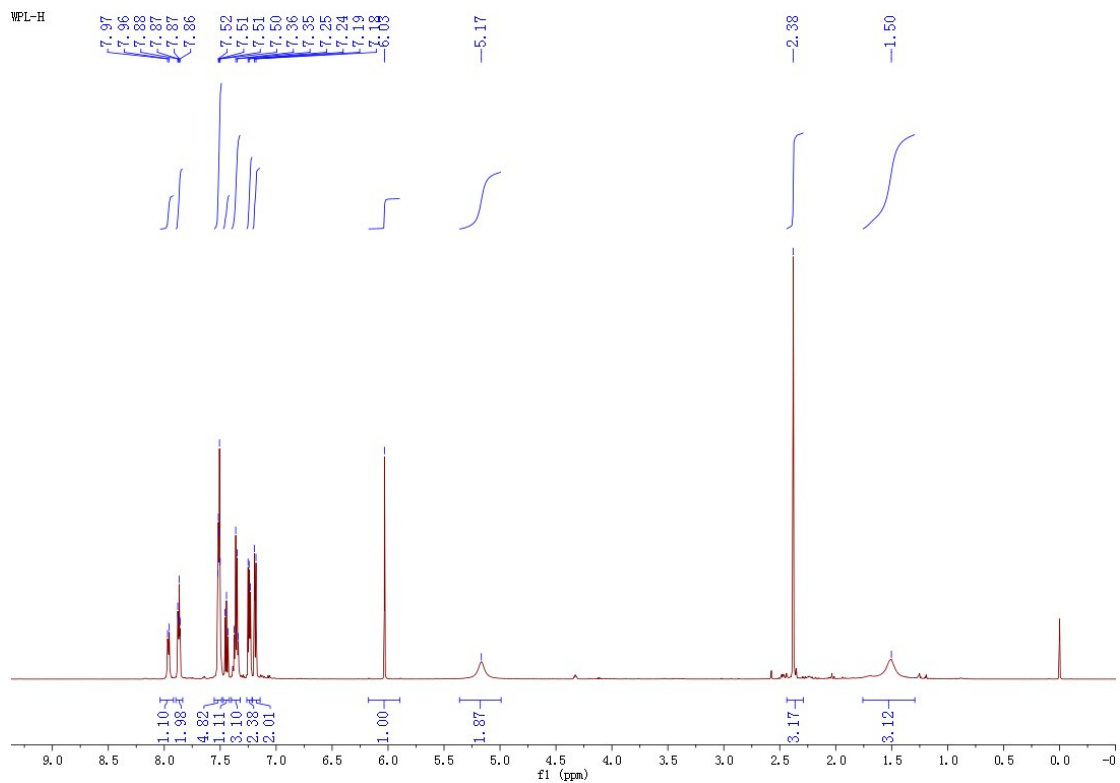
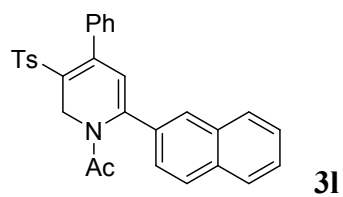


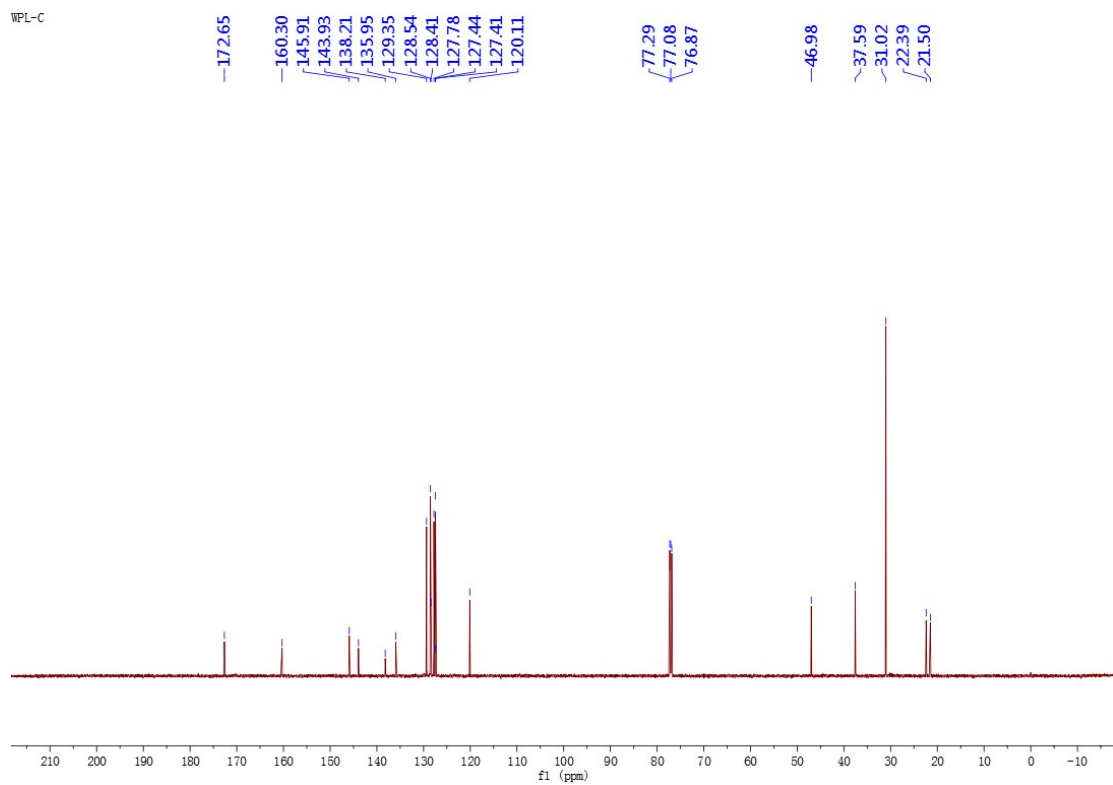
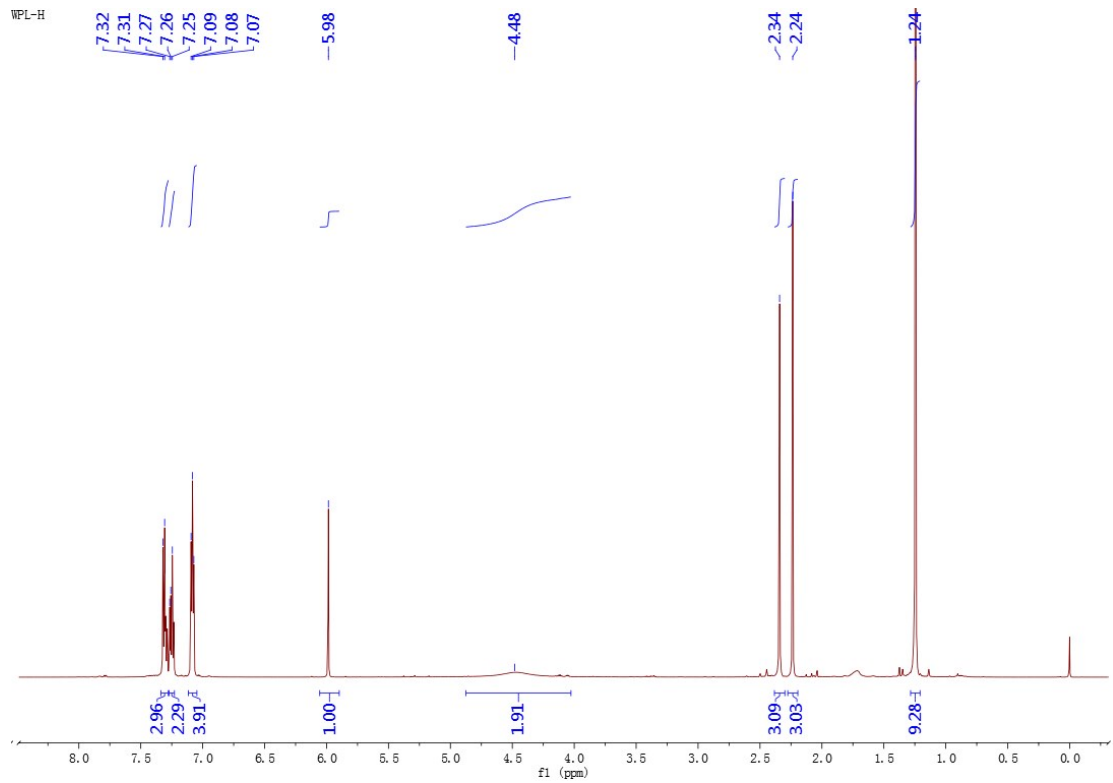
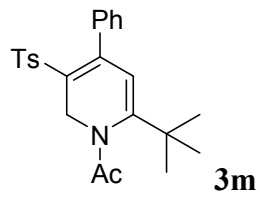


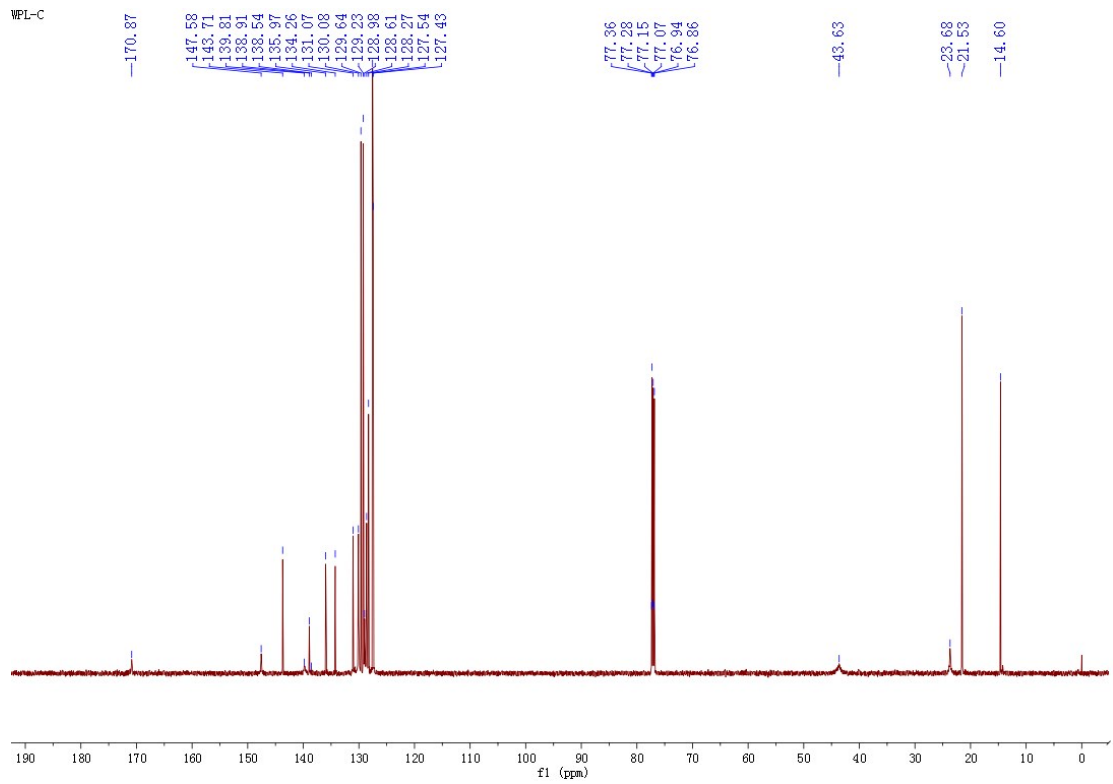
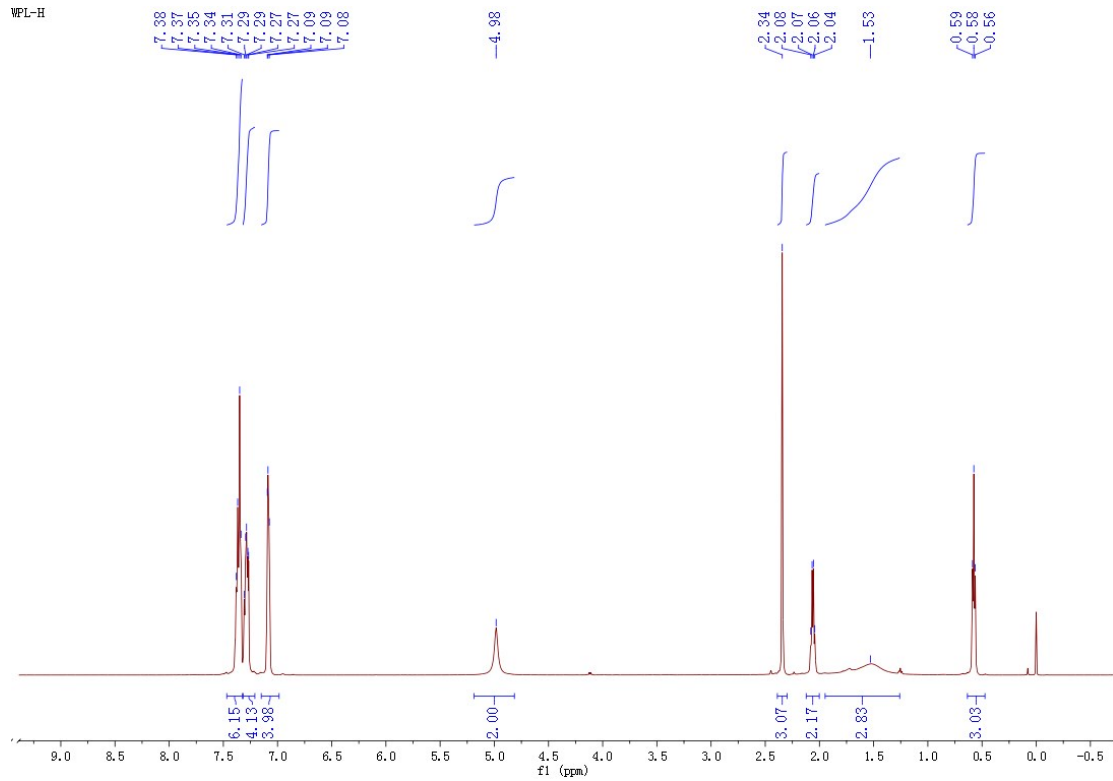
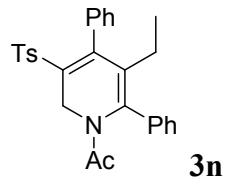


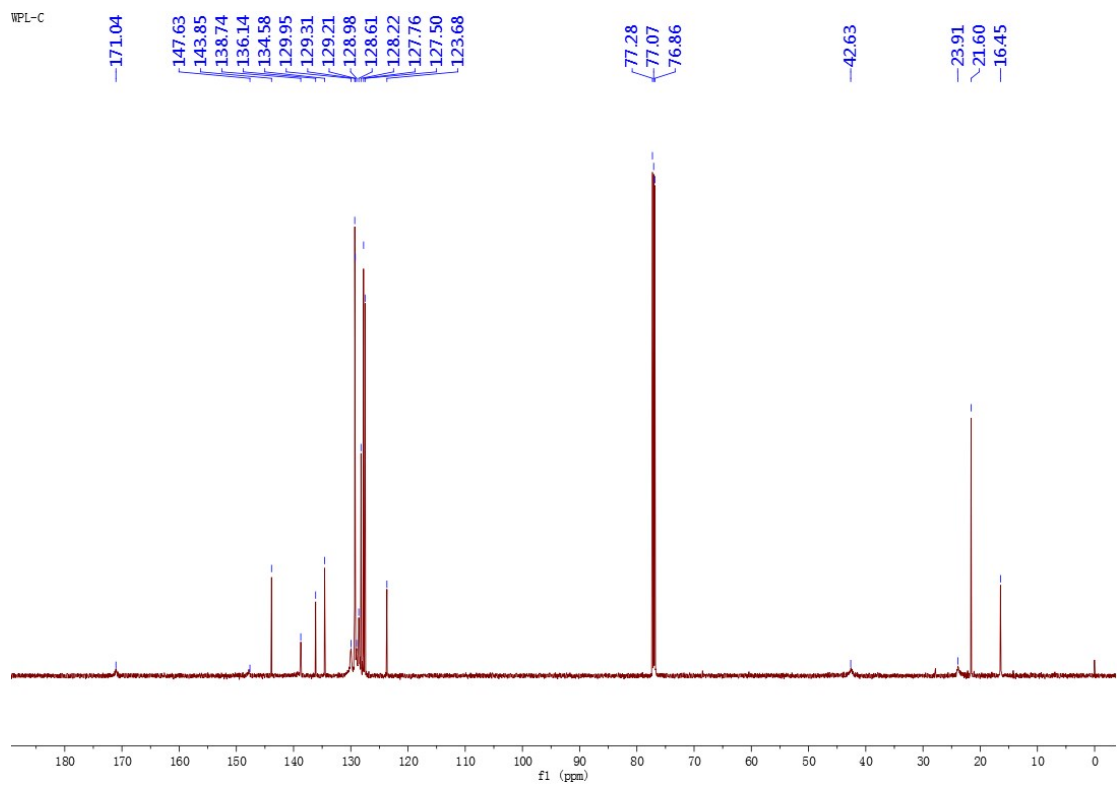
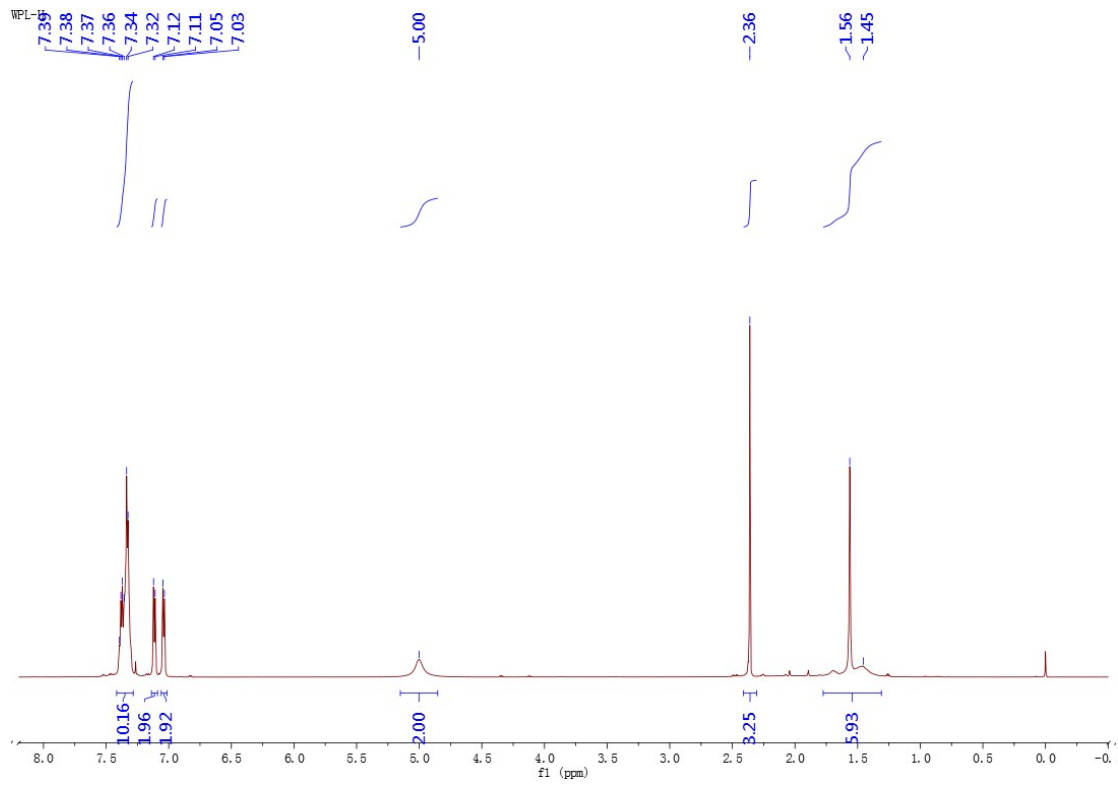
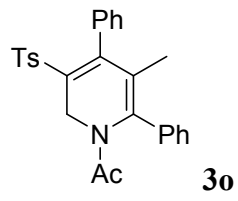


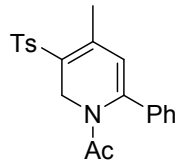






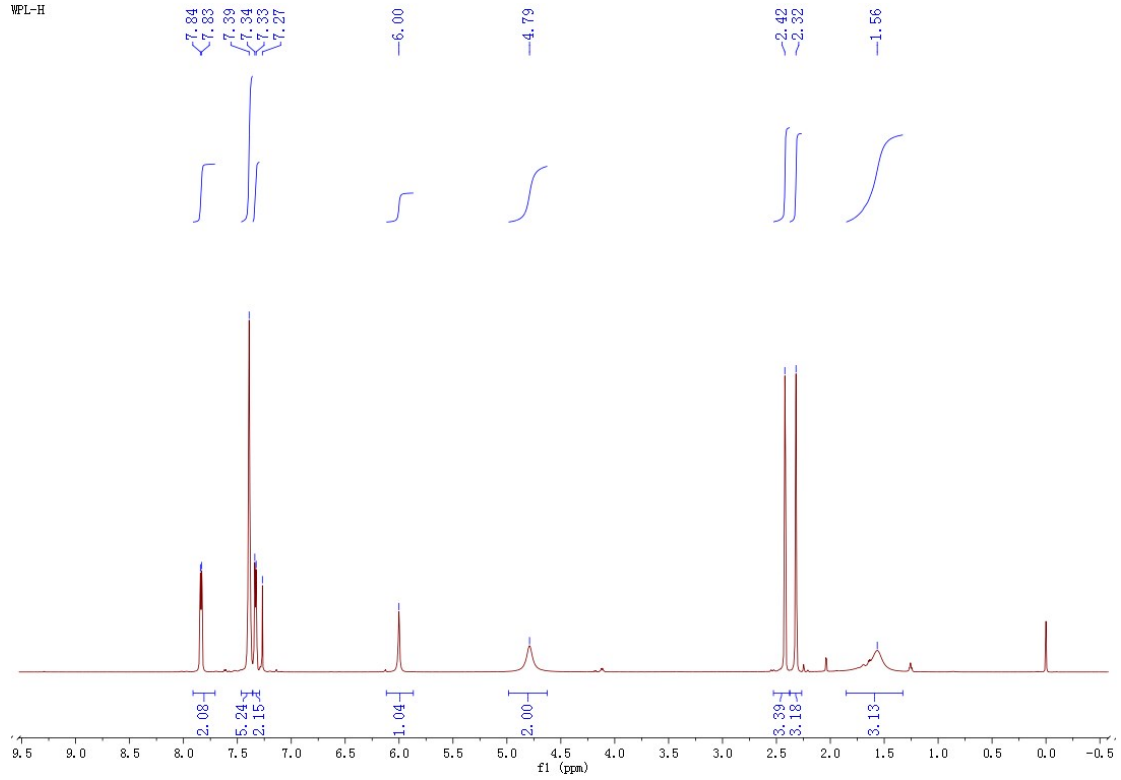




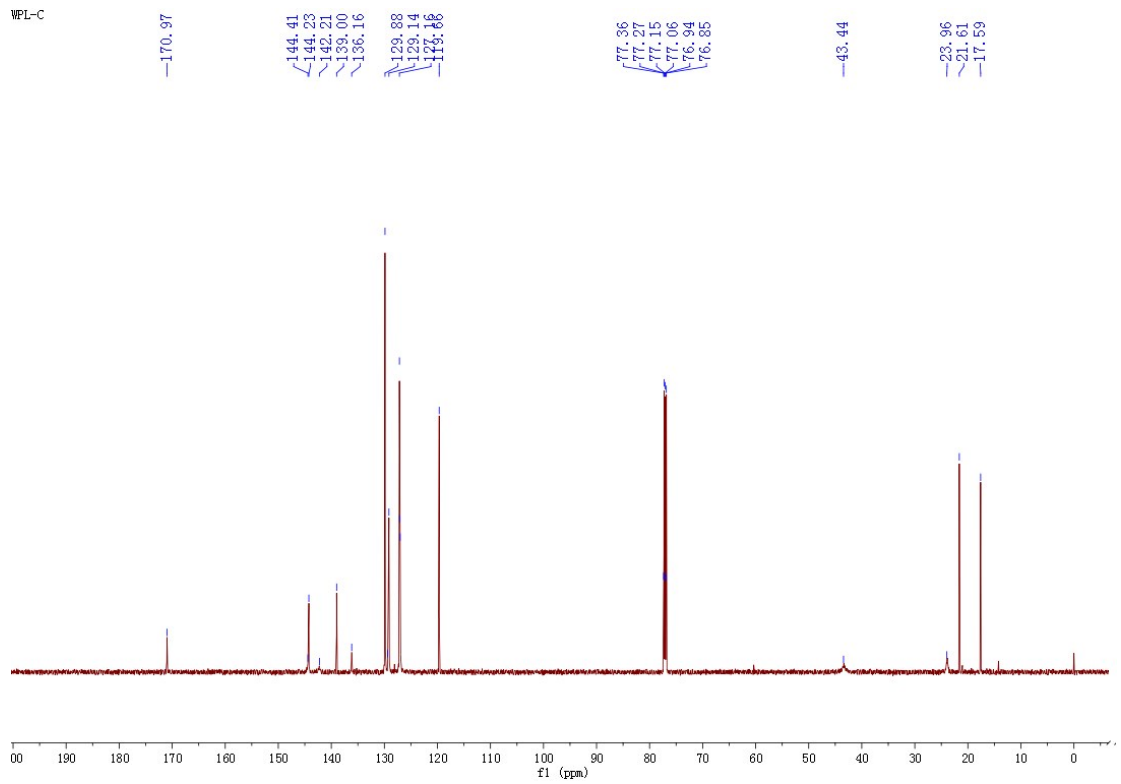


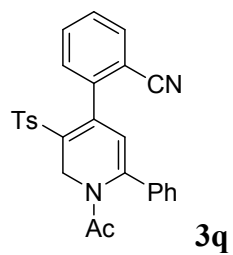
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WFL-H

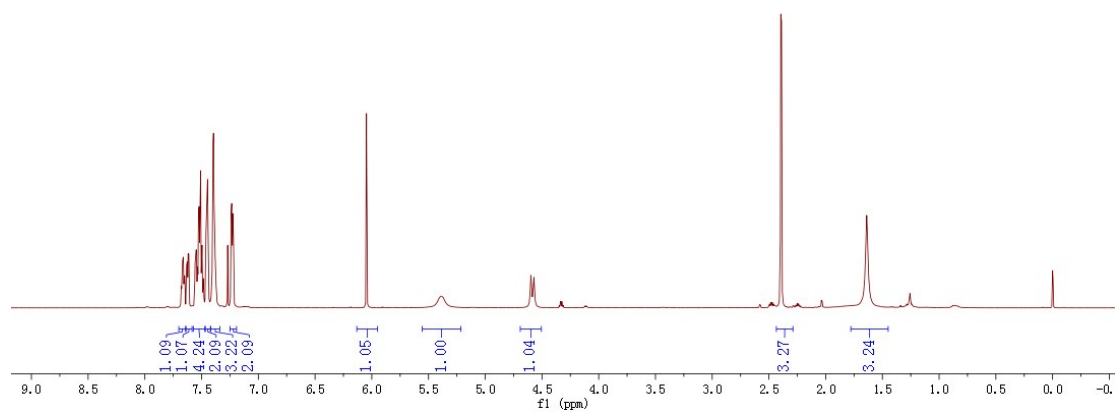


WFL-C

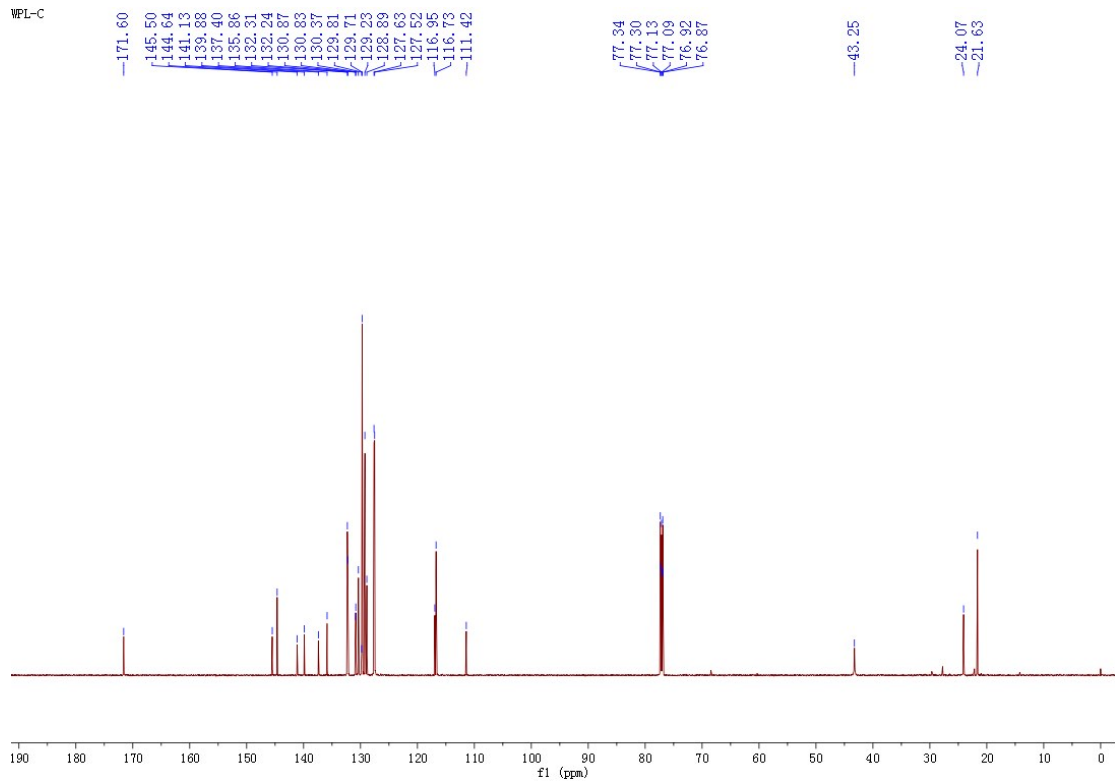


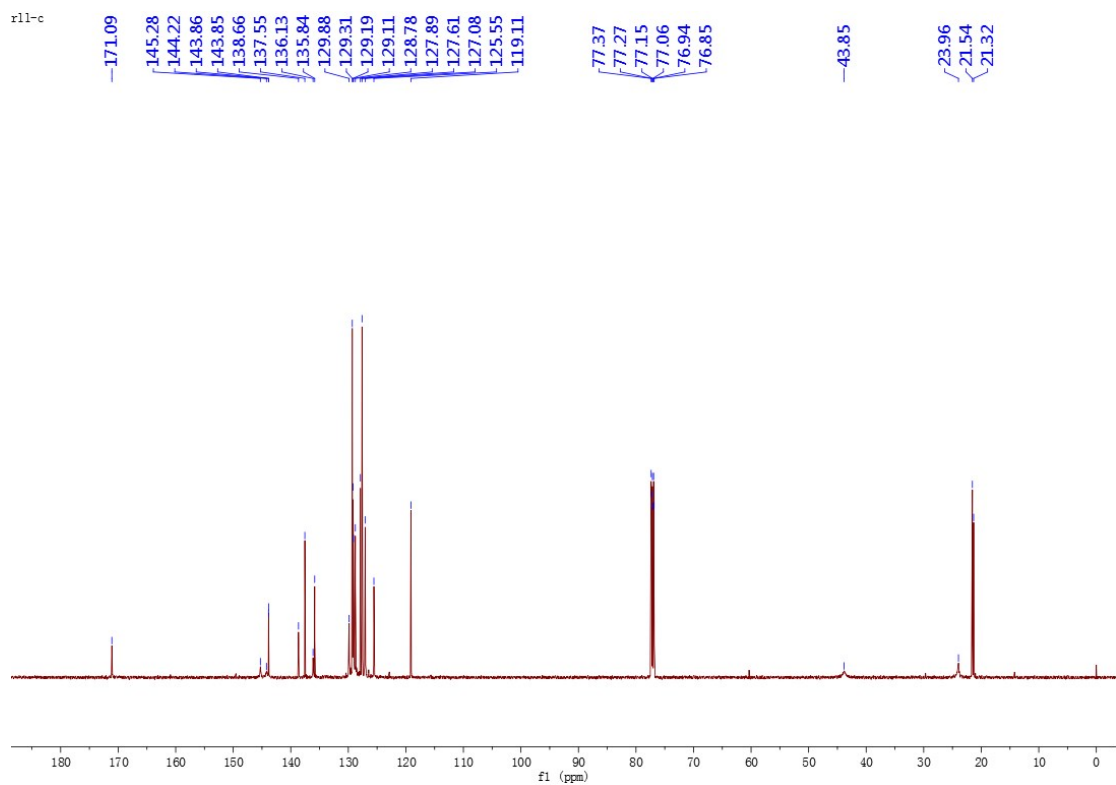
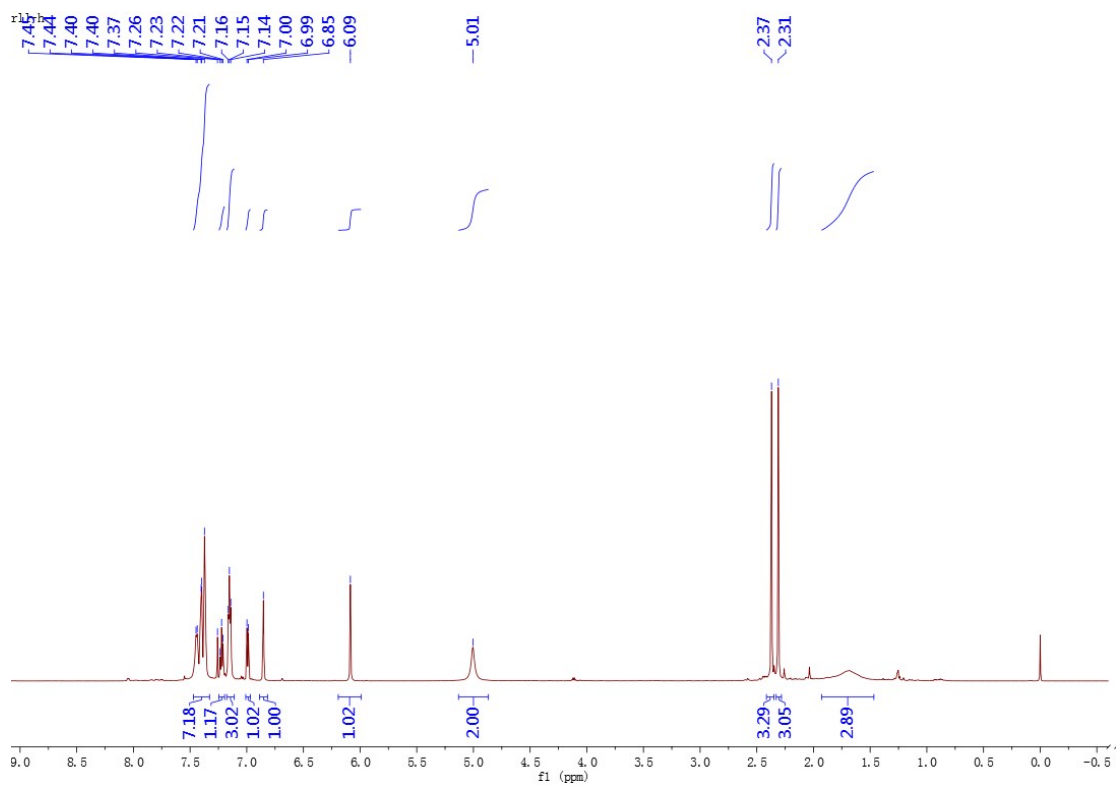
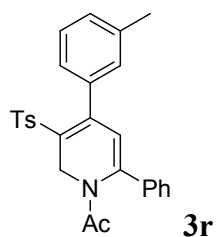


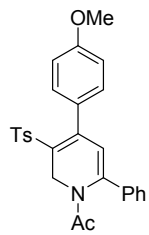
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WPL-C

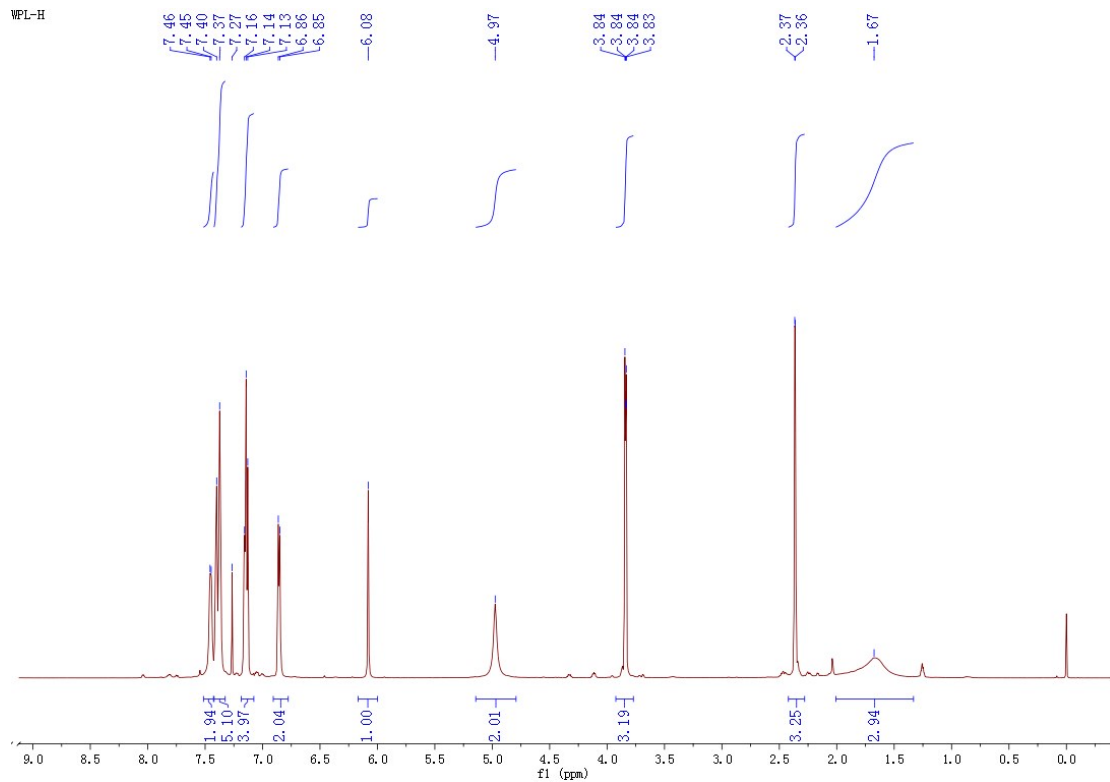




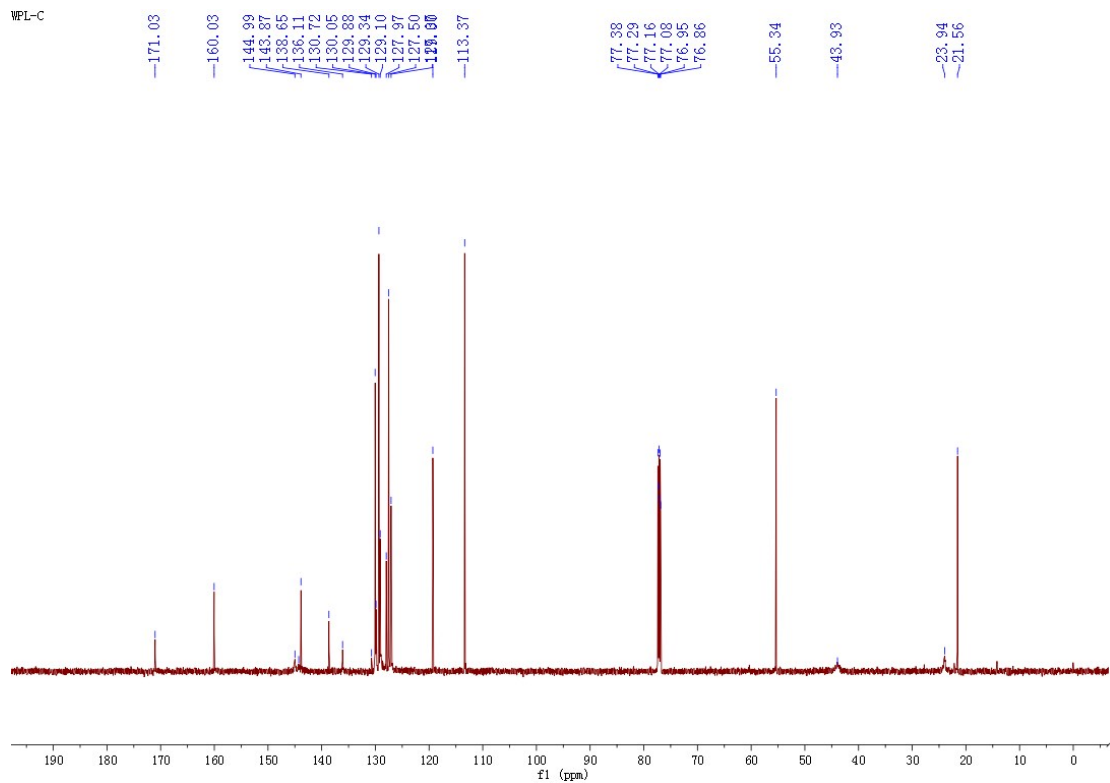


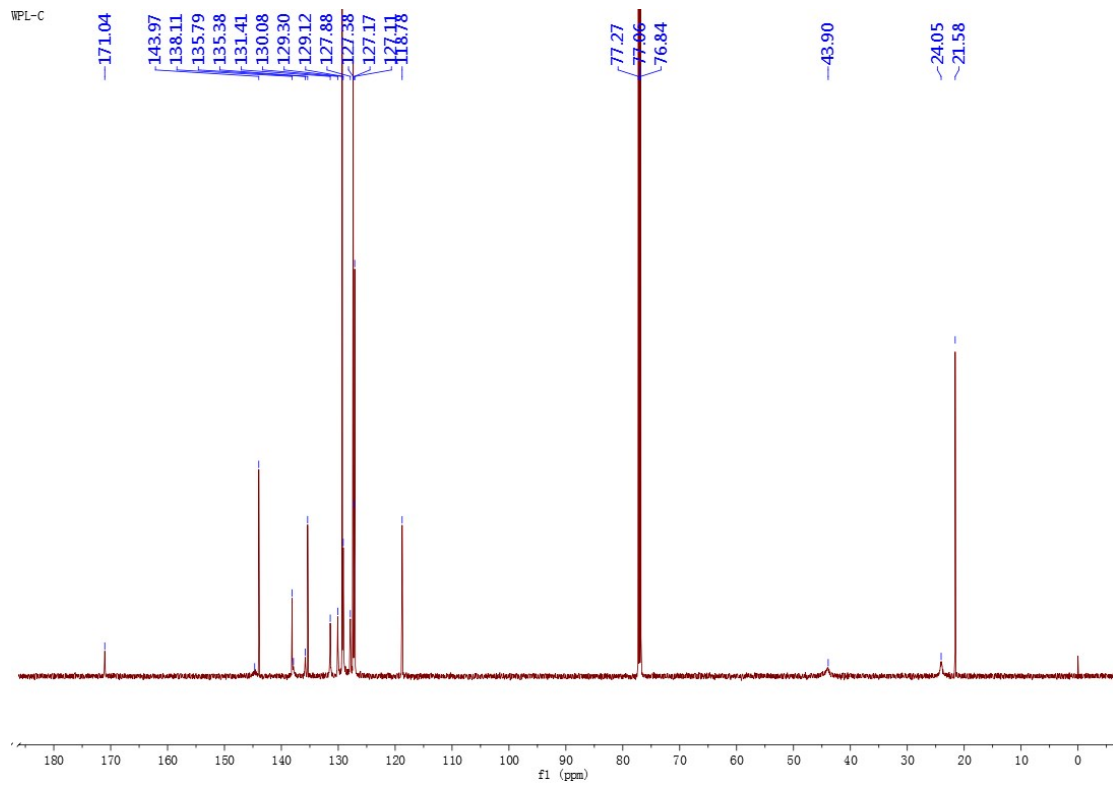
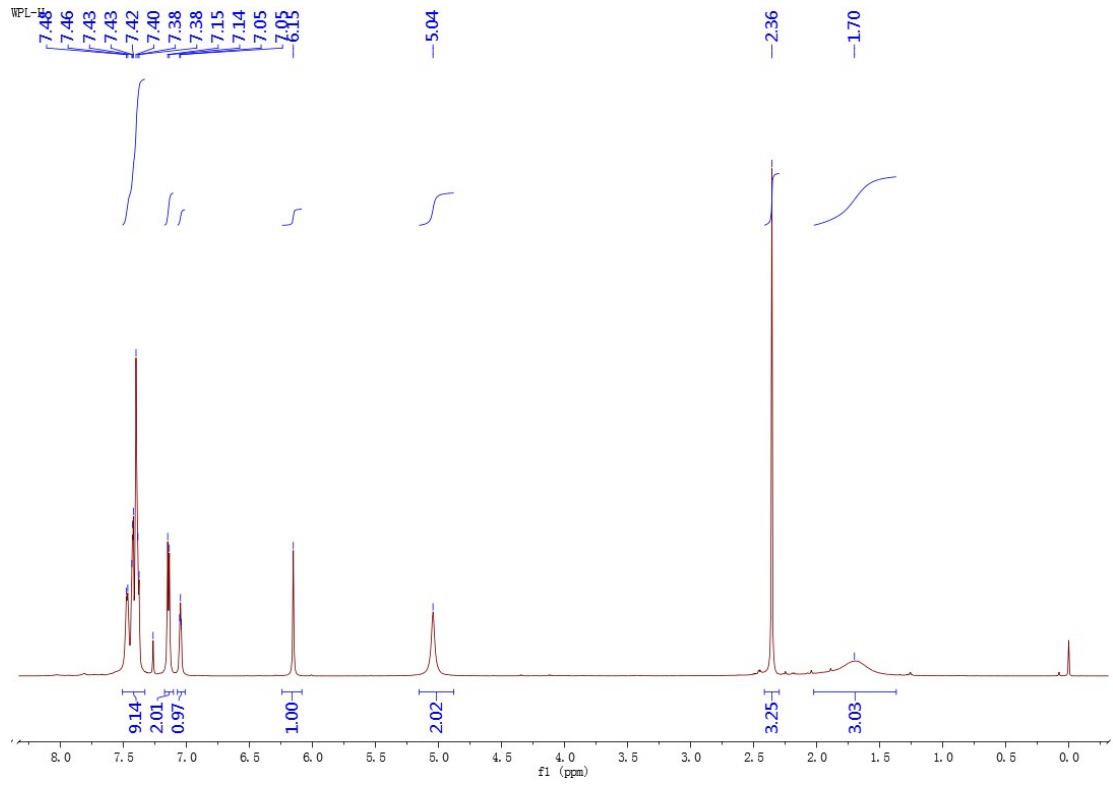
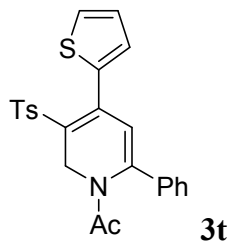
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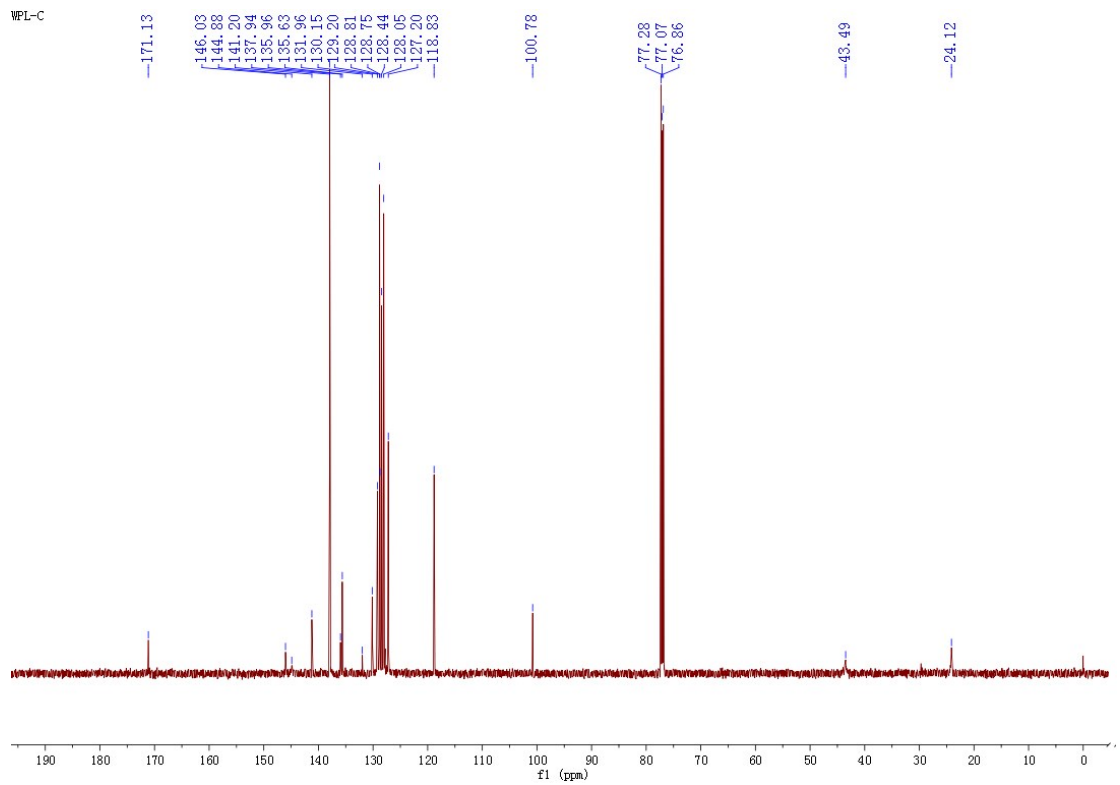
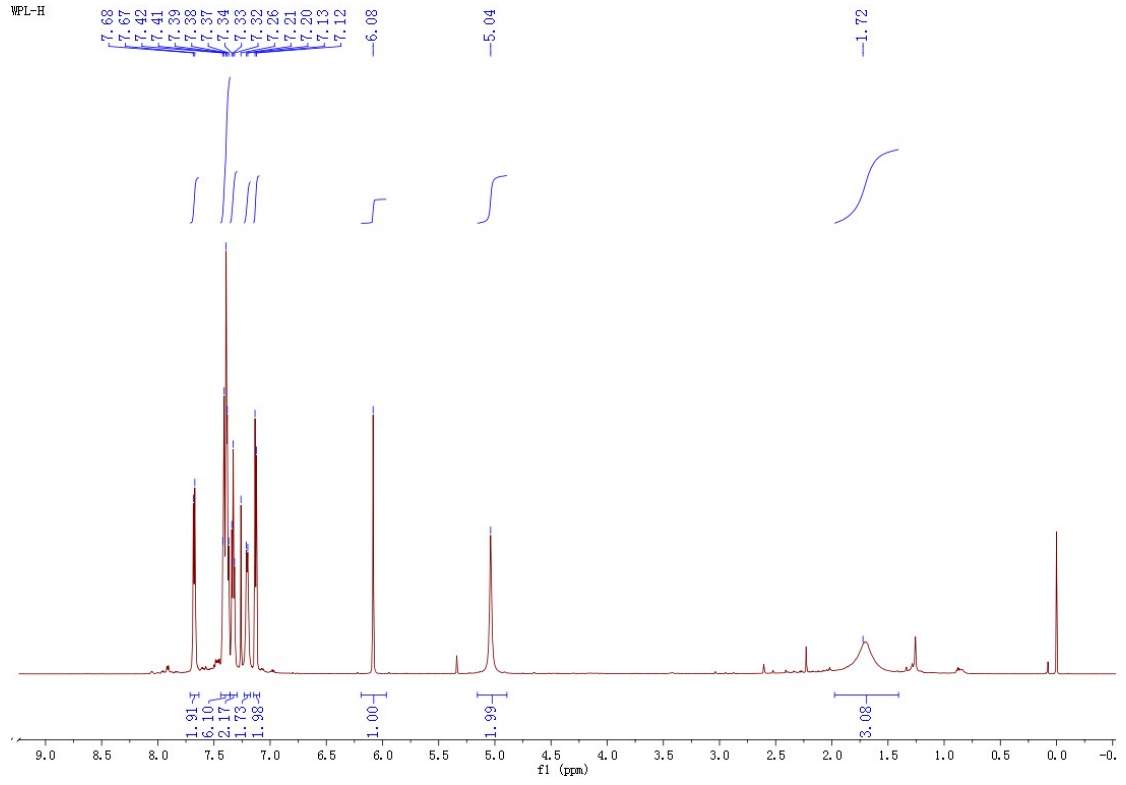
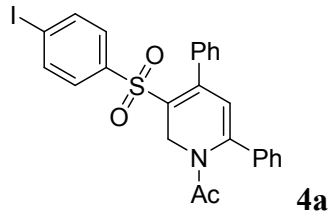
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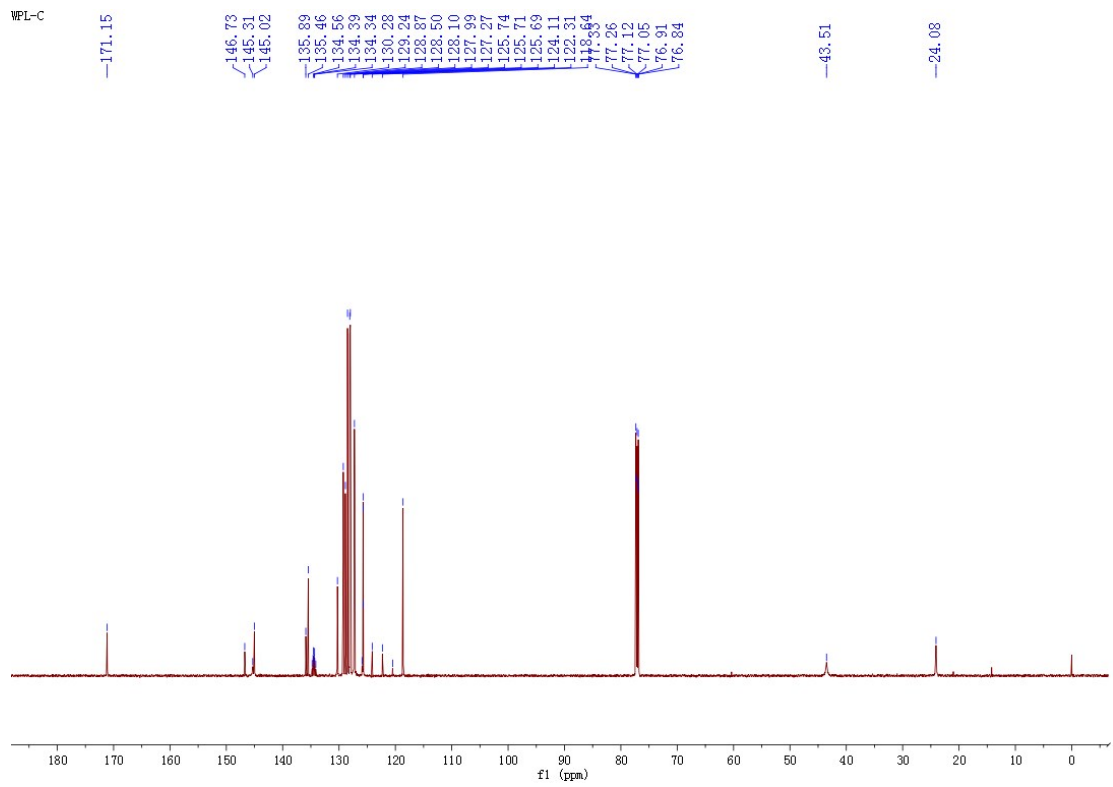
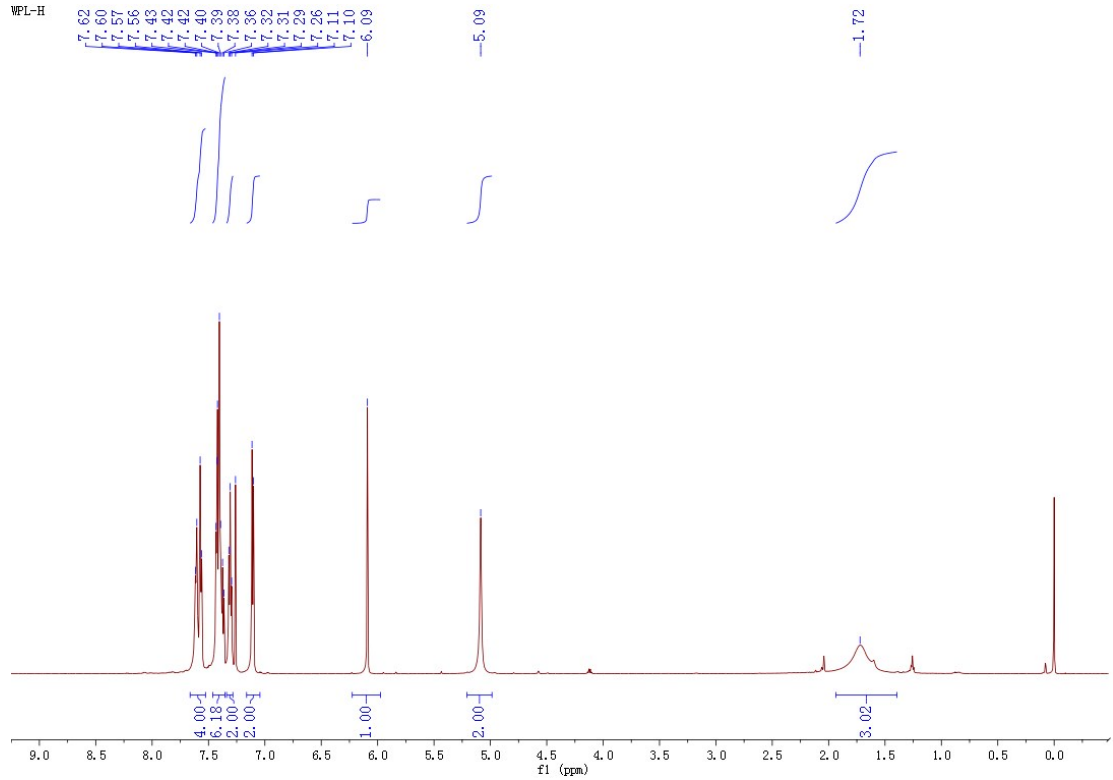
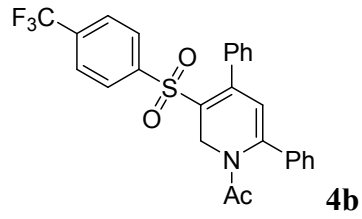


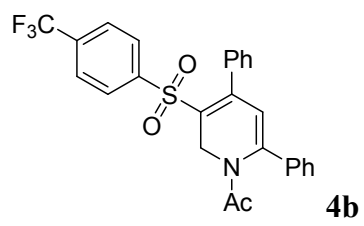
WPL-C











wp1-f

63.19
63.22

