

Supporting Information

for

A copper anchored on phosphorus g-C₃N₄ as a highly efficient photocatalyst for synthesis of *N*-arylpyridin-2-amines

Jia-Qi Di, Mo Zhang, Yu-Xuan Chen, Jin-Xin Wang, Shan-Shan Geng, Jia-Qi Tang and Zhan-Hui Zhang*

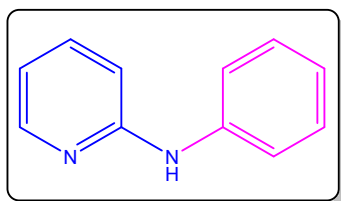
Hebei Key Laboratory of Organic Functional Molecules, National Demonstration Center for Experimental Chemistry Education, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, P. R. China.

Table of Contents

Spectra data of all products.....	S2-S10
Copies of NMR spectra for all products.....	S11-
	S46

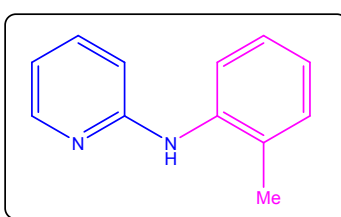
Spectra data of products:

N-Phenylpyridin-2-amine (**3a**)



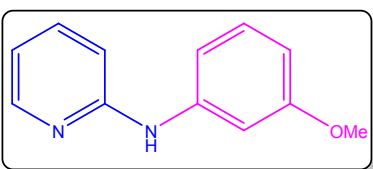
White solid, m.p.: 107-108 °C; IR (KBr): 3475, 1327, 1279, 1253, 1153, 1074, 1028, 767, 750, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 7.54 (m, 1H), 7.38 (d, *J* = 4.8 Hz, 4H), 7.09 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.83–6.76 (m, 1H), 6.71 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 148.3, 140.4, 137.8, 129.2, 122.7, 120.2, 115.0, 108.1 ppm; ESI-MS: *m/z* = 171 (M + H)⁺.

N-(*o*-Tolyl)pyridin-2-amine (**3b**)



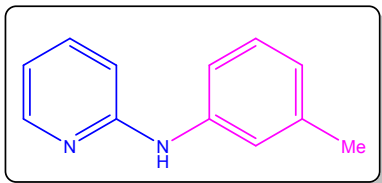
Brown solid, m.p. : 75-76 °C; IR (KBr): 3428, 2918, 1433, 1156, 1072, 779, 704, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (t, *J* = 4.4 Hz, 1H), 7.43 (m, 2H), 7.21 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.73–6.58 (m, 2H), 6.46 (s, 1H), 2.27 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 148.3, 138.4, 137.9, 131.5, 131.0, 126.8, 124.4, 122.9, 114.5, 107.5, 19.2 ppm; ESI-MS: *m/z* = 185 (M + H)⁺.

N-(3-Methoxyphenyl)pyridin-2-amine (**3c**)



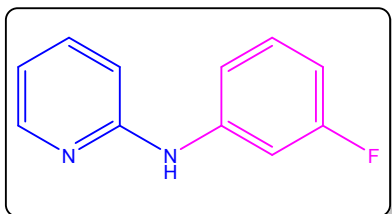
Semi solid; IR (KBr): 3470, 1595, 1151, 767 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 7.57–7.43 (m, 1H), 7.30–7.16 (m, 1H), 6.98–6.82 (m, 4H), 6.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.50–6.32 (m, 1H), 3.81 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 155.8, 148.2, 141.6, 137.9, 123.0, 115.2, 108.2, 108.1, 101.7, 55.3, 29.7 ppm; ESI-MS: *m/z* = 201 (M + H)⁺.

N-(*m*-Tolyl)pyridin-2-amine (**3d**)



Semi solid; IR (KBr): 3422, 1577, 1150, 1075, 763 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 2H), 6.89 (t, *J* = 7.6 Hz, 3H), 6.72 (t, *J* = 6.0 Hz, 1H), 2.35 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 147.7, 140.1, 139.3, 137.8, 128.9, 124.0, 117.2, 114.9, 108.4, 19.2 ppm; ESI-MS: *m/z* = 185 (M + H)⁺.

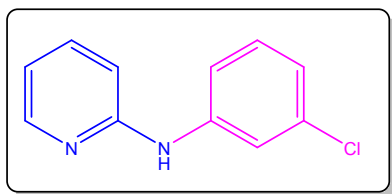
N-(3-Fluorophenyl)pyridin-2-amine (**3e**)



Yellow solid, m.p.: 65-66 °C; IR (KBr): 3421, 1588, 1338, 1152, 856, 768, 736, 682 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.23–8.20 (m, 1H),

7.50 (m, 1H), 7.40 (s, 1H), 7.23 (m, 2H), 7.03 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.86 (m, 1H), 6.80–6.62 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 162.2, 155.4, 148.1, 142.5, 138.0, 130.6(d, $J_{\text{C-F}} = 138.0$ Hz), 115.6(d, $J_{\text{C-F}} = 23.0$ Hz), 115.0(d, $J_{\text{C-F}} = 21.2$ Hz), 109.0, 106.4 ppm; ESI-MS: $m/z = 189$ ($\text{M} + \text{H}$) $^+$.

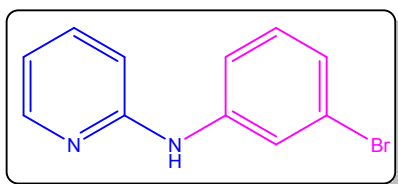
N-(3-Chlorophenyl)pyridin-2-amine (**3f**)



Yellow solid, m.p.: 102–103 °C; IR (KBr): 3462, 1640, 1479, 767, 747 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.32–8.15 (m, 1H), 7.64–7.47 (m, 2H), 7.43 (s, 1H), 7.24–7.11 (m, 2H), 6.99 (m, 1H), 6.87 (m, 1H), 6.76 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 148.3, 142.1,

138.2, 134.8, 130.2, 122.5, 119.4, 117.8, 115.7, 109.2 ppm; ESI-MS: $m/z = 205$ ($\text{M} + \text{H}$) $^+$.

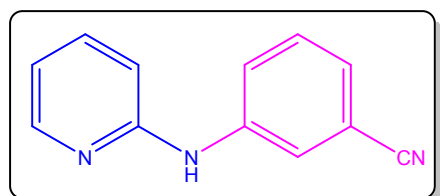
N-(3-Bromophenyl)pyridin-2-amine (**3g**)



Brown yellow solid, m.p.: 87–88 °C; IR (KBr): 3409, 2184, 1584, 1478, 1441, 991, 767 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.25–8.18 (m, 1H), 7.54–7.45 (m, 1H), 7.22–7.13 (m, 3H), 7.10–6.97 (m, 3H), 6.92 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 155.0,

141.7, 138.3, 138.10, 130.5, 122.9, 122.6, 122.4, 115.8, 114.8, 109.3 ppm; ESI-MS: $m/z = 249$ ($\text{M} + \text{H}$) $^+$.

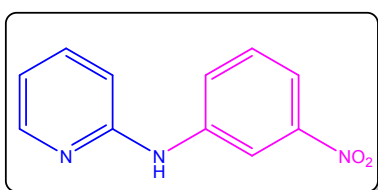
3-(Pyridin-2-ylamino)benzonitrile (**3h**)



White solid, m.p.: 121–122 °C; IR (KBr): 3367, 2230, 1593, 771, 734, 682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, $J = 4.8, 0.8$ Hz, 1H), 7.96–7.86 (m, 1H), 7.61–7.53 (m, 2H), 7.40 (m, 1H), 7.29–7.23 (m, 1H), 6.85 (m, 3H) ppm; ^{13}C NMR (100 MHz,

CDCl_3) δ 154.6, 147.9, 141.5, 138.3, 130.2, 125.1, 123.3, 121.8, 119.0, 116.5, 113.0, 110.1 ppm; ESI-MS: $m/z = 196$ ($\text{M} + \text{H}$) $^+$.

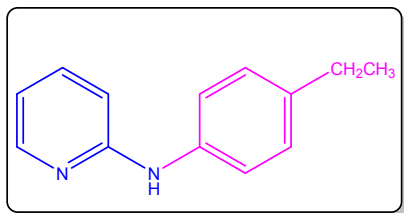
N-(3-Nitrophenyl)pyridin-2-amine (**3i**)



Yellow solid, m.p.: 115–116 °C; IR (KBr): 3426, 1604, 1530, 1515, 1344, 878, 734 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 8.26 (d, $J = 3.2$ Hz, 1H), 7.75 (m, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ

154.6, 148.9, 148.0, 142.0, 138.2, 133.1, 129.8, 124.5, 116.4, 113.0, 110.2 ppm; ESI-MS: $m/z = 216$ ($\text{M} + \text{H}$) $^+$.

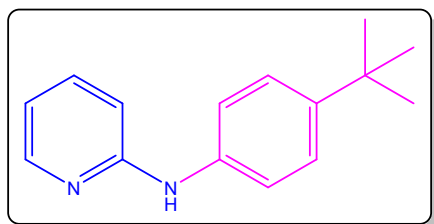
N-(4-Ethylphenyl)pyridin-2-amine (**3j**)



Yellow solid, m.p.: 108-109 °C; IR (KBr): 3390, 2944, 1598, 1422, 1230, 861, 788, 662 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 1H), 6.73–6.63 (m, 1H), 6.57 (s, 1H), 2.63 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100

MHz, CDCl_3) δ 156.5, 139.3, 137.9, 128.7, 121.2, 121.0, 114.6, 112.5, 107.9, 28.3, 15.8 ppm; ESI-MS: $m/z = 199$ (M + H) $^+$.

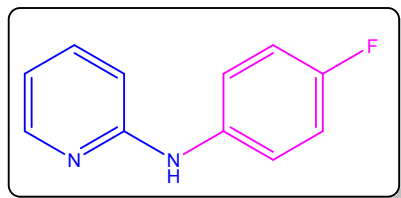
***N*-(4-(*tert*-Butyl)phenyl)pyridin-2-amine (3k)**



Brown solid, m.p.: 114-115 °C; IR (KBr): 3384, 1594, 1571, 1455, 1363, 1335, 1280, 1267, 898, 852, 841, 809, 770, 739 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.37–7.31 (m, 2H), 7.23 (d, $J = 6.8$ Hz, 2H), 7.05 (s, 1H), 6.86 (d,

$J = 8.4$ Hz, 1H), 6.68 (s, 1H), 1.32 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 156.5, 148.1, 146.1, 138.0, 137.7, 126.0, 120.7, 114.7, 108.1, 34.4, 31.4 ppm; ESI-MS: $m/z = 227$ (M + H) $^+$.

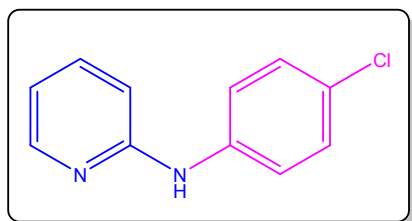
***N*-(4-Fluorophenyl)pyridin-2-amine (3l)**



Brown solid, m.p.: 122-123 °C; IR (KBr): 3415, 1588, 1331, 1265, 1152, 878, 768, 738, 682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.30 (dd, $J = 8.4, 4.8$ Hz, 2H), 7.03 (m, 2H), 6.73 (s, 2H), 6.62 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3)

δ 159.0 (d, $J_{\text{C-F}} = 240.7$ Hz), 156.6, 148.1, 137.9, 123.1, 116.1, 115.9 (d, $J_{\text{C-F}} = 22.3$ Hz), 114.8, 107.9 ppm; ESI-MS: $m/z = 189$ (M + H) $^+$.

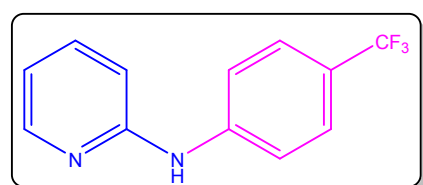
***N*-(4-Chlorophenyl)pyridin-2-amine (3m)**



Yellow solid, m.p.: 99-100 °C; IR (KBr): 3427, 1629, 1589, 1574, 1330, 1287, 1157, 1089, 1073, 840, 809, 767, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 4.8$ Hz, 1H), 7.56–7.39 (m, 1H), 7.32–7.17 (m, 4H), 7.07 (d, $J = 4.0$ Hz, 1H), 6.88–6.67 (m, 2H) ppm; ^{13}C

NMR (100 MHz, CDCl_3) δ 155.7, 148.1, 139.2, 138.0, 129.3, 127.42, 121.4, 115.4, 108.8 ppm; ESI-MS: $m/z = 205$ (M + H) $^+$.

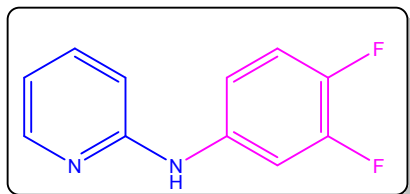
***N*-(4-(Trifluoromethyl)phenyl)pyridin-2-amine (3n)**



White solid, m.p.: 94-95 °C; IR (KBr): 3471, 1605, 1327, 1167,

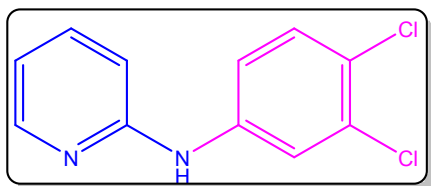
1152, 849, 819, 771, 732 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.27 (s, 1H), 7.57 (dd, $J = 12.9, 5.1$ Hz, 3H), 7.48 (d, $J = 8.6$ Hz, 2H), 7.01–6.79 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 148.3, 143.9, 138.0, 137.8, 126.5 (q, $J_{\text{C-F}} = 270.0$ Hz), 123.5 (q, $J_{\text{C-F}} = 33.0$ Hz), 118.3, 116.4, 109.7 ppm; ESI-MS: $m/z = 239$ ($\text{M} + \text{H}$) $^+$.

N-(3,4-Difluorophenyl)pyridin-2-amine (**3o**)



Yellow solid, m.p.: 101-102 $^{\circ}\text{C}$; IR (KBr): 3446, 1602, 1587, 1347, 1306, 1283, 1258, 1206, 1160, 1150, 789, 770, 753, 735, 654 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.39 (dd, $J = 10.8, 8.4$ Hz, 1H), 7.16–7.03 (m, 1H), 6.98 (s, 1H), 6.82–6.64 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 150.4 (d, $J_{\text{C-F}} = 245.0$ Hz), 148.1, 146.1 (d, $J_{\text{C-F}} = 242.0$ Hz), 138.0, 137.8, 137.2, 117.5, 115.7, 109.4, 108.7 ppm; ESI-MS: $m/z = 207$ ($\text{M} + \text{H}$) $^+$.

N-(3,4-Dichlorophenyl)pyridin-2-amine (**3p**)

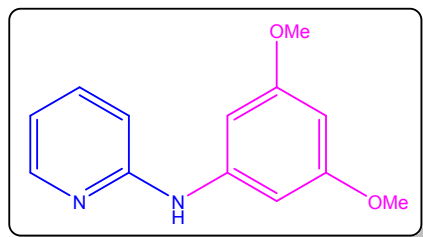


White solid, m.p.: 147-148 $^{\circ}\text{C}$; IR (KBr): 3482, 1592, 879, 845, 814, 761, 739 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.22 (s, 1H), 7.55 (dd, $J = 21.2, 14.2$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 1H), 7.19 (d, $J = 8.8$ Hz, 1H), 7.05 (s, 1H), 6.80 (d, $J = 7.2$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 148.1, 140.3, 138.1, 132.8, 130.6, 125.0, 120.9, 118.8, 116.1, 109.5 ppm; ESI-MS: $m/z = 240$ ($\text{M} + \text{H}$) $^+$.

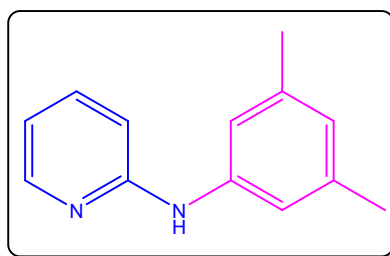
N-(3,5-Dimethoxyphenyl)pyridin-2-amine (**3q**)

White solid, m.p.: 107-108 $^{\circ}\text{C}$; IR (KBr): 3470, 1592, 1455, 1203, 1151, 770 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.52 (t, $J = 8$ Hz, 1H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.75 (s, 1H), 6.51 (s, 2H), 6.19 (s, 1H), 3.79 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 161.5, 155.5, 148.4, 147.4, 141.9, 138.3, 98.7, 95.2, 55.3, 29.7 ppm; ESI-MS: $m/z = 231$ ($\text{M} + \text{H}$) $^+$.

N-(3,5-dimethylphenyl)pyridin-2-amine (**3r**)



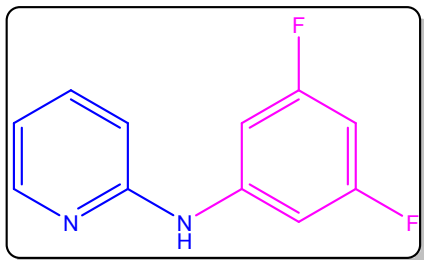
δ 8.20 (s, 1H), 7.65–7.42 (m, 1H), 6.92



Brown solid, m.p.: 72-73 $^{\circ}\text{C}$; IR (KBr): 3446, 2922, 1595, 1443, 1339, 835, 770 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) (s, 3H), 6.71 (s, 3H), 2.31 (s,

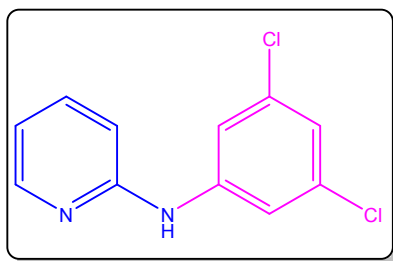
6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 148.3, 140.3, 139.0, 137.8, 124.9, 118.5, 114.9, 108.3, 21.5 ppm; ESI-MS: $m/z = 199$ ($\text{M} + \text{H}$) $^+$.

N-(3,5-Difluorophenyl)pyridin-2-amine (**3s**)



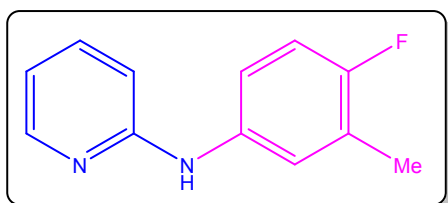
Yellow solid, m.p.: 109-110 °C; IR (KBr): 3438, 1637, 1585, 1545, 1285, 1155, 1111, 835, 804, 763, 738, 718, 670 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.31–8.15 (m, 1H), 7.60–7.37 (m, 2H), 6.96 (d, $J = 9.2$ Hz, 2H), 6.91–6.71 (m, 2H), 6.41 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 163.6 (d, $J_{\text{C-F}} = 244.0$ Hz), 143.3, 138.0 (d, $J_{\text{C-F}} = 17.0$ Hz), 116.3 (d, $J_{\text{C-F}} = 17.8$ Hz), 110.0 (d, $J_{\text{C-F}} = 19.0$ Hz), 101.5, 97.2, 96.9, 96.7 ppm; ESI-MS: $m/z = 207$ ($\text{M} + \text{H}$) $^+$.

N-(3,5-Dichlorophenyl)pyridin-2-amine (**3t**)



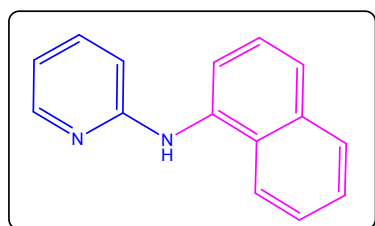
Yellow solid, m.p.: 162-163 °C; IR (KBr): 3462, 1640, 1444, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 4.4$ Hz, 1H), 7.56 (m, 1H), 7.35 (d, $J = 1.2$ Hz, 2H), 6.97 (s, 1H), 6.83 (m, 2H), 6.62 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 148.2, 142.7, 138.1, 135.3, 121.9, 119.7, 116.5, 110.0 ppm; ESI-MS: $m/z = 240$ ($\text{M} + \text{H}$) $^+$.

N-(4-Fluoro-3-methylphenyl)pyridin-2-amine (**3u**)



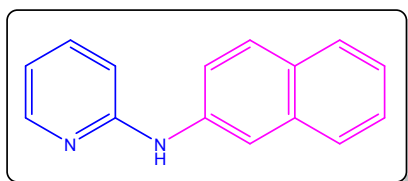
Yellow solid, m.p.: 73-74 °C; IR (KBr): 3424, 2926, 1583, 1461, 1442, 1336, 1279, 1210, 1150, 882, 810, 763, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 4.4$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.18–7.06 (m, 2H), 6.97 (m, 2H), 6.84–6.38 (m, 2H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 157.6 (d, $J_{\text{C-F}} = 240.0$ Hz), 156.7, 148.2, 137.9, 136.1, 132.3, 128.9, 125.5, 115.5, 114.6 (d, $J_{\text{C-F}} = 14.0$ Hz), 107.7 (d, $J_{\text{C-F}} = 18.0$ Hz), 14.6 ppm; ESI-MS: $m/z = 203$ ($\text{M} + \text{H}$) $^+$.

N-(Naphthalen-1-yl)pyridin-2-amine (**3v**)



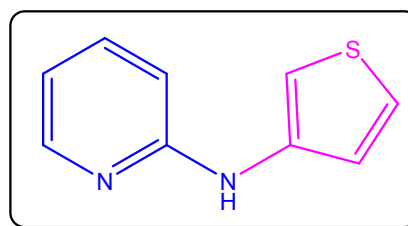
Yellow solid, m.p.: 102-103 °C; IR (KBr): 3474, 1632, 1439, 722, 458 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.61–7.45 (m, 5H), 6.92 (s, 1H), 6.71 (t, $J = 5.6$ Hz, 1H), 6.62 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 157.7, 148.6, 137.9, 136.0, 134.7, 129.2, 128.5, 126.5, 125.4, 122.4, 120.3, 114.8, 114.7, 107.7 ppm; ESI-MS: $m/z = 221$ ($\text{M} + \text{H}$) $^+$.

***N*-(Naphthalen-2-yl)pyridin-2-amine (3w)**



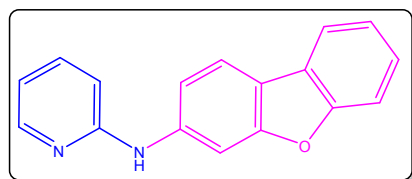
Light brown solid; m.p.: 138-139 °C; IR (KBr): 3462, 1597, 812, 743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (s, 1H), 7.86–7.68 (m, 4H), 7.54 (m, 1H), 7.47–7.31 (m, 3H), 6.98 (d, $J = 8.4$ Hz, 1H), 6.79 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 148.4, 138.0, 134.3, 130.0, 129.1, 127.7, 127.6, 127.1, 127.0, 124.5, 121.2, 115.5 ppm; ESI-MS: $m/z = 221$ (M + H) $^+$.

***N*-(Thiophen-3-yl)pyridin-2-amine (3x)**



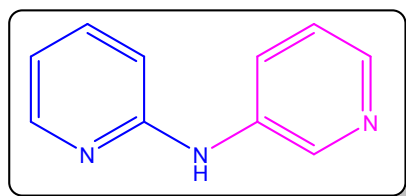
Semi solid, IR (KBr): 3428, 1602, 1481, 1441, 1283, 768 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, $J = 4.8, 1.2$ Hz, 1H), 7.51–7.45 (m, 1H), 7.30–7.20 (m, 3H), 6.99 (dd, $J = 4.8, 1.2$ Hz, 2H), 6.84–6.61 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 148.1, 138.7, 137.8, 124.8, 123.0, 114.5, 108.2, 108.0 ppm; ESI-MS: $m/z = 176$ (M + H) $^+$.

***N*-(Dibenzo[*b,d*]furan-3-yl)pyridin-2-amine (3y)**



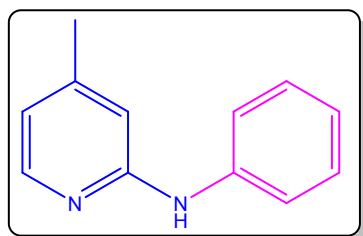
Yellow-brown solid, m.p.: 110-111°C; IR (KBr): 3447, 1636, 1603, 1522, 1450, 1289, 1189, 1120 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 4.4$ Hz, 1H), 8.02–7.89 (m, 2H), 7.62 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.60–7.54 (m, 2H), 7.50–7.42 (m, 1H), 7.40–7.29 (m, 2H), 7.21 (s, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 6.81 (dd, $J = 6.8, 5.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 155.8, 155.4, 147.9, 138.0, 130.9, 128.9, 127.2, 126.1, 124.7, 123.4, 123.0, 115.6, 114.4, 111.8, 109.6 ppm; ESI-MS: $m/z = 261$ (M + H) $^+$.

***N*-(Pyridin-3-yl)pyridin-2-amine (3z)**



White Semi-solid; IR (KBr): 3530, 3065, 3017, 1503, 1322, 1283, 1150, 860, 762, 738 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 4.1$ Hz, 1H), 7.49–7.35 (m, 1H), 7.30–7.23 (m, 3H), 7.06–6.93 (m, 1H), 6.90–6.77 (m, 2H), 6.66 (dd, $J = 8.8, 3.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 148.1, 140.4, 137.9, 129.3, 123.0, 120.5, 115.0, 108.3 ppm; ESI-MS: $m/z = 172$ (M + H) $^+$.

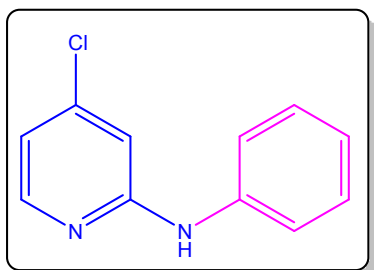
4-Methyl-*N*-phenylpyridin-2-amine (3aa)



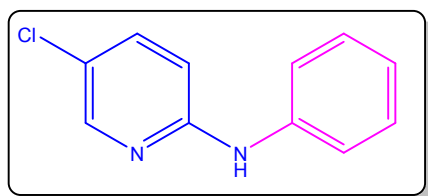
Yellow solid, m.p.: 106-107 °C; IR (KBr): 1614, 1592, 1568, 1558, 1488, 1471, 1441, 672 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 4.8$ Hz,

1H), 7.41–7.29 (m, 4H), 7.04 (t, $J = 6.4$ Hz, 1H), 6.71 (s, 1H), 6.63–6.39 (m, 2H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 148.9, 148.1, 140.6, 129.2, 122.8, 120.3, 116.6, 108.4, 21.2 ppm; ESI-MS: $m/z = 185$ ($\text{M} + \text{H}$) $^+$.

4-Chloro-*N*-phenylpyridin-2-amine (**3ab**)



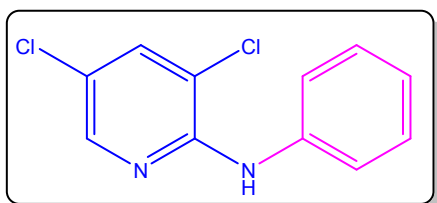
Yellow solid, m.p.: 102-103 °C; IR (KBr): 3335, 1578, 791, 760, 705 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (t, $J = 5.6$ Hz, 1H), 7.53 (dd, $J = 6.0, 3.6$ Hz, 1H), 7.39–7.29 (m, 4H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 1.2$ Hz, 1H), 6.71–6.69 (dd, $J = 5.6, 1.6$ Hz 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 157.5, 149.2, 145.3, 139.7, 129.5, 123.8, 121.5, 115.3, 107.5 ppm; ESI-MS: $m/z = 205$ ($\text{M} + \text{H}$) $^+$.



5-Chloro-*N*-phenylpyridin-2-amine (**3ac**)

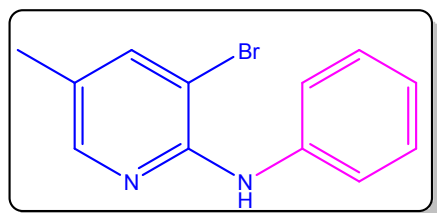
Pale yellow solid, m.p.: 100-101 °C; IR (KBr): 3325, 1603, 1588, 1574, 755, 707, 680 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 2.4$ Hz, 1H), 7.43 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.38–7.28 (m, 4H), 7.09 (d, $J = 6.8$ Hz, 1H), 7.05 (d, $J = 9.2$ Hz, 1H), 6.82 (d, $J = 8.8$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 146.6, 140.1, 137.4, 129.3, 123.1, 121.6, 120.4, 109.1 ppm; ESI-MS: $m/z = 205$ ($\text{M} + \text{H}$) $^+$.

3,5-Dichloro-*N*-phenylpyridin-2-amine (**3ad**)



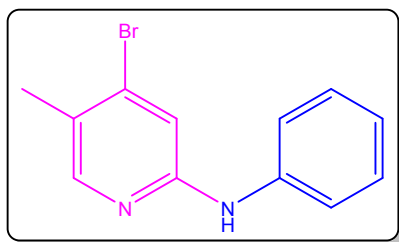
Semi-solid ; IR (KBr): 3462, 1599, 1578, 1560, 746, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.4$ Hz, 1H), 7.60 (dd, $J = 5.6, 1.2$ Hz, 3H), 7.36 (m, 2H), 7.09 (m, 1H), 6.95 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 149.7, 144.2, 139.2, 136.3, 131.0, 129.1, 123.2, 120.0, 116.1 ppm; ESI-MS: $m/z = 240$ ($\text{M} + \text{H}$) $^+$.

3-Bromo-5-methyl-*N*-phenylpyridin-2-amine (**3ae**)



Dark green solid, m.p.: 85-86 °C; IR (KBr): 3410, 1510, 1498, 1454, 623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 2.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.43–7.28 (m, 3H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.13 (s, 1H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 143.4, 140.3, 137.2, 128.9, 128.8, 122.5, 121.8, 119.6, 17.1 ppm; ESI-MS: $m/z = 264$ ($\text{M} + \text{H}$) $^+$.

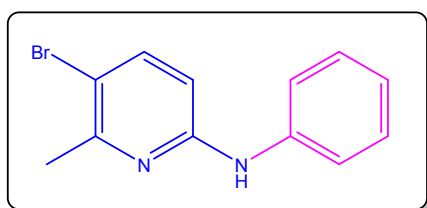
4-Bromo-5-methyl-*N*-phenylpyridin-2-amine (**3af**)



Yellow solid, m.p.: 113-114 °C; IR (KBr): 3447, 2926, 1590, 1567, 1464, 1437, 1235, 1189, 1173, 840, 767 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.37–7.28 (m, 4H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.76 (s, 1H), 6.64 (s, 1H), 2.30 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 155.2, 149.4, 148.2, 140.1, 129.2, 122.9, 120.4, 112.5,

109.9, 22.7 ppm; ESI-MS: *m/z* = 264 (M + H)⁺.

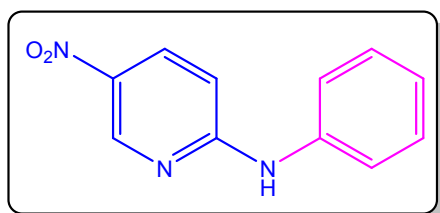
5-Bromo-6-methyl-*N*-phenylpyridin-2-amine (**3ag**)



Dark brown liquid, IR (KBr): 3404, 2925, 1575, 1436, 1392, 1141, 742, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, *J* = 8.8, 4.0 Hz, 1H), 7.35–7.26 (m, 4H), 7.07–7.02 (m, 1H), 6.71 (s, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 2.52 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃)

δ 155.5, 154.3, 141.3, 140.2, 129.4, 123.2, 120.4, 109.7, 107.0, 24.6 ppm; ESI-MS: *m/z* = 264 (M + H)⁺.

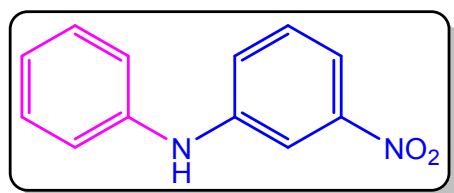
5-Nitro-*N*-phenylpyridin-2-amine (**3ah**)



Yellow solid, m.p.: 108-109 °C; IR (KBr): 3436, 1607, 1581, 1332, 1287, 1231, 1119, 827, 754, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.09 (d, *J* = 2.4 Hz, 1H), 8.25 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.47–7.33 (m, 5H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 9.2 Hz,

1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 146.8, 133.6, 129.9, 125.8, 122.8, 106.5 ppm; ESI-MS: *m/z* = 216 (M + H)⁺.

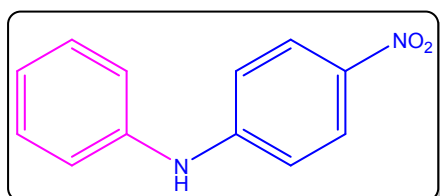
3-Nitro-*N*-phenylaniline (**5a**)



Yellow solid, m.p.: 87-88 °C; IR (KBr): 3379, 1599, 1337, 1279, 1093, 1076, 866, 829, 754, 697, 676, 665 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.40–7.24 (m, 4H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 6.8

Hz, 1H), 5.96 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 141.1, 130.2, 129.9, 123.4, 122.0, 120.0, 114.9, 110.4 ppm; ESI-MS: *m/z* = 215 (M + H)⁺.

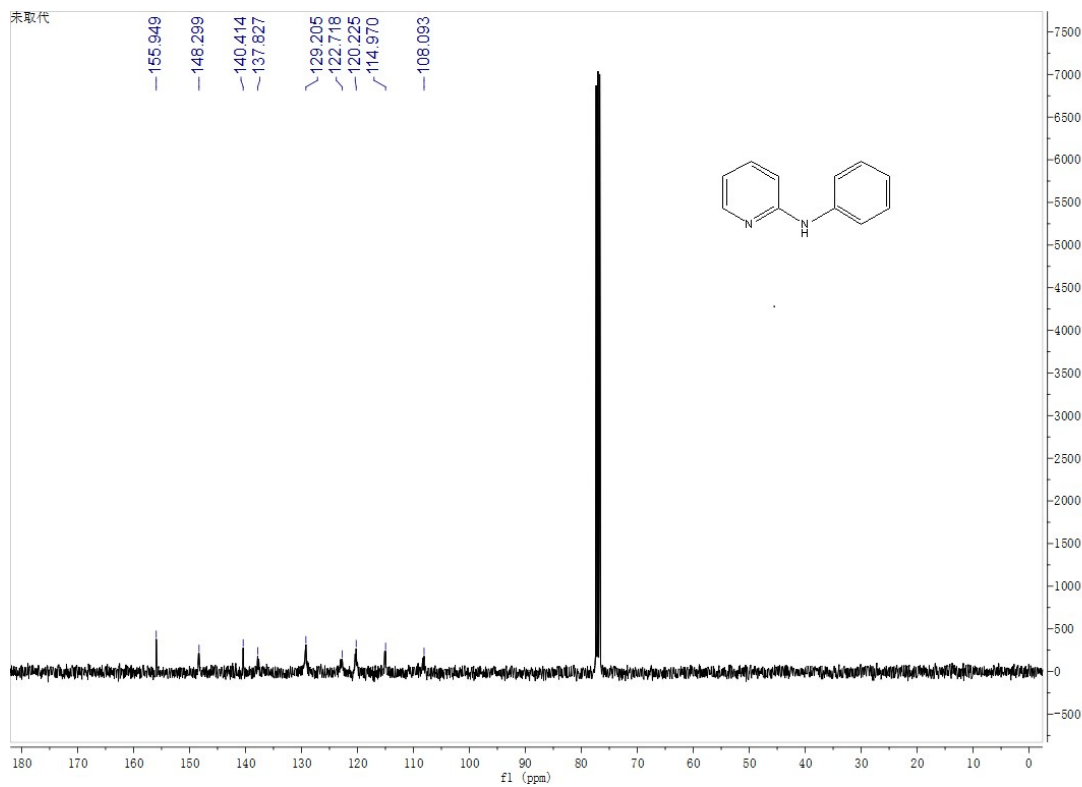
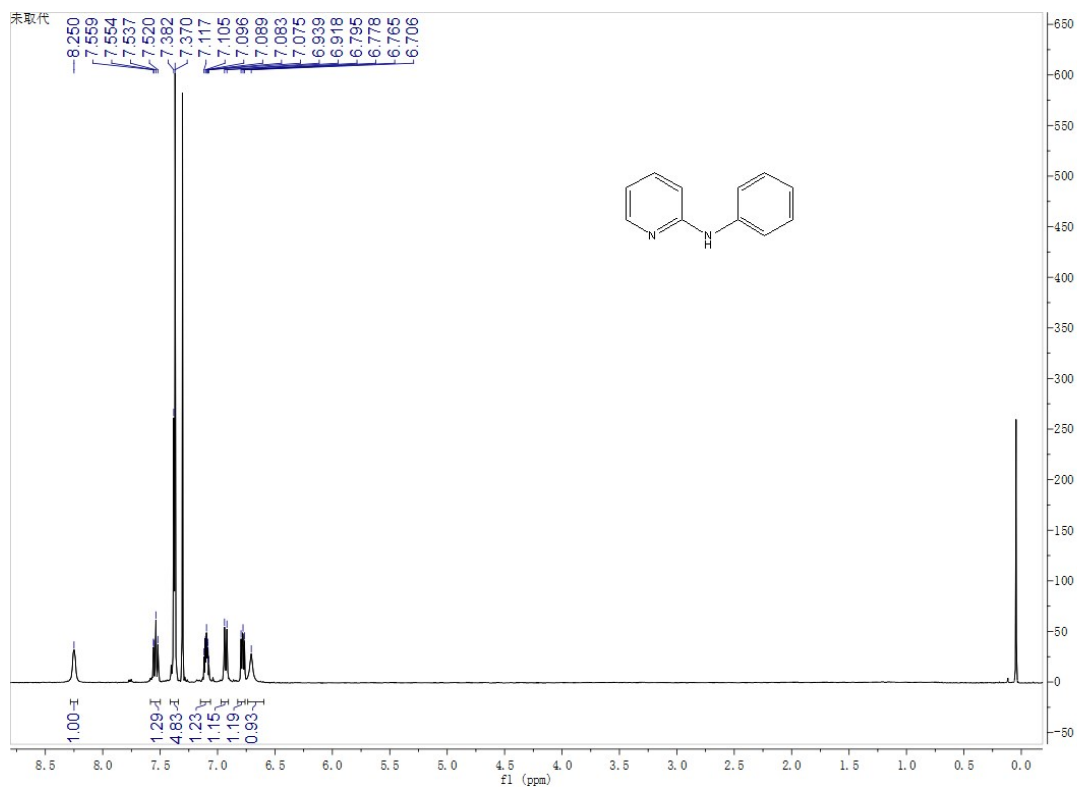
4-Nitro-*N*-phenylaniline (**5b**)



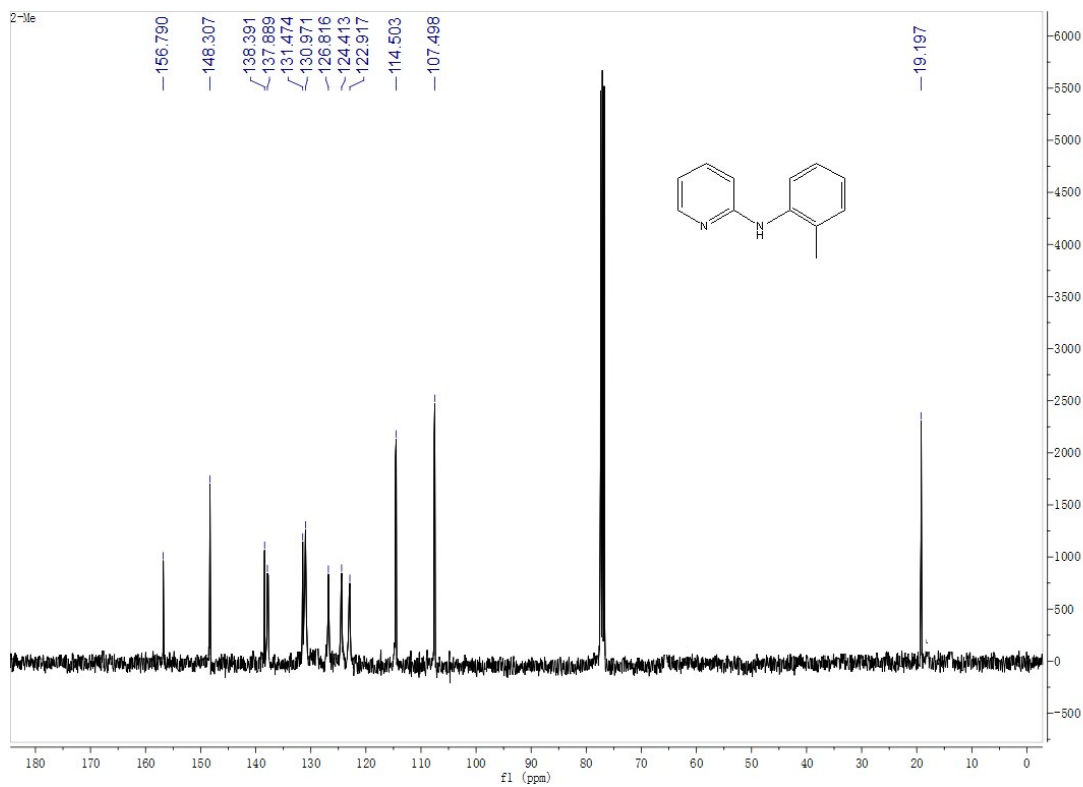
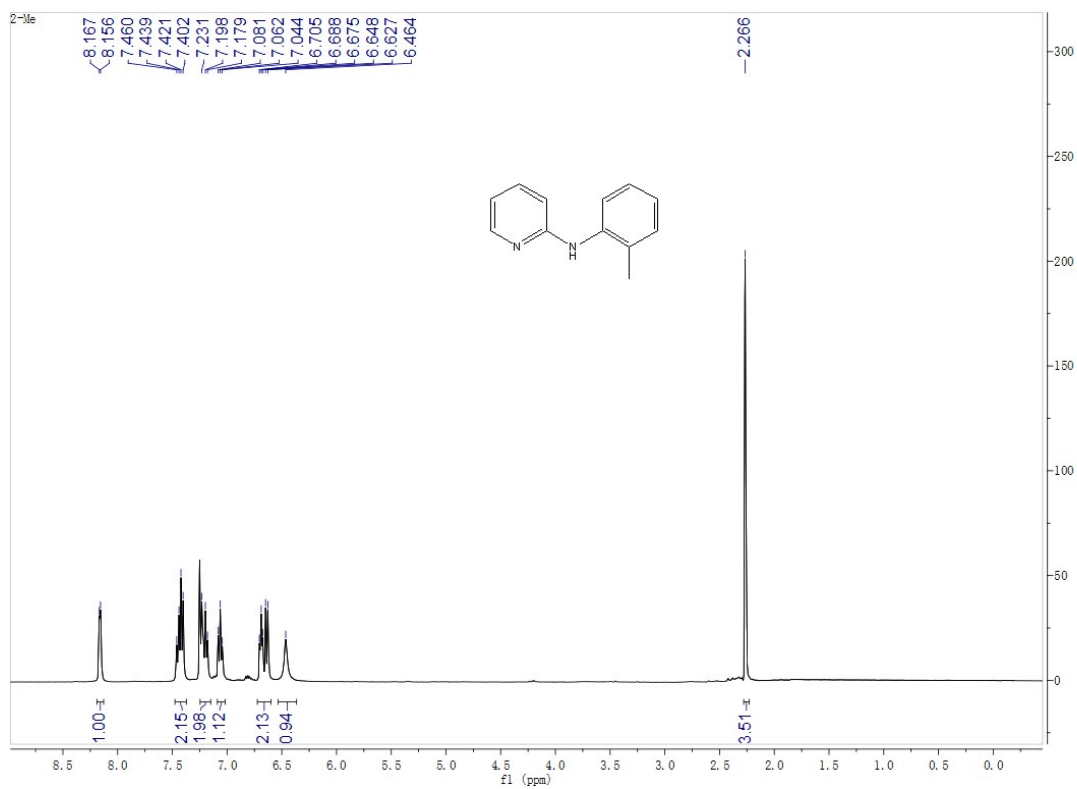
Yellow solid, m.p.: 132-133 °C; IR (KBr): 3343, 1604, 1585, 1303, 1186, 1112, 879, 842, 748, 691, 670 cm⁻¹; ¹H NMR (400

MHz, CDCl₃) δ 8.11 (d, *J* = 9.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.23–7.11 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.38 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 139.6, 139.4, 129.7, 126.2, 124.6, 121.9, 113.6 ppm; ESI-MS: *m/z* = 215 (M + H).

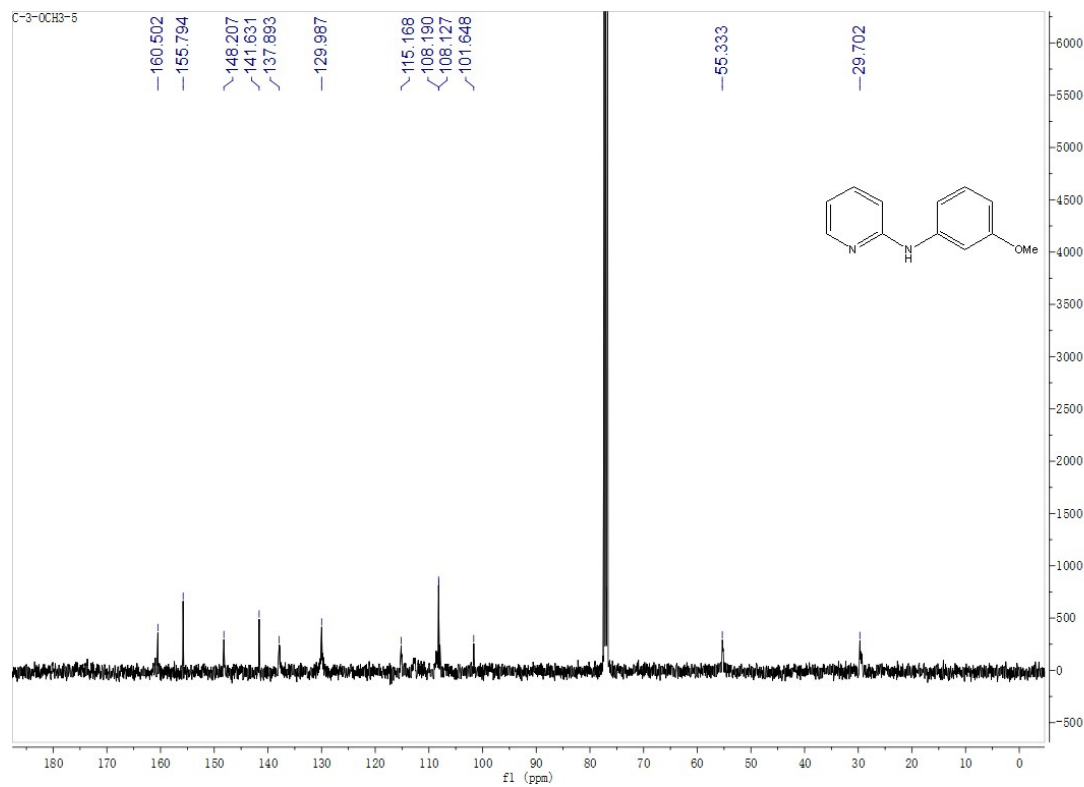
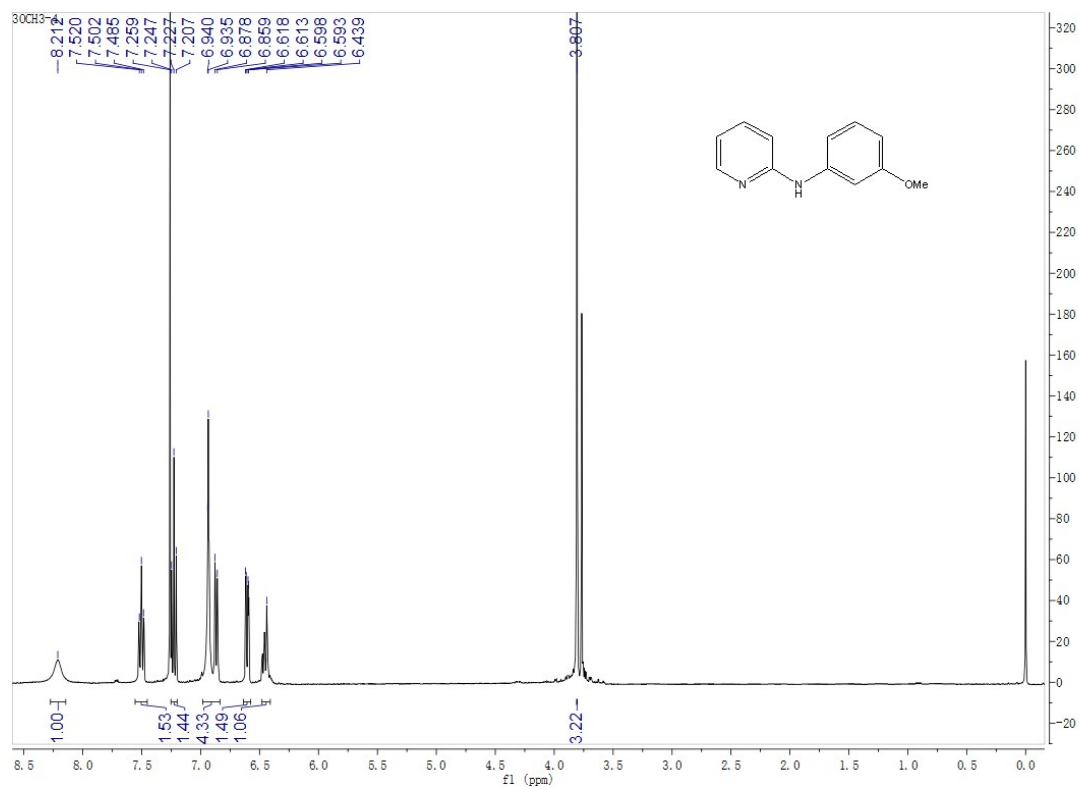
¹H NMR and ¹³C NMR of compound **3a**



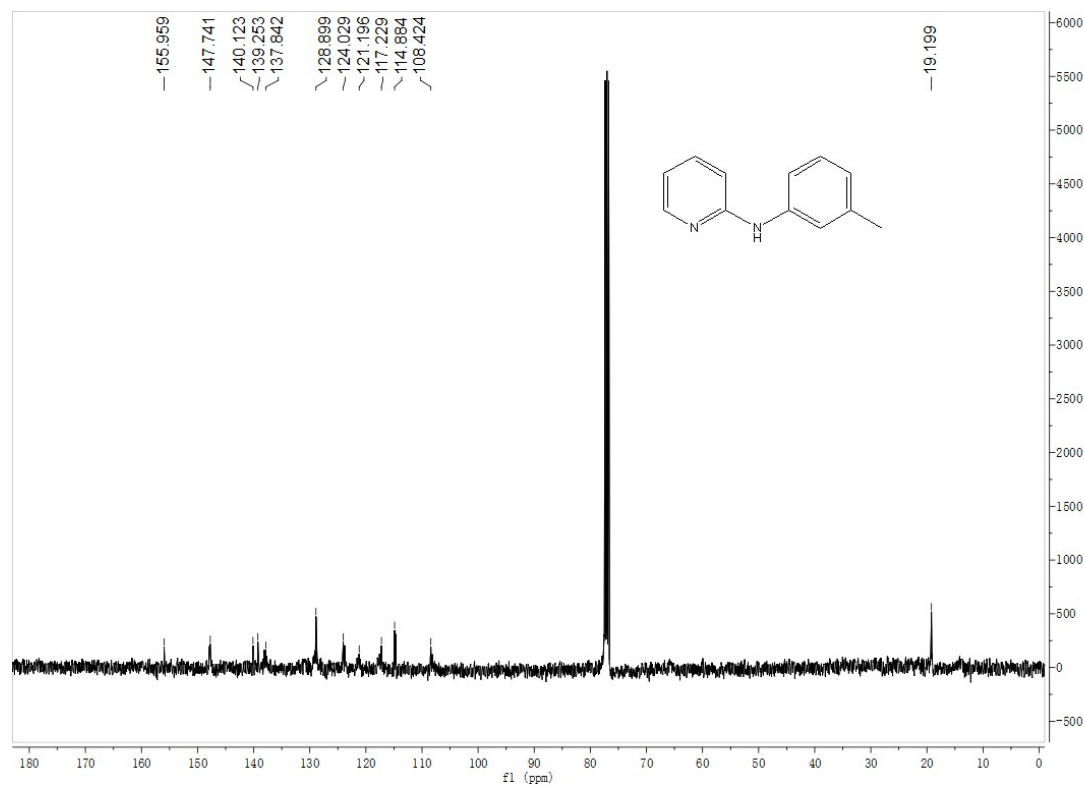
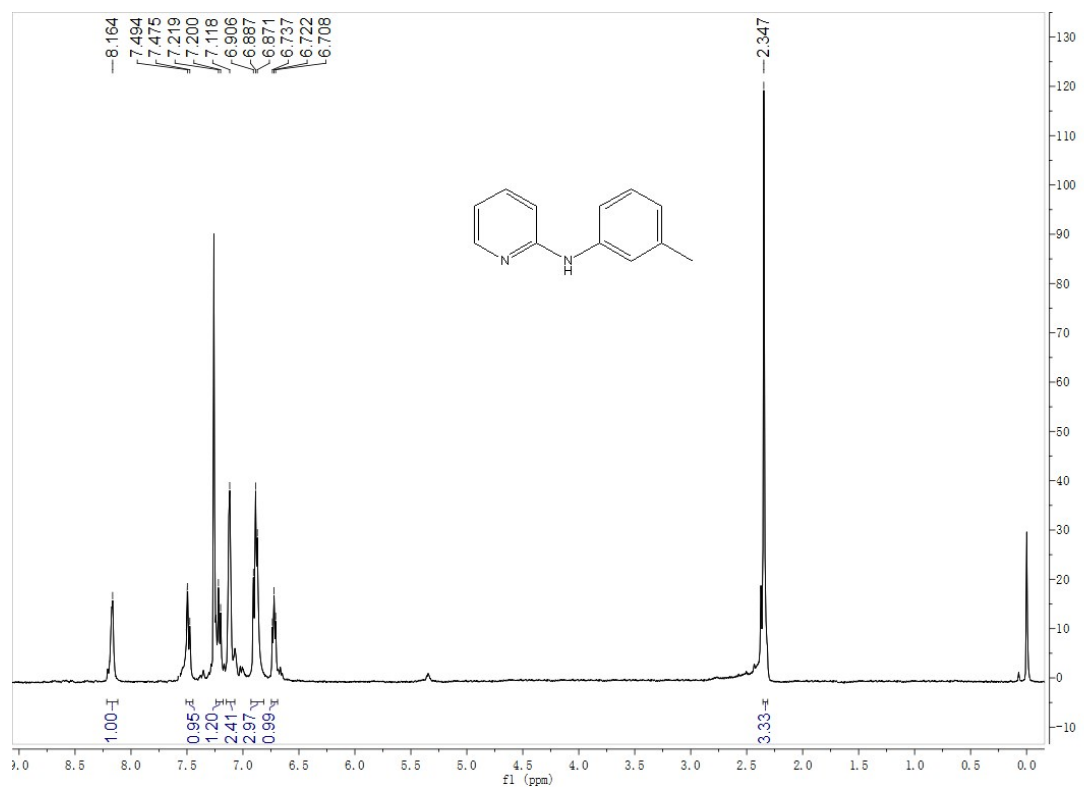
^1H NMR and ^{13}C NMR of compound **3b**



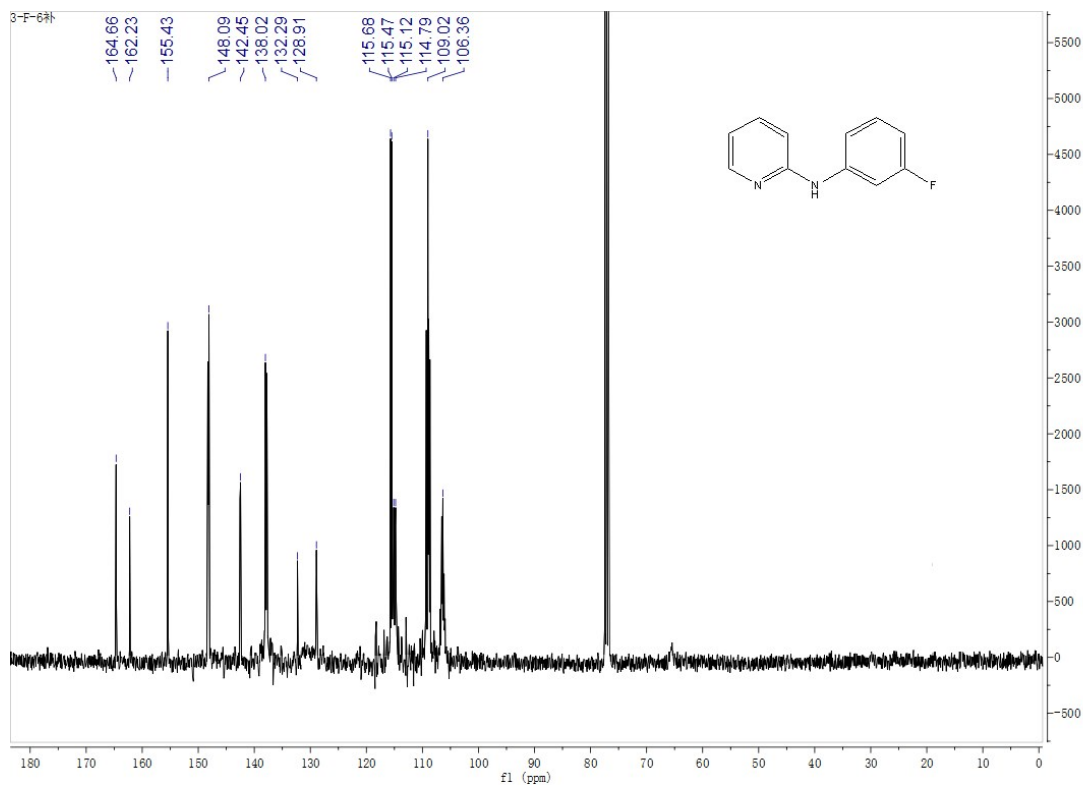
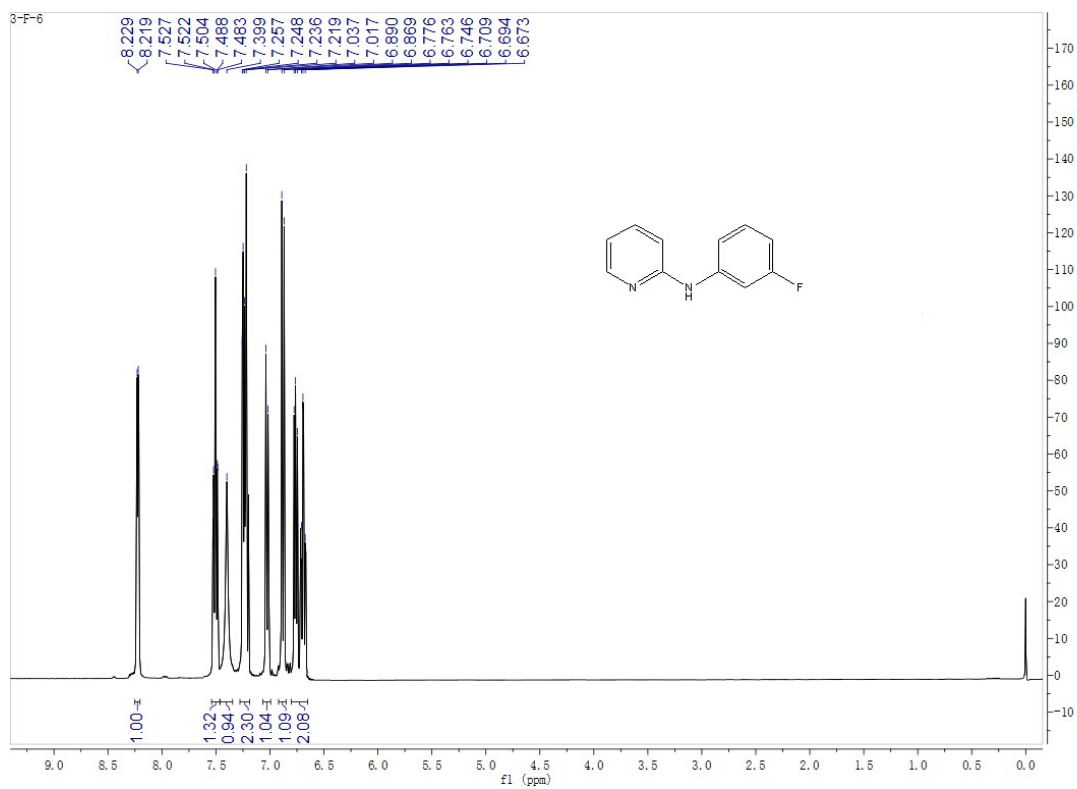
¹H NMR and ¹³C NMR of compound **3c**



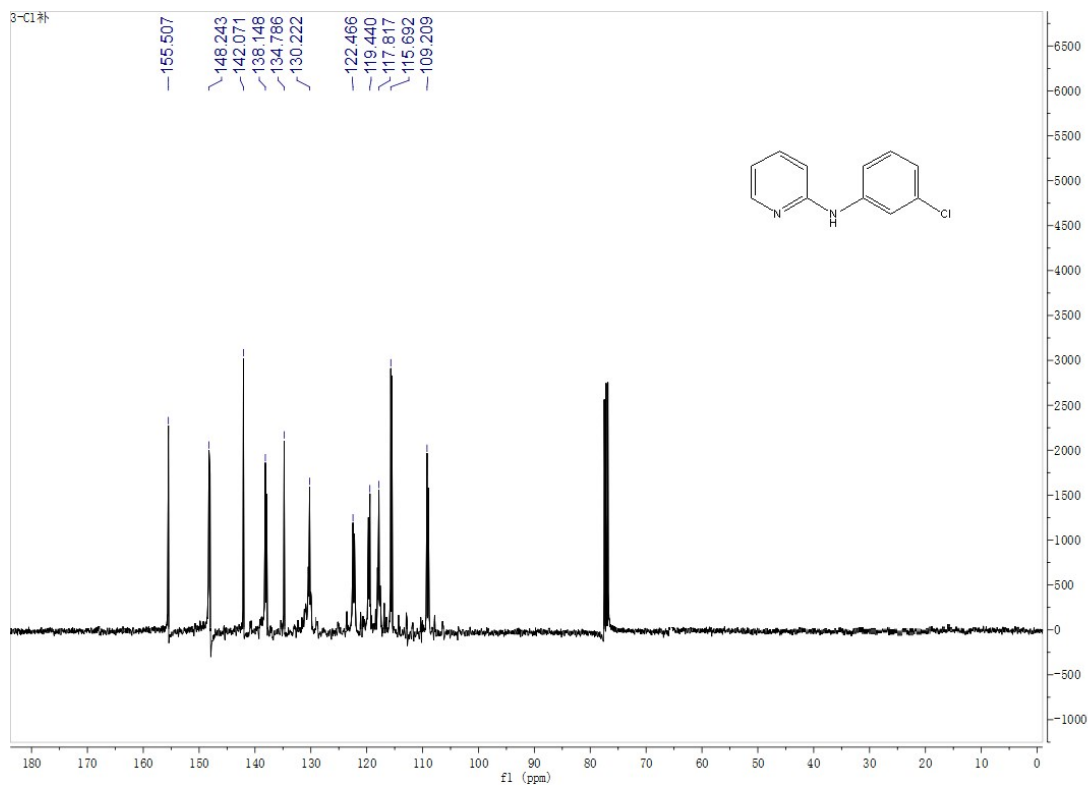
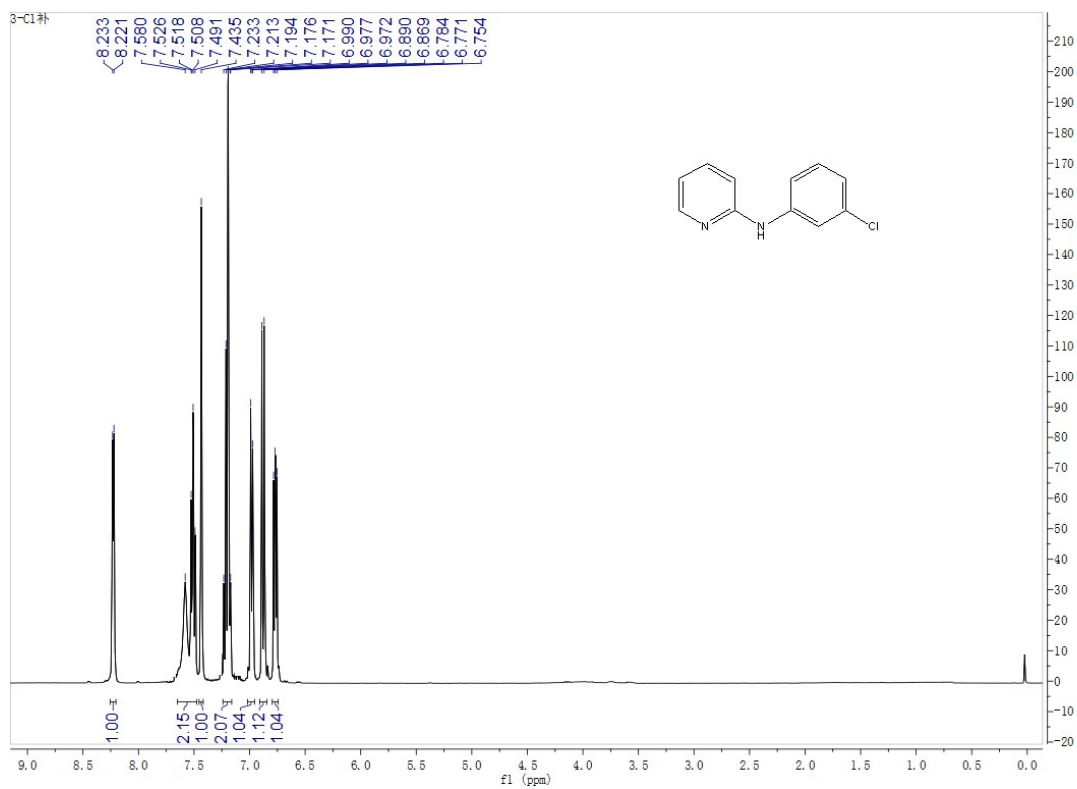
¹H NMR and ¹³C NMR of compound **3d**



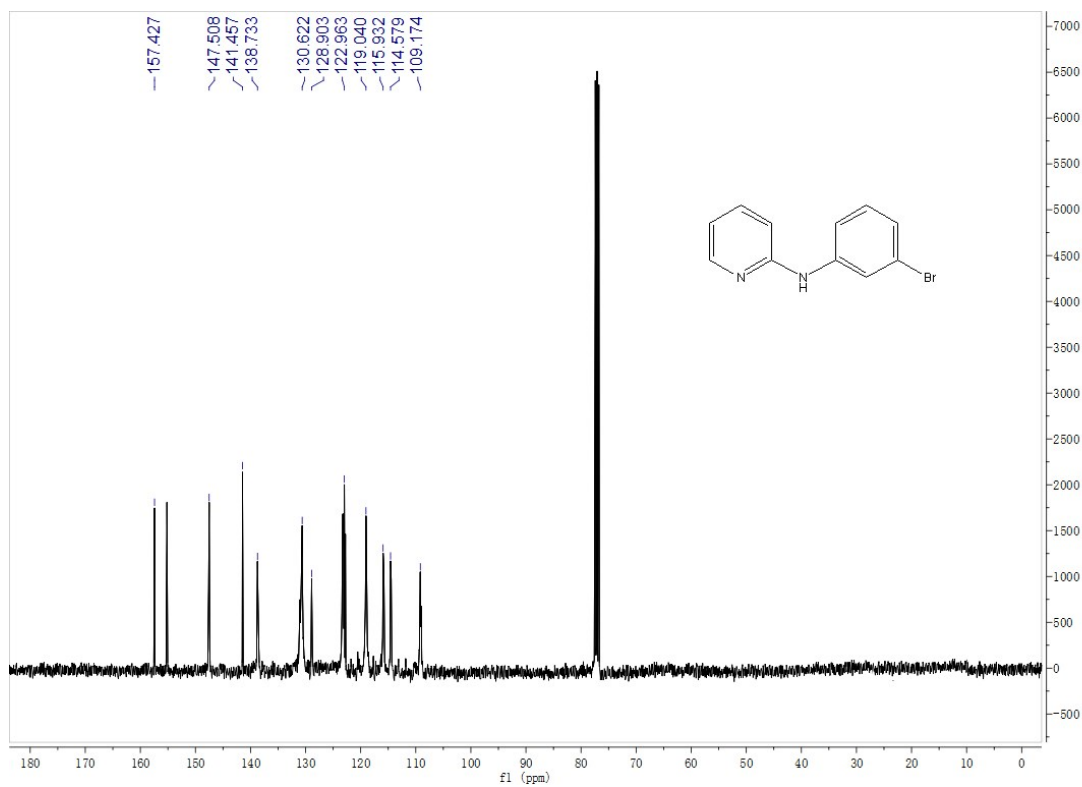
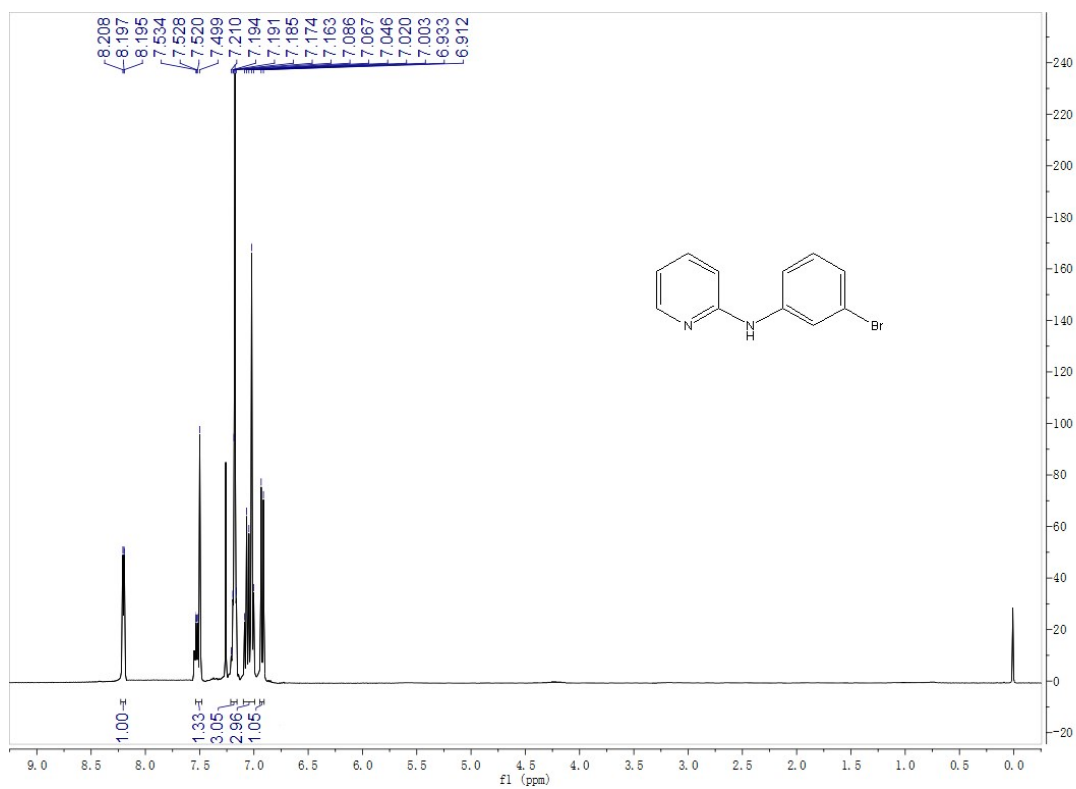
¹H NMR and ¹³C NMR of compound **3e**



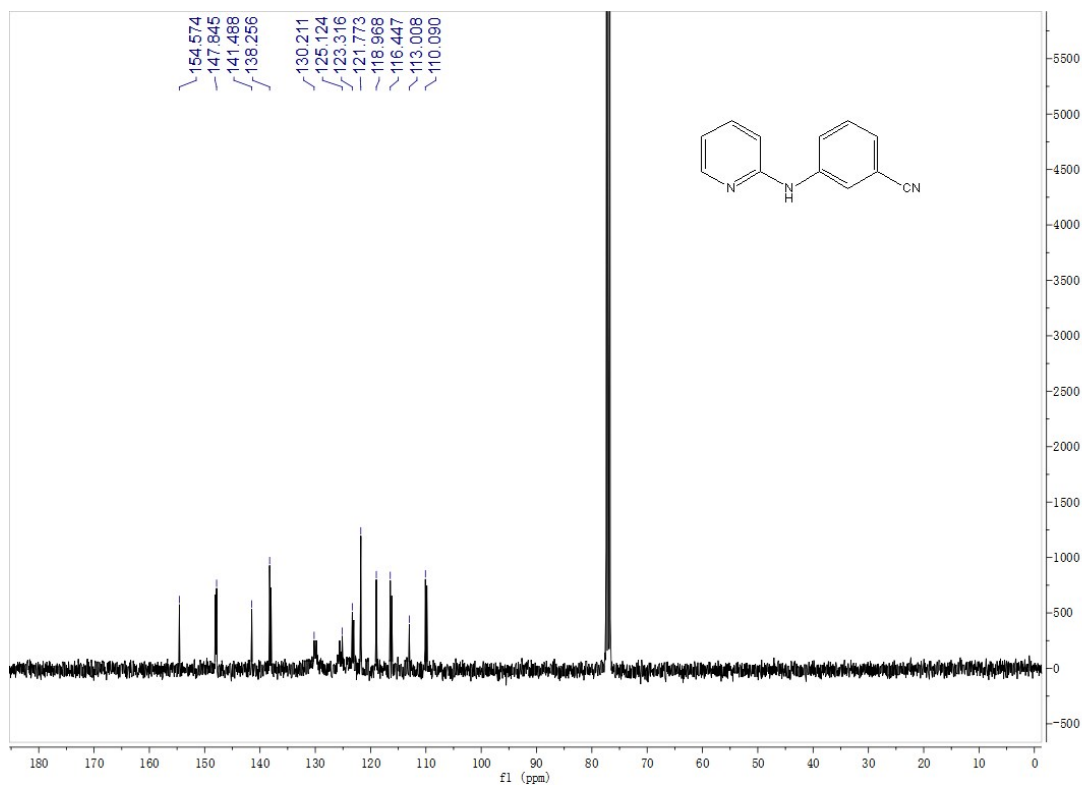
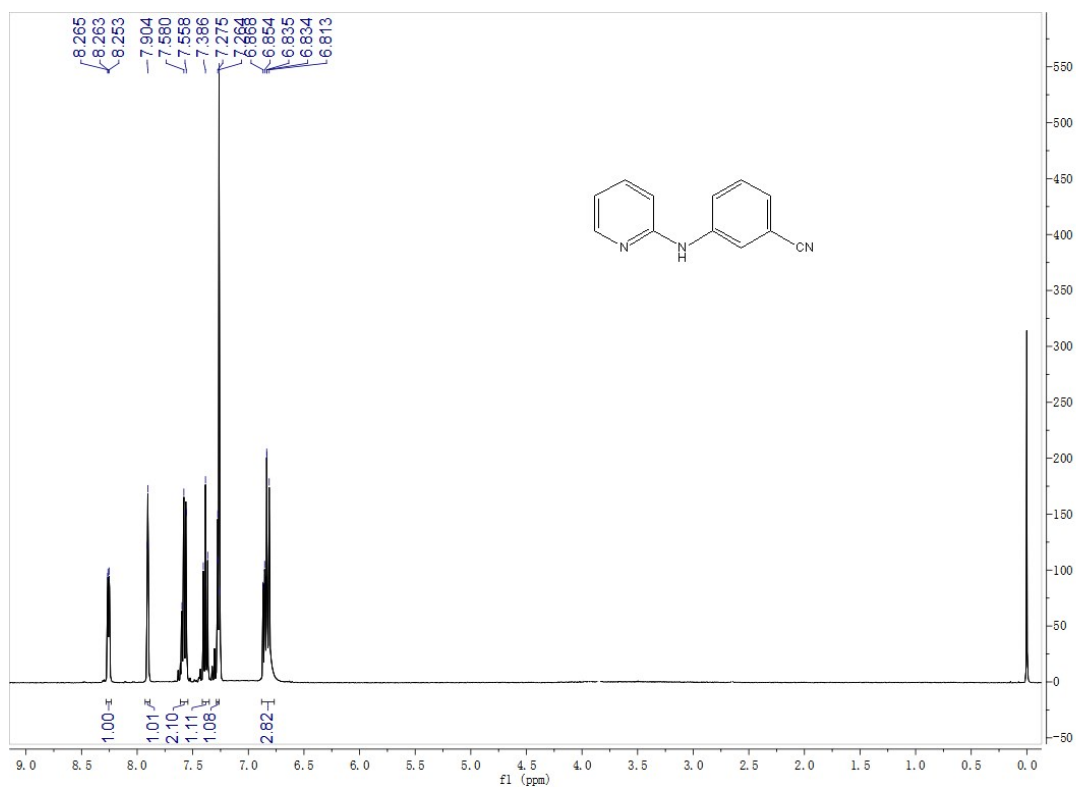
^1H NMR and ^{13}C NMR of compound **3f**



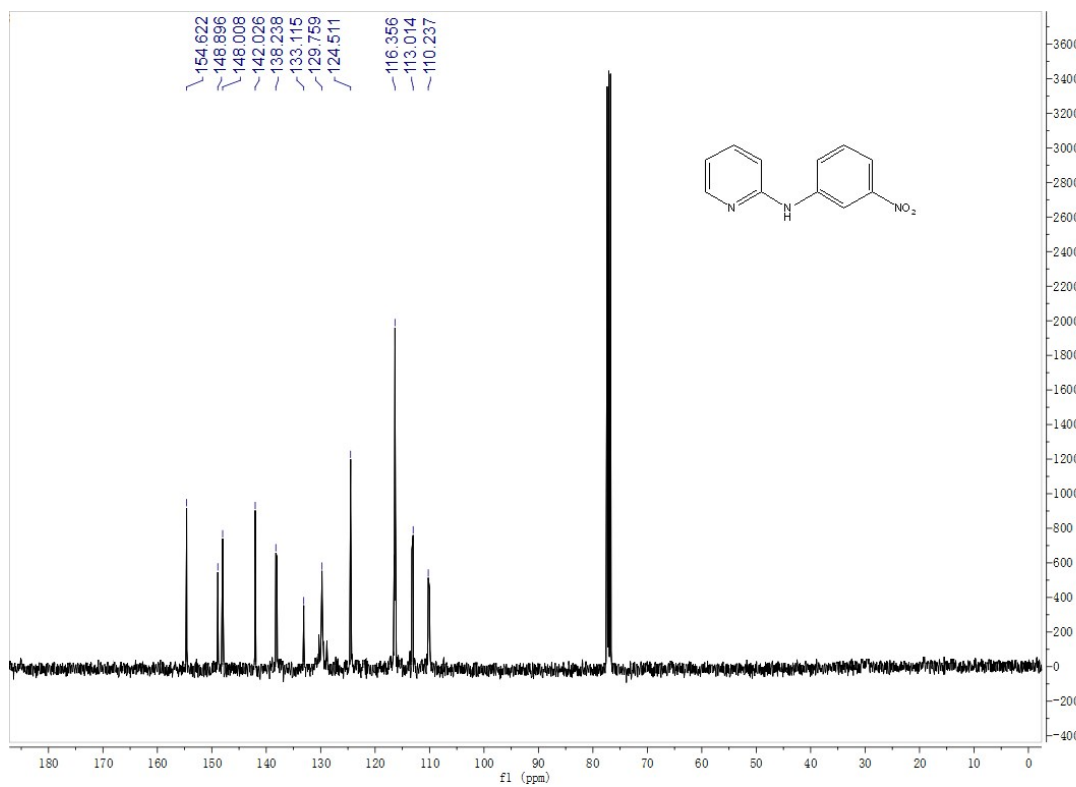
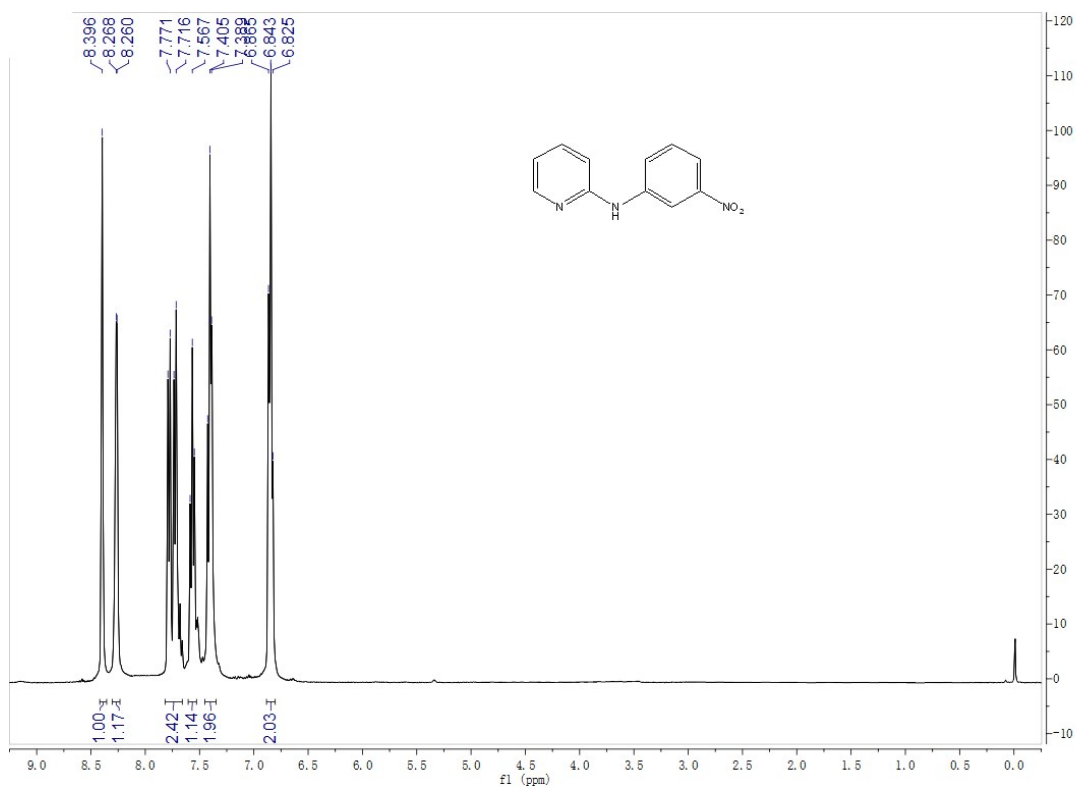
^1H NMR and ^{13}C NMR of compound **3g**



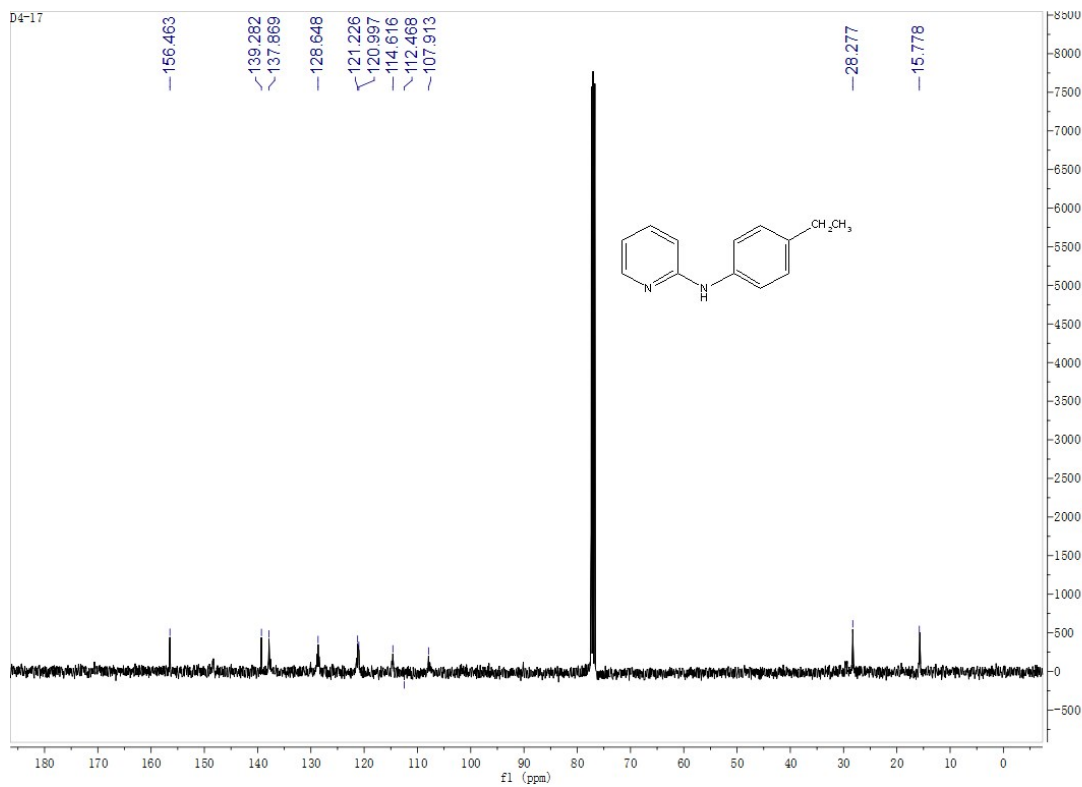
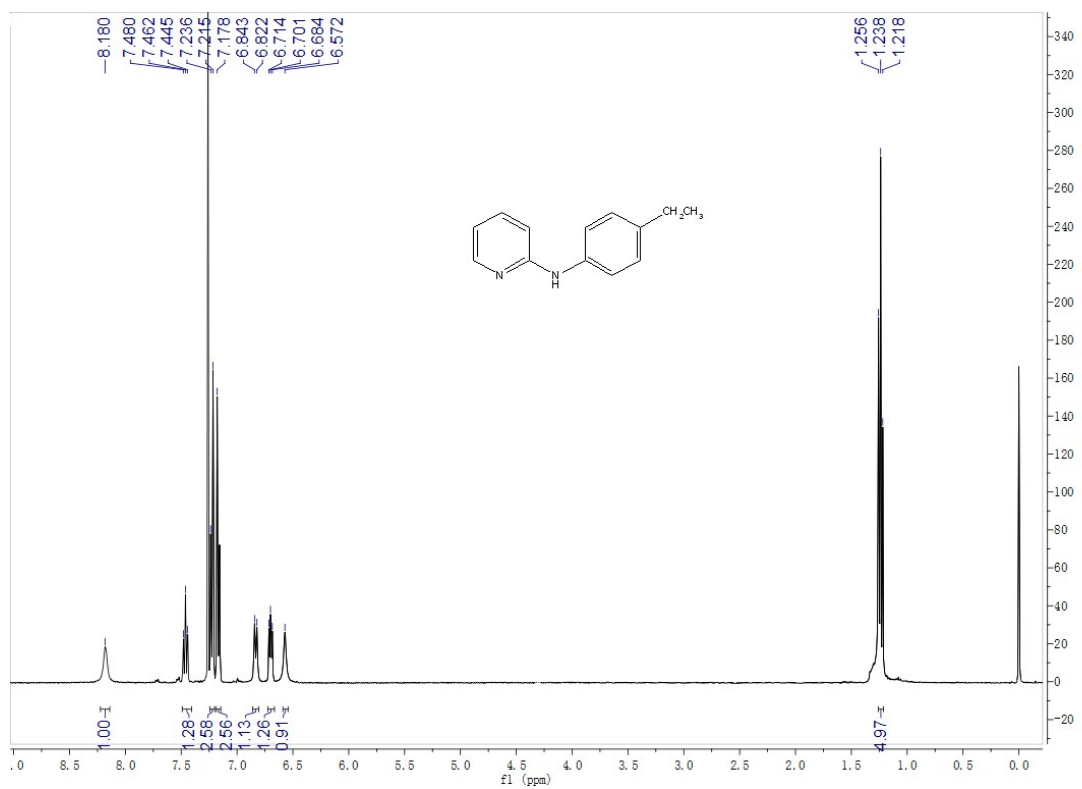
¹H NMR and ¹³C NMR of compound **3h**



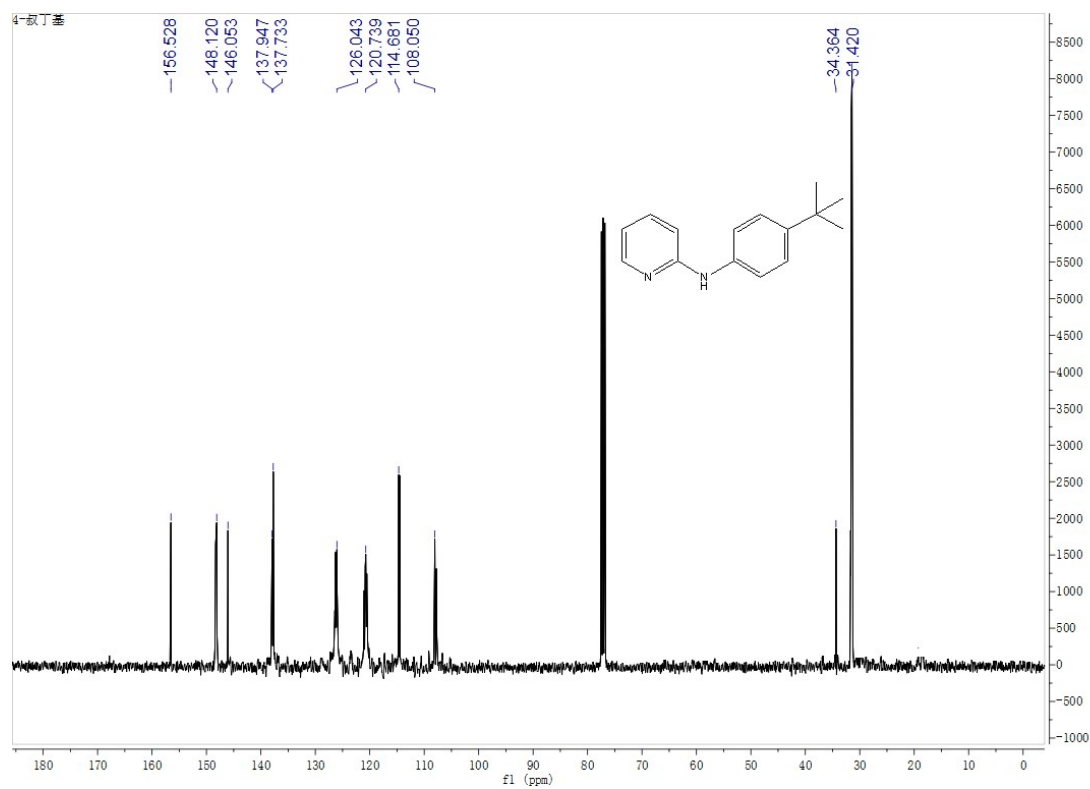
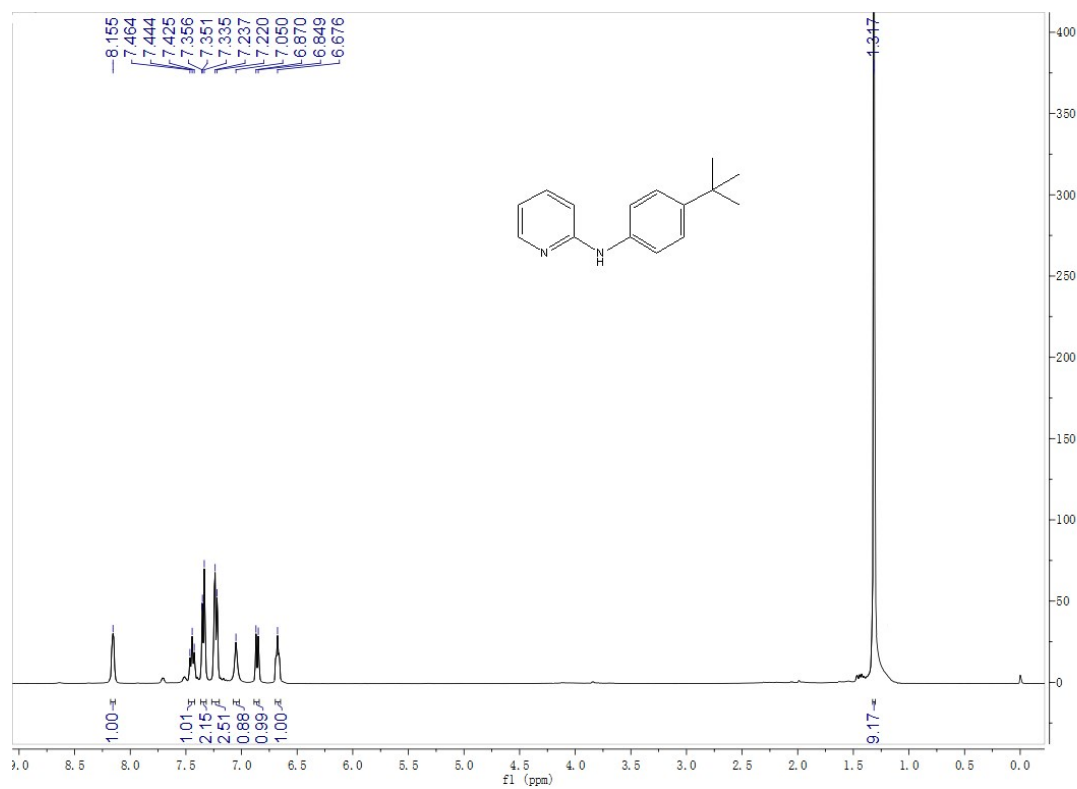
^1H NMR and ^{13}C NMR of compound **3i**



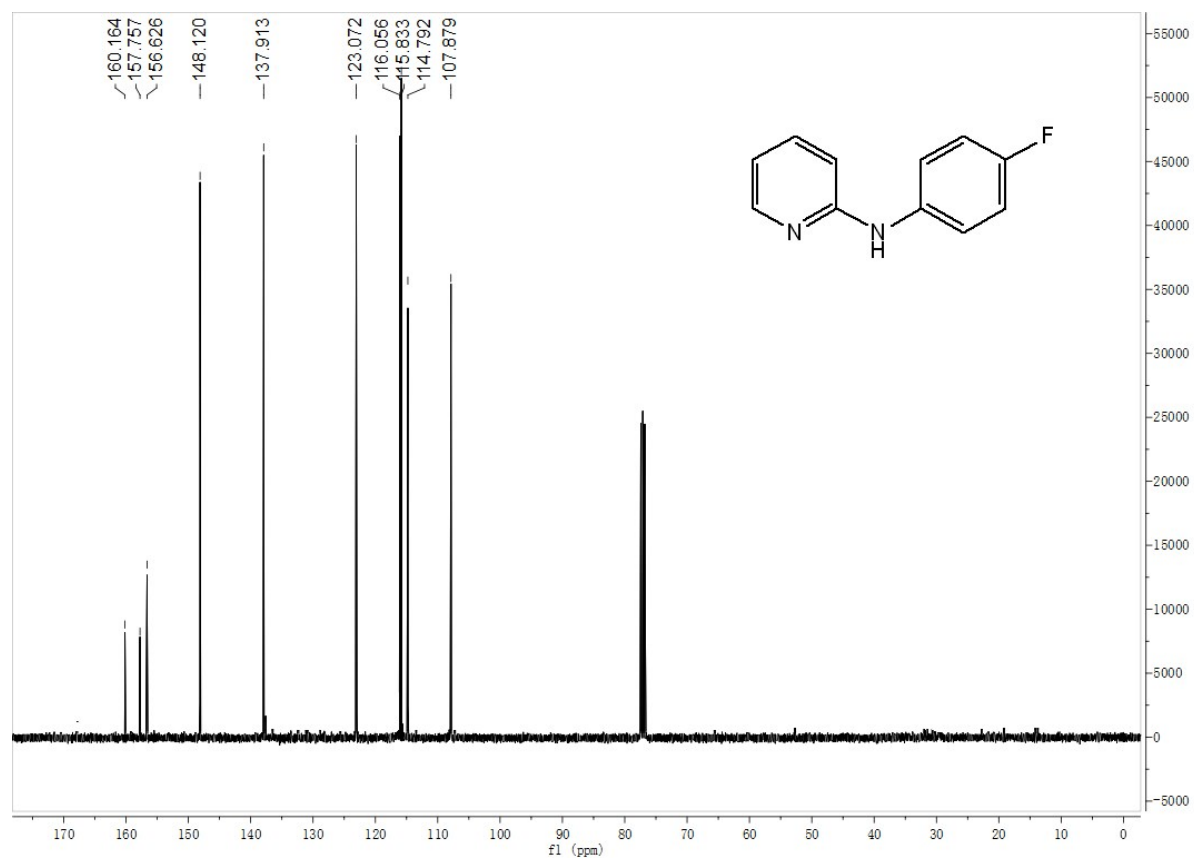
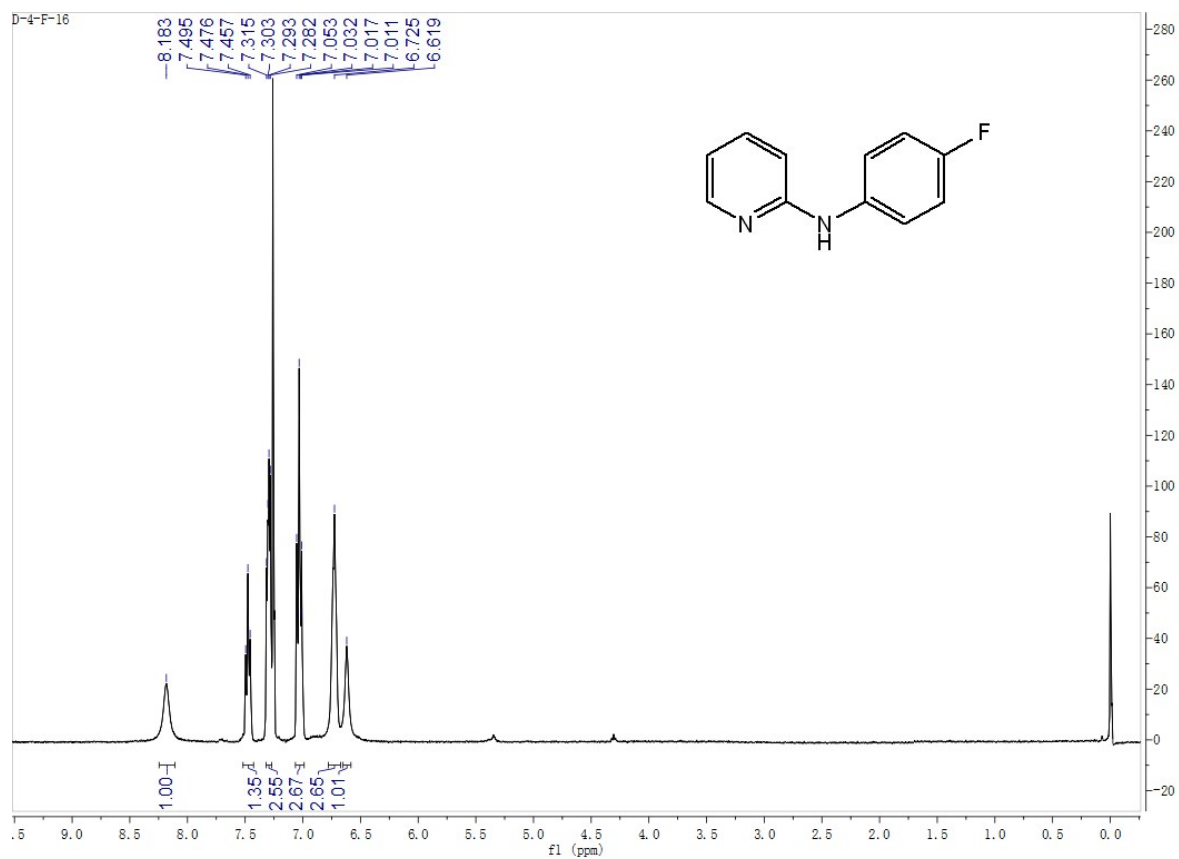
¹H NMR and ¹³C NMR of compound **3j**



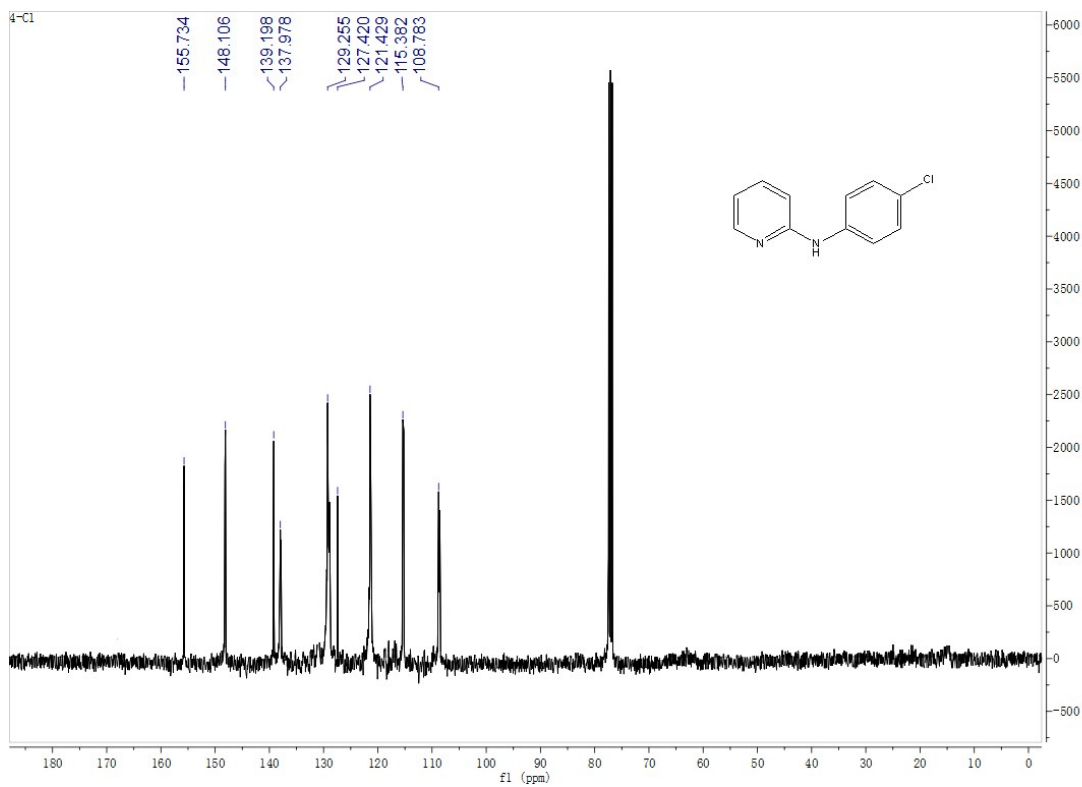
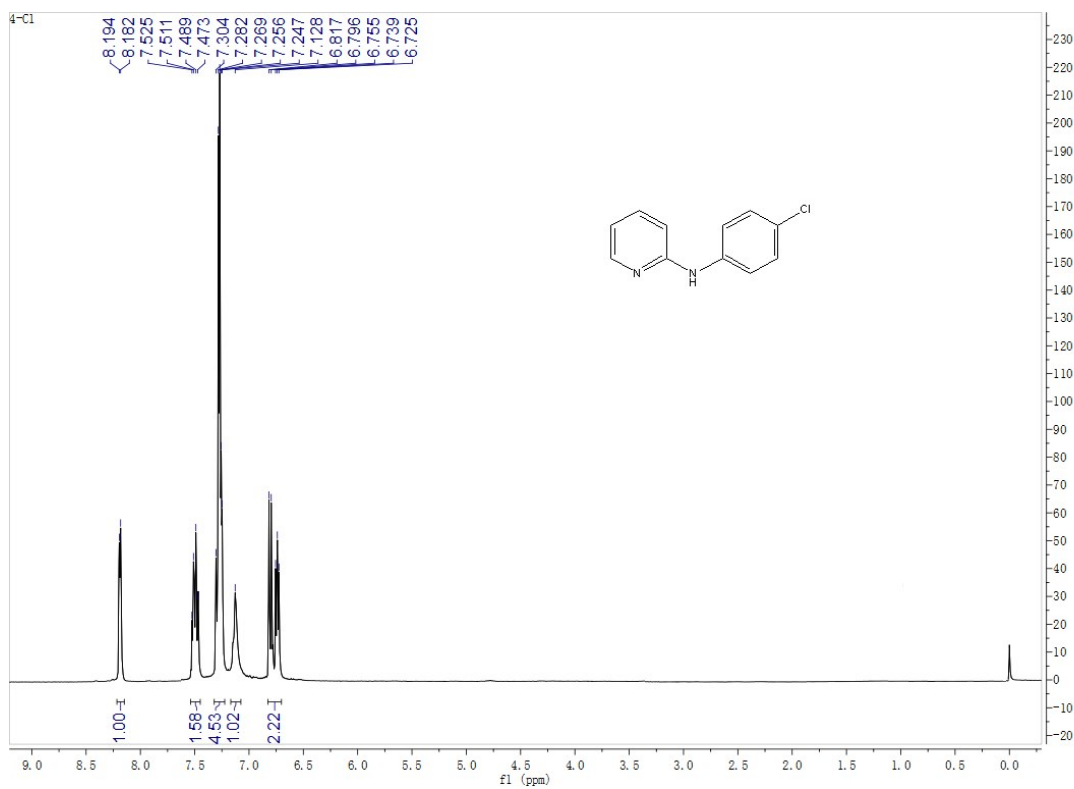
¹H NMR and ¹³C NMR of compound **3k**



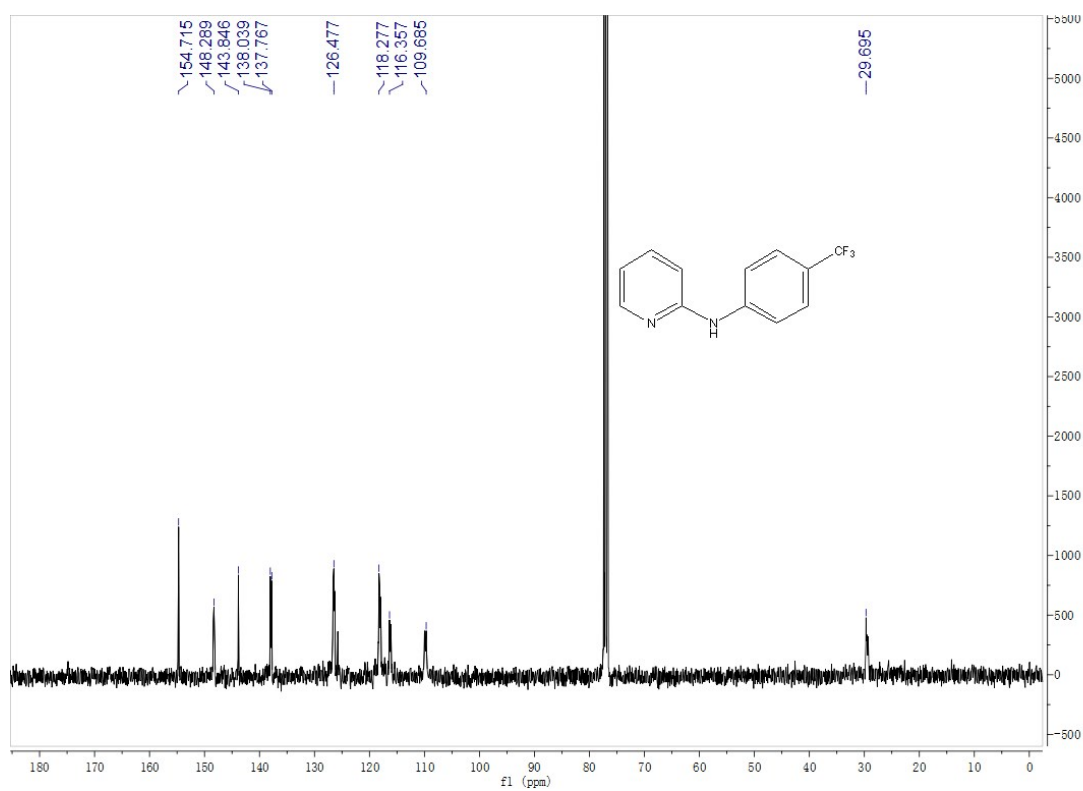
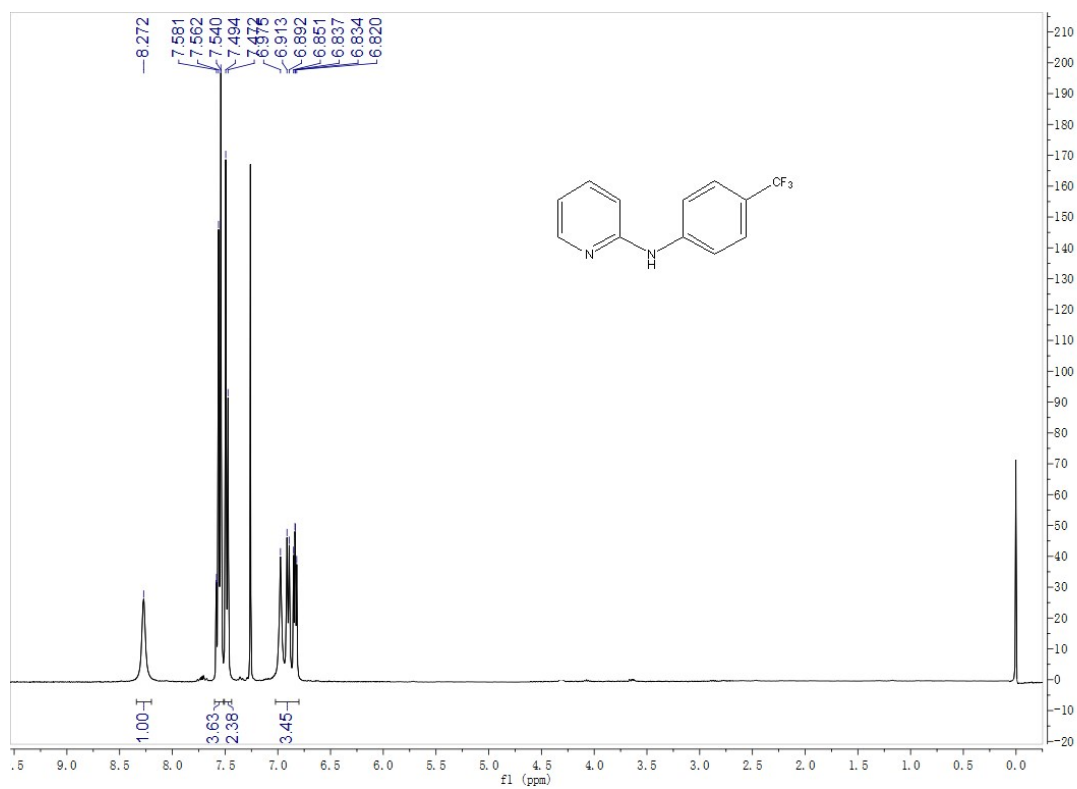
¹H NMR and ¹³C NMR of compound 31



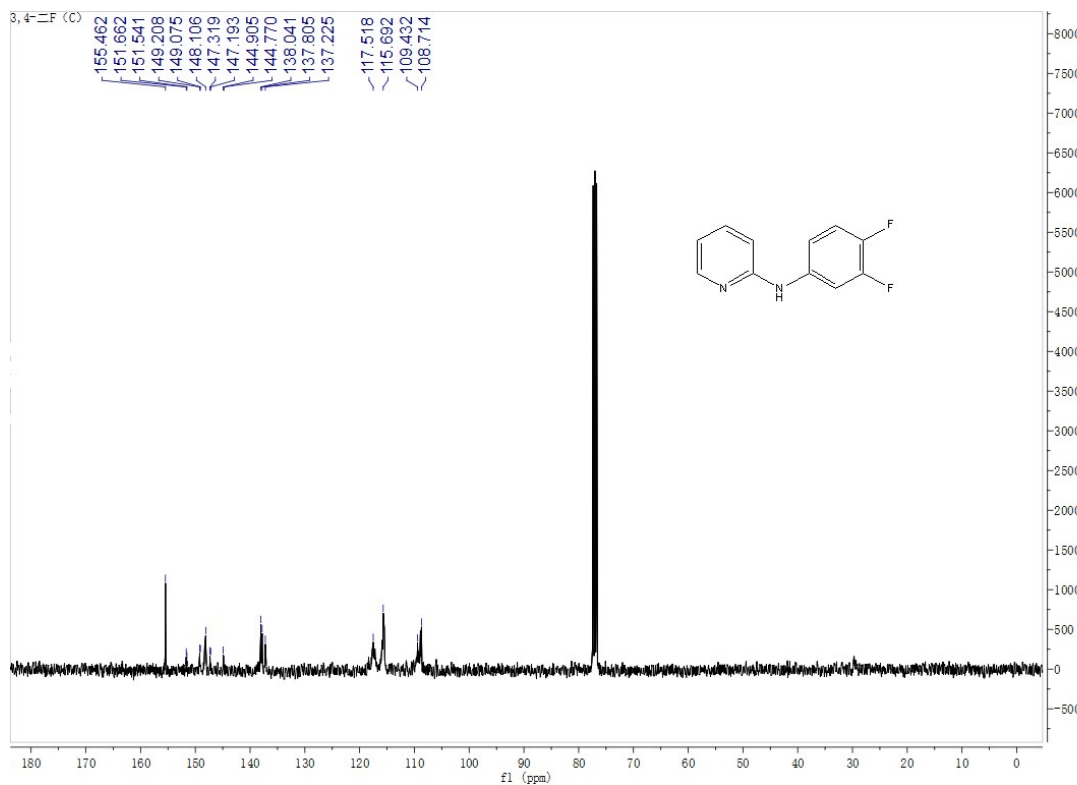
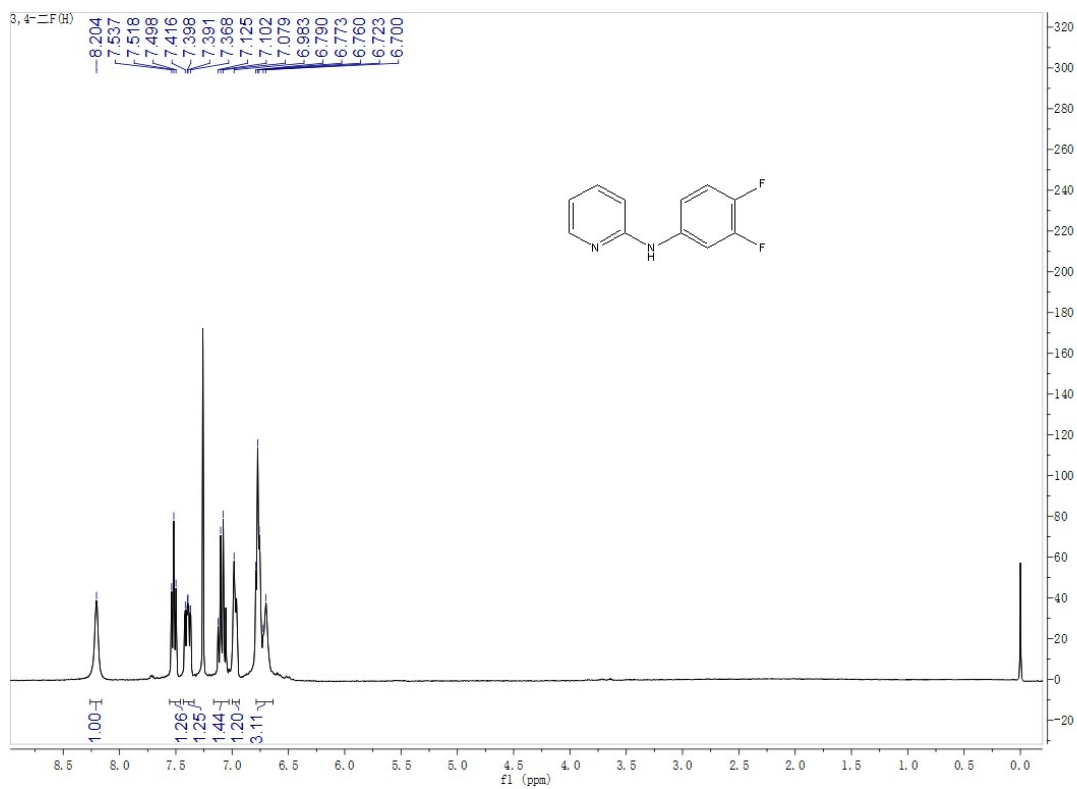
^1H NMR and ^{13}C NMR of compound **3m**



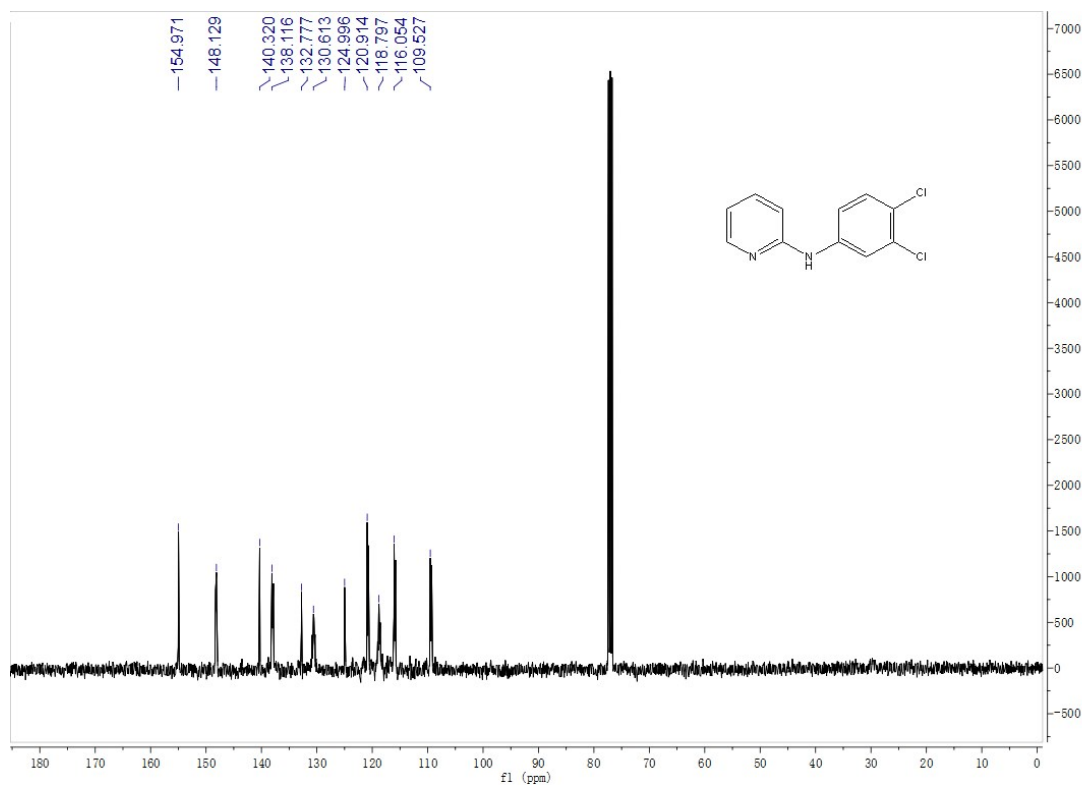
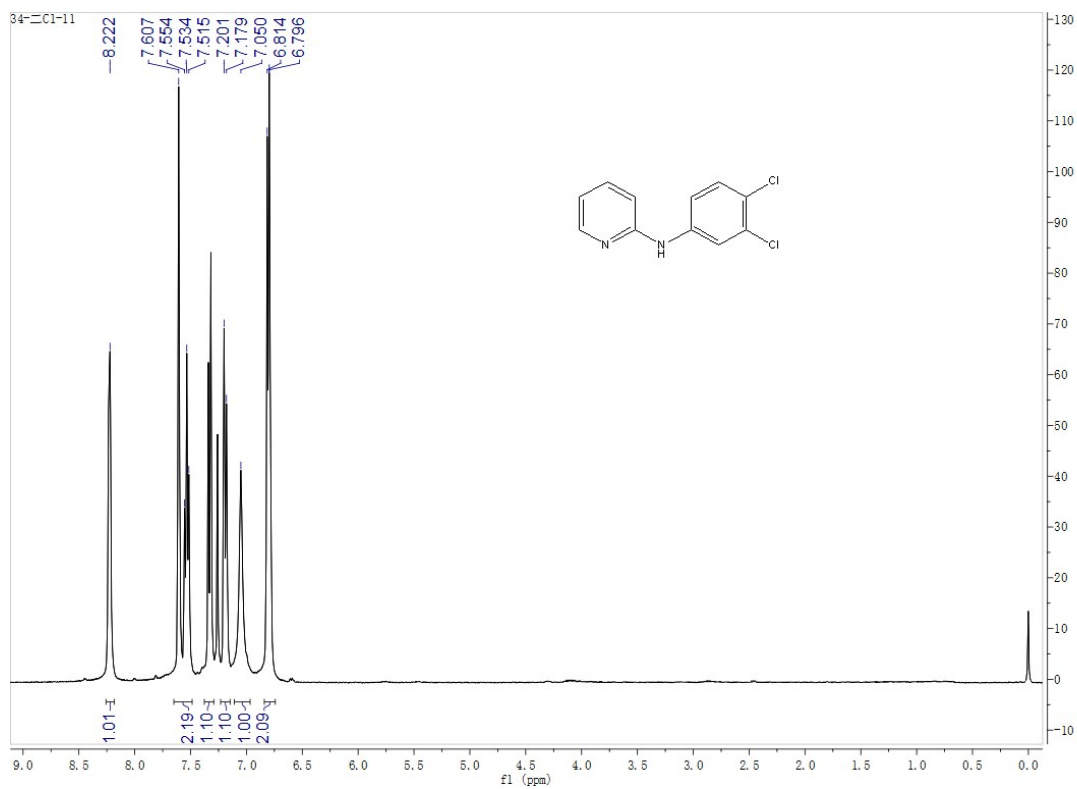
^1H NMR and ^{13}C NMR of compound **3n**



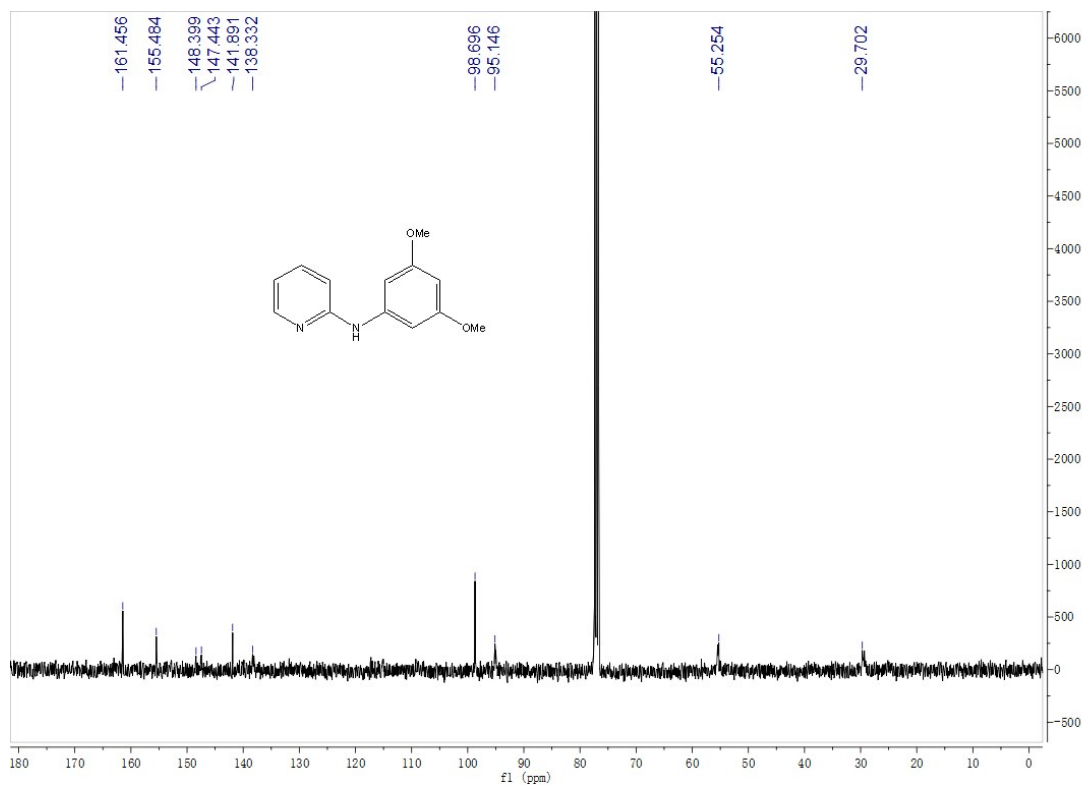
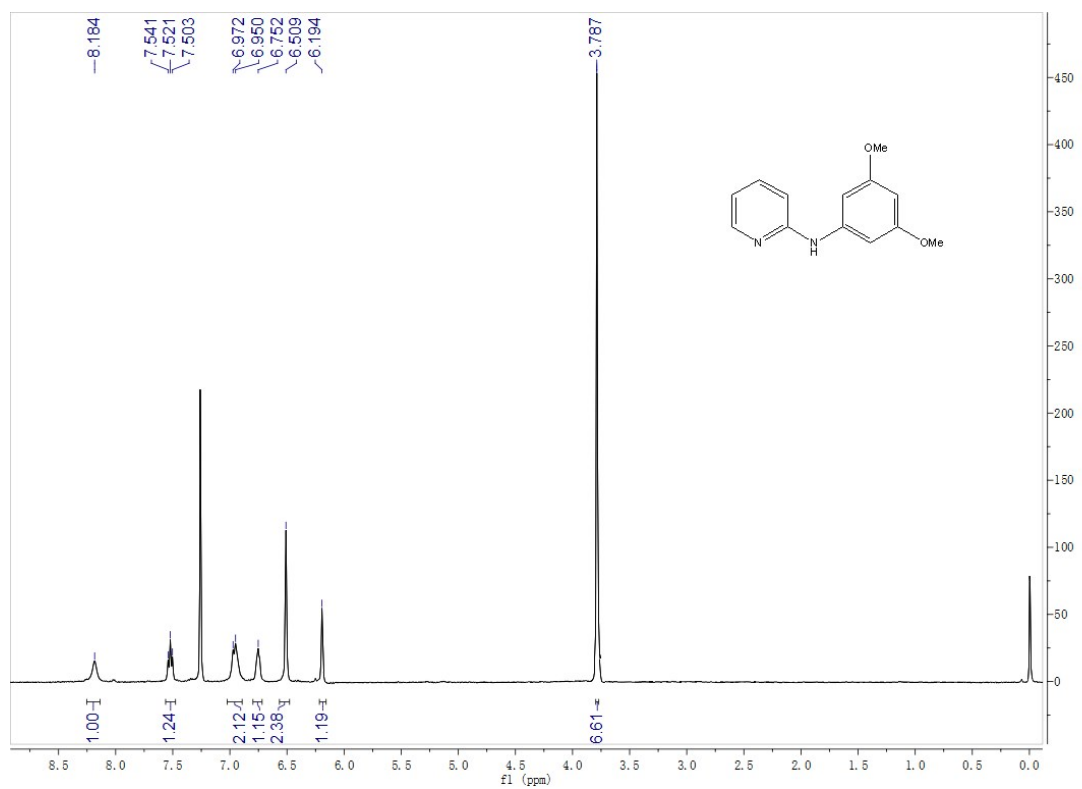
¹H NMR and ¹³C NMR of compound **3o**



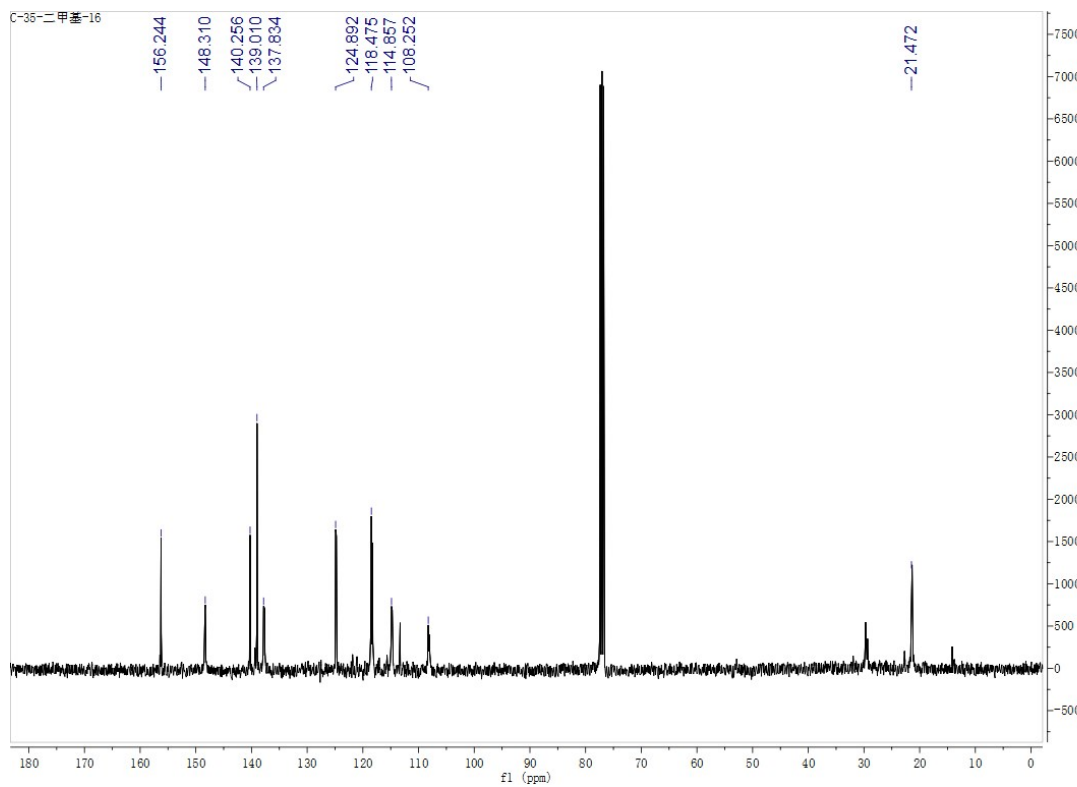
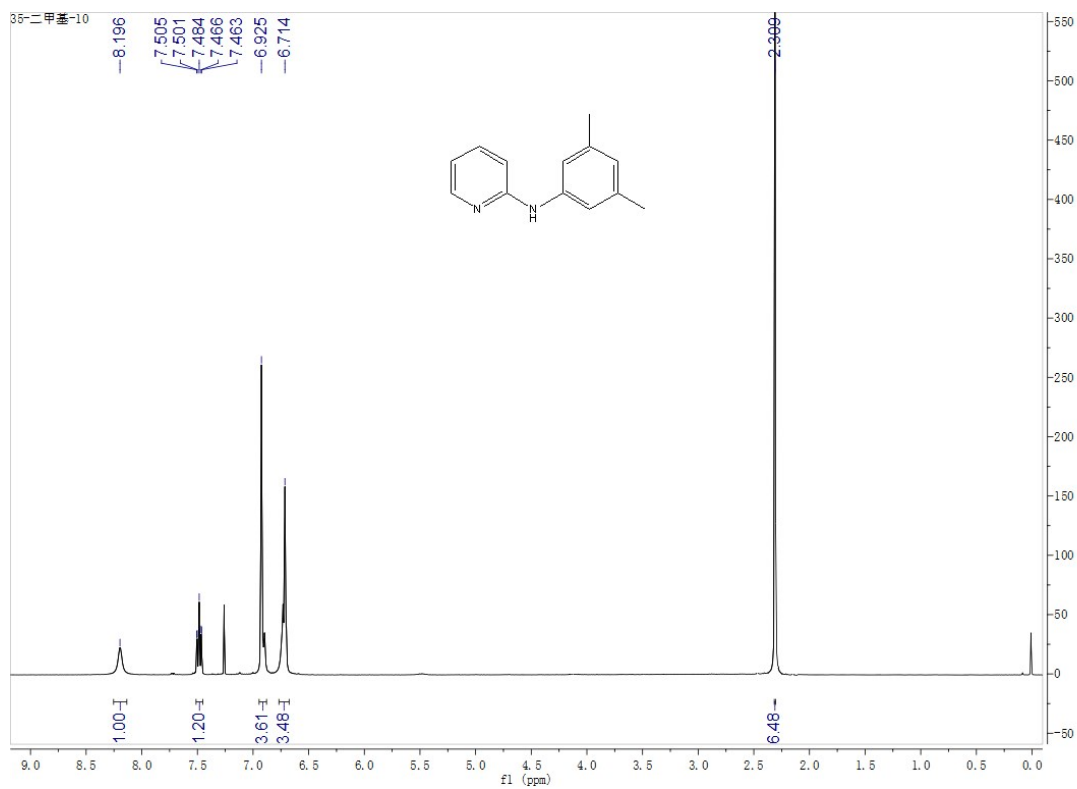
¹H NMR and ¹³C NMR of compound **3p**



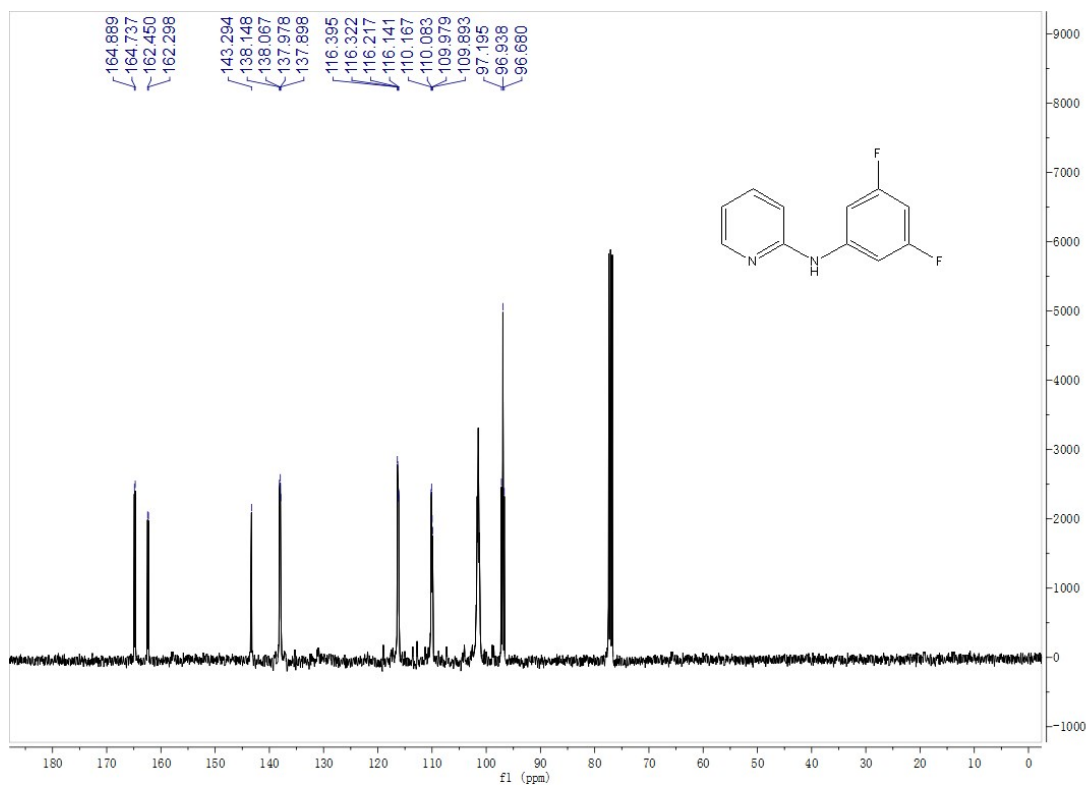
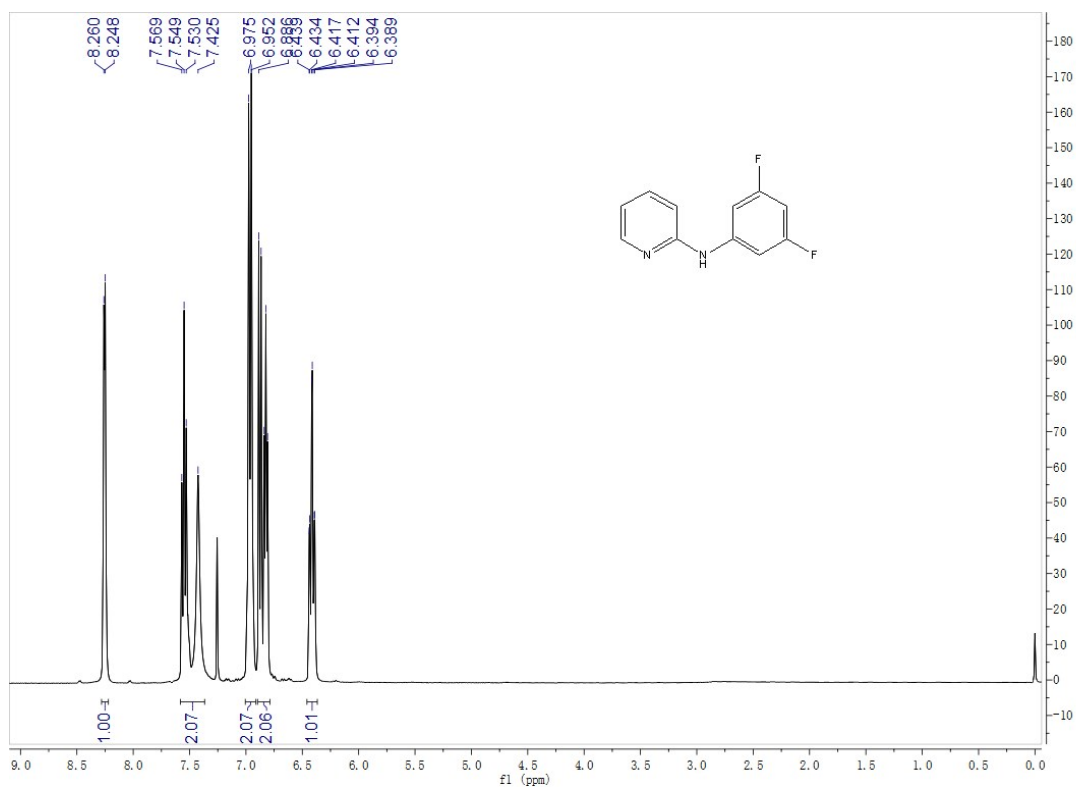
^1H NMR and ^{13}C NMR of compound **3q**



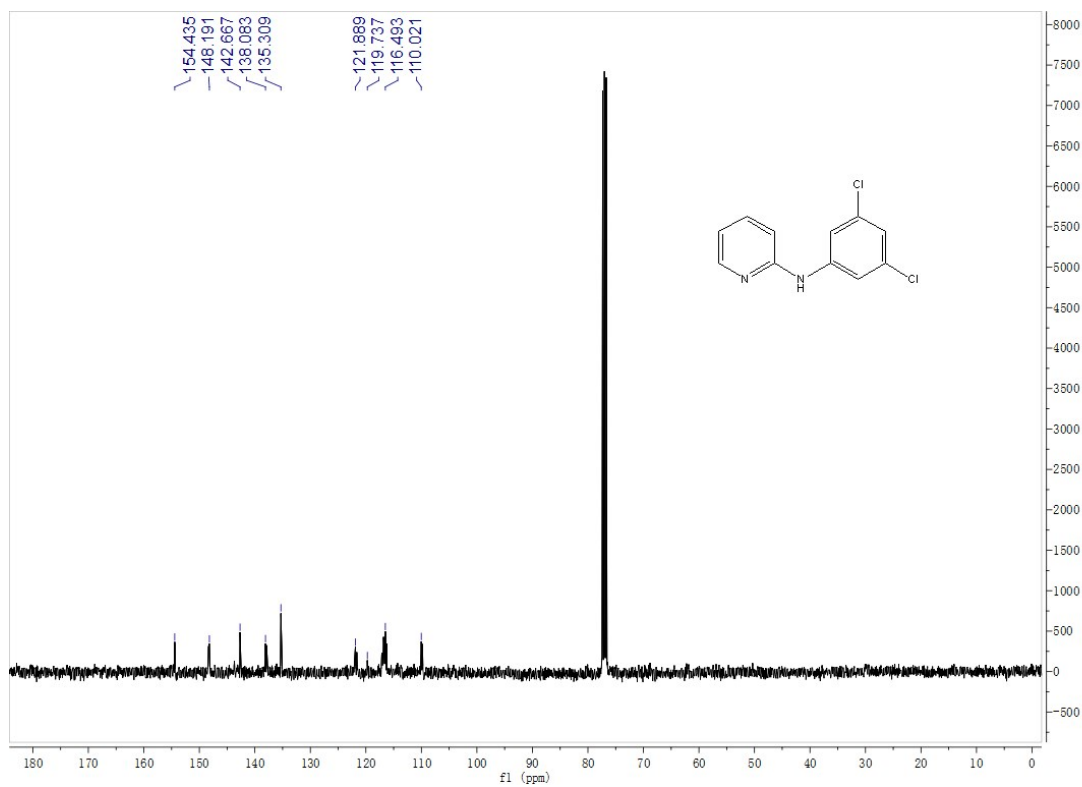
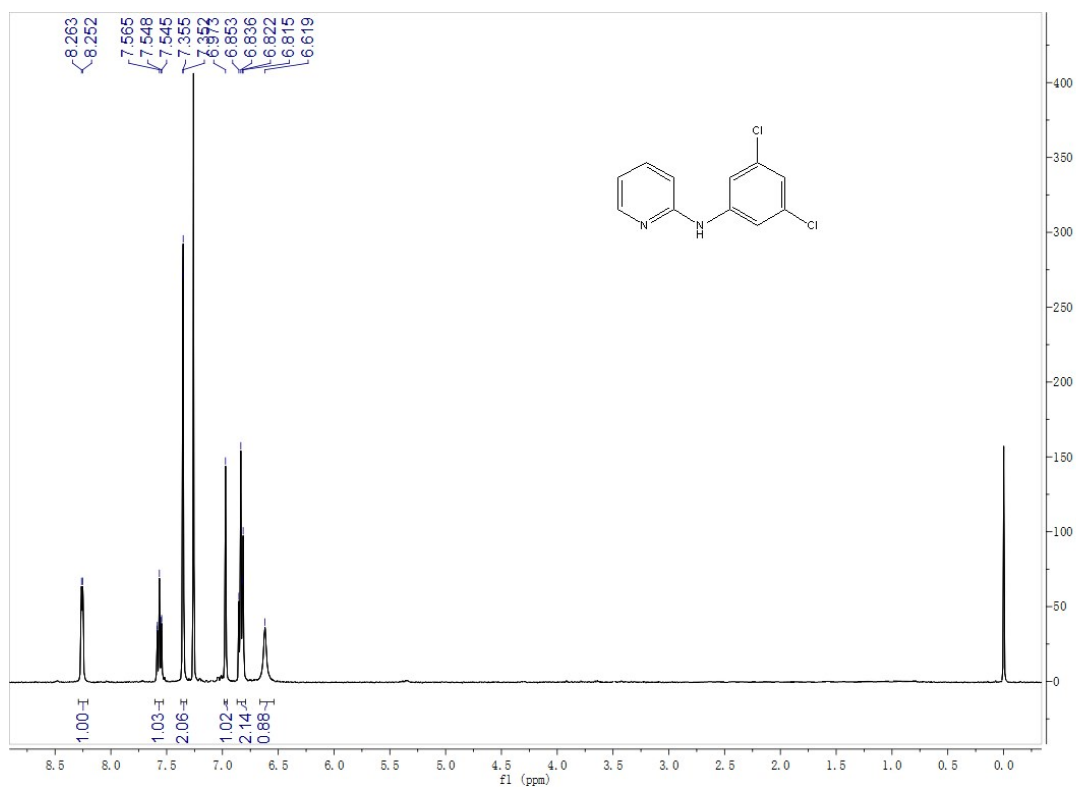
¹H NMR and ¹³C NMR of compound **3r**



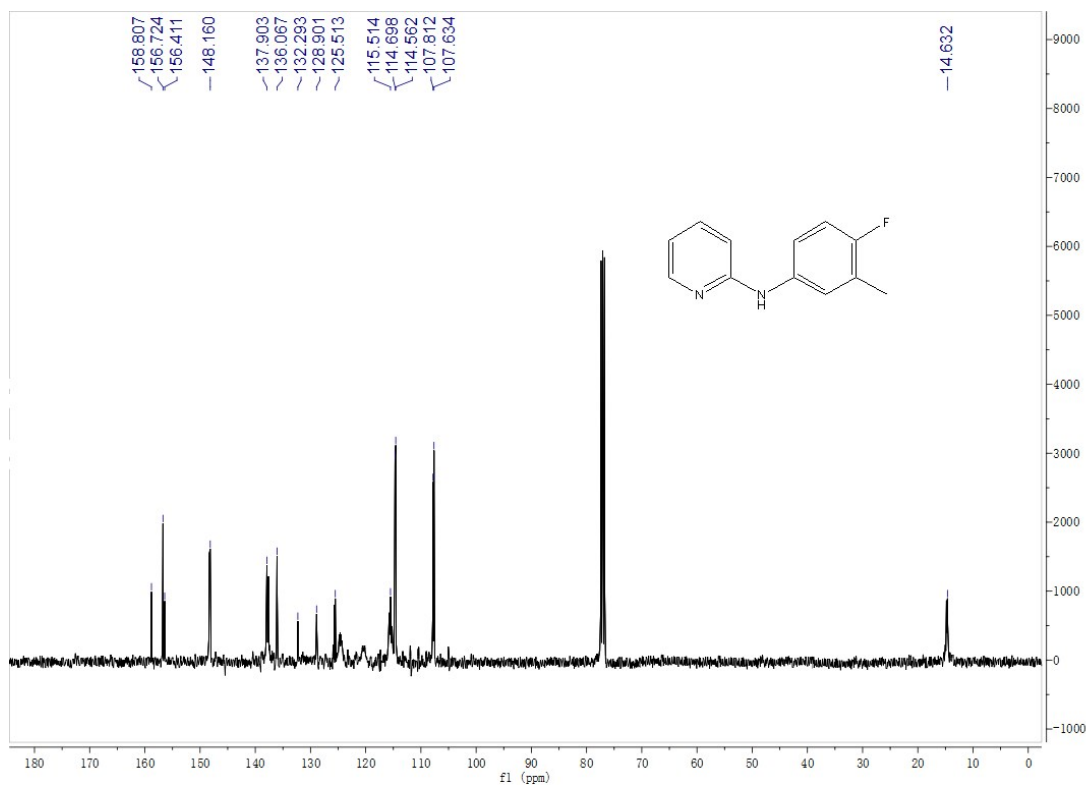
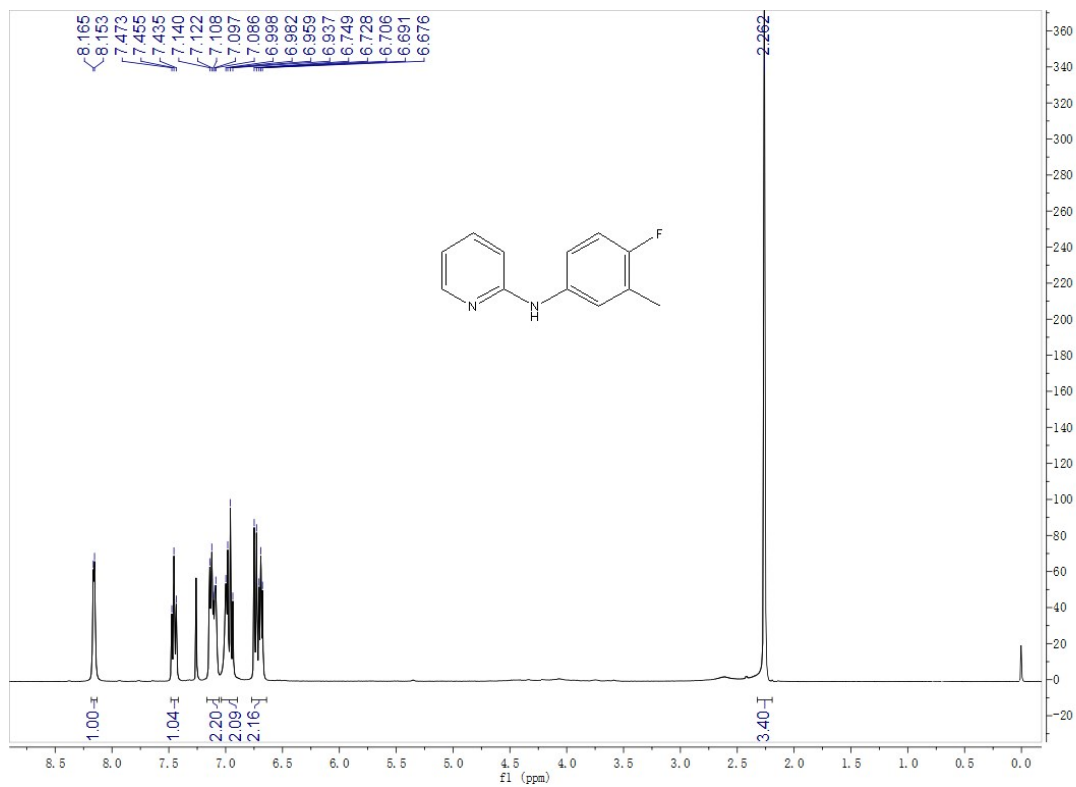
^1H NMR and ^{13}C NMR of compound **3s**



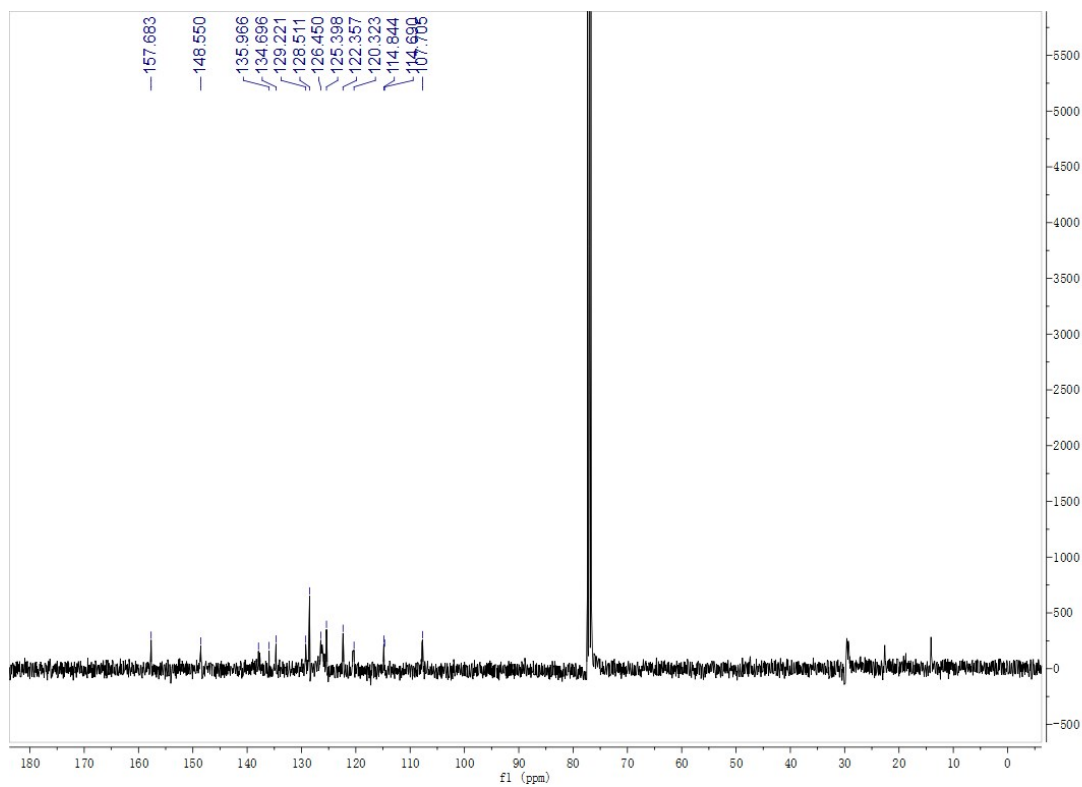
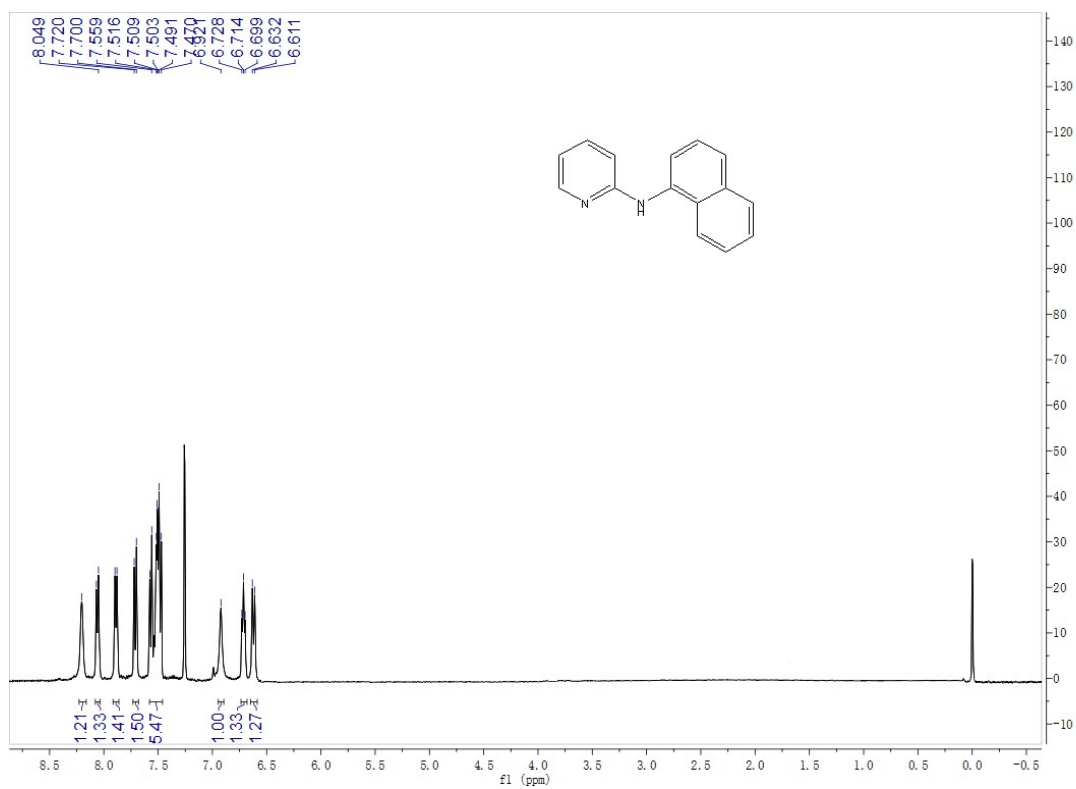
¹H NMR and ¹³C NMR of compound **3t**



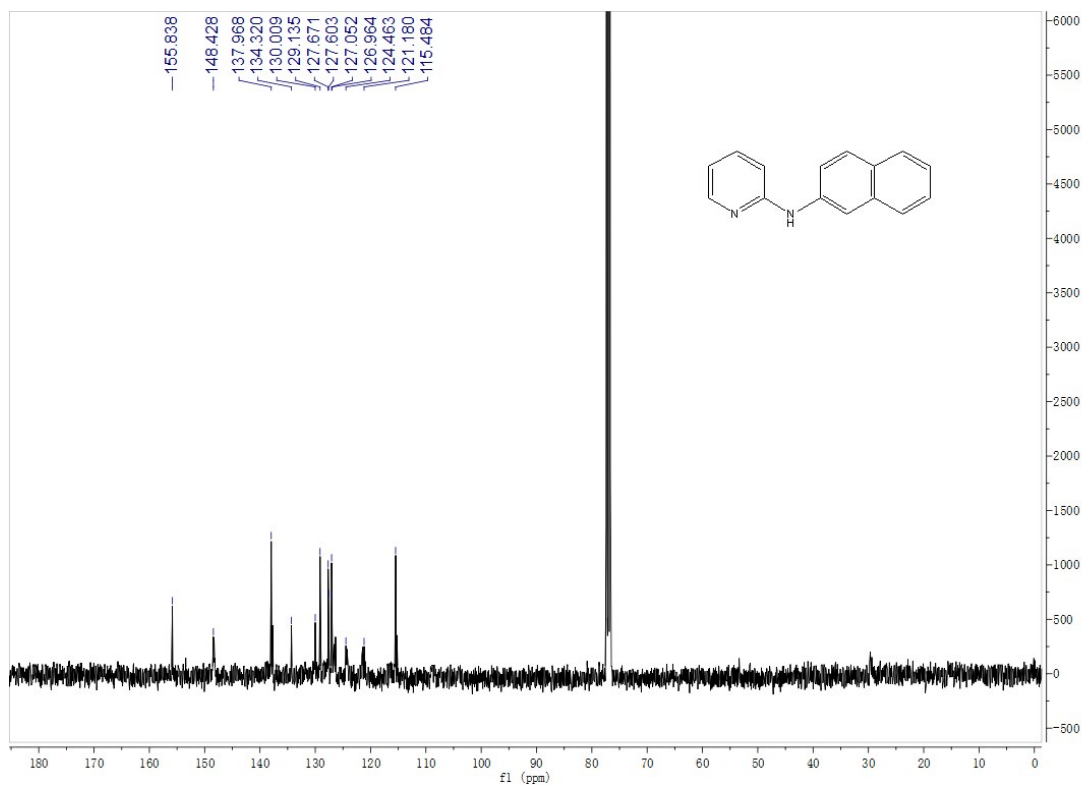
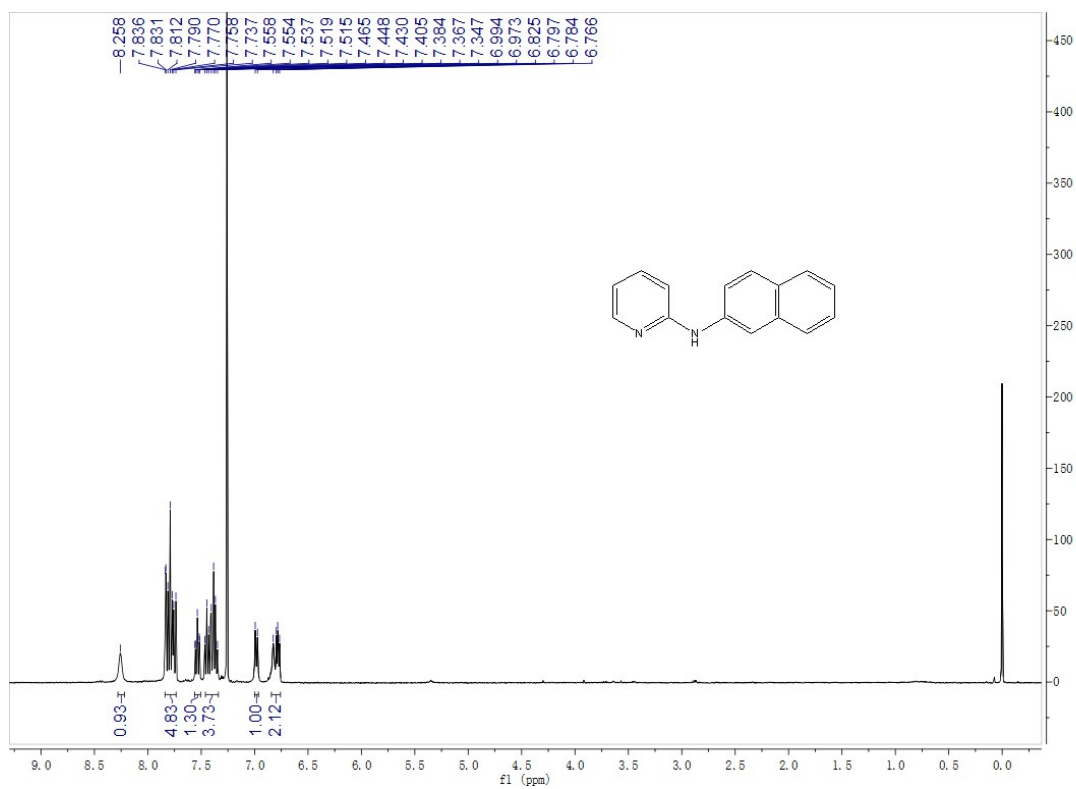
¹H NMR and ¹³C NMR of compound **3u**



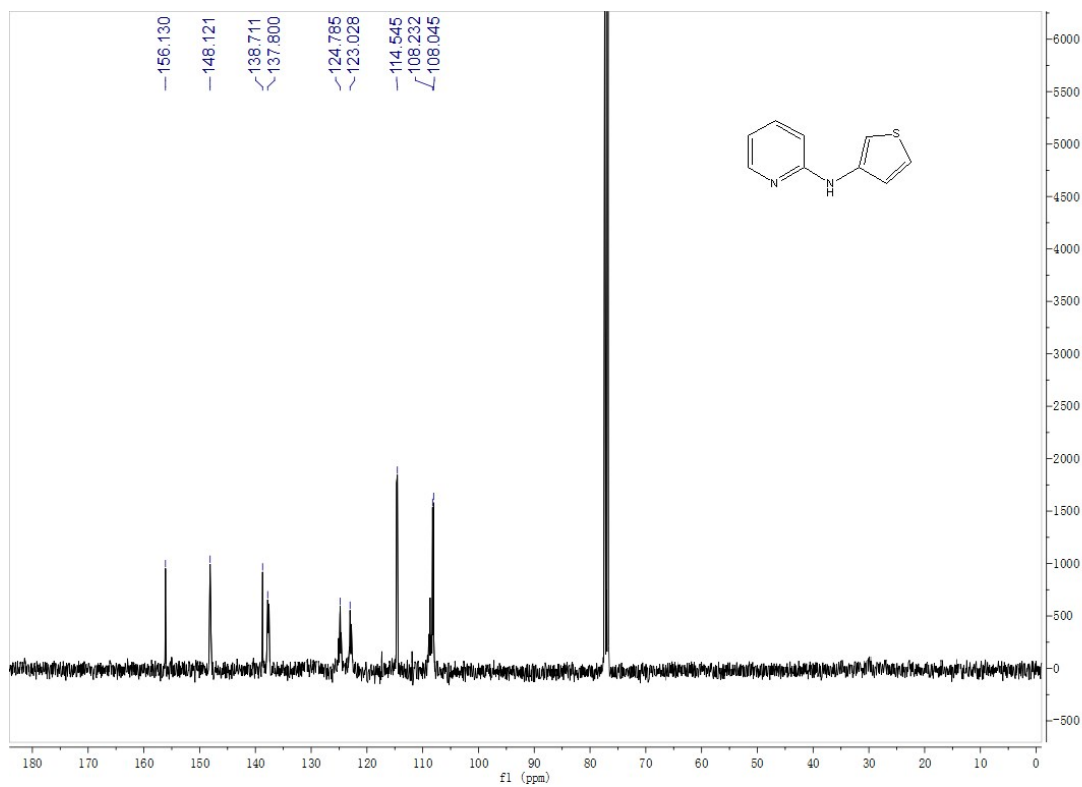
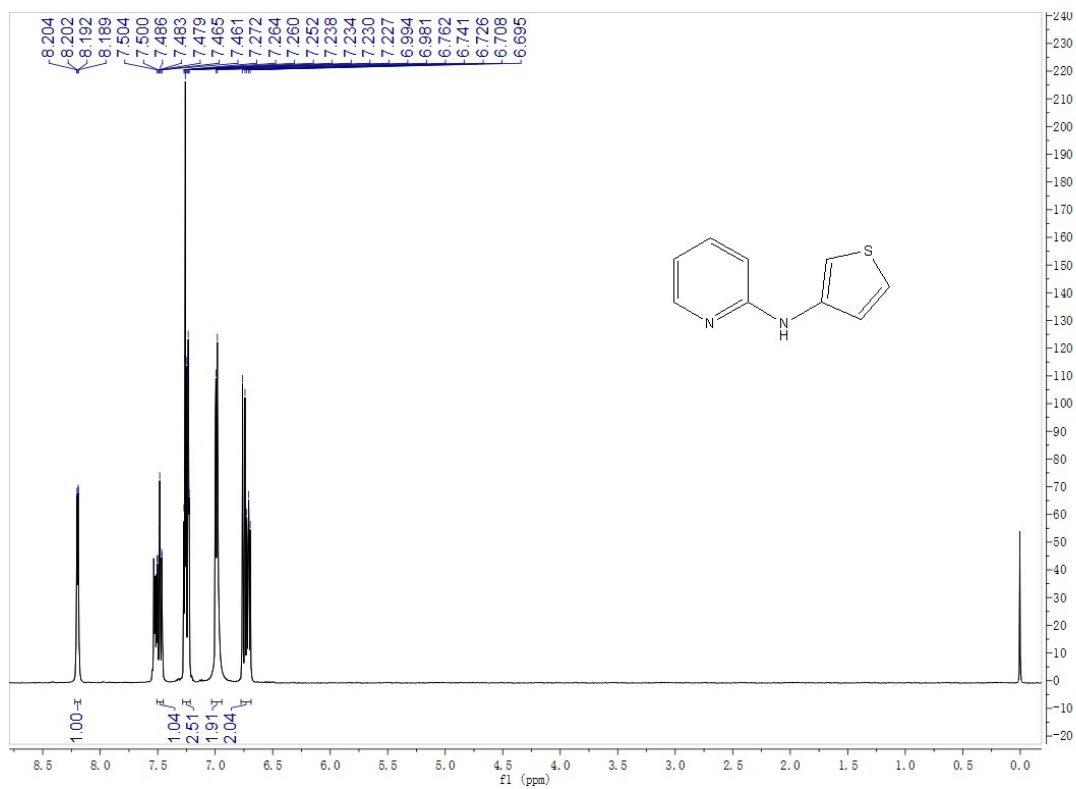
¹H NMR and ¹³C NMR of compound **3v**



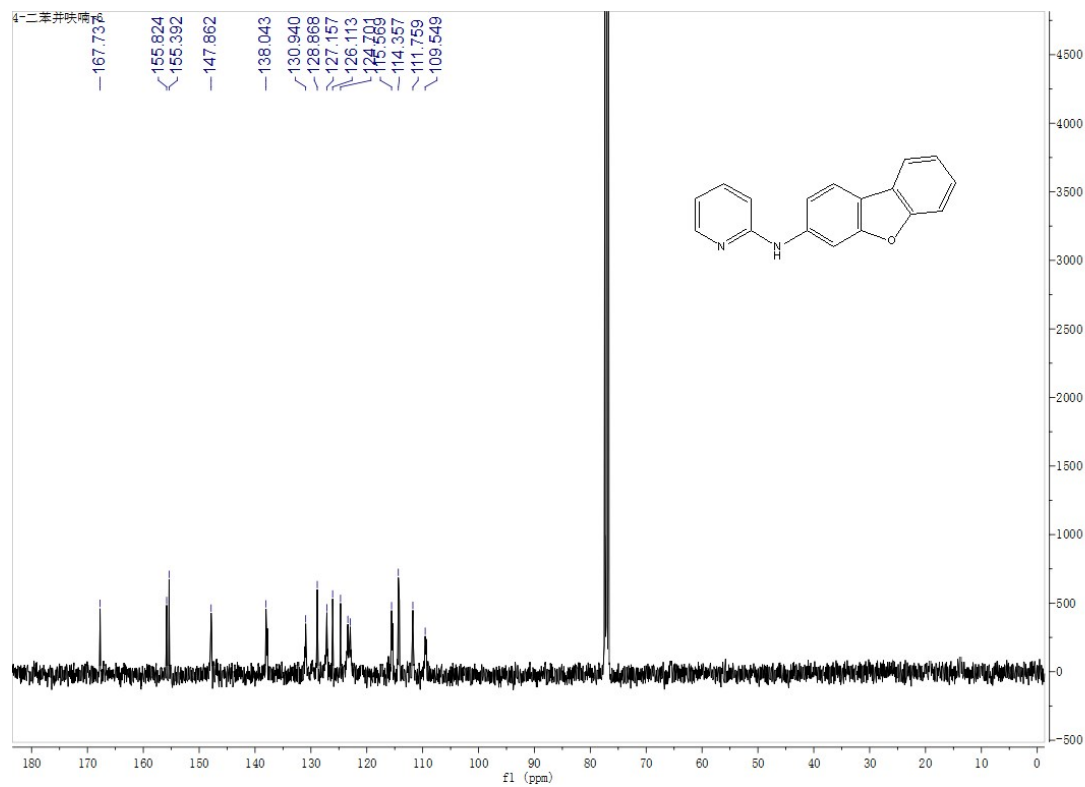
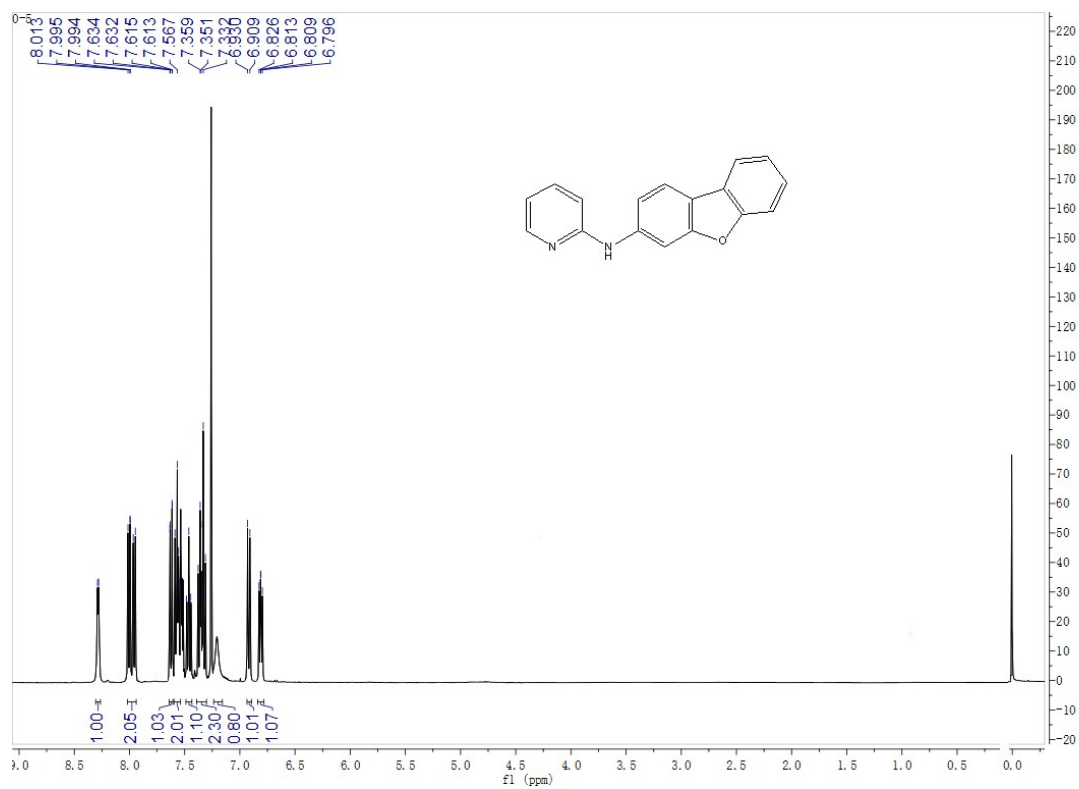
¹H NMR and ¹³C NMR of compound **3w**



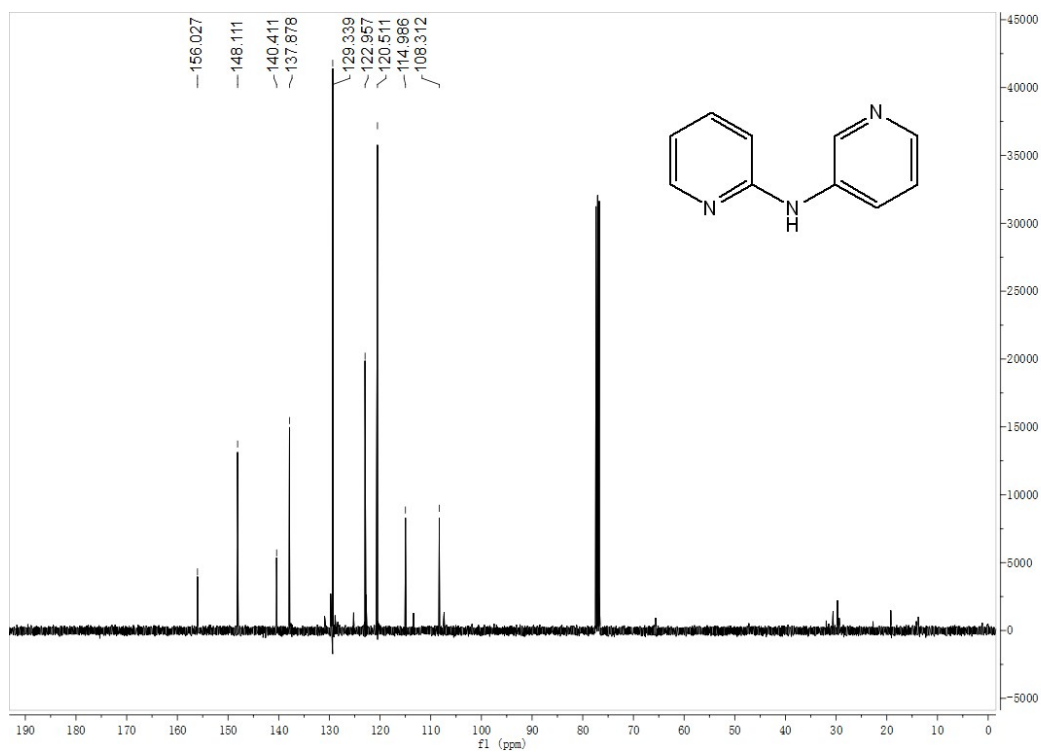
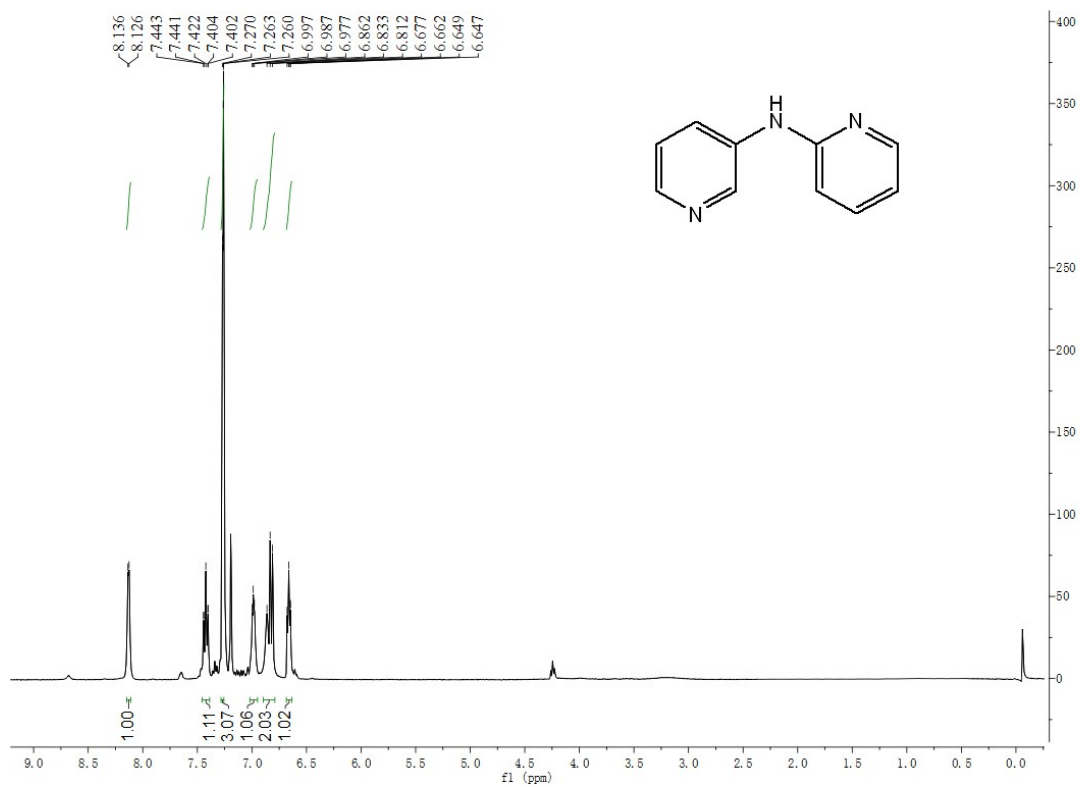
^1H NMR and ^{13}C NMR of compound **3x**



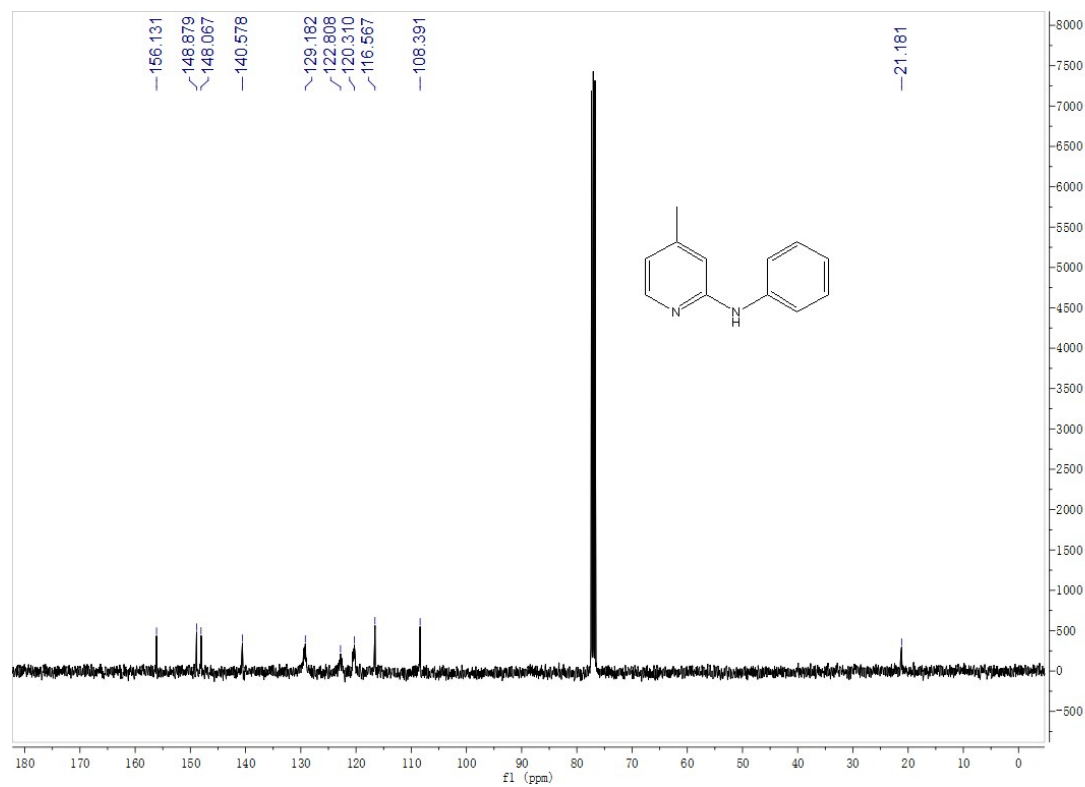
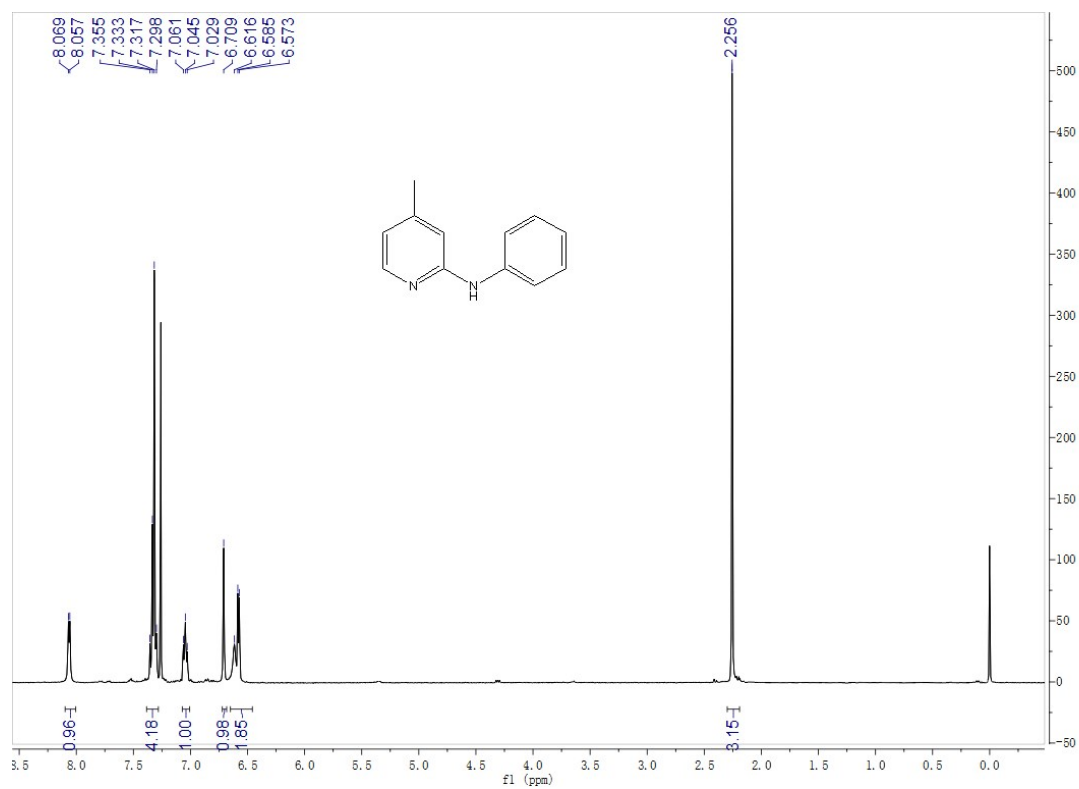
¹H NMR and ¹³C NMR of compound 3y



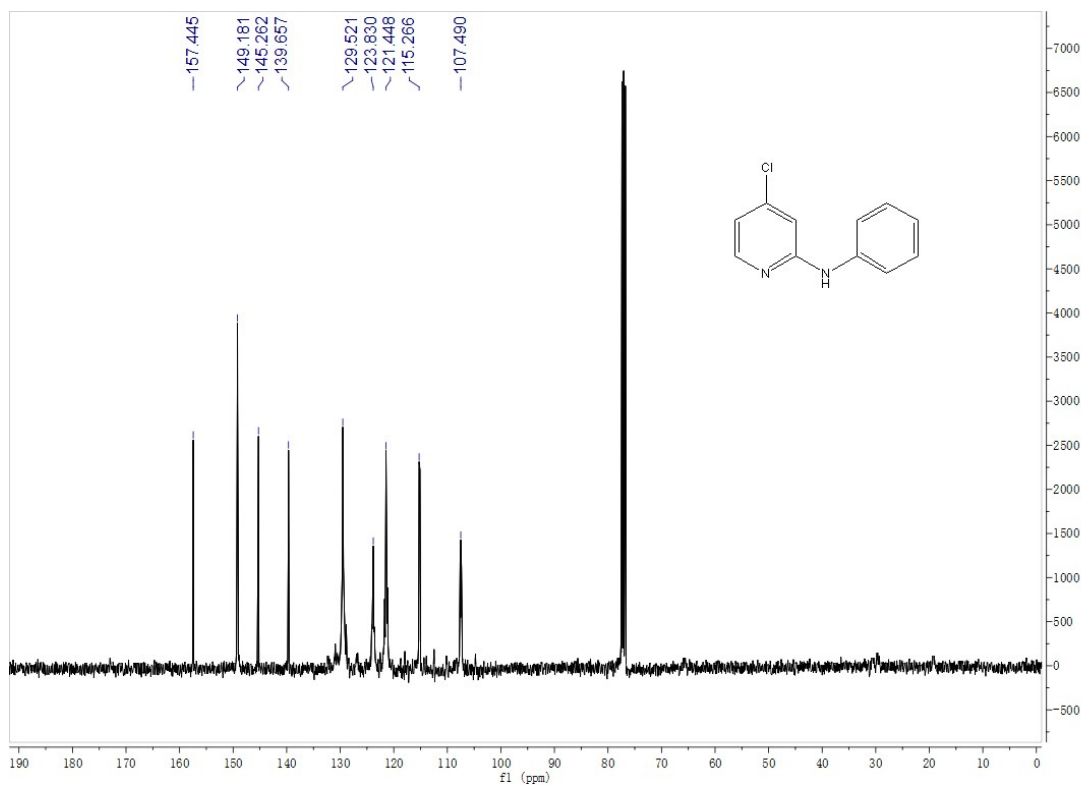
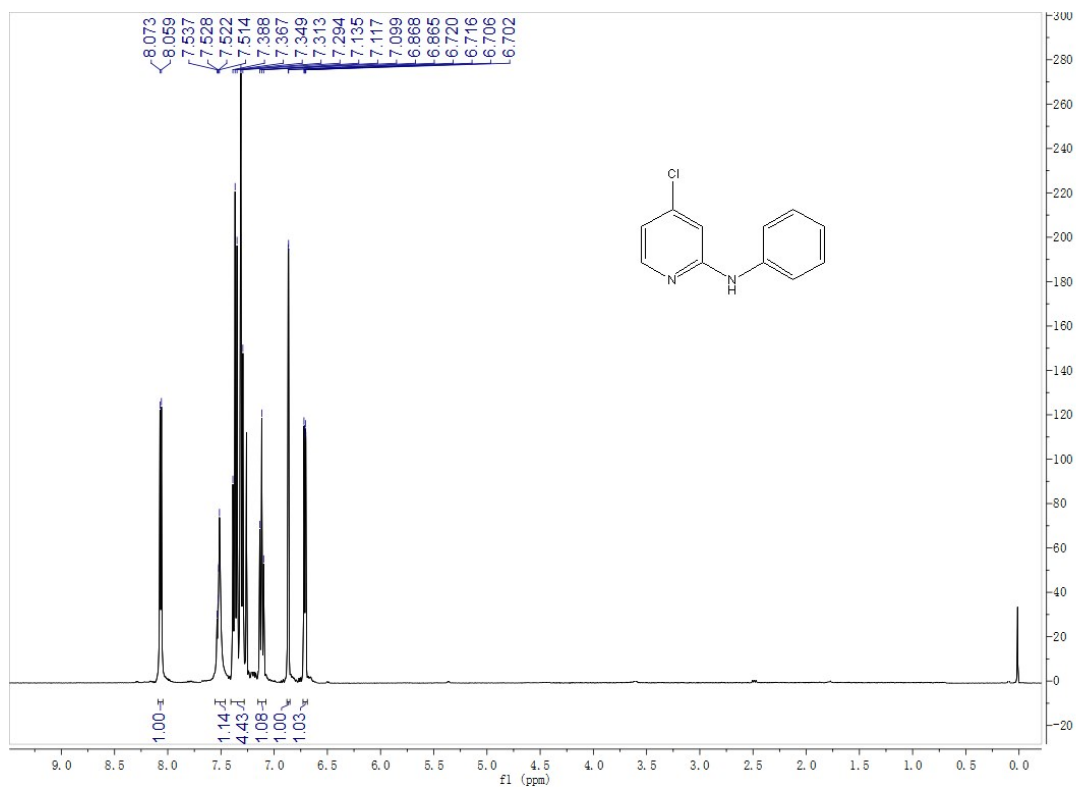
^1H NMR and ^{13}C NMR of compound **3z**



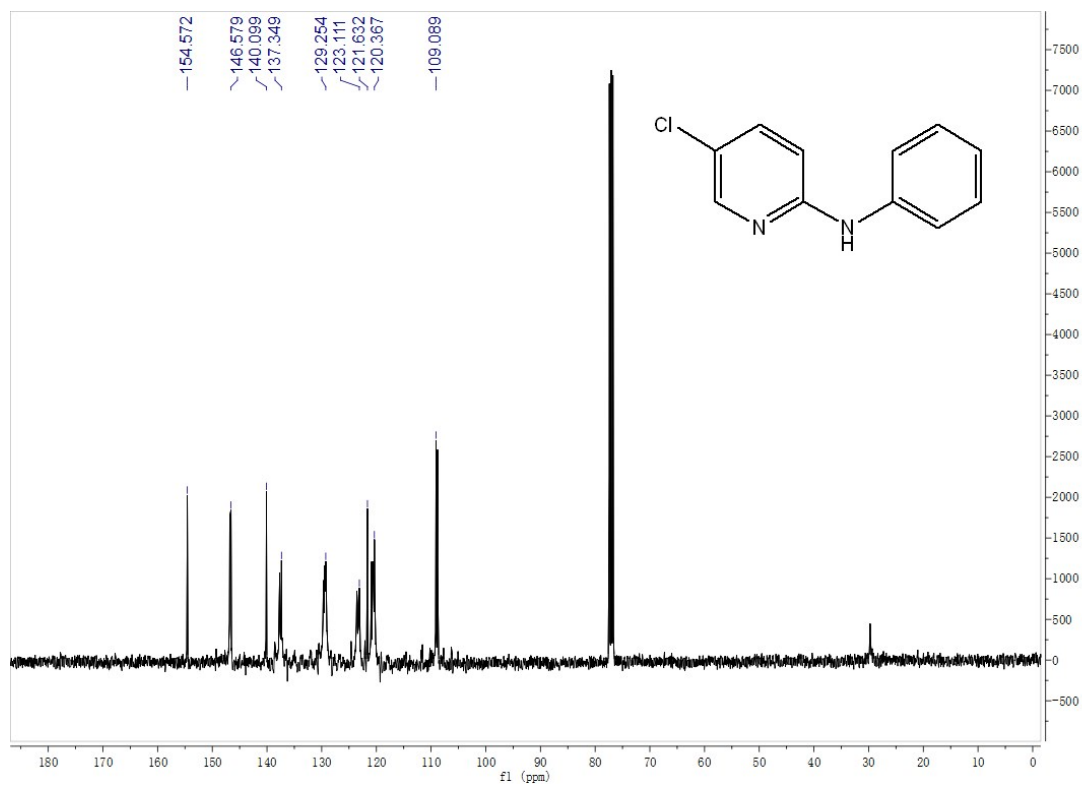
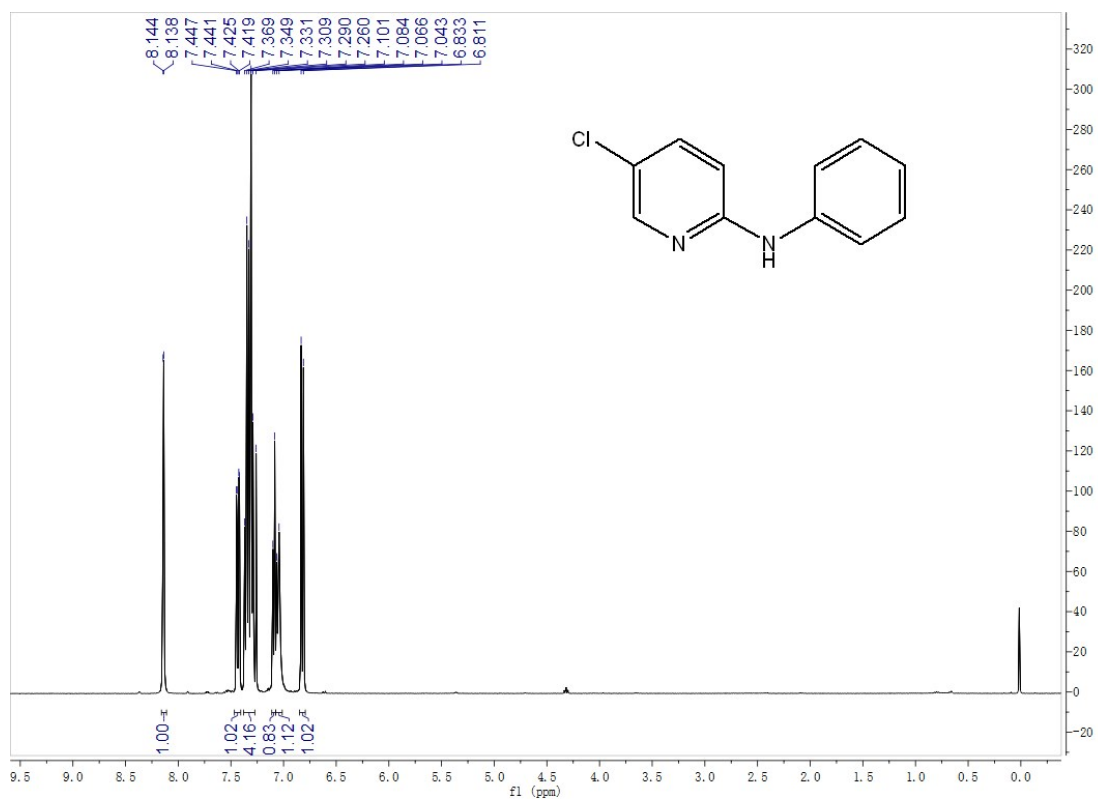
¹H NMR and ¹³C NMR of compound 3aa



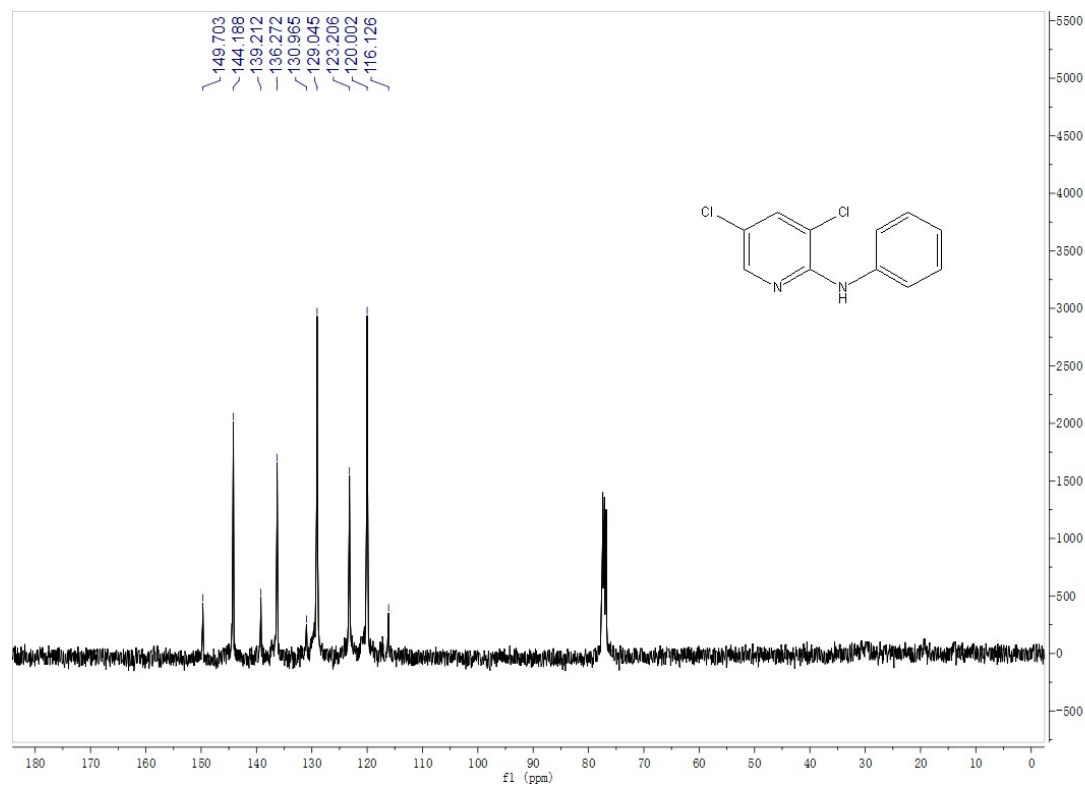
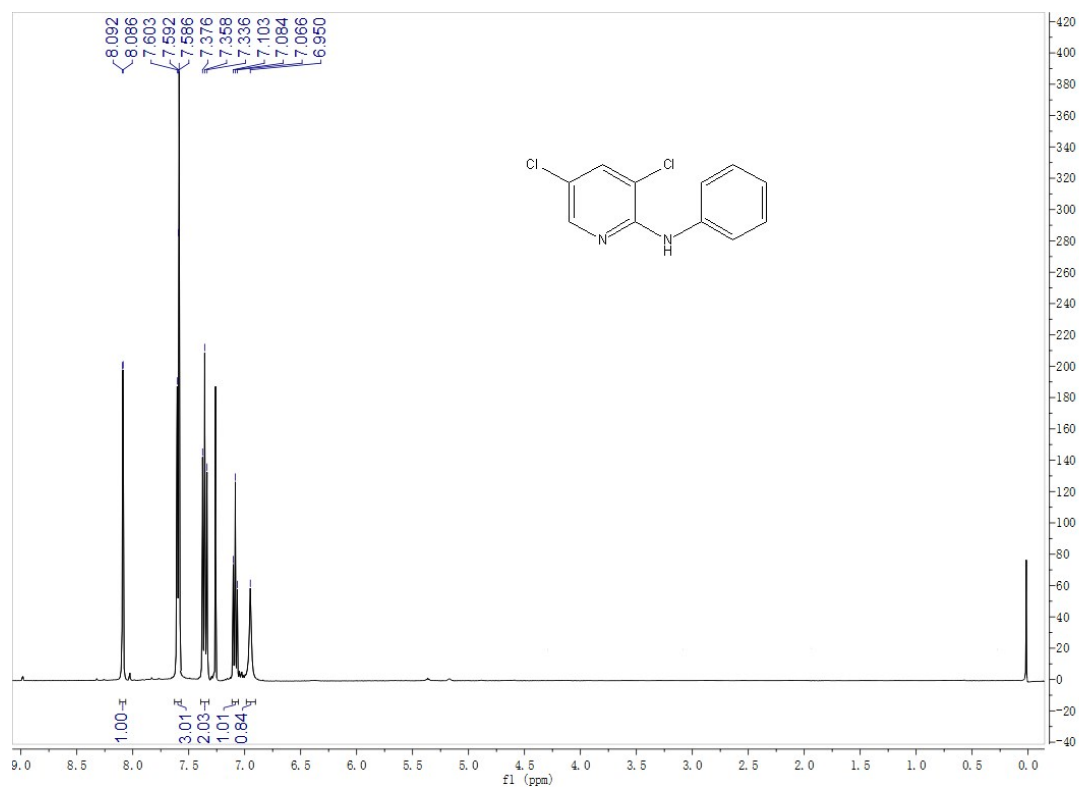
¹H NMR and ¹³C NMR of compound **3ab**



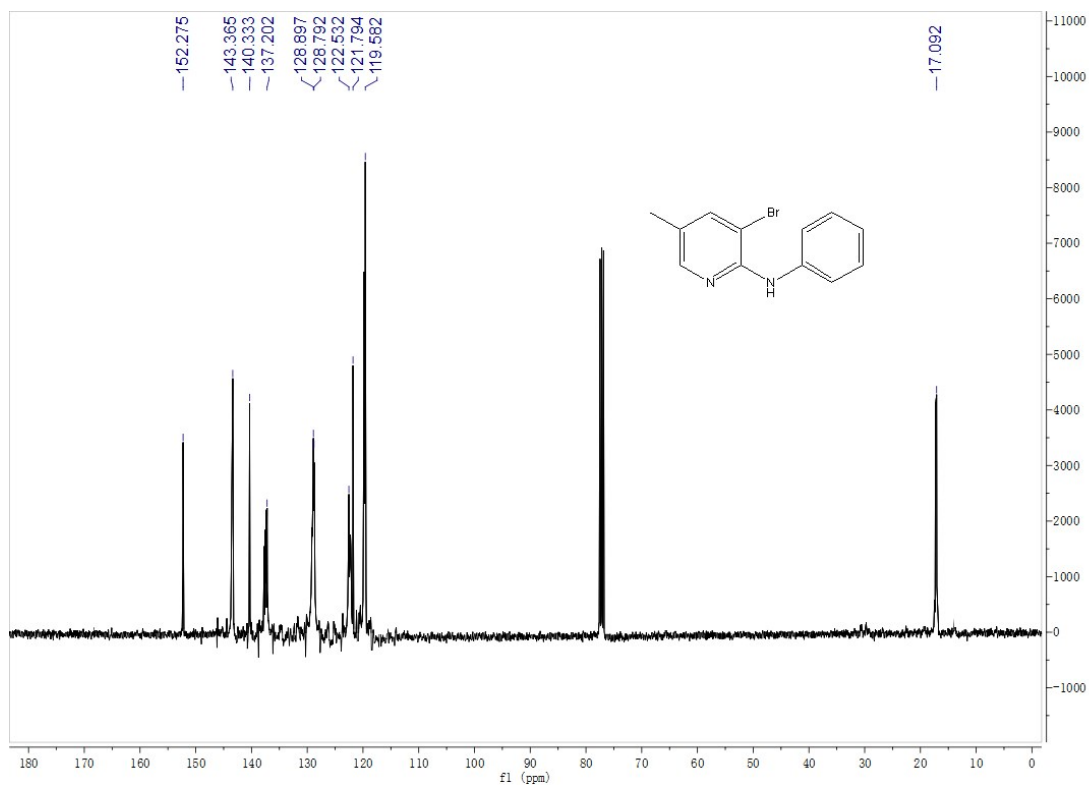
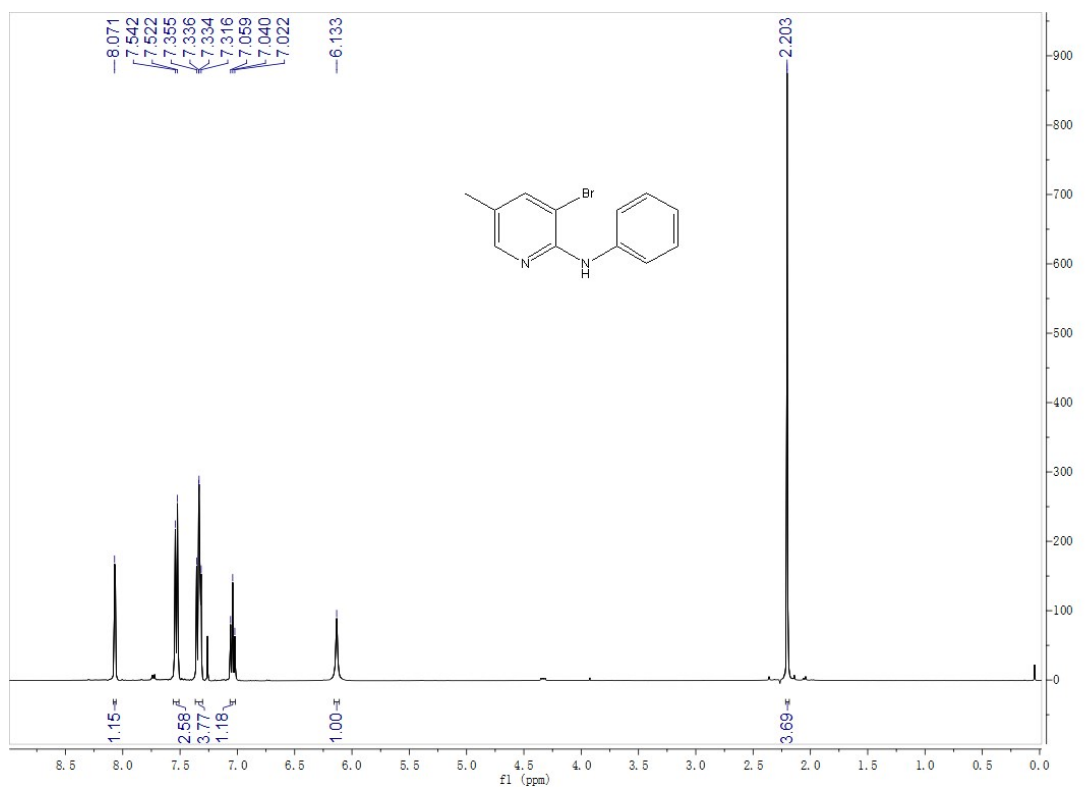
^1H NMR and ^{13}C NMR of compound **3ac**



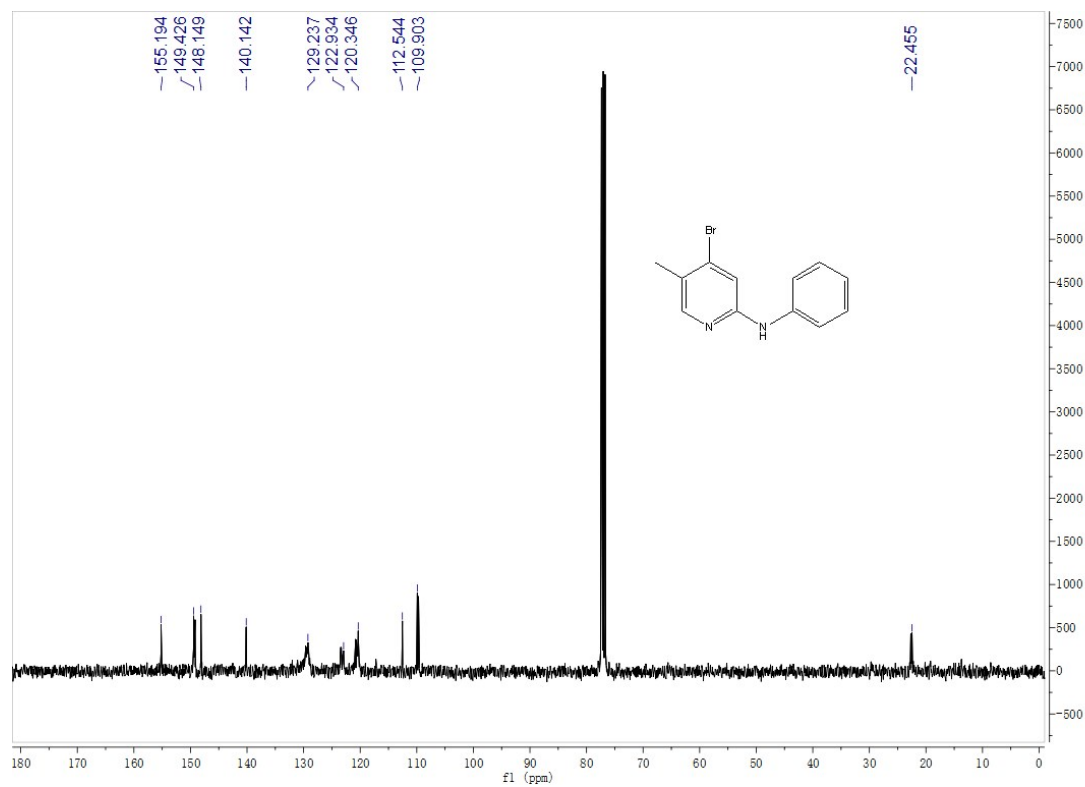
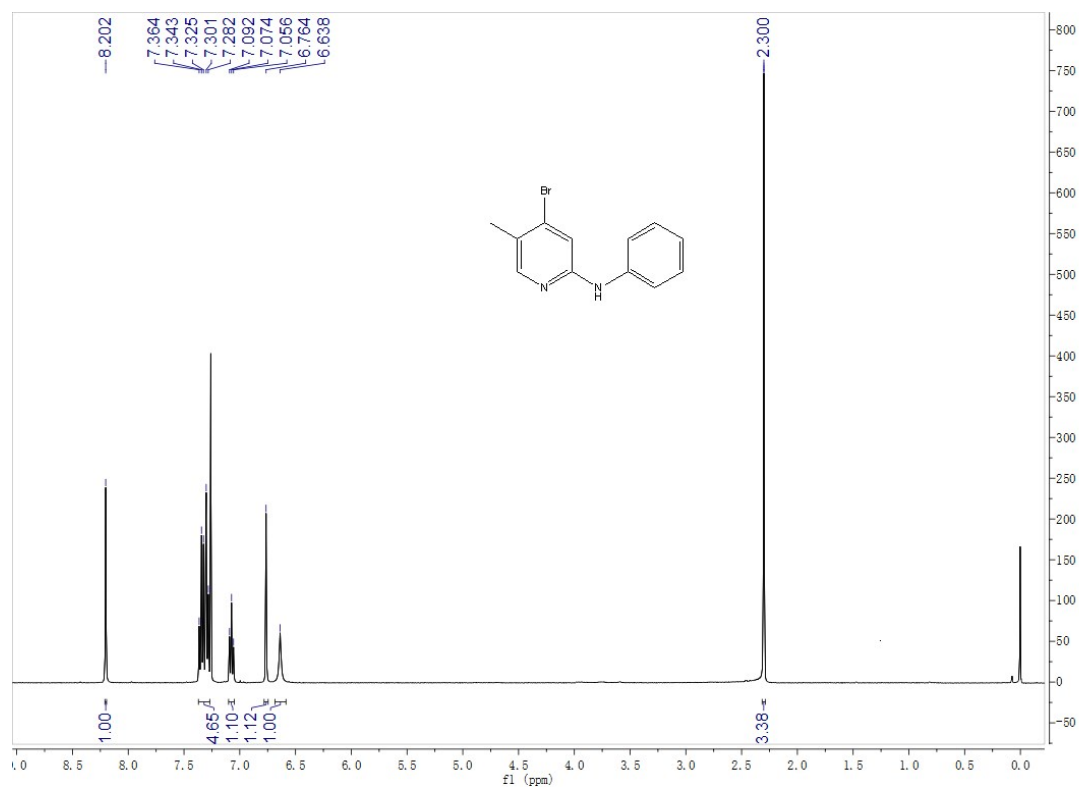
¹H NMR and ¹³C NMR of compound **3ad**.



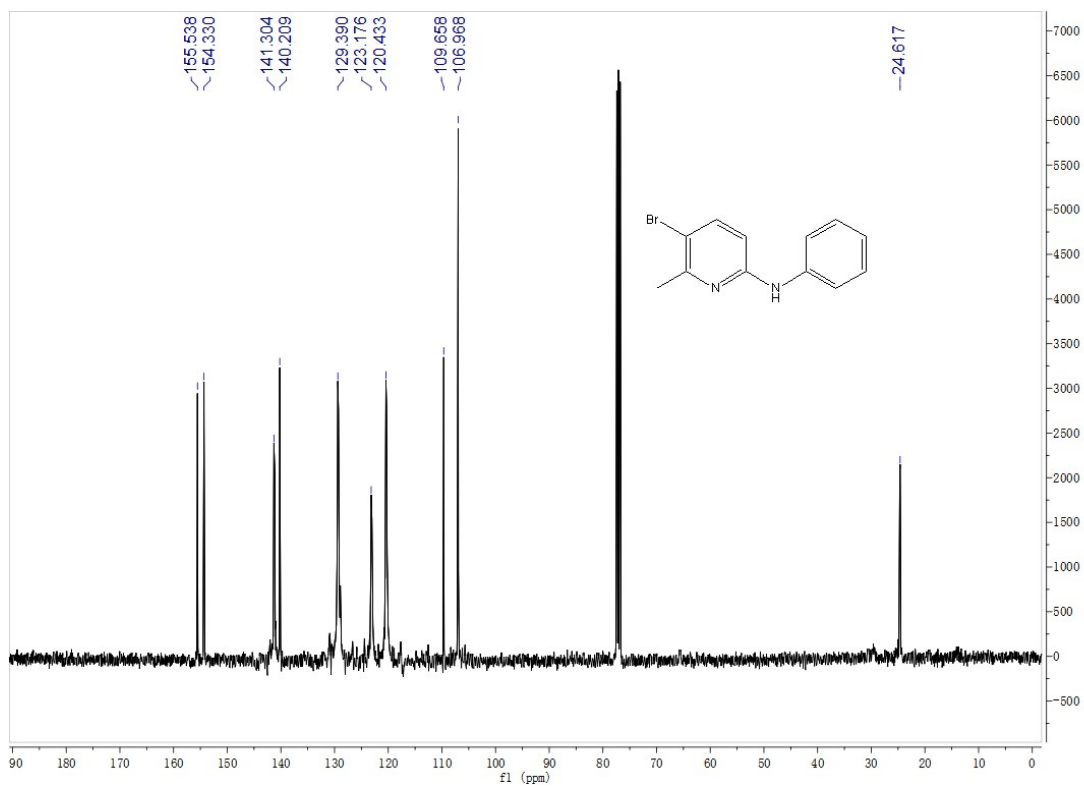
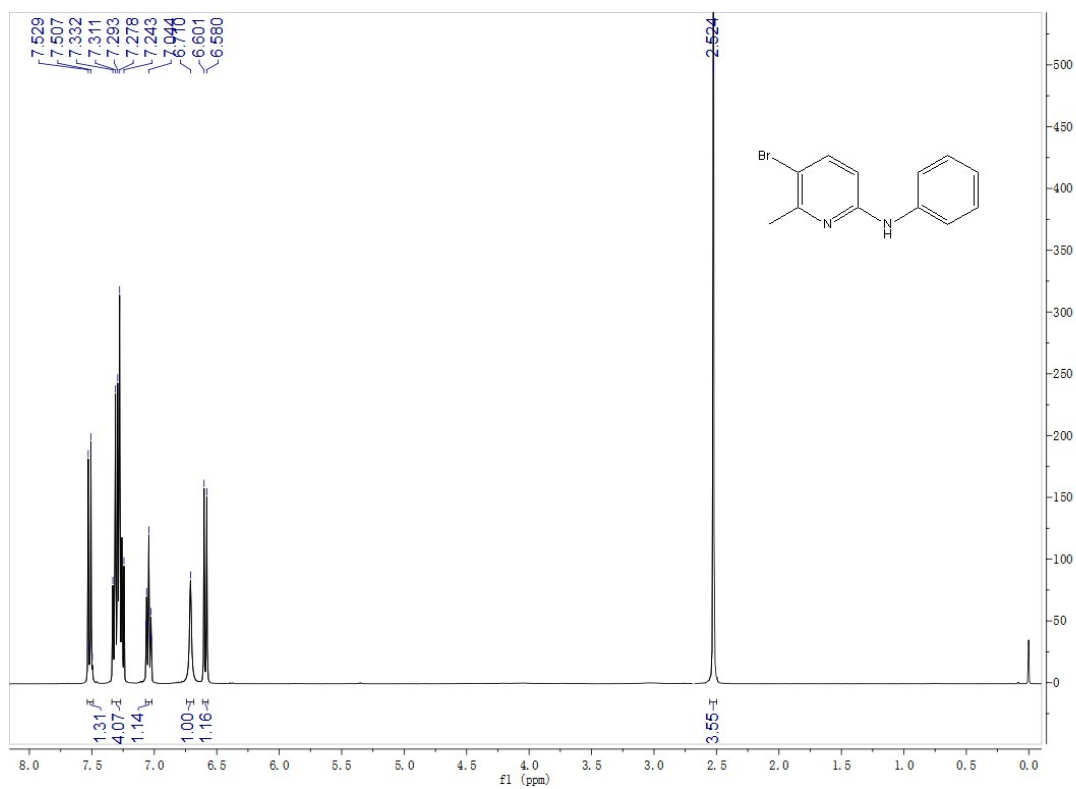
^1H NMR and ^{13}C NMR of compound **3ae**



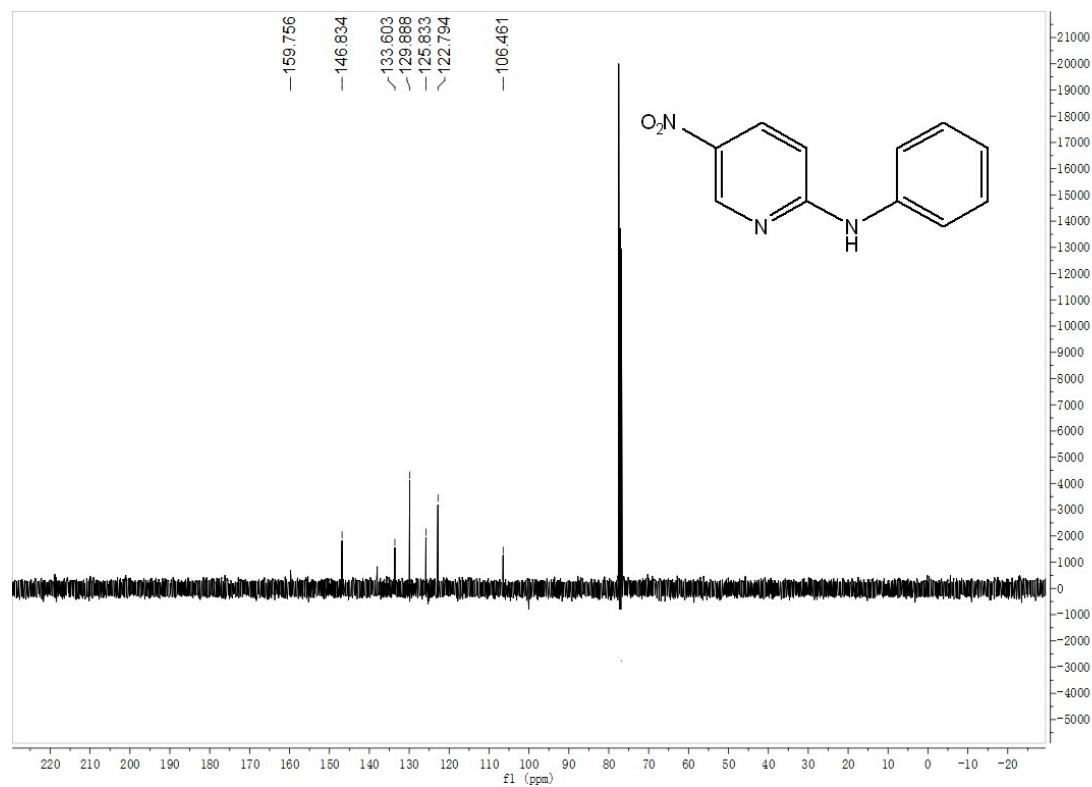
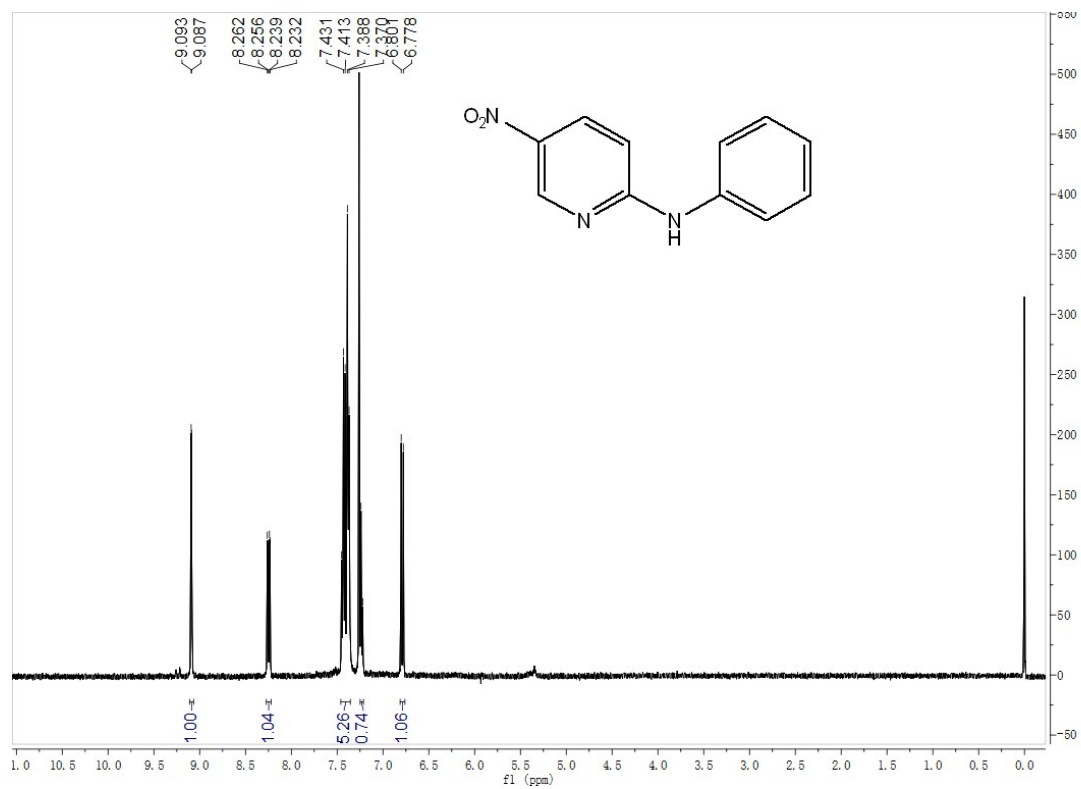
¹H NMR and ¹³C NMR of compound **3af**



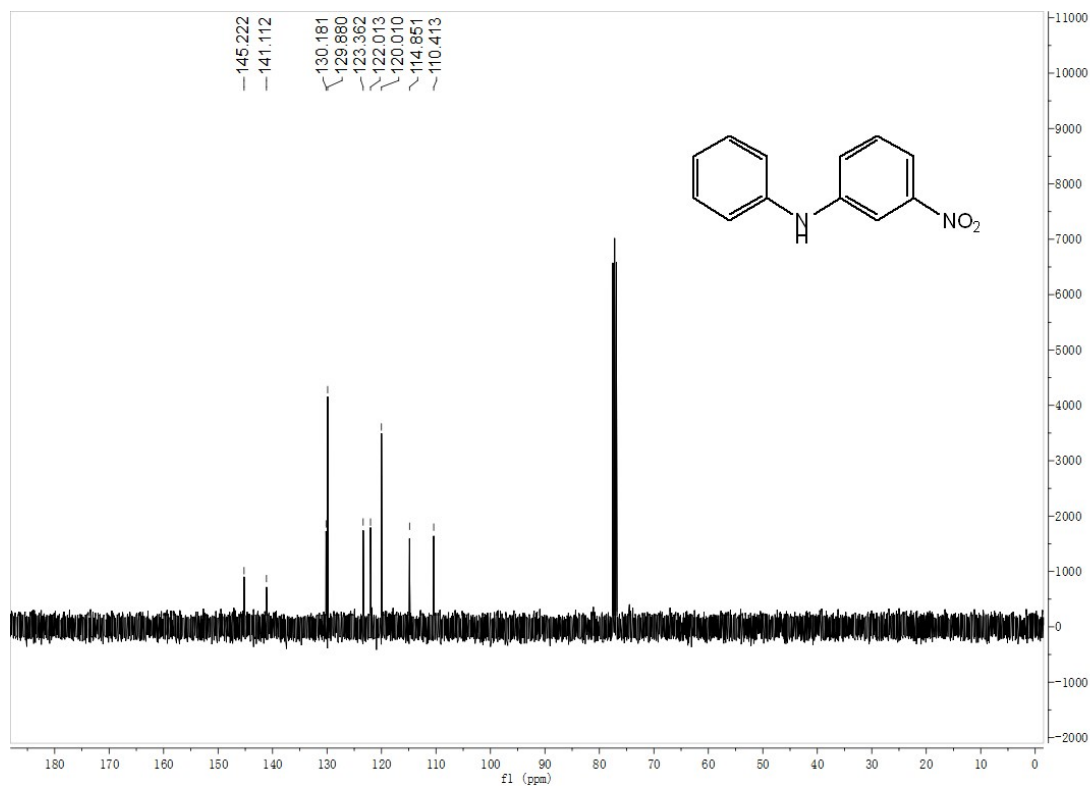
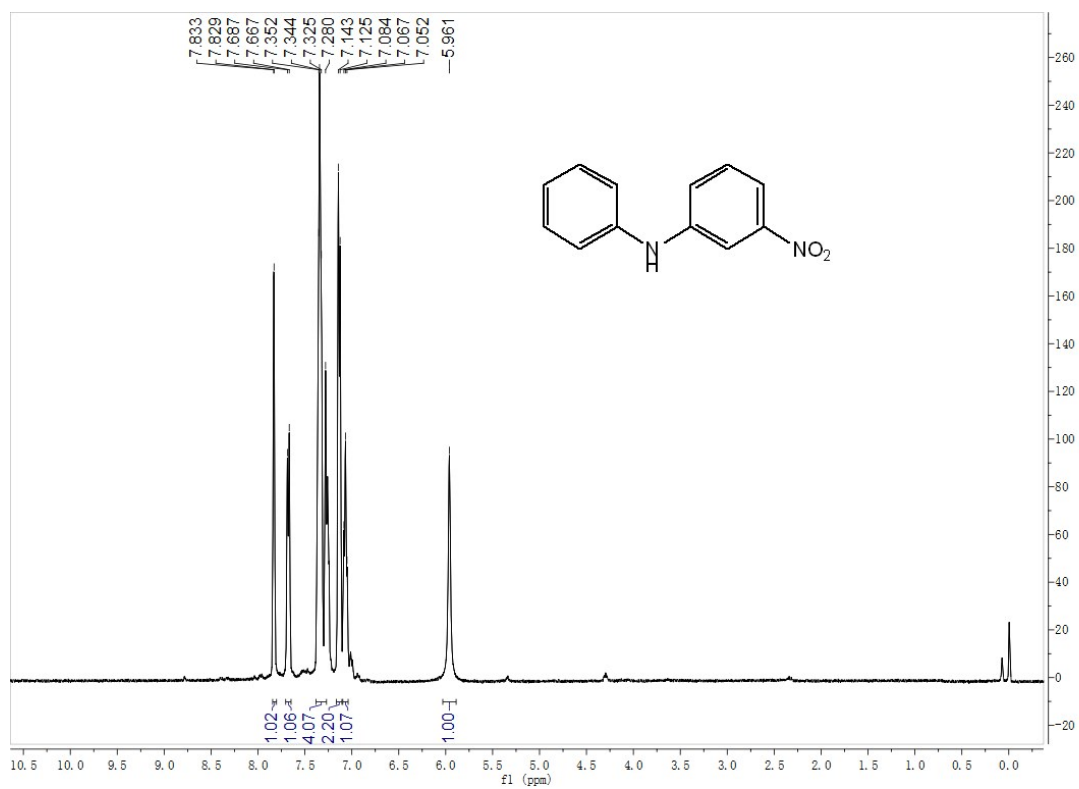
¹H NMR and ¹³C NMR of compound **3ag**



¹H NMR and ¹³C NMR of compound **3ah**



¹H NMR and ¹³C NMR of compound 5a



¹H NMR and ¹³C NMR of compound **5b**

