Bulky α-Diimine Palladium Complexes: Highly Efficient for Direct C-H Bond Arylation of Heteroarenes under Aerobic Conditions

Jia-Sheng Ouyang,[†] Yan-Fang Li,[†] Dong-Dong Lu,[†] Dong-Sheng Shen,[†] Zhuofeng Ke,[,‡] and Feng-Shou Liu[*,†]*

[†]*School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan, Guangdong, 528458, China*

[‡]*School of Materials Science and Engineering, MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, Sun Yat-sen University, Guangzhou 510275, China*

Content of Supporting Information

General Information for NMR data

The NMR data of compounds were obtained on a Varian Mercury-Plus 400 MHz spectrometer at ambient temperature, using $CDCl_3$ as solvent and referenced *versus* TMS as standard. Chemical shifts are reported in ppm and coupling constants are reported in Hz.

3a: 2-(2-methylnaphthalen-1-yl)benzo[b]thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, Ar-H, 1H), 7.89 (dd, *J* = 8.3, 2.3 Hz, Ar-H, 3H), 7.72 (d, *J* = 8.3 Hz, Ar-H, 1H), 7.51 – 7.38 (m, Ar-H, 5H), 7.29 (s, Ar-H, 1H), 2.44 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 141.0, 140.3, 135.8, 133.6, 131.8, 130.1, 128.7, 128.4, 127.7, 126.4, 125.9, 125.1, 124.6, 124.3, 124.1, 123.5, 122.2, 20.9.

3b: 2-(naphthalen-1-yl)benzo[b]thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (t, *J* =8.26 Hz, Ar-H, 1H), 7.96 – 7.83 (m, Ar-H, 4H), 7.67 (dd, *J* = 7.1, 1.1 Hz, Ar-H, 1H), 7.53 (ddd, *J* = 6.8, 5.2, 3.5 Hz, Ar-H, 3H), 7.47 (s, Ar-H, 1H), 7.40 (dtd, *J* = 16.4, 7.2, 1.3 Hz, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 140.3, 140.2, 133.8, 132.4, 131.8, 128.9, 128.5, 128.4, 126.6, 126.1, 125.8, 125.2, 124.5, 124.2, 124.0, 123.6, 122.1.

3c: 2-(4-methoxyphenyl)benzo[b]thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 19.4, 7.9 Hz, Ar-H, 2H), 7.65 (d, *J* = 8.8 Hz, Ar-H, 2H), 7.43 (s, Ar-H, 1H), 7.37 – 7.27 (m, Ar-H, 2H), 6.96 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.87 (s, OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 144.1, 140.8,

139.1, 127.7, 127.0, 124.4, 123.9, 123.2, 122.1, 118.2, 114.3, 55.4.

3d: 2-phenylbenzo[b]thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.68 (m, 4H), 7.55 (s, Ar-H, 1H), 7.43 (t, *J* = 7.5 Hz, Ar-H, 2H), 7.38 – 7.28 (m, Ar-H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.6, 139.4, 134.2, 128.9, 128.2, 126.4, 124.5, 124.3, 123.5, 122.2, 119.4.

3e: 2-(o-tolyl)benzo[b]thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, Ar-H, 1H), 7.48 (dd, *J* = 6.2, 1.7 Hz, Ar-H, 1H), 7.41 – 7.26 (m, Ar-H, 6H), 2.50 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.1, 140.0, 136.4, 134.1, 130.7, 130.6, 128.3, 125.9, 124.3, 124.0, 123.4, 123.0, 122.0, 21.1.

3f: 4-(benzo[b]thiophen-2-yl)benzonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, Ar-H, 4H), 7.76 – 7.72 (m, Ar-H, 2H), 7.69 (d, *J* = 6.4 Hz, Ar-H, 1H), 7.43 – 7.39 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 138.6, 132.7, 131.1, 130.1, 126.7, 125.3, 124.9, 124.1, 122.4, 121.8, 118.7, 111.4.

4a: 2-methyl-5-(2-methylnaphthalen-1-yl)thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, *J* = 8.8 Hz, Ar-H, 2H), 7.69 (d, *J* = 6.8 Hz, Ar-H, 1H), 7.40 (d, *J* = 7.3 Hz, Ar-H, 3H), 6.84 (d, *J* = 1.5 Hz, Ar-H, 1H), 6.75 (d, *J* = 3.3 Hz, Ar-H, 1H), 2.60 (s, CH_3, 3H), 2.39 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 137.6, 135.8, 134.2, 131.8, 130.7, 128.3, 128.1, 127.6, 127.2, 126.1, 126.0, 125.2, 124.8, 20.9, 15.3.

4b: 2-methyl-5-(naphthalen-1-yl)thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (t, *J* = 5.2 Hz, Ar-H, 1H), 7.86 (dd, *J* = 15.9, 8.5 Hz, Ar-H, 2H), 7.59 – 7.42 (m, Ar-H, 4H), 7.04 (d, *J* = 2.8 Hz, Ar-H, 1H), 6.84 (d, *J* = 2.0 Hz, Ar-H, 1H), 2.59 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.4, 133.9, 132.8, 131.8, 128.3, 128.1, 127.9, 127.2, 126.3, 125.9, 125.8, 125.5, 125.2, 15.3.

4c: 2-(4-methoxyphenyl)-5-methylthiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.9 Hz, Ar-H, 2H), 6.98 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.89 (d, *J* = 8.9 Hz, Ar-H, 2H), 6.69 (d, *J* = 2.4 Hz, Ar-H, 1H), 3.82 (s, OCH_3, 3H), 2.49 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 141.9, 138.4, 126.8, 126.0, 121.8, 114.2, 100.0, 55.3, 15.4.

4g: 2-(4-(tert-butyl)phenyl)-5-methylthiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, Ar-H, 2H), 7.38 (d, *J* = 8.4 Hz, Ar-H, 2H), 7.06 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.71 (d, *J* = 2.5 Hz, Ar-H, 1H), 2.50 (s, CH_3, 3H), 1.34 (s, CH_3, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 142.0, 139.0, 132.0, 126.1, 125.7, 125.3, 122.4, 34.5, 31.3, 15.4.

5a: 2-ethyl-5-(2-methylnaphthalen-1-yl)thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.73 (m, Ar-H, 3H), 7.50 – 7.43 (m, Ar-H, 3H), 6.93 (d, *J* = 3.0 Hz, Ar-H, 1H), 6.84 (d, *J* = 3.3 Hz, Ar-H, 1H), 3.00 (dd, *J* = 7.4, 3.1 Hz, CH_2, 2H), 2.45 (s, CH_3, 3H), 1.46 (t, *J* = 7.5 Hz, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 137.1, 135.9, 134.2, 131.8, 130.8, 128.3, 128.1, 127.6, 127.4, 126.1, 126.0, 124.9, 123.1, 23.5, 21.0, 15.8.

5b: 2-ethyl-5-(naphthalen-1-yl)thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 5.6 Hz, Ar-H, 1H), 7.92 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.86 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.59 (d, *J* = 7.0 Hz, Ar-H, 1H), 7.52 (dt, *J* = 8.4, 4.6 Hz, Ar-H, 3H), 7.10 (d, *J* = 3.2 Hz, Ar-H, 1H), 6.90 (d, *J* = 3.0 Hz, Ar-H, 1H), 2.97 (dd, *J* = 7.5 Hz, CH_2, 2H), 1.43 (t, *J* = 7.5 Hz, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 139.0, 133.9, 132.9, 131.8, 128.3, 128.0, 127.9, 127.0, 126.3, 125.9, 125.9, 125.2, 123.6, 23.5, 15.9.

6b: 2-chloro-5-(naphthalen-1-yl)thiophene

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.5 Hz, Ar-H, 1H), 7.89 (dd, *J* = 10.5, 5.5 Hz, Ar-H, 2H), 7.50 (dt, *J* = 15.8, 6.2 Hz, Ar-H, 4H), 7.00 (s, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 133.9, 131.8, 131.5, 129.8, 128.8, 128.4, 128.2, 126.7, 126.4, 126.2, 125.4, 125.2, 125.1.

7b: 5-(naphthalen-1-yl)thiophene-2-carbonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J* = 6.7 Hz, Ar-H, 1H), 7.97 (dd, *J* = 8.7, 2.6 Hz, Ar-H, 2H), 7.72 (d, *J* = 3.8 Hz, Ar-H, 1H), 7.63 – 7.50 (m, Ar-H, 4H), 7.27 (t, *J* = 4.9 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 137.6, 133.7, 131.2, 129.9, 129.7, 128.6, 127.6, 127.1, 126.4, 125.1, 124.8, 114.2, 109.4.

8a: 5-(2-methylnaphthalen-1-yl)thiophene-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, CHO, 1H), 7.92 – 7.83 (m, Ar-H, 3H), 7.53 – 7.37 (m, Ar-H, 4H), 7.11 (d, *J* = 3.7 Hz, Ar-H, 2H), 2.35 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.9, 151.1, 144.4, 136.6, 135.6, 133.2, 131.8, 129.5, 129.3, 128.8, 128.4, 127.9, 126.7, 125.3, 125.3, 20.8.

8b: 5-(naphthalen-1-yl)thiophene-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, CHO, 1H), 8.22 – 8.10 (m, Ar-H, 1H), 7.96 – 7.91 (m, Ar-H, 3H), 7.85 (d, *J* = 3.8 Hz, Ar-H, 1H), 7.56 (dt, *J* = 9.5, 3.7 Hz, Ar-H, 3H), 7.36 (d, *J* = 3.8 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.8, 152.3, 143.6, 136.5, 133.9, 131.2, 131.1, 129.8, 128.6, 128.6, 128.3, 127.0, 126.4, 125.2, 125.1.

8g: 5-(4-(tert-butyl)phenyl)thiophene-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, CHO, 1H), 7.73 (d, *J* = 3.9 Hz, Ar-H, 1H), 7.61 (d, *J* = 8.4 Hz, Ar-H, 2H), 7.46 (d, *J* = 8.4 Hz, Ar-H, 2H), 7.37 (d, *J* = 3.9 Hz, Ar-H, 1H), 1.35 (s, CH_3, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 154.5, 152.9, 142.0, 137.5, 130.2, 126.2, 126.1, 123.6, 34.8, 31.1.

9b: 3-(naphthalen-1-yl)-2-phenylimidazo[1, 2-a]pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 20.1, 8.0 Hz, Ar-H, 2H), 7.78 (d, *J* = 9.1 Hz, Ar-H, 1H), 7.69 – 7.53 (m, Ar-H, 5H), 7.48 – 7.36 (m, Ar-H, 3H), 7.31 – 7.15 (m, Ar-H, 4H), 6.66 (t, *J* = 6.8 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 143.3, 134.1, 134.0, 132.3, 130.3, 130.0, 128.8, 128.2, 127.5, 127.4, 127.3, 127.2, 126.6, 126.1, 125.1, 124.7, 123.9, 119.0, 117.4, 112.1.

10a: 2, 4-dimethyl-5-(2-methylnaphthalen-1-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, Ar-H, 2H), 7.52 (d, *J* = 7.4 Hz, Ar-H, 1H), 7.48 – 7.30 (m, Ar-H, 3H), 2.77 (s, CH_3, 3H), 2.31 (s, CH_3, 3H), 2.08 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 149.6, 136.6, 133.5, 131.9, 128.7, 128.4, 127.9, 127.0, 126.8, 126.5, 125.3, 125.1, 20.6, 19.3, 15.2.

11a: 2-methyl-5-(2-methylnaphthalen-1-yl)-4-phenylthiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 12.3, 5.0 Hz, Ar-H, 2H), 7.71 (d, *J* = 7.7 Hz, Ar-H, 1H), 7.49 – 7.35 (m, Ar-H, 5H), 7.17 – 7.08 (m, Ar-H, 3H), 2.86 (s, CH_3, 3H), 2.21 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 150.9, 136.3, 134.7, 133.5, 132.0, 128.9, 128.6, 128.2, 128.0, 128.0, 127.3, 127.3, 127.2, 126.7, 125.4, 125.2, 20.6, 19.3.

11b: 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole

NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, Ar-H, 2H), 7.83 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.53 – 7.37 (m, Ar-H, 6H), 7.12 (t, *J* = 1.8 Hz, Ar-H, 3H), 2.84 (s, CH_3, 3H). NMR (101 MHz, $CDCl_3$) δ 164.7, 150.9, 134.5, 133.6, 132.3, 130.8, 129.6, 129.4, 129.3, 129.1, 128.8, 128.3, 128.1, 128.0, 127.3, 126.6, 126.1, 125.6, 125.4, 19.2.

12b: 4-methyl-5-(naphthalen-1-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, Ar-H, 1H), 7.74 (d, *J* = 7.8 Hz, Ar-H, 2H), 7.54 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.38 – 7.24 (m, Ar-H, 4H), 2.14 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 150.6, 133.5, 132.3, 129.2, 129.0, 128.9, 128.6, 128.3, 126.5, 126.0, 125.4, 125.0, 15.6.

13b: 1-methyl-5-(naphthalen-1-yl)-1H-imidazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, Ar-H, 2H), 7.65 (d, *J* = 8.1 Hz, Ar-H, 2H), 7.57 – 7.42 (m, Ar-H, 4H), 7.16 (s, Ar-H, 1H), 3.42 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 133.7, 132.9, 131.1, 129.4, 129.2, 129.0, 128.4, 127.2, 126.7, 126.2, 125.5, 125.2, 32.0.

14b: 1, 2-dimethyl-5-(naphthalen-1-yl)-1H-imidazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, Ar-H, 2H), 7.66 (d, *J* = 8.1, Ar-H, 1H),

7.54 – 7.38 (m, Ar-H, 4H), 7.00 (s, Ar-H, 1H), 3.25 (s, CH_3, 3H), 2.50 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 133.5, 132.8, 131.0, 129.0, 128.9, 128.3, 127.8, 126.8, 126.6, 126.0, 125.5, 125.2, 30.9, 13.5.

16a: 3-(benzo[b]thiophen-2-yl)pyridine

^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, Ar-H, 1H), 8.58 (d, *J* = 1.9 Hz, Ar-H, 1H), 8.07 – 7.93 (m, Ar-H, 1H), 7.83 (m, Ar-H, 2H), 7.60 (d, *J* = 1.9 Hz, Ar-H, 1H), 7.47 – 7.31 (m, Ar-H, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 147.4, 140.3, 140.2, 139.6, 133.5, 130.3, 124.8, 124.7, 123.8, 123.7, 122.3, 120.7.

16b: 4-(benzo[b]thiophen-2-yl)isoquinoline

^1H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, Ar-H, 1H), 8.73 (s, Ar-H, 1H), 8.29 (d, *J* = 8.4 Hz, Ar-H, 1H), 8.07 – 7.96 (m, Ar-H, 1H), 7.88 (m, Ar-H,2H), 7.76 – 7.57 (m, Ar-H, 2H), 7.54 – 7.35 (m, Ar-H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 143.5, 140.2, 139.8, 138.0, 133.9, 130.9 128.0, 127.8, 127.3, 126.1, 124.6, 124.6, 124.4, 124.2, 123.5, 121.9.

17a: 3-(5-methylthiophen-2-yl)pyridine

^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, Ar-H, 1H), 8.47 (d, *J* = 4.7 Hz, Ar-H, 1H), 7.80 (d, *J* = 8.0 Hz, Ar-H, 1H), 7.31 – 7.27 (m, Ar-H, 1H), 7.16 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.77 (d, *J* = 4.2 Hz, Ar-H, 1H), 2.54 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 146.6, 140.9, 137.9, 132.4, 130.7, 126.45 (s), 124.1, 123.5, 15.4.

17b: 4-(5-methylthiophen-2-yl)isoquinoline

^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, Ar-H, 1H), 8.57 (s, Ar-H, 1H), 8.25 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.96 (d, *J* = 8.0 Hz, Ar-H, 1H), 7.75 – 7.53 (m, Ar-H, 2H), 7.11 – 7.02

(m, Ar-H, 1H), 6.84 (d, *J* = 1.1 Hz, Ar-H, 1H), 2.55 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 143.1, 141.2, 135.3, 134.0, 130.7, 128.2, 127.9, 127.8, 127.2, 126.4, 125.8, 124.5, 15.2.

17c: 5-(5-methylthiophen-2-yl)pyrimidine

^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, Ar-H, 1H), 8.90 (s, Ar-H, 2H), 7.23 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.85 – 6.79 (m, Ar-H, 1H), 2.55 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 152.9, 142.4, 133.7, 128.9, 126.8, 125.2, 15.4.

18a: 3-(5-ethylthiophen-2-yl)pyridine

^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, Ar-H, 1H), 8.45 – 8.22 (m, Ar-H, 1H), 7.89 – 7.59 (m, Ar-H, 1H), 7.19 – 7.00 (m, Ar-H, 2H), 6.83 – 6.51 (m, Ar-H, 1H), 2.76 (q, *J* = 7.5 Hz, CH_2, 2H), 1.23 (m, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.3, 146.0, 137.0, 131.9, 130.3, 124.2, 123.5, 123.1, 23.1, 15.4.

18b: 4-(5-ethylthiophen-2-yl)isoquinoline

^1H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, Ar-H, 1H), 8.57 (s, Ar-H, 1H), 8.24 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.92 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.69 – 7.59 (m, Ar-H, 1H), 7.54 (t, *J* = 7.1 Hz, Ar-H, 1H), 7.06 (d, *J* = 3.4 Hz, Ar-H, 1H), 6.85 (dd, *J* = 2.4, 0.9 Hz, Ar-H, 1H), 2.88 (q, *J* = 7.5 Hz, CH_2, 2H), 1.35 (t, *J* = 7.5 Hz, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 148.7, 143.0, 134.7, 133.8, 130.5, 128.1, 127.6, 127.5, 127.0, 126.4, 124.4, 123.8, 23.3, 15.7.

18c: 5-(5-methylthiophen-2-yl)pyrimidine

^1H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, Ar-H, 1H), 8.88 (s, Ar-H, 2H), 7.23 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.83 (d, *J* = 3.3 Hz, Ar-H, 1H), 2.89 (q, *J* = 7.5 Hz, CH_2, 2H), 1.34

(t, J = 7.5 Hz, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 152.9, 150.1, 133.3, 128.9, 125.0, 124.9, 23.6, 15.8.

19a: 5-(5-methylthiophen-2-yl)pyrimidine

^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, Ar-H, 1H), 8.47 (s, Ar-H, 1H), 7.79 (d, J = 7.9 Hz, Ar-H, 1H), 7.36 – 7.20 (m, Ar-H, 1H), 7.08 (s, Ar-H, 1H), 2.39 (s, CH_3, 3H), 2.18 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.4, 135.0, 134.4, 134.0, 132.2, 130.6, 127.0, 123.5, 13.6, 13.2.

19b: 4-(4, 5-dimethylthiophen-2-yl)isoquinoline

^1H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, Ar-H, 1H), 8.57 (s, Ar-H, 1H), 8.31 (d, J = 8.5 Hz, Ar-H, 1H), 7.99 (d, J = 8.1 Hz, Ar-H, 1H), 7.71 (t, J = 7.6 Hz, Ar-H, 1H), 7.61 (t, J = 7.5 Hz, Ar-H, 1H), 2.43 (s, CH_3, 3H), 2.23 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 143.0, 134.4, 134.0, 133.8, 132.7, 130.9, 130.7, 128.3, 127.8, 127.2, 126.6, 124.7, 13.6, 13.0.

19c: 5-(4, 5-dimethylthiophen-2-yl)pyrimidine

^1H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, Ar-H, 1H), 8.83 (s, Ar-H, 2H), 7.09 (s, Ar-H, 1H), 2.37 (s, CH_3, 3H), 2.15 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 152.7, 135.5, 134.9, 130.8, 128.8, 128.0, 13.5, 13.2.

20a: 3-(5-chlorothiophen-2-yl)pyridine

^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, Ar-H, 1H), 8.49 (d, J = 4.4 Hz, Ar-H, 1H), 7.77 – 7.67 (m, Ar-H, 1H), 7.30 – 7.26 (m, Ar-H, 1H), 7.08 (m, Ar-H, 1H), 6.89 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 146.5, 138.8, 132.6, 130.6, 127.3, 124.9, 123.7, 123.5.

20b: 4-(5-chlorothiophen-2-yl)isoquinoline

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, Ar-H, 1H), 8.54 (s, Ar-H, 1H), 8.17 (d, *J* = 8.5 Hz, Ar-H, 1H), 8.00 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.68 (m, Ar-H, 2H), 7.10 – 6.97 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 143.3, 136.4, 134.0, 131.1, 130.8, 128.2, 128.0, 127.5, 127.3, 126.7, 125.4, 124.1.

20c: 5-(5-chlorothiophen-2-yl)pyrimidine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, Ar-H, 1H), 8.86 (s, Ar-H, 2H), 7.19 (d, *J* = 3.9 Hz, Ar-H, 1H), 6.99 (d, *J* = 3.9 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 153.1, 134.7, 132.1, 128.0, 127.7, 124.7.

21b: 4-(5-isocyanothiophen-2-yl)isoquinoline

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, Ar-H, 1H), 8.59 (s, Ar-H, 1H), 8.08 (m, Ar-H, 2H), 7.84 – 7.62 (m, Ar-H, 3H), 7.30 (d, *J* = 3.8 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 153.9, 148.3, 145.5, 143.7, 137.8, 133.7, 131.7, 128.3, 128.0, 123.9, 123.7, 113.9, 110.5.

22b: 5-(isoquinolin-4-yl)thiophene-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, Ar-H, 1H), 8.95 (s, Ar-H, 1H), 8.63 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.94 (d, *J* = 7.9 Hz, Ar-H, 1H), 7.79 (d, *J* = 3.9 Hz, Ar-H, 1H), 7.47 (d, *J* = 3.9 Hz, Ar-H, 1H), 7.39 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.8, 153.7, 148.0, 144.3, 143.5, 136.6, 133.5, 131.5, 129.1, 128.2, 128.1, 127.8, 125.1, 123.9.

23a: 2-phenyl-3-(pyridin-3-yl)imidazo[1,2-a]pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.68 (m, Ar-H, 2H), 7.96 (m, Ar-H, 1H), 7.74 (m, Ar-H, 2H), 7.65 – 7.56 (m, Ar-H, 2H), 7.46 (m, Ar-H, 1H), 7.34 – 7.27 (m, Ar-H, 3H), 6.80 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 149.7, 145.2, 143.7, 138.2, 133.5, 128.4, 128.1, 127.8, 126.2, 125.2, 124.1, 122.7, 117.7, 117.3, 112.7.

23c: 2-phenyl-3-(pyrimidin-5-yl)imidazo[1,2-a]pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, Ar-H, 1H), 8.86 (s, Ar-H, 2H), 8.00 (d, *J* = 6.9 Hz, Ar-H, 1H), 7.79 (d, *J* = 9.1 Hz, Ar-H, 1H), 7.63 – 7.51 (m, Ar-H, 2H), 7.41 – 7.29 (m, Ar-H, 4H), 6.89 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 158.2, 146.0, 145.2, 133.0, 128.8, 128.3, 128.2, 125.9, 125.1, 122.4, 118.1, 113.9, 113.4.

23d: 3-(5-methylthiophen-2-yl)-2-phenylimidazo[1,2-a]pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.9 Hz, Ar-H, 1H), 7.80 (d, *J* = 6.9 Hz, Ar-H, 2H), 7.72 (d, *J* = 9.0 Hz, Ar-H, 1H), 7.32 (m, Ar-H, 3H), 7.26 – 7.22 (m, Ar-H, 1H), 7.00 (d, *J* = 3.4 Hz, Ar-H, 1H), 6.92 – 6.86 (m, Ar-H, 1H), 6.81 (m, Ar-H, 1H), 2.57 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.1, 143.5, 133.8, 130.5, 128.2, 127.9, 127.7, 127.2, 126.2, 125.0, 123.9, 117.3, 113.9, 112.4, 15.5.

24a: 2-methyl-4-phenyl-5-(pyridin-3-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, Ar-H, 1H), 8.54 – 8.47 (m, Ar-H, 1H), 7.61 – 7.53 (m, Ar-H, 1H), 7.46 (m, Ar-H, 2H), 7.28 (m, Ar-H, 3H), 7.24 – 7.16 (m, Ar-H, 1H), 2.76 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 150.8, 149.8, 148.7, 136.5, 134.1, 128.8, 128.4, 124.3, 128.1, 128.0, 123.2, 19.1.

25a: 2,4-dimethyl-5-(pyridin-3-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, Ar-H, 1H), 8.53 (t, *J* = 3.5 Hz, Ar-H, 1H), 7.68 (d, *J* = 7.9 Hz, Ar-H, 1H), 7.32 (dd, *J* = 7.5, 5.1 Hz, Ar-H, 1H), 2.67 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 149.5, 148.4, 148.3, 136.0, 128.5, 127.3, 123.3, 19.0, 15.8.

25b: 5-(isoquinolin-4-yl)-2,4-dimethylthiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, Ar-H, 1H), 8.49 (s, Ar-H, 1H), 8.04 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.83 – 7.57 (m, Ar-H, 3H), 2.76 (s, CH_3, 3H), 2.22 (s, CH_3, 3H). ^{13}C NMR (101 MHz,) δ 165.4, 153.0, 150.4, 144.7, 135.0, 131.1, 128.3, 128.0, 127.6, 124.6, 124.5, 123.3, 19.2, 15.7.

26a: 4-methyl-5-(pyridin-3-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, Ar-H, 1H), 8.70 (s, Ar-H, 1H), 8.59 (d, J = 4.1 Hz, Ar-H, 1H), 7.79 – 7.71 (m, Ar-H, 1H), 7.37 (m, Ar-H, 1H), 2.53 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 149.7, 149.6, 148.8, 136.3, 128.2, 128.0, 123.4, 15.9.

26c: 4-methyl-5-(pyrimidin-5-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, Ar-H, 1H), 8.85 (s, Ar-H, 3H), 2.58 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 156.3, 152.2, 151.0, 126.9, 124.2, 16.0.

26d: 4-methyl-5-(5-methylthiophen-2-yl)thiazole

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, Ar-H, 1H), 6.93 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.79 – 6.67 (m, Ar-H, 1H), 2.59 (s, CH_3, 3H), 2.51 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 148.5, 141.0, 130.8, 129.3, 127.1, 125.8, 16.5, 15.2.

27a: 3-(1-methyl-1H-imidazol-5-yl)pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 – 8.26 (m, Ar-H, 2H), 7.82 – 6.94 (m, Ar-H, 4H), 3.63 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 139.7, 135.4, 129.8, 128.8, 125.8, 125.7, 123.4, 32.4.

27b: 4-(1-methyl-1H-imidazol-5-yl)isoquinoline

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, Ar-H, 1H), 8.47 (s, Ar-H, 1H), 8.05 (d, J = 8.0 Hz, Ar-H, 1H), 7.74 – 7.62 (m, Ar-H, 4H), 7.20 (d, J = 0.9 Hz, Ar-H, 1H), 3.46 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 144.4, 139.2, 135.3, 131.3, 130.4, 128.0, 127.7, 124.4, 121.0, 32.1.

27c: 5-(1-methyl-1H-imidazol-5-yl)pyrimidine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, Ar-H, 1H), 8.80 (s, Ar-H, 1H), 7.61 (s, Ar-H, 1H), 7.24 (s, Ar-H, 1H), 3.71 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 155.4, 140.7, 130.0, 126.4, 124.5, 32.7.

28a: 3-(1,2-dimethyl-1H-imidazol-5-yl)pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, Ar-H, 1H), 8.55 (d, J = 6.4 Hz, Ar-H, 1H), 7.64 (d, J = 9.8 Hz, Ar-H, 1H), 7.38 – 7.29 (m, Ar-H, 1H), 6.99 (s, Ar-H, 1H), 3.51 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.7, 146.9, 135.6, 129.9, 126.7, 126.6, 123.4, 31.3, 13.5.

28b: 4-(1, 2-dimethyl-1H-imidazol-5-yl)isoquinoline

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, Ar-H, 1H), 8.43 (s, Ar-H, 1H), 8.08 – 7.92 (m, Ar-H, 1H), 7.78 – 7.55 (m, Ar-H, 3H), 7.04 (s, Ar-H, 1H), 3.30 (s, CH_3, 3H), 2.48 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 146.3, 144.5, 135.3, 131.0, 128.2, 127.9, 127.5, 124.4, 121.8, 31.1, 13.6.

28c: 5-(1, 2-dimethyl-1H-imidazol-5-yl)pyrimidine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, Ar-H, 1H), 8.77 (s, Ar-H, 1H), 7.10 (s, Ar-H, 1H), 3.57 (s, CH_3, 3H), 2.48 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 155.5, 148.0, 128.1, 126.5, 125.1, 31.5, 13.7.

29a: 5,7-di(pyridin-3-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 1.3 Hz, Ar-H, 2H), 8.47 (dd, *J* = 4.6, 1.1 Hz, Ar-H, 2H), 8.06 – 7.97 (m, Ar-H, 2H), 7.37 – 7.26 (m, Ar-H, 2H), 4.41 (s, OCH_2, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.1, 139.6, 132.8, 128.9, 123.4, 112.7, 64.6.

29b: 5,7-di(isoquinolin-4-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, Ar-H, 2H), 8.70 (s, Ar-H, 2H), 8.20 (d, *J* = 8.4 Hz, Ar-H, 2H), 8.02 (d, *J* = 8.1 Hz, Ar-H, 2H), 7.78 (t, *J* = 7.6 Hz, Ar-H, 2H), 7.65 (t, *J* = 7.5 Hz, Ar-H, 2H), 4.31 (s, OCH_2, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 144.5, 138.9, 134.1, 130.6, 128.4, 127.9, 127.4, 125.3, 123.5, 111.9, 64.6.

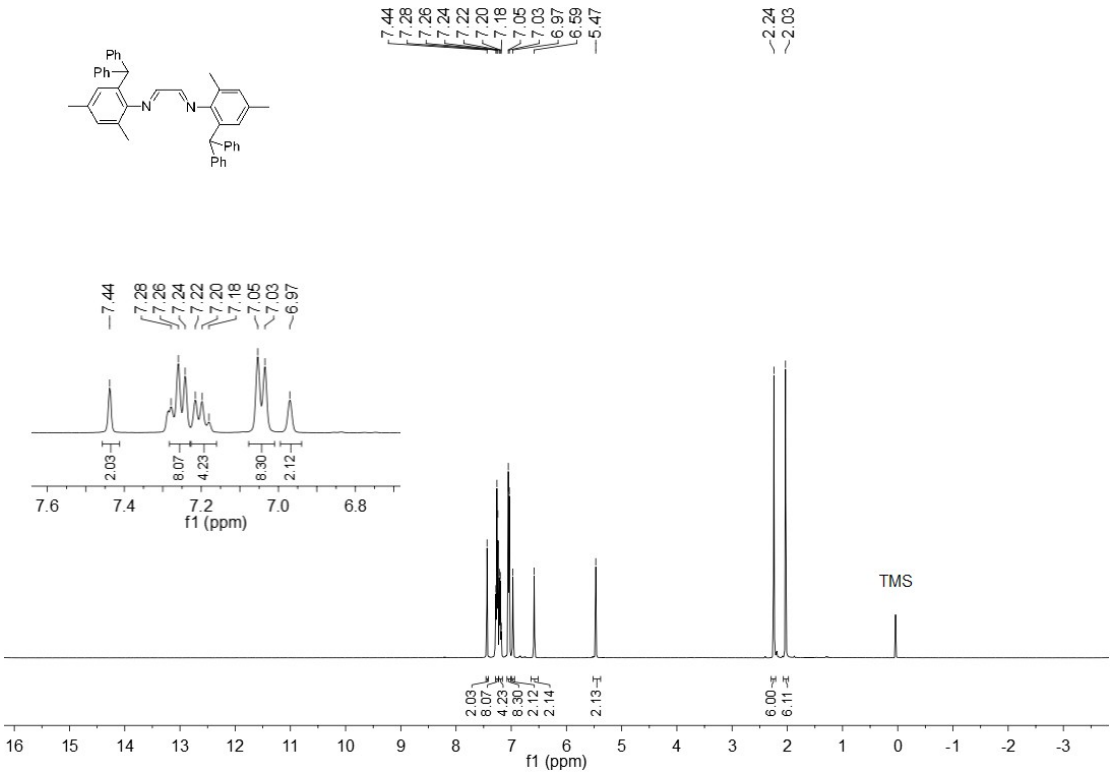
30: 3,5-bis(4-methylthiazol-5-yl)pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, Ar-H, 2H), 8.70 (d, *J* = 2.0 Hz, Ar-H, 2H), 7.81 (d, *J* = 2.0 Hz, Ar-H, 2H), 2.59 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 150.3, 148.8, 136.5, 128.3, 127.4, 16.1.

31: 3,5-bis(1-methyl-1H-imidazol-5-yl)pyridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.0 Hz, Ar-H, 2H), 7.73 (t, *J* = 1.9 Hz, Ar-H, 1H), 7.60 (s, Ar-H, 2H), 7.22 (s, Ar-H, 2H), 3.74 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 140.1, 134.7, 129.5, 129.3, 126.0, 32.6.

Figure **S1**. The NMR spectrums of ligand **L1**



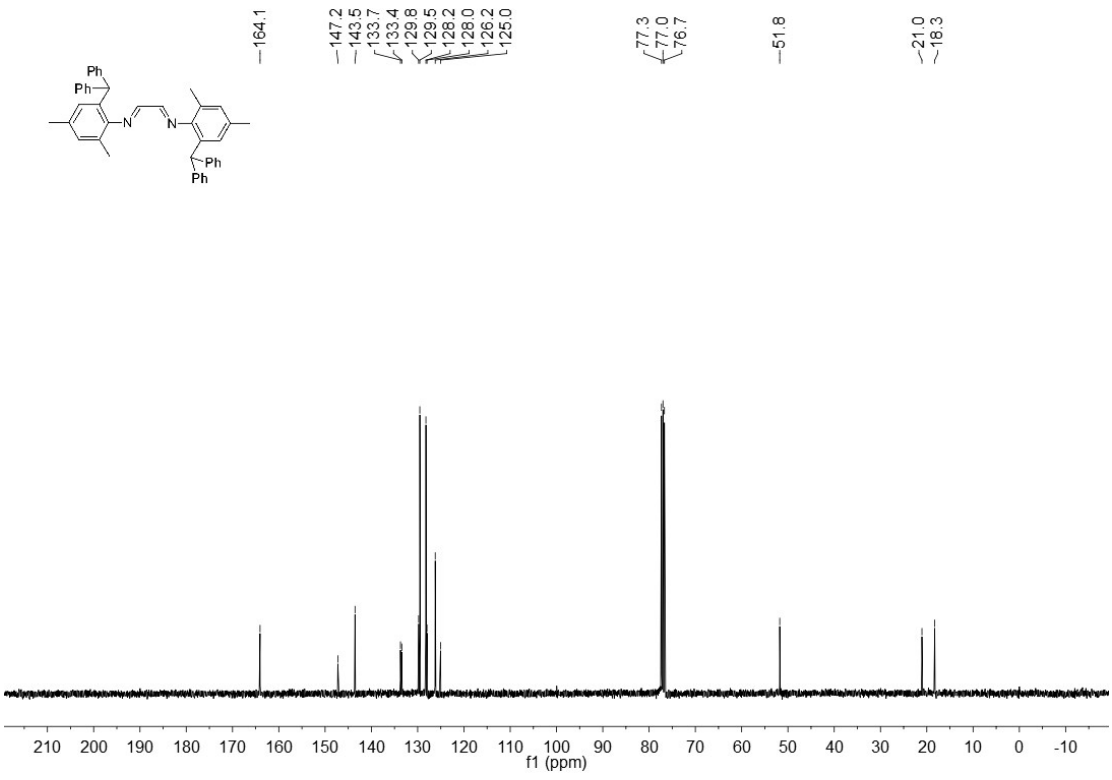
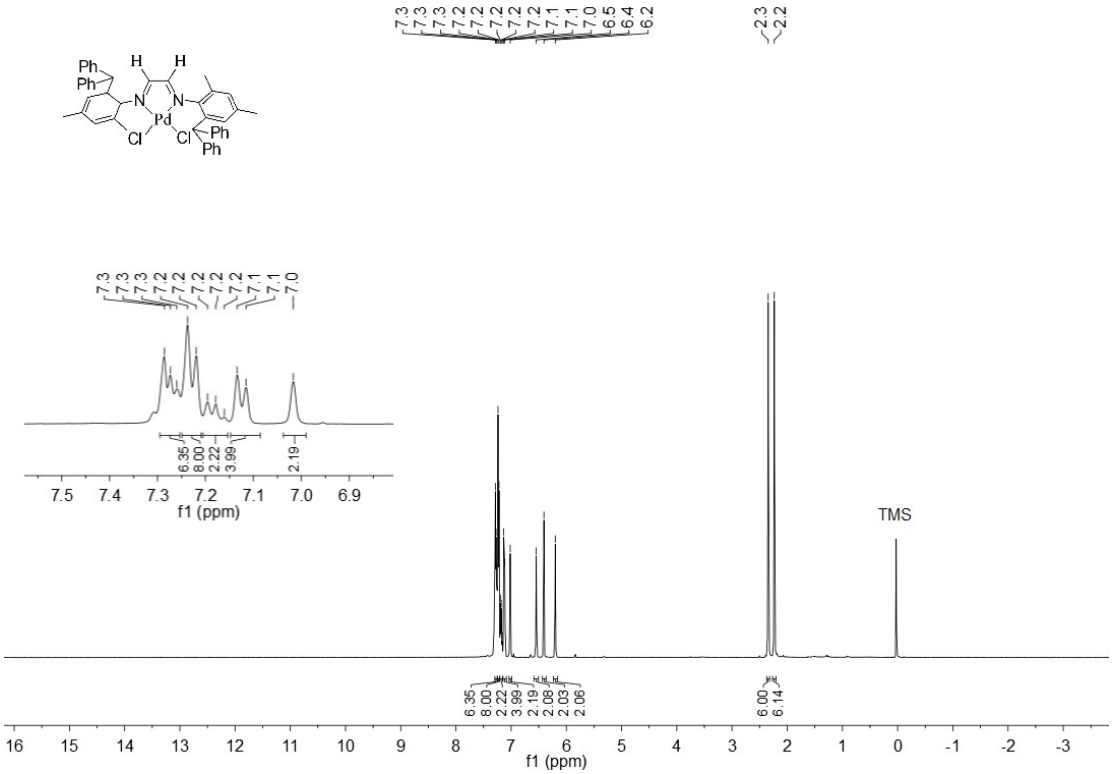


Figure **S2**. The NMR spectrums of Palladium complexes **C1**



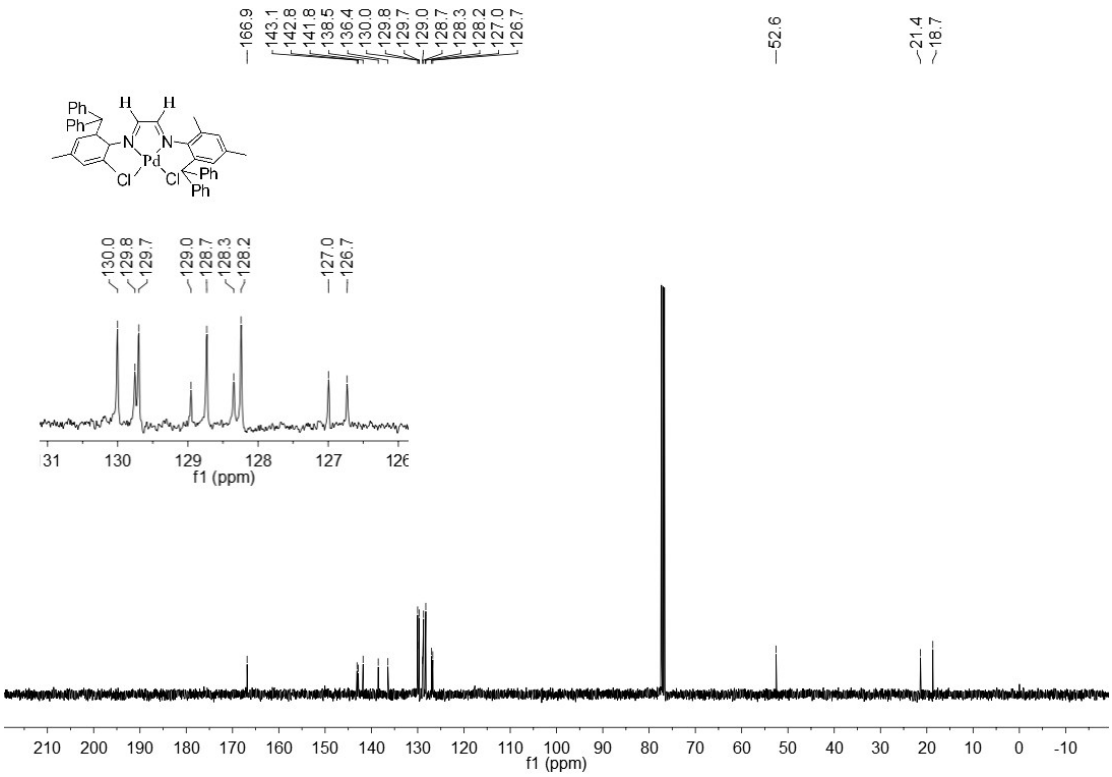
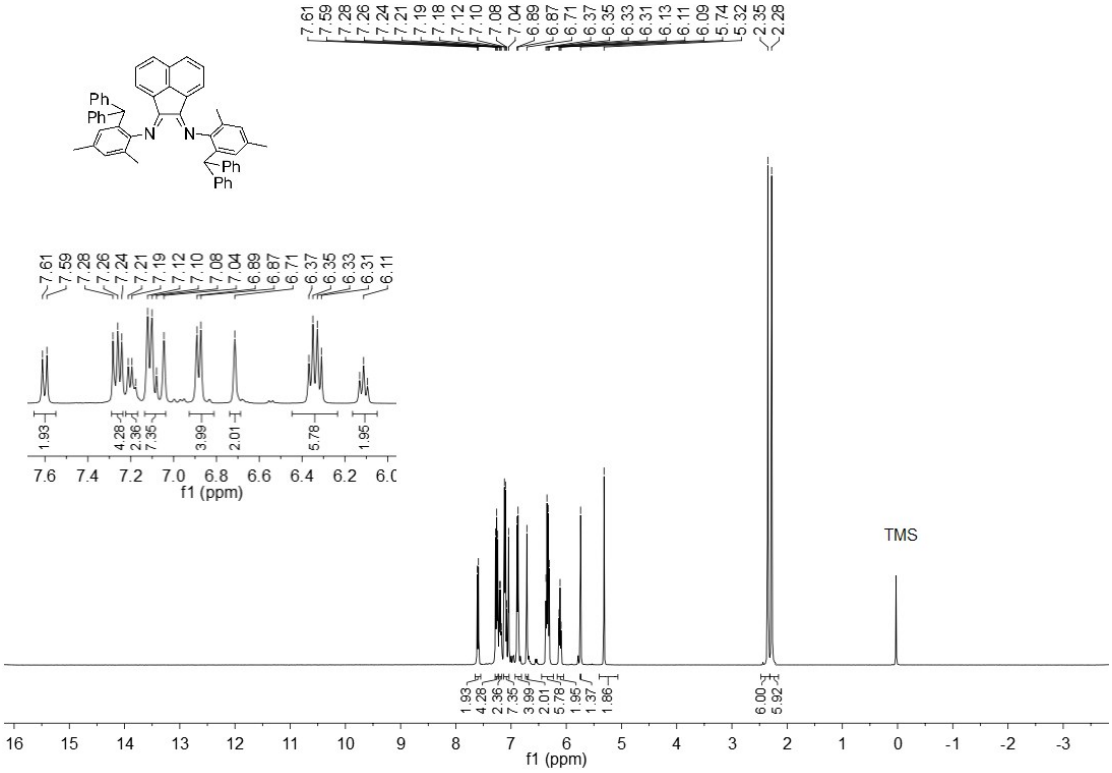


Figure **S3**. The NMR spectrums of ligand **L2**



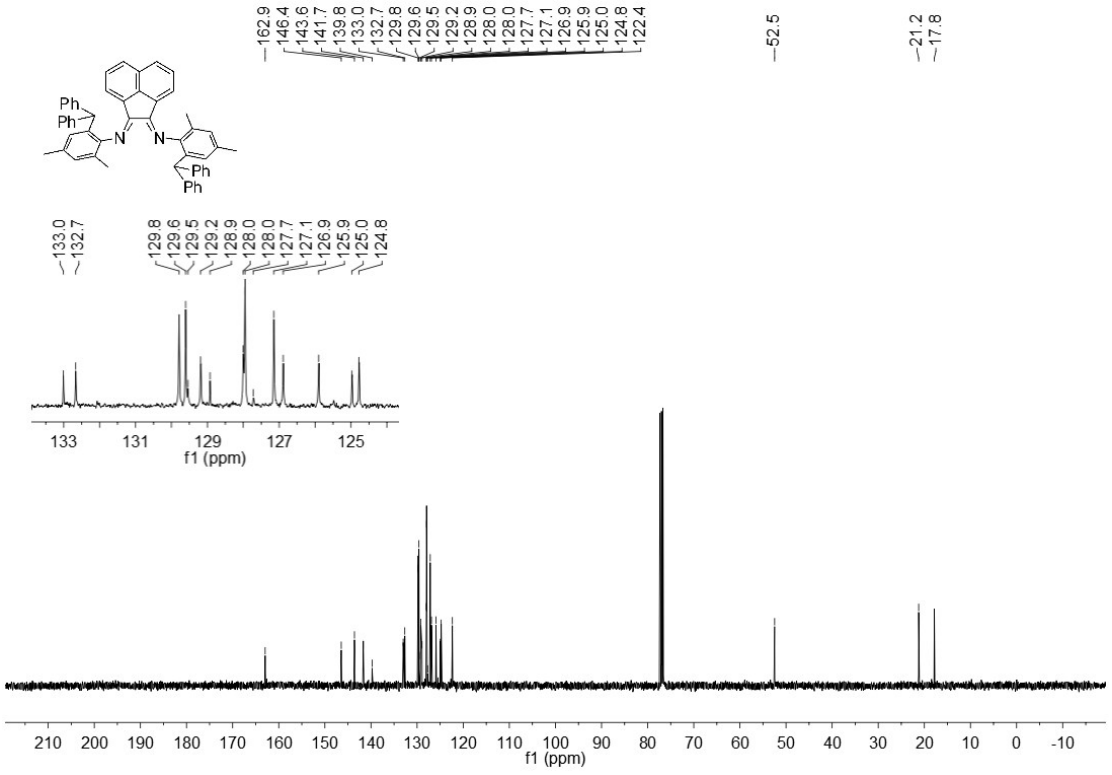
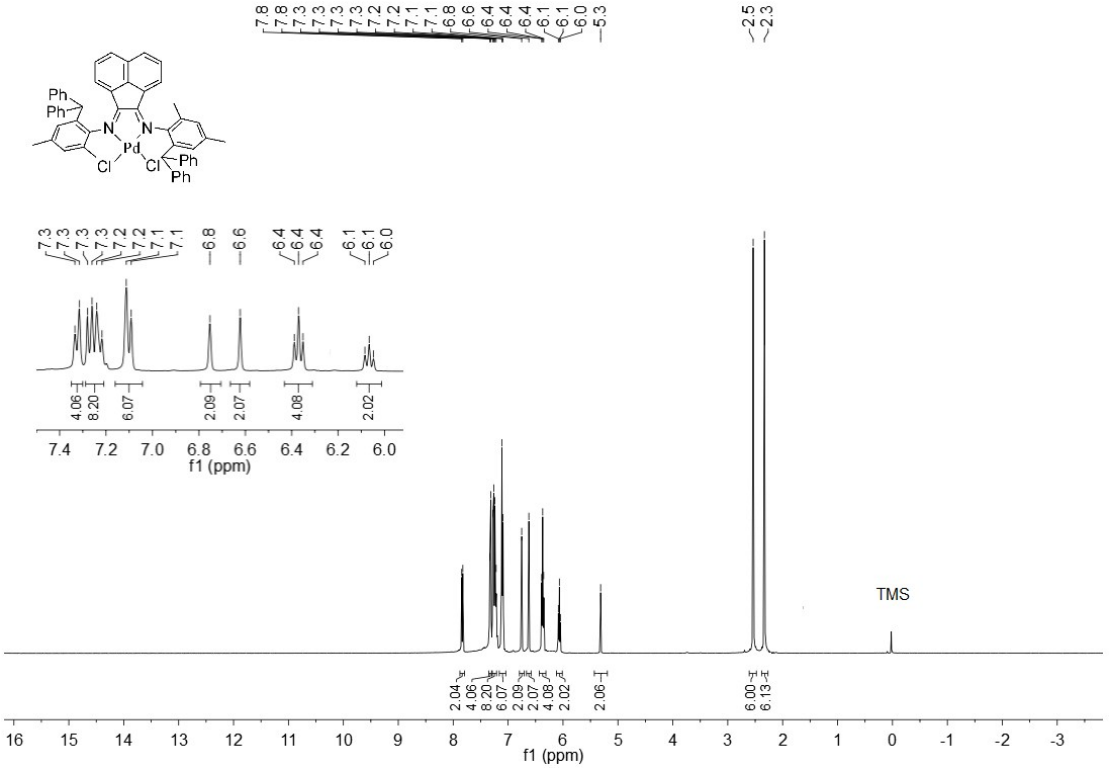


Figure **S4**. The NMR spectrums of Palladium complexes **C2**



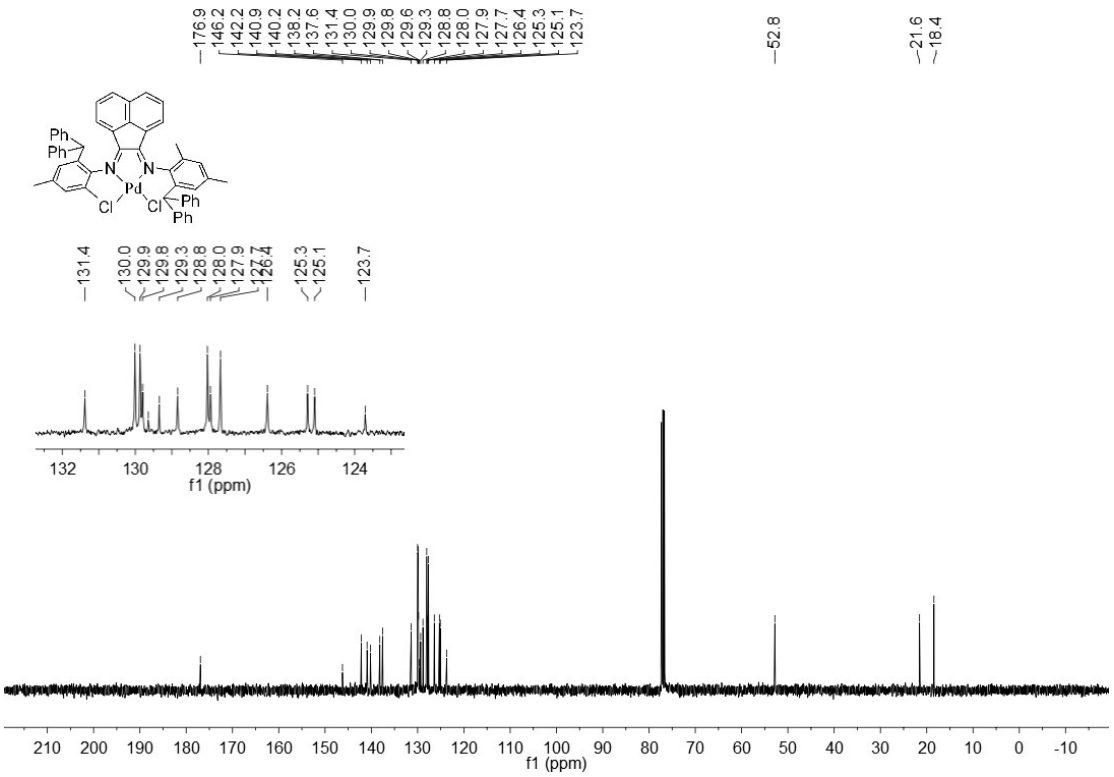
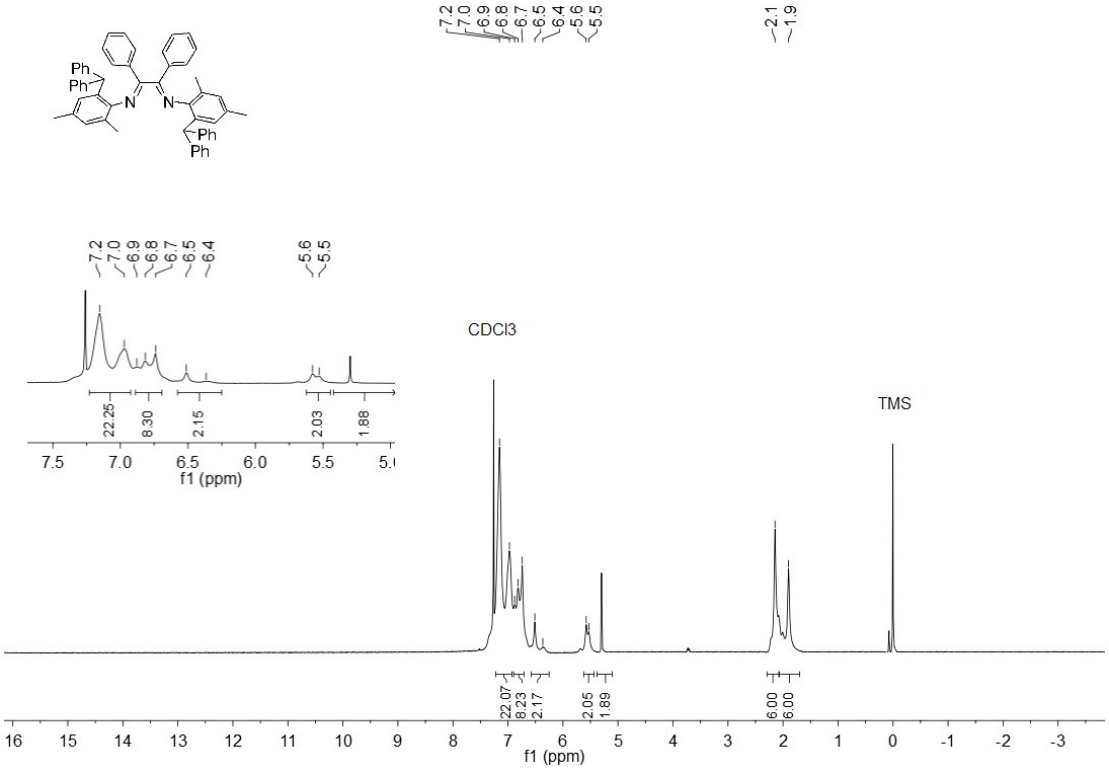


Figure **S5**. The NMR spectrums of ligand L3



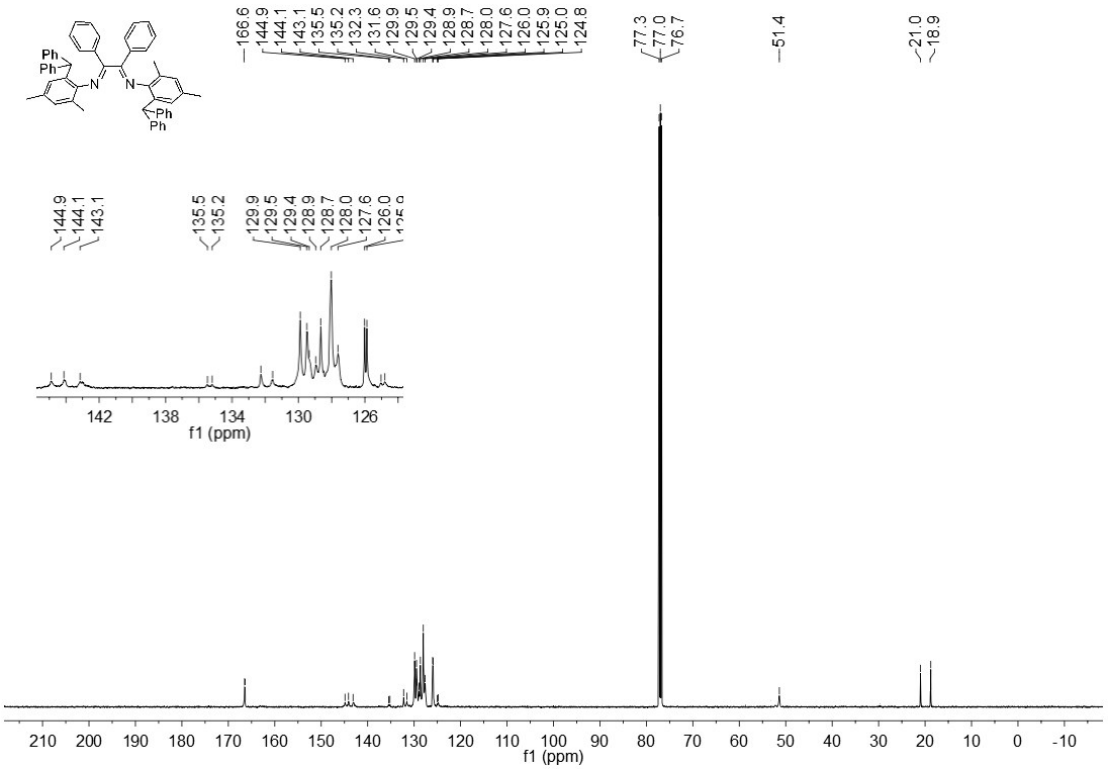
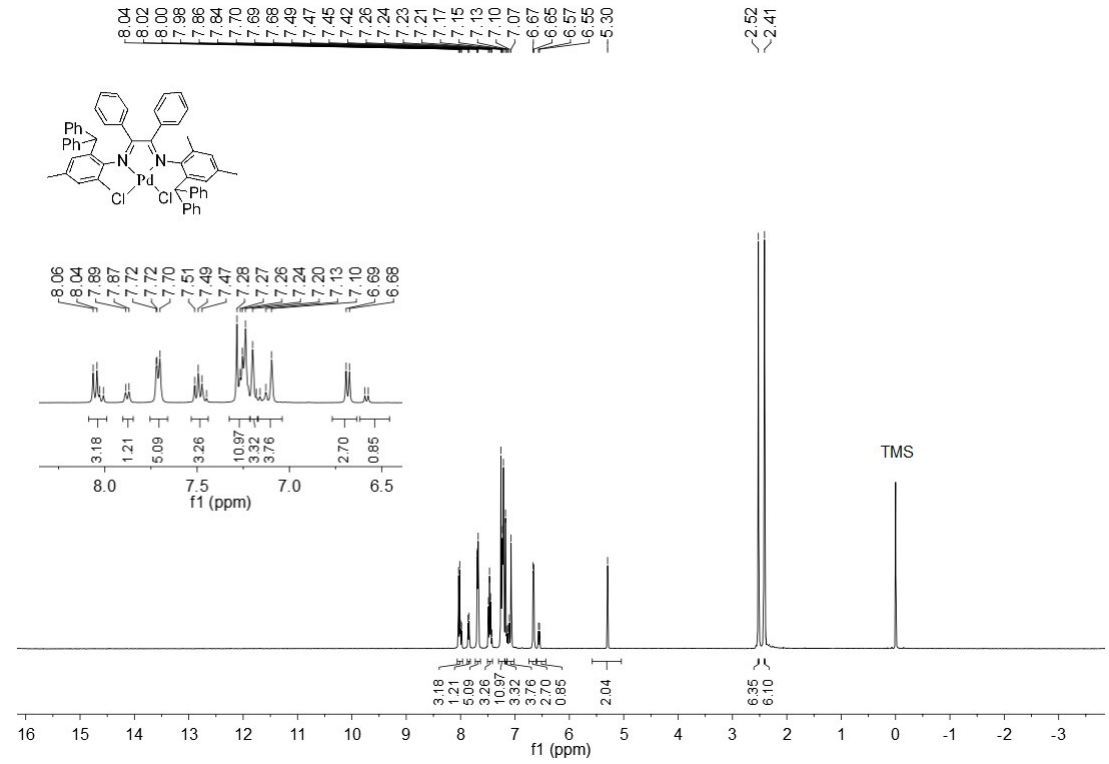


Figure **S6**. The NMR spectrums of Palladium complexes **C3**



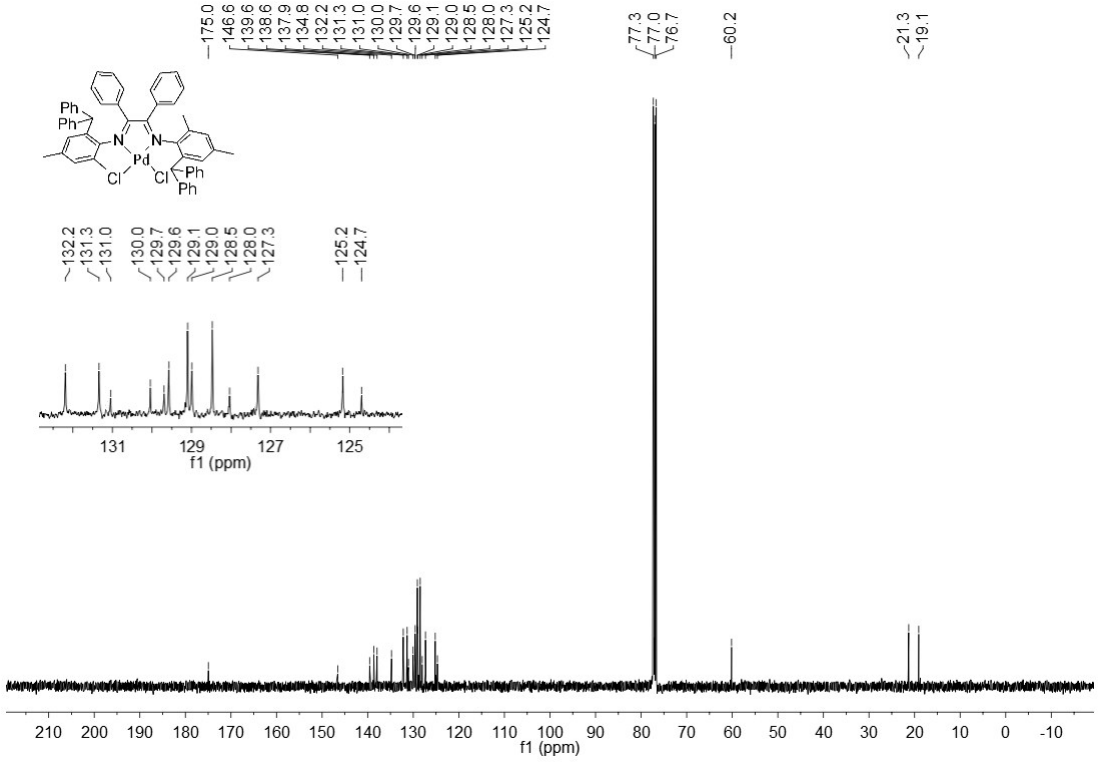
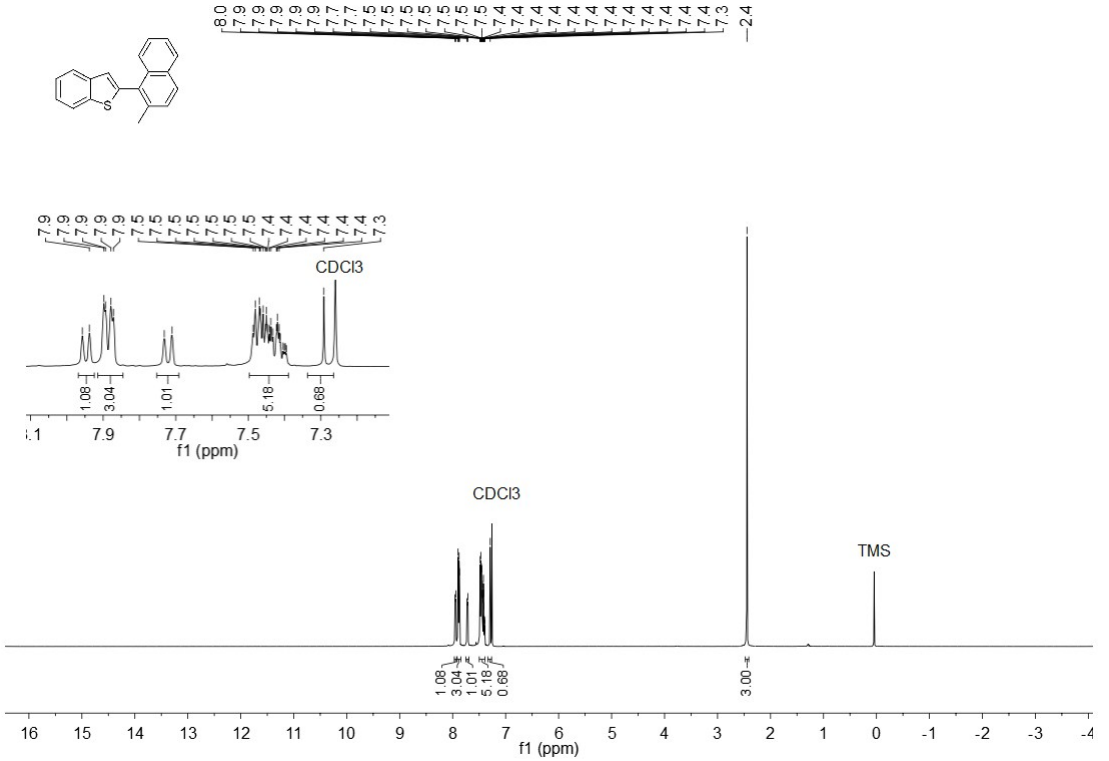


Figure **S7**. The NMR spectrums of 2-(2-methylnaphthalen-1-yl)benzo[b]thiophene (**3a**)



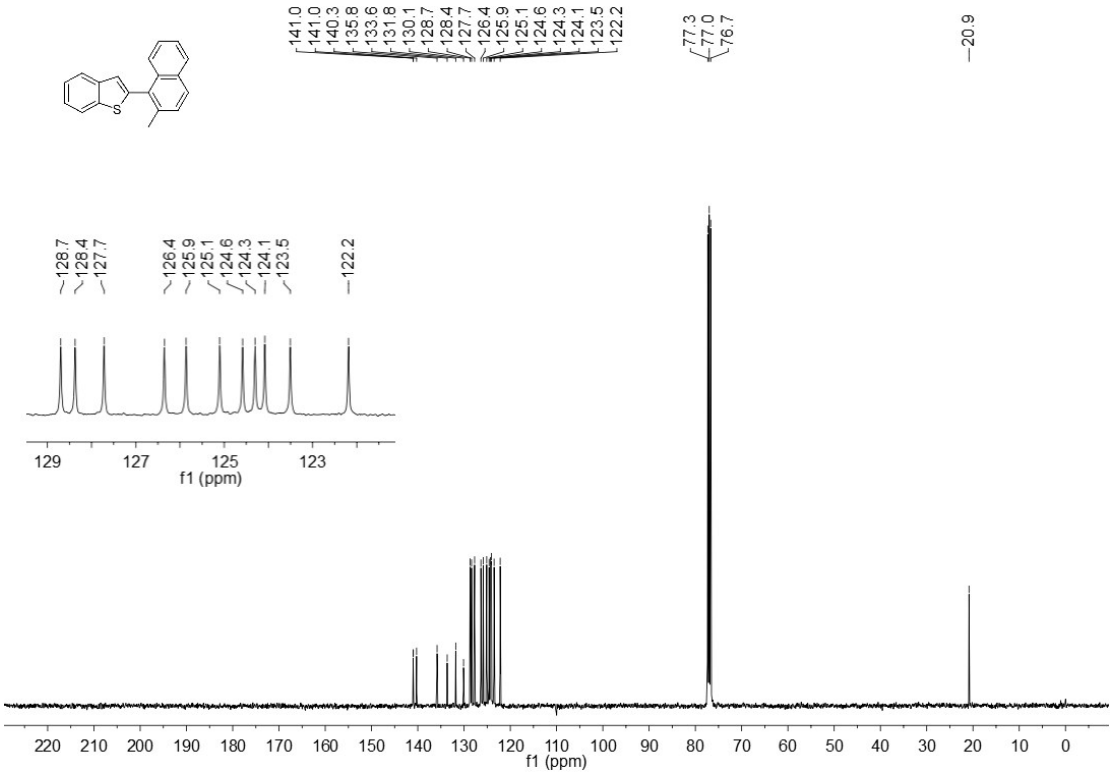
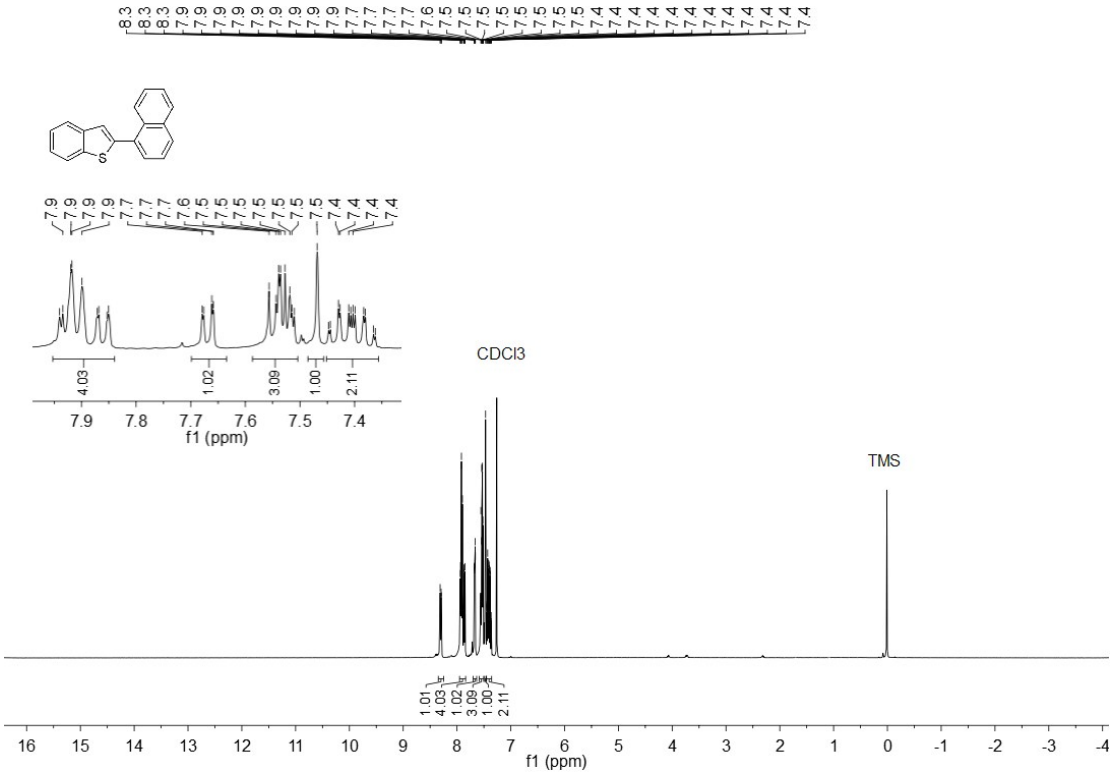


Figure **S8**. The NMR spectrums of 2-(naphthalen-1-yl)benzo[b]thiophene (**3b**)



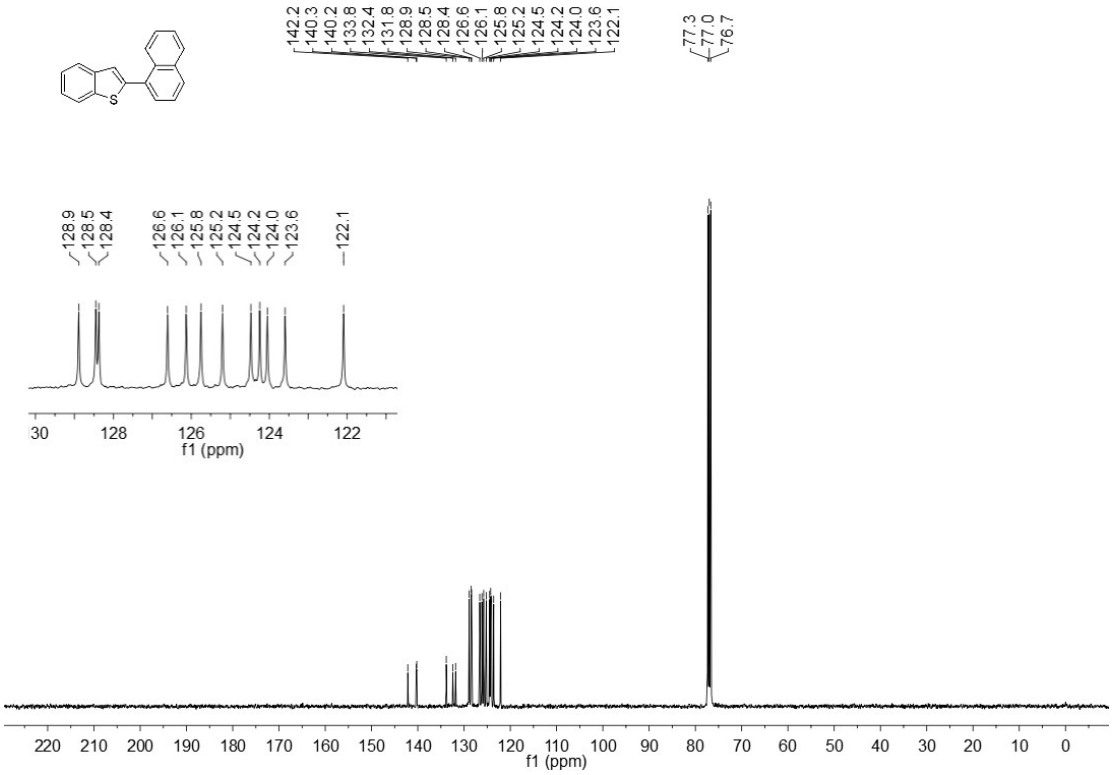


Figure **S9**. The NMR spectrums of 2-(4-methoxyphenyl)benzo[b]thiophene (**3c**)

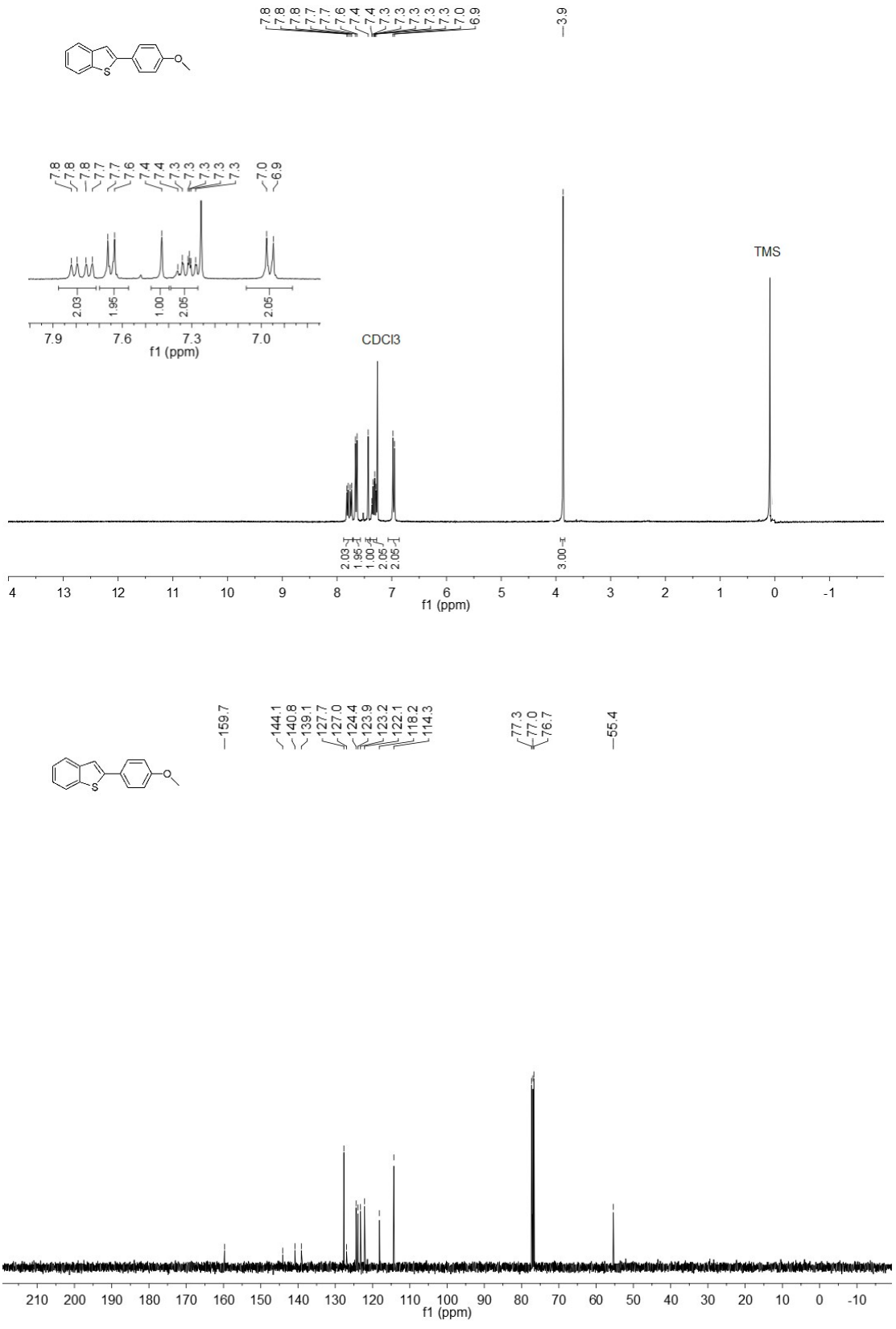
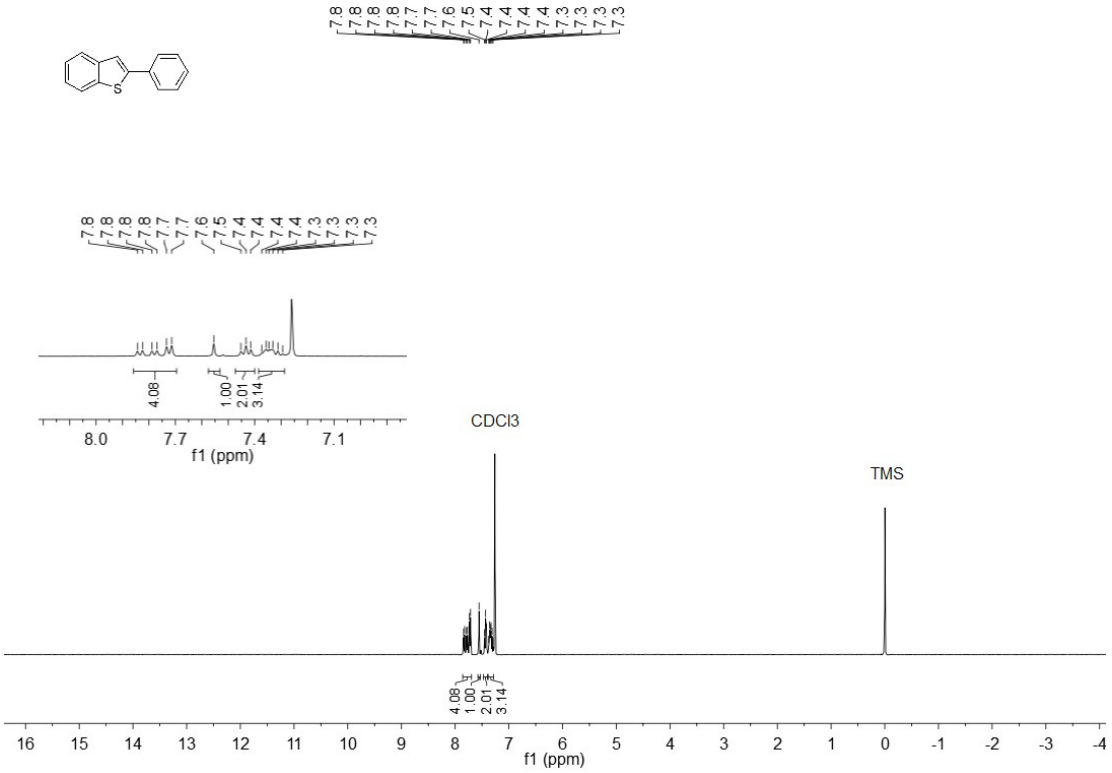


Figure **S10**. The NMR spectrums of 2-phenylbenzo[b]thiophene (**3d**)



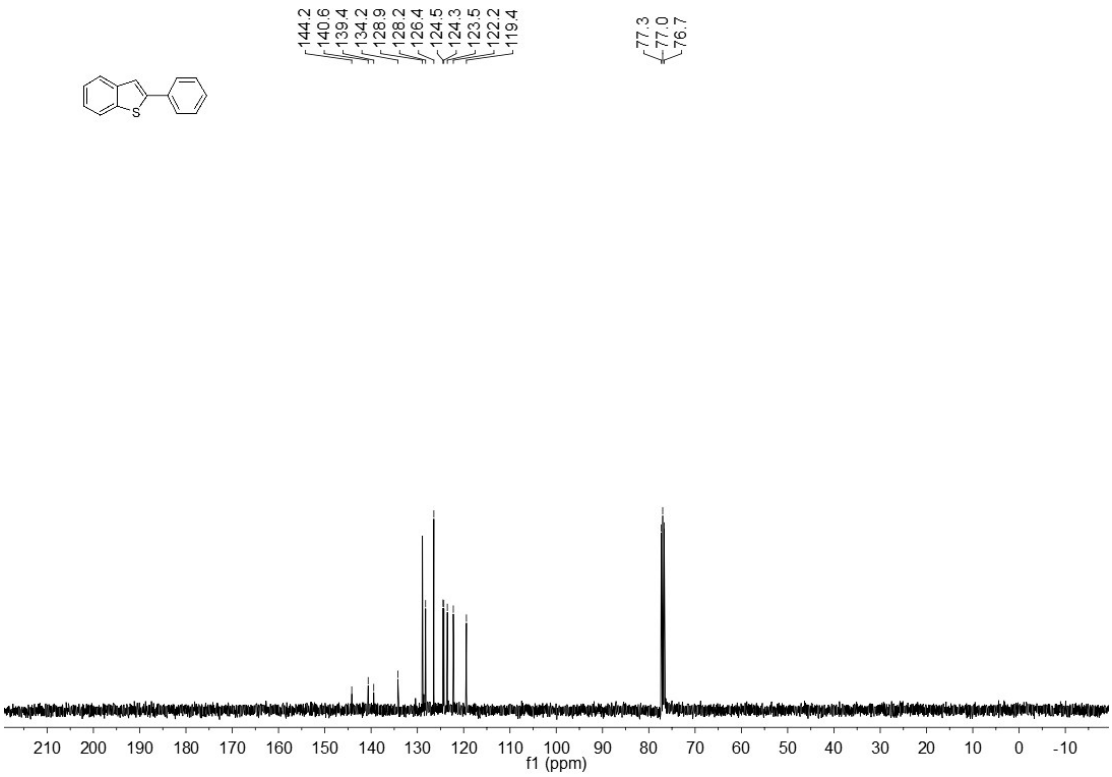
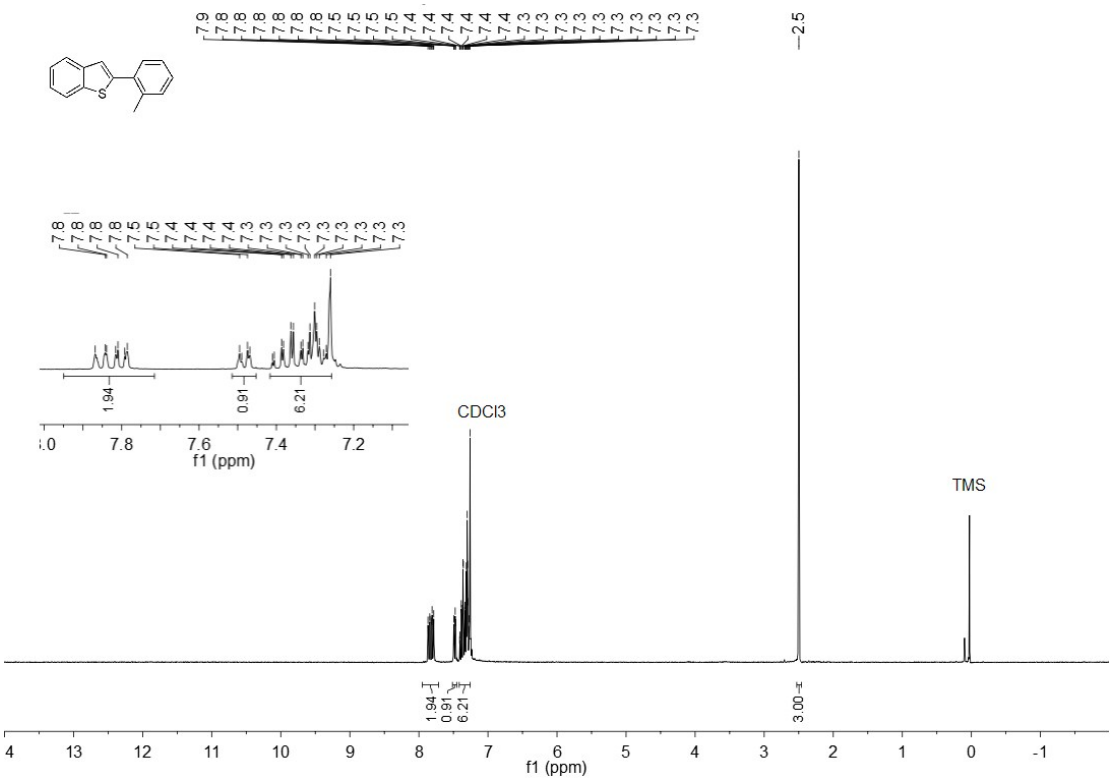


Figure **S11**. The NMR spectrums of 2-(o-tolyl)benzo[b]thiophene (**3e**)



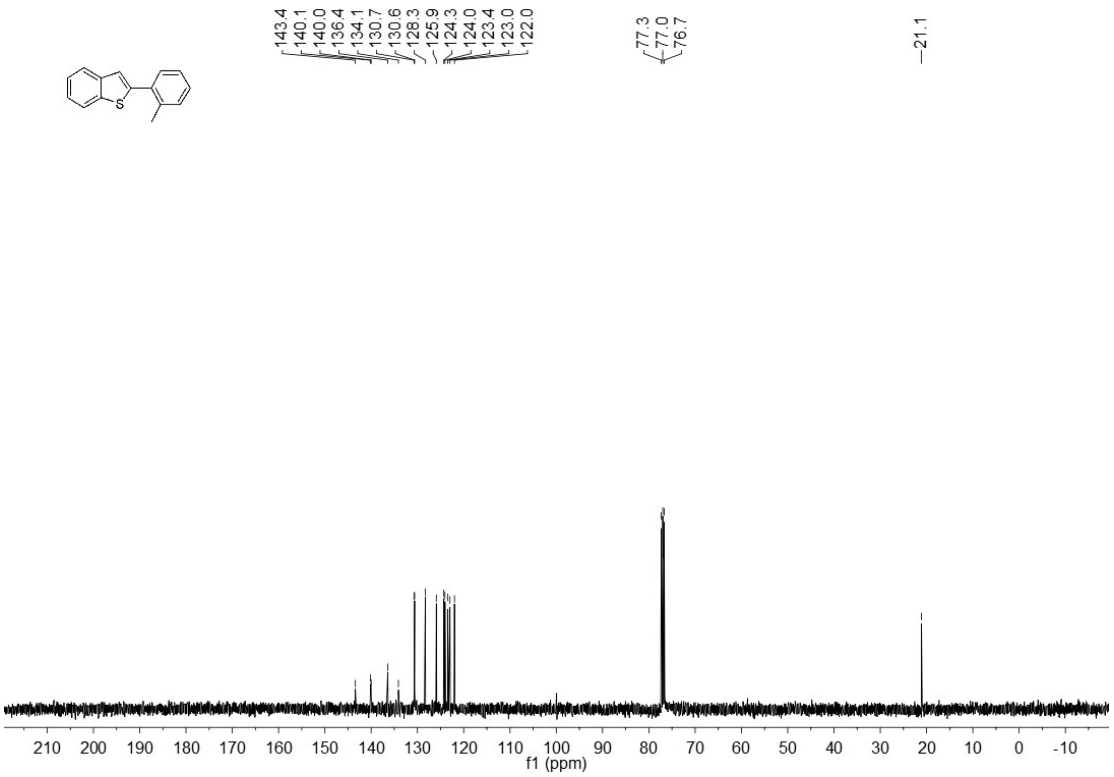
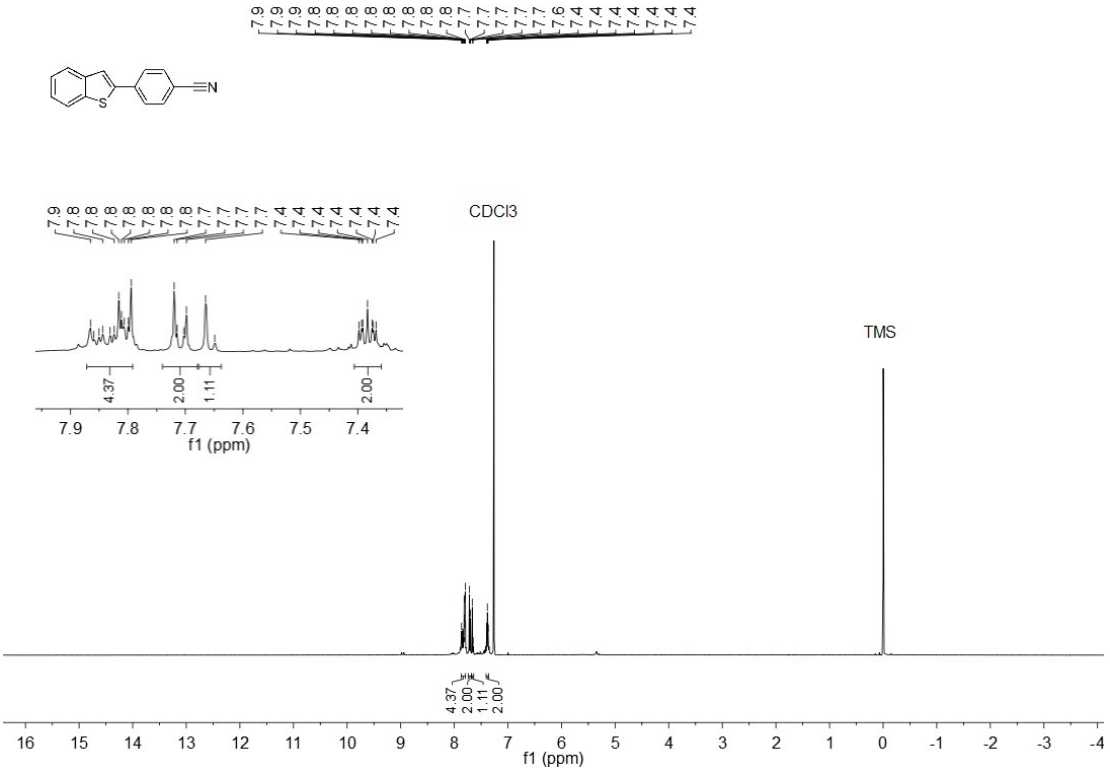


Figure **S12**. The NMR spectrums of 4-(benzo[b]thiophen-2-yl)benzonitrile (**3f**)



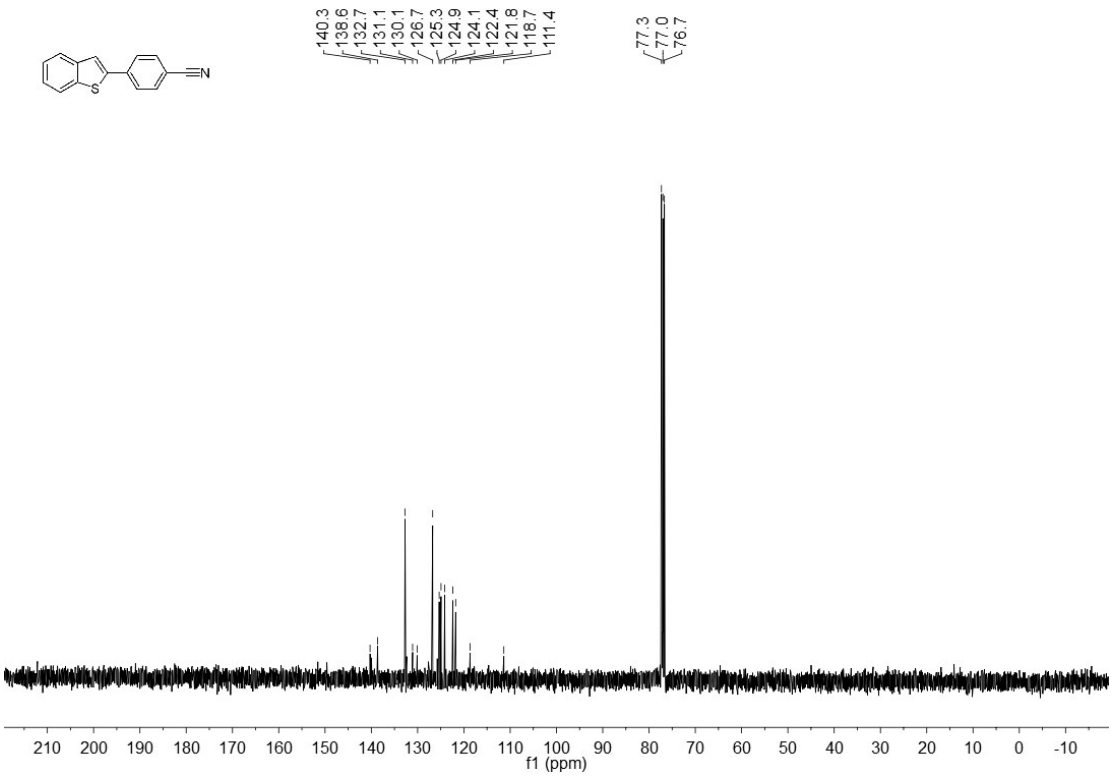
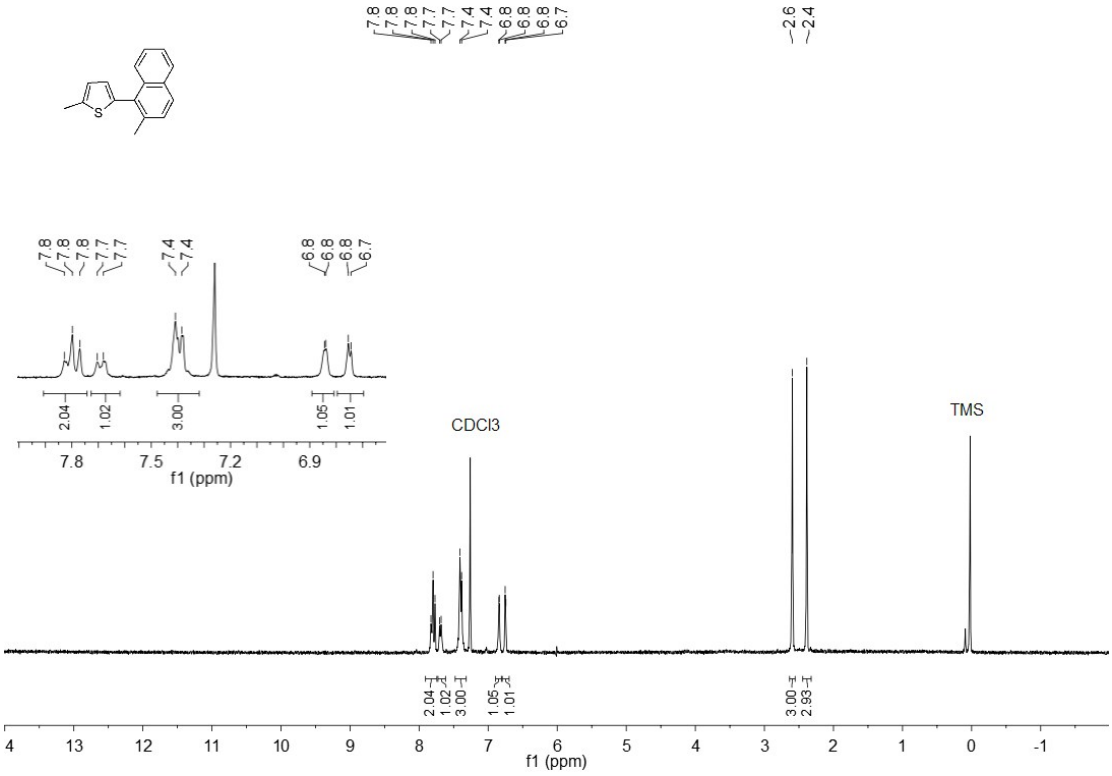


Figure **S13**. The NMR spectrums of 2-methyl-5-(2-methylnaphthalen-1-yl)thiophene (**4a**)



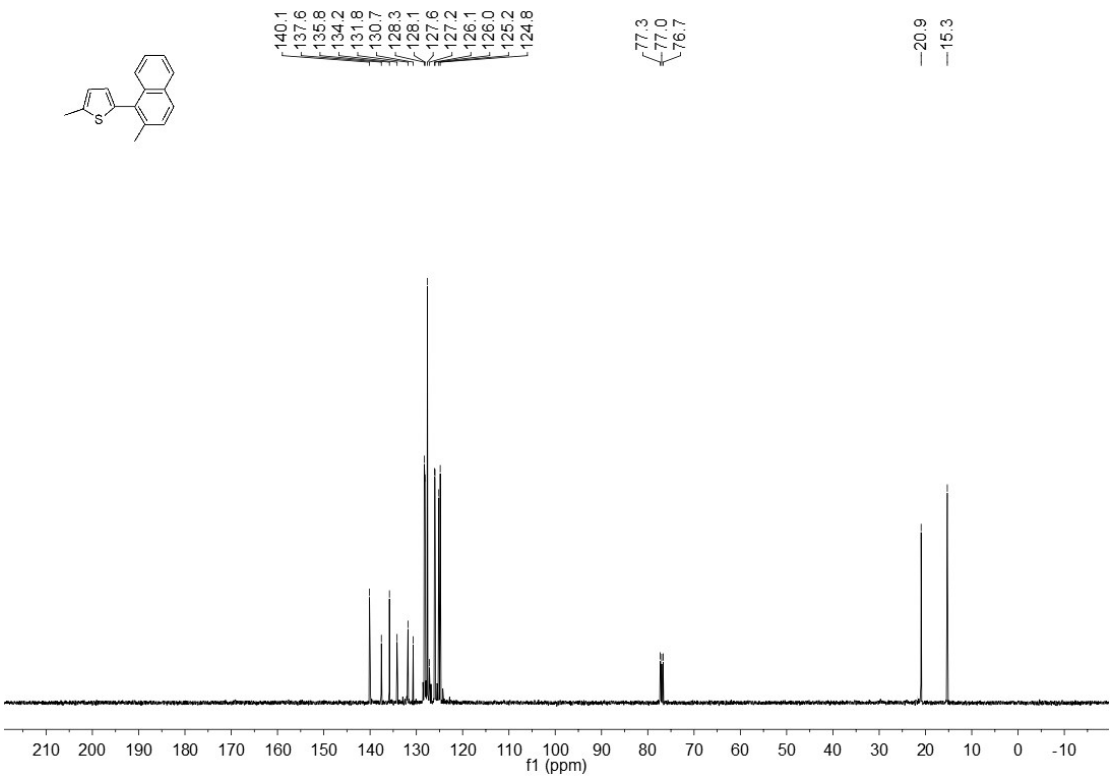


Figure **S14**. The NMR spectrums of 2-methyl-5-(naphthalen-1-yl)thiophene (**4b**)

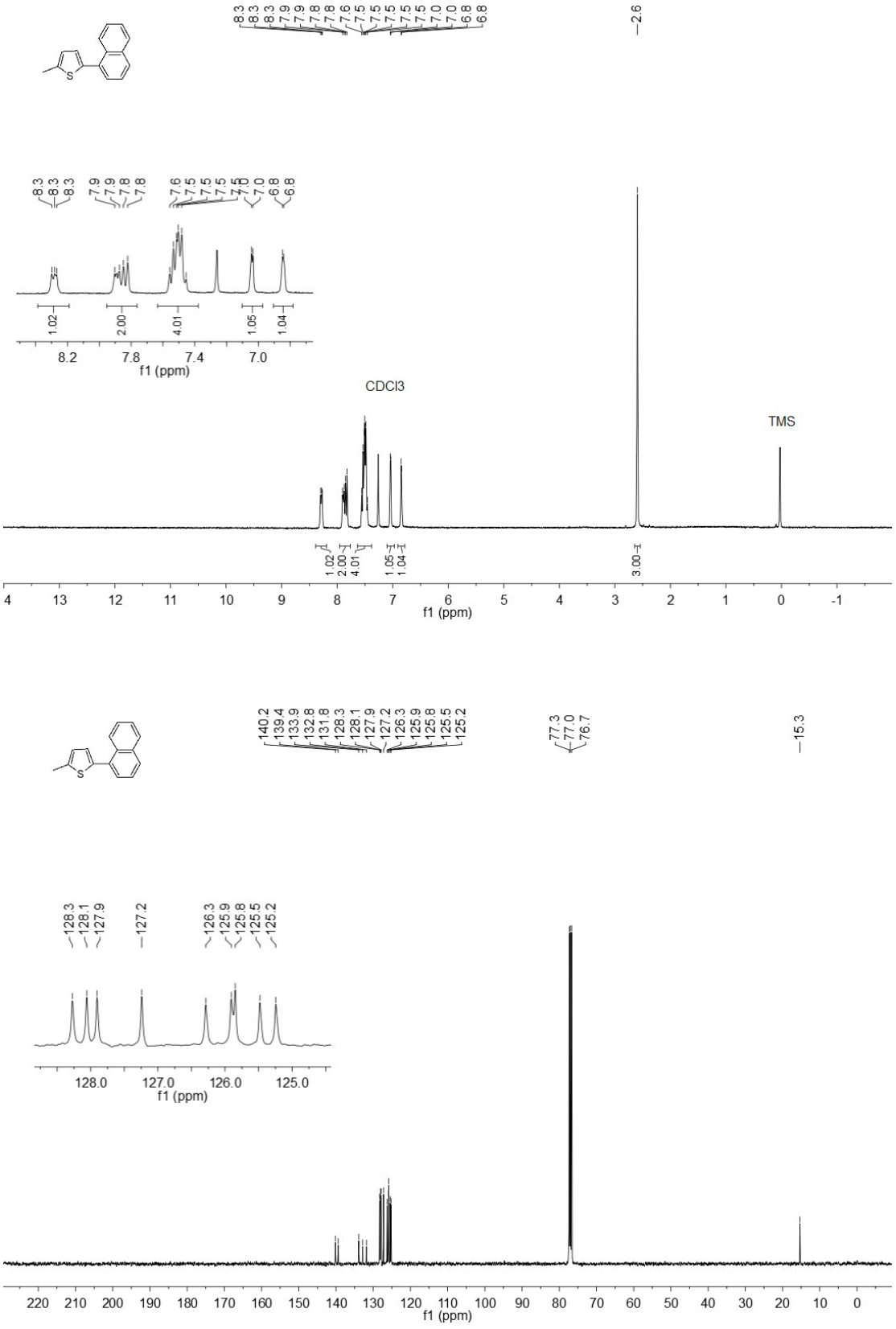
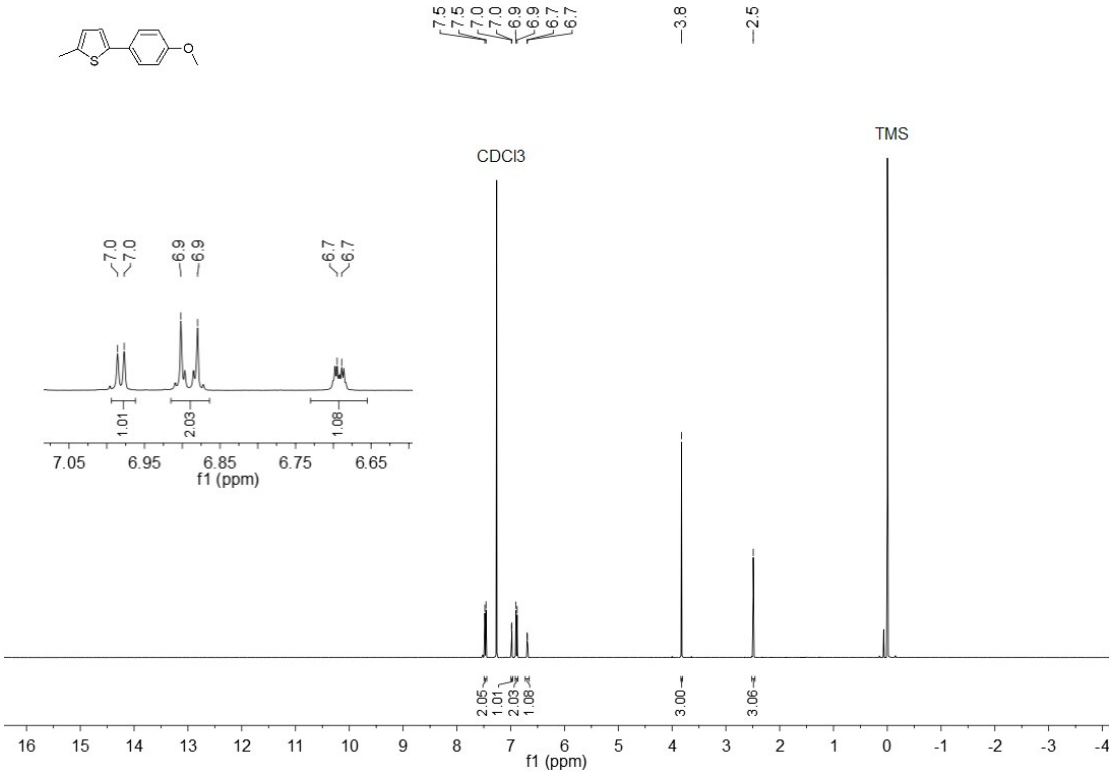


Figure **S15**. The NMR spectrums of 2-(4-methoxyphenyl)-5-methylthiophene (**4c**)



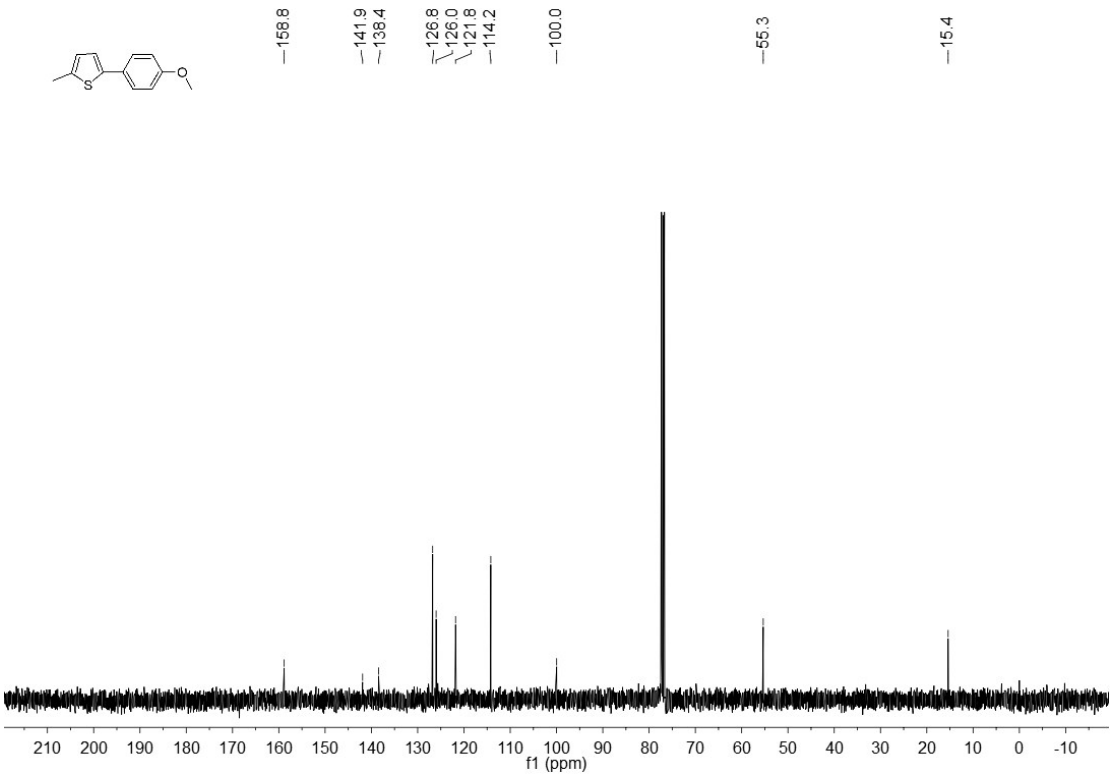
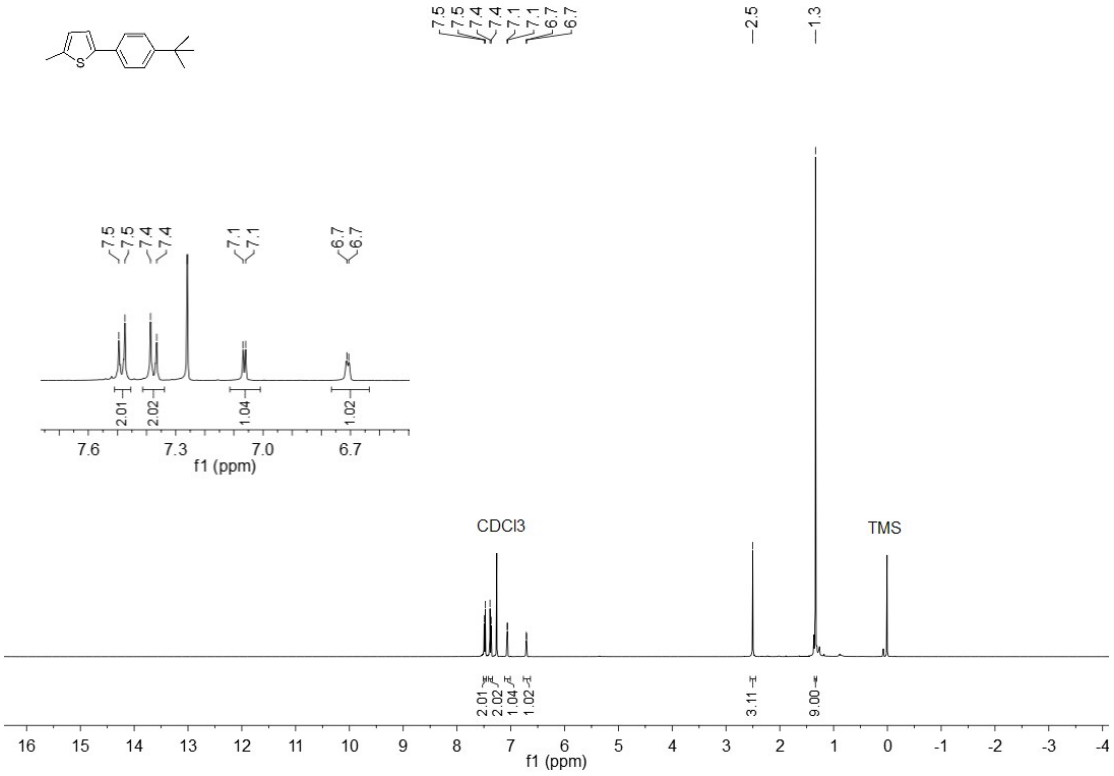


Figure **S16**. The NMR spectrums of 2-(4-(tert-butyl)phenyl)-5-methylthiophene (**4g**)



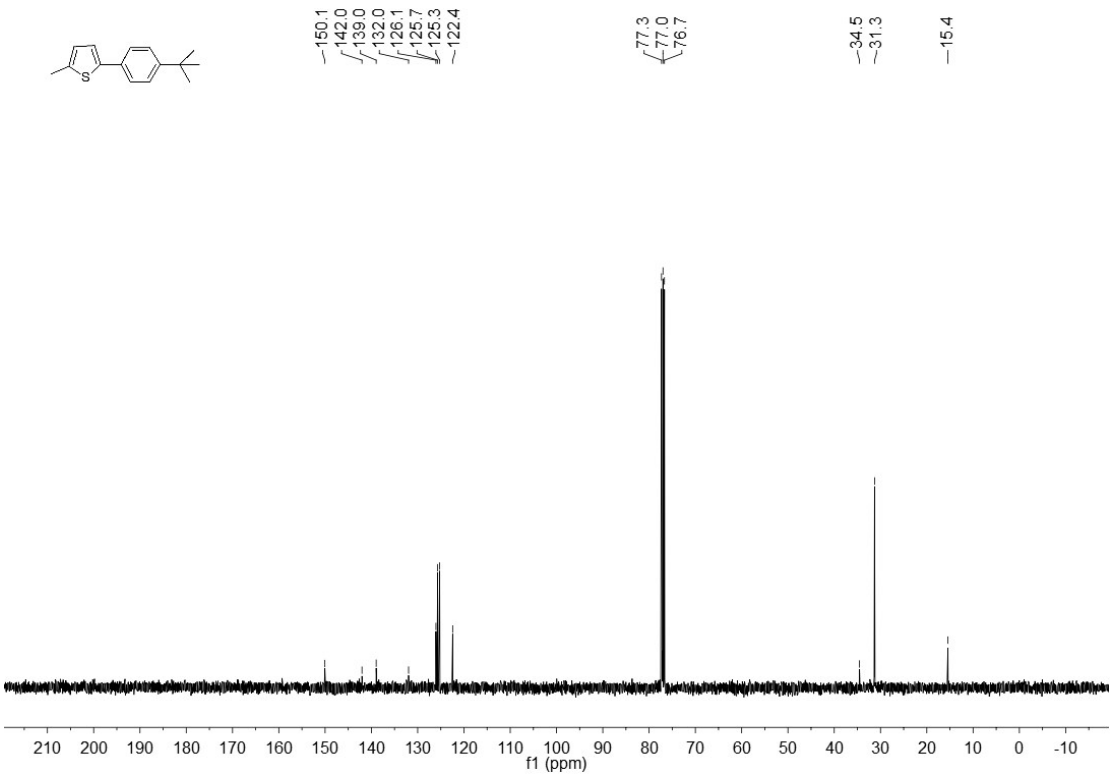


Figure **S17**. The NMR spectrums of 2-ethyl-5-(2-methylnaphthalen-1-yl)thiophene (**5a**)

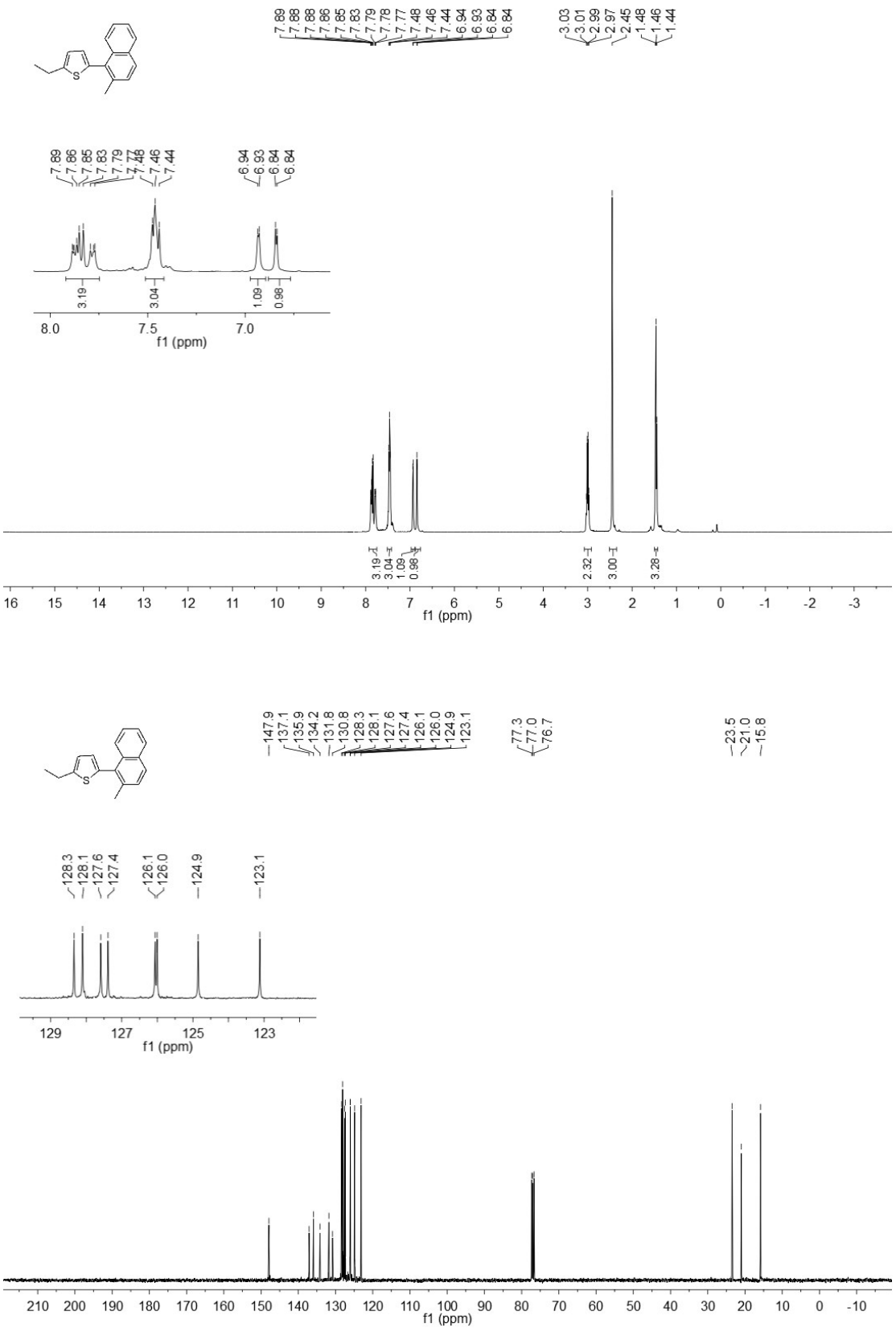
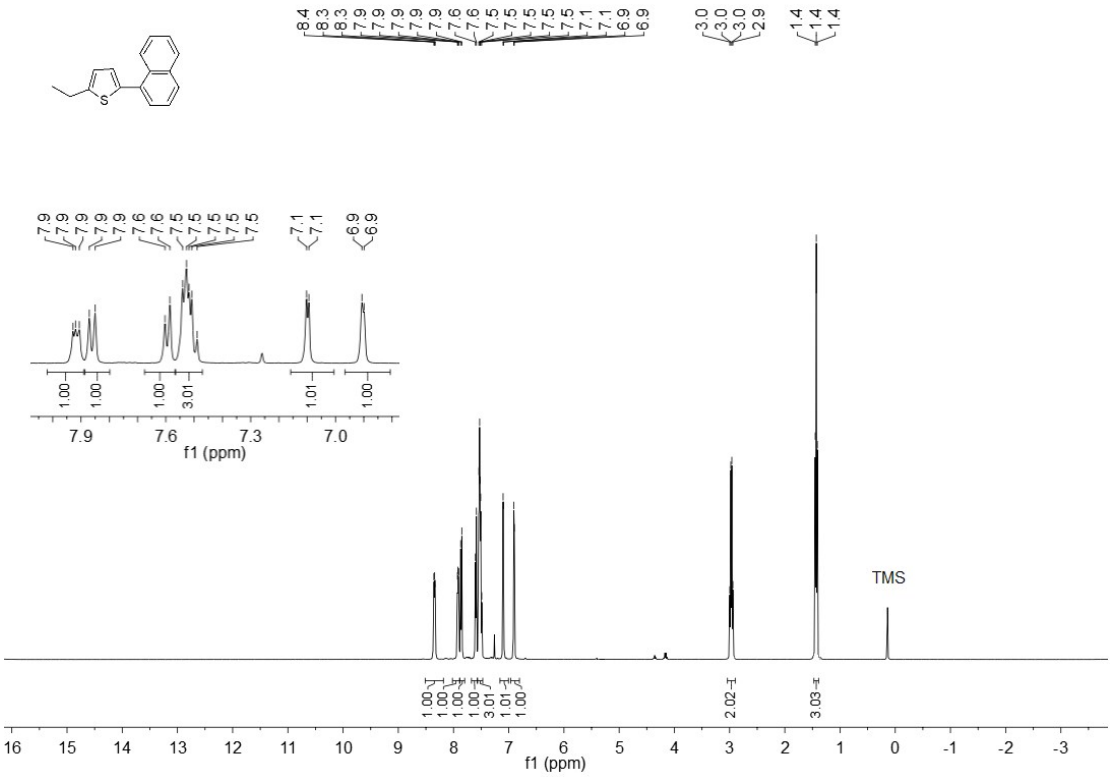


Figure **S18**. The NMR spectrums of 2-ethyl-5-(naphthalen-1-yl)thiophene (**5b**)



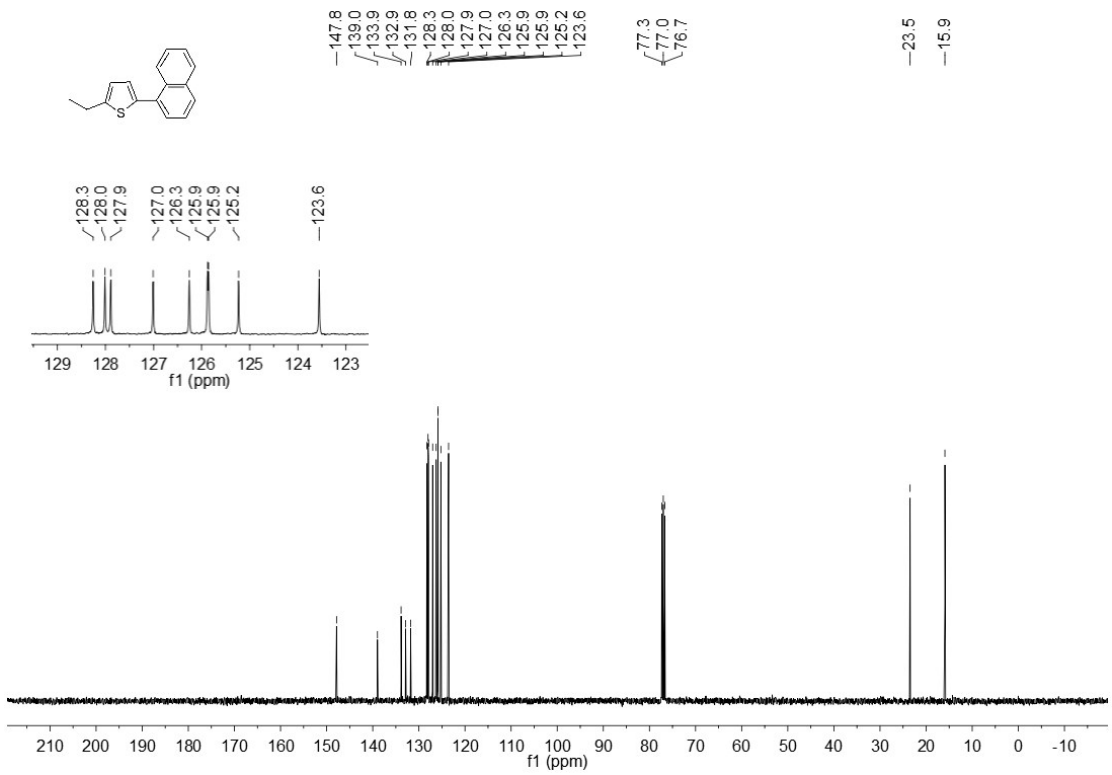


Figure **S19**. The NMR spectrums of 2-chloro-5-(naphthalen-1-yl)thiophene (**6b**)

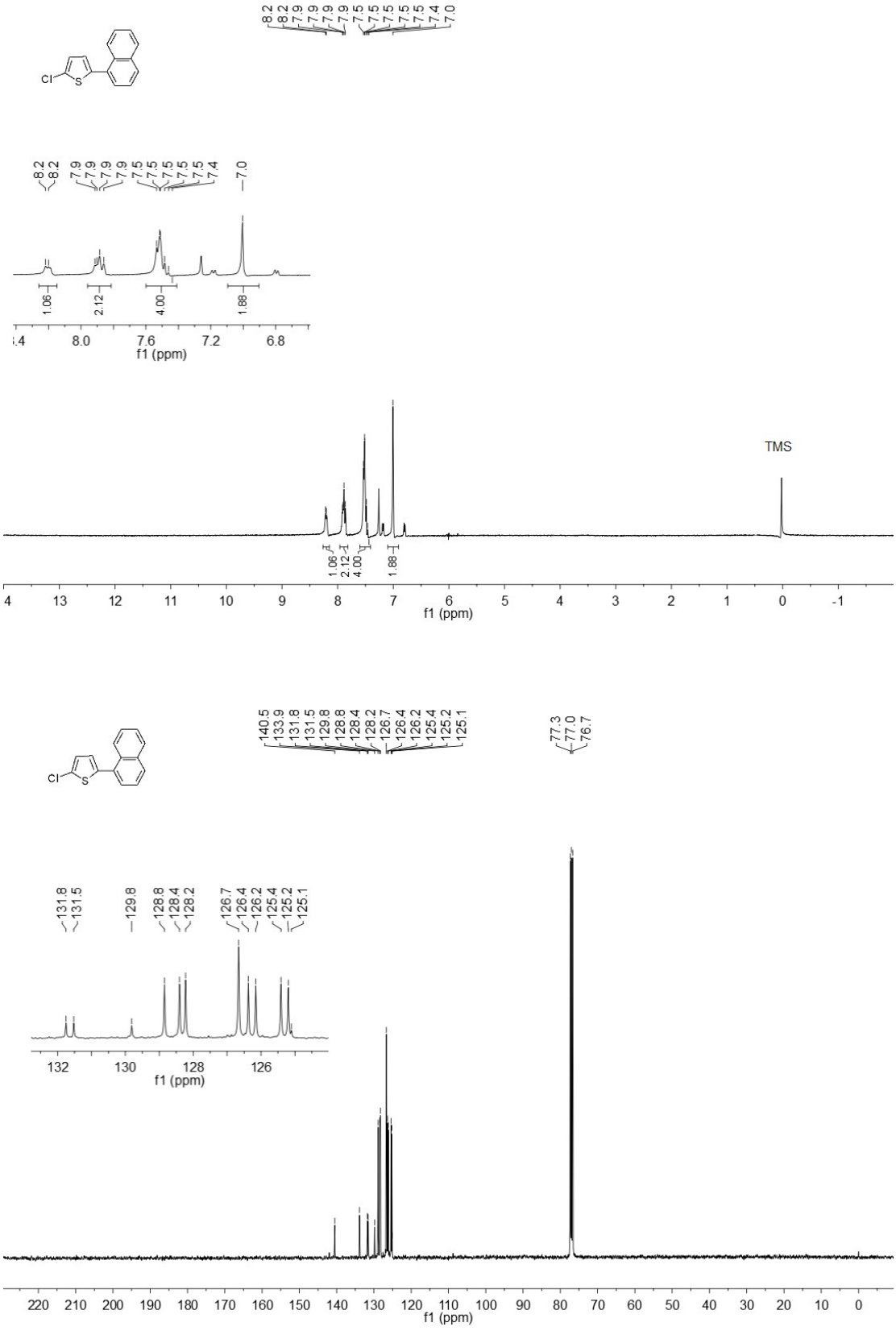


Figure **S20**. The NMR spectrums of 5-(naphthalen-1-yl)thiophene-2-carbonitrile (**7b**)

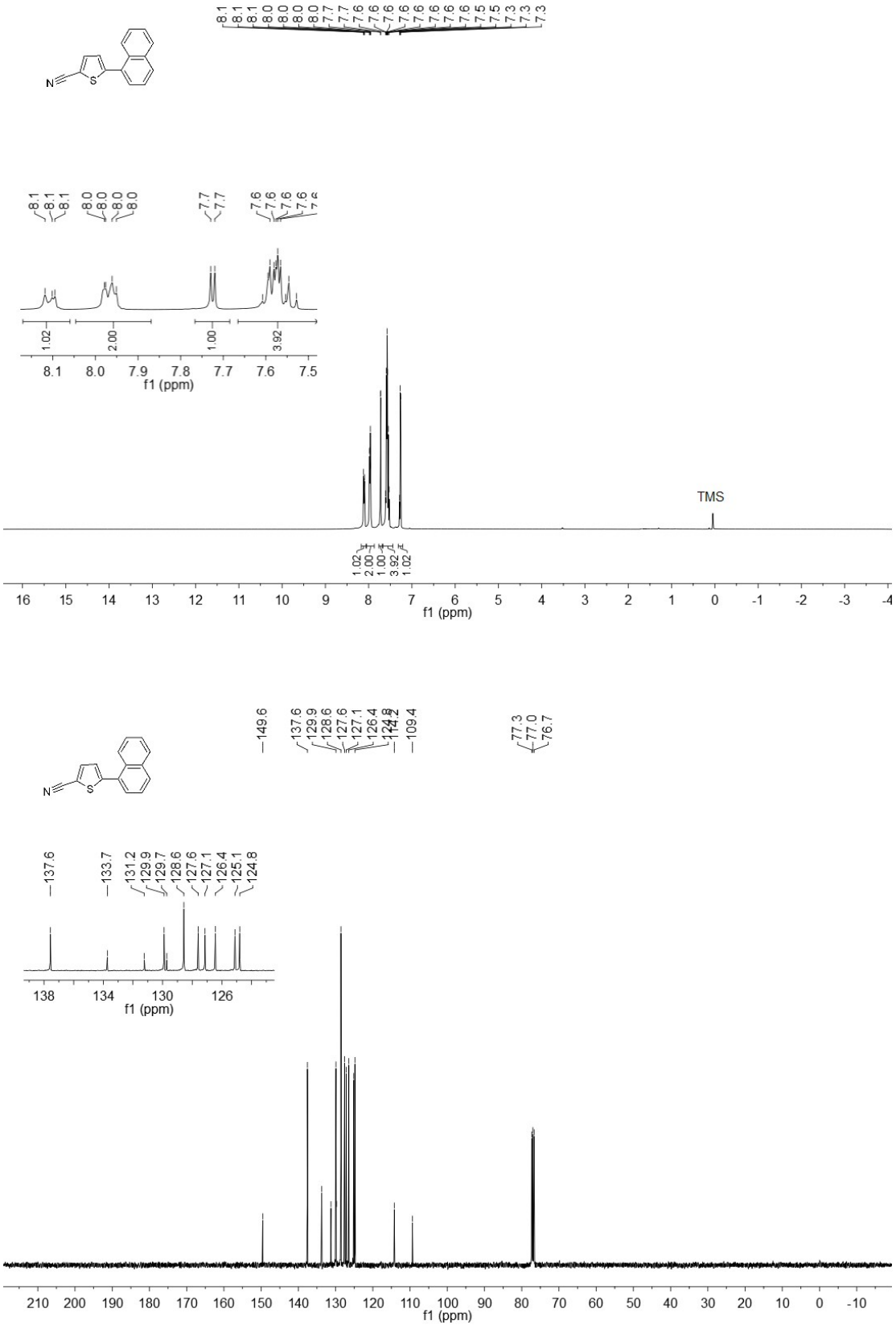


Figure **S21**. The NMR spectrums of 5-(2-methylnaphthalen-1-yl)thiophene-2-carbaldehyde (**8a**)

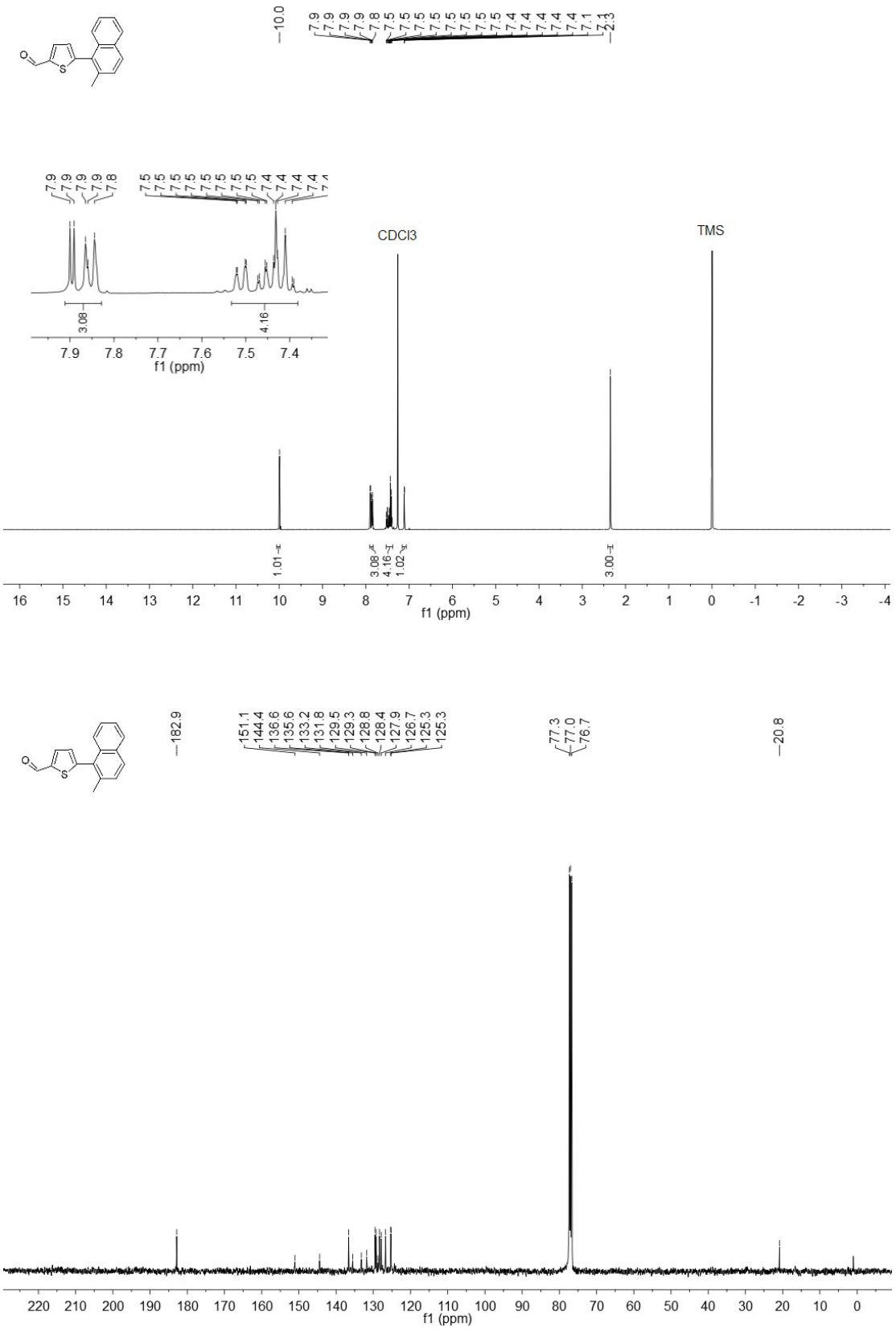
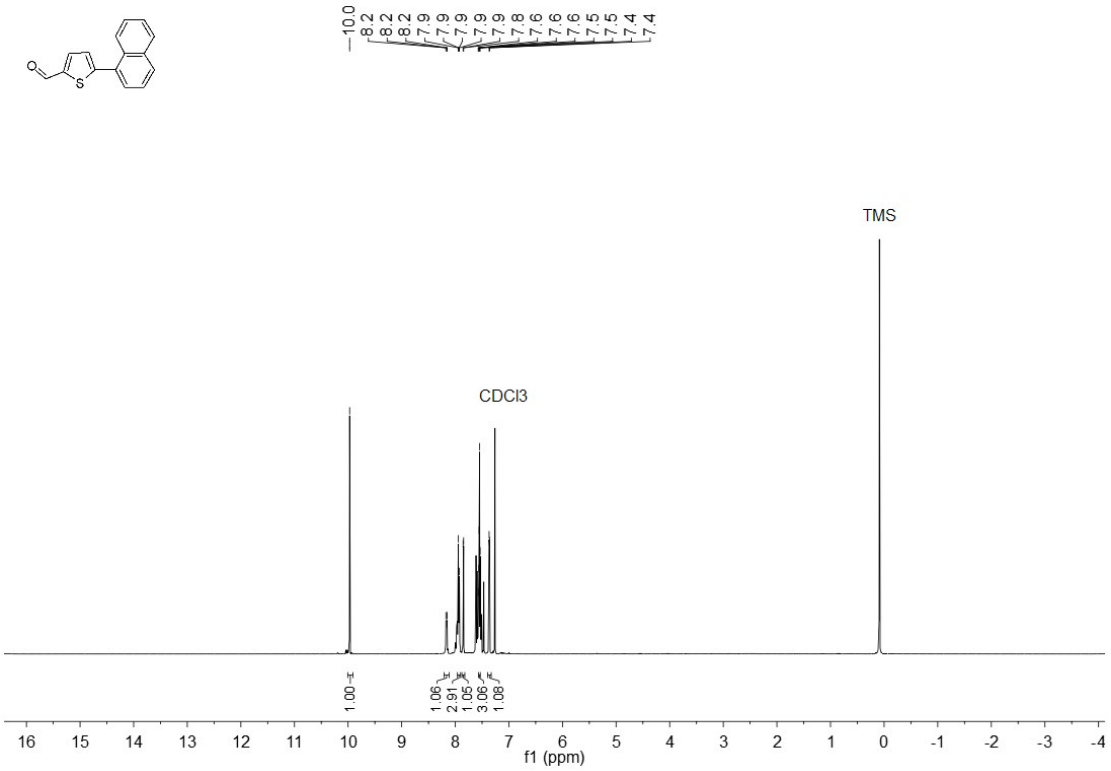


Figure **S22**. The NMR spectrums of 5-(naphthalen-1-yl)thiophene-2-carbaldehyde (**8b**)



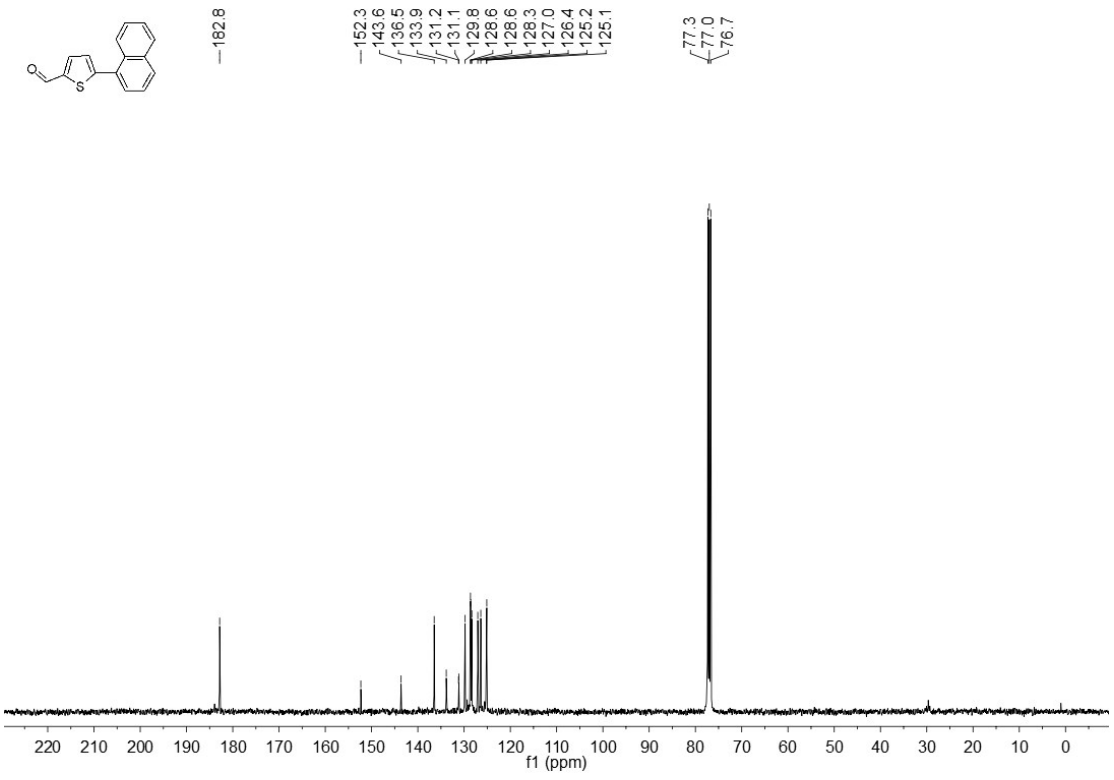


Figure **S23**. The NMR spectrums of 5-(4-(tert-butyl)phenyl)thiophene-2-carbaldehyde (**8g**)

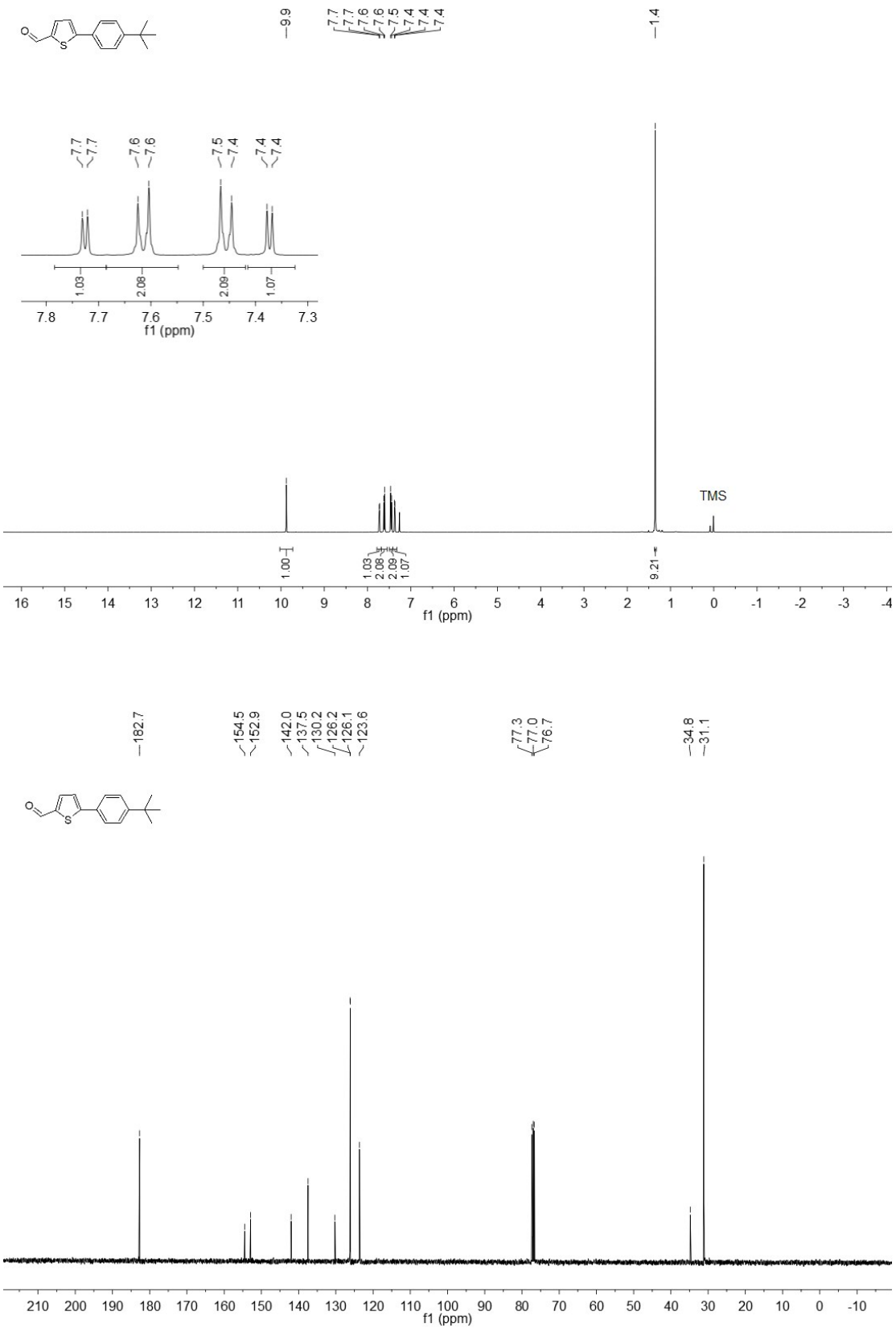
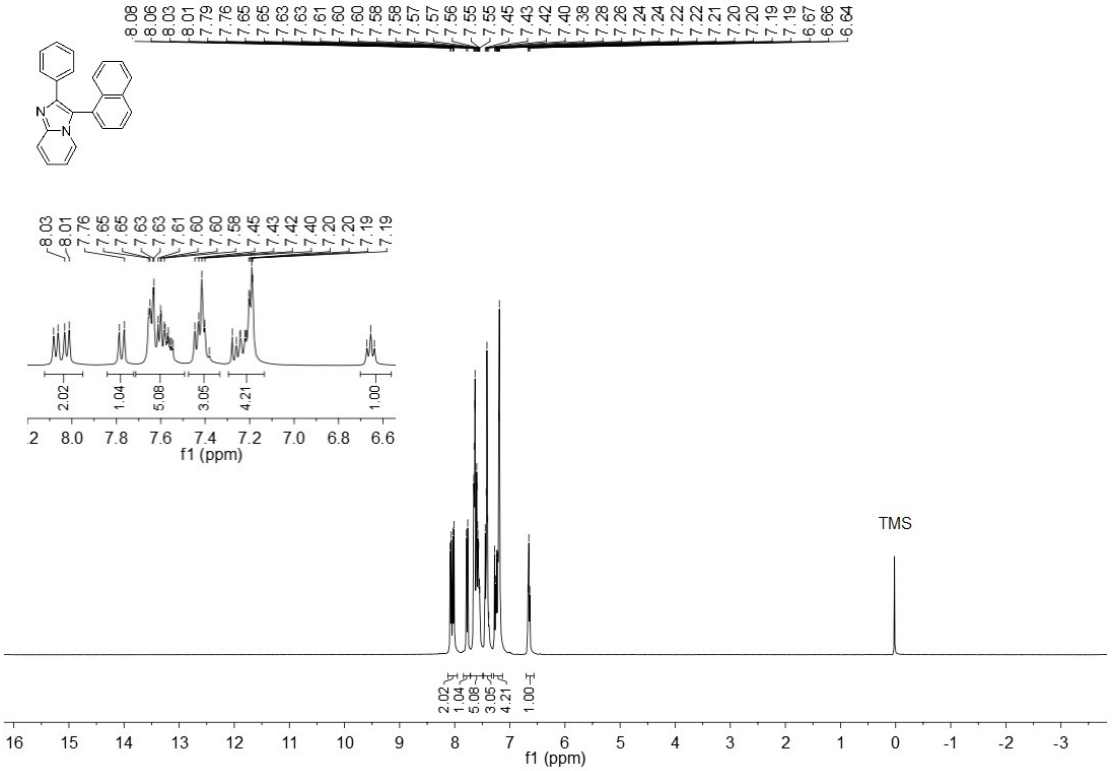


Figure **S24**. The NMR spectrums of 3-(naphthalen-1-yl)-2-phenylimidazo[1, 2-a]pyridine (**9b**)



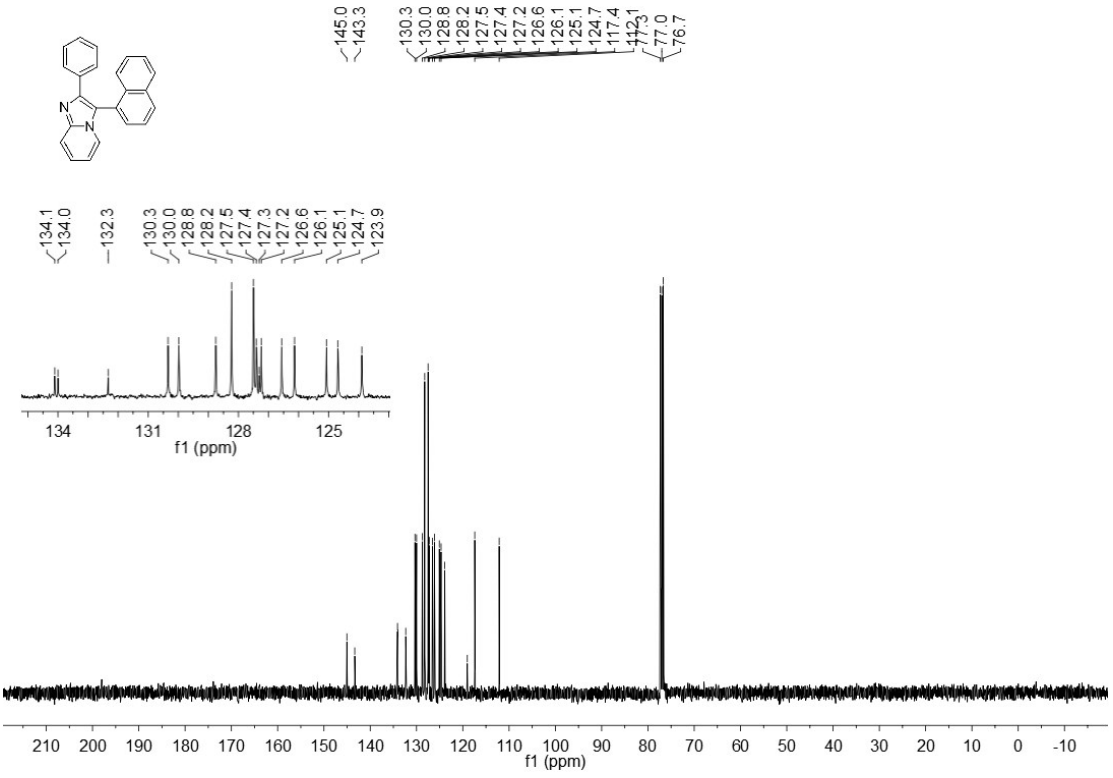


Figure **S25**. The NMR spectrums of 2, 4-dimethyl-5-(2-methylnaphthalen-1-yl)thiazole (**10a**)

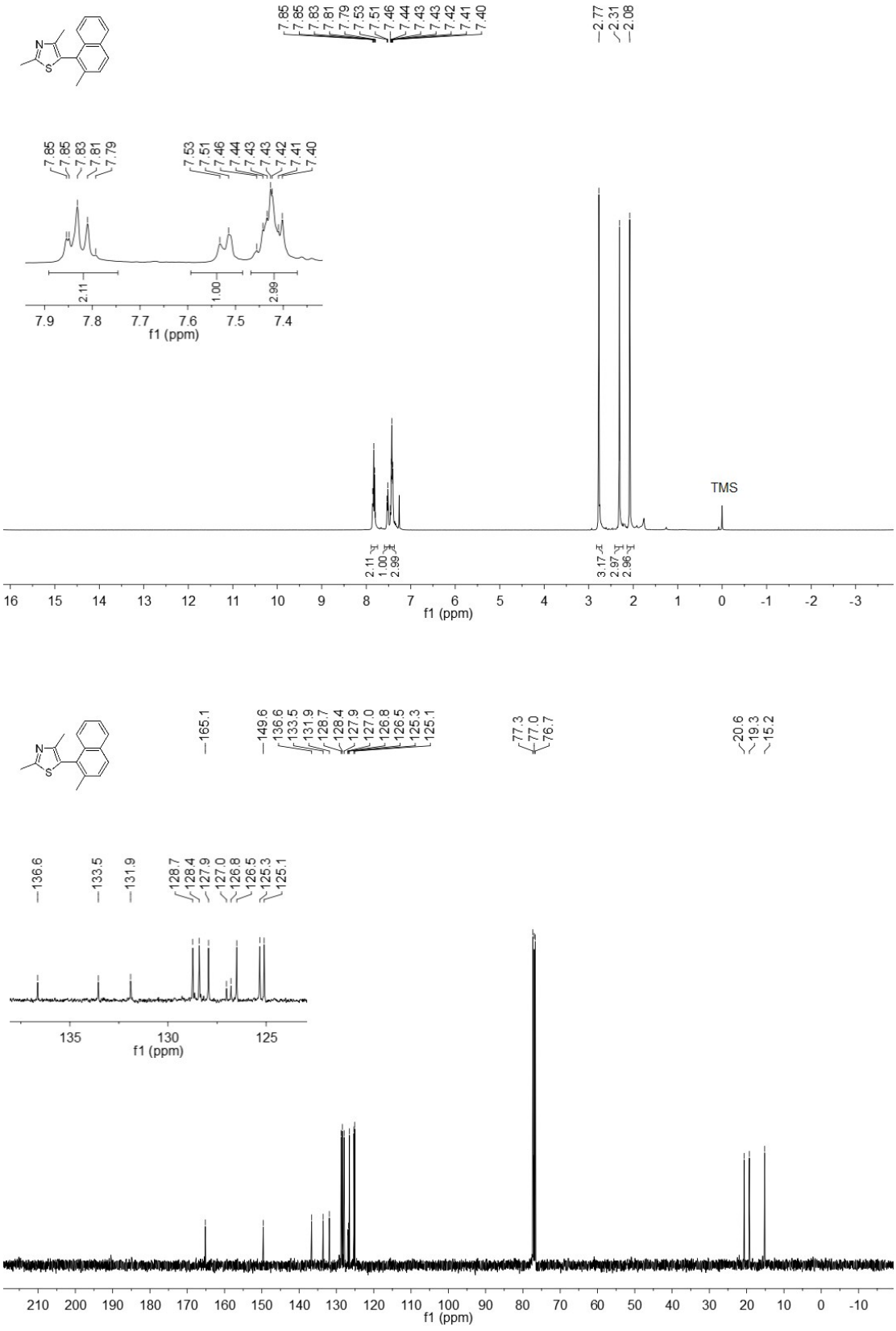


Figure **S26**. The NMR spectrums of 2-methyl-5-(2-methylnaphthalen-1-yl)-4-phenylthiazole (**11a**)

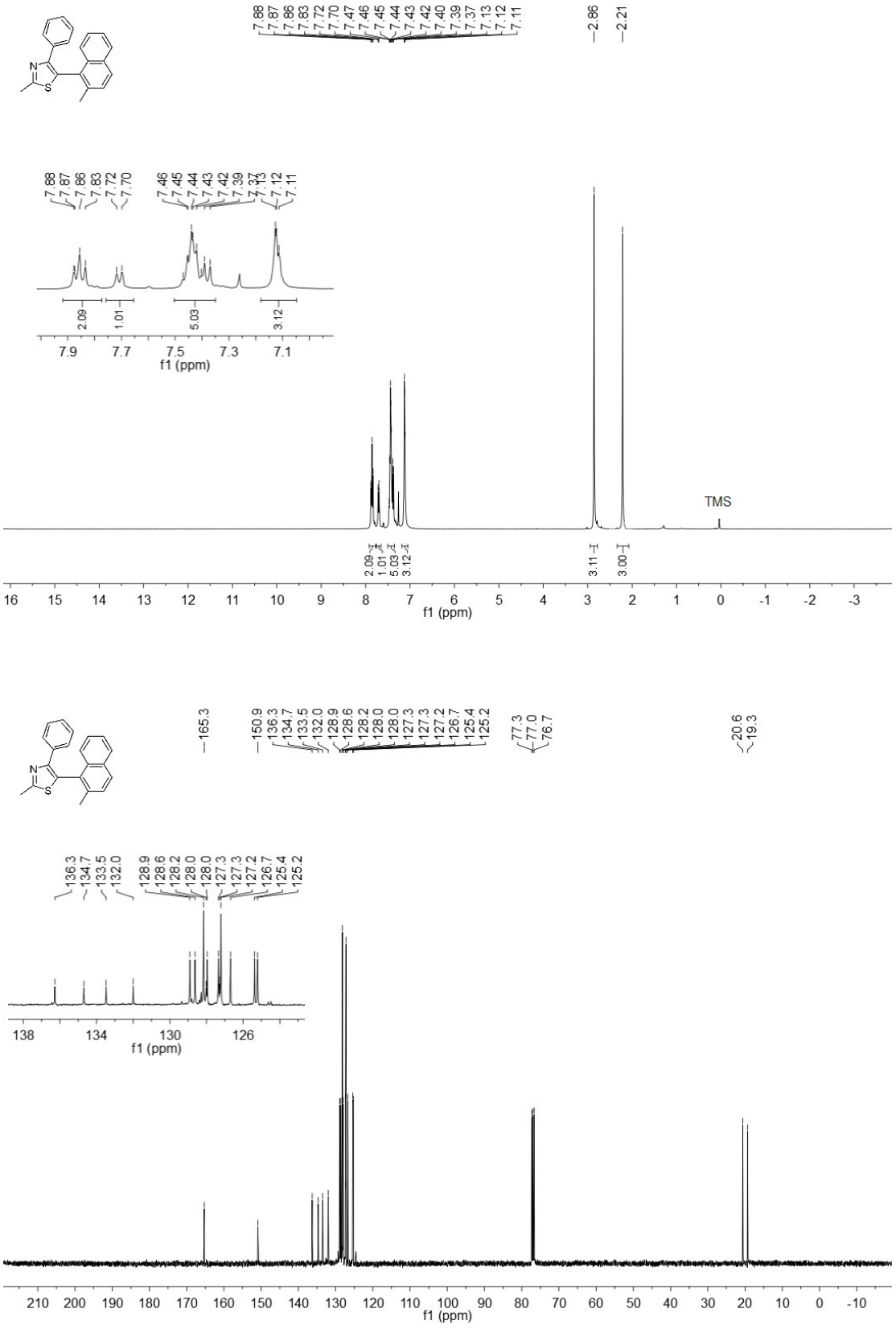


Figure **S27**. The NMR spectrums of 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole (**11b**)

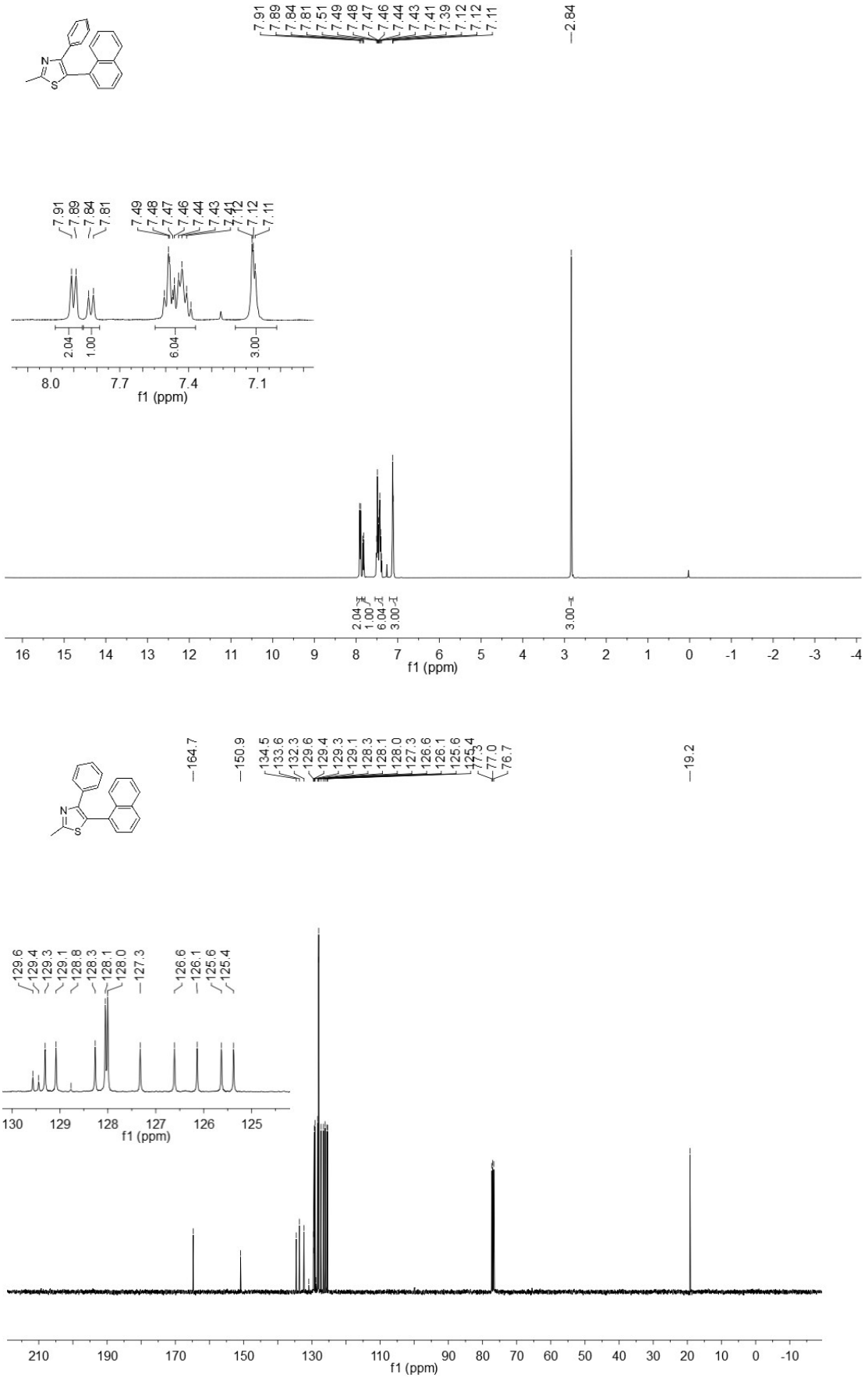
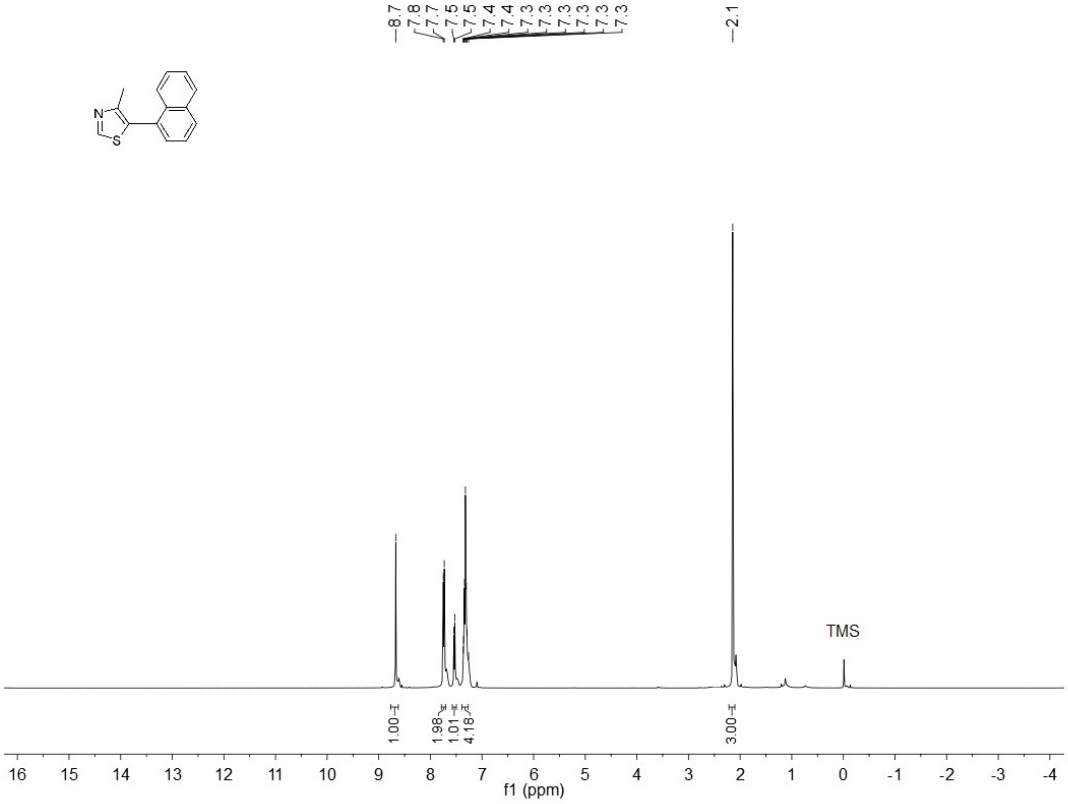


Figure **S28**. The NMR spectrums of 4-methyl-5-(naphthalen-1-yl)thiazole (**12b**)



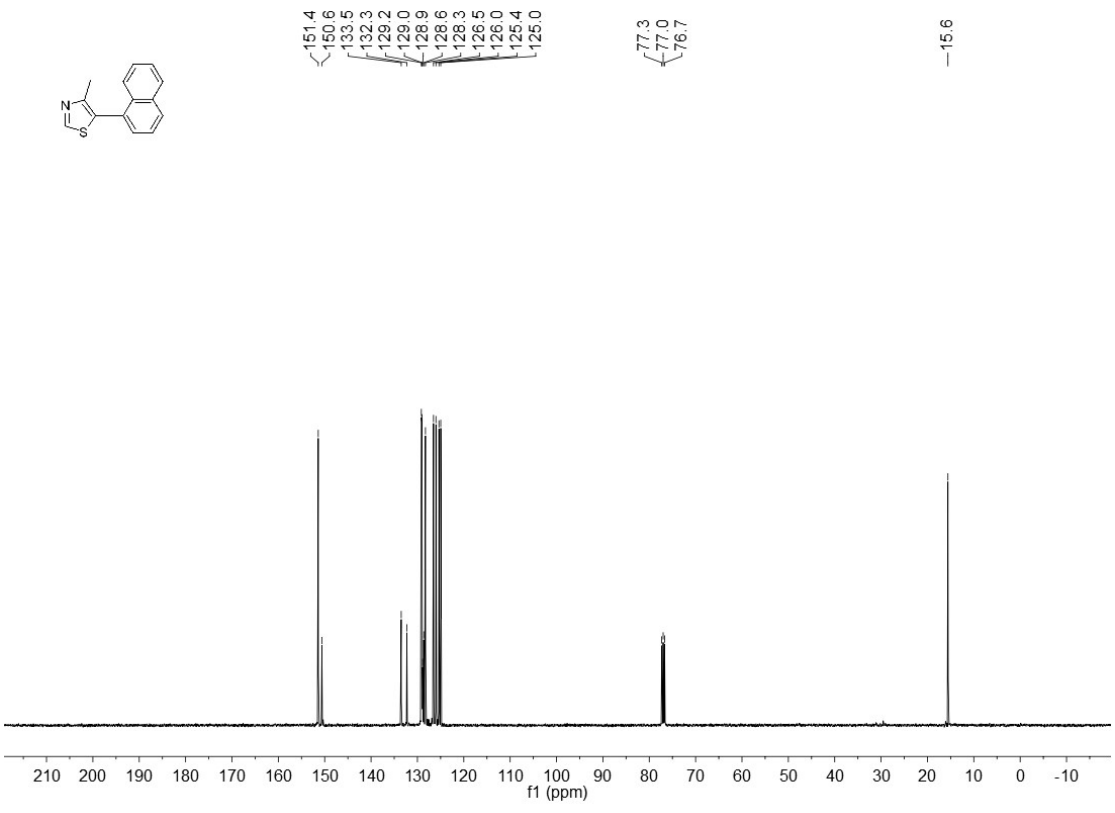
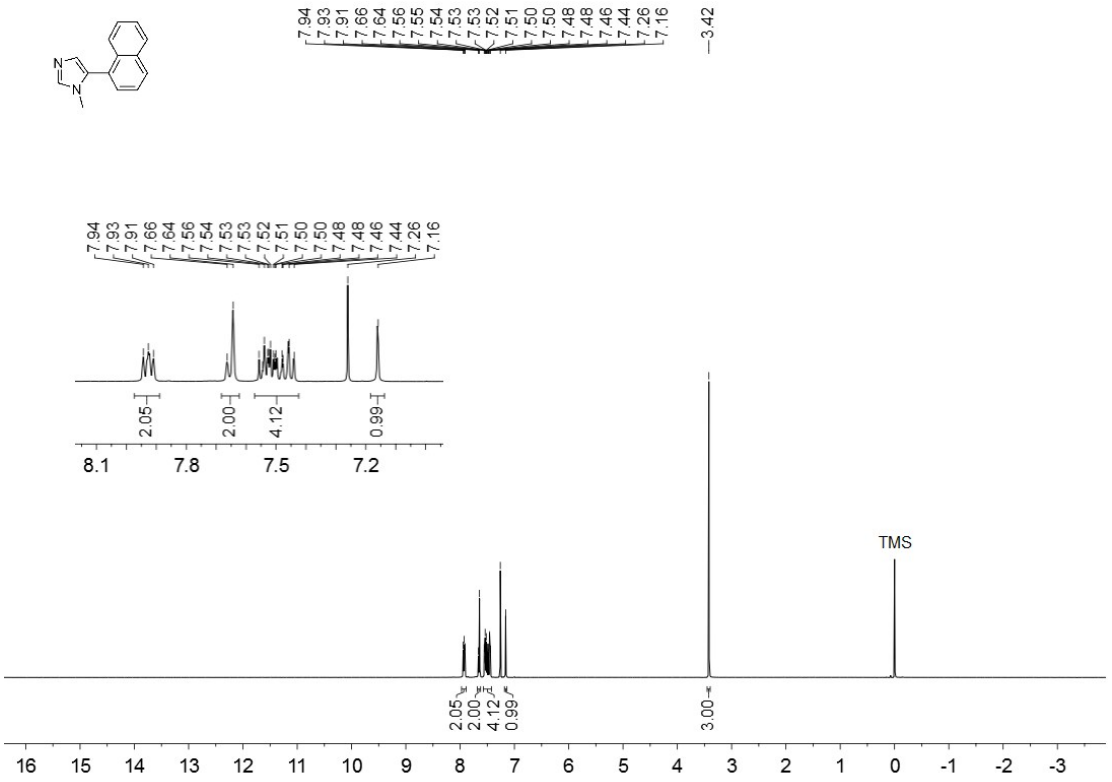


Figure **S29**. The NMR spectrums of 1-methyl-5-(naphthalen-1-yl)-1H-imidazole (**13b**)



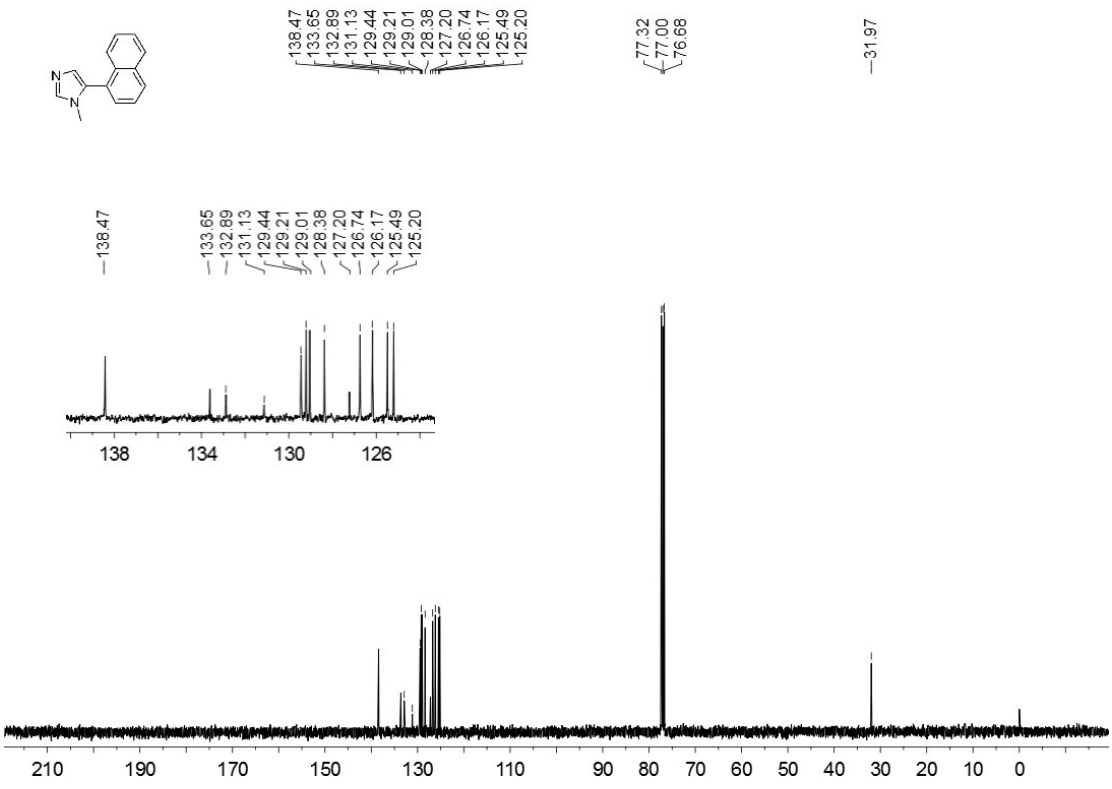


Figure **S30**. The NMR spectrums of 1, 2-dimethyl-5-(naphthalen-1-yl)-1H-imidazole (**14b**)

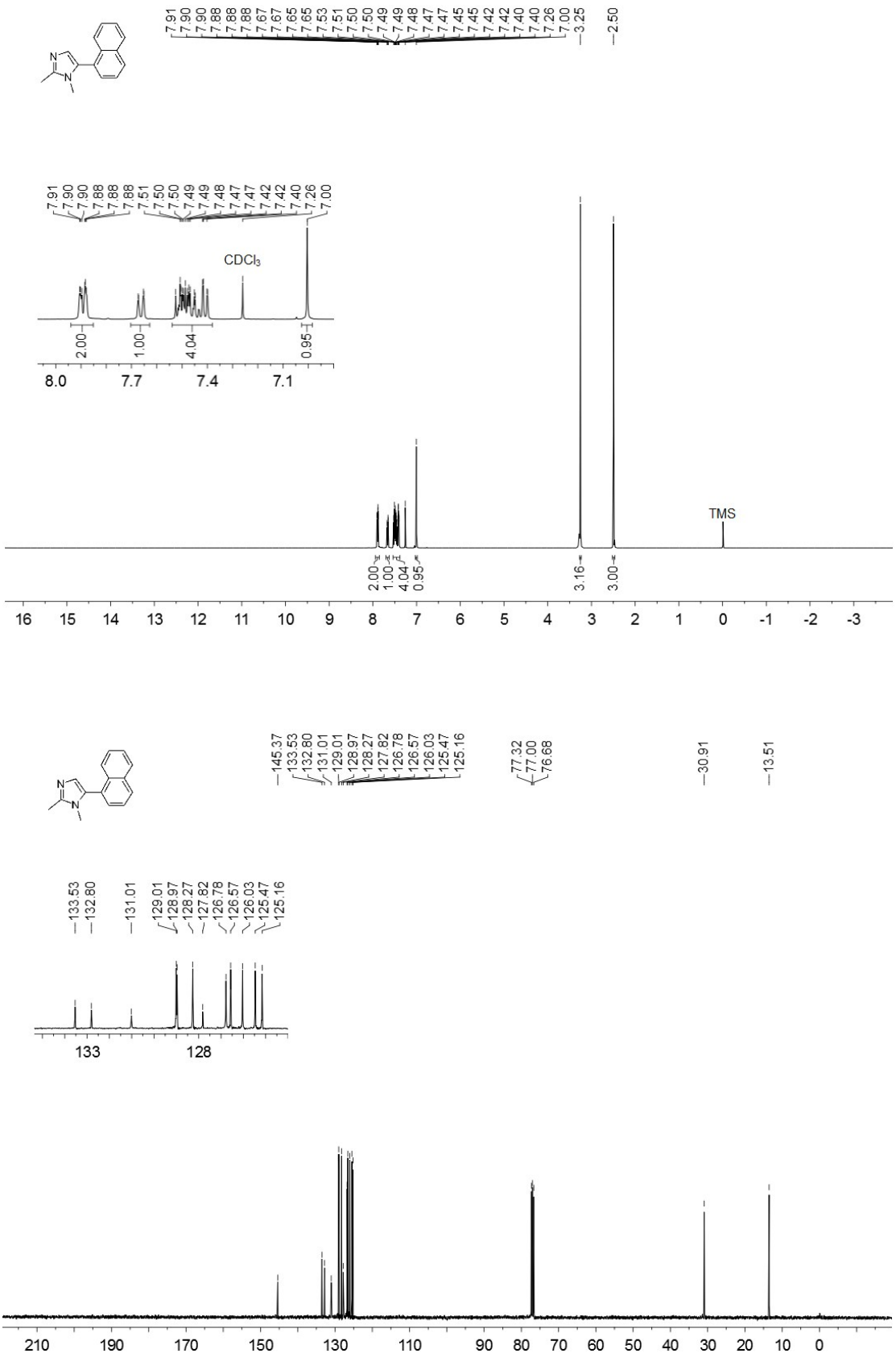


Figure **S31**. The NMR spectrums of 3-(benzo[b]thiophen-2-yl)pyridine (**16a**)

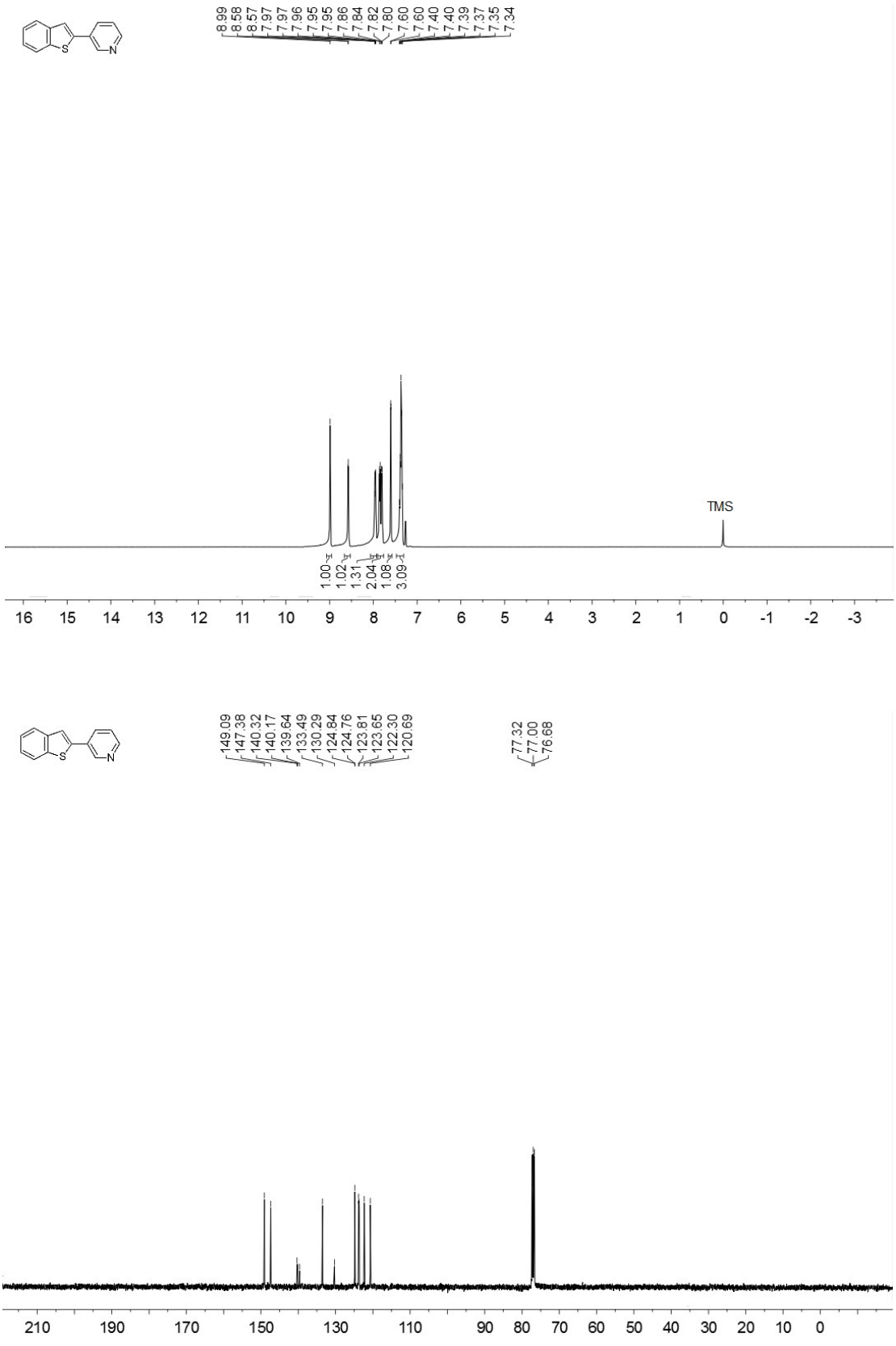
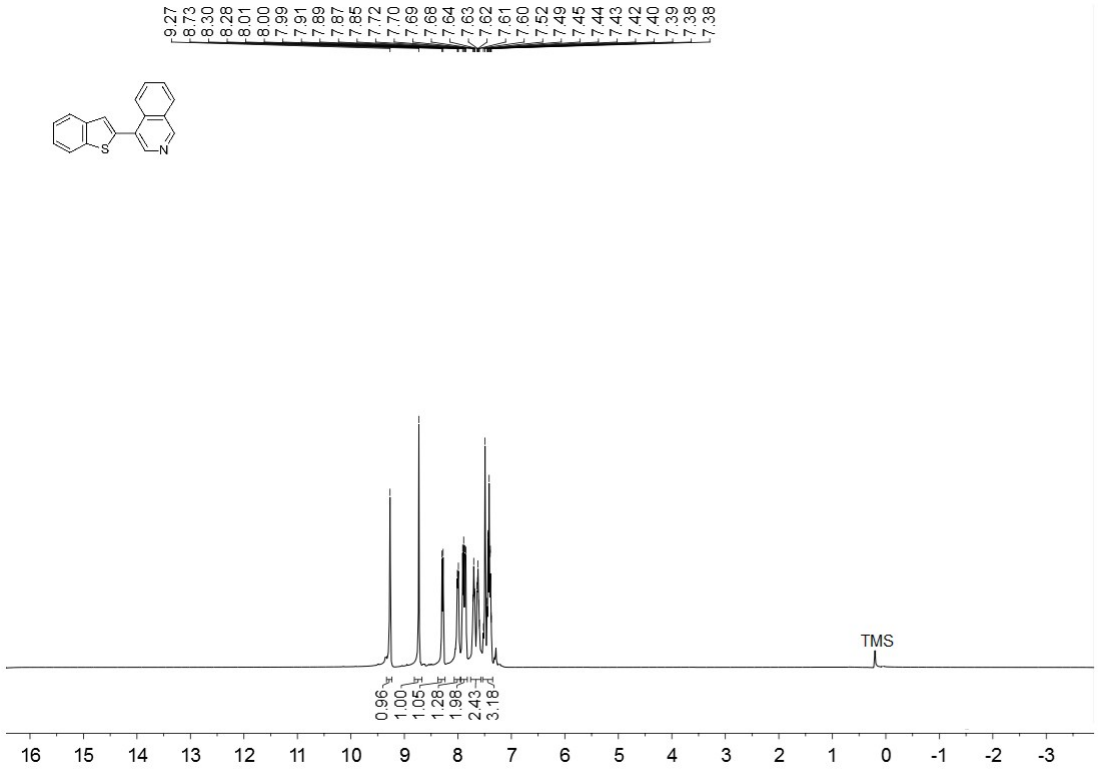


Figure **S32**. The NMR spectrums of 4-(benzo[b]thiophen-2-yl)isoquinoline (**16b**)



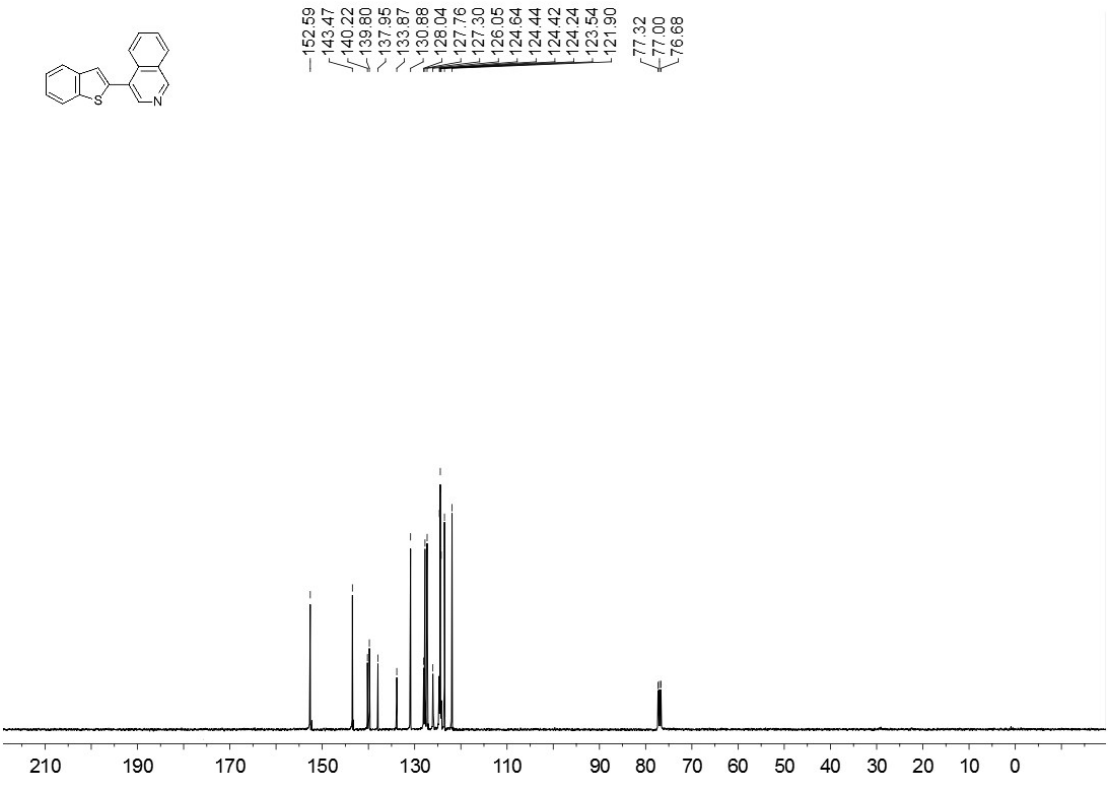
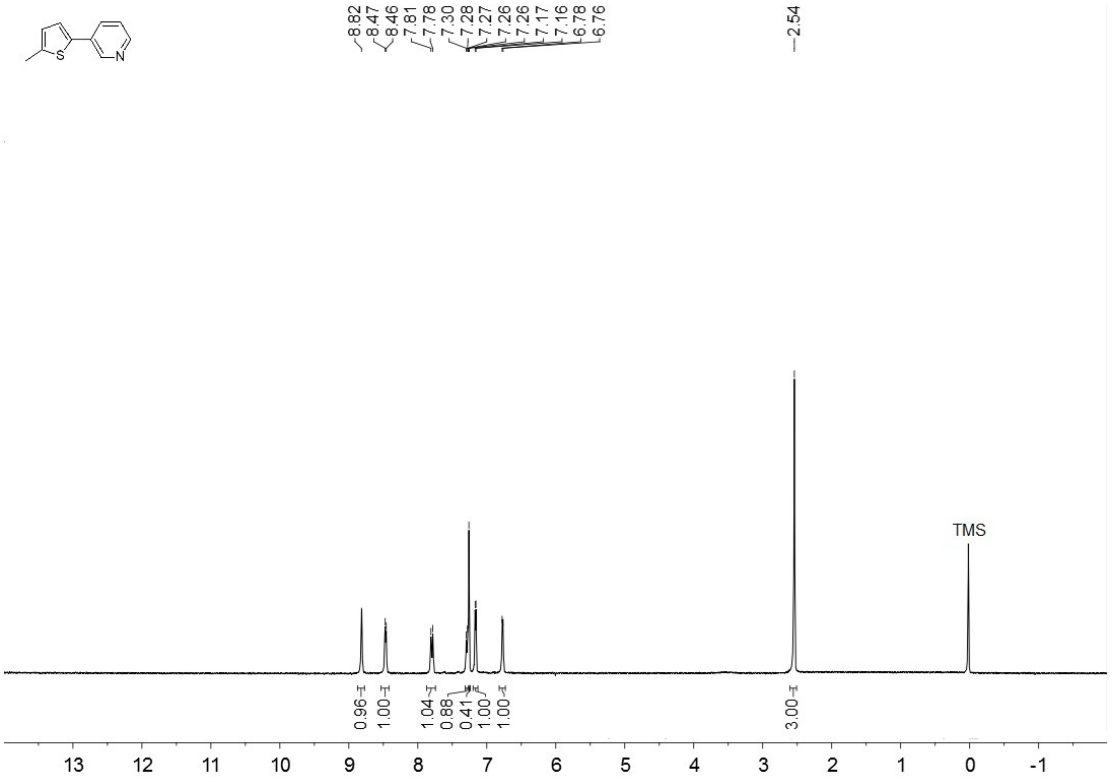


Figure **S33**. The NMR spectrums of 3-(5-methylthiophen-2-yl)pyridine (**17a**)



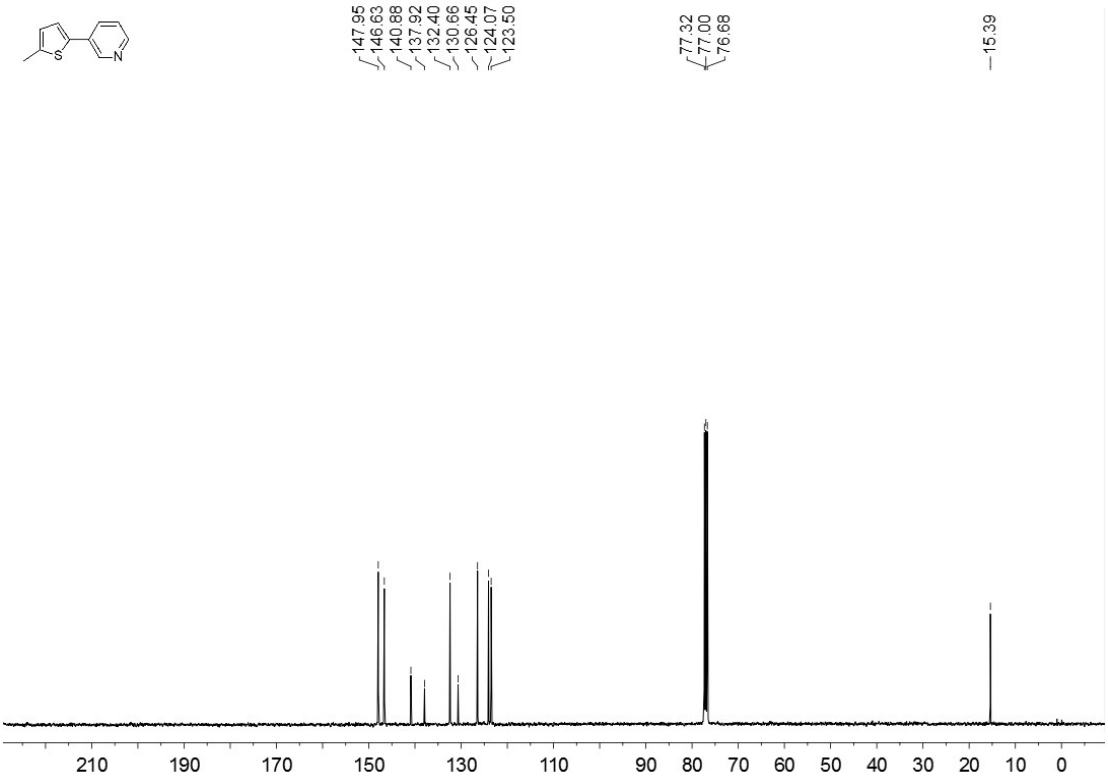
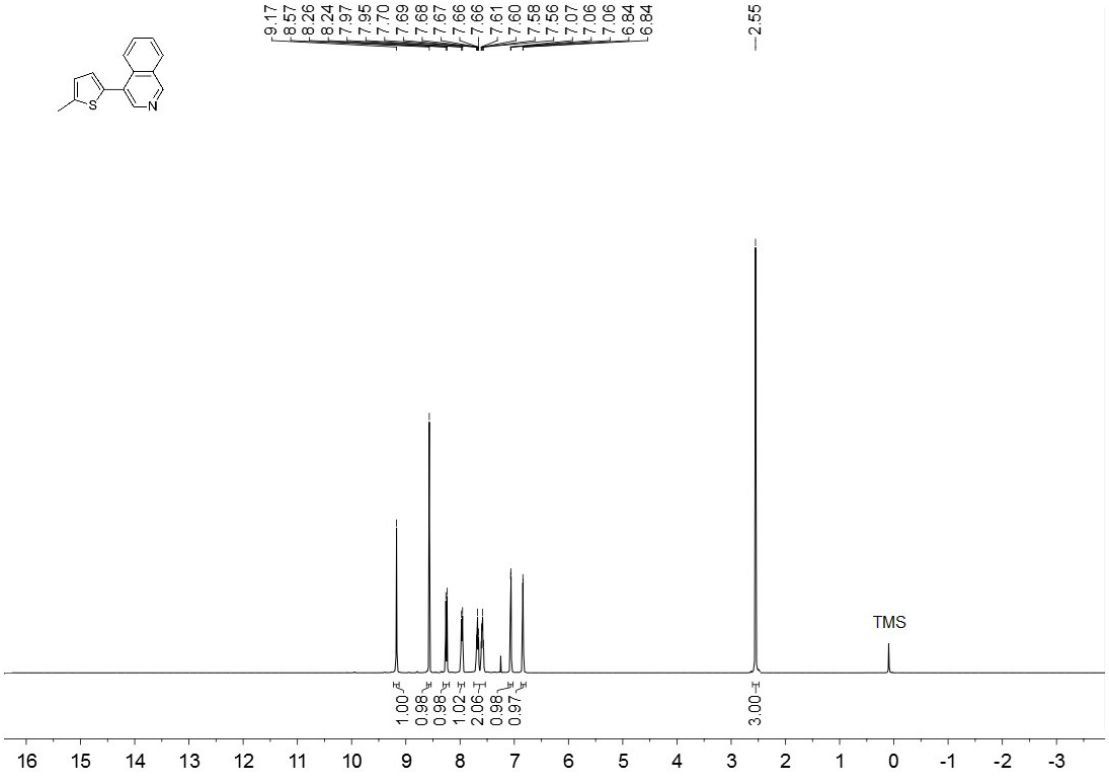


Figure **S34**. The NMR spectrums of 4-(5-methylthiophen-2-yl)isoquinoline (**17b**)



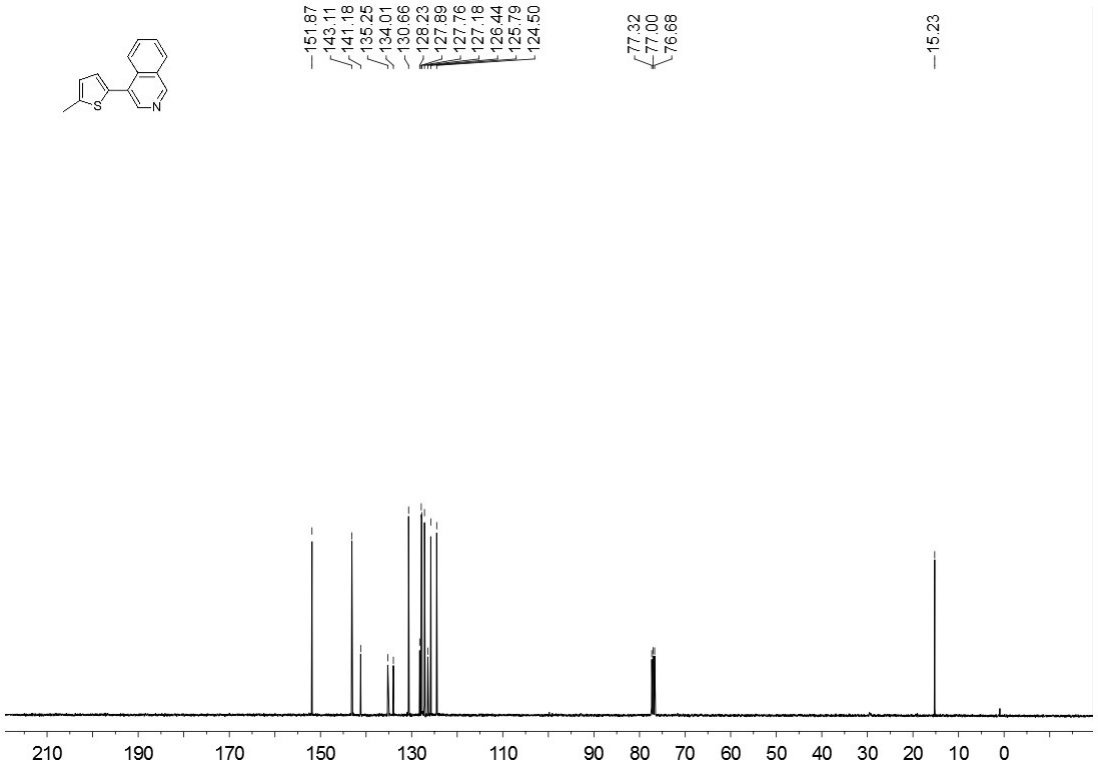


Figure **S35**. The NMR spectrums of 5-(5-methylthiophen-2-yl)pyrimidine (**17c**)

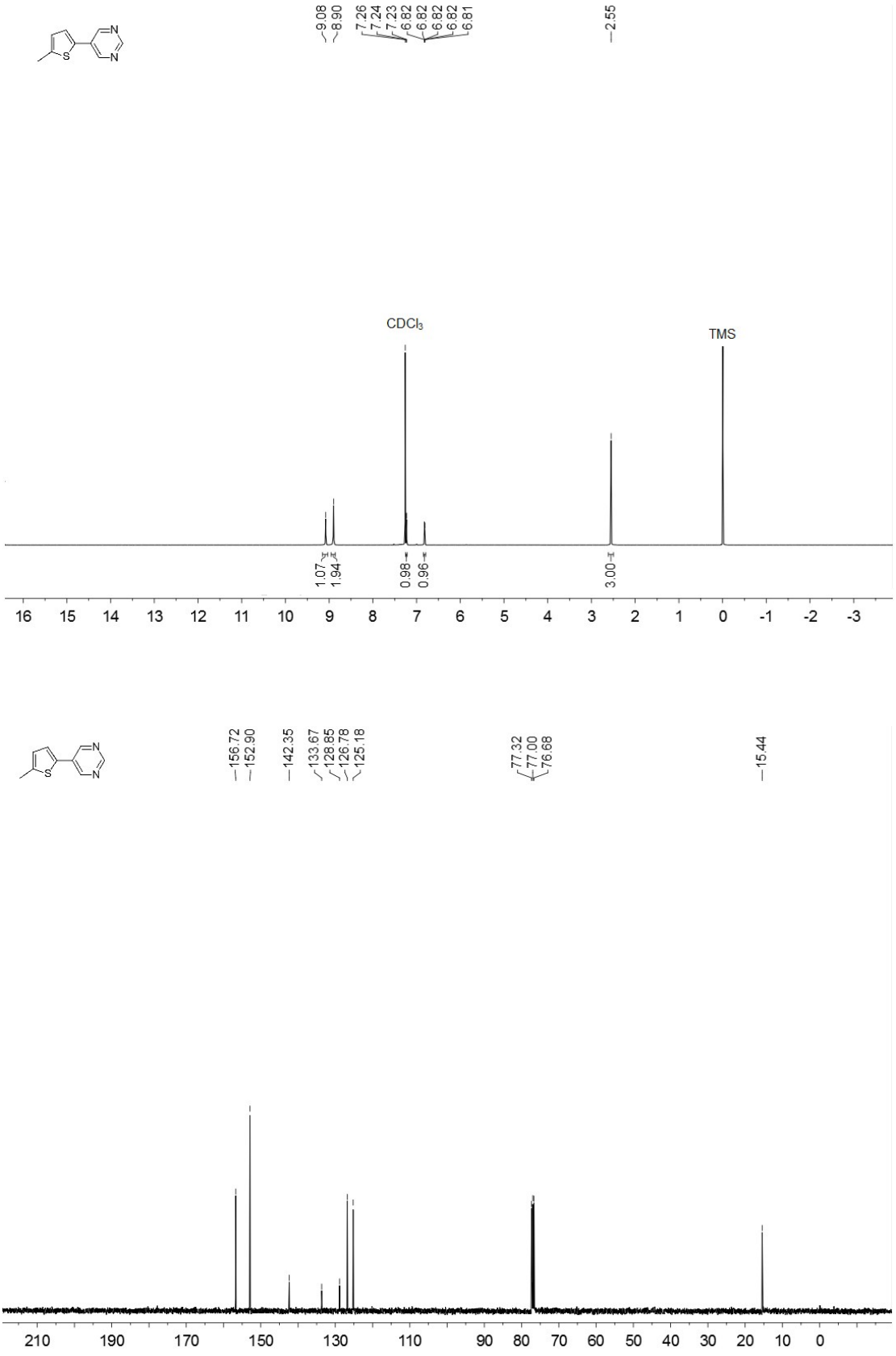


Figure **S36**. The NMR spectrums of 3-(5-ethylthiophen-2-yl)pyridine (**18a**)

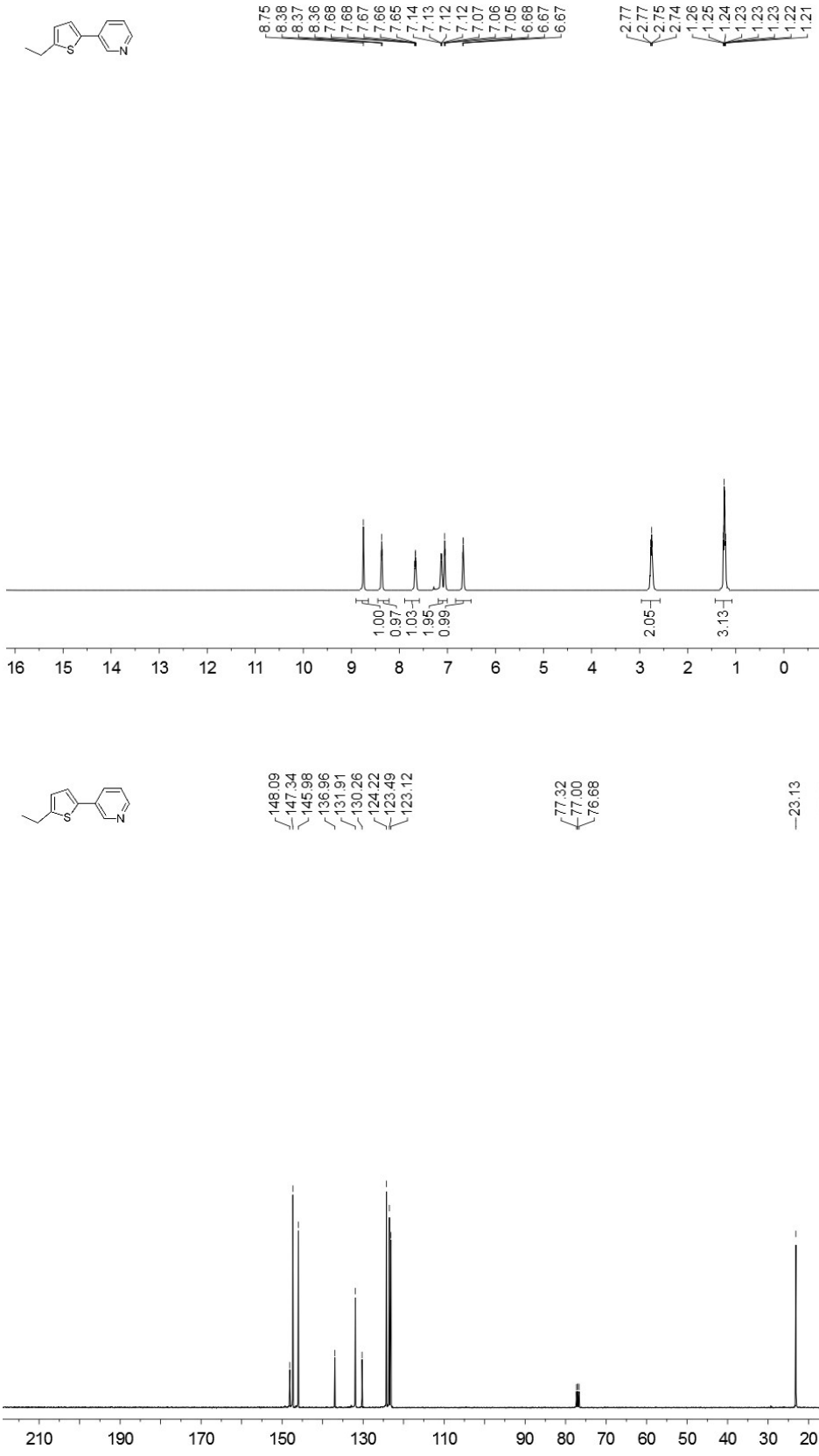


Figure **S37**. The NMR spectrums of 4-(5-ethylthiophen-2-yl)isoquinoline (**18b**)

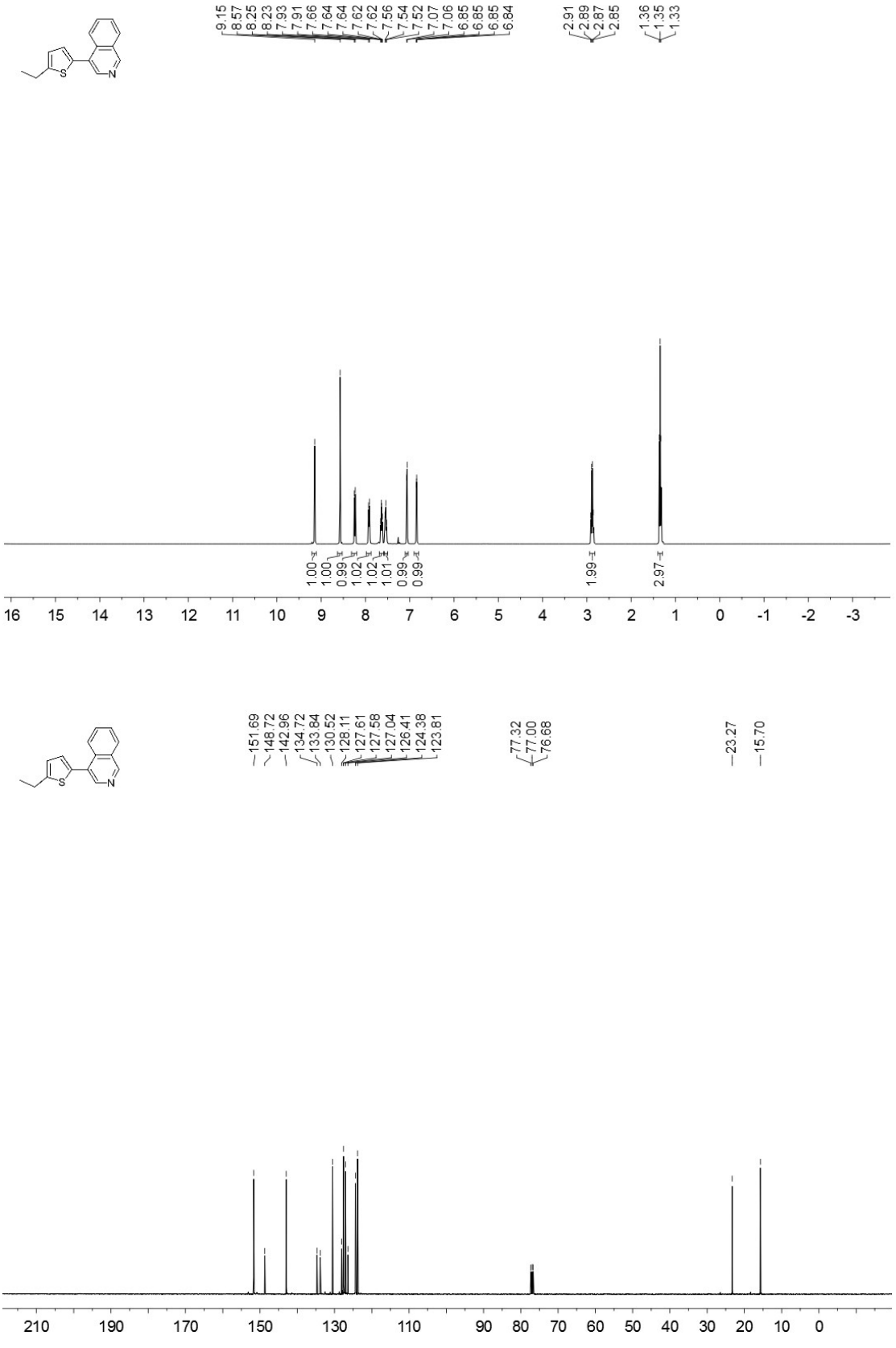


Figure **S38**. The NMR spectrums of 5-(5-methylthiophen-2-yl)pyrimidine (**18c**)

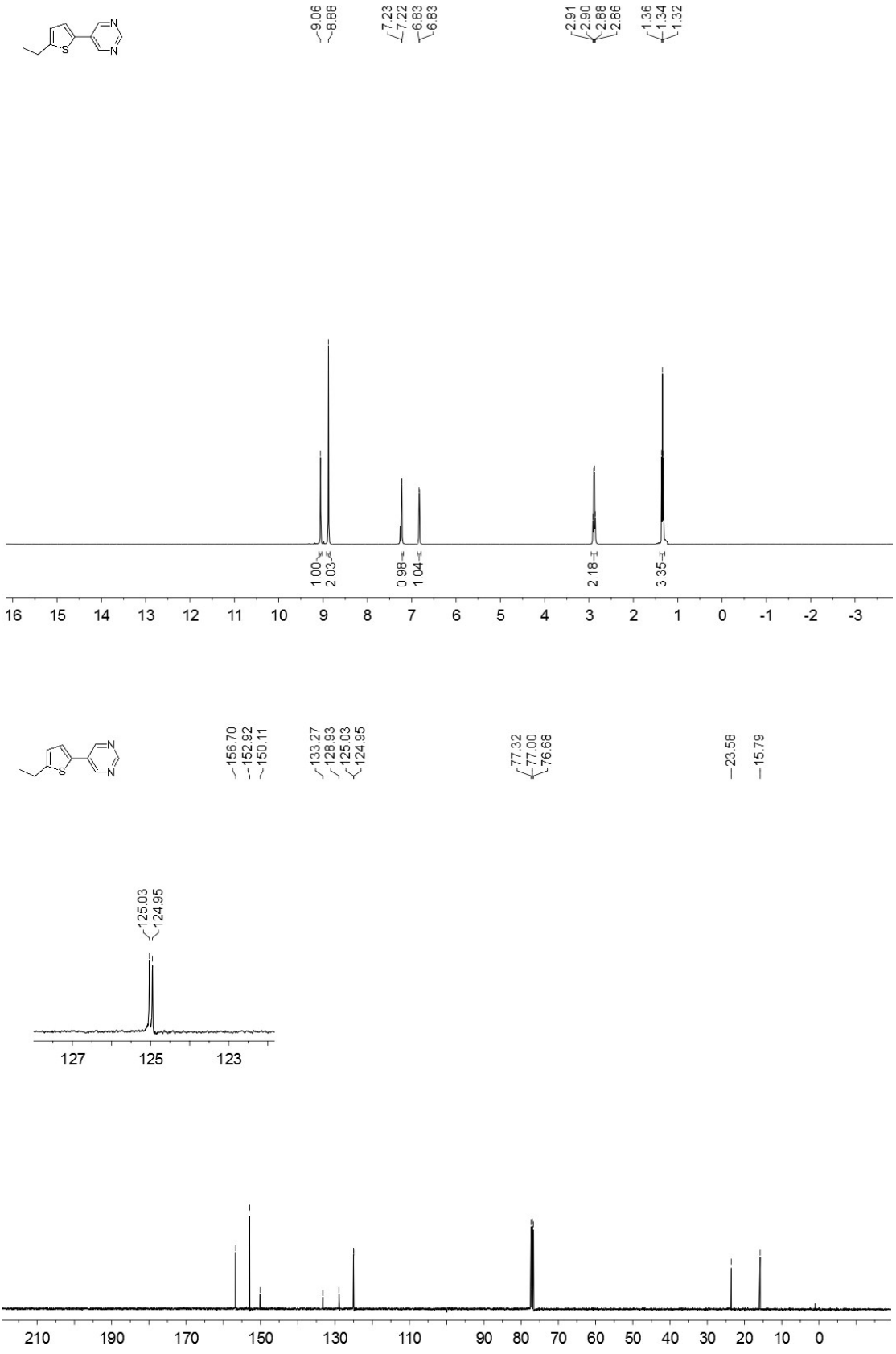


Figure **S39**. The NMR spectrums of 5-(5-methylthiophen-2-yl)pyrimidine (**19a**)

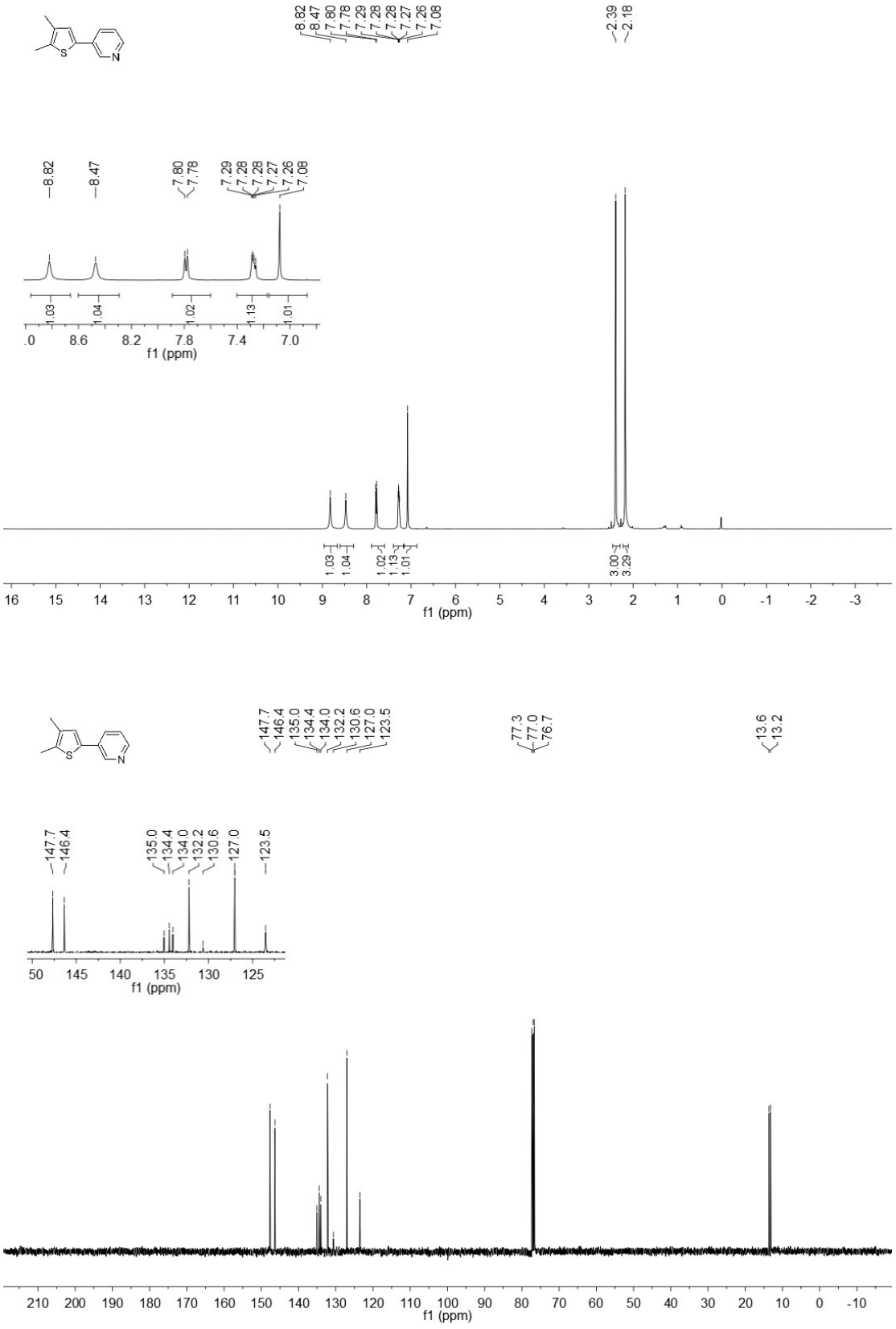
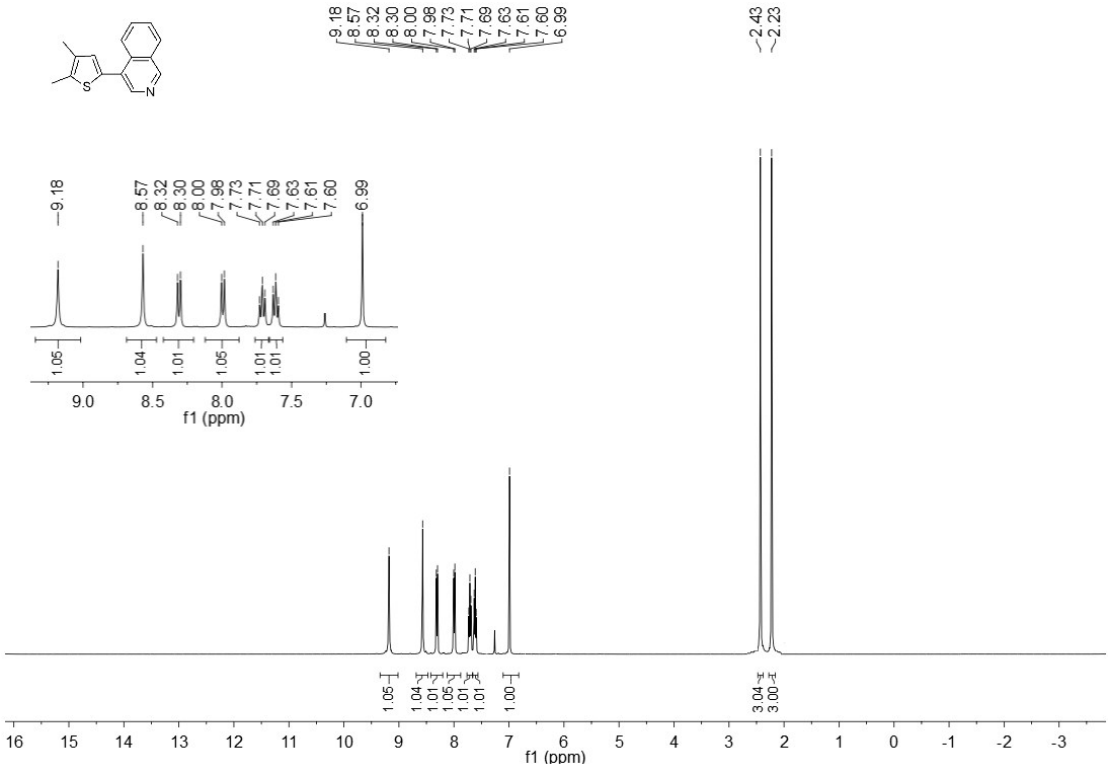


Figure **S40**. The NMR spectrums of 4-(4, 5-dimethylthiophen-2-yl)isoquinoline (**19b**)



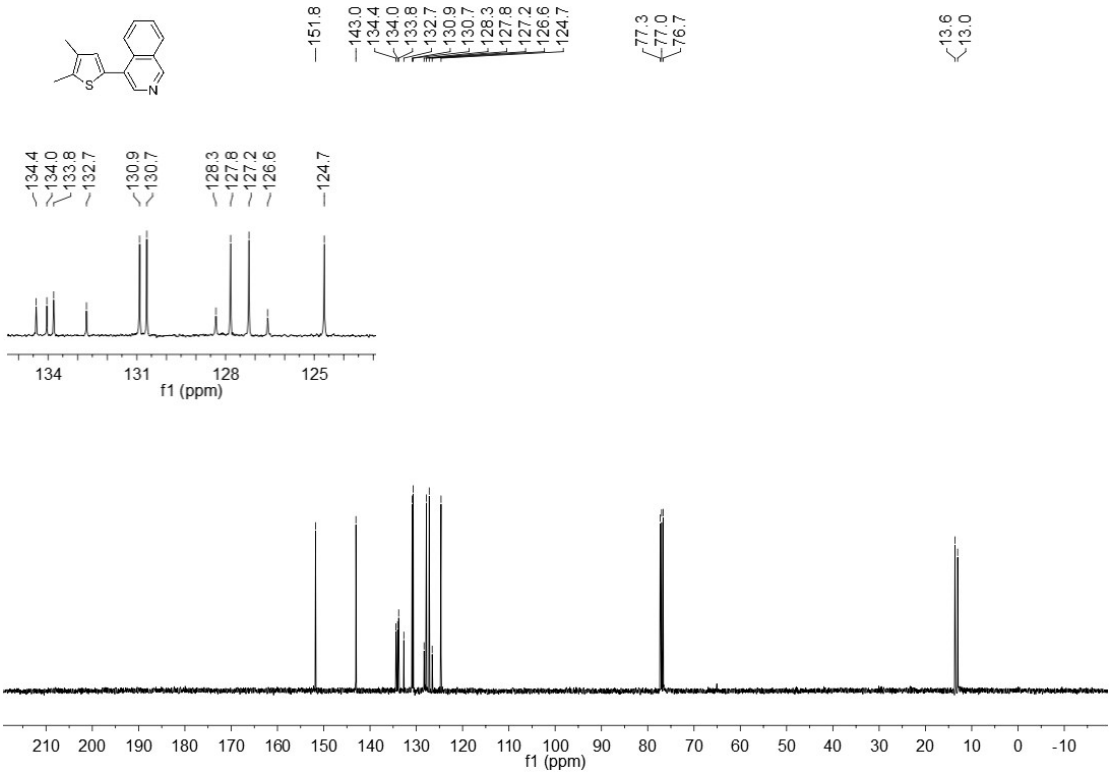
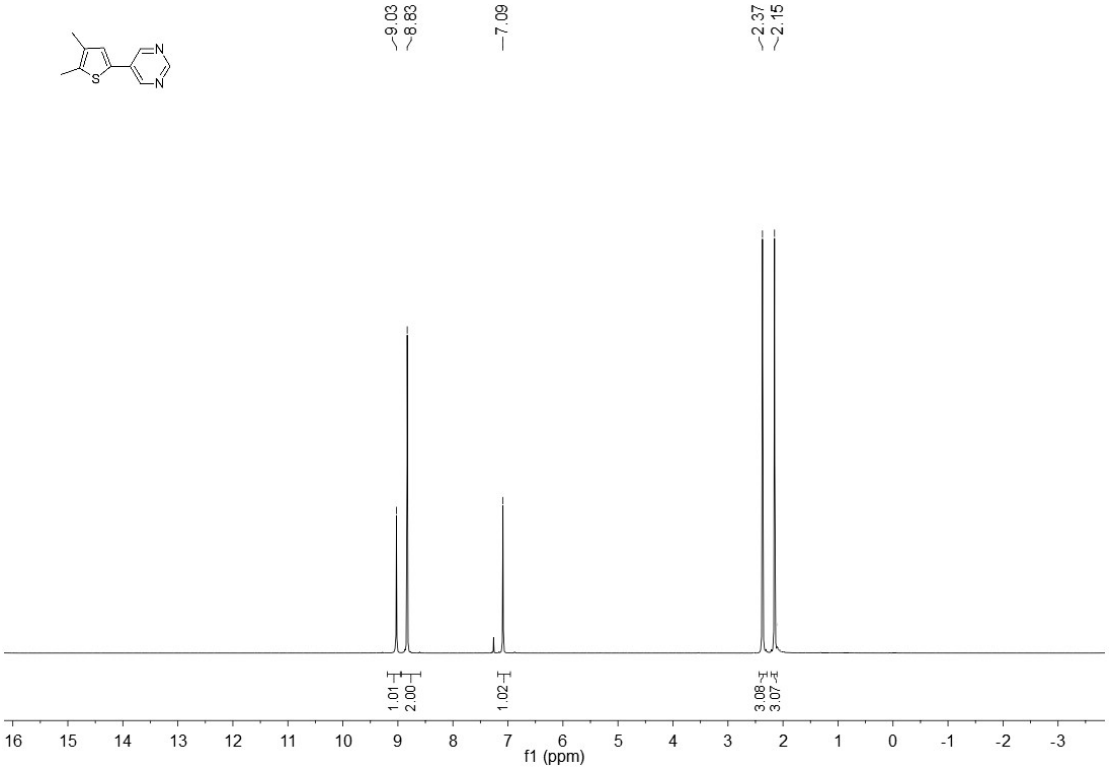


Figure **S41**. The NMR spectrums of 5-(4, 5-dimethylthiophen-2-yl)pyrimidine (**19c**)



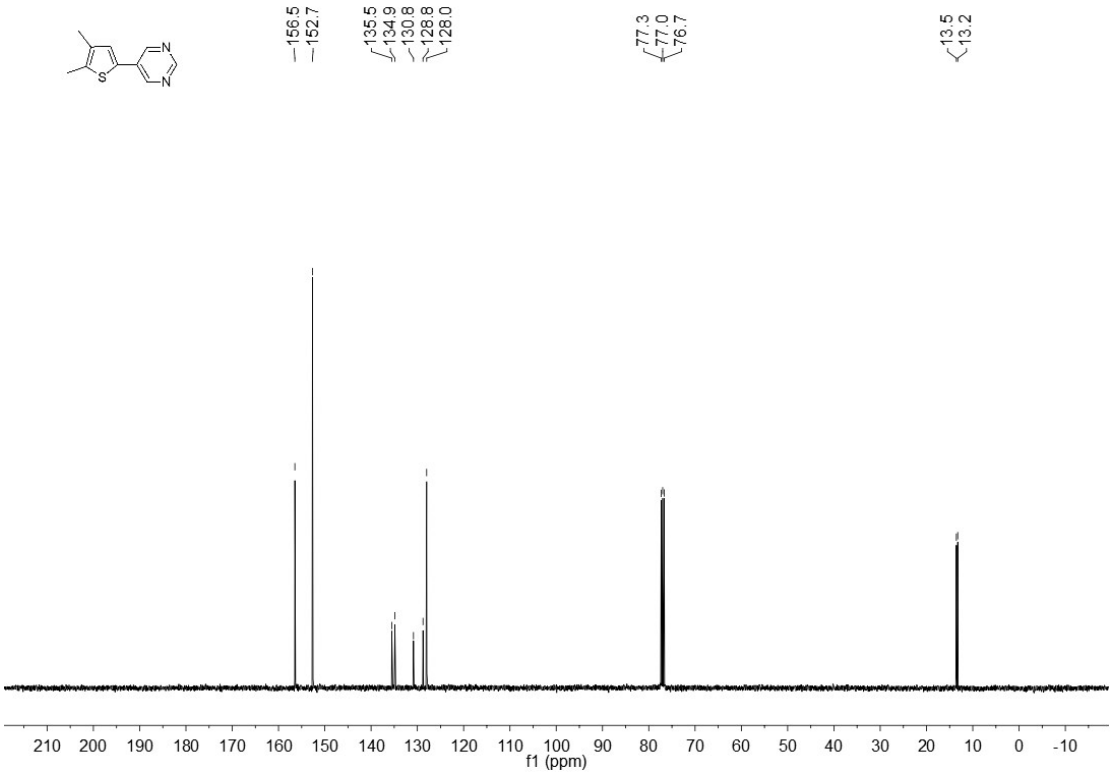
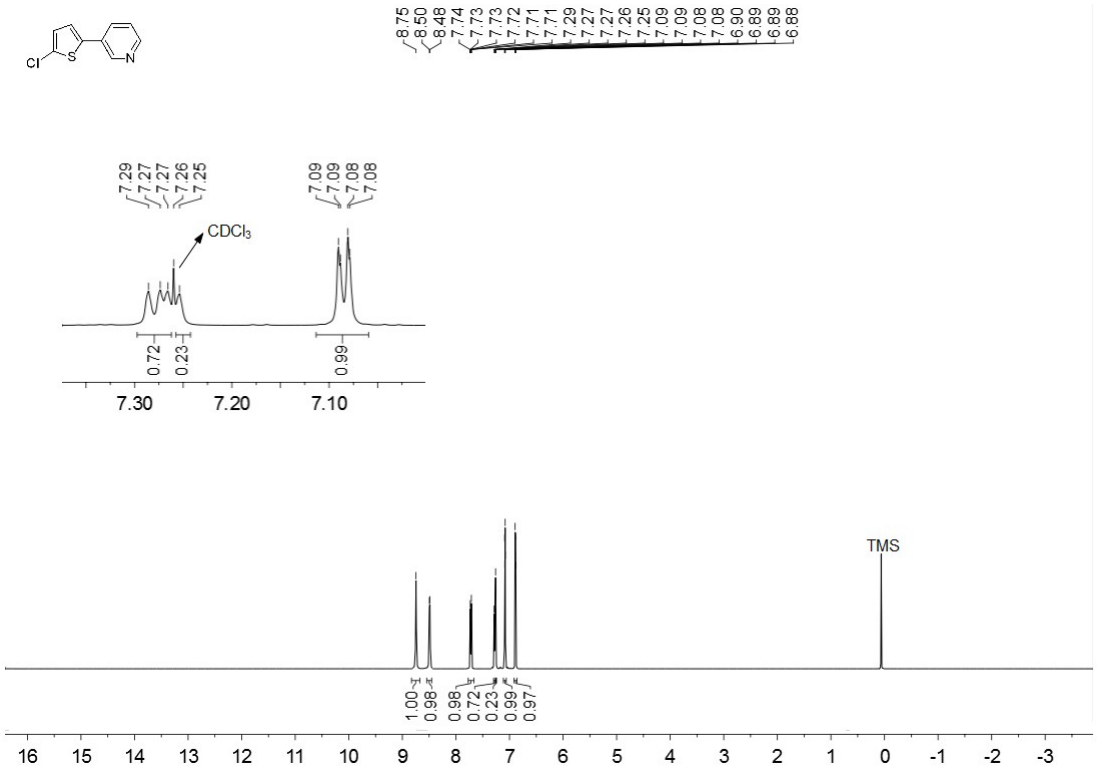


Figure **S42**. The NMR spectrums of 3-(5-chlorothiophen-2-yl)pyridine (**20a**)



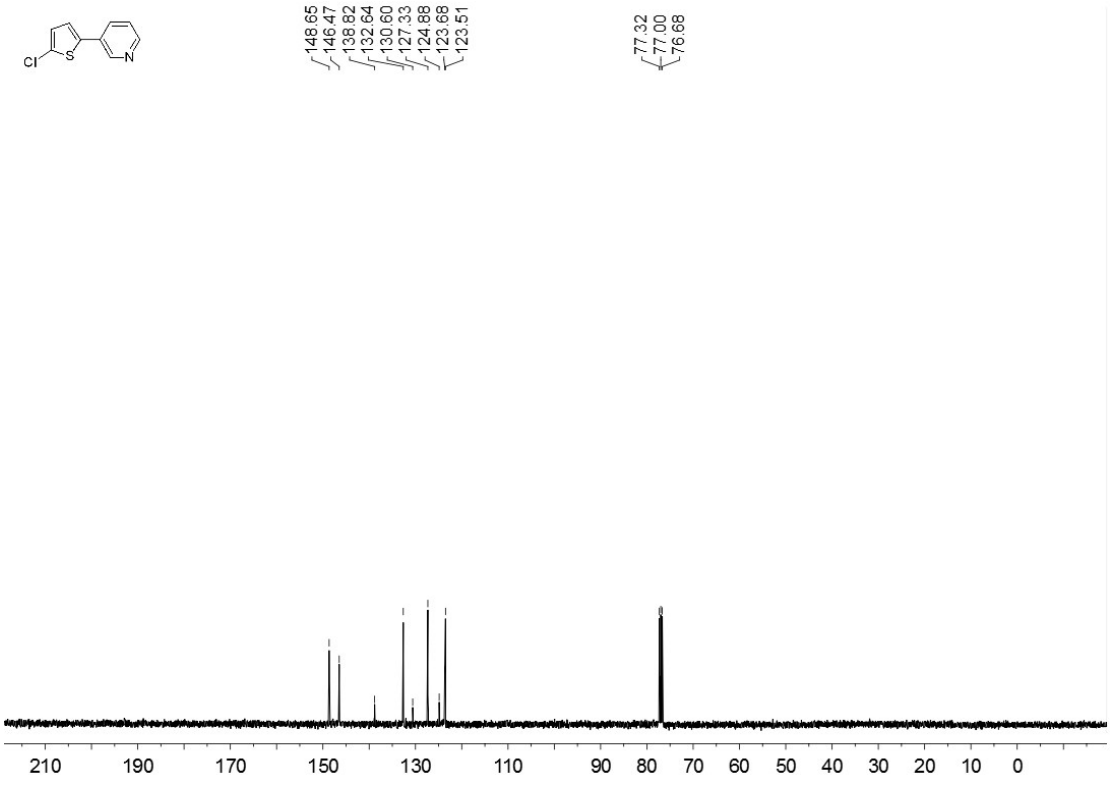
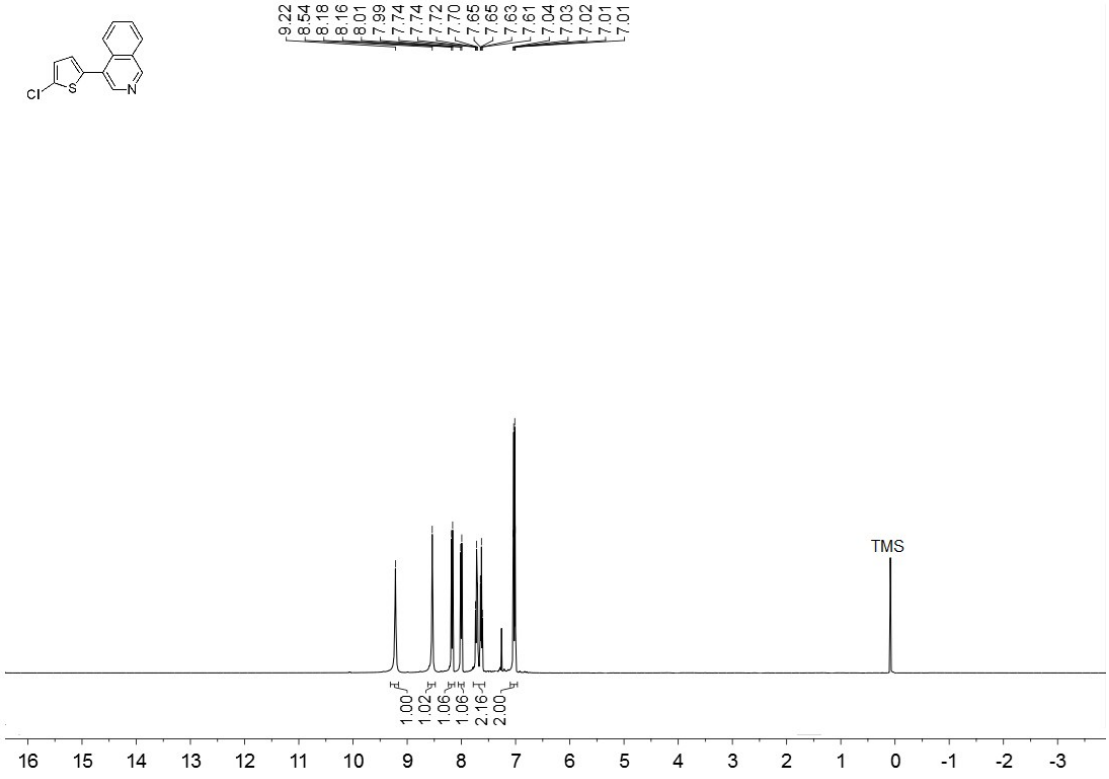


Figure **S43**. The NMR spectrums of 4-(5-chlorothiophen-2-yl)isoquinoline (**20b**)



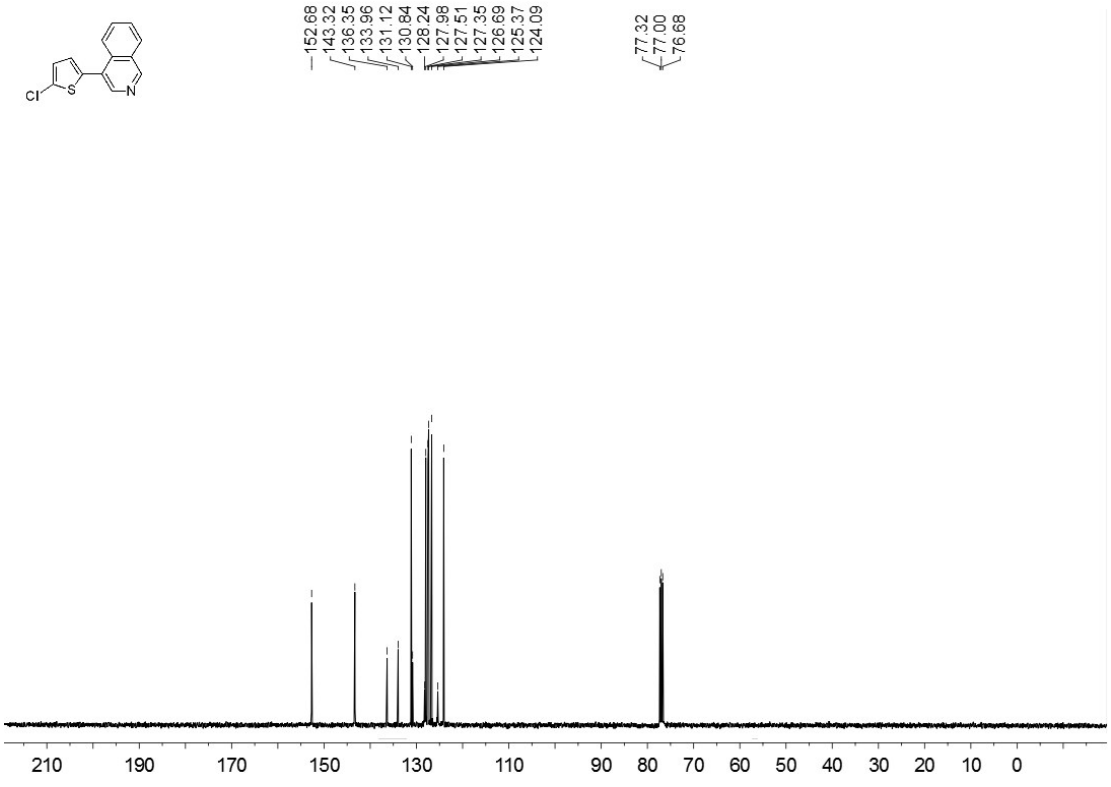
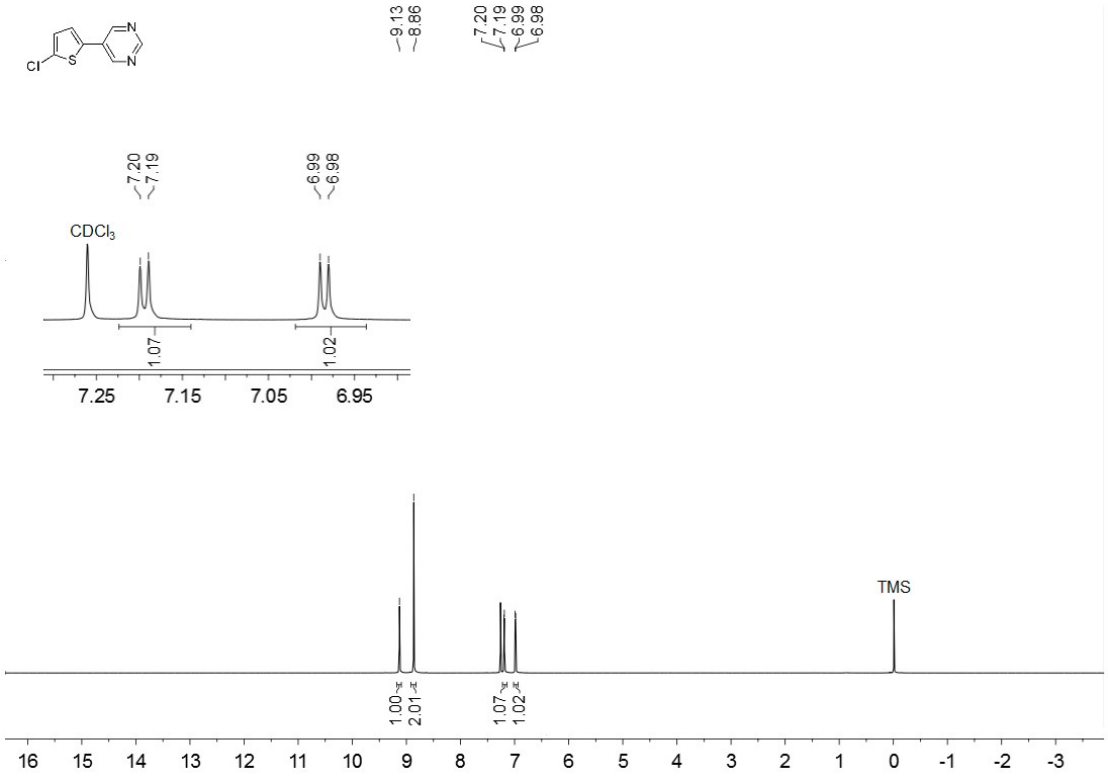


Figure **S44**. The NMR spectrums of 5-(5-chlorothiophen-2-yl)pyrimidine (**20c**)



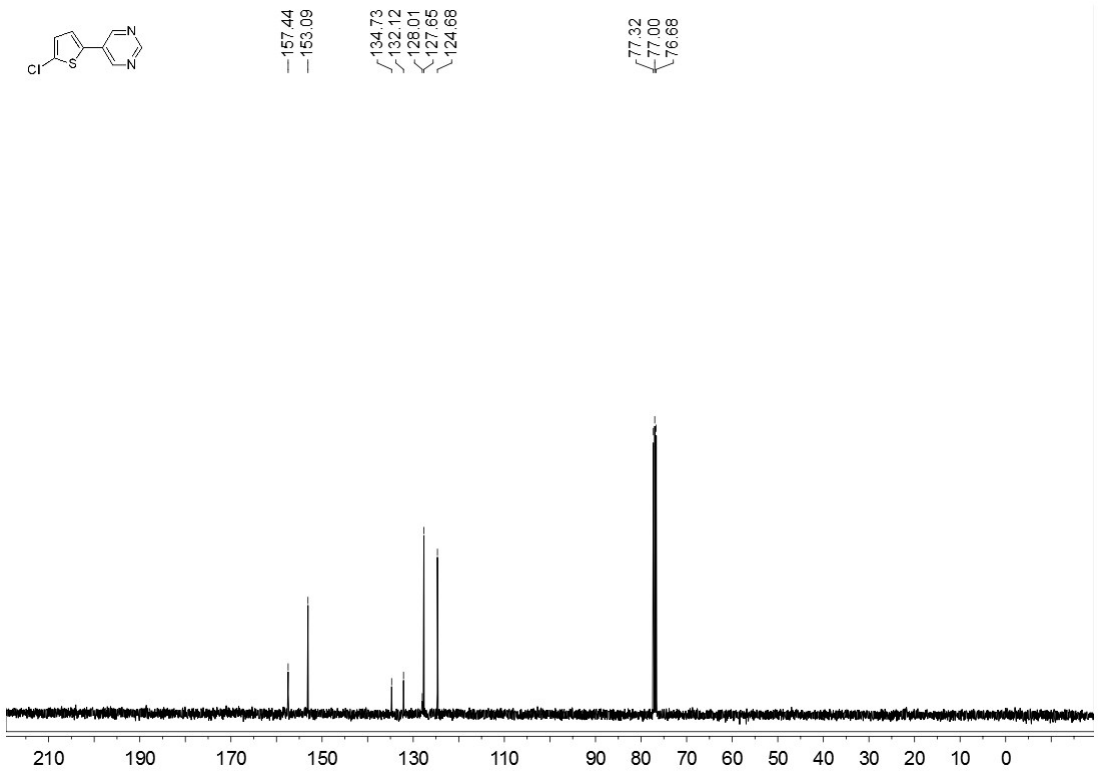
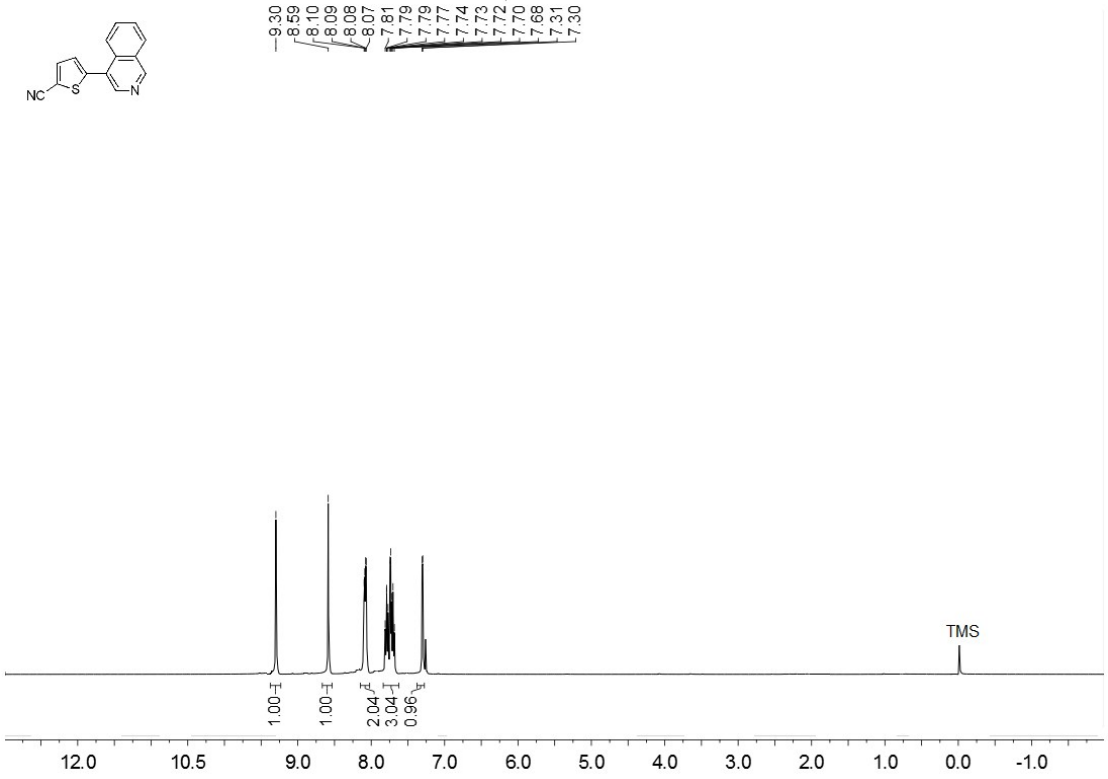


Figure **S45**. The NMR spectrums of 4-(5-isocyanothiophen-2-yl)isoquinoline (**21b**)



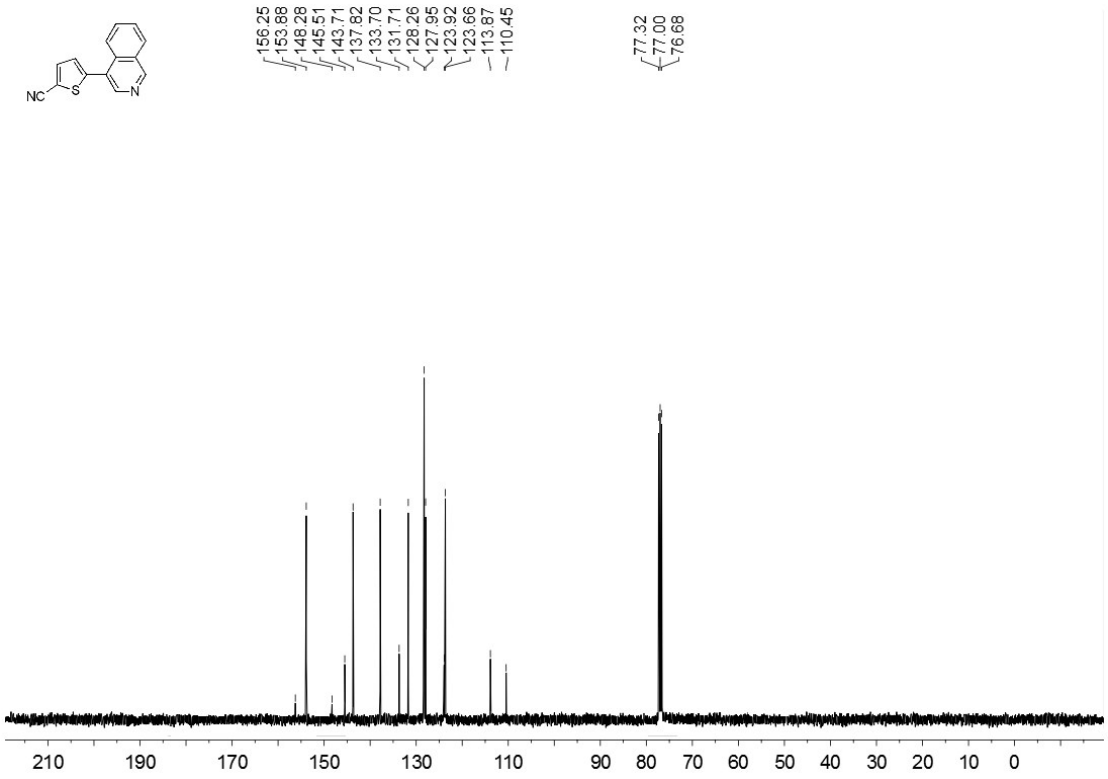
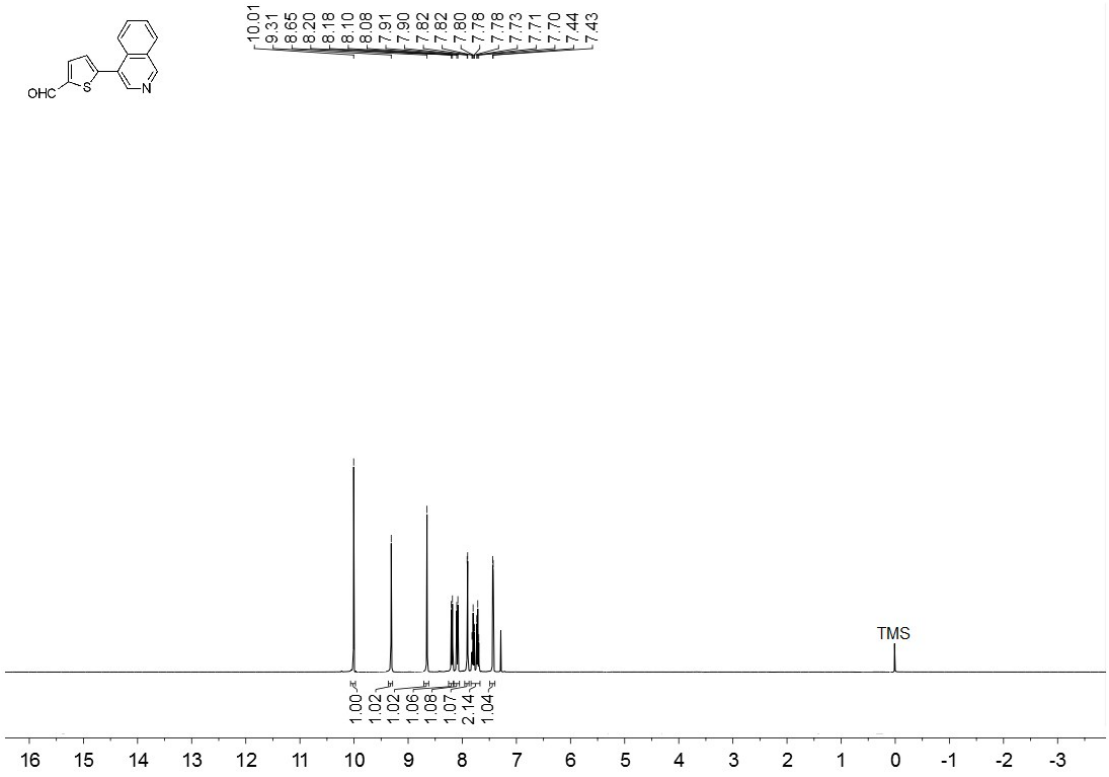


Figure **S46**. The NMR spectrums of 5-(isoquinolin-4-yl)thiophene-2-carbaldehyde (**22b**)



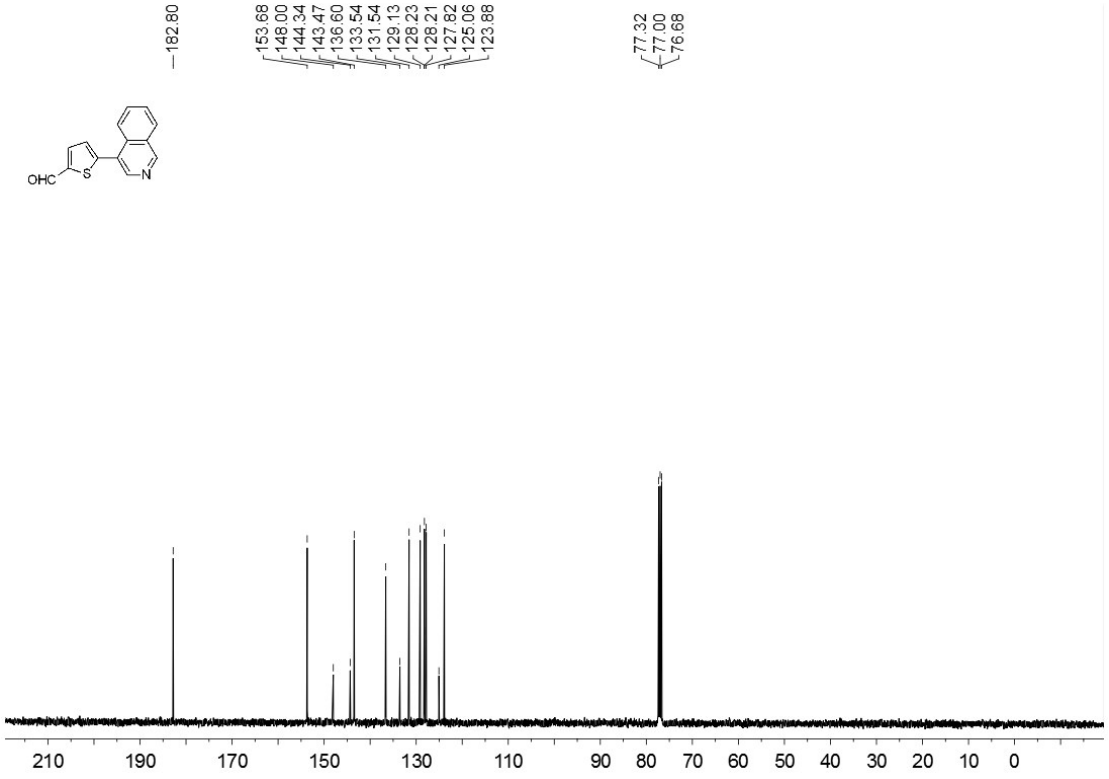


Figure **S47**. The NMR spectrums of 2-phenyl-3-(pyridin-3-yl)imidazo[1,2-a]pyridine (**23a**)

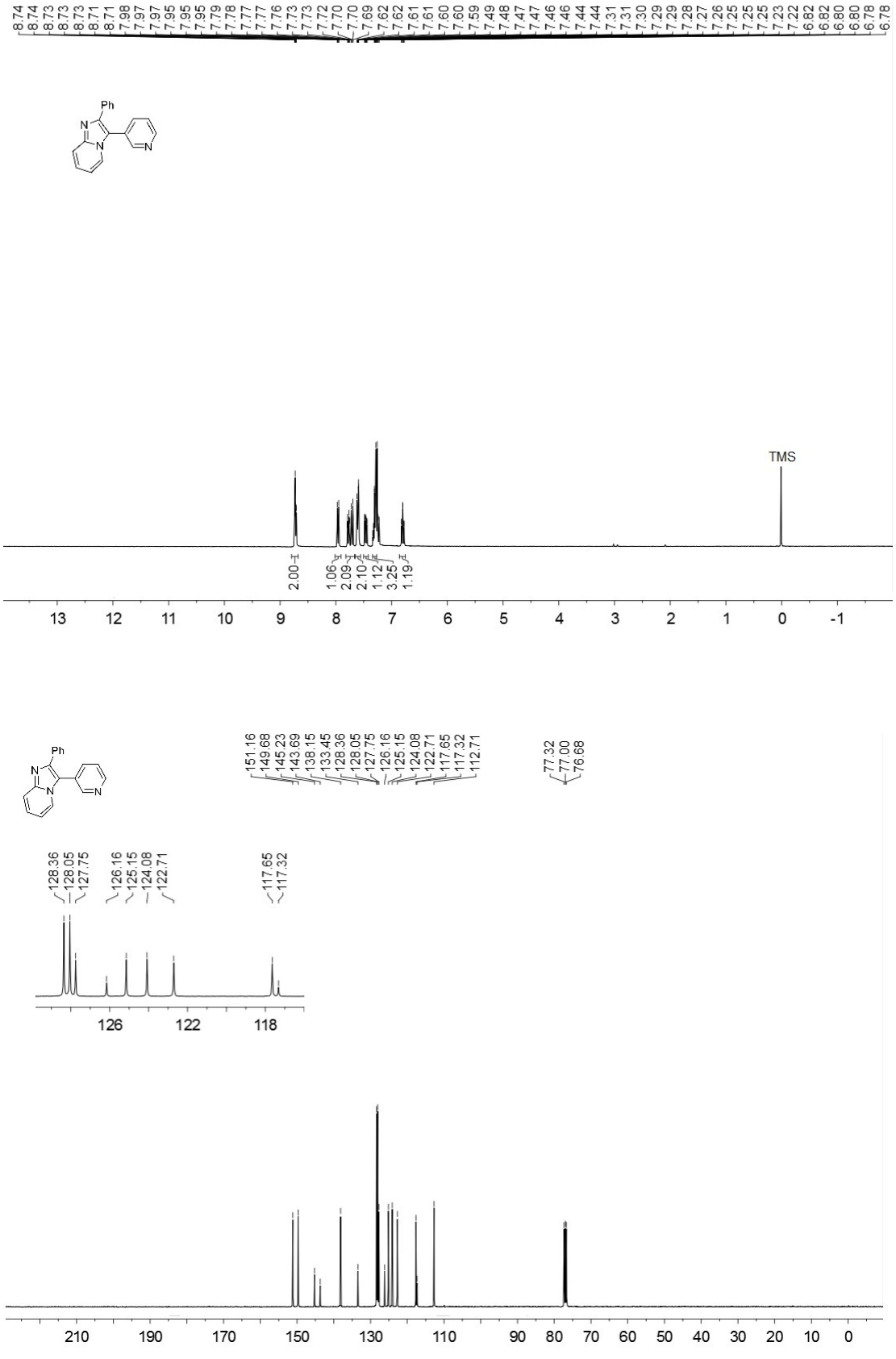


Figure **S48**. The NMR spectrums of 2-phenyl-3-(pyrimidin-5-yl)imidazo[1,2-a]pyridine (**23c**)

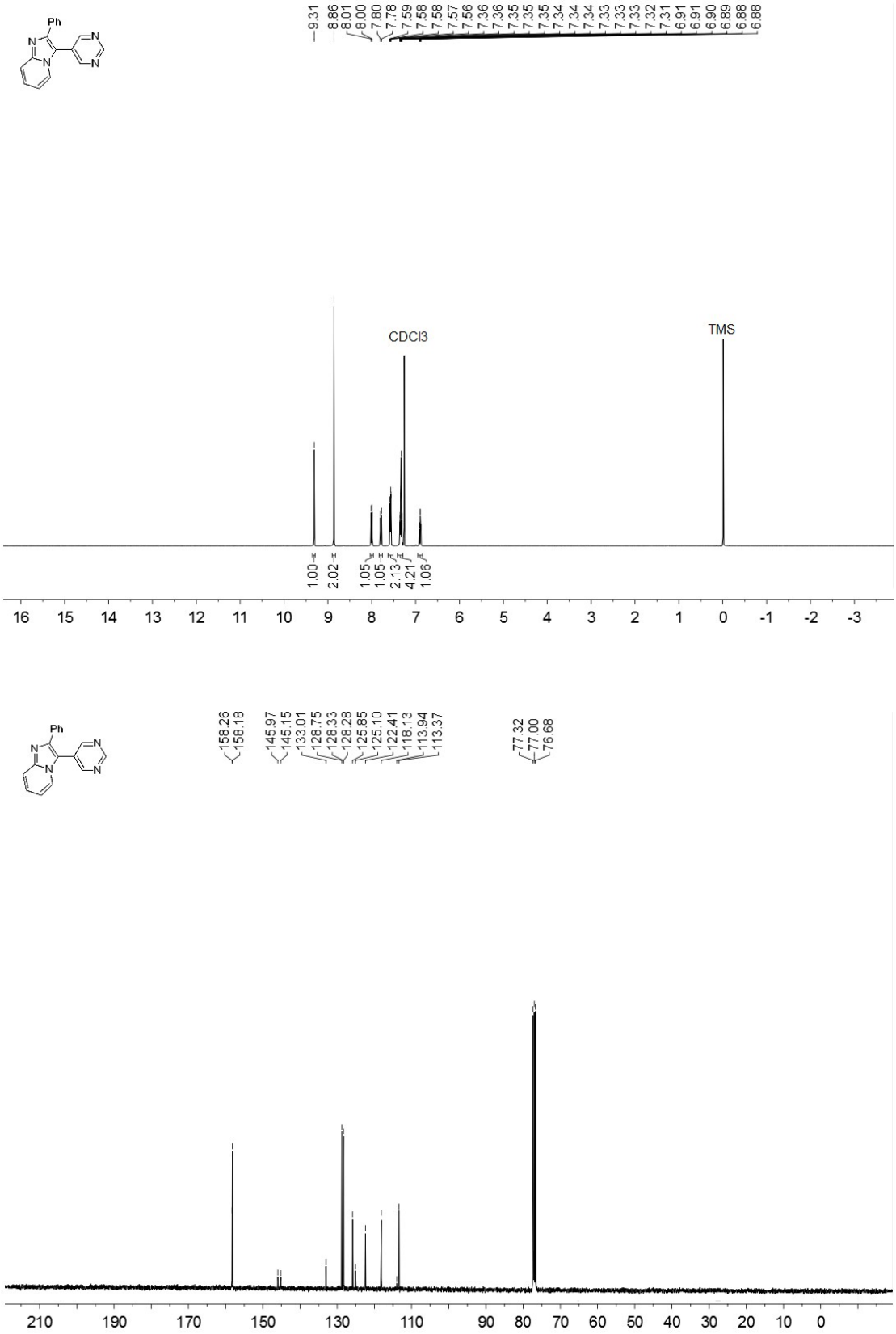
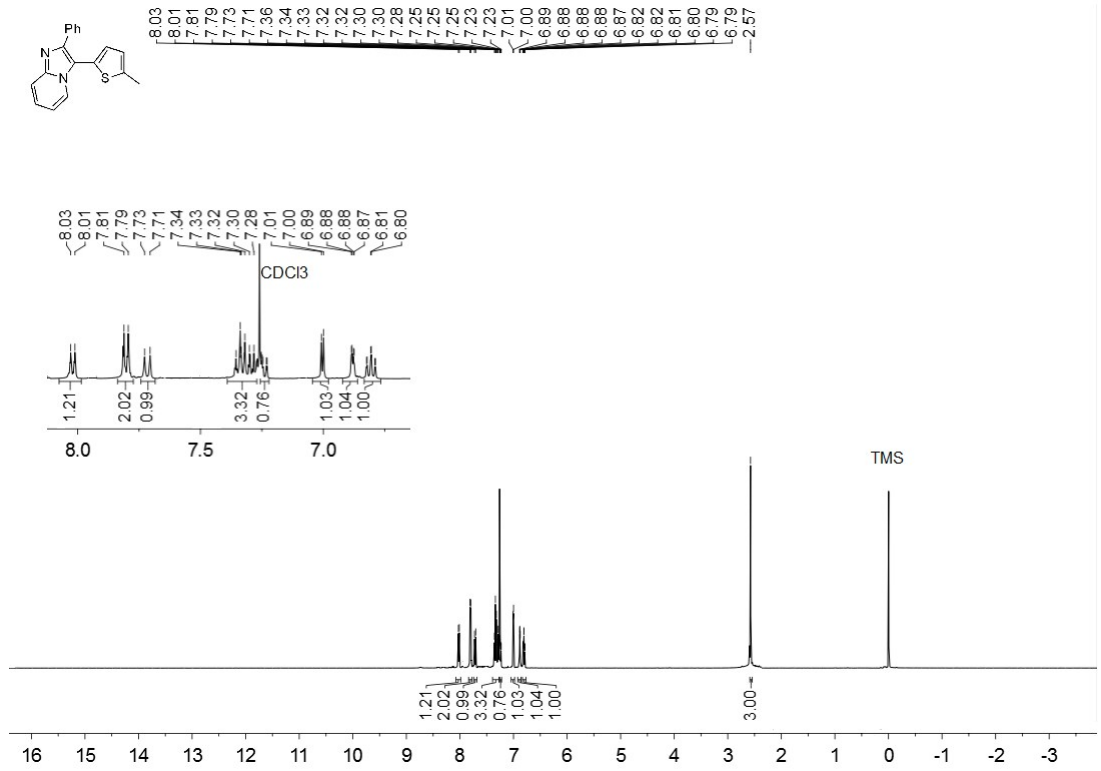


Figure **S49**. The NMR spectrums of 3-(5-methylthiophen-2-yl)-2-phenylimidazo[1,2-a]pyridine (**23d**)



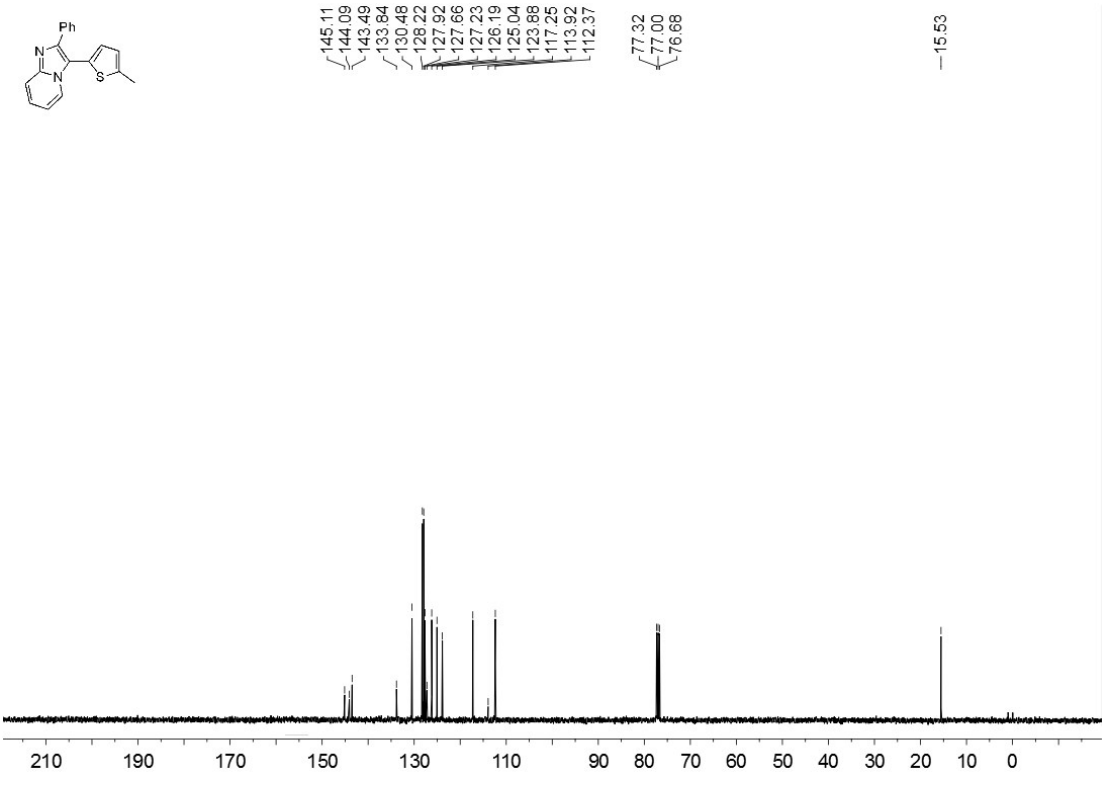


Figure **S50**. The NMR spectrums of 2-methyl-4-phenyl-5-(pyridin-3-yl)thiazole (**24a**)

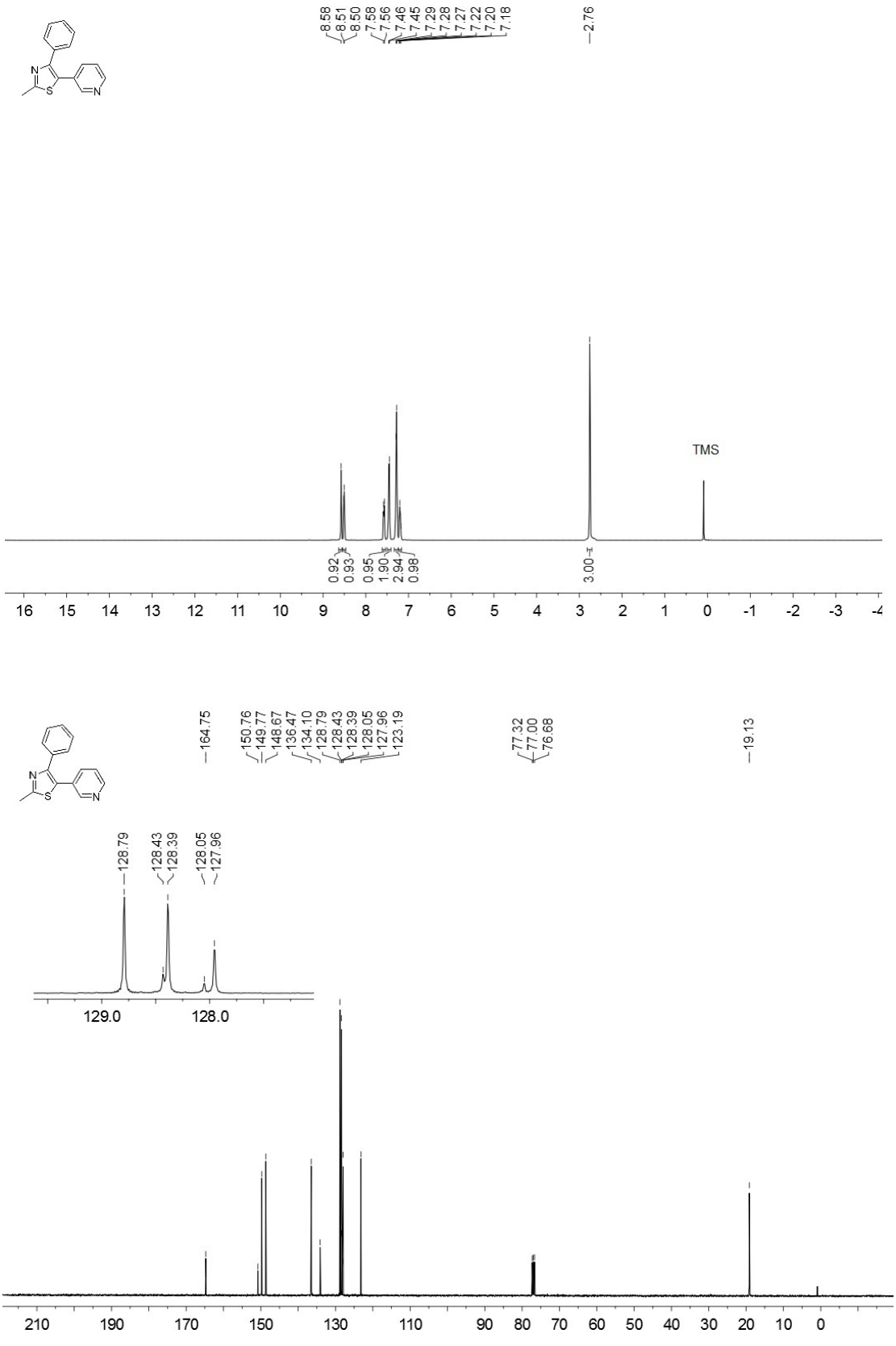


Figure **S51**. The NMR spectrums of 2,4-dimethyl-5-(pyridin-3-yl)thiazole (**25a**)

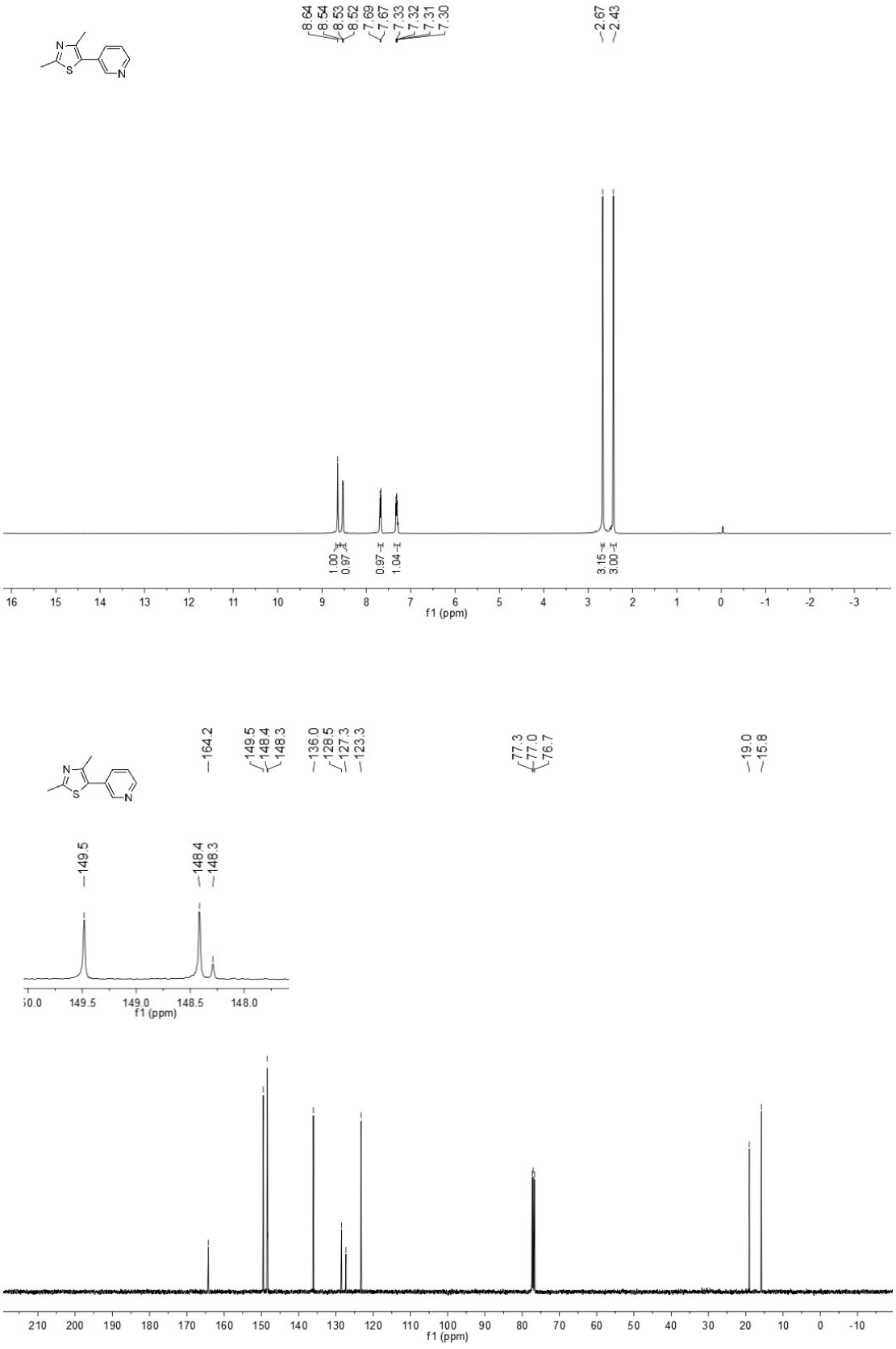


Figure **S52**. The NMR spectrums of 5-(isoquinolin-4-yl)-2,4-dimethylthiazole (**25b**)

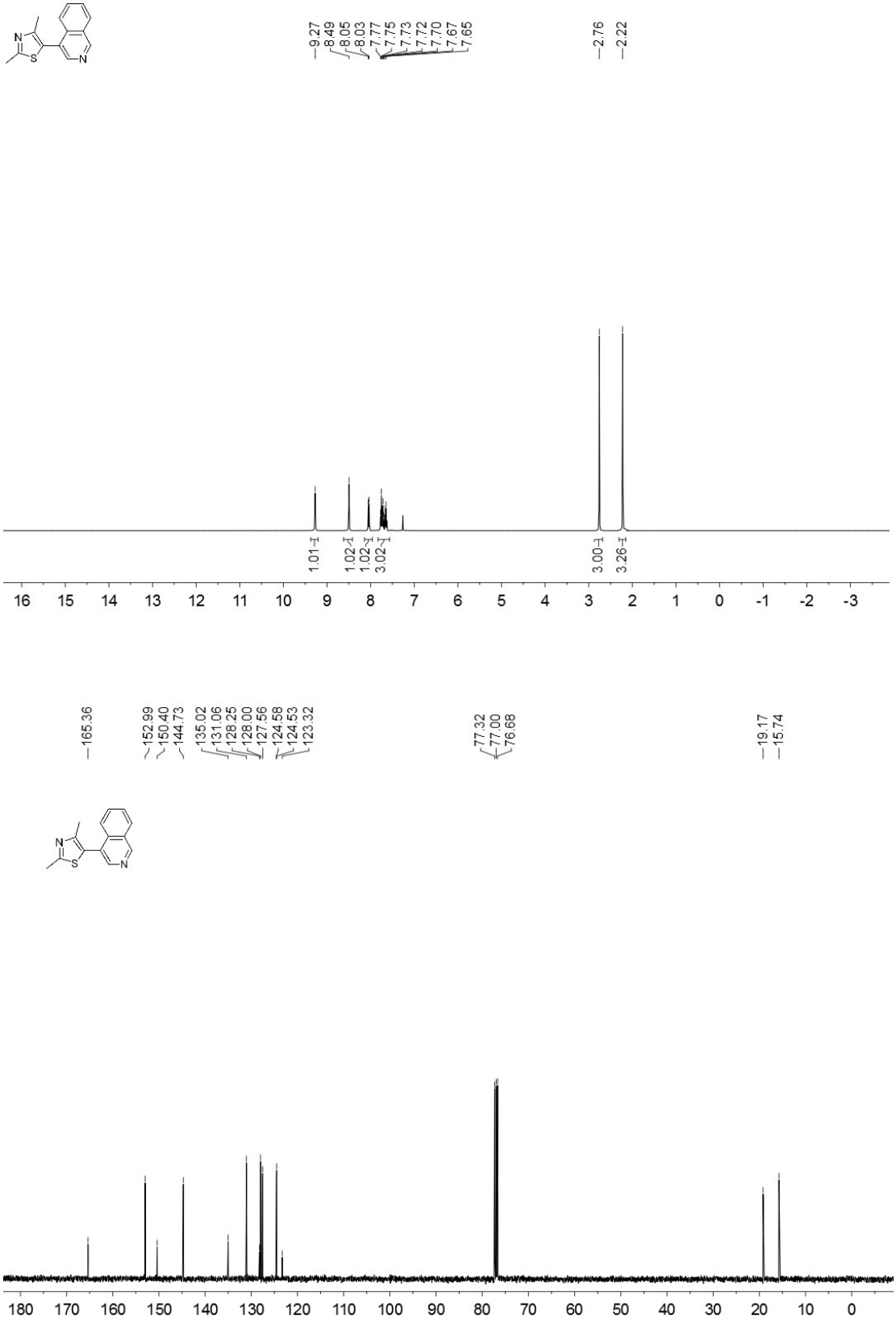
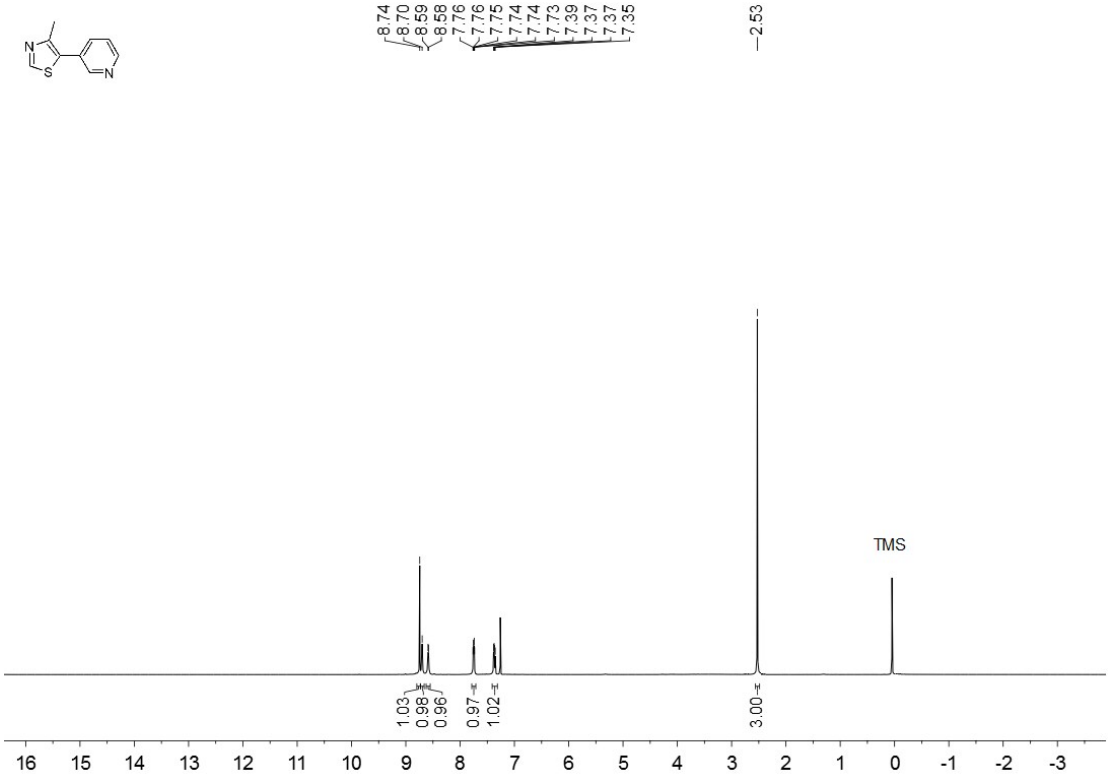


Figure **S53**. The NMR spectrums of 4-methyl-5-(pyridin-3-yl)thiazole (**26a**)



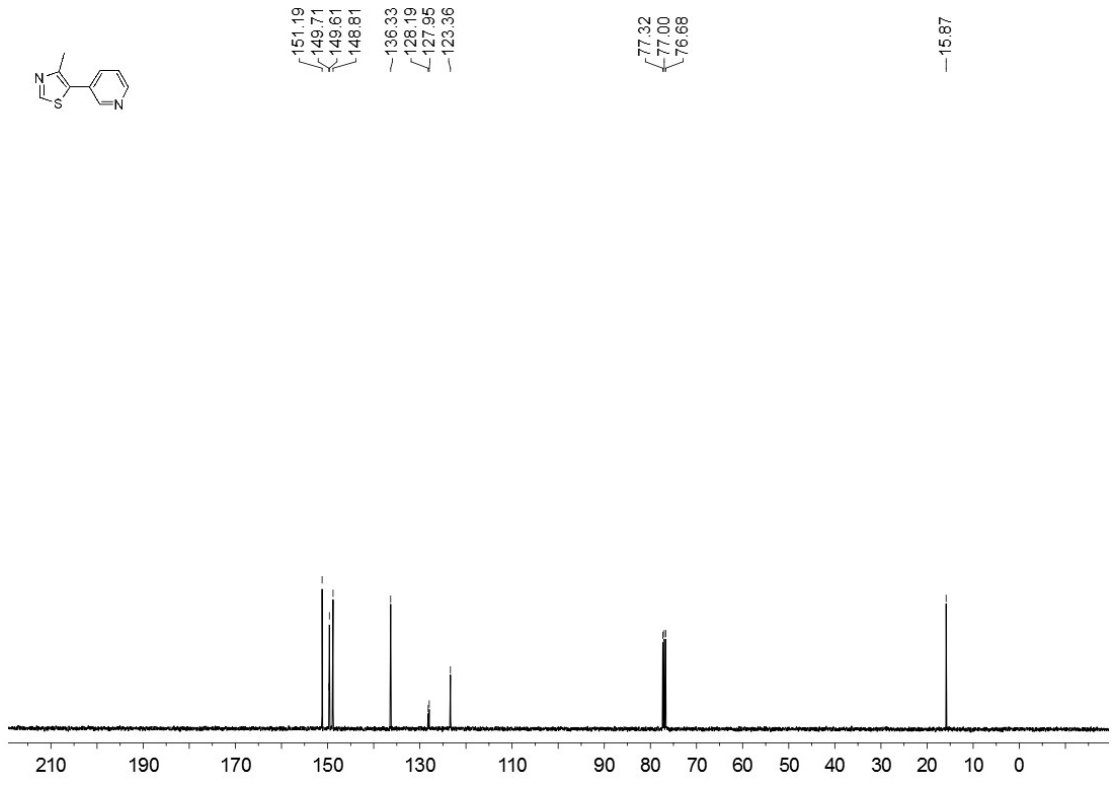


Figure **S54**. The NMR spectrums of 4-methyl-5-(pyrimidin-5-yl)thiazole (**26c**)

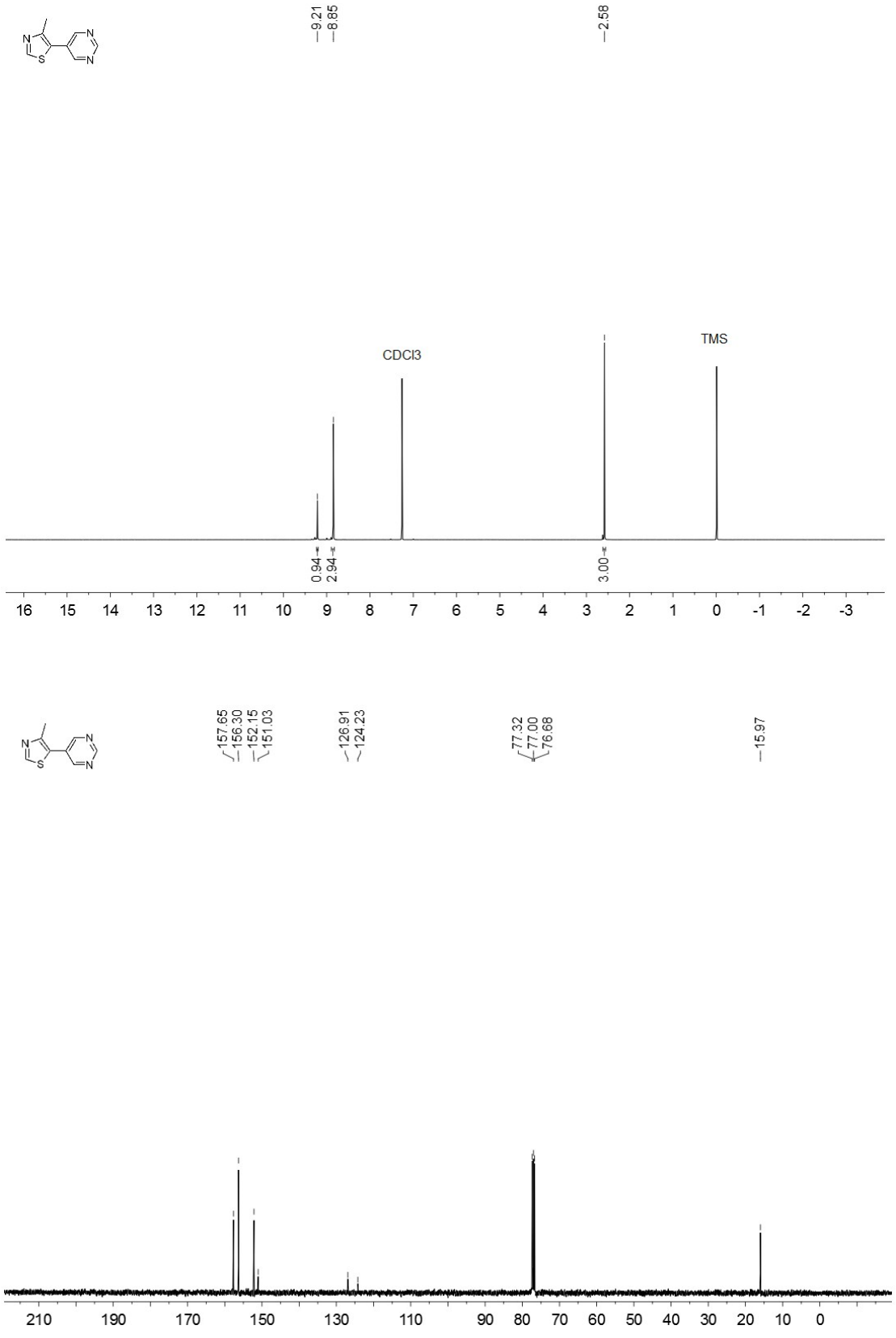


Figure **S55**. The NMR spectrums of 4-methyl-5-(5-methylthiophen-2-yl)thiazole (**26d**)

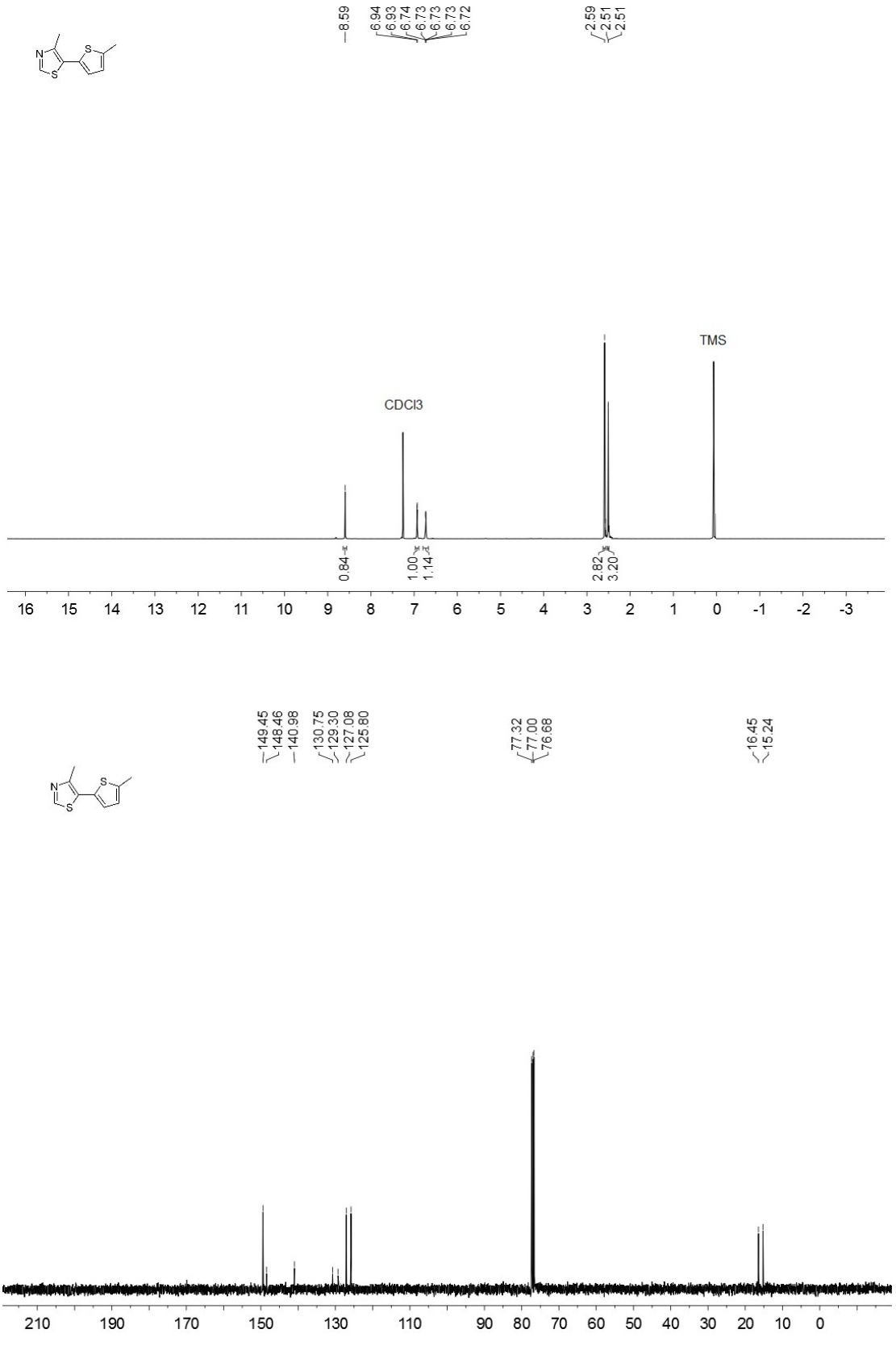


Figure **S56**. The NMR spectrums of 3-(1-methyl-1H-imidazol-5-yl)pyridine (**27a**)

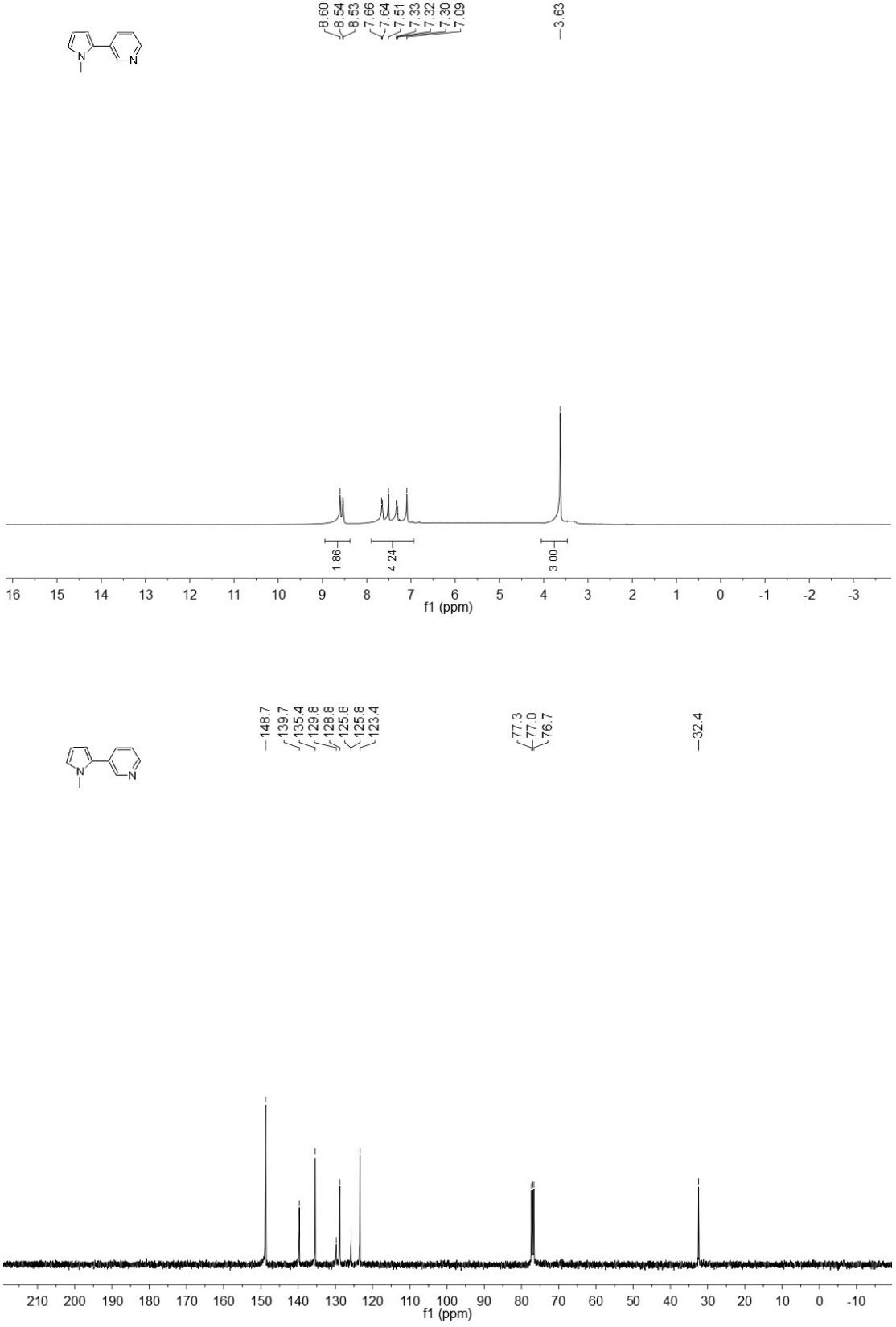
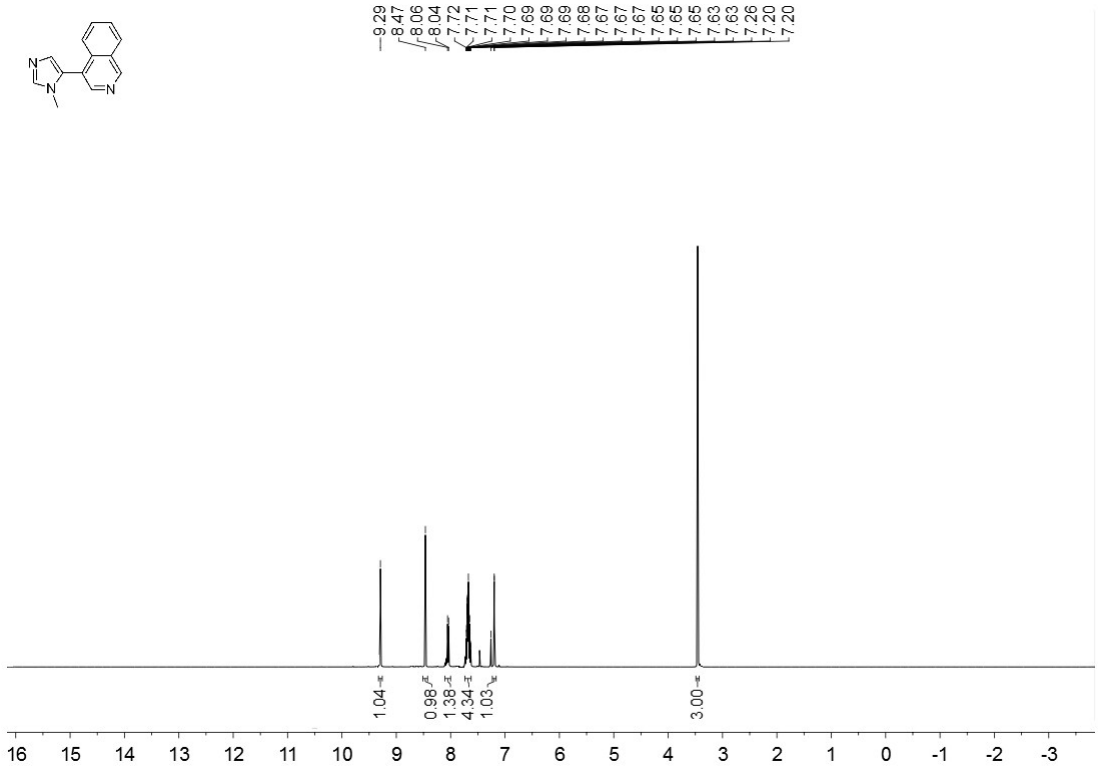


Figure **S57**. The NMR spectrums of 4-(1-methyl-1H-imidazol-5-yl)isoquinoline (**27b**)



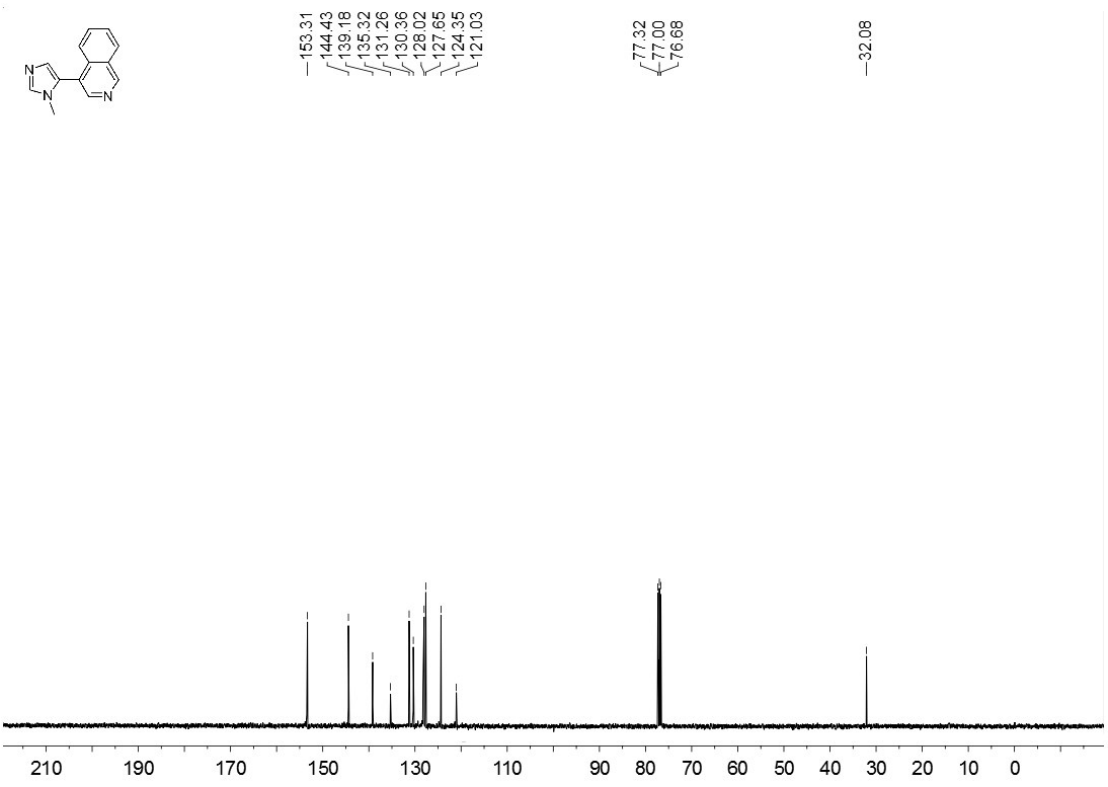
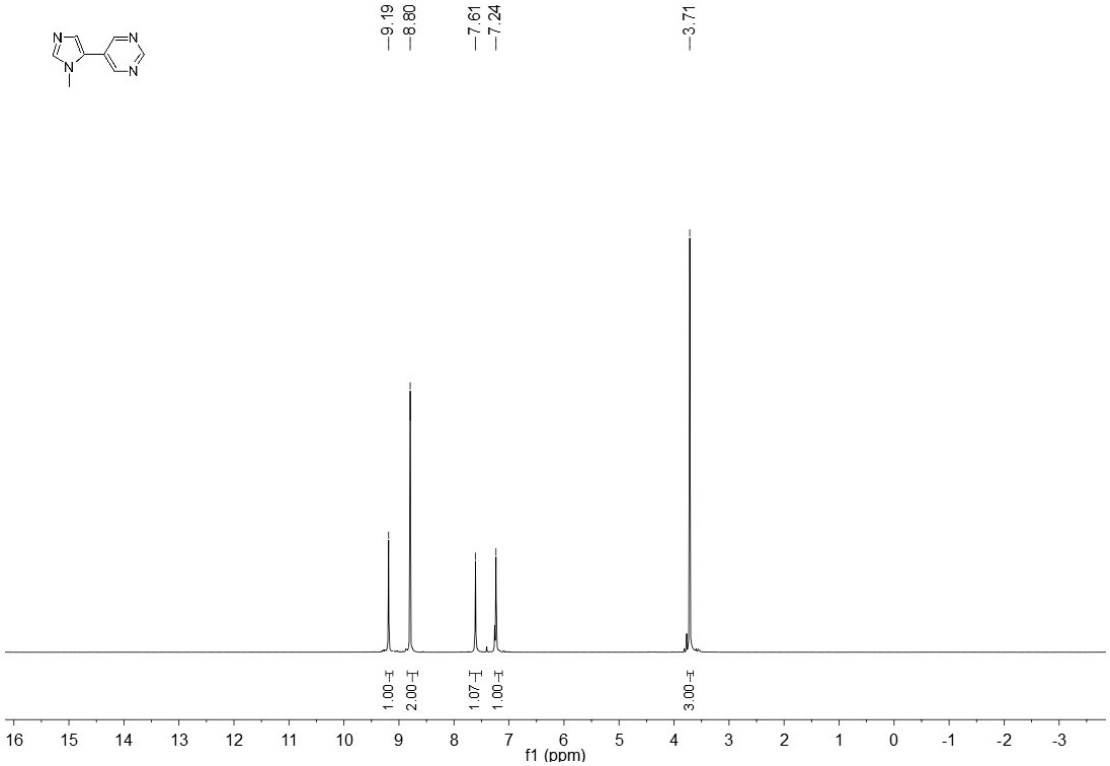


Figure **S58**. The NMR spectrums of 5-(1-methyl-1H-imidazol-5-yl)pyrimidine (**27c**)



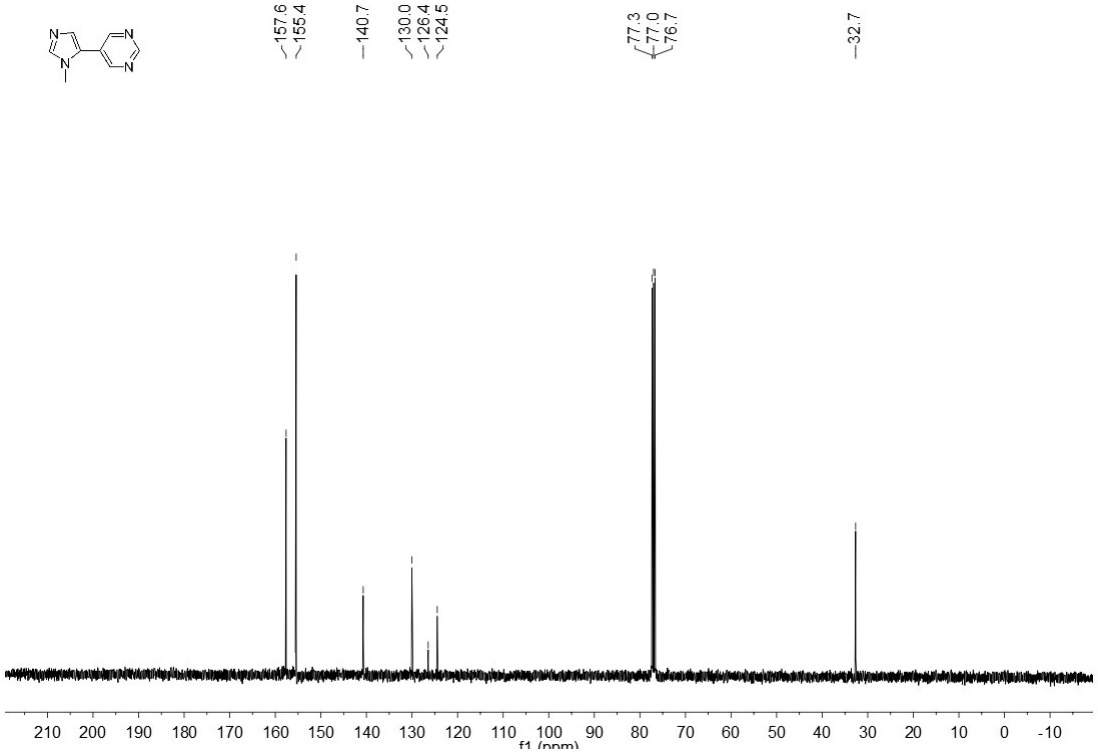
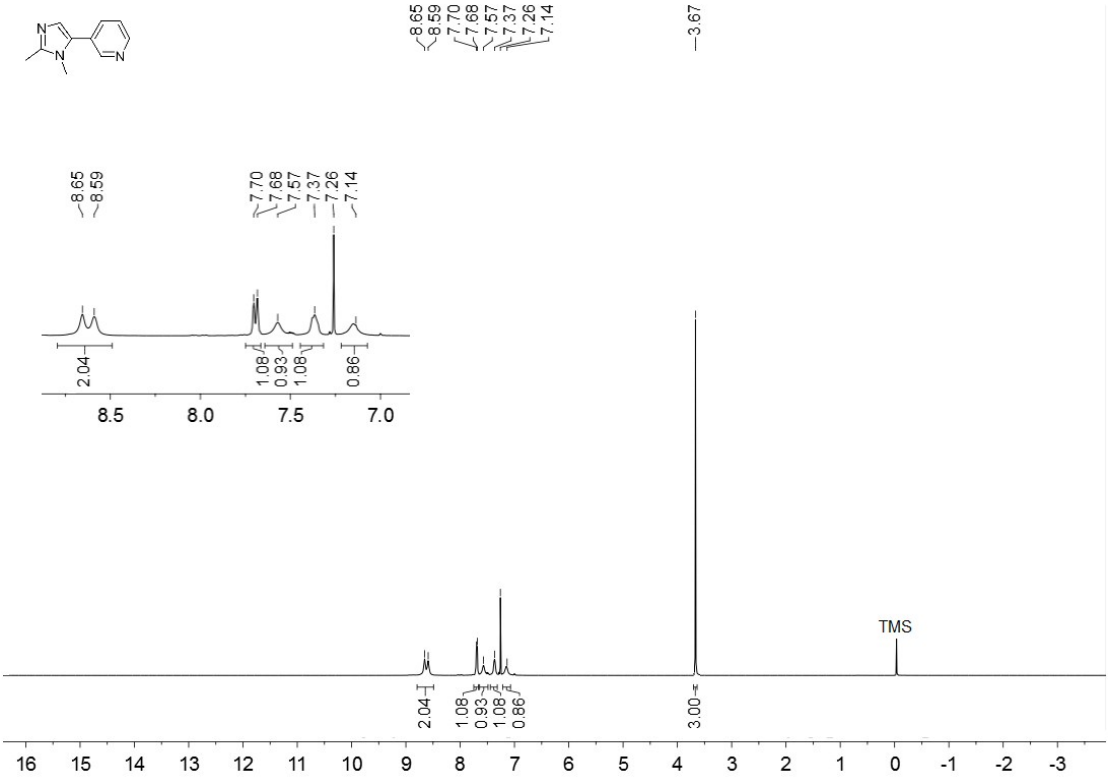


Figure **S59**. The NMR spectrums of 3-(1,2-dimethyl-1H-imidazol-5-yl)pyridine (**28a**)



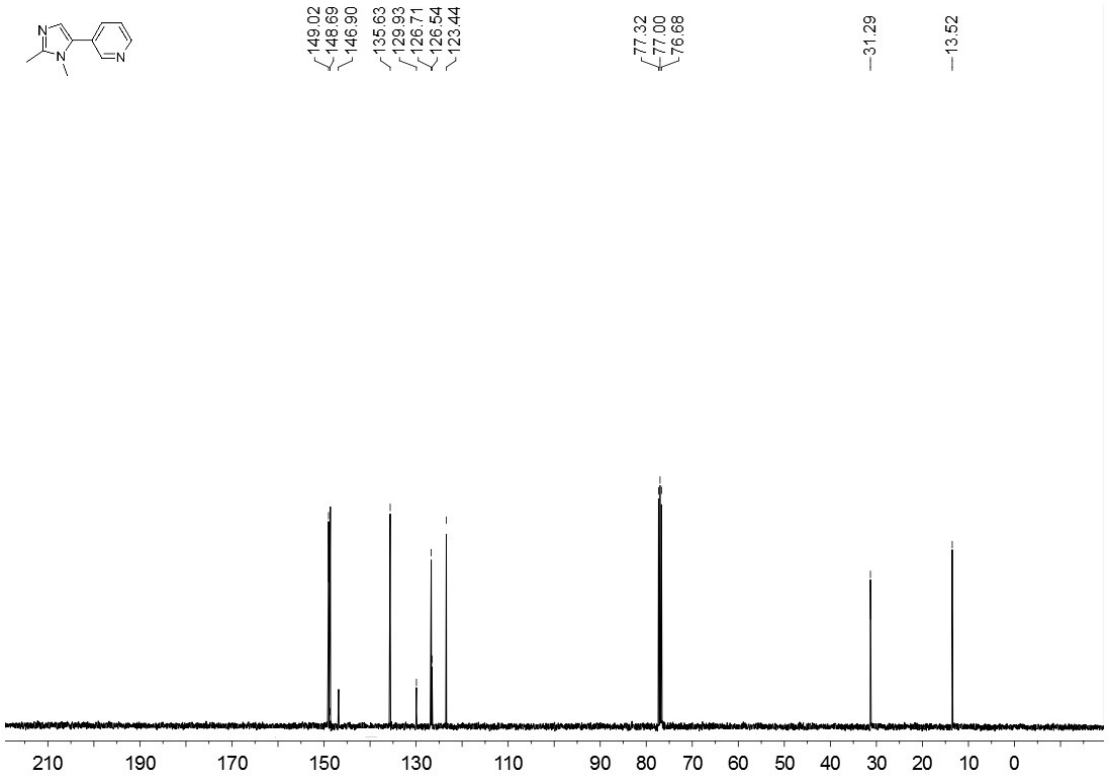
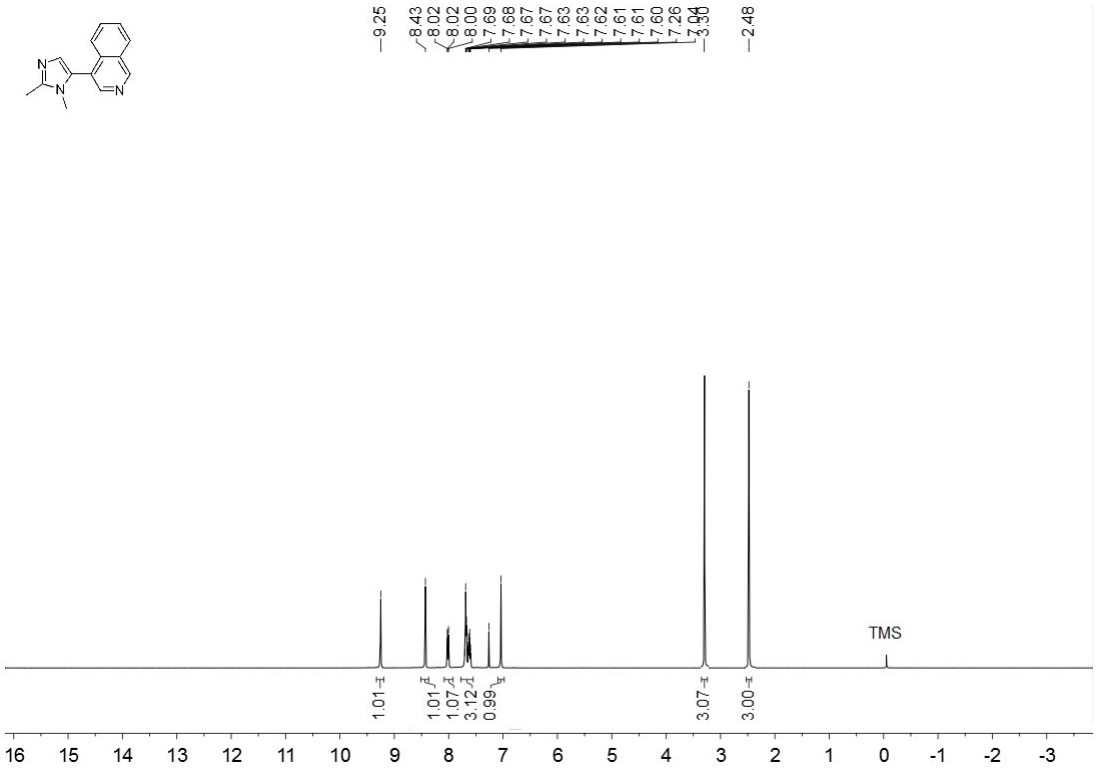


Figure **S60**. The NMR spectrums of 4-(1, 2-dimethyl-1H-imidazol-5-yl)isoquinoline (**28b**)



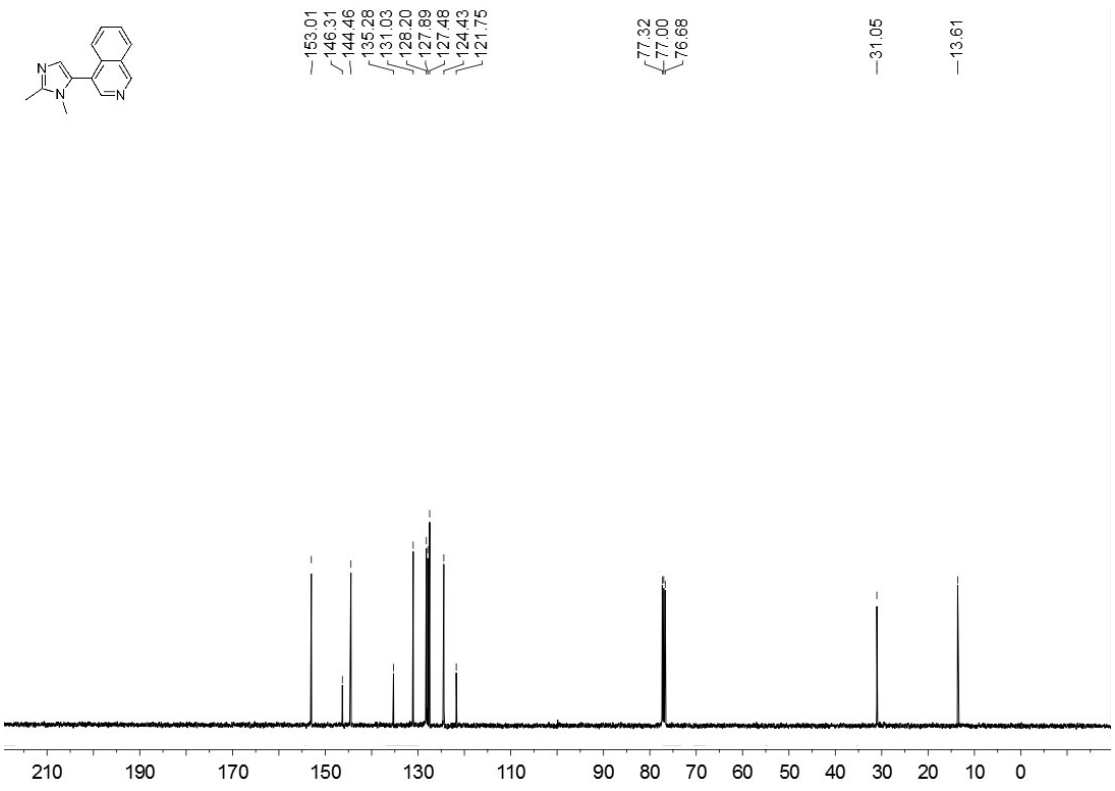
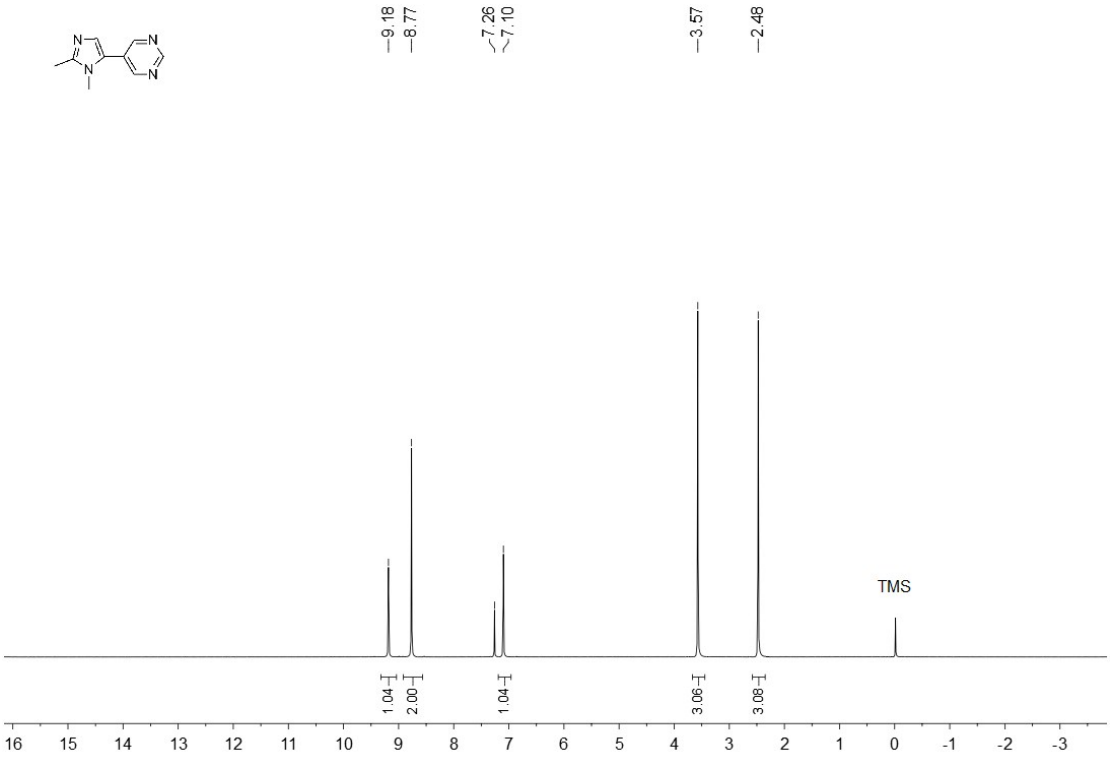


Figure **S61**. The NMR spectrums of 5-(1, 2-dimethyl-1H-imidazol-5-yl)pyrimidine (**28c**)



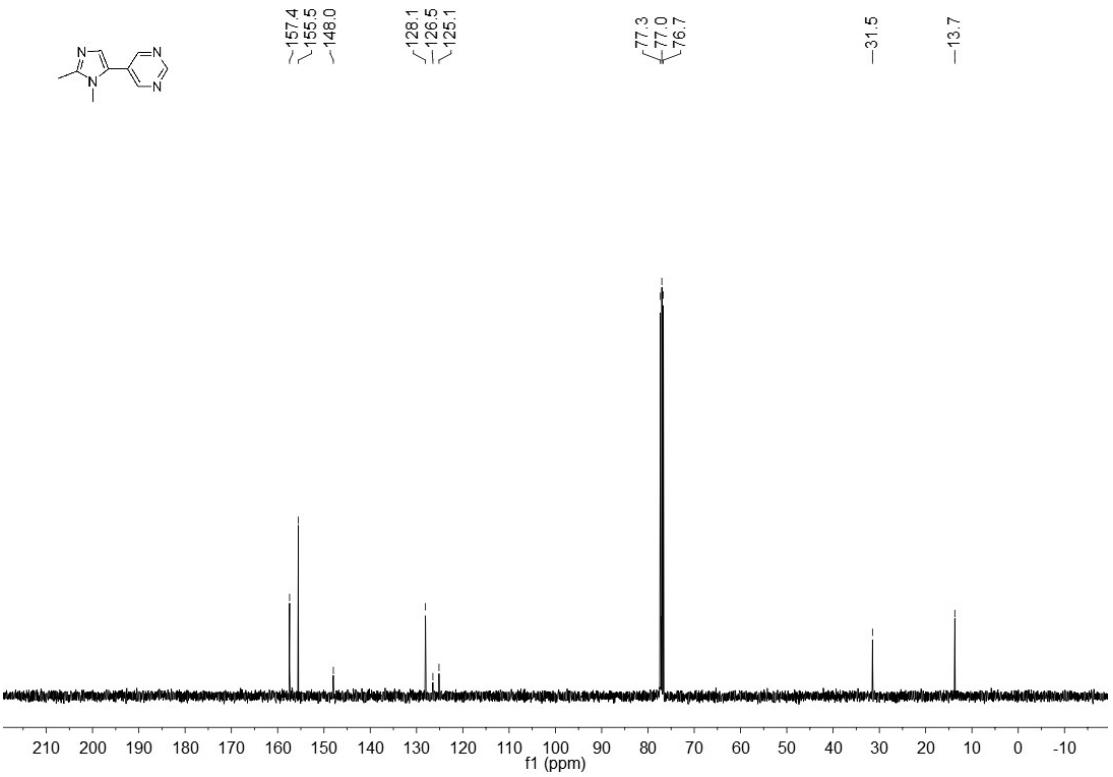
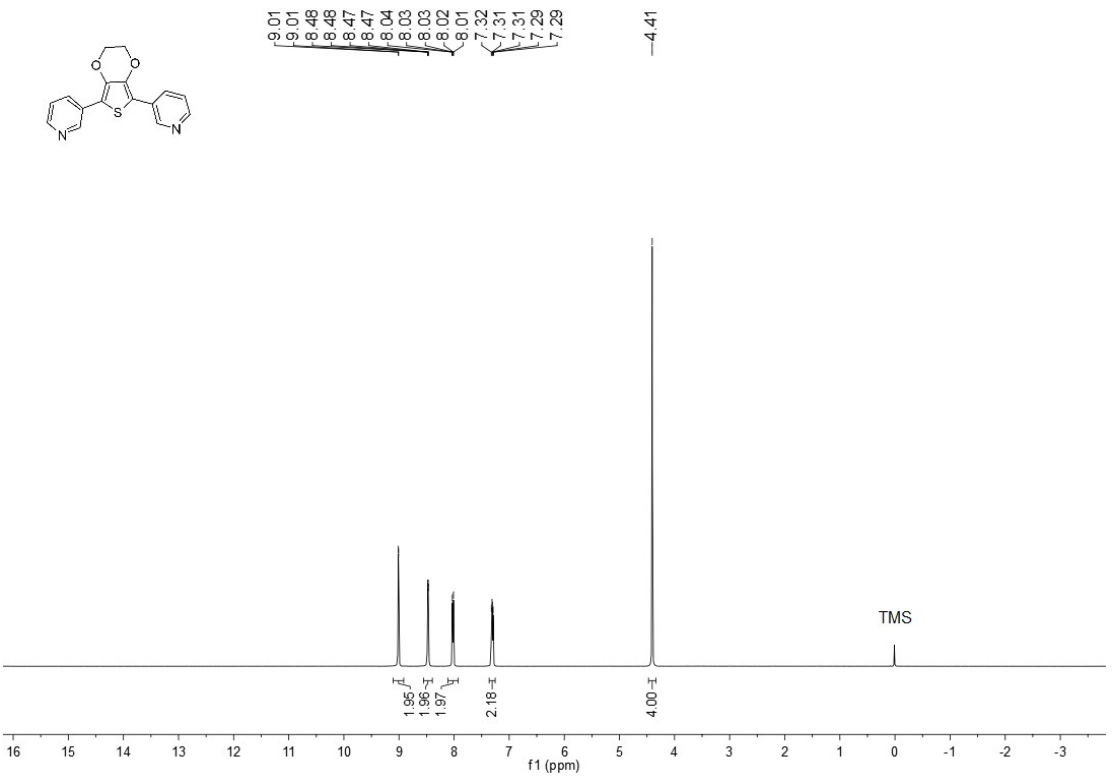


Figure **S62**. The NMR spectrums of 5,7-di(pyridin-3-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (**29a**)



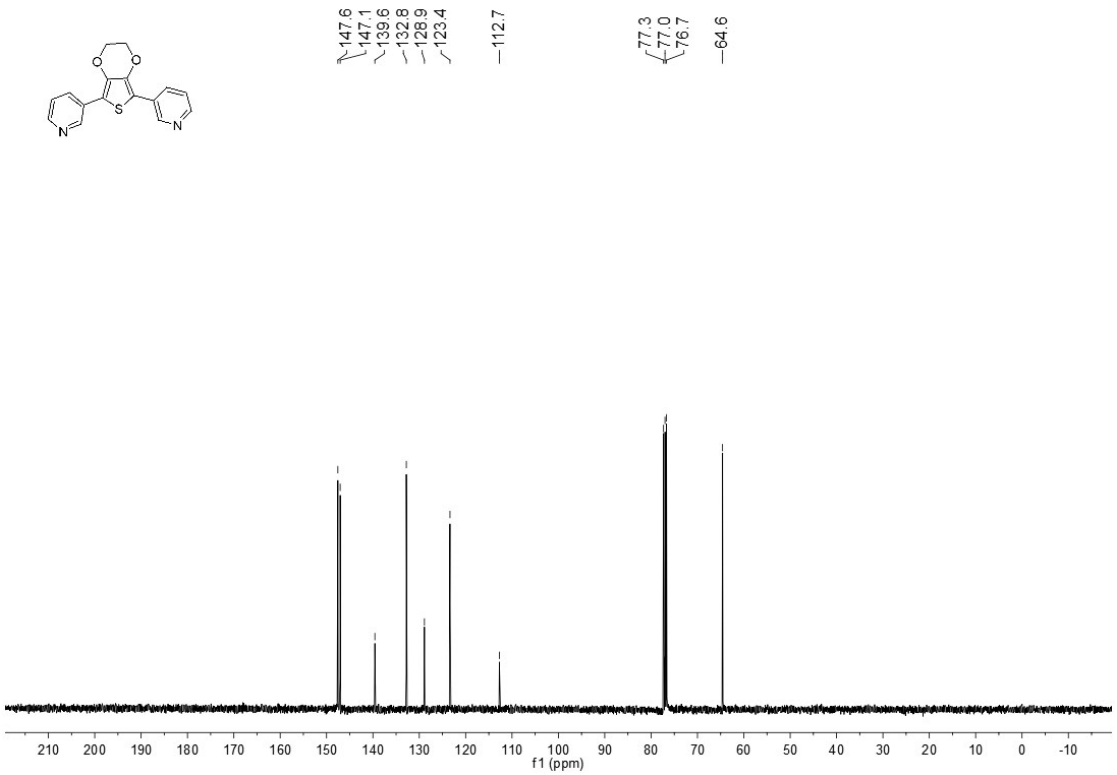
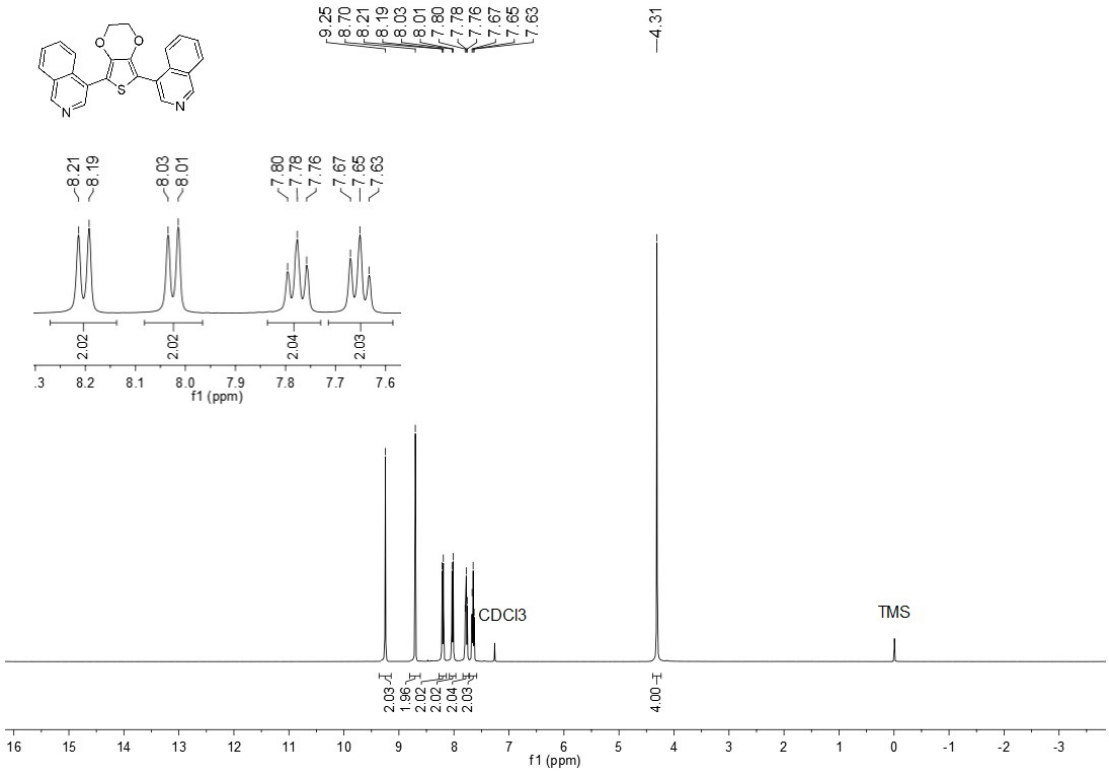


Figure **S63**. The NMR spectrums of 5,7-di(isoquinolin-4-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (**25b**)



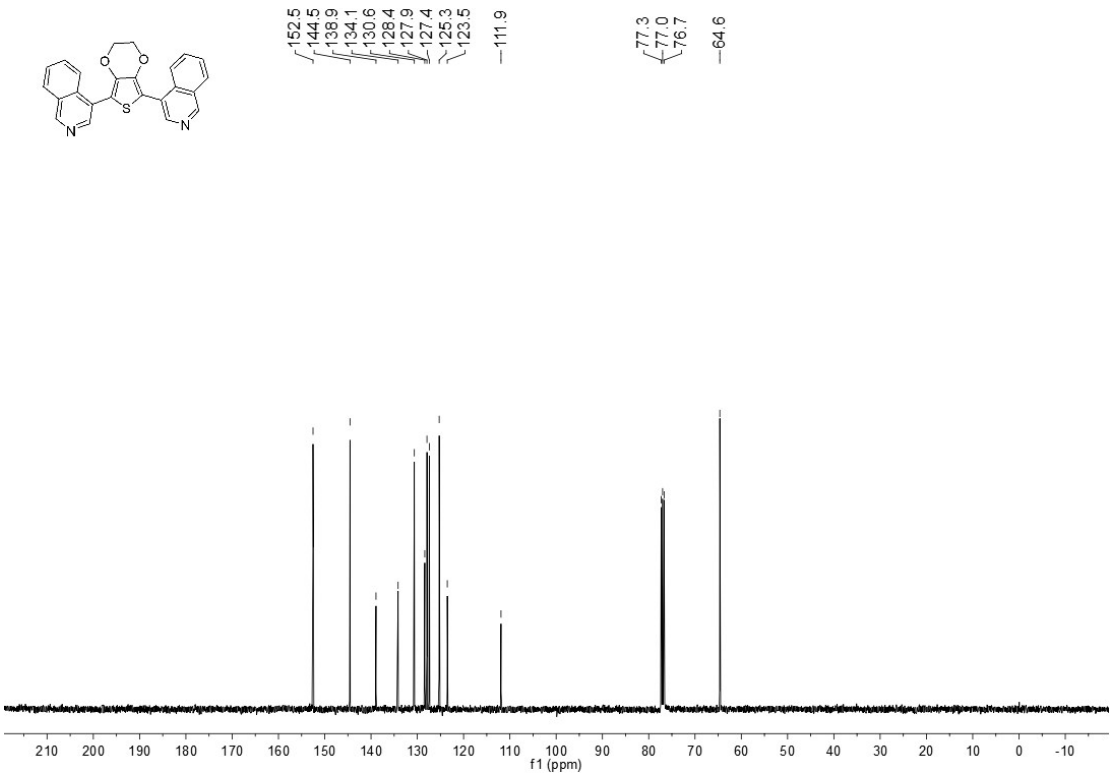
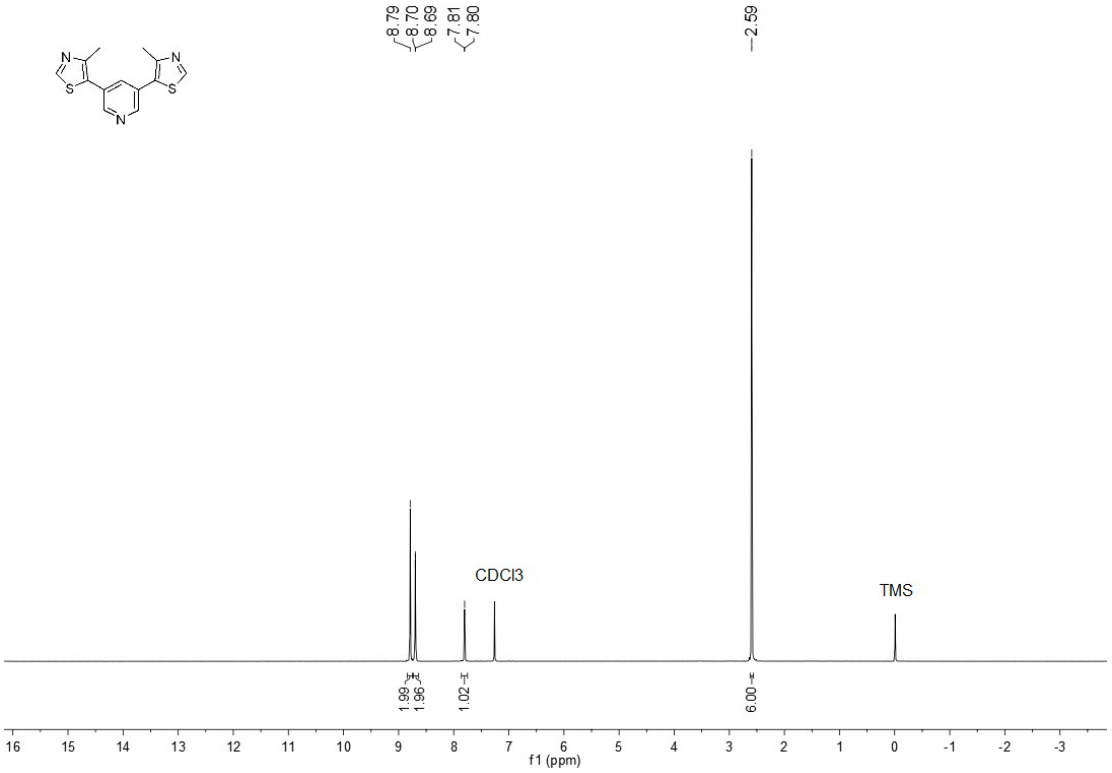


Figure **S64**. The NMR spectrums of 3,5-bis(4-methylthiazol-5-yl)pyridine (**30**)



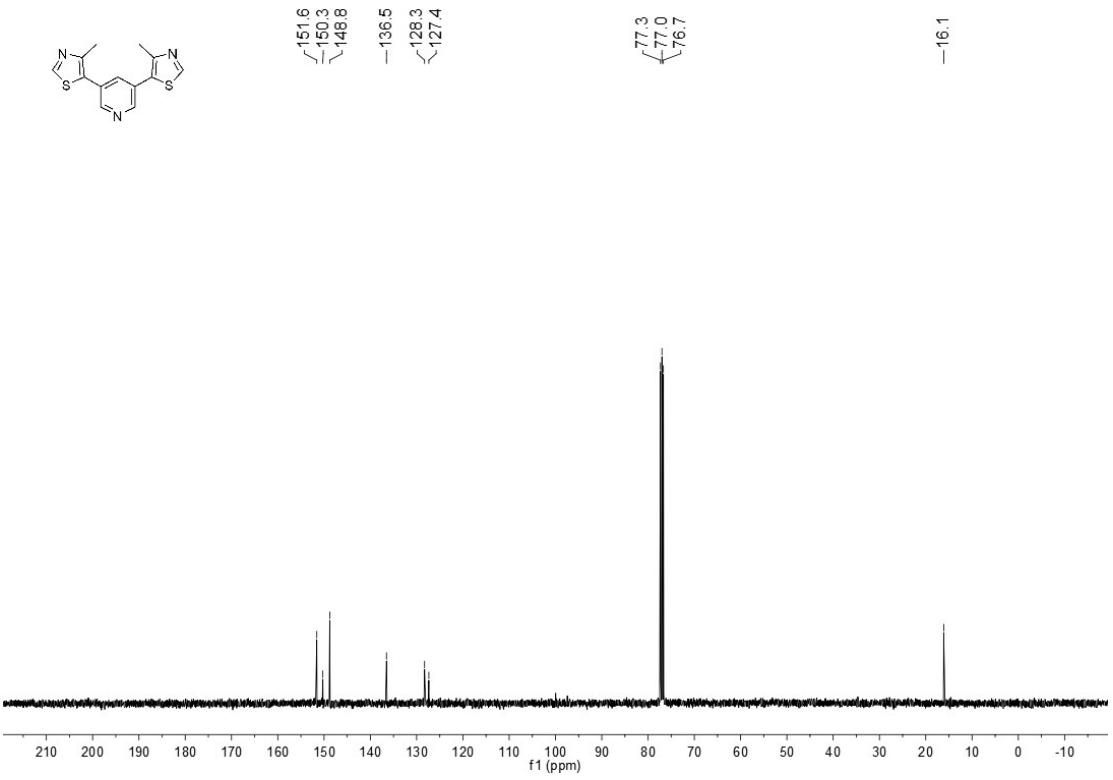


Figure **S65**. The NMR spectrums of 3,5-bis(1-methyl-1H-imidazol-5-yl)pyridine (**31**)