Supporting Information

for

Fast Regio-selective Sulfonylation of Pyridines/Quinolines *N*-Oxide Induced by Iodine

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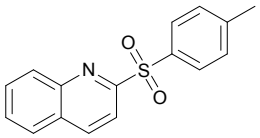
General information

All product mixtures were analyzed by thin layer chromatography glass-backed silica TLC plates with a fluorescent indicator from Branch of Qingdao Haiyang Chemical CO. LTD. UV-active compounds were detected with a UV lamp (λ = 254 nm). For flash column chromatography, silica gel (200-300 mesh) was used as stationary phase. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 in deuterated chloroform at 25 °C with residue solvent peaks as internal standards. Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (J) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), and m (multiplet). High resolution mass spectra (HRMS) were obtained using GCT-TOF instrument with the ESI technique. IR spectra were recorded as KBr disks on an FT-IR spectrometer. Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.

All other reagents were purchased from commercial companies and used without further purification.

Data

2-Tosyl quinoline(3aa)[2]



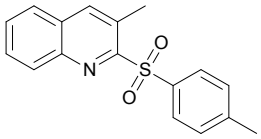
Follow the general procedure A, **3aa** was obtained as white solid 124.5 mg (88%) with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 7.33 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 8.18 (t, J = 8.0 Hz, 2H), 8.36 (d, J = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 117.6, 127.6, 128.8, 129.09, 129.13, 129.7, 130.4, 130.9, 136.1, 138.6, 144.8, 147.4, 158.3 (ppm).

HRMS (ESI): $[C_{16}H_{13}NO_2S + H]^+$ calcd. for 284.0667; found 284.0670.

3-Methyl-2-tosylquinoline(3ba)



Follow the general procedure A, **3ba** was obtained 106.9 mg (72%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 111 - 113 ^{o}C.

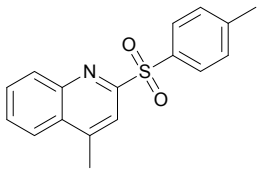
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.46 (s, 3H), 2.86 (s, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.76(d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 12.0Hz, 3H), 8.05(s, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.8, 21.7, 126.6, 128.5, 128.9, 129.1, 129.3, 129.4, 129.7, 129.9, 135.8, 139.8, 144.4, 144.7, 157.1 (ppm).

IR (in KBr): ν = 3733, 3075, 1590, 1390, 540, 513, 430 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{15}NO_2S+H]^+$ calcd. for 298.0823; found 298.0825.

4-methyl-2-tosylquinoline(3ca)[2]



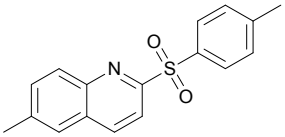
Follow the general procedure A, **3ca** was obtained 121.8 mg (82%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 2.79 (s, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 8.01 (m, 4H), 8.16 (d, *J* = 12.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.1, 21.6, 118.0, 123.7, 128.7, 128.8, 129.0, 129.7, 130.5, 131.0, 136.2, 144.6, 147.2, 147.8, 157.9 (ppm).

HRMS (ESI): $[C_{17}H_{15}NO_2S+H]^+$ calcd. for 298.0823; found 298.0827.

6-methyl-2-tosylquinoline(3da)[2]



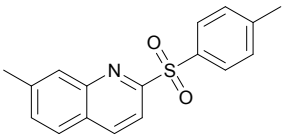
Follow the general procedure A, **3da** was obtained 118.8 mg (80%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.38 (s, 3H), 2.53 (s, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 12.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.5, 21.7, 117.7, 126.3, 128.89, 128.96, 129.7, 129.9, 133.3, 136.3, 137.7, 139.5, 144.6, 146.0, 157.4 (ppm).

HRMS (ESI): $[C_{17}H_{15}NO_2S+H]^+$ calcd. for 298.0823; found 298.0826.

7-methyl-2-tosylquinoline(3ea)



Follow the general procedure A, **3ea** was obtained 115.8 mg (78%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 209 - 210 ^{o}C.

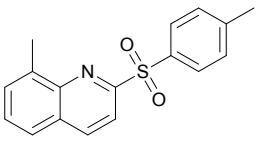
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 2.55 (s, 3H), 7.32 (d, *J*= 8.0 Hz, 2H), 7.48 (d, *J*= 8.0 Hz, 1H), 7.76 (d, *J*= 8.0 Hz, 1H), 7.95 (s, 1H) , 8.01 (d, *J*= 8.0 Hz, 2H), 8.13 (d, *J*= 8.0 Hz, 1H), 8.30 (d, *J*= 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 21.8, 116.8, 126.9, 127.2, 129.0, 129.2, 129.7, 131.4, 136.3, 138.2, 141.6, 144.6, 147.7, 158.3 (ppm).

IR (in KBr): ν =3852, 2930, 1550, 1320, 1160, 854, 555 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{15}NO_2S+H]^+$ calcd. for 298.0823; found 298.0825.

8-methyl-2-tosylquinoline(3fa)



Follow the general procedure A, **3fa** was obtained 112.8 mg (76%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

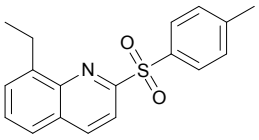
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.41 (s, 3H), 2.68 (s, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 21.6, 116.7, 125.5, 128.81, 128.88, 129.38, 129.49, 130.8, 135.9, 138.3, 138.6, 144.6, 146.4, 157.3 (ppm).

IR (in KBr): ν = 3819, 3030, 2958, 1477, 1322, 580, 513 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{15}NO_2S + H]^+$ calcd. for 298.0823; found 298.0821.

8-ethyl-2-tosylquinoline(3ga)



Follow the general procedure A, **3ga** was obtained 102.6 mg (66%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 100 - 101 ^{o}C.

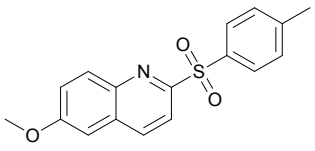
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.19 (t, *J*= 8.0 Hz, 3H), 2.41 (s, 3H), 3.11-3.17 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.52-7.60 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.0, 21.6, 24.6, 116.5, 125.5, 128.93, 129.05, 129.43, 129.46, 135.8, 138.8, 144.1, 144.6, 145.7, 157.4 (ppm).

IR (in KBr): ν = 3670, 3043, 1325, 1130, 570, 515, 447 (cm^{-1}).

HRMS (ESI): $[C_{18}H_{17}NO_2S + H]^+$ calcd. for 312.0980; found 312.0985.

6-methoxy-2-tosylquinoline(3ha)



Follow the general procedure B, **3ha** was obtained 134.6 mg (86%) as white solid with *n*-hexane/ethyl acetate (2/1) used as eluent.

Melting point: 152 - 154 ^{o}C.

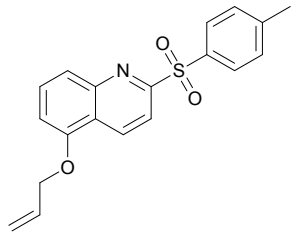
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.38 (s, 3H), 3.92 (s, 3H), 7.07 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 12.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 55.7, 104.6, 118.1, 124.2, 128.8, 129.7, 130.3, 131.7, 136.5, 136.7, 143.6, 144.5, 155.7, 159.7 (ppm).

IR (in KBr): ν = 3628, 2925, 1506, 1326, 1162, 689, 653 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{15}NO_3S+H]^+$ calcd. for 314.0773; found 314.0776.

5-(allyloxy)-2-tosylquinoline(3ia)



Follow the general procedure A, **3ia** was obtained 133.9 mg (79%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

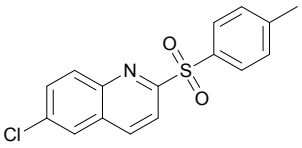
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 4.73 (d, *J* = 4.0 Hz, 2H), 5.36 (d, *J* = 8.0 Hz, 1H), 5.49 (d, *J* = 20.0Hz, 1H), 6.08-6.18 (m, 1H) , 6.93 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 1H) , 7.74 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.82 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 69.4, 107.5, 116.7, 118.2, 121.7, 122.4, 129.1, 129.7, 130.9, 132.4, 133.8, 136.2, 144.7, 148.3, 153.8, 158.7 (ppm).

IR (in KBr): ν = 3743, 3381, 1669, 1325, 1150, 854, 685 (cm^{-1}).

HRMS (ESI): $[C_{19}H_{17}NO_3S+H]^+$ calcd. for 340.0929; found 340.0927.

6-chloro-2-tosylquinoline(3ja)



Follow the general procedure B, **3ja** was obtained 112.5 mg (71%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 175 – 176 °C.

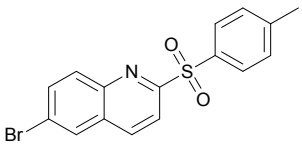
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.41 (s, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 118.6, 126.3, 129.1, 129.3, 129.8, 131.9, 132.0, 135.2, 135.8, 137.7, 145.0, 145.7, 158.7 (ppm).

IR (in KBr): ν = 3852, 2968, 1558, 1324, 951, 849, 518 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}ClNO_2S+H]^+$ calcd. for 318.0277; found 318.0279.

6-bromo-2-tosylquinoline(3ka)



Follow the general procedure B, **3ka** was obtained 113.7 mg (63%) as yellow solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 185 - 188°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.01 (t, *J* = 8.0 Hz, 4H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H) (ppm).

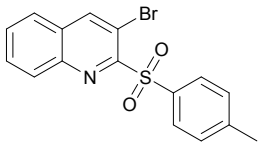
^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 118.6, 123.5, 129.1, 129.74, 129.84, 131.9, 134.5, 135.8, 137.6, 145.0,

145.9, 158.8 (ppm).

IR (in KBr): ν = 3640, 2950, 1760, 1318, 1162, 825, 695 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}BrNO_2S +H]^+$ calcd. for 361.9772; found 361.9775.

3-bromo-2-tosylquinoline(3la)[2]



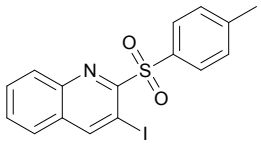
Follow the general procedure B, **3la** was obtained 108.2 mg (60%) as yellow solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.47 (s, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 4.0 Hz, 1H), 7.77 (m, 2H), 7.98 (t, *J* = 8.0 Hz, 3H), 8.52 (s, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 111.4, 126.5, 129.4, 129.80, 129.85, 130.0, 130.3, 131.0, 135.0, 142.9, 144.5, 144.9, 154.5 (ppm).

HRMS (ESI): $[C_{16}H_{12}BrNO_2S +H]^+$ calcd. for 361.9772; found 361.9770.

3-iodo-2-tosylquinoline(3ma)



Follow the general procedure B, **3ma** was obtained 132.9 mg (65%) as yellow solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 137 - 139 ^{o}C.

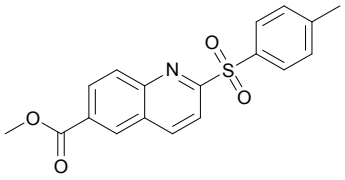
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.48 (s, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.86 (s, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 79.9, 126.3, 129.3, 129.80, 129.84, 130.0, 130.14, 131.1, 134.5 144.7, 144.8, 150.5, 156.3 (ppm).

IR (in KBr): ν = 3734, 2961, 1699, 1324, 1081, 750, 656 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}INO_2S + H]^+$ calcd. for 409.9633; found 409.9636

methyl 2-tosylquinoline-6-carboxylate(3na)



Follow the general procedure B, **3na** was obtained 107.4 mg (63%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 170 - 171 °C.

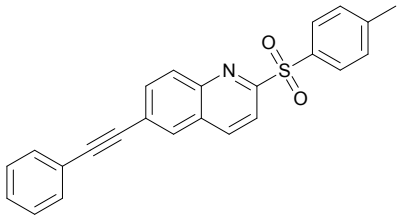
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.42 (s, 3H), 4.00 (s, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 12.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.62 (s, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 52.7, 118.3, 128.0, 129.3, 129.8, 130.3, 130.4, 130.6, 130.7, 135.6, 140.1, 145.1, 149.1, 160.5, 166.0 (ppm).

IR (in KBr): ν = 3676, 2924, 1780, 1323, 1075, 691, 577 (cm^{-1}).

HRMS (ESI): $[C_{18}H_{15}NO_4S + H]^+$ calcd. for 342.0722; found 342.0725.

6-(phenylethynyl)-2-tosylquinoline(3oa)



Follow the general procedure A, **3oa** was obtained 134.0 mg (70%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 282 - 283 °C.

^{1}H NMR (400 MHz, CDCl3) δ = 2.42 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 4.0 Hz, 3H), 7.56-7.58 (m,

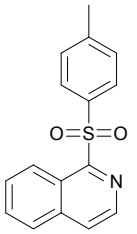
2H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.01-8.04 (m, 3H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H) , 8.32 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 88.4, 92.4, 118.3, 122.5, 124.4, 128.5, 128.6, 128.9, 129.1, 129.8, 130.47, 130.61, 131.8, 133.6, 136.0, 138.2, 144.9, 146.7, 158.7 (ppm).

IR (in KBr): ν = 3688, 2961, 2853, 1324, 1261, 812, 636 (cm^{-1}).

HRMS (ESI): $[C_{24}H_{17}NO_2S + H]^+$ calcd. for 384.0980; found 384.0983.

1-tosylisoquinoline(3pa)[2]



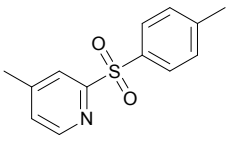
Follow the general procedure B, **3pa** was obtained 94.8 mg (67%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.43 (s, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.75-7.78 (m, 3H), 7.89-7.90 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.42 (d, *J* = 4.0 Hz, 1H), 9.16 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 124.2, 124.9, 125.3, 127.5, 129.19, 129.22, 129.5, 131.1, 136.0, 137.7, 140.5, 144.7, 157.2 (ppm).

HRMS (ESI): $[C_{16}H_{13}NO_2S + H]^+$ calcd. for 284.0667; found 284.0669.

4-methyl-2-tosylpyridine(3qa)[2]



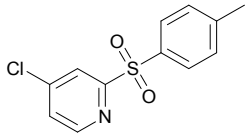
Follow the general procedure C, **3qa** was obtained 81.5 mg (66%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.41 (s, 3H), 2.45 (s, 3H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 8.01 (s, 1H), 8.50 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.2, 21.6, 122.7, 127.5, 128.9, 129.7, 136.1, 144.7, 149.9, 150.1, 158.9 (ppm).

HRMS (ESI): $[C_{13}H_{13}NO_2S+H]^+$ calcd. for 248.0667; found 248.0665.

4-chloro-2-tosylpyridine(3ra)[2]



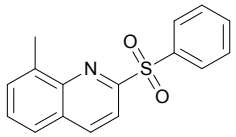
Follow the general procedure C, **3ra** was obtained 86.7 mg (65%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.42 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.19 (s, 1H), 8.54 (d, *J* = 4.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 122.5, 126.9, 129.1, 129.9, 135.3, 145.3, 146.3, 151.2, 160.4 (ppm).

HRMS (ESI): $[C_{12}H_{10}ClNO_2S+H]^+$ calcd. for 268.0121; found 268.0123.

8-methyl-2-(phenylsulfonyl)quinoline(3fb)



Follow the general procedure A, **3fb** was obtained 116.0 mg (82%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 106 - 108 ^{o}C.

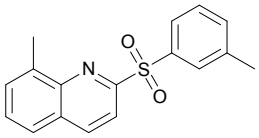
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.65 (s, 3H), 7.50-7.64 (m, 5H), 7.69 (d, *J* = 8.0 Hz, 1H), 8.17-8.22 (m, 3H), 8.33 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 116.7, 125.5, 128.81, 128.87, 128.98, 129.39, 130.9, 133.6, 138.4, 138.7, 138.9, 146.3,157.1 (ppm).

IR (in KBr): ν = 3743, 3058, 2923, 1493, 1477, 1320, 536 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{13}NO_2S+H]^+$ calcd. for 284.0667; found 284.0669.

8-methyl-2-(m-tolylsulfonyl)quinoline(3fc)



Follow the general procedure A, **3fc** was obtained obtained 103.9 mg (70%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

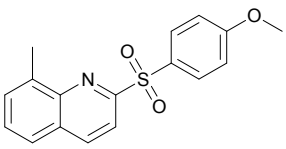
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.42 (s, 3H), 2.68 (s, 3H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.97-8.00 (m, 2H), 8.20 (d, *J* = 8.0 Hz, 1H) , 8.32 (d, *J* = 12.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 21.2, 116.7, 125.5, 126.5, 128.6, 128.85, 128.93, 129.7, 130.8, 134.4, 138.4, 138.71, 138.75, 139.0, 146.4, 157.2 (ppm).

IR (in KBr): ν = 3793, 3002, 1644, 1326, 852, 686, 533 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{15}NO_2S+H]^+$ calcd. for 298.0823; found 298.0825.

2-((4-methoxyphenyl)sulfonyl)-8-methylquinoline(3fd)



Follow the general procedure B, **3fd** was obtained 108.0 mg (69%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 143 - 145 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.68 (s, 3H), 3.85 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H) (ppm).

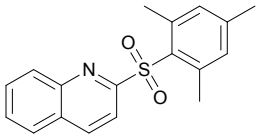
^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.5, 55.6, 114.1, 116.5, 125.5, 128.78, 128.82, 130.3, 130.8, 131.5, 138.3,

138.6, 146.3, 157.6, 163.8 (ppm).

IR (in KBr): ν = 3645, 2950, 1621, 1320, 1180, 634, 456 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{15}NO_3S + H]^+$ calcd. for 314.0773; found 314.0773.

2-(mesitylsulfonyl)quinoline(3ae)



Follow the general procedure A, **3ae** was obtained 127.5 mg (82%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 120 - 123 °C.

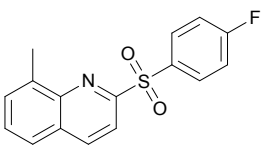
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.30 (s, 3H), 2.68 (s, 6H), 6.95 (s, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.0, 23.0, 116.9, 127.7, 128.92, 128.94, 130.5, 130.7, 131.9, 132.9, 138.4, 141.2, 143.5, 147.1, 159.6 (ppm).

IR (in KBr): ν = 3891, 3689, 2925, 1569, 1305, 684, 408 (cm^{-1}).

HRMS (ESI): $[C_{18}H_{17}NO_2S + H]^+$ calcd. for 312.0980; found 312.0984.

2-((4-fluorophenyl)sulfonyl)-8-methylquinoline(3ff)



Follow the general procedure A, **3ff** was obtained 102.3 mg (68%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.65 (s, 3H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0

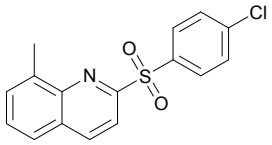
Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 8.18-8.21 (m, 3H), 8.36 (d, *J* = 12.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 116.0, 116.2, 116.5, 125.6, 128.94, 129.09, 131.0, 132.28, 132.38, 134.8, 138.3, 138.9, 146.3, 157.0, 164.7, 167.2 (ppm).

IR (in KBr): ν = 3820, 2993, 1753, 1326, 1150, 762, 549 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}FNO_2S + H]^+$ calcd. for 302.0573; found 302.0577.

2-((4-chlorophenyl)sulfonyl)-8-methylquinoline(3fg)



Follow the general procedure A, **3fg** was obtained 126.8 mg (80%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 110 - 111 °C.

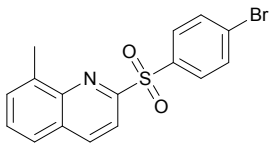
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.66 (s, 3H), 7.53 (t, *J* = 8.0 Hz, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 12.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 116.6, 125.6, 128.96, 129.15, 130.8, 131.0, 137.4, 138.3, 138.9, 140.4, 146.4, 156.8 (ppm).

IR (in KBr): ν = 3679, 3001, 1653, 1321, 1109, 848, 539 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}ClNO_2S + H]^+$ calcd. for 318.0277; found 318.0279.

2-((4-bromophenyl)sulfonyl)-8-methylquinoline(3fh)



Follow the general procedure A, **3fh** was obtained 137.1 mg (76%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 120 – 122 °C.

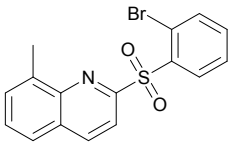
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.67 (s, 3H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 4.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 3H), 8.04 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.5, 116.6, 125.6, 128.9, 129.13, 129.17, 130.9, 131.1, 132.1, 137.9, 138.3, 138.9, 146.4, 156.7 (ppm).

IR (in KBr): ν = 3701, 3006, 1593, 1324, 1149, 843, 520 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}BrNO_2S + H]^+$ calcd. for 361.9772; found 361.9776.

2-((2-bromophenyl)sulfonyl)-8-methylquinoline(3fi)



Follow the general procedure A, **3fi** was obtained 129.9 mg (72%) as yellow solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 135 – 138 °C.

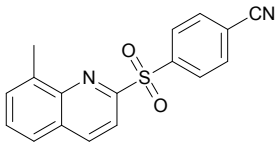
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.45(s, 3H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.54-7.66 (m, 4H), 7.74 (d, *J* = 8.0 Hz, 1H) , 8.30 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.1, 117.5, 121.8, 125.6, 127.5, 129.05, 129.08, 130.9, 132.7, 134.6, 134.8, 138.3, 138.4, 138.5, 146.0, 156.0 (ppm).

IR (in KBr): ν = 3642, 3012, 1687, 1536, 1321, 1086, 749 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}BrNO_2S + H]^+$ calcd. for 361.9772; found 361.9775.

4-((8-methylquinolin-2-yl)sulfonyl)benzonitrile(3fj)



Follow the general procedure A, **3fj** was obtained 115.5 mg (75%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 144 - 146 °C.

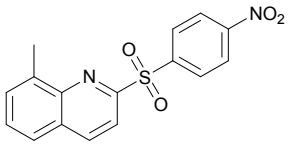
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.62 (s, 3H), 7.56 (t, *J*= 8.0 Hz, 1H), 7.63 (d, *J*= 8.0 Hz, 1H), 7.72 (d, *J*= 8.0 Hz, 1H), 7.85 (d, *J*= 8.0Hz, 2H), 8.21 (d, *J*= 8.0 Hz, 1H), 8.30 (d, *J*= 8.0 Hz, 2H), 8.39 (d, *J*= 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 116.6, 117.2, 117.3, 125.6, 129.0, 129.4, 130.1, 131.3, 132.4, 138.2, 139.1, 143.1, 146.3, 156.1 (ppm).

IR (in KBr): ν = 3748, 3093, 2959, 2232, 1472, 1322, 835 (cm^{-1}).

HRMS (ESI): $[C_{17}H_{12}N_2O_2S +H]^+$ calcd. for 309.0619; found 309.0617.

8-methyl-2-((4-nitrophenyl)sulfonyl)quinoline(3fk)



Follow the general procedure A, **3fk** was obtained 118.0 mg (72%) as yellow solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 162 - 164 ^{o}C.

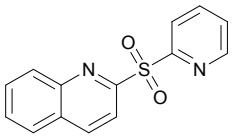
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.63 (s, 3H), 7.57 (t, *J*= 8.0 Hz, 1H), 7.63 (d, *J*= 4.0 Hz, 1H), 7.73 (d, *J*= 8.0 Hz, 1H), 8.23 (d, *J*= 8.0 Hz, 1H), 8.39 (d, *J*= 12.0 Hz, 5H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.4, 116.6, 123.9, 125.7, 129.15, 129.52, 130.8, 131.3, 138.3, 139.2, 144.7, 146.4, 150.8, 156.0 (ppm).

IR (in KBr): ν = 3738, 3108, 2928, 1687, 1312, 1075, 738 (cm^{-1}).

HRMS (ESI): $[C_{16}H_{12}N_2O_4S +H]^+$ calcd. for 329.0518; found 329.0521.

2-(pyridin-2-ylsulfonyl)quinoline(3al)



Follow the general procedure A, **3al** was obtained 91.8mg (68%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 151 - 153°C.

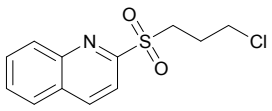
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.52 (m, 1H), 7.69 (t, *J*= 8.0 Hz, 1H), 7.81 (t, *J*= 8.0 Hz, 1H), 7.90 (d, *J*= 8.0 Hz, 1H), 8.13 (d, *J*= 8.0 Hz, 1H), 8.24 (d, *J*= 12.0 Hz, 1H), 8.44 (t, *J*= 8.0 Hz, 2H), 8.83 (d, *J*= 4.0 Hz, 1H), 9.34 (s, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 117.3, 123.6, 127.8, 129.0, 129.5, 130.3, 131.2, 135.6, 136.9, 139.0, 147.4, 150.0, 154.1, 157.5 (ppm).

IR (in KBr): ν = 3743, 3648, 2922, 2851, 1616, 1317, 649 (cm^{-1}).

HRMS (ESI): $[C_{14}H_{10}N_2O_2S +H]^+$ calcd. for 271.0463; found 271.0466.

2-((3-chloropropyl)sulfonyl)quinoline(3am)



Follow the general procedure A, **3am** was obtained 91.4 mg (68%) as white viscous oil with *n*-hexane/ethyl acetate (2/1) used as eluent.

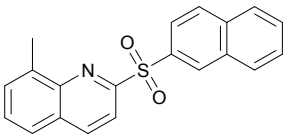
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.33-2.40 (m, 2H), 3.69-3.76 (m, 4H), 7.73 (t, *J*= 8.0 Hz, 1H), 7.87 (t, *J*= 8.0 Hz, 1H), 7.95 (d, *J*= 8.0 Hz, 1H), 8.13 (d, *J*= 8.0 Hz, 1H), 8.23 (d, *J*= 8.0 Hz, 1H), 8.45 (d, *J*= 8.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.6, 42.8, 49.2, 116.9, 127.9, 129.2, 129.4, 130.2, 131.3, 139.0, 147.1, 156.7 (ppm).

IR (in KBr): ν = 3891, 3776, 3648, 2924, 1646, 668, 443 (cm^{-1}).

HRMS (ESI): $[C_{12}H_{12}ClNO_2S +H]^+$ calcd. for 270.0277; found 270.0275.

8-methyl-2-(naphthalen-2-ylsulfonyl)quinoline(3fn)



Follow the general procedure A, **3fn** was obtained 103.2 mg (62%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 100 - 101 °C.

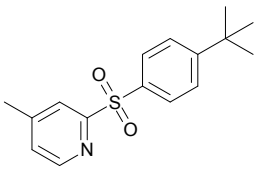
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.66 (s, 3H), 7.51 (t, 1H, *J*= 8.0 Hz), 7.57-7.69 (m, 4H), 7.90 (d, 1H, *J*= 8.0 Hz), 7.99 (t, 2H, *J*= 8.0 Hz), 8.19 (d, 1H, *J*= 8.0 Hz), 8.26 (d, 1H, *J*= 8.0 Hz), 8.35 (d, 1H, *J*=12.0 Hz), 8.75 (s, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.5, 116.8, 124.3, 125.5, 127.4, 127.9, 128.8, 128.9, 129.2, 129.4, 130.9, 131.0, 132.1, 135.3, 136.0, 138.4, 138.7, 146.4, 157.2 (ppm).

IR (in KBr): ν = 3880, 3668, 3648, 2922, 1652, 1317, 686 (cm^{-1}).

HRMS (ESI): $[C_{20}H_{15}NO_2S +H]^+$ calcd. for 334.0823; found 334.0826.

2-((4-(tert-butyl)phenyl)sulfonyl)-4-methylpyridine(3qo)



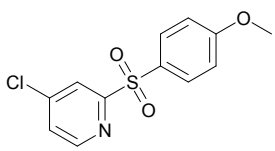
Follow the general procedure C, **3qo** was obtained 83.8 mg (58%) as white viscous oil with *n*-hexane/ethyl acetate (2/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.31 (s, 9H), 2.46 (s, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.02 (s, 1H), 8.53 (d, *J* = 4.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.2, 31.0, 35.2, 122.9, 126.1, 127.5, 128.7, 136.0, 149.9, 150.1, 157.5, 158.9 (ppm).

HRMS (ESI): $[C_{16}H_{19}NO_2S +H]^+$ calcd. for 290.1140; found 290.1138.

4-chloro-2-((4-methoxyphenyl)sulfonyl)pyridine(3rd)



Follow the general procedure C, **3rd** was obtained 79.2 mg (56%) as white viscous oil with *n*-hexane/ethyl acetate (2/1) used as eluent.

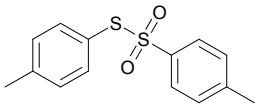
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.86 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* =

8.0 Hz, 2H), 8.17 (s, 1H), 8.54 (d, *J* = 4.0 Hz, 1H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.7, 114.5, 122.3, 126.8, 129.5, 131.4, 146.3, 151.1, 160.7, 164.2 (ppm).

HRMS (ESI): $[C_{12}H_{10}ClNO_3S+H]^+$ calcd. for 284.0065; found 284.0072.

S-p-tolyl 4-methylbenzenesulfonothioate(4b)



Follow the **eq. 4**, **4b** was obtained 27.8 mg (20%) as white solid with *n*-hexane/ethyl acetate (30/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.37 (s, 3H), 2.42 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.23 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H) (ppm).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.4, 21.6, 124.5, 127.5, 129.3, 130.2, 136.4, 140.4, 142.0, 144.5 (ppm).

HRMS (ESI): $[C_{14}H_{14}O_2S_2+H]^+$ calcd. for 279.0437; found 279.0441.

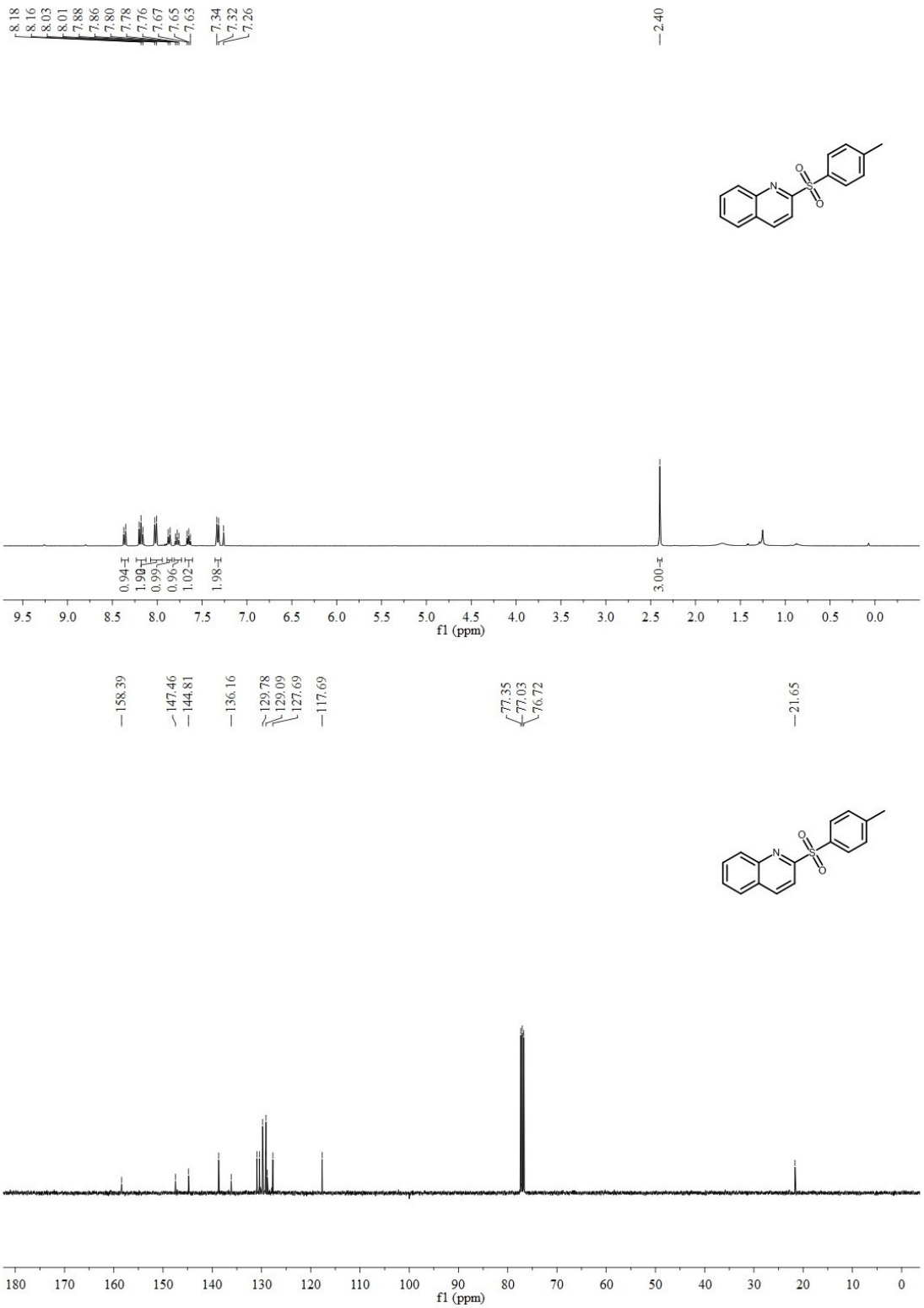
References:

[S1] E. M. Simmons , J. F. Hartwig. *Angew. Chem. Int. Ed*. 2012, **51**, 3066-3072.

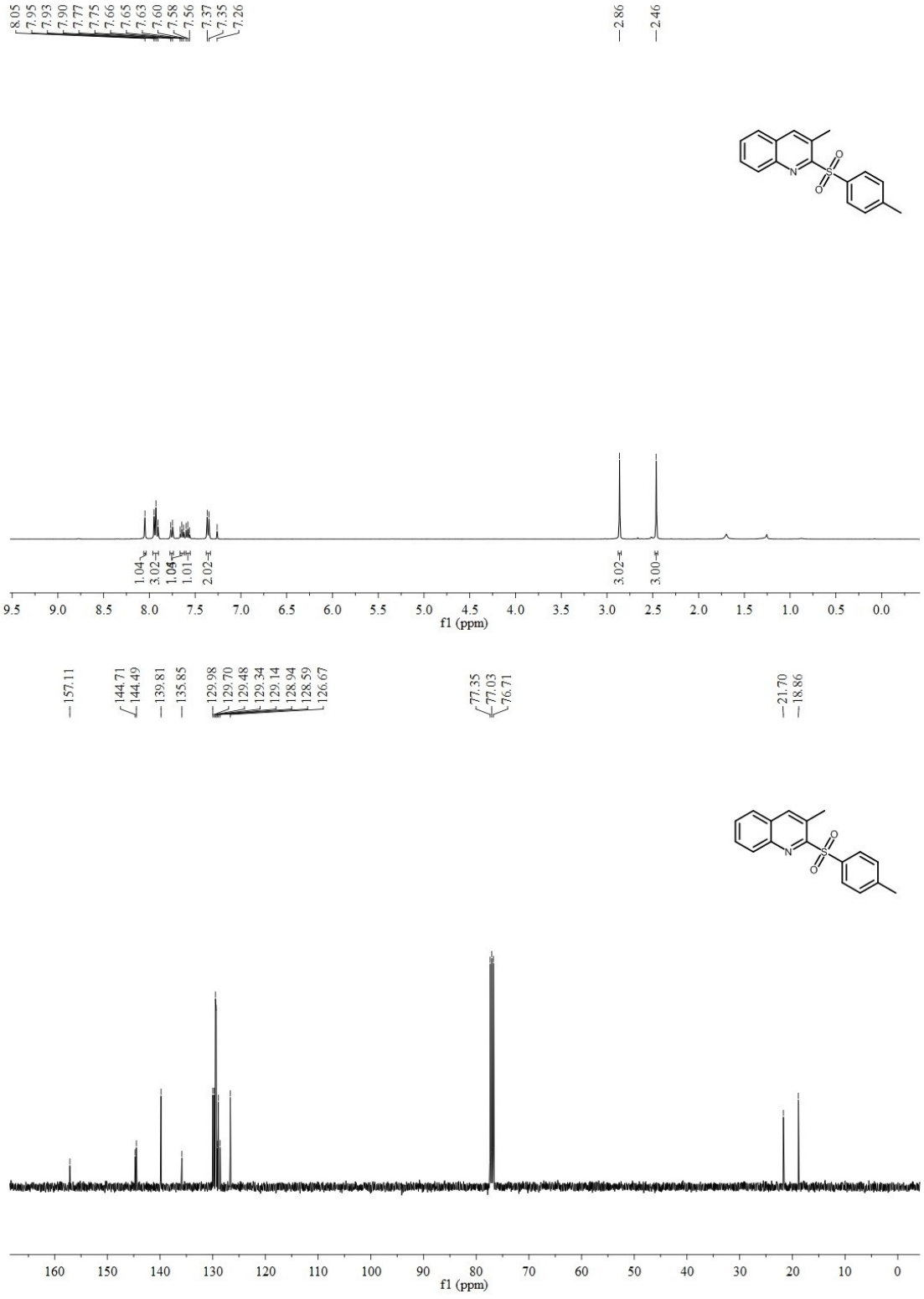
[S2] K. Sun, X. Chen, X. Li, L. Qu, W. Bi, XChen, H. Ma, S. Zhang, B. Han, Y. Zhao, C. Li. *Chem. Commun.* 2015, **51**, 12111-12114.

Spectra:

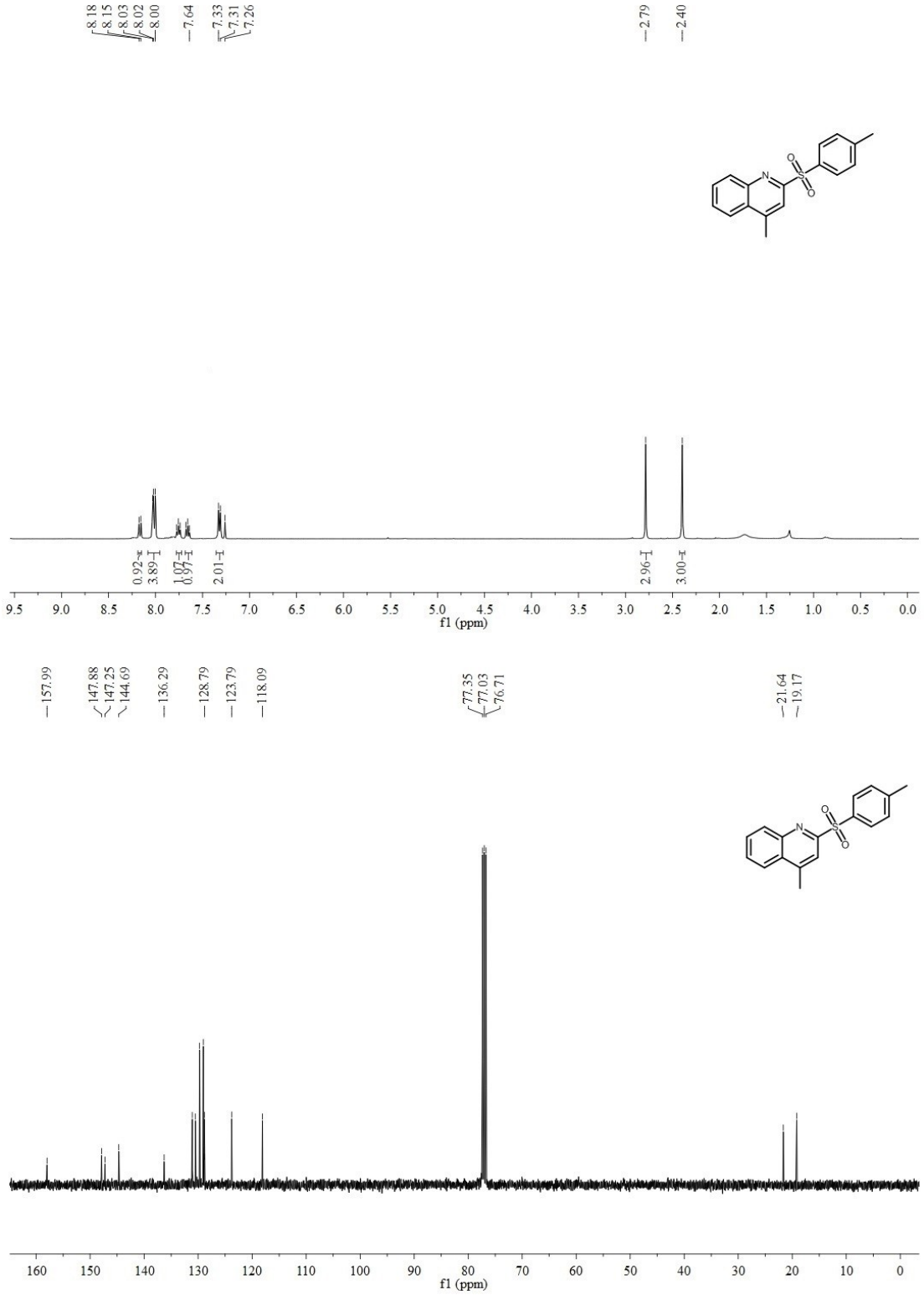
^{1}H, ^{13}C-NMR spectra of **3aa**



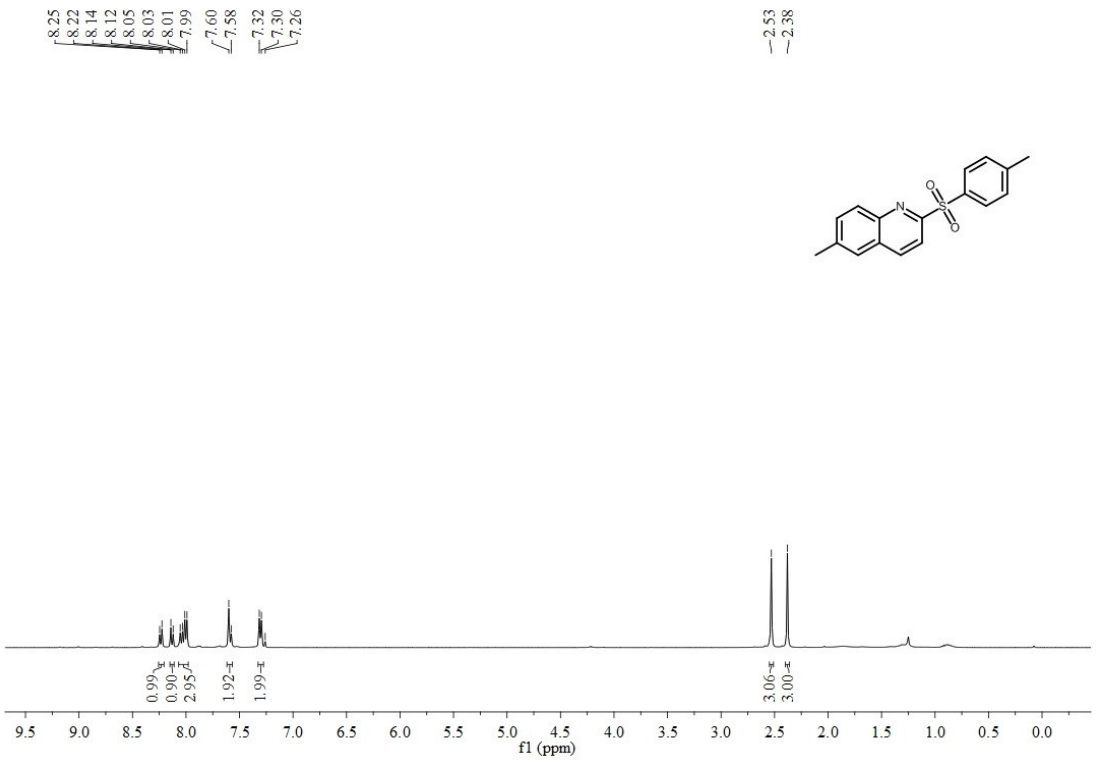
^{1}H, ^{13}C-NMR spectra of **3ba**

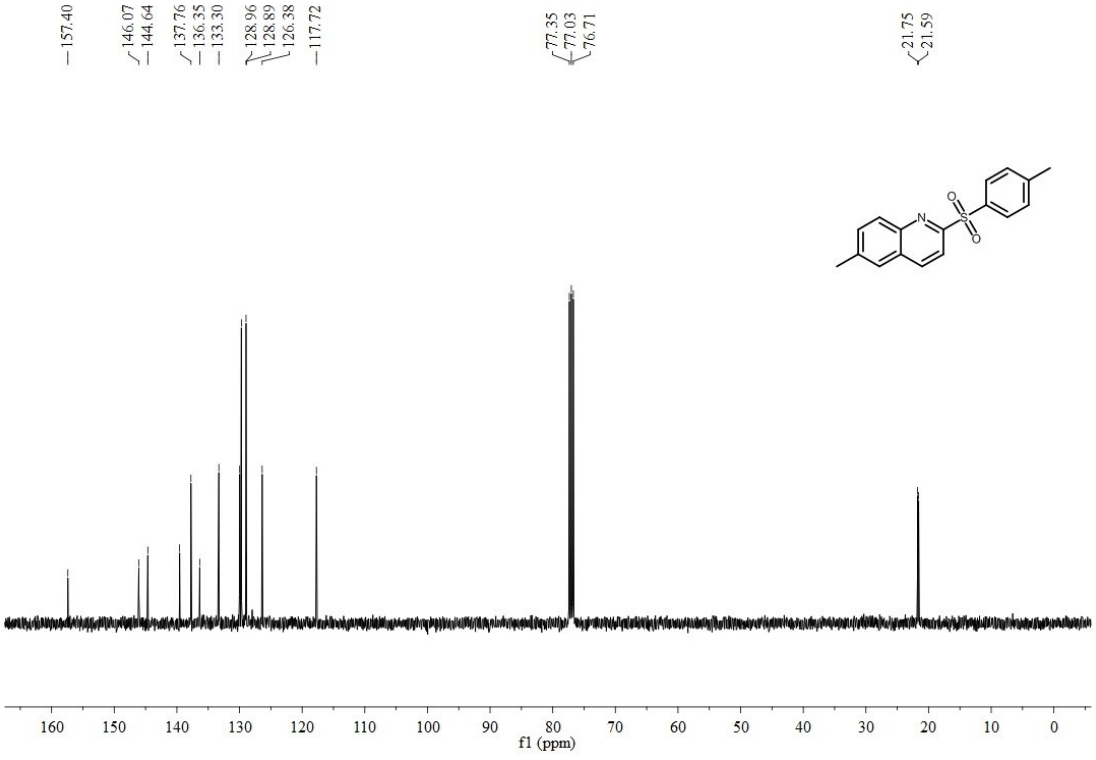


^{1}H, ^{13}C-NMR spectra of **3ca**

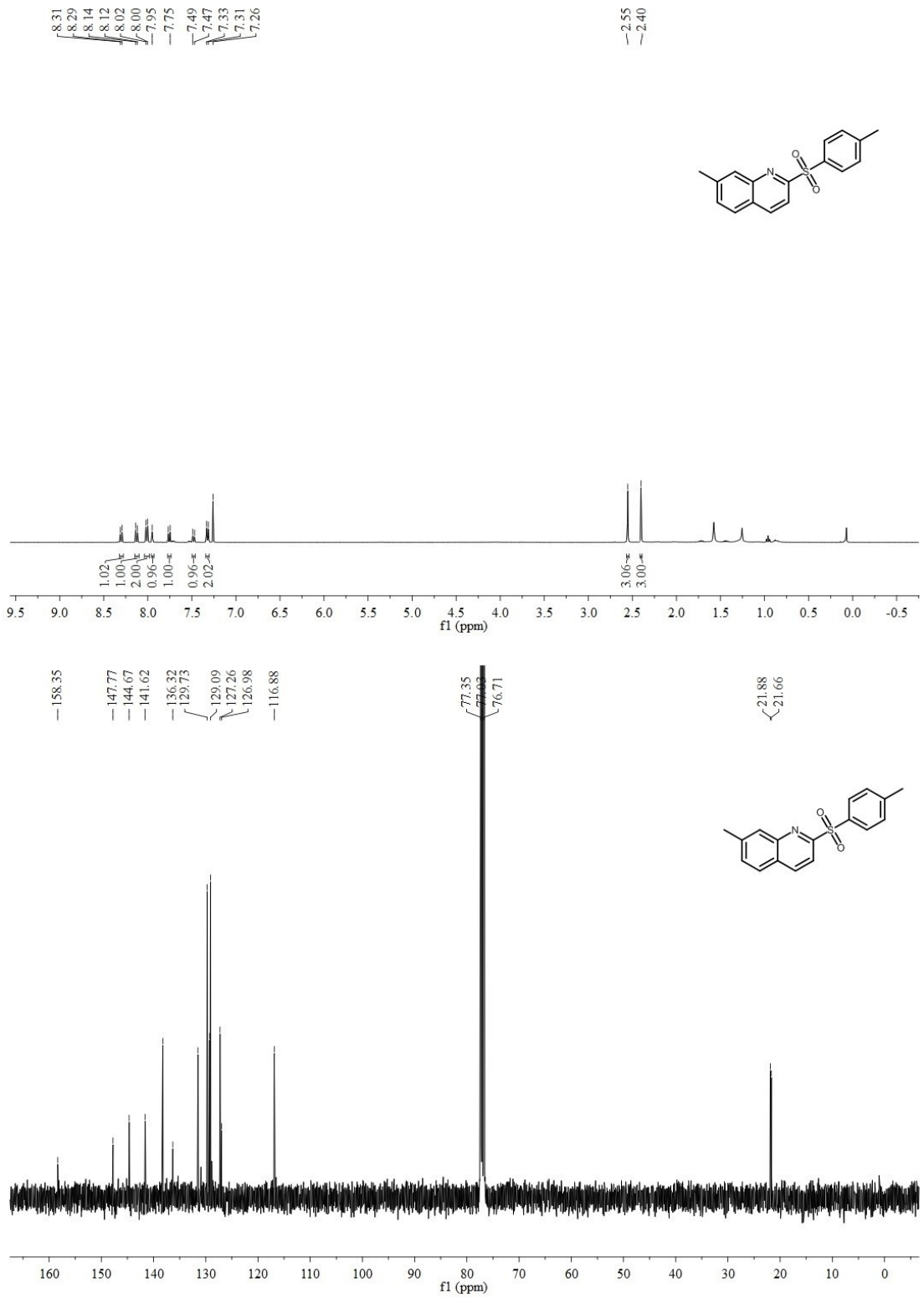


^{1}H, ^{13}C-NMR spectra of **3da**

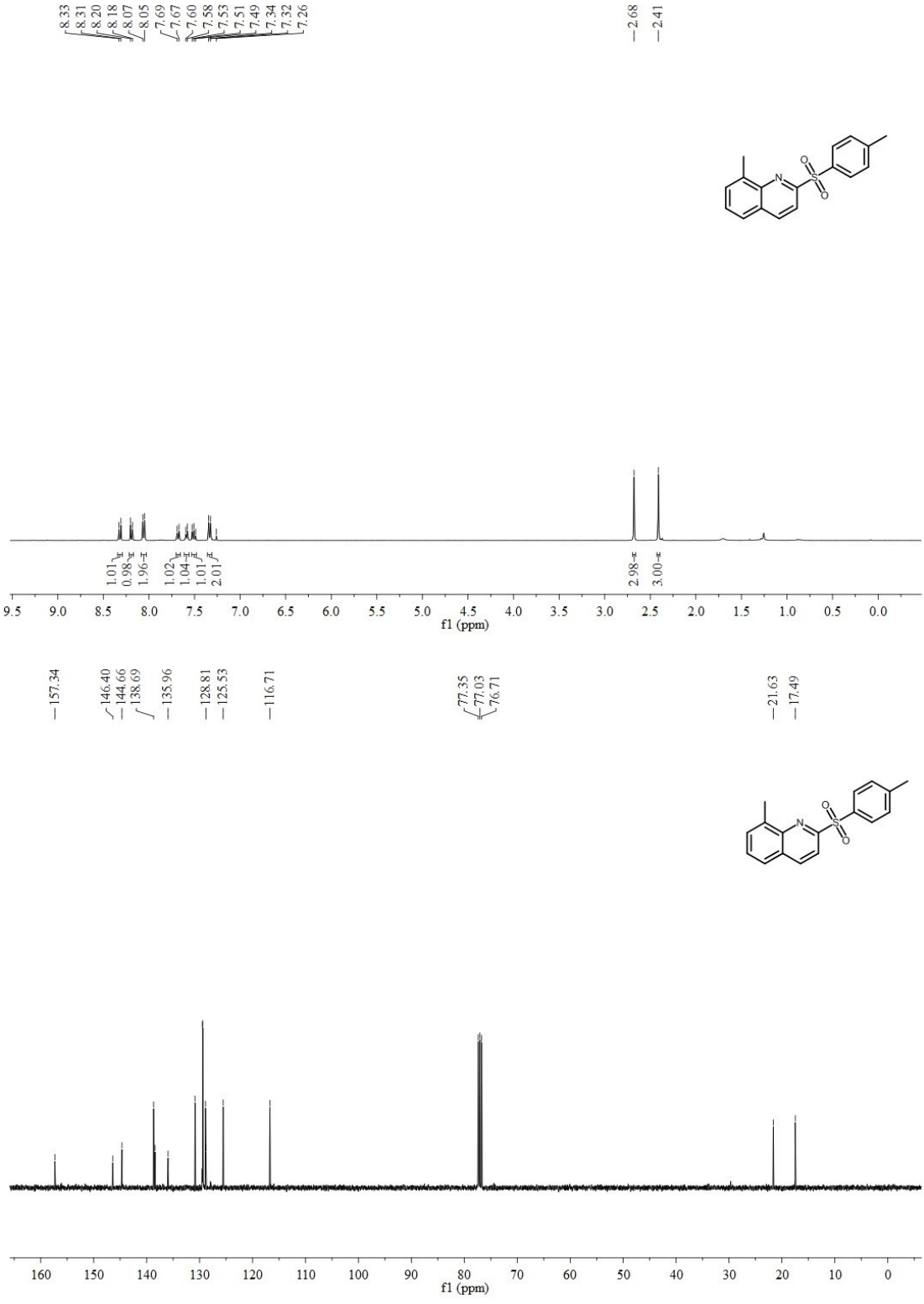




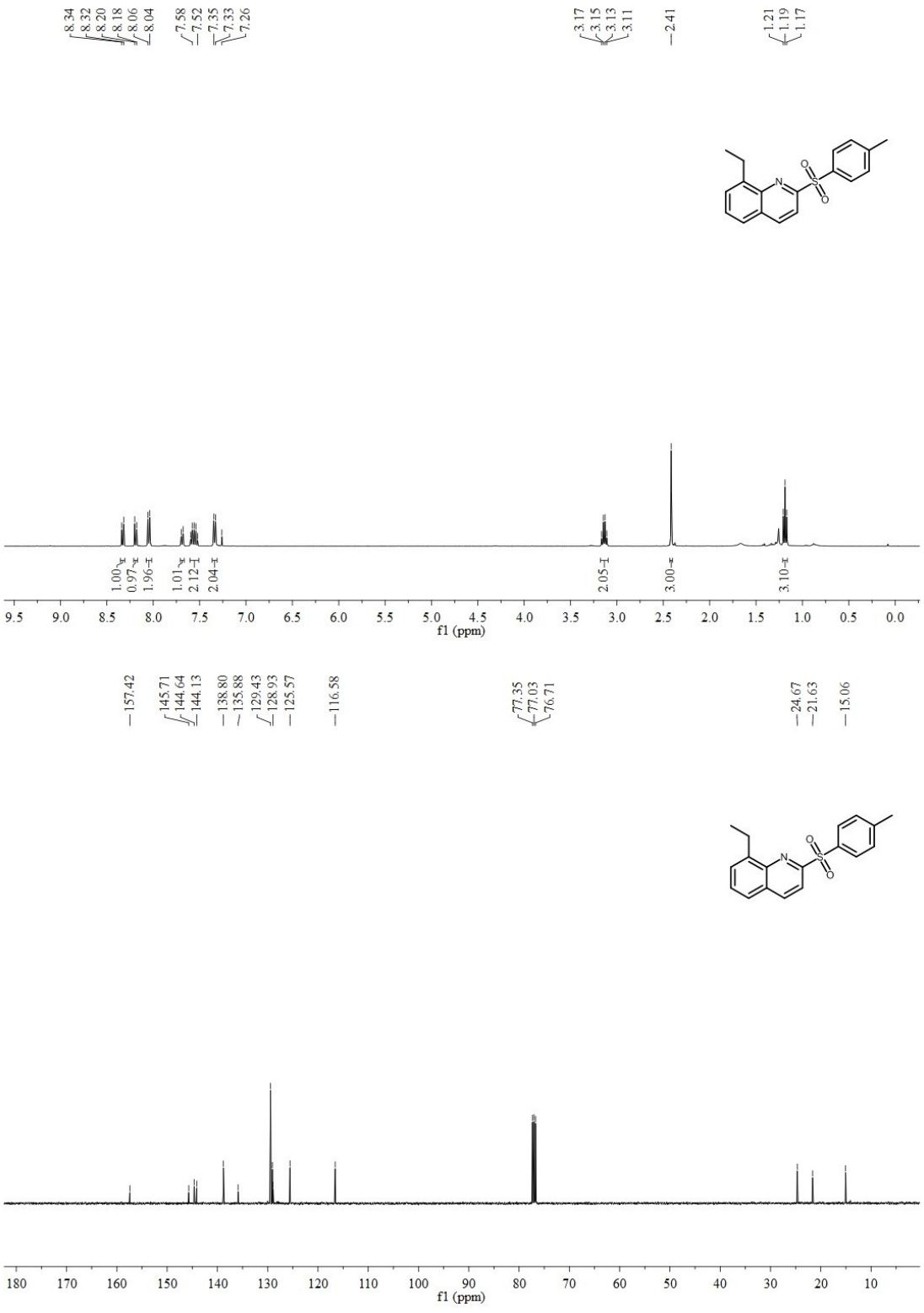
^{1}H, ^{13}C-NMR spectra of **3ea**



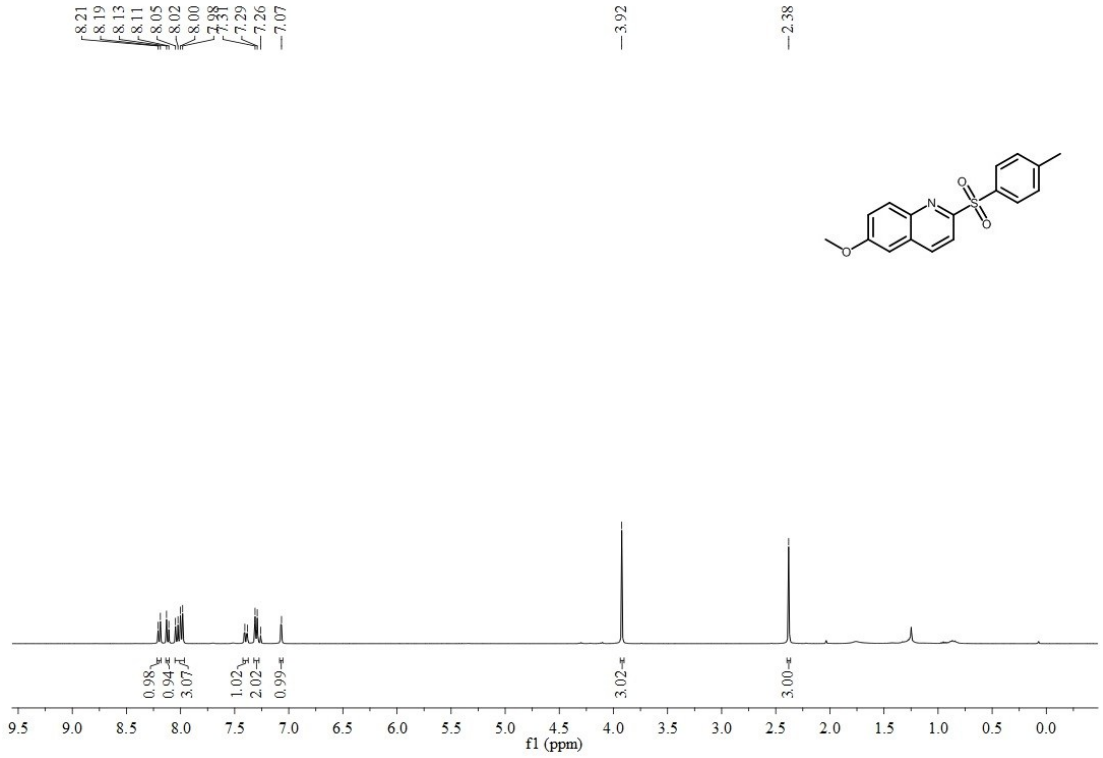
^{1}H, ^{13}C-NMR spectra of **3fa**

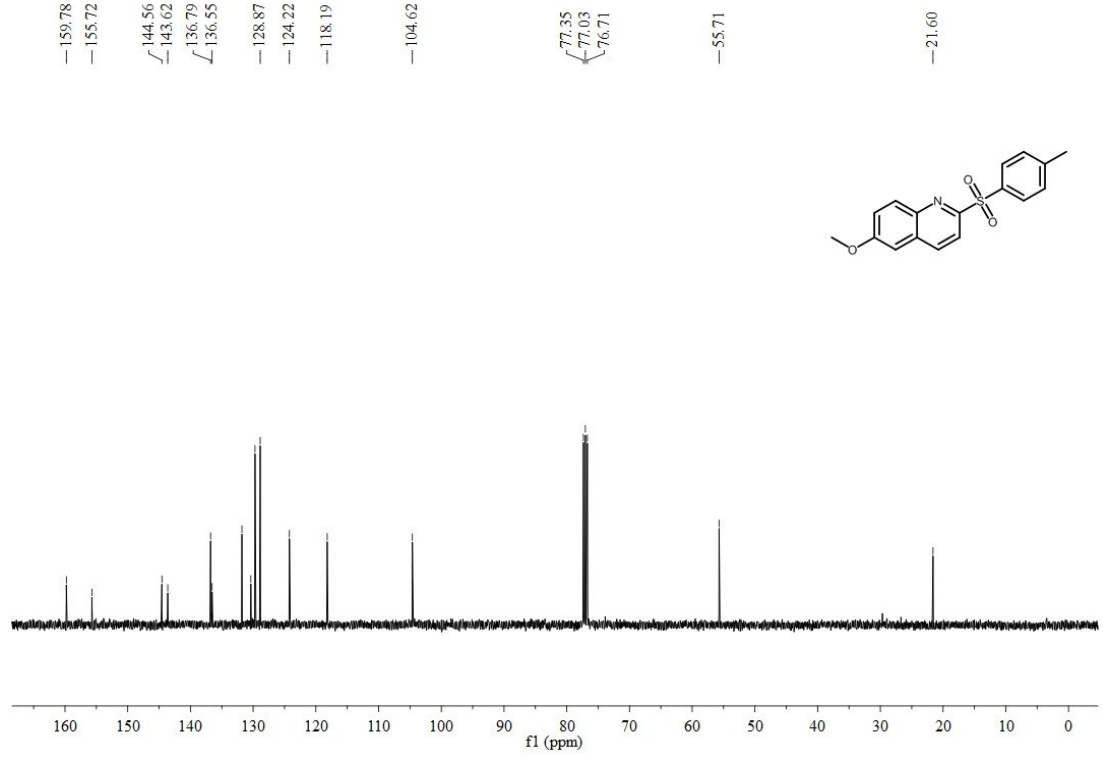


^{1}H, ^{13}C-NMR spectra of **3ga**

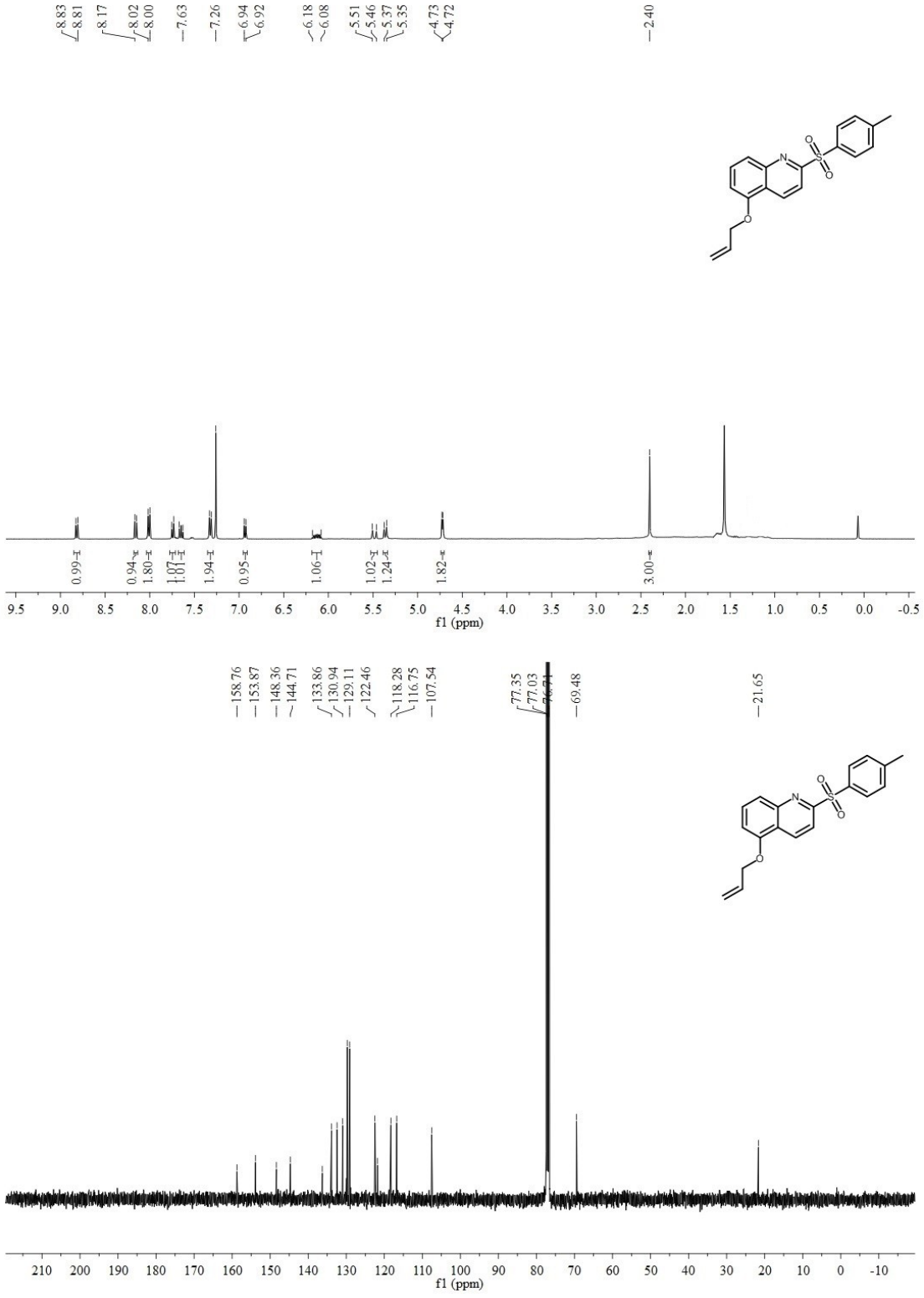


^{1}H, ^{13}C-NMR spectra of **3ha**

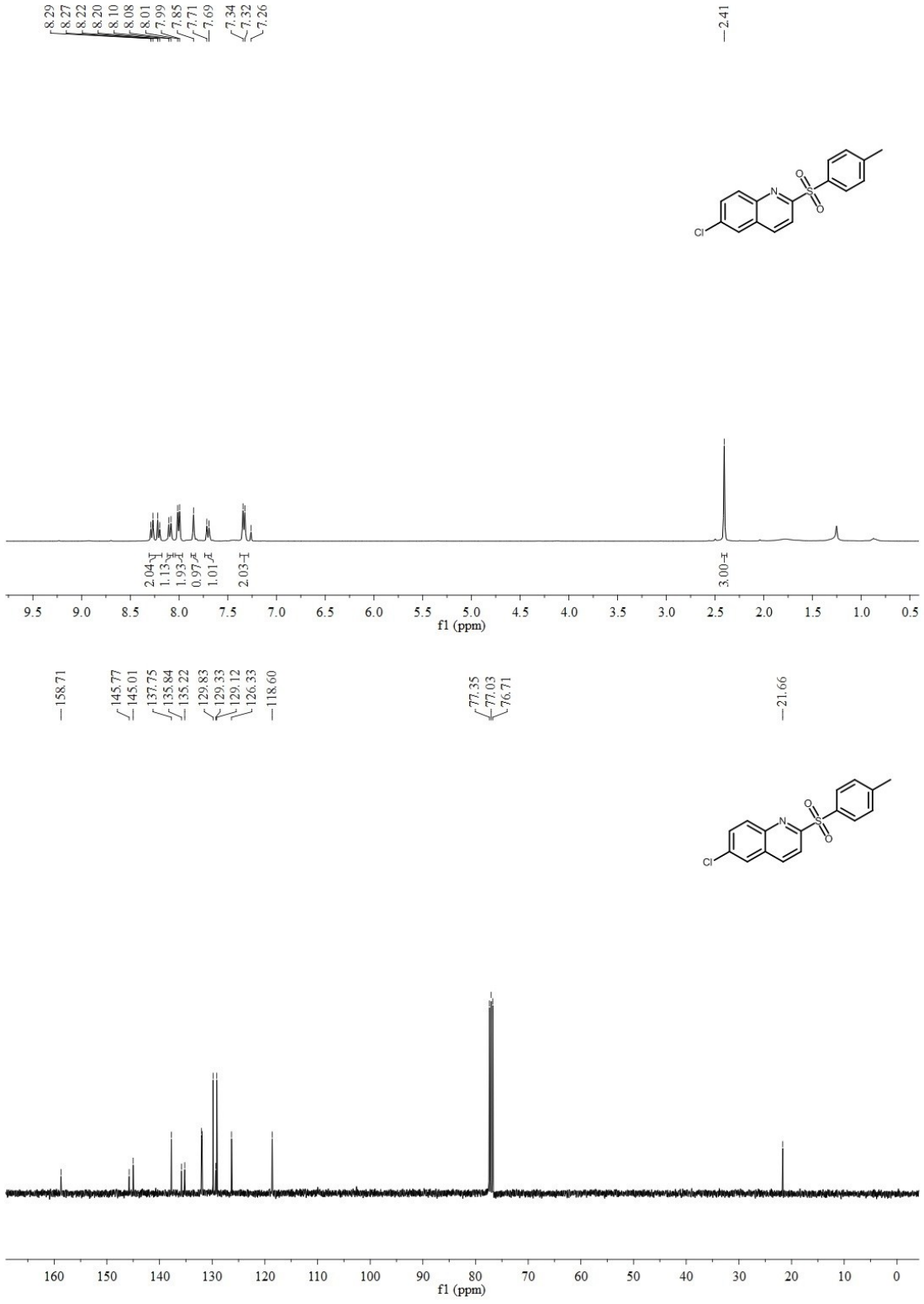




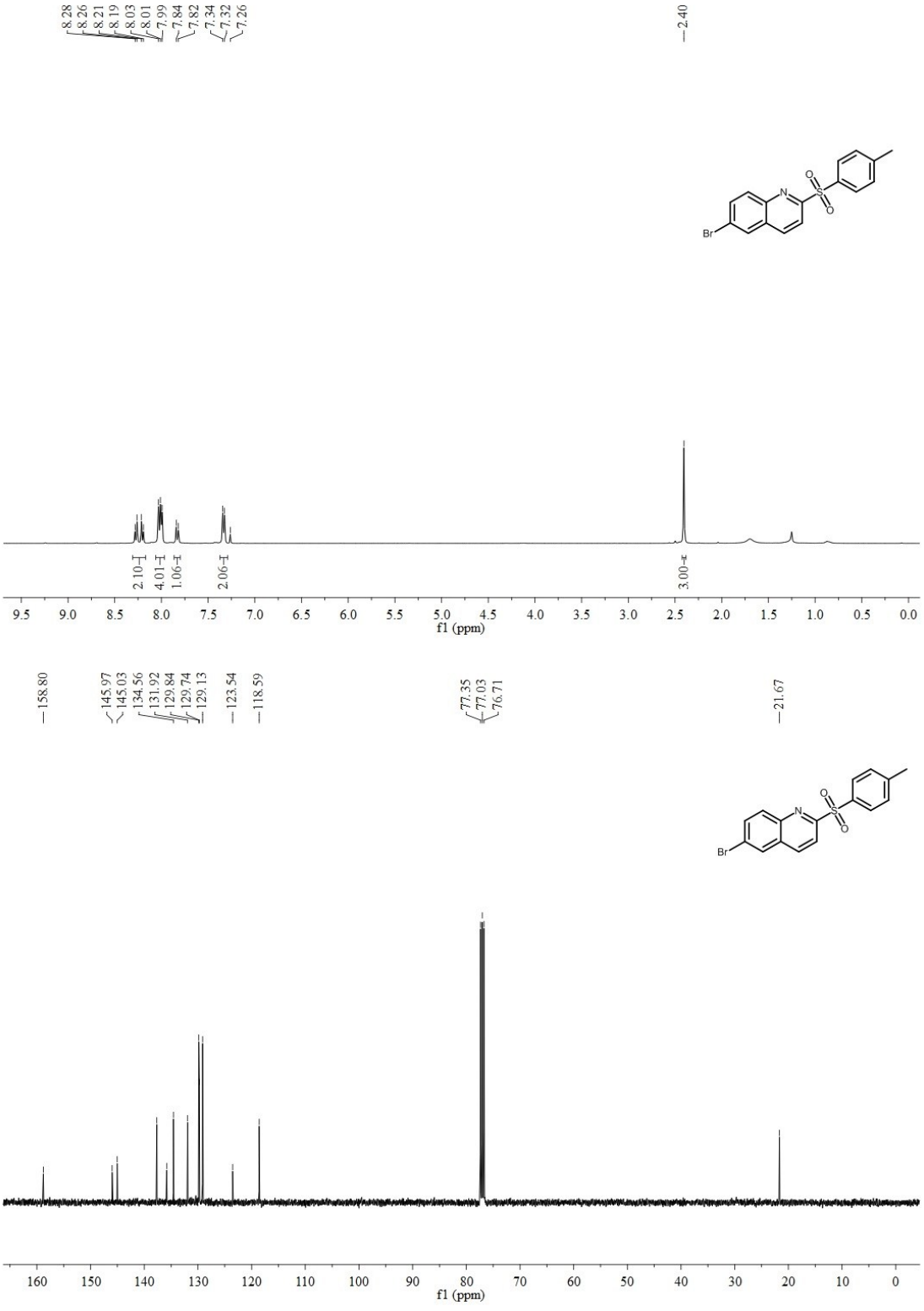
^{1}H, ^{13}C-NMR spectra of **3ia**



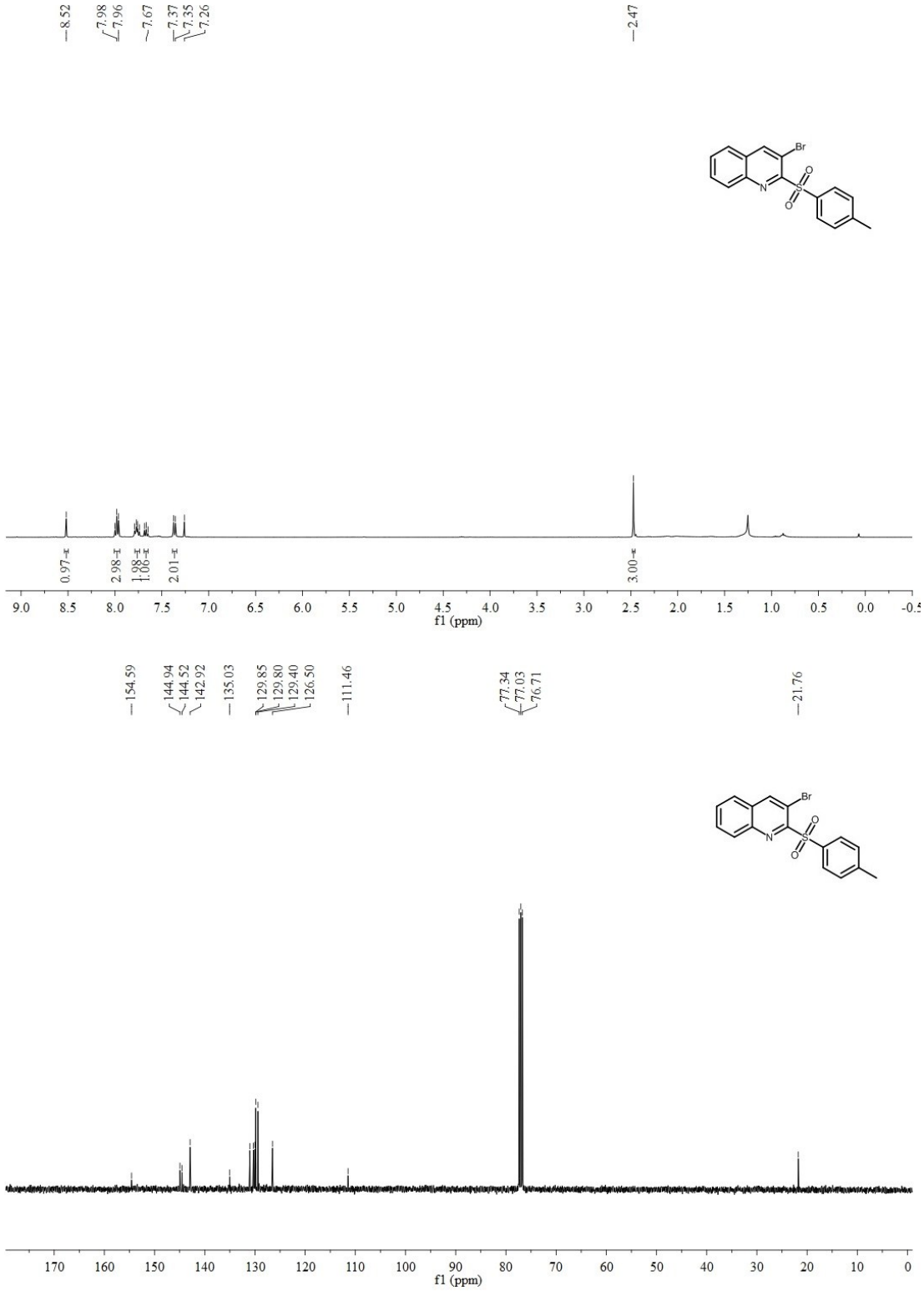
^{1}H, ^{13}C-NMR spectra of **3ja**



^{1}H, ^{13}C-NMR spectra of **3ka**



^{1}H, ^{13}C-NMR spectra of **3la**



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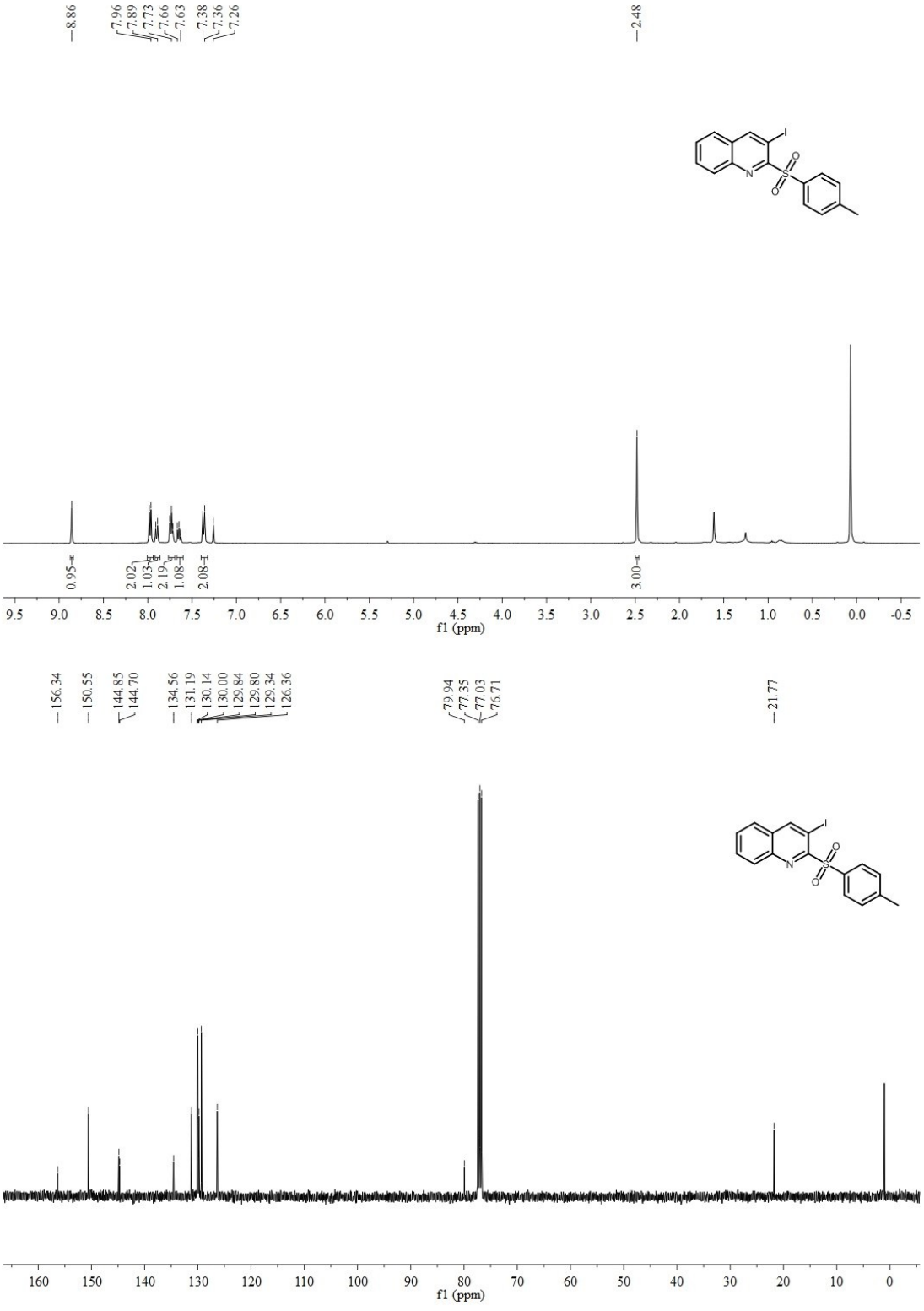
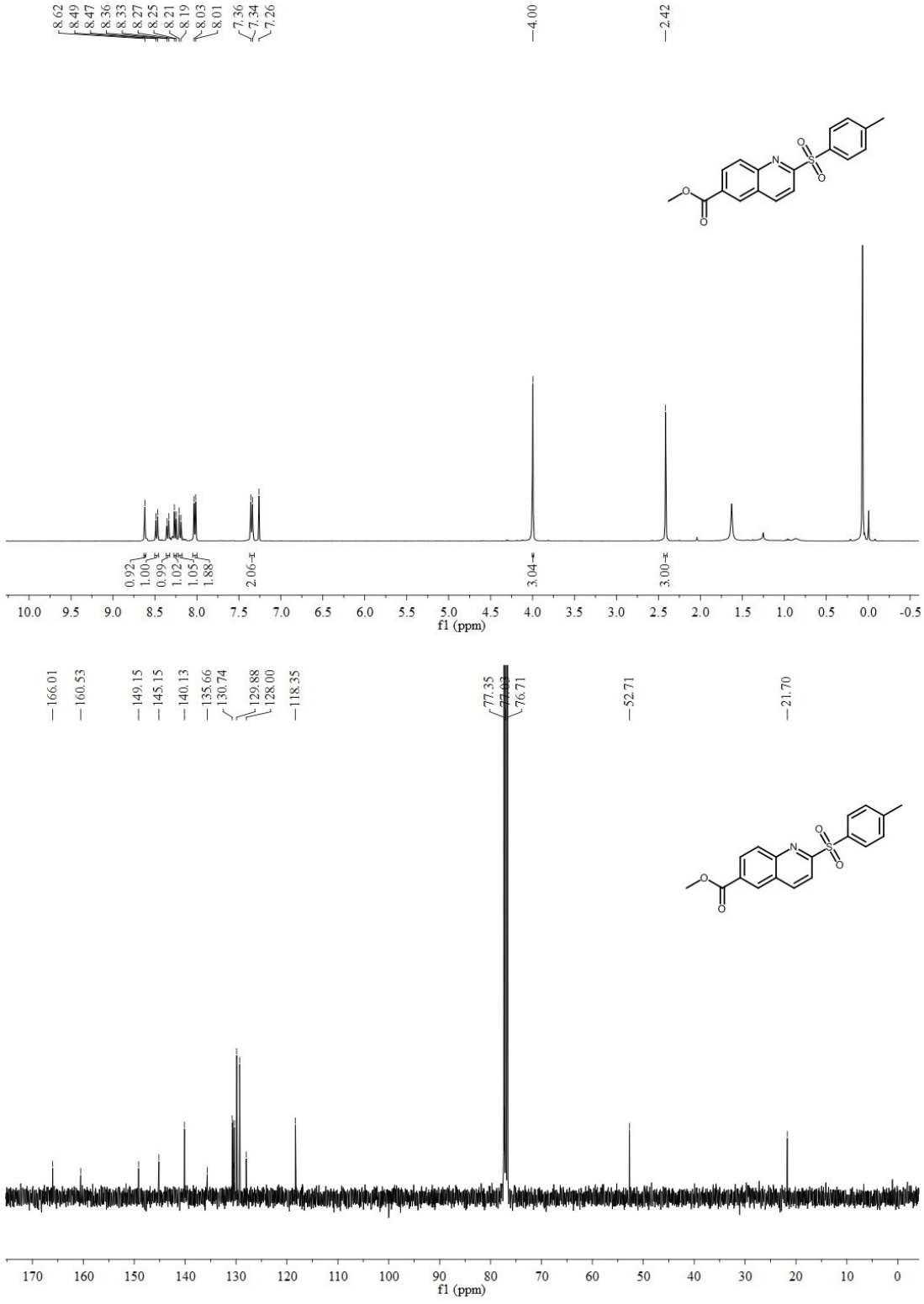
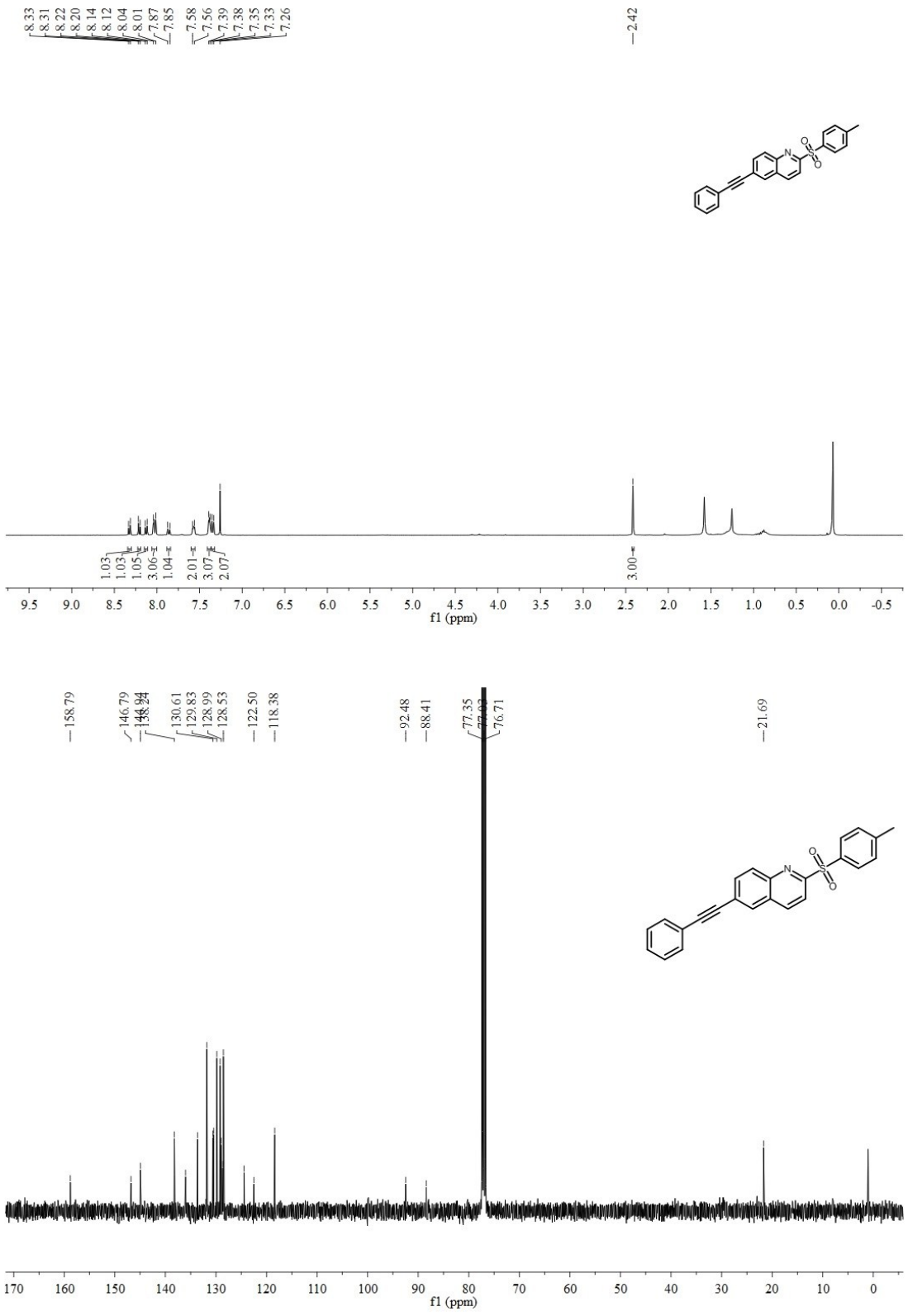


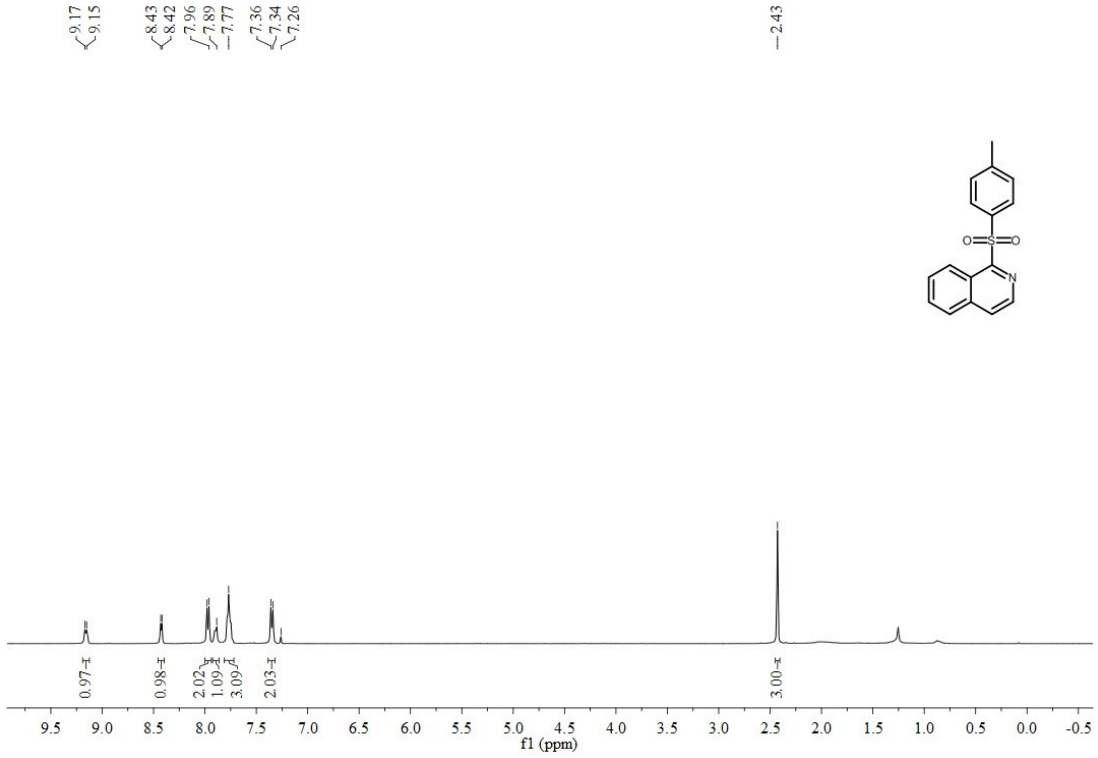
^{1}H, ^{13}C-NMR spectra of **3na**

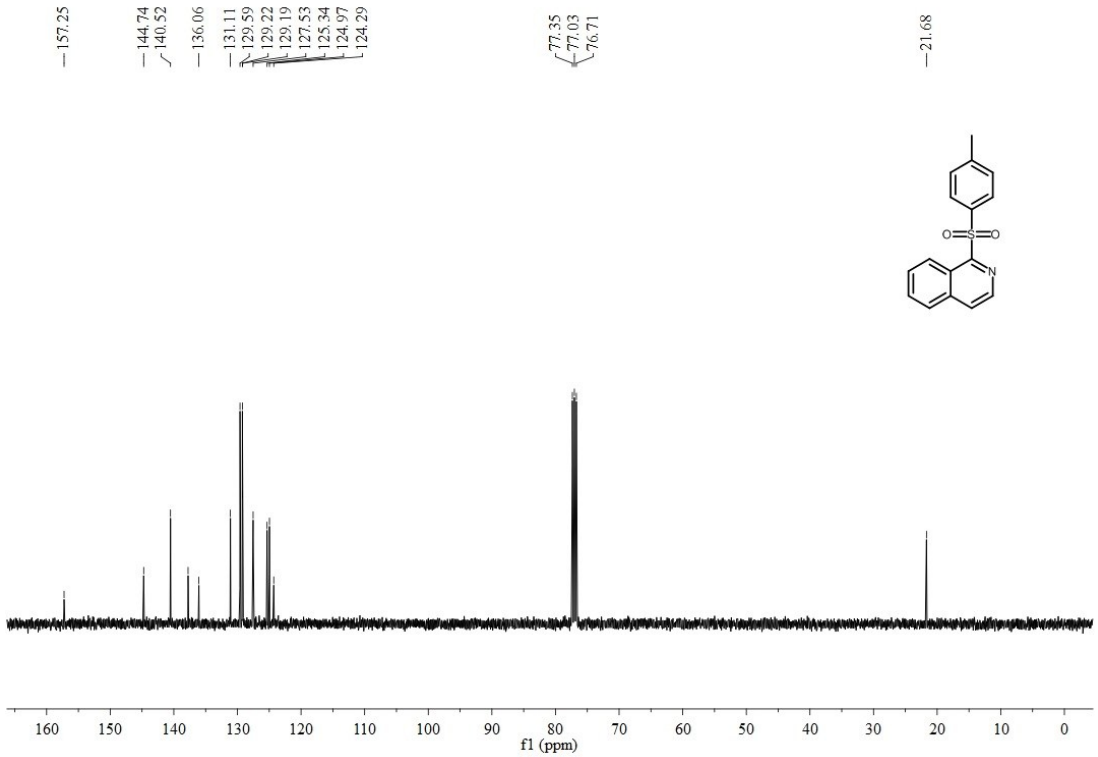


^{1}H, ^{13}C-NMR spectra of **3oa**

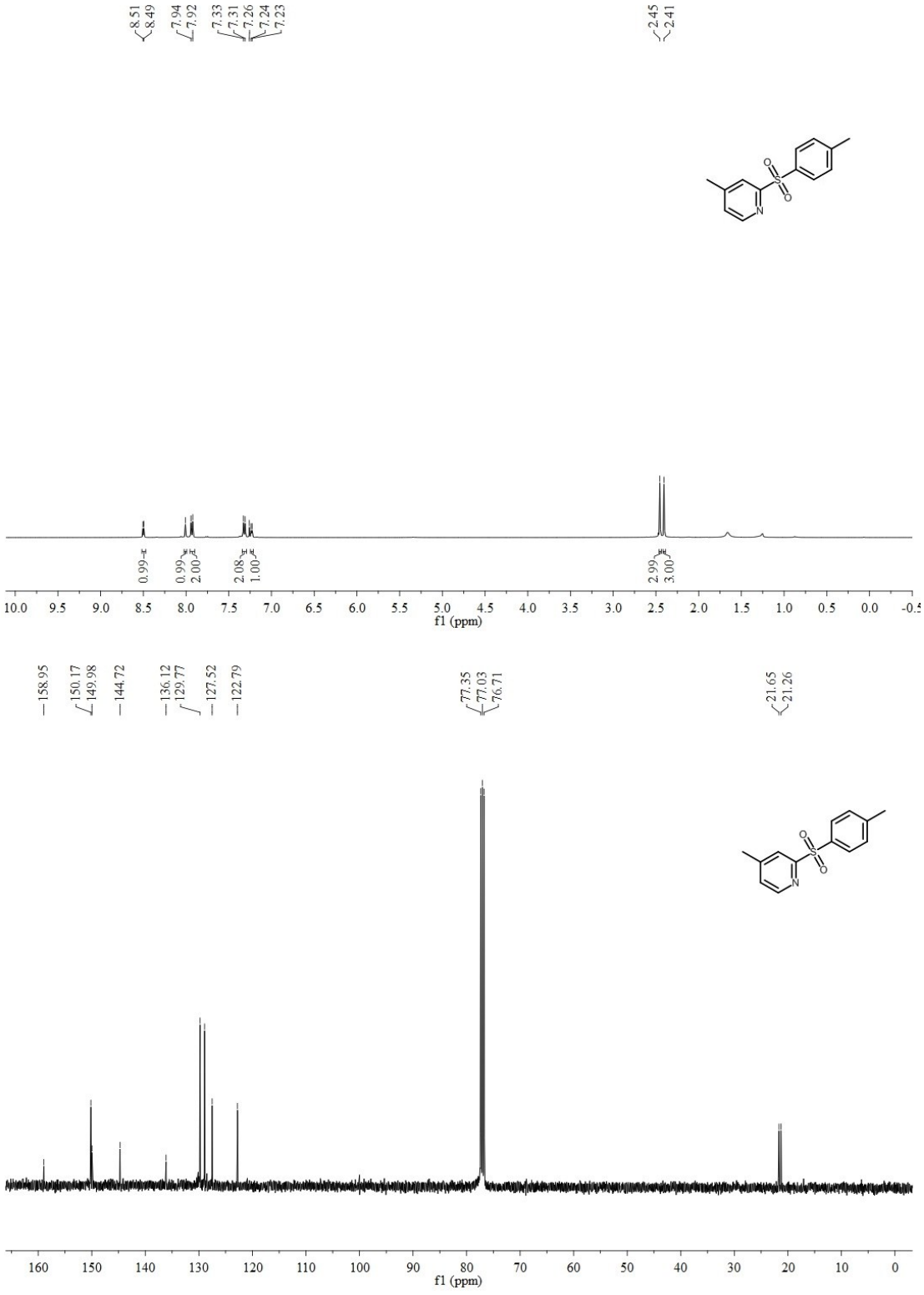


^{1}H, ^{13}C-NMR spectra of **3pa**

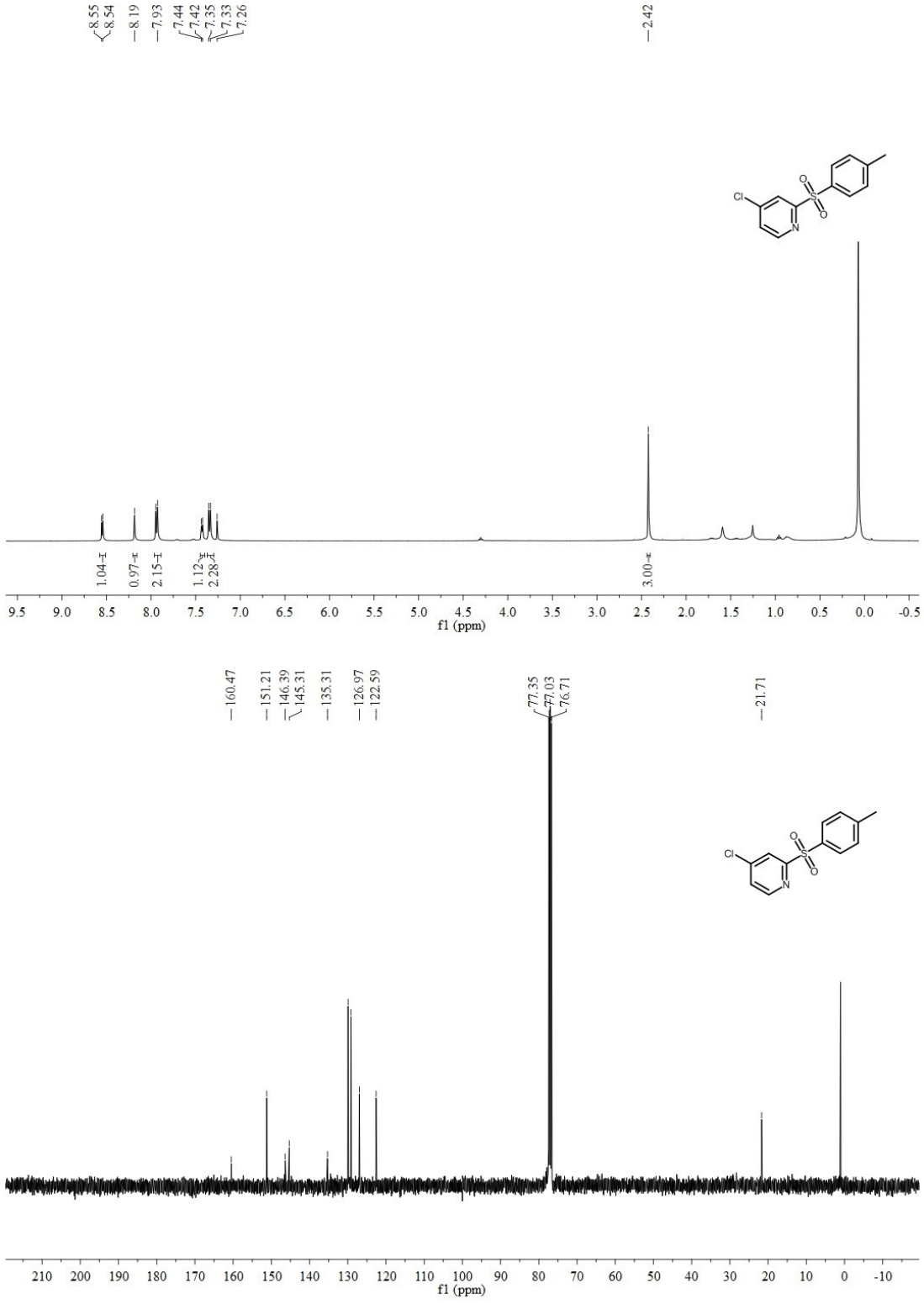




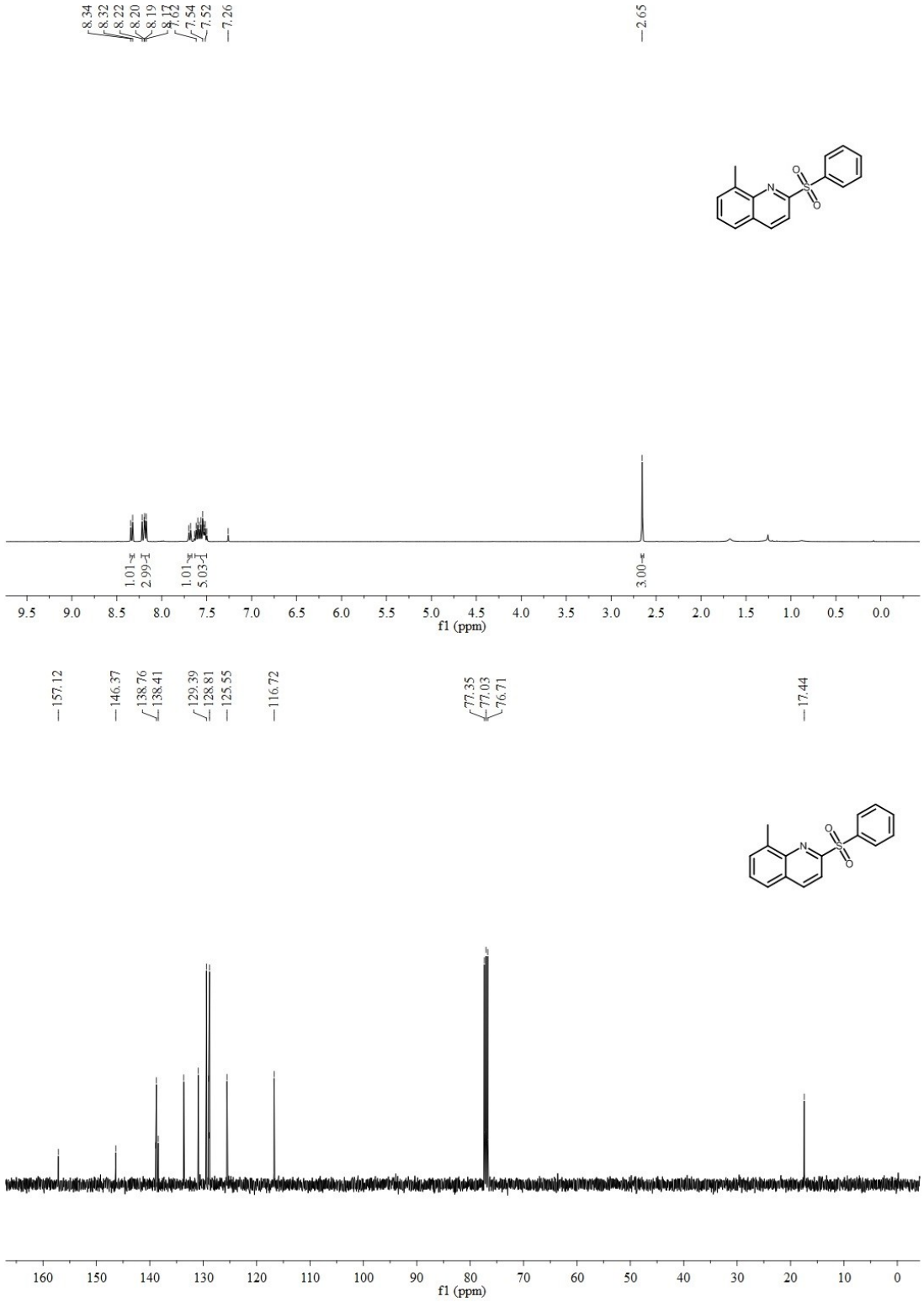
^{1}H, ^{13}C-NMR spectra of **3qa**



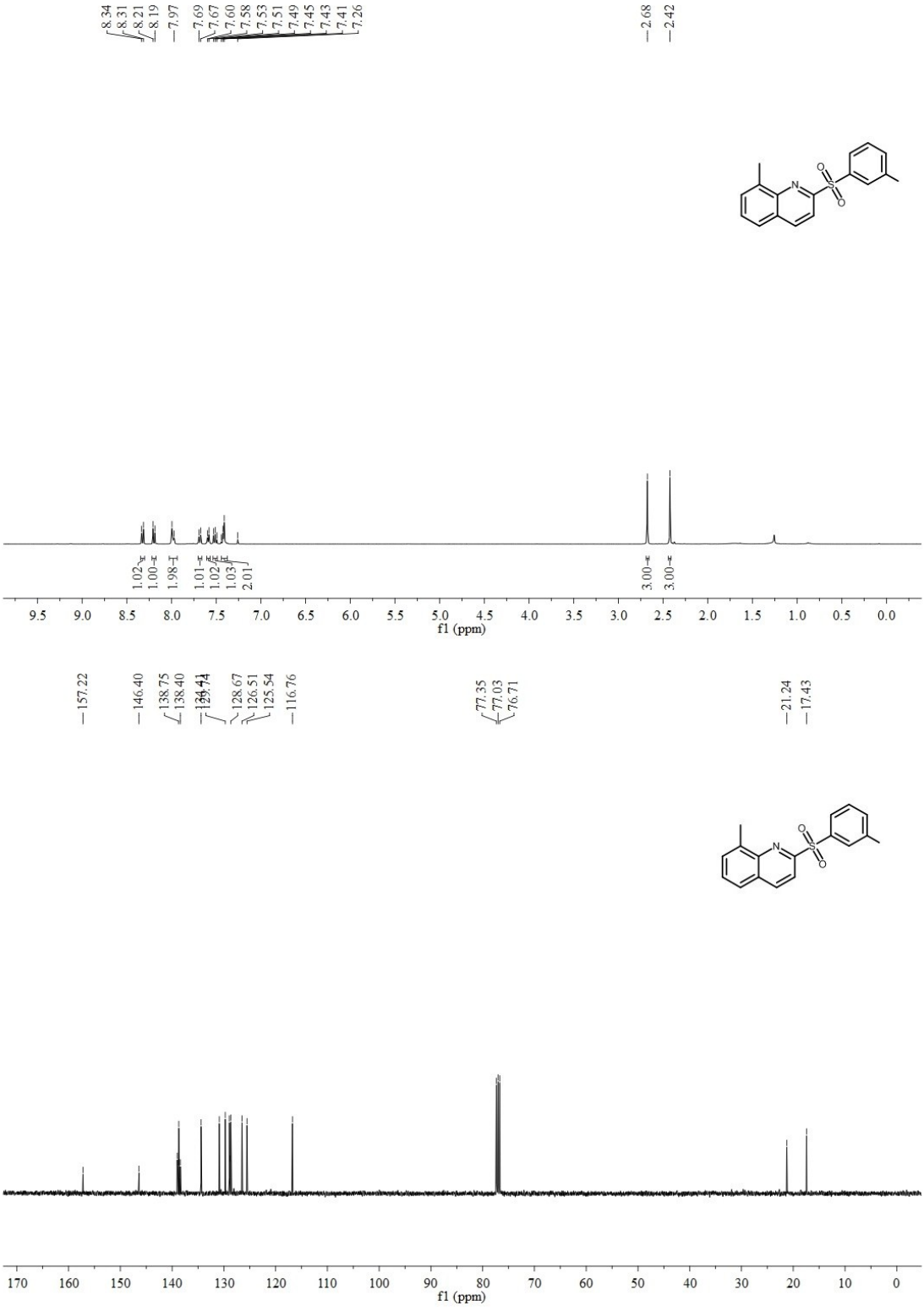
^{1}H, ^{13}C-NMR spectra of **3ra**



^{1}H, ^{13}C-NMR spectra of **3fb**



^{1}H, ^{13}C-NMR spectra of **3fc**



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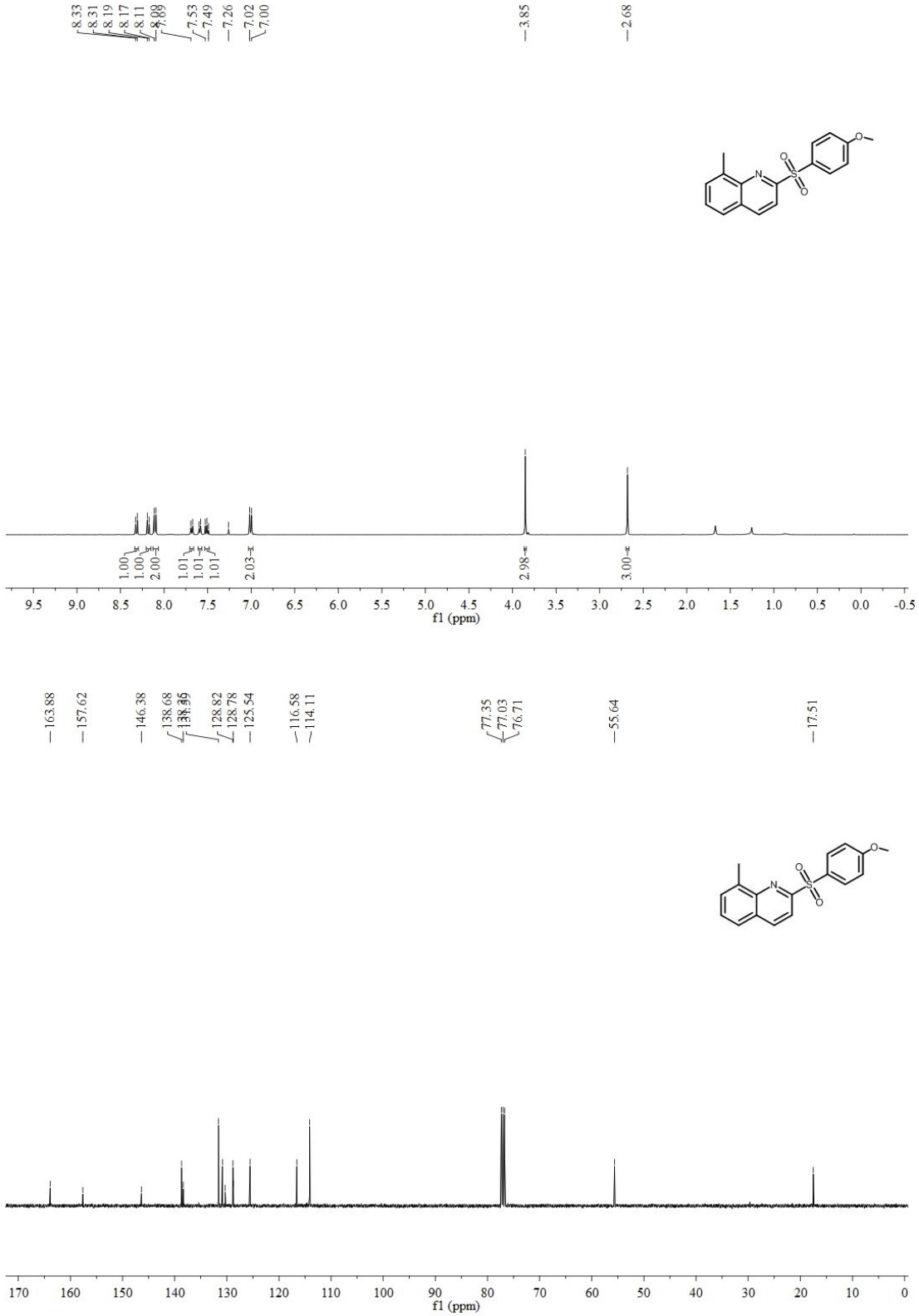
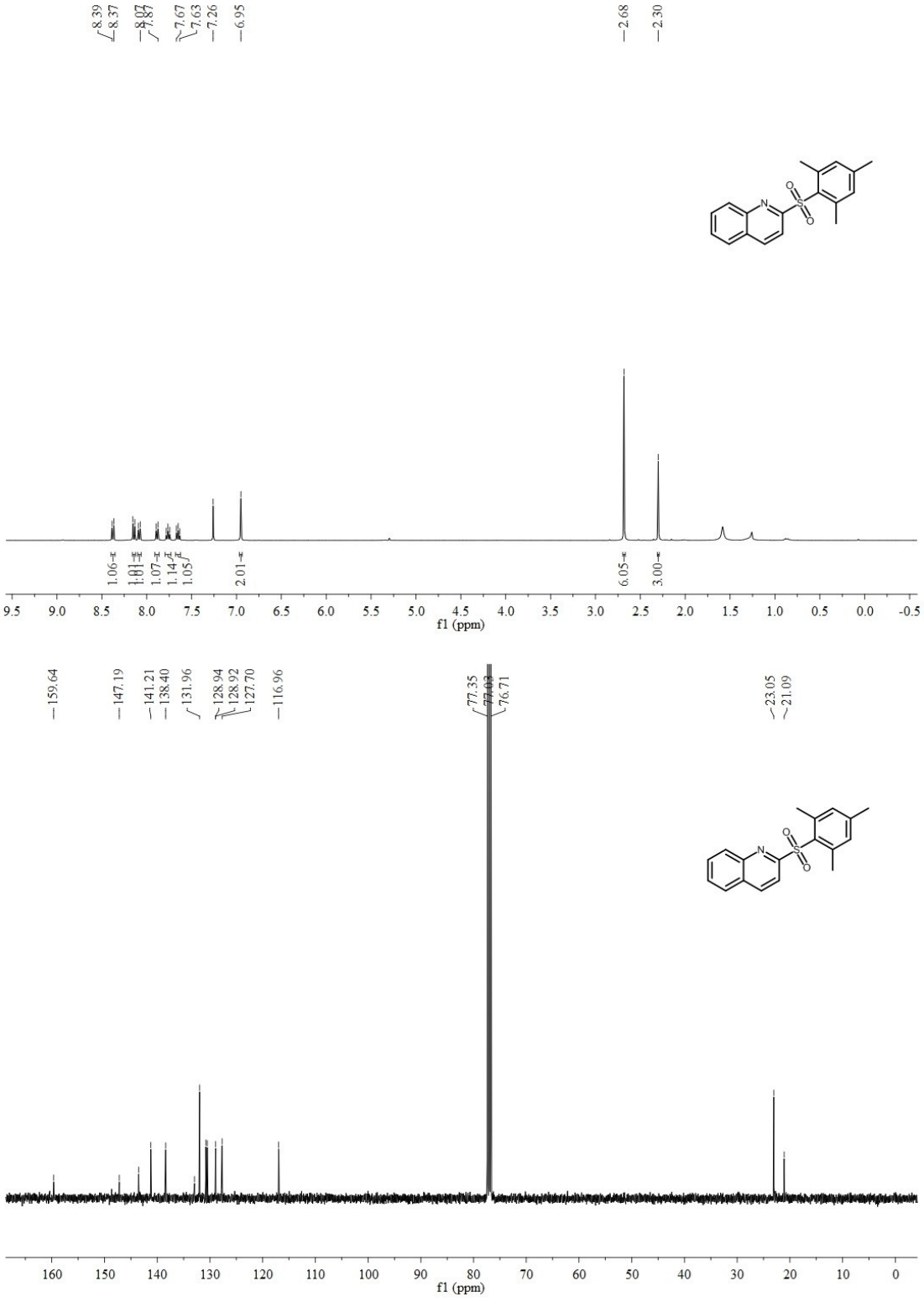
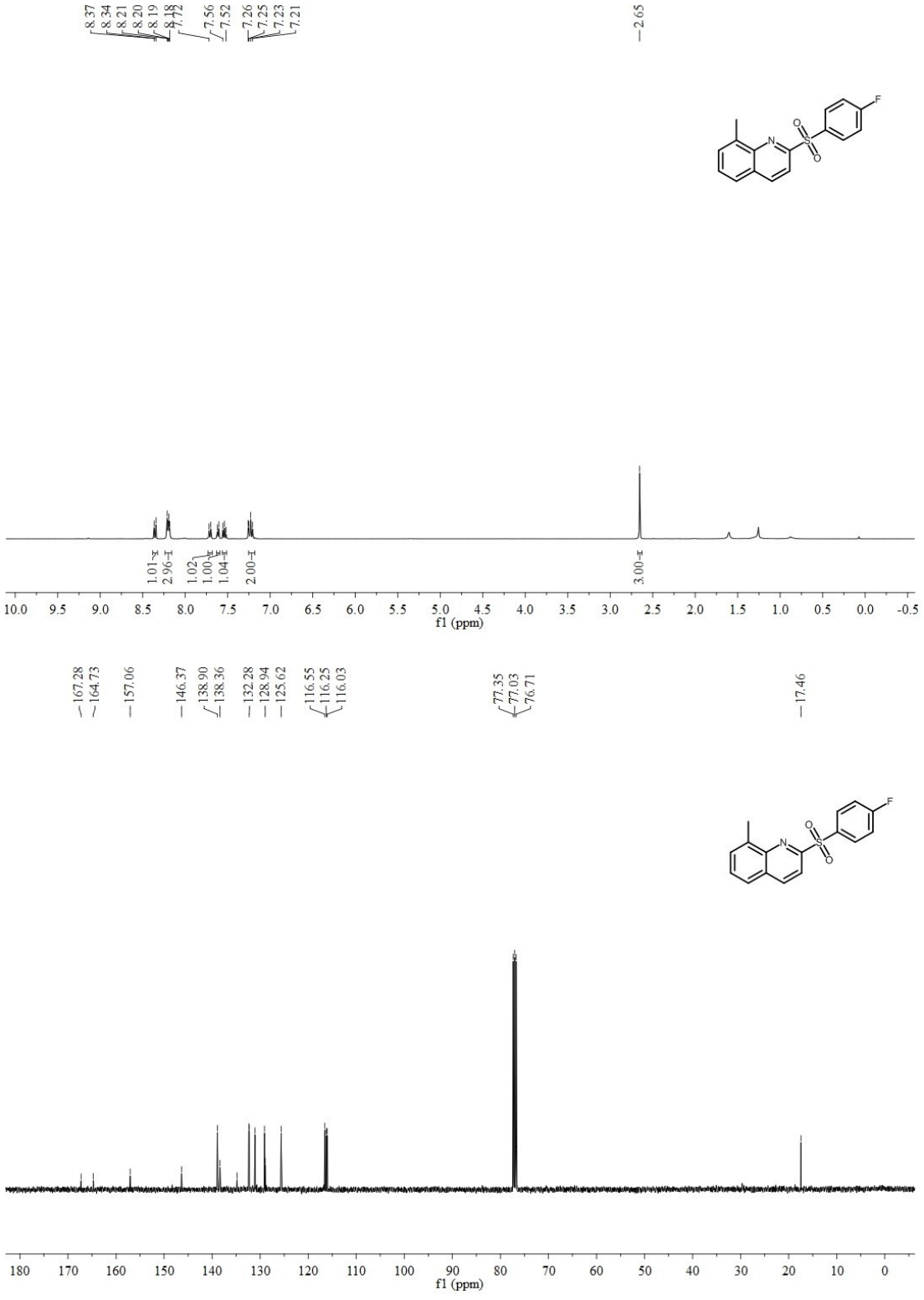


^{1}H, ^{13}C-NMR spectra of **3ae**



^{1}H, ^{13}C-NMR spectra of **3ff**



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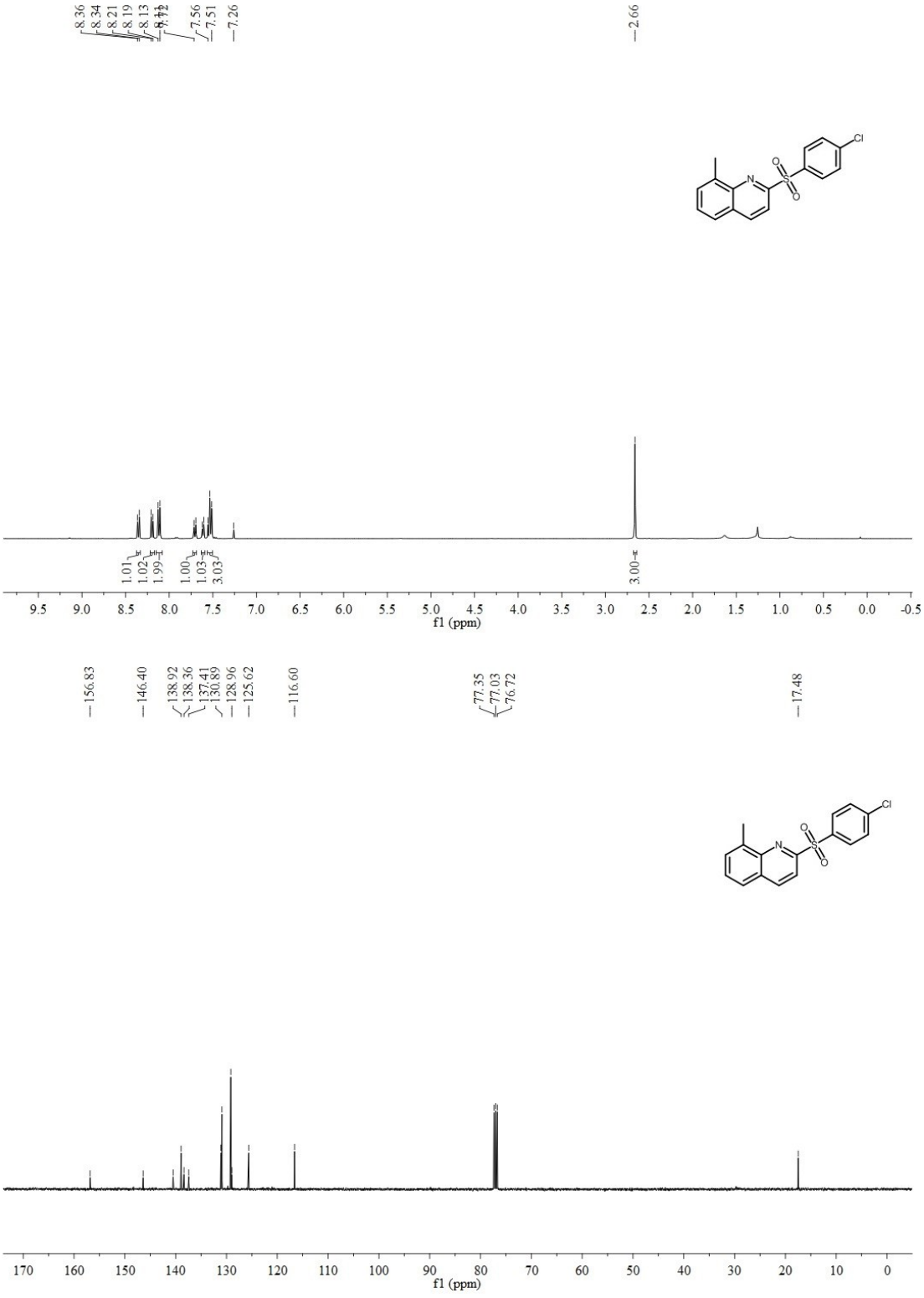
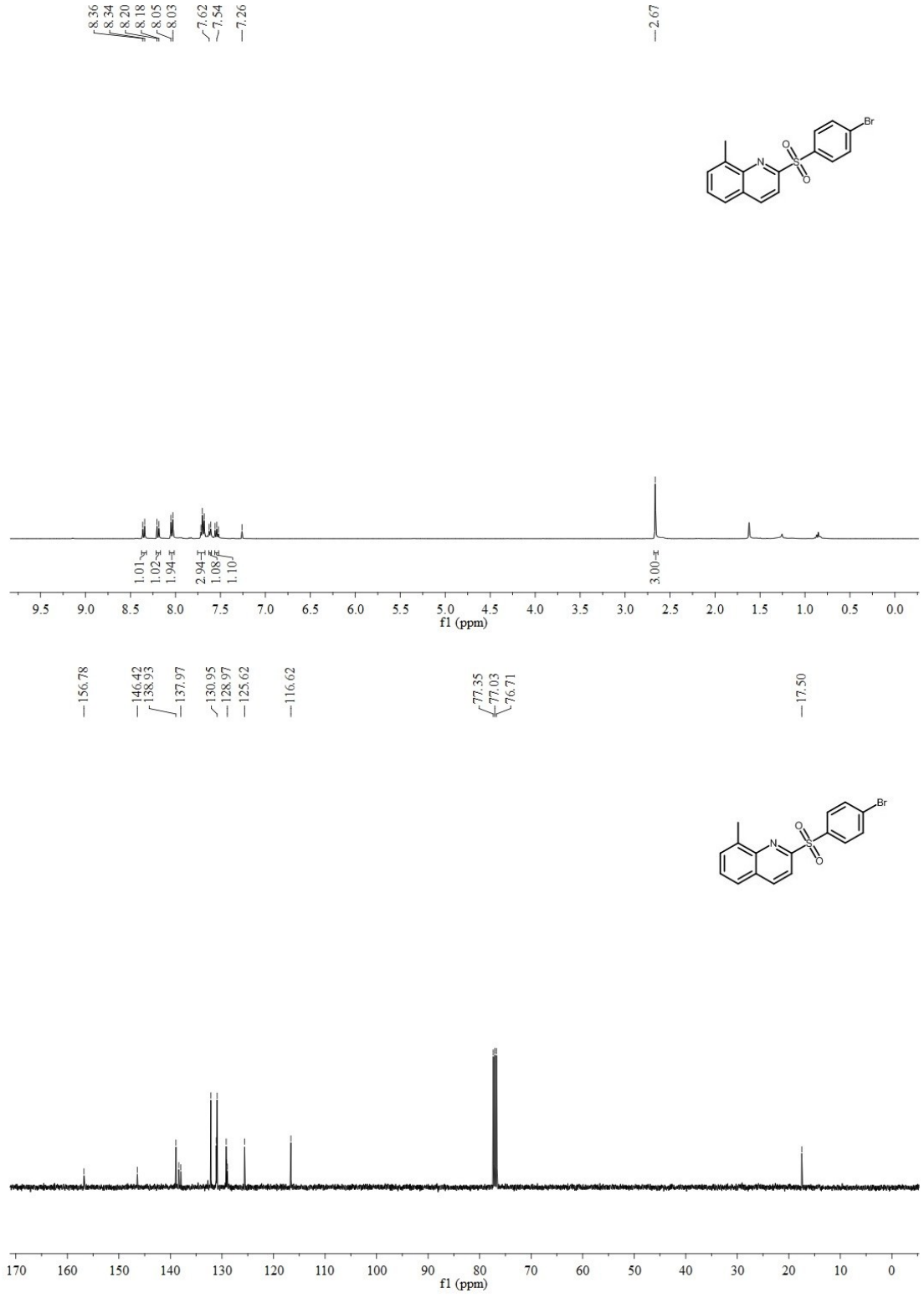


^{1}H, ^{13}C-NMR spectra of **3fh**



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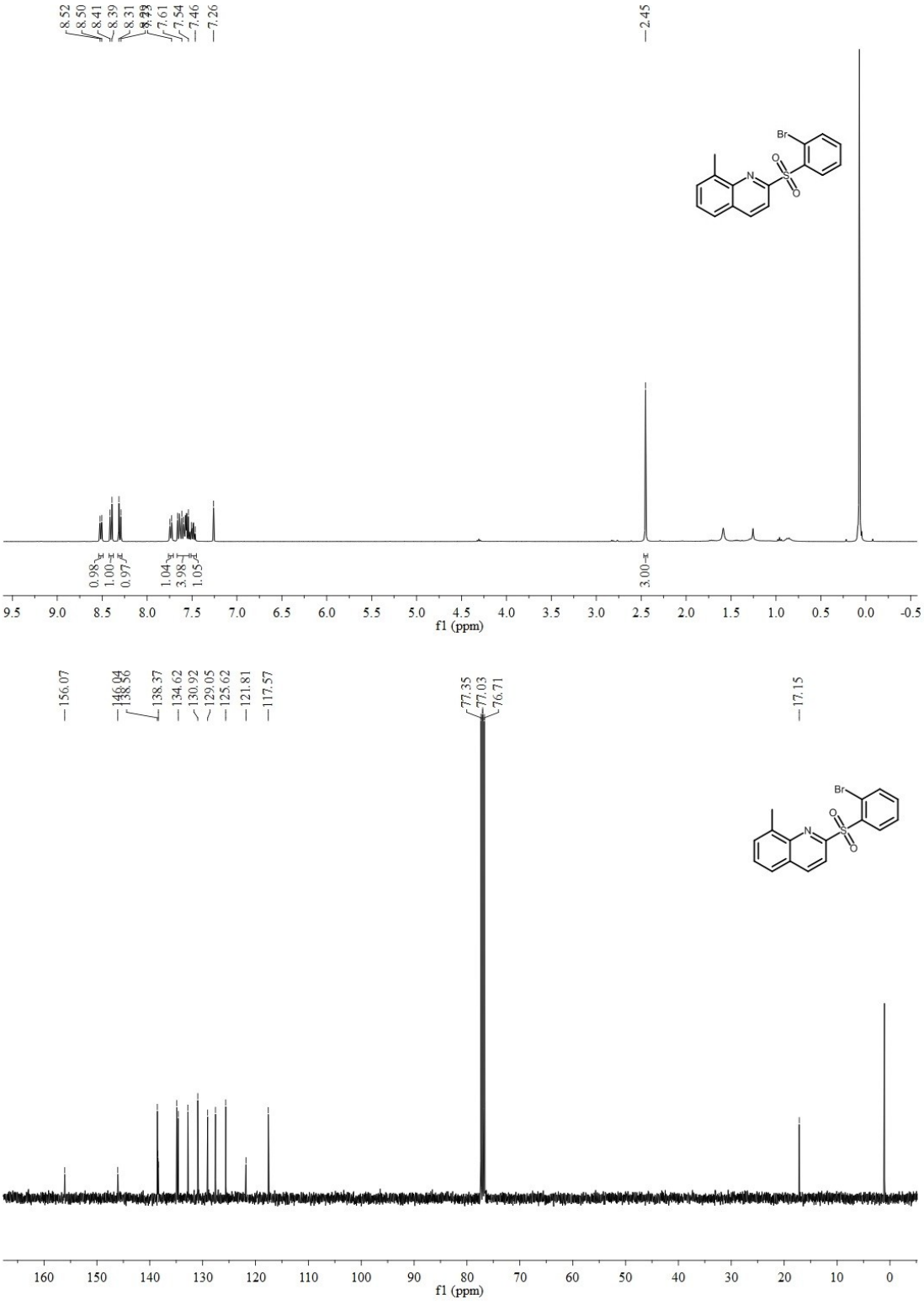

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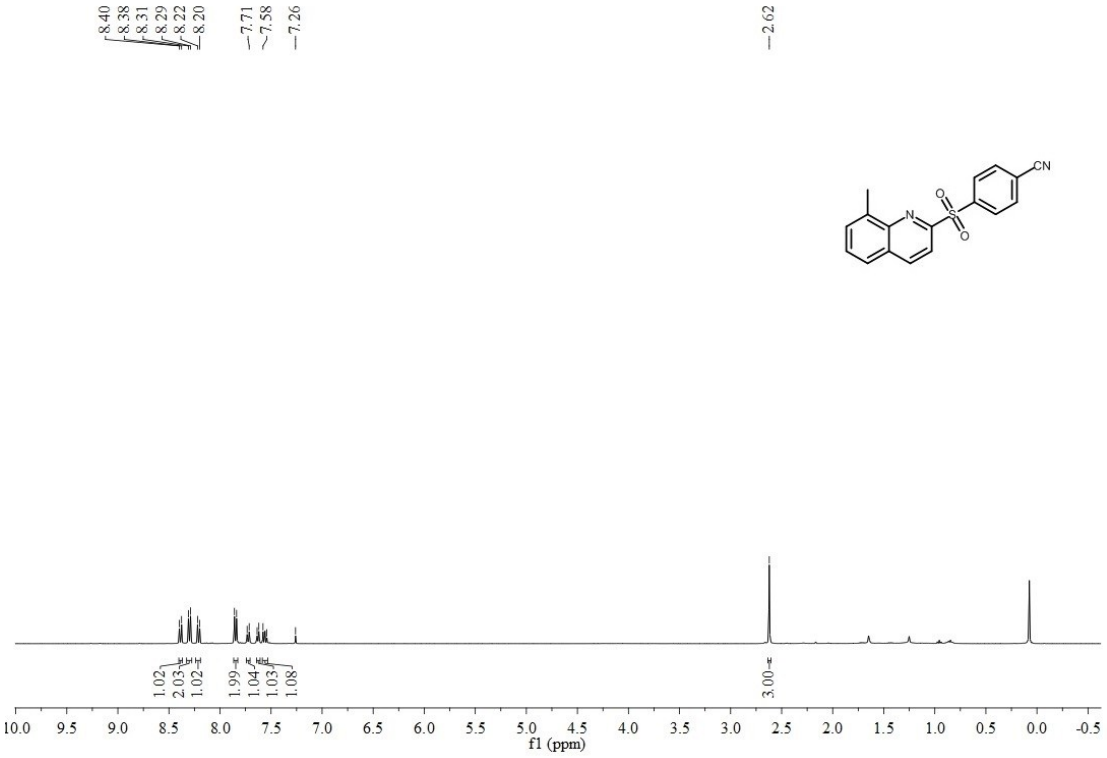
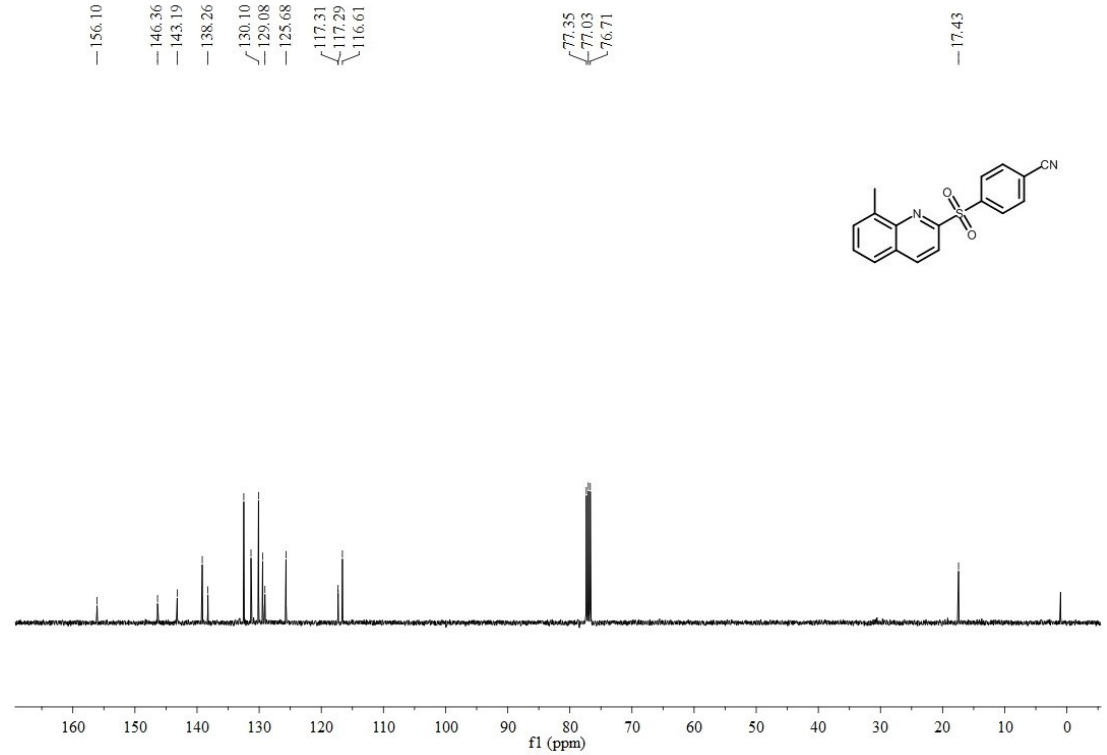
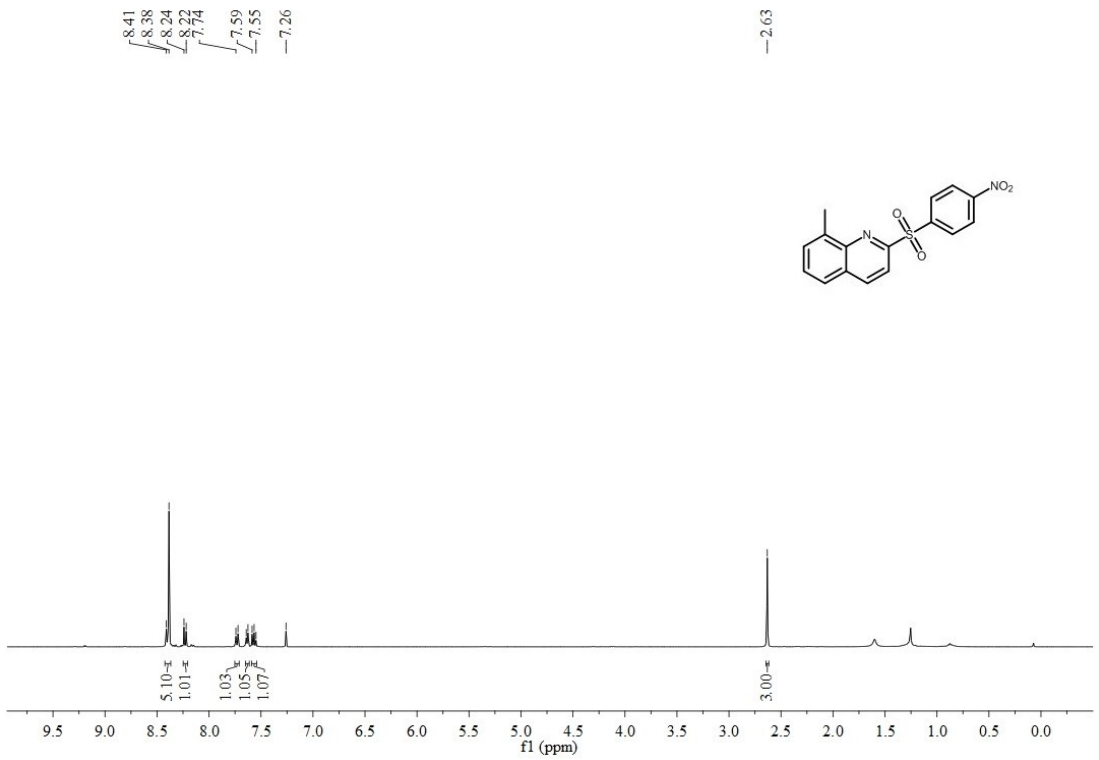
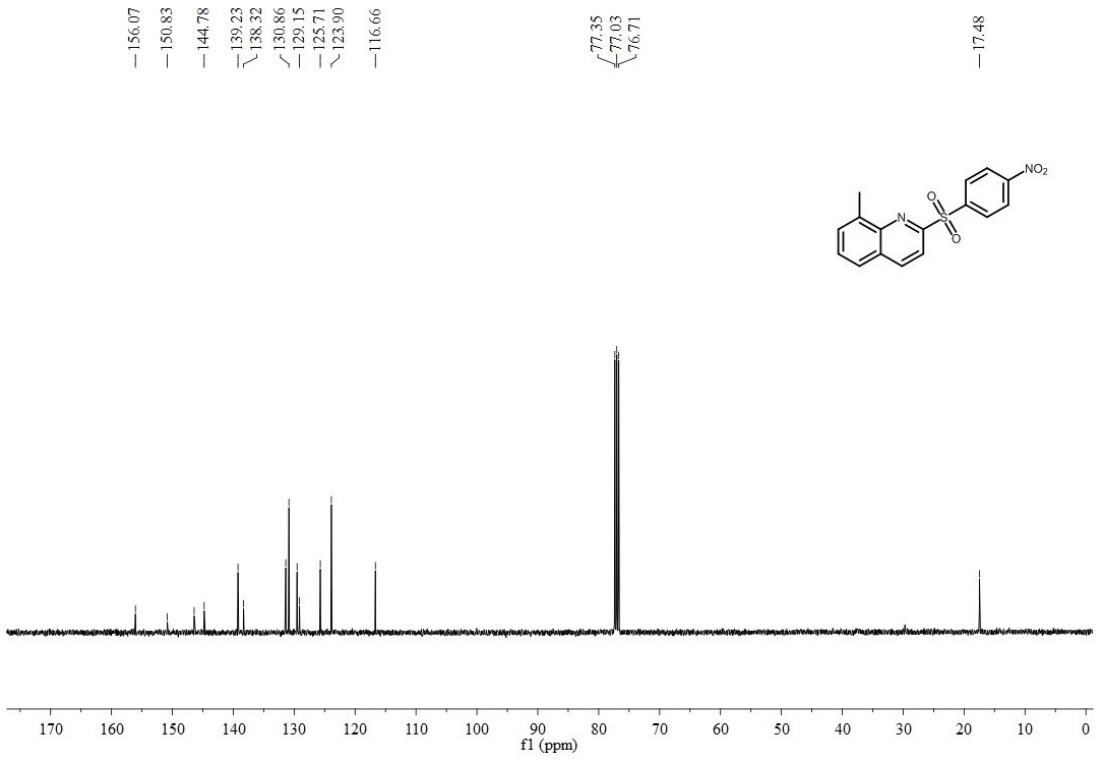


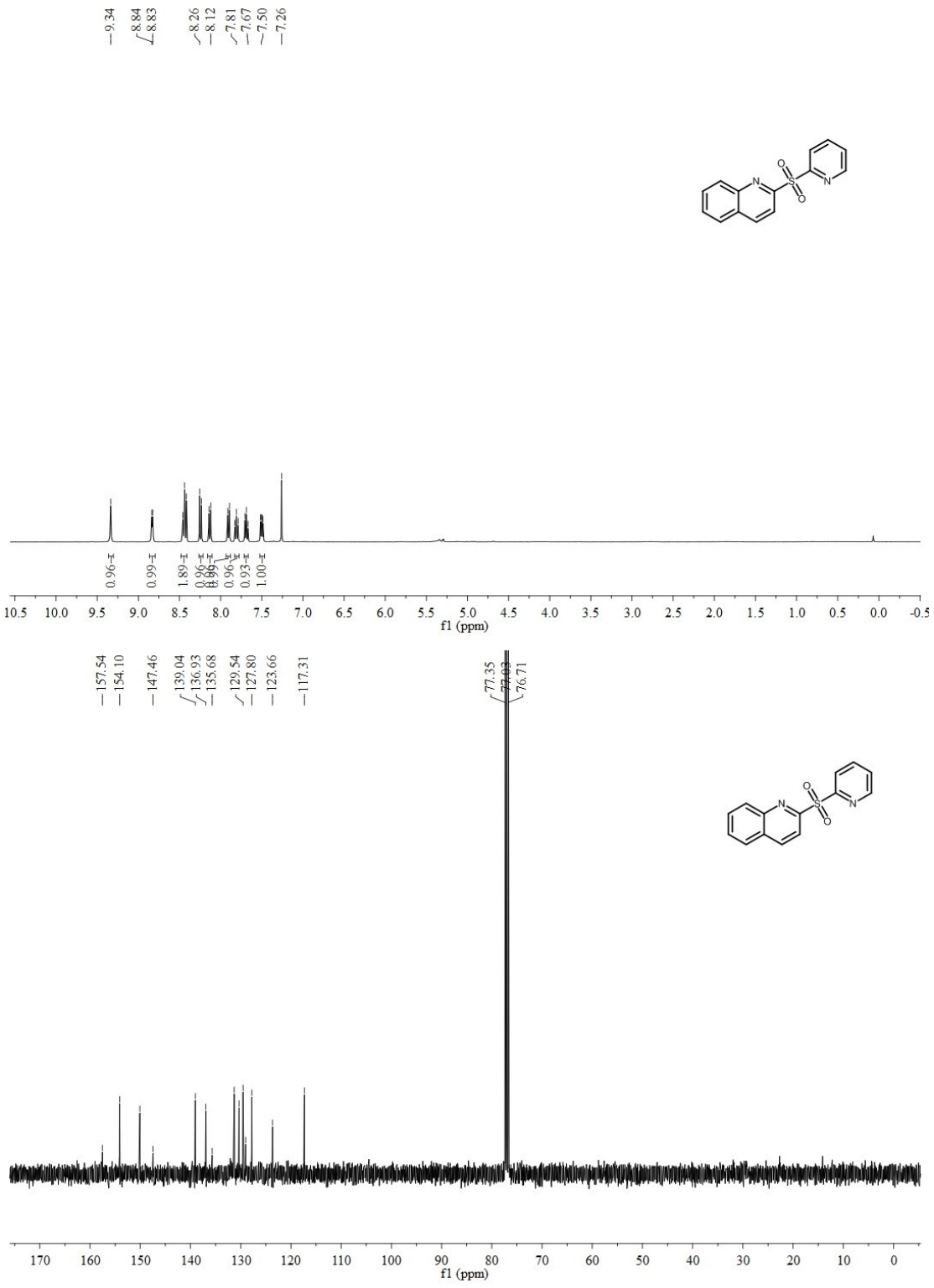


^{1}H, ^{13}C-NMR spectra of **3fk**

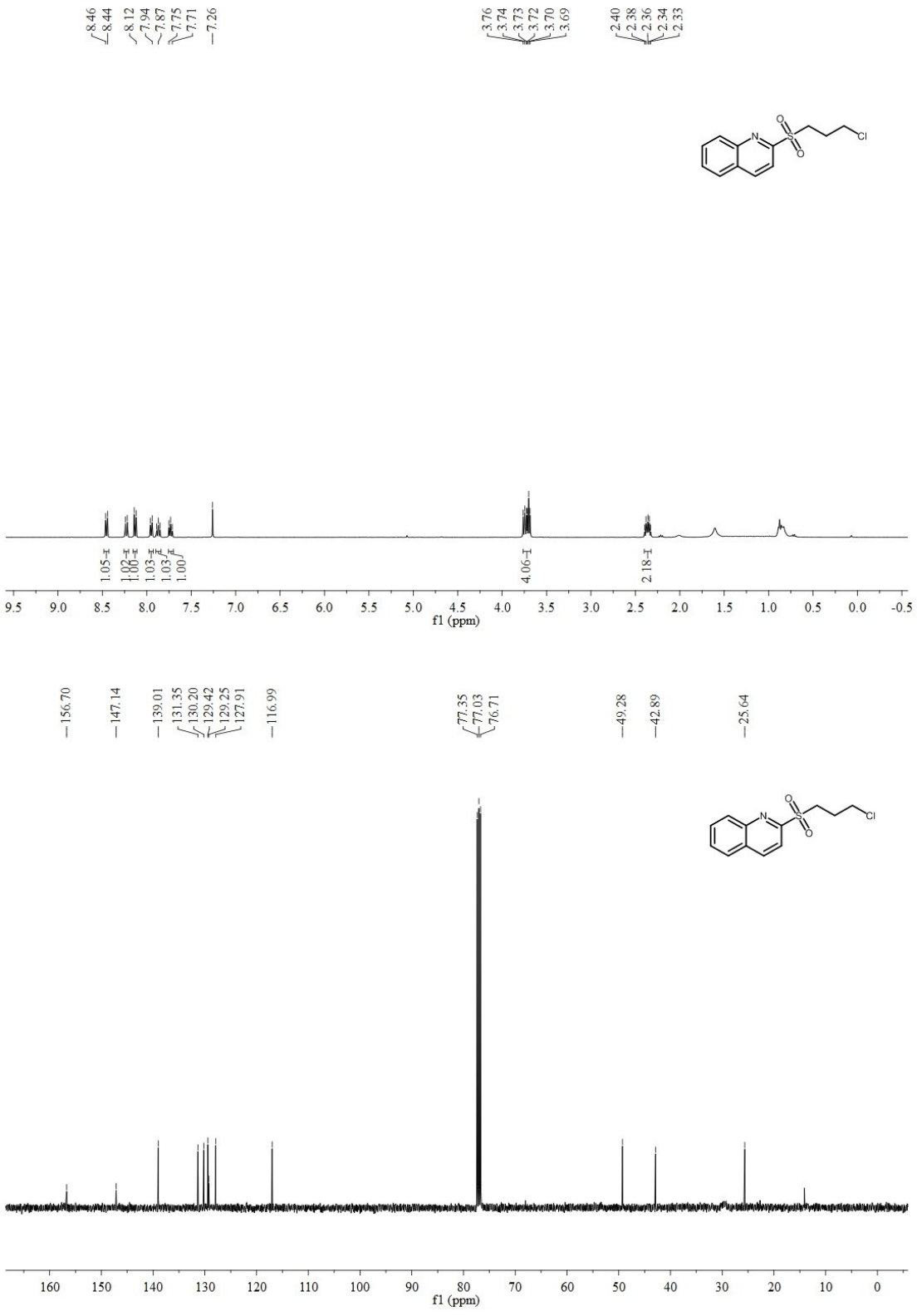




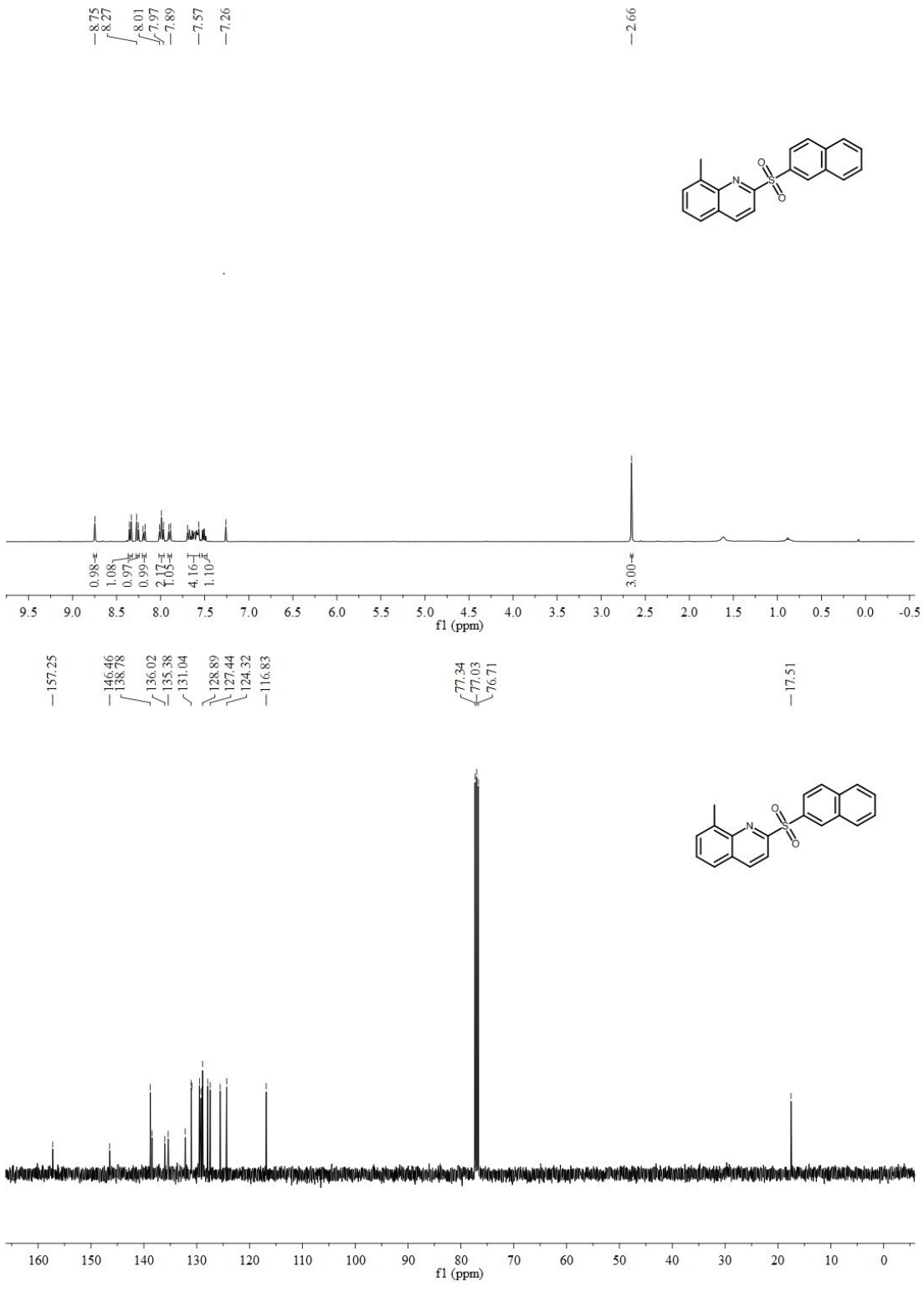
^{1}H, ^{13}C-NMR spectra of **3al**



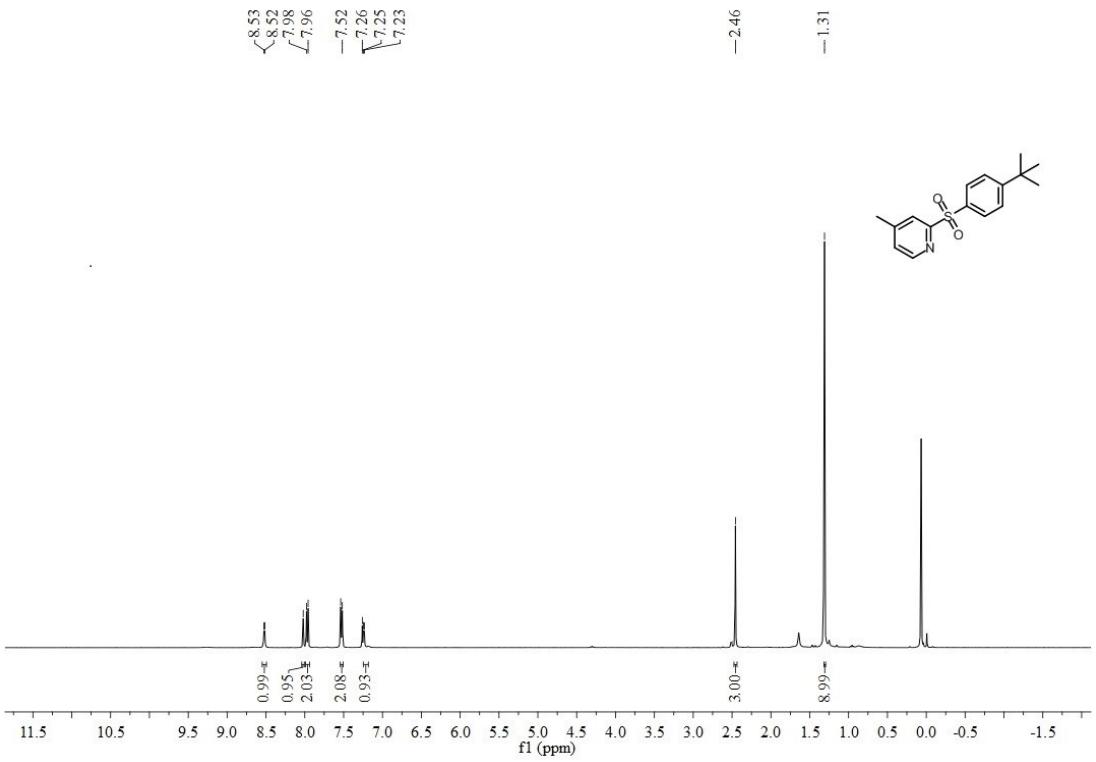
^{1}H, ^{13}C-NMR spectra of **3am**

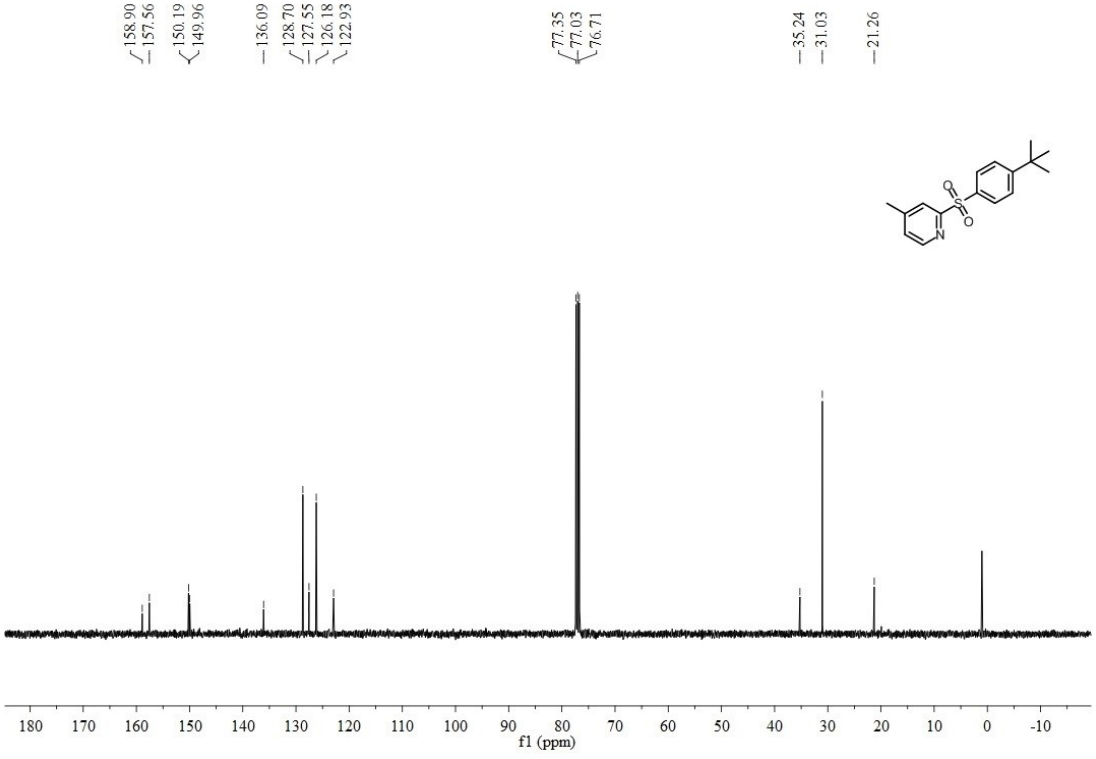


^{1}H, ^{13}C-NMR spectra of **3fn**

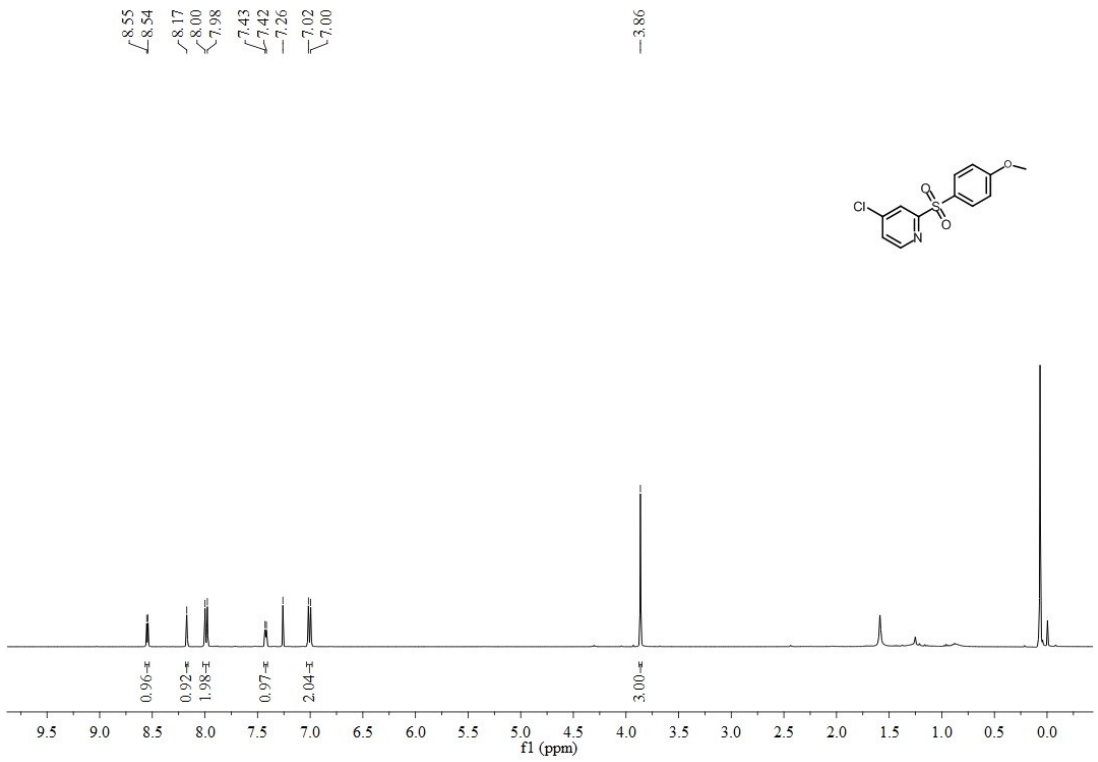


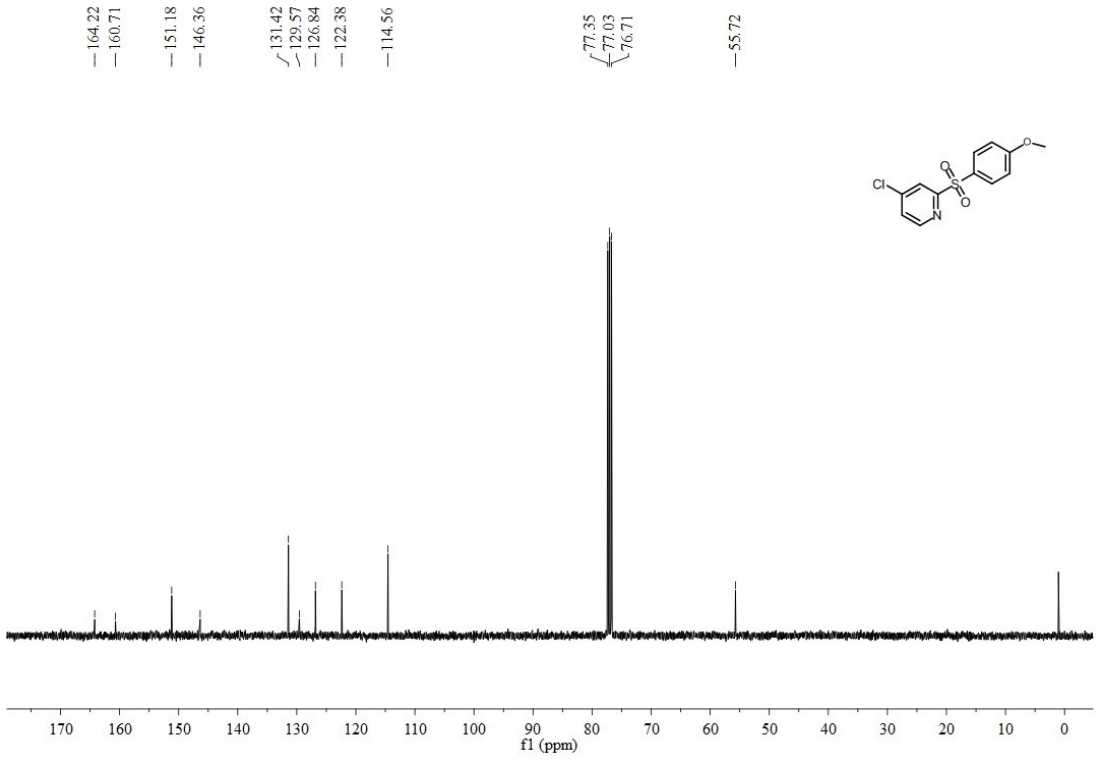
^{1}H, ^{13}C-NMR spectra of **3qo**





^{1}H, ^{13}C-NMR spectra of **3rd**





^{1}H, ^{13}C-NMR spectra of **4b**