Supporting Information

Synthesis of 1,3,4-thiadiazoles from elemental sulfur via three-component cyclization under metal-free conditions

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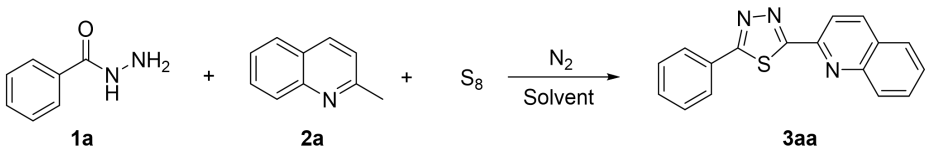
1. General information

All reactions were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (HRMS) was performed on Agilent 6230 TOF LC/MS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Most reagents were obtained from commercial suppliers and used without further purification.

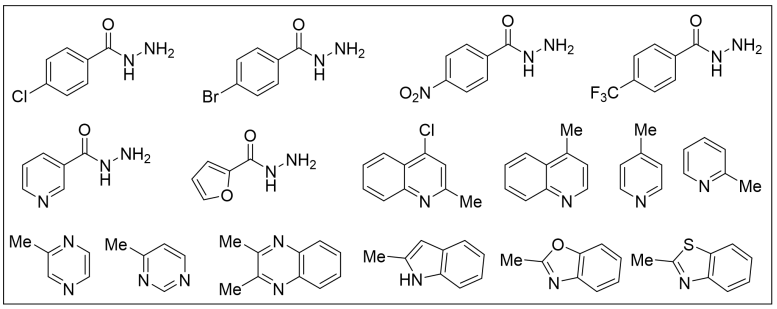
2. General procedure for Synthesis of 1,3,4-thiadiazoles from elemental sulfur via three-component cyclization under metal-free condition



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

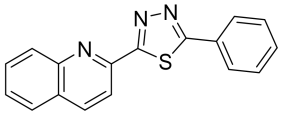
A 10 mL reaction vessel was charged with **1a** (0.2 mmol), **2a** (0.4 mmol), S_8 (0.075 mmol, 32 g/mol), DMSO (1.0 mL), under N_2(Repeat the vacuuming and nitrogen filling steps three times in total). The reaction vessel was stirred at 100 ^{o}C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL), then suction filtration and washed with saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.

3. Unsuccessful substrates



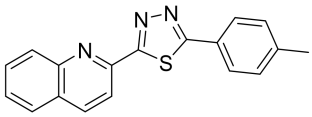
Scheme S1. Unsuccessful substrates.

4. Characterization data of products



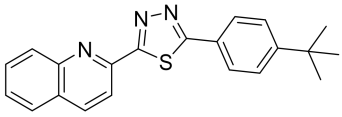
2-Phenyl-5-(quinolin-2-yl)-1,3,4-thiadiazole (3aa)[1] : 48.8 mg, 84%. Yellow solid. M.p. 240-242 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, J = 8.5, 2.4 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 8.03 (dd, J = 23.4, 6.0 Hz, 3H), 7.78 (d, J = 8.2 Hz, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.47 – 7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 149.1, 147.9, 137.2, 131.3, 130.2, 130.2, 129.5, 129.2, 128.8, 128.0, 127.8, 127.7, 118.3.



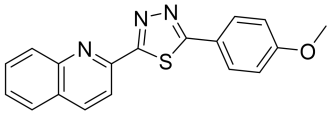
2-(Quinolin-2-yl)-5-(*p*-tolyl)-1,3,4-thiadiazole (3ba)[1] : 46.0 mg, 76%. White solid. M.p. 167-169 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.1 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 169.8, 149.0, 147.7, 141.6, 136.9, 130.0, 129.7, 129.3, 128.6, 127.8, 127.6, 127.5, 127.4, 118.1, 21.4.



2-(4-(Tert-butyl)phenyl)-5-(quinolin-2-yl)-1,3,4-thiadiazole (3ca) : 51.8 mg, 75%. White solid. M.p. 178-179 ℃.

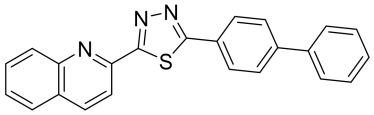
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.1 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.57 (dd, J = 30.9, 8.2 Hz, 3H), 1.37 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.0, 154.9, 149.2, 147.9, 137.1, 130.2, 129.4, 128.7, 127.8, 127.6, 127.5, 126.2, 118.3, 35.0, 31.1. HRMS (ESI) m/z calcd for $C_{21}H_{20}N_3S^+$ $(M+H)^+$ 346.1372, found 346.1359.



2-(4-Methoxyphenyl)-5-(quinolin-2-yl)-1,3,4-thiadiazole (3da)[1] : 44.7 mg, 70%. White solid. M.p. 178-180 ℃.

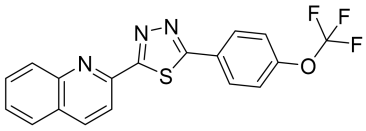
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.6

Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 169.6, 162.0, 149.2, 147.9, 137.1, 130.1, 129.5, 129.4, 128.6, 127.7, 127.6, 122.9, 118.3, 114.5, 55.4.



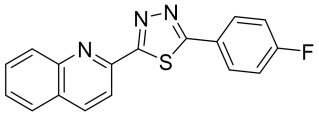
2-([1,1'-Biphenyl]-4-yl)-5-(quinolin-2-yl)-1,3,4-thiadiazole (3ea) : 51.8 mg, 71%. Orange solid. M.p. 185-187 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.3 Hz, 3H), 7.87 (d, J = 7.9 Hz, 1H), 7.80 – 7.70 (m, 3H), 7.69 – 7.63 (m, 2H), 7.63 – 7.56 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 170.1, 149.1, 147.9, 144.0, 139.8, 137.2, 130.2, 129.5, 129.1, 128.9, 128.8, 128.4, 128.0, 127.8, 127.8, 127.7, 127.1, 118.3. HRMS (ESI) m/z calcd for $C_{23}H_{16}N_3S^+$ $(M+H)^+$ 366.1059, found 366.1034.



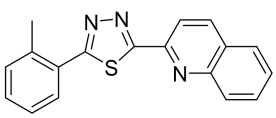
2-(Quinolin-2-yl)-5-(4-(trifluoromethoxy)phenyl)-1,3,4-thiadiazole (3fa) : 23.9 mg, 32%, Yellow solid. M.p. 204-206 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.12 (t, J = 8.0 Hz, 3H), 7.88 (d, J = 8.1 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 168.8, 151.2, 148.9, 147.9, 137.3, 130.3, 129.6, 129.5, 128.8, 128.8, 127.8, 127.8 121.4, 118.3 (d, J = 256.9 Hz), 118.3. HRMS (ESI) m/z calcd for $C_{18}H_{11}F_3N_3OS^+$ $(M+H)^+$ 374.0569, found 374.0553.



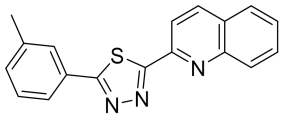
2-(4-Fluorophenyl)-5-(quinolin-2-yl)-1,3,4-thiadiazole (3ga)[1] : 29.5 mg, 48%, Yellow solid. M.p. 213-215 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 8.5 Hz, 1H), 8.30 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.07 (dd, J = 8.6, 5.3 Hz, 2H), 7.87 (d, J = 8.1 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 169.2, 164.5 (d, J = 251.1 Hz), 149.0, 147.9, 137.2, 130.3, 130.0 (d, J = 8.7 Hz), 129.5, 128.8, 127.8, 127.8, 126.6 (d, J = 3.3 Hz), 118.3, 116.4 (d, J = 22.0 Hz).



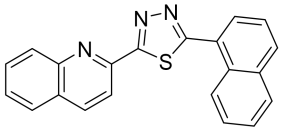
2-(Quinolin-2-yl)-5-(*o*-tolyl)-1,3,4-thiadiazole (3ha)[1] : 38.2 mg, 63%, Yellowish solid. M.p. 143-145 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 8.5 Hz, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 7.4 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.9, 149.2, 147.8, 137.4, 131.7, 130.8, 130.6, 130.3, 129.4, 129.4, 128.8, 127.8, 127.8, 126.3, 118.4, 21.8.



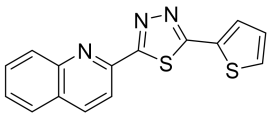
2-(Quinolin-2-yl)-5-(*m*-tolyl)-1,3,4-thiadiazole (3ia)[1] : 51.5 mg, 85%, Yellowish solid. M.p. 140-142 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.91 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.79 – 7.73 (m, 1H), 7.63 – 7.55 (m, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.3, 149.1, 147.9, 139.0, 137.1, 132.1, 130.2, 130.1, 129.5, 129.1, 128.7, 128.5, 127.8, 127.7, 125.2, 118.3, 21.3.



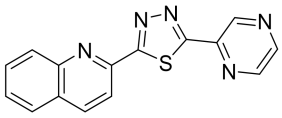
2-(Naphthalen-1-yl)-5-(quinolin-2-yl)-1,3,4-thiadiazole (3ja) : 21.0 mg, 31%. White solid. M.p. 200-202 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, J = 8.5 Hz, 1H), 8.55 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.90 (s, 1H), 7.81 – 7.71 (m, 1H), 7.67 – 7.54 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 169.8, 149.2, 148.0, 137.3, 133.9, 131.6, 130.6, 130.3, 129.9, 129.5, 128.8, 128.5, 127.8, 127.8, 127.8, 127.0, 126.7, 125.7, 125.1, 118.3. HRMS (ESI) m/z calcd for $C_{21}H_{14}N_3S^+$ $(M+H)^+$ 340.0903, found 340.0887.



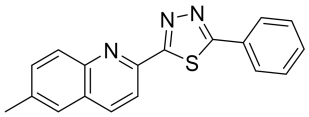
2-(Quinolin-2-yl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (3ka)[1] : 18.8 mg, 32%. Red solid. M.p. 212-214 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, J = 8.5 Hz, 1H), 8.30 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.67 (d, J = 3.6 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.20 – 7.15 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 164.2, 14 9.0, 147.9, 137.2, 132.6, 130.3, 130.0, 129.7, 129.4, 128.8, 128.1, 127.8, 127.7, 118.4.



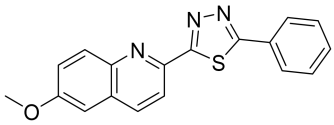
2-(Pyrazin-2-yl)-5-(quinolin-2-yl)-1,3,4-thiadiazole (3la) : 16.2 mg, 28%. Yellow solid. M.p. 24 4-246 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.76 – 8.64 (m, 2H), 8.50 (d, J = 8.5 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.62 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 169.6, 148.8, 147.9, 145.9, 145.1, 144.3, 142. 5, 137.3, 130.3, 129.6, 128.9, 127.9, 127.8, 118.3. HRMS (ESI) m/z calcd for $C_{15}H_{10}N_5S^+$ $(M+H)^+$ 292. 0651, found 292.0638.



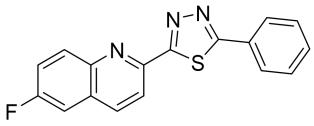
2-(6-Methylquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3ab)[1] : 46.1 mg, 76%. Yellow solid. M. p. 162-164 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 8.06 (dd, J = 6.6, 2.9 Hz, 2H), 8.00 (d, J = 8.5 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.54 – 7.48 (m, 3H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 170.1, 148.2, 146.5, 137.9, 136.4, 132.5, 131.2, 130.2, 129.1, 129.1, 128.8, 127.9, 126.6, 118.3, 21.7.



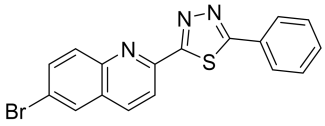
2-(6-Methoxyquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3ac)[1] : 28.1 mg, 44%. White solid. M. p. 217-219 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.12 – 7.96 (m, 3H), 7.51 (s, 3H), 7.40 (d, J = 8.1 Hz, 1H), 7.10 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 158.7, 146.8, 144.0, 135.6, 131.1, 130.9, 130.4, 130.1, 129.2, 127.9, 123.1, 118.6, 105. 2, 55.6.



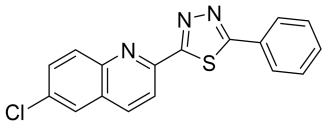
2-(6-Fluoroquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3ad)[1] : 29.5mg, 48%. Orange solid. M.p. 211-213 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.15 – 8.09 (m, 1H), 8.06 (d, *J* = 4.7 Hz, 2H), 7.50 (d, *J* = 13.2 Hz, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.4, 170.0, 161.1 (d, *J* = 249.3 Hz), 148.6, 145.0, 136.5 (d, *J* = 5.49 Hz), 132.0 (d, *J* = 9.5 Hz), 131.3, 130.2, 129.5 (d, *J* = 10.3 Hz), 129.2, 128.0, 120.6(d, *J* = 25.8 Hz), 119.1, 110.9(d, *J* = 21.9 Hz).



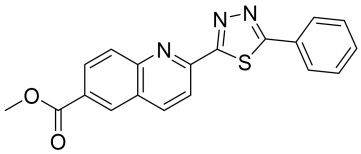
2-(6-Bromoquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3ae)[1] : 40.4 mg, 55%. Orange solid. M.p. 194-196 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.48 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 8.10 – 8.04 (m, 2H), 8.02 (d, *J* = 1.9 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.81 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.55 – 7.49 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 170.6, 169.9, 149.4, 146.4, 136.1, 133.7, 131.4, 131.1, 130.1, 129.8, 129.7, 129.2, 128.0, 121.8, 119.2.



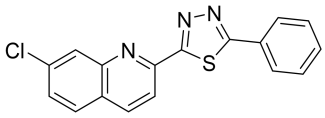
2-(6-Chloroquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3af) : 35.5 mg, 55%. Yellow solid. M.p. 90-92 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 3H), 7.83 (s, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.5, 169.9, 149.4, 146.2, 136.2, 133.5, 131.3, 131.2, 131.0, 130.1, 129.2, 129.2, 128.0, 126.5, 119.2. HRMS (ESI) m/z calcd for $C_{17}H_{10}ClN_3NaS^+$ $(M+Na)^+$ 346.0176, found 346.0159.



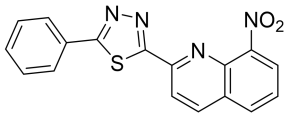
Methyl 2-(5-phenyl-1,3,4-thiadiazol-2-yl)quinoline-6-carboxylate (3ag) : 32.6 mg, 47%. Pale pink solid. M.p. 206-208 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 1.6 Hz, 1H), 8.51 (d, J = 8.6 Hz, 1H), 8.37 (d, J = 8.6 Hz, 1H), 8.32 (dd, J = 8.8, 1.8 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.06 (dd, J = 6.5, 3.1 Hz, 2H), 7.51 (dd, J = 5.0, 1.8 Hz, 3H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 169.8, 166.3, 151.0, 149.7, 138.4, 131.4, 130.7, 130.1, 129.7, 129.2, 128.9, 128.0, 127.8, 119.1, 52.5. HRMS (ESI) m/z calcd for $C_{19}H_{14}N_3O_2S^+$ $(M+H)^+$ 348.0801, found 348.0787.



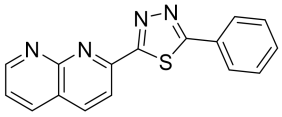
2-(7-Chloroquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3ah)[1] : 31.0 mg, 48%. Yellow solid. M.p. 218-220 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 1.7 Hz, 1H), 8.06 (dd, J = 6.5, 3.1 Hz, 2H), 7.78 (d, J = 8.7 Hz, 1H), 7.55 – 7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.9, 150.0, 148.2, 137.0, 136.2, 131.4, 130.1, 129.2, 128.9, 128.7, 128.4, 128.0, 127.0, 118.5.



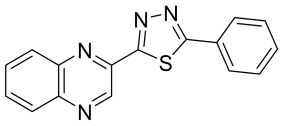
2-(8-Nitroquinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (3ai) : 30.7 mg, 46%. Yellow solid. M.p. 211-213 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (d, J = 8.6 Hz, 1H), 8.49 (d, J = 8.6 Hz, 1H), 8.34 (d, J = 7.9 Hz, 2H), 8.12 – 7.98 (m, 2H), 7.80 (t, J = 7.9 Hz, 1H), 7.54 (d, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.0, 169.4, 150.7, 147.6, 139.3, 138.5, 133.0, 132.3, 130.0, 129.8, 129.5, 128.4, 127.6, 125.5, 120.1. HRMS (ESI) m/z calcd for $C_{17}H_{11}N_4O_2S^+$ $(M+H)^+$ 335.0597, found 335.0584.



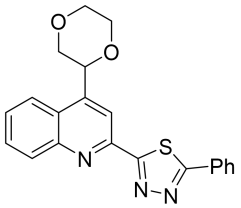
2-(1,8-Naphthyridin-2-yl)-5-phenyl-1,3,4-thiadiazole (3aj) : 26.0 mg, 45%. White solid. M.p. 231-233 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, J = 4.2, 1.9 Hz, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.25 (dd, J = 8.1, 1.9 Hz, 1H), 8.05 (dd, J = 6.7, 2.9 Hz, 2H), 7.56 – 7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 169.6, 155.5, 154.5, 152.2, 138.5, 137.0, 131.4, 130.0, 129.2, 128.0, 123.6, 122.9, 119.5. HRMS (ESI) m/z calcd for $C_{16}H_{11}N_4S^+$ $(M+H)^+$ 291.0699, found 291.0681.



2-Phenyl-5-(quinoxalin-2-yl)-1,3,4-thiadiazole (3ak)[1] : 43.9 mg, 76%. Orange solid. M.p. 193-195 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.15 (dd, J = 6.3, 3.5 Hz, 1H), 8.11 (dd, J = 6.3, 3.5 H z, 1H), 8.06 (dd, J = 7.3, 2.0 Hz, 2H), 7.81 (dd, J = 6.4, 3.4 Hz, 2H), 7.51 (t, J = 5.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 167.9, 143.8, 142.8, 142.6, 141.7, 131.5, 131.1, 130.8, 129.7, 129.4, 129.3, 129.2, 128.0.



2-(4-(1,4-Dioxan-2-yl)quinolin-2-yl)-5-phenyl-1,3,4-thiadiazole (4) : 36.0mg, 48%. White solid. M.p. 232-234℃.

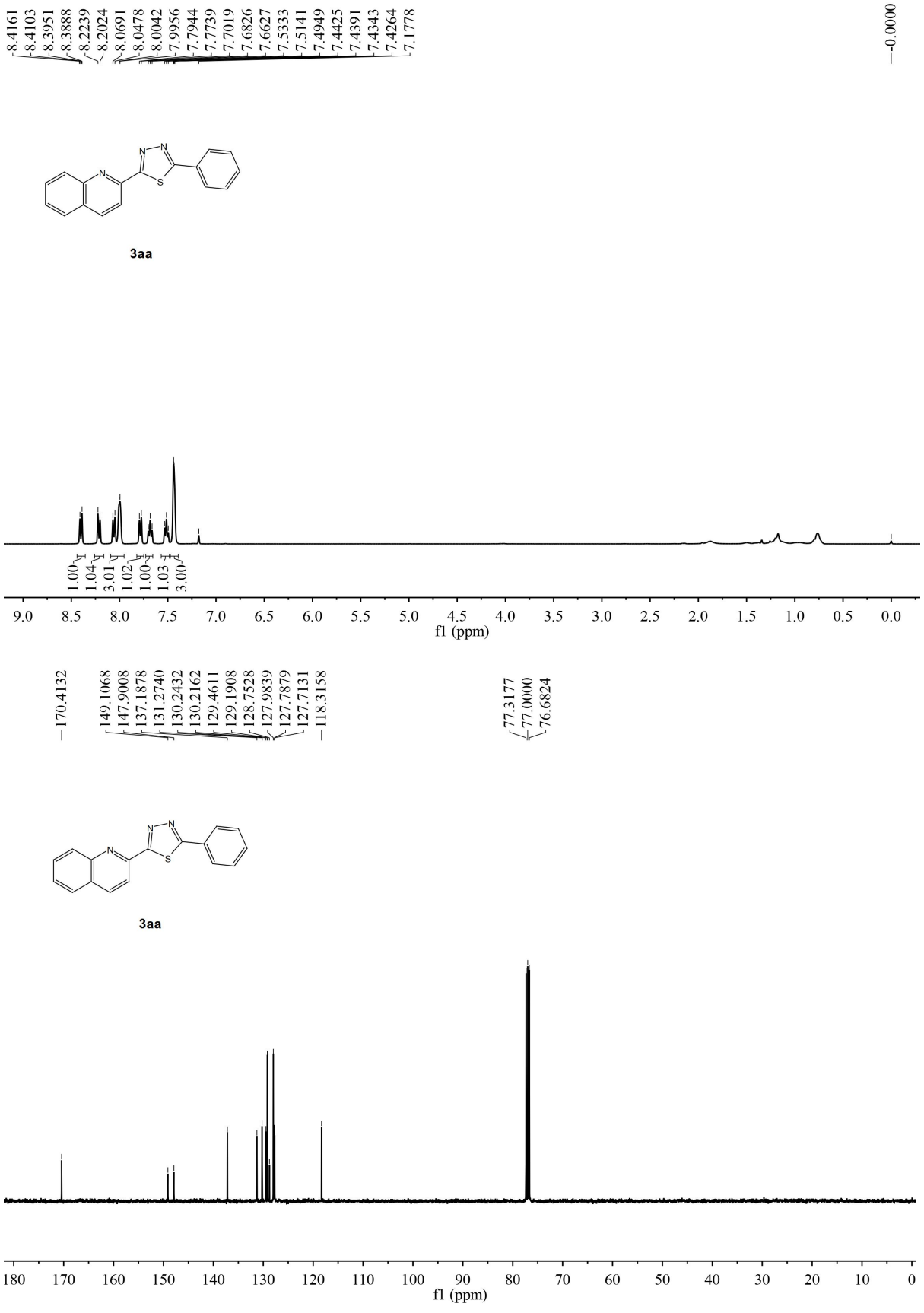
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.26 – 7.99 (m, 4H), 7.77 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (s, 3H), 5.42 (d, J = 9.7 Hz, 1H), 4.22 – 4.01 (m, 3H), 3.90 (t, J = 14.6 Hz, 2H), 3.58 (t, J = 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.4, 149.2, 147.9, 145.1, 131.3, 130.5, 130.3, 130.0, 129.2, 128.0, 127.9, 125.9, 122.8, 115.9, 74.1, 71.7, 67.2, 66.6. HRMS (ESI) m/z calcd for $C_{21}H_{18}N_3O_2S^+$ $(M+H)^+$ 376.1114, found 376.1997.

5. References

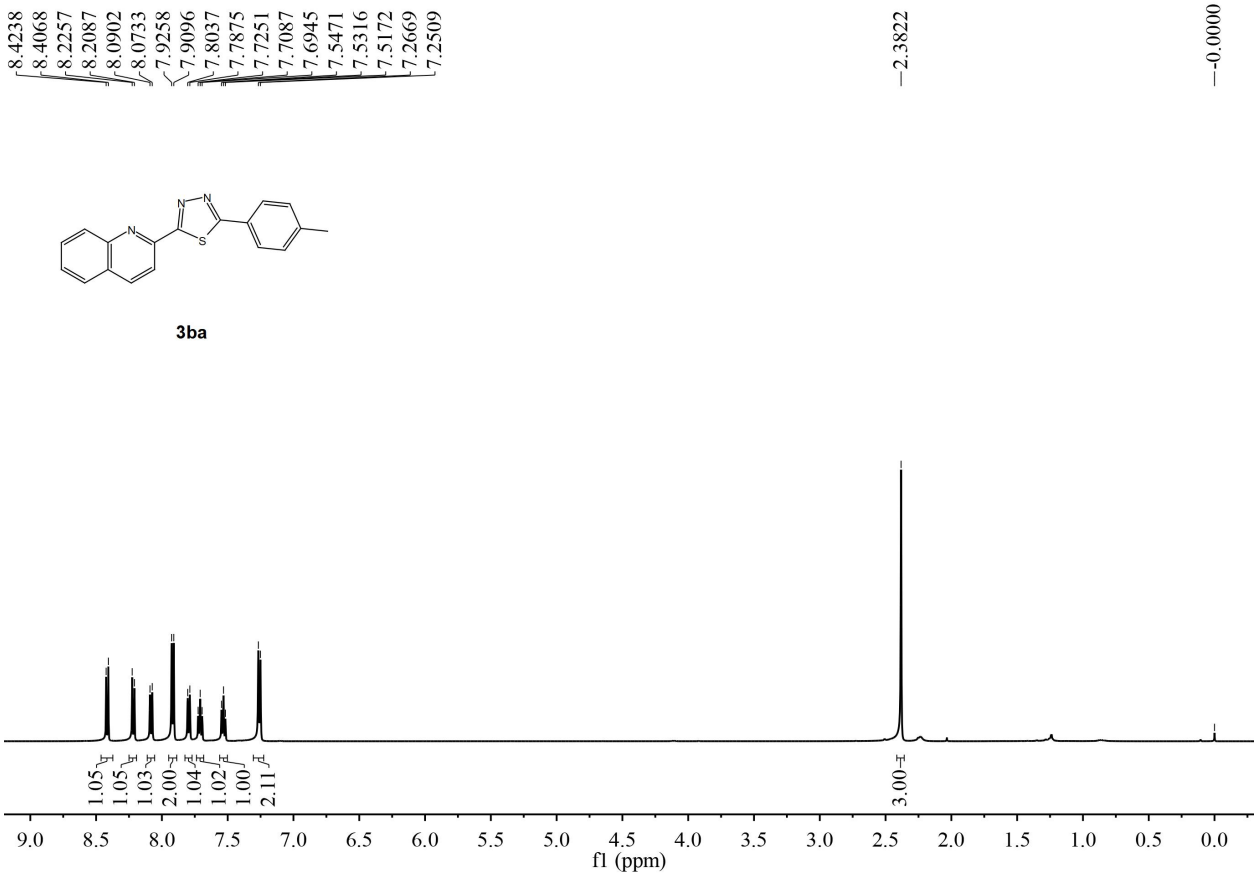
[1] C. Wen, G. Sun, L. Liu, J. Zhang, M. She, Z. Yang, P. Liu, S. Zhang, J. L, *Green Chem.*, **2024**, *26*, 7944-7950.

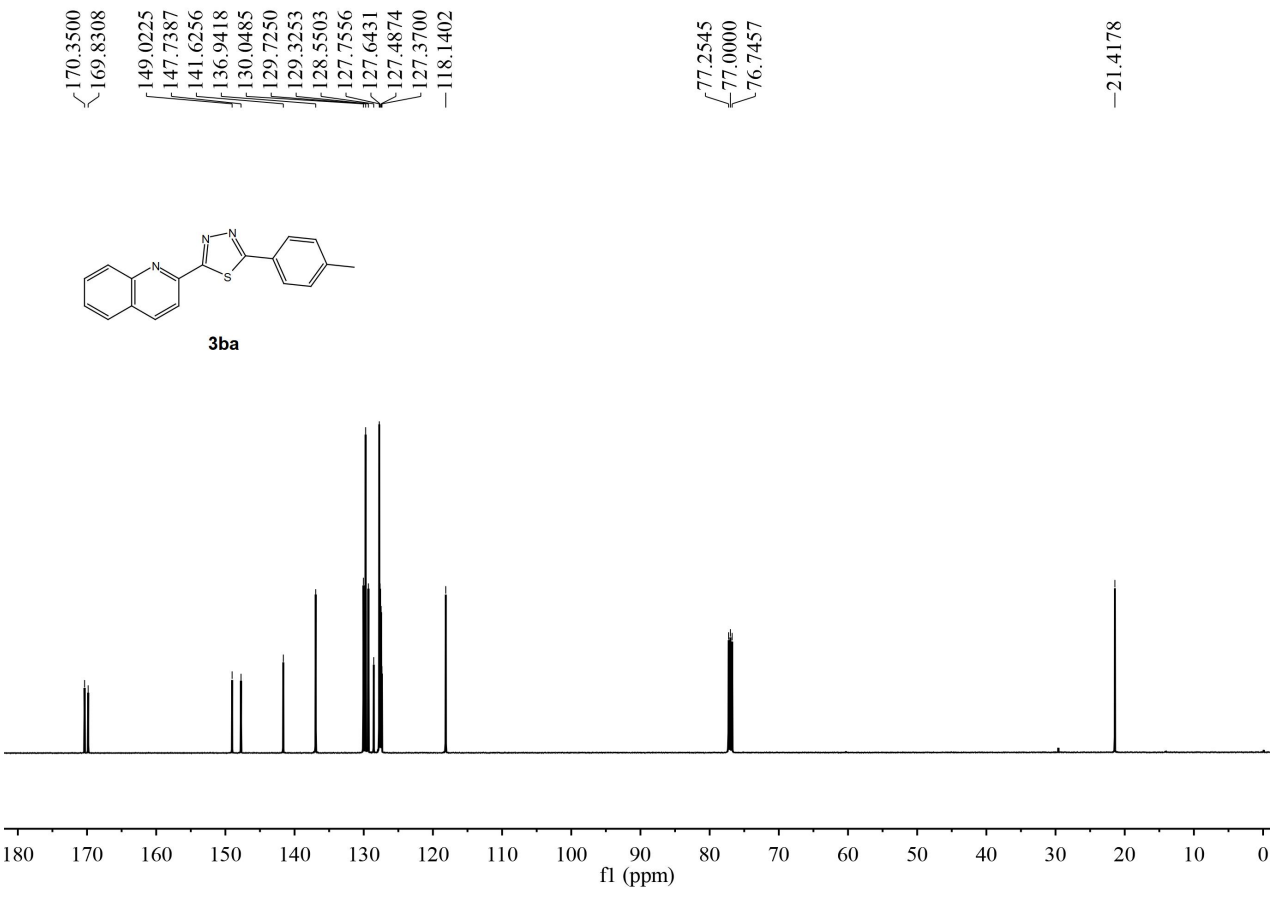
6. Copies of NMR spectra for all products

[1] H NMR and [13]C NMR of Compound **3aa**

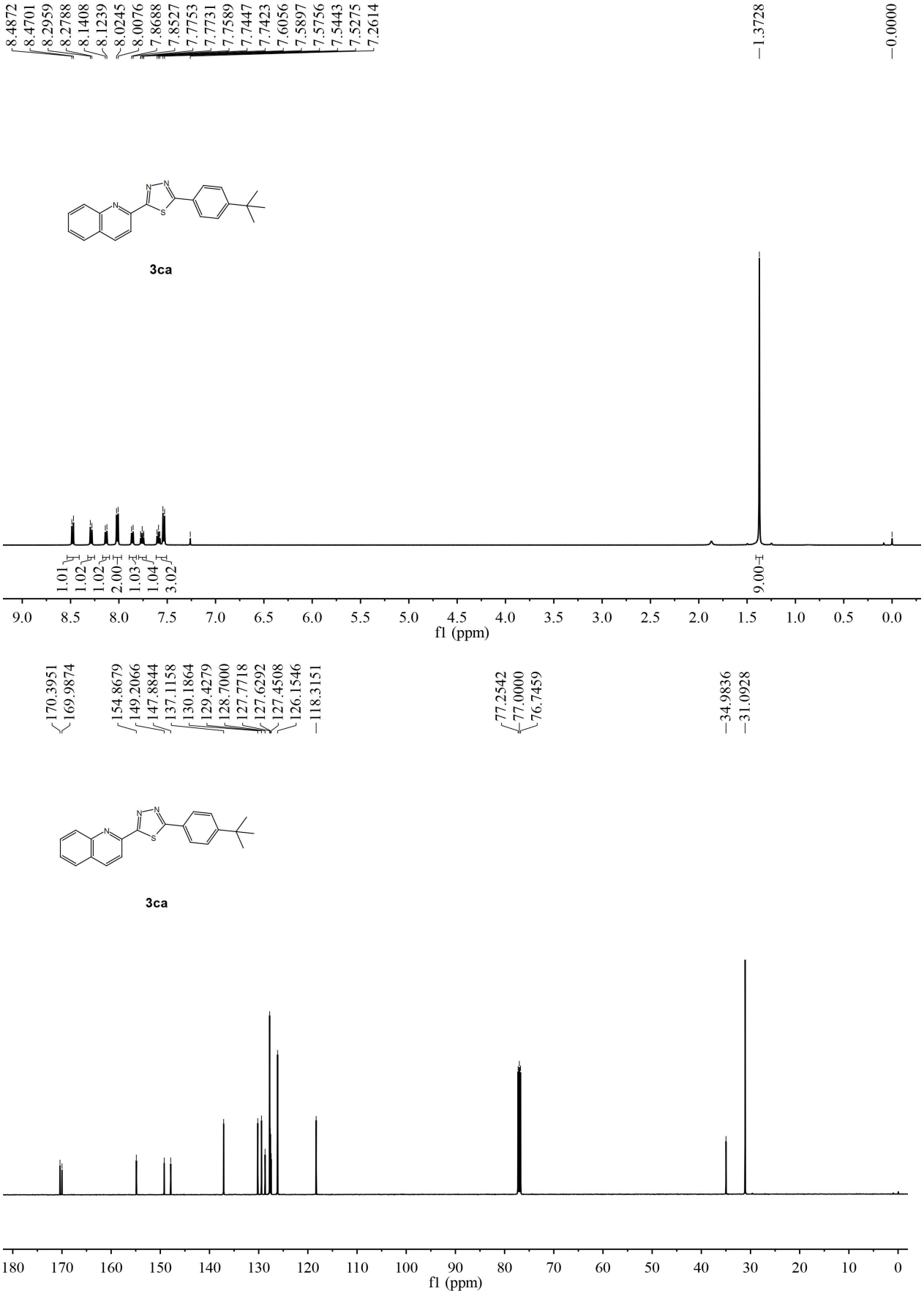


^{1} H NMR and ^{13}C NMR of Compound **3ba**

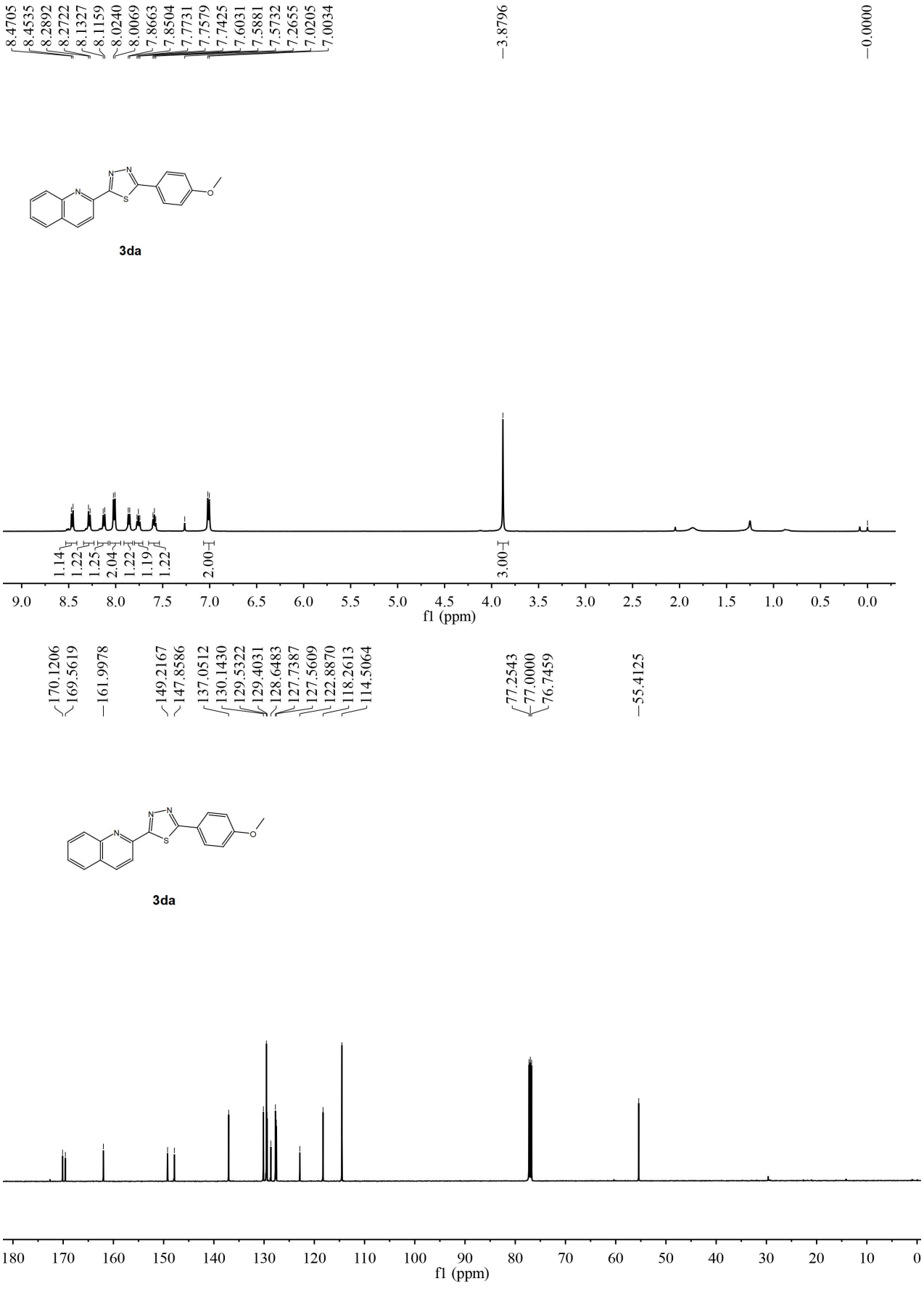




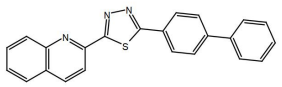
^{1}H NMR and ^{13}C NMR of Compound **3ca**



[1] H NMR and [13]C NMR of Compound **3da**



[1] H NMR and [13]C NMR of Compound **3ea**



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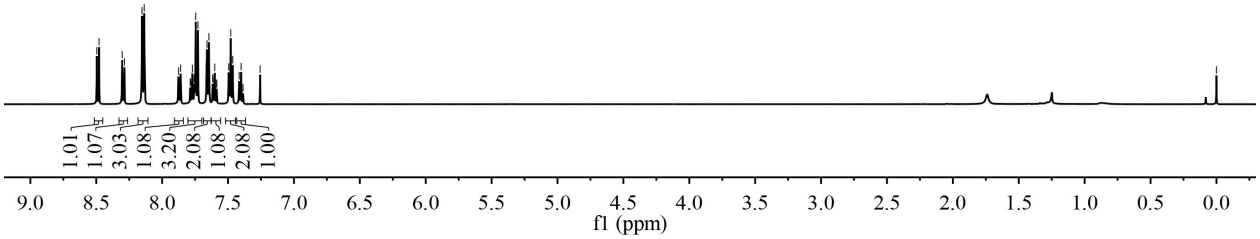

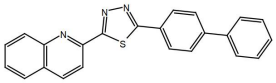

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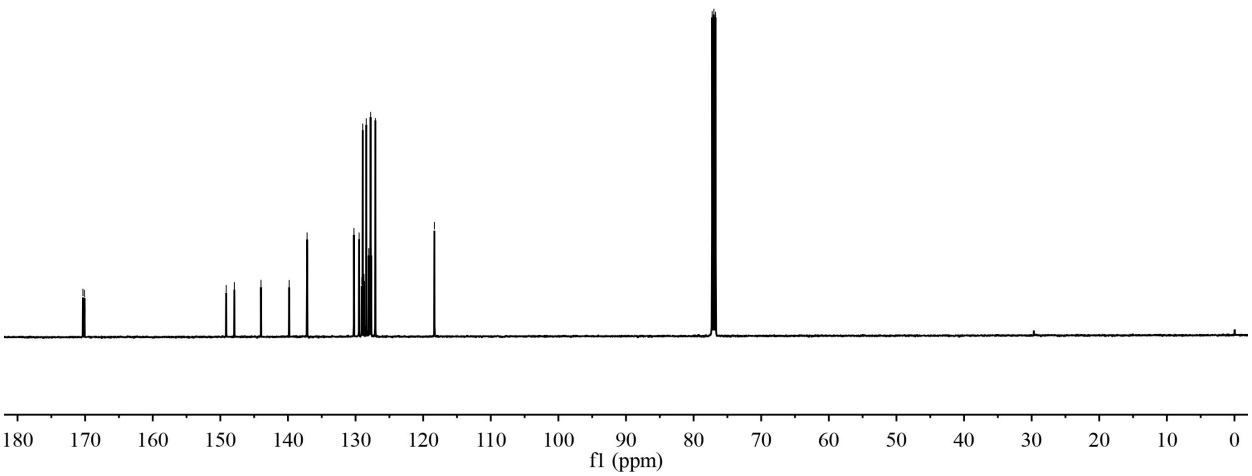
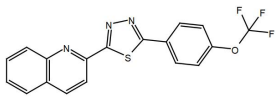


^{1} H NMR and ^{13}C NMR of Compound **3fa**



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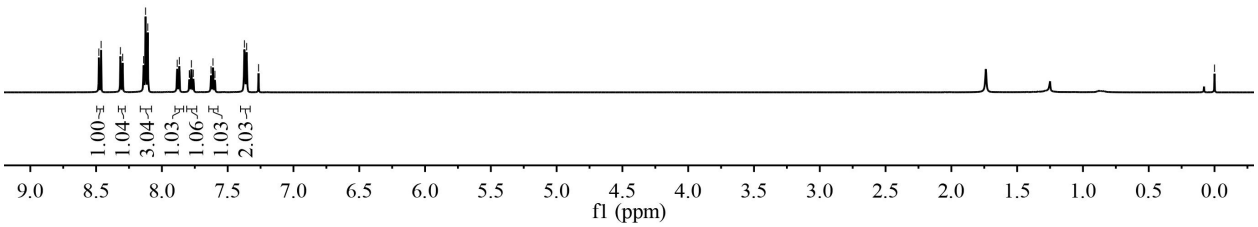

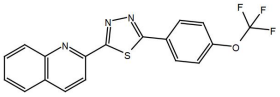

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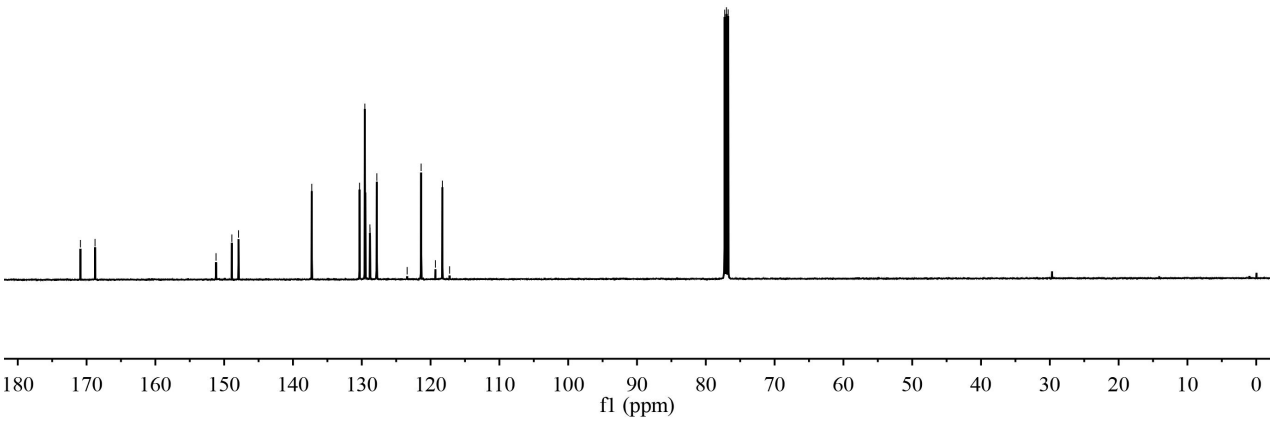
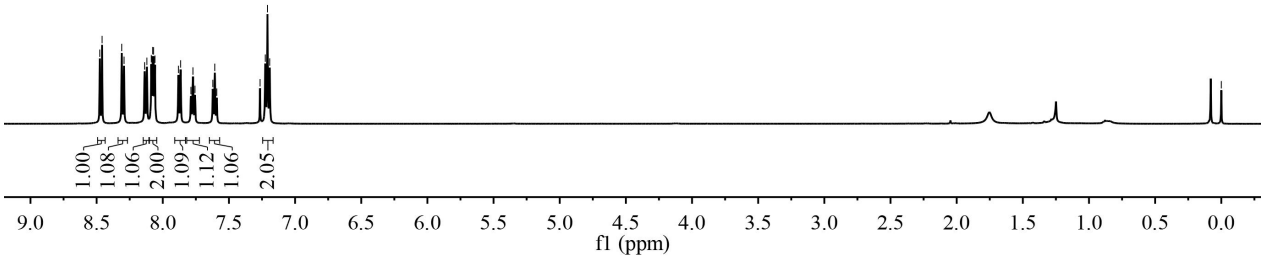
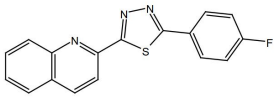


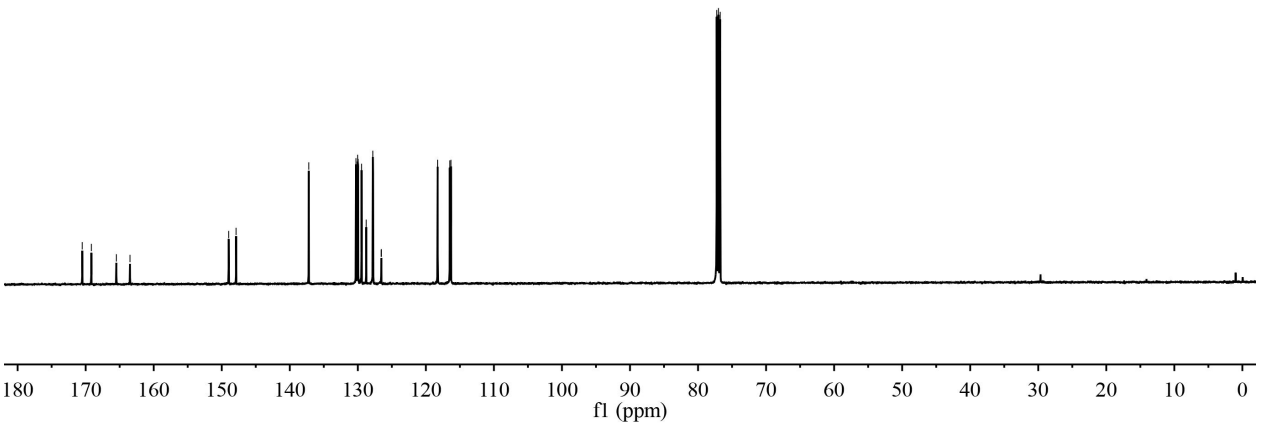
[1] H NMR and [13]C NMR of Compound **3ga**

3ga

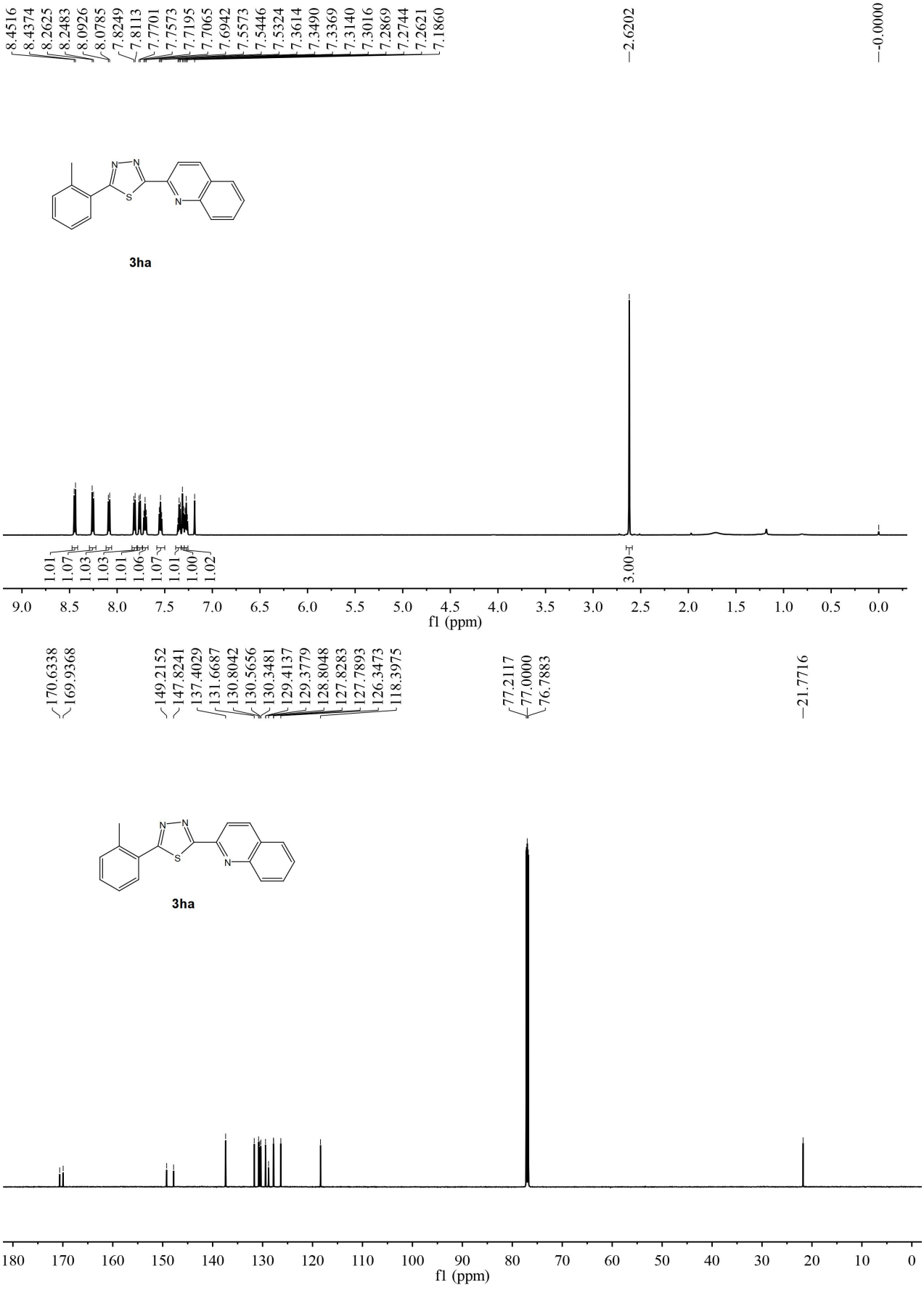




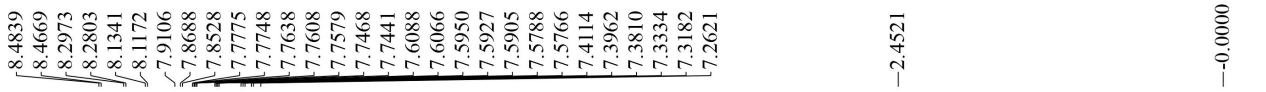
3ga

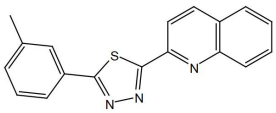


[1] H NMR and [13]C NMR of Compound **3ha**

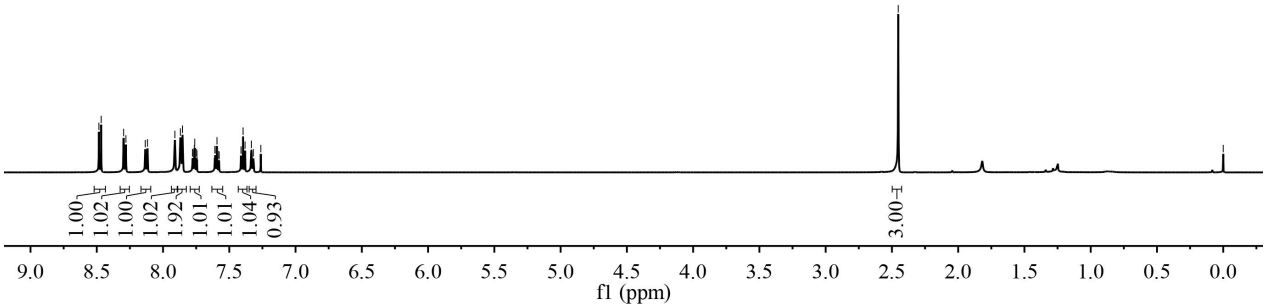


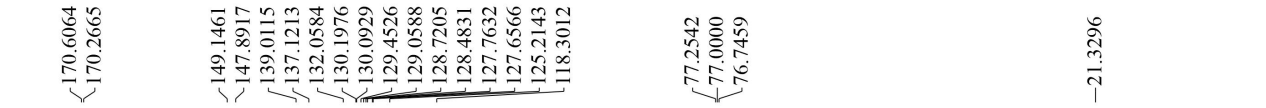
[1] H NMR and [13]C NMR of Compound **3ia**

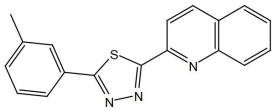




3ia







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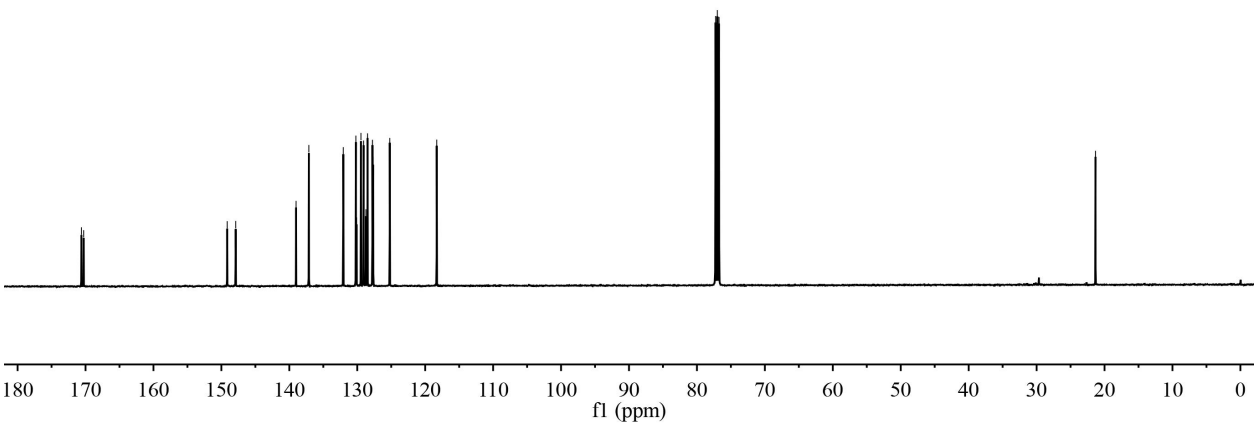
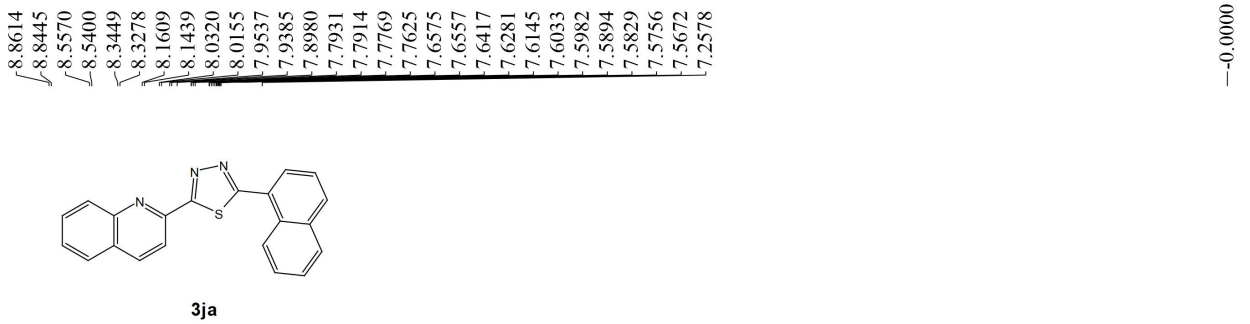


^{1} H NMR and ^{13}C NMR of Compound **3ja**



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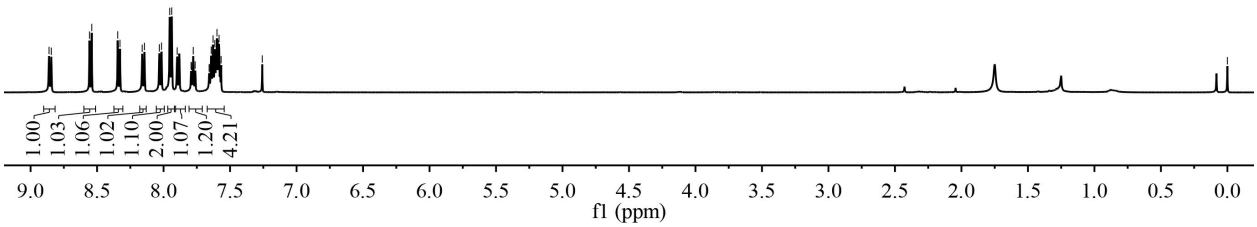

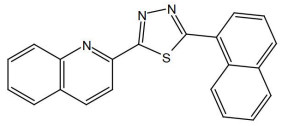

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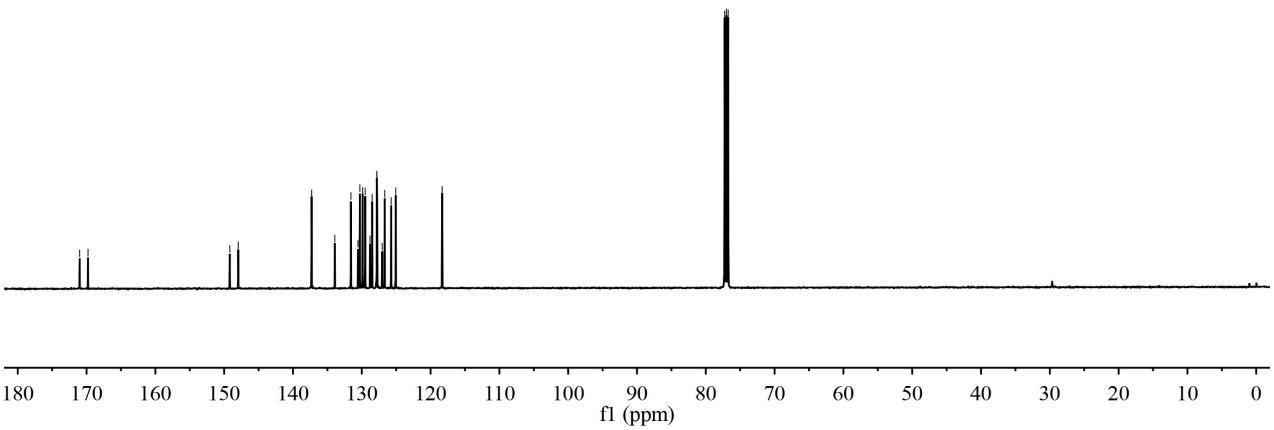
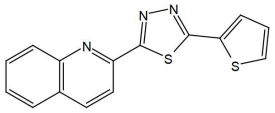


[1] H NMR and [13]C NMR of Compound **3ka**



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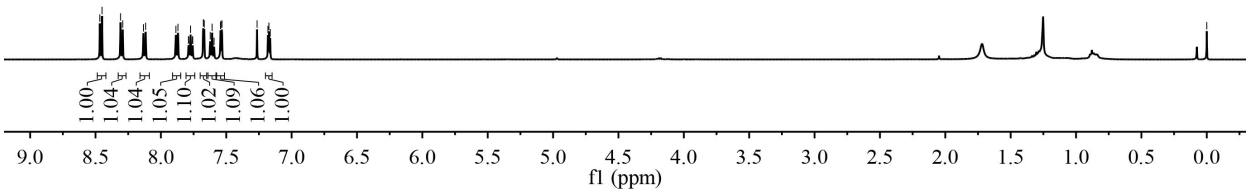

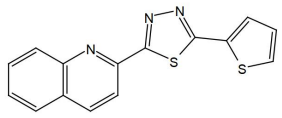

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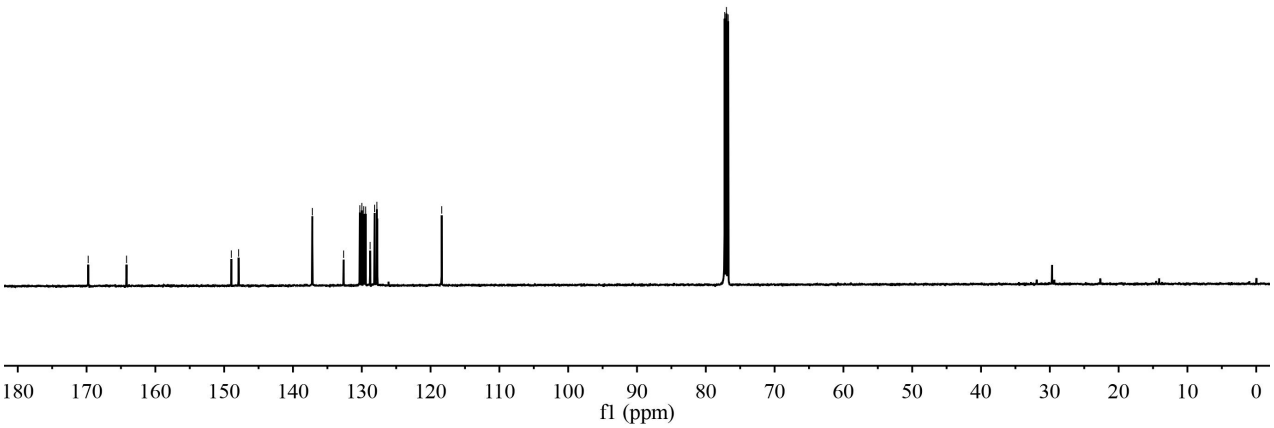
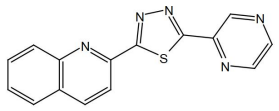


[1] H NMR and [13]C NMR of Compound **3la**



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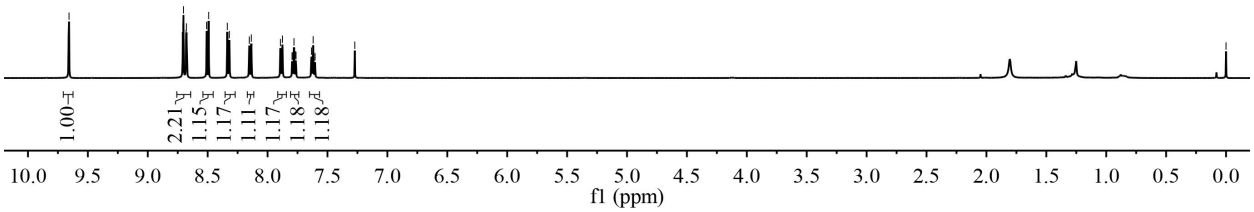

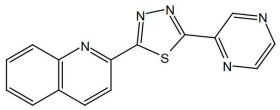

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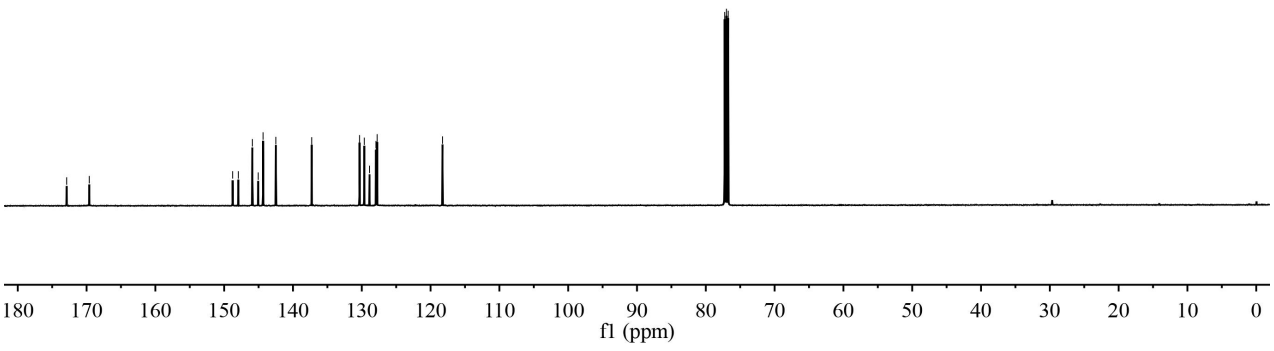
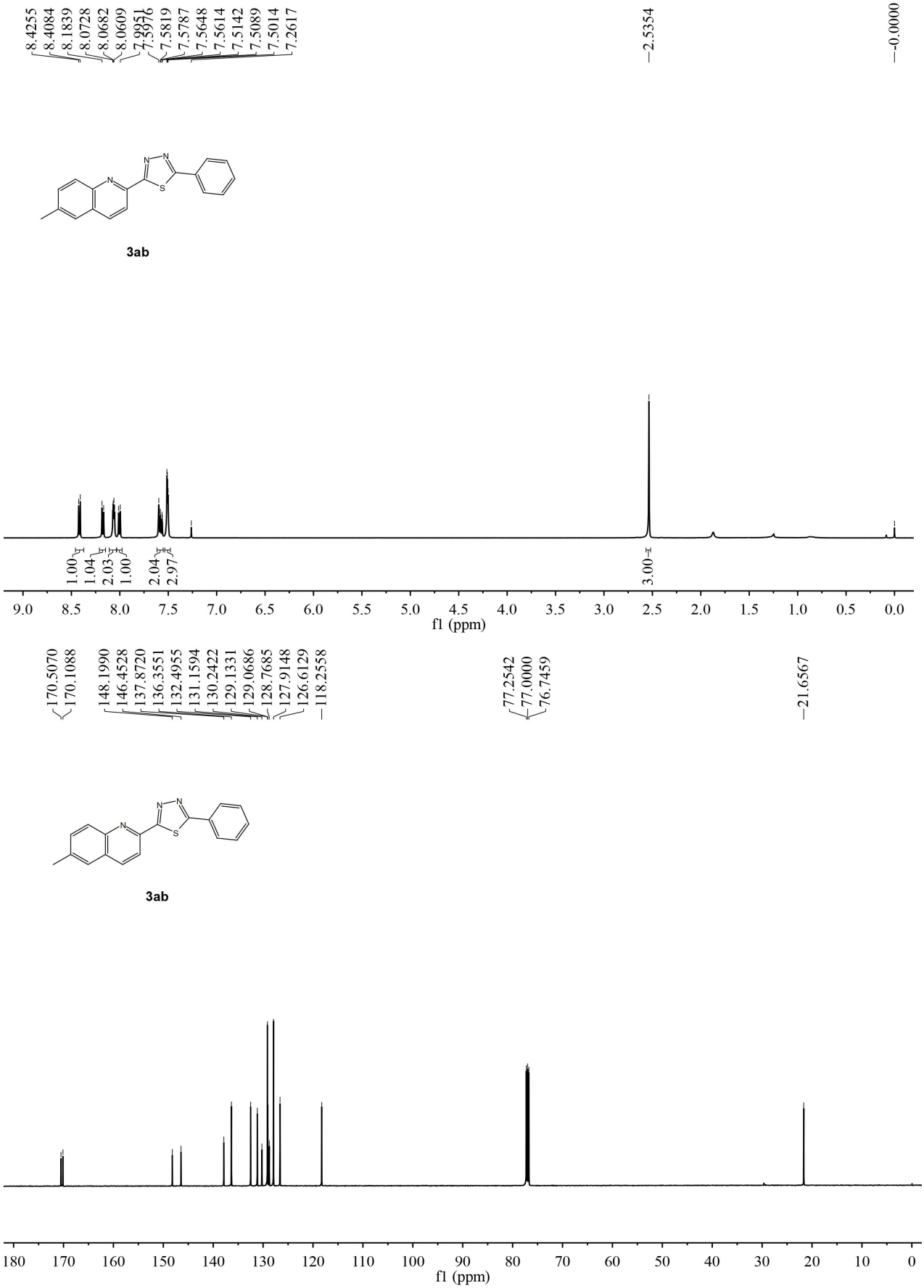
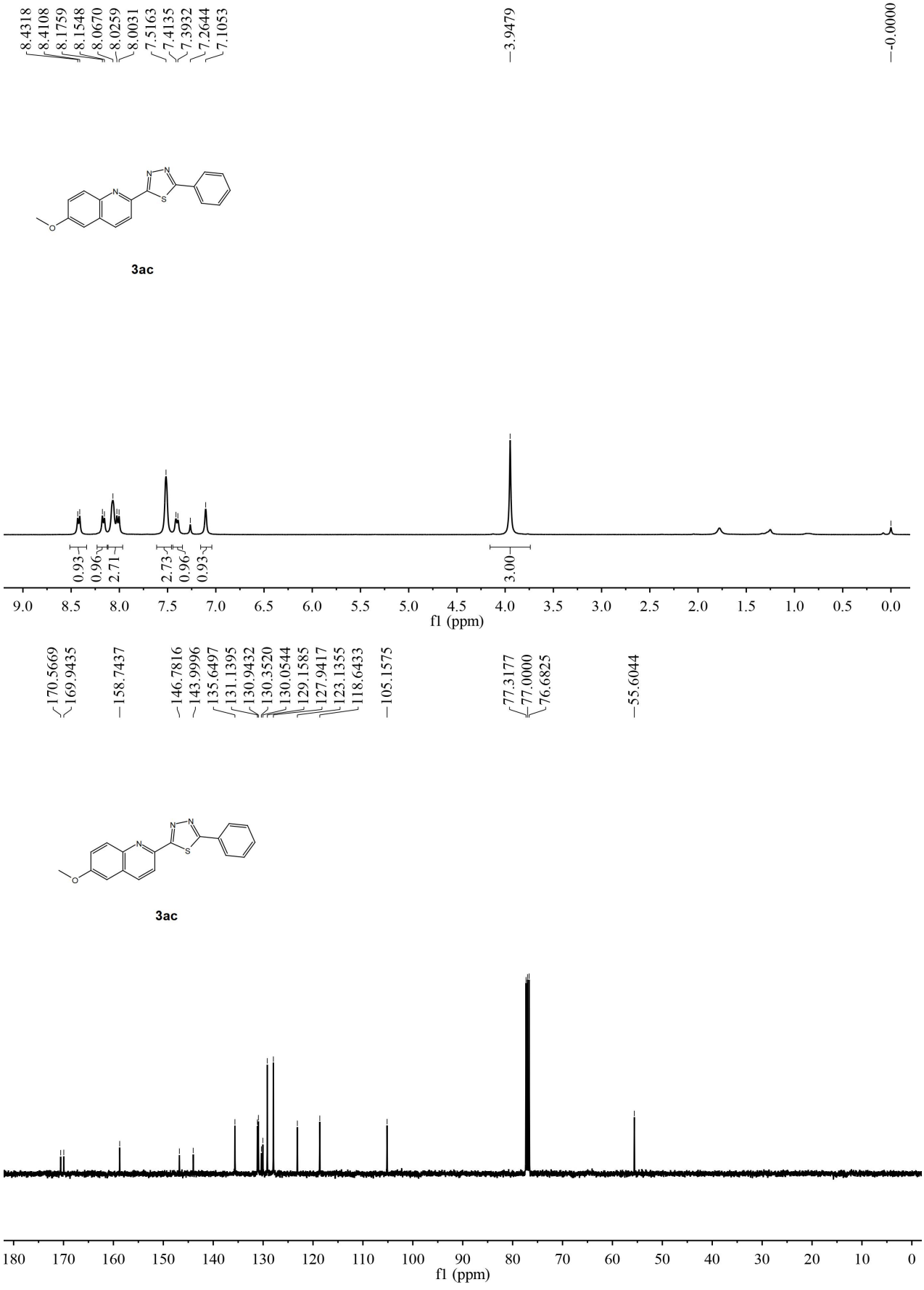


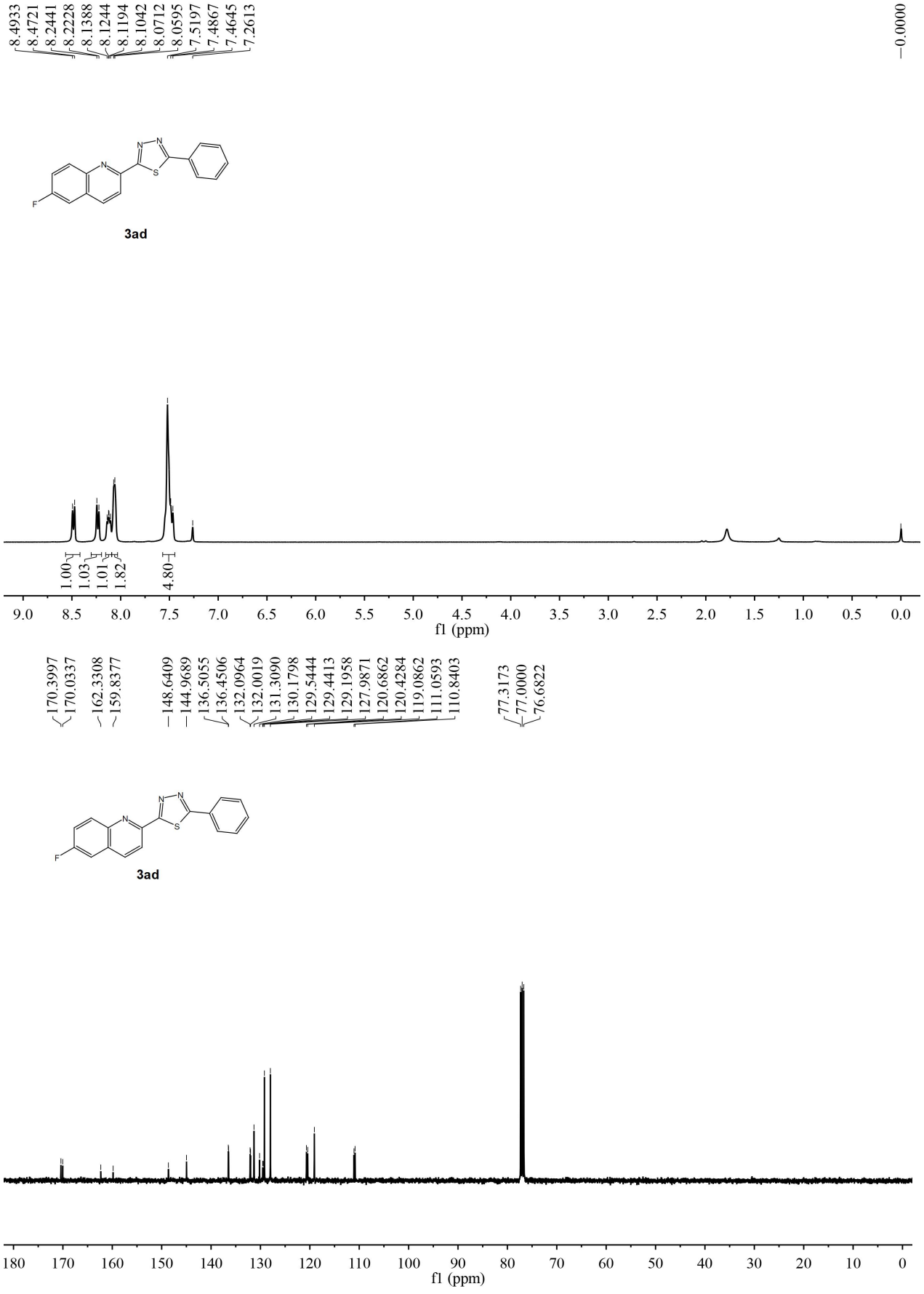
[1] H NMR and [13]C NMR of Compound **3ab**



[1] H NMR and [13]C NMR of Compound **3ac**

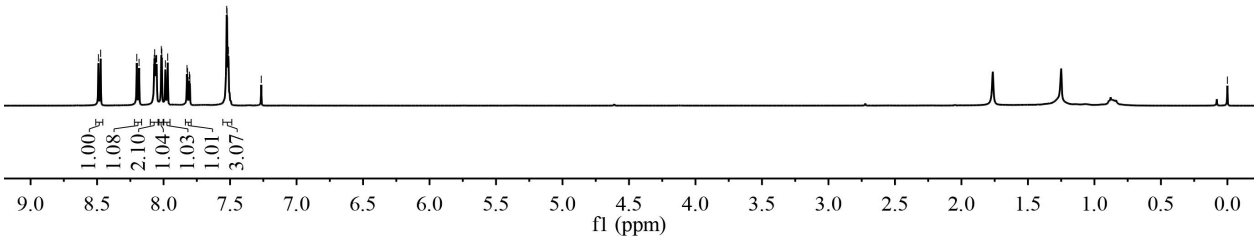


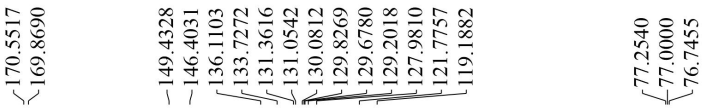
[1] H NMR and [13]C NMR of Compound **3ad**

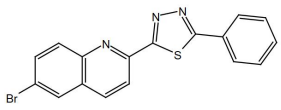


[1] H NMR and [13]C NMR of Compound **3ae**

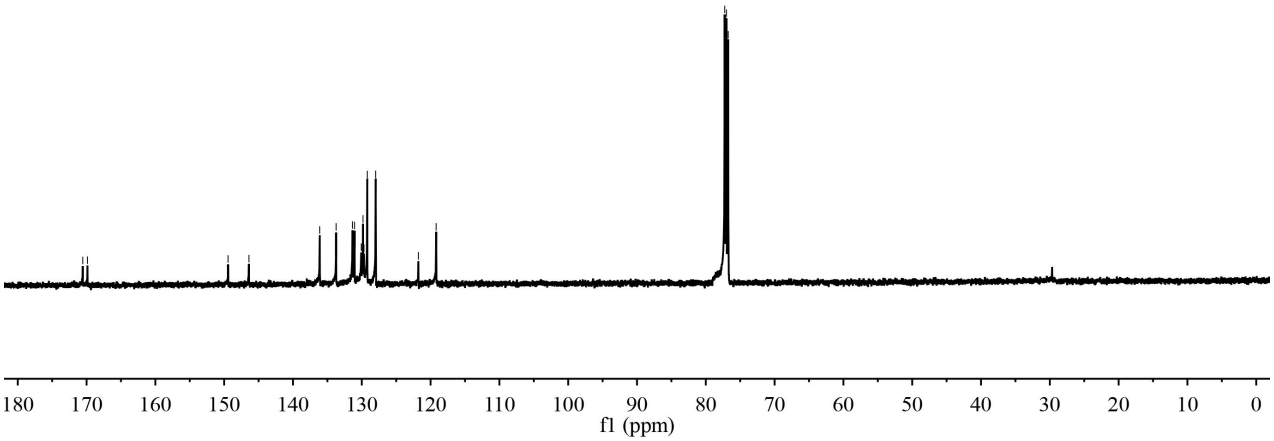
3ae



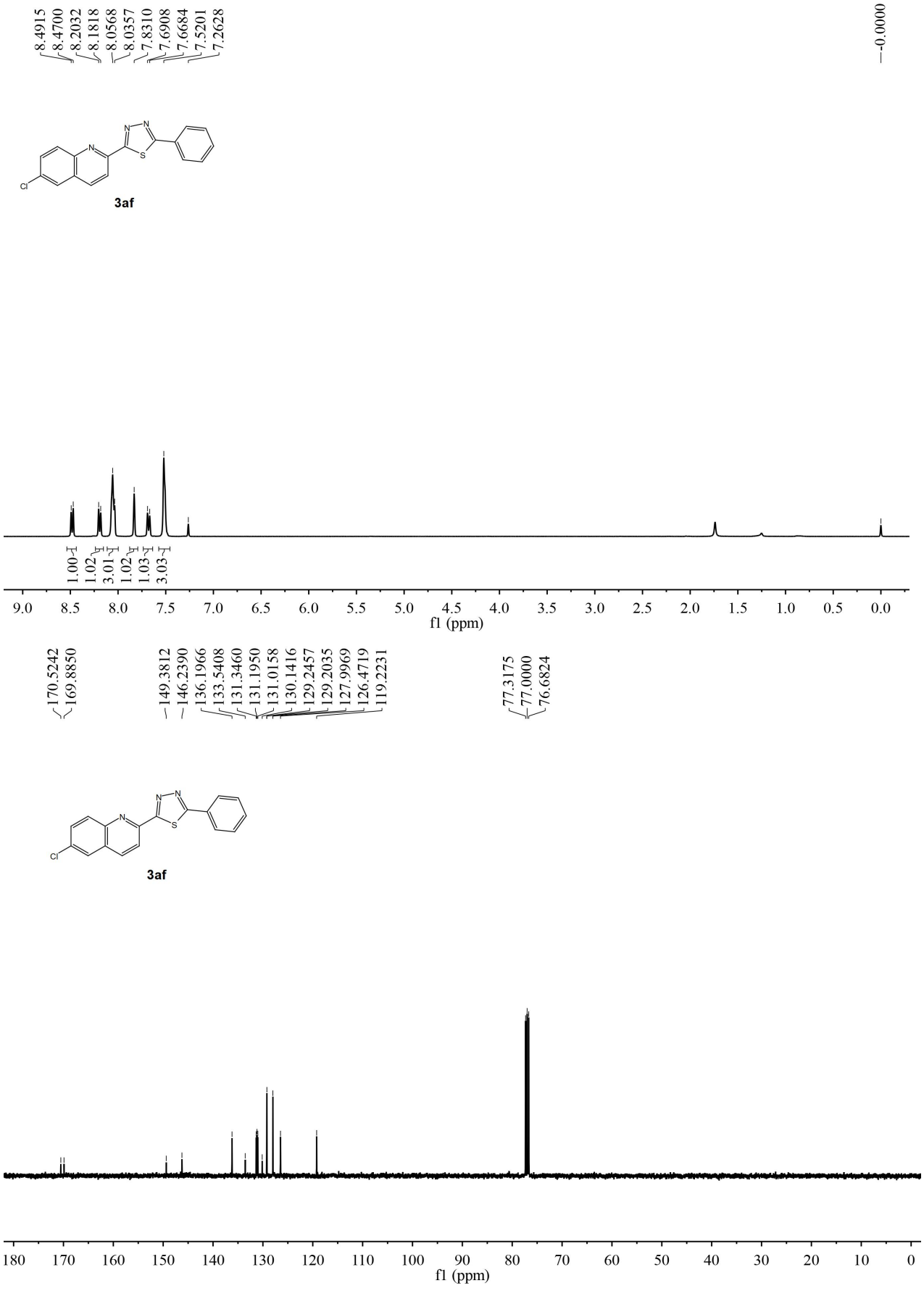




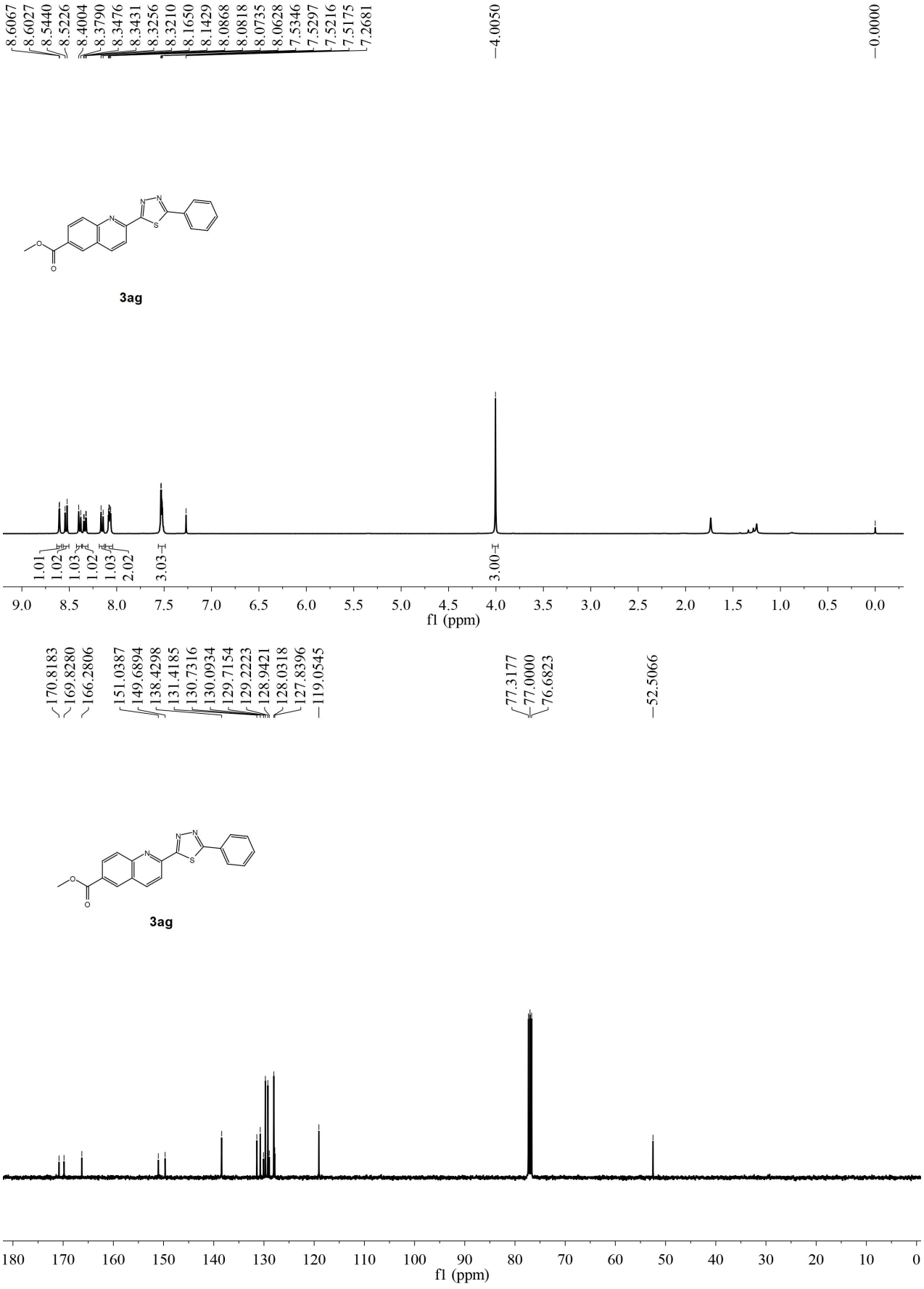
3ae



[1] H NMR and [13]C NMR of Compound **3af**

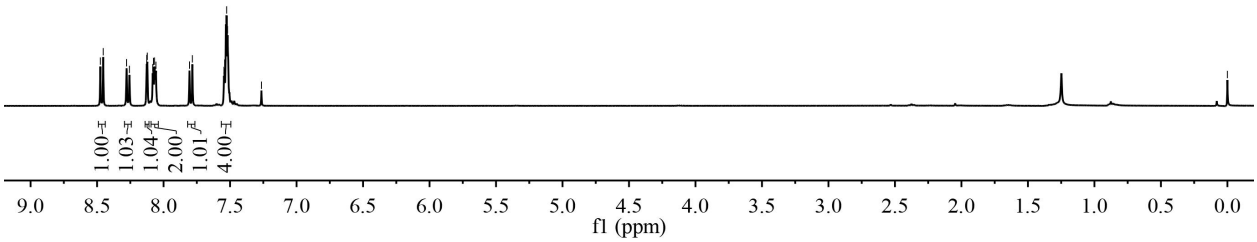


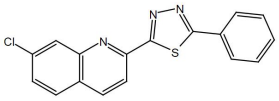
[1] H NMR and [13]C NMR of Compound **3ag**



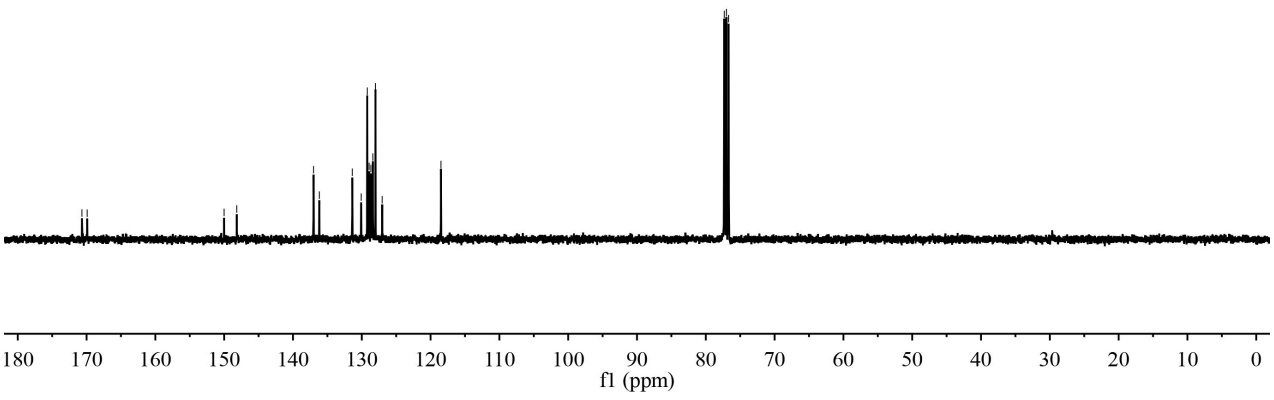
[1] H NMR and [13]C NMR of Compound **3ah**

3ah

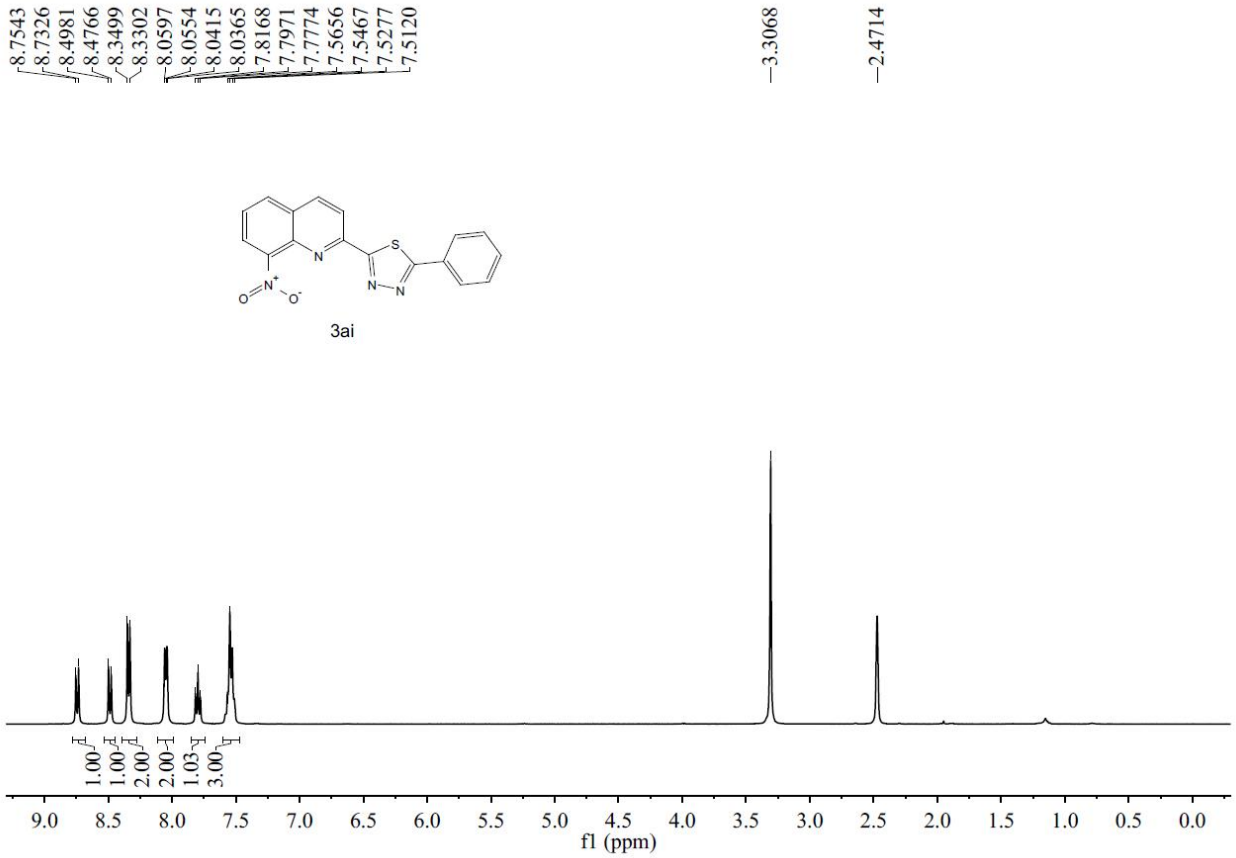


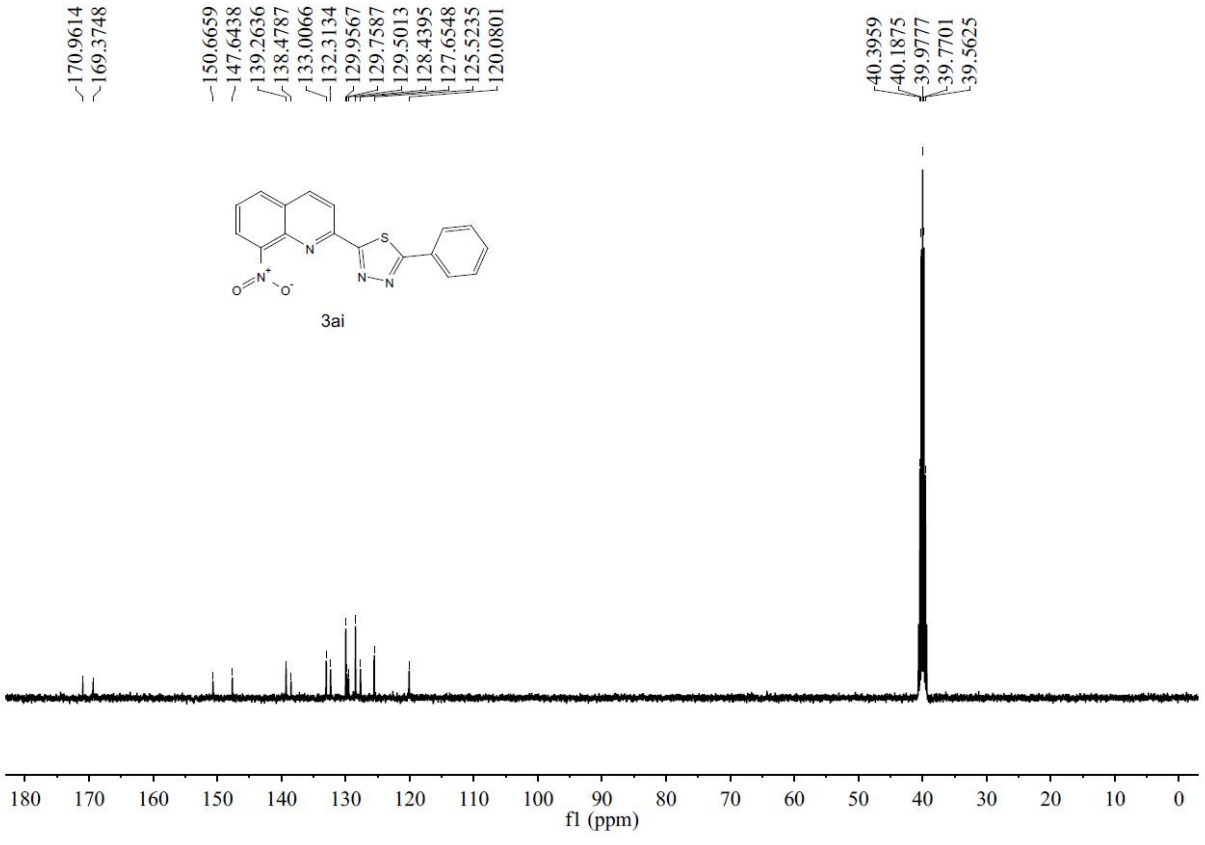


3ah

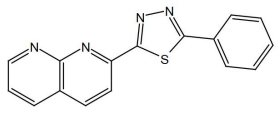


[1] H NMR and [13]C NMR of Compound **3ai**

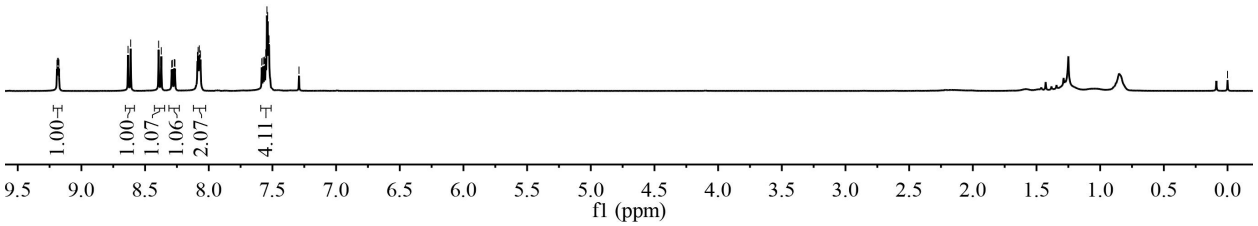


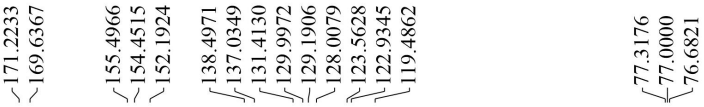


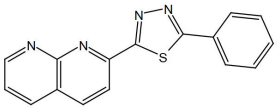
[1] H NMR and [13]C NMR of Compound **3aj**



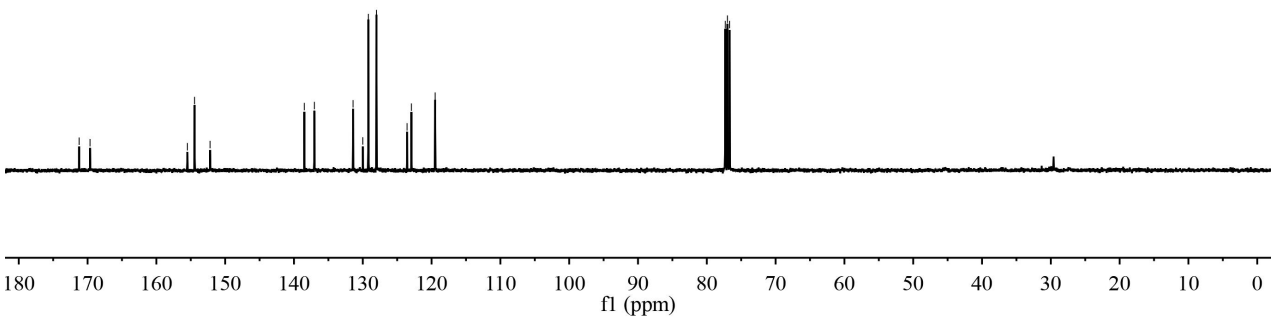
3aj





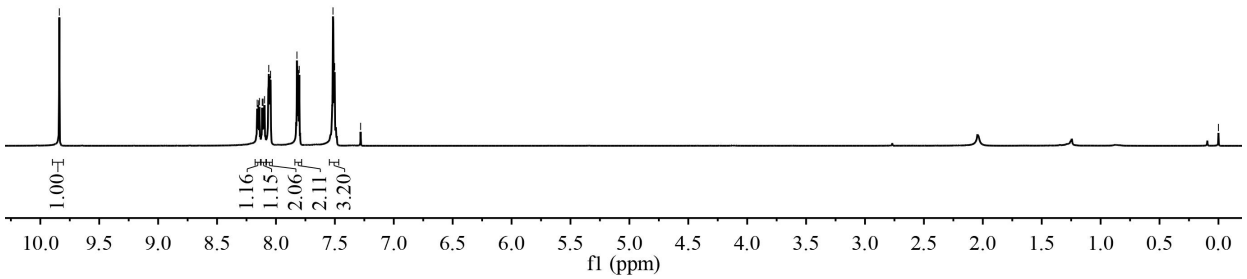


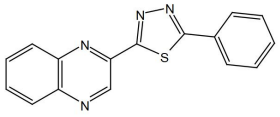
3aj



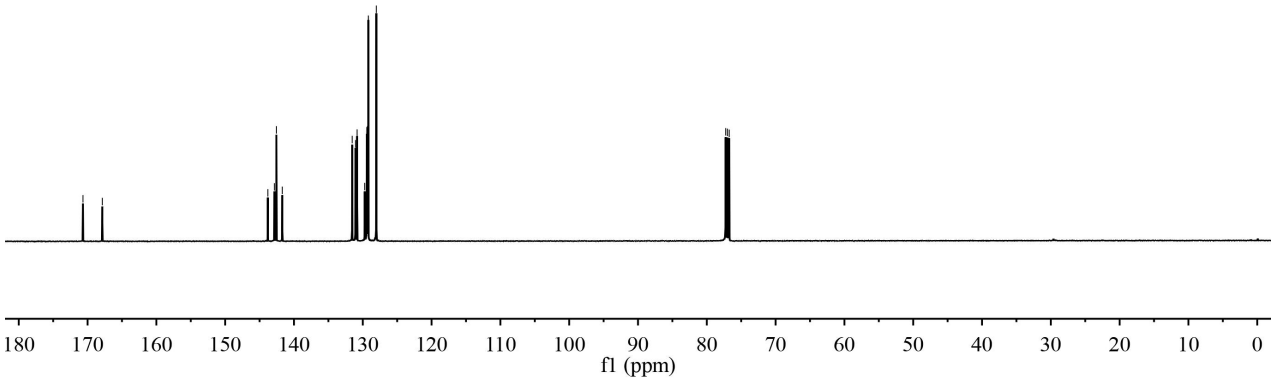
[1] H NMR and [13]C NMR of Compound **3ak**

3ak

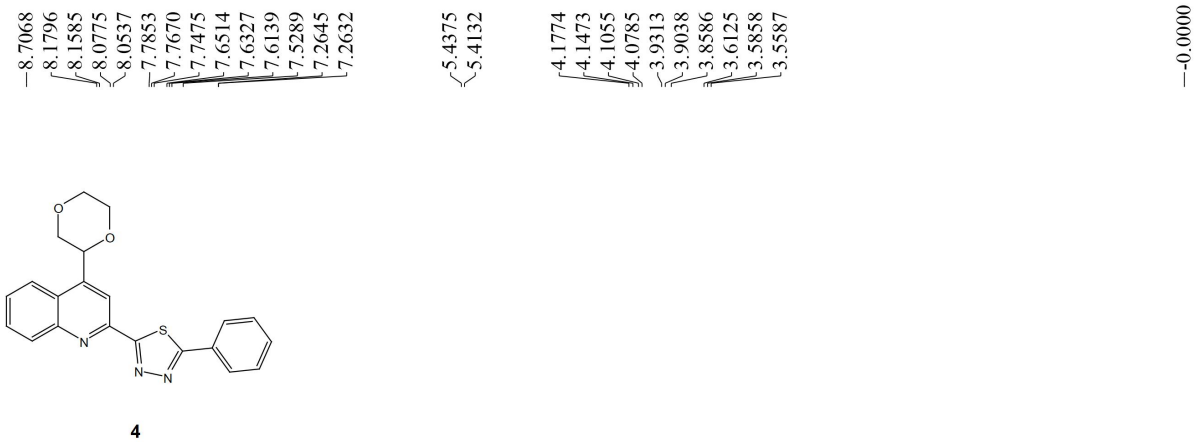




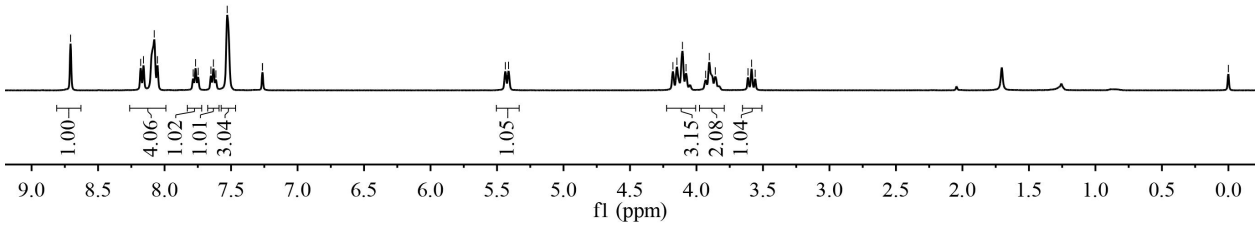
3ak

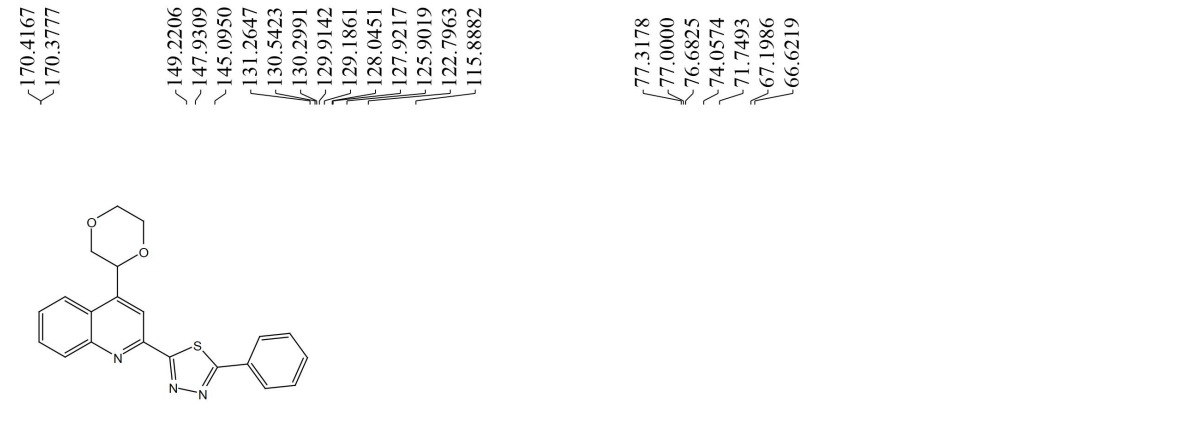


^{1} H NMR and ^{13}C NMR of Compound **4**

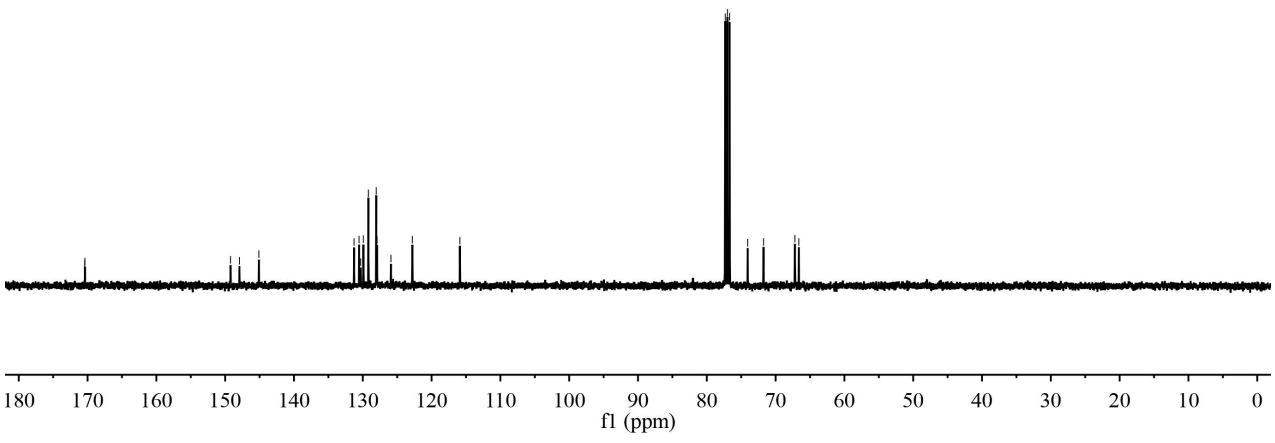


4





4



H-H Cosy spectrum of compound **4**