Supporting Information for

One-Pot Synthesis of 2,2'-Biquinolines from Aromatic Amines under Oxygen as Oxidant and Metal-Free Conditions

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1. General information:

All reactions were carried out under an atmosphere of air 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 internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra was measured on bruker 15T HRMS instrument (maldi). Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. All reagents were obtained from commercial suppliers and used without further purification.

2. General procedure for preparation (4a):

A 10 mL sealed tube was charged with 4-methoxyaniline (**1a**, 49.2 mg, 0.4 mmol) and was purged with oxygen for three times. Then, 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol), 55%HI (9.5 μL, 0.08 mmol) and 1,4-dioxane (1.5 mL) were added to the sealed reaction vessel by syringe. The reaction vessel was stirred at 130 ^{o}C for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **4a** as white solid (37.8 mg, 66% yield).

3. General procedure for preparation (5a):

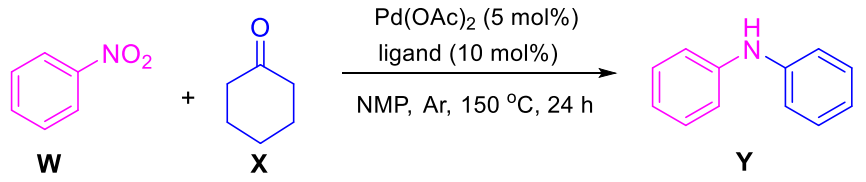
A 10 mL sealed tube was purged with oxygen for three times and was added aniline (**1m**, 18.2 μL, 0.2 mmol), 55%HI (11.9 μL, 0.1 mmol) and 1,4-dioxane (1.5 mL) by syringe. The reaction vessel was stirred at 110 ^{o}C for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **5a** as white solid (18.5 mg, 72% yield).

4. Gram-scale reaction

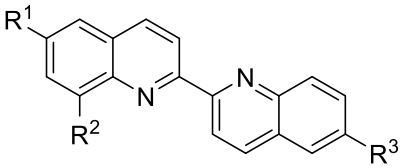
A 100 mL three neck flask with reflow condenser tube was added *p*-toluidine (**1d**, 1.2840 g, 12.0 mmol) and 6-methoxy-2-methylquinoline (**2c**, 1.0381 g, 6.0 mmol) and was purged with oxygen for three times. Next, 55%HI (0.357 mL, 3.0 mmol) and 1,4-dioxane (45 mL) were purged by

syringe. Reaction apparatus loaded with oxygen bulb. The reaction vessel was stirred at 100 °C for 16 h. After cooling to room temperature, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4v** as yellow solid (1.0793 g, 60%), mp 249.3-253.2 °C.

5. Application of 2,2′-biquinoline ligands for dehydrogenation and borrowing hydrogen reaction[1]



W + **X** → **Y**



5a, R^1 = H, R^2 = H, R^3 = H
4w, R^1 = CH_3, R^2 = H, R^3 = F
4v, R^1 = CH_3, R^2 = H, R^3 = OCH_3
4d, R^1 = CH_3, R^2 = H, R^3 = H
4e, R^1 = CH_3, R^2 = CH_3, R^3 = H

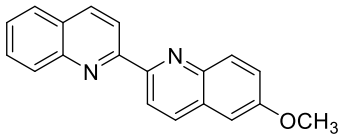
entry	ligand	yield[a]
1	**5a**	68%
2	**4w**	70%
3	**4v**	65%
4	**4d**	50%
5	**4e**	55%

[a] Isolated yield of diphenylamine based on nitrobenzene.

A 10 mL sealed tube was charged with $Pd(OAc)_2$ (0.01 mmol, 5 mol%), ligands (0.02 mmol, 10 mol%). The reaction vessel was purged with argon for three times and was added nitrobenzene (**W**, 0.2 mmol), cyclohexanone (**X**, 0.4 mmol) and NMP (0.3 mL) by syringe. The sealed vessel was stirred at 150 °C for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 98:2) to give the corresponding product **Y.**

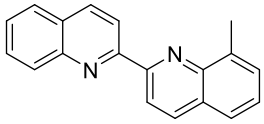
6. Characterization data of products

6-methoxy-2, 2'-biquinoline (4a) [2]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (dd, *J* = 8.4, 2.0 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 9.2 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.77-7.73 (m, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.2, 156.4, 154.0, 147.9, 143.9, 136.7, 135.5, 131.3, 129.8, 129.5, 129.5, 128.3, 127.6, 126.7, 122.3, 119.7, 119.2, 105.1, 55.6; HRMS (maldi, m/z): calcd. for $C_{19}H_{15}N_2O$ $[M+H]^+$ 287.1184, found 287.1176.

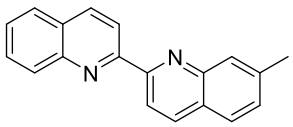
8-methyl-2, 2'-biquinoline (4b)



The reaction was conducted with *o*-toluidine (**1b**, 42.7 μL, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4b** as yellow solid (41.1 mg, 76%), mp 114.8-118.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (d, *J* = 8.4 Hz, 1H), 8.85 (d, *J* = 8.4 Hz, 1H), 8.31 - 8.27 (m, 2H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77-7.69 (m, 2H), 7.60-7.54 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.6, 154.7, 147.9, 146.8, 137.8, 136.9, 136.6, 129.8, 129.6, 129.4, 128.4, 128.4, 127.6, 126.8, 126.7, 125.6, 119.5, 118.8, 17.9; HRMS (maldi, m/z): calcd. for $C_{19}H_{15}N_2$ $[M+H]^+$ 271.1235, found 271.1236.

7-methyl-2, 2'-biquinoline (4c)

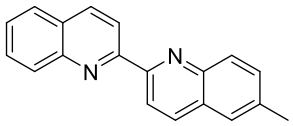


The reaction was conducted with *m*-toluidine (**1c**, 42.9 μL, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum

ether/EtOAc = 5:1 to 2:1) afforded the product **4c** as yellow solid (39.4 mg, 73%), mp 136.5-139.1 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.83 (d, *J* = 8.8 Hz, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.02 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.79-7.74 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.4, 156.2, 148.1, 147.9, 139.8, 136.7, 136.4, 129.9, 129.5, 129.2, 128.9, 128.4, 127.6, 127.3, 126.9, 126.5, 119.4, 118.6, 21.9; HRMS (maldi, m/z): calcd. for $C_{19}H_{15}N_2$ $[M+H]^+$ 271.1235, found 271.1232.

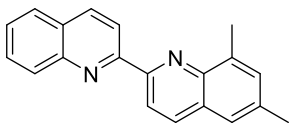
6-methyl-2, 2'-biquinoline (4d)



The reaction was conducted with *p*-toluidine (**1d**, 42.9 mg, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4d** as yellow solid (36.7 mg, 68%), mp 198.4-202.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.83-8.79 (m, 2H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.25-8.22 (m, 2H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.78-7.74 (m, 1H), 7.65 (s, 1H), 7.61-7.56 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.4, 155.4, 147.9, 146.5, 137.0, 136.7, 136.1, 131.9, 129.9, 129.6, 129.5, 128.5, 128.4, 127.6, 126.8, 126.6, 119.4, 119.4, 21.7; HRMS (maldi, m/z): calcd. for $C_{19}H_{14}N_2Na$ $[M+Na]^+$ 293.1055, found 293.1056.

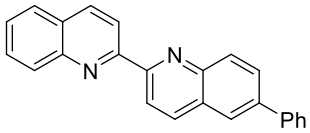
6, 8-dimethyl-2, 2'-biquinoline (4e)



The reaction was conducted with 2,4-dimethylaniline (**1e**, 49.5 μL, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4e** as red solid (23.9 mg, 42%), mp 122.4-125.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (d, *J* = 8.4 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.21 (t, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.77-7.73 (m, 1H), 7.58-7.55 (m, 1H), 7.48 (s, 1H), 7.45 (s, 1H), 2.92 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.8, 153.9, 147.9, 145.4, 137.4, 136.6, 136.5, 136.2, 132.0, 129.8, 129.4, 128.5, 128.4, 127.6, 126.7, 124.5, 119.5, 118.9, 21.7, 17.8; HRMS (maldi, m/z): calcd. for $C_{20}H_{16}N_2Na$ $[M+Na]^+$ 307.1211, found 307.1213.

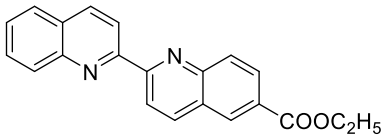
6-phenyl-2, 2'-biquinoline (4f)



The reaction was conducted with [1,1'-biphenyl]-4-amine (**1f**, 67.7 mg, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4f** as yellow solid (45.8 mg, 69%), mp 251.5-255.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (dd, *J* = 8.4, 5.2 Hz, 2H), 8.33-8.27 (m, 2H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.01 (s, 1H), 7.97 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.71-7.69 (m, 3H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.2, 148.0, 147.3, 140.4, 139.7, 136.9, 136.8, 130.3, 129.9, 129.6, 129.3, 129.0, 128.6, 128.5, 127.8, 127.7, 127.4, 127.0, 125.4, 119.8, 119.4; HRMS (maldi, m/z): calcd. for $C_{24}H_{16}N_2Na$ $[M+Na]^+$ 355.1211, found 355.1215.

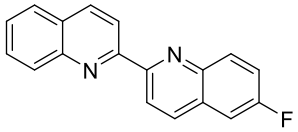
ethyl [2, 2'-biquinoline]-6-carboxylate (4g)



The reaction was conducted with ethyl 4-aminobenzoate (**1g**, 66.0 mg, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 1:1) afforded the product **4g** as white solid (40.4 mg, 62%), mp 202.2-206.0 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.93 (d, *J* = 8.8 Hz, 1H), 8.86 (d, *J* = 8.8 Hz, 1H), 8.65 (d, *J* = 1.6 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 8.8 Hz, 2H), 8.25 (t, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.80-7.76 (m, 1H), 7.62-7.59 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.2, 158.1, 155.7, 149.8, 147.9, 137.9, 136.9, 130.7, 130.1, 130.0, 129.7, 129.1, 128.6, 128.6, 127.7, 127.5, 127.2, 120.1, 119.4, 61.4, 14.4; HRMS (maldi, m/z): calcd. for $C_{21}H_{16}N_2NaO_2$ $[M+Na]^+$ 351.1109, found 351.1114.

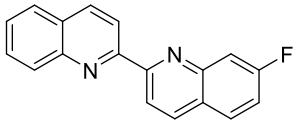
6-fluoro-2, 2'-biquinoline (4h)



The reaction was conducted with 4-fluoroaniline (**1h**, 37.9 μL, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4h** as yellow solid (13.2 mg, 24%), mp 232.7-236.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.17-8.14 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.48-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.8 (d, *J* = 247.4 Hz), 155.9, 155.7, 147.9, 145.0, 136.8, 136.1 (d, *J* = 5.3 Hz), 132.4 (d, *J* = 9.1 Hz), 129.9, 129.6, 129.1 (d, *J* = 10.1 Hz), 128.5, 127.7, 127.0, 120.2, 119.8 (d, *J* = 25.6 Hz), 119.2, 110.7 (d, *J* = 21.5 Hz); HRMS (maldi, m/z): calcd. for $C_{18}H_{11}FN_2Na$ $[M+Na]^+$ 297.0804, found 297.0808.

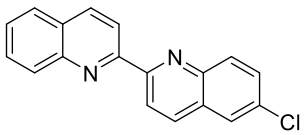
7-fluoro-2, 2'-biquinoline (4i)



The reaction was conducted with 3-fluoroaniline (**1i**, 38.4 μL, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4i** as yellow solid (48.8 mg, 89%), mp 160.4-162.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.74 (d, *J* = 8.8 Hz, 2H), 8.26 (t, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.83-7.76 (m, 3H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.30 (td, *J* = 8.8, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.2 (d, *J* = 248.1 Hz), 157.2, 155.9, 148.9 (d, *J* = 12.7 Hz), 147.9, 136.8, 136.6, 129.9, 129.6, 129.5, 128.5, 127.7, 127.1, 125.4, 119.4, 118.8 (d, *J* = 2.5 Hz), 117.4 (d, *J* = 25.3 Hz), 113.4 (d, *J* = 20.1 Hz); HRMS (maldi, m/z): calcd. for $C_{18}H_{12}FN_2$ $[M+H]^+$ 275.0985, found 275.0984.

6-chloro-2, 2'-biquinoline (4j)

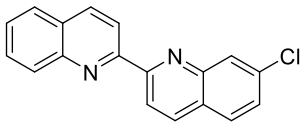


The reaction was conducted with 4-chloroaniline (**1j**, 51.0 mg, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4j** as yellow solid (9.9 mg, 17%), mp 194.3-198.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 8.4 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.23 (t, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.90-7.87 (m, 2H), 7.79-7.75 (m, 1H), 7.69 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.61-7.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.4, 155.7, 147.9, 146.3, 136.9, 135.8, 132.7, 131.5, 130.5, 129.9, 129.7, 129.0, 128.5, 127.7,

127.1, 126.4, 120.3, 119.3; HRMS (maldi, m/z): calcd. for $C_{18}H_{11}ClN_2Na$ $[M+Na]^+$ 313.0508, found 313.0502.

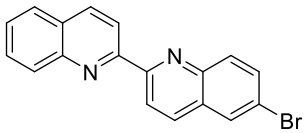
7-chloro-2, 2'-biquinoline (4k)



The reaction was conducted with 3-chloroaniline (**1k**, 42.3 μL, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4k** as yellow solid (11.6 mg, 20%), mp 205.6-209.2 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.76 (dd, *J* = 17.2, 8.4 Hz, 2H), 8.25 (dd, *J* = 14.0, 8.4 Hz, 2H), 8.17-8.15 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.72-7.68 (m, 1H), 7.54-7.51 (m, 1H), 7.46 (dd, *J* = 8.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.2, 155.8, 148.3, 147.9, 136.8, 136.5, 135.4, 130.0, 129.6, 128.9, 128.8, 128.5, 127.9, 127.7, 127.1, 126.8, 119.6, 119.3; HRMS (maldi, m/z): calcd. for $C_{18}H_{11}ClN_2Na$ $[M+Na]^+$ 313.0508, found 313.0513.

6-bromo-2, 2'-biquinoline (4l)

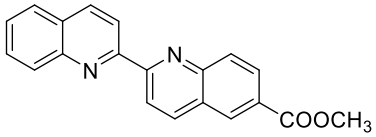


The reaction was conducted with 4-bromoaniline (**1l**, 83.4 mg, 0.4 mmol) and 2-methylquinoline (**2a**, 27.1 μL, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4l** as yellow solid (13.4 mg, 20%), mp 285.0-288.2 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (d, *J* = 8.8 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.17-8.14 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.97 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76-7.68 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.6, 155.8,

147.9, 146.5, 136.8, 135.7, 133.0, 131.6, 129.9, 129.7, 129.7, 129.5, 128.5, 127.7, 127.1, 120.8, 120.3, 119.3; HRMS (maldi, m/z): calcd. for $C_{18}H_{11}BrN_2Na$ $[M+Na]^+$ 357.0003, found 356.9992.

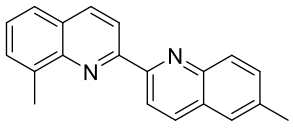
methyl [2, 2'-biquinoline]-6-carboxylate (4m)



The reaction was conducted with aniline (**1m**, 36.4 μL, 0.4 mmol) and methyl 2-methylquinoline-6-carboxylate (**2g**, 80.5 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 1:1) afforded the product **4m** as yellow solid (23.2 mg, 37%), mp 266.4-269.8 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 8.8 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 8.59 (s, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 8.30-8.27 (m, 2H), 8.18 (t, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 158.2, 155.7, 149.8, 147.9, 138.0, 136.9, 130.8, 130.2, 130.0, 129.7, 129.1, 128.6, 128.3, 127.7, 127.6, 127.3, 120.2, 119.4, 52.4; HRMS (maldi, m/z): calcd. for $C_{20}H_{14}N_2O_2Na$ $[M+Na]^+$ 337.0953, found 337.0953.

6, 8'-dimethyl-2, 2'-biquinoline (4n)

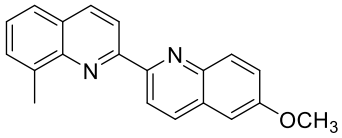


The reaction was conducted with *o*-toluidine (**1b**, 42.7 μL, 0.4 mmol) and 2,6-dimethylquinoline (**2b**, 31.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4n** as red solid (37.4 mg, 66%), mp 263.2-266.1 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 8.4 Hz, 1H), 8.84 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.61-7.57 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 2.96 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$, ppm) δ 155.8, 154.9, 146.8, 146.5, 137.8, 136.9, 136.8, 135.9, 131.8, 129.6, 128.5, 128.3, 126.6, 126.6, 125.6, 119.5, 118.8, 21.7, 17.9; HRMS (maldi, m/z): calcd. for $C_{20}H_{16}N_2Na$ $[M+Na]^+$ 307.1211, found 307.1214.

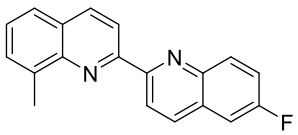
6-methoxy-8'-methyl-2, 2'-biquinoline (4o)



The reaction was conducted with *o*-toluidine (**1b**, 42.7 μL, 0.4 mmol) and 6-methoxy-2-methylquinoline (**2c**, 34.6 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 1:1) afforded the product **4o** as red solid (32.5 mg, 54%), mp 175.3-178.6 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.82 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.40-7.32 (m, 2H), 7.08 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.1, 154.9, 154.4, 146.8, 143.9, 137.7, 136.9, 135.3, 131.3, 129.5, 129.5, 128.3, 126.5, 125.6, 122.2, 119.8, 118.7, 105.2, 55.6, 17.9; HRMS (maldi, m/z): calcd. for $C_{20}H_{16}N_2NaO$ $[M+Na]^+$ 323.1160, found 323.1166.

6-fluoro-8'-methyl-2, 2'-biquinoline (4p)

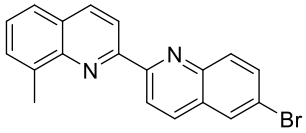


The reaction was conducted with *o*-toluidine (**1b**, 42.7 μL, 0.4 mmol) and 6-fluoro-2-methylquinoline (**2d**, 32.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4p** as white solid (14.4 mg, 27%), mp 205.1-208.4 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.95 (d, *J* = 8.4 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.30 - 8.20 (m, 3H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.54-7.44 (m, 3H), 2.96 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7 (d, *J* = 247.0 Hz), 156.1, 154.4, 146.8, 145.0, 137.8, 137.0, 135.9 (d, *J* = 5.2 Hz), 132.3 (d, *J* = 9.2 Hz), 129.7, 129.1 (d, *J* = 10.0 Hz), 128.4, 126.8, 125.6, 120.3, 119.6 (d, *J* = 25.6 Hz), 118.7, 110.7 (d, *J* = 21.5 Hz), 17.9; HRMS (maldi, m/z): calcd. for $C_{19}H_{13}FN_2Na$ $[M+Na]^+$ 311.0960, found 311.0966.

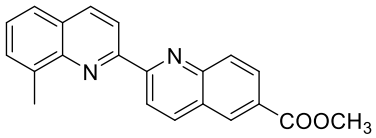
6-bromo-8'-methyl-2, 2'-biquinoline (4q)



The reaction was conducted with *o*-toluidine (**1b**, 42.7 μL, 0.4 mmol) and 6-bromo-2-methylquinoline (**2e**, 44.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4q** as yellow solid (19.2 mg, 28%), mp 260.3-263.7 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.0, 154.3, 146.8, 146.5, 137.9, 137.0, 135.5, 135.5, 132.9, 131.6, 129.7, 129.5, 128.5, 126.9, 125.6, 120.7, 120.4, 118.7, 17.9; HRMS (maldi, m/z): calcd. for $C_{19}H_{13}BrN_2Na$ $[M+H]^+$ 349.0340, found 349.0337.

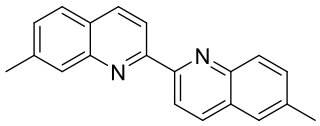
methyl 8'-methyl-[2, 2'-biquinoline]-6-carboxylate (4r)



The reaction was conducted with *o*-toluidine (**1b**, 42.7 μL, 0.4 mmol) and methyl 2-methylquinoline-6-carboxylate (**2g**, 40.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 1:1) afforded the product **4r** as white solid (29.9 mg, 46%), mp 228.5-231.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (d, *J* = 8.8 Hz, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.56 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 8.24 (t, *J* = 9.2 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 3.94 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 158.6, 154.2, 149.8, 146.8, 137.9, 137.8, 137.1, 130.8, 130.1, 129.7, 129.0, 128.6, 128.1, 127.5, 127.1, 125.6, 120.3, 118.9, 52.4, 17.9; HRMS (maldi, m/z): calcd. for $C_{21}H_{16}N_2NaO_2$ $[M+Na]^+$ 351.1109, found 351.1114.

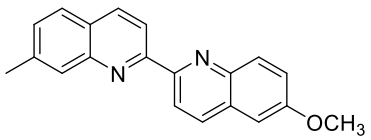
6, 7'-dimethyl-2, 2'-biquinoline (4s)



The reaction was conducted with *m*-toluidine (**1c**, 42.9 μL, 0.4 mmol) and 2,6-dimethylquinoline (**2b**, 31.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4s** as red solid (35.3 mg, 62%), mp 258.6-263.7 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.69 (dd, *J* = 12.0, 8.4 Hz, 2H), 8.17 (dd, *J* = 15.6, 8.8 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.3, 155.6, 148.2, 146.5, 139.7, 136.9, 136.4, 136.0, 131.8, 129.6, 129.1, 128.9, 128.4, 127.3, 126.5, 126.4, 119.4, 118.6, 21.9, 21.7; HRMS (maldi, m/z): calcd. for $C_{20}H_{16}N_2Na$ $[M+Na]^+$ 307.1211, found 307.1219.

6-methoxy-7'-methyl-2, 2'-biquinoline (4t)

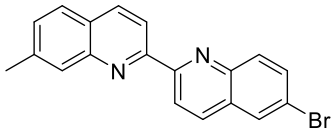


The reaction was conducted with *m*-toluidine (**1c**, 42.9 μL, 0.4 mmol) and 6-methoxy-2-methylquinoline (**2c**, 34.6 mg, 0.2 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4t** as yellow solid (51.2 mg, 85%), mp 245.4-248.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.92 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.07 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.2, 156.4, 154.2, 148.2, 144.0, 139.7, 136.4, 135.4, 131.4, 129.5, 129.0, 128.8, 127.3, 126.4, 122.3, 119.7, 118.4, 105.2, 55.6, 21.9; HRMS (maldi, m/z): calcd. for $C_{20}H_{16}N_2NaO$ $[M+Na]^+$ 323.1160, found 323.1170.

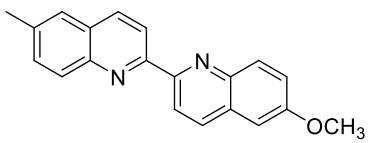
6-bromo-7'-methyl-2, 2'-biquinoline (4u)



The reaction was conducted with *m*-toluidine (**1c**, 42.9 μL, 0.4 mmol) and 6-bromo-2-methylquinoline (**2e**, 44.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4u** as yellow solid (57.3 mg, 82%), mp 260.2-264.0 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.78 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.02-7.94 (m, 3H), 7.75-7.70 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.8, 155.7, 148.2, 146.5, 140.0, 136.5, 135.6, 133.0, 131.6, 129.7, 129.5, 129.4, 128.9, 127.3, 126.6, 120.7, 120.3, 118.5, 21.9; HRMS (maldi, m/z): calcd. for $C_{19}H_{14}BrN_2$ $[M+H]^+$ 349.0340, found 349.0336.

6-methoxy-6'-methyl-2, 2'-biquinoline (4v)

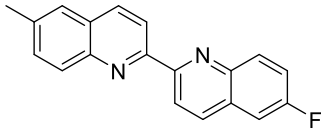


The reaction was conducted with *p*-toluidine (**1d**, 42.9 mg, 0.4 mmol) and 6-methoxy-2-methylquinoline (**2c**, 34.6 mg, 0.2 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4v** as yellow solid (43.7 mg, 73%), mp 249.3-253.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.69 (t, *J* = 8.4 Hz, 2H), 8.15 (dd, *J* = 8.8, 3.2 Hz, 2H), 8.04 (dd, *J* = 9.2, 4.8 Hz, 2H), 7.57 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 3.90 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.1, 155.6, 154.2, 146.5, 144.0, 136.7, 136.0, 135.4, 131.8, 131.3, 129.5, 129.4, 128.3, 126.6, 122.2, 119.7, 119.2, 105.2, 55.6, 21.7; HRMS (maldi, m/z): calcd. for $C_{20}H_{16}N_2NaO$ $[M+Na]^+$ 323.1160, found 323.1170.

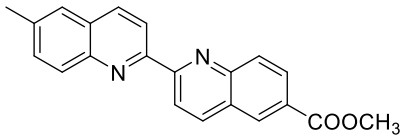
6-fluoro-6'-methyl-2, 2'-biquinoline (4w)



The reaction was conducted with *p*-toluidine (**1d**, 42.9 mg, 0.4 mmol) and 6-fluoro-2-methylquinoline (**2d**, 32.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4w** as yellow solid (31.2 mg, 54%), mp 263.7-266.0 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.78 (d, *J* = 8.8 Hz, 1H), 8.69 (d, *J* = 8.8 Hz, 1H), 8.21-8.13 (m, 3H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.48-7.41 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7 (d, *J* = 247.1 Hz), 155.9, 155.1, 146.5, 145.0, 137.0, 136.1, 136.0 (d, *J* = 5.3 Hz), 132.3 (d, *J* = 9.1 Hz), 131.9, 129.6, 129.0 (d, *J* = 10.1 Hz), 128.5, 126.6, 120.1, 119.7 (d, *J* = 25.6 Hz), 119.2, 110.7 (d, *J* = 21.6 Hz), 21.7; HRMS (maldi, m/z): calcd. for $C_{19}H_{13}FN_2Na$ $[M+Na]^+$ 311.0960, found 311.0965.

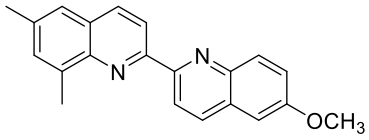
methyl 6'-methyl-[2, 2'-biquinoline]-6-carboxylate (4x)



The reaction was conducted with *p*-toluidine (**1d**, 42.9 mg, 0.4 mmol) and methyl 2-methylquinoline-6-carboxylate (**2g**, 40.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 1:1) afforded the product **4x** as red solid (33.0 mg, 50%), mp 281.6-284.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.83 (d, *J* = 8.8 Hz, 1H), 8.73 (d, *J* = 8.8 Hz, 1H), 8.57 (d, *J* = 1.6 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.28-8.25 (m, 1H), 8.18 (d, *J* = 7.6 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.59 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 3.95 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 158.4, 154.8, 149.8, 146.5, 137.9, 137.3, 136.2, 132.0, 130.8, 130.1, 129.7, 129.0, 128.6, 128.2, 127.5, 126.6, 120.2, 119.4, 52.4, 21.7; HRMS (maldi, m/z): calcd. for $C_{21}H_{16}N_2NaO_2$ $[M+Na]^+$ 351.1109, found 351.1108.

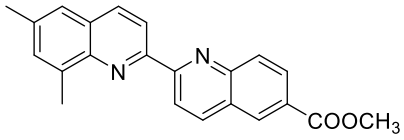
6'-methoxy-6, 8-dimethyl-2, 2'-biquinoline (4y)



The reaction was conducted with 2,4-dimethylaniline (**1e**, 49.5 μL, 0.4 mmol) and 6-methoxy-2-methylquinoline (**2c**, 34.6 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **4y** as yellow solid (25.5 mg, 41%), mp 255.8-259.4 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.87 (d, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 8.19 (t, *J* = 7.6 Hz, 2H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.47-7.38 (m, 3H), 7.14 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H), 2.92 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.1, 154.6, 154.1, 145.4, 143.9, 137.3, 136.4, 136.2, 135.3, 131.9, 131.3, 129.4, 128.3, 124.5, 122.1, 119.8, 118.7, 105.2, 55.6, 21.7, 17.8; HRMS (maldi, m/z): calcd. for $C_{21}H_{18}N_2NaO$ $[M+Na]^+$ 337.1317, found 337.1321.

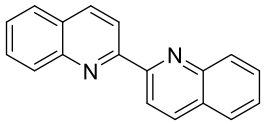
methyl 6', 8'-dimethyl-[2, 2'-biquinoline]-6-carboxylate (4z)



The reaction was conducted with 2,4-dimethylaniline (**1e**, 49.5 μL, 0.4 mmol) and 2-methylquinoline-6-carboxylate (**2g**, 40.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 1:1) afforded the product **4y** as white solid (23.9 mg, 35%), mp 280.1-283.0 ^{o}C

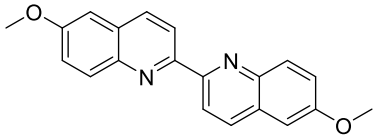
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.99 (d, *J* = 8.4 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.64 (s, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.23 (t, *J* = 9.6 Hz, 2H), 7.49 (s, 1H), 7.46 (s, 1H), 4.02 (s, 3H), 2.92 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.8, 158.8, 153.4, 149.8, 145.5, 137.7, 137.5, 137.0, 136.4, 132.1, 130.8, 130.1, 129.0, 128.7, 128.0, 127.5, 124.5, 120.3, 118.9, 52.4, 21.7, 17.8; HRMS (maldi, m/z): calcd. for $C_{22}H_{18}N_2NaO_2$ $[M+Na]^+$ 365.1266, found 365.1261.

2, 2'-biquinoline (5a) [3]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.76 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.2, 147.9, 136.7, 129.9, 129.5, 128.4, 127.6, 126.9, 119.4; HRMS (maldi, m/z): calcd. for $C_{18}H_{13}N_2$ $[M+H]^+$ 257.1079, found 257.1071.

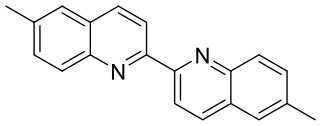
6, 6'-dimethoxy-2, 2'-biquinoline (5b) [2]



The reaction was conducted with 4-methoxyaniline (**1a**, 24.6 mg, 0.2 mmol) and 1,4-dioxane (1.5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **5b** as yellow solid (18.7 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.68 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 9.2 Hz, 2H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.08 (d, *J* = 2.4 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.1, 154.2, 144.0, 135.4, 131.3, 129.4, 122.2, 119.5, 105.2, 55.6; HRMS (maldi, m/z): calcd. for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290, found 317.1277.

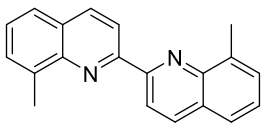
6, 6'-dimethyl-2, 2'-biquinoline (5c) [3]



The reaction was conducted with *p*-toluidine (**1d**, 21.4 mg, 0.2 mmol) and 1,4-dioxane (1.5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **5c** as white solid (23.0 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.70 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.56 (s, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.6, 146.5, 136.8, 136.0, 131.8, 129.5, 128.4, 126.5, 119.4, 21.7; HRMS (maldi, m/z): calcd. for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392, found 285.1382.

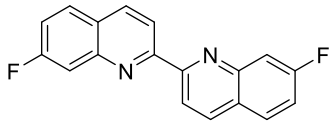
8, 8'-dimethyl-2, 2'-biquinoline (5d) [2]



The reaction was conducted with *o*-toluidine (**1b**, 21.3 μL, 0.2 mmol) and 1,4-dioxane (1.5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **5d** as yellow solid (13.9 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 6.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.1, 146.8, 137.8, 136.8, 129.5, 128.3, 126.6, 125.6, 118.9, 17.9; HRMS (maldi, m/z): calcd. for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392, found 285.1388.

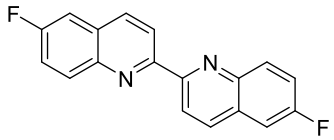
7, 7'-difluoro-2, 2'-biquinoline (5e)



The reaction was conducted with 3-fluoroaniline (**1i**, 19.2 μL, 0.2 mmol) and 1,4-dioxane (1.5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **5e** as red solid (9.9 mg, 34%), mp 246.5-249.3 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.72 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 2H), 7.82-7.76 (m, 4H), 7.31 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.3 (d, *J* = 248.4 Hz), 156.8, 148.9 (d, *J* = 12.7 Hz), 136.7, 129.6 (d, *J* = 9.8 Hz), 125.5, 118.8 (d, *J* = 2.5 Hz), 117.5 (d, *J* = 25.3 Hz), 113.5 (d, *J* = 20.1 Hz); HRMS (maldi, m/z): calcd. for $C_{18}H_{10}F_2N_2Na$ $[M+Na]^+$ 315.0710, found 315.0716.

6, 6'-difluoro-2, 2'-biquinoline (5f) [2]

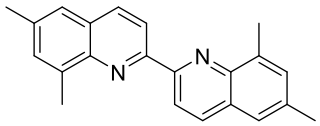


The reaction was conducted with 4-fluoroaniline (**1h**, 19.0 μL, 0.2 mmol) and 1,4-dioxane (1.5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **5f** as red solid (9.9 mg, 34%)

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.76 (d, *J* = 8.4 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.15 (dd, *J* = 9.2, 5.2 Hz, 2H), 7.49-7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.8 (d, *J* = 247.5 Hz), 155.4, 145.0, 136.1 (d, *J* = 5.3 Hz), 132.4 (d, *J* = 9.2 Hz), 129.1 (d, *J* = 10.1 Hz), 120.0,

119.7, 110.7 (d, J = 21.6 Hz); HRMS (maldi, m/z): calcd. for $C_{18}H_{11}F_2N_2$ $[M+H]^+$ 293.0890, found 293.0884.

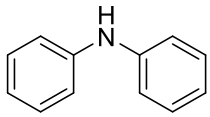
6, 6', 8, 8'-tetramethyl-2, 2'-biquinoline (5g)



The reaction was conducted with 2,4-dimethylaniline (**1e**, 24.7 μL, 0.2 mmol) and 1,4-dioxane (1.5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1) afforded the product **5g** as yellow solid (20.3 mg, 65%), mp 233.1-236.2 ^oC

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.87 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 7.47 (s, 2H), 7.44 (s, 2H), 2.92 (s, 6H), 2.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.5, 145.4, 137.3, 136.3, 136.0, 131.8, 128.4, 124.5, 118.9, 21.7, 17.8; HRMS (maldi, m/z): calcd. for $C_{22}H_{21}N_2$ $[M+H]^+$ 313.1705, found 313.1706.

Diphenylamine (Y) [1]



The reaction was conducted with nitrobenzene (**W**, 0.2 mmol) and cyclohexanone (**X**, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 98:2) afforded the product **Y** as white solid (23.7 mg, 70%, **4w** as ligand), mp 52.7-54.0 ^oC.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.28-7.24 (m, 4H), 7.07 (d, J = 8.4 Hz, 4H), 6.92 (td, J = 7.2 Hz, 0.8 Hz, 4H), 5.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.1, 129.3, 120.9, 117.7; HRMS (maldi, m/z): calcd. for $C_{12}H_{12}N$ $[M+H]^+$ 170.0964, found 170.0972. The experimental data of **Y** matched with those reported in the literature.[1]

7. References

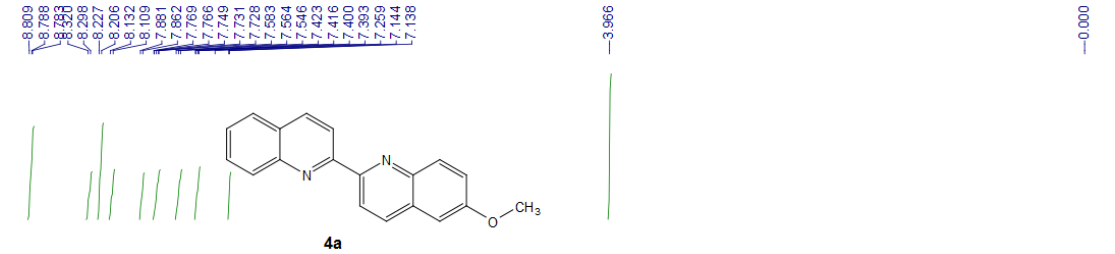
[1] Y. Xie, S. Liu, Y. Liu, Y. Wen, and G.-J. Deng, *Org. Lett.*, 2012, **14**, 1692-1695.

[2] W. Ma, J. Zhang, C. Xu, F. Chen, Y.-M. He, Q.-H. Fan, *Angew. Chem.* 2016, **128**,

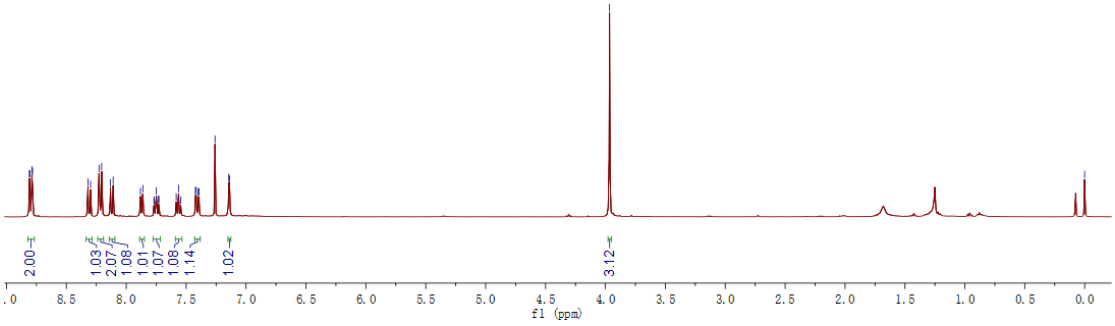
13083-13086,4; *Angew. Chem. Int. Ed.* **2016**, 55, 12891-12894.

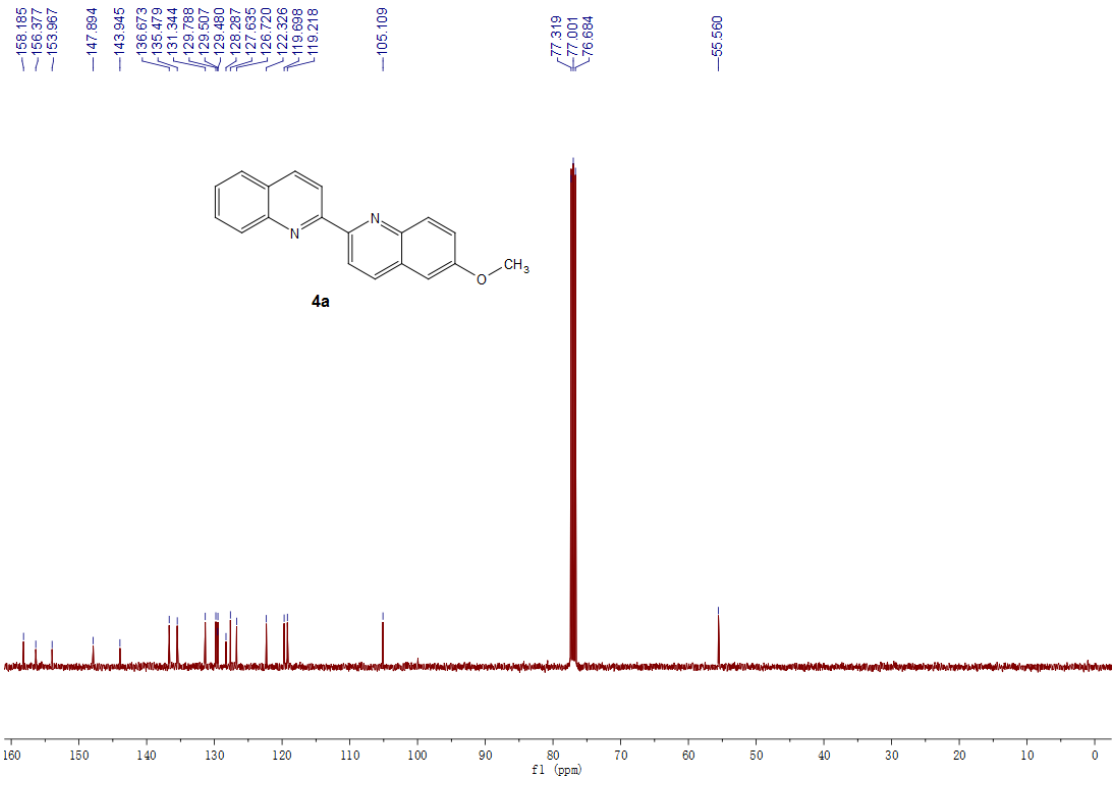
[3] W.-W. Xie, Y. Liu, R. Yuan, D. Zhao, T.-Z. Yu, J. Zhang, and C.-S. Da, *Adv. Synth. Catal.* 2016, **358**, 994-1002.

8. Copies of ^{1}H and ^{13}C NMR spectra of all products

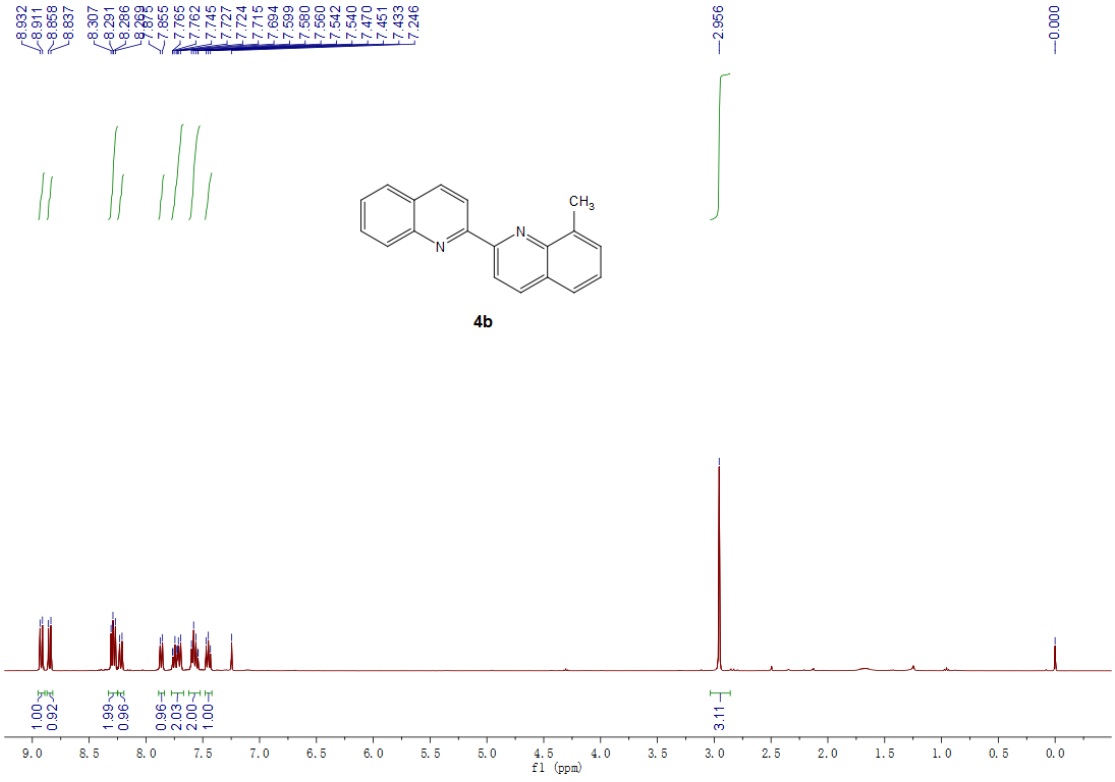


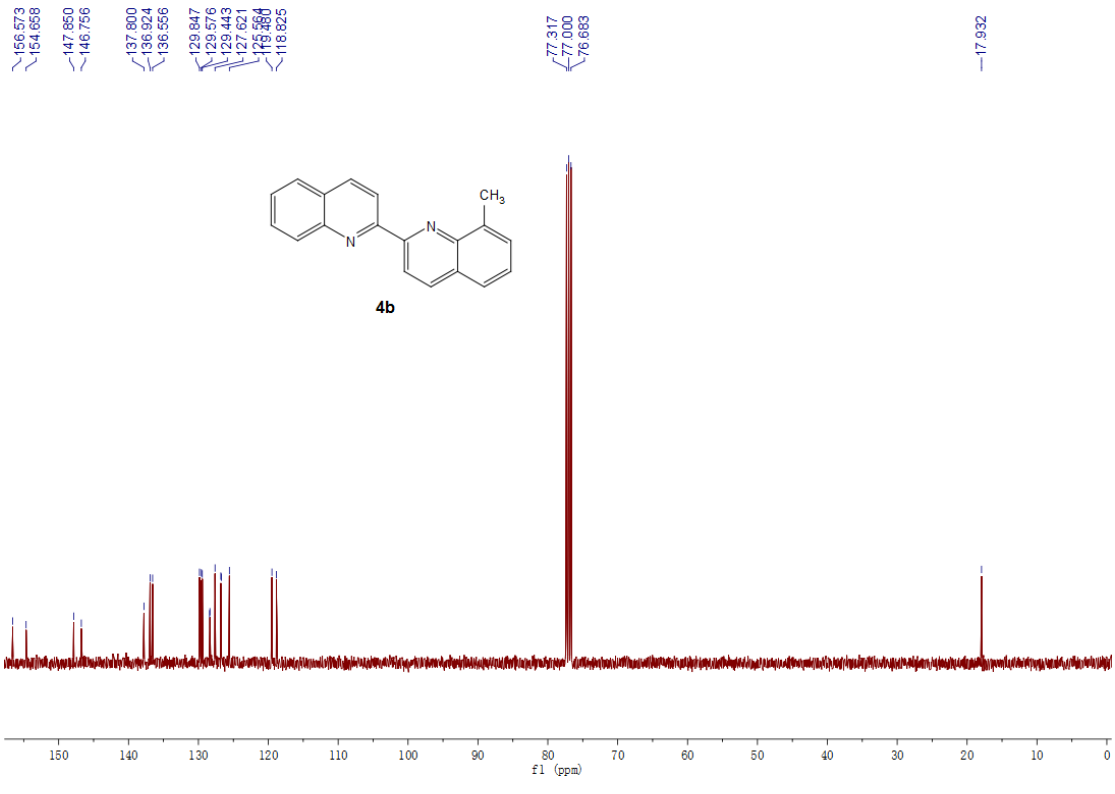
4a

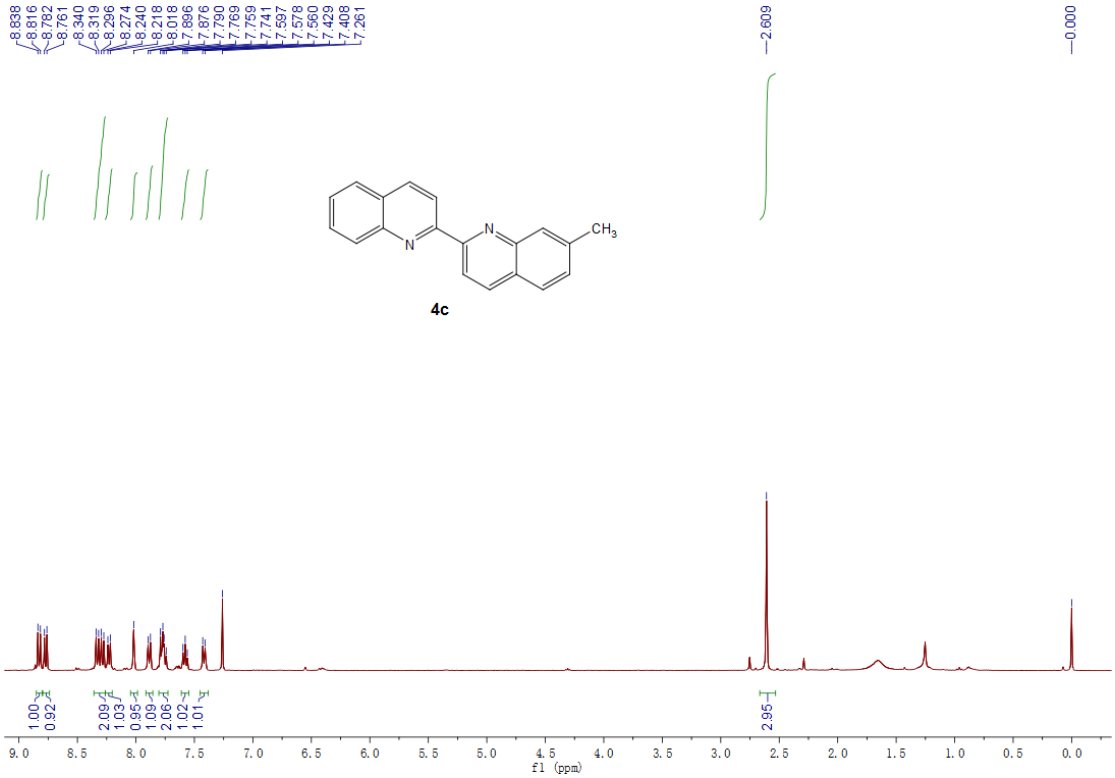


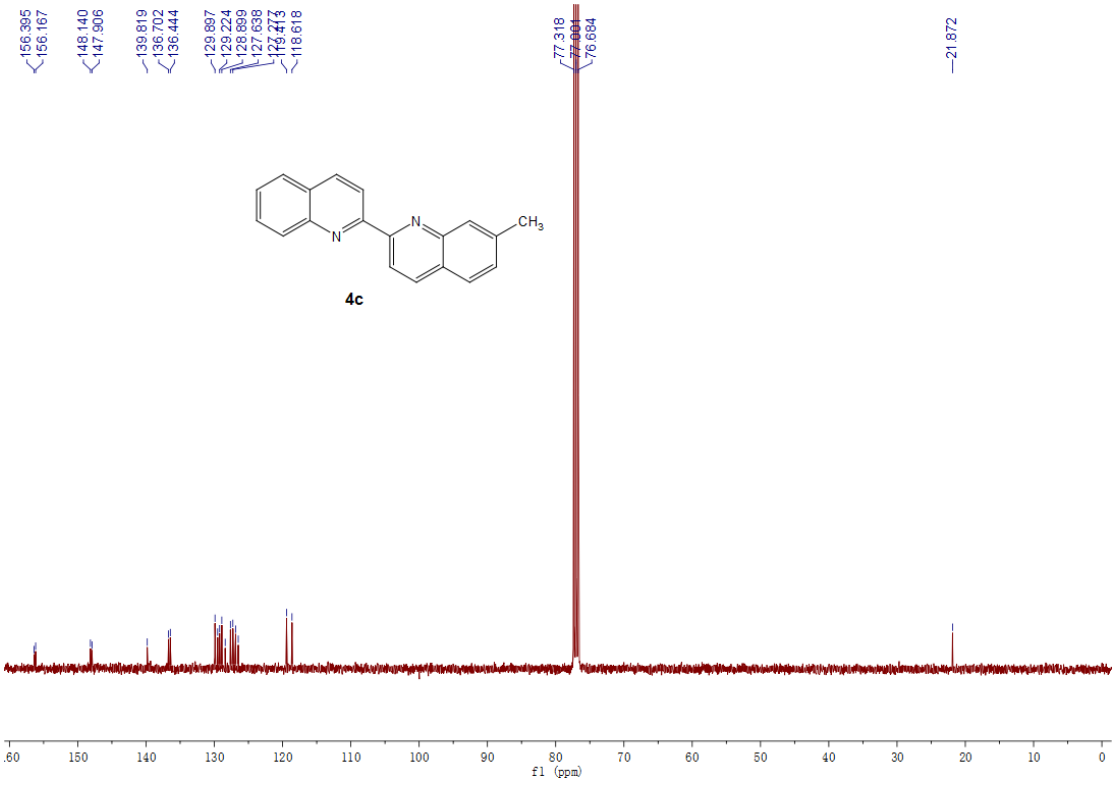


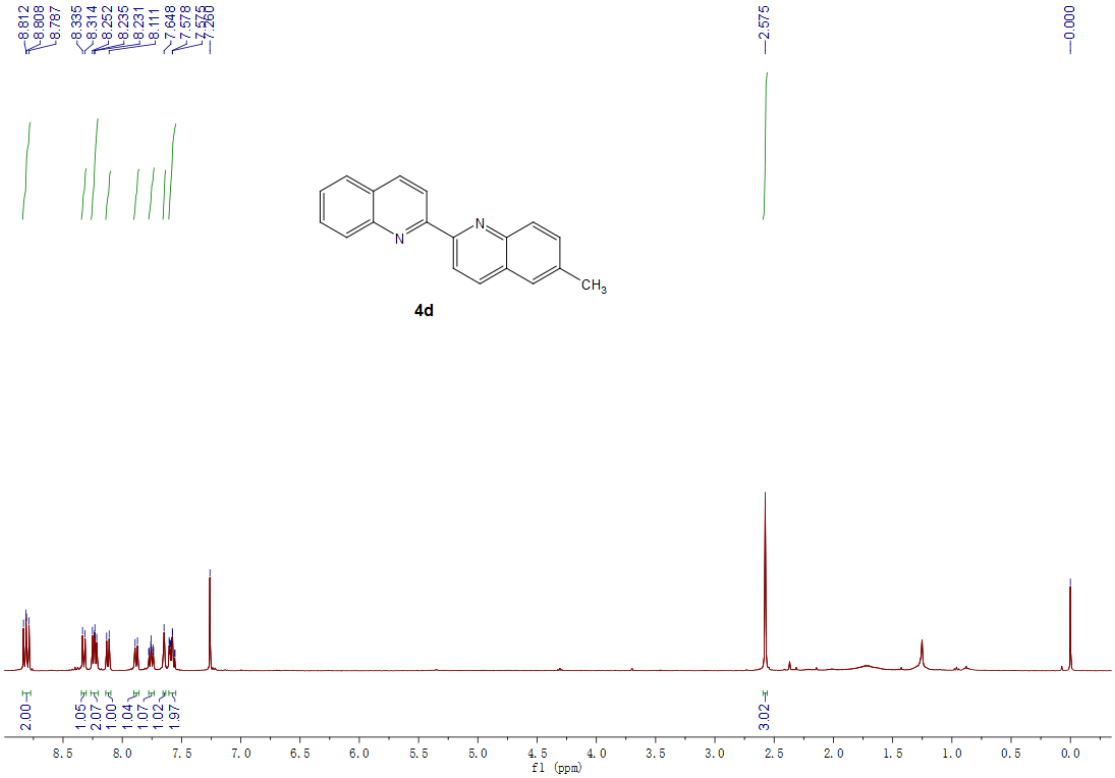
4a

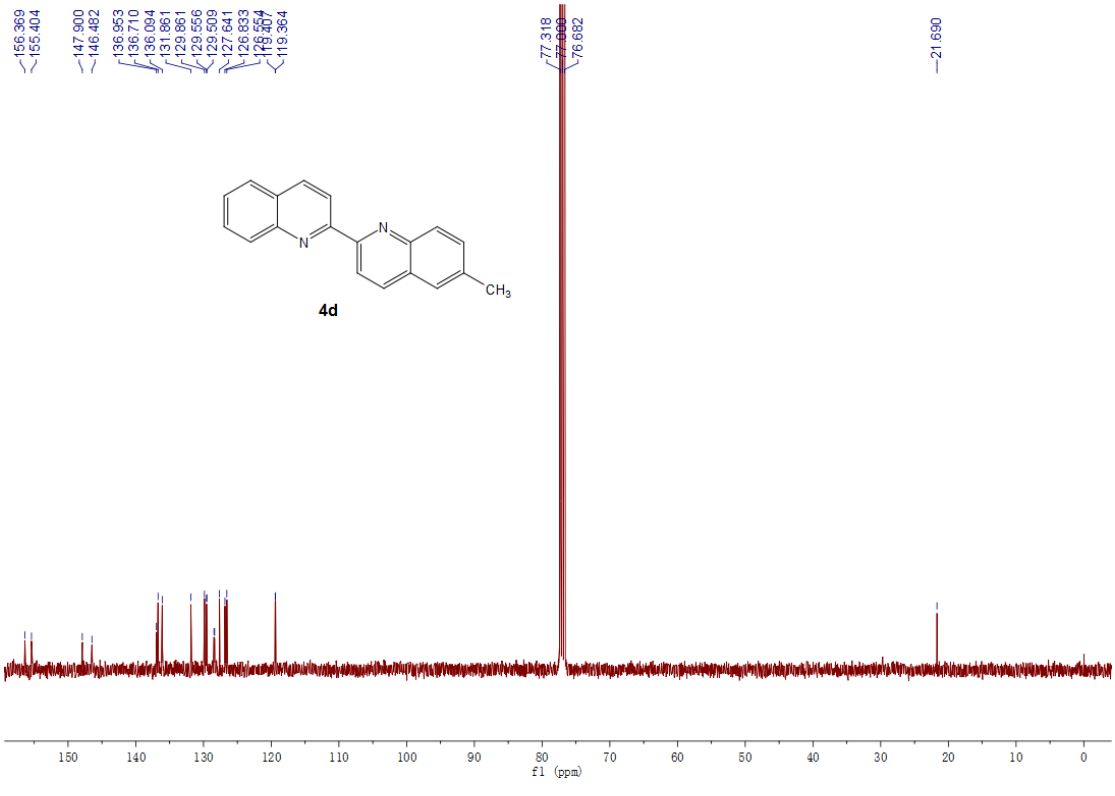

8.932
8.911
8.858
8.837
8.307
8.291
8.286
7.855
7.765
7.762
7.745
7.727
7.724
7.715
7.694
7.599
7.580
7.560
7.542
7.540
7.470
7.451
7.433
7.246
2.956
0.000
CH3
N
N
4b
1.00
0.92
1.99
0.96
0.96
2.03
2.00
1.00
3.11
f1 (ppm)


156.573
154.658
147.850
146.756
137.800
136.924
136.556
129.847
129.576
129.443
127.621
118.825
77.317
77.000
76.683
17.932
CH3
N
N
4b
f1 (ppm)


8.838
8.816
8.782
8.761
8.340
8.319
8.296
8.274
8.240
8.218
8.018
7.896
7.876
7.790
7.769
7.759
7.741
7.597
7.578
7.560
7.429
7.408
7.261
2.609
0.000
N
N
CH3
4c
1.00
0.92
2.09
1.03
0.95
1.09
2.06
1.02
1.01
2.95
f1 (ppm)


156.395
156.167
148.140
147.906
139.819
136.702
136.444
129.897
129.224
128.899
127.638
124.473
124.417
118.618
77.318
77.001
76.684
21.872
N
N
CH3
4c
f1 (ppm)


8.812
8.808
8.787
8.335
8.314
8.252
8.235
8.231
8.111
7.648
7.578
2.575
0.000
N
N
CH3
4d
2.00
1.05
2.07
1.00
1.04
1.07
1.02
1.97
3.02
f1 (ppm)


156.369
155.404
147.900
146.482
136.953
136.710
136.094
131.861
129.861
129.556
129.509
127.641
126.833
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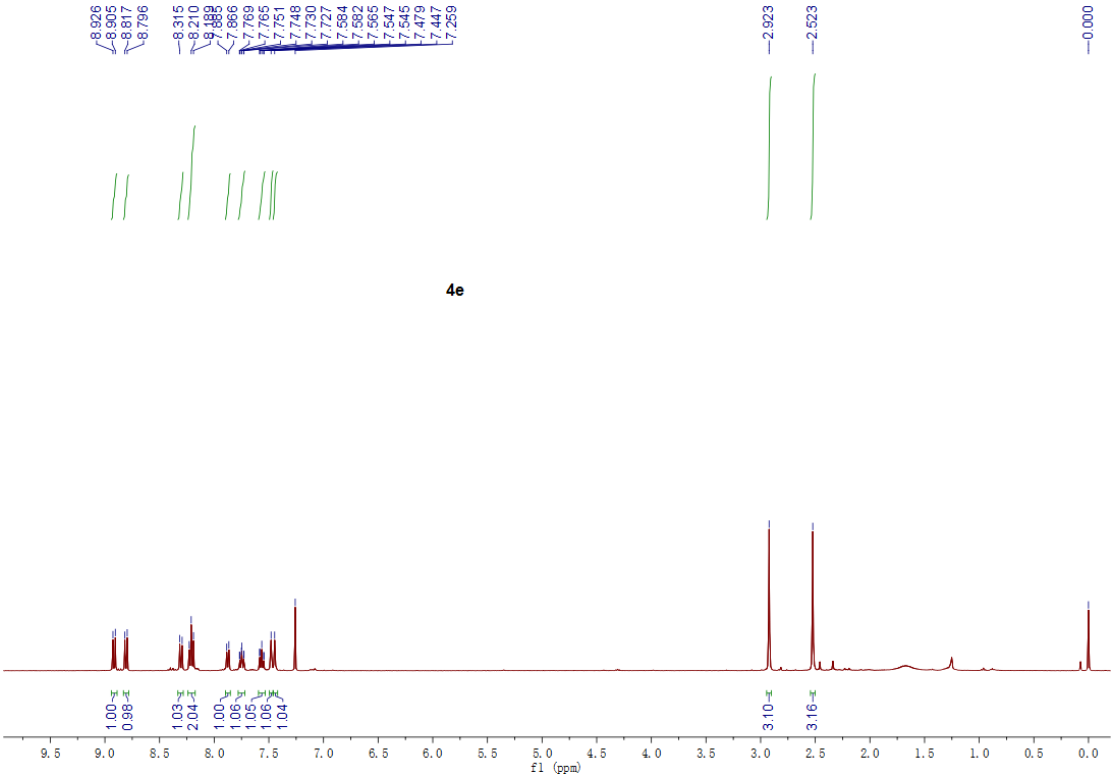
21.690
N
N
CH3
4d
f1 (ppm)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8.905
8.817
8.796
8.315
8.210
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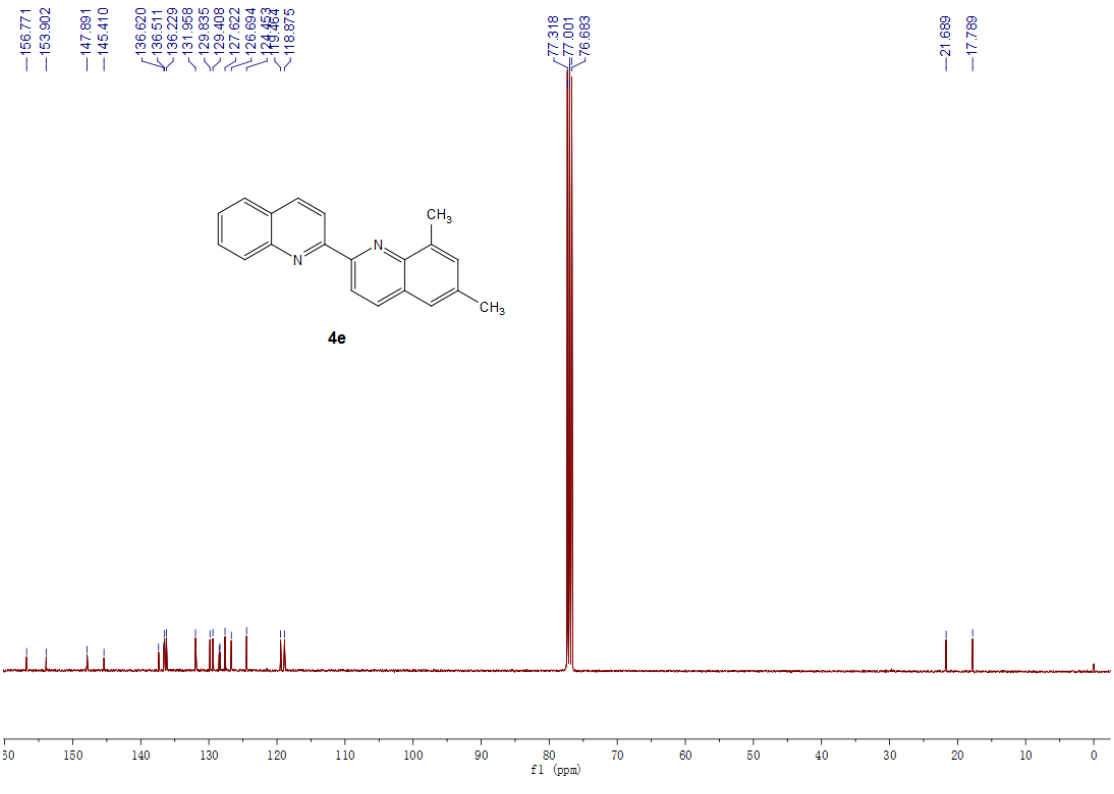
7.866
7.769
7.765
7.751
7.748
7.730
7.727
7.584
7.582
7.565
7.547
7.545
7.479
7.447
7.259
2.923
2.523
0.000
1.00
0.98
1.03
2.04
1.00
1.06
1.05
1.06
1.04
3.10
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4e


156.771
153.902
147.891
145.410
136.620
136.511
136.229
131.958
129.835
129.408
127.622
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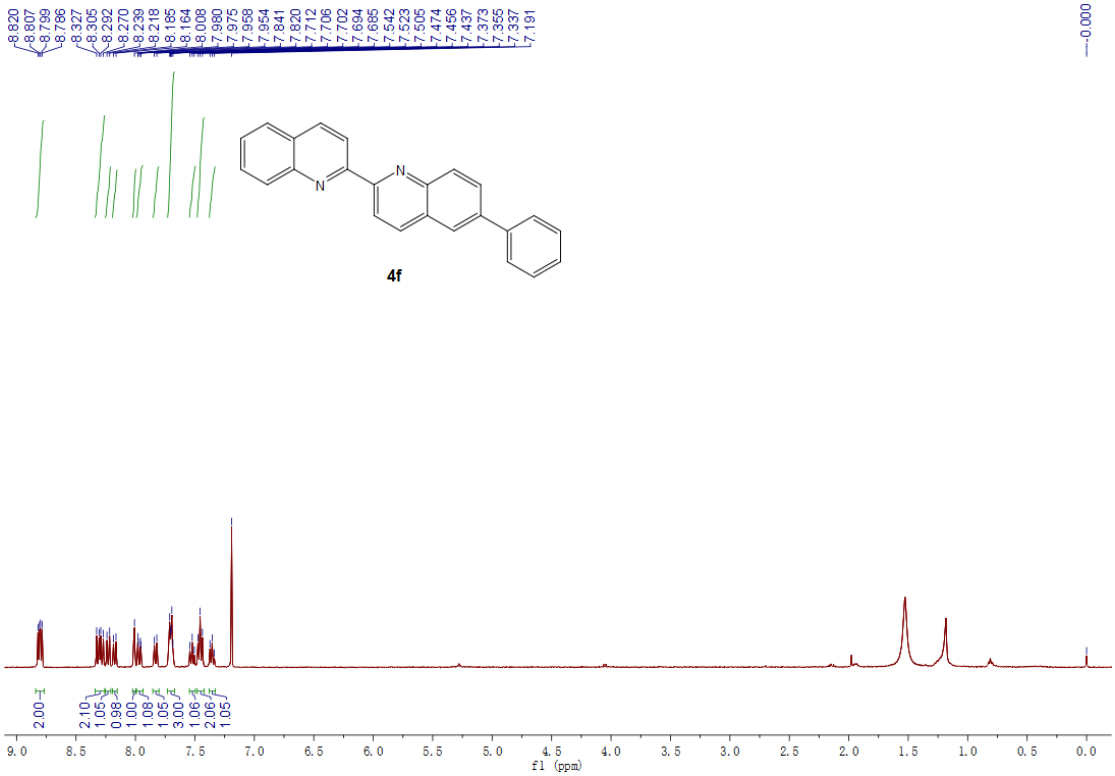
124.453
118.875
77.318
77.001
76.683
21.689
17.789
CH3
CH3
N
N
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4e


8.820
8.807
8.799
8.786
8.327
8.305
8.292
8.270
8.239
8.218
8.185
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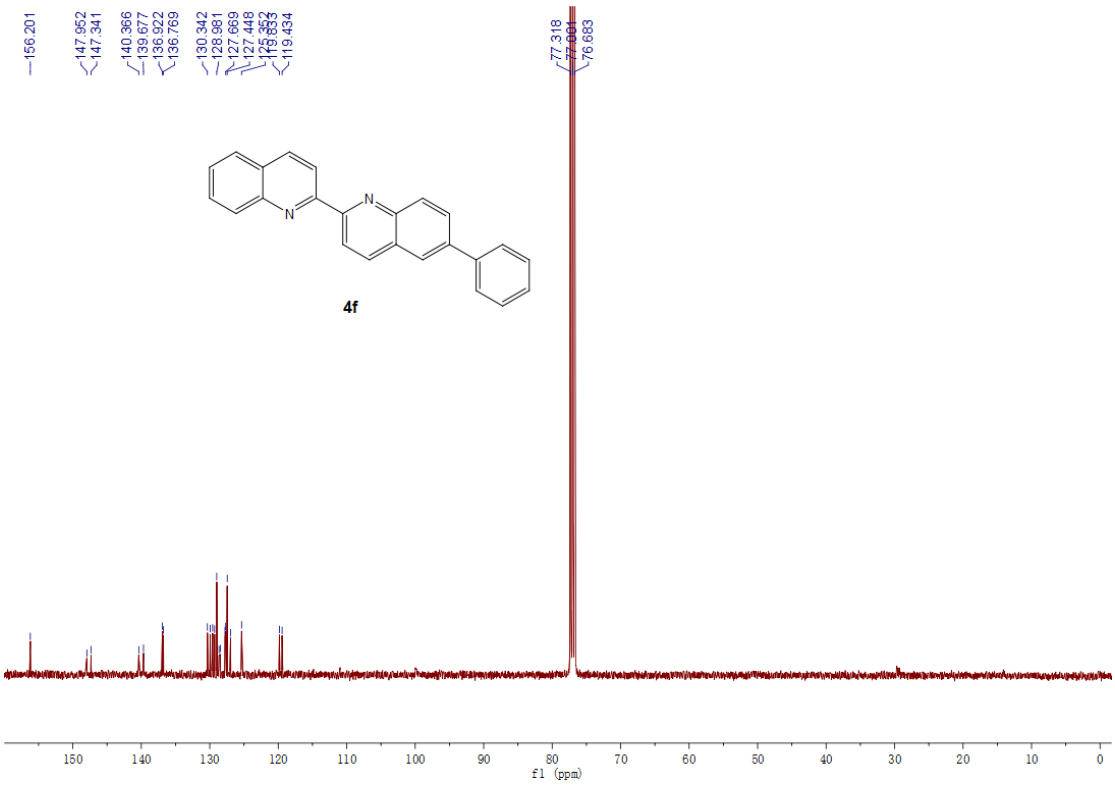
8.008
7.980
7.975
7.958
7.954
7.841
7.820
7.712
7.706
7.702
7.694
7.685
7.542
7.523
7.505
7.474
7.456
7.437
7.373
7.355
7.337
7.191
0.000
4f
2.00
2.10
1.05
0.98
1.00
1.08
1.05
3.00
1.06
2.06
1.05
f1 (ppm)


156.201
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140.366
139.677
136.922
136.769
130.342
128.981
127.669
127.448
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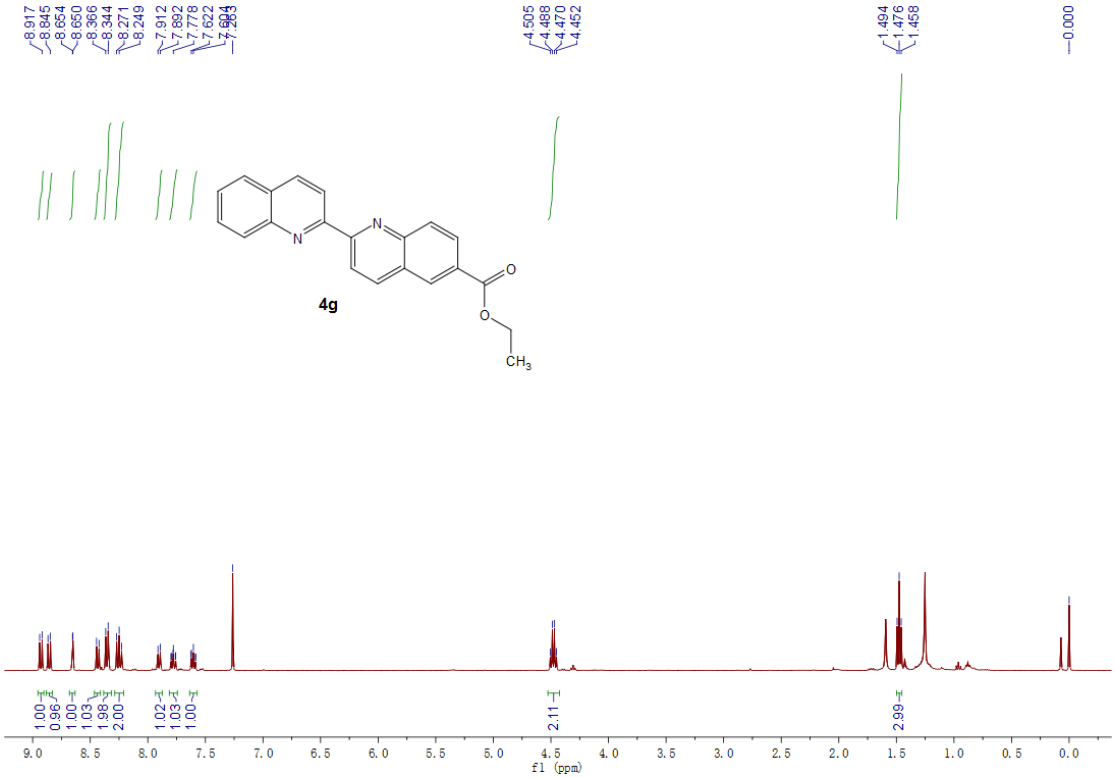
119.434
77.318
77.001
76.683
4f
f1 (ppm)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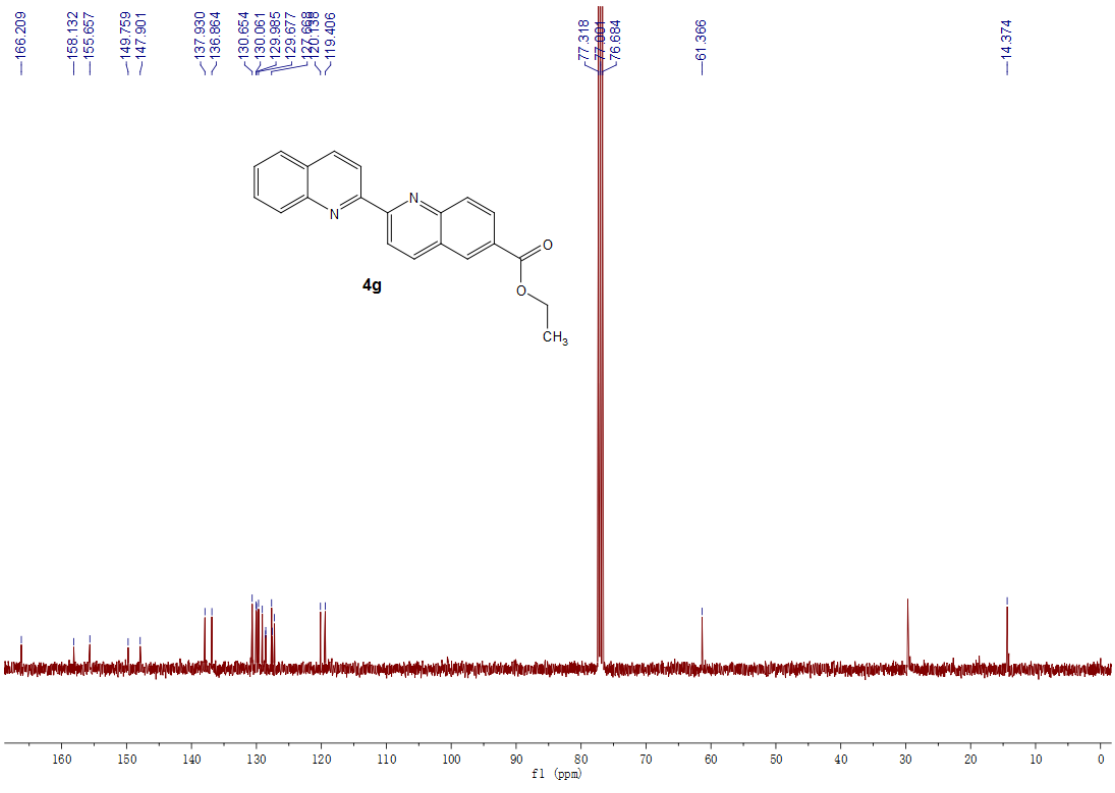
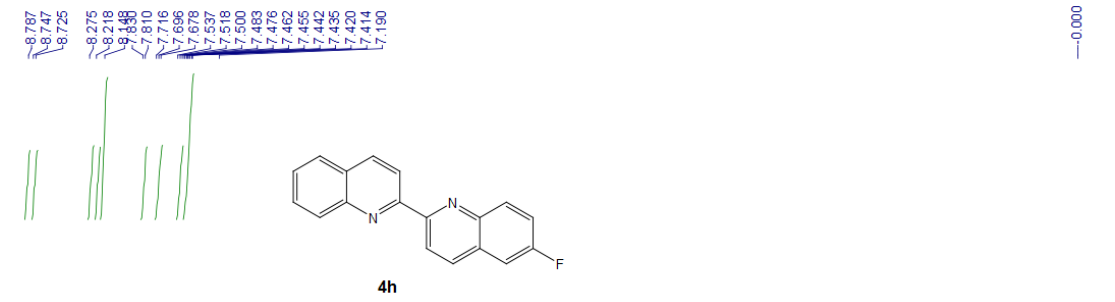
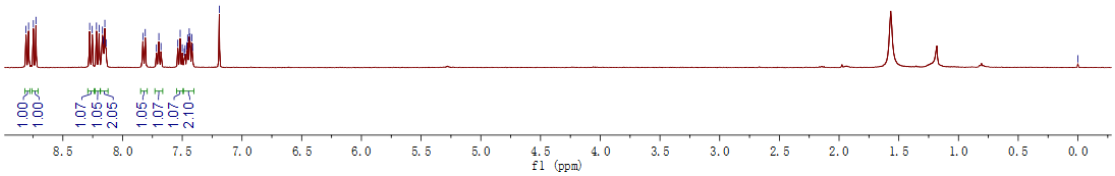
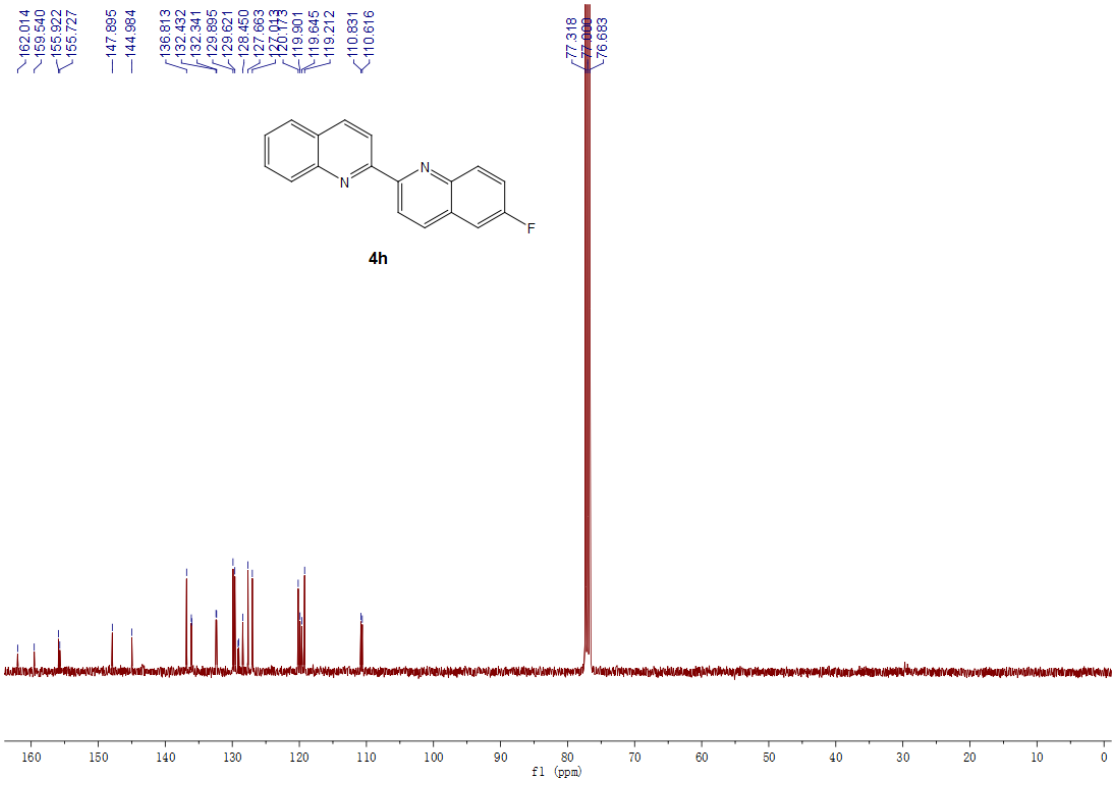
8.845
8.654
8.650
8.366
8.344
8.271
8.249
7.912
7.892
7.778
7.622
4.505
4.488
4.470
4.452
1.494
1.476
1.458
0.000
4g
1.00
0.96
1.00
1.03
1.98
2.00
1.02
1.03
1.00
2.11
2.99
f1 (ppm)


166.209
158.132
155.657
149.759
147.901
137.930
136.864
130.654
130.061
129.985
129.677
127.668
120.138
119.406
77.318
77.001
76.684
61.366
14.374
4g
f1 (ppm)

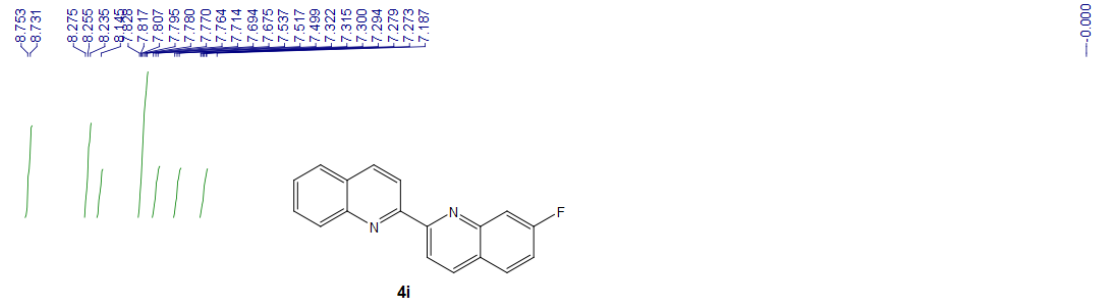

8.787
8.747
8.725
8.275
8.218
7.716
7.696
7.678
7.537
7.518
7.500
7.483
7.476
7.462
7.455
7.442
7.436
7.420
7.414
7.190
0.000
N
N
F

4h

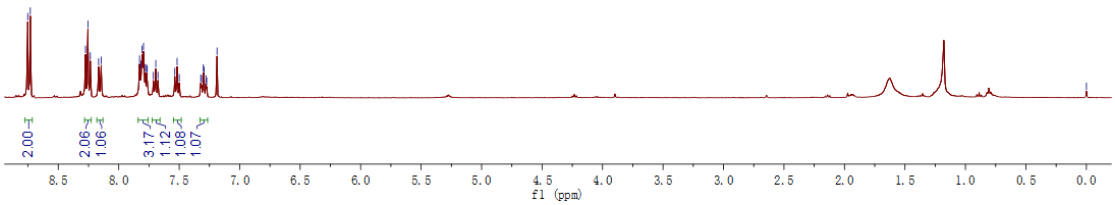

1.00
1.00
1.07
1.05
2.05
1.05
1.07
1.07
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

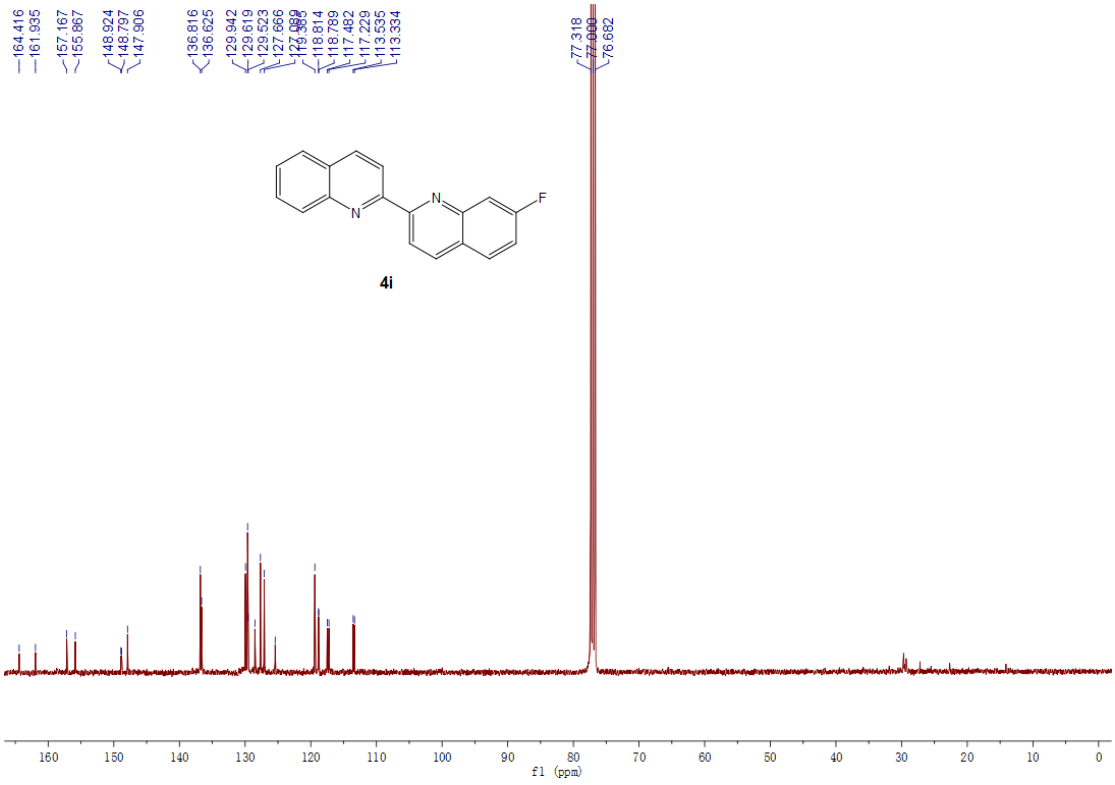

162.014
159.540
155.922
155.727
147.895
144.984
136.813
132.432
132.341
129.895
129.621
128.450
127.663
120.173
120.013
119.901
119.645
119.212
110.831
110.616
77.318
77.000
76.683
N
N
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4h

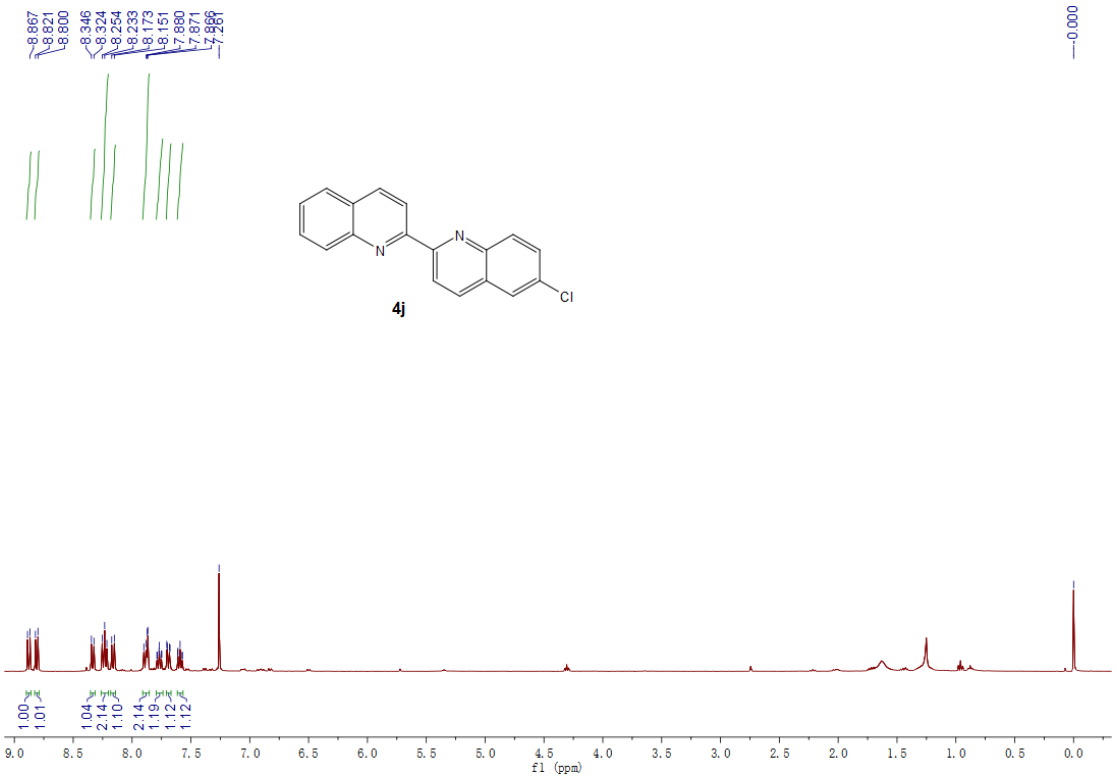

8.753
8.731
8.275
8.255
8.236
7.817
7.807
7.796
7.780
7.770
7.764
7.714
7.694
7.675
7.537
7.517
7.499
7.322
7.315
7.300
7.294
7.279
7.273
7.187
0.000
N
N
F

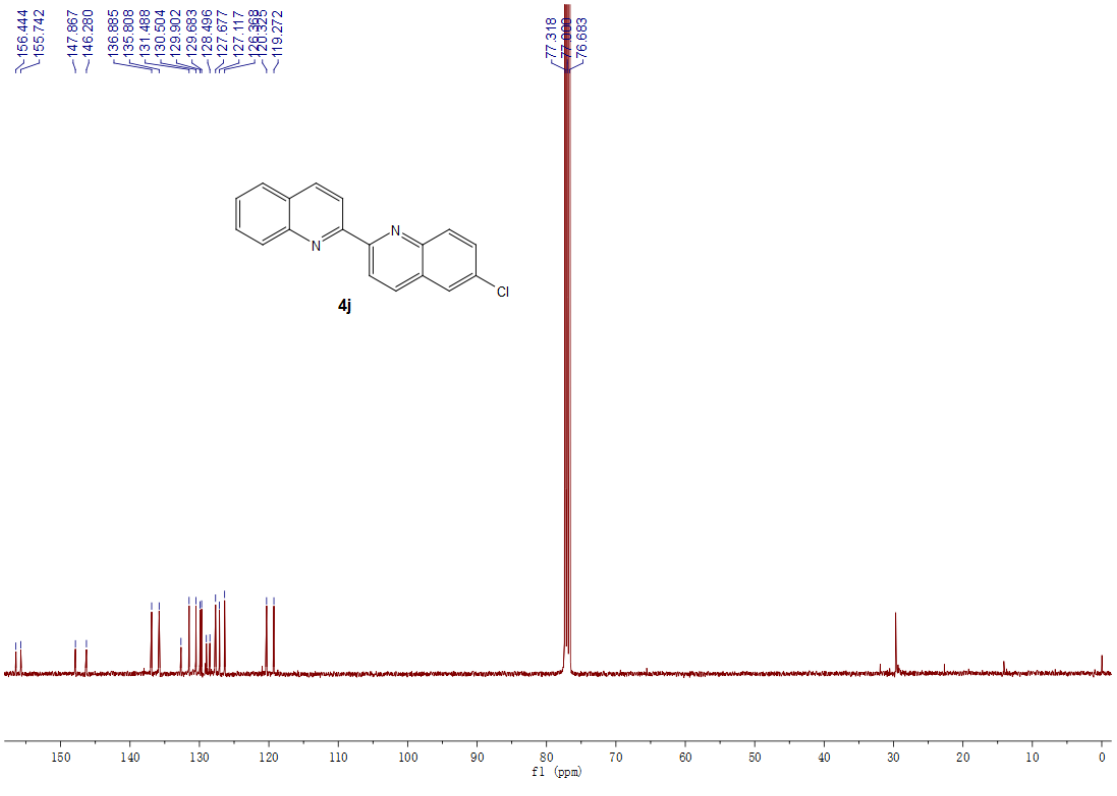
4i

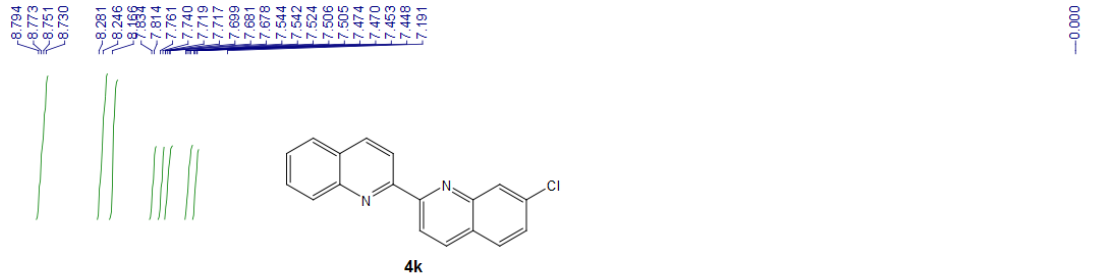

2.00
2.06
1.06
3.17
1.12
1.08
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.416
161.935
157.167
155.867
148.924
148.797
147.906
136.816
136.625
129.942
129.619
129.523
127.666
118.814
118.789
117.482
117.229
113.535
113.334
77.318
77.000
76.682
N
N
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

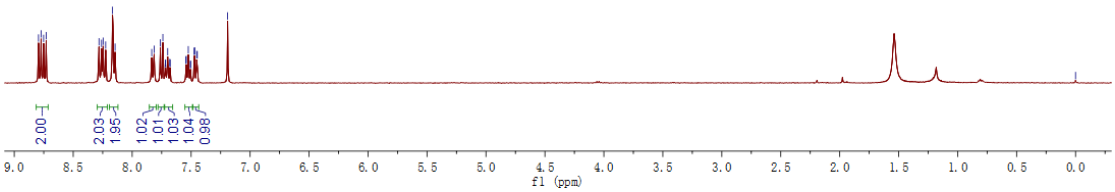
4i

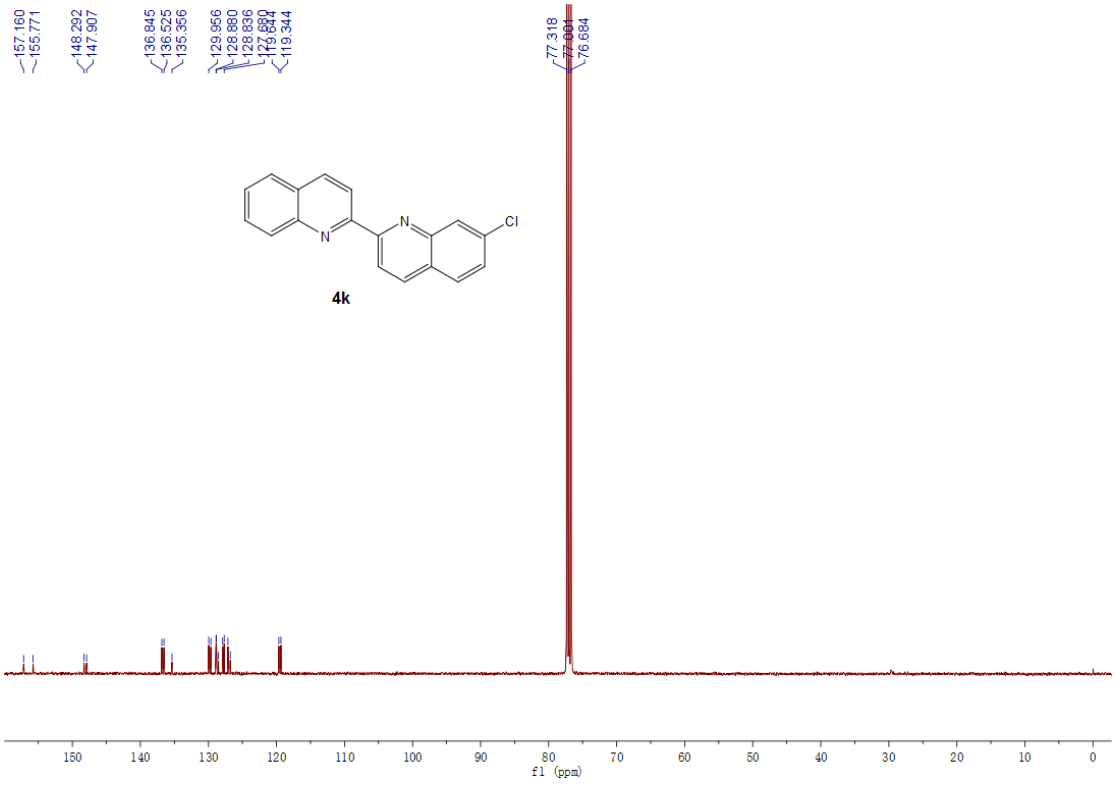

8.867
8.821
8.800
8.346
8.324
8.254
8.233
8.173
8.151
7.880
7.871
7.866
7.261
0.000
N
N
Cl
4j
1.00
1.01
1.04
2.14
1.10
2.14
1.19
1.12
1.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.444
155.742
147.867
146.280
136.885
135.808
131.488
130.504
129.902
129.683
128.496
127.677
127.117
126.368
126.328
119.272
77.318
77.000
76.683
N
N
Cl
4j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

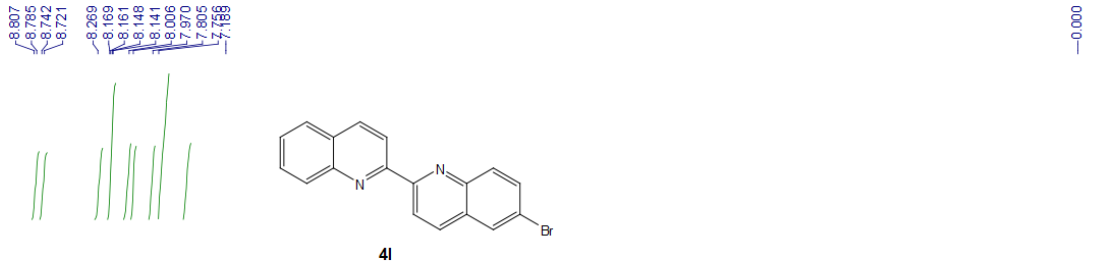

8.794
8.773
8.751
8.730
8.281
8.246
7.814
7.761
7.740
7.719
7.717
7.699
7.681
7.678
7.544
7.542
7.524
7.506
7.505
7.474
7.470
7.453
7.448
7.191
0.000
N
N
Cl

4k

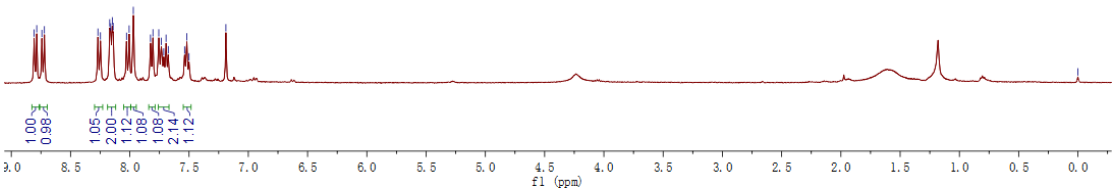

2.00
2.03
1.95
1.02
1.01
1.03
1.04
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

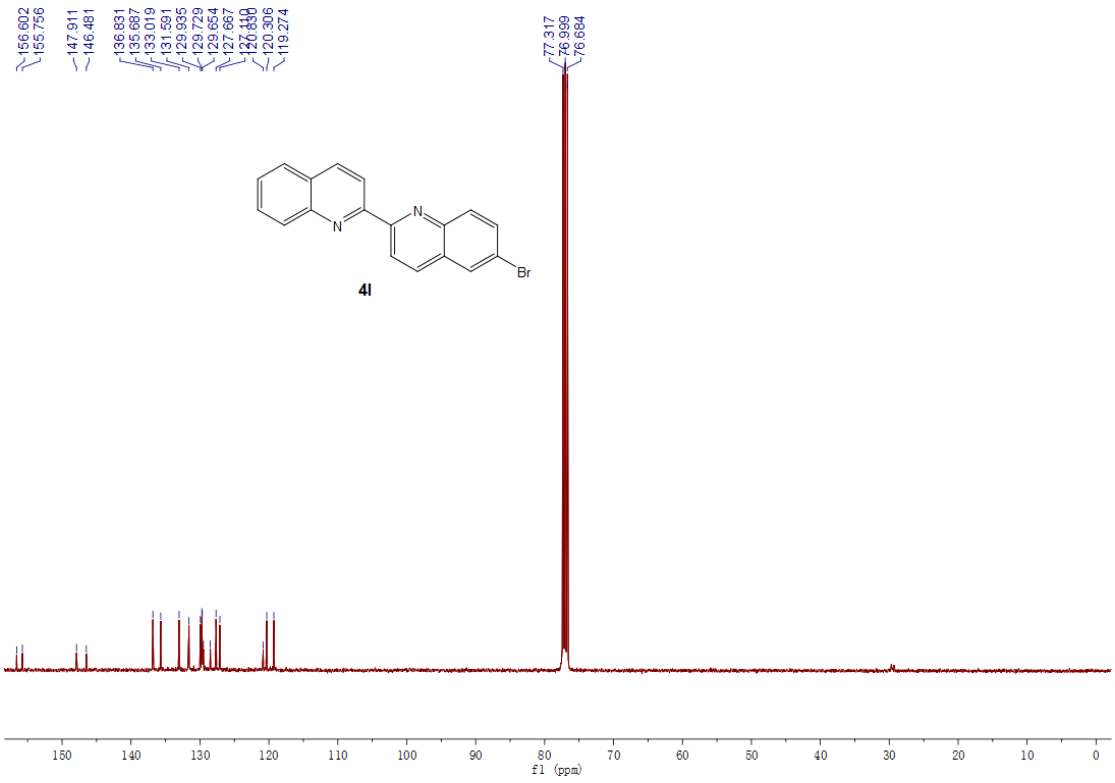

157.160
155.771
148.292
147.907
136.845
136.525
135.356
129.956
128.880
128.836
127.680
119.644
119.344
77.318
77.001
76.684
N
N
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4k

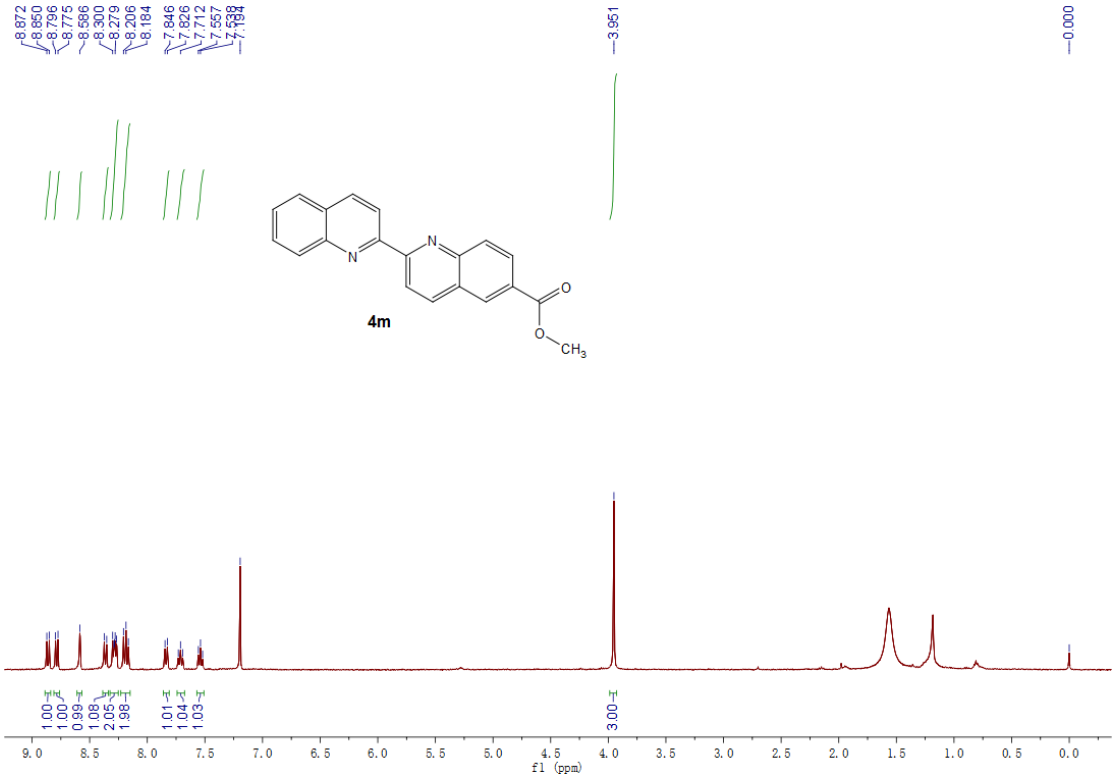

8.807
8.785
8.742
8.721
8.269
8.169
8.161
8.148
8.141
8.006
7.970
7.805
7.758
7.189
0.000
N
N
Br

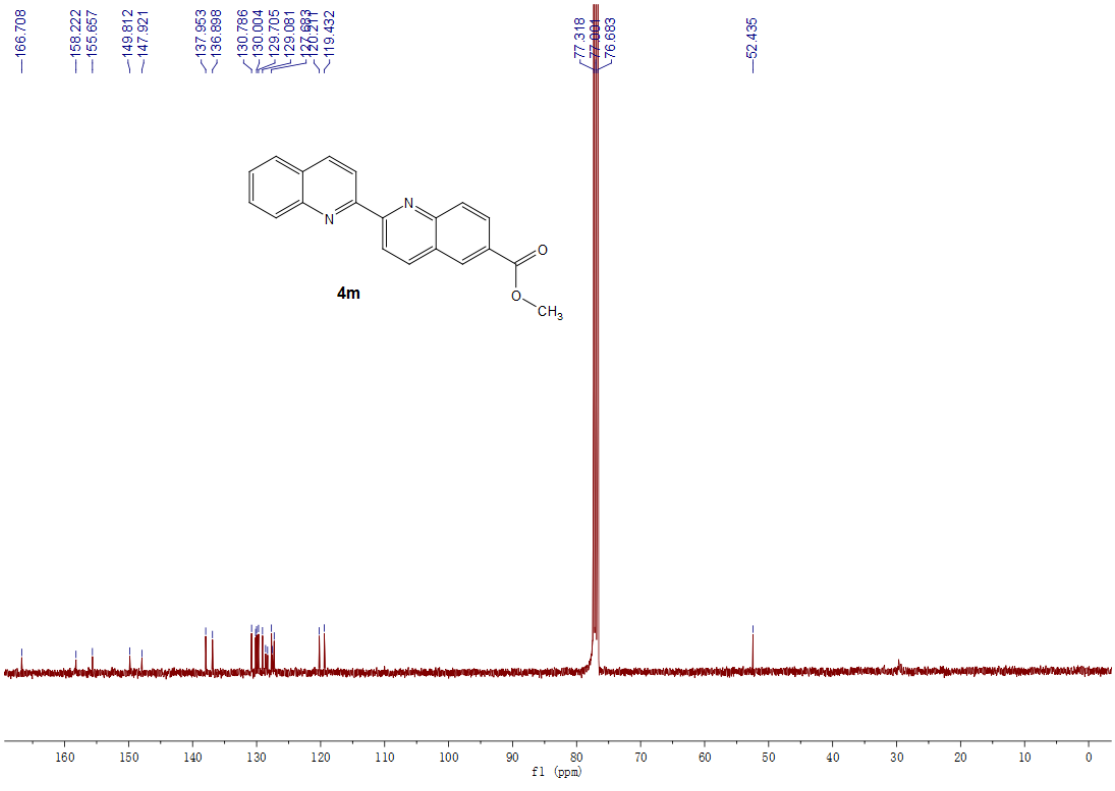
4l

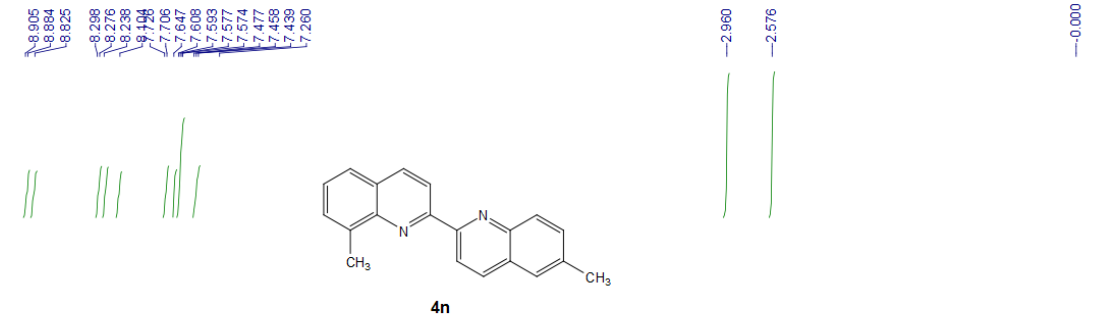

1.00
0.98
1.05
2.00
1.12
1.08
1.08
2.14
1.12
f1 (ppm)


156.602
155.756
147.911
146.481
136.831
135.687
133.019
131.591
129.935
129.729
129.654
127.667
120.306
119.274
77.317
76.999
76.684
N
N
Br
f1 (ppm)

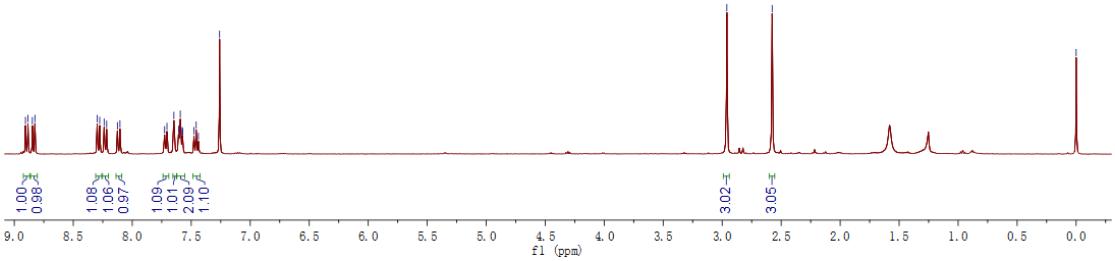
4l

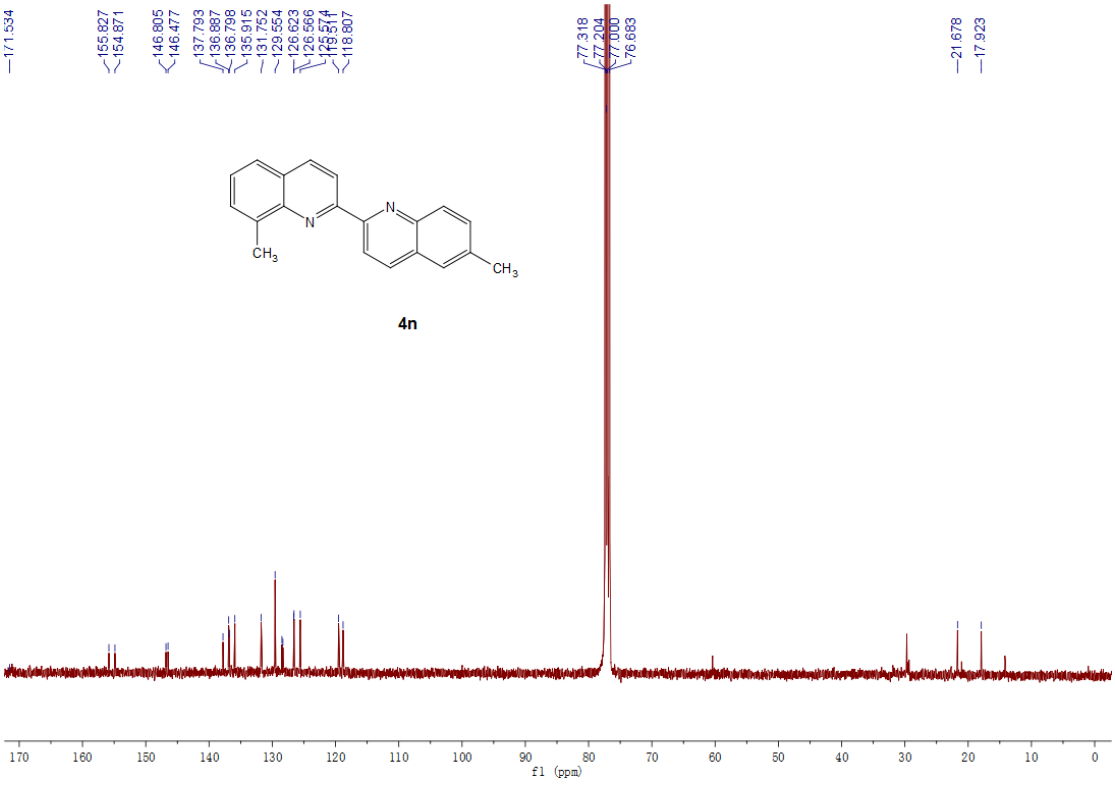

8.872
8.850
8.796
8.775
8.586
8.300
8.279
8.206
8.184
7.846
7.826
7.712
7.557
7.538
7.194
3.951
0.000
4m
1.00
1.00
0.99
1.08
2.05
1.98
1.01
1.04
1.03
3.00
f1 (ppm)


166.708
158.222
155.657
149.812
147.921
137.953
136.898
130.786
130.004
129.705
129.081
127.693
120.211
119.432
77.318
77.001
76.683
52.435
4m
f1 (ppm)

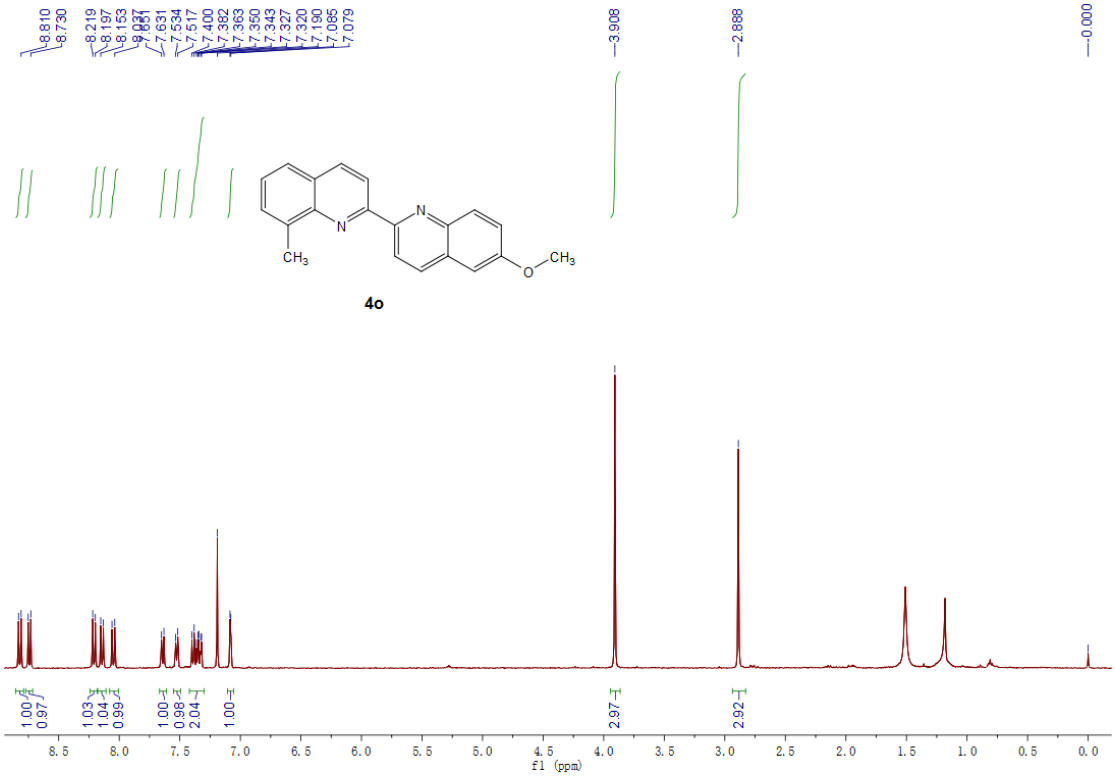

8.905
8.884
8.825
8.298
8.276
8.238
7.706
7.647
7.608
7.593
7.577
7.574
7.477
7.458
7.439
7.260
2.960
2.576
0.000
N
N
CH3
CH3

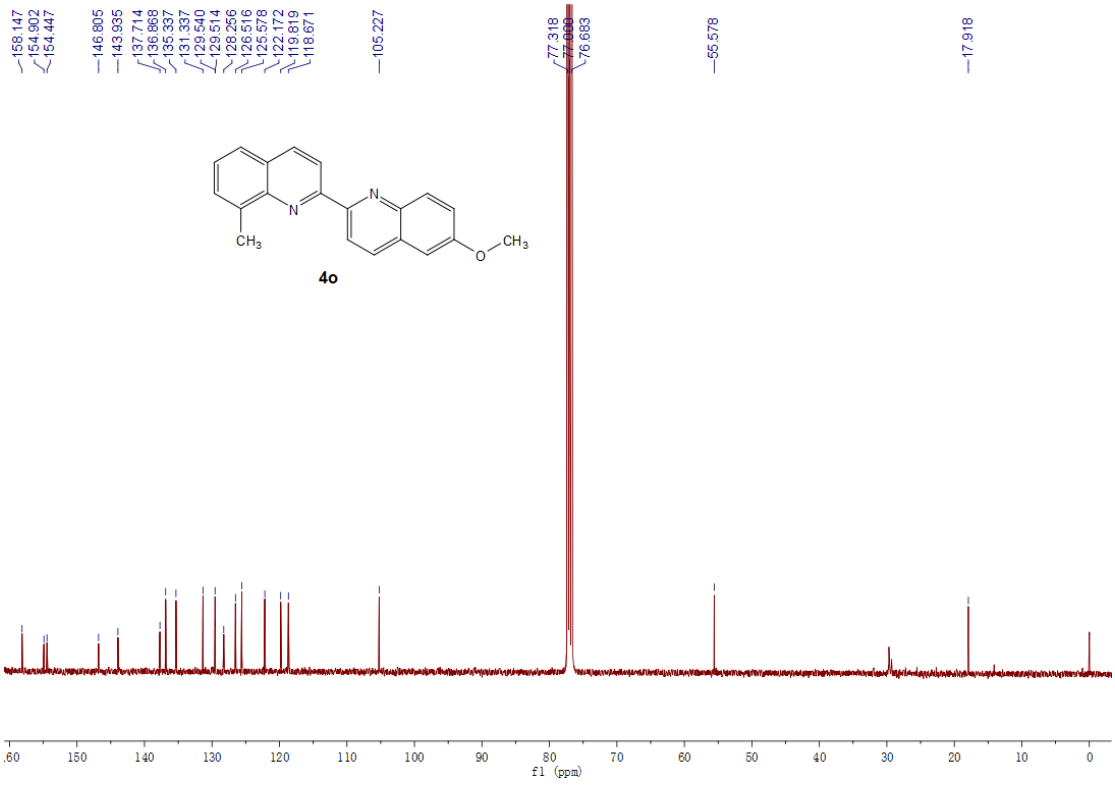
4n

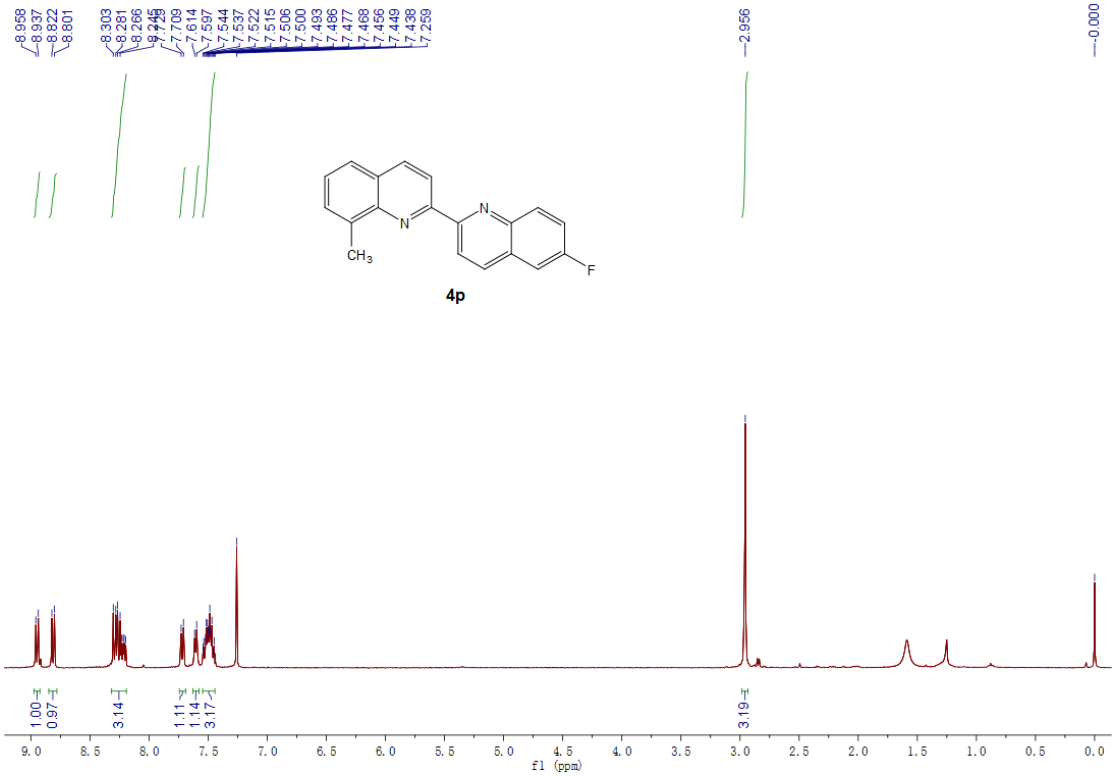

1.00
0.98
1.08
1.06
0.97
1.09
1.01
2.09
1.10
3.02
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

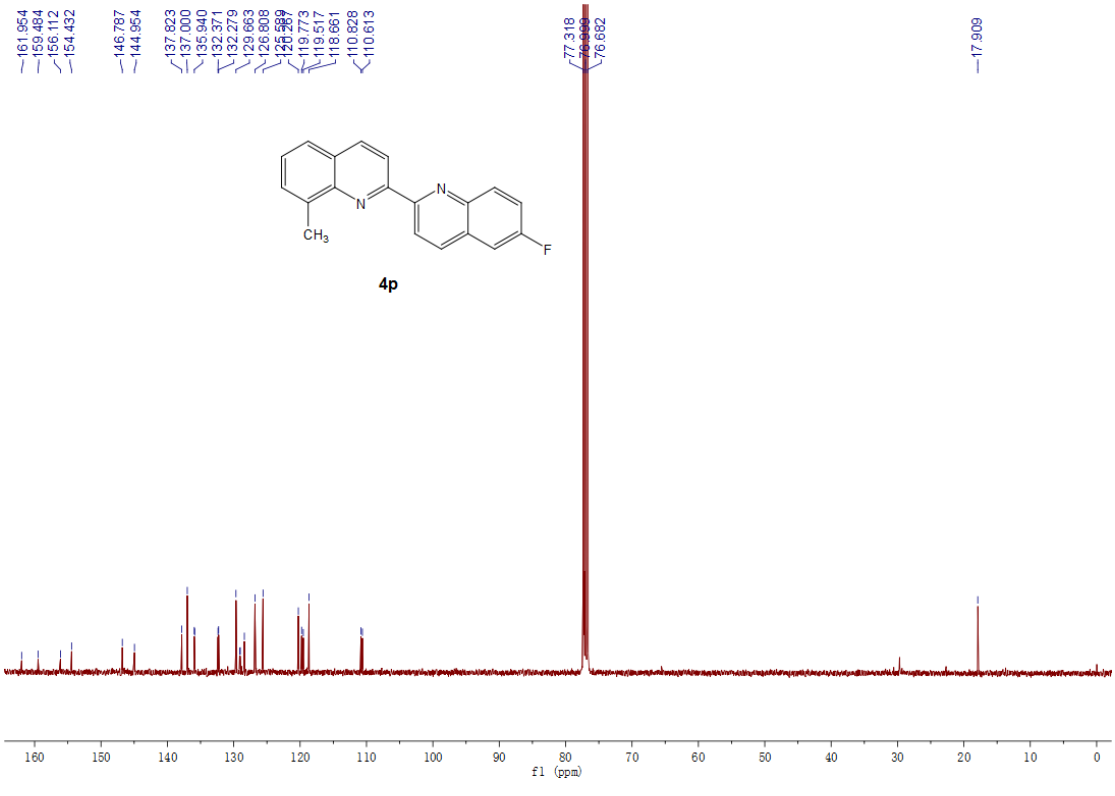

171.534
155.627
154.871
146.805
146.477
137.793
136.887
136.798
135.915
131.752
129.554
126.623
126.566
126.514
119.511
118.807
77.318
77.204
77.000
76.683
21.678
17.923
N
N
CH3
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

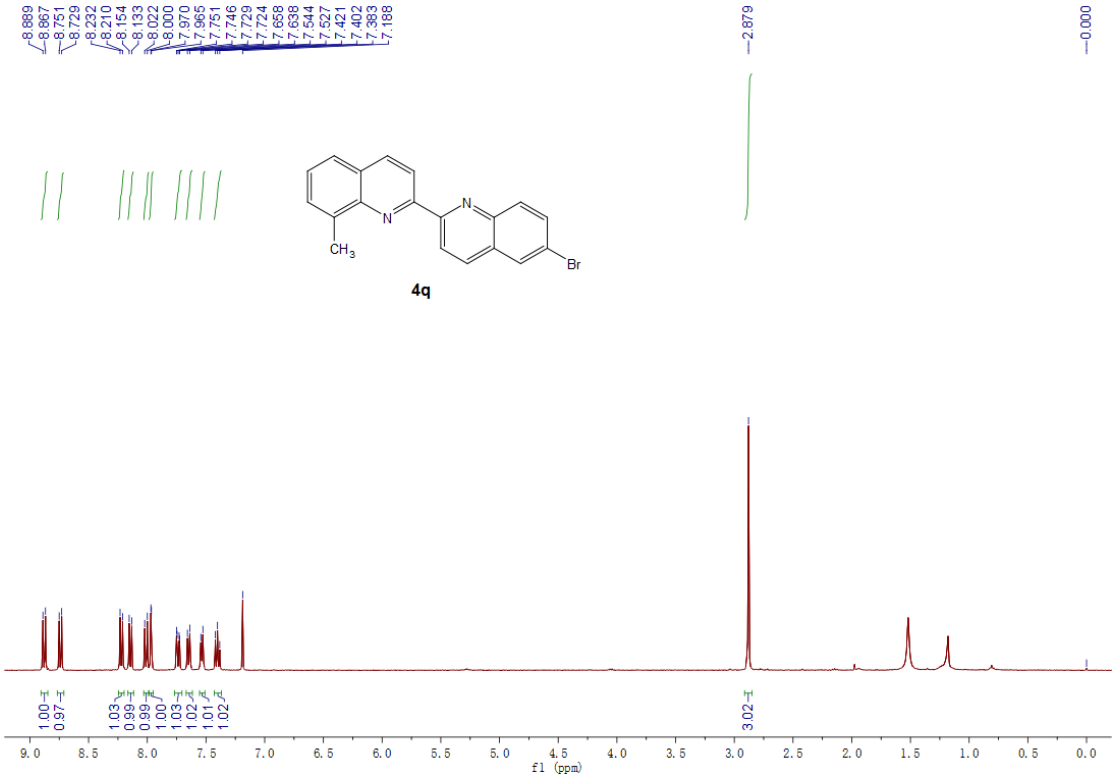
4n

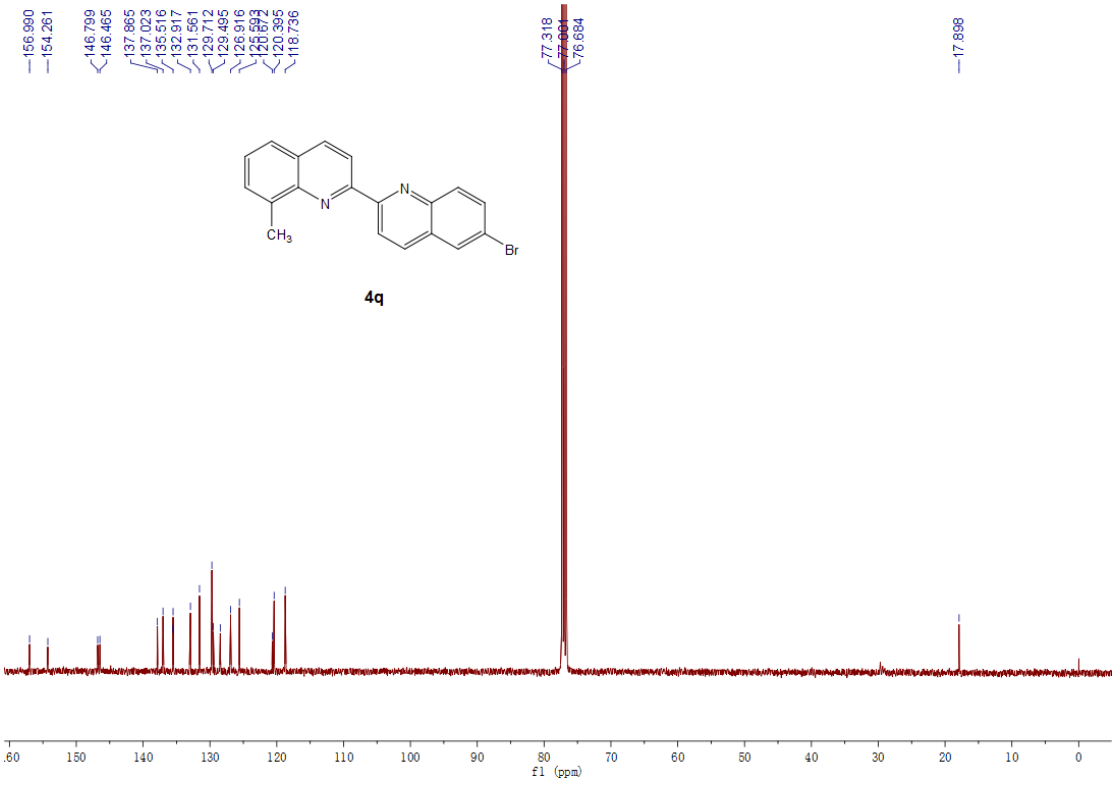

8.810
8.730
8.219
8.197
8.153
7.631
7.534
7.517
7.400
7.382
7.363
7.350
7.343
7.327
7.320
7.190
7.085
7.079
3.908
2.888
0.000
N
N
CH3
O
CH3
4o
1.00
0.97
1.03
1.04
0.99
1.00
0.98
2.04
1.00
2.97
2.92
f1 (ppm)


158.147
154.902
154.447
146.805
143.935
137.714
136.868
135.337
131.337
129.540
129.514
128.256
126.516
125.578
122.172
119.819
118.671
105.227
77.318
77.000
76.683
55.578
17.918
N
N
CH3
O
CH3
4o
f1 (ppm)


8.958
8.937
8.822
8.801
8.303
8.281
8.266
7.709
7.614
7.597
7.544
7.537
7.522
7.515
7.506
7.500
7.493
7.486
7.477
7.468
7.456
7.449
7.438
7.259
2.956
0.000
N
N
CH3
F
4p
1.00
0.97
3.14
1.11
1.14
3.17
3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.954
159.484
156.112
154.432
146.787
144.954
137.823
137.000
135.940
132.371
132.279
129.663
126.808
125.589
120.287
119.773
119.517
118.661
110.828
110.613
77.318
77.000
76.682
17.909
N
N
CH3
F
4p
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.889
8.867
8.751
8.729
8.232
8.210
8.154
8.133
8.022
8.000
7.970
7.965
7.751
7.746
7.729
7.724
7.658
7.638
7.544
7.527
7.421
7.402
7.383
7.188
2.879
0.000
N
N
CH3
Br
4q
1.00
0.97
1.03
0.99
0.99
1.00
1.03
1.02
1.01
1.02
3.02
f1 (ppm)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154.261
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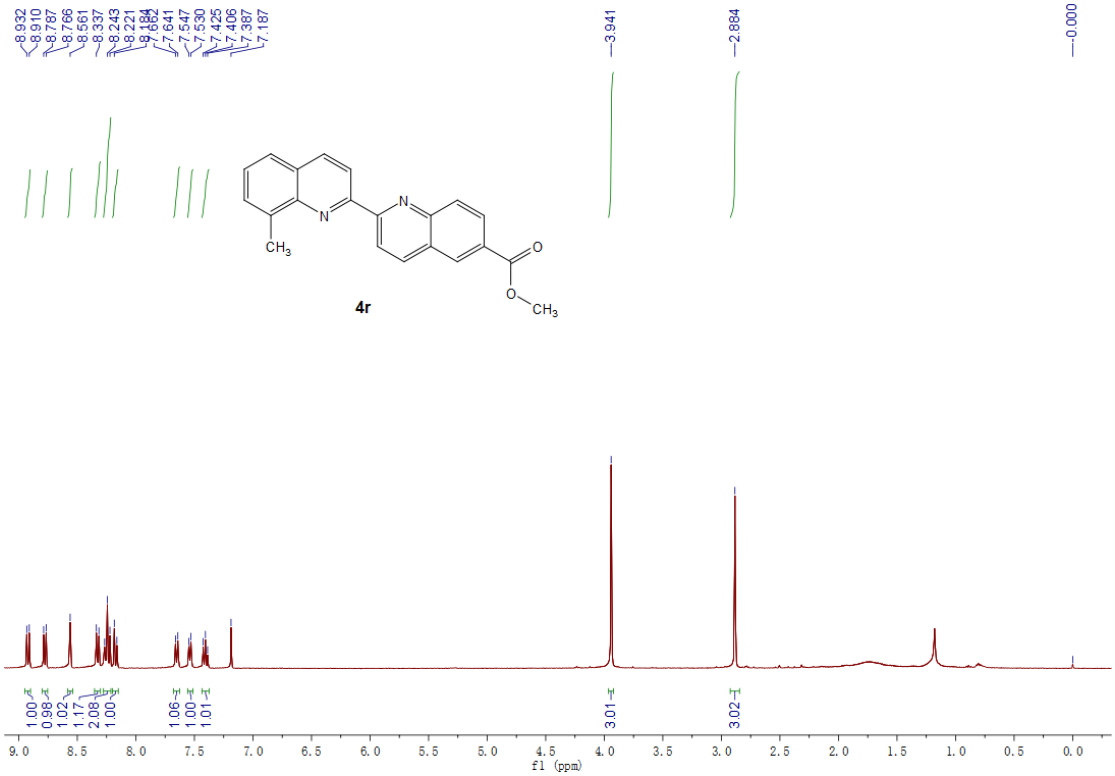
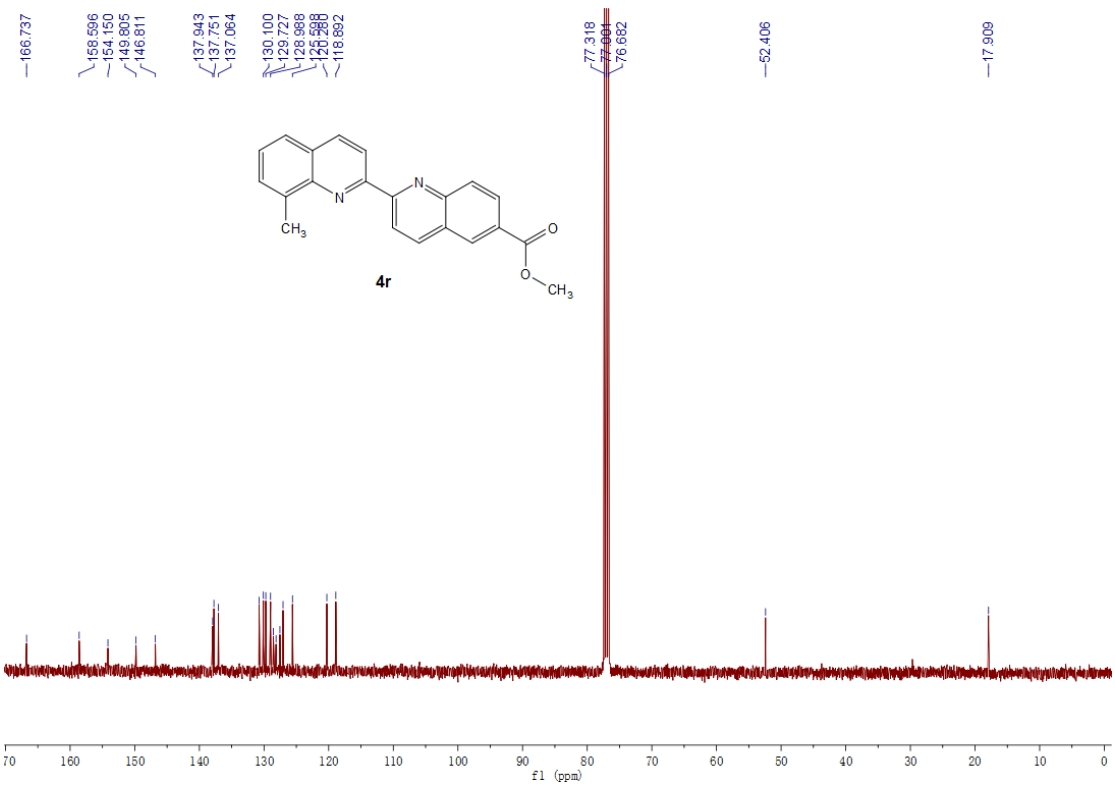
146.465
137.865
137.023
135.516
132.917
131.561
129.712
129.495
126.916
120.395
118.736
77.318
77.084
76.684
17.898
N
N
CH3
Br
4q
f1 (ppm)


8.932
8.910
8.787
8.766
8.561
8.337
8.243
8.221
7.641
7.547
7.530
7.425
7.406
7.387
7.187
3.941
2.884
0.000
4r
1.00
0.98
1.02
1.17
2.08
1.00
1.06
1.00
1.01
3.01
3.02
f1 (ppm)


166.737
158.596
154.150
149.805
146.811
137.943
137.751
137.064
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129.727
128.988
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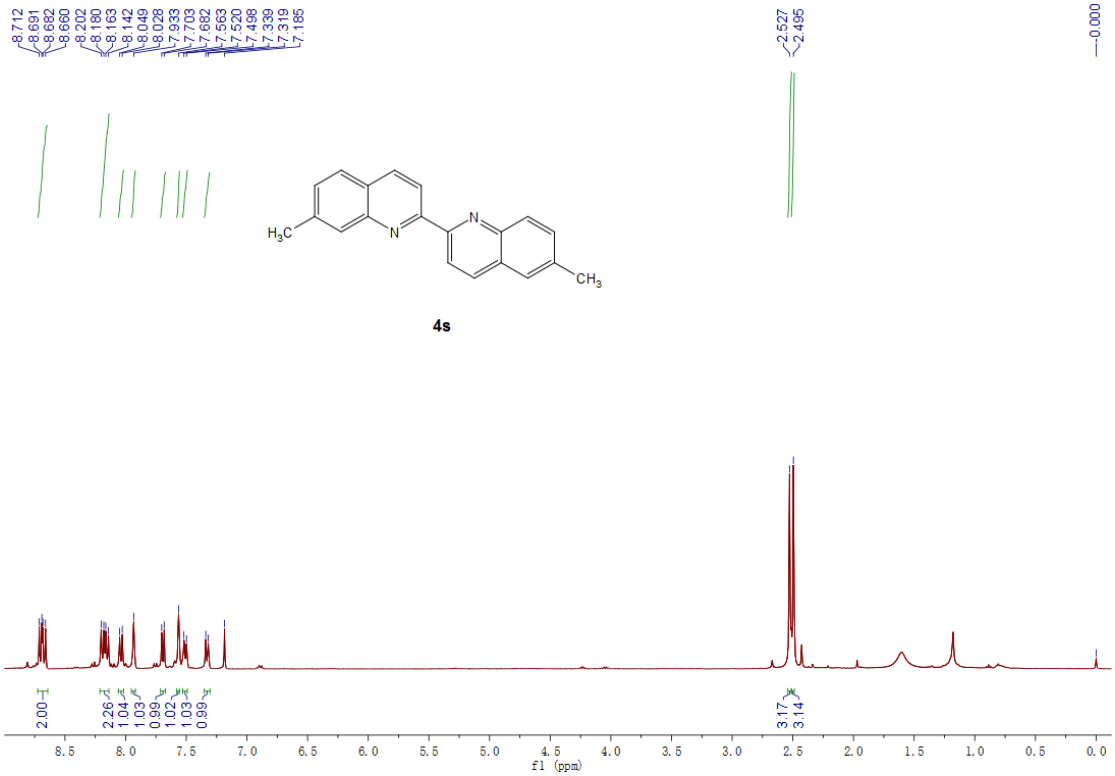
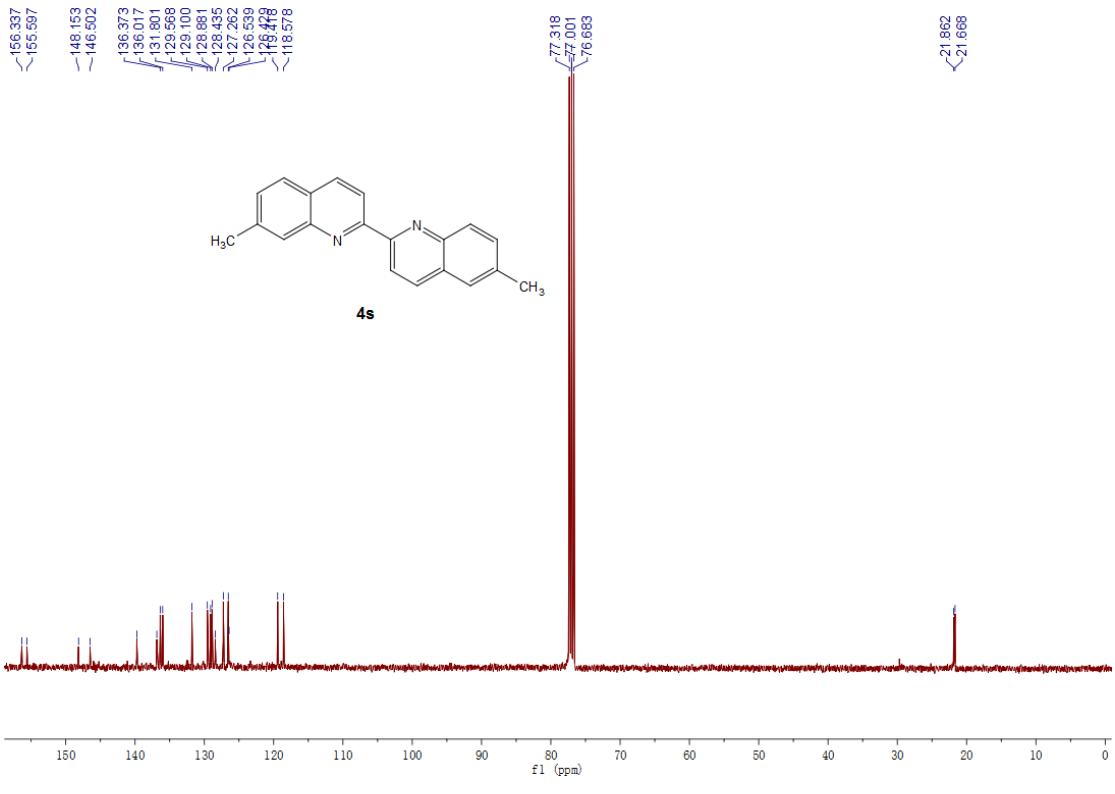
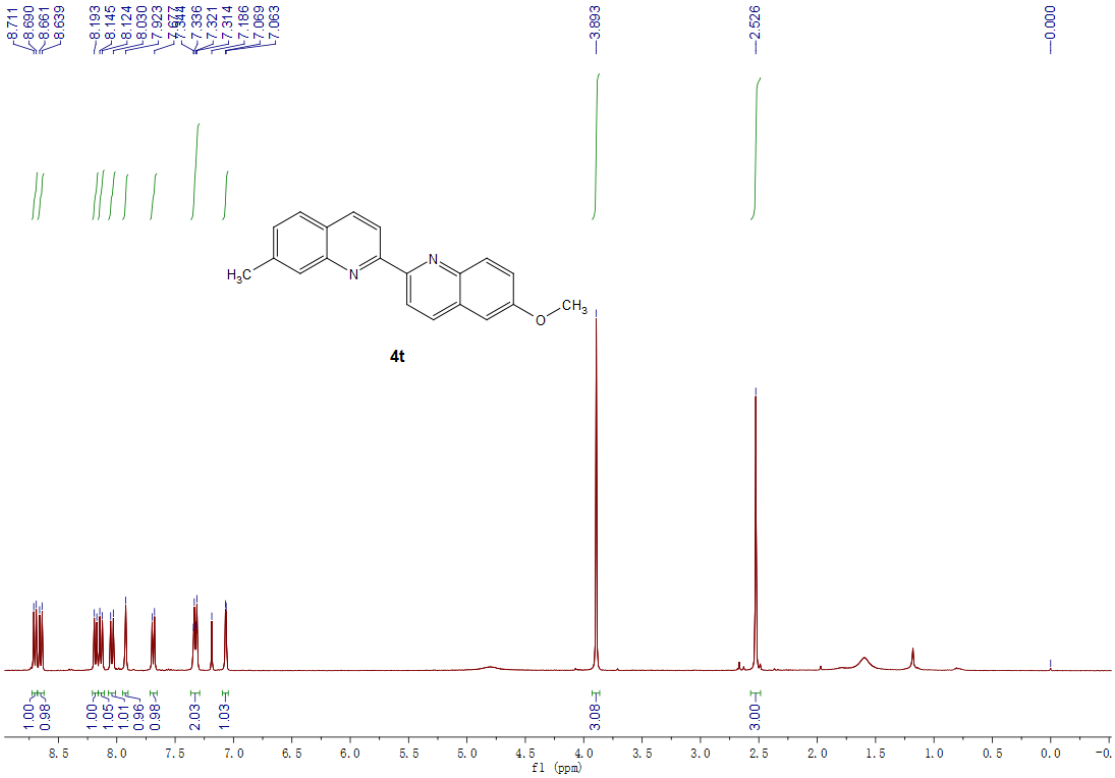
76.682
52.406
17.909
4r
f1 (ppm)


8.712
8.691
8.682
8.660
8.202
8.180
8.163
8.142
8.049
8.028
7.933
7.703
7.682
7.563
7.520
7.498
7.339
7.319
7.185
2.527
2.495
0.000
H3C
N
N
CH3
4s
2.00
2.26
1.04
1.03
0.99
1.02
1.03
0.99
3.17
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.337
155.597
148.153
146.502
136.373
136.017
131.801
129.568
129.100
128.881
128.435
127.262
126.539
126.429
126.418
119.418
118.578
77.318
77.001
76.683
21.862
21.668
H3C
N
N
CH3
4s
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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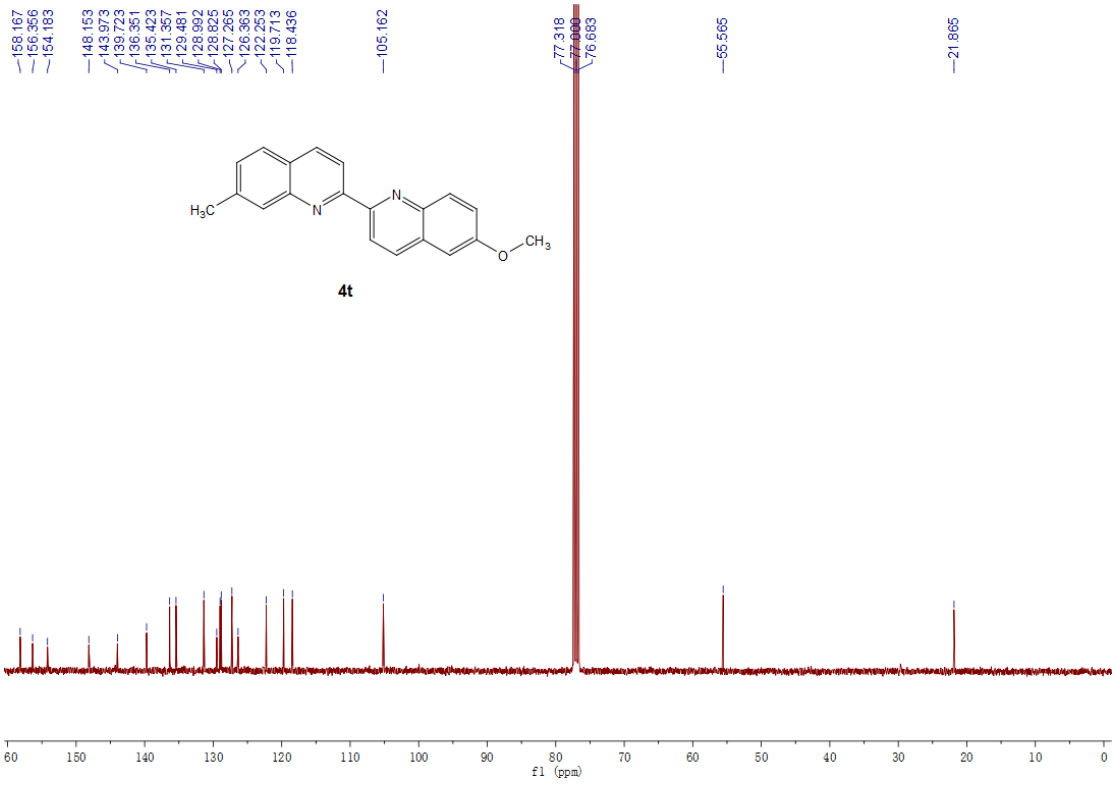
8.690
8.661
8.639
8.193
8.145
8.124
8.030
7.923
7.336
7.321
7.314
7.186
7.069
7.063
3.893
2.526
0.000
4t
1.00
0.98
1.00
1.05
1.01
0.96
0.98
2.03
1.03
3.08
3.00
f1 (ppm)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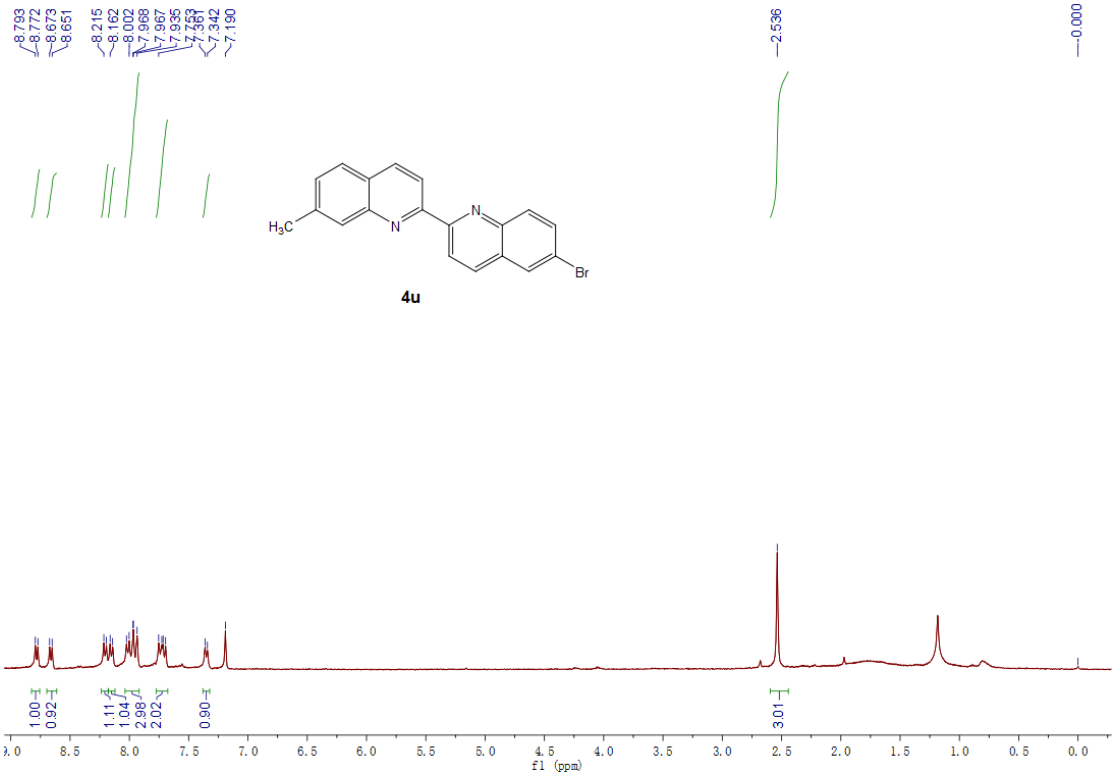
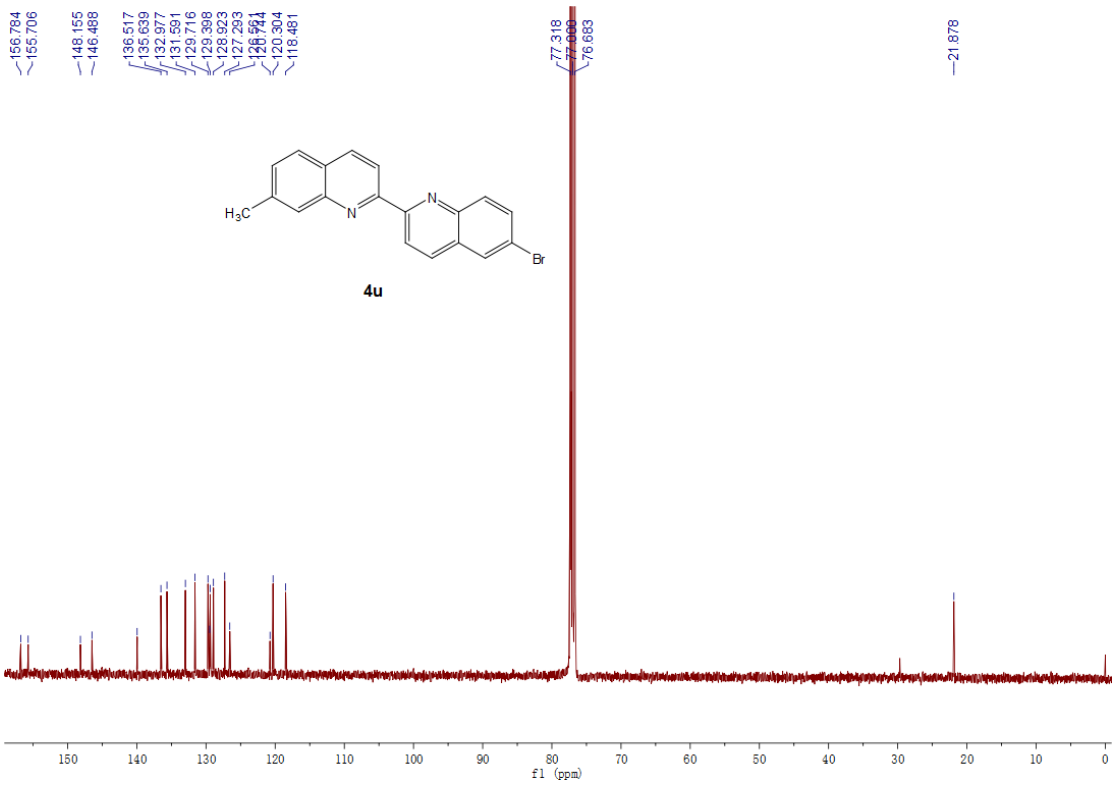
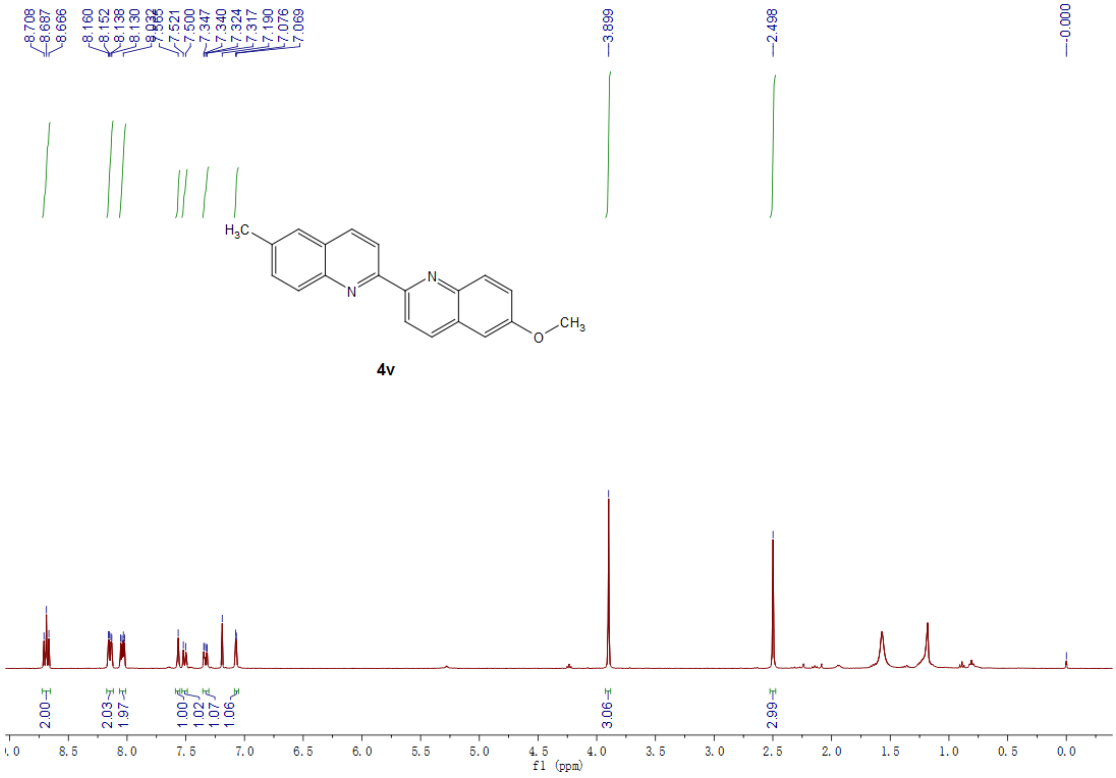
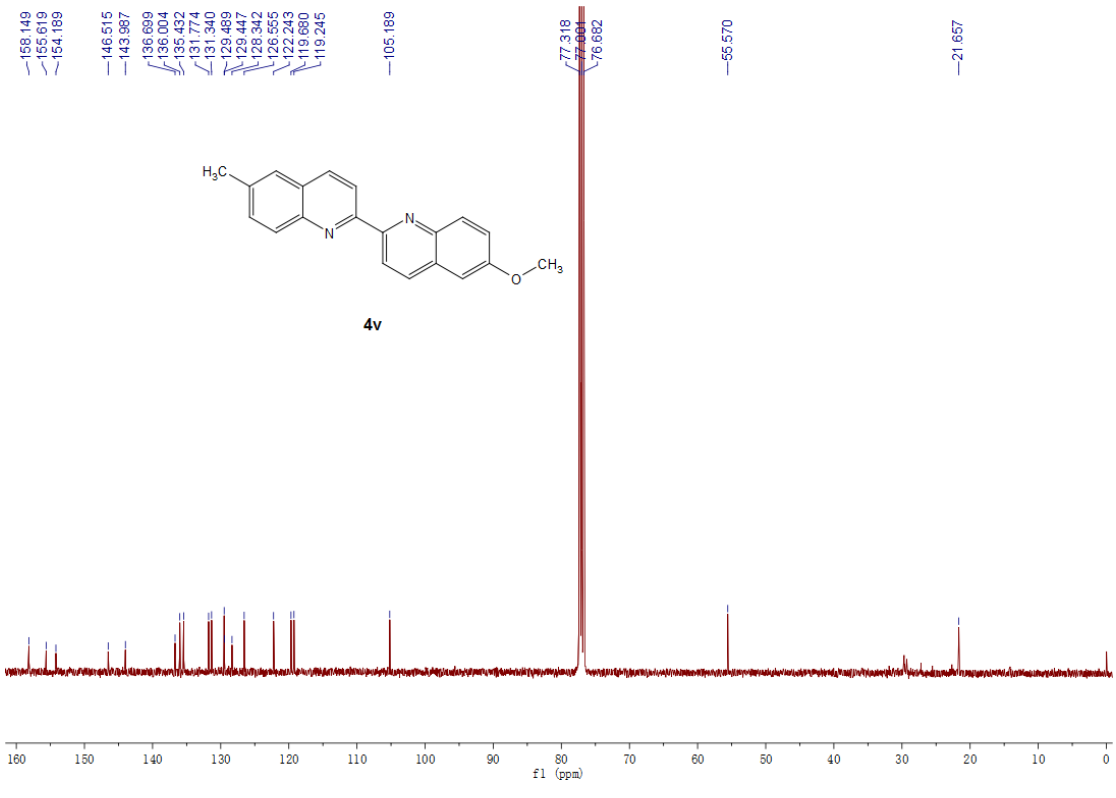
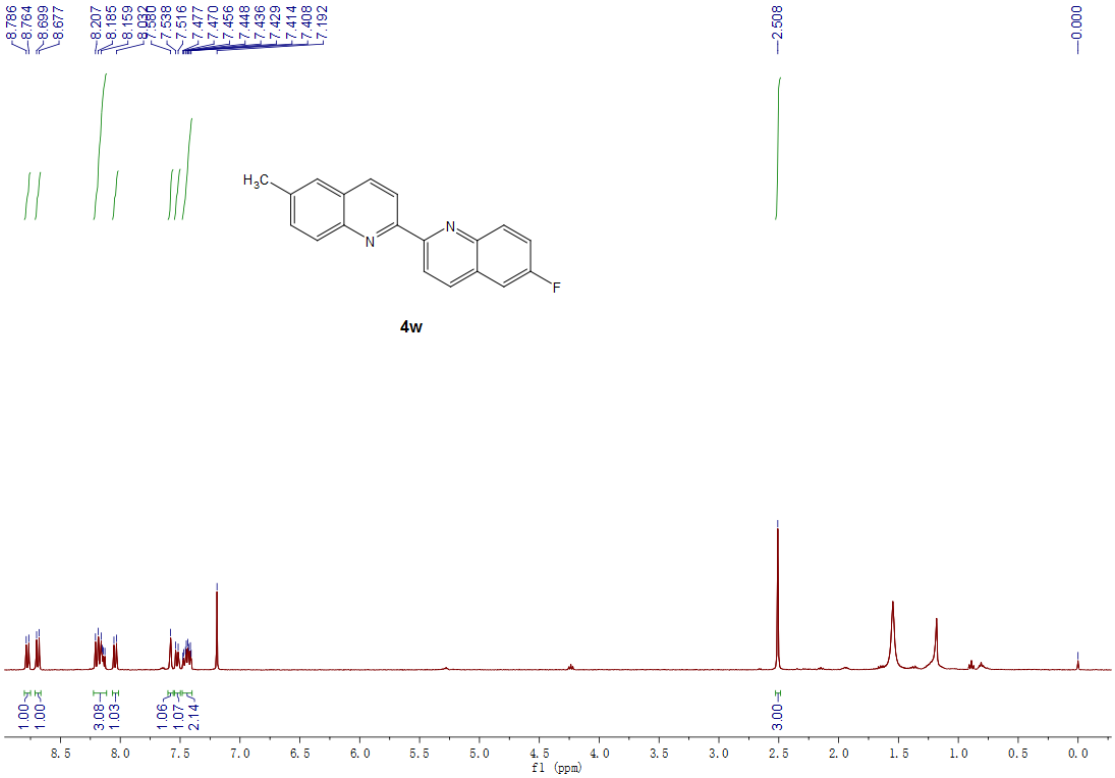
156.356
154.183
148.153
143.973
139.723
136.351
135.423
131.357
129.481
128.992
128.825
127.265
126.363
122.253
119.713
118.436
105.162
77.318
77.000
76.683
55.565
21.865
4t
f1 (ppm)

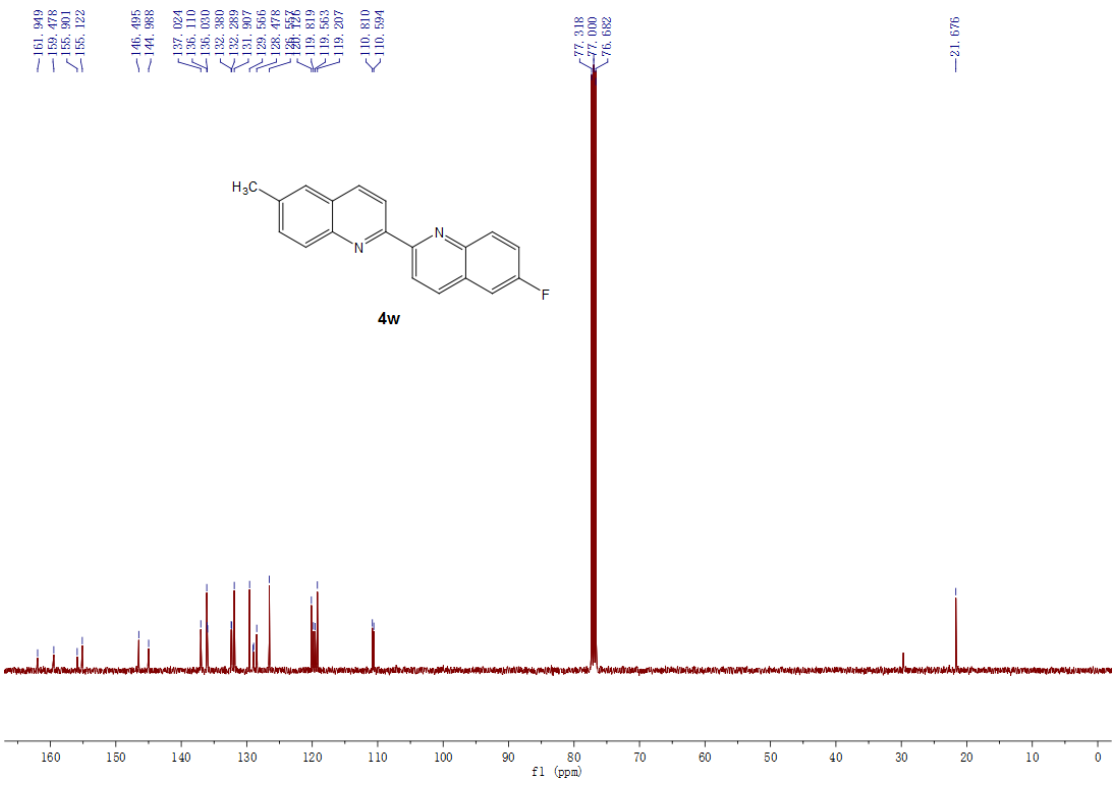

8.799
8.772
8.673
8.651
8.215
8.162
8.002
7.988
7.967
7.935
7.553
7.351
7.342
7.190
2.536
0.000
H3C
N
N
Br
4u
1.00
0.92
1.11
1.04
2.98
2.02
0.90
3.01
f1 (ppm)

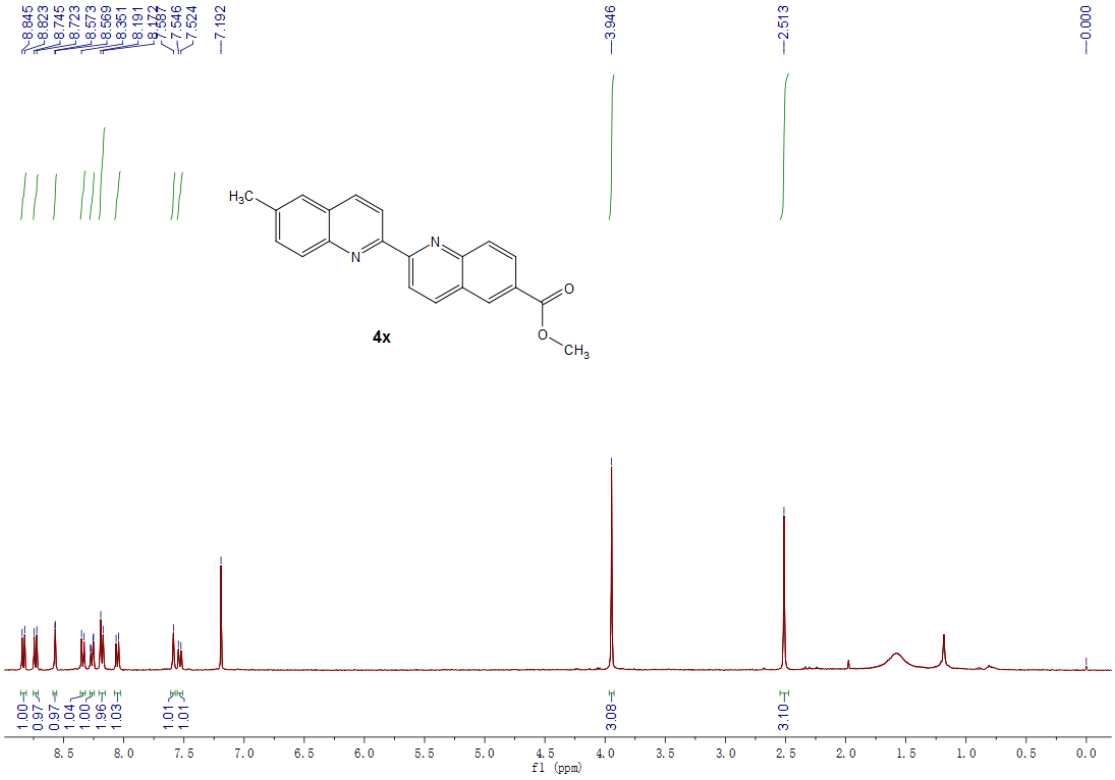

156.784
155.706
148.155
146.488
136.517
135.639
132.977
131.591
129.716
129.398
128.923
127.293
120.304
118.481
77.318
77.000
76.683
21.878
H3C
N
N
Br
4u
f1 (ppm)

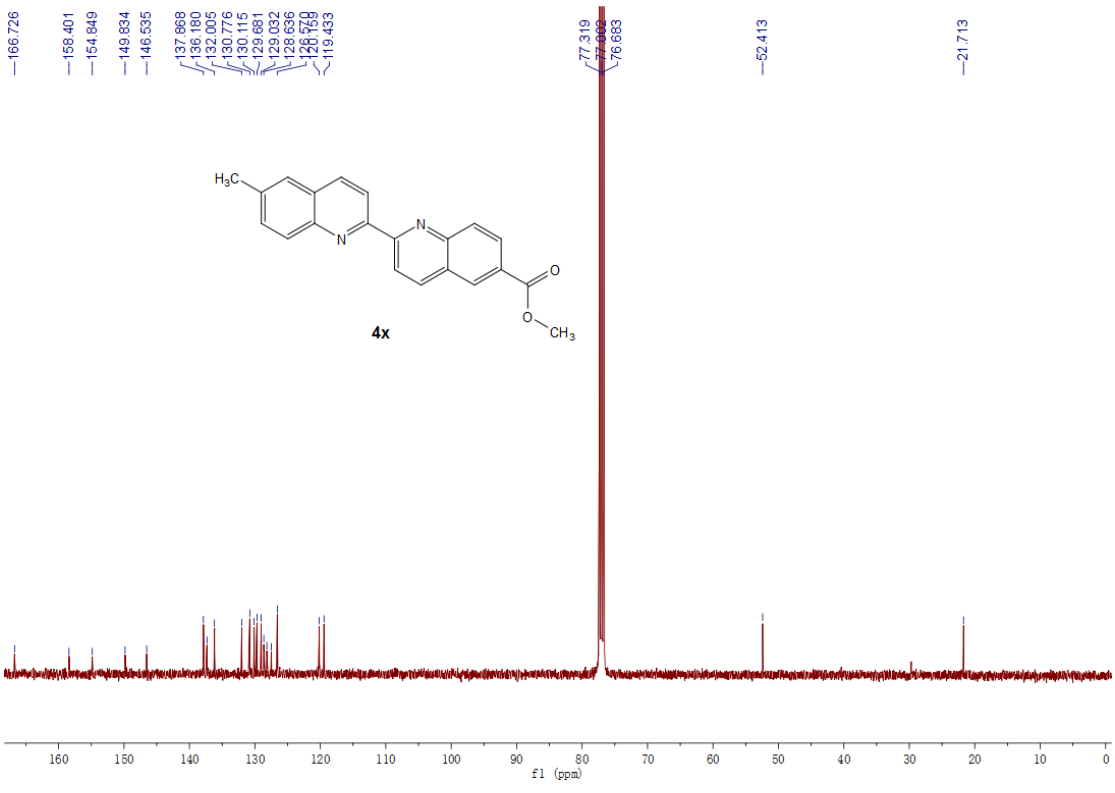

8.708
8.687
8.666
8.160
8.152
8.138
8.130
7.521
7.500
7.347
7.340
7.324
7.317
7.190
7.076
7.069
3.899
2.498
0.000
H3C
N
N
O
CH3
4v
2.00
2.03
1.97
1.00
1.02
1.07
1.06
3.06
2.99
f1 (ppm)


158.149
155.619
154.189
146.515
143.987
136.699
136.004
135.432
131.774
131.340
129.489
129.447
128.342
126.555
122.243
119.680
119.245
105.189
77.318
77.001
76.682
55.570
21.657
H3C
N
N
O
CH3
4v
f1 (ppm)


8.786
8.764
8.699
8.677
8.207
8.185
8.159
7.538
7.516
7.477
7.470
7.456
7.448
7.436
7.429
7.414
7.408
7.192
2.508
0.000
H3C
N
N
F
4w
1.00
1.00
3.08
1.03
1.06
1.07
2.14
3.00
f1 (ppm)


161.949
159.478
155.901
155.122
146.495
144.988
137.024
136.110
136.030
132.380
132.289
131.907
129.566
128.478
119.819
119.563
119.207
110.810
110.594
77.318
77.000
76.682
21.676
H3C
N
N
F
4w
f1 (ppm)


8.845
8.823
8.745
8.723
8.573
8.569
8.351
8.191
8.172
7.587
7.546
7.524
7.192
3.946
2.513
0.000
H3C
N
N
O
O
CH3
4x
1.00
0.97
0.97
1.04
1.00
1.96
1.03
1.01
1.01
3.08
3.10
f1 (ppm)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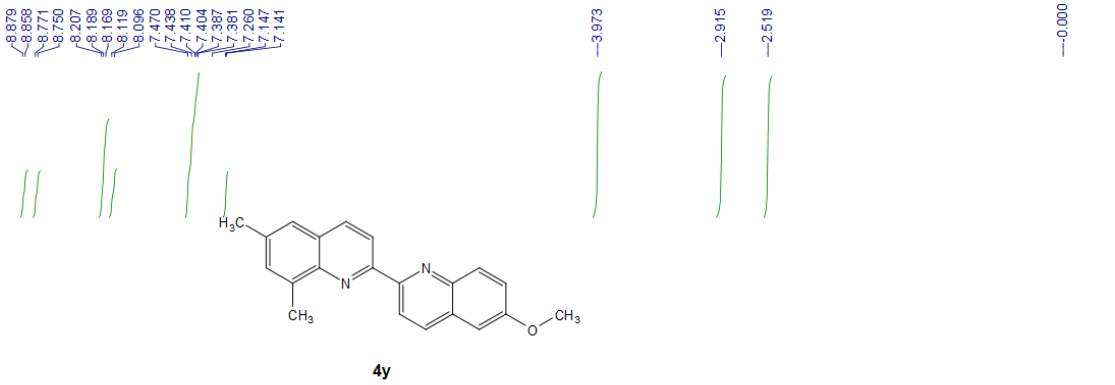
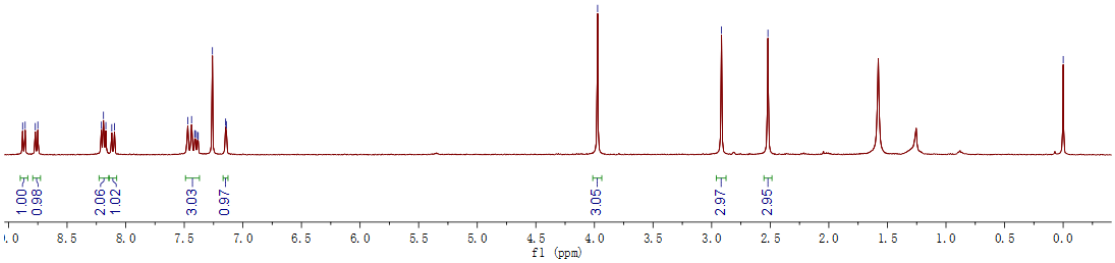
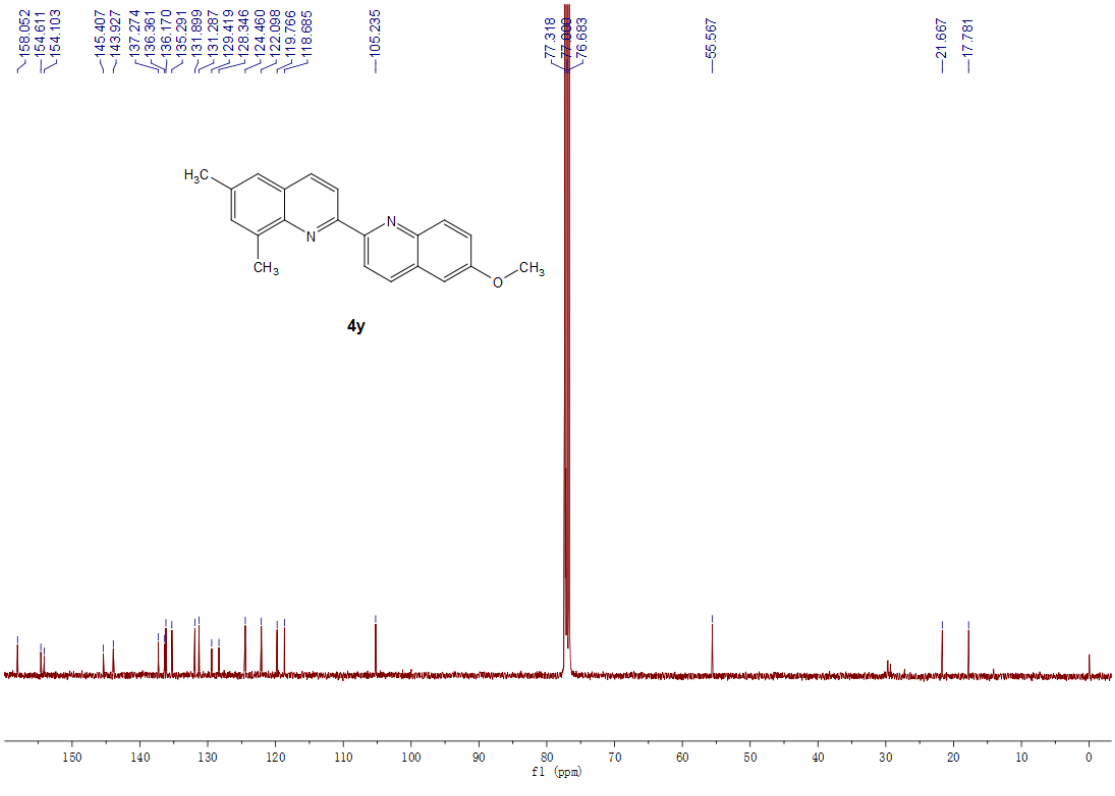
158.401
154.849
149.834
146.535
137.868
136.180
132.005
130.776
130.115
129.681
129.032
128.636
126.570
120.159
119.433
77.319
77.000
76.683
52.413
21.713
H3C
N
N
O
O
CH3
4x
f1 (ppm)

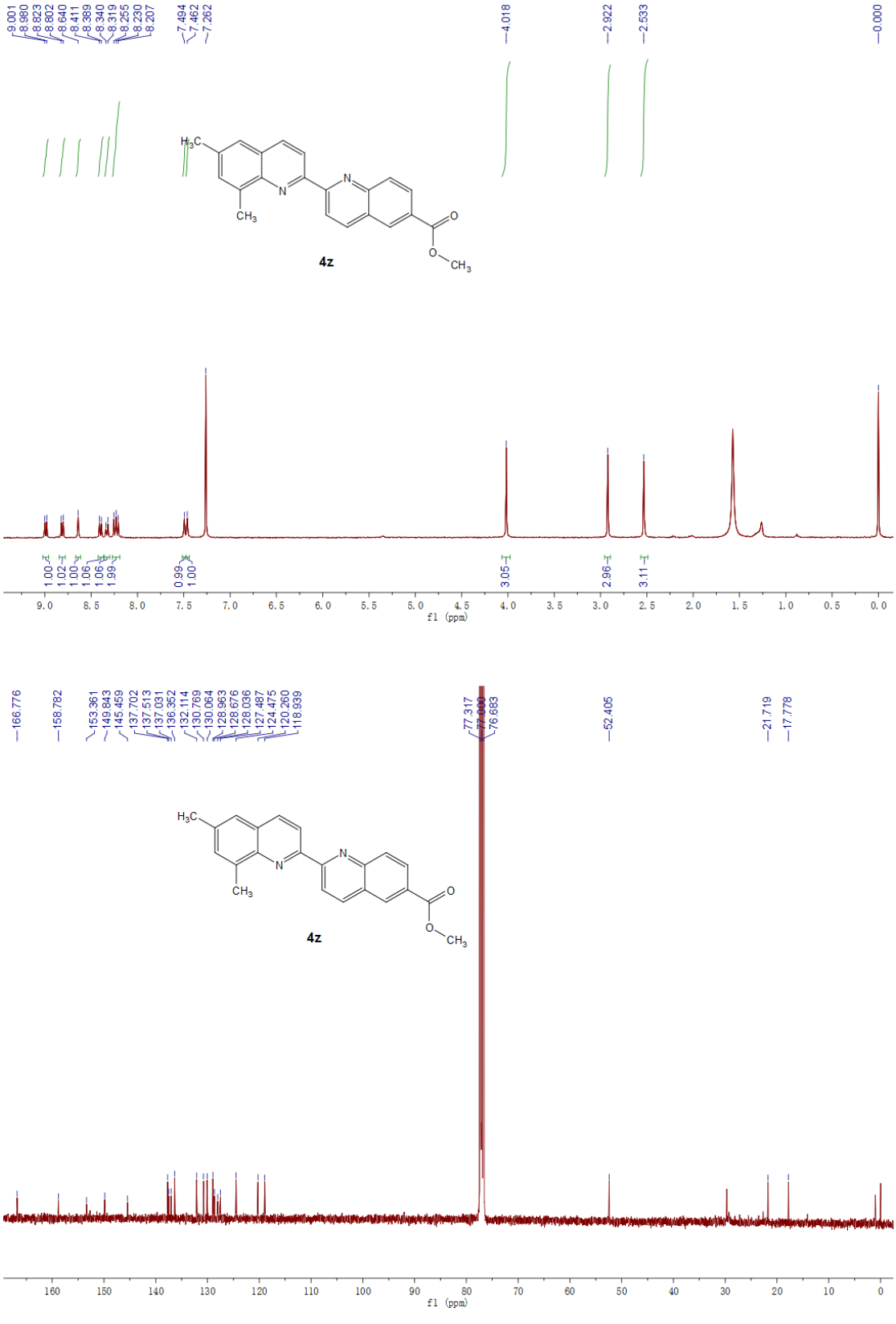

8.879
8.858
8.771
8.750
8.207
8.189
8.169
8.119
8.096
7.470
7.438
7.410
7.404
7.387
7.381
7.260
7.147
7.141
3.973
2.915
2.519
0.000
H3C
CH3
N
N
O
CH3

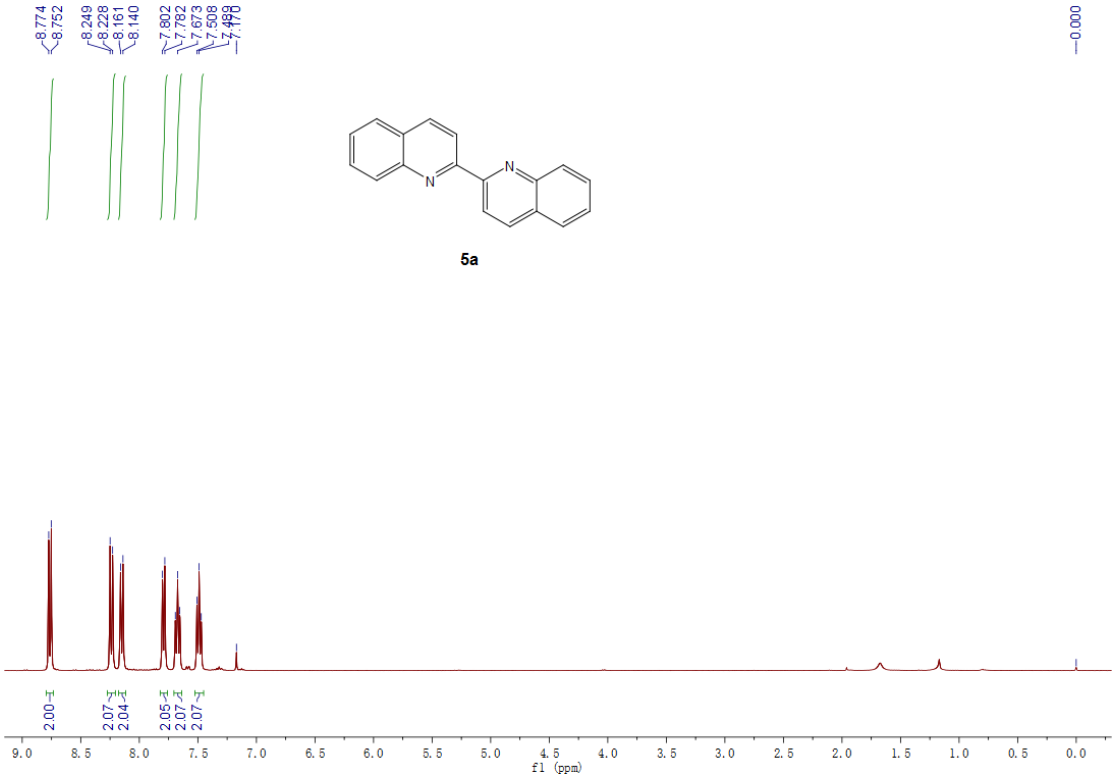
4y

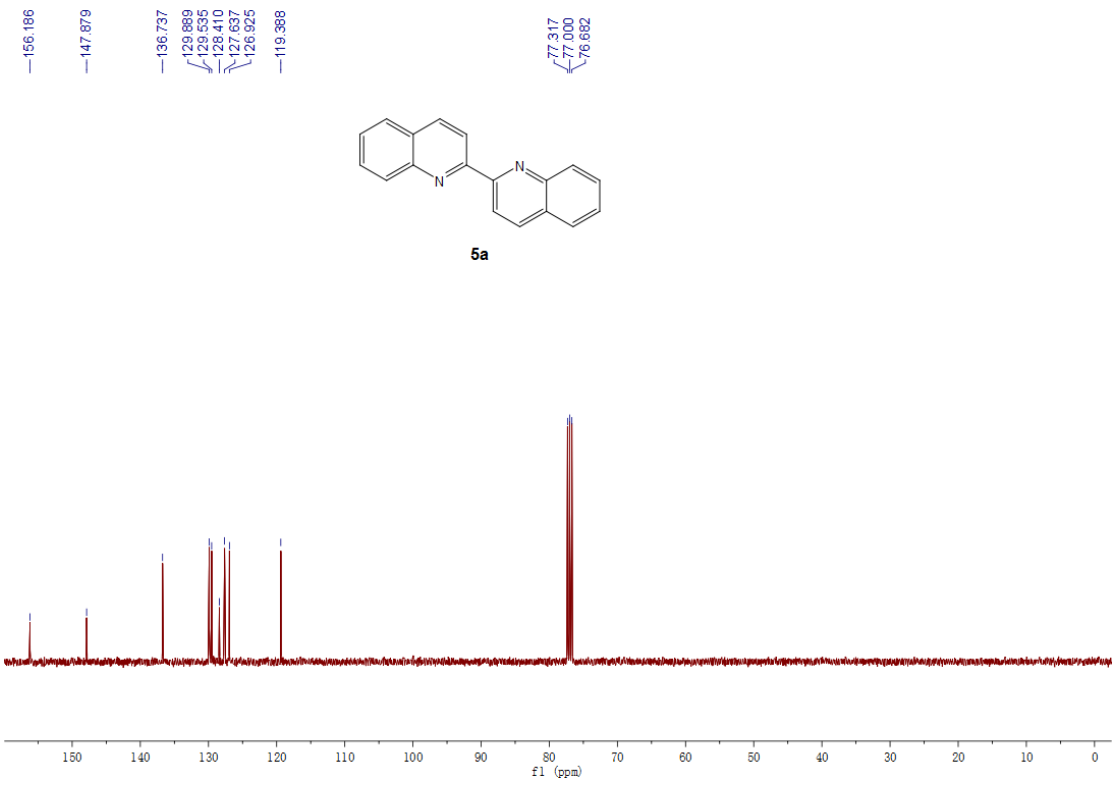

1.00
0.98
2.06
1.02
3.03
0.97
3.05
2.97
2.95
f1 (ppm)

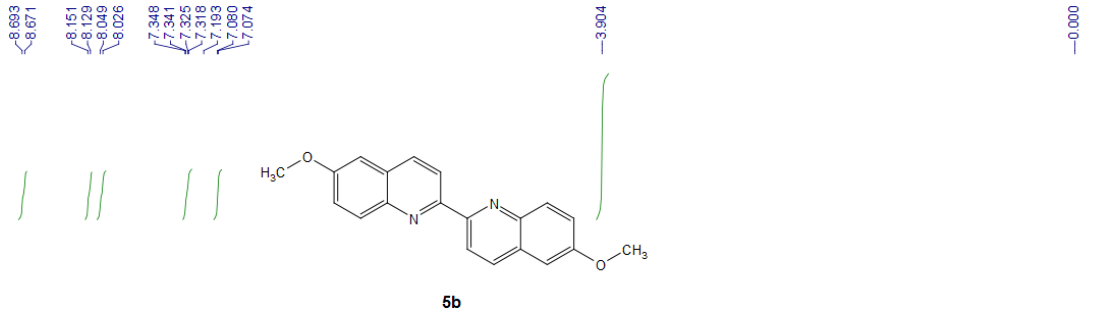

158.052
154.611
154.103
145.407
143.927
137.274
136.361
136.170
135.291
131.899
131.287
129.419
128.346
124.460
122.098
119.766
118.685
105.235
77.318
77.000
76.683
55.567
21.667
17.781
H3C
CH3
N
N
O
CH3
f1 (ppm)

4y

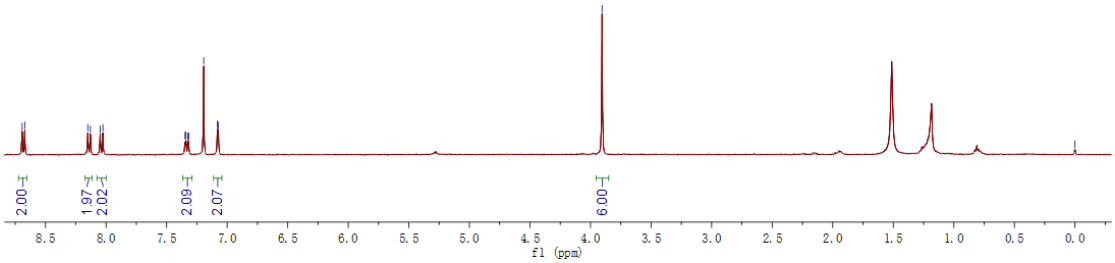

9.001
8.980
8.823
8.802
8.640
8.411
8.389
8.340
8.319
8.255
8.230
8.207
7.494
7.462
7.262
4.018
2.922
2.533
0.000
4z
1.00
1.02
1.00
1.06
1.06
1.99
0.99
1.00
3.05
2.96
3.11
f1 (ppm)
166.776
158.782
153.361
149.843
145.459
137.702
137.513
137.031
136.352
132.114
130.769
130.064
128.963
128.676
128.036
127.487
124.475
120.260
118.939
77.317
77.000
76.683
52.405
21.719
17.778
4z
f1 (ppm)

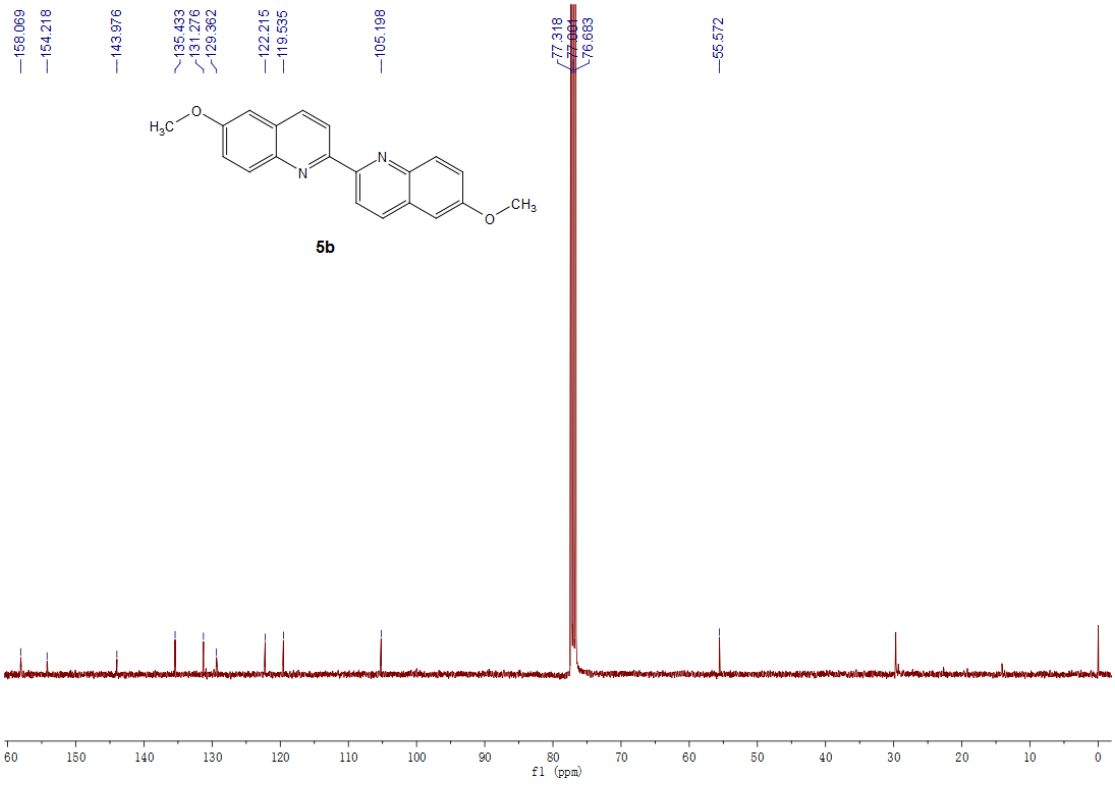

8.774
8.752
8.249
8.228
8.161
8.140
7.802
7.782
7.673
7.508
7.488
7.470
0.000
N
N
5a
2.00
2.07
2.04
2.05
2.07
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.186
147.879
136.737
129.889
129.535
128.410
127.637
126.925
119.388
77.317
77.000
76.682
N
N
5a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

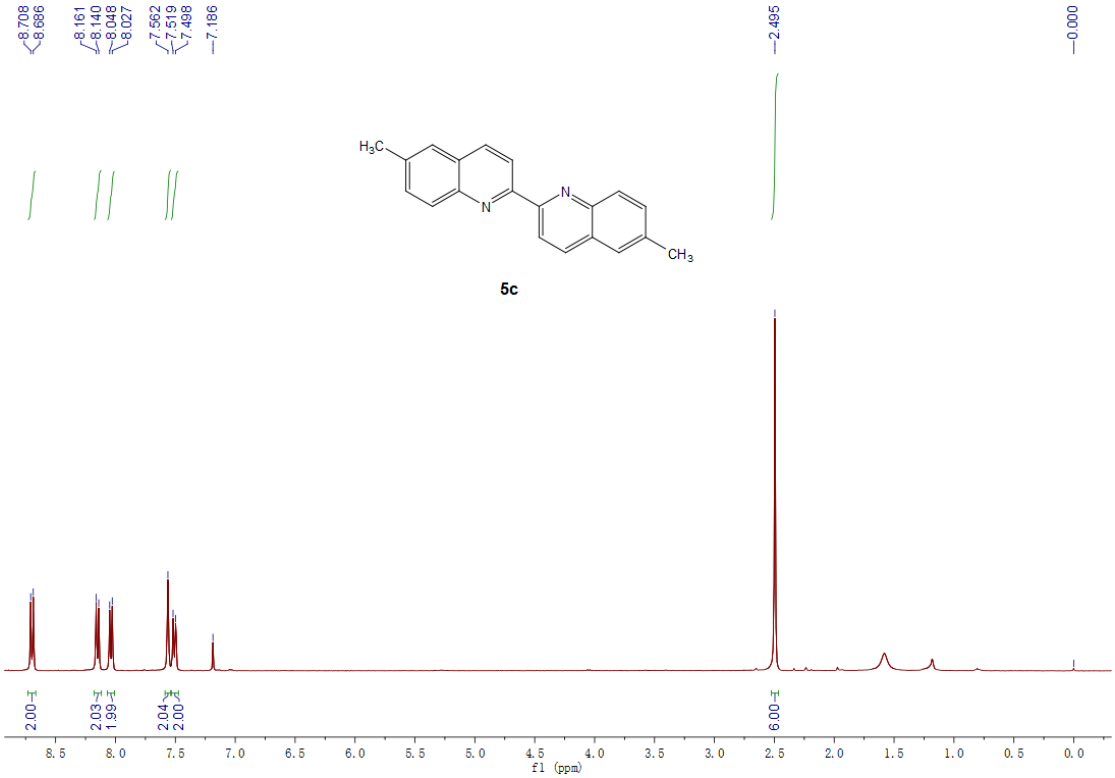

8.693
8.671
8.151
8.129
8.049
8.026
7.348
7.341
7.325
7.318
7.193
7.080
7.074
3.904
0.000
O
H3C
N
N
O
CH3

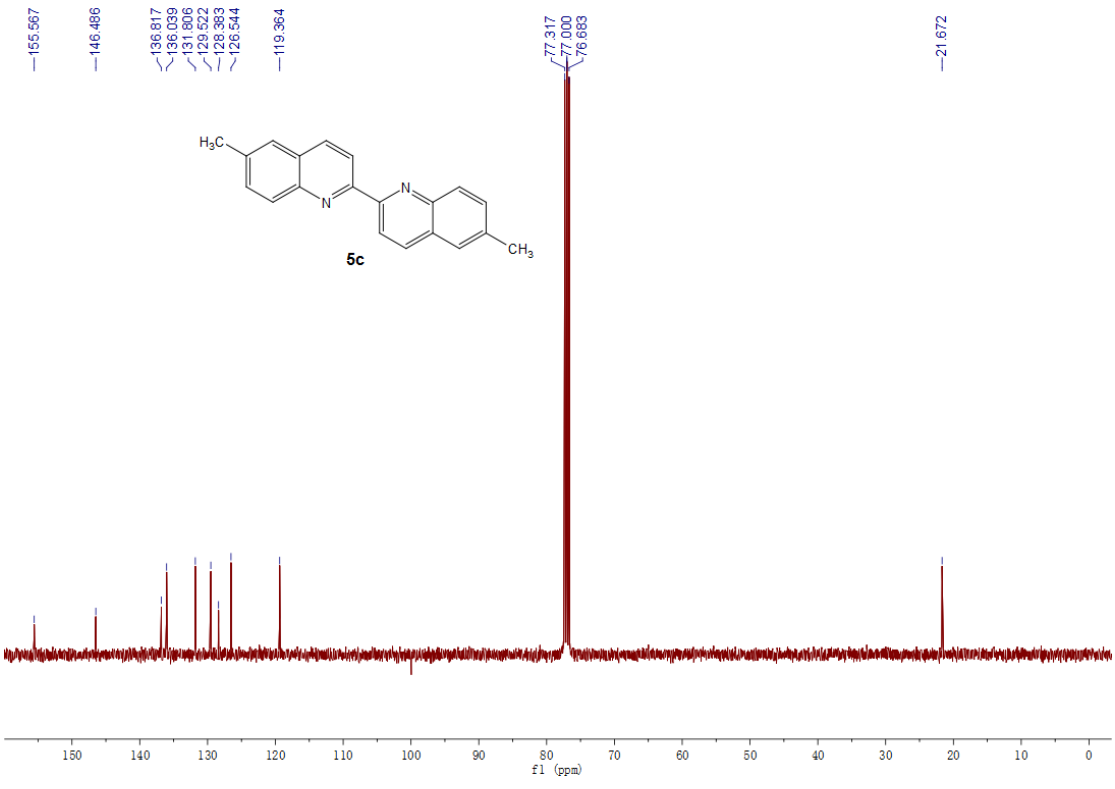
5b

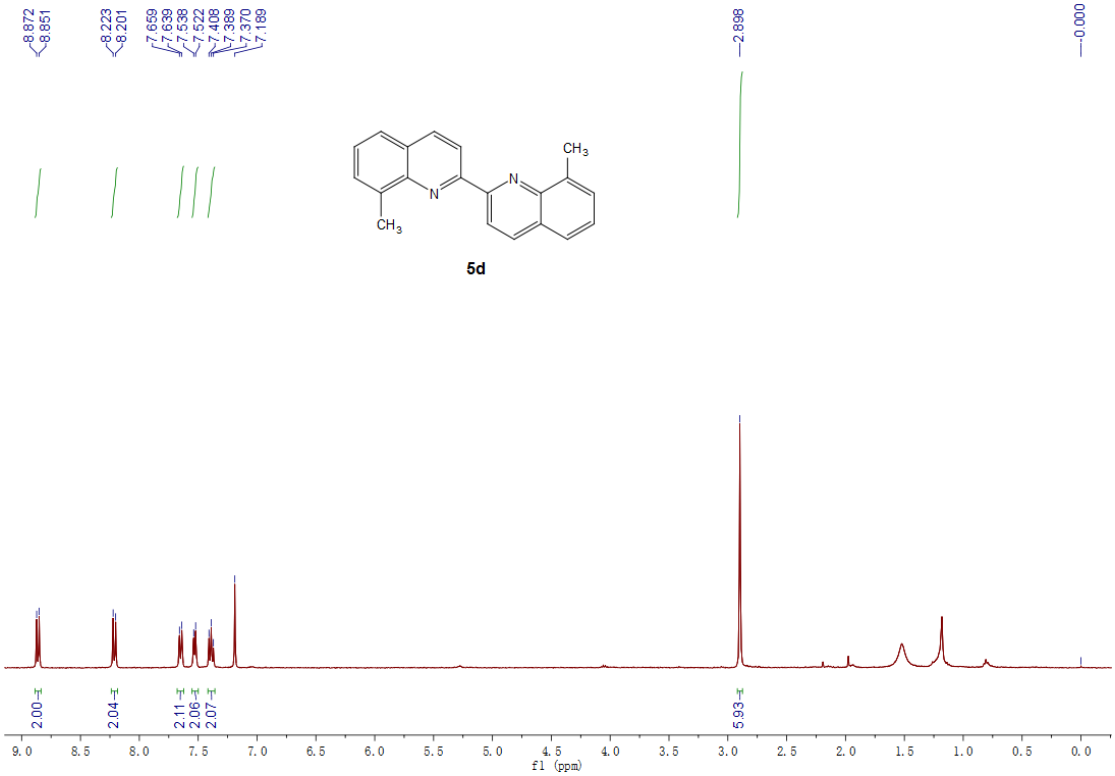

2.00
1.97
2.02
2.09
2.07
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.069
154.218
143.976
135.433
131.276
129.362
122.215
119.535
105.198
77.318
77.001
76.683
55.572
O
H3C
N
N
O
CH3
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5b


8.708
8.686
8.161
8.140
8.048
8.027
7.562
7.519
7.498
7.186
2.495
0.000
H3C
N
N
CH3
5c
2.00
2.03
1.99
2.04
2.00
6.00
f1 (ppm)


155.567
146.486
136.817
136.039
131.806
129.522
128.383
126.544
119.364
77.317
77.000
76.683
21.672
H3C
N
N
CH3
5c
f1 (ppm)


8.872
8.851
8.223
8.201
7.659
7.639
7.538
7.522
7.408
7.389
7.370
7.189
2.898
0.000
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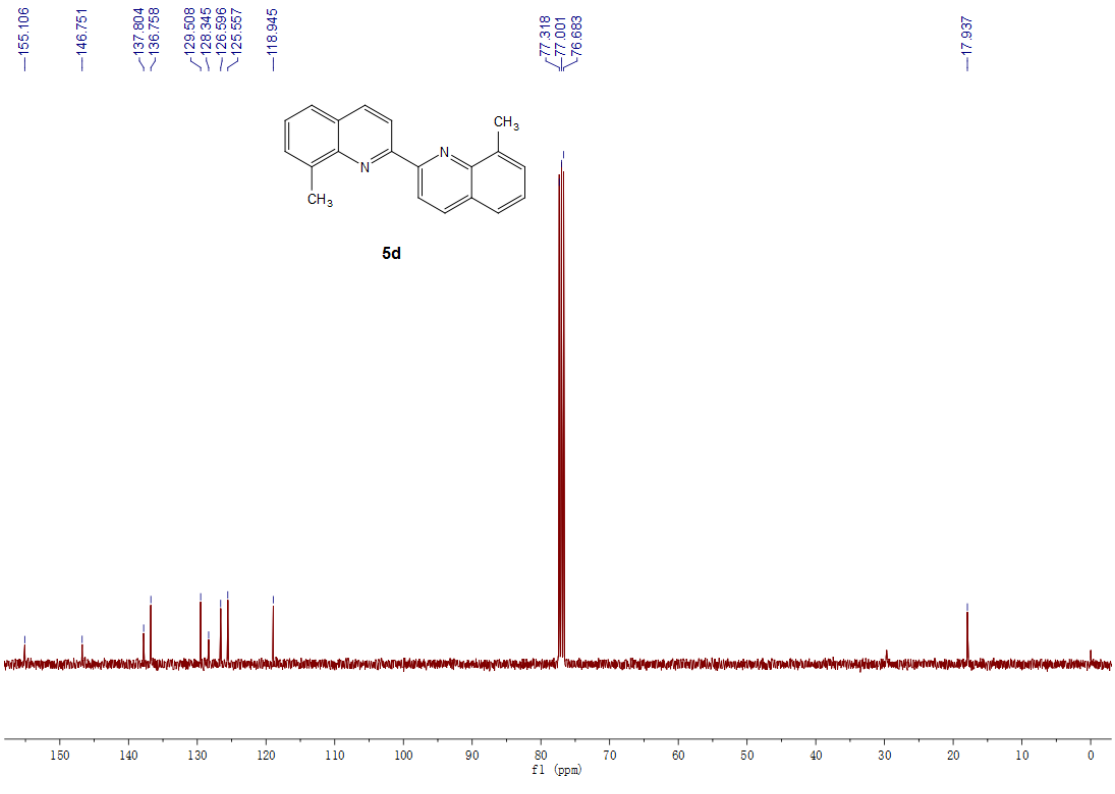
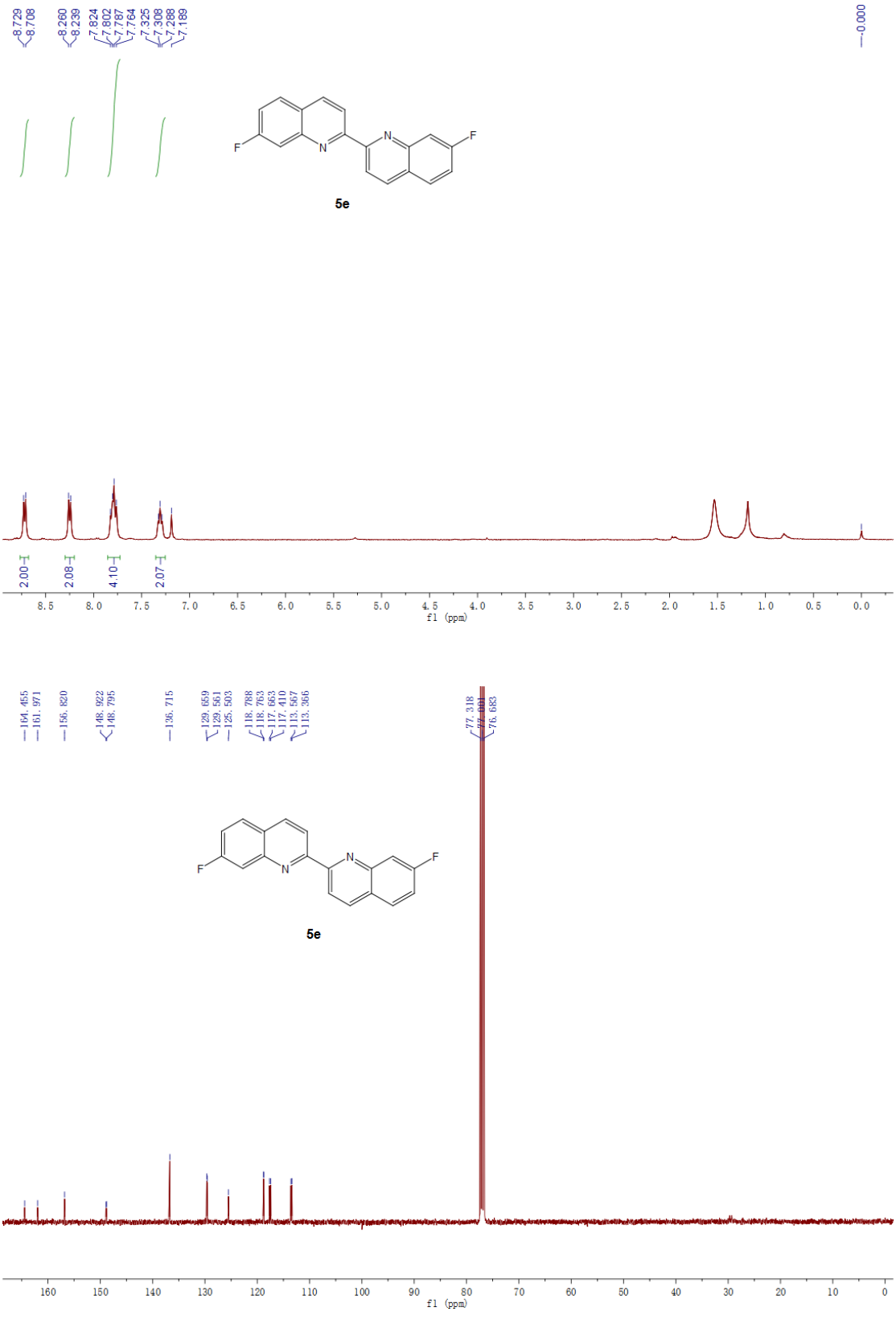
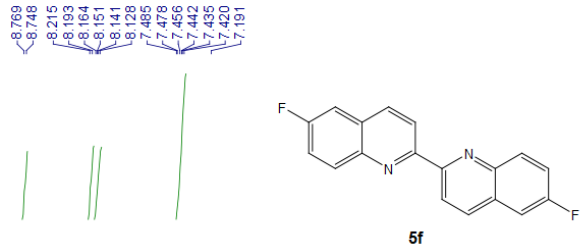
N
CH3
5d
2.00
2.04
2.11
2.06
2.07
5.93
f1 (ppm)


155.106
146.751
137.804
136.758
129.508
128.345
126.596
125.557
118.945
77.318
77.001
76.683
17.937
CH3
N
CH3
5d
f1 (ppm)


8.729
8.708
8.260
8.239
7.824
7.802
7.787
7.764
7.325
7.308
7.288
7.189
0.000
F
N
N
F
5e
2.00
2.08
4.10
2.07
f1 (ppm)
164.455
161.971
156.820
148.922
148.795
136.715
129.659
129.561
125.503
118.788
118.763
117.663
117.410
113.567
113.366
77.318
77.001
76.683
F
N
N
F
5e
f1 (ppm)


8.769
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8.215
8.193
8.164
8.151
8.141
8.128
7.485
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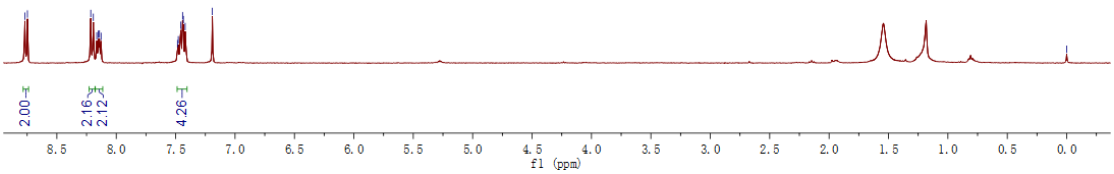
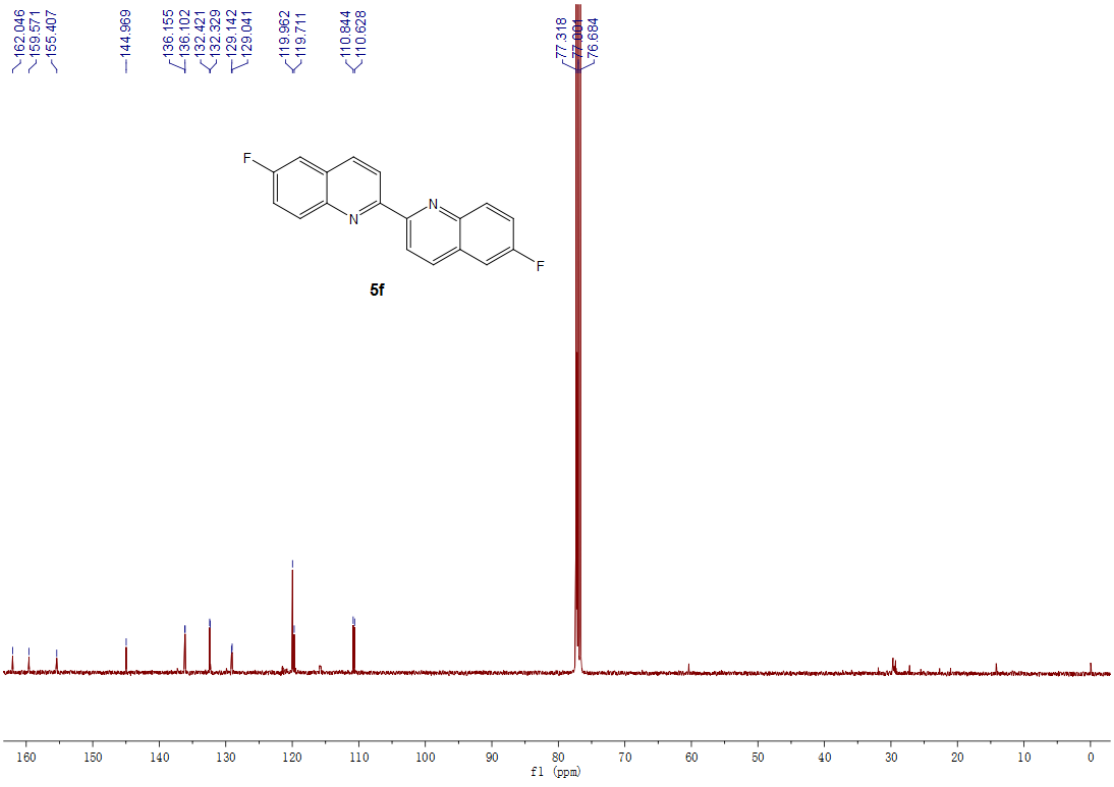
7.456
7.442
7.435
7.420
7.191
0.000
F
N
N
F

5f


2.00
2.16
2.12
4.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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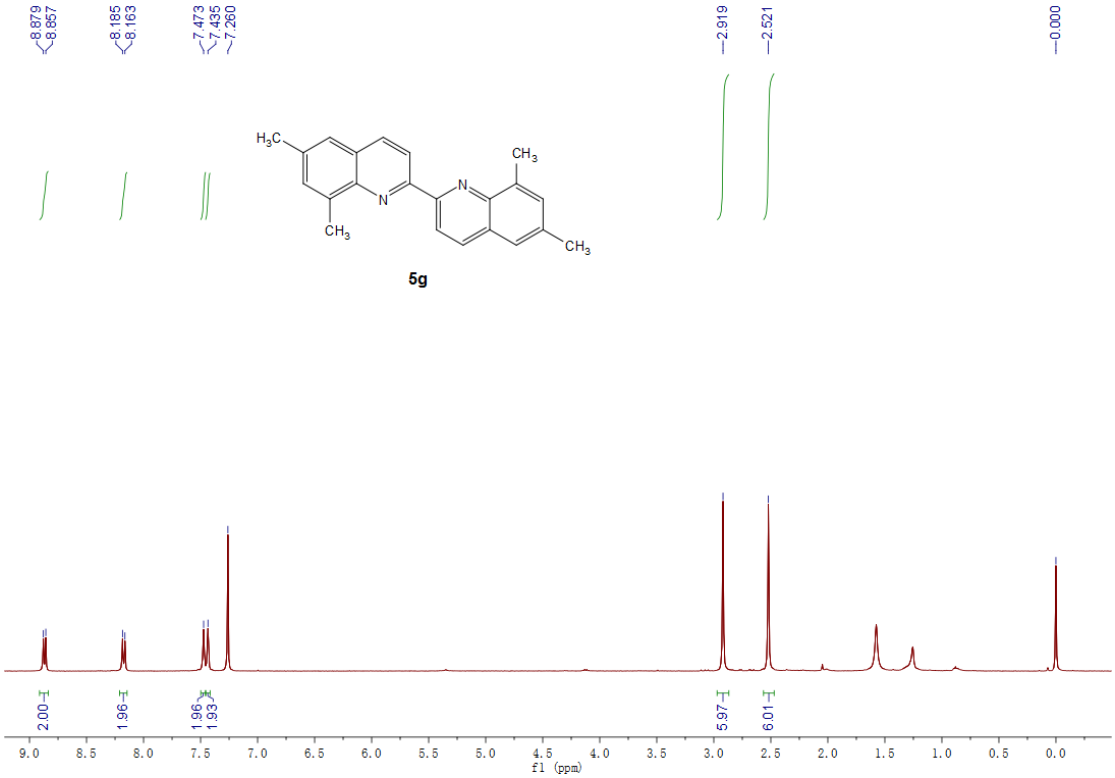
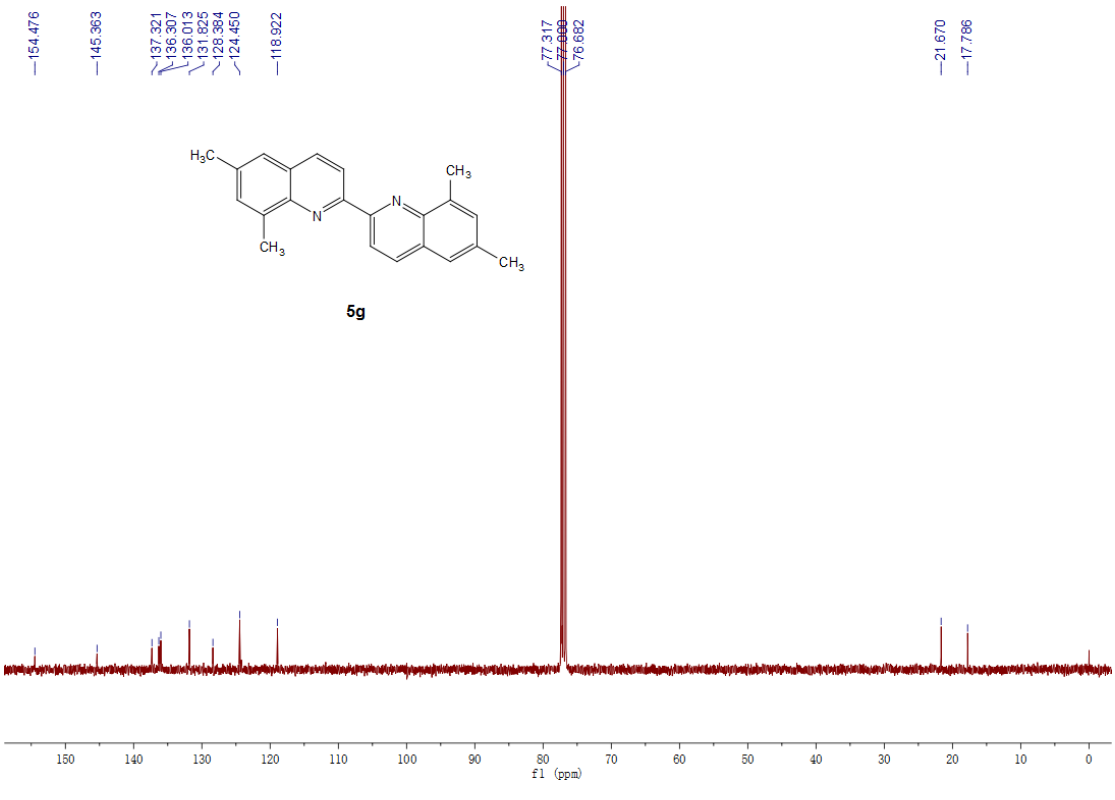
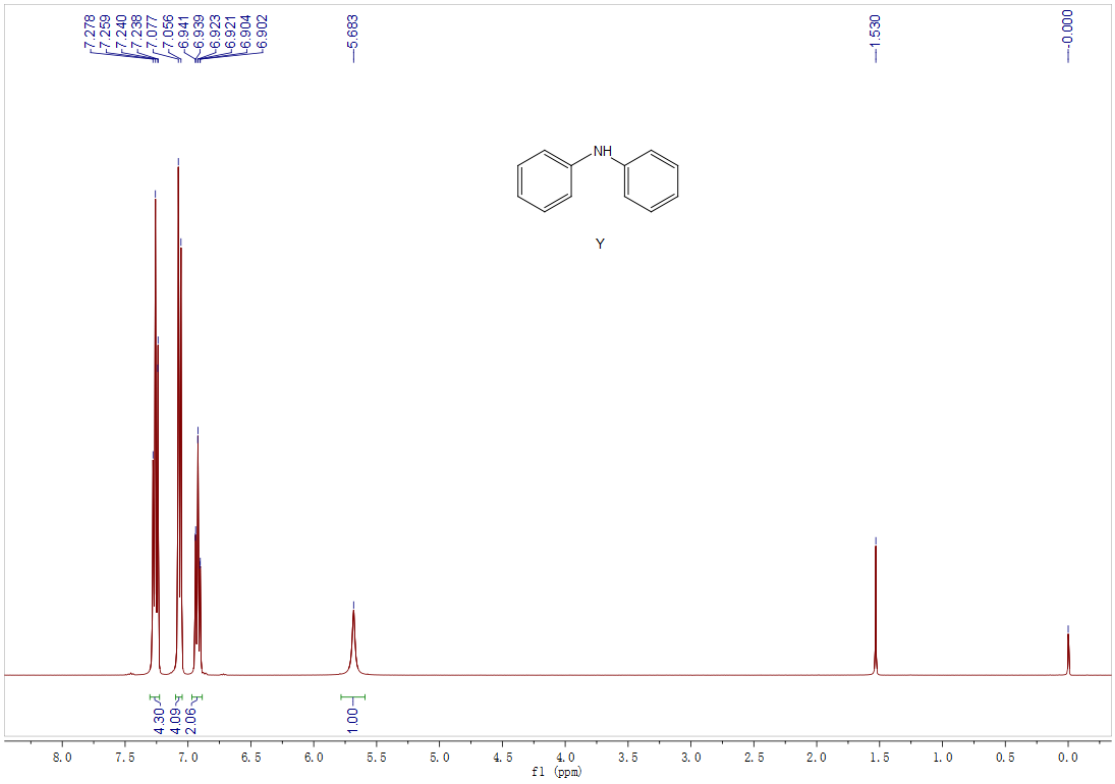
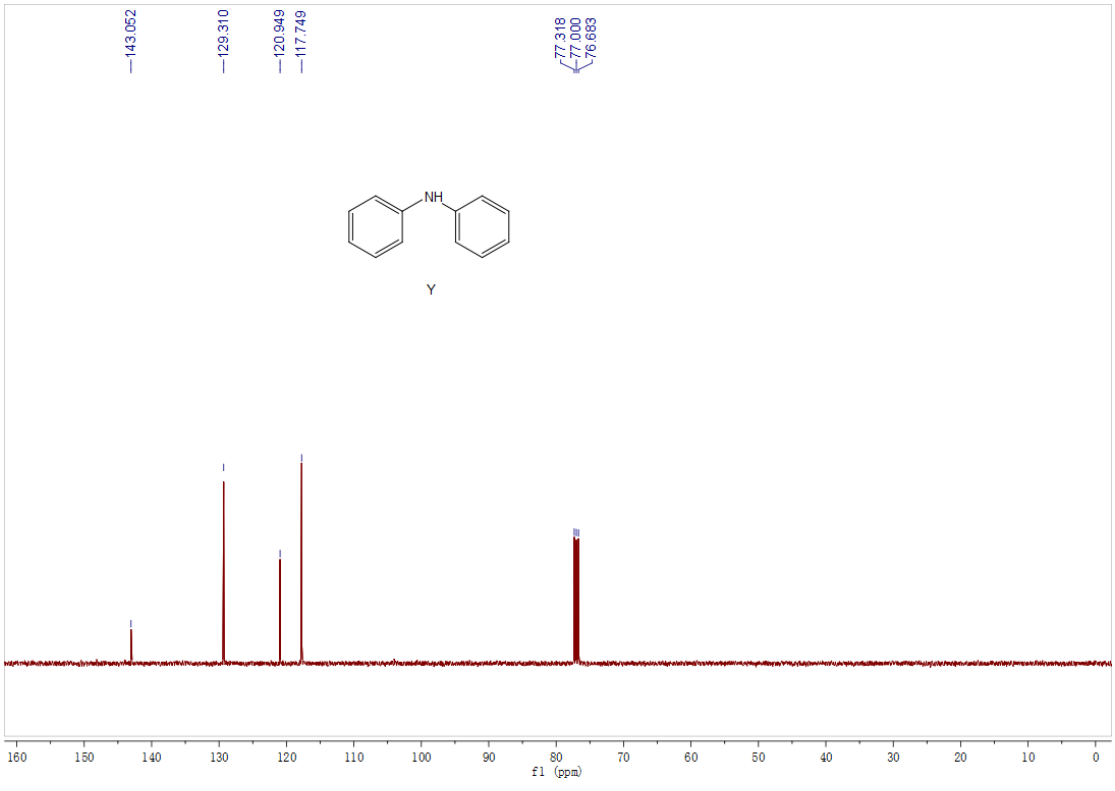
159.571
155.407
144.969
136.155
136.102
132.421
132.329
129.142
129.041
119.962
119.711
110.844
110.628
77.318
77.001
76.684
F
N
N
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5f


8.879
8.857
8.185
8.163
7.473
7.435
7.260
2.919
2.521
0.000
H3C
CH3
N
N
CH3
CH3
5g
2.00
1.96
1.96
1.93
5.97
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.476
145.363
137.321
136.307
136.013
131.825
128.384
124.450
118.922
77.317
77.000
76.682
21.670
17.786
H3C
CH3
N
N
CH3
CH3
5g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.278
7.259
7.240
7.238
7.077
7.056
6.941
6.939
6.923
6.921
6.904
6.902
5.683
1.530
0.000
NH
Y
4.30
4.09
2.06
1.00
f1 (ppm)


143.052
129.310
120.949
117.749
77.318
77.000
76.683
NH
Y
f1 (ppm)