Supporting Information for

Cu(II)-Promoted Three-Component Coupling Sequence for the Efficient Synthesis of Substituted Quinolines

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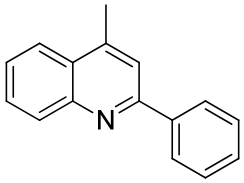
General information:

All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over aluminum oxide 40-60 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the Center for Mass Spectrometry, Peking University. The structures of known compounds were further corroborated by comparing their ^{1}H NMR data and MS data with those of literature. All reagents were used as received from commercial sources without further purification. Aldehydes, amines and acetone employed were reagent grade materials and used as received.

General procedure: (4a):

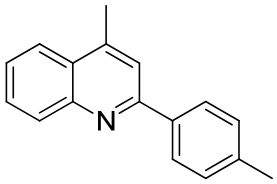
A 10 mL oven-dried reaction vessel was charged with $CuCl_2$ (1.3 mg, 5 mol %), benzaldehyde (**1a**, 30.6 μL, 0.3 mmol), aniline (**2a**, 18.3 μL, 0.2 mmol), trifluoromethanesulfonic acid (18.6 μL, 0.2 mmol) and charged with oxygen (1 atm). Acetone (0.2 mL) and ethanol (0.3 mL) were added to the sealed reaction vessel by syringe. The resulting solution was stirred at 50 ^{o}C for 24 h. After cooling to room temperature the volatiles were removed under vacuum and the residue was purified by column chromatography (aluminum oxide, petroleum ether/ dichloromethane = 4:1) to give **4a** as pale yellow solid; yield: 35.1 mg (80%).

2-Phenyl-4-methylquinoline (4a, CAS: 4789-76-8) [1]



^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20-8.15 (m, 3H), 8.01 (d, J = 8.2 Hz, 1H), 7.74-7.71 (m, 2 H), 7.57-7.44 (m, 4H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.1, 148.3, 144.8, 13 9.9, 130.4, 129.3, 129.2, 128.8, 127.6, 127.3, 126.0, 123.6, 119.7, 18.9; MS (EI) m/z (%): 219 (100), 204, 189, 115, 108, 77.

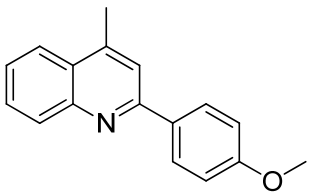
4-Methyl-2-(4'-methylphenyl)quinoline (4b) [2]



4-Methylbenzaldehyde (**1b**, 35.5 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4b** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 34.0 mg (73%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 7.6 Hz, 2H), 7.99 (d, J = 8.2 Hz, 1H), 7.71-7.69 (m, 2H), 7.55-7.51 (m, 1H), 7.33 (d, J =7.6 Hz, 2H), 2.76 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.0, 148.3, 144.6, 139.2, 137.1, 130.3, 129.5, 129.2, 127.4, 127.2, 125.8, 123.6, 119.6, 21.3, 18.9; MS (EI) *m/z* (%)：233 (100), 218, 189, 115, 108, 75.

4-Methyl-2-(4'-methoxyphenyl)quinoline (4c, CAS: 14428-50-3) [3]

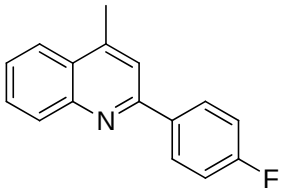


4-Methoxybenzaldehyde (**1c**, 36.5 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4c** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 3:1); yield: 35.4 mg (71%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13 (d, J = 8.5 Hz, 3H), 7.98 (d, J = 8.2 Hz, 1H), 7.72-7.68 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H), 2.76 (s, 3H); ^{13}C NMR

($CDCl_3$, 100 MHz, ppm): δ 160.7, 156.7, 148.2, 144.6, 132.4, 130.1, 129.3, 128.9, 127.0, 125.7, 123.6, 119.3, 114.2, 55.4, 19.0; MS (EI) *m/z* (%)：249 (100), 234, 206, 191, 77.

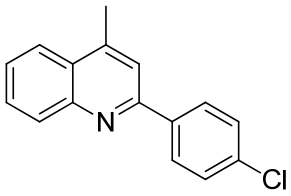
2-(4-Fluorophenyl)-4-methyl-quinoline (4d)



4-Fluorobenzaldehyde (**1d**, 32.2 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4d** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 38.4 mg (81%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16-8.15 (m, 3H), 8.00 (d, J = 8.2 Hz, 1H), 7.74-7.67 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.26-7.18 (m, 2H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 163.8 (d, J = 247.0 Hz), 155.9, 148.2, 144.9, 136.0 (d, J = 3.0 Hz), 130.3, 129.4, 129.3 (d, J = 8.4 Hz), 127.2, 126.1, 123.6, 119.3, 115.7 (d, J = 21.4 Hz), 18.9; MS (EI) *m/z* (%)：237 (100), 222, 216, 117, 75; HRMS calcd. for : $C_{16}H_{13}FN$ $[M+H]^+$ 238.1026, found 238.1025.

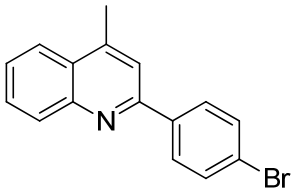
2-(4-Chlorophenyl)-4-methylquinoline (4e, CAS: 14428-49-0) [4]



4-Chlorobenzaldehyde (**1e**, 32.2 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4e** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 43.0 mg (85%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17-8.10 (m, 3H), 8.00 (d, J = 8.2 Hz, 1H), 7.75-7.68 (m, 2H), 7.57-7.48 (m, 3H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.7, 148.2, 145.0, 138.2, 135.4, 130.3, 129.5, 128.9, 128.8, 127.3, 126.2, 123.6, 119.3, 18.9; MS (EI) *m/z* (%)：253 (100), 238, 217, 203, 108, 75.

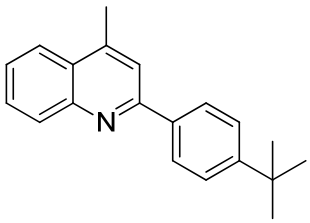
2-(4-Bromophenyl)-4-methylquinoline (4f, CAS: 14444-95-2) [4]



4-Bromobenzaldehyde (**1f**, 55.5 mg, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4f** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 51.7 mg (87%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.15 (d, J = 8.4 Hz, 1H), 8.05-7.99 (m, 3H), 7.74-7.54 (m, 5H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.7, 148.2, 145.0, 138.7, 131.9, 130.3, 129.5, 127.2, 127.4, 126.3, 123.8, 123.6, 119.3, 18.9; MS (EI) *m/z* (%)：297 (100), 284, 217, 203, 108, 75.

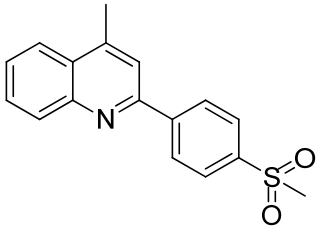
2-(4-tert-Butylphenyl)-4-methylquinoline (4g, CAS: 863487-45-0)



4-(*tert*-Butyl)benzaldehyde (**1g**, 50.2 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone to give **4g** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 40.7 mg (74%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 7.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 3H), 2.77 (s, 3H), 1.38 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.2, 152.4, 148.2, 144.7, 137.1, 130.3, 129.3, 128.2, 127.3, 125.9, 125.8, 123.7, 119.8, 34.8, 31.4, 19.0; MS (EI) *m/z* (%)：275, 260 (100), 244, 116, 108, 75; HRMS calcd. for : $C_{20}H_{22}N$ $[M+H]^+$ 276.1747, found 276.1750.

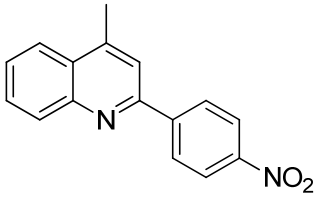
4-Methyl-2-(4-methylsulfonylphenyl)quinoline (4h)



4-(Methylsulfonyl)benzaldehyde (**1h**, 55.3 mg, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4h** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 2:1); yield: 50.5 mg (85%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.36 (d, J = 8.2 Hz, 2H), 8.19 (d, J = 8.4 Hz, 1H), 8.09(d, J = 8.2 Hz, 2H), 8.04 (d, J = 8.2 Hz, 1H), 7.78-7.76 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 3.10 (s, 3H), 2.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.6, 148.1, 145.5, 144.8, 140.8, 130.5, 129.7, 128.3, 127.7, 127.6, 126.8, 123.7, 119.5, 44.6, 19.0; MS (EI) *m/z* (%)： 297, 282, 234, 218 (100), 108, 75; HRMS calcd. for : $C_{17}H_{16}NO_2S$ $[M+H]^+$ 298.0896, found 298.0901.

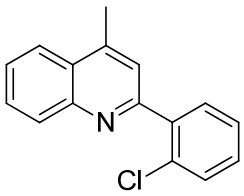
4-Methyl-2-(4-nitrophenyl)quinoline (4i, CAS: 14365-92-5) [5]



4-Nitrobenzaldehyde (**1i**, 30.3 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone to give **4i** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 38.0 mg (72%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.39-8.37 (m, 4H), 8.19 (d, J = 8.4 Hz, 1H), 8.04(d, J = 8.3 Hz, 1H), 7.77 (t, J = 7.0 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.2, 148.3, 148.2, 145.7, 145.6, 130.6, 129.9, 128.3, 127.7, 127.0, 123.9, 123.7. 119.5, 19.0; MS (EI) *m/z* (%)： 264, 234, 218 (100), 191, 75.

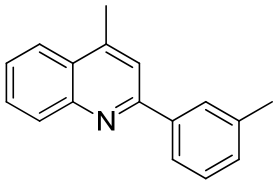
2-(2'-Chlorophenyl)-4-methylquinoline (4j, CAS: 1131453-82-1) [6]



2-Chlorobenzaldehyde (**1j**, 33.7 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4j** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 30.4 mg (60%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.18 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.74-7.50 (m, 5H), 7.42-7.35 (m, 2H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.2, 148.0, 143.9, 139.9, 132.4, 131.7, 130.3, 130.1, 129.7, 129.3, 127.3, 127.1, 126.5, 123.7, 123.4, 18.8; MS (EI) *m/z* (%)：253, 238, 218 (100), 203, 108, 75.

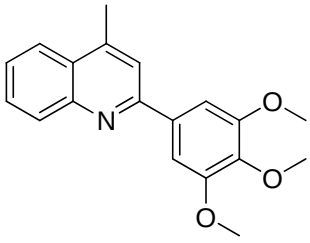
4-Methyl-2-*m*-tolylquinoline (4k, CAS: 1039775-39-7) [7]



3-Methylbenzaldehyde (**1k**, 35.3 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4k** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 36.4 mg (78%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (d, J = 8.3 Hz, 1H), 8.01-7.99 (m, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.74-7.71 (m, 2H), 7.54 (t, J = 7.4 Hz , 1H), 7.41 (t, J = 7.5 Hz , 1H), 7.28-7.26 (m, 1H), 2.77 (s, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.3, 148.3, 144.7, 139.9, 138.4, 130.4, 130.0, 129.3, 128.7, 128.3, 127.3, 126.0, 124.7, 123.6, 119.9, 21.6, 18.9; MS (EI) *m/z* (%)：233 (100), 218, 203, 115, 108, 75.

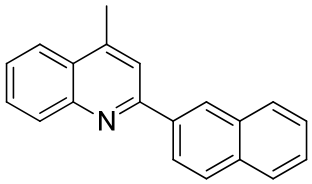
4-Methyl-2-(3,4,5-trimethoxyphenyl)quinoline (4l)



3,4,5-Trimethoxybenzaldehyde (**1l**, 58.9 mg, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4l** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 3:1); yield: 50.1 mg (81%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.73 (t, J = 7.4 Hz, 1H), 7.76 (s, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.39 (s, 2H), 4.02 (s, 6H), 3.92 (s, 3H), 2.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.7, 153.6, 148.1, 144.8, 139.6, 135.5, 130.2, 129.4, 127.3, 126.0, 123.6, 119.5, 105.1, 60.9, 56.4, 18.9; MS (EI) *m/z* (%)： 309 (100), 294, 264, 236, 180, 77; HRMS calcd. for : $C_{19}H_{20}NO_3$ $[M+H]^+$ 310.1438, found 310.1441.

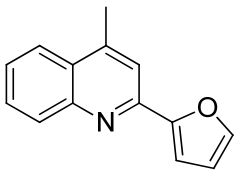
4-Methyl-2-(naphthalen-2-yl)quinoline (4m) [8]



2-Naphthaldehyde (**1m**, 46.9 mg, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4m** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 3:1); yield: 48.4 mg (90%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.62 (s, 1H), 8.37 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 8.04-7.89 (m, 5H), 7.75 (t, J = 7.4 Hz, 1H), 7.59-7.53 (m, 3H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.9, 148.3, 144.9, 137.1, 133.9, 133.6, 130.3, 129.5, 128.9, 128.6, 127.8, 127.4, 127.1, 126.7, 126.3, 126.1, 125.2, 123.7, 119.9, 19.1; MS (EI) *m/z* (%)： 269 (100), 254, 239, 133, 127, 75.

2-(Furan-2-yl)-4-methylquinoline (4n, CAS: 20364-42-5) [9]

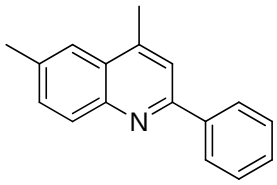


Furan-2-carbaldehyde (**1n**, 24.9 μL, 0.3 mmol) reacted with aniline (**2a**, 18.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4n** as pale yellow solid; yield (aluminum oxide, petroleum ether/dichloromethane = 4:1): 21.3 mg (51%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.72-7.68 (m, 2H), 7.63 (s, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.21 (s, 1H), 6.59 (s, 1H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 153.9, 148.8, 148.0, 144.7, 143.9, 130.0, 129.5, 127.3, 125.9, 123.6,

118.0, 112.1, 109.9, 18.8; MS (EI) *m/z* (%)：209 (100), 180, 152, 115, 77.

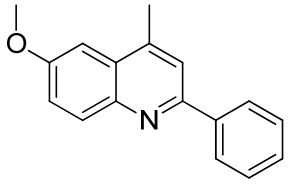
4,6-Dimethyl-2-phenyl-quinoline (4o) [10]



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with *p*-toluidine (**2b**, 22.3 μL, 0.2 mmol) and acetone (0.2 mL) to give **4o** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 37.8 mg (81%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.14 (d, J = 7.3 Hz, 2H), 8.06 (d, J = 8.5 Hz, 1H), 7.75 (s, 1H), 7.68 (s, 1H), 7.56-7.44 (m, 4H), 2.74 (s, 3H), 2.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.3, 146.7, 144.1, 140.0, 135.9, 131.6, 130.0, 129.0, 128.8, 127.5, 127.2, 122.7, 119.8, 22.0, 19.1; MS (EI) *m/z* (%)：233 (100), 218, 108, 89, 77.

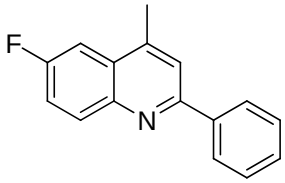
6-Methoxy-4-methyl-2-phenylquinoline (4p, CAS: 171774-27-9) [11]



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with 4-methoxyaniline (**2c**, 22.6 μL, 0.2 mmol) and acetone (0.2 mL) to give **4p** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 3:1); yield: 27.9 mg (56%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13-8.08 (m, 3H), 7.70 (s, 1H), 7.53-7.37 (m, 4H), 7.21 (s, 1H), 4.00 (s, 3H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.6, 154.8, 144.1, 143.3, 140.0, 131.8, 128.9, 128.8, 128.1, 127.3, 121.5, 120.0, 101.9, 55.6, 19.3; MS (EI) *m/z* (%)：249 (100), 234, 206, 191, 102, 77.

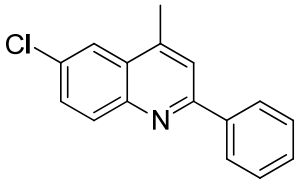
6-Fluoro-4-methyl-2-phenylquinoline (4q)



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with 4-fluoroaniline (**2d**, 19.0 μL, 0.2 mmol) and acetone (0.2 mL) to give **4q** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 25.6 mg (56%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18-8.12 (m, 3H), 7.74 (s, 1H), 7.60-7.46 (m, 5H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 160.4 (d, J = 246.0 Hz), 156.5 (d, J = 2.6 Hz), 145.3, 144.2 (d, J = 5.4 Hz), 139.6, 132.8 (d, J = 9.1 Hz), 129.3, 128.8, 128.0 (d, J = 9.2 Hz), 127.4, 120.3, 119.3 (d, J = 25.4 Hz), 107.2 (d, J = 22.1 Hz), 19.0; MS (EI) *m/z* (%)：237 (100), 222, 158, 133, 117, 77; HRMS calcd. for : $C_{16}H_{13}FN$ $[M+H]^+$ 238.1026, found 238.1028.

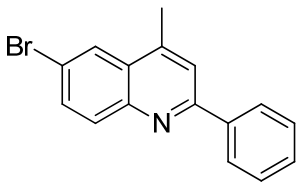
6-Chloro-4-methyl-2-phenylquinoline (4r) [12]



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with 4-chloroaniline (**2e**, 22.5 mg, 0.2 mmol) and acetone (0.2 mL) to give **4r** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 33.5 mg (66%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.15-8.09 (m, 3H), 7.97 (s, 1H), 7.74 (s, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.54-7.46 (m, 3H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.2, 146.5, 144.0, 139.4, 131.9, 131.8, 130.2, 129.5, 128.9, 128.0, 127.5, 122.8, 120.0, 18.9; MS (EI) *m/z* (%)：253 (100), 238, 217, 203, 108, 75.

6-Bromo-4-methyl-2-phenyl-quinoline (4s)

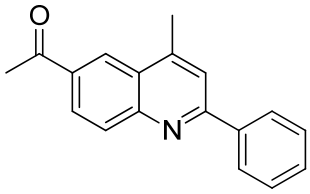


Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with 4-bromoaniline (**2f**, 34.4 mg, 0.2 mmol) and

acetone (0.2 mL) to give **4s** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 47.5 mg (80%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.15-8.14 (m, 3H), 8.04 (d, J = 8.8 Hz, 1H), 7.79-7.74 (m, 2H), 7.55-7.45 (m, 3H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.3, 146.7, 144.0, 139.3, 132.7, 132.0, 129.5, 128.9, 128.5 127.5, 126.2, 120.4, 120.0, 19.0; MS (EI) *m/z* (%)：297 (100), 282, 217, 203, 108, 75; HRMS calcd. for : $C_{16}H_{13}BrN$ $[M+H]^+$ 298.0226, found 298.0233.

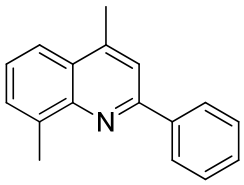
1-(4-Methyl-2-phenylquinolin-6-yl)ethanone (4t)



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with 1-(4-aminophenyl)ethanone (**2g**, 34.4 mg, 0.2 mmol) and acetone (0.2 mL) to give **4t** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 31.8 mg (61%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.65 (s, 1H), 8.27-8.18 (m, 4H), 7.80 (s, 1H), 7.56-7.49 (m, 3H), 2.86 (s, 3H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 197.6, 159.1, 150.0, 146.5, 139.2, 134.3, 130.8, 129.8, 128.9, 127.8, 127.7, 126.6, 125.5, 120.4, 26.8, 19.0; MS (EI) *m/z* (%)：261, 246 (100), 217, 189, 108, 77; HRMS calcd. for: $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1230.

4, 8-Dimethyl-2-phenylquinoline (4u)

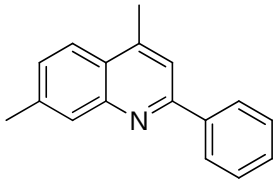


Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with *o*-toluidine (**2h**, 21.2 μL, 0.2 mmol) and acetone (0.2 mL) to give **4u** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 29.4 mg (63%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.26 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.75 (s, 1H), 7.58-7.41 (m, 5H), 2.92 (s, 3H), 2.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.1,

147.1, 144.7, 140.1, 138.2, 129.4, 129.1, 128.7, 127.5, 127.2, 125.7, 121.5, 119.0, 19.3, 18.3; MS (EI) *m/z* (%)：233 (100), 218, 154, 128, 116, 77; HRMS calcd. for : $C_{17}H_{16}N$ $[M+H]^+$ 234.1277, found 234.1278.

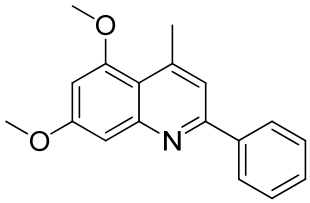
4,7-Dimethyl-2-phenyl-quinoline (4v)



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with *m*-toluidine (**2i**, 21.6 μL, 0.2 mmol) and acetone (0.2 mL) to give **4v** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 31.7 mg (68%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.14 (d, J = 7.6 Hz, 2H), 7.96 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.64 (s, 1H), 7.53-7.37 (m, 4H), 2.74 (s, 3H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.1, 148.5, 144.8, 140.1, 139.4, 129.4, 129.0, 128.7, 128.2, 127.5, 125.3, 123.3, 119.0, 21.7, 18.9; MS (EI) *m/z* (%)：233 (100), 218, 203, 108, 77; HRMS calcd. for : $C_{17}H_{16}N$ $[M+H]^+$ 234.1277, found 234,1279.

5,7-Dimethoxy-4-methyl-2-phenylquinoline (4w)



Benzaldehyde (**1a**, 30.6 μL, 0.3 mmol) reacted with 3,5-dimethoxyaniline (**2j**, 30.6 mg, 0.2 mmol) and acetone (0.2 mL) to give **4w** as pale yellow solid (aluminum oxide, petroleum ether/dichloromethane = 4:1); yield: 36.8 mg (66%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.10 (d, J = 7.3 Hz, 2H), 7.52-7.43 (m, 4H), 7.11 (s, 1H), 6.49 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 160.5, 158.6, 157.3, 151.9, 146.2, 139.8, 129.0, 128.7, 127.4, 119.2, 115.7, 101.2, 98.5, 55.54, 55.51, 24.5; MS (EI) *m/z* (%)：279 (100), 264, 250, 236, 221, 139, 102, 77; HRMS calcd. for : $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, found 280.1330.

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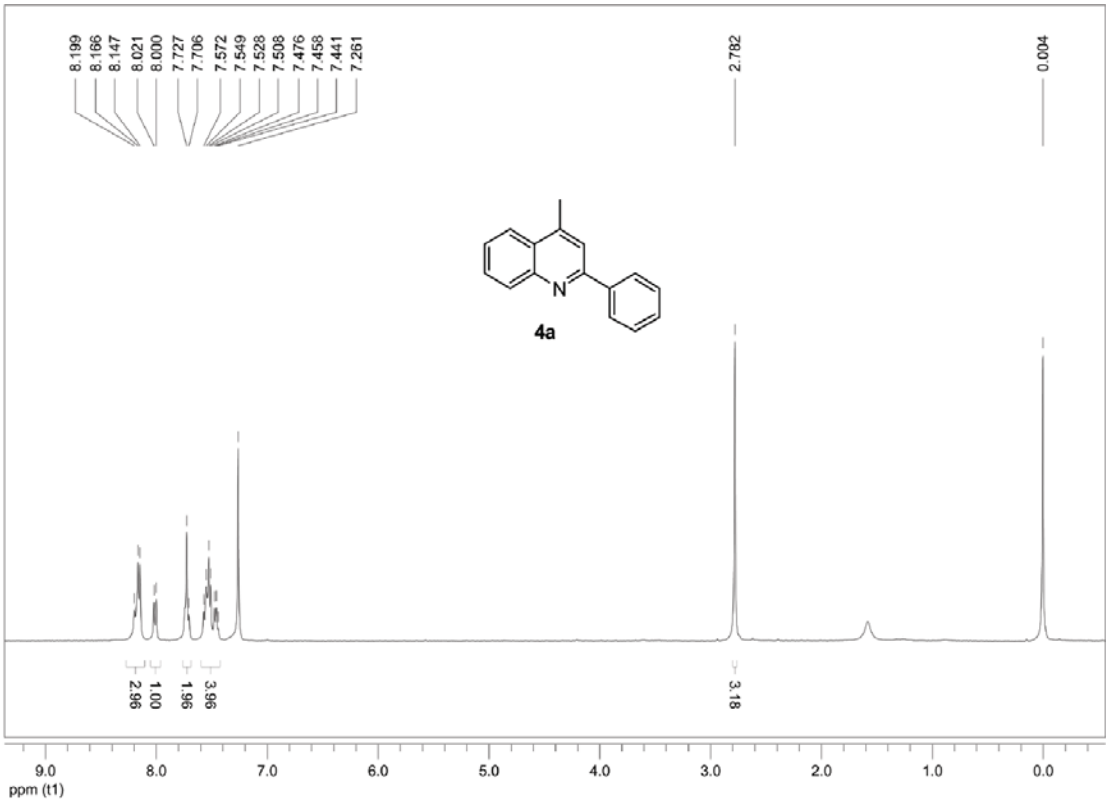
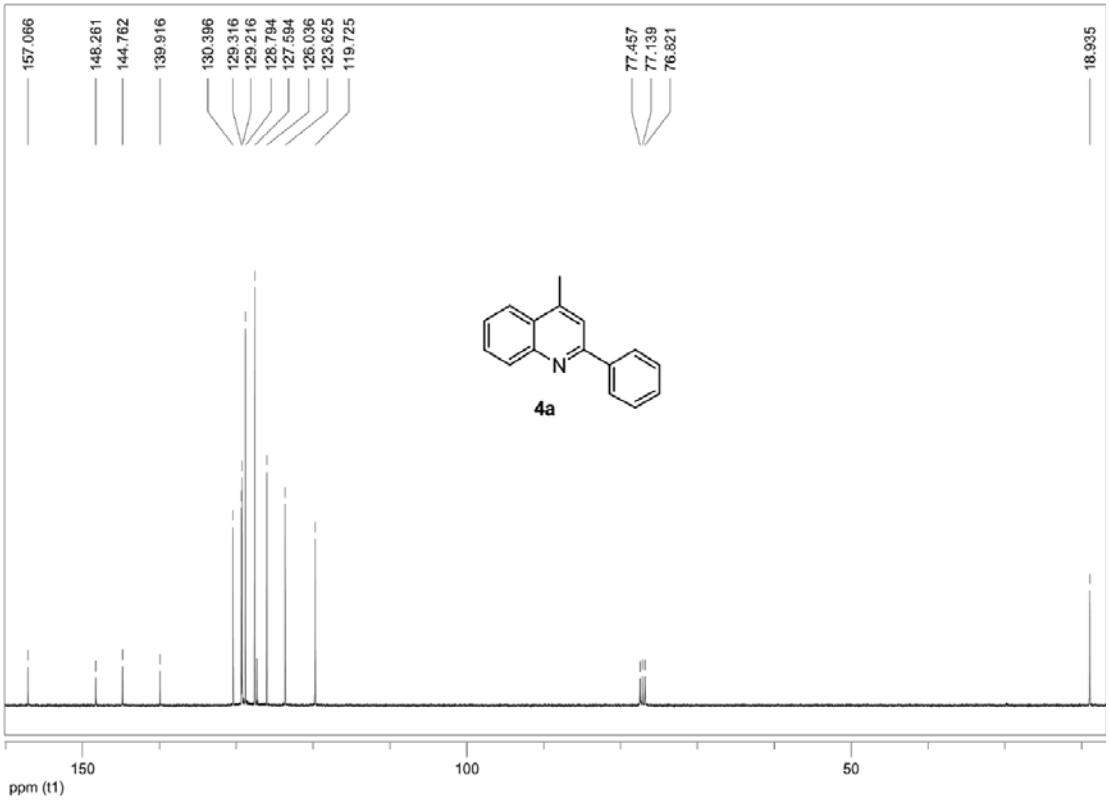
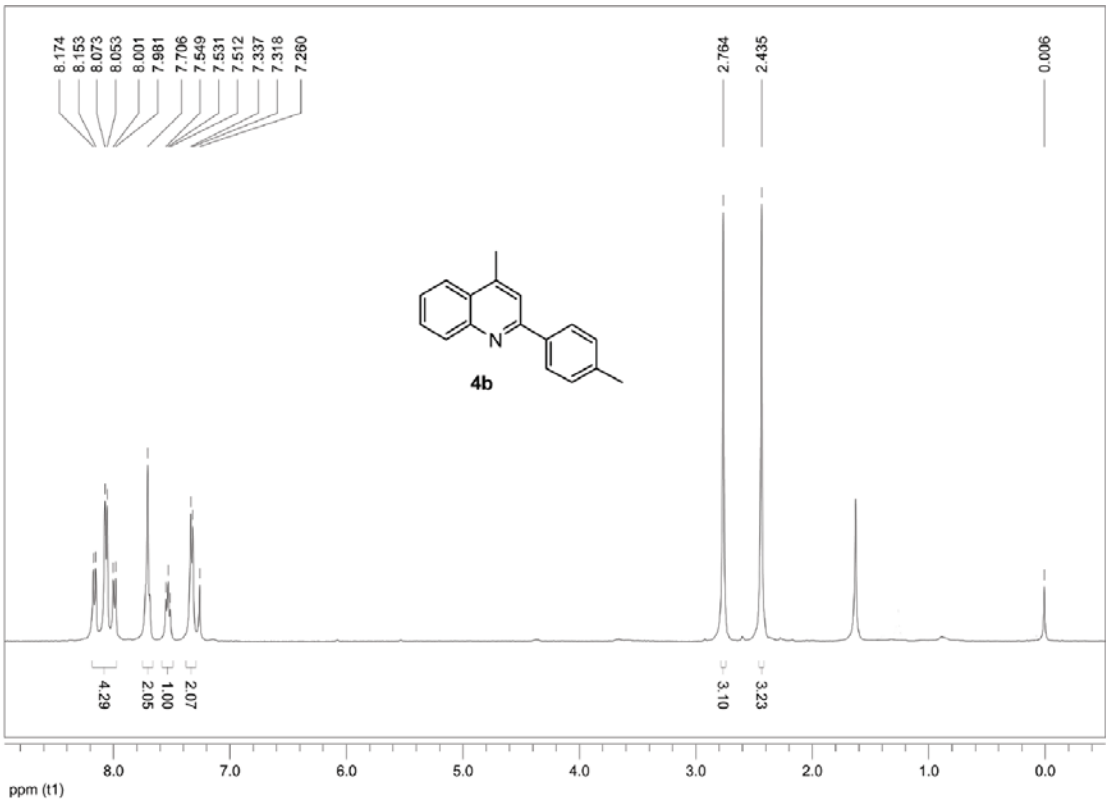
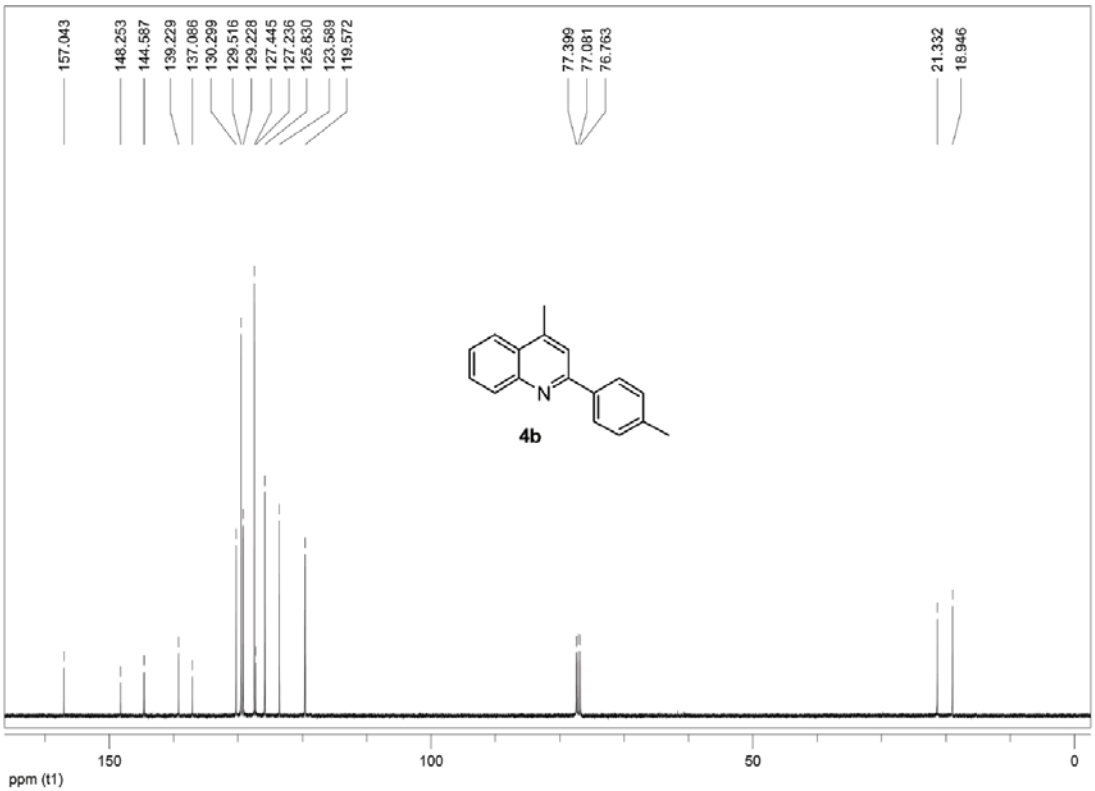
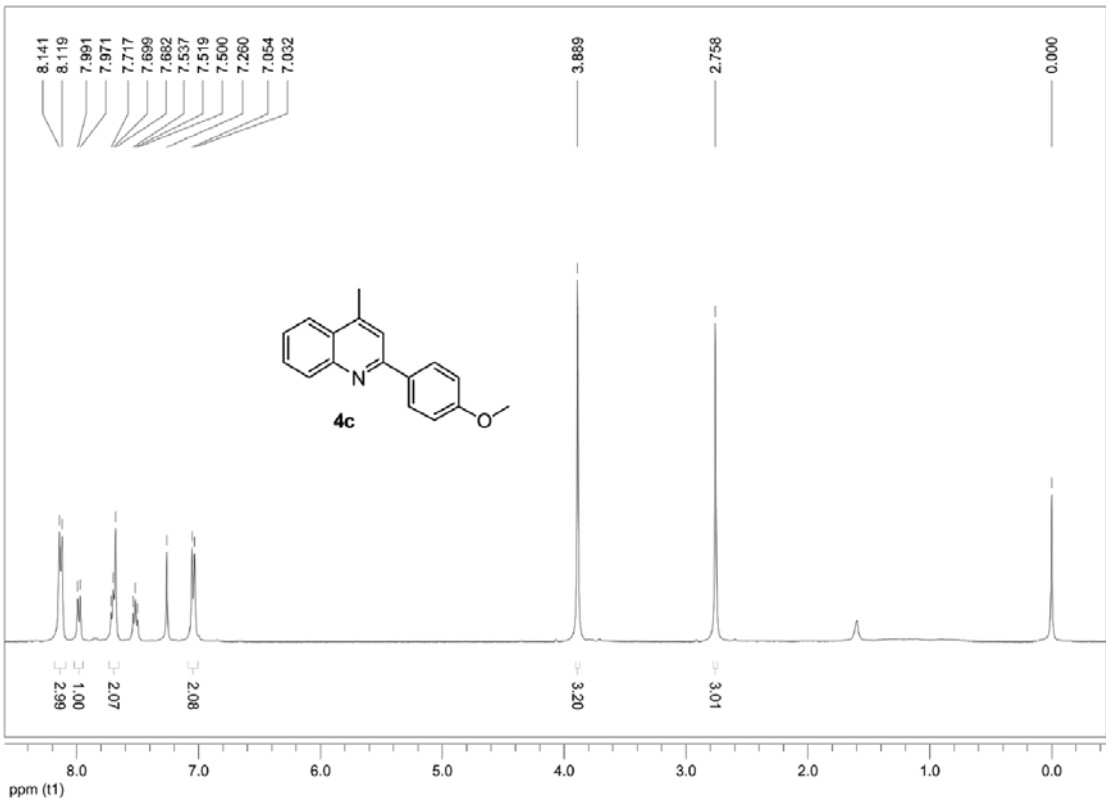
^{1}H NMR and ^{13}C NMR spectra for all products

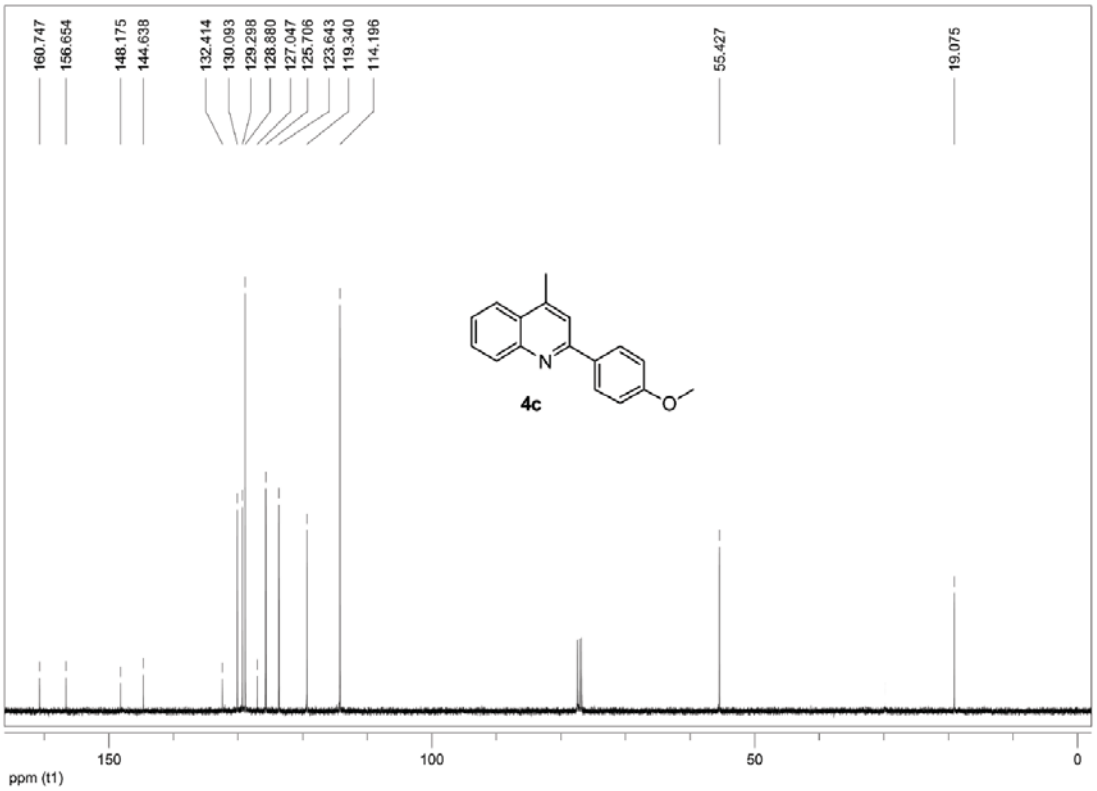


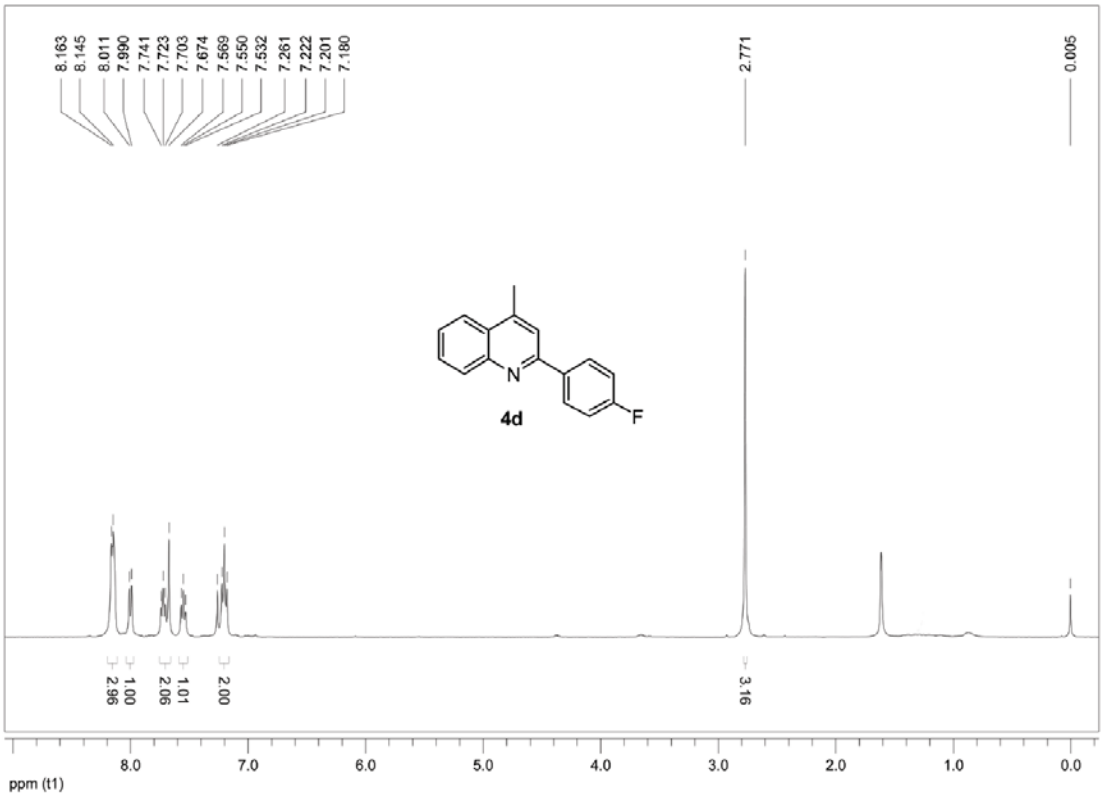


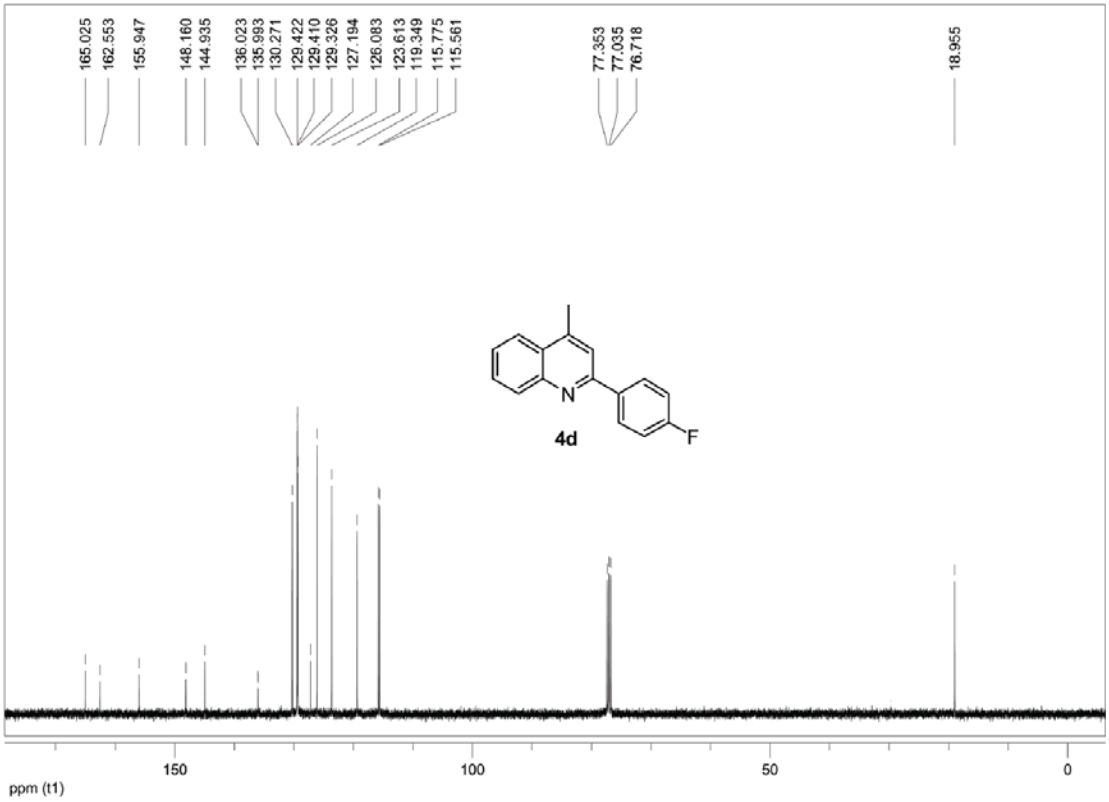


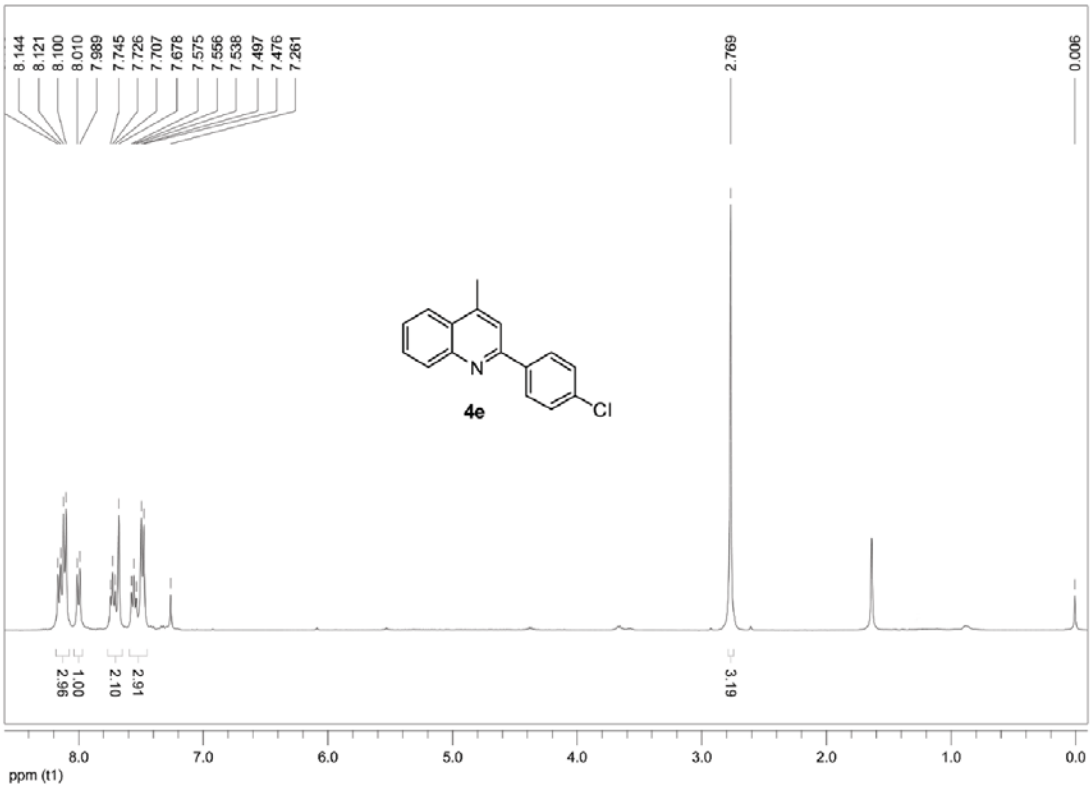


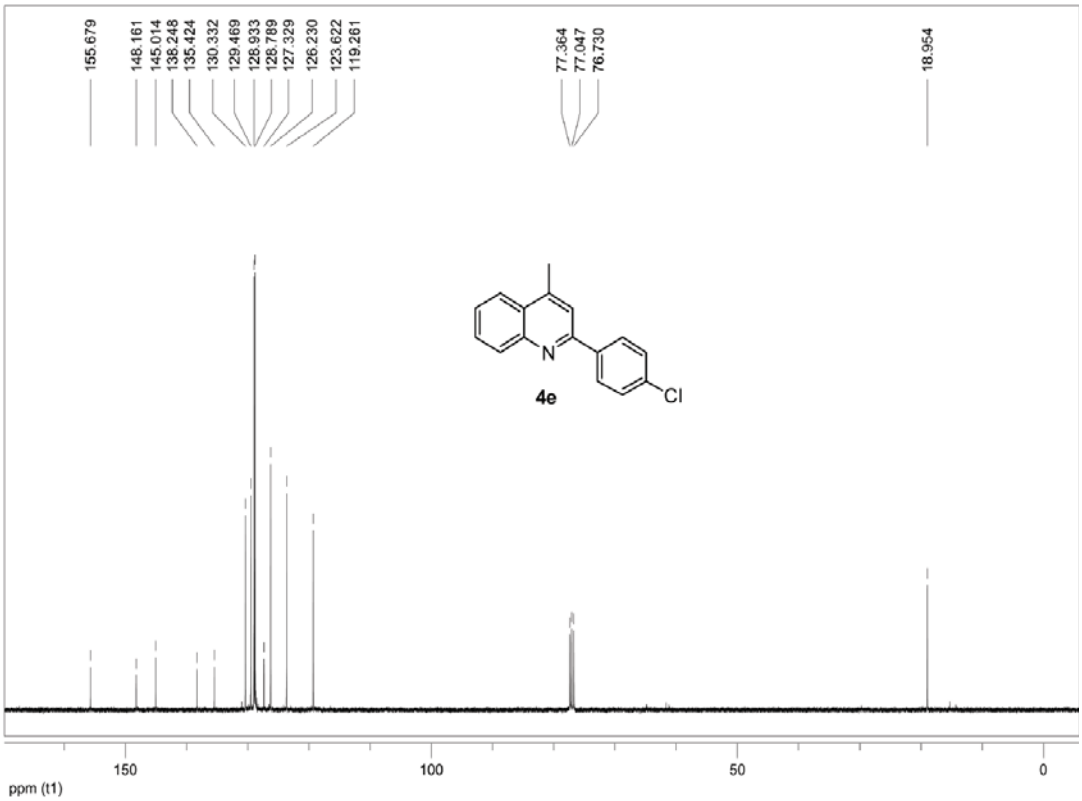


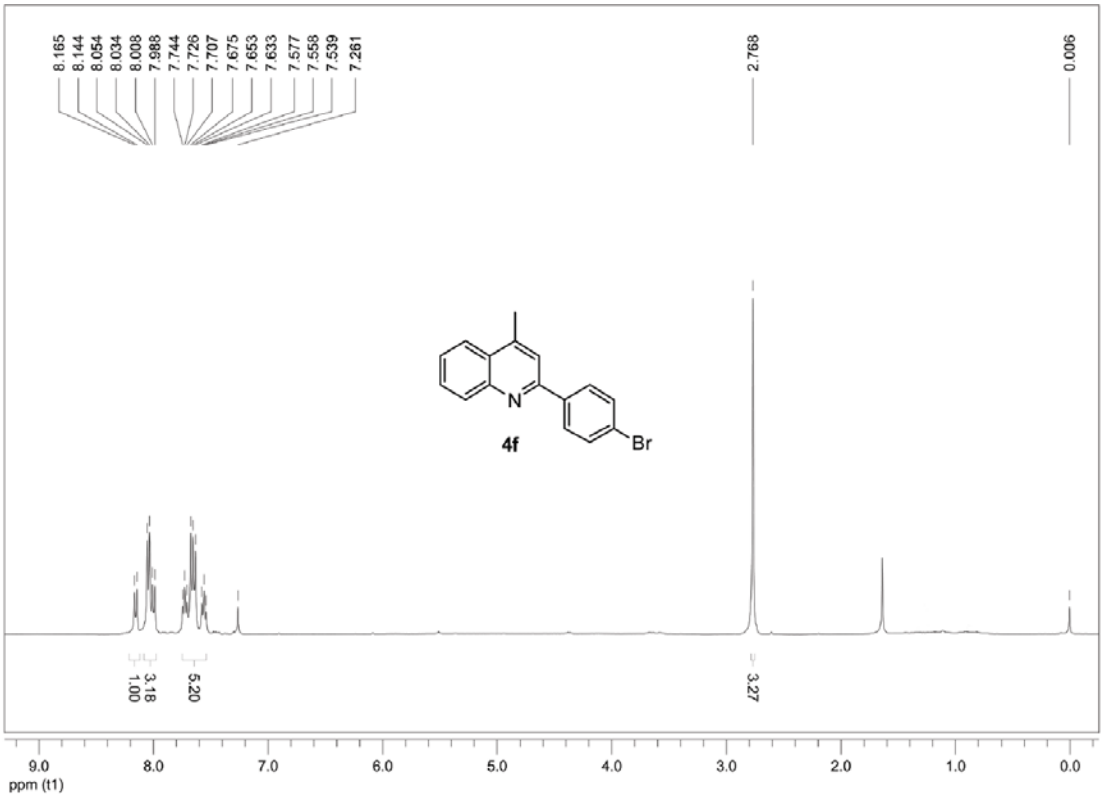


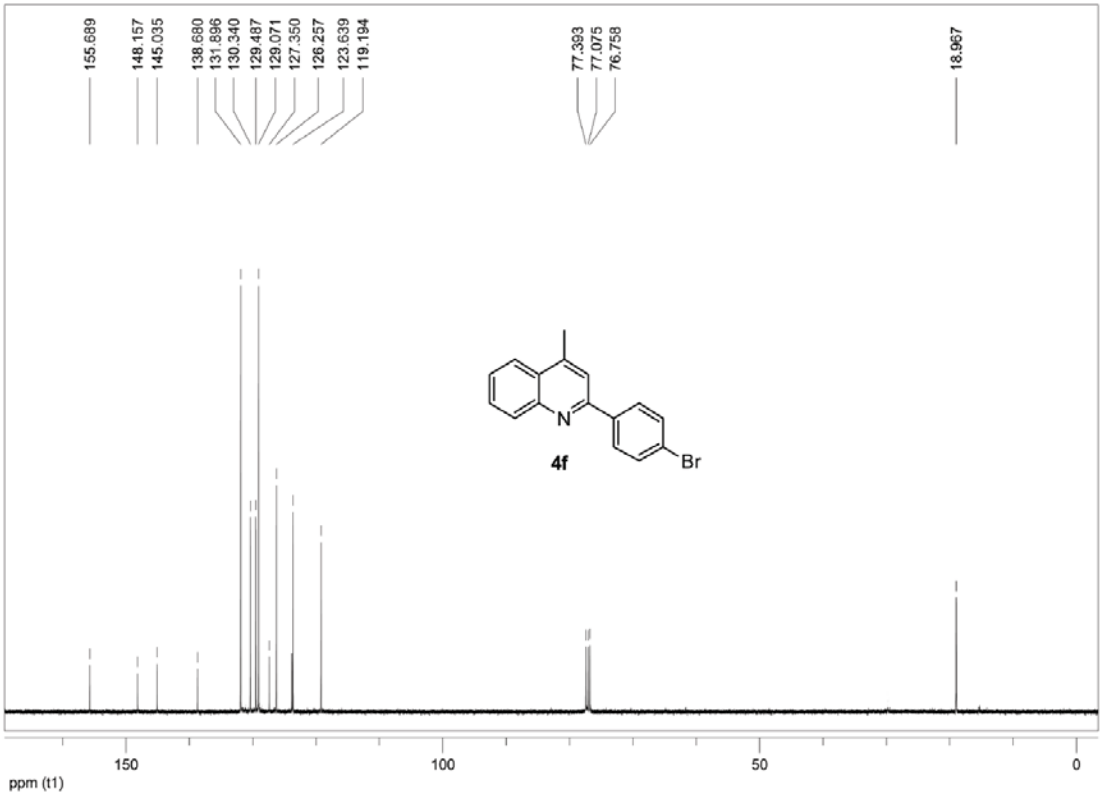


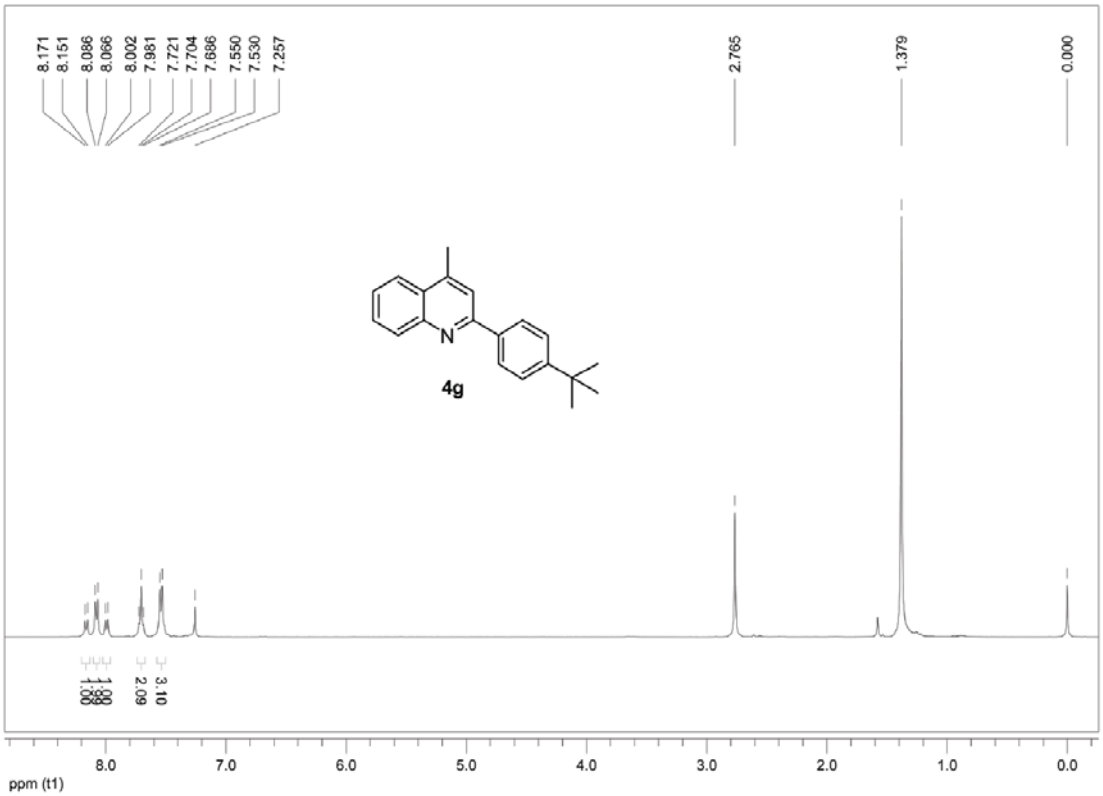


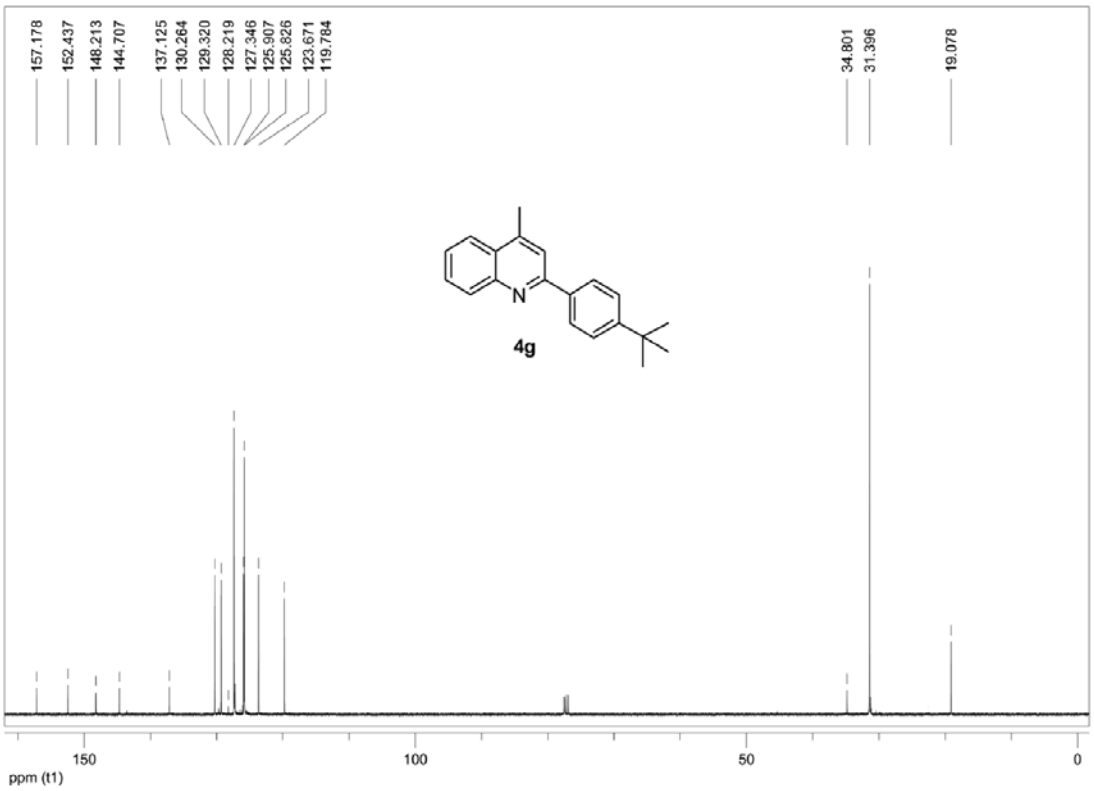


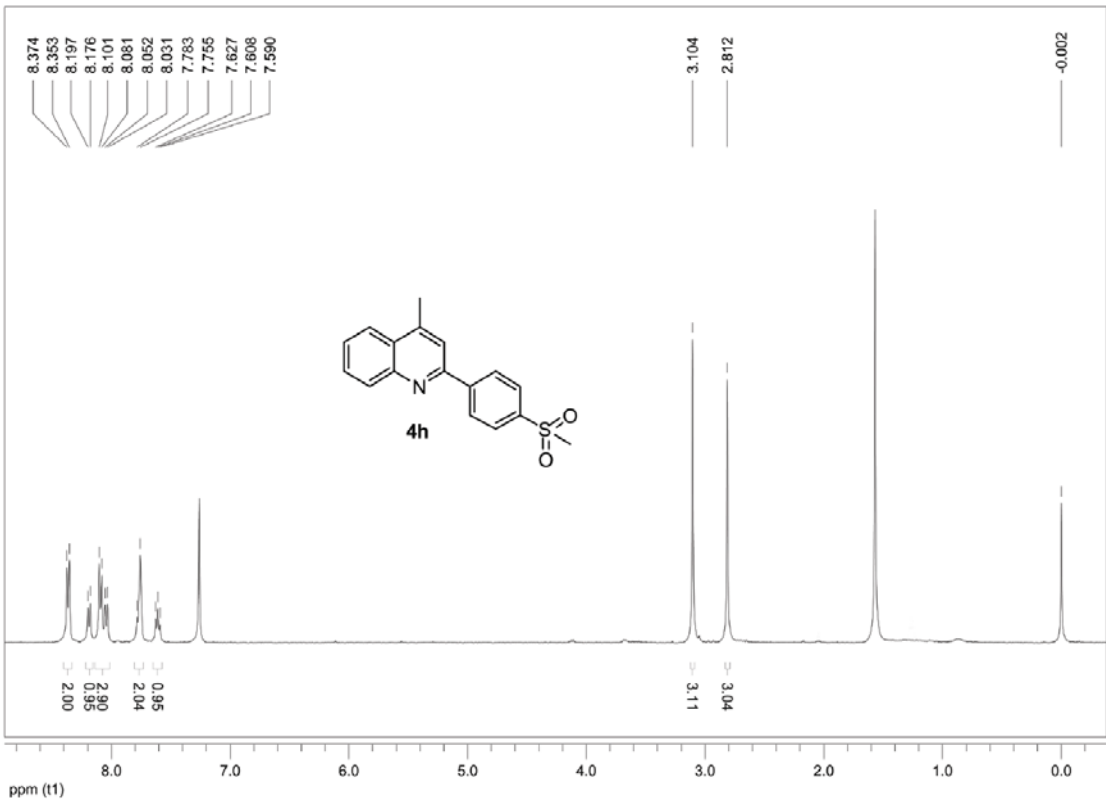


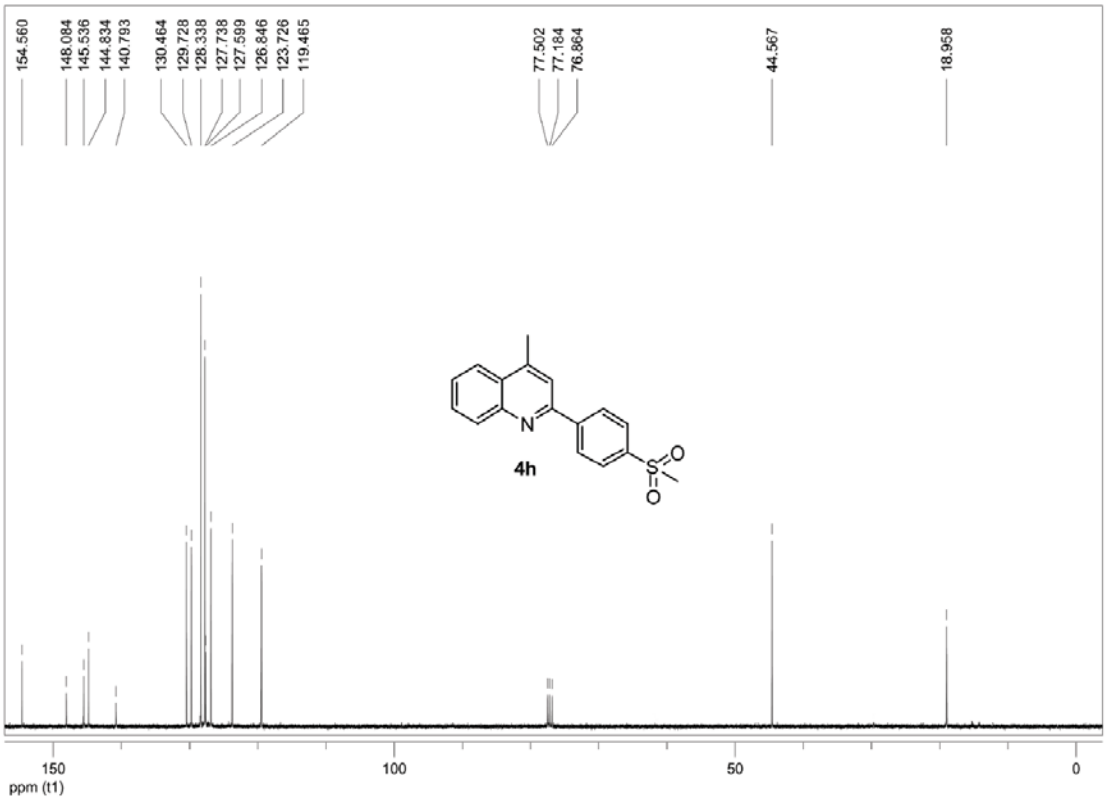


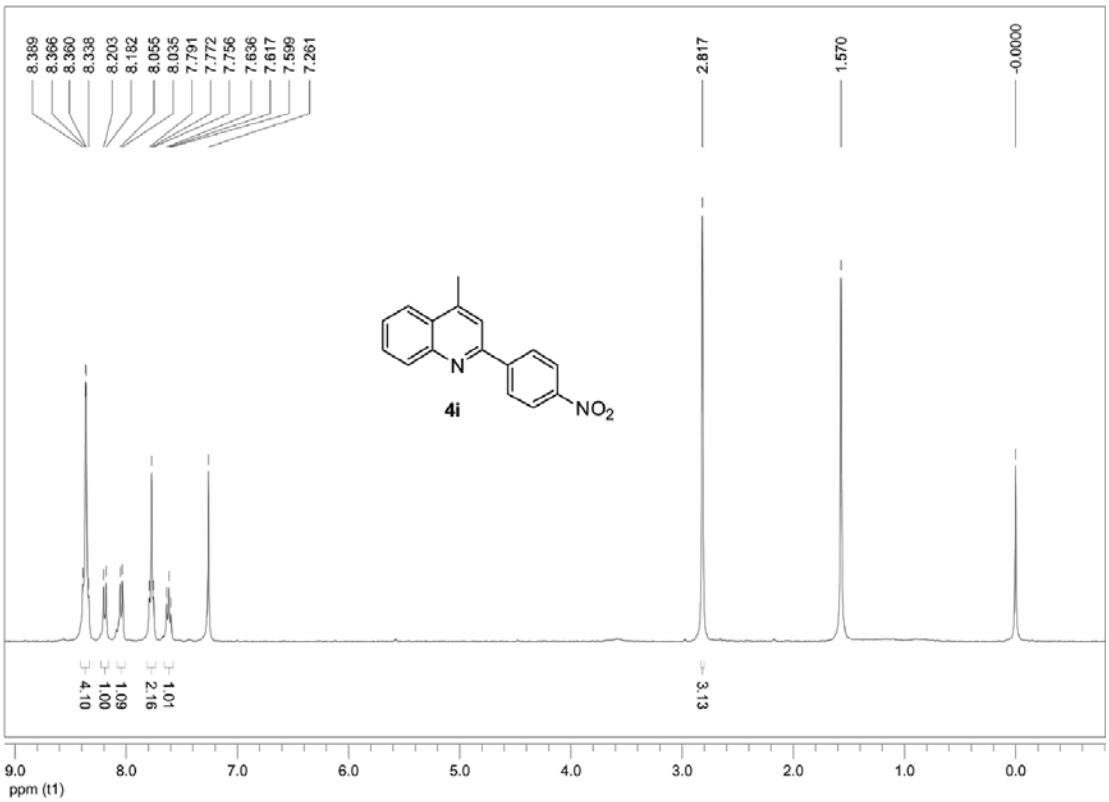


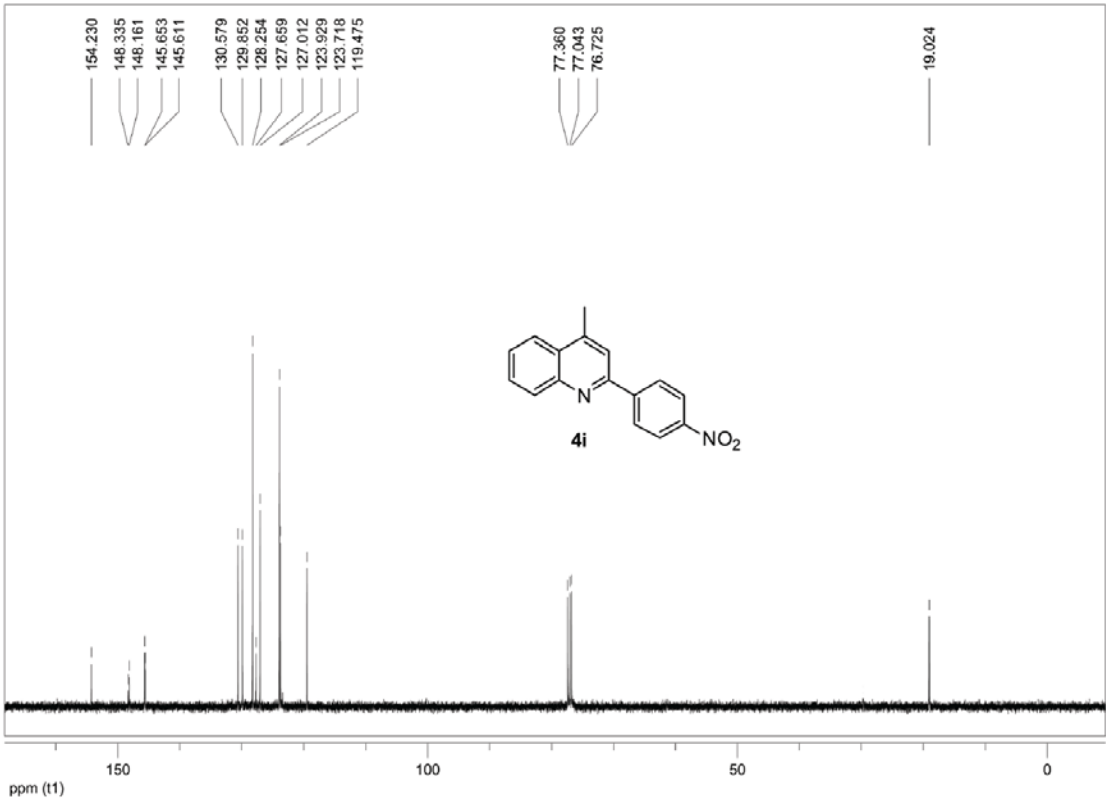


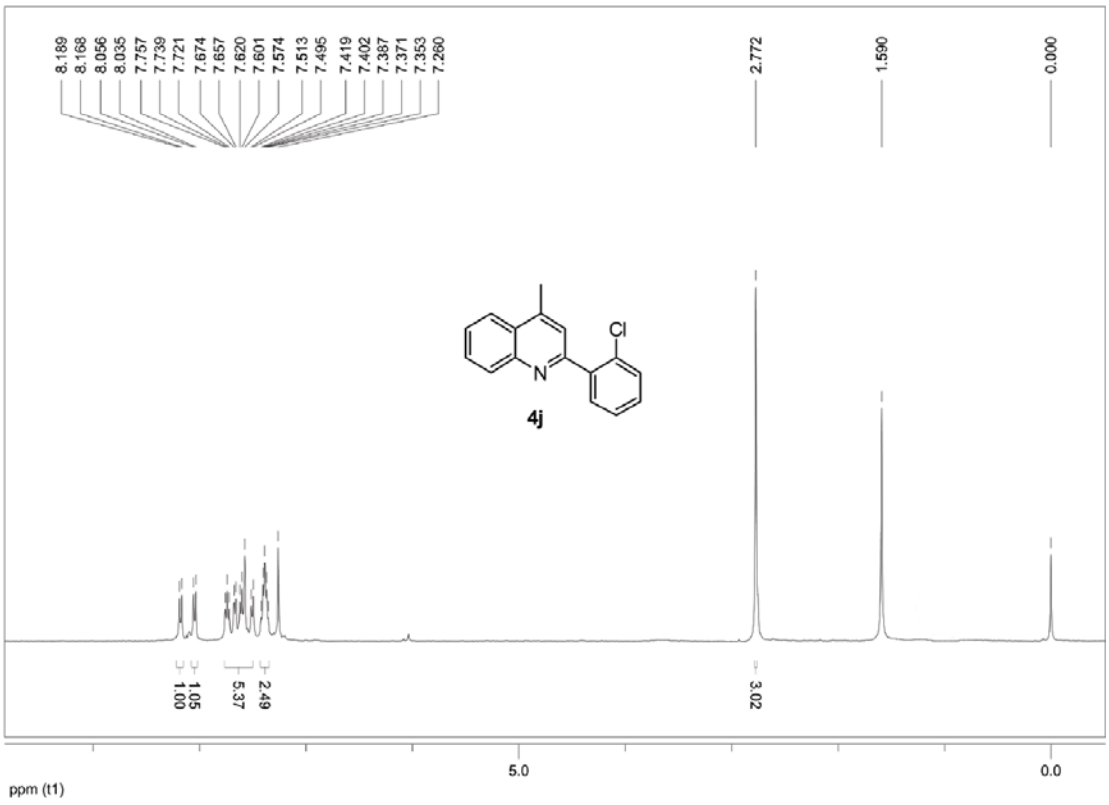


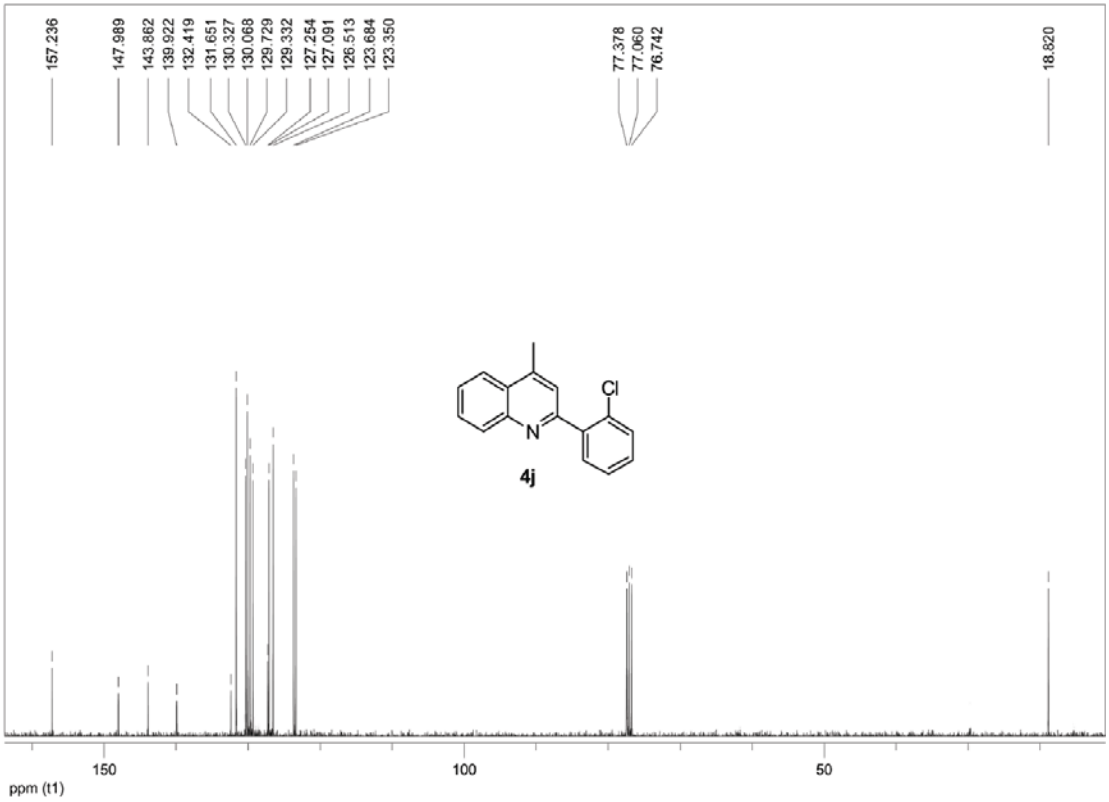


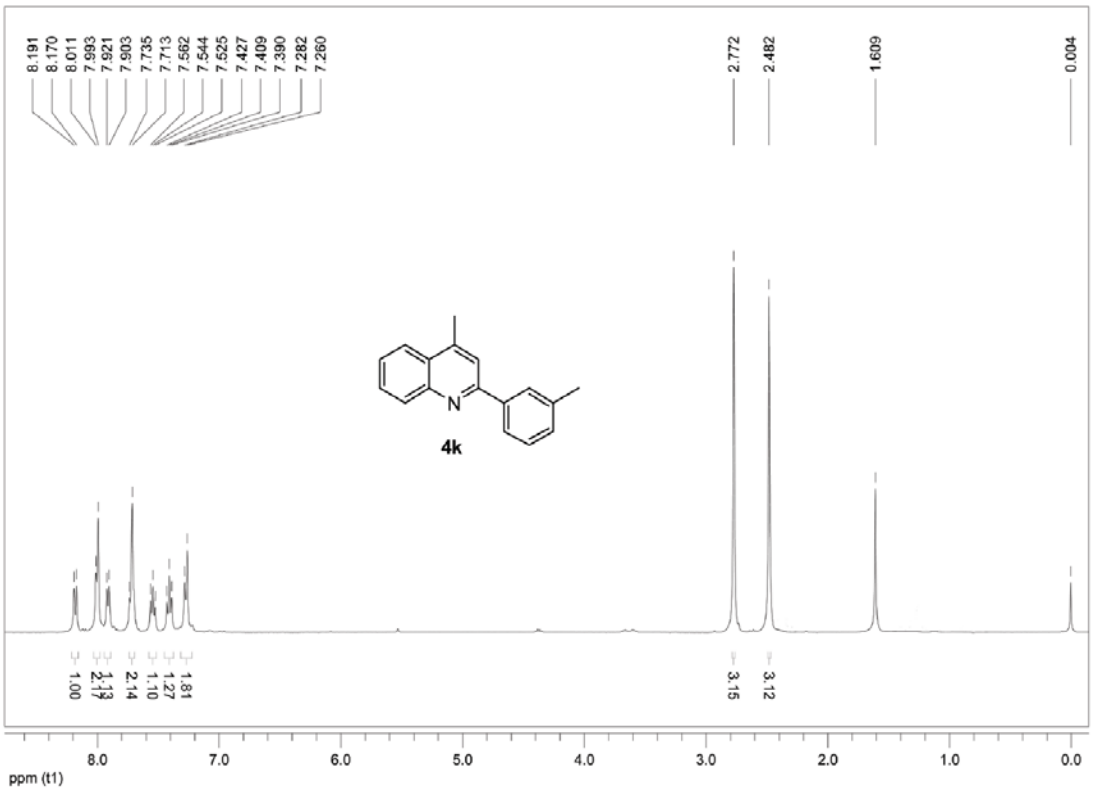


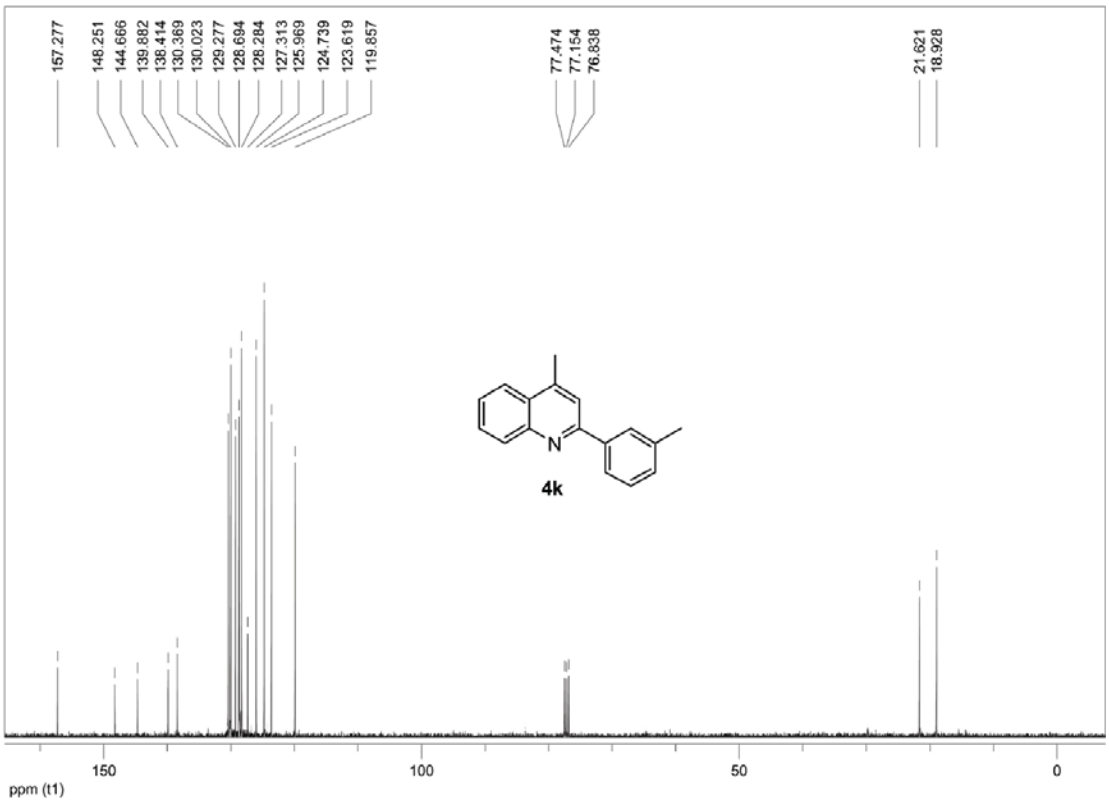


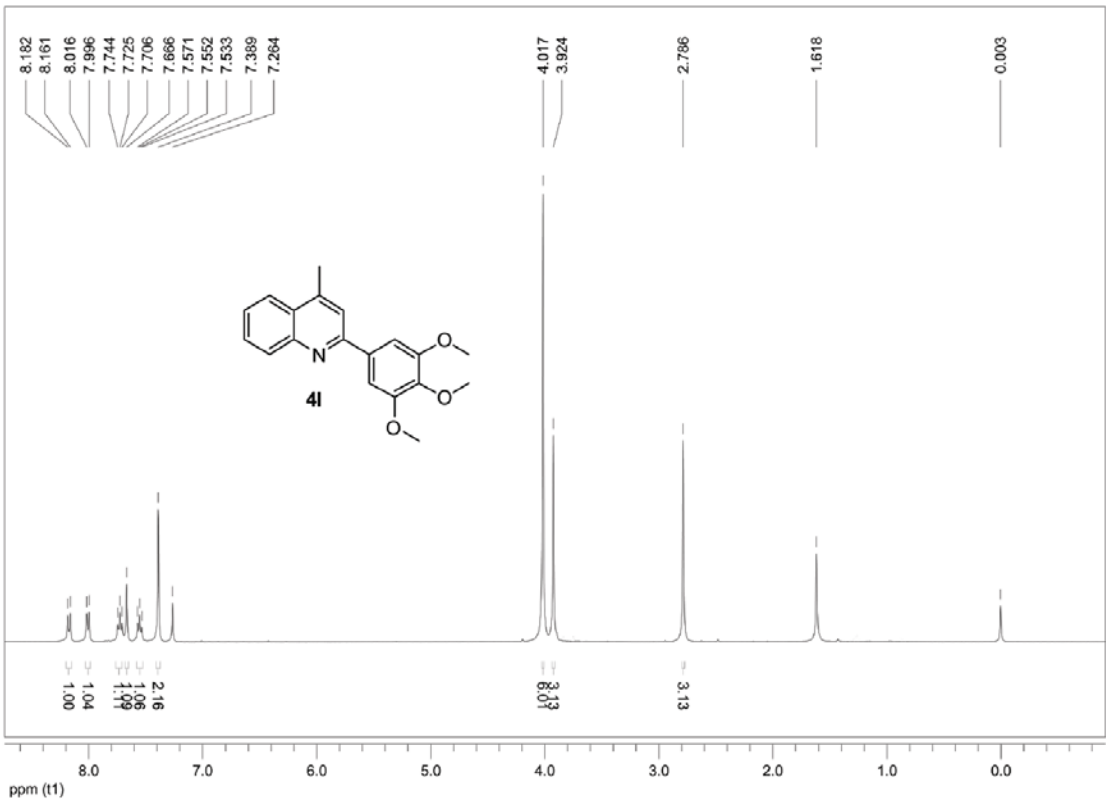








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3.924
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0.003
4l
1.00
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1.09
1.06
2.16
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7.0
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2.0
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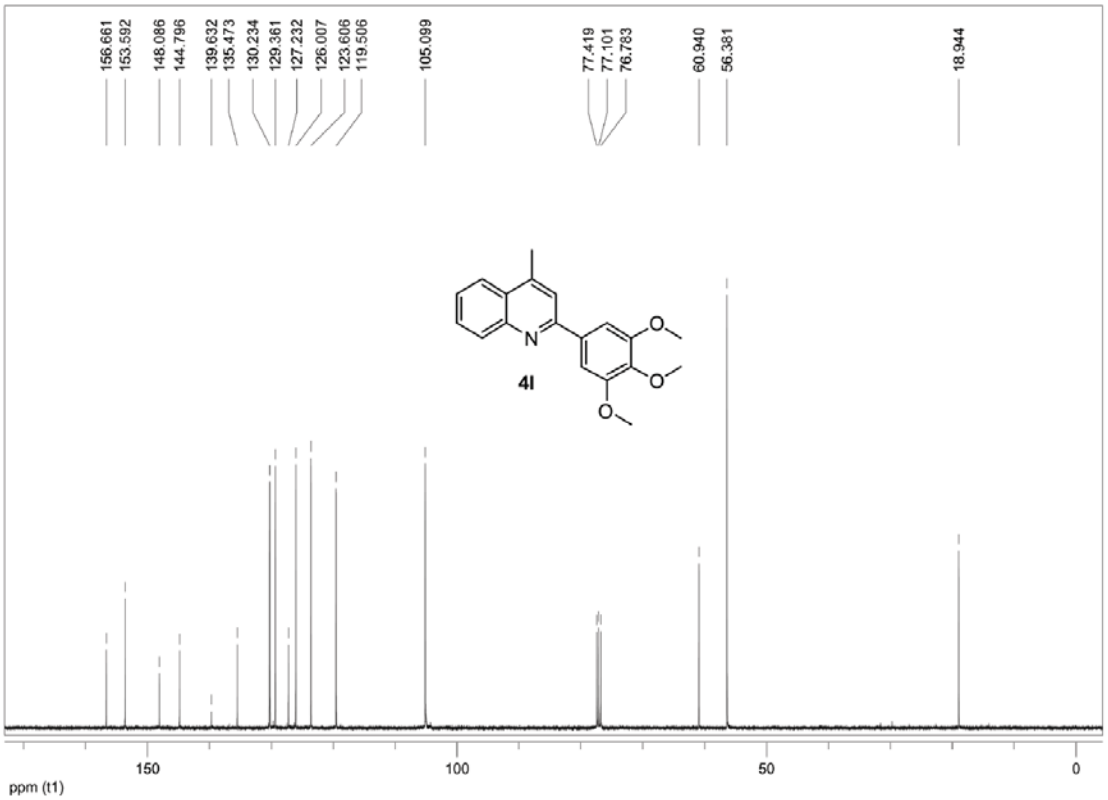
0.0
ppm (t1)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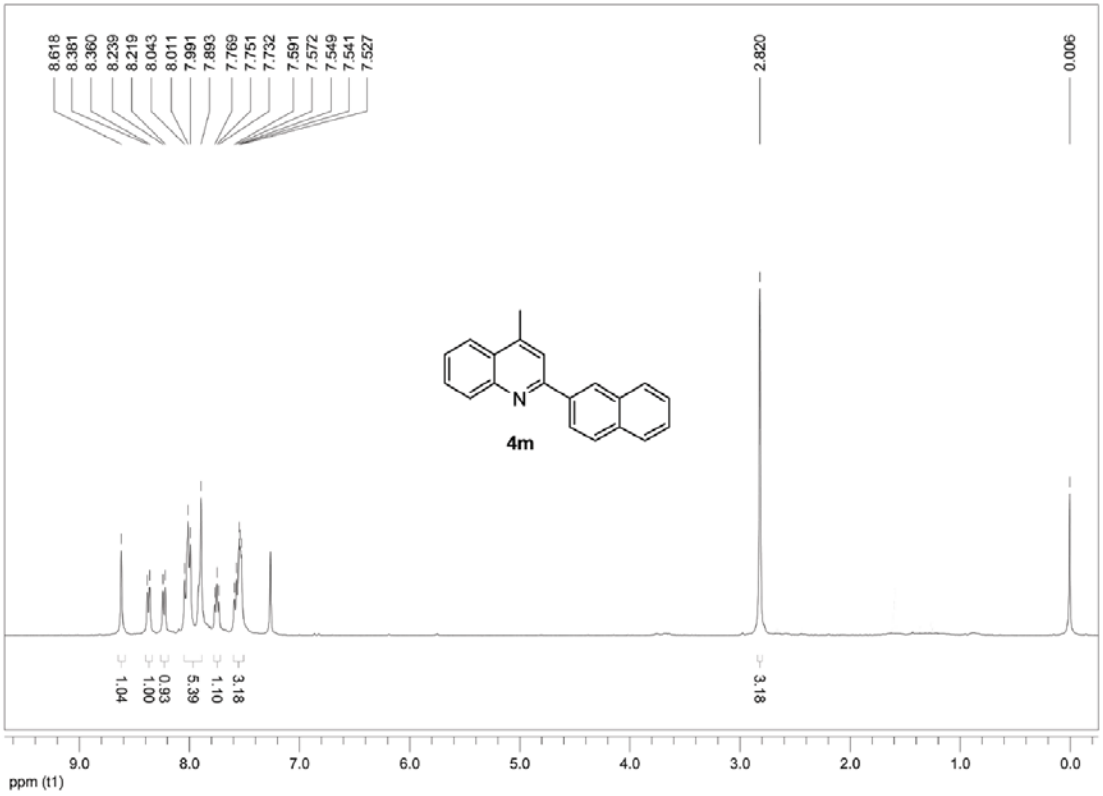
ppm (t1)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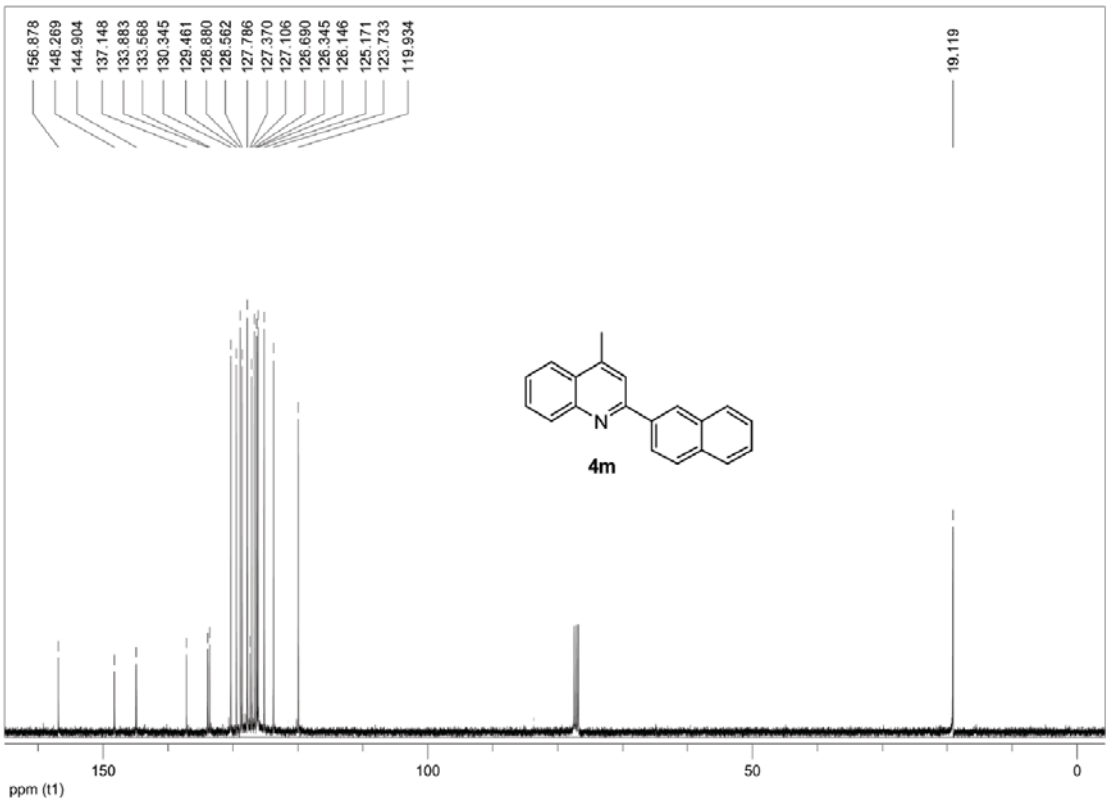
ppm (t1)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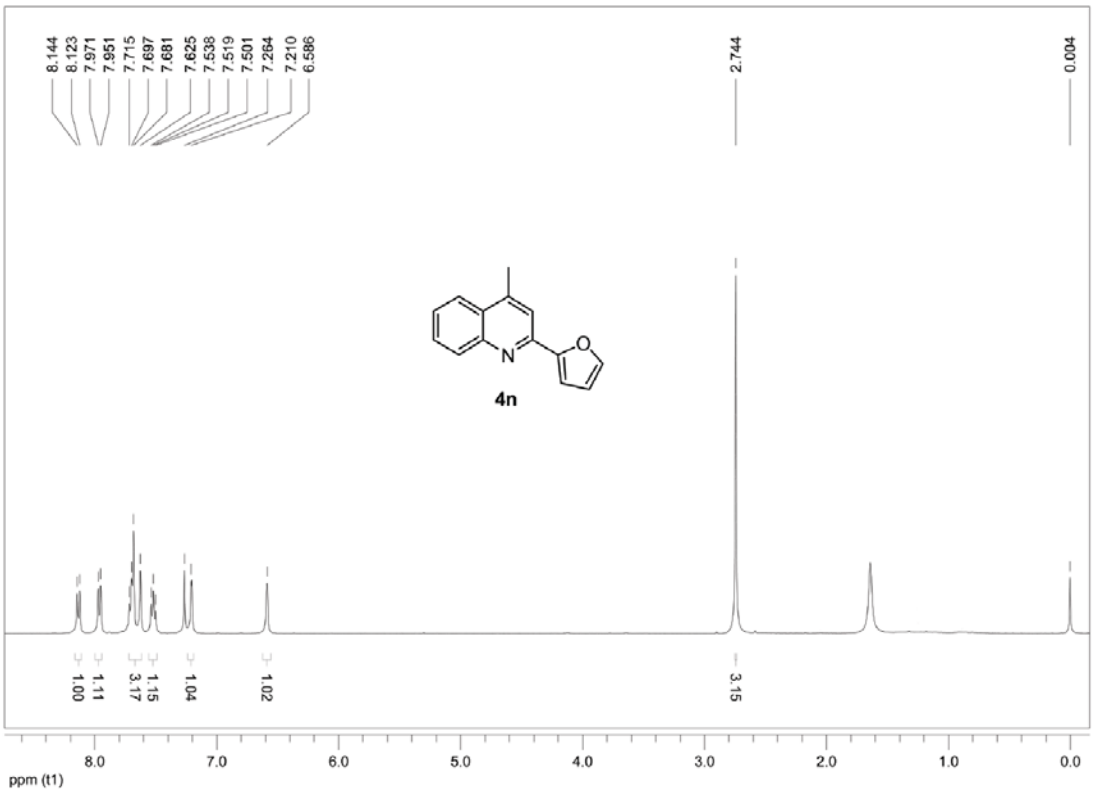
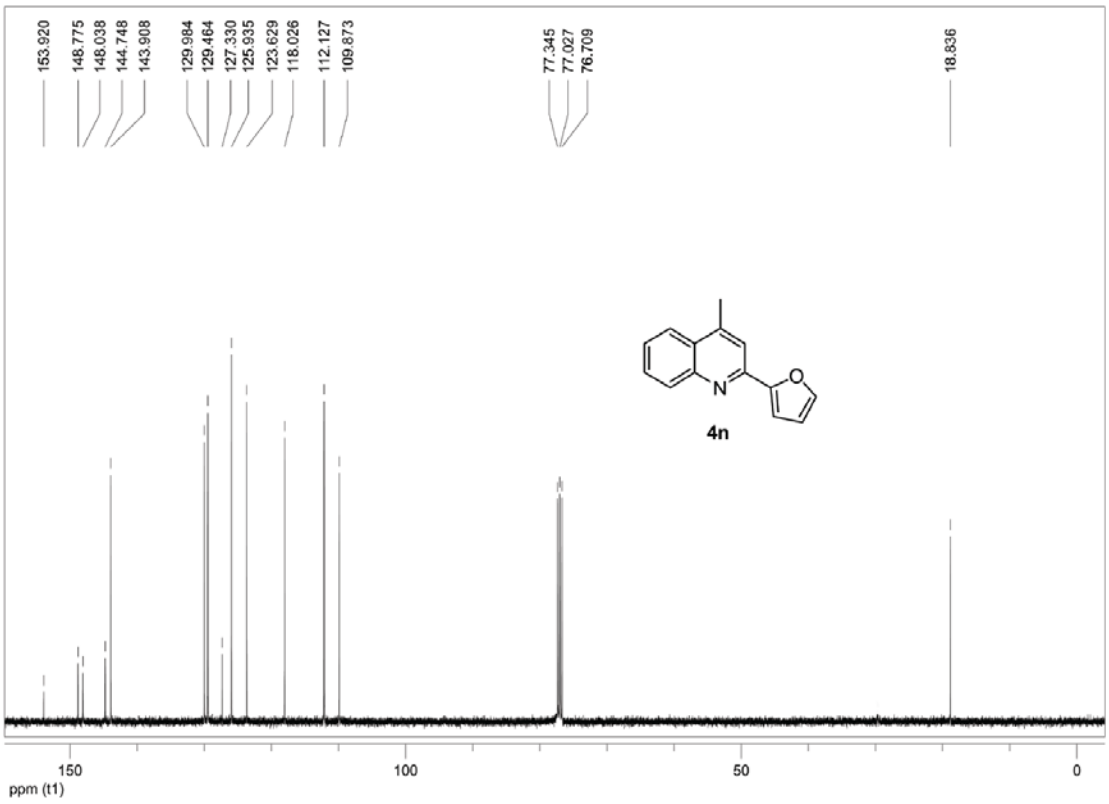
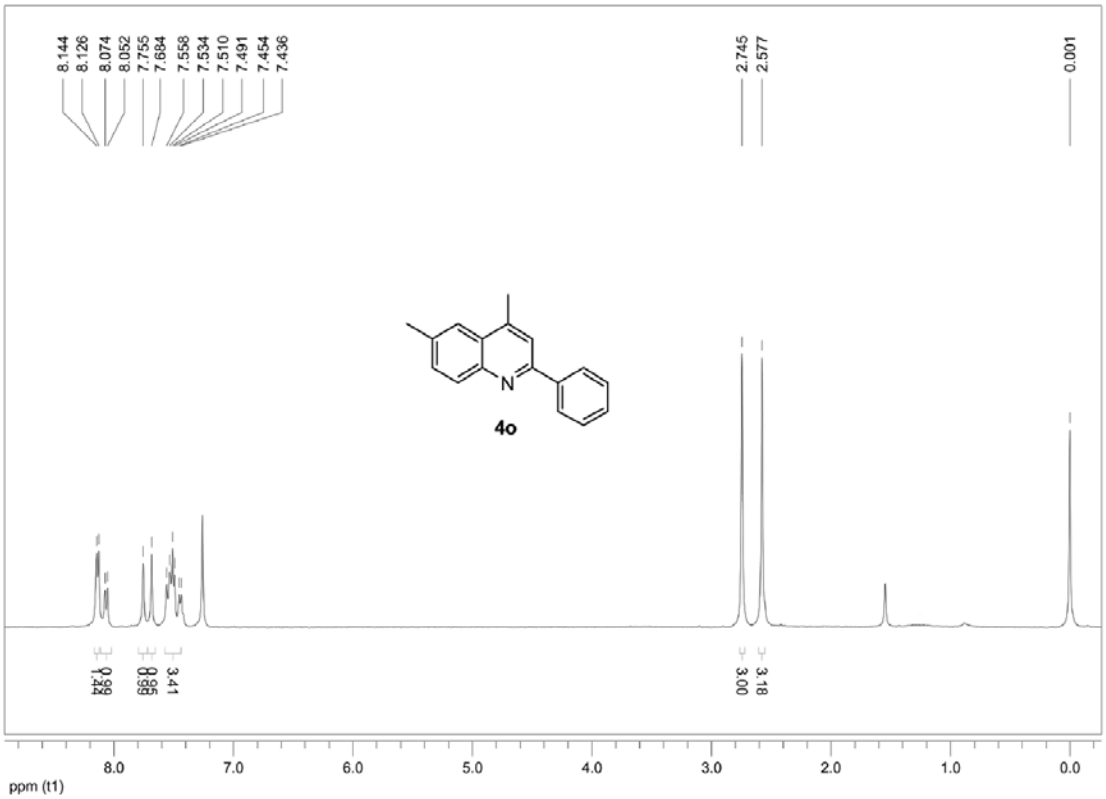
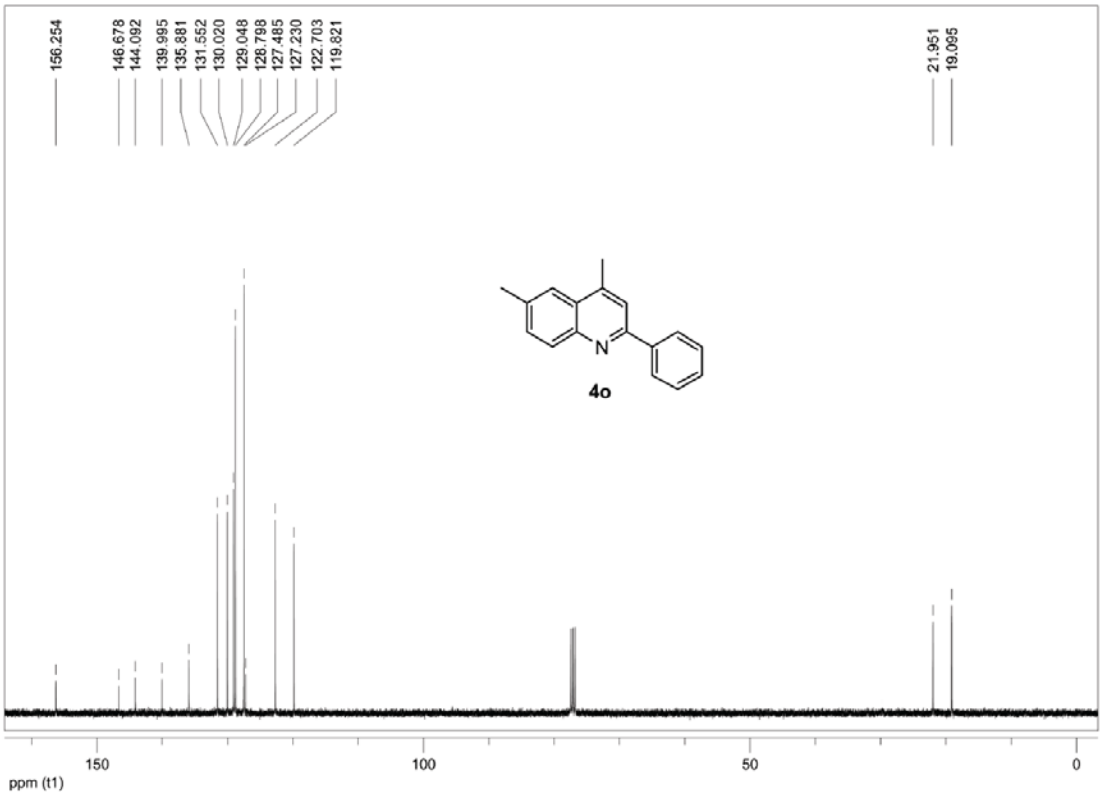
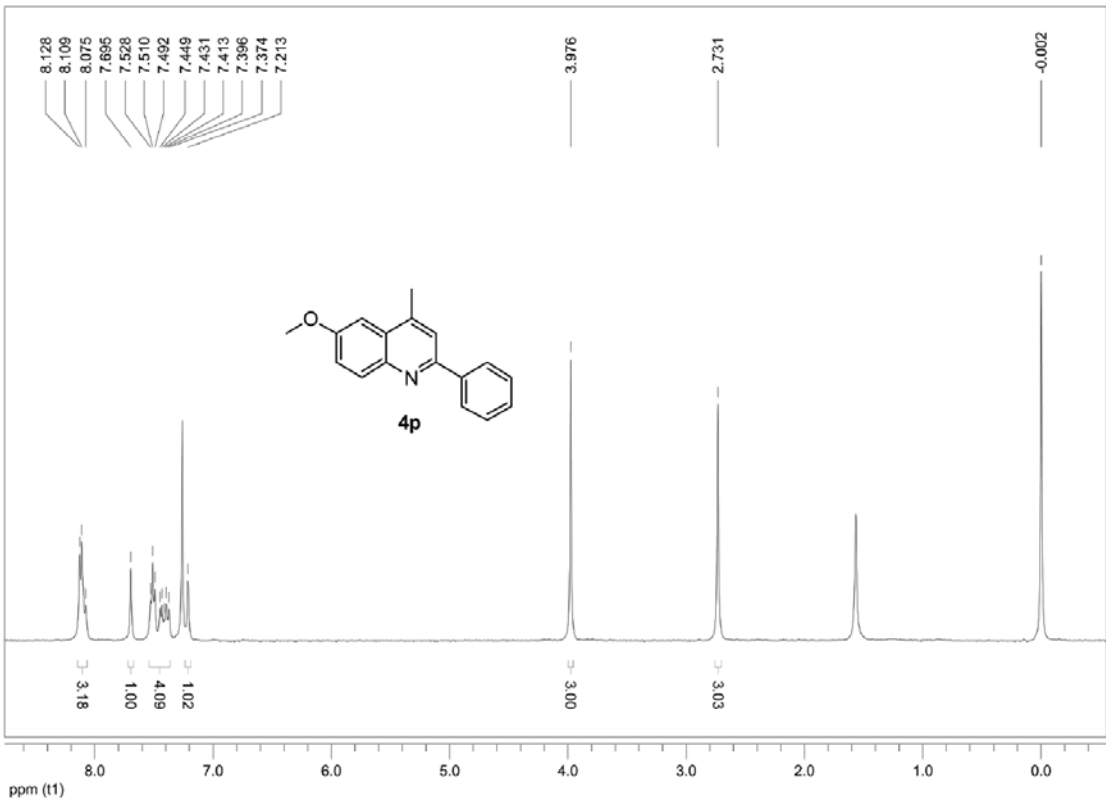
ppm (t1)

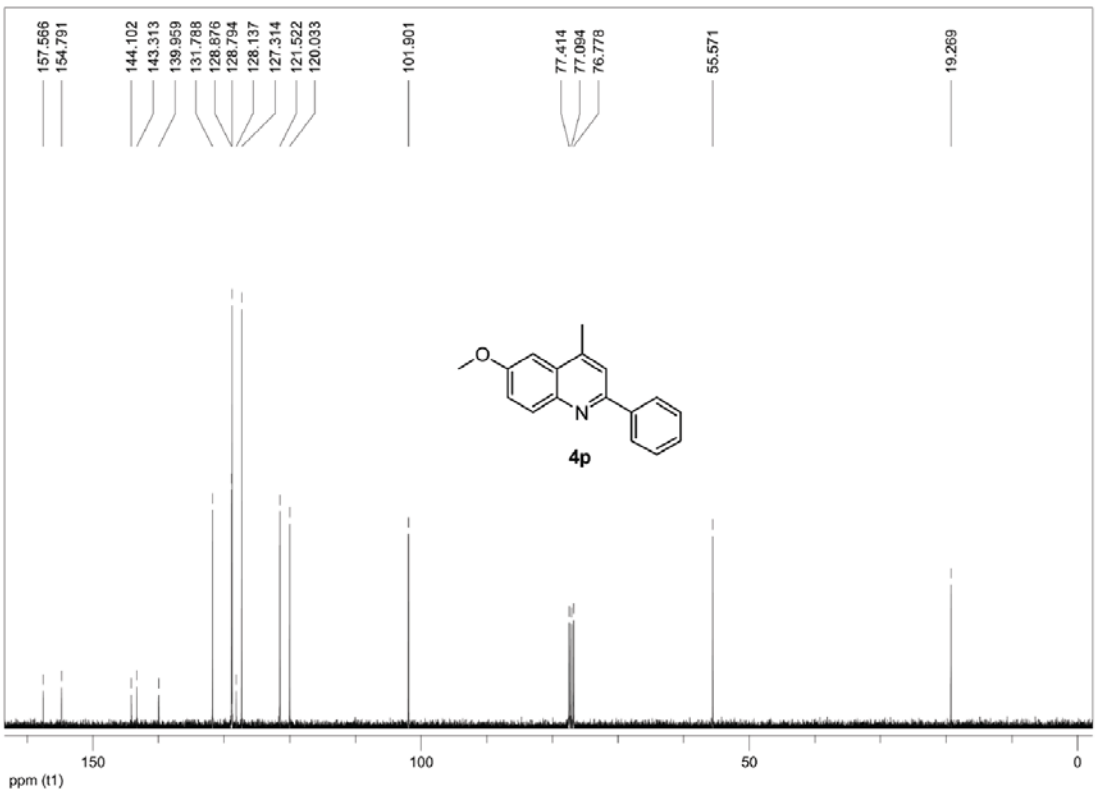









8.128
8.109
8.075
7.695
7.528
7.510
7.492
7.449
7.431
7.413
7.396
7.374
7.213
3.976
2.731
-0.002
4p
3.18
1.00
4.09
1.02
3.00
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


157.566
154.791
144.102
143.313
139.959
131.788
128.876
128.794
128.137
127.314
121.522
120.033
101.901
77.414
77.094
76.778
55.571
19.269
4p
150
100
50
0
ppm (t1)