Supporting Information For

Tertiary amines as a C1 synthon: metal-free synthesis of quinolines and 2-substituted quinolines *via* [3+2+1] aerobic cyclization and C–N bond cleavage

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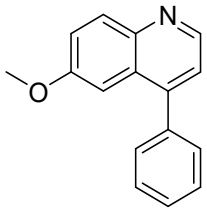
1. General

All other substrates and reagents were commercially available and used without further purification. The products were purified by flash column chromatography on silica gel (300-400 meshes). ^{1}H spectra were recorded in $CDCl_3$ on 500 MHz NMR spectrometers and resonances (δ) are given in parts per million relatives to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, etc.), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ on 125 MHz NMR spectrometers and resonances (δ) are given in ppm. ^{19}F spectra were recorded in $CDCl_3$ on 470 MHz NMR spectrometers and resonances (δ) are given in ppm. High-resolution mass spectral (HRMS) were obtained on a Waters XEVO G2-XS QTOF mass spectrometer with ESI resource. All GC analyses were performed on Shimadzu GC 2014C. Compound 4-methoxy-2-(1-phenylvinyl)aniline **5a** and N-phenylmethanimine **6** were prepared according to the reported literature.[1]

2. General procedure for the synthesis of 4 (4a as an example)

An oven dried Schlenk tube of 10 mL equipped with a magnetic stir bar was charged with phenylacetylene **1a** (0.5 mmol), 4-methoxyaniline **2a** (1.0 mmol, 2.0 equiv.), TMEDA **3a** (1.0 mmol, 2.0 equiv.) and I_2 (1.0 mmol), $TsOH{\cdot}H_2O$ (1.0 equiv.) in TFE (1.0 mL), The mixture was stirred at 130 ^{o}C for 12 hours under an atmosphere of O_2. After the reaction finished, the reaction mixtures were quenched with saturation $Na_2S_2O_3$ solution (20 mL), extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc = 5:1) to afford the product **4a** as a yellow solid (82.2 mg, 70% yield).

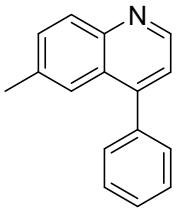
3. Characterization data for compounds 4



6-Methoxy-4-phenylquinoline (4a) [2]**:**

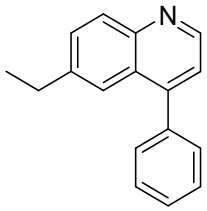
Obtained as a yellow solid (82.2 mg, 70% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ

(ppm) 8.79 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H), 7.55-7.45 (m, 5H), 7.38 (dd, J = 9.2, 2.8 Hz, 1H), 7.27 (d, J = 4.4 Hz, 1H), 7.19 (d, J = 2.7 Hz, 1H), 3.78 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.8, 147.5, 147.1, 144.8, 138.3, 131.2, 129.3, 128.6, 128.3, 127.7, 121.7, 121.6, 103.7, 55.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO$: 236.1075, found: 236.1091.



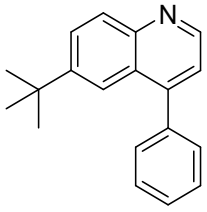
6-Methyl-4-phenylquinoline (4b) [2]**:**

Obtained as a colorless liquid (85.5 mg, 78% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.86 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.65 (s, 1H), 7.59-7.43 (m, 6H), 7.27 (d, J = 4.4 Hz, 1H), 2.46 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 149.0, 147.7, 147.3, 138.2, 136.5, 131.5, 129.54, 129.47, 128.5, 128.2, 126.7, 124.5, 121.4, 21.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}N$: 220.1126, found: 220.1146.



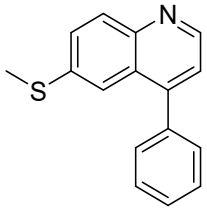
6-Ethyl-4-phenylquinoline (4c) [3]**:**

Obtained as a brown liquid (62.9 mg, 54% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.86 (d, J = 4.4 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.68 (s, 1H), 7.58 (dd, J = 8.7, 2.0 Hz, 1H), 7.55-7.44 (m, 5H), 7.26 (d, J = 4.4 Hz, 1H), 2.74 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 149.0, 147.8, 147.4, 142.7, 138.2, 130.3, 129.6, 129.4, 128.4, 128.2, 126.6, 123.3, 121.3, 29.0, 15.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}N$: 234.1282, found: 234.1279.



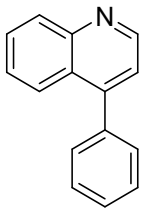
6-(*tert*-Butyl)-4-phenylquinoline (4d) [2]**:**

Obtained as a colorless liquid (78.3 mg, 60% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.88 (d, J = 4.4 Hz, 1H), 8.12 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 2.2 Hz, 1H), 7.82 (dd, J = 8.9, 2.2 Hz, 1H), 7.63-7.41 (m, 5H), 7.29 (d, J = 4.4 Hz, 1H), 1.33 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 149.3, 149.25, 148.3, 147.2, 138.2, 129.5, 129.3, 128.5, 128.3, 128.1, 126.2, 121.3, 120.6, 35.0, 31.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}N$: 262.1595, found: 262.1593.



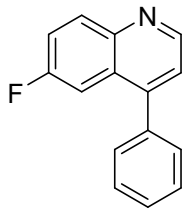
6-(Methylthio)-4-phenylquinoline (4e) [4]**:**

Obtained as a white solid (54.0 mg, 43% yield);^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.85 (d, J = 4.4 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 2.2 Hz, 1H), 7.61 (dd, J = 8.9, 2.1 Hz, 1H), 7.56-7.45 (m, 6H), 7.30 (d, J = 4.4 Hz, 1H), 2.45 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 149.1, 147.1, 146.9, 137.8, 137.5, 130.1, 129.4, 128.7, 128.6, 128.5, 127.1, 121.9, 121.0, 15.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NS$: 252.0847, found: 252.0850.



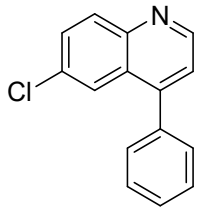
4-Phenylquinoline (4f) [4]**:**

Obtained as a yellow liquid (49.2 mg, 48% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.93 (d, J = 4.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.79-7.63 (m, 1H), 7.59-7.40 (m, 6H), 7.31 (d, J = 4.4 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 149.9, 148.6, 148.4, 137.9, 129.8, 129.4, 129.2, 128.5, 128.3, 126.7, 126.5, 125.8, 121.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}N$: 206.0969, found: 206.0969.



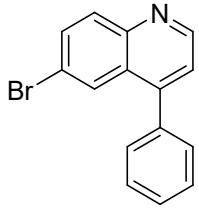
6-Fluoro-4-phenylquinoline (4g) [4]**:**

Obtained as a white solid (100.4 mg, 90% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.88 (d, J = 4.4 Hz, 1H), 8.16 (dd, J = 9.2, 5.6 Hz, 1H), 7.61-7.39 (m, 7H), 7.30 (d, J = 4.4 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 160.5 (d, J = 247.7 Hz), 149.1 (d, J = 2.5 Hz), 147.8 (d, J = 5.5 Hz), 145.7, 137.4, 132.2 (d, J = 9.2 Hz), 129.2, 128.6, 128.5, 127.4 (d, J = 9.6 Hz), 121.7, 119.4 (d, J = 25.8 Hz), 109.0 (d, J = 23.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -112.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}FN$: 224.0875, found: 224.0879.



6-Chloro-4-phenylquinoline (4h) [4]**:**

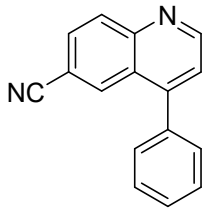
Obtained as a white solid (102.8 mg, 86% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.92 (d, J = 4.4 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 9.0, 2.3 Hz, 1H), 7.62-7.41 (m, 5H), 7.35 (d, J = 4.4 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 150.1, 147.8, 147.1, 137.3, 132.6, 131.5, 130.3, 129.4, 128.8, 128.7, 127.5, 124.7, 122.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}ClN$: 240.0580, found: 240.0586.



6-Bromo-4-phenylquinoline (4i) [4]**:**

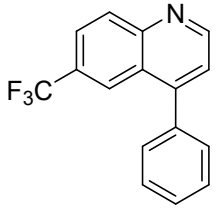
Obtained as a white solid (63.7 mg, 45% yield);^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.95 (d, J = 4.4 Hz, 1H), 8.06-8.03 (m, 2H), 7.80 (dd, J = 9.0, 2.2 Hz, 1H), 7.61-7.44 (m,

5H), 7.36 (d, J = 4.4 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 150.30, 147.7, 147.3, 137.3, 132.8, 131.6, 129.4, 128.8, 128.7, 127.98, 127.96, 122.0, 120.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}BrN$: 284.0075, found: 284.0080.



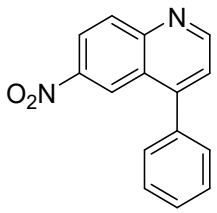
4-Phenylquinoline-6-carbonitrile (4j) [5]**:**

Obtained as a yellow solid (43.7 mg, 38% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.07 (d, J = 4.5 Hz, 1H), 8.33 (d, J = 1.8 Hz, 1H), 8.26 (d, J = 8.7 Hz, 1H), 7.87 (dd, J = 8.8, 1.9 Hz, 1H), 7.69-7.53 (m, 3H), 7.53-7.43 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 152.7, 149.6, 149.1, 136.4, 132.6, 131.4, 129.9, 129.4, 129.2, 129.0, 126.3, 122.7, 118.7, 110.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{11}N_2$: 231.0922, found: 231.0931.



4-Phenyl-6-(trifluoromethyl) quinoline (4k) [4]**:**

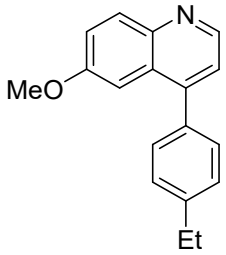
Obtained as a yellow liquid (46.4 mg, 34% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.05 (d, J = 4.4 Hz, 1H), 8.29 (d, J = 8.8 Hz, 1H), 8.25 (s, 1H), 7.90 (dd, J = 8.8, 2.1 Hz, 1H), 7.61-7.48 (m, 5H), 7.44 (d, J = 4.4 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 152.0, 149.7, 149.5, 137.0, 131.2, 129.4, 129.0, 128.9, 128.5(q, J = 32.3 Hz), 125.9, 125.0 (q, J = 2.9 Hz), 124.02(q, J = 270.8 Hz), 123.95 (q, J = 4.6 Hz), 122.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -62.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{11}F_3N$: 274.0843, found: 274.0845.



6-Nitro-4-phenylquinoline (4l) [6]**:**

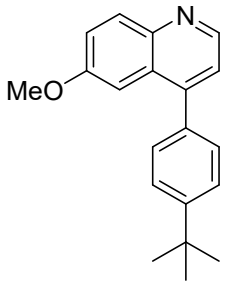
Obtained as a yellow solid (32.5 mg, 26% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.11 (d, J = 4.4 Hz, 1H), 8.89 (d, J = 2.5 Hz, 1H), 8.49 (dd, J = 9.2, 2.5 Hz, 1H),

8.30 (d, J = 9.3 Hz, 1H), 7.65-7.57 (m, 3H), 7.54-7.50 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 153.2, 150.8, 150.7, 145.8, 136.4, 131.8, 129.5, 129.4, 129.1, 125.9, 123.1, 122.9, 122.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}N_2O_2$: 251.0820, found: 251.0821.



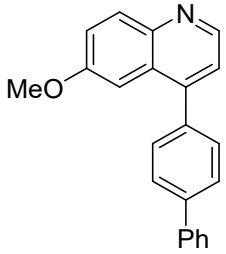
4-(4-Ethylphenyl)-6-methoxyquinoline (4m):

Obtained as a yellow solid (84.2 mg, 64% yield), m.p.: 51-52 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.76 (d, J = 4.4 Hz, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.45-7.39 (m, 2H), 7.38-7.31 (m, 3H), 7.26-7.21 (m, 2H), 3.76 (s, 3H), 2.74 (q, J = 7.6 Hz, 2H), 1.31 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.6, 147.4, 147.0, 144.7, 144.3, 135.5, 131.1, 129.1, 128.0, 127.6, 121.50, 121.48, 103.7, 55.2, 28.5, 15.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}NO$: 264.1388, found: 264.1384.



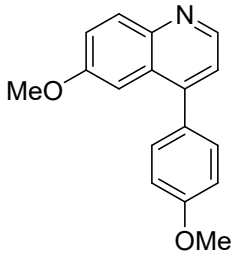
4-(4-(*tert*-Butyl)phenyl)-6-methoxyquinoline (4n) [7]**:**

Obtained as a yellow liquid (101.9 mg, 70% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.78 (d, J = 4.5 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H), 7.61-7.52 (m, 2H), 7.50-7.44 (m, 2H), 7.38 (dd, J = 9.2, 2.9 Hz, 1H), 7.28 (m, 2H), 3.81 (s, 3H), 1.41 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.8, 151.4, 147.6, 147.0, 144.8, 135.3, 131.3, 129.0, 127.7, 125.6, 121.7, 121.5, 104.3, 55.5, 34.7, 31.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO$: 292.1701, found: 292.1705.



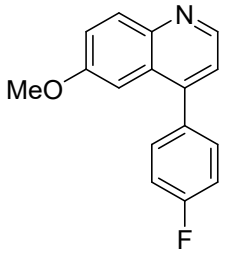
4-([1,1'-biphenyl]-4-yl)-6-Methoxyquinoline (4o):

Obtained as a white solid (101.1 mg, 65% yield), m.p.: 163-164 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.80 (d, J = 4.4 Hz, 1H), 8.09 (d, J = 9.2 Hz, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.42-7.36 (m, 2H), 7.31 (d, J = 4.4 Hz, 1H), 7.27 (d, J = 2.8 Hz, 1H), 3.79 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.9, 147.5, 146.6, 144.9, 141.1, 140.3, 137.2, 131.3, 129.7, 128.9, 127.62, 127.60, 127.3, 127.0, 121.7, 121.6, 103.7, 55.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO$: 312.1388, found: 312.1395.



6-Methoxy-4-(4-methoxyphenyl) quinoline (4p) [8]**:**

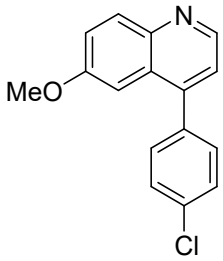
Obtained as a yellow liquid (37.1 mg, 28% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.77 (d, J = 4.4 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.51-7.41 (m, 2H), 7.37 (dd, J = 9.2, 2.8 Hz, 1H), 7.30-7.21 (m, 2H), 7.14-6.99 (m, 2H), 3.90 (s, 3H), 3.80 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 159.7, 157.8, 147.5, 146.8, 144.8, 131.2, 130.6, 130.5, 127.8, 121.64, 121.58, 114.1, 103.7, 55.4, 55.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO_2$: 266.1181, found: 266.1194.



4-(4-Fluorophenyl)-6-methoxyquinoline (4q) [7]**:**

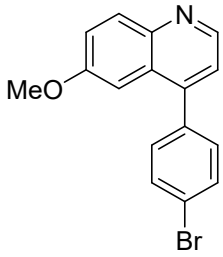
Obtained as a white solid (97.4 mg, 77% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.78 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 7.47 (dd, J = 8.5, 5.5 Hz, 2H), 7.38 (dd, J = 9.3, 2.8 Hz, 1H), 7.26-7.17 (m, 3H), 7.11 (d, J = 2.9 Hz, 1H), 3.78 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 163.7, 161.8, 157.9, 147.5, 145.9, 144.8, 134.3 (d, J = 3.6 Hz), 131.4, 131.0 (d, J = 8.2 Hz), 127.6, 121.7 (d, J = 11.7 Hz), 115.7 (d, J = 21.6 Hz), 103.4, 55.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -113.3. HRMS (ESI) m/z: $[M+H]^+$

calcd for $C_{16}H_{13}FNO$: 254.0981, found: 254.0989.



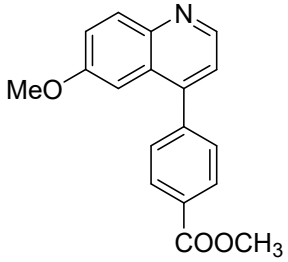
4-(4-Chlorophenyl)-6-methoxyquinoline (4r) [7]**:**

Obtained as a white solid (103.6 mg, 77% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.76 (d, J = 4.4 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.48 (dd, J = 8.4, 1.6 Hz, 2H), 7.45-7.39 (m, 2H), 7.36 (dd, J = 9.2, 2.8 Hz, 1H), 7.20 (d, J = 4.4 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 3.76 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.9, 147.3, 145.5, 144.7, 136.6, 134.3, 131.2, 130.4, 128.8, 127.2, 121.7, 121.4, 103.1, 55.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}ClNO$: 270.0685, found: 270.0689.



4-(4-Bromophenyl)-6-methoxyquinoline (4s) [7]**:**

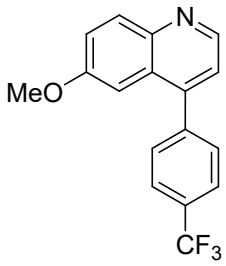
Obtained as a white solid (115.8 mg, 74% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.66 (d, J = 4.4 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.32-7.19 (m, 3H), 7.10 (d, J = 4.3 Hz, 1H), 6.98 (d, J = 2.8 Hz, 1H), 3.66 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.9, 147.3, 145.5, 144.7, 137.1, 131.8, 131.3, 130.8, 127.2, 122.6, 121.8, 121.4, 103.1, 55.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}BrNO$: 314.0180, found: 314.0180.



Methyl 4-(6-methoxyquinolin-4-yl)benzoate (4t):

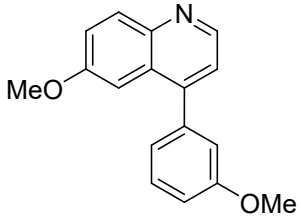
Obtained as a yellow solid (89.4 mg, 61% yield), m.p.: 104-105 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.82 (d, J = 4.5 Hz, 1H), 8.21 (d, J = 7.9 Hz, 2H), 8.09 (d, J = 9.2

Hz, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.40 (dd, J = 9.2, 2.4 Hz, 1H), 7.29 (d, J = 4.3 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 3.99 (s, 3H), 3.78 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 166.7, 158.1, 147.5, 145.8, 144.8, 143.0, 131.4, 130.1, 129.9, 129.4, 127.2, 122.0, 121.5, 103.2, 55.4, 52.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NO_3$: 294.1130, found: 294.1137.



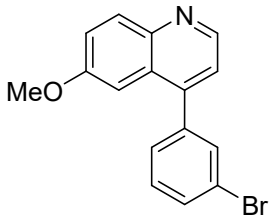
6-Methoxy-4-(4-(trifluoromethyl)phenyl) quinoline (4u) [7]**:**

Obtained as a white solid (95.5 mg, 63% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.82 (d, J = 4.3 Hz, 1H), 8.10 (d, J = 9.2 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.41 (dd, J = 9.2, 2.8 Hz, 1H), 7.27 (d, J = 4.3 Hz, 1H), 7.07 (d, J = 2.7 Hz, 1H), 3.80 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 158.2, 147.4, 145.4, 144.8, 142.1 (d, J = 1.7 Hz), 131.5, 130.6 (d, J = 32.7 Hz), 129.7, 127.2, 125.7 (q, J = 3.9 Hz), 124.0 (d, J = 272.2 Hz), 122.0, 121.6, 103.2, 55.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -62.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3NO$: 304.0949, found: 304.0958.



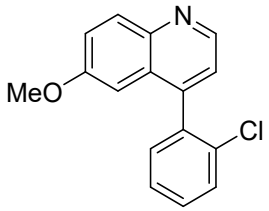
6-Methoxy-4-(3-methoxyphenyl) quinoline (4v):

Obtained as a yellow liquid (95.5 mg, 75% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.78 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H), 7.43 (t, J = 7.9 Hz, 1H), 7.37 (dd, J = 9.2, 2.8 Hz, 1H), 7.27 (d, J = 4.3 Hz, 1H), 7.22 (d, J = 2.8 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.07-7.04 (m, 1H), 7.04-7.00 (m, 1H), 3.85 (s, 3H), 3.78 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 159.7, 157.8, 147.4, 146.8, 144.8, 139.6, 131.2, 129.6, 127.5, 121.7, 121.6, 121.5, 114.8, 113.8, 103.6, 55.34, 55.26. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO_2$: 266.1181, found: 266.1184.



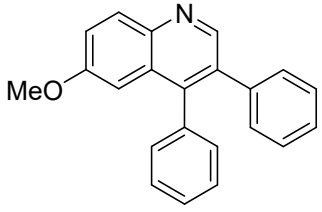
4-(3-Bromophenyl)-6-methoxyquinoline (4w) [7]**:**

Obtained as a yellow liquid (112.7 mg, 72% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.79 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H), 7.67 (t, J = 1.8 Hz, 1H), 7.66-7.58 (m, 1H), 7.44 (m, 1H), 7.42-7.36 (m, 2H), 7.25 (d, J = 4.4 Hz, 1H), 7.11 (d, J = 2.8 Hz, 1H), 3.80 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 158.0, 147.4, 145.3, 144.8, 140.3, 132.2, 131.4, 131.4, 130.1, 127.9, 127.3, 122.8, 121.9, 121.5, 103.2, 55.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}BrNO$: 314.0180, found: 314.0179.



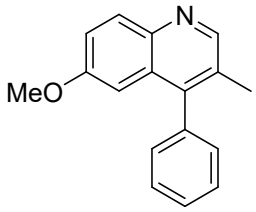
4-(2-Chlorophenyl)-6-methoxyquinoline (4x):

Obtained as a yellow liquid (94.2 mg, 70% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.71 (d, J = 4.4 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.45 (dd, J = 7.8, 1.5 Hz, 1H), 7.34-7.25 (m, 3H), 7.22 (dd, J = 7.3, 2.0 Hz, 1H), 7.14 (d, J = 4.4 Hz, 1H), 6.64 (d, J = 2.8 Hz, 1H), 3.62 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.8, 147.2, 144.4, 144.3, 136.8, 133.1, 131.2, 131.1, 129.8, 129.7, 127.7, 126.8, 122.0, 121.8, 103.5, 55.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}ClNO$: 270.0685, found: 270.0683.



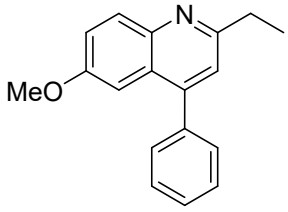
6-Methoxy-3,4-diphenylquinoline (4y) [9]**:**

Obtained as a yellow solid (24.9 mg, 16% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.85 (s, 1H), 8.09 (d, J = 9.1 Hz, 1H), 7.45-7.30 (m, 4H), 7.29-7.10 (m, 7H), 6.95 (d, J = 2.8 Hz, 1H), 3.73 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 158.0, 149.4, 144.2, 143.7, 138.3, 136.6, 133.4, 131.0, 130.4, 130.1, 128.24, 128.22, 128.0, 127.7, 127.0, 121.4, 104.6, 55.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO$: 312.1388, found: 312.1390.



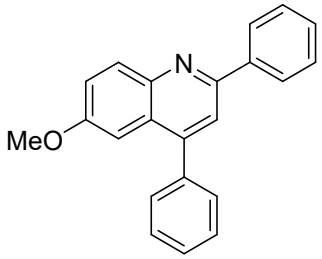
6-Methoxy-3-methyl-4-phenylquinoline (4z):

Obtained as a white solid (67.3 mg, 54% yield), m.p.: 78-79 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.70 (s, 1H), 8.01 (d, J = 9.1 Hz, 1H), 7.57-7.49 (m, 2H), 7.49-7.43 (m, 1H), 7.32-7.22 (m, 3H), 6.69 (d, J = 2.8 Hz, 1H), 3.67 (s, 3H), 2.22 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.7, 150.2, 145.0, 143.0, 137.1, 130.8, 129.1, 128.6, 128.5, 128.2, 127.8, 120.3, 104.0, 55.2, 17.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO$: 250.1232, found: 250.1235.



2-Ethyl-6-methoxy-4-phenylquinoline (4zb) [10]**:**

Obtained as a yellow solid (32.9 mg, 25% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 9.1 Hz, 1H), 7.55-7.50 (m, 4H), 7.50-7.46 (m, 1H), 7.35 (dd, J = 9.2, 2.9 Hz, 1H), 7.21 (s, 1H), 7.16 (d, J = 2.8 Hz, 1H), 3.77 (s, 3H), 3.00 (q, J = 7.6 Hz, 2H), 1.41 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 161.0, 157.3, 147.4, 144.4, 138.7, 130.6, 129.3, 128.6, 128.2, 126.0, 121.34, 121.27, 103.9, 55.4, 32.0, 14.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}NO$: 264.1388, found: 264.1398.



6-Methoxy-2,4-diphenylquinoline (4zc) [11]**:**

Obtained as a white solid (96.5 mg, 62% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.20-8.08 (m, 3H), 7.77 (s, 1H), 7.60-7.52 (m, 4H), 7.53-7.47 (m, 3H), 7.46-7.41 (m, 1H), 7.39 (dd, J = 9.2, 2.8 Hz, 1H), 7.19 (d, J = 2.8 Hz, 1H), 3.79 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 157.8, 154.6, 147.8, 144.9, 139.7, 138.7, 131.6, 129.3, 129.0, 128.8, 128.7, 128.3, 127.3, 126.6, 121.8, 119.7, 103.7, 55.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for

$C_{22}H_{18}NO$: 312.1388, found: 312.1396.

4. References

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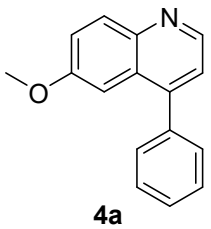
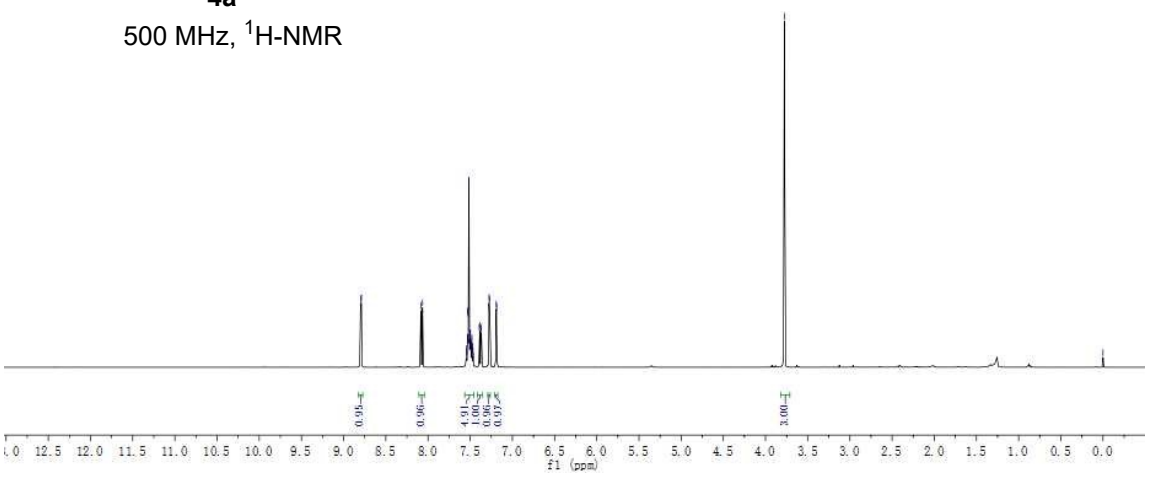
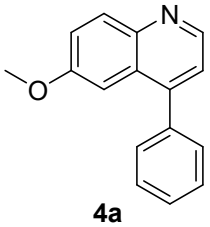
5. ^{1}H, ^{19}F and ^{13}C NMR spectra of compounds 4



4a

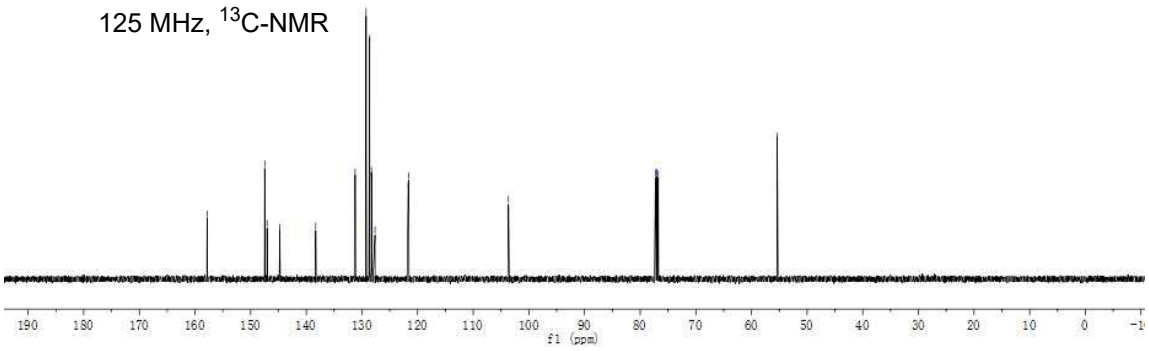
500 MHz, ^{1}H-NMR

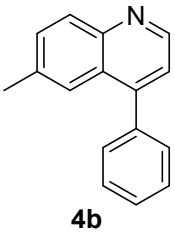




4a

125 MHz, ^{13}C-NMR





4b

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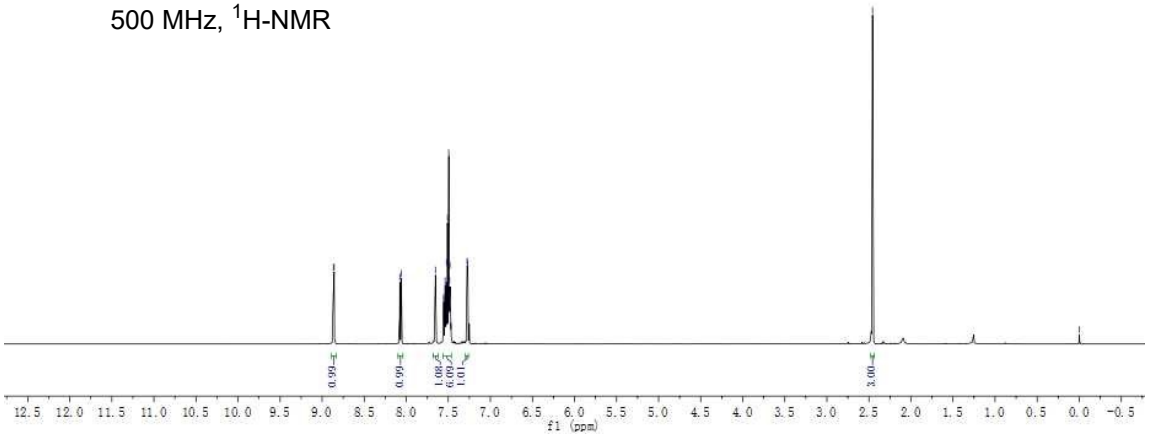
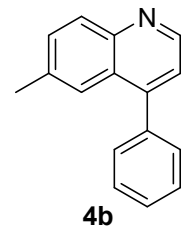
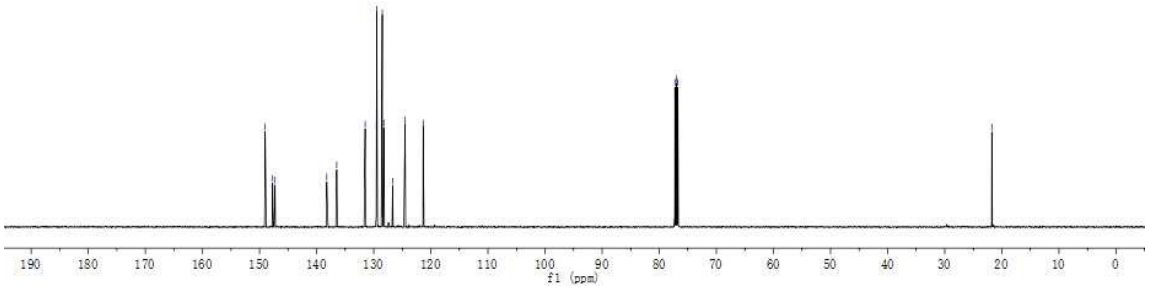
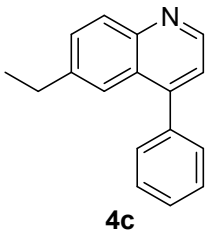




4b

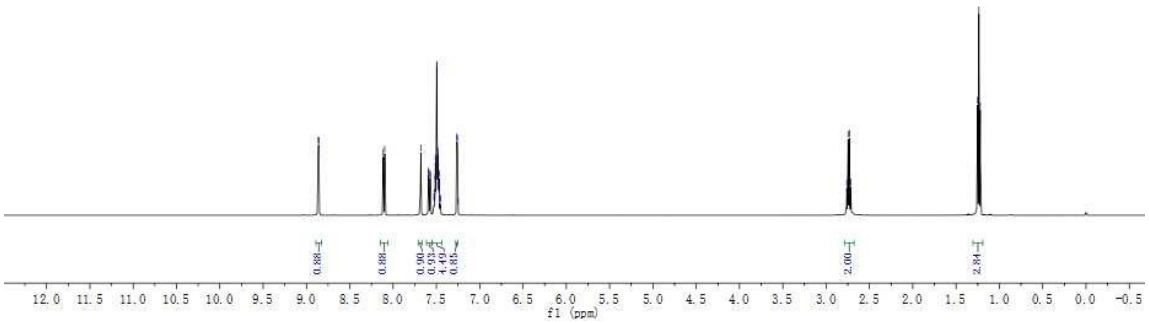
125 MHz, ^{13}C-NMR

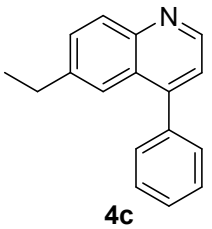




4c

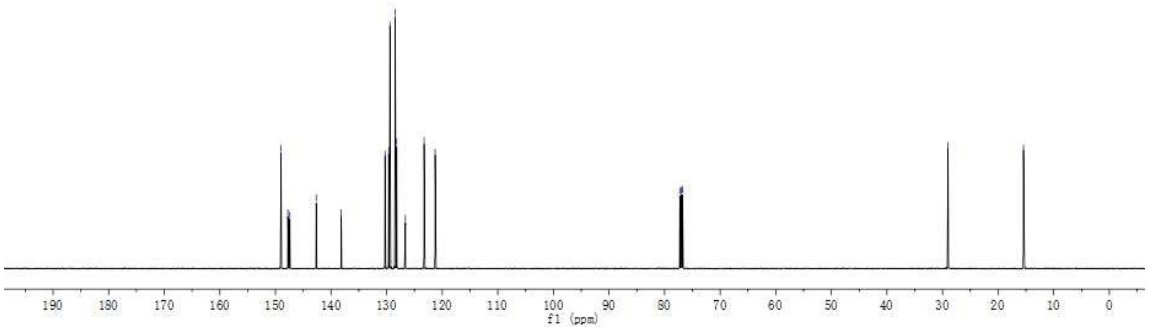
500 MHz, ^{1}H-NMR

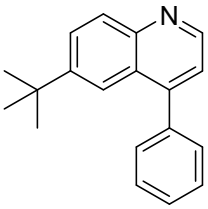




4c

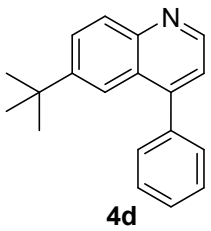
125 MHz, ^{13}C-NMR





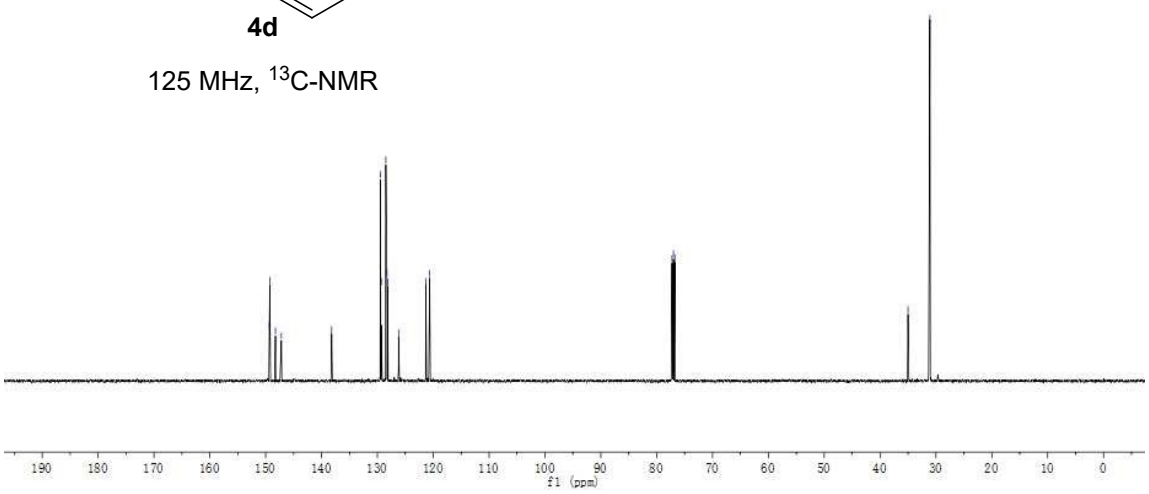
4d

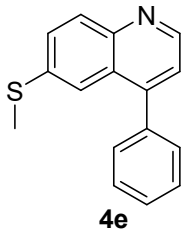
500 MHz, ^{1}H-NMR



4d

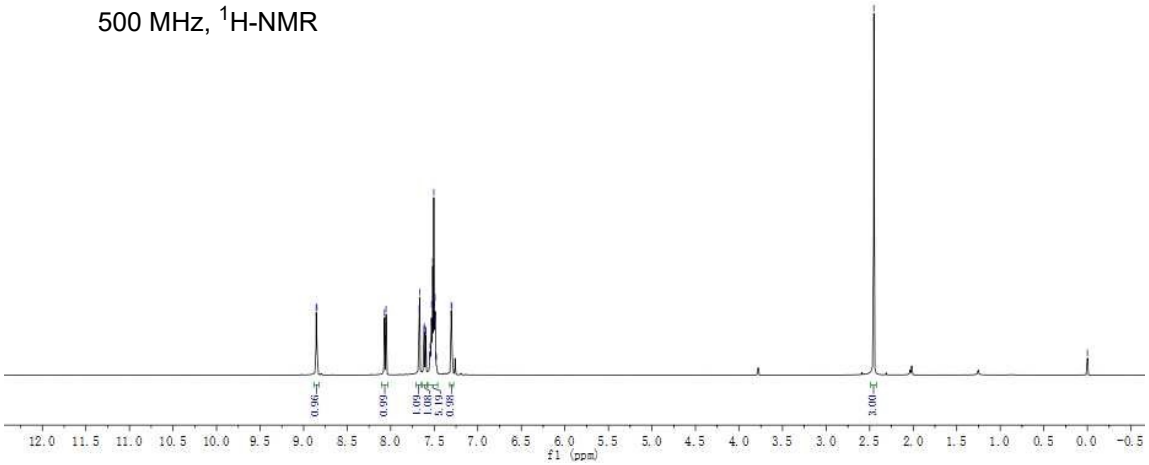
125 MHz, ^{13}C-NMR

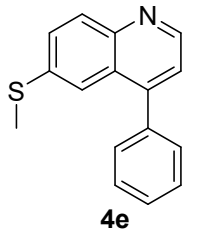




4e

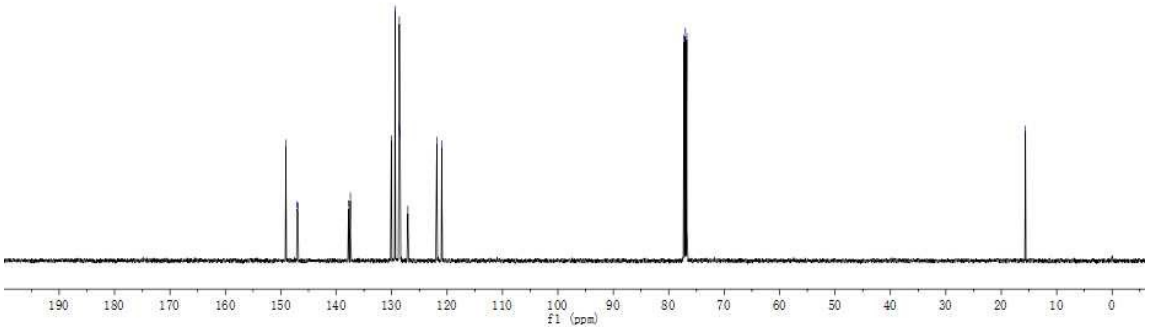
500 MHz, ^{1}H-NMR





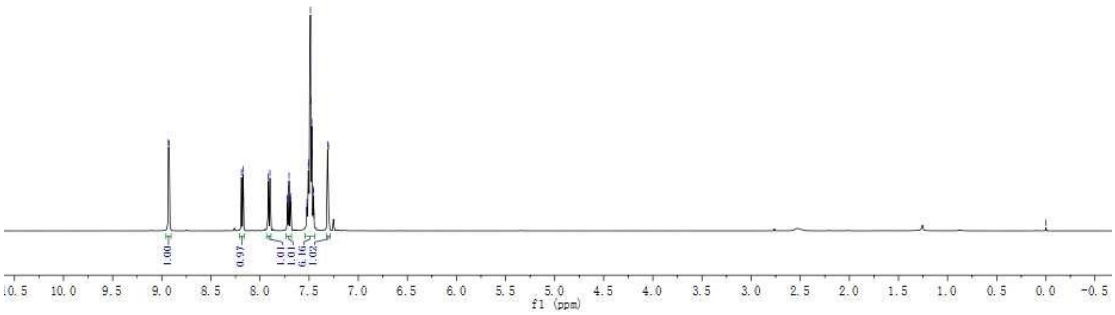
4e

125 MHz, ^{13}C-NMR



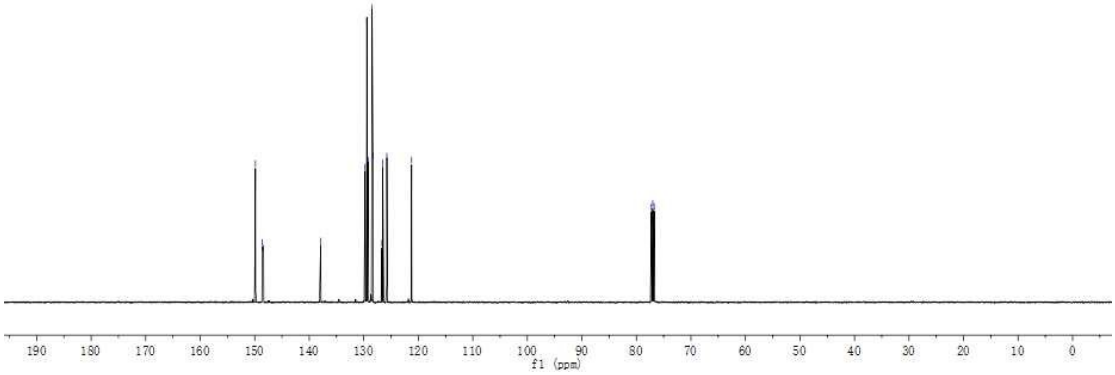
4f

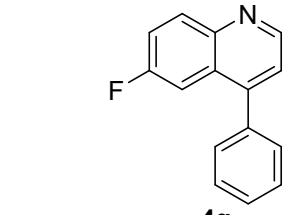
500 MHz, ^{1}H-NMR



4f

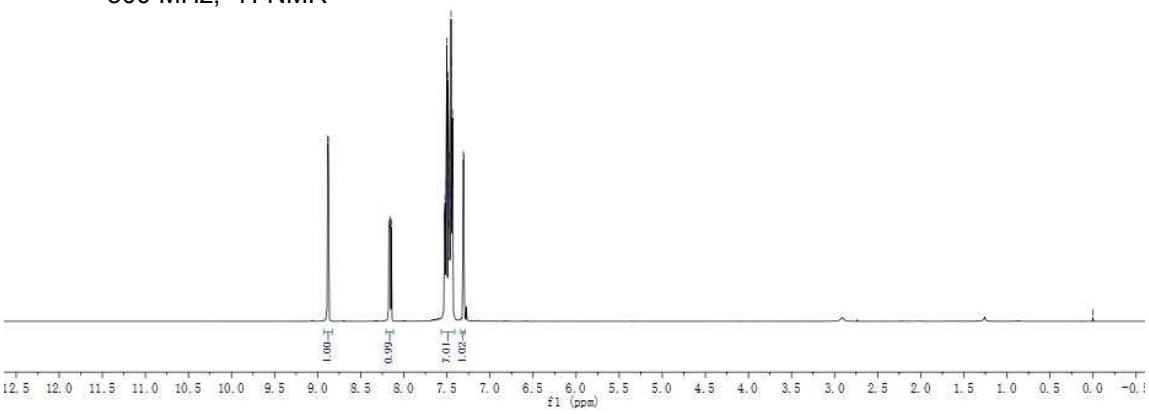
125 MHz, ^{13}C-NMR

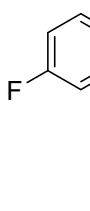




4g

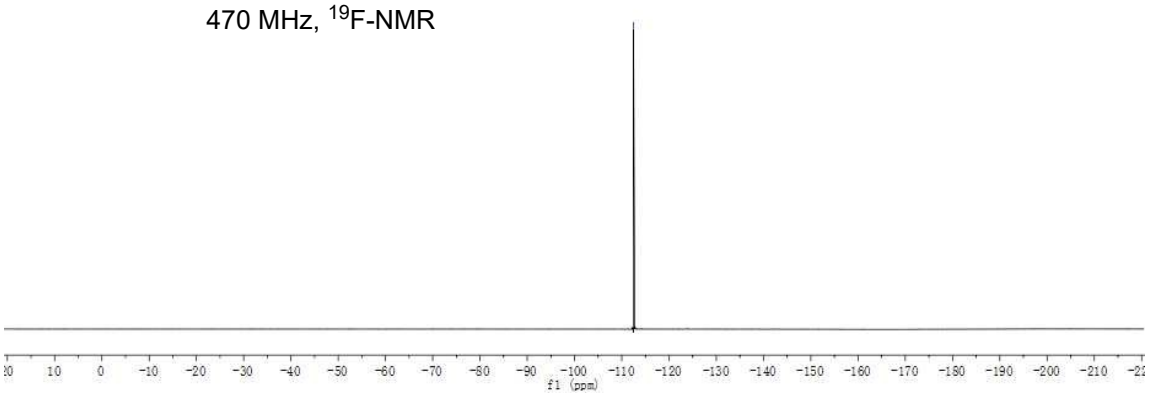
500 MHz, ^{1}H-NMR

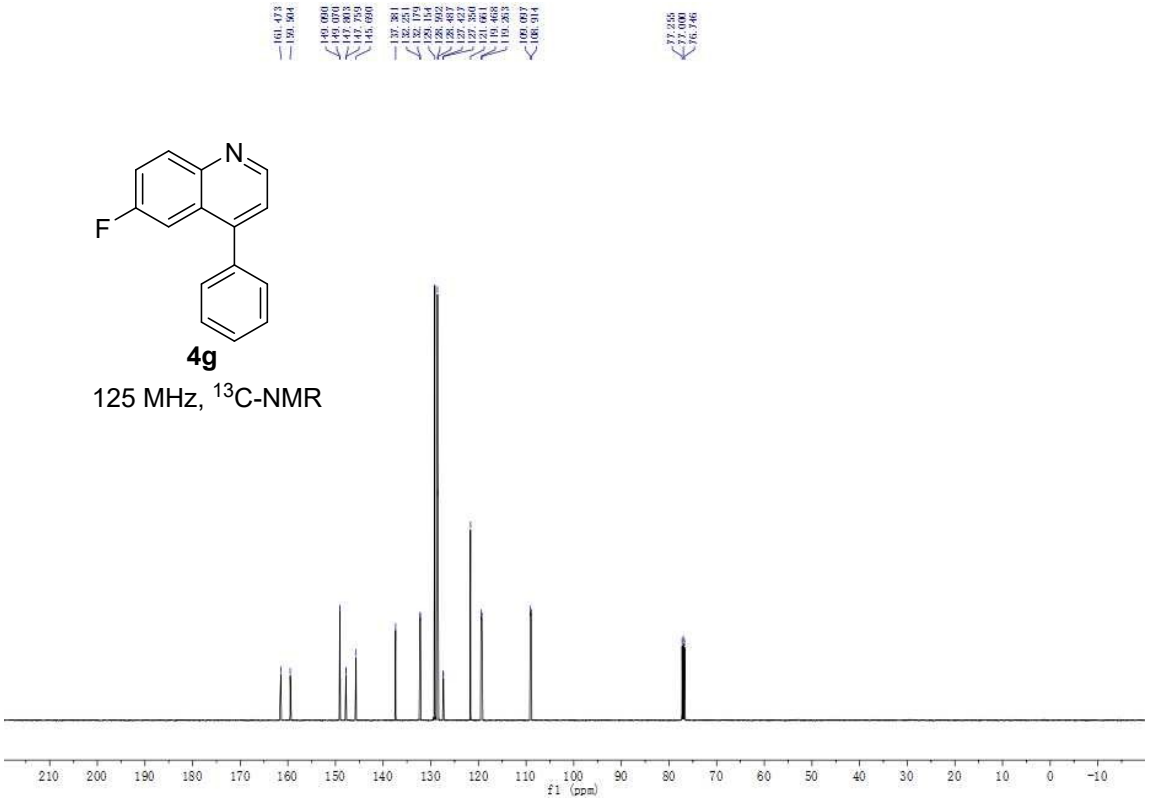




4g

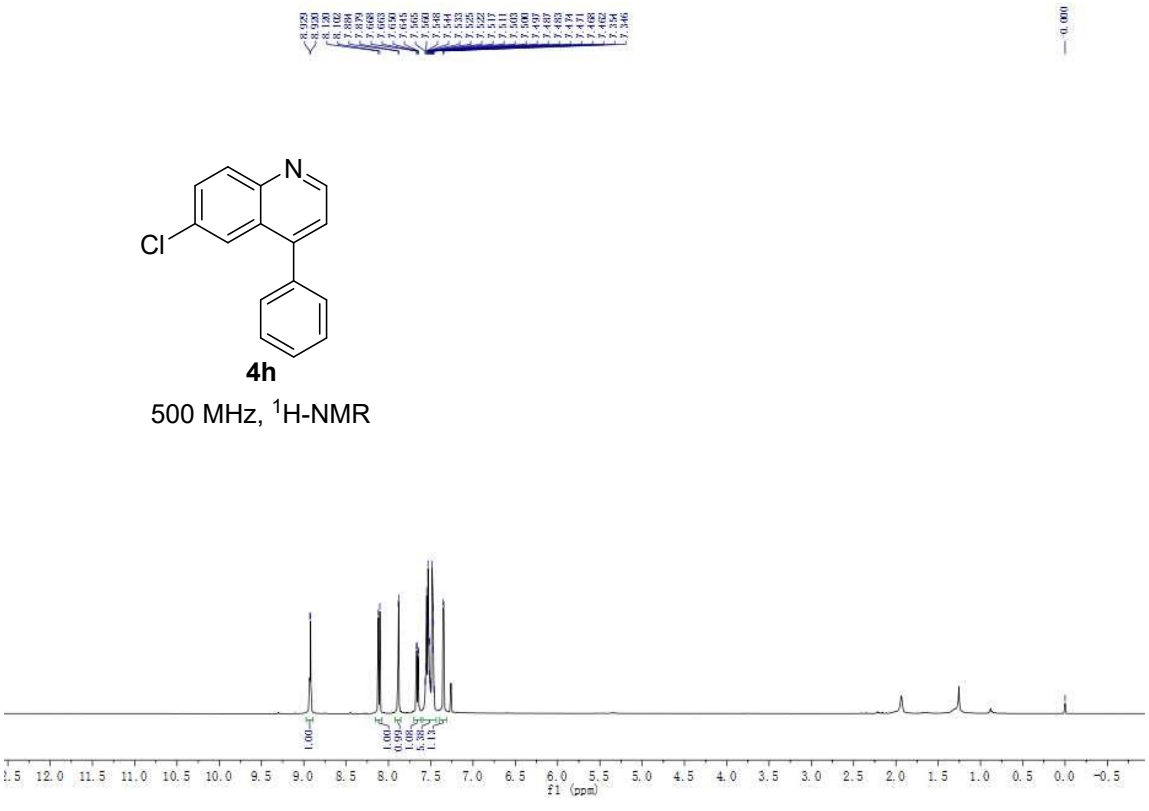
470 MHz, ^{19}F-NMR





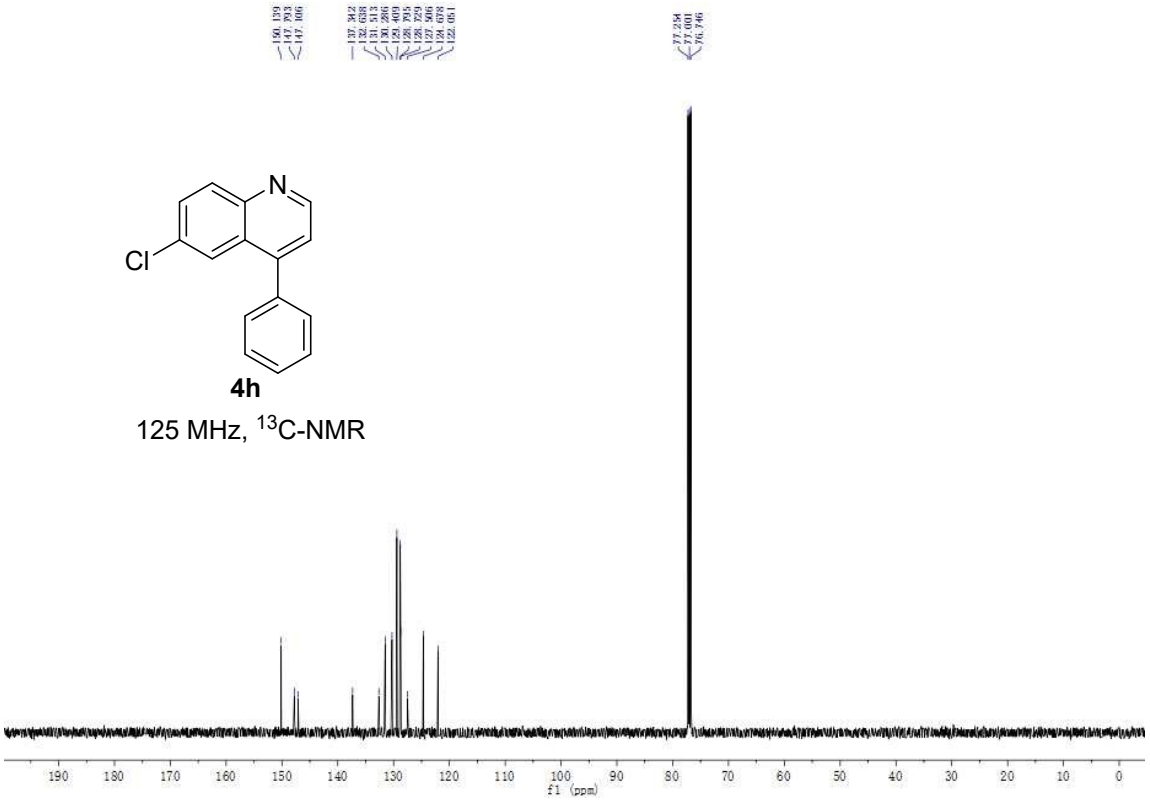
4g

125 MHz, ^{13}C-NMR



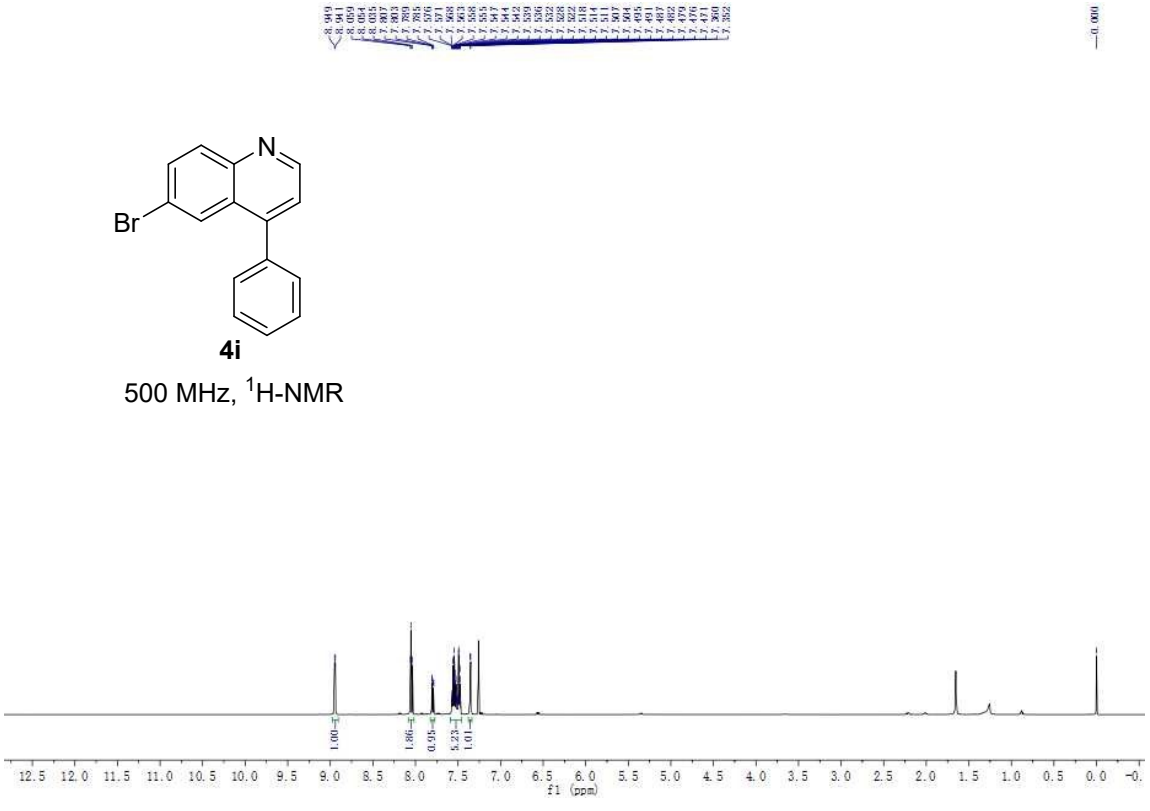
4h

500 MHz, ^{1}H-NMR



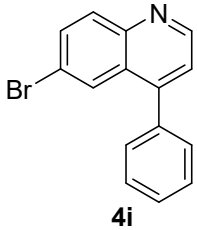
4h

125 MHz, ^{13}C-NMR



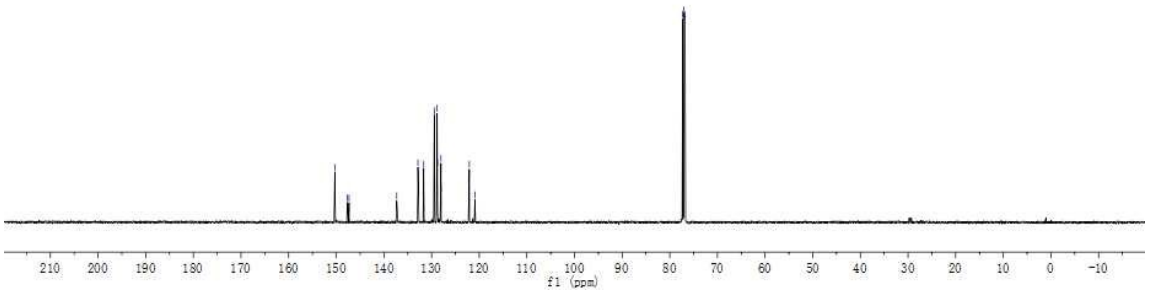
4i

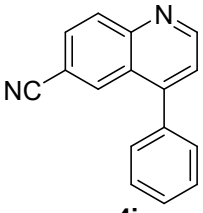
500 MHz, ^{1}H-NMR



4i

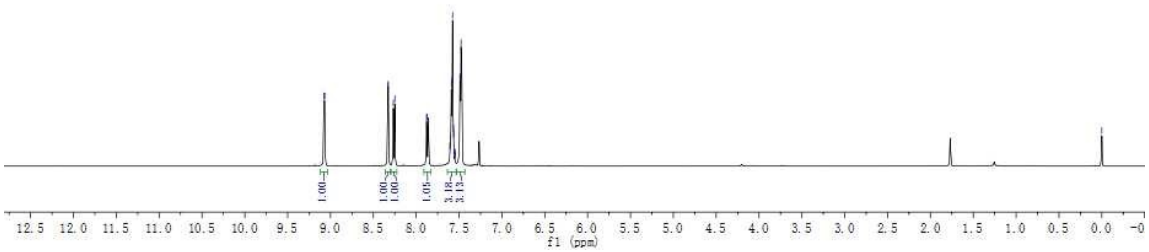
125 MHz, ^{13}C-NMR

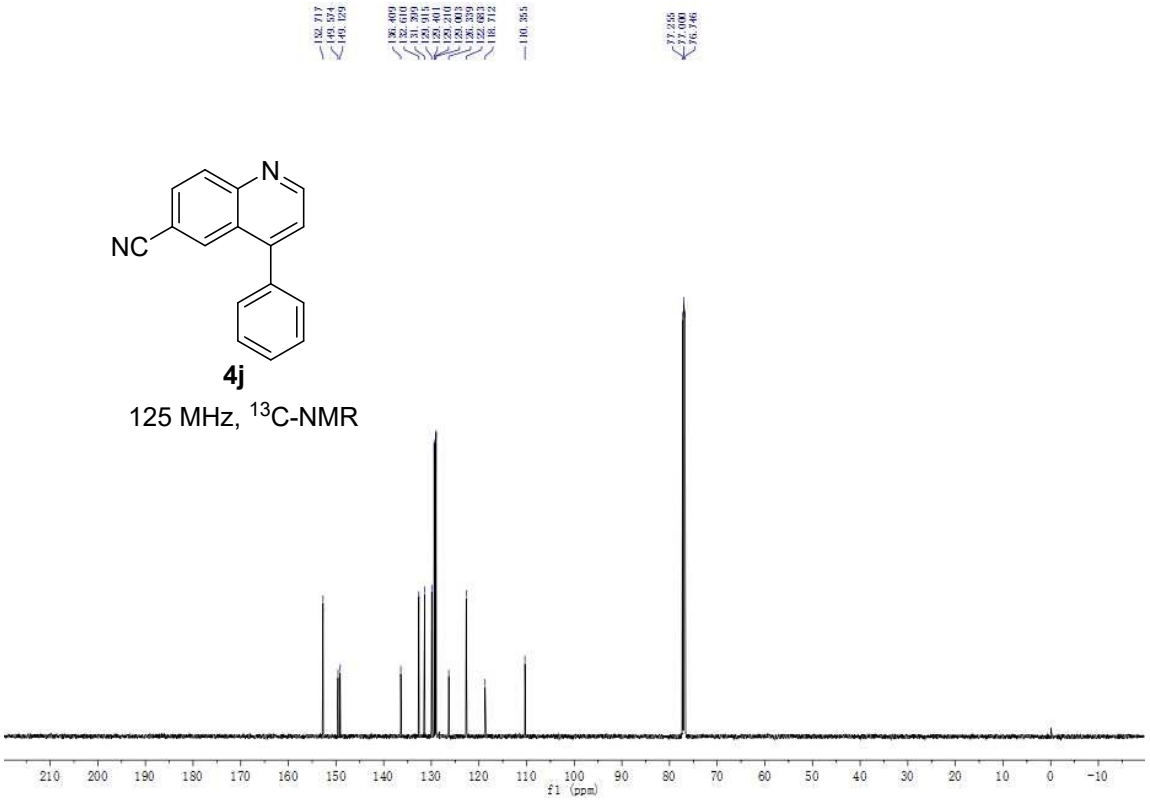




4j

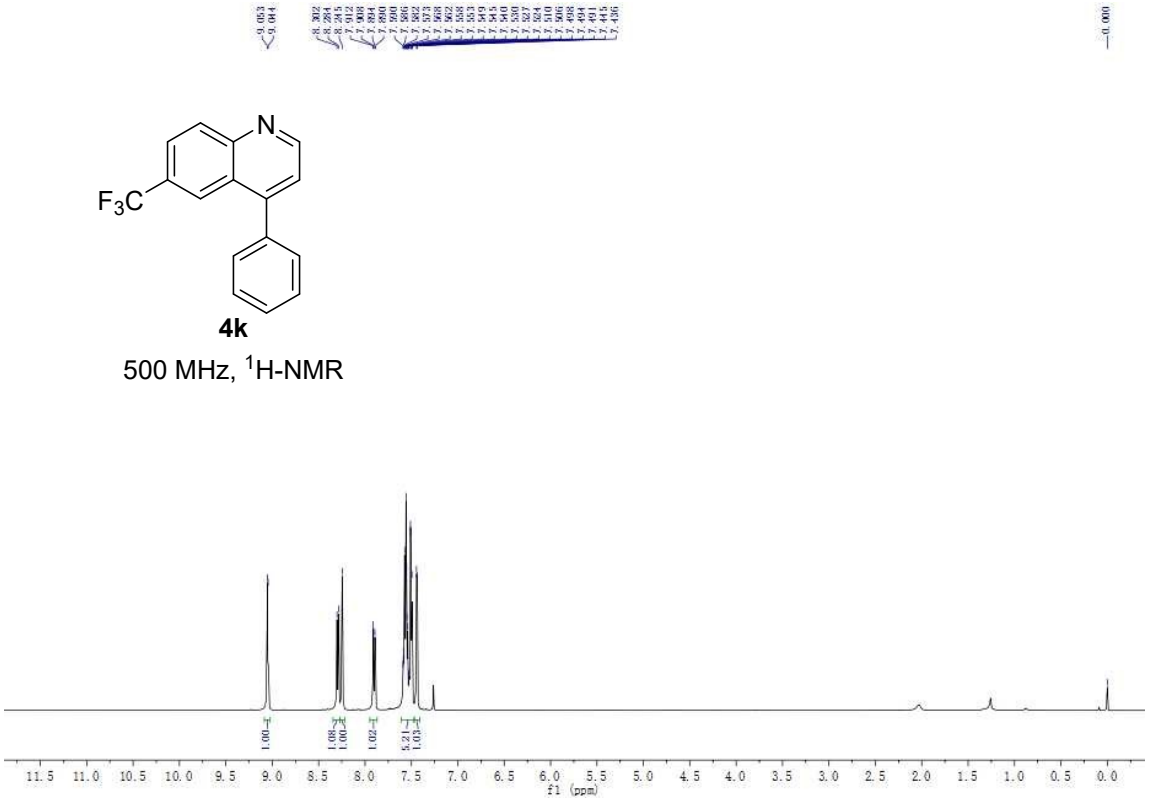
500 MHz, ^{1}H-NMR





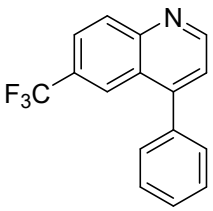
4j

125 MHz, ^{13}C-NMR



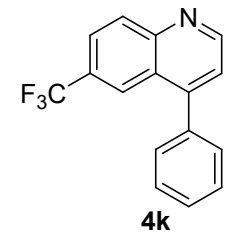
4k

500 MHz, ^{1}H-NMR



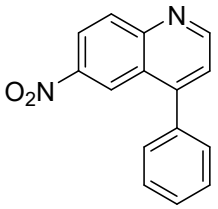
4k

470 MHz, ^{19}F-NMR



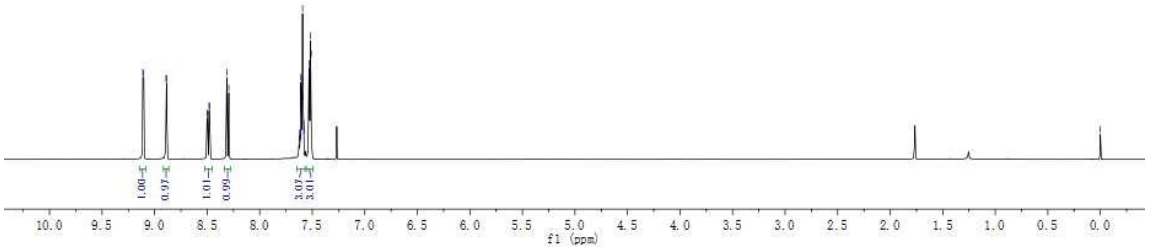
4k

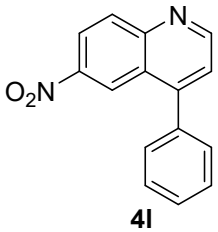
125 MHz, ^{13}C-NMR



4l

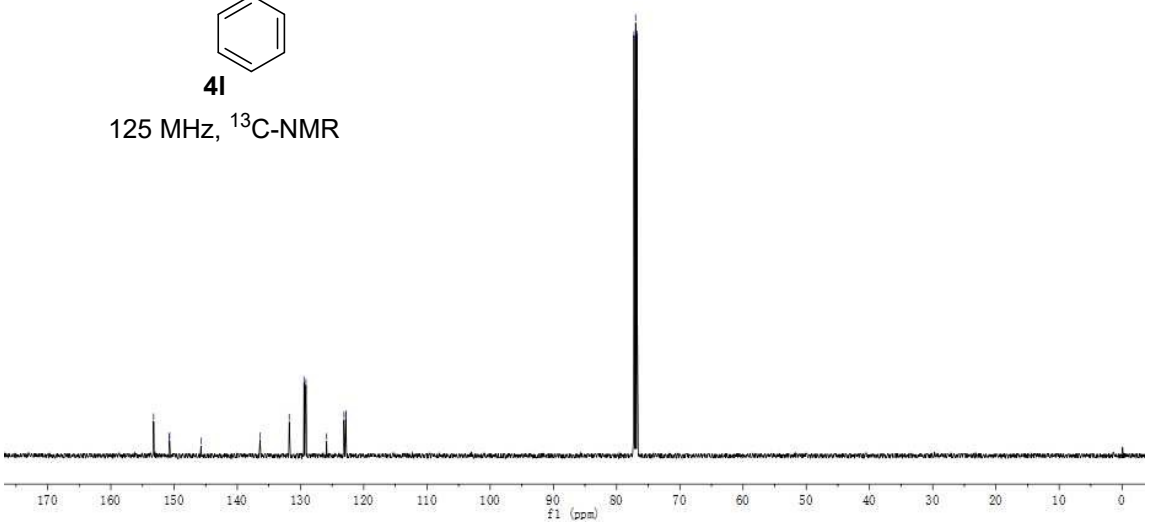
500 MHz, ^{1}H-NMR

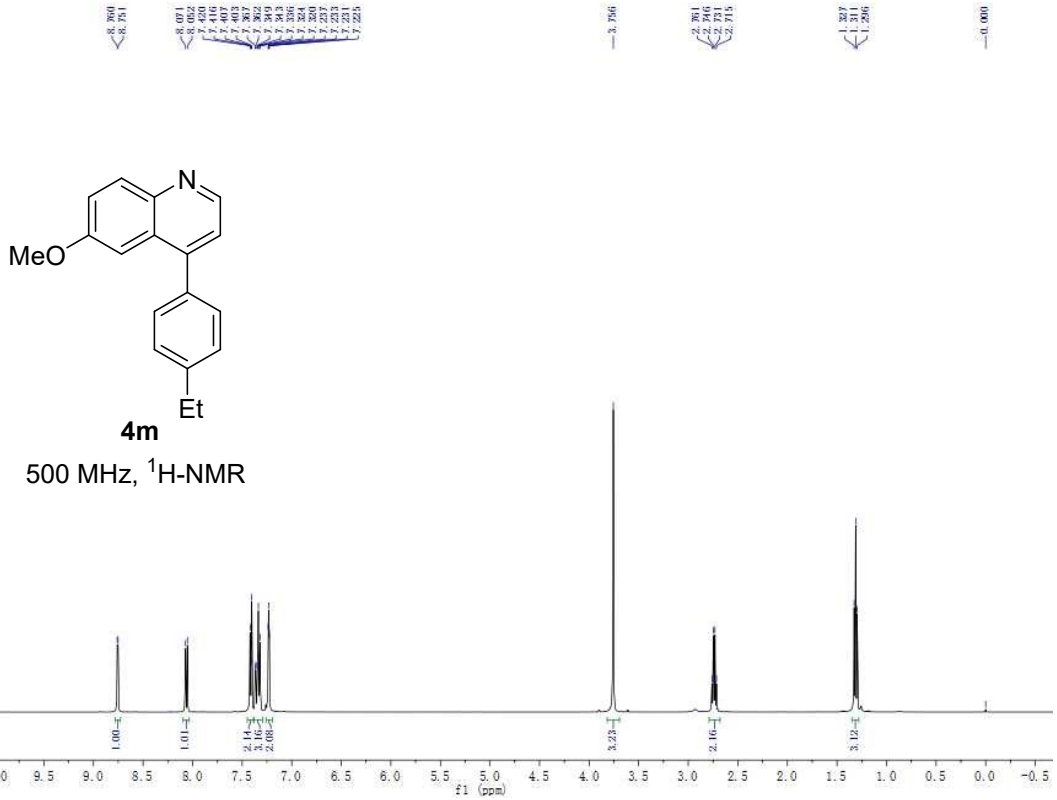




4l

125 MHz, ^{13}C-NMR



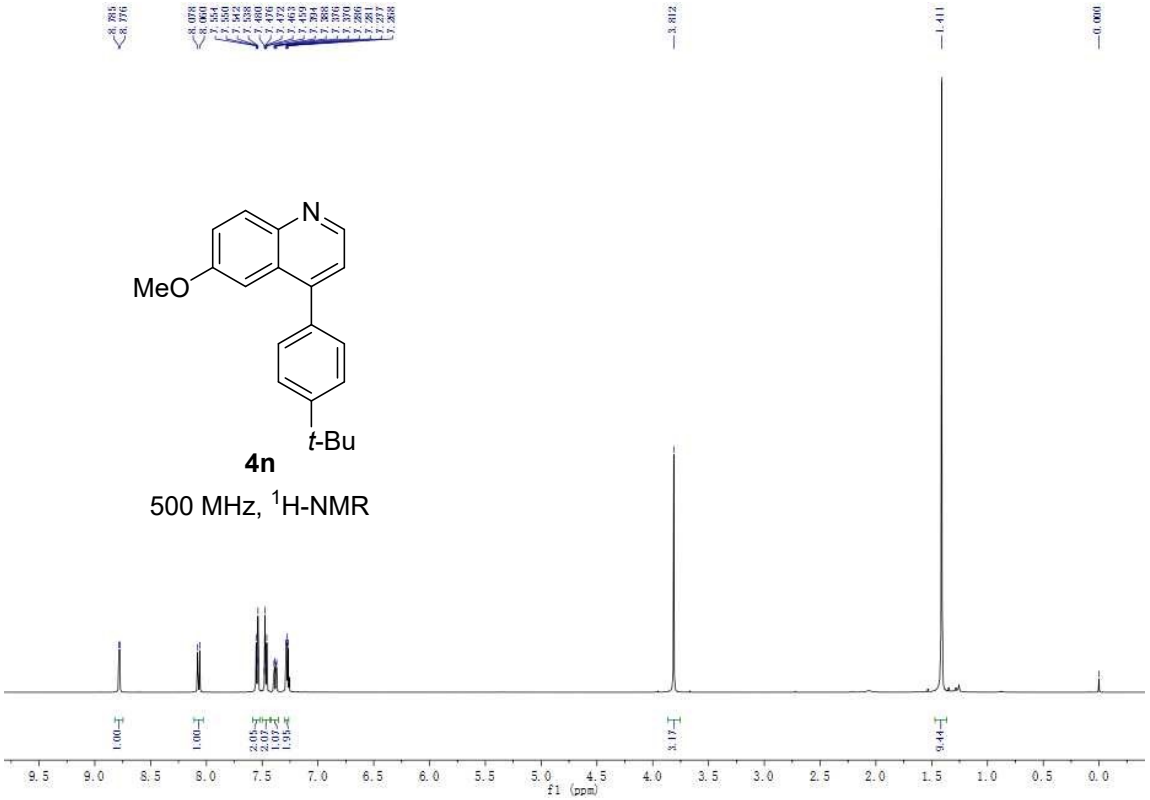


4m

500 MHz, ^{1}H-NMR

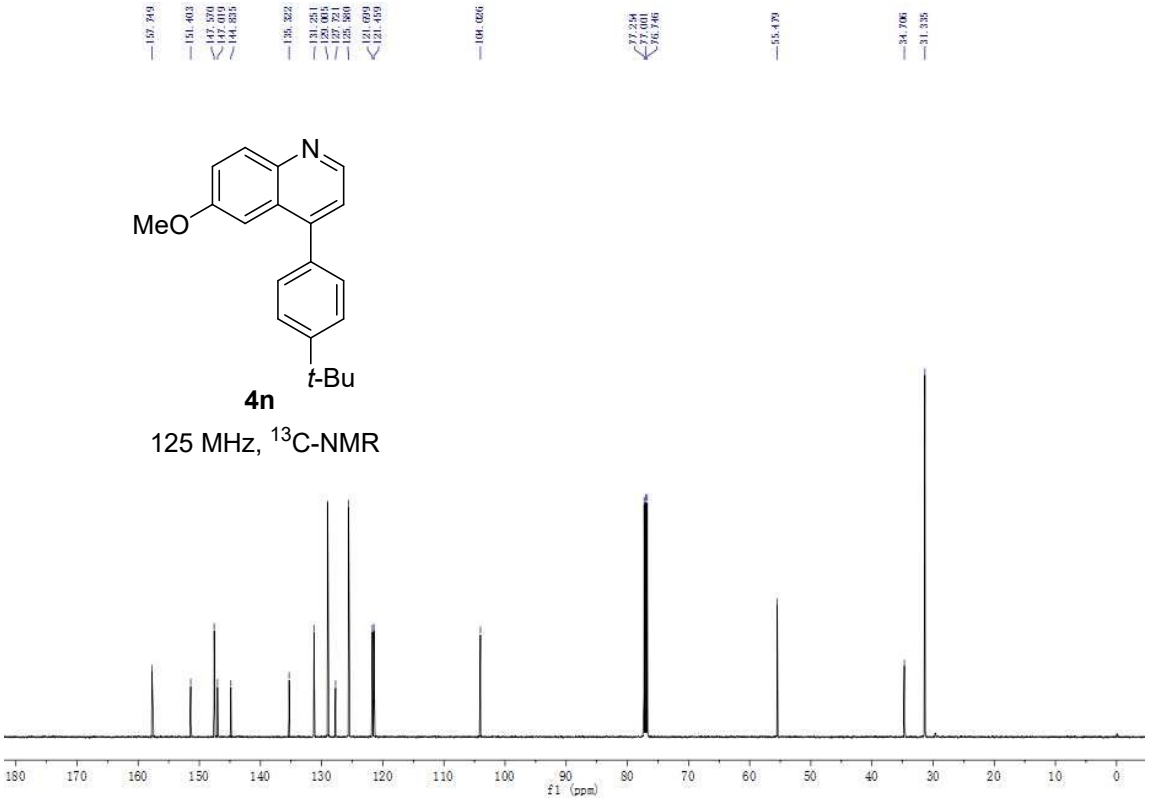
4m

125 MHz, ^{13}C-NMR



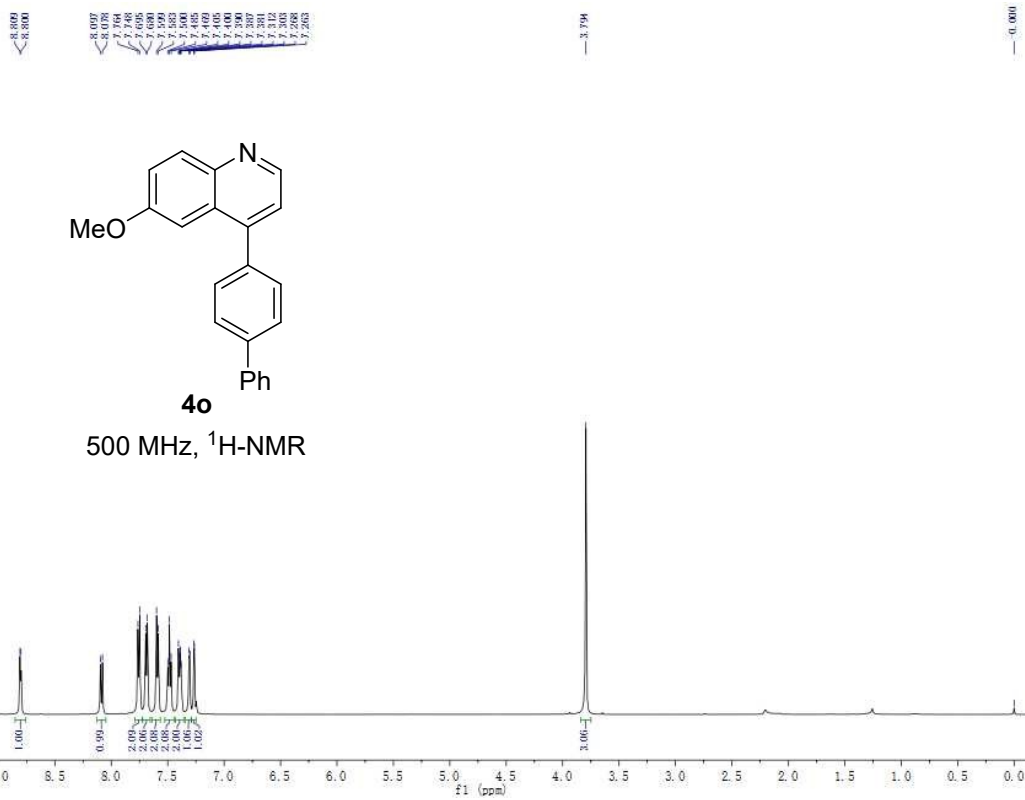
4n

500 MHz, ^{1}H-NMR



4n

125 MHz, ^{13}C-NMR

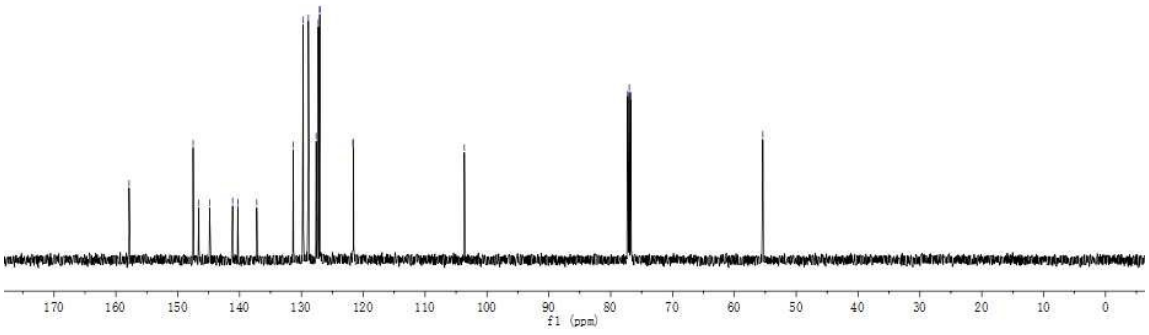


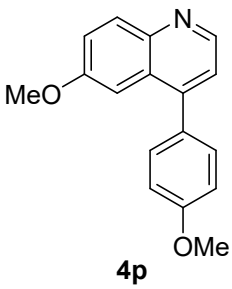
4o

500 MHz, ^{1}H-NMR

4o

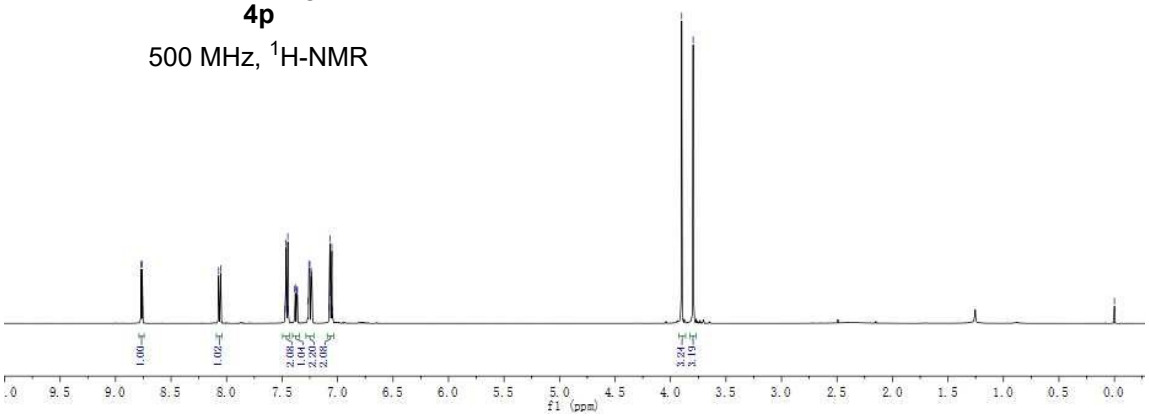
125 MHz, ^{13}C-NMR

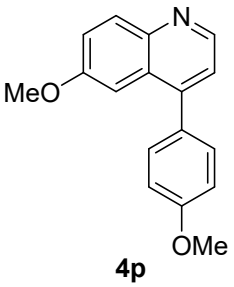




4p

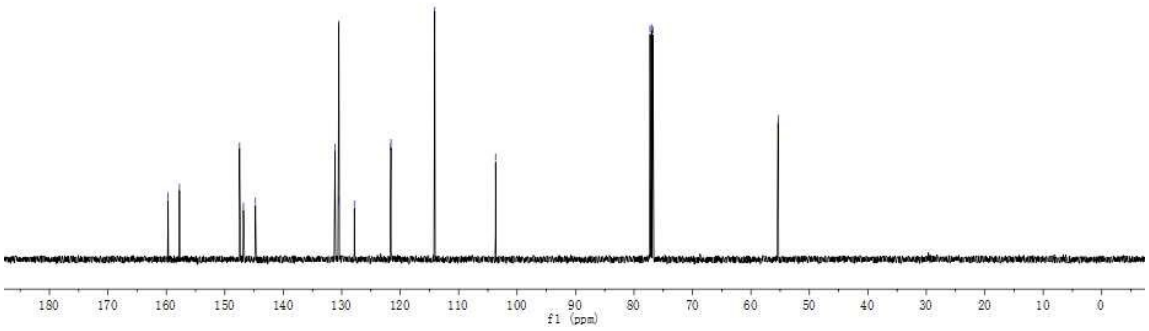
500 MHz, ^{1}H-NMR

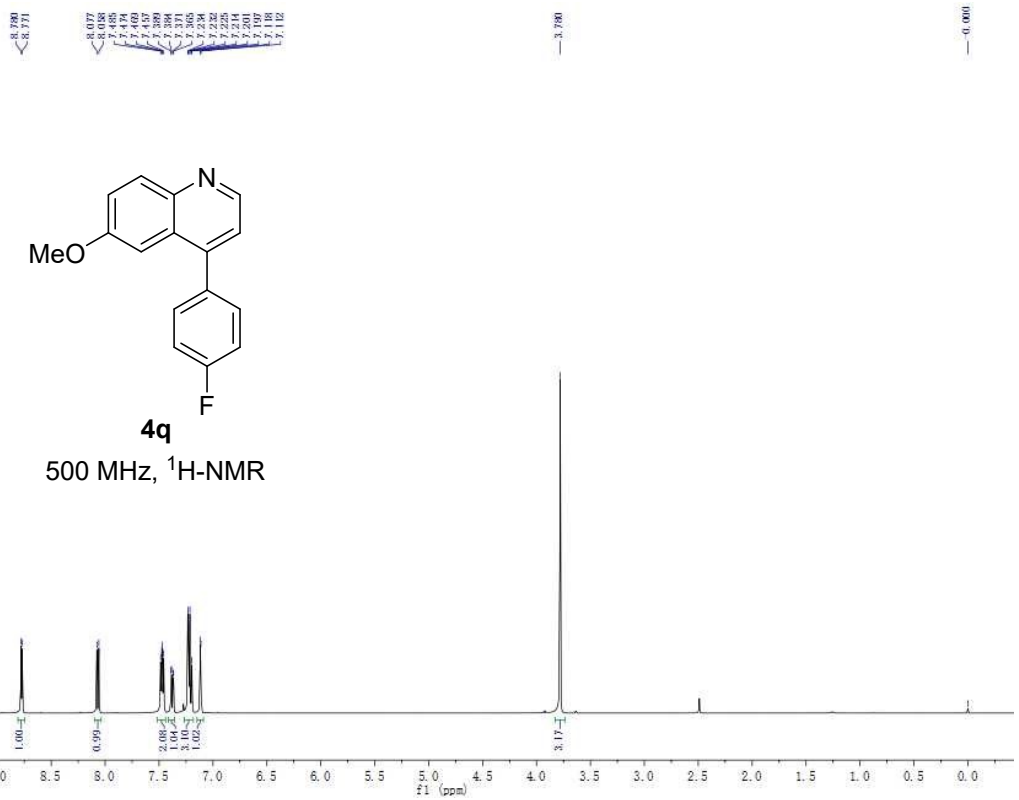




4p

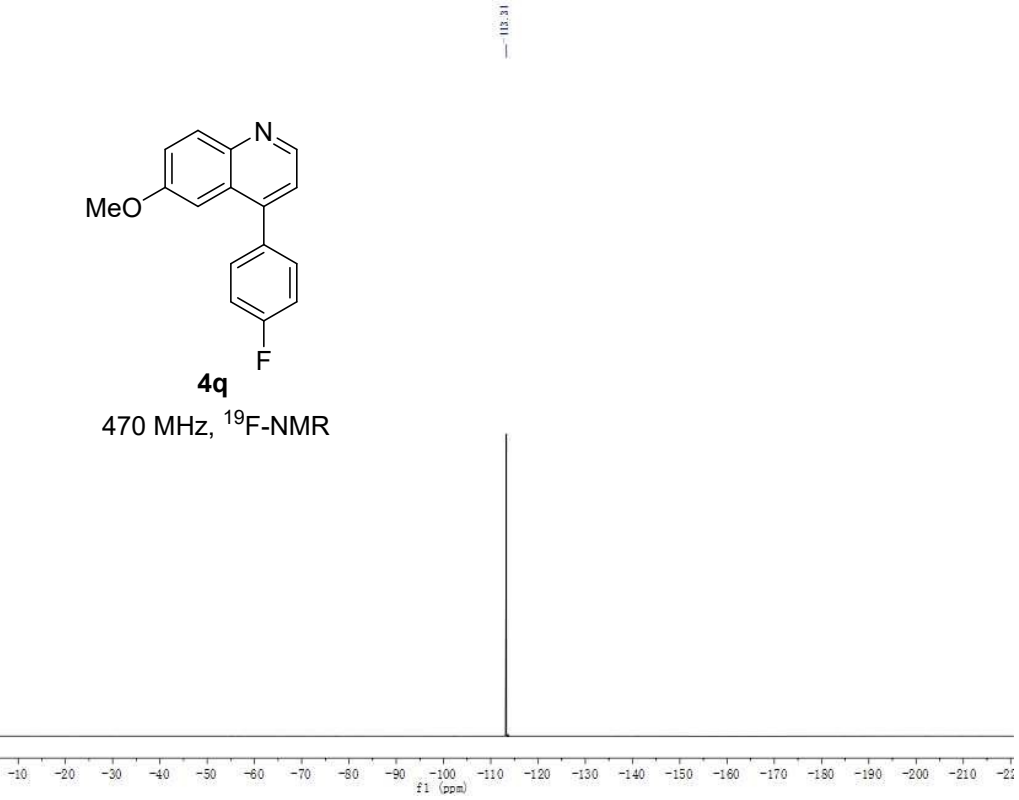
125 MHz, ^{13}C-NMR





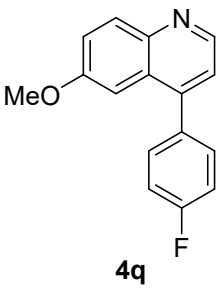
4q

500 MHz, ^{1}H-NMR



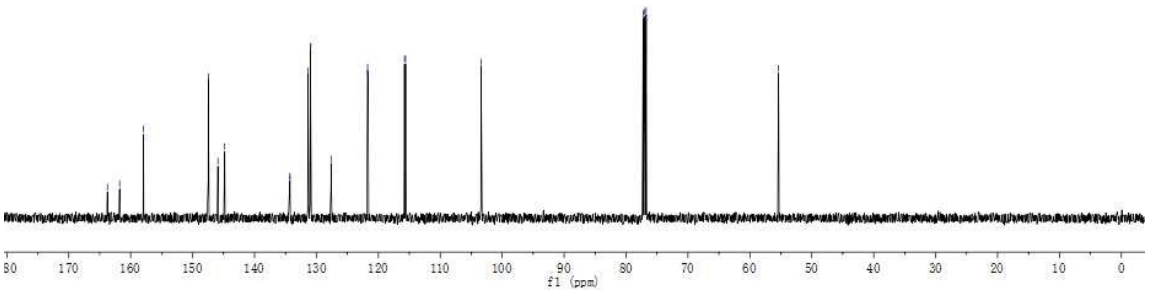
4q

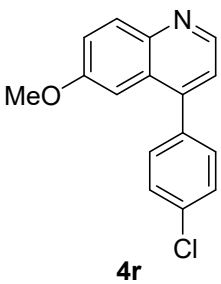
470 MHz, ^{19}F-NMR



4q

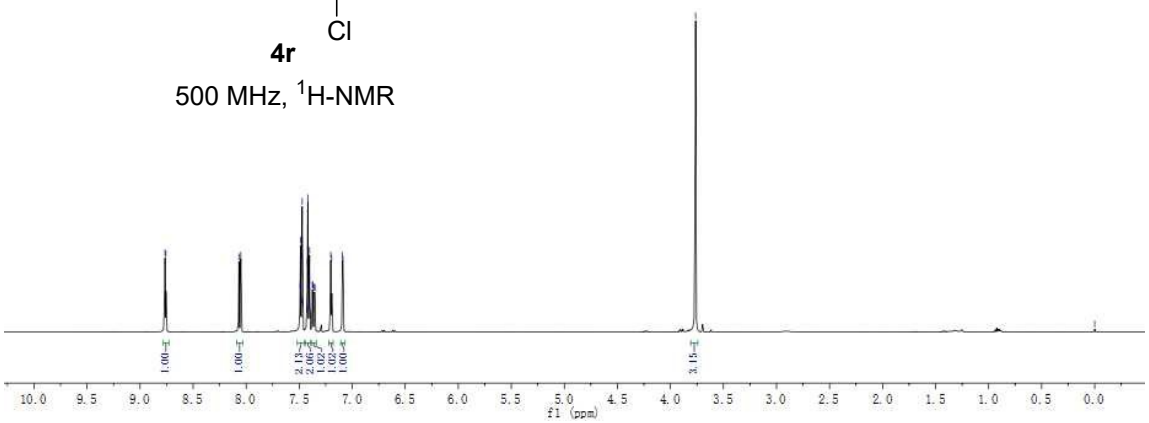
125 MHz, ^{13}C-NMR

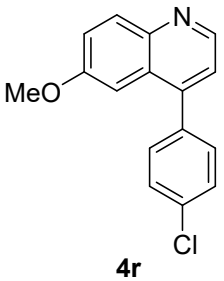




4r

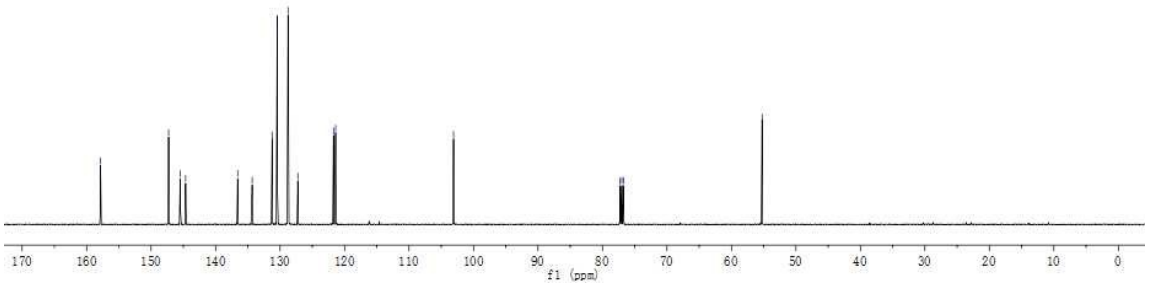
500 MHz, ^{1}H-NMR

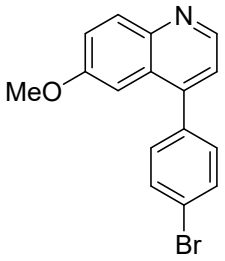




4r

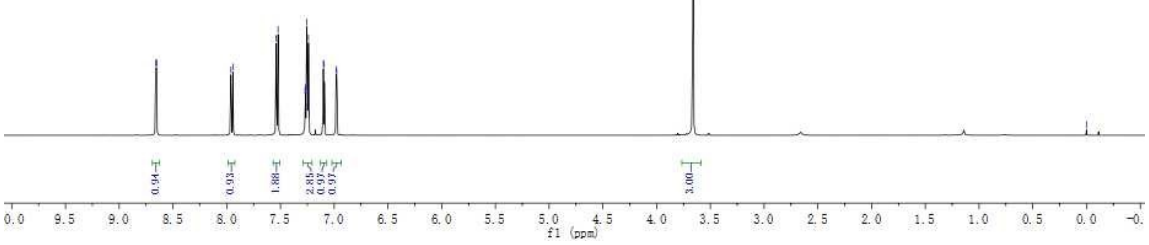
125 MHz, ^{13}C-NMR

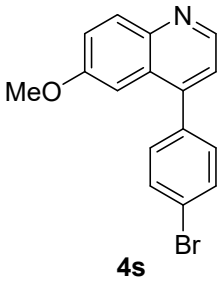




4s

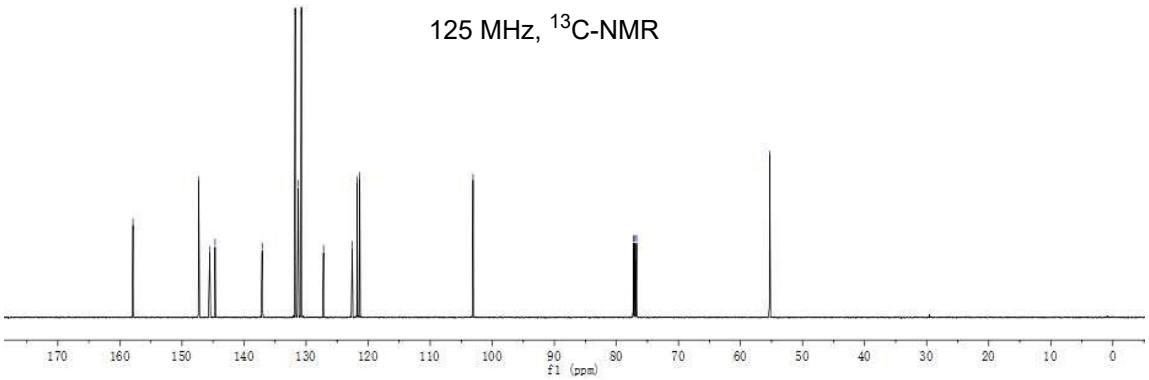
500 MHz, ^{1}H-NMR

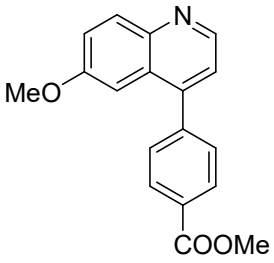




4s

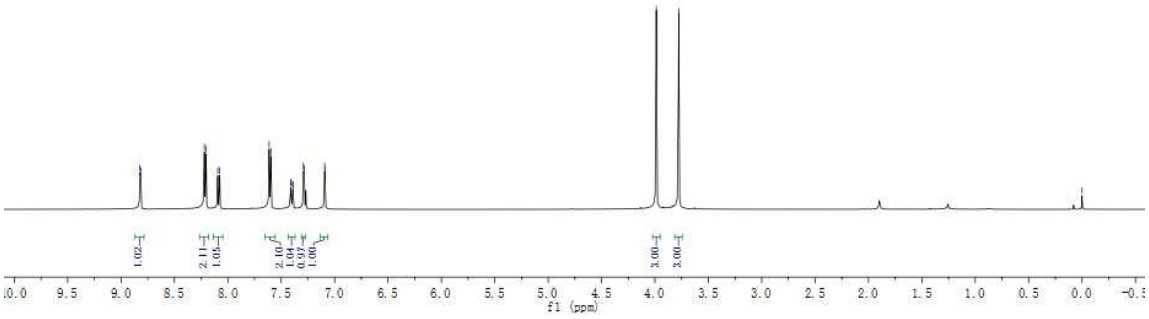
125 MHz, ^{13}C-NMR

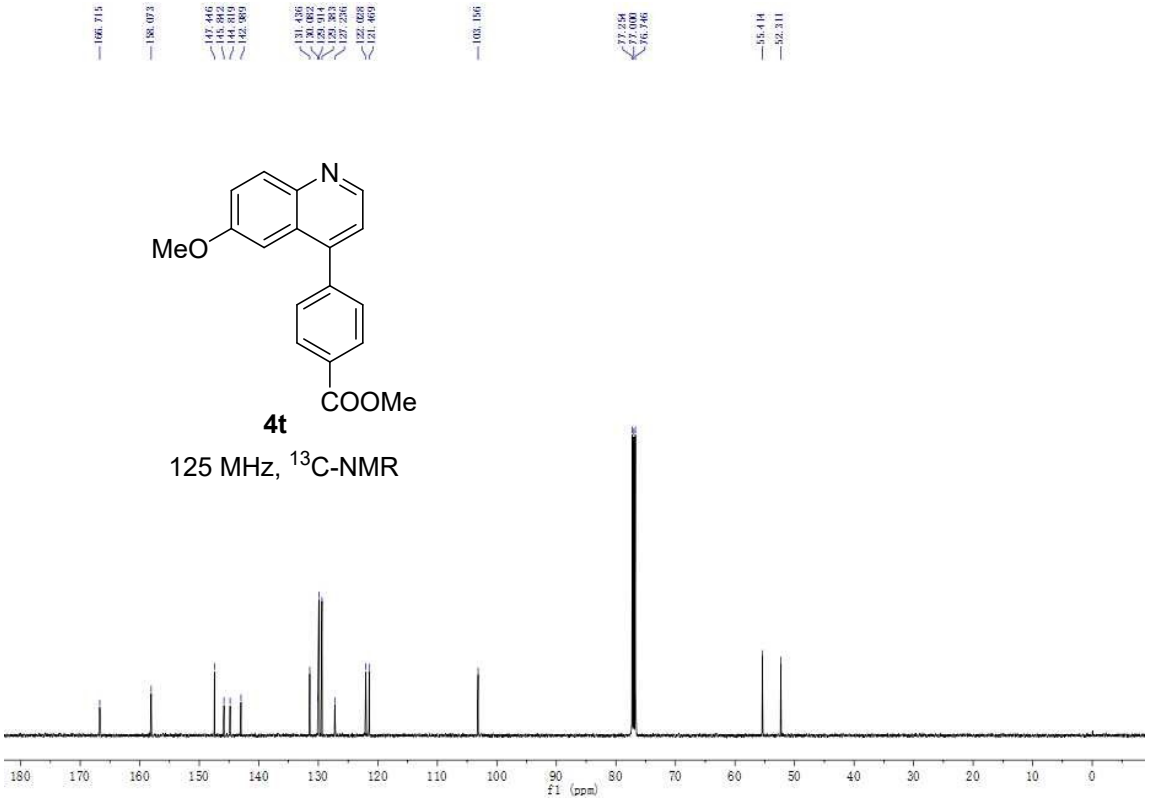




4t

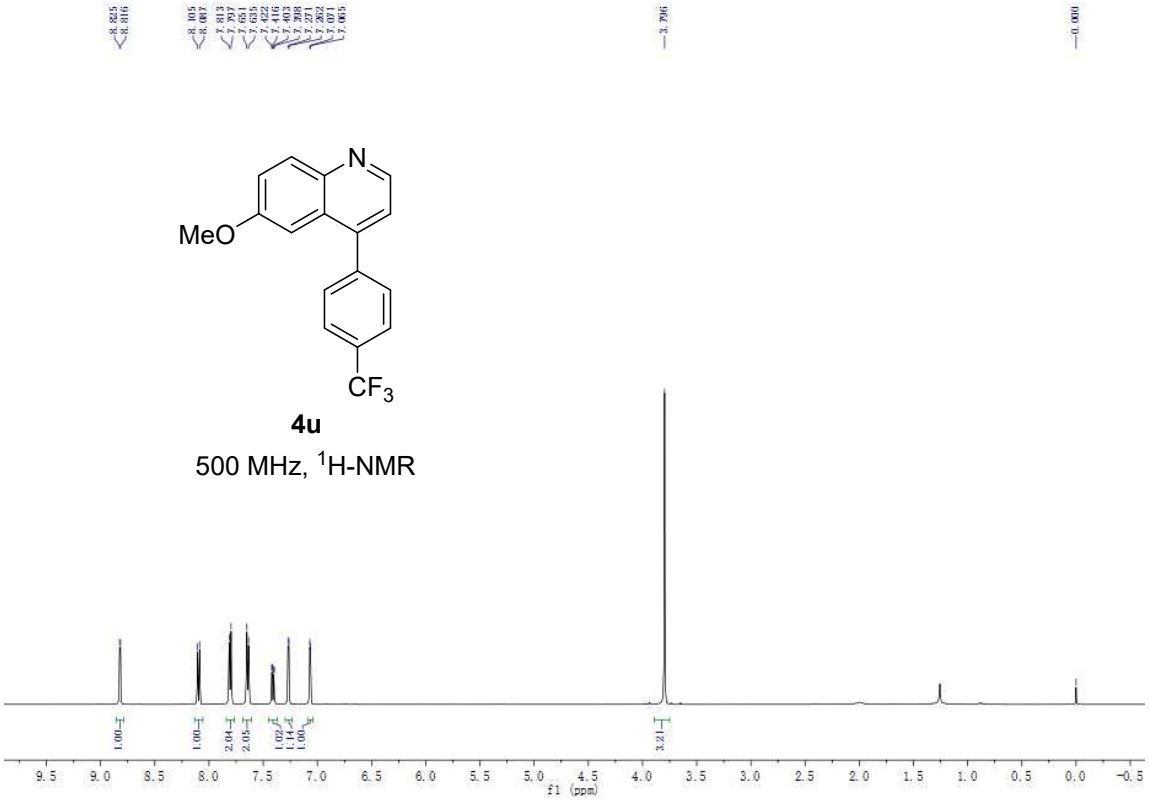
500 MHz, ^{1}H-NMR





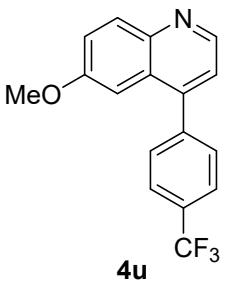
4t

125 MHz, ^{13}C-NMR



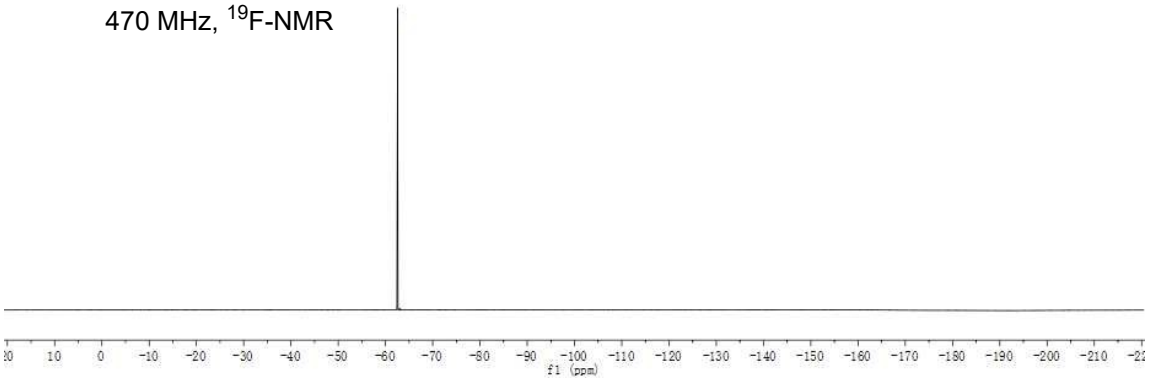
4u

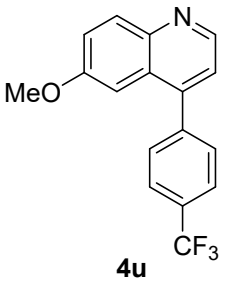
500 MHz, ^{1}H-NMR



4u

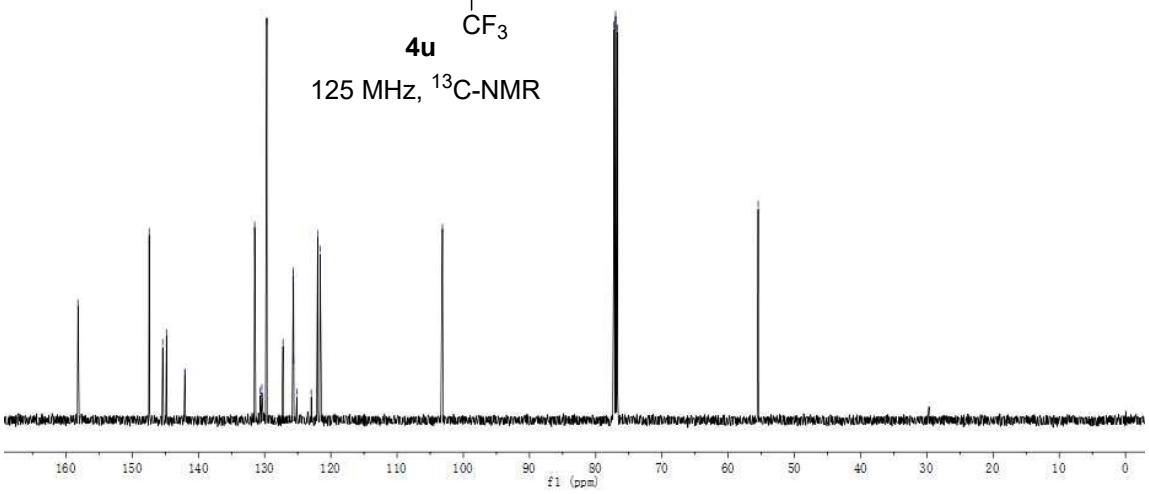
470 MHz, ^{19}F-NMR

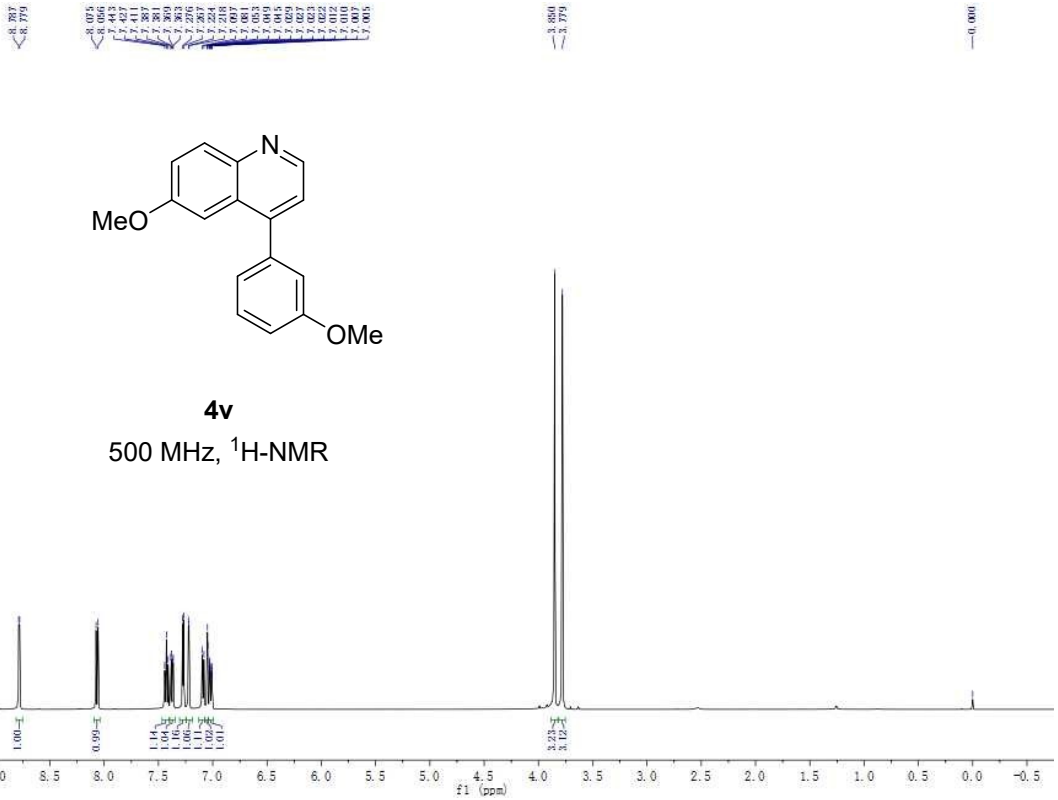




4u

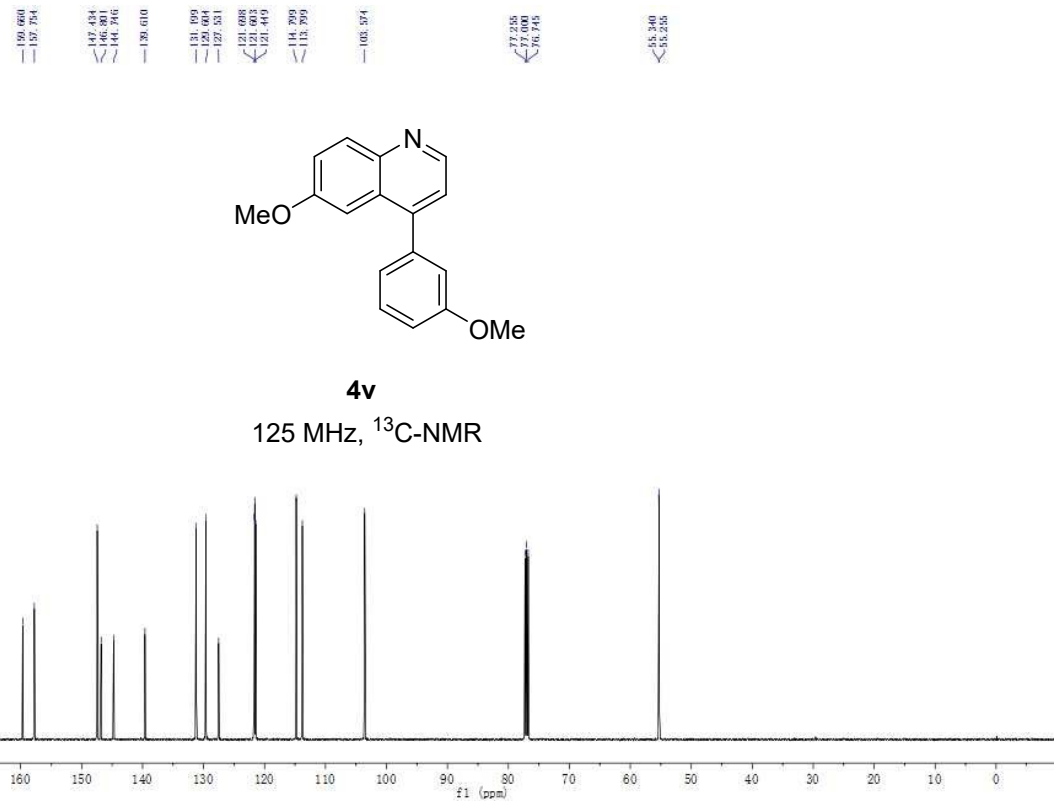
125 MHz, ^{13}C-NMR





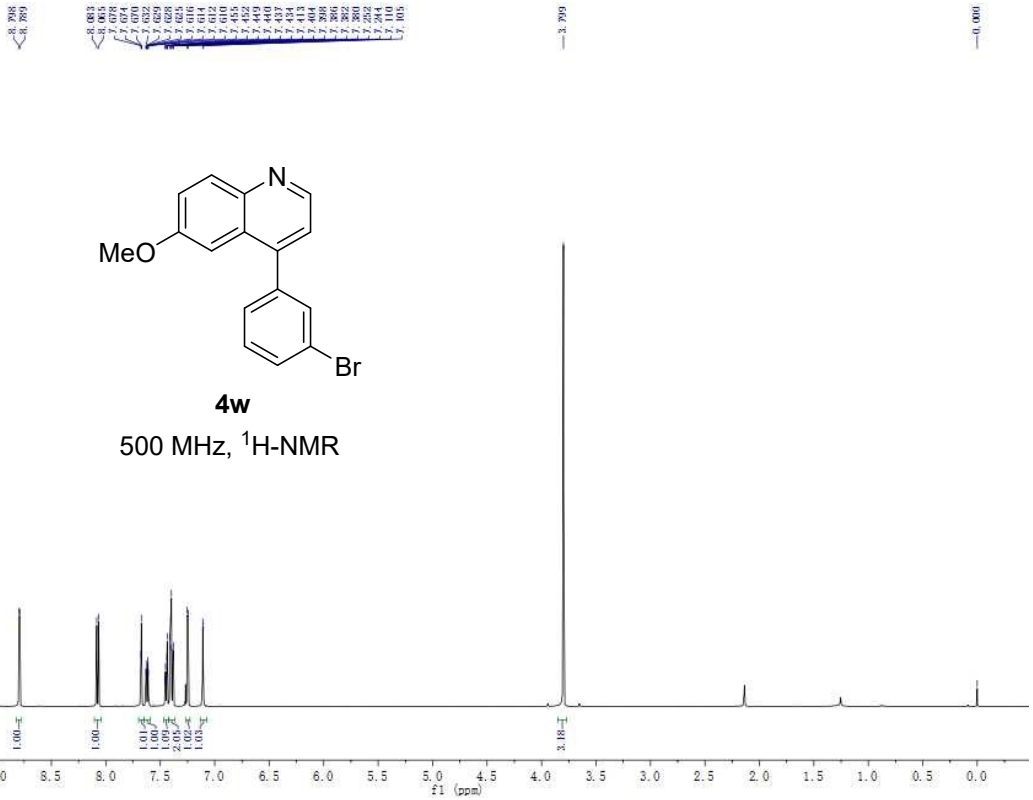
4v

500 MHz, ^{1}H-NMR



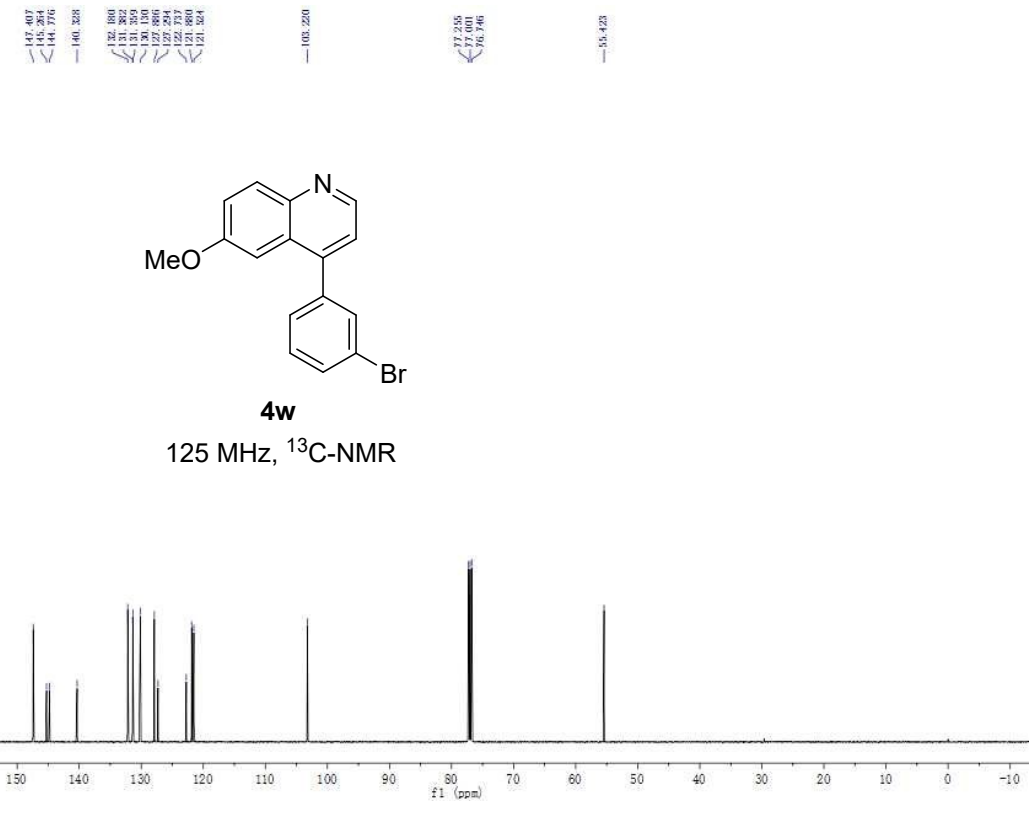
4v

125 MHz, ^{13}C-NMR



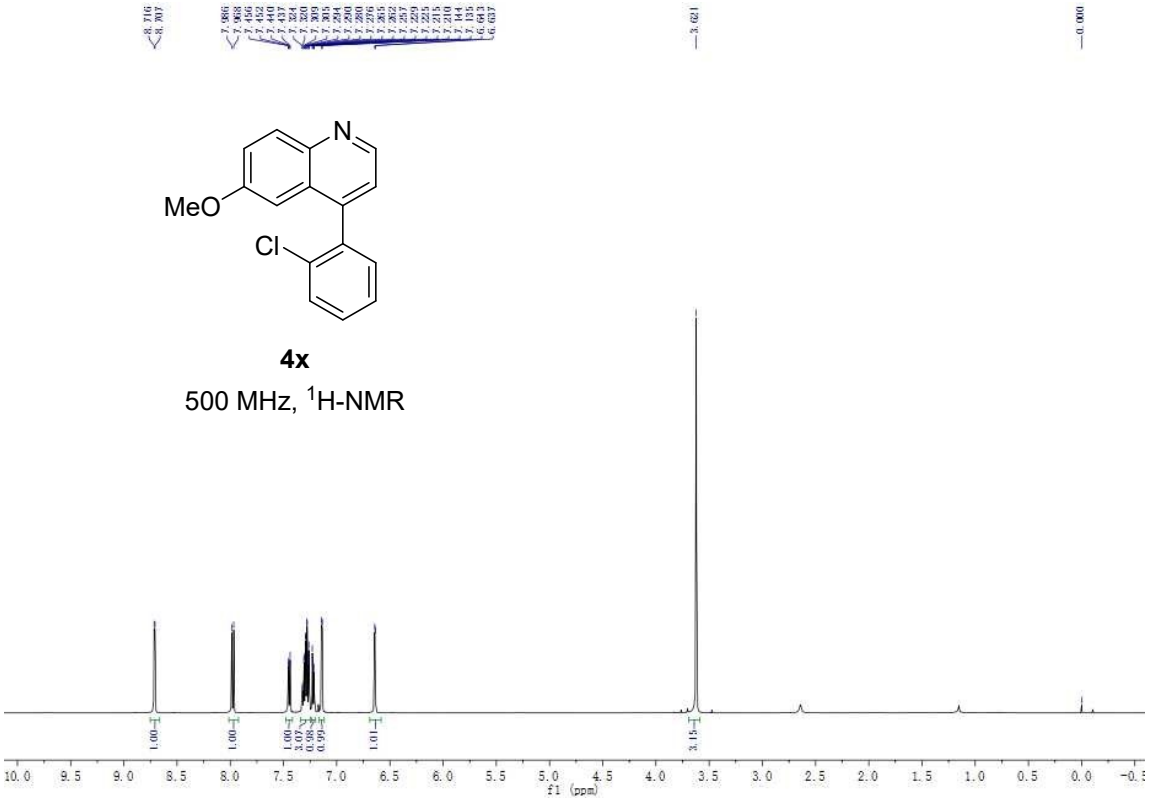
4w

500 MHz, ^{1}H-NMR



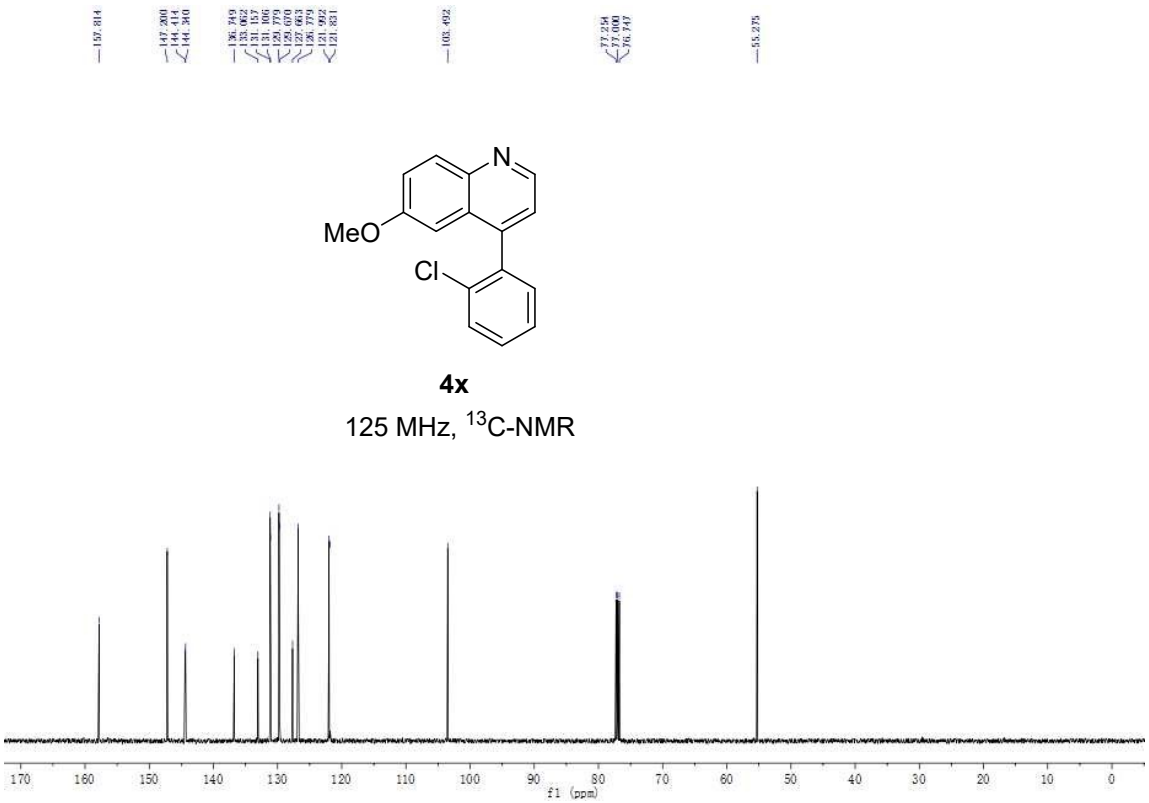
4w

125 MHz, ^{13}C-NMR



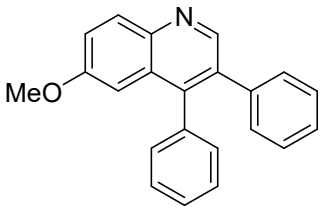
4x

500 MHz, ^{1}H-NMR



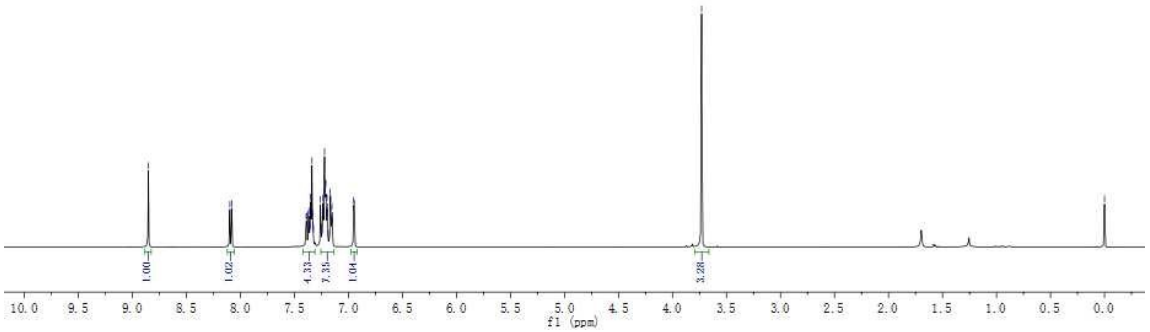
4x

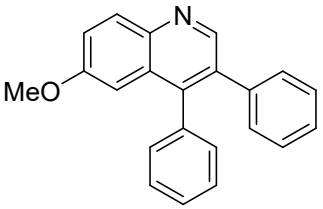
125 MHz, ^{13}C-NMR



4y

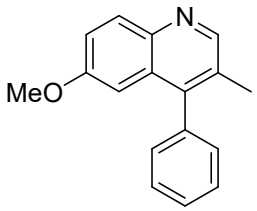
500 MHz, ^{1}H-NMR





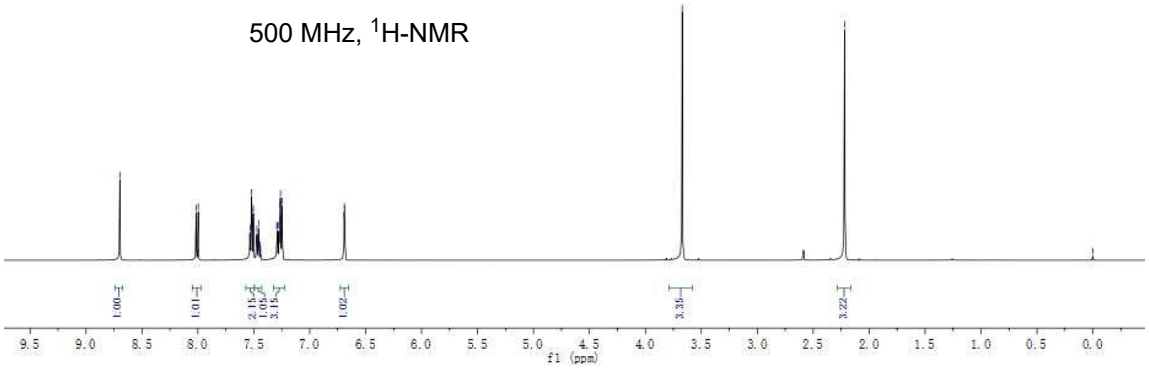
4y

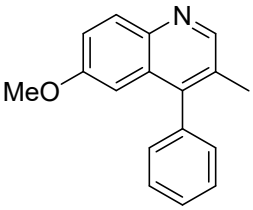
125 MHz, ^{13}C-NMR



4z

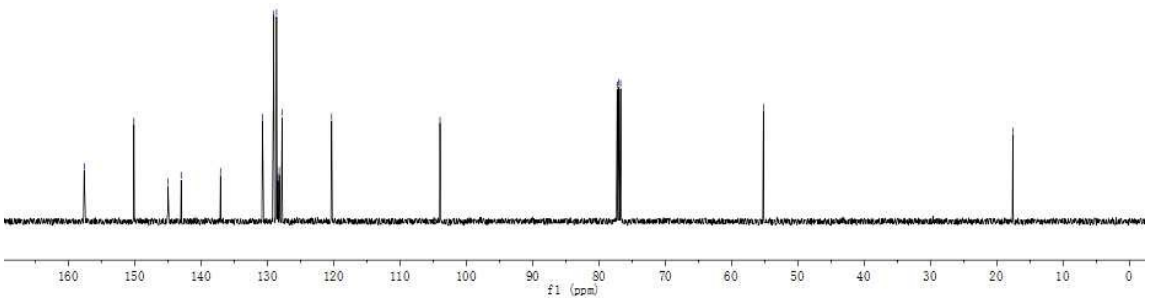
500 MHz, ^{1}H-NMR

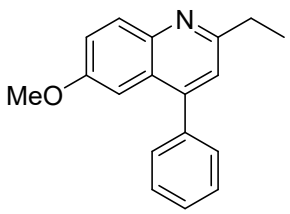




4z

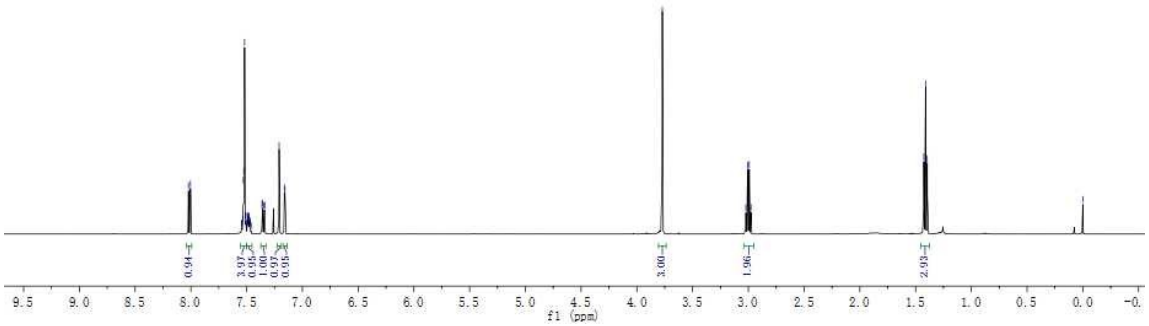
125 MHz, ^{13}C-NMR

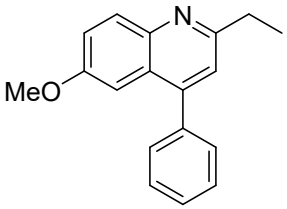




4zb

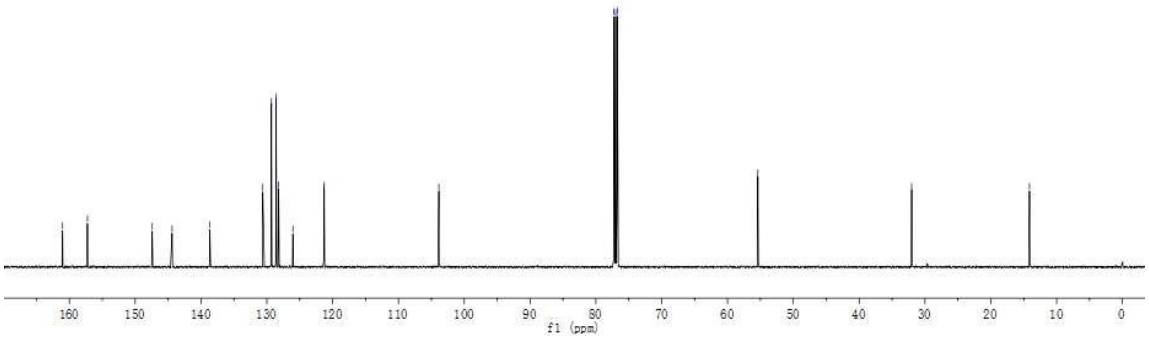
500 MHz, ^{1}H-NMR

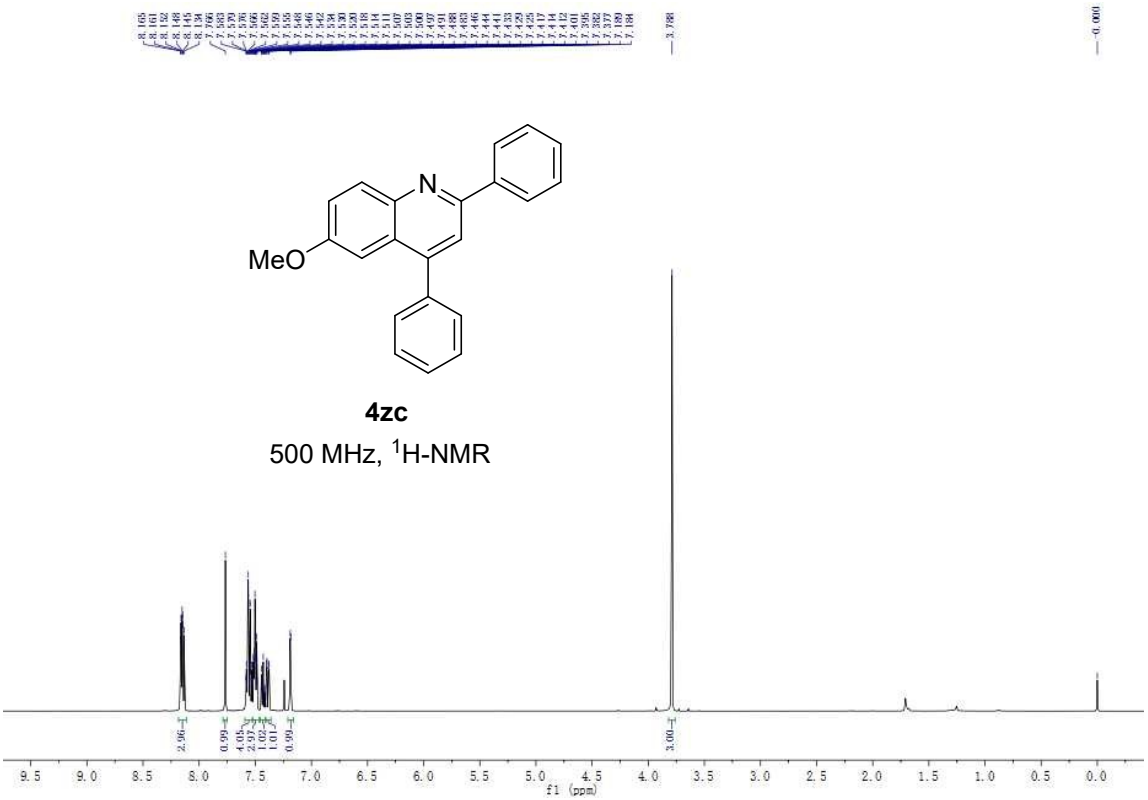




4zb

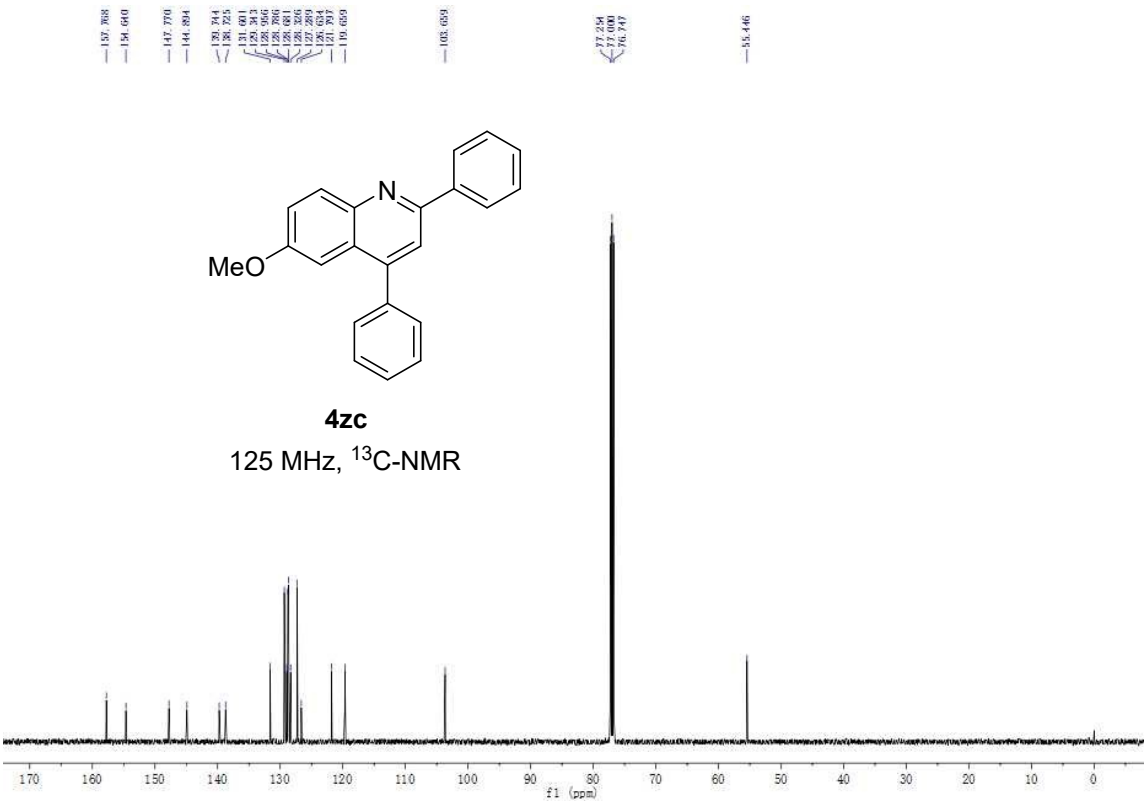
125 MHz, ^{13}C-NMR





4zc

500 MHz, ^{1}H-NMR



4zc

125 MHz, ^{13}C-NMR