Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

One-pot synthesis of pyranoquinolin-1-ones via Rh(III)-catalysed redox annulation of 3-carboxyquinolines and alkynes

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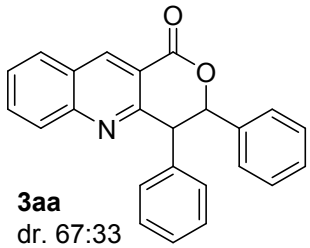
1. General Information

Unless otherwise noted, all of the reagents were purchased from commercial suppliers and used without purification. 1,2-Dichloroethane was dried by calcium hydride. Melting point was measured on a microscopic apparatus and uncorrected. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in deuterated chloroform or dimethyl sulfoxide. The chemical shifts (δ) are reported in relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet). Coupling constants (*J*) are reported in hertz. ^{13}C NMR spectra were recorded using a 100 MHz spectrometer. ^{19}F NMR spectra were recorded using a 376 MHz spectrometer. High-resolution mass spectrometry (HRMS) was performed on a Q-TOF spectrometer with micromass MS software using electrospray ionization (ESI). Column chromatography was carried out on silica gel (230-400 mesh) from Qingdao Marine Chemical Co. X-ray analysis was performed with a single-crystal X-ray diffractometer. **1a** was purchased from Bide Pharmatech Ltd., **2a**, **2q**, and **2u** were purchased from Sigma Aldrich and used without further purification. Other alkynes[1,2] and quinoline-3-carboxylic acids[3,4] were prepared according to the literature.

2. General catalytic procedure

$[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), quinolone-3-carboxylic acids (0.18 mmol, 1.8 equiv) and alkynes (0.1 mmol, 1.0 equiv) were weighted and placed in a dried Schlenk tube. Then 2.0 mL of DCE was added. The reaction mixture was stirred at 80 °C for 12 h (or 120 °C for 24 h). After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford the desired product.

3. Characterization of Products



3aa
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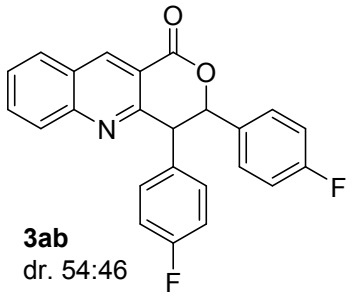
***trans*-3,4-Diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (22.2 mg, 63% yield); m. p. 160-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.63 – 7.56 (m, 1H), 7.32 – 7.17 (m, 10H), 6.00 (d, *J* = 5.3 Hz, 1H), 4.97 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 157.8, 150.3, 140.3, 138.4, 137.8, 132.6, 129.3, 128.8, 128.8, 128.6, 128.4, 127.5, 127.4, 127.0, 126.4, 119.0, 84.0, 52.3; HRMS (ESI)

Calcd. for $C_{24}H_{17}NO_2$: $[M+H]^+$, 352..1332. Found: m/z 352.1336.

***cis*-3,4-Diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (10.9 mg, 31% yield); m. p. 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.69 – 7.62 (m, 1H), 7.30 – 7.26 (m, 3H), 7.17 – 7.04 (m, 5H), 6.72 (d, J = 7.1 Hz, 2H), 6.11 (d, J = 3.1 Hz, 1H), 4.74 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 159.2, 150.3, 140.8, 136.1, 134.7, 133.0, 129.6, 129.4, 129.2, 128.2, 128.1, 127.6, 127.4, 127.3, 126.1, 118.9, 82.1,53.7; HRMS (ESI) Calcd. for $C_{24}H_{17}NO_2$: $[M+H]^+$, 352..1332. Found: m/z 352.1336.



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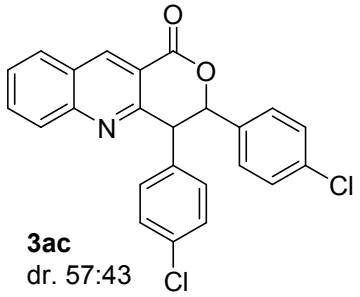
***trans*-3,4-Bis(4-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (19.1 mg, 49% yield); m. p. 162-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.00 (t, J = 9.0 Hz, 2H), 7.86 – 7.81 (m, 1H), 7.66 – 7.61 (m, 1H), 7.25 – 7.20 (m, 2H), 7.12 – 7.07 (m, 2H), 7.01 – 6.93 (m, 4H), 5.84 (d, J = 7.2 Hz, 1H), 4.86 (d, J = 7.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7, -114.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 162.6 (d, J = 248.2 Hz, J_{CF}), 162.1 (d, J = 246.0 Hz, J_{CF}), 161.3, 160.8, 157.7, 150.2, 140.6, 133.3 (d, J = 3.4 Hz, J_{CF}), 132.9, 130.8 (d, J = 8.0 Hz, J_{CF}), 129.3 (d, J = 3.8 Hz, J_{CF}), 128.5 (d, J = 8.3 Hz, J_{CF}), 127.7, 127.0, 118.7, 115.7 (d, J = 13.5 Hz, J_{CF}), 115.5 (d, J = 13.9 Hz, J_{CF}), 83.6, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{15}F_2NO_2$: $[M+H]^+$, 388.1144. Found: m/z 388.1145.

***cis*-3,4-Bis(4-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (15.8 mg, 41% yield); m. p. 183-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.08 (dd, J = 16.2, 8.6 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.70 – 7.65 (m, 1H), 7.13 – 7.07 (m, 2H), 7.02 – 6.96 (m, 2H), 6.84 – 6.77 (m, 2H), 6.70 – 6.64 (m, 2H), 6.08 (d, J = 3.2 Hz, 1H), 4.69 (d, J = 3.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.12, -114.43; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.4 (d, J = 235.8 Hz, J_{CF}), 163.2 (d, J = 245.0 Hz, J_{CF}), 158.6, 150.4, 141.1, 133.2, 131.1, 131.0, 129.5, 129.2, 127.9, 127.8, 127.3, 118.6, 115.4 (d, J = 4.4 Hz, J_{CF}), 115.2 (d, J = 4.3 Hz, J_{CF}), 81.3, 52.9; HRMS (ESI) Calcd. for $C_{24}H_{15}F_2NO_2$: $[M+H]^+$, 388.1144. Found: m/z 388.1145.



3ac
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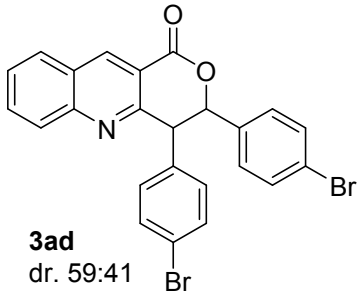
***trans*-3,4-Bis(4-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (19.6 mg, 48% yield); m. p. 200 – 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.00 (t, J = 8.7 Hz, 2H), 7.86 – 7.81 (m, 1H), 7.66 – 7.61 (m, 1H), 7.29 – 7.23 (m, 4H), 7.21 – 7.17 (m, 2H), 7.10 – 7.05 (m, 2H), 5.84 (d, J = 7.2 Hz, 1H), 4.84 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.3, 150.2, 140.7, 135.9, 135.7, 134.6, 133.6, 132.9, 130.5, 129.3, 129.3, 129.0, 128.8, 128.0, 127.7, 127.0, 118.6, 83.3, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{15}Cl_2NO_2$: $[M+H]^+$, 420.0553. Found: m/z 420.0555.

***cis*-3,4-Bis(4-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (14.8 mg, 36% yield); m. p. 206 – 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.07 (dd, J = 13.8, 8.6 Hz, 2H), 7.92 – 7.87 (m, 1H), 7.71 – 7.65 (m, 1H), 7.31 – 7.27 (m, 2H), 7.12 – 7.06 (m, 4H), 6.68 – 6.64 (m, 2H), 6.08 (d, J = 3.2 Hz, 1H), 4,69 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 150.3, 141.2, 134.4, 134.3, 133.7, 133.3, 133.0, 130.8, 129.5, 129.2, 128.6, 128.5, 127.9, 127.4, 127.3, 118.5, 81.1, 52.9; HRMS (ESI) Calcd. for $C_{24}H_{15}Cl_2NO_2$: $[M+H]^+$, 420.0553. Found: m/z 420.0555.



3ad
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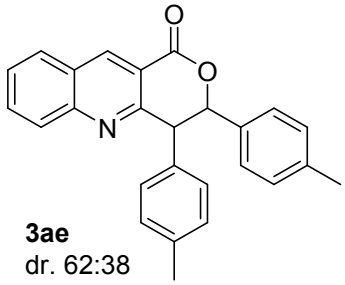
***trans*-3,4-Bis(4-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (26.2 mg, 51% yield); m. p. 182-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.99 (t, J = 9.2 Hz, 2H), 7.83 (t, J = 7.4 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 8.1 Hz, 4H), 7.13 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 5.83 (d, J = 7.0 Hz, 1H), 4.82 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.2, 150.2, 140.7, 136.5, 136.3, 132.9, 131.9, 131.8, 130.8, 129.3, 129.3, 128.3, 127.7, 127.0, 122.8, 121.7, 118.6, 83.3, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{15}Br_2NO_2$: $[M+H]^+$, 509.9522. Found: m/z 509.9528.

***cis*-3,4-Bis(4-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (17.8 mg, 35% yield); m. p. 200 – 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.07 (dd, J = 14.1, 8.6 Hz, 2H), 7.92 – 7.86 (m, 1H), 7.71 – 7.65 (m, 1H), 7.47 – 7.42 (m, 2H), 7.25 – 7.22 (m, 2H), 7.04 (d, J = 8.3 Hz, 2H), 6.64 – 6.58 (m, 2H), 6.06 (d, J = 3.2 Hz, 1H), 4.68 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 158.2, 150.3, 141.2, 134.9, 133.5, 133.3, 131.6, 131.5, 131.1, 129.5, 129.2, 127.9, 127.7, 127.3, 122.4, 121.9, 118.5, 81.1, 52.8; HRMS (ESI) Calcd. for $C_{24}H_{15}Br_2NO_2$: $[M+H]^+$, 509.9522. Found: m/z 509.9524.



3ae
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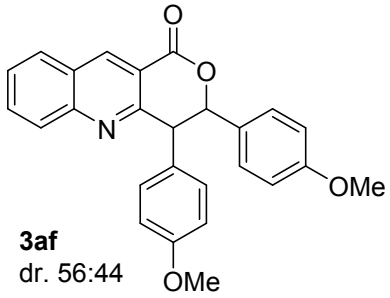
***trans*-3,4-Di-p-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (19.9 mg, 53% yield); m. p. 169-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.62 – 7.56 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.10 (s, 4H), 7.05 (d, J = 8.0 Hz, 2H), 5.98 (d, J = 4.6 Hz, 1H), 4.95 (d, J = 4.6 Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 158.0, 150.3, 140.2, 138.1, 137.1, 135.7, 135.0, 132.5, 129.5, 129.3, 129.3, 129.2, 128.5, 127.3, 127.0, 126.3, 119.1, 83.9, 51.6, 21.1, 21.0; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_2$: $[M+H]^+$, 380.1645. Found: m/z 380.1649.

***cis*-3,4-Di-p-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (12.6 mg, 33% yield); m. p. 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.08 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.85 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.64 (d, J = 7.8 Hz, 2H), 6.05 (d, J = 2.3 Hz, 1H), 4.68 (d, J = 2.4 Hz, 1H), 2.33 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.6, 150.3, 140.8, 137.8, 137.0, 133.1, 132.9, 131.8, 129.4, 129.4, 129.2, 128.9, 128.8, 127.5, 127.2, 126.1, 118.9, 82.2, 53.3, 21.2, 21.0; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_2$: $[M+H]^+$, 380.1645. Found: m/z 380.1650.



3af
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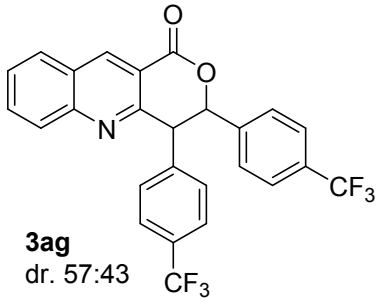
***trans*-3,4-Bis(4-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (16.5 mg, 40% yield); m. p. 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.63 – 7.57 (m, 1H), 7.20 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.85 – 6.80 (m, 2H), 6.80 – 6.74 (m, 2H), 5.90 (d, J = 5.6 Hz, 1H), 4.90 (d, J = 5.6 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 159.4, 158.7, 158.4, 150.2, 140.3, 132.6, 130.4, 129.9, 129.9, 129.3, 127.9, 127.4, 126.9, 119.0, 83.9, 55.2, 55.2, 51.4; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_4$: $[M+H]^+$, 412.1543. Found: m/z 412.1545.

***cis*-3,4-Bis(4-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (12.9 mg, 31% yield); m. p. 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 7.7 Hz, 1H), 7.89 – 7.83 (m, 1H),

7.03 (d, J = 8.6 Hz, 2H), 6.80 (dd, J = 6.9, 1.9 Hz, 2H), 6.64 (s, 4H), 6.02 (d, J = 3.2 Hz, 1H), 4.64 (d, J = 3.1 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.6, 159.4, 158.7, 150.3, 140.8, 132.9, 130.7, 129.4, 129.2, 128.3, 127.6, 127.5, 127.2, 126.9, 118.9, 55.2, 55.1, 53.1; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_4$: $[M+H]^+$, 412.1543. Found: m/z 412.1546.



3ag
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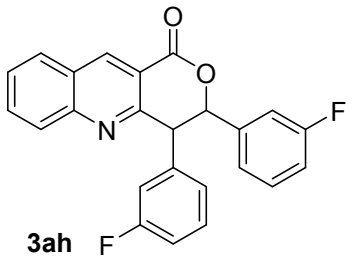
***trans*-3,4-Bis(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (24.2 mg, 50% yield); m. p. 149-150 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.99 (t, J = 8.1 Hz, 2H), 7.84 (t, J = 8.1 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 8.8 Hz, 4H), 7.40 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.98 (d, J = 6.9 Hz, 1H), 4.97 (d, J = 6.9 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6, -62.8; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 156.7, 150.2, 141.2 (d, J = 38.2 Hz, J_{CF}), 140.8, 133.1, 131.0 (d, J = 32.8 Hz, J_{CF}), 130.0 (d, J = 32.4 Hz, J_{CF}), 129.5, 129.4, 127.9, 127.1, 127.0, 125.8 (q, J = 3.7 Hz, J_{CF}), 125.7 (q, J = 4.5 Hz, J_{CF}), 123.9 (q, J = 274.3 Hz, J_{CF}), 123.7 (q, J = 274.3 Hz, J_{CF}), 118.5, 83.0, 52.6; HRMS (ESI) Calcd. for $C_{26}H_{15}F_6NO_2$: $[M+H]^+$, 488.1080. Found: m/z 488.1082.

***cis*-3,4-Bis(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (18.1 mg, 37% yield); m. p. 202-203 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.08 (t, J = 9.2 Hz, 2H), 7.94 – 7.87 (m, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.35 (dd, J = 11.7, 8.3 Hz, 4H), 6.88 (d, J = 8.1 Hz, 2H), 6.21 (d, J = 2.8 Hz, 1H), 4.85 (d, J = 3.1 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6, -62.8; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 157.7, 150.4, 141.3, 139.6, 138.5, 133.5, 130.7 (d, J = 31.7 Hz, J_{CF}), 130.3 (d, J = 31.7 Hz, J_{CF}), 129.8, 129.5, 129.2, 128.0, 127.3, 126.3, 125.5 (q, J = 3.6 Hz, J_{CF}), 125.3 (q, J = 4.3 Hz, J_{CF}), 123.8 (q, J = 273.5 Hz, J_{CF}), 123.7 (q, J = 272.8 Hz, J_{CF}), 118.4, 80.9, 53.0; HRMS (ESI) Calcd. for $C_{26}H_{15}F_6NO_2$: $[M+H]^+$, 488.1080. Found: m/z 488.1082.



3ah
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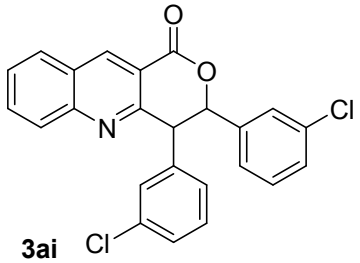
***trans*-3,4-Bis(3-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (19.9 mg, 51% yield); m. p. 169-170 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.86 – 7.81 (m, 1H),

7.30 – 7.20 (m, 2H), 7.03 (d, J = 7.6 Hz, 2H), 7.00 – 6.92 (m, 3H), 6.89 (dt, J = 9.8, 2.0 Hz, 1H), 5.92 (d, J = 6.3 Hz, 1H), 4.89 (d, J = 6.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7, -112.1; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 162.8 (d, J = 247.3 Hz, J_{CF}), 162.7 (d, J = 247.3 Hz, J_{CF}), 156.9, 150.2, 140.6, 140.0 (d, J = 6.9 Hz, J_{CF}), 139.8 (d, J = 6.9 Hz, J_{CF}), 132.9, 130.3 (d, J = 7.0 Hz, J_{CF}), 130.2 (d, J = 6.9 Hz, J_{CF}), 129.4 (d, J = 1.4 Hz, J_{CF}), 127.7, 127.0, 124.7 (d, J = 2.8 Hz, J_{CF}), 122.2 (d, J = 3.0 Hz, J_{CF}), 118.6, 116.0 (d, J = 22.0 Hz, J_{CF}), 115.7 (d, J = 21.0 Hz, J_{CF}), 114.7 (d, J = 20.9 Hz, J_{CF}), 113.7 (d, J = 18.4 Hz, J_{CF}), 83.1, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{15}F_2NO_2$: $[M+H]^+$, 388.1144. Found: m/z 388.1146.

***cis*-3,4-Bis(3-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (17.1 mg, 44% yield); m. p. 150-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.71 – 7.65 (m, 1H), 7.33 – 7.28 (m, 1H), 7.11 – 7.04 (m, 1H), 7.03 – 6.97 (m, 2H), 6.92 – 6.81 (m, 2H), 6.54 (d, J = 7.8 Hz, 1H), 6.46 (dt, J = 9.7, 2.1 Hz, 1H), 6.11 (d, J = 3.2 Hz, 1H), 4.74 (d, J = 3.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.2, -112.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.7 (d, J = 246.3 Hz, J_{CF}), 162.4 (d, J = 246.3 Hz, J_{CF}), 158.1, 150.3, 141.2, 138.4 (d, J = 4.6 Hz, J_{CF}), 136.9 (d, J = 7.1 Hz, J_{CF}), 133.3, 130.0 (d, J = 8.1 Hz, J_{CF}), 129.8 (d, J = 8.6 Hz, J_{CF}), 129.5, 129.2, 127.9, 127.3, 125.1 (d, J = 3.0 Hz, J_{CF}), 121.5 (d, J = 2.9 Hz, J_{CF}), 118.5, 116.5 (d, J = 22.3 Hz, J_{CF}), 115.4 (d, J = 21.1 Hz, J_{CF}), 114.6 (d, J = 20.8 Hz, J_{CF}), 113.2 (d, J = 23.2 Hz, J_{CF}), 80.9, 53.1; HRMS (ESI) Calcd. for $C_{24}H_{15}F_2NO_2$: $[M+H]^+$, 388.1144. Found: m/z 388.1148.

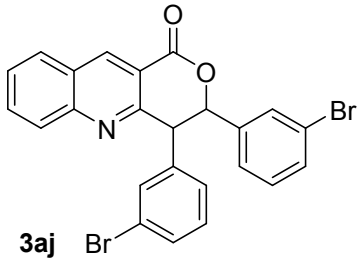


3ai
dr. 60:40

***trans*-3,4-Bis(3-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (21.6 mg, 52% yield); m. p. 158 – 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.01 (dd, J = 15.4, 8.6 Hz, 2H), 7.87 – 7.81 (m, 1H), 7.67 – 7.61 (m, 1H), 7.33 (d, 1.7 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.25 (d, J = 1.2 Hz, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.17 (t, J = 1.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.04 (dt, J = 7.2, 1.4 Hz, 1H), 5.88 (d, J = 6.4 Hz, 1H), 4.86 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 156.8, 150.2, 140.7, 139.5, 139.2, 134.7, 134.6, 133.0, 130.0, 129.8, 129.4, 129.4, 129.1, 128.9, 128.0, 127.8, 127.2, 127.0, 126.7, 124.6, 118.5, 83.0, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{15}Cl_2NO_2$: $[M+H]^+$, 420.0553. Found: m/z 420.0556.

***cis*-3,4-Bis(3-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (14.8 mg, 35% yield); m. p. 166 – 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.08 (dd, J = 17.6, 8.5 Hz, 2H), 7.93 – 7.87 (m, 1H), 7.71 – 7.66 (m, 1H), 7.31 – 7.27 (m, 1H), 7.24 (d, J = 7.9 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.08 – 7.02 (m,

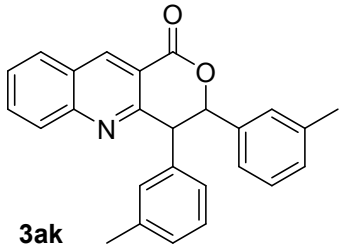
2H), 6.70 (t, *J* = 1.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 4.70 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 157.9, 150.4, 141.2, 137.7, 136.4, 134.4, 134.2, 133.3, 129.7, 129.6, 129.5, 129.5, 129.2, 128.6, 127.9, 127.6, 127.3, 126.3, 124.1, 118.5, 80.9, 53.0; HRMS (ESI) Calcd. for $C_{24}H_{15}Cl_2NO_2$: $[M+H]^+$, 420.0553. Found: m/z 420.0558.



3aj
dr. 63:37

***trans*-3,4-Bis(3-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (28.3 mg, 56% yield); m. p. 178 – 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.05 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.67 – 7.61 (m, 1H), 7.48 (s, 1H), 7.45 – 7.36 (m, 2H), 7.33 (t, *J* = 1.7 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 5.1 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 5.86 (d, *J* = 6.5 Hz, 1H), 4.84 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 163.9, 156.8, 150.2, 140.7, 139.8, 139.4, 133.0, 132.0, 131.8, 130.9, 130.3, 130.1, 129.6, 129.4, 129.4, 127.8, 127.7, 127.1, 125.0, 122.8, 118.5, 83.0, 52.4; HRMS (ESI) Calcd. for $C_{24}H_{15}Br_2NO_2$: $[M+H]^+$, 509.9522. Found: m/z 509.9520.

***cis*-3,4-Bis(3-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (16.8 mg, 33% yield); m. p. 183-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.17 (s, 1H), 8.08 (dd, *J* = 17.8, 8.5 Hz, 2H), 7.93 – 7.86 (m, 1H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 12.8 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.84 (s, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 3.1 Hz, 1H), 4.68 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.6, 157.9, 150.4, 141.2, 137.9, 136.7, 133.3, 132.5, 131.6, 130.8, 129.9, 129.7, 129.5, 129.3, 129.2, 128.0, 127.9, 127.3, 124.6, 122.5, 122.4, 118.5, 80.9, 53.0; HRMS (ESI) Calcd. for $C_{24}H_{15}Br_2NO_2$: $[M+H]^+$, 509.9522. Found: m/z 509.9519.

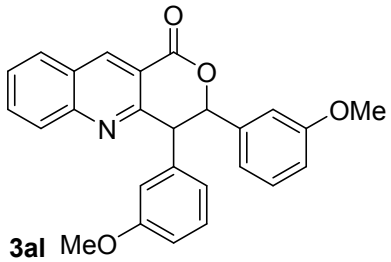


3ak
dr. 64:36

***trans*-3,4-Di-m-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (22.6 mg, 60% yield); m. p. 151 – 152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.01 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.61 – 7.55 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 3.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.08 – 6.99 (m, 5H), 6.00 (d, *J* = 4.2 Hz, 1H), 4.95 (d, *J* = 4.2 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.6, 157.7, 150.3, 140.1, 138.8,

138.4, 138.3, 138.0, 132.5, 129.3, 129.2, 129.2, 129.0, 128.7, 128.4, 128.2, 127.3, 127.0, 126.9, 125.6, 123.2, 119.1, 83.8 51.9, 21.4, 21.4; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_2$: $[M+H]^+$, 380.1645. Found: m/z 380.1647.

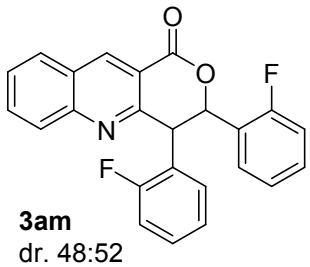
***cis*-3,4-Di-m-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (12.9 mg, 34% yield); m. p. 186 – 187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.68 – 7.62 (m, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.00 – 6.88 (m, 4H), 6.50 (t, J = 7.3 Hz, 2H), 6.05 (d, J = 3.1 Hz, 1H), 4.68 (d, J = 3.2 Hz, 1H), 2.26 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 159.4, 150.3, 140.8, 137.7, 137.6, 135.9, 134.6, 132.9, 130.3, 129.4, 129.2, 128.9, 128.1, 127.9, 127.9, 127.5, 127.2, 127.0, 126.7, 123.2, 119.0, 82.3, 53.6, 21.3, 21.3; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_2$: $[M+H]^+$, 380.1645. Found: m/z 380.1646.



3al
dr. 67:33

***trans*-3,4-Bis(3-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (23.3 mg, 57% yield); m. p. 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.83 – 7.78 (m, 1H), 7.63 – 7.57 (m, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.82 – 6.73 (m, 4H), 5.98 (d, J = 4.8 Hz, 1H), 4.93 (d, J = 4.8 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 159.8, 159.7, 157.5, 150.3, 140.2, 140.0, 139.4, 132.6, 129.8, 129.6, 129.3, 129.3, 127.4, 127.0, 120.9, 119.0, 118.5, 114.9, 113.9, 112.7, 112.1, 83.6, 55.2, 52.1; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_4$: $[M+H]^+$, 412.1543. Found: m/z 412.1545.

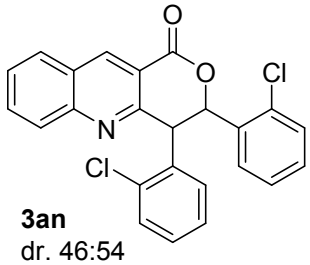
***cis*-3,4-Bis(3-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (11.6 mg, 28% yield); m. p. 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.68 – 7.62 (m, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.71 – 6.65 (m, 1H), 6.63 (s, 1H), 6.32 (d, J = 7.7 Hz, 1H), 6.24 (t, J = 2.0 Hz, 1H), 6.07 (d, J = 3.2 Hz, 1H), 4.70 (d, J = 3.2 Hz, 1H), 3.64 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 159.5, 159.2, 158.9, 150.3, 140.8, 137.6, 136.2, 133.0, 129.4, 129.2, 129.2, 129.1, 127.6, 127.3, 121.8, 118.9, 118.3, 115.4, 114.7, 113.1, 111.2, 81.9, 55.2, 55.0, 53.6; HRMS (ESI) Calcd. for $C_{26}H_{21}NO_4$: $[M+H]^+$, 412.1543. Found: m/z 412.1544.



3am
dr. 48:52

***trans*-3,4-Bis(2-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (14.1 mg, 36% yield); m. p. 163 – 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.11(d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.88 (td, J = 7.0, 1.2 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.16 – 7.06 (m, 2H), 7.01 – 6.95 (m, 1H), 6.91 (t, J = 8.2 Hz, 2H), 6.83 – 6.70 (m, 2H), 6.41 (d, J = 3.2 Hz, 1H), 5.27 (d, J = 3.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6, -119.1; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 160.6 (d, J = 245.3 Hz, J_{CF}), 159.4 (d, J = 248.8 Hz, J_{CF}), 158.0, 150.4, 140.8, 133.1, 130.5 (d, J = 3.5 Hz, J_{CF}), 129.9 (d, J = 8.2 Hz, J_{CF}), 129.4 (d, J = 2.6 Hz, J_{CF}), 129.3 (d, J = 2.7 Hz, J_{CF}), 127.7, 127.5 (d, J = 3.2 Hz, J_{CF}), 127.3, 123.9 (d, J = 3.6 Hz, J_{CF}), 123.8 (d, J = 3.6 Hz, J_{CF}), 123.3 (d, J = 12.5 Hz, J_{CF}), 122.6 (d, J = 14.7 Hz, J_{CF}), 119.1, 115.4 (d, J = 22.9 Hz, J_{CF}), 114.8 (d, J = 20.7 Hz, J_{CF}), 75.9 (d, J = 3.1 Hz, J_{CF}), 44.6; HRMS (ESI) Calcd. for $C_{24}H_{15}F_2NO_2$: $[M+H]^+$, 388.1144. Found: m/z 388.1147.

***cis*-3,4-Bis(2-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (15.0 mg, 39% yield); m. p. 173 – 174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.03 – 7.93 (m, 2H), 7.79 (td, J = 7.0, 1.3 Hz, 1H), 7.61 (t, J = 7.9 Hz, 1H), 7.45 (td, J = 7.6, 1.3 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.06 – 6.97 (m, 2H), 6.97 – 6.89 (m, 2H), 6.25 (d, J = 9.2 Hz, 1H), 5.18 (d, J = 9.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8, -116.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.1 (d, J = 245.3 Hz, J_{CF}), 160.0 (d, J = 248.8 Hz, J_{CF}), 157.3, 150.1, 140.6, 132.7, 131.3 (d, J = 4.4 Hz, J_{CF}), 130.6 (d, J = 8.5 Hz, J_{CF}), 129.6, 129.5, 129.3, 128.3 (d, J = 3.1 Hz, J_{CF}), 127.5, 126.9, 124.3, 124.2 (d, J = 3.6 Hz, J_{CF}), 124.2 (d, J = 3.7 Hz, J_{CF}), 123.9 (d, J = 13.8 Hz, J_{CF}), 118.5, 115.7 (d, J = 6.0 Hz, J_{CF}), 115.5 (d, J = 5.8 Hz, J_{CF}), 48.1; HRMS (ESI) Calcd. for $C_{24}H_{15}F_2NO_2$: $[M+H]^+$, 388.1144. Found: m/z 388.1147.

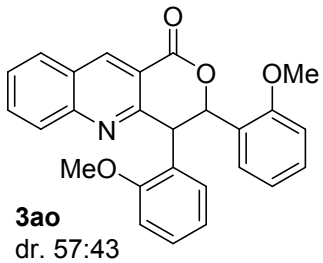


3an
dr. 46:54

***trans*-3,4-Bis(2-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (13.0 mg, 31% yield); m. p. 170 – 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.69 – 7.63 (m, 1H), 7.37 (dd, J = 8.0, 1.0 Hz, 1H), 7.24 (td, J = 7.7, 1.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.12 – 7.04 (m, 2H), 7.03 – 6.97 (m ,1H), 6.85 – 6.78 (m, 2H), 6.50 (d,

J = 3.3 Hz, 1H), 5.66 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.3, 158.5, 150.6, 140.9, 135.7, 133.1, 133.0, 132.9, 132.5, 130.6, 129.7, 129.6, 129.4, 129.4, 128.9, 128.6, 128.3, 127.7, 127.2, 126.6, 126.3, 119.1, 78.6, 45.9; HRMS (ESI) Calcd. for $C_{24}H_{15}Cl_2NO_2$: $[M+H]^+$, 420.0553. Found: m/z 420.0554.

***cis*-3,4-Bis(2-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (15.4 mg, 37% yield); m. p. 173 – 174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.09 (s, 1H), 7.99 (dd, *J* = 11.5, 8.5 Hz, 2H), 7.84 – 7.78 (m, 1H), 7.66 – 7.59 (m, 2H), 7.34 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.17 (m, 3H), 7.14 (td, *J* = 7.6, 1.4 Hz, 1H), 7.03 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.51 (d, *J* = 9.8 Hz, 1H), 5.51 (d, *J* = 9.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 158.0, 150.2, 140.7, 134.9, 134.3, 134.2, 133.9, 132.7, 131.7, 130.2, 129.9, 129.7, 129.5, 129.2, 129.1, 128.9, 127.5, 127.0, 126.9, 126.8, 118.5, 79.2, 49.8; HRMS (ESI) Calcd. for $C_{24}H_{15}Cl_2NO_2$: $[M+H]^+$, 420.0553. Found: m/z 420.0552.



3ao
dr. 57:43

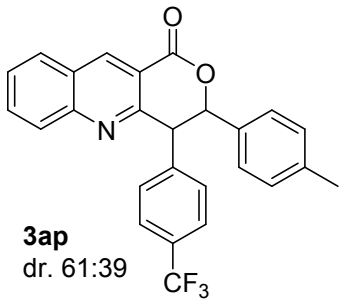
(20.6 mg, 50% yield)

***trans*-3,4-Bis(2-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.75 (td, *J* = 6.9, 1.2 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.90 – 6.79 (m, 6H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 6.6 Hz, 1H), 5.30 (d, *J* = 6.7 Hz, 1H), 3.68 (s, 3H), 3.62 (s, 3H).

***cis*-3,4-Bis(2-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.82 (td, *J* = 7.0, 1.3 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.10 – 7.04 (m, 1H), 6.68 (q, *J* = 6.6 Hz, 2H), 6.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 3.3 Hz, 1H), 5.42 (d, *J* = 3.0 Hz, 1H), 3.90 (s, 3H), 3.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.6, 160.1, 159.1, 157.4, 157.1, 156.8, 155.8, 150.2, 150.1, 140.0, 139.6, 132.5, 132.2, 130.8, 130.3, 129.5, 129.3, 129.2, 129.2, 129.2, 128.6, 128.5, 128.4, 127.6, 127.2, 127.1, 127.0, 126.9, 126.9, 126.8, 126.3, 125.0, 124.4, 120.5, 120.2, 120.1, 120.0, 119.8, 119.6, 111.0, 110.5, 110.2, 108.9, 78.5, 77.2, 77.2, 55.3, 55.3, 55.3, 54.7, 47.4.

HRMS (ESI) Calcd. for $C_{26}H_{21}NO_4$: $[M+H]^+$, 412.1543. Found: m/z 412.1547.



3ap
dr. 61:39

(39.4 mg, 91% yield);

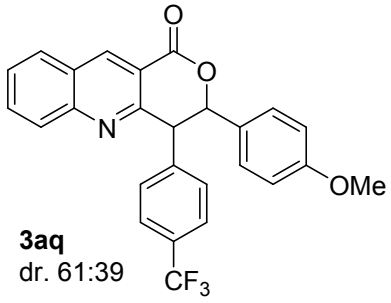
***trans*-3-(P-tolyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.97 (t, *J* = 6.4 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.62 – 7.58 (m, 1H), 7.52 (d, *J* = 9.9 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 1.8 Hz, 2H), 5.92 (d, *J* = 6.2 Hz, 1H), 5.00 (d, *J* = 6.2 Hz, 1H), 2.27 (s, 3H).

***cis*-3-(P-tolyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.02 (t, *J* = 5.7 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.64 – 7.62 (m, 1H), 7.55 (s, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.05 (s, 2H), 5.99 (d, *J* = 6.0 Hz, 1H), 4.88 (d, *J* = 6.0 Hz, 1H), 2.32 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56, -62.72.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 165.0, 158.9, 158.4, 150.4, 150.3, 141.1, 141.0, 140.2, 139.1, 138.3, 137.4, 133.2, 133.1, 132.6, 131.2, 129.9, 129.5, 129.4, 129.2, 129.2, 129.2, 129.1, 129.1, 127.8, 127.7, 127.3, 127.2, 126.5, 125.8, 125.2 (q, *J* = 3.8 Hz, J_{CF}), 125.0 (q, *J* = 3.6 Hz, J_{CF}), 124.0 (q, *J* = 282.5 Hz, J_{CF}), 123.9 (q, *J* = 283.0 Hz, J_{CF}), 118.8, 118.6, 81.7, 81.4, 53.4, 53.0, 21.2, 21.0.

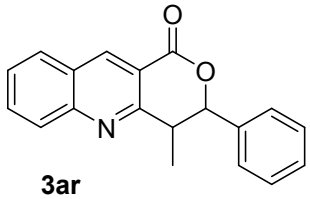
HRMS (ESI) Calcd. for $C_{26}H_{18}F_3NO_2$: $[M+H]^+$, 434.1362. Found: m/z 434.1365.



3aq
dr. 61:39

***trans*-3-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (24.3 mg, 54% yield); m. p. 166 – 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.00 (t, J = 9.1 Hz, 2H), 7.86 – 7.80 (m, 1H), 7.66 – 7.61 (m, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 5.88 (d, J = 6.6 Hz, 1H), 4.99 (d, J = 6.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.7, 157.4, 150.2, 142.1, 140.6, 132.8, 129.8, 129.5, 129.5, 129.3, 129.1, 128.0, 127.7, 127.0, 125.6 (q, *J* = 3.6 Hz, J_{CF}), 124.0 (q, *J* = 273.4 Hz, J_{CF}), 118.9, 114.0, 83.6, 55.2, 52.5; HRMS (ESI) Calcd. for $C_{26}H_{18}F_3NO_3$: $[M+H]^+$, 450.1312. Found: m/z 450.1314.

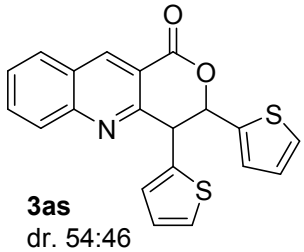
***cis*-3-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (15.1 mg, 34% yield); m. p. 175 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.07 (dd, J = 12.4, 8.5 Hz, 2H), 7.92 – 7.86 (m, 1H), 7.71 – 7.65 (m, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.10 (d, J = 3.2 Hz, 1H), 4.77 (d, J = 3.3 Hz, 1H), 3.80 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 159.6, 158.4, 150.3, 141.1, 139.1, 133.2, 130.0, 129.5, 129.2, 127.8, 127.7, 127.3, 127.3, 125.2, 125.1 (q, J = 4.2 Hz, J_{CF}), 123.9 (q, J = 272.4 Hz, J_{CF}), 118.8, 113.7, 81.6, 55.3, 53.5; HRMS (ESI) Calcd. for $C_{26}H_{18}F_3NO_3$: $[M+H]^+$, 450.1312. Found: m/z 450.1316.



3ar
dr. 88:12

***trans*-4-Methyl-3-phenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (17.6 mg, 61% yield); m. p. 168 – 169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.64 – 7,58 (m, 1H), 7.47 – 7.34 (m, 5H), 5.40 (d, J = 8.6 Hz, 1H), 3.75 – 3.64 (m, 1H), 1.48 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 159.8, 150.0, 140.3, 137.4, 132.6, 129.3, 129.2, 128.9, 128.7, 127.2, 127.1, 126.8, 118.4, 85.3, 40.9, 14.8; HRMS (ESI) Calcd. for $C_{19}H_{15}NO_2$: $[M+H]^+$, 290.1176. Found: m/z 290.1181.

***cis*-4-Methyl-3-phenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (2.3 mg, 8% yield); m. p. 154 – 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.2Hz, 1H), 7.92 – 7.86 (m, 1H), 7.67 – 7.61 (m, 1H), 7.53 – 7.43 (m, 4H), 7.41 – 7.36 (m, 1H), 5.90 (d, J = 2.7 Hz, 1H), 3.64 – 3.55 (m, 1H), 1.17 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 162.3, 149.9, 141.1, 136.5, 132.9, 129.4, 128.9, 128.6, 128.2, 127.3, 127.1, 125.6, 117.6, 81.2, 42.1, 13.4; HRMS (ESI) Calcd. for $C_{19}H_{15}NO_2$: $[M+H]^+$, 290.1176. Found: m/z 290.1130.

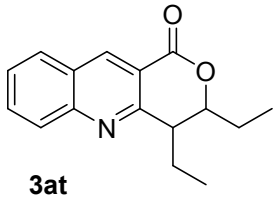


3as
dr. 54:46

***trans*-3,4-Di(thiophen-2-yl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Black solid (4.5 mg, 13% yield); m. p. 185 – 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.13 (dd, J = 8.5, 0.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.66 – 7.60 (m, 1H), 7.26 – 7.24 (m, 1H), 7.20 (dd, J = 5.1, 1.2 Hz, 1H), 6.99 (dt, J = 3.6, 1.1 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.85 (dd, J = 5.0, 3.6 Hz, 1H), 6.31 (dd, J = 2.7, 1.0 Hz, 1H), 5.27 (d, J = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 156.9, 150.2,

140.8, 140.7, 132.9, 129.4, 129.3, 127.7, 127.2, 127.0, 126.9, 126.7, 126.5, 126.4, 125.5, 118.4, 79.9, 47.6; HRMS (ESI) Calcd. for $C_{20}H_{13}NO_2S_2$: $[M+H]^+$, 364.0460. Found: m/z 434.1363.

***cis*-3,4-Di(thiophen-2-yl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Black solid (4.0 mg, 11% yield); m. p. 235 – 236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.69 – 7.63 (m, 1H), 7.29 (dd, J = 5.0, 1.2 Hz, 1H), 7.16 (dd, J = 5.1, 1.0 Hz, 1H), 7.07 (dd, J = 2.6, 1.0 Hz, 1H), 6.99 (dd, J = 5.0, 3.6 Hz, 1H), 6.86 (dd, J = 5.1, 3.6 Hz, 1H), 6.79 (d, J = 3.5 Hz, 1H), 6.33 (dd, J = 3.0, 0.8 Hz, 1H), 5.09 (d, J = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 158.4, 150.0, 141.5, 138.1, 136.5, 133.2, 129.4, 129.2, 127.8, 127.3, 126.7, 126.5, 126.2, 126.1, 126.0, 117.7, 78.7, 49.3; HRMS (ESI) Calcd. for $C_{20}H_{13}NO_2S_2$: $[M+H]^+$, 364.0460. Found: m/z 434.1365.



3at
dr. 60:40

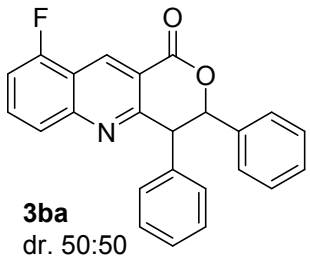
(14.0 mg, 55% yield)

***trans*-3,4-Diethyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.10 (d, J = 3.2 Hz, 1H), 7.95 (s, 1H), 7.61 (t, J = 7.9 Hz, 2H), 4.70 - 4.65 (m, 1H), 3.13 – 3.06 (m, 1H), 2.09 – 1.93 (m, 2H), 1.82 – 1.70 (m, 2H), 1.10 – 1.01 (m, 6H).

***cis*-3,4-Diethyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.13 (d, J = 3.1 Hz, 1H), 7.97 (s, 1H), 7.85 (td, J = 7.2, 1.2 Hz, 2H), 4.65 – 4.59 (m, 1H), 3.20 – 3.13 (m, 1H), 1.93 – 1.82 (m, 2H), 1.66 – 1.55 (m, 2H), 1.12 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.2, 161.0, 159.9, 149.9, 149.4, 140.4, 140.0, 132.5, 132.4, 129.3, 129.3, 129.0, 128.9, 127.1, 127.0, 127.0, 118.5, 118.4, 82.7, 82.4, 77.2, 45.9, 44.9, 27.6, 26.4, 24.5, 20.4, 11.4, 11.2, 10.1, 10.0.

HRMS (ESI) Calcd. for $C_{16}H_{17}NO_2$: $[M+H]^+$, 256.1332. Found: m/z 256.1335.

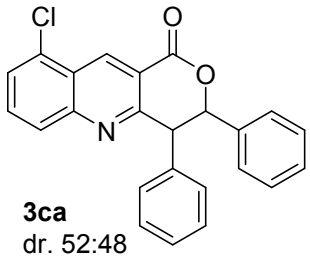


3ba
dr. 50:50

9-Fluoro-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (16.8 mg, 46% yield); m. p. 164 – 166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.33 – 7.22 (m, 8H), 7.19 (dd, J = 7.9, 1.8 Hz, 2H), 6.01 (d, J = 5.4 Hz, 1H), 4.96 (d, J = 5.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.0; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.9, 158.5 (d, J = 259.6 Hz, J_{CF}), 157.3, 150.6, 138.0, 137.6, 134.1 (d, J = 4.5 Hz, J_{CF}), 132.4 (d, J = 8.9 Hz, J

$_{CF}$), 128.8 (d, J = 5.9 Hz, J_{CF}), 128.6, 128.5, 127.6, 126.4, 125.2 (d, J = 4.2 Hz, J_{CF}), 119.2, 118.2 (d, J = 16.2 Hz, J_{CF}), 111.0 (d, J = 18.9 Hz, J_{CF}), 83.9, 52.4; HRMS (ESI) Calcd. for $C_{24}H_{16}FNO_2$: $[M+H]^+$, 370.1238. Found: m/z 370.1240.

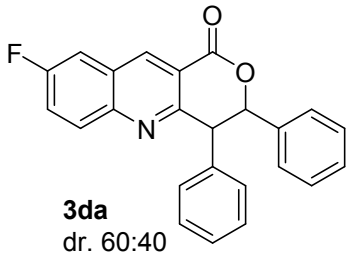
9-Fluoro-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (16.8 mg, 46% yield); m. p. 196 – 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.34 – 7.30 (m, 1H), 7.30 – 7.26 (m, 3H), 7.17 – 7.11 (m, 3H), 7.11 – 7.05 (m, 2H), 6.74 – 6.69 (m, 2H), 6.11 (d, J = 3.2 Hz, 1H), 4.73 (d, J = 3.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.7; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 160.2, 158.6 (d, J = 259.3 Hz, J_{CF}), 150.6, 135.9, 134.7 (d, J = 4.6 Hz, J_{CF}), 134.5, 132.9 (d, J = 9.1 Hz, J_{CF}), 129.5, 128.3, 128.2 (d, J = 3.7 Hz, J_{CF}), 127.5, 126.1, 125.1 (d, J = 4.3 Hz, J_{CF}), 119.1, 118.6, 111.1 (d, J = 18.7 Hz, J_{CF}), 82.0, 53.7; HRMS (ESI) Calcd. for $C_{24}H_{16}FNO_2$: $[M+H]^+$, 370.1238. Found: m/z 370.1237.



3ca
dr. 52:48

9-Chloro-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (18.4 mg, 48% yield); m. p. 191 – 193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.66 (dd, J = 7.5, 1.3 Hz, 1H), 7.32 – 7.23 (m, 8H), 7.19 (dd, J = 7.9, 1.8 Hz, 2H), 6.01 (d, J = 5.5 Hz, 1H), 4.97 (d, J = 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.7, 150.9, 138.0, 137.6, 137.4, 133.1, 132.2, 128.8, 128.8, 128.6, 128.5, 128.4, 127.6, 127.4, 126.4, 125.6, 119.7, 83.9, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{16}ClNO_2$: $[M+H]^+$, 386.0942. Found: m/z 386.0944.

9-Chloro-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (17.4 mg, 45% yield); m. p. 186 – 188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.71 (dd, J = 7.5, 1.2 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.17 – 7.11 (m, 3H), 7.11 – 7.05 (m, 2H), 6.74 – 6.68 (m, 2H), 6.11 (d, J = 3.2 Hz, 1H), 4.74 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 160.0, 150.9, 138.0, 135.8, 134.5, 133.2, 132.6, 129.5, 128.3, 128.2, 128.2, 127.6, 127.5, 126.1, 125.8, 119.6, 82.0, 53.5; HRMS (ESI) Calcd. for $C_{24}H_{16}ClNO_2$: $[M+H]^+$, 386.0942. Found: m/z 386.0945.

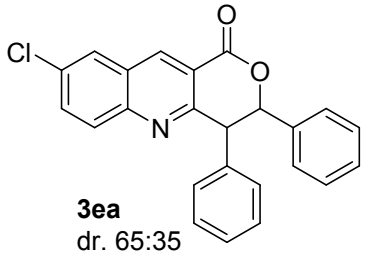


3da
dr. 60:40

8-Fluoro-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (18.6

mg, 50% yield); m. p. 174 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.02 (q, *J* = 5.2 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.33 – 7.22 (m, 8H), 7.18 (dd, *J* = 7.9, 1.8 Hz, 2H), 5.99 (d, *J* = 5.6 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.3; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.7 (d, *J* = 249.6 Hz, J_{CF}), 157.2, 147.4, 139.5 (d, *J* = 5.6 Hz, J_{CF}), 138.1, 137.6, 132.0 (d, *J* = 9.0 Hz, J_{CF}), 128.8 (d, *J* = 2.1 Hz, J_{CF}), 128.6, 128.5, 127.6, 126.4, 123.0 (d, *J* = 25.7 Hz, J_{CF}), 119.7, 112.0 (d, *J* = 22.7 Hz, J_{CF}), 84.1, 52.3; HRMS (ESI) Calcd. for $C_{24}H_{16}FNO_2$: $[M+H]^+$, 370.1238. Found: m/z 370.1237.

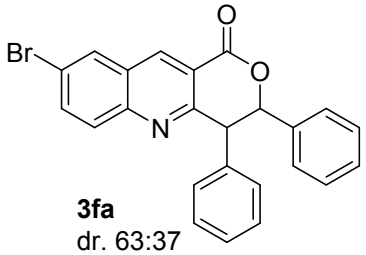
8-Fluoro-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (12.6 mg, 34% yield); m. p. 216 – 218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.10 (q, *J* = 5.2 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.30 – 7.26 (m, 3H), 7.16 – 7.04 (m, 5H), 6.70 (d, *J* = 7.1 Hz, 2H), 6.11 (d, *J* = 3.2 Hz, 1H), 4.72 (d, *J* = 3.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 160.7 (d, *J* = 243.1 Hz, J_{CF}), 158.5, 147.5, 140.0 (d, *J* = 5.4 Hz, J_{CF}), 135.9, 134.6, 131.8 (d, *J* = 9.0 Hz, J_{CF}), 129.5, 128.3, 128.2 (d, *J* = 2.1 Hz, J_{CF}), 127.9, 127.5, 126.1, 123.4 (d, *J* = 28.6 Hz, J_{CF}), 119.6, 112.1 (d, *J* = 24.2 Hz, J_{CF}), 82.1, 53.5; HRMS (ESI) Calcd. for $C_{24}H_{16}FNO_2$: $[M+H]^+$, 370.1238. Found: m/z 370.1237.



3ea
dr. 65:35

8-Chloro-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (18.0 mg, 47% yield); m. p. 181 – 183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.97 (s, 1H), 7.94 (t, *J* = 3.8 Hz, 1H), 7.35 – 7.21 (m, 8H), 7.20 – 7.15 (m, 2H), 5.98 (d, *J* = 5.7 Hz, 1H), 4.93 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.2, 148.6, 139.2, 138.0, 137.6, 133.5, 133.4, 130.9, 128.8, 128.6, 128.5, 127.6, 127.6, 126.4, 119.8, 84.1, 52.4; HRMS (ESI) Calcd. for $C_{24}H_{16}ClNO_2$: $[M+H]^+$, 386.0942. Found: m/z 386.0945.

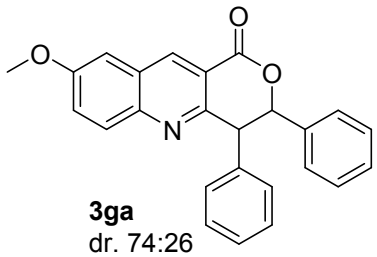
8-Chloro-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (9.8 mg, 25% yield); m. p. 202 – 203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.04 (s, 1H), 8.01 (d, *J* = 2.4 Hz, 1H), 7.28 (d, *J* = 2.5 Hz, 2H), 7.16 – 7.05 (m, 6H), 6.73 – 6.68 (m, 2H), 6.10 (d, *J* = 3.2 Hz, 1H), 4.72 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.4, 148.7, 139.8, 135.9, 134.5, 133.8, 133.5, 130.8, 129.5, 128.3, 128.2, 128.2, 127.8, 127.8, 127.4, 126.1, 119.7, 82.1, 53.6; HRMS (ESI) Calcd. for $C_{24}H_{16}ClNO_2$: $[M+H]^+$, 386.0942. Found: m/z 386.0945.



3fa
dr. 63:37

8-Bromo-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (18.0 mg, 42% yield); m. p. 195 – 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.11 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.32 – 7.22 (m, 8H), 7.17 (dd, *J* = 7.9, 1.8 Hz, 2H), 5.98 (d, *J* = 5.7 Hz, 1H), 4.93 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.3, 148.8, 139.1, 138.0, 137.5, 136.0, 131.0, 131.0, 128.8, 128.6, 128.5, 128.1, 127.6, 126.4, 121.4, 119.8, 84.0, 52.4; HRMS (ESI) Calcd. for $C_{24}H_{16}BrNO_2$: $[M+H]^+$, 430.0437. Found: m/z 430.0441.

8-Bromo-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (10.8 mg, 25% yield); m. p. 187 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.19 (d, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.91 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.58 (t, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 2.4 Hz, 2H), 7.15 – 7.05 (m, 4H), 6.70 (d, *J* = 7.1 Hz, 2H), 6.10 (d, *J* = 3.2 Hz, 1H), 4.71 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.6, 148.9, 139.7, 136.3, 135.8, 134.5, 132.6, 131.1, 130.8, 129.5, 128.3, 128.2, 128.2, 127.5, 126.1, 121.6, 119.7, 82.1, 53.6; HRMS (ESI) Calcd. for $C_{24}H_{16}BrNO_2$: $[M+H]^+$, 430.0437. Found: m/z 430.0438.



3ga
dr. 74:26

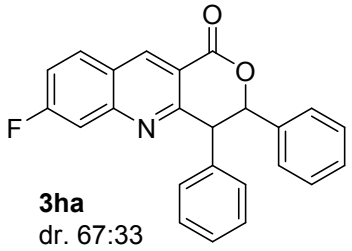
(32.0 mg, 84% yield)

8-Methoxy-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.43 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.32 – 7.21 (m, 7H), 7.14 – 7.03 (m, 3H), 5.96 (d, *J* = 5.4 Hz, 1H), 4.91 (d, *J* = 5.4 Hz, 1H), 3.93 (s, 3H).

8-Methoxy-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.49 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.32 – 7.21 (m, 3H), 7.17 (d, *J* = 6.0 Hz, 5H), 6.70 (d, *J* = 7.2 Hz, 2H), 6.09 (d, *J* = 2.9 Hz, 1H), 4.69 (d, *J* = 2.9 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.7, 158.4, 158.3, 156.6, 155.2, 146.6, 146.6, 139.0, 138.5, 137.8, 136.2, 134.9, 130.6, 130.5, 129.5, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 128.1, 128.1, 127.4, 127.3, 126.4, 126.2, 126.1, 125.7, 119.2, 119.0, 105.9, 105.9, 84.2, 82.2, 55.7, 55.7, 53.4, 52.1.

HRMS (ESI) Calcd. for $C_{25}H_{19}NO_3$: $[M+H]^+$, 382.1438. Found: m/z 382.1439.



3ha
dr. 67:33

(28.4 mg, 77% yield)

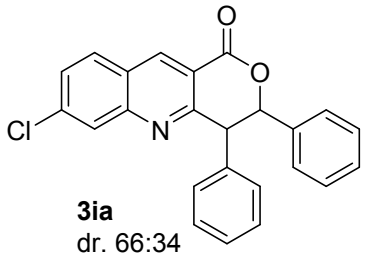
7-Fluoro-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.01 – 7.93 (m, 1H), 7.65 (dd, *J* = 9.9, 2.0 Hz, 1H), 7.38 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.34 – 7.21 (m, 7H), 7.16 – 7.04 (m, 3H), 5.99 (d, *J* = 5.6 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 1H);

7-Fluoro-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.09 – 8.02 (m, 1H), 7.72 (dd, *J* = 9.7, 1.9 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.34 – 7.21 (m, 4H), 7.21 – 7.16 (m, 4H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.10 (d, *J* = 3.1 Hz, 1H), 4.71 (d, *J* = 3.1 Hz, 1H);

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.7, -103.3.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 234.7 Hz, J_{CF}), 164.4, 164.1 (d, *J* = 230.4 Hz, J_{CF}), 160.4, 159.1, 151.7 (d, *J* = 9.9 Hz, J_{CF}), 151.5 (d, *J* = 9.9 Hz, J_{CF}), 140.6, 140.1, 138.1, 137.6, 135.9, 134.5, 131.8 (d, *J* = 9.4 Hz, J_{CF}), 131.6 (d, *J* = 10.5 Hz, J_{CF}), 129.5, 128.8, 128.6, 128.5, 128.3, 128.2, 128.2, 127.6, 127.5, 126.4, 126.1, 124.4, 124.1, 118.5 (d, *J* = 19.1 Hz, J_{CF}), 118.3 (d, *J* = 19.1 Hz, J_{CF}), 113.3 (d, *J* = 21.0 Hz, J_{CF}), 113.1 (d, *J* = 21.5 Hz, J_{CF}), 83.9, 82.0, 53.6, 52.4.

HRMS (ESI) Calcd. for $C_{24}H_{16}FNO_2$: $[M+H]^+$, 370.1238. Found: m/z 370.1239.



3ia
dr. 66:34

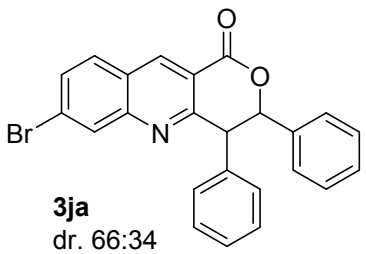
(33.4 mg, 87% yield)

7-Chloro-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.03 (d, *J* = 1.5 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.33 – 7.05 (m, 10H), 5.98 (d, *J* = 5.8 Hz, 1H), 4.93 (d, *J* = 5.8 Hz, 1H).

7-Chloro-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.09 (d, *J* = 1.5 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.60 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.33 – 7.05 (m, 8H), 6.71 (d, *J* = 7.1 Hz, 2H), 6.11 (d, *J* = 3.2 Hz, 1H), 4.72 (d, *J* = 3.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.2, 160.4, 159.2, 150.6, 150.5, 140.5, 140.0, 139.3, 138.9, 137.9, 137.5, 135.9, 134.5, 130.5, 130.4, 129.5, 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 128.2, 127.6, 127.5, 126.4, 126.1, 125.6, 125.3, 119.1, 119.0, 83.9, 82.0, 53.6, 52.4.

HRMS (ESI) Calcd. for $C_{24}H_{16}ClNO_2$: $[M+H]^+$, 386.0942. Found: m/z 386.0941.



3ja
dr. 66:34

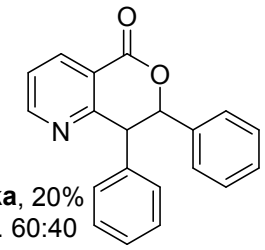
(34.8 mg, 81% yield)

7-Bromo-*trans*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.23 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.34 – 7.21 (m, 7H), 7.16 – 7.04 (m, 3H), 5.98 (d, *J* = 5.8 Hz, 1H), 4.93 (d, *J* = 5.8 Hz, 1H).

7-Bromo-*cis*-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.29 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.73 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.20 – 7.16 (m, 4H), 6.71 (d, *J* = 7.2 Hz, 2H), 6.11 (d, *J* = 3.1 Hz, 1H), 4.71 (d, *J* = 3.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.2, 160.3, 159.1, 150.7, 150.6, 140.6, 140.1, 137.9, 137.5, 135.8, 134.5, 131.8, 131.7, 131.3, 131.2, 130.4, 130.3, 129.5, 128.8, 128.8, 128.6, 128.5, 128.3, 128.2, 128.2, 127.8, 127.6, 127.5, 127.5, 126.5, 126.1, 125.8, 125.6, 119.2, 119.2, 83.9, 81.97, 53.6, 52.4.

HRMS (ESI) Calcd. for $C_{24}H_{16}BrNO_2$: $[M+H]^+$, 430.0437. Found: m/z 430.0438.



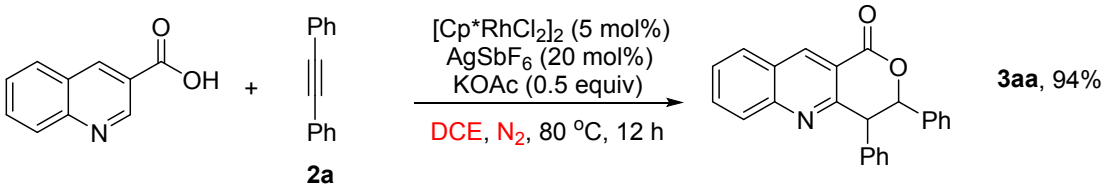
3ka, 20%
dr. 60:40

***trans*-7,8-Diphenyl-7,8-dihydro-5H-pyrano[4,3-b]pyridin-5-one.** White solid (3.6 mg, 12% yield); m. p. 159 – 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 4.74, 1.60 Hz, 1H), 8.46 (dd, *J* = 7.89, 1.69 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 7.30 – 7.26 (m, 4H), 7.23 – 7.17 (m, 3H), 7.11 – 7.02 (m, 2H), 5.81 (d, *J* = 7.68 Hz, 1H), 4.74 (d, *J* = 7.38 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 160.2, 154.7, 137.9, 137.6, 137.3, 129.3, 129.1, 128.8, 128.5, 128.4, 127.7, 126.7, 123.2, 84.6, 52.5; HRMS (ESI) Calcd. for $C_{20}H_{15}NO_2$: $[M+H]^+$, 302.1176. Found: m/z 302.1174.

***cis*-7,8-Diphenyl-7,8-dihydro-5H-pyrano[4,3-b]pyridin-5-one.** White solid (2.4 mg, 8% yield); m. p. 186 – 187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.79, 1.58 Hz, 1H), 8.56 (dd, *J* = 7.87, 1.62, 1H), 7.48 (q, *J* = 4.87 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.16 – 7.05 (m, 5H), 6.72 – 6.67 (m, 2H), 6.05 (d, *J* = 3.52 Hz, 1H), 4.55 (d, *J* = 3.52 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 161.2, 154.9, 138.2, 136.0, 134.3, 129.4, 128.2, 128.2, 128.1, 127.5, 126.1, 123.6, 121.2, 82.1, 53.0; HRMS (ESI) Calcd. for $C_{20}H_{15}NO_2$: $[M+H]^+$, 302.1176. Found: m/z 302.1172.

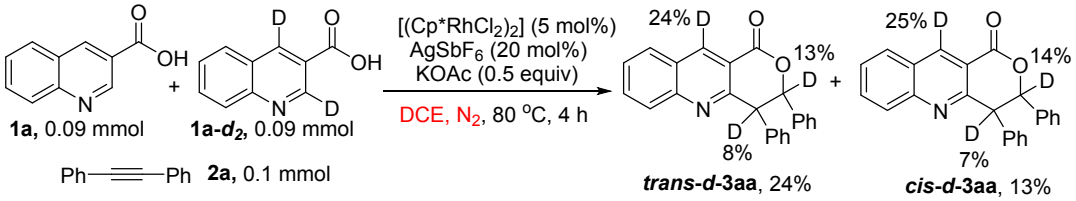
4. Control experiments

(a) Under no O_2 and H_2O reaction conditions

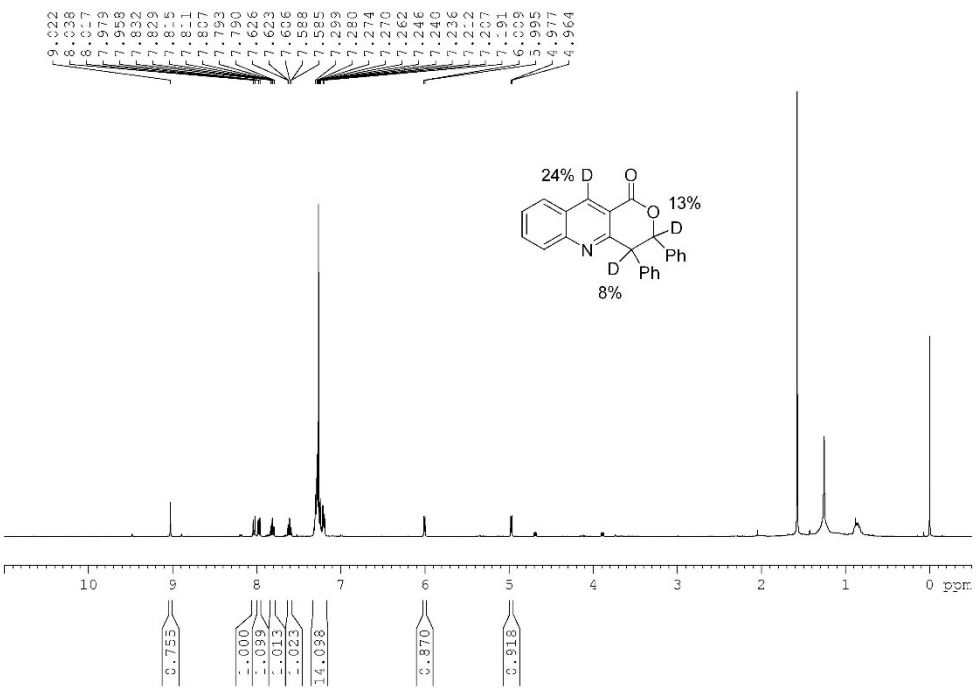


$[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), **1a** (0.18 mmol, 1.8 equiv) and **2a** (0.1 mmol, 1.0 equiv) were weighted and placed in a dried Schlenk tube. Then 2.0 mL of anhydrous DCE was added. The reaction mixture was stirred at 80 °C for 12 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford the desired product **3aa** was obtained in 94% yield, indicating that external oxygen and water are no necessary for this reaction.

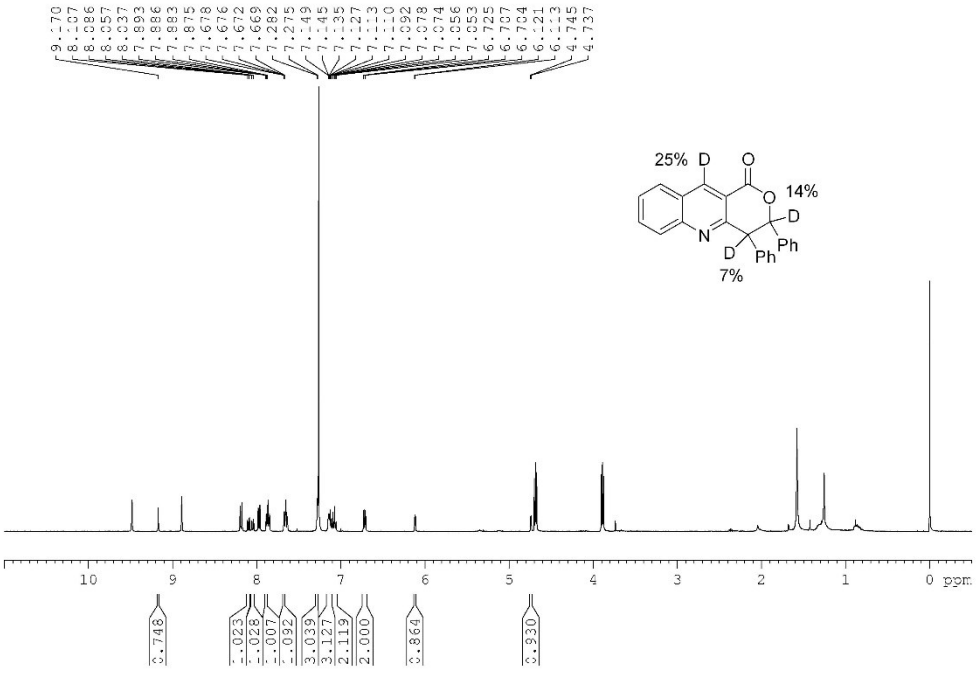
(b) *d*-Incorporation reaction



$[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), **1a-*d*$_2$** (0.09 mmol, 0.9 equiv), **1a** (0.09 mmol, 0.9 equiv) and **2a** (0.1 mmol, 1.0 equiv) were weighted and placed in same dried Schlenk tube. Then 2.0 mL of anhydrous DCE was added. The reaction mixture was stirred at 80 °C for 4 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford ***d*-3aa (trans)** and ***d*-3aa (cis)** in 24% and 13% yield, and *d*-incorporation occurred at the two C_{sp3}-H, suggesting that two C_{sp3}-H in the products are partially derived from the *ortho* C-H of the carboxylic acid. The *d*-incorporation was calculated from ^1H NMR spectrum (see the following ^1H NMR spectrum).

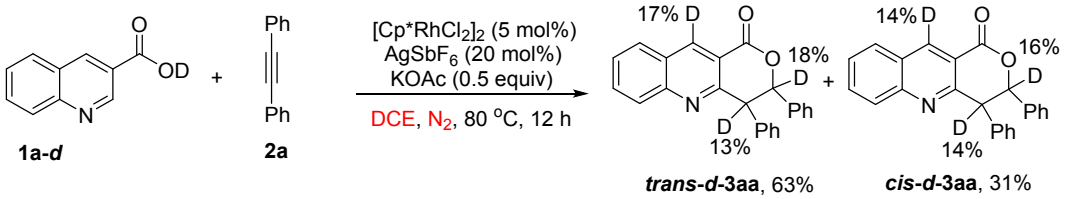


^{1}H NMR spectrum of compound 3aa (trans)

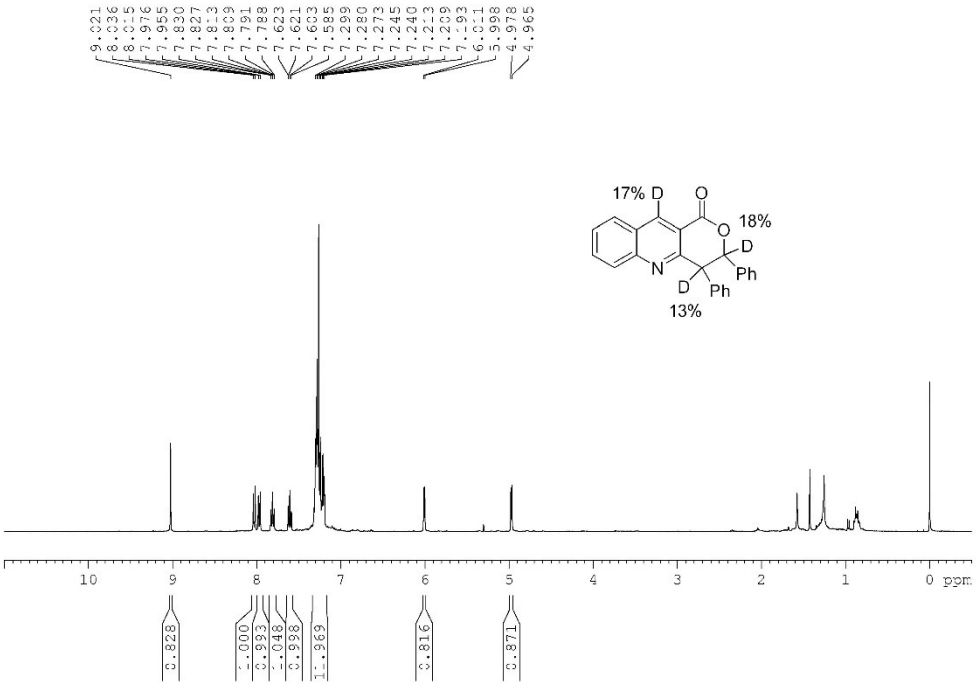


^{1}H NMR spectrum of compound 3aa (cis)

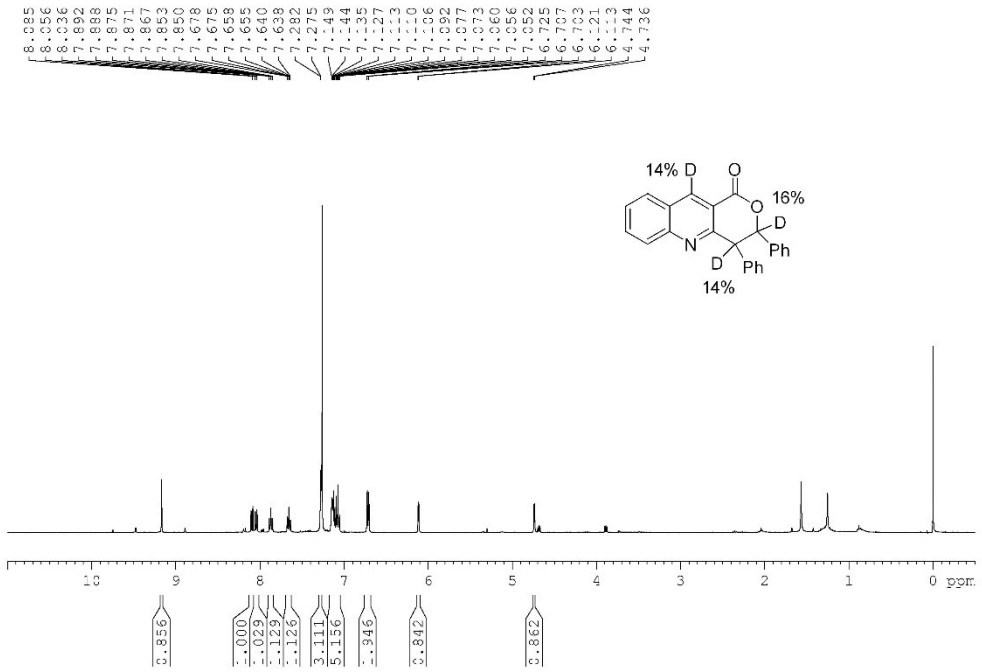
(c) *d*-Incorporation reaction



$[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), **1a-*d*** (0.18 mmol, 1.8 equiv) and **2a** (0.1 mmol, 1.0 equiv) were weighted and placed in a dried Schlenk tube. Then 2.0 mL of anhydrous DCE was added. The reaction mixture was stirred at 80 °C for 12 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford *d*-incorporation on the three positions of ***d*-3aa (trans)** and ***d*-3aa (cis)**, indicates that two C_{sp3}-H in the products are partially derived from carboxylic acid. The *d*-incorporation was calculated from ^{1}H NMR spectrum (see the following ^{1}H NMR spectrum).

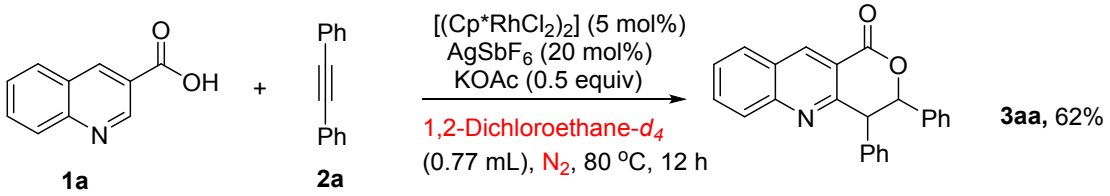


^{1}H NMR spectrum of compound 3aa (trans)



^{1}H NMR spectrum of compound 3aa (cis)

(d) Under the reaction conditions of 1,2-dichloroethane–d_4 as solvent



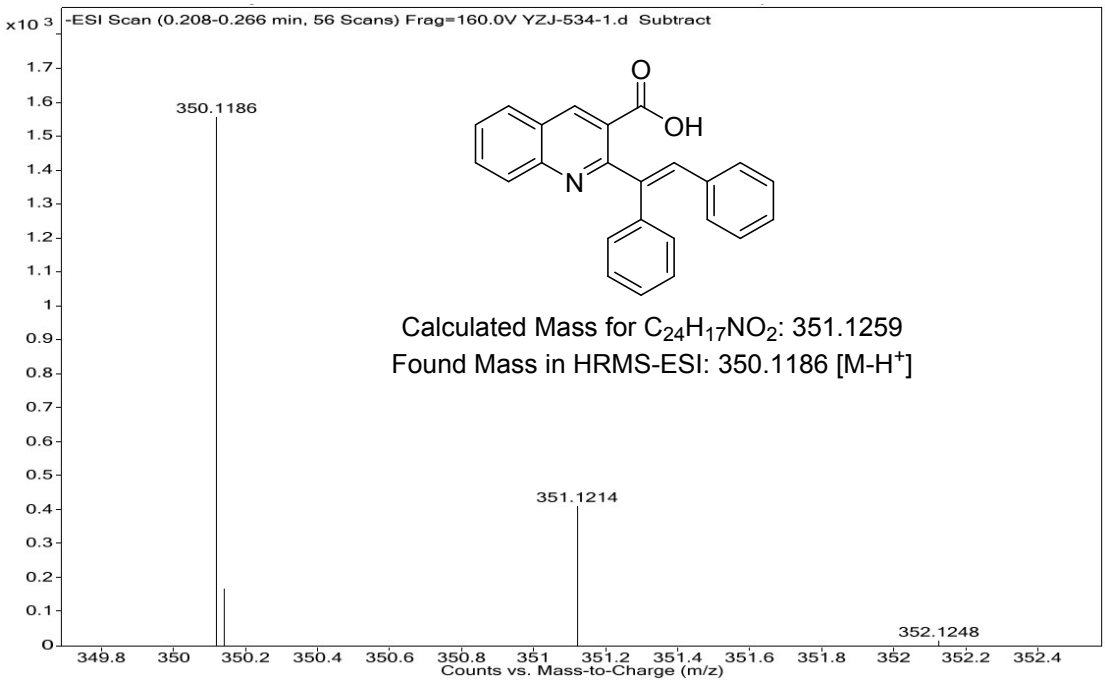
$[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), **1a** (0.18 mmol, 1.8 equiv) and **2a** (0.1 mmol, 1.0 equiv) were weighted and placed in a dried Schlenk tube. Then 0.77 mL of 1,2-dichloroethane–d_4 was added. The reaction mixture was stirred at 80 °C for 12 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford the desired product **3aa** was obtained in 62% yield, and no *d*-incorporation occurred at the two C_{sp3}-H.

5. Mechanistic studies

Possible intermediate detection in reaction system

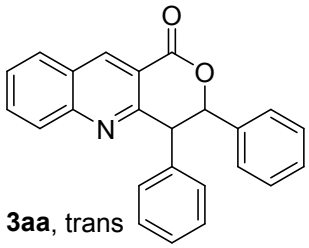
To a dried Schlenk tube was added $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), quinolone-3-carboxylic acids (0.18 mmol, 1.8 equiv), alkynes (0.1 mmol, 1.0 equiv) in DCE (2.0 mL) under air. The reaction mixture was stirred at 80 °C for 4 h, and then

cooled down to room temperature. The reaction solution is detected by high resolution mass spectrometry. Calculated Mass for $C_{24}H_{17}NO_2$: 351.1259. Found Mass in HRMS-ESI: 350.1186 [M-H^+] (see the following HRMS spectrum).

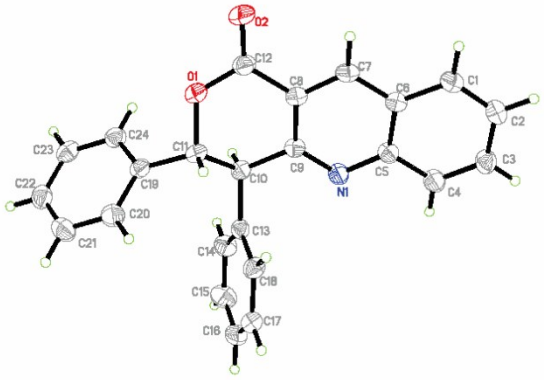


6. X-Ray Crystallographic Data of 3aa and 3ap

X-Ray Crystallographic Data of 3aa (trans)



3aa, trans



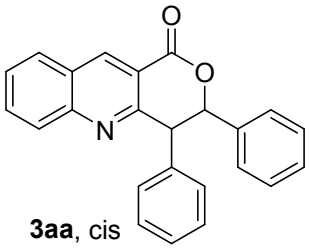
Single-crystal X-Ray Molecular Structure of 3aa (trans)

The structure of **3aa** (trans) was determined by the X-ray diffraction. Recrystallized from chloroform/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1850247.

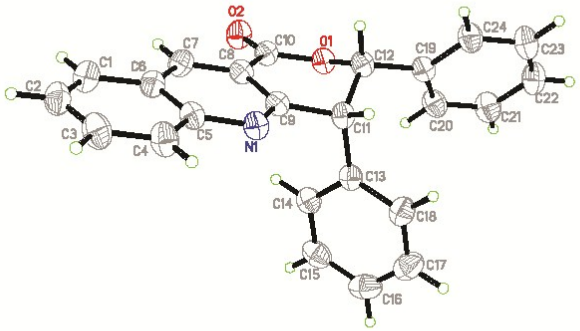
Table S1 Crystal data and structure refinement for 3aa (trans).

Identification code	**3aa** (trans)
Empirical formula	$C_{24}H_{17}NO_2$
Formula weight	351.38
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.0804(3)
b/Å	12.2799(5)
c/Å	13.6018(4)
α/°	75.764(3)
β/°	84.604(3)
γ/°	89.194(3)
Volume/Å^3	1785.88(11)
Z	4
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	0.083
F(000)	736.0
Crystal size/mm^3	0.18 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.788 to 52.744
Index ranges	$-13 \le h \le 9$, $-15 \le k \le 15$, $-16 \le l \le 16$
Reflections collected	14984
Independent reflections	7283 [R_{int} = 0.0263, R_{sigma} = 0.0401]
Data/restraints/parameters	7283/0/487
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.0931
Final R indexes [all data]	R_1 = 0.0668, wR_2 = 0.1062
Largest diff. peak/hole / e Å^{-3}	0.12/-0.21

X-Ray Crystallographic Data of 3aa (cis)



3aa, cis



Single-crystal X-Ray Molecular Structure of 3aa (cis)

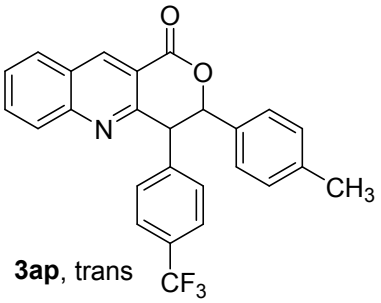
The structure of **3aa** (cis) was determined by the X-ray diffraction. Recrystallized from chloroform/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1850250.

Table S2 Crystal data and structure refinement for 3aa (cis).

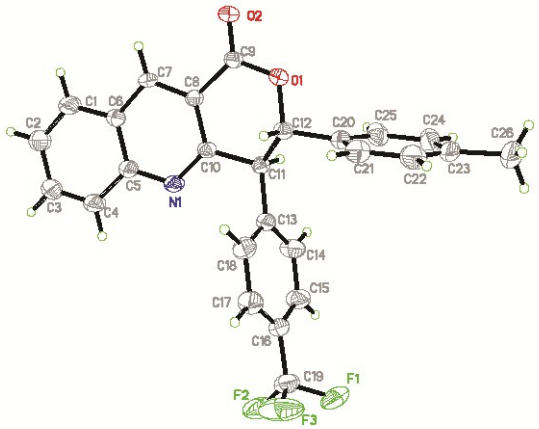
Identification code	**3aa** (cis)
Empirical formula	$C_{24}H_{17}NO_2$
Formula weight	351.38
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.5534(8)
b/Å	5.4976(2)
c/Å	37.5979(18)
α/°	90
β/°	93.982(6)
γ/°	90
Volume/Å^3	1763.7(2)
Z	4

ρ_{calc}g/cm^3	1.323
μ/mm^{-1}	0.669
F(000)	736.0
Crystal size/mm^3	0.2 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.432 to 134.156
Index ranges	$-10 \le h \le 9$, $-3 \le k \le 6$, $-35 \le l \le 44$
Reflections collected	6515
Independent reflections	3151 [R_{int} = 0.0416, R_{sigma} = 0.0558]
Data/restraints/parameters	3151/0/244
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1361
Final R indexes [all data]	R_1 = 0.0824, wR_2 = 0.1614
Largest diff. peak/hole / e Å^{-3}	0.16/-0.19

X-Ray Crystallographic Data of 3ap (trans)



3ap, trans



Single-crystal X-Ray Molecular Structure of 3ap (trans)

The structure of **3ap** (trans) was determined by the X-ray diffraction. Recrystallized from chloroform/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1850256.

Table S3 Crystal data and structure refinement for 3ap (trans).

Identification code	**3ap** (trans)
Empirical formula	$C_{26}H_{18}F_3NO_2$
Formula weight	433.41
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.4787(5)
b/Å	10.7989(7)
c/Å	16.2052(6)
α/°	79.201(4)
β/°	85.566(5)
γ/°	73.057(7)
Volume/Å^3	1065.03(12)
Z	2
ρ_{calc}g/cm^3	1.352
μ/mm^{-1}	0.868
F(000)	448.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.69 to 134.156
Index ranges	$-7 \le h \le 5$, $-12 \le k \le 11$, $-19 \le l \le 19$
Reflections collected	7706
Independent reflections	3782 [R_{int} = 0.0240, R_{sigma} = 0.0383]
Data/restraints/parameters	3782/21/325
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0857, wR_2 = 0.2528
Final R indexes [all data]	R_1 = 0.1246, wR_2 = 0.2922
Largest diff. peak/hole / e Å^{-3}	0.39/-0.38

7. References

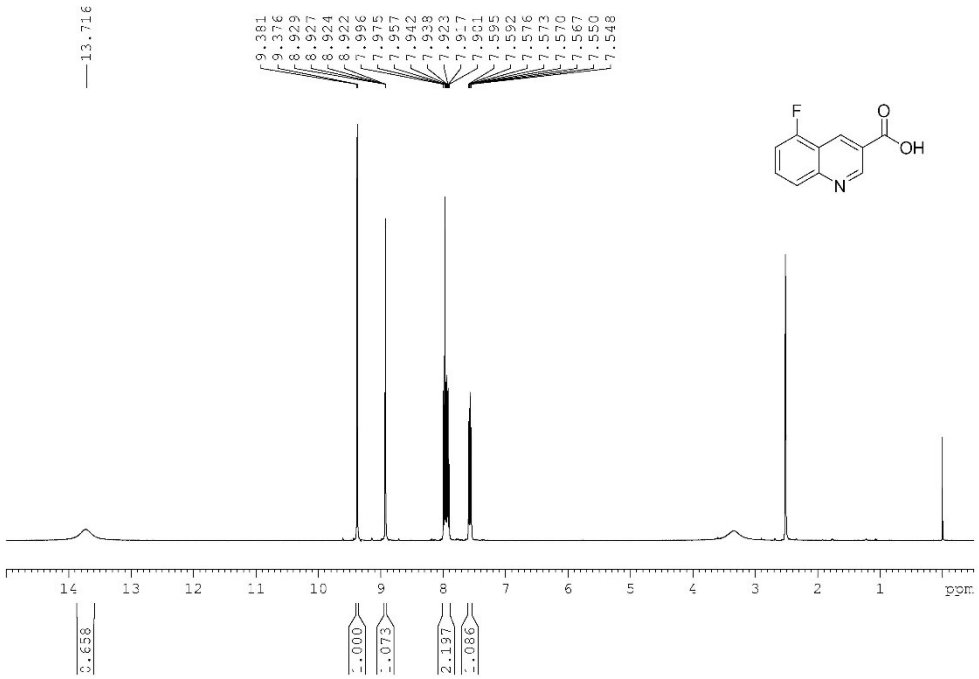
(1) Yan, H.; Wang, H. L.; Li, X. C.; Xin, X. Y.; Wang, C. X.; Wan, B. S. *Angew, Chem., Int. Ed*. **2015**, *54*, 10613-10617.

(2) Jia, X. D.; Petrone, D. A.; Lautens, M. *Angew. Chem., Int. Ed*. **2012**, *51*, 9870-9872.

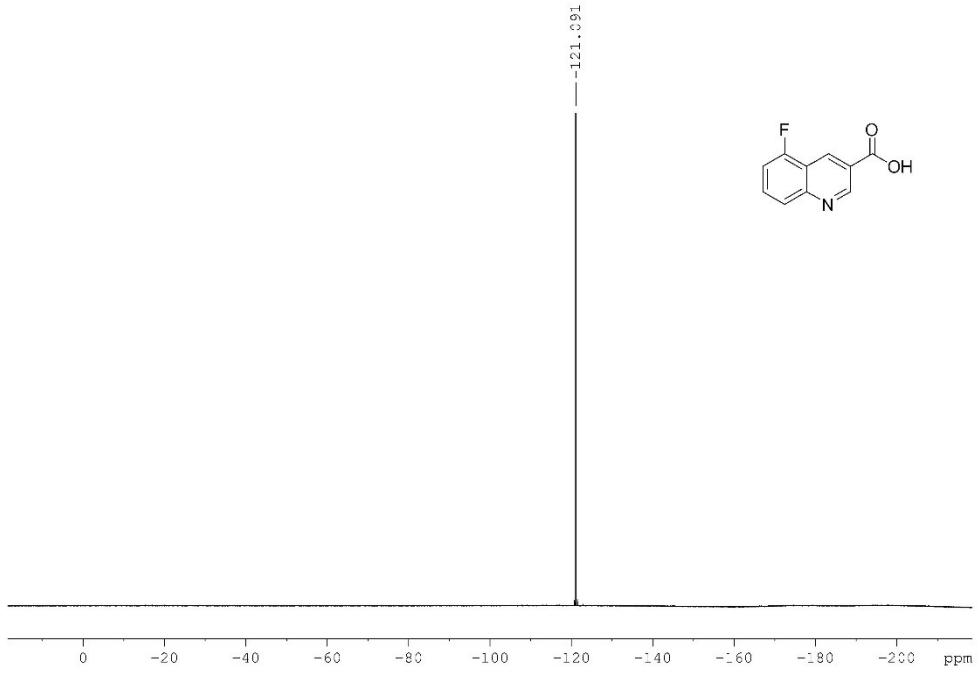
(3) Venkatesan, H.; Hocutt, F. M.; Jones, T. K.; Rabinowitz, M. H. *J. Org. Chem*. **2010**, *75*, 3488-3491.

(4) Bailly, J. U.S. Patent 2009040288, 2009.

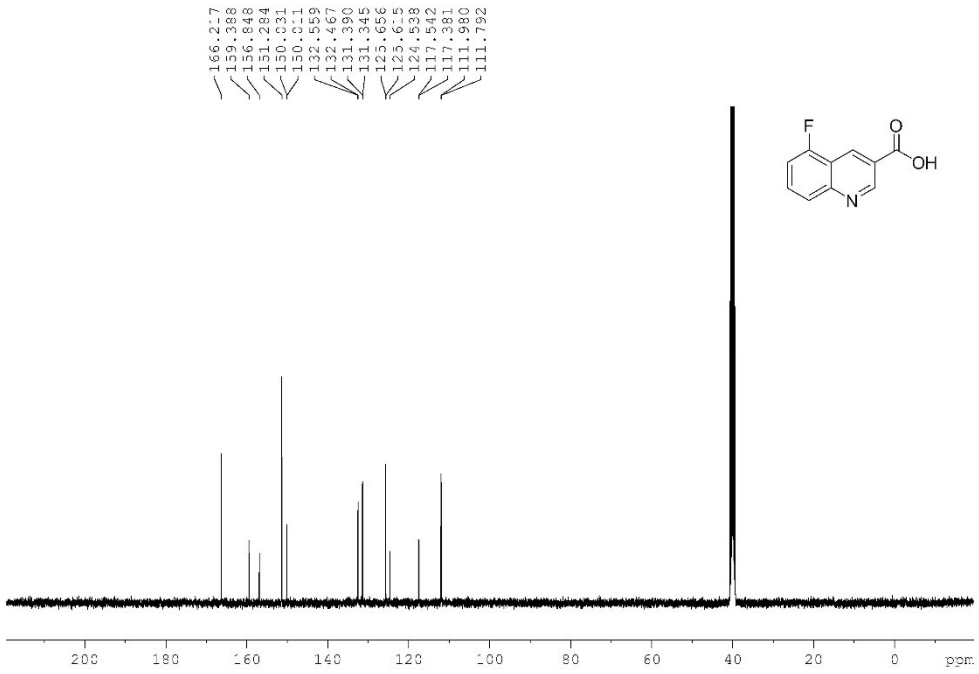
8. NMR spectra of the substrates and products



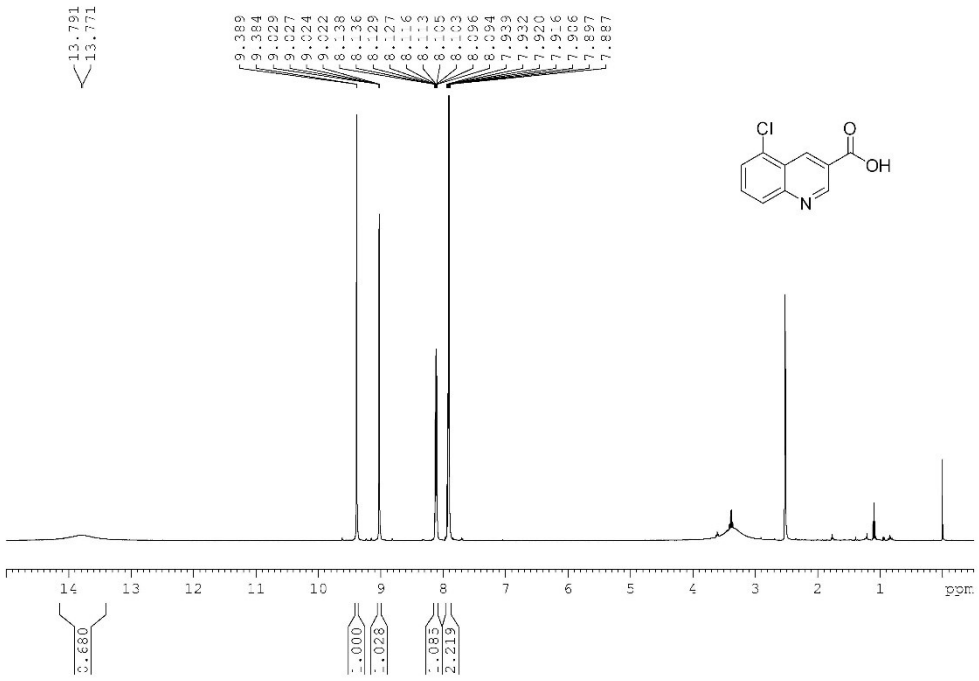
^{1}H NMR spectrum of compound 1b



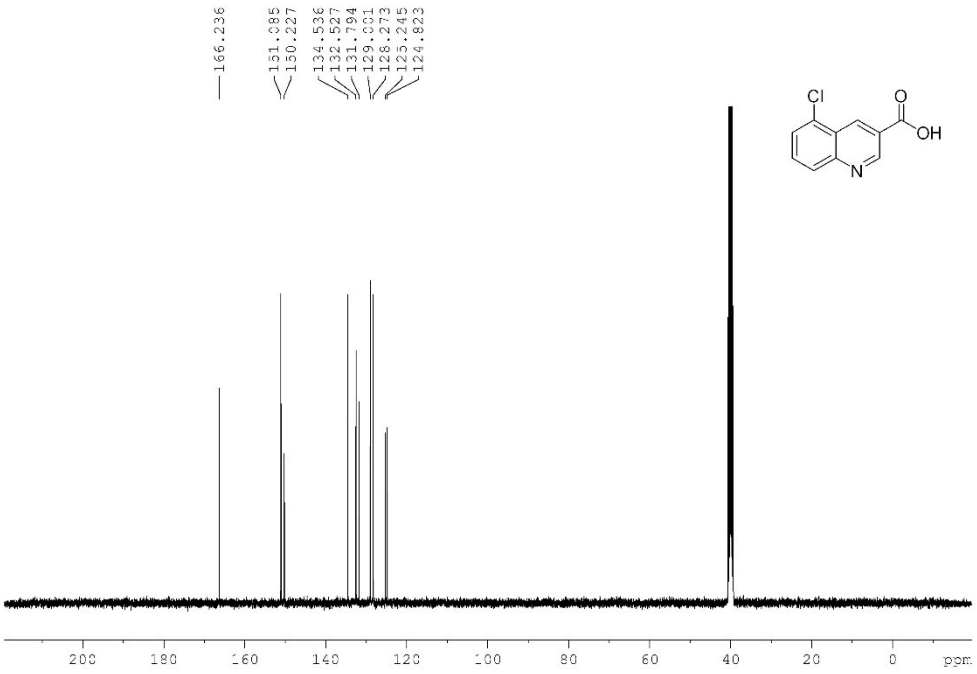
^{19}F NMR spectrum of compound 1b



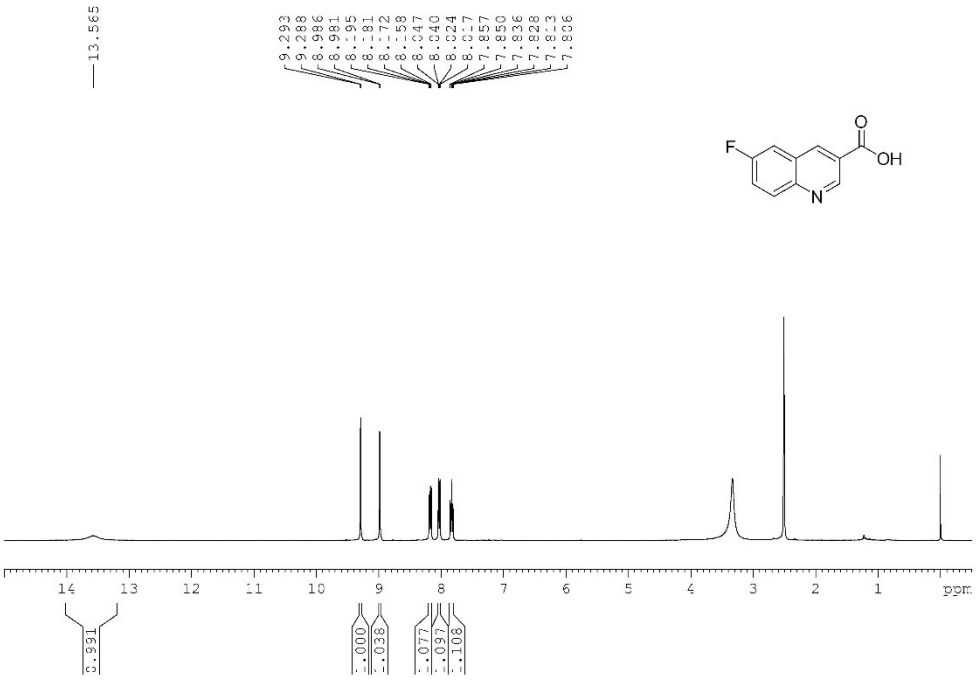
^{13}C NMR spectrum of compound 1b



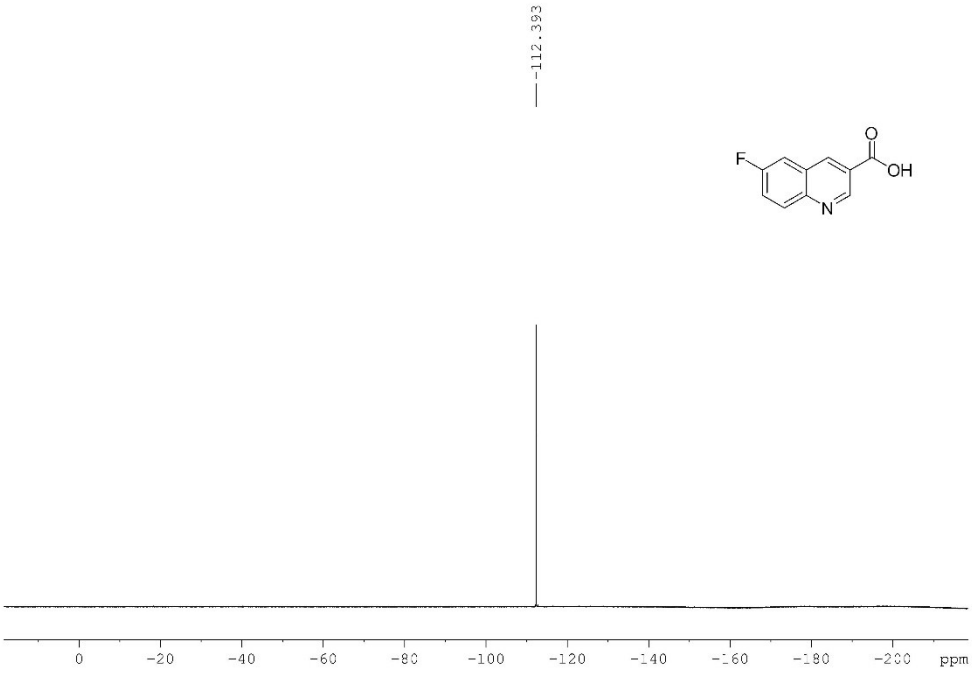
^{1}H NMR spectrum of compound 1c



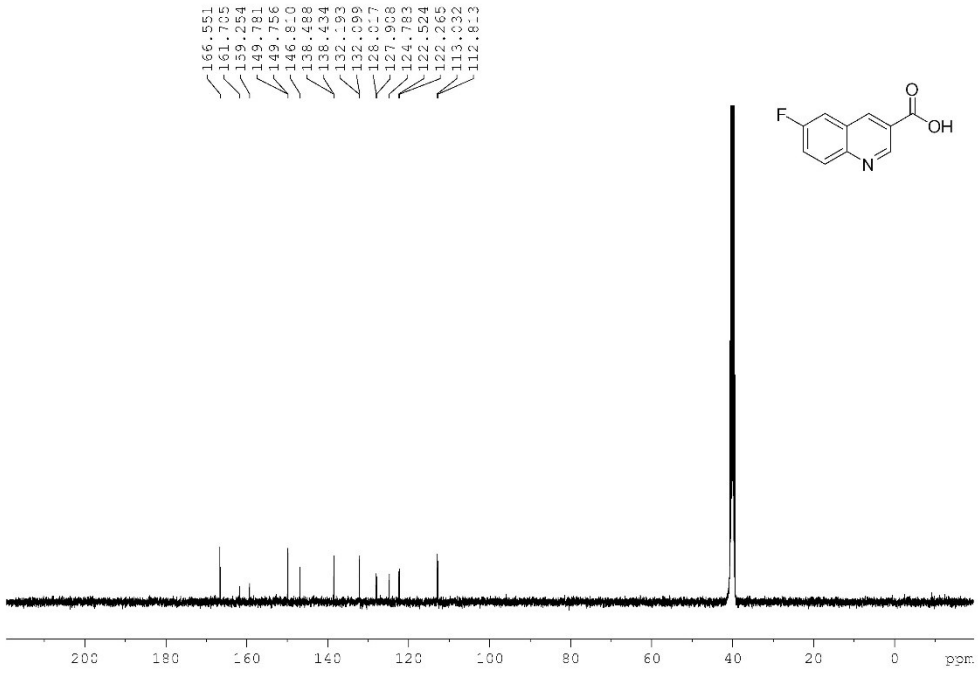
^{13}C NMR spectrum of compound 1c



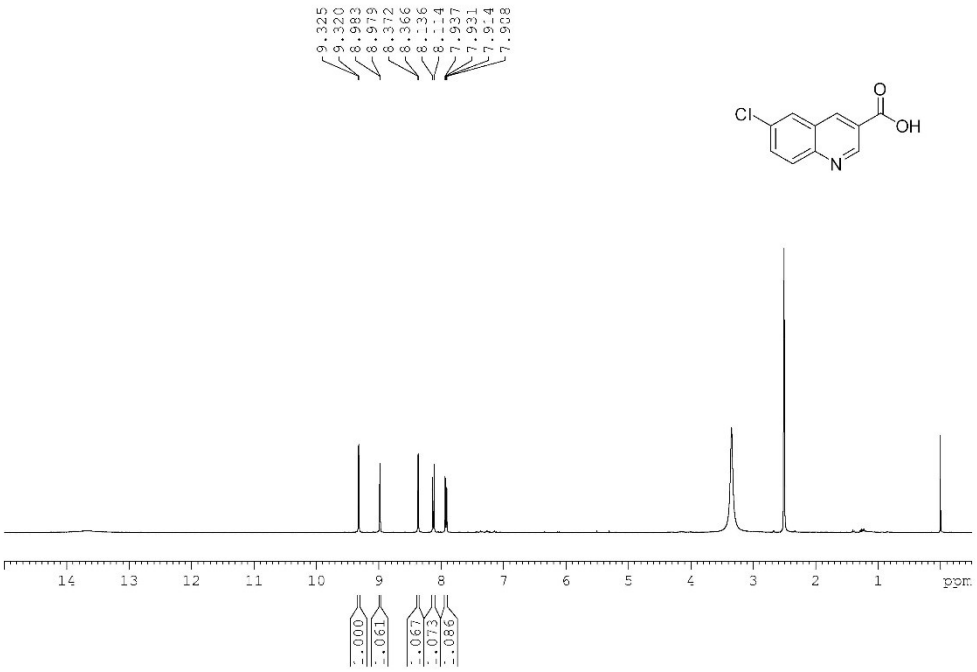
^{1}H NMR spectrum of compound 1d



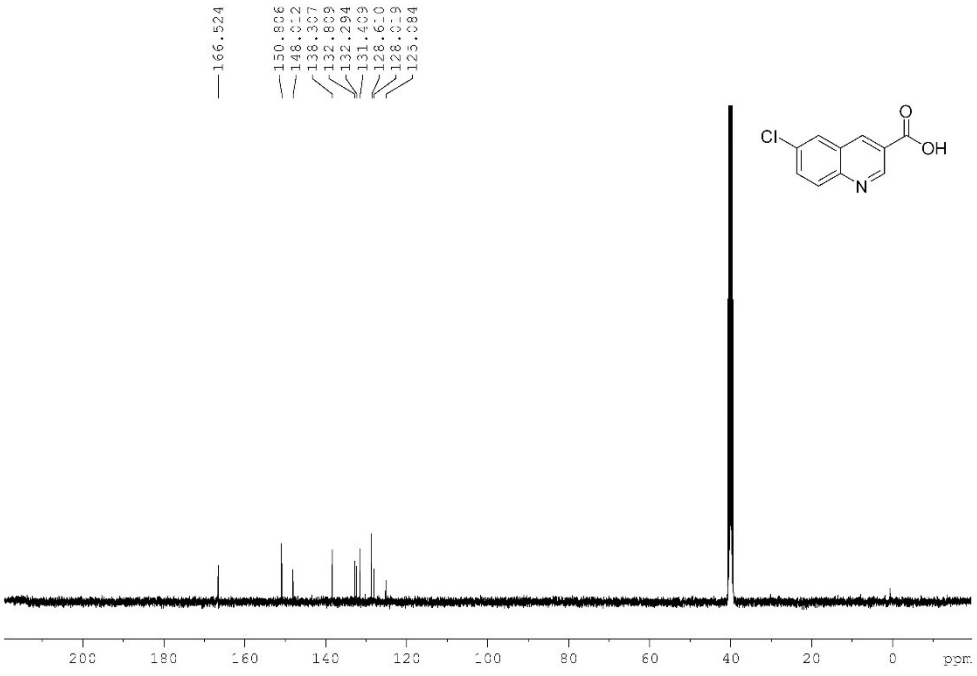
^{19}F NMR spectrum of compound 1d



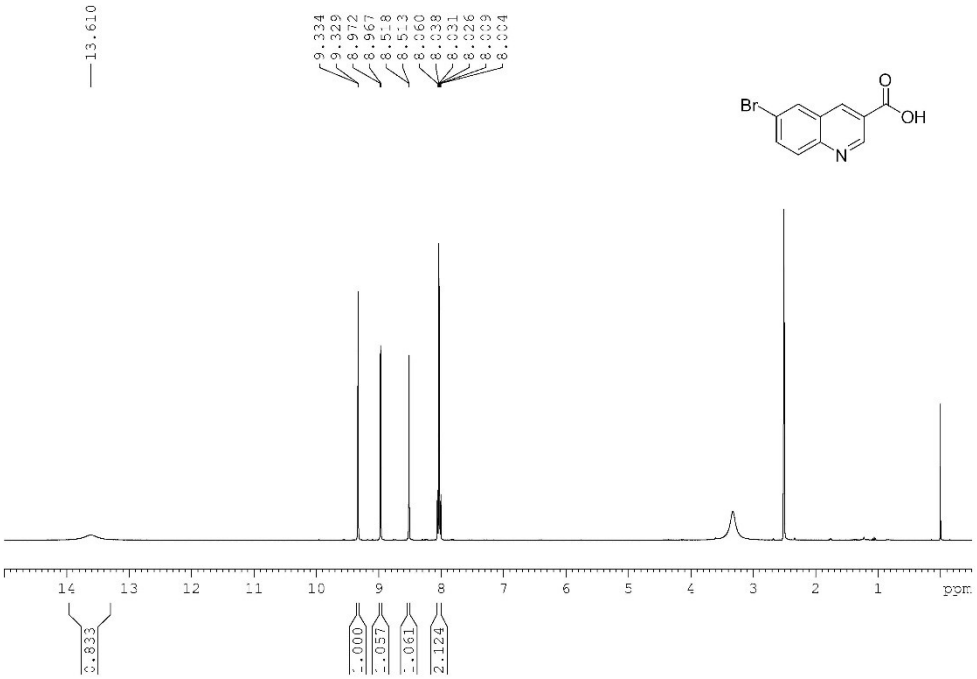
^{13}C NMR spectrum of compound 1d



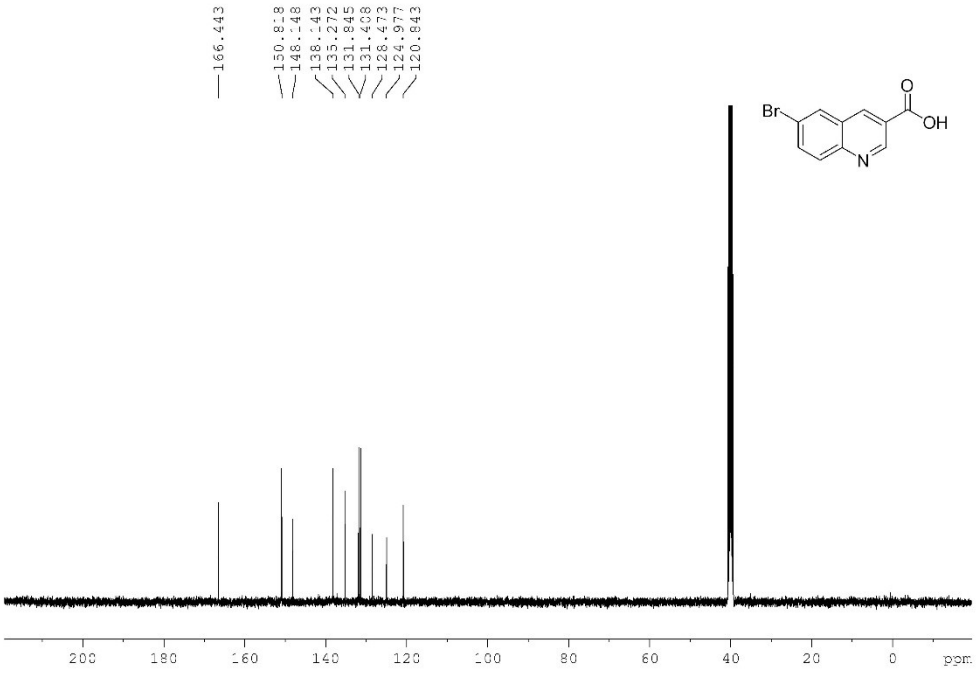
^{1}H NMR spectrum of compound 1e



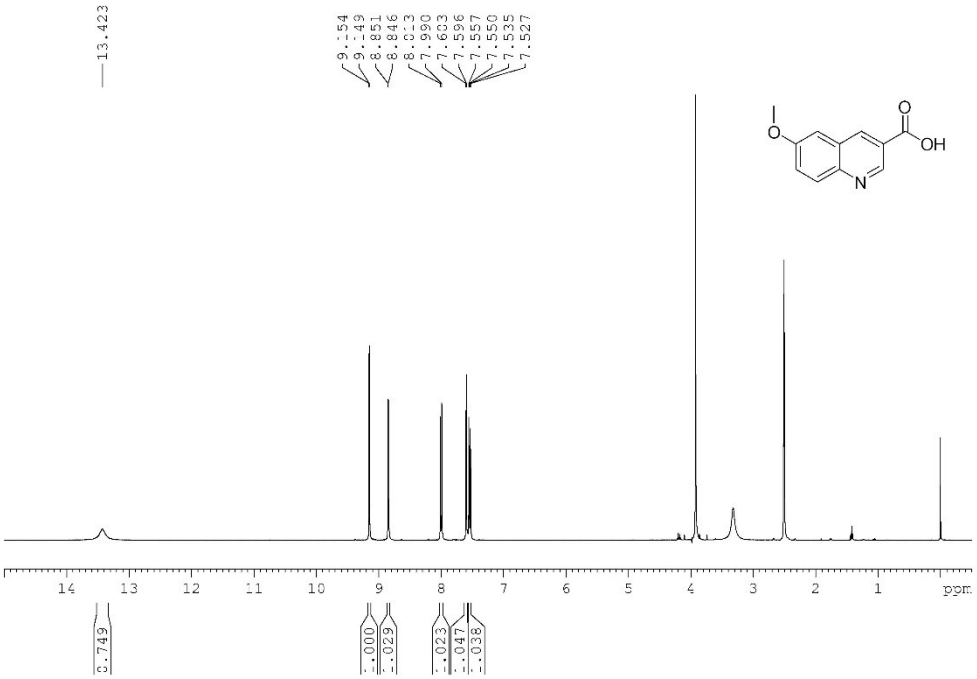
^{13}C NMR spectrum of compound 1e



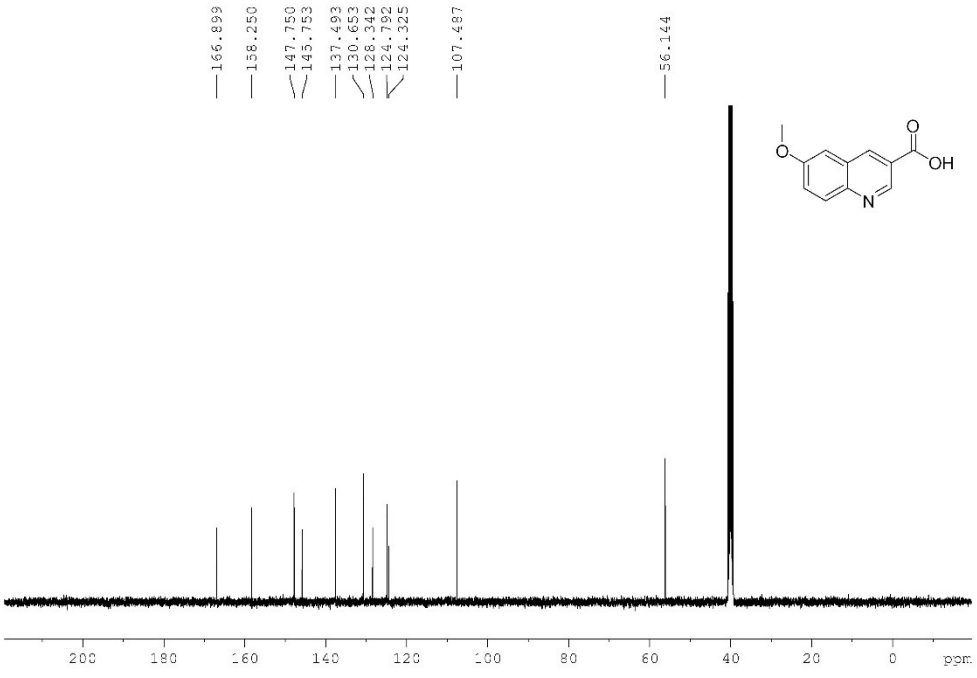
^{1}H NMR spectrum of compound 1f



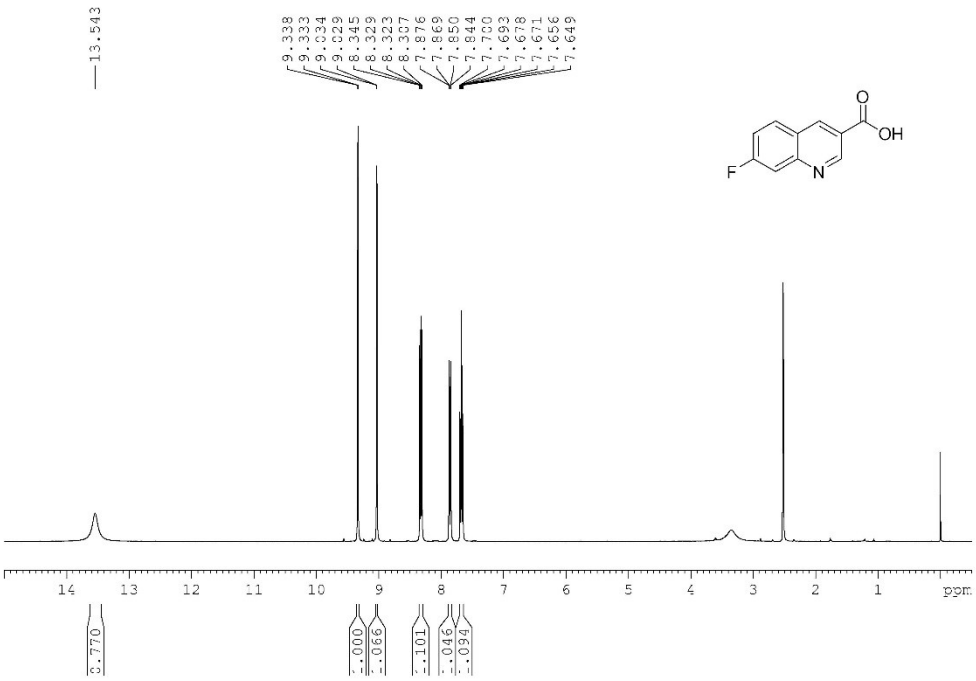
^{13}C NMR spectrum of compound 1f



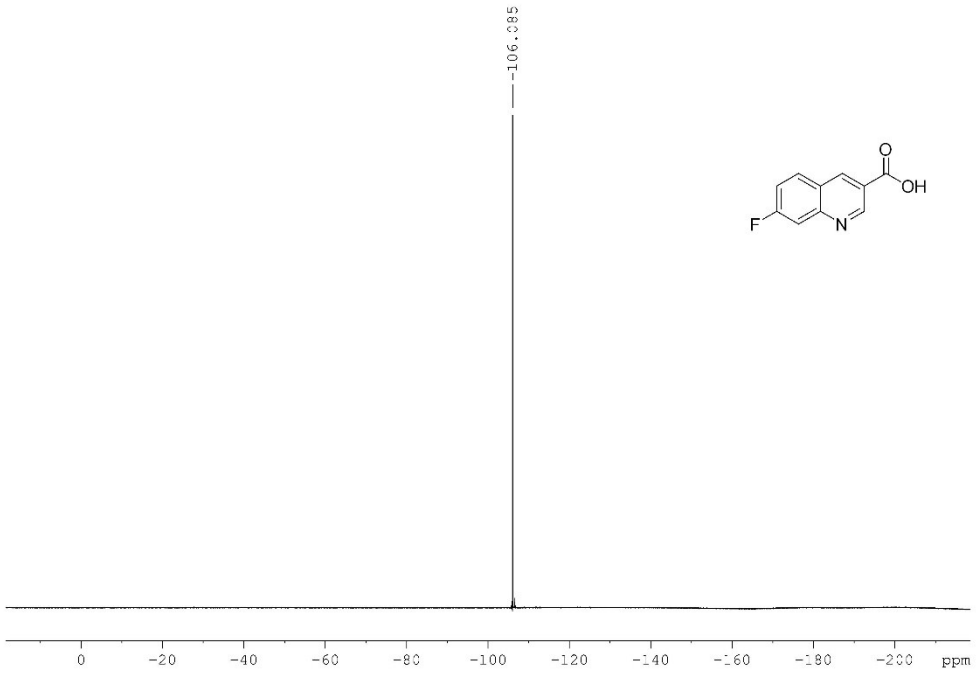
^{1}H NMR spectrum of compound 1g



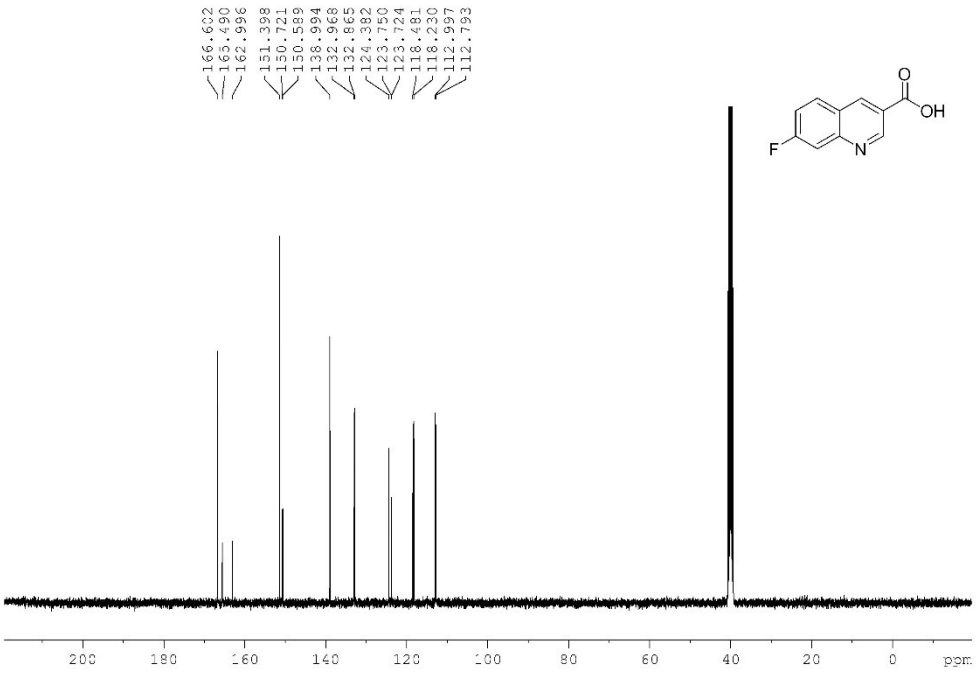
^{13}C NMR spectrum of compound 1g



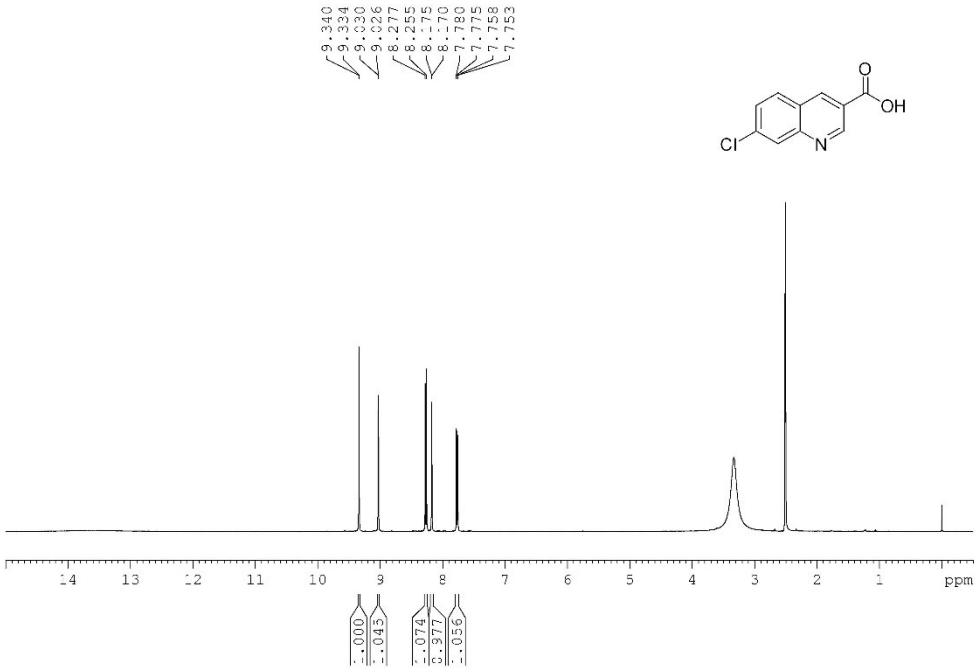
[1]H NMR spectrum of compound 1h



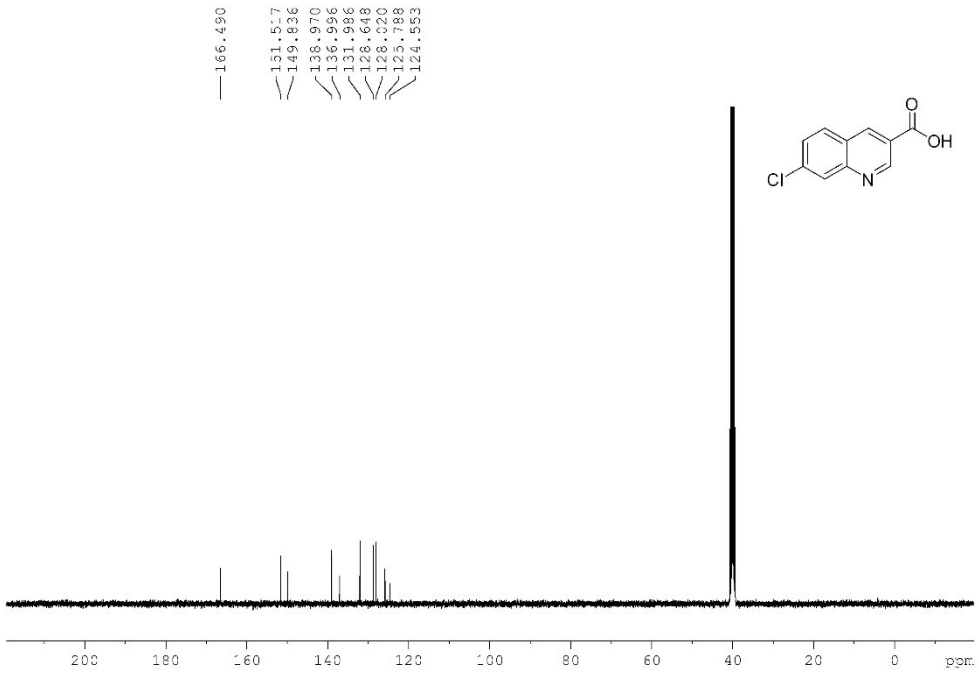
[19]F NMR spectrum of compound 1h



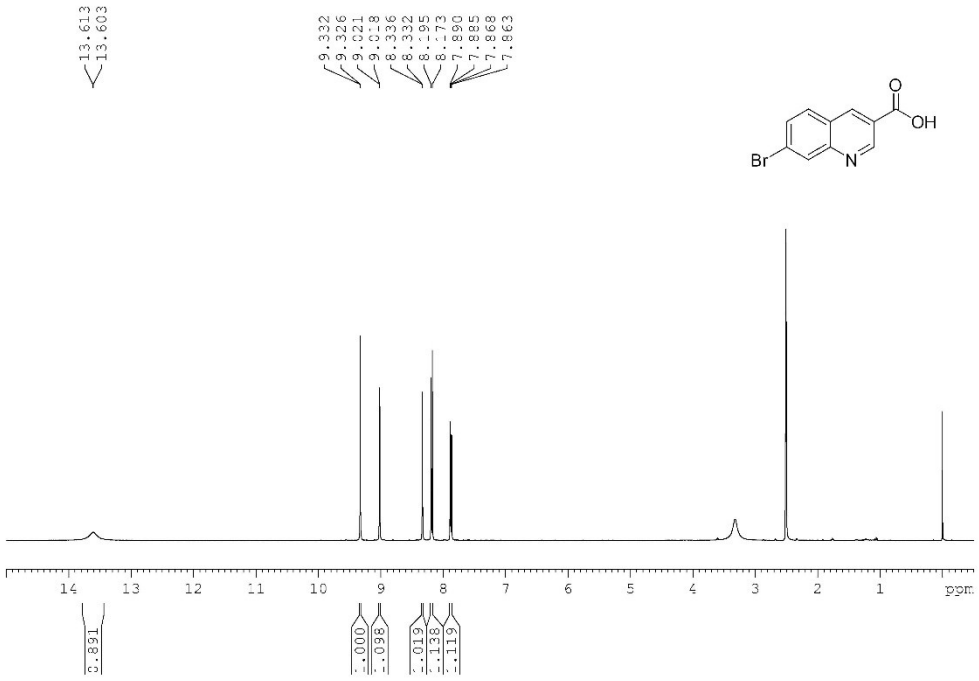
^{13}C NMR spectrum of compound 1h



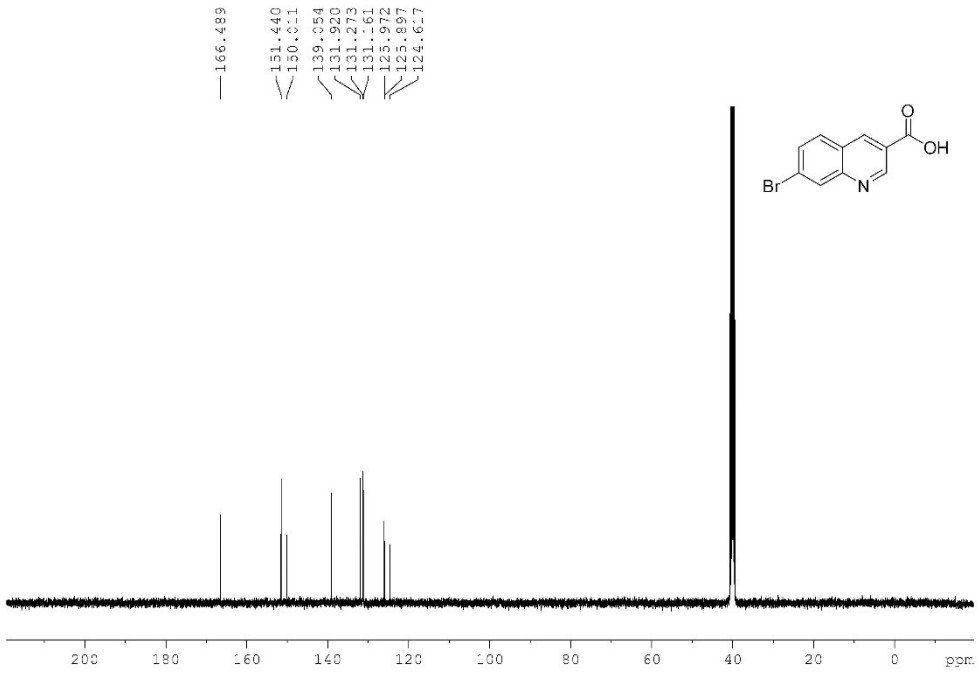
^{1}H NMR spectrum of compound 1i



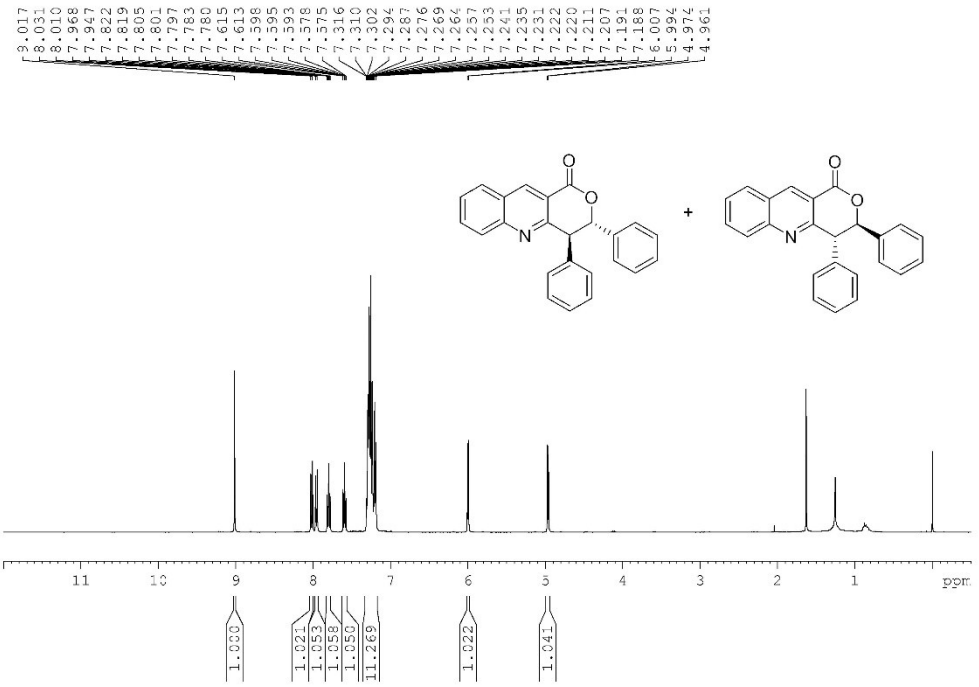
^{13}C NMR spectrum of compound 1i



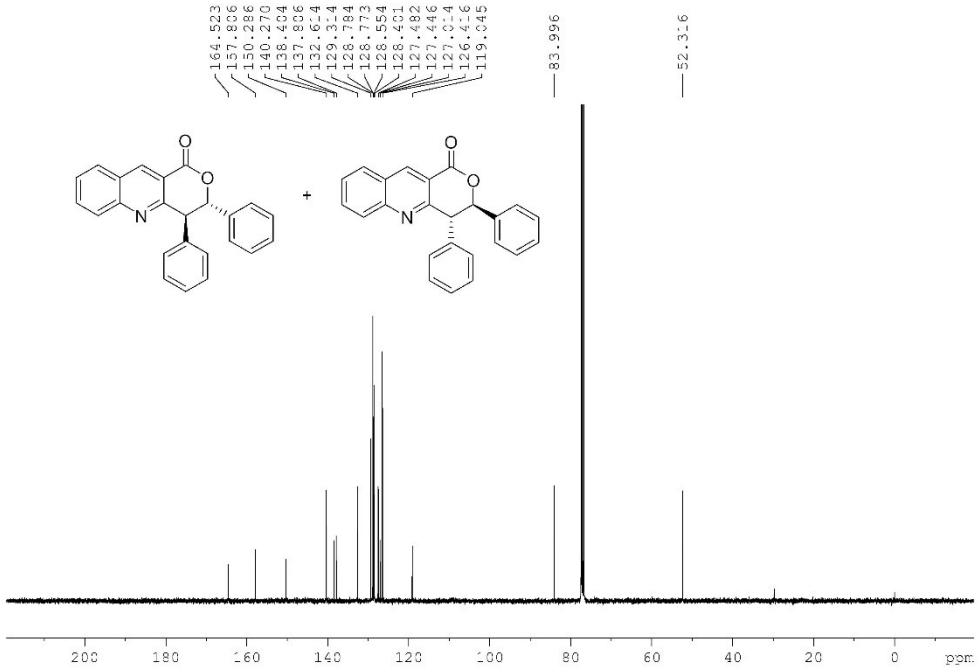
^{1}H NMR spectrum of compound 1j



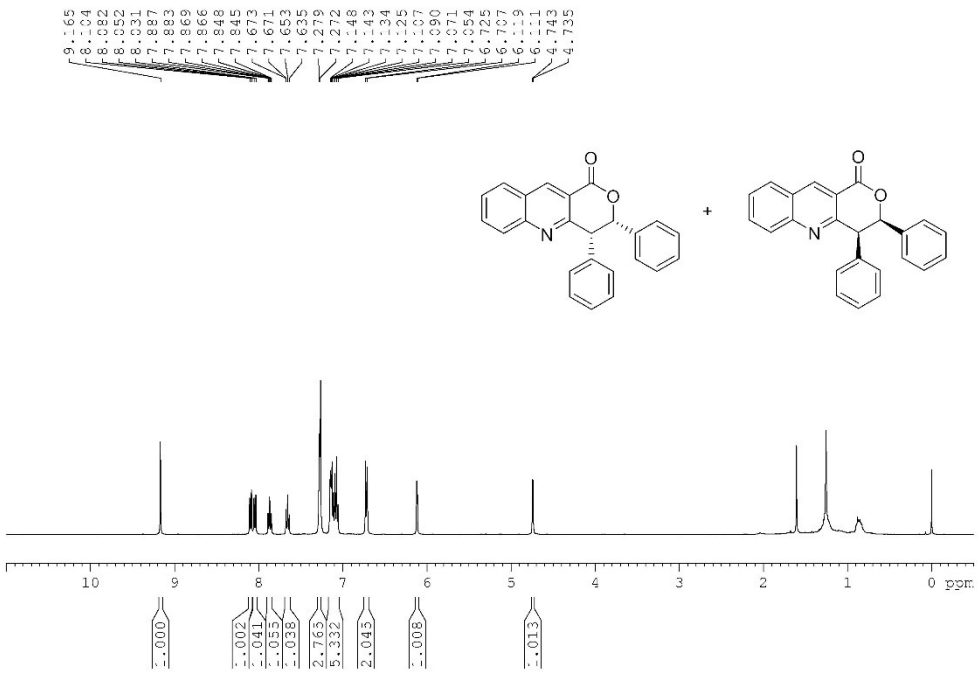
^{13}C NMR spectrum of compound 1j



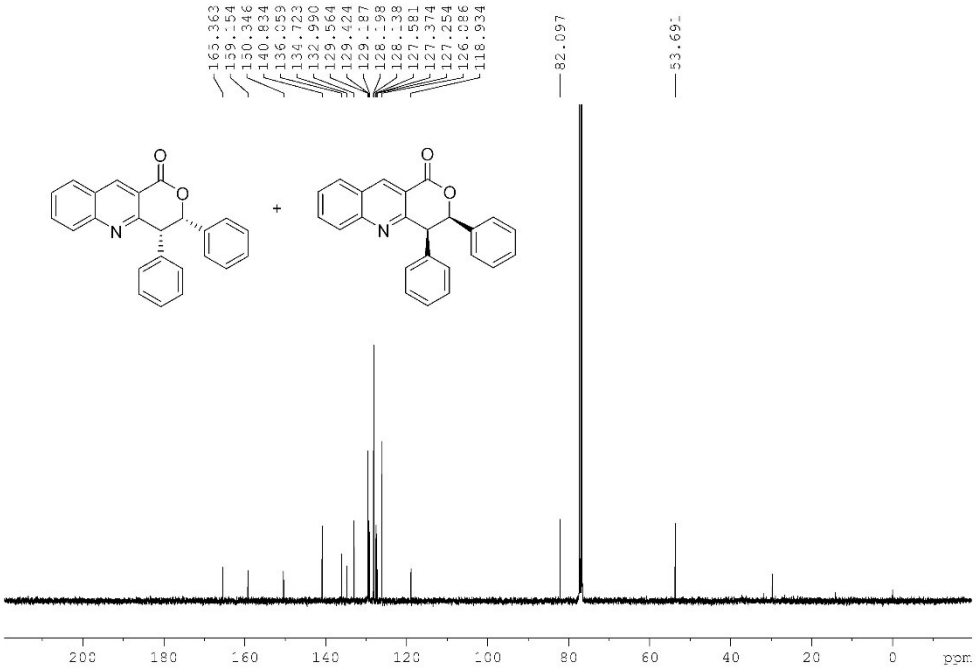
^{1}H NMR spectrum of compound 3aa (trans)



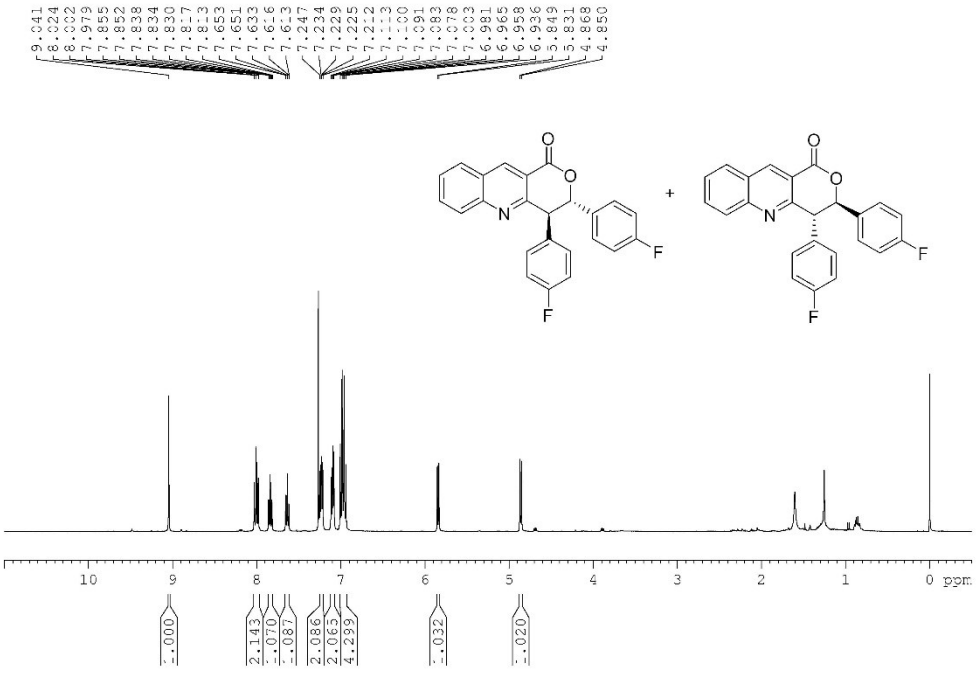
^{13}C NMR spectrum of compound 3aa (trans)



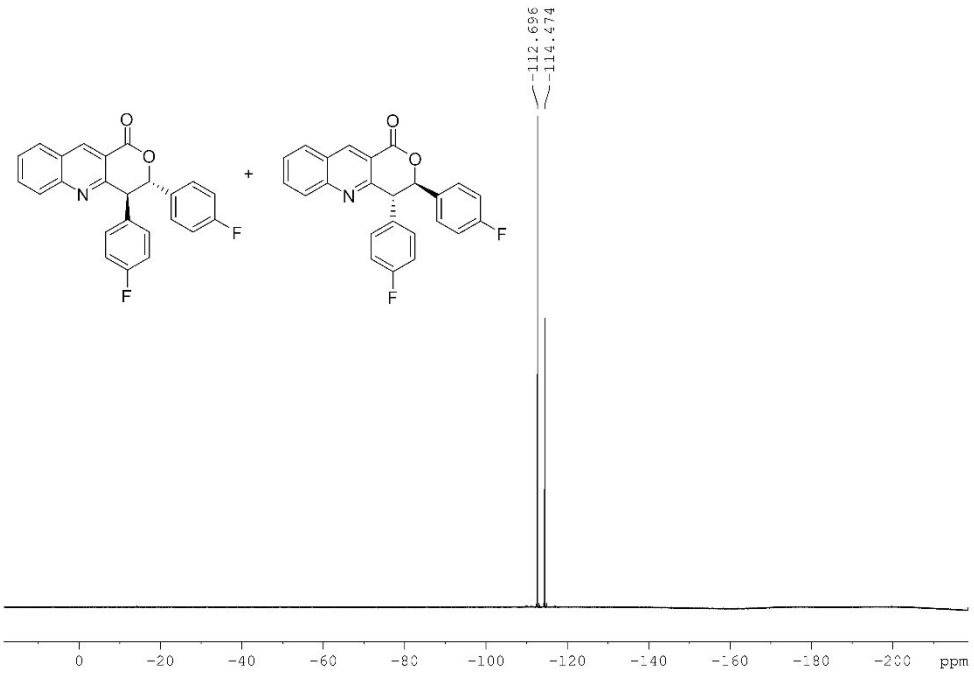
^{1}H NMR spectrum of compound 3aa (cis)



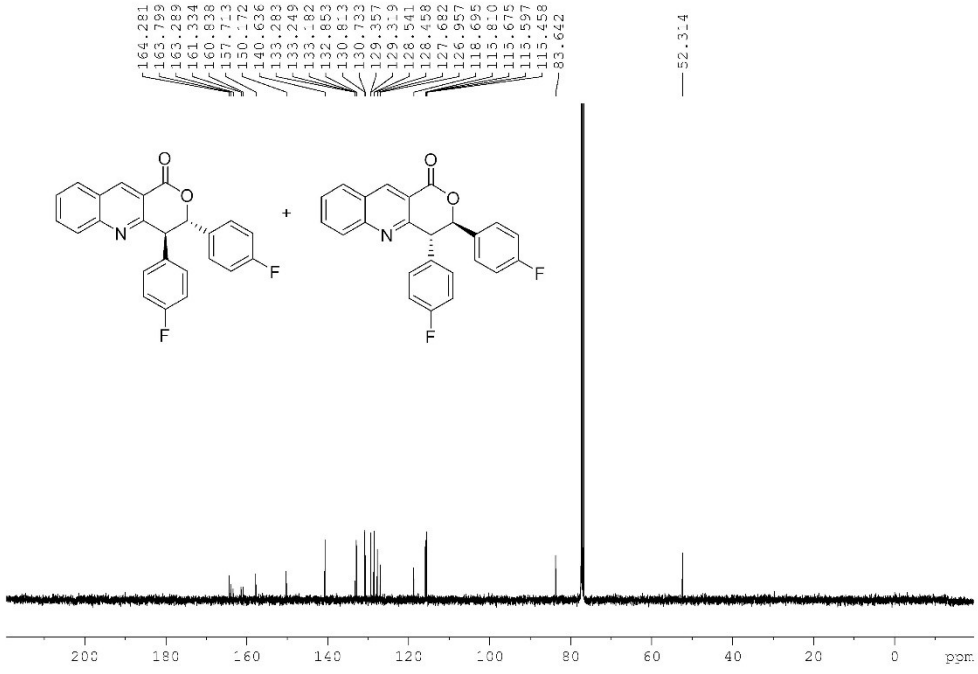
^{13}C NMR spectrum of compound 3aa (cis)



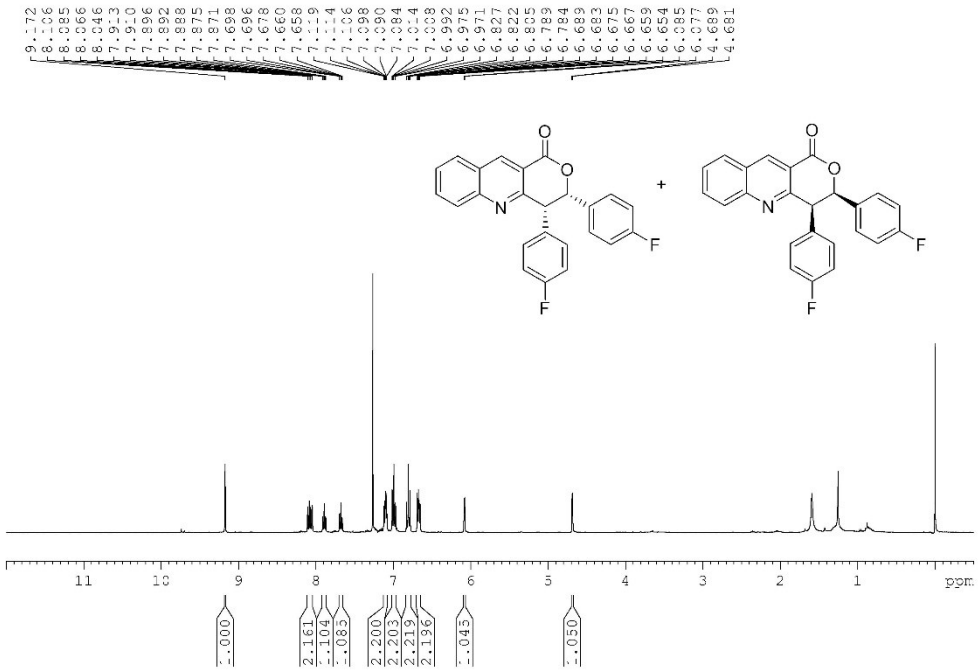
^{1}H NMR spectrum of compound 3ab (trans)



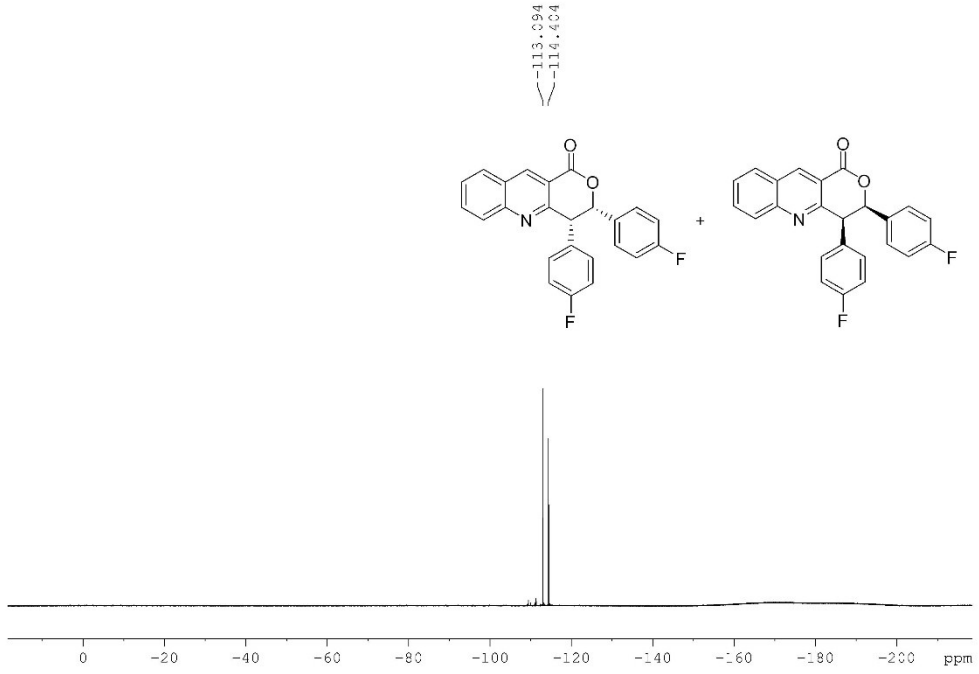
^{19}F NMR spectrum of compound 3ab (trans)



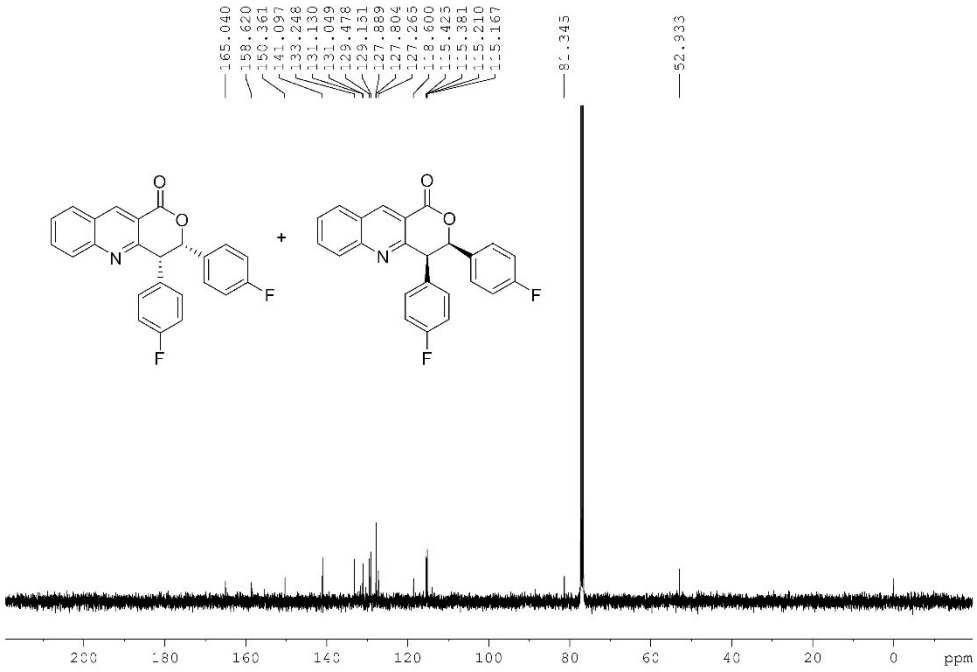
^{13}C NMR spectrum of compound 3ab (trans)



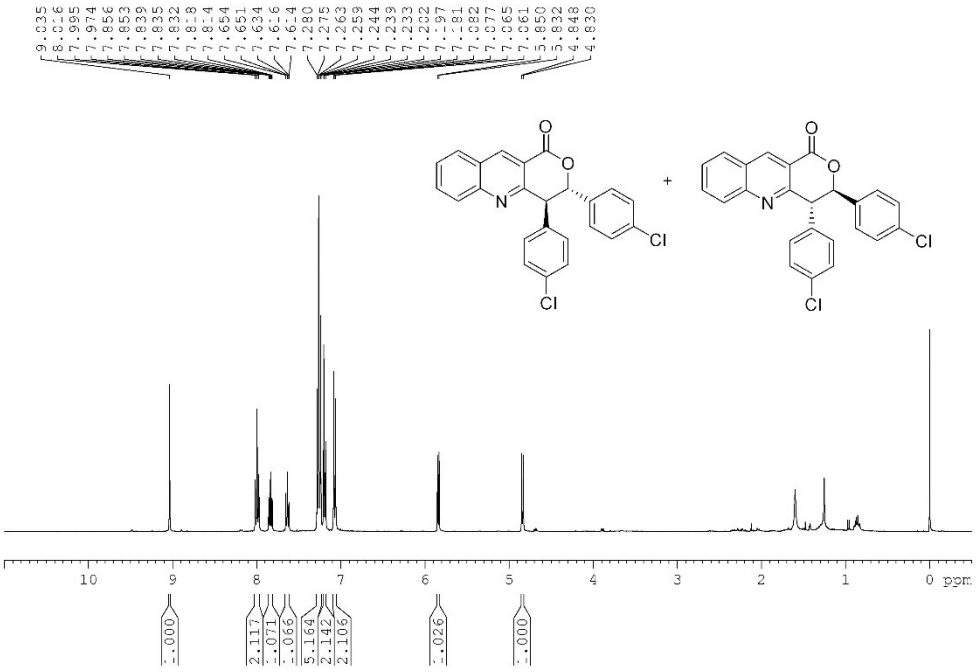
^{1}H NMR spectrum of compound 3ab (cis)



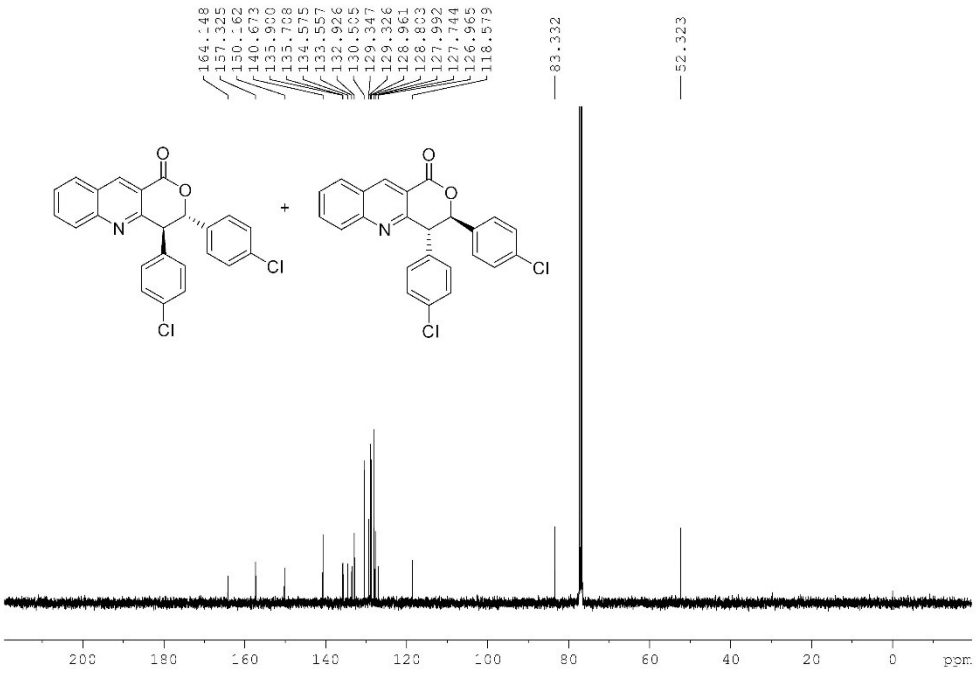
^{19}F NMR spectrum of compound 3ab (cis)



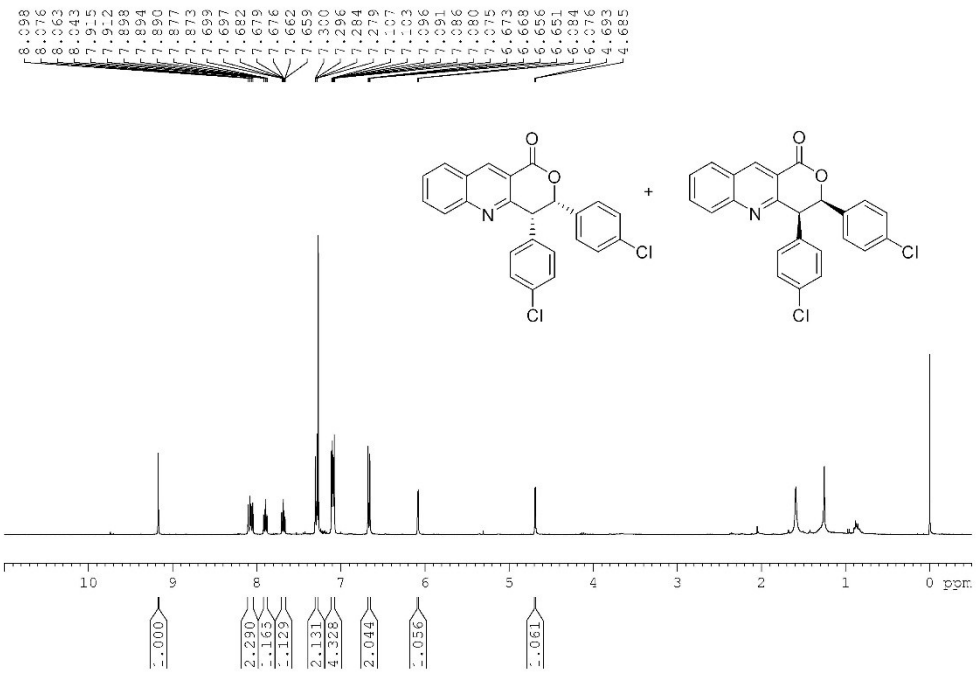
^{13}C NMR spectrum of compound 3ab (cis)



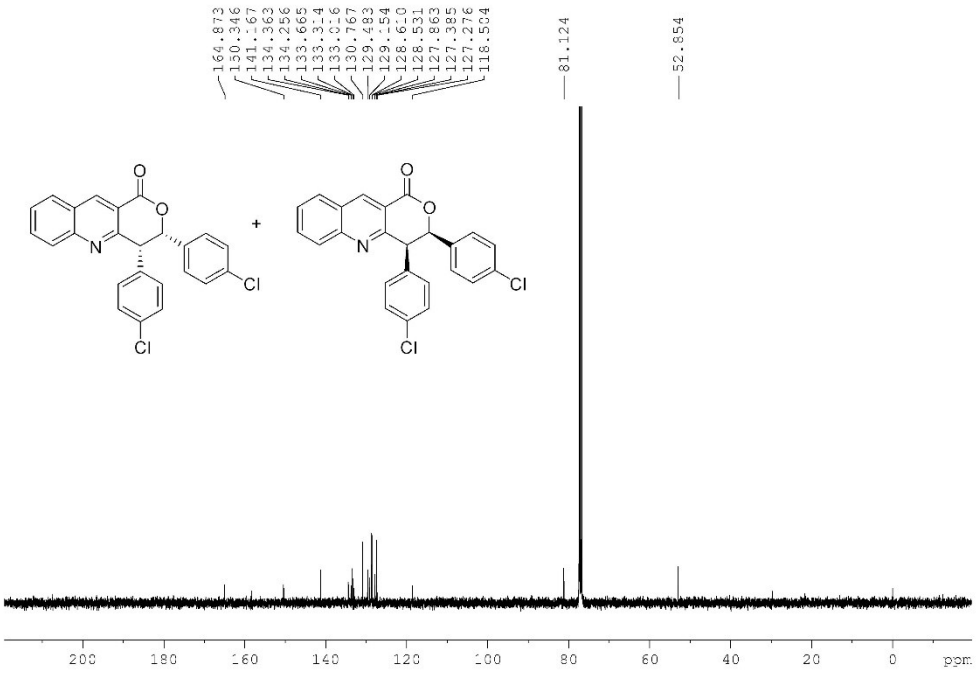
^{1}H NMR spectrum of compound 3ac (trans)



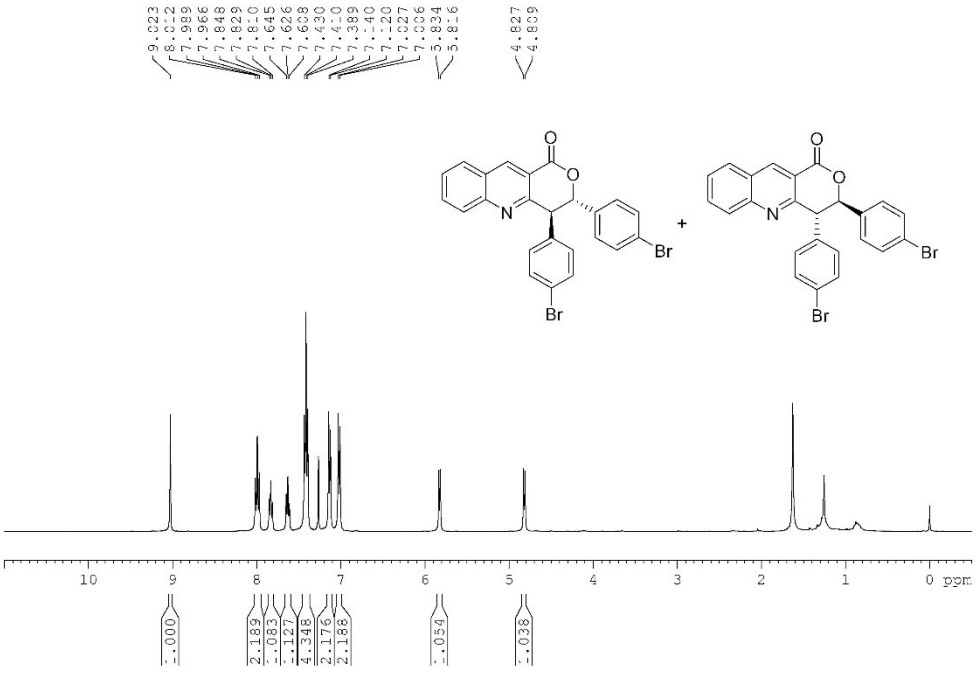
^{13}C NMR spectrum of compound 3ac (trans)



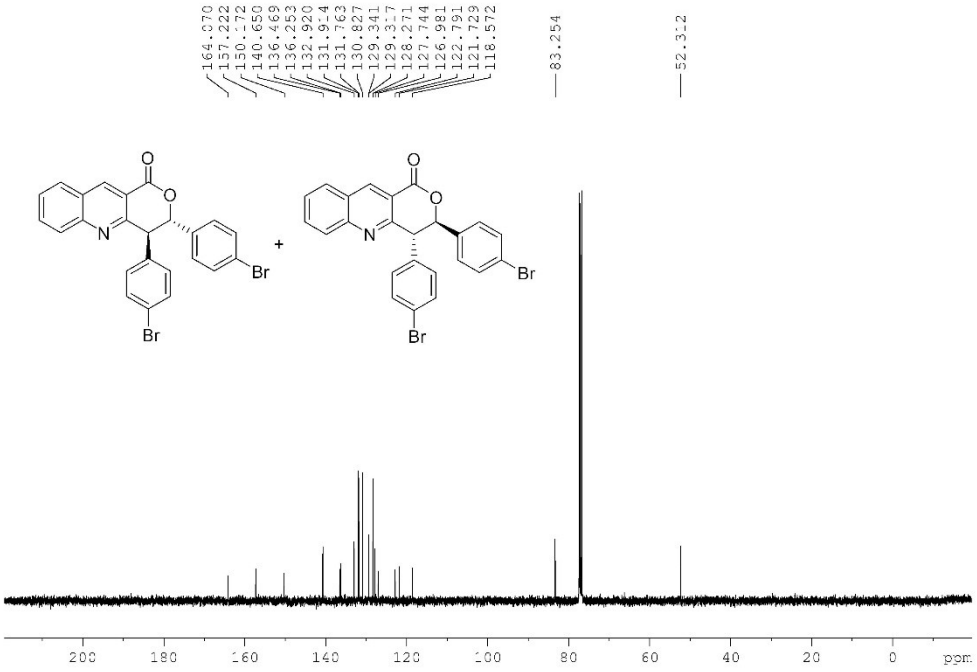
^{1}H NMR spectrum of compound 3ac (cis)



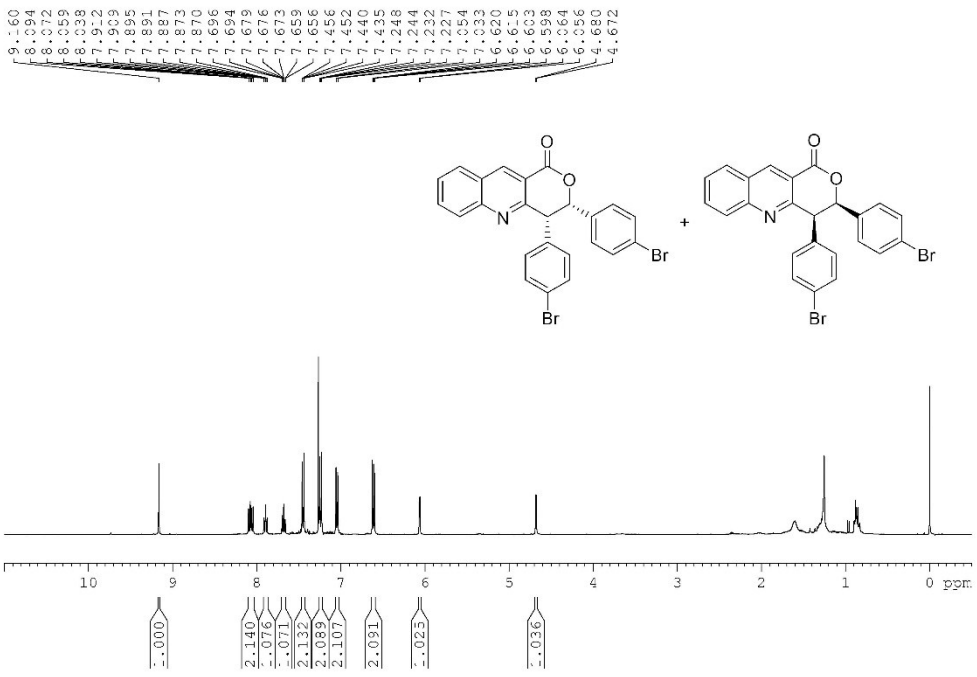
^{13}C NMR spectrum of compound 3ac (cis)



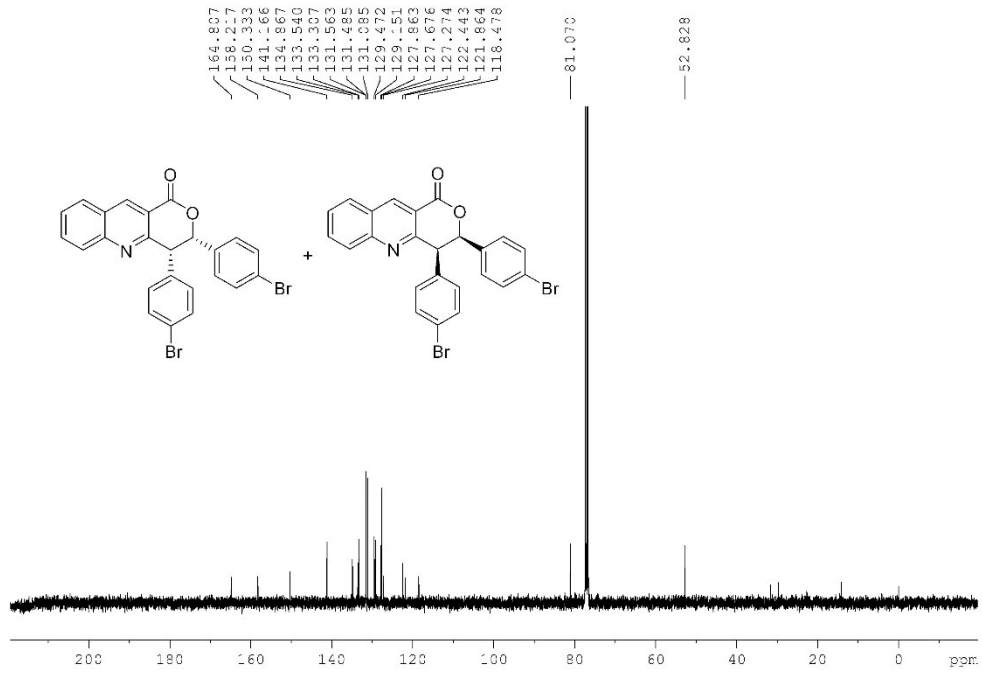
^{1}H NMR spectrum of compound 3ad (trans)



^{13}C NMR spectrum of compound 3ad (trans)

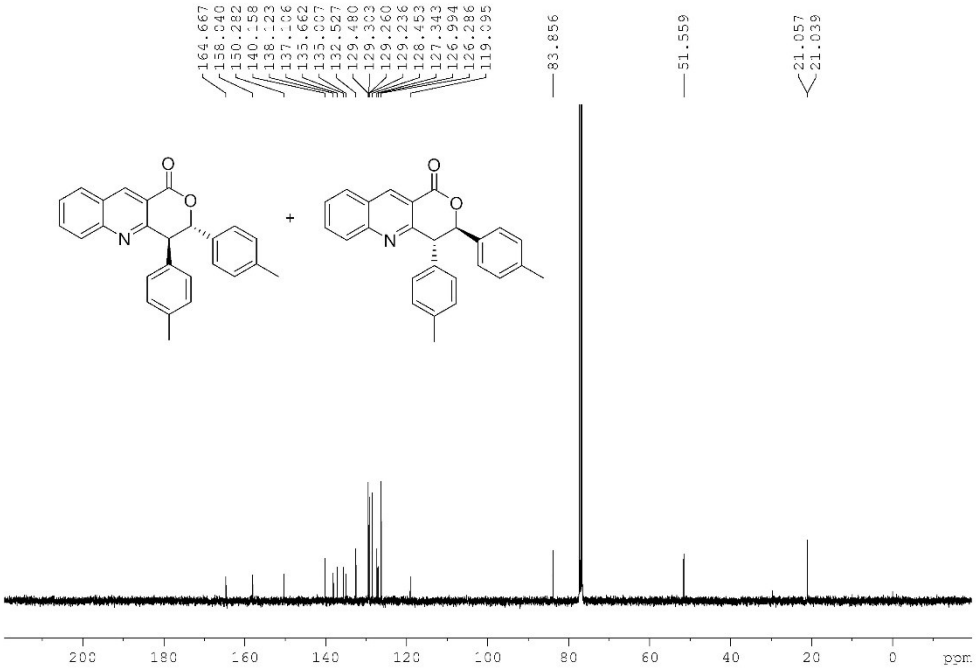


^{1}H NMR spectrum of compound 3ad (cis)

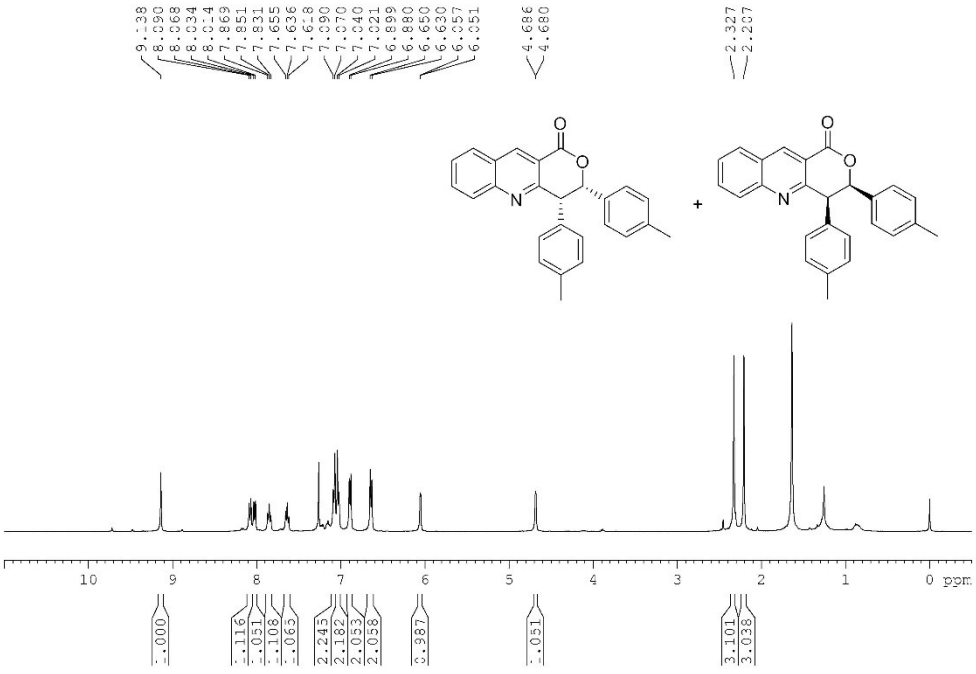


^{13}C NMR spectrum of compound 3ad (cis)

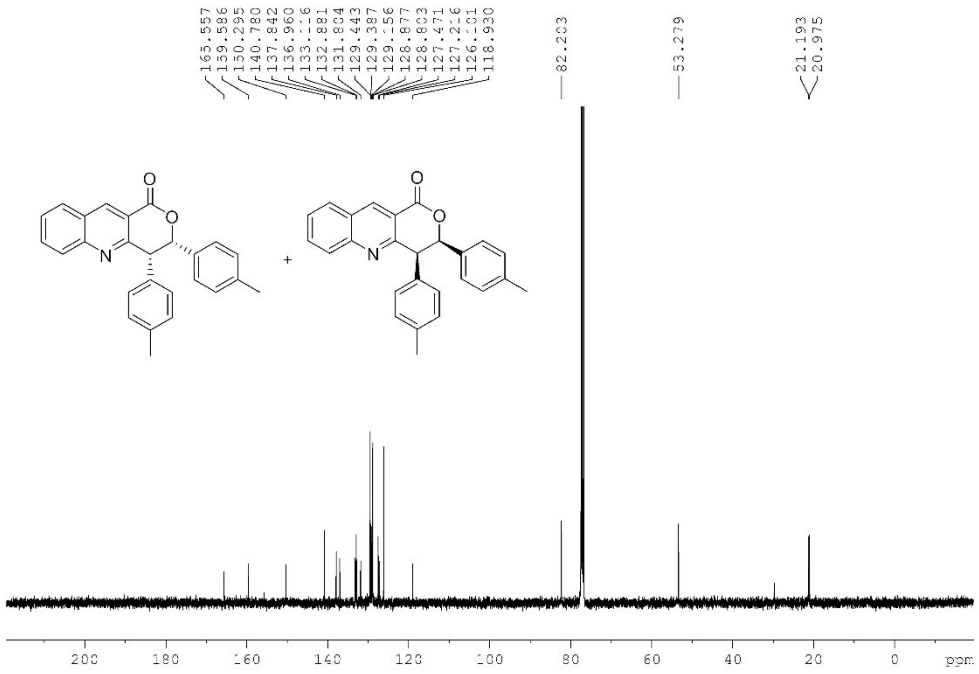
^{1}H NMR spectrum of compound 3ae (trans)



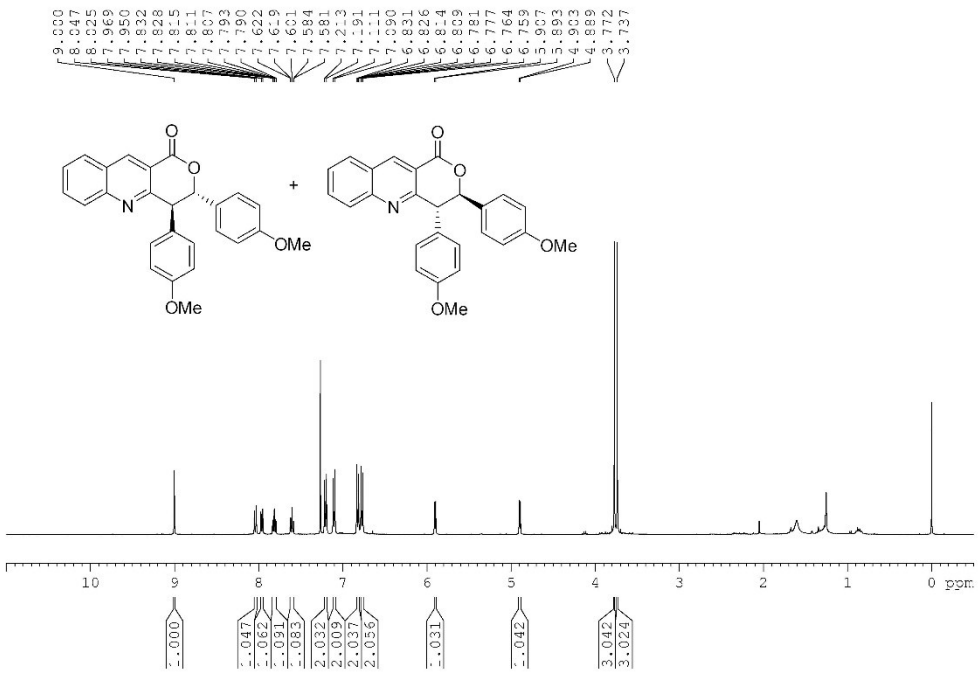
^{13}C NMR spectrum of compound 3ae (trans)



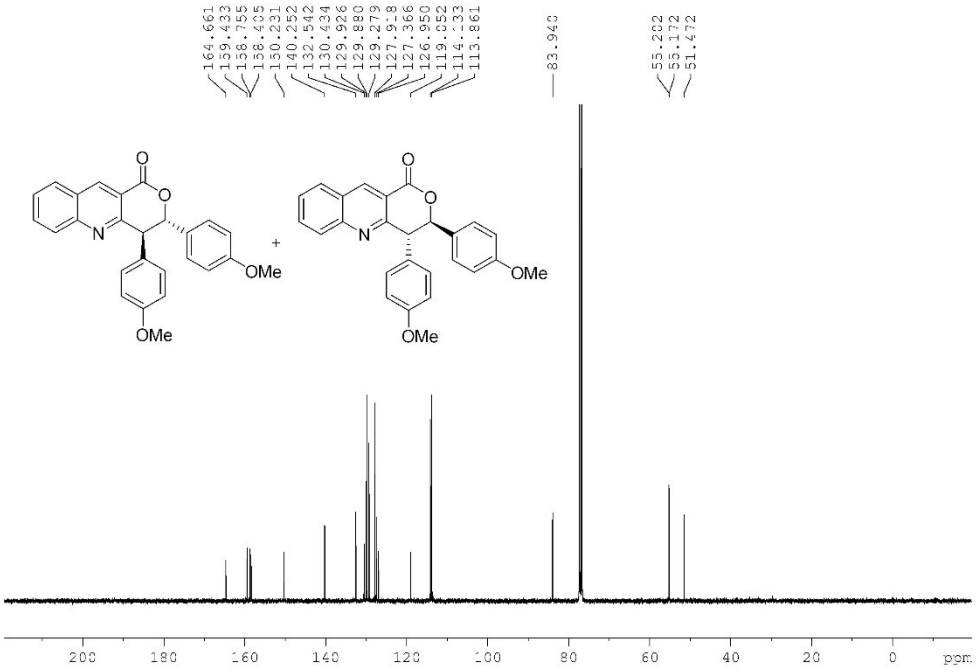
^{1}H NMR spectrum of compound 3ae (cis)



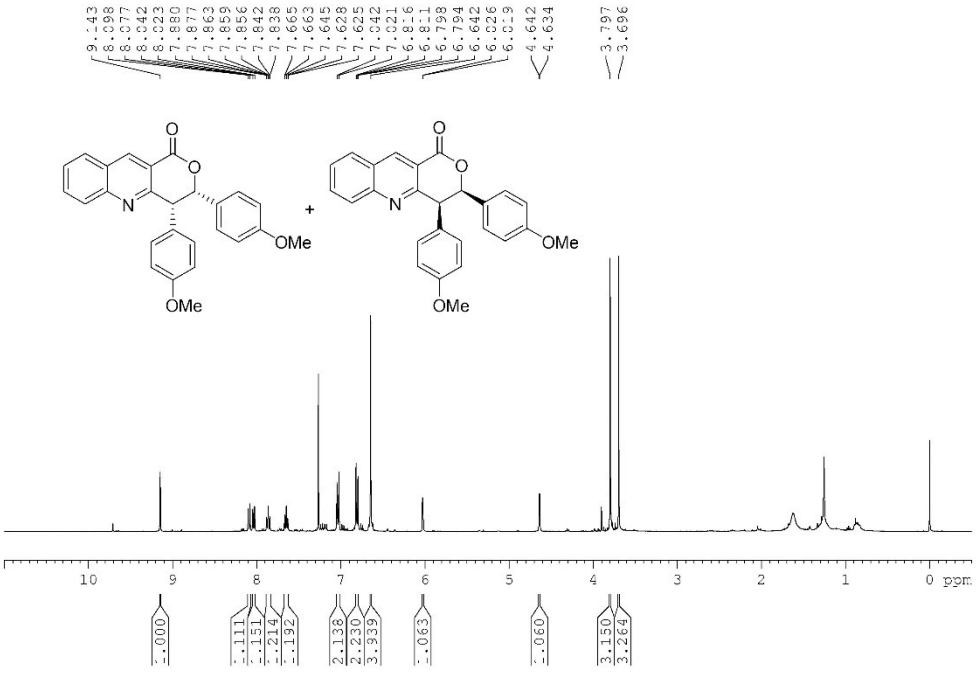
^{13}C NMR spectrum of compound 3ae (cis)



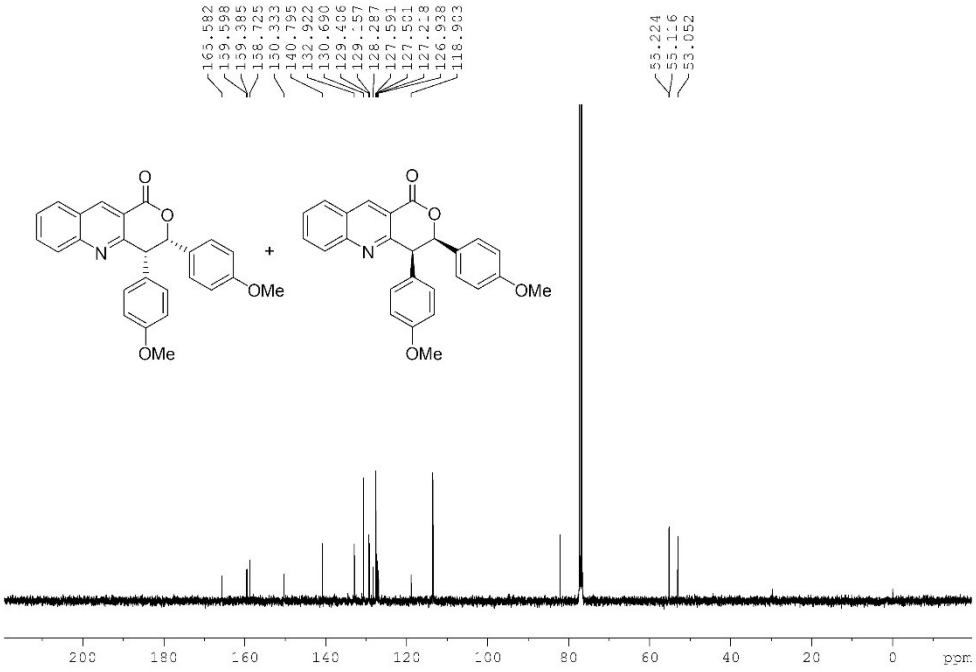
^{1}H NMR spectrum of compound 3af (trans)



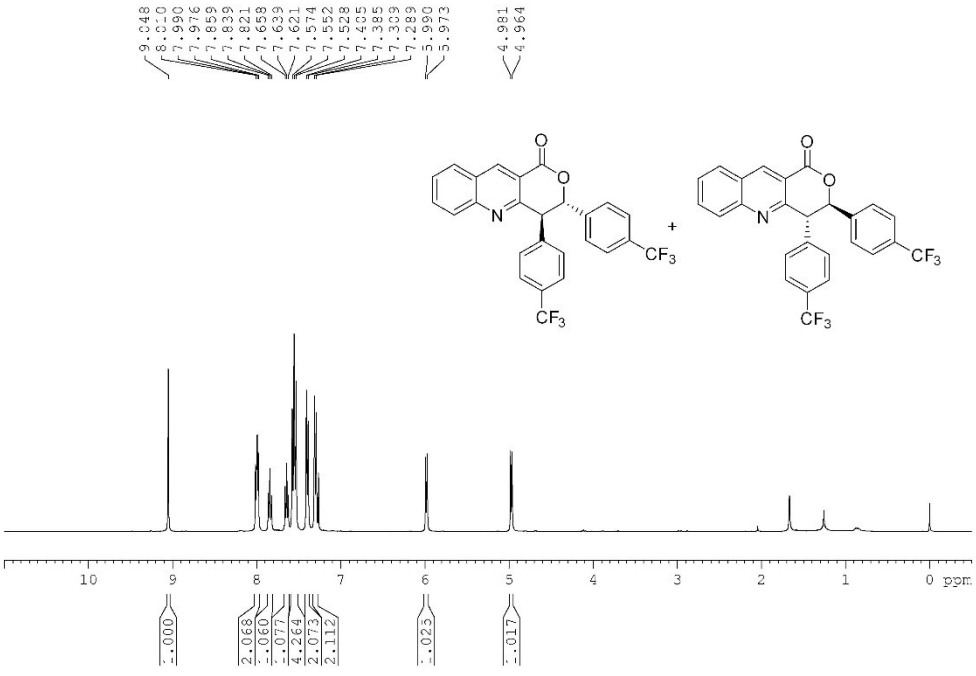
^{13}C NMR spectrum of compound 3af (trans)



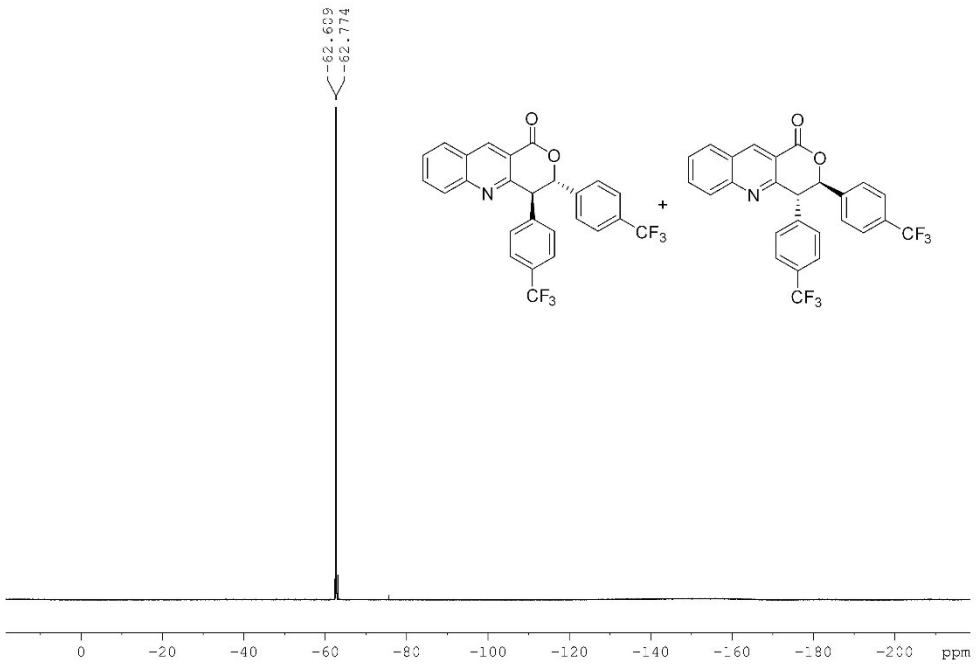
^{1}H NMR spectrum of compound 3af (cis)



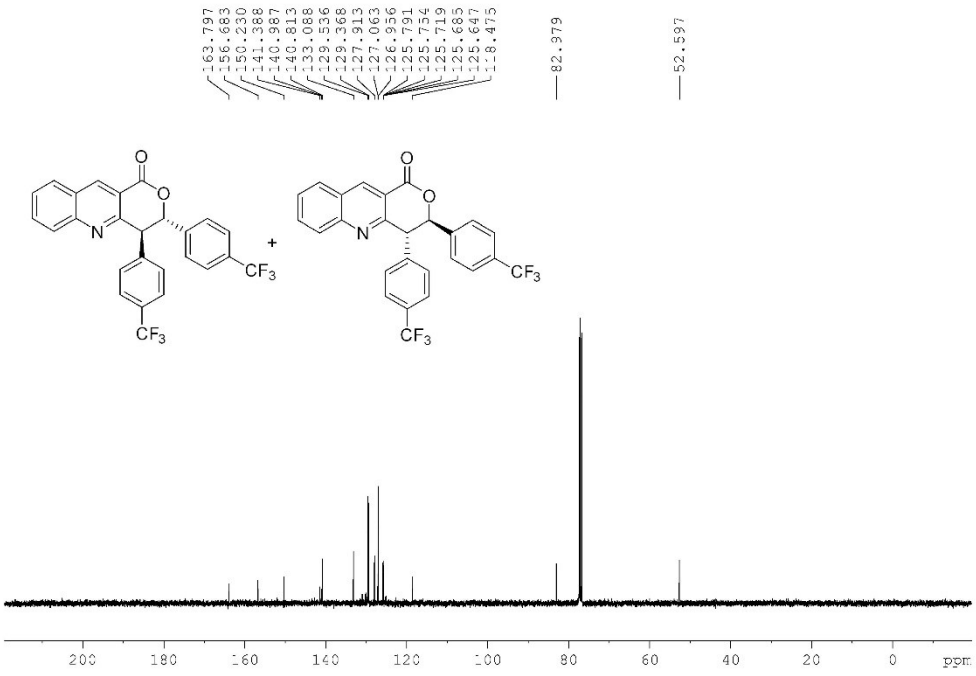
^{13}C NMR spectrum of compound 3af (cis)



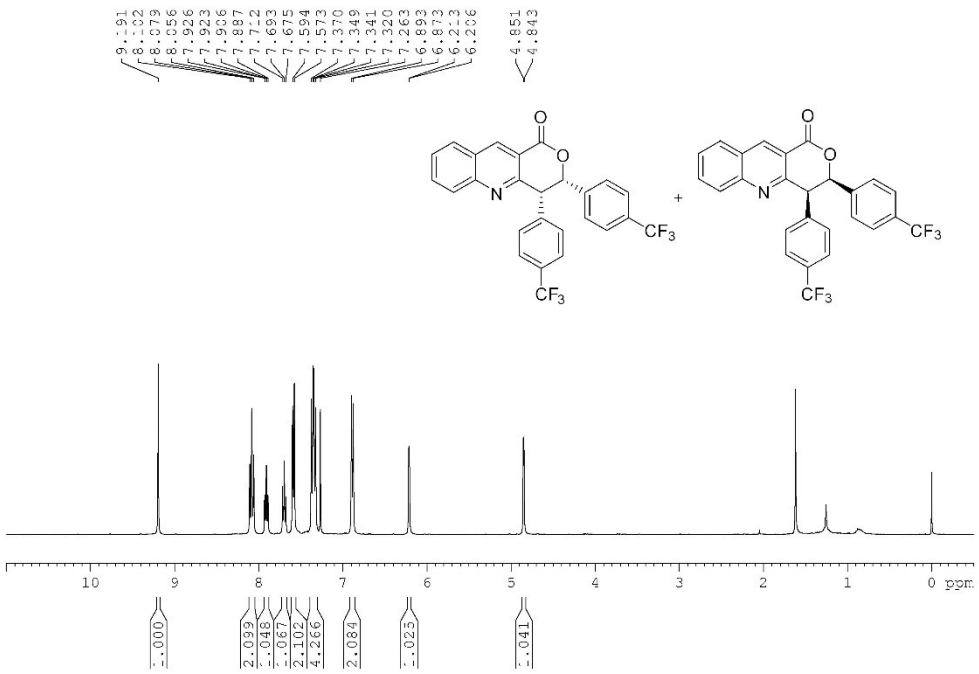
^{1}H NMR spectrum of compound 3ag (trans)



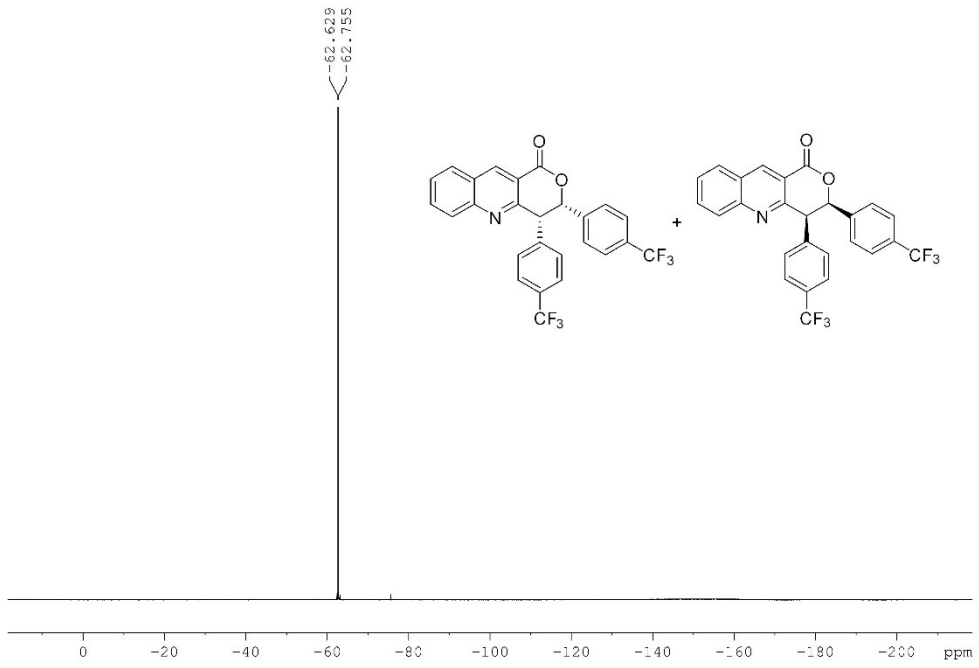
^{19}F NMR spectrum of compound 3ag (trans)



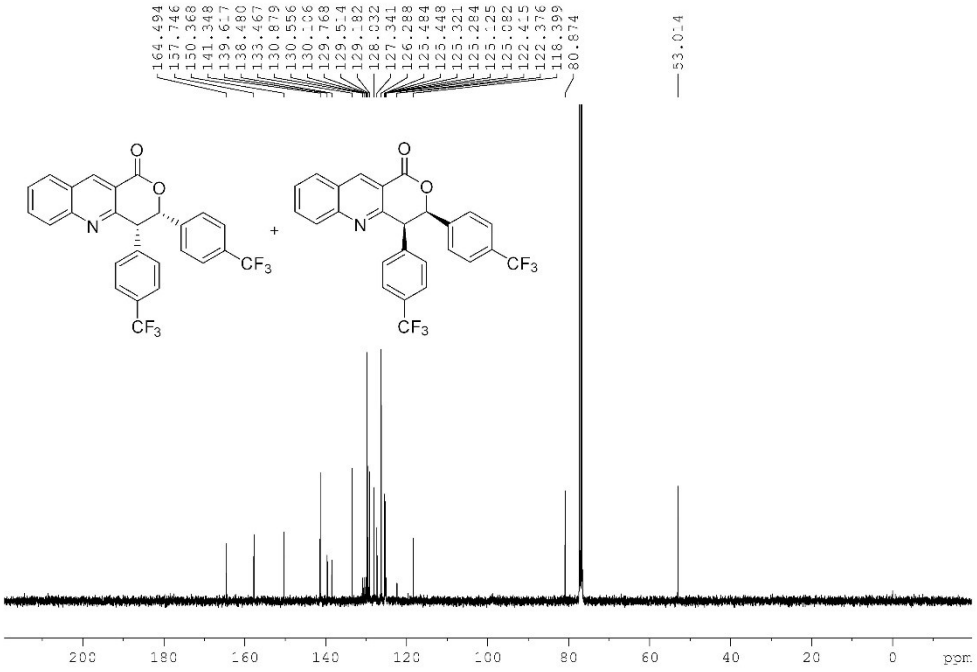
^{13}C NMR spectrum of compound 3ag (trans)



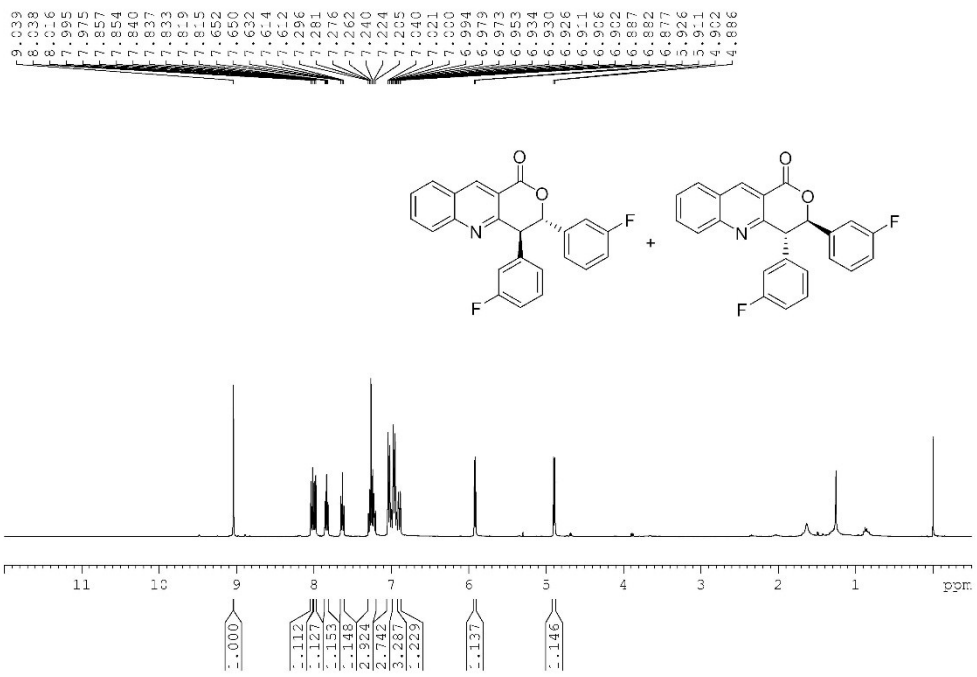
^{1}H NMR spectrum of compound 3ag (cis)



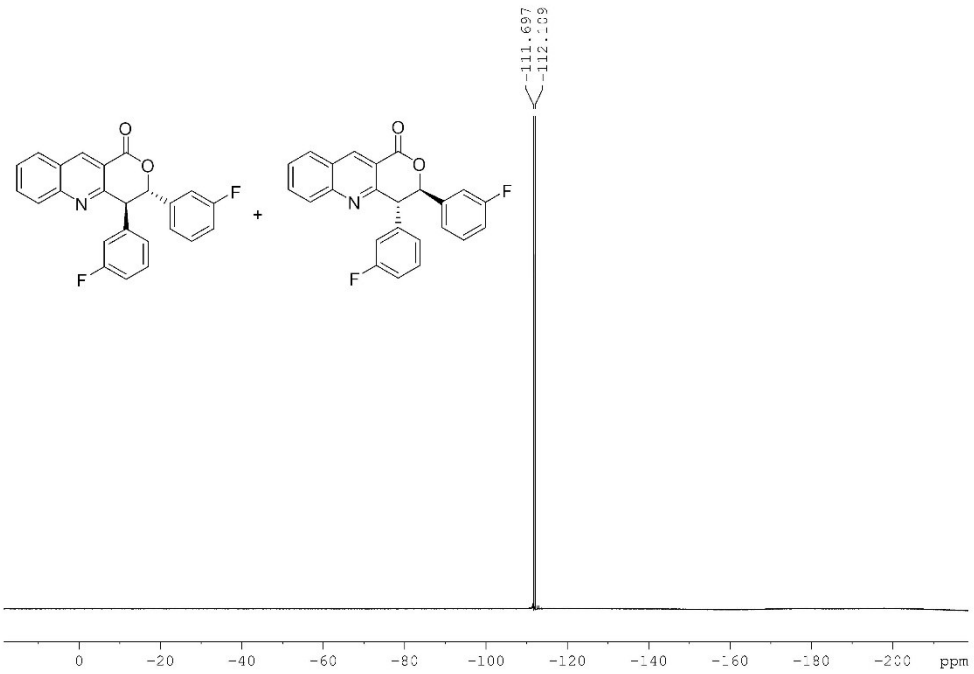
^{19}F NMR spectrum of compound 3ag (cis)



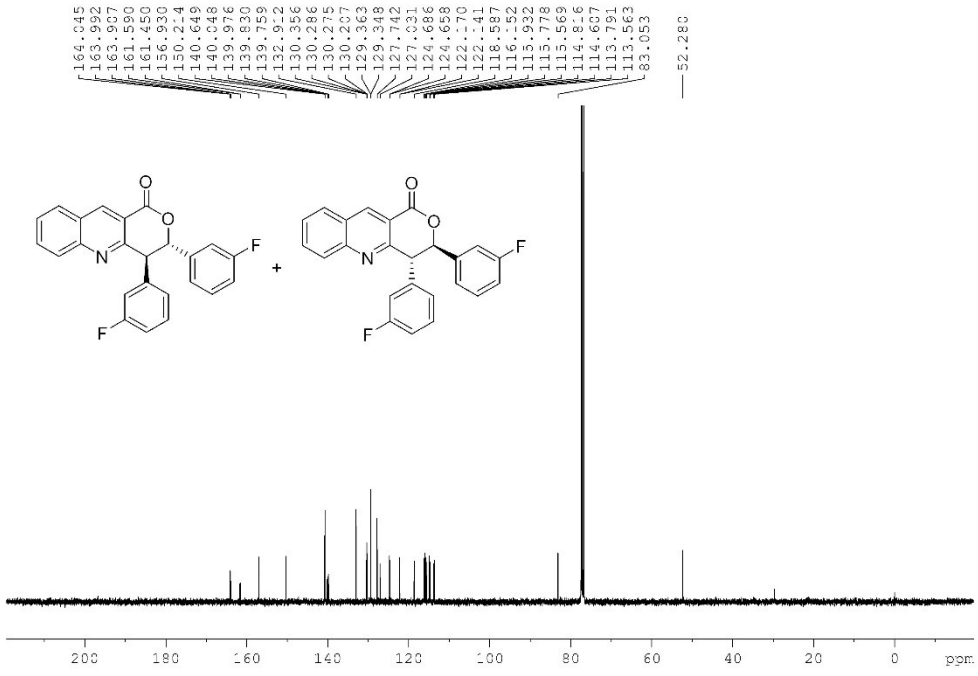
^{13}C NMR spectrum of compound 3ag (cis)



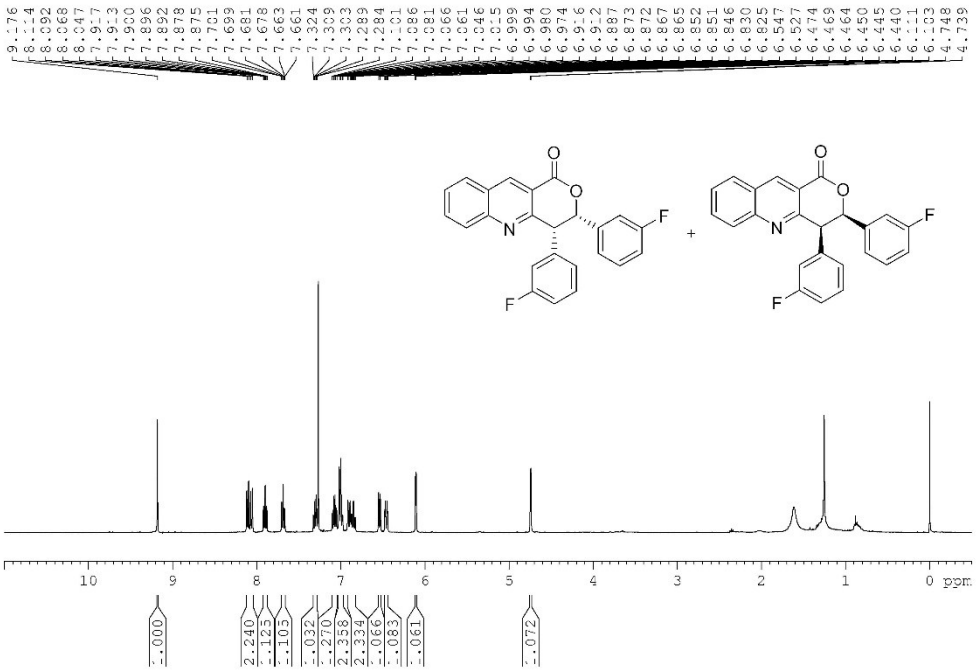
^{1}H NMR spectrum of compound 3ah (trans)



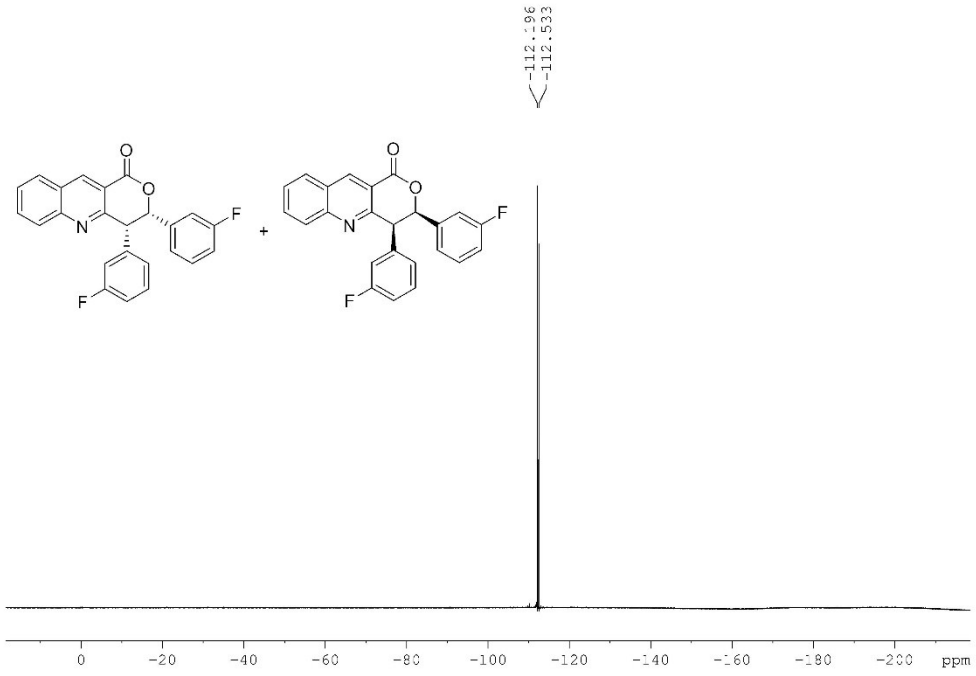
^{19}F NMR spectrum of compound 3ah (trans)



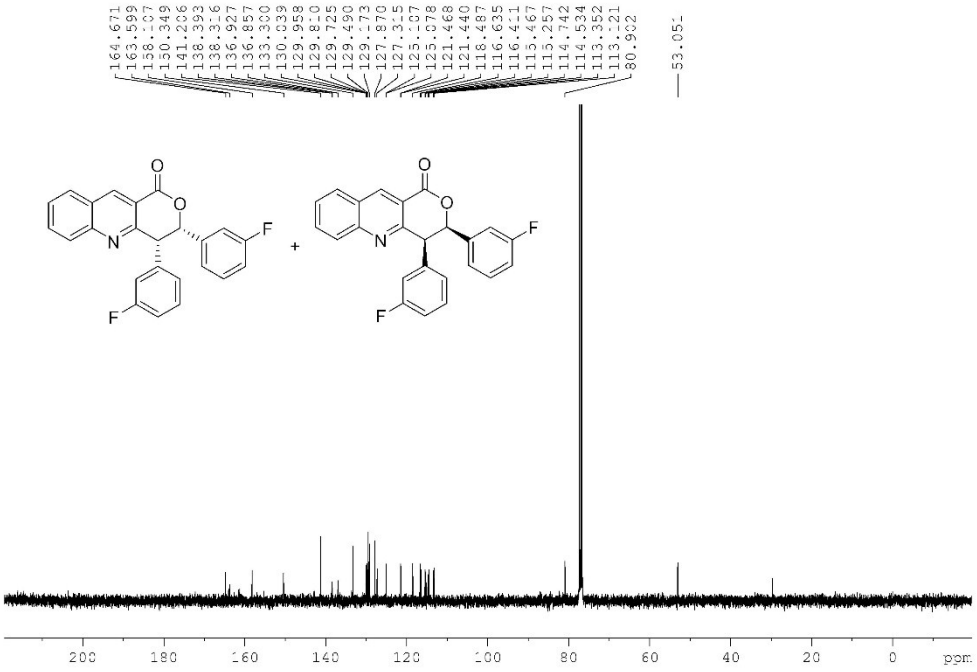
^{13}C NMR spectrum of compound 3ah (trans)



^{1}H NMR spectrum of compound 3ah (cis)

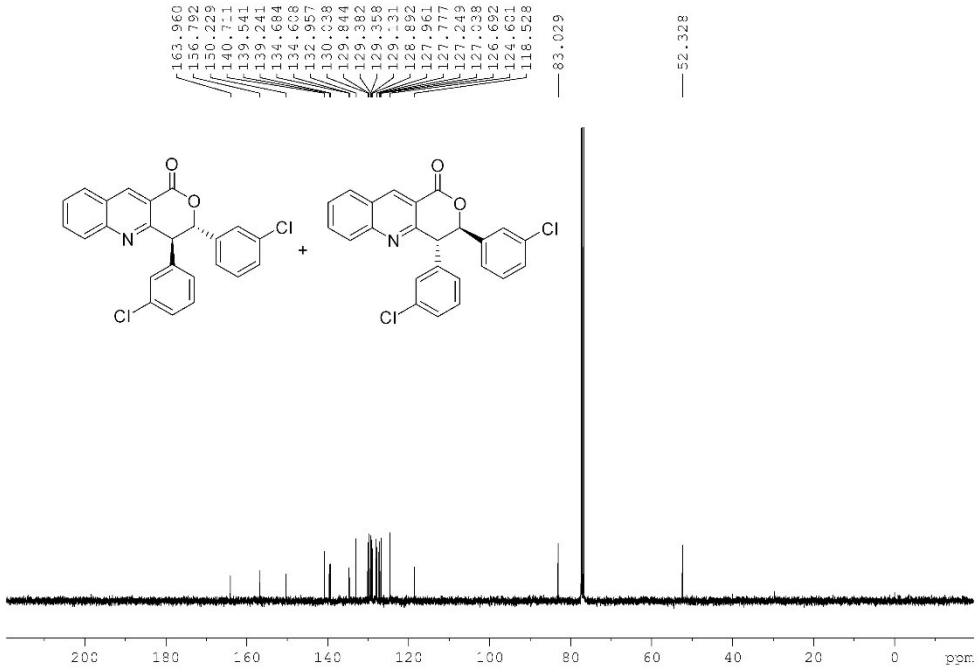


^{19}F NMR spectrum of compound 3ah (cis)

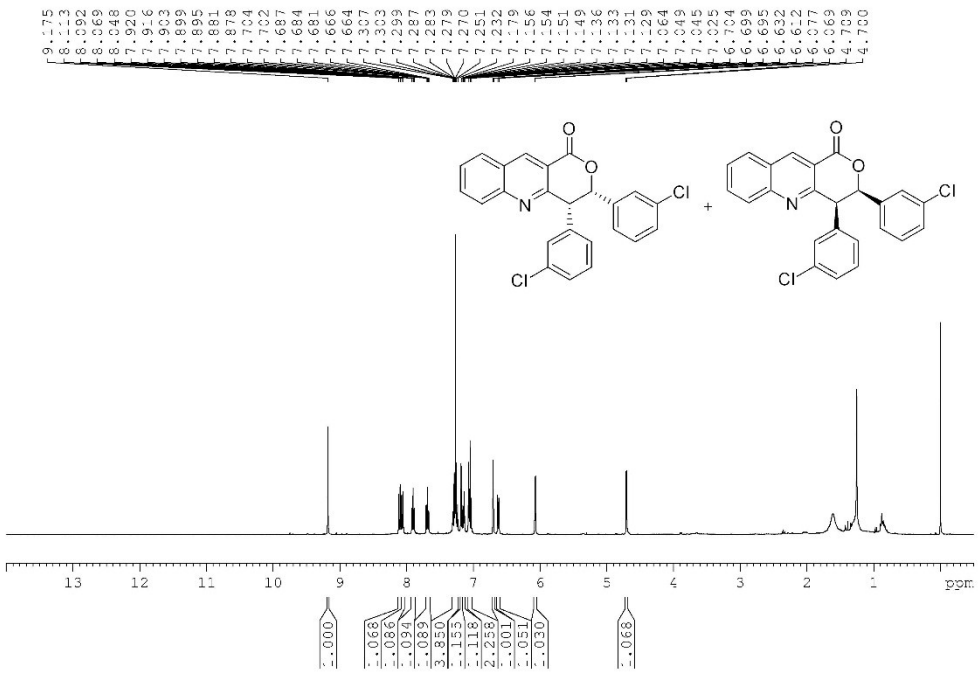


^{13}C NMR spectrum of compound 3ah (cis)

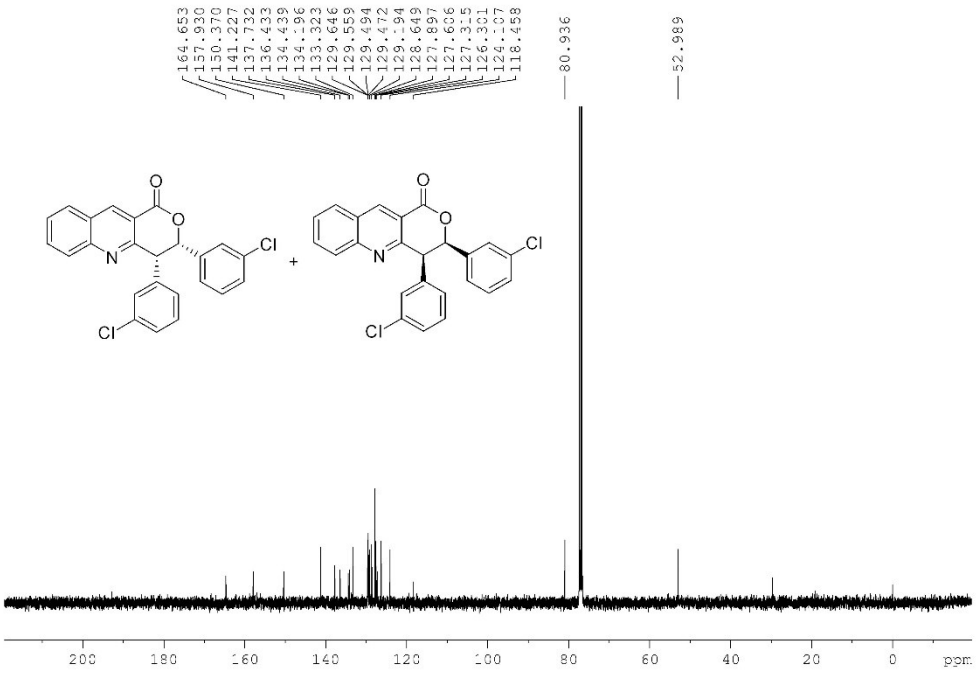
^{1}H NMR spectrum of compound 3ai (trans)



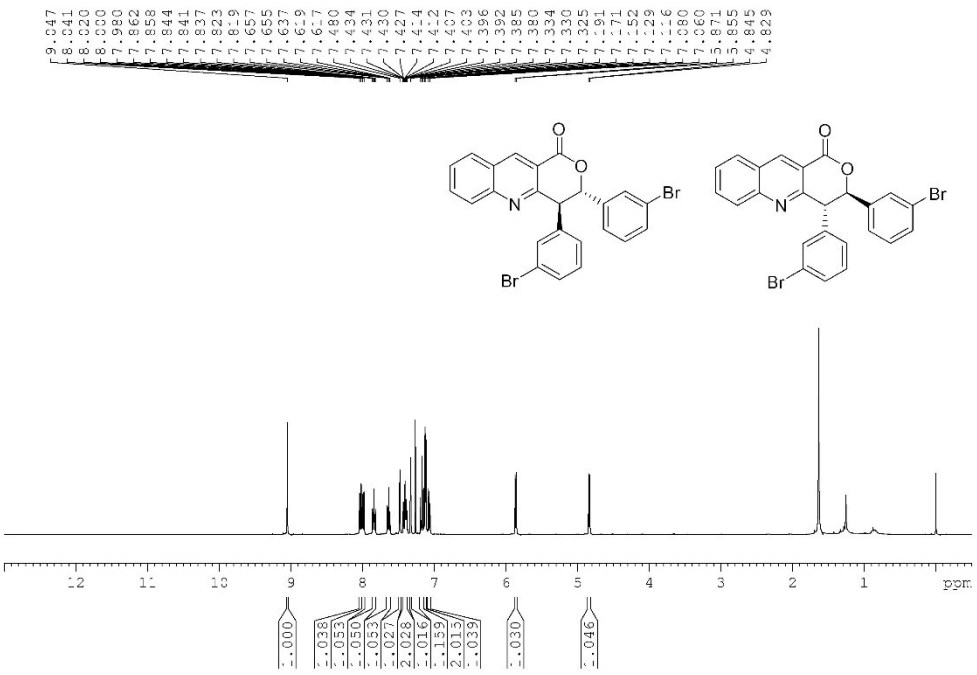
^{13}C NMR spectrum of compound 3ai (trans)



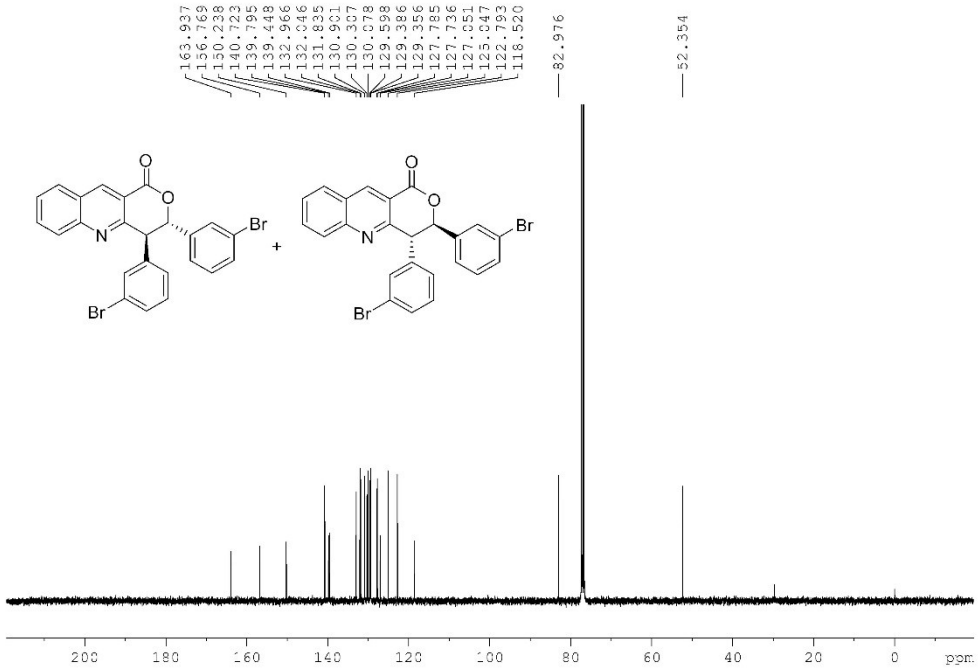
^{1}H NMR spectrum of compound 3ai (cis)



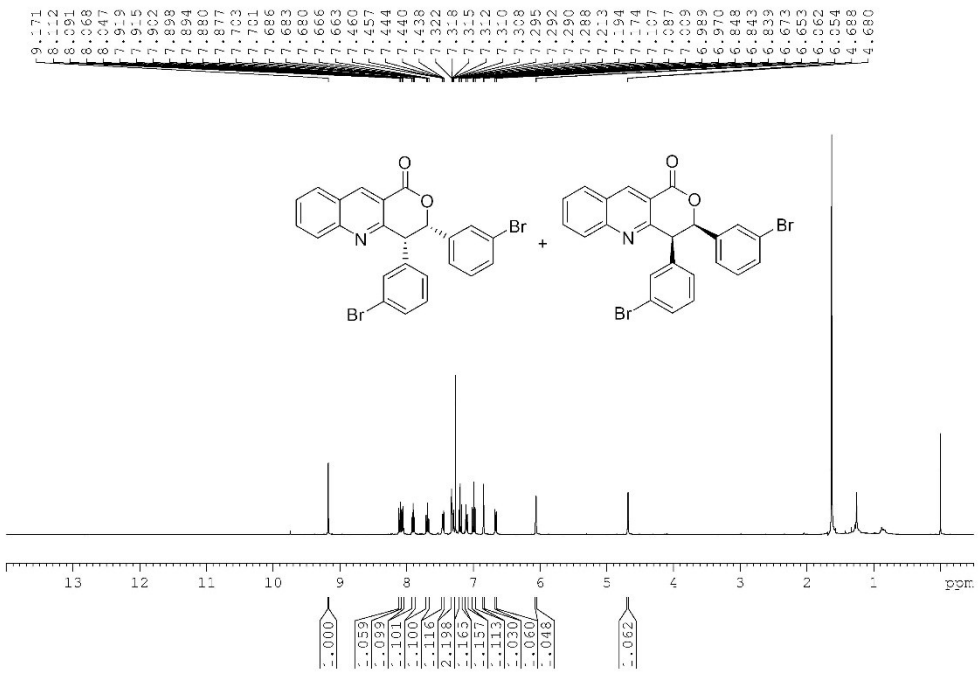
^{13}C NMR spectrum of compound 3ai (cis)



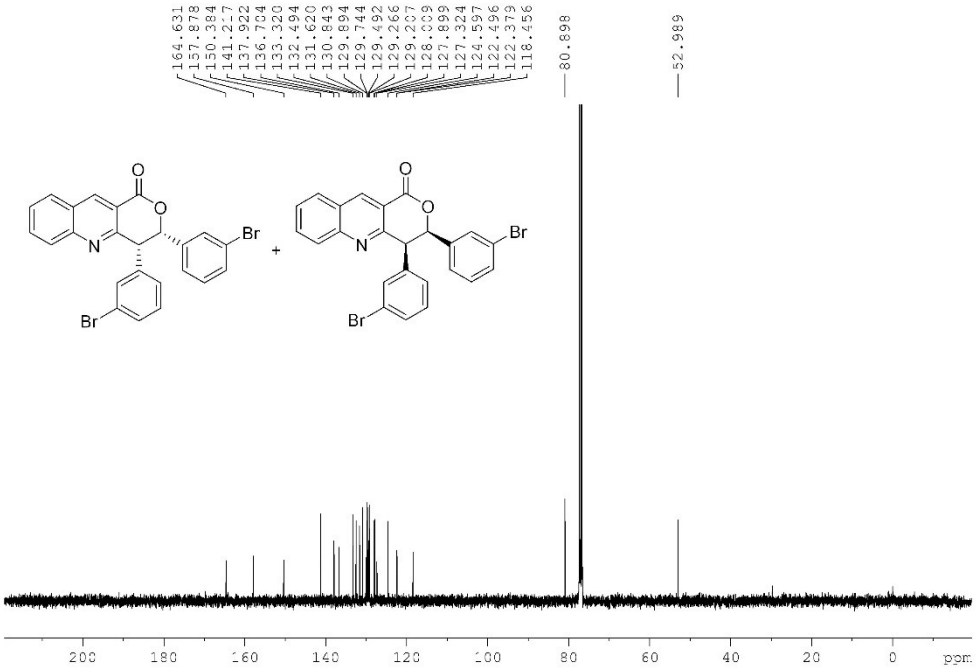
^{1}H NMR spectrum of compound 3aj (trans)



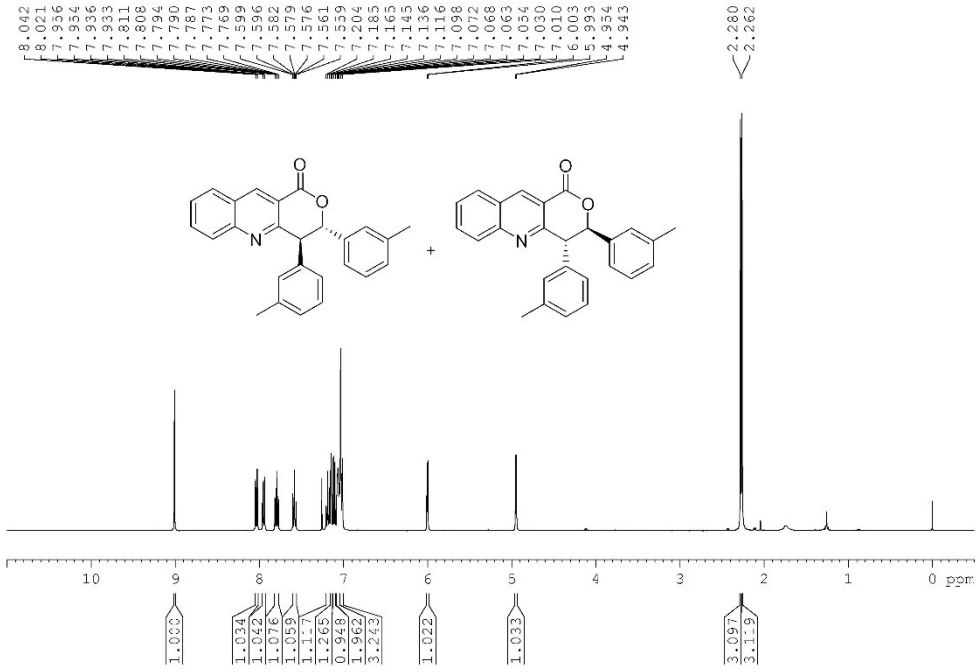
^{13}C NMR spectrum of compound 3aj (trans)



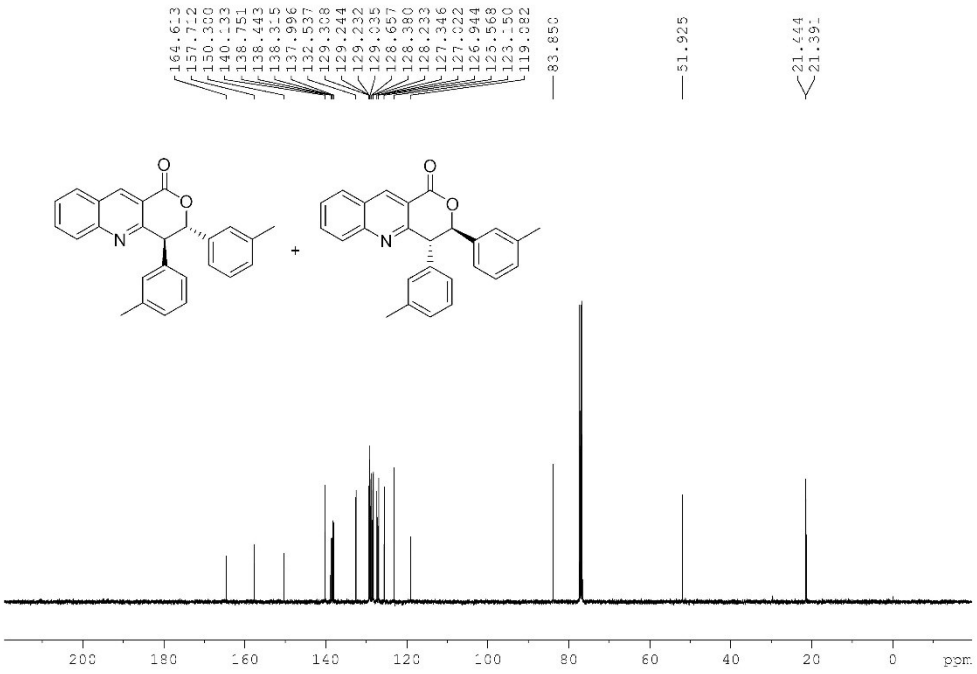
^{1}H NMR spectrum of compound 3aj (cis)



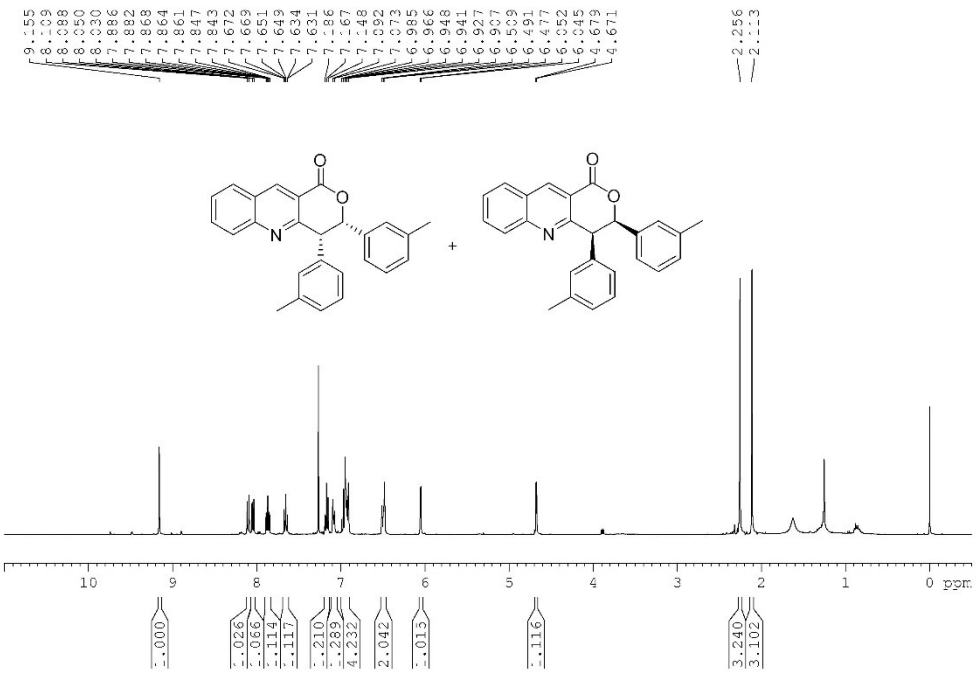
^{13}C NMR spectrum of compound 3aj (cis)



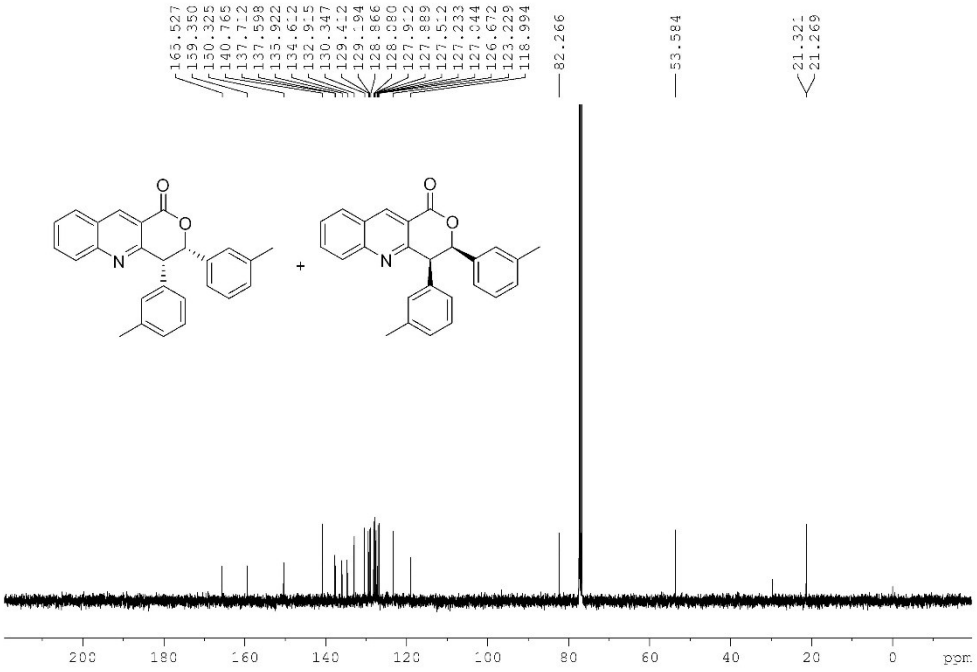
^{1}H NMR spectrum of compound 3ak (trans)



^{13}C NMR spectrum of compound 3ak (trans)

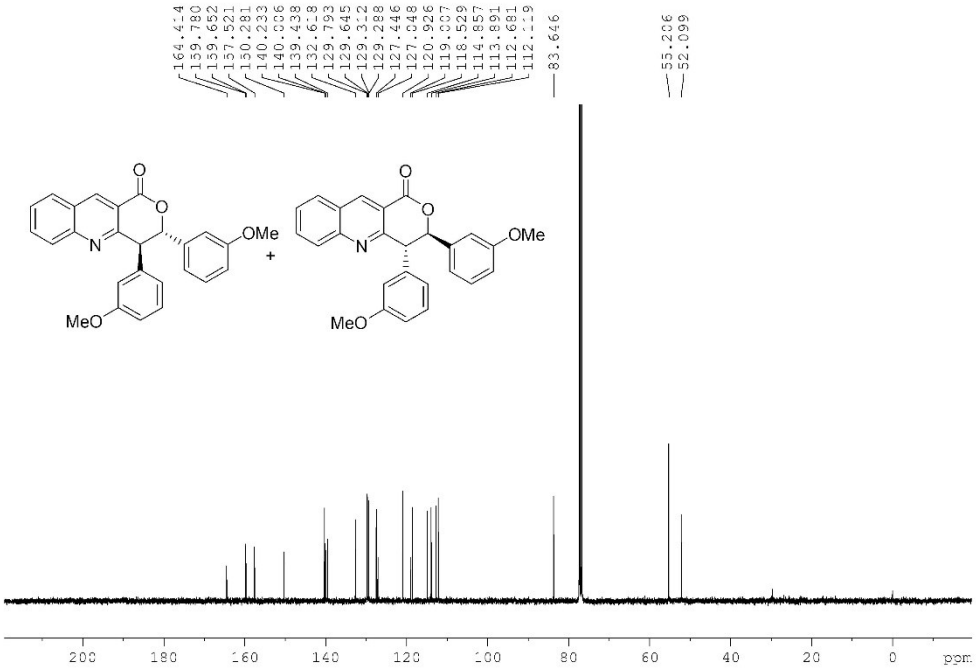


^{1}H NMR spectrum of compound 3ak (cis)

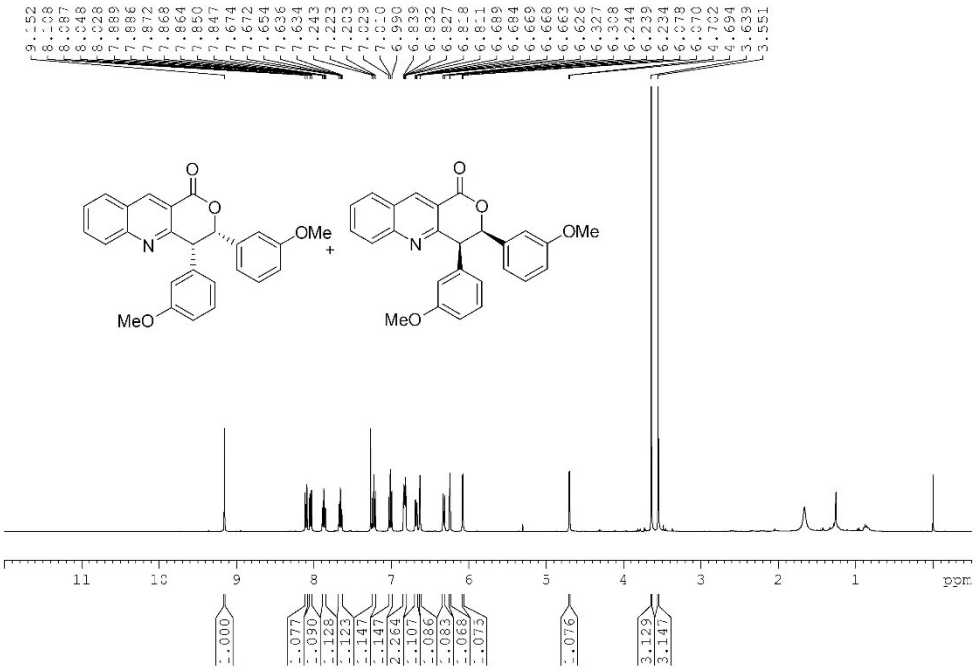


^{13}C NMR spectrum of compound 3ak (cis)

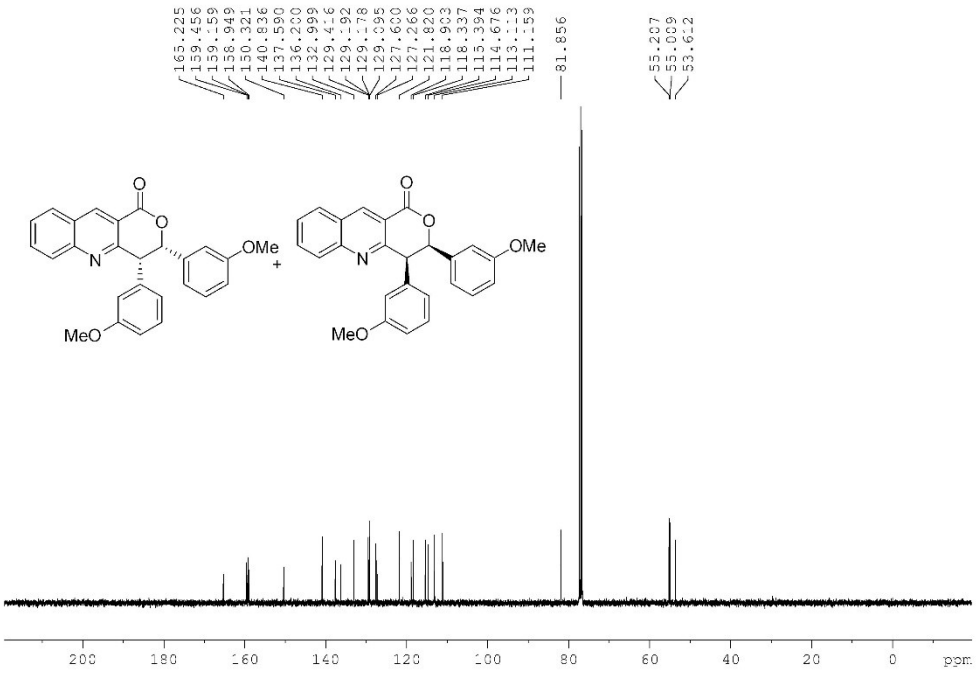
^{1}H NMR spectrum of compound 3al (trans)



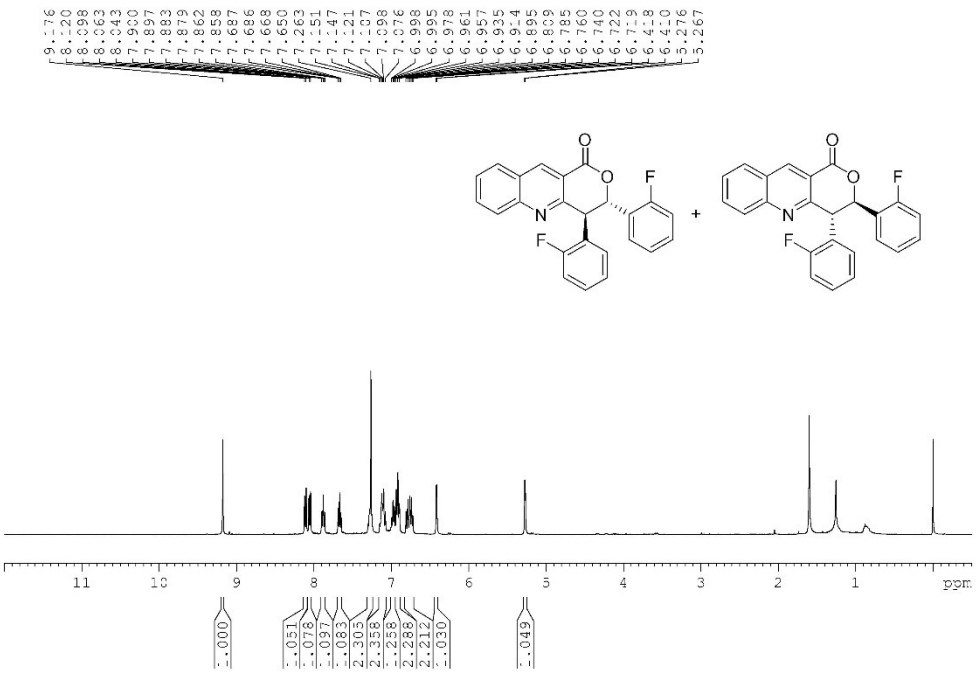
^{13}C NMR spectrum of compound 3al (trans)



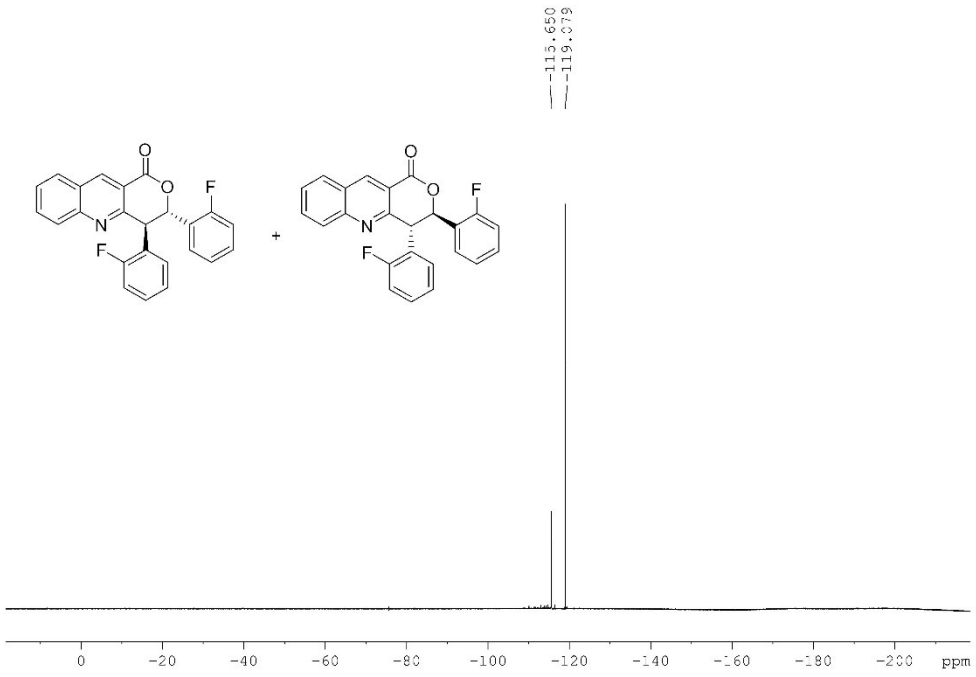
^{1}H NMR spectrum of compound 3al (cis)



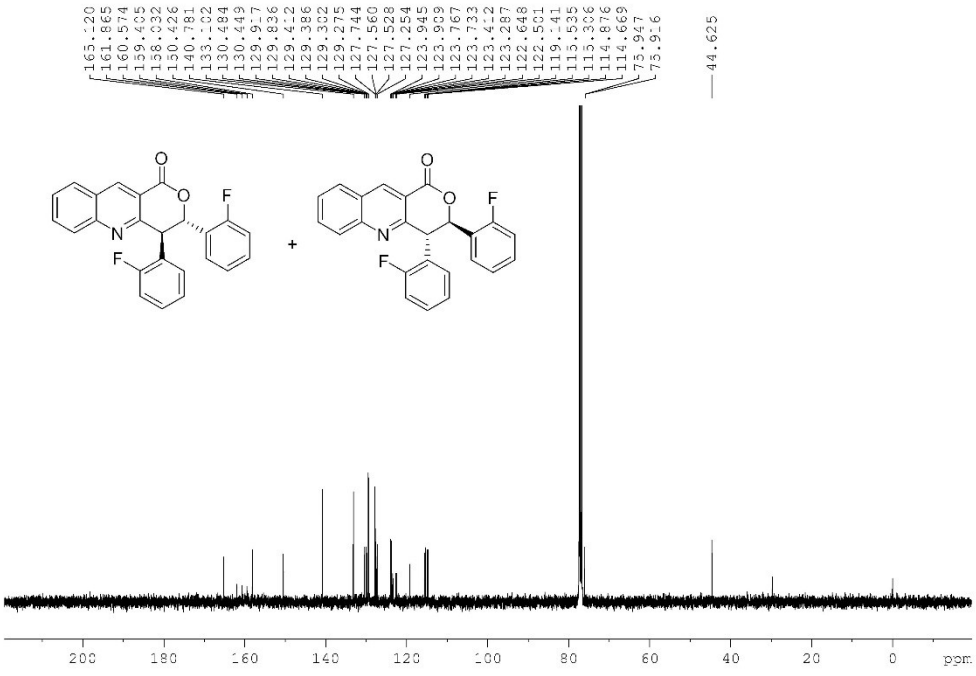
^{13}C NMR spectrum of compound 3al (cis)



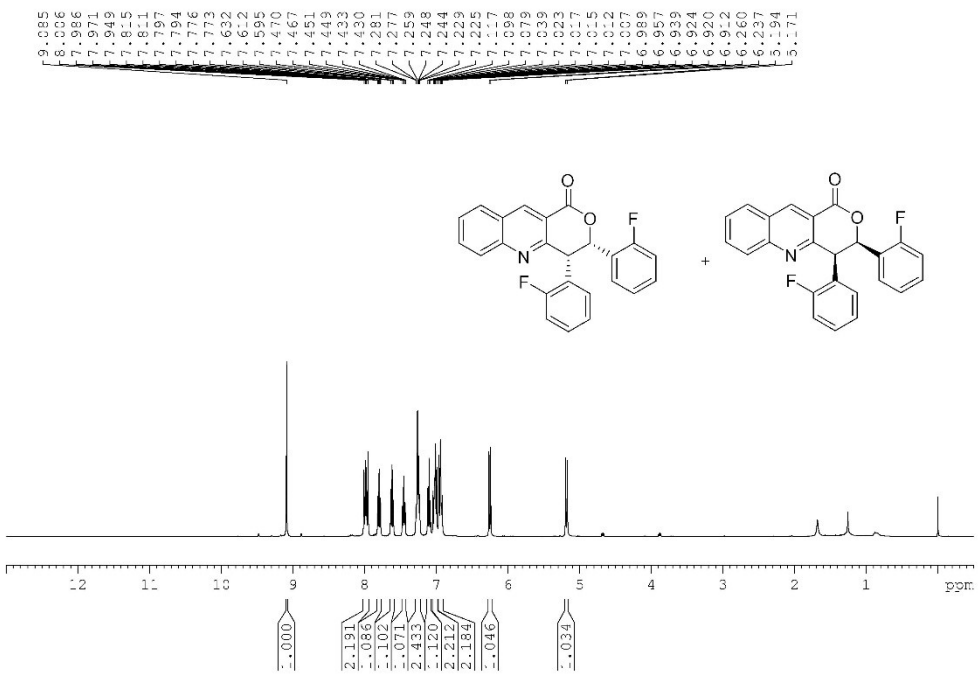
^{1}H NMR spectrum of compound 3am (trans)



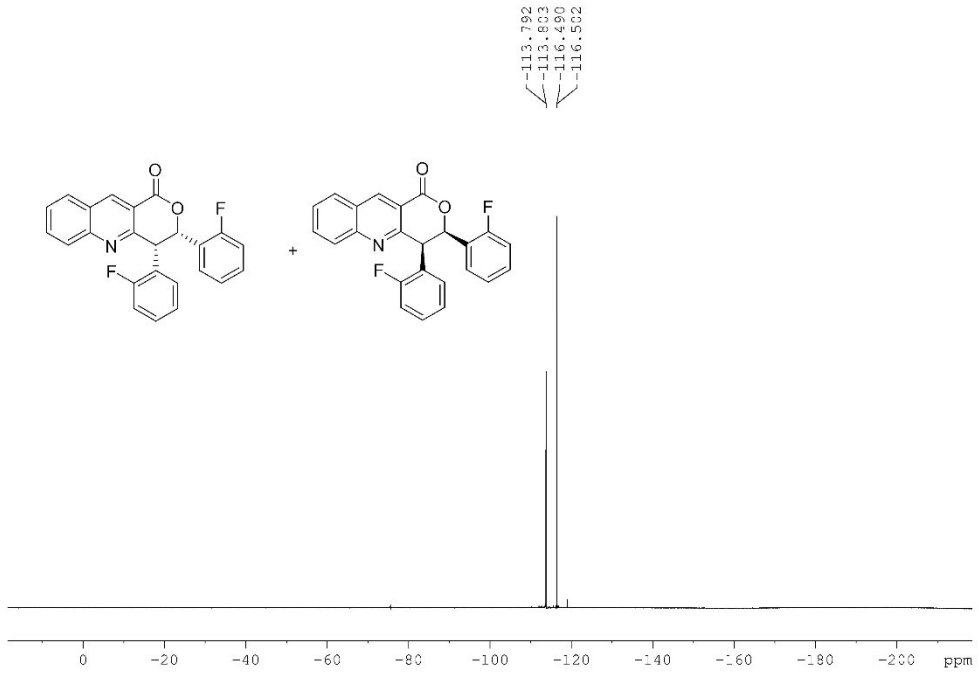
^{19}F NMR spectrum of compound 3am (trans)



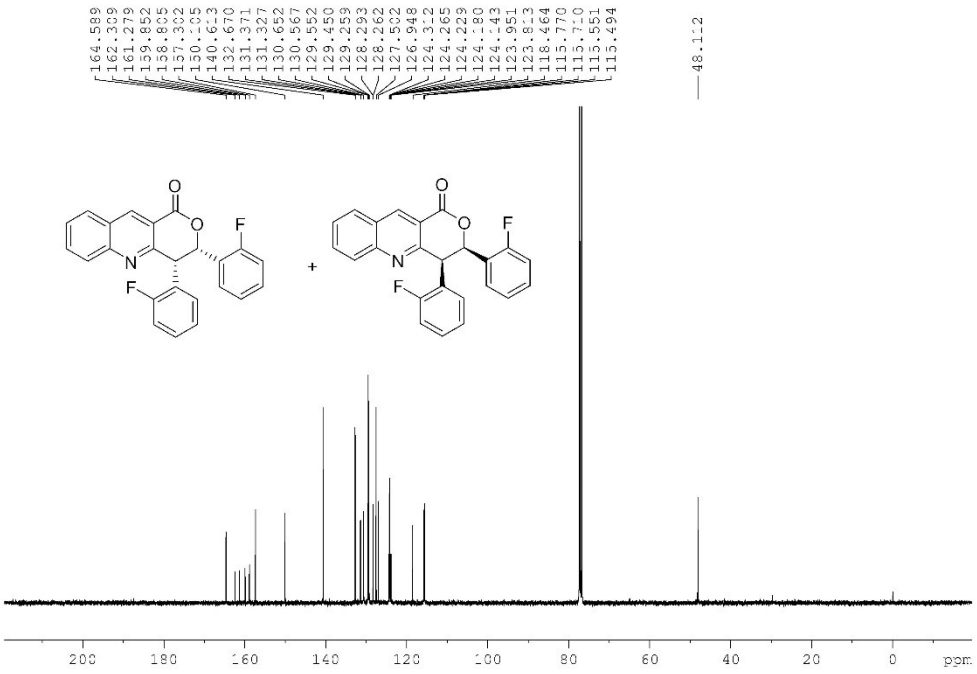
^{13}C NMR spectrum of compound 3am (trans)



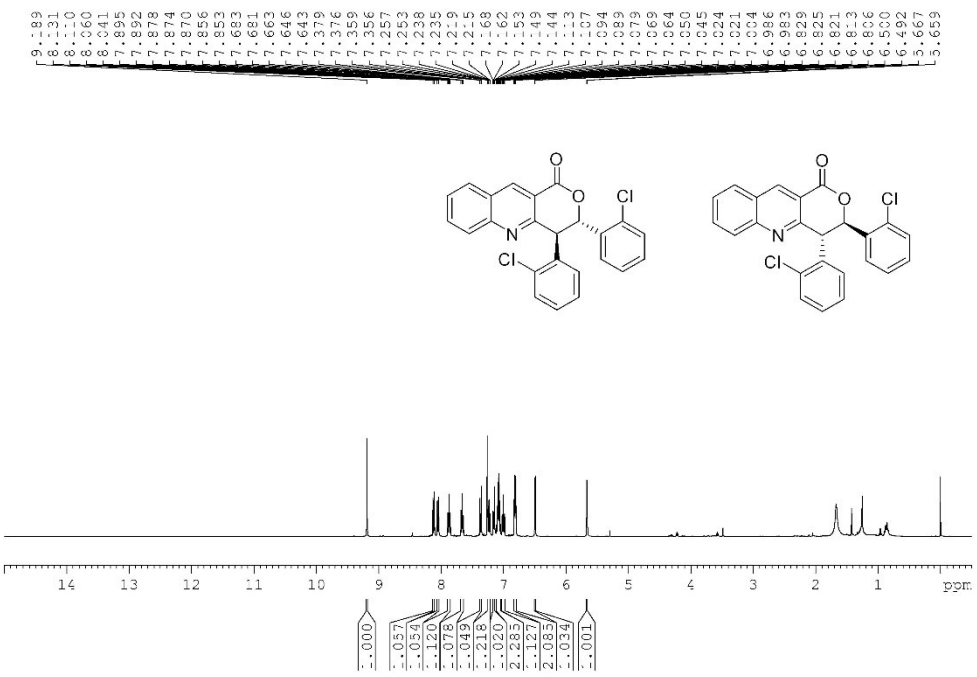
^{1}H NMR spectrum of compound 3am (cis)



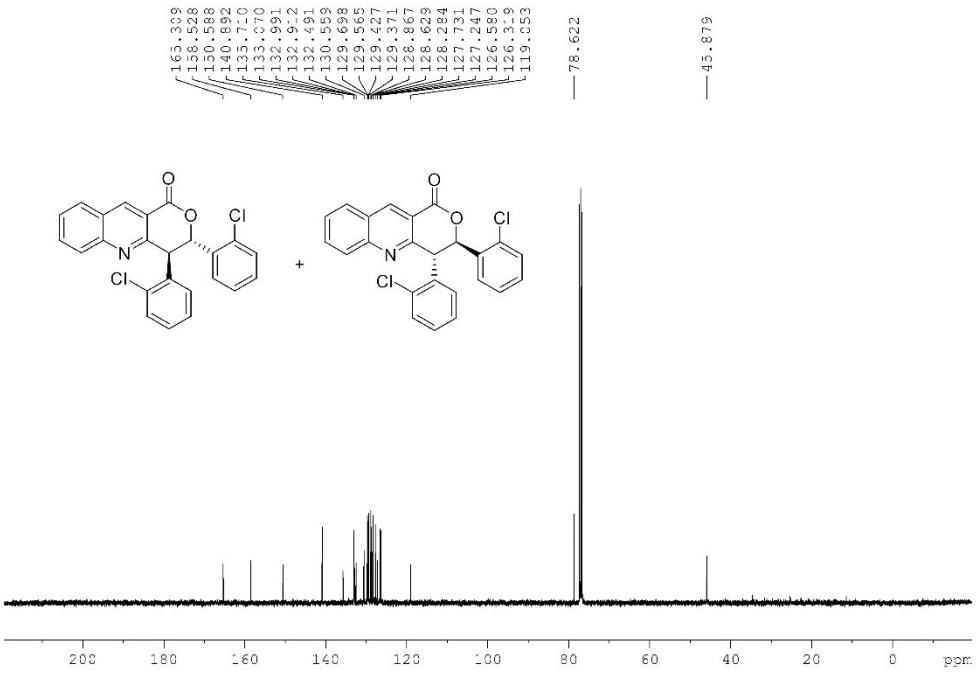
^{19}F NMR spectrum of compound 3am (cis)



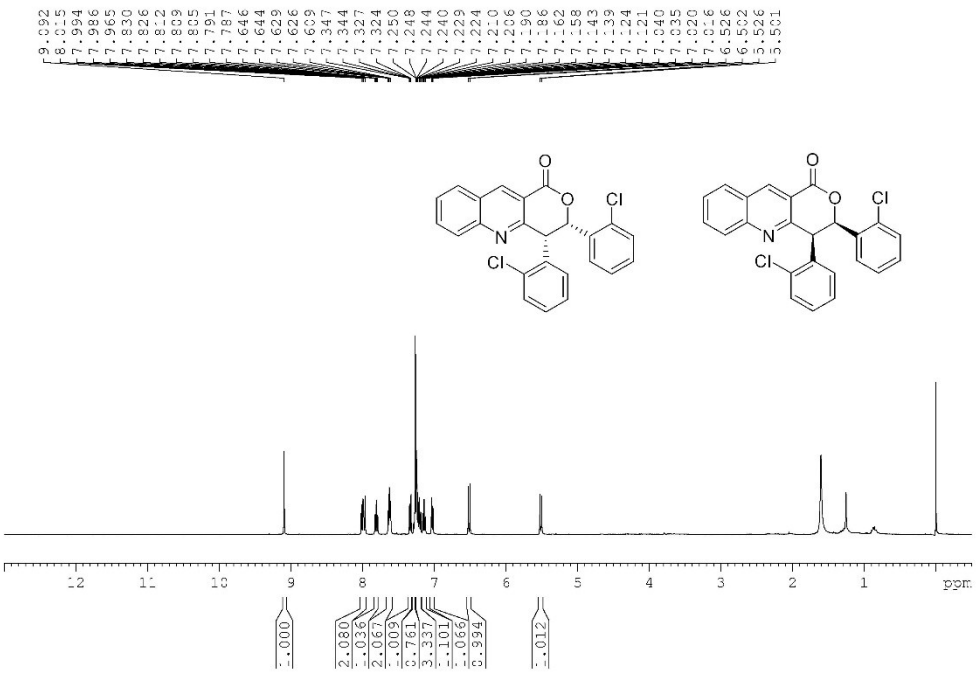
^{13}C NMR spectrum of compound 3am (cis)



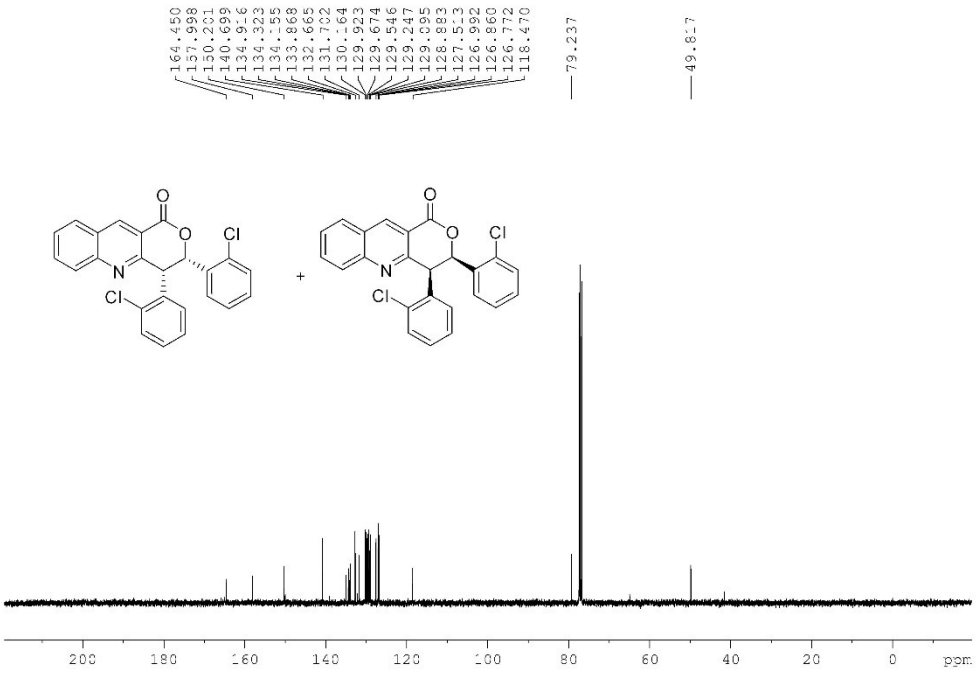
^{1}H NMR spectrum of compound 3an (trans)



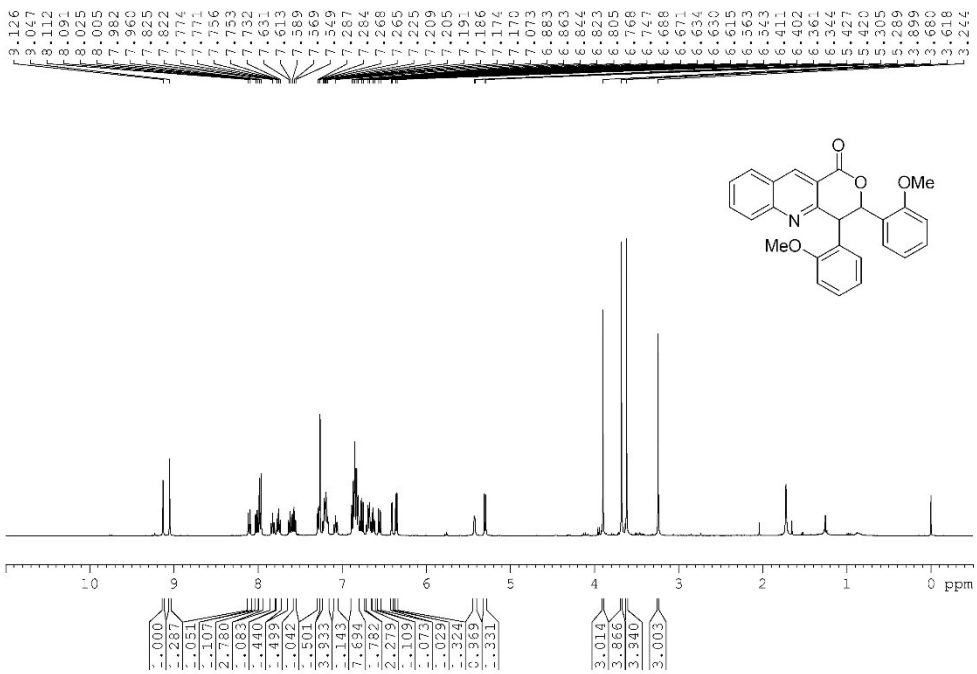
^{13}C NMR spectrum of compound 3an (trans)



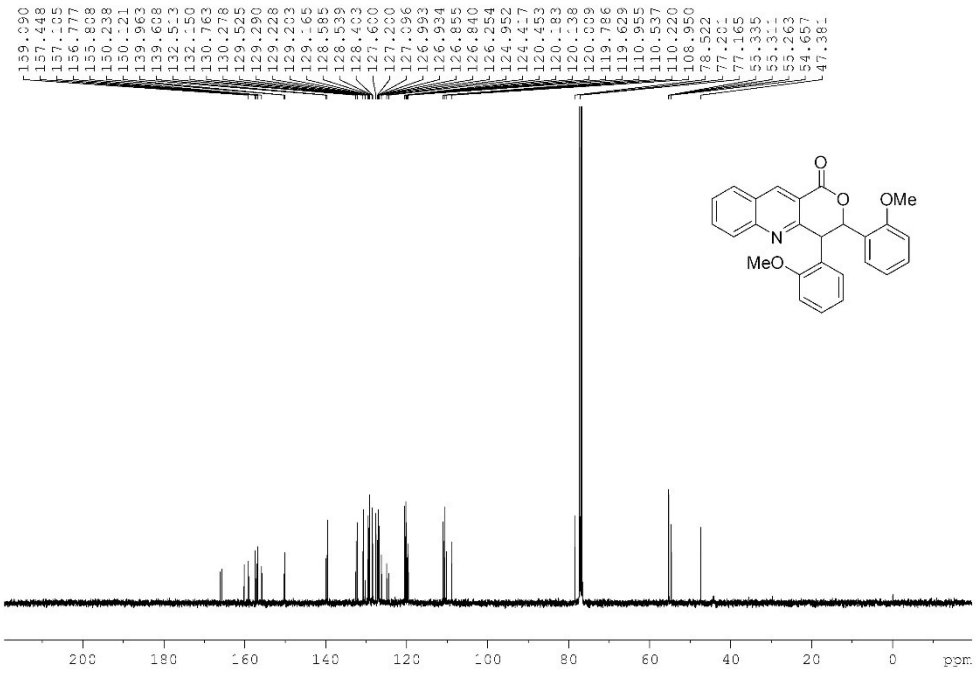
^{1}H NMR spectrum of compound 3an (cis)



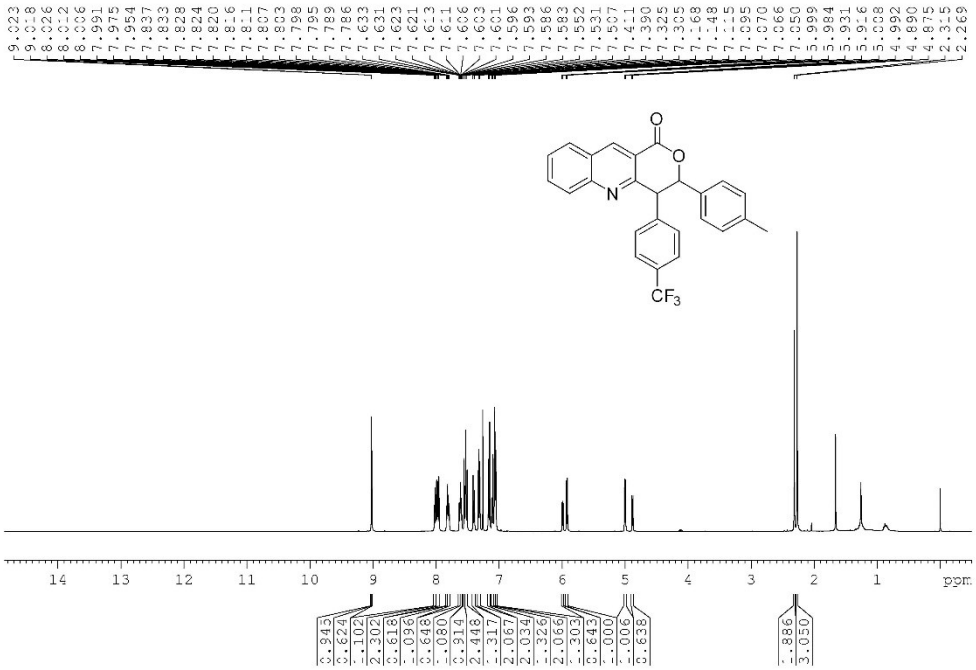
^{13}C NMR spectrum of compound 3an (cis)



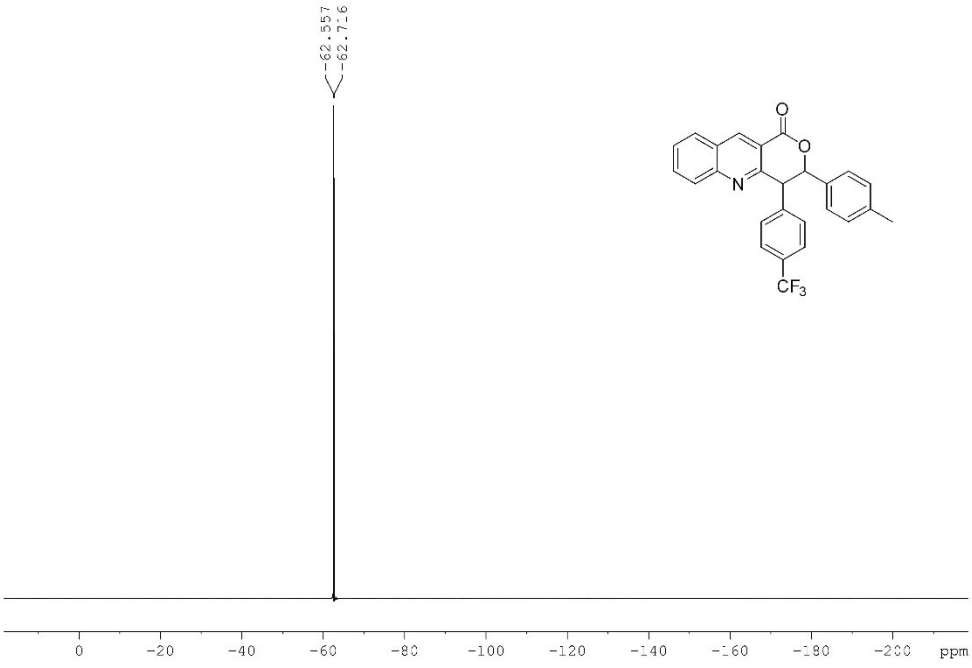
^{1}H NMR spectrum of compound 3ao



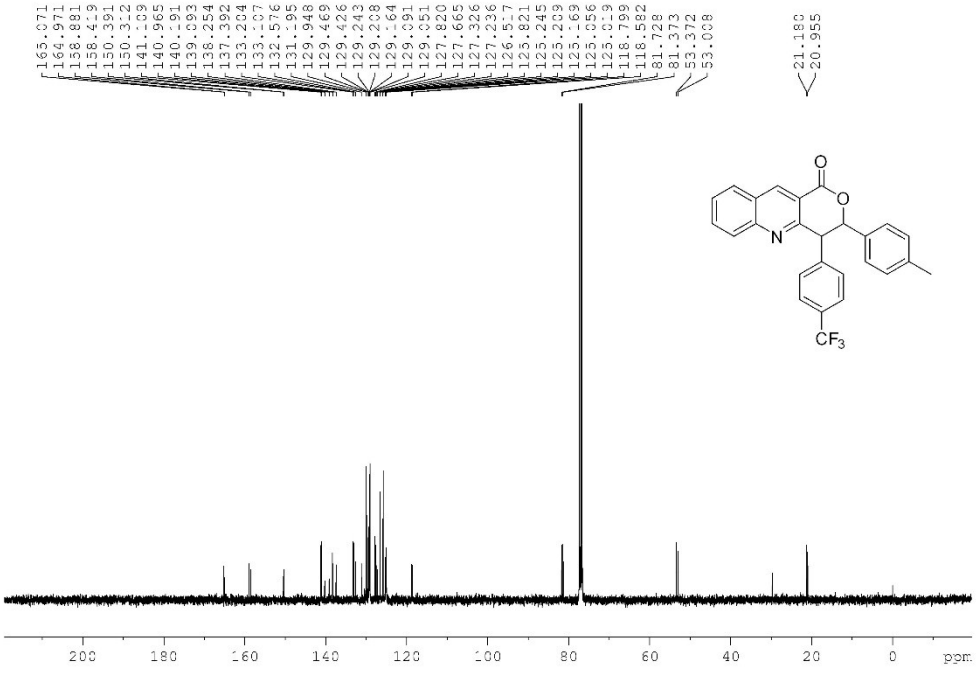
^{13}C NMR spectrum of compound 3ao



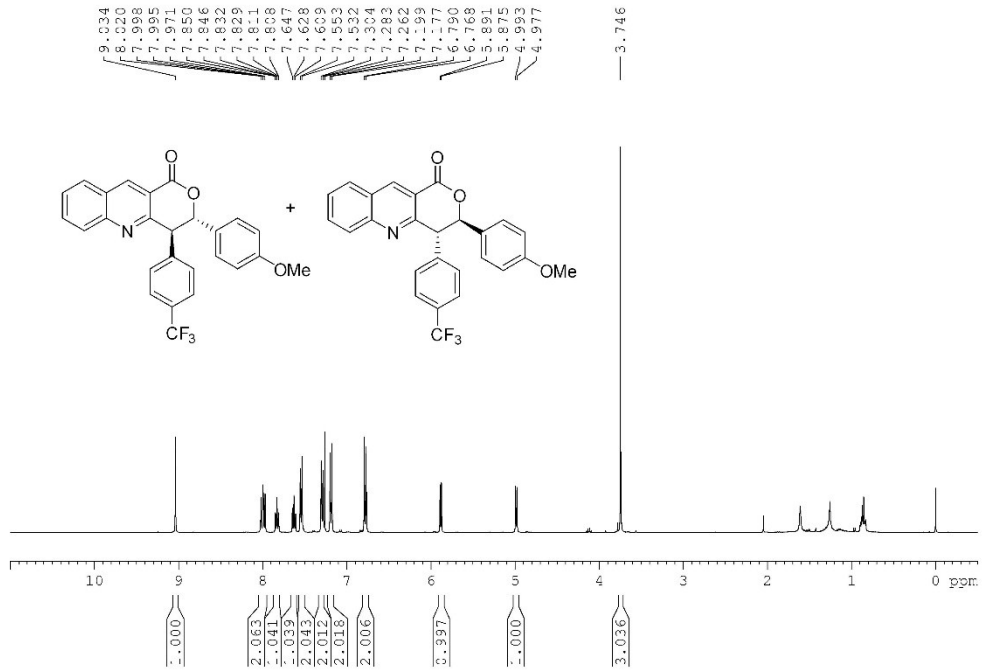
^{1}H NMR spectrum of compound 3ap



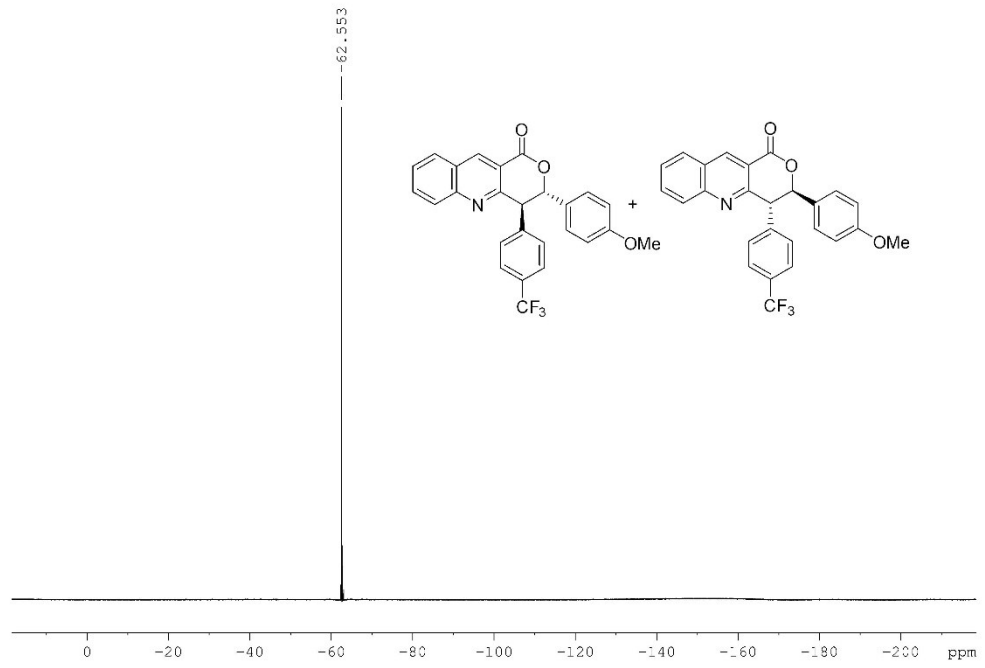
^{19}F NMR spectrum of compound 3ap



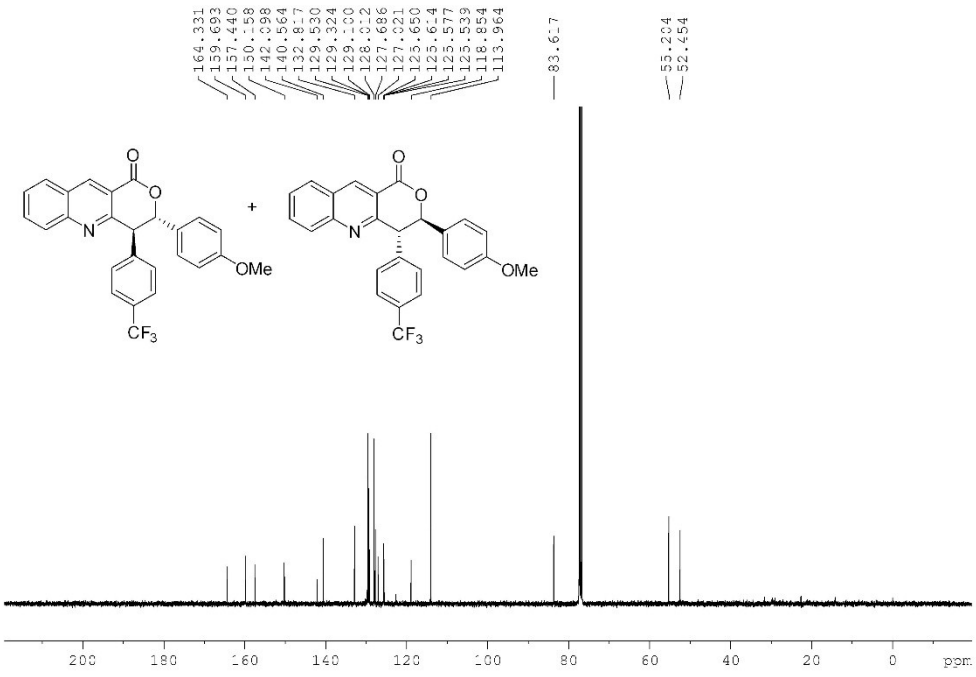
^{13}C NMR spectrum of compound 3ap



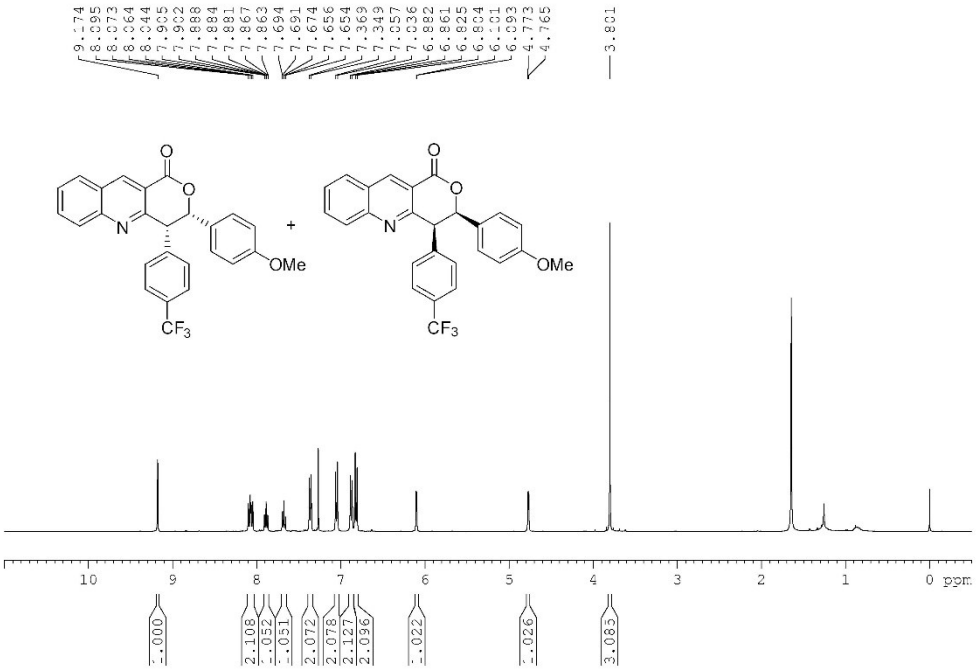
^{1}H NMR spectrum of compound 3aq (trans)



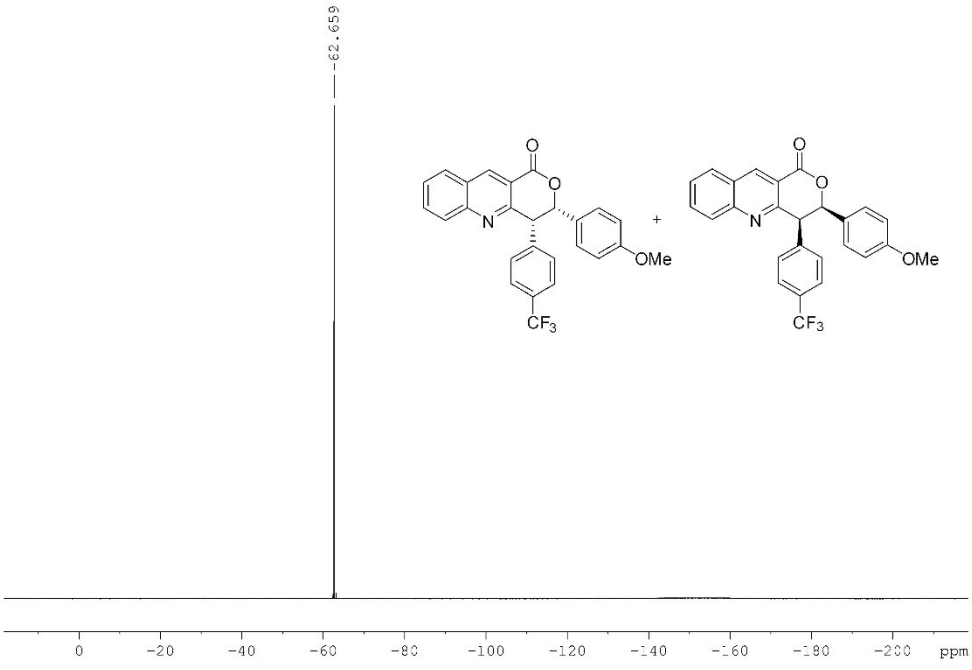
^{19}F NMR spectrum of compound 3aq (trans)



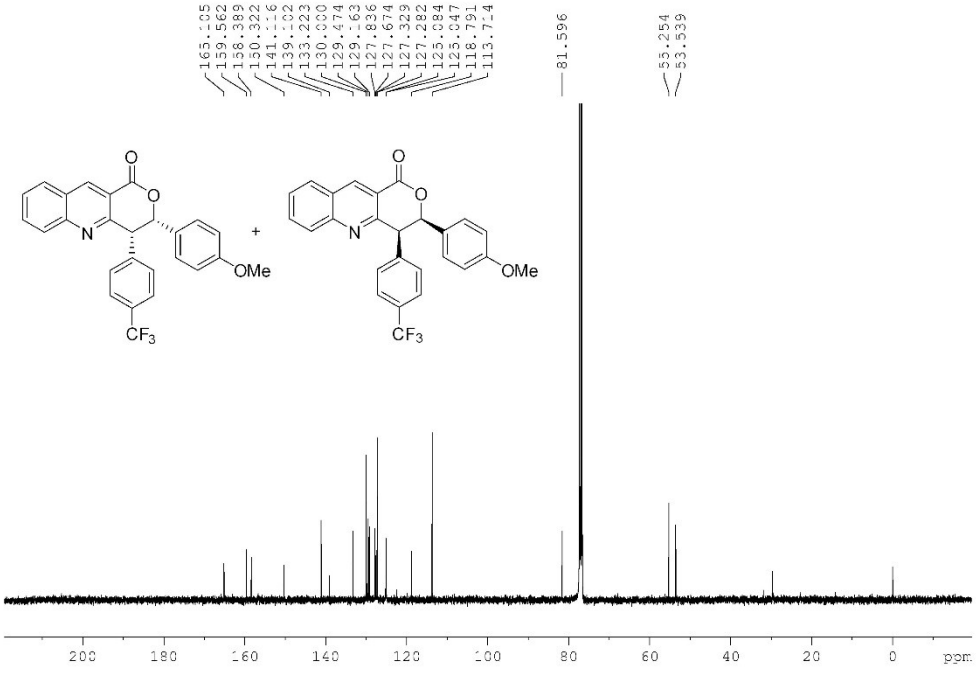
^{13}C NMR spectrum of compound 3aq (trans)



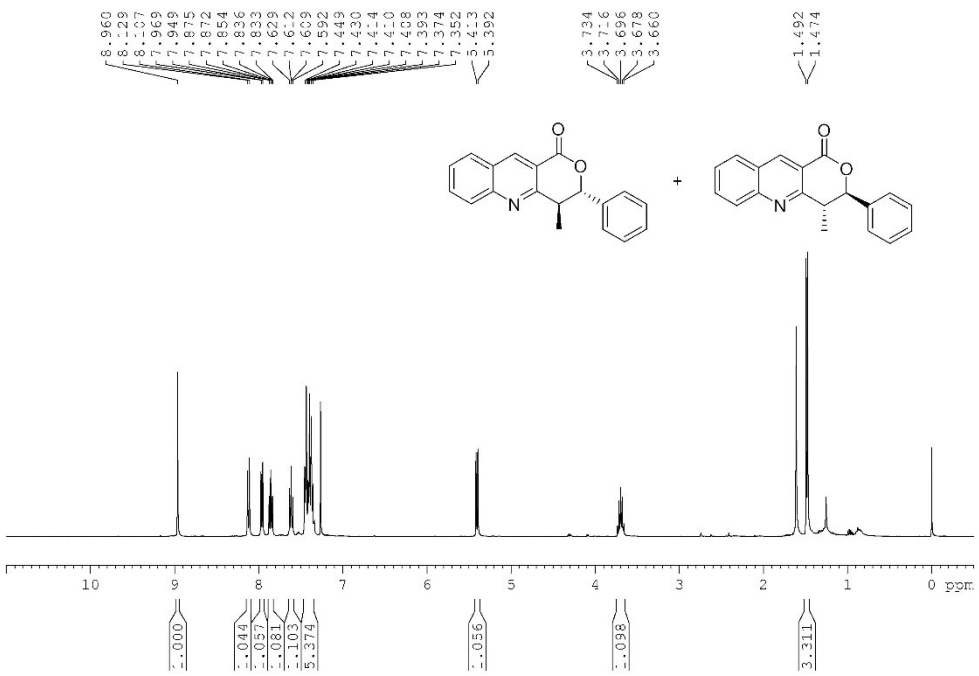
^{1}H NMR spectrum of compound 3aq (cis)



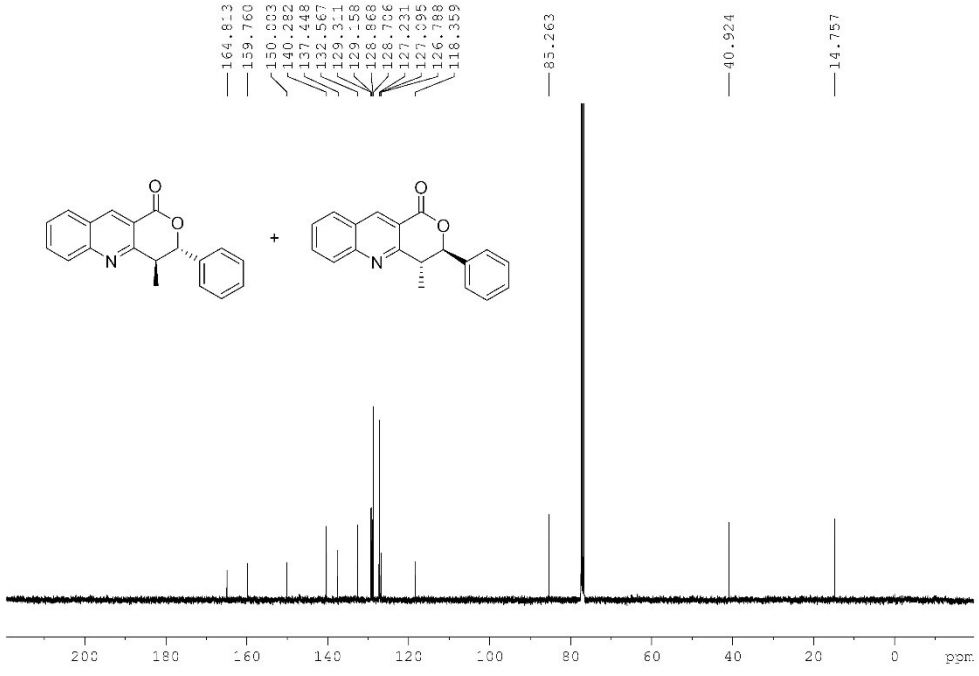
^{19}F NMR spectrum of compound 3aq (cis)



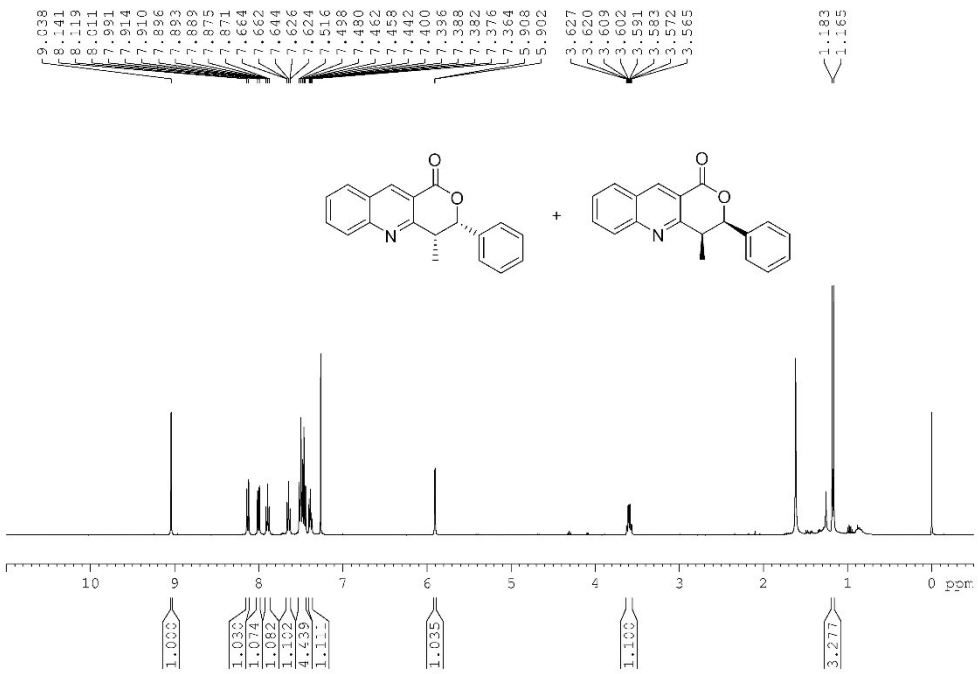
^{13}C NMR spectrum of compound 3aq (cis)



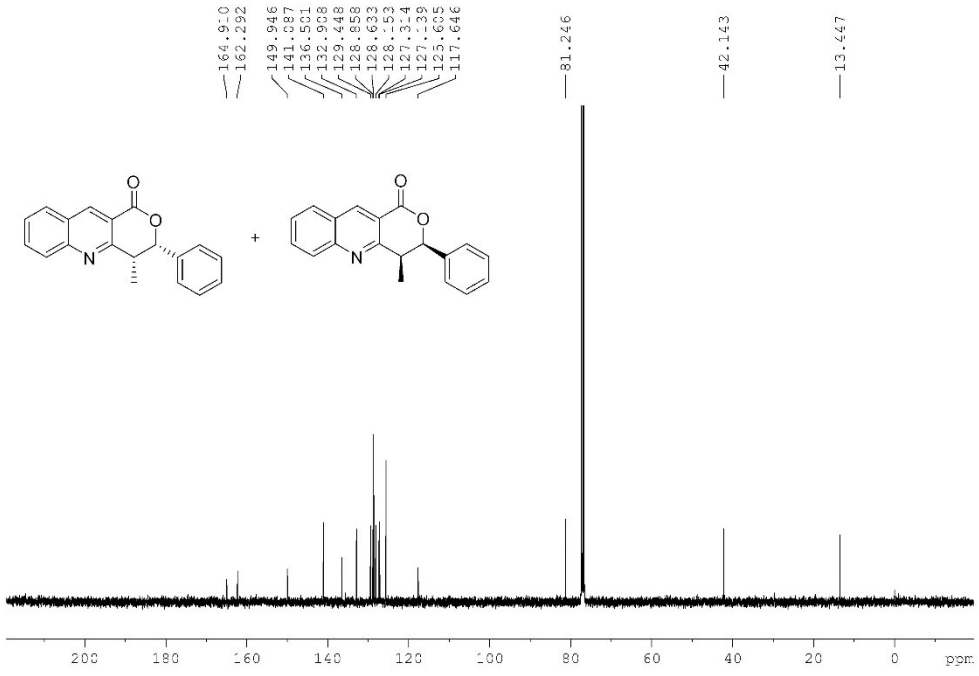
^{1}H NMR spectrum of compound 3ar (trans)



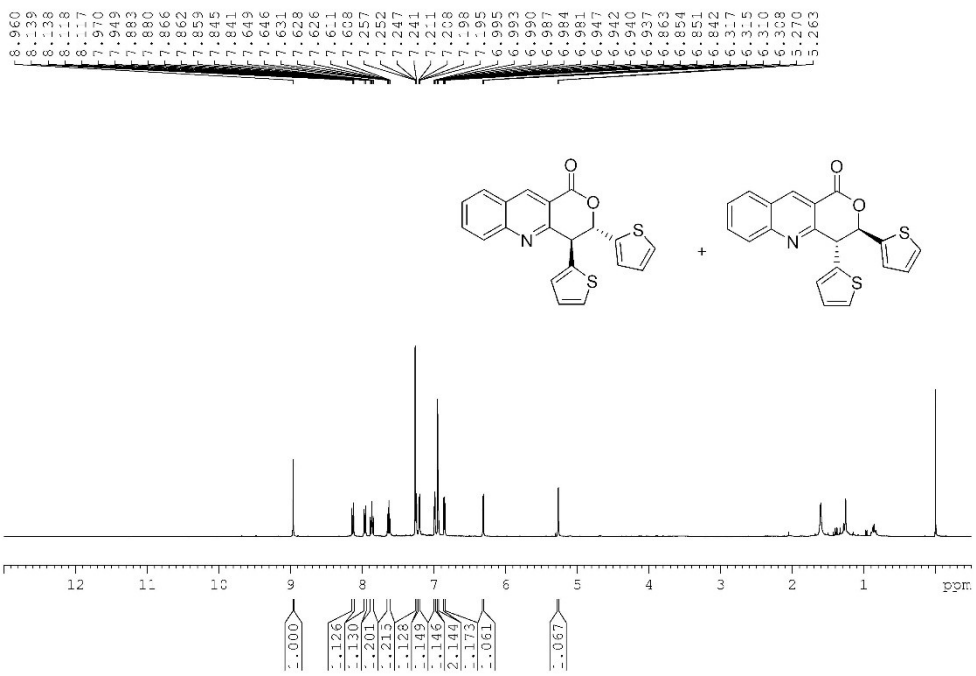
^{13}C NMR spectrum of compound 3ar (trans)



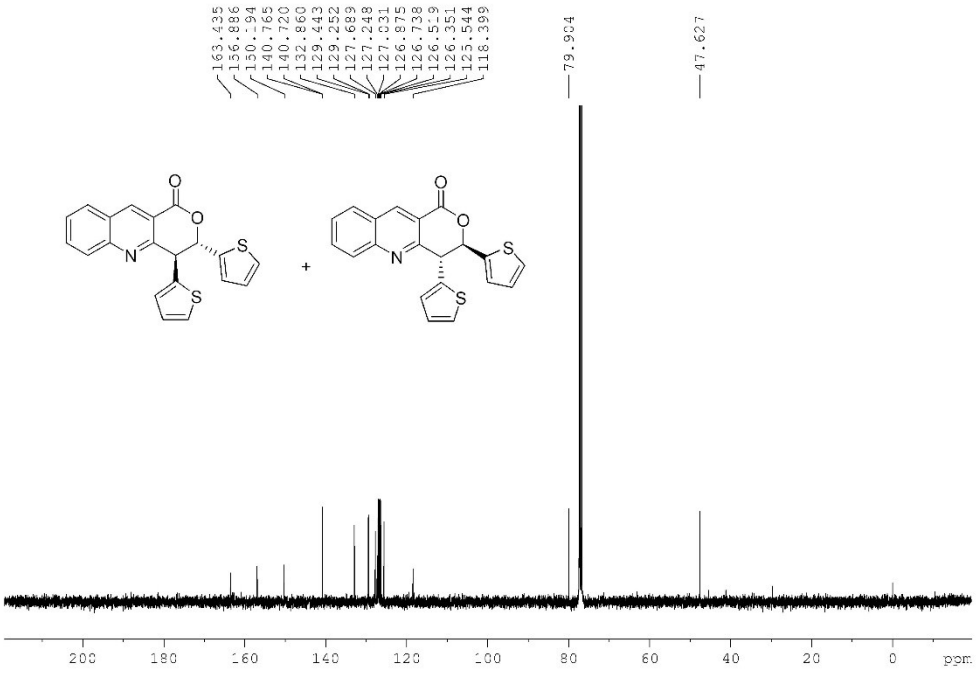
^{1}H NMR spectrum of compound 3ar (cis)



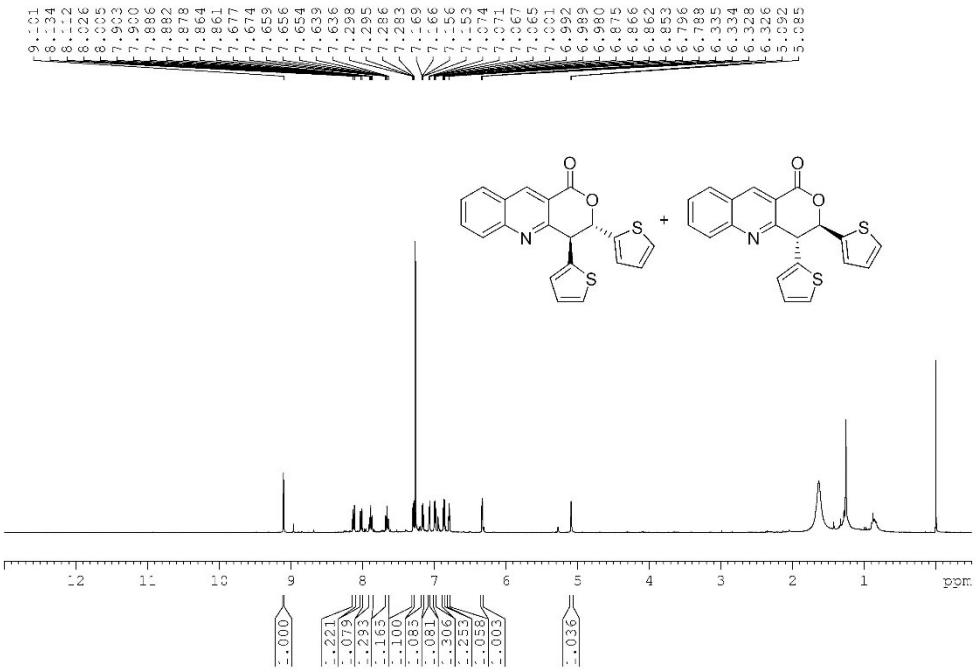
^{13}C NMR spectrum of compound 3ar (cis)



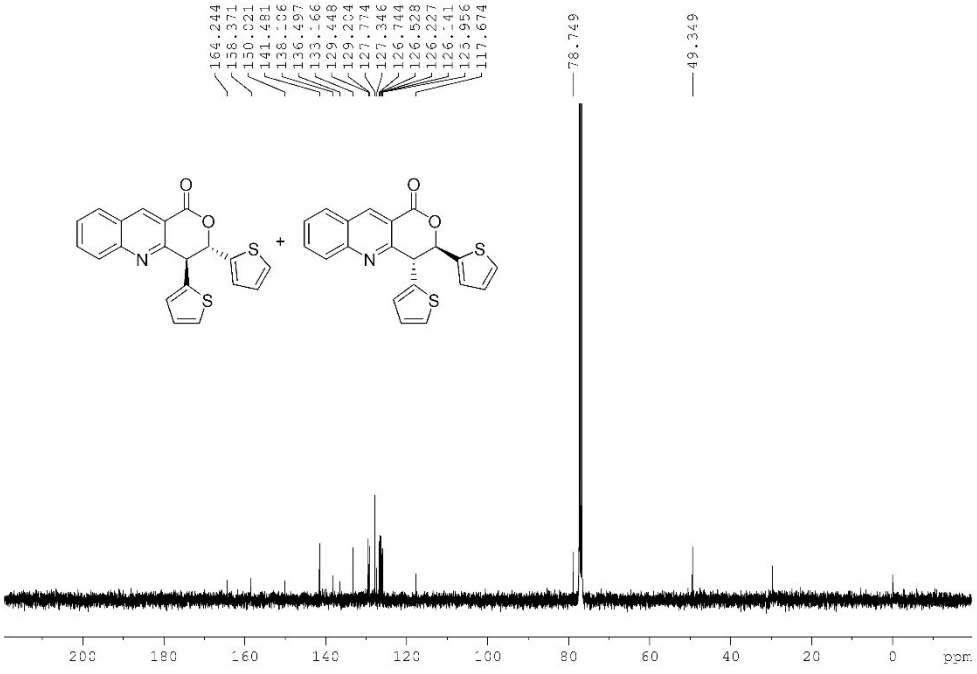
^{1}H NMR spectrum of compound 3as (trans)



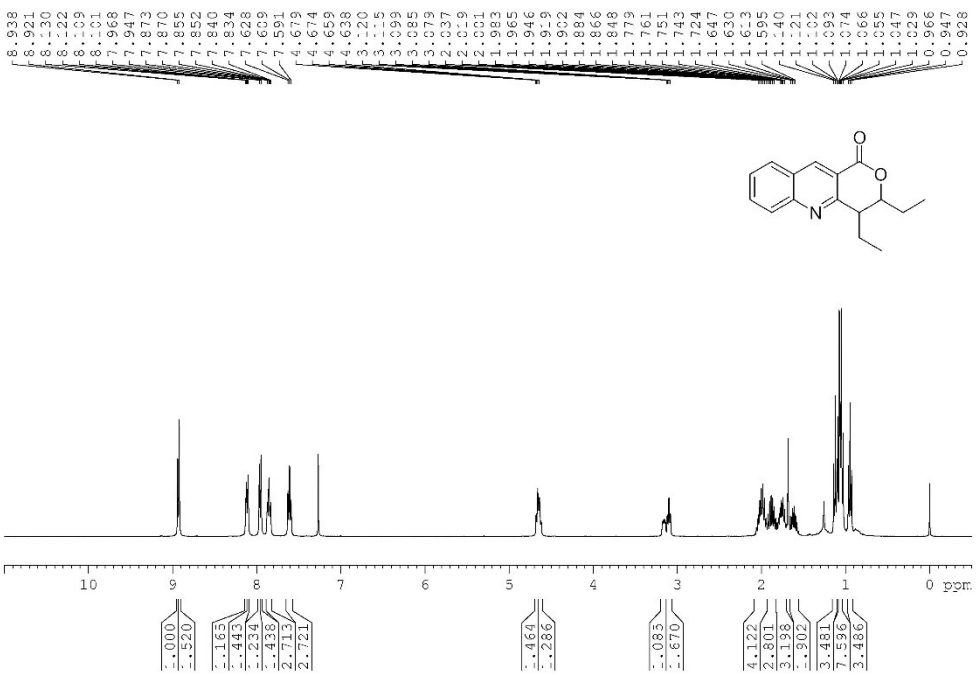
^{13}C NMR spectrum of compound 3as (trans)



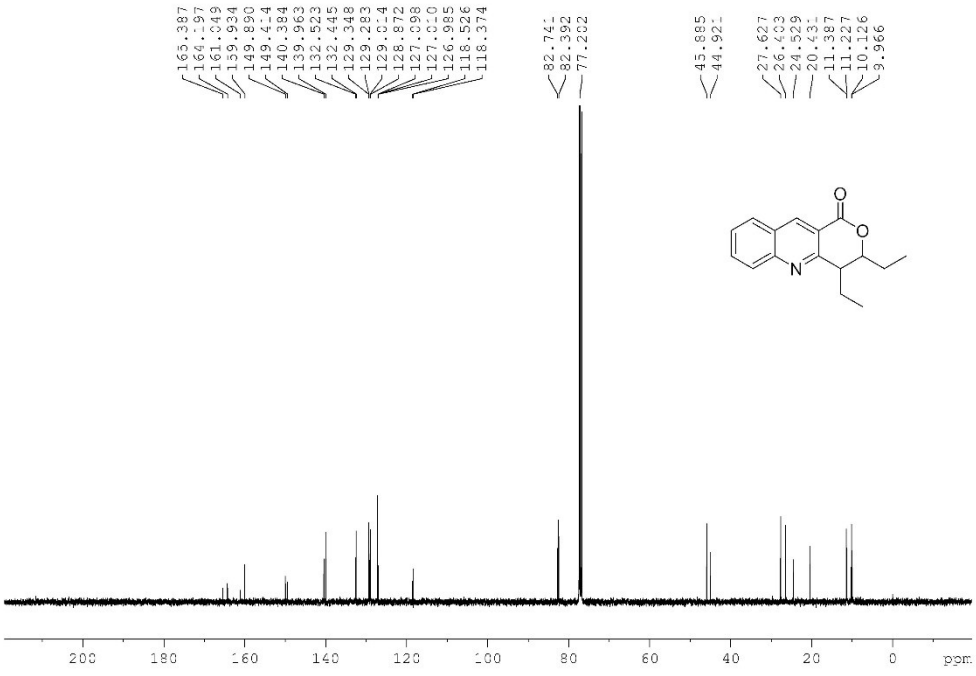
^{1}H NMR spectrum of compound 3as (cis)



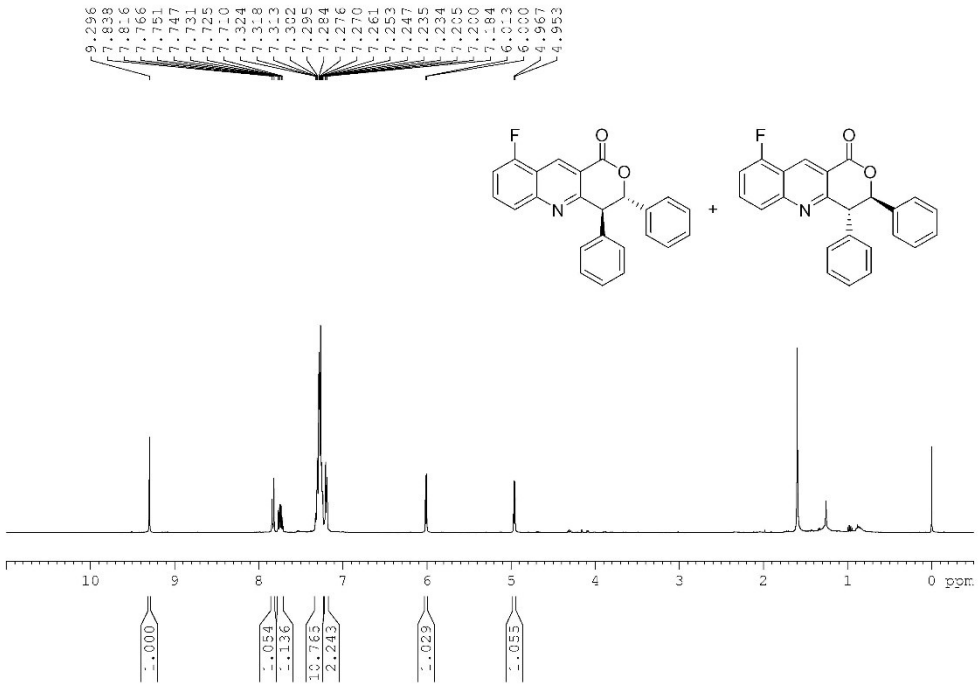
^{13}C NMR spectrum of compound 3as (cis)



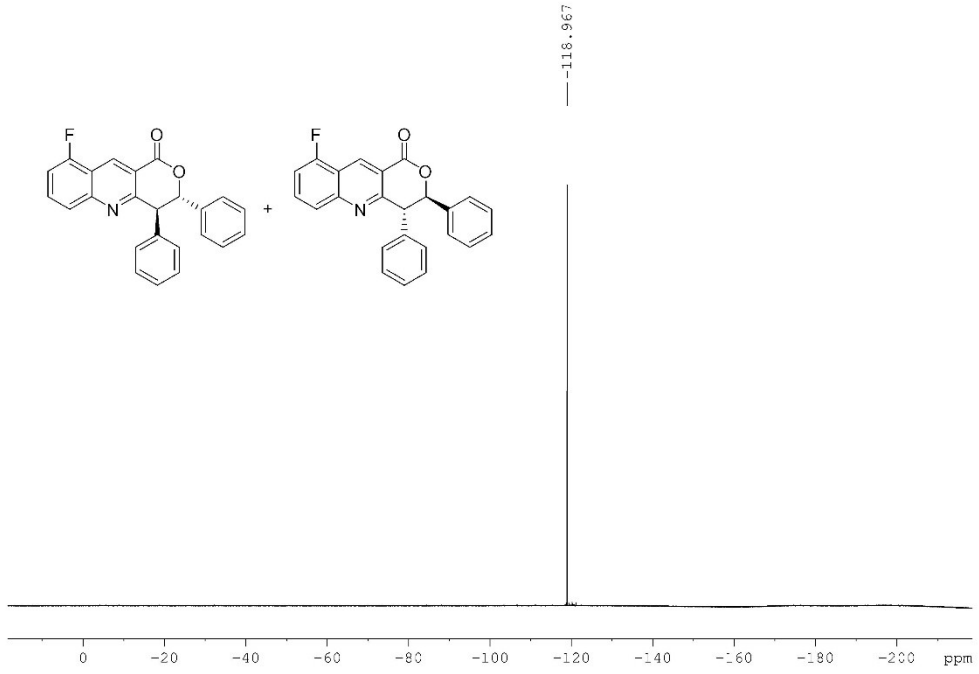
^{1}H NMR spectrum of compound 3at



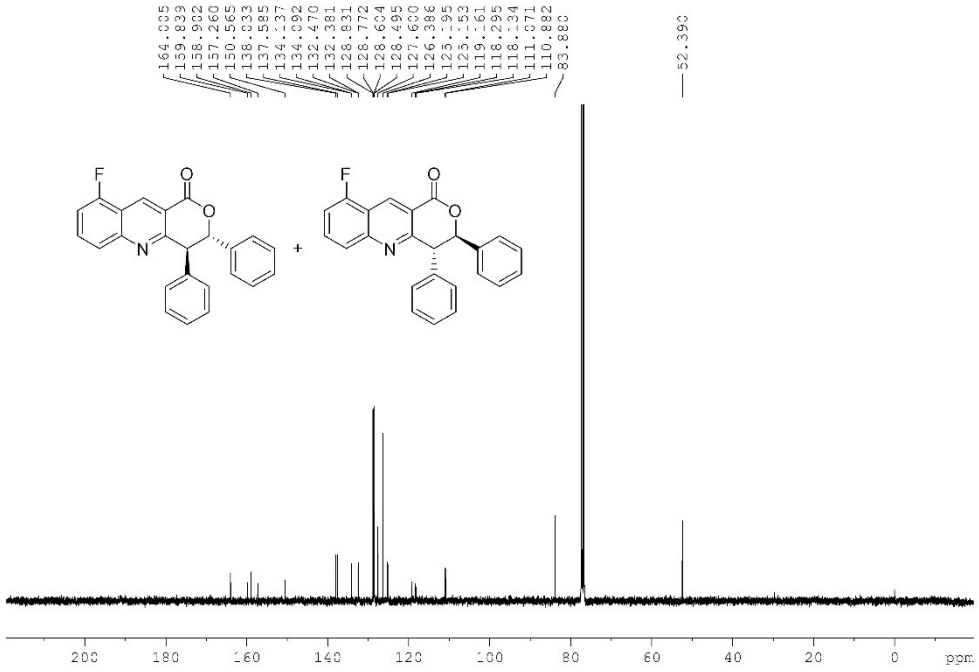
^{13}C NMR spectrum of compound 3at



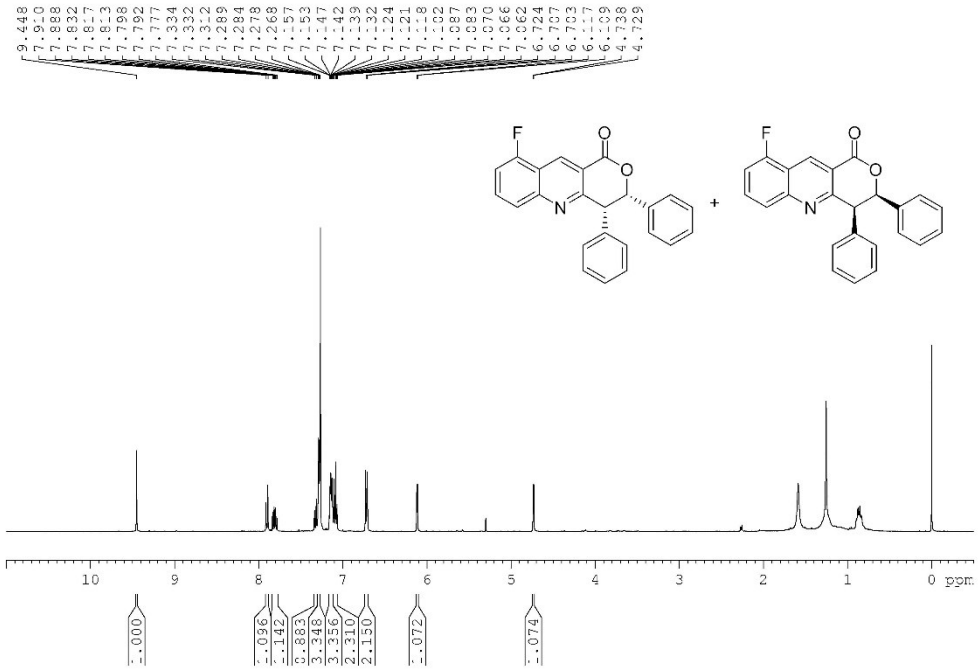
^{1}H NMR spectrum of compound 3ba (trans)



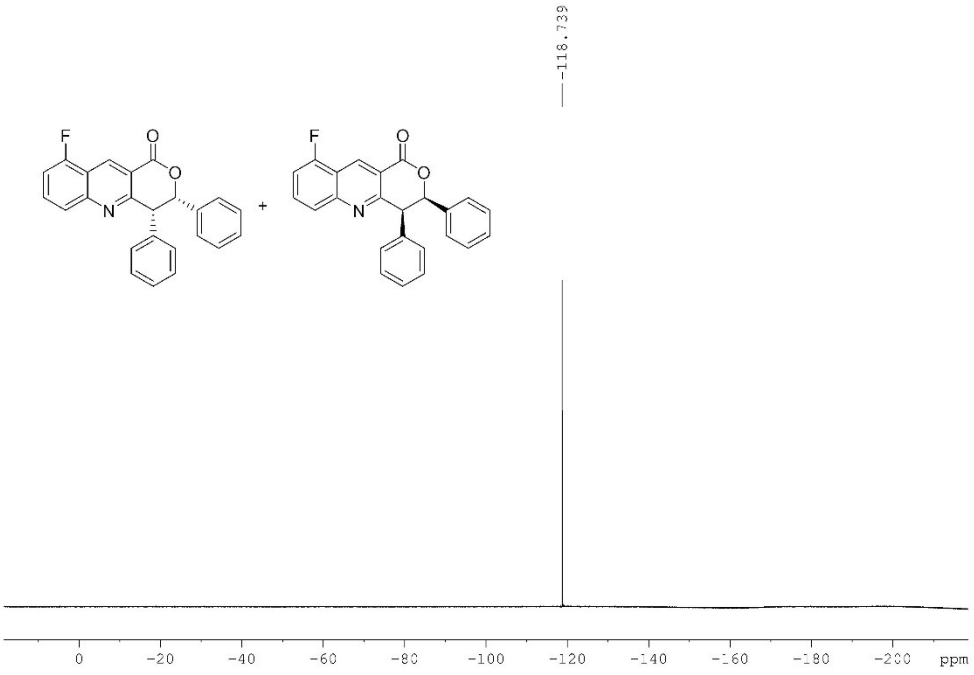
^{19}F NMR spectrum of compound 3ba (trans)



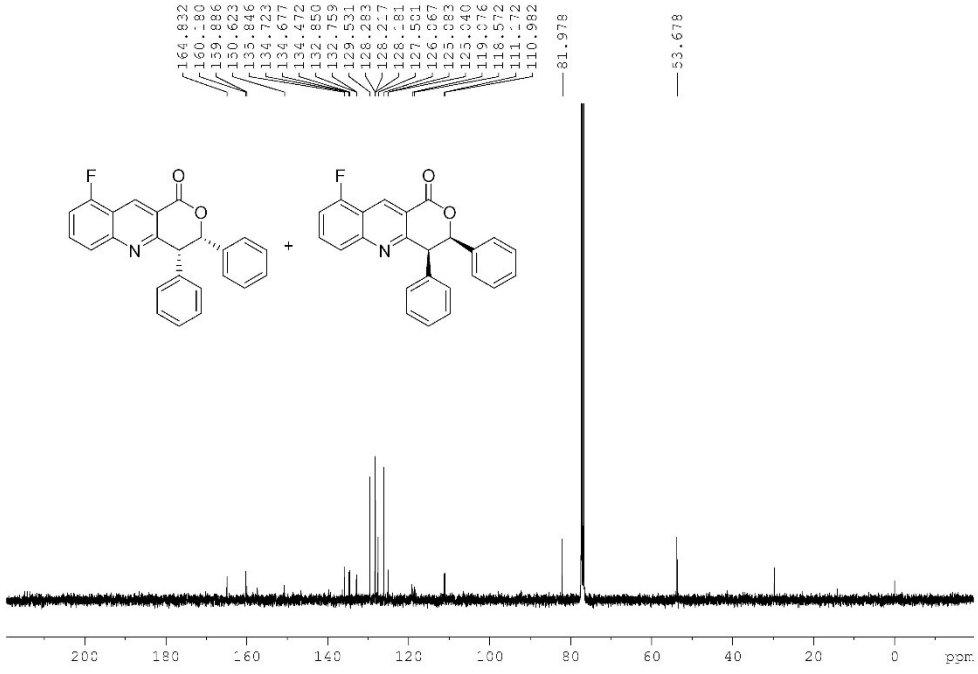
^{13}C NMR spectrum of compound 3ba (trans)



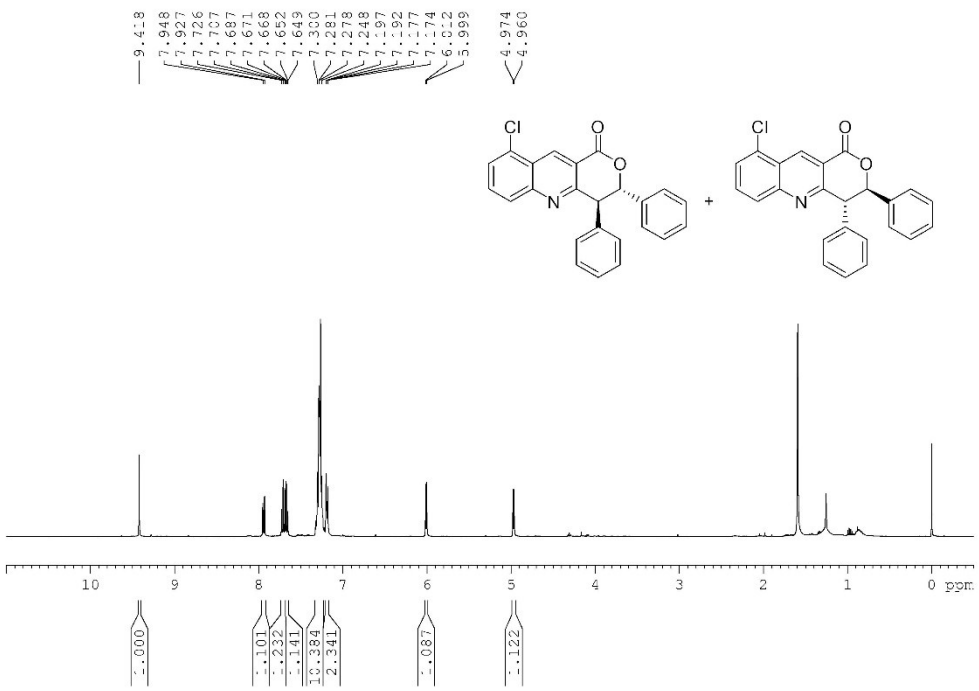
^{1}H NMR spectrum of compound 3ba (cis)



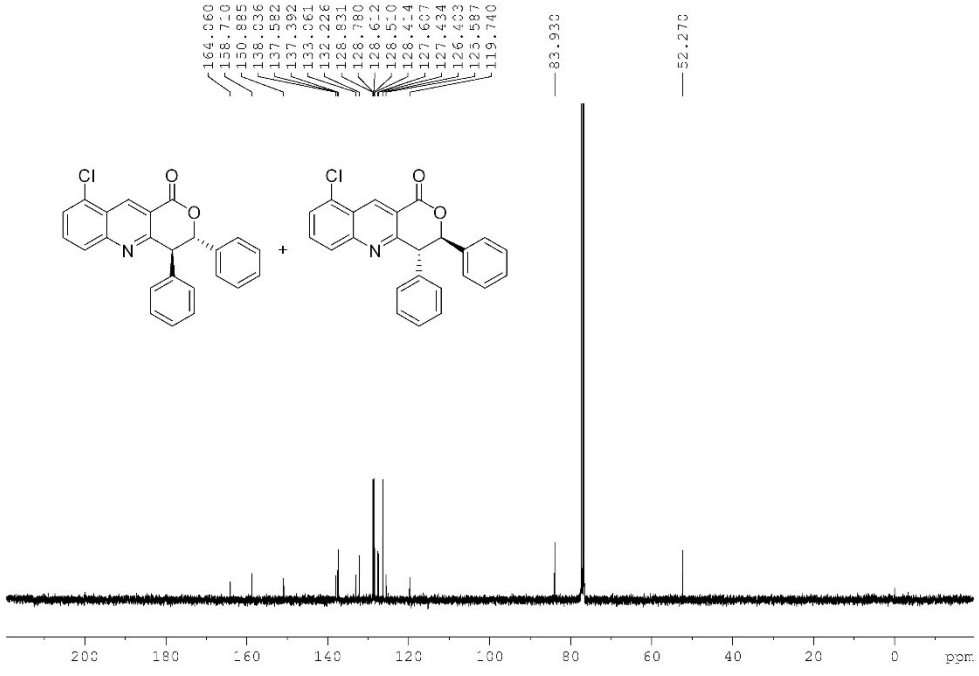
^{19}F NMR spectrum of compound 3ba (cis)



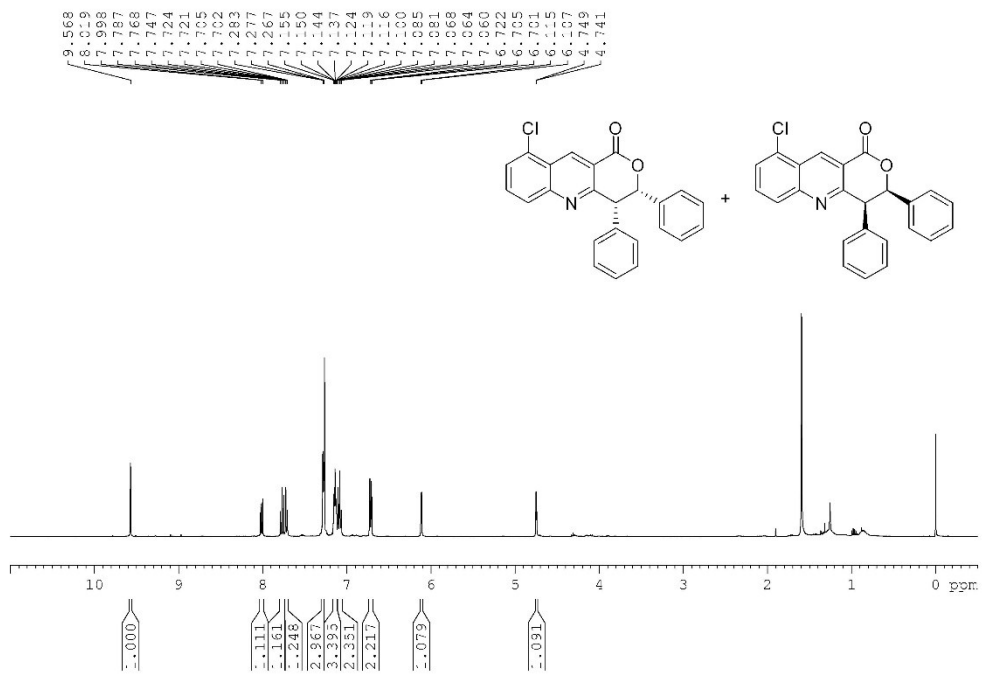
^{13}C NMR spectrum of compound 3ba (cis)



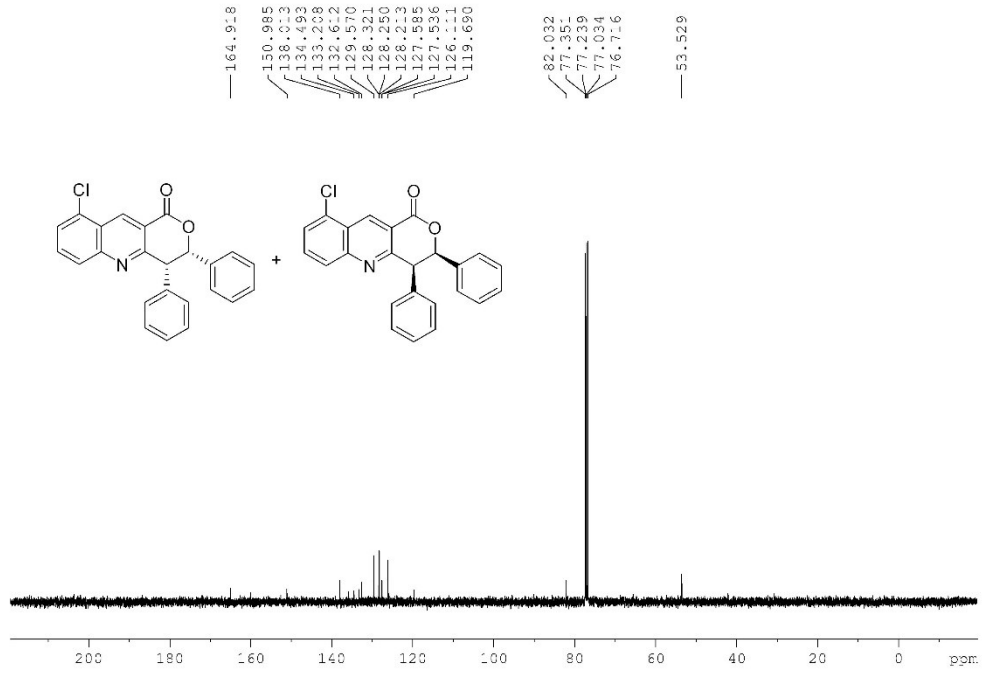
^{1}H NMR spectrum of compound 3ca (trans)



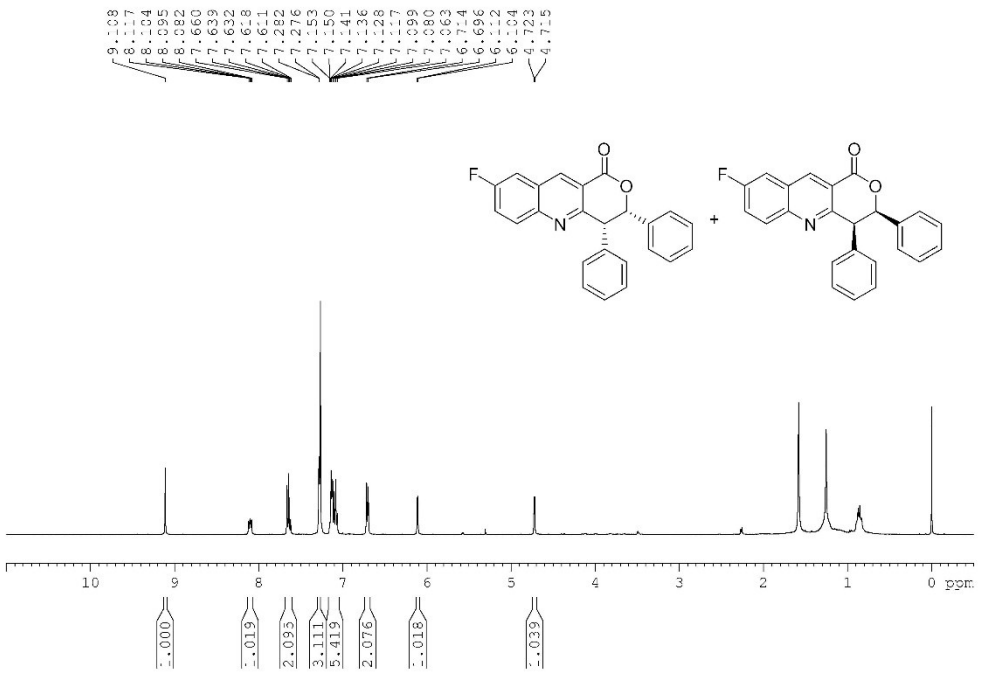
^{13}C NMR spectrum of compound 3ca (trans)



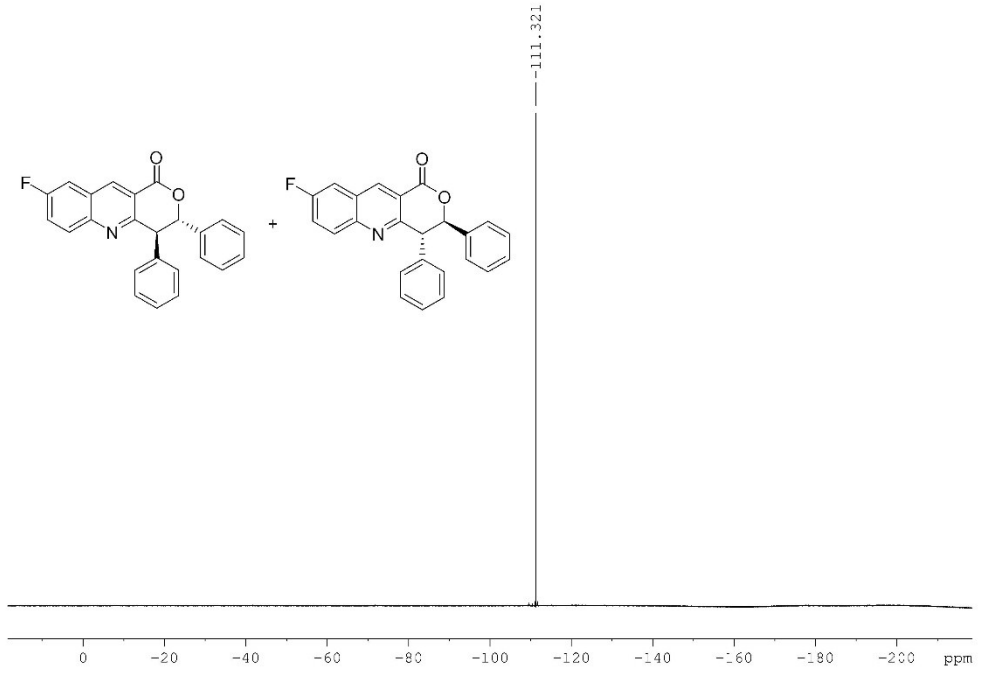
^{1}H NMR spectrum of compound 3ca (cis)



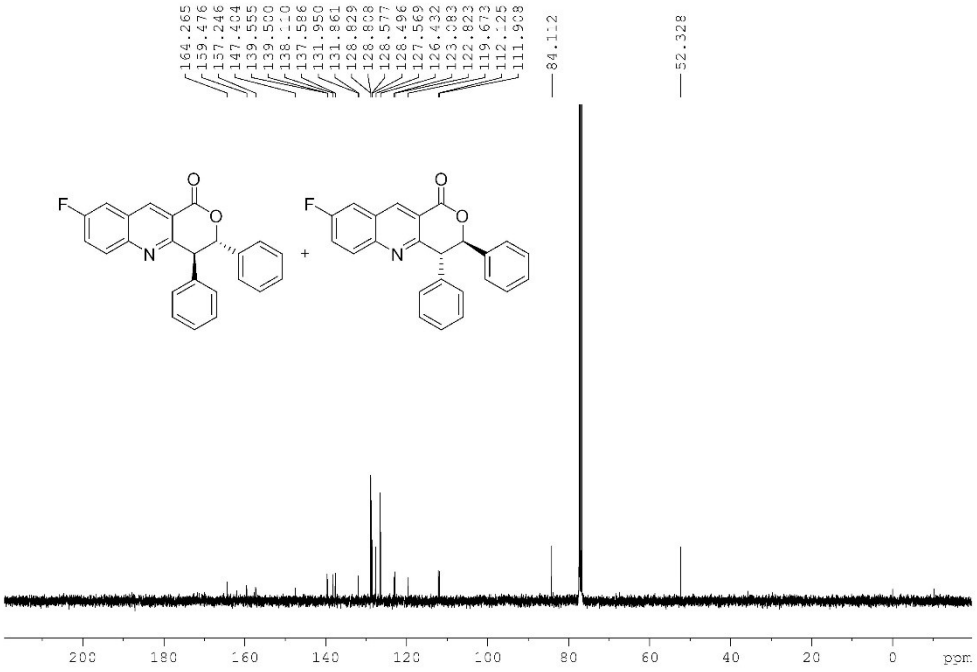
^{13}C NMR spectrum of compound 3ca (cis)



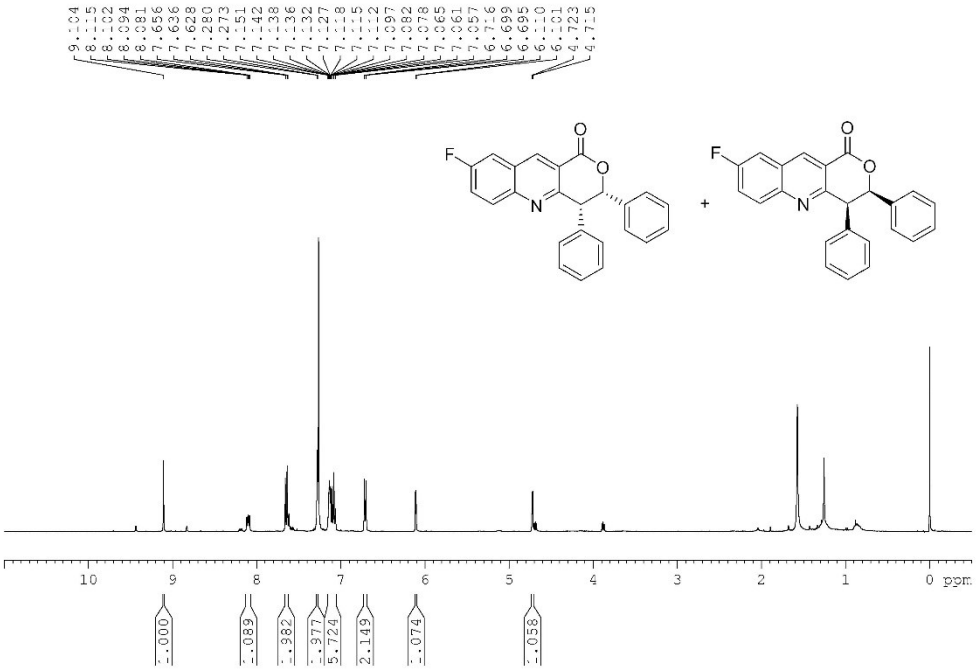
^{1}H NMR spectrum of compound 3da (trans)



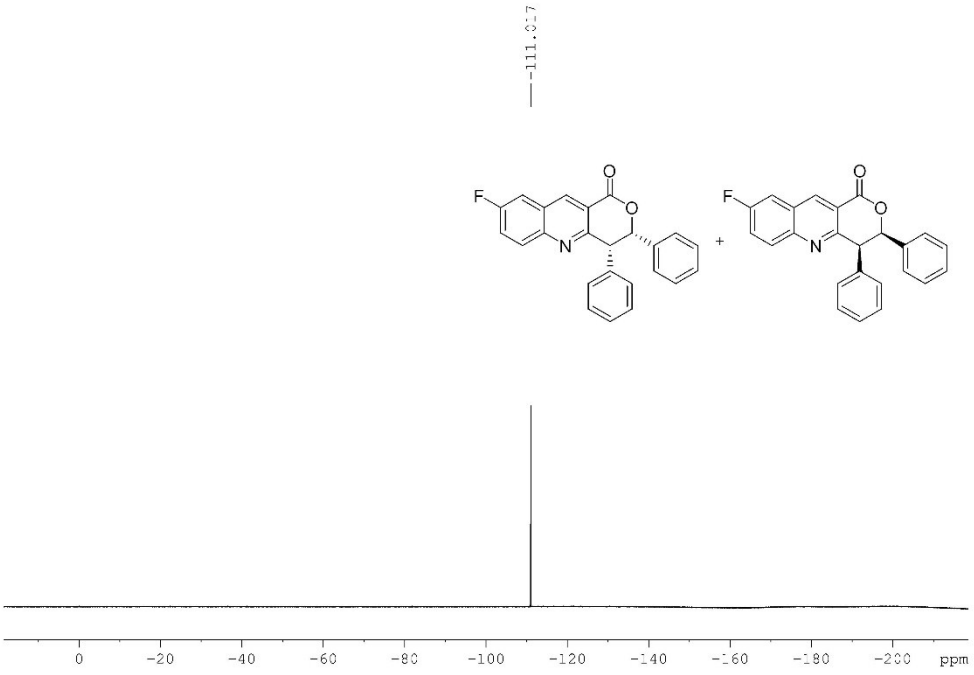
^{19}F NMR spectrum of compound 3da (trans)



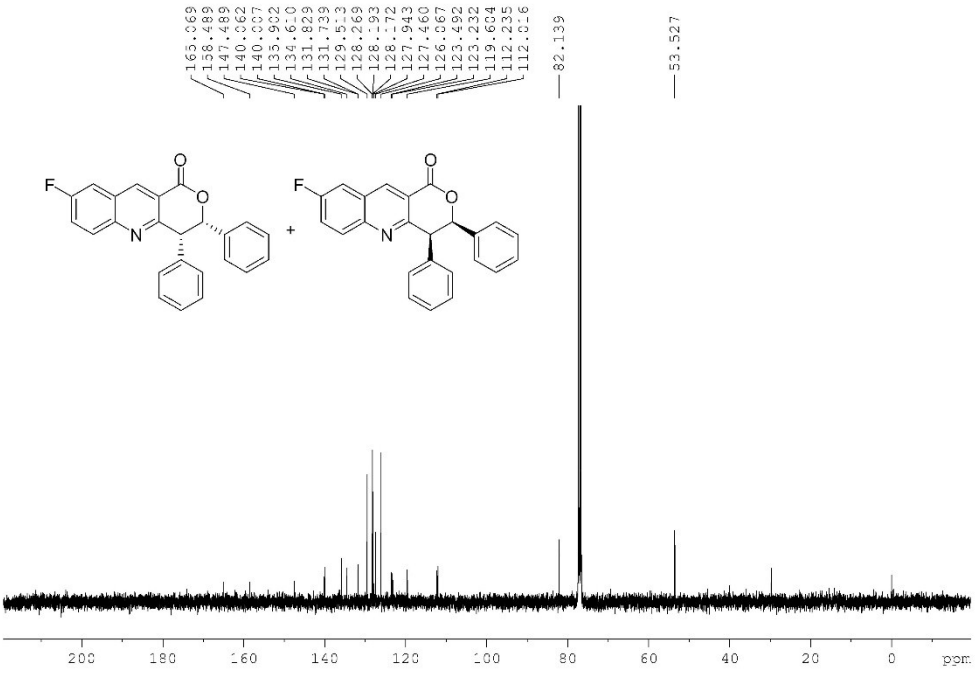
^{13}C NMR spectrum of compound 3da (trans)



^{1}H NMR spectrum of compound 3da (cis)

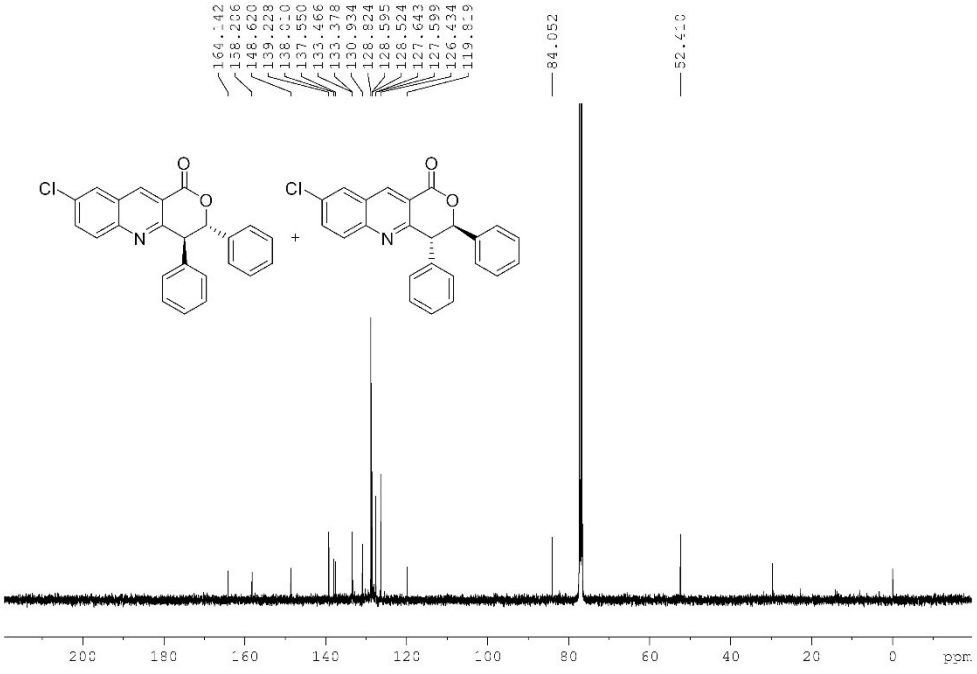


^{19}F NMR spectrum of compound 3da (cis)

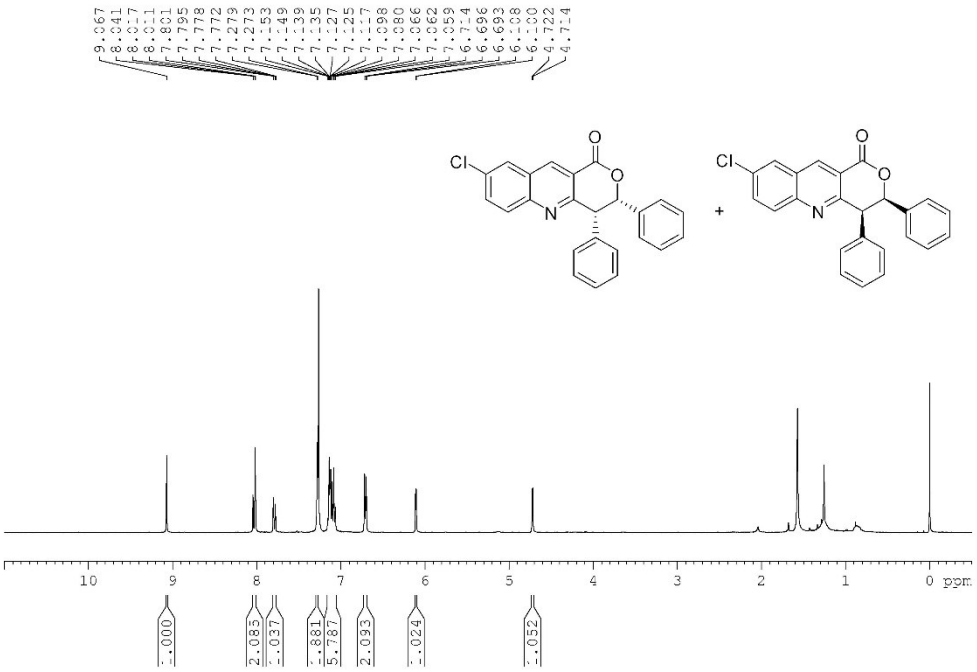


^{13}C NMR spectrum of compound 3da (cis)

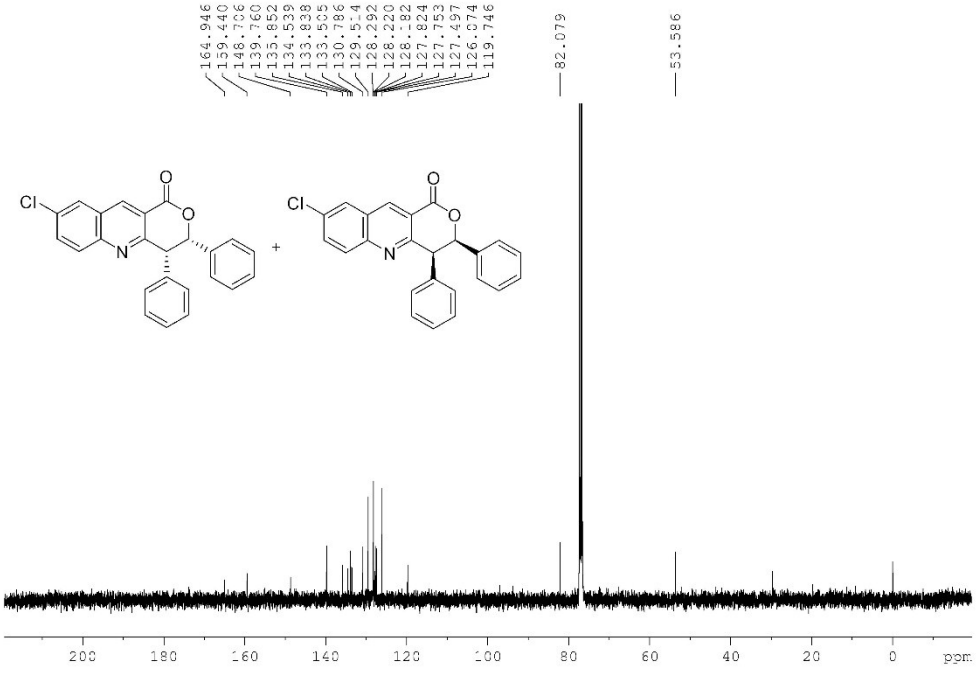
^{1}H NMR spectrum of compound 3ea (trans)



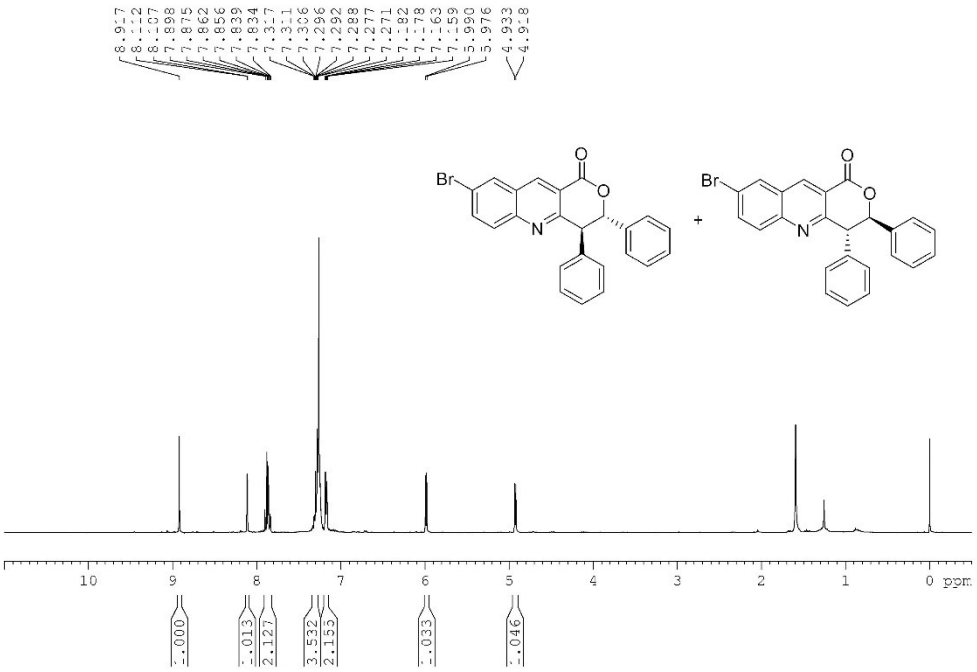
^{13}C NMR spectrum of compound 3ea (trans)



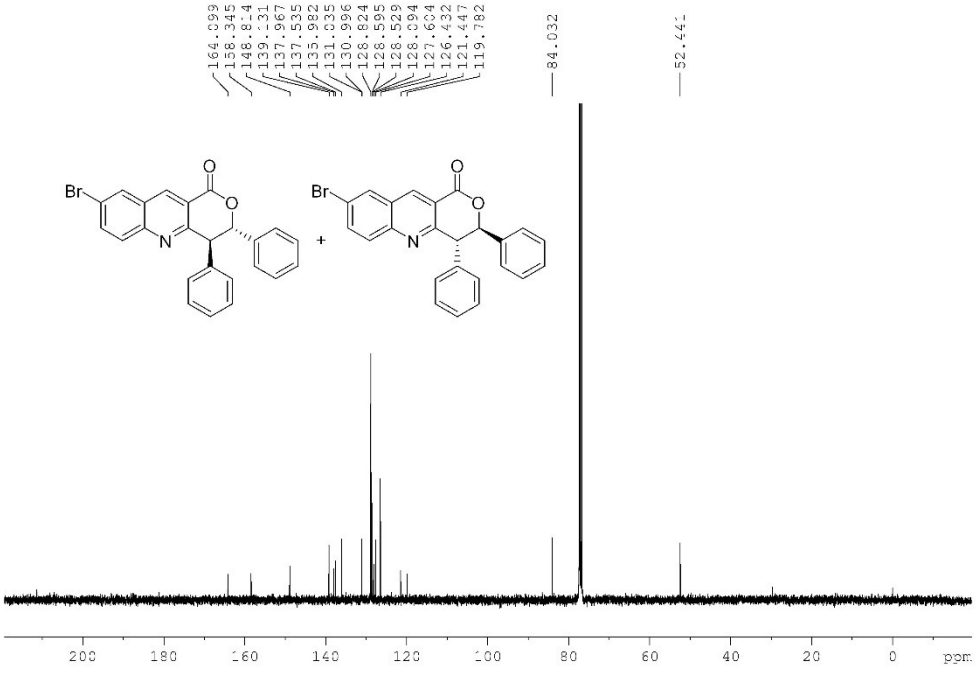
^{1}H NMR spectrum of compound 3ea (cis)



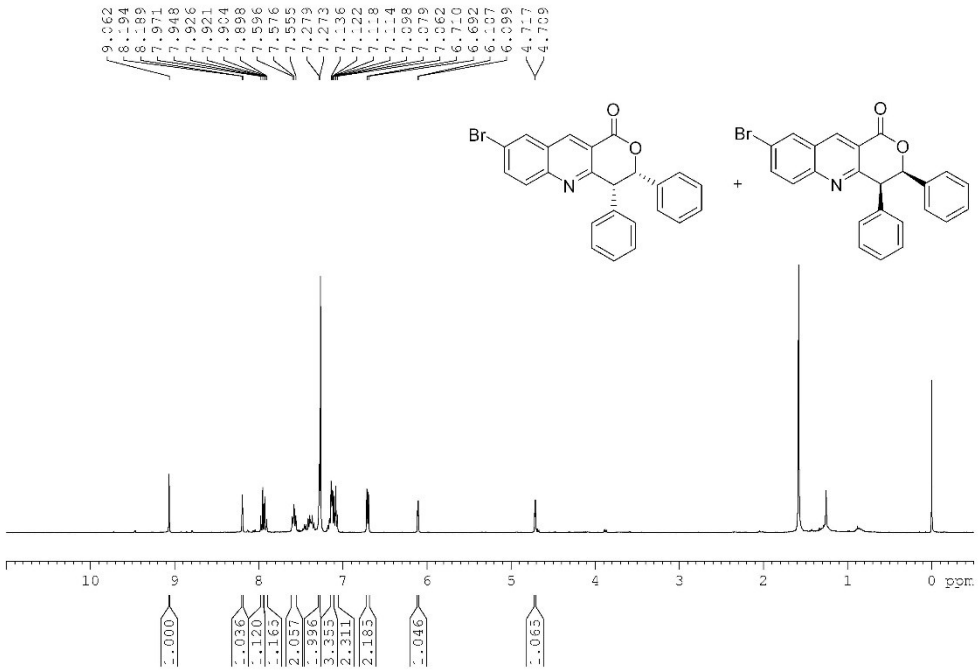
^{13}C NMR spectrum of compound 3ea (cis)



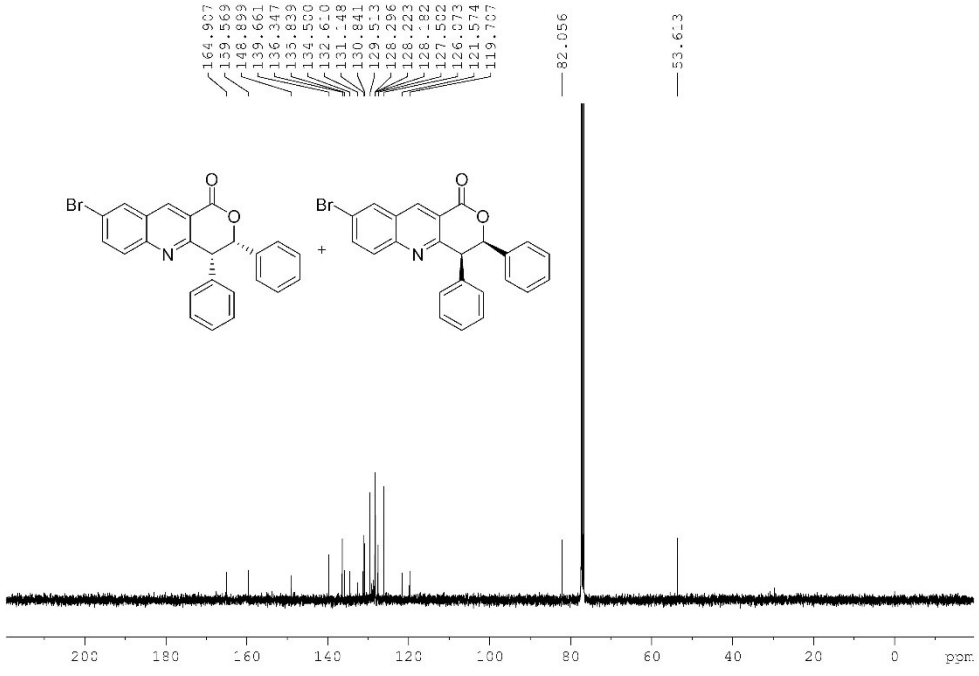
^{1}H NMR spectrum of compound 3fa (trans)



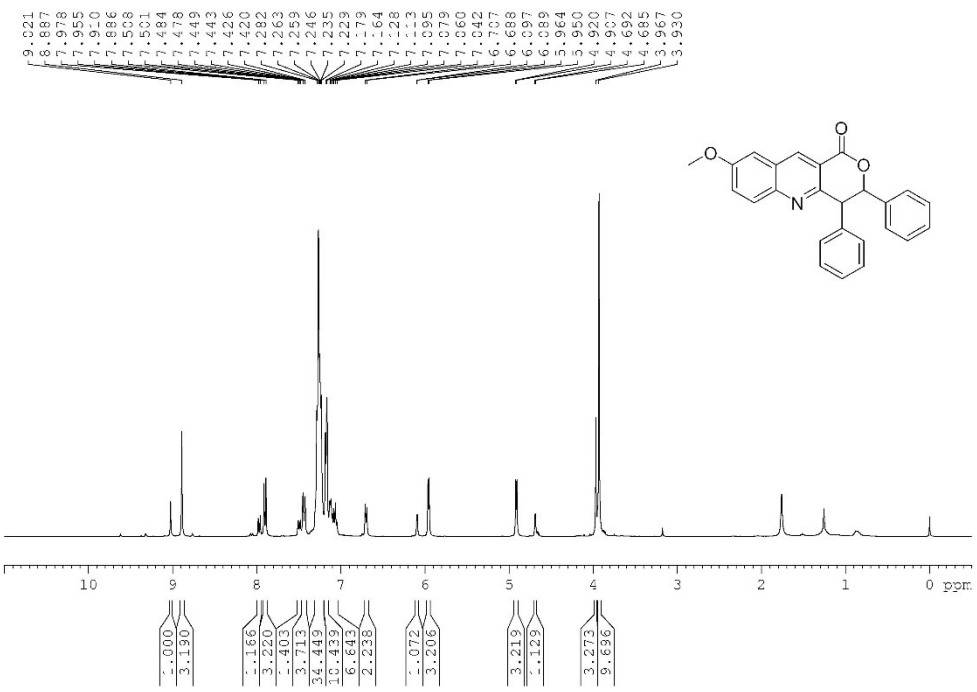
^{13}C NMR spectrum of compound 3fa (trans)



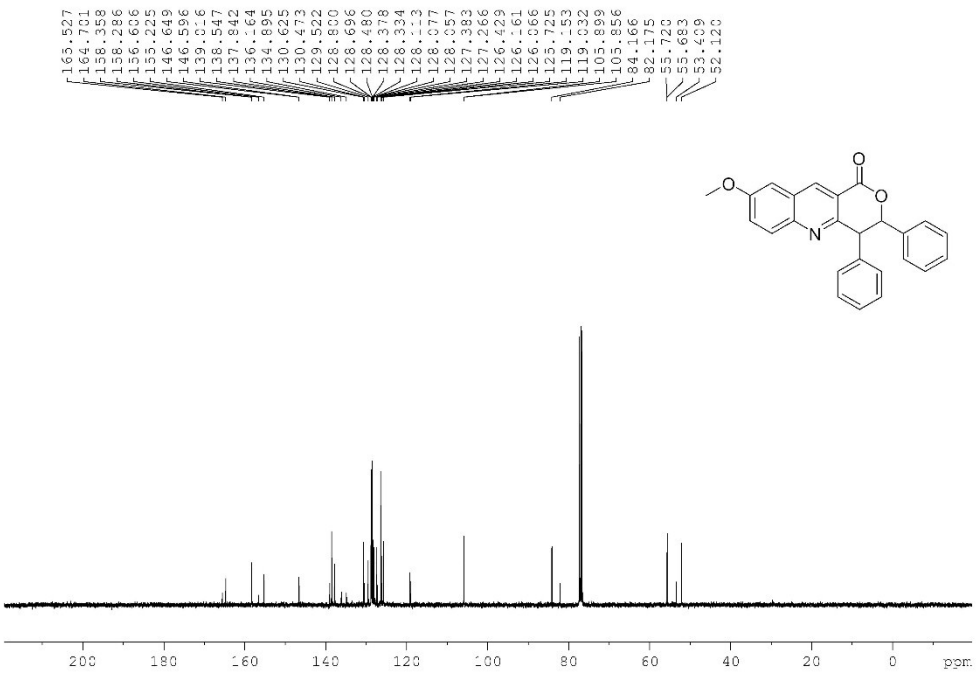
^{1}H NMR spectrum of compound 3fa (cis)



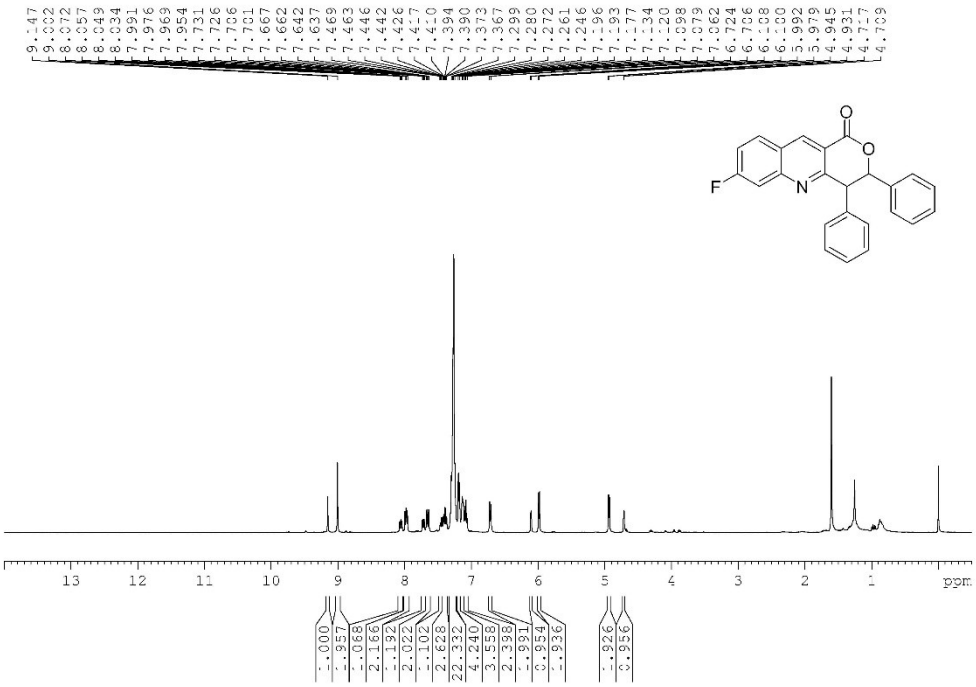
^{13}C NMR spectrum of compound 3fa (cis)



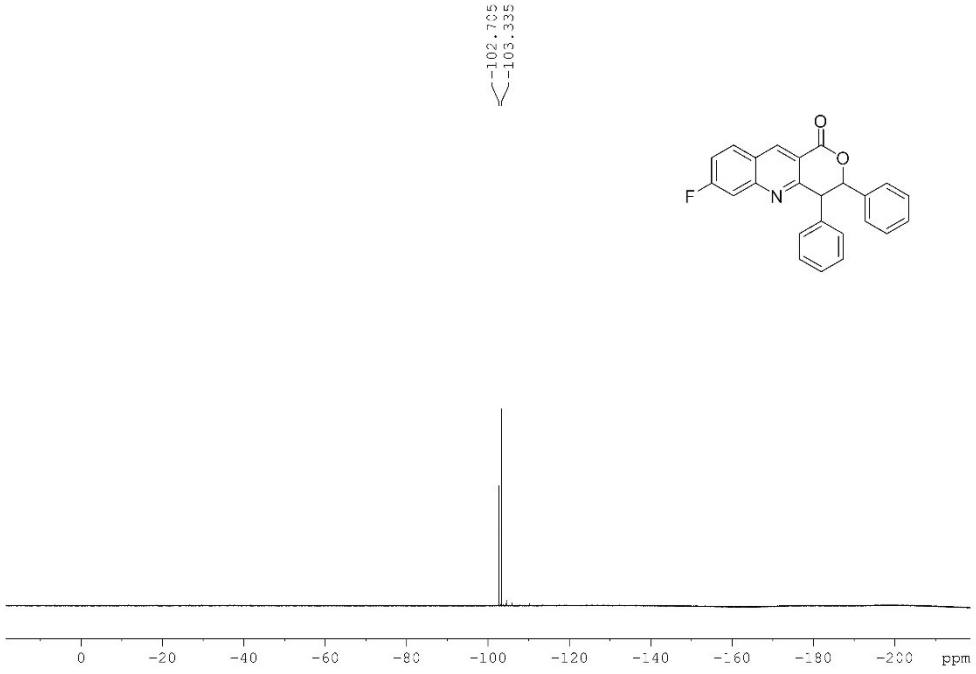
^{1}H NMR spectrum of compound 3ga



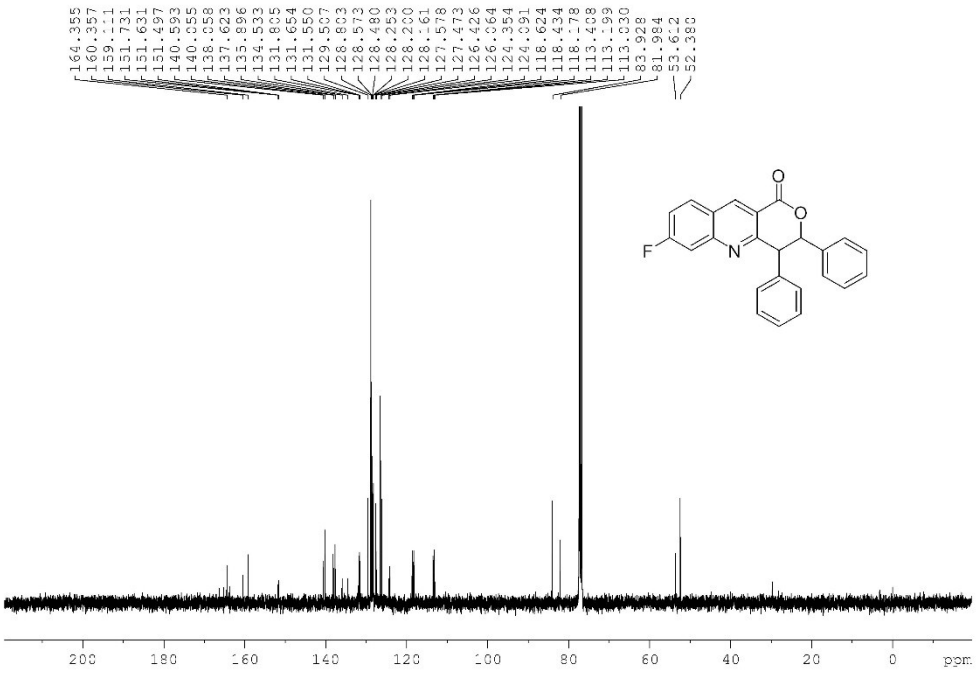
^{13}C NMR spectrum of compound 3ga



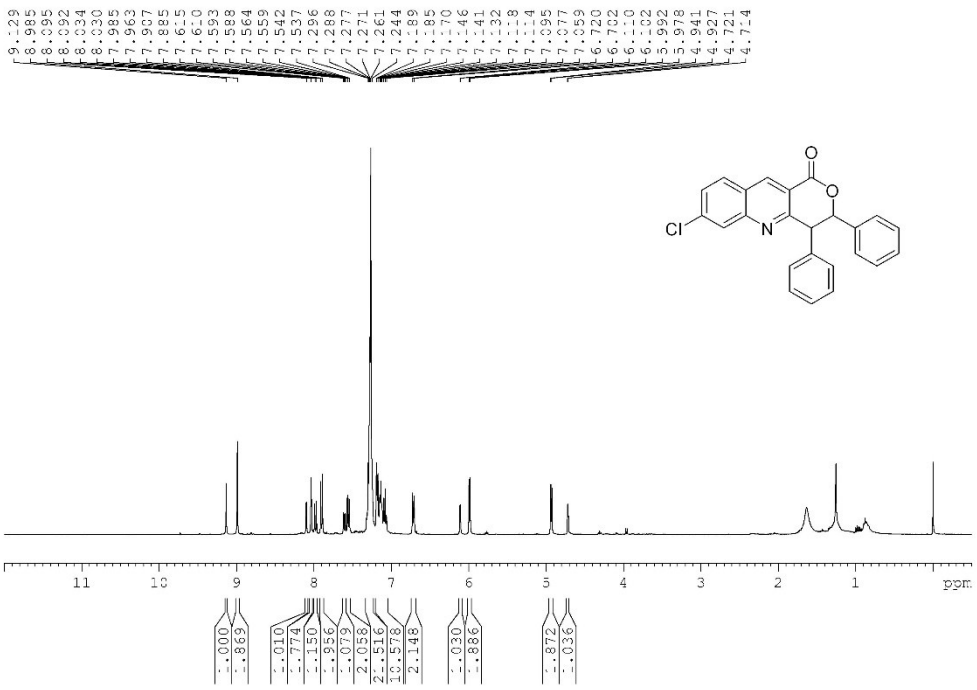
^{1}H NMR spectrum of compound 3ha



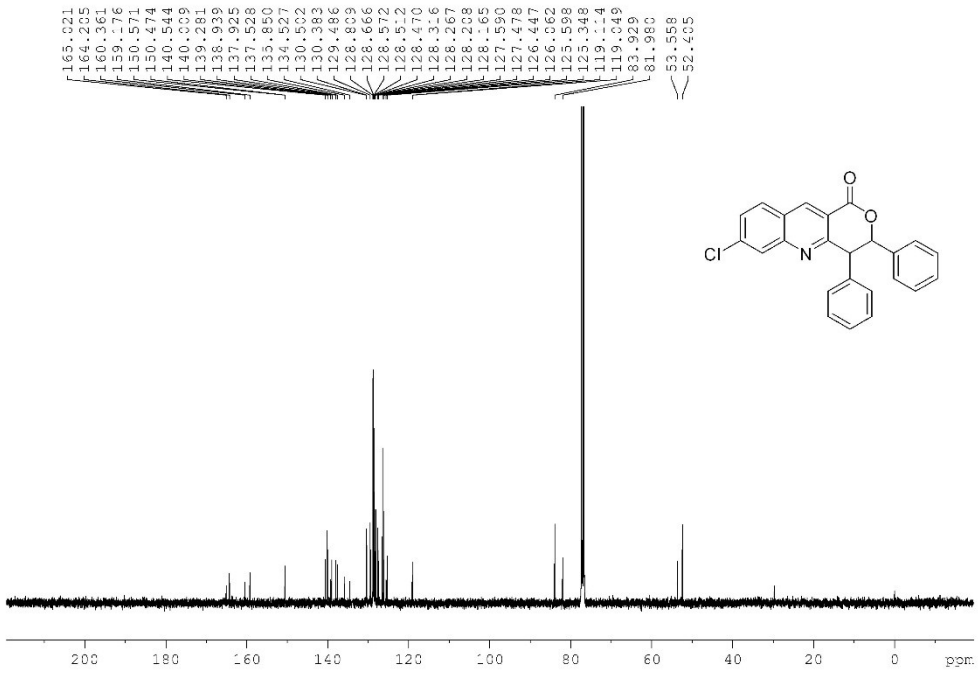
^{19}F NMR spectrum of compound 3ha



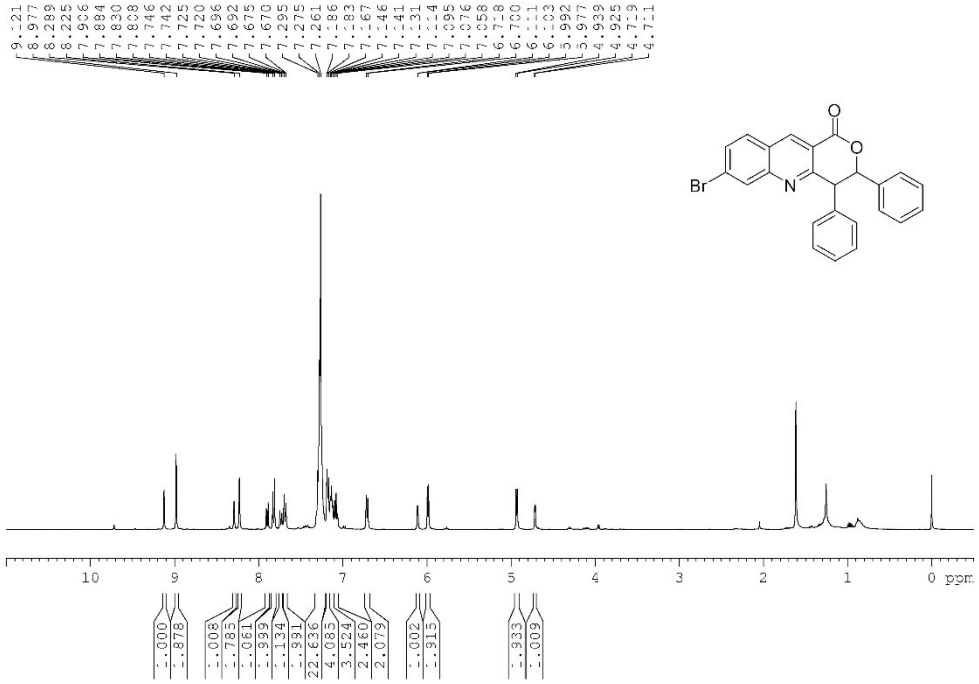
^{13}C NMR spectrum of compound 3ha



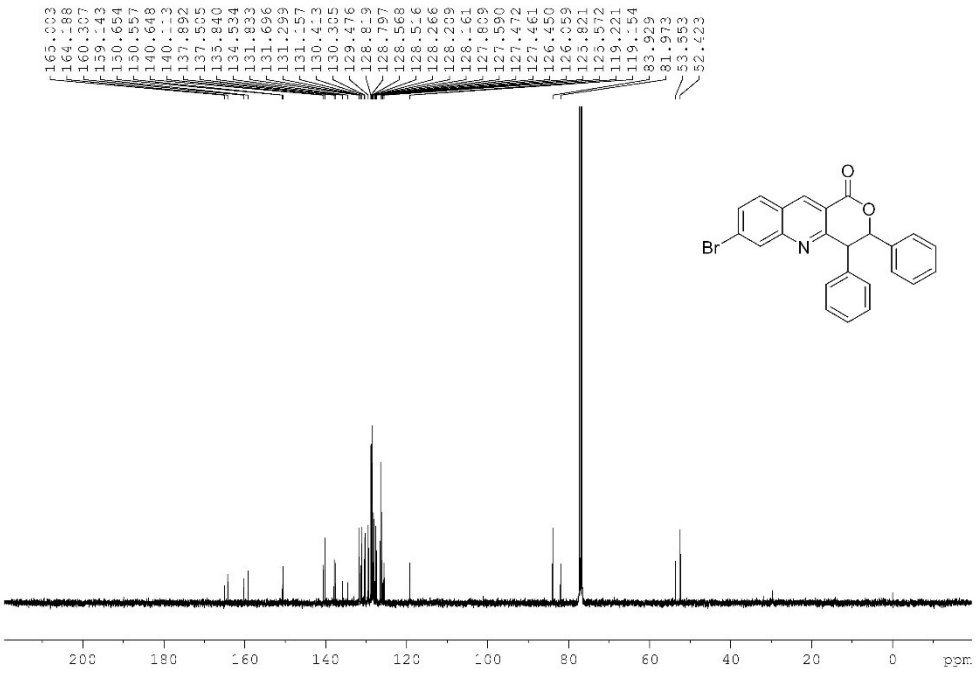
^{1}H NMR spectrum of compound 3ia



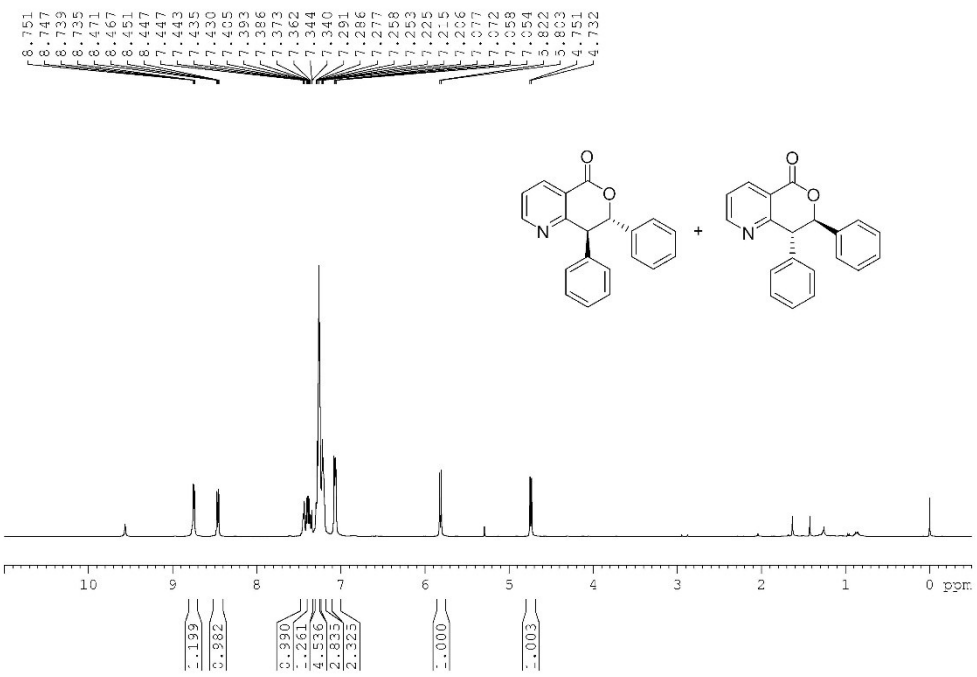
^{13}C NMR spectrum of compound 3ia



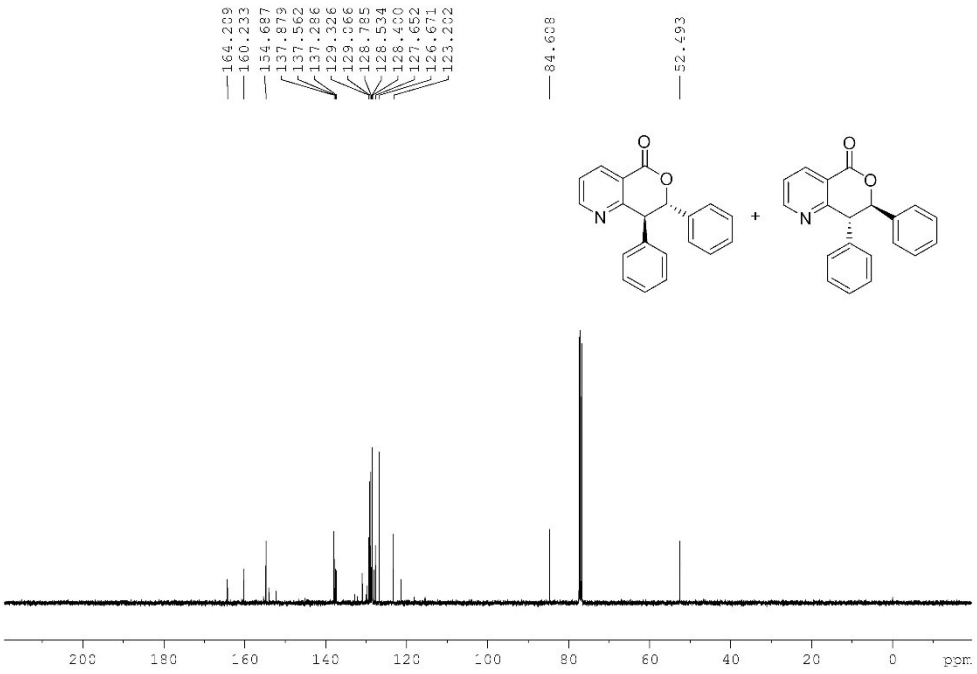
^{1}H NMR spectrum of compound 3ja



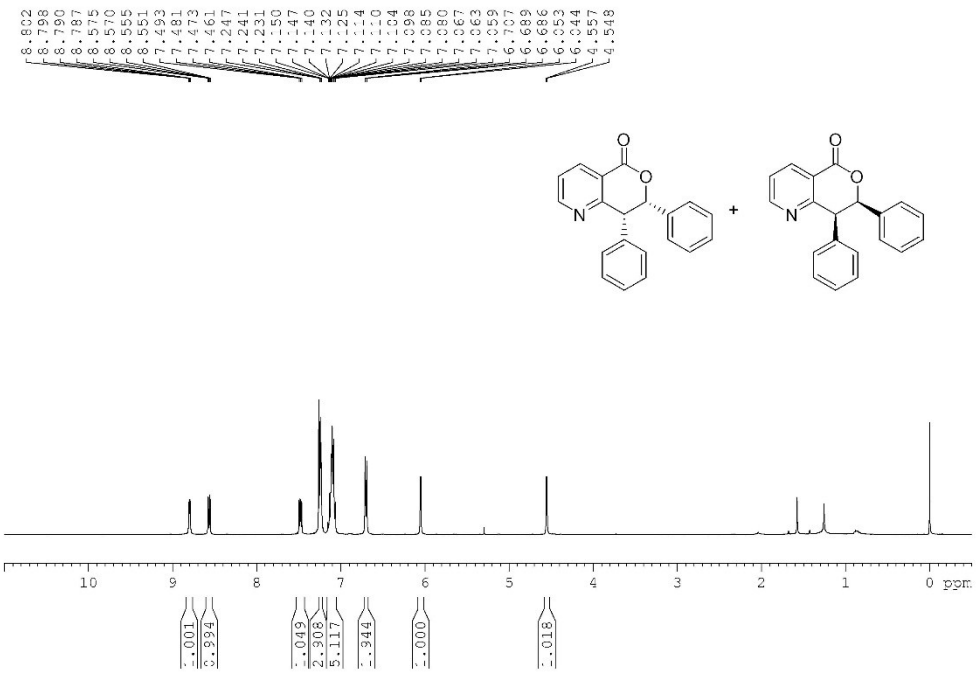
^{13}C NMR spectrum of compound 3ja



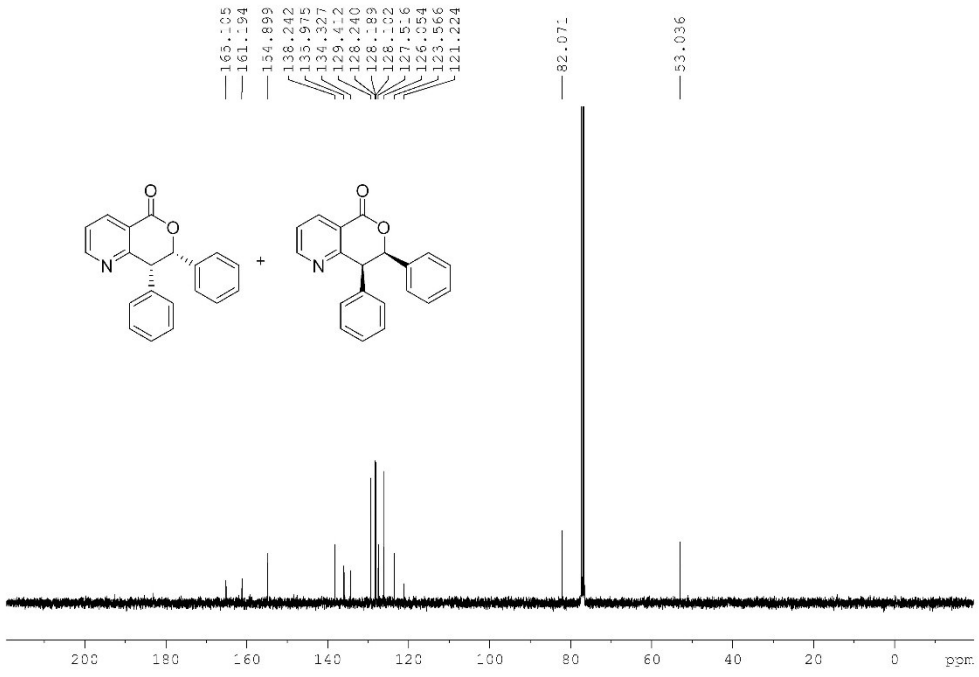
^{1}H NMR spectrum of compound 3ka (trans)



^{13}C NMR spectrum of compound 3ka (trans)



^{1}H NMR spectrum of compound 3ka (cis)



^{13}C NMR spectrum of compound 3ka (cis)