Supporting Information

Oxidation of Active *sp*^{3} C-H Bond Initiated Consecutive Intermolecular/intramolecular Cyclization between Glycine Derivatives and *o*-Vinylphenols: Construction of Polycyclic Benzofuroquinoline Skeleton

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Supporting Information

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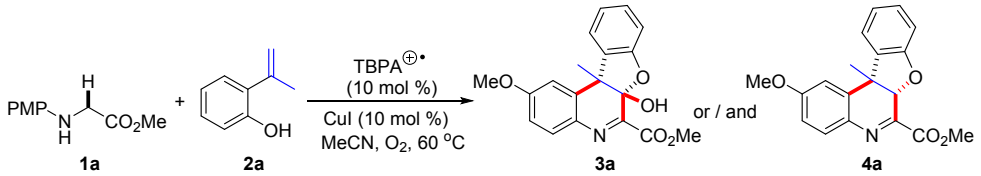
General

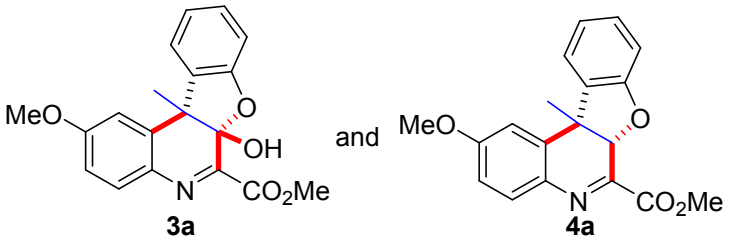
Solvents are anhydrous. $TBPA^{+\cdot}$ was purchased from commercial sources and used without treatment. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. The high resolution mass spectra (HRMS) were measured on an electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry.

General Experimental Procedure

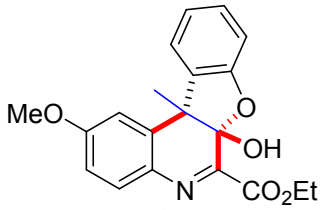


A solution of **1a** (1 mmol), **2a** (1.5 mmol) and CuI (10 mol %) in MeCN (10 ml) was mixed fully, then $TBPA^{+\cdot}$ (10 mol %) was added dropwise. The reaction solution was stirred at 60°C under O_2 atmosphere. After completion monitored by TLC (by UV visualization), the reaction was quenched by addition of NEt_3 (1 ml). The mixture was poured into a separator funnel with the addition of excess DCM (10 ml), and then the crude organic solution was extracted three times with water to remove inorganic salts. The organic phase was then dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 15:1) to afford the products.

Analytical data for compounds

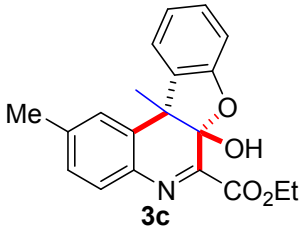


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.7 Hz, 0.3H), 7.58 (d, J = 8.7 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1.3H), 7.20 – 7.09 (m, 1.4H), 7.03 – 6.95 (m, 1.5H), 6.93 (d, J = 2.7 Hz, 1H), 6.87 – 6.79 (m, 1.5H), 6.77 (dd, J = 8.6, 2.6 Hz, 1.2H), 6.54 (s, 1H), 5.31 (s, 0.3H), 4.02 (s, 3H), 4.00 (s, 0.7H), 3.78 (s, 0.8H), 3.77 (s, 3H), 1.64 (s, 3H), 1.60 (s, 0.8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.1, 162.0, 161.8, 158.1, 156.2, 148.7, 147.0, 136.0, 133.8, 133.5, 132.9, 132.8, 132.7, 132.5, 128.6 (two ^{13}C), 123.7 (two ^{13}C), 122.1, 121.7, 113.7, 113.2, 112.1, 111.9, 110.6, 110.2, 103.4, 79.6, 55.5, 53.6, 53.3, 50.5, 45.5, 26.8, 21.8; HRMS (ESI) m/z calculated for $C_{19}H_{17}NO_5 + Na^+$ (**3a**), 362.1004, found: 362.1005; $C_{19}H_{17}NO_4 + Na^+$, 346.1055 (**4a**), found: 346.1058.



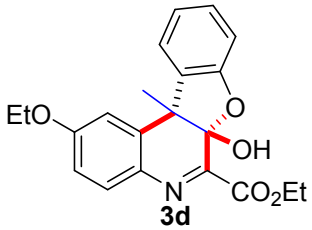
3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.7 Hz, 1H), 7.49 – 7.38 (m, 1H), 7.17 (td, *J* = 7.9, 1.2 Hz, 1H), 7.01 (td, *J* = 7.5, 0.8 Hz, 1H), 6.94 (d, *J* = 2.7 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.62 (s, *OH*, 1H), 4.51 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.64 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 161.9, 156.3, 147.3, 135.9, 132.8, 132.6, 128.6, 123.7, 122.1, 113.6, 112.0, 110.6, 103.6, 63.0, 55.5, 50.5, 21.7, 14.2; HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5$ + Na^+, 376.1161, found: 376.1155.



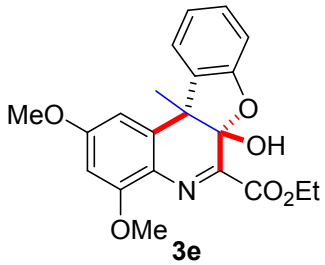
3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.23 (s, 1H), 7.17 (td, *J* = 7.8, 1.3 Hz, 1H), 7.09 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.03 (td, *J* = 7.5, 0.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.55 (s, *OH*, 1H), 4.52 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.66 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 156.3, 149.3, 142.1, 136.4, 133.4, 133.0, 130.9, 128.7, 128.5, 127.6, 124.0, 122.1, 110.6, 103.6, 63.1, 50.1, 21.8, 21.8, 14.2; HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_4$ + Na^+, 360.1212, found: 360.1198.



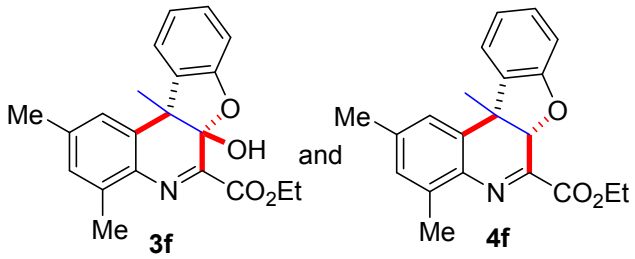
3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.63 (s, *OH*, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.64 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 161.3, 156.3, 147.2, 135.9, 132.9, 132.8, 132.5, 128.6, 123.8, 122.1, 114.0, 112.4, 110.6, 103.6, 63.8, 63.0, 50.5, 21.8, 14.6, 14.2; HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_5$ + Na^+, 390.1317; found: 390.1306.

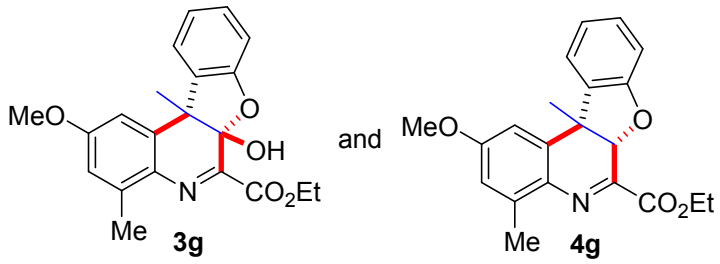


3e

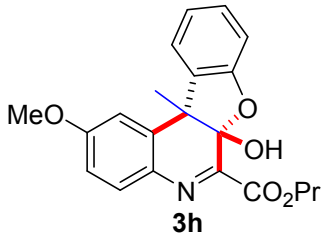
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.72 (s, 1H), 6.52 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 2.2 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 3H), 1.61 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.1, 157.9, 156.4, 145.1, 137.3, 132.8, 128.6, 123.7, 122.5, 122.0, 110.6, 104.4, 103.7, 96.7, 62.9, 56.3, 55.4, 50.7, 21.4, 14.1; HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_6$ + Na^+, 406.1267; found: 406.1277.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.4 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.17 – 7.08 (m, 2H), 7.00 – 6.90 (m, 3H), 6.83 (d, J = 7.9 Hz, 1H), 6.55 (s, *OH*, 0.3H), 5.30 (s, 1H), 4.54 – 4.39 (m, 2.5H), 2.54 (s, 3H), 2.51 (s, 1H), 2.30 (s, 4H), 2.29 (s, 1H), 1.63 (s, 1H), 1.60 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 164.9, 158.2, 149.3, 146.0, 141.0, 139.2, 139.0, 135.8, 133.5, 132.5, 131.3, 130.5 (two ^{13}C), 128.4, 128.3, 125.6, 125.3, 124.7, 124.0, 123.9, 122.0, 121.5, 116.0, 110.5, 110.1, 79.9, 62.7, 62.1, 45.5, 31.5, 30.1, 26.7, 21.7, 21.6, 17.7, 14.2, 14.1; HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_4$ + Na^+ (**3f**), 374.1368; found: 374.1358; $C_{21}H_{21}NO_3$ + Na^+, 358.1419; found: 358.1411 (**4f**).

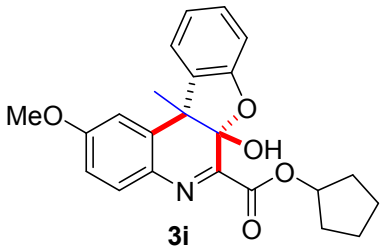


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 1H), 7.20 – 7.09 (m, 1H), 7.04 – 6.92 (m, 1H), 6.87 – 6.80 (m, 2H), 6.76 (d, J = 2.7 Hz, 1H), 6.69 – 6.61 (m, 1H), 5.28 (s, 1H), 4.57 – 4.35 (m, 2H), 3.78 (s, 3H), 3.77 (s, 1H), 2.56 (s, 3H), 2.54 (s, 1H), 1.62 (s, 1H), 1.58 (s, 3H), 1.49 – 1.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 164.9, 161.3, 161.0, 158.2, 156.3, 147.2, 141.6, 141.4, 136.1, 133.7, 133.3, 132.2, 131.2, 128.5, 128.4, 123.8, 123.7, 122.0, 121.5, 113.6, 113.6, 111.2, 110.6, 110.6, 110.1, 103.6, 79.7, 62.5, 62.0, 55.3, 50.6, 45.8, 26.5, 21.6, 18.1, 18.1, 14.2, 14.1; HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_4$ + Na^+ (**3g**), 374.1368; found: 374.1381; $C_{21}H_{21}NO_5$ + Na^+, 390.1317; found: 390.1330 (**4g**).



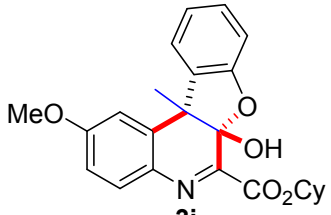
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.94 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.7 Hz, 1H), 6.57 (s,

OH, 1H), 4.47 – 4.34 (m, 2H), 3.80 (s, 3H), 1.92 – 1.82 (m, 2H), 1.65 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 161.8, 156.3, 147.5, 135.8, 132.9, 132.8, 132.7, 128.6, 123.7, 122.1, 113.5, 112.0, 110.6, 103.6, 68.3, 55.5, 50.4, 21.9, 21.7, 10.3; HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_5 + Na^+$, 390.1317; found: 390.1325.



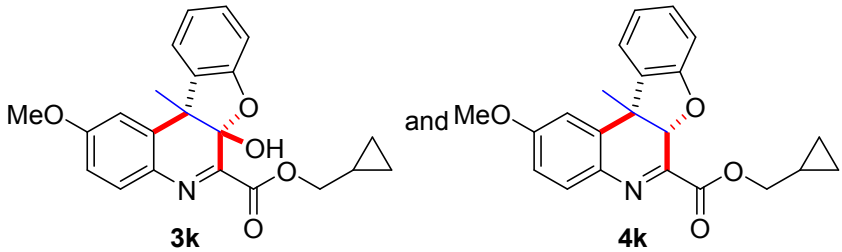
3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.77 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.61 (s, *OH*, 1H), 5.53 – 5.39 (m, 1H), 3.80 (s, 3H), 2.10 – 1.99 (m, 2H), 1.99 – 1.89 (m, 2H), 1.89 – 1.78 (m, 2H), 1.74 – 1.57 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 161.7, 156.3, 147.7, 135.7, 132.9, 132.7, 129.6, 128.6, 123.7, 122.0, 115.3, 113.4, 112.0, 110.6, 103.7, 80.1, 55.5, 50.4, 32.6, 32.5, 23.9, 23.8, 21.7; HRMS (ESI) m/z calculated for $C_{23}H_{23}NO_5 + Na^+$, 416.1474; found: 416.1465.



3j

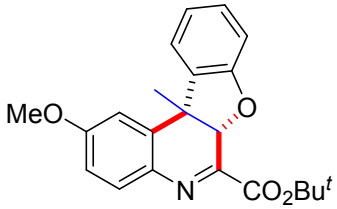
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.78 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.62 (s, *OH*, 1H), 5.14 – 4.97 (m, 1H), 3.80 (s, 3H), 2.11 – 1.99 (m, 2H), 1.90 – 1.78 (m, 2H), 1.74 – 1.56 (m, 5H), 1.50 – 1.36 (m, 2H), 1.36 – 1.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 161.7, 156.3, 147.8, 135.7, 133.0, 132.8, 128.6, 123.7, 122.0, 113.4, 111.9, 110.6, 103.7, 76.0, 55.5, 50.4, 31.4, 31.4, 26.9, 25.2, 24.0, 21.7; HRMS (ESI) m/z calculated for $C_{24}H_{25}NO_5 + Na^+$, 430.1630; found: 430.1628.



3k **4k**

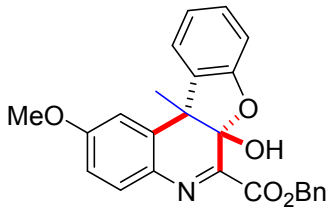
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 0.2H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 2.7 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.59 (s, *OH*, 1H), 5.32 (s, 0.2H), 4.28 (d, *J* = 7.3 Hz, 2H), 3.80 (s, 0.6H), 3.79 (s, 3H), 1.65 (s, 3H), 1.62 (s, 0.6H), 1.36 (m, 0.6H), 0.91 – 0.82 (m, 0.6H), 0.66 (q, *J* = 5.5 Hz, 2H), 0.43 (q, *J* = 5.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 161.9, 156.3, 147.5, 135.9, 132.9, 132.7, 128.7, 123.8, 122.1, 113.6, 112.0, 110.7, 103.6, 71.9, 55.5, 50.5, 21.7, 9.8, 3.8 (two ^{13}C); HRMS (ESI)

m/z calculated for $C_{22}H_{21}NO_5 + Na^+$ (**3k**), 402.1317; found: 402.1300; $C_{22}H_{21}NO_4 + Na^+$ (**4k**), 386.13687; found: 386.1347.



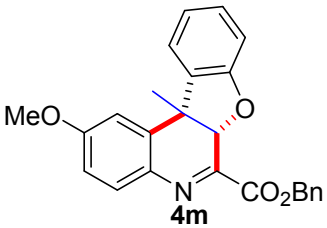
4l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 8.7, 1.7 Hz, 1H), 5.25 (s, 1H), 3.80 (s, 3H), 1.64 (s, 9H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 161.4, 158.2, 150.6, 133.7, 133.5, 133.1, 132.6, 128.5, 123.7, 121.5, 112.9, 111.8, 110.1, 83.1, 80.0, 55.4, 45.6, 28.1, 26.8; HRMS (ESI) m/z calculated for $C_{22}H_{23}NO_4 + H^+$, 366.1705; found: 366.1695.



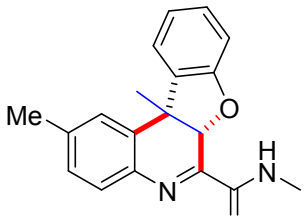
3m

and



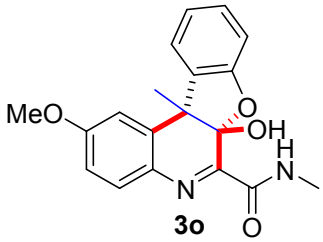
4m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 0.3H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.32 (m Hz, 4.5H), 7.18 – 7.12 (m, 1.4H), 7.06 – 6.92 (m, 2.5H), 6.87 – 6.73 (m, 2.4H), 6.46 (s, *OH*, 0.3H), 5.49 (d, *J* = 12.5 Hz, 1H), 5.44 (d, *J* = 12.4 Hz, 1H), 5.32 (s, 1H), 3.81 (s, 3H), 3.80 (s, 1H), 1.64 (s, 1H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 161.8, 158.1, 149.0, 135.5, 133.7, 133.0, 132.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 123.7, 123.7, 122.1, 121.7, 113.5, 113.1, 111.9, 110.6, 110.2, 103.6, 79.9, 68.2, 67.7, 55.5, 45.6, 31.6, 26.9, 21.7, 14.1; HRMS (ESI) m/z calculated for $C_{25}H_{21}NO_4 + Na^+$ (**3m**), 422.1368; found: 422.1361; $C_{25}H_{21}NO_5 + H^+$ (**4m**), 416.1493; found: 416.1484.



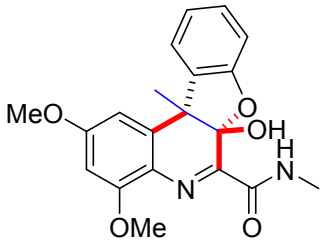
4n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 3.4 Hz, *NH*, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.26 (s, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.49 (s, 1H), 3.02 (d, *J* = 5.1 Hz, 3H), 2.33 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 158.5, 152.4, 141.1, 136.8, 133.2, 132.0, 129.7, 128.6, 128.3, 127.3, 123.9, 121.4, 110.2, 77.9, 45.1, 26.8, 26.2, 21.7; HRMS (ESI) m/z calculated for $C_{19}H_{18}N_2O_2 + Na^+$, 329.1266; found: 329.1248.



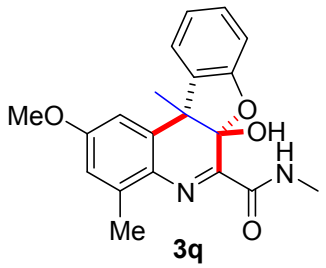
3o

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, *OH*, 1H), 7.84 (d, *J* = 4.2 Hz, *NH*, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.75 (dd, *J* = 8.6, 2.6 Hz, 1H), 3.78 (s, 3H), 3.01 (d, *J* = 5.2 Hz, 3H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 161.3, 156.5, 147.5, 136.7, 132.7, 131.9, 131.4, 128.5, 123.8, 121.9, 113.7, 112.1, 110.7, 104.5, 55.5, 50.4, 26.0, 21.9; HRMS (ESI) m/z calculated for $C_{19}H_{18}N_2O_4$ + Na^+, 361.1164; found:361.1156.



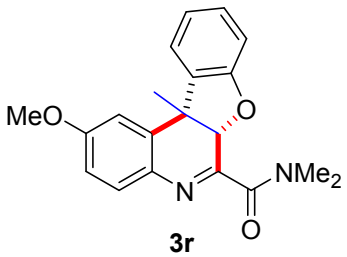
3p

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, *OH*, 1H), 7.95 (d, *J* = 4.1 Hz, *NH*, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 2.99 (d, *J* = 5.1 Hz, 3H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 162.3, 157.0, 156.6, 145.6, 138.0, 132.8, 128.5, 123.8, 121.9, 121.8, 110.7, 104.7, 104.5, 97.0, 56.1, 55.4, 50.6, 26.0, 21.6; HRMS (ESI) m/z calculated for $C_{20}H_{20}N_2O_5$ + Na^+, 391.1270; found: 391.1258.



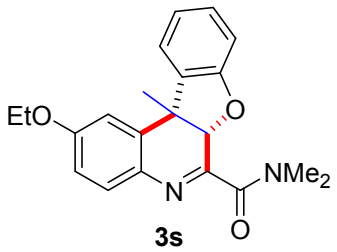
3q

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, *NH*, 1H), 7.34 – 7.22 (m, 2H), 7.09 – 7.02 (m, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.61 (s, *OH*, 1H), 3.93 (s, 3H), 2.94 (d, *J* = 5.1 Hz, 3H), 2.78 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 158.3, 154.0, 145.7, 144.8, 140.7, 139.7, 130.5, 130.2, 129.4, 129.2, 127.8, 122.5, 120.7, 117.9, 99.9, 55.4, 26.5, 18.1, 16.4; HRMS (ESI) m/z calculated for $C_{21}H_{20}N_2O_4$ + H^+, 353.1496; found: 353.1489.



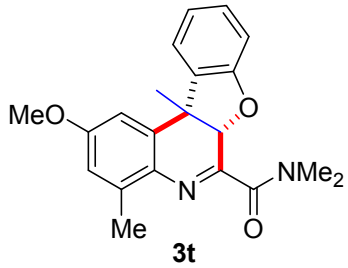
3r

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.80 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.46 (s, 1H), 3.85 (s, 3H), 3.10 (s, 3H), 3.01 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 160.5, 157.6, 155.6, 133.5, 133.3, 131.9, 130.8, 128.6, 123.6, 121.7, 112.9, 111.7, 110.0, 81.9, 55.5, 45.2, 38.2, 35.2, 27.6; HRMS (ESI) m/z calculated for $C_{20}H_{20}N_2O_3$ + H^+, 337.1547; found: 337.1533.



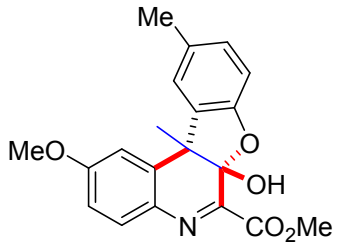
3s

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.46 (s, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.10 (s, 3H), 3.00 (s, 3H), 1.68 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 159.9, 157.6, 155.5, 133.6, 133.2, 131.9, 130.8, 128.6, 123.7, 121.7, 113.4, 112.2, 109.9, 81.9, 63.8, 45.2, 38.2, 35.2, 27.7, 14.8; HRMS (ESI) m/z calculated for $C_{21}H_{22}N_2O_3$ + H^+, 351.1709; found: 351.1716.



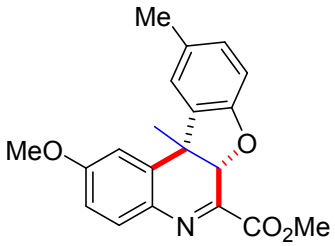
3t

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.10 (td, *J* = 8.0, 1.3 Hz, 1H), 6.95 – 6.87 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 5.44 (s, 1H), 3.81 (s, 3H), 3.12 (s, 3H), 3.09 (s, 3H), 2.43 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 159.8, 157.8, 153.0, 139.5, 133.8, 132.1, 131.6, 128.4, 123.7, 121.6, 113.6, 110.4, 109.9, 81.3, 55.3, 45.4, 38.5, 35.6, 27.3, 18.2; HRMS (ESI) m/z calculated for $C_{21}H_{22}N_2O_3$ + H^+, 351.1703, found: 351.1692.



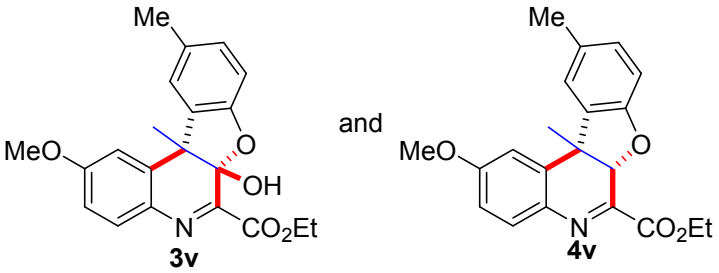
3u

and

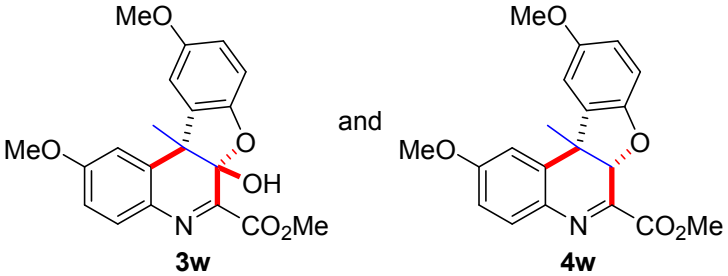


4u

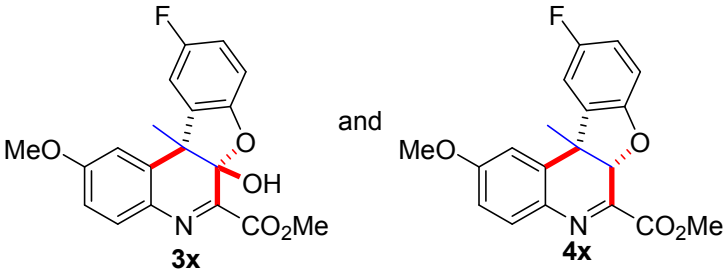
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 0.2H), 7.22 (s, 1.3H), 7.01 (d, *J* = 2.7 Hz, 1.1H), 6.98 – 6.89 (m, 1.5H), 6.81 (dd, *J* = 8.7, 2.7 Hz, 1.3H), 6.75 – 6.69 (m, 1.2H), 6.43 (s, *OH*, 0.2H), 5.28 (s, 1H), 4.03 (s, 0.4H), 4.00 (s, 3H), 3.82 (s, 3H), 3.81 (s, 0.5H), 2.34 (s, 0.5H), 2.33 (s, 3H), 1.62 (s, 0.6H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 161.7, 156.1, 149.0, 133.9, 133.6, 132.9, 132.7, 131.1, 128.9, 124.1, 113.4, 111.6, 109.7, 79.8, 55.5, 53.2, 45.6, 26.9, 21.0; HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_4$ + H^+ (**3u**), 360.1211; found: 360.1199; $C_{20}H_{19}NO_4$ + H^+ (**4u**), 338.1387, found: 338.1377.



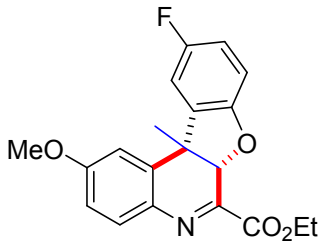
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.7 Hz, 0.4H), 7.22 (s, 1.4H), 7.00 (s, 1H), 6.98 – 6.88 (m, 1.8H), 6.84 – 6.76 (m, 1.5H), 6.73 (t, J = 6.8 Hz, 1.4H), 6.51 (s, 0.4H), 5.28 (s, 1H), 4.57 – 4.40 (m, 2.8H), 3.82 (s, 4H), 2.33 (s, 4H), 1.62 (s, 1H), 1.59 (s, 3H), 1.50 – 1.39 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 164.7, 161.8, 161.6, 156.1, 154.2, 149.4, 147.6, 136.0, 133.8, 133.7, 132.9, 132.7, 132.7, 132.7, 131.5, 131.0, 129.0, 128.9, 124.3, 124.2, 113.8, 113.3, 111.7, 111.6, 110.1, 109.7, 103.6, 79.9, 63.0, 62.3, 55.5, 50.5, 45.6, 26.8, 21.7, 21.1, 21.0, 14.3, 14.2; HRMS (ESI) m/z calculated for $C_{21}H_{21}NO_5 + Na^+$ (**3v**), 390.1317, found: 390.1315; $C_{21}H_{21}NO_4 + Na^+$, 374.1368 (**4v**), found: 374.1375.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 1H), 7.58 (d, J = 8.7 Hz, 0.2H), 7.02 – 6.92 (m, 2.2H), 6.84 – 6.77 (m, 1.3H), 6.74 (m, 1.2H), 6.70 – 6.62 (m, 1.3H), 6.42 (s, *OH*, 0.2H), 5.28 (s, 1H), 4.02 (s, 1H), 4.00 (s, 3H), 3.81 (s, 3H), 3.80 (s, 1H), 3.78 (s, 3.4H), 1.61 (s, 1H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 161.8, 155.0, 152.3, 149.0, 134.0, 133.6, 133.5, 132.8, 113.7, 113.2, 112.7, 111.9, 110.9, 110.6, 110.1, 79.9, 56.1, 55.5, 53.2, 45.9, 26.6, 21.7; HRMS (ESI) m/z calculated for $C_{20}H_{19}NO_5 + Na^+$ (**3w**), 376.1161, found: 376.1153; $C_{20}H_{19}NO_6 + Na^+$ (**4w**), 392.1110, found: 392.0999.

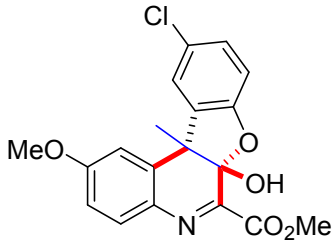


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.7 Hz, 0.2H), 7.16 – 7.08 (m, 1.2H), 6.94 (d, J = 2.7 Hz, 1H), 6.89 (d, J = 2.7 Hz, 0.2H), 6.86 – 6.78 (m, 2.2H), 6.77 – 6.70 (m, 1.2H), 6.55 (s, *OH*, 0.2H), 5.33 (s, 1H), 4.03 (s, 0.5H), 4.00 (s, 3H), 3.82 (s, 3H), 3.81 (s, 0.6H), 1.61 (s, 0.6H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 161.9, 159.2, 156.8, 154.1, 148.5, 134.4, 134.4, 133.5, 133.0, 132.9, 115.0, 114.7, 113.6, 113.1, 112.1, 111.1, 110.8, 110.6, 110.5, 104.0, 55.5, 53.6, 53.2, 45.9, 26.8, 26.6, 21.6; HRMS (ESI) m/z calculated for $C_{19}H_{16}FNO_5 + Na^+$ (**3x**), 380.0910, found: 380.0894; $C_{19}H_{16}FNO_4 + Na^+$ (**4x**), 364.0961, found: 364.0944.



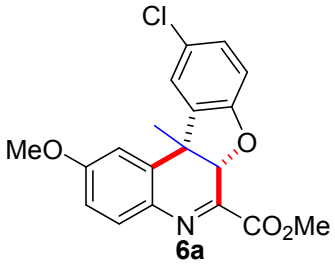
4y

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.94 (s, 1H), 6.87 – 6.78 (m, 2H), 6.77 – 6.68 (m, 1H), 5.33 (s, 1H), 4.57 – 4.41 (m, 2H), 3.82 (s, 3H), 1.59 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 161.8, 159.2, 156.8, 154.1, 149.0, 134.4, 133.6, 132.9, 114.9, 114.7, 113.0, 112.0, 111.1, 110.8, 110.6, 110.5, 80.3, 62.4, 55.5, 45.9, 26.6, 14.3; HRMS (ESI) m/z calculated for $C_{20}H_{18}FNO_4 + Na^+$, 378.1118; found: 378.1116.



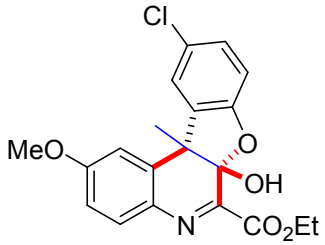
5a

and



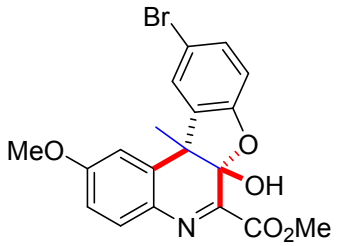
6a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.17 – 7.04 (m, 2H), 6.95 (s, 1H), 6.89 (s, 1H), 6.82 (t, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 8.4, 3.9 Hz, 2H), 6.59 (s, *OH*, 1H), 5.34 (s, 1H), 4.04 (s, 3H), 4.01 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 164.9, 162.1, 161.9, 156.8, 154.9, 148.4, 146.6, 135.2, 134.9, 134.8, 133.5, 133.0, 132.9, 132.5, 128.6, 128.52 126.8, 126.4, 124.0, 123.9, 113.8, 113.2, 112.1, 112.0, 111.7, 111.2, 104.1, 80.3, 55.6, 53.7, 53.3, 50.7, 45.8, 26.8, 21.6; HRMS (ESI) m/z calculated for $C_{19}H_{16}ClNO_4 + Na^+$ (**5a**), 380.0666, found: 380.0653; $C_{19}H_{16}ClNO_5 + Na^+$ (**6a**), 396.0615, found: 396.0601.



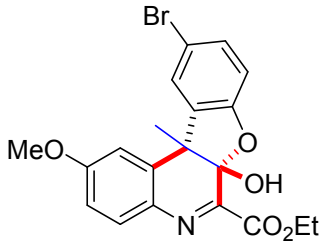
5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.37 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.89 (s, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.68 (s, *OH*, 1H), 4.51 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 1.62 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 162.0, 155.0, 146.9, 135.1, 134.9, 133.0, 132.6, 128.5, 126.7, 124.0, 113.7, 112.0, 111.7, 104.2, 63.1, 55.6, 50.7, 26.9, 21.6, 14.1; HRMS (ESI) m/z calculated for $C_{20}H_{18}ClNO_5 + Na^+$, 410.0771; found: 410.0784.



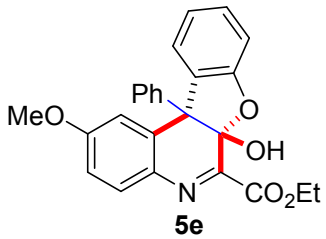
5c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.89 (d, *J* = 2.7 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.60 (s, *OH*, 1H), 4.03 (s, 3H), 3.82 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 162.1, 155.5, 146.6, 135.3, 135.1, 133.0, 132.5, 131.5, 126.8, 113.9, 113.8, 112.3, 112.1, 104.1, 55.6, 53.6, 50.7, 21.6; HRMS (ESI) m/z calculated for $C_{19}H_{16}BrNO_5 + Na^+$, 440.0110; found: 440.0108.



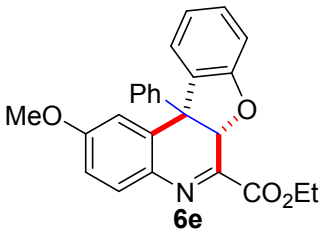
5d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.51 (s, 1H), 7.26 (d, *J* = 9.4 Hz, 2H), 6.88 (s, 1H), 6.85 – 6.78 (m, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.69 (s, *OH*, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.61 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ165.8, 162.0, 155.5, 146.9, 135.4, 135.0, 133.0, 132.6, 131.5, 126.8, 113.8, 113.7, 112.3, 112.0, 104.2, 63.1, 55.6, 50.7, 21.6, 14.1; HRMS (ESI) m/z calculated for $C_{20}H_{18}BrNO_5 + Na^+$, 454.0266; found: 454.0255.



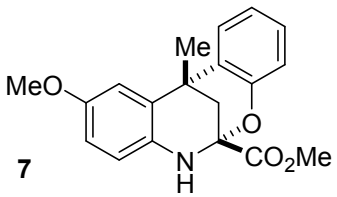
5e

and



6e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 0.3H), 7.46 (d, *J* = 7.4 Hz, 0.3H), 7.36 (d, *J* = 7.4 Hz, 1.2H), 7.22 (m, 5.6H), 7.11 – 6.86 (m, 6.4H), 6.82 (s, 1.4H), 6.73 (s, 0.4H), 6.63 (s, *OH*, 0.4H), 5.53 (s, 1H), 4.52 – 4.33 (m, 2.7H), 3.74 (s, 3H), 3.71 (s, 0.8H), 1.46 – 1.33 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 161.9, 161.7, 159.6, 148.7, 143.0, 135.2, 132.6, 132.6, 132.0, 131.9, 129.8, 128.9, 128.8, 128.7, 128.1, 127.9, 127.6, 127.5, 126.2, 125.8, 122.1, 122.0, 115.2, 114.9, 113.1, 112.9, 111.0, 110.3, 103.1, 81.7, 63.1, 62.4, 60.2, 55.6, 55.5, 14.2, 14.1; HRMS (ESI) m/z calculated for $C_{25}H_{22}NO_5 + H^+$ (**5e**), 416.1493, found: 416.1491; $C_{25}H_{22}NO_4 + H^+$ (**6e**), 400.1543, found: 400.1540.

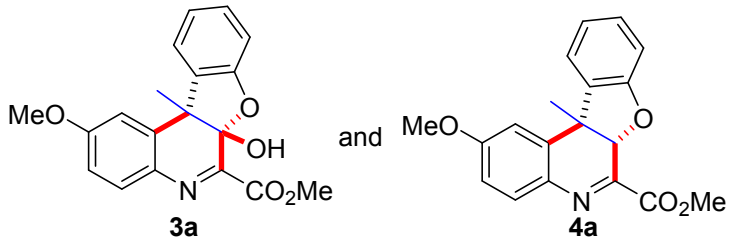


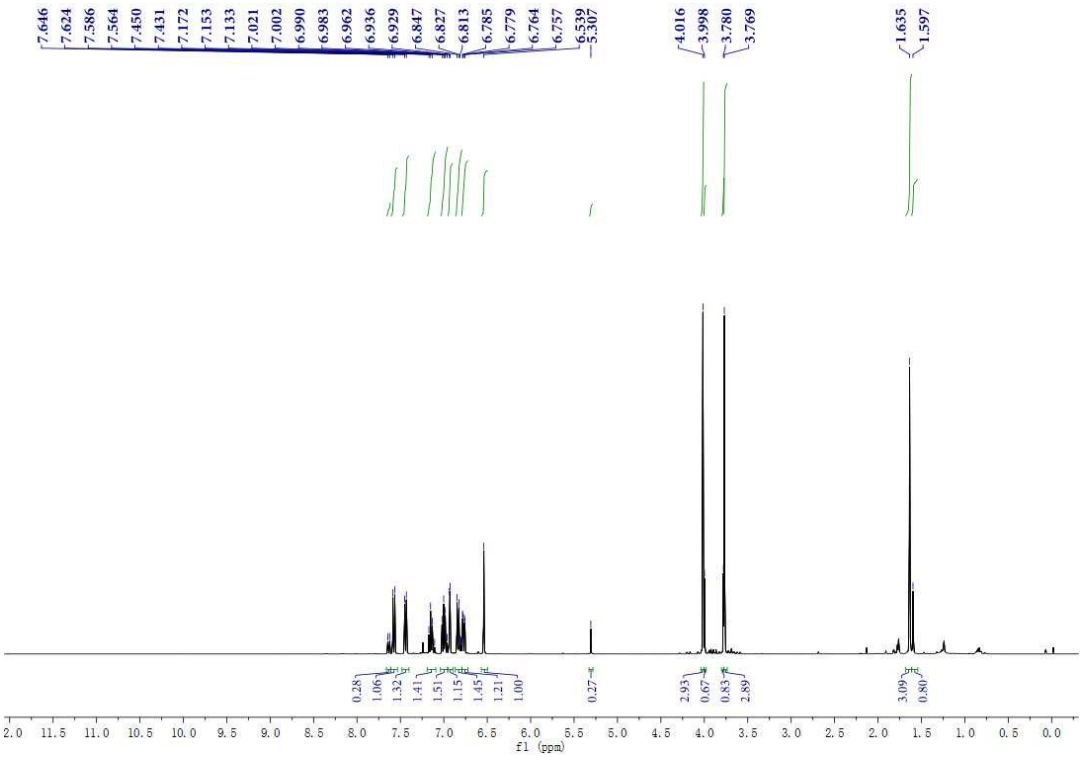
7

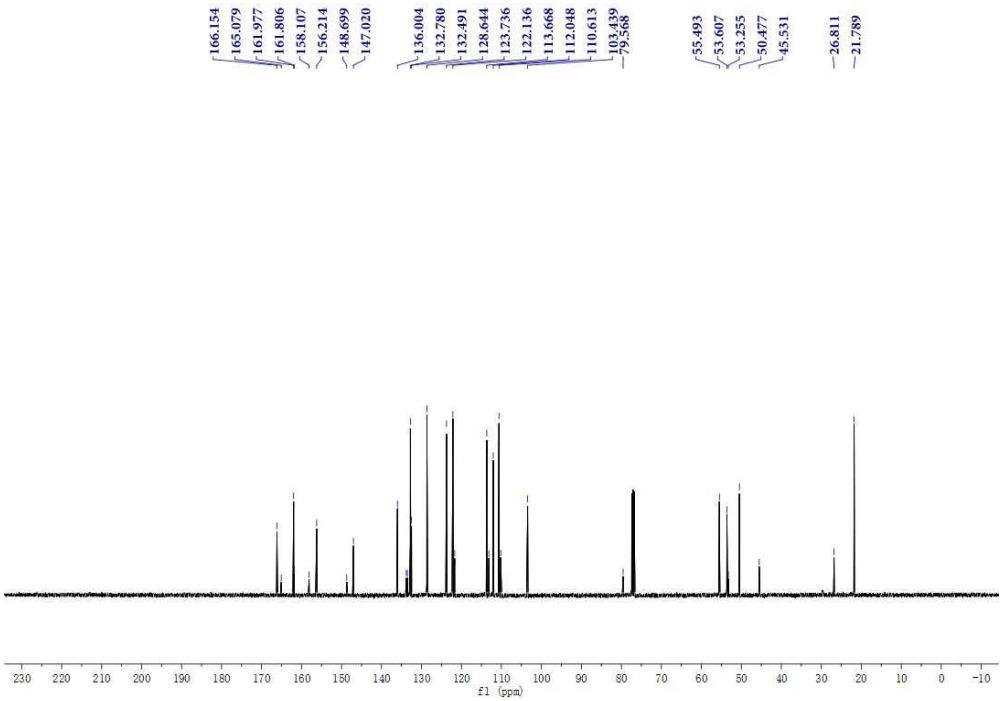
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.92 (d, *J* = 2.6 Hz,

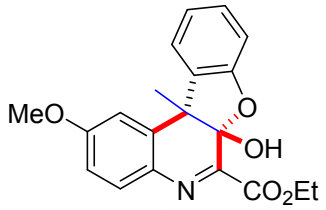
1H), 6.89 – 6.81 (m, 2H), 6.60 – 6.48 (m, 2H), 5.40 (s, *NH*, 1H), 3.91 (s, 3H), 3.73 (s, 3H), 2.47 (dd, J = 12.9, 1.7 Hz, 1H), 2.13 (d, J = 12.9 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 153.1, 152.1, 133.6, 130.6, 129.5, 127.2, 125.4, 121.2, 117.0, 114.7, 111.9, 110.3, 83.2, 55.8, 53.2, 36.0, 33.3, 23.2; HRMS (ESI) m/z calculated for $C_{19}H_{19}NO_4 + Na^+$, 348.1206, found: 348.1218.

^{1}H and ^{13}C spectra

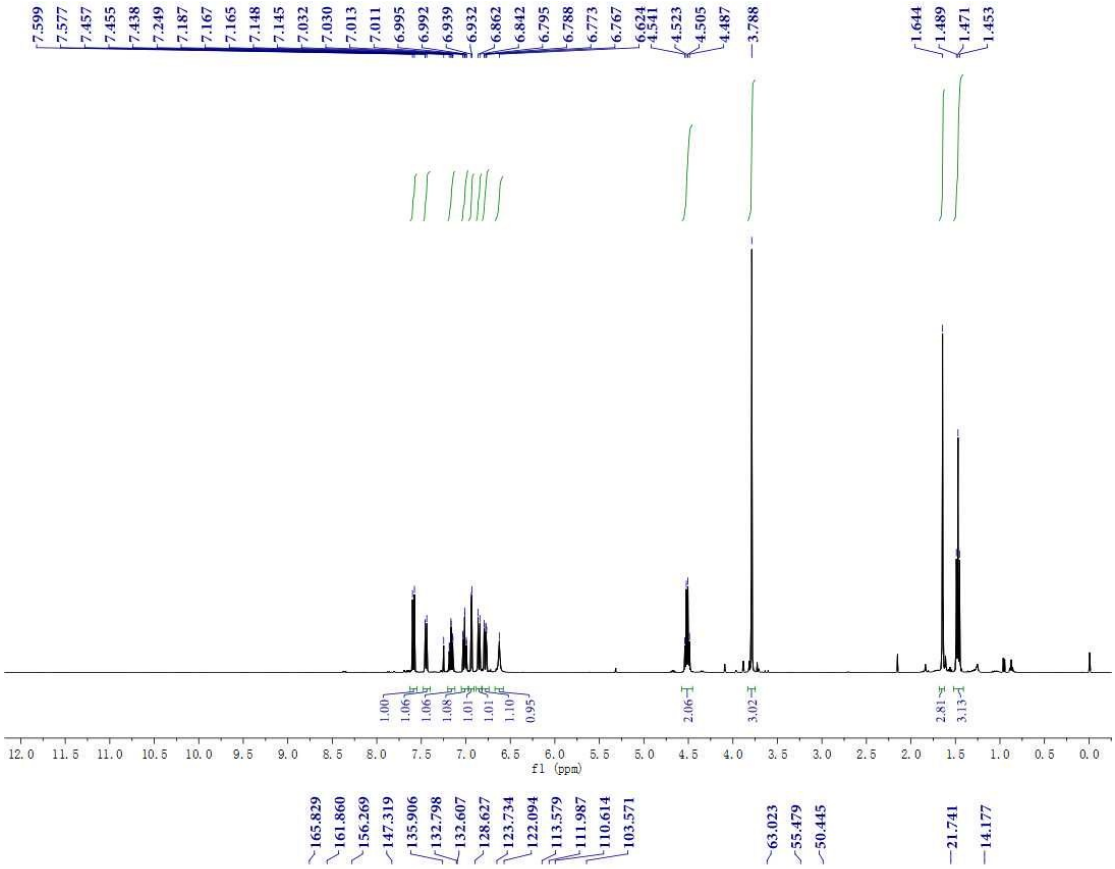


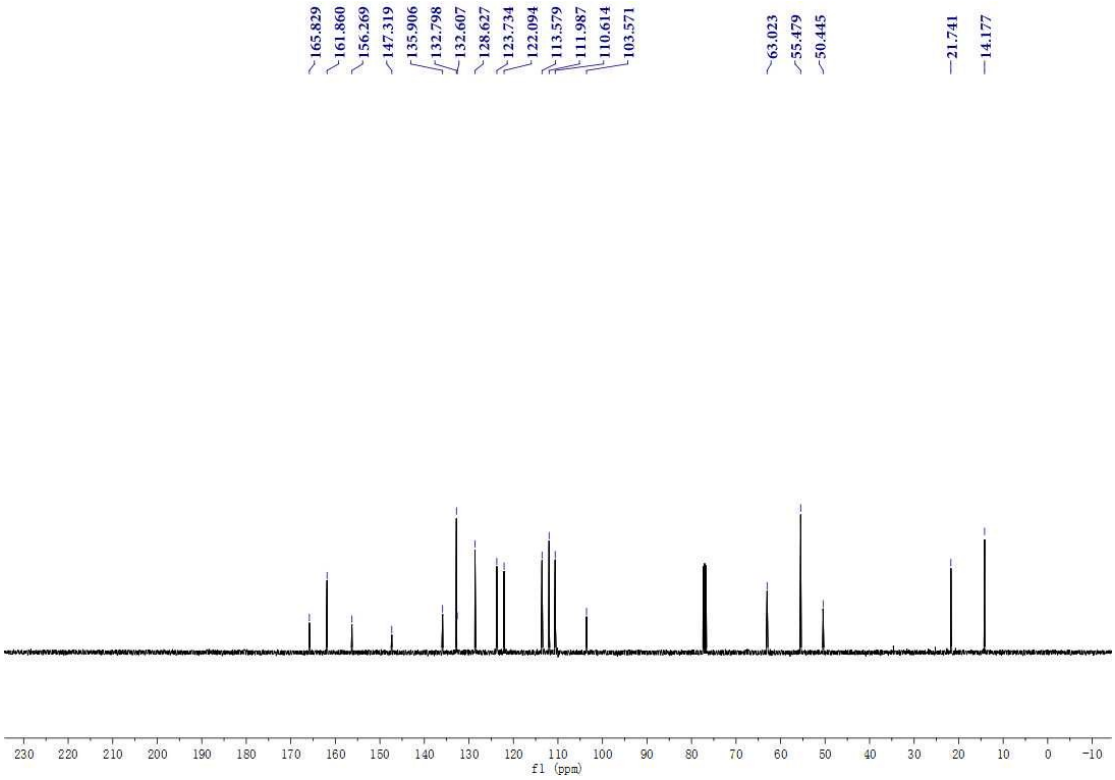


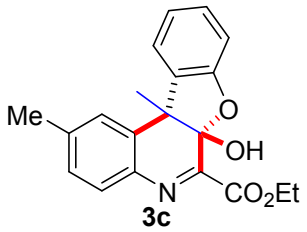



MeO
O
OH
N
CO2Et

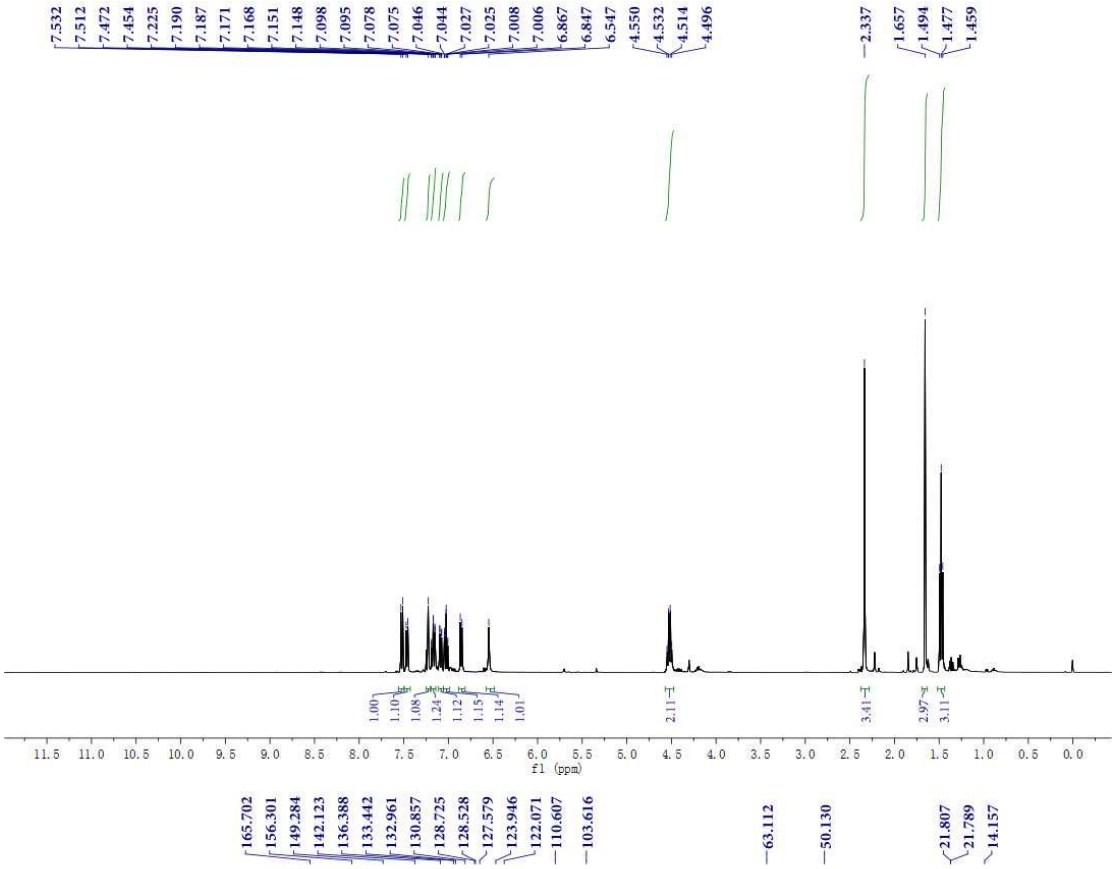
3b

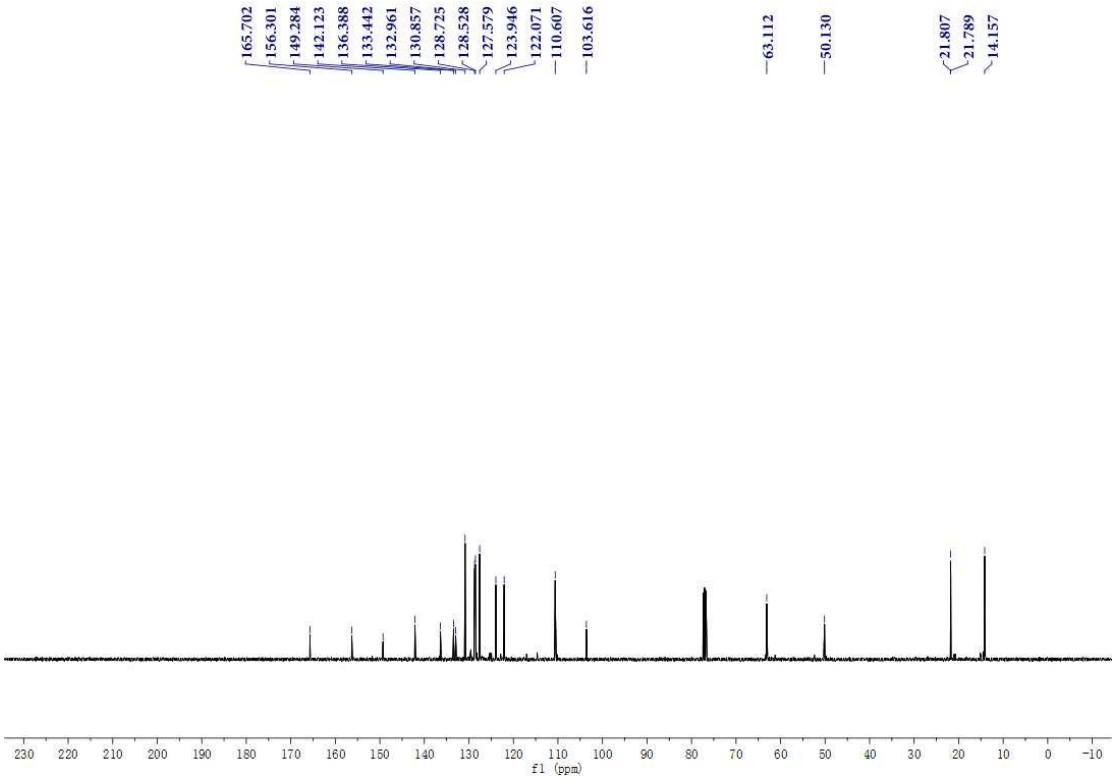

7.599
7.577
7.457
7.455
7.438
7.249
7.187
7.167
7.165
7.148
7.145
7.032
7.030
7.013
7.011
6.995
6.992
6.939
6.932
6.862
6.842
6.795
6.788
6.773
6.767
6.624
4.541
4.523
4.505
4.487
3.788
1.644
1.489
1.471
1.453
1.00
1.06
1.06
1.08
1.01
1.01
1.10
0.95
2.06
3.02
2.81
3.13
f1 (ppm)

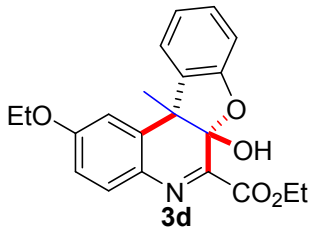

165.829
161.860
156.269
147.319
135.906
132.798
132.607
128.627
123.734
122.094
113.579
111.987
110.614
103.571
63.023
55.479
50.445
21.741
14.177
f1 (ppm)


Me
O
OH
N
CO2Et

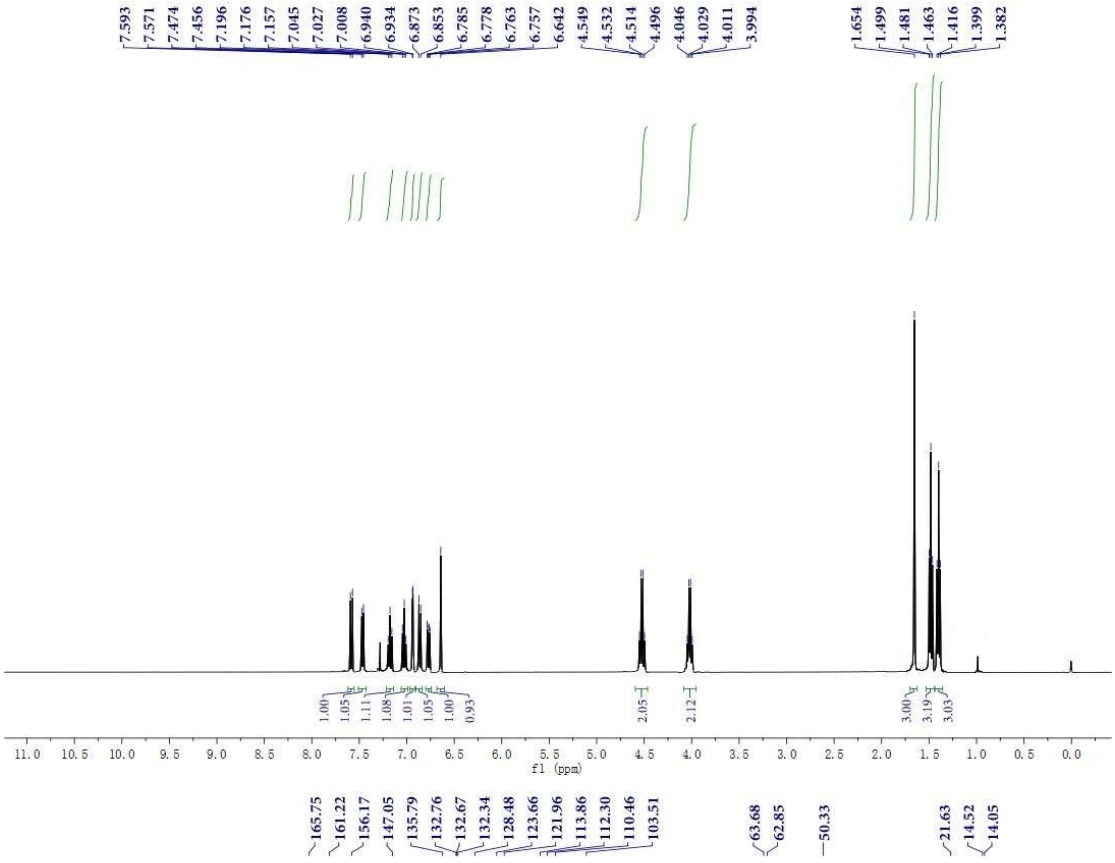
3c

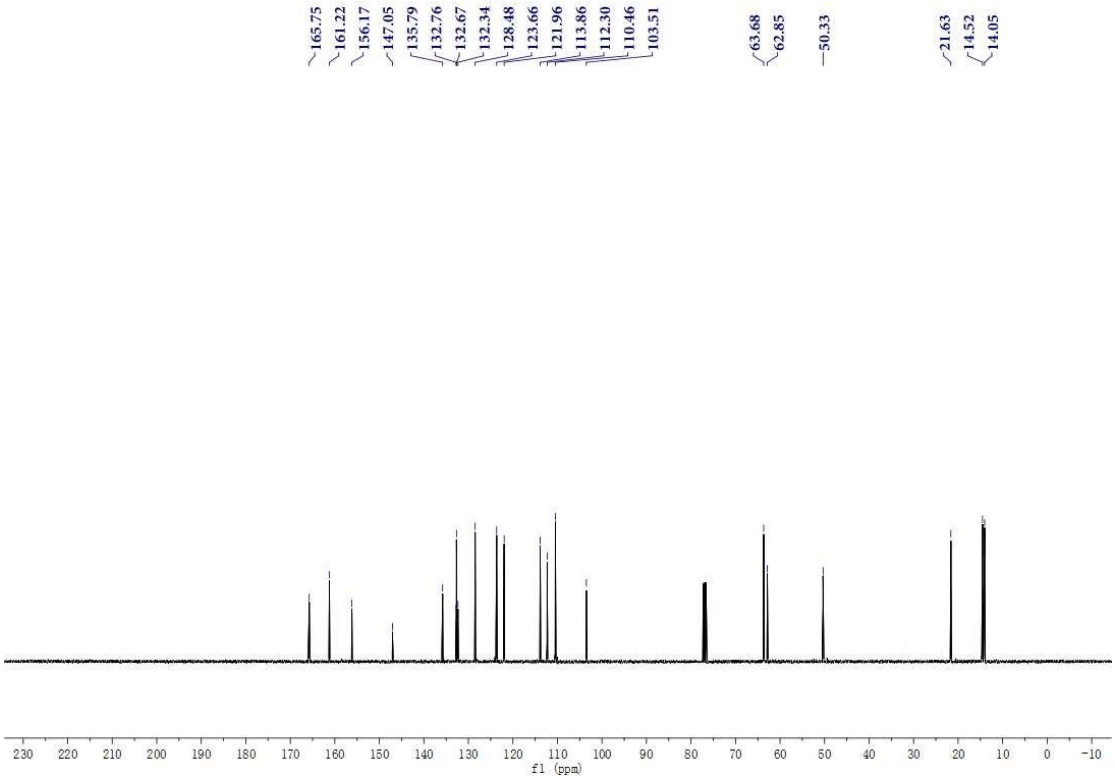

7.532
7.512
7.472
7.454
7.225
7.190
7.187
7.171
7.168
7.151
7.148
7.098
7.095
7.078
7.075
7.046
7.044
7.027
7.025
7.008
7.006
6.867
6.847
6.547
4.550
4.532
4.514
4.496
2.337
1.657
1.494
1.477
1.459
1.00
1.10
1.08
1.24
1.12
1.15
1.14
1.01
2.11
3.41
2.97
3.11
f1 (ppm)

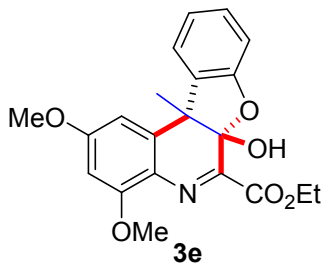

165.702
156.301
149.284
142.123
136.388
133.442
132.961
130.857
128.725
128.528
127.579
123.946
122.071
110.607
103.616
63.112
50.130
21.807
21.789
14.157
f1 (ppm)


EtO
O
OH
N
CO2Et

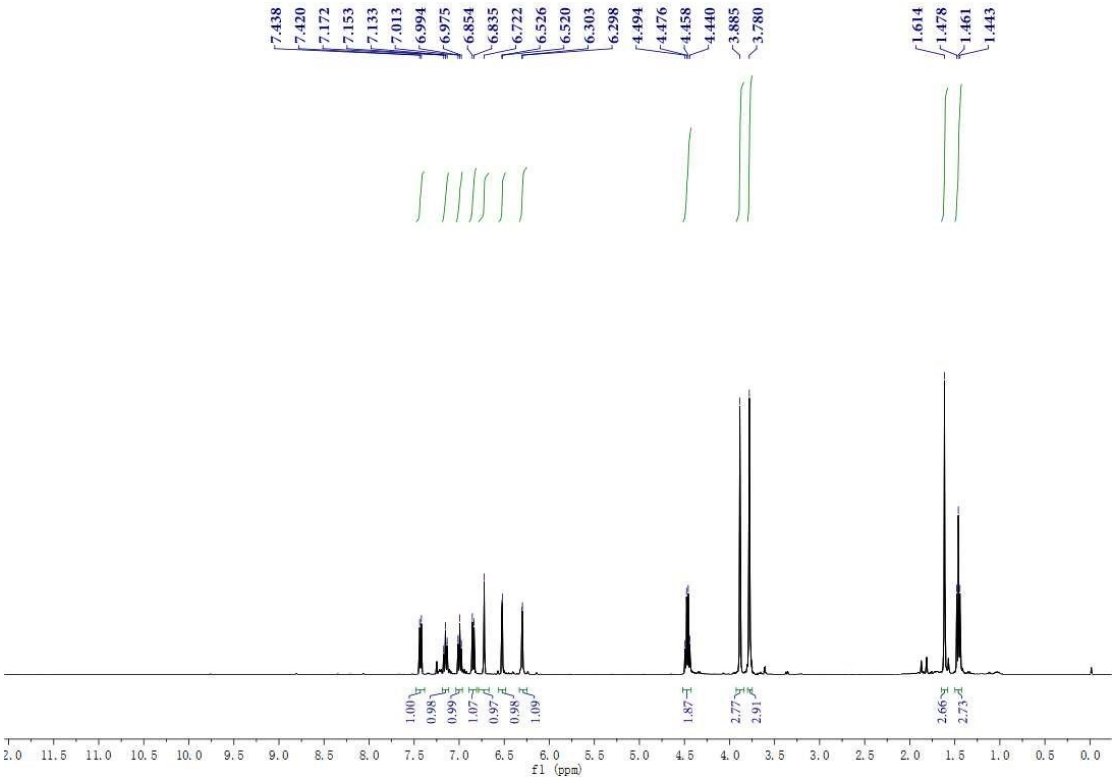
3d

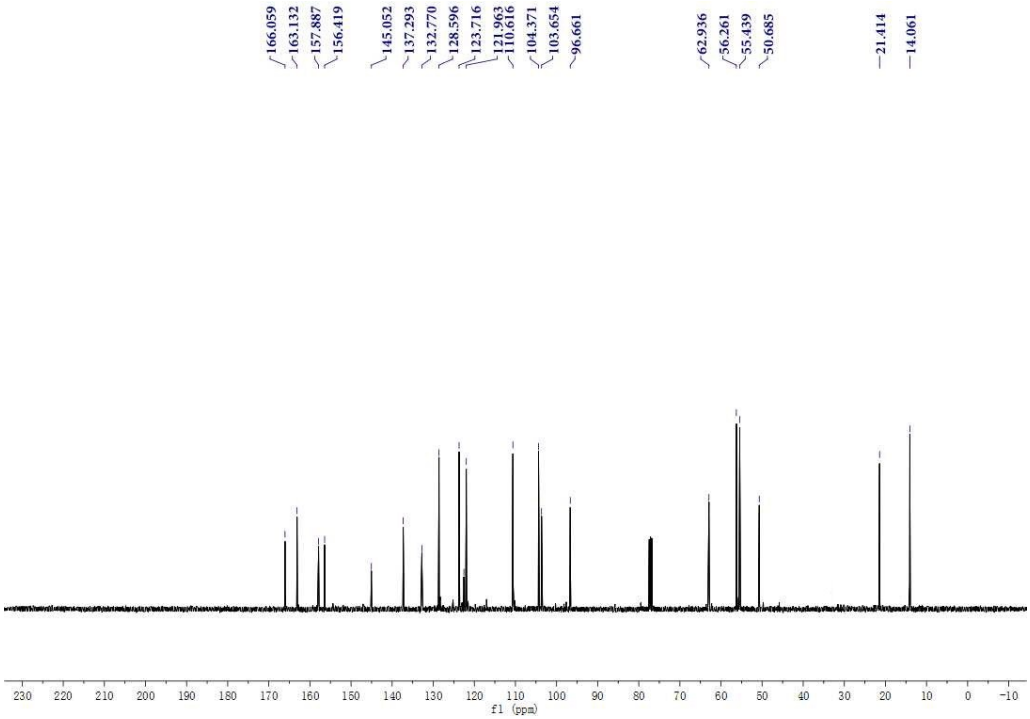

7.593 7.571 7.474 7.456 7.196 7.176 7.157 7.045 7.027 7.008 6.940 6.934 6.873 6.853 6.785 6.778 6.763 6.757 6.642
4.549 4.532 4.514 4.496 4.046 4.029 4.011 3.994
1.654 1.499 1.481 1.463 1.416 1.399 1.382
1.00 1.05 1.11 1.08 1.01 1.05 1.00 0.93
2.05
2.12
3.00 3.19 3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

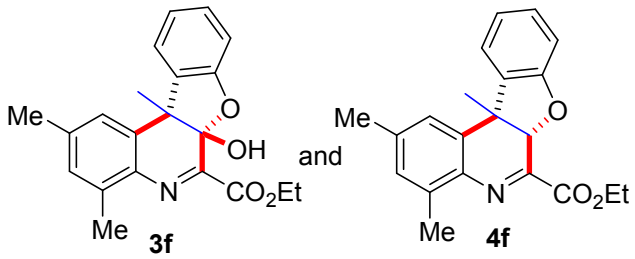

165.75 161.22 156.17 147.05 135.79 132.76 132.67 132.34 128.48 123.66 121.96 113.86 112.30 110.46 103.51
63.68 62.85
50.33
21.63 14.52 14.05
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

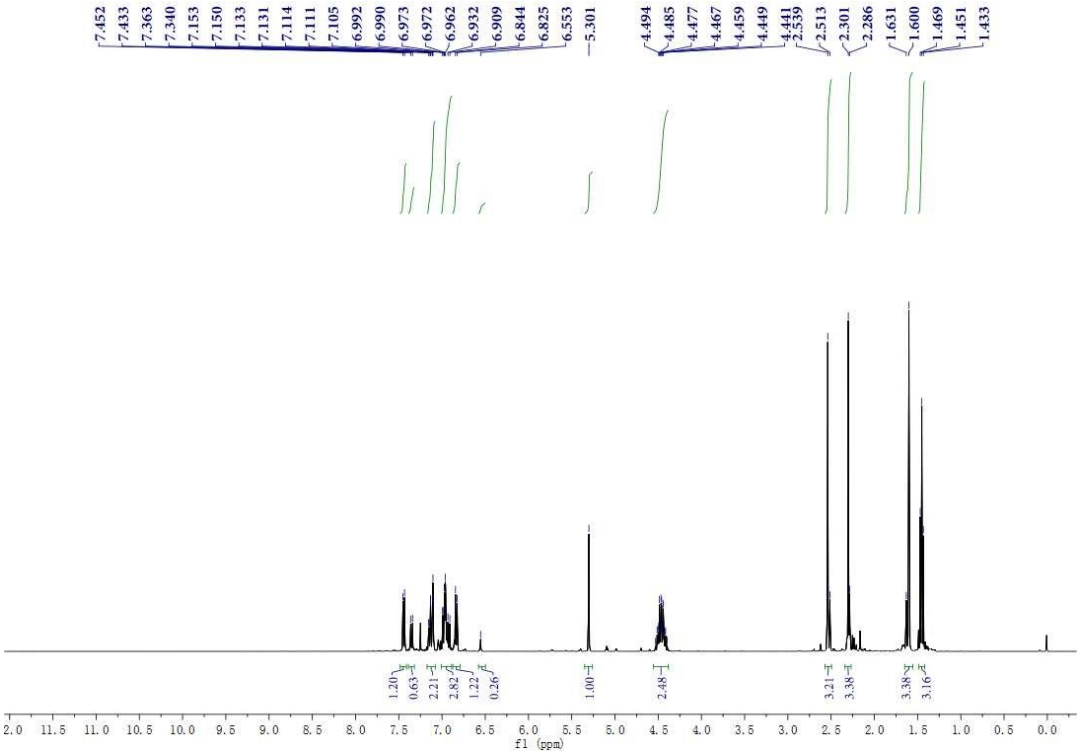

MeO
O
OH
N
CO2Et
OMe

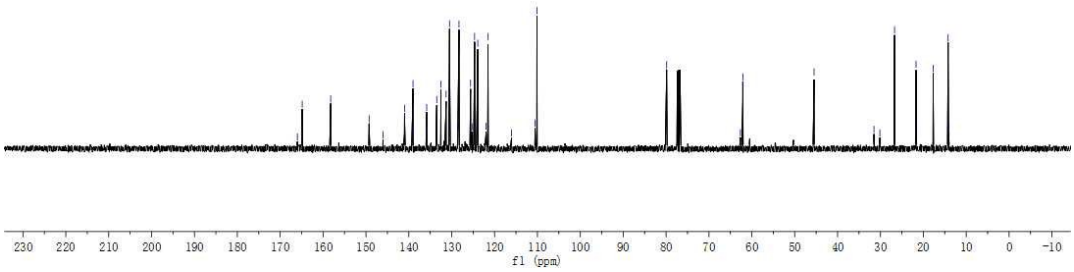
3e

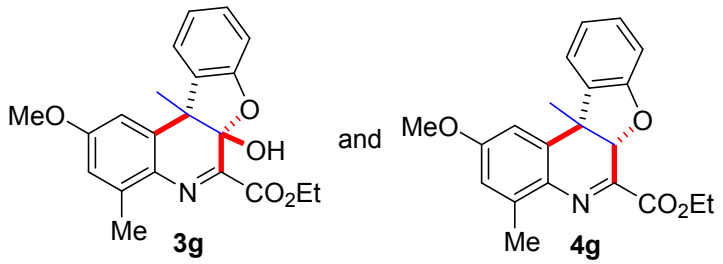

7.438
7.420
7.172
7.153
7.133
7.013
6.994
6.975
6.854
6.835
6.722
6.526
6.520
6.303
6.298
4.494
4.476
4.458
4.440
3.885
3.780
1.614
1.478
1.461
1.443
1.00
0.98
0.99
1.07
0.97
0.98
1.09
1.87
2.77
2.91
2.66
2.73
f1 (ppm)

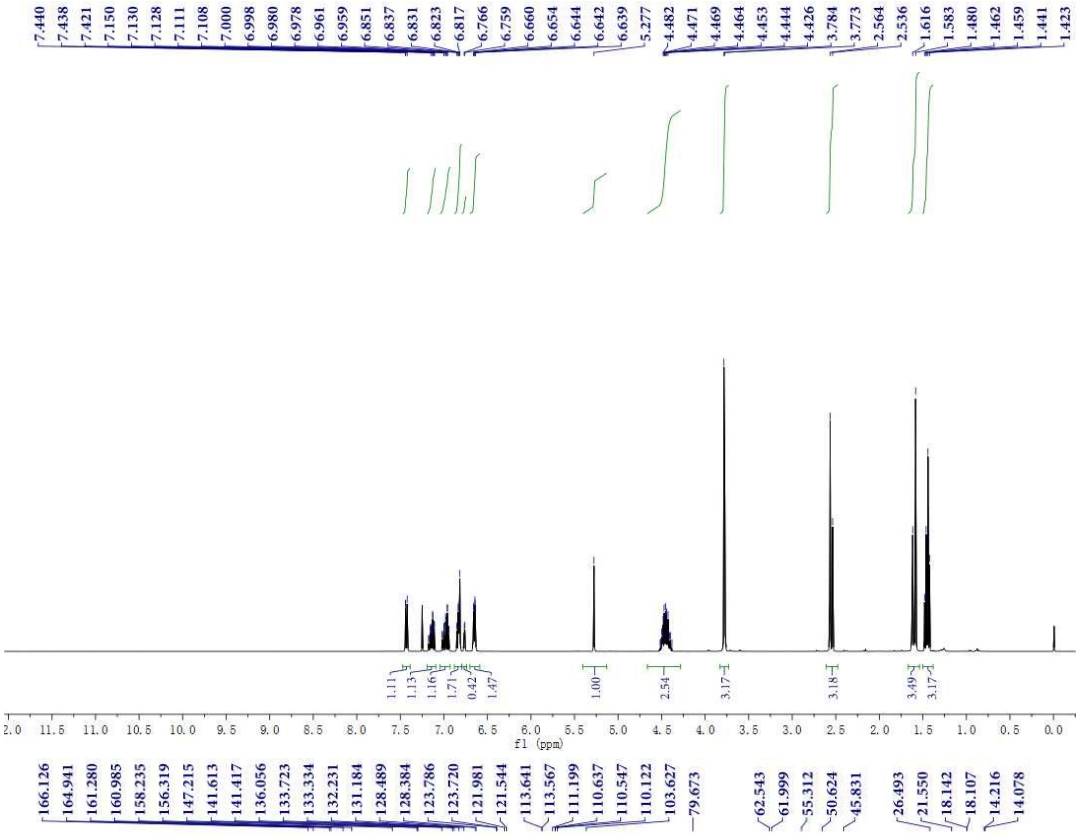

166.059
163.132
157.887
156.419
145.052
137.293
132.770
128.596
123.716
121.963
110.616
104.371
103.654
96.661
62.936
56.261
55.439
50.685
21.414
14.061
f1 (ppm)

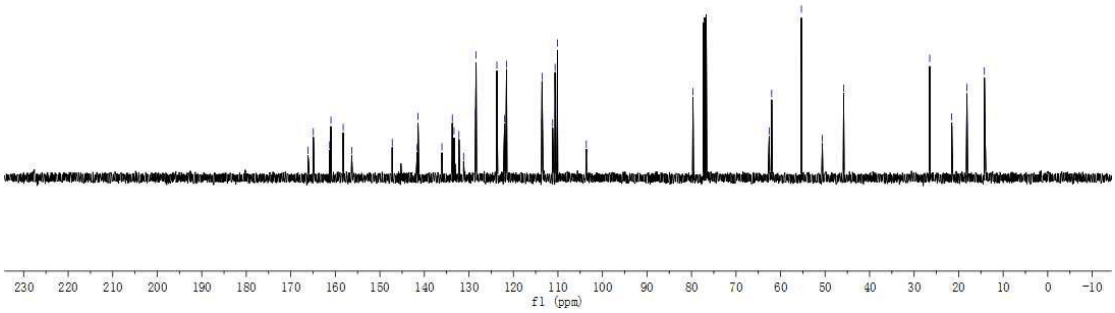

Me
O
OH
N
CO2Et
Me
3f
and
Me
O
N
CO2Et
Me
4f

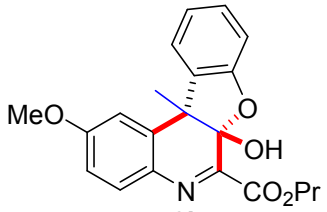

7.452 7.433 7.363 7.340 7.153 7.150 7.133 7.131 7.114 7.111 7.105 6.992 6.990 6.973 6.972 6.962 6.932 6.909 6.844 6.825 6.553 5.301
4.494 4.485 4.477 4.467 4.459 4.449 4.441 2.539 2.513 2.301 2.286 1.631 1.600 1.469 1.451 1.433
1.20 0.63 2.21 2.82 1.22 0.26 1.00 2.48 3.21 3.38 3.38 3.16
f1 (ppm)
165.988 164.869 158.224 149.260 146.034 141.006 139.146 139.029 135.836 133.486 132.509 131.307 130.504 130.463 128.397 128.299 125.602 125.260 124.664 124.016 123.917 121.971 121.535 116.044 110.540 110.117 79.865 62.659 62.100 45.488 31.512 30.137 26.702 21.703 21.643 17.704 14.217 14.079


f1 (ppm)

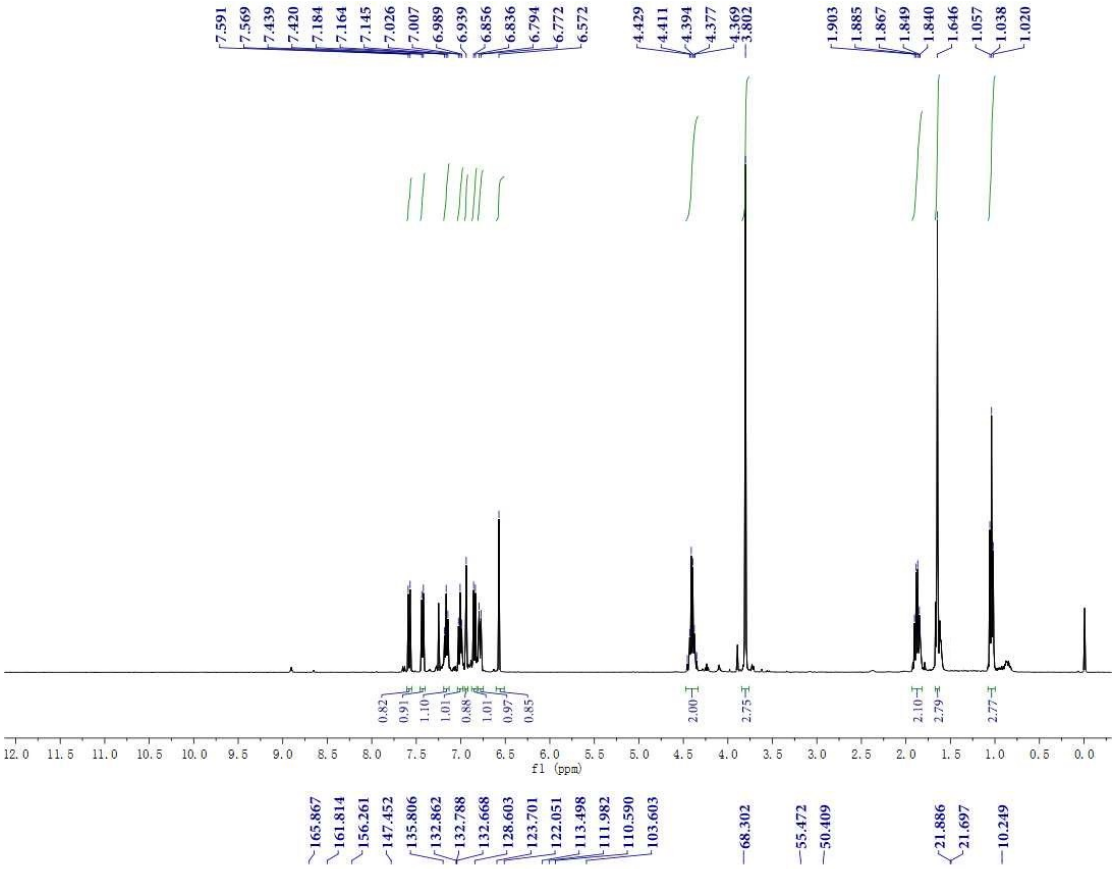

MeO
O
OH
N
CO2Et
Me
3g
and
MeO
O
N
CO2Et
Me
4g


7.440 7.438 7.421 7.150 7.130 7.128 7.111 7.108 7.000 6.998 6.980 6.978 6.961 6.959 6.851 6.837 6.831 6.823 6.817 6.766 6.759 6.660 6.654 6.644 6.642 6.639 5.277 4.482 4.471 4.469 4.464 4.453 4.444 4.426 3.784 3.773 2.564 2.536 1.616 1.583 1.480 1.462 1.459 1.441 1.423
1.11 1.13 1.16 1.71 0.42 1.47 1.00 2.54 3.17 3.18 3.49 3.17
f1 (ppm)


166.126 164.941 161.280 160.985 158.235 156.319 147.215 141.613 141.417 136.056 133.723 133.334 132.231 131.184 128.489 128.384 123.786 123.720 121.981 121.544 113.641 113.567 111.199 110.637 110.547 110.122 103.627 79.673 62.543 61.999 55.312 50.624 45.831 26.493 21.550 18.142 18.107 14.216 14.078
f1 (ppm)


MeO
O
OH
N
CO2Pr

3h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7.184
7.164
7.145
7.026
7.007
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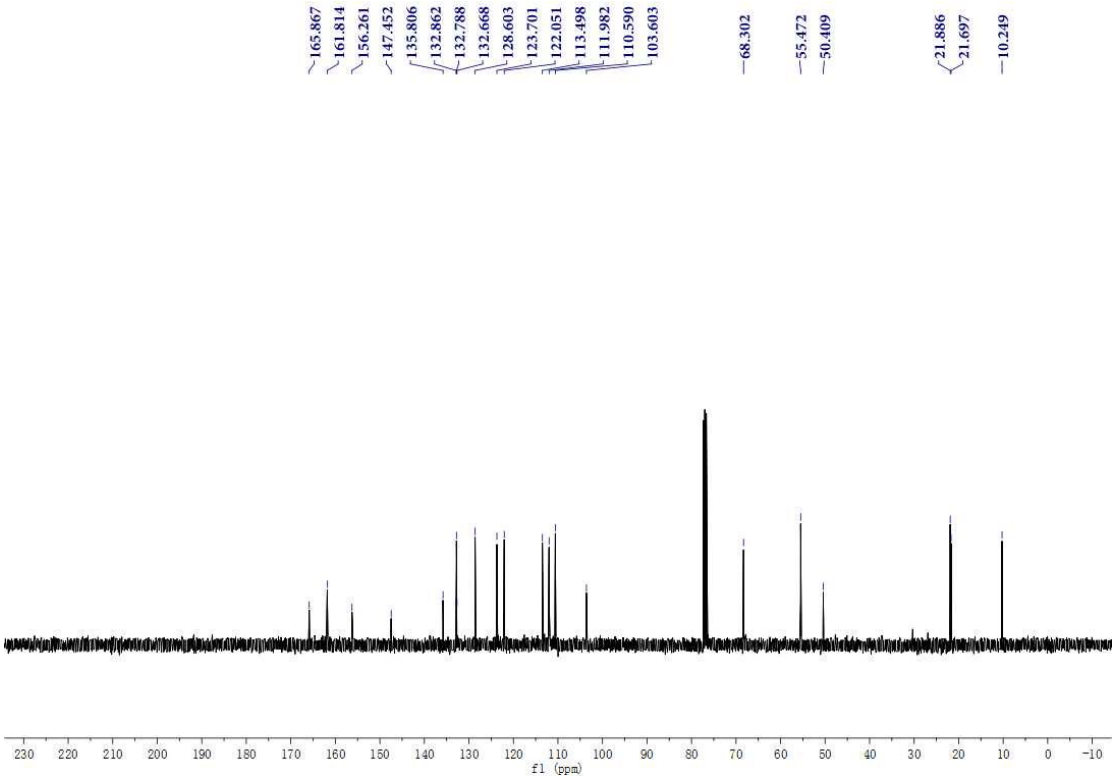
6.939
6.856
6.836
6.794
6.772
6.572
4.429
4.411
4.394
4.377
4.369
3.802
1.903
1.885
1.867
1.849
1.840
1.646
1.057
1.038
1.020
0.82
0.91
1.10
1.01
0.88
1.01
0.97
0.85
2.00
2.75
2.10
2.79
2.77
f1 (ppm)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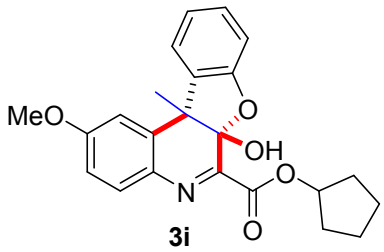
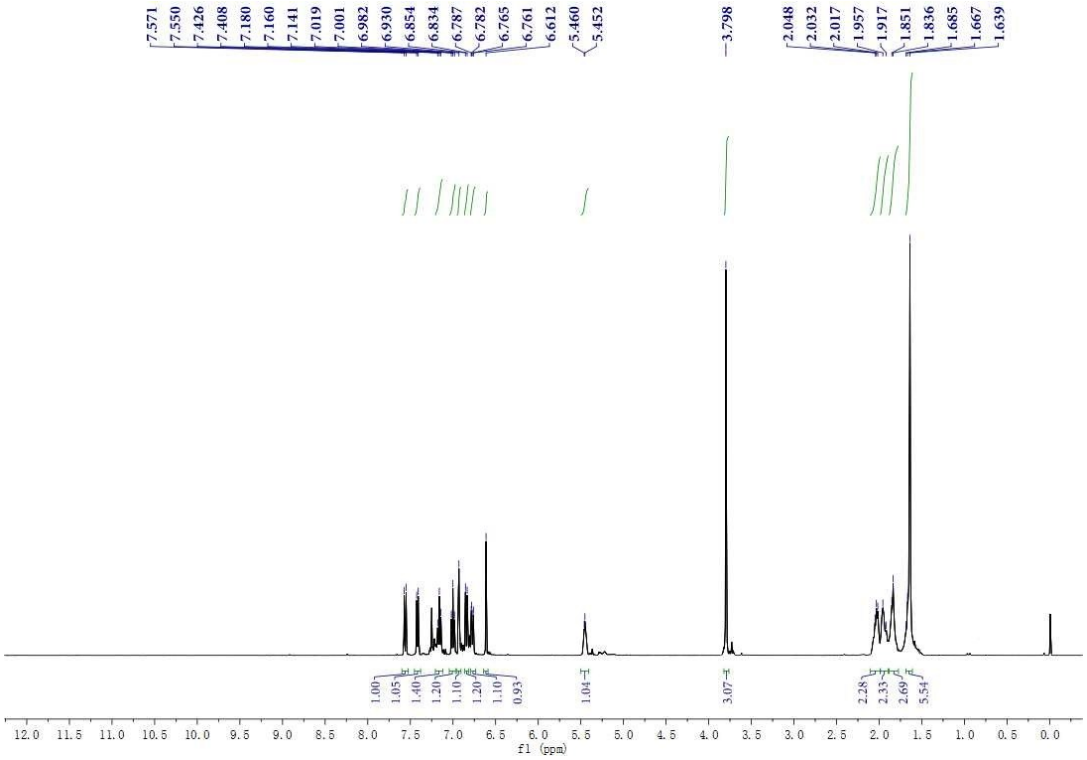
156.261
147.452
135.806
132.862
132.788
132.668
128.603
123.701
122.051
113.498
111.982
110.590
103.603
68.302
55.472
50.409
21.886
21.697
10.249
f1 (ppm)


MeO
O
OH
O
N
O

3i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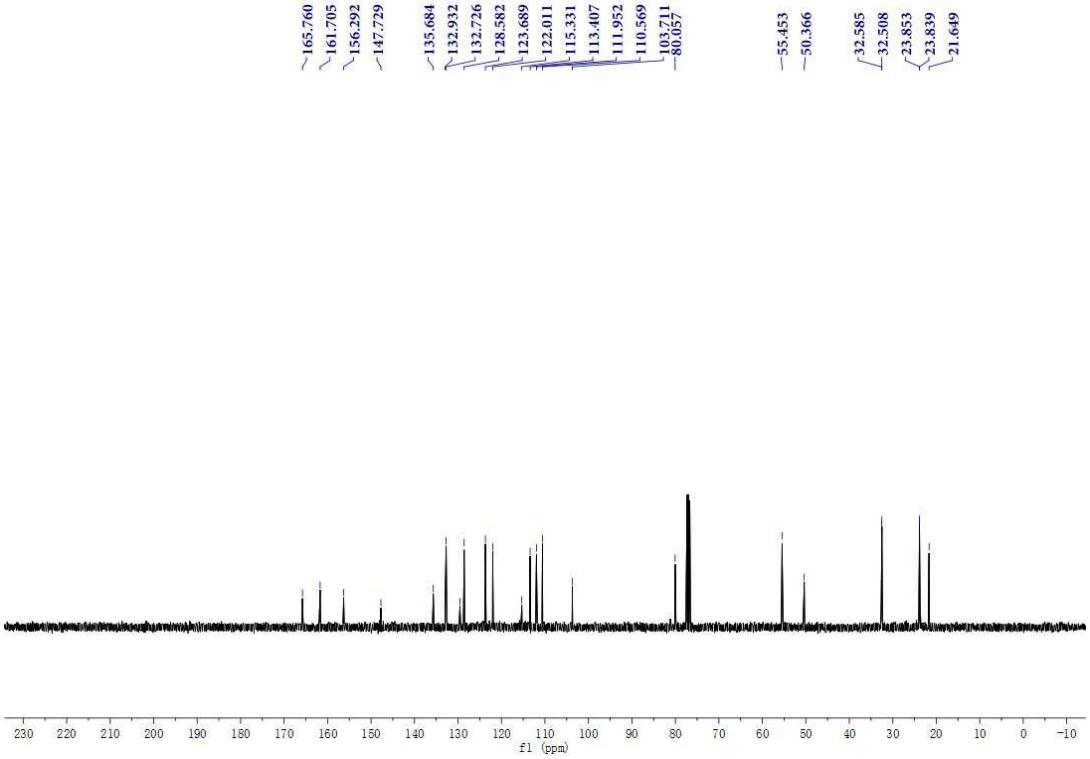
7.180
7.160
7.141
7.019
7.001
6.982
6.930
6.854
6.834
6.787
6.782
6.765
6.761
6.612
5.460
5.452
3.798
2.048
2.032
2.017
1.957
1.917
1.851
1.836
1.685
1.667
1.639
1.00
1.05
1.40
1.20
1.10
1.20
1.10
0.93
1.04
3.07
2.28
2.33
2.69
5.54
f1 (ppm)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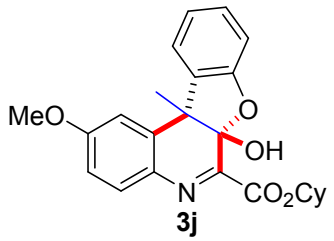
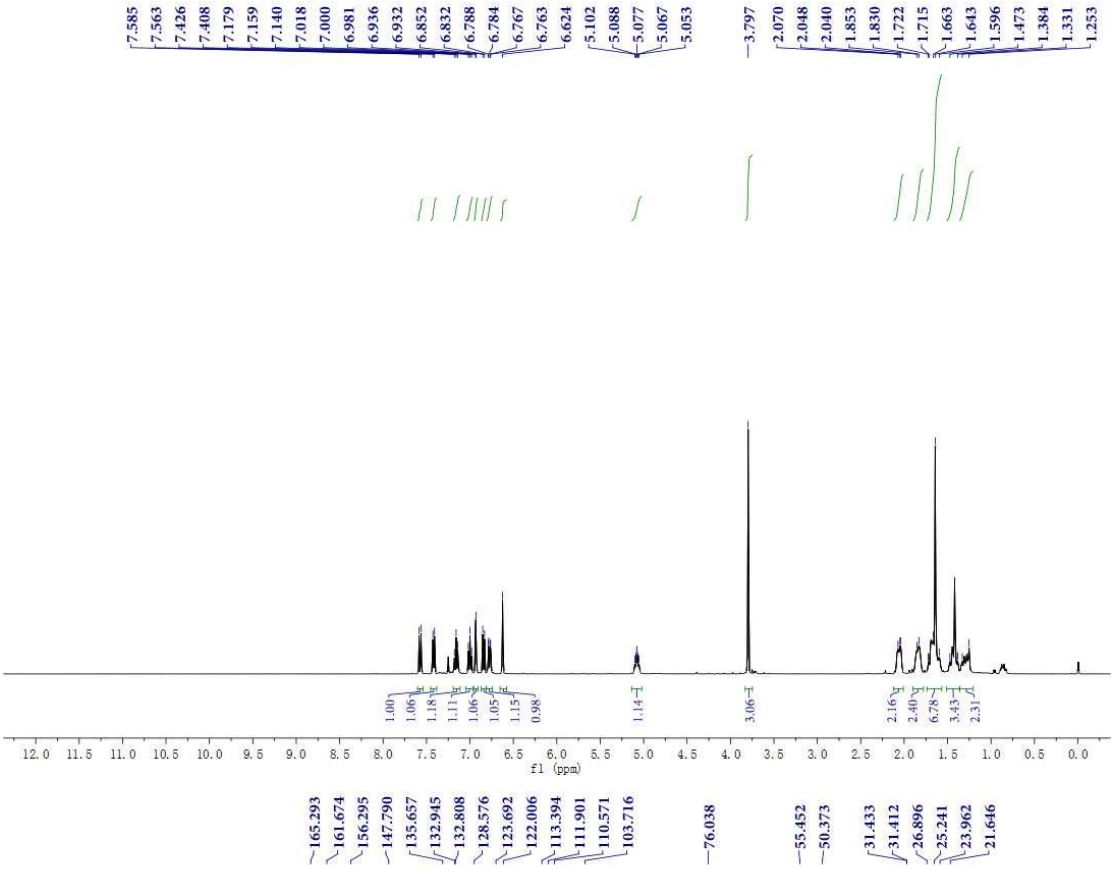
147.729
135.684
132.932
132.726
128.582
123.689
122.011
115.331
113.407
111.952
110.569
103.711
80.057
55.453
50.366
32.585
32.508
23.853
23.839
21.649
f1 (ppm)


MeO
O
OH
N
CO2Cy

3j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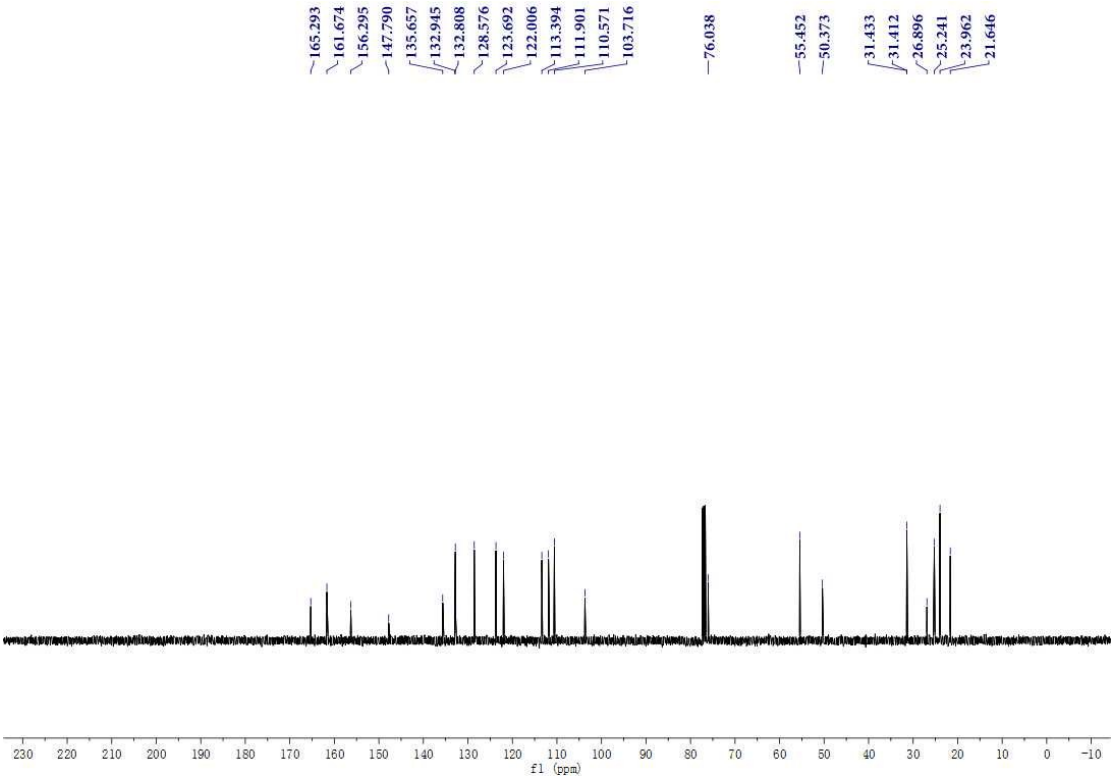
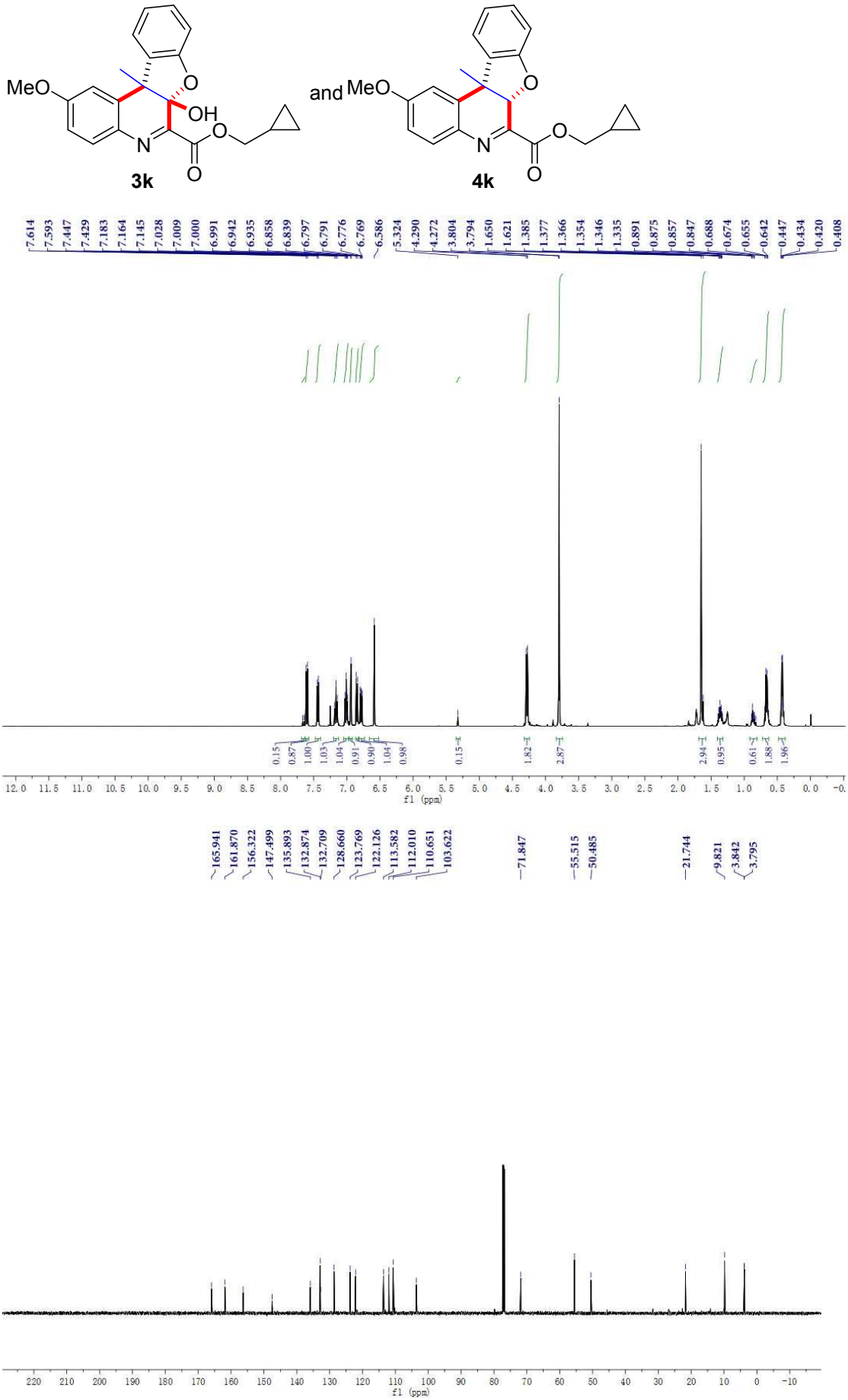
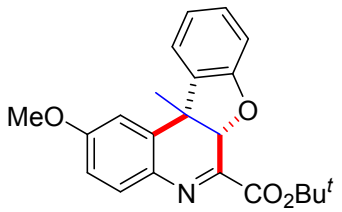
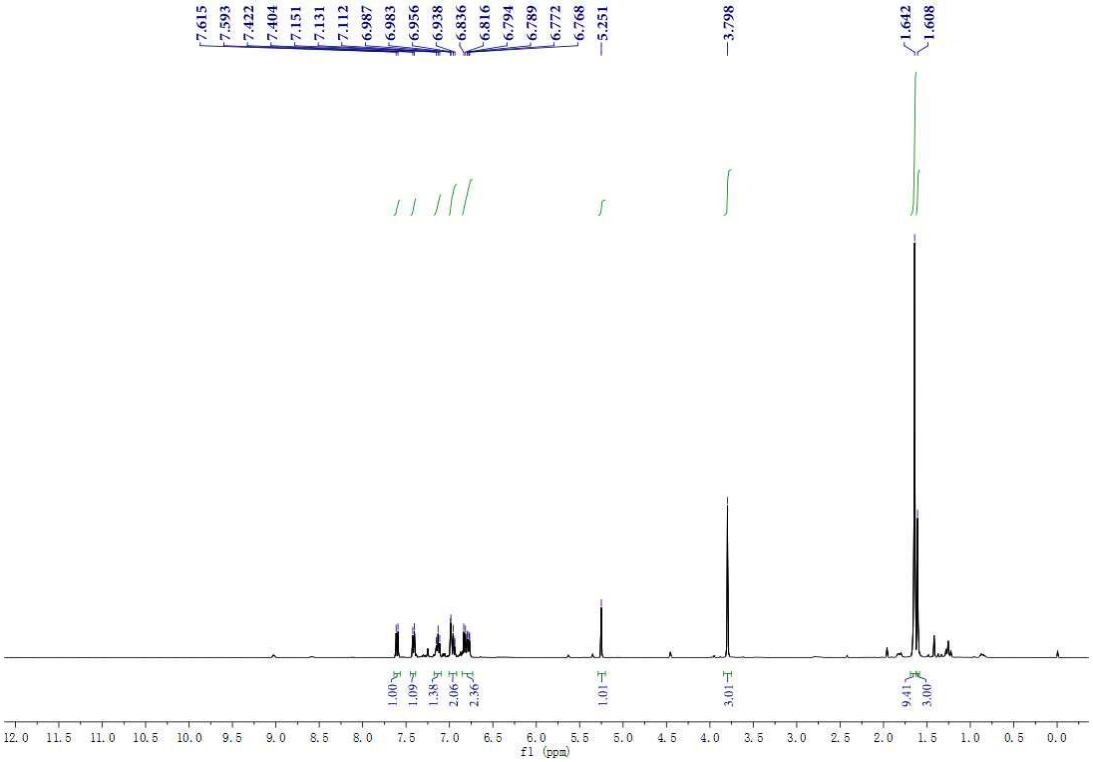
1.00 1.06 1.18 1.11 1.06 1.05 1.15 0.98 1.14 3.06 2.16 2.40 6.78 3.43 2.31
f1 (ppm)

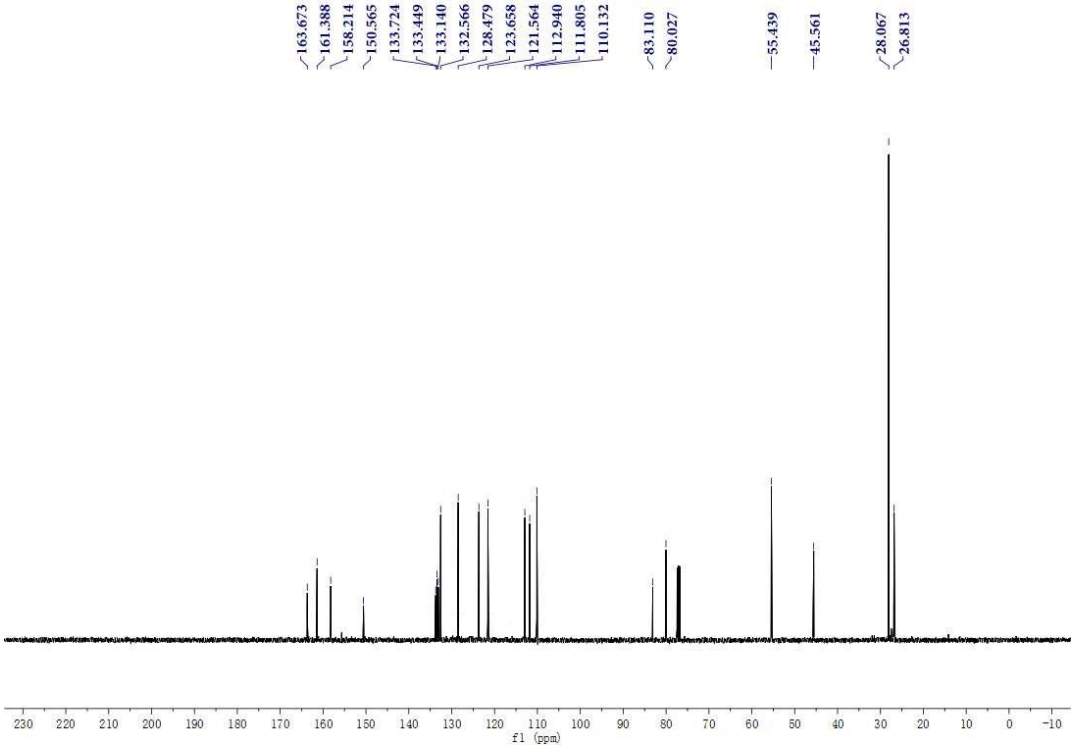

165.293 161.674 156.295 147.790 135.657 132.945 132.808 128.576 123.692 122.006 113.394 111.901 110.571 103.716 76.038 55.452 50.373 31.433 31.412 26.896 25.241 23.962 21.646
f1 (ppm)

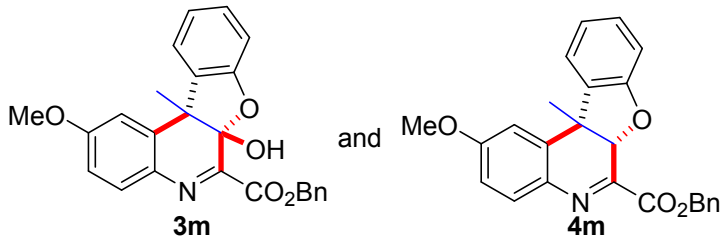

MeO
OH
O
N
O
O
3k
and MeO
4k
7.614 7.593 7.447 7.429 7.183 7.164 7.145 7.028 7.009 7.000 6.991 6.942 6.935 6.858 6.839 6.797 6.791 6.776 6.769 6.586 5.324 4.290 4.272 3.804 3.794 1.650 1.621 1.385 1.377 1.366 1.354 1.346 1.335 0.891 0.875 0.857 0.847 0.688 0.674 0.655 0.642 0.447 0.434 0.420 0.408
0.15 0.87 1.00 1.03 1.04 0.91 0.90 1.04 0.98 0.15 1.82 2.87 2.94 0.95 0.61 1.88 1.96
f1 (ppm)
165.941 161.870 156.322 147.499 135.893 132.874 132.709 128.660 123.769 122.126 113.582 112.010 110.651 103.622 71.847 55.515 50.485 21.744 9.821 3.842 3.795
f1 (ppm)

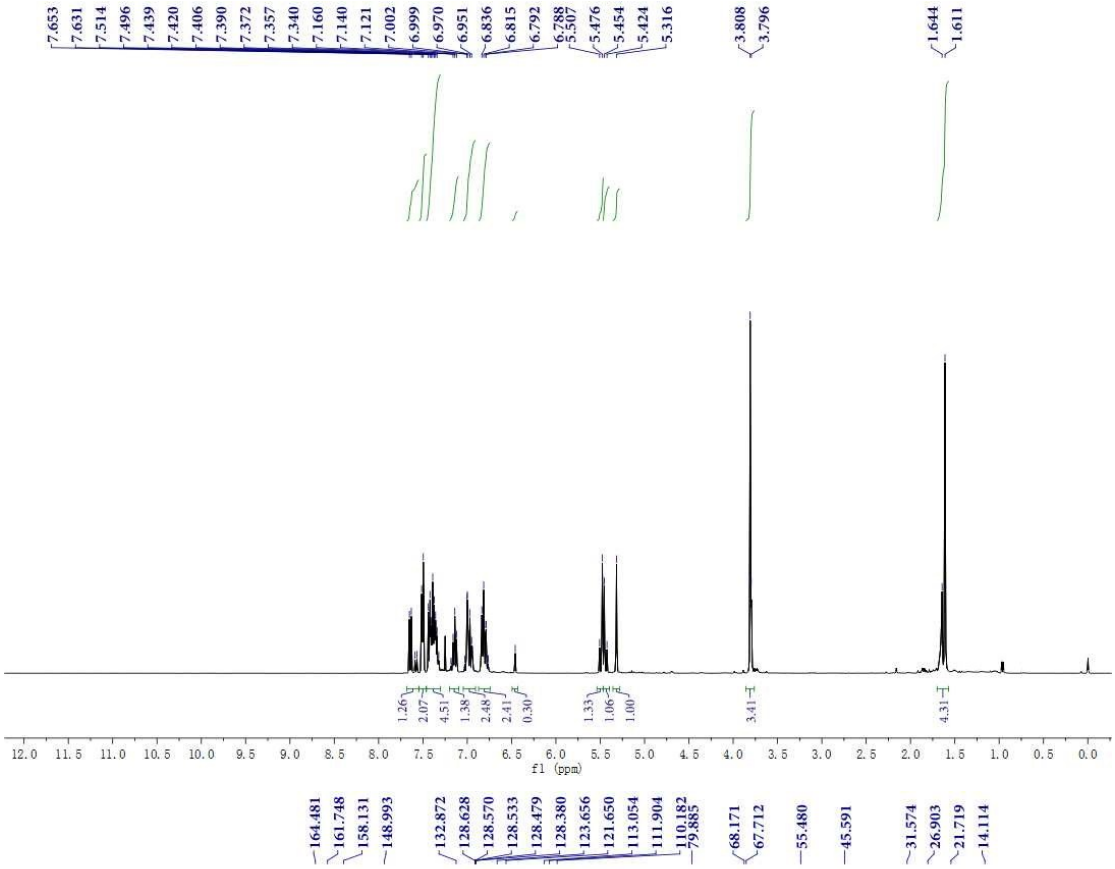

MeO
O
N
CO2Bu^t

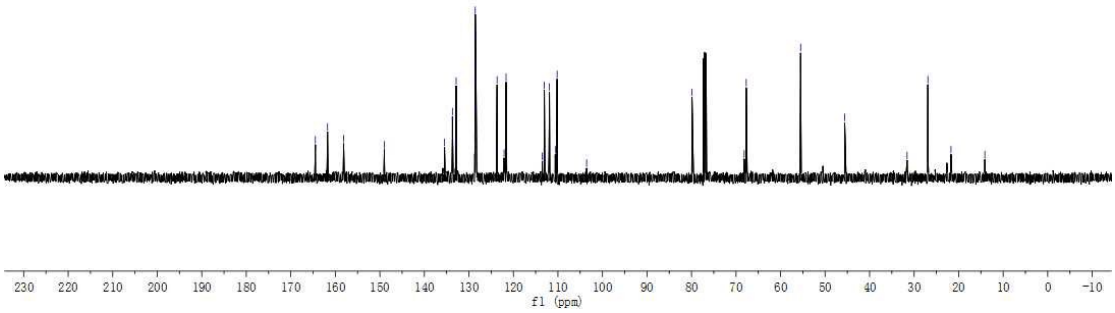
4l

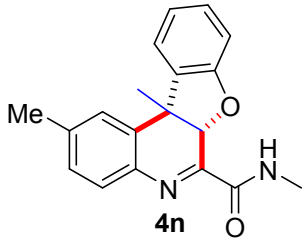

7.615
7.593
7.422
7.404
7.151
7.131
7.112
6.987
6.983
6.956
6.938
6.836
6.816
6.794
6.789
6.772
6.768
5.251
3.798
1.642
1.608
1.00
1.09
1.38
2.06
2.36
1.01
3.01
9.41
3.00
f1 (ppm)


163.673
161.388
158.214
150.565
133.724
133.449
133.140
132.566
128.479
123.658
121.564
112.940
111.805
110.132
83.110
80.027
55.439
45.561
28.067
26.813
f1 (ppm)

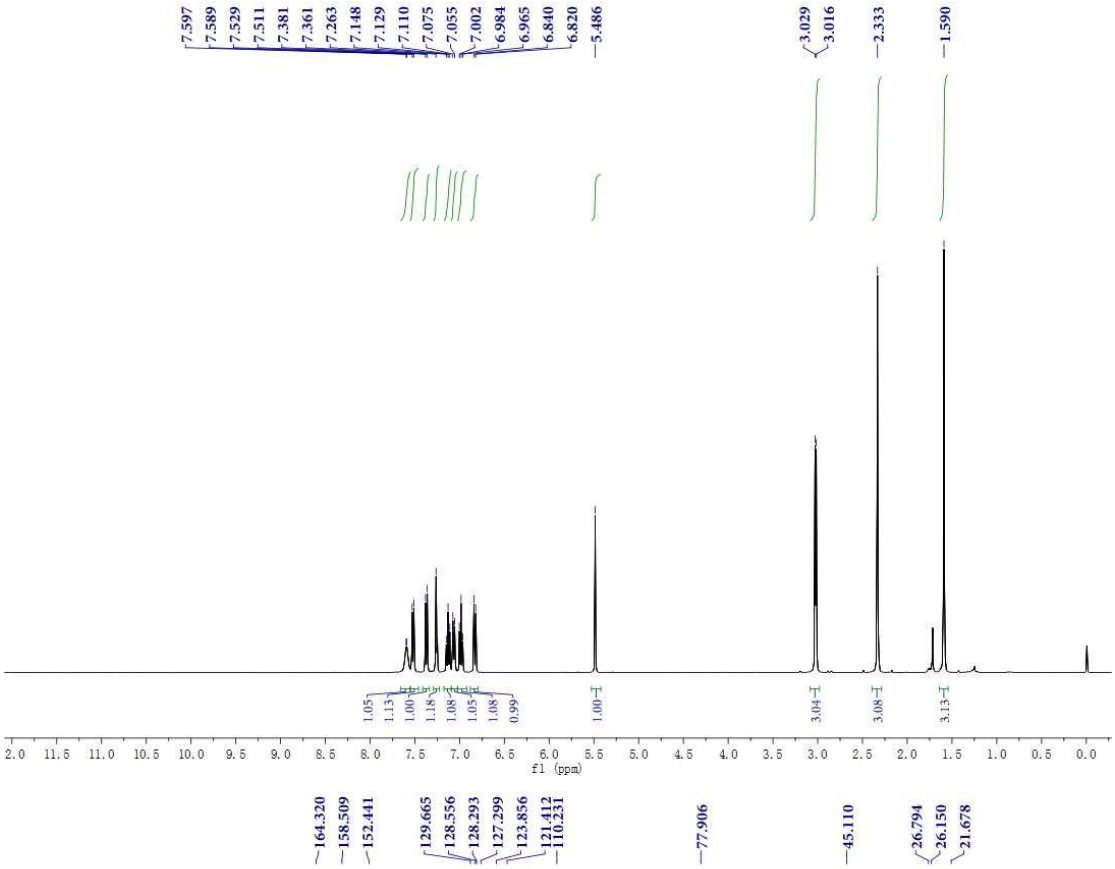

MeO
O
OH
N
CO2Bn
3m
and
MeO
O
N
CO2Bn
4m

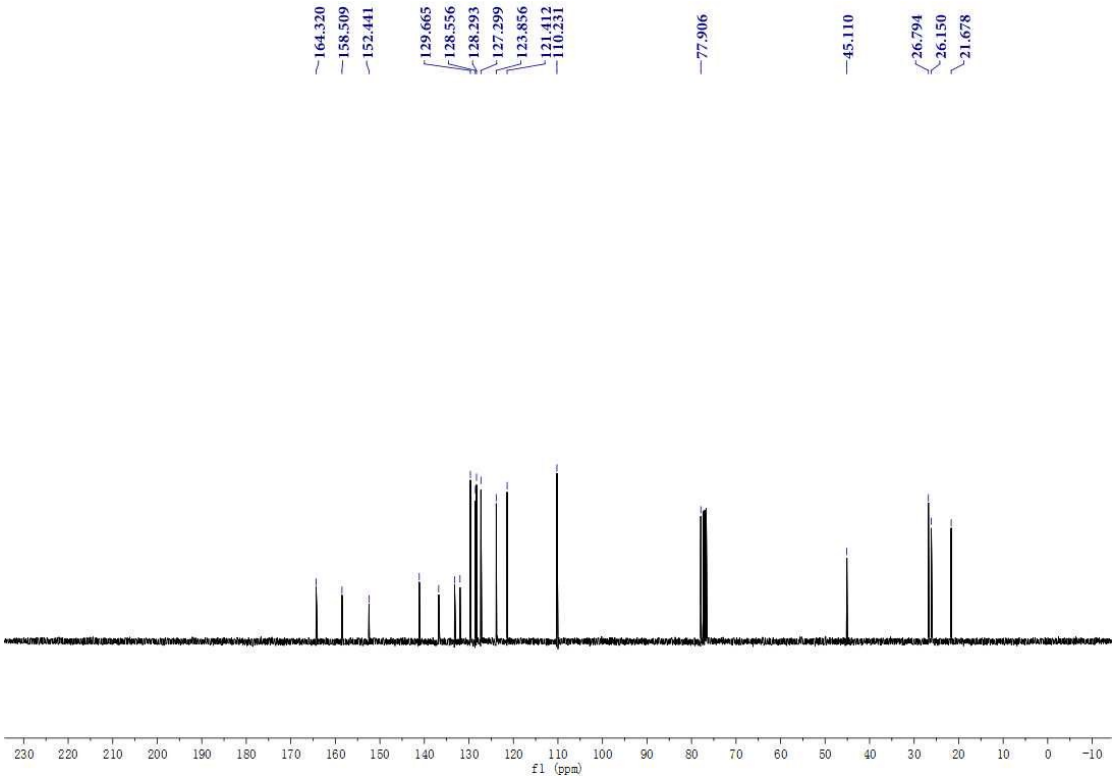

7.653 7.631 7.514 7.496 7.439 7.420 7.406 7.390 7.372 7.357 7.340 7.160 7.140 7.121 7.002 6.999 6.970 6.951 6.836 6.815 6.792 6.788 5.507 5.476 5.454 5.424 5.316
3.808 3.796
1.644 1.611
1.26 2.07 4.51 1.38 2.48 2.41 0.30 1.33 1.06 1.00 3.41 4.31
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
164.481 161.748 158.131 148.993 132.872 128.628 128.570 128.533 128.479 128.380 123.656 121.650 113.054 111.904 110.182 79.885 68.171 67.712 55.480 45.591 31.574 26.903 21.719 14.114

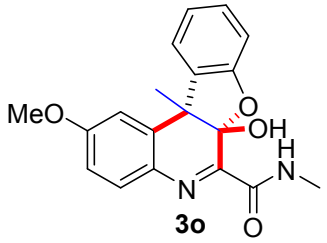

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
O
H
N
N
O

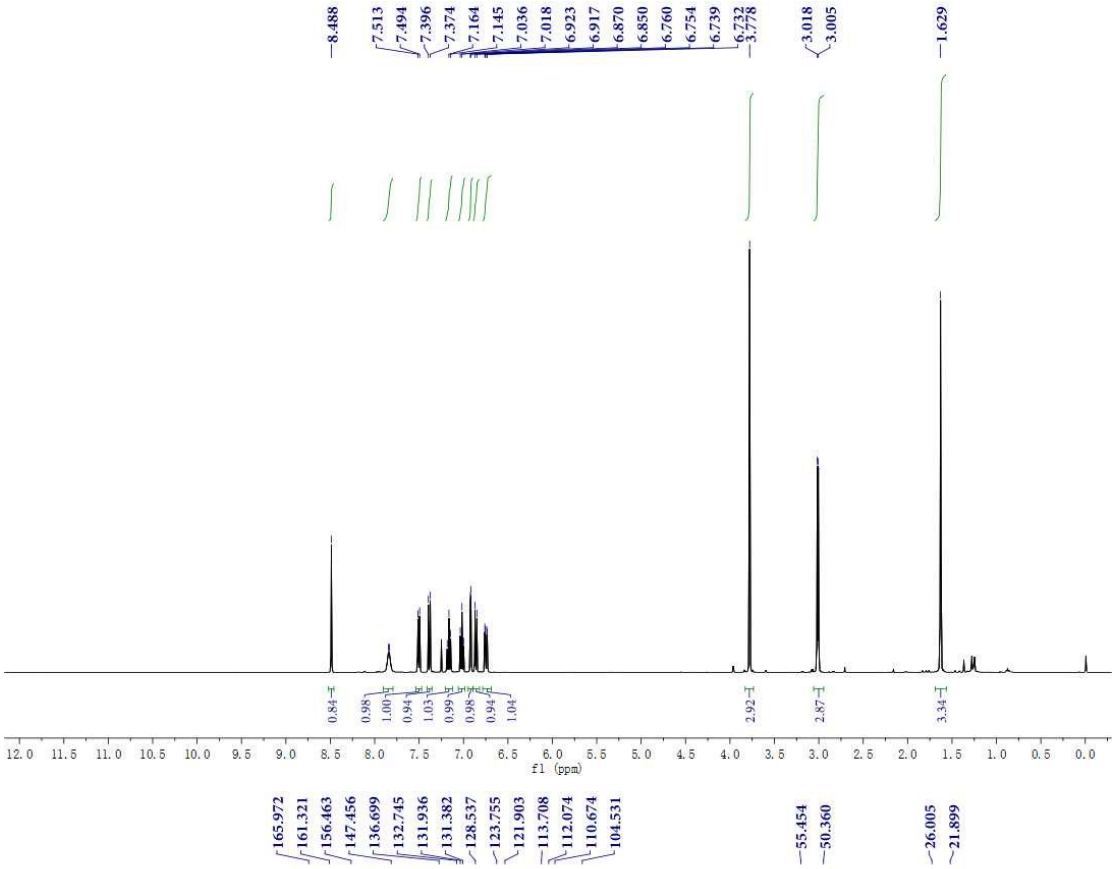
4n

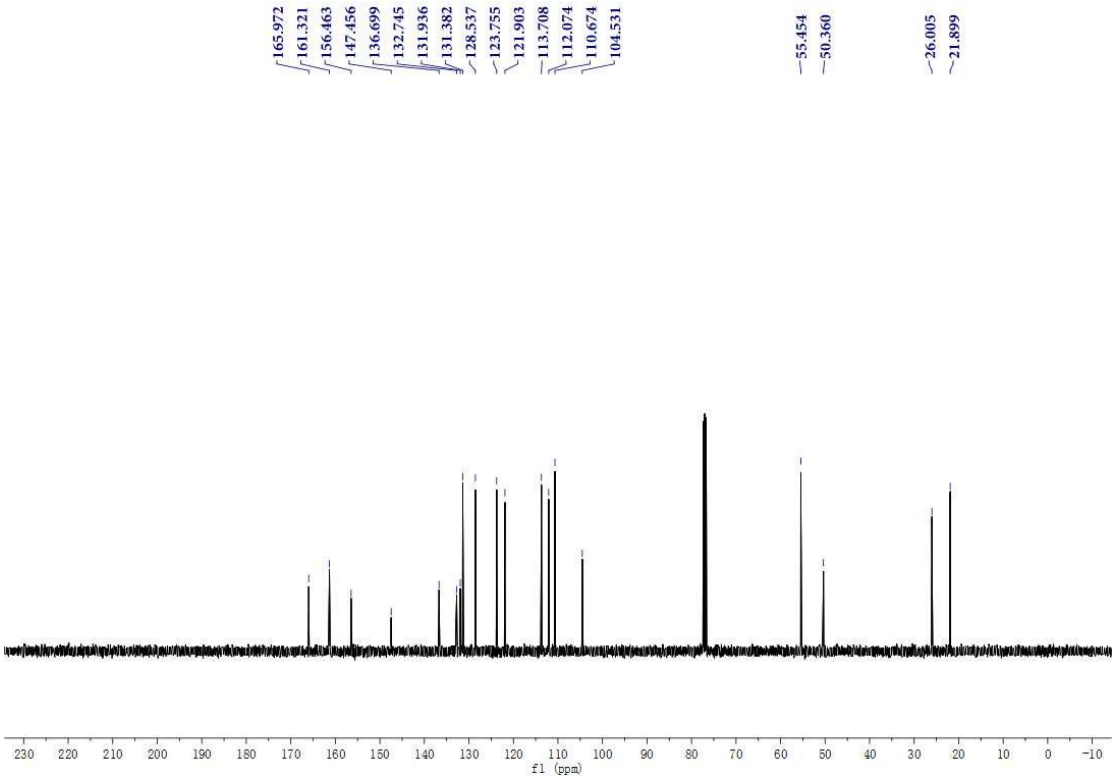

7.597
7.589
7.529
7.511
7.381
7.361
7.263
7.148
7.129
7.110
7.075
7.055
7.002
6.984
6.965
6.840
6.820
5.486
3.029
3.016
2.333
1.590
1.05
1.13
1.00
1.18
1.08
1.05
1.08
0.99
1.00
3.04
3.08
3.13
f1 (ppm)

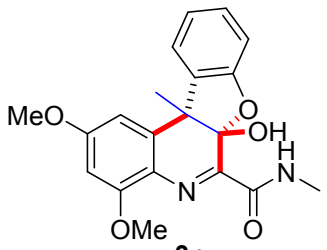

164.320
158.509
152.441
129.665
128.556
128.293
127.299
123.856
121.412
110.231
77.906
45.110
26.794
26.150
21.678
f1 (ppm)


MeO
O
OH
H
N
N
O

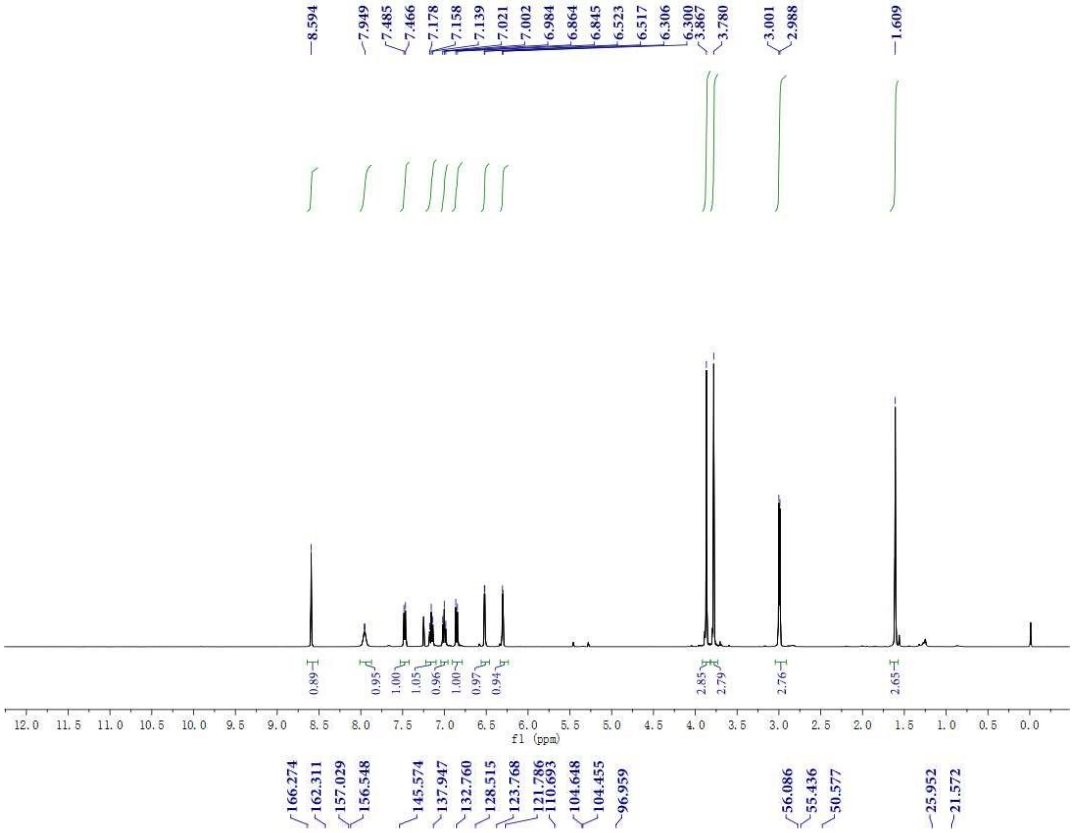
3o

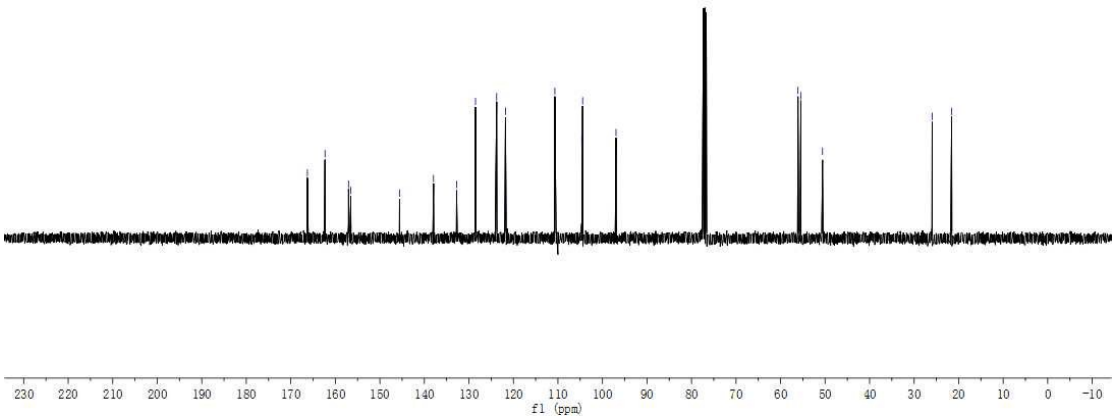

8.488
7.513
7.494
7.396
7.374
7.164
7.145
7.036
7.018
6.923
6.917
6.870
6.850
6.760
6.754
6.739
6.732
3.778
3.018
3.005
1.629
0.84
0.98
1.00
0.94
1.03
0.99
0.98
0.94
1.04
2.92
2.87
3.34
f1 (ppm)

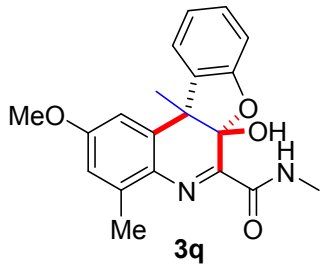

165.972
161.321
156.463
147.456
136.699
132.745
131.936
131.382
128.537
123.755
121.903
113.708
112.074
110.674
104.531
55.454
50.360
26.005
21.899
f1 (ppm)

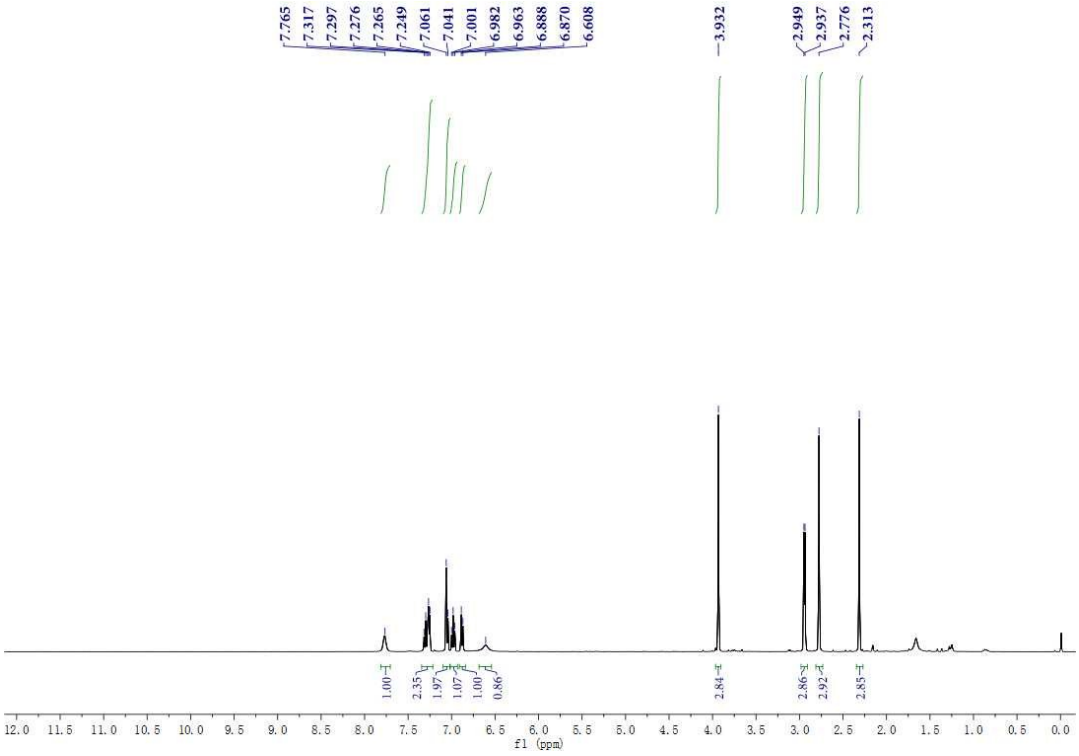

MeO
O
OH
H
N
N
OMe
O

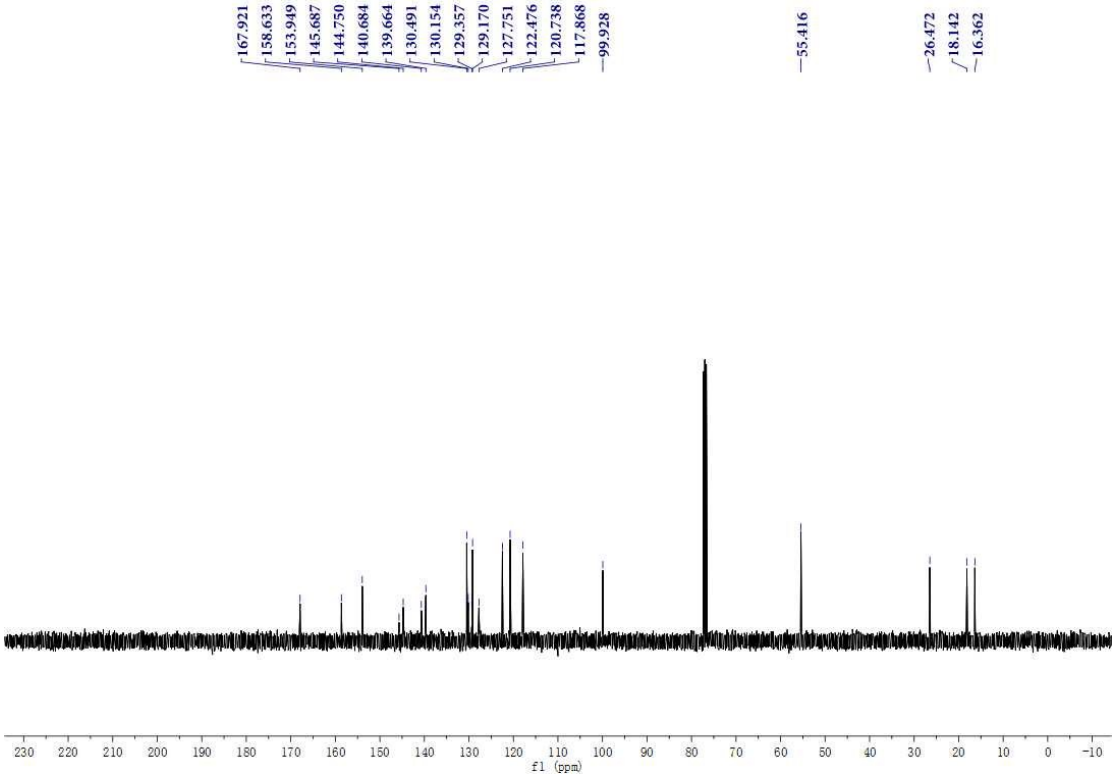
3p

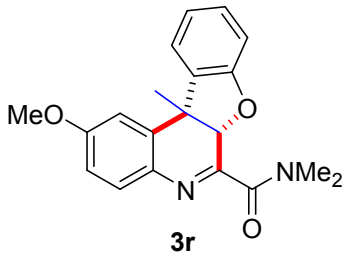

8.594
7.949
7.485
7.466
7.178
7.158
7.139
7.021
7.002
6.984
6.864
6.845
6.523
6.517
6.306
6.300
3.867
3.780
3.001
2.988
1.609
0.89
0.93
1.00
1.05
0.96
1.00
0.97
0.94
2.85
2.79
2.76
2.65
f1 (ppm)
166.274
162.311
157.029
156.548
145.574
137.947
132.760
128.515
123.768
121.786
110.693
104.648
104.455
96.959
56.086
55.436
50.577
25.952
21.572


f1 (ppm)

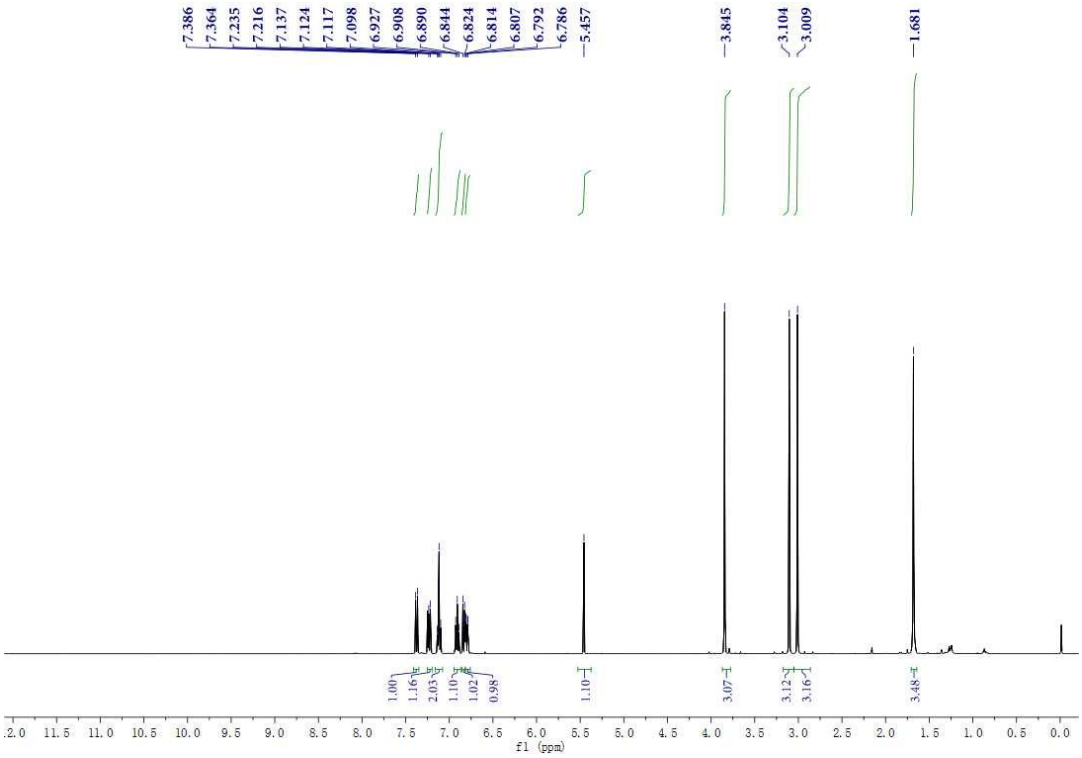

MeO
O
OH
H
N
N
Me
O
3q

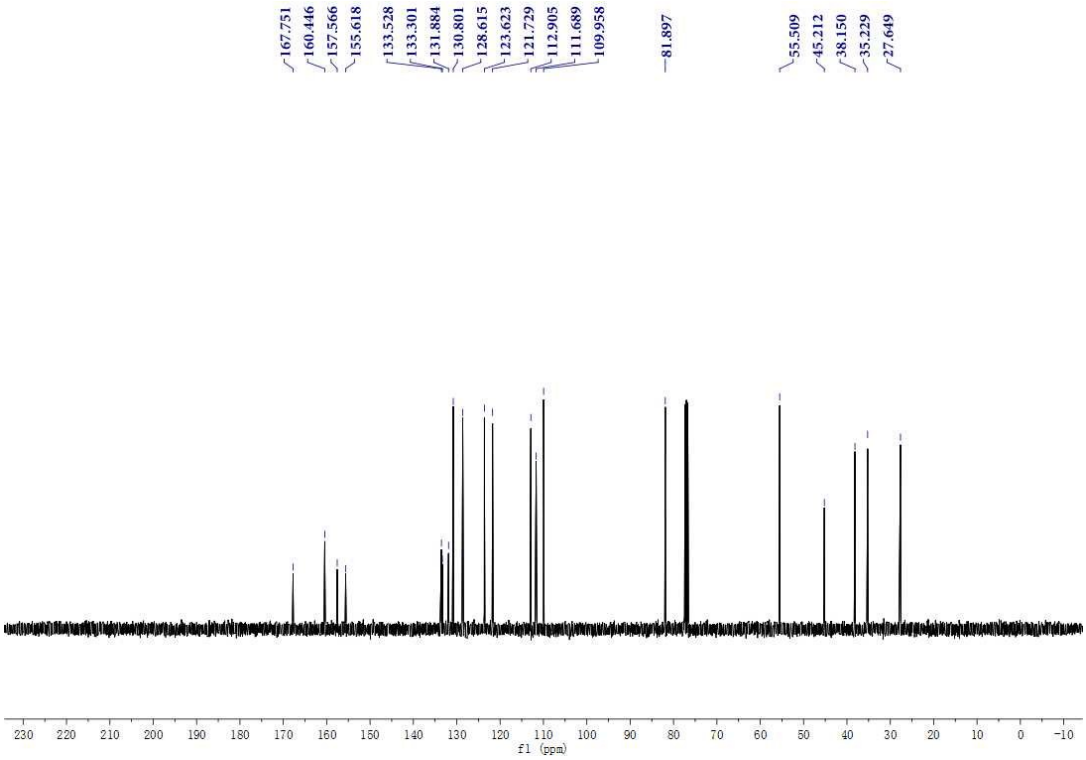

7.765
7.317
7.297
7.276
7.265
7.249
7.061
7.041
7.001
6.982
6.963
6.888
6.870
6.608
3.932
2.949
2.937
2.776
2.313
1.00
2.35
1.97
1.07
1.00
0.86
2.84
2.86
2.92
2.85
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

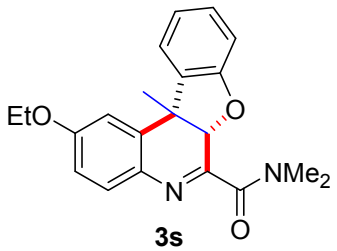

167.921
158.633
153.949
145.687
144.750
140.684
139.664
130.491
130.154
129.357
129.170
127.751
122.476
120.738
117.868
99.928
55.416
26.472
18.142
16.362
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
O
NMe2
N
O

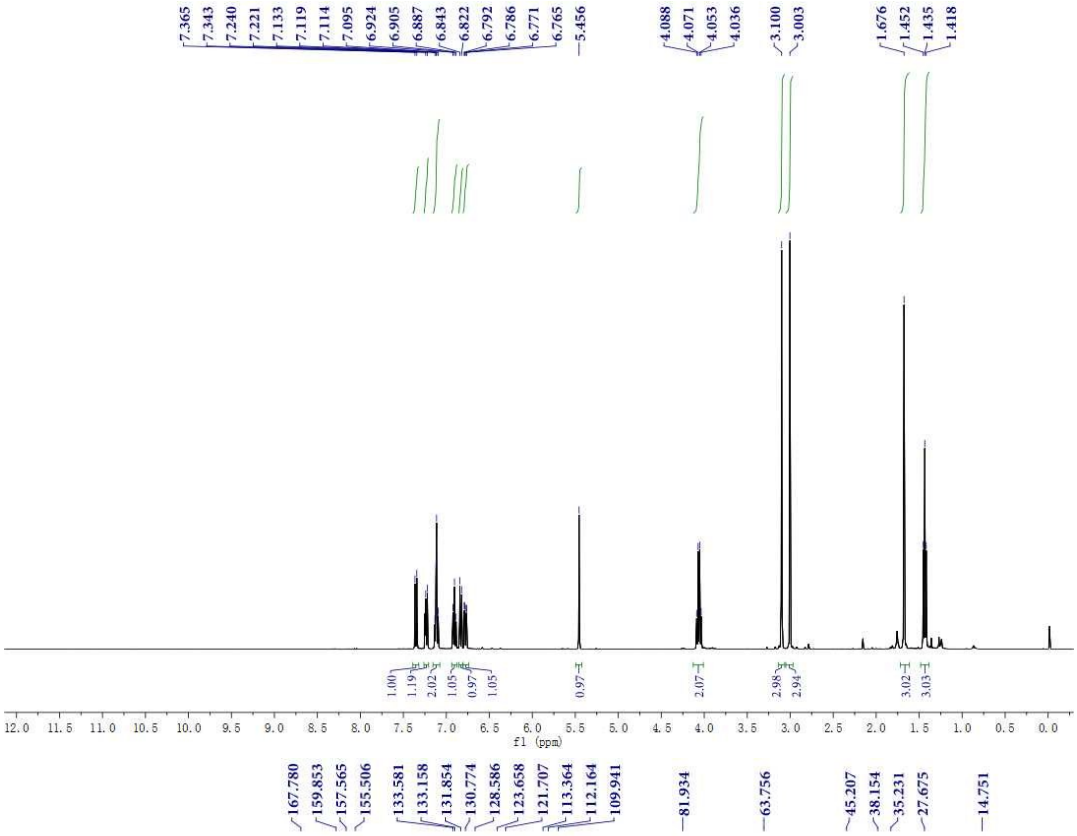
3r

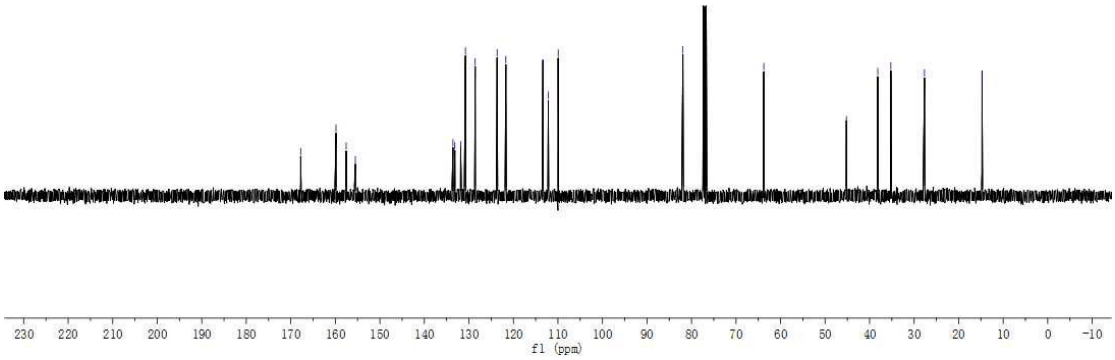

7.386
7.364
7.235
7.216
7.137
7.124
7.117
7.098
6.927
6.908
6.890
6.844
6.824
6.814
6.807
6.792
6.786
5.457
3.845
3.104
3.009
1.681
1.00
1.16
2.03
1.10
1.02
0.98
1.10
3.07
3.12
3.16
3.48
f1 (ppm)

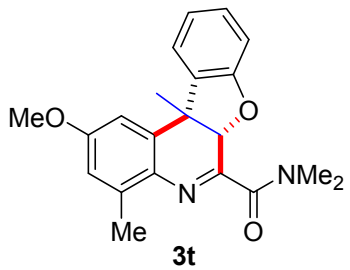

167.751
160.446
157.566
155.618
133.528
133.301
131.884
130.801
128.615
123.623
121.729
112.905
111.689
109.958
81.897
55.509
45.212
38.150
35.229
27.649
f1 (ppm)


EtO
O
NMe2
N
O

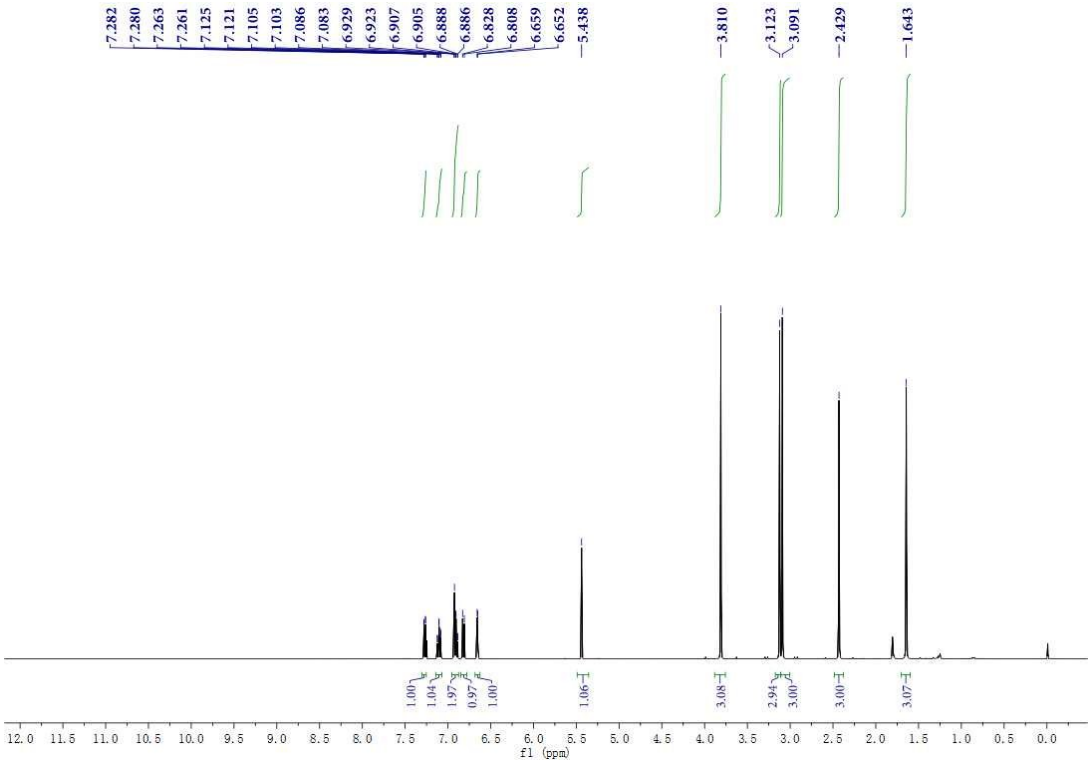
3s

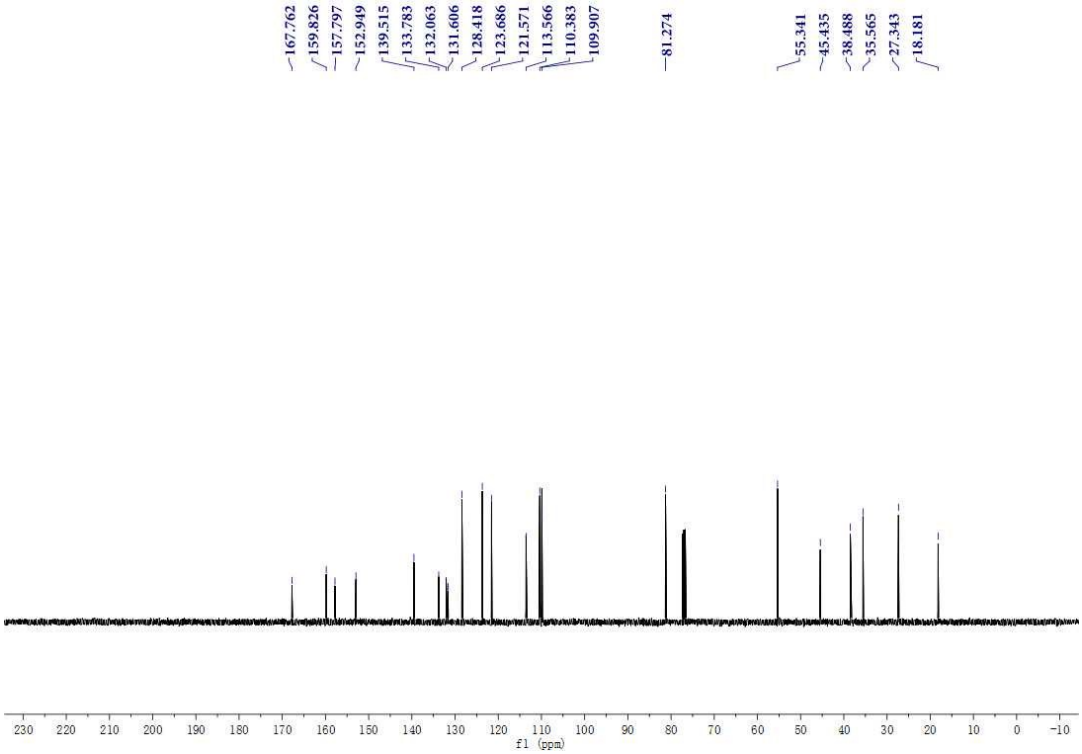

7.365
7.343
7.240
7.221
7.133
7.119
7.114
7.095
6.924
6.905
6.887
6.843
6.822
6.792
6.786
6.771
6.765
5.456
4.088
4.071
4.053
4.036
3.100
3.003
1.676
1.452
1.435
1.418
1.00
1.19
2.02
1.05
0.97
1.05
0.97
2.07
2.98
2.94
3.02
3.03
f1 (ppm)

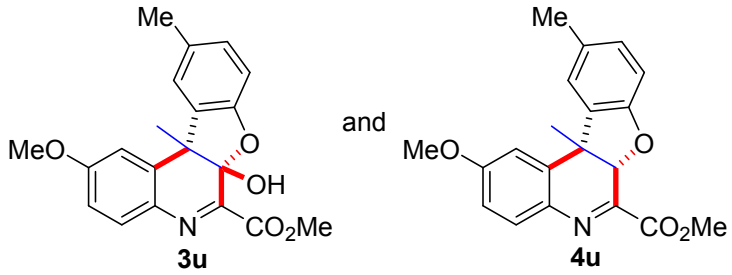

167.780
159.853
157.565
155.506
133.581
133.158
131.854
130.774
128.586
123.658
121.707
113.364
112.164
109.941
81.934
63.756
45.207
38.154
35.231
27.675
14.751
f1 (ppm)

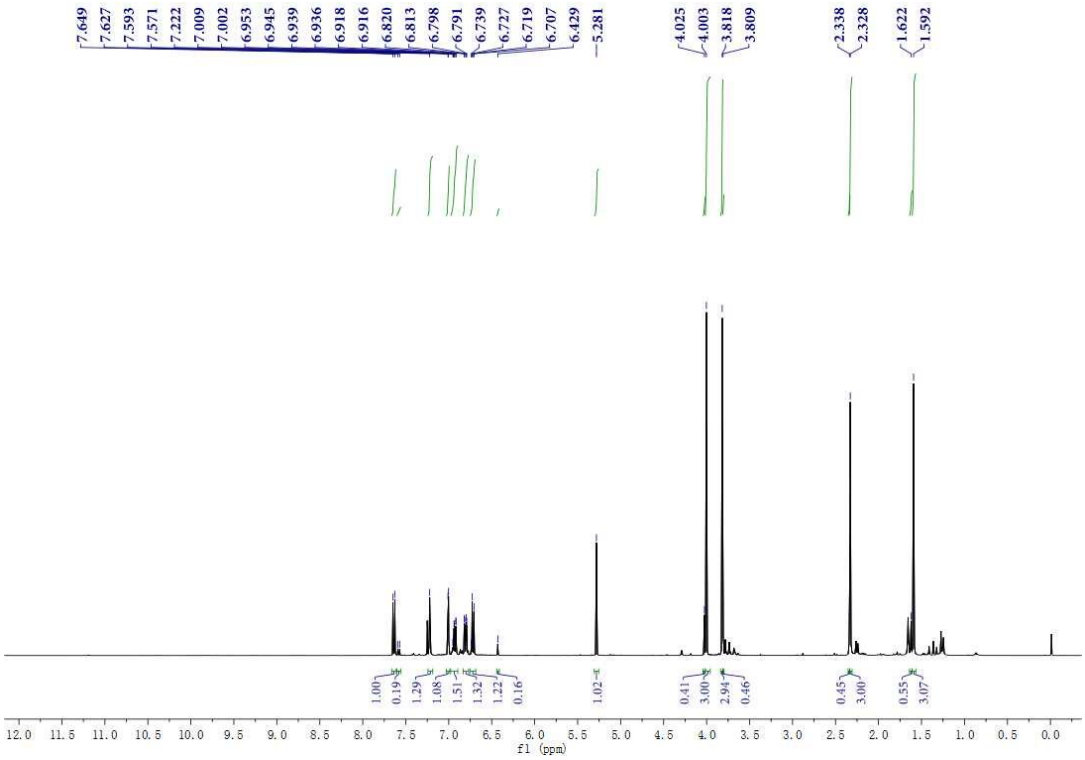

MeO
O
NMe2
N
Me
O

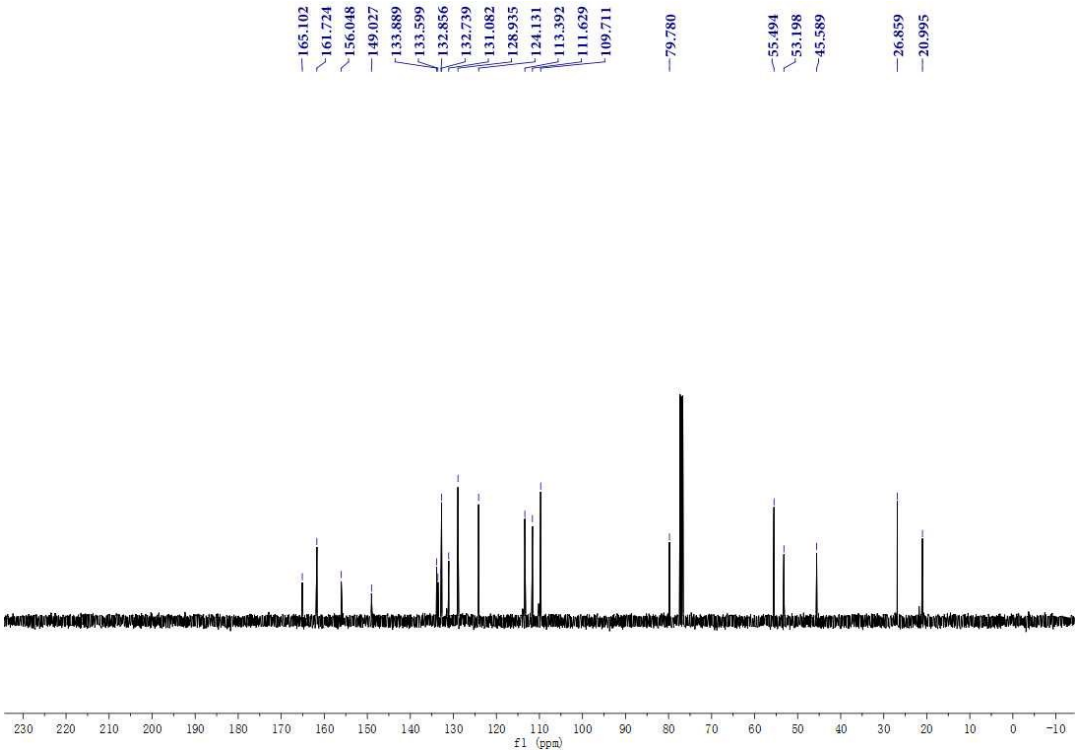
3t

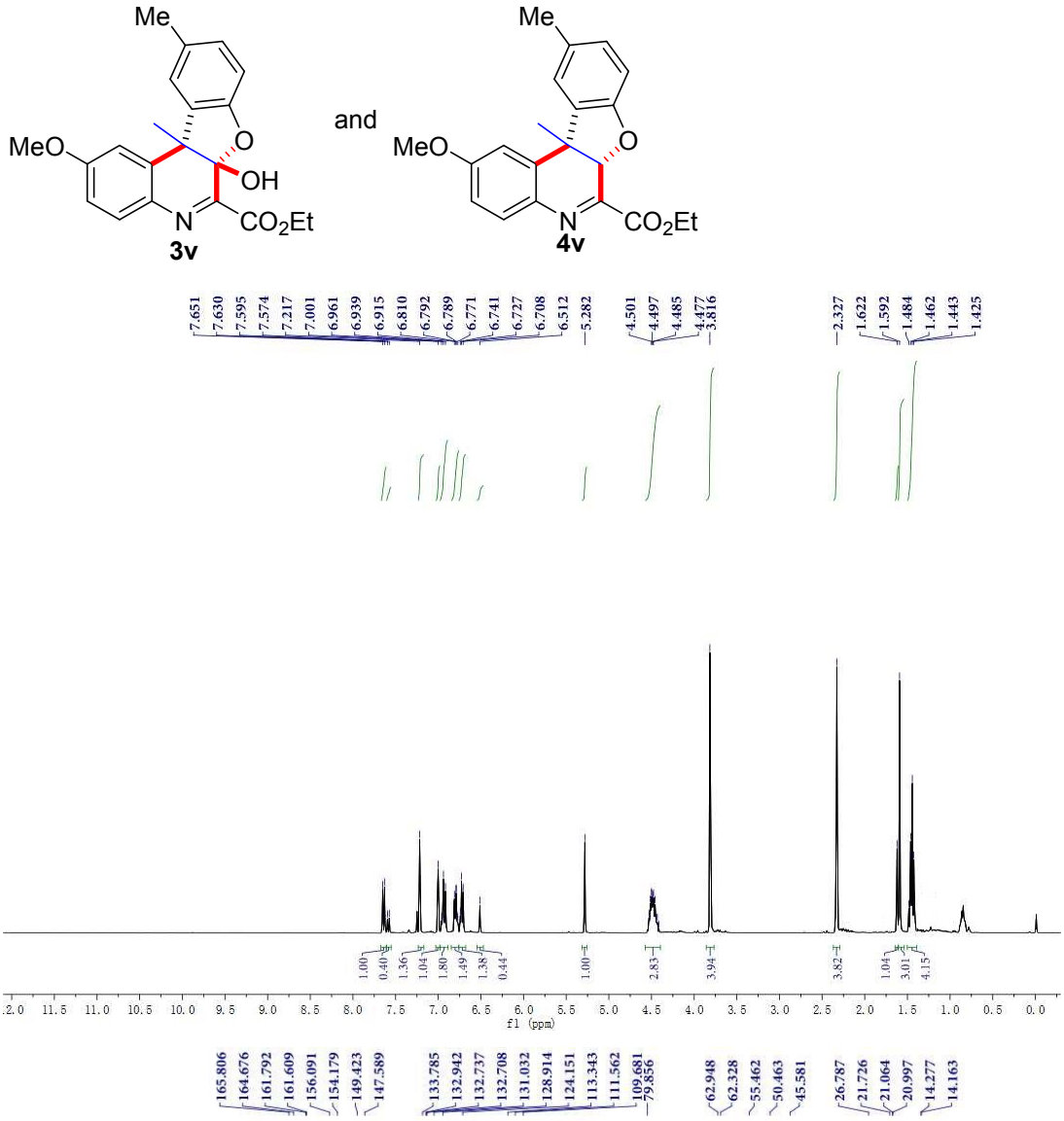

7.282
7.280
7.263
7.261
7.125
7.121
7.105
7.103
7.086
7.083
6.929
6.923
6.907
6.905
6.888
6.886
6.828
6.808
6.659
6.652
5.438
3.810
3.123
3.091
2.429
1.643
1.00
1.04
1.97
0.97
1.00
1.06
3.08
2.94
3.00
3.00
3.07
f1 (ppm)

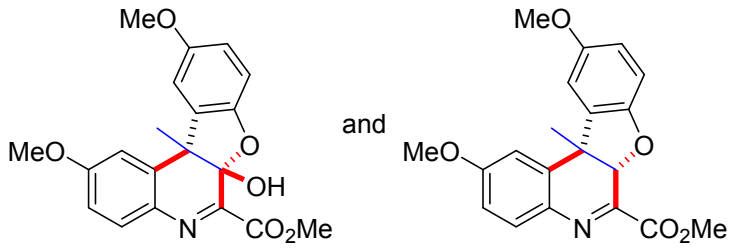

167.762
159.826
157.797
152.949
139.515
133.783
132.063
131.606
128.418
123.686
121.571
113.566
110.383
109.907
81.274
55.341
45.435
38.488
35.565
27.343
18.181
f1 (ppm)


Me
MeO
O
OH
N
CO2Me
3u
and
Me
MeO
O
N
CO2Me
4u

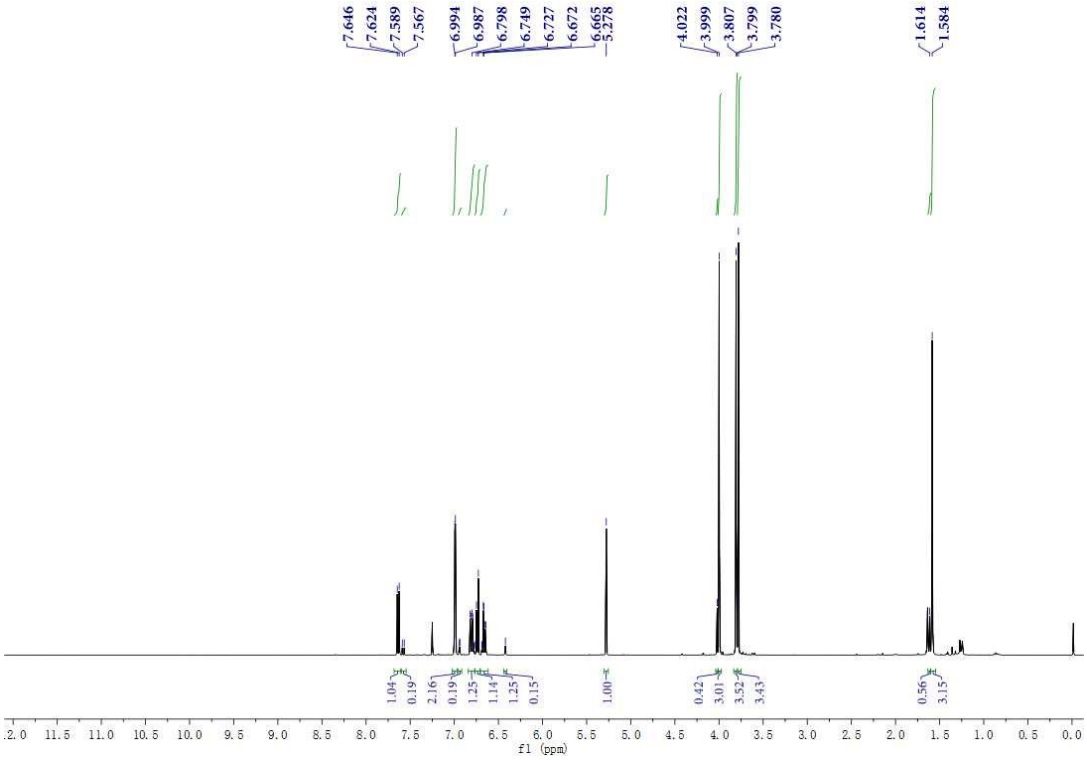

7.649
7.627
7.593
7.571
7.222
7.009
7.002
6.953
6.945
6.939
6.936
6.918
6.916
6.820
6.813
6.798
6.791
6.739
6.727
6.719
6.707
6.429
5.281
4.025
4.003
3.818
3.809
2.338
2.328
1.622
1.592
1.00
0.19
1.29
1.08
1.51
1.32
1.22
0.16
1.02
0.41
3.00
2.94
0.46
0.45
3.00
0.55
3.07
f1 (ppm)

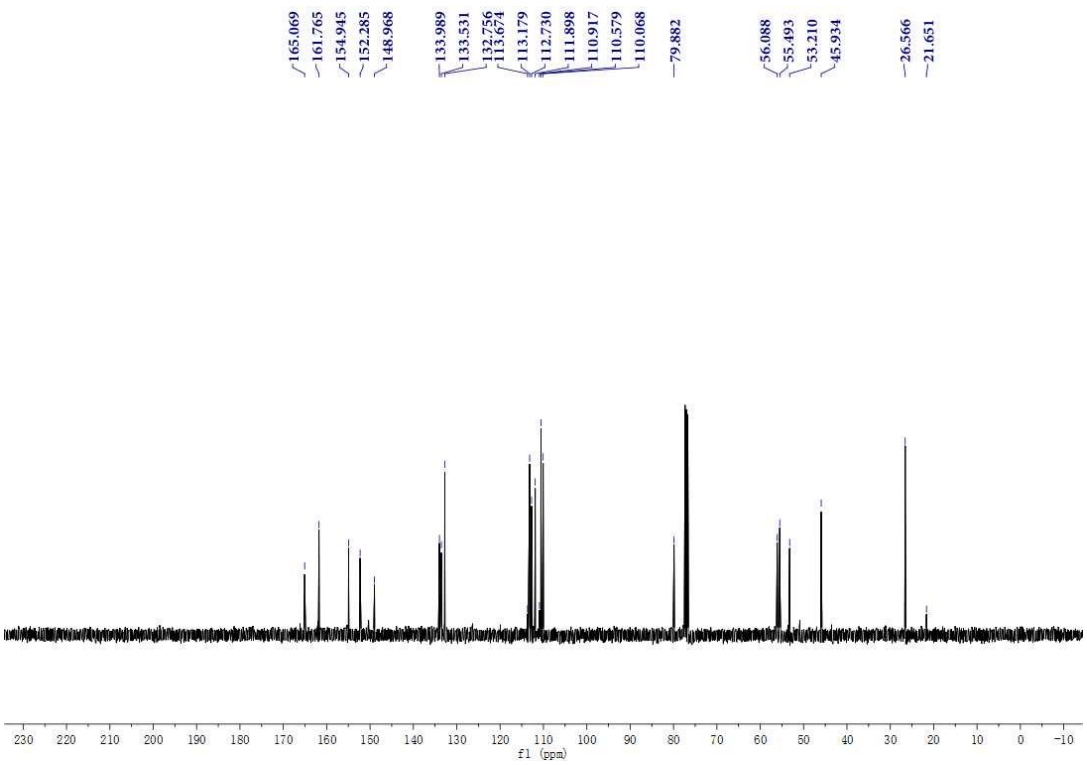

165.102
161.724
156.048
149.027
133.889
133.599
132.856
132.739
131.082
128.935
124.131
113.392
111.629
109.711
79.780
55.494
53.198
45.589
26.859
20.995
f1 (ppm)

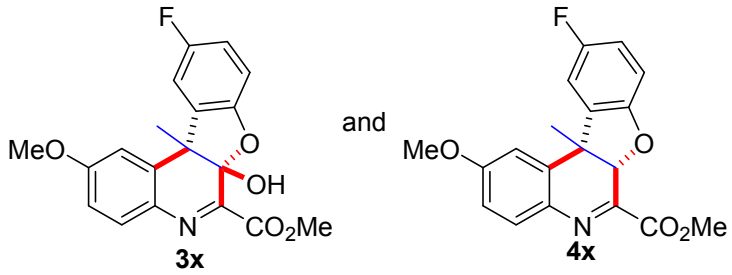

Me
MeO
O
OH
N
CO2Et
3v
and
Me
MeO
O
N
CO2Et
4v
7.651 7.630 7.595 7.574 7.217 7.001 6.961 6.939 6.915 6.810 6.792 6.789 6.771 6.741 6.727 6.708 6.512 5.282 4.501 4.497 4.485 4.477 3.816 2.327 1.622 1.592 1.484 1.462 1.443 1.425
1.00 0.40 1.36 1.04 1.80 1.49 1.38 0.44 1.00 2.83 3.94 3.82 1.04 3.01 4.15
f1 (ppm)
165.806 164.676 161.792 161.609 156.091 154.179 149.423 147.589 133.785 132.942 132.737 132.708 131.032 128.914 124.151 113.343 111.562 109.681 79.856 62.948 62.328 55.462 50.463 45.581 26.787 21.726 21.064 20.997 14.277 14.163
f1 (ppm)

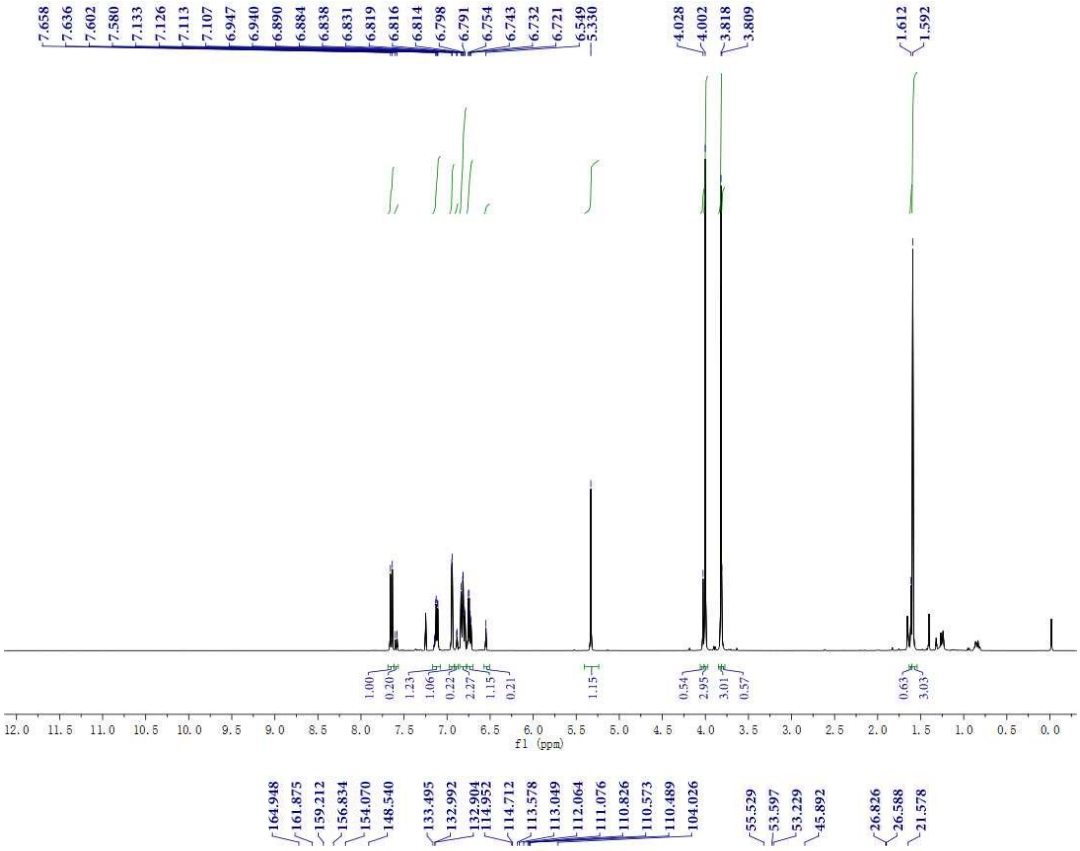

MeO
MeO
O
OH
N
CO2Me
and
MeO
MeO
O
N
CO2Me

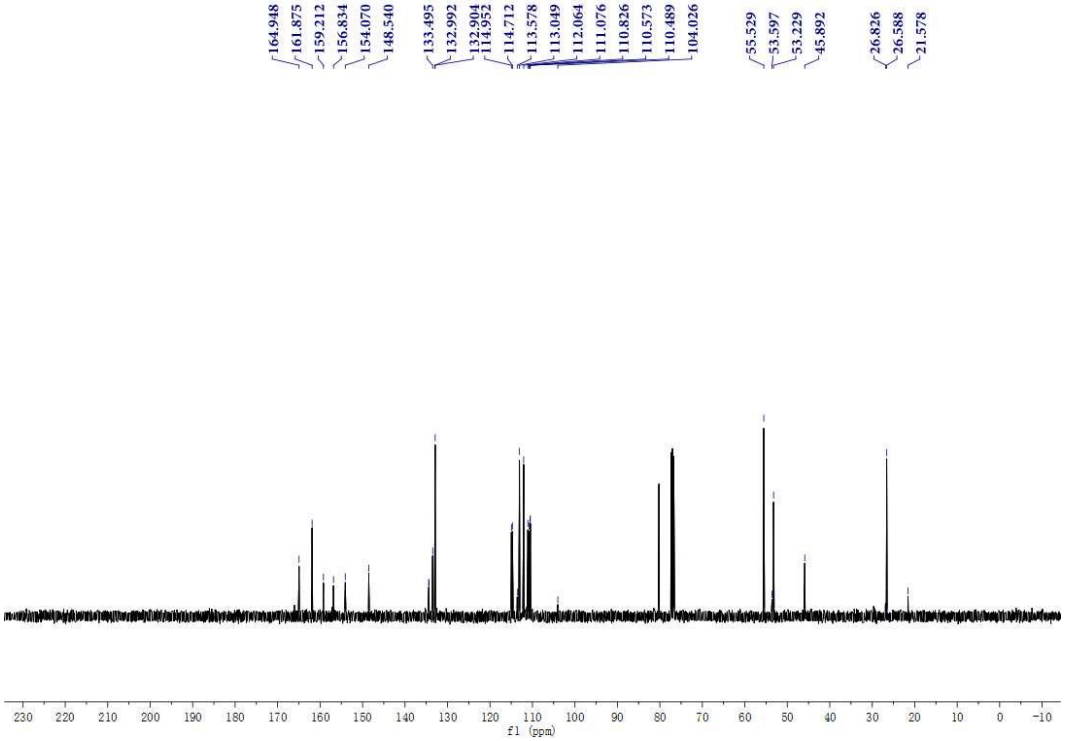
3w **4w**

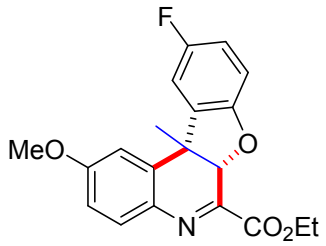

7.646
7.624
7.589
7.567
6.994
6.987
6.798
6.749
6.727
6.672
6.665
5.278
4.022
3.999
3.807
3.799
3.780
1.614
1.584
1.04
0.19
2.16
0.19
1.25
1.14
1.25
0.15
1.00
0.42
3.01
3.52
3.43
0.56
3.15
f1 (ppm)


165.069
161.765
154.945
152.285
148.968
133.989
133.531
132.756
113.674
113.179
112.730
111.898
110.917
110.579
110.068
79.882
56.088
55.493
53.210
45.934
26.566
21.651
f1 (ppm)

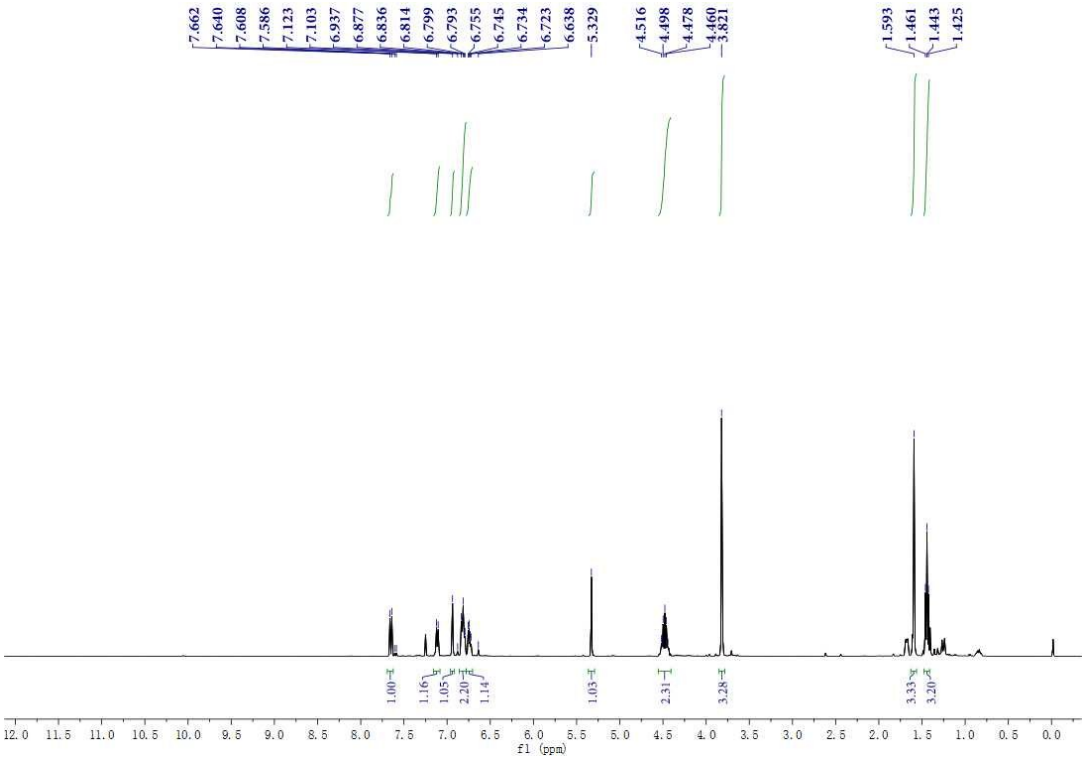

F
MeO
O
OH
N
CO2Me
3x
and
F
MeO
O
N
CO2Me
4x

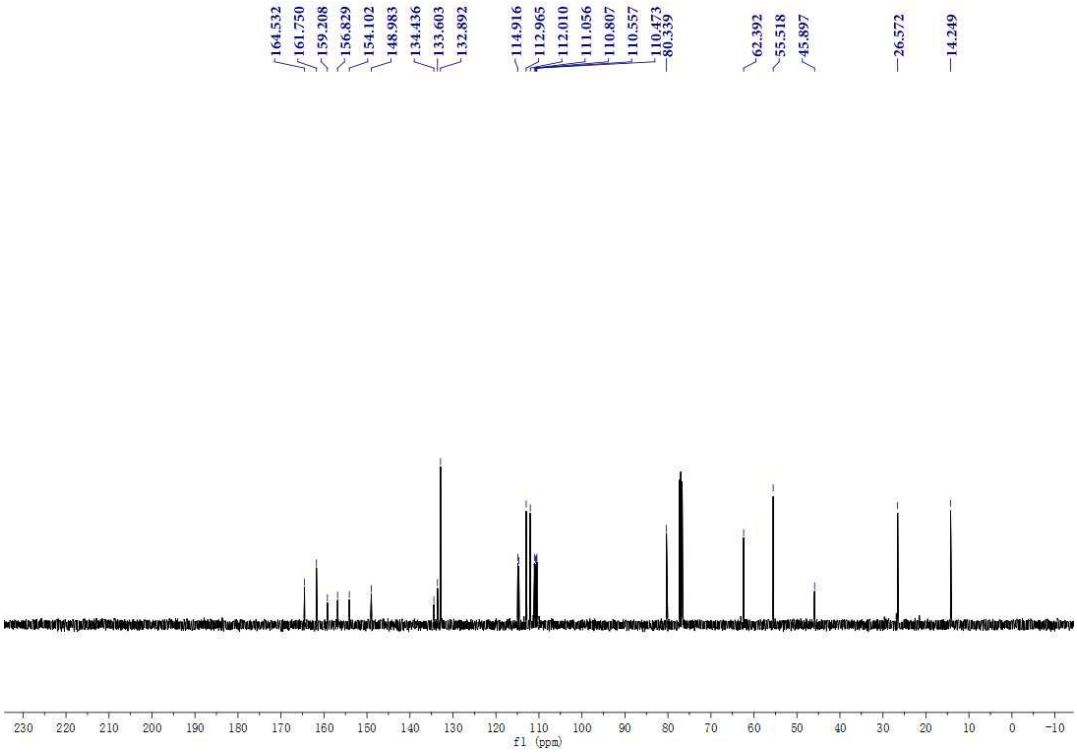

7.658
7.636
7.602
7.580
7.133
7.126
7.113
7.107
6.947
6.940
6.890
6.884
6.838
6.831
6.819
6.816
6.814
6.798
6.791
6.754
6.743
6.732
6.721
6.549
5.330
4.028
4.002
3.818
3.809
1.612
1.592
1.00
0.20
1.23
1.06
0.22
2.27
1.15
0.21
1.15
0.54
2.95
3.01
0.57
0.63
3.03
f1 (ppm)

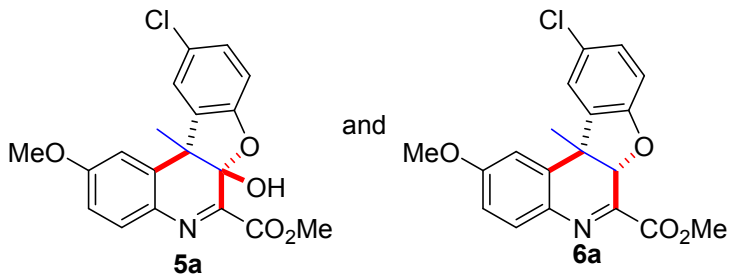

164.948
161.875
159.212
156.834
154.070
148.540
133.495
132.992
132.904
114.952
114.712
113.578
113.049
112.064
111.076
110.826
110.573
110.489
104.026
55.529
53.597
53.229
45.892
26.826
26.588
21.578
f1 (ppm)

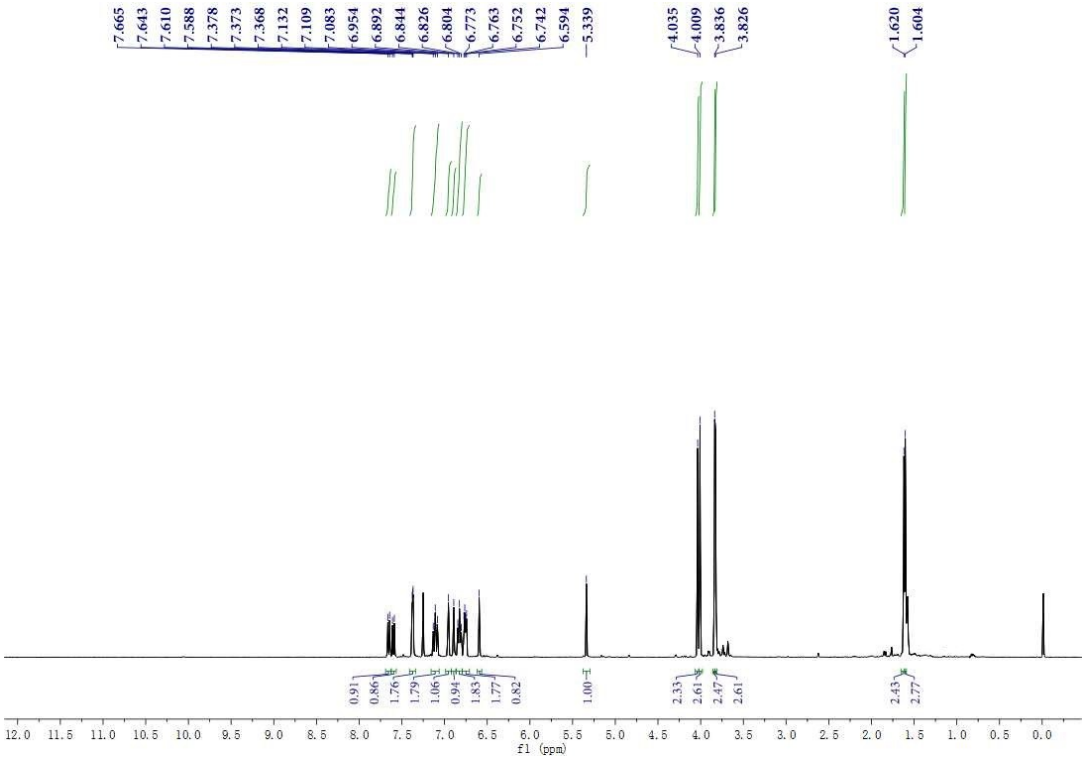

F
MeO
O
N
CO2Et

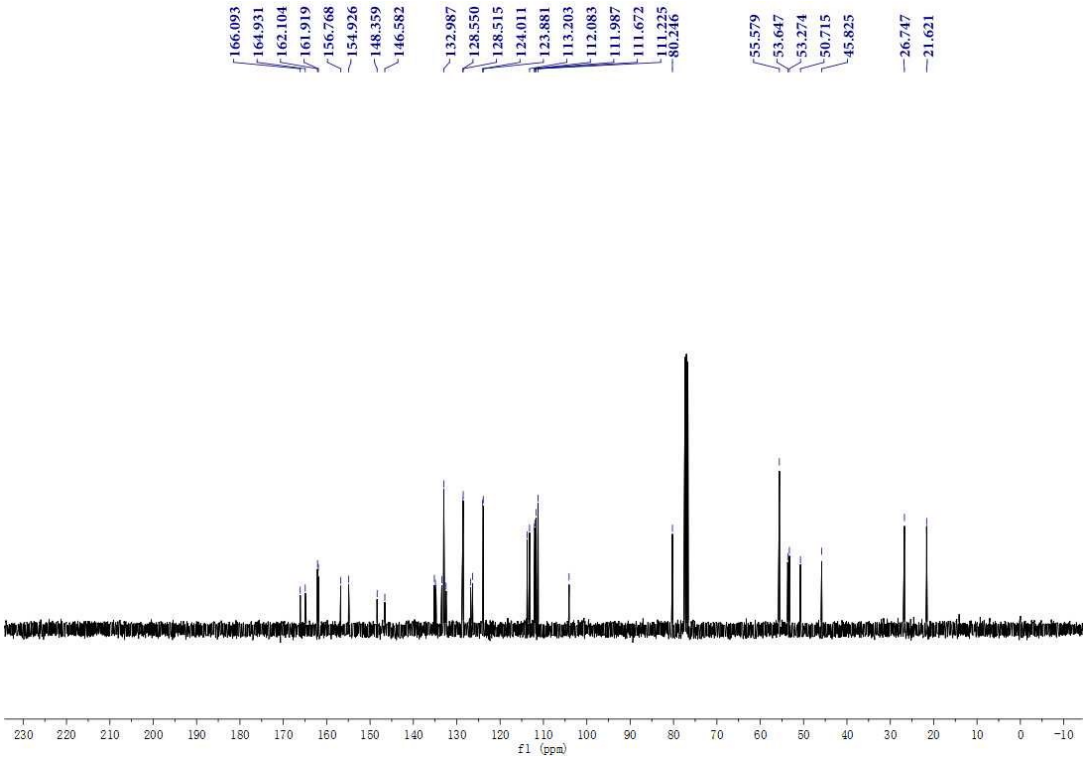
4y

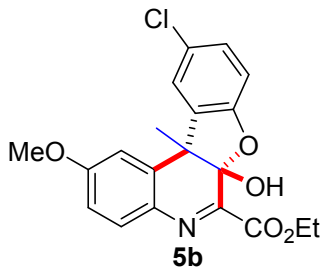

7.662
7.640
7.608
7.586
7.123
7.103
6.937
6.877
6.836
6.814
6.799
6.793
6.755
6.745
6.734
6.723
6.638
5.329
4.516
4.498
4.478
4.460
3.821
1.593
1.461
1.443
1.425
1.00
1.16
1.05
2.20
1.14
1.03
2.31
3.28
3.33
3.20
f1 (ppm)


164.532
161.750
159.208
156.829
154.102
148.983
134.436
133.603
132.892
114.916
112.965
112.010
111.056
110.807
110.557
110.473
80.339
62.392
55.518
45.897
26.572
14.249
f1 (ppm)

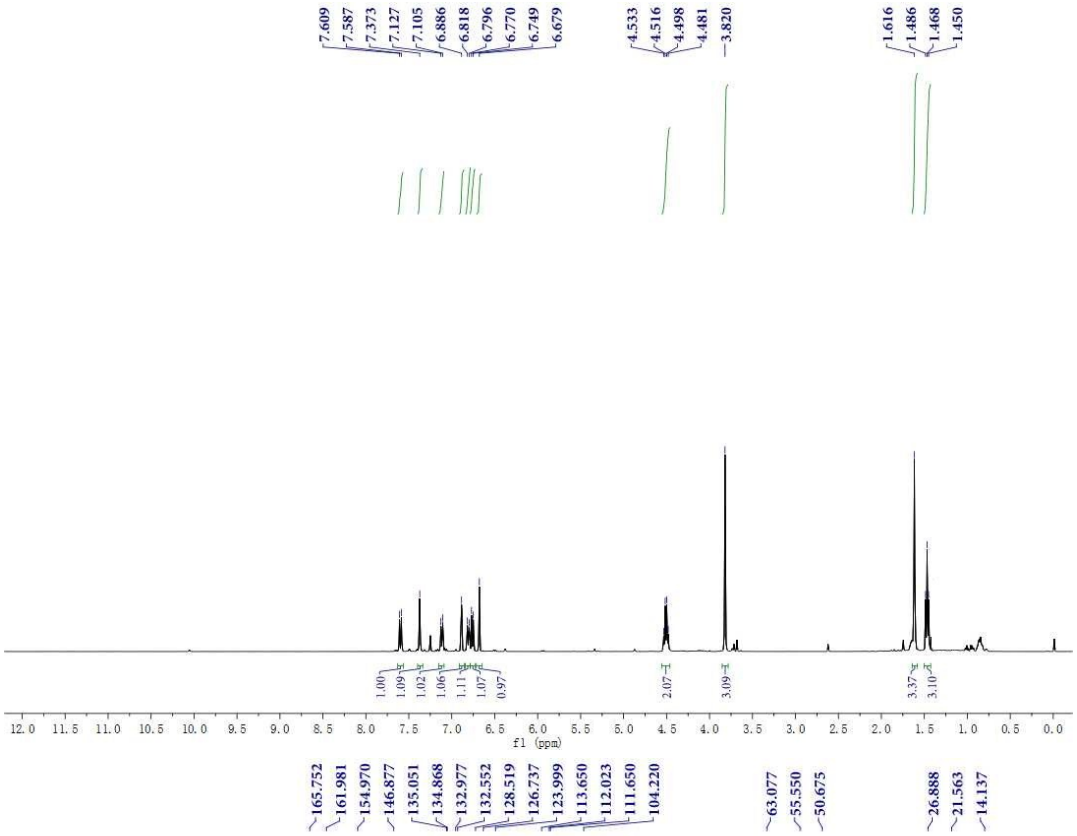

Cl
MeO
O
OH
N
CO2Me
5a
and
Cl
MeO
O
N
CO2Me
6a

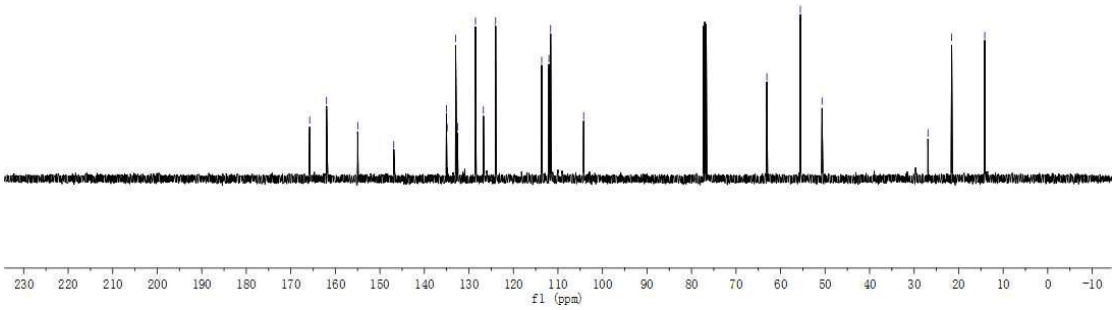

7.665
7.643
7.610
7.588
7.378
7.373
7.368
7.132
7.109
7.083
6.954
6.892
6.844
6.826
6.804
6.773
6.763
6.752
6.742
6.594
5.339
4.035
4.009
3.836
3.826
1.620
1.604
0.91
0.86
1.76
1.79
1.06
0.94
1.83
1.77
0.82
1.00
2.33
2.61
2.47
2.61
2.43
2.77
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

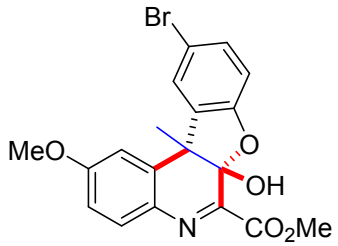

166.093
164.931
162.104
161.919
156.768
154.926
148.359
146.582
132.987
128.550
128.515
124.011
123.881
113.203
112.083
111.987
111.672
111.225
80.246
55.579
53.647
53.274
50.715
45.825
26.747
21.621
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
MeO
O
OH
N
CO2Et

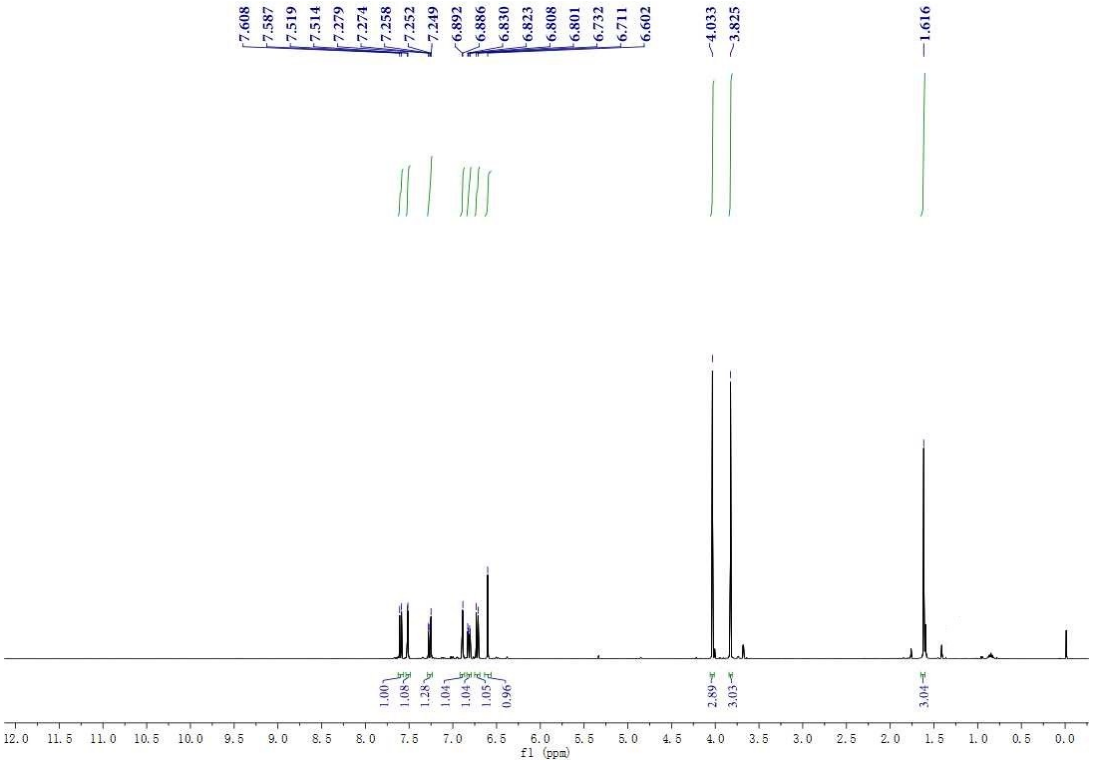
5b

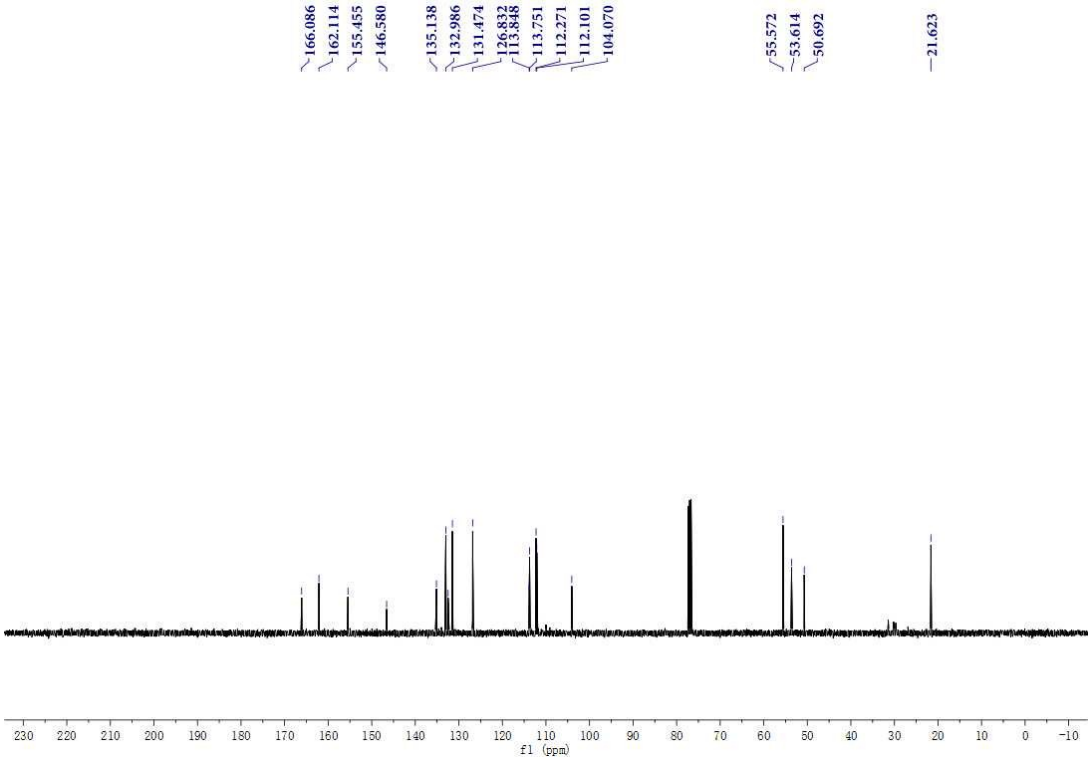

7.609
7.587
7.373
7.127
7.105
6.886
6.818
6.796
6.770
6.749
6.679
4.533
4.516
4.498
4.481
3.820
1.616
1.486
1.468
1.450
1.00
1.09
1.02
1.06
1.11
1.07
0.97
2.07
3.09
3.37
3.10
f1 (ppm)
165.752
161.981
154.970
146.877
135.051
134.868
132.977
132.552
128.519
126.737
123.999
113.650
112.023
111.650
104.220
63.077
55.550
50.675
26.888
21.563
14.137

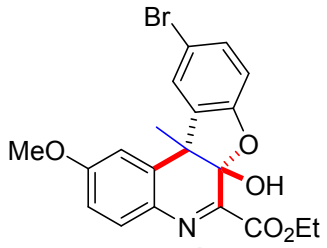

f1 (ppm)


Br
MeO
O
OH
N
CO2Me

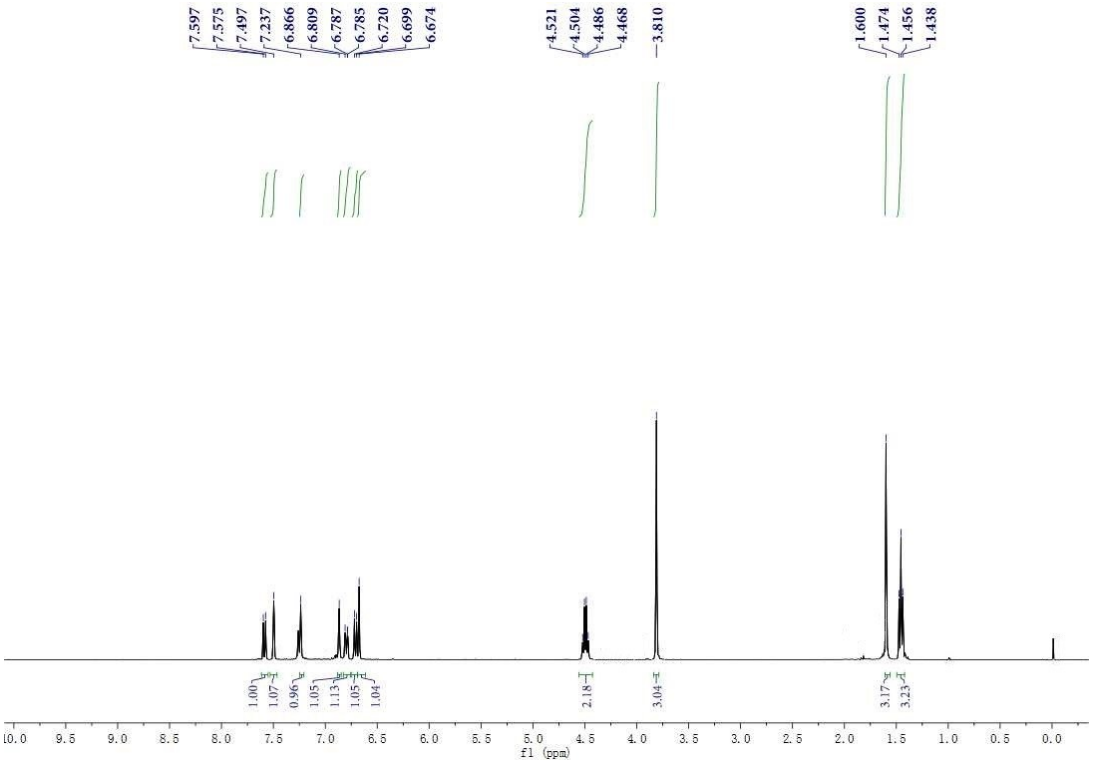
5c

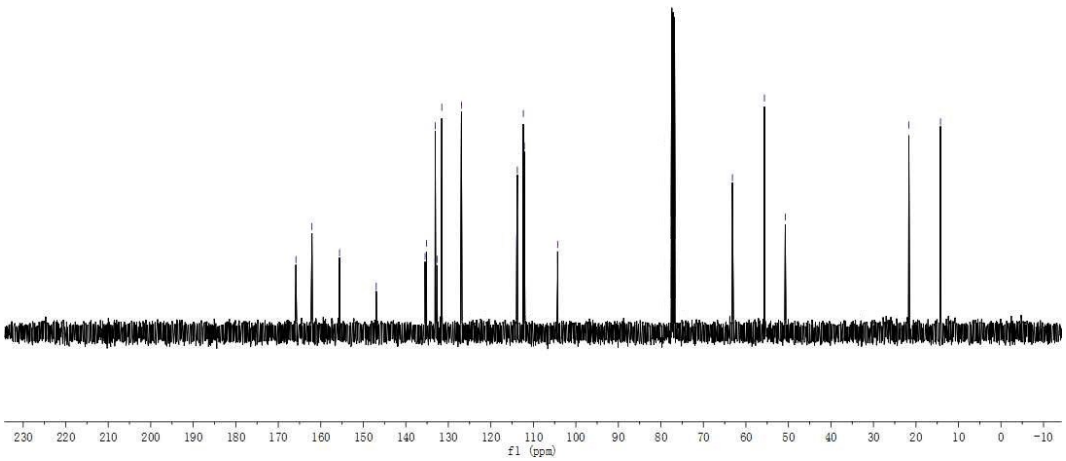

7.608
7.587
7.519
7.514
7.279
7.274
7.258
7.252
7.249
6.892
6.886
6.830
6.823
6.808
6.801
6.732
6.711
6.602
4.033
3.825
1.616
1.00
1.08
1.28
1.04
1.04
1.05
0.96
2.89
3.03
3.04
f1 (ppm)

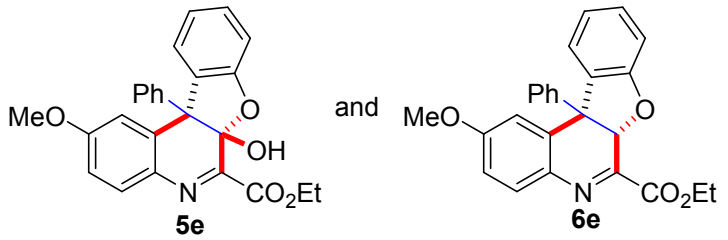

166.086
162.114
155.455
146.580
135.138
132.986
131.474
126.832
113.848
113.751
112.271
112.101
104.070
55.572
53.614
50.692
21.623
f1 (ppm)

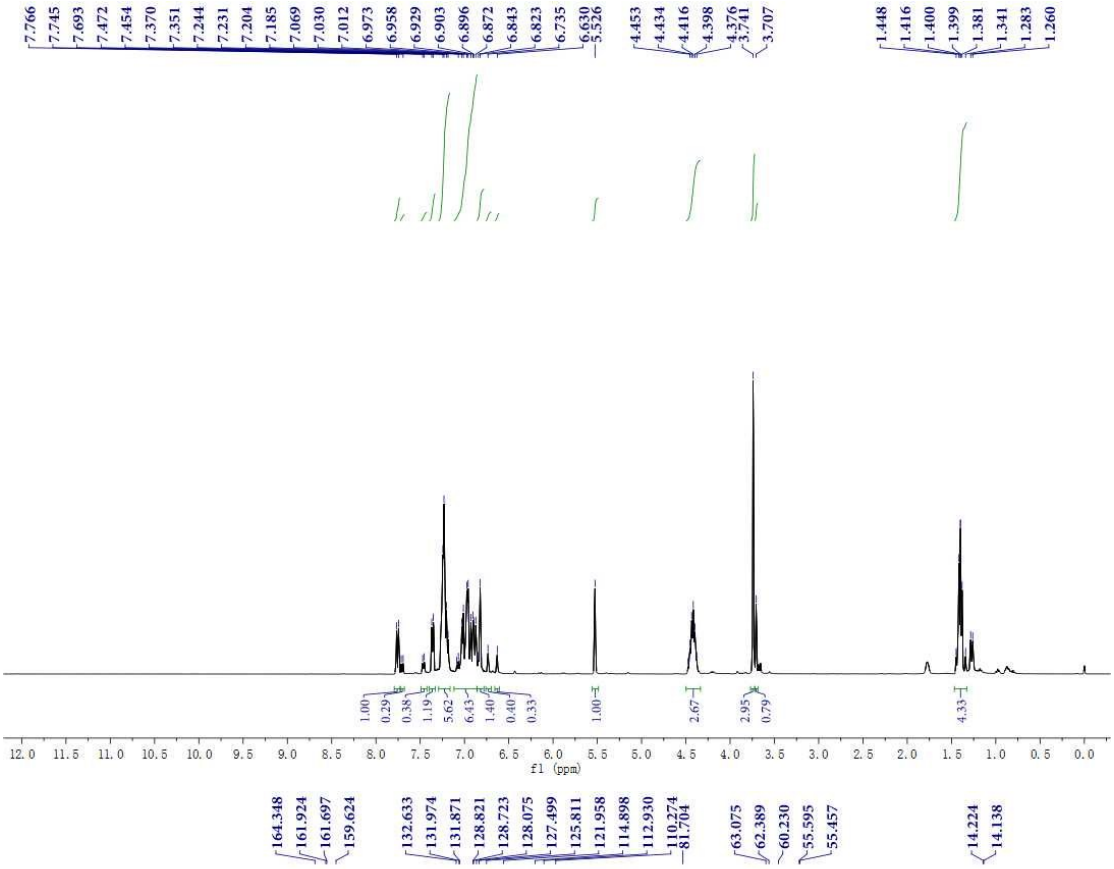

Br
MeO
O
OH
N
CO2Et

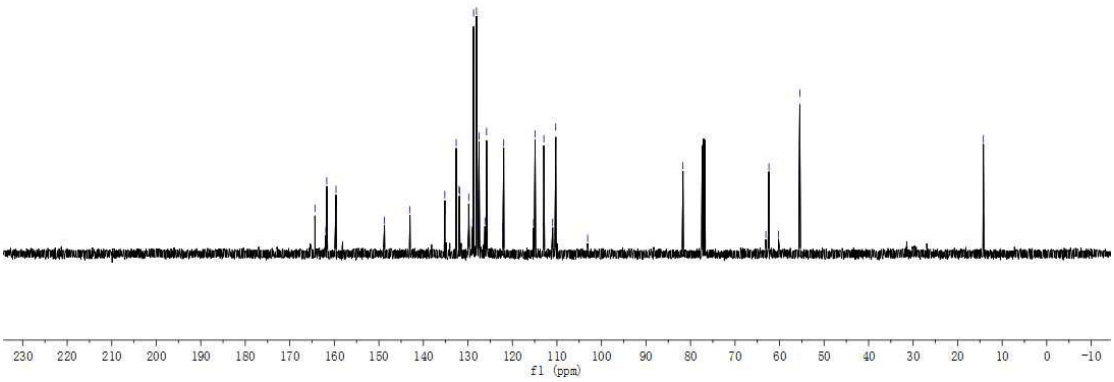
5d

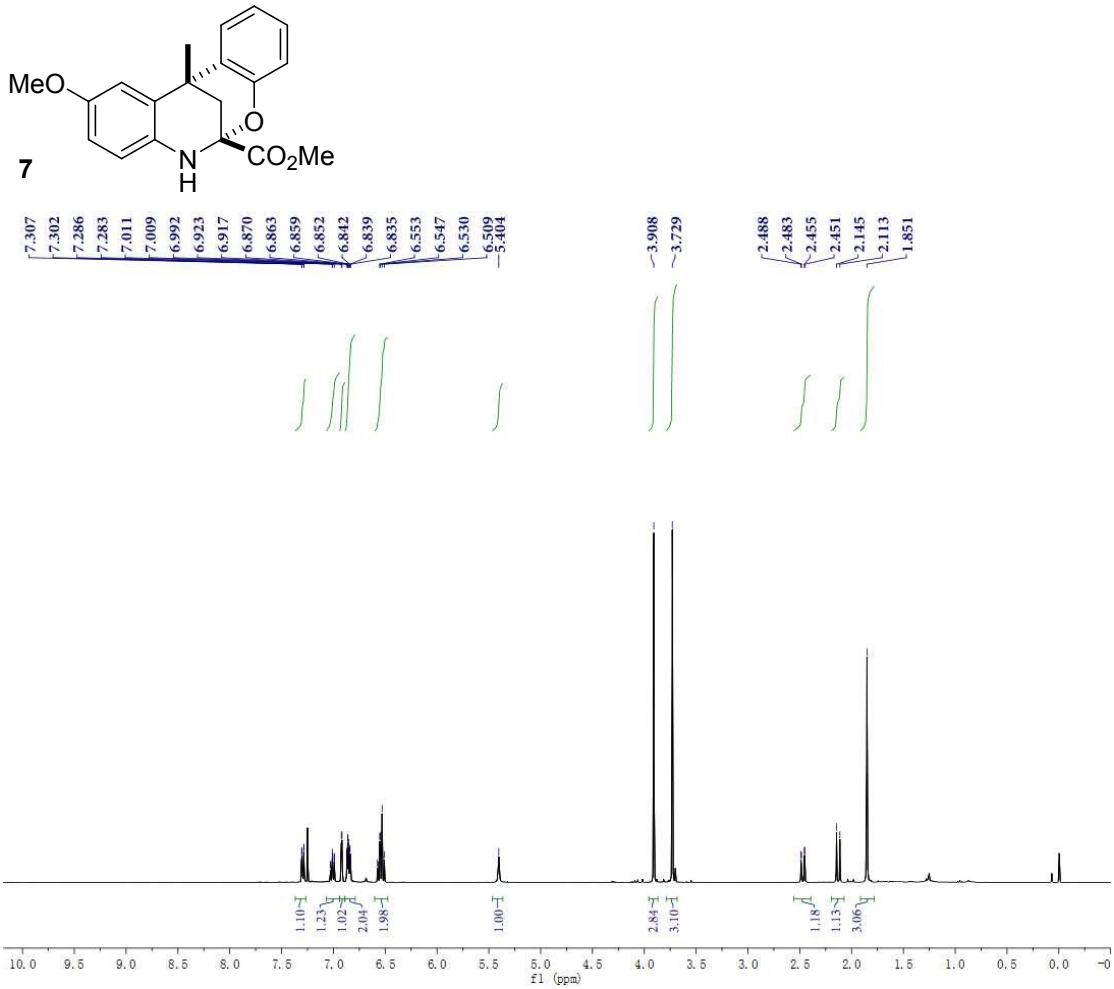

7.597
7.575
7.497
7.237
6.866
6.809
6.787
6.785
6.720
6.699
6.674
4.521
4.504
4.486
4.468
3.810
1.600
1.474
1.456
1.438
1.00
1.07
0.96
1.05
1.13
1.05
1.04
2.18
3.04
3.17
3.23
f1 (ppm)

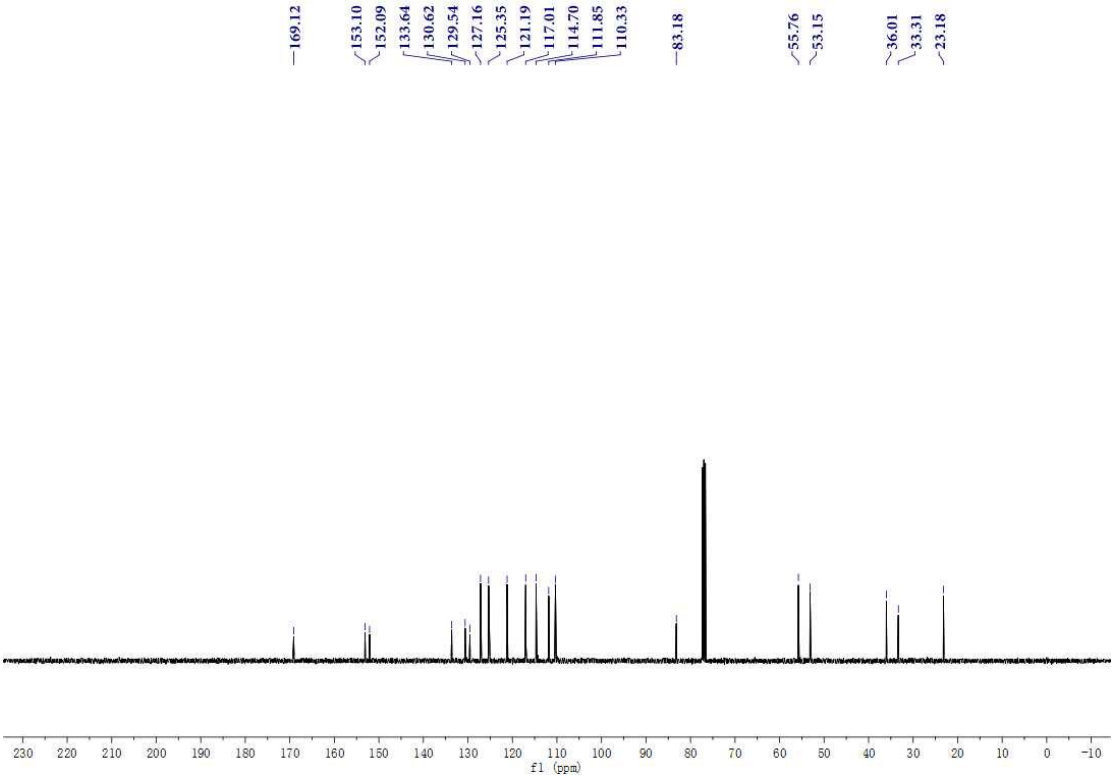

165.85
162.08
155.59
146.95
135.13
133.08
131.54
126.92
113.90
113.77
112.36
112.12
104.29
63.17
55.65
50.75
21.67
14.23
f1 (ppm)


MeO
Ph
O
OH
N
CO2Et
5e
and
MeO
Ph
O
N
CO2Et
6e


7.766 7.745 7.693 7.472 7.454 7.370 7.351 7.244 7.231 7.204 7.185 7.069 7.030 7.012 6.973 6.958 6.929 6.903 6.896 6.872 6.843 6.823 6.735 6.630 5.526
4.453 4.434 4.416 4.398 4.376 3.741 3.707
1.448 1.416 1.400 1.399 1.381 1.341 1.283 1.260
1.00 0.29 0.38 1.19 5.62 6.43 1.40 0.40 0.33 1.00 2.67 2.95 0.79 4.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
164.348 161.924 161.697 159.624 132.633 131.974 131.871 128.821 128.723 128.075 127.499 125.811 121.958 114.898 112.930 110.274 81.704 63.075 62.389 60.230 55.595 55.457 14.224 14.138


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
O
N
H
CO2Me
7
7.307
7.302
7.286
7.283
7.011
7.009
6.992
6.923
6.917
6.870
6.863
6.859
6.852
6.842
6.839
6.835
6.553
6.547
6.530
6.509
5.404
3.908
3.729
2.488
2.483
2.455
2.451
2.145
2.113
1.851
1.10
1.23
1.02
2.04
1.98
1.00
2.84
3.10
1.18
1.13
3.06
f1 (ppm)


169.12
153.10
152.09
133.64
130.62
129.54
127.16
125.35
121.19
117.01
114.70
111.85
110.33
83.18
55.76
53.15
36.01
33.31
23.18
f1 (ppm)