Supporting Information

Oxidative N-heterocyclic carbene catalyzed [3+3] annulation reaction of enals with benzofuran-3-ones: efficient access to benzofuran fused δ-lactones

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1. General Information

NMR spectra were obtained in $CDCl_3$ using TMS as the internal standard at 400 (for ^1H NMR) or 100 MHz (for ^{13}C NMR), respectively. ^1H NMR spectra: J-values are reported in Hz. Organic solvents used were treated by general methods. Commercially obtained reagents were used without further purification. Column chromatography was performed using Huanghai 300-400 mesh silica gel at increased pressure. HRMS (m/z) were measured using Thermo Scientific™ Q Exactive. The benzofuran-3-one **1**[1] and the NHC precursor **E**[2] were prepared according to literature methods.

1. D. Wu, H. Mei, P. Tan, W. Lu, J. Zhu, W. Wang, J. Huang and J. Li, *Tetrahedron letters*, 2015, **56**, 4383–4387.
2. F. Romanov-Michailidis, C. Besnard and A. Alexakis, *Organic letters*, 2012, **14**, 4906–4909.

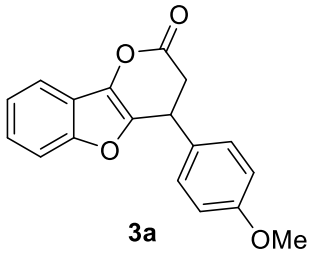
General procedure for the NHC-catalyzed annulation of benzofuran-3-ones 1 with enals 2.

Under N_2 atmosphere, benzofuran-3-ones **1** (0.1 mmol), α,β-unsaturated aldehydes **2** (0.12 mmol), NHC precursor **E** (0.01 mmol), DQ (0.12 mmol) and K_2CO_3 (0.01 mmol) were successively added into a 10 ml reaction tube, then dry toluene (1 ml) was added with stirring. The resulting mixture was continuously stirred at rt. After completion and removal of the solvent, the product **3** was obtained by column chromatography on a silica gel column eluting with petroleum ether-ethyl acetate mixture (PE:EA = 5:1) in 47% - 99% yields.

A typical procedure for one-pot stepwise reaction to obtain benzofuran fused pyraones.

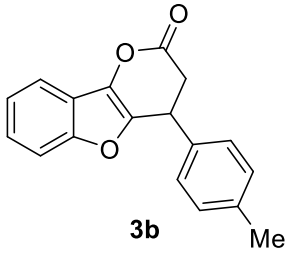
Under standard conditions, the reaction between benzofuran-3-ones **1** and α,β-unsaturated aldehydes **2** was monitored by TLC. After completion DDQ (0.3 mmol) with toluene (1 ml) was added directly into the reaction mixture with stirring. The resulting mixture keepping stir at rt for the required period of time. The solvent was removed under reduced pressure and the product **4** was obtained by column chromatography on a silica gel column eluting with petroleum ether-ethyl acetate mixture (PE:EA = 5:1) in 93% - 96% yields.

2. The data of the products 3, 4



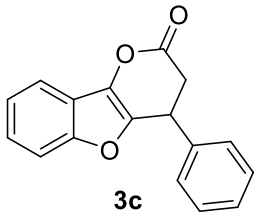
3a

4-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3a: white solid, 96%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 1H), 7.41 – 7.37 (m, 1H), 7.33 – 7.27 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.51 (dd, *J* = 7.5, 5.6 Hz, 1H), 3.79 (s, 3H), 3.38 (dd, *J* = 16.3, 7.7 Hz, 1H), 3.09 (dd, *J* = 16.3, 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 159.3, 153.3, 138.2, 135.3, 131.1, 128.2, 125.1, 123.4, 119.7, 117.8, 114.7, 112.0, 55.4, 37.9, 36.6; HRMS (FT-APCI): $[M - H]^-$ calcd for $C_{18}H_{13}O_4$-: 293.0819; found: 293.0822.



3b

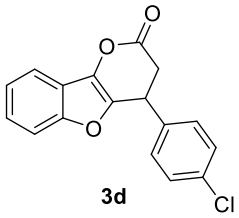
4-(*p*-tolyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3b: white solid, 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.27 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.53 (dd, *J* = 7.7, 5.5 Hz, 1H), 3.39 (dd, *J* = 16.4, 7.8 Hz, 1H), 3.11 (dd, *J* = 16.4, 5.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 153.3, 138.0, 137.9, 136.1, 135.3, 130.0, 126.9, 125.1, 123.4, 119.7, 117.8, 112.0, 37.8, 37.0, 21.1; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{18}H_{15}O_3$+: 279.1016; found: 279.1010.



3c

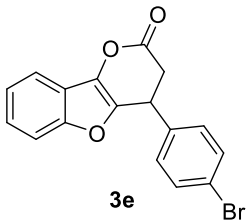
4-phenyl-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3c: white solid, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 1H), 7.41 – 7.28 (m, 6H), 7.24 – 7.22 (m, 2H), 4.56 (dd, *J* = 7.8,

5.3 Hz, 1H), 3.42 (dd, *J* = 16.4, 7.9 Hz, 1H), 3.13 (dd, *J* = 16.4, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 153.4, 139.1, 137.8, 135.5, 129.3, 128.1, 127.1, 125.2, 123.4, 119.7, 117.8, 112.0, 37.7, 37.3; HRMS (FT-APCI): [M - H]$^-$ calcd for $C_{17}H_{11}O_3$-: 263.0714; found: 263.0714.



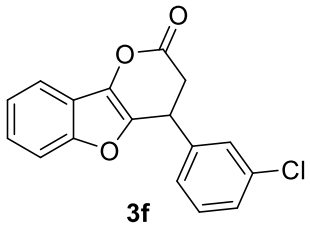
3d

4-(4-chlorophenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3d: white solid, 74%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.41 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.55 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.41 (dd, *J* = 16.4, 7.8 Hz, 1H), 3.09 (dd, *J* = 16.4, 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 153.4, 137.5, 137.1, 135.6, 134.0, 129.5, 128.5, 125.4, 123.5, 119.5, 117.9, 112.1, 37.6, 36.7; HRMS (FT-APCI): [M - H]$^-$ calcd for $C_{17}H_{10}ClO_3$-: 297.0324; found: 297.0327.



3e

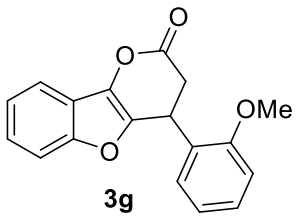
4-(4-bromophenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3e: white solid, 73%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.40 (m, 1H), 7.36 – 7.29 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.54 (dd, *J* = 7.7, 5.4 Hz, 1H), 3.41 (dd, *J* = 16.4, 7.8 Hz, 1H), 3.08 (dd, *J* = 16.4, 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 153.4, 138.1, 137.0, 135.7, 132.5, 128.8, 125.4, 123.6, 122.1, 119.5, 117.9, 112.1, 37.5, 36.8; HRMS (FT-APCI): [M - H]$^-$ calcd for $C_{17}H_{10}BrO_3$-: 340.9819; found: 340.9820.



3f

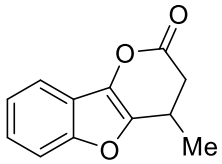
4-(3-chlorophenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3f: white solid, 64%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 1H), 7.43 – 7.41 (m, 1H), 7.37 – 7.28 (m, 4H), 7.22 (s, 1H), 7.13 – 7.09 (m, 1H), 4.55 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.42 (dd, *J* = 16.4, 7.9 Hz, 1H), 3.11 (dd,

J = 16.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 153.4, 141.0, 136.8, 135.8, 135.2, 130.6, 128.4, 127.4, 125.5, 125.2, 123.6, 119.5, 118.0, 112.1, 37.4, 37.0; HRMS (FT-ESI): $[M + H]^+$ calcd for $C_{17}H_{12}ClO_3$+: 299.0469; found: 299.0463.



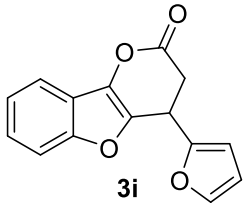
3g

4-(2-methoxyphenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3g: white solid, 88%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 1H), 7.38 – 7.53 (m, 1H), 7.30 – 7.27 (m, 3H), 7.13 – 7.11 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 4.64 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.77 (s, 3H), 3.35 (dd, *J* = 16.7, 8.9 Hz, 1H), 3.08 (dd, *J* = 16.7, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 157.1, 153.2, 137.0, 135.2, 129.4, 128.9, 127.4, 124.8, 123.2, 120.9, 119.9, 117.7, 111.9, 111.0, 54.8, 35.8, 34.2; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{18}H_{15}O_4$+: 295.0965; found: 295.0961.



3h

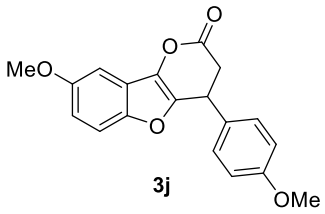
4-methyl-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3h: white solid, 98%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 1H), 7.44 – 7.42 (m, 1H), 7.33 – 7.25 (m, 2H), 3.53 – 3.39 (m, 1H), 3.14 (dd, *J* = 16.2, 6.9 Hz, 1H), 2.73 (dd, *J* = 16.2, 8.0 Hz, 1H), 1.44 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 153.0, 140.5, 133.9, 124.8, 123.3, 119.8, 117.6, 111.8, 37.3, 26.2, 18.5; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{12}H_{11}O_3$+: 203.0703; found: 203.0700.



3i

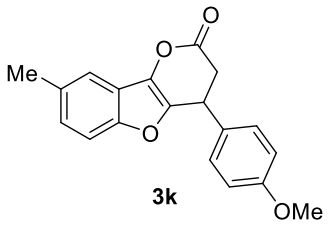
4-(furan-2-yl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3i: white solid, 98%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.0 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 0.9 Hz, 1H), 7.36 – 7.28 (m, 2H), 6.33 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 4.65 (dd, *J* = 7.3, 4.9

Hz, 1H), 3.32 (qd, *J* = 16.3, 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 153.3, 151.0, 142.9, 135.5, 135.3, 125.4, 123.5, 119.6, 117.9, 112.1, 110.6, 107.0, 34.7, 31.2; HRMS (FT-APCI): [M + H]$^+$ calcd for $C_{15}H_{11}O_4$+: 255.0652; found: 255.0646.



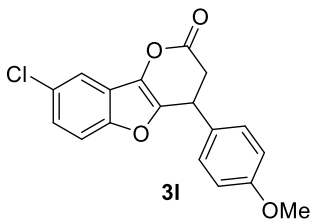
3j

8-methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3j: white solid, 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.91 – 6.87 (m, 3H), 4.49 (dd, *J* = 7.4, 5.8 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.37 (dd, *J* = 16.4, 7.7 Hz, 1H), 3.07 (dd, *J* = 16.4, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 159.3, 156.3, 148.2, 139.0, 135.3, 131.0, 128.2, 120.0, 114.6, 114.2, 112.7, 99.7, 55.9, 55.4, 38.0, 36.6; HRMS (FT-APCI): [M + H]$^+$ calcd for $C_{19}H_{17}O_5$+: 325.1071; found: 325.1067.



3k

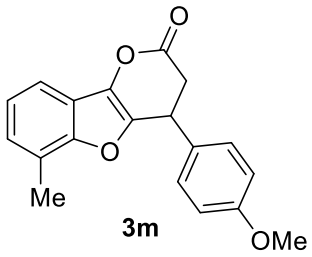
4-(4-methoxyphenyl)-8-methyl-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3k: white solid, 62%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.14 – 7.10 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.49 (dd, *J* = 7.5, 5.6 Hz, 1H), 3.79 (s, 3H), 3.37 (dd, *J* = 16.3, 7.7 Hz, 1H), 3.07 (dd, *J* = 16.3, 5.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.3, 151.8, 138.2, 135.0, 133.1, 131.1, 128.2, 126.4, 119.7, 117.5, 114.6, 111.5, 55.4, 38.0, 36.6, 21.4; HRMS (FT-APCI): [M + H]$^+$ calcd for $C_{19}H_{17}O_4$+: 309.1121; found: 309.1115.



3l

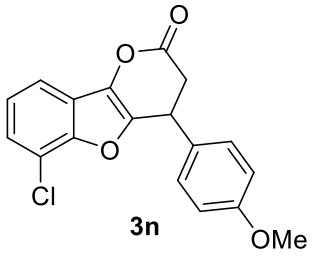
8-chloro-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3l: white solid, 52%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.51 (dd, *J* = 7.5, 5.7 Hz, 1H), 3.79 (s,

3H), 3.38 (dd, *J* = 16.4, 7.7 Hz, 1H), 3.09 (dd, *J* = 16.4, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 159.4, 151.6, 139.9, 134.6, 130.6, 129.2, 128.1, 125.4, 120.9, 117.5, 114.7, 113.1, 55.4, 37.8, 36.6; HRMS (FT-APCI): $[M - H]^-$ calcd for $C_{18}H_{12}ClO_4$-: 327.0430; found: 327.0432.



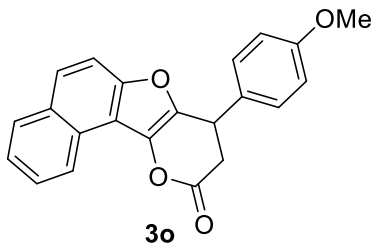
3m

4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3m: white solid, 99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.11 (m, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.50 (dd, *J* = 7.7, 4.6 Hz, 1H), 3.79 (s, 3H), 3.38 (dd, *J* = 16.3, 7.9 Hz, 1H), 3.07 (dd, *J* = 16.3, 4.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 159.2, 152.3, 137.9, 135.6, 131.4, 128.1, 126.1, 123.4, 122.2, 119.2, 115.2, 114.6, 55.4, 38.1, 36.52, 14.7; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{19}H_{17}O_4$+: 309.1121; found: 309.1115.



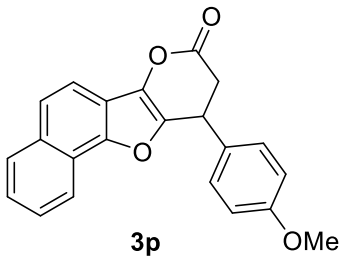
3n

6-chloro-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-2-one 3n: white solid, 70%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.55 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.79 (s, 3H), 3.40 (dd, *J* = 16.3, 7.9 Hz, 1H), 3.11 (dd, *J* = 16.3, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.4, 149.0, 139.4, 135.4, 130.8, 128.0, 125.4, 124.3, 121.3, 117.5, 116.4, 114.7, 55.4, 37.8, 36.4; HRMS (FT-APCI): $[M - H]^-$ calcd for $C_{18}H_{12}ClO_4$-: 327.0430; found: 327.0433.



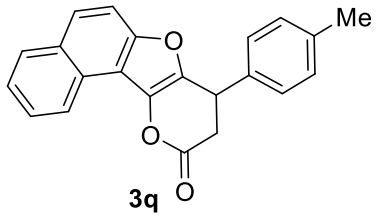
3o

8-(4-methoxyphenyl)-8,9-dihydro-10*H*-naphtho[1',2':4,5]furo[3,2-*b*]pyran-10-one 3o: white solid, 76%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.59 (dd, *J* = 7.4, 5.8 Hz, 1H), 3.79 (s, 3H), 3.44 (dd, *J* = 16.3, 7.7 Hz, 1H), 3.14 (dd, *J* = 16.3, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 159.3, 150.9, 137.34, 137.30, 131.3, 130.4, 128.4, 128.2, 126.9, 126.3, 126.0, 125.2, 124.4, 114.7, 113.8, 112.6, 55.4, 38.0, 36.7; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{22}H_{17}O_4$+: 345.1121; found: 345.1116.



3p

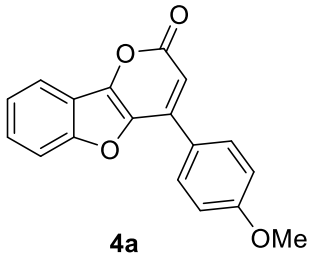
10-(4-methoxyphenyl)-9,10-dihydro-8*H*-naphtho[2',1':4,5]furo[3,2-*b*]pyran-8-one 3p: white solid, 47%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.63 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.80 (s, 3H), 3.44 (dd, *J* = 16.3, 7.8 Hz, 1H), 3.12 (dd, *J* = 16.3, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 159.3, 149.0, 137.3, 136.4, 131.7, 131.5, 128.6, 128.1, 126.8, 125.7, 124.2, 121.3, 119.7, 116.0, 115.0, 114.6, 55.4, 38.2, 36.7; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{22}H_{17}O_4$+: 345.1121; found: 345.1113.



3q

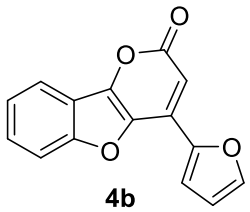
8-(*p*-tolyl)-8,9-dihydro-10*H*-naphtho[1',2':4,5]furo[3,2-*b*]pyran-10-one 3q: white solid, 64%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.55 – 7.51 (m, 2H), 7.17 (q, *J* = 8.2 Hz, 4H), 4.61 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.45 (dd, *J* = 16.3, 7.7 Hz, 1H), 3.16 (dd, *J* = 16.3, 5.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.9, 137.9, 137.4, 137.2, 136.3, 130.4, 130.0, 128.4, 127.0, 126.9,

126.3, 126.0, 125.2, 124.4, 113.8, 112.6, 37.8, 37.1, 21.1; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{22}H_{17}O_3$+: 329.1172; found: 329.1167.



4a

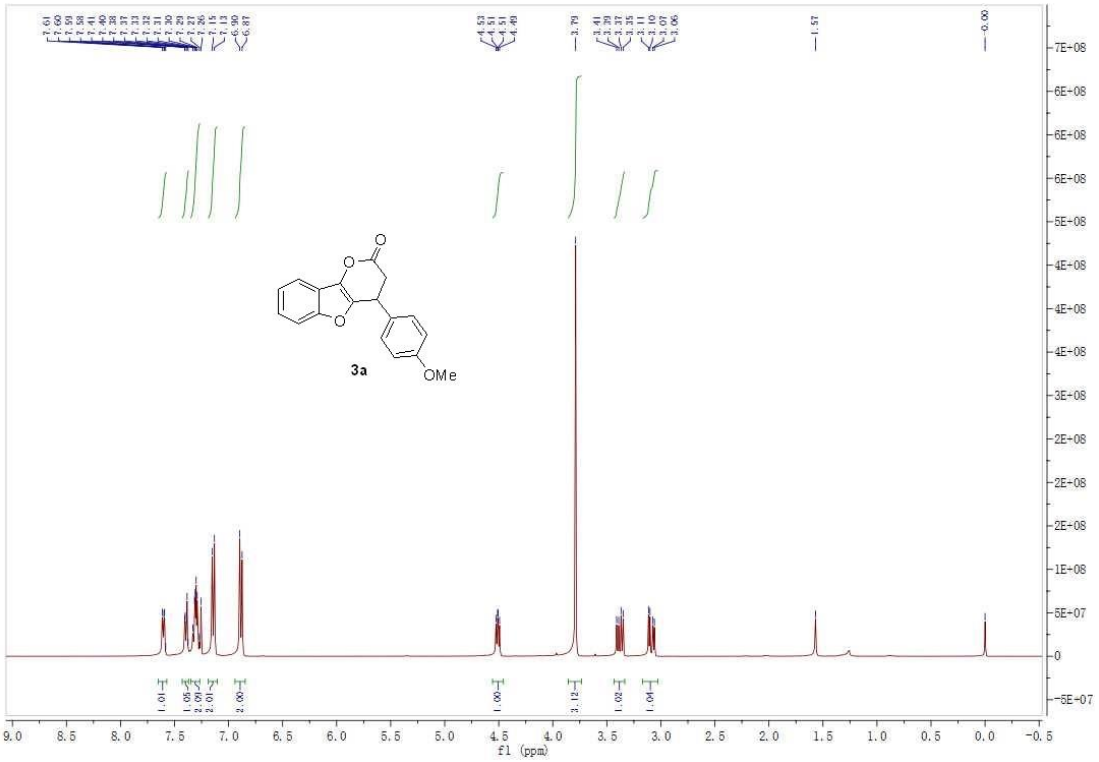
4-(4-methoxyphenyl)-2*H*-pyrano[3,2-*b*]benzofuran-2-one 4a: yellow solid, 93%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 126.2, 154.9, 145.3, 143.9, 136.7, 130.2, 128.4, 124.2, 123.7, 119.6, 118.2, 114.7, 112.7, 106.1, 55.6; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{18}H_{13}O_4$+: 293.0808; found: 293.0802.

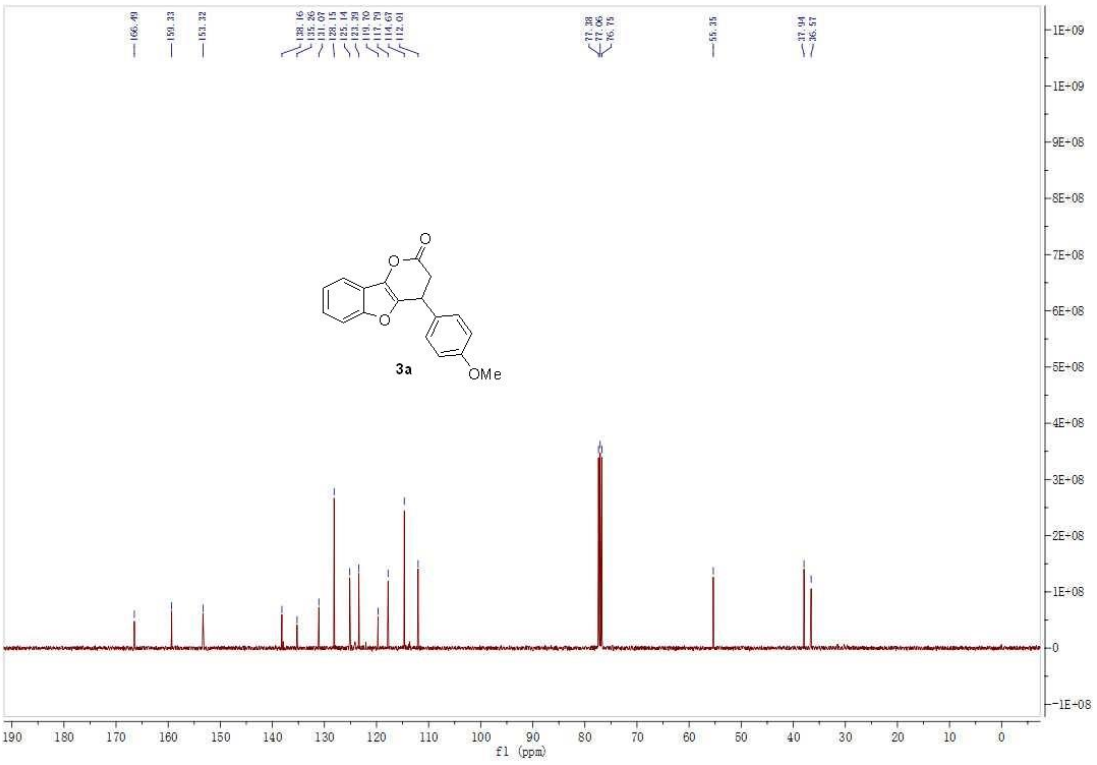


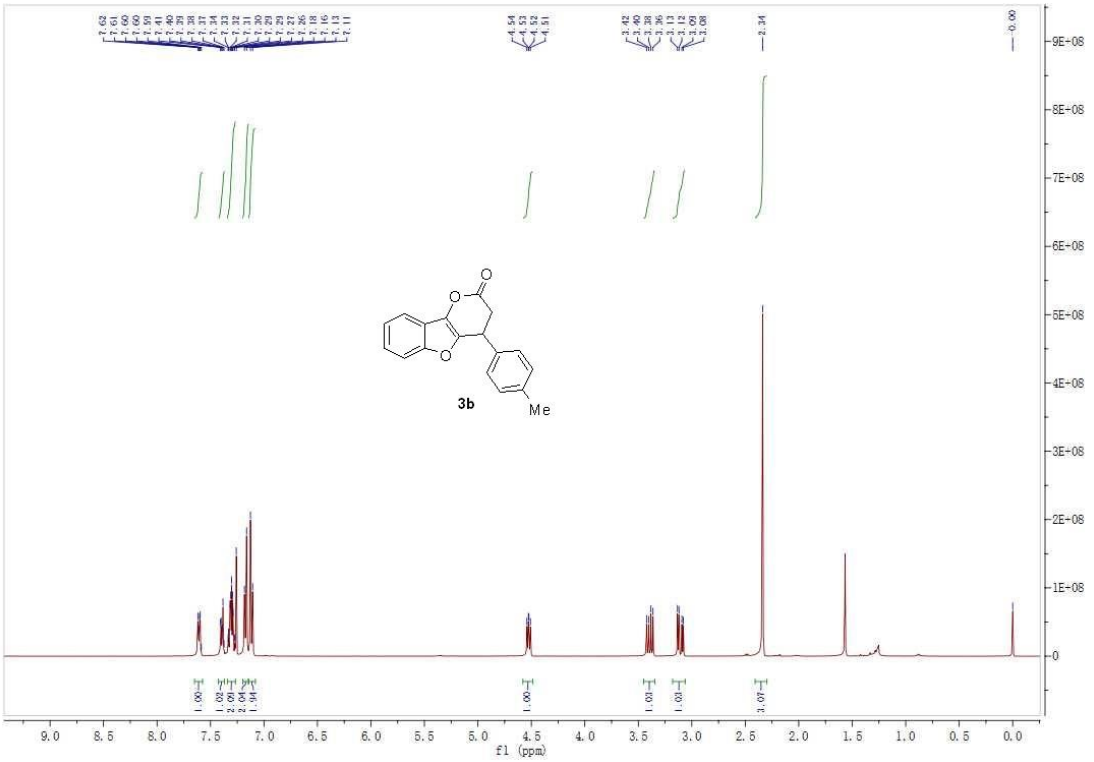
4b

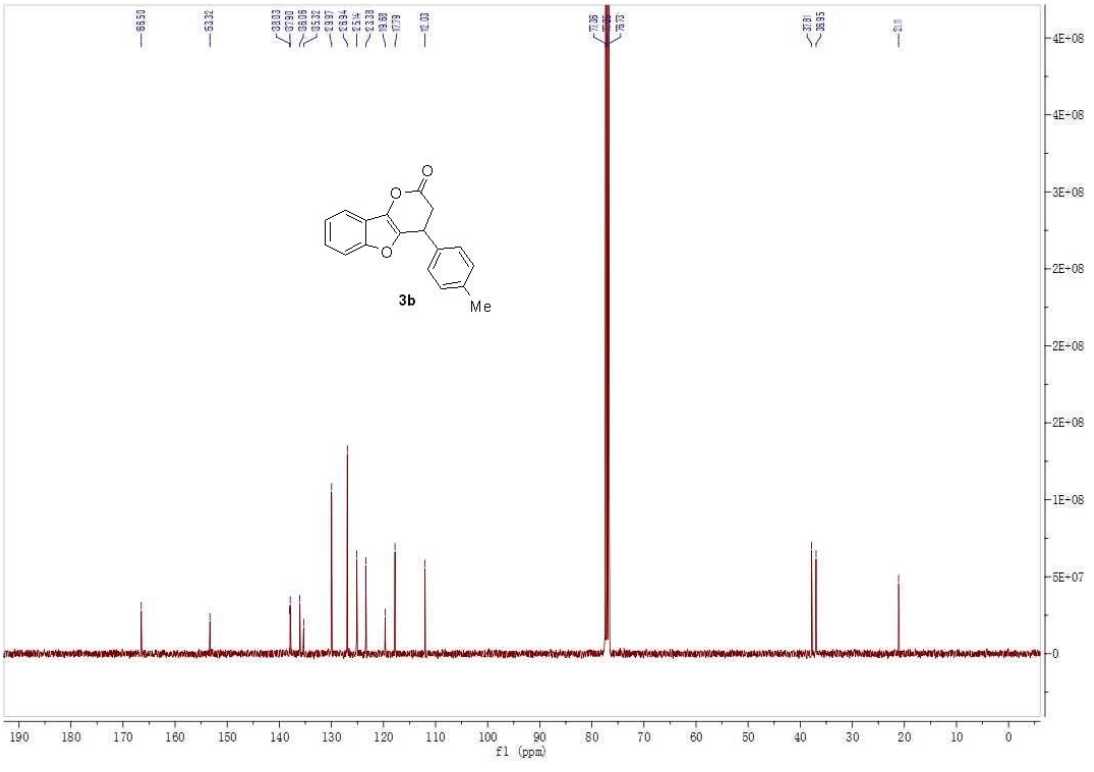
4-(furan-2-yl)-2*H*-pyrano[3,2-*b*]benzofuran-2-one 4b: yellow solid, 96%, 1H NMR (400 MHz, CDCl3) δ 7.82 (d, J = 7.8 Hz, 1H), 7.72 (s, 1H), 7.63 (d, J = 3.6 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 6.70 (dd, J = 3.2, 1.5 Hz, 1H), 6.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 154.9, 146.4, 145.0, 144.0, 134.2, 133.6, 128.4, 124.3, 119.6, 118.3, 113.2, 112.6, 102.1; HRMS (FT-APCI): $[M + H]^+$ calcd for $C_{15}H_9O_4$+: 253.0495; found: 253.0490.

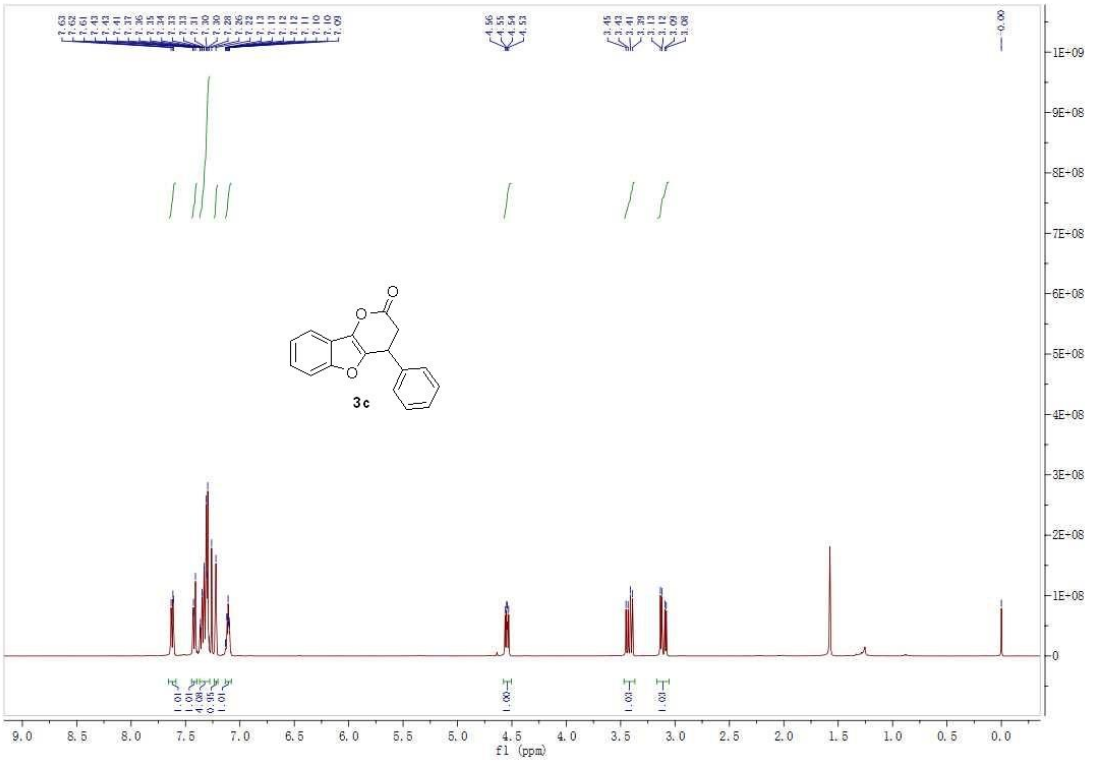
3. The NMR of 3, 4






3b
Me
f1 (ppm)


3b
Me
f1 (ppm)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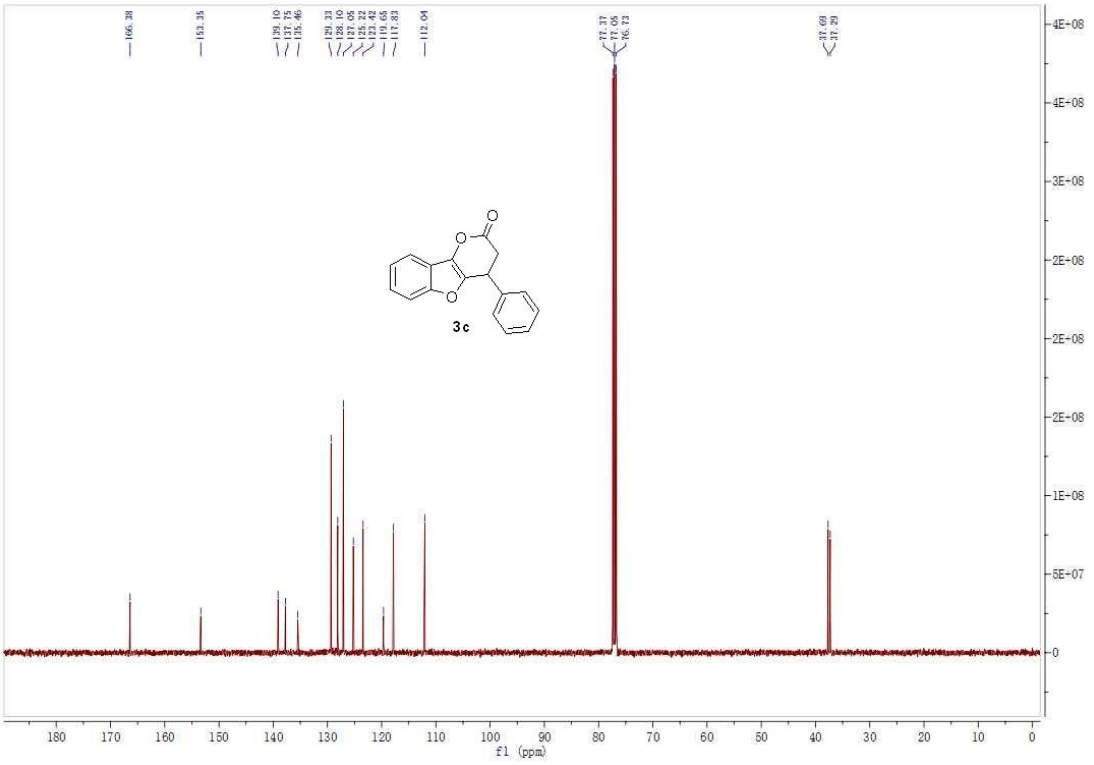
f1 (ppm)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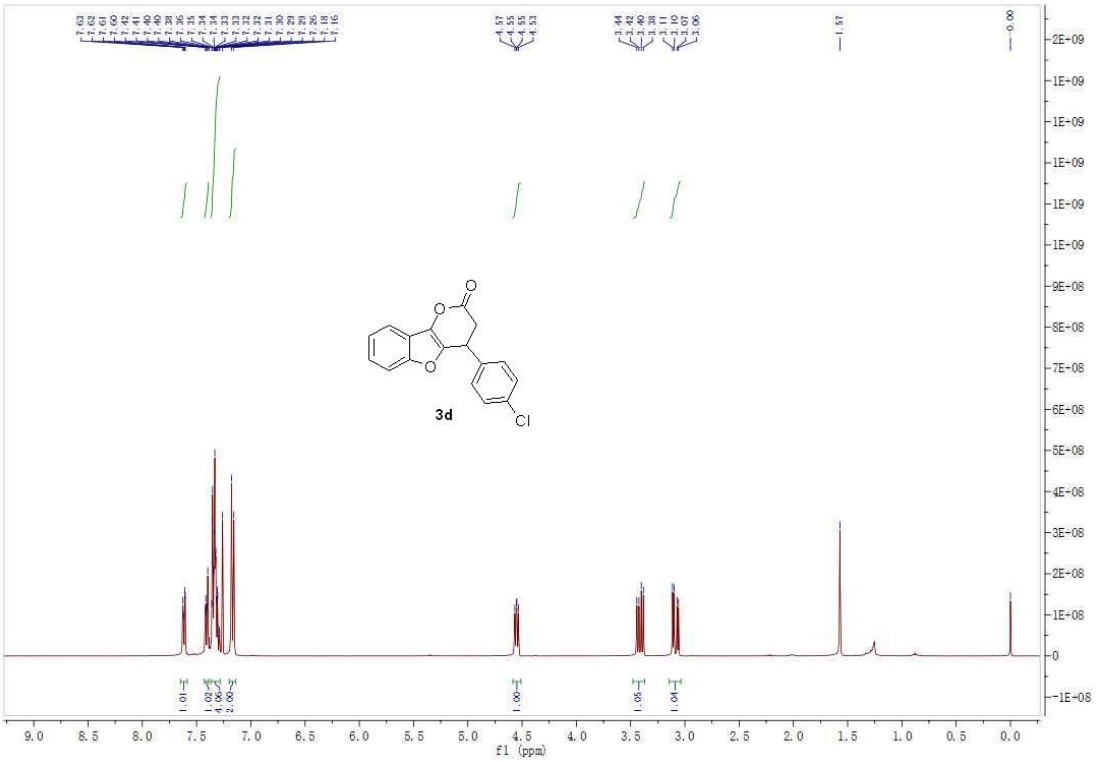
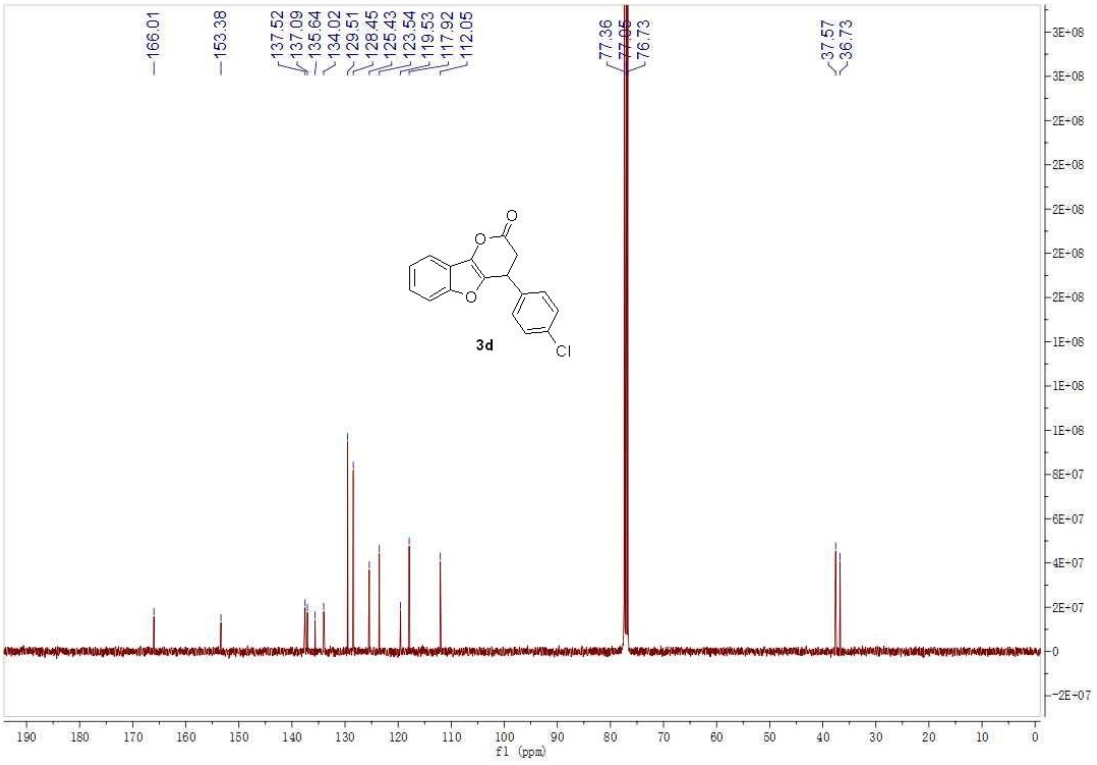
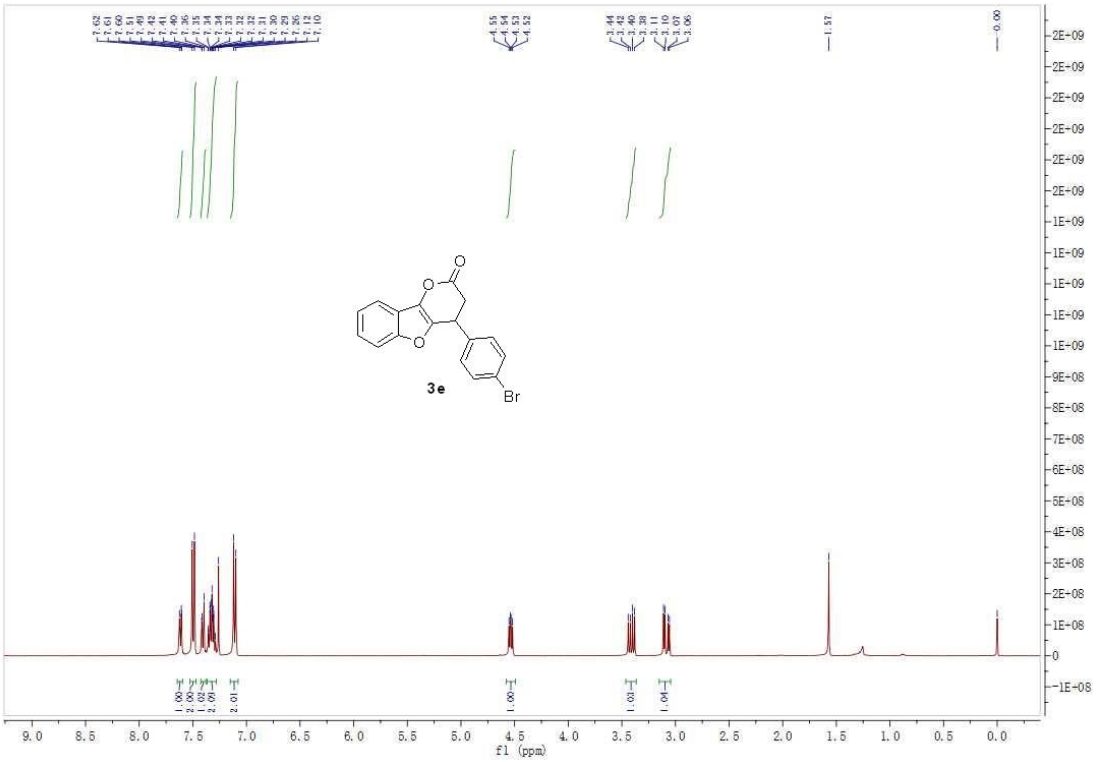
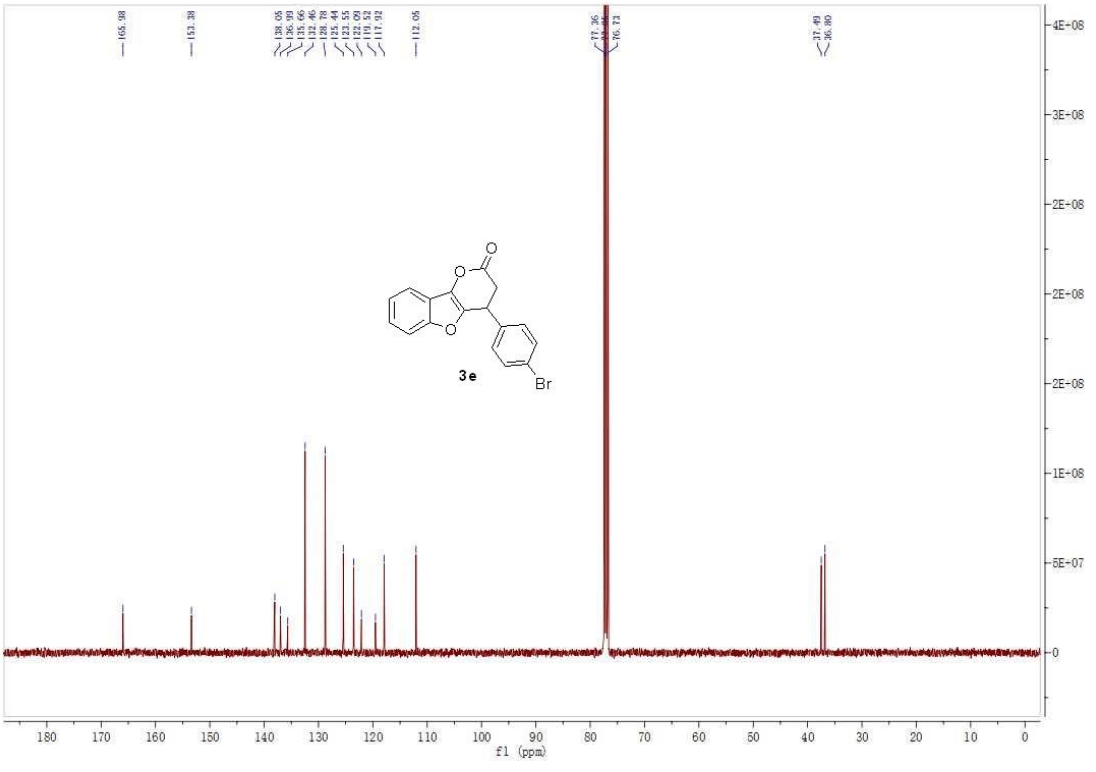
f1 (ppm)


3d
Cl
f1 (ppm)


166.01
153.38
137.52
137.09
135.64
134.02
129.51
128.45
125.43
123.54
119.53
117.92
112.05
77.36
77.05
76.73
37.57
36.73
3d
Cl
f1 (ppm)


3e
Br
f1 (ppm)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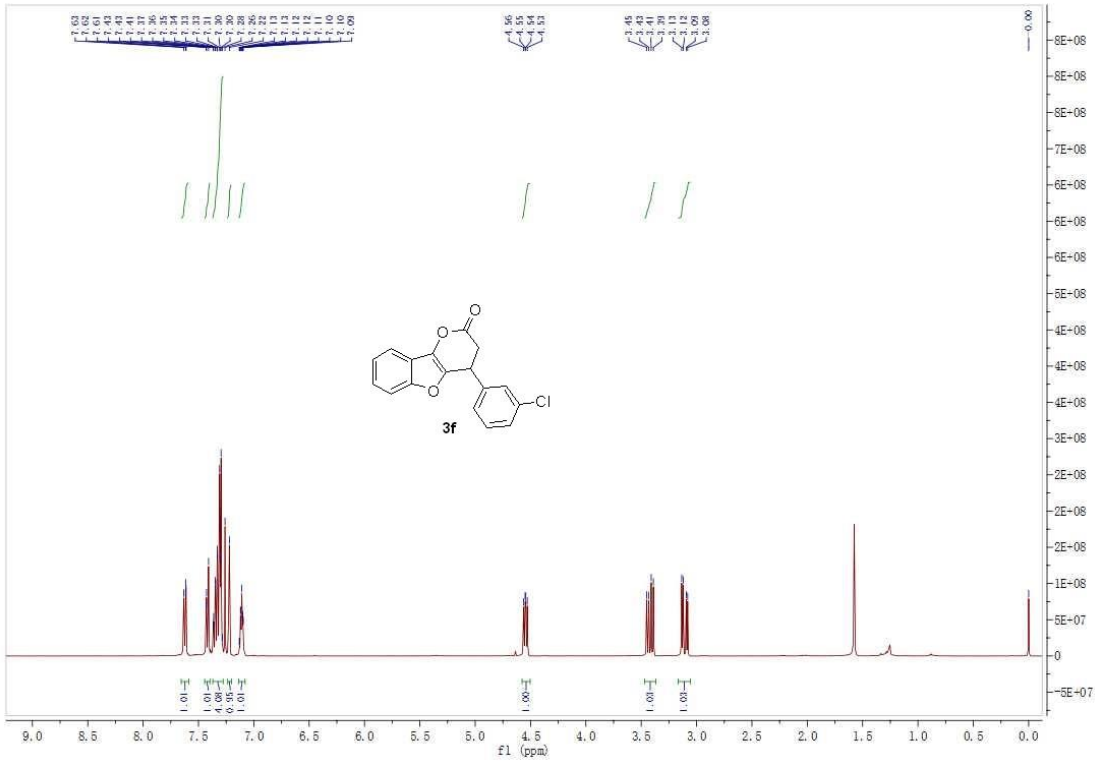
Br
f1 (ppm)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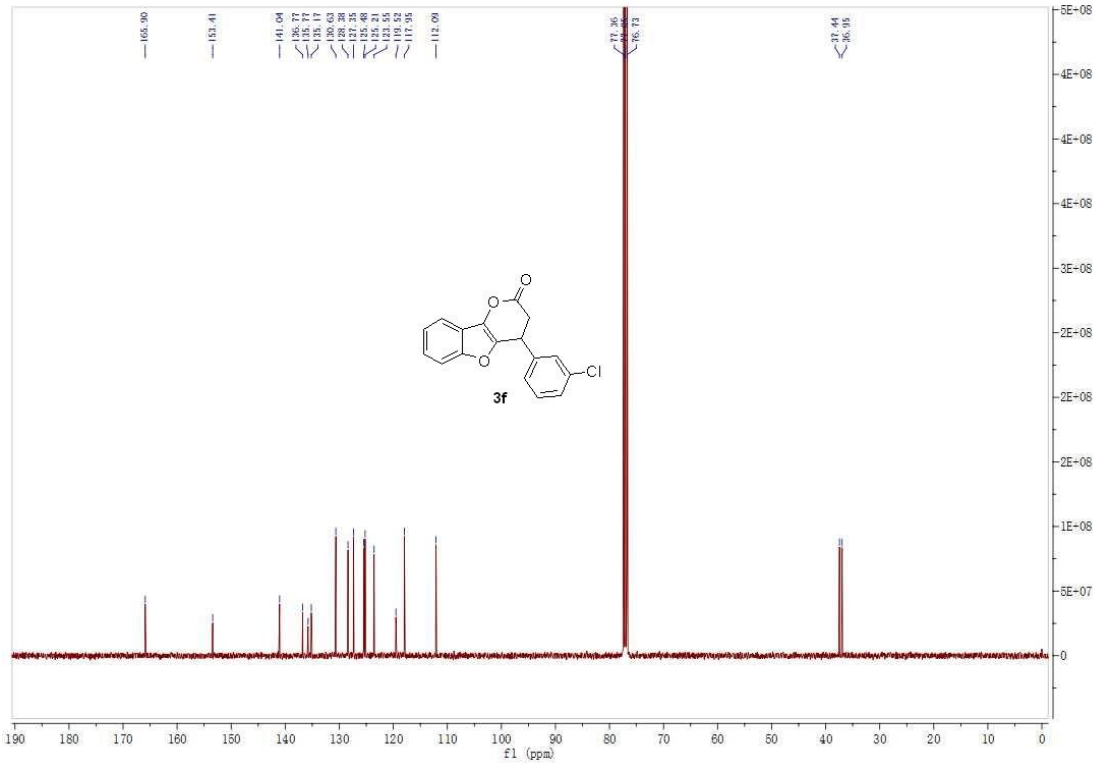
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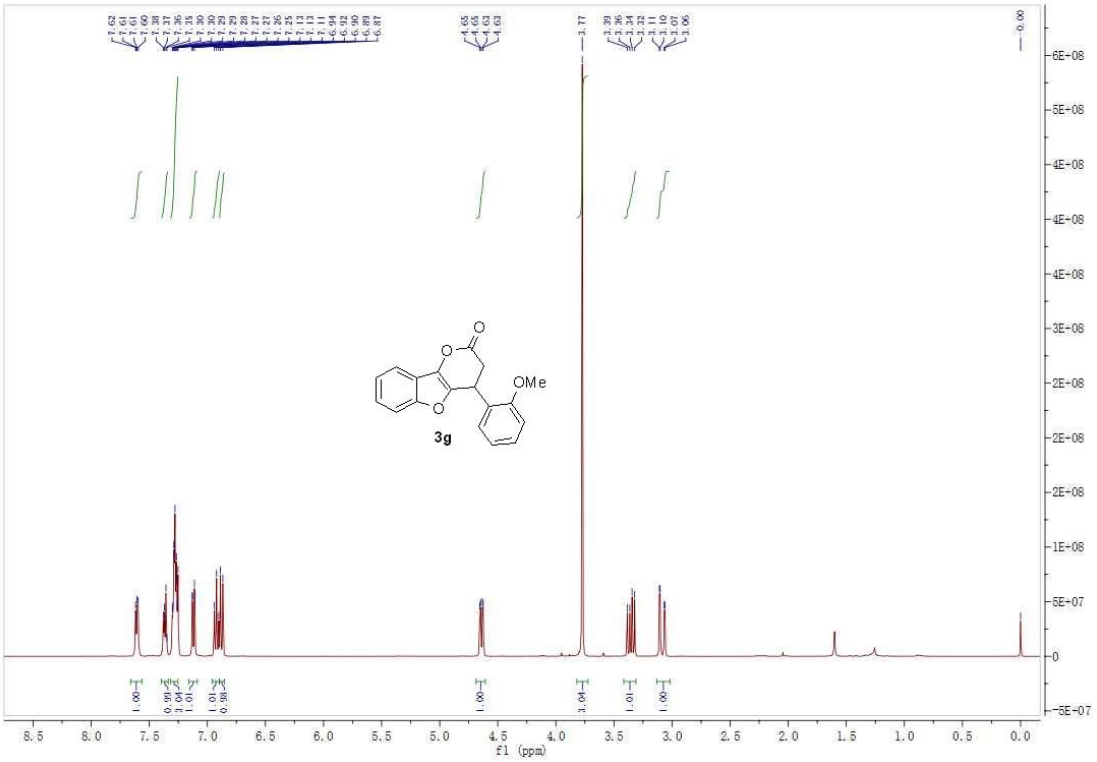
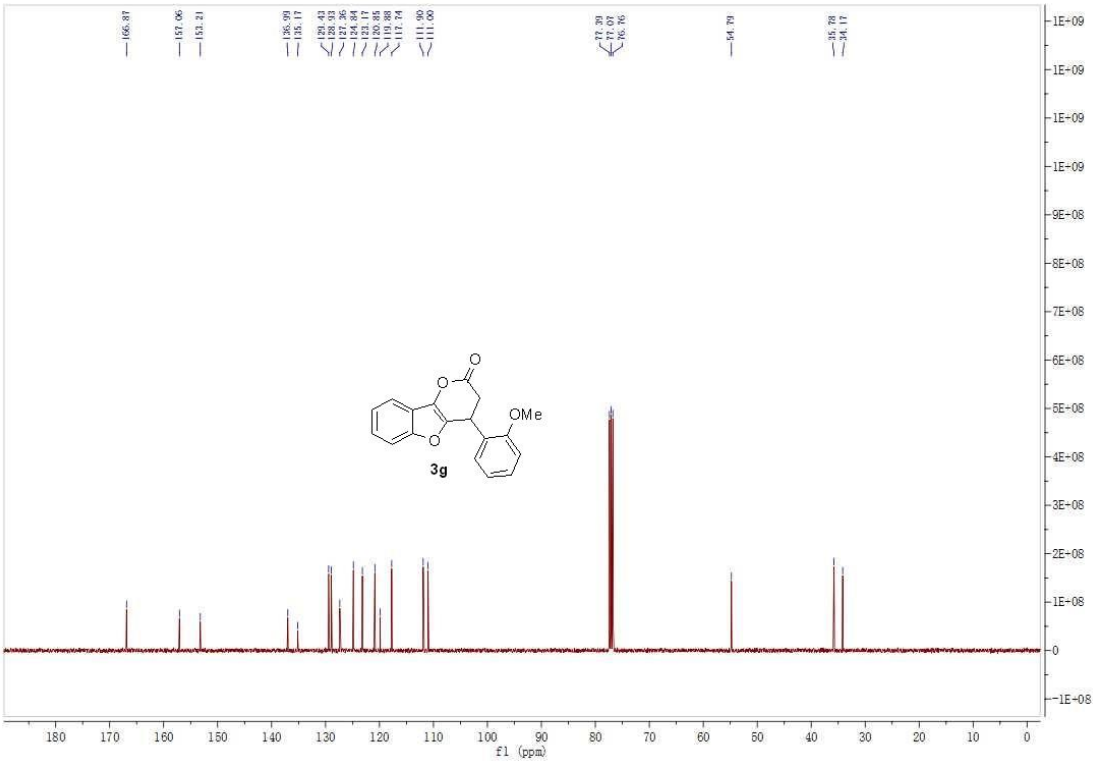

OMe
3g
f1 (ppm)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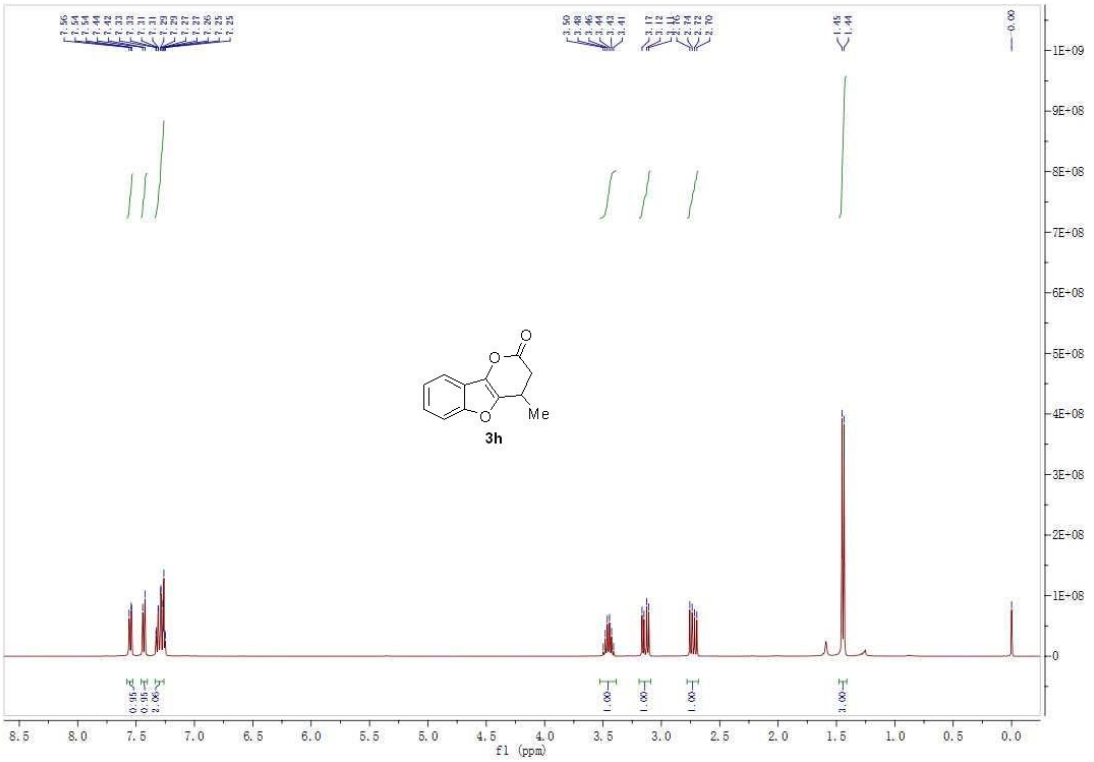
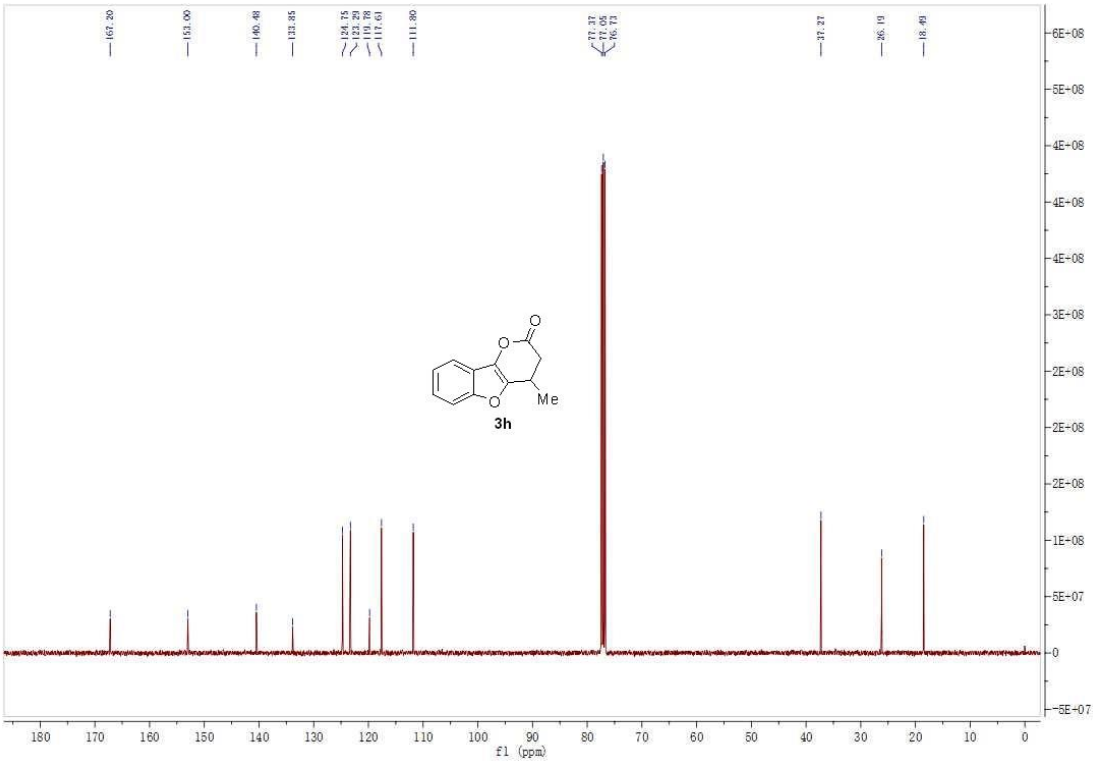
f1 (ppm)


Me
3h
f1 (ppm)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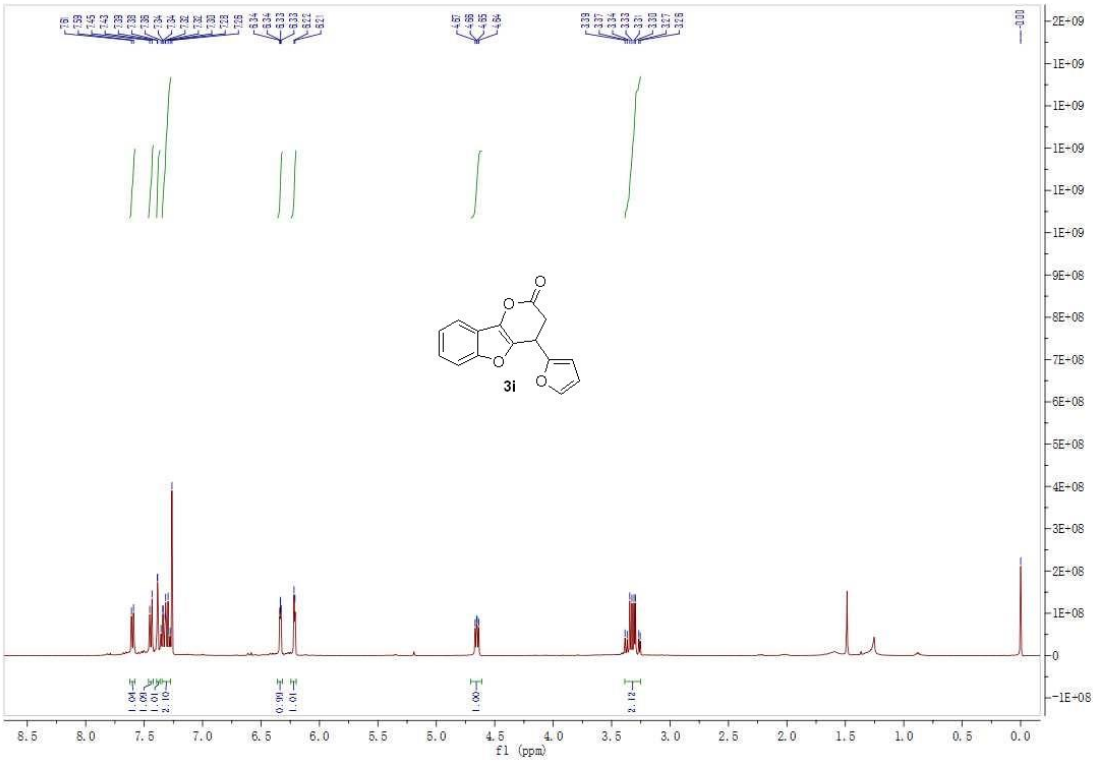
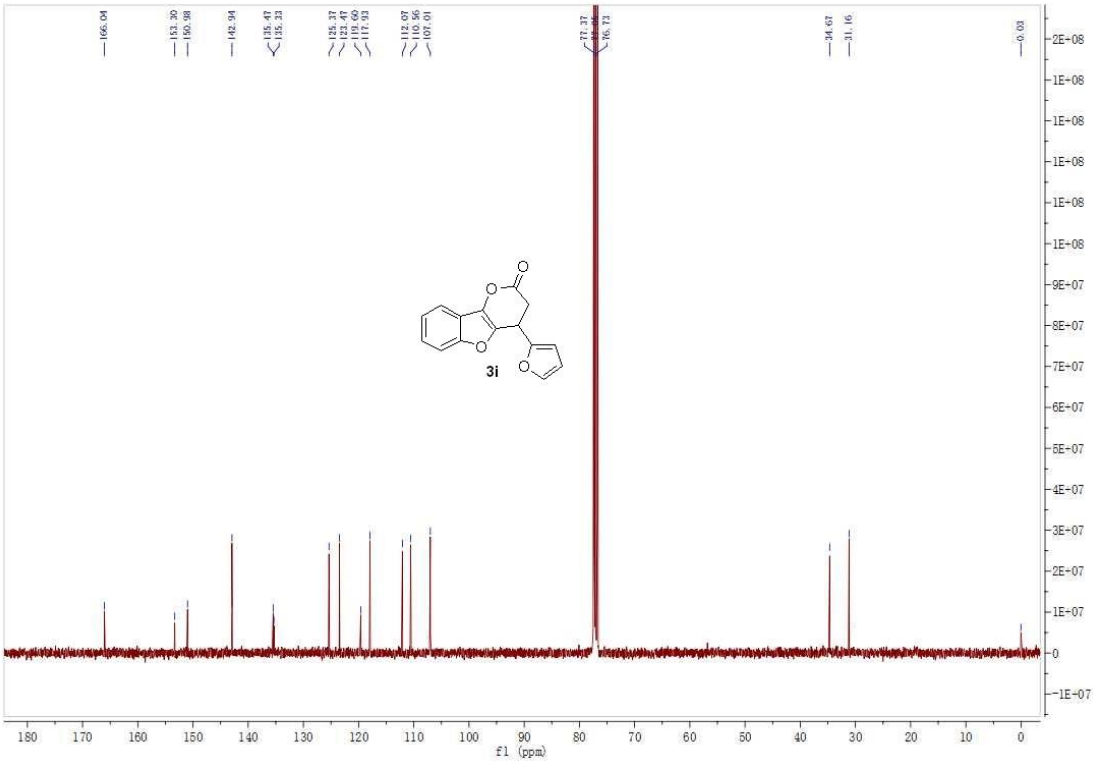
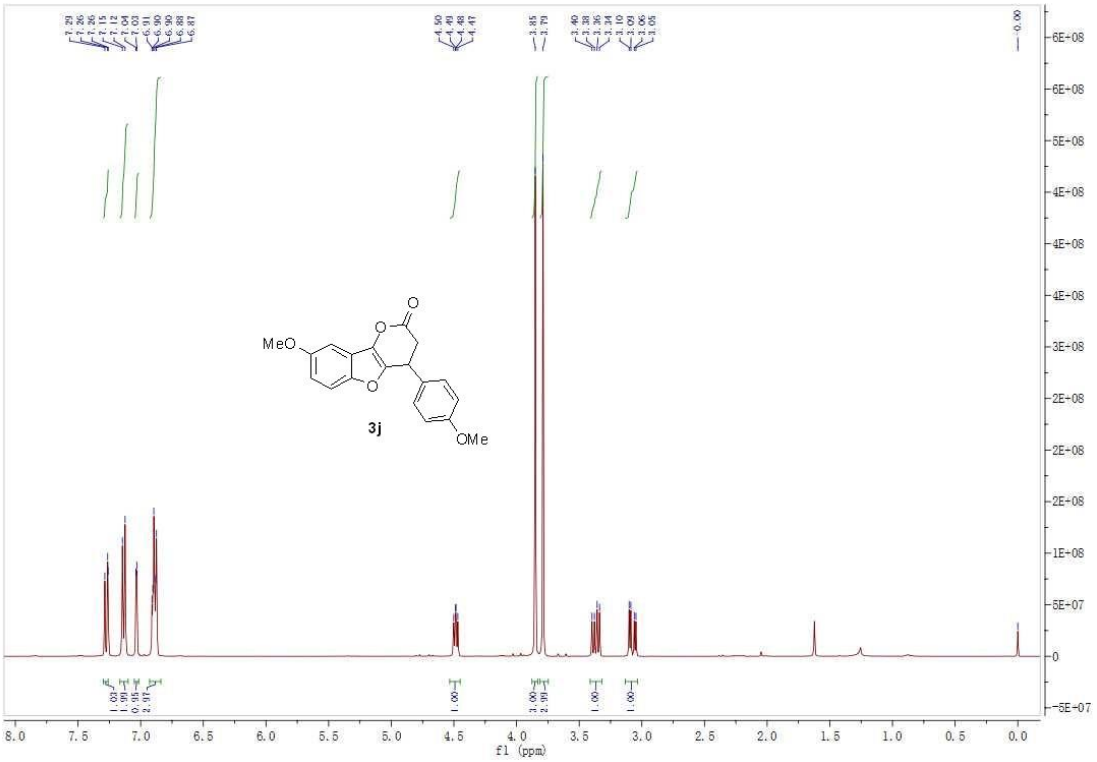
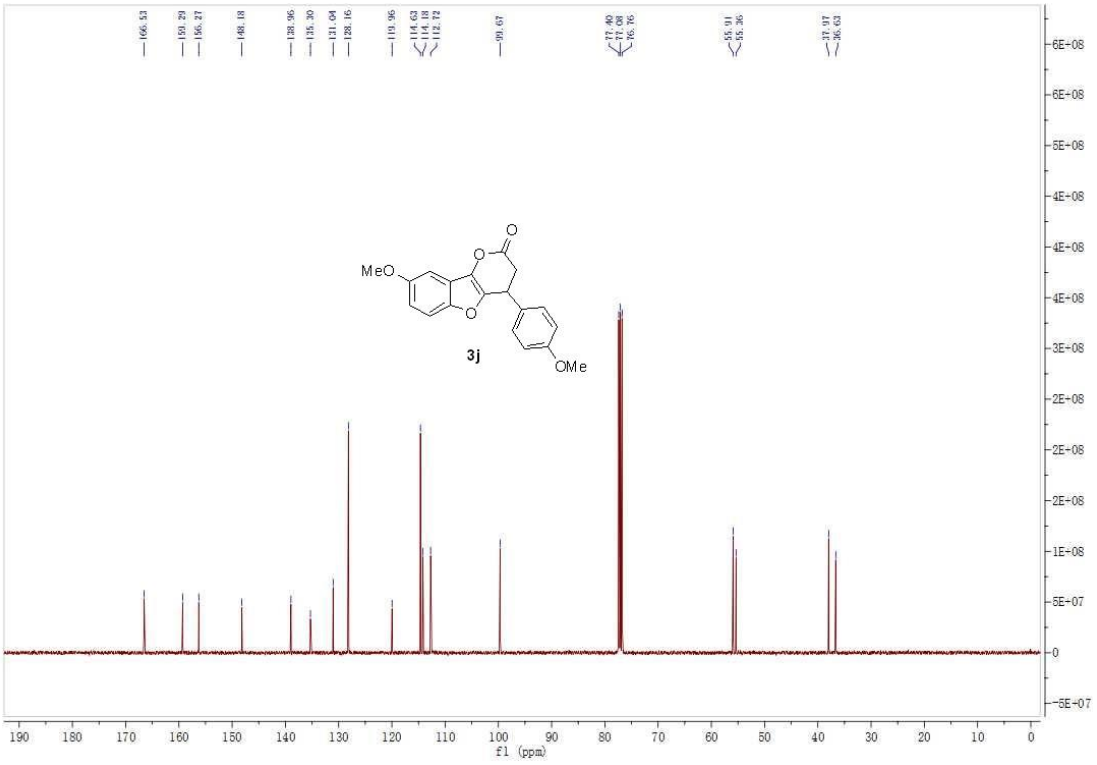
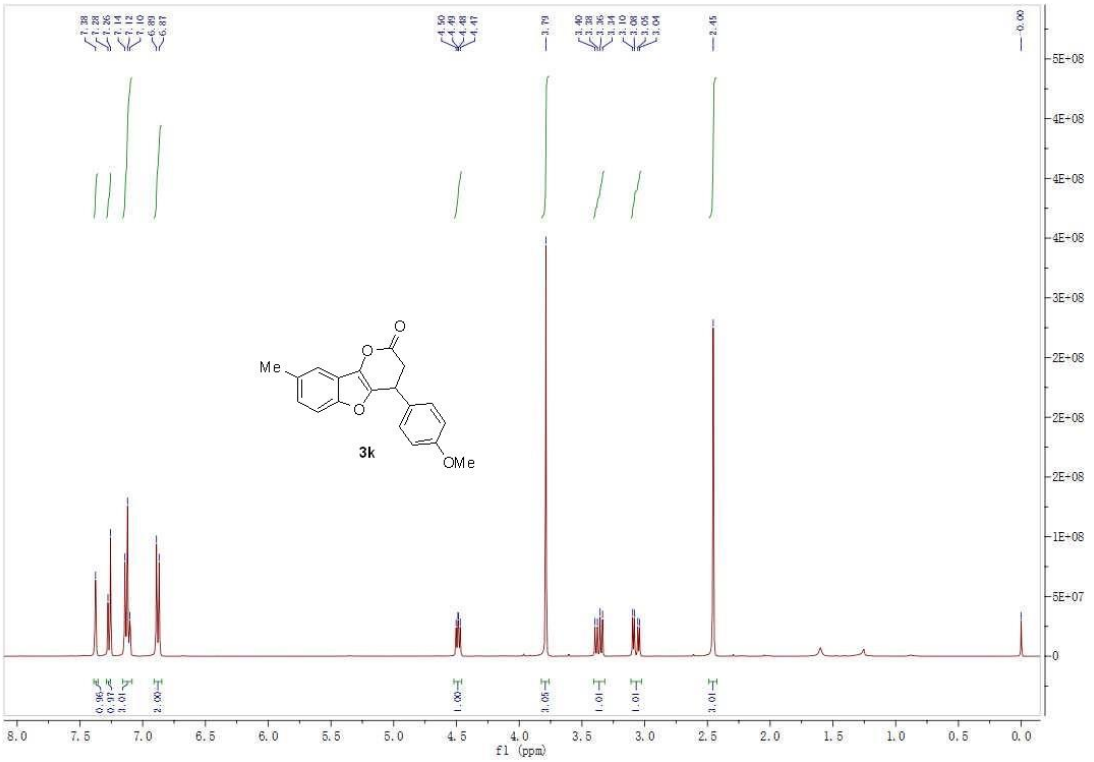
3h
f1 (ppm)

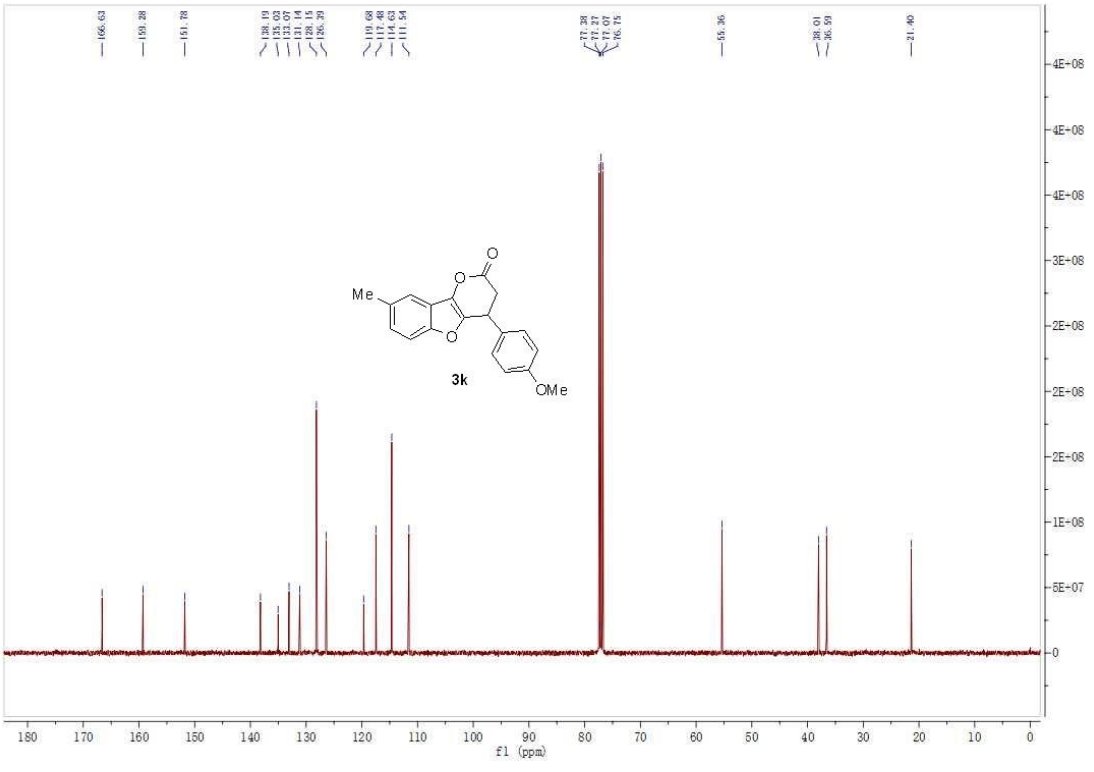

3i
f1 (ppm)


3i
f1 (ppm)


MeO
O
O
O
OMe
3j
f1 (ppm)


MeO
O
O
O
OMe
3j
f1 (ppm)


Me
O
O
O
OMe
3k
f1 (ppm)


Me
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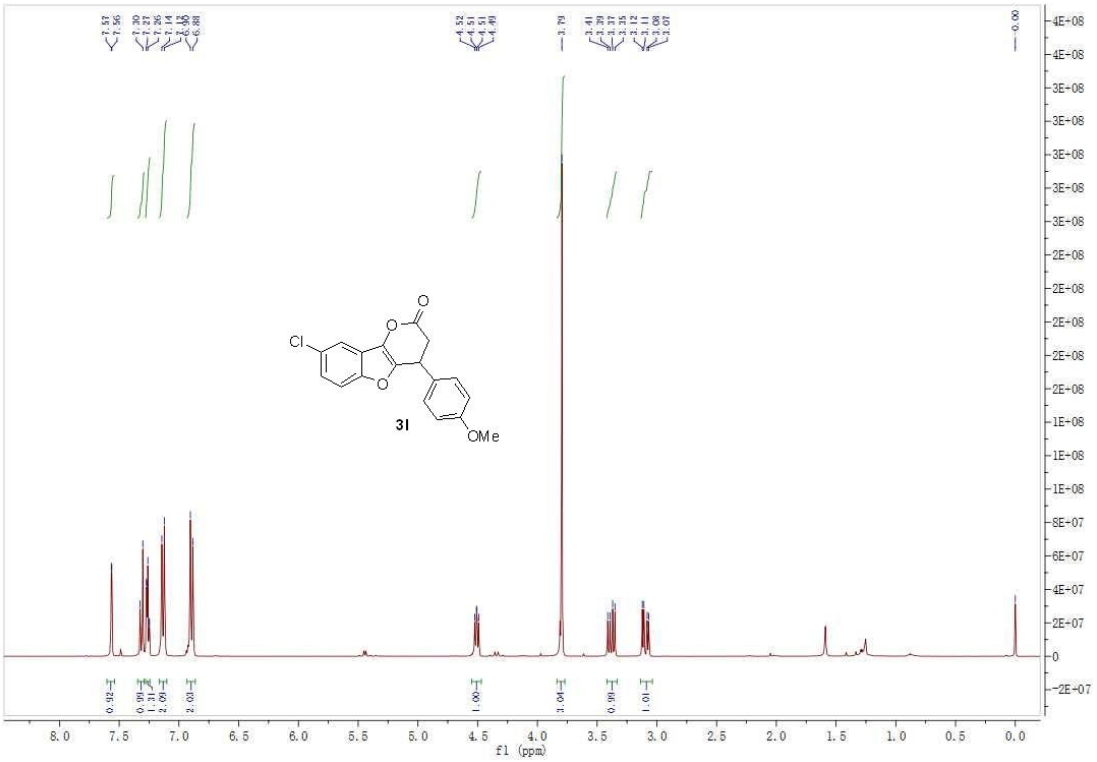
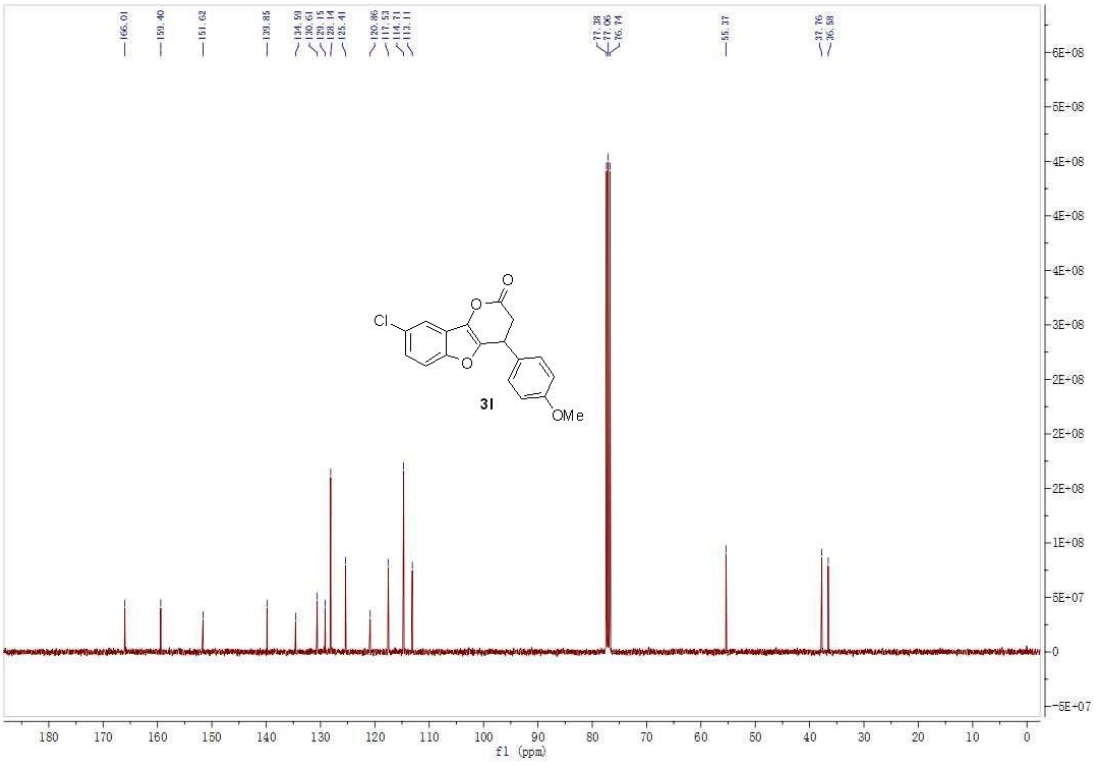
O
O
OMe
3k
f1 (ppm)


Cl
O
O
O
3l
OMe
f1 (ppm)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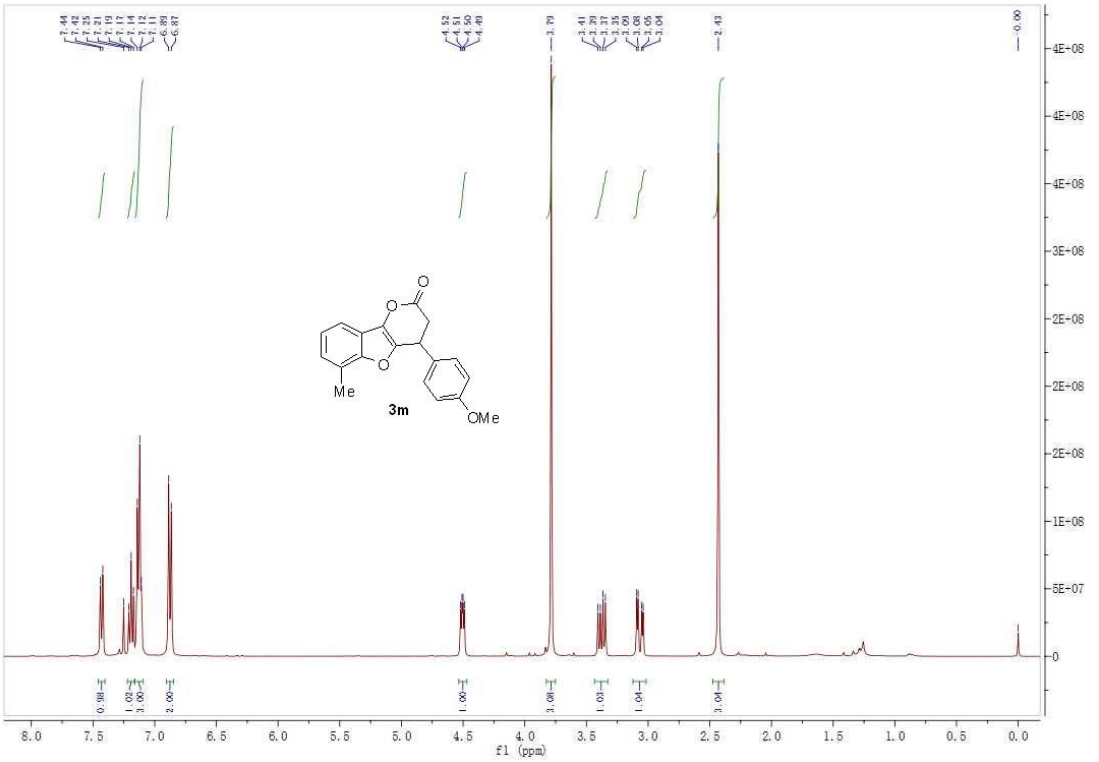
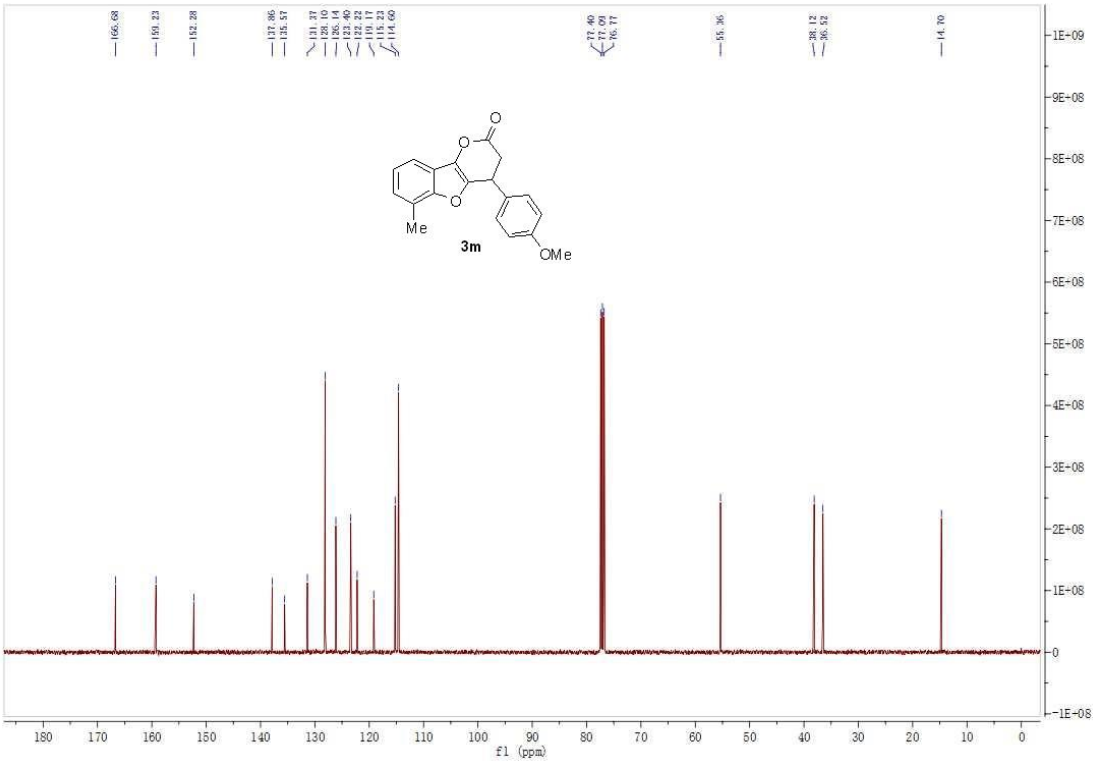
O
O
3l
OMe
f1 (ppm)


Me
3m
OMe
f1 (ppm)


Me
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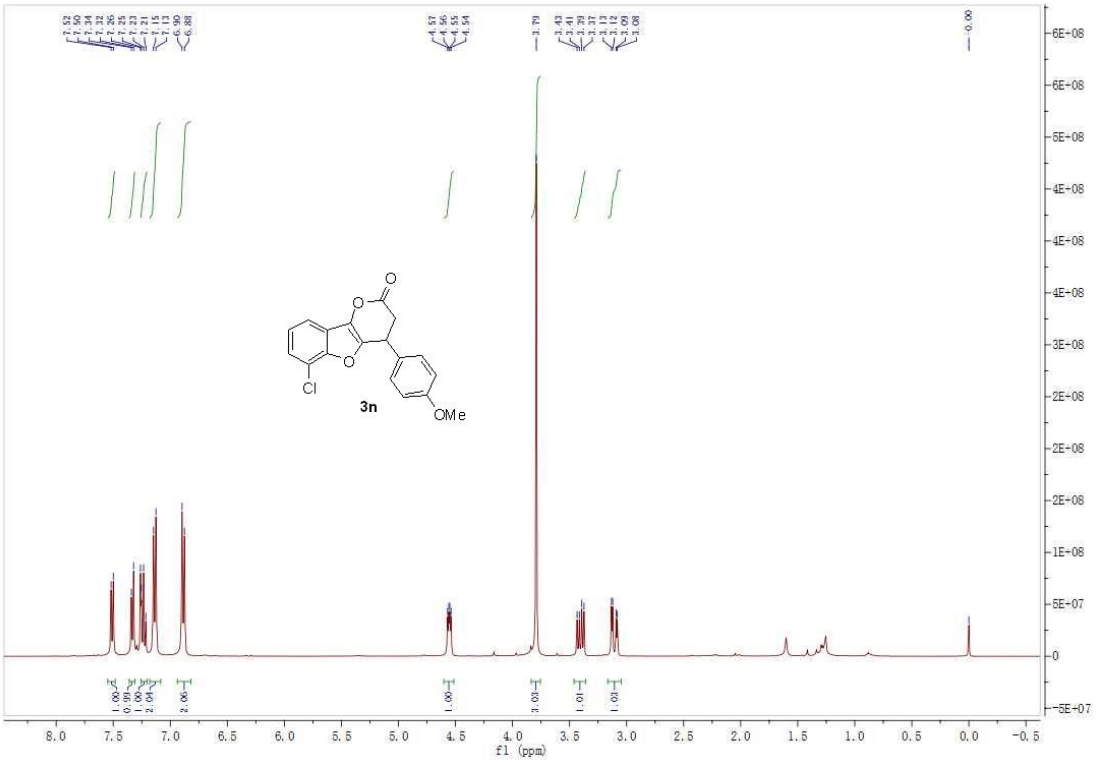
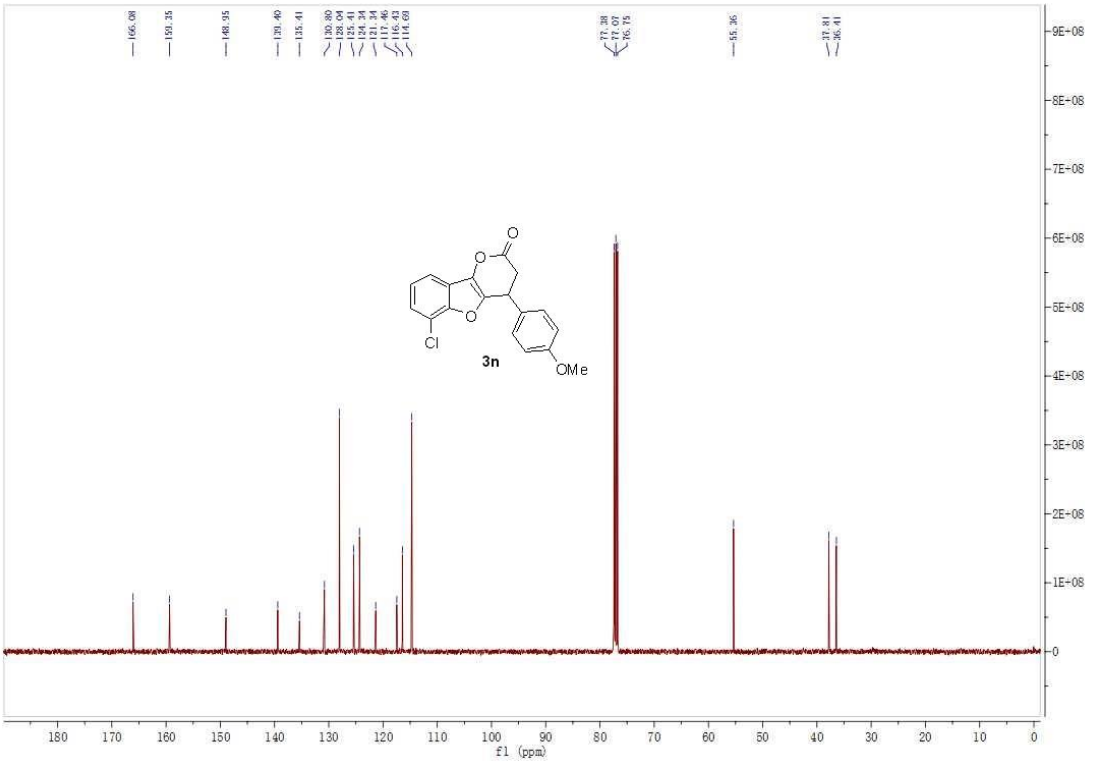
OMe
f1 (ppm)


3n
Cl
OMe
f1 (ppm)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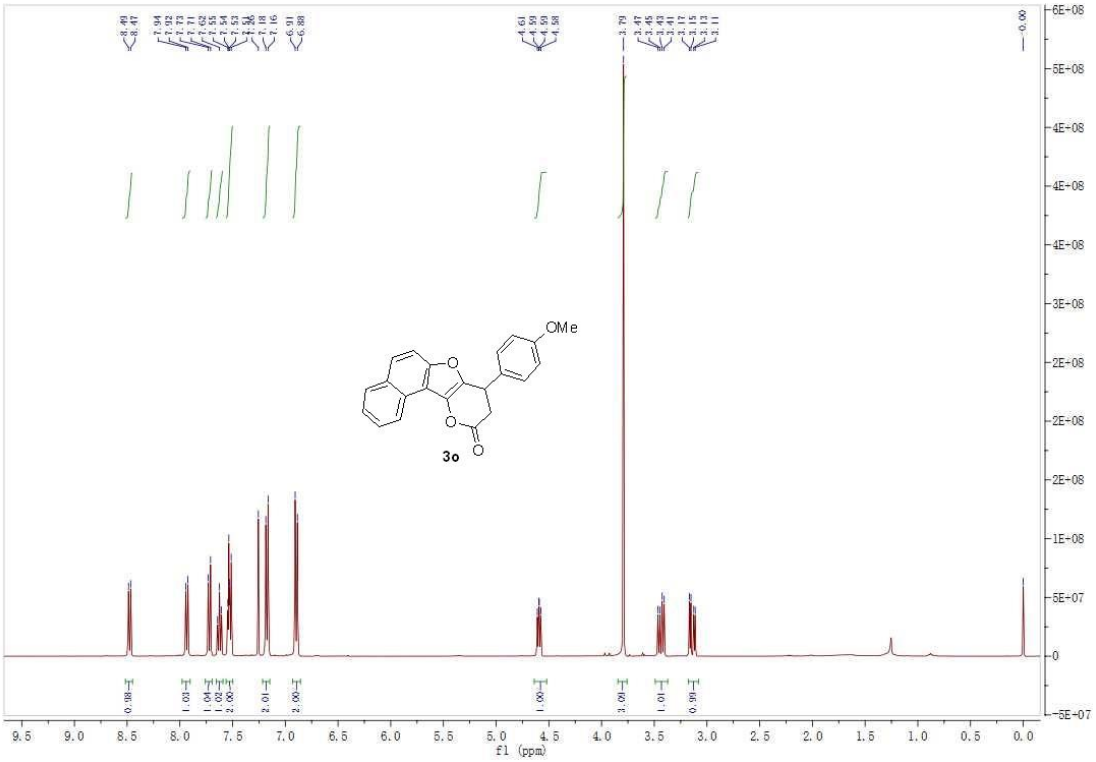
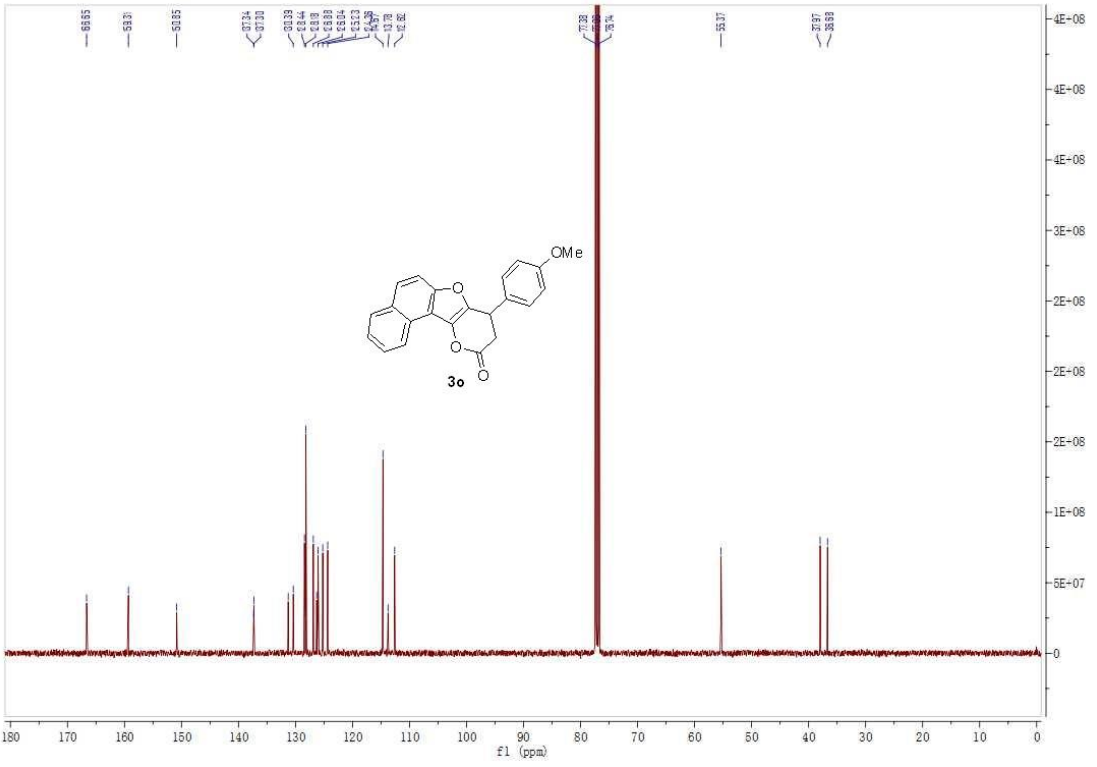
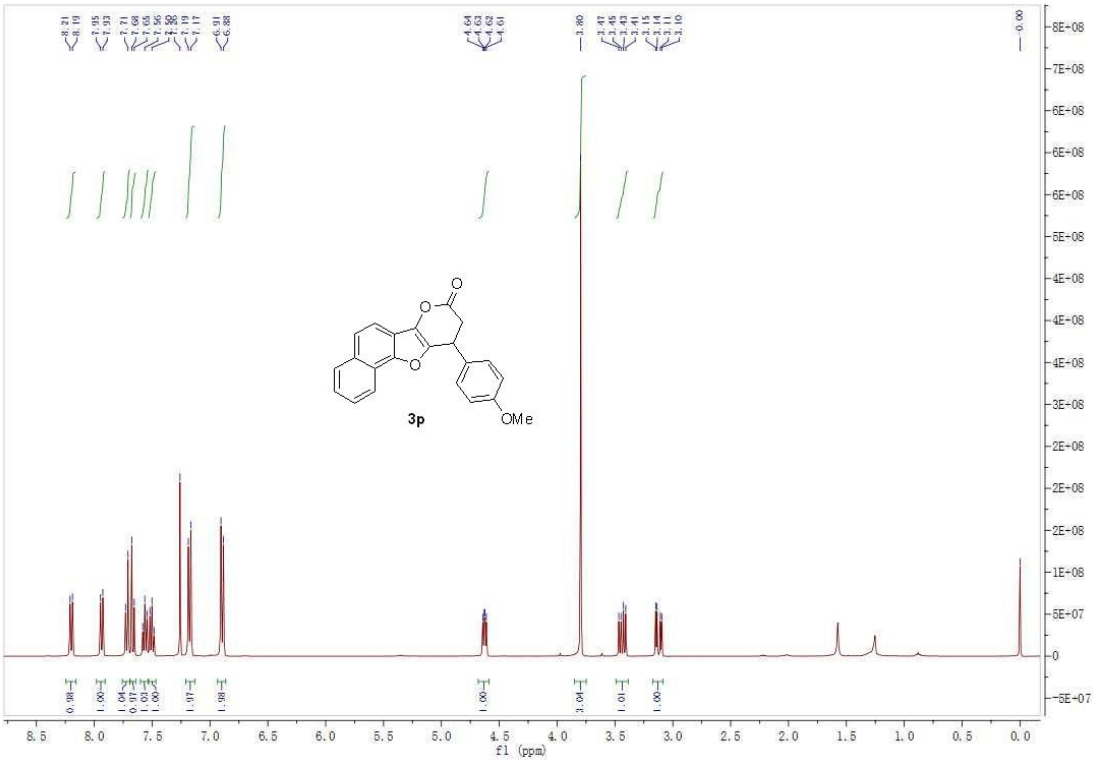
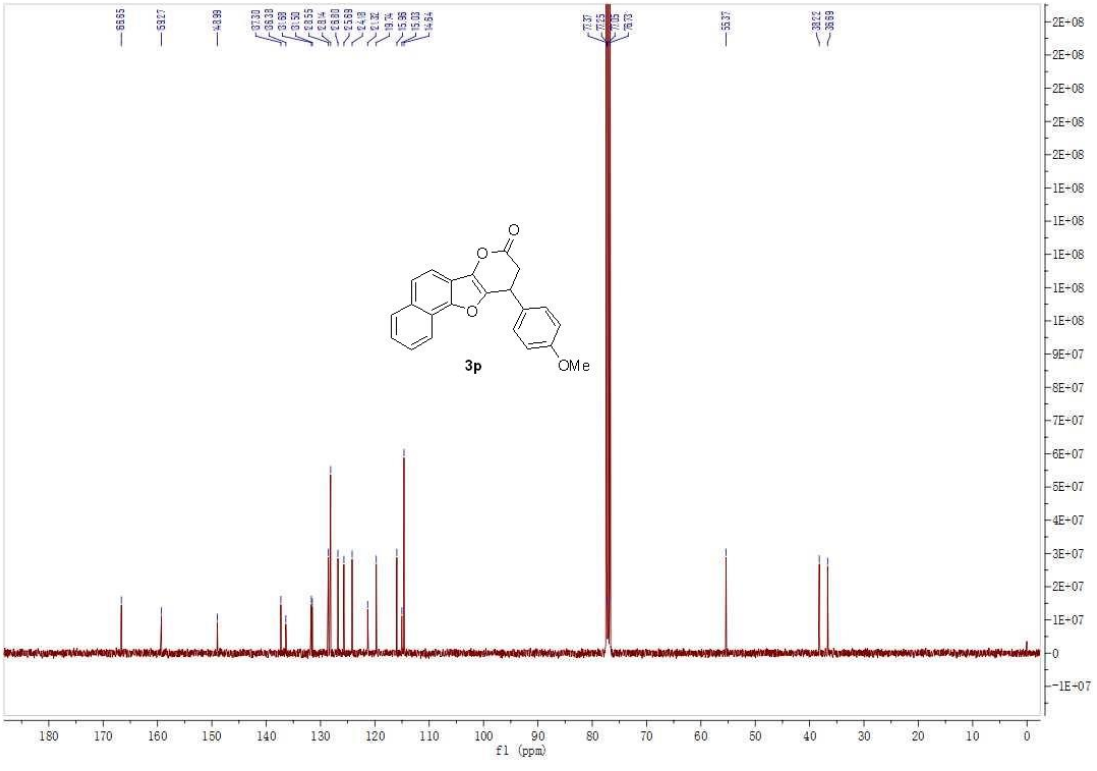

OMe
O
O
O
3o
f1 (ppm)


OMe
O
O
O
3o
f1 (ppm)


3p
OMe
f1 (ppm)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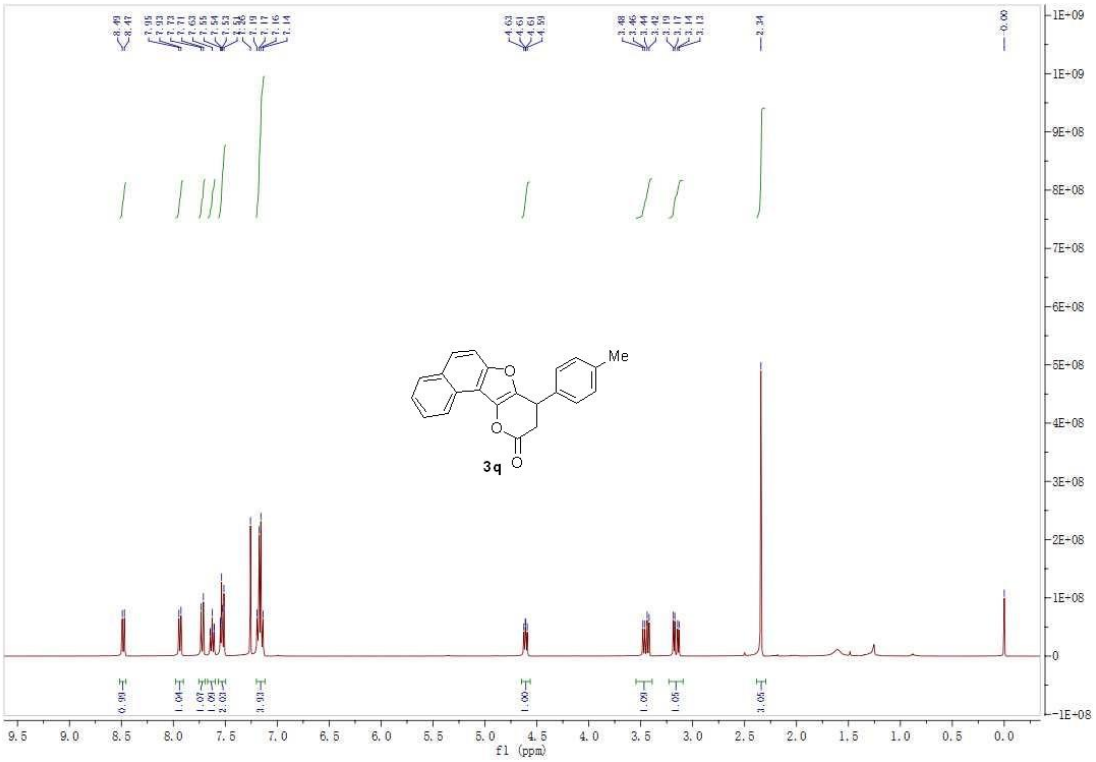
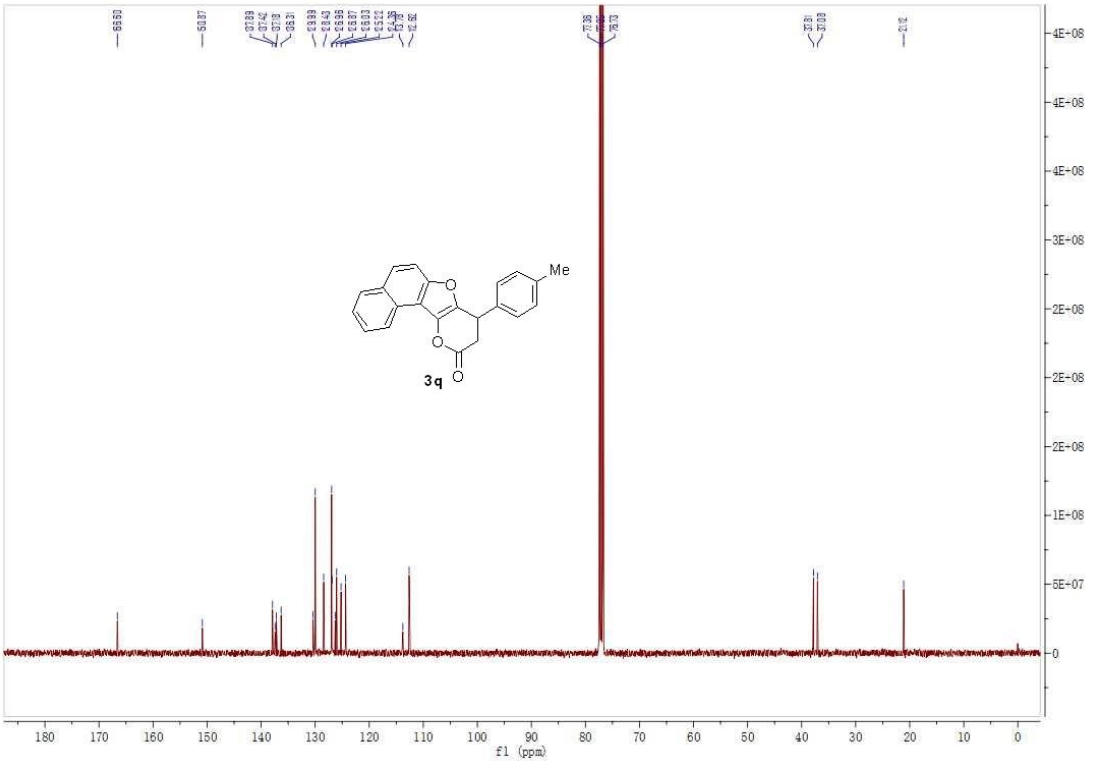
OMe
f1 (ppm)


Me
3q
f1 (ppm)


Me
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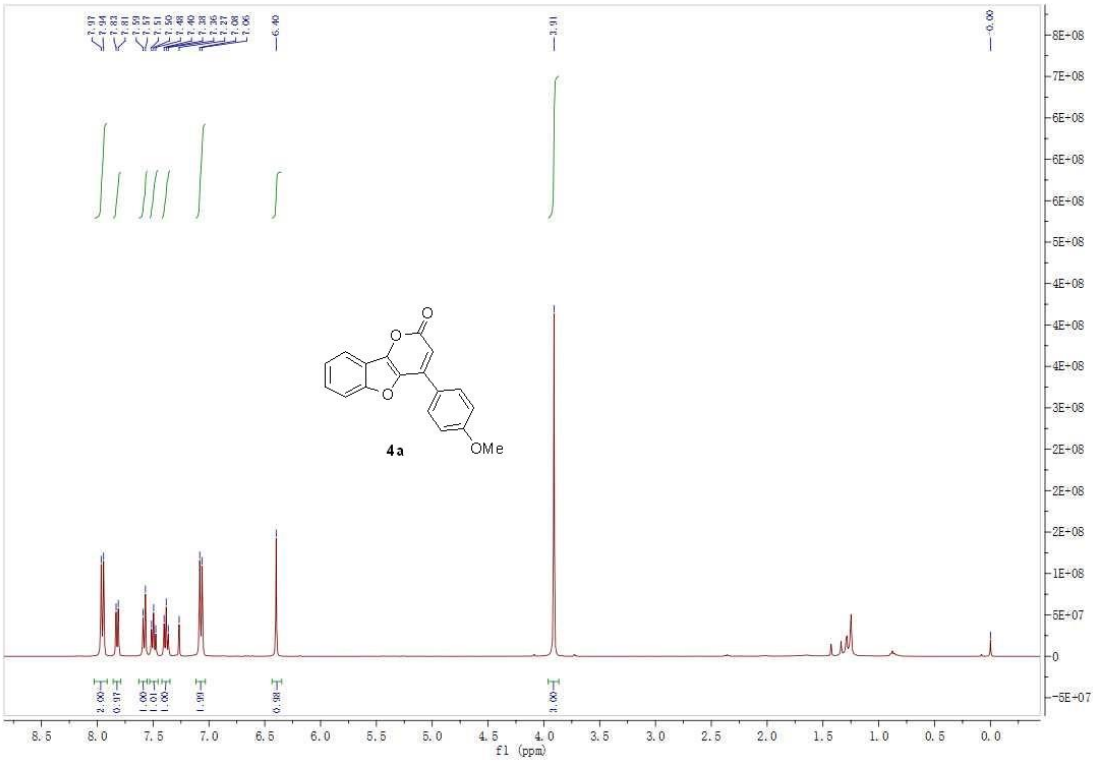
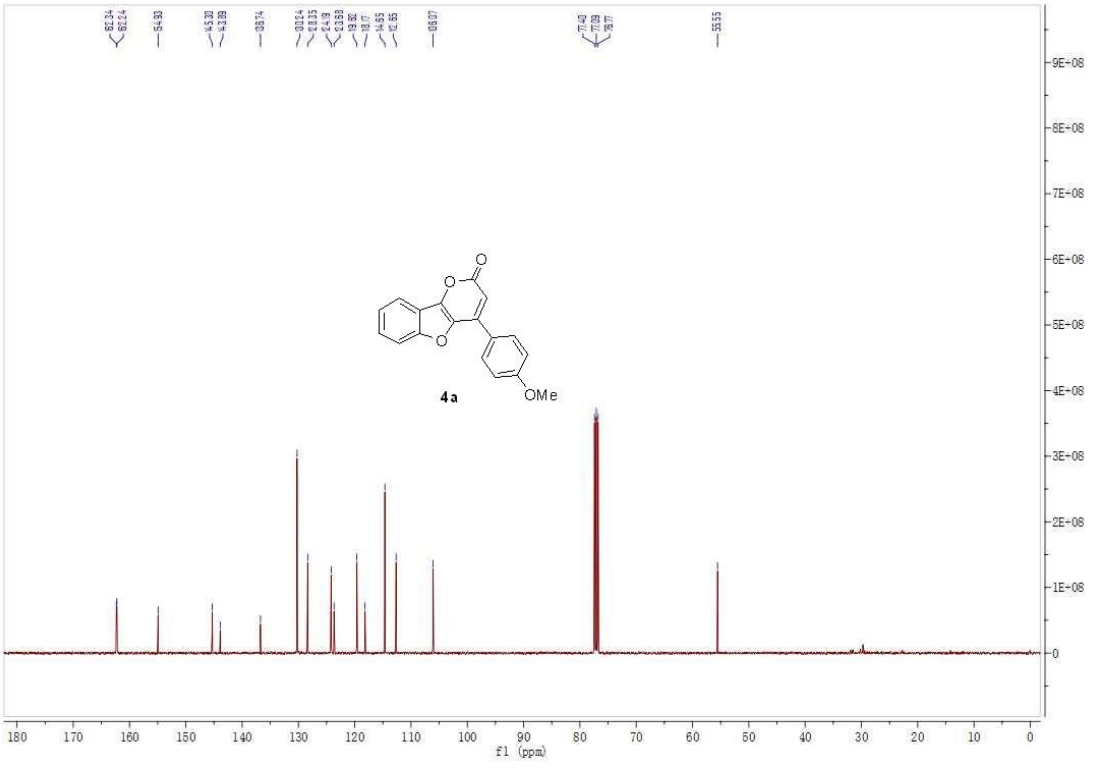
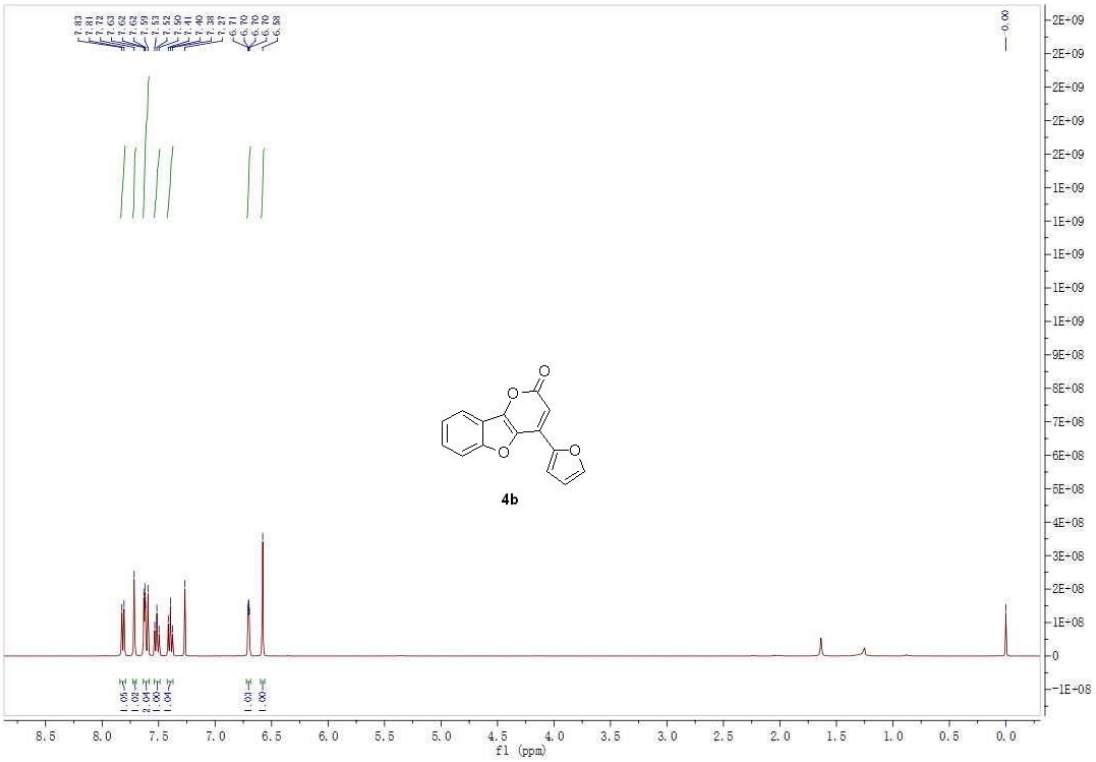
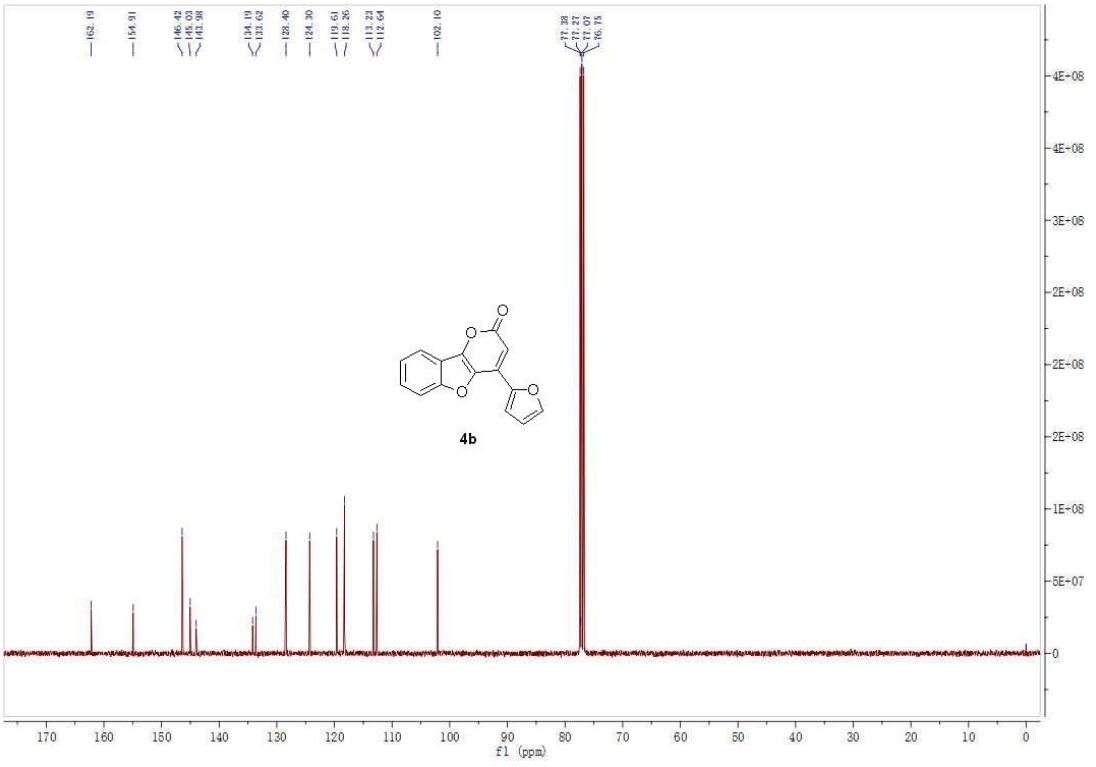

4a
OMe
f1 (ppm)

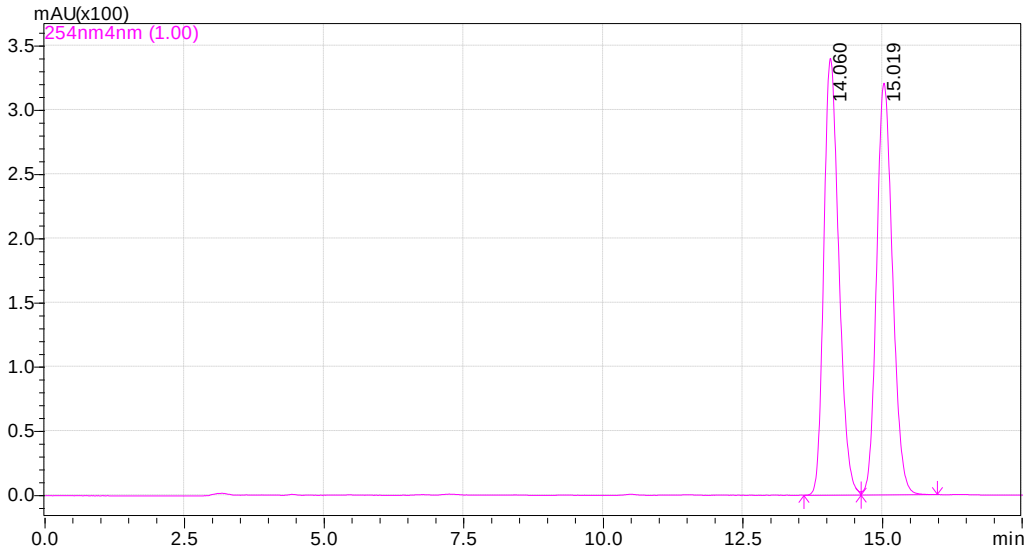

4a
OMe
f1 (ppm)


4b
f1 (ppm)


4b
f1 (ppm)

4. The HPLC of 3a, 3h, 3i

HPLC data of compound **3a**: AD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 96% ee.



Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
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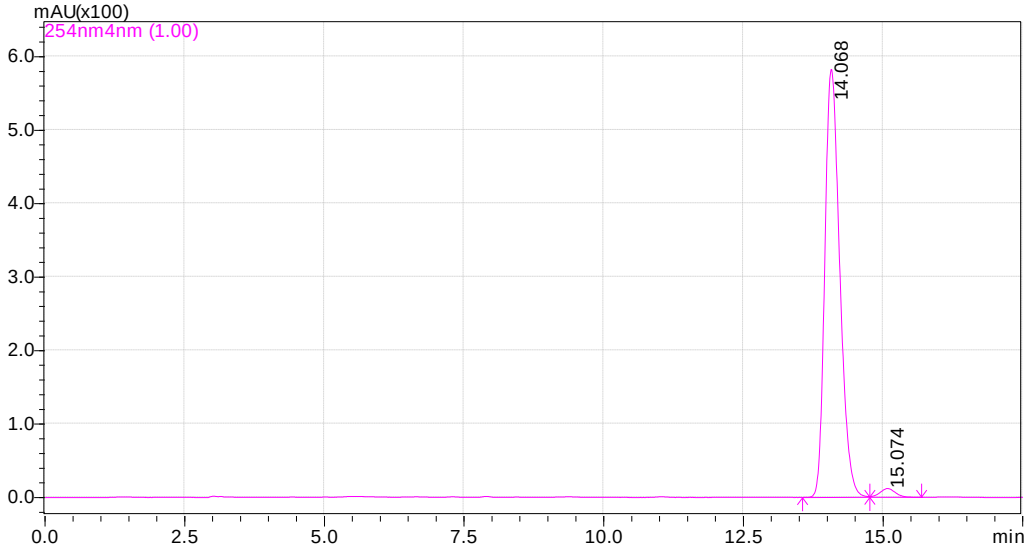
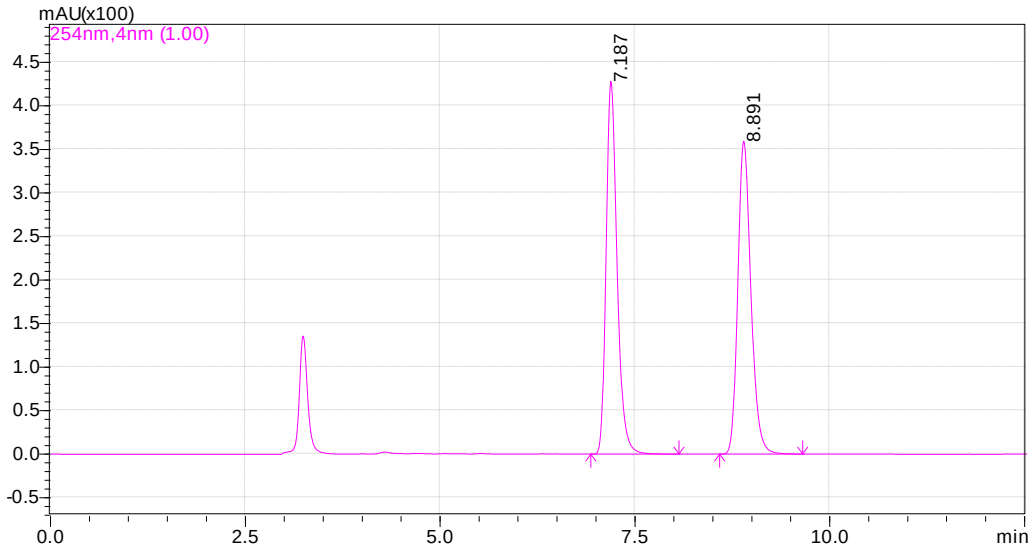
2	15.019	6369271	320392	14.613	15.979	50.0499

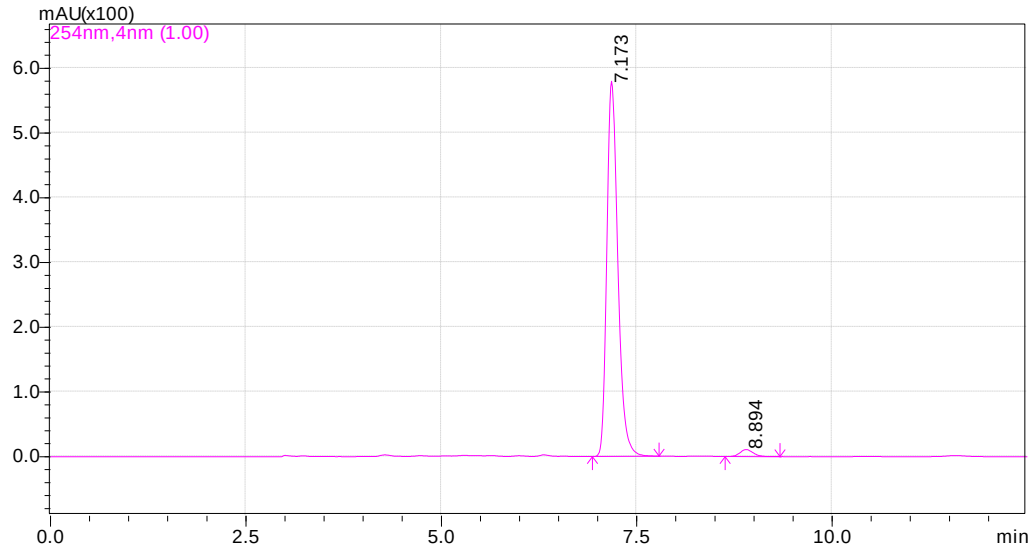


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	14.068	10837216	582650	13.557	14.763	97.9310
2	15.074	228964	11932	14.763	15.691	2.0690

HPLC data of compound **3h**: OD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 96% ee.

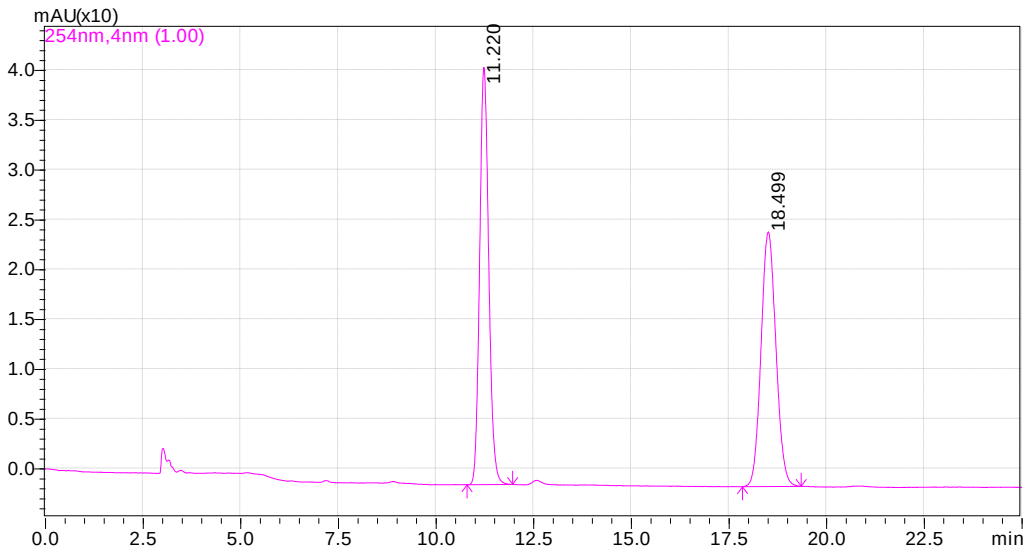


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	7.187	4220308	428273	6.933	8.064	49.9849
2	8.891	4222862	359705	8.587	9.653	50.0151

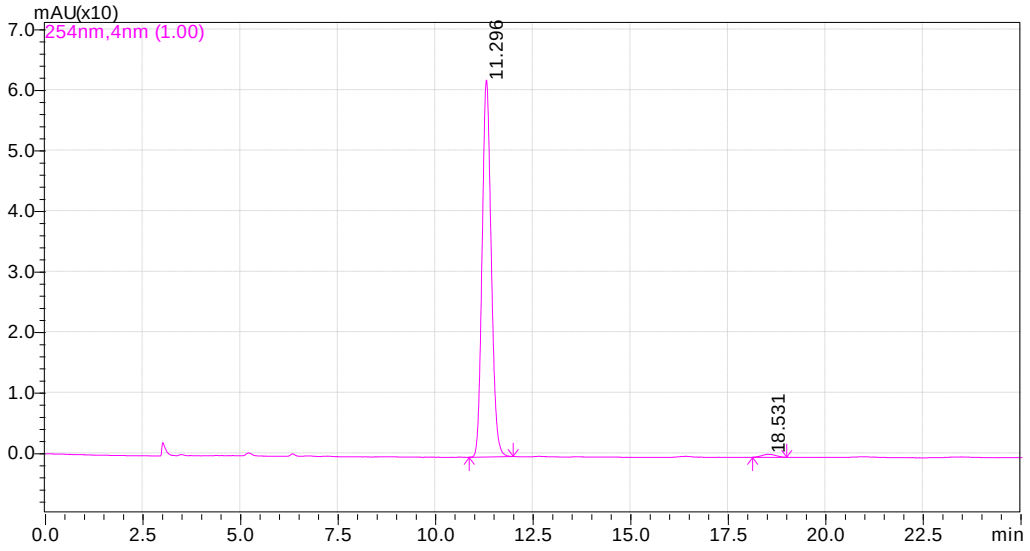


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	7.173	5683905	579564	6.933	7.787	97.8193
2	8.894	126712	10886	8.629	9.333	2.1807

HPLC data of compound **3i**: OD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 98% ee.

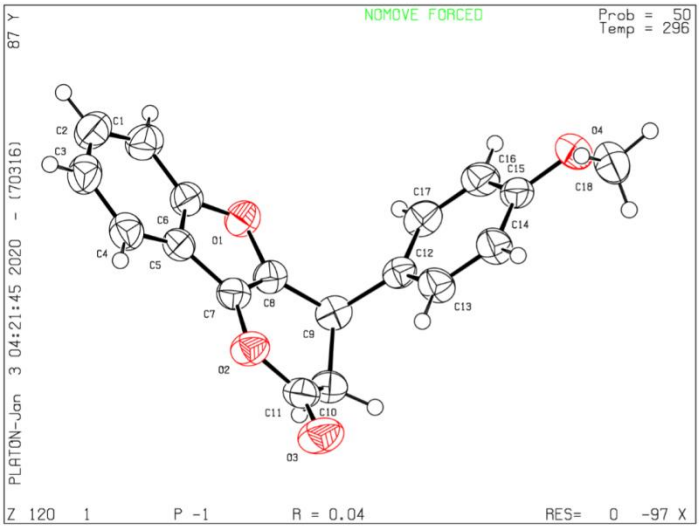


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	11.220	677719	41891	10.795	11.957	50.0394
2	18.499	676652	25548	17.845	19.349	49.9606



Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	11.296	1013965	62260	10.859	11.989	98.7951
2	18.531	12366	504	18.123	18.997	1.2049

5 The data of crystal structure



Datablock: 1

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=5.7002(12) b=8.4405(18) c=14.914(3)
alpha=85.171(3) beta=80.701(3) gamma=84.498(4)
Temperature: 296 K

	Calculated	Reported
Volume	703.1(3)	703.2(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H14 O4	?
Sum formula	C18 H14 O4	C18 H14 O4
Mr	294.29	294.29
Dx,g cm-3	1.390	1.390
Z	2	2
Mu (mm-1)	0.098	0.098
F000	308.0	308.0
F000'	308.17	
h,k,lmax	6,10,17	6,9,17
Nref	2475	2460
Tmin,Tmax	0.975,0.981	
Tmin'	0.975	

Correction method= Not given

Data completeness= 0.994 Theta(max)= 24.995

R(reflections)= 0.0397(1987) wR2(reflections)= 0.1137(2460)

S = 1.106 Npar= 199

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
