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Supplementary Information

Metal-Free Oxidative Cyclization Reaction of Enynals to Access Pyrane-2-one Derivatives

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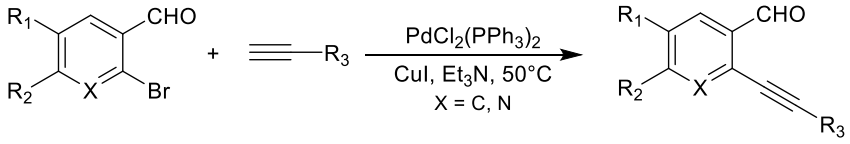
A. General Consideration

Synthesis of o-Alkynyl Aldehyde derivatives were performed according to literature procedures;[1-8] other reagents were purchased from Merck and used without further purification. Flash column chromatography was carried out using 63-200 mesh silica gel. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254) and visualized by exposure to UV light (254 nm). Uncorrected melting points were reported using an Electrothermal *9100* apparatus. ^{1}H and ^{13}C NMR spectra were recorded with Varian - INOVA 500MHz (at 500 and 125 MHz) instrument at room temperature, using $CDCl_3$ as a solvent. Chemical shifts are referenced to tetramethylsilane as an internal standard (TMS: δ 0.00 ppm). ^{13}C NMR spectra are referenced from the solvent central peak (77.26 ppm). Chemical shifts are given in ppm. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. Mass spectra were recorded on an Agilent Technologies (HP) 5973 Mass spectrometer operating at an ionization potential of 20 eV. Elemental analysis (CHN) were recorded on a Thermo Finnigan Flash EA 1112 elemental analyzer.

B. Experimental procedures

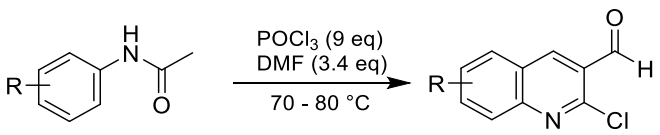
B1. Typical Procedure for the Synthesis of ortho-alkynylbenzaldehyde derivatives (Sonogashira coupling reaction)



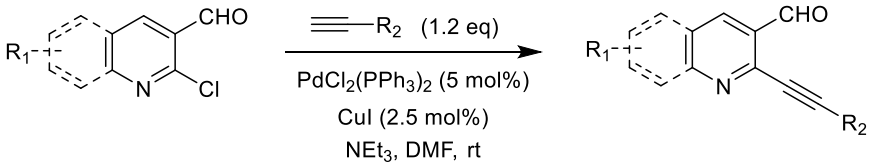
Sonogashira coupling reactions were performed following a reported method.[1]
To a solution of the corresponding 2-bromobenzaldehyde (1 eq), $PdCl_2(PPh_3)_2$ (2 mol%), and CuI (1 mol%) in NEt_3 (0.25 M) was added the appropriate acetylene (1.2 eq). The resulting mixture was heated under Ar atmosphere at 50°C for 6-18 hours. After the reaction was completed, the reaction mixture was quenched by addition of distilled water and extracted with CH_2Cl_2 (three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired products **1m, 1n, 1o,** and **1p**.

B2. Typical Procedure for the Synthesis of quinoline-based starting materials

2-chloroquinoline-3-carbaldehydes: They were prepared by the reported procedure.[9, 10]

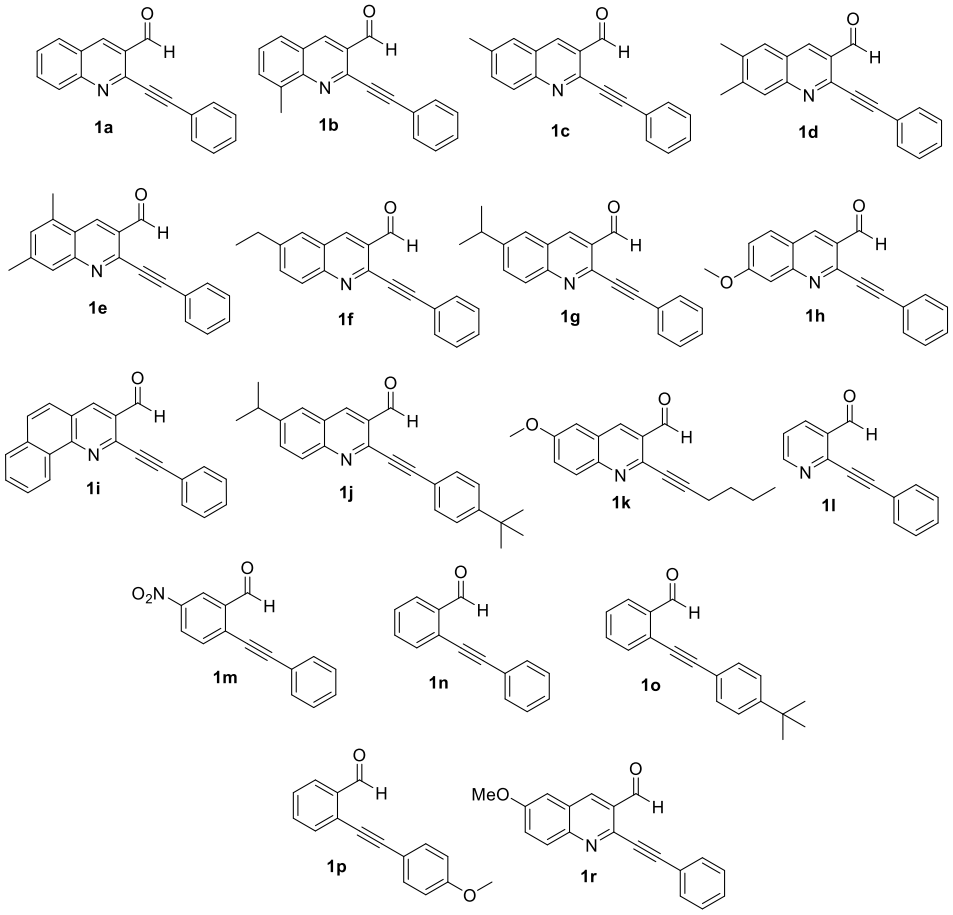


2-(alkylethynyl)quinoline-3-carbaldehydes and 2-(alkylethynyl)nicotinaldehyde:

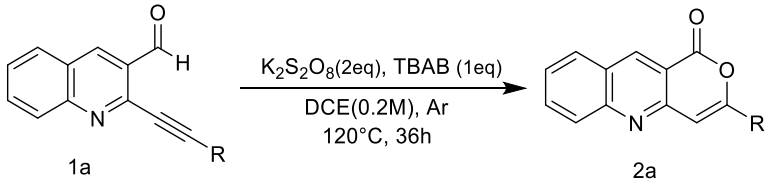


They were prepared by the Sonogashira coupling reaction of 2-chloroquinoline-3-carbaldehydes and 2-Chloro-3-pyridine carboxaldehyde with terminal alkynes.[2] All commercially available compounds were used as received.

Table S1. Starting materials

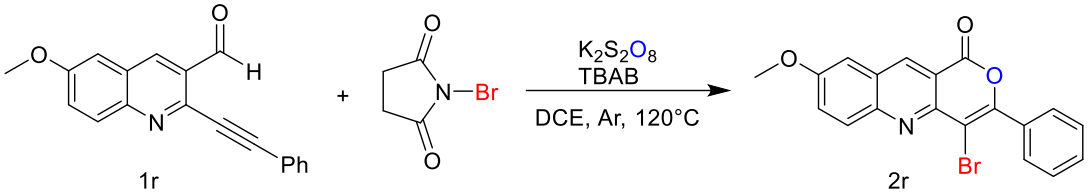


B3. General Procedure for the Synthesis of 2 using 1a as the Examples



To a 10 mL dried Schlenk tube were added TBAB (128.9 mg, 0.4 mmol), $K_2S_2O_8$ (216.2 mg, 0.8 mmol) and followed by addition of compound **1a** (102.9 mg, 0.4mmol) and DCE (2.0 mL, 0.2M). The formed mixture was sealed and was stirred at 120 ºC under Ar atmosphere for 36 h. The solution was then cooled to rt, and DCE was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (eluent: *n*-Hexane/ethyl acetate 5: 1) to afford the desired product **2a**.

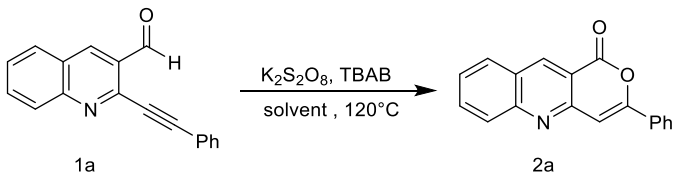
B4. General Procedure for the Synthesis of 4-bromo-8-methoxy-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one 2q (Control Experiment)



To a 10 mL dried Schlenk tube were added TBAB (128.9 mg, 0.4 mmol), $K_2S_2O_8$ (216.2 mg, 0.8 mmol), NBS (71 mg, 0.4 mmol) and followed by addition of compound **1r** (102.9 mg, 0.4mmol) and DCE (2.0 mL, 0.2M). The formed mixture was sealed and was stirred at 120 ºC under Ar atmosphere for 36 h. The solution was then cooled to rt, and DCE was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (eluent: *n*-Hexane/ethyl acetate 5: 1) to afford the desired product **2q**.

C. Solvent Screening with 2-(phenylethynyl)quinoline-3-carbaldehyde, 1a

Table S2. Solvent screening[a] with 2-(phenylethynyl)quinoline-3-carbaldehyde, 1a



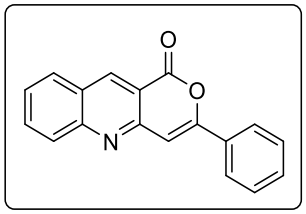
entry	solvent	yield (%)[b]
1	PhCl	50
2	**DCE**	**82**
3	DCE/H_2O	55
4	DMSO	ND[c]
5	Benzene	25
6	Toluene	Trace
7	ACN	23
8	Neat	Trace

[a]Reaction conditions: 1a (51.0 mg, 0.2 mmol), $K_2S_2O_8$ (2.0 equiv.), TBAB (1.0 equvi.), DCE (1.0 ml), under Ar atmosphere,120 ºC and 36 h. [b] Isolated yields, [c]ND = Not detected.

D. Compounds Characterization Data

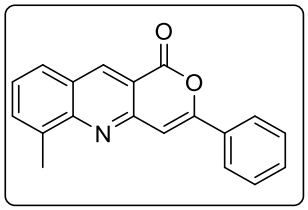
D1. Characterization Data for final compounds

3-phenyl-1H-pyrano [4,3-b]quinolin-1-one (2a)



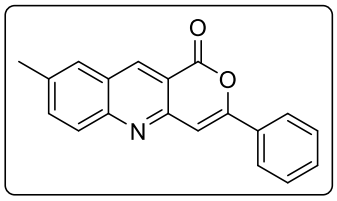
Yellow solid; Yield 82% (89mg); m.p. 132-134°C; R_f = 0.18 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.27 (s, 1H), 7.44-7.50 (m, 3H), 7.57 (t, J = 7.5 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.90-7.97 (m, 3H), 8.08 (d, J = 8.5 Hz, 1H), 9.10 (s, 1H) **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.1, 157.0, 152.7, 151.8, 140.6, 133.6, 131.5, 130.9, 129.6, 129.1, 127.1, 127.1, 125.7, 115.7, 103.8. **IR (cm^{-1}) *ν*** 3053, 2924, 1733, 1603, 1489, 1364, 1269, 1206, 1160, 1045. **MS (EI, 70 eV)** m/z [M]+ found for $C_{18}H_{11}NO_2$: 273. **Anal. Calcd** for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13; Found: C, 78.84; H, 3.97; N, 5.00.

6-methyl-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2b)



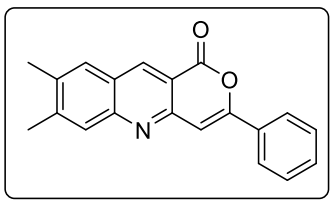
Yellow solid; Yield 88% (101mg); m.p. 137-139°C; R_f = 0.53 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 2.79 (s, 3H),7.27 (s, 1H) 7.37 – 7.51 (m, 4H), 7.64 (d, J = 6.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.1 Hz, 2H), 8.98 (s, 1H) **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.3, 156.3, 151.6, 150.9, 140.4, 137.2, 133.3, 131.6, 130.7, 130.6, 129.0, 127.5, 127.0, 126.8, 125.6, 115.2, 104.3, 18.2. **IR (cm^{-1}) *ν*** 3056, 2916, 2852, 1736, 1621, 1583, 1489, 1445, 1369, 1267, 1215, 1161, 1082, 1038. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{19}H_{13}NO_2$: 287. **Anal. Calcd** for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88; Found: C, 79.74; H, 4.67; N, 5.01.

8-methyl-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2c)



Yellow solid; Yield 81% (93mg); m.p. 156-160°C; R_f = 0.18 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.08 (s, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.98 – 7.94 (m, 2H), 7.76 – 7.72 (m, 2H), 7.53 – 7.48 (m, 3H), 7.35 (s, 1H), 2.58 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.3, 156.6, 152.0, 150.5, 139.8, 137.4, 136.2, 131.7, 130.8, 129.1, 128.7, 128.2, 127.2, 125.7, 115.7, 103.9, 32.1 **IR (cm^{-1}) *ν*** 2917, 1728, 1625, 1589, 1486, 1374, 1269, 1184, 1049. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{19}H_{13}NO_2$: 287. **Anal. Calcd** for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88; Found: C, 79.11; H, 4.40; N, 4.69.

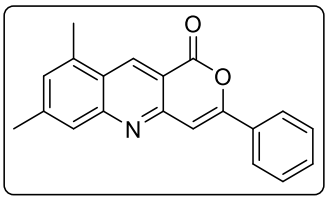
7,8-dimethyl-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2d)



Yellow solid; Yield 78% (94mg); m.p. 157-159°C; R_f = 0.14 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.97 (s, 1H), 7.93 (d, J = 6.5 Hz, 2H), 7.86 (s, 1H), 7.68 (s, 1H), 7.44- 7.52 (m, J = 6.1, 5.4 Hz, 3H), 7.28 (s, 1H), 2.50 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.4, 156.3, 152.0, 151.0, 145.1, 139.2, 137.6 131.8, 130.7, 129.1, 128.5, 128.3, 125.9, 125.6, 124.5, 115.0, 104.0, 21.1, 20.2 **IR (cm^{-1}) *ν*** 3033, 2919, 2852, 1734, 1624, 1585, 1546, 1487, 1448, 1373, 1111, 1072.

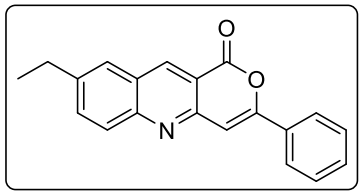
MS (ESI)$^+$ m/z $[M]^+$ found for $C_{20}H_{15}NO_2$: 301.3. **Anal. Calcd** for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65; Found: C, 79.37; H, 4.94; N, 4.46.

7,9-dimethyl-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2e)



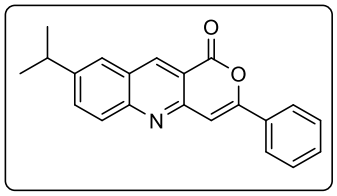
Yellow solid; Yield 77% (93mg); m.p 159-163°C; R_f = 0.23 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.01 (s, 1H), 7.85 (d, J = 6.0 Hz, 2H), 7.58 (s, 1H), 7.42 – 7.45 (m, 3H), 7.10 (d, J = 10.9 Hz, 2H), 2.63 (s, 3H), 2.42 (s, 3H).) **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.2, 156.4, 152.3, 152.1, 144.4, 136.3, 131.5, 130.6, 129.9, 128.9, 126.0, 125.5, 124.8, 114.0, 103.6, 22.3, 18.7. **IR (cm^{-1})** ***v*** 3057, 2922, 2858, 1726, 1584, 1499, 1449, 1376, 1242, 1189, 1061. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{20}H_{15}NO_2$: 301. **Anal. Calcd** for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65; Found: C, 79.98; H, 5.21; N, 4.83.

8-ethyl-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2f)



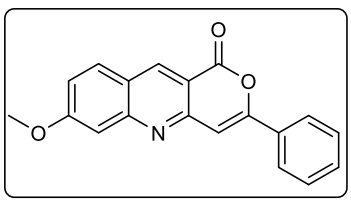
Yellow solid; Yield 84% (101mg); m.p. 161-163°C; R_f = 0.25 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.96 (s, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 6.7 Hz, 2H), 7.64 – 7.68 (m, 2H), 7.44 (d, J = 6.9 Hz, 3H), 7.19 (s, 1H), 2.81 (q, 2H), 1.32 (t, J = 7.6 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.1, 156.3, 151.8, 150.6, 143.3, 139.7, 135.0, 132.4, 131.5, 130.6, 129.0, 128.8, 127.1, 126.7, 125.7, 115.5, 103.8, 28.8, 15. **IR (cm^{-1})** ***v*** 2926, 1727, 1624, 1588, 1475, 1373, 1264, 1197, 1054**. MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{20}H_{15}NO_2$: 301. **Anal. Calcd** for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65; Found: C, 79.88; H, 5.19; N, 4.80.

8-isopropyl-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2g)



Yellow solid; Yield 84% (106mg); m.p. 149-151°C; R_f = 0.25 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 1.36 (d, J = 6.9 Hz, 6H), 3.12 (hept, J = 6.9 Hz, 1H), 7.28 (s, 1H), 7.44-7.50 (m, 3H), 7.74 (s, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 6.9 Hz, 2H), 8.03 (d, J = 8.8 Hz,1H), 9.07 (s, 1H) **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.3, 156.5, 152.0, 150.8, 148.0, 140.0, 133.9, 131.7, 130.7, 129.1, 128.9, 127.2, 125.7, 125.4, 115.6, 103.9, 34.2, 23.7 **IR (cm^{-1})** ***v*** 3057, 2928, 2863, 1880, 1728, 1621, 1588, 1486, 1370, 1270, 1204, 1166, 1056. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{21}H_{17}NO_2$: 315. **Anal. Calcd** for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44; Found: C, 79.65; H, 5.29; N, 4.30.

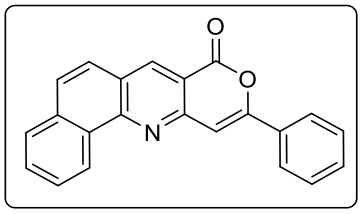
7-methoxy-3-phenyl-1H-pyrano [4,3-b]quinolin-1-one (2h)



Yellow solid; Yield 84% (101mg); m.p. 182-184°C; R_f = 0.2 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 4.00 (s, 3H), 7.20 – 7.29 (m, 2H), 7.39 (d, J = 2.4 Hz, 1H), 7.44 – 7.55 (m, 3H), 7.85 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 9.02 (s, 1H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 164.3, 162.4, 157.1, 154.1, 153.3, 139.8, 131.8, 130.8, 130.8, 129.1, 125.8, 122.8, 121.3, 113.7, 106.5, 103.9, 56.0. **IR (cm^{-1})** ***v*** 3020, 2921, 2852, 1729, 1609, 1497, 1456, 1382, 1247, 1156, 1060,

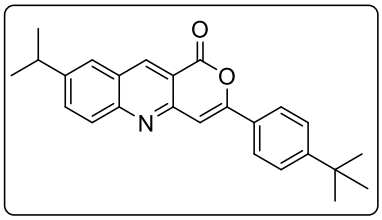
1014. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{19}H_{13}NO_3$: 303. **Anal. Calcd** for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62; Found: C, 75.58; H, 4.43; N, 4.82.

10-phenyl-8H-benzo[h]pyrano[4,3-b]quinolin-8-one (2i)



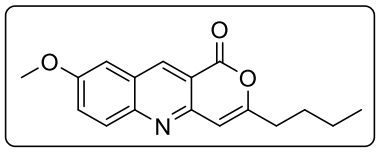
Yellow solid; Yield 87% (112mg); m.p. 218-221°C; R_f = 0.55 on silica gel (Hexane/EtOAc 5:1)**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.35 – 9.30 (m, 1H), 9.00 (d, J = 9.4 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.90 – 7.87 (m, 1H), 7.79 – 7.75 (m, 3H), 7.72 (d, J = 8.9 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.41 (s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.4, 156.8, 152.3, 151.4, 138.6, 135.2, 131.7, 130.8, 130.3, 129.6, 129.1, 128.6, 128.4, 128.2, 127.7, 125.8, 125.6, 125.6, 115.6, 104.3 **IR (cm^{-1}) *v*** 3048, 2958, 2907, 1734, 1627, 1584, 1498, 1397, 1348, 1225, 1161, 1066. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{22}H_{13}NO_2$: 323. **Anal. Calcd** for $C_{22}H_{13}NO_2$: C, 81.72; H, 4.05; N, 4.33; Found: C, 81.89; H, 4.14; N, 4.51.

3-(4-(tert-butyl)phenyl)-8-isopropyl-1H-pyrano[4,3-b]quinolin-1-one (2j)



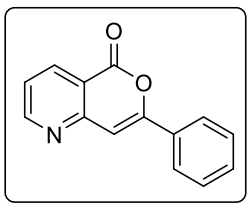
Yellow solid; Yield 79% (117mg); m.p. 154-157°C; R_f=0.225 on silica gel (Hexane/EtOAc 5:1)**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.36 (s, 15H), 3.12 (hept, J = 7.0 Hz, 1H), 7.29 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H), 7.75 (s, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.8 Hz, 1H), 9.07 (s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.3, 156.9, 154.4, 152.1, 150.6, 147.9, 140.2, 134.0, 128.8, 128.7, 127.2, 126.1, 125.6, 125.4, 115.6, 103.0, 35.1, 34.1,31.3, 23.7 **IR (cm^{-1}) *v*** 3083, 2957, 2871, 1731, 1629, 1590, 1466, 1374, 1269, 1198, 1115, 1057, 1018. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{25}H_{25}NO_2$: 371. **Anal. Calcd** for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.77; Found: C, 80.92; H, 6.87; N, 3.98.

3-butyl-8-methoxy-1H-pyrano[4,3-b]quinolin-1-one (2k)



Yellow solid; Yield 62% (70mg); m.p. 157-160°C; R_f =0.27 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.97(t, J = 7.4 Hz, 3H), 1.39 – 1.50 (m, 2H), 1.74(p, J = 7.5 Hz, 2H), 2.61(t, J = 7.6 Hz, 2H), 3.97(s, 3H), 6.61(s, 1H), 7.18(d, J = 2.8 Hz, 1H), 7.54(dd, J = 9.3, 2.8 Hz, 1H), 8.01(d, J = 9.3 Hz, 1H), 8.99(s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.2, 156.8 150.6, 130.1, 128.1, 127.4, 127.4, 120.1, 115.6, 105.9, 104.9, 55.9, 33.6, 28.8, 22.2, 13.9. **IR (cm^{-1}) *v*** 2950, 2871, 1733, 1653, 1589, 1489, 1427, 1380, 1222, 1180,1108, 1021**. MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{17}H_{17}NO_3$: 283. **Anal. Calcd** for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94; Found: 71.80; H, 5.93; N, 4.80.

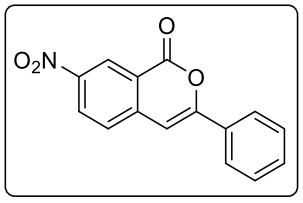
7-phenyl-5H-pyrano [4,3-b]pyridin-5-one (2l)



Pale yellow solid; yield 87% (78mg); m.p. 137-139°C; R_f = 0.13 on silica gel (Hexane/EtOAc 5:1)**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.22 (s, 1H), 7.41 (dd, J = 8.0, 4.7 Hz, 1H), 7.48(dd, J = 5.4, 2.2 Hz, 3H), 7.89 – 7.93 (m, 2H), 8.53(d, J = 8.0, 1H), 8.92 (d, J = 4.4 Hz, 1H) **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.1, 157.4, 156.5, 155.1, 137.7, 131.4, 130.9, 129.1, 125.8, 123.0, 117.1, 103.8 **IR (cm^{-1}) *v*** 3067, 2919, 1787, 1721, 1617, 1557, 1430, 1280, 1223,

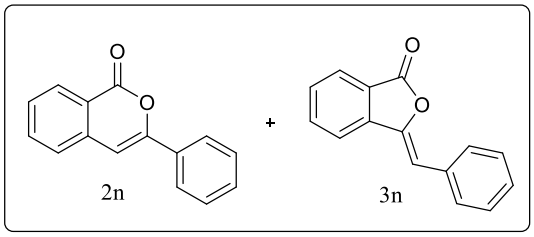
1070, 1037. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{14}H_9NO_2$: 223. **Anal. Calcd** for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27; Found: C, 75.12; H, 3.97; N, 6.02.

7-nitro-3-phenyl-1H-isochromen-1-one (2m)



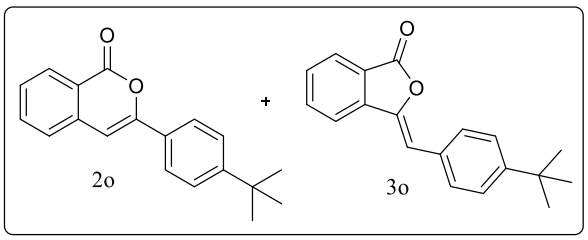
Yellow solid; Yield 73% (78mg); m.p. 196-200°C; R_f = 0.44 on silica gel (Hexane/EtOAc 5:1)**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.05 (s, 1H), 7.48 – 7.54 (m, 3H), 7.66 (d, J = 8.6 Hz, 1H), 7.90 – 7.95 (m, 2H), 8.52 (dd, J = 8.6, 2.4 Hz, 1H), 9.15 (d, J = 2.1 Hz, 1H)**. ^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.3, 142.7, 131.4, 131.1, 130.3, 129.3, 129.2, 128.6, 127.4, 126.0, 125.9, 120.9, 100.8**. IR (cm^{-1}) *ν*** 2918, 2854, 1716, 1619, 1519, 1458, 1337, 1254, 1088, 1027. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{15}H_9NO_4$: 267. Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42; H, 3.39; N, 5.24; Found: C, 67.80; H, 3.54; N, 5.40.

3-phenyl-1H-isochromen-1-one (2n)



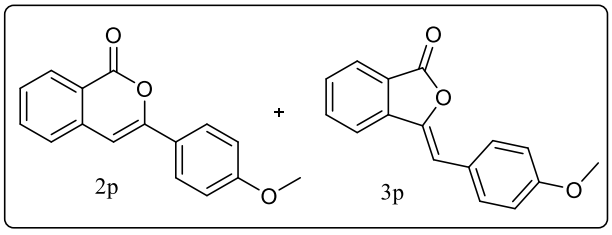
The compounds exist as a 22:3 mixture of 2n and 3n. Yellow solid; Yield 78% (69mg); R_f = 0.52 on silica gel (Hexane/EtOAc 5:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.32 (d, J = 8.1 Hz, 1H), 7.89 (d, J =7.0 Hz, 2H), 7.73 (dd, J = 7.6, 1.3 Hz, 1H), 7.42− 7.52 (m, 6H), 6.96 (s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.4, 153.8, 137.7, 135.0, 132.1, 130.3, 130.1, 129.8, 129.0, 128.9, 128.3, 126.1, 125.4, 120.7, 102.0. **IR (cm^{-1}) *ν*** 3057, 2957, 1771, 1719, 1635, 1480, 1268, 1072. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{15}H_{10}O_2$: 222. **Anal. Calcd** for $C_{15}H_{10}O_2$: C, 81.07; H, 4.54; Found: C, 81.49; H, 4.71.

3-(4-(tert-butyl) phenyl)-1H-isochromen-1-one (2o)



The compounds exist as a 23:2 mixture of 2o and 3o. Yellow oil; Yield 70% (78mg); R_f =0.5 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.36 (s, 9H), 6.91 (s, 1H), 7.43 – 7.52 (m, 4H), 7.70 (t, J = 8.2 Hz, 1H), 7.82 (d, J = 8.5 Hz, 2H), 8.30 (d, J = 8.1 Hz, 1H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.5, 153.9, 153.5, 137.8, 134.9, 129.8, 129.7, 129.3, 128.0, 125.9, 125.2, 120.6, 101.3, 35.0, 29.8 **IR (cm^{-1}) *ν*** 2918, 2856, 1734, 1634, 1463, 1371, 1231, 1064, 1017. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{19}H_{18}O_2$: 278. **Anal. Calcd** for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52; Found: C, 82.34; H, 6.66.

3-(4-methoxyphenyl)-1H-isochromen-1-one (2p)

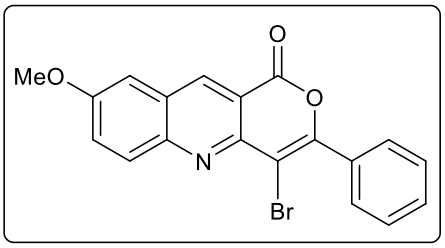


The compounds exist as a 19:1 mixture of 2p and 3p. Red solid; Yield 76% (76mg); R_f = 0.3 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.85(s, 3H), 6.8(s, 1H), 6.95(d, J = 8.2 Hz, 2H), 7.40 – 7.48 (m, 2H), 7.67(t, J = 7.6 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 8.27(d, J = 8.1 Hz, 1H) **^{13}C NMR (125 MHz,**

$CDCl_3$) δ 162.6, 161.2, 153.8, 138.0, 134.9, 131.8, 129.7, 127.7, 126.9, 125.8, 124.6, 120.2, 114.3, 100.3, 55.5 **IR** (cm^{-1}) *v* 3063, 1780, 1719, 1487, 1247, 1070, 1005. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{16}H_{12}O_3$: 252. **Anal. Calcd** for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79; Found: C, 76.44; H, 4.90.

D2. Characterization Data of compound 2q

4-bromo-8-methoxy-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (2q)



Yellow solid; Yield 77% (93mg); m.p. 239-241°C; R_f = 0.3 on silica gel (Hexane/EtOAc 5:1); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.04 (s, 3H), 7.30 (dt, J = 9.0, 2.5 Hz, 1H), 7.50 – 7.55 (m, J = 4.3, 3.5 Hz, 2H), 7.55 – 7.59 (dd, J = 6.9, 2.4 Hz, 1H), 7.90 (d, J = 8.9 Hz, 3H), 7.94 – 7.99 (m, 1H), 9.05 (d, J = 7.7 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 56.2, 107.3, 122.2, 123.0, 128.3, 128.4, 129.6, 129.9, 130.5, 130.6, 130.7, 130.8, 132.9, 140.2, 140.3, 154.0, 161.4, 164.5 **IR** (cm^{-1}) *v* 2931, 1744, 1593, 1486, 1373, 1242, 1159, 1022. **MS (EI, 70 eV)** m/z $[M]^+$ found for $C_{19}H_{12}BrNO_3$: 381. **Anal. Calcd** for $C_{19}H_{12}BrNO_3$: C, 59.71; H, 3.16; Found: C, 59.86; H, 3.24.

E. X-ray crystallographic data of compound (2a)

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the

data can be obtained free of charge on quoting the depository numbers CCDC-2051315 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, www.ccdc.cam.ac.uk)

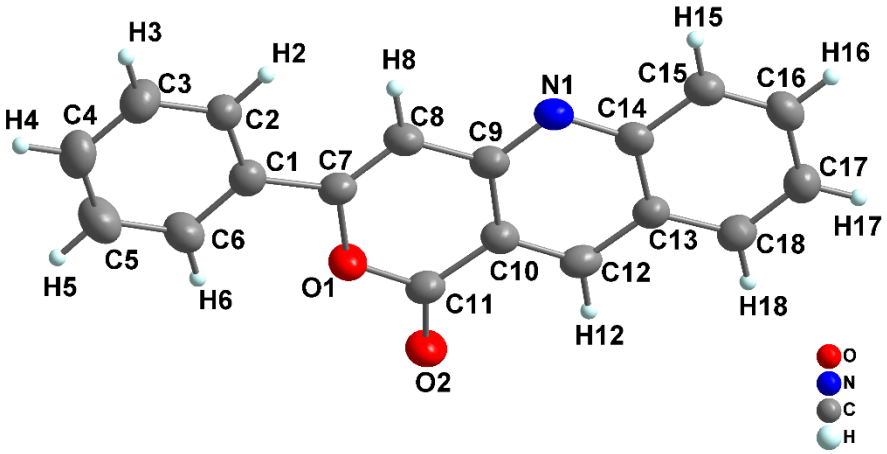


Figure 1. a view of the asymmetric unit of 3-phenyl-1H-pyrano[4,3-b]quinolin-1-one with the labelling scheme, showing displacement ellipsoids at the 50% probability level.

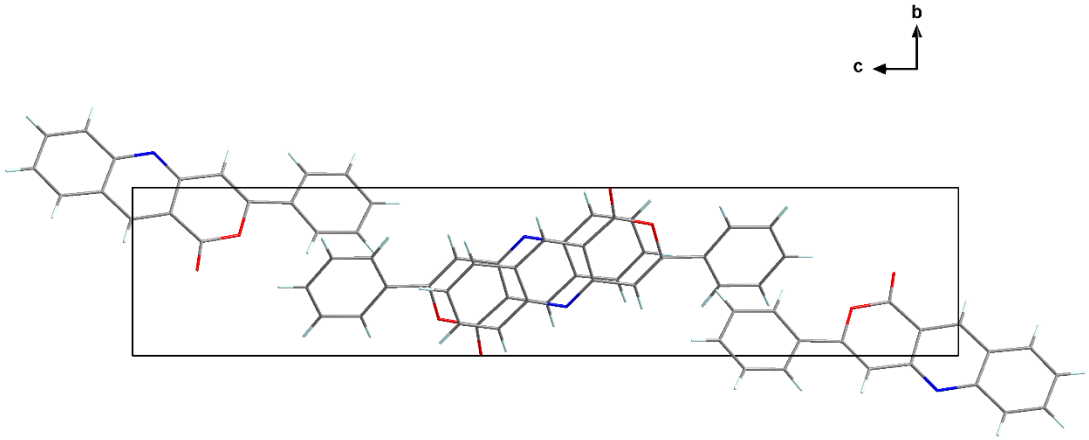


Figure 2. Packing diagram looking along the crystallographic *a* axis of 3-phenyl-1H-pyrano[4,3-b]quinolin-1-one, Color legend: O (red), N (blue), C (gray).

Table 1. Crystal data and structure refinement for 3-phenyl-1H-pyrano[4,3-b]quinolin-1-one.

Identification code	865
Empirical formula	C18H11NO2
Formula weight	273.28

Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.1600(16) Å	α= 90°.
	b = 5.6000(11) Å	β= 94.00(3)°.
	c = 27.700(6) Å	γ = 90°.
Volume	1262.7(4) $Å^3$	
Z	4	
Density (calculated)	1.438 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	568	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.559 to 27.048°.	
Index ranges	-10<=h<=10, -7<=k<=7, -34<=l<=33	
Reflections collected	11016	
Independent reflections	2697 [R(int) = 0.0836]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2697 / 0 / 190	
Goodness-of-fit on F^2	1.331	
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.1455	
R indices (all data)	R1 = 0.1256, wR2 = 0.1550	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.225 and -0.249 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for 3-phenyl-1H-pyrano[4,3-b]quinolin-1-one.

Bond lengths	
O(1)-C(7)	1.385(4)
O(1)-C(11)	1.387(4)
O(2)-C(11)	1.191(4)
N(1)-C(9)	1.313(4)
N(1)-C(14)	1.369(4)
C(1)-C(6)	1.381(4)
C(1)-C(2)	1.390(4)
C(1)-C(7)	1.488(4)
C(2)-C(3)	1.383(5)
C(2)-H(2)	0.9400
C(3)-C(4)	1.365(5)
C(3)-H(3)	0.9400
C(4)-C(5)	1.367(5)
C(4)-H(4)	0.9400
C(5)-C(6)	1.393(5)
C(5)-H(5)	0.9400
C(6)-H(6)	0.9400
C(7)-C(8)	1.322(4)
C(8)-C(9)	1.454(4)
C(8)-H(8)	0.9400
C(9)-C(10)	1.414(4)
C(10)-C(12)	1.379(4)
C(10)-C(11)	1.456(4)
C(12)-C(13)	1.399(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.415(4)
C(13)-C(18)	1.429(4)
C(14)-C(15)	1.411(4)
C(15)-C(16)	1.360(4)
C(15)-H(15)	0.9400
C(16)-C(17)	1.406(5)
C(16)-H(16)	0.9400
C(17)-C(18)	1.347(4)

C(17)-H(17)	0.9400
C(18)-H(18)	0.9400

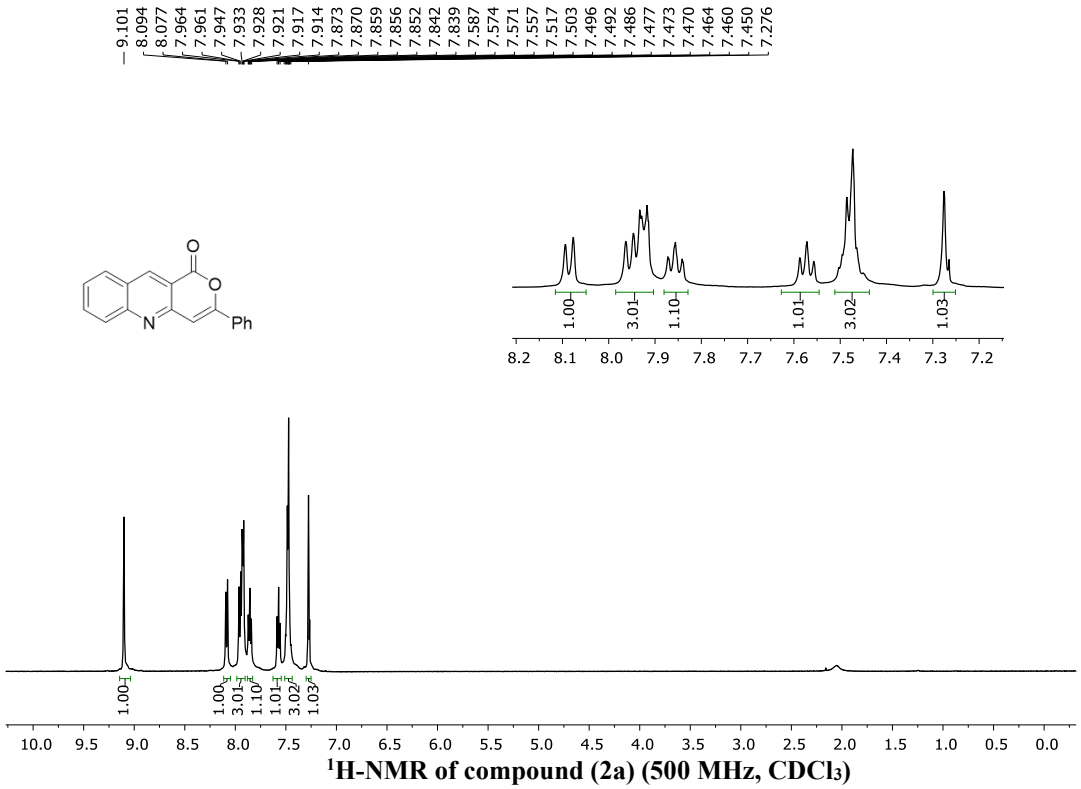
Angles

C(7)-O(1)-C(11)	123.0(2)
C(9)-N(1)-C(14)	117.6(3)
C(6)-C(1)-C(2)	117.5(3)
C(6)-C(1)-C(7)	121.4(3)
C(2)-C(1)-C(7)	121.0(3)
C(3)-C(2)-C(1)	121.5(3)
C(3)-C(2)-H(2)	119.3
C(1)-C(2)-H(2)	119.3
C(4)-C(3)-C(2)	120.5(4)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	118.8(3)
C(3)-C(4)-H(4)	120.6
C(5)-C(4)-H(4)	120.6
C(4)-C(5)-C(6)	121.4(4)
C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(1)-C(6)-C(5)	120.3(3)
C(1)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(8)-C(7)-O(1)	120.8(3)
C(8)-C(7)-C(1)	128.0(3)
O(1)-C(7)-C(1)	111.2(3)
C(7)-C(8)-C(9)	121.5(3)
C(7)-C(8)-H(8)	119.3
C(9)-C(8)-H(8)	119.3
N(1)-C(9)-C(10)	123.3(3)
N(1)-C(9)-C(8)	119.0(3)
C(10)-C(9)-C(8)	117.6(3)
C(12)-C(10)-C(9)	119.0(3)
C(12)-C(10)-C(11)	121.0(3)
C(9)-C(10)-C(11)	120.0(3)

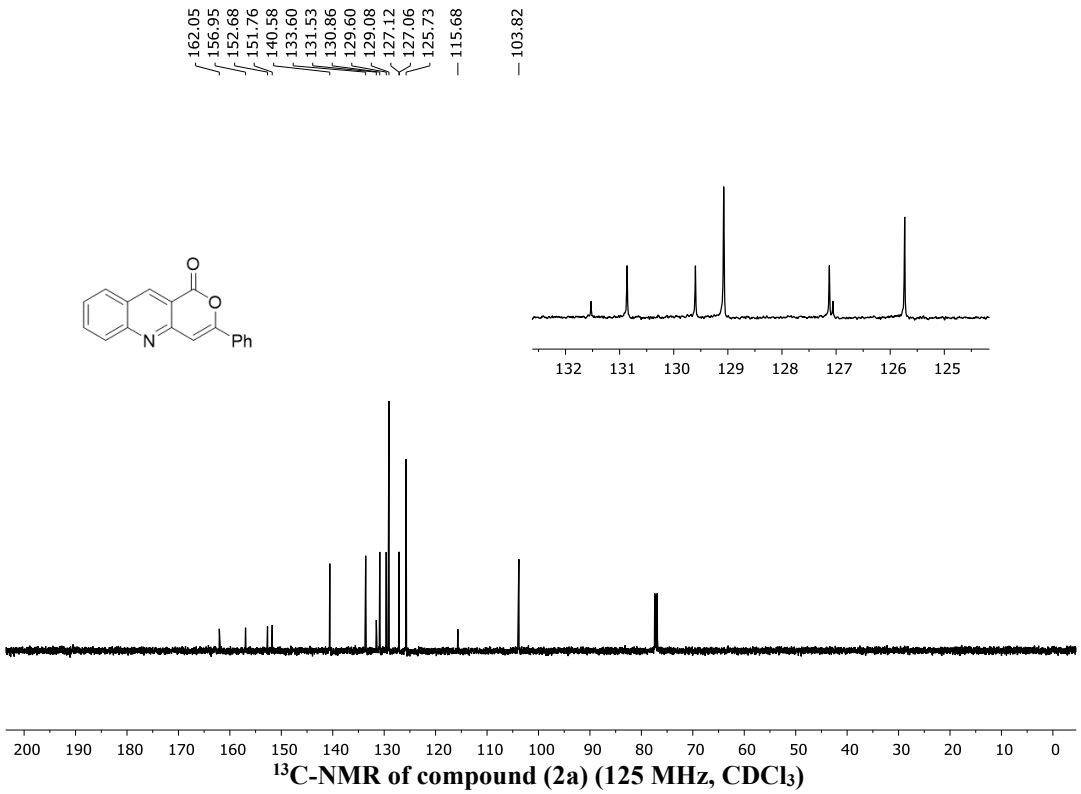
O(2)-C(11)-O(1)	117.6(3)
O(2)-C(11)-C(10)	125.6(3)
O(1)-C(11)-C(10)	116.8(3)
C(10)-C(12)-C(13)	119.5(3)
C(10)-C(12)-H(12)	120.2
C(13)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	117.1(3)
C(12)-C(13)-C(18)	122.9(3)
C(14)-C(13)-C(18)	120.0(3)
N(1)-C(14)-C(15)	118.7(3)
N(1)-C(14)-C(13)	123.4(3)
C(15)-C(14)-C(13)	117.9(3)
C(16)-C(15)-C(14)	120.4(3)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(15)-C(16)-C(17)	121.8(3)
C(15)-C(16)-H(16)	119.1
C(17)-C(16)-H(16)	119.1
C(18)-C(17)-C(16)	119.8(3)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(17)-C(18)-C(13)	120.2(3)
C(17)-C(18)-H(18)	119.9
C(13)-C(18)-H(18)	119.9

F. Copies of ^{1}H and ^{13}C NMR Spectra

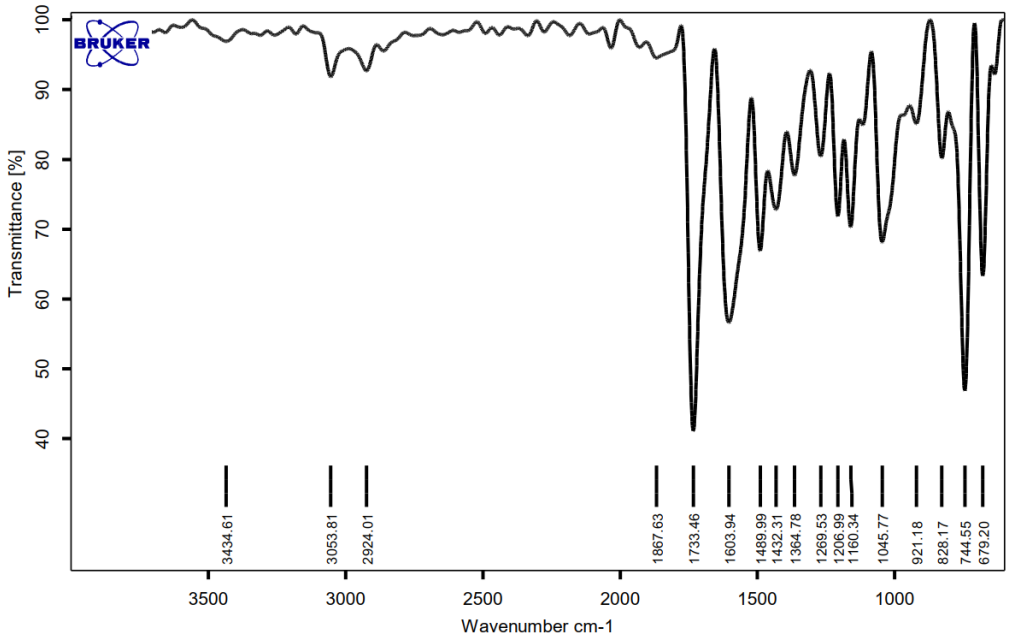
F1. ^{1}H NMR and ^{13}C NMR spectra of final compounds



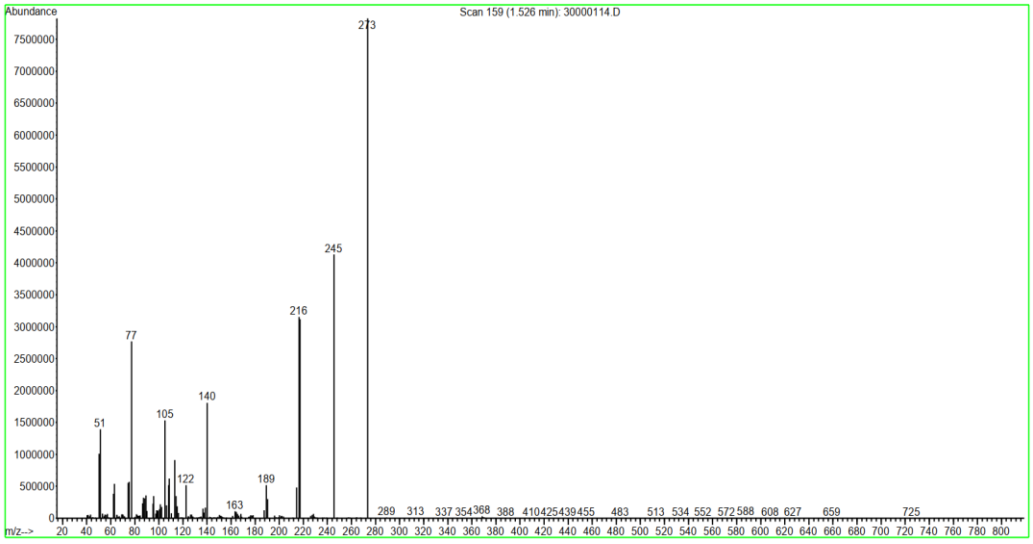
^{1}H-NMR of compound (2a) (500 MHz, $CDCl_3$)



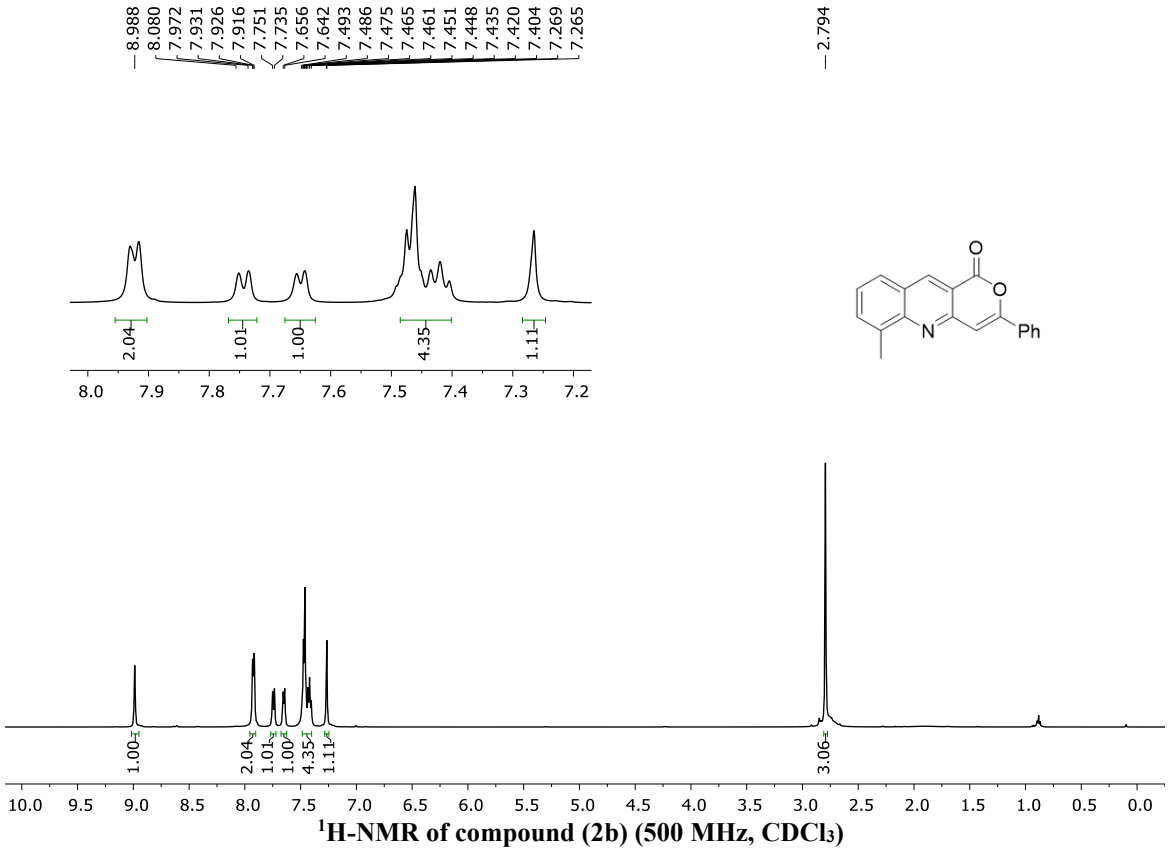
^{13}C-NMR of compound (2a) (125 MHz, $CDCl_3$)



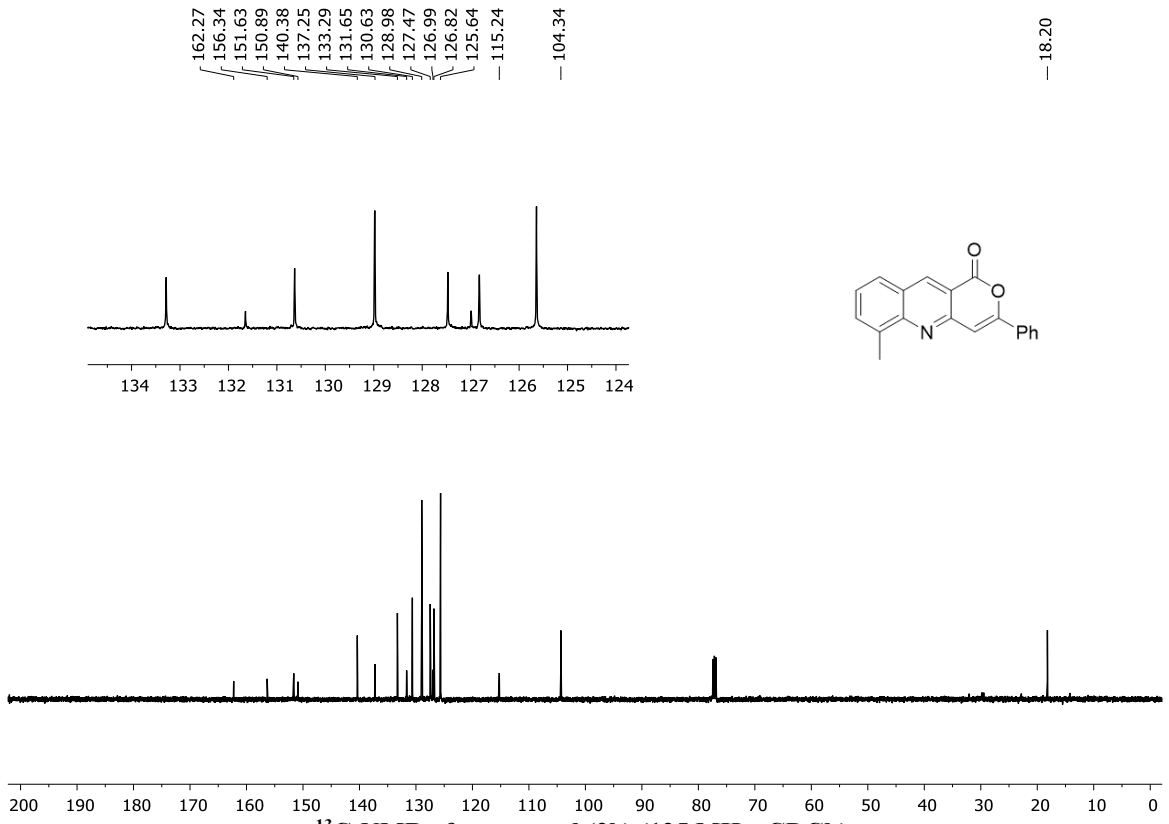
IR spectrum of compound 2a



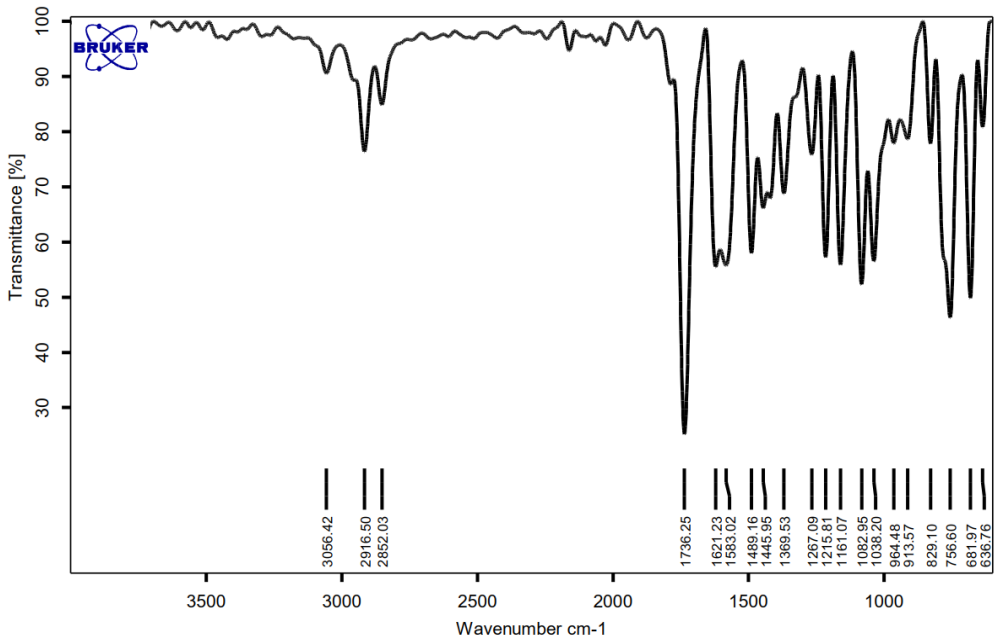
Mass spectrum of compound 2a with the molecular ion peak at 273



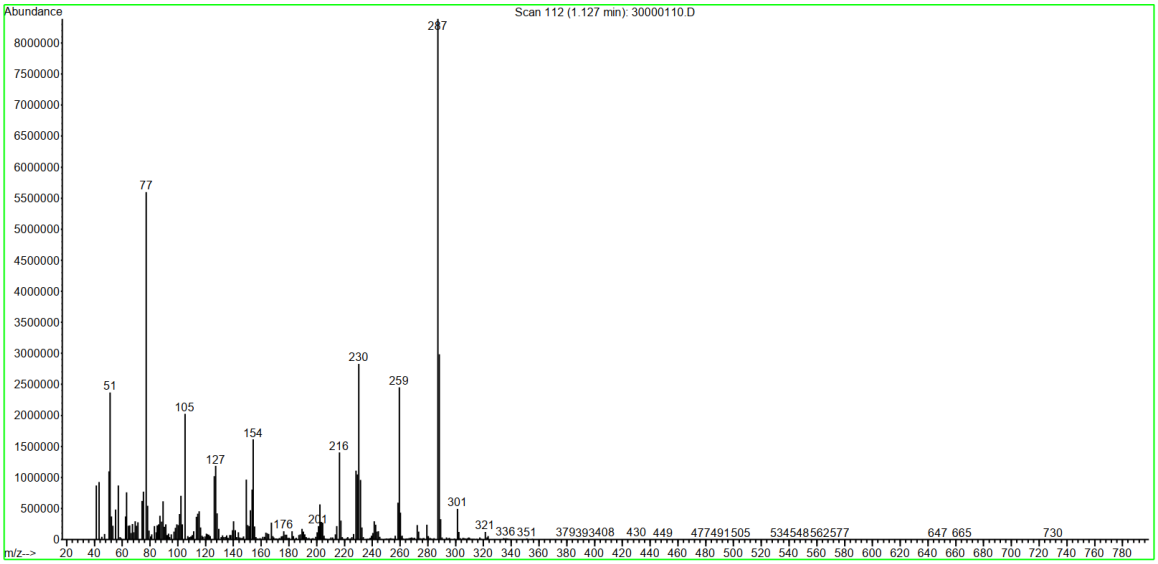
^{1}H-NMR of compound (2b) (500 MHz, $CDCl_3$)



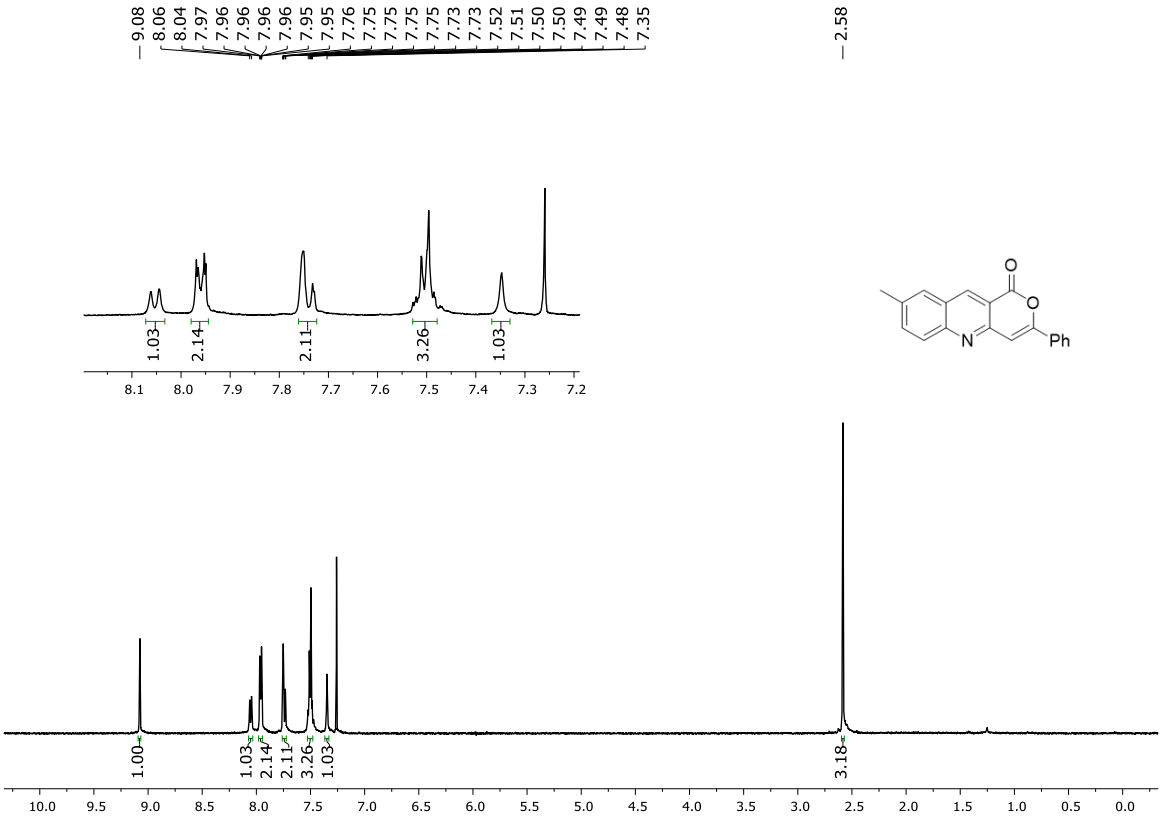
^{13}C-NMR of compound (2b) (125 MHz, $CDCl_3$)



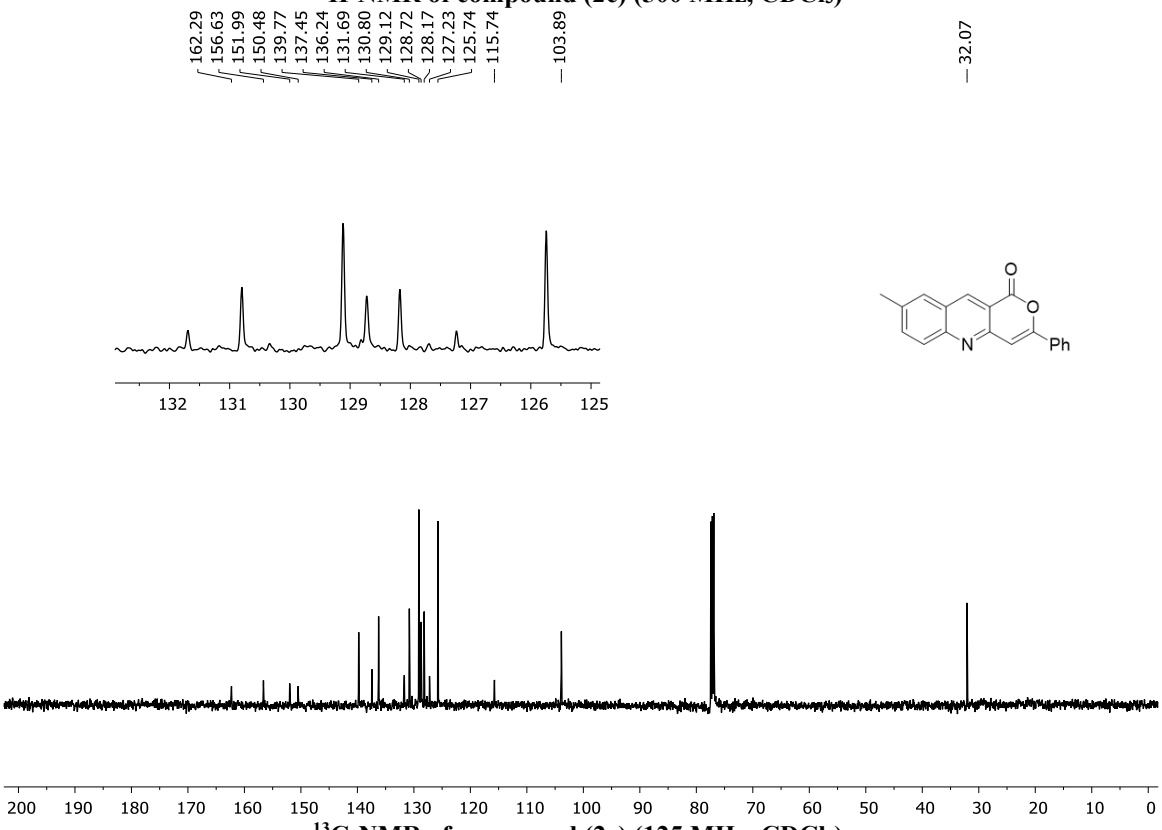
IR spectrum of compound 2b



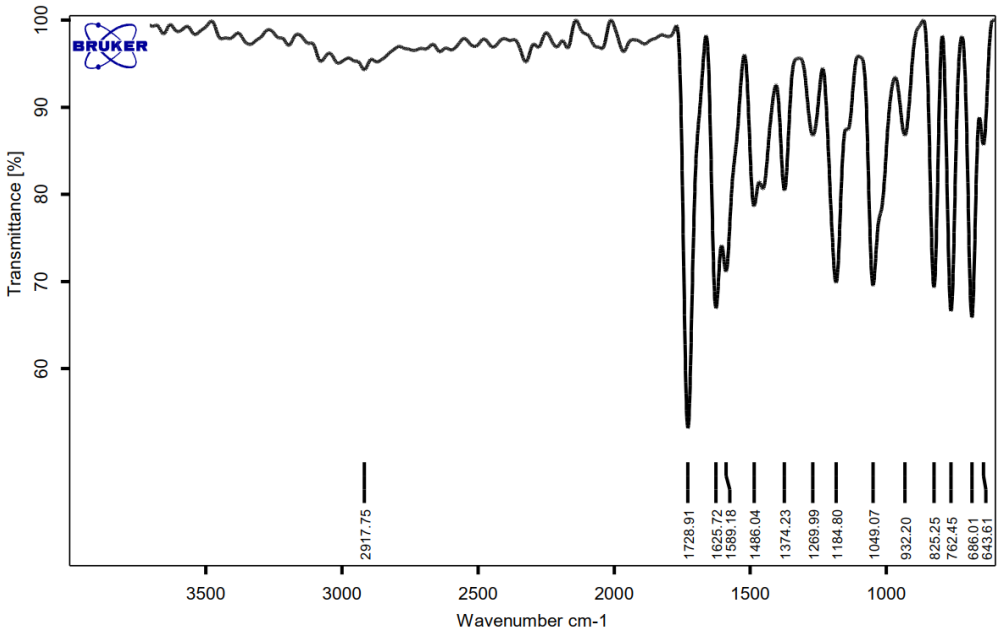
Mass spectrum of compound 2b with the molecular ion peak at 287



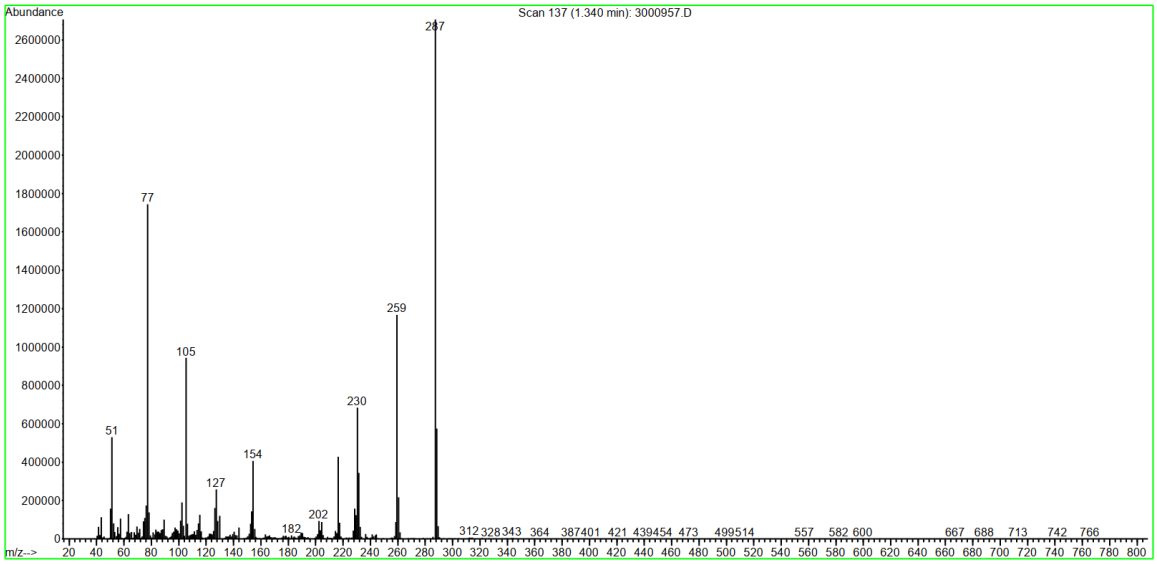
^{1}H-NMR of compound (2c) (500 MHz, $CDCl_3$)



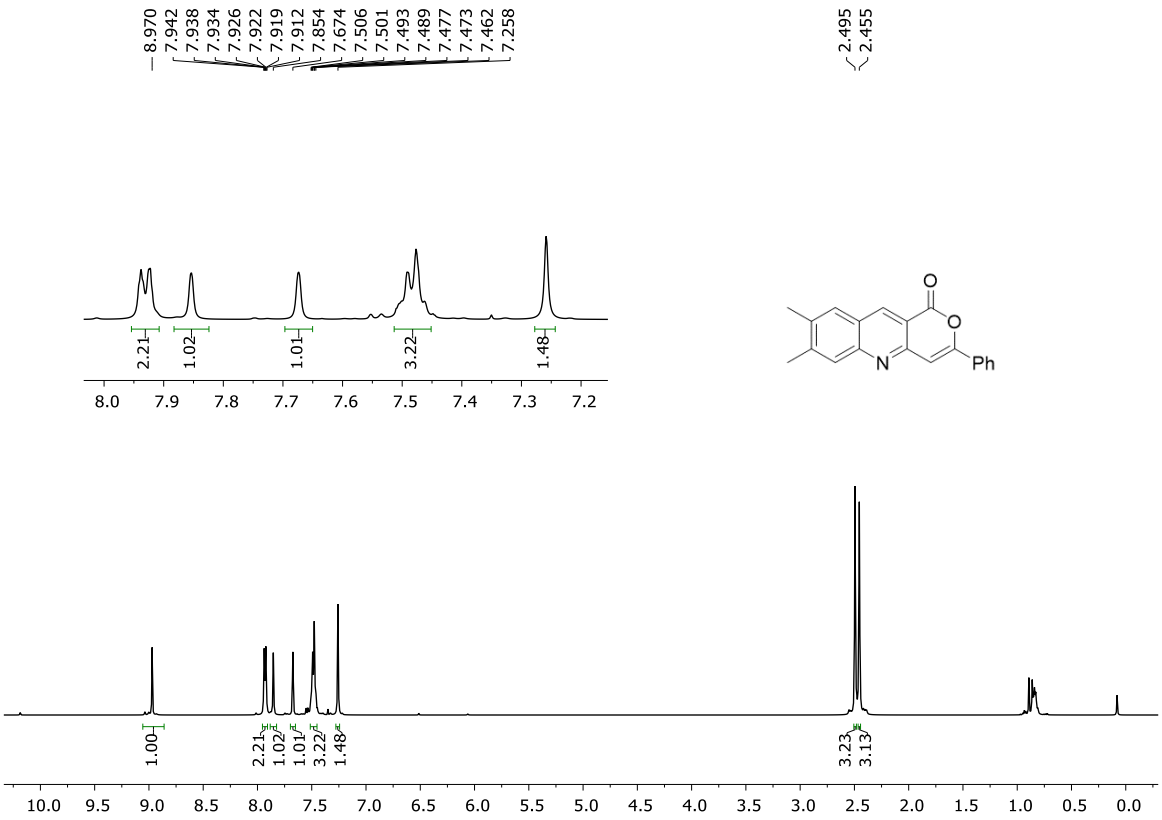
^{13}C-NMR of compound (2c) (125 MHz, $CDCl_3$)



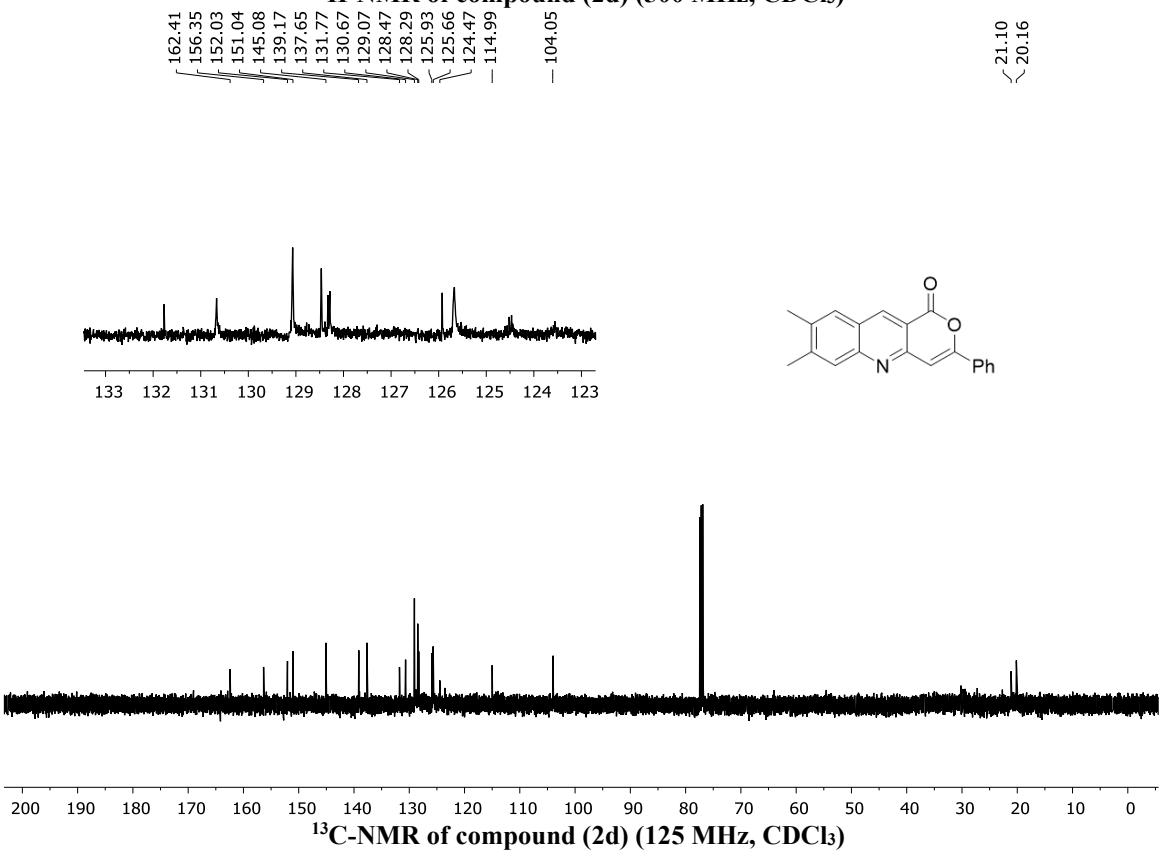
IR spectrum of compound 2c



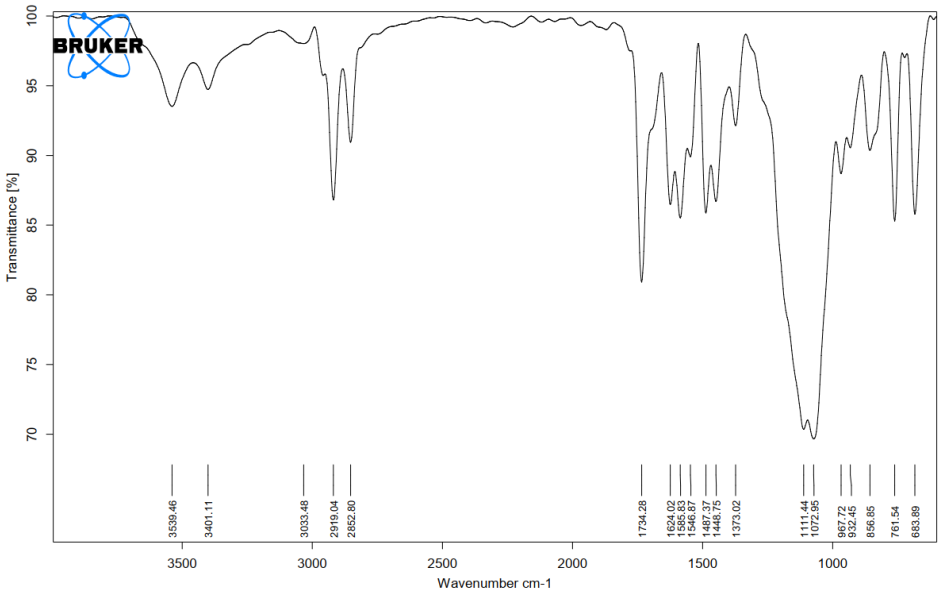
Mass spectrum of compound 2c with the molecular ion peak at 287



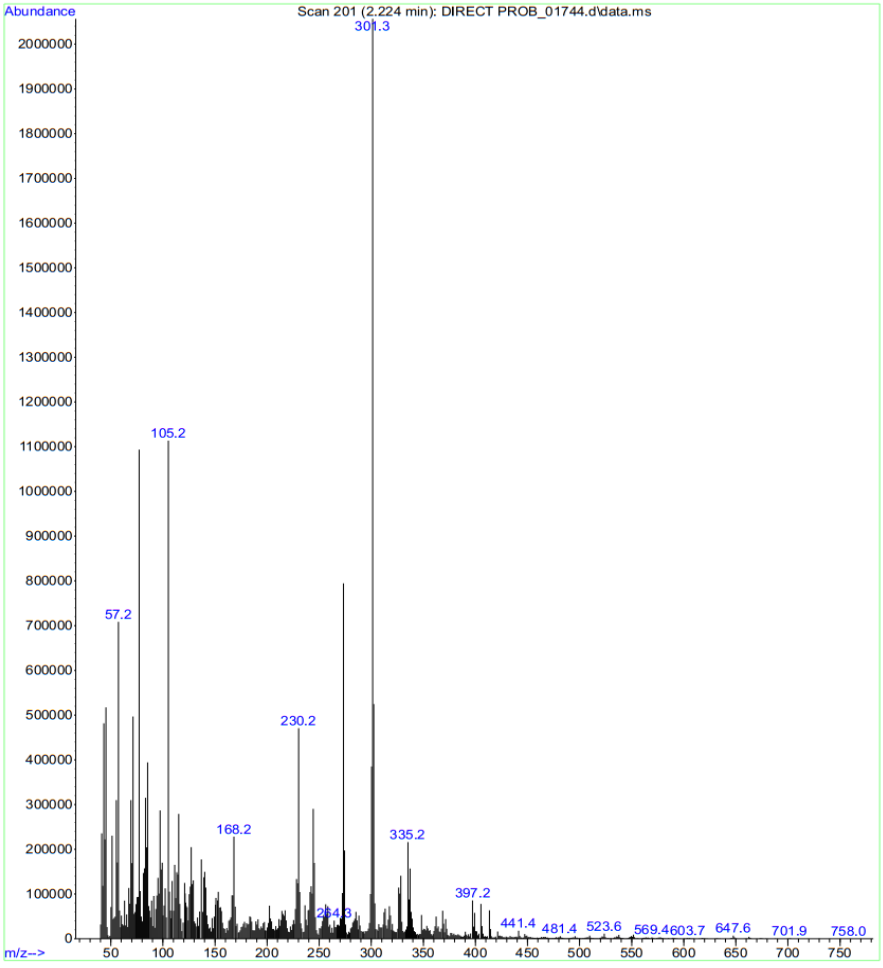
^{1}H-NMR of compound (2d) (500 MHz, $CDCl_3$)



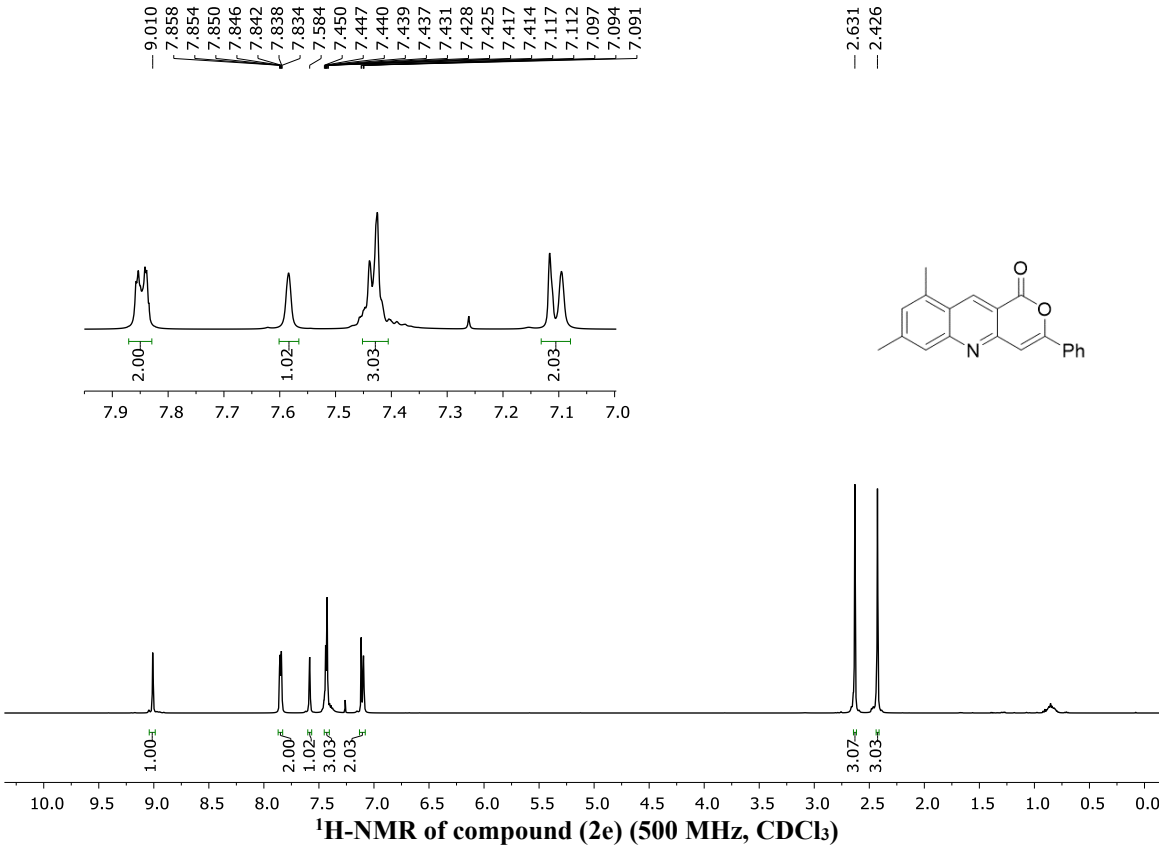
^{13}C-NMR of compound (2d) (125 MHz, $CDCl_3$)



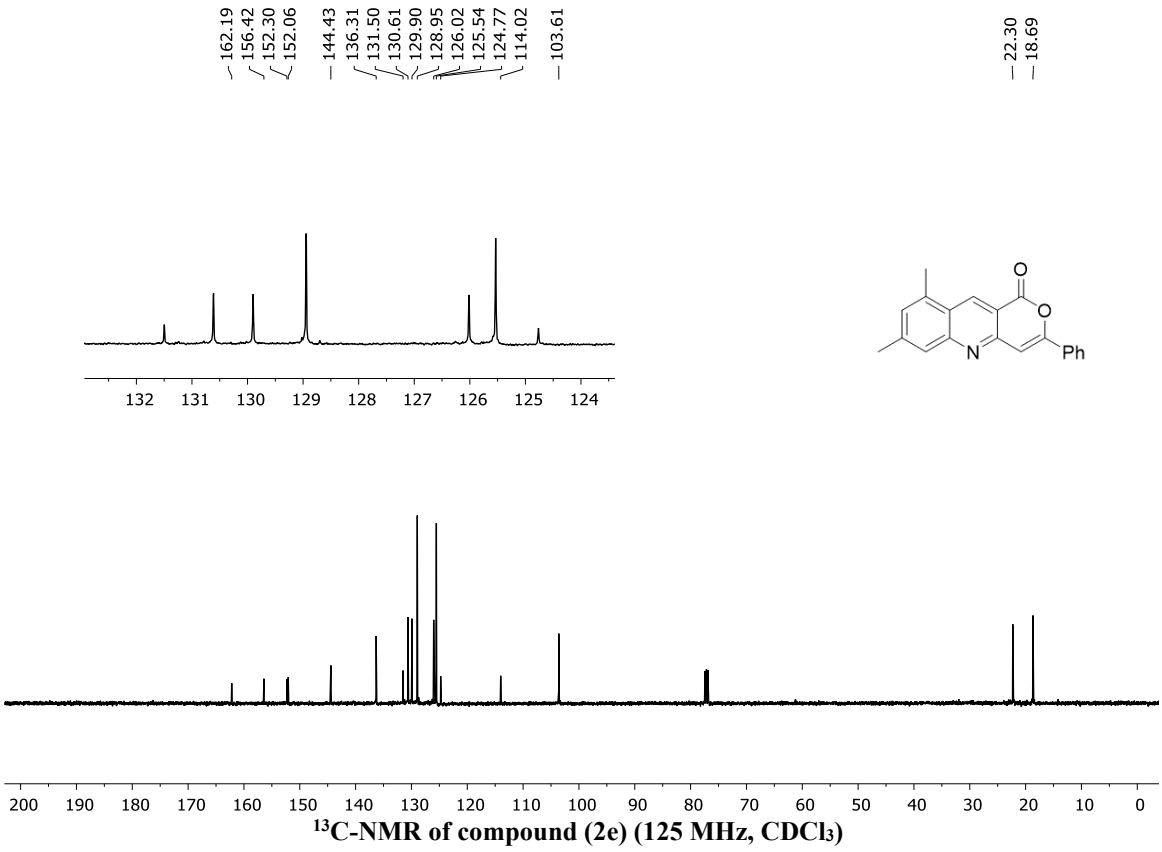
IR spectrum of compound 2d



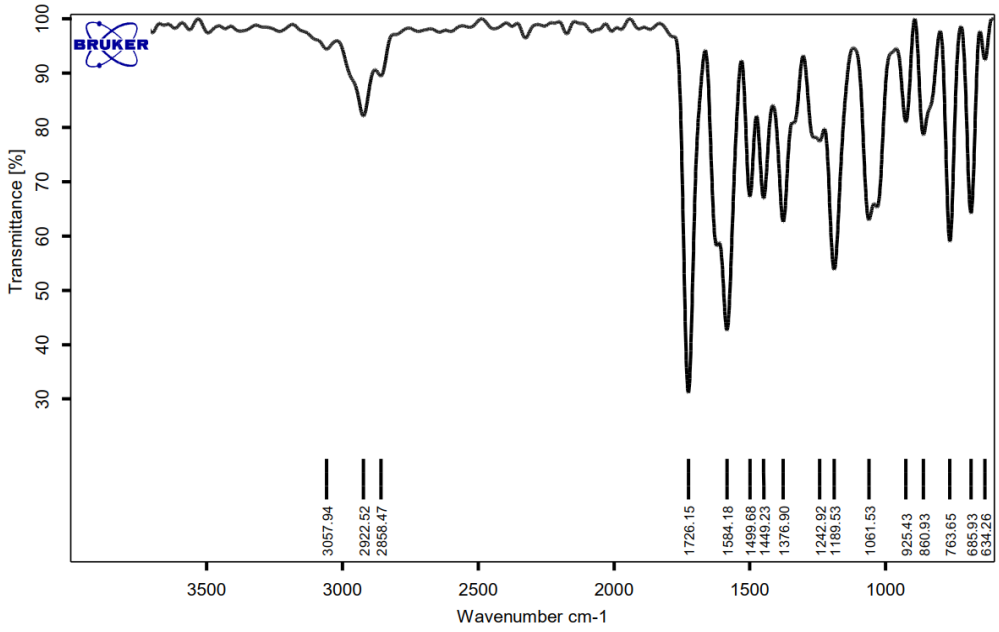
Mass spectrum of compound 2d with the molecular ion peak at 301



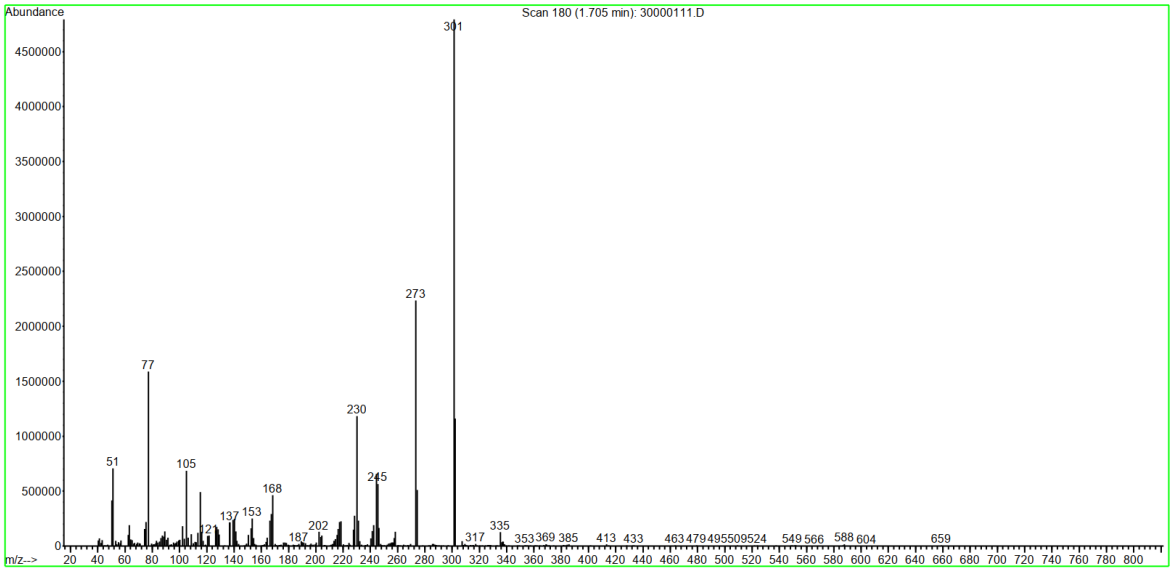
^{1}H-NMR of compound (2e) (500 MHz, $CDCl_3$)



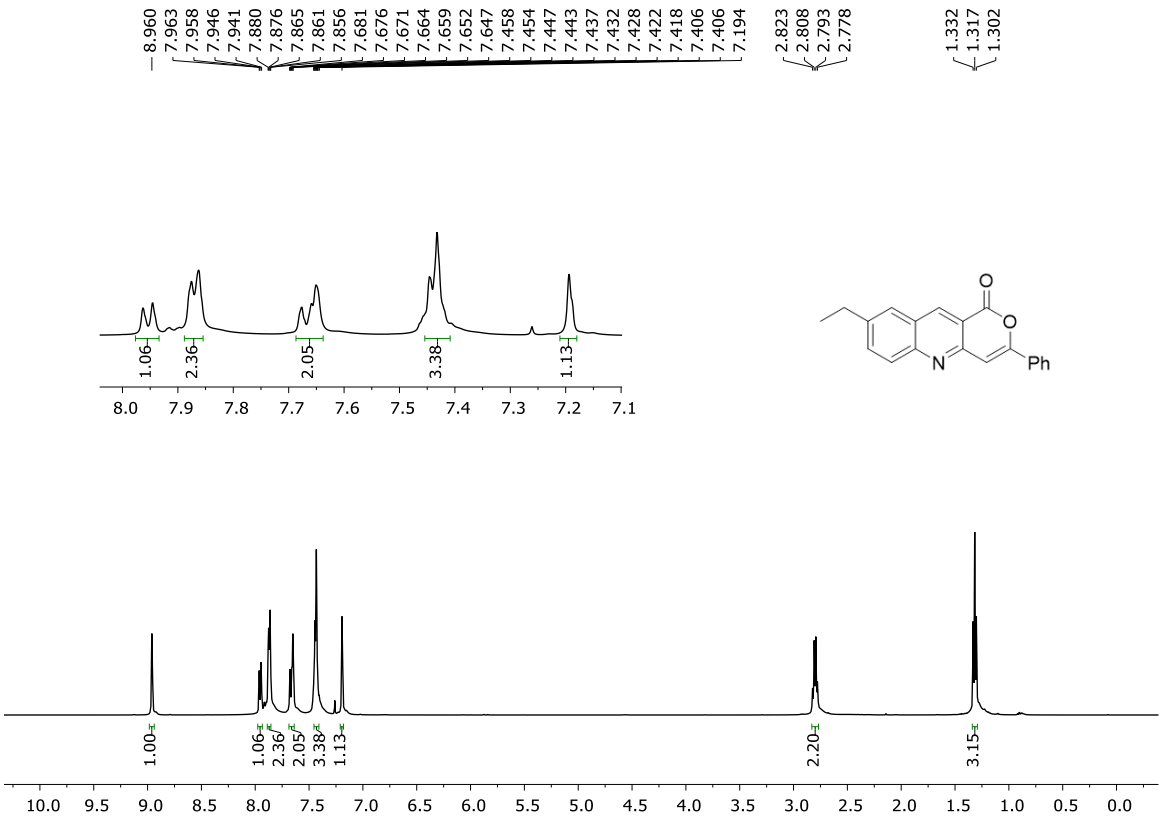
^{13}C-NMR of compound (2e) (125 MHz, $CDCl_3$)



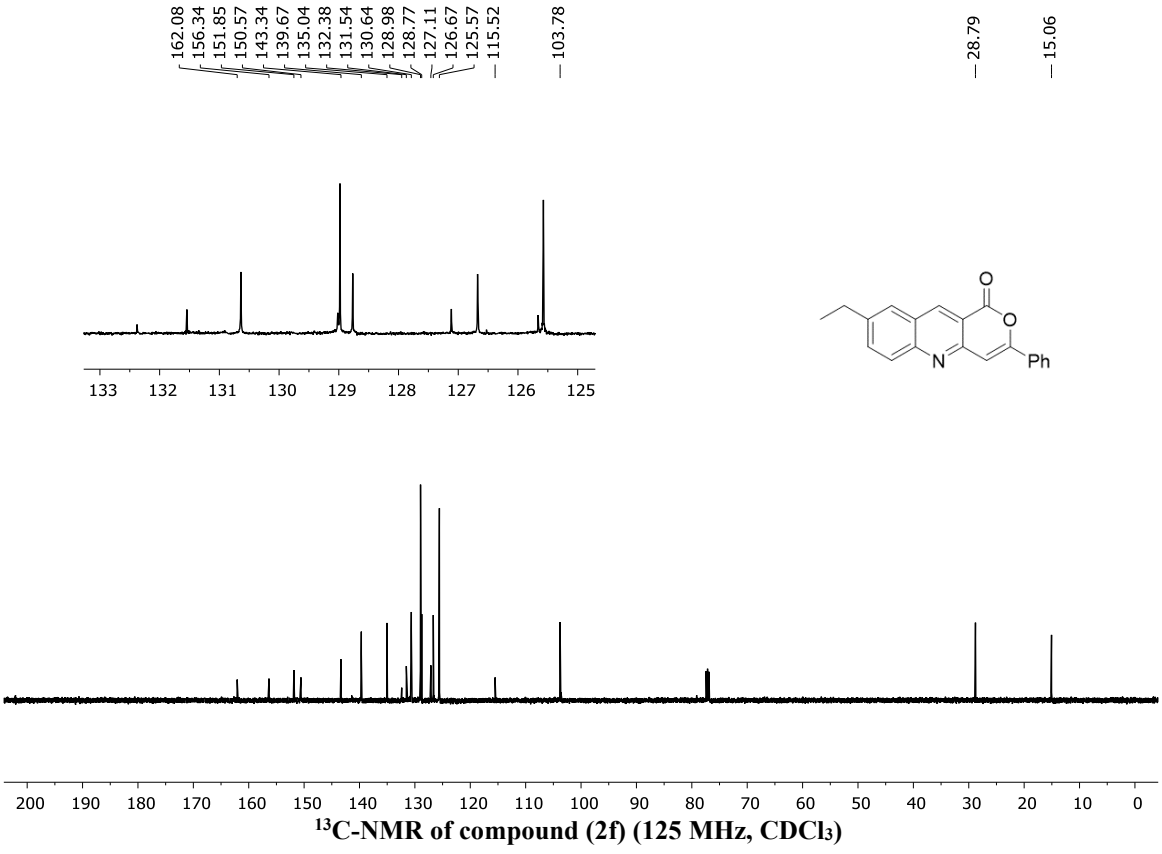
IR spectrum of compound 2e



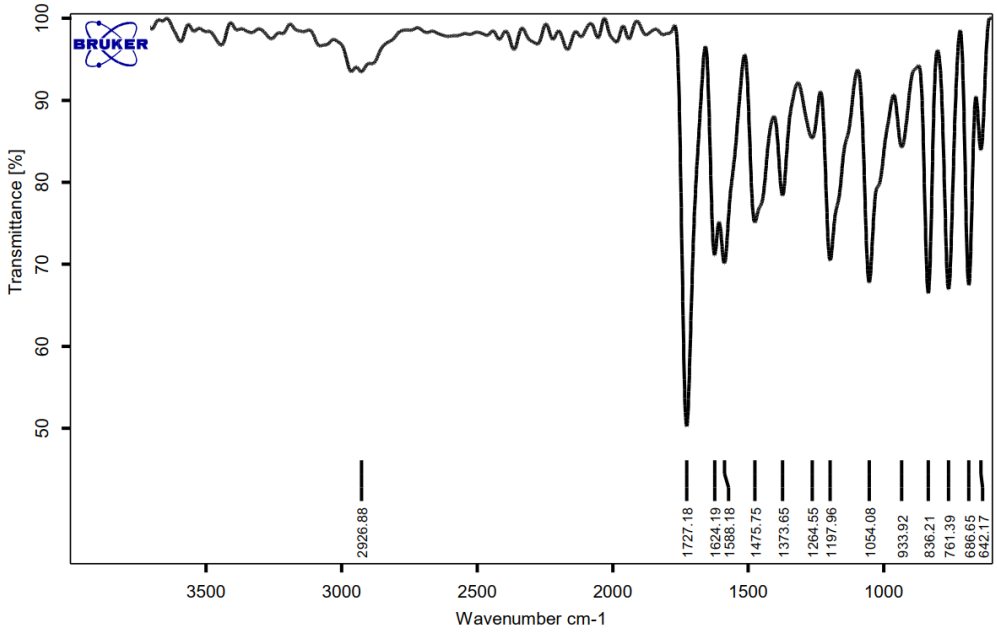
Mass spectrum of compound 2e with the molecular ion peak at 301



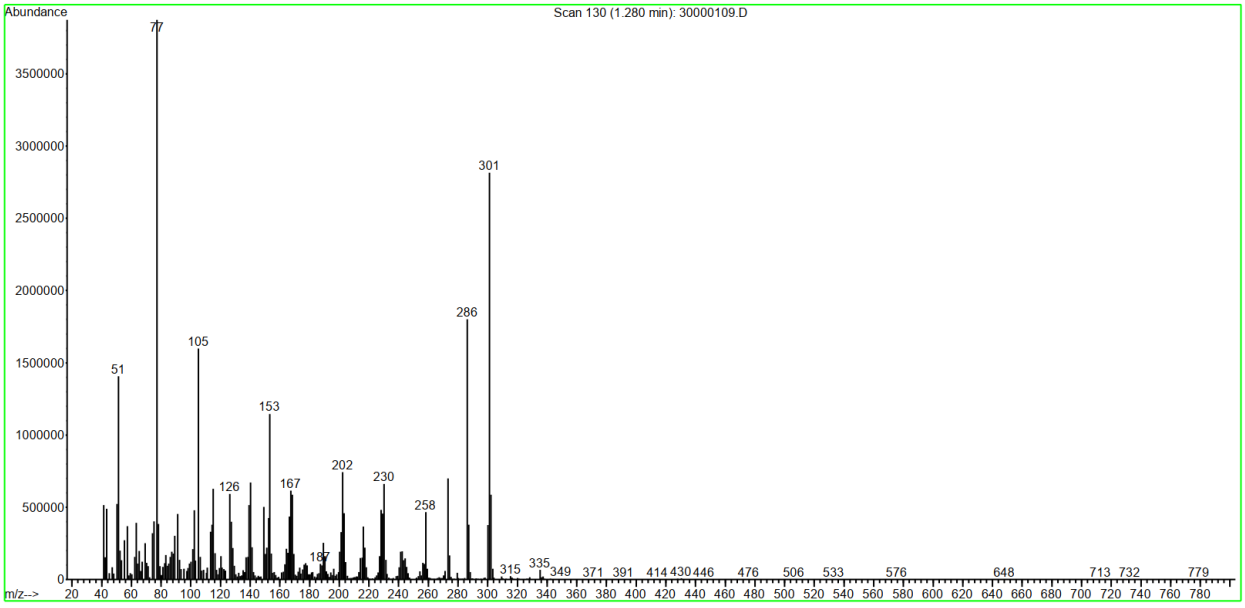
^{1}H-NMR of compound (2f) (500 MHz, $CDCl_3$)



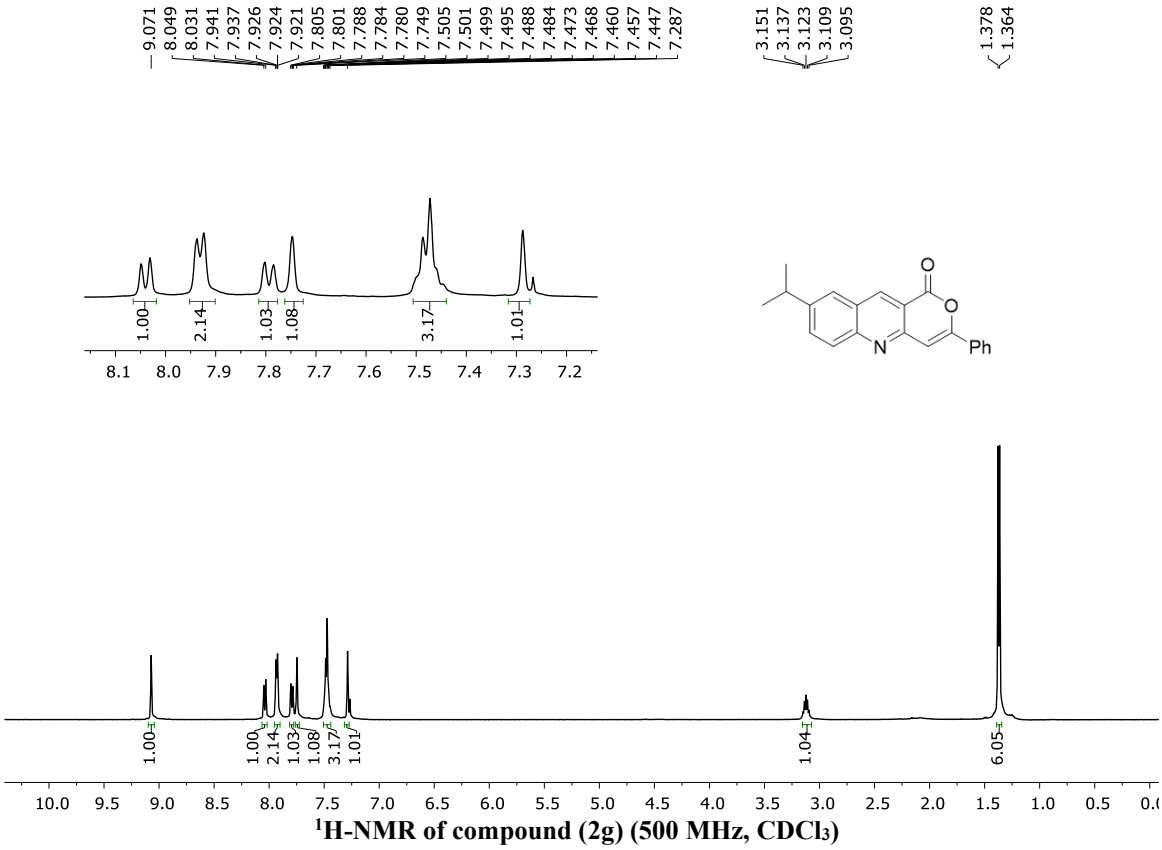
^{13}C-NMR of compound (2f) (125 MHz, $CDCl_3$)



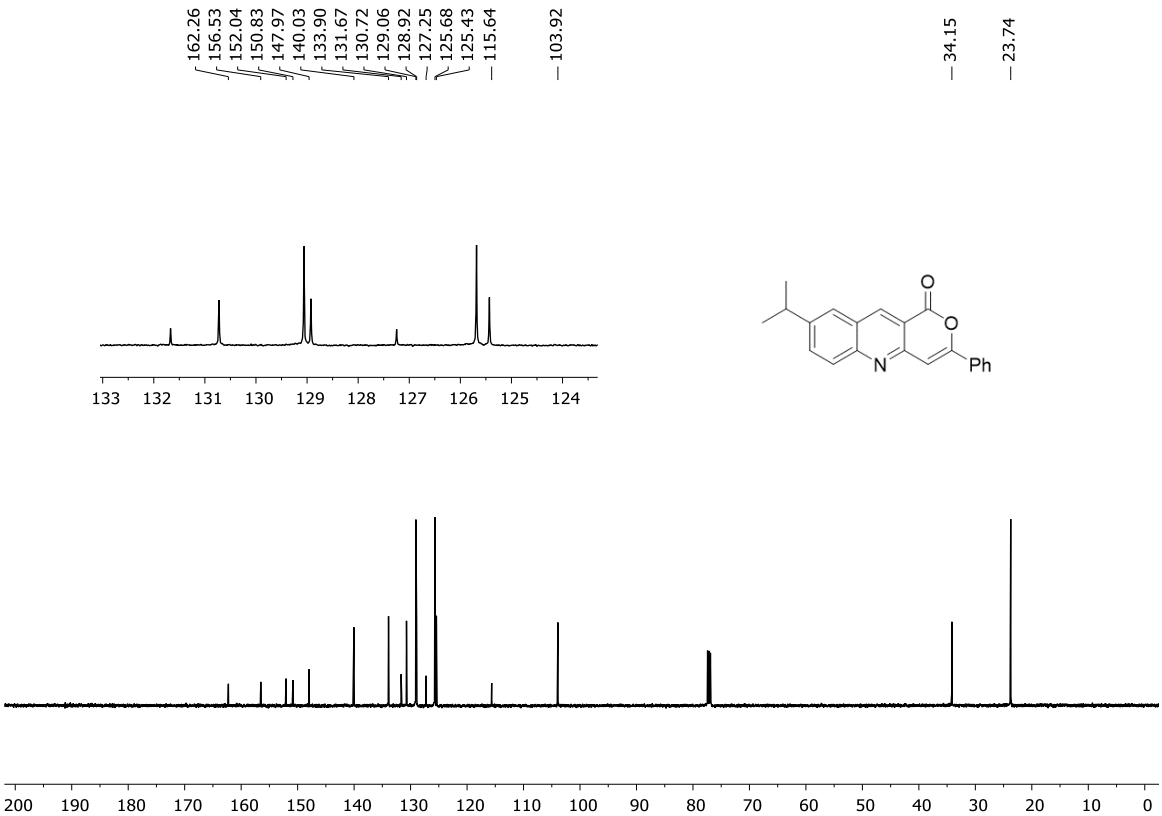
IR spectrum of compound 2f



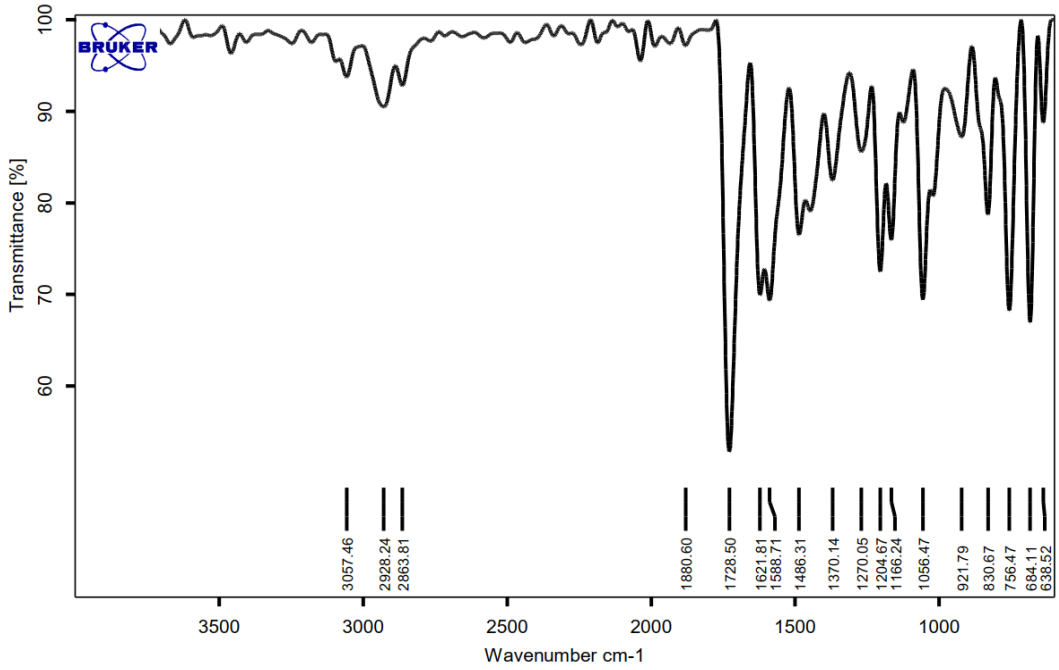
Mass spectrum of compound 2f with the molecular ion peak at 301



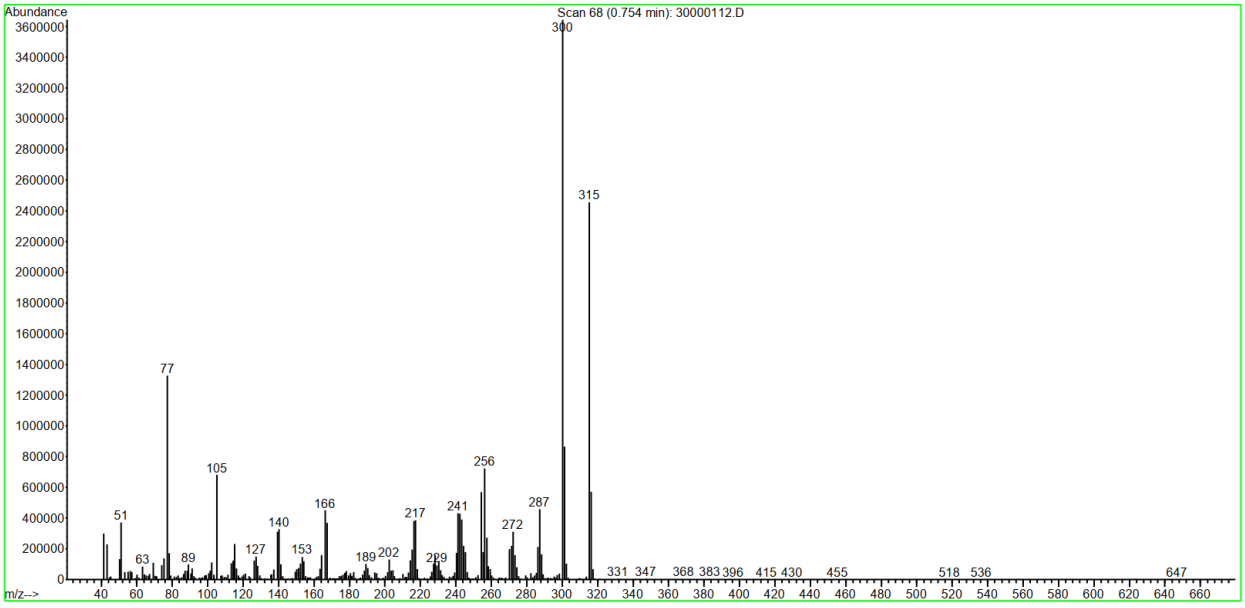
^{1}H-NMR of compound (2g) (500 MHz, $CDCl_3$)



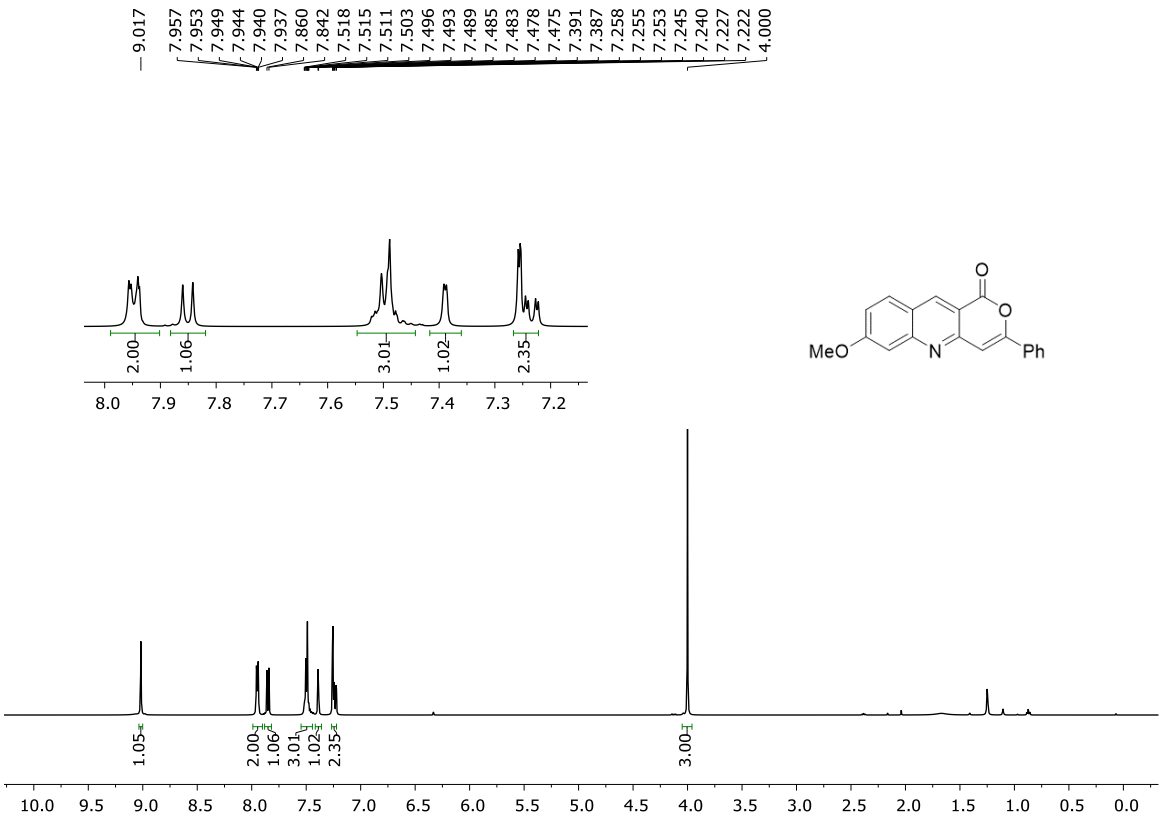
^{13}C-NMR of compound (2g) (125 MHz, $CDCl_3$)



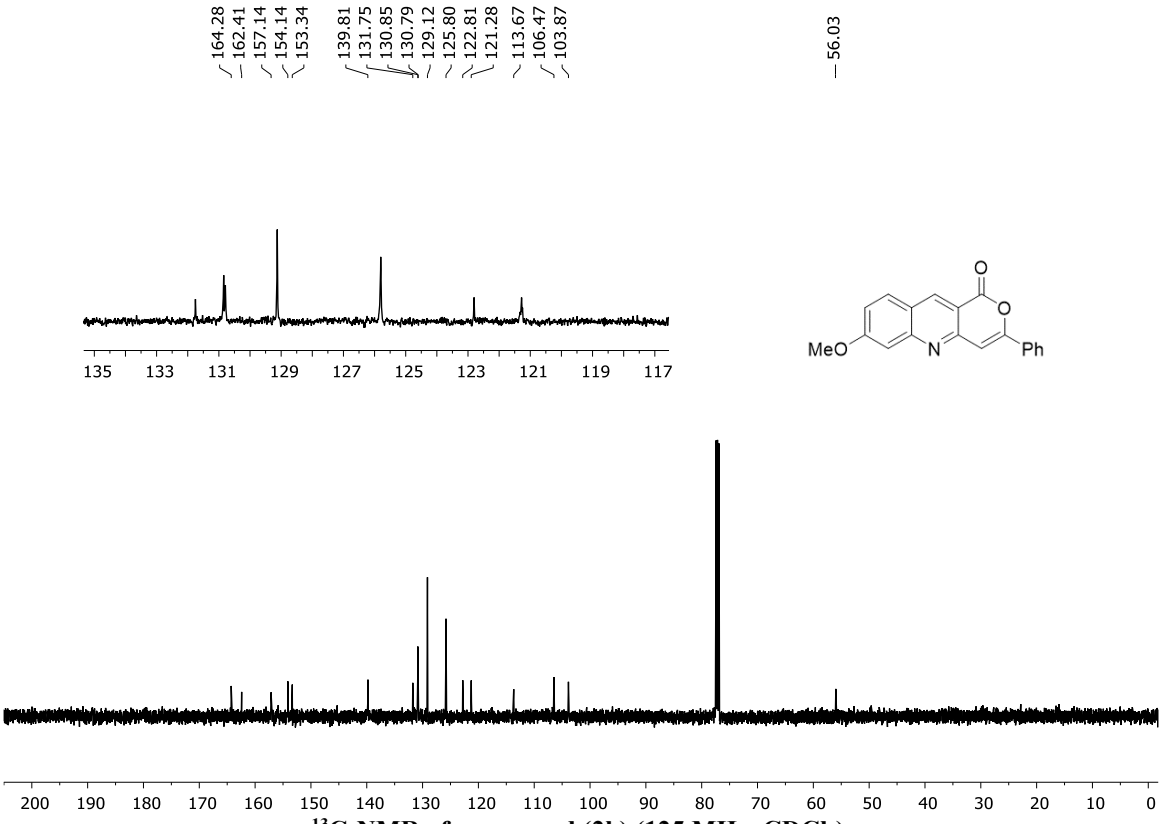
IR spectrum of compound 2g



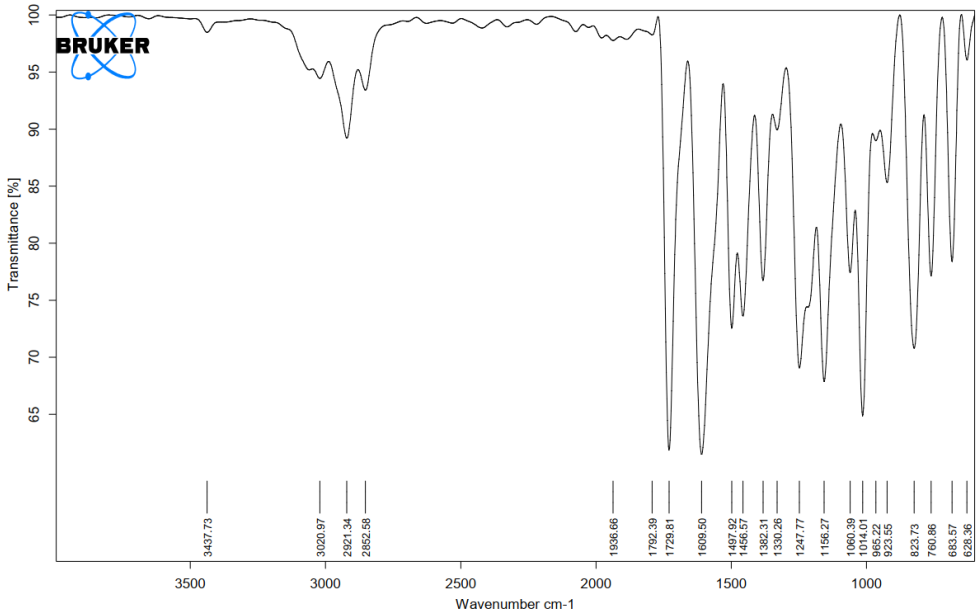
Mass spectrum of compound 2g with the molecular ion peak at 315



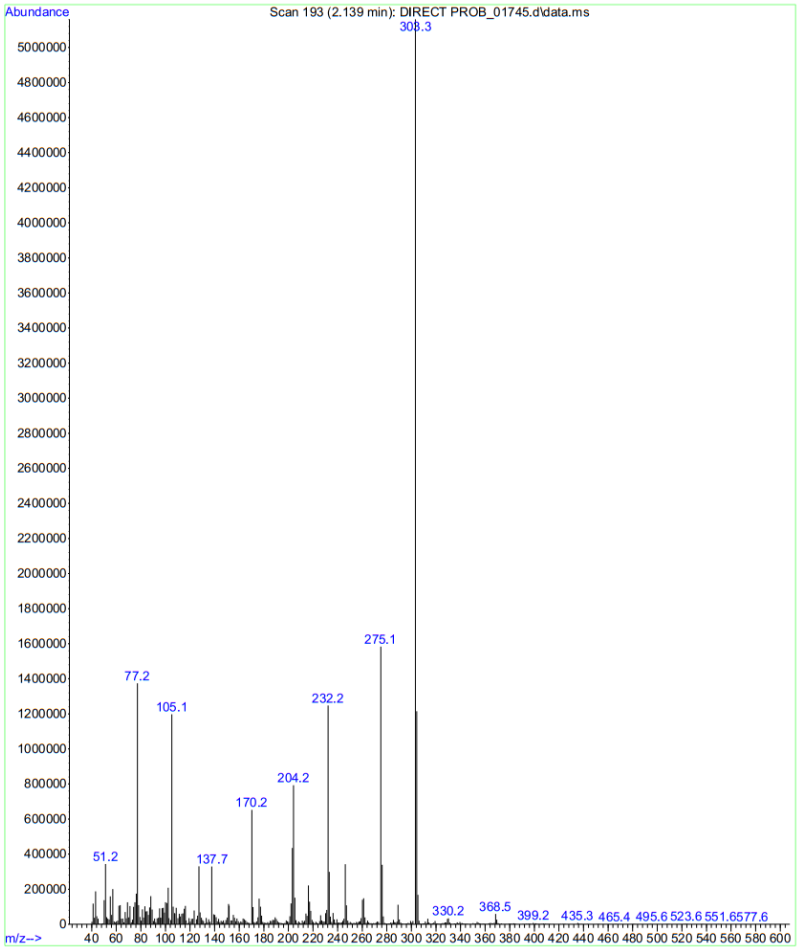
^{1}H-NMR of compound (2h) (500 MHz, $CDCl_3$)



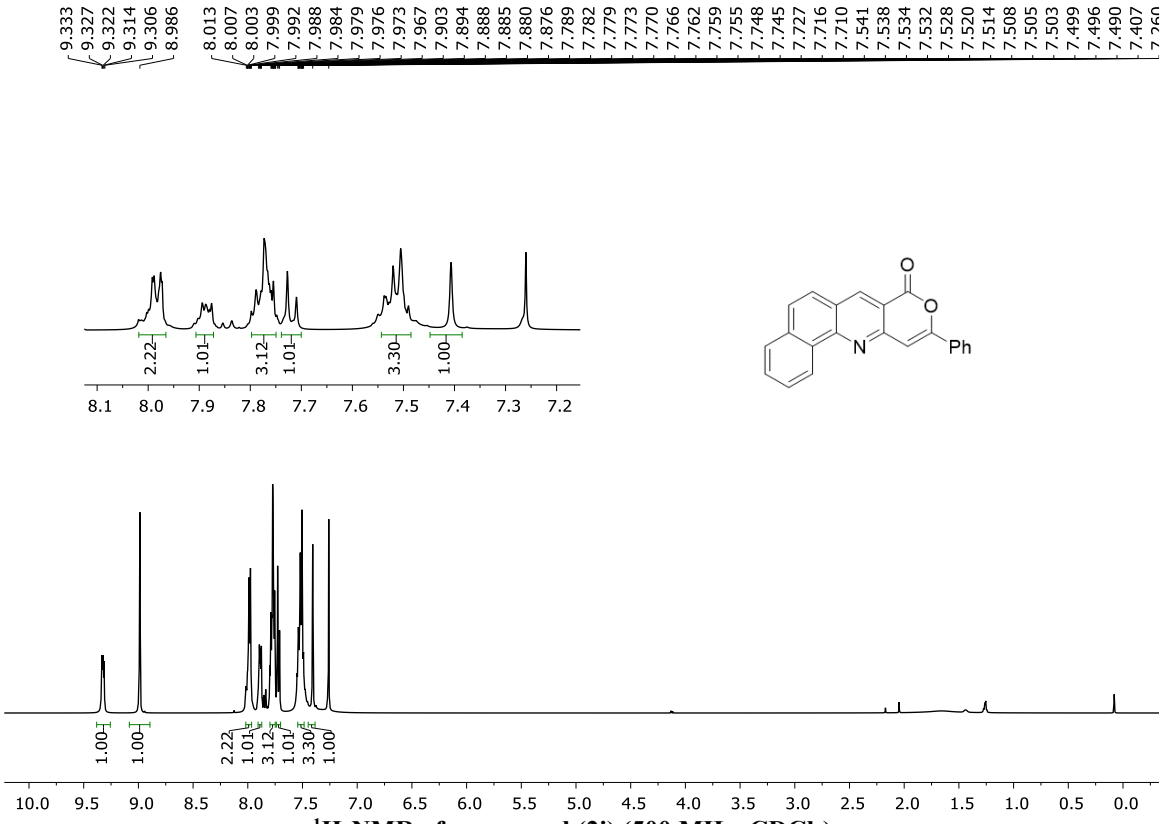
^{13}C-NMR of compound (2h) (125 MHz, $CDCl_3$)



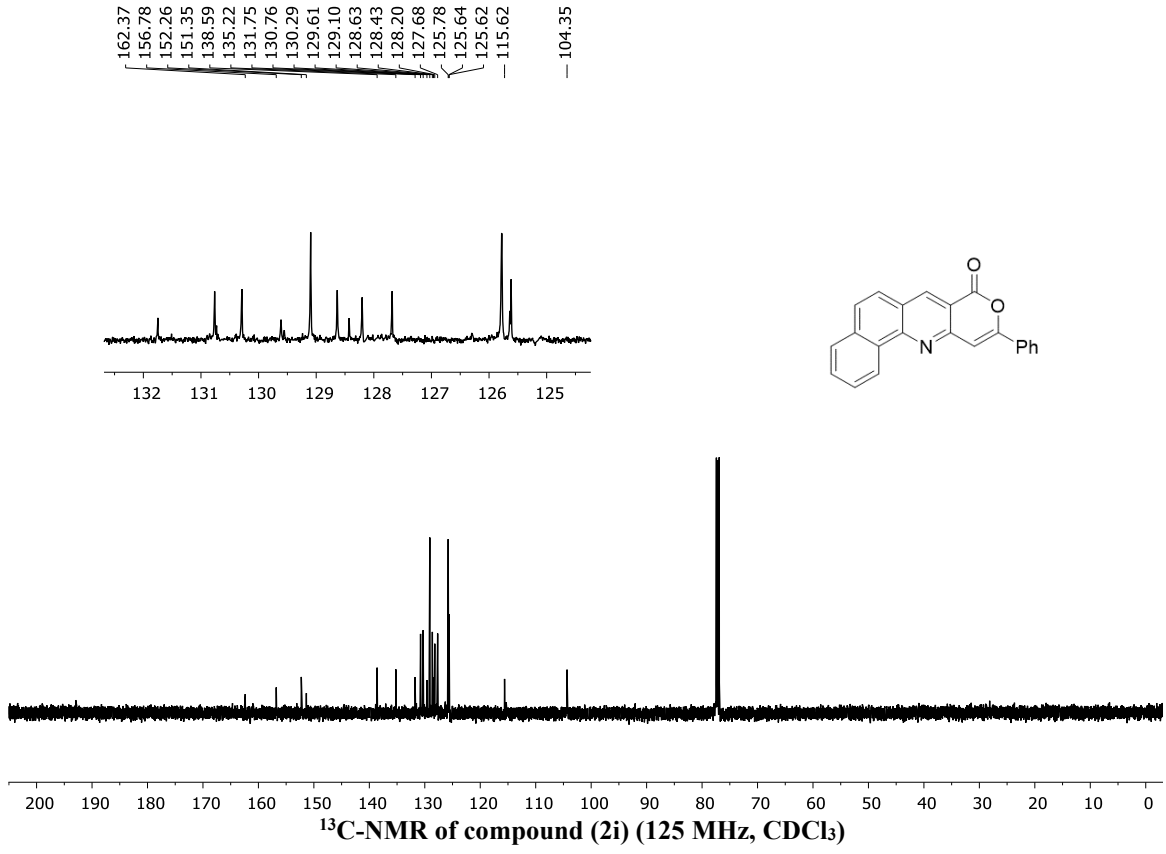
IR spectrum of compound 2h



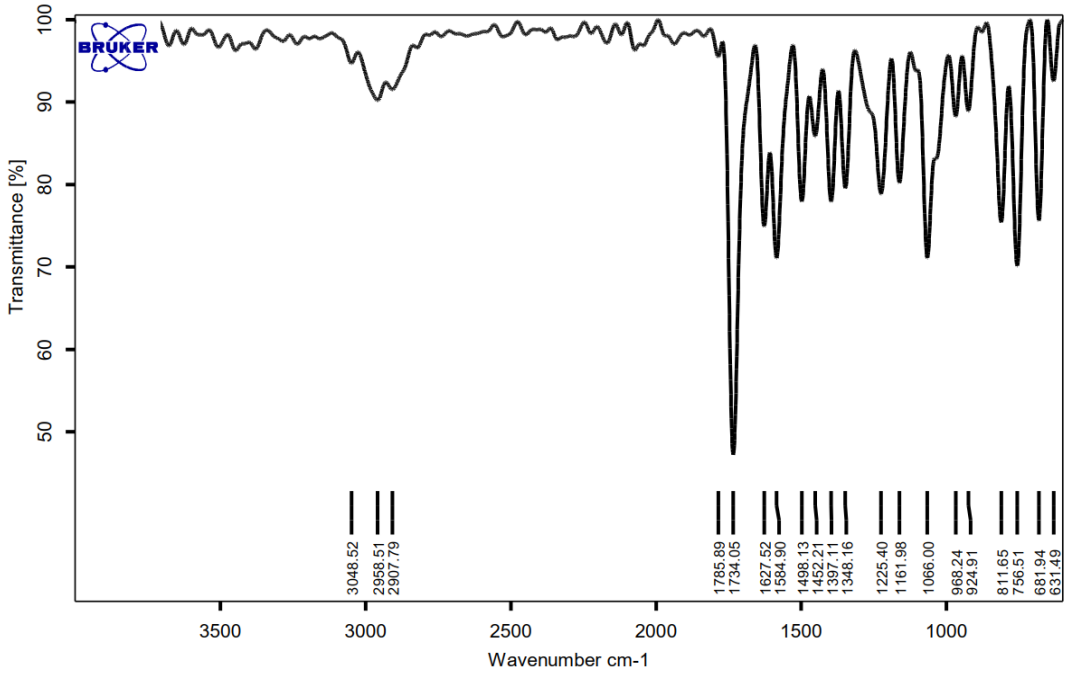
Mass spectrum of compound 2h with the molecular ion peak at 303



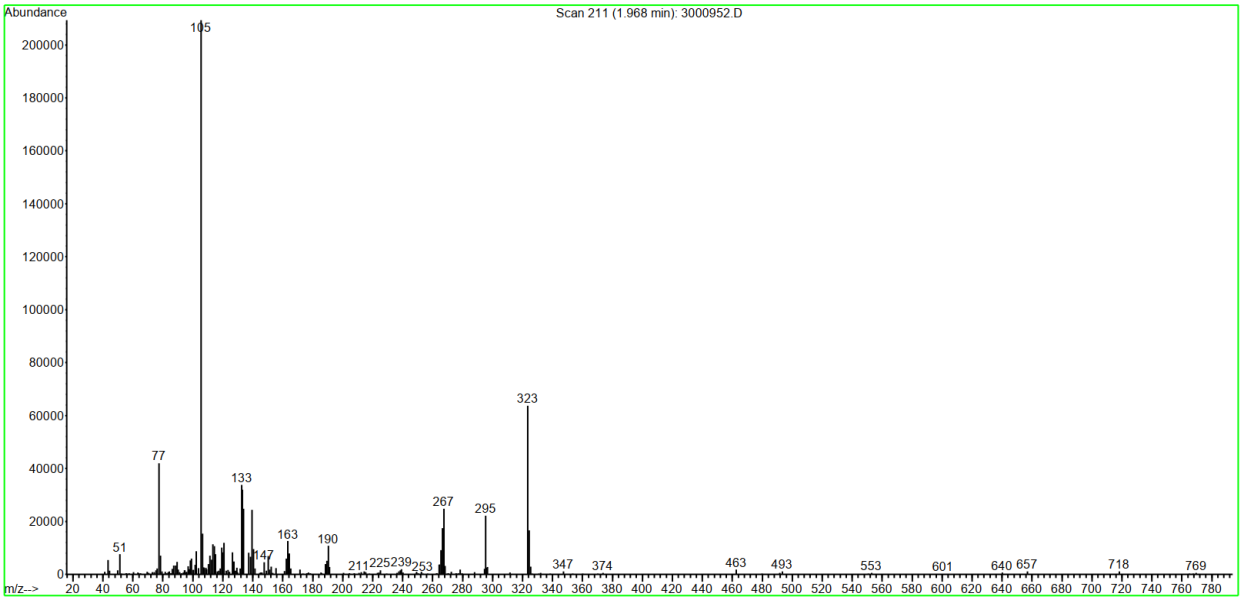
^{1}H-NMR of compound (2i) (500 MHz, $CDCl_3$)



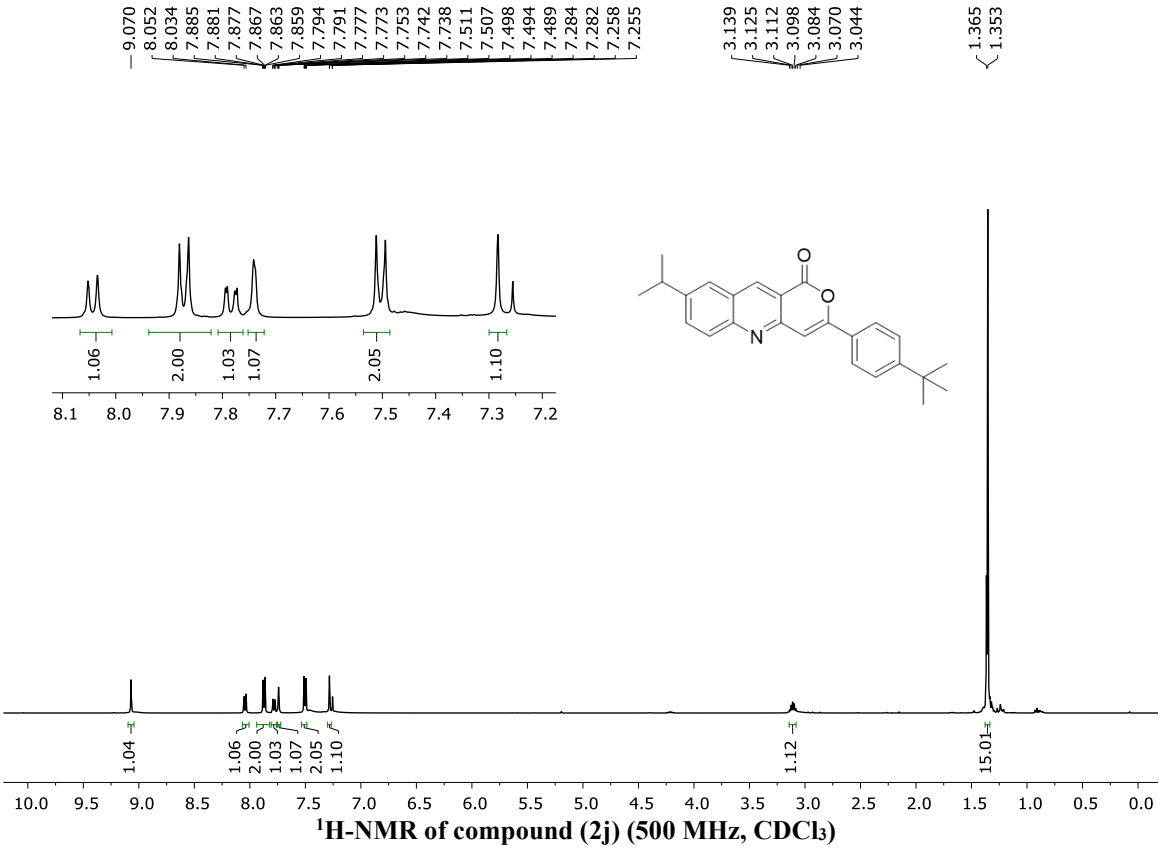
^{13}C-NMR of compound (2i) (125 MHz, $CDCl_3$)



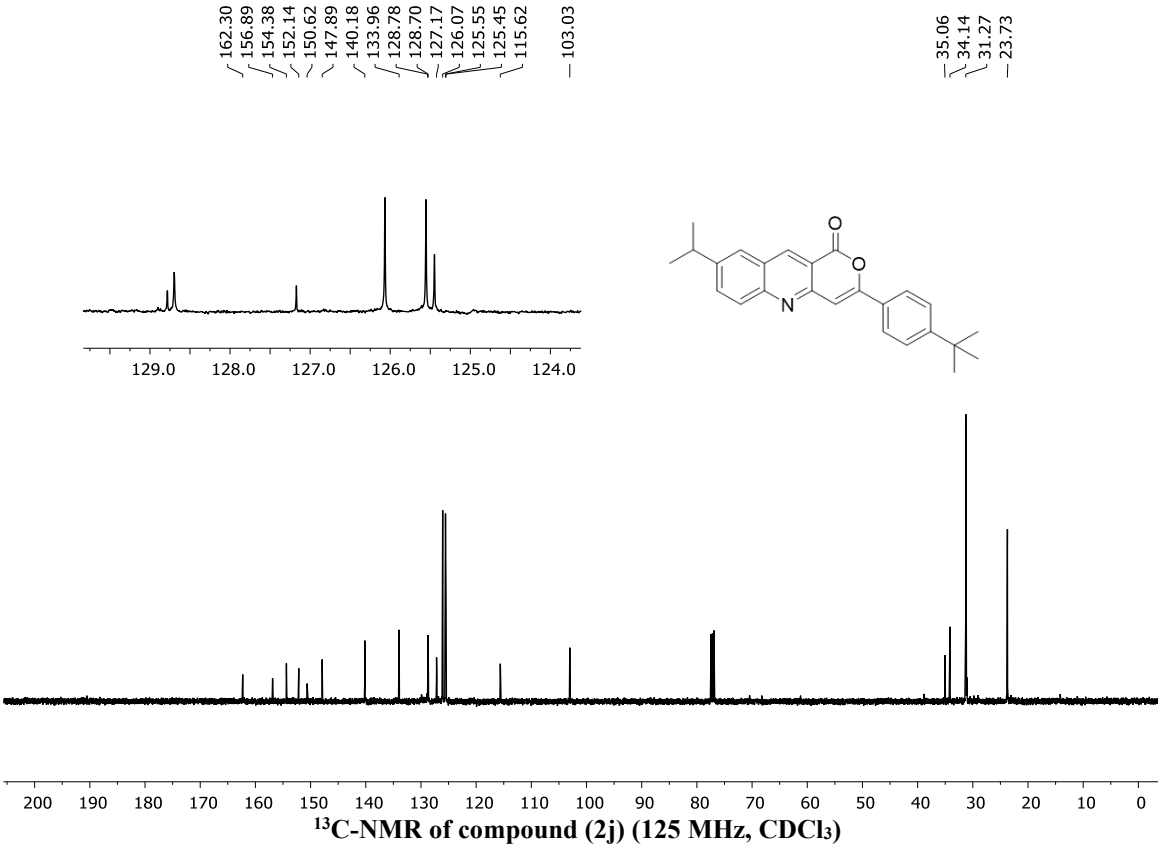
IR spectrum of compound 2i



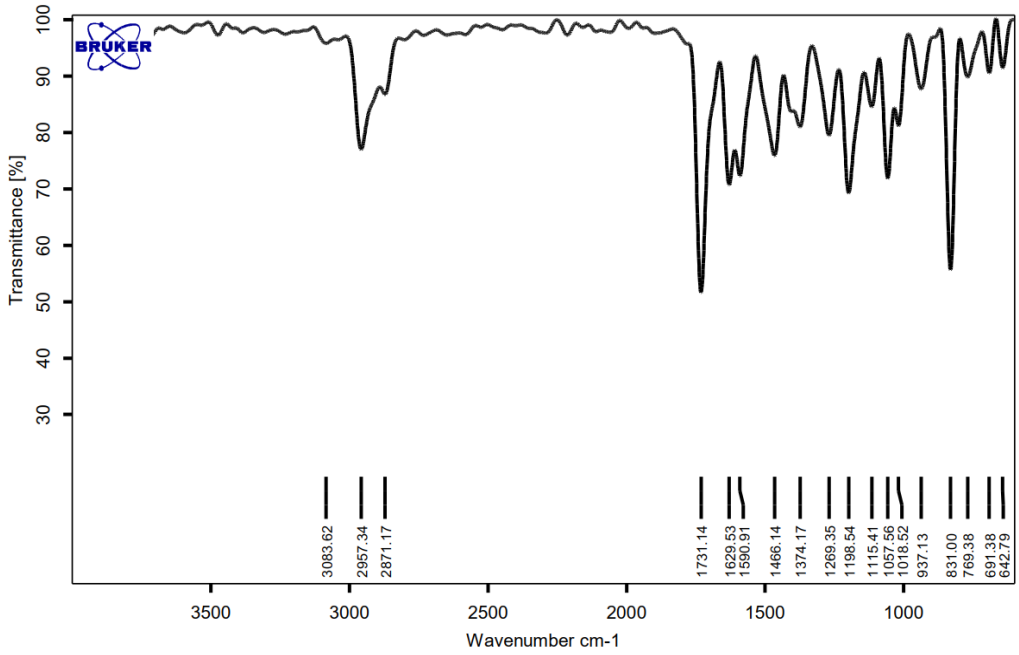
Mass spectrum of compound 2i with the molecular ion peak at 323



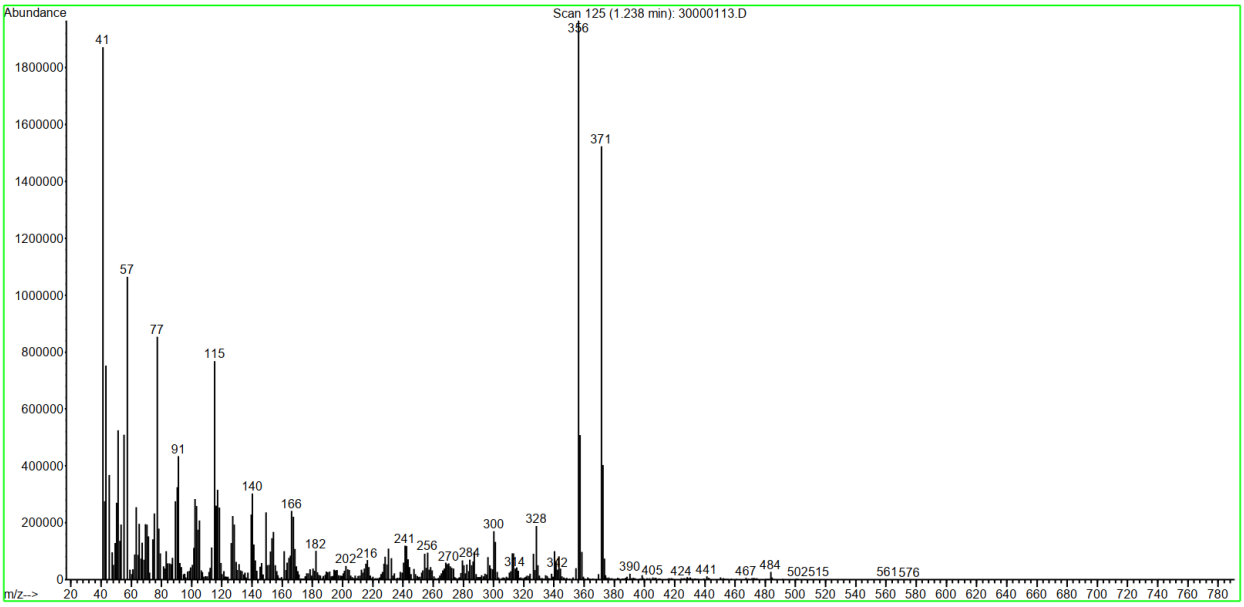
^{1}H-NMR of compound (2j) (500 MHz, $CDCl_3$)



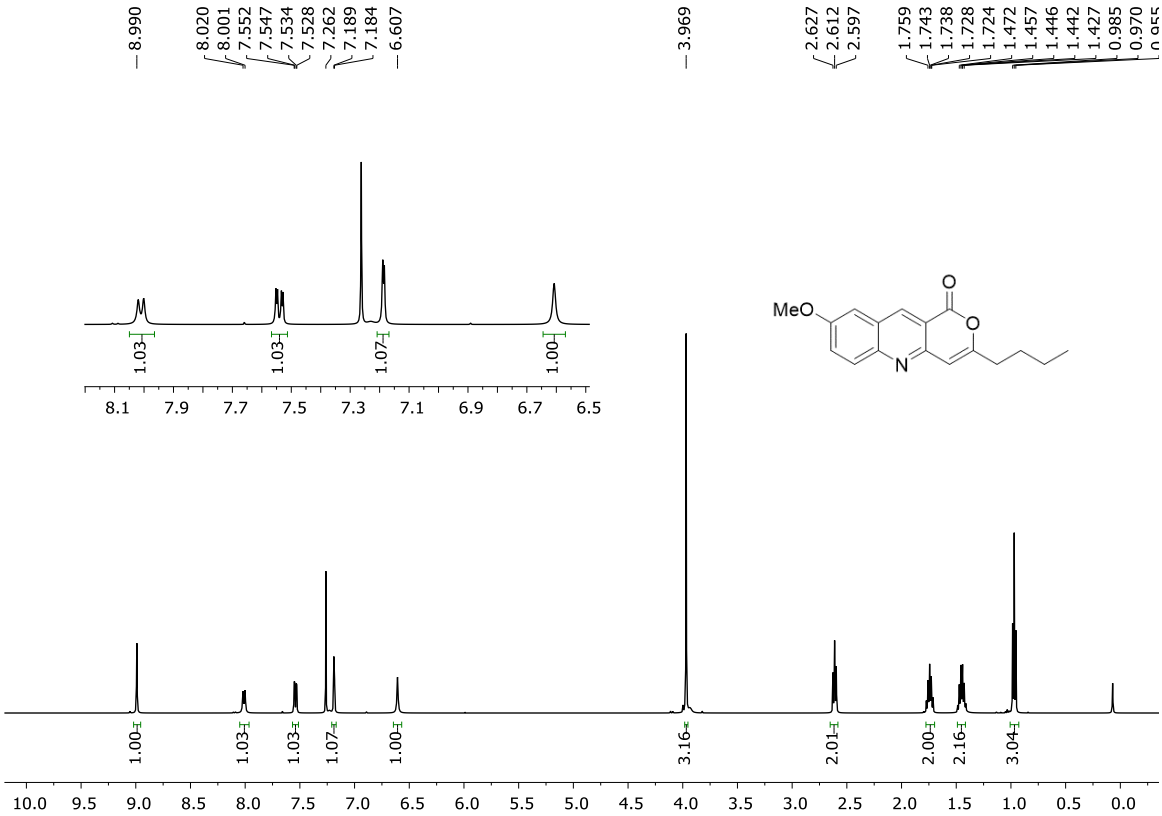
^{13}C-NMR of compound (2j) (125 MHz, $CDCl_3$)



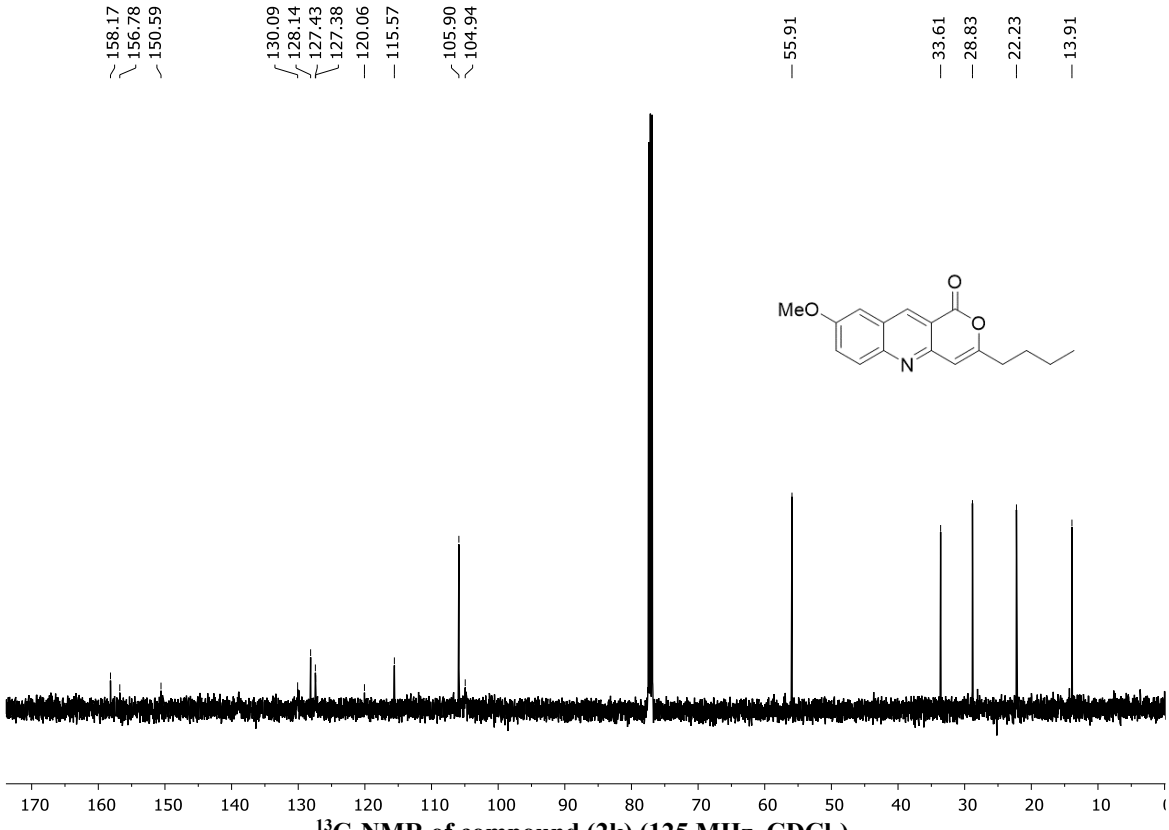
IR spectrum of compound 2j



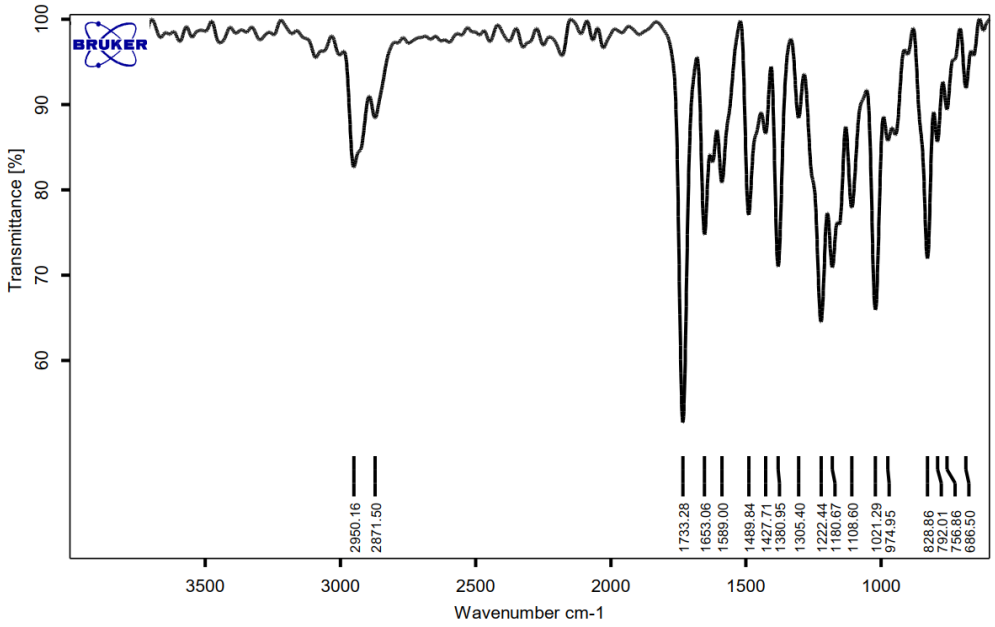
Mass spectrum of compound 2j with the molecular ion peak at 371



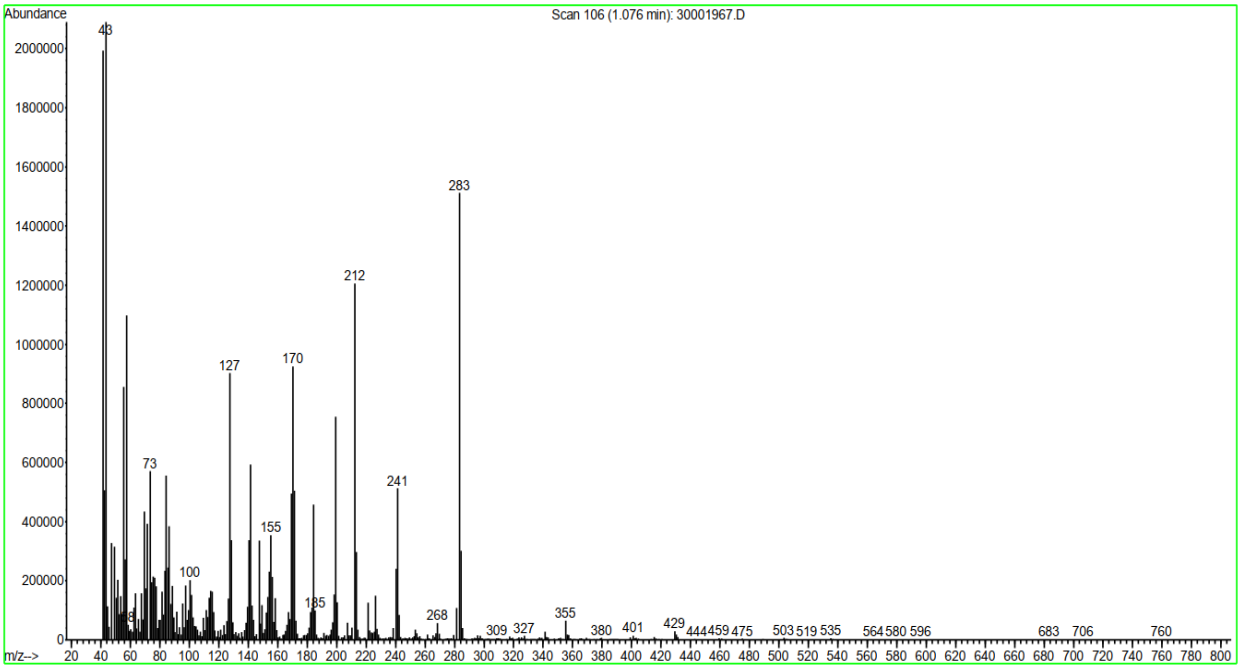
^{1}H-NMR of compound (2k) (500 MHz, $CDCl_3$)



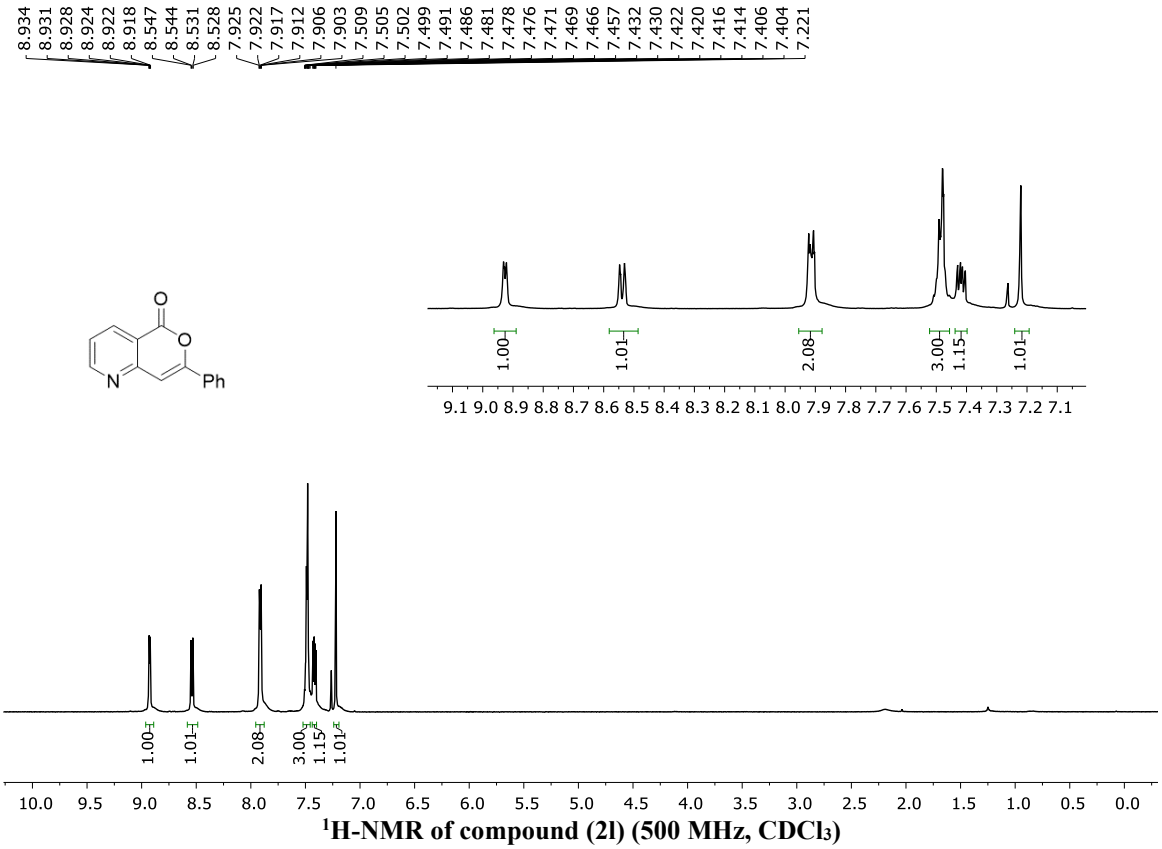
^{13}C-NMR of compound (2k) (125 MHz, $CDCl_3$)



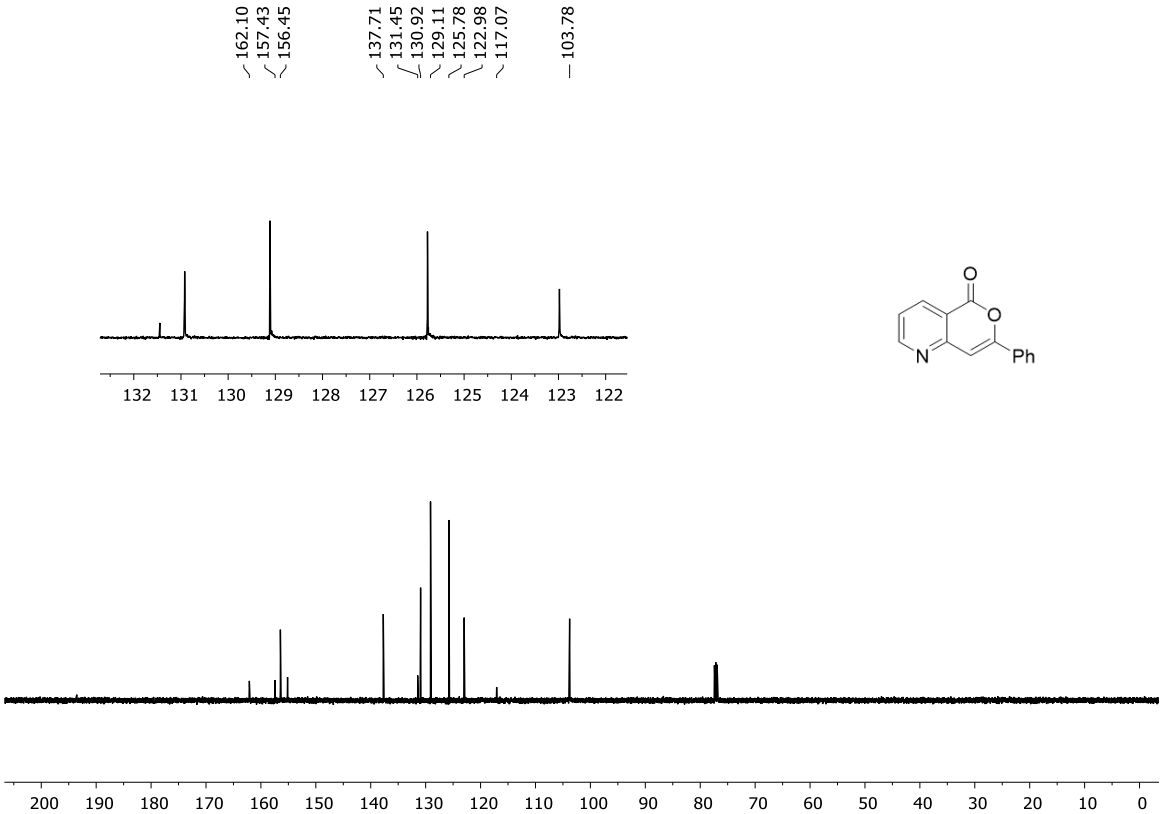
IR spectrum of compound 2k



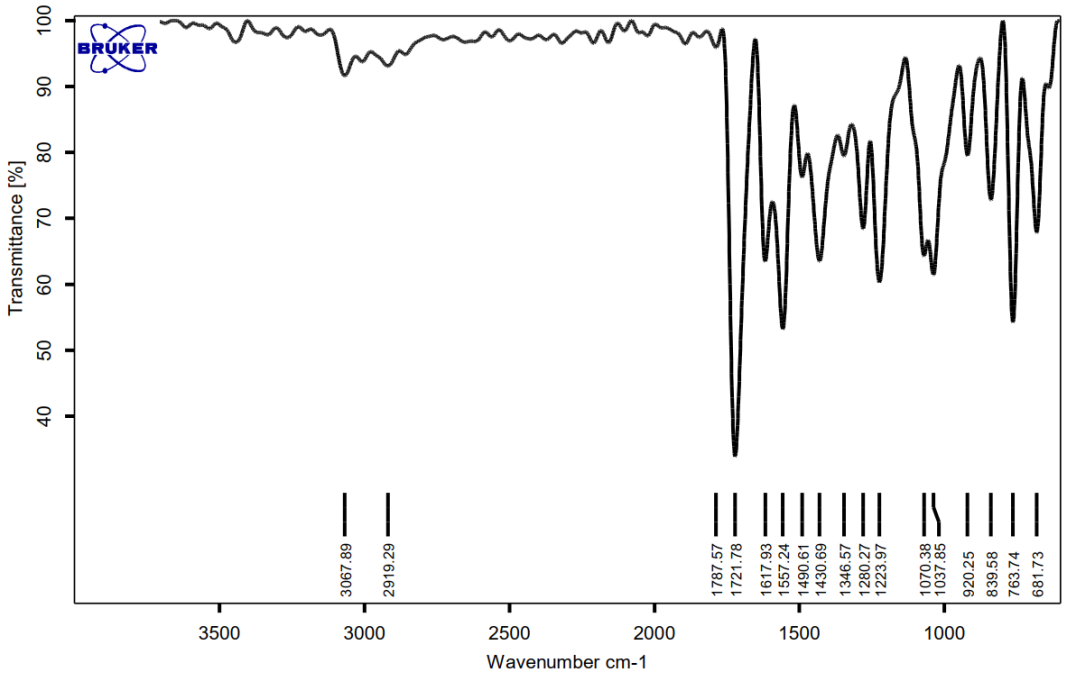
Mass spectrum of compound 2k with the molecular ion peak at 283



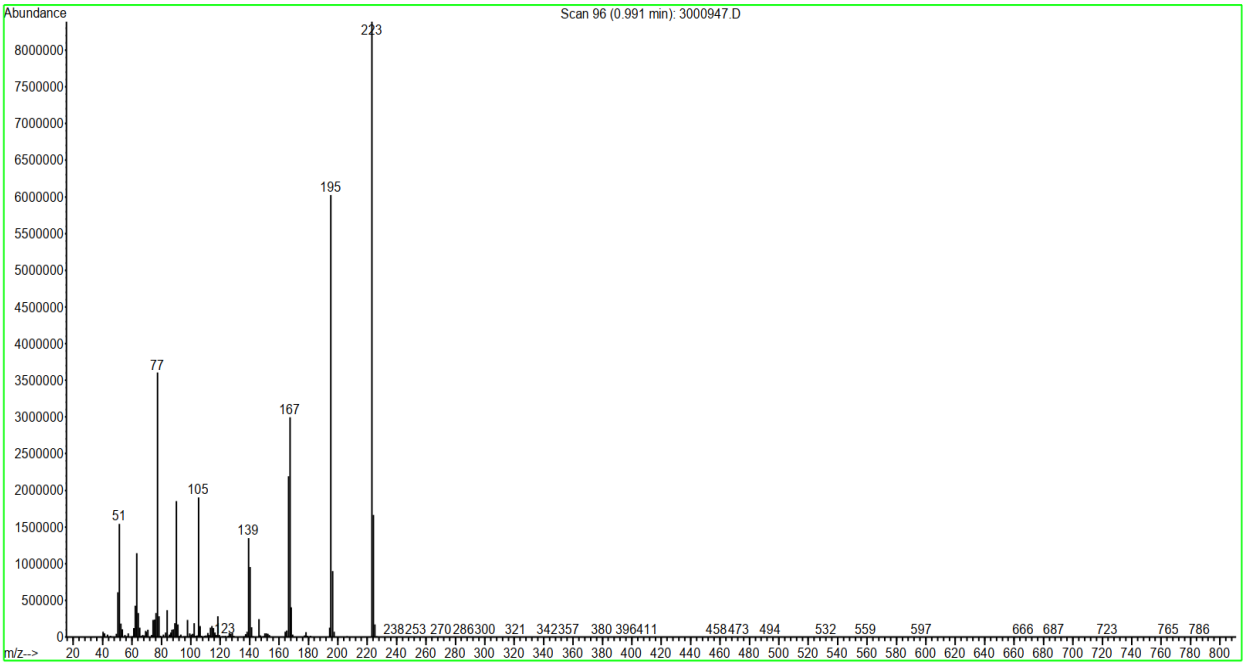
^{1}H-NMR of compound (2l) (500 MHz, $CDCl_3$)



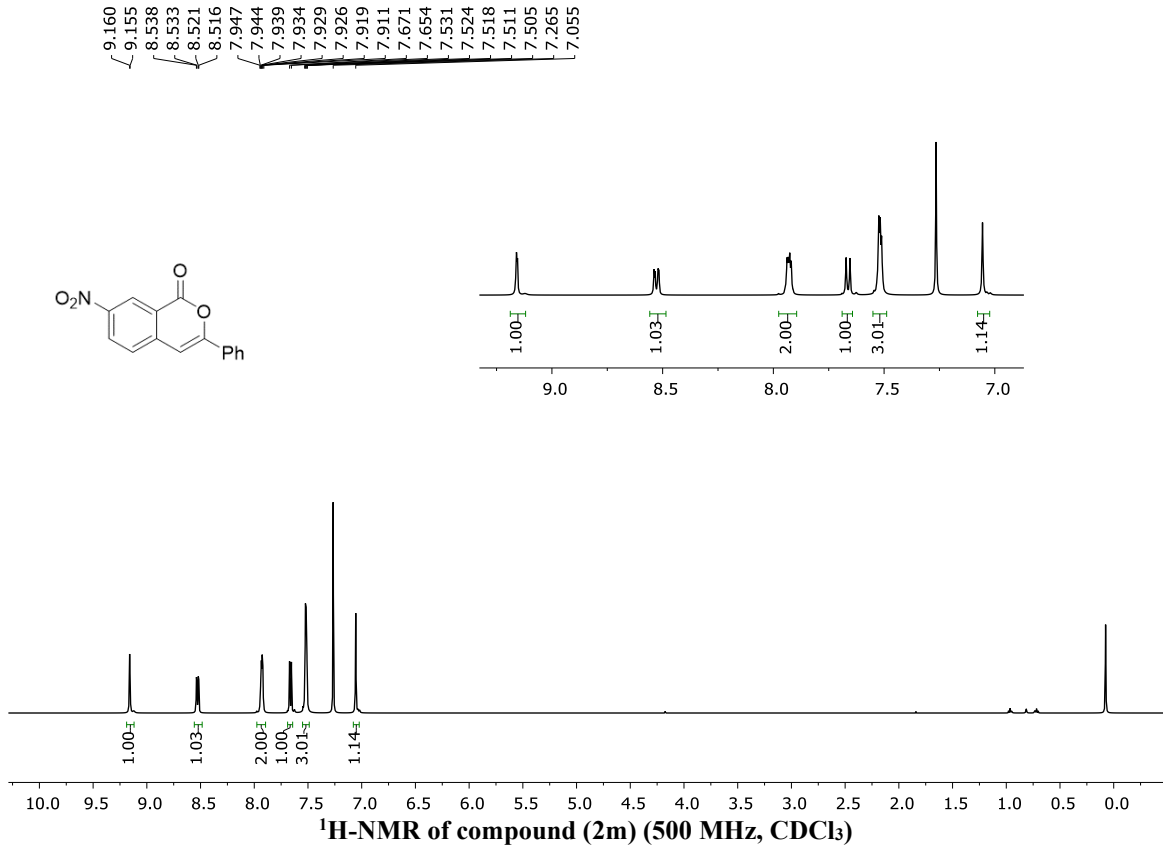
^{13}C-NMR of compound (2l) (125 MHz, $CDCl_3$)



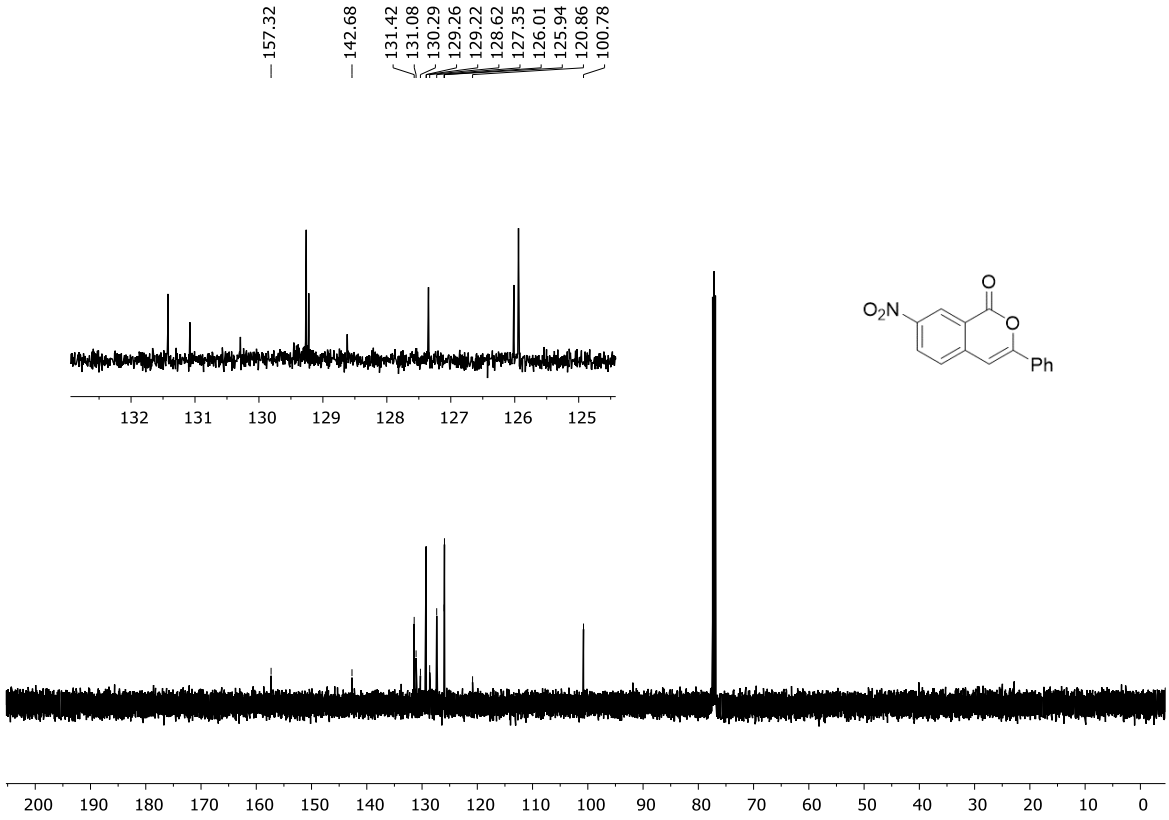
IR spectrum of compound 2l



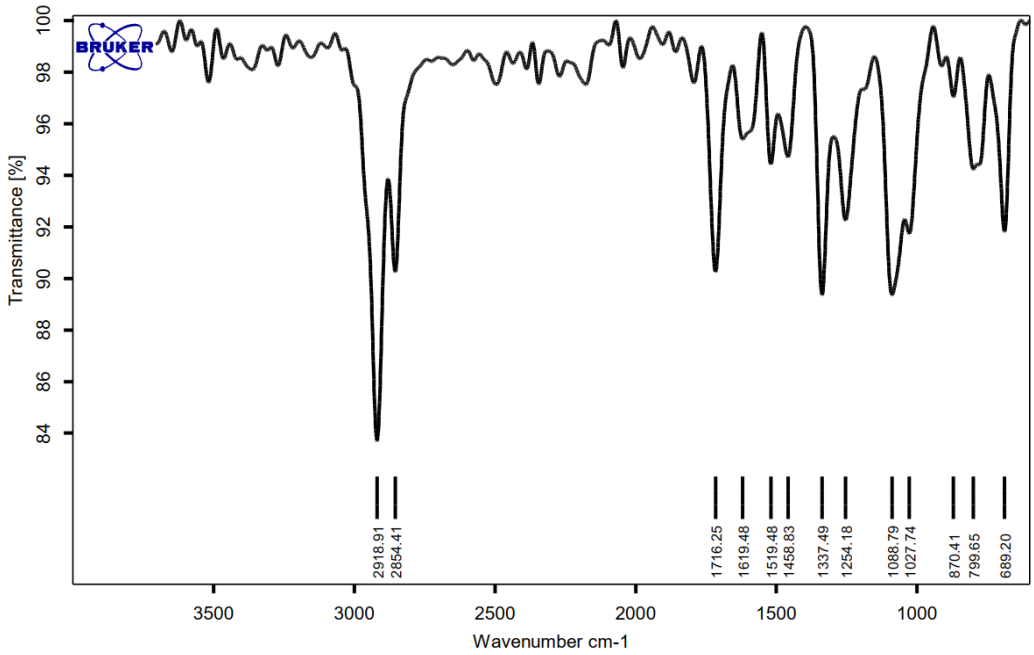
Mass spectrum of compound 2l with the molecular ion peak at 323



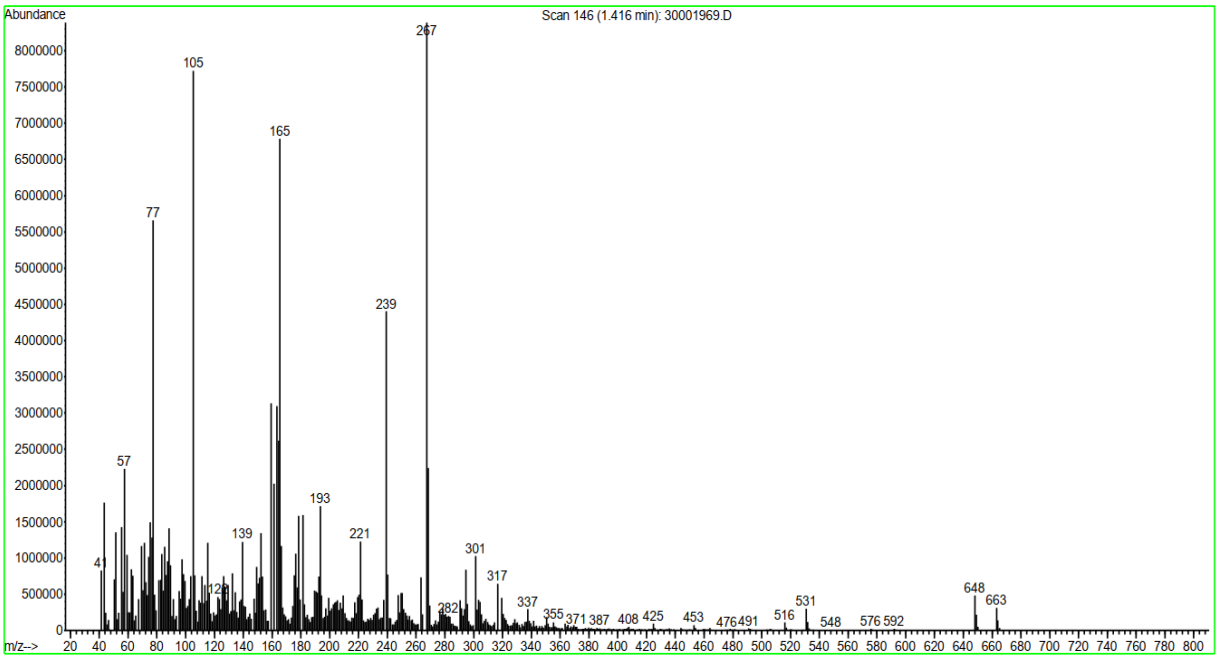
^{1}H-NMR of compound (2m) (500 MHz, $CDCl_3$)



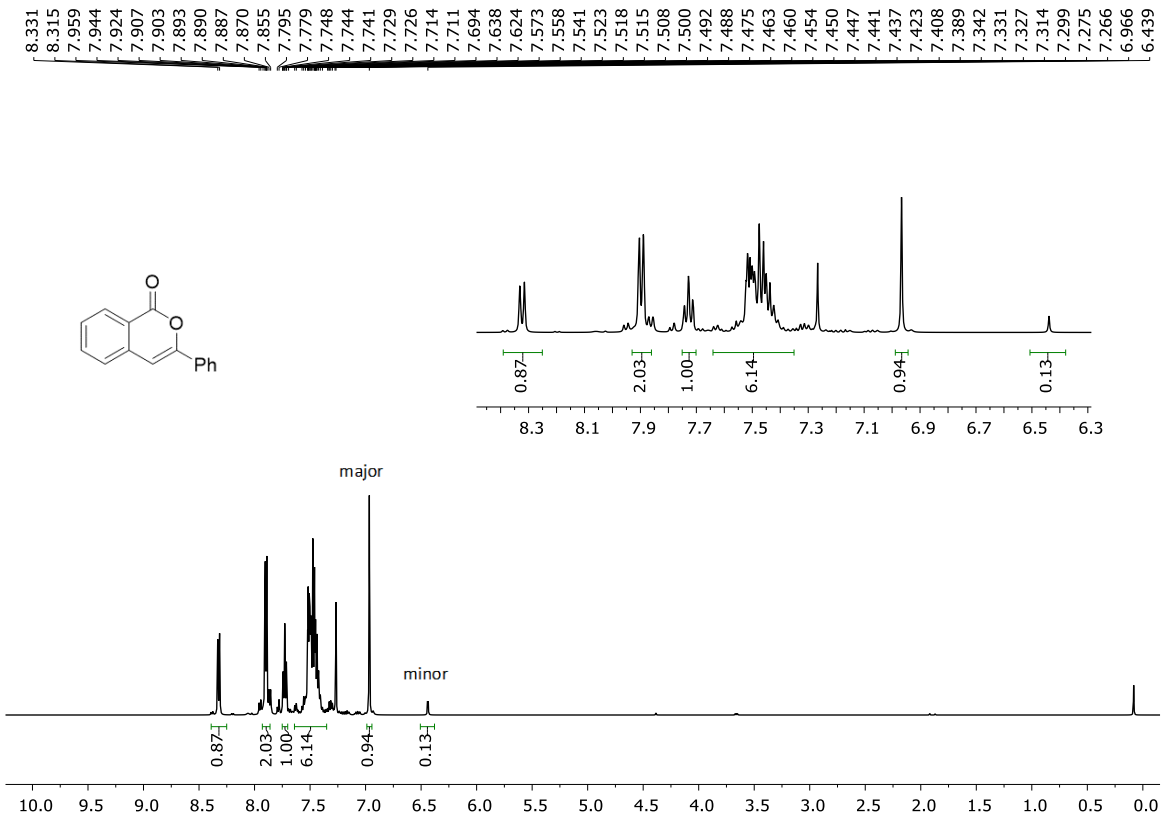
^{13}C-NMR of compound (2m) (125 MHz, $CDCl_3$)



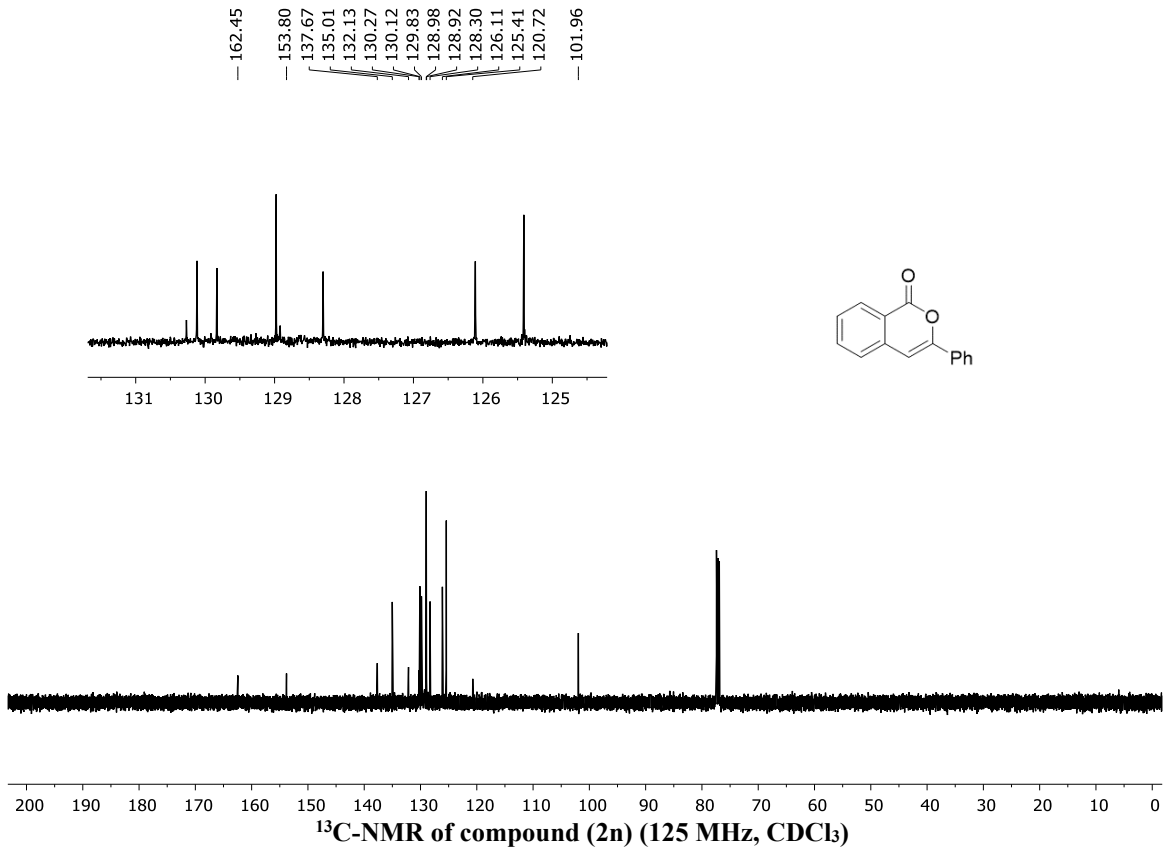
IR spectrum of compound 2m



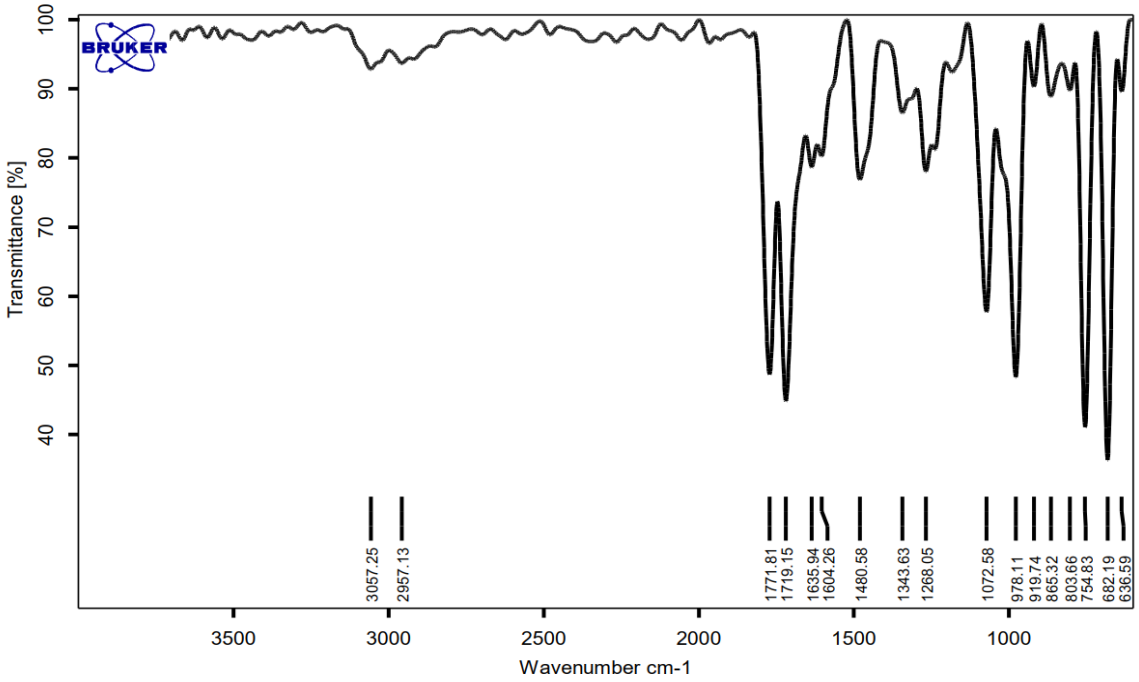
Mass spectrum of compound 2m with the molecular ion peak at 267



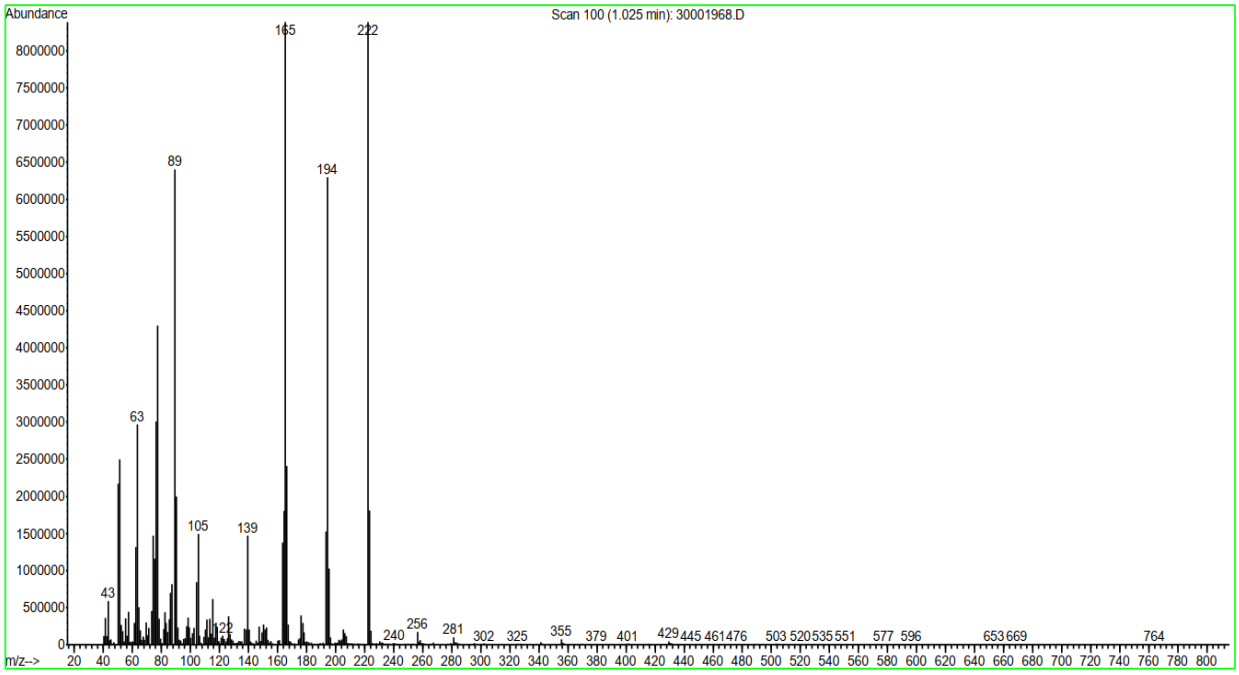
^{1}H-NMR of compound (2n) (500 MHz, $CDCl_3$)



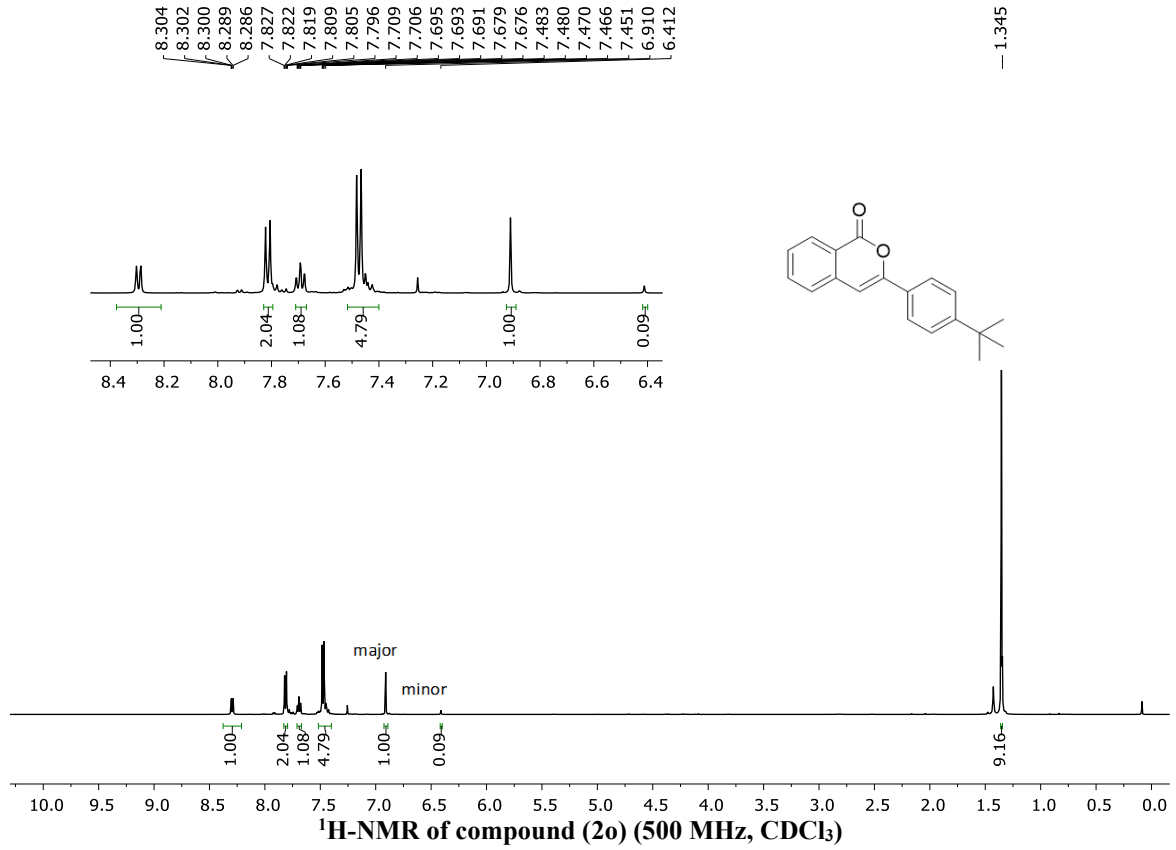
^{13}C-NMR of compound (2n) (125 MHz, $CDCl_3$)



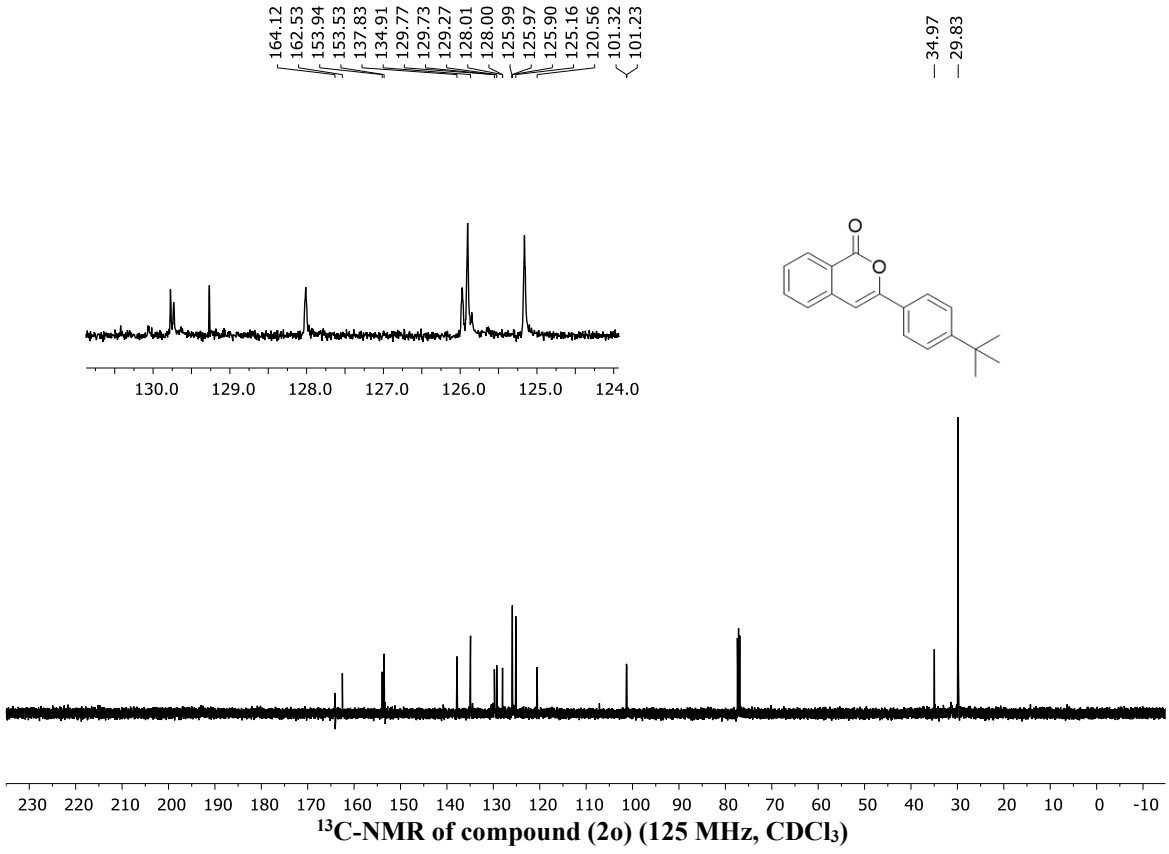
IR spectrum of compound 2n



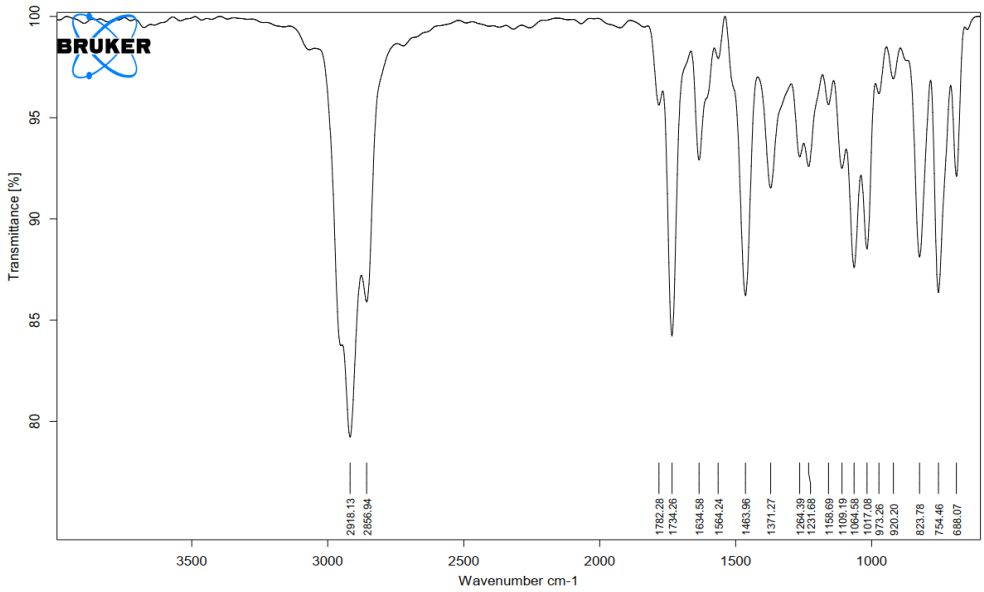
Mass spectrum of compound 2n with the molecular ion peak at 222



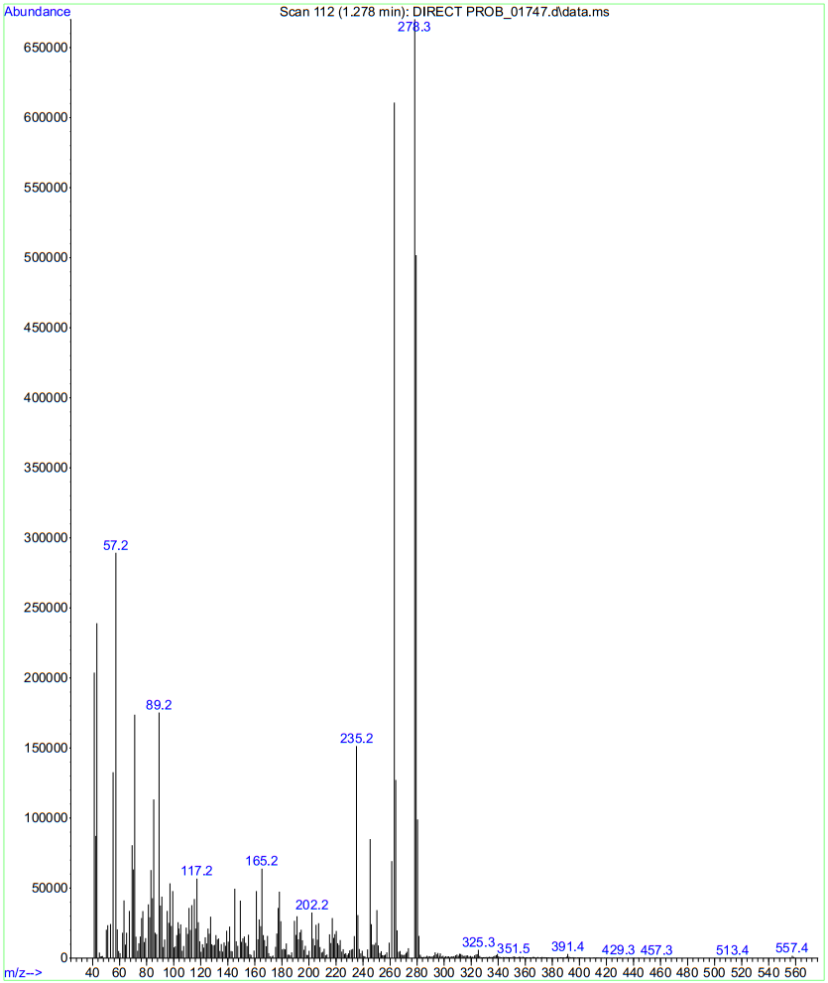
^{1}H-NMR of compound (2o) (500 MHz, $CDCl_3$)



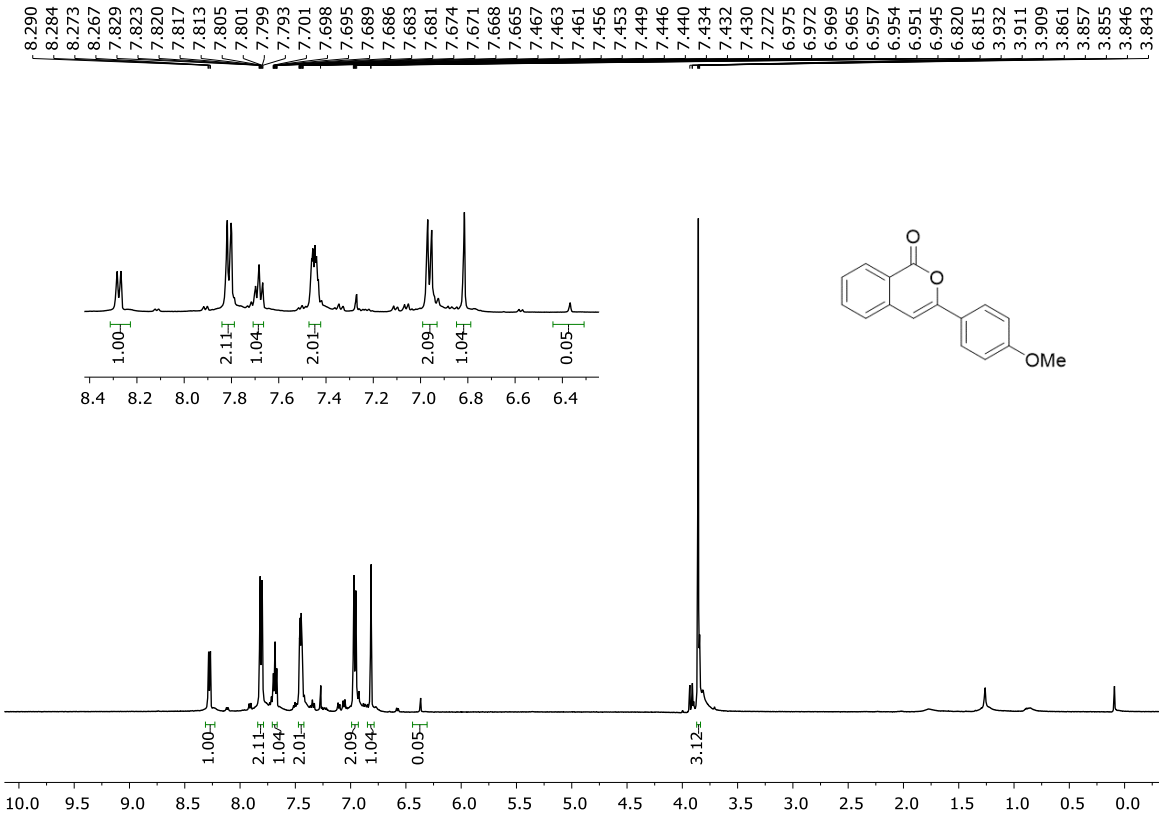
^{13}C-NMR of compound (2o) (125 MHz, $CDCl_3$)



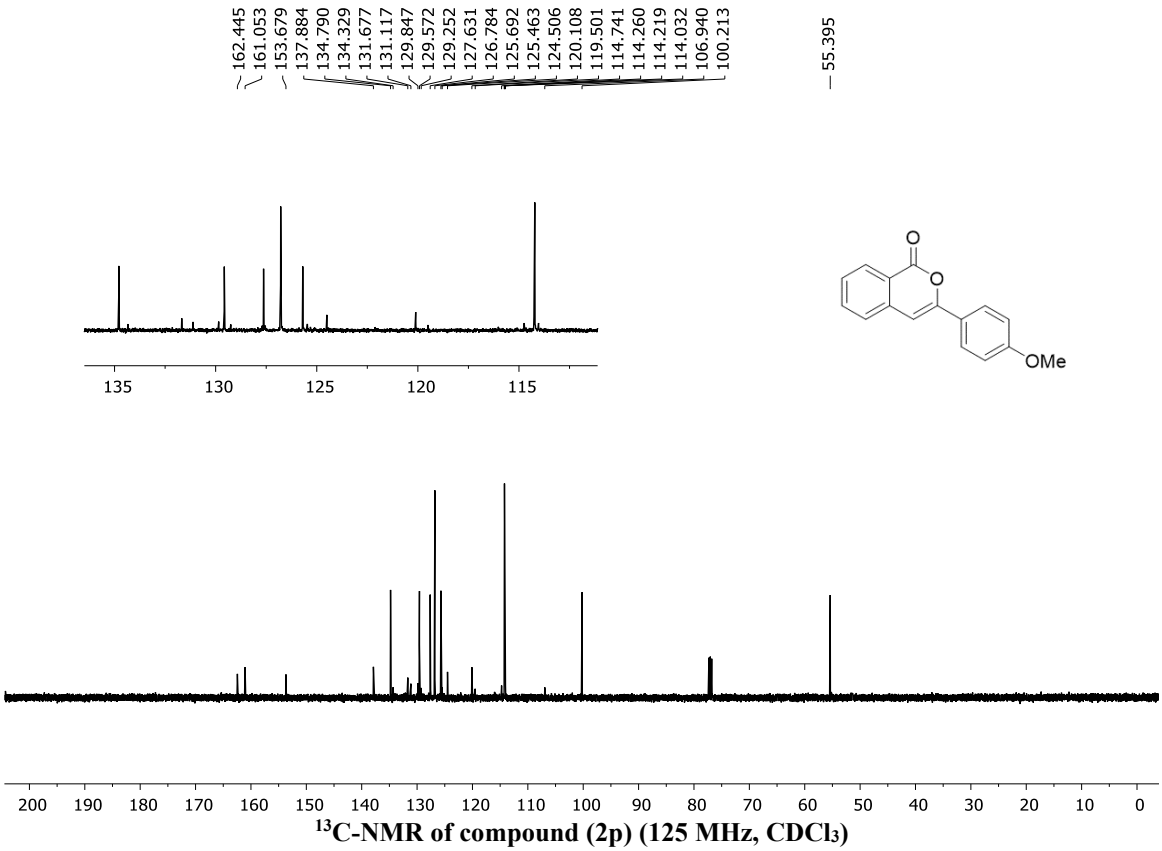
IR spectrum of compound 2o



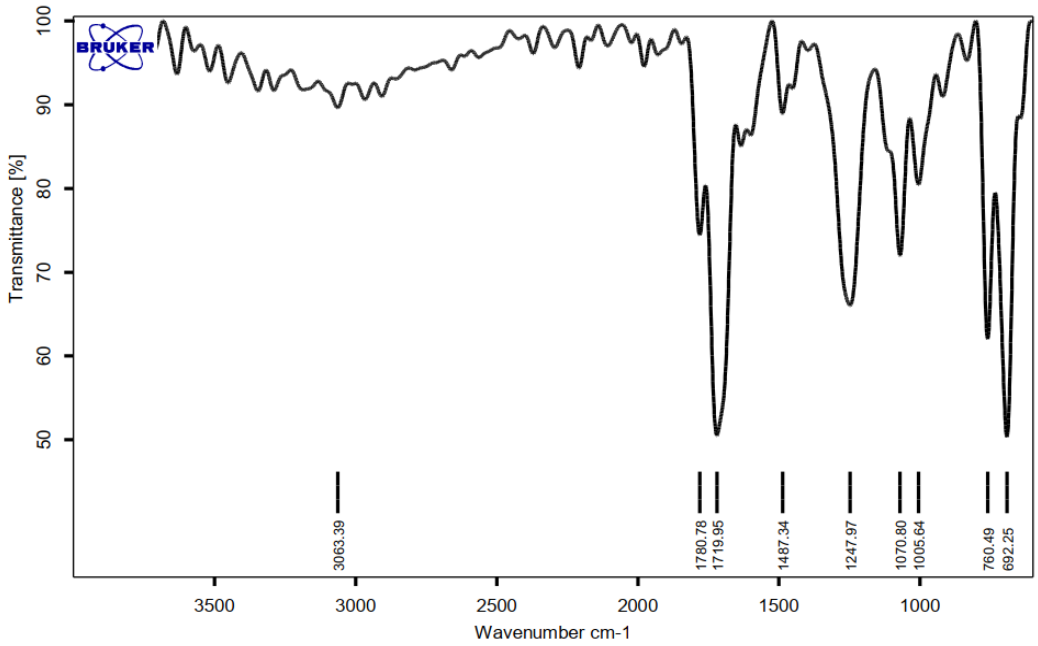
Mass spectrum of compound 2o with the molecular ion peak at 278



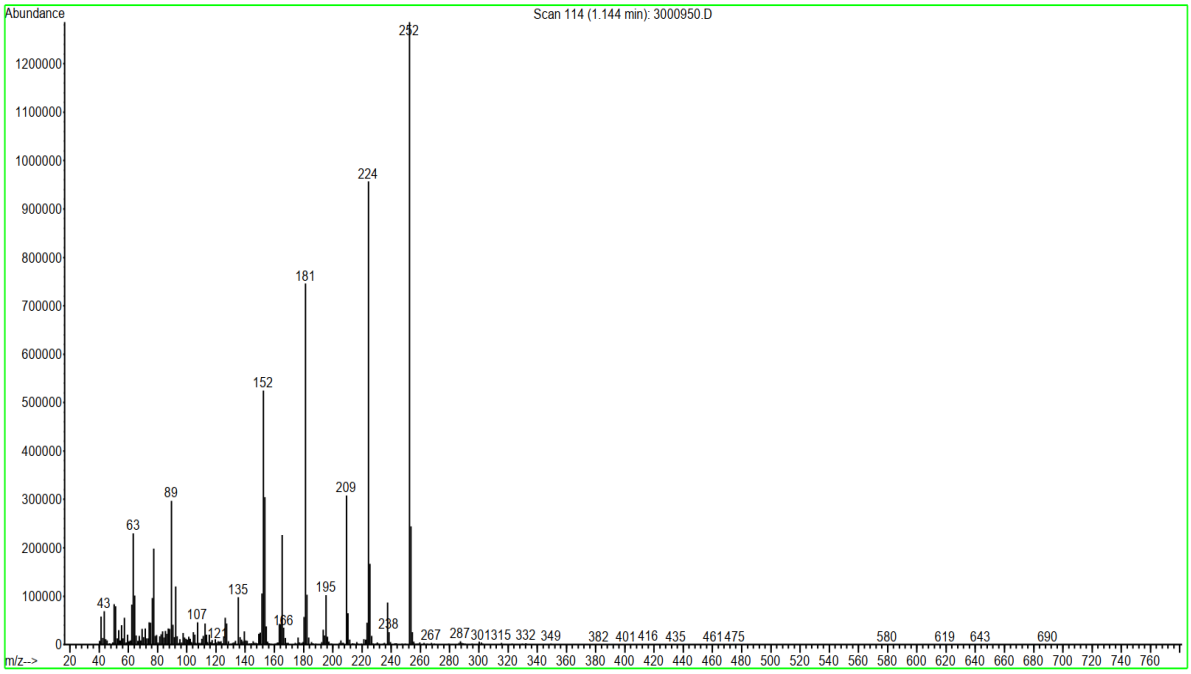
^{1}H-NMR of compound (2p) (500 MHz, $CDCl_3$)



^{13}C-NMR of compound (2p) (125 MHz, $CDCl_3$)

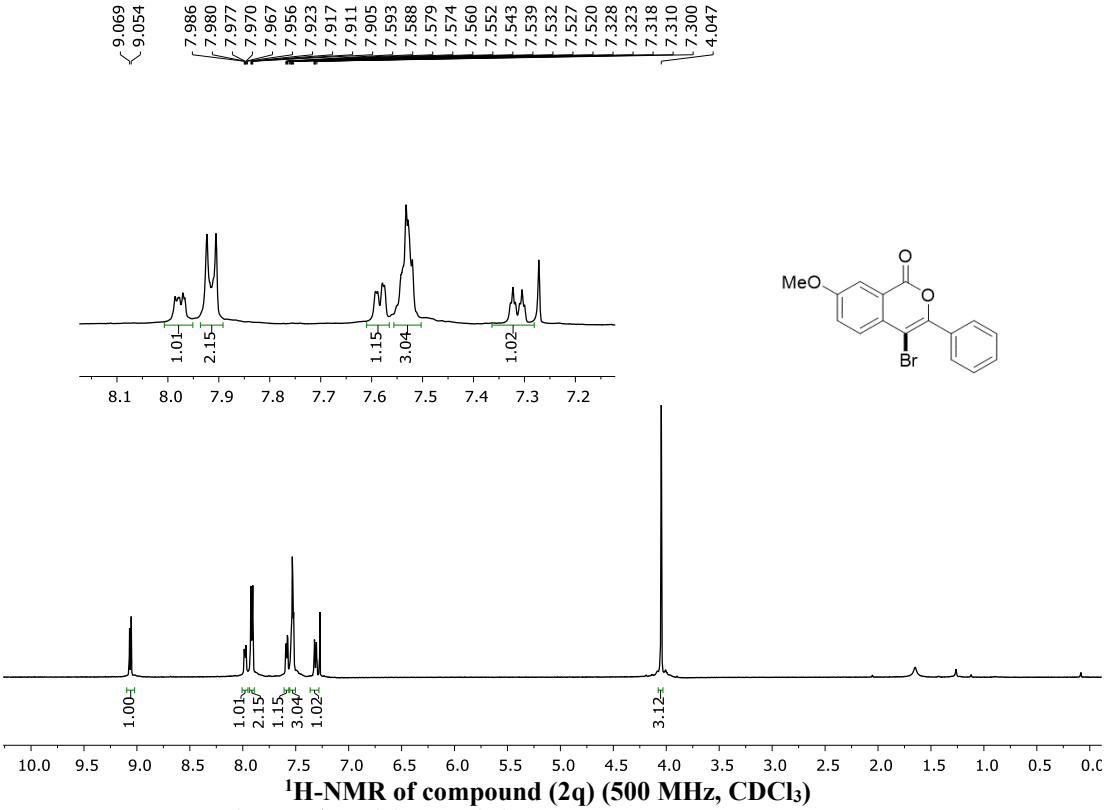


IR spectrum of compound 2p

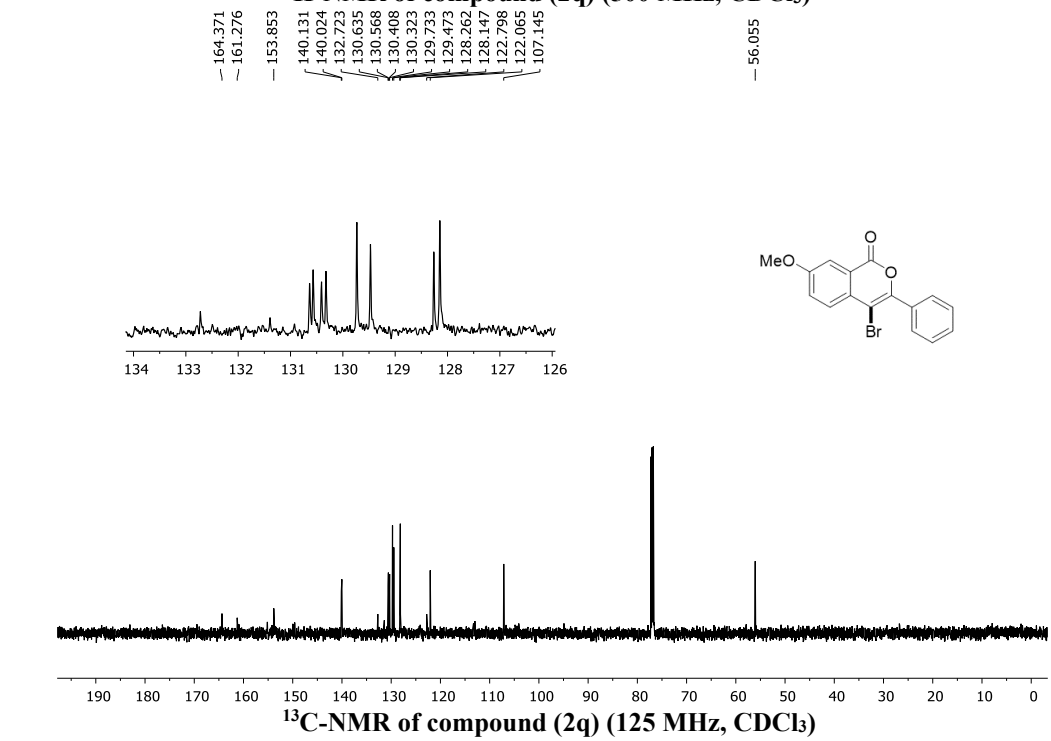


Mass spectrum of compound 2p with the molecular ion peak at 252

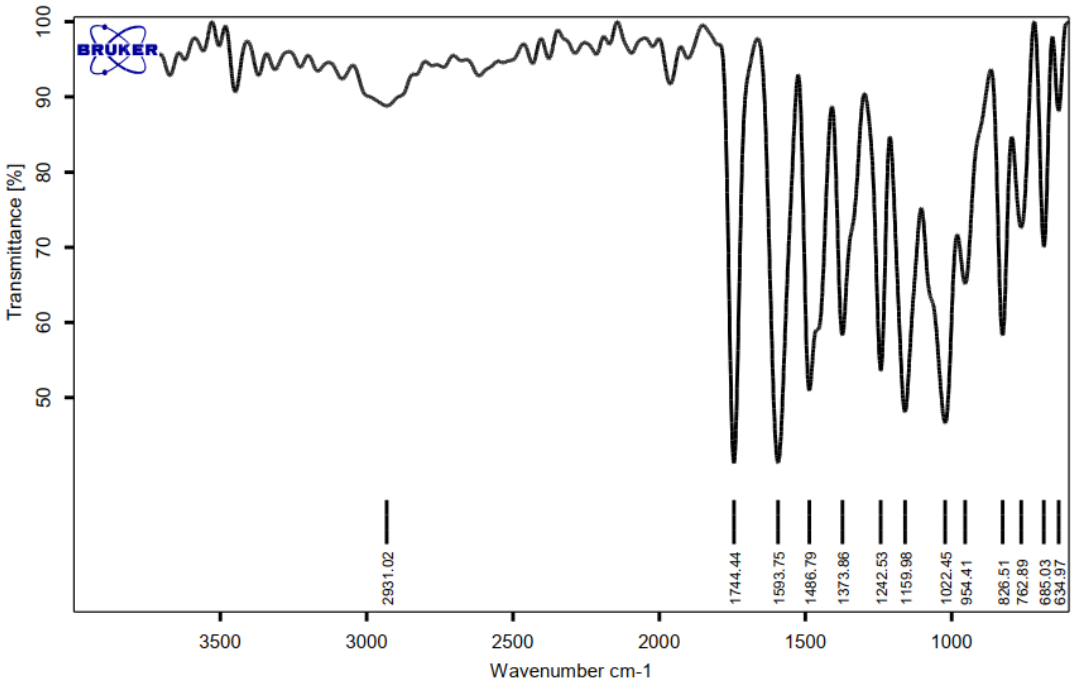
F2. 1H NMR and 13C NMR spectra of compound 2q



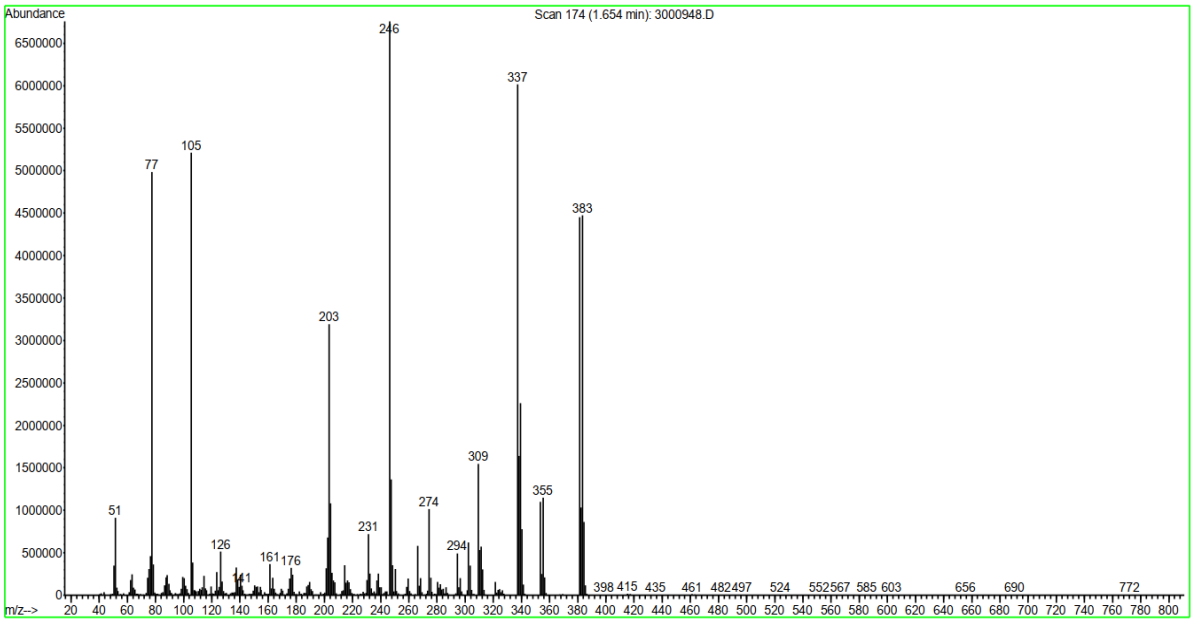
^{1}H-NMR of compound (2q) (500 MHz, $CDCl_3$)



^{13}C-NMR of compound (2q) (125 MHz, $CDCl_3$)



IR spectrum of compound 2q



Mass spectrum of compound 2q with the molecular ion peak at 381

Z- matrices

INT1

C	-0.21184600	3.50645100	-0.00017000
C	0.03427300	2.11526300	-0.00008300
C	1.38930900	1.68033500	-0.00003500
C	2.42374700	2.62996100	-0.00007800
C	2.15424400	3.99226400	-0.00016100
C	0.82610500	4.42887700	-0.00020700
H	-1.24361400	3.84204600	-0.00020700
H	3.44604100	2.26898000	-0.00004300
H	2.97058700	4.70800300	-0.00018900
H	0.59894200	5.49137000	-0.00027100
C	-1.10047000	1.26017000	-0.00005400
C	-2.14136900	0.63093400	-0.00004600
C	-3.31891700	-0.16884200	-0.00009600
C	-4.59579800	0.42737600	-0.00035900
C	-3.22017400	-1.57524000	0.00012500
C	-5.74026500	-0.36481500	-0.00040100
H	-4.67466400	1.51020300	-0.00052800
C	-4.37011800	-2.35885900	0.00008400
H	-2.23627100	-2.03337200	0.00032900
C	-5.63193700	-1.75787400	-0.00017900
H	-6.71991000	0.10512100	-0.00060500
H	-4.28291200	-3.44186600	0.00025600
H	-6.52749000	-2.37310300	-0.00021200

C	1.81346100	0.25742800	0.00005600
O	3.01581000	-0.04874700	0.00000500
O	0.84879300	-0.64945900	0.00019900
H	1.29156300	-1.53523300	0.00025000
Br	3.33141200	-2.60505900	0.00026300

Electronic Energy (EE) = -3299.706887 Hartree

EE + Thermal Free Energy Correction = -3299.550476 Hartree

Imaginary Freq = 0

TS1-*endo*

C	2.21115100	1.72216000	-1.26604100
C	1.71793400	0.83918900	-0.27320500
C	2.63925600	0.19062500	0.59947700
C	4.00125400	0.46614300	0.46336500
C	4.47091400	1.32730000	-0.52794800
C	3.57187000	1.95630500	-1.39591600
H	1.49933300	2.21301200	-1.92163200
H	4.68798300	-0.00822900	1.15592700
H	5.53726500	1.51165200	-0.61999500
H	3.93357900	2.62988500	-2.16709300
C	0.32531900	0.66951300	-0.17089700
C	-0.88417700	0.37235100	-0.17491900
C	-2.27474900	0.61557700	0.10888800
C	-3.14927100	-0.41086800	0.50444800
C	-2.74838600	1.93996500	0.02753600

C	-4.46875700	-0.11029100	0.82778500
H	-2.78325400	-1.43055400	0.53265000
C	-4.07071800	2.22827100	0.35256000
H	-2.07260700	2.72974400	-0.28531200
C	-4.93308100	1.20570000	0.75461700
H	-5.13901500	-0.90840200	1.13353700
H	-4.42830300	3.25196500	0.28813400
H	-5.96585800	1.43256200	1.00401800
C	2.26608700	-0.74233300	1.72976000
O	2.89845500	-0.72940600	2.76303400
O	1.24547100	-1.59764300	1.56889200
H	0.86941200	-1.62104600	0.66264000
Br	-0.60965200	-1.85148100	-1.25129500

Electronic Energy (EE) = -3299.704418 Hartree

EE + Thermal Free Energy Correction = -3299.544605 Hartree

Imaginary Freq = -120.06

TS1-*exo*

C	-3.30913500	-0.37719900	1.48303200
C	-2.41572600	0.25592900	0.58557900
C	-2.91497400	1.19508100	-0.35196100
C	-4.27198600	1.48492800	-0.38332700
C	-5.14712200	0.85399900	0.50895600
C	-4.66322100	-0.07489400	1.43833300
H	-2.92239100	-1.09785600	2.19626300

H	-4.65324500	2.20217800	-1.10404900
H	-6.20815600	1.08518100	0.47945700
H	-5.34803300	-0.56275700	2.12567300
C	-1.04100700	-0.01727400	0.61154300
C	0.17002400	-0.27498900	0.48761800
C	1.56396600	-0.06741600	0.78999400
C	2.34629600	0.86922800	0.07257100
C	2.13829400	-0.78385600	1.85461200
C	3.67035800	1.08529400	0.46875100
C	3.46544500	-0.57369600	2.21252000
H	1.52733300	-1.50162300	2.39218900
C	4.23408200	0.36440500	1.51868400
H	4.24552300	1.83462100	-0.06448200
H	3.89744200	-1.13719700	3.03443900
H	5.26918700	0.53727600	1.79857100
Br	0.17445000	-1.99272800	-1.26655200
H	-2.22125500	1.66987500	-1.03861200
C	1.84200700	1.72602500	-1.06484200
O	2.23886800	2.86066700	-1.21325200
O	0.94797600	1.20020200	-1.92302300
H	0.80930600	0.23546100	-1.79231800

Electronic Energy (EE) = -3299.705907 Hartree

EE + Thermal Free Energy Correction = -3299.546454 Hartree

Imaginary Freq = -102.01

INT2-*endo*

C	-2.16164600	-0.89065000	-1.84643600
C	-1.69927100	-0.48061300	-0.55776300
C	-2.66500300	-0.33475400	0.49689000
C	-4.00351600	-0.62409300	0.23201400
C	-4.43093700	-1.01696200	-1.03684700
C	-3.50156400	-1.14328400	-2.07896500
H	-1.43037800	-1.00259400	-2.64037300
H	-4.70907900	-0.52846100	1.05014400
H	-5.48226500	-1.22346500	-1.21319000
H	-3.82839100	-1.44570600	-3.06978000
C	-0.33250800	-0.31116000	-0.38220100
C	0.87121700	0.16348600	-0.33165800
C	2.15931900	-0.50908200	-0.08292400
C	3.33662400	0.18457400	0.22876000
C	2.19410500	-1.91533300	-0.14451700
C	4.51879600	-0.51205400	0.47789600
H	3.32294900	1.26706200	0.27925900
C	3.37568800	-2.60437300	0.10556800
H	1.28727800	-2.45945200	-0.39166200
C	4.54494900	-1.90500500	0.41793200
H	5.42178500	0.04097900	0.72067300
H	3.38506000	-3.68949500	0.05262400
H	5.46849800	-2.44374700	0.61055400
C	-2.36186100	0.09950400	1.90885500

O	-3.09725900	-0.18752100	2.82715100
O	-1.26254300	0.84673500	2.14054900
H	-0.78557600	1.07309000	1.32272100
Br	0.94749100	2.16962500	-0.59720500

Electronic Energy (EE) = -3299.709192 Hartree

EE + Thermal Free Energy Correction = -3299.551472 Hartree

Imaginary Freq = 0

INT2-*exo*

C	3.22410500	0.27415100	1.49412400
C	2.34945000	-0.20096500	0.47674600
C	2.86955200	-1.06201900	-0.53314700
C	4.20869300	-1.41895200	-0.51777000
C	5.05911500	-0.94089000	0.48872200
C	4.56000900	-0.09567400	1.48943500
H	2.83047400	0.92858200	2.26521200
H	4.59849100	-2.07301000	-1.29243400
H	6.10710100	-1.22625900	0.49381400
H	5.22266600	0.27356200	2.26699200
C	1.00309300	0.13624800	0.45980000
C	-0.18834700	0.54776000	0.26009400
C	-1.51699300	0.05712900	0.66849300
C	-2.16199100	-0.99742800	-0.01472900
C	-2.13226300	0.63359100	1.78907600
C	-3.38796400	-1.47133100	0.47155300

C	-3.36249900	0.16679900	2.24267400
H	-1.62906500	1.44770000	2.30155800
C	-3.99181600	-0.89173800	1.58321000
H	-3.85169600	-2.30529100	-0.04435900
H	-3.82534700	0.62411400	3.11261000
H	-4.94848000	-1.26574200	1.93628600
Br	-0.38789600	2.23097000	-0.97910800
H	2.19938500	-1.42426100	-1.30644400
C	-1.61655500	-1.71242500	-1.22705300
O	-1.85138400	-2.88167000	-1.43198800
O	-0.87177400	-1.01197200	-2.11238900
H	-0.83543900	-0.05976700	-1.89681600

Electronic Energy (EE) = -3299.707567 Hartree

EE + Thermal Free Energy Correction = -3299.548712 Hartree

Imaginary Freq = 0

TS2-*endo*

C	-2.26658000	-1.47942800	0.48271600
C	-1.77162400	-0.21086400	0.11024200
C	-2.69873000	0.84318400	-0.10221900
C	-4.06937100	0.61176300	0.00669800
C	-4.54288400	-0.65403300	0.34404100
C	-3.63662500	-1.69186600	0.58781900
H	-1.57435400	-2.29086800	0.66590800
H	-4.74371200	1.44545000	-0.15971400

H	-5.61104300	-0.83039700	0.43102400
H	-4.00119300	-2.67767100	0.86328300
C	-0.37364400	0.11895500	-0.03990800
C	0.84876800	-0.42640800	-0.02029900
C	2.12204500	0.30392000	0.09403300
C	2.12290800	1.59279300	0.66696900
C	3.34070700	-0.22827000	-0.36202900
C	3.30226600	2.32401200	0.76327300
H	1.19847100	2.01911800	1.04135000
C	4.51773100	0.50918500	-0.26199400
H	3.36195200	-1.21904000	-0.80120000
C	4.50539700	1.78663200	0.29987600
H	3.28075600	3.31407900	1.20948300
H	5.44755700	0.08189800	-0.62666200
H	5.42603000	2.35773300	0.38044200
C	-2.25421200	2.25088900	-0.39582200
O	-3.03808300	3.17407000	-0.54193800
O	-0.94369100	2.46817800	-0.48269900
H	-0.38928200	1.35591900	-0.34345400
Br	0.98806000	-2.35991400	-0.21439200

Electronic Energy (EE) = -3299.691577 Hartree

EE + Thermal Free Energy Correction = -3299.536048 Hartree

Imaginary Freq = -1471.30

TS2-*exo*

C	-2.90052400	-0.38998000	0.90813400
C	-2.13959600	0.52607800	0.14745300
C	-2.80278500	1.58509700	-0.51085800
C	-4.18652500	1.70018000	-0.44323300
C	-4.93040600	0.77446200	0.29467600
C	-4.28327600	-0.26726800	0.96907100
H	-2.39493300	-1.19807200	1.42486400
H	-4.68662600	2.51431400	-0.95970400
H	-6.01147400	0.86732200	0.35049800
H	-4.86162300	-0.98239900	1.54729800
C	-0.70061200	0.45055600	0.08119800
C	0.24252100	-0.48174000	-0.02871500
C	1.70603400	-0.29545000	0.11548400
C	2.37290200	0.97055500	0.06133700
C	2.50105300	-1.43781500	0.33128400
C	3.77010600	1.00257800	0.19537400
C	3.88119100	-1.37238300	0.48342200
H	2.01687000	-2.40429000	0.38046100
C	4.52793000	-0.14267700	0.40802800
H	4.24884800	1.97245900	0.12876400
H	4.44276100	-2.28623400	0.65579400
H	5.60628400	-0.07068300	0.51450000
Br	-0.38344100	-2.27477300	-0.49017500
H	-2.21599100	2.30926700	-1.06829400

C	1.79952900	2.35773100	-0.13974400
O	2.52563000	3.31460500	-0.38263500
O	0.51104700	2.61591200	-0.01561700
H	-0.16235700	1.57169500	0.13049400

Electronic Energy (EE) = -3299.687080 Hartree

EE + Thermal Free Energy Correction = -3299.532167 Hartree

Imaginary Freq = -1212.75

INT3-*endo*

C	-1.52208500	1.91417700	0.88166800
C	-1.50177900	0.91897400	-0.08991500
C	-2.66592300	0.25693300	-0.45625900
C	-3.89679000	0.55364400	0.12483500
C	-3.92755800	1.55172000	1.09839200
C	-2.75203300	2.22204100	1.47096300
H	-0.61600300	2.43210600	1.18387200
H	-4.79147900	0.01877200	-0.17911800
H	-4.86701300	1.81422900	1.57627200
H	-2.79883100	2.99429900	2.23396100
C	-0.35899600	0.36497600	-0.92172000
C	0.77810400	-0.22318700	-0.14226300
C	2.14174600	0.18729800	-0.18876000
C	2.57485000	1.22179400	-1.07210600
C	3.13685900	-0.40411200	0.64218100
C	3.90120300	1.62463900	-1.11330900

H	1.86979900	1.70549200	-1.73872000
C	4.45865500	0.00990400	0.59076400
H	2.84561600	-1.19286100	1.32550900
C	4.85735300	1.02710200	-0.28429700
H	4.19478400	2.41195300	-1.80234400
H	5.18902200	-0.46557700	1.23982200
H	5.89439800	1.34725300	-0.32150000
C	-2.33814100	-0.74198700	-1.49833200
O	-3.05218200	-1.51860600	-2.07841900
O	-0.98517400	-0.64937100	-1.75070700
H	0.02208400	1.13091000	-1.60298900
Br	0.22981900	-1.65017900	0.98477700

Electronic Energy (EE) = -3299.748361 Hartree

EE + Thermal Free Energy Correction = -3299.584792 Hartree

Imaginary Freq = 0

INT3-*exo*

C	-2.81124600	-0.07343100	-0.64302000
C	-2.10913400	0.48589900	0.44188100
C	-2.83981800	1.16075800	1.43984800
C	-4.22798100	1.23499900	1.38432200
C	-4.91236200	0.66029400	0.31116600
C	-4.19861900	0.01692600	-0.70346800
H	-2.26822400	-0.55460800	-1.44656700
H	-4.77417000	1.74928900	2.16992200

H	-5.99573400	0.72430800	0.25850600
H	-4.72577000	-0.40898200	-1.55251100
C	-0.65588800	0.45879200	0.57748600
C	0.27937700	-0.45878200	0.18284000
C	1.72288700	-0.23686300	0.35324800
C	2.30486400	0.97688900	-0.07360800
C	2.53493900	-1.20594100	0.96754100
C	3.66101500	1.21774200	0.16798900
C	3.88032400	-0.94917800	1.20870200
H	2.09565200	-2.15246600	1.26662600
C	4.44551700	0.26917400	0.81713800
H	4.08179100	2.15016700	-0.19483600
H	4.49017800	-1.70015200	1.70303600
H	5.49820900	0.46605300	0.99891300
Br	-0.20034500	-2.14448500	-0.57580000
H	-2.30682800	1.62071900	2.26833500
C	1.55986700	2.00235700	-0.88923300
O	2.14873800	2.93243000	-1.44306100
O	0.27219200	1.88703500	-1.02956400
H	-0.25292700	1.24911300	1.20557000

Electronic Energy (EE) = -3299.710768 Hartree

EE + Thermal Free Energy Correction = -3299.550230 Hartree

Imaginary Freq = 0

TS3-*endo*

C	-2.57089400	-0.63799000	-1.97798000
C	-1.70245800	-0.58650100	-0.87527400
C	-2.24060400	-0.49365900	0.42800100
C	-3.62035100	-0.38659100	0.60116800
C	-4.47158700	-0.38352100	-0.50375400
C	-3.94617300	-0.52212700	-1.79268300
H	-2.15920100	-0.73644900	-2.97904700
H	-4.00571400	-0.34017500	1.61468900
H	-5.54527400	-0.30035300	-0.36072900
H	-4.60981500	-0.54081700	-2.65267500
C	-0.25947400	-0.67511800	-1.03094700
C	0.64582500	0.08764200	-0.30107900
C	2.07987100	-0.24087500	-0.24372200
C	3.08889700	0.72538000	-0.38751500
C	2.44584400	-1.58977600	-0.07512600
C	4.42901100	0.34634500	-0.39434800
H	2.81820600	1.76902400	-0.50138100
C	3.78685400	-1.96167900	-0.07704000
H	1.67325500	-2.33029500	0.10180500
C	4.78241900	-0.99572300	-0.24210300
H	5.19878900	1.10301100	-0.51603300
H	4.05545000	-3.00431800	0.06693200
H	5.82932100	-1.28646200	-0.23922600
C	-1.37505200	-0.65058600	1.65607900

O	-1.87435300	-0.74532100	2.77284900
O	-0.07260200	-0.72945300	1.50419600
Br	0.16384300	1.90578000	0.12066400
H	0.15332800	-1.44860600	-1.67599200

Electronic Energy (EE) = -3299.702160 Hartree

EE + Thermal Free Energy Correction = -3299.540149 Hartree

Imaginary Freq = -337.01

INT4-*exo*

C	2.71460500	-0.56667200	-0.61832700
C	2.22348000	-0.21319900	0.66853500
C	3.15590100	-0.14441400	1.74031900
C	4.49817000	-0.42926400	1.54352900
C	4.96025400	-0.78173200	0.26923700
C	4.06200800	-0.84253600	-0.80343200
H	2.03221300	-0.60852200	-1.45718600
H	5.19081400	-0.37454600	2.37880400
H	6.01240400	-1.00236800	0.11275200
H	4.42054900	-1.10541000	-1.79475700
C	0.86034900	0.08856300	0.94636100
C	-0.27187700	0.03627200	0.04838000
C	-1.65452200	-0.05786100	0.61091200
C	-2.34502100	-1.01074100	-0.13188800
C	-2.27325800	0.61077100	1.66321000
C	-3.67077400	-1.34082500	0.13911800

C	-3.59995300	0.28068300	1.94885700
H	-1.75660500	1.37922300	2.23005900
C	-4.29407000	-0.68247000	1.19841500
H	-4.18705700	-2.08632200	-0.45762000
H	-4.10906100	0.78598400	2.76479100
H	-5.32654100	-0.91063200	1.44585600
Br	-0.25116100	1.97131300	-0.97514100
H	2.79916600	0.13284700	2.72930200
C	-1.43996800	-1.54028000	-1.16720800
O	-1.60568500	-2.35907400	-2.02817100
O	-0.20298900	-0.90790300	-0.98274200
H	0.63219100	0.49182200	1.92914500

Electronic Energy (EE) = -3299.752911 Hartree

EE + Thermal Free Energy Correction = -3299.590367 Hartree

Imaginary Freq = 0

INT4-*endo*

C	-2.62801300	0.79047700	-1.43201700
C	-1.68910800	0.01785300	-0.72699200
C	-2.14206900	-1.08504500	0.02589000
C	-3.50663300	-1.40332700	0.07781900
C	-4.42136900	-0.62959400	-0.62370000
C	-3.97696200	0.46729900	-1.37928200
H	-2.28843200	1.65304300	-1.99766200
H	-3.82004200	-2.25648800	0.67006400

H	-5.47944500	-0.87062400	-0.58638100
H	-4.69546200	1.07260600	-1.92474200
C	-0.27108900	0.30443400	-0.76220000
C	0.62297900	-0.57429200	-0.15783700
C	2.07556600	-0.53088900	-0.28248100
C	2.73128400	0.64799900	-0.69183800
C	2.83984200	-1.68219900	-0.00635600
C	4.11281100	0.65980300	-0.84558300
H	2.16425800	1.56383400	-0.82001200
C	4.22139000	-1.66039000	-0.16675400
H	2.34040500	-2.58657100	0.32222400
C	4.86165100	-0.49338800	-0.59151500
H	4.61011700	1.57667800	-1.14838200
H	4.80031200	-2.55577100	0.04048000
H	5.94128200	-0.47814700	-0.71238700
C	-1.18872500	-1.92317600	0.75886300
O	-1.44159800	-2.86696500	1.46252100
O	0.17013900	-1.59674100	0.60182200
Br	-0.09589800	2.29064000	0.91364600
H	0.10579000	0.98529500	-1.51167300

Electronic Energy (EE) = -3299.767921 Hartree

EE + Thermal Free Energy Correction = -3299.603380 Hartree

Imaginary Freq = 0

TS1-SRA

C	-2.15659000	-1.62189700	0.06004500
C	-1.95398600	-0.22414500	0.05948500
C	-3.08384400	0.64106200	0.02799300
C	-4.36857200	0.08568300	-0.02727200
C	-4.55650300	-1.29195200	-0.03556600
C	-3.44596900	-2.14035700	0.01205800
H	-1.28829900	-2.27816200	0.09305900
H	-5.20962800	0.76992100	-0.05900400
H	-5.56253500	-1.70252200	-0.07402300
H	-3.57953700	-3.21933500	0.00961900
C	-0.61511500	0.27503100	0.06913600
C	0.62667100	0.38343100	-0.06018300
C	1.77877700	1.26143800	-0.03944300
C	1.59421200	2.61229600	-0.39717100
C	3.05711400	0.81892900	0.34301600
C	2.66511000	3.50224300	-0.36788900
H	0.61024300	2.95425000	-0.70412400
C	4.11903300	1.72061900	0.36913700
H	3.18741000	-0.22038900	0.62993800
C	3.93291700	3.05933800	0.01503600
H	2.50743000	4.54042100	-0.65011600
H	5.10348500	1.37022000	0.66969800
H	4.77046200	3.75311900	0.03547800
C	-3.02895500	2.14384900	0.07068600

O	-4.00927500	2.83889700	-0.11216100
O	-1.84373700	2.72834000	0.35129500
H	-1.14975600	2.03709300	0.47756100
S	1.67638300	-2.56149300	0.00819200
O	2.52967900	-3.21559000	-1.02969400
O	0.43331900	-3.30260800	0.32629600
O	1.28094900	-1.25422300	-0.88672400
O	2.40941500	-2.09158400	1.20679200

Electronic Energy (EE) = -1427.063433 Hartree

EE + Thermal Free Energy Correction = -1426.893245 Hartree

Imaginary Freq = -519.62

HBr

Br	0.00000000	0.00000000	0.03994000
H	0.00000000	0.00000000	-1.39789000

Electronic Energy (EE) = -2572.301284 Hartree

EE + Thermal Free Energy Correction = -2572.314619 Hartree

Imaginary Freq = 0

CR

C	3.64700200	-2.11293200	-0.00001800
C	4.45442500	-0.96991900	-0.00007100
C	3.86296900	0.29024700	-0.00009800
C	2.47191400	0.41493400	-0.00007200
C	1.64690600	-0.73405400	-0.00001700

H	4.46336700	1.19525400	-0.00014000
C	0.23141700	-0.60674400	0.00000600
C	-0.98574600	-0.52494400	0.00002600
C	-2.39620600	-0.34146000	0.00004900
C	-3.27079000	-1.44591200	0.00011200
C	-2.93003100	0.96387800	0.00000800
C	-4.64815300	-1.24529900	0.00013200
H	-2.85949400	-2.45065500	0.00014400
C	-4.30887400	1.15093600	0.00002900
H	-2.25042400	1.80995300	-0.00004000
C	-5.17066300	0.05057700	0.00009100
H	-5.31619900	-2.10214100	0.00018100
H	-4.71316700	2.15934300	-0.00000300
H	-6.24651300	0.20239400	0.00010700
C	1.88076100	1.77131300	-0.00010500
O	2.54025400	2.82961300	-0.00007600
O	0.60722800	1.95609300	-0.00000800
H	5.53612300	-1.06464800	-0.00009200
H	4.10374900	-3.09874800	0.00000100
C	2.25974600	-2.00185000	0.00000800
H	1.63465000	-2.88902300	0.00004700

Electronic Energy (EE) = -727.364050 Hartree

EE + Thermal Free Energy Correction = -727.215752 Hartree

Imaginary Freq = 0

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