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Rhodium(III)-catalyzed C–H annulation for the construction of antifungal agents based on isocoumarin framework

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1. X-ray diffraction study

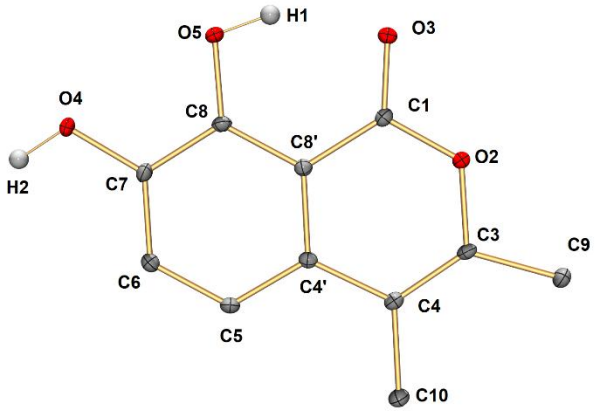


Figure S1. General view of **3** in the representation of atoms as 50% probability ellipsoids; hydrogen atoms (except two at the O4 and O5 atoms) are omitted. Selected bond lengths [Å]: C1−O2 1.3408(19), C4'−C5 1.394(2), C1−O3 1.2392(19), C4'−C8' 1.419(2), C1−C8' 1.442(2), C4−C10 1.505(2), O2−C3 1.4020(19), O5−C8 1.3541(19), C3−C4 1.344(2), C5−C6 1.388(2), C3−C9 1.491(2), C6−C7 1.392(2), O4−C7 1.3586(19), C7−C8 1.397(2), C4'−C4 1.457(2), C8−C8' 1.406(2).

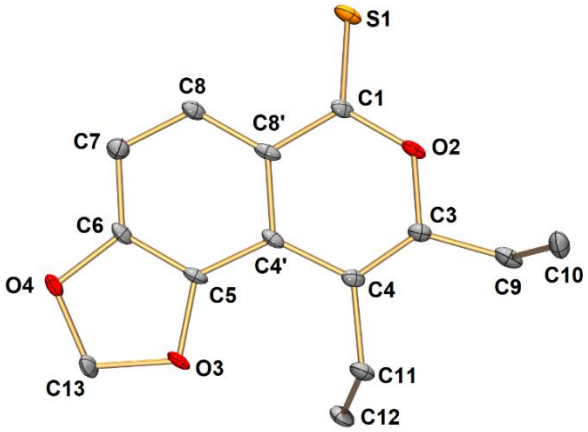


Figure S2. General view of **12** in the representation of atoms as 50% probability ellipsoids; hydrogen atoms are omitted. Selected bond lengths [Å]: S1−C1 1.655(5), C4−C4' 1.442(8), C1−O2 1.349(7), C4−C11 1.519(6), C1−C8' 1.451(7), C4'−C5 1.397(7),O2−C3 1.397(6), C4'−C8' 1.442(6), O3−C5 1.394(5), C5−C6 1.355(8), O3−C13 1.434(7), C6−C7 1.391(7), C3−C4 1.337(7), C7−C8 1.386(7), C3−C9 1.491(9), C8−C8' 1.375(8), O4−C6 1.370(6), C9−C10 1.537(8), O4−C13 1.429(6), C11−C12 1.543(6).

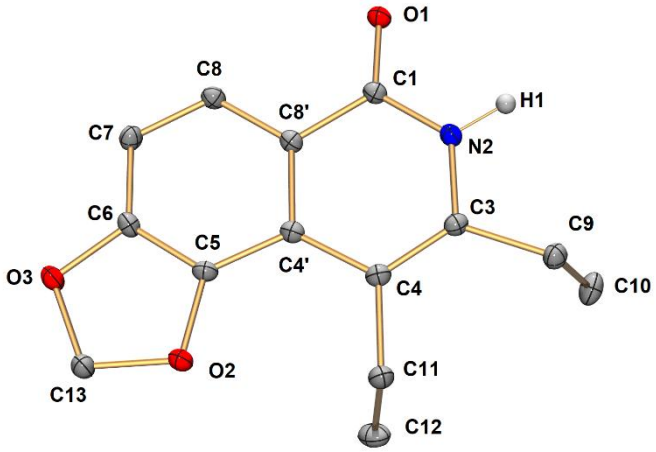


Figure S3. General view of **13** in the representation of atoms as 50% probability ellipsoids; hydrogen atoms (except one at the nitrogen atom) are omitted. Selected bond lengths [Å]: O1−C1 1.2518(19), C1−N2 1.355(2), C1−C8' 1.457(2), O2−C5 1.3814(19), O2−C13 1.432(2), N2−C3 1.396(2), O3−C6 1.3706(19), O3−C13 1.431(2), C3−C4 1.357(2), C3−C9 1.512(2), C4'−C4 1.451(2), C4'−C5 1.403(2), C4'−C8' 1.429(2), C4−C11 1.512(2), C5−C6 1.378(2), C6−C7 1.379(2), C7−C8 1.382(2), C8'−C8 1.400(2), C9−C10 1.534(9), C9−C10' 1.527(10), C11−C12 1.527(2).

X-ray crystallography. Crystals of **3**, **12** and **13** were obtained by slow interdiffusion of a two-phase system containing petroleum ether and a solution of the compound in dichloromethane. X-ray diffraction data for **13** were collected at 100K at the K4.4 station of the Kurchatov Center for Synchrotron Radiation and Nanotechnology in Moscow (Russia) at a wavelength of 0.7527 Å. For **3** and **12**, they were collected at 100 K with a Bruker APEX2 Quazar CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Using Olex2,[S1] the structures were solved with the ShelXT[S2] structure solution program using Intrinsic Phasing and refined with the XL[S3] refinement package using Least-Squares minimization against F^2 in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of OH groups were located from difference

Fourier synthesis while positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation in the riding model. Crystal data and structure refinement parameters are given in Table S1.

Table S1. Crystal data and structure refinement parameters for **3**, **12** and **13**.

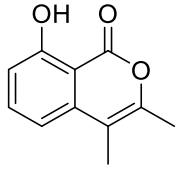
	3	**12**	**13**
Formula unit	$C_{11}H_{10}O_4$	$C_{14}H_{14}O_3S$	$C_{14}H_{15}NO_3$
Formula weight	206.19	262.31	245.27
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c	P-1	Pbca
Z	8	2	16
a, Å	11.853(6)	7.899(5)	16.613(3)
b, Å	14.981(8)	8.852(5)	16.788(3)
c, Å	10.767(6)	10.051(6)	17.172(3)
α, °	90	114.282(7)	90
β, °	108.589(6)	106.279(7)	90
γ, °	90	93.792(7)	90
V, Å^3	1812.0(17)	601.6(6)	4789.3(17)
D_{calc} (g cm^{-1})	1.512	1.448	1.361
Linear absorption, μ (cm^{-1})	1.16	2.66	1.09
F(000)	864	276	2080
$2\Theta_{max}$, °	58	50	60
Reflections measured	8400	3919	27055
Independent reflections	2381	2008	5818
Observed reflections [$I > 2\sigma(I)$]	1729	1127	4103
Parameters	138	165	340
R1	0.0507	0.0880	0.0452
wR2	0.1421	0.2443	0.1215
GOOF	1.035	0.994	1.027
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.368/-0.295	0.552/-0.706	0.351/-0.229

Synthetic procedures

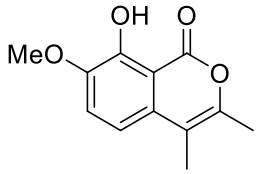
Unless otherwise stated, all reactions were carried out under argon using distilled solvents. Isolation of all products was carried out in air. All other reagents were purchased from Acros or Aldrich and used as received. Column chromatography was carried out using Macherey-Nagel silica gel 60 (particle size: 0.04−0.063 mm). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Varian Inova 400 spectrometer and a Brucker Avance 300 spectrometer operating at 400 and 101 MHz, respectively. Chemical shifts are given in ppm using residual solvent signals as an internal standard. High-resolution mass spectra were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Measurements were carried out in positive ion mode; samples were dissolved in acetonitrile and injected into the mass-spectrometer chamber from an HPLC system LC-40 Nexera (Shimadzu, Japan). The following parameters were used: capillary voltage 4.0 kV; mass scanning range: m/z 150–2000; external calibration with solution NaI in MeOH/H_2O; drying and heating gases (nitrogen) (each 10 L/min); nebulizing gas (nitrogen) (3 L/min); interface temperature: 250 C; flow rate 100% acetonitrile 0.4 mL/min. Molecular ions in the spectra were analyzed and matched with the appropriately calculated *m*/*z* and isotopic profiles in the LabSolutions v.5.114 program

General procedure for isocoumarin preparation

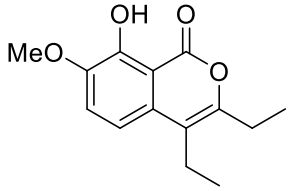
Carboxylic acid (0.25 mmol, 1 equiv), alkyne (0.5 mmol, 2 equiv), $[Cp^{Ph3}RhCl_2]_2$ (3.2 mg, 1 mol %), AgOAc (63 mg, 0.375 mmol, 1.5 equiv), and MeOH (2 mL) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred in air at 80°C (an oil bath) for 8 h. Then, the formed precipitate was centrifuged, the solvent was removed in vacuo, and the residue was chromatographed on silica (1 × 15 cm). The first colorless band containing unreacted alkyne was eluted with petroleum ether. The second band was eluted with a mixture of dichloromethane with petroleum ether or ethyl acetate.



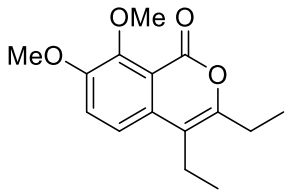
8-Hydroxy-3,4-dimethyl-1*H*-isochromen-1-one (1). Colorless crystals. Yield: 46 mg (98%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.25 (s, 1H), 7.56 (t, J = 8.1 Hz, 1H), 6.87 (t, J = 8.6 Hz, 2H), 2.26 (s, 3H), 2.08 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 161.9, 149.6, 139.2, 137.2, 114.5, 112.9, 109.2, 105.9, 17.2, 12.6.NMR data are in agreement with previously reported data.[S4]



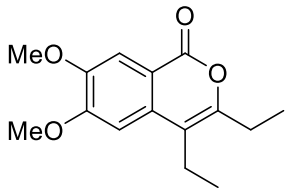
8-Hydroxy-7-methoxy-3,4-dimethyl-1*H*-isochromen-1-one (2). White crystals. Eluent: petroleum ether/CH_2Cl_2 (1:1). Yield: 49 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.41 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H), 2.21 (s, 3H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.0, 151.3, 147.5, 146.2, 131.2, 119.7, 112.5, 108.9, 106.4, 56.6, 16.9, 12.4. NMR data are in agreement with previously reported data.[S5] HRMS (ESI+) of $C_{12}H_{12}O_4$, *m*/*z*: calcd for $[M+H]^+$ 221.0809, found 221.0813.



3,4-Diethyl-8-hydroxy-7-methoxy-1*H*-isochromen-1-one (4). White solid. Yield: 52 mg (80%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H), 2.54 – 2.48 (m, 4H), 1.18 (t, *J* = 7.4 Hz, 3H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)δ 167.2, 152.4, 151.6, 146.1, 130.2, 119.8, 114.3, 112.6, 106.9, 56.6, 23.7, 19.5, 14.2, 12.6. HRMS (ESI+) of $C_{14}H_{16}O_4$, *m*/*z*: calcd for $[M+H]^+$ 249.1122, found 249.1129.

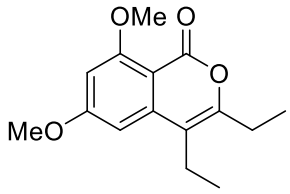


3,4-Diethyl-7,8-dimethoxy-1*H*-isochromen-1-one (5). White oily crystals. Yield: 59 mg (90%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.58 – 2.45 (m, 4H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.11 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.5, 153.1, 151.9, 151.2, 132.3, 119.8, 118.4, 115.6, 112.2, 61.5, 56.6, 23.8, 19.5, 14.3, 12.6. HRMS (ESI+) of $C_{15}H_{18}O_4$, *m*/*z*: calcd for $[M+H]^+$ 263.1278, found 263.1277.

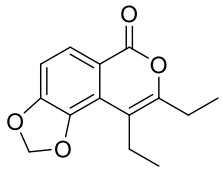


3,4-Diethyl-6,7-dimethoxy-1*H*-isochromen-1-one (6). Colorless solid. Yield: 61 mg (94%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 6.86 (s, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 2.66 – 2.54 (m, 4H), 1.25 (t, J = 7.5 Hz, 3H), 1.19 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.0, 155.1, 154.3, 149.0, 133.6, 114.2, 112.9,

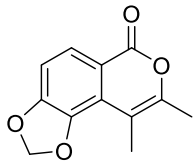
110.1, 103.6, 56.4, 56.3, 24.2, 19.7, 14.5, 12.8. NMR data are in agreement with previously reported data.[S6]



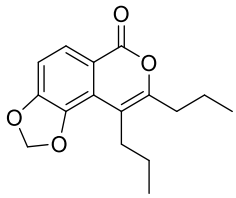
3,4-Diethyl-6,8-dimethoxy-1*H*-isochromen-1-one (7). Colorless solid. Yield: 61 mg (93%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (d, *J* = 2.2 Hz, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 2.56 – 2.46 (m, 4H), 1.19 (t, *J* = 7.5 Hz, 3H), 1.12 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)δ 165.5, 163.9, 159.8, 156.1, 142.5, 112.5, 103.7, 98.1, 97.3, 56.3, 55.5, 24.2, 19.8, 14.1, 12.5. HRMS (ESI+) of $C_{15}H_{18}O_4$, *m*/*z*: calcd for $[M+H]^+$ 263.1278, found 263.1279



8,9-Diethyl-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (8a). Colorless crystals. Yield: 57 mg (98%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.08 (s, 2H), 2.66 (q, J = 7.4 Hz, 2H), 2.53 (q, J = 7.5 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H), 1.12 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.3, 154.9, 152.7, 141.4, 126.4, 122.5, 115.9, 111.3, 108.8, 101.9, 23.7, 20.8, 15.4, 12.7.NMR data are in agreement with previously reported data.[S6]

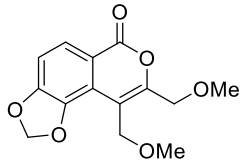


8,9-Dimethyl-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (8b). Colorless solid. Yield: 52 mg (95%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 2H), 2.21 – 2.18 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1, 152.6, 149.7, 141.9, 126.1, 122.9, 115.3, 108.8, 105.7, 102.0, 17.0, 14.0. HRMS (ESI+) of $C_{15}H_{18}O_4$, *m*/*z*: calcd for $[M+H]^+$ 219.0652, found 219.0656. NMR data are in agreement with previously reported data.[S7]

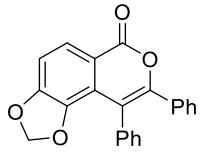


8,9-Dipropyl-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (8c). Colorless solid. Yield: 64 mg (95%). Eluent: petroleum ether/CH_2Cl_2 (3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.07 (s, 2H), 2.62 – 2.54 (m, 2H), 2.51 – 2.43 (m, 2H), 1.68

(sx, *J* = 7.4 Hz, 2H), 1.49 (sx, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)δ 162.3, 153.8, 152.6, 141.5, 126.4, 122.6, 115.7, 110.4, 108.8, 101.8, 32.3, 29.4, 24.0, 21.3, 14.0, 13.9. HRMS (ESI+) of $C_{16}H_{19}O_4$, *m*/*z*: calcd for $[M+H]^+$ 275.1278, found 275.1273.



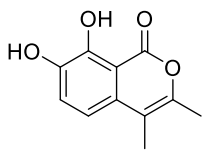
8,9-Bis(methoxymethyl)-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (8d). Colorless crystals. Yield: 57 mg (82%). Eluent: ethyl acetate/CH_2Cl_2 (1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.14 (s, 2H), 4.55 (s, 2H), 4.34 (s, 2H), 3.41 (s, 3H), 3.39 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0, 153.1, 152.9, 142.4, 126.5, 120.5, 115.8, 110.7, 109.9, 102.4, 68.7, 66.3, 58.9, 58.2. HRMS (ESI+) of $C_{14}H_{14}O_6$, *m*/*z*: calcd for $[M+H]^+$ 279.0863, found 279.0863.



8,9-Diphenyl-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (8e). Pale yellow solid. Yield: 78 mg (95%). Eluent: petroleum ether/CH_2Cl_2 (2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.24 – 7.06 (m, 10H), 6.93 (d, J = 8.3 Hz, 1H), 5.72 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6, 153.3, 151.3, 142.7, 135.1, 133.0, 131.2, 129.4, 128.9, 128.1, 127.9, 127.8, 126.3, 122.0, 115.0, 113.5, 109.6, 102.1. NMR data are in agreement with previously reported data.[S6]

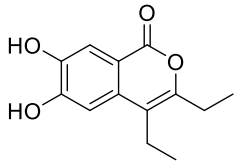
Typical procedure for dealkylation reaction

Alkoxy-substitute isocoumarin (0.2 mmol, 1 equiv.) and absolute benzene (3 ml) were placed in a Schlenk tube equipped with a magnetic stirring bar, the solution was cooled in an ice bath, and BBr_3 (1.5 equiv per OR fragment) was added slowly. The reaction mixture was allowed to warm to room temperature and heated for 2h at 80°C. Then the reaction was cooled in an ice bath and H_2O (2 ml) was added. The reaction was heated at 100°C for 2h and white precipitate was formed. After cooling the precipitate was filtered and dried in vacuo. In the case of **3**, the precipitate was chromatographed on SiO_2 with CH_2Cl_2/acetone (10:1) eluent. Compounds **6′** and **8′a** can be additionally purified by chromatography on SiO_2 with CH_2Cl_2/ethyl acetate (4:1) as eluent.

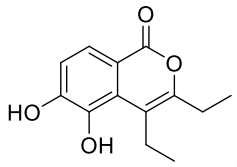


7,8-Dihydroxy-3,4-dimethyl-1*H*-isochromen-1-one (3). White crystals. Yield: 30 mg (74%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 9.70 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 2.25 (s, 3H), 2.07 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2CO$) δ 167.4,

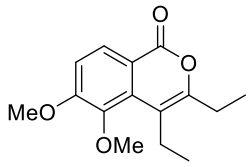
149.4, 147.9, 144.5, 131.2, 124.6, 114.0, 109.7, 106.9, 16.7, 12.3. NMR data are in agreement with previously reported data[5]. HRMS (ESI+) of $C_{11}H_{10}O_4$, *m*/*z*: calcd for $[M+H]^+$ 207.0652, found 207.0652.



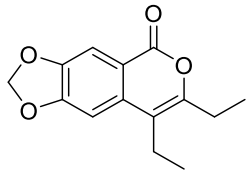
3,4-Diethyl-6,7-dihydroxy-1*H*-isochromen-1-one (6′). White solid. Yield 42 (89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ δ 11.04 – 9.06 (br s, 2H), 7.45 (s, 1H), 6.94 (s, 1H), 2.53 (s, 4H, overlapped with dmso), 1.19 – 1.06 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 161.4, 153.1, 152.2, 145.9, 131.6, 113.6, 112.2, 112.1, 108.1, 23.2, 18.9, 14.3, 12.5. HRMS (ESI+) of $C_{13}H_{15}O_4$, *m*/*z*: calcd for $[M+H]^+$ 235.0965, found 235.0966.



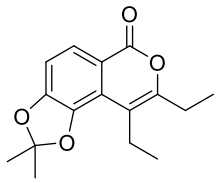
5,6-Dihydroxy-3,4-diethyl-1*H*-isochromen-1-one (8′a). White solid. Yield 41 (87%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70 (d, J = 8.2 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 3.02 – 2.89 (m, 2H), 2.61 – 2.53 (m, 2H), 1.25 – 1.16 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$) δ 162.0, 153.2, 149.8, 140.4, 125.4, 122.2, 114.6, 113.0, 108.0, 23.6, 21.2, 15.5, 12.3. HRMS (ESI+) of $C_{13}H_{15}O_4$, *m*/*z*: calcd for $[M+H]^+$ 235.0965, found 235.0966.



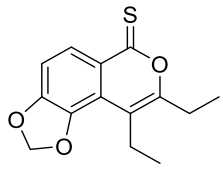
3,4-Diethyl-5,6-dimethoxy-1*H*-isochromen-1-one (9). Crude (not purified by column chromatography) dihydroxy isocoumarin **8′a** (41 mg, 0.18 mmol, 1 equiv.) and DMF (2 ml) were placed in a Schlenk tube equipped with a magnetic stirring bar, the solution was cooled in an ice bath, and NaH (11 mg, 0.45 mmol, 2.5 equiv.) was added. The reaction mixture was stirred for 20 minutes, and MeI (128 mg, 0.9 mmol, 5 equiv.) was added. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with 10 ml of water and the product was extracted with CH_2Cl_2 (3 × 5 ml). The organic layers were combined, dried with Na_2SO_4 and concentrated under vacuum. The resulting residue was chromatographed on silica gel (1 × 15 cm) with petroleum ether CH_2Cl_2/ (1:1) as an eluent. Yield: 42 mg (75% for two steps starting from **8a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 3.96 (s, 3H), 3.83 (s, 3H), 2.76 (q, *J* = 7.3 Hz, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.8, 158.4, 155.1, 131.6, 127.6, 115.4, 112.8, 111.8, 110.8, 61.5, 56.2, 24.2, 21.3, 15.5, 12.8. HRMS (ESI+) of $C_{15}H_{18}O_4$, *m*/*z*: calcd for $[M+H]^+$ 263.1278, found 263.1277.



7,8-Diethyl-5*H*-[1,3]dioxolo[4,5-*g*]isochromen-5-one (10). Dihydroxy isocoumarin **6′** (30 mg, 0.12 mmol, 1 equiv.), KF (35 mg, 0.6 mmol, 5 equiv.) and DMF (2 ml) were placed in a Schlenk tube equipped with a magnetic stirring bar, and were stirred for 20 minutes, then CH_2I_2 (48 mg, 0.18 mmol, 1.5 equiv.) was added. The reaction mixture was stirred for 10 hours at 110°C (an oil bath) and was cooled. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (1 × 15 cm) with pure CH_2Cl_2 as an eluent. Yield: 29 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 6.88 (s, 1H), 6.06 (s, 2H), 2.59 – 2.51 (m, 4H), 1.23 (t, J = 7.5 Hz, 3H), 1.14 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.6, 154.2, 153.9, 147.4, 135.7, 115.6, 113.1, 107.8, 102.2, 101.6, 24.1, 19.8, 14.3, 12.7. Although the synthesis of compound **10** has been published earlier,[S8] its structure was assigned incorrectly. In fact, the NMR spectra from the earlier work correspond to the nonlinear isomer **8a**. So, compound **10** was synthesized by us for the first time.

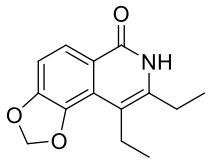


8,9-Diethyl-2,2-dimethyl-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (11). Dihydroxy isocoumarin **8′a** (40 mg, 0.16 mmol, 1 equiv.), acetone (19 mg, 0,32 mmol, 2 equiv.) and benzene (3 ml) were placed in a Schlenk tube equipped with a magnetic stirring bar, and P_2O_5 (100 mg) was added. The reaction mixture was stirred for 4 hours at 80°C (an oil bath) and was quenched with 10 ml of water. The product was extracted with CH_2Cl_2 (3 × 5 ml). The organic layers were combined, dried with Na_2SO_4 and concentrated under vacuum. The resulting residue was chromatographed on silica gel (1 × 15 cm) with petroleum ether CH_2Cl_2/ (2:1) as an eluent. Yield: 34 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 2.67 (q, *J* = 7.4 Hz, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.71 (s, 6H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.7, 154.4, 152.4, 128.9, 125.9, 122.2, 119.3, 115.3, 111.5, 108.8, 26.0, 23.7, 20.8, 15.4, 12.8. HRMS (ESI+) of $C_{16}H_{18}O_4$, *m/z*: calcd for $[M+H]^+$ 275.1278, found 275.1280.



8,9-Diethyl-6*H*-[1,3]dioxolo[4,5-*f*]isochromene-6-thione (12). Isocoumarin **8a** (60 mg, 0.24 mmol, 1 equiv), the Lawesson's reagent (118 mg, 0.29 mmol, 1.2 equiv.) and toluene (2 mL) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at

110 °C (an oil bath) for 4 h. Then, the reaction was cooled and the solvent was evaporated. The residue was chromatographed on silica (1 × 15 cm). The product was eluted with pure dichloromethane. Yield: 61 mg (98%). Eluent: petroleum ether/ CH_2Cl_2 (15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.7 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.11 (s, 2H), 2.72 – 2.61 (m, 4H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)δ 199.9, 158.3, 153.2, 141.4, 130.9, 125.8, 117.9, 114.3, 110.2, 102.3, 23.7, 20.9, 15.2, 13.0. HRMS (ESI+) of $C_{14}H_{14}O_4S$, *m*/*z*: calcd for $[M+H]^+$ 263.0737, found 263.0733.



8,9-Diethyl-[1,3]dioxolo[4,5-*f*]isoquinolin-6(7*H*)-one (13). Isocoumarin **8a** (37 mg, 0.15 mmol, 1 equiv), ammonium formate (75 mg, 8 equiv) and DMSO (1 mL) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 110 °C (an oil bath) for 2 h. Then, the reaction was quenched with 10 ml of water and the product was extracted with dichloromethane (3×10 ml), the organic layer was combined and dried with Na_2SO_4. Solvent was removed in vacuo. The residue was chromatographed on silica (1 × 15 cm). The product was eluted with a mixture of acetone and dichloromethane (1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (br s, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.07 (s, 2H), 2.79 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.57 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.1, 150.4, 141.4, 139.3, 123.7, 123.5, 121.0, 111.9, 108.1, 101.3, 23.9, 21.0, 16.1, 14.1. HRMS (ESI+) of $C_{14}H_{15}NO_3$, *m*/*z*: calcd for $[M+H]^+$ 246.1122, found 246.1122.

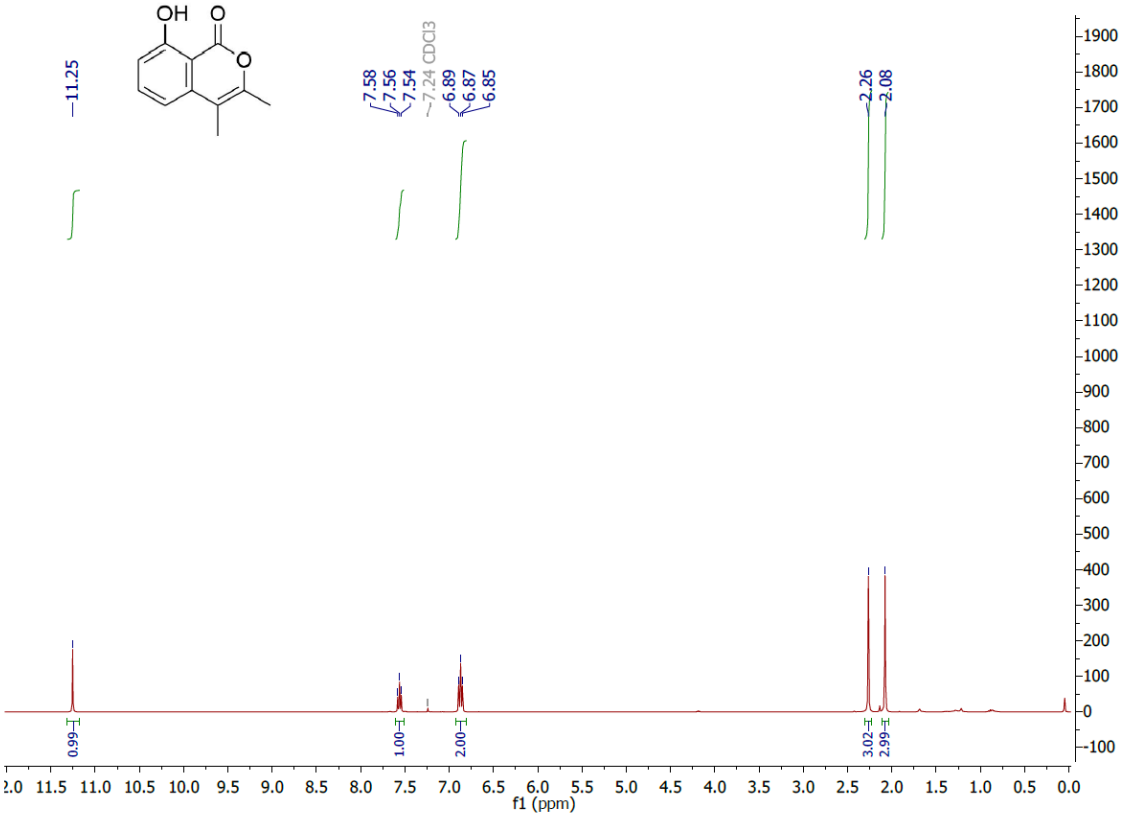
Bioassay of fungicidal activities

The effect of the chemicals on mycelial radial growth was determined by dissolving compounds in the cprresponding solvents. All compounds except **6′** and **8′a** were dissolved in methanol at a concentration of 3 mg/mL. In the case of **6′** and **8′a**, dmso was used as a solvent at the same concentration. Then aliquots were suspended in potato-saccharose agar at 50 °C to give the concentration 30 μg/mL. Petri dishes containing 15 mL of the agar medium were inoculated by placing 2-mm mycelial agar discs on the agar surface. Plates were incubated at 25 °C and radial growth was measured after 72 h. The agar medium without sample was used as the blank control. Three replicates of each test were carried out. The mycelium elongation diameter (mm) of fungi settlements was measured after 72 h of culture. The growth inhibition rates (***I***) were calculated using the following equation:

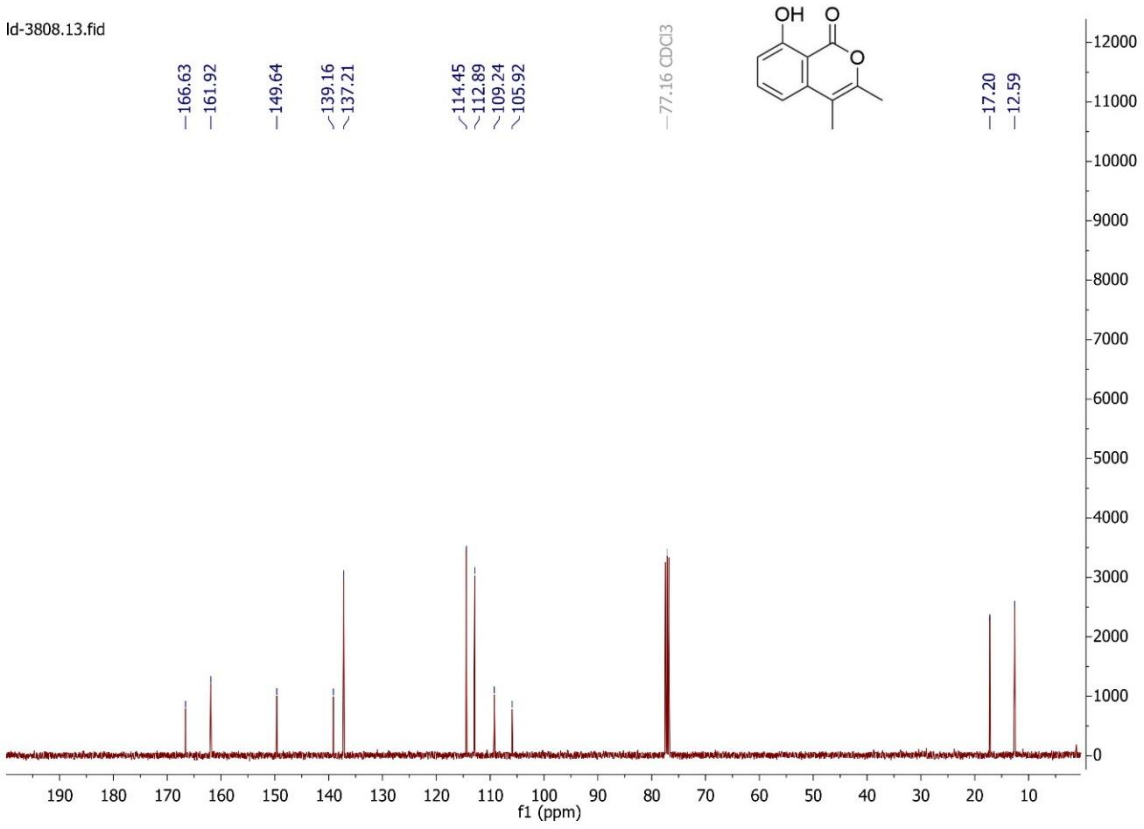
$$I = \frac{Control\ settlement\ diameter\ (mm)\ -\ Test\ settlement\ diameter\ (mm)}{Control\ settlement\ diameter\ (mm)} * 100\%$$

Copies of NMR spectra

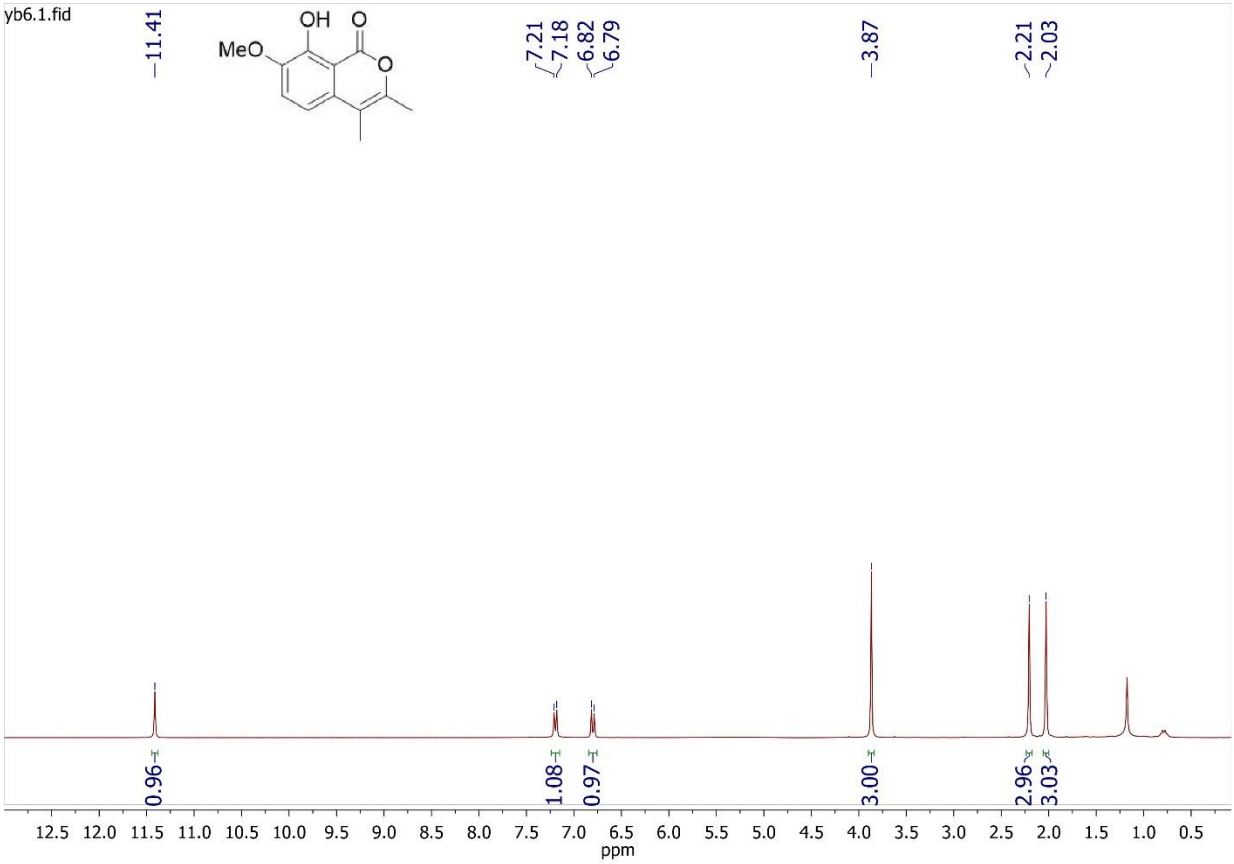
^{1}H NMR (400 MHz) spectrum of **1** in $CDCl_3$



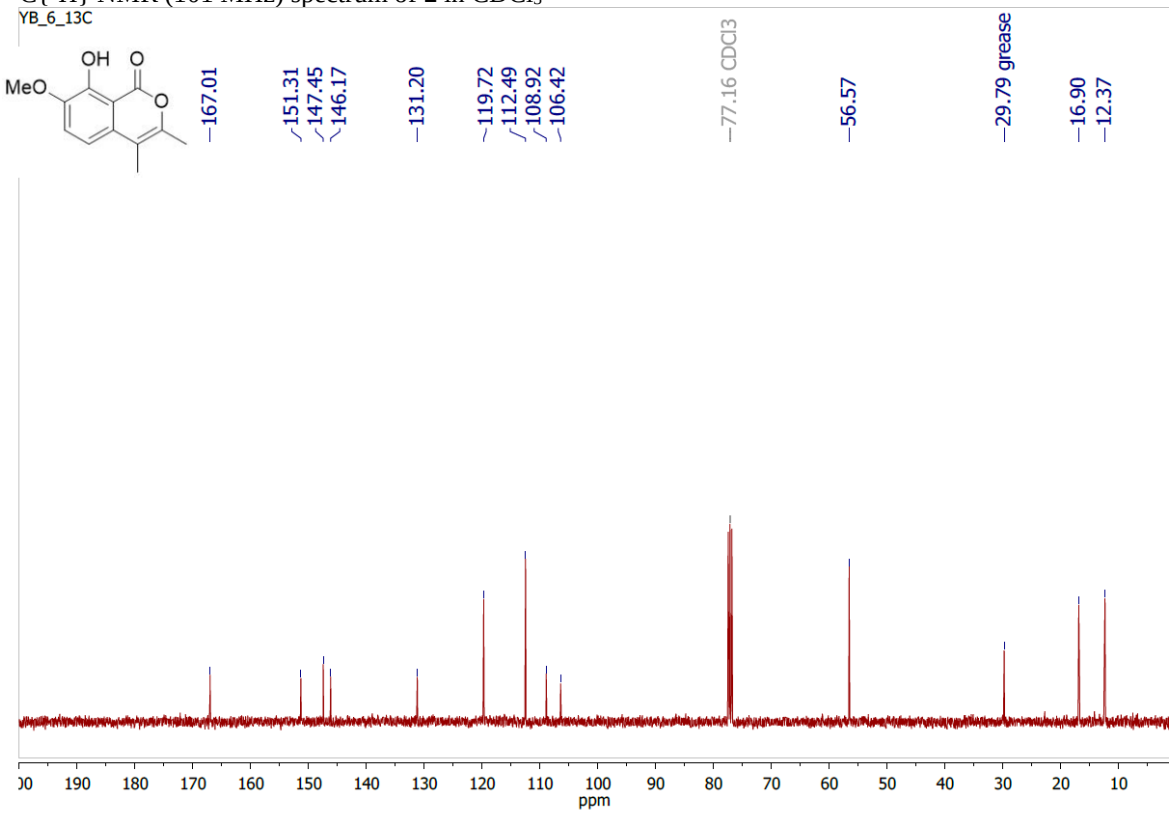
^{13}C{^{1}H} NMR (101 MHz) spectrum of **1** in $CDCl_3$



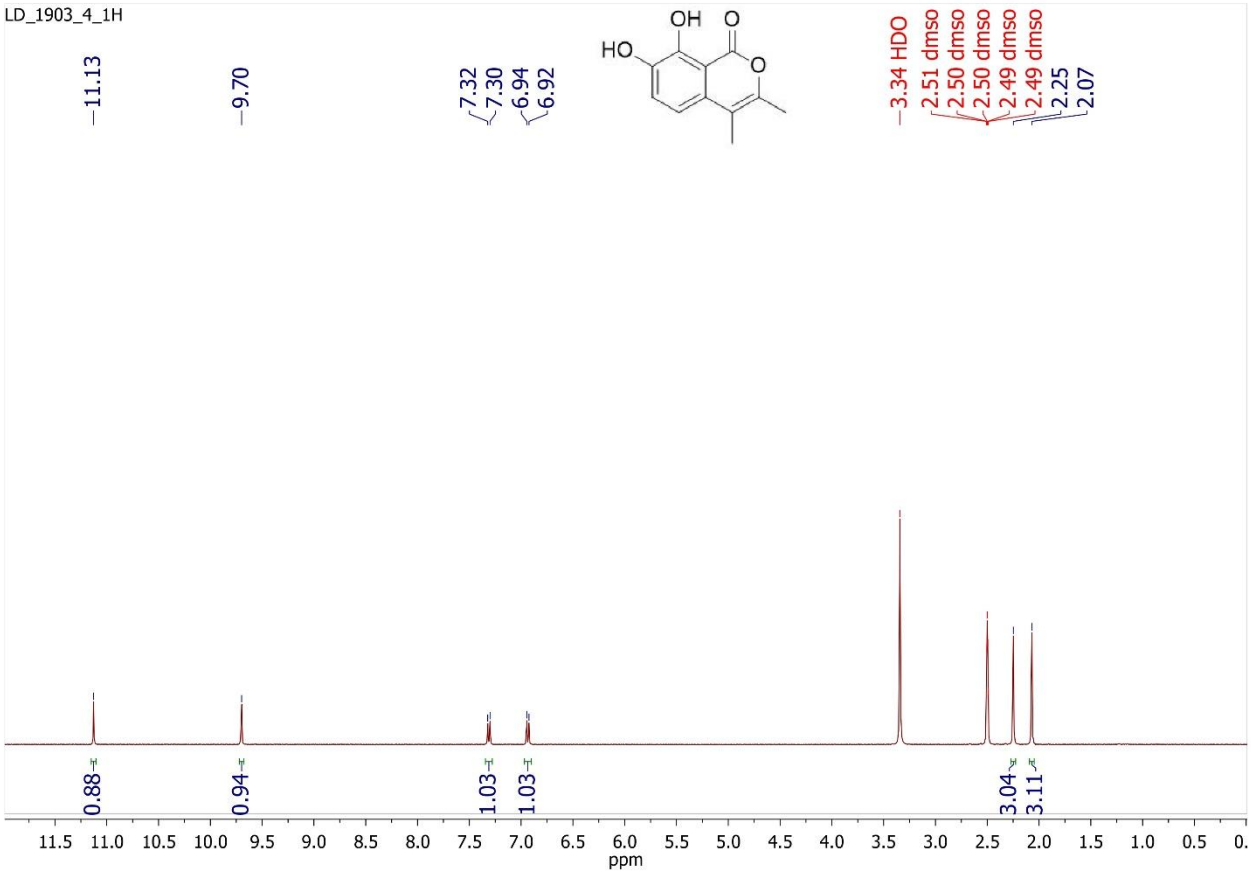
^{1}H NMR (400 MHz) spectrum of **2** in $CDCl_3$



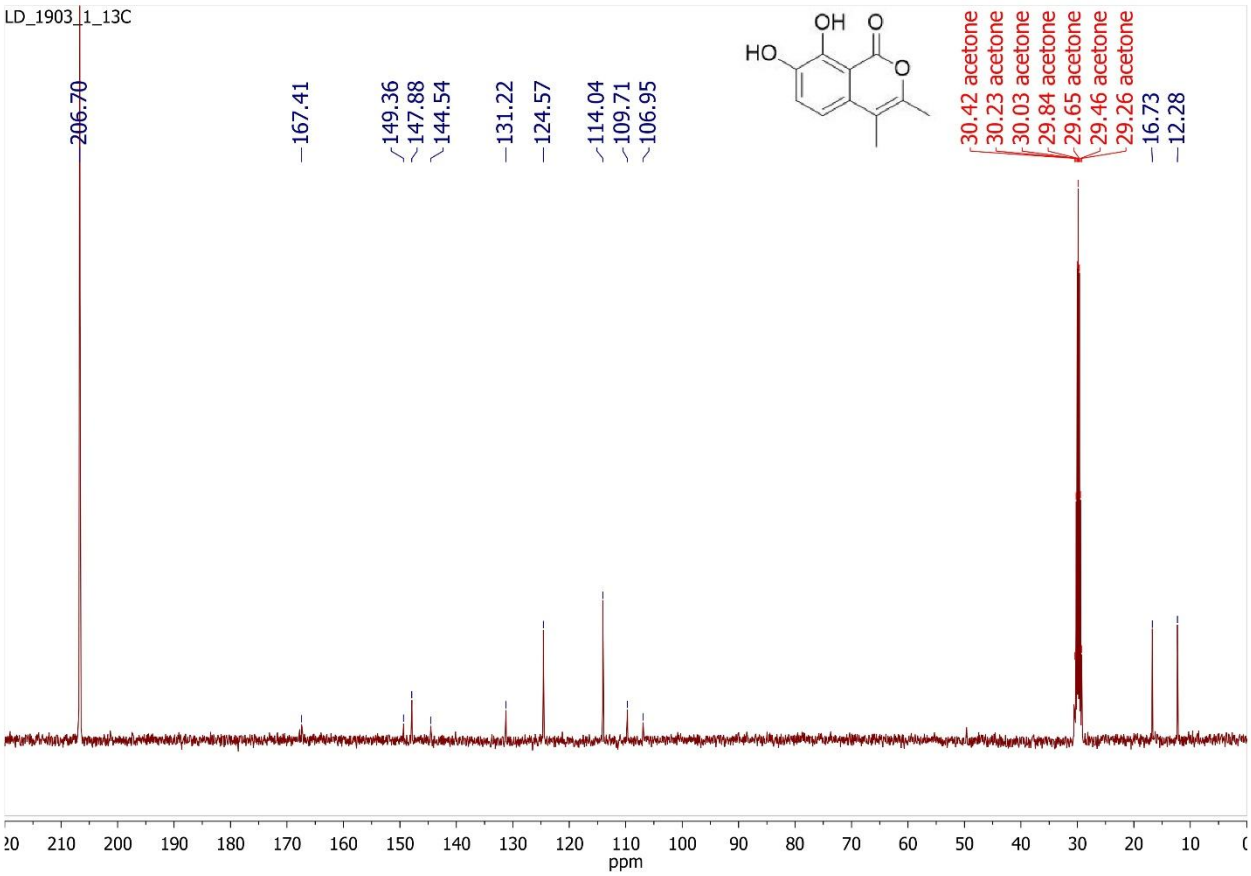
^{13}C{^{1}H} NMR (101 MHz) spectrum of **2** in $CDCl_3$



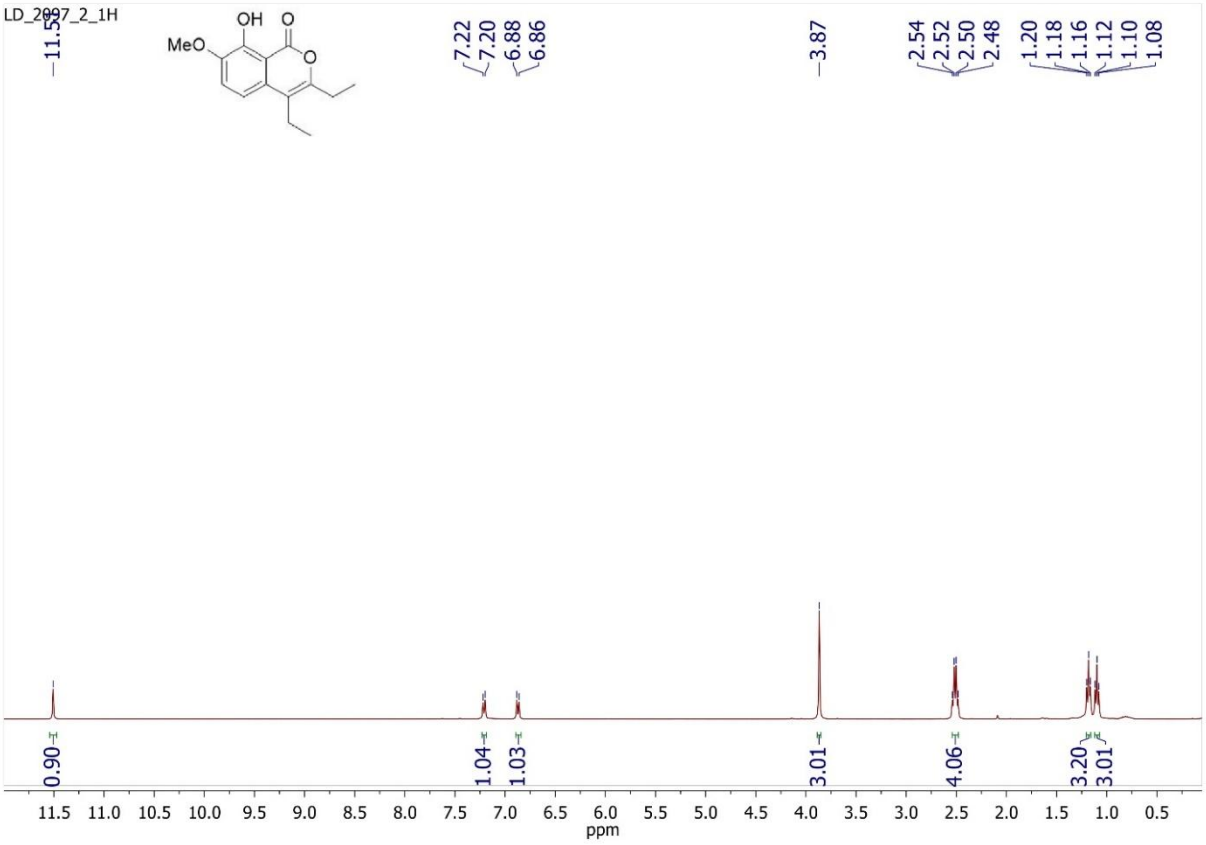
^{1}H NMR (400 MHz) spectrum of **3** in dmso-d_6



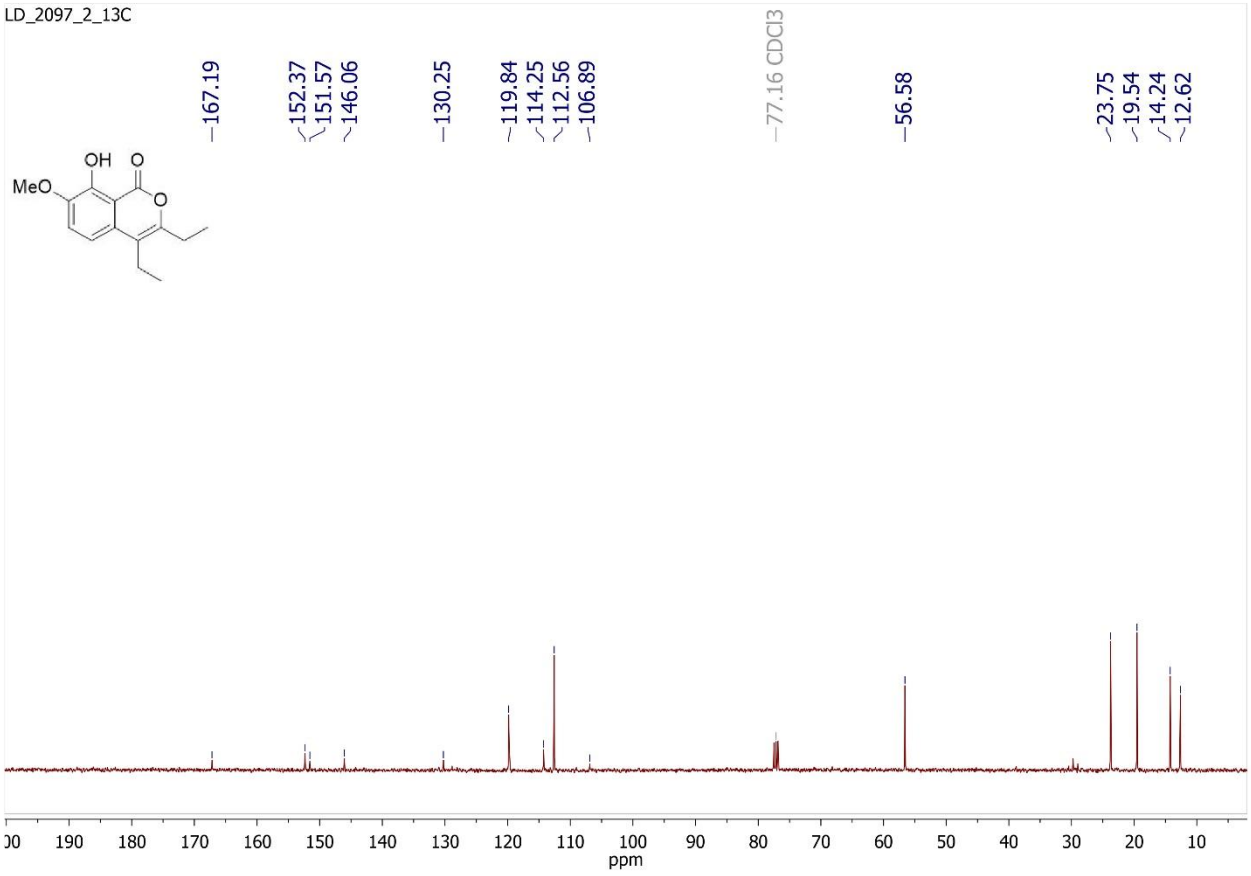
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3** in $(CD_3)_2CO$



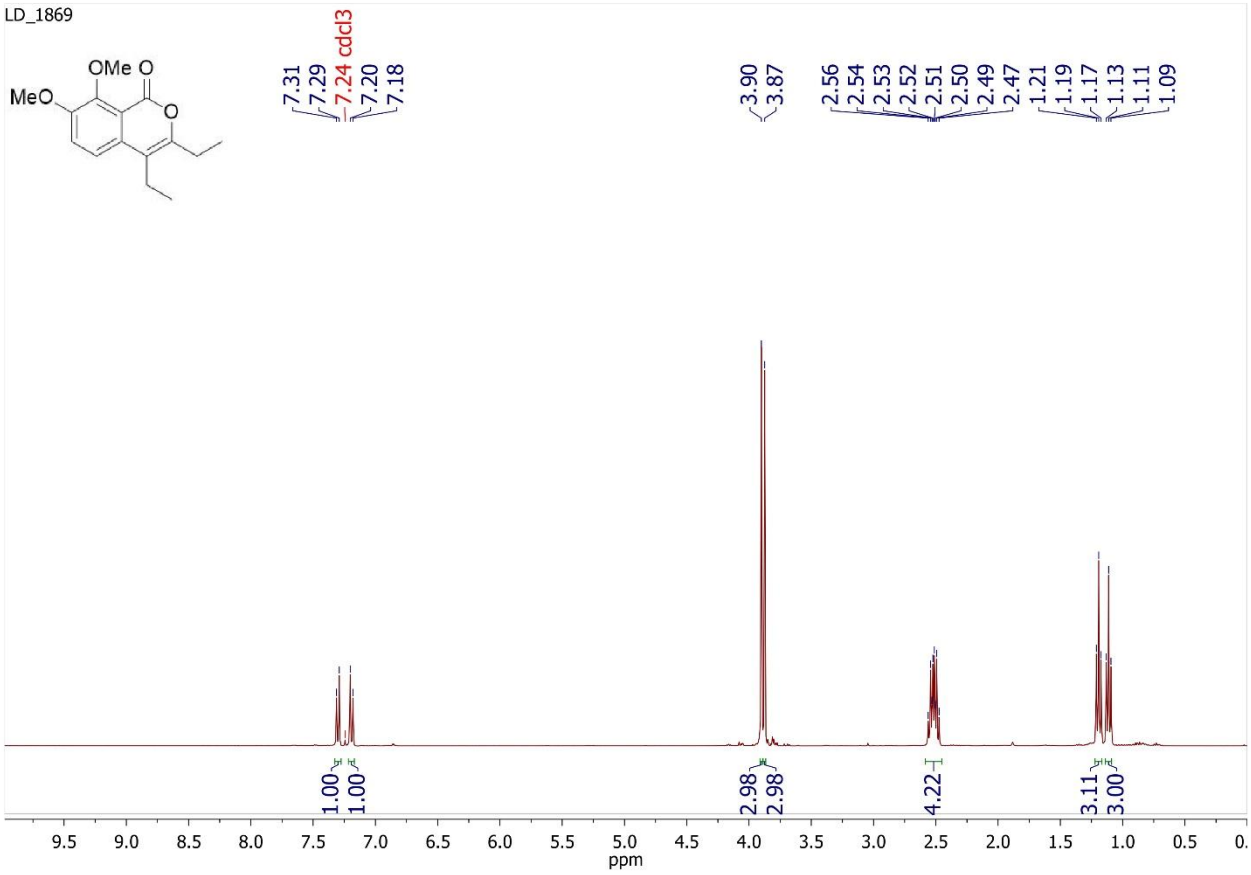
^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$



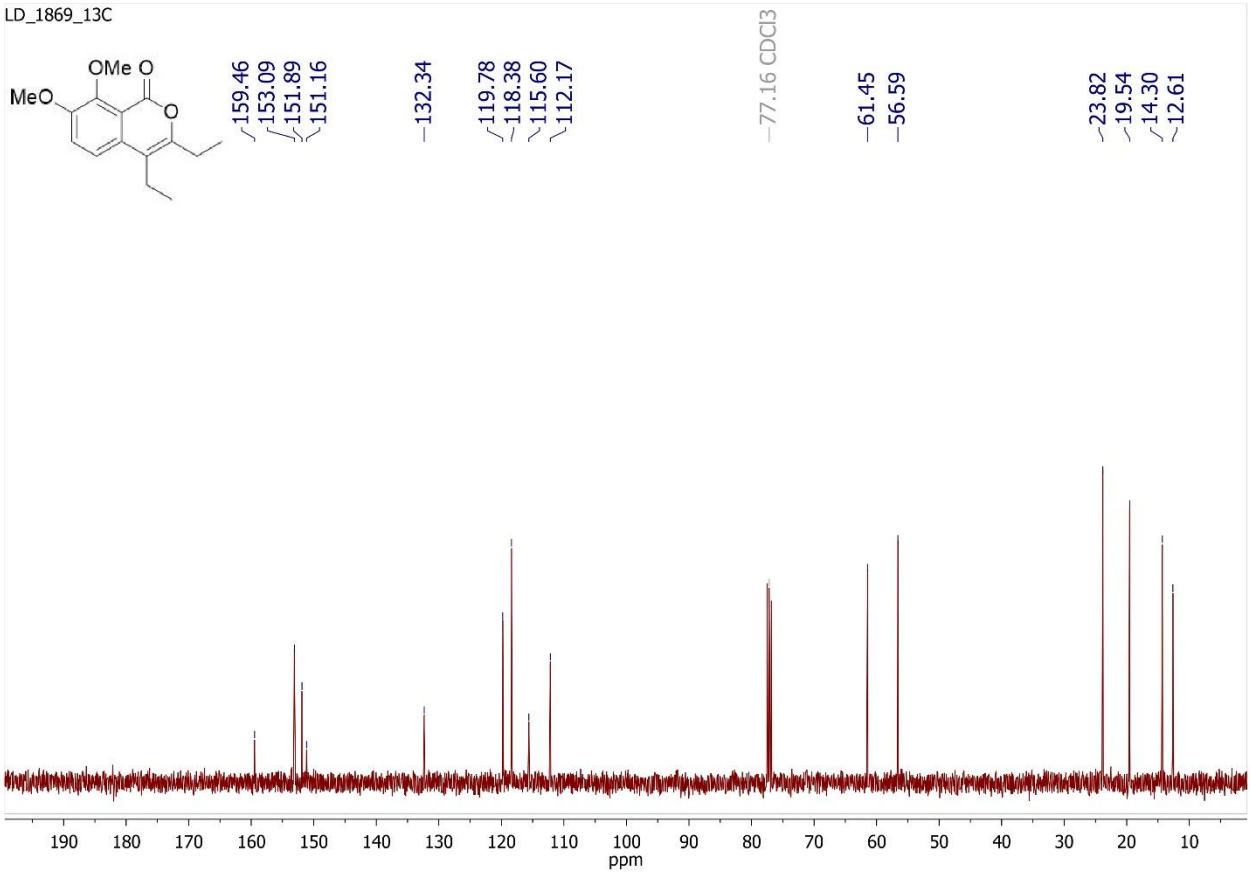
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4** in $CDCl_3$



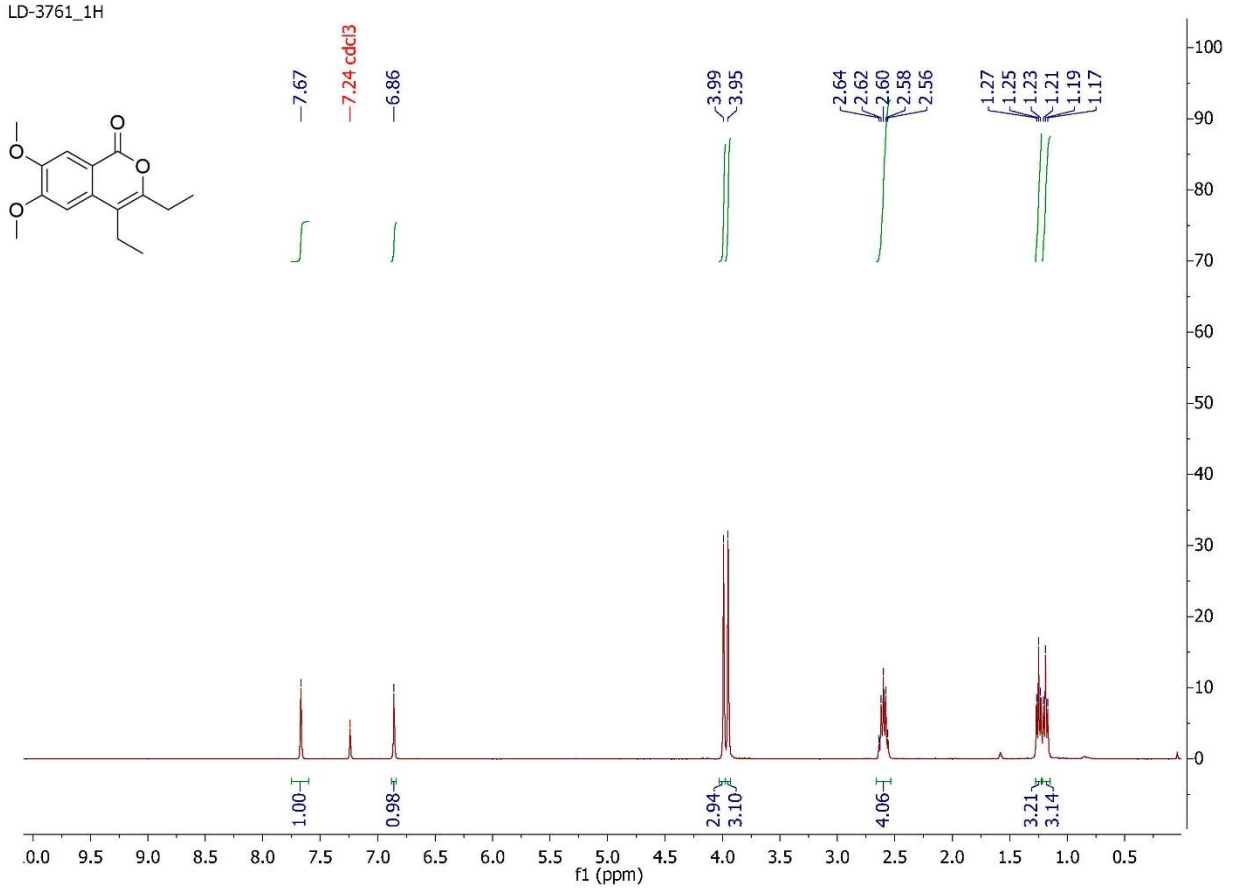
^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$



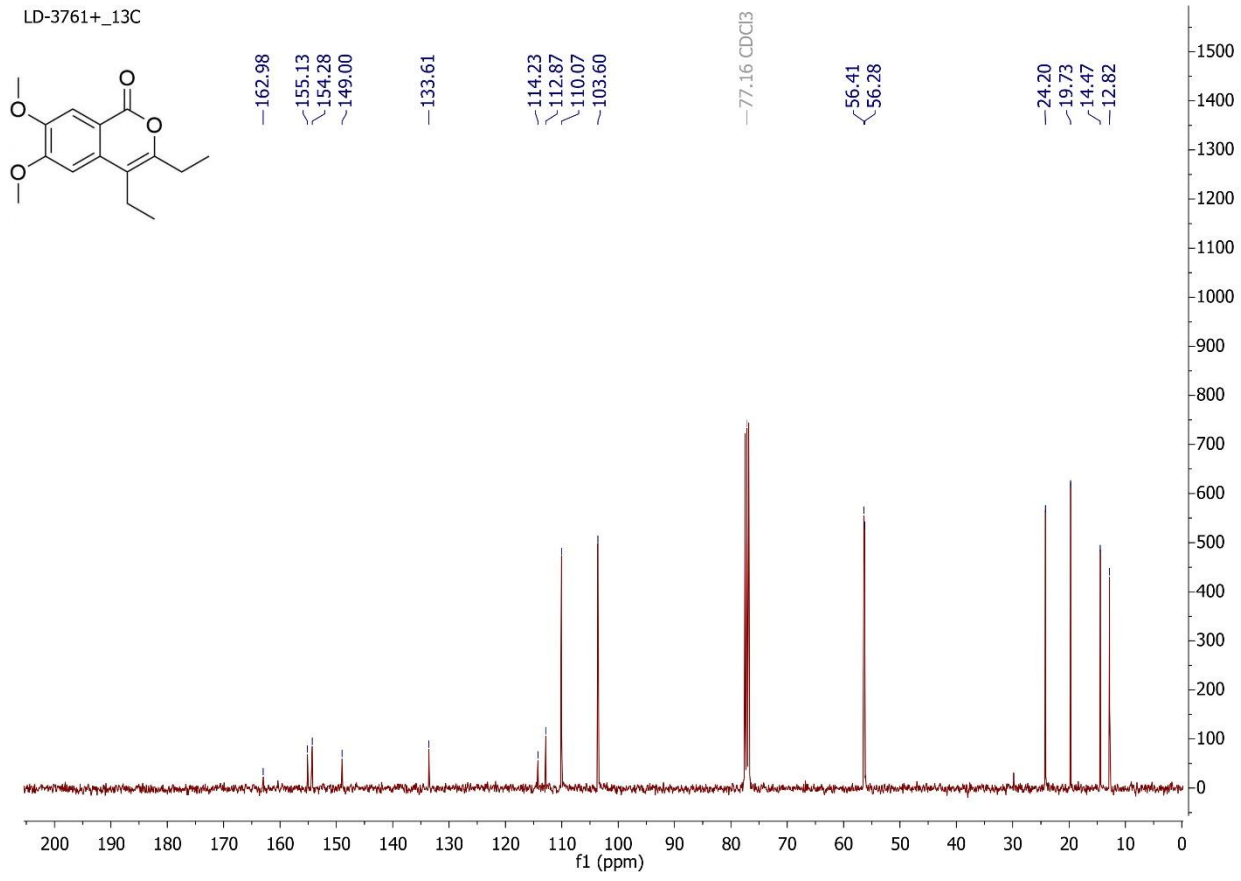
^{13}C{^{1}H} NMR (101 MHz) spectrum of **5** in $CDCl_3$



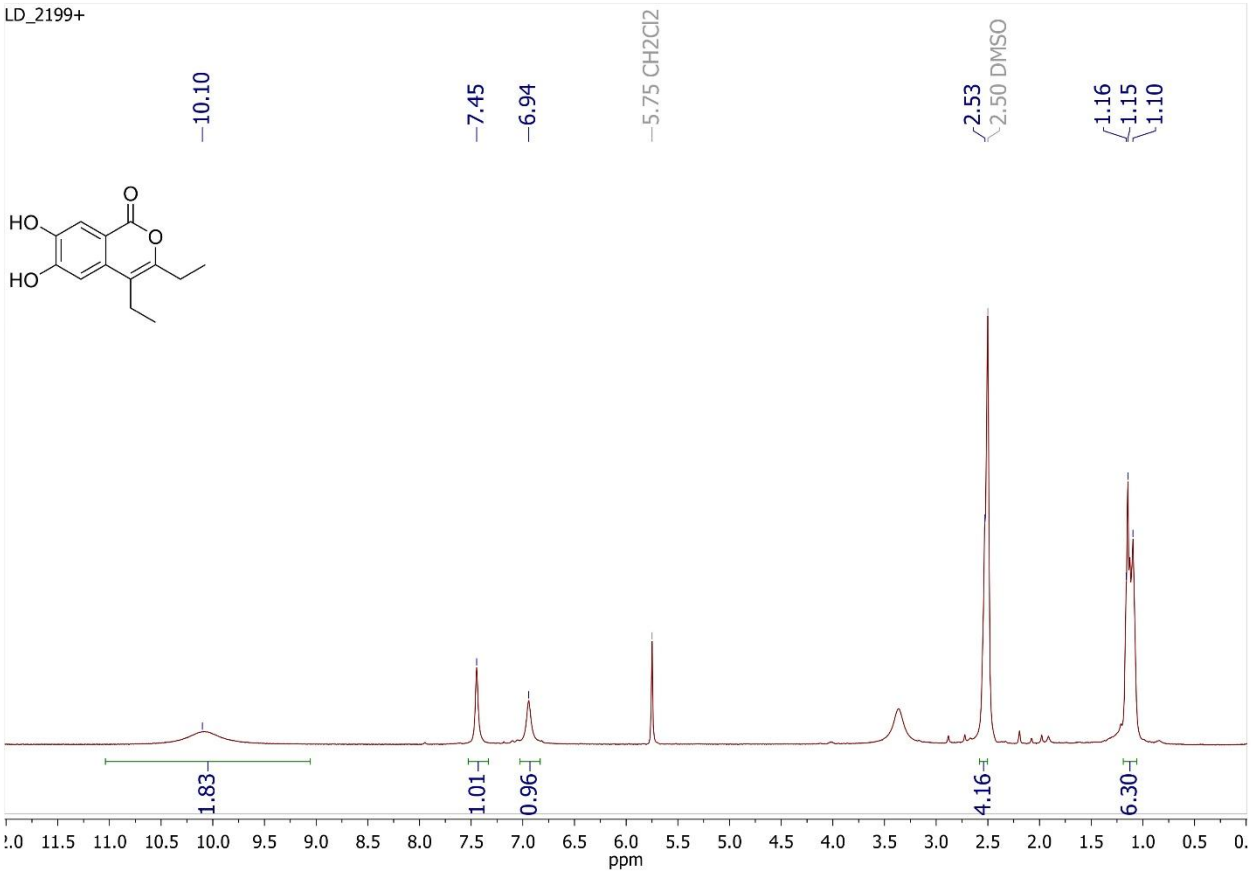
^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$



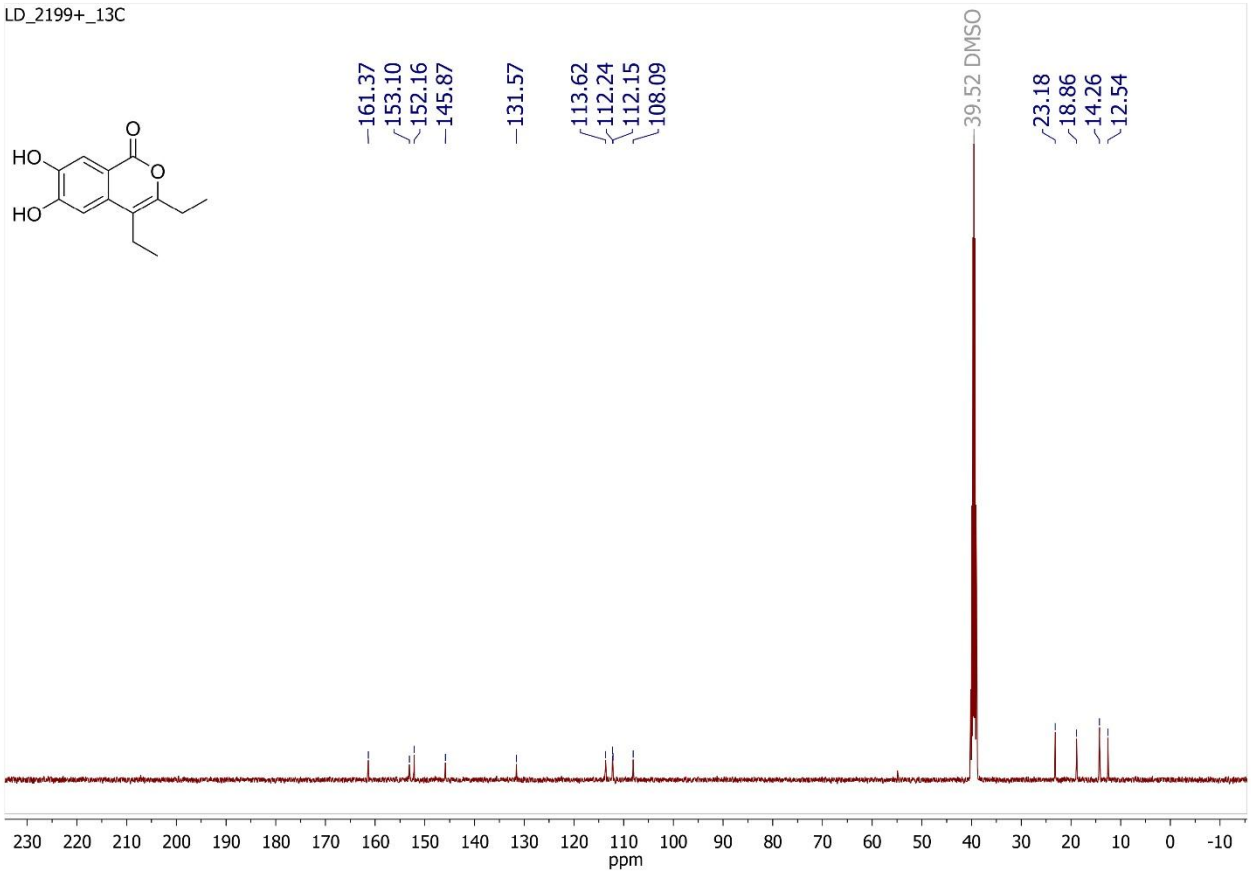
^{13}C{^{1}H} NMR (101 MHz) spectrum of **6** in $CDCl_3$



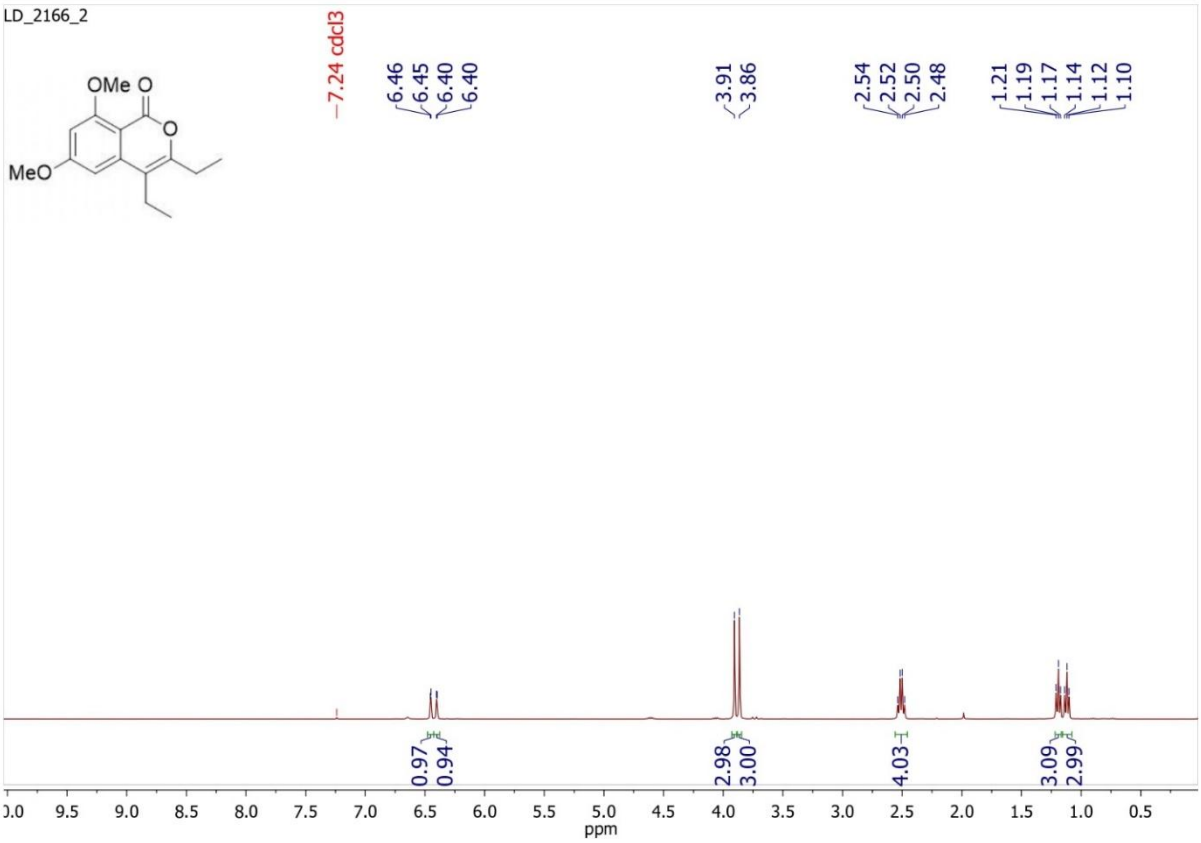
^{1}H NMR (400 MHz) spectrum of **6'** in dmso-d_6



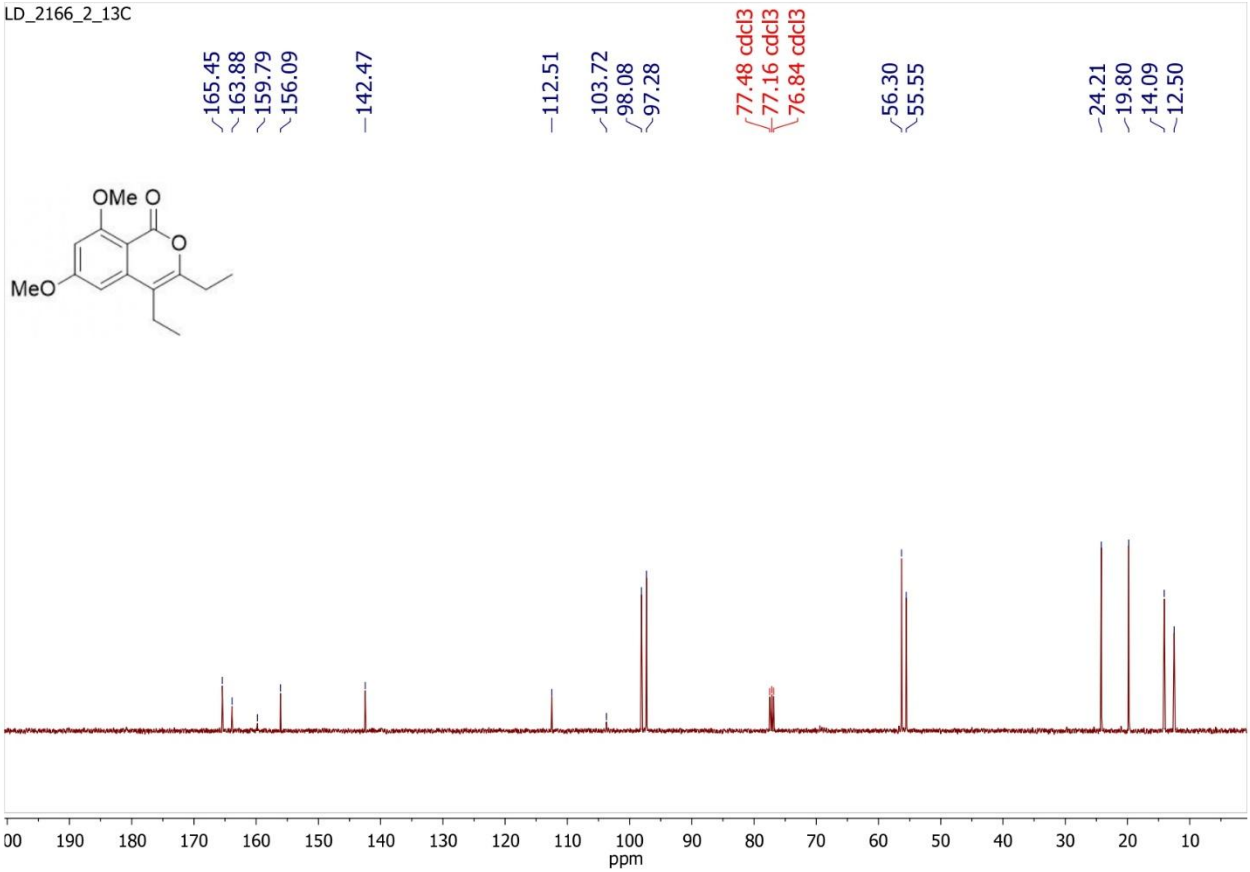
^{13}C{^{1}H} NMR (101 MHz) spectrum of **6'** in dmso-d_6



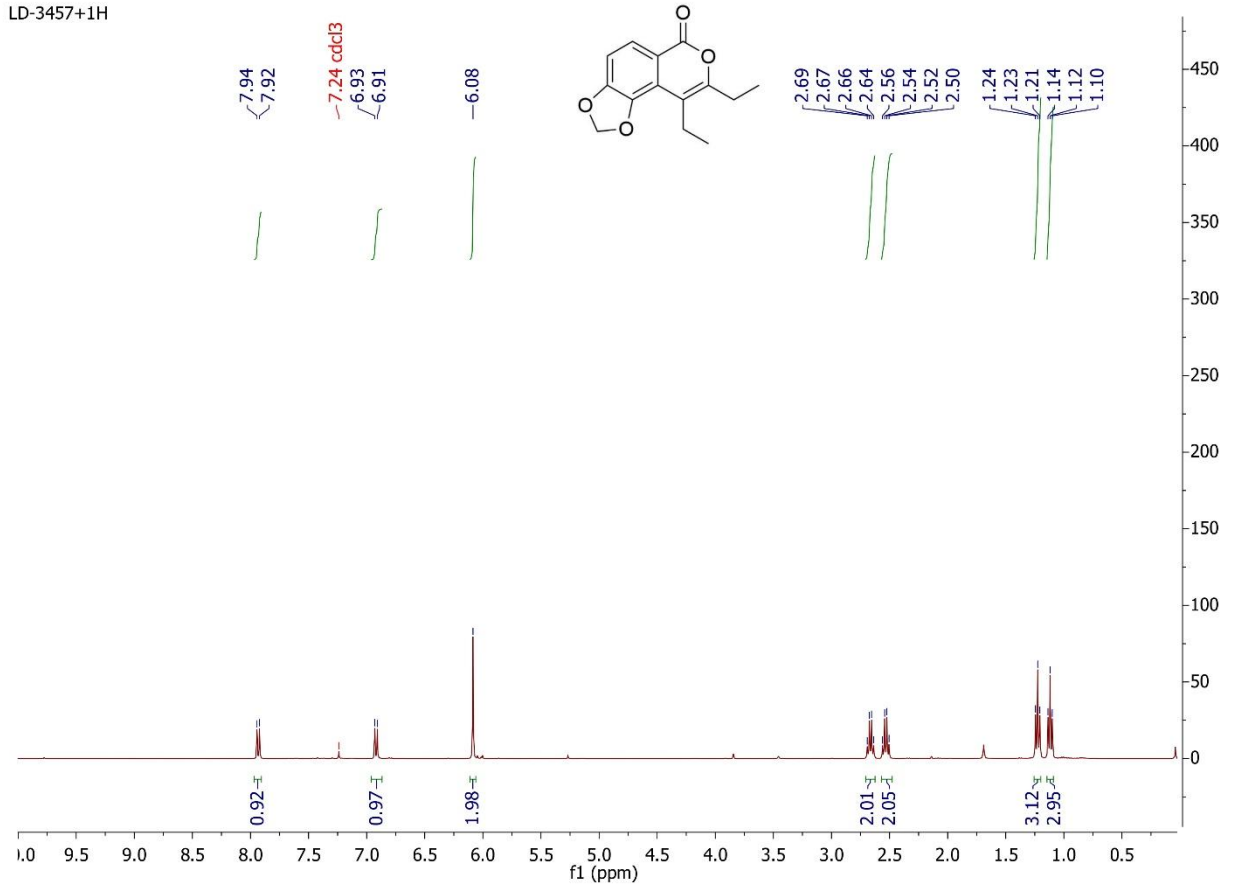
^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$



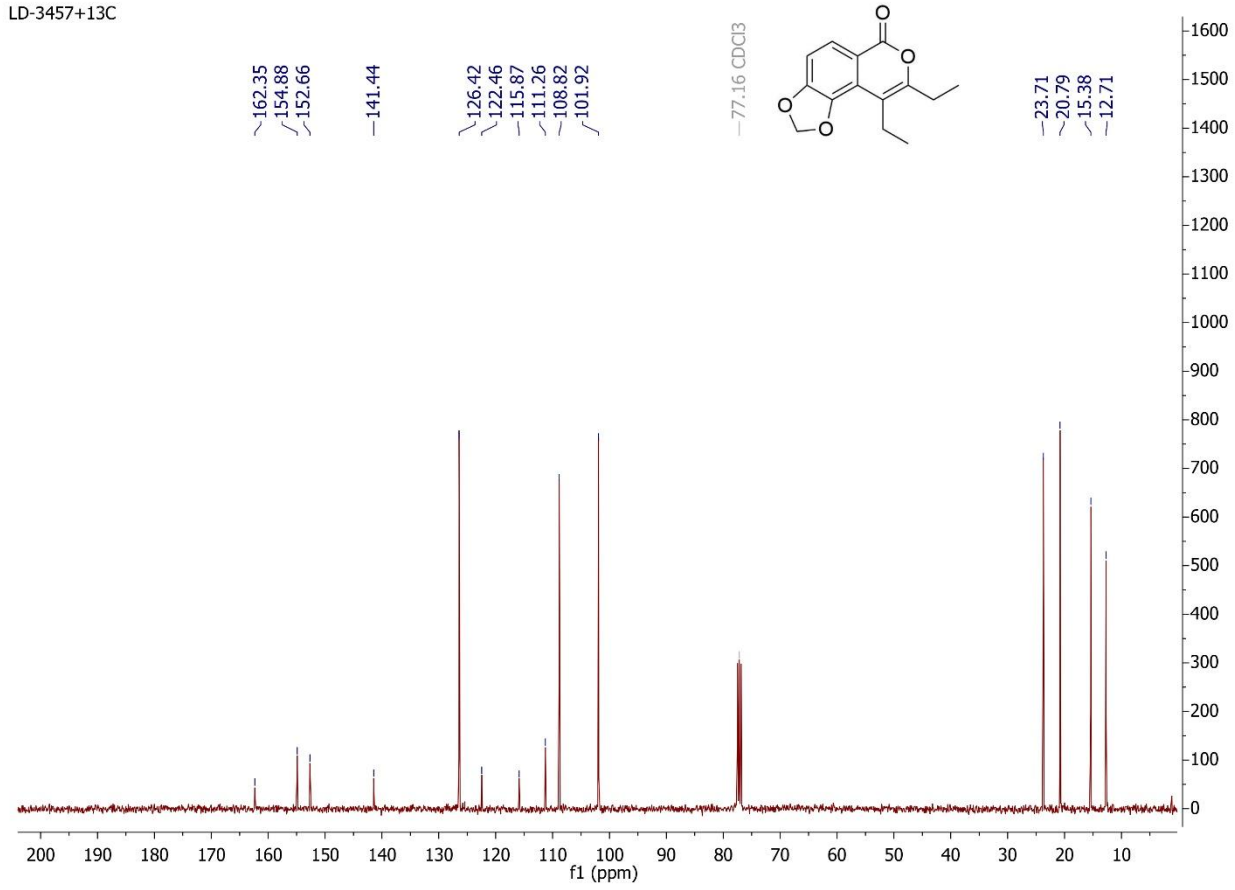
^{13}C{^{1}H} NMR (101 MHz) spectrum of **7** in $CDCl_3$



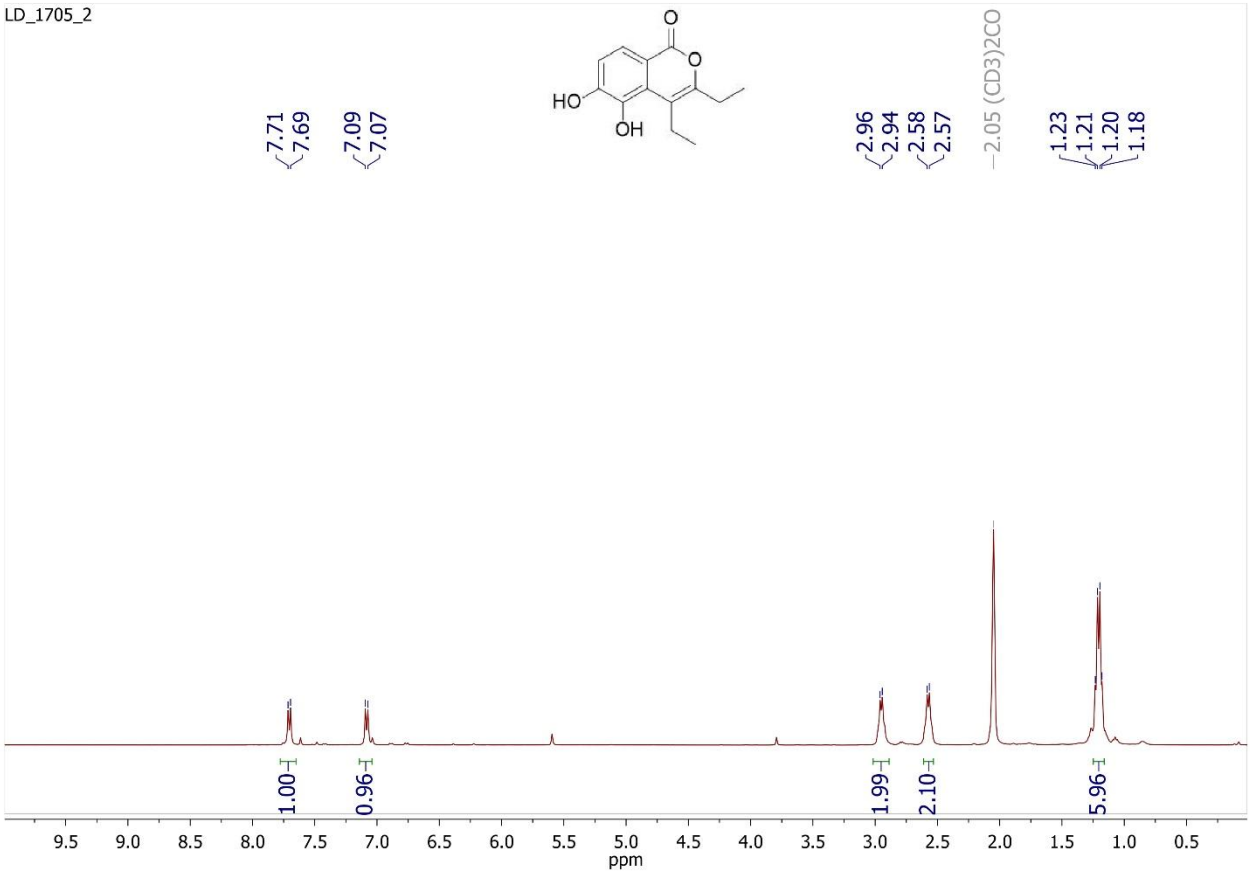
^{1}H NMR (400 MHz) spectrum of **8a** in $CDCl_3$



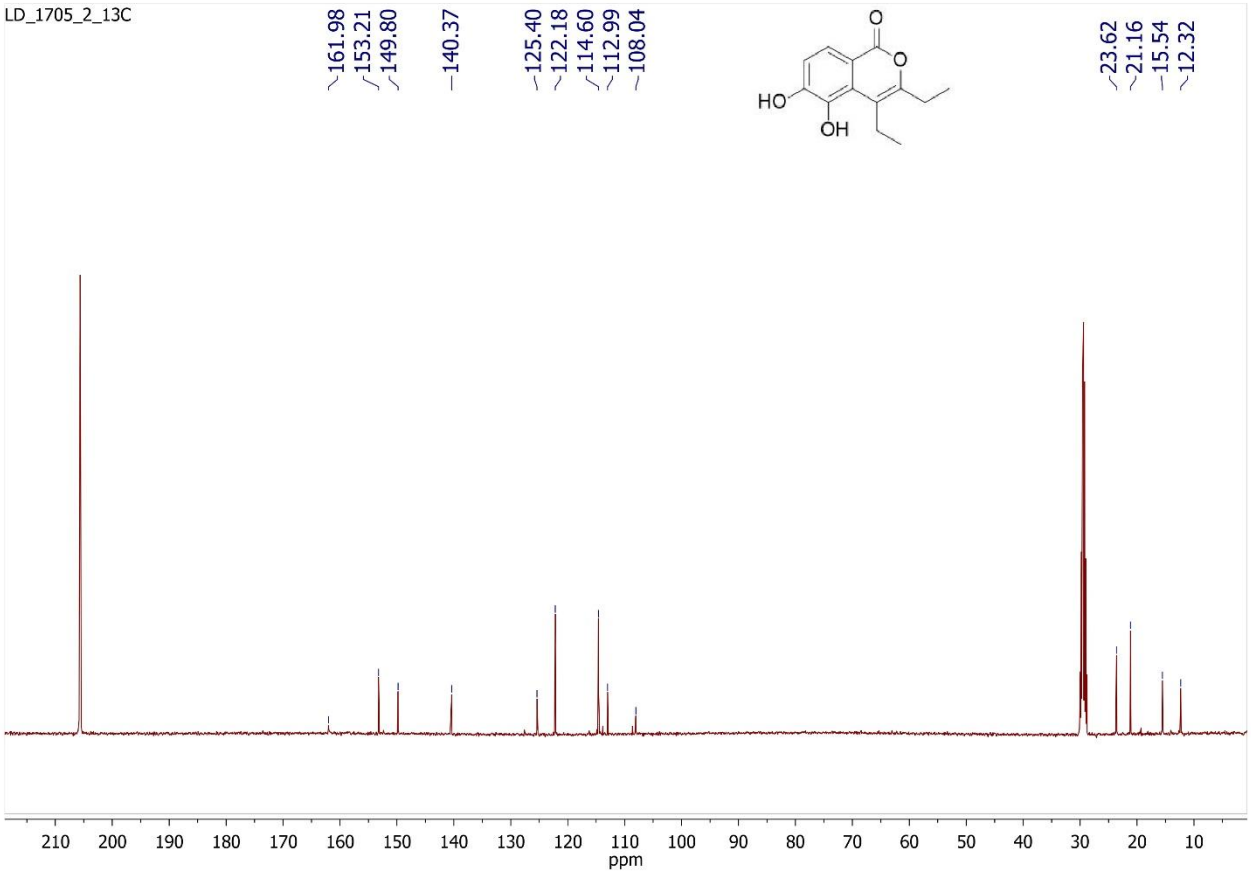
^{13}C{^{1}H} NMR (101 MHz) spectrum of **8a** in $CDCl_3$



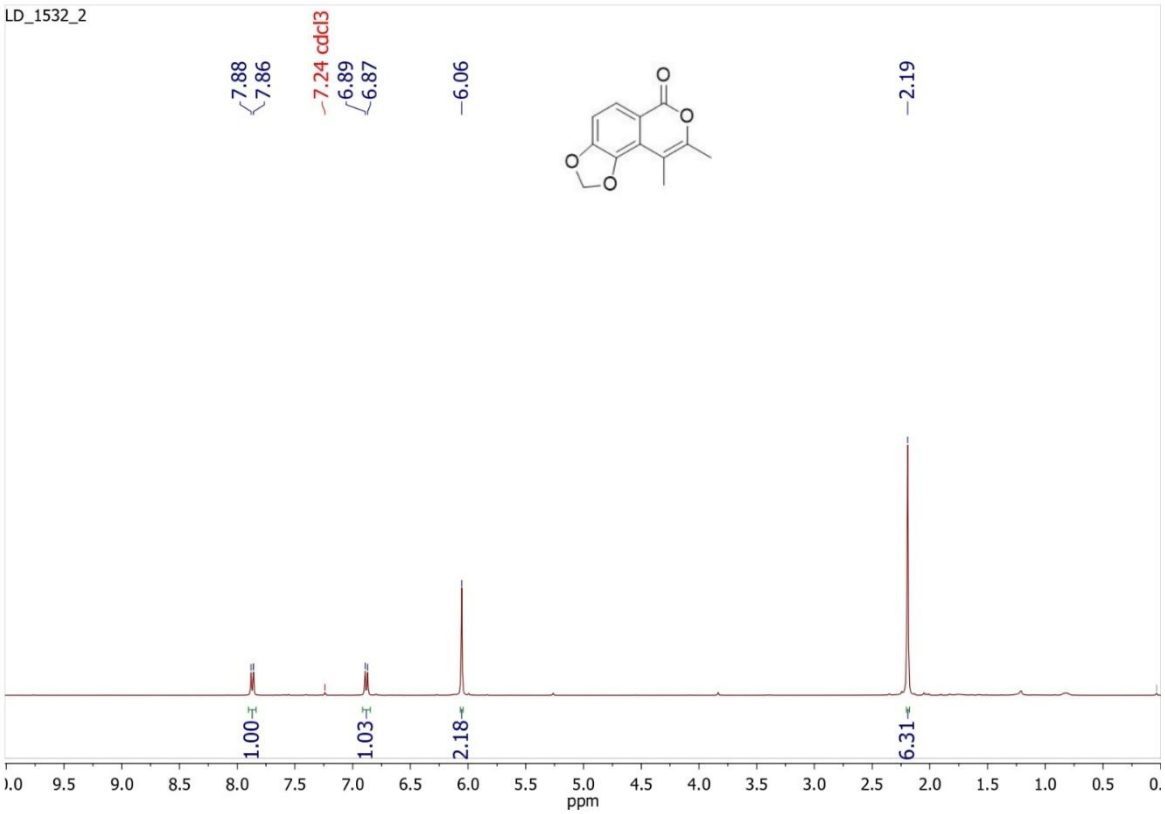
^{1}H NMR (400 MHz) spectrum of **8′a** in $(CD_3)_2CO$



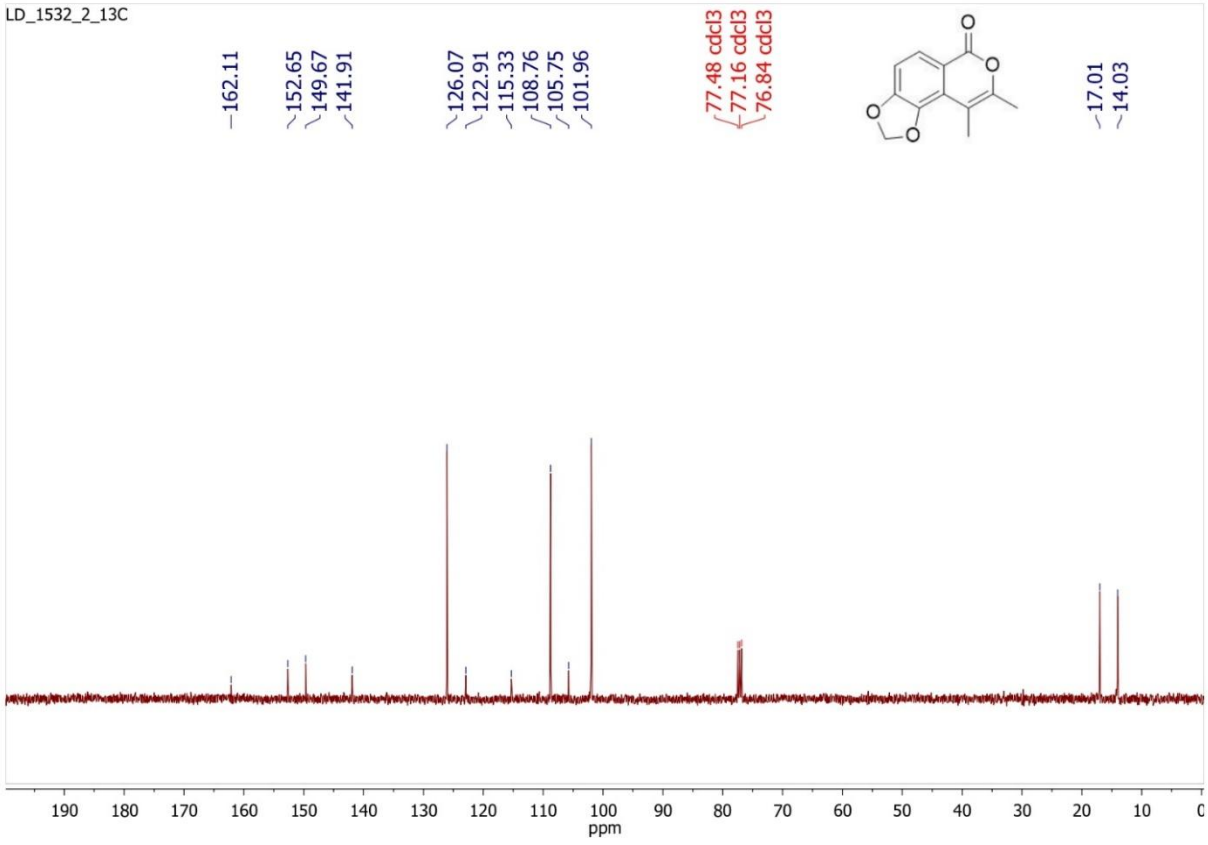
^{13}C{^{1}H} NMR (101 MHz) spectrum of **8′a** in $(CD_3)_2CO$



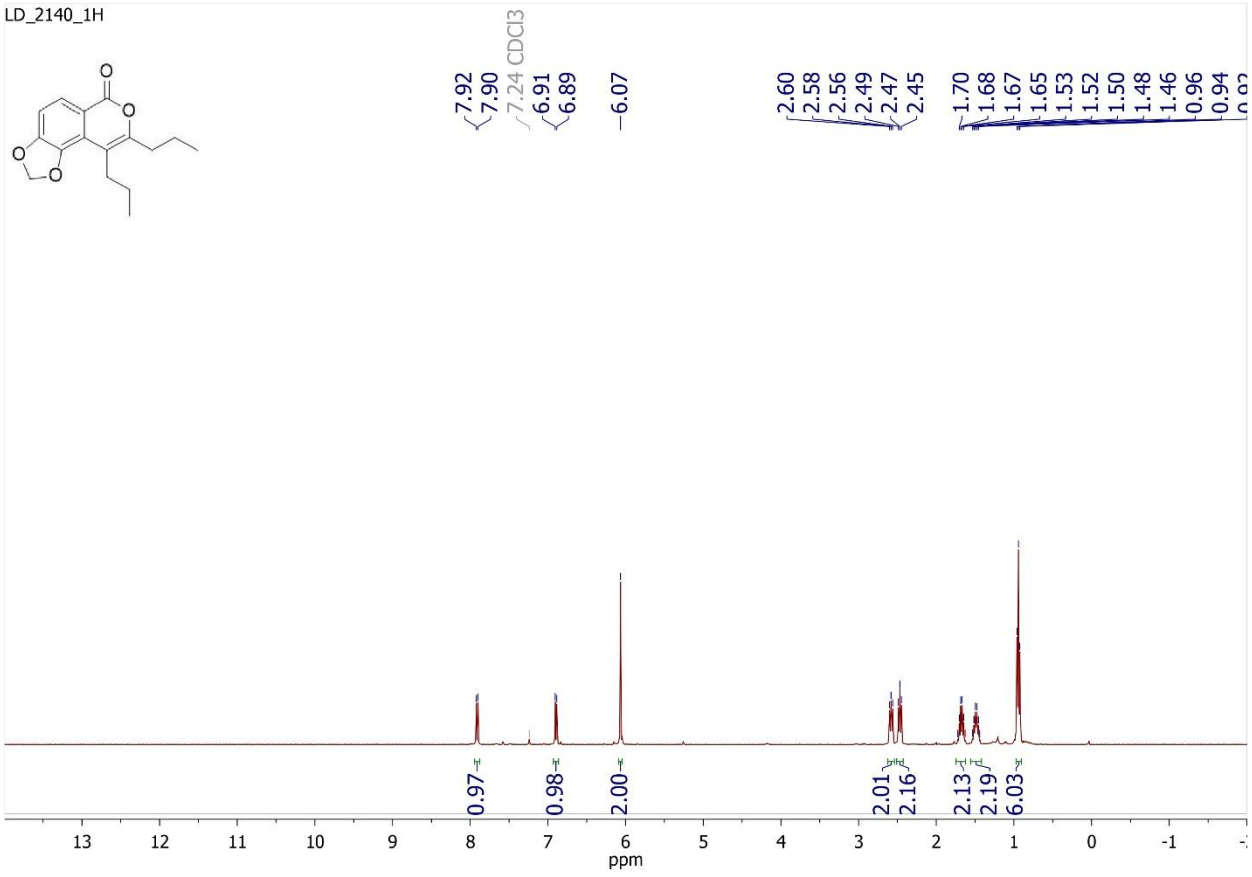
^{1}H NMR (400 MHz) spectrum of **8b** in $CDCl_3$



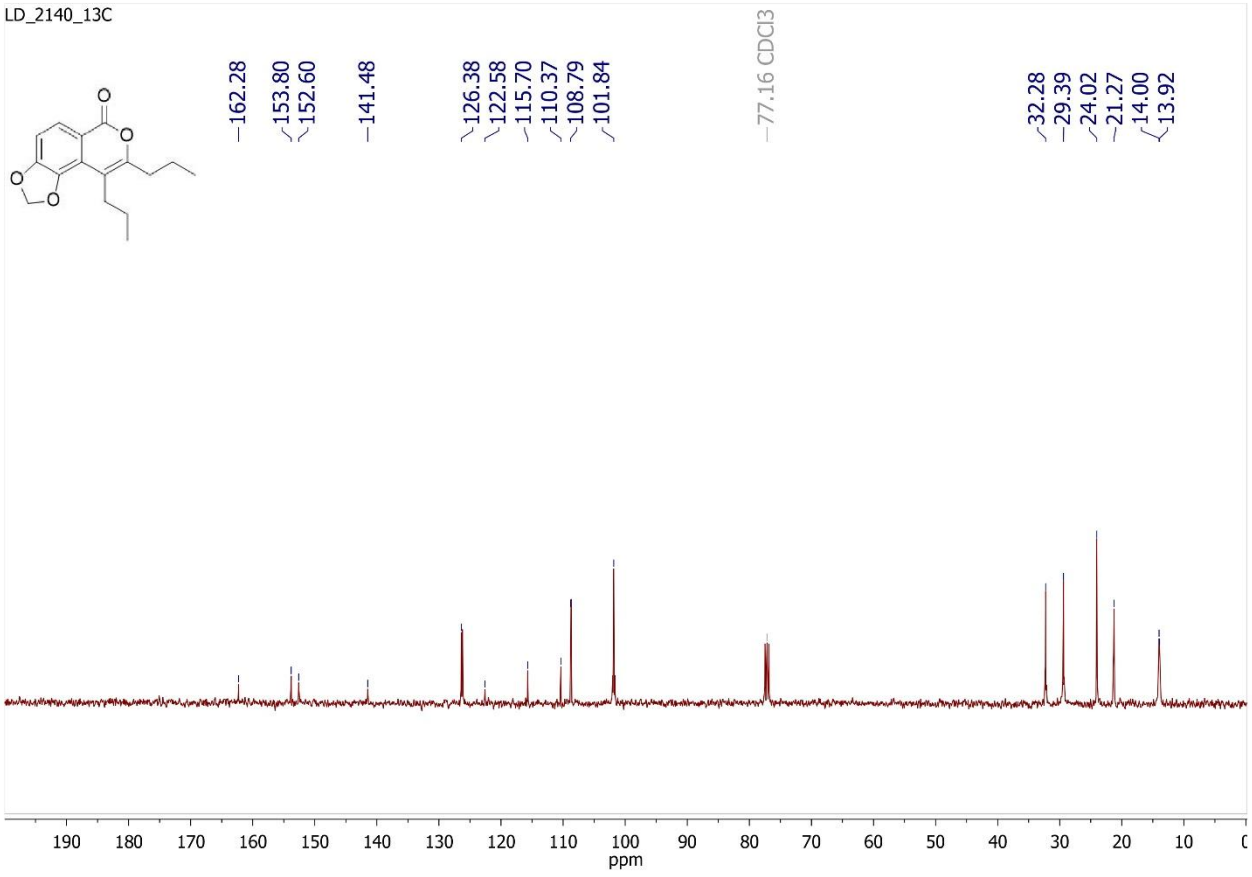
^{13}C{^{1}H} NMR (101 MHz) spectrum of **8b** in $CDCl_3$



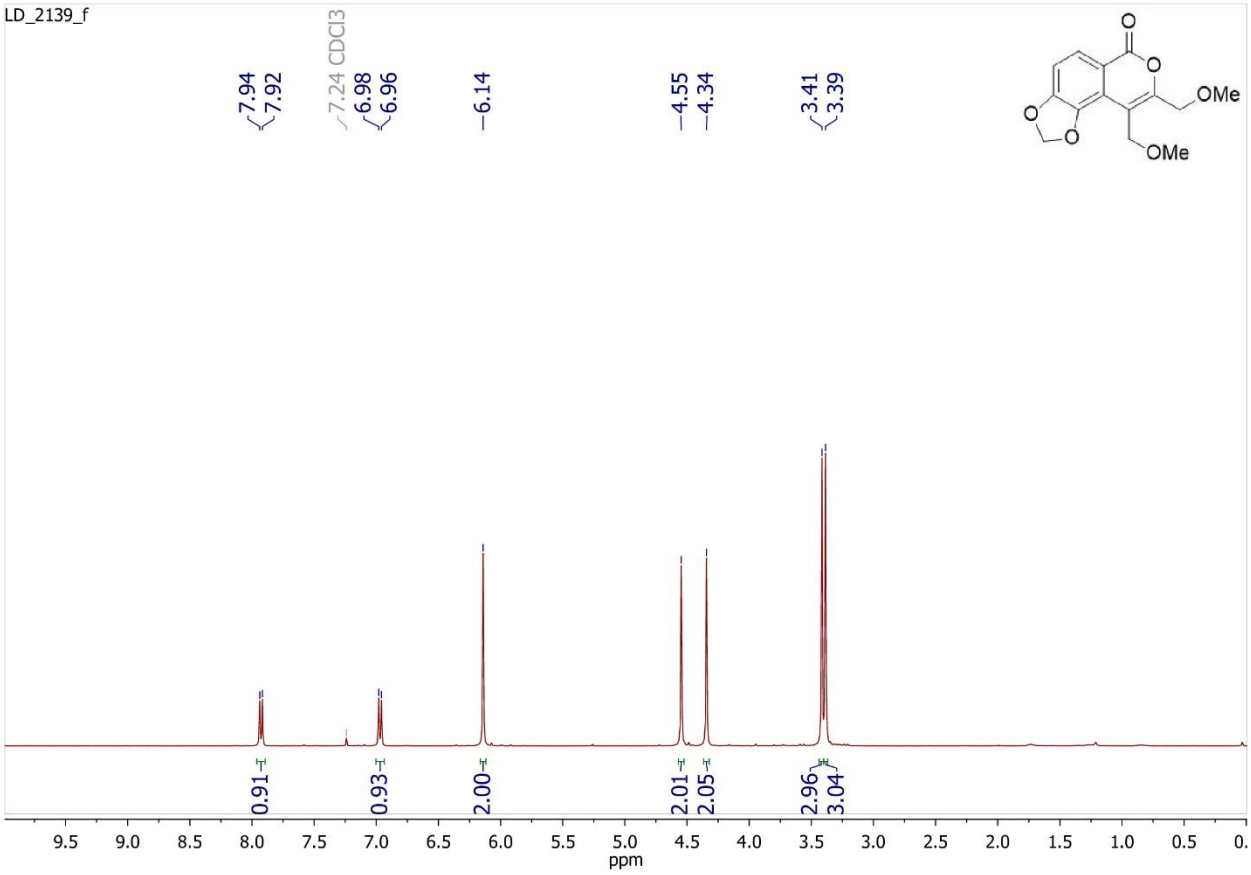
^{1}H NMR (400 MHz) spectrum of **8c** in $CDCl_3$



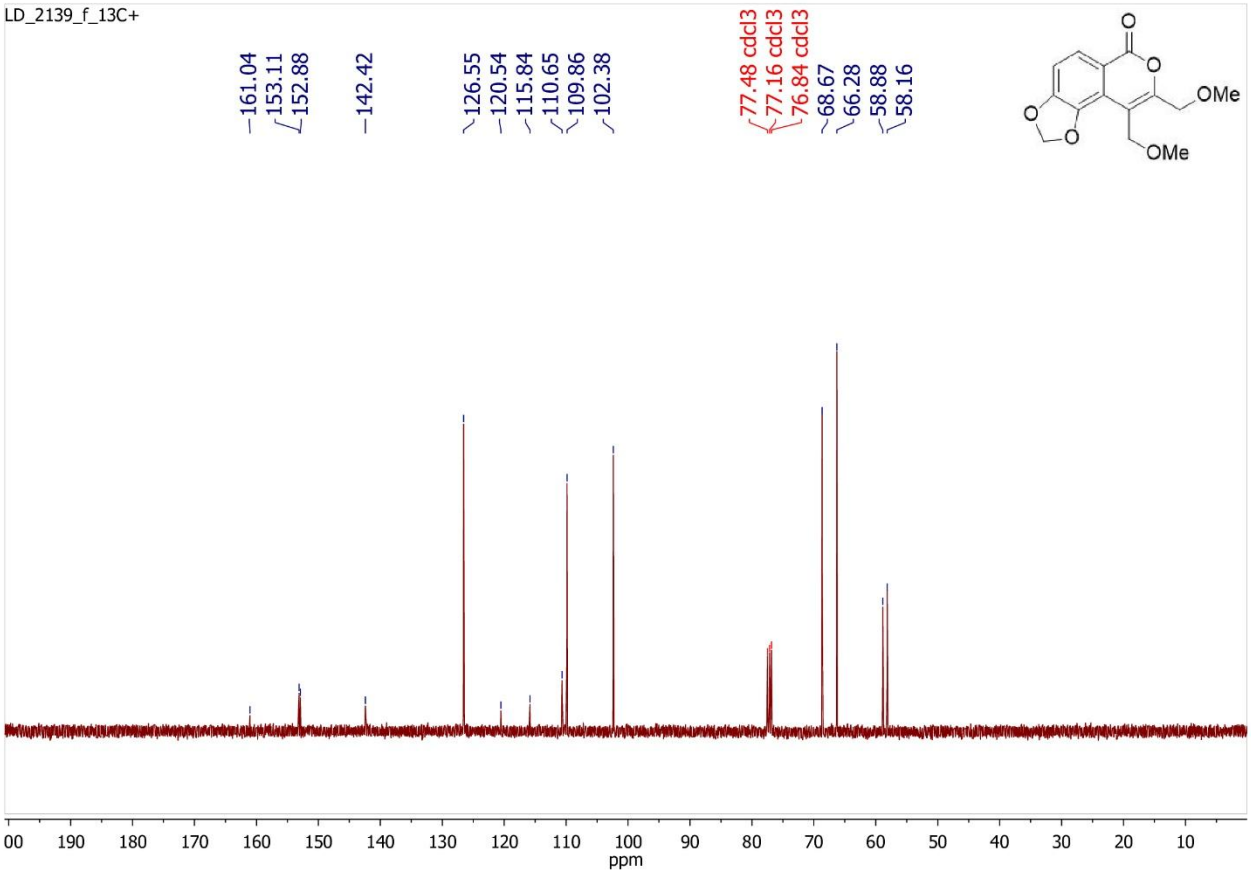
^{13}C{^{1}H} NMR (101 MHz) spectrum of **8c** in $CDCl_3$



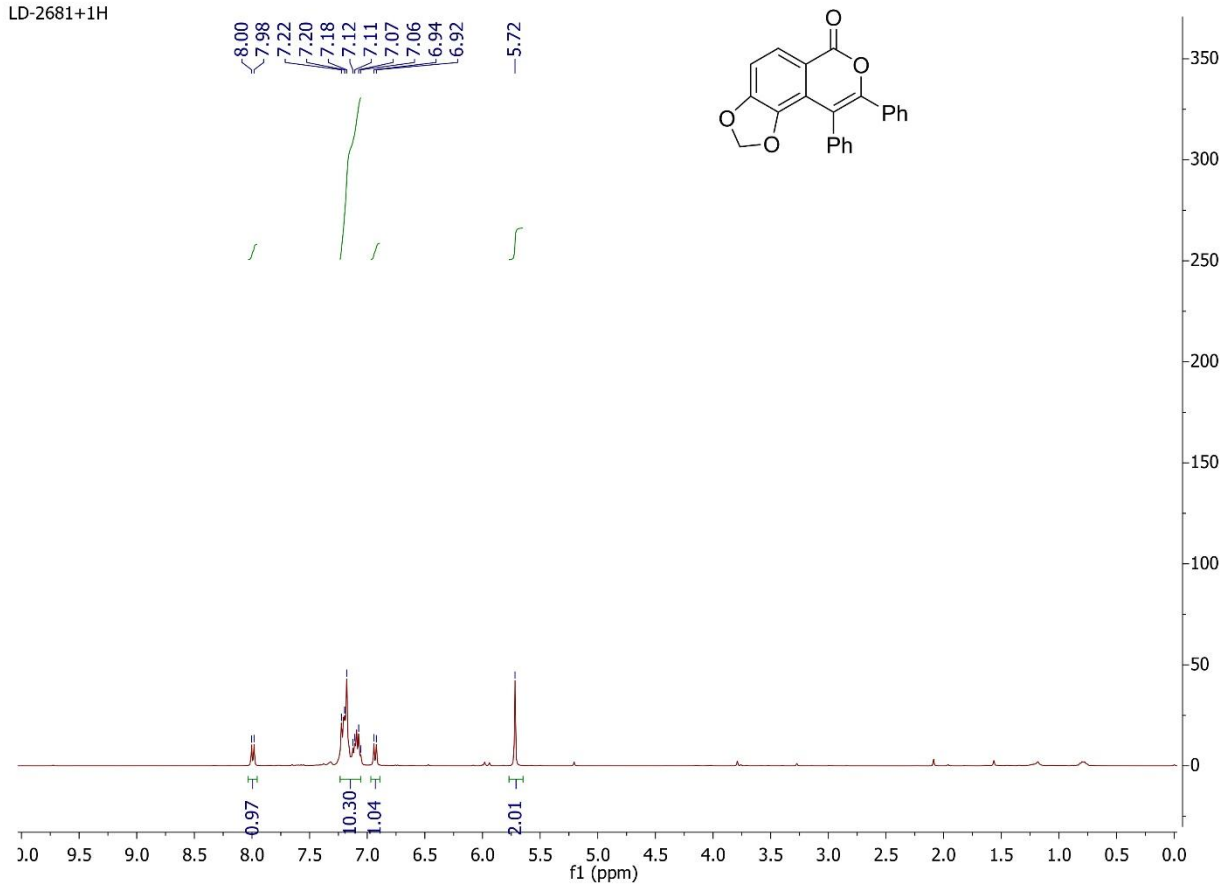
^{1}H NMR (400 MHz) spectrum of **8d** in $CDCl_3$



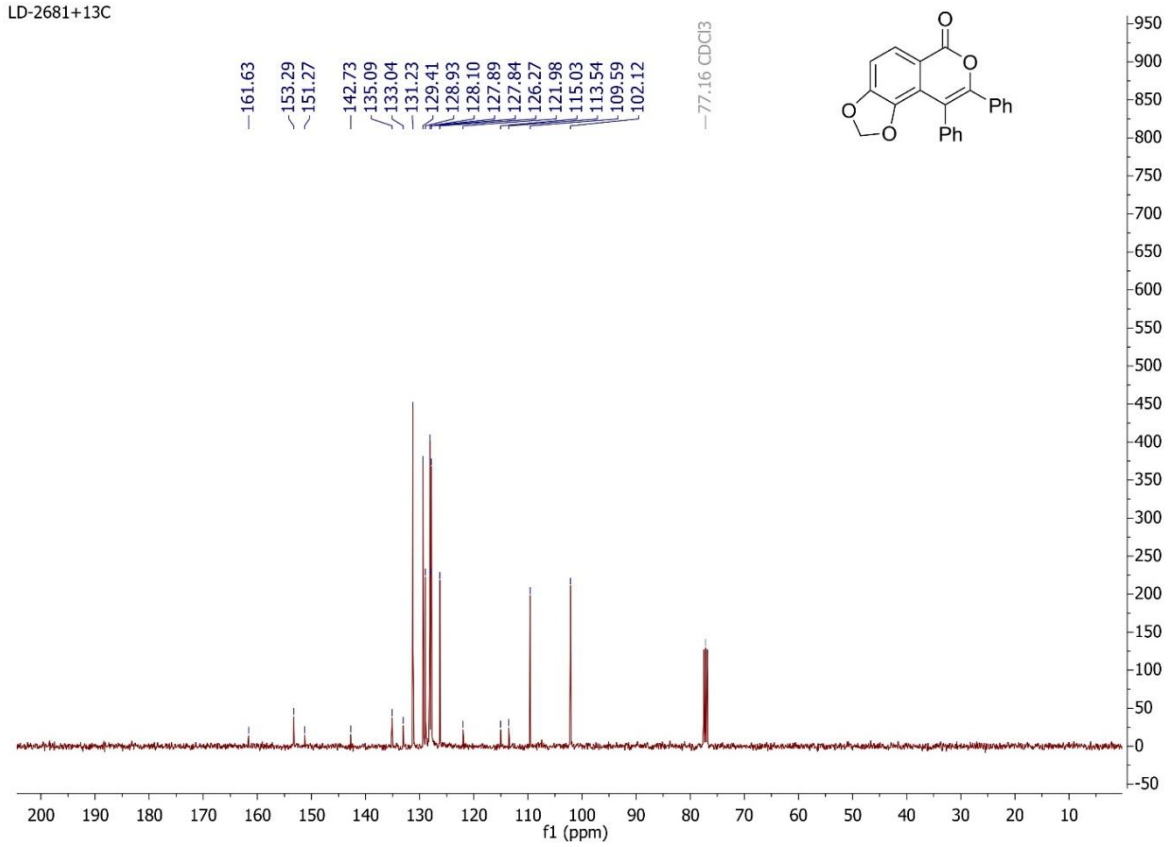
^{13}C{^{1}H} NMR (101 MHz) spectrum of **8d** in $CDCl_3$



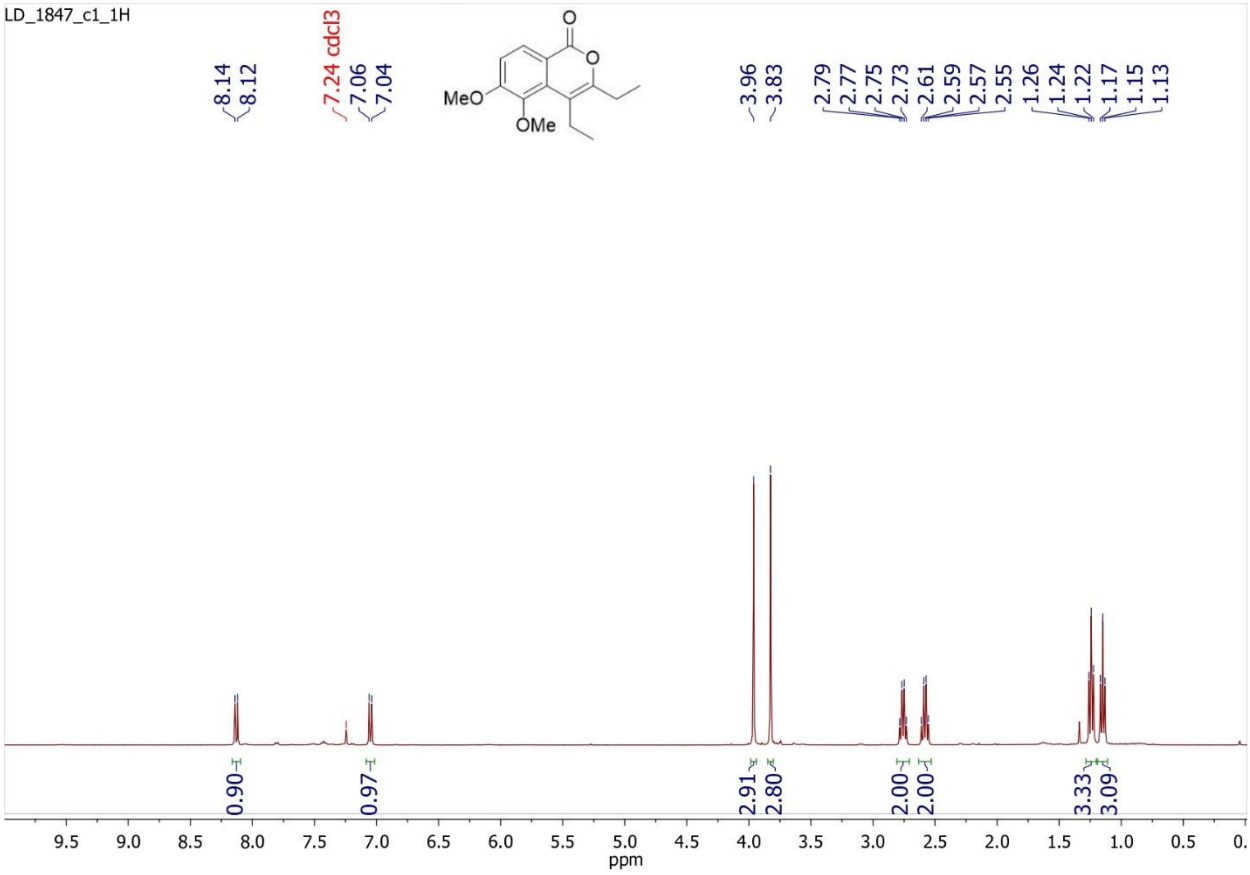
^{1}H NMR (400 MHz) spectrum of **8e** in $CDCl_3$



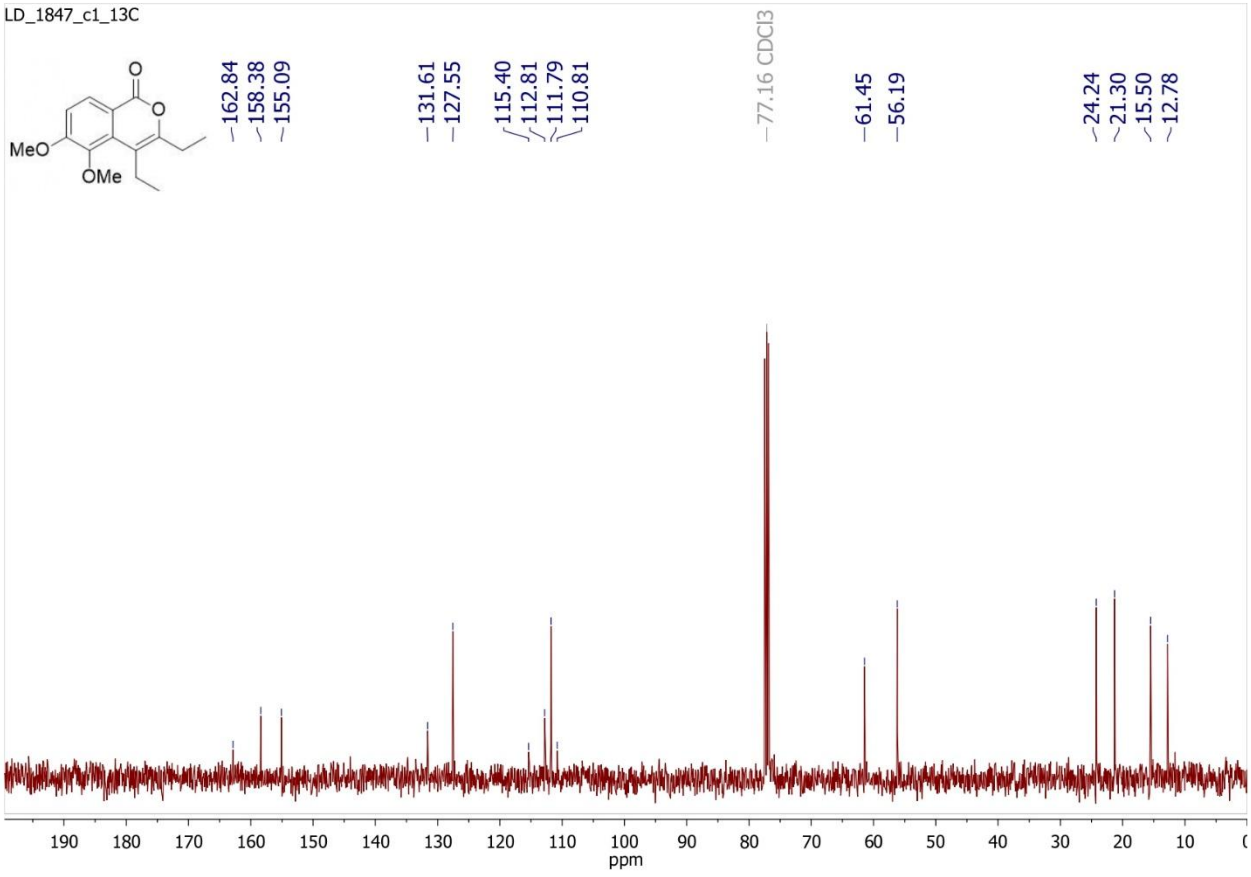
^{13}C{^{1}H} NMR (101 MHz) spectrum of **8e** in $CDCl_3$



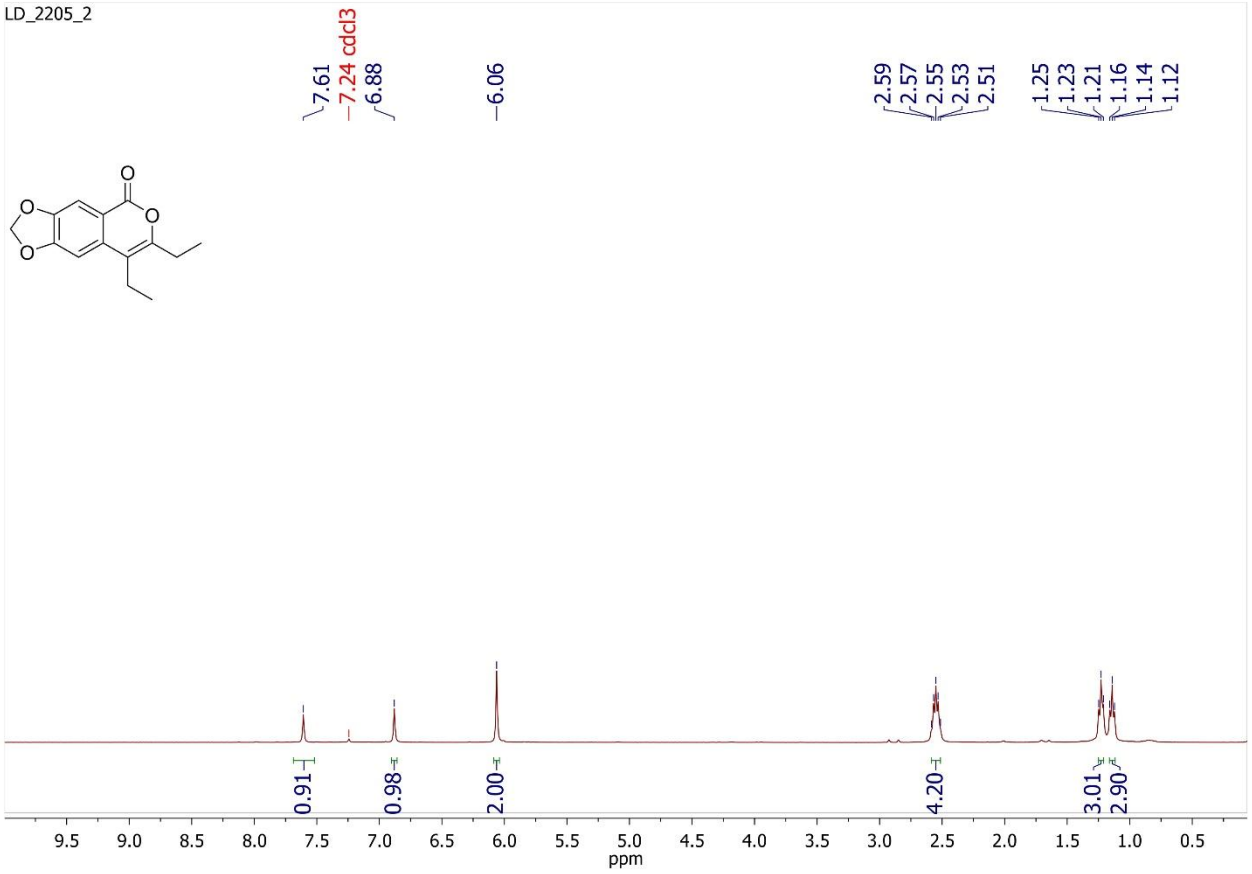
^{1}H NMR (400 MHz) spectrum of **9** in $CDCl_3$



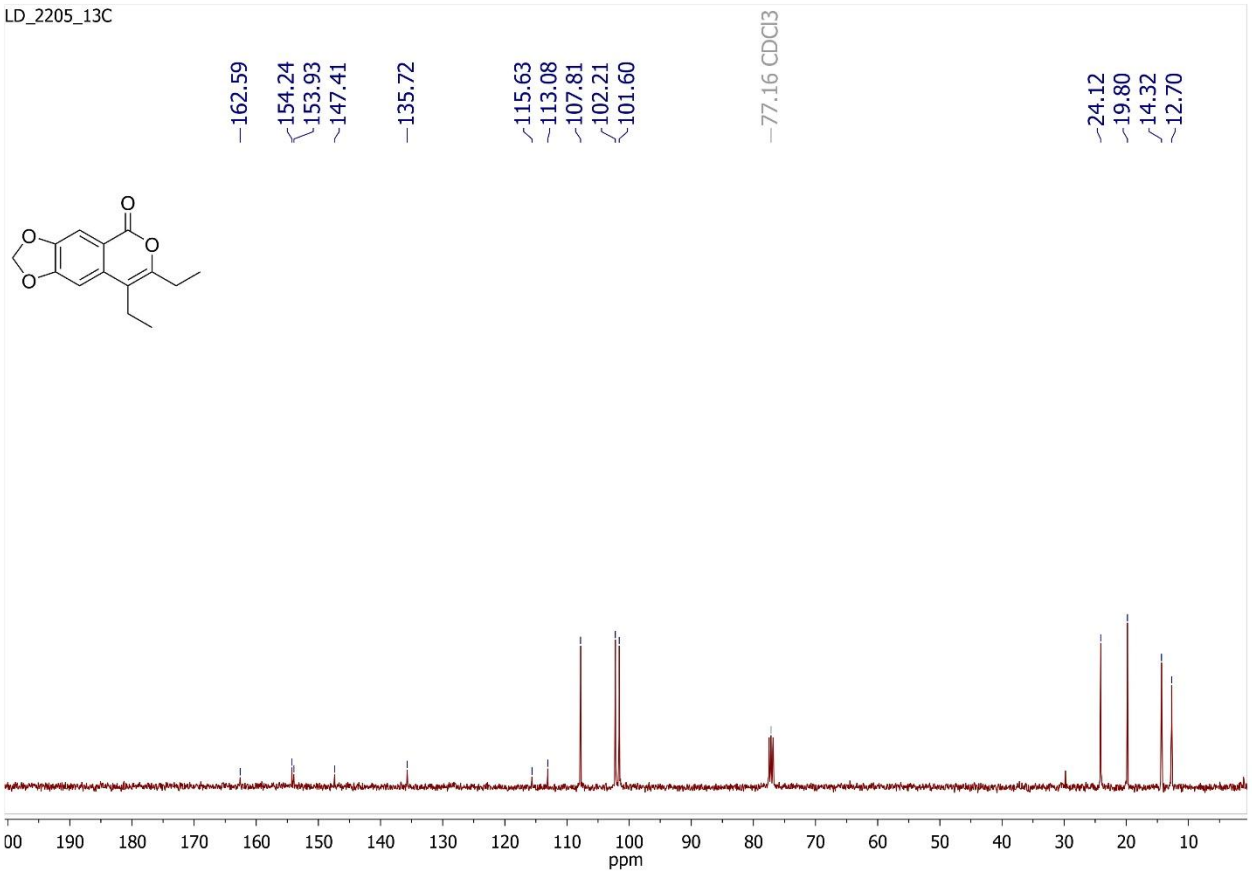
^{13}C{^{1}H} NMR (101 MHz) spectrum of **9** in $CDCl_3$



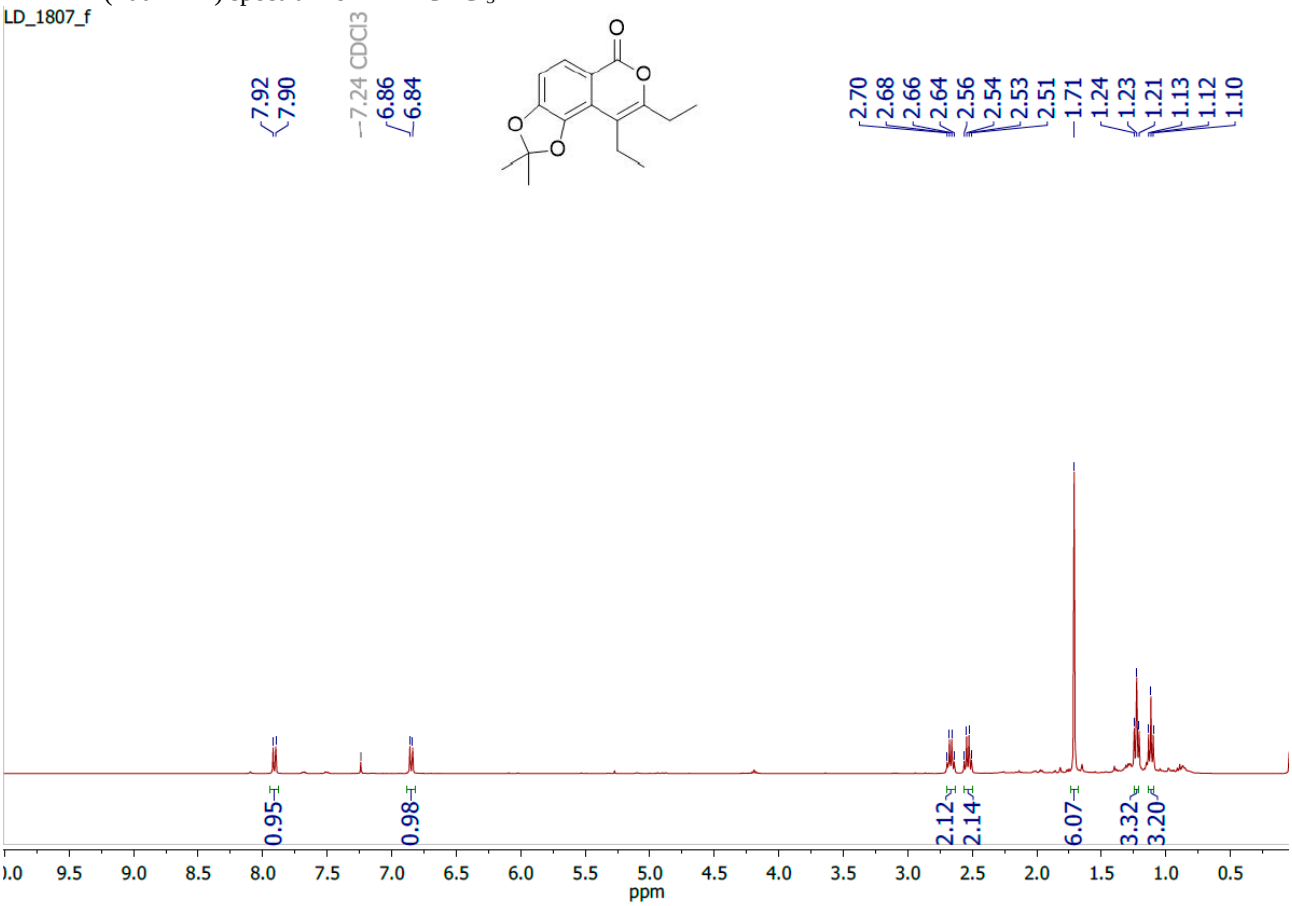
^{1}H NMR (400 MHz) spectrum of **10** in $CDCl_3$



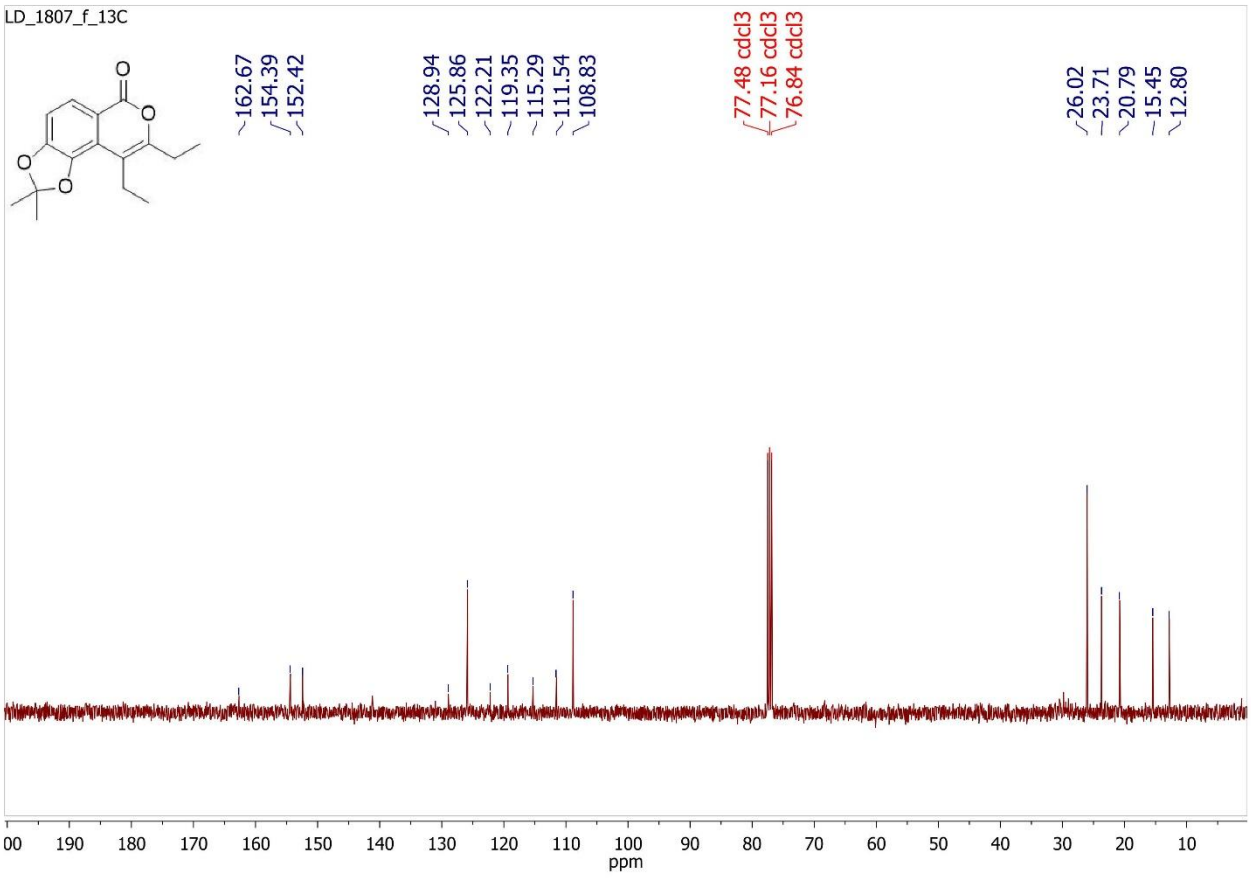
^{13}C{^{1}H} NMR (101 MHz) spectrum of **10** in $CDCl_3$



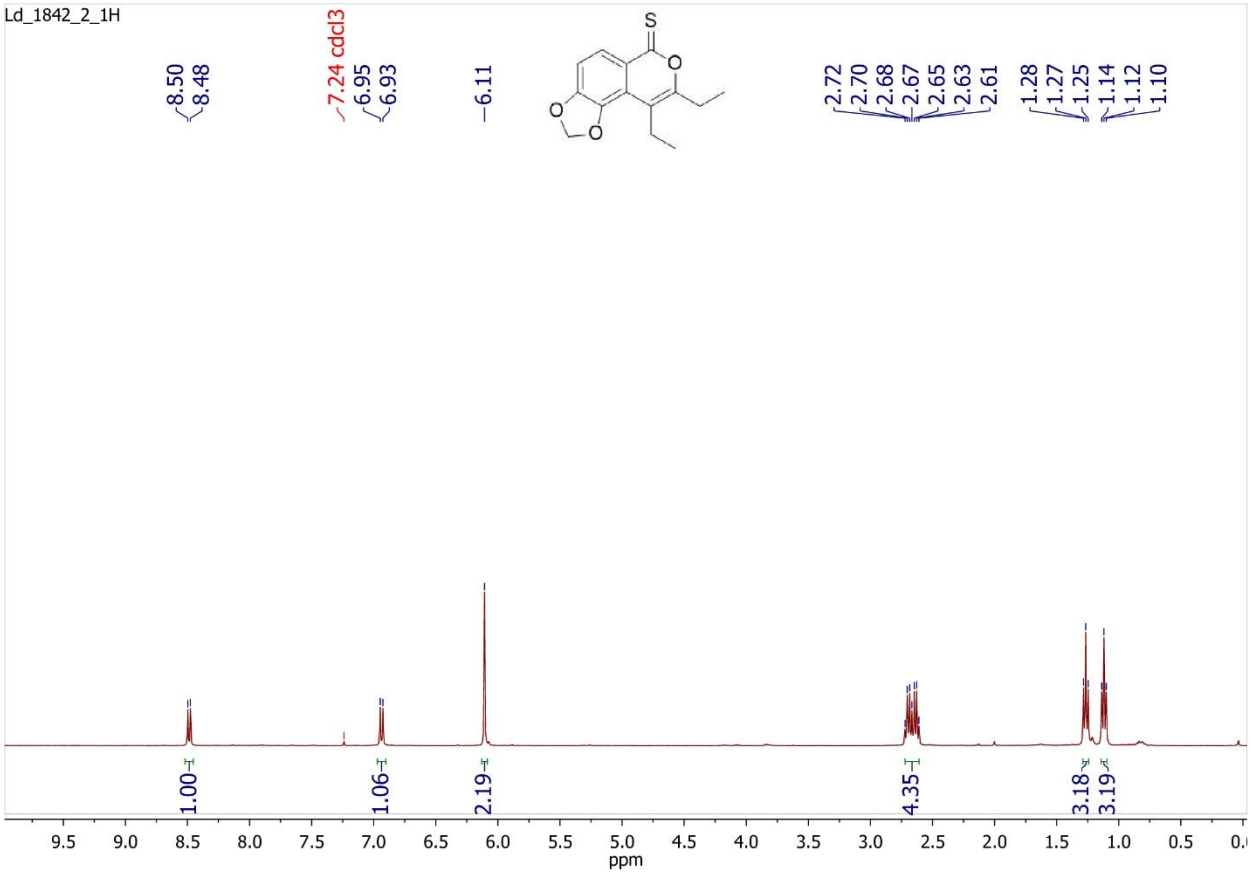
^{1}H NMR (400 MHz) spectrum of **11** in $CDCl_3$



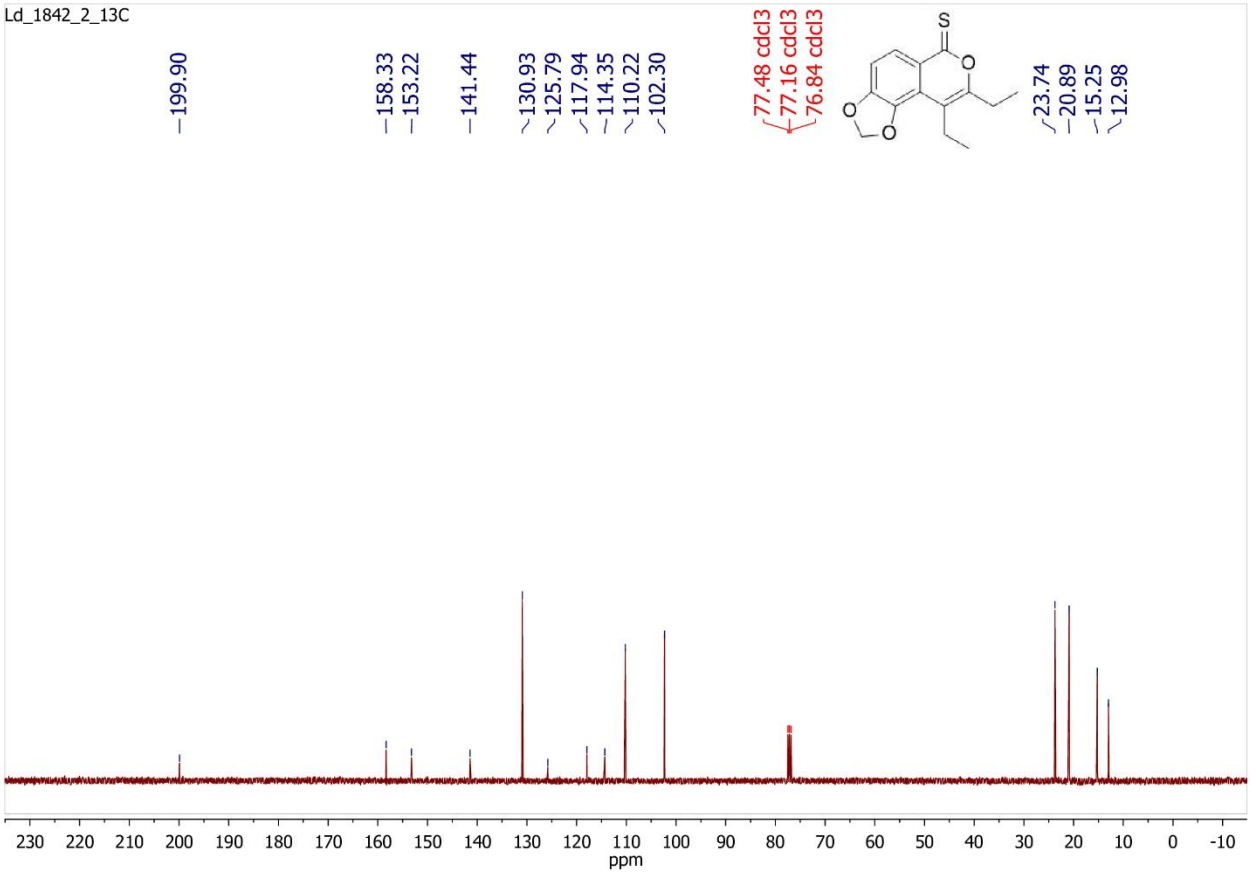
^{13}C{^{1}H} NMR (101 MHz) spectrum of **11** in $CDCl_3$



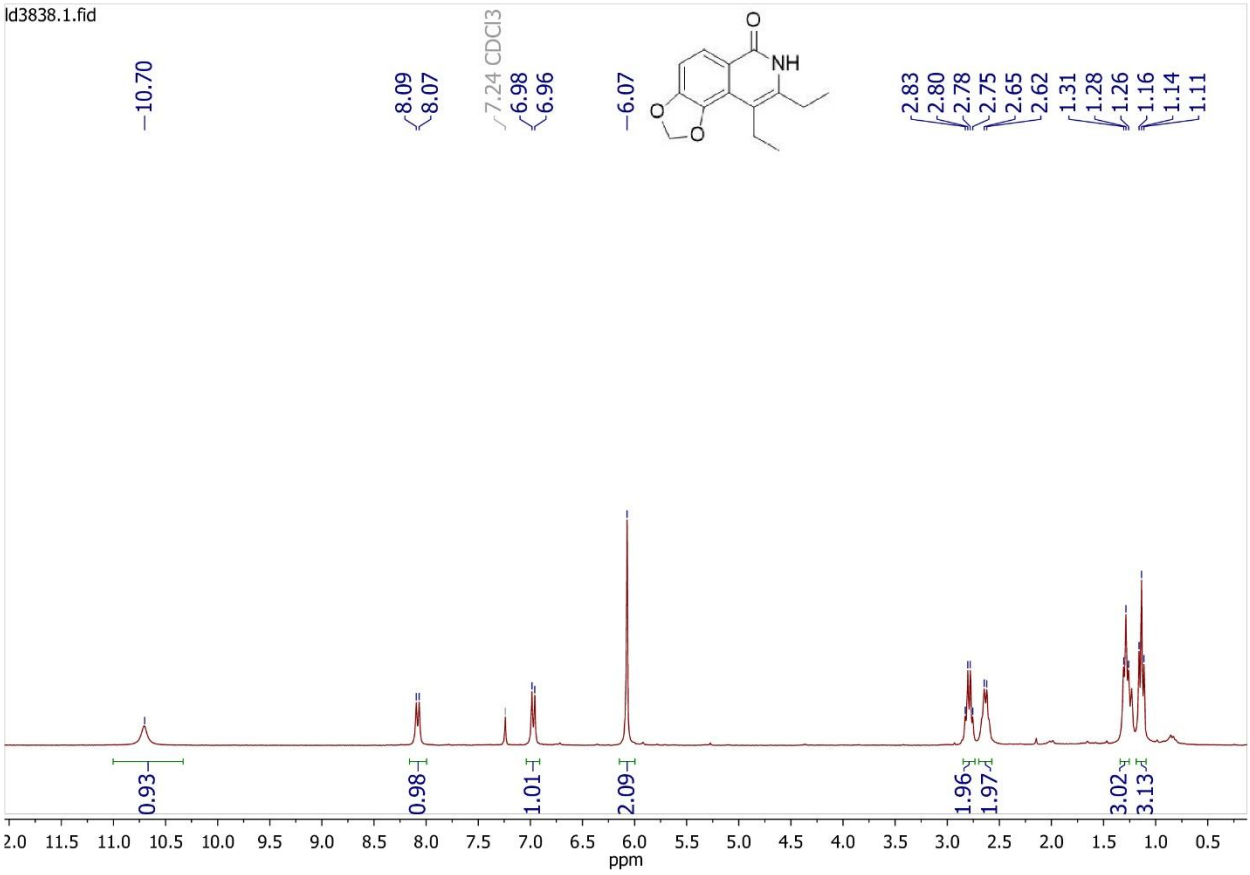
^{1}H NMR (400 MHz) spectrum of **12** in $CDCl_3$



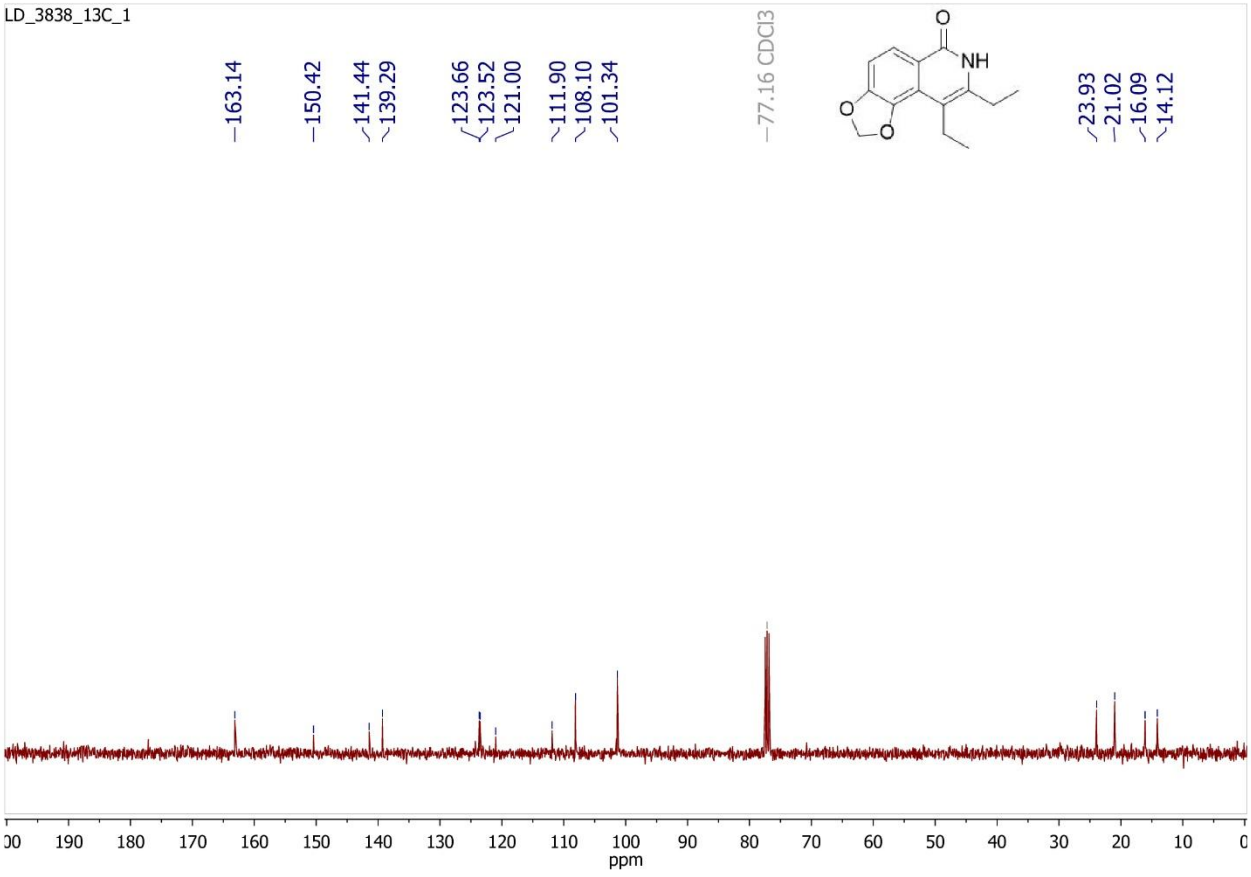
^{13}C{^{1}H} NMR (101 MHz) spectrum of **12** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **13** in $CDCl_3$



^{13}C{^{1}H} NMR (101 MHz) spectrum of **13** in $CDCl_3$



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