Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 342–344

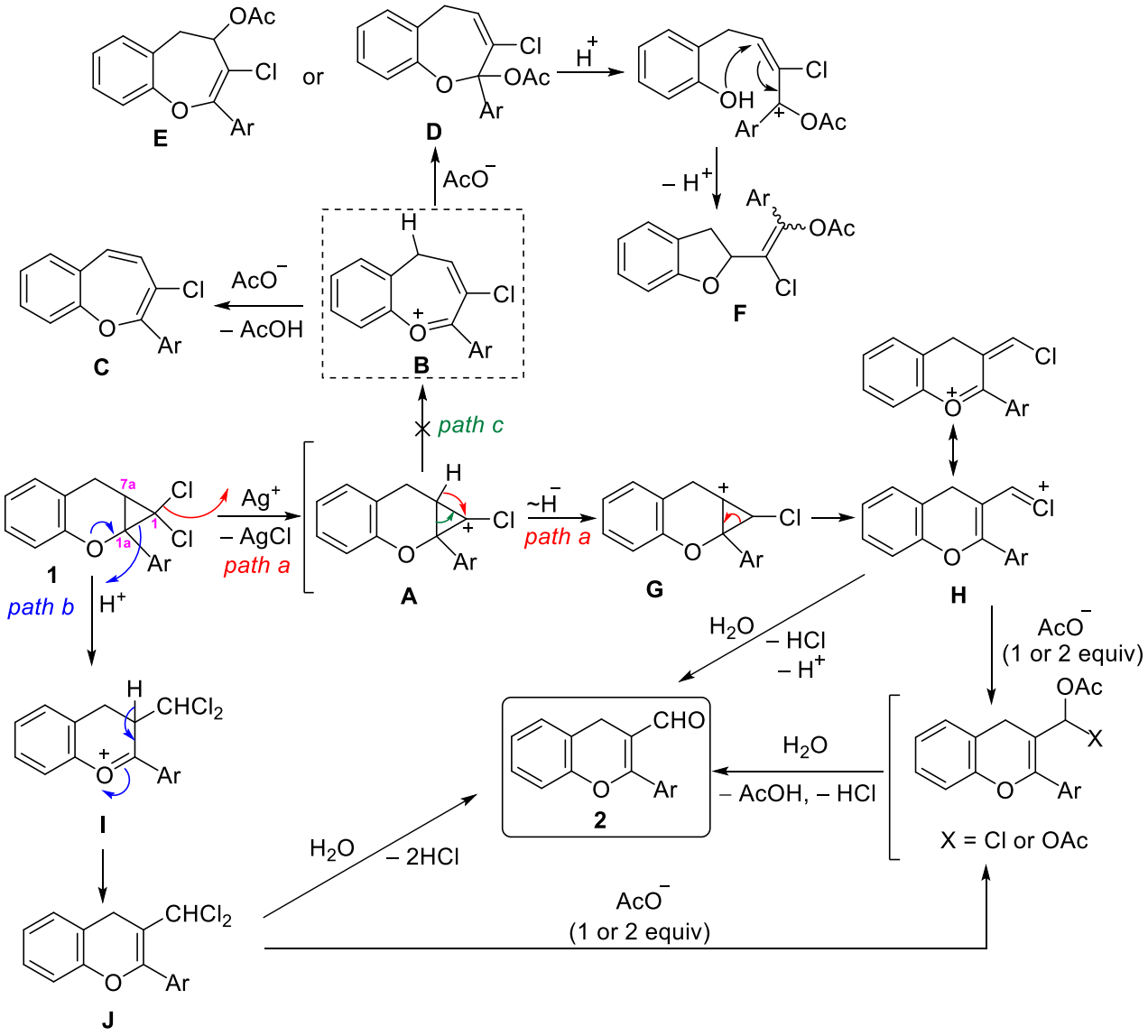
Synthesis of 4*H*-chromene-3-carbaldehydes *via* ring-opening of *gem*-dichlorocyclopropane-fused 4*H*-chromenes

Irina A. Semenova and Vitaly A. Osyanin

Discussion of the reaction mechanism

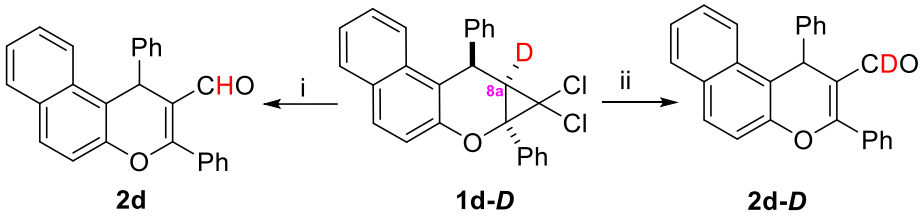
The mechanism of the discovered transformation of *gem*-dichlorocyclopropane-fused 4*H*-chromenes into 4*H*-chromene-3-carbaldehydes is currently under discussion. As a role, in the presence of halophilic Ag^I ions, 7,7-dichloro-2-oxabicyclo[4.1.0]heptanes initially undergo elimination of one chlorine atom (or another halogen) to form a cyclopropyl cation **A**, which, as a result of 2π disrotatory electrocyclic opening accompanied by expansion of the six-membered ring to a seven-membered ring, is transformed into an oxonium-stabilized allylic intermediate **B** of the oxepine type (*path c*) (Scheme S1). The latter can potentially be stabilized into oxepine derivatives **C–E** either by proton elimination under the action of a base or by the addition of a nucleophile. In this case, product **D** can undergo acid-promoted recyclization with ring contraction to a five-membered ring (compound **F**). However, in the case of 1,1-dichloro-1,1a,7,7a-tetrahydrocyclopropa[*b*]chromenes **1**, the formation of such products is not observed. It could be assumed that aldehyde **2** is also formed from cation **A**, which, as a result of hydride ion migration and electrocyclic opening, is converted into a resonance-stabilized cation **H** (*path a*). Subsequent hydrolysis by traces of water present in acetic acid or in the course of workup of the reaction mixture would yield aldehyde **2**.

Another possible explanation for the formation of aldehyde **2** could involve an initial opening of the cyclopropane ring at the C(1)–C(1a) bond, initiated by electrophilic attack by a proton or silver ions (*path b*).[S1] Although halocyclopropanes are generally resistant to acidic cleavage, stabilization of the positive charge by the heteroatom and the aryl substituent at the α-position to the cyclopropane ring may be an energetically more favorable process than concerted or non-concerted elimination of the halide ion. Subsequent elimination of a proton from intermediate **I** yields the dichloromethyl derivative of the allyl type **J**, which is further transformed to aldehyde **2** (Scheme S1).



Scheme S1

However, the proposed mechanisms for the formation of aldehydes **2** are not consistent with experimental data for the rearrangement of 8,8-dichloro-7a,9-diphenyl-7a,8,8a,9-tetrahydrobenzo[*f*]cyclopropa[*b*]chromene **1d-*D*** deuterated at the position 8a into aldehyde **2d-*D*** (Scheme S2).

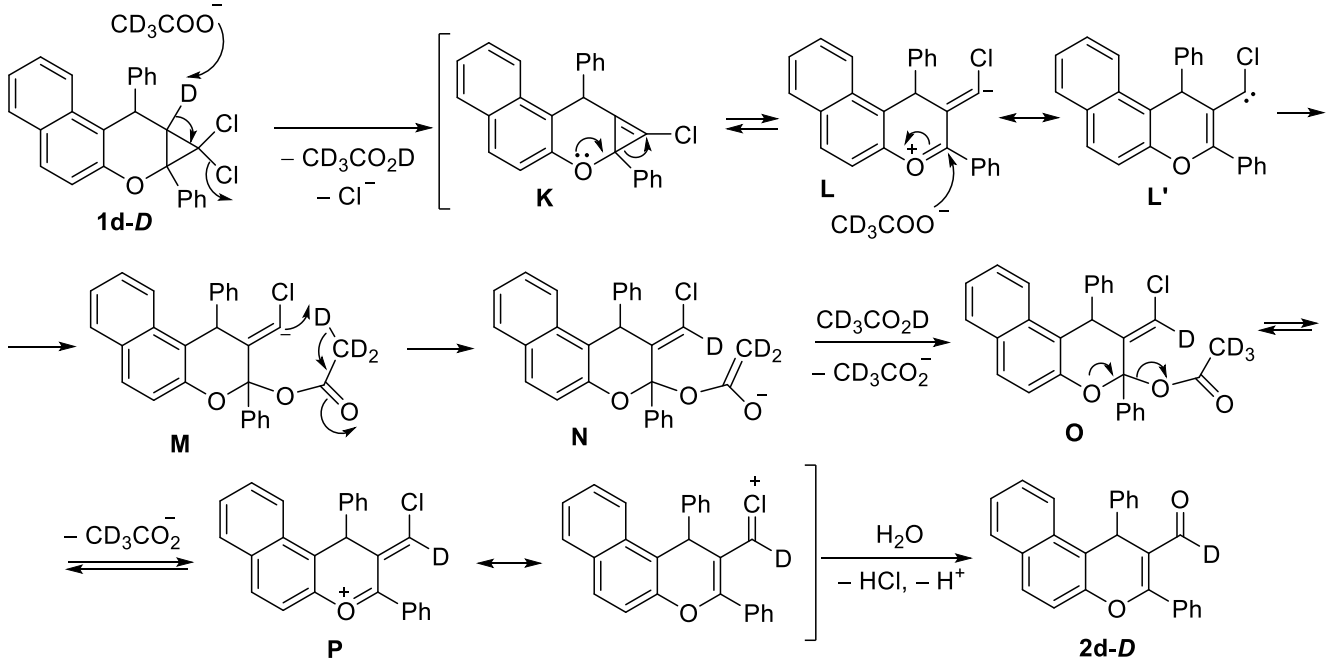


Scheme S2 *Reagents and conditions*: i, AcOAg (2 equiv.), AcOD or AcOH, Δ, 4 h; ii, CD_3CO_2Ag (2 equiv.), CD_3CO_2D, Δ, 4 h.

Since deuterium is not retained in the aldehyde during the rearrangement in AcOH or AcOD, this rules out *path a*. 'Protonation' of the starting tetrahydrocyclopropa[*b*]chromene **1** with AcOD (*path b*) should also lead to monodeuterated product **2**, but this does not occur. Therefore, during the reaction, deuterium is eliminated from the β-carbon of the dihydropyran ring and subsequently reincorporated

during the rearrangement promoted by CD_3CO_2Ag in CD_3CO_3D, with the deuterium source being the methyl group of perdeuterated acetic acid or its salt.

The following reaction mechanism is more consistent with these experimental facts. It can be proposed that the reaction initially proceeds *via* a base-promoted elimination of DCl, affording chlorocyclopropene **K**, which then ring-opens to generate a zwitterionic intermediate **L** – a structure that may also be represented as carbene **L'**. Subsequent nucleophilic attack by acetate anion at the α-carbon of the pyran ring, followed by an intramolecular deuterium transfer, leads to enolate **N**. This enolate, upon protonation, elimination of $CD_3CO_2^-$, and hydrolysis, is transformed into aldehyde **2d-*D*** (Scheme S3). The formation of cyclopropene-type intermediates such as **K** has previously been postulated in several base-promoted conversions of *gem*-dihalogenated fused cyclopropanes.[S2–S5]

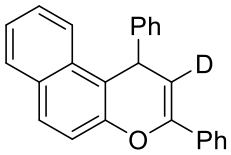


Scheme S3

Experimental

Solvents were purified and dried by standard procedures before use. ^{1}H and ^{13}C NMR spectra (400 and 100 MHz, respectively), as well as DEPT-135 spectra were acquired on a JEOL JNM-ECX400 spectrometer in $CDCl_3$ or DMSO-d_6 using residual solvent signals (DMSO-d_6: 2.50 ppm for ^{1}H nuclei, 39.5 ppm for ^{13}C nuclei; $CDCl_3$: 7.26 ppm for ^{1}H nuclei, 77.2 ppm for ^{13}C nuclei) as internal standards. Chemical shifts are reported in δ unit-parts per million (ppm). Splitting patterns are designated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet; m = multiplet. Elemental analysis was performed on a Euro Vector EA-3000 CHNS-analyzer. Melting points were determined by the capillary method on an SRS OptiMelt MPA100 apparatus. Reaction progress and purity of the obtained compounds were monitored by thin-layer chromatography (TLC) on Merck Silica gel 60 F_{254} plates, eluted with $CHCl_3$, and visualized under UV light and iodine vapor. The starting dichlorotetrahydro(benzo)cyclopropa[*b*]chromenes **1a**–**c**, **e**–**g**, **i** were prepared according to a literature procedure.[S6]

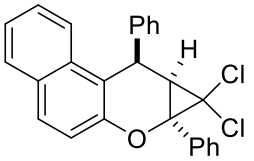
1,3-Diphenyl-1*H*-benzo[*f*]chromene-2-*d*.



A solution of 670 mg (2 mmol) of 1,3-diphenyl-1*H*-benzo[*f*]chromene in 25 mL of CH_3CO_2D was heated under reflux for 10 h. The solvent was then removed under reduced pressure. This procedure was repeated twice more using fresh portions of CH_3CO_2D (25 mL each time). As a result, a monodeuterated product was obtained with a purity of approximately 95% (as determined by ^{1}H NMR spectroscopy). Yield 670 mg (99%), colorless crystals, mp 201–202 ºC. IR spectrum, ν, cm^{-1}: 3059, 3021, 2928, 1667, 1620, 1597, 1512, 1493, 1450, 1396, 1227, 1099, 1018, 841, 822, 752, 698. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 5.44 (1H, s, H-1); 7.10 (1H, t, *J* = 6.8, H Ar); 7.20–7.42 (9H, m, H Ar); 7.49 (1H, d, *J* = 8.9, H Ar); 7.74–7.92 (5H, m, H Ar). Found, %: C 89.49; H 5.69. $C_{25}H_{17}DO$. Calculated, %: C 89.52; H 5.71.

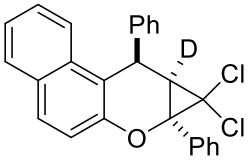
Synthesis of cyclopropa[*b*]chromenes 1d, 1d-*D*, 1h (general procedure). Aqueous NaOH (50%, 2 mL) and TEBA (4 mg) were added to a solution of 1,3-diphenyl-1*H*-benzo[*f*]chromene (335 mg, 1 mmol), 1,3-diphenyl-1*H*-benzo[*f*]chromene-2-*d* (335 mg, 1 mmol) or 2-(4-methoxyphenyl)-4*H*-chromene (240 mg, 1 mmol) in $CHCl_3$ (5 mL). The resulting mixture was vigorously stirred at room temperature for 2–4 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2, the combined organic phases were washed with H_2O until neutral, dried with Na_2SO_4, and evaporated to dryness. The residue was purified by recrystallization from EtOH.

(7a*R,8a*R**,9*R**)-8,8-Dichloro-7a,9-diphenyl-7a,8,8a,9-tetrahydrobenzo[*f*]cyclopropa[*b*]chromene (1d).**



Reaction time 4 h. Yield 365 mg (87%), colorless crystals, mp 233–234 ºC. IR spectrum, ν, cm^{-1}: 1625, 1600, 1513, 1482, 1464, 1405, 1225, 1170, 1140, 1128, 1085, 980, 933, 878, 811, 747, 700. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.76 (1H, s, H-8a); 5.07 (1H, s, H-9); 7.18 (1H, d, *J* = 8.9, H Ar); 7.21–7.35 (7H, m, H Ar); 7.39–7.48 (5H, m, H Ar); 7.67–7.74 (3H, m, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.8 (9-CH); 39.1 (8a-CH); 63.8 (CCl_2); 66.2 (C-7a); 112.0 (C); 118.2 (CH); 123.1 (CH); 123.7 (CH); 126.7 (CH); 127.2 (CH); 127.7 (2CH); 128.6 (CH); 128.7 (2CH); 128.8 (2CH); 129.3 (CH); 129.4 (2CH); 129.5 (CH); 130.1 (C); 131.6 (C); 135.2 (C); 144.7 (C); 149.7 (C-6a). Found, %: C 74.76; H 4.30. $C_{26}H_{18}Cl_2O$. Calculated, %: C 74.83; H 4.35.

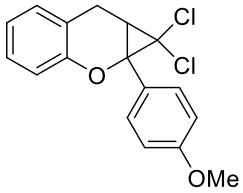
(7a*R,8a*R**,9*R**)-8,8-Dichloro-7a,9-diphenyl-7a,8,8a,9-tetrahydrobenzo[*f*]cyclopropa[*b*]chromene-8a-*d* (1d-*D*)**



Reaction time 4 h. Yield 360 mg (86%), colorless crystals, mp 232–234 ºC. IR spectrum, ν, cm^{-1}: 1625, 1601, 1511, 1483, 1464, 1404, 1225, 1171, 1139, 1128, 1085, 978, 932, 878, 810, 746, 701. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 5.07 (1H, s, H-9); 7.18 (1H, d, *J* = 8.9, H Ar); 7.21–7.35 (7H, m, H Ar); 7.39–7.48 (5H, m, H Ar); 7.67–7.74 (3H, m, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*,

Hz): 35.8 (9-CH); 38.7 (t, $^1J_{CD}$ = 25.4, 8a-CH); 63.8 (CCl_2); 66.2 (C-7a); 112.0 (C); 118.2 (CH); 123.1 (CH); 123.7 (CH); 126.7 (CH); 127.2 (CH); 127.7 (2CH); 128.6 (CH); 128.7 (2CH); 128.8 (2CH); 129.3 (CH); 129.4 (2CH); 129.5 (CH); 130.1 (C); 131.6 (C); 135.2 (C); 144.7 (C); 149.7 (C-6a). Found, %: C 74.60; H 4.55. $C_{26}H_{17}DCl_2O$. Calculated, %: C 74.65; H 4.58.

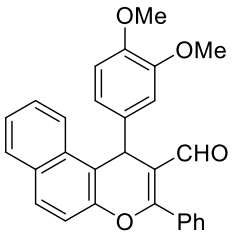
1,1-Dichloro-1a-(4-methoxyphenyl)-1,1a,7,7a-tetrahydrocyclopropa[*b*]chromene (1h).



Reaction time 2 h. Yield 225 mg (70%), colorless crystals, mp 149–150 ºC. IR spectrum, ν, cm^{-1}: 1611, 1583, 1517, 1480, 1469, 1449, 1415, 1339, 1250, 1239, 1218, 1112, 1020, 885, 861, 840, 755. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.57 (1H, dd, *J* = 9.2, *J* = 2.1, H-7a); 3.08 (1H, d, *J* = 17.6, CH_2); 3.34 (1H, dd, *J* = 17.6, *J* = 9.2, CH_2); 3.82 (3H, s, OCH_3); 6.88–6.94 (4H, m, H Ar); 7.07–7.13 (2H, m, H Ar); 7.47 (2H, d, *J* = 8.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.0 (CH_2); 29.6 (7a-CH); 55.4 (OCH_3); 65.8 (C-1a); 67.4 (CCl_2); 113.8 (2CH); 117.3 (CH); 119.2 (C); 121.9 (CH); 127.5 (C); 127.7 (CH); 128.8 (CH); 129.6 (2CH); 152.1 (C–O); 160.0 (C–O). Found, %: C 63.61; H 4.34. $C_{17}H_{14}Cl_2O_2$. Calculated, %: C 63.57; H 4.39.

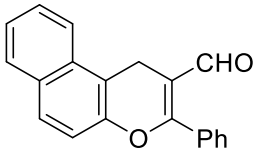
Synthesis of chromenecarbaldehydes 2a–i (general procedure). A solution of 1 mmol of dichlorotetrahydro(benzo)cyclopropa[*b*]chromene **1a–i** in 7 mL of AcOH was treated with 334 mg (2 mmol) of AgOAc and refluxed for 4 h with stirring. The hot reaction mixture was filtered, and the filtrate was poured into 15 mL of cold water. The precipitated solid was collected by filtration, washed with water, and purified by column chromatography (silica gel, eluent $CHCl_3$). After removal of the solvent, the residue was suspended in 3 mL of MeOH, heated to reflux, cooled to –30 °C, and kept at this temperature for 1 h. The precipitate was filtered off, washed with ice-cold methanol, and dried in air.

1-(3,4-Dimethoxyphenyl)-3-phenyl-1*H*-benzo[*f*]chromene-2-carbaldehyde (2a).



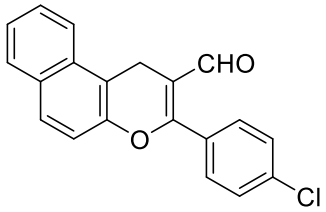
Yield 320 mg (76%), yellow crystals, mp 138−139 °C. IR spectrum, ν, cm^{-1}: 1655, 1632, 1616, 1589, 1512, 1462, 1450, 1435, 1400, 1339, 1269, 1254, 1227, 1196, 1138, 1115, 1084, 1069, 1030, 1011, 937, 914, 887, 860, 818, 806. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.76 (3H, s, CH_3O); 3.81 (3H, s, CH_3O); 5.81 (1H, s, H-1); 6.67 (1H, d, *J* = 8.5, H Ar); 6.78 (1H, dd, *J* = 8.2, *J* = 2.0, H Ar); 7.05 (1H, d, *J* = 2.0, H Ar); 7.40−7.58 (6H, m, H Ar); 7.62−7.65 (2H, m, H Ar); 7.83 (2H, d, *J* = 8.7, H Ar); 8.02 (1H, d, *J* = 8.3, H Ar); 9.64 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 34.5 (1-CH); 55.8 (CH_3O); 55.9 (CH_3O); 111.2 (CH); 111.7 (CH); 117.1 (CH); 117.7 (C); 118.1 (C); 120.4 (CH); 123.7 (CH); 125.3 (CH); 127.3 (CH); 128.6 (CH); 128.7 (2CH); 129.1 (CH); 130.5 (2CH); 131.2 (C); 131.4 (C); 131.5 (CH); 131.8 (C); 137.3 (C); 147.7 (C); 148.4 (C); 148.9 (C); 166.4 (C); 190.8 (CHO). Found, %: C 79.58; H 5.19. $C_{28}H_{22}O_4$. Calculated, %: C 79.60; H 5.25.

3-Phenyl-1*H*-benzo[*f*]chromene-2-carbaldehyde (2b).



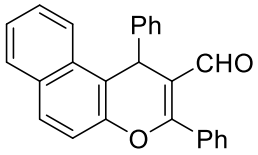
Yield 230 mg (80%), yellow crystals, mp 185−186 °C. IR spectrum, ν, cm^{-1}: 1639, 1616, 1593, 1574, 1516, 1493, 1466, 1450, 1431, 1400, 1362, 1339, 1265, 1238, 1200, 1169, 1126, 1069, 1007, 957, 945, 914, 860, 806. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.97 (2H, s, CH_2); 7.26 (1H, d, *J* = 8.9, H Ar); 7.47–7.68 (7H, m, H Ar); 7.75 (1H, d, *J* = 8.9, H Ar); 7.85 (1H, d, *J* = 8.0, H Ar); 7.96 (1H, d, *J* = 8.5, H Ar); 9.74 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.9 (CH_2); 113.06 (C); 113.12 (C); 117.2 (CH); 123.2 (CH); 125.3 (CH); 127.2 (CH); 128.46 (CH); 128.55 (CH); 128.63 (2CH); 130.1 (2CH); 131.07 (CH); 131.10 (C); 131.6 (C); 131.9 (C); 147.5 (C); 167.0 (C); 191.9 (CHO). Found, %: C 83.81; H 5.00. $C_{20}H_{14}O_2$. Calculated, %: C 83.90; H 4.93.

3-(4-Chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbaldehyde (2c).



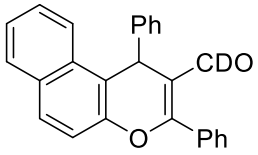
Yield 230 mg (72%), pale yellow crystals, mp 169−170 °C. IR spectrum, ν, cm^{-1}: 1639, 1624, 1589, 1512, 1489, 1462, 1435, 1400, 1366, 1339, 1258, 1234, 1207, 1173, 1126, 1107, 1088, 1042, 1003, 957, 941, 868, 837, 806. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.96 (2H, s, CH_2); 7.24 (1H, d, *J* = 8.9, H Ar); 7.48–7.52 (3H, m, H Ar); 7.57–7.64 (3H, m, H Ar); 7.75 (1H, d, *J* = 8.9, H Ar); 7.85 (1H, d, *J* = 8.0, H Ar); 7.94 (1H, d, *J* = 8.5, H Ar); 9.72 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.9 (CH_2); 112.9 (C); 113.5 (C); 117.1 (CH); 123.2 (CH); 125.4 (CH); 127.3 (CH); 128.5 (CH); 128.7 (CH); 129.0 (2CH); 130.0 (C); 131.1 (C); 131.4 (2CH); 131.8 (C); 137.4 (C); 147.3 (C); 165.7 (C); 191.3 (CHO). Found, %: C 74.81; H 4.13. $C_{20}H_{13}ClO_2$. Calculated, %: C 74.89; H 4.09.

1,3-Diphenyl-1*H*-benzo[*f*]chromene-2-carbaldehyde (2d).



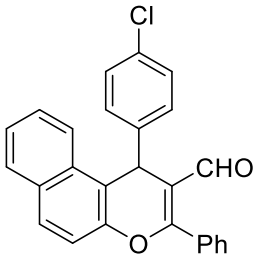
Yield 272 mg (75%), colorless crystals, mp 232−234 °C. IR spectrum, ν, cm^{-1}: 1655, 1612, 1589, 1520, 1504, 1393, 1350, 1331, 1258, 1231, 1200, 1184, 1157, 1142, 1126, 1072, 1038, 1011, 945, 930, 914, 883, 864, 814, 802. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 5.87 (1H, s, H-1); 7.09−7.13 (1H, m, H Ar); 7.20−7.24 (2H, m, H Ar); 7.39−7.43 (3H, m, H Ar); 7.46−7.52 (4H, m, H Ar); 7.54−7.58 (1H, m, H Ar); 7.62−7.65 (2H, m, H Ar); 7.83 (2H, d, *J* = 8.7, H Ar); 8.04 (1H, d, *J* = 8.5, H Ar); 9.64 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.1 (1-CH); 117.1 (CH); 117.7 (C); 118.0 (C); 123.7 (CH); 125.3 (CH); 126.7 (CH); 127.3 (CH); 128.4 (2CH); 128.59 (CH); 128.64 (2CH); 128.67 (2CH); 129.1 (CH); 130.6 (2CH); 131.2 (C); 131.3 (C); 131.5 (CH); 131.8 (C); 144.5 (C); 148.3 (C); 166.5 (C); 190.6 (CHO). Found, %: C 86.08; H 4.96. $C_{26}H_{18}O_2$. Calculated, %: C 86.16; H 5.01.

1,3-Diphenyl-1*H*-benzo[*f*]chromene-2-carbaldehyde-*d* (2d-*D*).



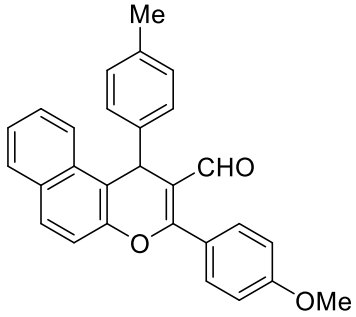
This compound was obtained according to the general procedure from 420 mg (1 mmol) of chromene **1d-*D*** and 340 mg (2 mmol) of CD_3CO_2Ag in 7 mL of CD_3CO_2D. Yield 265 mg (73%), colorless crystals, mp 233−234 °C. IR spectrum, ν, cm^{-1}: 1655, 1612, 1589, 1520, 1504, 1393, 1350, 1331, 1258, 1231, 1200, 1184, 1157, 1142, 1126, 1072, 1038, 1011, 945, 930, 914, 883, 864, 814, 802. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 5.87 (1H, s, H-1); 7.09−7.13 (1H, m, H Ar); 7.20−7.24 (2H, m, H Ar); 7.39−7.43 (3H, m, H Ar); 7.46−7.52 (4H, m, H Ar); 7.54−7.58 (1H, m, H Ar); 7.62−7.65 (2H, m, H Ar); 7.83 (2H, d, *J* = 8.7, H Ar); 8.04 (1H, d, *J* = 8.5, H Ar). Found, %: C 85.89; H 5.24. $C_{26}H_{17}DO_2$. Calculated, %: C 85.93; H 5.27.

1-(4-Chlorophenyl)-3-phenyl-1*H*-benzo[*f*]chromene-2-carbaldehyde (2e).



Yield 293 mg (74%), colorless crystals, mp 174−176 °C. IR spectrum, ν, cm^{-1}: 1651, 1636, 1612, 1585, 1512, 1489, 1462, 1396, 1366, 1354, 1339, 1315, 1292, 1254, 1231, 1204, 1180, 1161, 1123, 1096, 1038, 1011, 891, 841, 826, 810. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 5.84 (1H, s, H-1); 7.18 (2H, d, *J* = 8.5, H Ar); 7.34 (2H, d, *J* = 8.5, H Ar); 7.41−7.59 (6H, m, H Ar); 7.62 (2H, d, *J* = 8.2, H Ar); 7.82−7.85 (2H, m, H Ar); 7.96 (1H, d, *J* = 8.2, H Ar); 9.63 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 34.6 (1-CH); 117.08 (C); 117.13 (CH); 117.5 (C); 123.5 (CH); 125.4 (CH); 127.4 (CH); 128.7 (3CH); 128.8 (2CH); 129.4 (CH); 129.8 (2CH); 130.5 (2CH); 131.0 (C); 131.1 (C); 131.6 (CH); 131.8 (C); 132.5 (C); 143.0 (C); 148.3 (C); 166.6 (C); 190.5 (CHO). Found, %: C 78.77; H 4.27. $C_{26}H_{17}ClO_2$. Calculated, %: C 78.69; H 4.32.

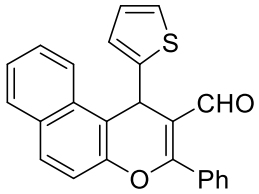
3-(4-Methoxyphenyl)-1-(*p*-tolyl)-1*H*-benzo[*f*]chromene-2-carbaldehyde (2f).



Yield 270 mg (67%), colorless crystals, mp 150−152 °C. IR spectrum, ν, cm^{-1}: 1651, 1636, 1593, 1512, 1458, 1439, 1420, 1393, 1354, 1327, 1300, 1258, 1234, 1211, 1204, 1177, 1111, 1069, 1018, 945, 845, 814, 783, 745, 718. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.22 (3H, s, CH_3); 3.88 (3H, s, CH_3O); 5.81 (1H, s, H-1); 6.97−7.02 (4H, m, H Ar); 7.27 (2H, d, *J* = 8.0, H Ar); 7.38−7.49 (3H, m, H Ar); 7.58 (2H, d, *J* = 8.7, H Ar); 7.81 (2H, d, *J* = 8.7, H Ar); 8.03 (1H, d, *J* = 8.2, H Ar); 9.63 (1H, s,

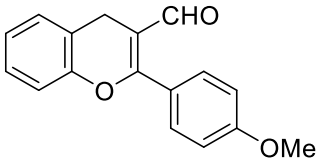
CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.1 (CH_3); 34.7 (1-CH); 55.6 (CH_3O); 114.1 (2CH); 117.1 (CH); 117.4 (C); 118.2 (C); 123.5 (C); 123.7 (CH); 125.1 (CH); 127.2 (CH); 128.2 (2CH); 128.5 (CH); 128.9 (CH); 129.3 (2CH); 131.3 (C); 131.7 (C); 132.2 (2CH); 136.1 (C); 141.8 (C); 148.3 (C); 162.3 (C); 166.5 (C); 190.6 (CHO). Found, %: C 82.67; H 5.49. $C_{28}H_{22}O_3$. Calculated, %: C 82.74; H 5.46.

3-Phenyl-1-(thiophen-2-yl)-1*H*-benzo[*f*]chromene-2-carbaldehyde (2g).



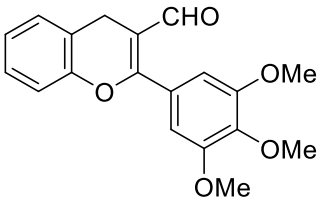
Yield 295 mg (80%), yellow crystals, mp 171−172 °C. IR spectrum, ν, cm^{-1}: 1651, 1636, 1612, 1589, 1574, 1516, 1489, 1462, 1435, 1393, 1335, 1231, 1211, 1192, 1177, 1157, 1142, 1123, 1076, 1069, 1034, 1011, 930, 914, 887, 853, 833, 814. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.17 (1H, s, H-1); 6.78−6.84 (2H, m, H Ar); 7.06 (1H, dd, *J* = 5.0, *J* = 1.1, H Ar); 7.43−7.59 (6H, m, H Ar); 7.66 (2H, d, *J* = 8.0, H Ar); 7.83−7.86 (2H, m, H Ar); 8.11 (1H, d, *J* = 8.5, H Ar); 9.69 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 29.8 (1-CH); 117.1 (CH); 117.2 (C); 117.4 (C); 123.5 (CH); 124.5 (CH); 125.1 (CH); 125.4 (CH); 126.7 (CH); 127.5 (CH); 128.6 (CH); 128.7 (2CH); 129.4 (CH); 130.6 (2CH); 131.0 (C); 131.3 (C); 131.6 (CH); 131.7 (C); 148.2 (2C); 166.9 (C); 190.3 (CHO). Found, %: C 78.31; H 4.32; S 8.60. $C_{24}H_{16}O_2S$. Calculated, %: C 78.24; H 4.38; S 8.70.

2-(4-Methoxyphenyl)-4*H*-chromene-3-carbaldehyde (2h).



Yield 232 mg (87%), colorless crystals, mp 119–120 ºC. IR spectrum, ν, cm^{-1}: 2839, 1659, 1636, 1605, 1578, 1508, 1493, 1458, 1396, 1366, 1304, 1288, 1246, 1223, 1173, 1107, 1030, 972, 841, 822. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.67 (2H, s, CH_2); 3.88 (3H, s, OCH_3); 6.99 (2H, d, *J* = 8.7, H Ar), 7.05–7.12 (2H, m, H Ar), 7.18–7.22 (2H, m, H Ar), 7.54 (2H, d, *J* = 8.7, H Ar), 9.64 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 22.0 (CH_2); 55.6 (OCH_3); 112.6 (C); 114.0 (2CH); 116.7 (CH); 120.7 (C); 123.9 (C); 125.0 (CH); 127.8 (CH); 129.5 (CH); 131.7 (2CH); 150.5 (C); 161.9 (C); 167.5 (C); 191.5 (CHO). Found, %: C 76.60; H 5.26. $C_{17}H_{14}O_3$. Calculated, %: C 76.68; H 5.30.

2-(3,4,5-Trimethoxyphenyl)-4*H*-chromene-3-carbaldehyde (2i).



Yield 285 mg (88%), colorless crystals, mp 167−168 °C. IR spectrum, ν, cm^{-1}: 2839, 1659, 1636, 1609, 1582, 1508, 1493, 1458, 1416, 1393, 1366, 1335, 1308, 1288, 1227, 1173, 1123, 1111, 1030, 1003, 972, 891, 872, 841, 822. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.68 (2H, s, CH_2); 3.90 (6H, s, 2OCH_3); 3.91 (3H, s, OCH_3); 6.79 (2H, s, H Ar); 7.06–7.14 (2H, m, H Ar); 7.19–7.23 (2H, m,

H Ar); 9.68 (1H, s, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 22.0 (CH_2); 56.5 ($2OCH_3$); 61.1 (OCH_3); 107.5 (2CH); 113.1 (C); 116.8 (CH); 120.4 (C); 125.2 (CH); 126.9 (C); 127.9 (CH); 129.6 (CH); 140.5 (C); 150.4 (C); 153.3 (C); 167.3 (2C); 191.5 (CHO). Found, %: C 70.02; H 5.50. $C_{19}H_{18}O_5$. Calculated, %: C 69.93; H 5.56.

References

[S1] P. E. Brown, W. Clegg, Q. Islam and J. E. Steele, *J. Chem. Soc., Perkin Trans. 1*, 1990, 139; https://doi.org/10.1039/P19900000139.

[S2] R. J. Lepage, P. W. Moore, R. J. Hewitt, P. H. Teesdale-Spittle, E. H. Krenske and J. E. Harvey, *J. Org. Chem*., 2022, **87**, 301; https://doi.org/10.1021/acs.joc.1c02366.

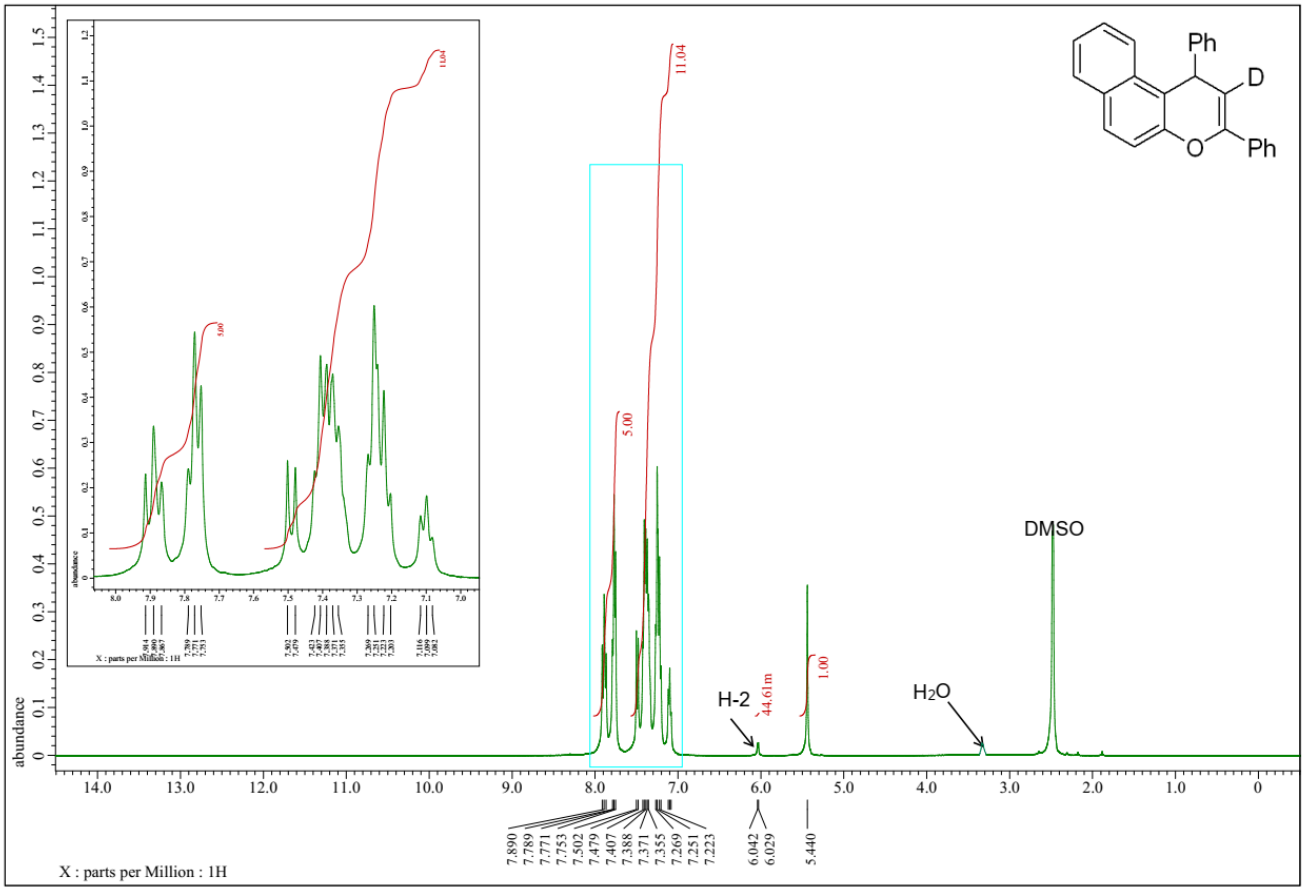
[S3] P. Müller and N. Pautex, *Helv. Chim. Acta*, 1991, **74**, 55; https://doi.org/10.1002/hlca.19910740108.

[S4] A. C. Bissember, A. T. Phillis, M. G. Banwell and A. C. Willis, *Org. Lett*., 2007, **9**, 5421; https://doi.org/10.1021/ol7021774.

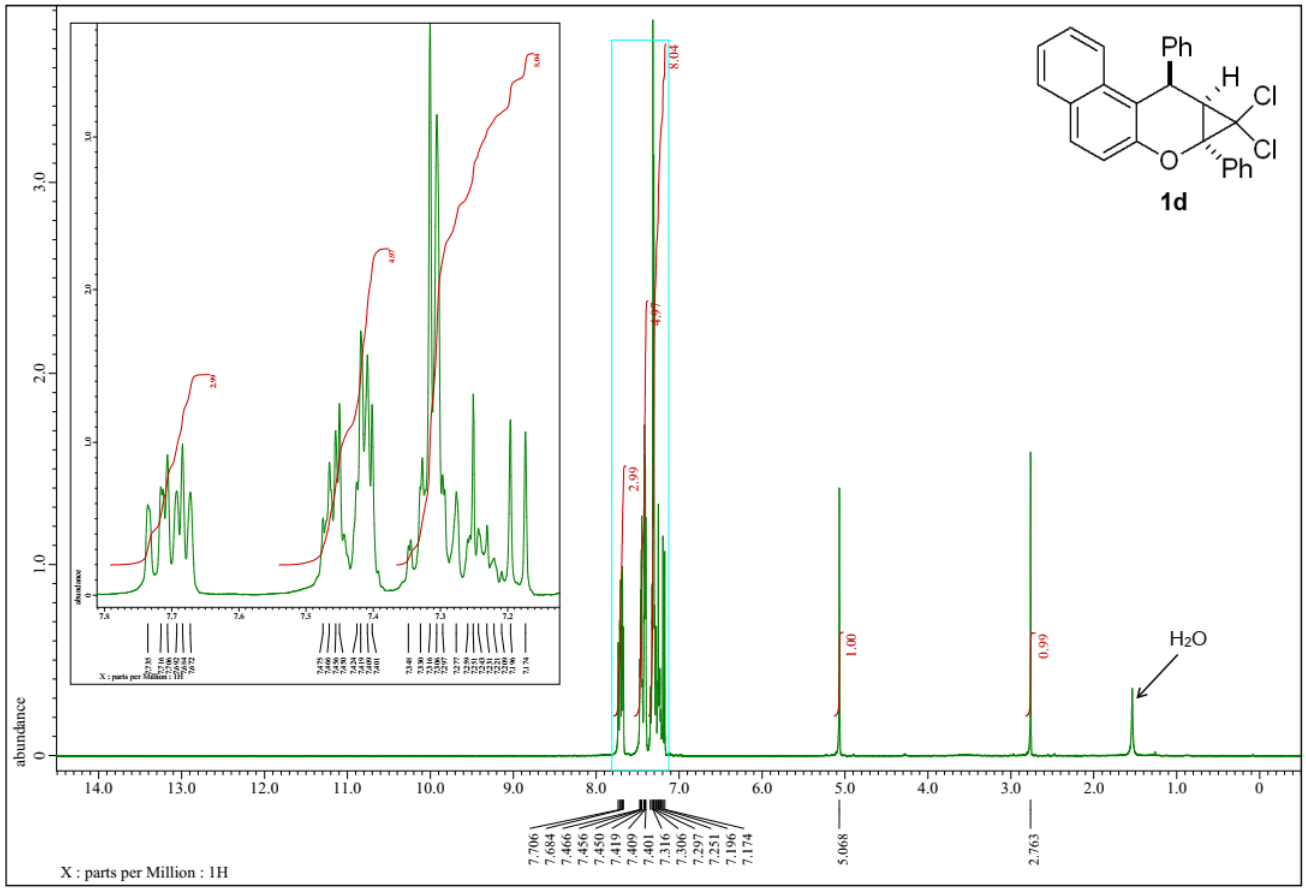
[S5] P. P. Sharp, J. Mikusek, J. Ho, E. H. Krenske, M. G Banwell, M. L. Coote, J. S. Ward and A. C. Willis, *J. Org. Chem*., 2018, **83**, 13678; https://doi.org/10.1021/acs.joc.8b01766.

[S6] I. A. Semenova, V. A. Osyanin, M. R. Demidov, D. V. Osipov and Yu. N. Klimochkin. *Chem. Heterocycl. Compd*., 2020, **56**, 1417; https://doi.org/10.1007/s10593-020-02831-0.

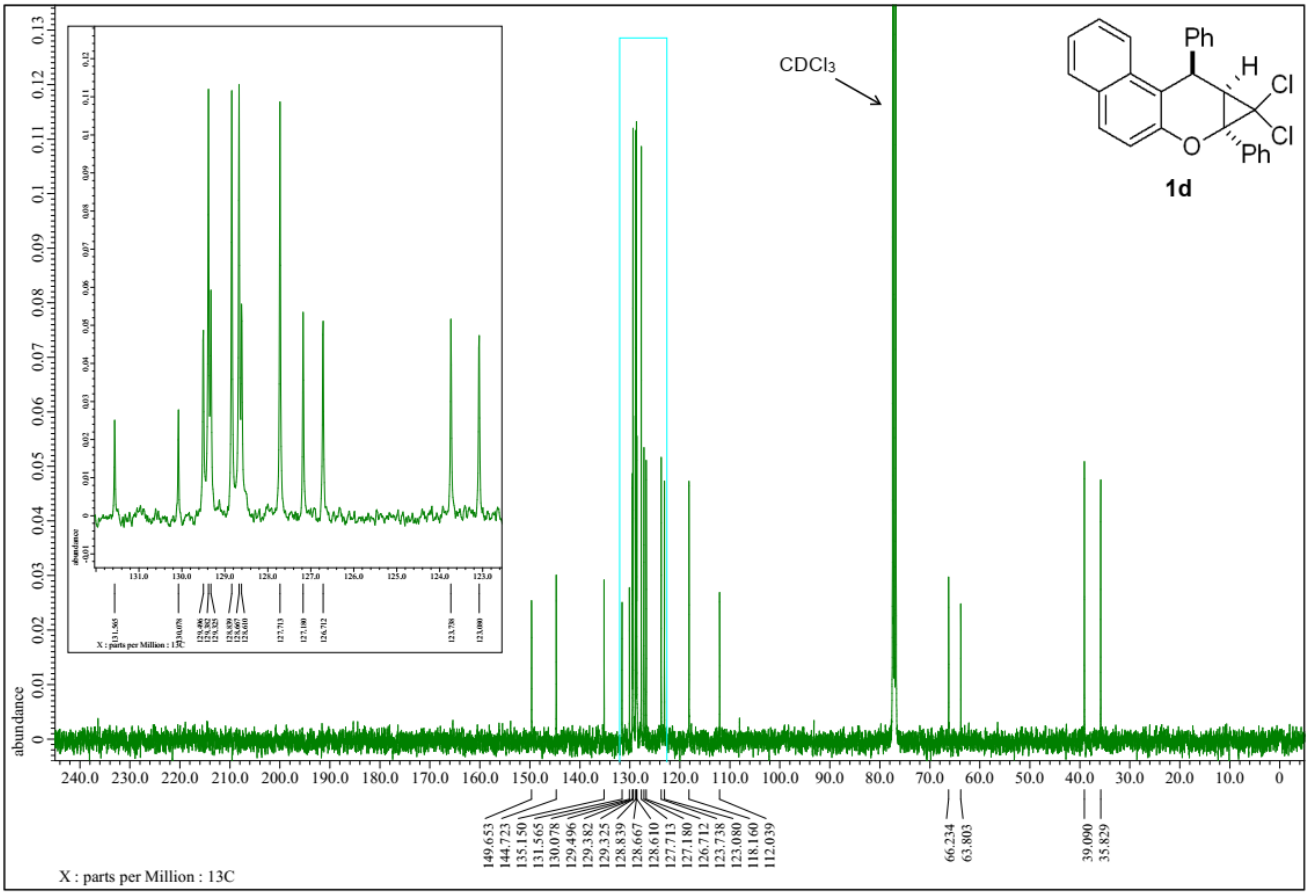
^{1}H NMR


Ph
D
O
Ph
DMSO
H-2
H2O
5.00
11.04
1.00
44.61m
abundance
X : parts per Million : 1H

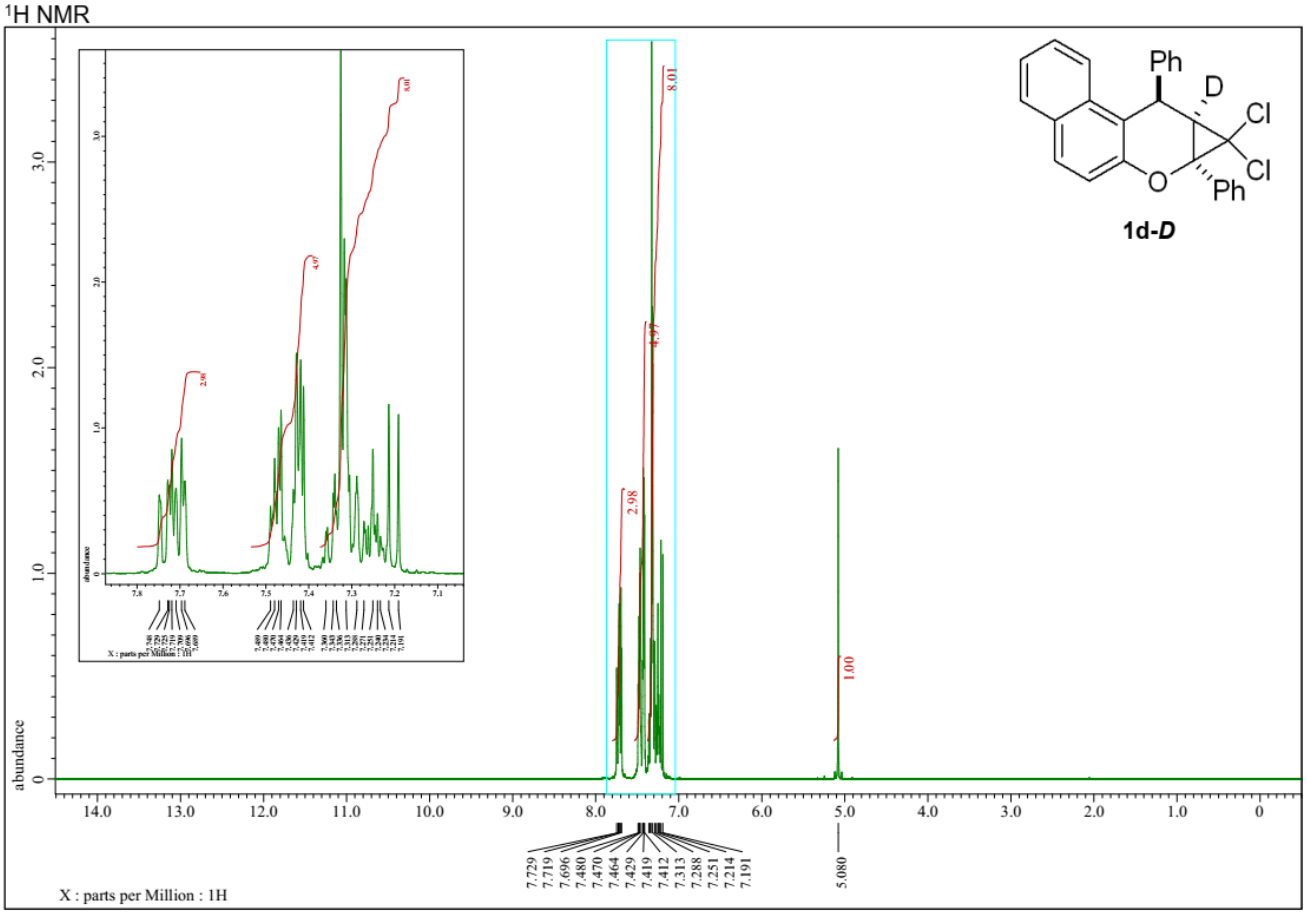
^{1}H NMR



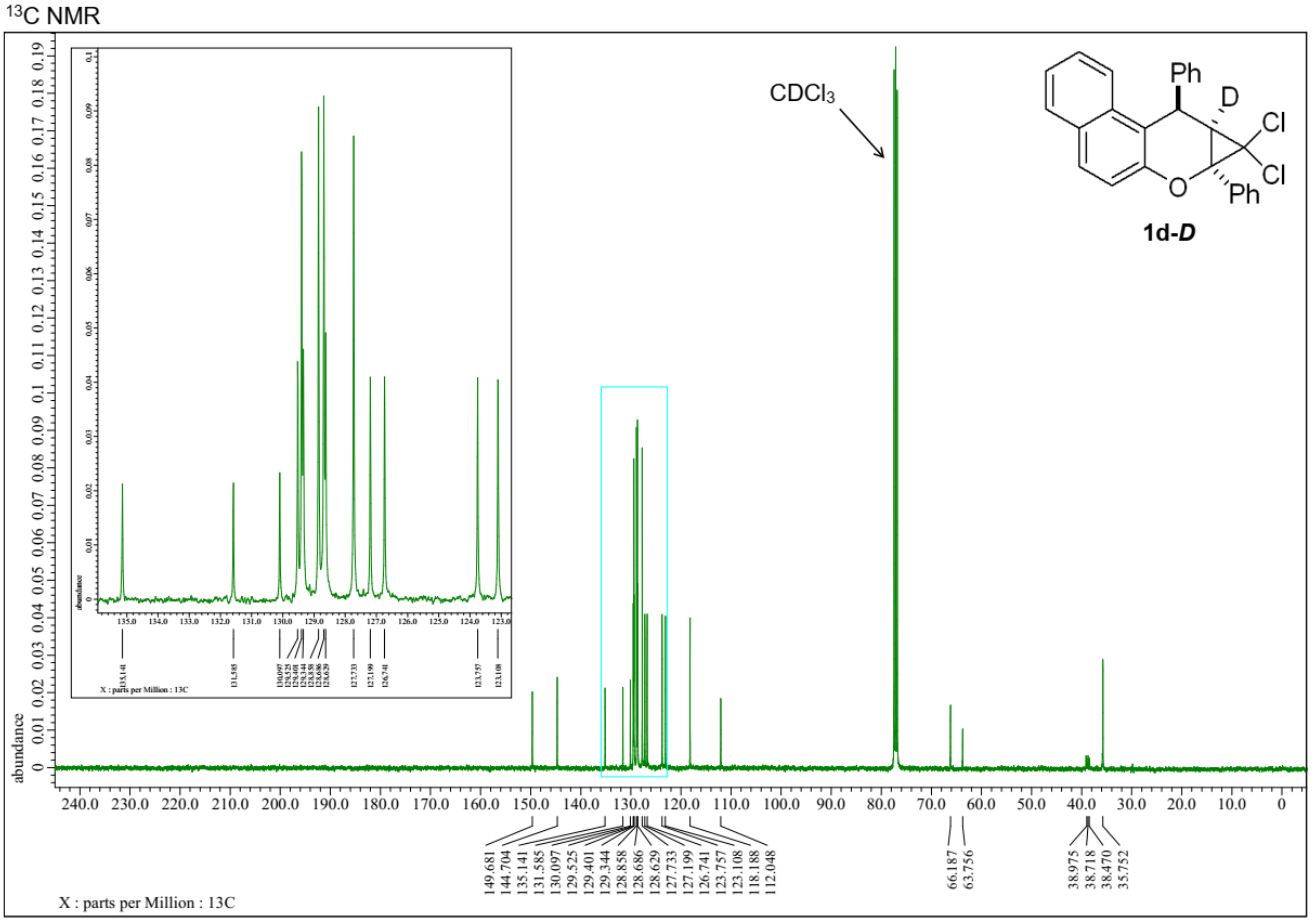
^{13}C NMR



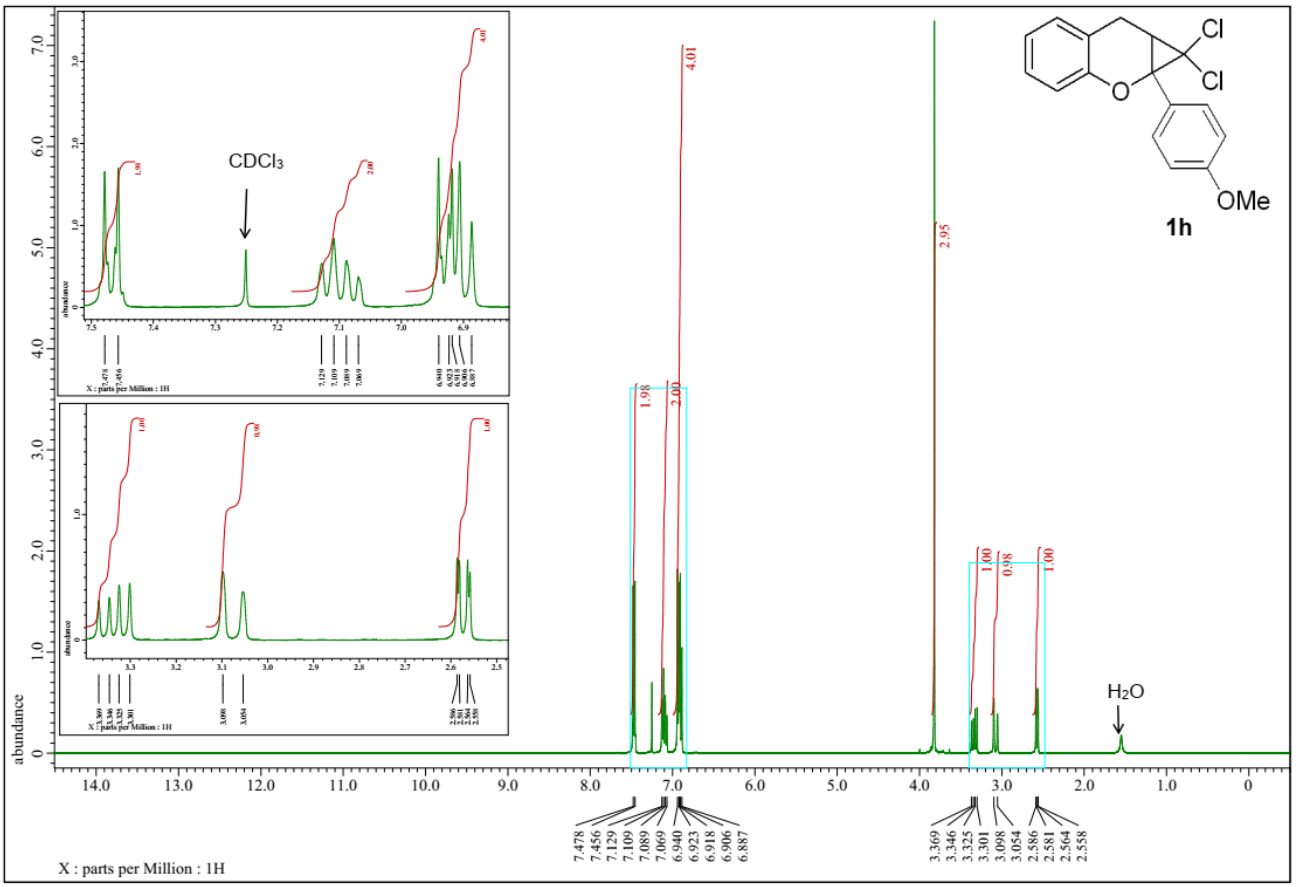
^{1}H NMR



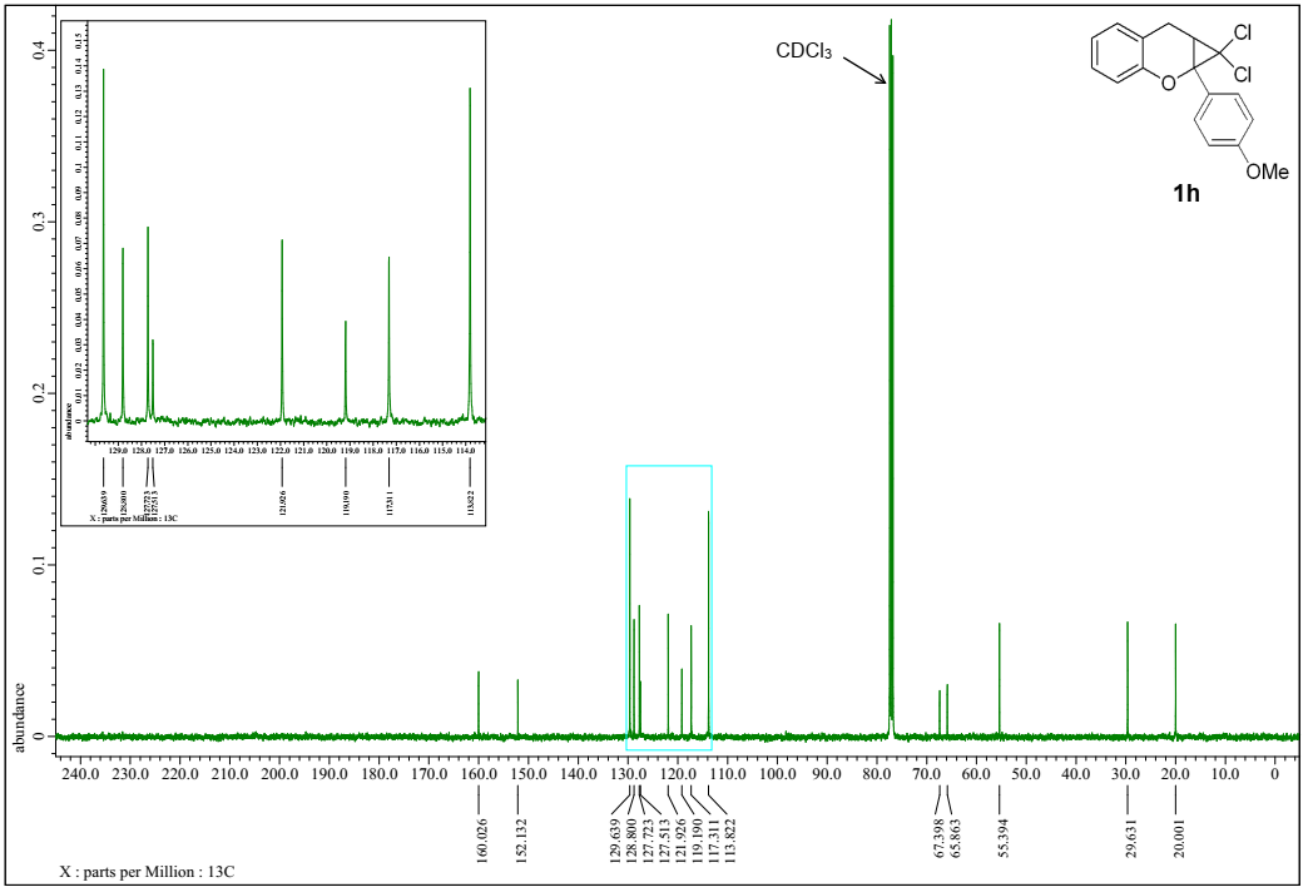
^{13}C NMR



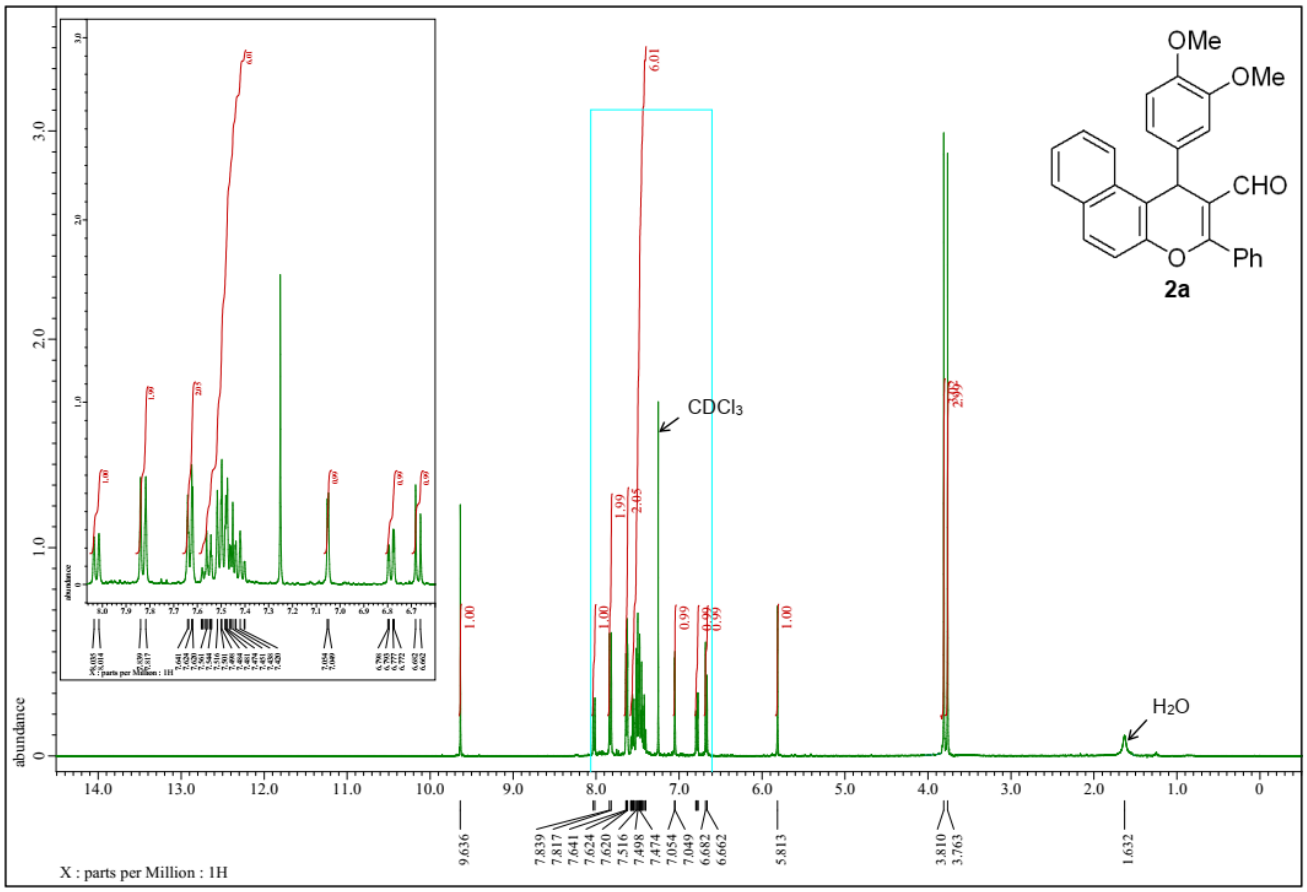
^{1}H NMR



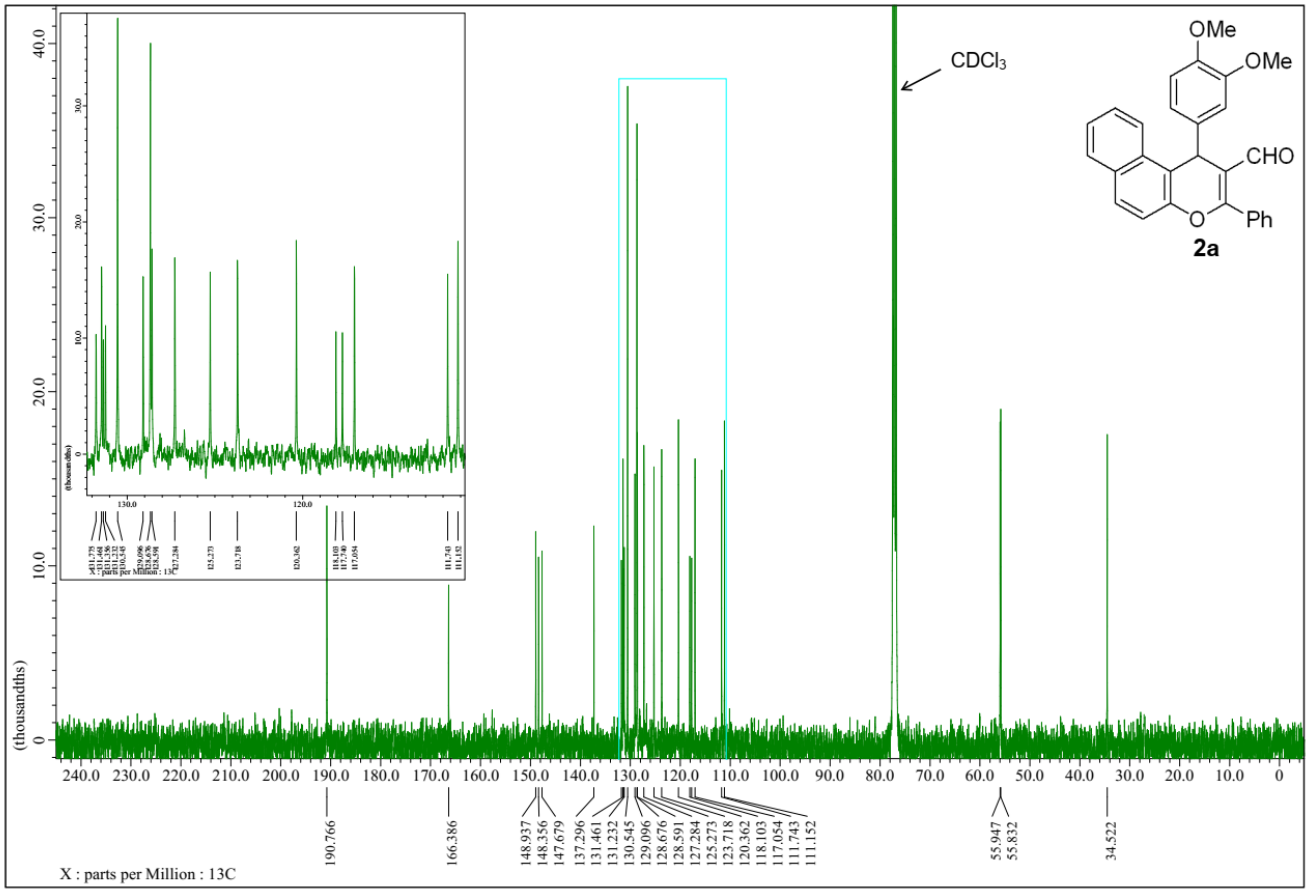
^{13}C NMR



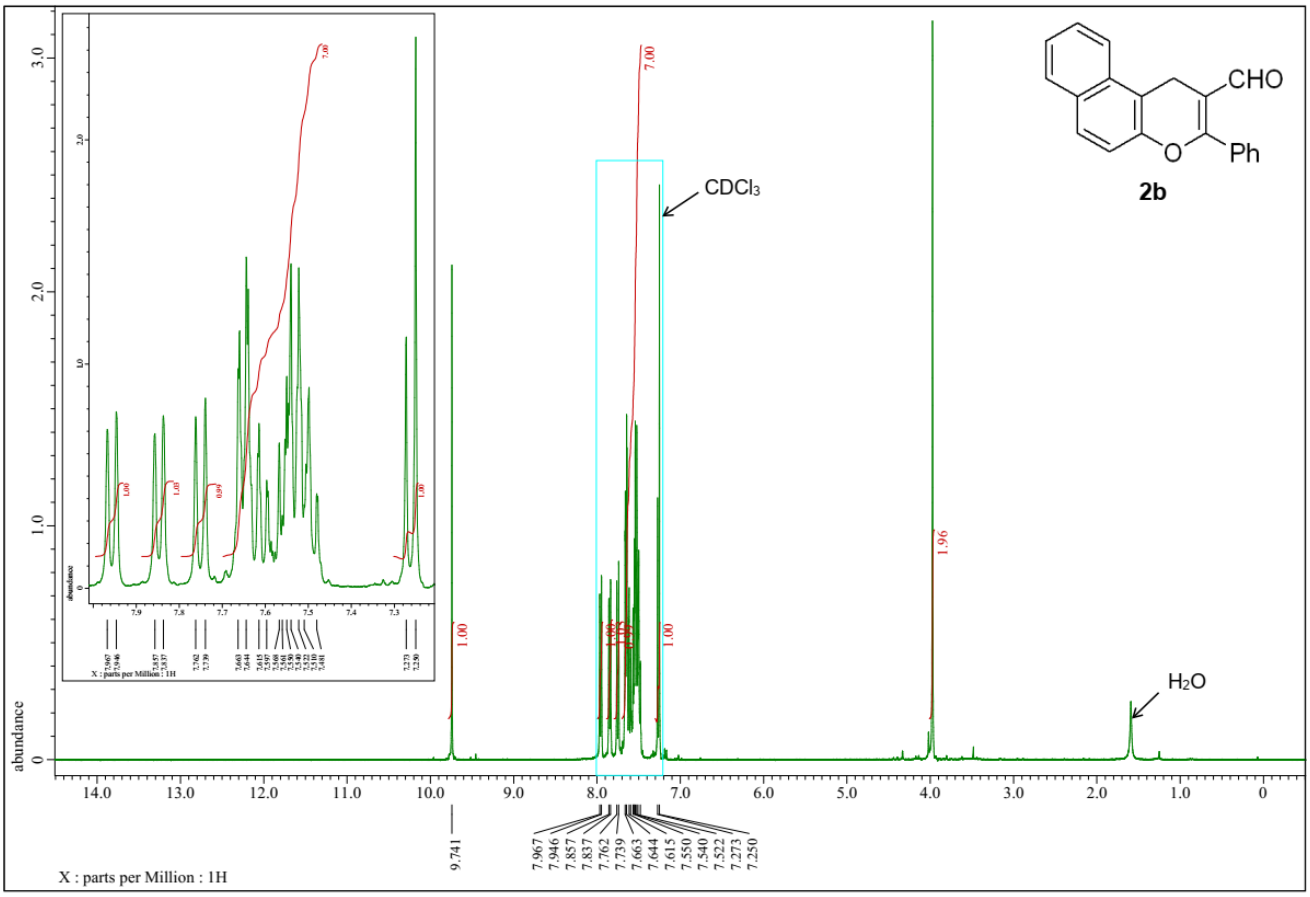
^{1}H NMR



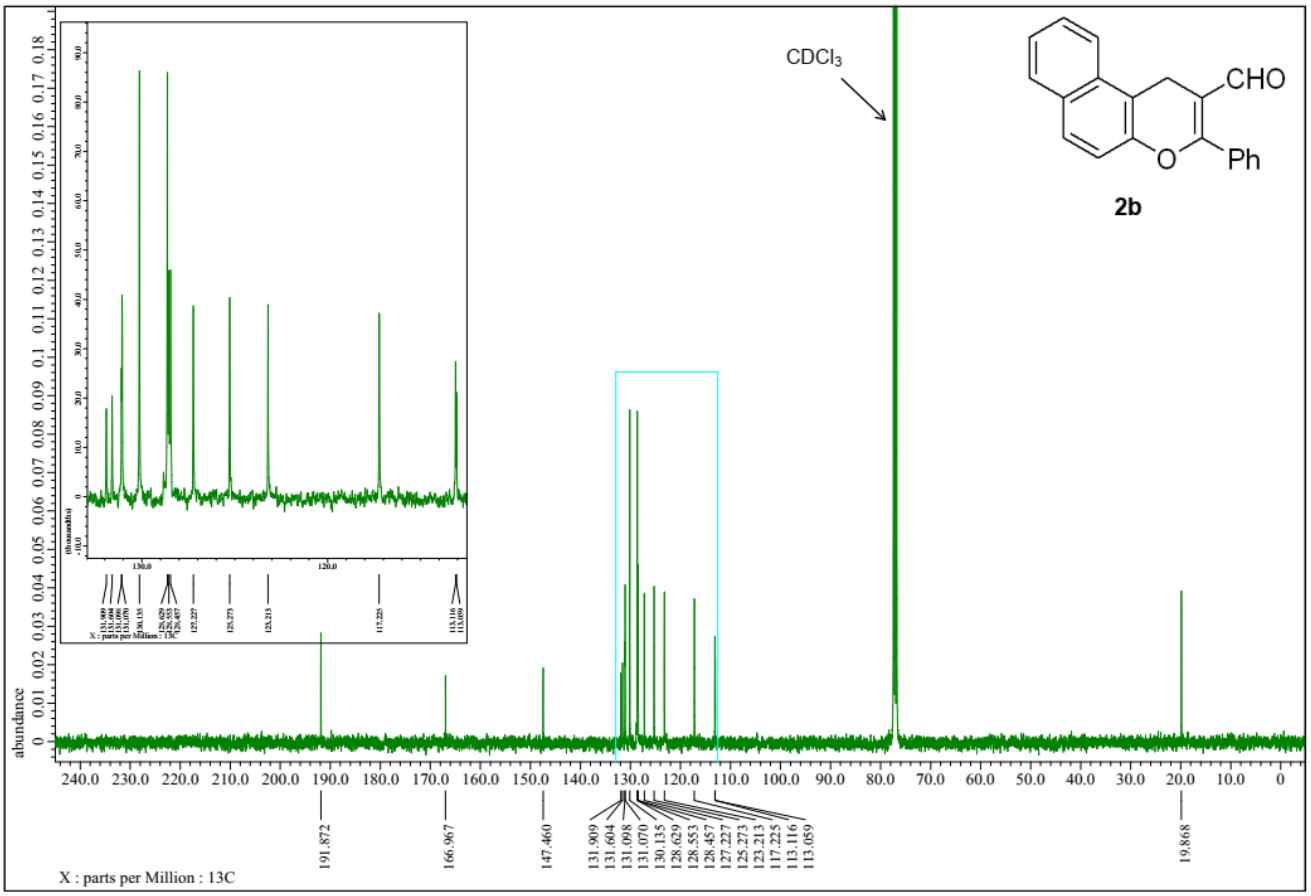
^{13}C NMR



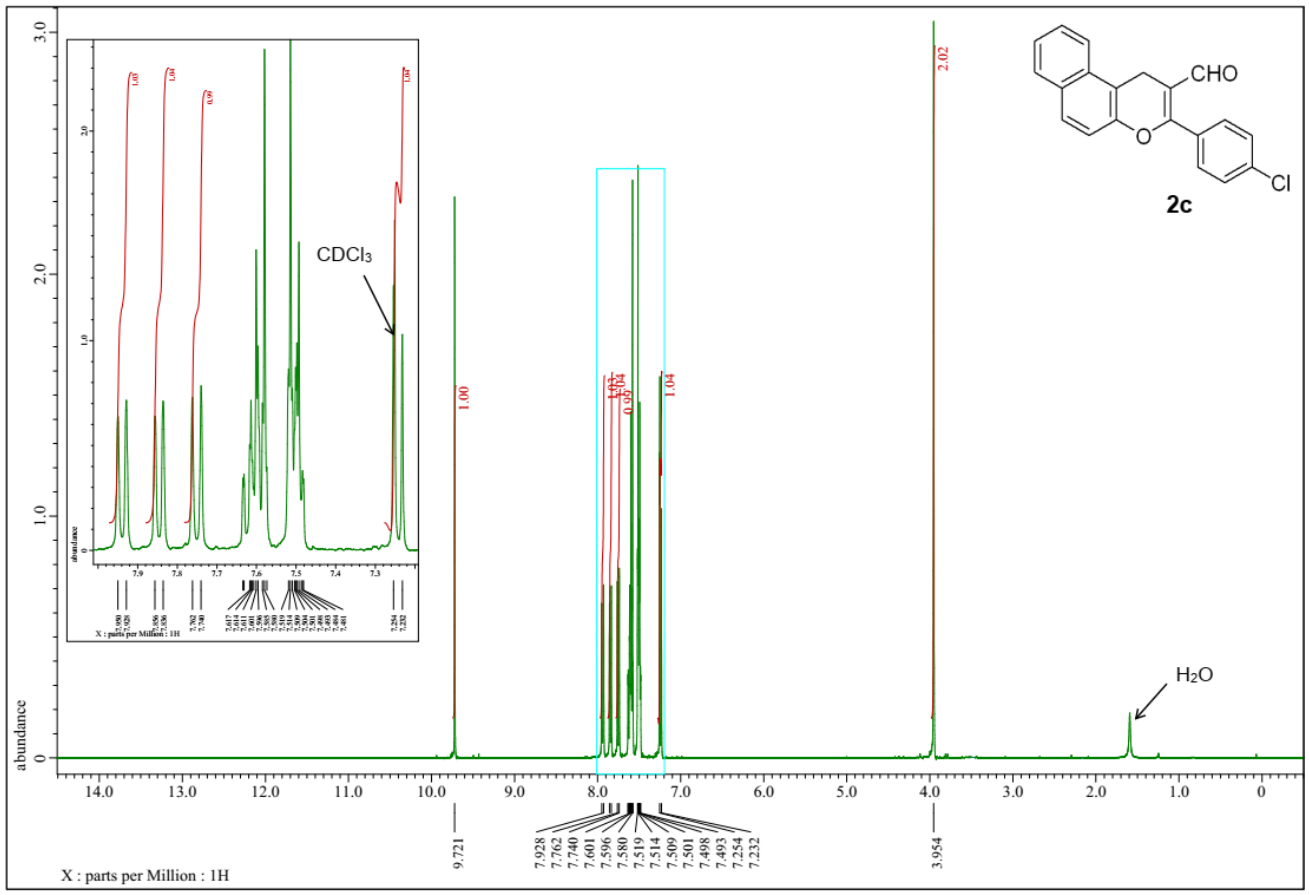
^{1}H NMR



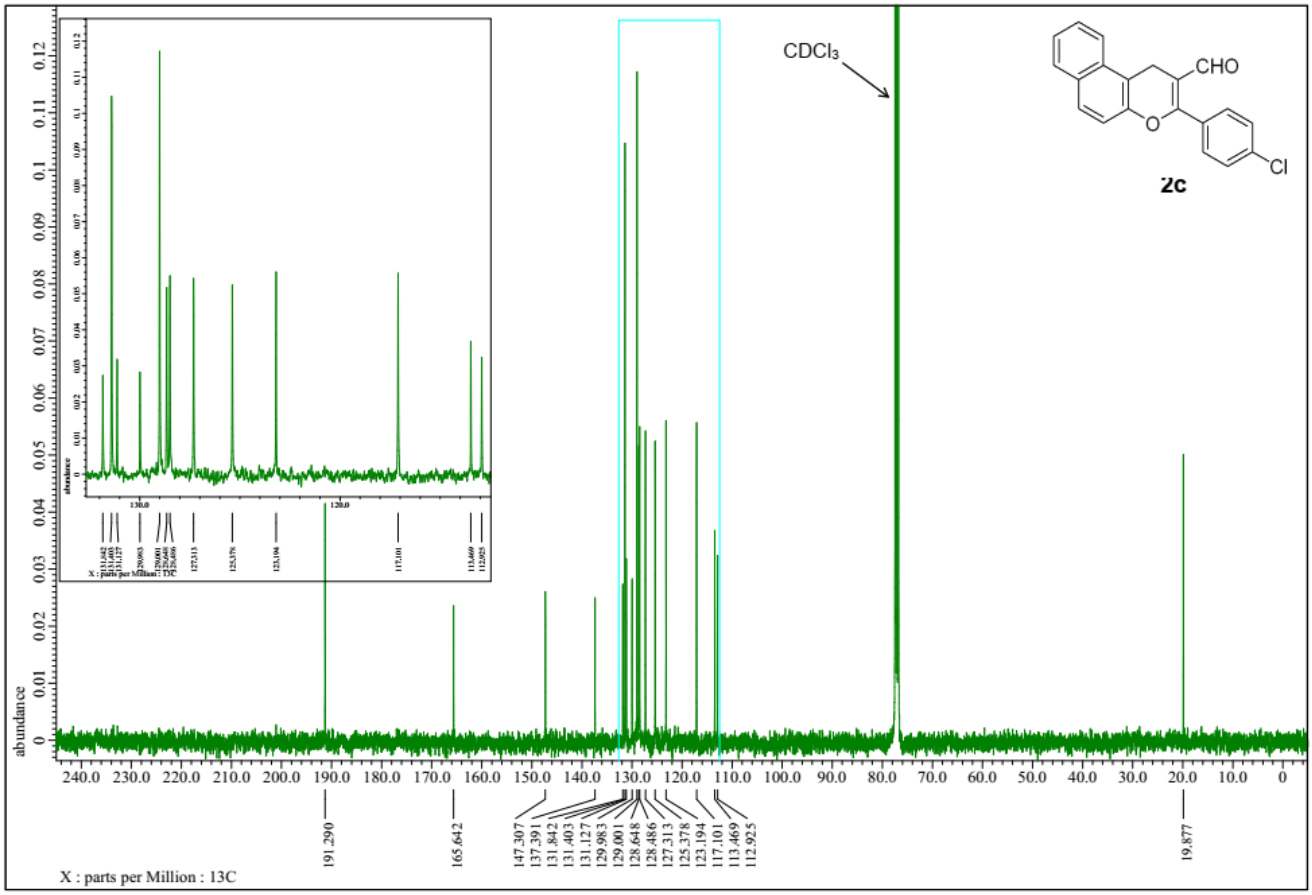
^{13}C NMR



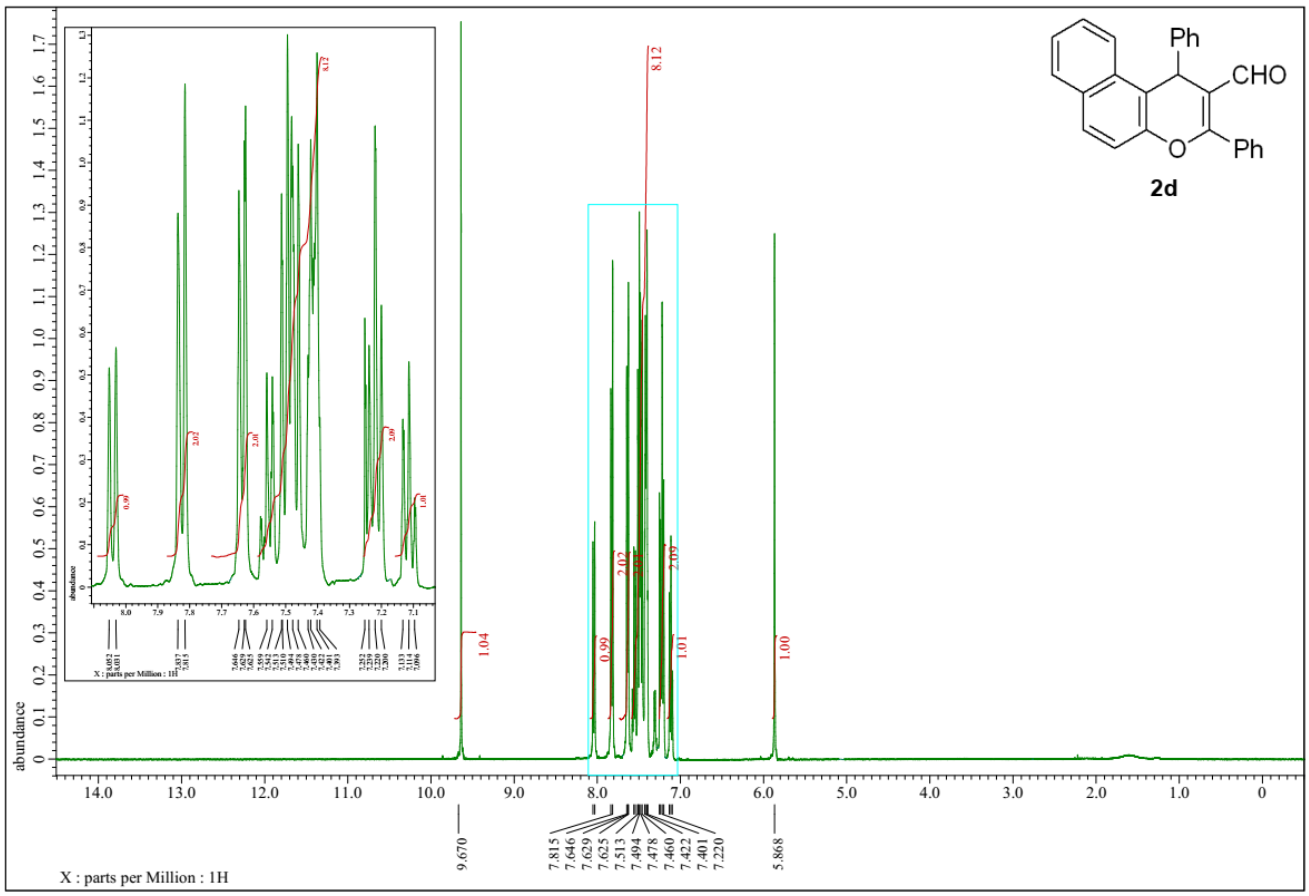
^{1}H NMR



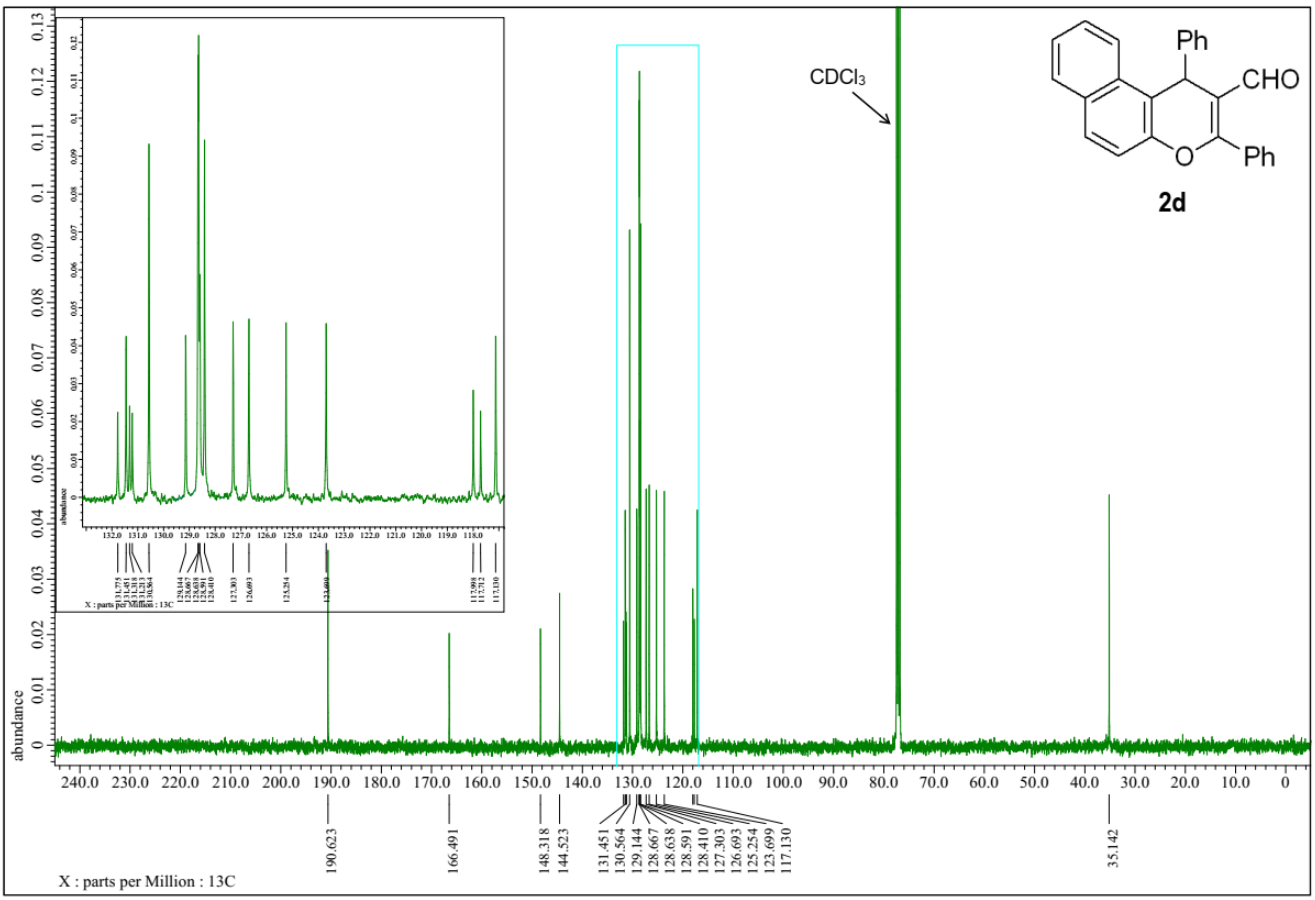
^{13}C NMR



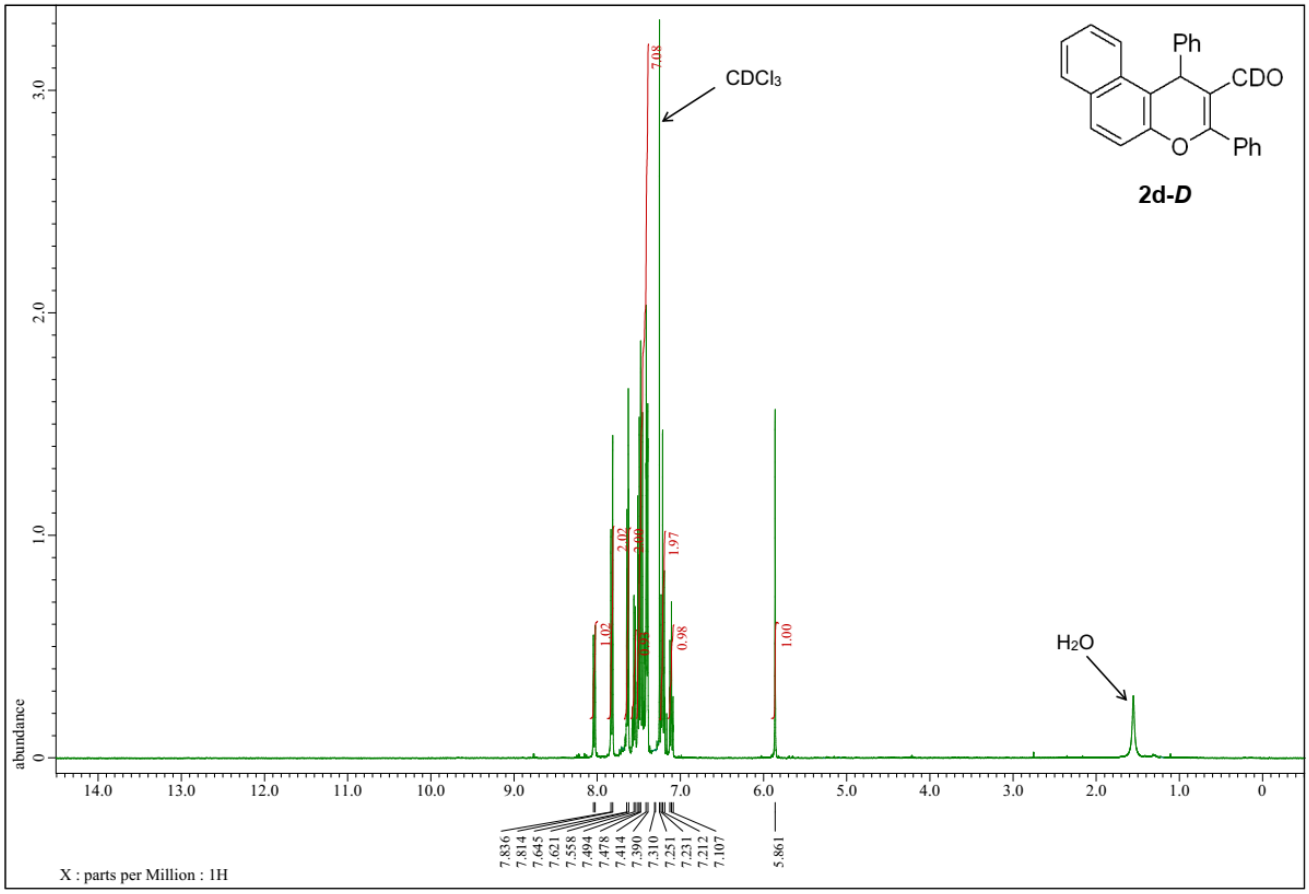
^{1}H NMR



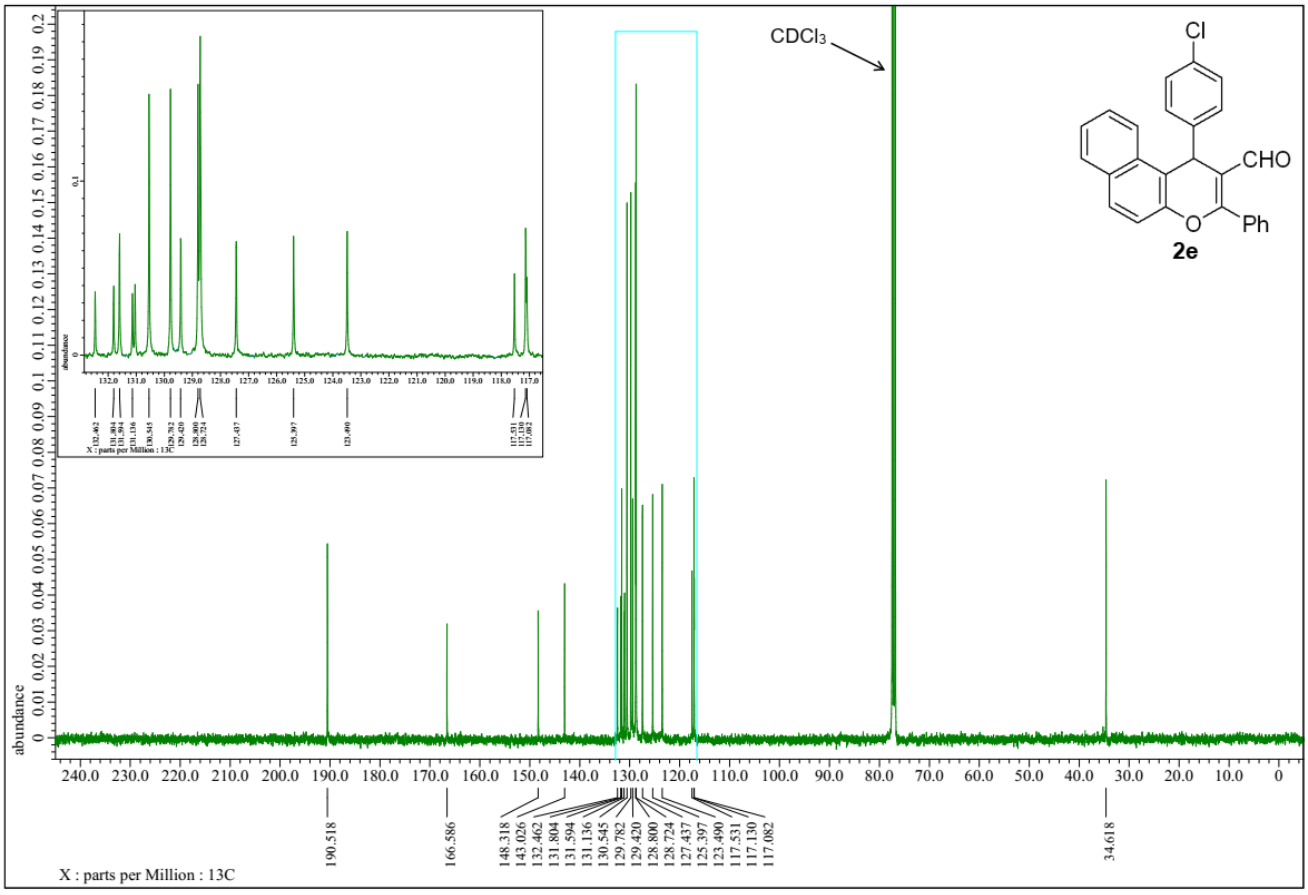
^{13}C NMR



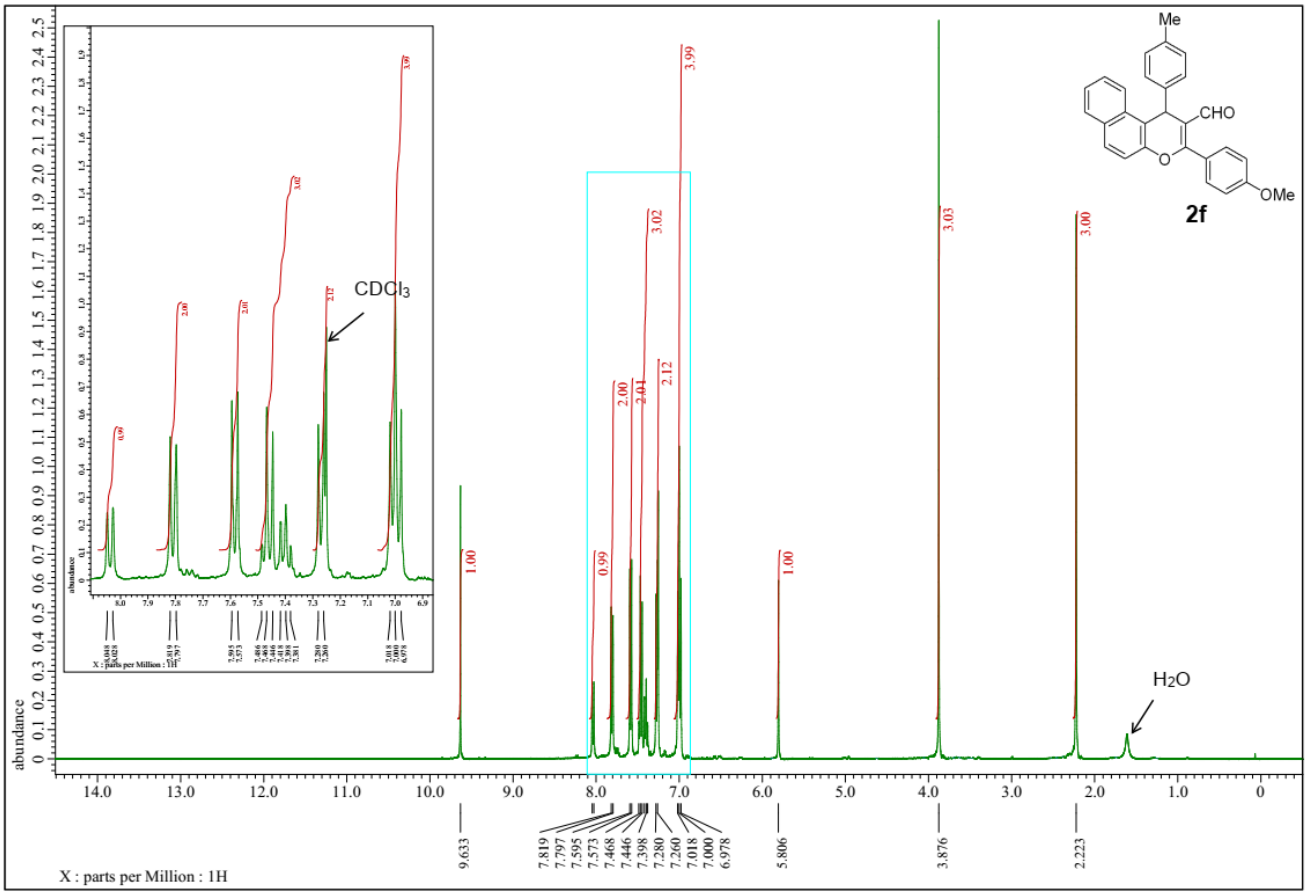
^{1}H NMR


CDCl3
H2O
Ph
CDO
Ph
O
2d-D
abundance
X : parts per Million : 1H
7.836
7.814
7.645
7.621
7.558
7.494
7.478
7.414
7.390
7.310
7.251
7.231
7.212
7.107
5.861

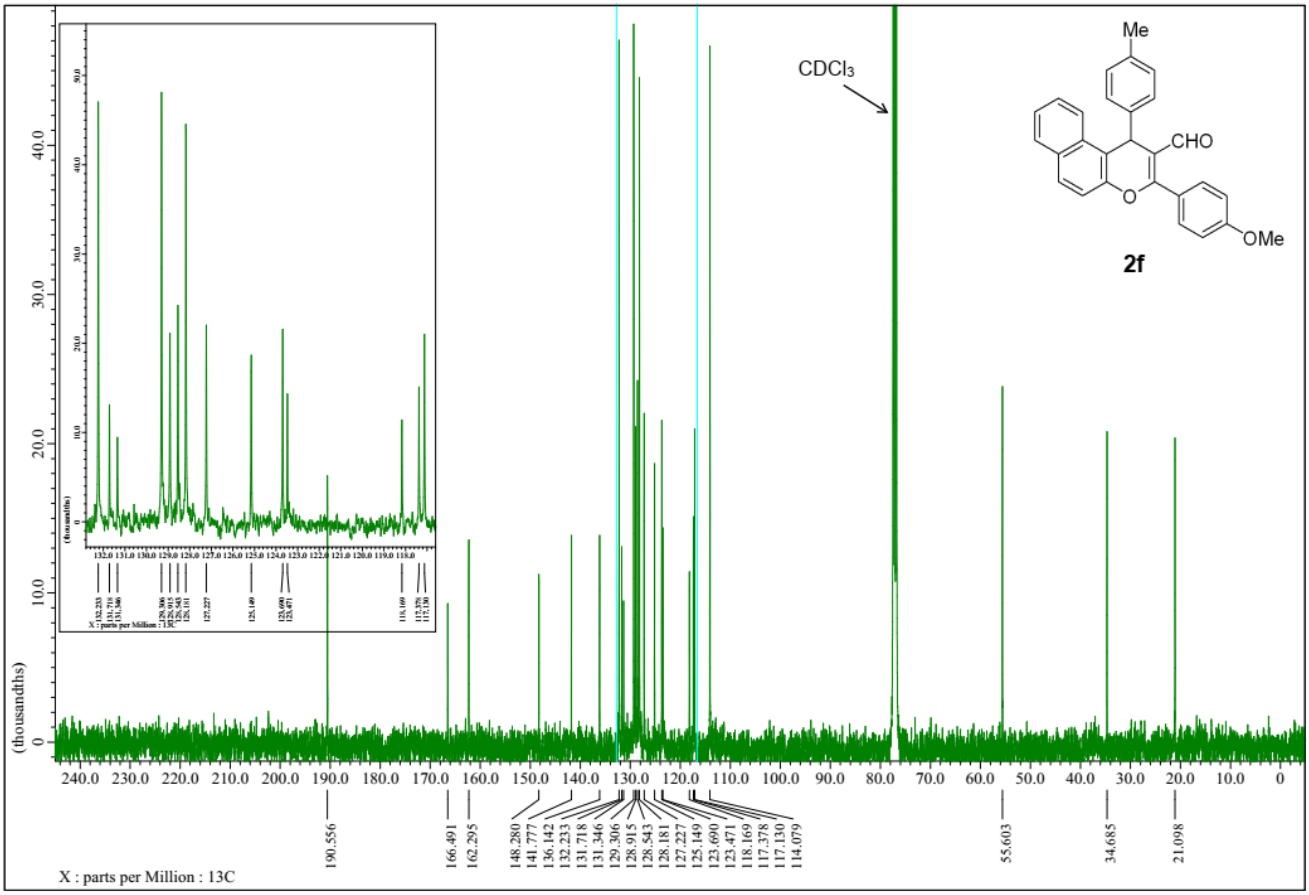
^{13}C NMR


CDCl3
Cl
CHO
Ph
O
2e
abundance
X : parts per Million : 13C
190.518
166.586
148.318
143.026
132.462
131.804
131.594
131.136
130.545
129.782
129.420
128.800
128.724
127.437
125.397
123.490
117.531
117.130
117.082
34.618

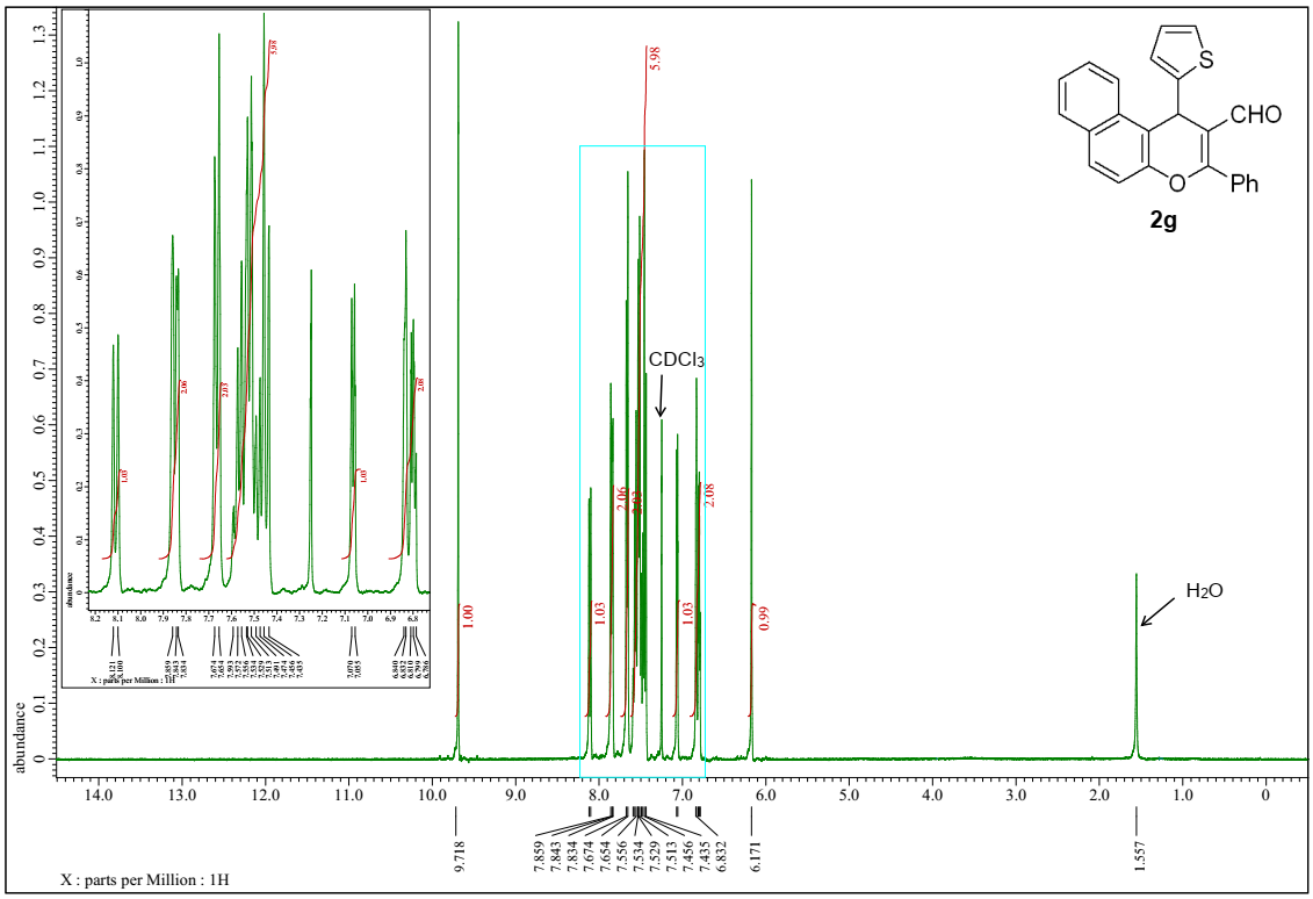
^{1}H NMR



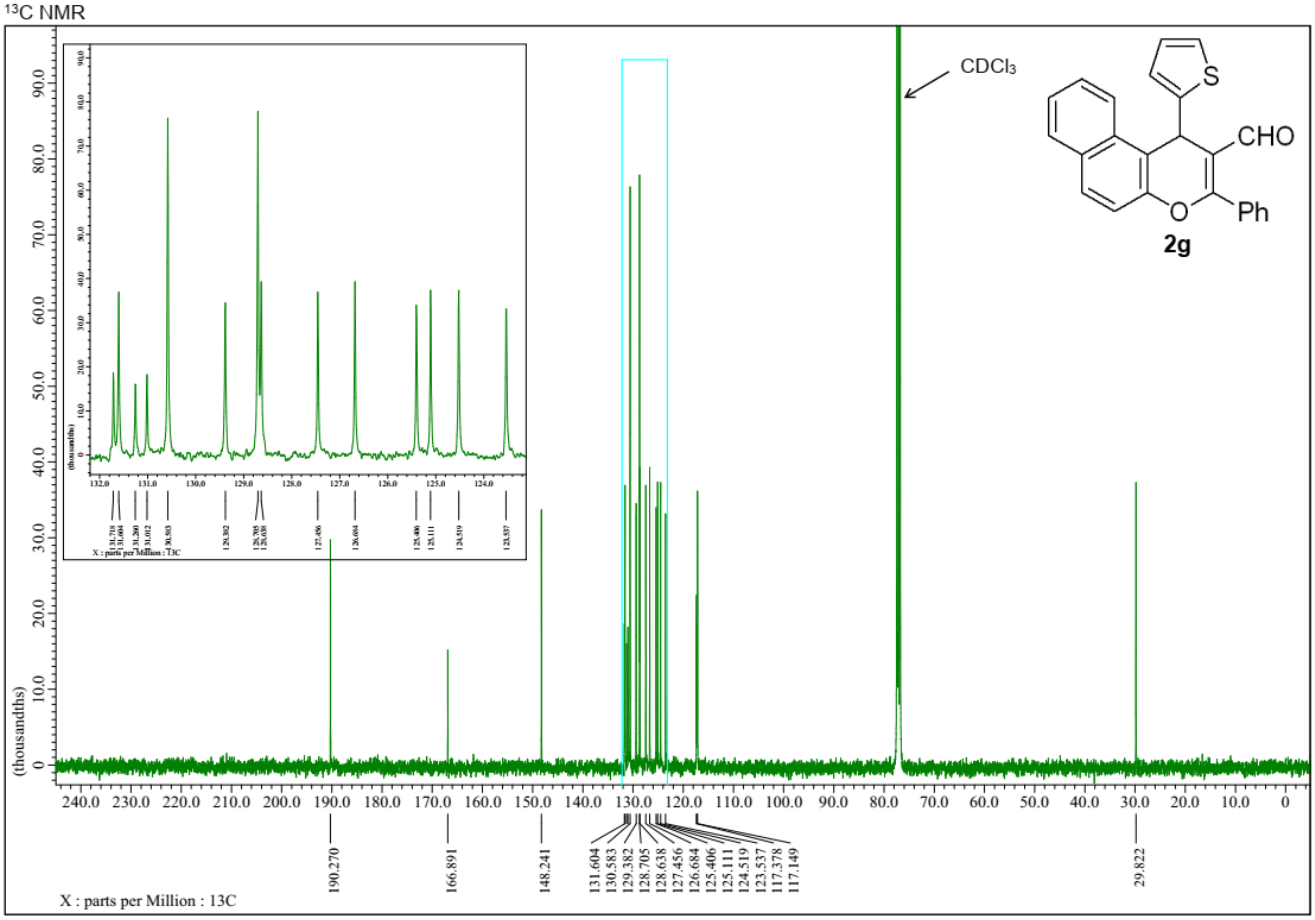
^{13}C NMR



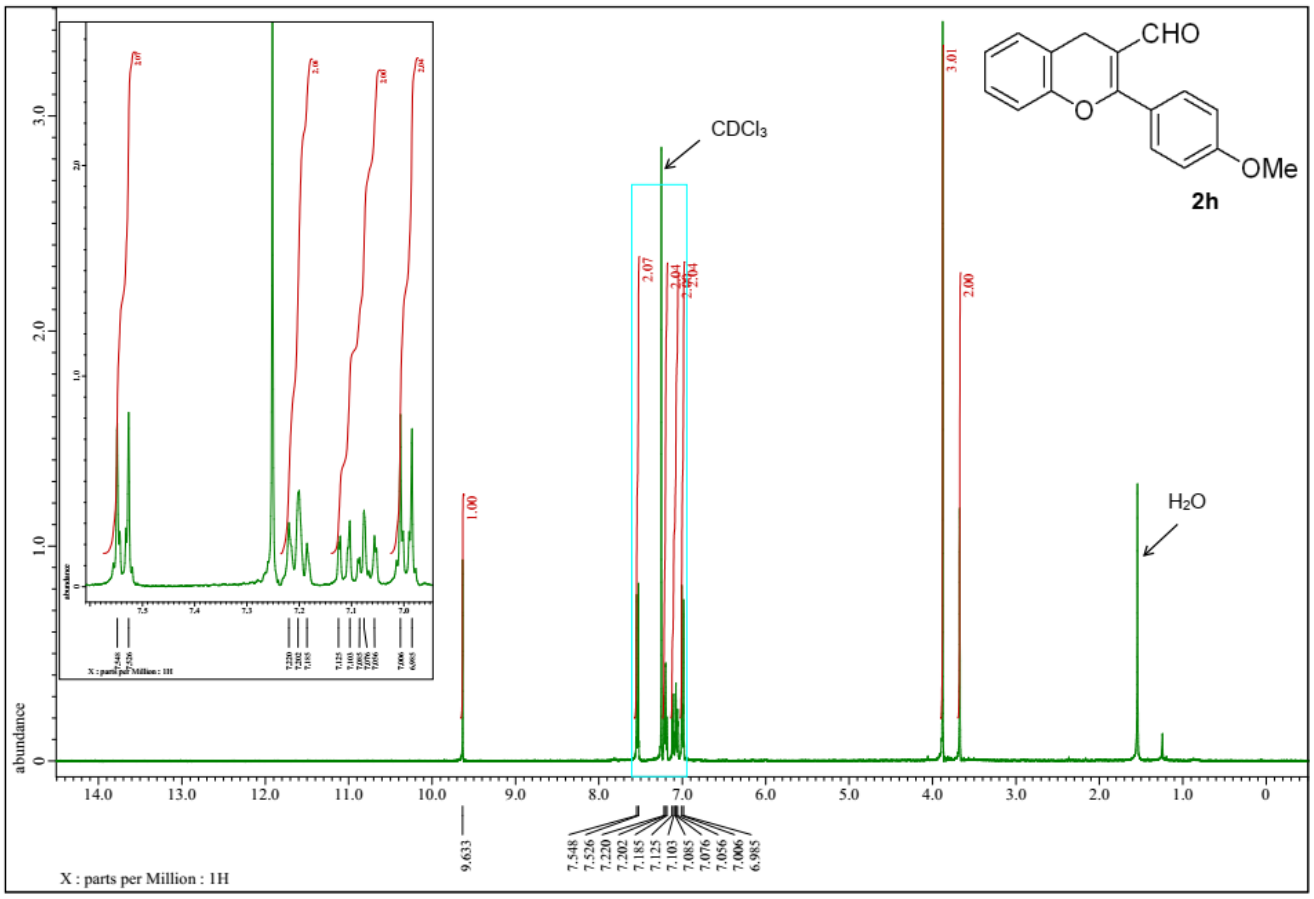
^{1}H NMR



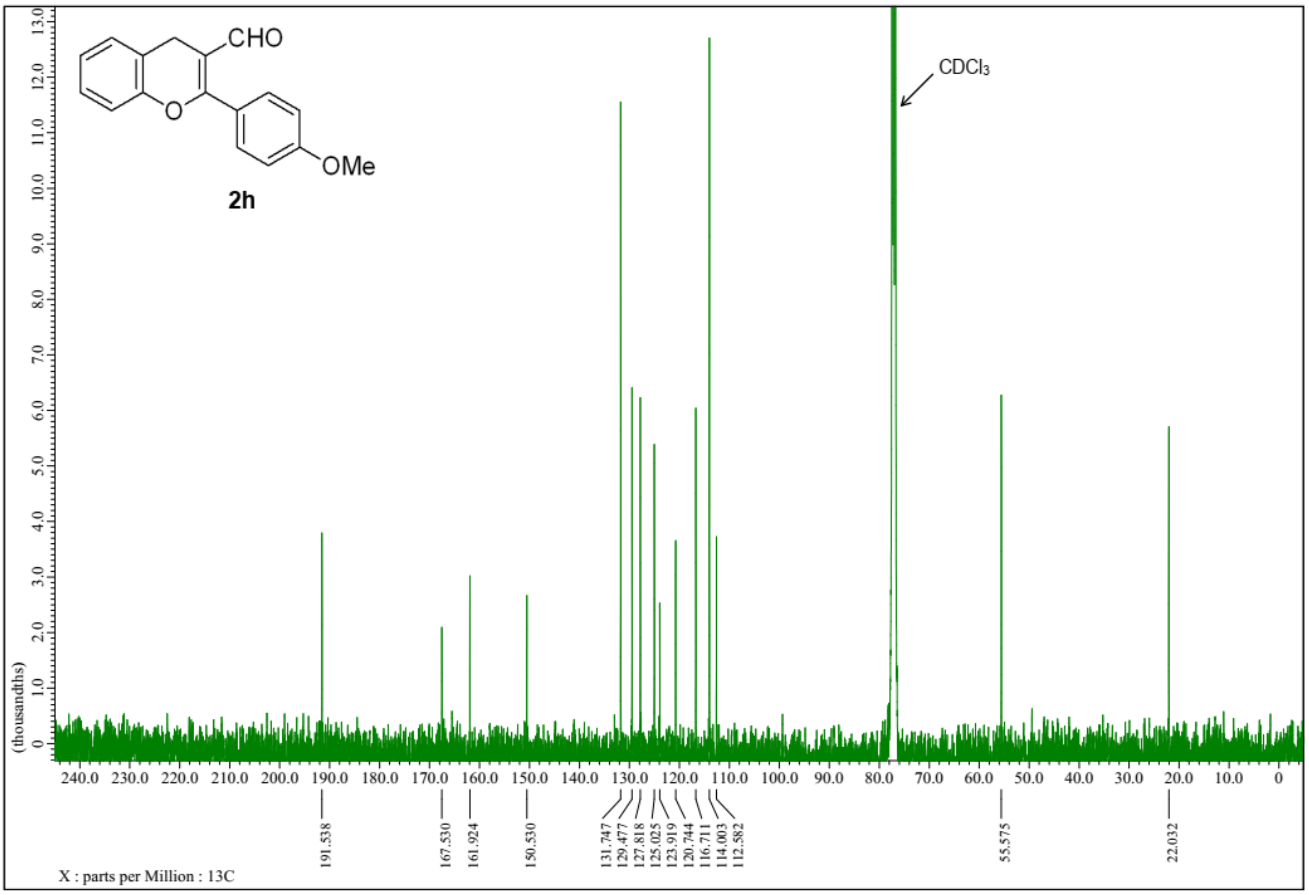
^{13}C NMR



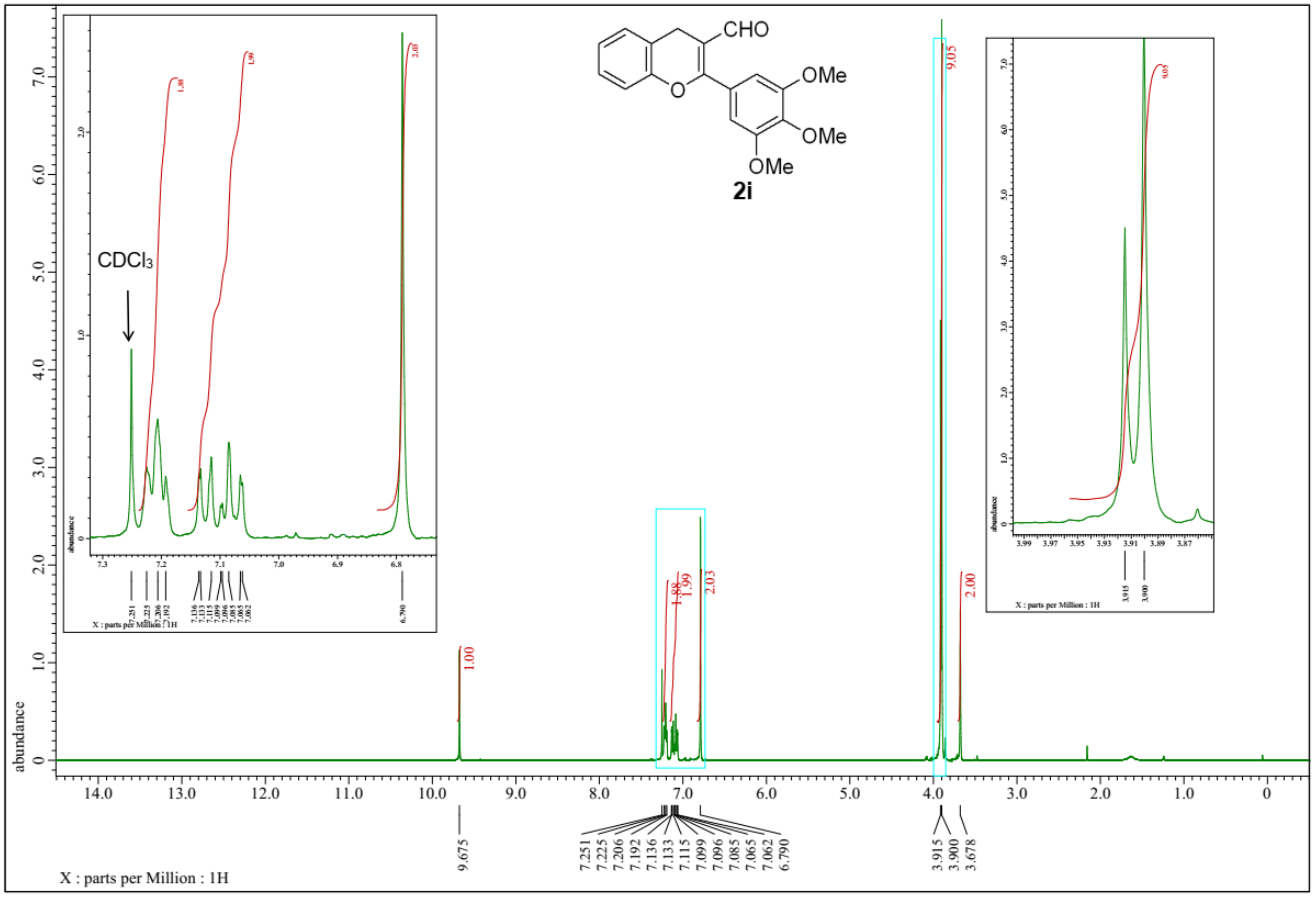
^{1}H NMR



^{13}C NMR



^{1}H NMR



^{13}C NMR