Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of *Cis*/*trans*-dihydrochromenones *via* Photoinduced Rearrangement of 4-Phenyl-3-aryl/cyclohexenylcoumarins

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Synthesis of *Cis*/*trans*-dihydrochromenones *via* Photoinduced Rearrangement of 4-Phenyl-3-aryl/cyclohexenylcoumarins

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Contents

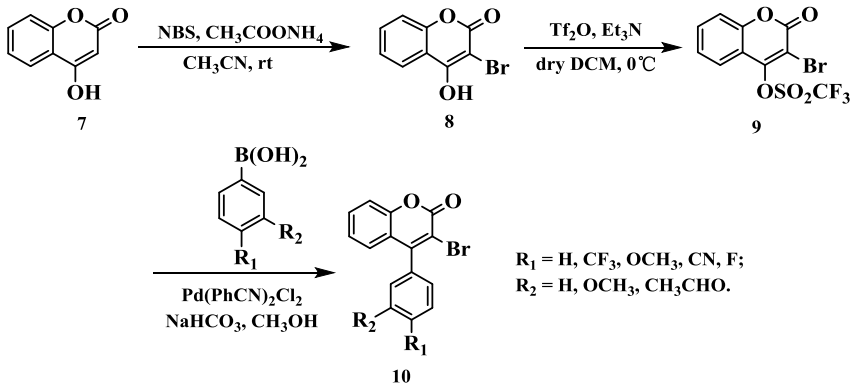
1. General Information

Unless otherwise noted, all reagents and solvents of reaction were purchased from commercial suppliers and used without purification. Thin-layer chromatography (TLC) used silica gel 60 GF254 plate. The silica gel (size 200−300 mesh) used for the column chromatography was purchased from Qingdao Haiyang Chemistry Plant (China). Melting points were measured in a X-5 micromelting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained by Bruker 400 or 600 MHz spectrometers using $CDCl_3$ as an NMR solvent at room temperature. All chemical shifts were reported in ppm and was referenced with internally residual protons or carbon atoms in $CDCl_3$ (^{1}H-NMR, δ = 7.26, ^{13}C-NMR, δ =77.16). High-resolution mass spectrometry (HRMS) was recorded using the electron-spray ionization quadrupole-time-of-flight (ESI-Q-TOF) technique. The infrared spectra were recorded on a Nicollet 170SX FTIR spectrophotometer with KBr pellets in the 4000−500 cm^{-1} region. All of the irradiation experiments were performed in a photochemical reactor equipped with a 30 W lamp at room temperature. The emission wavelength of the 64 W lamp was 313 nm.

All calculations were performed utilizing the Gaussian 09 program package. Geometry optimizations were conducted in the framework of the DFT at the B3LYP level. The 6-311G+ (d, p) basis set was used for all the elements.

2. Synthetic Schemes

General procedure for the synthesis of 3-bromo-4-phenyl-2*H*-chromen-2-one derivatives (10)



7 8 9 10

Scheme S1 Synthesis of 3-bromo-4-phenyl-2*H*-chromen-2-one derivatives(**10**)

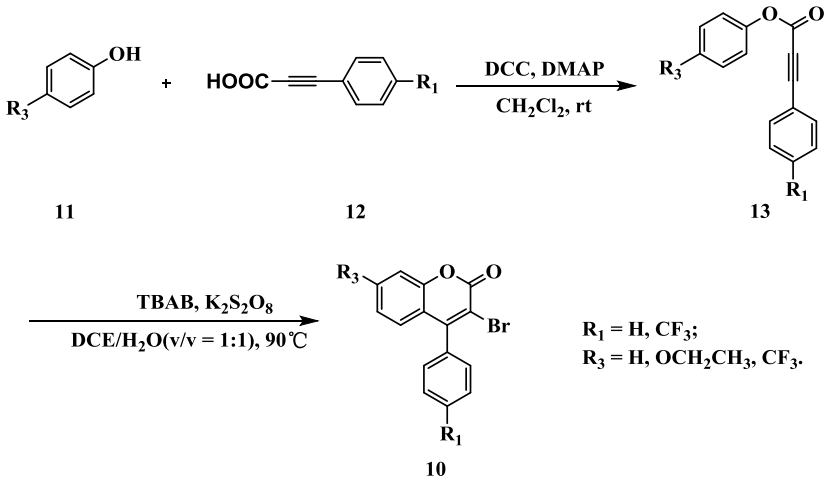
Synthesis of 3-Bromo-4-hydroxy-2H-chromen-2-ones. The N-bromosuccinimide(1.05 eq, 13.0 mmol) was added to a solution of 4-hydroxycoumarin(**7**) (2.21 g, 12.5 mmol) in acetonitrile (63mL), followed by ammonium acetate (0.1 g, 1.5 mmol). The resulting mixture was stirred at room temperature for 3 h. Then the volatiles were removed under reduced pressure, and the residue was taken in an ethyl acetate and water mixture (50 mL, 1:1). The mixture was extracted with ethyl acetate (3 × 20 mL). The organic layer was collected, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column

chromatography (ethyl acetate/petroleum ether, 1:30) to give 3-bromo-4-hydroxycoumarin as a yellow solid (3.01 g, 88%), which was used for the next step without characterization.[1]

Synthesis of 3-Bromo-2-oxo-2H-chromen-4-yltrifluoromethanesulfonate. A hot-oven-dried Schlenk test tube containing a magnetic stirring bar was charged with 3-bromo-4-hydroxycoumarin (**8**) (1.0 g, 4.0 mmol) and dry DCM (80 mL). The mixture was cooled to ice bath temperature. Then, Et_3N (0.7 mL, 5.1 mmol) was added and stirred for 5 min followed by adding trifluoromethane sulfonic anhydride (2.6 mL, 15 mmol) dropwise. After the reaction mixture was stirred at 0 °C for 8 h, it was poured into water and extracted with DCM (3 × 20 mL). The organic layer was concentrated under reduced pressure and the residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:30) to give a white solid (1.23 g, 72%).[1]

Synthesis of 3-bromo-4-phenyl-2H-chromen-2-one. According to a typical procedure, a hot-oven dried Schlenk tube was charged with **9** (1.0 mmol, 0.36 g), phenylboronic acid (1.0 mmol, 0.12 g), $NaHCO_3$ (2.0 mmol, 0.14 g), $Pd(PhCN)_2Cl_2$(0.5 mol %), and CH_3OH (20 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1.5 h. Then the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was combined and the volatiles were removed under reduced pressure. The crude product was purified on silica gel column chromatography (ethyl acetate/petroleum ether, 1:60) and was used directly in the next step. [1]

General procedure for the synthesis of 3-bromo-4-phenyl-2*H*-chromen-2-one derivatives (10)

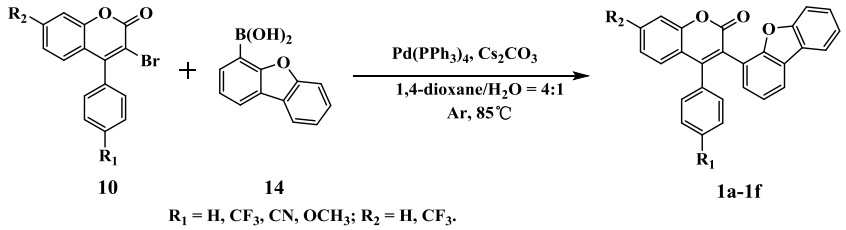


Scheme S2 Synthesis of 3-bromo-4-phenyl-2*H*-chromen-2-one derivatives (**10**)

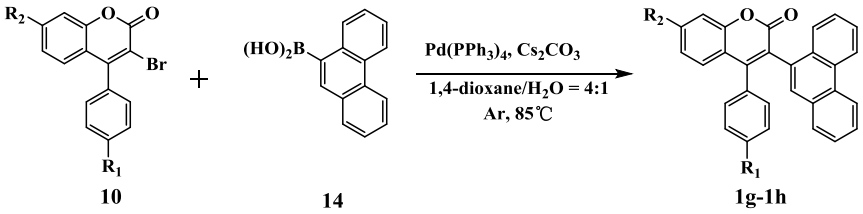
Synthesis of 3-bromo-4-phenyl-7-(trifluoromethyl/Ethoxy)-2H-chromen-2-ones(10). To a solute-on of the p-trifluoromethylphenol (**11**) (9.3 mmol, 1.0 equiv) in CH_2Cl_2 (45.0 mL) was added 3-phenylpropiolic acid (**12**) (10.2 mmol, 1.1 equiv) at 0 °C, then a mixture of DCC (13.9 mmol, 1.5 equiv) and DMAP (0.9 mmol, 0.1 equiv) in CH_2Cl_2 (22.0 mL) was added dropwise. The resulting mixture was stirred at room temperature for 12 h. Then the crude mixture was filtered and washed with CH_2Cl_2 (50.0 mL). The combined organic phase was concentrated under reduced pressure to give a residue which was purified by a silica gel column chromatography (petroleum ether/ ethyl acetate = 10:1) to give the alkynoate products(**13**). A hot-oven dried Schlenk tube was charged with **13** (7.3 mmol, 2.12 g), TBAB (14.6 mmol, 4.7g), $K_2S_2O_8$ (10.95 mmol, 1.5 g) and DCE/H_2O = 1:1 (72 mL). The reaction mixture was stirred in an oil bath at 90 °C for 8 h. Then,

the crude reaction mixture was poured into water (40 mL) and extracted with EtOAc (3 × 40 mL). The volatiles were removed under reduced pressure, and the residue was purified on silica gel column chromatography (EtOAc/ petroleum ether, 1:70) to give a white solid(**10**) (1.6 g, 60%).[2]

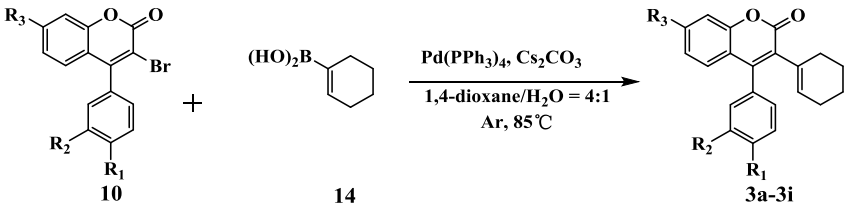
General procedure for the synthesis of 4-phenyl-3- aryl-2*H*-chromen-2-one derivatives (1)/4-phenyl-3- alkenyl-2*H*-chromen-2-one derivatives (3)



R_1 = H, CF_3, CN, OCH_3; R_2 = H, CF_3.



R_1 = H, CF_3; R_2 = H, CF_3.



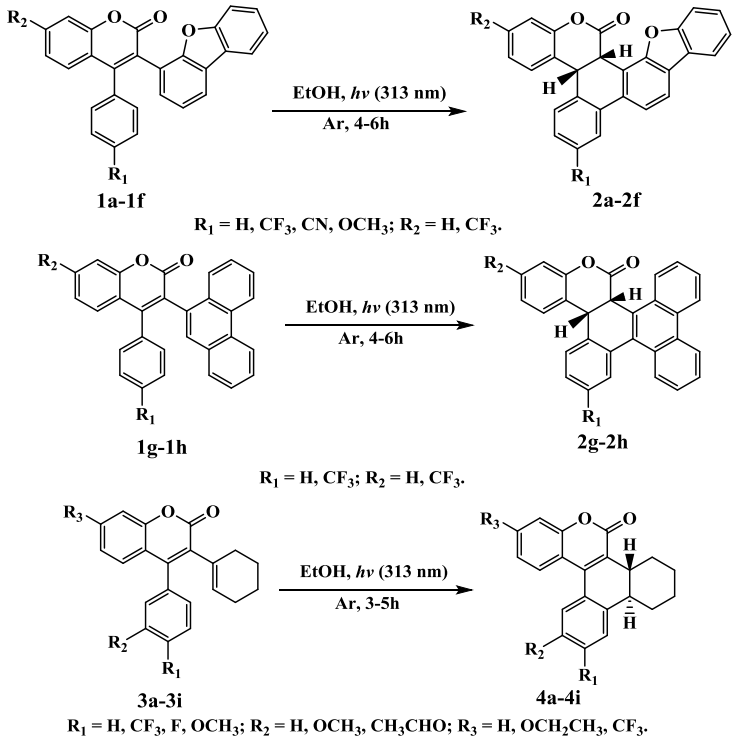
R_1 = H, CF_3, F, OCH_3; R_2 = H, OCH_3, CH_3CHO; R_3 = H, OCH_2CH_3, CF_3.

Scheme S3 Synthesis of 4-phenyl-3- aryl-2*H*-chromen-2-one derivatives(**1**)/4-phenyl-3-alkenyl-2*H*-chromen-2-one derivatives (**3**)

Synthesis of trans-1,2,3,4,4a,14b-hexahydro-5H-phenanthro[9,10-c]chromen-5-one (3a)

The mixture of 3-bromo-4-phenyl-2H-chromen-2-one **10a** (1 mmol) , cyclohex-1-en-1-ylboronic acid **14** (3 eq, 3 mmol), $Pd(PPh_3)_4$ (5% mmol, 57 mg) and Cs_2CO_3 (5 eq, 5 mmol, 1.6 g) was dissolved in a mixed solvent composed of 1,4-dioxane : H_2O = 4:1 (12 ml : 3 ml). The reaction mixture was stirred at 85 ℃ for 6.5-9 h under argon atmosphere. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature, and the volatiles were removed under reduced pressure. Then, the mixture was poured into the water and extracted with ethyl acetate (40 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel by column chromatography(EtOAc/petroleum ether, 1:60) to give **3a** in 76.3%. Analogously, **1** were prepared according to this methodology as described above, with yields 67−88%.

General procedure for the synthesis of cis-4b,15c-dihydro-16*H*- benzofuro[3',2':7,8]phenanthro[9,10-c]chromen-16-ones(2)/ cis-8c,14b-dihydro- 9*H*-benzo [11,12]chryseno[5,6-c]chromen-9-ones(2)/ trans-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-c]chromen-5-ones (4)



Scheme S4 Synthesis of cis-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro [9,10-c] chromen-16-ones(**2**)/cis-8c,14b-dihydro-9*H*-benzo[11,12]chryseno[5,6-c]chromen-9-ones (**2**)/trans-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-c]chromen-5-ones (**4**)

Synthesis of trans-1,2,3,4,4a,14b-hexahydro-5H-phenanthro[9,10-c]chromen-5-ones (4a)

Substrate 3-(cyclohex-1-en-1-yl)-4-phenyl-2H-chromen-2-one (**3a**) (150mg, 0.5 mmol) was dissolved in EtOH (100 mL) at ambient temperature in a quartz tube (100 mL). The solution was degassed (ultrasound) for 30 min, deaerated by bubbling argon for 30 min, irradiated with a lamp (30W, 313 nm) at room temperature until reactant was consumed completely as indicated by thin-layer chromatography(TLC). Then, the volatiles were removed under reduced pressure, and the residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:70) to give **4a** (135 mg, 90%). Analogously, compounds **2** were synthesized using the same methodology described above, with yields 33-93%.

3. UV absorption spectra of 1a and 3a.

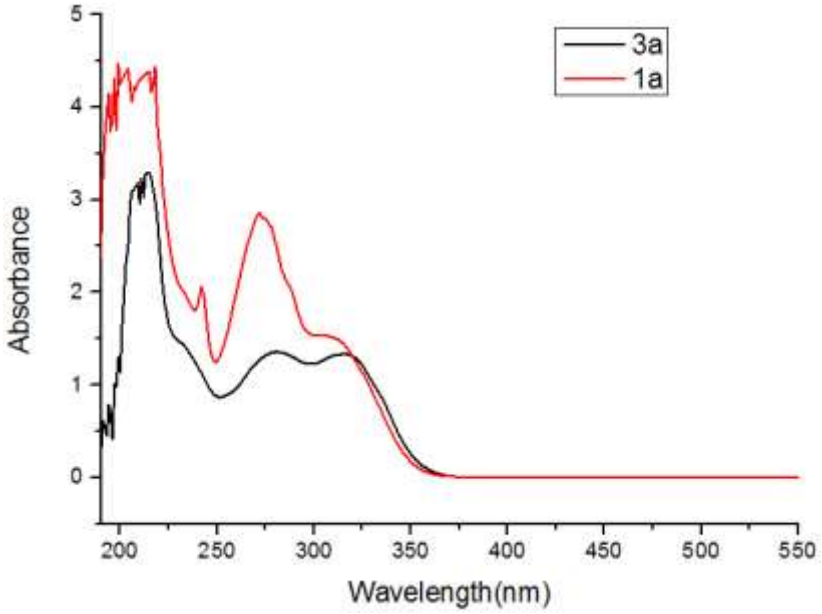


Figure S1. UV-visible absorption spectrum of **1a** and **3a** in EtOH solution(10^{-5} M).

4. X-ray Parameters and Structure of 4b

Table S1 Crystal and Structure Refinement Data for 4b

Identification code	**4b**
CCDC	2047431
Empirical formula	$C_{22}H_{17}F_3O_2$
Formula weight	370.35
Temperature/K	182.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.1778(10)
b/Å	11.4254(7)
c/Å	18.2577(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3374.7(4)
Z	8
ρ_{calc}g/cm^3	1.458

μ/mm^{-1}	0.115
F(000)	1536.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.462 to 52.754
Index ranges	-20 ≤ h ≤ 20, -14 ≤ k ≤ 14, -21 ≤ l ≤ 22
Reflections collected	59881
Independent reflections	3453 [R_{int} = 0.0456, R_{sigma} = 0.0163]
Data/restraints/parameters	3453/0/244
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0917
Final R indexes [all data]	R_1 = 0.0391, wR_2 = 0.0958
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.19

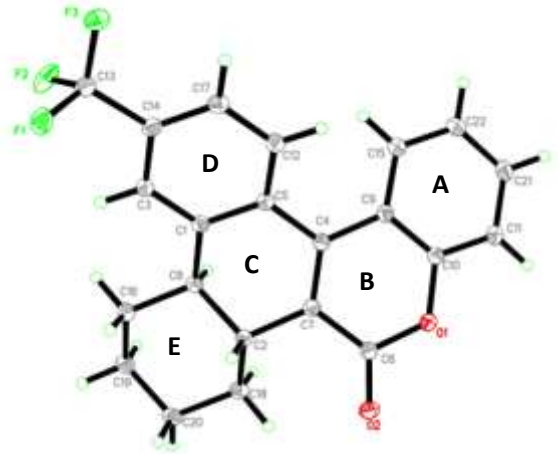


Figure S2 Thermal ellipsoid ORTEP diagram of **4b**

5. The atom coordinates for the optimized geometries of 2a and 2a'

2a

C	-1.29369	1.86299	-1.1671
C	-2.51091	0.94317	-1.39224
C	-0.18948	1.38705	-0.54119
C	-2.4829	-0.34369	-0.96249
C	-0.16582	-0.07933	-0.0582
C	-1.23274	-0.88931	-0.24857

C	2.16598	1.53024	-0.52769
C	2.30111	0.08972	-0.01323
C	1.09037	-0.56385	0.65858
O	0.9487	2.25865	-0.32514
O	3.11898	2.06516	-1.15156
C	1.18594	-2.12438	0.60969
C	-0.13462	-2.91597	0.70005
C	2.37028	-2.81821	0.49817
C	-0.12609	-4.26994	0.73742
C	2.37134	-4.35673	0.57813
C	1.20624	-5.03495	0.69128
C	3.66677	-0.58397	0.04034
C	3.707	-2.09163	0.28229
C	4.82601	0.08332	-0.11795
C	4.89927	-2.77108	0.29899
C	6.13773	-0.65792	-0.01439
C	6.22742	-1.99152	0.13987
C	6.44467	1.70085	-0.24483
C	7.19375	0.39673	-0.09761
C	7.11041	2.87369	-0.22895
C	8.65886	2.8353	-0.13283
C	9.32516	1.63678	-0.06221
C	8.53248	0.30953	-0.04124
O	4.9993	1.51053	-0.39847
H	-1.32078	2.8778	-1.50526
H	-3.38029	1.32091	-1.88857
H	-3.32953	-0.97886	-1.11955
H	-1.20781	-1.90242	0.09488
H	-1.06596	-2.39056	0.73868
H	-1.04871	-4.80802	0.80186
H	1.21208	-6.10355	0.74585
H	3.29729	-4.89152	0.53889
H	4.91113	-3.83344	0.42609
H	7.17404	-2.48997	0.15789
H	9.02856	-0.63649	0.02073
H	10.39416	1.62141	-0.01895
H	9.21236	3.75095	-0.12363
H	6.5859	3.80459	-0.28632
H	2.59794	0.39497	0.96843
H	1.03819	-0.24604	1.67897

Zero-point correction=	0.355722 (Hartree/Particle)
Thermal correction to Energy=	0.376218
Thermal correction to Enthalpy=	0.377163
Thermal correction to Gibbs Free Energy=	0.306578

Sum of electronic and zero-point Energies= -1263.868561
Sum of electronic and thermal Energies= -1263.848064
Sum of electronic and thermal Enthalpies= -1263.847120
Sum of electronic and thermal Free Energies= -1263.917705
B3LYP/6-31G(d, p)-SDD

2a'

C	-4.85798	5.45718	-1.01965
C	-3.40754	5.79567	-1.4141
C	-5.21042	4.18173	-0.74647
C	-2.46785	4.82033	-1.47525
C	-4.13972	3.07133	-0.84768
C	-2.8567	3.36135	-1.1645
C	-7.03029	2.58201	-0.80267
C	-6.078	1.38146	-0.78541
C	-4.6158	1.65769	-0.5785
O	-6.58165	3.88136	-0.36112
O	-8.20699	2.44128	-1.21785
C	-3.68479	0.50588	-0.19202
C	-2.41123	0.72717	0.21985
C	-4.24865	-0.91916	-0.28238
C	-1.4942	-0.47518	0.52453
C	-3.43464	-1.97732	-0.02391
C	-1.97291	-1.73899	0.39957
C	-6.57734	-0.07035	-0.87693
C	-5.739	-1.138	-0.66504
C	-8.02144	-0.36488	-1.27992
C	-6.27317	-2.59552	-0.80977
C	-8.47662	-1.61089	-1.34165
C	-7.58232	-2.82585	-1.12021
C	-10.23618	-0.22782	-1.69987
C	-9.94786	-1.51764	-1.62979
C	-11.68597	0.23111	-1.83876
C	-12.65485	-0.70966	-1.96971
C	-12.29111	-2.22459	-1.96563
C	-11.00143	-2.62244	-1.79886
O	-9.0468	0.61777	-1.62843
H	-5.58968	6.23888	-0.9598
H	-3.15064	6.79954	-1.63784
H	-1.46337	5.06389	-1.73813
H	-2.11576	2.59395	-1.20455
H	-2.03554	1.7277	0.33827
H	-0.4895	-0.31392	0.83738
H	-1.33489	-2.57427	0.60479

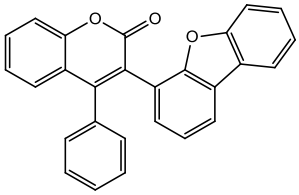
H	-3.805	-2.97278	-0.10689
H	-5.61064	-3.42276	-0.6673
H	-7.96816	-3.81507	-1.20497
H	-10.73114	-3.658	-1.77901
H	-13.05214	-2.96078	-2.08436
H	-13.67446	-0.40999	-2.07494
H	-11.92972	1.27514	-1.83936
H	-6.23028	1.34406	0.28082
H	-4.46369	1.46537	-1.62438

Zero-point correction= 0.355645 (Hartree/Particle)
Thermal correction to Energy= 0.376070
Thermal correction to Enthalpy= 0.377014
Thermal correction to Gibbs Free Energy= 0.306915
Sum of electronic and zero-point Energies= -1263.847672
Sum of electronic and thermal Energies= -1263.827248
Sum of electronic and thermal Enthalpies= -1263.826303
Sum of electronic and thermal Free Energies= -1263.896402
B3LYP/6-31G(d, p)-SDD

6. Characterization Data for Products

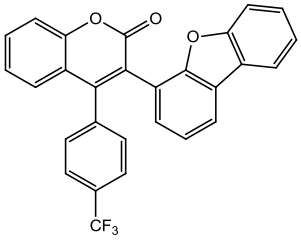
The data of 1a-1h, 3a-3i

3-(dibenzo[*b*,*d*]furan-4-yl)-4-phenyl-2*H*-chromen-2-one (1a)



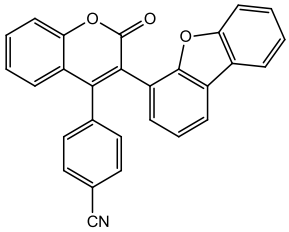
Yield: 88% (213 mg). White solid. m.p. 254.6-256.9° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.79 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.08 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 156.0, 154.0, 153.8, 153.7, 134.3, 131.8, 129.1, 128.7, 128.7, 128.5, 128.2, 127.9, 127.8, 127.1, 124.2, 124.1, 124.1, 122.7, 122.4, 120.7, 120.4, 118.8, 117.0, 111.6. HRMS (ESI) m/z calcd for. $C_{27}H_{16}O_3$ $[M+Na]^+$ 411.0992, found 411.0986.

3-(dibenzo[*b*,*d*]furan-4-yl)-4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-2-one (1b)



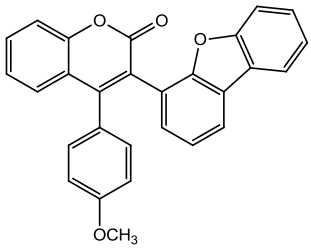
Yield: 86% (214 mg). White solid. m.p. 221.5-222.7° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.49 (dd, *J* = 17.9, 9.0 Hz, 3H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.23 (d, *J* = 5.7 Hz, 1H), 7.19 (d, *J* = 6.7 Hz, 1H), 7.15 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 156.0, 153.8, 153.7, 152.2, 138.1, 132.2, 130.7 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 129.2, 128.8, 127.4, 127.3, 125.2 (q, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.0 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 124.5, 124.3, 124.0, 123.0, 122.9, 122.6, 121.1, 121.1 (q, $^{1}J_{C\text{-}F}$ = 272.6 Hz), 120.8, 118.2, 117.2, 111.6. HRMS (ESI) m/z calcd for. $C_{28}H_{15}F_3O_3$ $[M+Na]^+$ 479.0866, found 479.0859.

4-(3-(dibenzo[*b*,*d*]furan-4-yl)-2-oxo-2*H*-chromen-4-yl)benzonitrile (1c)



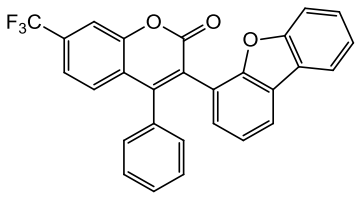
Yield: 84% (217 mg). White solid. m.p. 285.1-287.8° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.80 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.38 (dd, *J* = 8.7, 7.7 Hz, 3H), 7.32 – 7.25 (m, 3H), 7.22 – 7.14 (m, 3H), 7.08 (dd, *J* = 8.0, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 155.8, 153.7, 153.6, 151.6, 139.1, 132.4, 131.9, 131.8, 129.7, 129.6, 128.8, 127.5, 127.1, 124.6, 124.4, 123.9, 123.0, 123.0, 122.7, 121.3, 120.9, 119.5, 117.3, 112.6, 111.5. HRMS (ESI) m/z calcd for. $C_{28}H_{15}NO_3$ $[M+Na]^+$ 436.0944, found 436.0945.

3-(dibenzo[*b*,*d*]furan-4-yl)-4-(4-methoxyphenyl)-2*H*-chromen-2-one (1d)



Yield: 84% (207 mg). Yellow solid. m.p. 209.1-211.3° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.79 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 7.13 – 7.02 (m, 2H), 6.74 (d, J = 7.5 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 159.6, 156.0, 154.1, 153.7, 131.8, 130.2, 129.1, 128.0, 127.1, 126.4, 124.2, 122.7, 122.5, 122.4, 120.7, 120.6, 119.1, 117.0, 113.6, 113.6, 113.4, 111.7, 105.4, 55.1. HRMS (ESI) m/z calcd for. $C_{28}H_{18}O_4$ $[M+Na]^+$ 441.1097, found 441.1094.

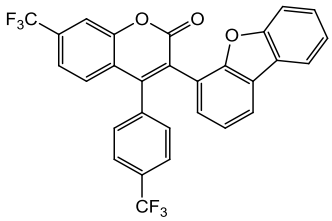
3-(dibenzo[*b*,*d*]furan-4-yl)-4-phenyl-7-(trifluoromethyl)-2*H*-chromen-2-one (1e)



Yield: 84% (204 mg). Yellow solid. m.p. 229.0-231.8° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.78 (dd, *J* = 5.3, 3.6 Hz, 1H), 7.70 (s, 1H), 7.47 – 7.36 (m, 4H), 7.29 – 7.20 (m, 2H), 7.18 – 7.07 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 156.0, 153.8, 153.3, 152.7, 133.6, 133.4 (q, $^{2}J_{C\text{-}F}$ = 33.3Hz), 129.0, 128.8, 128.8, 128.6, 128.4, 128.1, 127.4, 124.7, 124.3, 124.0, 123.3 (q, $^{1}J_{C\text{-}F}$ = 272.7

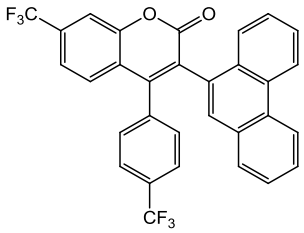
Hz), 123.2, 122.9, 122.5, 121.1, 120.7 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 118.2, 114.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 111.6. HRMS (ESI) m/z calcd for. $C_{28}H_{15}F_3O_3$ $[M+Na]^+$ 479.0866, found 479.0856.

3-(dibenzo[*b*,*d*]furan-4-yl)-7-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-2-one (1f)



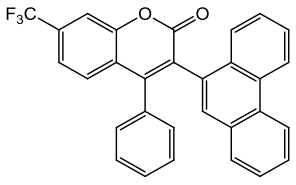
Yield: 83% (227 mg). White solid. m.p. 220.2-224.5° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 13.6, 7.6 Hz, 2H), 7.73 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.35 – 7.27 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 155.9, 153.6, 153.3, 151.0, 137.3, 133.7 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 131.1 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 129.2, 128.6, 128.3, 127.5, 125.5 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 125.2, 124.5, 123.8, 123.5 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 123.1 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 123.0, 122.6, 120.9 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 120.8, 117.5, 114.5 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 111.6, 104.0, 101.2. HRMS (ESI) m/z calcd for. $C_{29}H_{14}F_6O_3$ $[M+Na]^+$ 547.0739, found 547.0740.

3-(phenanthren-9-yl)-7-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-2-one (1g)



Yield: 79% (210 mg). Yellow solid. m.p. 252.0-255.5° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 8.6, 1.2 Hz, 2H), 7.61 – 7.53 (m, 3H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.27 (dd, *J* = 10.9, 6.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 153.3, 151.0, 137.3, 133.7 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 131.0 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 130.9, 130.6, 130.5, 130.4, 129.6, 129.3, 129.0, 128.8, 128.4, 128.0, 127.5, 127.1, 127.0, 126.8, 125.8 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 125.4, 125.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 123.5 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 123.3, 123.2 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 122.6, 121.0 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 114.6 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz). HRMS (ESI) m/z calcd for. $C_{31}H_{16}F_6O_2$ $[M+Na]^+$ 557.0947, found 557.0946.

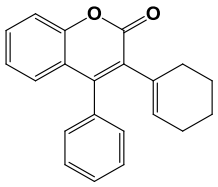
3-(phenanthren-9-yl)-4-phenyl-7-(trifluoromethyl)-2*H*-chromen-2-one (1h)



Yield: 81% (219 mg). Yellow solid. m.p. 222.7-226.5° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 7.81 (dd, *J* = 7.5, 6.6 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.69 – 7.57 (m, 3H), 7.56 – 7.49 (m, 2H), 7.47 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.06 – 6.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 153.3, 152.7, 133.6, 133.4 (q, $^{2}J_{C\text{-}F}$ = 34.3 Hz), 131.0, 130.8, 130.5, 130.3, 130.2, 129.7, 128.9, 128.8,

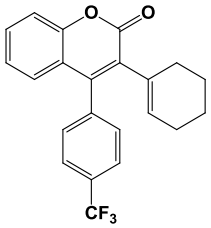
128.7, 128.6, 128.4, 128.2, 127.5, 127.2, 126.9, 126.7, 126.6, 125.7, 123.3 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 123.1, 122.5, 120.8 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 114.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz). HRMS (ESI) m/z calcd for. $C_{30}H_{17}F_3O_2$ $[M+Na]^+$ 489.1073, found 489.1067.

3-(cyclohex-1-en-1-yl)-4-phenyl-2*H*-chromen-2-one (3a)



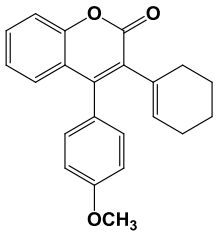
Yield: 85% (232 mg). White solid. m.p. 112.3-114.0 ° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 5H), 7.22 (d, *J* = 6.4 Hz, 2H), 7.13 (q, *J* = 7.8 Hz, 2H), 5.44 (s, 1H), 2.05 (s, 2H), 1.88 (d, *J* = 3.2 Hz, 2H), 1.56 – 1.49 (m, 2H), 1.46 – 1.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 152.9, 150.5, 135.2, 132.0, 130.9, 130.8, 129.9, 128.6, 128.3, 128.1, 127.6, 123.9, 120.7, 116.6, 28.6, 25.2, 22.4, 21.6. HRMS (ESI) m/z calcd for. $C_{21}H_{18}O_2$ $[M+Na]^+$ 325.1199, found 325.1195.

3-(cyclohex-1-en-1-yl)-4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-2-one (3b)



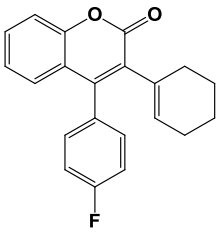
Yield: 83% (216 mg). Yellow solid. m.p. 158.6-162.1° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.44 (s, 1H), 2.08 (s, 2H), 1.87 (d, *J* = 2.9 Hz, 2H), 1.55 (dd, *J* = 11.0, 5.6 Hz, 2H), 1.44 (dd, *J* = 11.1, 5.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 152.9, 148.9, 139.0, 131.9, 131.4, 131.2, 130.5 (q, $^{2}J_{C\text{-}F}$ = 34.3 Hz), 129.2, 127.1, 125.2 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 124.1, 123.9 (q, $^{1}J_{C\text{-}F}$ =272.7 Hz), 122.6, 120.0, 116.8, 28.6, 25.1, 22.3, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3O_2$ $[M+Na]^+$ 393.1073, found 393.1072.

3-(cyclohex-1-en-1-yl)-4-(4-methoxyphenyl)-2*H*-chromen-2-one (3c)



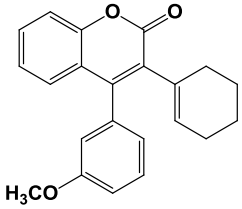
Yield: 92% (227 mg). White solid. m.p. 104.3-106.5° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 8.6, 7.0, 1.8 Hz, 1H), 7.34 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.20 – 7.10 (m, 4H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.50 – 5.43 (m, 1H), 3.88 (s, 3H), 2.08 – 2.00 (m, 2H), 1.93 (dt, *J* = 6.0, 3.0 Hz, 2H), 1.58 – 1.51 (m, 2H), 1.50 – 1.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 159.5, 152.9, 150.3, 132.1, 130.8, 130.6, 130.1, 129.8, 127.6, 127.2, 123.9, 120.9, 116.5, 113.6, 55.3, 28.5, 25.2, 22.5, 21.6. HRMS (ESI) m/z calcd for. $C_{22}H_{20}O_3$ $[M+Na]^+$ 355.1305, found 355.1308.

3-(cyclohex-1-en-1-yl)-4-(4-fluorophenyl)-2*H*-chromen-2-one (3d)



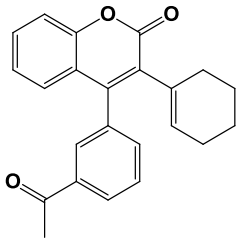
Yield: 93% (256 mg). White solid. m.p. 159.9-164.4° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.16 (t, *J* = 8.0 Hz, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 5.44 (d, *J* = 1.5 Hz, 1H), 2.04 (s, 2H), 1.91 (d, *J* = 2.0 Hz, 2H), 1.58 – 1.50 (m, 2H), 1.46 (dd, *J* = 10.8, 5.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ162.5 (d, $^{1}J_{C\text{-}F}$ = 249.5 Hz), 160.7, 152.9, 149.5, 132.0, 131.1, 131.0, 131.0, 130.5 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 130.3, 127.3, 124.0, 120.6, 116.7, 115.4 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 28.6, 25.2, 22.4, 21.6. HRMS (ESI) m/z calcd for. $C_{21}H_{17}FO_2$ $[M+Na]^+$ 343.1105, found 343.1101.

3-(cyclohex-1-en-1-yl)-4-(3-methoxyphenyl)-2*H*-chromen-2-one (3e)



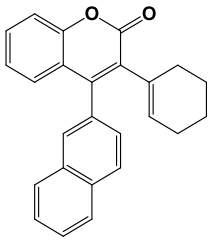
Yield: 91% (246 mg). White solid. m.p. 106.5-108.2° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (ddd, *J* = 8.5, 6.7, 2.1 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.16 – 7.09 (m, 2H), 6.94 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.77 (dd, *J* = 13.0, 4.4 Hz, 2H), 5.45 (s, 1H), 3.81 (s, 3H), 2.06 (s, 2H), 1.88 (d, *J* = 3.3 Hz, 2H), 1.53 (dd, *J* = 9.6, 5.2 Hz, 2H), 1.44 (dd, *J* = 11.1, 5.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 159.4, 152.9, 150.3, 136.4, 132.1, 130.9, 130.6, 129.7, 129.3, 127.6, 124.0, 121.1, 120.6, 116.6, 114.3, 113.80, 55.4, 28.6, 25.2, 22.5, 21.6. HRMS (ESI) m/z calcd for. $C_{22}H_{20}O_3$ $[M+Na]^+$ 355.1305, found 355.1301.

4-(3-acetylphenyl)-3-(cyclohex-1-en-1-yl)-2*H*-chromen-2-one (3f)



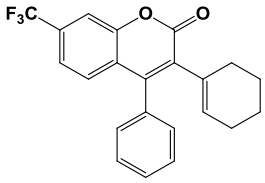
Yield: 90% (243 mg). White solid. m.p. 136.4-142.1° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 1H), 7.83 (t, *J* = 1.5 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.34 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.03 (dd, *J* = 8.0, 1.4 Hz, 1H), 5.44 – 5.38 (m, 1H), 2.61 (s, 3H), 2.06 – 1.99 (m, 2H), 1.85 – 1.79 (m, 2H), 1.49 (dt, *J* = 8.4, 6.0 Hz, 2H), 1.40 – 1.35 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 160.6, 152.9, 149.3, 137.0, 135.6, 133.3, 132.0, 131.2, 131.2, 130.3, 128.6, 128.6, 128.3, 127.2, 124.1, 120.2, 116.8, 28.6, 26.7, 25.2, 22.3, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{20}O_3$ $[M+Na]^+$ 367.1305, found 367.1306.

3-(cyclohex-1-en-1-yl)-4-(naphthalen-2-yl)-2*H*-chromen-2-one (3g)



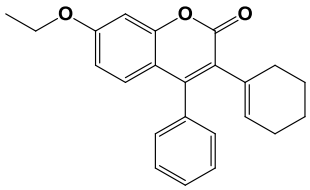
Yield: 92% (243 mg). Yellow solid. m.p. 199.2-203.1° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.8, 4.4 Hz, 2H), 7.89 – 7.83 (m, 1H), 7.72 (s, 1H), 7.58 – 7.52 (m, 2H), 7.46 (ddd, *J* = 8.5, 6.9, 1.8 Hz, 1H), 7.38 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.10 (dtd, *J* = 9.2, 8.0, 1.4 Hz, 2H), 5.53 – 5.45 (m, 1H), 2.12 (dd, *J* = 4.5, 1.8 Hz, 2H), 1.80 (td, *J* = 5.8, 3.2 Hz, 2H), 1.50 (dt, *J* = 11.9, 6.0 Hz, 2H), 1.36 (dt, *J* = 11.4, 5.8 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 153.0, 150.4, 132.9, 132.8, 132.6, 132.1, 131.0, 130.9, 130.2, 128.1, 127.9, 127.9, 127.7, 126.7, 126.7, 126.6, 124.0, 120.7, 116.7, 28.7, 25.2, 22.4, 21.6. HRMS (ESI) m/z calcd for. $C_{25}H_{20}O_2$ $[M+Na]^+$ 375.1356, found 375.1358.

3-(cyclohex-1-en-1-yl)-4-phenyl-7-(trifluoromethyl)-2*H*-chromen-2-one (3h)



Yield: 95% (245 mg). White solid. m.p. 125.8-130.4° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.9 Hz, 1H), 7.45 (dd, *J* = 12.5, 4.3 Hz, 3H), 7.35 (t, *J* = 8.6 Hz, 1H), 7.23 (dt, *J* = 17.8, 6.9 Hz, 4H), 5.46 (d, *J* = 2.1 Hz, 1H), 2.04 (s, 2H), 1.88 (s, 2H), 1.53 (d, *J* = 5.5 Hz, 2H), 1.43 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 152.5, 149.4, 134.4, 132.5 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 131.9, 131.7, 131.3, 128.7, 128.5, 128.4, 123.5, 123.3(q, $^1J_{C\text{-}F}$ = 273.7 Hz), 120.4 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 113.9 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 28.4, 25.1, 22.3, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3O_2$ $[M+Na]^+$ 393.1073, found 393.1066.

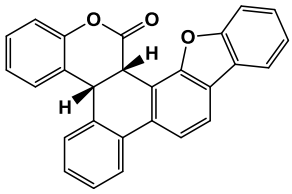
3-(cyclohex-1-en-1-yl)-7-ethoxy-4-phenyl-2*H*-chromen-2-one (3i)



Yield: 90% (233 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H), 7.19 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.44 – 5.35 (m, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 2.03 (dd, *J* = 7.8, 5.9 Hz, 2H), 1.85 (dt, *J* = 6.0, 3.6 Hz, 2H), 1.51 (ddd, *J* = 11.9, 6.0, 2.4 Hz, 2H), 1.45 – 1.37 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 161.4, 154.5, 150.9, 135.5, 132.1, 130.6, 128.6, 128.5, 128.1, 128.1, 126.5, 114.0, 112.4, 101.0, 64.1, 28.7, 25.2, 22.5, 21.6, 14.6. HRMS (ESI) m/z calcd for. $C_{23}H_{22}O_3$ $[M+Na]^+$ 369.1461, found 369.1460.

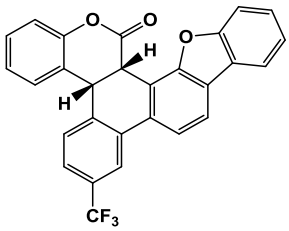
The data of 2a-2h, 4a-4i

cis-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromen-16-one (2a)



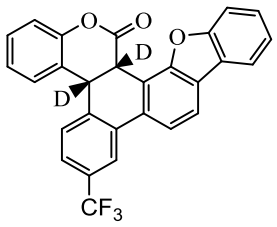
Yield: 58% (56 mg). White solid. m.p. 309.8-310.6° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.90 (dd, *J* = 12.1, 8.0 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.46 (dd, *J* = 13.5, 5.8 Hz, 3H), 7.38 (q, *J* = 6.9 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.21 (dd, *J* = 15.7, 7.8 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 4.81 (d, *J* = 6.4 Hz, 1H), 4.48 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 156.8, 154.5, 151.6, 133.9, 133.8, 132.8, 130.1, 129.5, 128.5, 128.3, 127.4, 127.1, 125.1, 124.6, 124.4, 124.1, 123.6, 123.1, 120.8, 119.1, 117.8, 115.4, 111.8, 39.6, 38.6. HRMS (ESI) m/z calcd for. $C_{27}H_{16}O_3$ $[M+Na]^+$ 411.0992, found 411.0991.

cis-7-(trifluoromethyl)-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromen-16-one (2b)



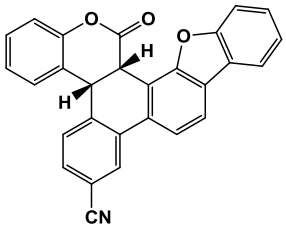
Yield: 63% (72 mg). White solid. m.p. 289.1-292.8° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.41 (ddd, *J* = 23.7, 16.5, 8.5 Hz, 6H), 7.23 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.85 (d, *J* = 6.6 Hz, 1H), 4.50 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 156.9, 154.4, 151.5, 137.5, 134.8, 131.3, 130.9 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 130.0, 129.9, 127.8, 127.8, 124.9, 124.7 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 124.1, 124.0 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 123.3, 122.7, 121.9 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 121.1, 121.0, 119.2, 118.0, 115.6, 39.6, 38.3. HRMS (ESI) m/z calcd for. $C_{28}H_{15}F_3O_3$ $[M+Na]^+$ 479.0866, found 479.0871.

cis-7-(trifluoromethyl)-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromen-16-one-4b,15c-d_2 (2b-2D)



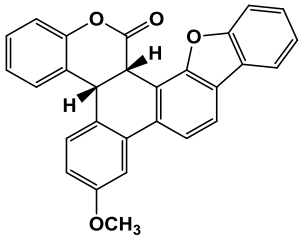
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.32 (m, 6H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H).

cis-16-oxo-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromene-7-carbonitrile (2c)



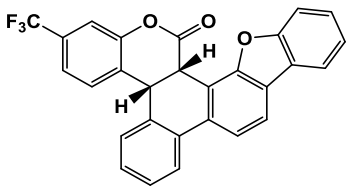
Yield: 59% (62 mg). Brown solid. m.p. 318.3-319.8° C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.21 (s, 1H), 8.10 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.57 – 7.46 (m, 5H), 7.40 (td, J = 7.2, 2.9 Hz, 2H), 7.26 (s, 1H), 7.00 (d, J = 8.0 Hz, 1H), 4.92 (d, J = 6.8 Hz, 1H), 4.54 (d, J = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 169.7, 157.0, 154.3, 151.0, 139.2, 135.4, 130.3, 130.1, 130.0, 128.8, 128.3, 128.2, 125.7, 125.6, 123.8, 123.5, 122.0, 121.6, 121.1, 119.2, 118.2, 115.7, 114.7, 112.9, 111.9, 111.6, 39.4, 38.3. HRMS (ESI) m/z calcd for. $C_{28}H_{15}NO_3$ $[M+Na]^+$ 436.0944, found 436.0942.

cis-7-methoxy-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromen-16-one (2d)



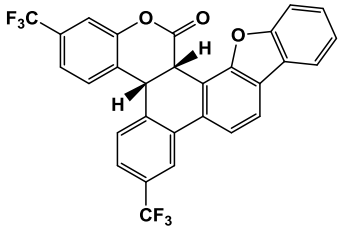
Yield: 44% (46 mg). Red solid. m.p. 235.8-241.4° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.48 – 7.41 (m, 4H), 7.36 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 6.79 – 6.66 (m, 2H), 4.78 (d, J = 6.2 Hz, 1H), 4.41 (d, J = 6.2 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 159.8, 156.8, 154.6, 151.6, 135.1, 132.7, 130.0, 129.4, 128.3, 127.4, 126.0, 124.6, 124.4, 124.2, 123.9, 123.1, 120.8, 120.7, 119.2, 117.8, 115.8, 113.4, 111.8, 111.0, 55.4, 39.1, 38.8. HRMS (ESI) m/z calcd for. $C_{28}H_{18}O_4$ $[M+Na]^+$ 441.1097, found 441.1084.

cis-2-(trifluoromethyl)-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromen-16-one (2e)



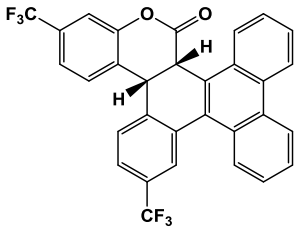
Yield: 61% (70 mg). White solid. m.p. 311.9-316.3° C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.06 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.62 (q, J = 7.9 Hz, 2H), 7.54 (d, J = 8.2 Hz, 1H), 7.48 (dd, J = 11.9, 4.5 Hz, 2H), 7.41 (dt, J = 15.5, 7.6 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 7.7 Hz, 1H), 4.85 (d, J = 6.4 Hz, 1H), 4.57 (d, J = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 169.5, 156.8, 154.4, 151.2, 133.8, 132.5, 132.3 (q, $^2J_{C-F}$ = 34.3 Hz), 132.3, 130.8, 129.0, 128.6, 127.7, 126.8, 125.3, 124.4, 124.1, 123.4 (q, $^1J_{C-F}$ = 273.3 Hz), 121.9 (q, $^3J_{C-F}$ = 4.0 Hz), 121.3, 120.9, 119.3, 115.7, 115.3 (q, $^3J_{C-F}$ = 4.0 Hz), 113.9, 112.9, 111.8, 39.3, 38.4. HRMS (ESI) m/z calcd for. $C_{28}H_{15}F_3O_3$ $[M+Na]^+$ 479.0866, found 479.0860.

cis-2,7-bis(trifluoromethyl)-4b,15c-dihydro-16*H*-benzofuro[3',2':7,8]phenanthro[9,10-*c*]chromen-16-one (2f)



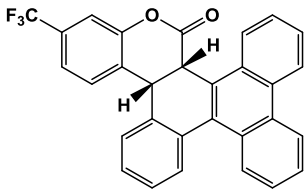
Yield: 67% (88 mg). White solid. m.p. 249.2-255.0° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.61 (q, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.86 (d, *J* = 6.5 Hz, 1H), 4.58 (d, *J* = 6.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 156.9, 154.3, 151.7, 136.4, 134.8, 132.5 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 131.3 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 131.1, 130.7, 127.9, 127.5, 126.8, 125.1, 124.9 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 124.0, 123.4, 123.9 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 123.3 (q, $^{1}J_{C\text{-}F}$ = 237.7 Hz), 122.1 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 121.6 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 121.4, 121.1, 119.3, 115.4 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 114.9, 111.9, 39.5, 38.0. HRMS (ESI) m/z calcd for. $C_{29}H_{14}F_6O_3$ $[M+Na]^+$ 547.0739, found 547.0744.

cis-12,17-bis(trifluoromethyl)-8c,14b-dihydro-9*H*-benzo[11,12]chryseno[5,6-*c*]chromen-9-one (2g)



Yield: 64% (86 mg). White solid. m.p. 269.8-275.4° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.66 – 7.58 (m, 2H), 7.52 (td, *J* = 7.6, 1.5 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.01 (td, *J* = 7.6, 0.9 Hz, 1H), 6.94 (s, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 4.76 (d, *J* = 5.9 Hz, 1H), 4.21 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 153.7, 143.0, 141.3, 134.3, 134.1, 133.6, 133.2(q, $^{2}J_{C\text{-}F}$ = 34.3 Hz), 132.6, 132.3(q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 131.7, 130.1, 129.1, 128.3, 128.3, 128.1, 127.8, 127.6, 127.2, 126.0, 125.1, 124.5 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 123.9, 123.6 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 123.4 (q, $^{1}J_{C\text{-}F}$ = 274.7 Hz), 120.9 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 120.8 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 115.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 42.4, 36.6. HRMS (ESI) m/z calcd for. $C_{31}H_{16}F_6O_2$ $[M+Na]^+$ 557.0947, found 557.0938.

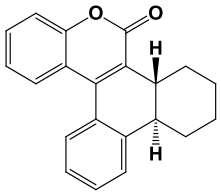
cis-12-(trifluoromethyl)-8c,14b-dihydro-9*H*-benzo[11,12]chryseno[5,6-*c*]chromen-9-one (2h)



Yield: 61% (71 mg). Yellow solid. m.p. 237.5-244.5° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.78 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 15.0, 8.2 Hz, 2H), 7.55 – 7.38 (m, 4H), 7.17 (dd, *J* = 13.0, 6.8 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 5.8 Hz, 1H), 4.21 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$)

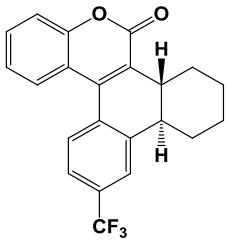
δ 161.1, 153.7, 144.3, 140.0, 134.9, 134.4, 134.3, 132.8 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 132.5, 130.9, 130.2, 129.4, 128.6, 128.0, 127.9, 127.9, 127.7, 127.5, 127.4, 126.7, 126.5, 126.1, 124.8, 123.6, 123.3 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 120.5 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 115.1 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 42.5, 36.6. HRMS (ESI) m/z calcd for. $C_{30}H_{17}F_3O_2$ $[M+Na]^+$ 489.1073, found 489.1065.

trans-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4a)



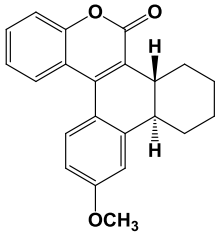
Yield: 90% (106 mg). Yellow solid. m.p. 139.3-143.9 ° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.33 (s, 2H), 7.27 (d, *J* = 9.1 Hz, 1H), 3.40 (d, *J* = 14.6 Hz, 1H), 2.47 (dd, *J* = 20.6, 10.8 Hz, 2H), 2.39 – 2.26 (m, 1H), 1.95 (dd, *J* = 11.2, 8.9 Hz, 2H), 1.56 (dt, *J* = 21.5, 10.8 Hz, 1H), 1.43 (p, *J* = 12.1 Hz, 2H), 1.28 – 1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 153.5, 145.8, 141.9, 130.4, 130.3, 130.0, 127.6, 127.1, 126.8, 125.9, 124.1, 123.6, 117.9, 117.0, 41.0, 39.9, 29.2, 28.9, 26.2, 25.9. HRMS (ESI) m/z calcd for. $C_{21}H_{18}O_2$ $[M+Na]^+$ 325.1199, found 325.1200.

trans-13-(trifluoromethyl)-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4b)



Yield: 93% (119 mg). Yellow solid. m.p. 175.8-178.8° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.69 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 3.42 (d, *J* = 13.4 Hz, 1H), 2.50 (t, *J* = 12.6 Hz, 2H), 2.35 (t, *J* = 12.3 Hz, 1H), 2.10 – 1.86 (m, 2H), 1.71 – 1.53 (m, 1H), 1.45 (t, *J* = 10.5 Hz, 2H), 1.26 (dd, *J* = 16.3, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 153.5, 144.4, 142.8, 133.2, 131.8 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 130.8, 128.2, 127.7, 126.5, 124.0 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 123.9, 122.9 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 121.1 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 117.4, 117.2, 40.9, 39.9, 29.1, 28.8, 26.1, 25.7. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3O_2$ $[M+Na]^+$ 393.1073, found 393.1074.

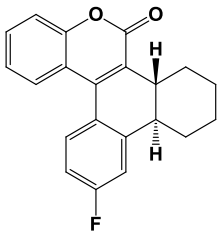
trans-13-methoxy-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4c)



Yield: 87% (124 mg). White solid. m.p. 154.0-157.4° C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.50 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.00 (d, *J* = 1.6 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.91 (s, 3H), 3.44 (d, *J* = 14.6 Hz, 1H),

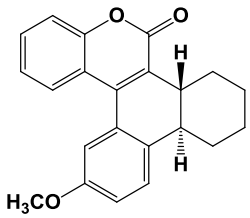
2.45 (dd, *J* = 17.7, 7.2 Hz, 2H), 2.35 (td, *J* = 12.6, 3.4 Hz, 1H), 2.02 – 1.92 (m, 2H), 1.55 (dt, *J* = 12.6, 8.9 Hz, 1H), 1.44 (dd, *J* = 20.6, 11.1 Hz, 2H), 1.27 – 1.23 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4, 159.9, 153.5, 145.8, 144.3, 130.3, 129.4, 127.1, 124.8, 123.5, 123.0, 118.1, 117.0, 110.8, 110.3, 55.4, 41.0, 39.8, 29.3, 28.9, 26.2, 25.9. HRMS (ESI) m/z calcd for. $C_{22}H_{20}O_3$ $[M+Na]^+$ 355.1305, found 355.1304.

trans-13-fluoro-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4d)



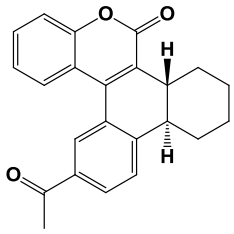
Yield: 89% (114 mg). White solid. m.p. 137.4-141.8° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.03 (td, *J* = 8.4, 2.5 Hz, 1H), 3.42 (d, *J* = 14.2 Hz, 1H), 2.43 (dd, *J* = 19.8, 11.2 Hz, 2H), 2.36 – 2.28 (m, 1H), 1.97 (dd, *J* = 17.8, 6.2 Hz, 2H), 1.56 – 1.48 (m, 1H), 1.43 (t, *J* = 10.7 Hz, 2H), 1.22 (dd, *J* = 11.7, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1(d, $^1J_{C\text{-}F}$ = 252.5 Hz), 159.6, 153.5, 145.2 (d, $^3J_{C\text{-}F}$ = 8.1Hz), 145.0, 130.6, 130.0(d, $^3J_{C\text{-}F}$ = 8.1Hz), 126.8, 126.2, 126.1, 123.7, 117.7, 117.1, 112.7(d, $^2J_{C\text{-}F}$ = 22.2 Hz), 111.9 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 40.9, 39.8, 29.2, 28.9, 26.1, 25.7. HRMS (ESI) m/z calcd for. $C_{21}H_{17}FO_2$ $[M+Na]^+$ 343.1105, found 343.1104.

trans-12-methoxy-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4e)



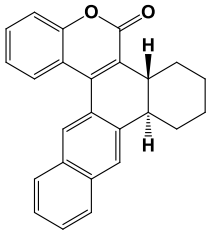
Yield: 87% (118 mg). White solid. m.p. 177.2-181.3° C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.22 (t, *J* = 8.3 Hz, 3H), 7.00 (p, *J* = 3.8 Hz, 1H), 3.80 (s, 3H), 3.33 (d, *J* = 13.4 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.59 (td, *J* = 12.4, 3.3 Hz, 1H), 2.44 (td, *J* = 12.1, 3.7 Hz, 1H), 1.94 – 1.7 5 (m, 3H), 1.46 – 1.36 (m, 1H), 1.27 (dd, *J* = 8.2, 4.8 Hz, 1H), 1.18 – 1.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 158.4, 153.4, 146.1, 132.7, 130.2, 128.7, 127.5, 127.2, 126.7, 123.4, 121.1, 118.3, 116.9, 115.1, 56.1, 43.1, 40.3, 30.7, 29.6, 27.1, 26.0. HRMS (ESI) m/z calcd for. $C_{22}H_{20}FO_3$ $[M+Na]^+$ 355.1305, found355.1312.

trans-12-acetyl-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4f)



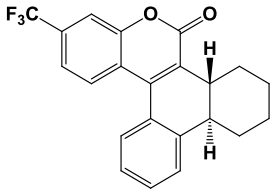
Yield: 82% (109 mg). Yellow solid. m.p. 149.6-153.2° C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.6 Hz, 1H), 8.05 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.40 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.33 – 7.28 (m, 1H), 3.45 – 3.39 (m, 1H), 2.62 (s, 3H), 2.50 (dd, *J* = 17.3, 7.4 Hz, 2H), 2.35 (td, *J* = 12.3, 3.5 Hz, 1H), 2.00 (d, *J* = 7.7 Hz, 1H), 1.95 (d, *J* = 6.1 Hz, 1H), 1.59 (dd, *J* = 12.5, 3.6 Hz, 1H), 1.46 – 1.40 (m, 2H), 1.24 – 1.20 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 159.5, 153.5, 147.2, 145.0, 135.1, 130.8, 130.4, 130.2, 127.3, 127.2, 126.6, 124.5, 124.0, 117.6, 117.2, 41.3, 39.8, 29.2, 28.9, 26.6, 26.1, 25.8. HRMS (ESI) m/z calcd for. $C_{23}H_{20}O_3$ $[M+Na]^+$ 367.1305, found 367.1307.

trans-6b,7,8,9,10,10a-hexahydro-6*H*-tetrapheno[5,6-*c*]chromen-6-one (4g)



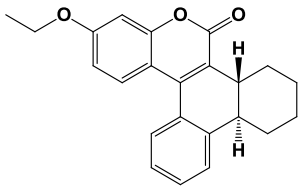
Yield: 80.0% (102.4mg). Yellow solid. m.p. 211.7-215.6° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 11.9, 8.2 Hz, 2H), 7.79 (s, 1H), 7.51 (dt, *J* = 14.8, 7.1 Hz, 3H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 3.43 (d, *J* = 12.0 Hz, 1H), 2.65 – 2.51 (m, 2H), 2.36 (td, *J* = 11.9, 3.3 Hz, 1H), 2.06 – 1.92 (m, 2H), 1.64 (d, *J* = 4.1 Hz, 1H), 1.47 (t, *J* = 10.3 Hz, 2H), 1.24 (dd, *J* = 10.7, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 153.5, 145.9, 139.1, 134.1, 131.4, 130.5, 128.5, 127.7, 127.7, 127.6, 127.5, 127.2, 127.1, 126.1, 123.7, 122.7, 118.1, 117.1, 41.4, 40.2, 29.3, 29.0, 26.2, 25.9. HRMS (ESI) m/z calcd for. $C_{25}H_{20}O_2$ $[M+Na]^+$ 375.1356, found 375.1359.

trans-8-(trifluoromethyl)-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4h)



Yield: 91.0% (112.2mg). White solid. m.p. 164.4-168.3° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.39 (dd, *J* = 14.5, 7.2 Hz, 3H), 7.28 (t, *J* = 6.7 Hz, 1H), 3.28 (d, *J* = 12.5 Hz, 1H), 2.38 (dd, *J* = 22.8, 12.0 Hz, 2H), 2.25 (t, *J* = 12.2 Hz, 1H), 1.88 (d, *J* = 13.8 Hz, 2H), 1.53 – 1.43 (m, 1H), 1.40 – 1.28 (m, 2H), 1.18 – 1.11 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 153.1, 144.8, 141.8, 132.1 (q, $^{2}J_{C\text{-}F}$ =33.3 Hz), 130.8, 129.4, 128.8, 127.9, 127.3, 126.1, 124.3, 123.3 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 120.7, 120.0 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 114.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 40.8, 40.0, 29.0, 28.9, 26.2, 25.8. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3O_2$ $[M+Na]^+$ 393.1073, found 393.1069.

trans-8-ethoxy-1,2,3,4,4a,14b-hexahydro-5*H*-phenanthro[9,10-*c*]chromen-5-one (4i)



Yield: 88.0% (105.5mg). White solid. m.p. 151.4-153.6° C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 6.85 – 6.77 (m, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.39 (d, *J* = 13.8 Hz, 1H), 2.42 (dd, *J* = 26.4, 12.8 Hz, 2H), 2.31 – 2.22 (m, 1H), 2.00 – 1.87 (m, 2H), 1.56 – 1.38 (m, 6H), 1.21 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 160.1, 155.2, 146.0, 142.1, 130.2, 130.2, 128.1, 127.6, 125.8, 124.0, 123.5, 112.0, 111.1, 101.3, 64.1, 41.0, 39.7, 29.3, 29.0, 26.2, 25.9, 14.6. HRMS (ESI) m/z calcd for. $C_{23}H_{22}O_3$ $[M+Na]^+$ 369.1461, found 369.1463.

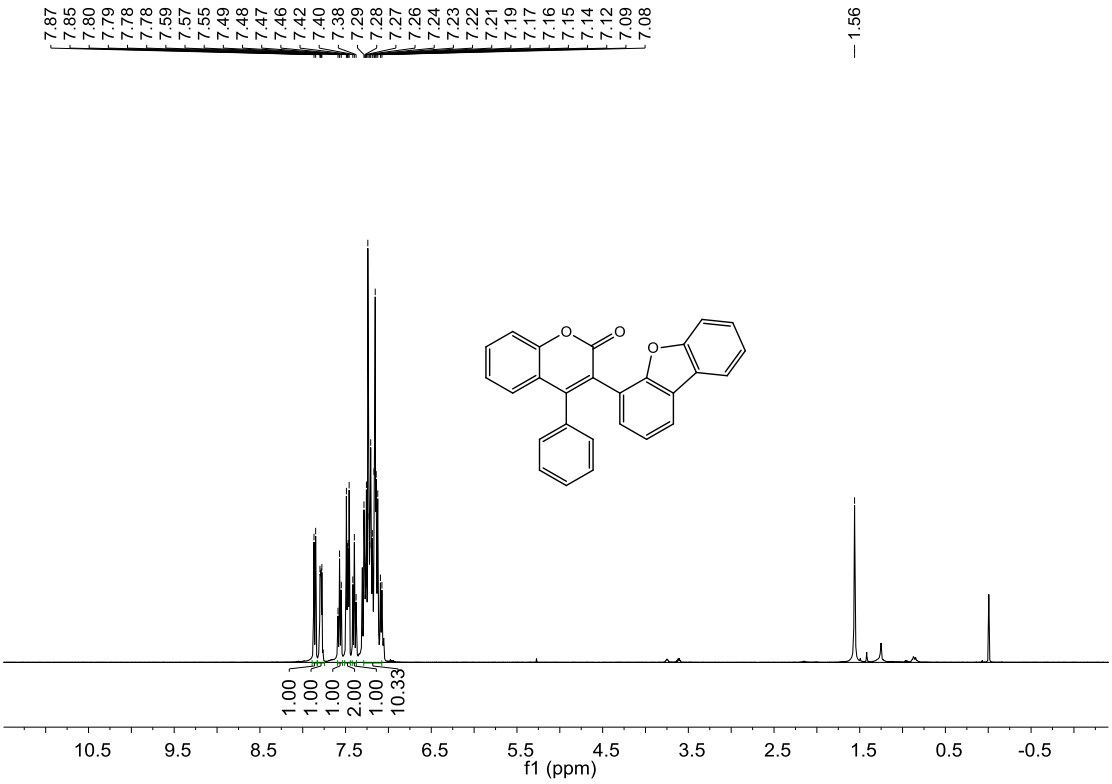
7. References

[1] J. Shi, Y. Kang, T. Wang, Y. Liang and Z. Zhang, *J. Org. Chem.*, 2018, 83, 13940-13948.

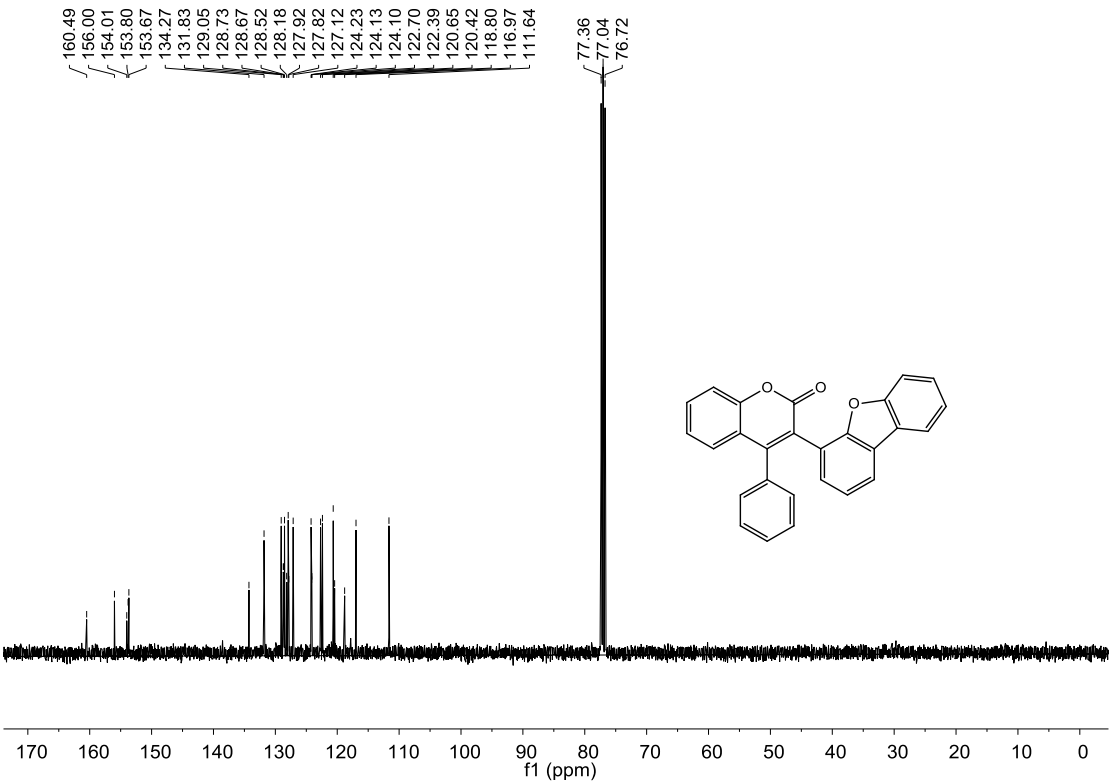
[2] G. Qiu, T. Liu and Q. Ding, *Org. Chem. Front.*, 2016, 3, 510-515.

8. ^{1} H NMR and ^{13} C NMR Spectra

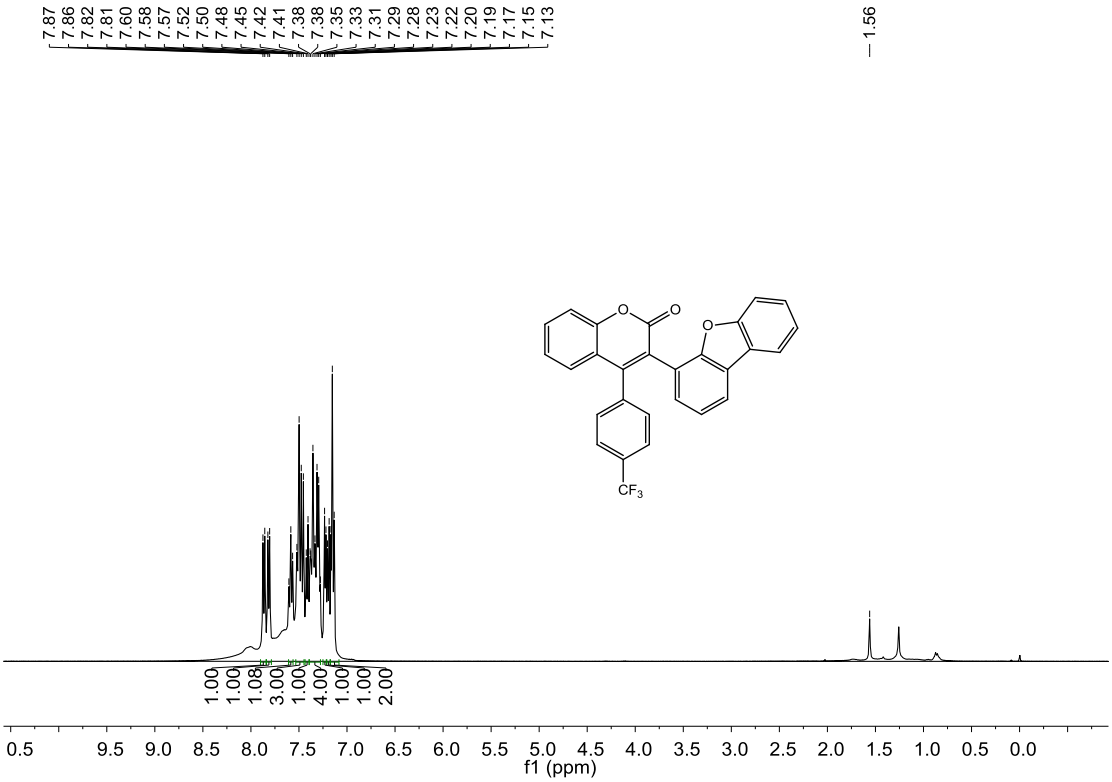
The spectra of 1a-1h, 3a-3i



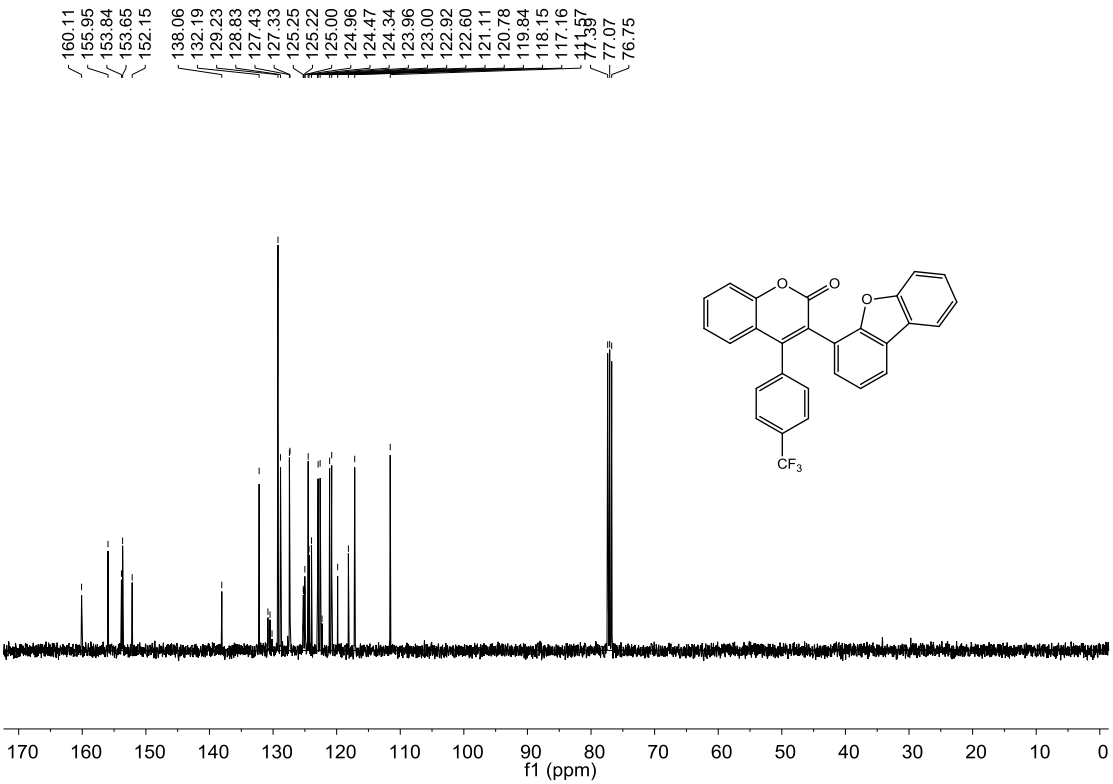
^{1}H NMR spectrum of **1a** ($CDCl_3$, 400MHz)



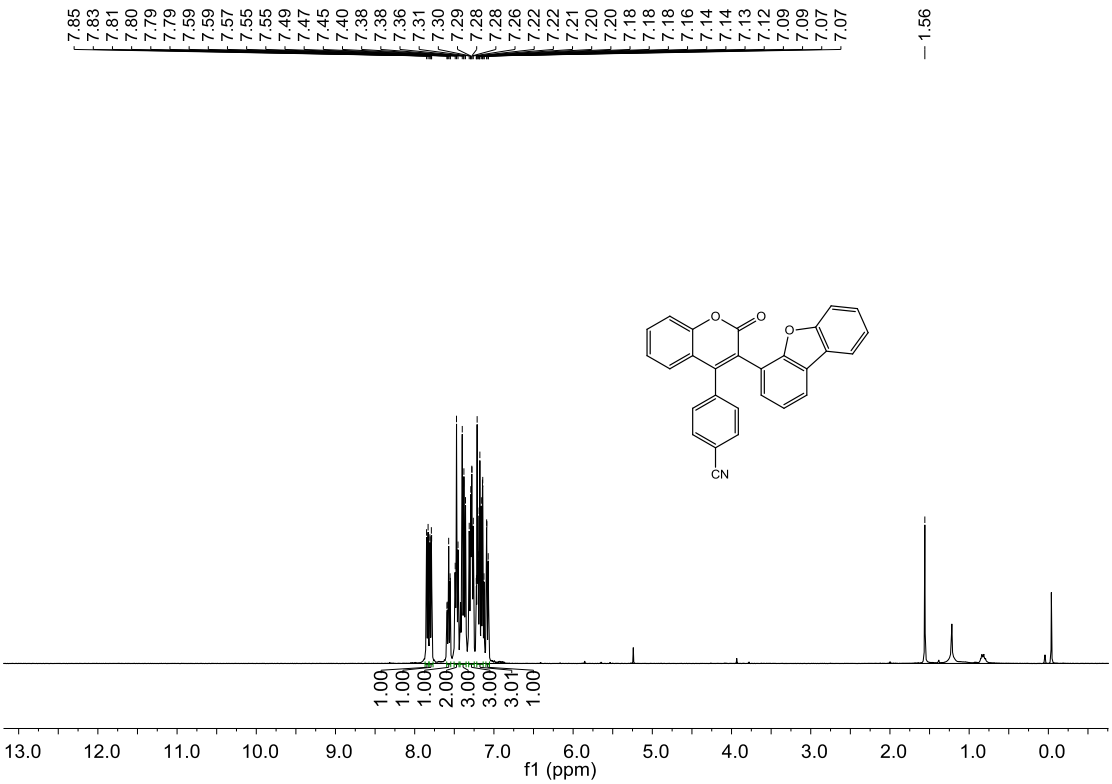
^{13}C NMR spectrum of **1a** ($CDCl_3$, 100MHz)



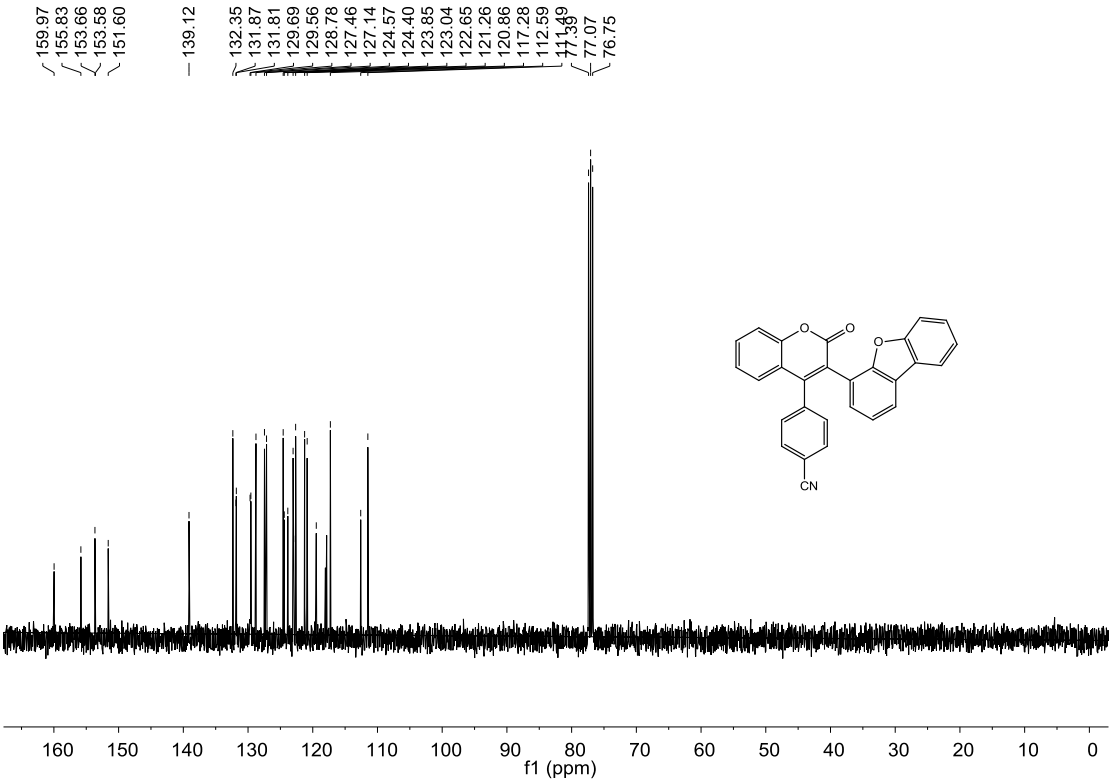
^{1}H NMR spectrum of **1b** ($CDCl_3$, 400MHz)



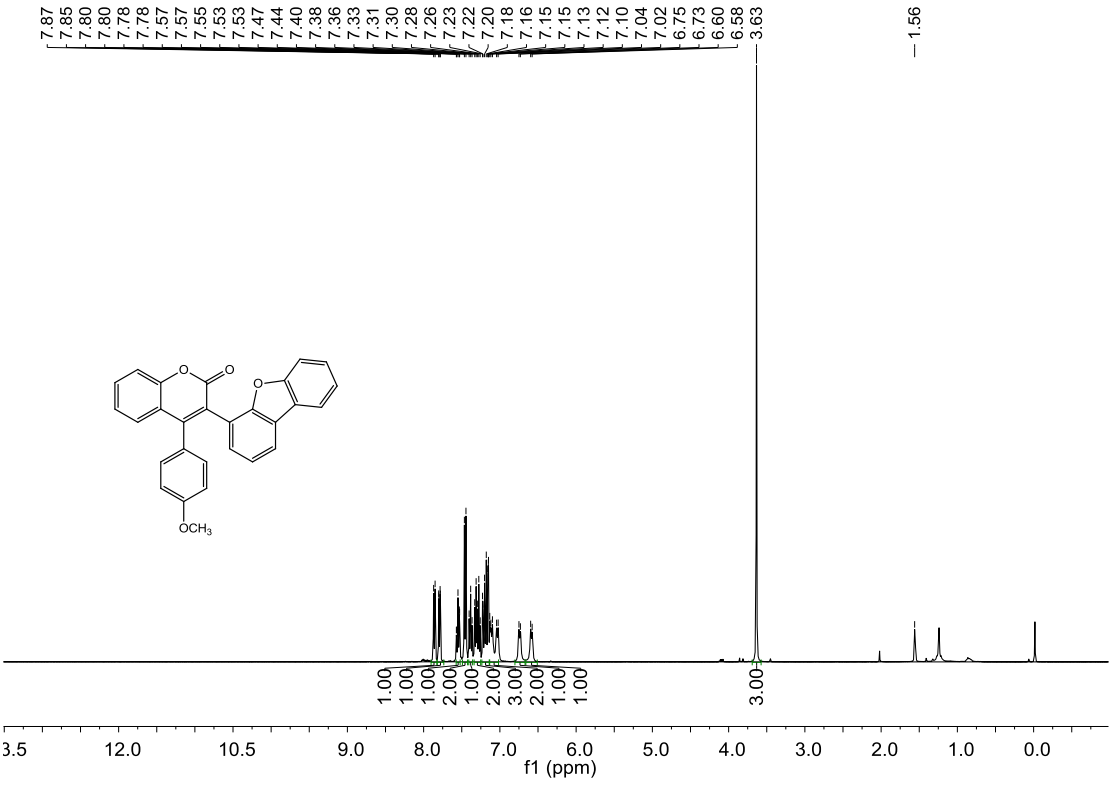
^{13}C NMR spectrum of **1b** ($CDCl_3$, 100MHz)



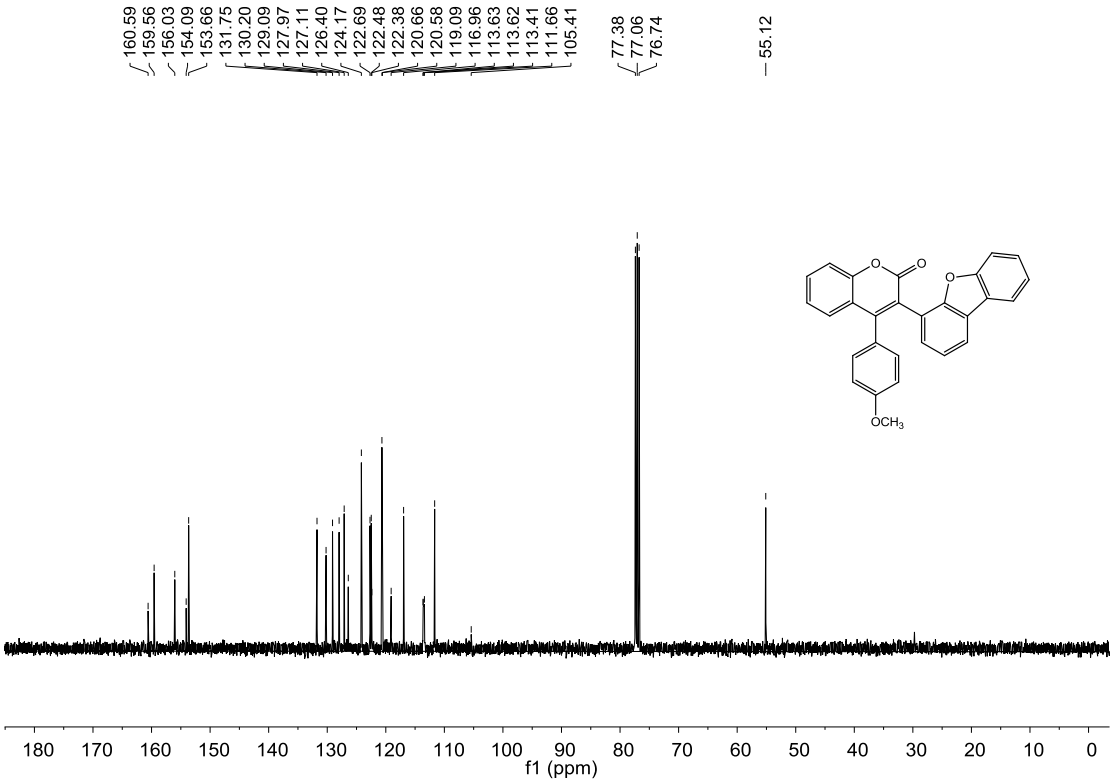
^{1}H NMR spectrum of **1c** ($CDCl_3$, 400MHz)



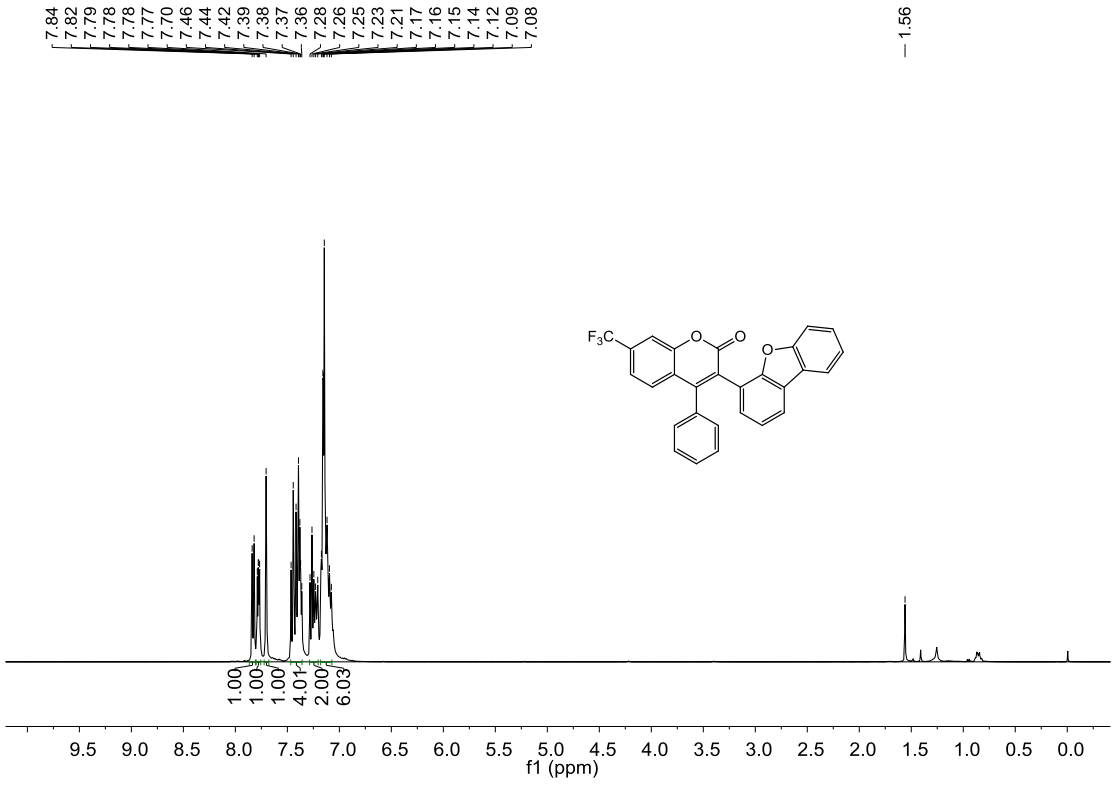
^{13}C NMR spectrum of **1c** ($CDCl_3$, 100MHz)



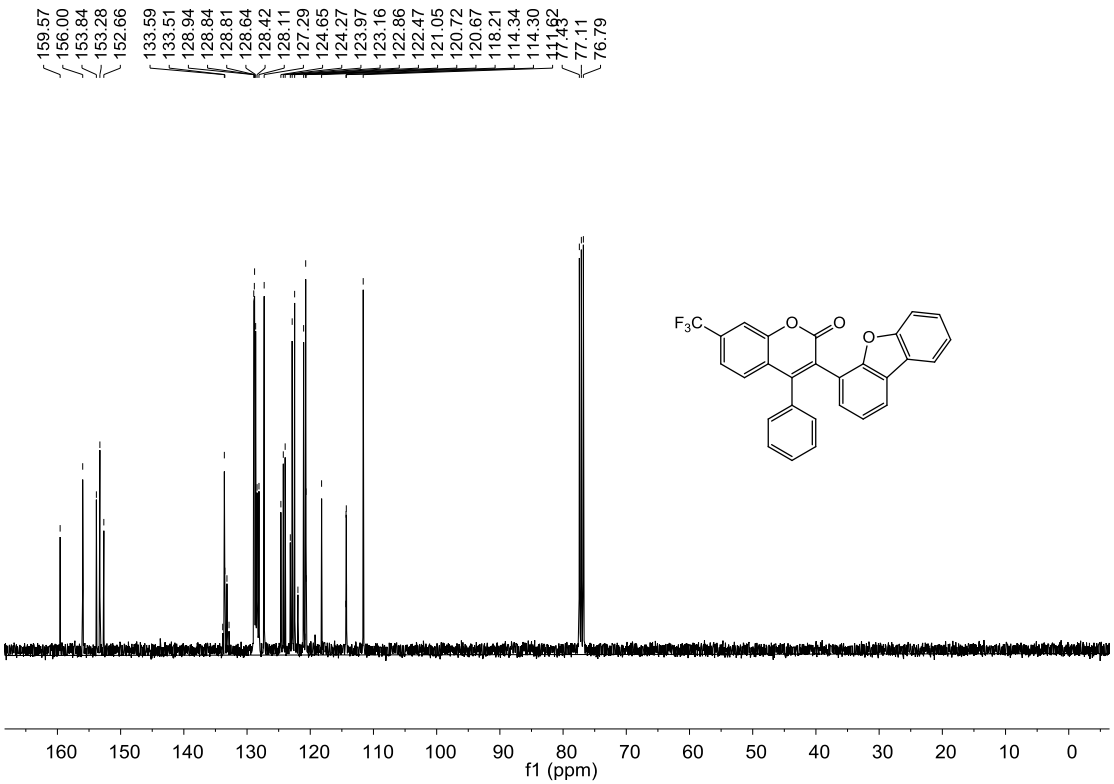
^{1}H NMR spectrum of **1d** ($CDCl_3$, 400MHz)



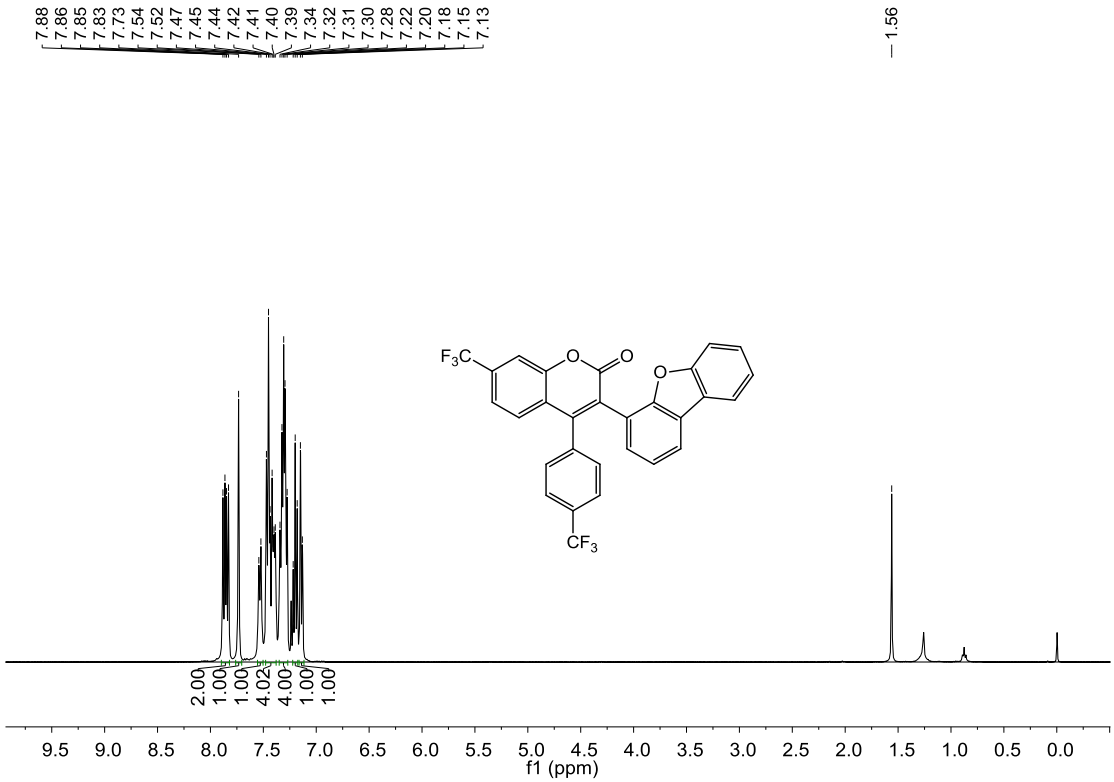
^{13}C NMR spectrum of **1d** ($CDCl_3$, 100MHz)



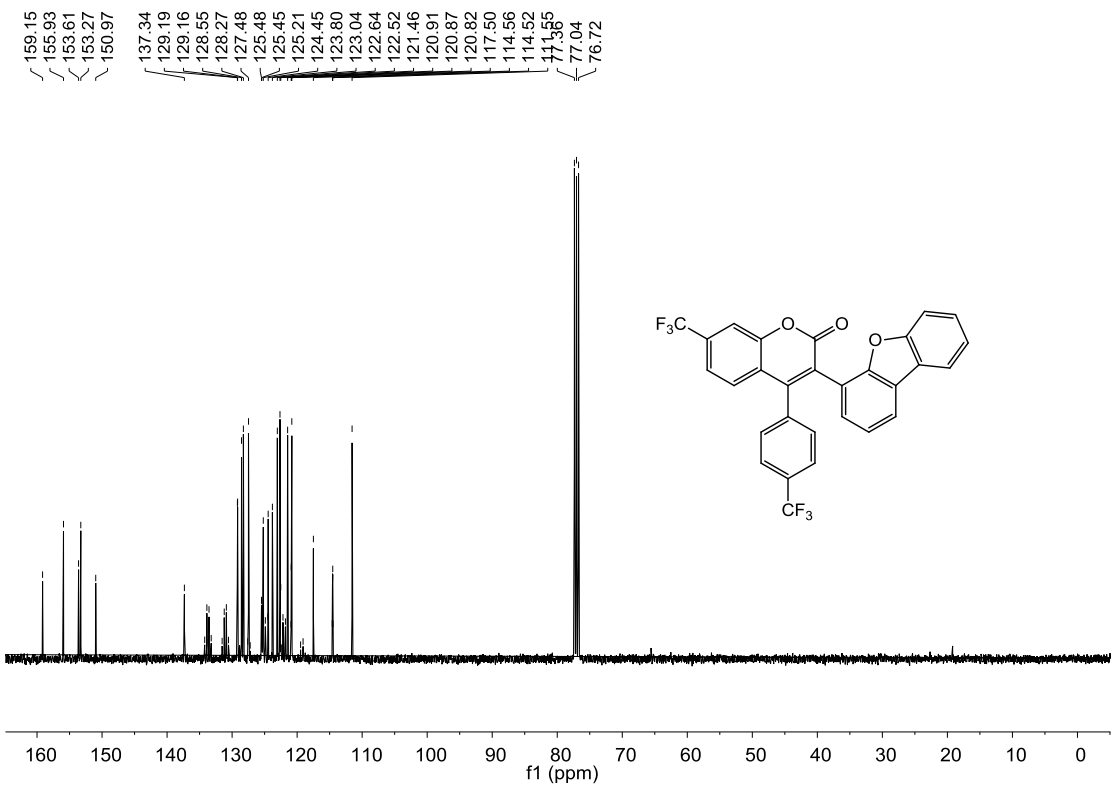
^{1}H NMR spectrum of **1e** ($CDCl_3$, 400MHz)



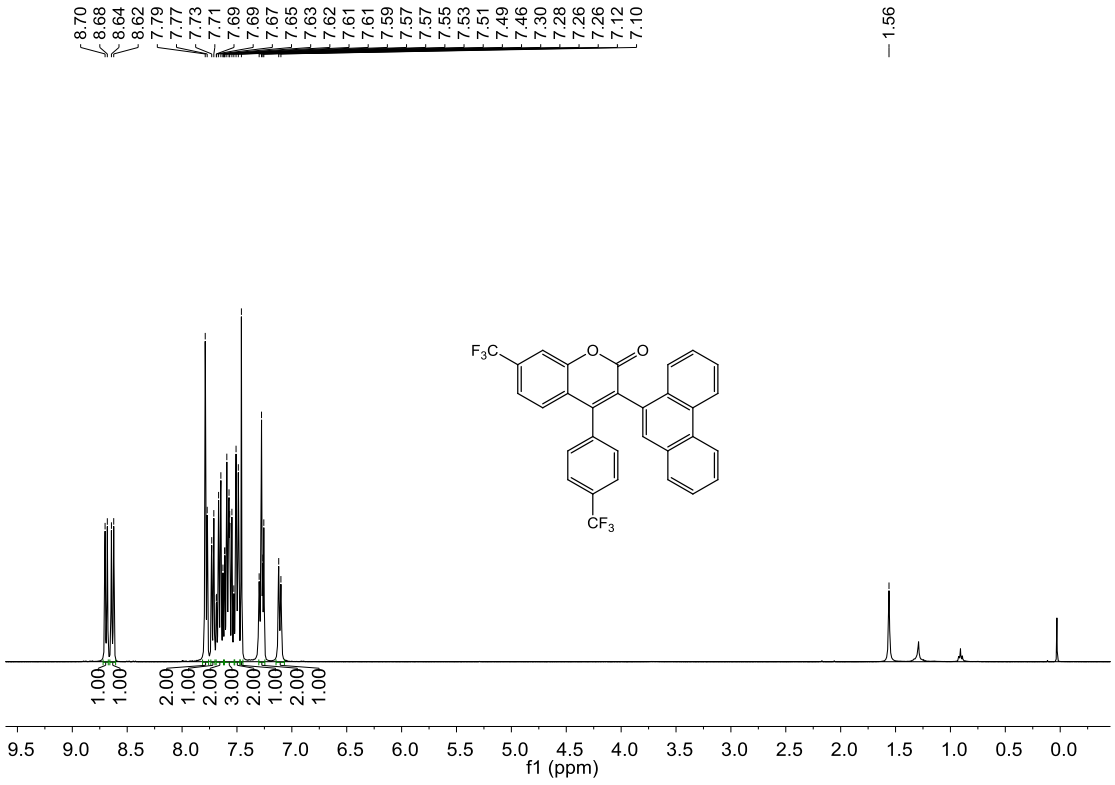
^{13}C NMR spectrum of **1e** ($CDCl_3$, 100MHz)



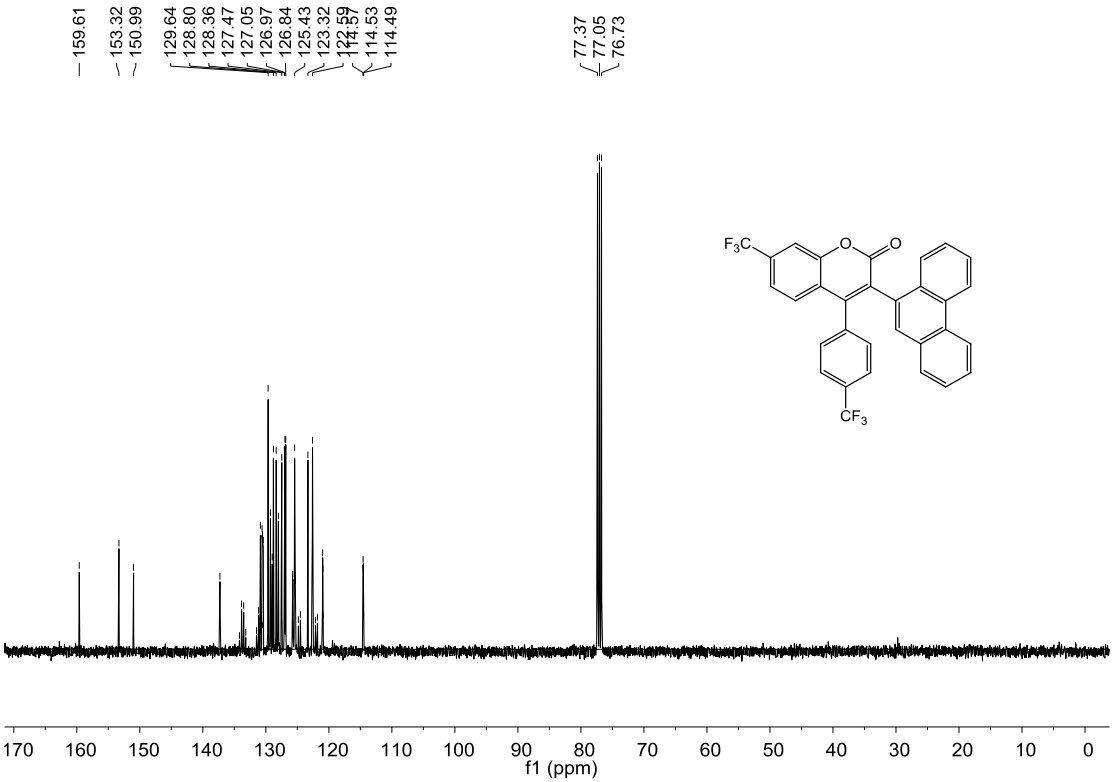
^{1}H NMR spectrum of **1f** ($CDCl_3$, 400MHz)



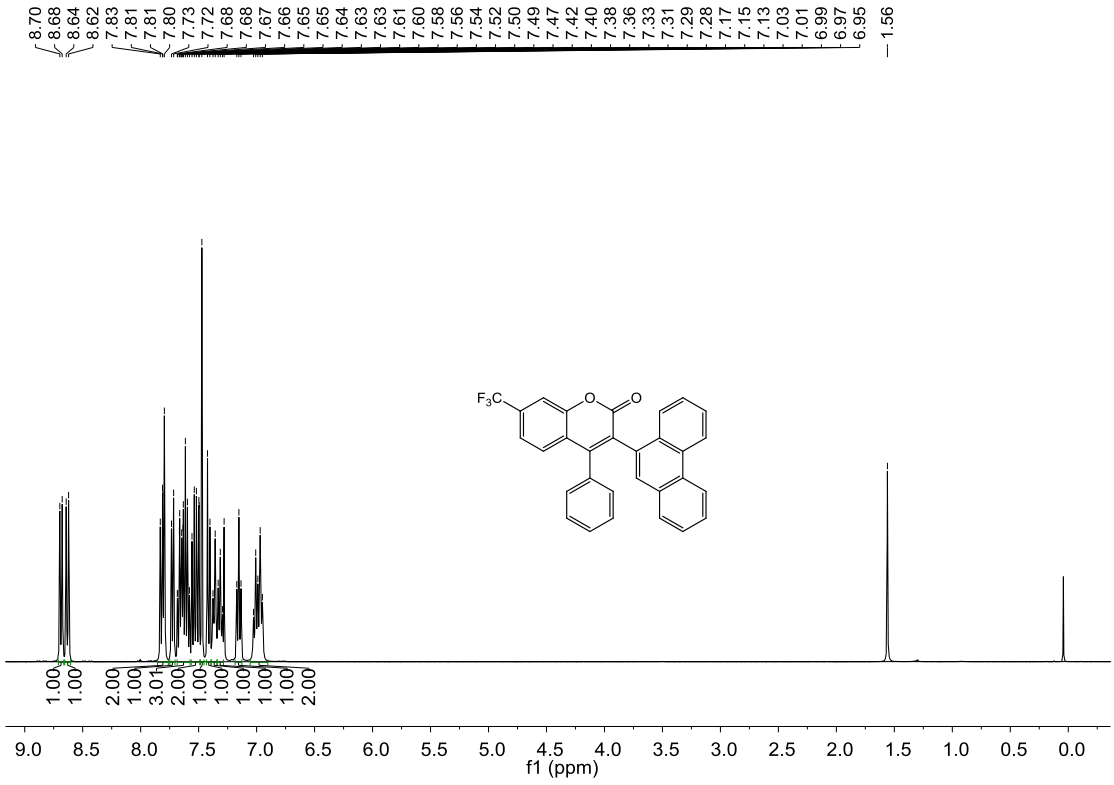
^{13}C NMR spectrum of **1f** ($CDCl_3$, 100MHz)



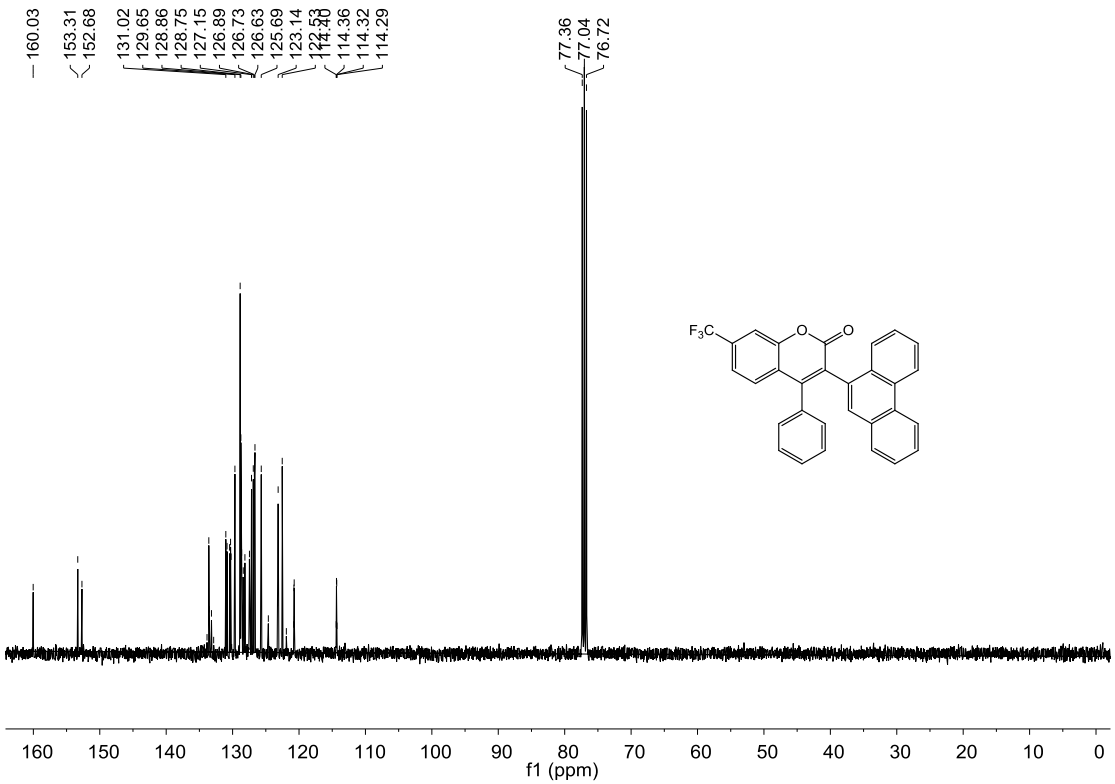
^{1}H NMR spectrum of **1g** ($CDCl_3$, 400MHz)



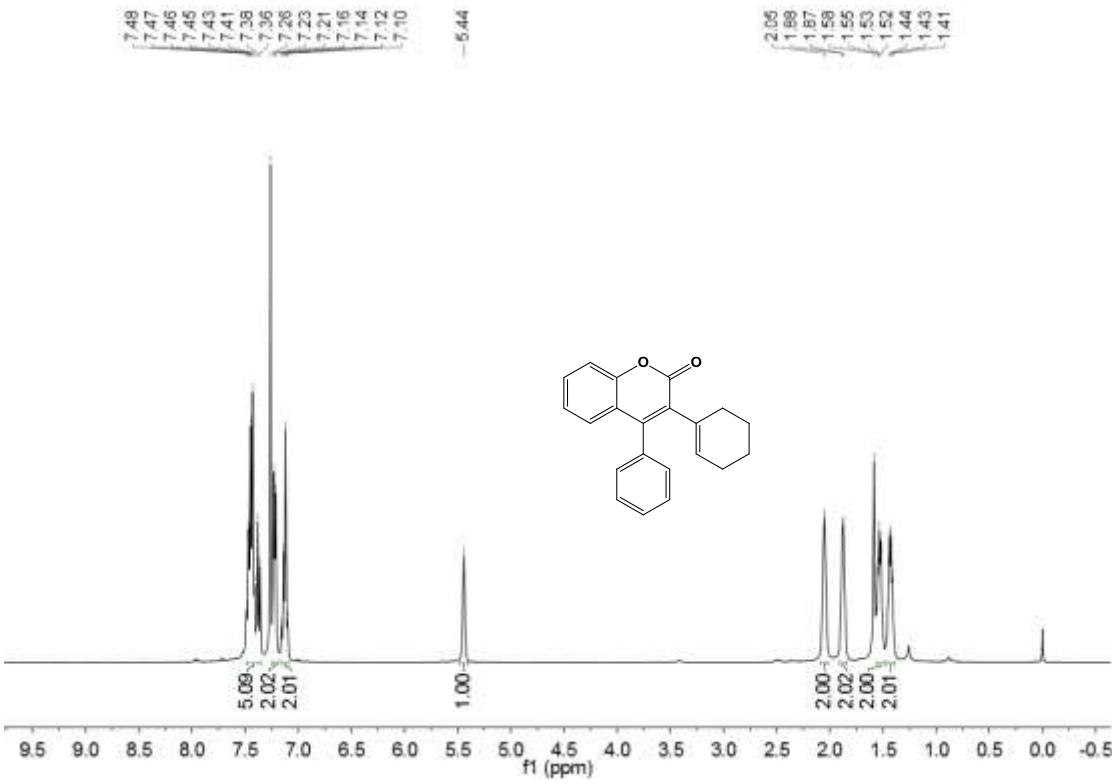
^{13}C NMR spectrum of **1g** ($CDCl_3$, 100MHz)



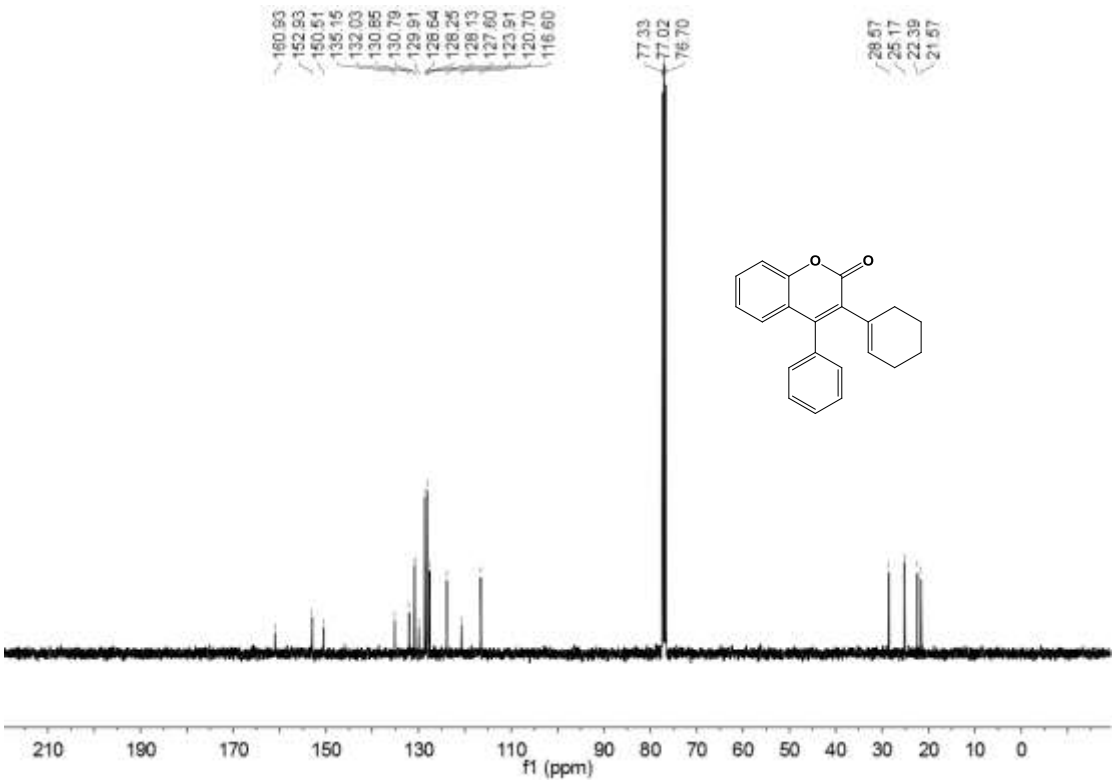
^{1}H NMR spectrum of **1h** ($CDCl_3$, 400MHz)



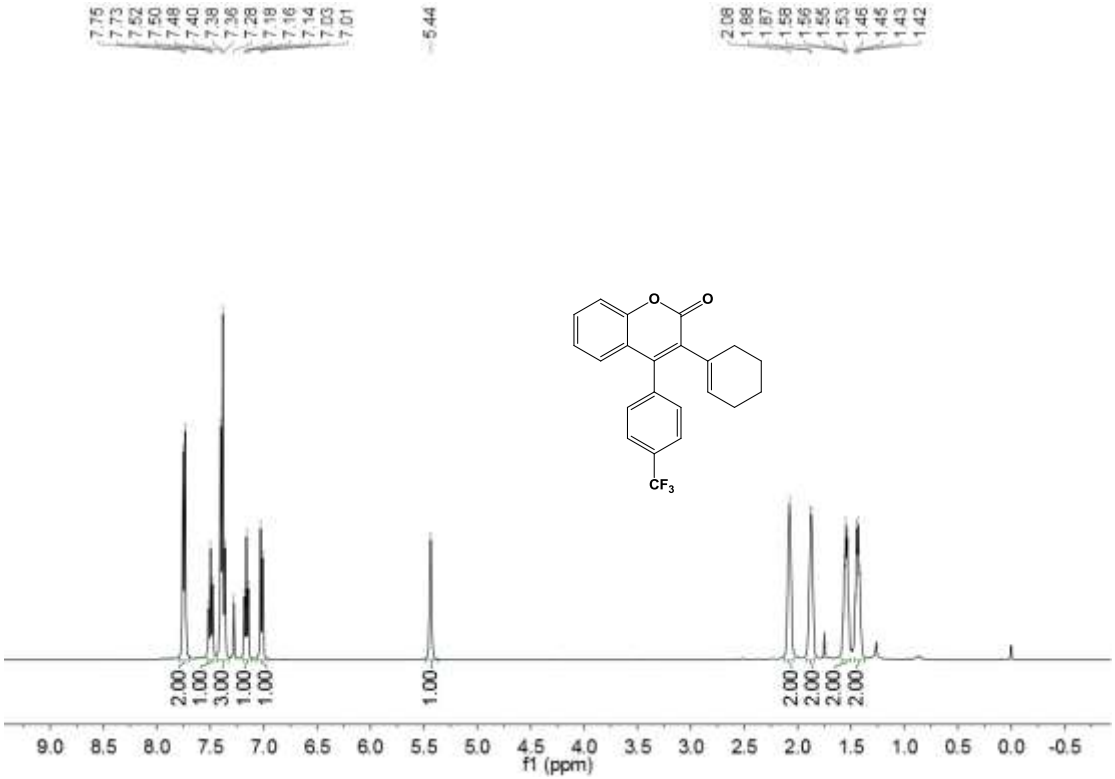
^{13}C NMR spectrum of **1h** ($CDCl_3$, 100MHz)



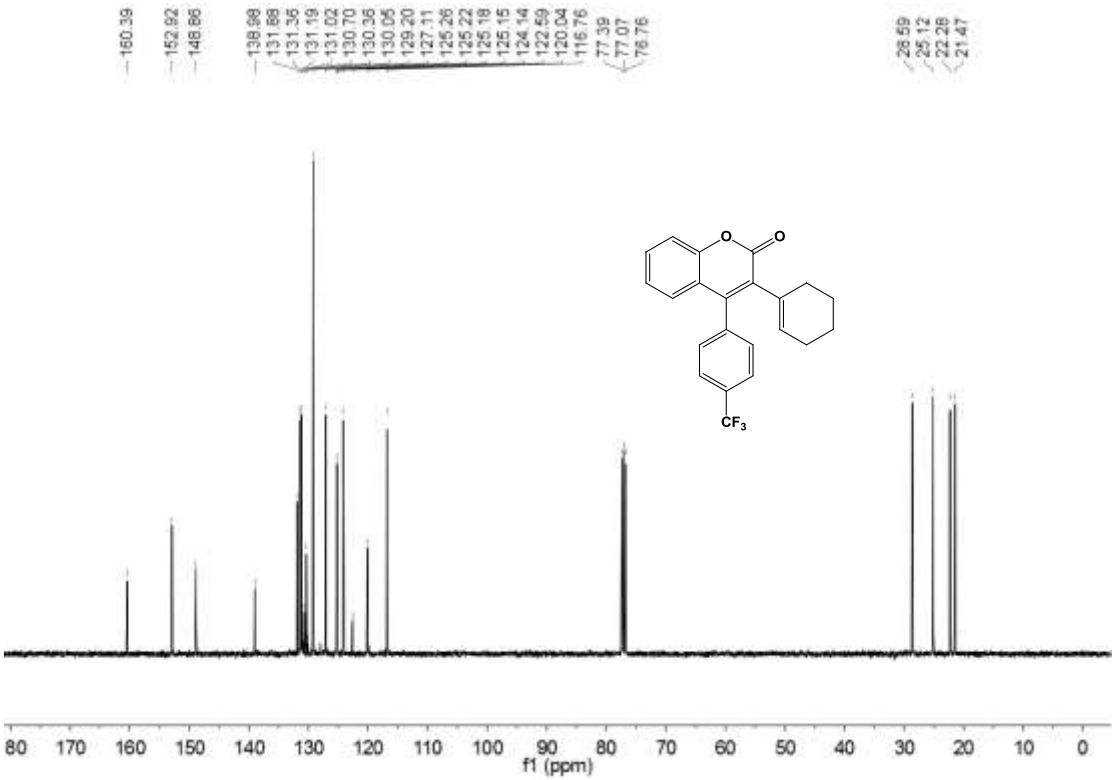
^{1}H NMR spectrum of **3a** ($CDCl_3$, 400MHz)



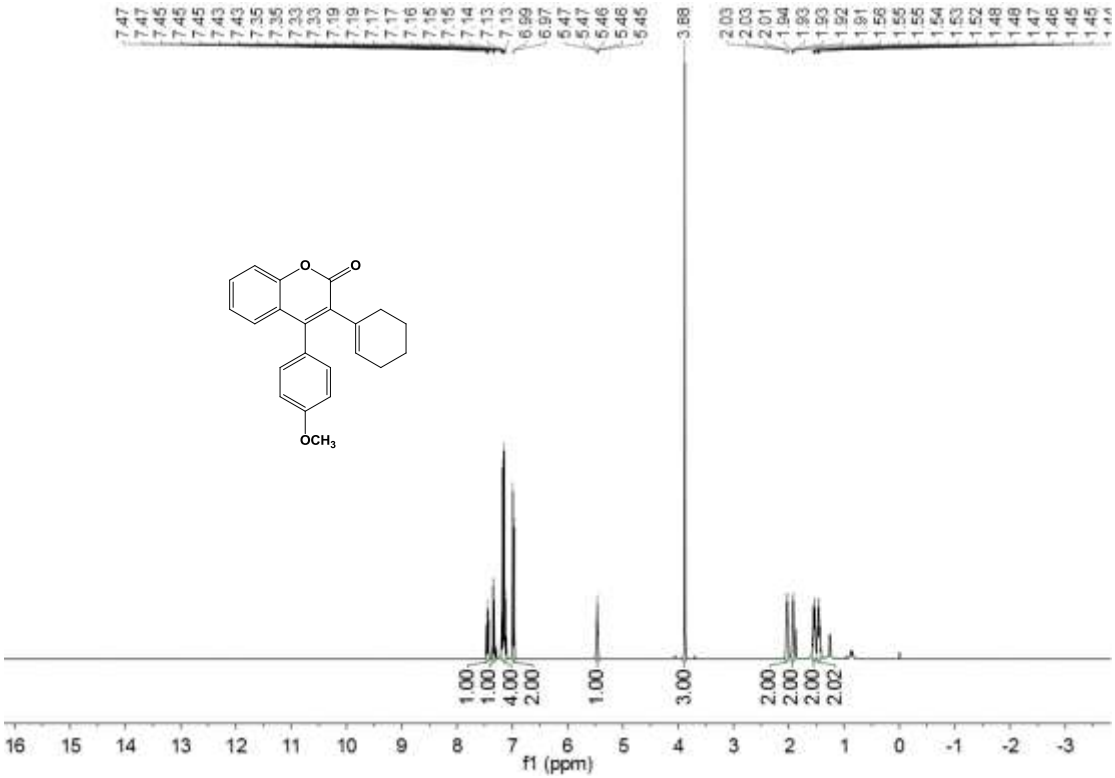
^{13}C NMR spectrum of **3a** ($CDCl_3$, 100MHz)



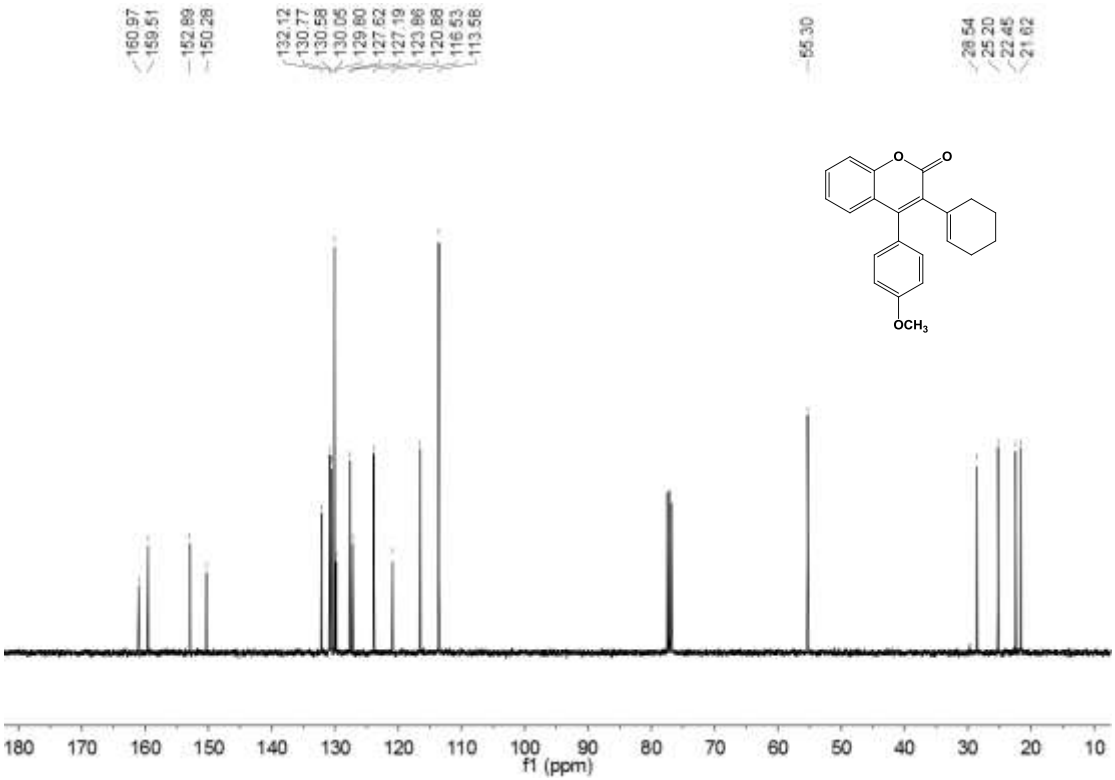
^{1}H NMR spectrum of **3b** ($CDCl_3$, 400MHz)



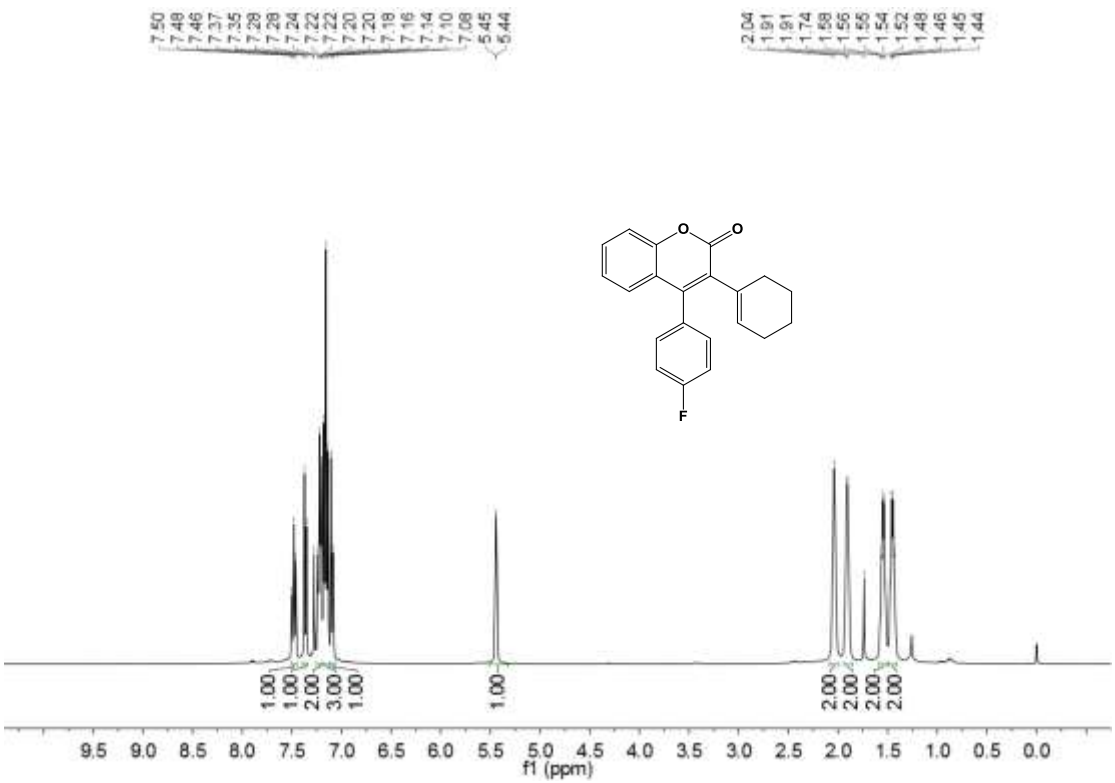
^{13}C NMR spectrum of **3b** ($CDCl_3$, 100MHz)



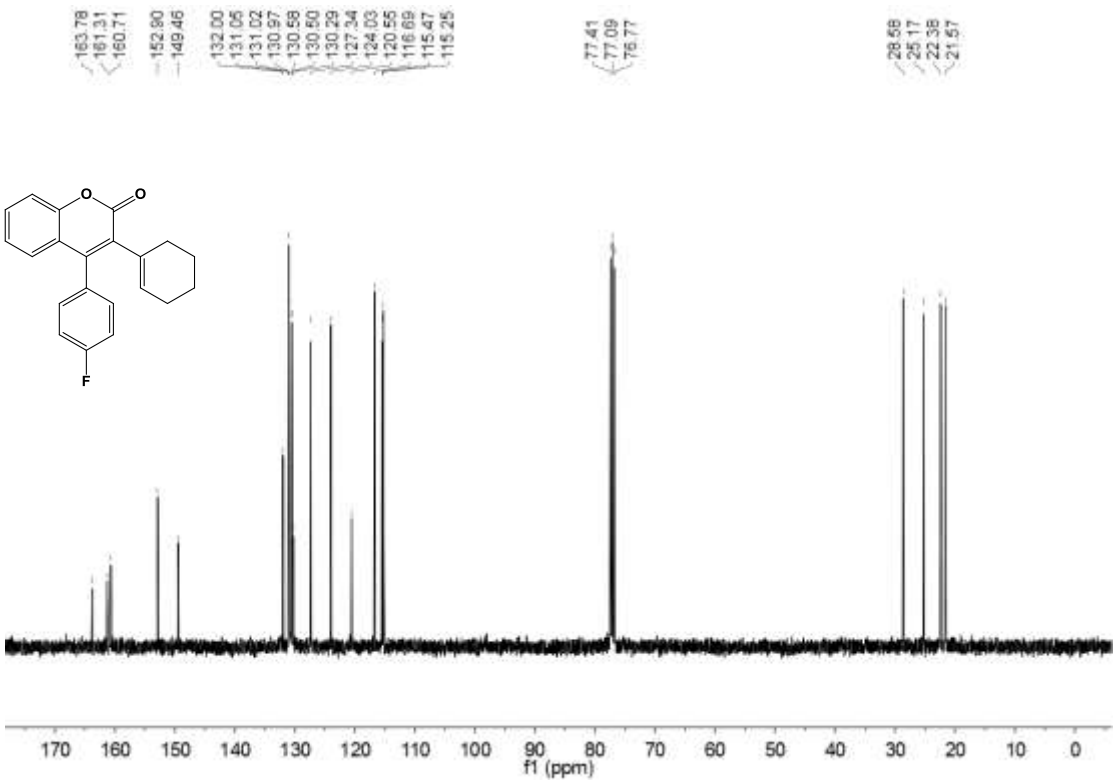
^{1}H NMR spectrum of **3c** ($CDCl_3$, 400MHz)



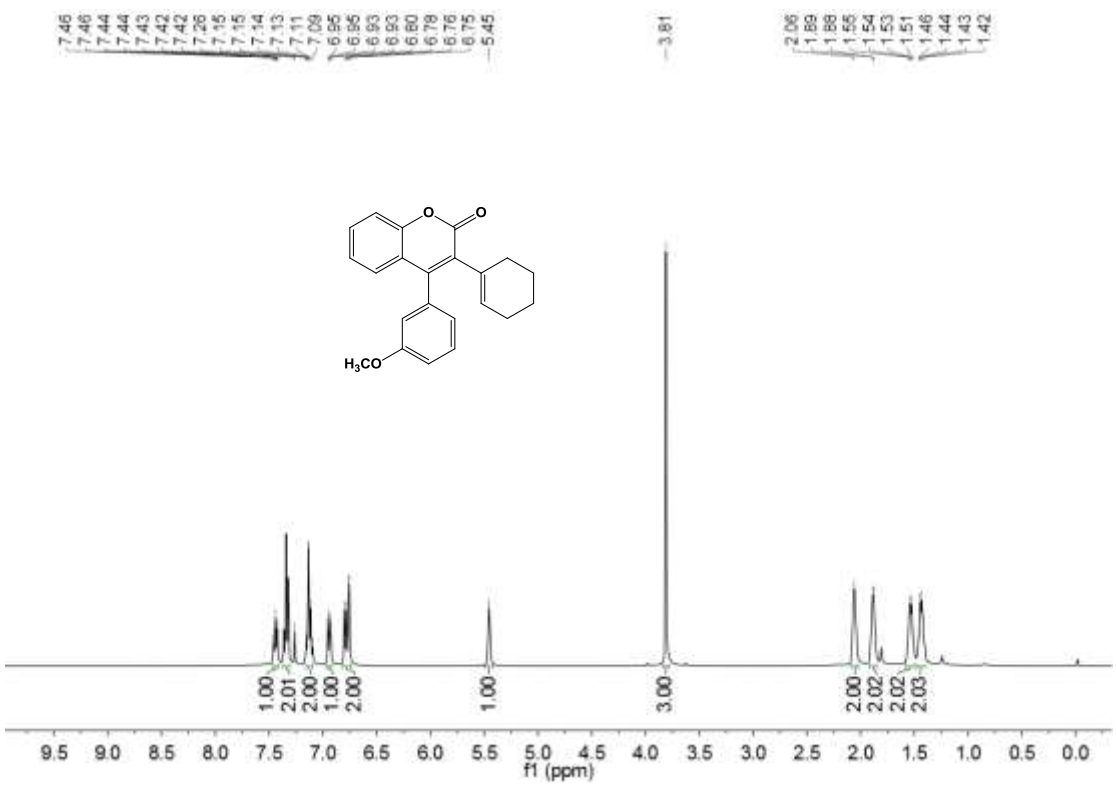
^{13}C NMR spectrum of **3c** ($CDCl_3$, 100MHz)



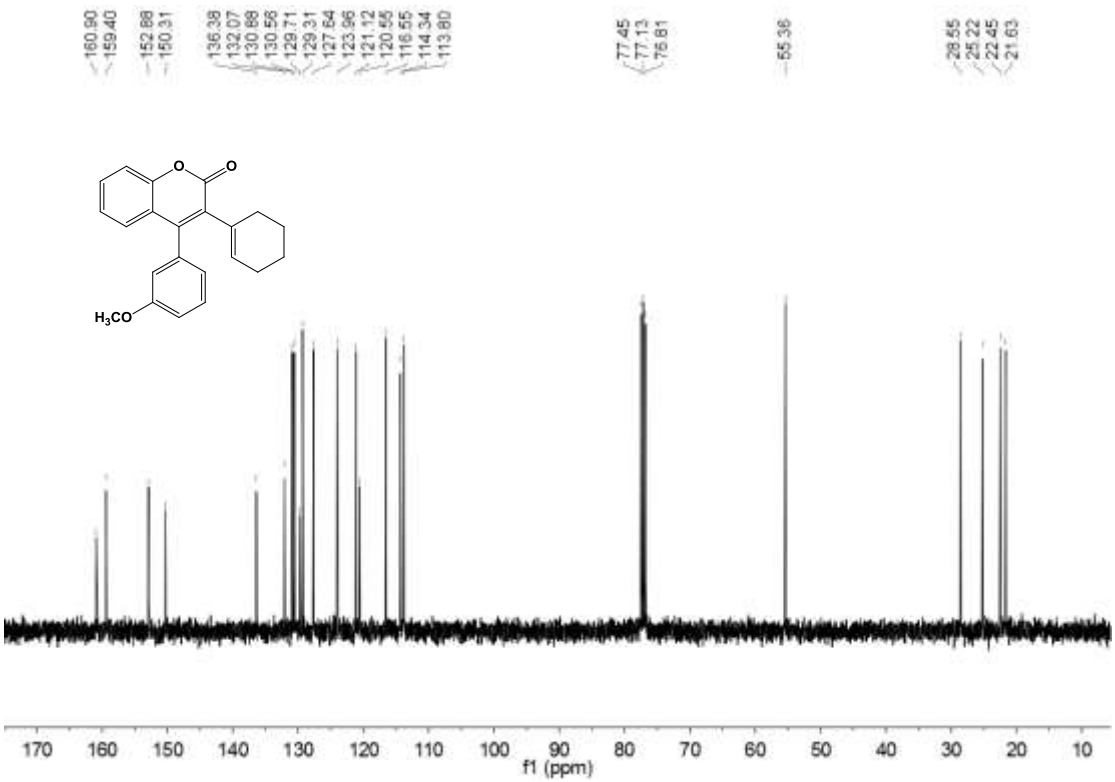
^{1}H NMR spectrum of **3d** ($CDCl_3$, 400MHz)



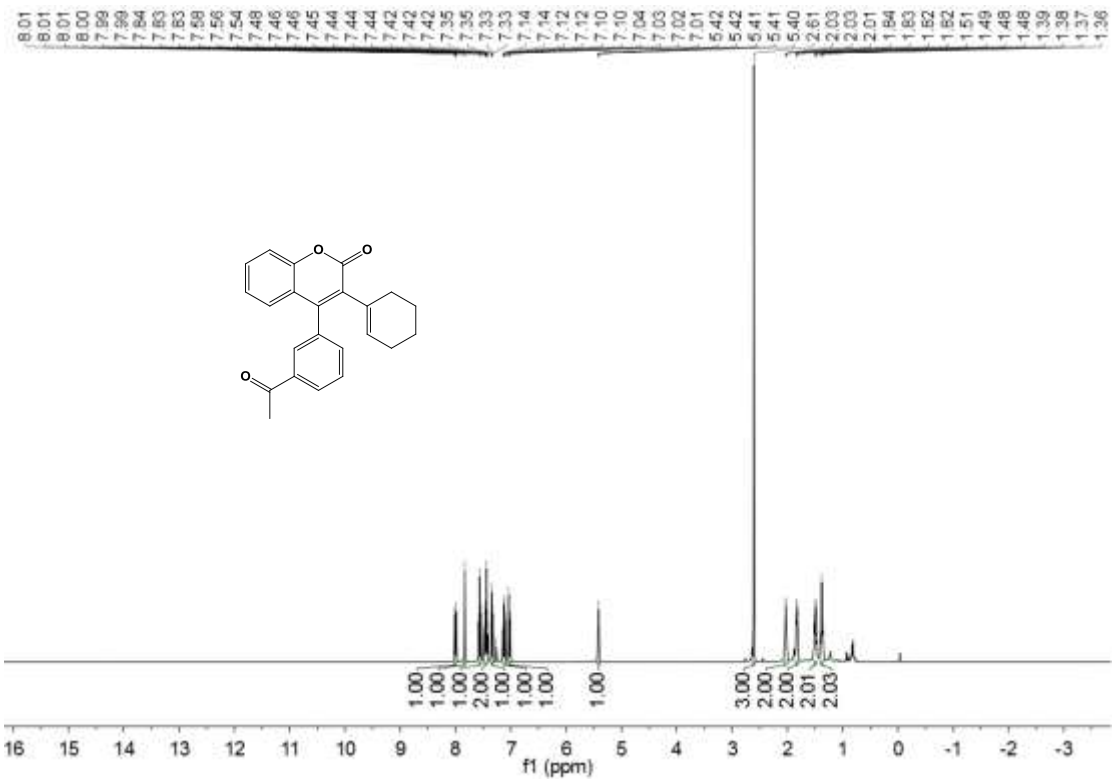
^{13}C NMR spectrum of **3d** ($CDCl_3$, 100MHz)



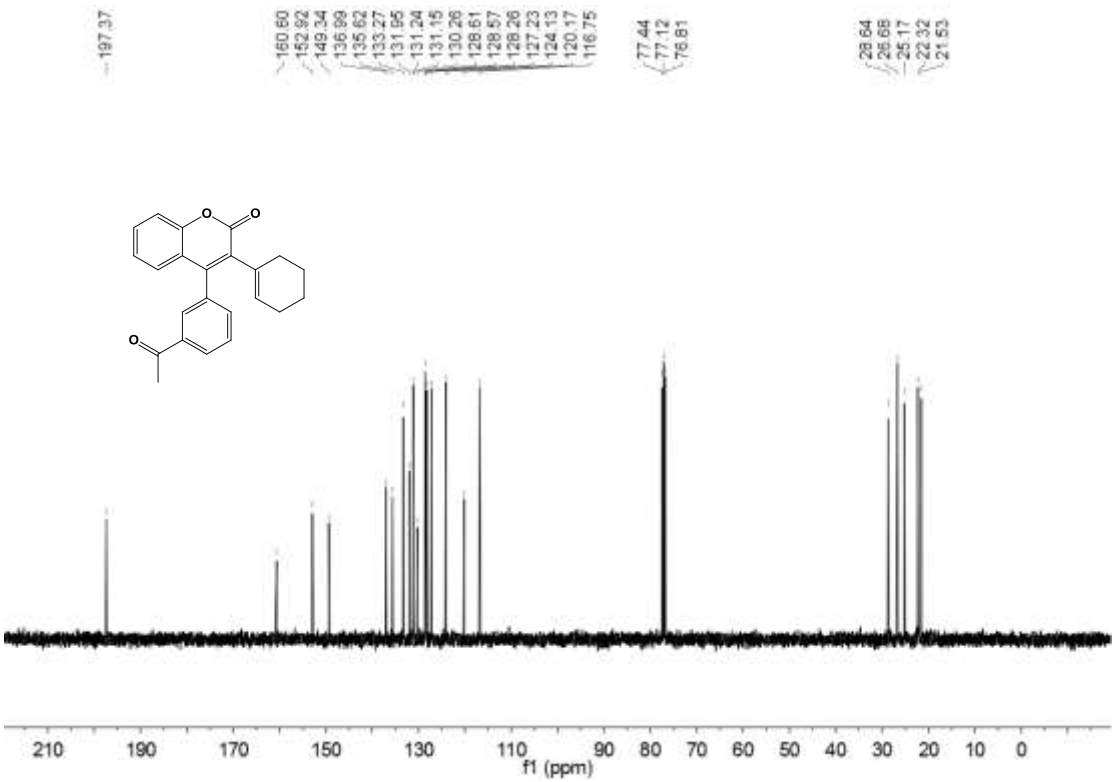
^{1}H NMR spectrum of **3e** ($CDCl_3$, 400MHz)



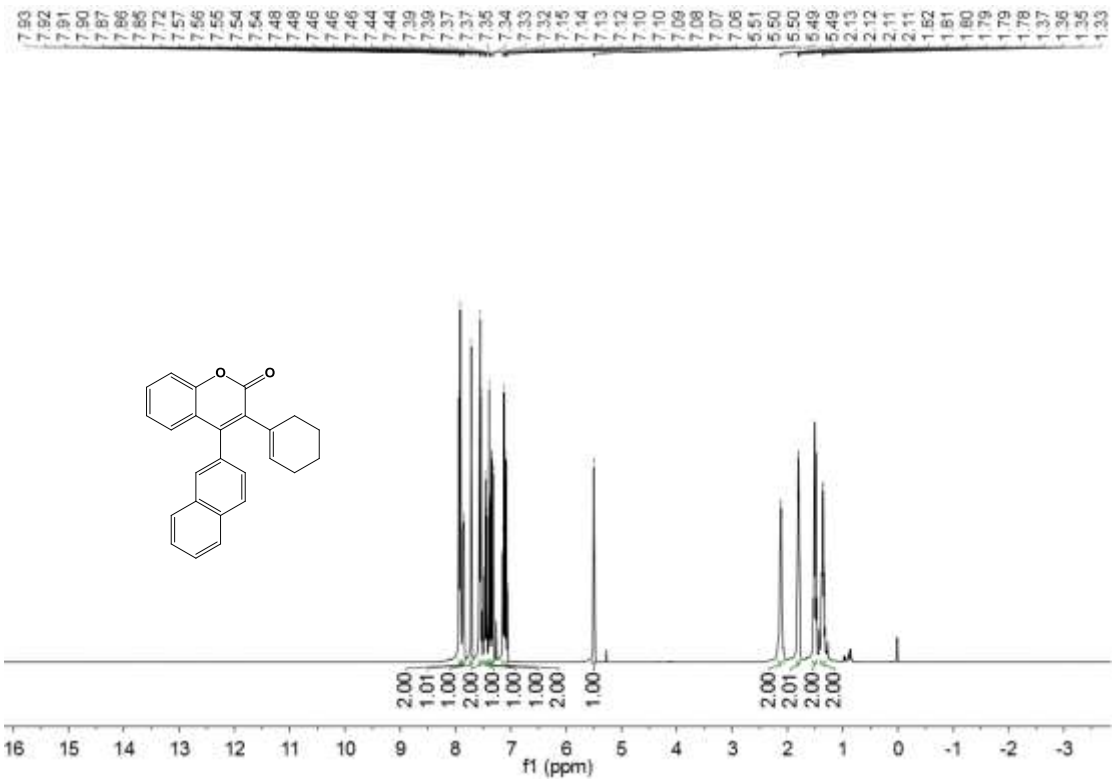
^{13}C NMR spectrum of **3e** ($CDCl_3$, 100MHz)



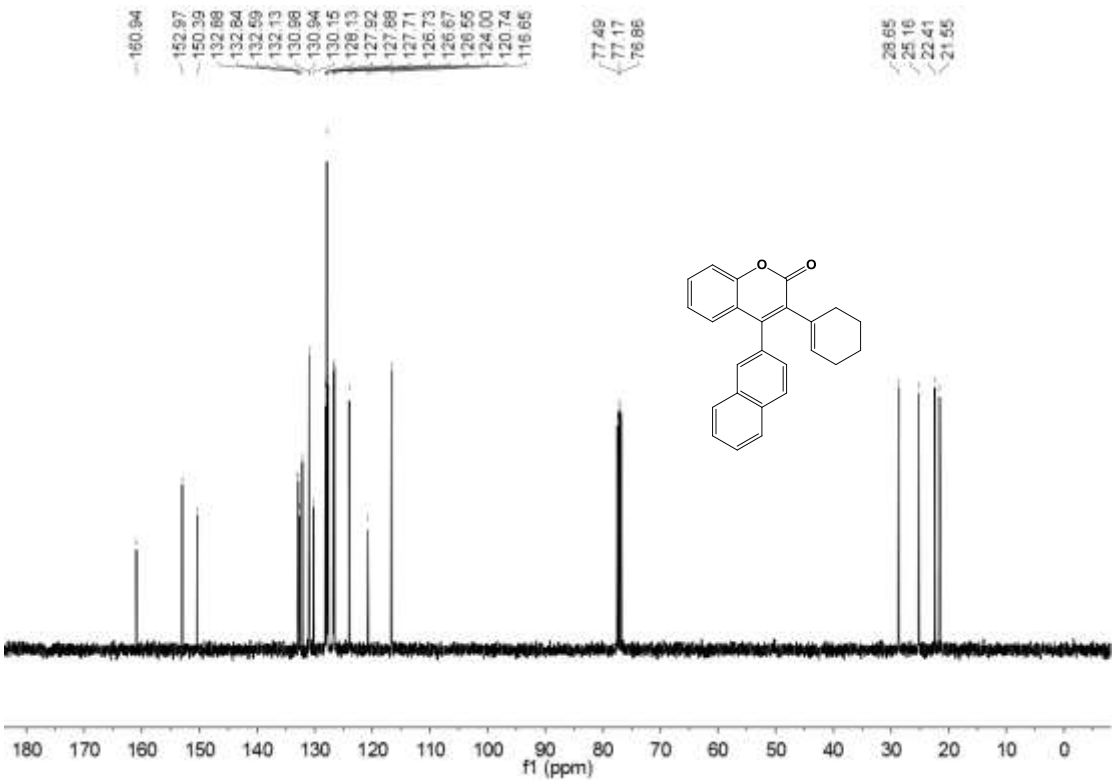
^{1}H NMR spectrum of **3f** ($CDCl_3$, 400MHz)



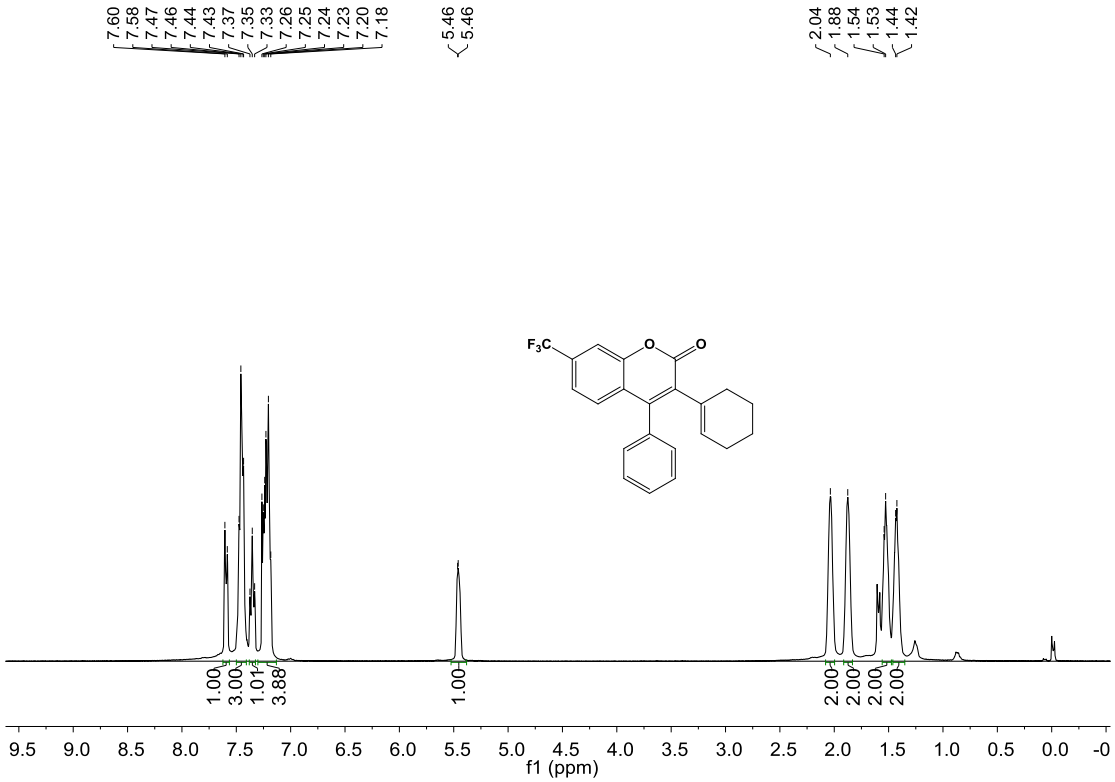
^{13}C NMR spectrum of **3f** ($CDCl_3$, 100MHz)



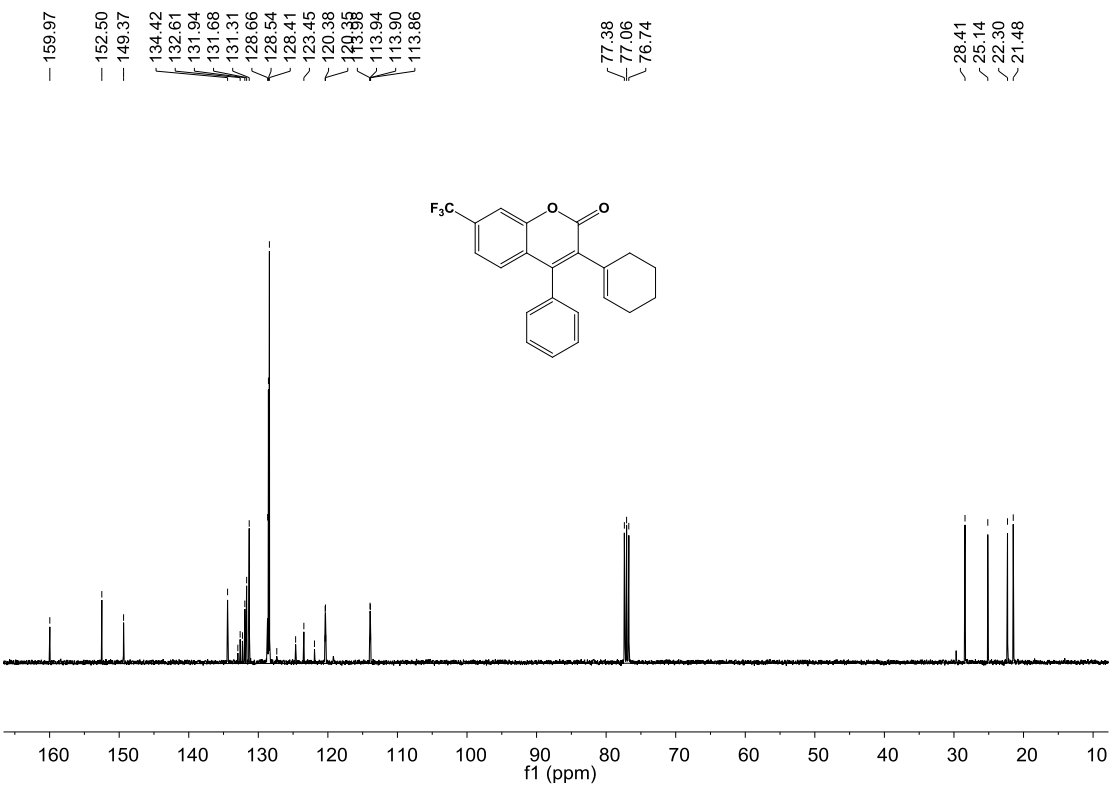
^{13}C NMR spectrum of **3g** ($CDCl_3$, 100MHz)



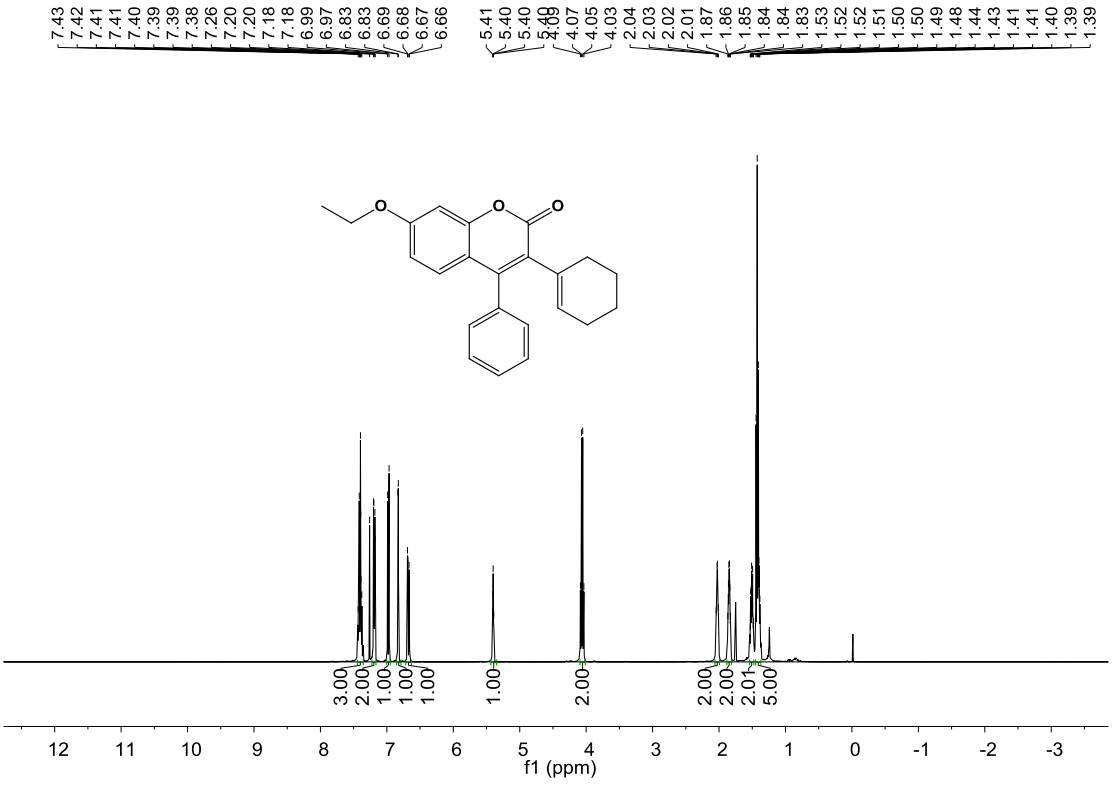
^{13}C NMR spectrum of **3g** ($CDCl_3$, 100MHz)



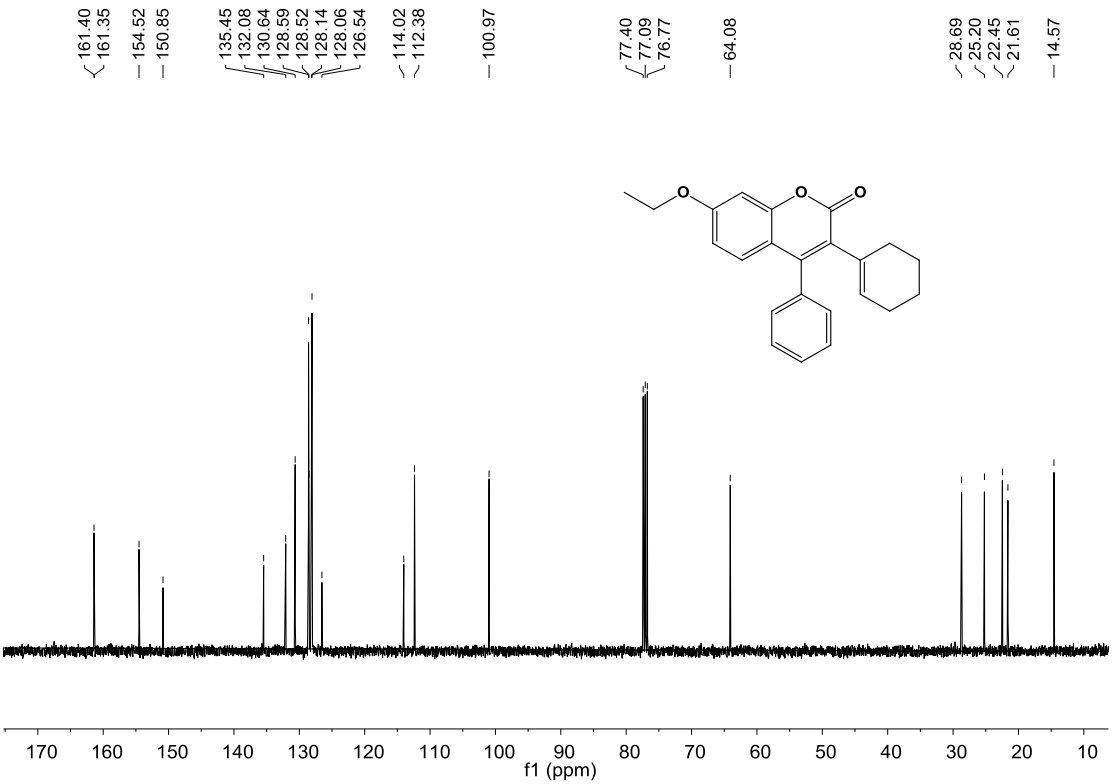
^{1}H NMR spectrum of **3h** ($CDCl_3$, 400MHz)



^{13}C NMR spectrum of **3h** ($CDCl_3$, 100MHz)

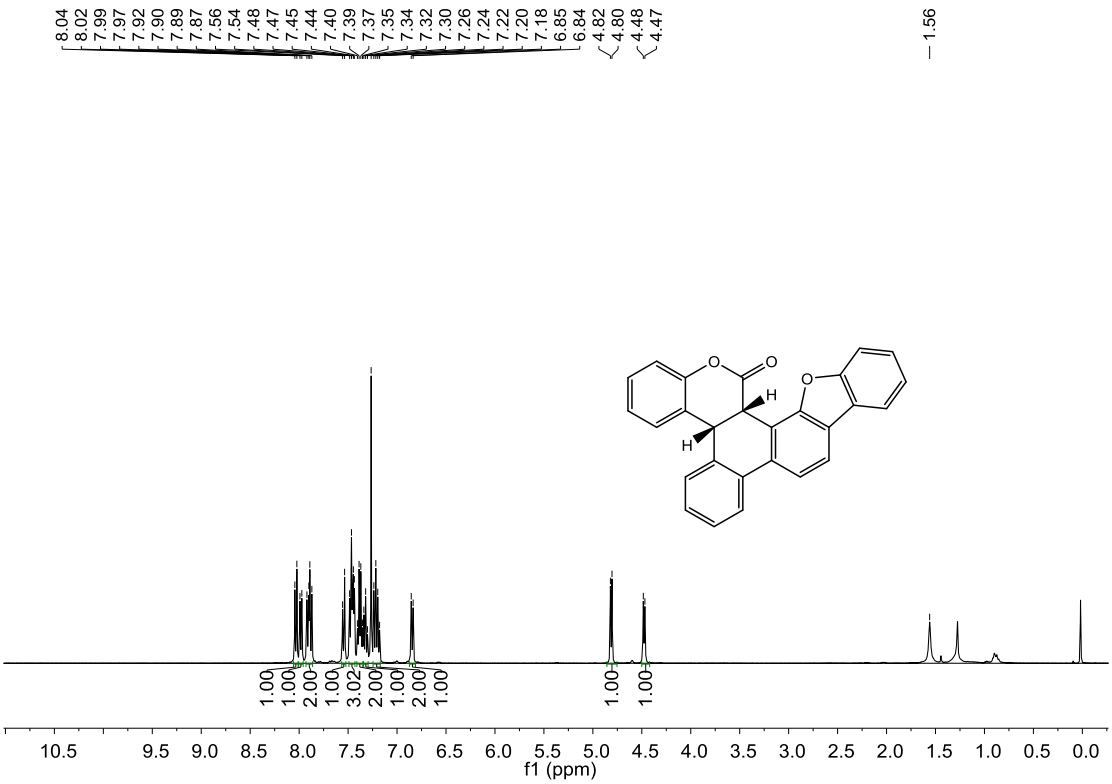


^{1}H NMR spectrum of **3i** ($CDCl_3$, 400MHz)

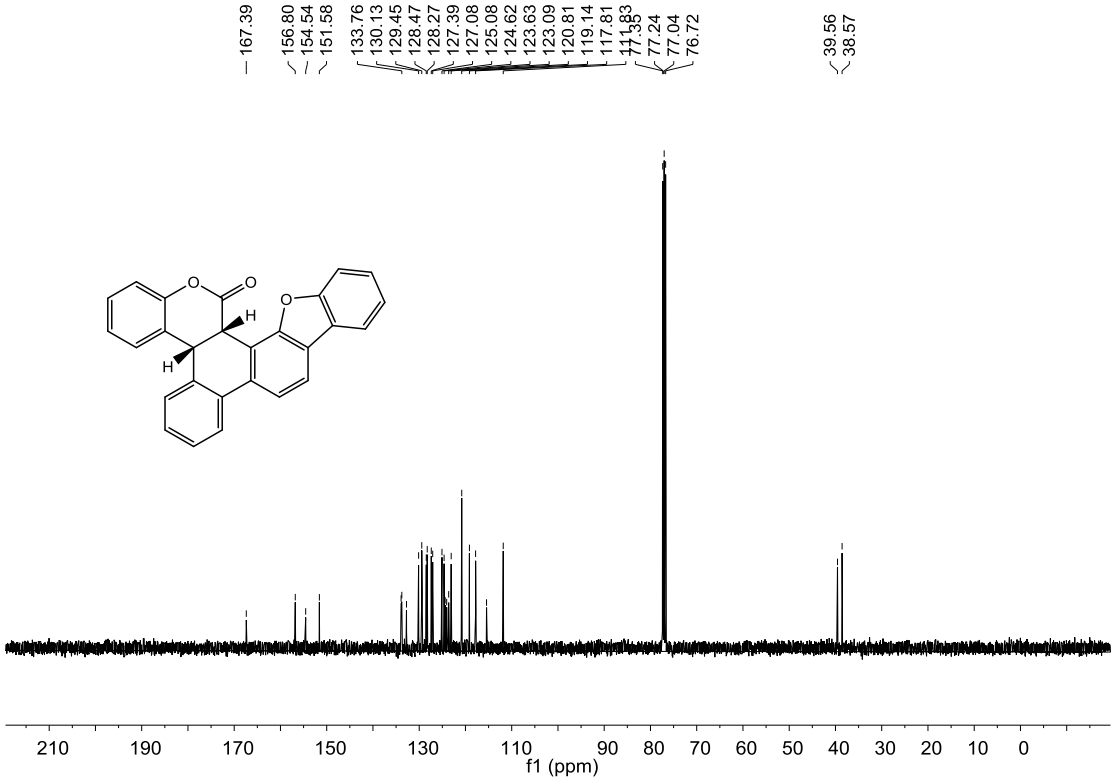


^{13}C NMR spectrum of **3i** ($CDCl_3$, 100MHz)

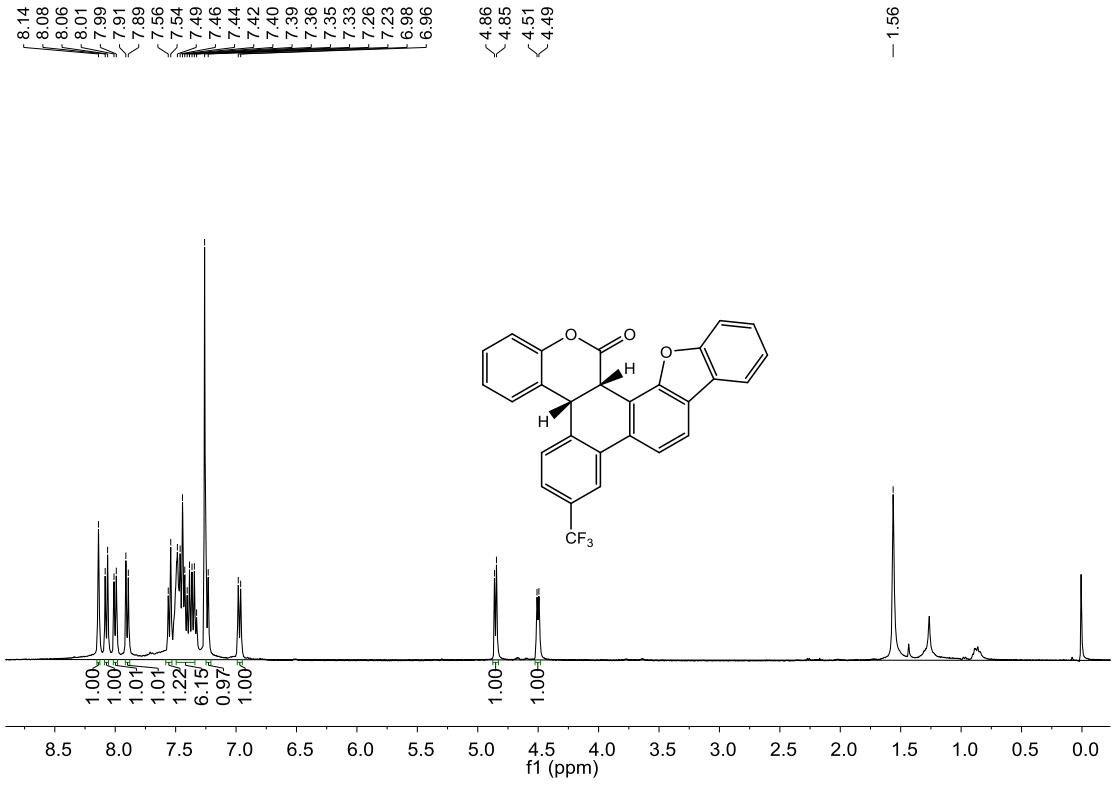
The spectra of 2a-2h, 4a-4i



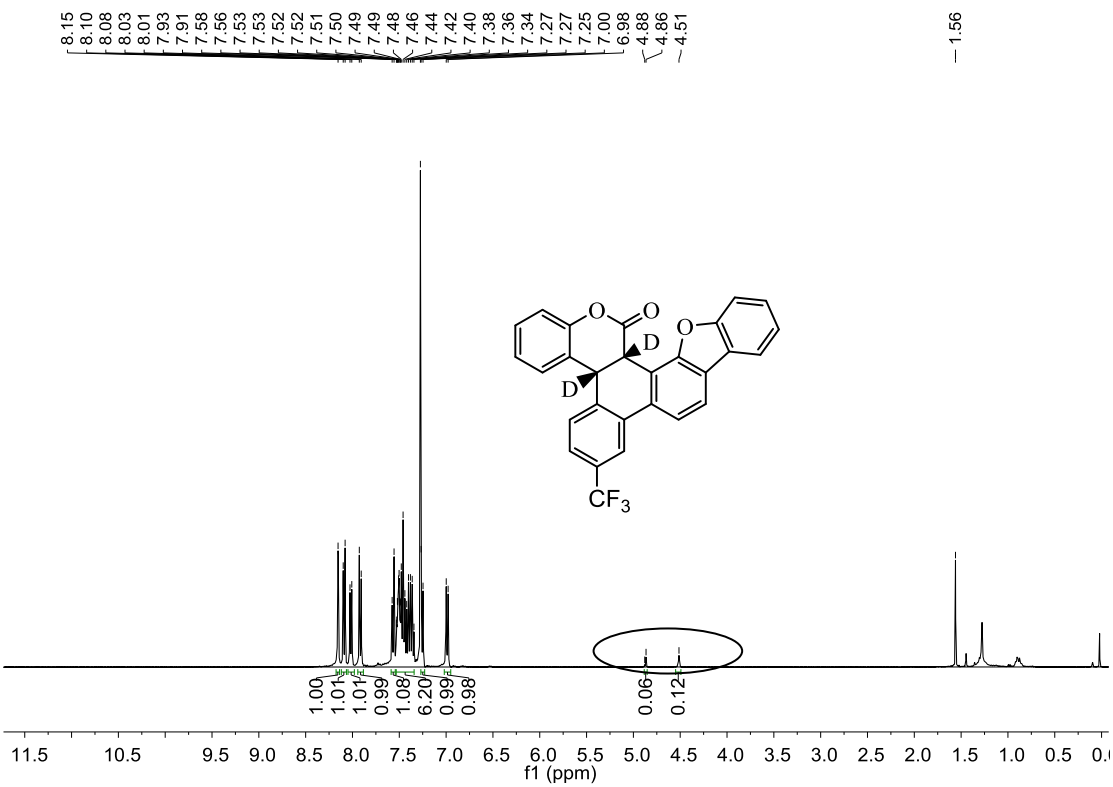
^{1}H NMR spectrum of **2a** ($CDCl_3$, 400MHz)



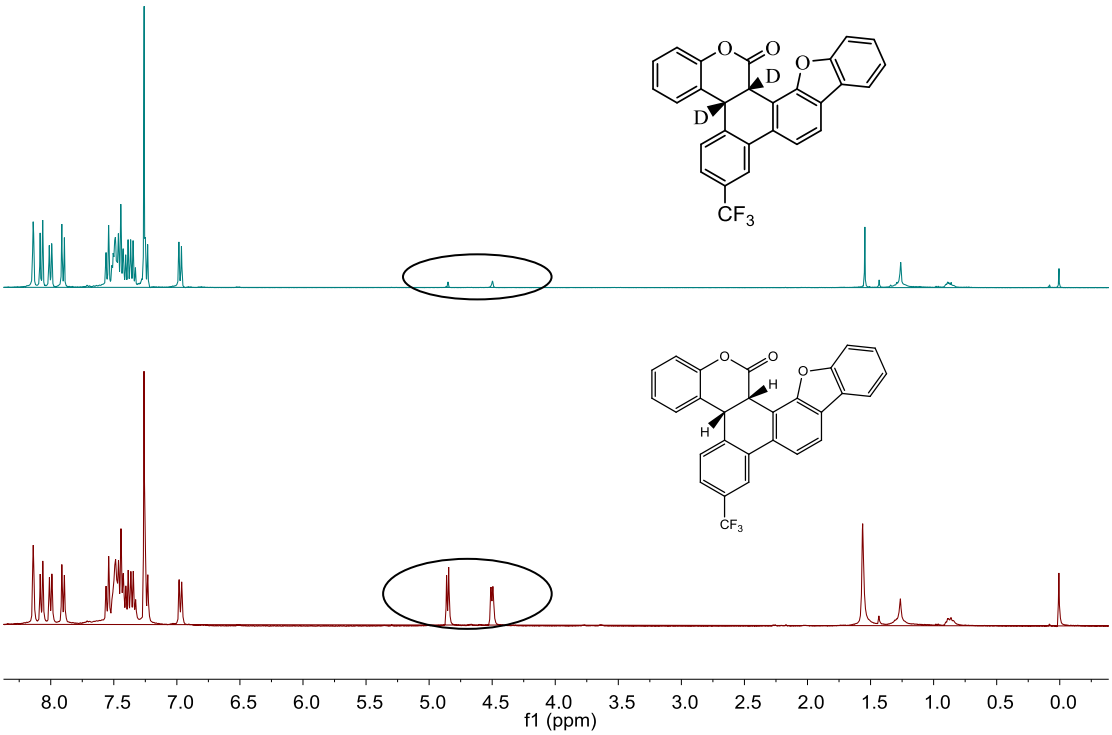
^{13}C NMR spectrum of **2a** ($CDCl_3$, 100MHz)



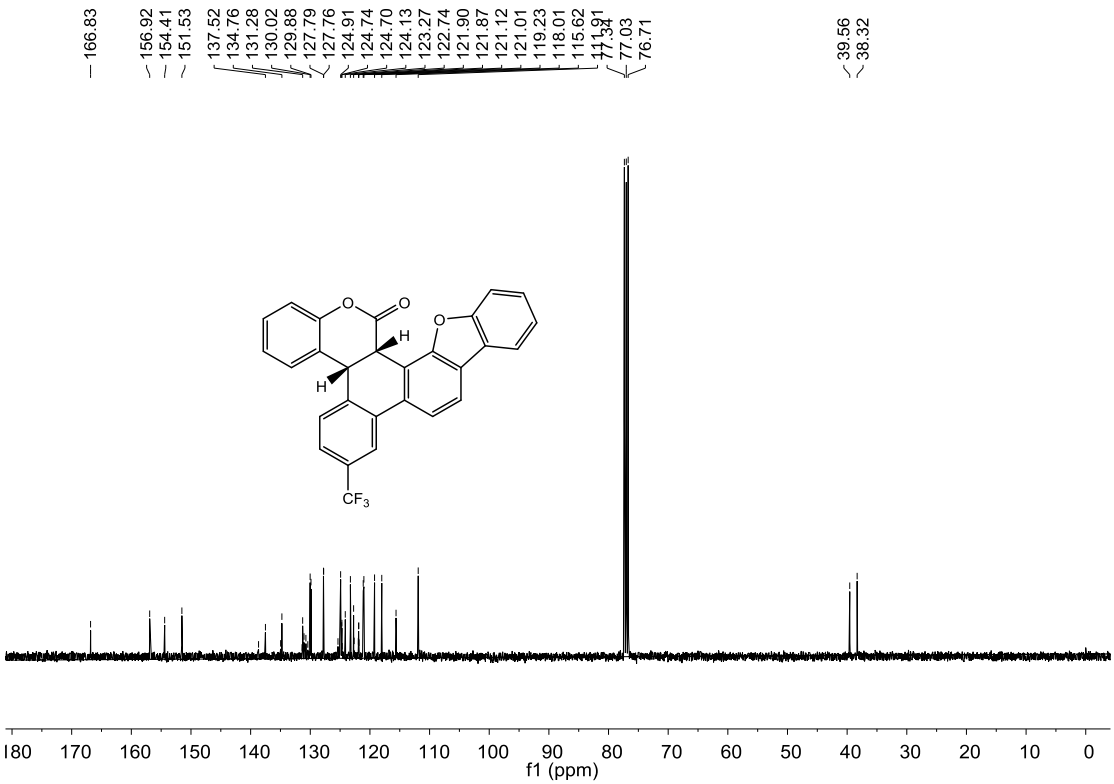
^{1}H NMR spectrum of **2b** ($CDCl_3$, 400MHz)



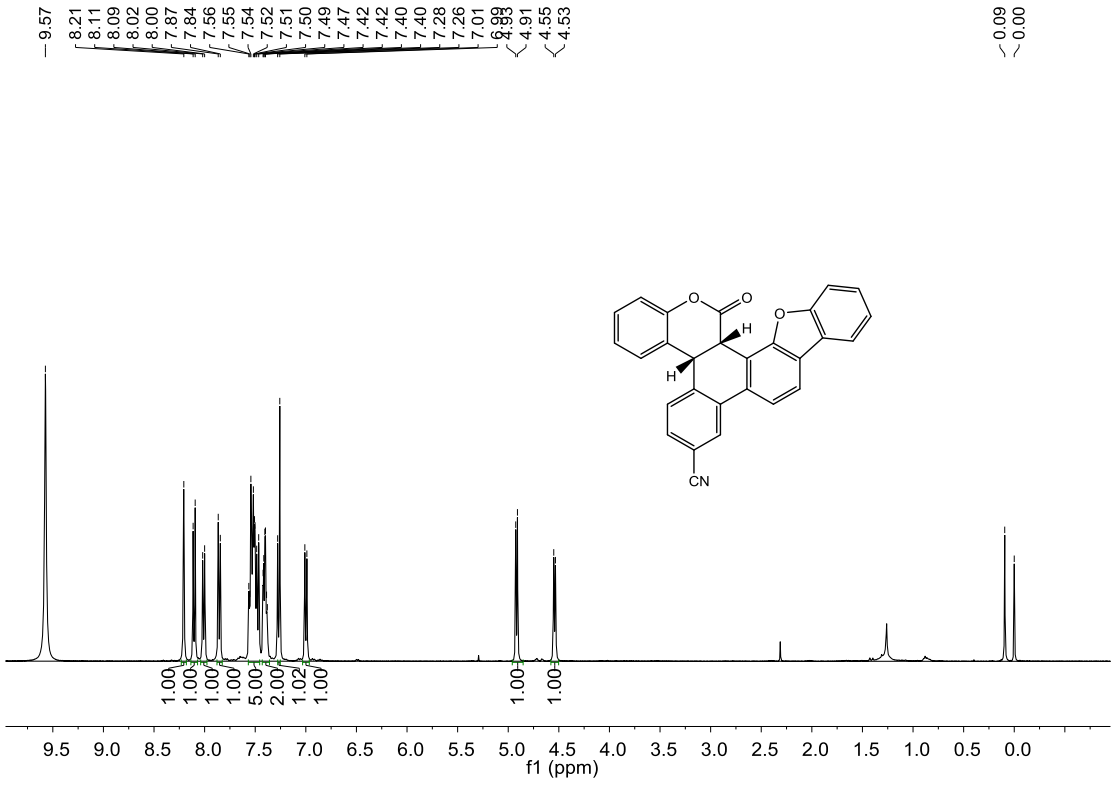
^{1}H NMR spectrum of **2b′** ($CDCl_3$, 400MHz)



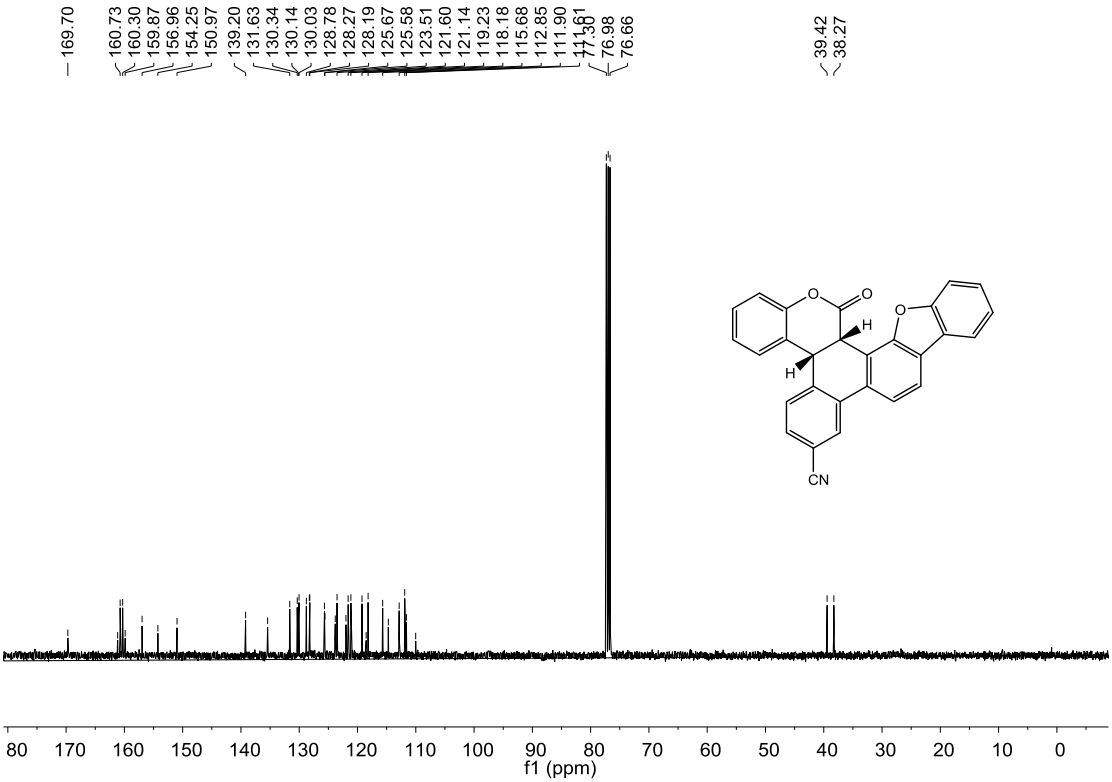
^{1}H NMR spectrum of **2b** and **2b-2D** ($CDCl_3$, 400MHz)



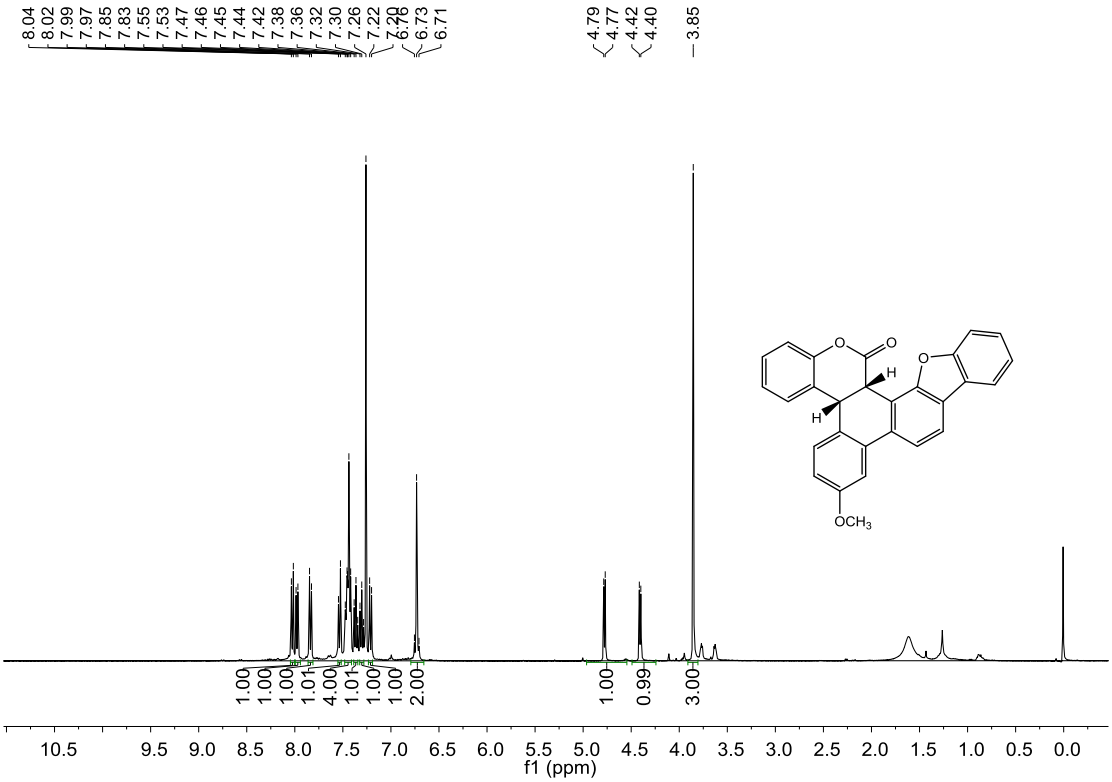
^{13}C NMR spectrum of **2b** ($CDCl_3$, 100MHz)



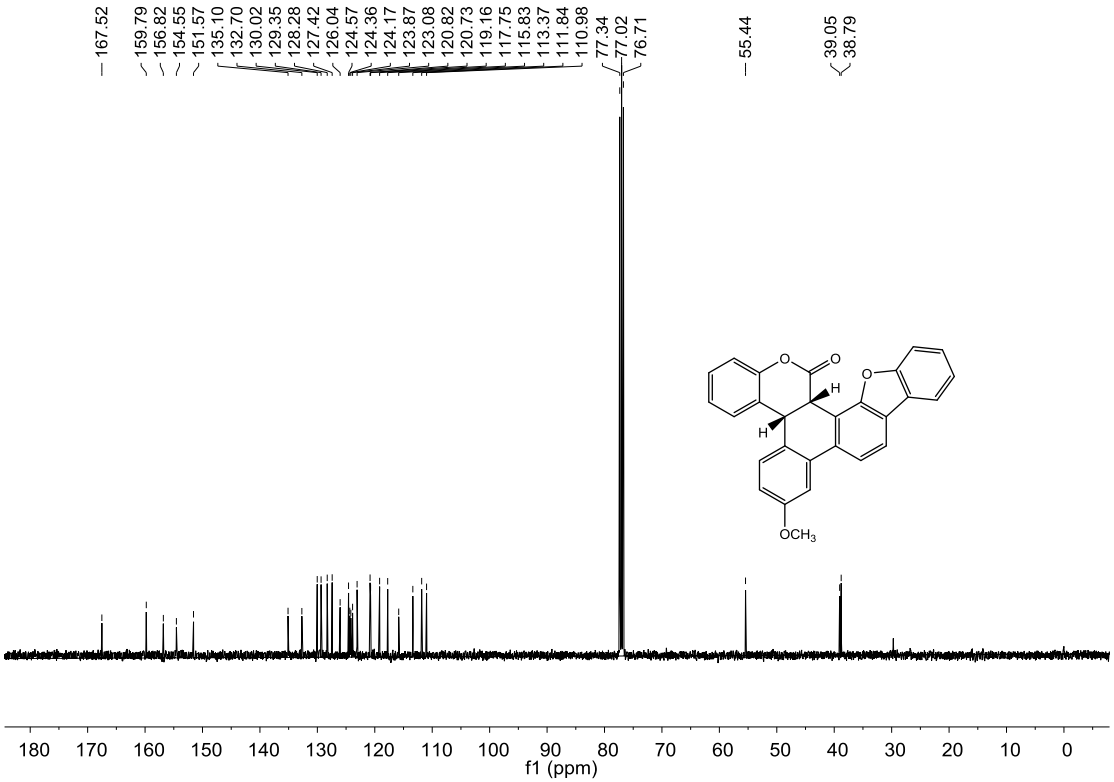
^{1}H NMR spectrum of **2c** ($CDCl_3$, 400MHz)



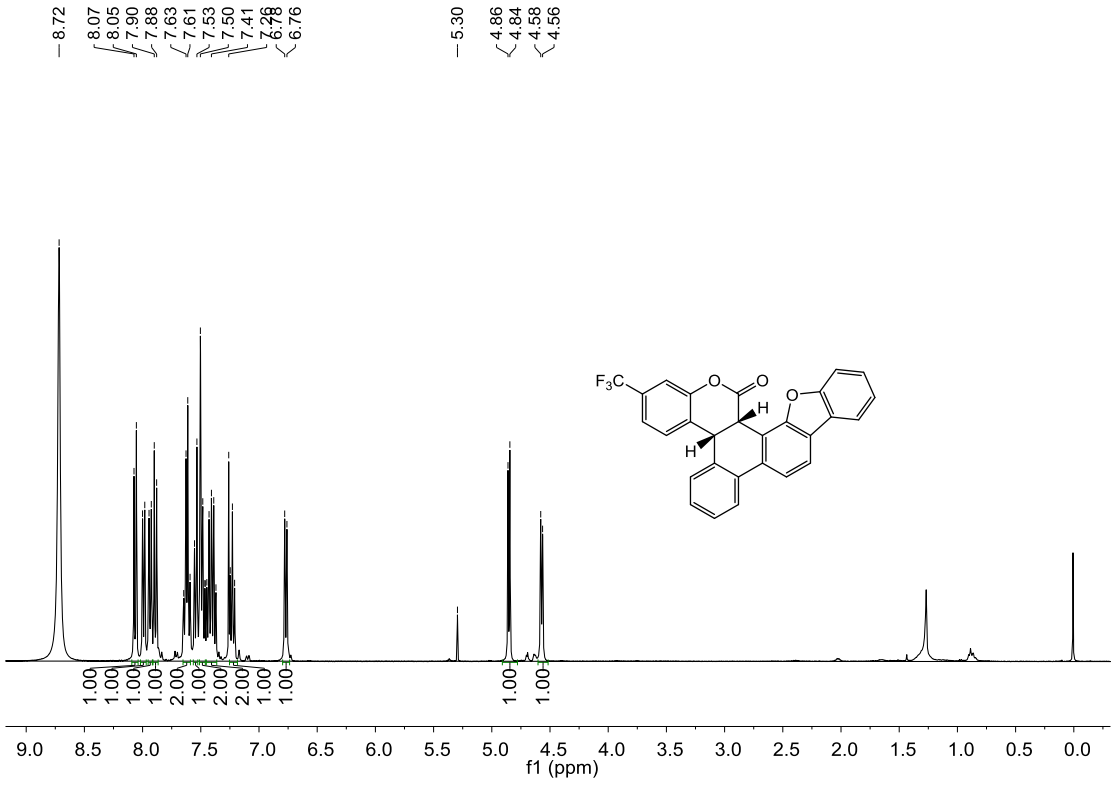
^{13}C NMR spectrum of **2c** ($CDCl_3$, 100MHz)



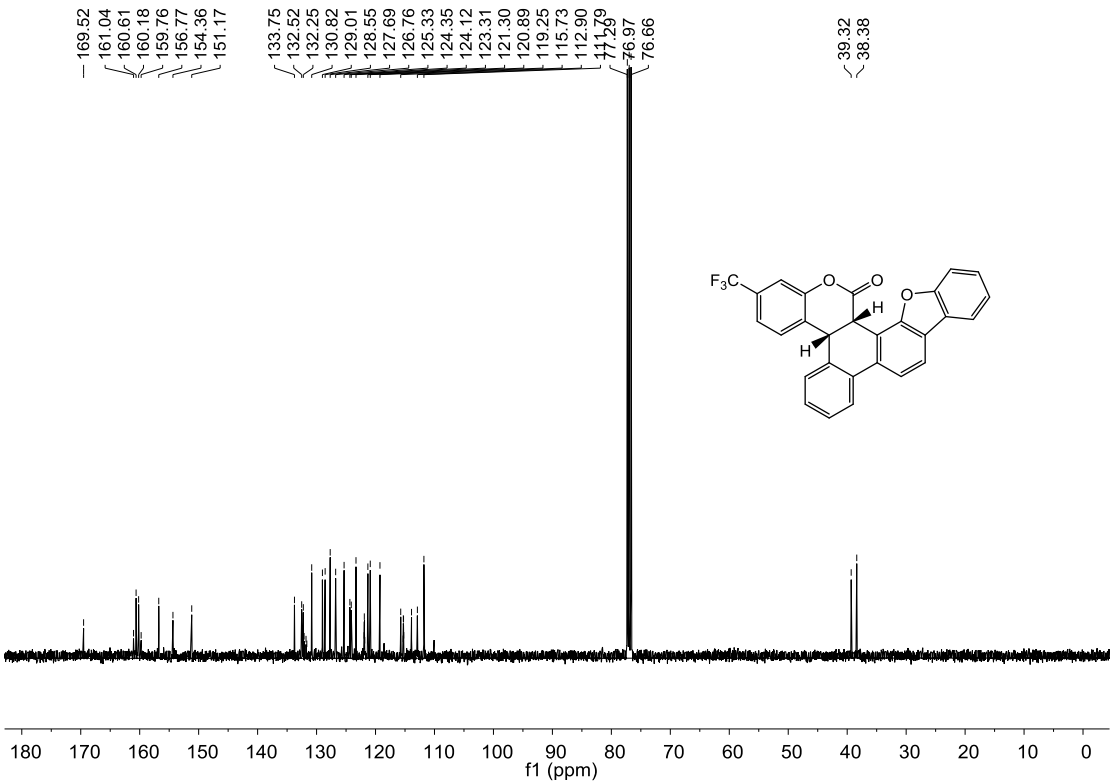
^{1}H NMR spectrum of **2d** ($CDCl_3$, 400MHz)



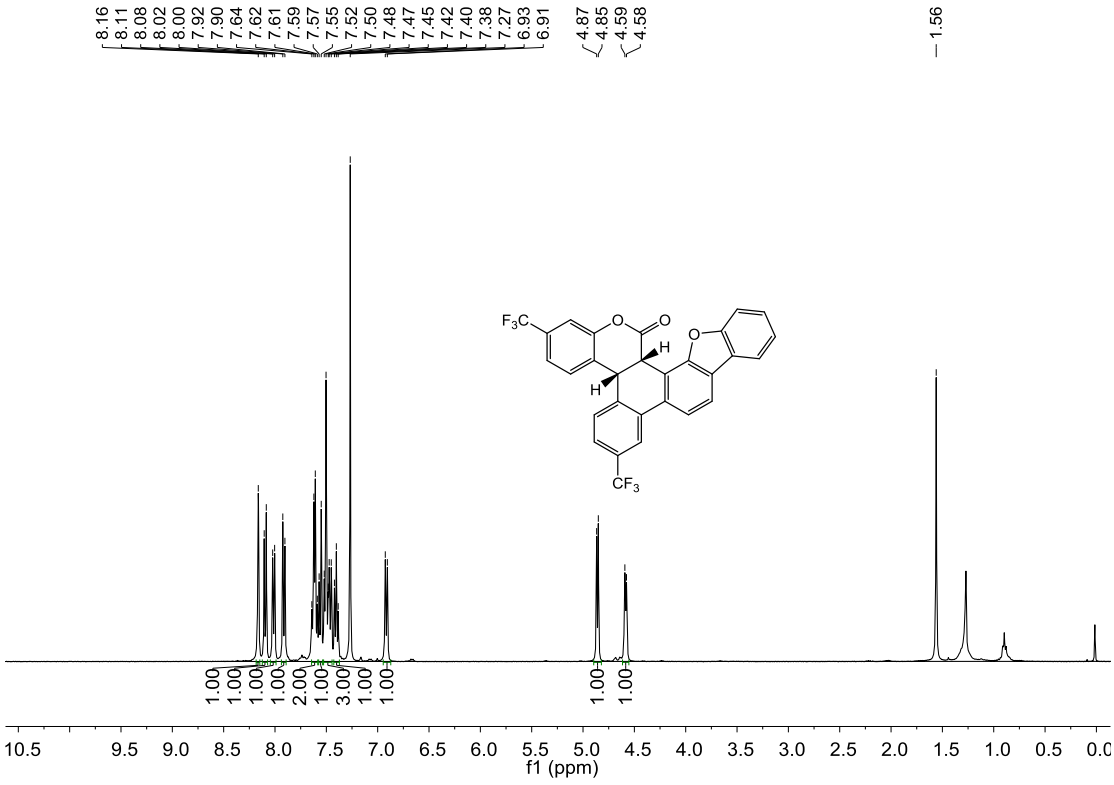
^{13}C NMR spectrum of **2d** ($CDCl_3$, 100MHz)



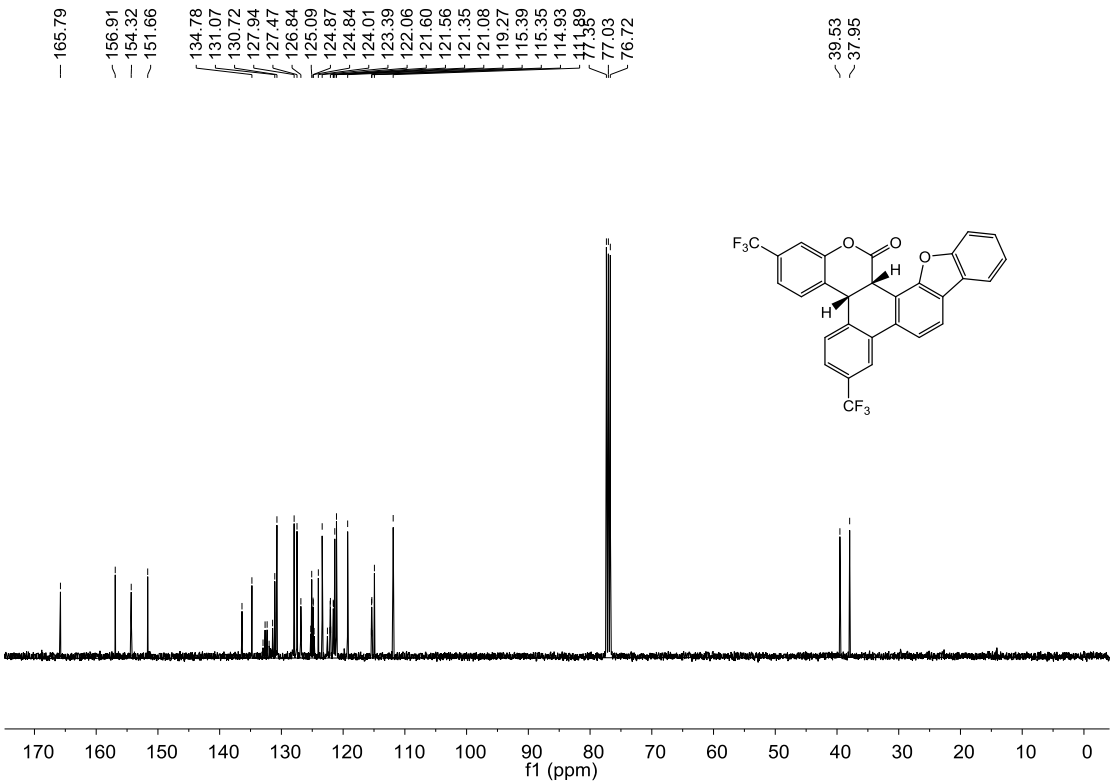
^{1}H NMR spectrum of **2e** ($CDCl_3$, 400MHz, TFA-d_1)



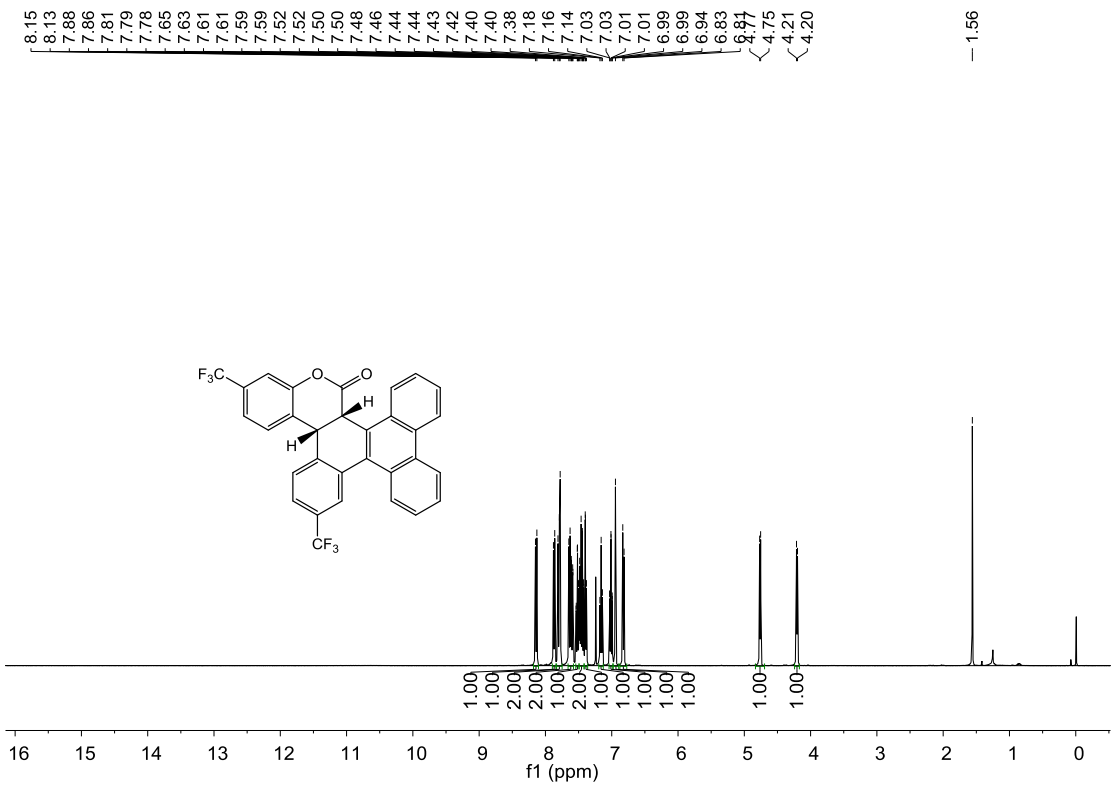
^{13}C NMR spectrum of **2e** ($CDCl_3$, 100MHz, TFA-d_1)



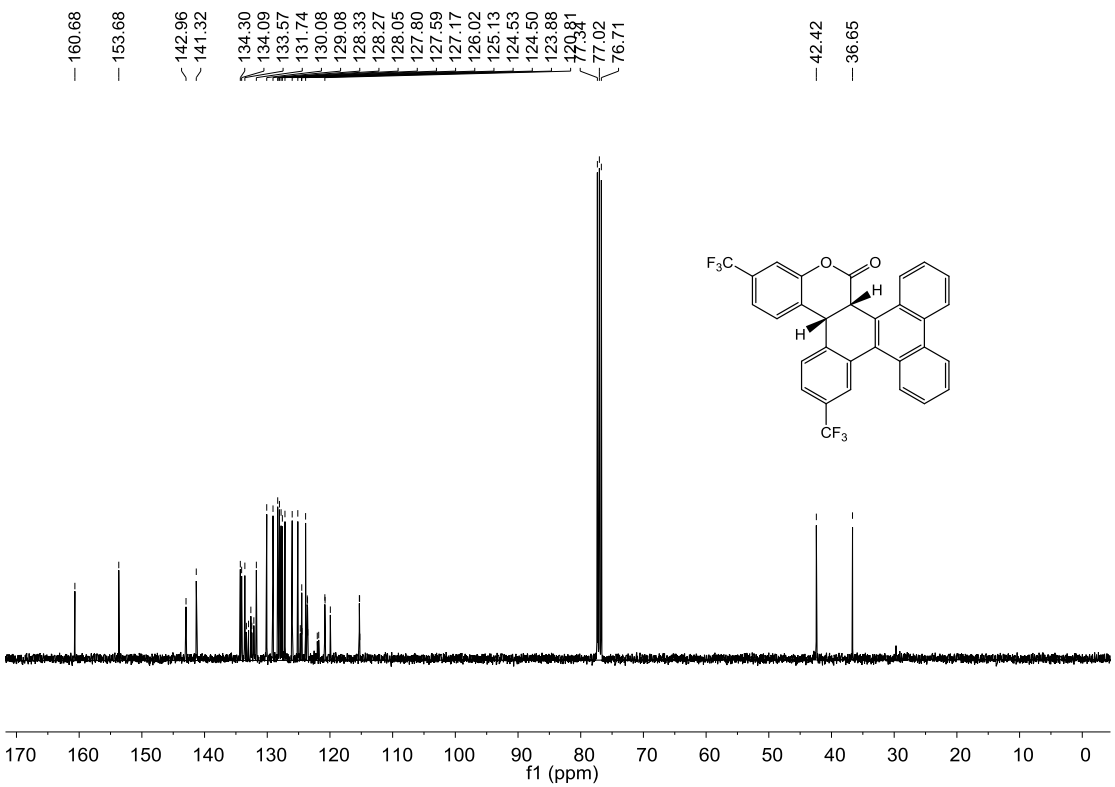
^{1}H NMR spectrum of **2f** ($CDCl_3$, 400MHz)



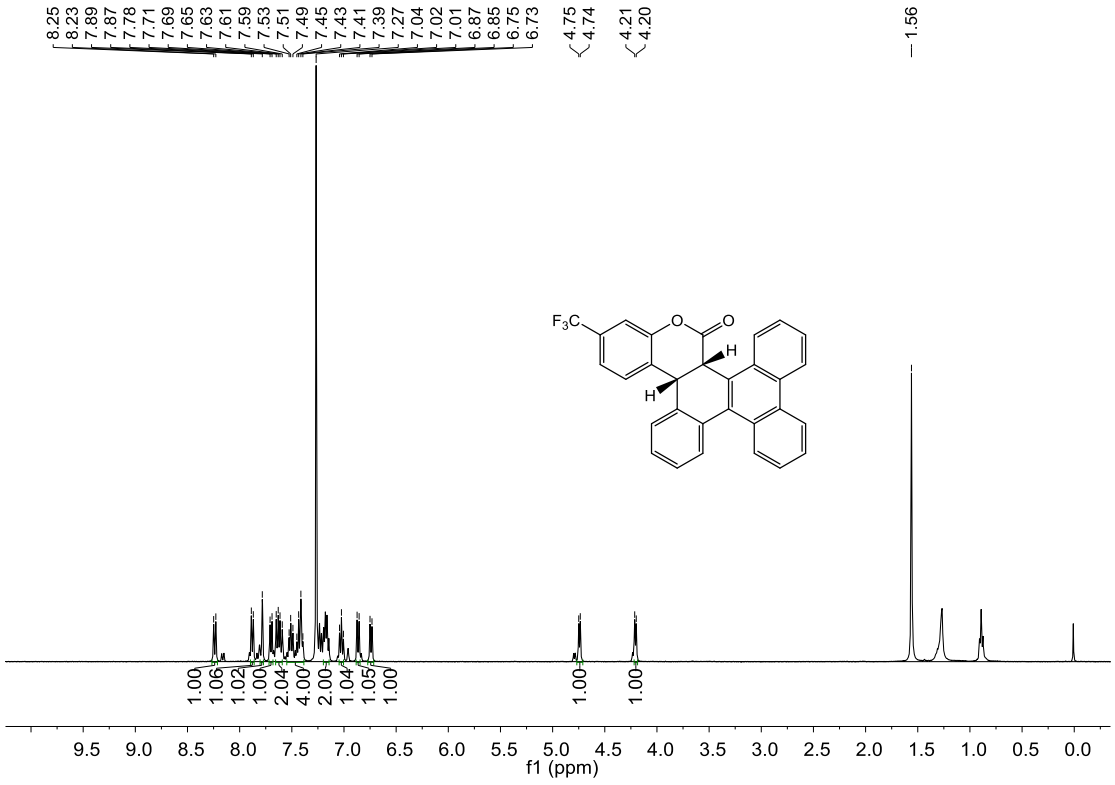
^{13}C NMR spectrum of **2f** ($CDCl_3$, 100MHz)



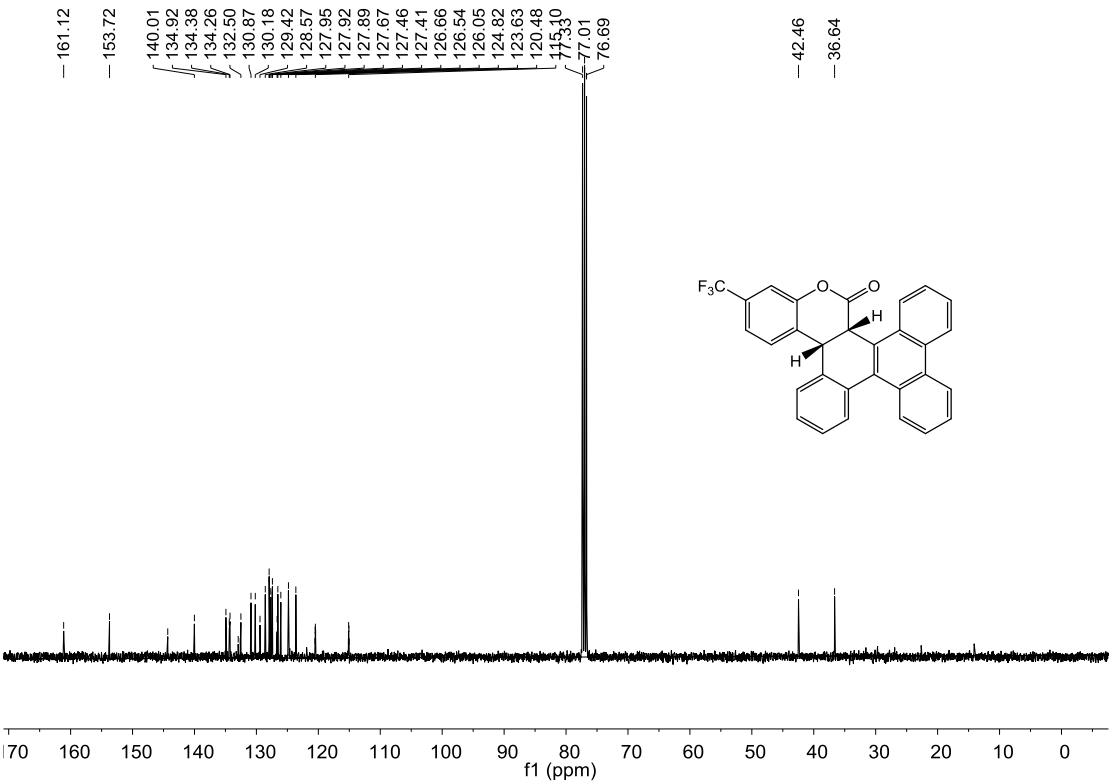
^{1}H NMR spectrum of **2g** ($CDCl_3$, 400MHz)



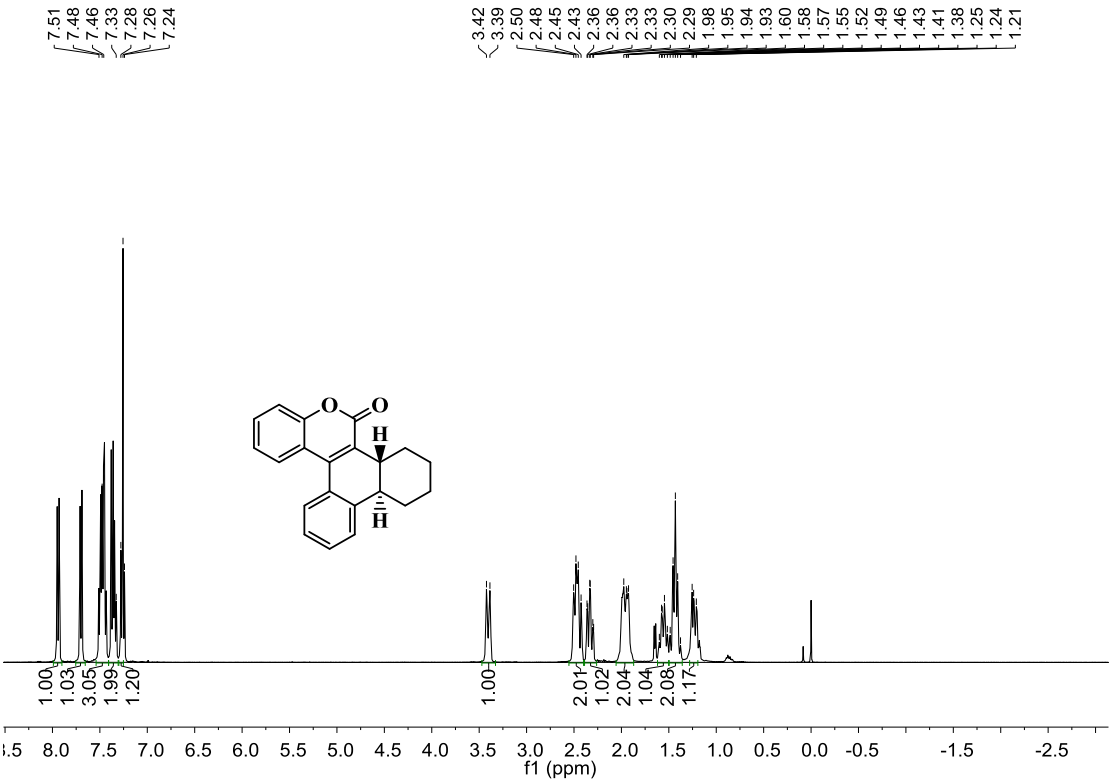
^{13}C NMR spectrum of **2g** ($CDCl_3$, 100MHz)



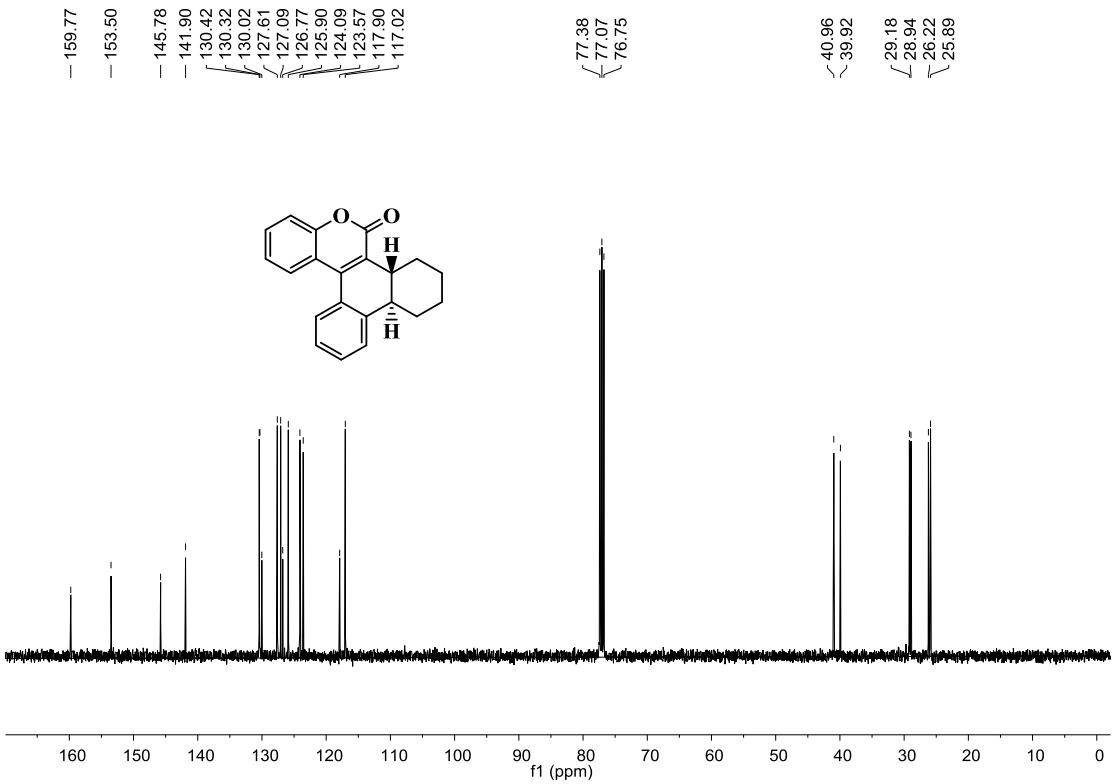
^{1}H NMR spectrum of **2h** ($CDCl_3$, 400MHz)



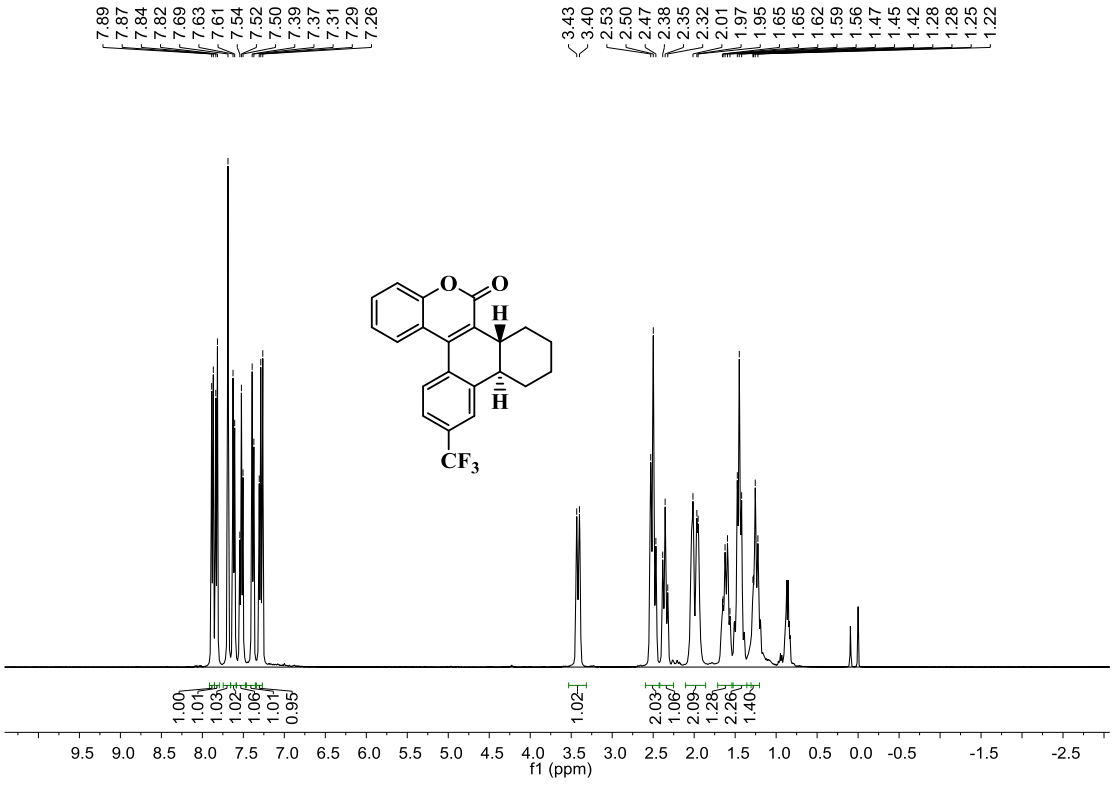
^{13}C NMR spectrum of **2h** ($CDCl_3$, 100MHz)



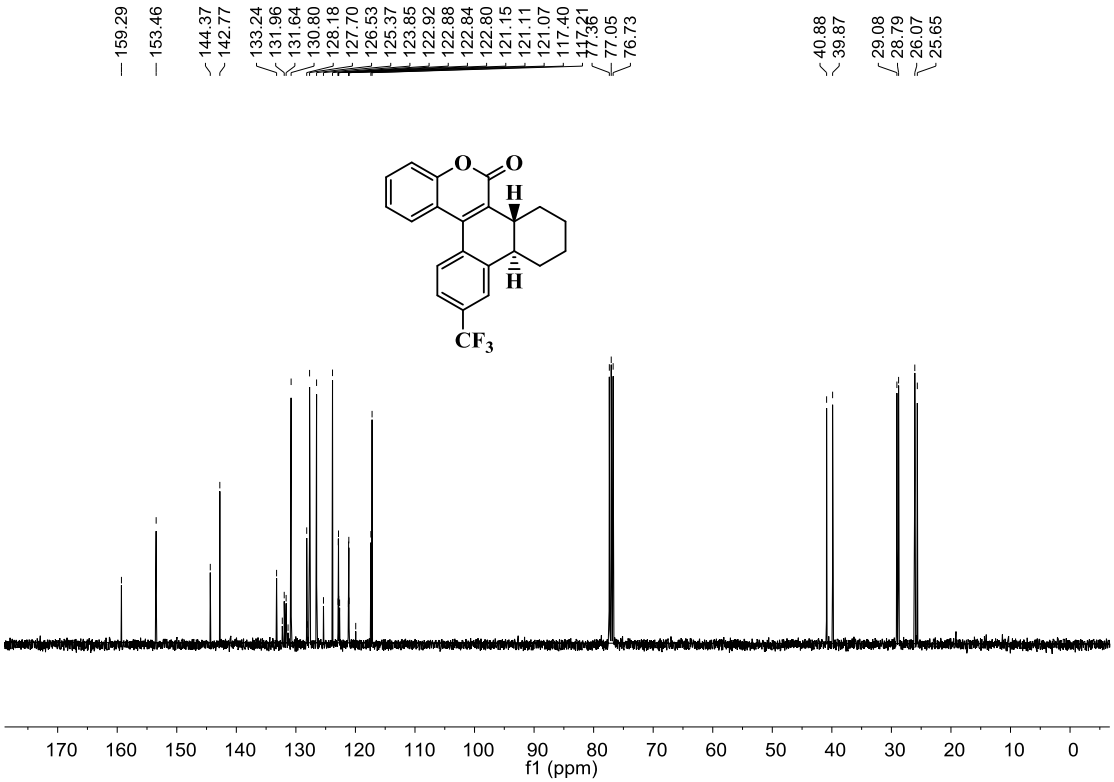
^{1}H NMR spectrum of **4a** ($CDCl_3$, 400MHz)



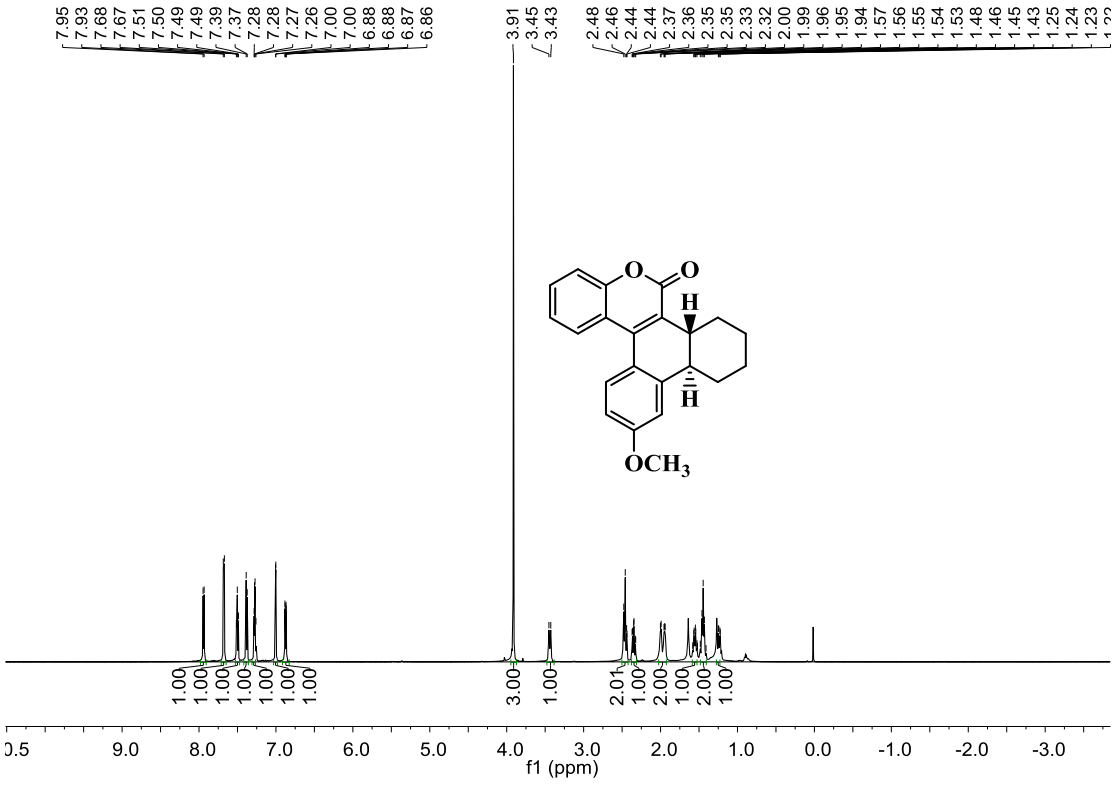
^{13}C NMR spectrum of **4a** ($CDCl_3$, 100MHz)



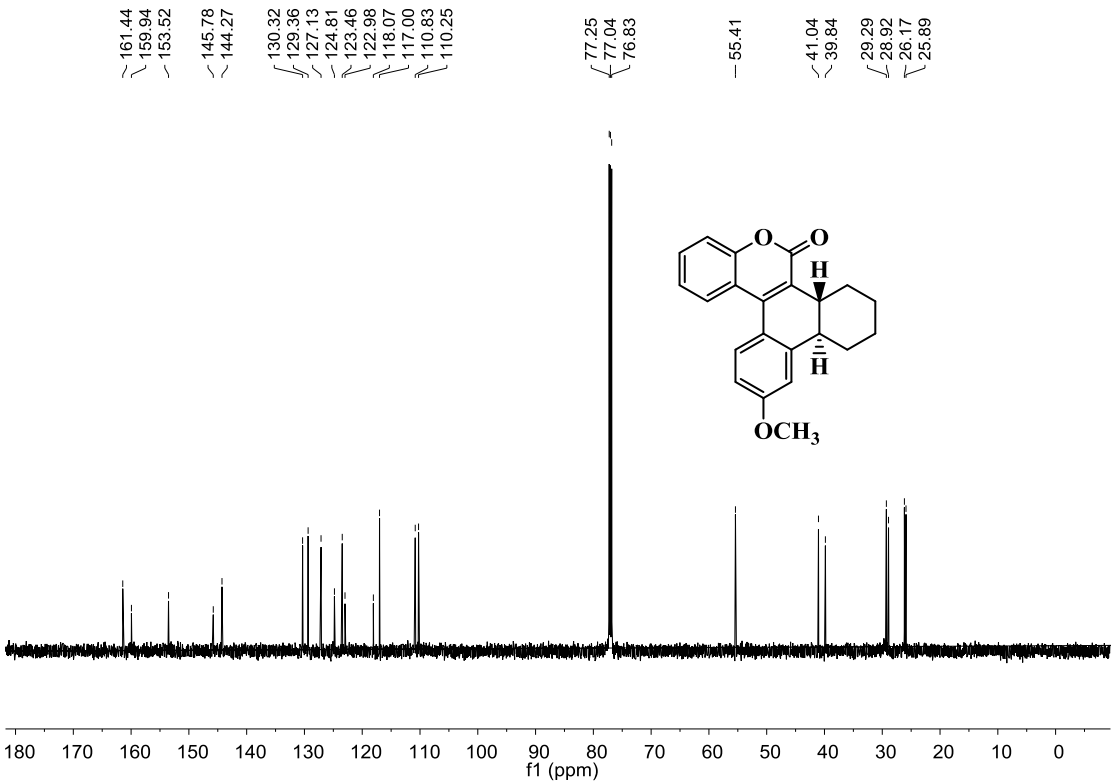
^{1}H NMR spectrum of **4b** ($CDCl_3$, 400MHz)



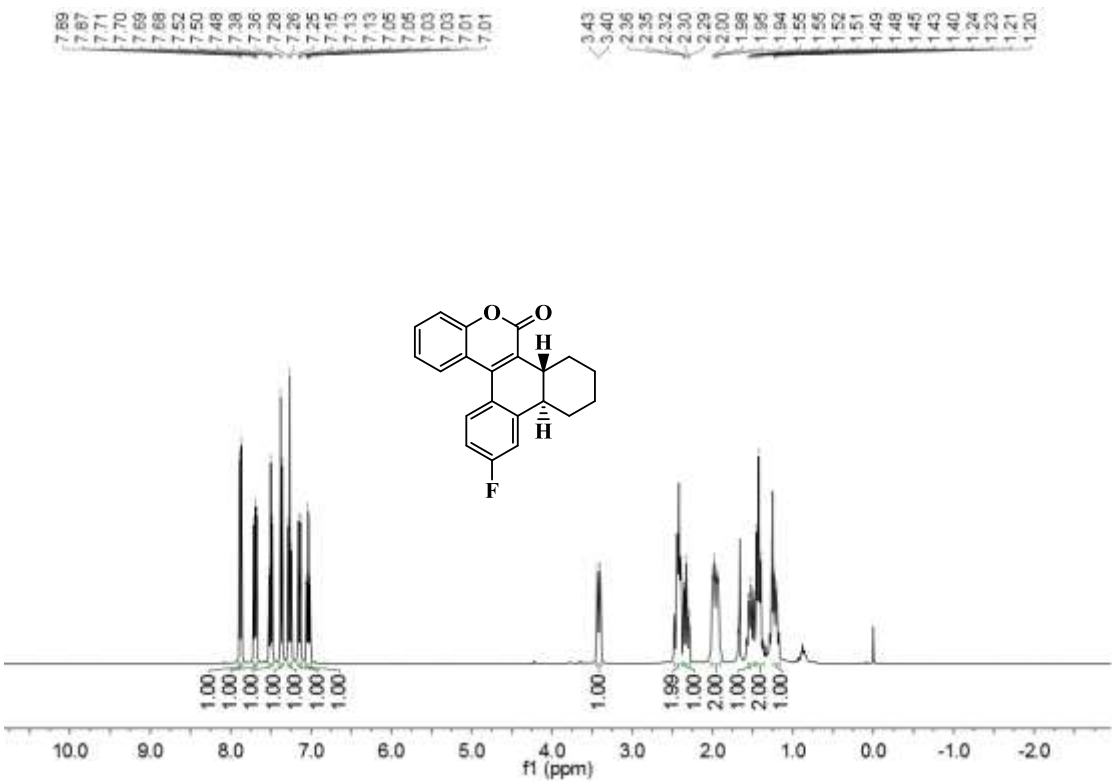
^{13}C NMR spectrum of **4b** ($CDCl_3$, 100MHz)



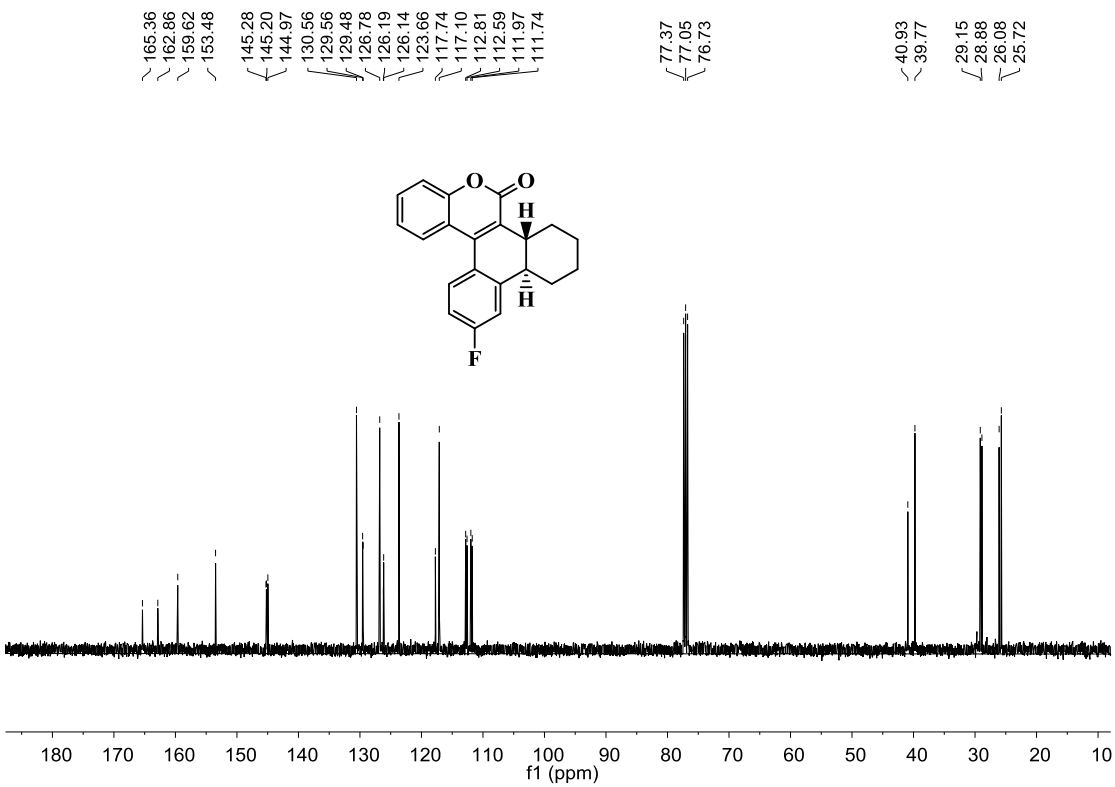
^{1}H NMR spectrum of **4c** ($CDCl_3$, 600MHz)



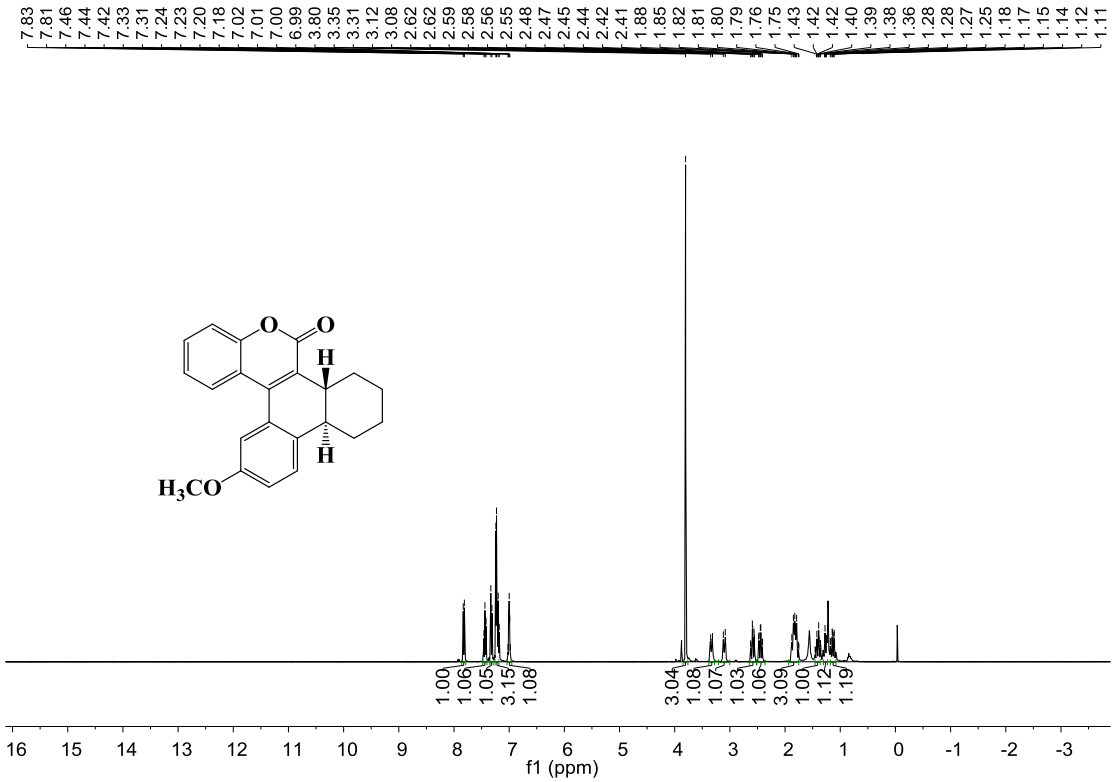
^{13}C NMR spectrum of **4c** ($CDCl_3$, 151MHz)



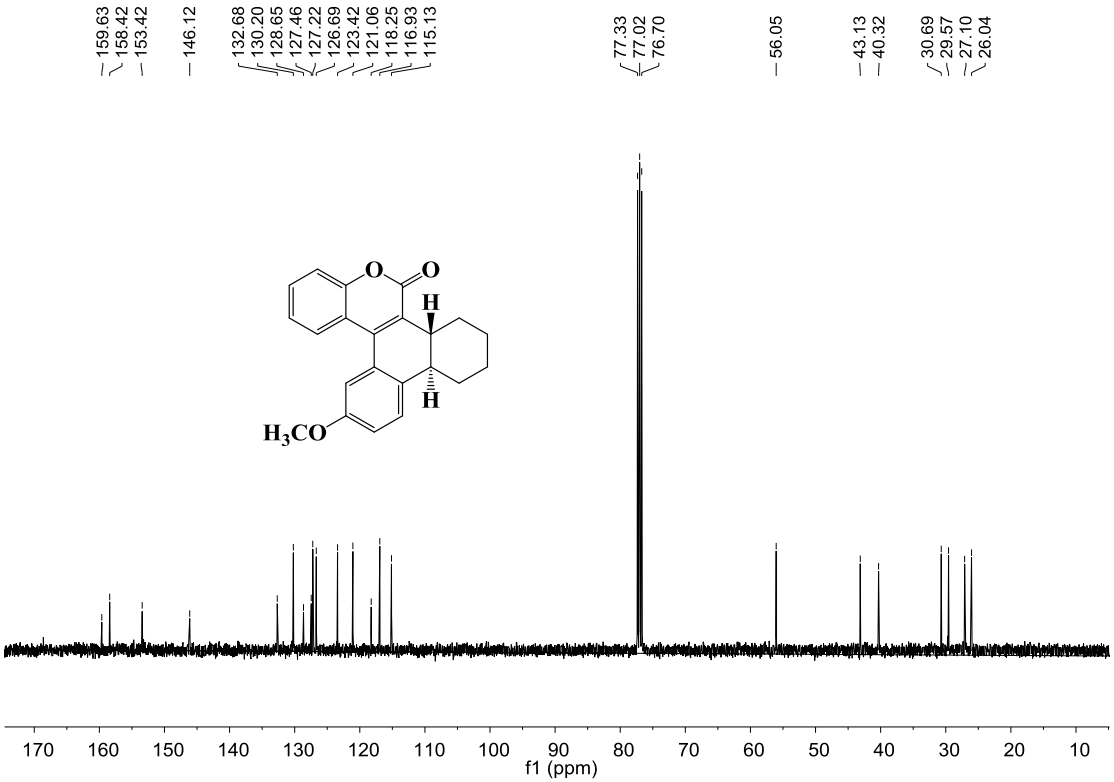
^{1}H NMR spectrum of **4d** ($CDCl_3$, 400MHz)



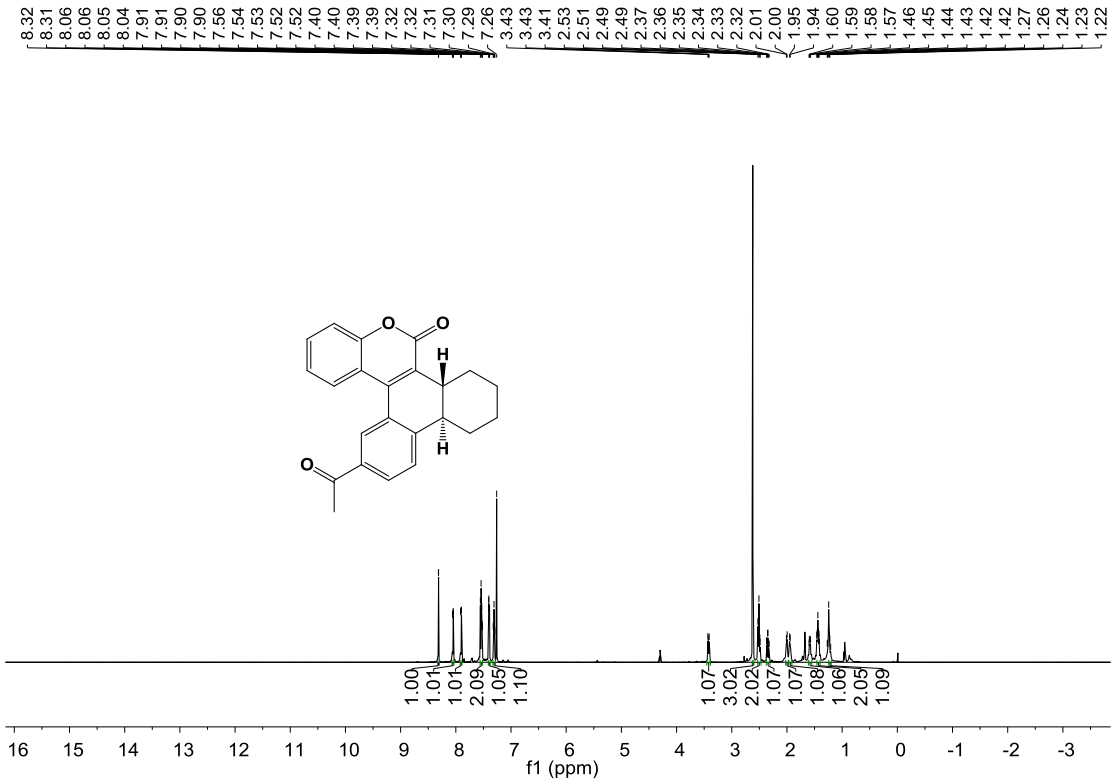
^{13}C NMR spectrum of **4d** ($CDCl_3$, 100MHz)



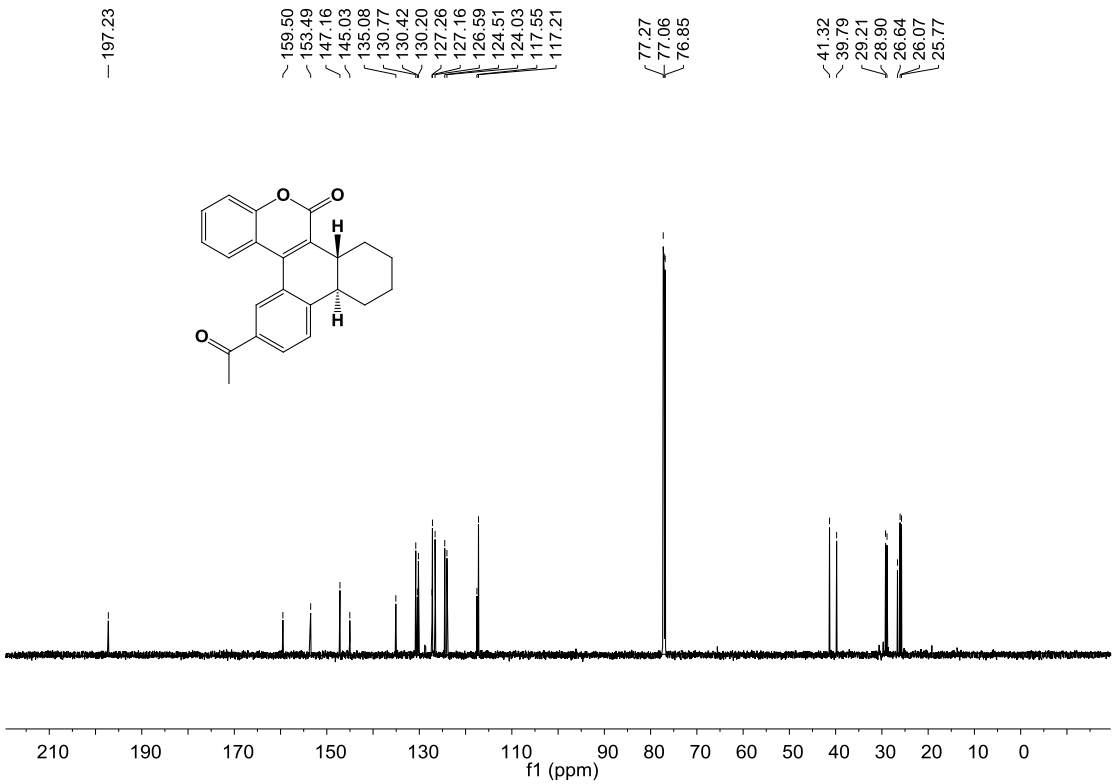
^{1}H NMR spectrum of **4e** ($CDCl_3$, 400MHz)



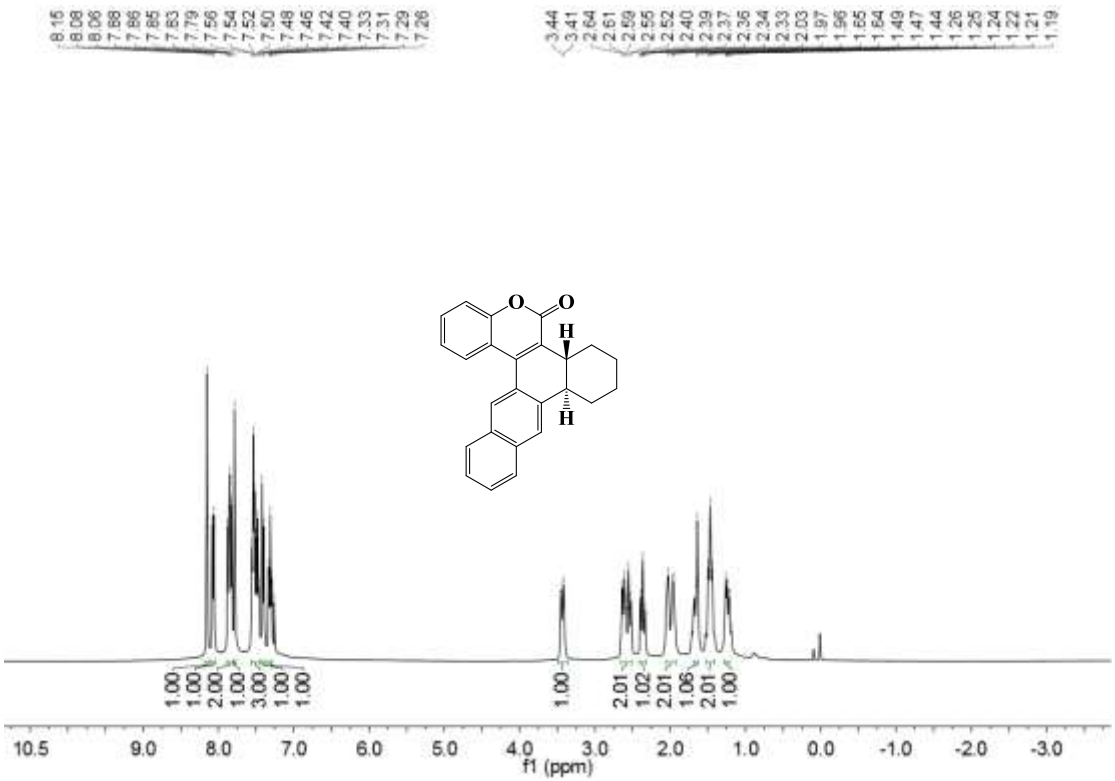
^{13}C NMR spectrum of **4e** ($CDCl_3$, 100MHz)



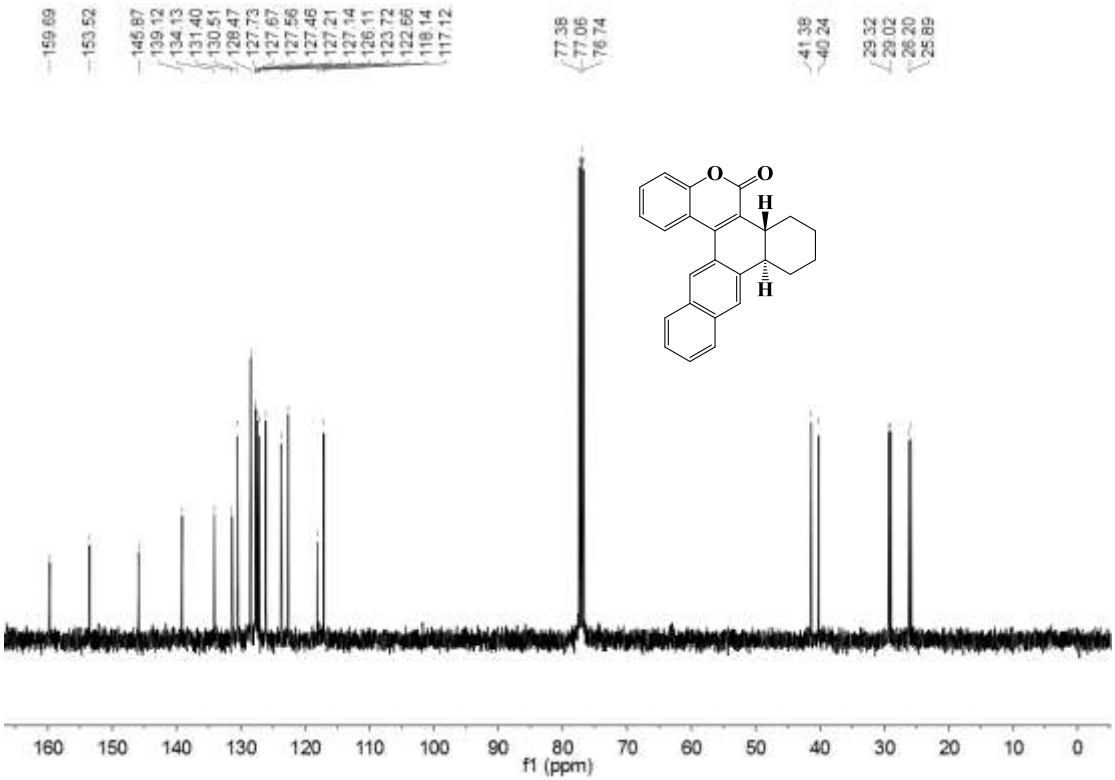
^{1}H NMR spectrum of **4f** ($CDCl_3$, 600MHz)



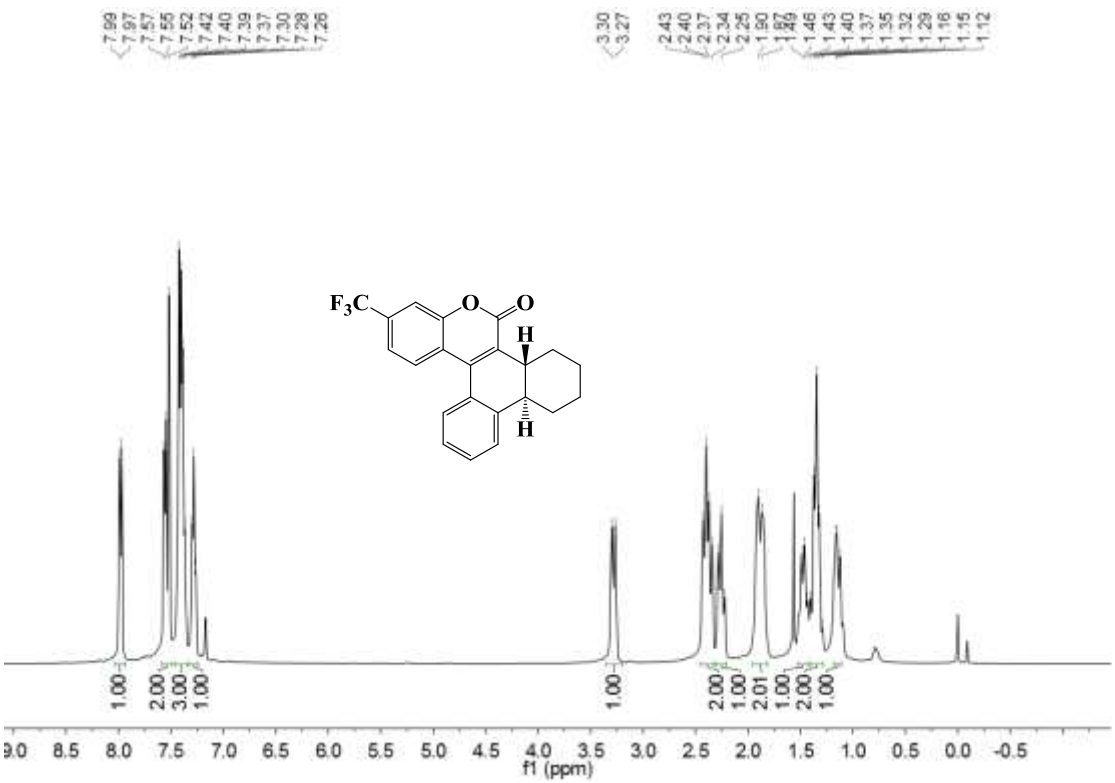
^{13}C NMR spectrum of **4f** ($CDCl_3$, 151MHz)



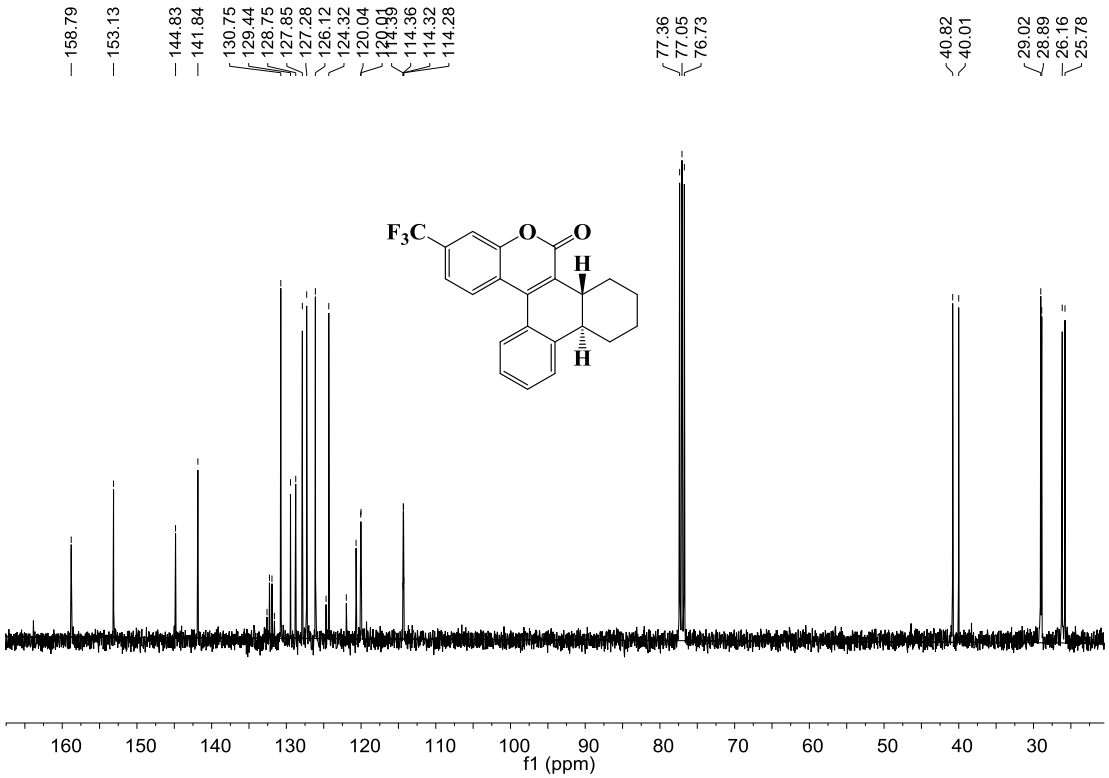
^{1}H NMR spectrum of **4g** ($CDCl_3$, 400MHz)



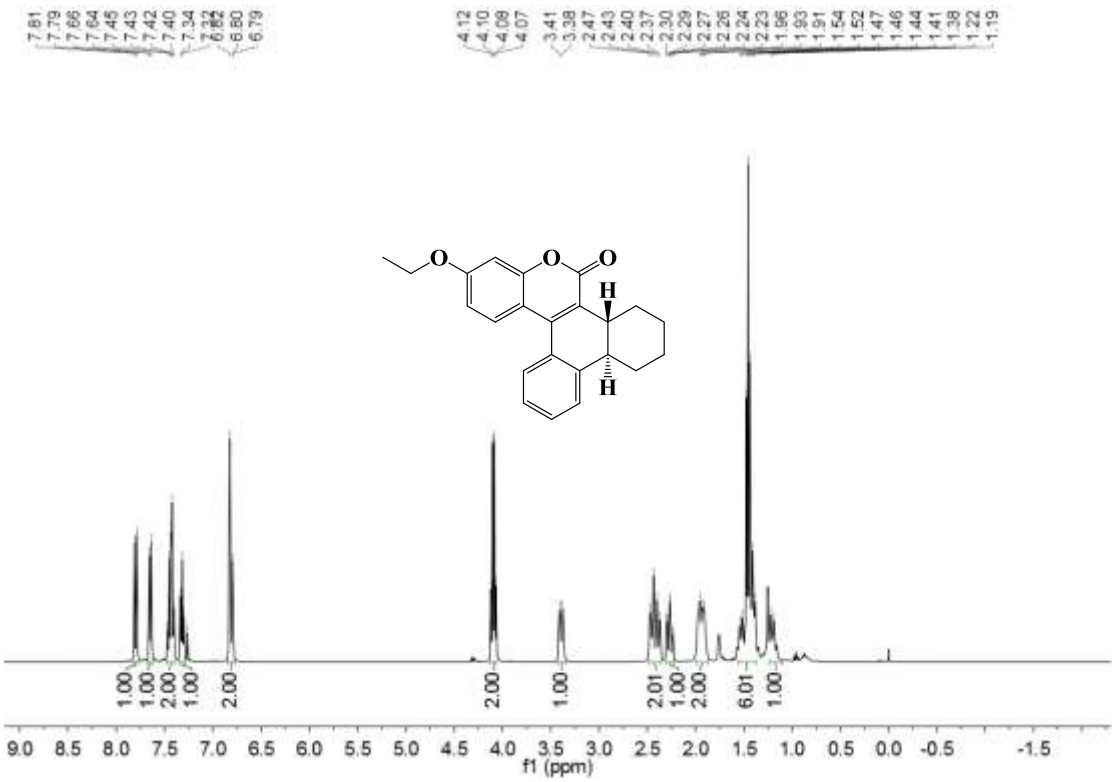
^{13}C NMR spectrum of **4g** ($CDCl_3$, 100MHz)



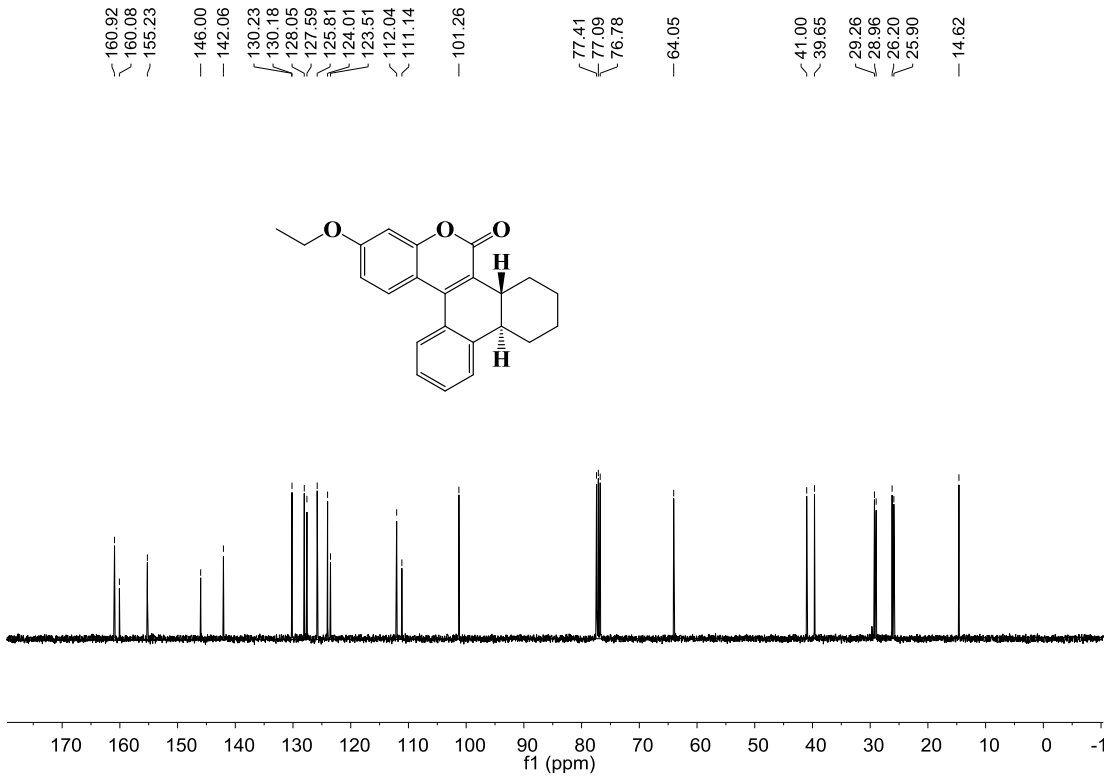
^{1}H NMR spectrum of **4h** ($CDCl_3$, 400MHz)



^{13}C NMR spectrum of **4h** ($CDCl_3$, 100MHz)



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



^{13}C NMR spectrum of **4i** ($CDCl_3$, 100MHz)