Supporting Information

Mn(III)-Catalysed Domino Process for C-3 Substituted Dihydrocoumarins from 2-hydroxybenzyl Alcohols and 4-hydroxy-2H-chromen-2-ones

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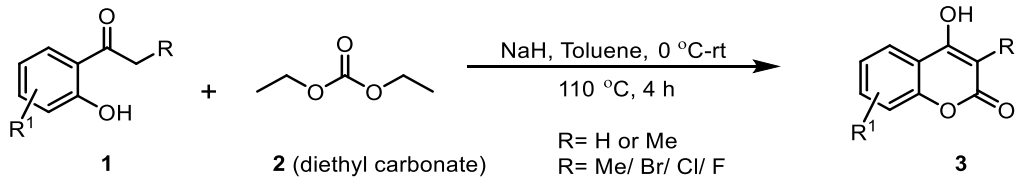
General information and data collection: Ketones, alcohols, catalysts, and all the reagents were purchased from Sigma-Aldrich. All the solvents used in the reactions were AR grade and purchased from Thermofisher Scientific. The column chromatographic separations were achieved over 100−200 mesh size silica gel, and visualization was completed with UV light. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker or JEOL spectrometer at 400 and

100 MHz, respectively. The following information was used in NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad; ddd, doublet of doublet of doublet. High-resolution mass spectra were recorded via a Waters Synapt G2 applying electrospray ionization (ESI). Infrared (IR) spectra were obtained with a Bruker Alpha-E infrared spectrometer. The melting point was measured using the BUCHI M-560 melting-point instrument. All melting points were measured in an open glass capillary tube. Single-crystal diffraction analysis data were collected at 100 K with a Bruker Kappa Apex III CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite monochromatic Cu Kα radiation. Deposition Number 2243887 (**5k**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Synthesis of 4-hydroxy coumarins using reported procedure A:[1]



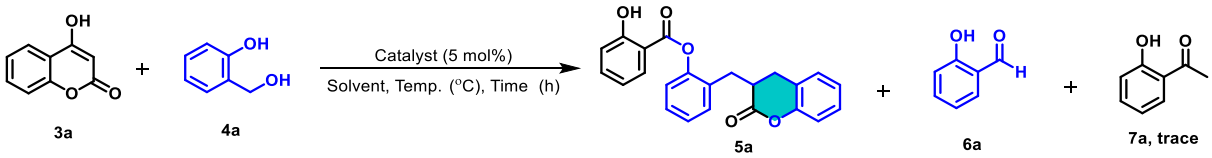
In an oven dried 100 mL round bottom flask 2-hydroxy acetophenone (1.0 equiv., 10.0 mmol) was suspended in anhydrous toluene (20 mL) at room temperature. The mixture was placed in an ice bath at 0 °C, and sodium hydride (10.0 equiv., 100.0 mmol) was added to this under Nitrogen atmosphere. The reaction mixture was vigorously stirred for 20 min at the same temperature and then warmed to room temperature. Diethyl carbonate (3.0 equiv., 30.0 mmol) was added to this, and the reaction mixture was refluxed at 110 °C for 4 h. After completion of the reaction, the reaction mixture was cooled to room temperature and then filtered through Buchner funnel under vacuum. The solid residue thus obtained was suspended in ice-cold water (50 mL) and acidified by adding 2 N HCl dropwise (pH 1-2). The solid precipitate obtained was filtered through a Buchner funnel under vacuum till dryness to get almost pure 4-hydroxy coumarins **3.** All the obtained results are shown in Scheme S1.

General experimental procedure B for the synthesis of 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoates: $Mn(OAc)_3.2H_2O$ catalyst (5 mol%), 4-hydroxy coumarins **3** (0.5 mmol, 1 equiv.), 2-hydoxy benzyl alcohols **4** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were added to an oven-dried 20 mL resealable pressure tube (equipped

with rubber septum) without maintaining any special reaction condition. The tube was sealed with a cap using a crimper, and the reaction mixture was stirred at 140 °C in a preheated oil bath for 24 h. The reaction mixture was cooled to room temperature and concentrated under a vacuum. The residue was purified by 100-200 mesh silica-gel column chromatography using (EtOAc: *n*-hexane 5:95 to 6:94) for 0.5 Retention factor (Rf) to afford the pure product of 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoates **5**.

Experimental procedure C for the synthesis of 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate 5a: $Mn(OAc)_3.2H_2O$ catalyst (5 mol%), 4-hydroxy-2*H*-chromen-2-one **3a** (10 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (20 mmol, 2 equiv.), and dichloroethane (30 mL) were added to an oven-dried 55 mL pressure tube (equipped with a septum). The reaction mixture was stirred at 140 °C in a parallel synthesizer for 24 h. The reaction mixture was cooled to room temperature and concentrated under a vacuum. The residue was purified by 100-200 mesh silica-gel column chromatography using (EtOAc: n-hexane 5:95) to afford the pure product of 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate **5a,** providing 66% yield.

Table S1: Optimization Study



Entry	Catalyst (5 mol%)	% Yield (5a: 6a)		Entry	Catalyst (5 mol%)	% Yield (5a: 6a)
1.	-	NR		**15.**	**$Mn(OAc)_3.2H_2O$**	**55: ND**
2.	$Ru(H_2)(CO)(PPh_3)_3$	20: 25		16.	$Mn(OTf)_2$	28: ND
3.	$Ru(H)(Cl)(CO)(PPh_3)_3$	15: 22		17.	$Mn(acac)_3$	51: ND
4.	$[Ru(p\text{-cymene})Cl_2]_2$	10: 20		18.	$CuCl_2$	ND: ND
5.	$RuCl_3.xH_2O$	Trace:trace		19.	CuCl	36: ND
6.	$FeCl_2$	07: ND		20.	CuBr	35: ND
7.	$Fe(OTf)_3$	Trace: ND		21.	$Cu(OTf)_2$	ND: ND
8.	$InCl_3$	Trace: ND		22.	$Cu(OAc)_2$	26: ND
9.	$In(OTf)_3$	Trace: ND		23.	$Fe(OAc)_3$	23: ND
10.	$NiCl_2.(PPh_3)_2$	28: ND		24.	$Zn(OAc)_2$	40: ND
11.	$Ni(OH)_2$	26: ND		25.	$Ni(OAc)_2$	48: ND
12.	$NiBr_2.xH_2O$	28: ND		26.	AcOH	16: ND
13.	$NiCl_2.6H_2O$	25: ND		27.[a]	AcOH	40: ND
14.	$MnCl_2$	26: ND		28.	*p*-TSA / Amberlyst-15	ND: ND

Reaction condition: catalyst (5 mol%), compound **1a** (0.3 mmol), compound **2a** (0.6 mmol), and toluene (3 mL) were stirred in a sealed tube in a preheated oil bath at 140 °C for 36 h. NR = No Reaction. ND = Not Detected. All mentioned yields are isolated yields. [a]1.0 equiv. of acetic acid (AcOH) used.

Xray Analysis:

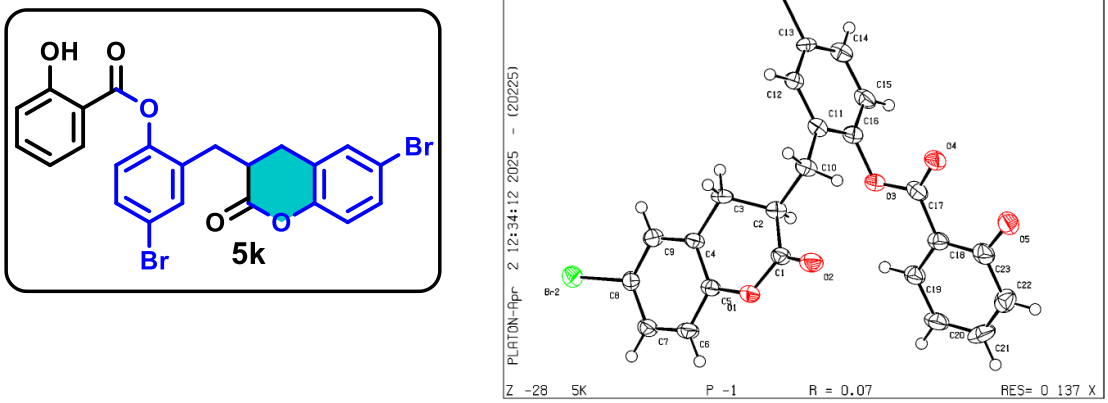


Fig. S1. ORTEP crystal structure of **5k** showing thermal ellipsoids at the 50% probability level (CCDC No. 2243887).

Crystallographic parameters of 5k:

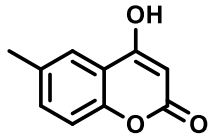
Parameters	**5k**
Empirical formula	$C_{23}H_{16}Br_2O_5$
Formula Mass/g mol	531.15
Experimental crystal description	Needles
Colour	Colourless
D calcd/g cm^{-3}	1.730
Crystal system	triclinic
Space group	P^{-1}
a/ Å	4.725(8)
b/ Å	13.22(5)
c/ Å	17.69(6)
α/ deg	112
β/ deg	92
γ/ deg	89
V/$Å^3$	1020(6)
Z	16
T / K	296 K
Diffraction Source	Cu K\a
Diffraction radiation wavelength/ Å	1.54178
Diffraction reflection theta full	0.999
Reflection number total	4270
Reflection number gt	3172
μ/mm^{-1}	5.335
F (000)	526

R_1, wR_2 [I>2σ(I)]	0.1918, 0.1735
R_1, wR_2 (all data)	0.0911, 0.0656
GoF	1.155

Crystal preparation: The crystal was grown by the recrystallization method, where the pure compound was dissolved in a mixture of dichloromethane & methanol (1:1) and kept at room temperature to get the pure crystal of compound **5k**. More information on crystal structures can be obtained from the Cambridge Crystallographic Data Centre (CCDC) with deposition number 2243887.

Characterization data of 4-hydroxy coumarins:

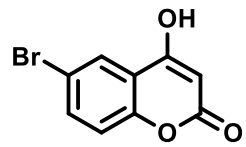
4-hydroxy-6-methyl-2H-chromen-2-one (3b): Prepared according to reported procedure **A**;



3b

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 12.43 (s, 1H), 7.58 (s, 1H), 7.41 (dd, J = 8.4, 1.6 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 5.56 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 165.7, 162.1, 151.7, 133.5, 133.1, 122.8, 116.1, 115.5, 90.9, 20.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_9O_3$, 177.0552; found, 177.0554.

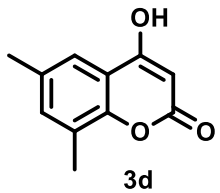
6-bromo-4-hydroxy-2H-chromen-2-one (3c): Prepared according to reported procedure **A**;



3c

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 12.79 (s, 1H), 7.86 (d, J = 2.3 Hz, 1H), 7.77 (dd, J = 8.8, 2.4 Hz, 1H), 7.33 (d, J = 8.8 Hz, 1H), 5.63 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 164.4, 161.4, 152.5, 135.1, 125.3, 118.8, 117.8, 115.7, 91.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_9H_6BrO_3$, 240.9500; found, 240.9495.

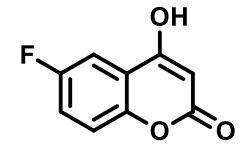
4-hydroxy-6,8-dimethyl-2H-chromen-2-one (3d): Prepared according to reported procedure



3d

A; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 12.30 (s, 1H), 7.34 (s, 1H), 7.17 (s, 1H), 5.54 (s, 1H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 134.4, 132.3, 124.8, 120.4, 115.3, 90.7, 20.3, 15.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{11}H_{11}O_3$, 191.0708; found, 191.0701.

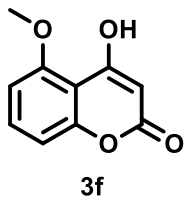
6-fluoro-4-hydroxy-2*H*-chromen-2-one (3e): Prepared according to reported procedure **A**;



3e

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 12.68 (s, 1H), 7.51 – 7.44 (m, 2H), 7.39 (dd, J = 9.8, 4.6 Hz, 1H), 5.62 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 164.8, 164.8, 161.7, 159.1, 156.7, 149.8, 120.1, 119.8, 118.5, 118.4, 117.0, 116.9, 108.8, 108.5, 91.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_9H_6FO_3$, 181.0301; found, 181.0304.

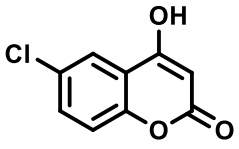
4-hydroxy-5-methoxy-2H-chromen-2-one (3f): Prepared according to reported procedure **A**;



3f

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.45 (t, J = 8.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 5.62 (s, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.9, 156.3, 155.1, 132.6, 111.3, 111.3, 105.7, 104.9, 92.9, 57.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_9O_4$, 193.0501; found, 193.0497.

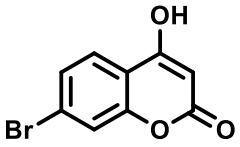
6-chloro-4-hydroxy-2H-chromen-2-one (3g): Prepared according to reported procedure **A**;



3g

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.80 (s, 1H), 7.71 (d, J = 2.6 Hz, 1H), 7.64 (dd, J = 8.8, 2.6 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 5.64 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 161.4, 152.1, 132.3, 128.0, 122.3, 118.5, 117.3, 91.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_9H_6ClO_3$, 197.0005; found, 197.0009.

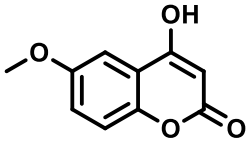
7-bromo-4-hydroxy-2H-chromen-2-one (3h): Prepared according to reported procedure **A**;



3h

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 5.61 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.2, 161.3, 153.9, 127.0, 125.4, 124.8, 119.3, 115.2, 91.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_9H_6BrO_3$, 240.9500; found, 240.9492.

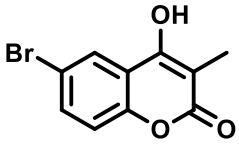
4-hydroxy-6-methoxy-2H-chromen-2-one (3i): Prepared according to reported procedure **A**;



3i

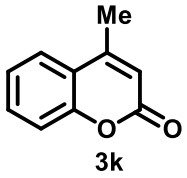
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (s, 1H), 7.27 (d, J = 8.6 Hz, 1H), 7.22 – 7.16 (m, 2H), 5.63 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.4, 162.1, 155.3, 147.9, 120.3, 117.6, 116.3, 105.0, 91.2, 55.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_9O_4$, 193.0501; found, 193.0508.

6-bromo-4-hydroxy-3-methyl-2*H*-chromen-2-one (3j): ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 7.96 (d, J = 2.2 Hz, 1H), 7.67 (dd, J = 8.8, 2.3 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.7, 158.5, 150.6, 133.7, 125.2, 118.3, 118.2, 115.6, 101.3, 9.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_8BrO_3$, 254.9657; found, 254.9654.



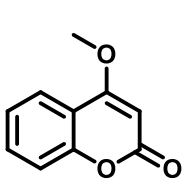
3i

4-methyl-2*H*-chromen-2-one (3k): Prepared using reported procedure:[2] To a mixture of 2-hydroxyacetophenone (1.0 equiv.) and acetic anhydride (2.0 equiv.) in acetonitrile was added DBU (3.0 equiv.) and the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was concentrated under vacuum and ethyl acetate (10 mL) was added. Then organic layer was washed with water, dried over anhydrous sodium sulfate, and then concentrated to dryness. The crude compound was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to afford 4-methyl-2*H*-chromen-2-one **3k** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.9, 1.2 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.36 – 7.28 (m, 2H), 6.30 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 153.7, 152.5, 131.9, 124.7, 124.3, 120.1, 117.2, 115.3, 18.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_9O_2$, 161.0603; found, 161.0609.



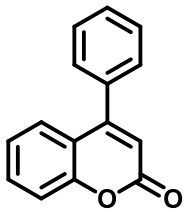
3k

4-methoxy-2*H*-chromen-2-one (3l): Prepared using reported procedure:[2] 4-Methoxycoumarin was prepared by heating 4-hydroxycoumarin with hydrogen chloride (HCl) in methanol at 80 °C and purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to afford 4-methoxy-2*H*-chromen-2-one **3l** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.9, 1.5 Hz, 1H), 7.53 (ddd, J = 8.7, 7.4, 1.6 Hz, 1H), 7.27 (ddd, J = 15.2, 8.6, 4.4 Hz, 2H), 5.69 (s, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 163.0, 153.4, 132.5, 124.0, 123.1, 116.9, 90.2, 56.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_9O_3$, 177.0552; found, 177.0550.



3l

4-phenyl-2*H*-chromen-2-one (3m): Prepared using reported procedure:[2] To a mixture of 2-hydroxybenzophenone (1.0 equiv.) and acetic anhydride (2.0 equiv.) in acetonitrile was added DBU (3.0 equiv.) and the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was concentrated under vacuum and ethyl acetate (10 mL) was added. Then organic layer was washed with water, dried over anhydrous sodium sulfate, and then concentrated to dryness. The crude compound was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to afford 4-phenyl-2*H*-chromen-2-one **3m** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (ddd, J = 10.7, 7.0, 2.2 Hz, 4H), 7.48 (dd, J = 8.0, 1.5 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.39 (dd, J = 8.3, 0.9 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 155.7, 154.2, 135.2, 132.0, 129.7, 128.9, 128.5, 127.0, 124.2,



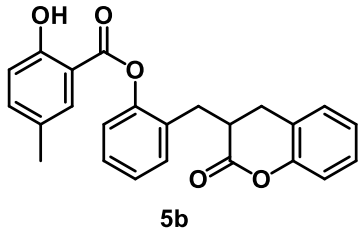
3m

119.0, 117.3, 115.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{15}H_{11}O_2$, 223.0759; found, 223.0750.

Synthesis of 1-methoxy-2-(methoxymethyl)benzene (4ac): Prepared using reported procedure:[3] To a solution of 2- methoxy benzylic alcohol (1.0 equiv.) in anhydrous THF was added sodium hydride (60% oil suspension, 1.5 equiv.) at 0 °C and stirred for 1 h. Then iodomethane (3.0 equiv.) was added at 0 °C and allowed to react for 15 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with $Na_2S_2O_3$ aq. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 30/1) to afford 1-methoxy-2-(methoxymethyl)benzene **4ac** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.4, 1.2 Hz, 1H), 7.30 (td, J = 7.9, 1.7 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 4.56 (s, 2H), 3.85 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 129.0, 128.7, 126.5, 120.3, 110.2, 77.1, 69.5, 58.2, 55.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_9H_{12}O_2Na$, 175.0735; found, 175.1034.

2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate (5a): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-2*H*-chromen-2-one **3a** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate **5a**(136 mg, 73%) as a white solid. Melting point: 110-112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.00 (dd, J = 8.0, 1.4 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.38 (dd, J = 11.4, 4.5 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.18 (m, 2H), 7.10 – 7.02 (m, 3H), 7.02 – 6.94 (m, 2H), 3.40 (dd, J = 14.1, 4.9 Hz, 1H), 3.00 (ddd, J = 16.1, 11.0, 5.4 Hz, 1H), 2.88 (dd, J = 15.7, 5.9 Hz, 1H), 2.83 – 2.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 168.9, 162.4, 151.6, 148.8, 136.9, 131.3, 130.5, 130.2, 128.5, 128.4, 128.3, 127.0, 124.5, 122.9, 122.2, 119.9, 118.1, 116.7, 111.5, 40.1, 30.2, 28.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{23}H_{19}O_5$, 375.1232; found, 375.1235. IR (neat): 3211, 2920, 1760, 1678, 1225 cm^{-1}.

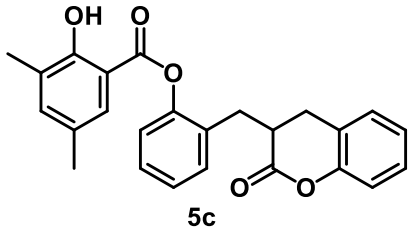
2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate (5b): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methyl-2*H*-chromen-2-one **3b** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate **5b** (120 mg, 62%) as a white solid. Melting point: 122-124 ℃.



5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.78 (d, J = 1.6 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.32 – 7.27 (m, 1H), 7.24 – 7.17 (m, 2H), 7.10 – 6.98 (m, 3H), 6.95 (d, J = 8.5 Hz, 1H), 3.41 (dd, J = 14.2, 4.9 Hz, 1H), 2.99 (ddd, J = 11.0, 7.3, 4.3 Hz, 1H), 2.87 (dd, J = 15.8, 5.9 Hz, 1H), 2.82 – 2.70 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.0, 160.4, 151.6, 148.9, 138.0, 131.3, 130.5, 129.8, 129.1, 128.5, 128.4, 128.3, 126.9, 124.5, 122.9, 122.3, 117.9, 116.7, 111.1, 40.1, 30.3, 28.8, 20.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{20}O_5Na$, 411.1208; found, 411.1203. IR (neat): 3215, 2916, 1758, 1671, 1220 cm^{-1}.

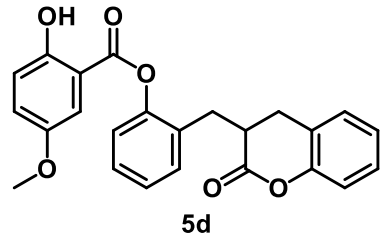
2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate (5c): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6,8-dimethyl-2*H*-chromen-2-one **3d** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate **5c** (132 mg, 66%) as a white solid.



5c

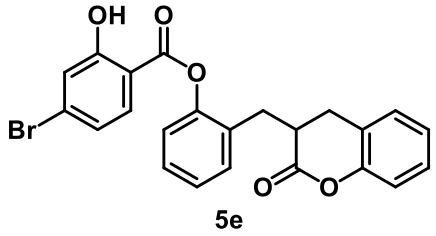
Melting point: 128-130 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.66 – 7.61 (m, 1H), 7.37 (dd, J = 11.7, 4.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.26 – 7.18 (m, 3H), 7.09 – 6.98 (m, 3H), 3.40 (dd, J = 14.2, 4.9 Hz, 1H), 3.06 – 2.95 (m, 1H), 2.91 – 2.70 (m, 3H), 2.28 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.4, 158.9, 151.6, 149.0, 138.9, 131.3, 130.6, 128.5, 128.4, 128.3, 127.2, 127.0, 126.9, 124.5, 122.9, 122.3, 116.7, 110.4, 40.0, 30.3, 28.8, 20.6, 15.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{22}O_5Na$, 425.1365; found, 425.1362. IR (neat): 3218, 2922, 1763, 1680, 1225 cm^{-1}.

2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate (5d): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methoxy-2*H*-chromen-2-one **3i** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate **5d** (157 mg, 78%) as a white solid. Melting point: 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.44 (d, J = 3.1 Hz, 1H), 7.38 (dd, J = 12.8, 4.9 Hz, 2H), 7.31 (dd, J = 10.6, 4.2 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.06 (dd, J = 11.3, 6.7 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H), 3.41 (dd, J = 14.2, 5.0 Hz, 1H), 3.06 – 2.95 (m, 1H), 2.88 (dd, J = 15.7, 5.9 Hz, 1H), 2.82 – 2.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 168.6, 157.0, 152.4, 151.6, 148.8, 131.4, 130.4, 128.5, 128.4, 128.3, 126.9, 125.4, 124.5, 122.8, 122.1, 119.1, 116.6, 111.8, 110.9, 56.0, 40.0, 30.4, 28.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{20}O_6Na$, 427.1158; found, 427.1163. IR (neat): 3249, 2919, 1690, 1618, 1220 cm^{-1}.



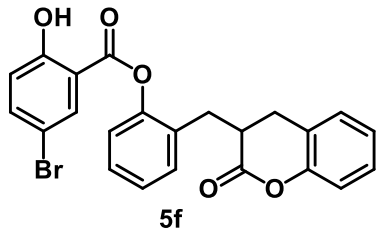
5d

2-((2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate (5e): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 7-bromo-4-hydroxy-2*H*-chromen-2-one **3h** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate **5e** (154 mg, 68%) as a white solid. Melting point: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.26 – 7.19 (m, 3H), 7.08 (ddd, J = 17.1, 8.2, 1.4 Hz, 3H), 7.00 (d, J = 8.0 Hz, 1H), 3.37 (dd, J = 14.2, 4.9 Hz, 1H), 3.01 – 2.93 (m, 1H), 2.87 (dd, J = 15.7, 5.9 Hz, 1H), 2.79 – 2.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.5, 162.7, 151.6, 148.6, 131.4, 131.3, 131.2, 130.4, 128.6, 128.5, 128.3, 127.1, 124.6, 123.5, 122.8, 122.0, 121.4, 116.8, 110.6, 40.1, 30.2, 28.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{23}H_{18}BrO_5$, 453.0338; found, 453.0331. IR (neat): 3324, 2930, 1687, 1605, 1170 cm^{-1}.



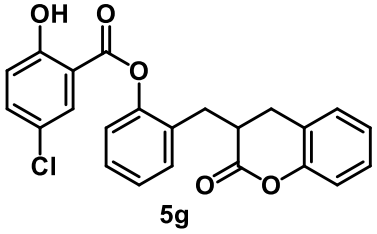
5e

2-((2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate (5f): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-bromo-4-hydroxy-2*H*-chromen-2-one **3c** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate **5f** (145 mg, 64%) as a white solid. Melting point: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.10 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 8.9, 2.5 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.20 (ddd, J = 12.1, 7.8, 1.6 Hz, 2H), 7.06 (ddd, J = 11.2, 8.3, 3.5 Hz, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.96 (d, J = 8.9 Hz, 1H), 3.35 (dd, J = 14.3, 5.1 Hz, 1H), 2.99 (ddt, J = 11.0, 9.0, 5.5 Hz, 1H), 2.90 (dd, J = 15.7, 5.9 Hz, 1H), 2.81 – 2.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 167.9, 161.4, 151.6, 148.6, 139.6, 132.4, 131.3, 130.5, 128.6, 128.5, 128.3, 127.2, 124.6, 122.6, 122.0, 120.1, 116.7, 113.0, 111.4, 40.1, 30.1, 28.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{17}BrO_5Na$, 475.0157; found, 475.0161. IR (neat): 3217, 2927, 1760, 1692, 1166 cm^{-1}.



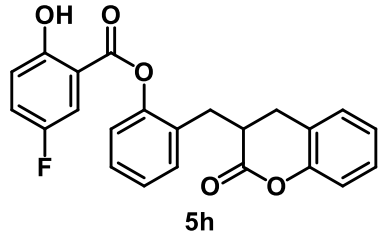
5f

2-((2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate (5g): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-chloro-4-hydroxy-2*H*-chromen-2-one **3g** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate **5g** (141 mg, 69%) as a white solid. Melting point: 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.95 (d, J = 2.6 Hz, 1H), 7.50 (dd, J = 8.9, 2.6 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.24 – 7.16 (m, 2H), 7.07 (dd, J = 14.9, 6.6 Hz, 2H), 7.01 (t, J = 5.9 Hz, 2H), 3.36 (dd, J = 14.3, 5.0 Hz, 1H), 3.04 – 2.95 (m, 1H), 2.90 (dd, J = 15.7, 5.9 Hz, 1H), 2.81 – 2.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.0, 160.9, 151.6, 148.6, 136.8, 131.3, 130.4, 129.3, 128.6, 128.5, 128.3, 127.2, 124.6, 122.7, 122.0, 119.7, 116.7, 112.4, 40.1, 30.1, 28.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{17}ClO_5Na$, 431.0662; found, 431.0657. IR (neat): 3378, 2917, 1765, 1693, 1175 cm^{-1}.



5g

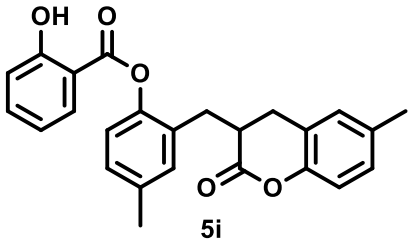
2-((2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate (5h): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-fluoro-4-hydroxy-2*H*-chromene-2-one **3e** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)phenol **4a** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate **5h** (137 mg, 70%) as a white solid. Melting point: 108-110 °C.



5h

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.60 (dd, J = 8.5, 3.2 Hz, 1H), 7.34 (dd, J = 11.3, 4.5 Hz, 2H), 7.29 (dd, J = 7.6, 2.1 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.17 (ddd, J = 9.4, 7.5, 1.8 Hz, 2H), 7.07 – 7.00 (m, 2H), 7.00 – 6.95 (m, 2H), 3.32 (dd, J = 14.2, 5.0 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.85 (dd, J = 15.7, 5.9 Hz, 1H), 2.72 (ddd, J = 15.8, 10.1, 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (s), 168.1 (d, J = 2.9 Hz), 158.7 (d, J = 1.5 Hz), 156.5 (s), 154.2 (s), 151.5 (s), 148.6 (s), 131.3 (s), 130.4 (s), 128.6 – 128.2 (m), 127.2 (s), 124.6 (t, J = 11.9 Hz), 122.7 (s), 122.0 (s), 119.5 (d, J = 7.4 Hz), 116.7 (s), 115.3 (s), 115.1 (s), 111.3(d, J = 7.5 Hz), 40.1(s), 30.1(s), 28.8(s). ^{19}F NMR (377 MHz, $CDCl_3$) δ -122.81 (s, 1F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{17}FO_5Na$, 415.0958; found, 415.0959. IR (neat): 3438, 3075, 1762, 1693, 1172 cm^{-1}.

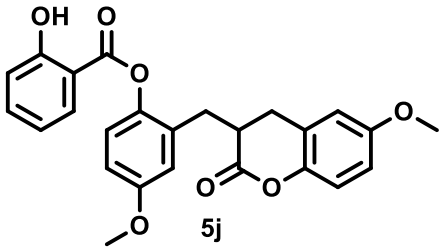
4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate (5i): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-2*H*-chromen-2-one **3a** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate **5i** (157 mg, 78%) as a white solid. Melting point: 107-109 °C.



5i

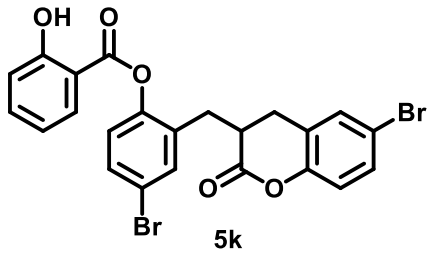
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.97 (dd, J = 8.0, 1.6 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.16 (d, J = 8.2 Hz, 2H), 7.11 – 6.93 (m, 4H), 6.91 – 6.86 (m, 2H), 3.34 (dd, J = 14.2, 4.8 Hz, 1H), 2.95 (dq, J = 15.6, 5.4 Hz, 1H), 2.83 (dd, J = 15.8, 5.9 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.39 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.1, 162.4, 149.5, 146.5, 136.8, 136.7, 134.1, 131.7, 130.2, 130.1, 128.9, 128.8, 128.7, 122.4, 121.9, 119.8, 118.0, 116.3, 111.6, 40.2, 30.1, 28.7, 21.0, 20.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{22}O_5Na$, 425.1365; found, 425.1368. IR (neat): 3219, 2923, 1760, 1685, 1298 cm^{-1}.

4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate (5j): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-2*H*-chromen-2-one **3a** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate **5j** (176 mg, 81%) as a white solid. Melting point: 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.97 (dd, J = 8.0, 1.6 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.13 (d, J = 8.6 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.98 – 6.85 (m, 4H), 6.73 (dd, J = 8.9, 2.9 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.34 (dd, J = 14.2, 4.8 Hz, 1H), 2.95 (dq, J = 15.8, 5.4 Hz, 1H), 2.84 (dd, J = 15.8, 5.9 Hz, 1H), 2.77 – 2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.3, 162.4, 157.9, 156.2, 145.5, 142.2, 136.8, 131.5, 130.2, 123.5, 123.1, 119.8, 118.1, 117.4, 116.2, 113.6, 113.3, 113.3, 111.6, 55.7, 40.0, 30.4, 29.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{25}H_{23}O_7$, 435.1444; found, 435.1449. IR (neat): 3222, 2926, 1758, 1685, 1297 cm^{-1}.



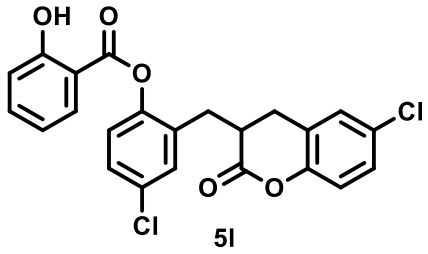
5j

4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate (5k): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-2*H*-chromen-2-one **3a** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate **5k** (175 mg, 66%) as a white solid. Melting point: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 8.6 Hz, 1H), 7.25 (d, J = 5.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 3.35 (dd, J = 14.2, 4.9 Hz, 1H), 2.93 (ddd, J = 14.3, 11.2, 5.5 Hz, 1H), 2.84 (dd, J = 15.8, 5.8 Hz, 1H), 2.79 – 2.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.4, 162.4, 150.5, 147.8, 137.1, 133.9, 132.5, 131.5, 131.0, 130.0, 124.6, 124.1, 120.0, 119.9, 118.4, 118.2, 117.1, 111.1, 39.5, 30.0, 28.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{16}Br_2O_5Na$, 552.9262; found, 552.9268. IR (neat): 3222, 2926, 1758, 1685, 1297 cm^{-1}.



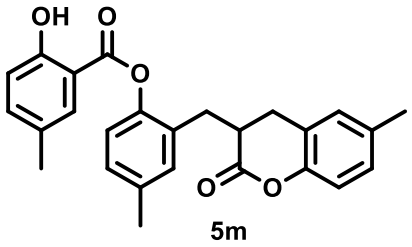
5k

4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate (5l): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-2H-chromen-2-one **3a** (0.5 mmol, 1 equiv.), 4-chloro-2-(hydroxymethyl)phenol **4c** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 2-hydroxybenzoate **5l** (142 mg, 64%) as a white solid. Melting point: 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.22 – 7.14 (m, 2H), 7.10 (d, J = 1.6 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 7.00 – 6.91 (m, 2H), 3.35 (dd, J = 14.2, 5.1 Hz, 1H), 2.94 (ddd, J = 14.3, 11.2, 5.5 Hz, 1H), 2.85 (dd, J = 15.8, 5.9 Hz, 1H), 2.79 – 2.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.6, 162.5, 150.1, 147.3, 137.2, 132.4, 132.2, 131.0, 130.1, 129.7, 128.6, 128.6, 128.2, 124.3, 123.7, 120.0, 118.3, 118.1, 111.2, 39.6, 30.1, 28.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{16}Cl_2O_5Na$, 465.0272; found, 465.0275. IR (neat): 3247, 2925, 1766, 1687, 1298 cm^{-1}.



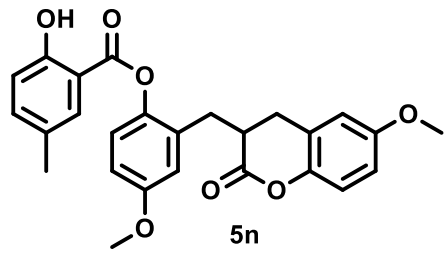
5l

4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate (5m): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methyl-2*H*-chromen-2-one **3b** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate **5m** (150 mg, 72%) as a white solid. Melting point: 137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.78 (d, J = 1.2 Hz, 1H), 7.36 (dd, J = 8.5, 2.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 3.35 (dd, J = 14.2, 4.8 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.83 (dd, J = 15.7, 5.9 Hz, 1H), 2.71 (dt, J = 15.6, 10.5 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.1, 160.3, 149.5, 146.6, 137.9, 136.6, 134.1, 131.7, 130.2, 129.8, 129.0, 128.9, 128.8, 128.7, 122.4, 122.0, 117.8, 116.3, 111.2, 40.2, 30.3, 28.8, 21.1, 20.8, 20.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}O_5Na$, 439.1521; found, 439.1521. IR (neat): 3235, 2923, 1764, 1687, 1187 cm^{-1}.

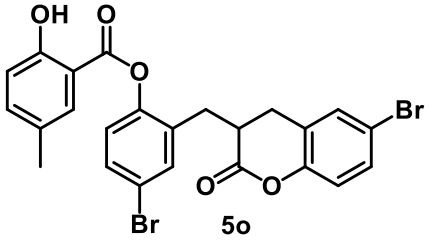


5m

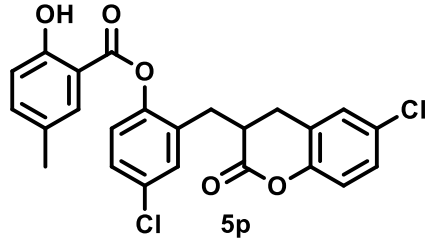
4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate (5n): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methyl-2*H*-chromen-2-one **3b** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate **5n** (184 mg, 82%) as a white solid. Melting point: 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.78 (d, J = 1.5 Hz, 1H), 7.35 (dd, J = 8.5, 2.1 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.90 – 6.85 (m, 2H), 6.73 (dd, J = 8.9, 2.9 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.36 (dd, J = 14.2, 4.8 Hz, 1H), 2.95 (ddd, J = 15.3, 8.2, 4.5 Hz, 1H), 2.83 (dd, J = 15.7, 5.9 Hz, 1H), 2.77 – 2.68 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.3, 160.3, 157.8, 156.2, 145.5, 142.2, 137.9, 131.6, 129.8, 129.0, 123.5, 123.2, 117.8, 117.4, 116.3, 113.6, 113.3, 113.2, 111.1, 55.7, 39.9, 30.5, 29.1, 20.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}O_7Na$, 471.1420; found, 471.1421. IR (neat): 3247, 2934, 1759, 1684, 1288 cm^{-1}.



4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate (5o): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methyl-2*H*-chromen-2-one **3b** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate **5o** (166 mg, 61%) as a white solid. Melting point: 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.75 (s, 1H), 7.51 – 7.45 (m, 2H), 7.36 (ddd, J = 17.7, 8.6, 1.9 Hz, 2H), 7.24 (s, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 3.37 (dd, J = 14.3, 5.2 Hz, 1H), 2.94 (ddt, J = 11.4, 8.8, 5.6 Hz, 1H), 2.87 – 2.69 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.5, 160.5, 150.6, 147.9, 138.3, 134.0, 132.7, 131.6, 131.1, 129.6, 129.2, 124.6, 124.3, 120.0, 118.4, 118.1, 117.1, 110.7, 39.6, 30.2, 28.8, 20.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{18}Br_2O_5Na$, 566.9419; found, 566.9420. IR (neat): 3258, 2923, 1768, 1687, 1164 cm^{-1}.

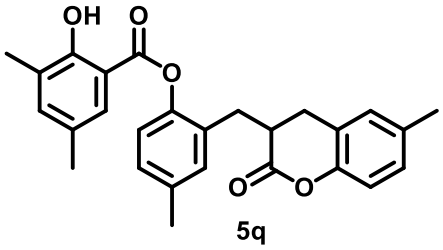


4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate (5p): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methyl-2*H*-chromen-2-one **3b** (0.5 mmol, 1 equiv.), 4-chloro-2-(hydroxymethyl)phenol **4c** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate **5p** (153 mg, 67%) as a white solid. Melting point: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.75 (d, J = 1.2 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.21 – 7.13 (m, 2H), 7.08 (d, J = 2.1 Hz, 1H), 6.94 (dd, J = 10.7, 8.7 Hz, 2H), 3.37 (dd, J = 14.3, 5.2 Hz, 1H), 3.01 – 2.90 (m, 1H), 2.84 (dd, J = 15.8, 5.9 Hz, 1H), 2.79 – 2.69 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.6, 160.5, 150.1, 147.3, 138.3, 132.3, 132.2, 131.0, 129.7, 129.6, 129.2, 128.6, 128.5 128.1, 124.2, 123.8, 118.1, 110.7, 39.5, 30.2, 28.9, 20.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{18}Cl_2O_5Na$, 479.0429; found, 479.0428. IR (neat): 3254, 2918, 1768, 1686, 1166 cm^{-1}.



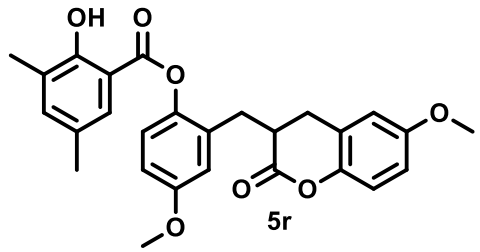
5p

4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate (5q): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6,8-dimethyl-2*H*-chromen-2-one **3d** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate **5q** (165 mg, 77%) as a white solid. Melting point: 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.63 (s, 1H), 7.23 (s, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 8.4 Hz, 2H), 2.38 (s, 3H), 2.28 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.6, 158.8, 149.6, 146.7, 138.8, 136.6, 134.1, 131.8, 130.2, 128.9, 128.8, 128.7, 128.2, 127.2, 126.9, 122.4, 122.1, 116.3, 110.4, 40.2, 30.3, 28.8, 21.1, 20.8, 20.6, 15.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{27}H_{26}O_5Na$, 453.1678; found, 453.1679. IR (neat): 3207, 2921, 1762, 1680, 1117 cm^{-1}.

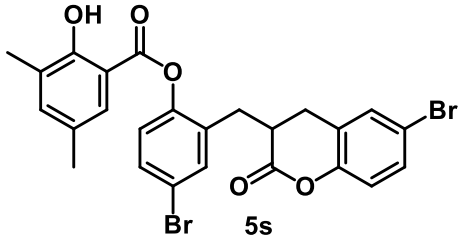


5q

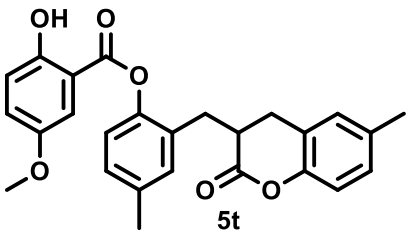
4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate (5r): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6,8-dimethyl-2*H*-chromen-2-one **3d** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate **5r** (150 mg, 65%) as a white solid. Melting point: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.63 (d, J = 0.8 Hz, 1H), 7.23 (s, 1H), 7.11 (d, J = 8.7 Hz, 1H), 6.92 (d, J = 8.9 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.73 (dd, J = 8.9, 2.9 Hz, 1H), 6.59 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.36 (dd, J = 14.2, 4.8 Hz, 1H), 3.00 – 2.89 (m, 1H), 2.83 (dd, J = 15.8, 5.9 Hz, 1H), 2.72 (ddd, J = 15.8, 10.6, 7.1 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.8, 158.8, 157.8, 156.2, 145.5, 142.3, 138.8, 131.6, 128.2, 127.2, 126.9, 123.5, 123.3, 117.4, 116.3, 113.6, 113.3, 113.2, 110.4, 55.7, 55.7, 39.9, 30.5, 29.1, 20.6, 15.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{27}H_{26}O_7Na$, 485.1576; found, 485.1584. IR (neat): 3218, 2919, 1753, 1681, 1185 cm^{-1}.



4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5-dimethylbenzoate (5s): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6,8-dimethyl-2*H*-chromen-2-one **3d** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-3,5- dimethylbenzoate **5s** (182 mg, 65%) as a white solid. Melting point: 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.59 (d, J = 0.9 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.34 (dd, J = 8.6, 2.3 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.09 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 8.6 Hz, 1H), 3.37 (dd, J = 14.3, 5.2 Hz, 1H), 2.92 (ddd, J = 11.3, 8.8, 5.8 Hz, 1H), 2.86 – 2.69 (m, 3H), 2.27 (d, J = 8.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 169.1, 159.0, 150.6, 148.0, 139.3, 134.0, 132.7, 131.6, 131.5, 131.1, 128.5, 127.2, 127.0, 124.6, 124.3, 120.0, 118.5, 117.2, 110.0, 39.6, 30.2, 28.8, 20.6, 15.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{20}Br_2O_5Na$, 580.9575; found, 580.9583. IR (neat): 3246, 2920, 1770, 1685, 1119 cm^{-1}.

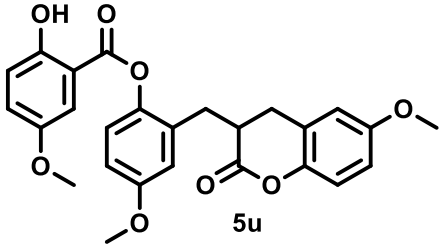


4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate (5t): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methoxy-2*H*-chromen-2-one **3i** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate **5t** (168 mg, 78%) as a white solid. Melting point: 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.43 (d, J = 3.1 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.09 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 7.8 Hz, 2H), 6.91 – 6.84 (m, 2H), 3.77 (s, 3H), 3.35 (dd, J = 14.2, 4.9 Hz, 1H), 3.01 – 2.90 (m, 1H), 2.83 (dd, J = 15.7, 5.9 Hz, 1H), 2.77 – 2.65 (m, 2H), 2.38 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 168.8, 156.9, 152.4, 149.5, 146.5, 136.7, 134.1, 131.8, 130.1, 129.0, 128.9, 128.7, 125.3, 122.4, 121.9, 119.1, 116.3, 111.8, 111.0, 55.9, 40.2, 30.4, 28.9, 21.1, 20.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}O_6Na$, 455.1471; found, 455.1466. IR (neat): 3317, 2922, 1762, 1690, 1180 cm^{-1}.



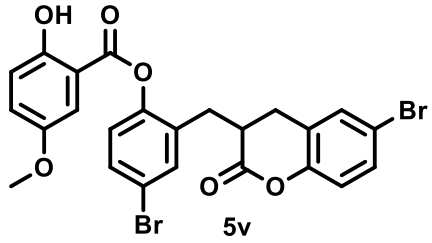
5t

4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate (5u): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methoxy-2*H*-chromen-2-one **3i** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate **5u** (179 mg, 77%) as a white solid. Melting point: 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.42 (d, J = 3.1 Hz, 1H), 7.17 (dd, J = 9.1, 3.1 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 9.1 Hz, 1H), 6.93 – 6.85 (m, 3H), 6.73 (dd, J = 8.9, 2.9 Hz, 1H), 6.59 (d, J = 2.9 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.36 (dd, J = 14.2, 4.9 Hz, 1H), 2.95 (ddt, J = 11.0, 9.4, 5.4 Hz, 1H), 2.84 (dd, J = 15.8, 5.9 Hz, 1H), 2.77 – 2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.0, 157.9, 156.9, 156.3, 152.4, 145.5, 142.2, 131.5, 125.3, 123.5, 123.2, 119.1, 117.4, 116.4, 113.6, 113.3, 113.2, 111.8, 111.0, 56.0, 55.8, 55.7, 40.0, 30.6, 29.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}O_8Na$, 487.1369; found, 487.1368. IR (neat): 3248, 2941, 1760, 1688, 1175 cm^{-1}.



5u

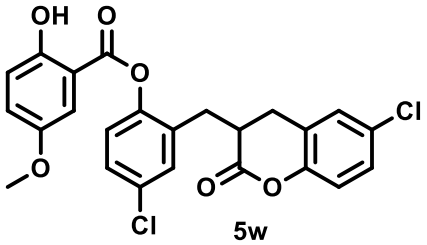
4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate (5v): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methoxy-2*H*-chromen-2-one **3i** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate **5v** (174 mg, 62%) as a white solid.



5v

Melting point: 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.51 – 7.46 (m, 2H), 7.40 (d, J = 3.1 Hz, 1H), 7.33 (dd, J = 8.6, 2.1 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.19 (dd, J = 9.1, 3.1 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 6.99 (d, J = 9.1 Hz, 1H), 6.86 (d, J = 8.6 Hz, 1H), 3.78 (s, 3H), 3.37 (dd, J = 14.3, 5.3 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.88 – 2.75 (m, 2H), 2.74 – 2.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.2, 157.0, 152.5, 150.5, 147.8, 134.0, 132.6, 131.6, 131.5, 131.1, 125.6, 124.6, 124.2, 120.0, 119.3, 118.4, 117.1, 111.8, 110.6, 56.0, 39.6, 30.3, 28.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{18}Br_2O_6Na$, 582.9368; found, 582.9373. IR (neat): 3251, 2918, 1767, 1690, 1169 cm^{-1}.

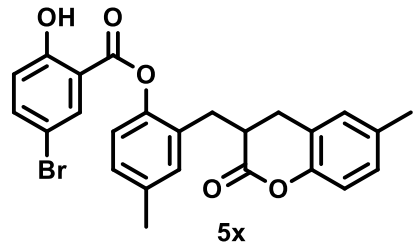
4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate (5w): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methoxy-2*H*-chromen-2-one **3i** (0.5 mmol, 1 equiv.), 4-chloro-2-(hydroxymethyl)phenol **4c** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methoxybenzoate **5w** (156 mg, 66%) as a white solid.



5w

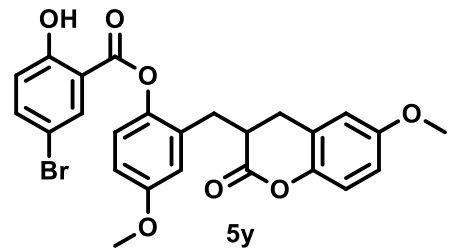
Melting point: 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.40 (d, J = 3.1 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.22 – 7.15 (m, 3H), 7.09 (d, J = 2.2 Hz, 1H), 6.99 (d, J = 9.1 Hz, 1H), 6.92 (d, J = 8.7 Hz, 1H), 3.78 (s, 3H), 3.37 (dd, J = 14.3, 5.3 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.85 (dd, J = 15.8, 5.9 Hz, 1H), 2.80 – 2.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.4, 157.0, 152.5, 150.1, 147.2, 132.3, 132.2, 131.1, 129.7, 128.7, 128.6, 128.1, 125.6, 124.2, 123.7, 119.3, 118.1, 111.8, 110.6, 56.0, 39.6, 30.4, 29.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{18}Cl_2O_6Na$, 495.0378; found, 495.0382. IR (neat): 3256, 2918, 1766, 1681, 1165 cm^{-1}.

4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate (5x): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-bromo-4-hydroxy-2*H*-chromen-2-one **3c** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate **5x** (154 mg, 64%) as a white solid. Melting point: 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 8.10 (d, J = 2.5 Hz, 1H), 7.62 (dd, J = 8.9, 2.5 Hz, 1H), 7.15 (d, J = 6.2 Hz, 2H), 7.07 – 7.03 (m, 1H), 7.01 (dd, J = 8.3, 1.4 Hz, 1H), 6.95 (d, J = 8.9 Hz, 1H), 6.91 – 6.88 (m, 2H), 3.31 (dd, J = 14.3, 5.1 Hz, 1H), 2.94 (ddt, J = 11.0, 8.8, 5.5 Hz, 1H), 2.84 (dd, J = 15.7, 5.9 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.1, 161.4, 149.5, 146.4, 139.6, 137.0, 134.1, 132.3, 131.8, 130.1, 129.0, 128.9, 128.7, 122.2, 121.8, 120.1, 116.4, 113.1, 111.4, 40.3, 30.1, 28.9, 21.1, 20.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}O_5BrNa$, 503.0469; found, 503.0473. IR (neat): 3328, 2920, 1760, 1693, 1184 cm^{-1}.



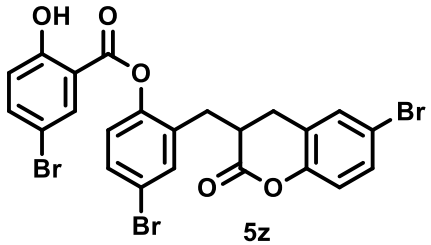
5x

4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate (5y): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-bromo-4-hydroxy-2*H*-chromen-2-one **3c** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate **5y** (154 mg, 60%) as a white solid. Melting point: 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.10 (d, J = 2.5 Hz, 1H), 7.61 (dd, J = 8.9, 2.5 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.94 (dd, J = 8.9, 6.2 Hz, 2H), 6.90 – 6.85 (m, 2H), 6.73 (dd, J = 8.9, 2.9 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.31 (dd, J = 14.2, 5.0 Hz, 1H), 2.94 (ddt, J = 11.0, 9.3, 5.5 Hz, 1H), 2.85 (dd, J = 15.7, 5.8 Hz, 1H), 2.77 – 2.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 168.2, 161.3, 158.0, 156.2, 145.4, 142.0, 139.5, 132.3, 131.5, 123.3, 123.0, 120.1, 117.4, 116.3, 113.6, 113.4, 113.2, 113.1, 111.4, 55.7, 40.0, 30.4, 29.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}BrO_7Na$, 535.0368; found, 535.0360. IR (neat): 3244, 2918, 1759, 1692, 1184 cm^{-1}.



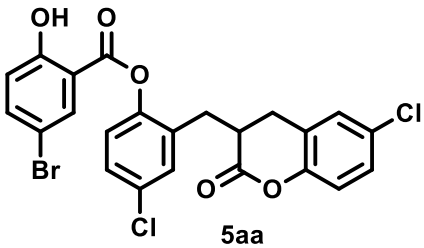
5y

4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate (5z): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-bromo-4-hydroxy-2*H*-chromen-2-one **3c** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate **5z** (208 mg, 68%) as a white solid. Melting point: 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.07 (d, J = 2.5 Hz, 1H), 7.64 (dd, J = 8.9, 2.5 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.34 (dd, J = 8.6, 2.2 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.07 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 8.9 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 3.33 (dd, J = 14.3, 5.3 Hz, 1H), 2.91 (s, 1H), 2.90 – 2.77 (m, 2H), 2.72 (dd, J = 14.4, 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.6, 161.4, 150.6, 147.6, 139.9, 134.1, 132.6, 132.2, 131.6, 131.1, 124.4, 124.1, 120.3, 120.3, 118.5, 117.2, 112.6, 111.5, 39.6, 30.1, 28.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Br_3O_5Na$, 630.8367; found, 630.8370. IR (neat): 3247, 2923, 1768, 1694, 1173 cm^{-1}.



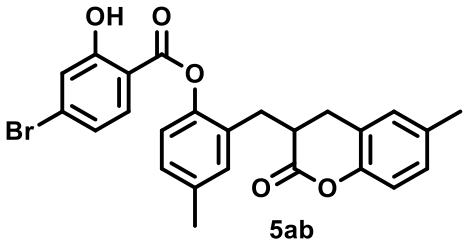
5z

4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate (5aa): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-bromo-4-hydroxy-2*H*-chromen-2-one **3c** (0.5 mmol, 1 equiv.), 4-chloro-2-(hydroxymethyl)phenol **4c** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 5-bromo-2-hydroxybenzoate **5aa** (177 mg, 68%) as a white solid. Melting point: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.07 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 8.9, 2.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.19 (dd, J = 8.6, 2.3 Hz, 1H), 7.12 (dd, J = 7.8, 5.4 Hz, 2H), 6.95 (t, J = 8.8 Hz, 2H), 3.33 (dd, J = 14.4, 5.4 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.90 – 2.83 (m, 1H), 2.81 – 2.76 (m, 1H), 2.75 – 2.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.6, 161.4, 150.0, 147.0, 139.9, 132.6, 132.2, 132.2, 131.1, 129.7, 128.7, 128.2, 124.0, 123.6, 120.3, 118.1, 112.7, 111.5, 39.6, 30.1, 29.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Cl_2BrO_5Na$, 542.9378; found, 542.9380. IR (neat): 3249, 2917, 1767, 1692, 1164 cm^{-1}.



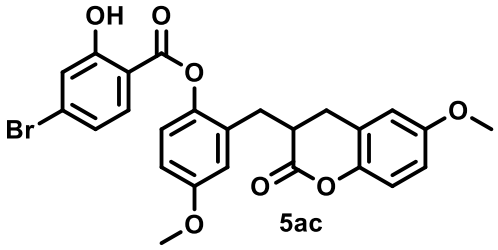
5aa

4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate (5ab): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 7-bromo-4-hydroxy-2*H*-chromen-2-one **3h** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate **5ab** (180 mg, 75%) as a white solid. Melting point: 178-180 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 7.01 (d, J = 8.3 Hz, 1H), 6.91 – 6.87 (m, 2H), 3.31 (dd, J = 14.2, 4.8 Hz, 1H), 2.92 (dt, J = 15.6, 5.4 Hz, 1H), 2.82 (dd, J = 15.7, 5.9 Hz, 1H), 2.74 – 2.64 (m, 2H), 2.38 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.7, 162.7, 149.5, 146.3, 136.9, 134.2, 131.7, 131.2, 131.1, 130.0, 129.0, 128.9, 128.7, 123.4, 122.3, 121.8, 121.3, 116.4, 110.7, 40.2, 30.2, 28.8, 21.1, 20.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}O_5BrNa$, 503.0469; found, 503.0459. IR (neat): 3202, 2924, 1763, 1688, 1194 cm^{-1}.



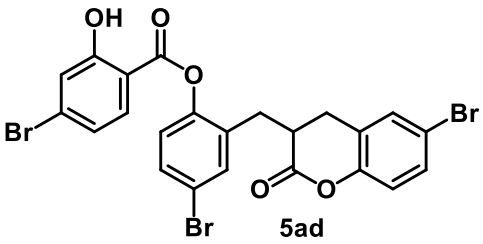
5ab

4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate (5ac): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 7-bromo-4-hydroxy-2*H*-chromen-2-one **3h** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methoxy-2-((6-methoxy-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate **5ac** (172 mg, 67%) as a white solid. Melting point: 162-164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.92 (d, J = 8.9 Hz, 1H), 6.87 (dt, J = 6.6, 2.9 Hz, 2H), 6.74 (dd, J = 8.9, 2.9 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.31 (dd, J = 14.2, 4.8 Hz, 1H), 2.93 (dq, J = 15.5, 5.3 Hz, 1H), 2.84 (dd, J = 15.8, 5.8 Hz, 1H), 2.75 – 2.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 168.9, 162.7, 158.0, 156.3, 145.5, 142.0, 131.4, 131.3, 131.1, 123.5, 123.4, 123.0, 121.4, 117.5, 116.3, 113.6, 113.4, 113.3, 110.6, 55.8, 40.0, 30.4, 29.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}BrO_7Na$, 535.0368; found, 535.0370. IR (neat): 3242, 2925, 1756, 1688, 1189 cm^{-1}.



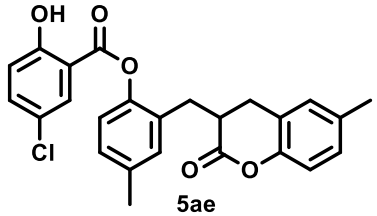
5ac

4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate (5ad): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 7-bromo-4-hydroxy-2*H*-chromen-2-one (

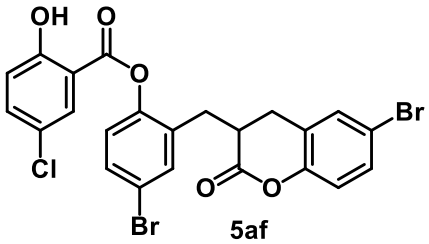


3h (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate **5ad** (232 mg, 76%) as a white solid. Melting point: 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.35 (dd, J = 8.6, 2.3 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.15 – 7.07 (m, 2H), 6.88 (d, J = 8.6 Hz, 1H), 3.34 (dd, J = 14.3, 4.9 Hz, 1H), 2.89 (ddd, J = 26.5, 13.7, 4.7 Hz, 2H), 2.79 – 2.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.2, 162.7, 150.6, 147.6, 134.0, 132.5, 131.8, 131.7, 131.1, 131.0, 124.5, 124.0, 123.6, 121.6, 120.3, 118.5, 117.2, 110.2, 39.6, 30.0, 28.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Br_3O_5Na$, 630.8367; found, 630.8371. IR (neat): 3221, 2918, 1735, 1691, 1175 cm^{-1}.

4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate (5ae): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-chloro-4-hydroxy-2*H*-chromen-2-one **3g** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate **5ae** (142 mg, 65%) as a white solid. Melting point: 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.94 (d, J = 2.6 Hz, 1H), 7.49 (dd, J = 8.9, 2.6 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.07 – 7.03 (m, 1H), 7.00 (d, J = 8.9 Hz, 2H), 6.91 – 6.88 (m, 2H), 3.31 (dd, J = 14.2, 5.0 Hz, 1H), 2.94 (ddt, J = 11.0, 8.9, 5.5 Hz, 1H), 2.84 (dd, J = 15.7, 5.9 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.2, 160.9, 149.5, 146.3, 137.0, 136.8, 134.2, 131.8, 130.1, 129.3, 129.0, 128.9, 128.7, 124.5, 122.2, 121.8, 119.7, 116.4, 112.5, 40.3, 30.1, 28.9, 21.1, 20.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}O_5ClNa$, 459.0975; found, 459.0985. IR (neat): 3226, 2924, 1762, 1692, 1186 cm^{-1}.

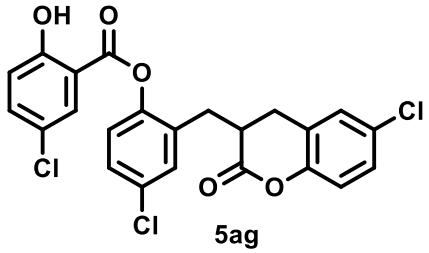


4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate (5af): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-chloro-4-hydroxy-2*H*-chromen-2-one **3g** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate **5af** (190 mg, 67%) as a white solid. Melting point: 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.93 (d, J = 2.6 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.34 (d, J = 8.6 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 7.02 (dd, J = 8.9, 1.8 Hz, 1H), 6.89 (dd, J = 8.6, 2.6 Hz, 1H), 3.34 (dd, J = 14.3, 5.2 Hz, 1H), 2.89 (dddd, J = 36.4, 30.6, 12.0, 4.7 Hz, 3H), 2.72 (dd, J = 14.4, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.7, 161.0, 150.6, 147.6, 137.2, 134.0, 132.6, 131.7, 131.1, 129.2, 124.7, 124.4, 124.0, 120.3, 119.9, 118.5, 117.2, 112.1, 39.7, 30.1, 28.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Br_2ClO_5Na$, 586.8872; found, 586.8864. IR (neat): 3250, 2919, 1768, 1695, 1171 cm^{-1}.



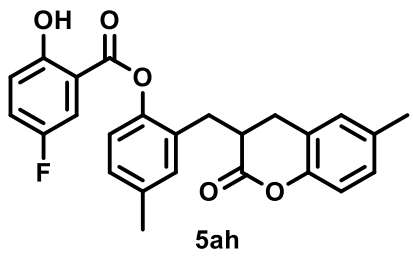
5af

4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate (5ag): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-chloro-4-hydroxy-2*H*-chromen-2-one **3g** (0.5 mmol, 1 equiv.), 4-chloro-2-(hydroxymethyl)phenol **4c** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 5-chloro-2-hydroxybenzoate **5ag** (148 mg, 62%) as a white solid. Melting point: 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.93 (d, J = 2.6 Hz, 1H), 7.51 (dd, J = 8.9, 2.6 Hz, 1H), 7.35 (dt, J = 8.5, 2.4 Hz, 2H), 7.19 (dd, J = 8.7, 2.4 Hz, 1H), 7.12 (dd, J = 9.8, 5.4 Hz, 2H), 7.02 (d, J = 9.0 Hz, 1H), 6.94 (d, J = 8.7 Hz, 1H), 3.33 (dd, J = 14.4, 5.4 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.90 – 2.83 (m, 1H), 2.81 – 2.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.8, 161.0, 150.0, 147.0, 137.2, 132.6, 132.2, 131.1, 129.7, 129.2, 128.7, 128.2, 124.7, 124.1, 123.6, 119.9, 118.1, 112.1, 39.6, 30.1, 29.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Cl_3O_5Na$, 498.9883; found, 498.9902. IR (neat): 3248, 2922, 1767, 1693, 1122 cm^{-1}.



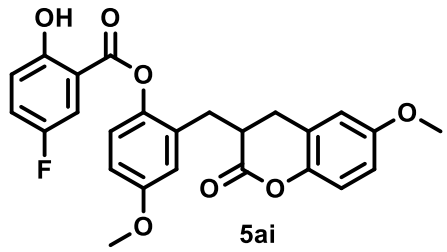
5ag

4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate (5ah): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-fluoro-4-hydroxy-2*H*-chromen-2-one **3e** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methylphenol **4d** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-methyl-2-((6-methyl-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate **5ah** (160 mg, 76%) as a white solid. Melting point: 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.62 (dd, J = 8.5, 3.2 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.16 (d, J = 6.9 Hz, 2H), 7.06 (d, J = 8.9 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.91 – 6.87 (m, 2H), 2.76 – 2.65 (m, 2H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4 (s), 168.3 (d, J = 2.8 Hz), 158.6 (s), 156.5 (s), 154.1 (s), 149.5 (s), 146.3 (s), 136.9 (s), 134.1 (s), 131.7 (s), 130.1 (s), 129.0 (d, J = 7.5 Hz), 128.7 (s), 124.6 (s), 124.3 (s), 122.3 (s), 121.8 (s), 119.4 (d, J = 7.5 Hz), 116.4 (s), 115.3 (s), 115.1 (s), 111.4 (d, J = 7.5 Hz), 40.3 (s), 30.1 (s), 28.8 (s), 21.0 (s), 20.8 (s). ^{19}F NMR (377 MHz, $CDCl_3$) δ -123.1 (s, 1F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}O_5FNa$, 443.1271; found, 443.1267. IR (neat): 3234, 2924, 1761, 1691, 1181 cm^{-1}.



5ah

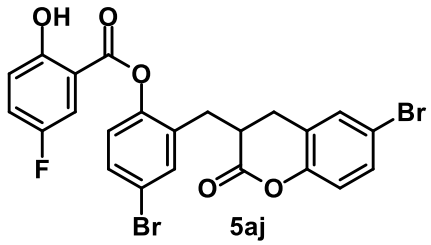
2-((6-(l1-oxidaneyl)-2-oxochroman-3-yl)methyl)-4-methoxyphenyl 5-fluoro-2-hydroxybenzoate (5ai): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-fluoro-4-hydroxy-2*H*-chromen-2-one **3e** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-4-methoxyphenol **4e** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-((6-(l1-oxidaneyl)-2-oxochroman-3-yl)methyl)-4-methoxyphenyl 5-fluoro-2-hydroxybenzoate **5ai** (140 mg, 62%) as a white solid. Melting point: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.63 (dd, J = 8.5, 3.1 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.10 (d, J = 8.9 Hz, 1H), 7.01 (dd, J = 9.2, 4.4 Hz, 1H), 6.93 (d, J = 8.9 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.74 (dd, J = 8.9, 2.9 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.32 (dd, J = 14.2, 4.9 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.85 (dd, J = 15.7, 5.8 Hz, 1H), 2.77 – 2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2 (s), 168.5 (d, J = 2.8 Hz), 158.7 (s), 158.0 (s), 156.5 (s), 156.3 (s), 154.2 (s), 145.4 (s), 142.0 (s), 131.5 (s), 124.6 (s), 124.4 (s), 123.4 (s), 123.0 (s), 119.4 (d, J = 7.4 Hz), 117.4 (s), 116.2 (s), 115.3 (s), 115.0 (s), 113.6 (s), 113.3 (d, J = 8.3 Hz), 111.4 (d, J = 7.4 Hz), 55.7 (d, J = 3.0 Hz), 40.0 (s), 30.3



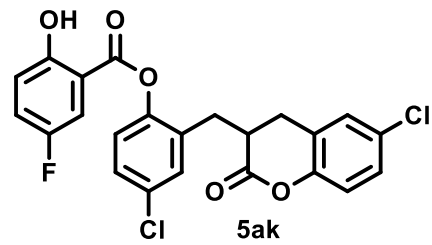
5ai

(s), 29.1 (s). ^{19}F NMR (377 MHz, $CDCl_3$) δ -122.6 (s, 1F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}FO_7Na$, 475.1169; found, 475.1166. IR (neat): 3329, 2925, 1760, 1692 1175 cm^{-1}.

4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate (5aj): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-fluoro-4-hydroxy-2*H*-chromen-2-one **3e** (0.5 mmol, 1 equiv.), 4-bromo-2-(hydroxymethyl)phenol **4b** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-bromo-2-((6-bromo-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate **5aj** (195 mg, 71%) as a white solid. Melting point: 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.62 (dd, J = 8.4, 3.0 Hz, 1H), 7.49 (d, J = 7.0 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.26 (s, 1H), 7.09 (d, J = 9.3 Hz, 1H), 7.03 (dd, J = 9.2, 4.3 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 3.34 (dd, J = 14.3, 5.1 Hz, 1H), 2.96 – 2.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 (s), 167.8 (d, J = 2.8 Hz), 158.8 (s), 156.6 (s), 154.22(s), 150.5 (s), 147.6 (s), 134.0 (s), 132.5 (s), 131.7 (s), 131.1 (s), 125.1 (s), 124.8 (s), 124.5 (s), 124.0 (s), 120.3 (s), 119.7 (d, J = 7.4 Hz), 118.5 (s), 117.2 (s), 115.2 (s), 115.0 (s), 111.0 (d, J = 7.5 Hz), 39.6 (s), 30.0 (s), 28.8 (s). ^{19}F NMR (377 MHz, $CDCl_3$) δ -122.27 (s, 1F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Br_2FO_5Na$, 570.9168; found, 570.9177. IR (neat): 3328, 2920, 1769, 1698, 1175 cm^{-1}.

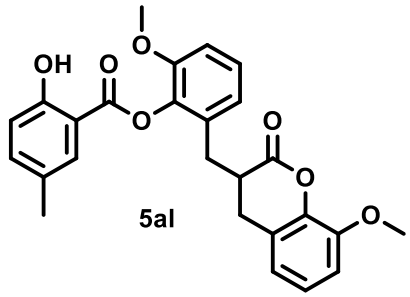


4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate (5ak): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-fluoro-4-hydroxy-2*H*-chromen-2-one **3e** (0.5 mmol, 1 equiv.), 4-chloro-2-(hydroxymethyl)phenol **4c** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 4-chloro-2-((6-chloro-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate **5ak** (161 mg, 70%) as a white solid. Melting point: 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.62 (dd, J = 8.4, 3.1 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.16 (ddd, J = 22.0, 10.7, 2.0 Hz, 3H), 7.03 (dd, J = 9.2, 4.4 Hz, 1H), 6.94 (d, J = 8.7 Hz, 1H), 3.34 (dd, J = 14.3, 5.2 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.86 (dd, J = 15.8, 5.9 Hz, 1H), 2.74 (dt, J = 14.4, 10.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1 (s), 167.9 (d, J = 2.8 Hz), 158.8 (s), 156.6 (s), 154.2 (s), 150.0 (s), 147.0 (s), 132.5 (s), 132.1 (s), 131.0 (s), 129.7 (s), 128.7 (d, J =

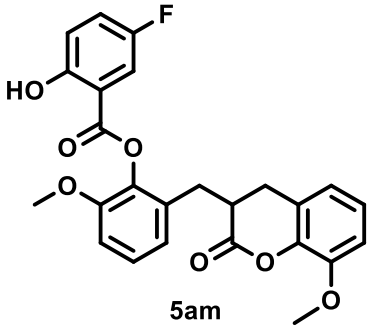


2.1 Hz), 128.2 (s), 125.0 (s), 124.8 (s), 124.1 (s), 123.5 (s), 119.7 (d, J = 7.5 Hz), 118.1 (s), 115.2 (s), 114.9 (s), 111.0 (d, J = 7.4 Hz), 39.6 (s), 30.0 (s), 28.8 (s). ^{19}F NMR (377 MHz, $CDCl_3$) δ -122.8 (s, 1F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{15}Cl_2FO_5Na$, 483.0178; found, 483.0181. IR (neat): 3261, 2921, 1766, 1694, 1163 cm^{-1}.

2-methoxy-6-((8-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate (5al): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 4-hydroxy-6-methyl-2*H*-chromen-2-one **3b** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-6-methoxyphenol **4f** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-methoxy-6-((8-methoxy-2-oxochroman-3-yl)methyl)phenyl 2-hydroxy-5-methylbenzoate **5al** (107 mg, 48%) as a colourless sticky solid. Melting point: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.86 (s, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 6.98 (td, J = 11.6, 8.2 Hz, 4H), 6.86 (d, J = 8.2 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.45 (d, J = 13.0 Hz, 1H), 3.02 – 2.72 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 168.3, 160.2, 151.5, 147.5, 140.8, 138.1, 137.7, 132.0, 130.1, 128.9, 127.1, 124.4, 123.5, 122.8, 122.4, 119.8, 119.6, 117.7, 111.1, 111.0, 108.9, 56.2, 56.1, 39.6, 28.8, 20.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}O_7Na$, 449.1620; found, 449.1618. IR (neat): 3221, 2938, 1764, 1688, 1163 cm^{-1}.

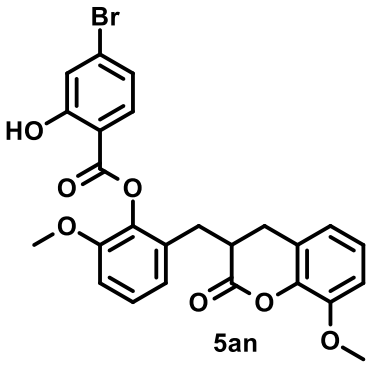


2-methoxy-6-((8-methoxy-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate (5am): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 6-fluoro-4-hydroxy-2*H*-chromen-2-one **3e** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-6-methoxyphenol **4f** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-methoxy-6-((8-methoxy-2-oxochroman-3-yl)methyl)phenyl 5-fluoro-2-hydroxybenzoate **5am** (90 mg, 40 %) as a colourless sticky solid. Melting point: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.58 (dd, J = 8.5, 3.1 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.06 (d, J = 8.9 Hz, 1H), 6.96 (dd, J = 9.2, 4.4 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.69 (dd, J = 8.9, 2.9 Hz, 1H), 6.56 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.27 (dd, J = 14.2, 4.9 Hz, 1H), 2.94 – 2.85 (m, 1H), 2.80 (dd, J = 15.7, 5.8 Hz, 1H), 2.72 – 2.62 (m, 2H). ^{13}C NMR



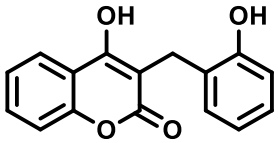
(100 MHz, $CDCl_3$) δ 170.3 (s), 168.5 (d, J = 2.8 Hz), 158.7 (s), 158.1 (s), 156.6 (s), 156.3 (s), 154.2 (s), 145.5 (s), 142.0 (s), 131.5 (s), 124.6 (s), 124.4 (s), 123.4 (s), 123.0 (s), 119.5 (d, J = 7.4 Hz), 117.5 (s), 116.2 (s), 115.3 (s), 115.1 (s), 113.6 (s), 113.3 (d, J = 8.3 Hz), 111.4 (d, J = 7.4 Hz), 55.7 (d, J = 3.0 Hz), 40.0 (s), 30.3 (s), 29.1 (s). ^{19}F NMR (377 MHz, $CDCl_3$) δ -123.1 (s, 1F). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}O_7FNa$, 475.1169; found, 475.1169. IR (neat): 3318, 2939, 1762, 1687, 1274 cm^{-1}.

2-methoxy-6-((8-methoxy-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate (5an): $Mn(OAc)_3.2H_2O$ catalyst (6.7 mg, 5 mol%), 7-bromo-4-hydroxy-2*H*-chromen-2-one **3h** (0.5 mmol, 1 equiv.), 2-(hydroxymethyl)-6-methoxyphenol **4f** (1.0 mmol, 2 equiv.), and dichloroethane (3 mL) were subjected to react according to general experimental procedure **B** to afford 2-methoxy-6-((8-methoxy-2-oxochroman-3-yl)methyl)phenyl 4-bromo-2-hydroxybenzoate **5an** (108 mg, 42%) as a colourless sticky solid. Melting point: 112-114 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.09 (dd, J = 8.5, 1.8 Hz, 1H), 7.01 – 6.89 (m, 3H), 6.82 (d, J = 8.1 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.37 (dd, J = 13.9, 3.3 Hz, 1H), 2.99 – 2.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.9, 162.6, 151.4, 147.5, 140.8, 137.9, 131.8, 131.5, 131.1, 127.4, 124.5, 123.4, 123.3, 122.4, 121.2, 119.8, 111.2, 111.1, 110.6, 56.1, 56.1, 39.7, 30.0, 28.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{25}H_{21}O_7BrNa$, 535.0368; found, 535.0372. IR (neat): 3315, 2930, 1759, 1685, 1194 cm^{-1}.



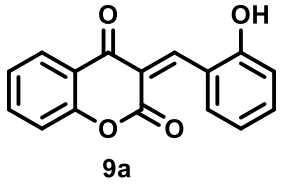
5an

4-hydroxy-3-(2-hydroxybenzyl)-2*H*-chromen-2-one (8a): ^1H NMR (400 MHz, DMSO) δ 10.47 (s, 1H), 7.94 (dd, J = 7.9, 1.4 Hz, 1H), 7.61 (s, 1H), 7.37 (dd, J = 8.0, 2.0 Hz, 2H), 7.00 (d, J = 1.1 Hz, 1H), 6.88 – 6.84 (m, 1H), 6.82 – 6.79 (m, 1H), 6.66 (d, J = 0.9 Hz, 1H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 162.9, 161.1, 154.9, 152.1, 131.8, 128.0, 126.8, 125.3, 123.9, 123.3, 118.9, 116.3, 116.1, 114.7, 102.8, 23.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{12}O_4Na$, 291.0633; found, 291.0631.



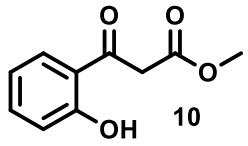
8a

(*Z*)-3-(2-hydroxybenzylidene)chromane-2,4-dione (9a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.96 (s, 1H), 7.71 – 7.63 (m, 1H), 7.60 (dd, J = 7.8, 1.4 Hz, 1H), 7.54 (dd, J = 13.2, 4.9 Hz, 2H), 7.45 – 7.34 (m, 2H), 7.06 (d, J = 8.3 Hz, 1H), 6.92 – 6.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.36, 163.37, 158.17, 154.70, 144.41, 137.71, 133.84, 132.66, 129.22, 126.55, 125.27, 119.32, 119.06, 118.77, 118.04, 117.17. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{16}H_{11}O_4$, 267.0657; found, 267.0664.



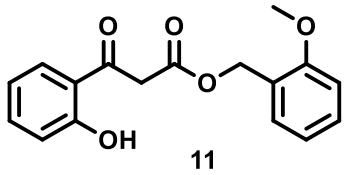
9a

Methyl 3-(2-hydroxyphenyl)-3-oxopropanoate (10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.83 (s, 1H), 7.66 (dd, J = 8.1, 1.5 Hz, 1H), 7.51 (ddd, J = 8.6, 7.4, 1.6 Hz, 1H), 7.00 (dd, J = 8.4, 0.8 Hz, 1H), 6.95 – 6.89 (m, 1H), 4.02 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 167.5, 162.9, 137.3, 130.4, 119.4, 119.1, 118.8, 52.8, 45.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{10}H_{11}O_4$, 195.0657; found, 195.0678.



10

2-methoxybenzyl 3-(2-hydroxyphenyl)-3-oxopropanoate (11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 1H), 7.64 (dd, J = 8.1, 1.5 Hz, 1H), 7.48 (dd, J = 4.8, 3.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 6.99 (dd, J = 8.4, 0.8 Hz, 1H), 6.93 (dd, J = 7.5, 0.9 Hz, 1H), 6.90 – 6.85 (m, 2H), 5.26 (s, 2H), 4.04 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 180.7, 166.9, 163.8, 162.8, 161.5, 157.7, 137.1, 130.5, 130.1, 130.0, 123.5, 120.5, 119.4, 119.1, 118.7, 110.6, 63.2, 55.5, 46.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{16}O_5Na$, 323.0895; found, 323.0899.



11

NMR Copies:

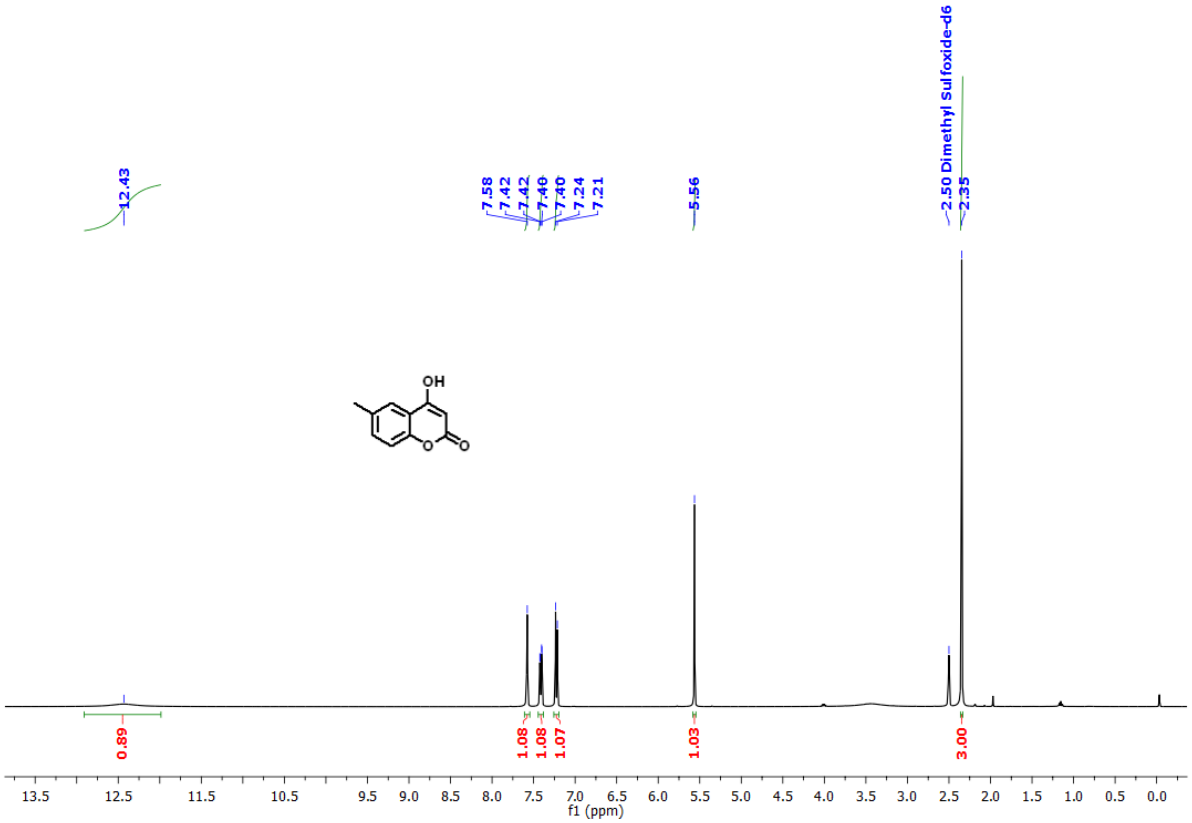


Fig. S3. ^{1}H NMR of **3b,** 400MHz, DMSO-d$_6$

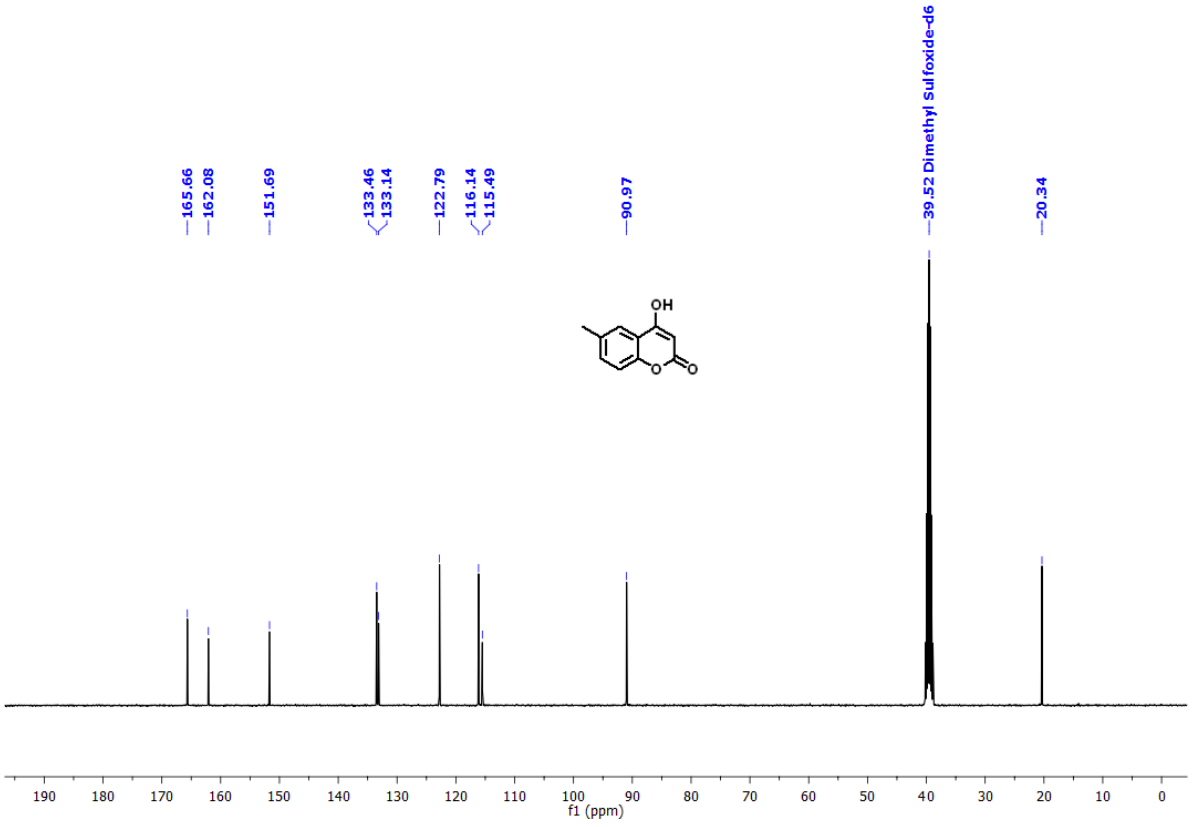


Fig. S4. ^{13}C NMR of **3b,** 100MHz, DMSO-d$_6$

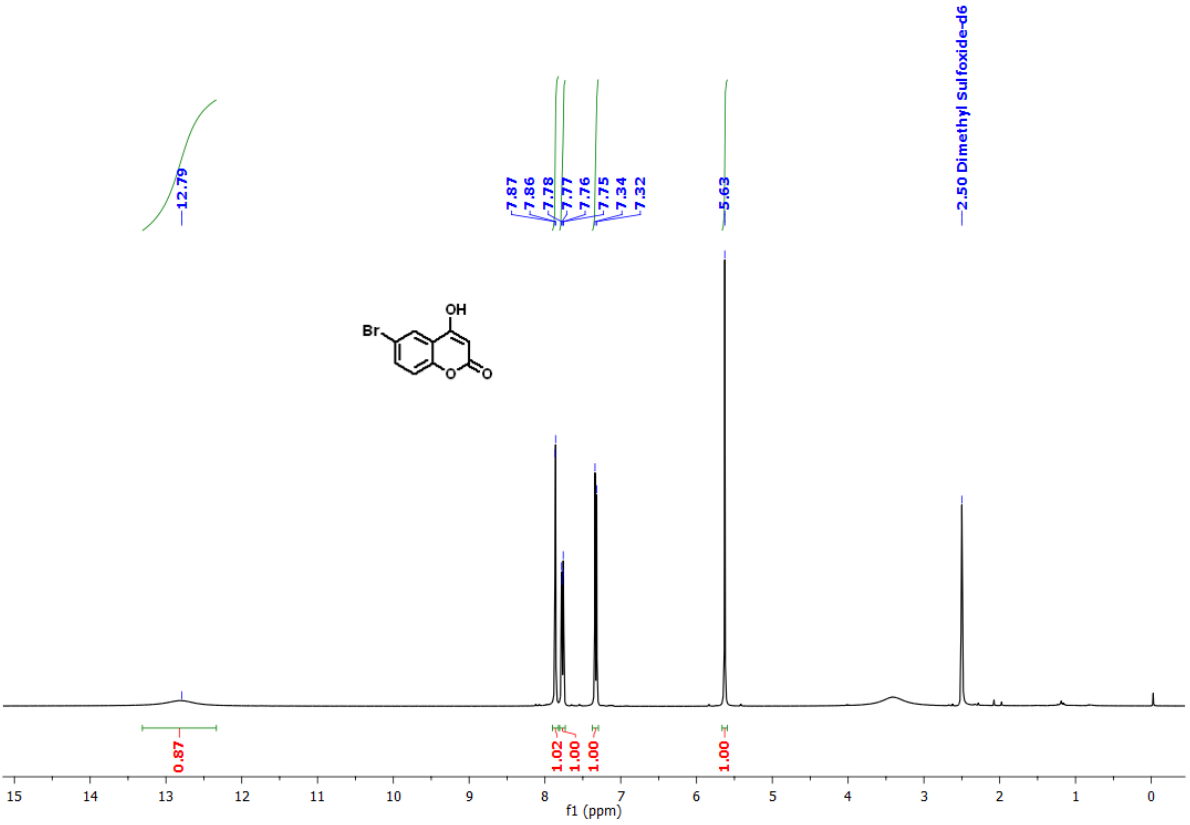


Fig. S5. ^{1}H NMR of **3c,** 400MHz, DMSO-d$_6$

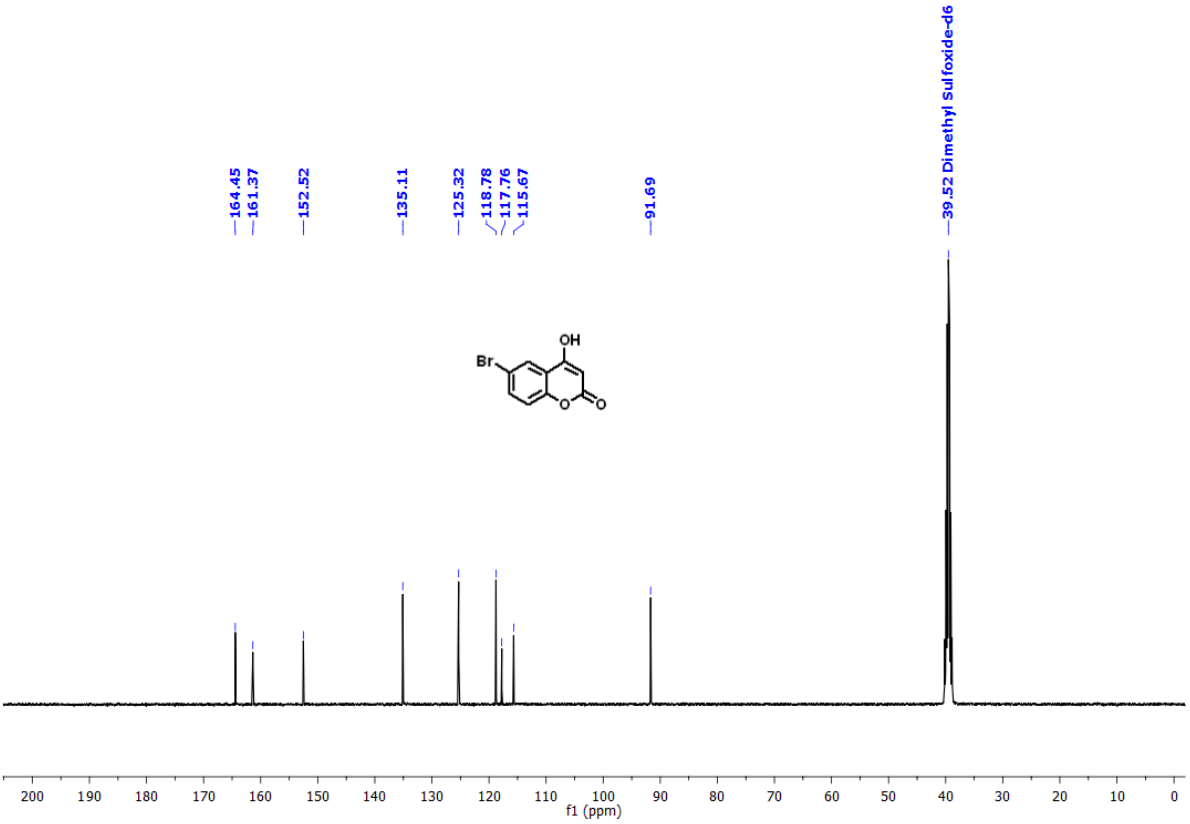


Fig. S6. ^{13}C NMR of **3c,** 100MHz, DMSO-d$_6$

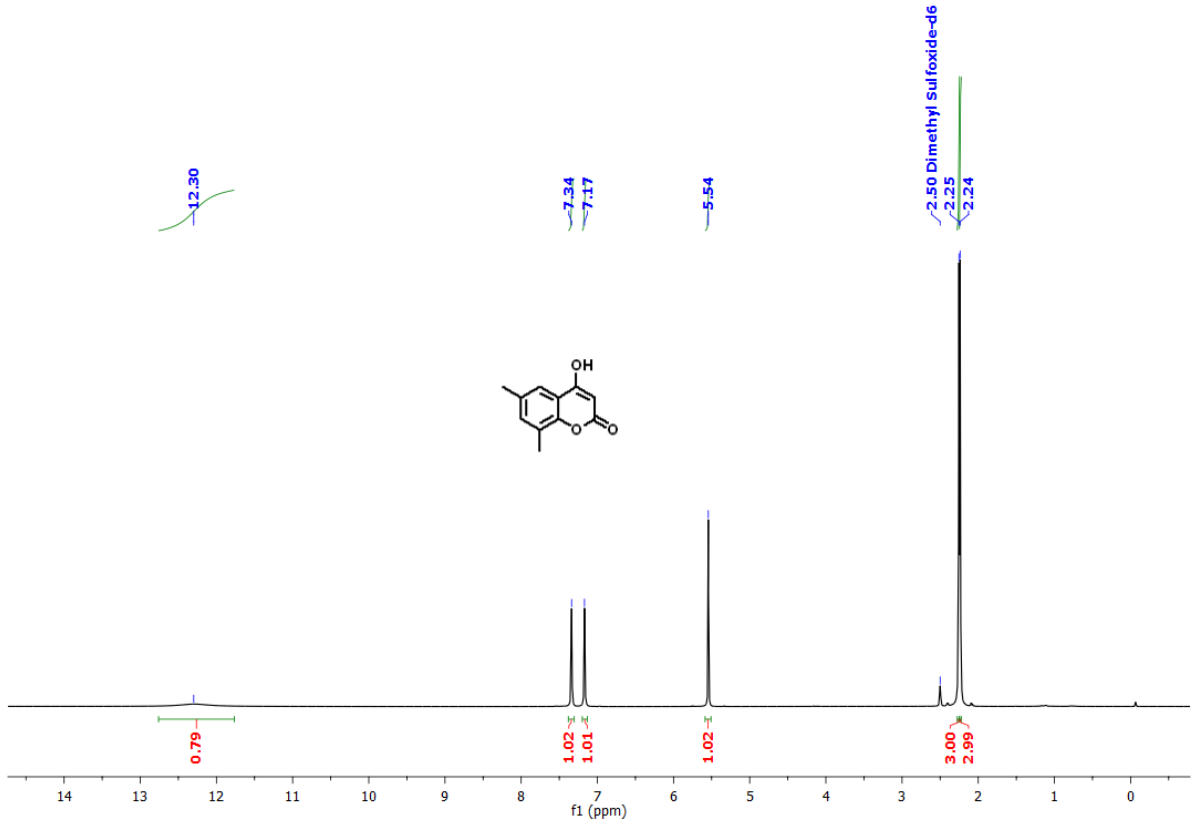


Fig. S7. ^{1}H NMR of **3d,** 400MHz, DMSO-d$_6$

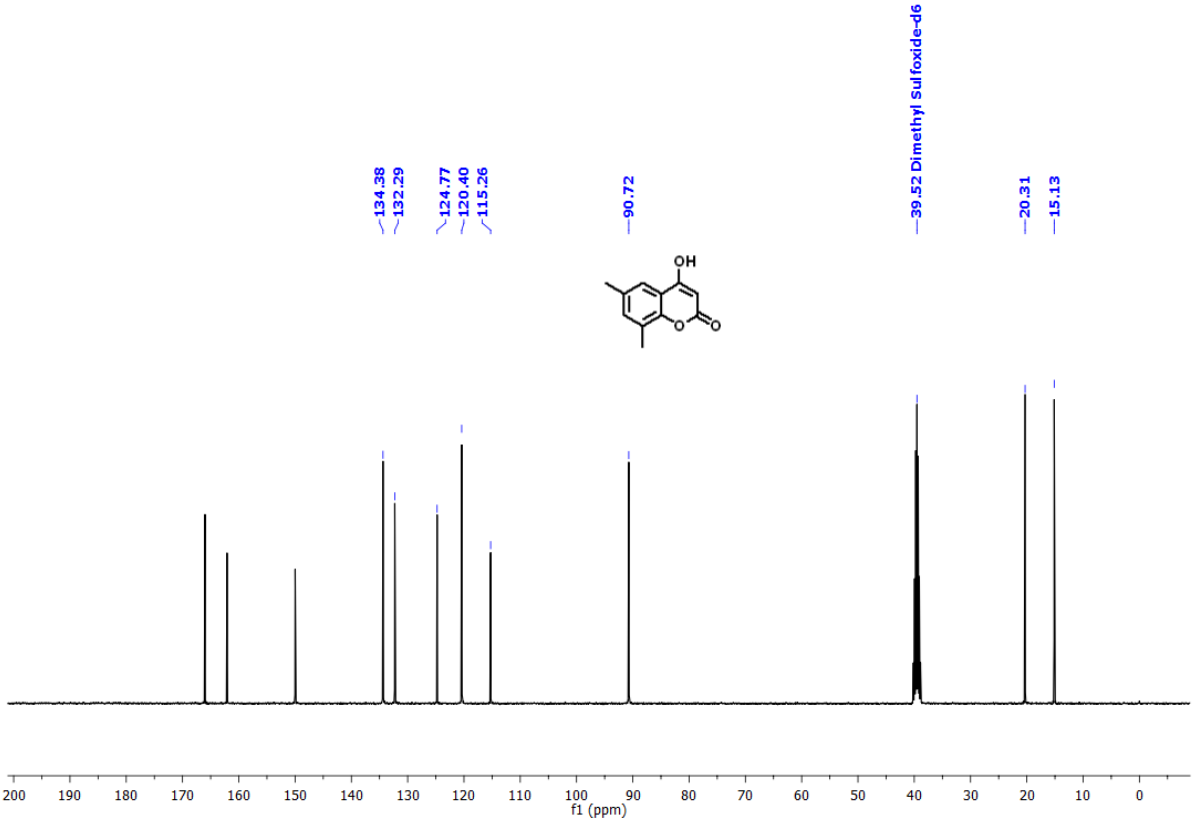


Fig. S8. ^{13}C NMR of **3d,** 100MHz, DMSO-d$_6$

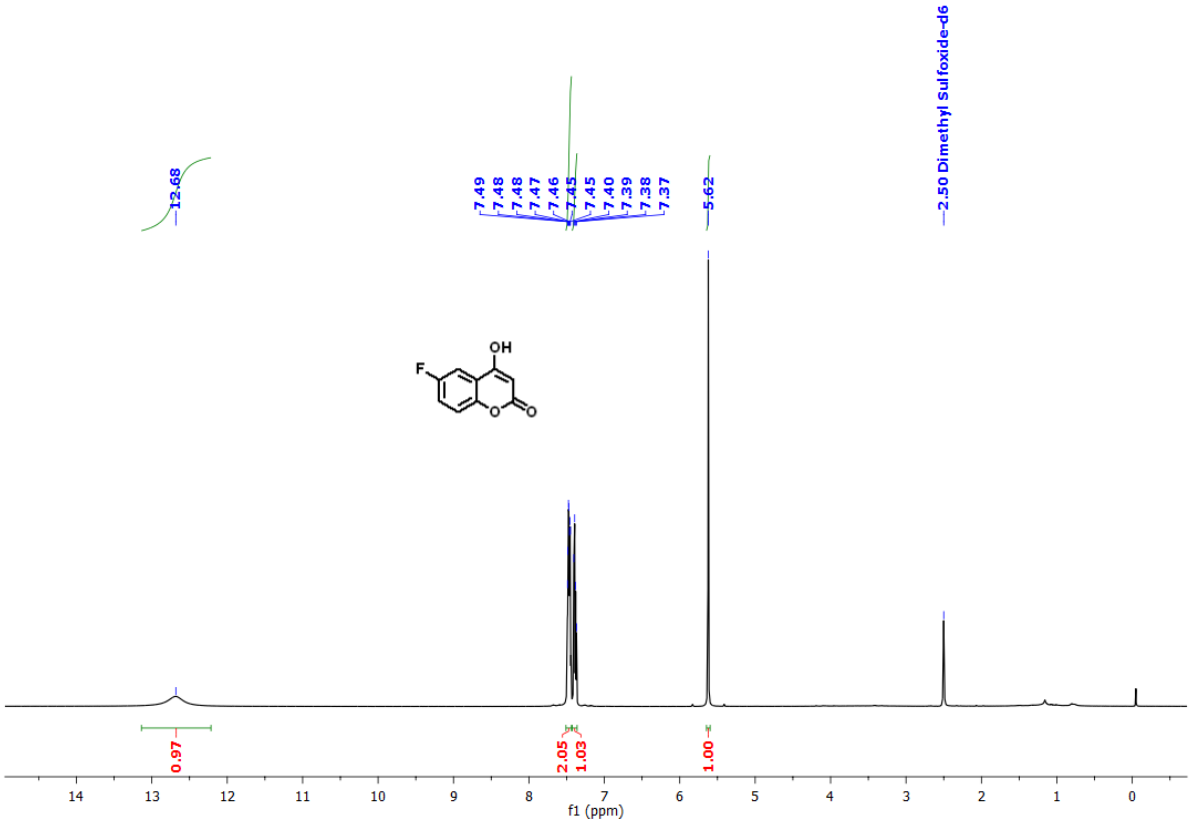


Fig. S9. ^{1}H NMR of **3e,** 400MHz, DMSO-d$_6$

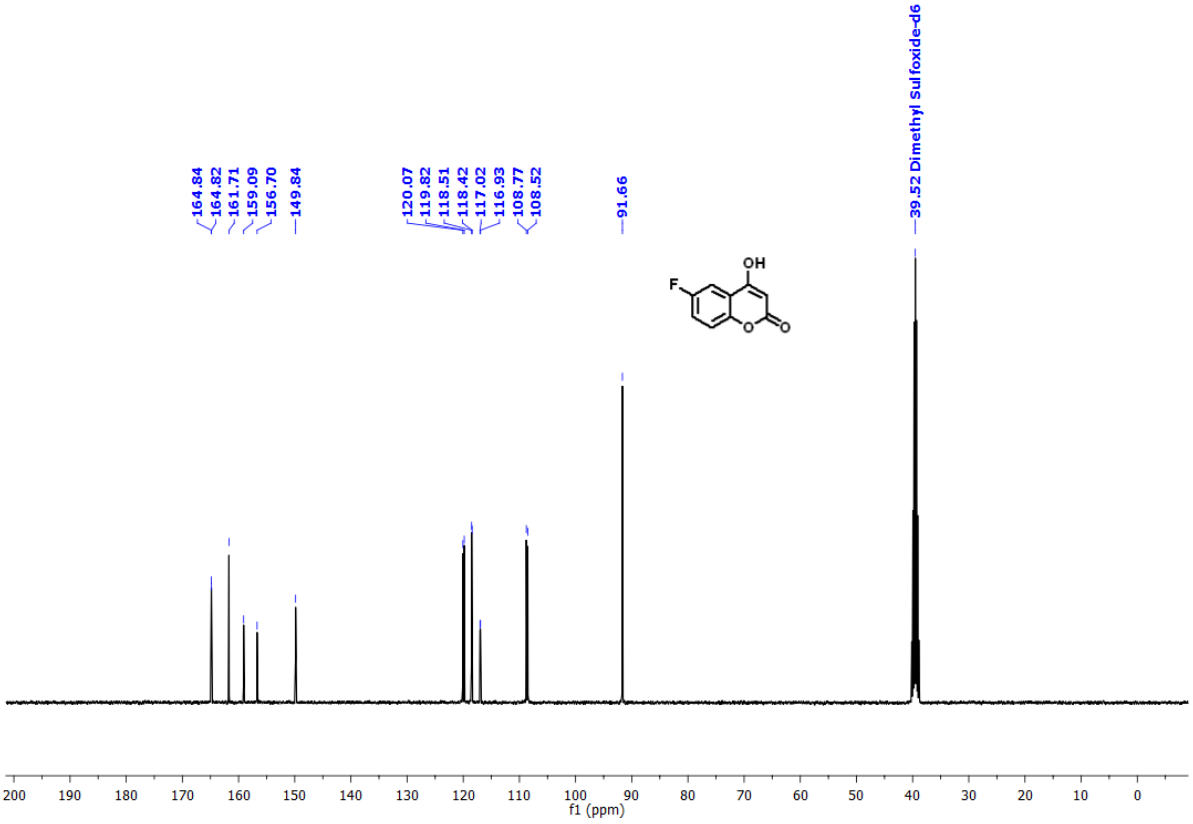


Fig. S10. ^{13}C NMR of **3e,** 100MHz, DMSO-d$_6$

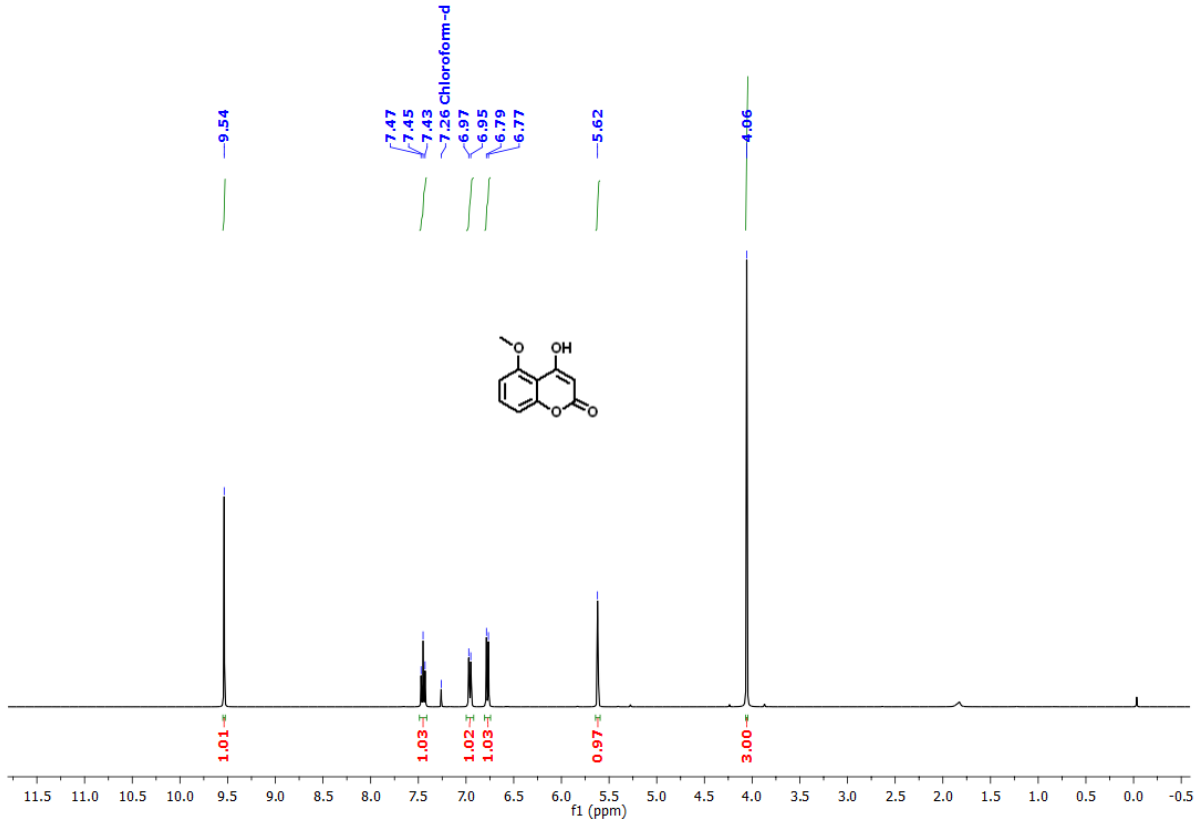


Fig. S11. ^{1}H NMR of **3f,** 400MHz, $CDCl_3$

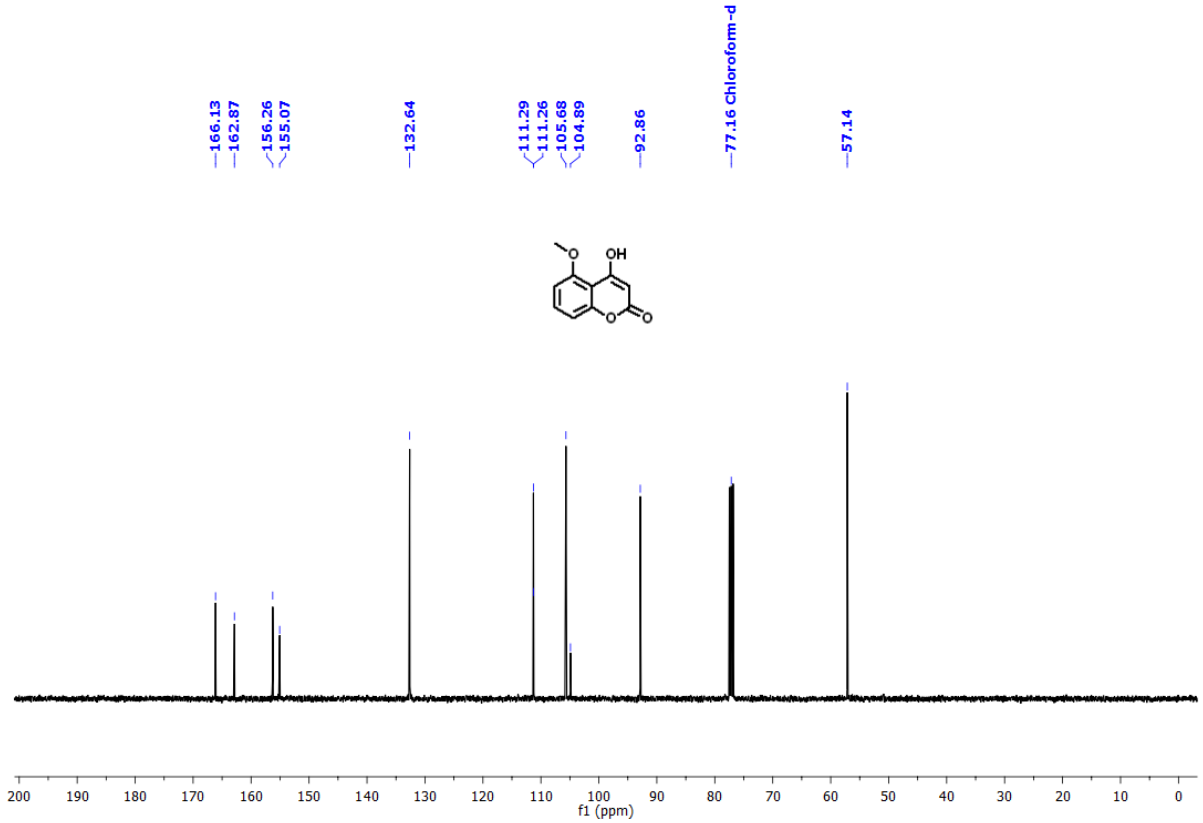


Fig. S12. ^{13}C NMR of **3f,** 100MHz, $CDCl_3$

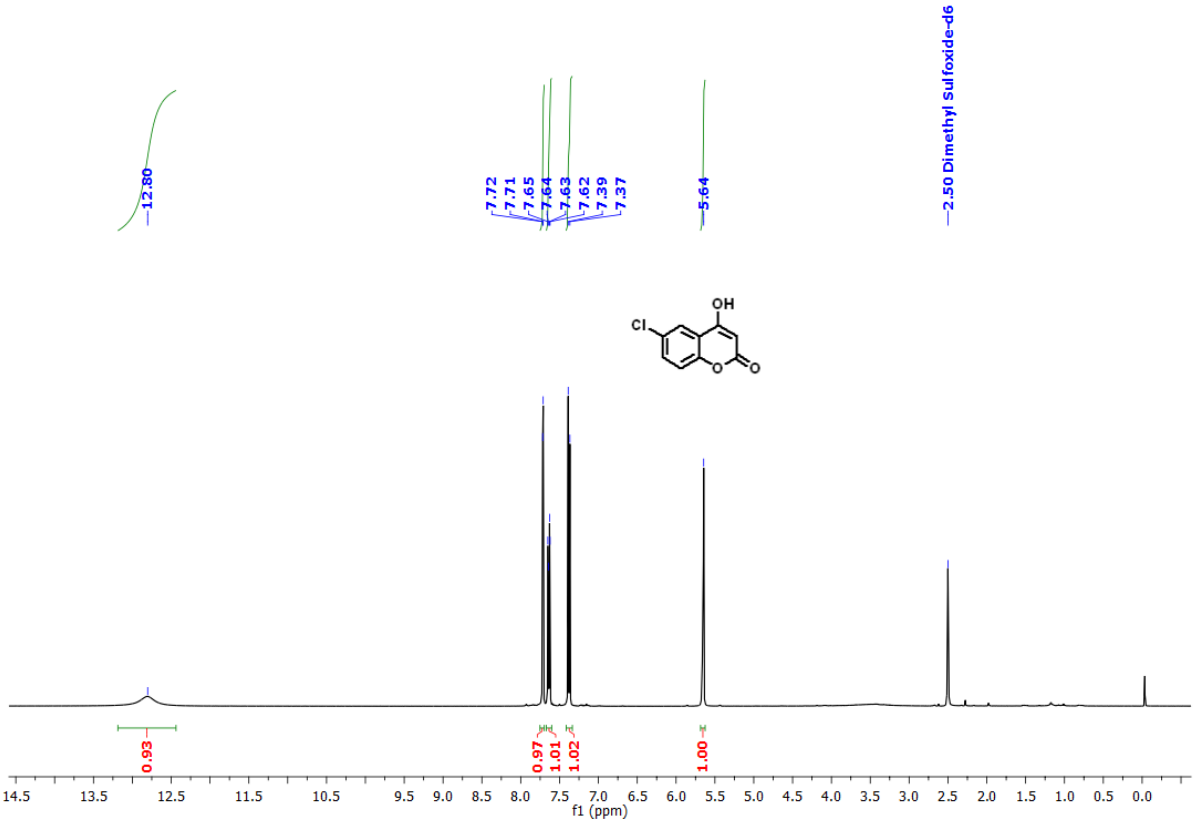


Fig. S13. ^{1}H NMR of **3g,** 400MHz, DMSO-d$_6$

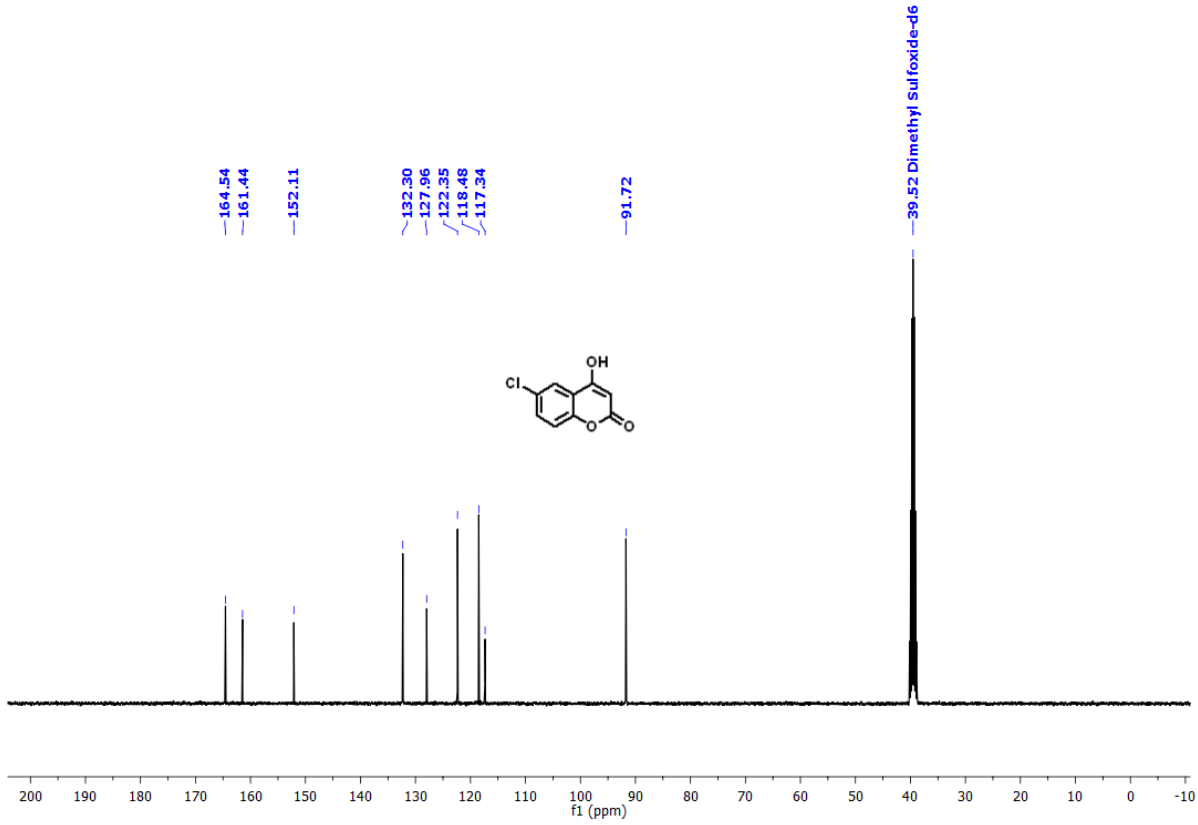


Fig. S14. ^{13}C NMR of **3g,** 100MHz, DMSO-d$_6$

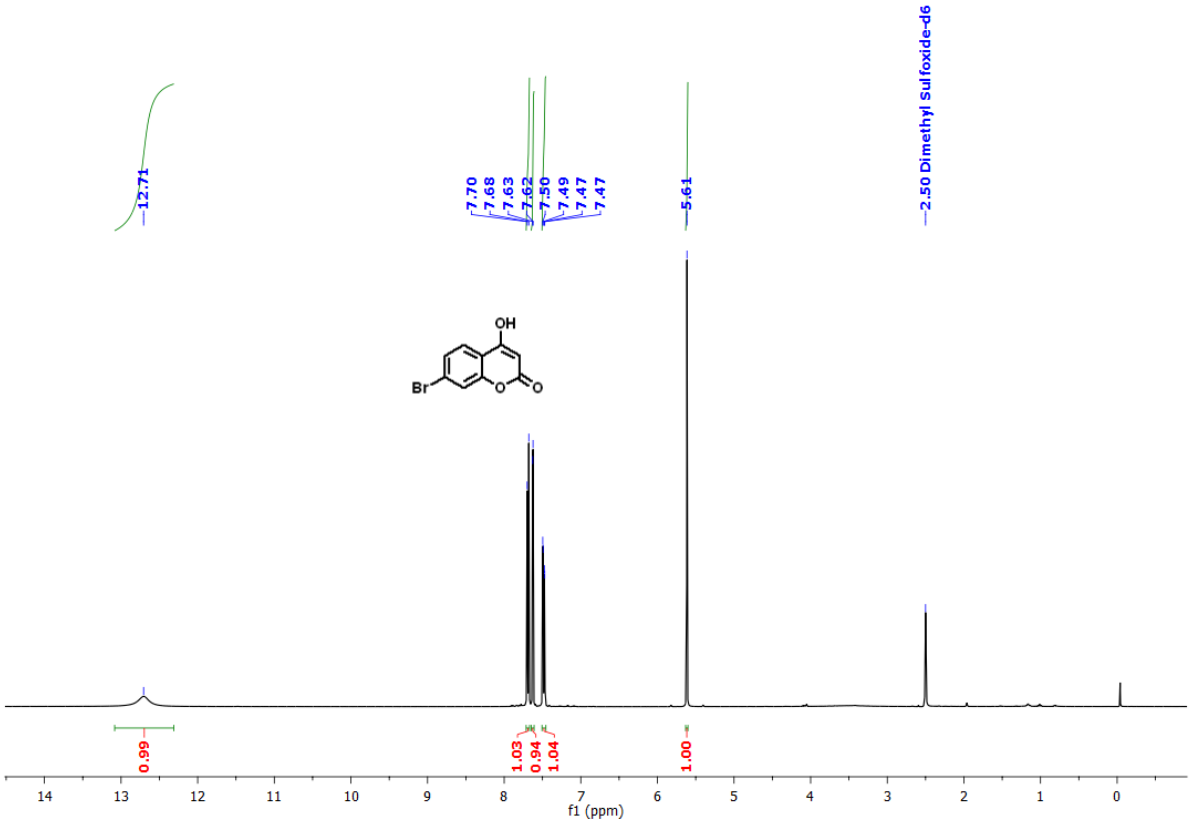


Fig. S15. ^{1}H NMR of **3h,** 400MHz, DMSO-d_6

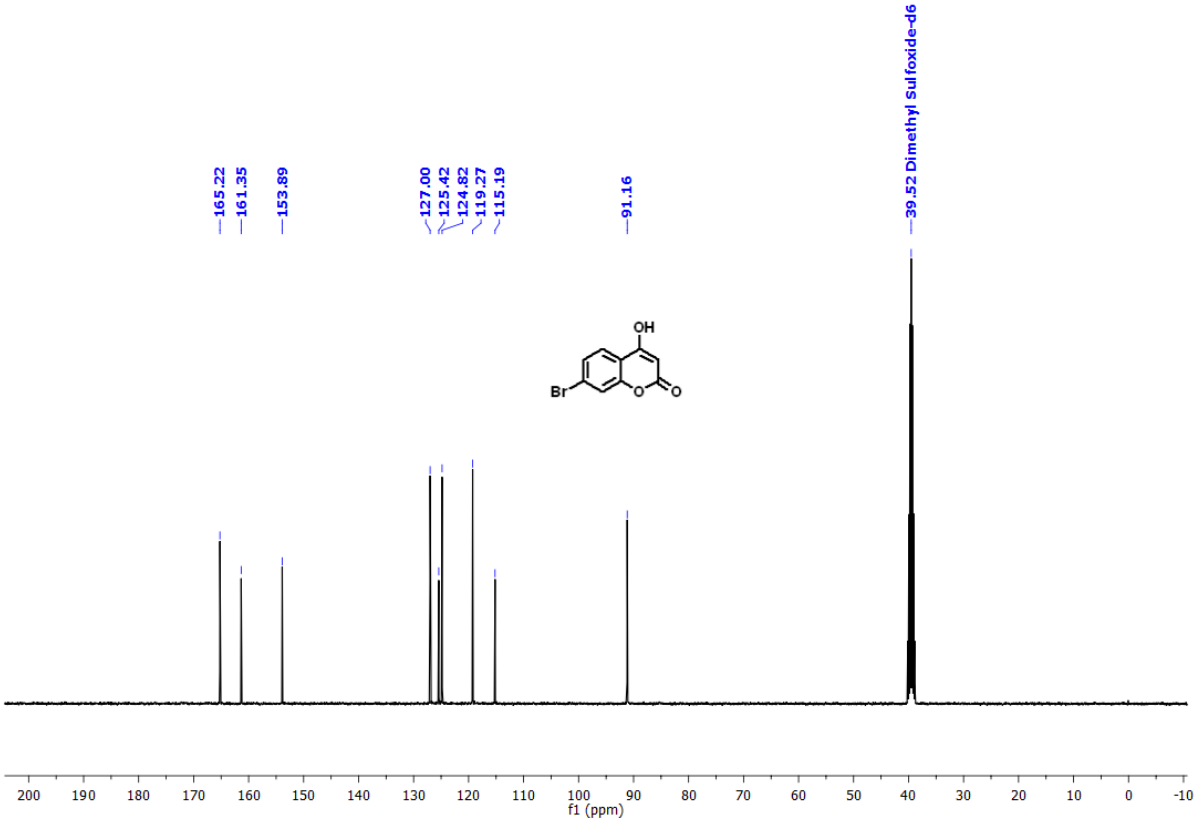


Fig. S16. ^{13}C NMR of **3h,** 100MHz, DMSO-d_6

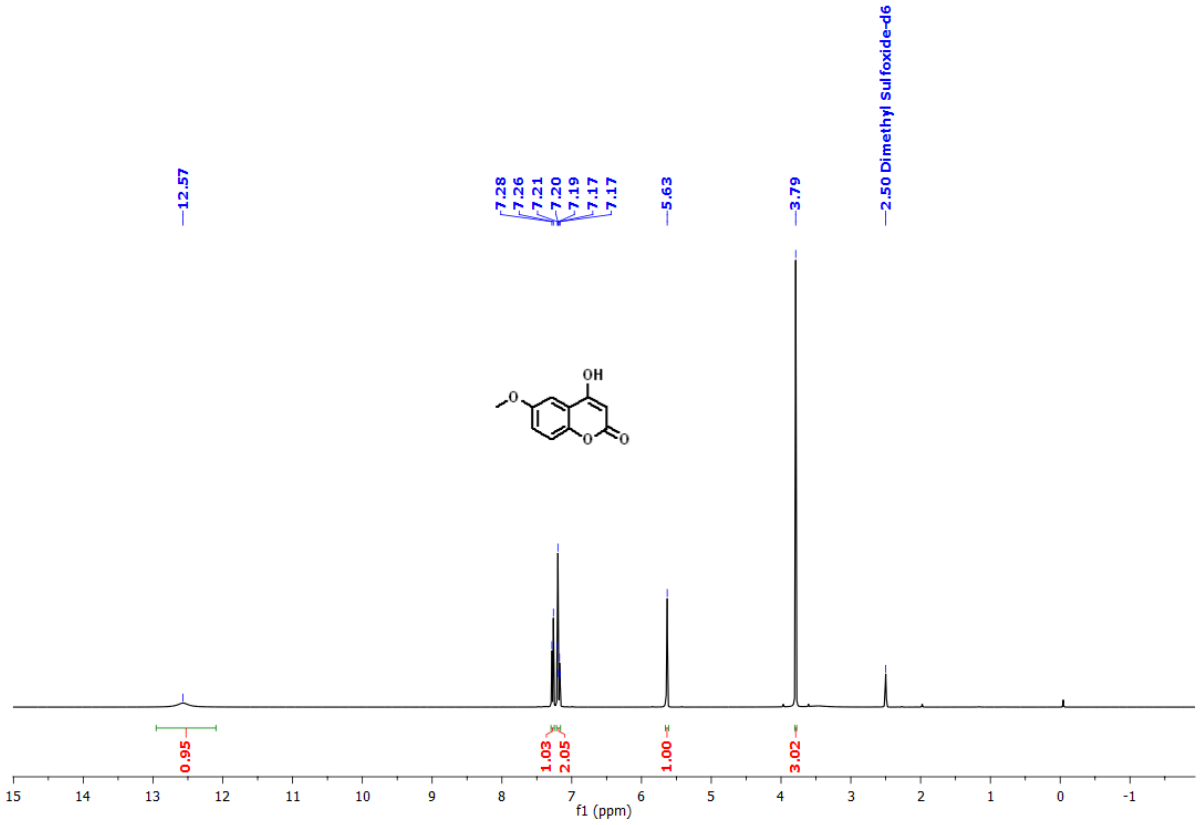


Fig. S17. ^{1}H NMR of **3i,** 400MHz, DMSO-d_6

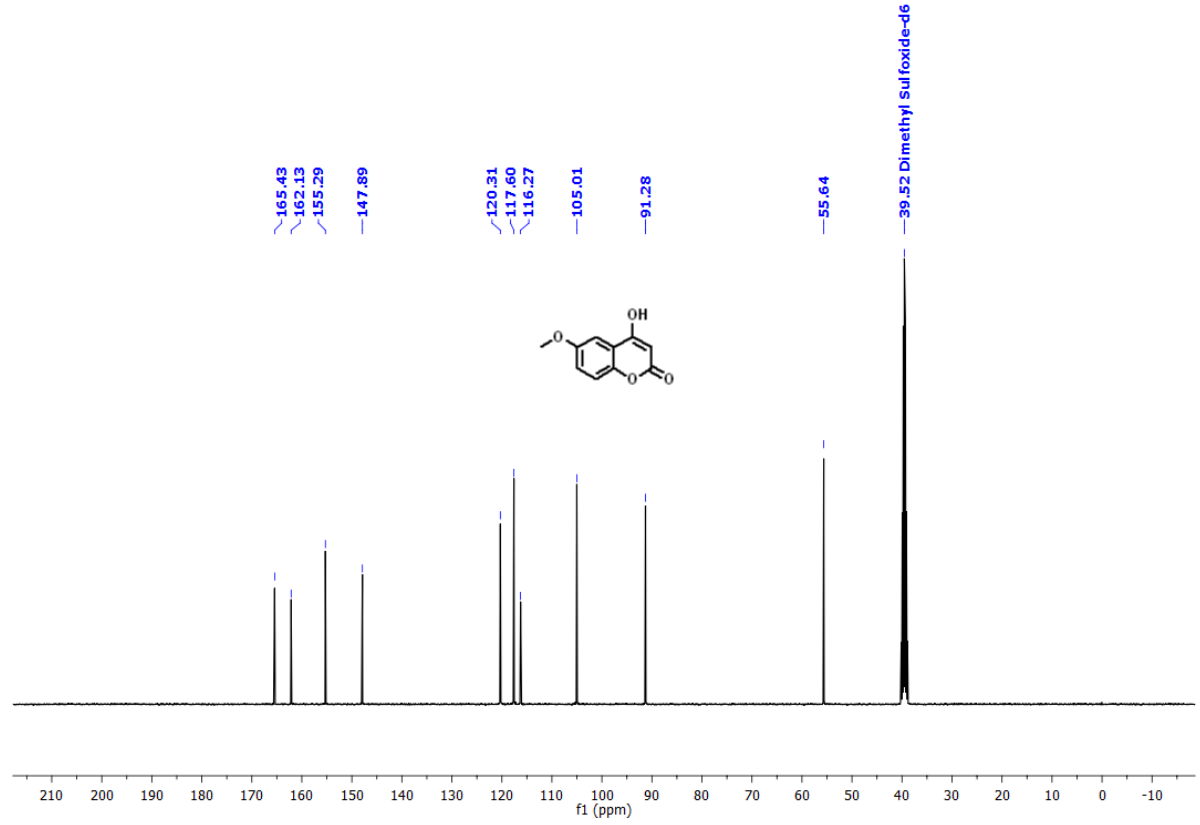


Fig. S18. ^{13}C NMR of **3i,** 100MHz, DMSO-d_6

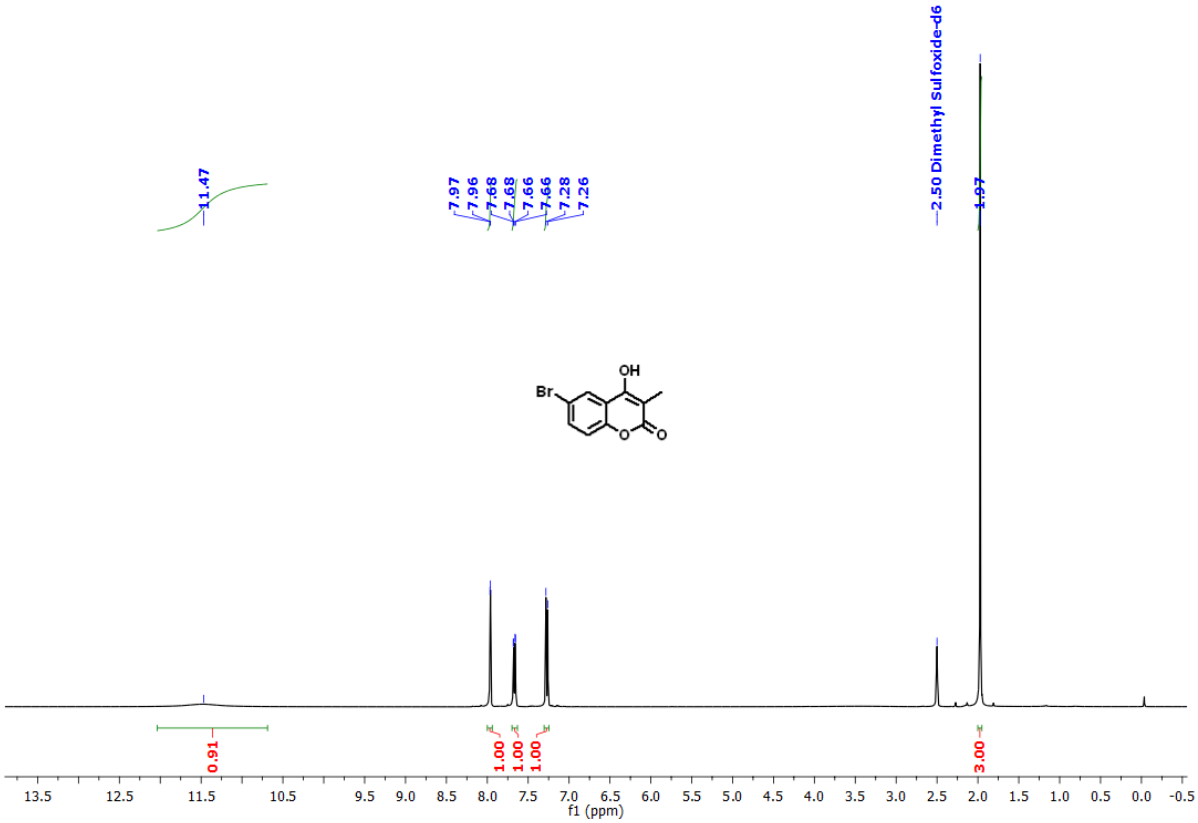


Fig. S19. ^{1}H NMR of **3j,** 400MHz, DMSO-d$_6$

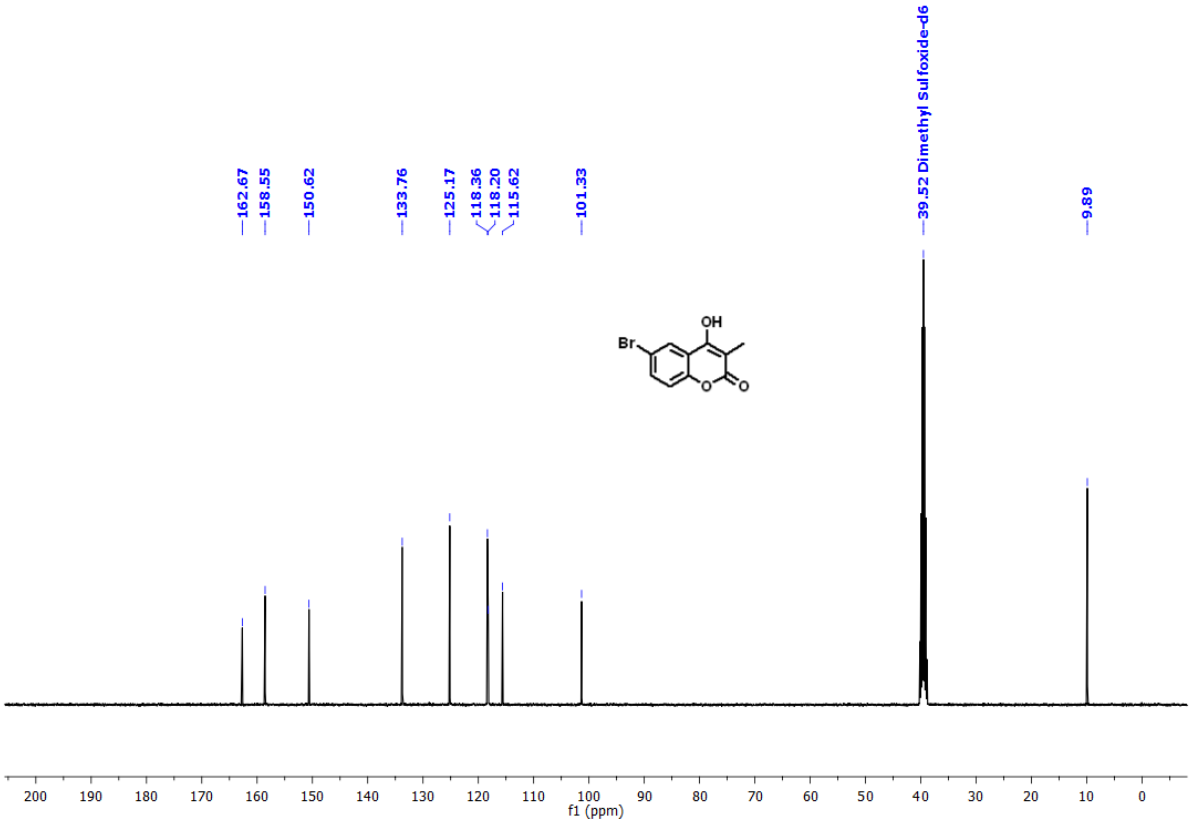


Fig. S20. ^{13}C NMR of **3j,** 100MHz, DMSO-d$_6$

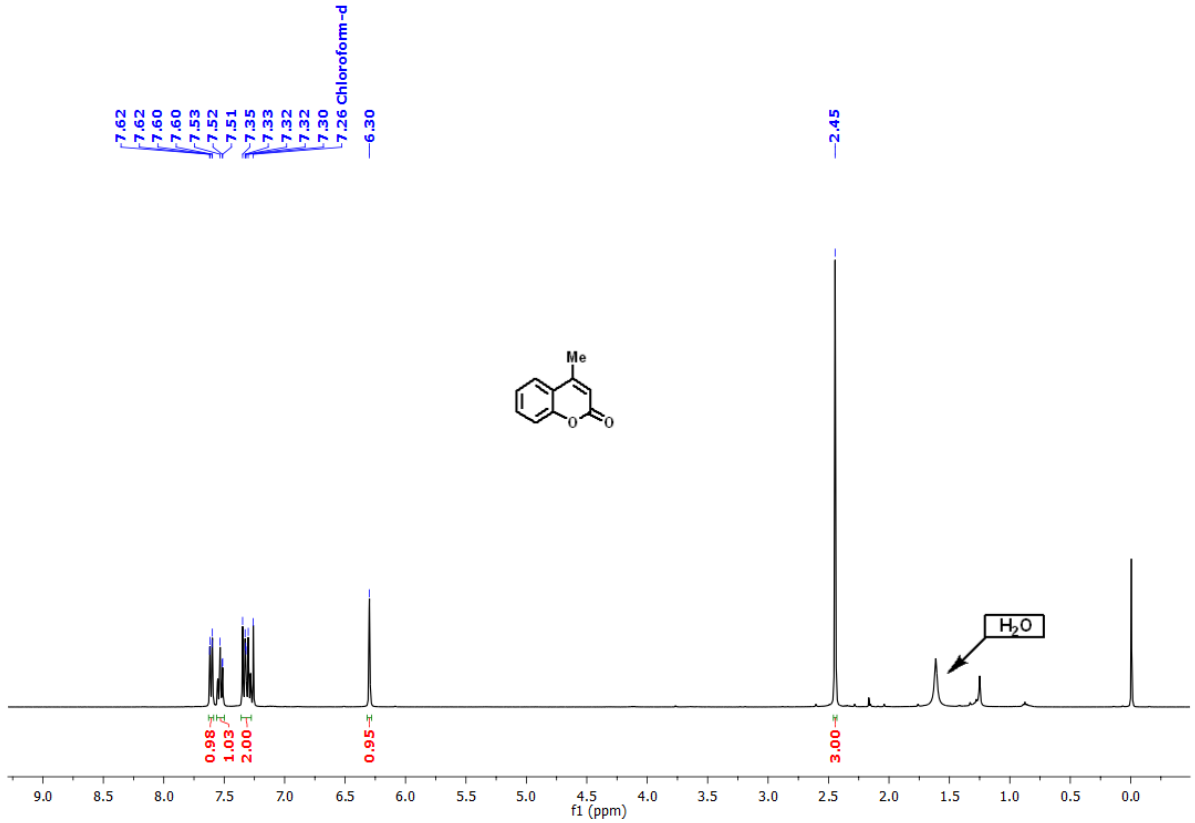


Fig. S21. ^{1}H NMR of **3k,** 400MHz, $CDCl_3$

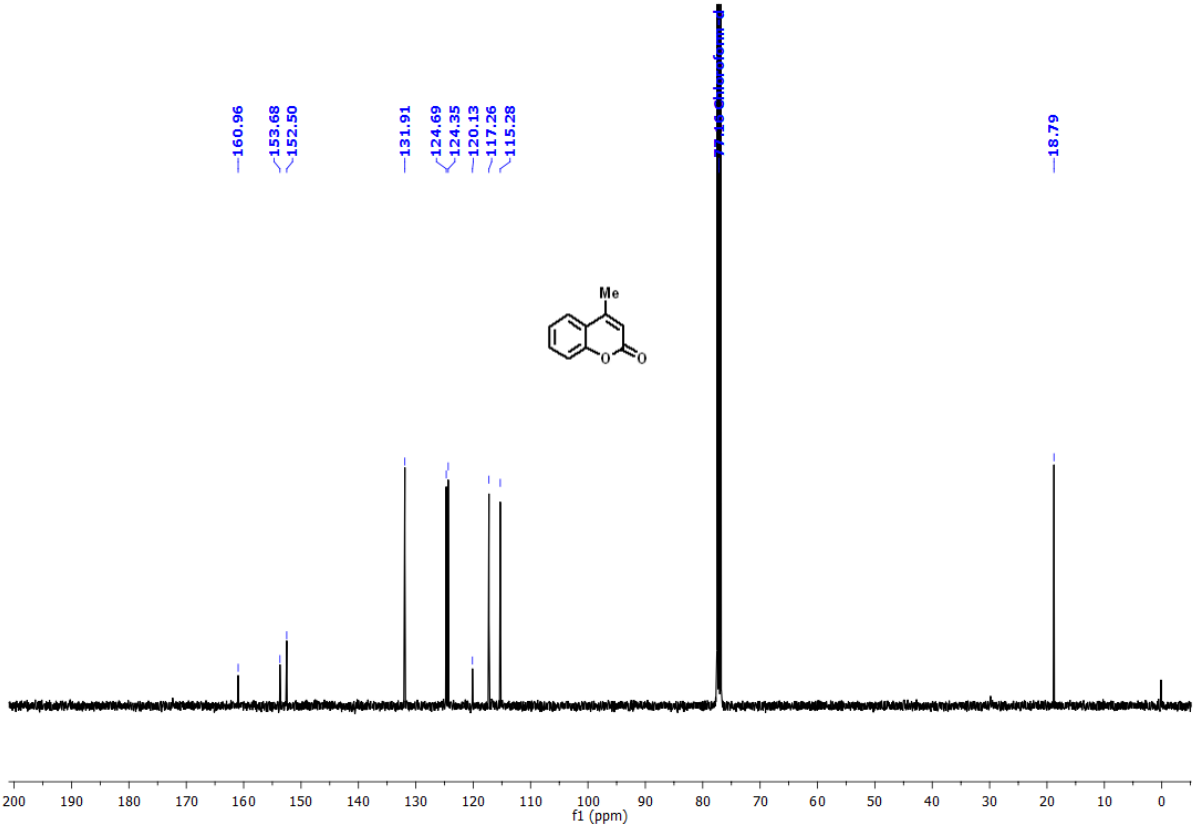


Fig. S22. ^{13}C NMR of **3k,** 100MHz, $CDCl_3$

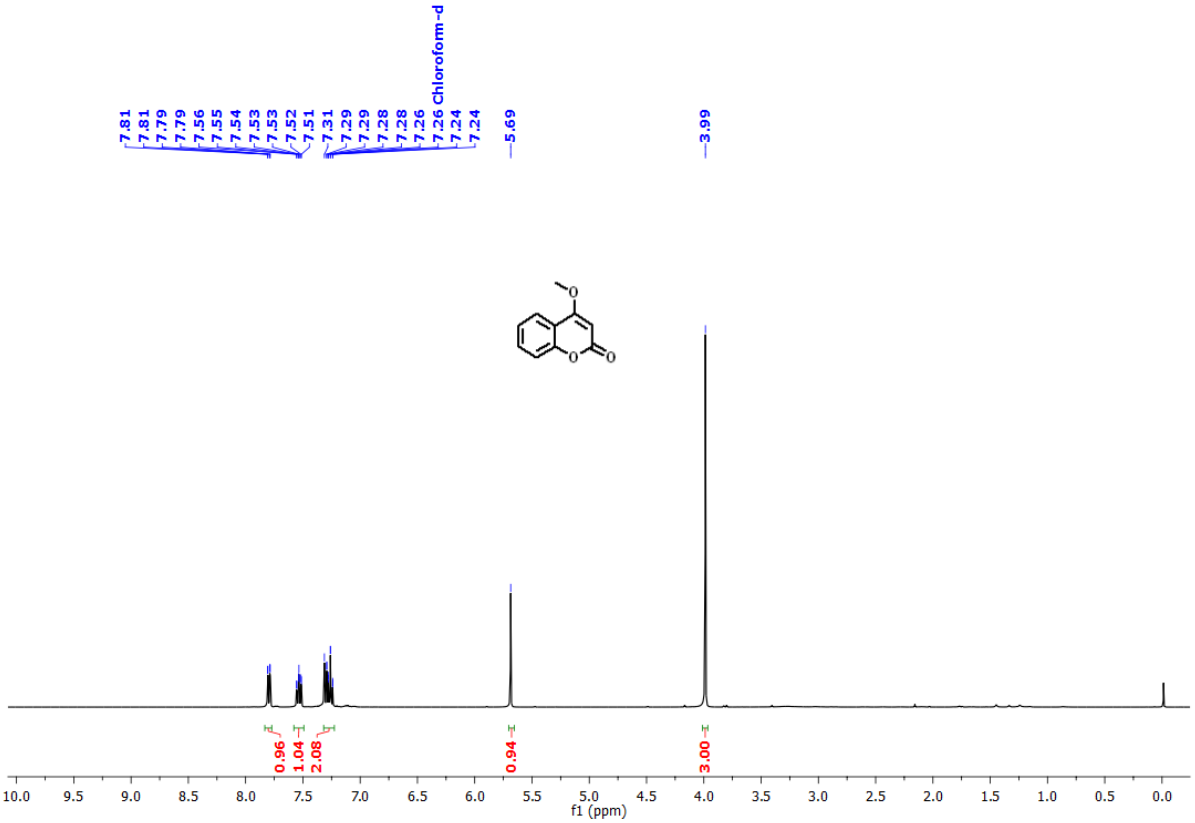


Fig. S23. ^{1}H NMR of **3l,** 400MHz, $CDCl_3$

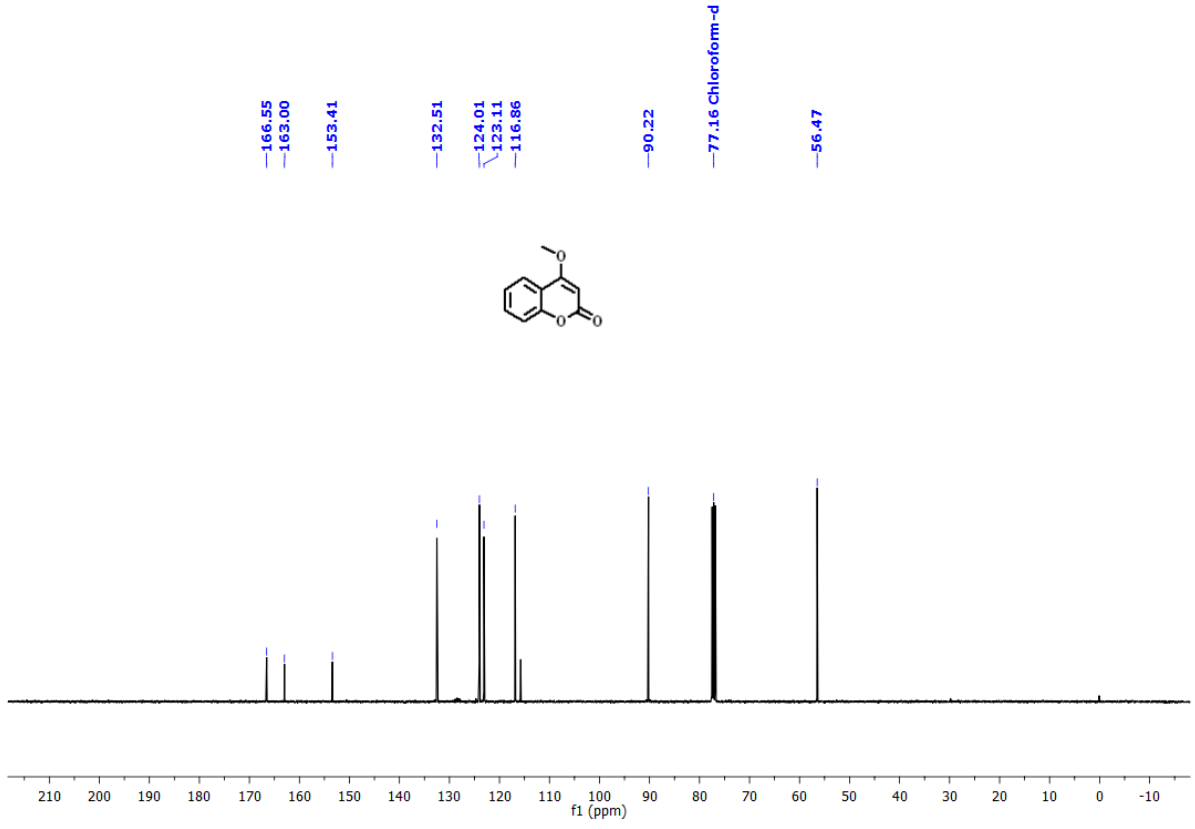


Fig. S24. ^{13}C NMR of **3l,** 100MHz, $CDCl_3$

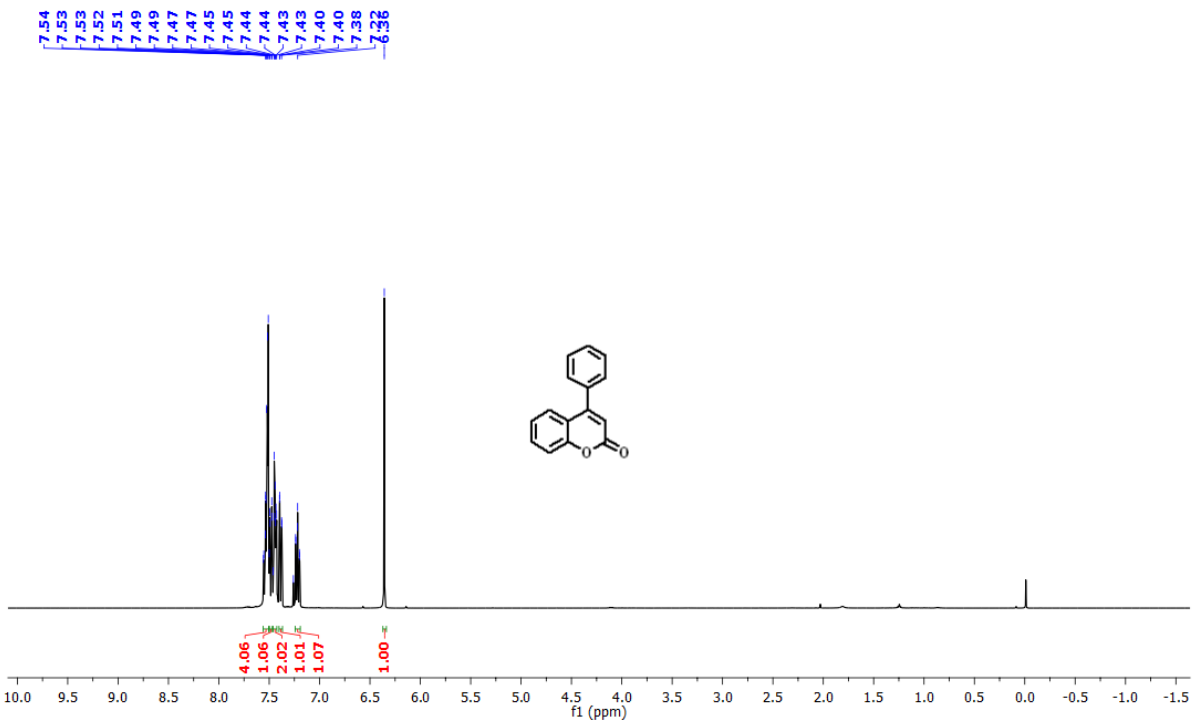


Fig. S25. ^{1}H NMR of **3m,** 400MHz, $CDCl_3$

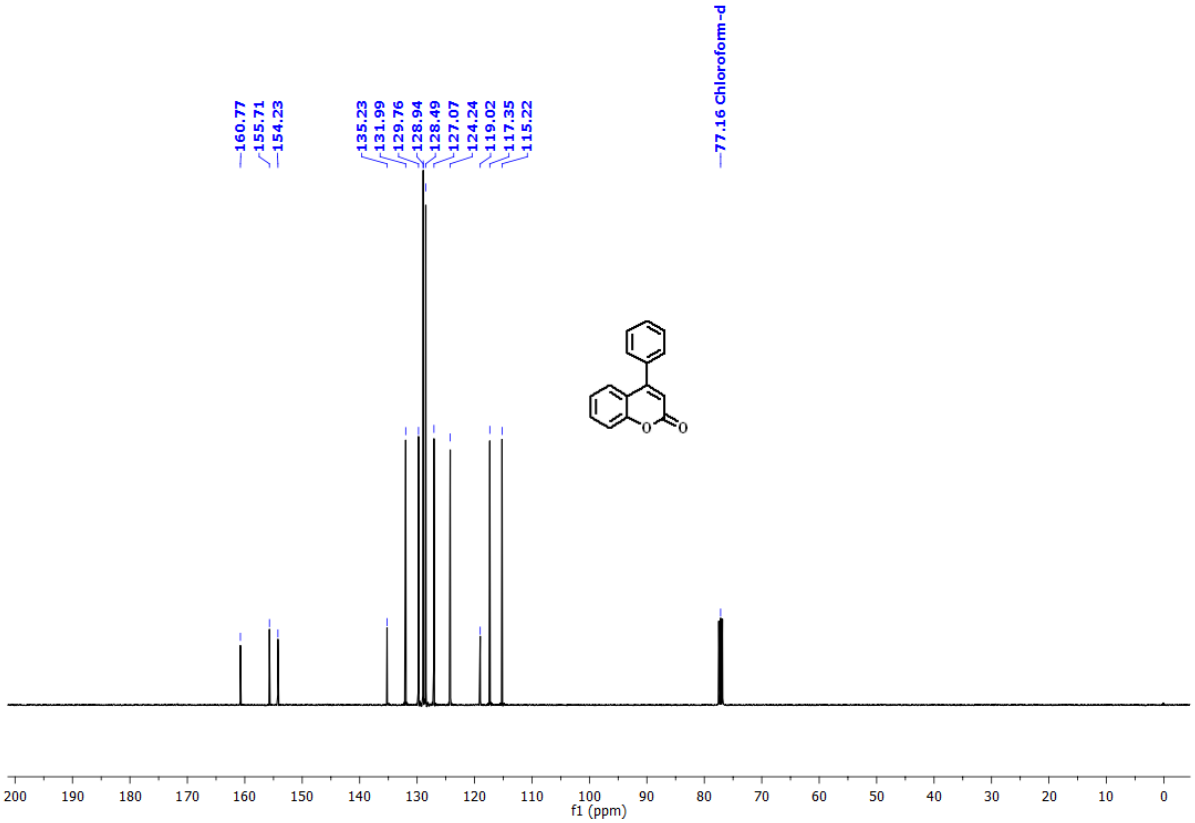


Fig. S26. ^{13}C NMR of **3m,** 100MHz, $CDCl_3$

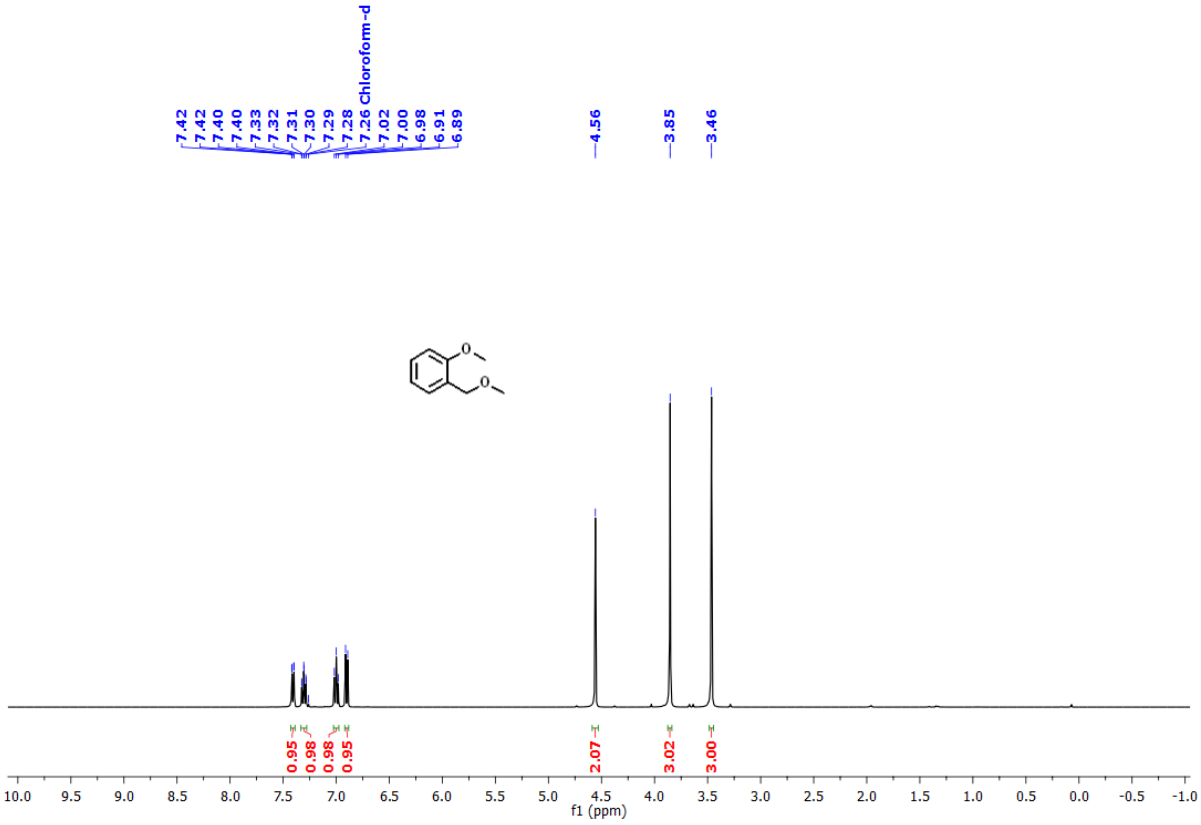


Fig. S27. ^{1}H NMR of **4ac,** 400MHz, $CDCl_3$

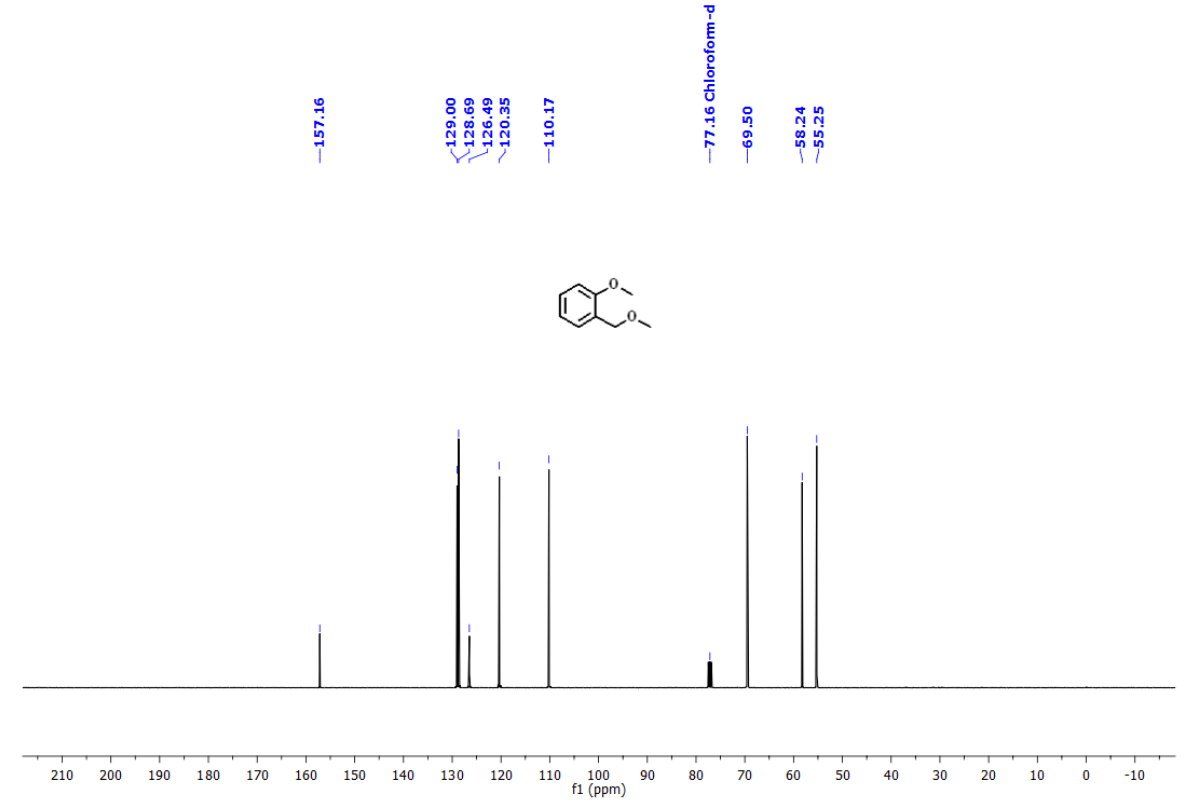


Fig. S28. ^{13}C NMR of **4ac,** 100MHz, $CDCl_3$

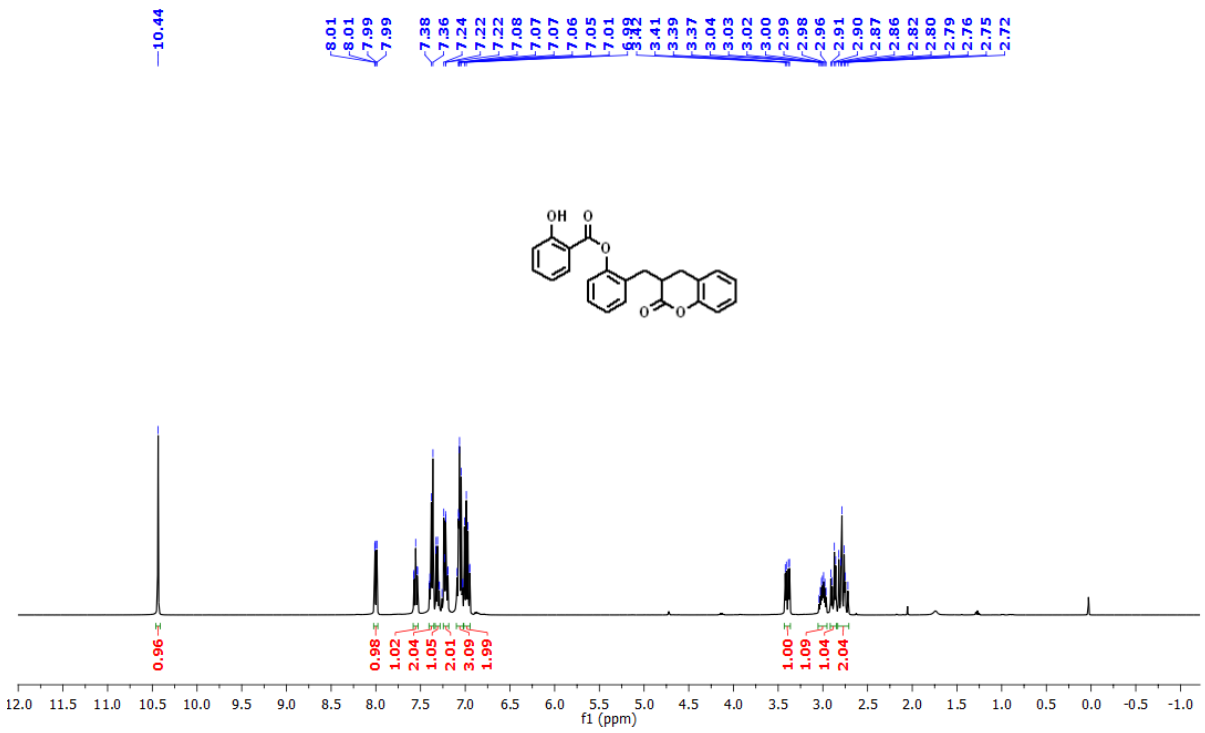


Fig. S27. ^{1}H NMR of **5a,** 400MHz, $CDCl_3$

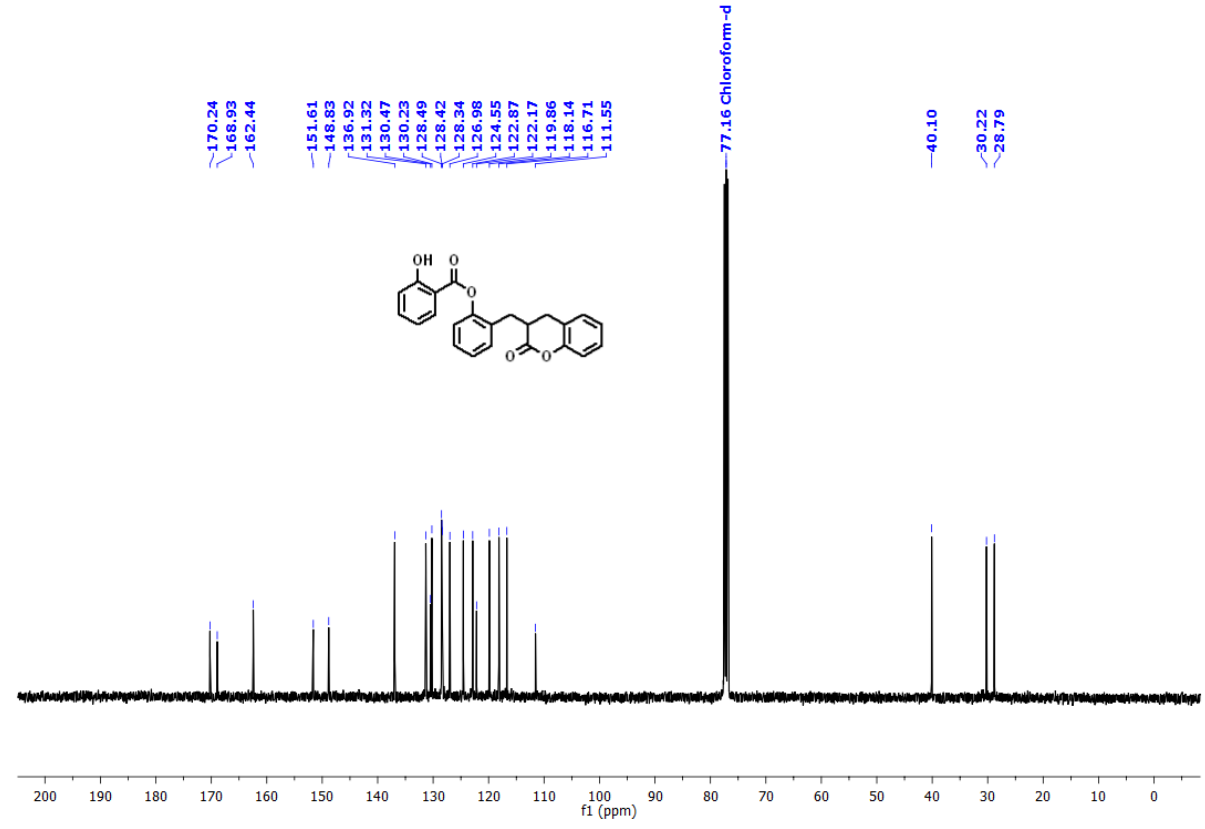


Fig. S28. ^{13}C NMR of **5a,** 100MHz, $CDCl_3$

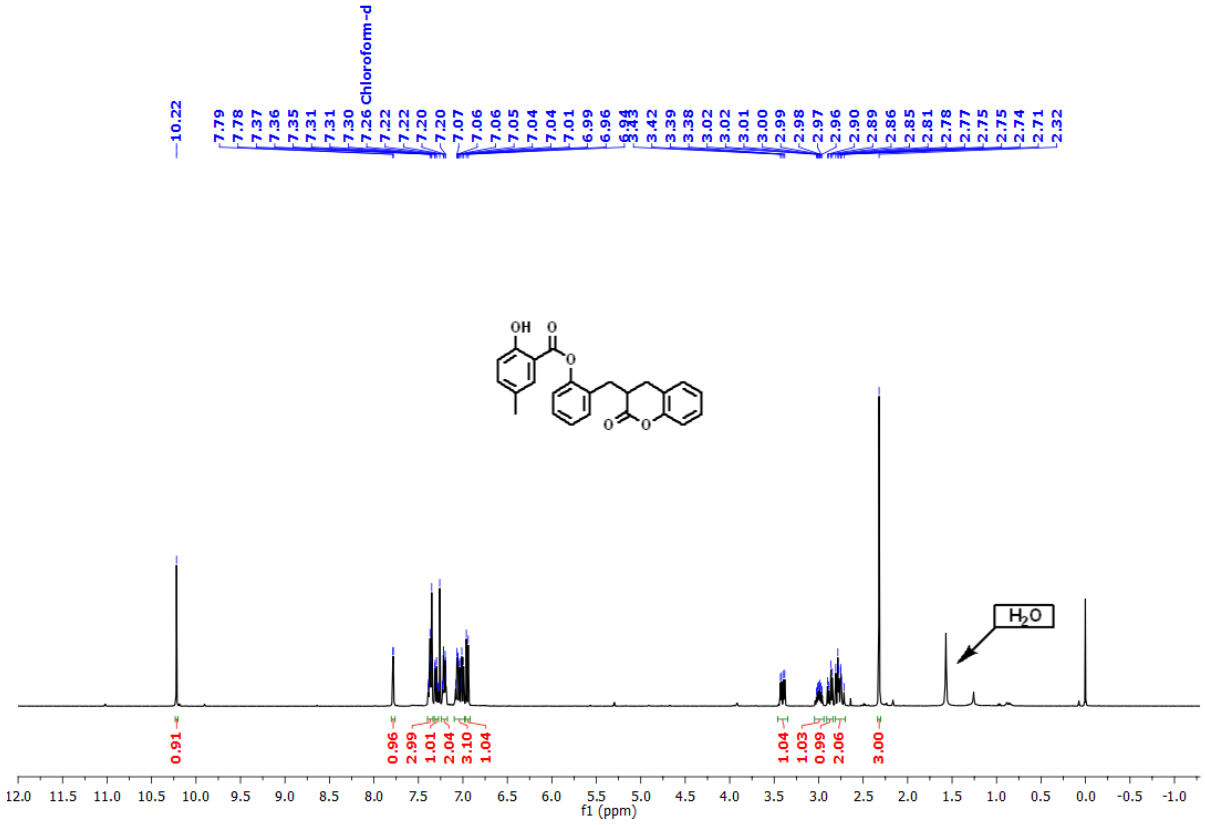


Fig. S29. ^{1}H NMR of **5b,** 400MHz, $CDCl_3$

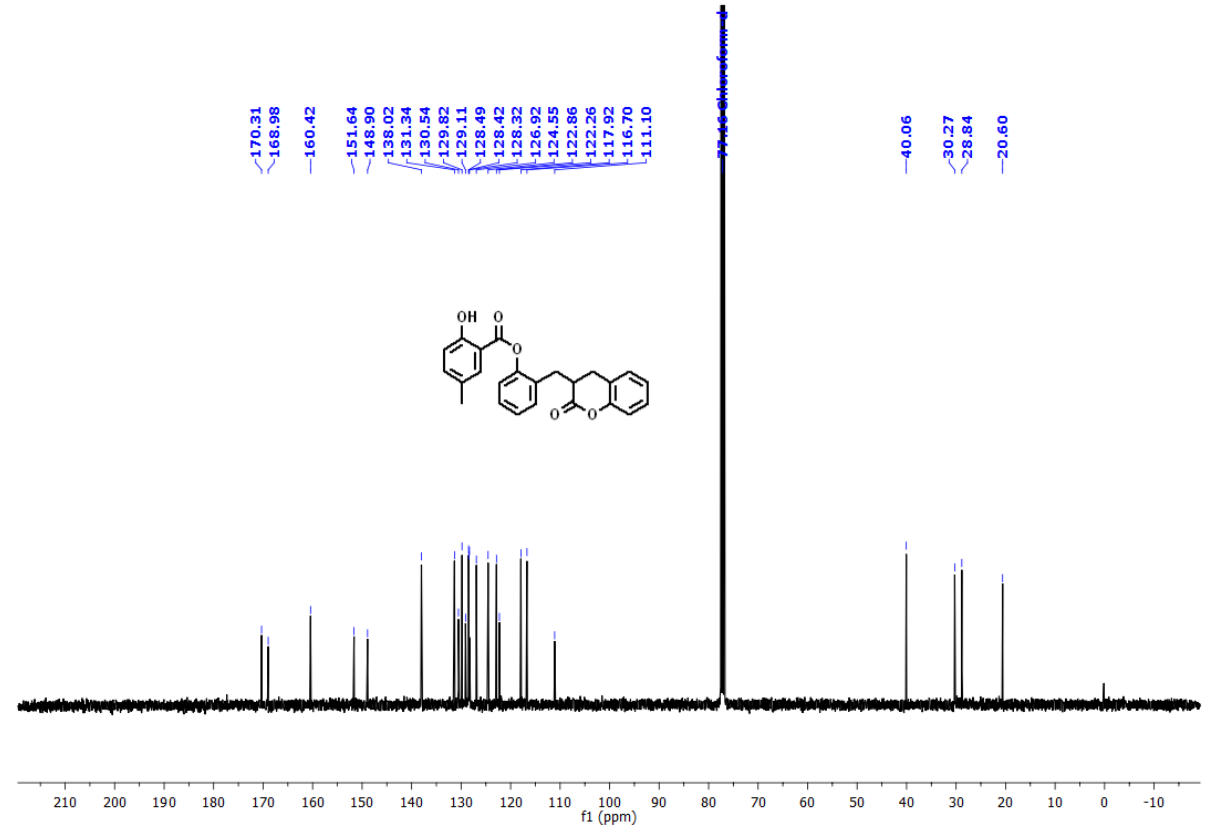


Fig. S30. ^{13}C NMR of **5b,** 100MHz, $CDCl_3$

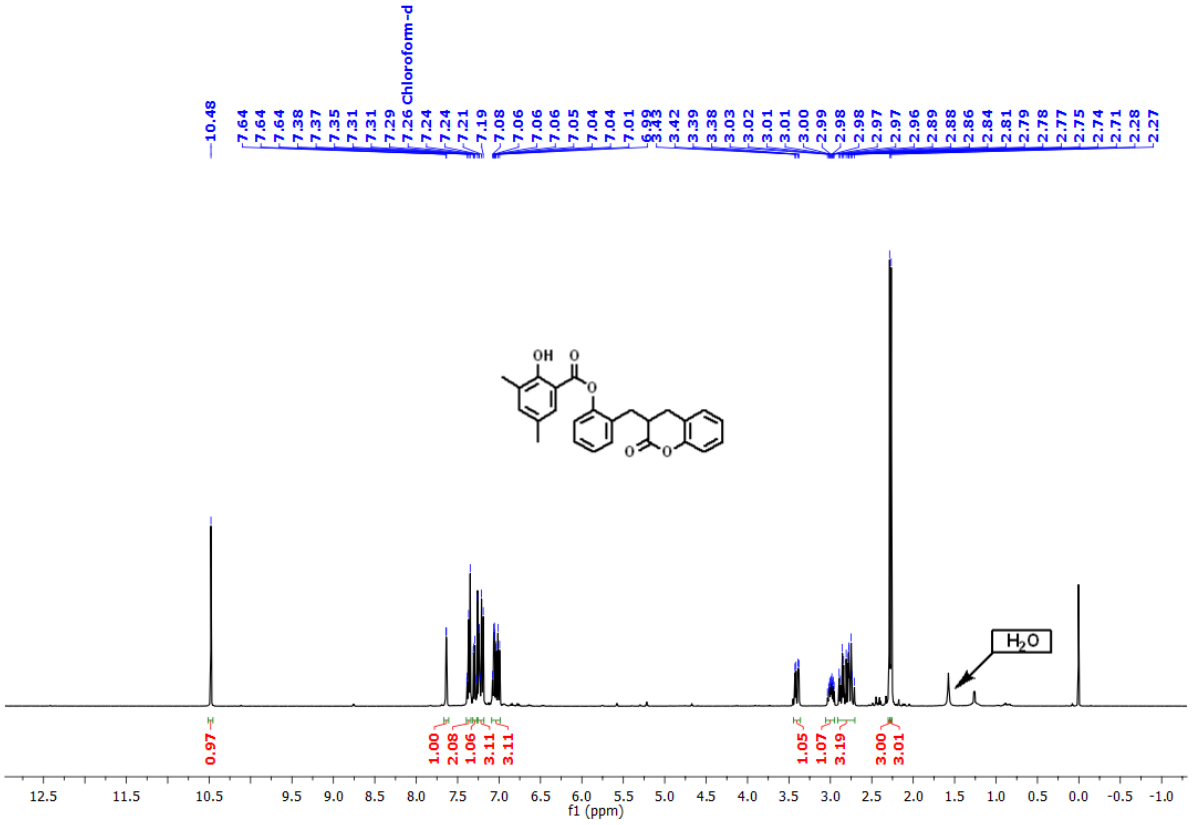


Fig. S31. ^{1}H NMR of **5c,** 400MHz, $CDCl_3$

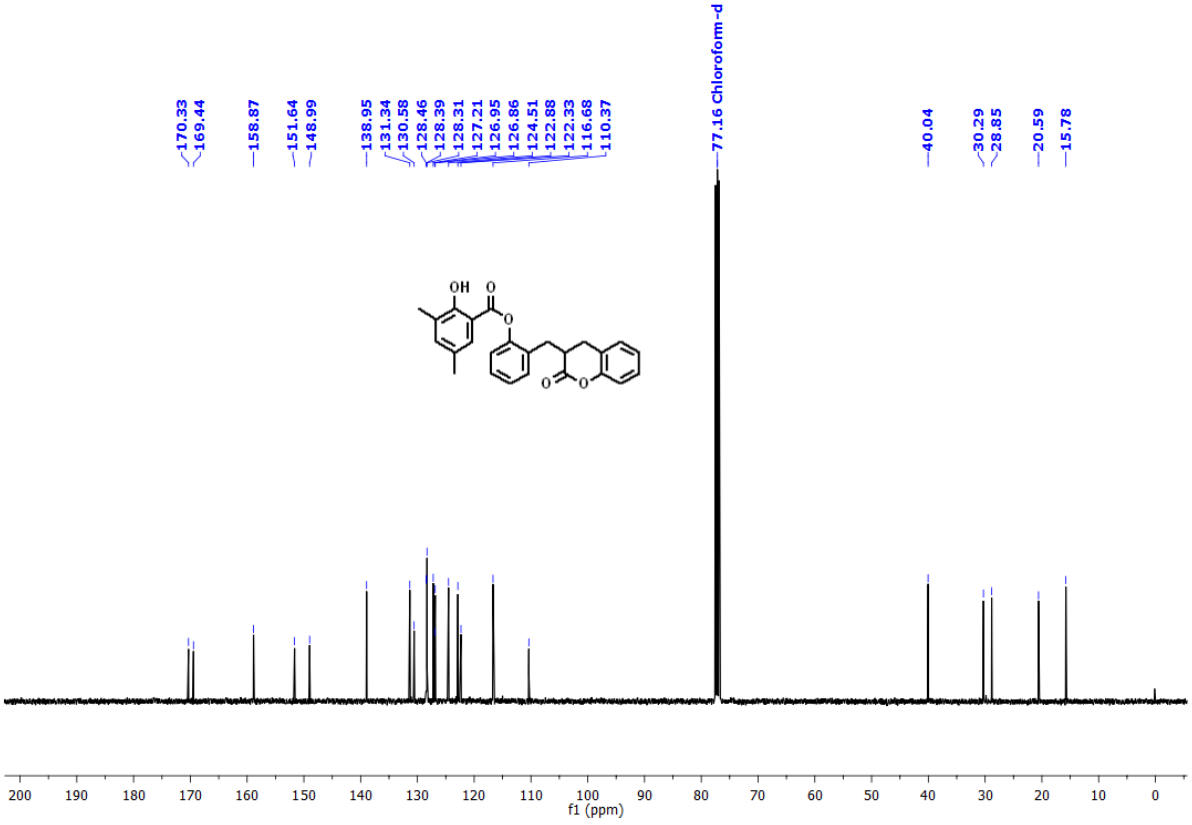


Fig. S32. ^{13}C NMR of **5c,** 100MHz, $CDCl_3$

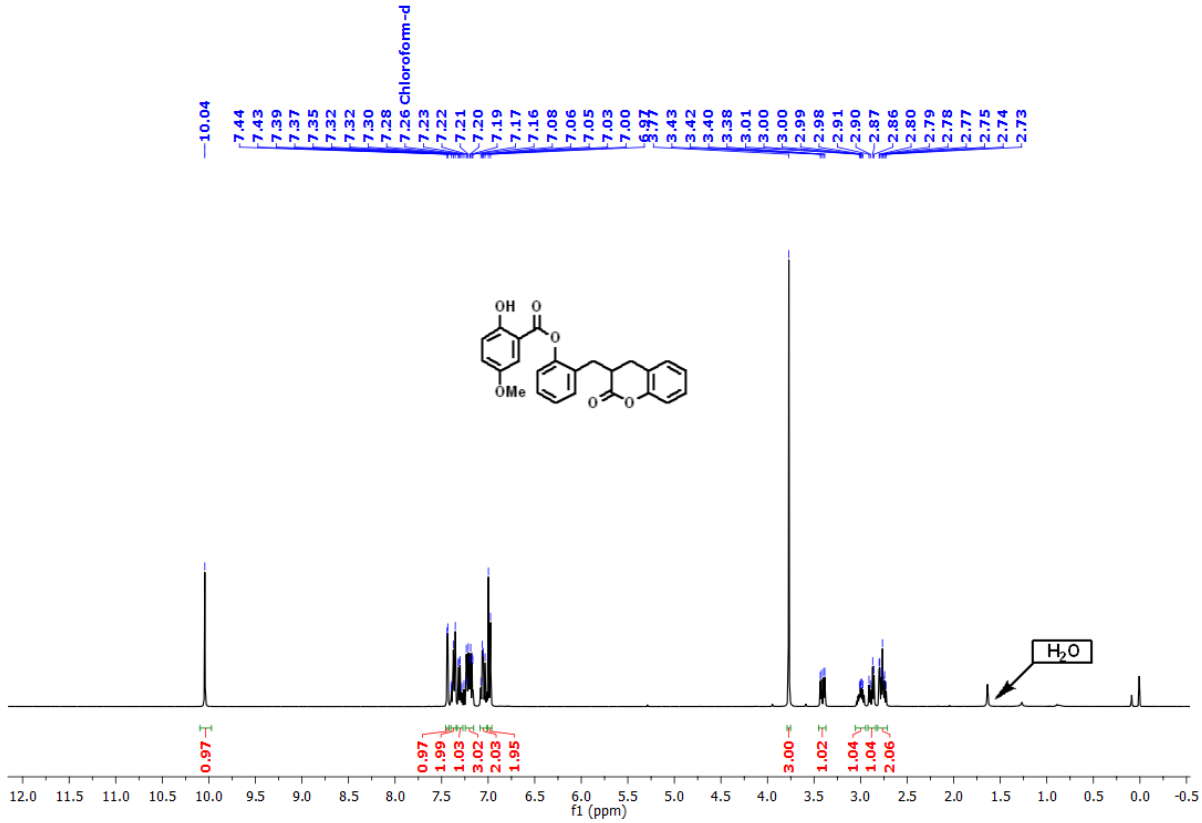


Fig. S33. ^{1}H NMR of **5d,** 400MHz, $CDCl_3$

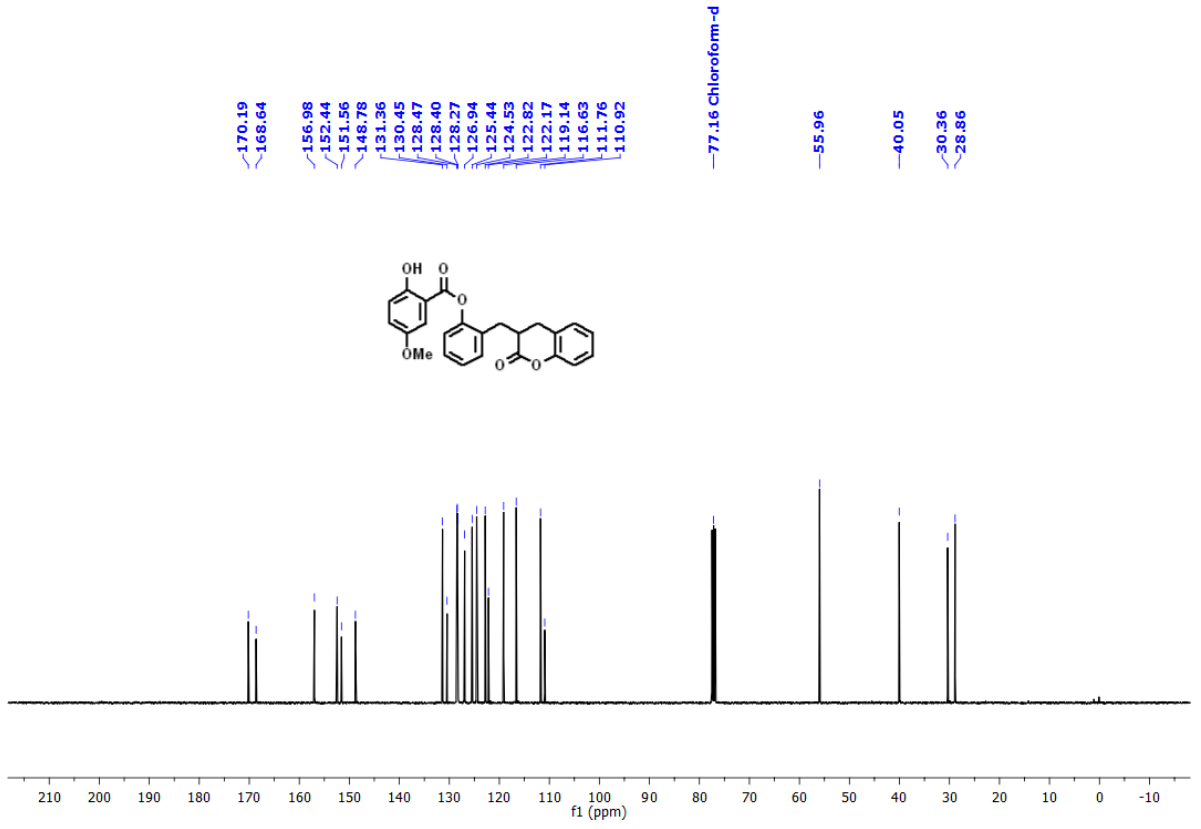


Fig. S34. ^{13}C NMR of **5d,** 100MHz, $CDCl_3$

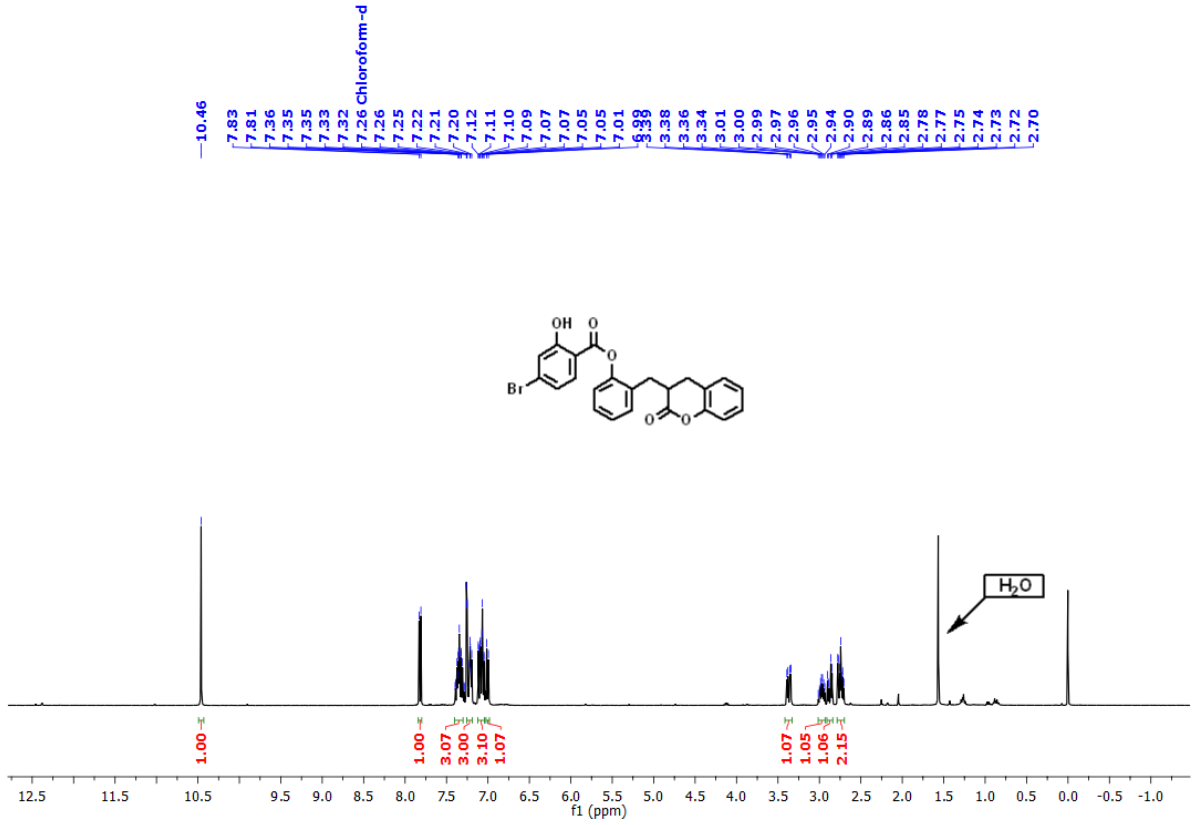


Fig. S35. ^{1}H NMR of **5e,** 400MHz, $CDCl_3$

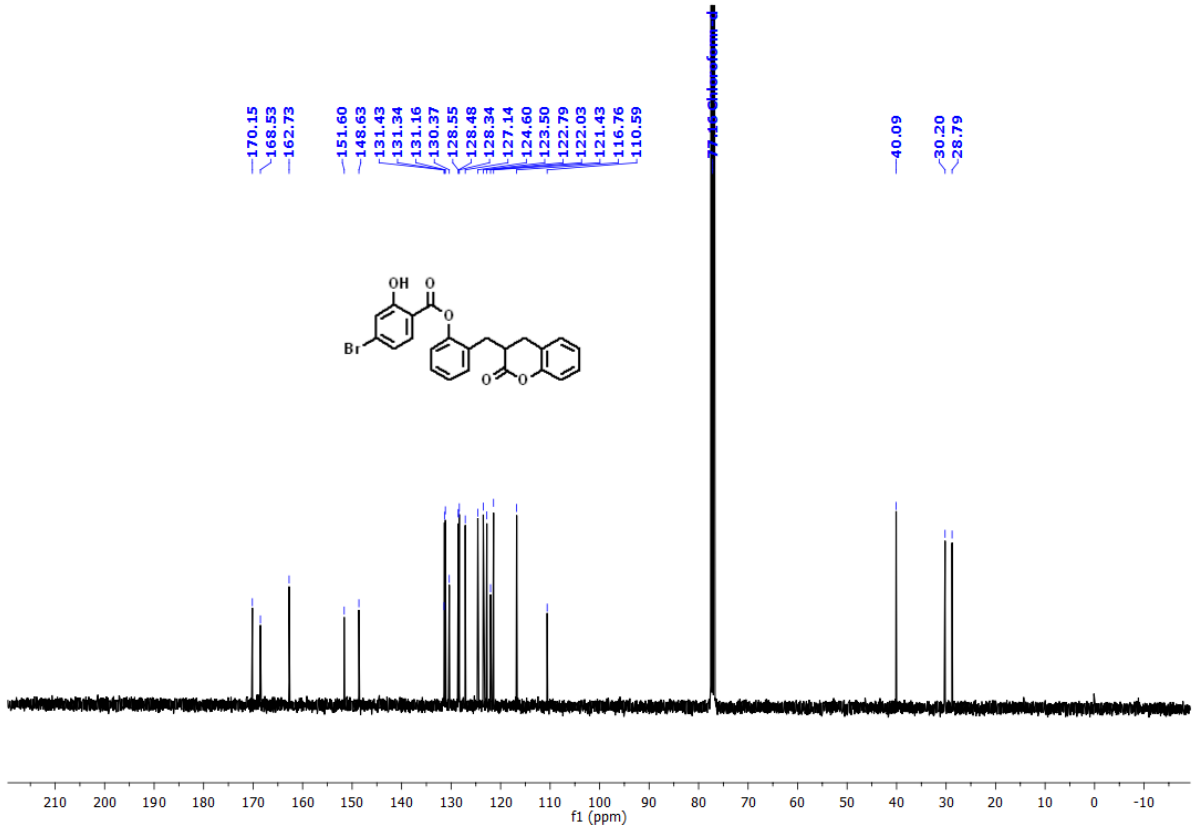


Fig. S36. ^{13}C NMR of **5e,** 100MHz, $CDCl_3$

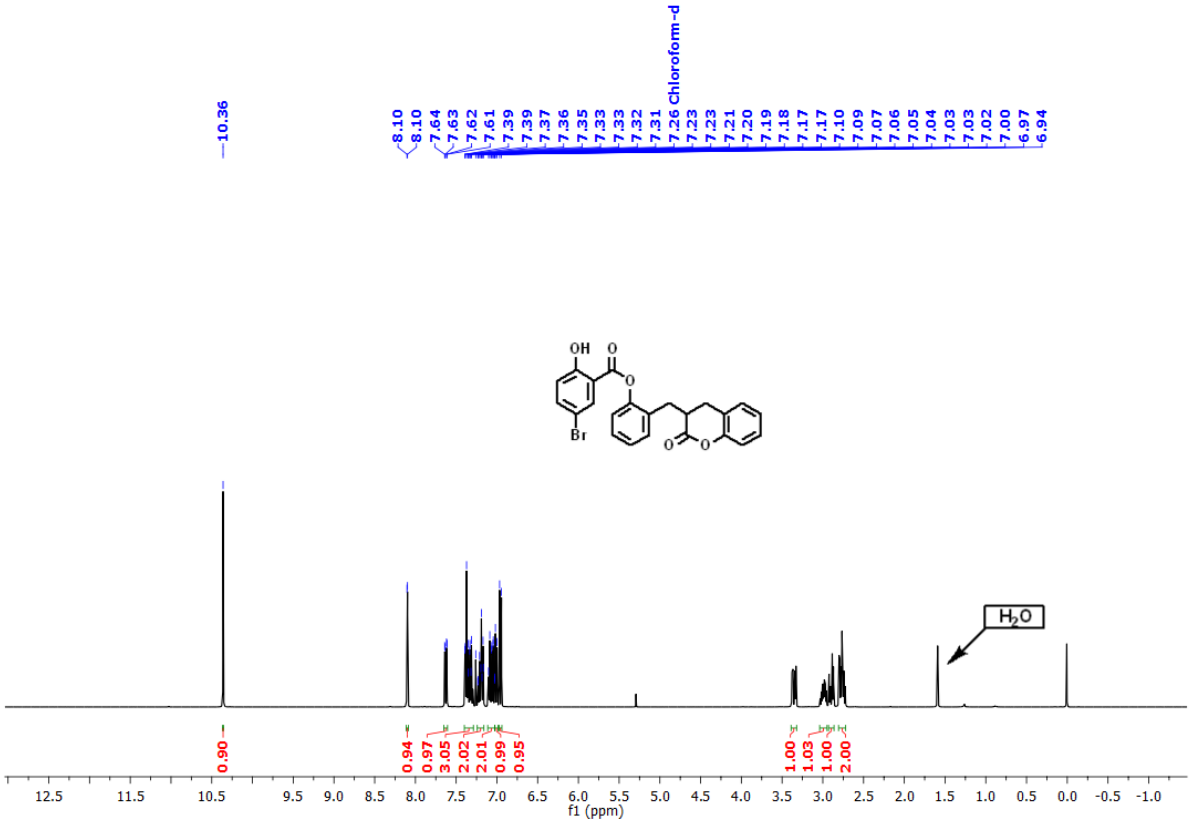


Fig. S37. ^{1}H NMR of **5f,** 400MHz, $CDCl_3$

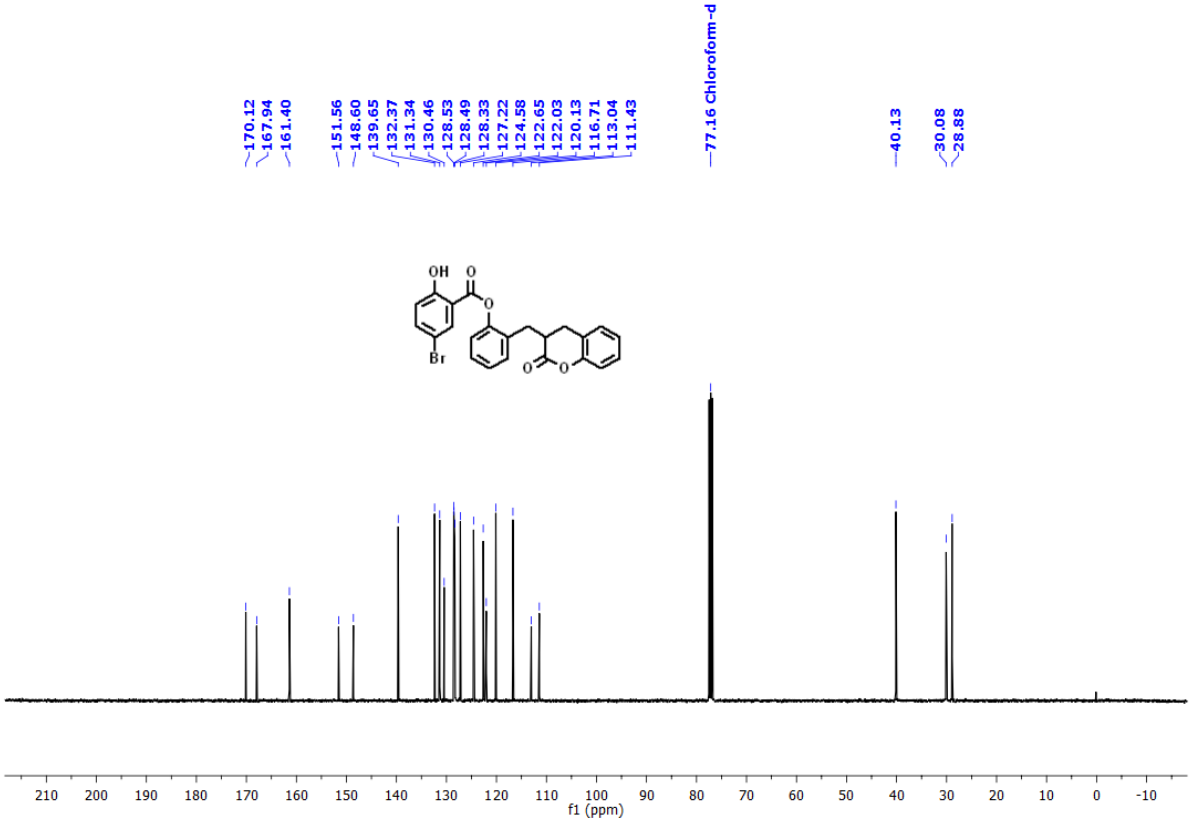


Fig. S38. ^{13}C NMR of **5f,** 100MHz, $CDCl_3$

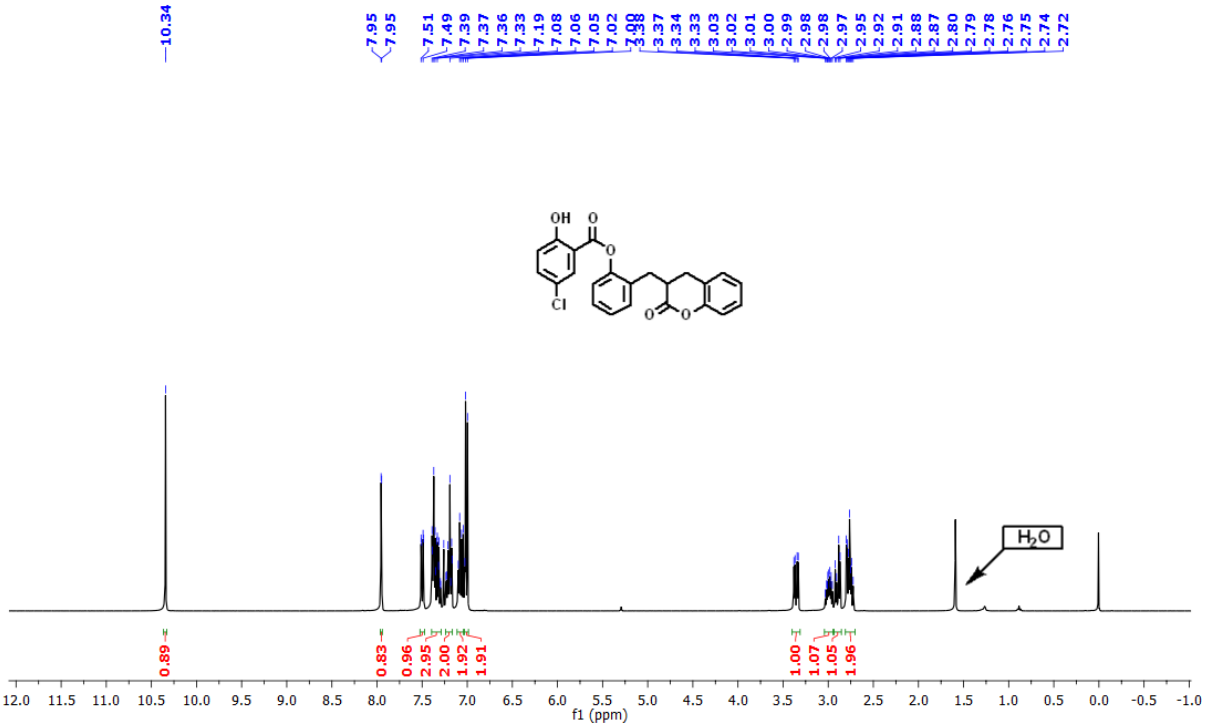


Fig. S39. ^{1}H NMR of **5g,** 400MHz, $CDCl_3$

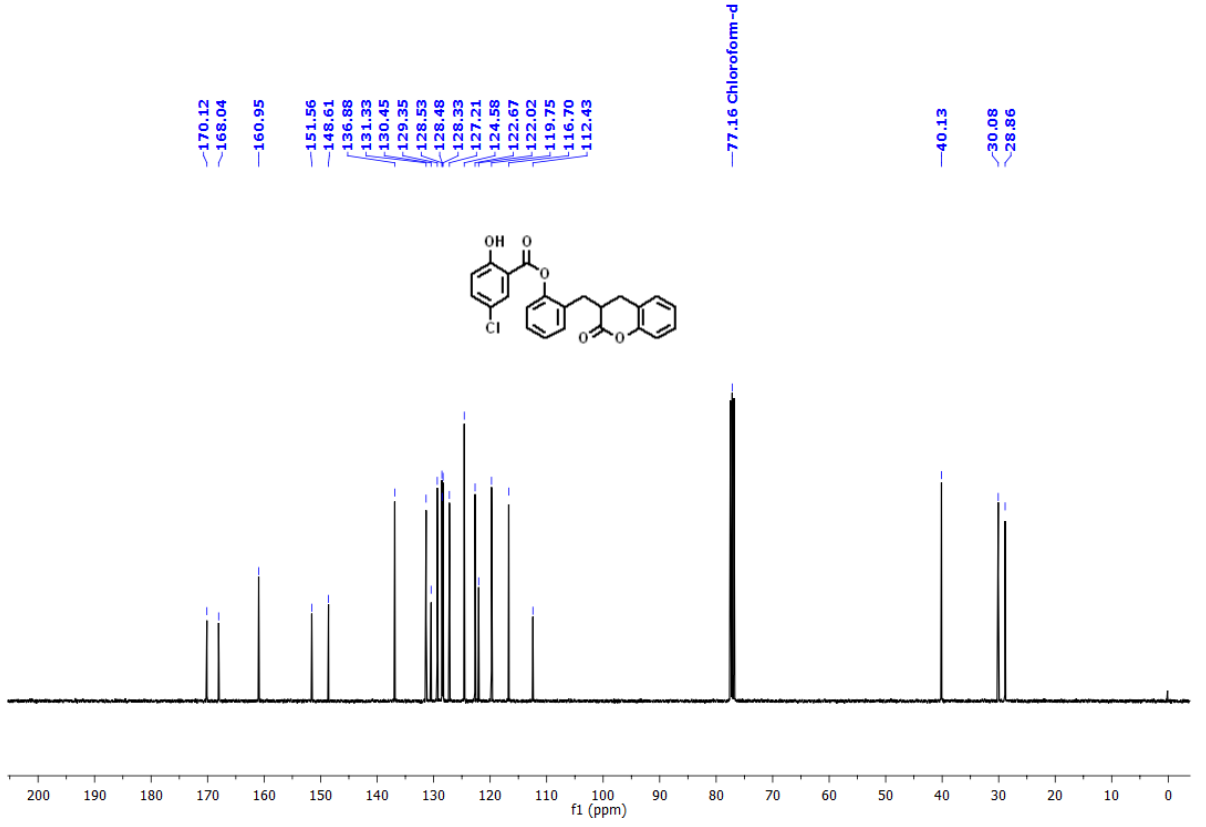


Fig. S40. ^{13}C NMR of **5g,** 100MHz, $CDCl_3$

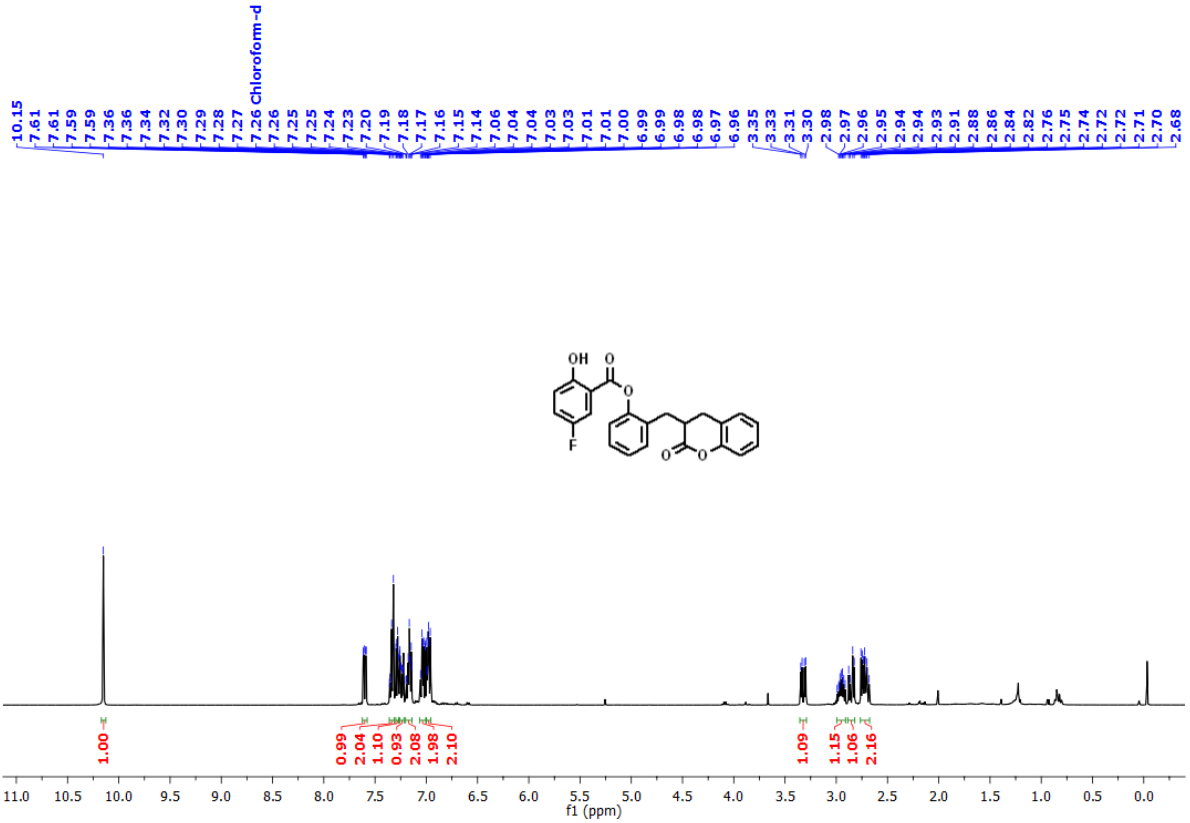


Fig. S41. ^{1}H NMR of **5h,** 400MHz, $CDCl_3$

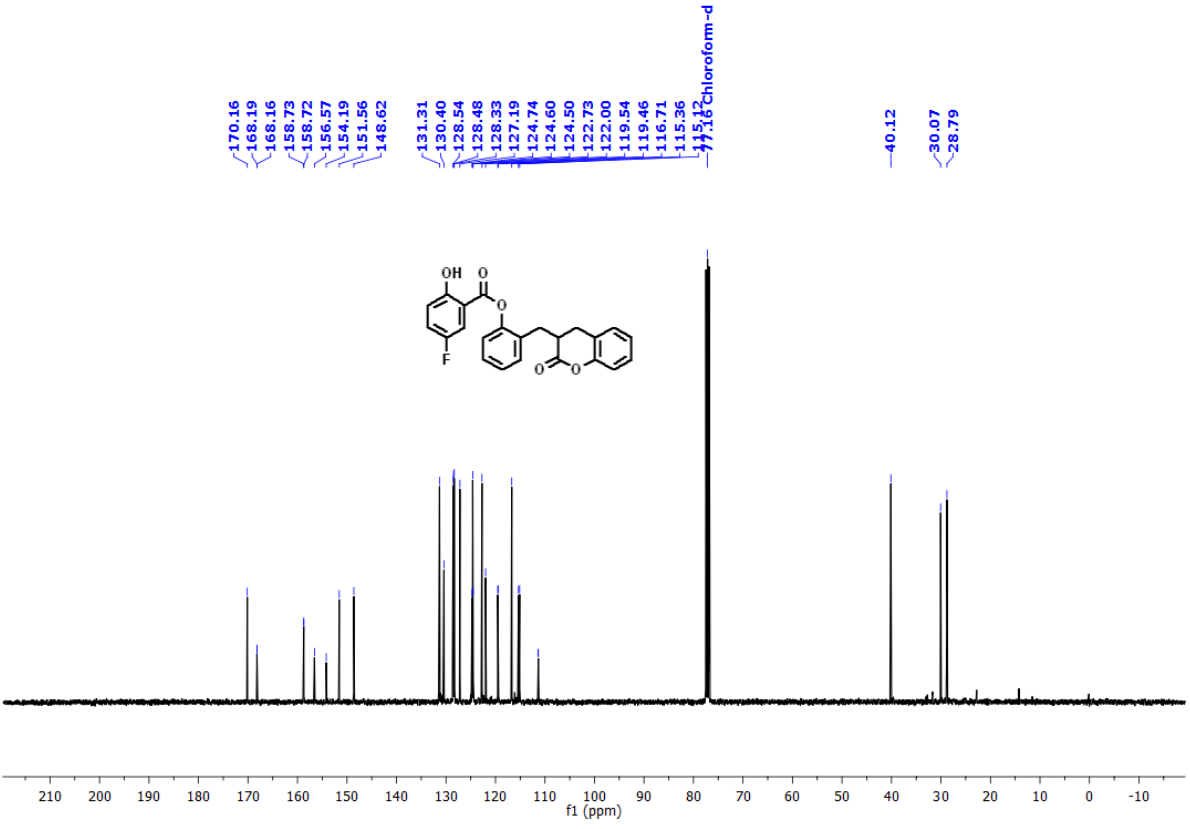


Fig. S42. ^{13}C NMR of **5h,** 100MHz, $CDCl_3$

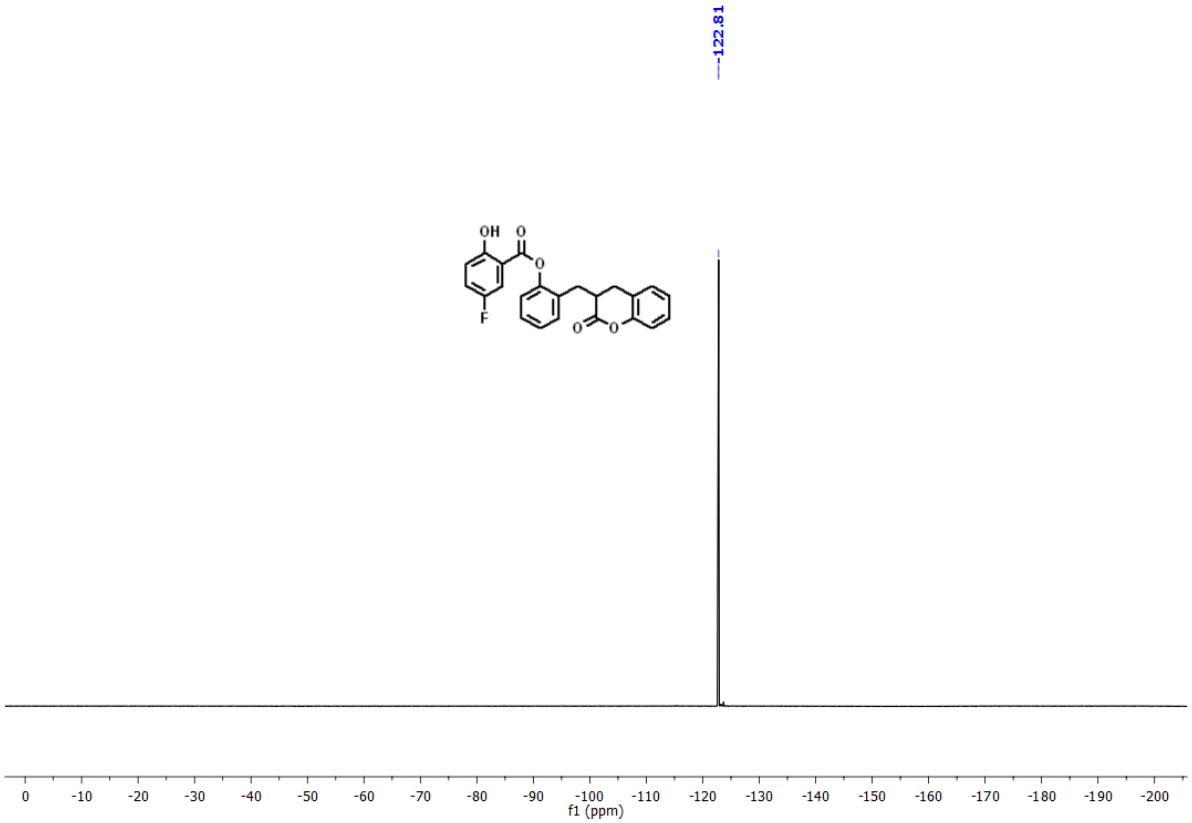


Fig. S43. ^{19}F NMR of **5h,** 377MHz, $CDCl_3$

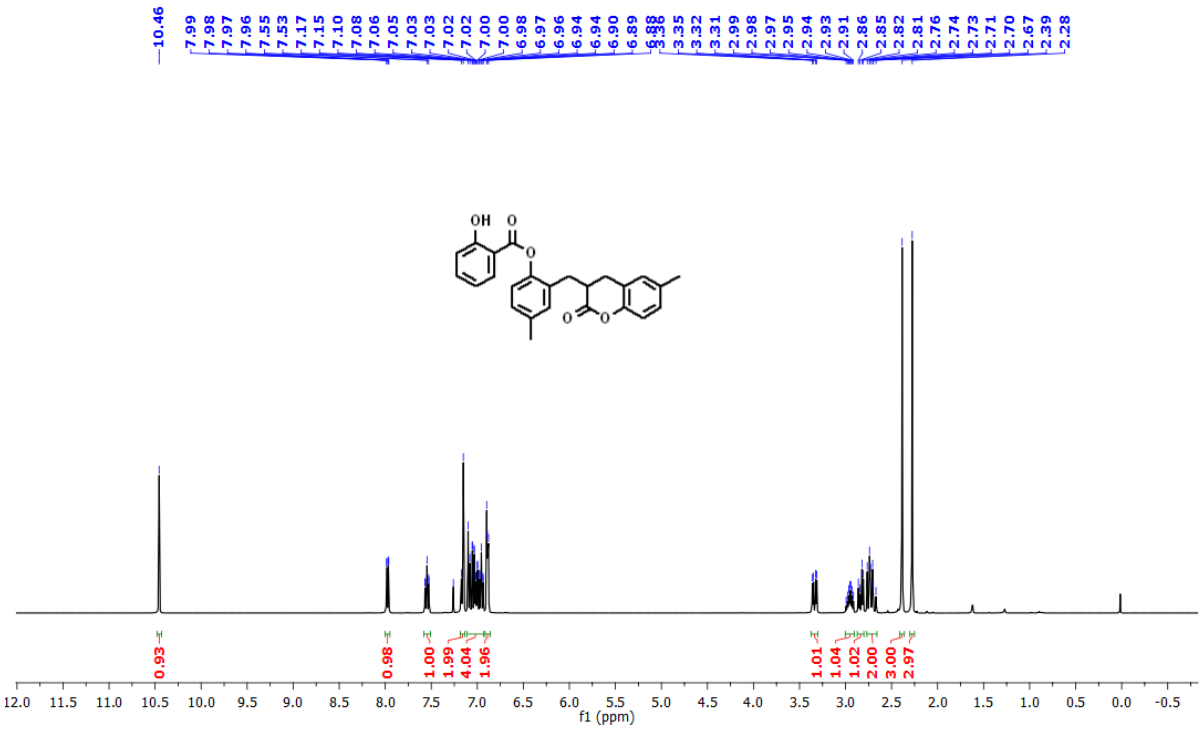


Fig. S44. ^{1}H NMR of **5i,** 400MHz, $CDCl_3$

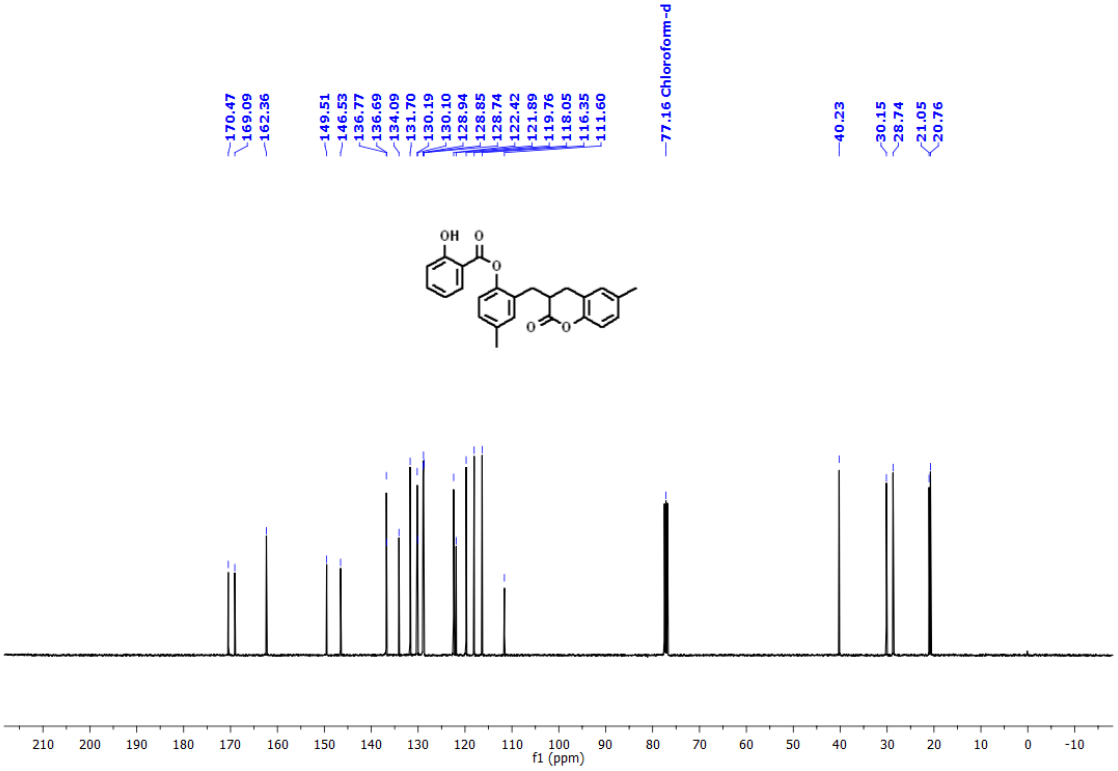


Fig. S45. ^{13}C NMR of **5i,** 100MHz, $CDCl_3$

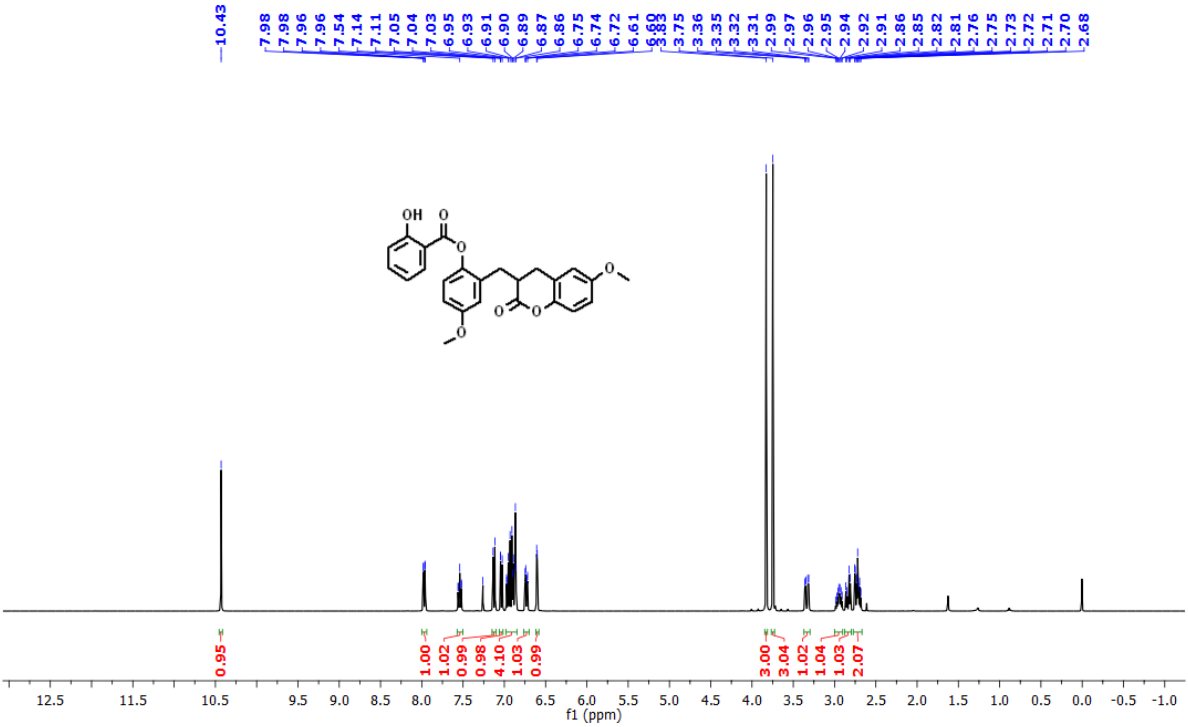


Fig. S46. ^{1}H NMR of **5j,** 400MHz, $CDCl_3$

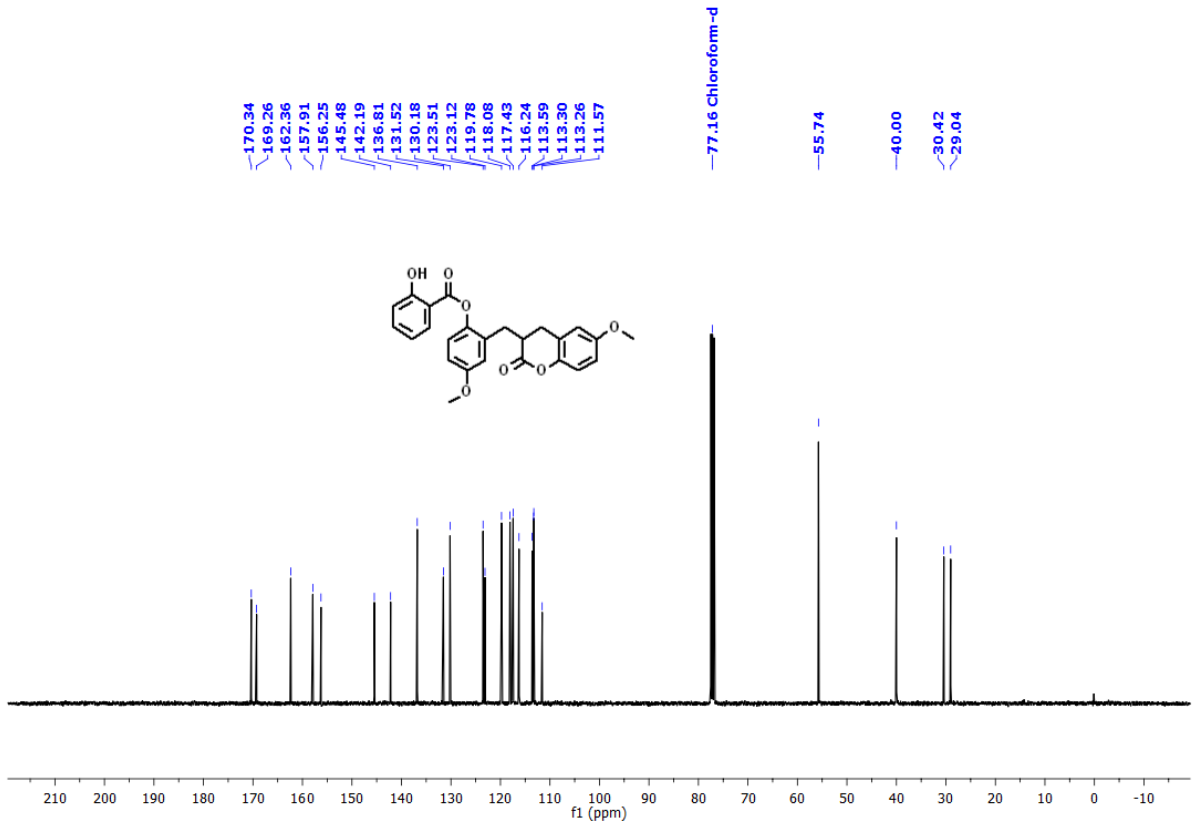


Fig. S47. ^{13}C NMR of **5j,** 100MHz, $CDCl_3$

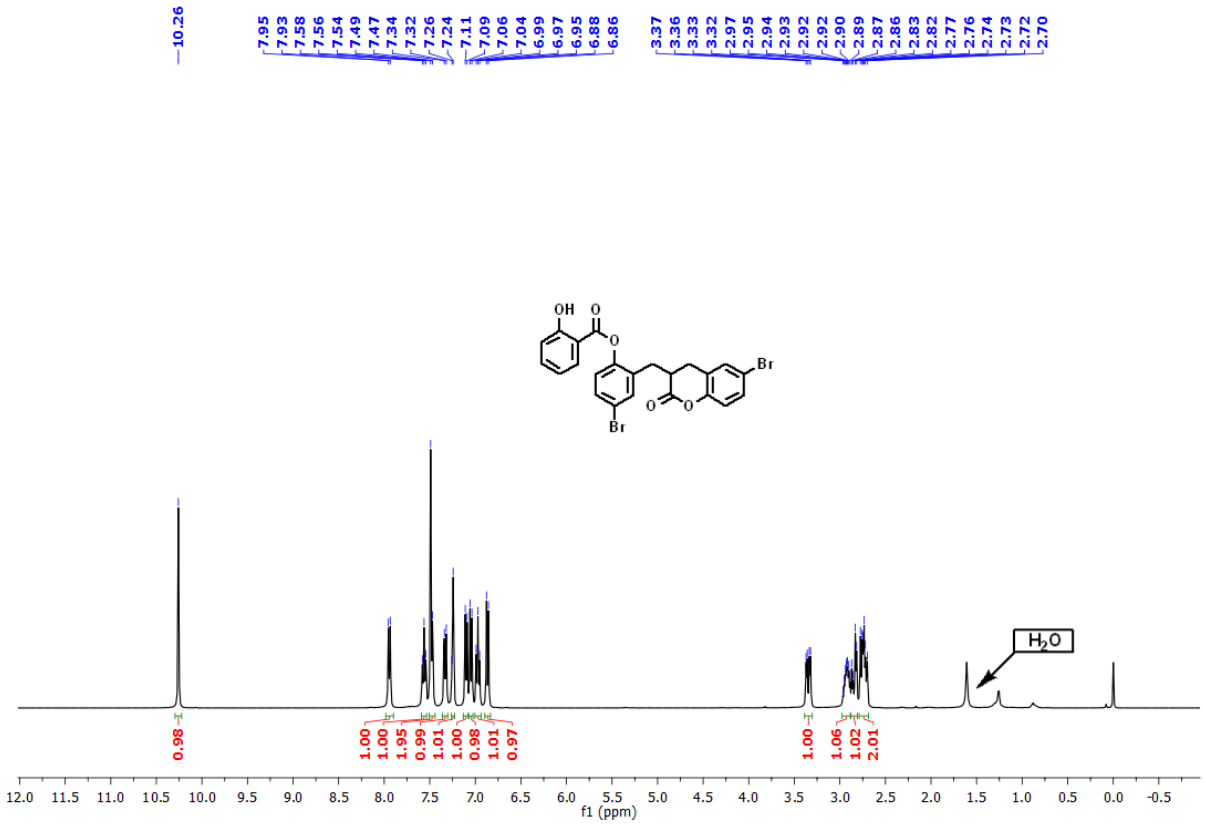


Fig. S48. ^{1}H NMR of **5k,** 400MHz, $CDCl_3$

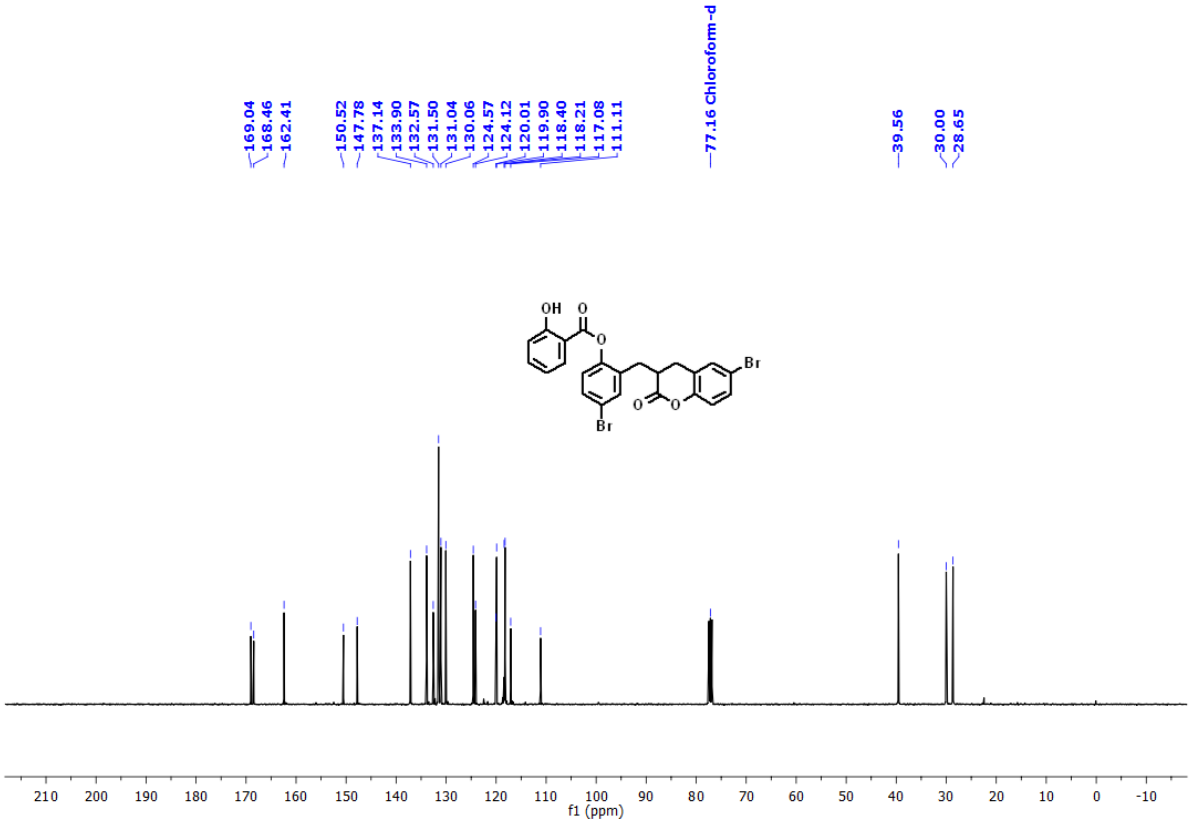


Fig. S49. ^{13}C NMR of **5k,** 100MHz, $CDCl_3$

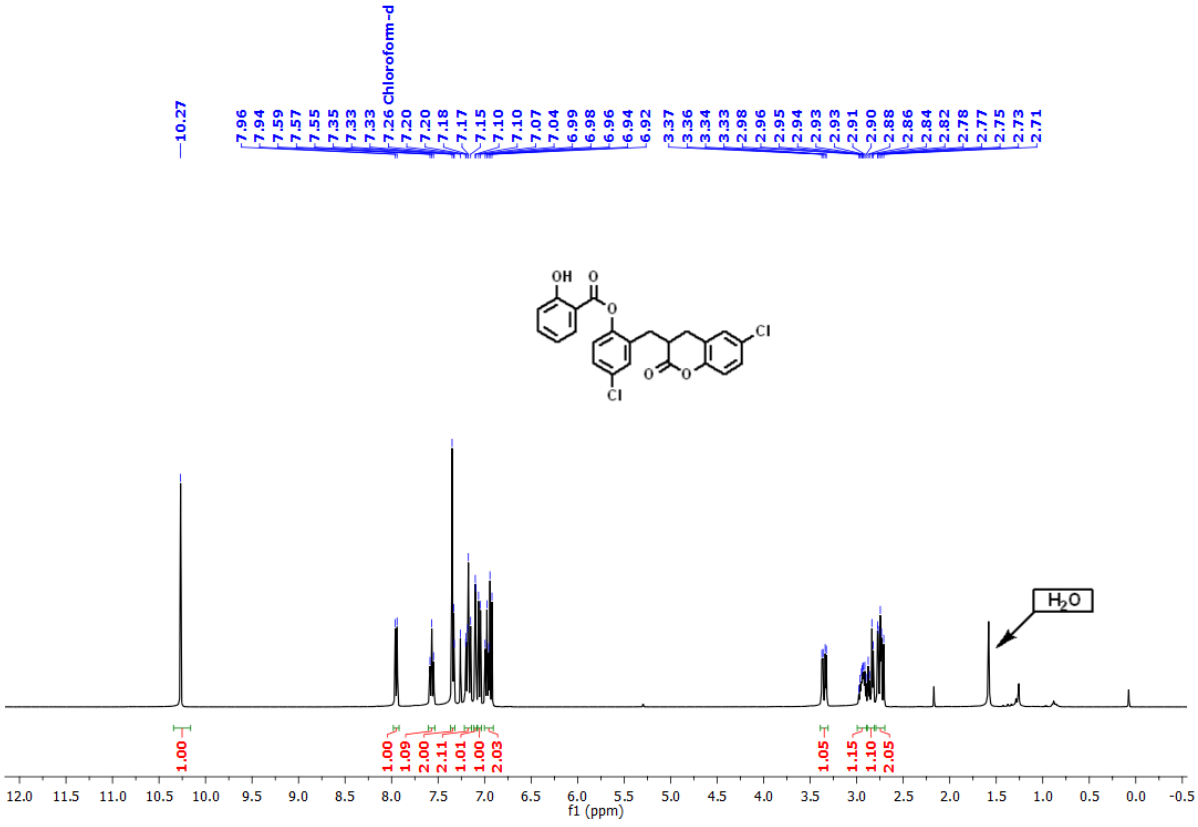


Fig. S50. ^{1}H NMR of **5l,** 400MHz, $CDCl_3$

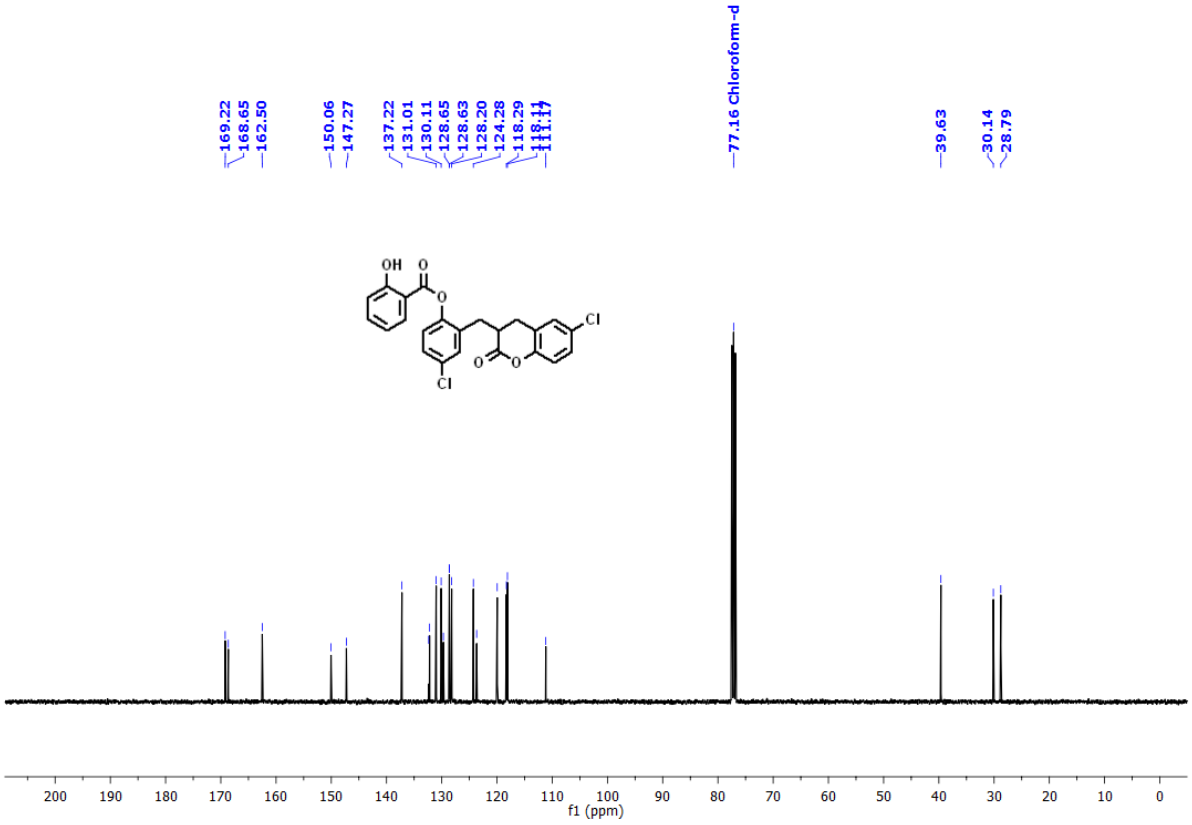


Fig. S51. ^{13}C NMR of **5l,** 100MHz, $CDCl_3$

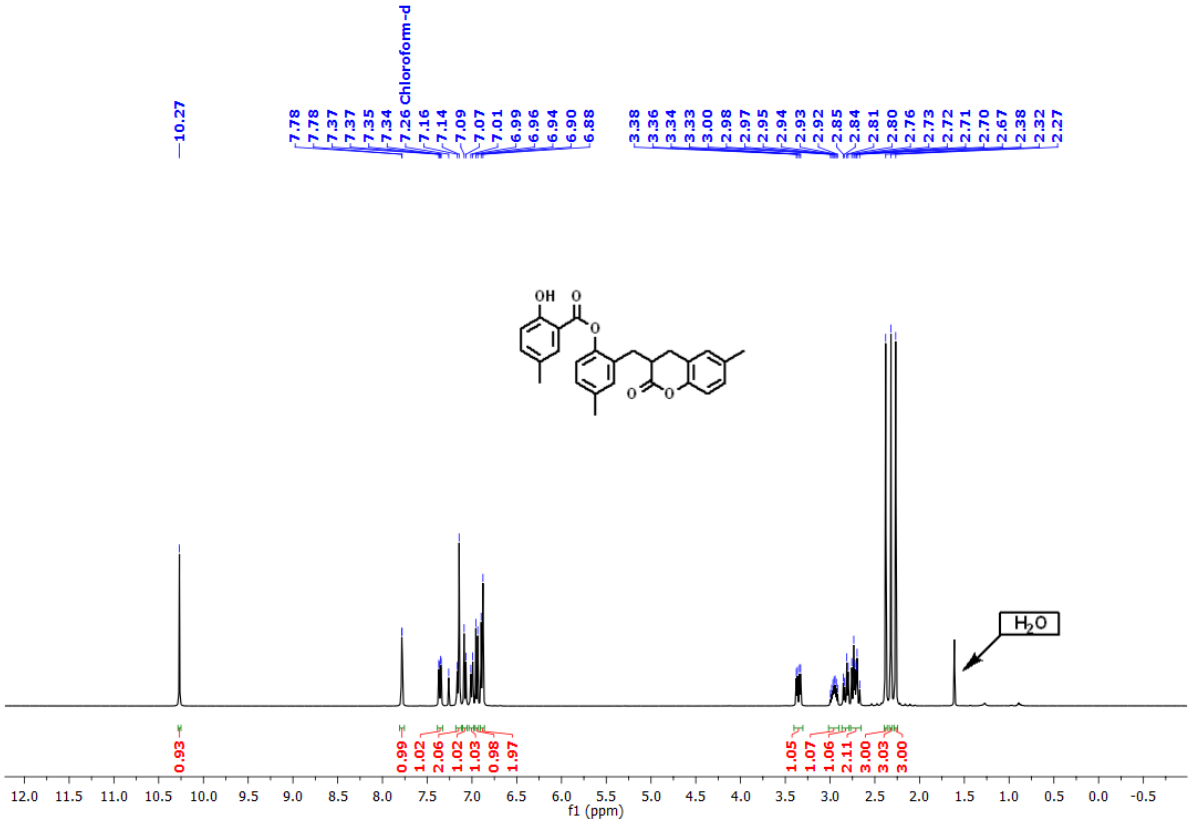


Fig. S52. ^{1}H NMR of **5m,** 400MHz, $CDCl_3$

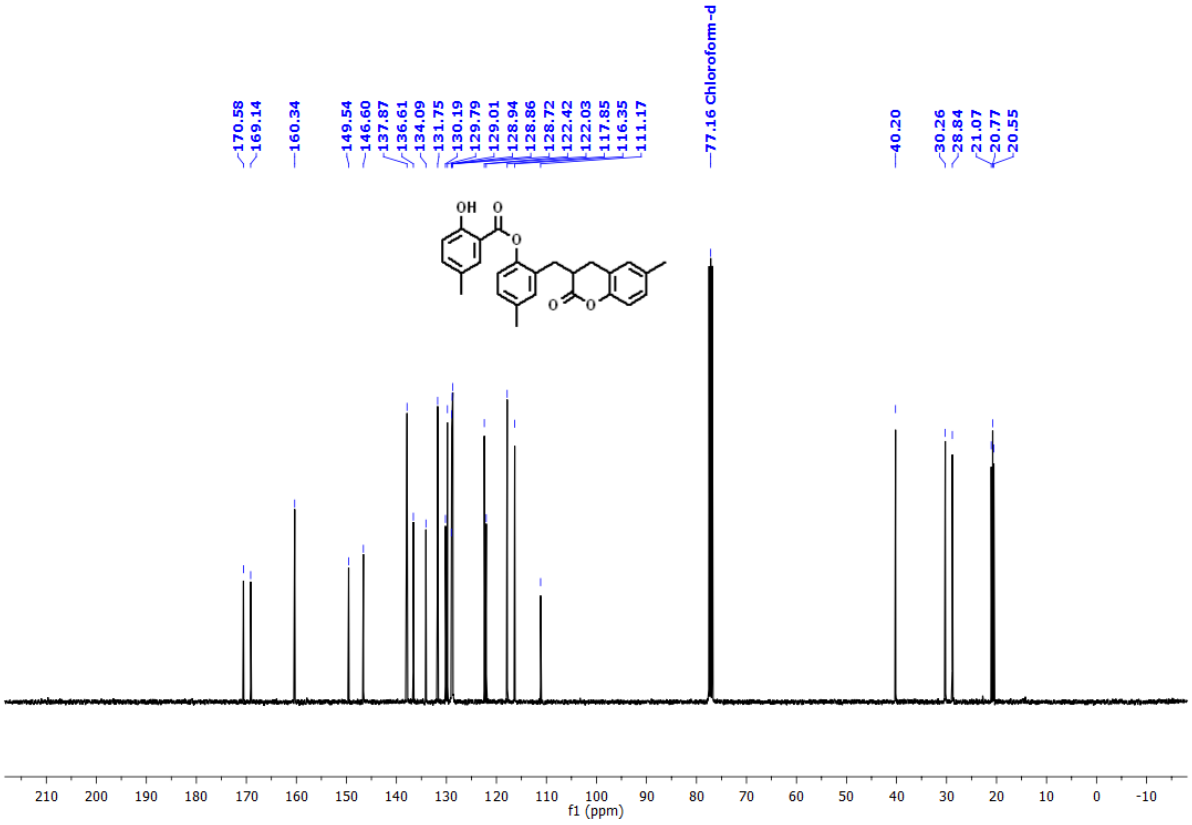


Fig. S53. ^{13}C NMR of **5m,** 100MHz, $CDCl_3$

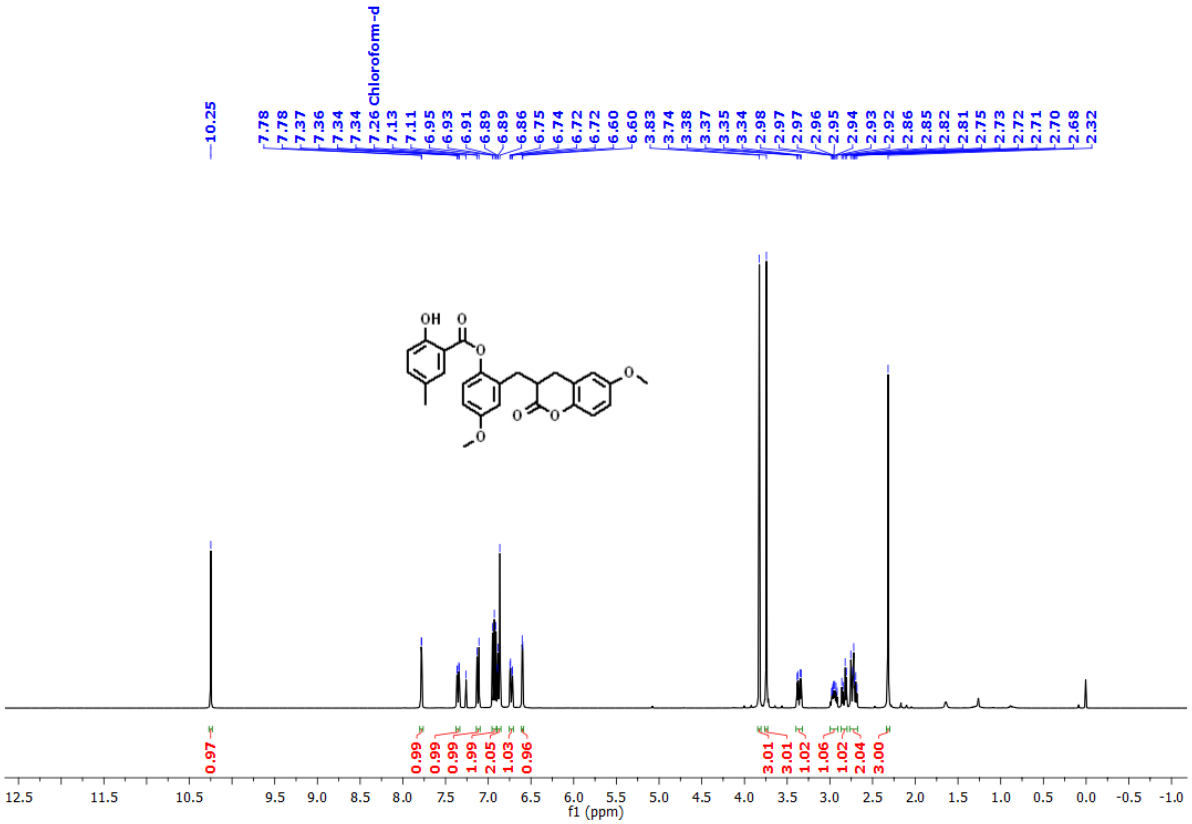


Fig. S54. ^{1}H NMR of **5n,** 400MHz, $CDCl_3$

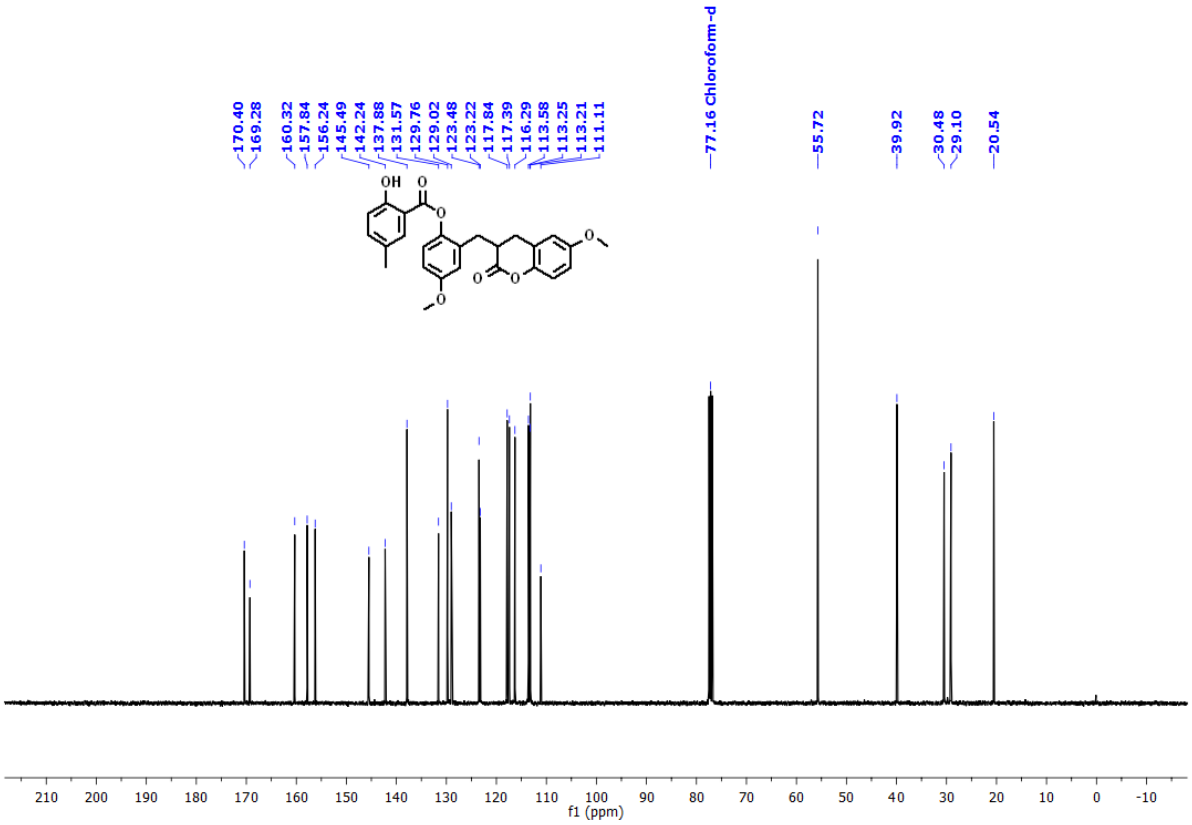


Fig. S55. ^{13}C NMR of **5n,** 100MHz, $CDCl_3$

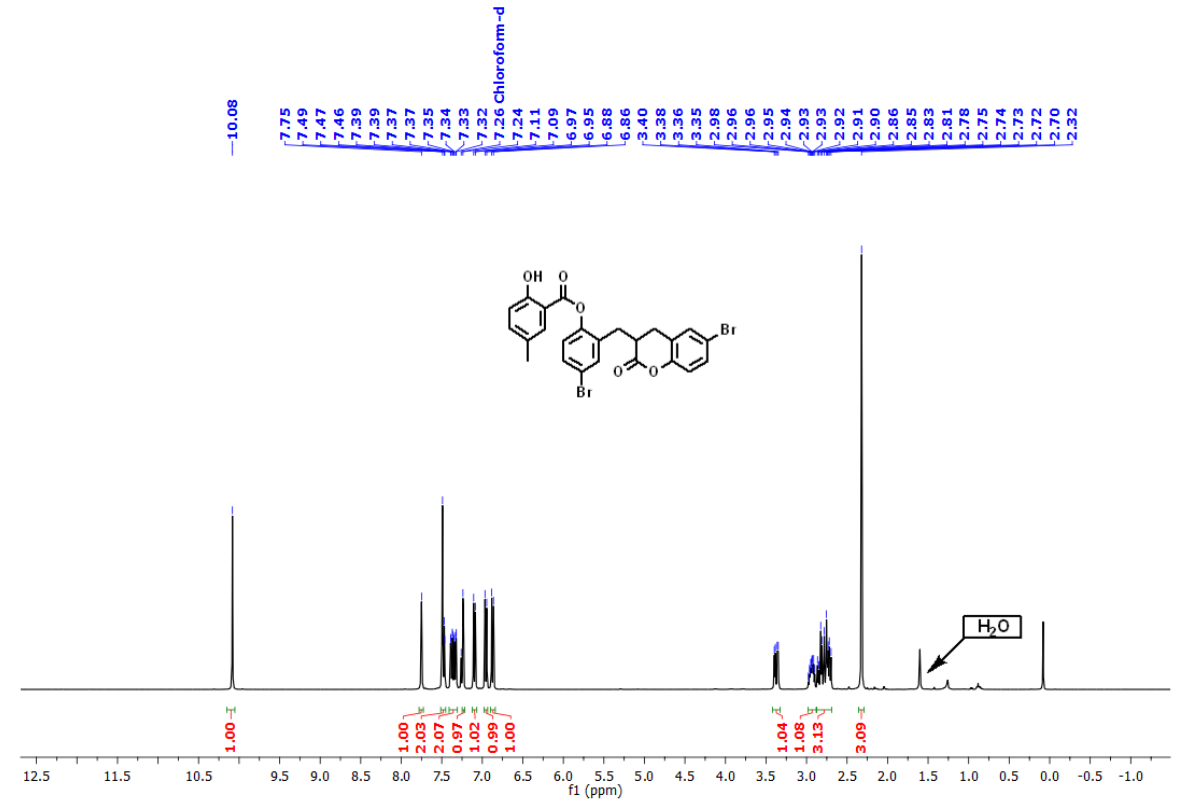


Fig. S56. ^{1}H NMR of **5o,** 400MHz, $CDCl_3$

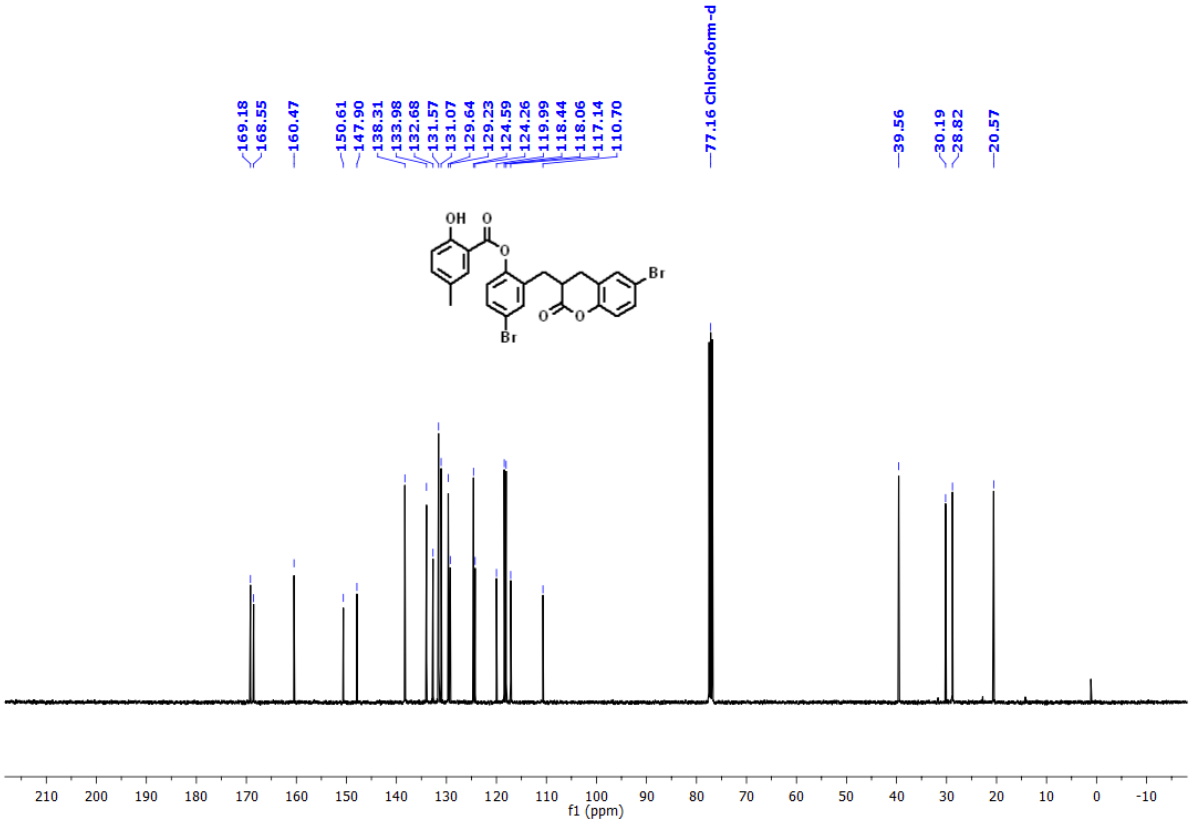


Fig. S57. ^{13}C NMR of **5o,** 100MHz, $CDCl_3$

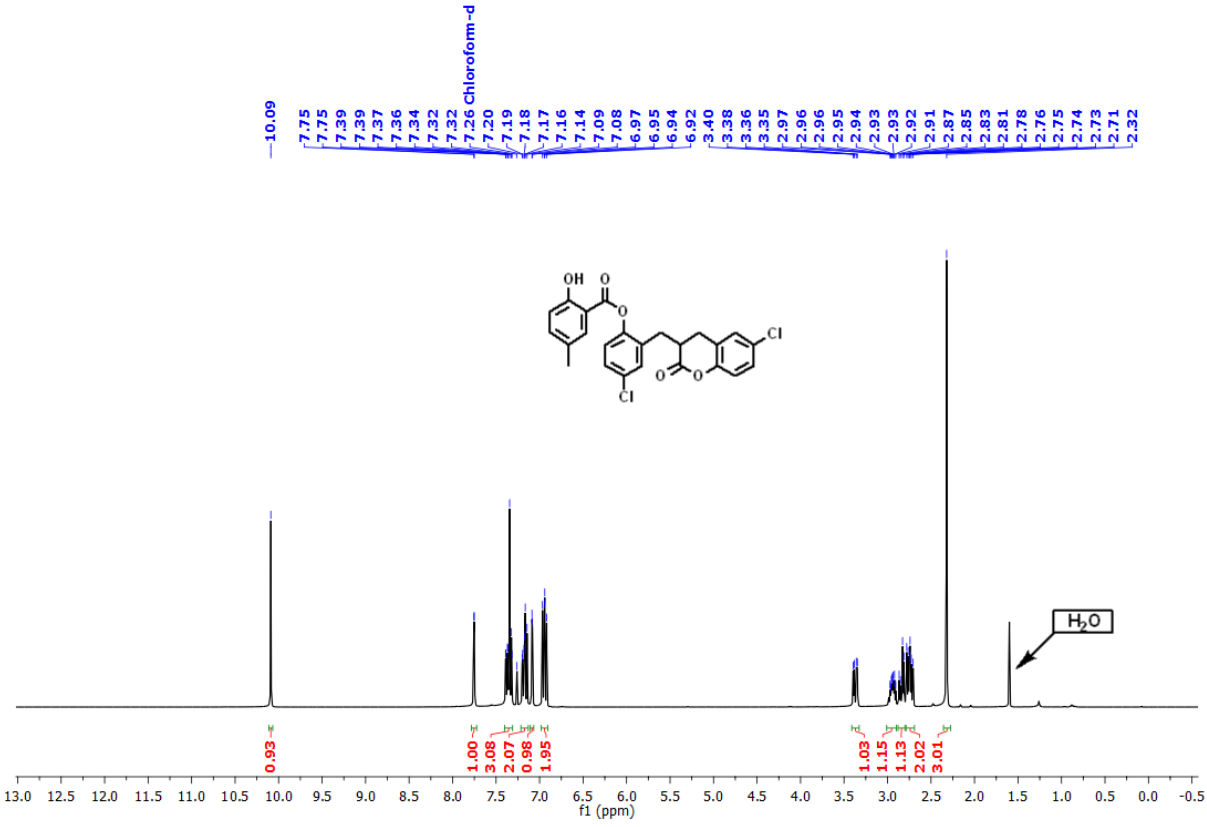


Fig. S58. ^{1}H NMR of **5p,** 400MHz, $CDCl_3$

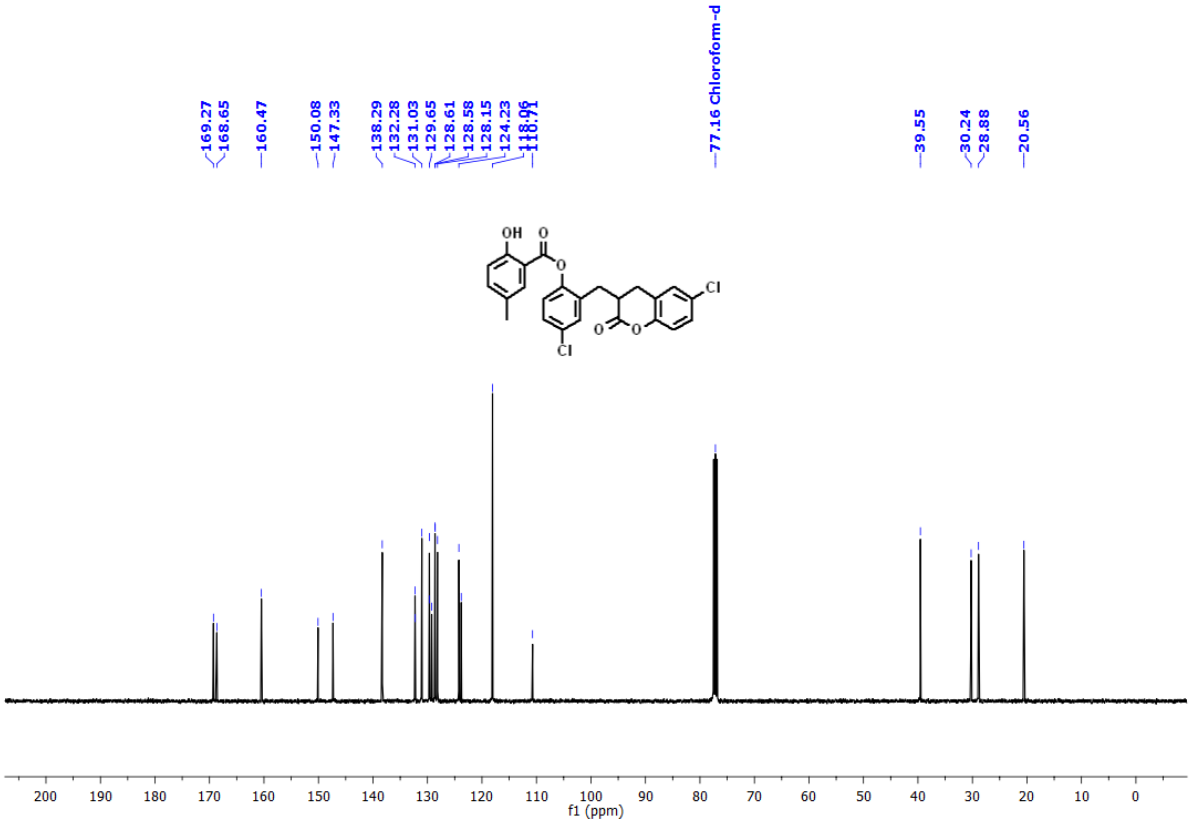


Fig. S59. ^{13}C NMR of **5p,** 100MHz, $CDCl_3$

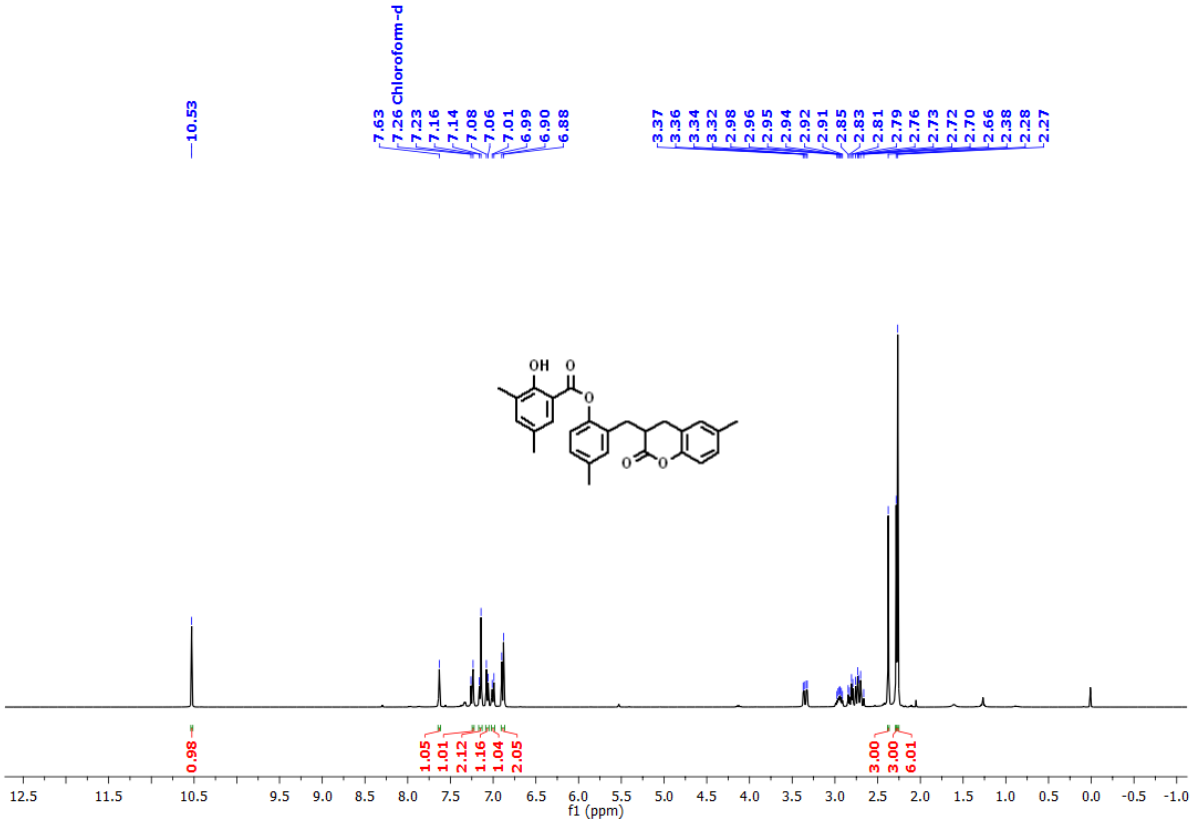


Fig. S60. ^{1}H NMR of **5q,** 400MHz, $CDCl_3$

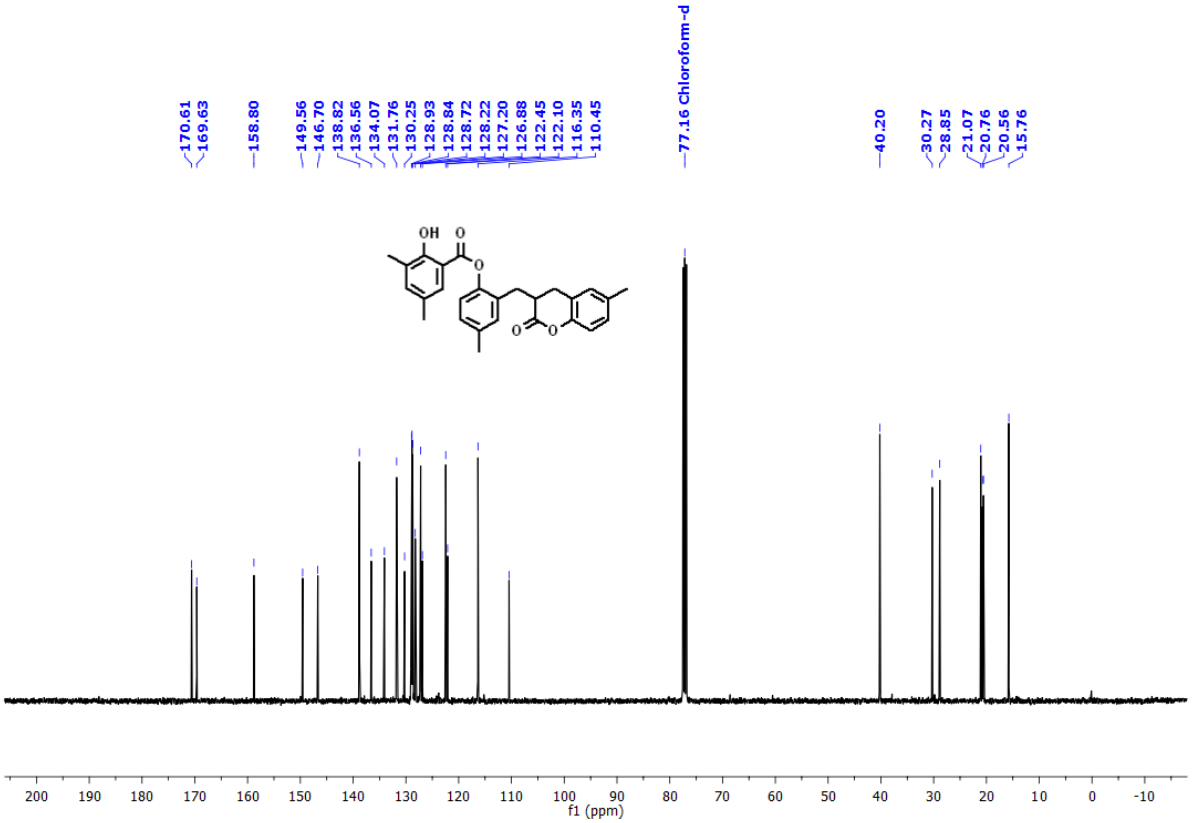


Fig. S61. ^{13}C NMR of **5q,** 100MHz, $CDCl_3$

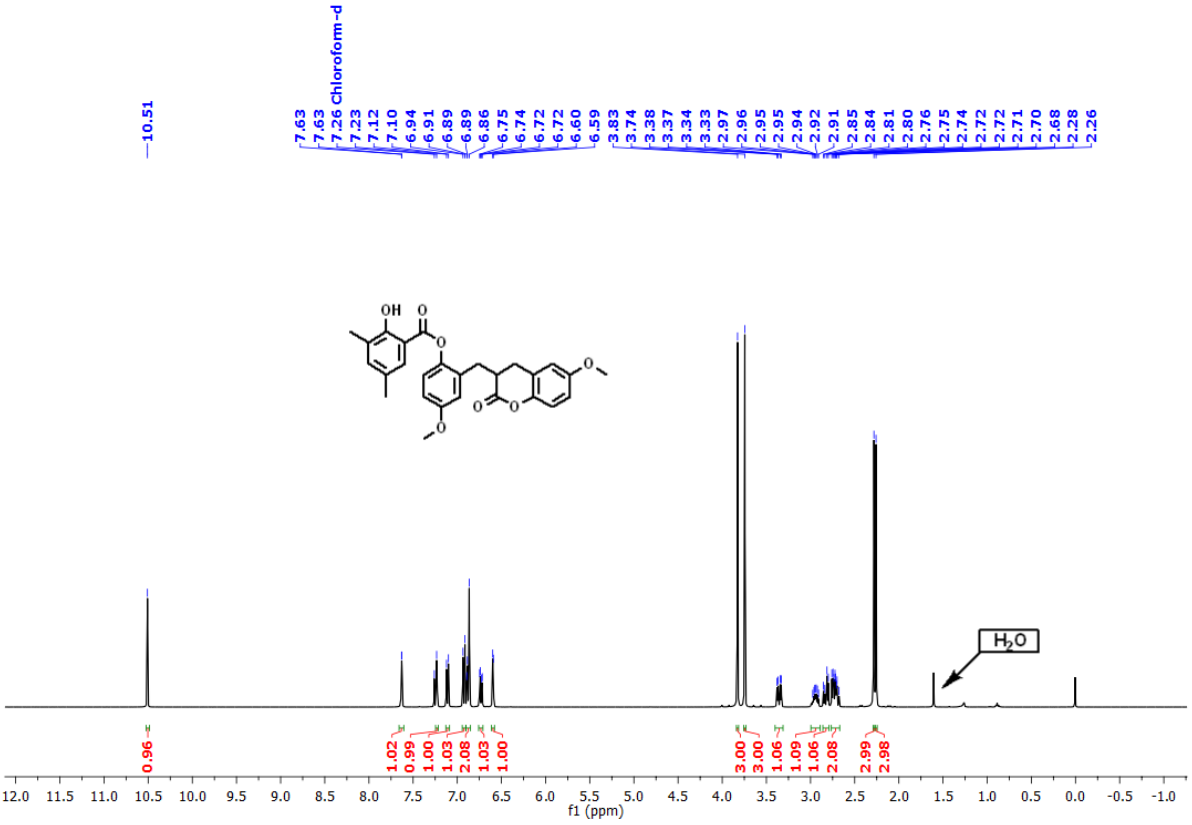


Fig. S62. ^{1}H NMR of **5r,** 400MHz, $CDCl_3$

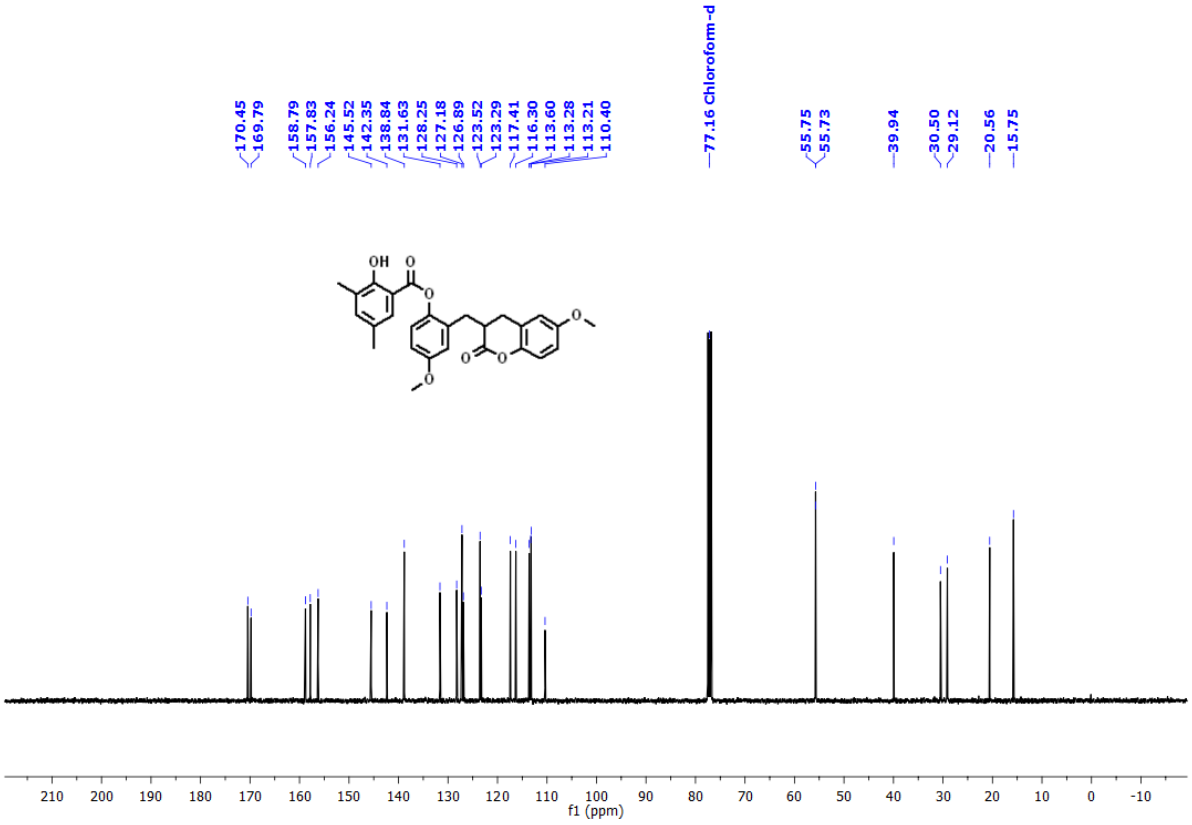


Fig. S63. ^{13}C NMR of **5r,** 100MHz, $CDCl_3$

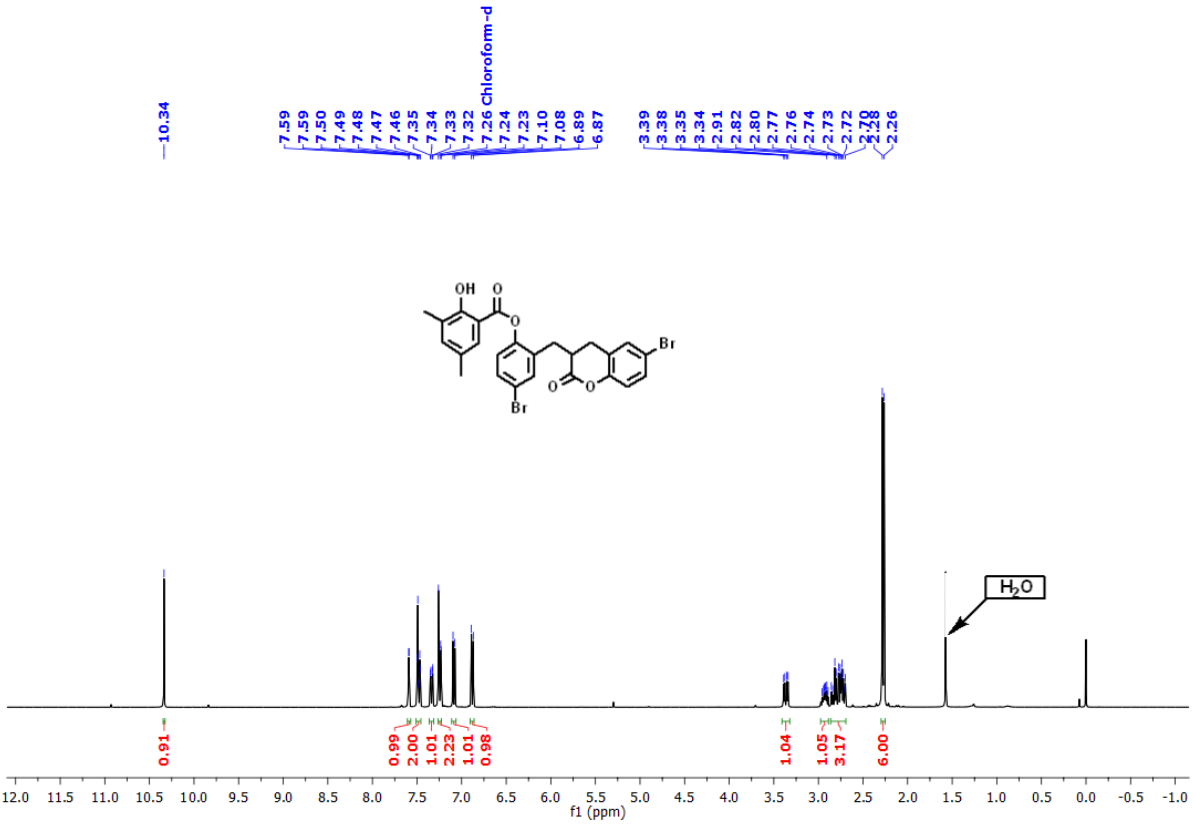


Fig. S64. ^{1}H NMR of **5s,** 400MHz, $CDCl_3$

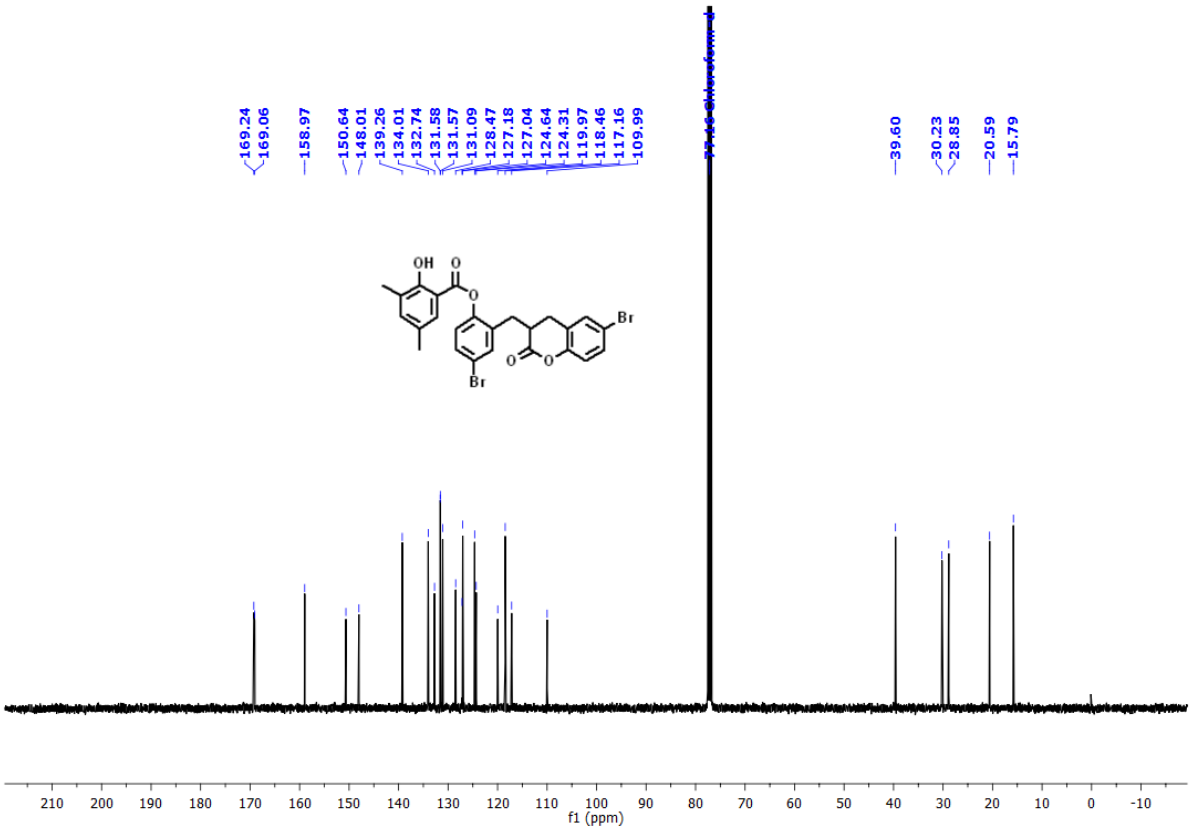


Fig. S65. ^{13}C NMR of **5s,** 100MHz, $CDCl_3$

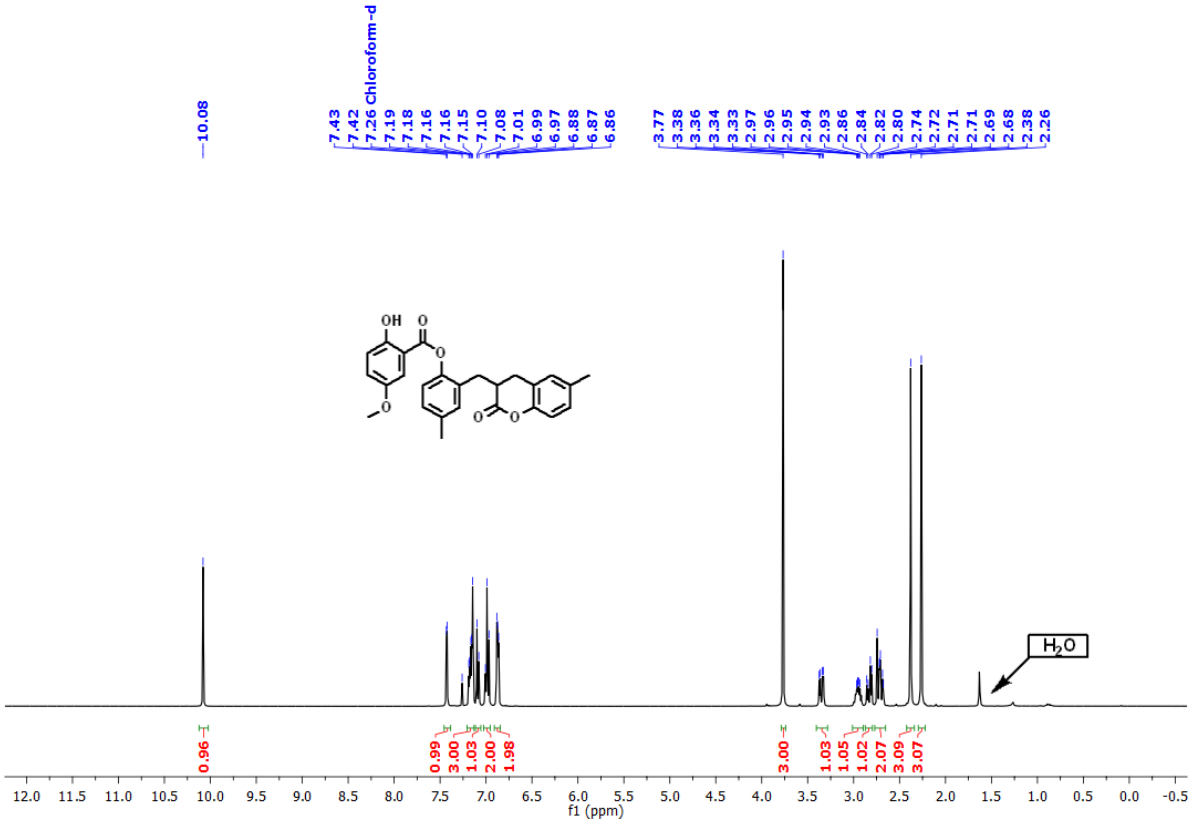


Fig. S66. ^{1}H NMR of **5t,** 400MHz, $CDCl_3$

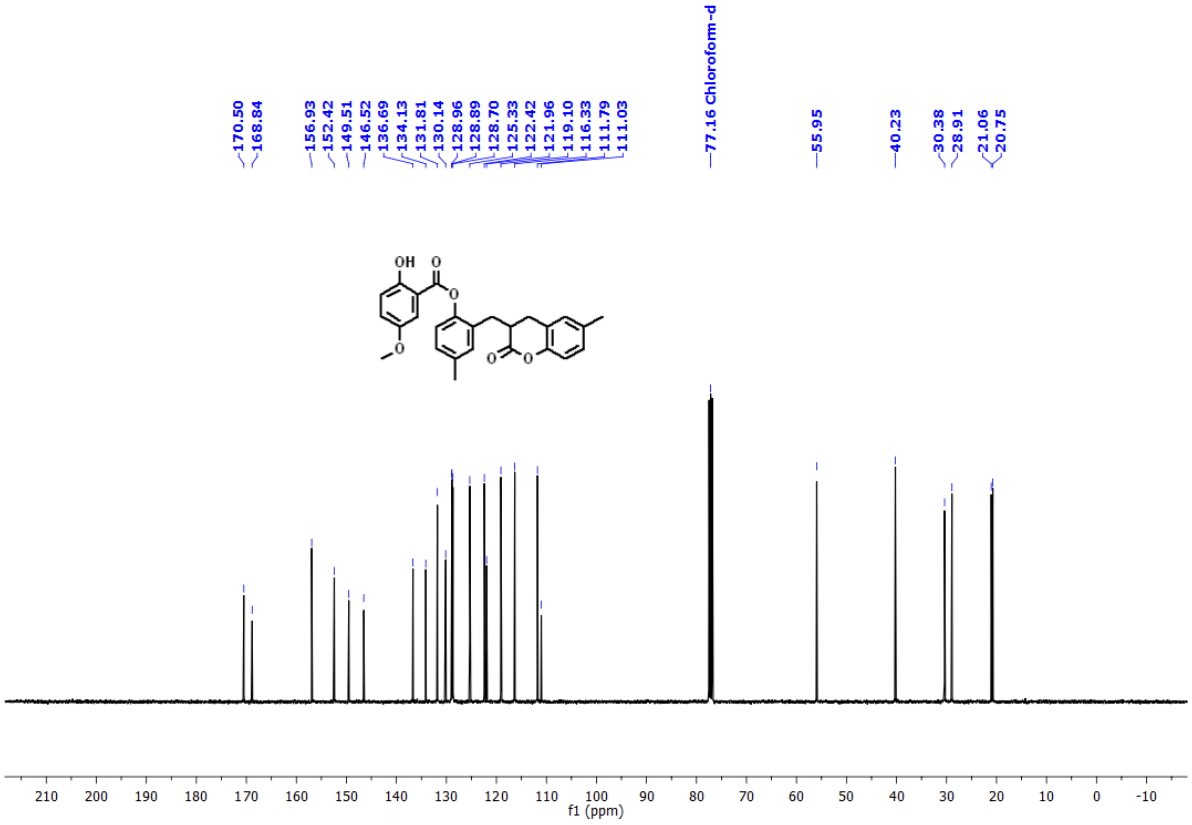


Fig. S67. ^{13}C NMR of **5t,** 100MHz, $CDCl_3$

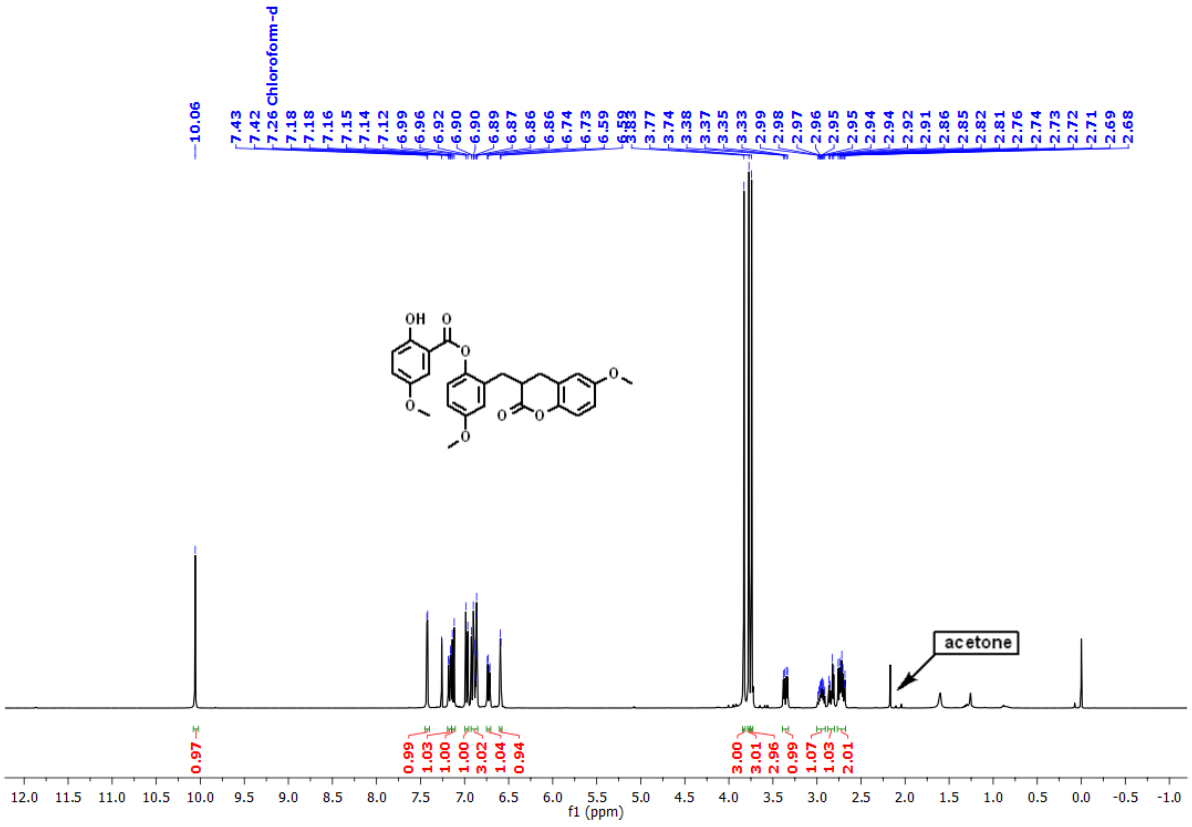


Fig. S68. ^{1}H NMR of **5u,** 400MHz, $CDCl_3$

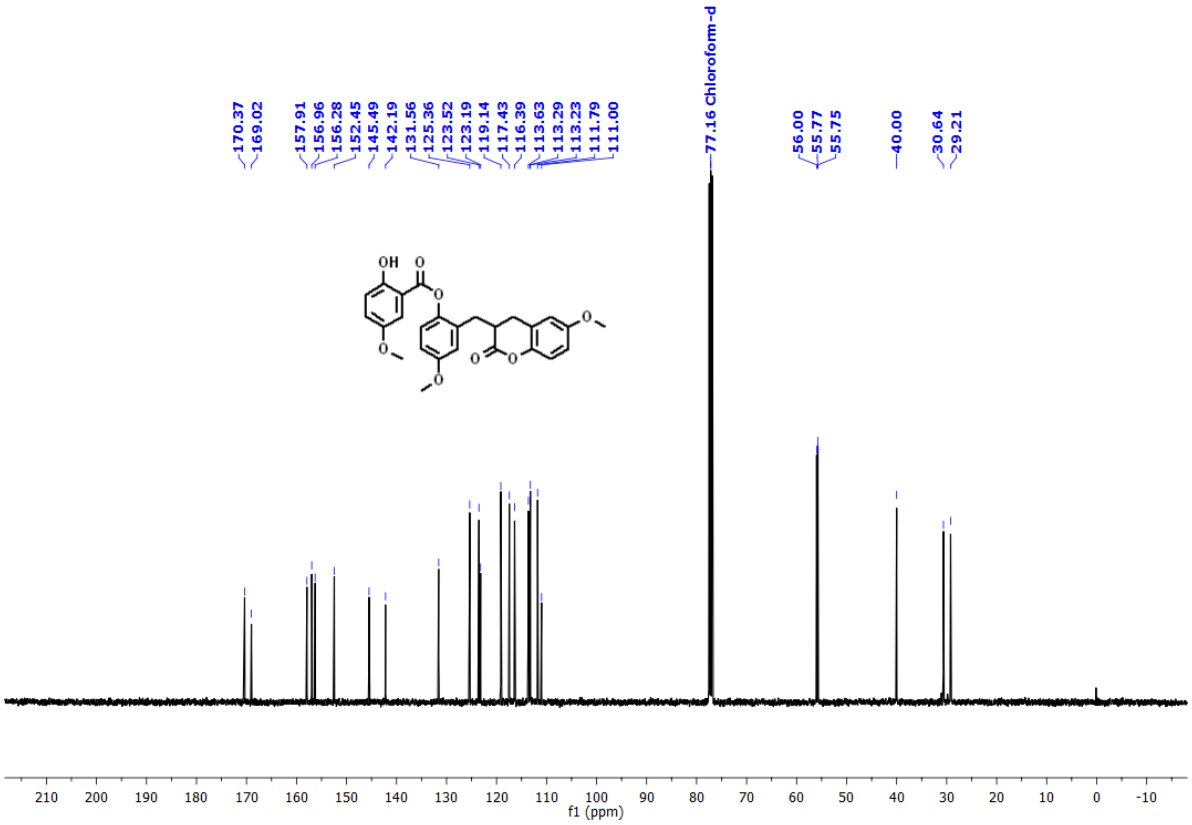


Fig. S69. ^{13}C NMR of **5u,** 100MHz, $CDCl_3$

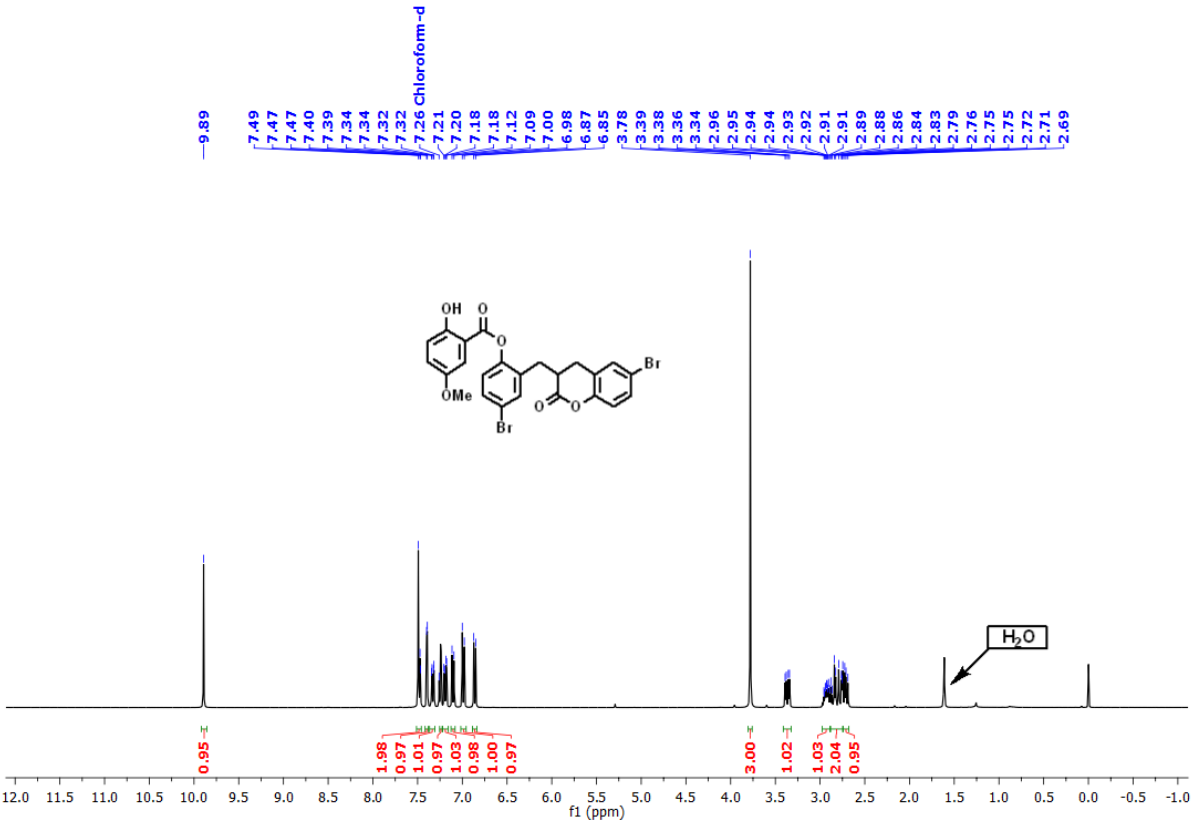


Fig. S70. ^{1}H NMR of **5v,** 400MHz, $CDCl_3$

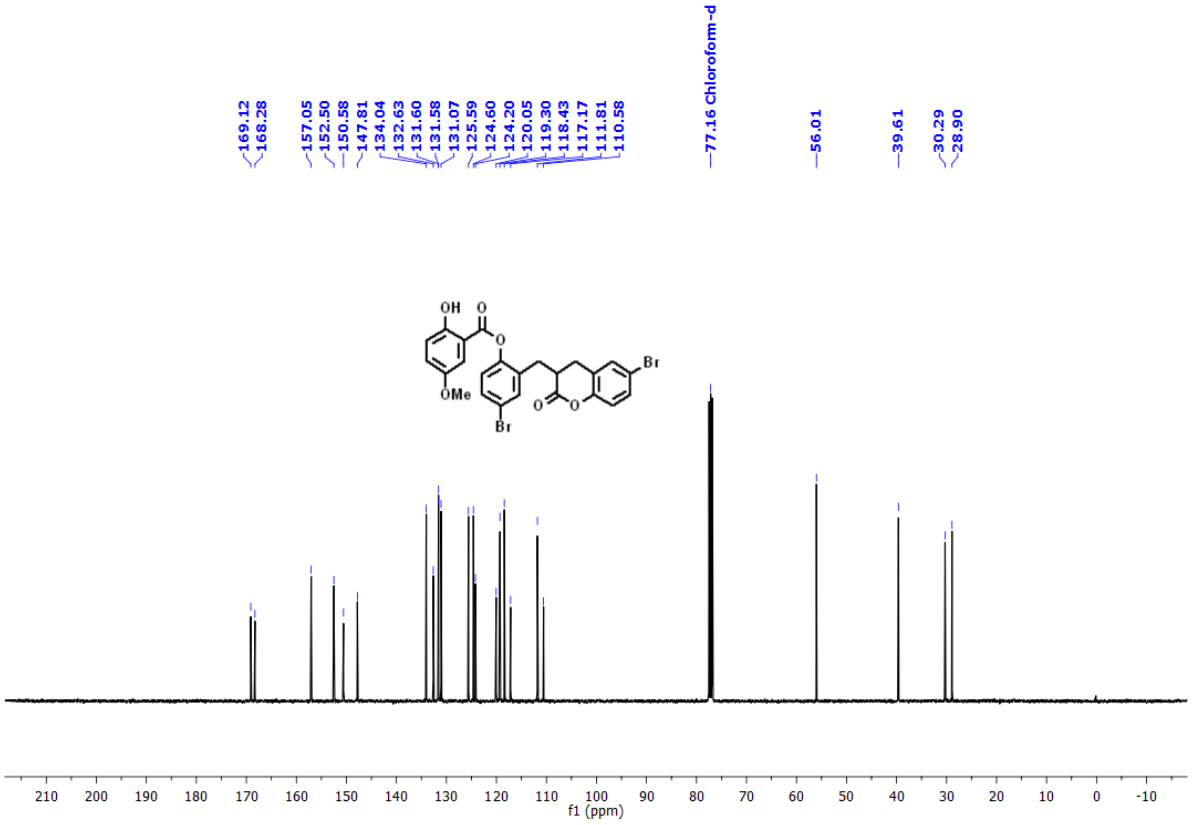


Fig. S71. ^{13}C NMR of **5v,** 100MHz, $CDCl_3$

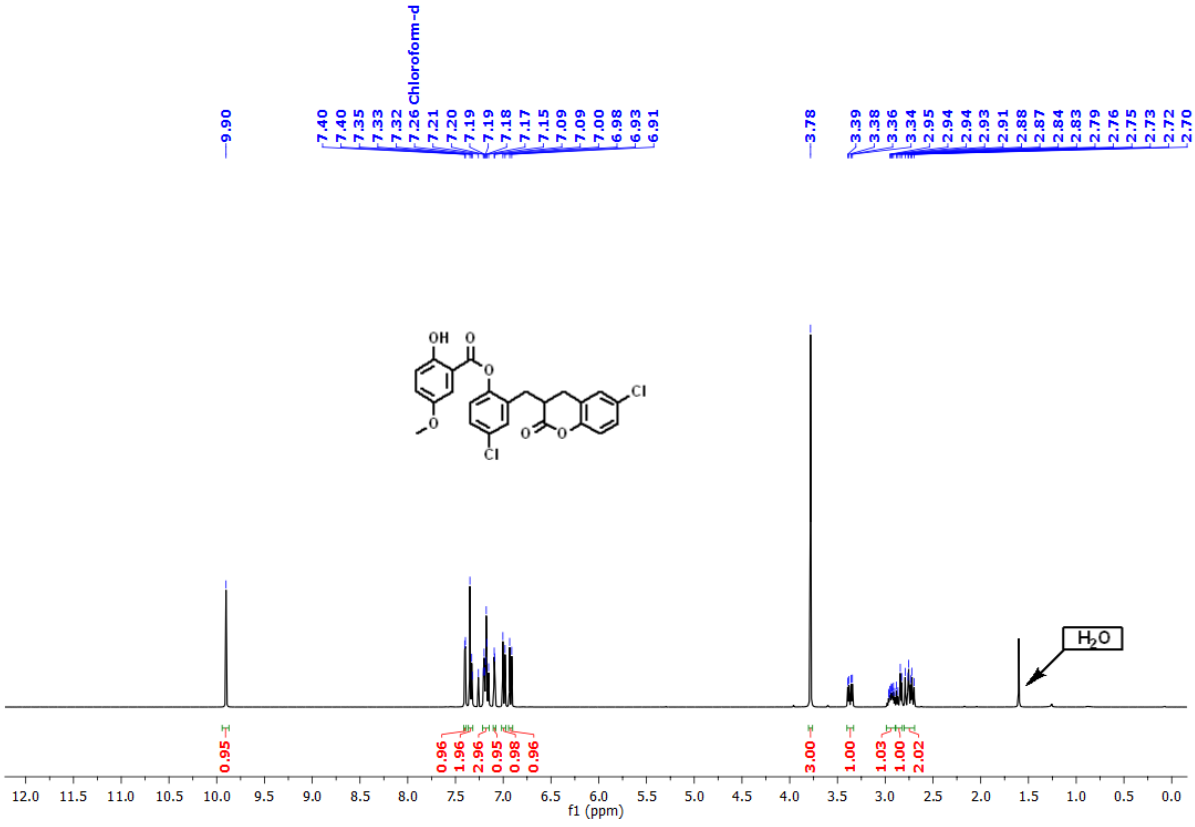


Fig. S72. ^{1}H NMR of **5w,** 400MHz, $CDCl_3$

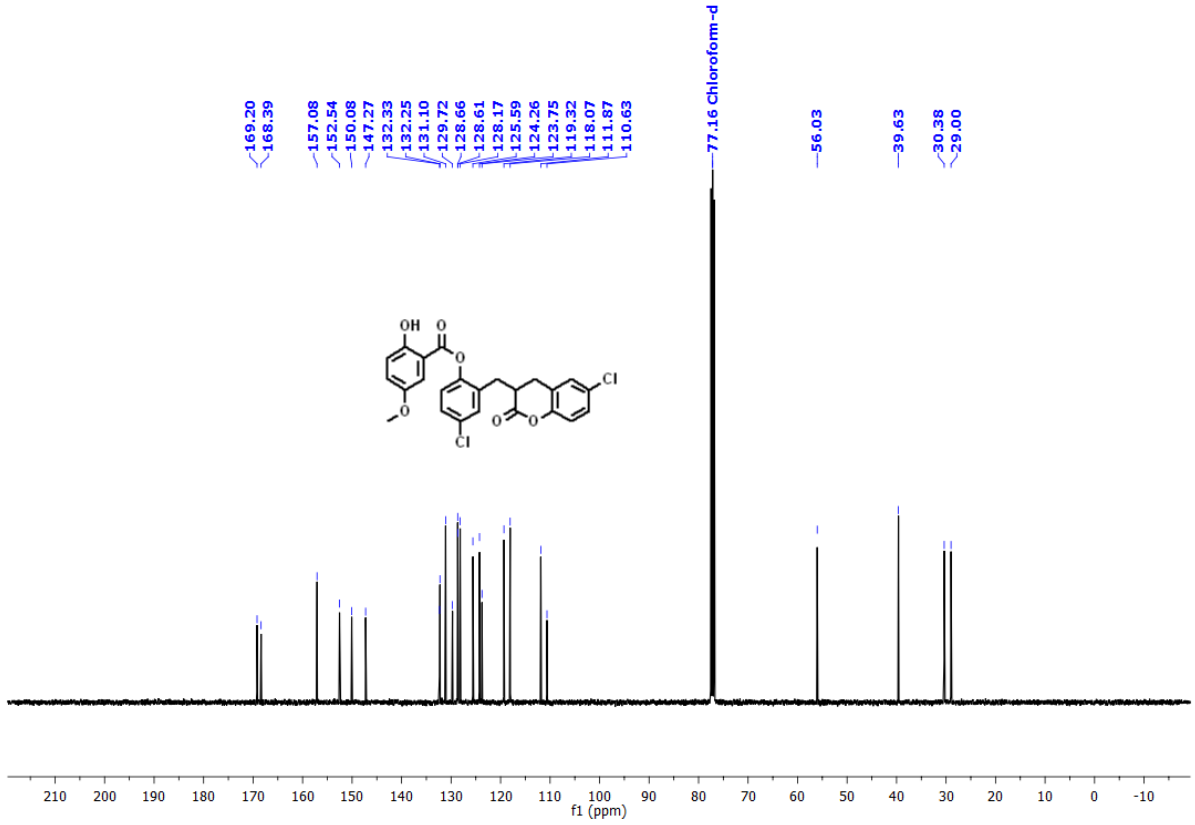


Fig. S73. ^{13}C NMR of **5w,** 100MHz, $CDCl_3$

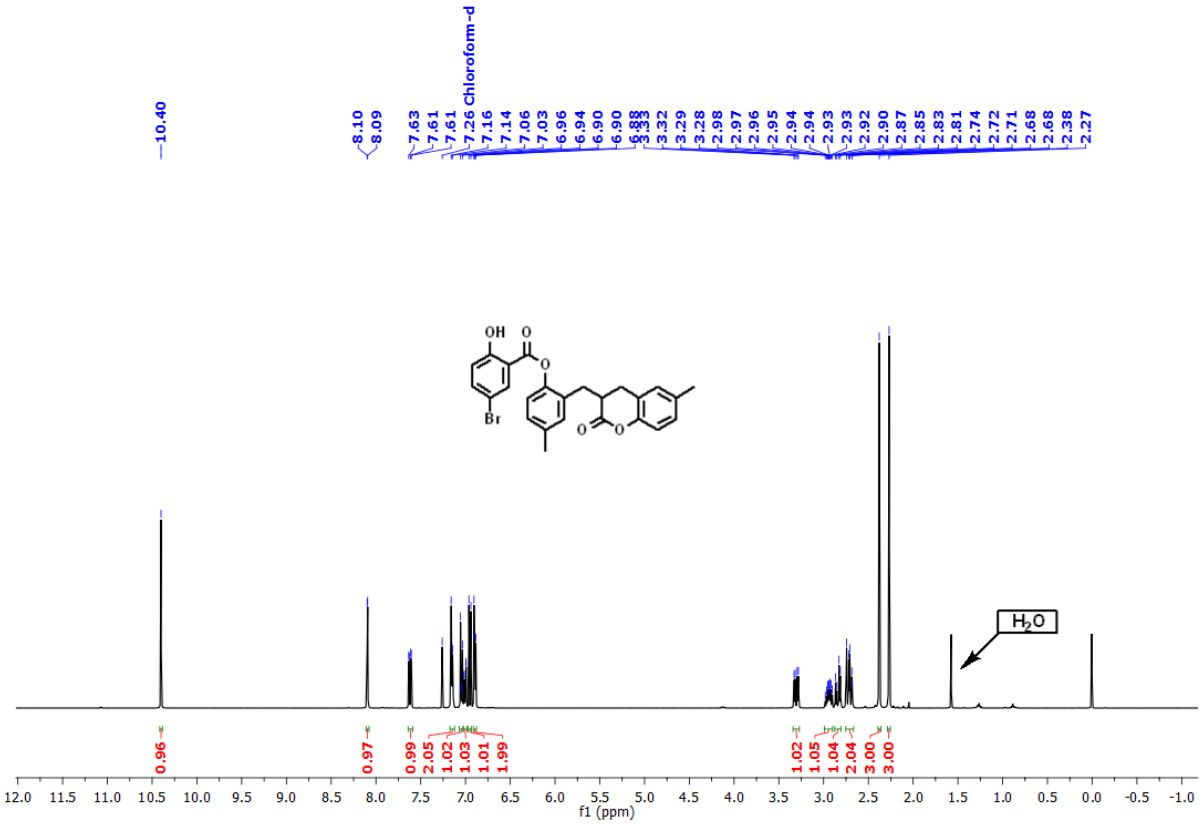


Fig. S74. ^{1}H NMR of **5x,** 400MHz, $CDCl_3$5

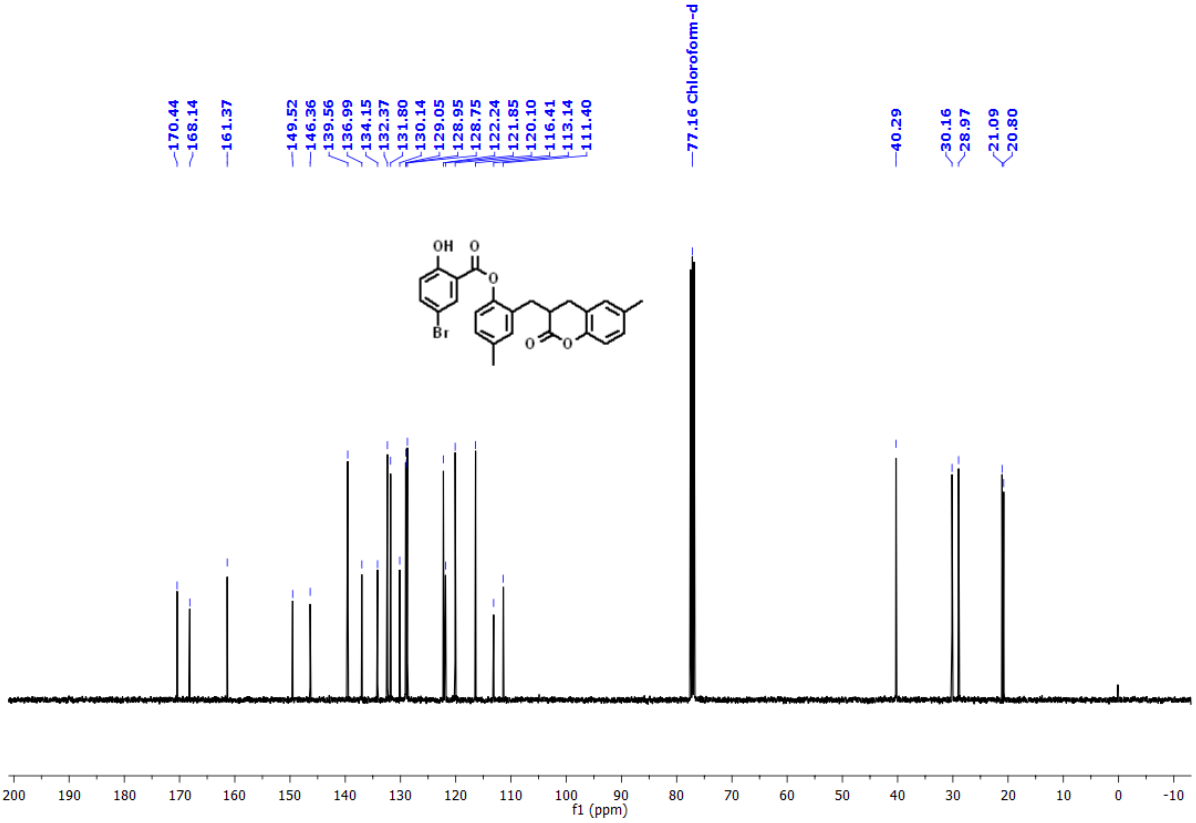


Fig. S75. ^{13}C NMR of **5x,** 100MHz, $CDCl_3$

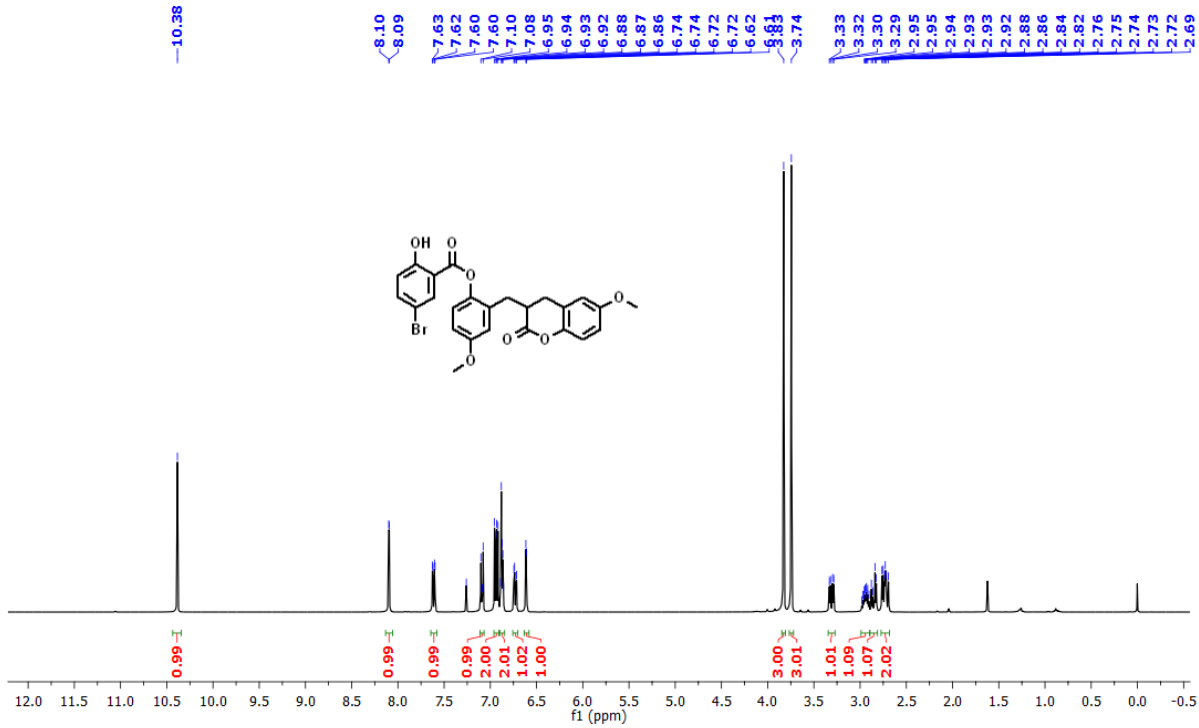


Fig. S76. ^{1}H NMR of **5y,** 400MHz, $CDCl_3$

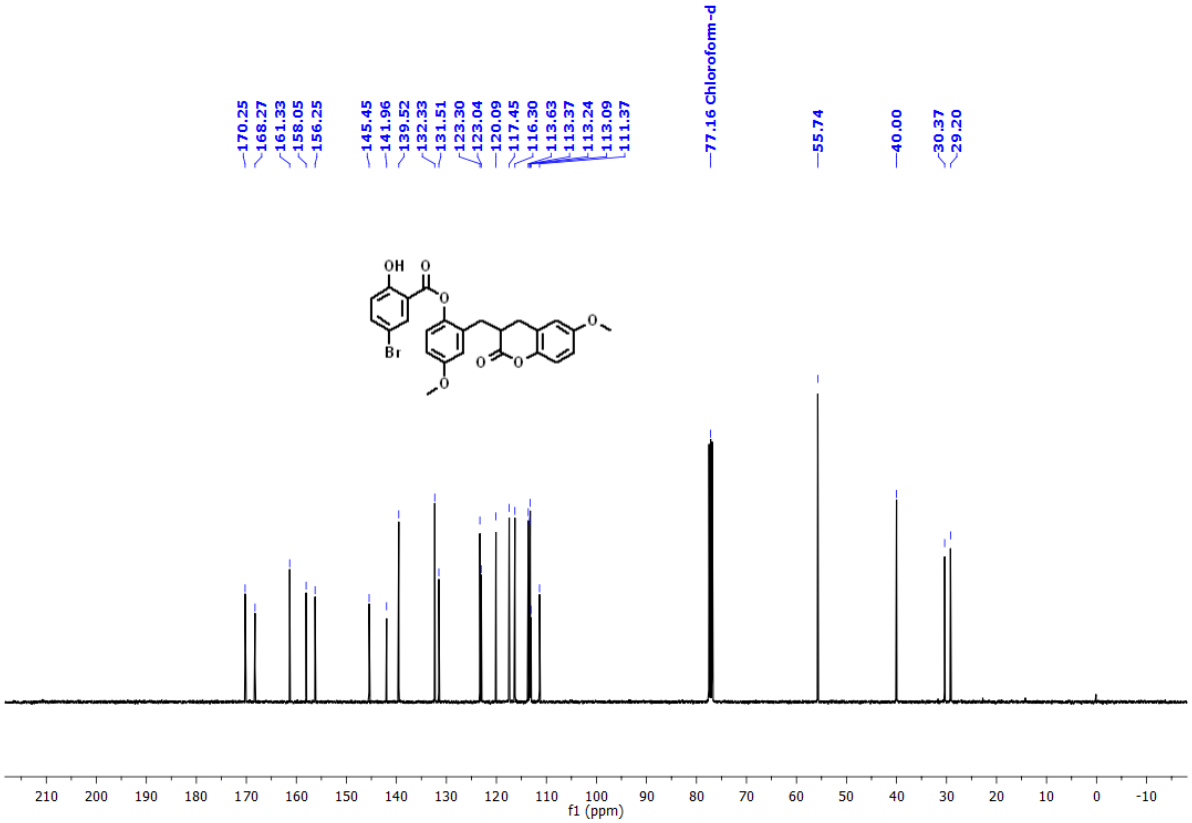


Fig. S77. ^{13}C NMR of **5y,** 100MHz, $CDCl_3$

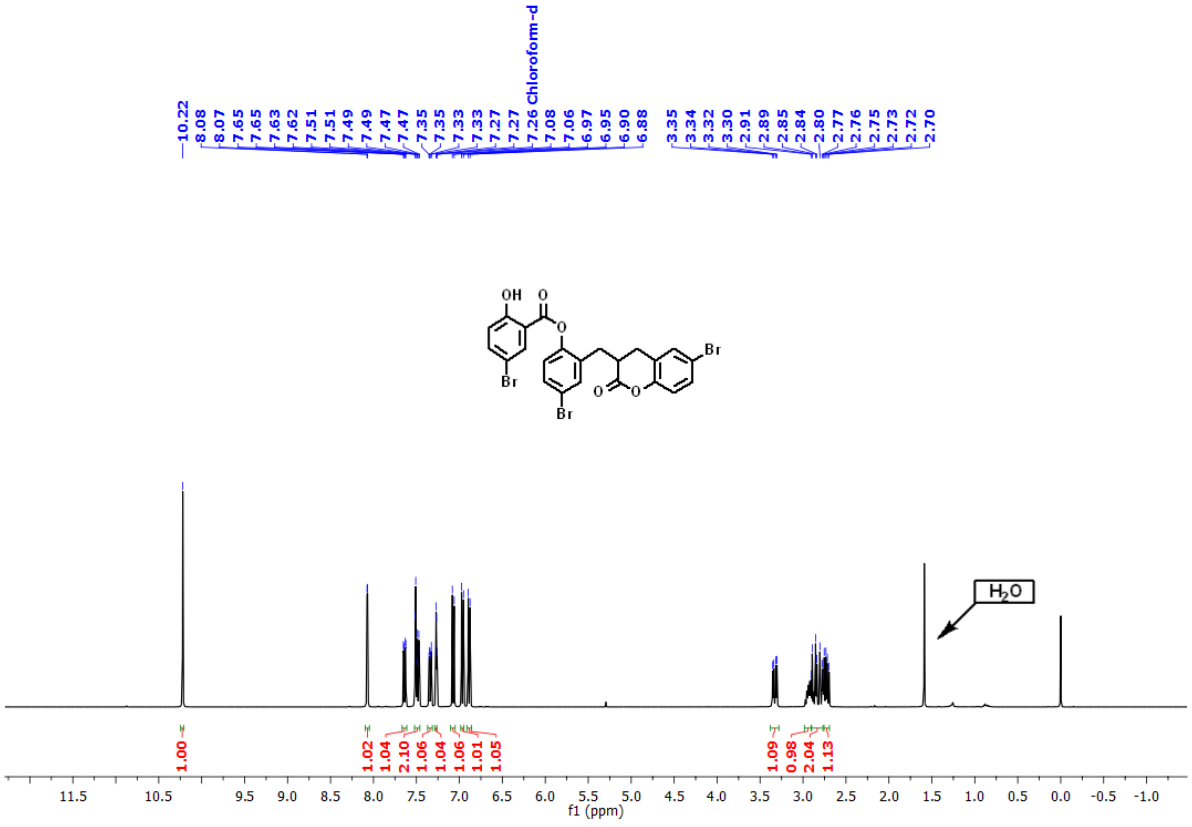


Fig. S78. ^{1}H NMR of **5z,** 400MHz, $CDCl_3$

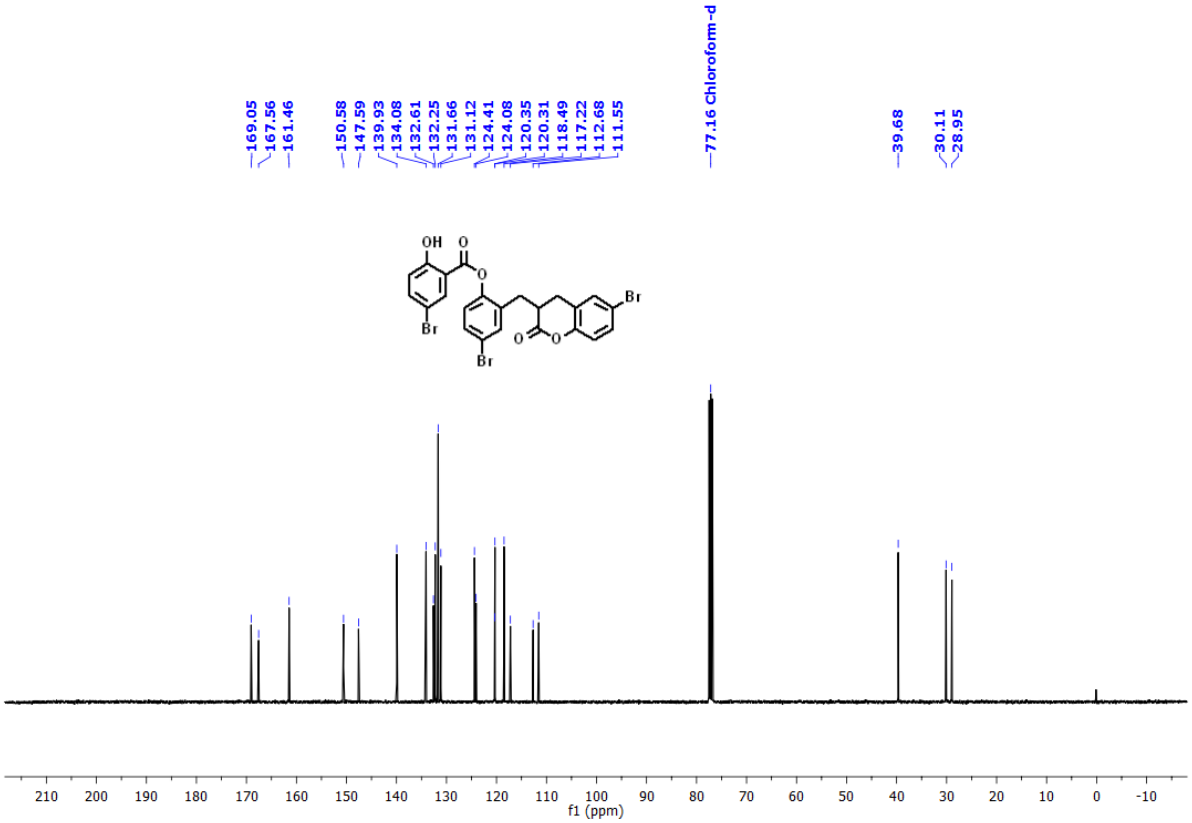


Fig. S79. ^{13}C NMR of **5z,** 100MHz, $CDCl_3$

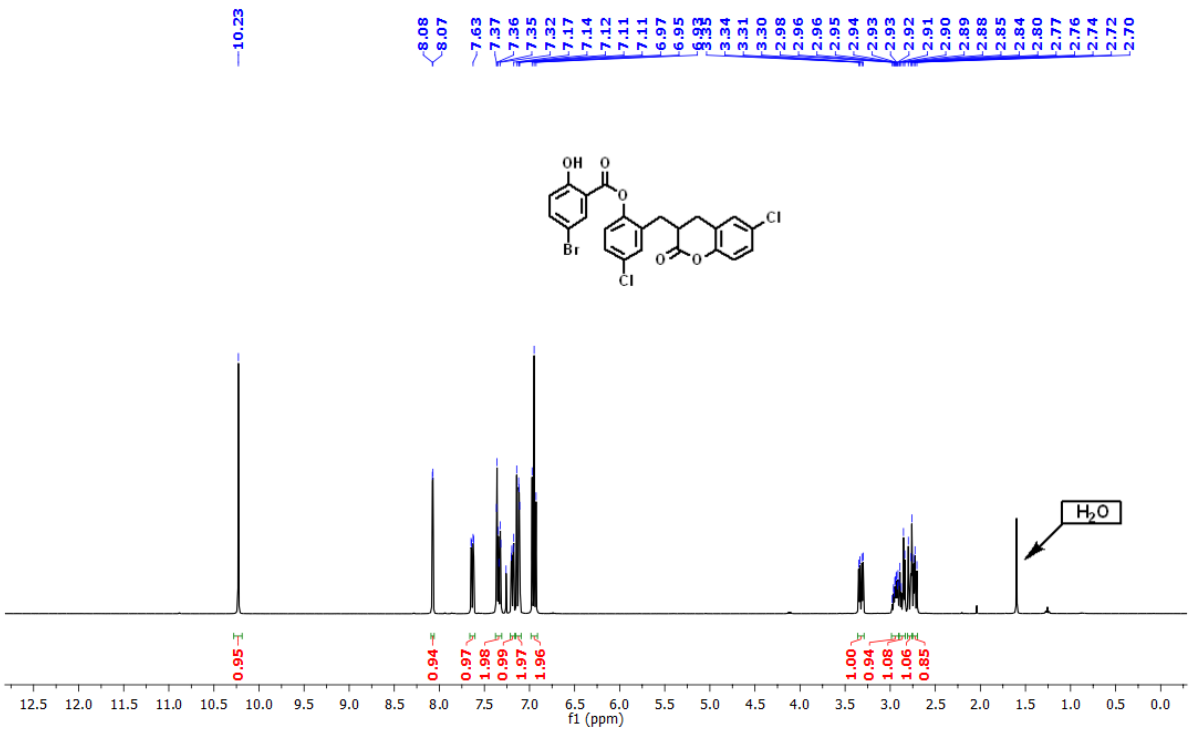


Fig. S80. ^{1}H NMR of **5aa,** 400MHz, $CDCl_3$

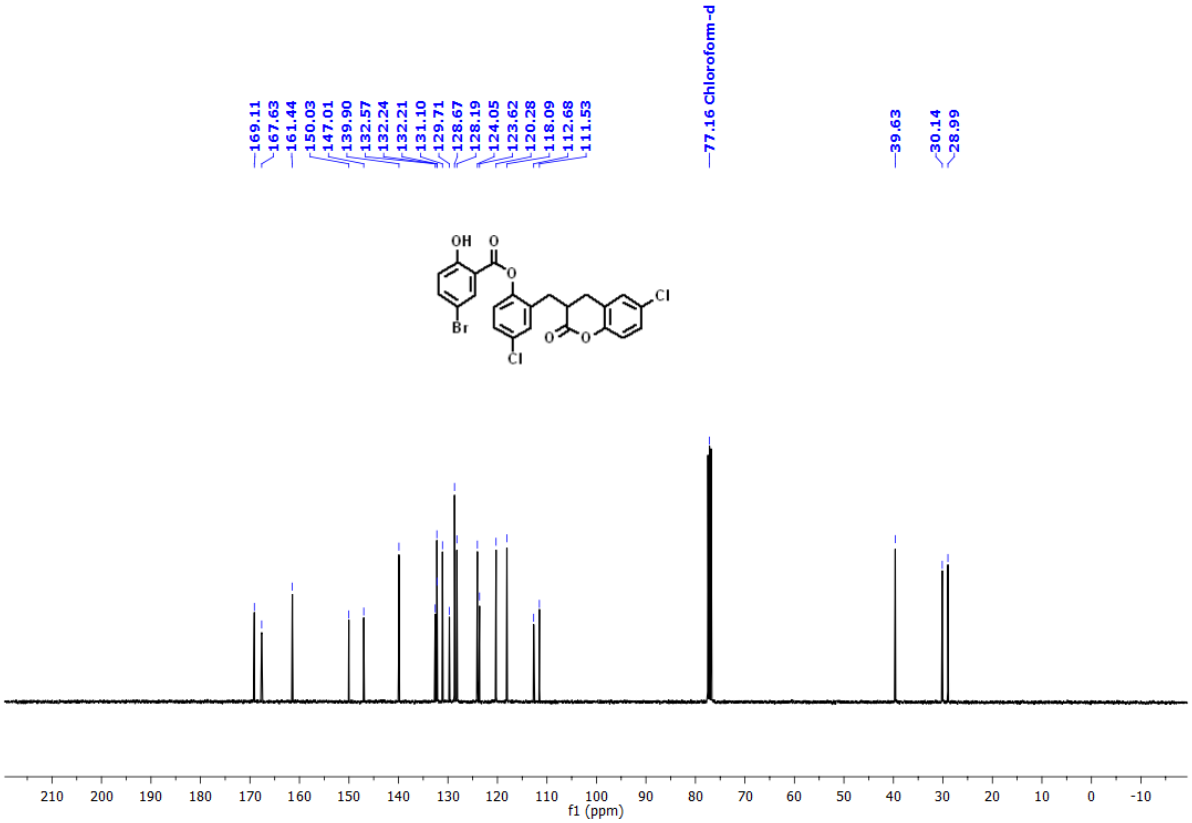


Fig. S81. ^{13}C NMR of **5aa,** 100MHz, $CDCl_3$

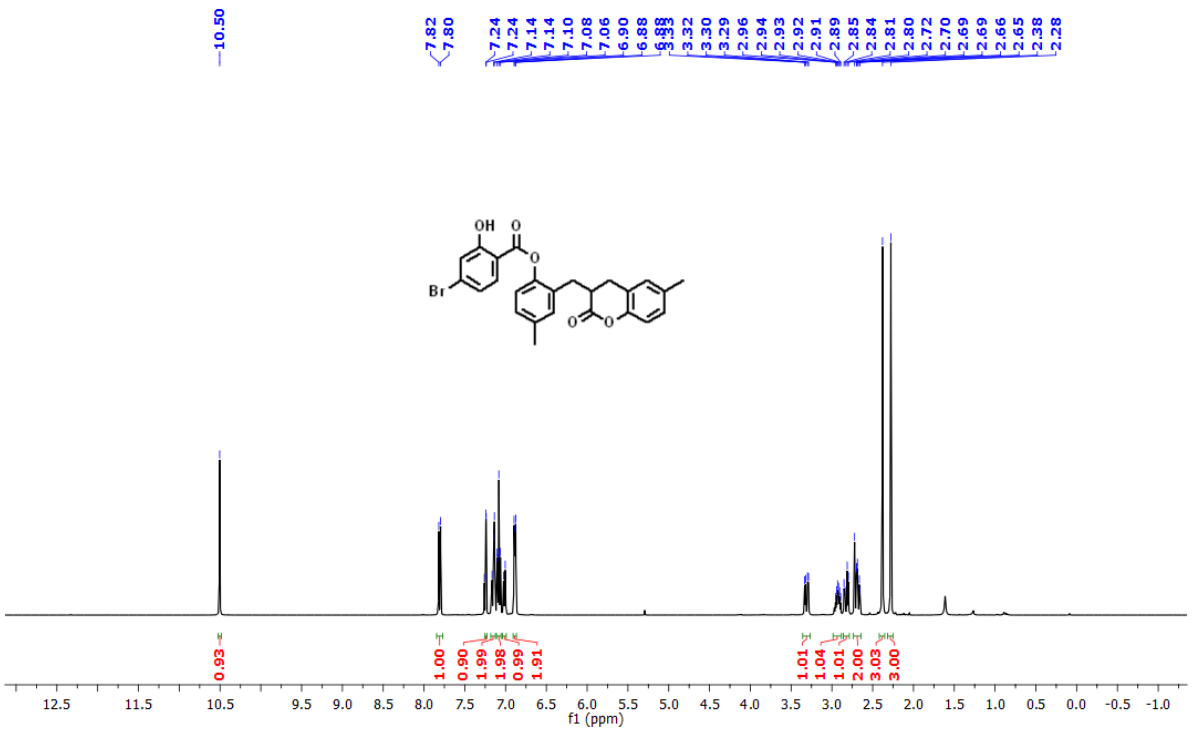


Fig. S82. ^{1}H NMR of **5ab,** 400MHz, $CDCl_3$

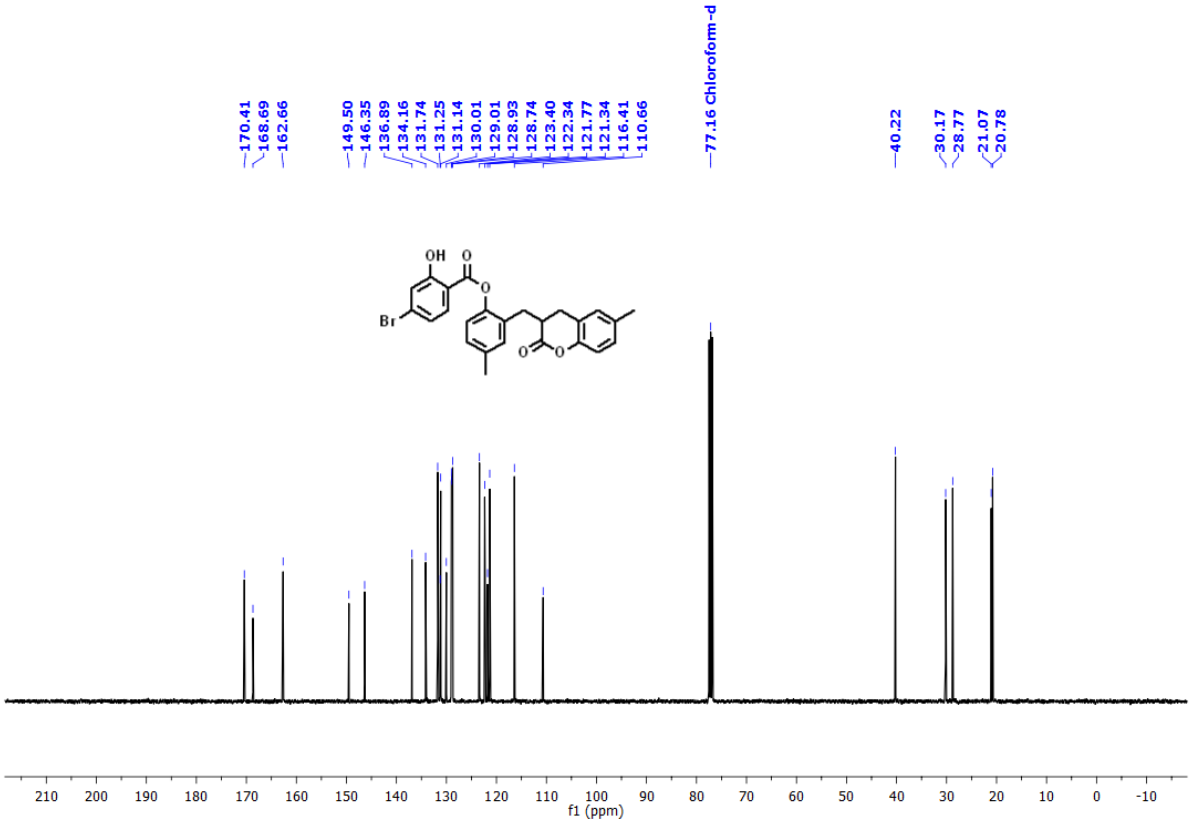


Fig. S83. ^{13}C NMR of **5ab,** 100MHz, $CDCl_3$

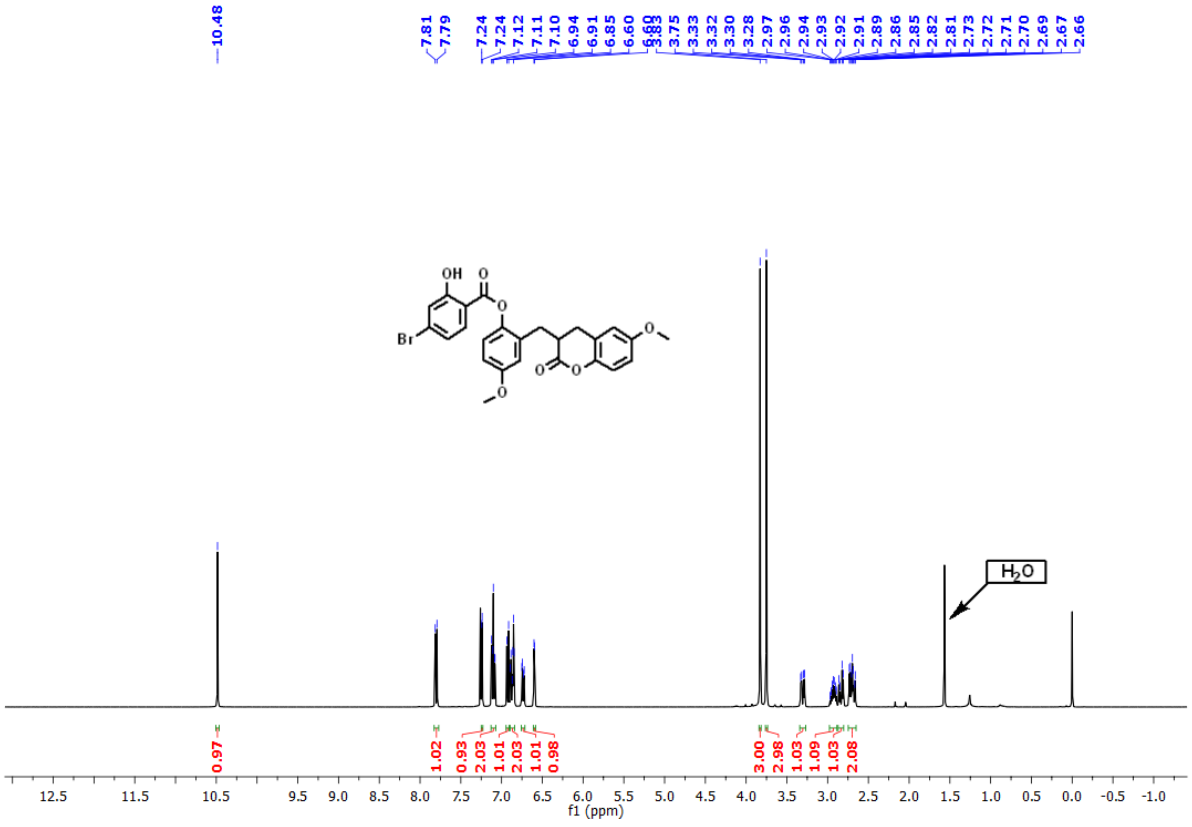


Fig. S84. ^{1}H NMR of **5ac,** 400MHz, $CDCl_3$

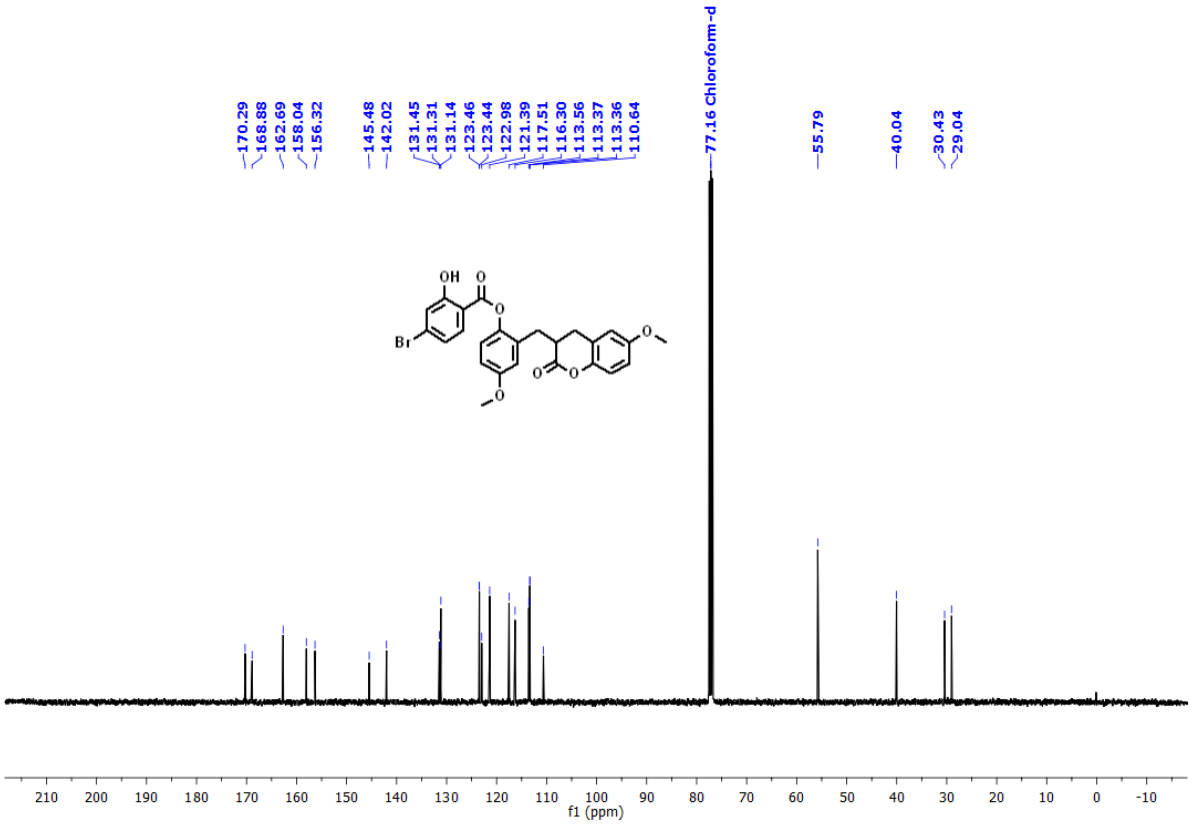


Fig. S85. ^{13}C NMR of **5ac,** 100MHz, $CDCl_3$

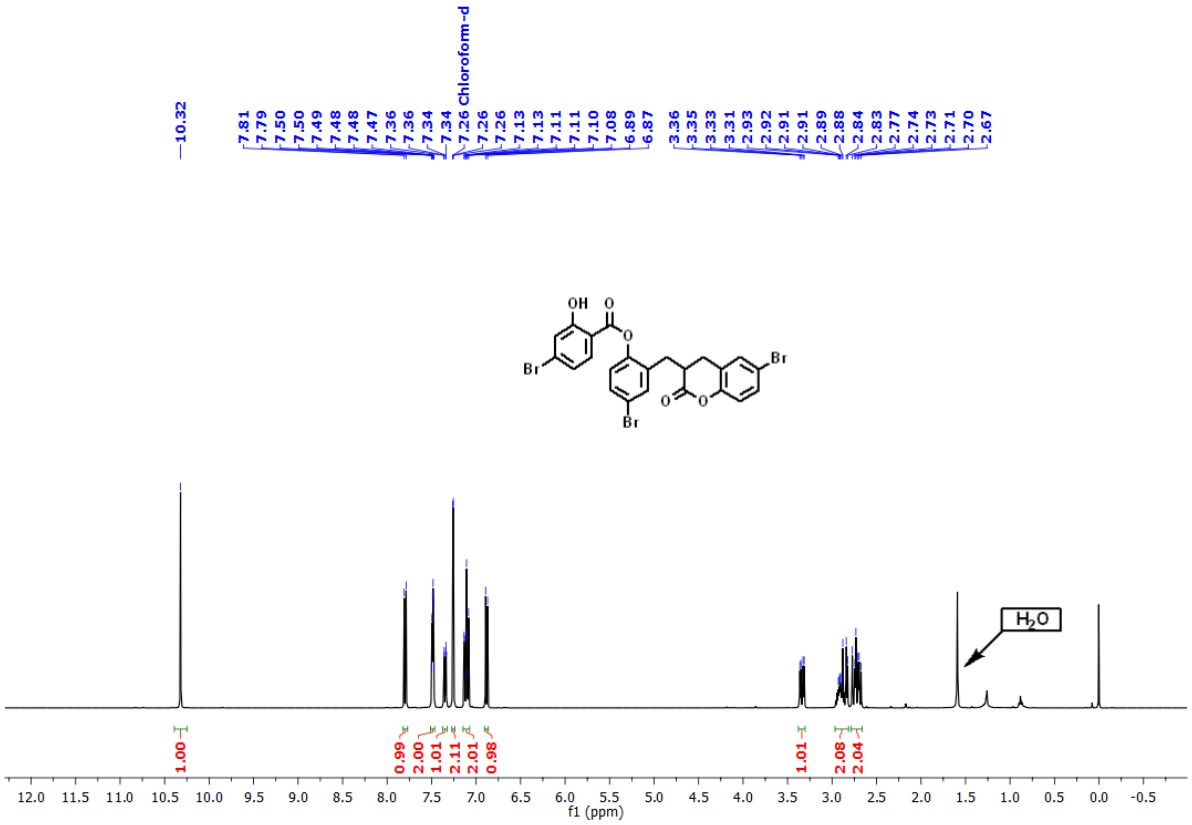


Fig. S86. ^{1}H NMR of **5ad,** 400MHz, $CDCl_3$

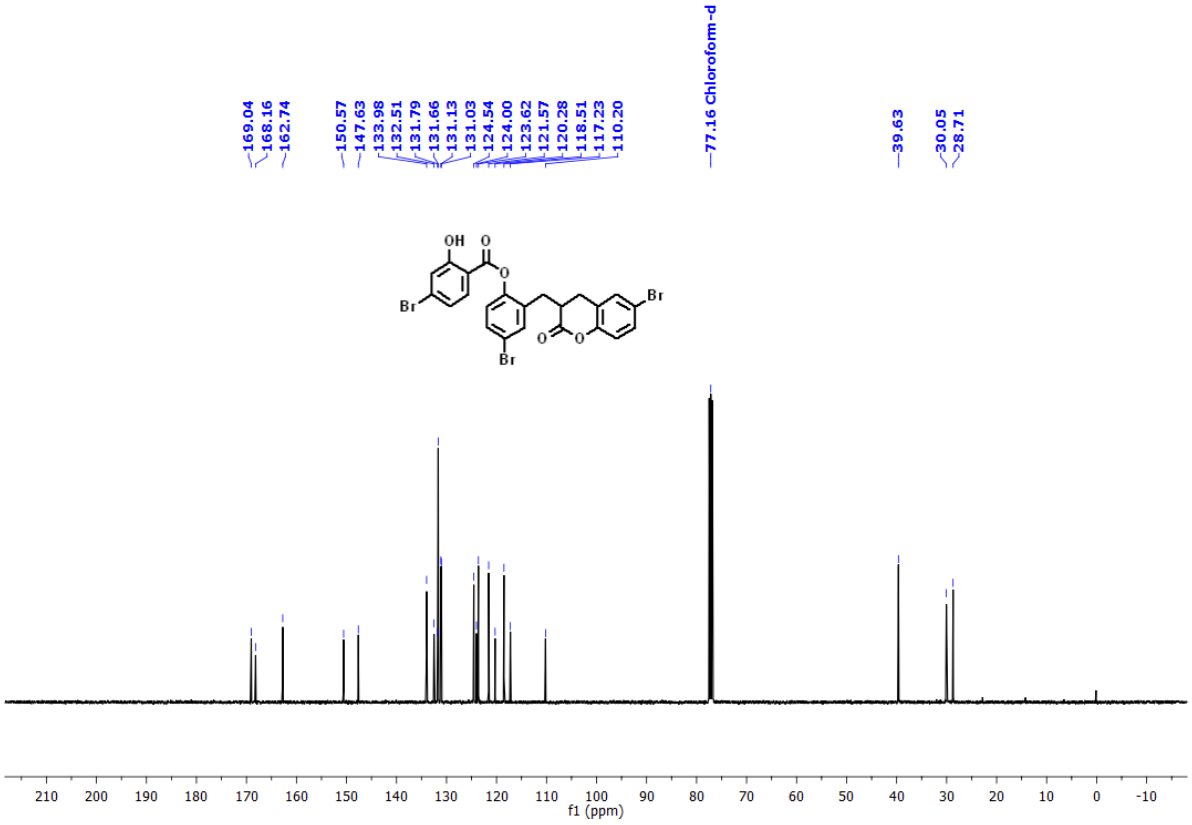


Fig. S87. ^{13}C NMR of **5ad,** 100MHz, $CDCl_3$

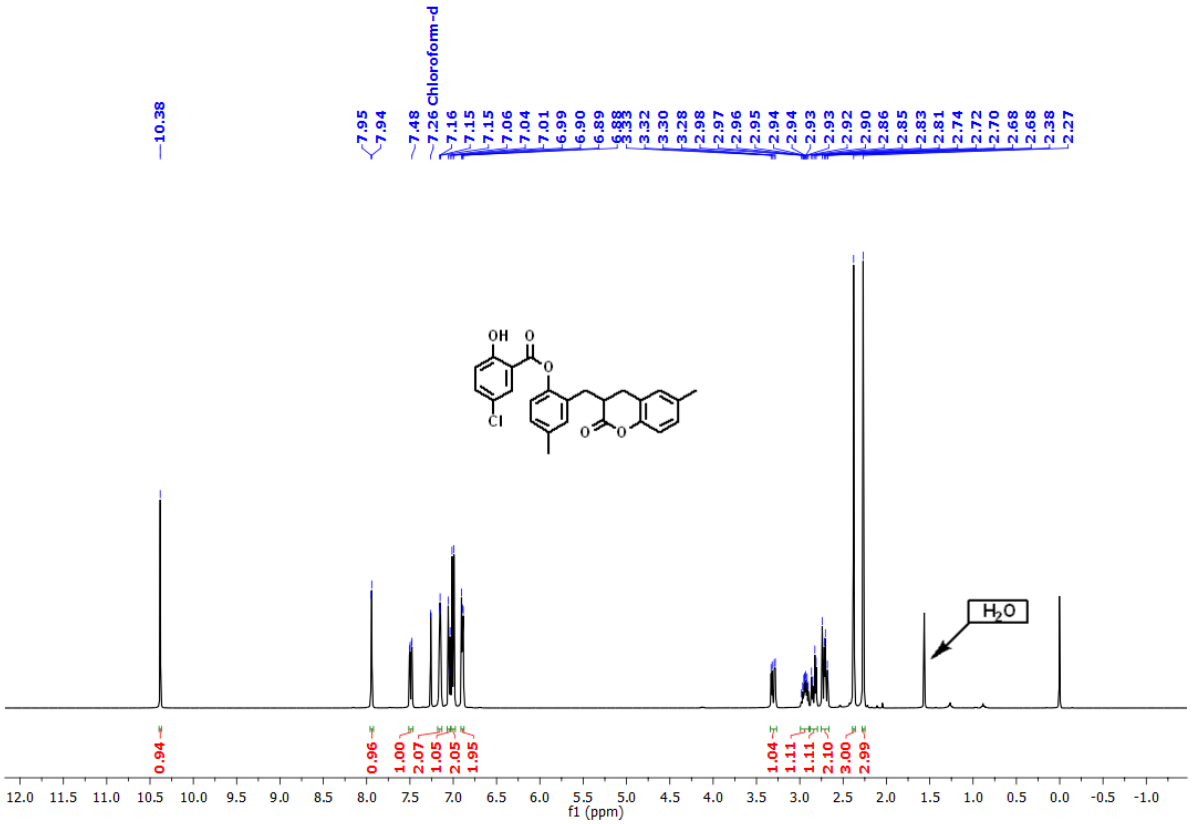


Fig. S88. ^{1}H NMR of **5ae,** 400MHz, $CDCl_3$

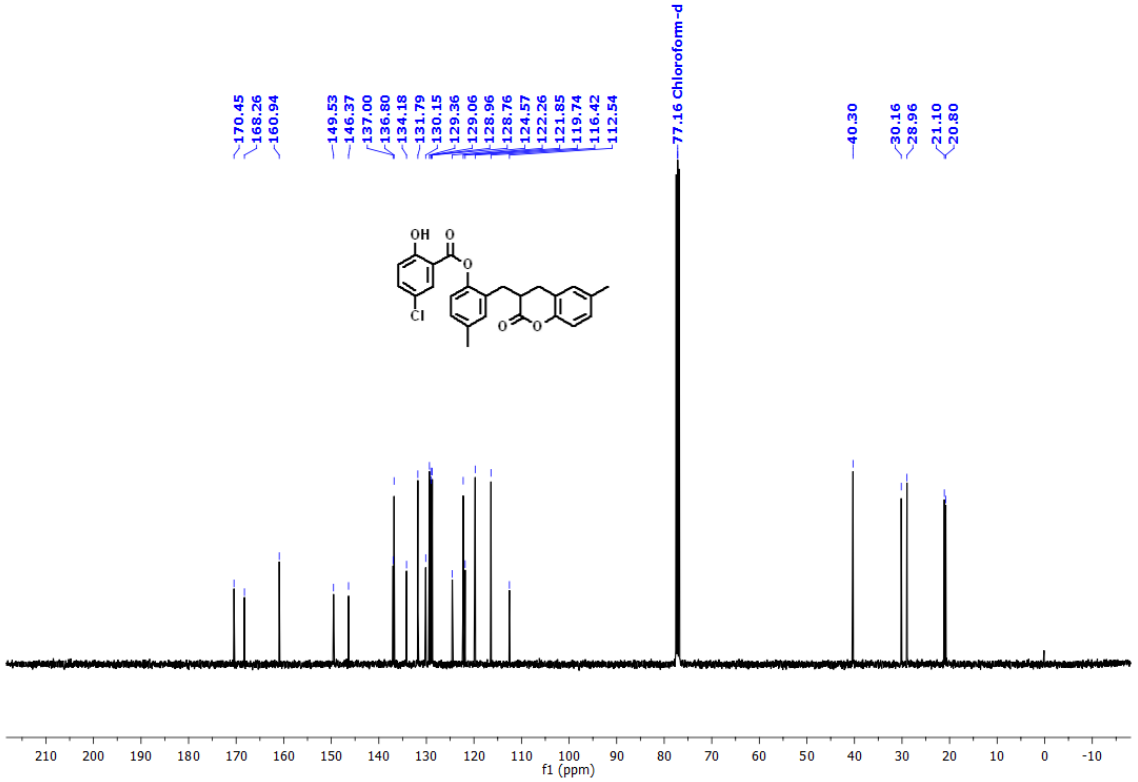


Fig. S89. ^{13}C NMR of **5ae,** 100MHz, $CDCl_3$

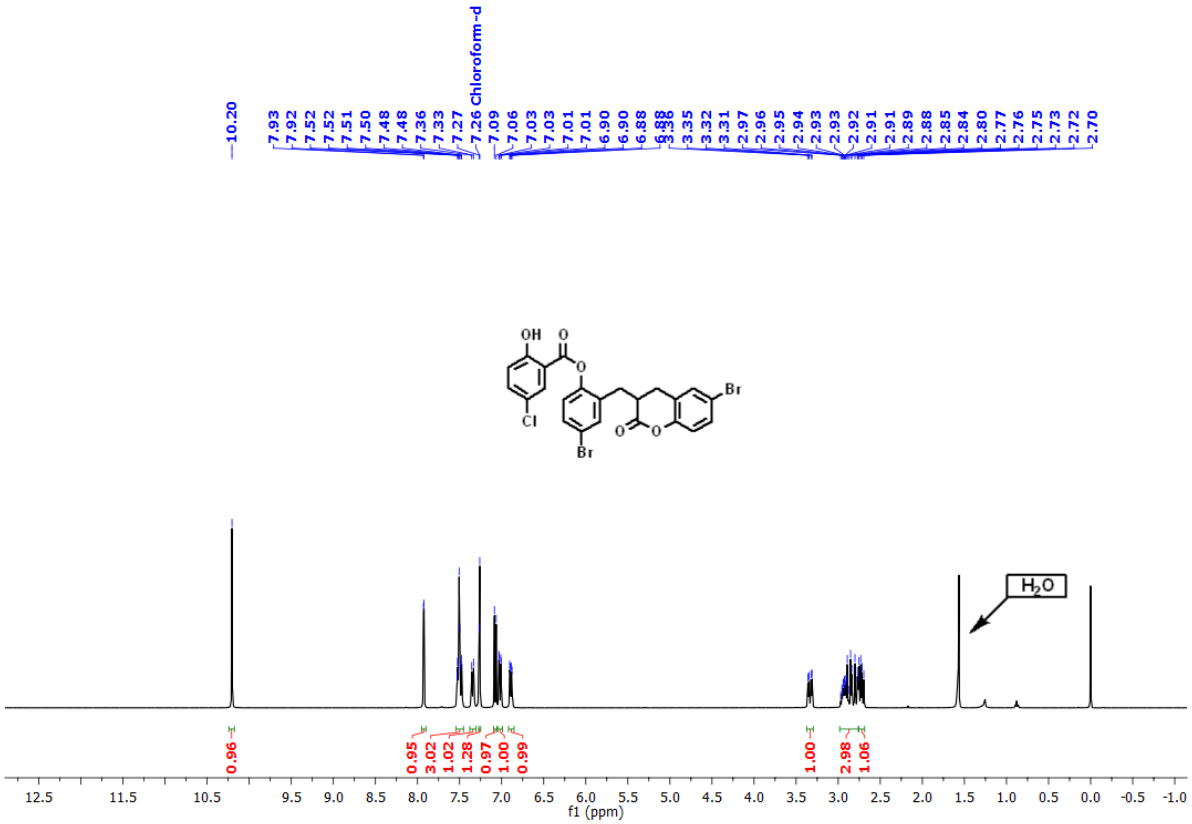


Fig. S90. ^{1}H NMR of **5af,** 400MHz, $CDCl_3$

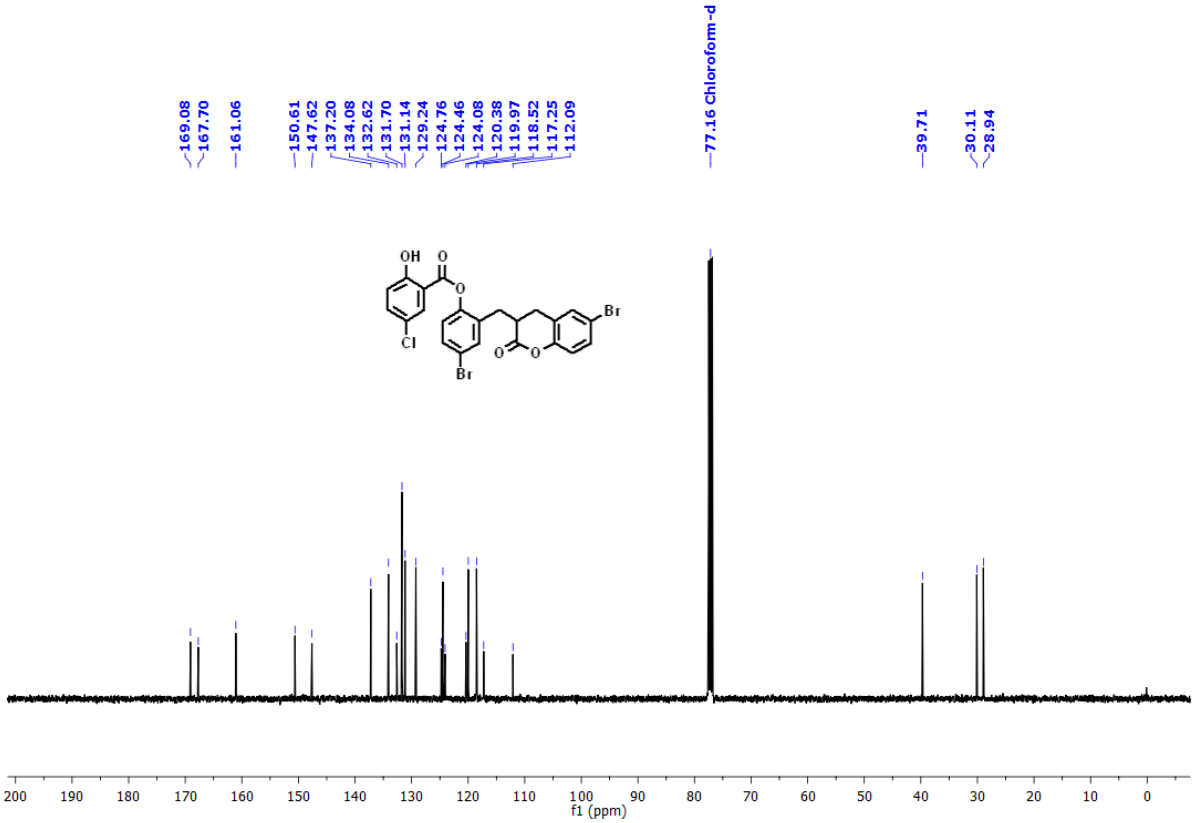


Fig. S91. ^{13}C NMR of **5af,** 100MHz, $CDCl_3$

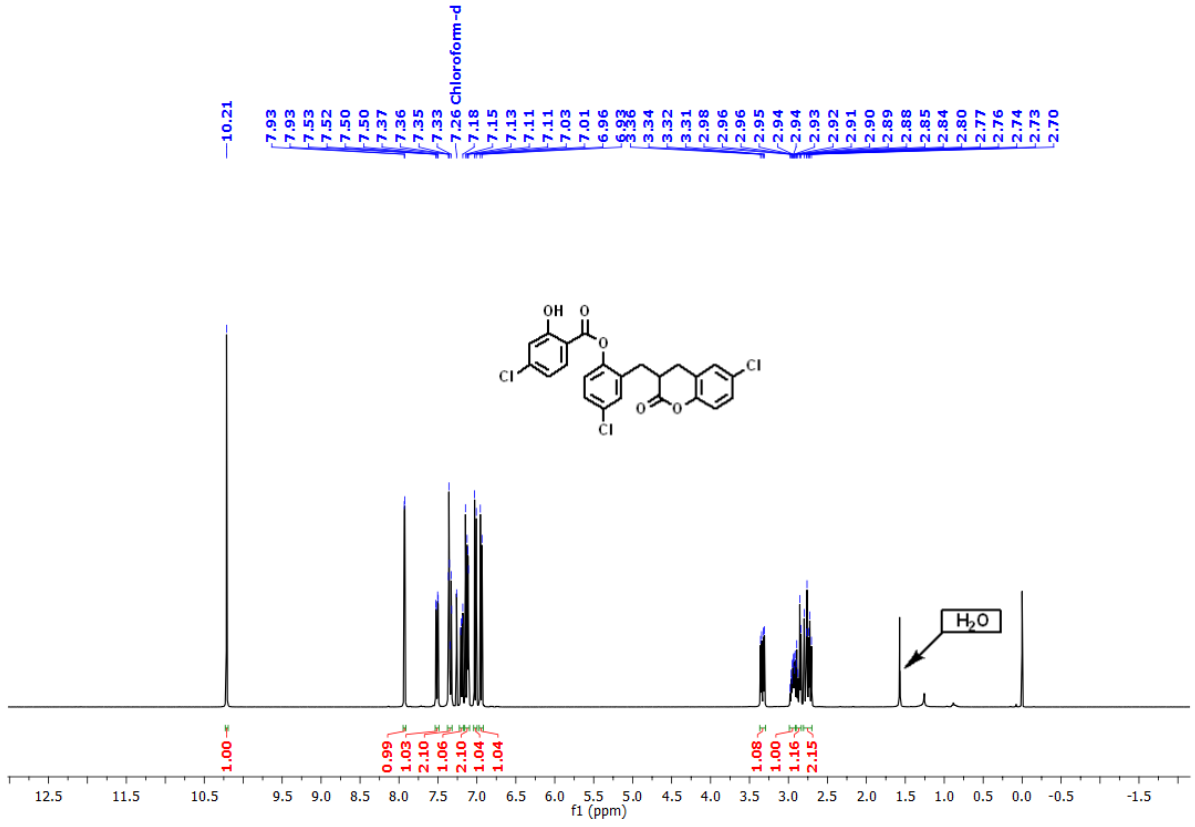


Fig. S92. ^{1}H NMR of **5ag,** 400MHz, $CDCl_3$

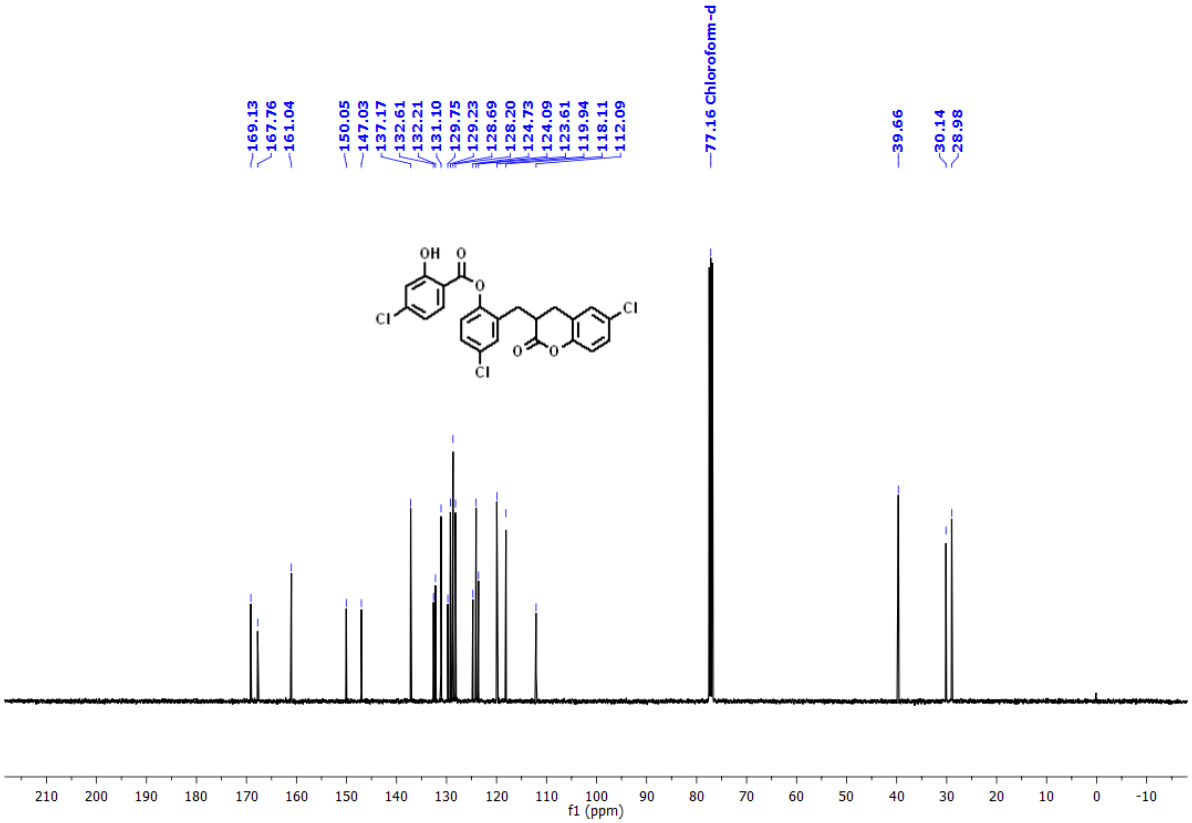


Fig. S93. ^{13}C NMR of **5ag,** 100MHz, $CDCl_3$

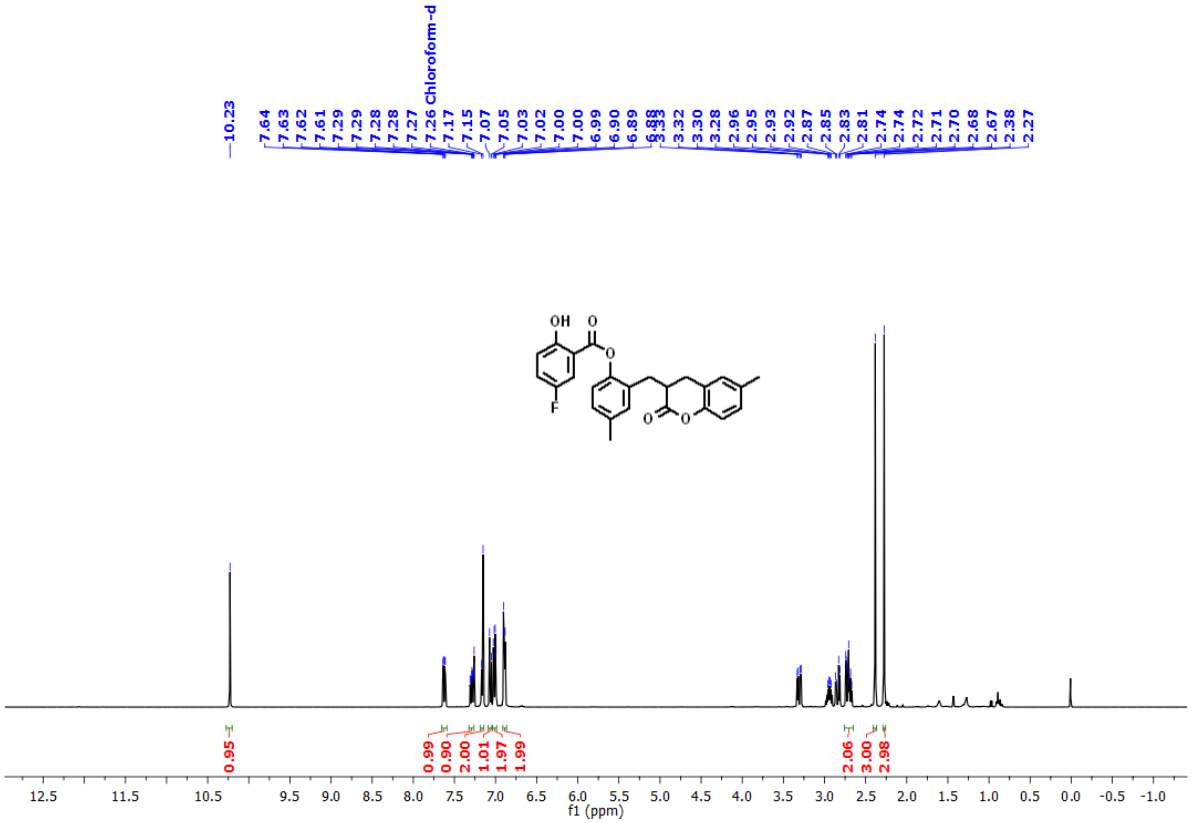


Fig. S94. ^{1}H NMR of **5ah,** 400MHz, $CDCl_3$

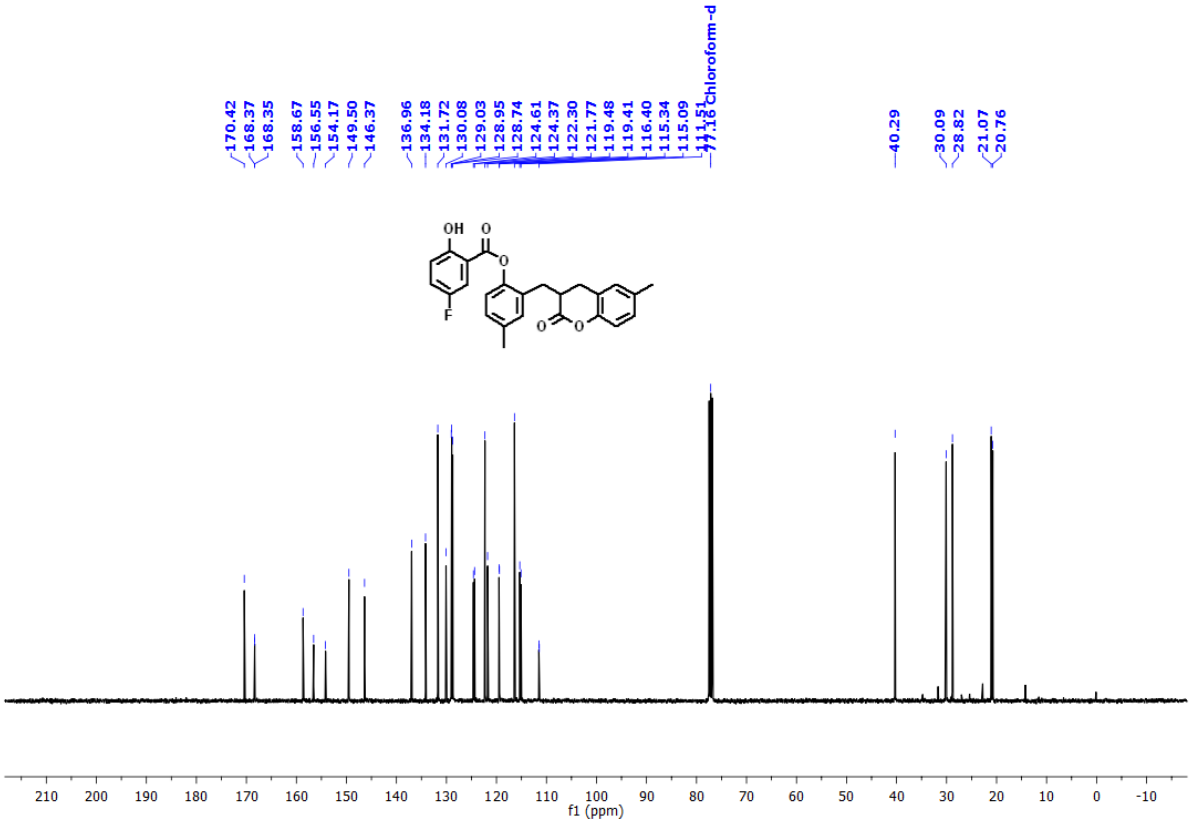


Fig. S95. ^{13}C NMR of **5ah,** 100MHz, $CDCl_3$

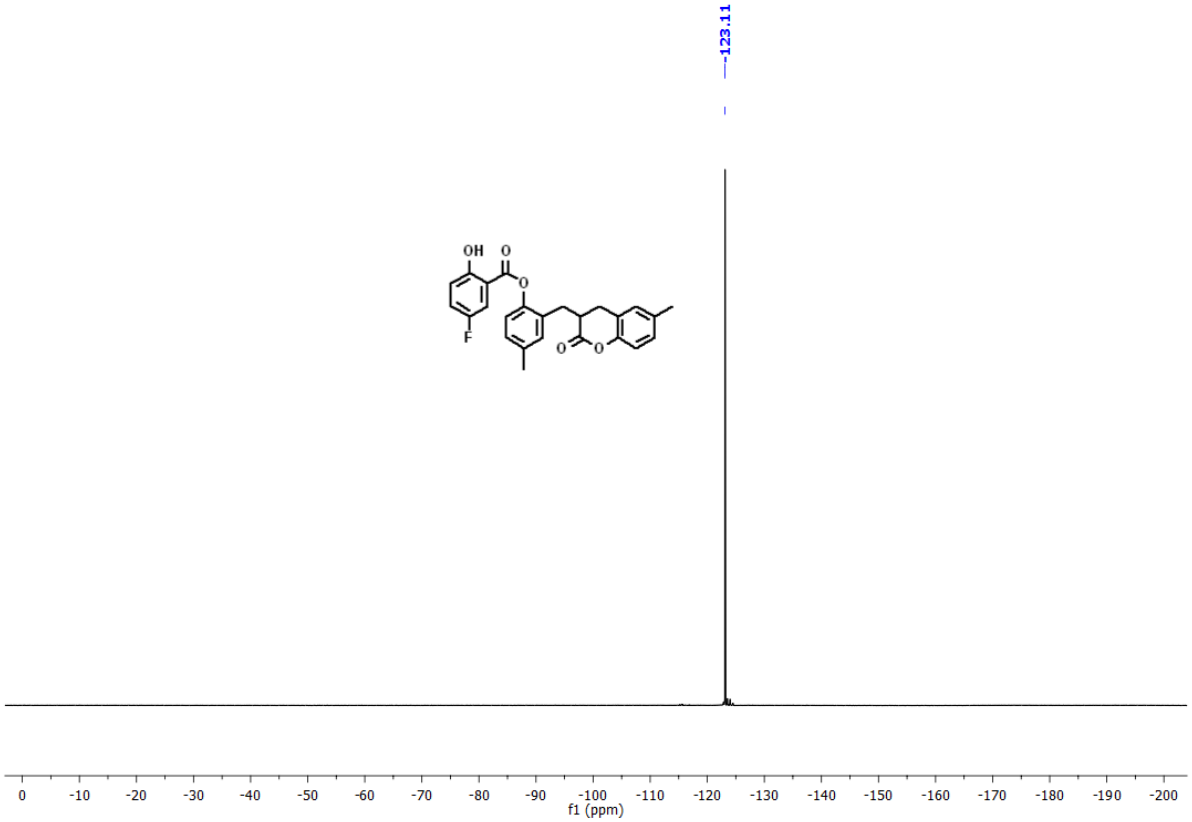


Fig. S96. ^{19}F NMR of **5ah,** 377 MHz, $CDCl_3$

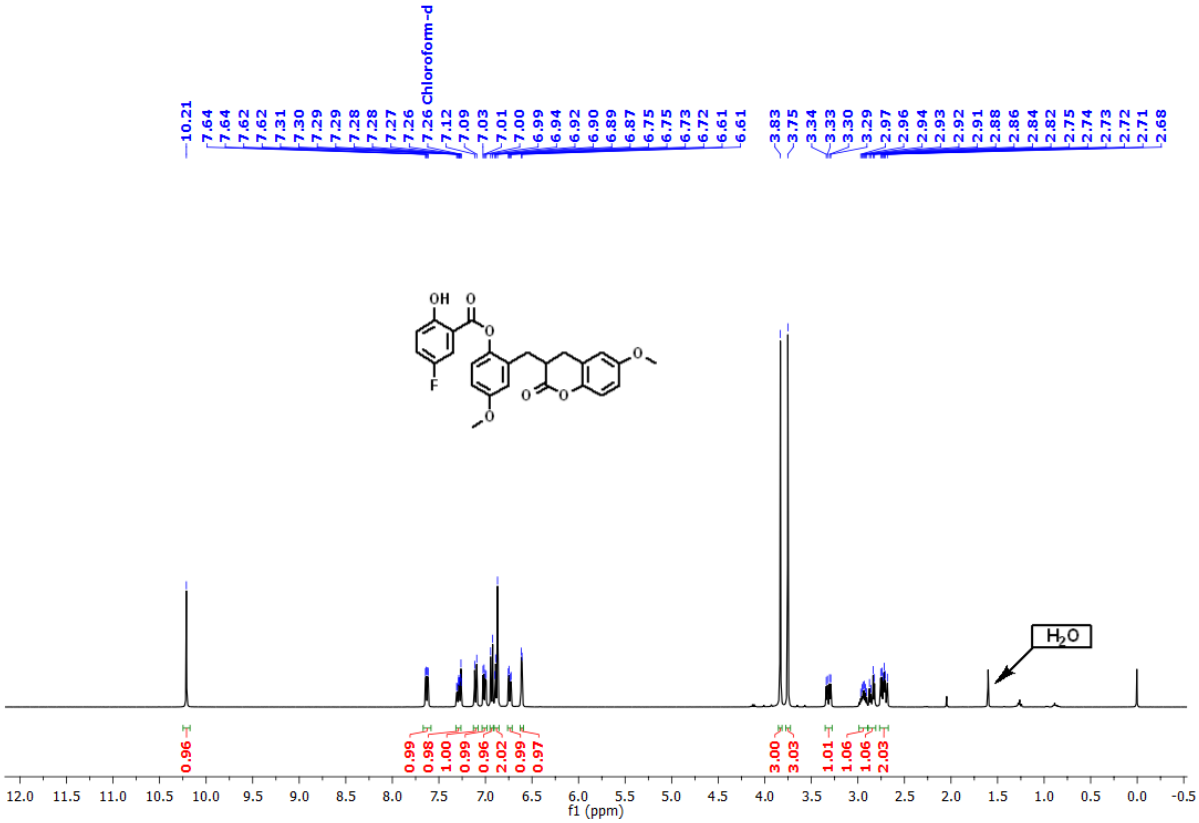


Fig. S97. ^{1}H NMR of **5ai,** 400MHz, $CDCl_3$

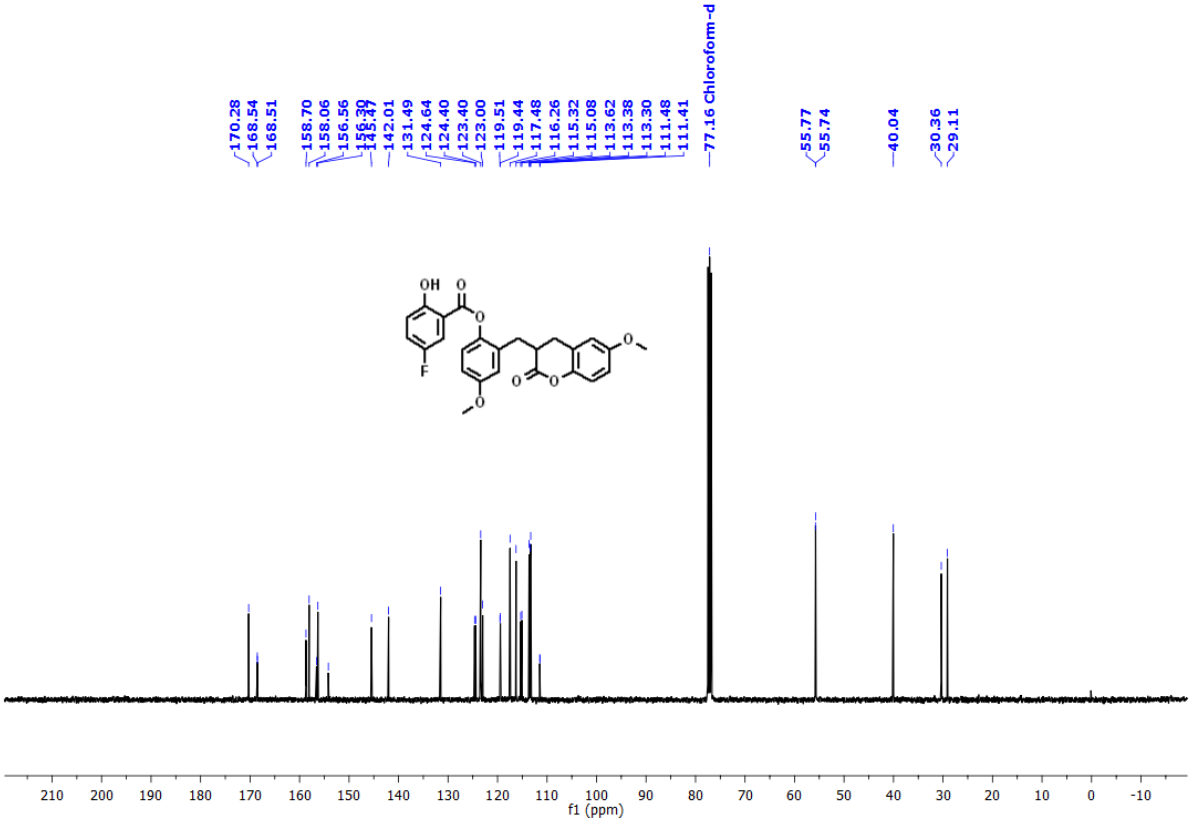


Fig. S98. ^{13}C NMR of **5ai,** 100MHz, $CDCl_3$

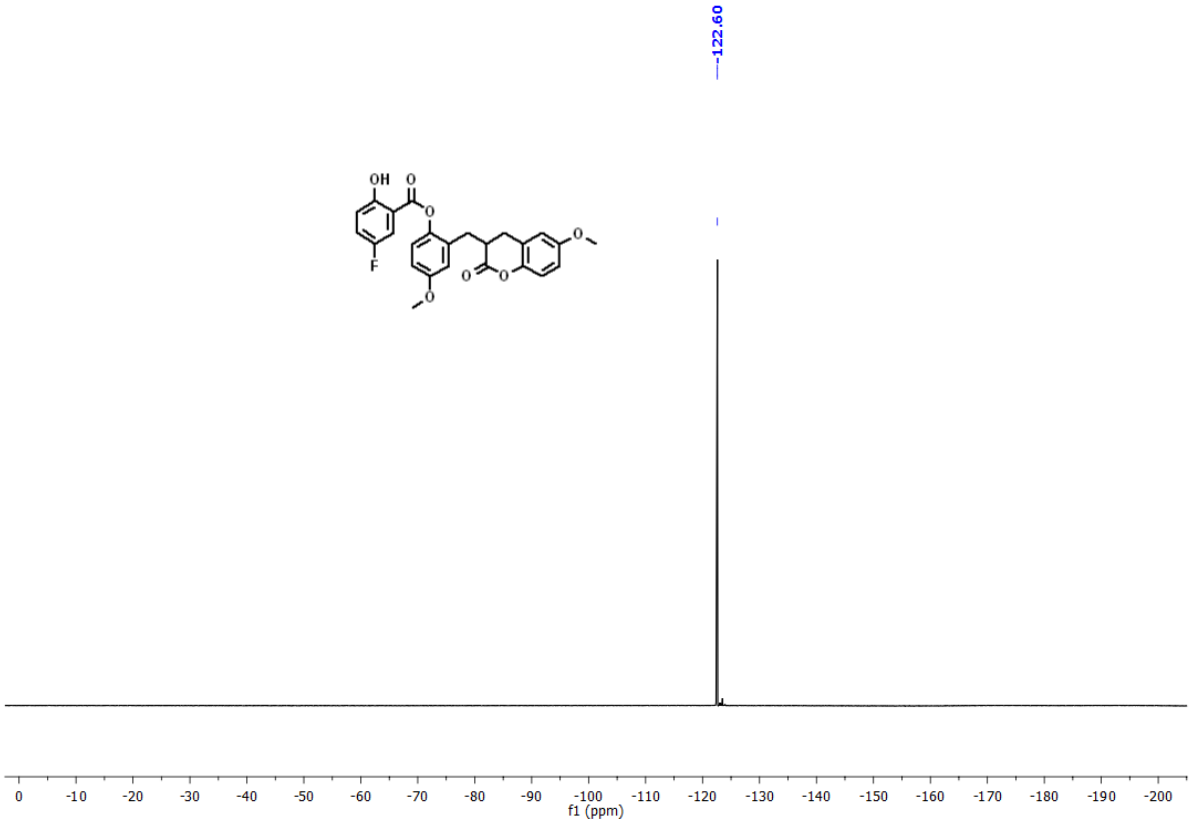


Fig. S99. ^{19}F NMR of **5ai,** 377 MHz, $CDCl_3$

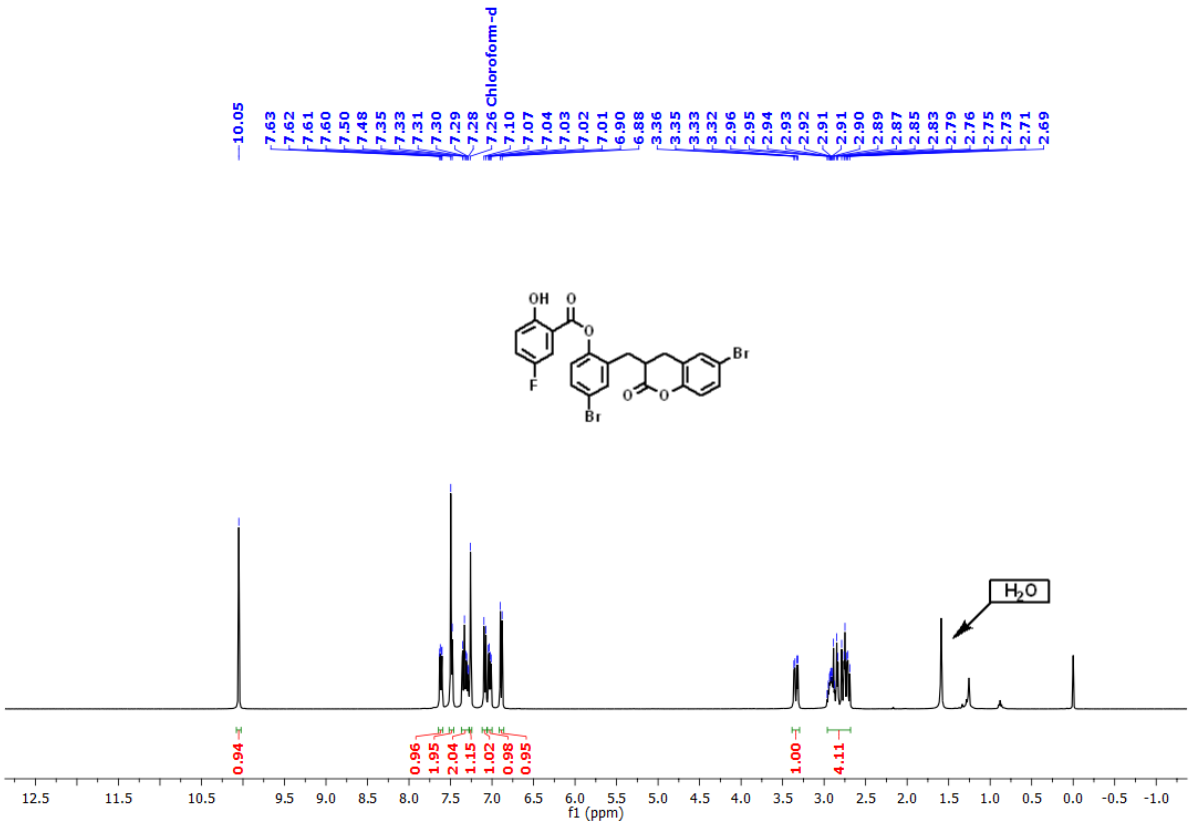


Fig. S100. ^{1}H NMR of **5aj,** 400MHz, $CDCl_3$

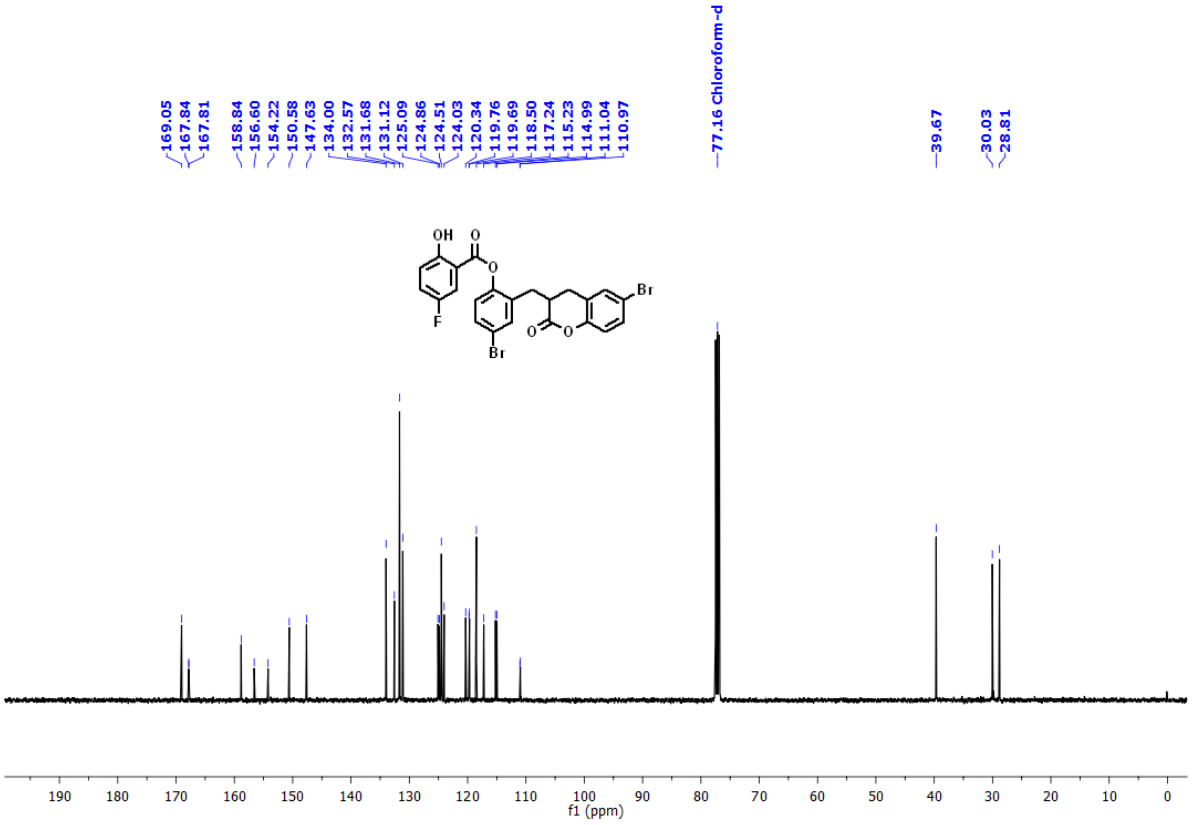


Fig. S101. ^{13}C NMR of **5aj,** 100MHz, $CDCl_3$

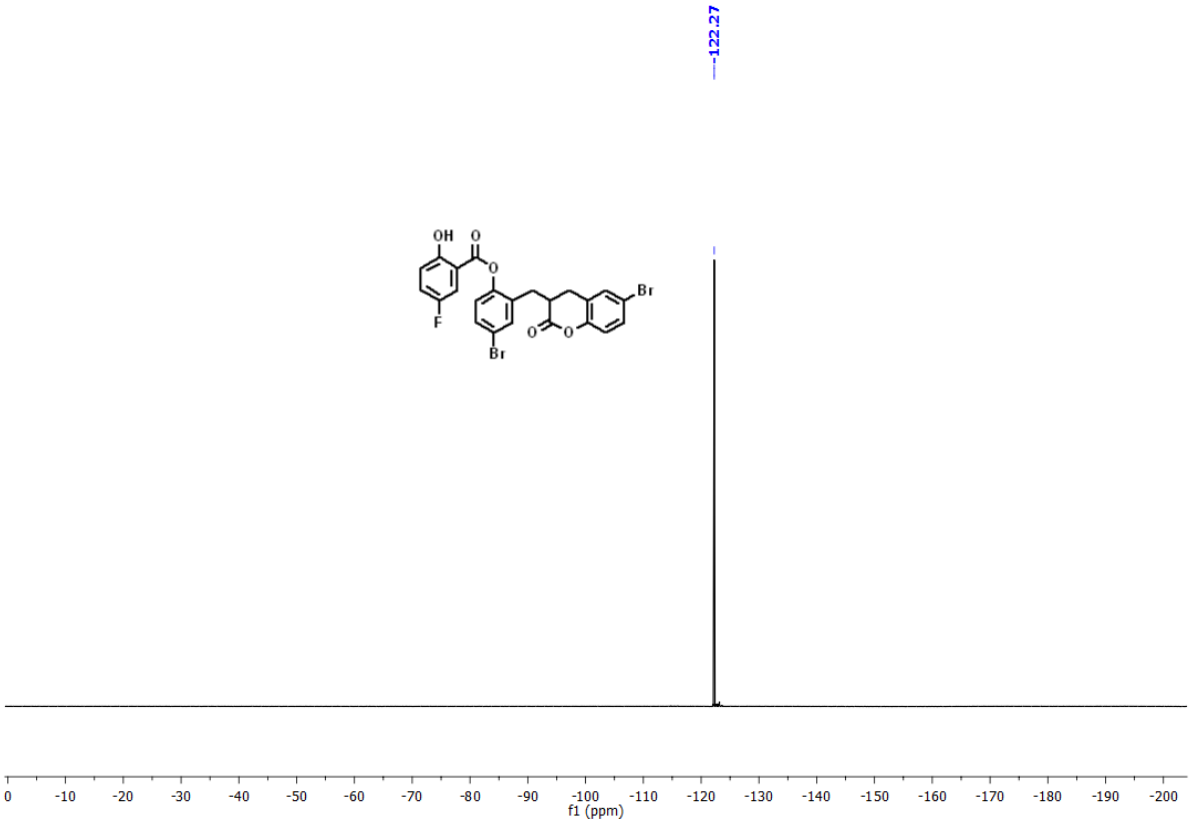


Fig. S102. ^{19}F NMR of **5aj,** 377 MHz, $CDCl_3$

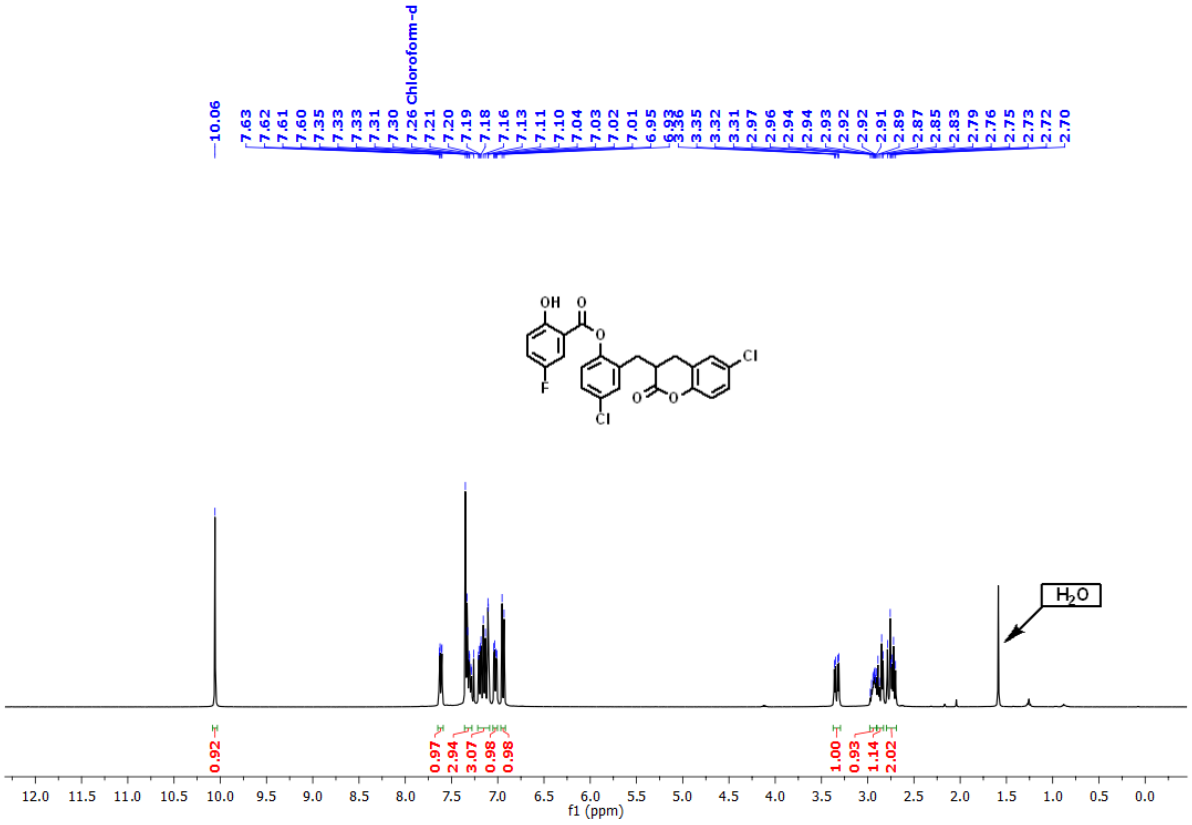


Fig. S103. ^{1}H NMR of **5ak,** 400MHz, $CDCl_3$

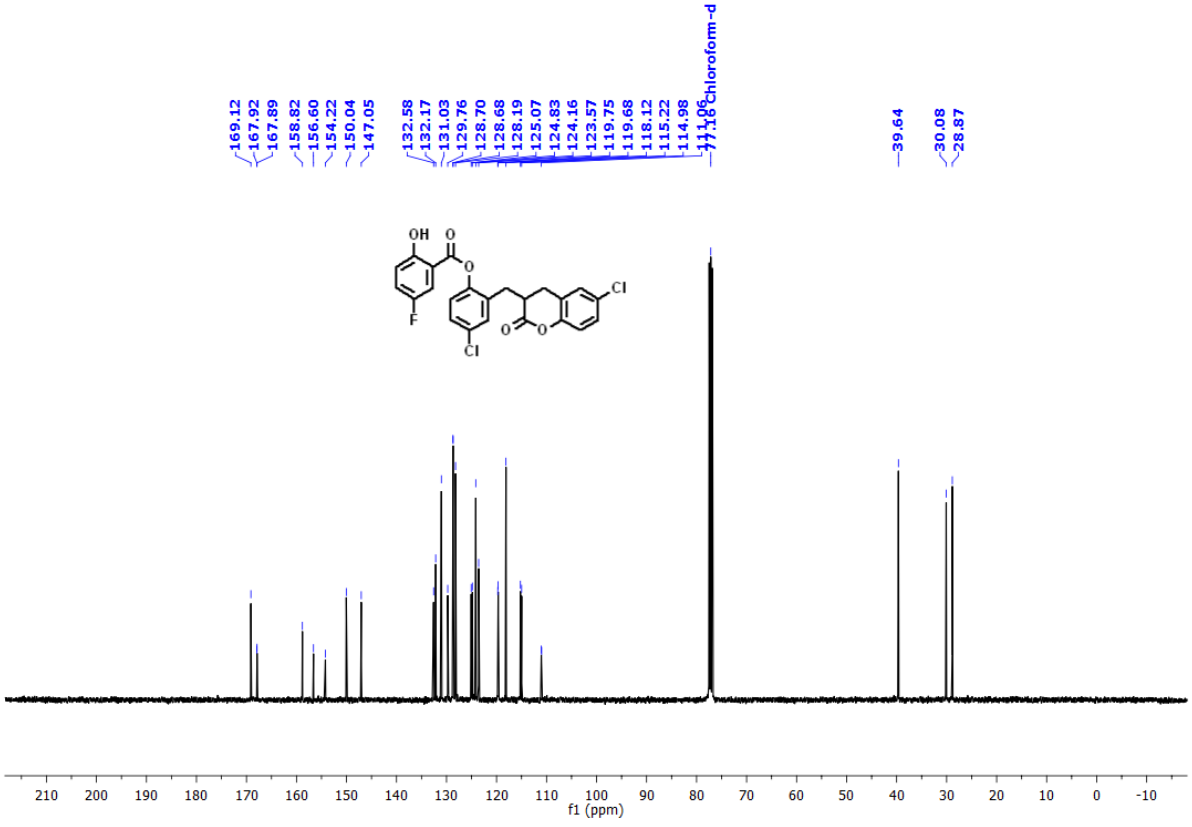


Fig. S104. ^{13}C NMR of **5ak,** 100MHz, $CDCl_3$

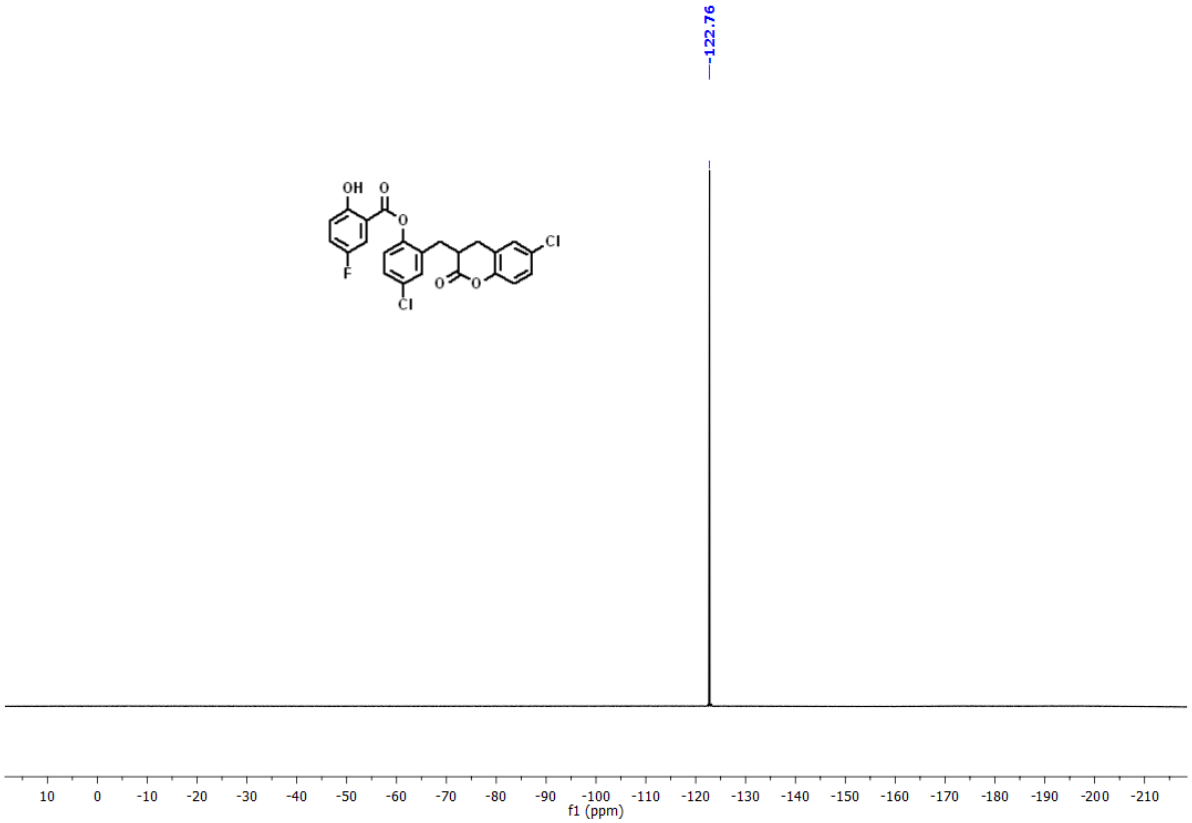


Fig. S105. ^{19}F NMR of **5ak,** 377 MHz, $CDCl_3$

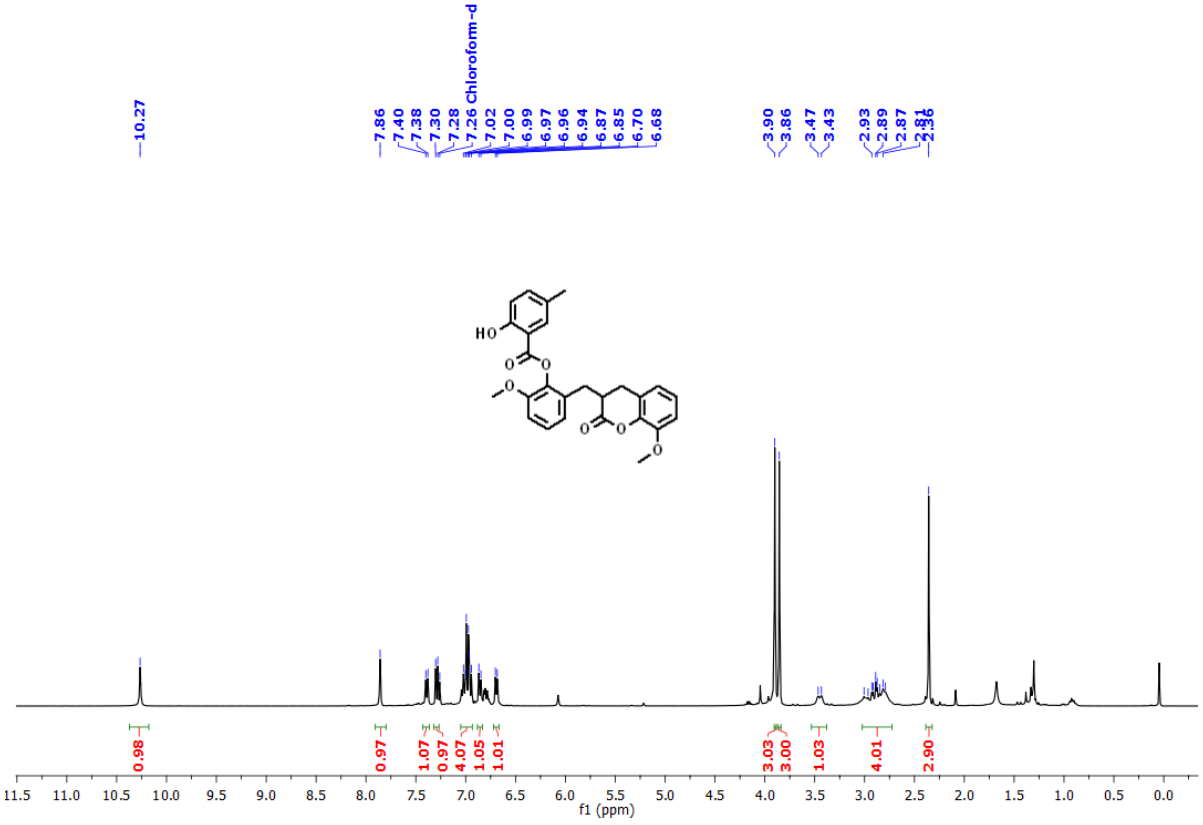


Fig. S106. ^{1}H NMR of **5al,** 400MHz, $CDCl_3$

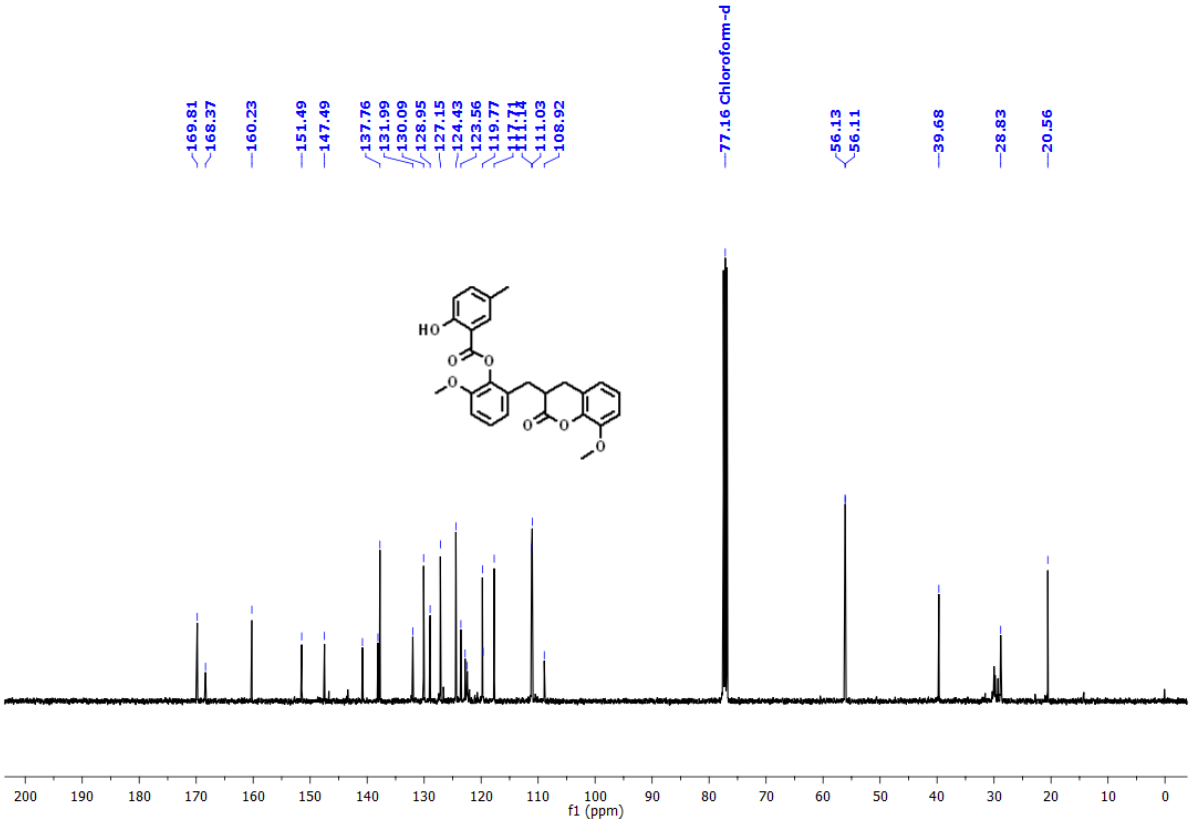


Fig. S107. ^{13}C NMR of **5al,** 100MHz, $CDCl_3$

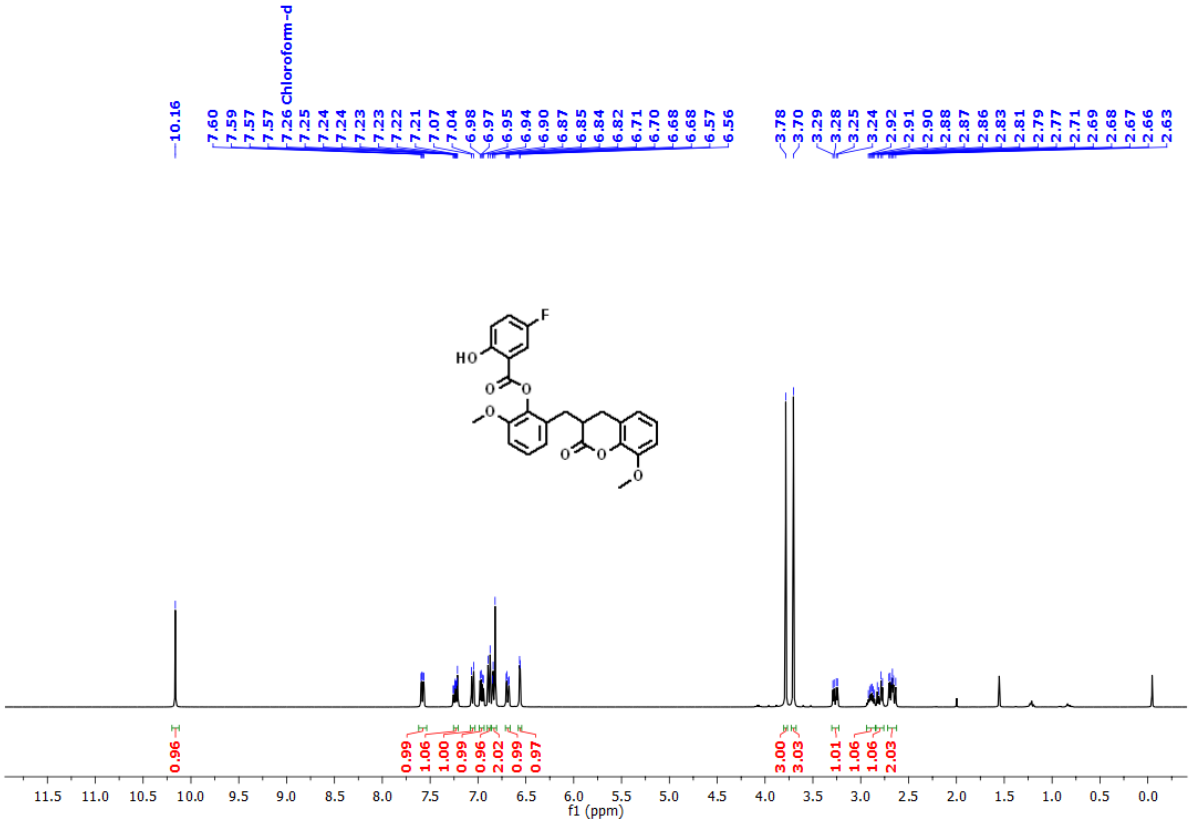


Fig. S108. ^{1}H NMR of **5am,** 400MHz, $CDCl_3$

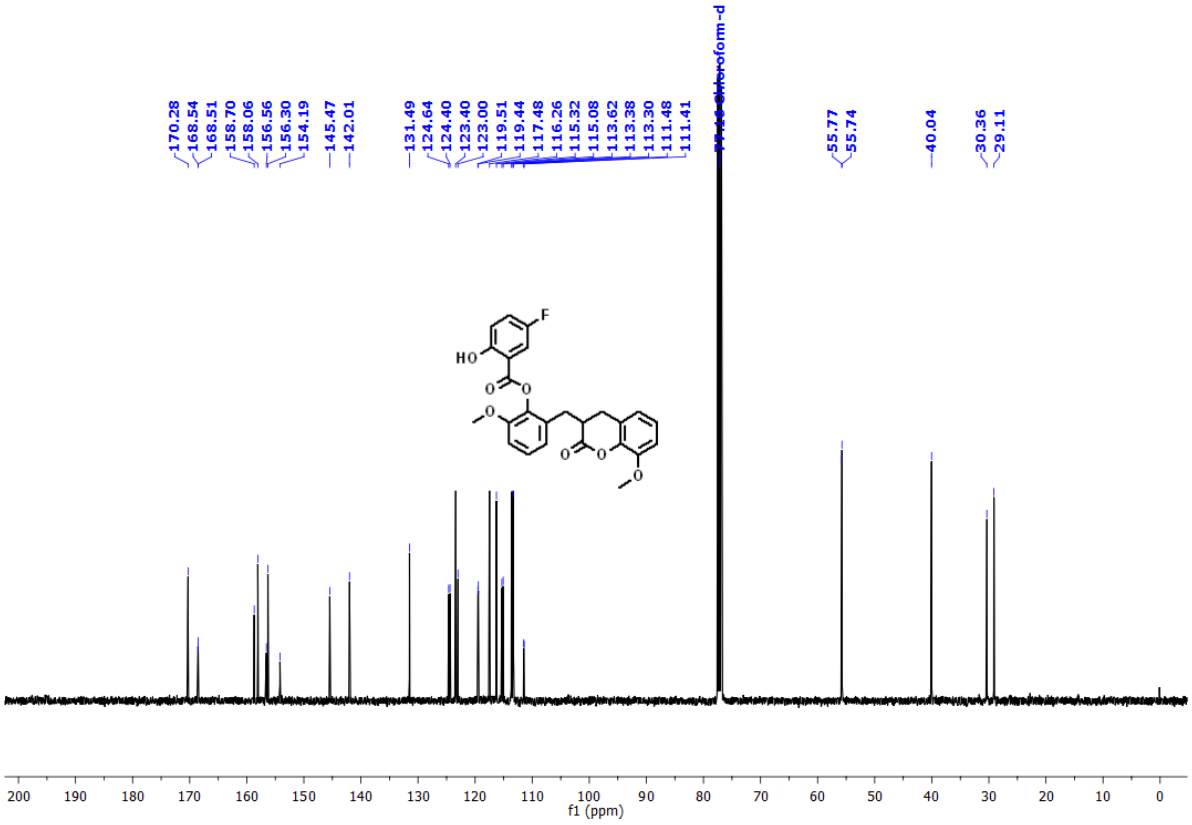


Fig. S109. ^{13}C NMR of **5am,** 100MHz, $CDCl_3$

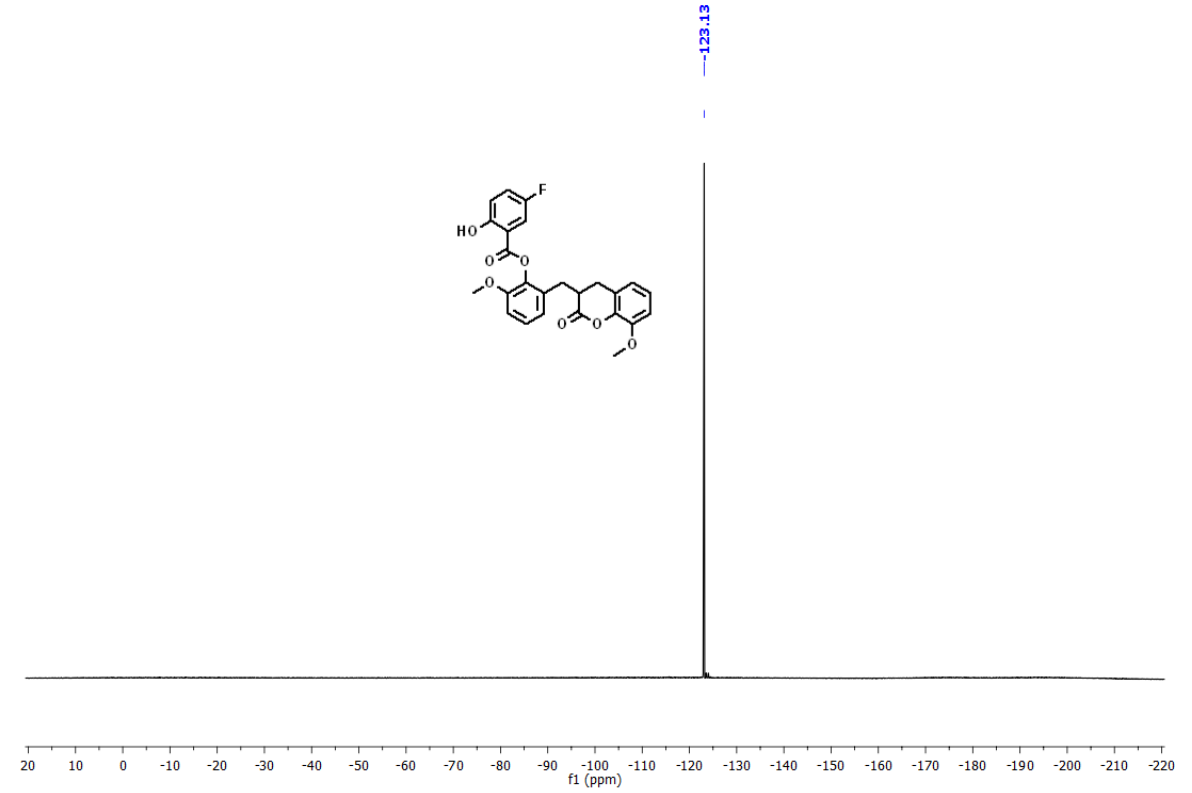


Fig. S110. ^{19}F NMR of **5am,** 377 MHz, $CDCl_3$

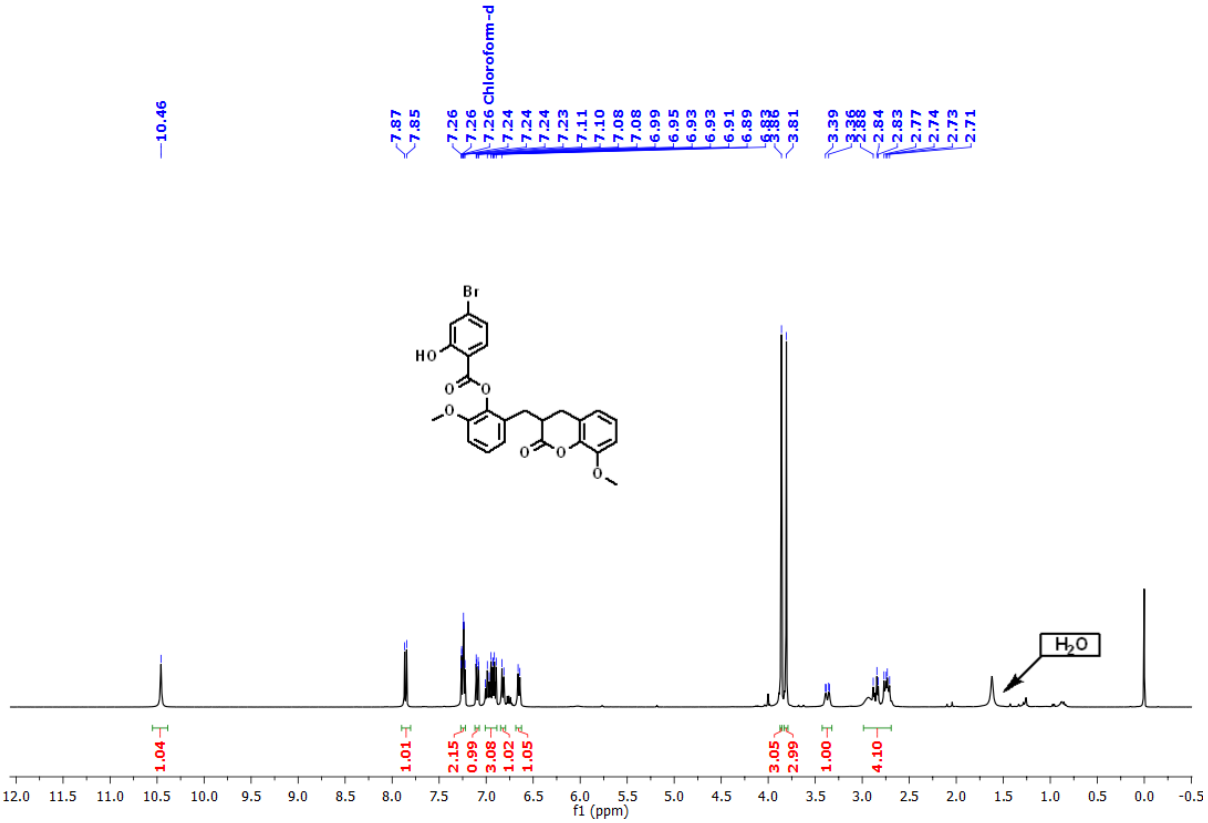


Fig. S111. ^{1}H NMR of **5an,** 400MHz, $CDCl_3$

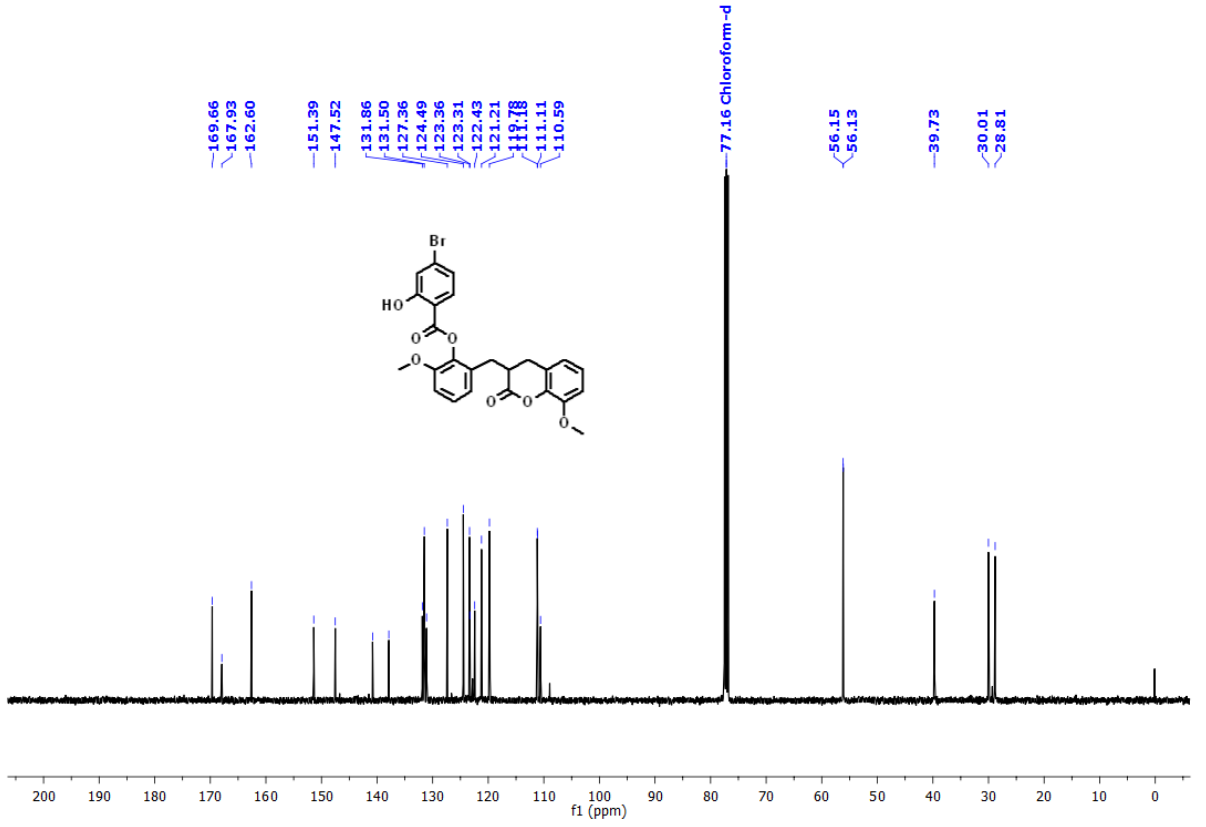


Fig. S112. ^{13}C NMR of **5an,** 100MHz, $CDCl_3$

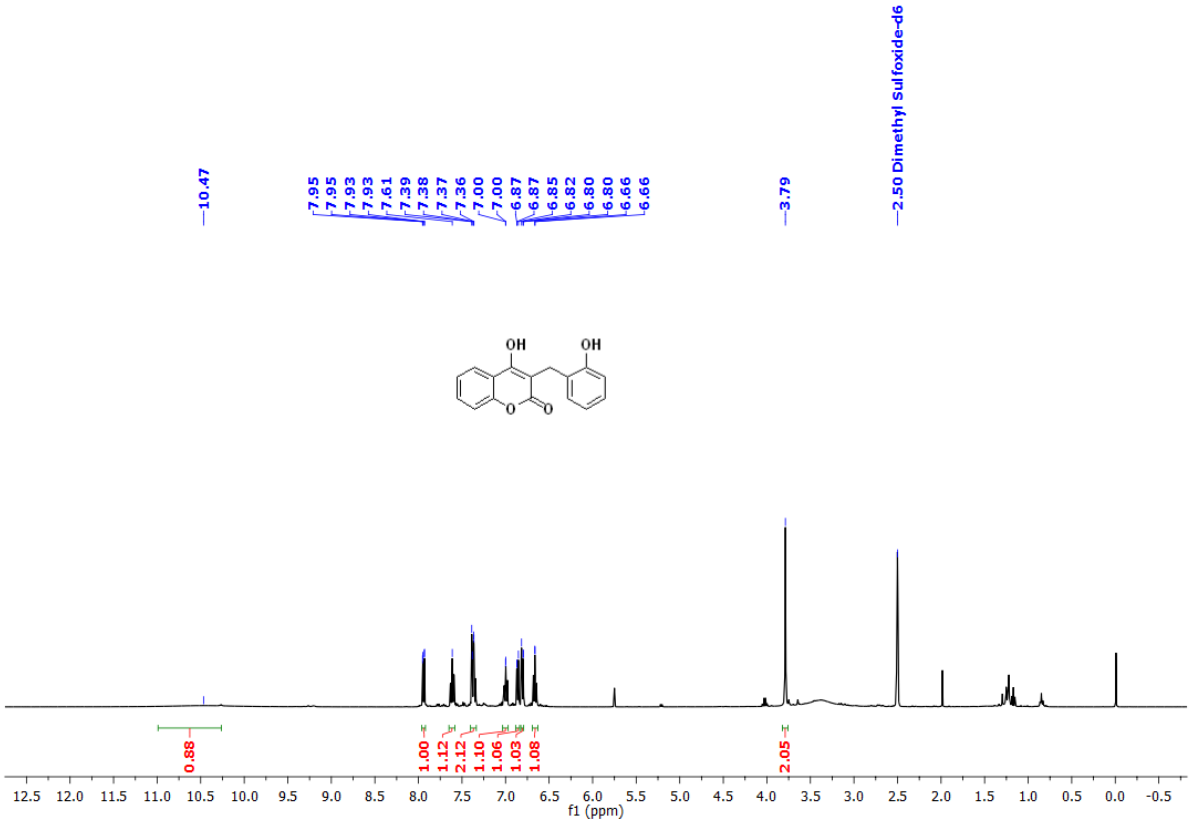


Fig. S113. ^{1}H NMR of **8a,** 400MHz, DMSO-d$_6$

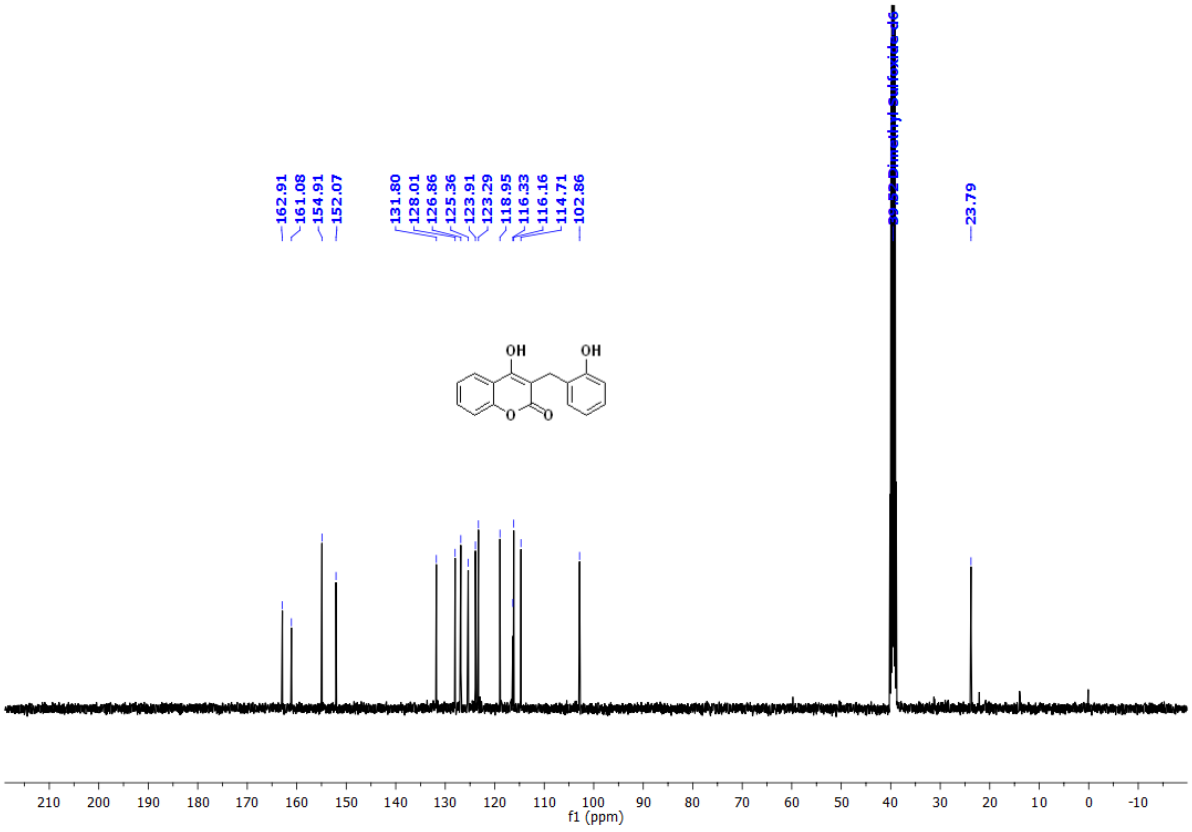


Fig. S114. ^{13}C NMR of **8a,** 100MHz, DMSO-d$_6$

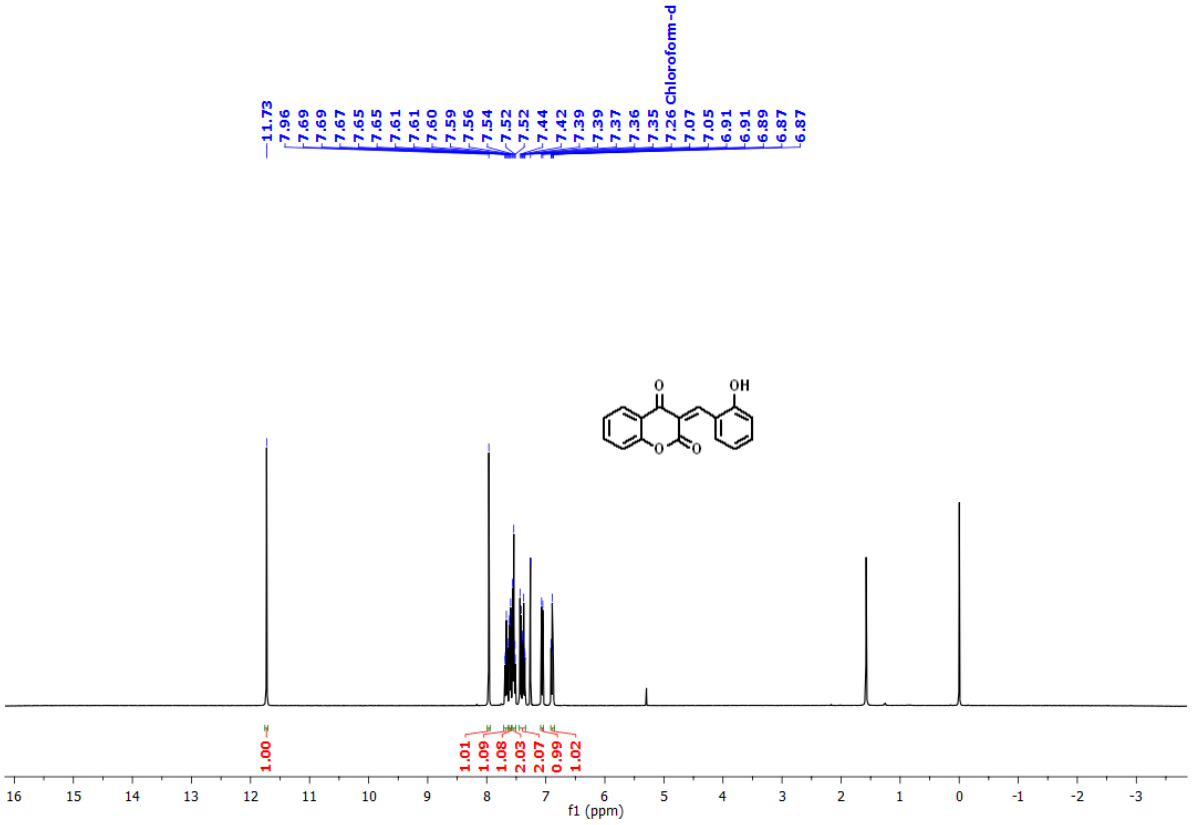


Fig. S115. ^{1}H NMR of **9a,** 400MHz, $CDCl_3$

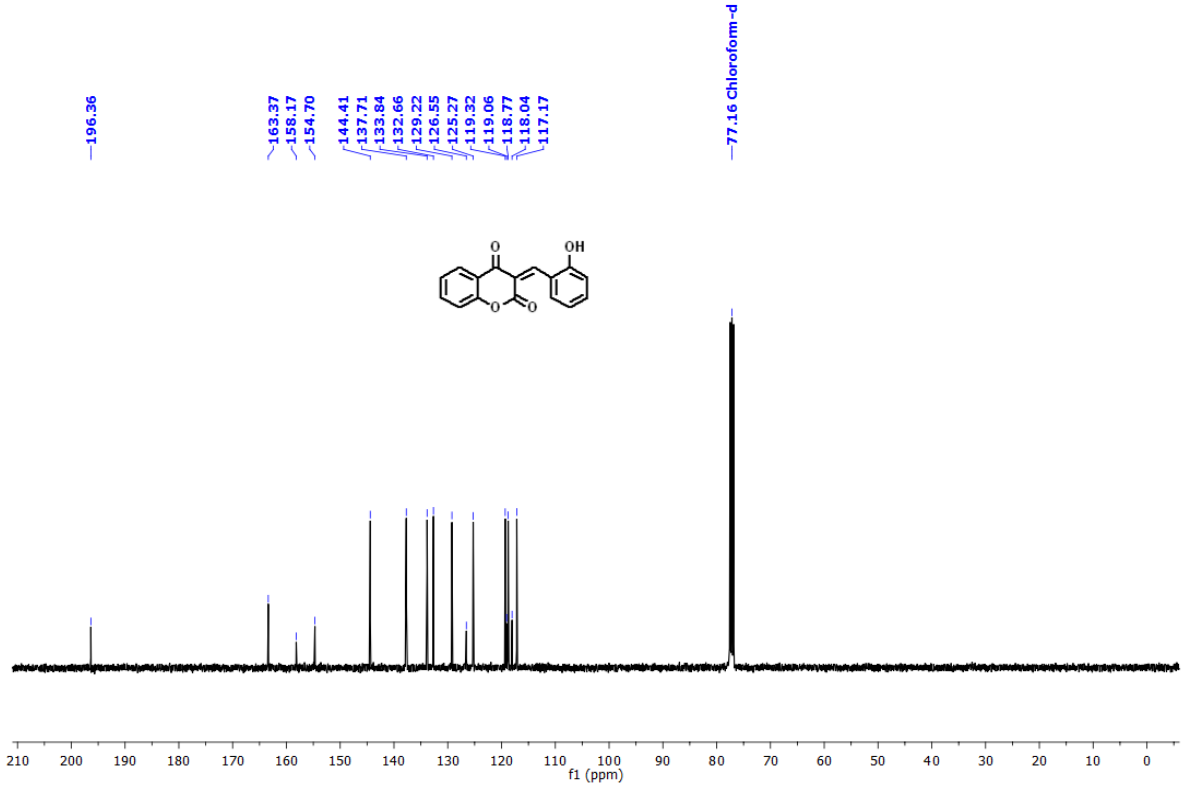


Fig. S116. ^{13}C NMR of **9a,** 100MHz, $CDCl_3$

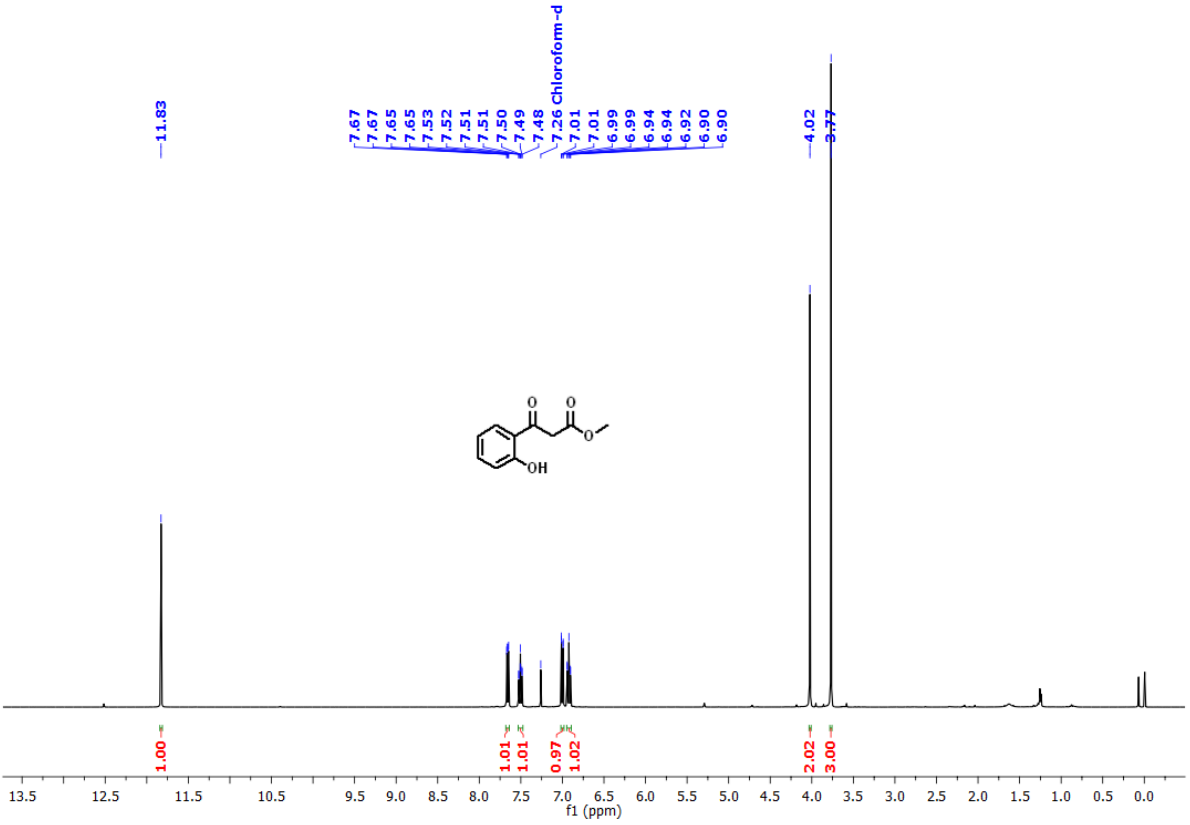


Fig. S117. ^{1}H NMR of **10,** 400MHz, $CDCl_3$

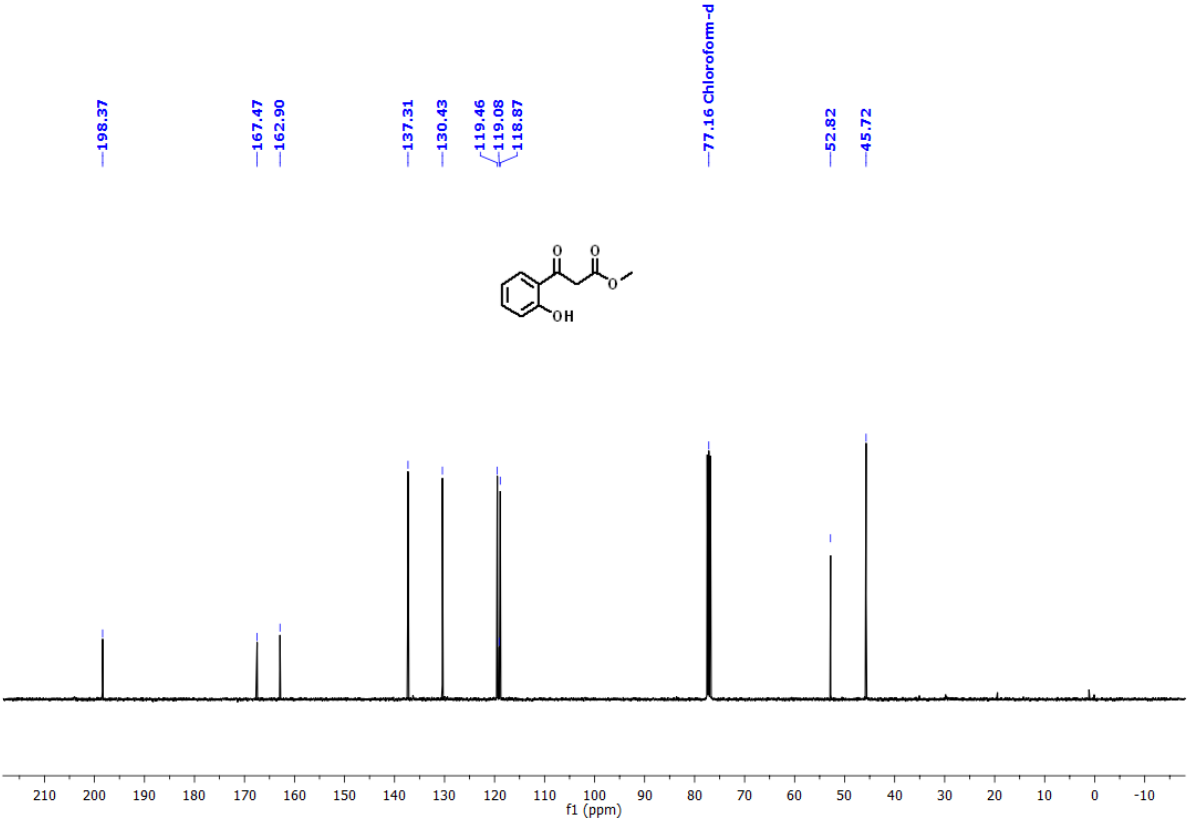


Fig. S118. ^{13}C NMR of **10,** 100MHz, $CDCl_3$

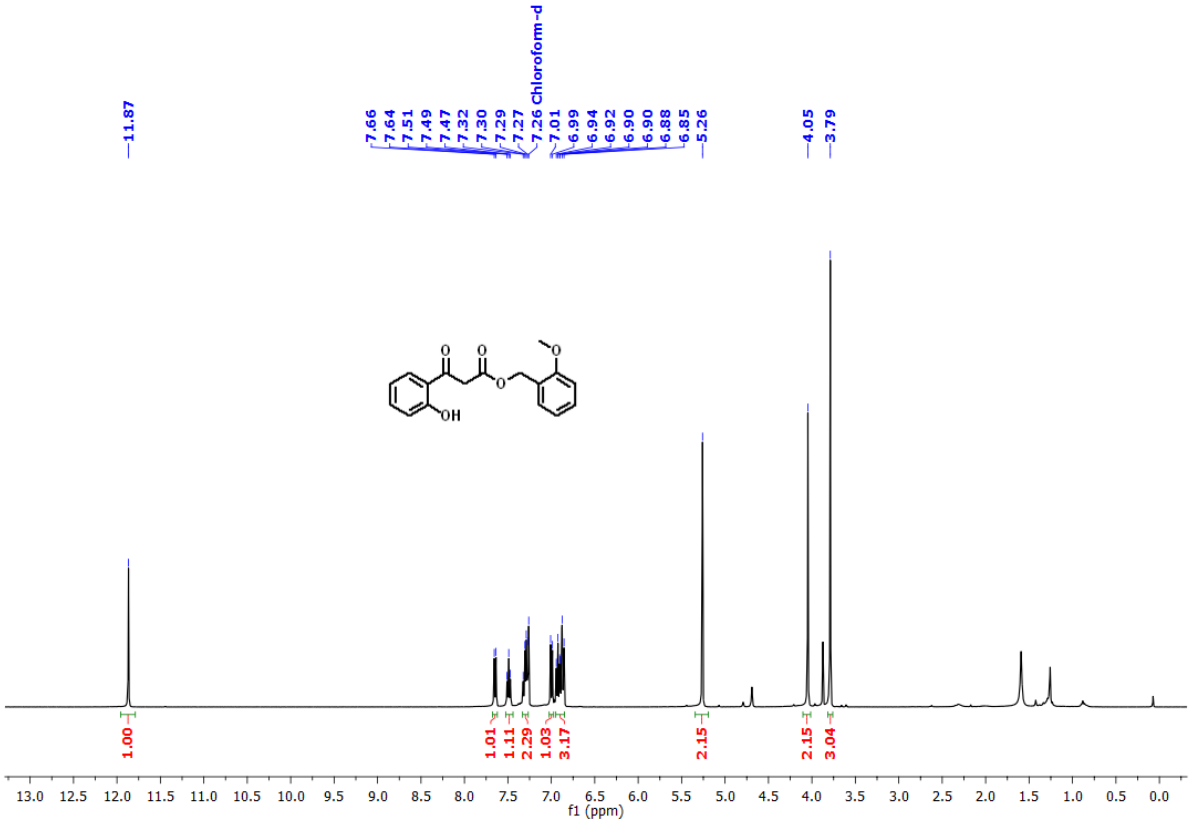


Fig. S119. ^{1}H NMR of **11,** 400MHz, $CDCl_3$

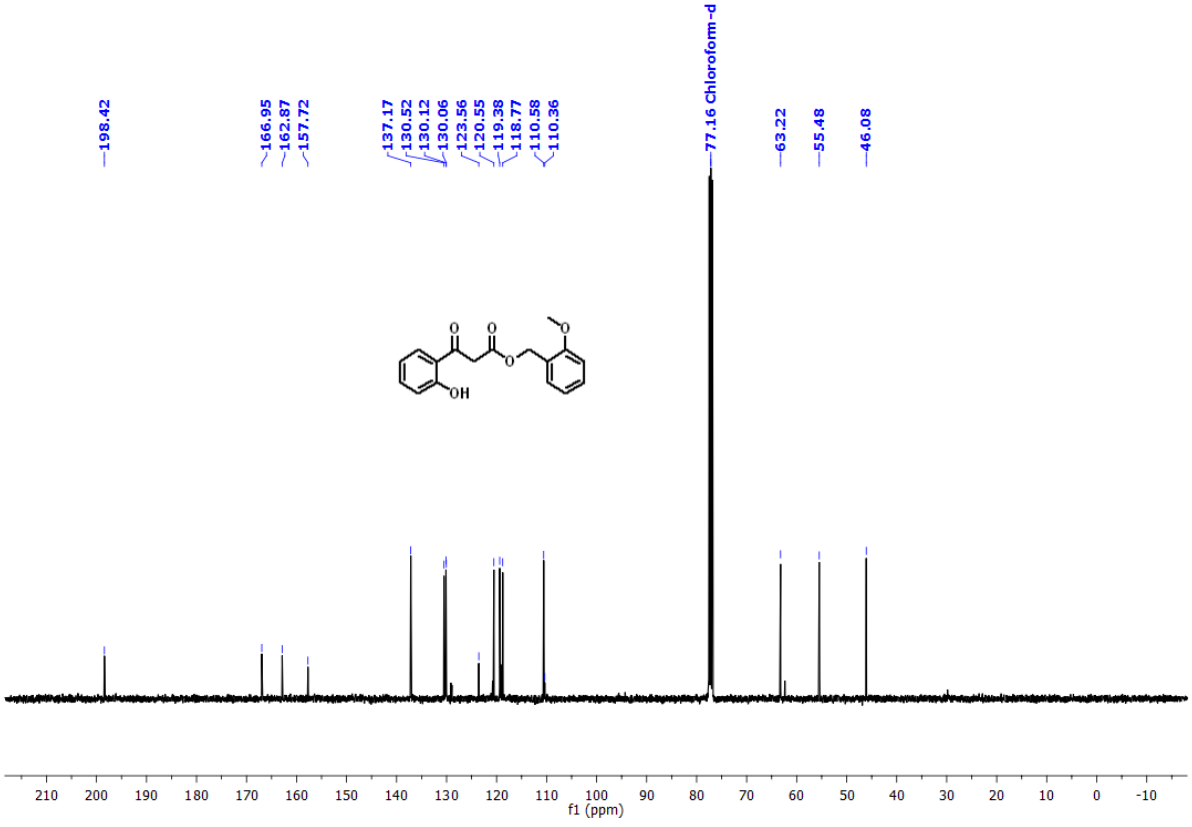


Fig. S120. ^{13}C NMR of **11,** 100MHz, $CDCl_3$

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2) Hwang, I. T. Lee, S. A. Hwang, J. S. and Lee, K. I. *Molecules*, 2011, ***16***, 6313-6321.
3) Kato, T. Maruoka, K. *Chem. Commun.* 2022, ***58***, 1021–1024.