Supporting information for

An Oxidant- and Catalyst-Free Electrooxidative Cross-Coupling Approach to 3-Tetrahydroisoquinoline Substituted Coumarins

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Experimental details and spectroscopic data

Contents

1. General Information

All reagents were used in analytical grades and were obtained from commercial sources without further purification unless otherwise noted. Coumarins were purchased from commercial suppliers and *N*-aryltetrahydroisoquinolines were prepared according to reported procedures.[1] Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light. Flash chromatography columns were packed with 200-300 mesh silica gel and silica gel was purchased from Qing Dao Hai Yang Chemical Industry. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro$^+$ and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee$^+$ were purchased from Dragon Laboratory Instruments Limited. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz relative to tetramethylsilane as internal standard (δ = 0 ppm). For the ^{19}F spectra, α-trifluorotoluene served as external standard (δ = -63.9 ppm). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). The Cyclic voltammetry (CV) was recorded in CH_3CN by CHI650A. Electrolysis was conducted using a IKA Electra 2.0 in constant current mode.

2. Experimental Procedures

General procedure for the synthesis of *N*-aryl-tetrahydroisoquinolines

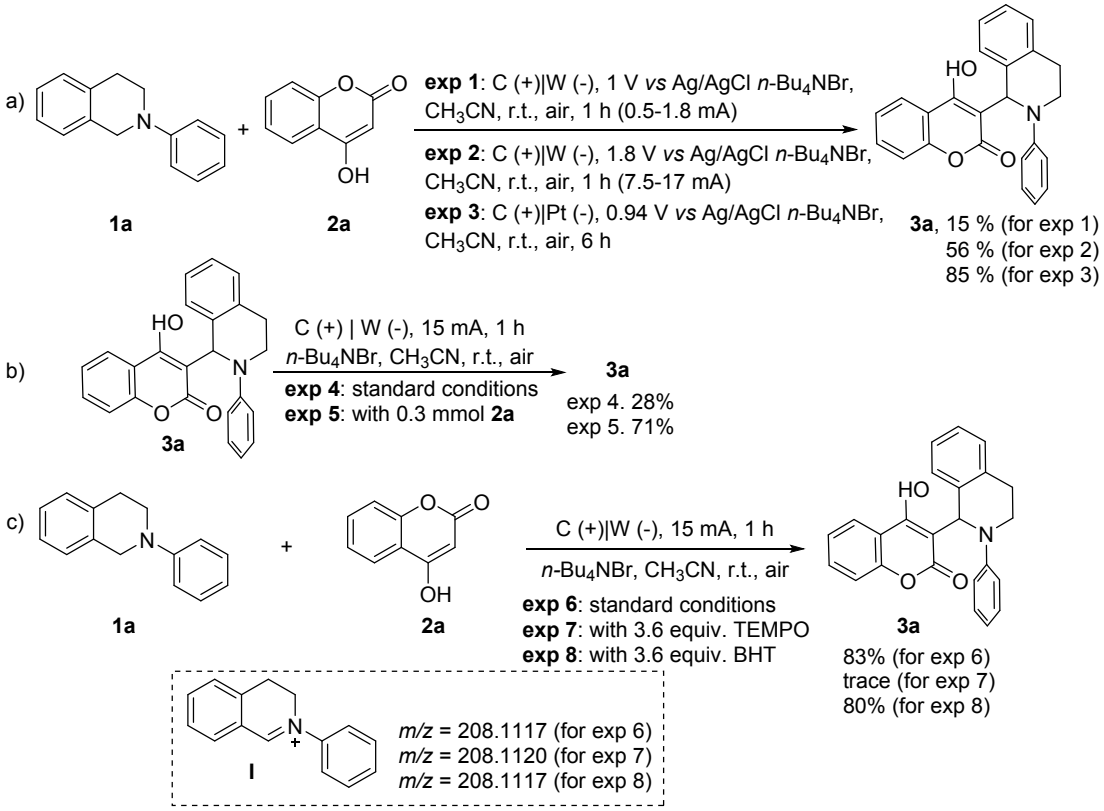
Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were added to an over-dried 50 mL three-neck flask. The flask was evacuated and back filled with Ar. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15 mmol) and iodobenzene (1.12 mL, 10.0mmol) were added successively by syringe at room temperature. The reaction mixture was heated at 85-90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:20) as an eluent to afford the desired product **1**.

General procedure for the electrochemical cross-dehydrogenative coupling of *N*-aryl-tetrahydroisoquinolines with 4-hydroxycoumarins

The ElectraSyn vial cap equipped with anode and cathode were inserted into the mixture. The Electrasyn vial cap was connected to the Electrasyn 2.0 and the reaction mixture was electrolyzed under a constant current of 15 mA by magnetic stirring (400 rpm). After the reaction, the ElectraSyn vial cap was removed, and electrodes were rinsed with DCM (3 mL),

which was combined with crude mixture. The product was purified by column chromatography on silica gel (ethylacetate/petroleum ether = 1:5 or 1:20, v/v) to give the desired product **3**.

3. Contorl Experiments



Scheme S1. Control experiments

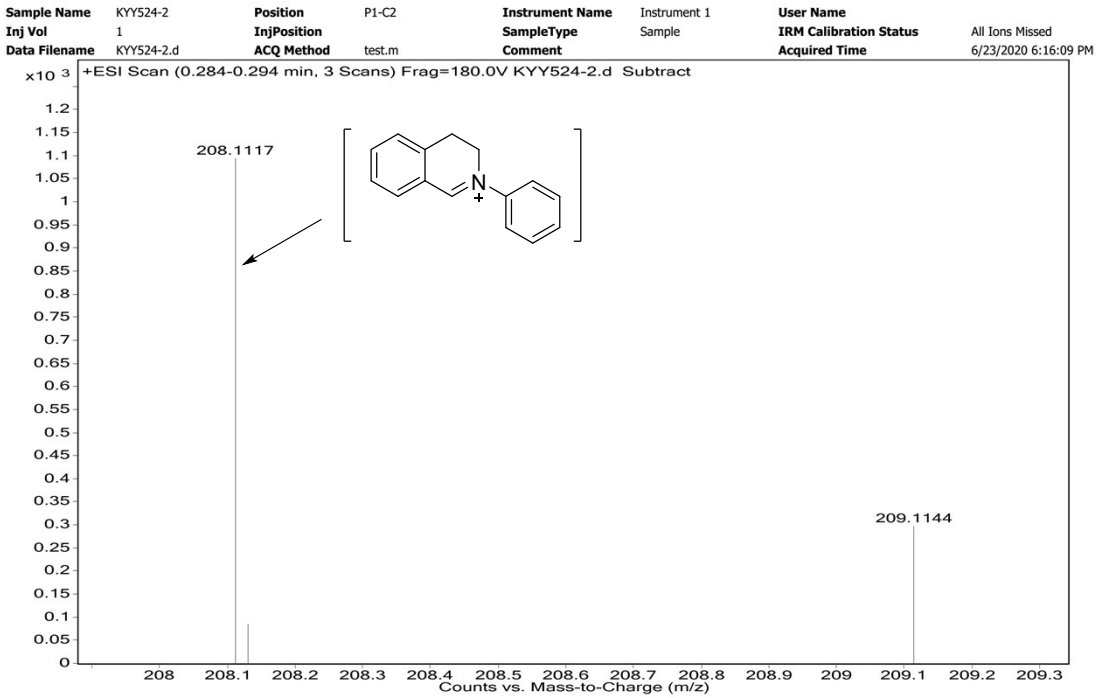


Figure S1. HRMS spectrum of compound **I** for exp 6

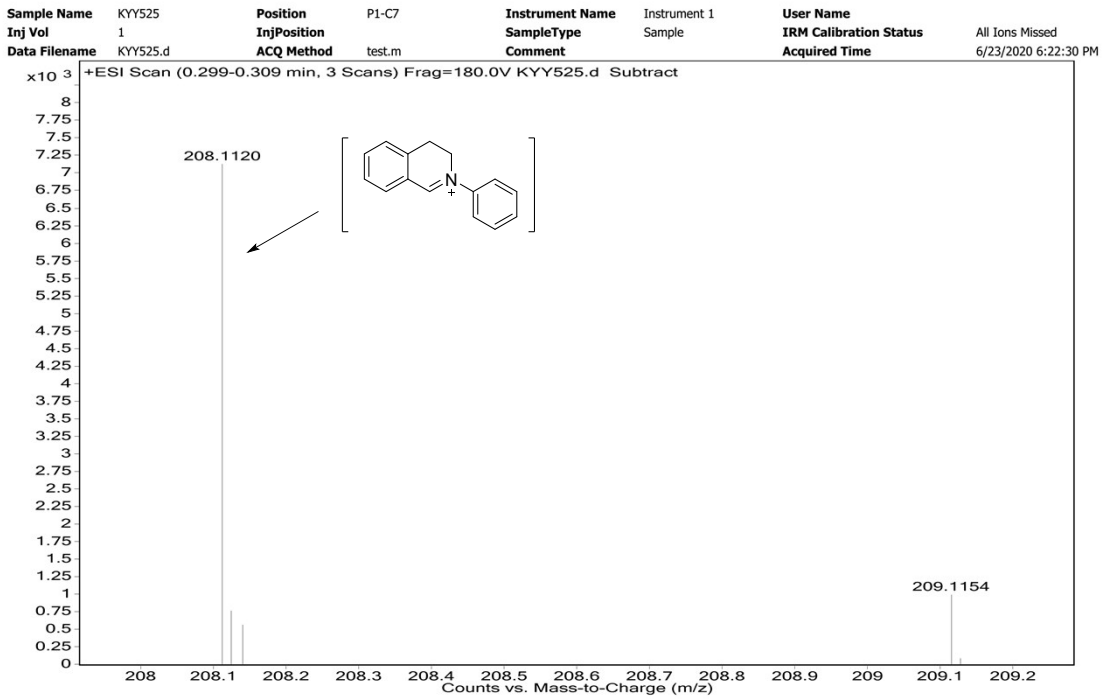


Figure S2. HRMS spectrum of compound **I** for exp 7

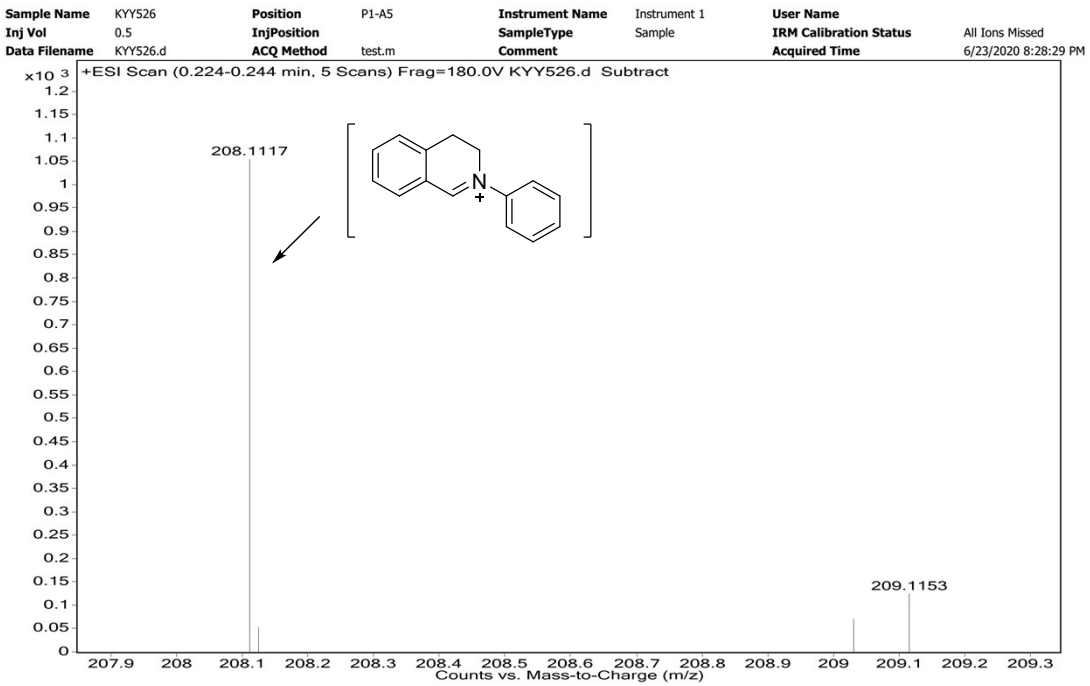


Figure S3. HRMS spectrum of compound **I** for exp 8

4. Cyclic Voltammetry Experiments

Cyclic voltammetry was measured in a glass cell with CHI 650A electrochemical workstation under Ar balloon protection with conventional three-electrode system. The working electrode was a steady glassy carbon disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 5 mL of CH_3CN containing 0.1 M *n*-Bu_4NPF_6 were poured into the electrochemical cell in all experiments. The CV of substrates (**1a**, **2a** and **3a**) were measured at the concentration of 5 mM. The scan rate was 0.1 V/s, ranging from 0 V to 2 V.

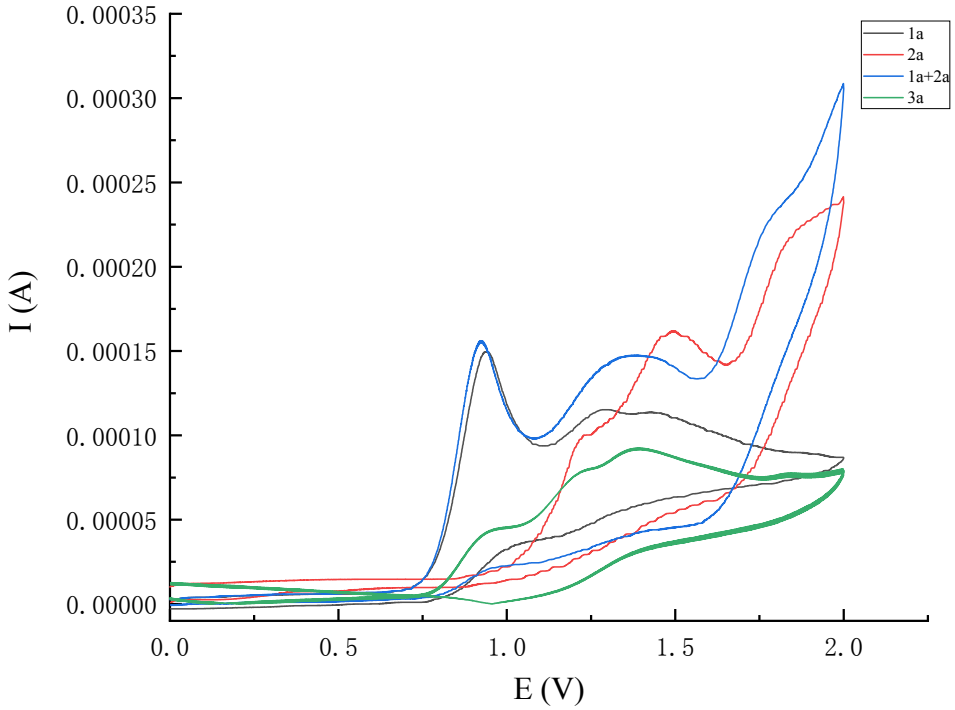


Figure S4. Cyclic voltammograms of compound **1a**, **2a** and **3a**

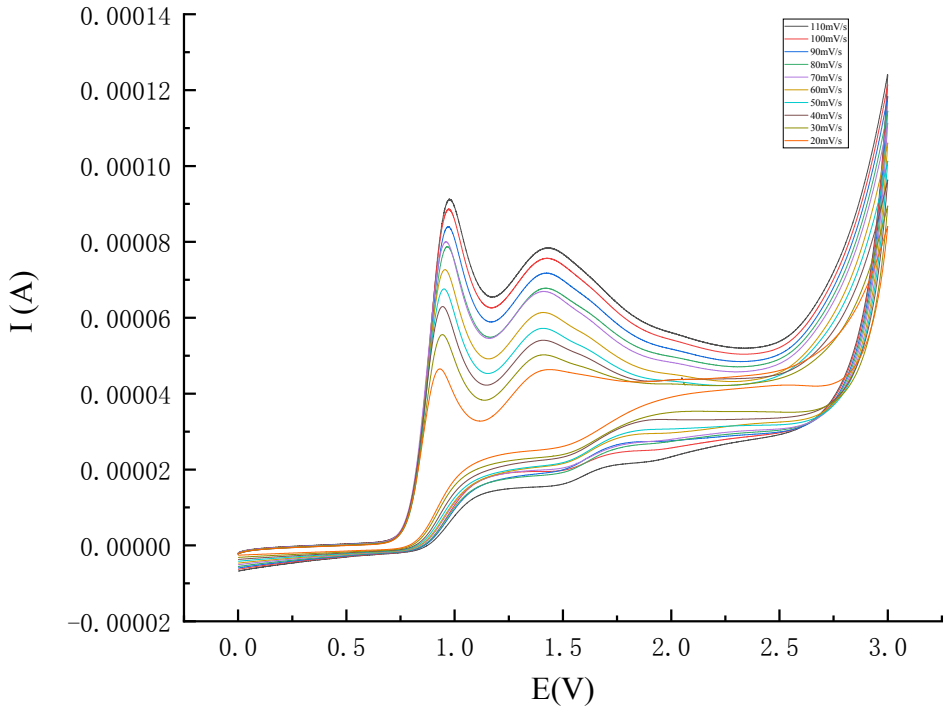


Figure S5. Cyclic voltammograms of 5 mM **1a** at different scan rates. Curves were obtained at 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 mV/s, respectively.

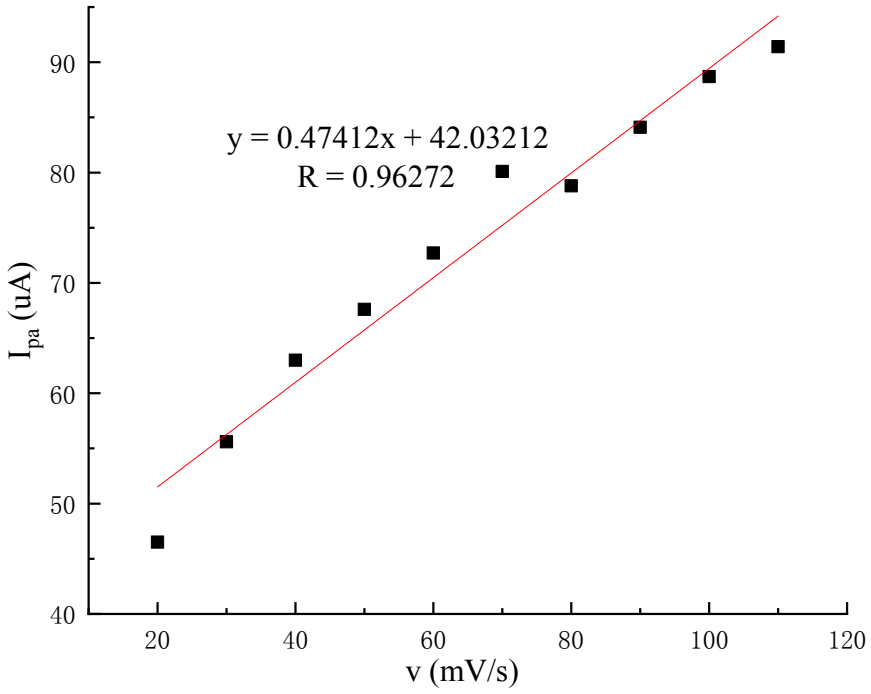


Figure S6. The plot of peak current *vs*. scan rate

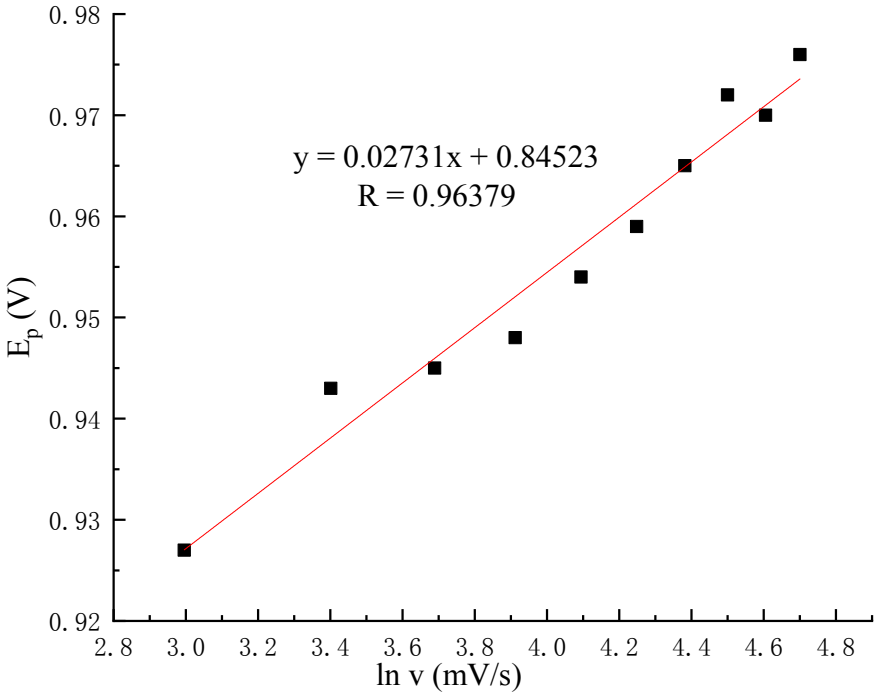


Figure S7. The relationship between E_{pa} and ln ν.

The peak current increased linearly with the scan rate in the range of 20-110 mV/s and the equation could be expressed as follows: y = 0.47412 x + 42.03212, R = 0.96272. It could be seen that the oxidation of compound **1a** was an absorption-controlled process. For an adsorption-controlled and irreversible electrode process, according to Laviron method, E_{pa} is defined by the following equation:

$E_{pa} = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln \nu$

where α is transfer coefficient, k^0 is standard rate constant of the reaction, n is electron transfer number involved in the rate-determining step, ν is scan rate, and E^0 is formal potential. Other symbols have their usual meanings. Thus, the value of α can be easily calculated from the slope of E_{pa}-ln*ν*. In this system, the slope is 0.02731. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 2.

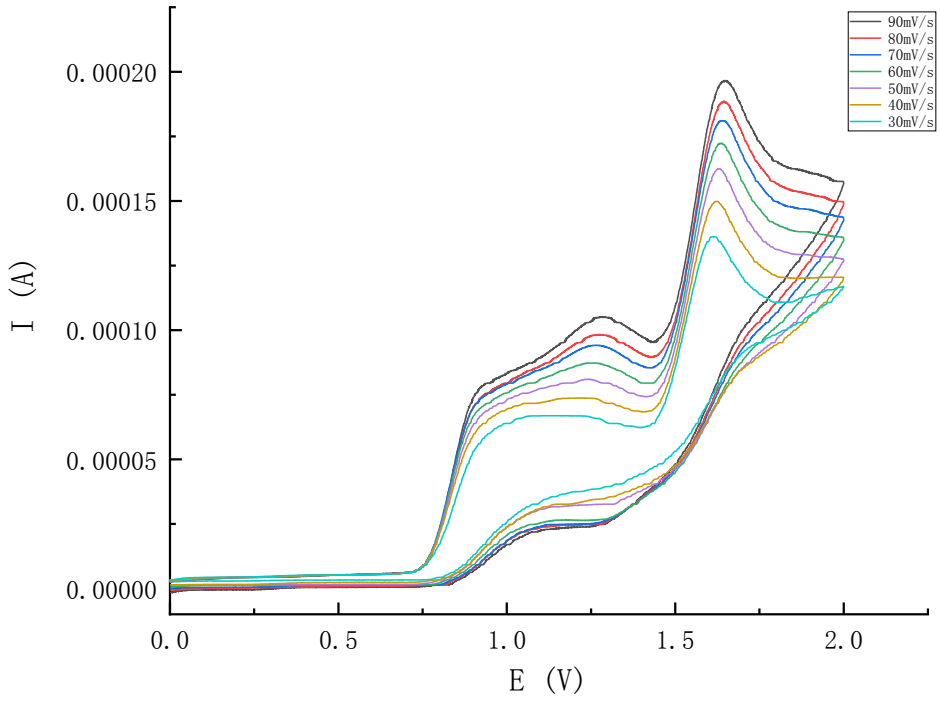


Figure S8. Cyclic voltammograms of 5 mM **2a** at different scan rates. Curves were obtained at 30, 40, 50, 60, 70, 80 and 90 mV/s, respectively.

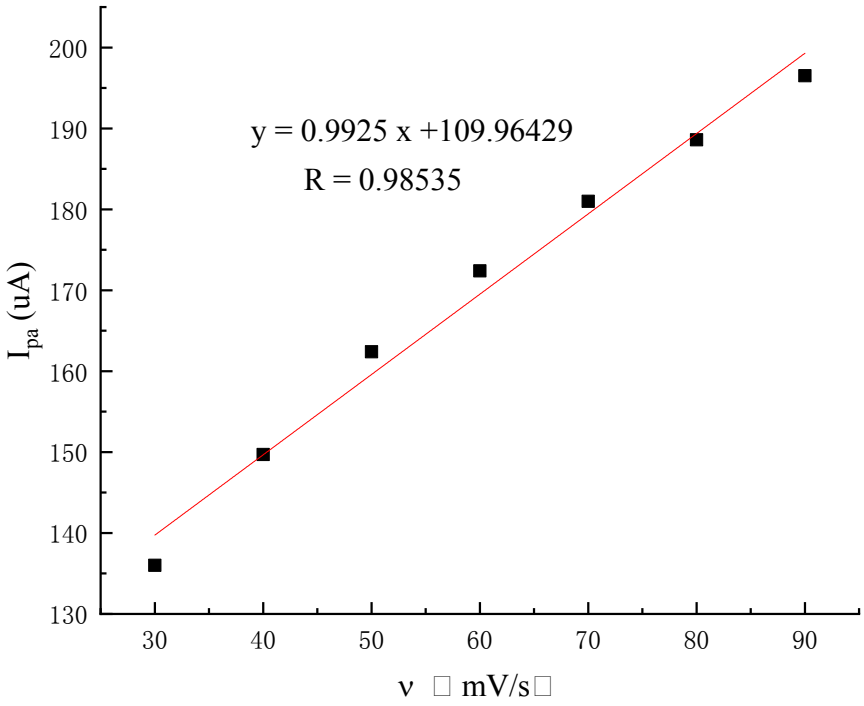


Figure S9. The plot of peak current *vs*. scan rate

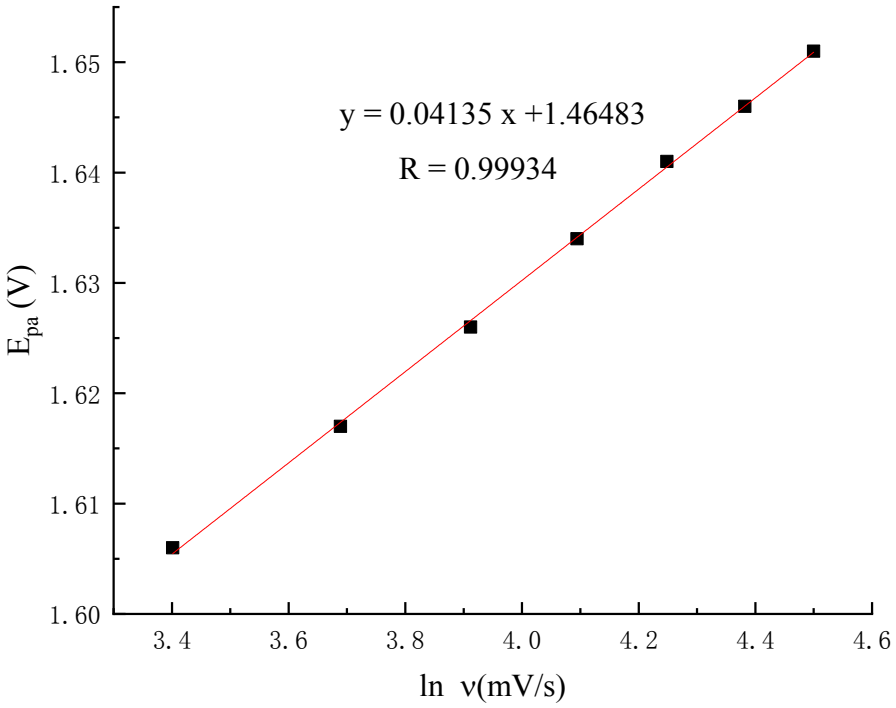


Figure S10. The relationship between E_{pa} and ln ν.

It could be seen that the oxidation of compound **2a** was an absorption-controlled process. According to Laviron method, E_{pa} is defined by the following equation:

$E_{pa} = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln \nu$

In this system, the slope of E_{pa}-lnν was 0.04135. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 1.

5. Computational Details

All the calculations were conducted by using the Gaussian 16 program package.[2] The B3LYP[3] functional together with Becke-Johnson damping corrections[4] (abbreviated as B3LYP-D3BJ) and the 6-311+G(d,p) basis sets[5] were used for all the calculations. The polarizable continuum model (PCM)[6] was employed to consider the solvent effect of CH_3CN. The intrinsic reaction coordinate (IRC)[6] analysis was carried out to confirm that all the saddle point connected the correct reactant and product on the potential energy surface. With the help of Multiwfn 3.7-dew[7] and VMD VERSION 1.9.3 program[8], we drawn and analysed **TS1**, **TS2** and **TS3**.

1a

Sum of electronic and zero-point Energies= -635.285019
Sum of electronic and thermal Energies= -635.272545
Sum of electronic and thermal Enthalpies= -635.271601
Sum of electronic and thermal Free Energies= -635.324631

C	-0.31502300	-0.76469500	0.44530500
H	-0.13981900	-0.84042800	1.53367300
C	-1.79198600	-0.53199400	0.20433000
C	-2.68983100	-1.58652800	0.41305000
H	-2.30959400	-2.55723200	0.71690100
H	-4.73993200	-2.23363400	0.39688100
C	-4.54456000	-0.15740900	-0.15798500
H	-5.60885300	-0.00513800	-0.29879300
C	-3.65622300	0.89316400	-0.36577600
H	-4.03267000	1.86557500	-0.66830400
C	-2.27688300	0.72079600	-0.18851300
C	-1.31454800	1.85969200	-0.43470400
H	-1.17494600	1.98872800	-1.51442900
H	-1.73767800	2.79673600	-0.05994900
C	0.05045700	1.62676400	0.21282000
H	0.75169600	2.36738700	-0.16970400
H	-0.01666500	1.76551800	1.30514200
N	0.53720600	0.28863200	-0.12386800
H	-0.03684900	-1.72738000	0.01858800
C	1.92827600	0.04603500	-0.06626200
C	2.84147000	0.98032000	0.45427100
C	2.44731900	-1.16100300	-0.57811300
C	4.21352200	0.72151200	0.44613100
H	2.49227200	1.91134700	0.87952700
C	3.81365800	-1.41491000	-0.57034100
H	1.77797900	-1.89500900	-1.00978700
C	4.71313300	-0.47457300	-0.06094800
H	4.89080600	1.46427200	0.85399100

H	4.17949200	-2.35060000	-0.97929700
H	5.77847000	-0.67306800	-0.06173600
C	-4.05780700	-1.40675500	0.23413100

2a

Sum of electronic and zero-point Energies=			-572.293384
Sum of electronic and thermal Energies=			-572.284585
Sum of electronic and thermal Enthalpies=			-572.283641
Sum of electronic and thermal Free Energies=			-572.327370
C	-1.95089200	0.70533600	-0.00001700
C	-0.74060100	1.33121200	-0.00000300
C	0.48326700	0.55996500	0.00000700
C	0.35797000	-0.83707000	0.00000100
O	-0.86602000	-1.44703700	-0.00001400
C	-2.05531800	-0.72711600	-0.00002300
C	1.76922800	1.12768200	0.00002200
C	2.89002000	0.31339200	0.00003000
C	2.74334900	-1.08082700	0.00002400
C	1.48213900	-1.66130000	0.00000900
O	-0.58421300	2.66458200	0.00000400
O	-3.08382600	-1.37593200	-0.00003600
H	-2.88155000	1.25816200	-0.00002500
H	1.86761100	2.20533600	0.00002600
H	3.87935800	0.75387600	0.00004200
H	3.62097600	-1.71629300	0.00003100
H	1.35116300	-2.73605300	0.00000400
H	-1.44006300	3.11442300	-0.00000300

3a

Sum of electronic and zero-point Energies=			-1206.378966
Sum of electronic and thermal Energies=			-1206.357143
Sum of electronic and thermal Enthalpies=			-1206.356199
Sum of electronic and thermal Free Energies=			-1206.430653
C	1.09356700	-0.02174700	-0.59549100
H	0.98899200	0.15737100	-1.67297400
C	2.03390000	-1.22924500	-0.46821100
C	1.65660700	-2.42444900	-1.09524000
H	0.72370400	-2.46900300	-1.64700100
H	2.14687800	-4.47378900	-1.51307300
C	3.66207000	-3.51050700	-0.31617300
H	4.29580600	-4.38800400	-0.25268900
C	4.04986000	-2.32228700	0.29396100
H	4.99278700	-2.27247000	0.82967900
C	3.24777100	-1.17573400	0.22595600

C	3.68282000	0.12027800	0.85806900
H	3.36811900	0.15476100	1.90670200
H	4.77376100	0.19933100	0.84154400
C	3.07084500	1.29651800	0.11160500
H	3.33474200	2.23182000	0.60008600
H	3.48055300	1.33974000	-0.91212100
N	1.60580400	1.18371200	0.07553100
C	0.89707100	2.39754600	-0.09043200
C	-0.02848500	2.62048100	-1.12331600
C	1.10888200	3.43966200	0.83553000
C	-0.71011300	3.83568600	-1.22241200
H	-0.22334700	1.85784300	-1.86382700
C	0.43752900	4.65078900	0.72158900
H	1.79188100	3.28635000	1.66276500
C	-0.48257400	4.86110200	-0.30939500
H	-1.41816800	3.97679000	-2.03223800
H	0.62154500	5.42985100	1.45358700
H	-1.01219900	5.80302000	-0.39224400
C	2.45791500	-3.55902600	-1.02120400
C	-0.29477100	-0.38411900	-0.06712100
C	-1.37541800	-0.51974900	-0.89656900
C	-0.44325400	-0.66094400	1.34868400
C	-2.69019000	-0.85827300	-0.38618700
C	-3.84458400	-1.00742500	-1.17738200
C	-2.80939300	-1.03681600	0.99903400
C	-5.06544100	-1.30901200	-0.59652400
H	-3.80199400	-0.89233800	-2.25503400
C	-4.03422400	-1.33884700	1.59306800
C	-5.15888400	-1.47185600	0.79195800
H	-5.94517400	-1.41964400	-1.21782000
H	-4.08210500	-1.46630200	2.66718600
H	-6.11396300	-1.70701900	1.24606600
O	-1.72802100	-0.93185300	1.81862100
O	0.43574100	-0.68664000	2.18210200
O	-1.19552200	-0.33262700	-2.22022600
H	-2.02905000	-0.37748500	-2.70407700

A2

Sum of electronic and zero-point Energies=	-634.669092
Sum of electronic and thermal Energies=	-634.656652
Sum of electronic and thermal Enthalpies=	-634.655708
Sum of electronic and thermal Free Energies=	-634.709169

C	-4.54982500	-0.15540100	0.06254000
C	-4.03166800	-1.44707600	-0.11677000

C	-2.66516900	-1.64840500	-0.21811700
C	-1.76039500	-0.55342500	-0.14145800
C	-2.29924200	0.76033400	0.00574100
C	-3.67194300	0.93513800	0.11644400
C	-0.36216100	-0.74744300	-0.23437600
N	0.54171400	0.27383700	-0.03838800
C	0.02147000	1.51533800	0.56856300
C	-1.32264700	1.90788400	-0.04227500
C	1.93450400	0.02587400	-0.01083000
C	2.44665000	-1.23323400	0.34674800
C	3.82032300	-1.46705600	0.33565400
C	4.71297400	-0.45661500	-0.01780100
C	4.21003700	0.79877000	-0.36663100
C	2.84039500	1.04017800	-0.36925200
H	-5.61875500	-0.00046800	0.15120200
H	-4.70425000	-2.29652100	-0.17059900
H	-2.27056000	-2.65135700	-0.34629100
H	-4.06941000	1.93917300	0.23359100
H	0.03938400	-1.70851500	-0.51834300
H	0.74752500	2.31216500	0.43162600
H	-0.09135000	1.34976200	1.64873700
H	-1.71414600	2.78051700	0.48697100
H	-1.16160100	2.21246300	-1.08476300
H	1.77634700	-2.02392700	0.65789500
H	4.19136700	-2.44518800	0.62136000
H	5.78060400	-0.64160500	-0.02159800
H	4.88743000	1.59518100	-0.65402700
H	2.47558300	2.01229900	-0.67612100

A

Sum of electronic and zero-point Energies=	-635.090960
Sum of electronic and thermal Energies=	-635.078487
Sum of electronic and thermal Enthalpies=	-635.077543
Sum of electronic and thermal Free Energies=	-635.131577

C	-0.38611700	-0.93405100	0.72990000
H	-0.42426800	-1.21913400	1.78873300
C	-1.77621200	-0.56012800	0.23407800
C	-2.71729900	-1.58843500	0.11100700
H	-2.44042800	-2.60506400	0.37092200
H	-4.72438500	-2.12016900	-0.43564400
C	-4.35611600	-0.00908800	-0.68330100
H	-5.35593600	0.21114800	-1.03907800
C	-3.42236100	1.01356200	-0.55793100
H	-3.69641700	2.03127900	-0.81527900

C	-2.12567300	0.75232300	-0.09796800
C	-1.11331100	1.86493000	0.03638700
H	-0.68834400	2.11882100	-0.94035200
H	-1.58663900	2.77055200	0.42284100
C	0.00982400	1.46915500	0.99607500
H	0.78681800	2.22159100	1.05571300
H	-0.39257600	1.32670400	2.00401400
N	0.57579000	0.17010400	0.60157000
H	-0.02943800	-1.78952800	0.16493000
C	1.86336100	-0.00813800	0.20204900
C	2.68444100	1.10977300	-0.14711800
C	2.43195300	-1.31817300	0.12560300
C	3.98592200	0.91473700	-0.55336100
H	2.28346800	2.11173900	-0.13817800
C	3.74078400	-1.48482500	-0.26910300
H	1.85885300	-2.18429900	0.41946500
C	4.52887500	-0.37704200	-0.61574000
H	4.58862800	1.76915400	-0.83369500
H	4.16329400	-2.48097700	-0.30160600
H	5.55512600	-0.51908000	-0.93069300
C	-4.00278600	-1.31684500	-0.34442400

A1

Sum of electronic and zero-point Energies=			-634.531842
Sum of electronic and thermal Energies=			-634.519744
Sum of electronic and thermal Enthalpies=			-634.518799
Sum of electronic and thermal Free Energies=			-634.570852
C	-4.50159300	-0.22055200	0.02869500
C	-3.96811300	-1.48567500	-0.23184500
C	-2.59472500	-1.63773100	-0.35175400
C	-1.75650900	-0.51974400	-0.18972900
C	-2.29468800	0.76203200	0.05915200
C	-3.67277700	0.89664300	0.16493300
C	-0.33426000	-0.67338700	-0.29735800
N	0.51178300	0.25236200	0.05590300
C	0.01383000	1.51651200	0.67446400
C	-1.33668300	1.92481100	0.10139900
C	1.93635100	0.01783100	0.01811500
C	2.45915700	-1.12163300	0.62921700
C	3.83269600	-1.34897500	0.57793900
C	4.66980100	-0.44309600	-0.07119000
C	4.13433200	0.69659800	-0.67247300
C	2.76395700	0.93584600	-0.62900400
H	-5.57478500	-0.10044700	0.12027400

H	-4.62249200	-2.34112000	-0.34188300
H	-2.16201000	-2.61048200	-0.55439000
H	-4.10685000	1.87246600	0.34943600
H	0.08203500	-1.59756800	-0.68247500
H	0.76314100	2.28574700	0.50759700
H	-0.04232000	1.32437200	1.75034300
H	-1.73657600	2.74246600	0.70290100
H	-1.20494000	2.31114100	-0.91628500
H	1.80710400	-1.80819600	1.15547500
H	4.24543200	-2.22869100	1.05649300
H	5.73777700	-0.62179000	-0.10589100
H	4.78157300	1.39905700	-1.18319600
H	2.34577500	1.80962600	-1.11308300

C

Sum of electronic and zero-point Energies=			-1206.802916
Sum of electronic and thermal Energies=			-1206.781359
Sum of electronic and thermal Enthalpies=			-1206.780415
Sum of electronic and thermal Free Energies=			-1206.854789
C	-1.11989700	4.48788000	0.19705600
C	-1.58069300	3.53434400	1.10352700
C	-0.93906300	2.30525400	1.20115000
C	0.16555100	1.99798000	0.39286700
C	0.64587700	2.96925500	-0.49749000
C	-0.00979700	4.20274900	-0.58687900
C	0.82790800	0.62652000	0.55279800
N	1.91071600	0.39429500	-0.50760300
C	2.74753000	1.63659200	-0.75941600
C	1.86345200	2.71371100	-1.35206700
C	2.75945800	-0.79440500	-0.24548000
C	3.50973200	-0.86991100	0.92402900
C	4.32330100	-1.98244200	1.12516900
C	4.38363500	-2.99467000	0.16739100
C	3.63136100	-2.89740800	-1.00106100
C	2.81299300	-1.78938700	-1.21595500
C	-0.15256300	-0.57674600	0.46875500
C	-0.99456900	-0.56822100	-0.80596000
C	-2.34812900	-1.09470500	-0.70552300
C	-2.85827700	-1.46487600	0.54543400
O	-2.13882000	-1.33222600	1.72266100
C	-0.88327400	-0.81975400	1.78065900
C	-3.16295400	-1.24596800	-1.84174300
C	-4.44314500	-1.75728500	-1.72196000
C	-4.92801400	-2.12325900	-0.45947700

C	-4.14184600	-1.97829000	0.67854700
O	-0.48181000	-0.17701100	-1.84835000
O	-0.38057600	-0.64478800	2.85688700
H	-1.61287800	5.44921100	0.11353500
H	-2.43229500	3.74536600	1.73903900
H	-1.30175100	1.59899000	1.93547100
H	0.36877000	4.94660600	-1.27966500
H	1.33191100	0.57214800	1.51695000
H	3.54643400	1.33909900	-1.43547600
H	3.17988300	1.93247700	0.19594600
H	2.45603300	3.62633900	-1.44438600
H	1.56787500	2.43436200	-2.37004500
H	3.47525400	-0.08724500	1.67151200
H	4.91050900	-2.05314200	2.03231000
H	5.01857200	-3.85675200	0.33212200
H	3.67714100	-3.67883400	-1.74936000
H	2.23146600	-1.70739400	-2.12734300
H	0.45918400	-1.48941600	0.38313900
H	-2.76099500	-0.95744200	-2.80479100
H	-5.06738300	-1.87595600	-2.59837500
H	-5.92951300	-2.52466400	-0.36171600
H	-4.50745400	-2.25238900	1.65961800
H	1.37241700	0.20902100	-1.37107100

TS1

Sum of electronic and zero-point Energies=	-1206.774338
Sum of electronic and thermal Energies=	-1206.752711
Sum of electronic and thermal Enthalpies=	-1206.751767
Sum of electronic and thermal Free Energies=	-1206.826170

C	-2.20255300	3.55934500	0.38211900
C	-1.91861600	2.90728400	1.58234400
C	-0.93365600	1.92598700	1.61796200
C	-0.23461000	1.57940000	0.45348800
C	-0.50027600	2.25338000	-0.74799000
C	-1.48737100	3.24062700	-0.76978900
C	0.81165900	0.50614300	0.51793500
N	1.77955200	0.50210000	-0.51187300
C	1.76081500	1.59294100	-1.52523200
C	0.34042100	1.93086700	-1.95742000
C	3.08296200	-0.03792300	-0.21585900
C	3.71267300	0.17248000	1.01583200
C	4.97536700	-0.36691300	1.25578500
C	5.62737300	-1.10565600	0.27024600
C	5.00920900	-1.30265400	-0.96423800

C	3.74407300	-0.77482900	-1.20642900
C	0.08849400	-1.13292700	0.56340400
C	-0.65765800	-1.35684400	-0.65122000
C	-2.07106900	-1.40779300	-0.64723200
C	-2.72200100	-1.37875500	0.60649000
O	-2.03321300	-1.31710500	1.78678700
C	-0.66138000	-1.28836500	1.84199000
C	-2.84932700	-1.49700300	-1.82753500
C	-4.22296200	-1.54674000	-1.74157700
C	-4.84641300	-1.51399100	-0.48163200
C	-4.10647200	-1.43383500	0.69137800
O	-0.02712100	-1.43167100	-1.79185800
O	-0.13367500	-1.33217600	2.91992200
H	-2.96516700	4.32879300	0.34861300
H	-2.45179600	3.16999400	2.48807500
H	-0.69780300	1.44006800	2.55817400
H	-1.68516900	3.77211500	-1.69435900
H	1.23989300	0.44201800	1.51609100
H	2.35534100	1.26494400	-2.37652500
H	2.24481700	2.47985300	-1.09866100
H	0.37427000	2.78760400	-2.63337400
H	-0.09057900	1.10035700	-2.52571500
H	3.23953800	0.77058400	1.78482500
H	5.45278600	-0.19510800	2.21334000
H	6.61015800	-1.52037200	0.46023200
H	5.50626000	-1.87386200	-1.73932600
H	3.27615700	-0.93375900	-2.17181800
H	1.01228700	-1.70837700	0.61706900
H	-2.34795700	-1.52193600	-2.78591100
H	-4.82351100	-1.61123300	-2.63936800
H	-5.92717100	-1.55426900	-0.41933600
H	-4.58163200	-1.41376900	1.66315400
H	0.92239800	-1.23609000	-1.67778300

Hradical

Sum of electronic and zero-point Energies=	-0.502177
Sum of electronic and thermal Energies=	-0.500761
Sum of electronic and thermal Enthalpies=	-0.499817
Sum of electronic and thermal Free Energies=	-0.512831

H	0.00000000	0.00000000	0.00000000

E

Sum of electronic and zero-point Energies=	-1206.939982
Sum of electronic and thermal Energies=	-1206.918219

Sum of electronic and thermal Enthalpies= -1206.917275

Sum of electronic and thermal Free Energies= -1206.992853

C	-1.83317900	4.01594200	0.33732500
C	-1.90254900	3.13101100	1.41386600
C	-1.03511600	2.04575300	1.47244200
C	-0.09536300	1.80940100	0.45717300
C	-0.00005200	2.72337400	-0.60247100
C	-0.87699500	3.81448400	-0.65113800
C	0.80286600	0.57933700	0.56173400
N	1.81391200	0.49624700	-0.53264300
C	2.26743600	1.80963200	-1.05193600
C	1.08518200	2.56547700	-1.63859600
C	2.94162400	-0.37018600	-0.23053600
C	3.67472600	-0.25446900	0.95540800
C	4.77463500	-1.08036600	1.18327100
C	5.15870500	-2.02145400	0.22828600
C	4.43739800	-2.13125500	-0.95969200
C	3.33324400	-1.31064600	-1.18695900
C	-0.00113100	-0.78379000	0.49352400
C	-0.83134200	-0.90826700	-0.74451200
C	-2.17519300	-1.29307400	-0.71276100
C	-2.78367300	-1.55526500	0.54111400
O	-2.05893300	-1.43692900	1.72619600
C	-0.75395600	-1.07988700	1.77891300
C	-2.99477300	-1.44631100	-1.86841800
C	-4.31937300	-1.83144600	-1.75095300
C	-4.88580500	-2.07944300	-0.49202600
C	-4.10328100	-1.93821700	0.66118400
O	-0.21480900	-0.68200200	-1.92421800
O	-0.22191200	-1.03663100	2.86276300
H	-2.50286400	4.86666200	0.28251300
H	-2.62071600	3.29018000	2.20994800
H	-1.08140000	1.38876900	2.33244100
H	-0.79190300	4.51945300	-1.47192800
H	1.28683500	0.60003200	1.54222800
H	3.01859500	1.61211700	-1.81753200
H	2.74550300	2.40217400	-0.25901400
H	1.41593300	3.54876000	-1.98296300
H	0.70783200	2.03312300	-2.51928500
H	3.39988200	0.48050700	1.70256900
H	5.33403000	-0.98286200	2.10676500
H	6.01379500	-2.66264100	0.40859800
H	4.72804800	-2.85843600	-1.70918600
H	2.77210500	-1.39751200	-2.11041100

H	0.78765100	-1.55309400	0.47716300
H	-2.55914300	-1.25402800	-2.84046800
H	-4.92463400	-1.94132400	-2.64363200
H	-5.92239900	-2.38018300	-0.40464600
H	-4.51261900	-2.12453300	1.64676100
H	0.66910000	-0.27842800	-1.70481300

TS3

Sum of electronic and zero-point Energies= -1206.930781
Sum of electronic and thermal Energies= -1206.908618
Sum of electronic and thermal Enthalpies= -1206.907674
Sum of electronic and thermal Free Energies= -1206.983802

C	-2.21028900	3.39364600	0.78528400
C	-1.82474900	2.72415800	1.94888600
C	-0.80502000	1.77922500	1.90097500
C	-0.16441400	1.48783600	0.68636600
C	-0.55078900	2.16488000	-0.48209100
C	-1.56785700	3.11704000	-0.42152300
C	0.90286800	0.47430800	0.62633300
N	1.89456500	0.64215300	-0.34791800
C	1.66594300	1.56309600	-1.47912100
C	0.18311700	1.81862100	-1.74812600
C	3.17929000	0.09363000	-0.17343200
C	3.45978100	-0.83407600	0.85273400
C	4.73838800	-1.36140800	1.00855700
C	5.77901000	-0.99176500	0.15810800
C	5.51462600	-0.07184800	-0.85466300
C	4.24199400	0.46704200	-1.02289500
C	0.03857100	-1.34570300	0.34752600
C	-0.73382100	-1.46338900	-0.84574800
C	-2.14265800	-1.33051900	-0.82310600
C	-2.77659700	-1.27287800	0.43963600
O	-2.04384800	-1.38715800	1.60793900
C	-0.67996800	-1.53421100	1.61154500
C	-2.96930500	-1.27643100	-1.97320200
C	-4.34368400	-1.14833400	-1.84794700
C	-4.94004700	-1.07532400	-0.58182200
C	-4.14884300	-1.14312200	0.56756000
O	-0.13775100	-1.61632000	-2.06171400
O	-0.14604000	-1.74502600	2.68240800
H	-2.99976500	4.13575500	0.82065100
H	-2.31064400	2.94628700	2.89204300
H	-0.49491600	1.27179400	2.80794400
H	-1.85651700	3.64735700	-1.32316700

H	1.30262400	0.22075100	1.60129300
H	2.11550100	1.13246900	-2.37466900
H	2.17452900	2.51307400	-1.27330600
H	0.10306600	2.62732300	-2.47796900
H	-0.26056100	0.93154700	-2.21066100
H	2.69165400	-1.16051600	1.53897500
H	4.91452400	-2.07387400	1.80683100
H	6.77121300	-1.40813200	0.28371900
H	6.30692200	0.24232400	-1.52515100
H	4.09307200	1.19115100	-1.81001400
H	0.99206200	-1.86536300	0.34757500
H	-2.50746700	-1.33078200	-2.95061300
H	-4.96092500	-1.10288100	-2.73775000
H	-6.01429000	-0.97316500	-0.48790100
H	-4.58667500	-1.10599300	1.55768600
H	0.81245800	-1.75301300	-1.95816800

H_2O

Sum of electronic and zero-point Energies=	-76.445024
Sum of electronic and thermal Energies=	-76.442189
Sum of electronic and thermal Enthalpies=	-76.441244
Sum of electronic and thermal Free Energies=	-76.462674

O	0.00000000	0.00000000	0.11797700
H	0.00000000	0.76214000	-0.47191000
H	0.00000000	-0.76214000	-0.47191000

B3

Sum of electronic and zero-point Energies=	-572.291027
Sum of electronic and thermal Energies=	-572.282085
Sum of electronic and thermal Enthalpies=	-572.281141
Sum of electronic and thermal Free Energies=	-572.325743

C	-2.92355700	0.30002800	-0.00891900
C	-1.81640600	1.13287500	-0.02304200
C	-0.51882200	0.59732400	-0.00311600
C	-0.36567600	-0.79421900	0.01646800
C	-1.46859800	-1.64165500	0.02464000
C	-2.74430400	-1.08850300	0.01619000
H	-3.92195300	0.71910000	-0.01620300
H	-1.92565600	2.21028600	-0.04049500
C	0.67186500	1.46140200	0.00007500
H	-1.31605300	-2.71337000	0.03162200
H	-3.60618500	-1.74507800	0.02611400
C	2.04831500	-0.71891400	-0.00583400
C	1.98434900	0.75702500	0.29230700

H	2.15524800	0.85587900	1.37382900
O	0.63536900	2.66710600	-0.17068400
O	0.87226400	-1.41671500	-0.01446700
O	3.06712100	-1.32780000	-0.19283700
H	2.81357700	1.26028800	-0.20358100

H+

Sum of electronic and zero-point Energies=	-0.162020
Sum of electronic and thermal Energies=	-0.160604
Sum of electronic and thermal Enthalpies=	-0.159660
Sum of electronic and thermal Free Energies=	-0.172020

H	0.00000000	0.00000000	0.00000000

B5

Sum of electronic and zero-point Energies=	-571.850464
Sum of electronic and thermal Energies=	-571.841932
Sum of electronic and thermal Enthalpies=	-571.840987
Sum of electronic and thermal Free Energies=	-571.884383

C	-2.89254500	0.28735800	0.00006500
C	-1.78044300	1.11837900	0.00005600
C	-0.48171200	0.58925700	0.00002000
C	-0.33047200	-0.80301500	-0.00000600
C	-1.44224200	-1.65108800	0.00000300
C	-2.71863600	-1.10302600	0.00003800
H	-3.89062500	0.70991900	0.00009200
H	-1.88786800	2.19661500	0.00007600
C	0.72688600	1.45816700	0.00001000
H	-1.28827600	-2.72371400	-0.00001900
H	-3.58167500	-1.75923800	0.00004500
C	2.08644900	-0.63271600	-0.00005400
C	1.95853900	0.76854900	-0.00002800
H	2.88063600	1.33724900	-0.00003800
O	0.60834800	2.71095600	0.00003300
O	0.89899200	-1.39894900	-0.00004200
O	3.11926800	-1.30601100	-0.00008800

OH-anion

Sum of electronic and zero-point Energies=	-75.948498
Sum of electronic and thermal Energies=	-75.946138
Sum of electronic and thermal Enthalpies=	-75.945194
Sum of electronic and thermal Free Energies=	-75.964749

O	0.00000000	0.00000000	0.10708300
H	0.00000000	0.00000000	-0.85666500

D

Sum of electronic and zero-point Energies= -1206.374418

Sum of electronic and thermal Energies= -1206.352629

Sum of electronic and thermal Enthalpies= -1206.351684

Sum of electronic and thermal Free Energies= -1206.427778

C	-1.18956400	0.22047800	0.56828300
H	-1.01410700	0.65224700	1.55815800
C	-2.69447300	0.00519000	0.45716000
C	-3.37686500	-0.51534100	1.56428100
H	-2.83277600	-0.73481300	2.47789500
H	-5.25779300	-1.15659300	2.38040900
C	-5.45574800	-0.46379000	0.34665800
H	-6.52391500	-0.64287000	0.29756700
C	-4.78717300	0.07490900	-0.74819000
H	-5.33775800	0.32321200	-1.64993400
C	-3.40868600	0.31366600	-0.70605700
C	-2.67550800	0.94207000	-1.86129600
H	-2.25489600	0.17007300	-2.51455500
H	-3.36125900	1.54227800	-2.46482400
C	-1.55585600	1.82568800	-1.33159000
H	-0.98436200	2.25123800	-2.15696000
H	-1.98583800	2.66542700	-0.76216400
N	-0.61607700	1.04726000	-0.49920200
C	0.57659200	1.78589100	-0.18924100
C	0.80122500	2.40707900	1.04553200
C	1.53959800	1.93204700	-1.19835000
C	1.96868300	3.13842000	1.26840900
H	0.07131600	2.33246100	1.84197400
C	2.69539100	2.67539900	-0.97942600
H	1.37461600	1.44857200	-2.15463000
C	2.91953600	3.27849500	0.25967900
H	2.12609900	3.60762200	2.23331400
H	3.42856600	2.77167300	-1.77248500
H	3.82428500	3.84893700	0.43551900
C	-4.74619200	-0.75429200	1.51355600
C	-0.42704100	-1.18171500	0.64071200
C	0.88490700	-1.05722100	1.40782100
C	-0.34689500	-1.81586800	-0.73030800
C	2.12669900	-1.30919000	0.66555400
C	3.38604300	-1.14505300	1.26523400
C	2.06768200	-1.71978800	-0.66999200
C	4.54641300	-1.37678800	0.54495500
H	3.42265700	-0.82907700	2.30046600
C	3.22461500	-1.95887200	-1.40465700

C	4.46058800	-1.78229100	-0.79289000
H	5.51464300	-1.24477000	1.01166500
H	3.14329200	-2.28024900	-2.43527600
H	5.36441900	-1.96558700	-1.36190300
O	0.87573700	-1.94160700	-1.33377300
O	-1.30465600	-2.21355600	-1.33846800
O	0.86018500	-0.76591300	2.59359600
H	-1.05859500	-1.83673500	1.24431700

B1

Sum of electronic and zero-point Energies= -572.049168
Sum of electronic and thermal Energies= -572.040124
Sum of electronic and thermal Enthalpies= -572.039180
Sum of electronic and thermal Free Energies= -572.084095

C	-2.87087500	0.31790300	0.00002500
C	-1.77158000	1.13806100	0.00010600
C	-0.47569300	0.57144700	0.00005500
C	-0.33996500	-0.85865800	-0.00008100
C	-1.46426200	-1.68413500	-0.00016300
C	-2.71286500	-1.09813700	-0.00011000
H	-3.86708500	0.73991500	0.00006300
H	-1.87272300	2.21431400	0.00020900
C	0.70857100	1.35716900	0.00012900
H	-1.33314400	-2.75762600	-0.00026800
H	-3.59465400	-1.72667400	-0.00017400
C	2.04006800	-0.73264200	-0.00006200
C	1.94497600	0.71005200	0.00007500
H	2.88315400	1.25054400	0.00012900
O	0.56812800	2.66737600	0.00024200
H	1.41396700	3.14114800	0.00028600
O	0.86019500	-1.46232800	-0.00013800
O	3.07420600	-1.35354700	-0.00011600

B2

Sum of electronic and zero-point Energies= -571.653261
Sum of electronic and thermal Energies= -571.644524
Sum of electronic and thermal Enthalpies= -571.643580
Sum of electronic and thermal Free Energies= -571.688139

C	2.89732300	0.28593100	0.00007400
C	1.79722800	1.12644000	0.00005100
C	0.49557000	0.59833000	0.00001500
C	0.33438200	-0.79381300	0.00000400
C	1.43217300	-1.64878800	0.00002700
C	2.71021100	-1.10307900	0.00006300

H	3.89850200	0.69832600	0.00010200
H	1.91405400	2.20305500	0.00006000
C	-0.69180900	1.46526800	-0.00000900
H	1.27253400	-2.71946800	0.00001800
H	3.56859400	-1.76417200	0.00008100
C	-2.06812000	-0.67883700	-0.00005600
C	-1.96414500	0.76825900	-0.00004300
O	-0.64868100	2.70027300	-0.00000100
O	-0.90738100	-1.40208400	-0.00003100
O	-3.12193200	-1.28192100	-0.00008700
H	-2.88662100	1.33383600	-0.00006200

B6

Sum of electronic and zero-point Energies= -572.386919
Sum of electronic and thermal Energies= -572.377328
Sum of electronic and thermal Enthalpies= -572.376384
Sum of electronic and thermal Free Energies= -572.422352

C	-2.91833200	0.28952200	0.00002900
C	-1.80726900	1.12634200	0.00000900
C	-0.48351000	0.58533900	0.00000100
C	-0.36428600	-0.83944700	0.00001300
C	-1.47364500	-1.66001300	0.00003300
C	-2.77377600	-1.10136400	0.00004000
H	-3.91183800	0.72729800	0.00003400
H	-1.93050400	2.20230300	0.00000000
C	0.70526100	1.32586300	-0.00002000
H	-1.32885700	-2.73486500	0.00004100
H	-3.64146300	-1.75022300	0.00005600
C	2.09259700	-0.69646600	-0.00001700
C	1.97164200	0.69333500	-0.00002900
H	2.88545700	1.27566400	-0.00004600
O	0.60005400	2.70351300	-0.00003100
H	1.48431400	3.08681600	-0.00004400
O	0.87888900	-1.44552000	0.00000700
O	3.11490700	-1.40120000	-0.00002500

B7

Sum of electronic and zero-point Energies= -571.850464
Sum of electronic and thermal Energies= -571.841932
Sum of electronic and thermal Enthalpies= -571.840987
Sum of electronic and thermal Free Energies= -571.884383

C	2.89254500	0.28735800	0.00013500
C	1.78044300	1.11837900	0.00012800
C	0.48171200	0.58925700	0.00004900

C	0.33047200	-0.80301500	-0.00002400
C	1.44224200	-1.65108800	-0.00001800
C	2.71863600	-1.10302600	0.00006200
H	3.89062500	0.70991900	0.00019600
H	1.88786900	2.19661500	0.00018400
C	-0.72688600	1.45816700	0.00004000
H	1.28827600	-2.72371400	-0.00007500
H	3.58167500	-1.75923800	0.00006600
C	-2.08644900	-0.63271600	-0.00011800
C	-1.95853900	0.76854900	-0.00004600
H	-2.88063600	1.33724900	-0.00005900
O	-0.60834800	2.71095600	0.00010400
O	-0.89899200	-1.39894900	-0.00010300
O	-3.11926800	-1.30601100	-0.00019600

B4

Sum of electronic and zero-point Energies=	-572.035800
Sum of electronic and thermal Energies=	-572.026485
Sum of electronic and thermal Enthalpies=	-572.025541
Sum of electronic and thermal Free Energies=	-572.071485

C	-2.89453800	0.38057500	-0.05063100
C	-1.73117600	1.19928200	-0.05555900
C	-0.48241900	0.63377900	-0.00031000
C	-0.38848500	-0.79340300	0.04769800
C	-1.56070500	-1.62032400	0.05486500
C	-2.79502800	-1.02602200	0.00758800
H	-3.86926200	0.85002300	-0.09127500
H	-1.82548700	2.27718800	-0.09516000
C	0.75982200	1.45333000	0.01821800
H	-1.42925300	-2.69379900	0.09062100
H	-3.69266200	-1.62950200	0.01061300
C	2.05153200	-0.74948200	-0.01460500
C	2.03374400	0.69811000	0.35664900
H	2.13938700	0.73639500	1.45118300
O	0.75652100	2.64472400	-0.17806300
O	0.75979500	-1.43231200	0.06011700
O	2.96059000	-1.43545000	-0.31659200
H	2.90554700	1.18893000	-0.07315000

TS2

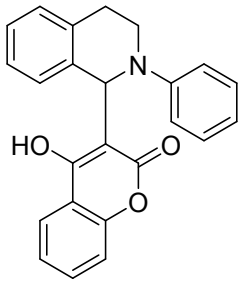
Sum of electronic and zero-point Energies=	-1206.370076
Sum of electronic and thermal Energies=	-1206.348310
Sum of electronic and thermal Enthalpies=	-1206.347365
Sum of electronic and thermal Free Energies=	-1206.423013

C	0.93190900	0.17848700	-0.28163100
H	0.18901100	-0.12305400	-1.00745900
C	2.27748900	-0.40988200	-0.48189200
C	2.49500200	-1.42394600	-1.41949200
H	1.66721500	-1.81025300	-2.00209100
H	3.94900300	-2.70987700	-2.34252100
C	4.84403500	-1.42245200	-0.86544100
H	5.84432900	-1.81292500	-1.01446700
C	4.62761700	-0.40748700	0.06860300
H	5.45899500	-0.01013200	0.64103000
C	3.34716300	0.10362900	0.26857800
C	3.02376600	1.18983300	1.25990900
H	2.59920100	0.75082400	2.16997600
H	3.92402800	1.72936300	1.55956900
C	2.02737600	2.18729600	0.66881800
H	1.66625000	2.85155100	1.45264000
H	2.51705500	2.80455200	-0.09381400
N	0.87508500	1.51036800	0.03331000
C	-0.20931600	2.32496600	-0.42014800
C	-0.68851000	2.19933500	-1.73060800
C	-0.78053700	3.28125000	0.42763900
C	-1.73649400	3.00254000	-2.17492500
H	-0.23213900	1.49146600	-2.41198400
C	-1.81676800	4.09162000	-0.02882500
H	-0.43717200	3.37290600	1.44958500
C	-2.30387200	3.95408300	-1.32866100
H	-2.09523400	2.89390400	-3.19202200
H	-2.25353700	4.82306100	0.64145400
H	-3.11388400	4.58326700	-1.67841200
C	3.77966900	-1.92786700	-1.61164100
C	0.20587000	-0.96550800	1.24187200
C	-0.24970200	-2.20796300	0.61967600
C	-0.77095400	-0.10014800	1.88326300
C	-1.66614600	-2.21163900	0.19124400
C	-2.19368100	-3.22328100	-0.62536200
C	-2.51703400	-1.18922500	0.62579700
C	-3.52721200	-3.20371800	-1.00468300
H	-1.52972900	-4.01444200	-0.95223600
C	-3.86179800	-1.16173900	0.25939500
C	-4.35944000	-2.16856300	-0.55898400
H	-3.92518400	-3.98404300	-1.64194300
H	-4.49463500	-0.36033900	0.61994300
H	-5.40332500	-2.14948300	-0.84974900
O	-2.08713300	-0.17860900	1.45731300

O	-0.51819800	0.74840000	2.71245000
O	0.50014400	-3.16687700	0.41798900
H	1.11507200	-1.05994600	1.82232100

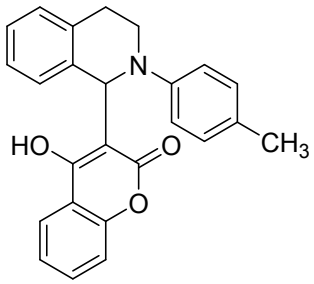
6. Characterization Data

4-hydroxy-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3a)[9,10,11,12,13]



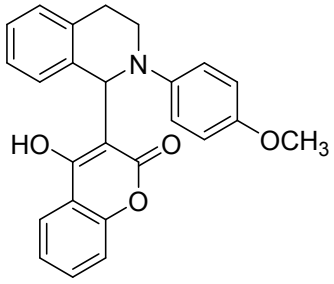
Yellow solid (76.7 mg, 83 %). mp. 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.5 Hz, 1H), 7.47-7.36 (m, 4H), 7.36-7.29 (m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 7.21-7.11 (m, 5H), 6.16 (s, 1H), 3.77-3.64 (m, 1H), 3.61-3.44 (m, 1H), 3.33-3.19 (m, 1H), 2.96 (d, J = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 164.1, 153.4, 148.5, 135.6, 132.7, 132.0, 129.7, 128.3, 127.5, 127.1, 127.0, 126.3, 123.7, 123.3, 122.4, 116.5, 116.5, 104.7, 58.4, 55.0, 30.4. HRMS (ESI), calcd. for $C_{24}H_{20}NO_3$ $(M+H)^+$: 370.1438, found: 370.1436.

4-hydroxy-3-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3b)[10,11]



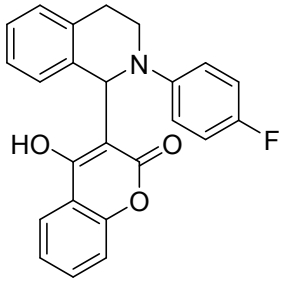
Yellow solid (80.5 mg, 84 %). mp. 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.8 Hz, 1H), 7.47-7.36 (m, 2H), 7.34-7.27 (m, 2H), 7.21 (d, J = 8.3 Hz, 1H), 7.19-7.06 (m, 6H), 6.12 (s, 1H), 3.70-3.60 (m, 1H), 3.59-3.47 (m, 1H), 3.32-3.19 (m, 1H), 2.94 (d, J = 16.3 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 164.2, 153.4, 145,7, 136.2, 135.7, 132.6, 131.9, 130.3, 128.2, 127.5, 127.0, 127.0, 123.6, 123.3, 122.2, 116.7, 116.5, 104.4, 58.8, 55.0, 30.3, 20.8. HRMS (ESI), calcd. for $C_{25}H_{22}NO_3$ $(M+H)^+$: 384.1594, found: 384.1597.

4-hydroxy-3-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3c)[10,11,12]



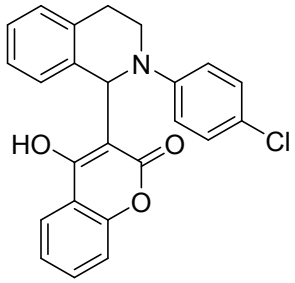
Orange solid (62.9 mg, 63 %). mp. 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.65 (m, 1H), 7.49-7.41 (m, 1H), 7.40-7.31 (m, 3H), 7.23 (d, J = 8.3 Hz, 1H), 7.20-7.09 (m, 4H), 6.88-6.78 (m, 2H), 6.07 (s, 1H), 3.74 (s, 3H), 3.64-3.47 (m, 2H), 3.34-3.20 (m, 1H), 3.00-2.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 164.1, 158.0, 153.4, 141.1, 135.7, 132.5, 131.9, 128.2, 127.5, 127.0, 125.7, 124.6, 123.6, 123.3, 116.7, 116.5, 114.8, 104.2, 59.3, 55.4, 55.0, 30.2. HRMS (ESI), calcd. for $C_{25}H_{22}NO_4$ $(M+H)^+$: 400.1543, found: 400.1546.

3-(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3d)[9,11]



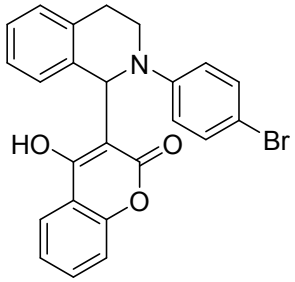
Orange solid (80.4 mg, 83 %). mp. 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.78 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.42-7.32 (m, 3H), 7.28-7.22 (m, 1H), 7.21-7.12 (m, 4H), 7.01 (t, J = 8.5 Hz, 2H), 6.07 (s, 1H), 3.65-3.58 (m, 1H), 3.57-3.46 (m, 1H), 3.30-3.19 (m, 1H), 2.96 (d, J = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 164.0, 160.7 (d, J = 245.8 Hz), 153.4, 144.8 (d, J = 2.9 Hz), 135.5, 132.7, 132.2, 128.3, 127.4, 127.1, 127.1, 124.2 (d, J = 8.1 Hz), 123.7, 123.3, 116.6, 116.4 (d, J = 19.8 Hz), 116.2, 104.8, 58.7, 55.2, 30.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.8. HRMS (ESI), calcd. for $C_{24}H_{19}FNO_3$ $(M+H)^+$: 388.1343, found: 388.1346.

3-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3e)[11]



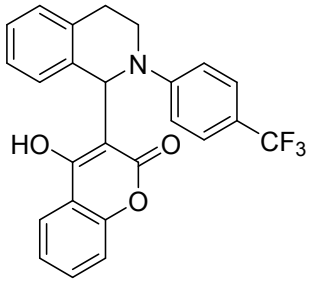
Yellow solid (97.9 mg, 97 %). mp. 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.41 (m, 3H), 7.40-7.29 (m, 5H), 7.21-7.09 (m, 4H), 6.09 (s, 1H), 3.76-6.61 (m, 1H), 3.60-3.41 (m, 1H), 3.31-3.14 (m, 1H), 2.96 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 164.0, 153.4, 147.5, 135.4, 132.9, 132.2, 131.4, 129.7, 128.3, 127.4, 127.1, 127.1, 123.8, 123.8, 123.3, 116.5, 116.1, 105.0, 58.0, 55.0, 30.4. HRMS (ESI), calcd. for $C_{24}H_{19}ClNO_3$ $(M+H)^+$: 404.1048, found: 404.1051.

3-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3f)[10,11]



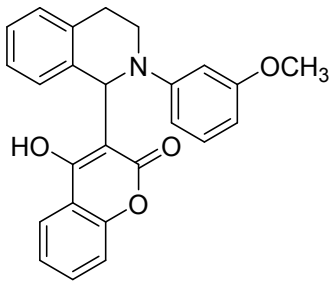
Yellow solid (96.4 mg, 86 %). mp. 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.59 (m, 1H), 7.55-7.28 (m, 7H), 7.22-7.08 (m, 4H), 6.09 (s, 1H), 3.75-3.60 (m, 1H), 3.59-3.41 (m, 1H), 3.31-3.14 (m, 1H), 2.96 (d, J = 15.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 164.0, 153.4, 148.0, 135.3, 132.7, 132.2, 128.3, 127.4, 127.1, 127.1, 124.2, 123.8, 123.3, 119.2, 116.6, 116.1, 105.0, 57.9, 55.0, 30.4. HRMS (ESI), calcd. for $C_{24}H_{19}BrNO_3$ $(M+H)^+$: 448.0543, found: 448.0544.

4-hydroxy-3-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3g)



Orange solid (83.1 mg, 76 %). mp. 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.55 (m, 3H), 7.55-7.42 (m, 3H), 7.41-7.33 (m, 1H), 7.31-7.07 (m, 5H), 6.18 (s, 1H), 3.87-3.74 (m, 1H), 3.62-3.46 (m, 1H), 3.33-3.19 (m, 1H), 3.00 (d, J = 16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 163.9, 153.3, 152.1, 135.2, 132.7, 132.3, 128.4, 127.7, 127.4, 127.2, 127.2, 126.8 (q, J = 3.7 Hz), 125.5, 123.9, 122.5, 123.3, 116.6, 115.9, 105.2, 57.4, 54.8, 30.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.3. HRMS (ESI), calcd. for $C_{25}H_{19}F_3NO_3$ $(M+H)^+$: 438.1312, found: 438.1314.

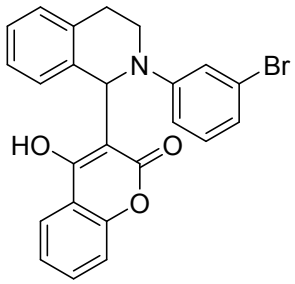
4-hydroxy-3-(2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3h)



Yellow solid (57.9 mg, 58 %). mp. 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 7.48-7.42 (m, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.25-7.19 (m, 2H), 7.19-7.12 (m, 4H), 7.02-6.97 (m, 1H), 6.96 (t, J = 2.3 Hz, 1H), 6.72-6.67 (m, 1H), 6.13 (s, 1H), 3.77 (s, 3H), 3.75-3.68 (m, 1H), 3.60-3.47 (m, 1H), 3.25 (dt, J_1 = 3.0 Hz, J_2 = 12.1 Hz, 1H), 2.96 (d, J =16.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 164.1, 160.5, 153.4, 150.0, 135.7,

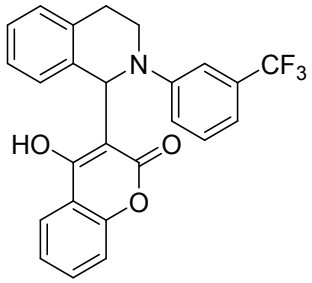
132.8, 132.0, 130.3, 128.3, 127.5, 127.0, 123.7, 123.3, 116.5, 114.7, 111.8, 108.2, 105.1, 58.2, 55.4, 55.0, 30.4. HRMS (ESI), calcd. for $C_{25}H_{22}NO_4$ $(M+H)^+$: 400.1543, found: 400.1545.

3-(2-(3-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3i)



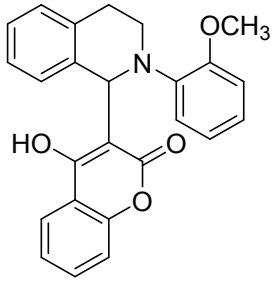
Yellow solid (71.7 mg, 64 %). mp. 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.62 (m, 1H), 7.56-7.52 (m, 1H), 7.50-7.44 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.29-7.23 (m, 2H), 7.22-7.11 (m, 5H), 6.11 (s, 1H), 3.76-3.67 (m, 1H), 3.58-3.44 (m, 1H), 3.23 (dt, J_1 = 2.8 Hz, J_2 = 12.1 Hz, 1H), 2.96 (d, J =16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 163.9, 153.3, 150.5, 135.3, 132.7, 132.2, 130.9, 129.1, 128.3, 127.4, 127.1, 127.1, 126.3, 123.8, 123.3, 123.1, 120.5, 116.5, 116.1, 105.1, 57.7, 55.1, 30.4. HRMS (ESI), calcd. for $C_{24}H_{19}BrNO_3$ $(M+H)^+$: 448.0543, found: 448.0546.

4-hydroxy-3-(2-(3-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3j)



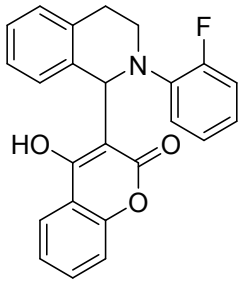
Orange solid (87.5, 80 %). mp. 177-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.57 (m, 3H), 7.51-7.42 (m, 2H), 7.41-7.33 (m, 2H), 7.25-7.09 (m, 5H), 6.17 (s, 1H), 3.81-3.71 (m, 1H), 3.61-3.47 (m, 1H), 3.34-3.20 (m, 1H), 2.99 (d, J = 16.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 163.8, 153.3, 149.6, 135.2, 132.7, 132.3, 132.2, 131.9, 130.2, 128.4, 127.4, 127.2, 127.2, 127.9, 123.8, 123.3, 122.5 (q, J = 3.7 Hz), 120.0 (q, J = 3.7 Hz), 116.5, 116.0, 105.1, 57.6, 55.1, 30.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.6. HRMS (ESI), calcd. for $C_{25}H_{19}F_3NO_3$ $(M+H)^+$: 438.1312, found: 438.1314.

4-hydroxy-3-(2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3k)[11]



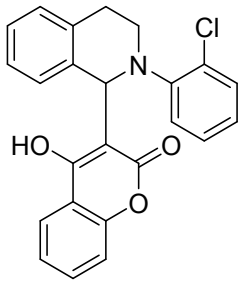
Yellow solid (74.9 mg, 75 %). mp. 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, J_1 = 1.5 Hz, J_2 = 7.8 Hz, 1H), 7.47-7.35 (m, 3H), 7.23-7.19 (m, 1H), 7.18-7.07 (m, 5H), 6.95-6.87 (m, 2H), 6.27 (s, 1H), 3.93 (s, 3H), 3.68-3.61 (m, 1H), 3.59-3.49 (m, 1H), 3.10-3.00 (m, 1H), 2.88 (d, J =16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 164.3, 153.8, 153.3, 136.5, 136.1, 133.4, 131.8, 128.3, 127.5, 126.8, 126.7, 126.6, 123.5, 123.4, 121.2, 121.2, 116.7, 116.4, 112.1, 104.7, 56.7, 55.9, 52.3, 30.1. HRMS (ESI), calcd. for $C_{25}H_{22}NO_4$ $(M+H)^+$: 400.1543, found: 400.1544.

3-(2-(2-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3l)



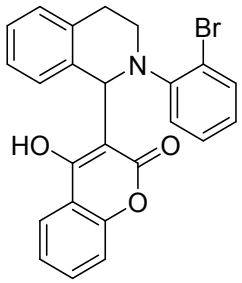
Yellow solid (83.9 mg, 97%). mp. 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.62 (m, 1H), 7.55-7.48 (m, 1H), 7.48-7.42 (m, 1H), 7.36-7.31 (m, 1H), 7.25-7.21 (m, 1H), 7.20-7.12 (m, 4H), 7.11-7.05 (m, 3H), 6.23 (s, 1H), 3.71-3.62 (m, 1H), 3.61-3.49 (m, 1H), 3.14 (dt, J_1 = 2.8 Hz, J_2 = 12.1 Hz, 1H), 2.93 (d, J =16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 164.1, 157.4 (d, J = 247.2 Hz), 153.3, 136.3 (d, J = 9.6 Hz), 135.4, 133.0, 132.1, 128.4, 127.4, 127.0 (d, J = 13.9 Hz), 126.7 (d, J = 8.1 Hz), 124.8, 124.8, 123.6 (d, J = 30.1 Hz), 122.1, 116.9, 116.7, 116.4, 116.1, 104.9, 56.6, 53.3 (d, J =2.9 Hz), 30.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.8. HRMS (ESI), calcd. for $C_{24}H_{19}FNO_3$ $(M+H)^+$: 388.1343, found: 388.1343.

3-(2-(2-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3m)



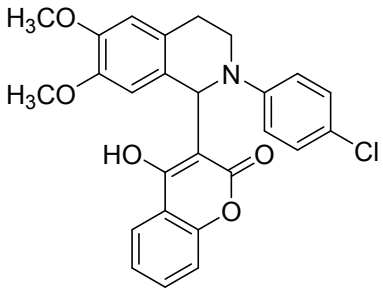
Yellow solid (74.7 mg, 74 %). mp. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.60 (s, 1H), 7.68-7.63 (m, 1H), 7.59-7.53 (m, 1H), 7.48-7.42 (m, 1H), 7.40 (dd, J_1 =1.5 Hz, J_2 = 8.0 Hz, 1H), 7.28-7.22 (m, 3H), 7.21-7.17 (m, 2H), 7.17-7.10 (m, 2H), 7.10-7.04 (m, 1H), 6.24 (s, 1H), 3.77-3.70 (m, 1H), 3.66-3.54 (m, 1H), 3.05-2.98 (m, 1H), 2.98-2.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.1, 153.3, 145.2, 135.6, 133.4, 132.2, 131.0, 130.1, 128.5, 128.1, 127.4, 127.1, 126.8, 126.6, 123.7, 123.5, 121.9, 116.4, 116.0, 105.0, 56.6, 53.4, 30.1. HRMS (ESI), calcd. for $C_{24}H_{19}ClNO_3$ $(M+H)^+$: 404.1048, found: 404.1047.

3-(2-(2-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3n)



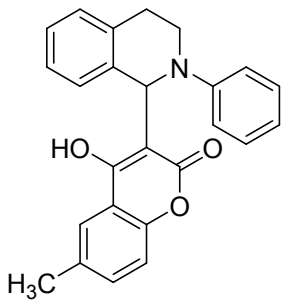
Yellow solid (71.7 mg, 64 %). mp. 179-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.34 (s, 1H), 7.74-7.52 (m, 3H), 7.50-7.40 (m, 1H), 7.35-7.07 (m, 8H), 7.05-6.93 (m, 1H), 6.22 (s, 1H), 3.86-3.55 (m, 2H), 3.09-2.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 164.1, 153.3, 146.5, 135.6, 134.3, 133.5, 132.2, 128.7, 128.5, 127.3, 127.1, 127.0, 126.7, 123.7, 123.5, 122.1, 120.8, 116.4, 116.0, 105.1, 56.8, 53.9, 30.1. HRMS (ESI), calcd. for $C_{24}H_{19}BrNO_3$ $(M+H)^+$: 448.0543, found: 448.0541.

3-(2-(4-chlorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3o)



Yellow oil (34.8 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, J_1 =1.5 Hz, J_2 = 8.0 Hz, 1H), 7.51-7.45 (m, 1H), 7.35-7.28 (m, 4H), 7.24 (s, 1H), 7.22-7.16 (m, 1H), 6.88 (s, 1H), 6.62 (s, 1H), 6.03 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.79-3.60 (m, 1H), 3.52-3.40 (m, 1H), 3.26-3.16 (m, 1H), 2.86 (d, J = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 164.1, 153.3, 148.3, 148.2, 147.4, 132.2, 131.4, 129.7, 127.2, 124.9, 123.8, 123.8, 123.3, 116.5, 116.2, 110.5, 109.6, 104.7, 58.0, 55.9, 55.9, 54.9, 30.0. HRMS (ESI), calcd. for $C_{26}H_{23}ClNO_5$ $(M+H)^+$: 464.1259, found: 464.1262.

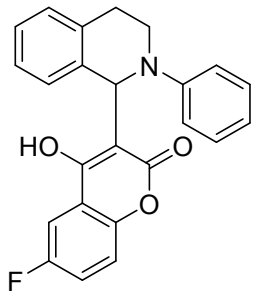
4-hydroxy-6-methyl-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3p)[10,11]



Yellow solid (80.5 mg, 84 %). mp. 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.36 (m, 4H), 7.35-7.29 (m, 2H), 7.25-7.22 (m, 1H), 7.19-7.10 (m, 5H), 6.15 (s, 1H), 3.74-3.66 (m, 1H),

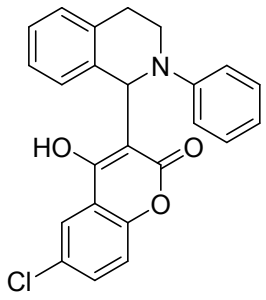
3.59-3.47 (m, 1H), 3.25 (dt, J_1 =3.0 Hz, J_2 = 12.3 Hz, 1H), 2.96 (d, J = 16.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 164.2, 151.5, 148.7, 135.7, 133.4, 133.0, 132.7, 129.6, 128.2, 127.5, 127.0, 127.0, 126.1, 122.9, 122.4, 116.2, 116.1, 104.8, 58.2, 55.0, 30.4, 20.8. HRMS (ESI), calcd. for $C_{25}H_{22}NO_3$ $(M+H)^+$: 384.1594, found: 384.1597.

6-fluoro-4-hydroxy-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3q)



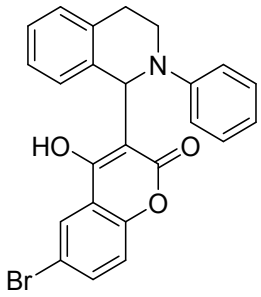
Yellow solid (63.0 mg, 65 %). mp. 173-175 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.35 (m, 4H), 7.35-7.30 (m, 2H), 7.23-7.11 (m, 6H), 6.16 (s, 1H), 3.74-3.66 (m, 1H), 3.60-3.49 (m, 1H), 3.28 (dt, J_1 = 3.0 Hz, J_2 = 12.3 Hz, 1H), 2.97 (d, J = 16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 163.8, 158.5 (d, J = 244.3 Hz), 149.5, 148.2, 135.3, 132.6, 129.8, 128.3, 127.4, 127.1, 127.1, 126.5, 122.3, 119.4 (d, J = 24.9 Hz), 118.1 (d, J = 8.1 Hz), 117.6 (d, J = 8.8 Hz), 109.0 (d, J = 24.9 Hz), 105.1, 58.6, 54.9, 30.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.8. HRMS (ESI), calcd. for $C_{24}H_{19}FNO_3$ $(M+H)^+$: 388.1343, found: 388.1342.

6-chloro-4-hydroxy-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3r)



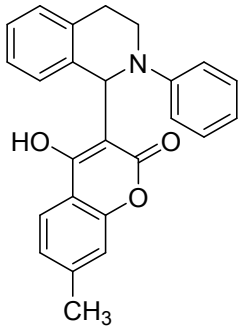
Yellow solid (70.7 mg, 70 %). mp. 143-145 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.50-7.30 (m, 6H), 7.23-7.09 (m, 5H), 6.15 (s, 1H), 3.77-3.64 (m, 1H), 3.63-3.47 (m, 1H), 3.37-3.23 (m, 1H), 2.98 (d, J = 16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 163.7, 151.8, 147.9, 135.2, 132.5, 132.0, 129.8, 129.3, 128.3, 127.3, 127.2, 127.2, 126.7, 123.0, 122.3, 118.0, 117.9, 104.8, 58.9, 54.9, 30.2. HRMS (ESI), calcd. for $C_{24}H_{19}ClNO_3$ $(M+H)^+$: 404.1048, found: 404.1047.

6-bromo-4-hydroxy-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3s)



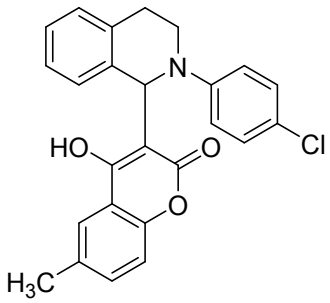
Yellow solid (74.0mg, 66 %). mp. 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.56-7.30 (m, 6H), 7.23-7.04 (m, 5H), 6.15 (s, 1H), 3.76-3.64 (m, 1H), 3.62-3.47 (m, 1H), 3.36-3.23 (m, 1H), 2.97 (d, J = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 163.6, 152.2, 147.9, 135.2, 134.7, 132.5, 129.8, 128.3, 127.3, 127.2,127.2, 126.7, 126.0, 122.3, 118.3, 118.2, 116.5, 104.9, 58.8, 54.9, 30.2. HRMS (ESI), calcd. for $C_{24}H_{19}BrNO_3$ $(M+H)^+$: 448.0543, found: 448.0545.

4-hydroxy-7-methyl-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2*H*-chromen-2-one (3t)



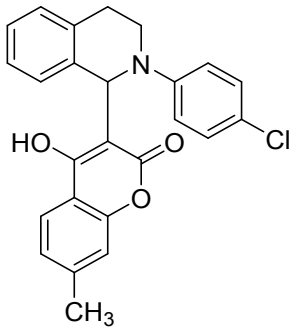
Yellow solid (79.6mg, 83 %). mp. 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.0 Hz, 1H), 7.45-7.35 (m, 3H), 7.31 (t, J = 7.5 Hz, 2H), 7.21-7.09 (m, 4H), 7.02 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.13 (s, 1H), 3.75-3.64 (m, 1H), 3.59-3.46 (m, 1H), 3.30-3.19 (m, 1H), 2.95 (d, J = 16.3 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 164.3, 153.5, 148.7, 143.2, 135.8, 132.7, 129.6, 128.2, 127.5, 127.0, 127.0, 126.1, 124.9, 123.0, 122.4, 116.6, 113.9, 104.0, 58.2, 55.0, 30.4, 21.7. HRMS (ESI), calcd. for $C_{25}H_{22}NO_3$ $(M+H)^+$: 384.1594, found: 384.1595.

3-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-6-methyl-2*H*-chromen-2-one (3u)



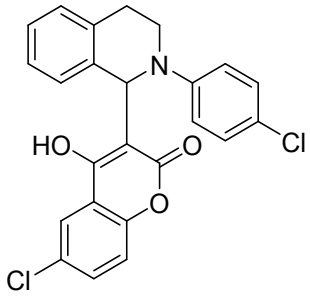
Orange solid (87.8mg, 84 %). mp. 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.40 (m, 1H), 7.36-7.30 (m, 3H), 7.29-7.23 (m, 3H), 7.21-7.10 (m, 4H), 6.08 (s, 1H), 3.71-3.61 (m, 1H), 3.56-3.45 (m, 1H), 3.21 (dt, J_1 = 3.0 Hz, J_2 = 12.1, 1H), 2.95 (d, J = 16.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 164.1, 151.5, 147.5, 135.4, 133.5, 133.2, 132.7, 131.3, 129.7, 128.3, 127.4, 127.1, 127.0, 123.8, 122.9, 116.3, 115.7, 104.9, 58.0, 55.0, 30.4, 20.8. HRMS (ESI), calcd. for $C_{25}H_{21}ClNO_3$ $(M+H)^+$: 418.1204, found: 418.1207.

3-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-7-methyl-2*H*-chromen-2-one (3v)



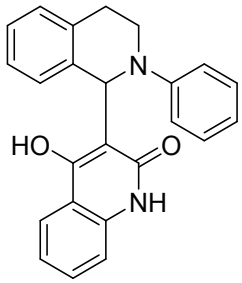
Orange solid (83.6mg, 80 %). mp. 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J =8.0 Hz, 1H), 7.36-7.30 (m, 3H), 7.29-7.24 (m, 2H), 7.21-7.11 (m, 3H), 7.05 (s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.06 (s, 1H), 3.69-3.61 (m, 1H), 3.56-3.44 (m, 1H), 3.21 (dt, J_1 = 3.0Hz, J_2 = 12.1 Hz, 1H), 2.95 (d, J = 16.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 164.2, 153.5, 147.6, 143.5, 135.5, 132.7, 131.3, 129.7, 128.3, 127.4, 127.1, 127.0, 125.0, 123.9, 123.0, 116.6, 113.6, 104.1, 58.0, 55.0, 30.4, 21.7. HRMS (ESI), calcd. for $C_{25}H_{21}ClNO_3$ $(M+H)^+$: 418.1204, found: 418.1206.

6-chloro-3-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2*H*-chromen-2-one (3w)



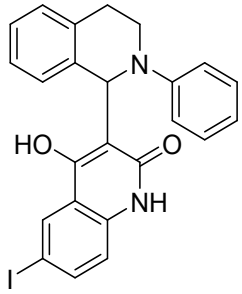
Yellow solid (76.7mg, 70 %). mp. 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.44-7.27 (m, 6H), 7.23-7.09 (m, 4H), 6.07 (s, 1H), 3.72-3.60 (m, 1H), 3.58-3.44 (m, 1H), 3.29-3.16 (m, 1H), 2.97 (d, J = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 163.5, 151.7, 147.2, 135.0, 132.6, 132.2, 131.7, 129.9, 129.4, 128.4, 127.3, 127.2, 124.8, 123.8, 122.9, 118.0, 117.3, 105.5, 58.3, 55.0, 30.3. HRMS (ESI), calcd. for $C_{24}H_{18}Cl_2NO_3$ $(M+H)^+$: 438.0658, found: 438.0659.

4-hydroxy-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)quinolin-2(1*H*)-one (3y)



Yellow solid (64.4mg, 70 %). mp. 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.59 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.50-7.37 (m, 4H), 7.35-7.26 (m, 3H), 7.19-7.13 (m, 2H), 7.11-7.03 (m, 3H), 6.42 (s, 1H), 3.81-3.71 (m, 1H), 3.64-3.50 (m, 1H), 3.28 (dt, J_1 = 2.8 Hz, J_2 = 12.1 Hz, 1H), 2.97 (d, J = 16.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 162.2, 149.5, 138.0, 136.5, 133.0, 130.7, 129.4, 128.2, 127.7, 126.8, 126.9, 125.4, 123.1, 122.5, 121.8, 115.9, 115.5, 111.1, 56.7, 55.3, 30.7. HRMS (ESI), calcd. for $C_{24}H_{21}N_2O_2$ $(M+H)^+$: 369.1598, found: 369.1600.

4-hydroxy-6-iodo-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)quinolin-2(1*H*)-one (3z)



Yellow solid (55.6mg, 45 %). mp. 230-232 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.59 (s, 1H), 7.84 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.46-7.36 (m, 2H), 7.34-7.26 (m, 2H), 7.25-7.10 (m, 4H), 7.09-7.00 (m, 2H), 6.15 (s, 1H), 3.81-3.69 (m, 1H), 3.54-3.41 (m, 1H), 3.30-3.17 (m, 1H), 2.97-2.85 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.4, 159.1, 149.7, 139.2, 137.8, 136.7, 134.0, 130.8, 129.5, 128.7, 127.1, 126.9, 126.9, 124.9, 122.0, 117.9, 117.2, 113.1, 85.0, 56.2, 53.8, 30.2. HRMS (ESI), calcd. for $C_{24}H_{20}IN_2O_2$ $(M+H)^+$: 495.0564, found: 495.0567.

7. References

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8. ^{1}H, ^{13}C and ^{19}F NMR Spectra

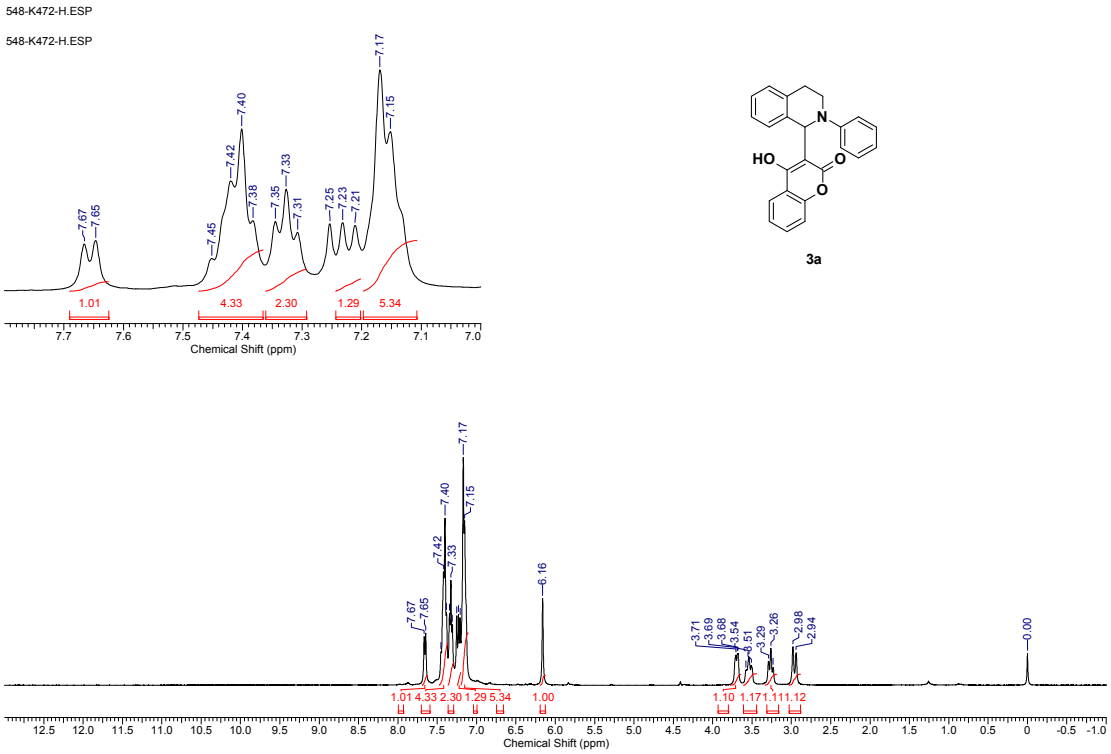


Figure S11. ^{1}H NMR spectrum of compound **3a**

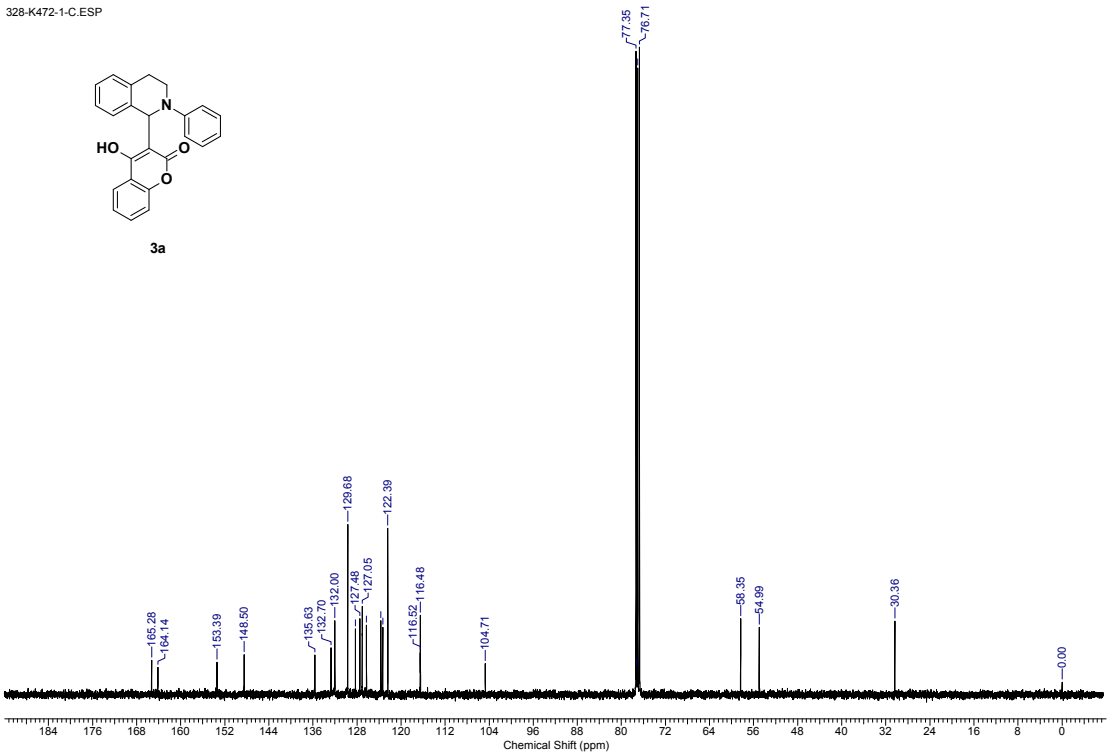


Figure S12. ^{13}C NMR spectrum of compound **3a**

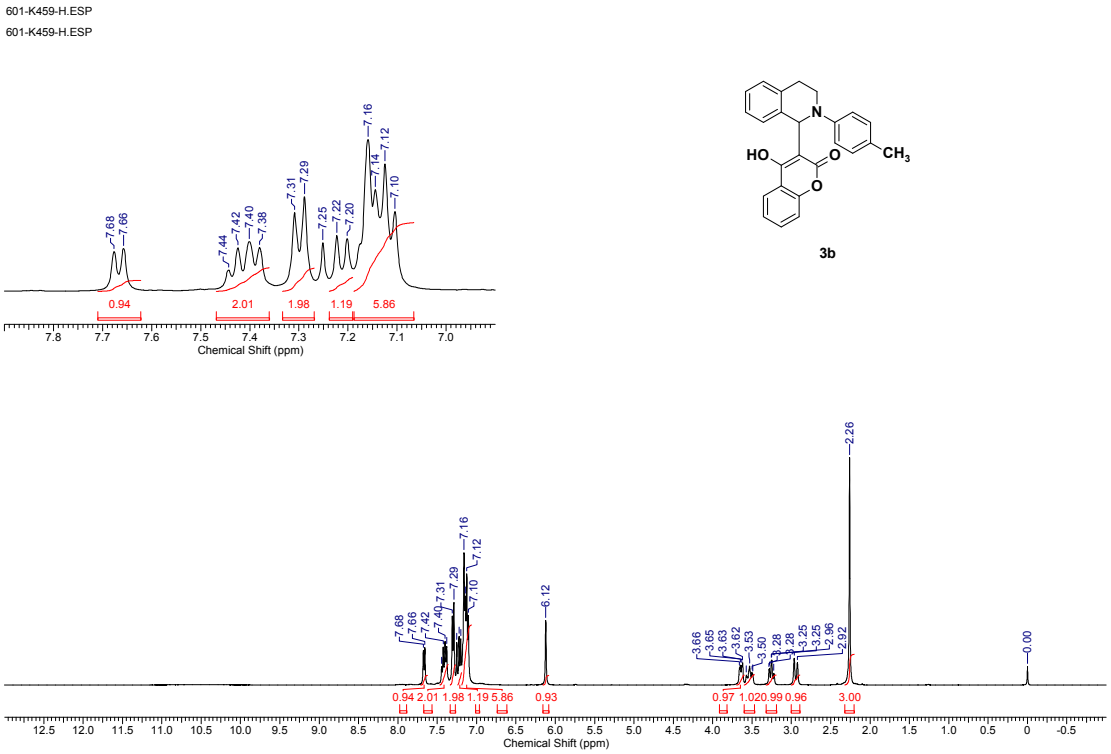


Figure S13. ^{1}H NMR spectrum of compound **3b**

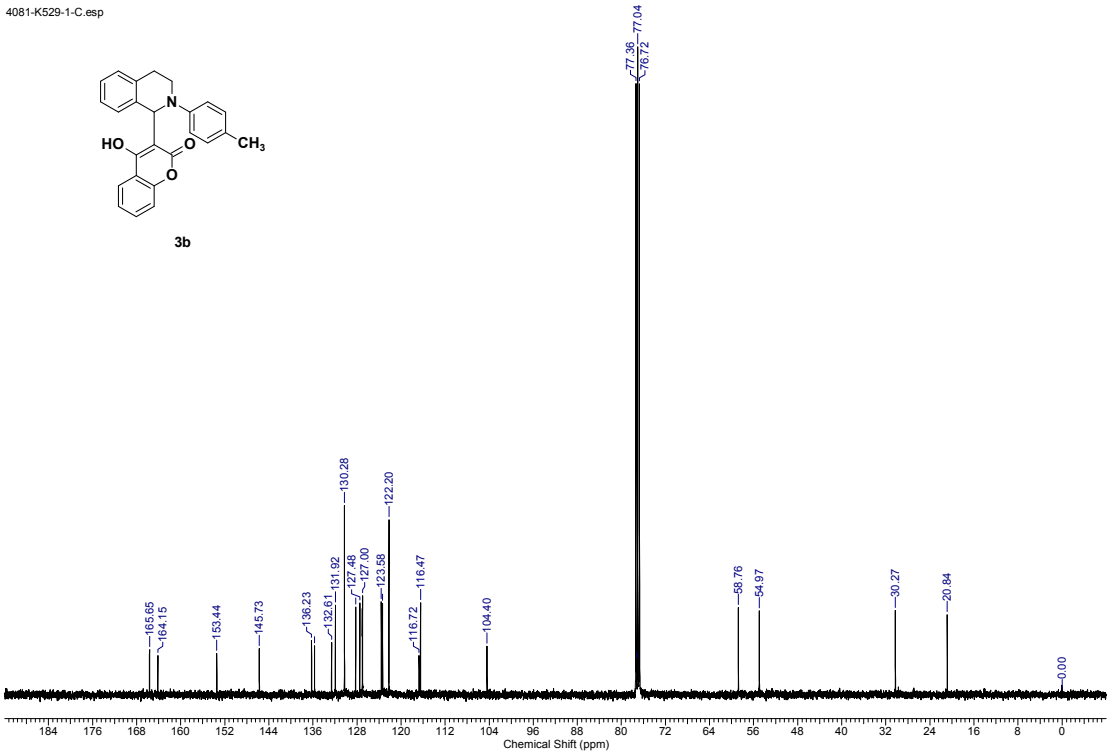


Figure S14. ^{13}C NMR spectrum of compound **3b**

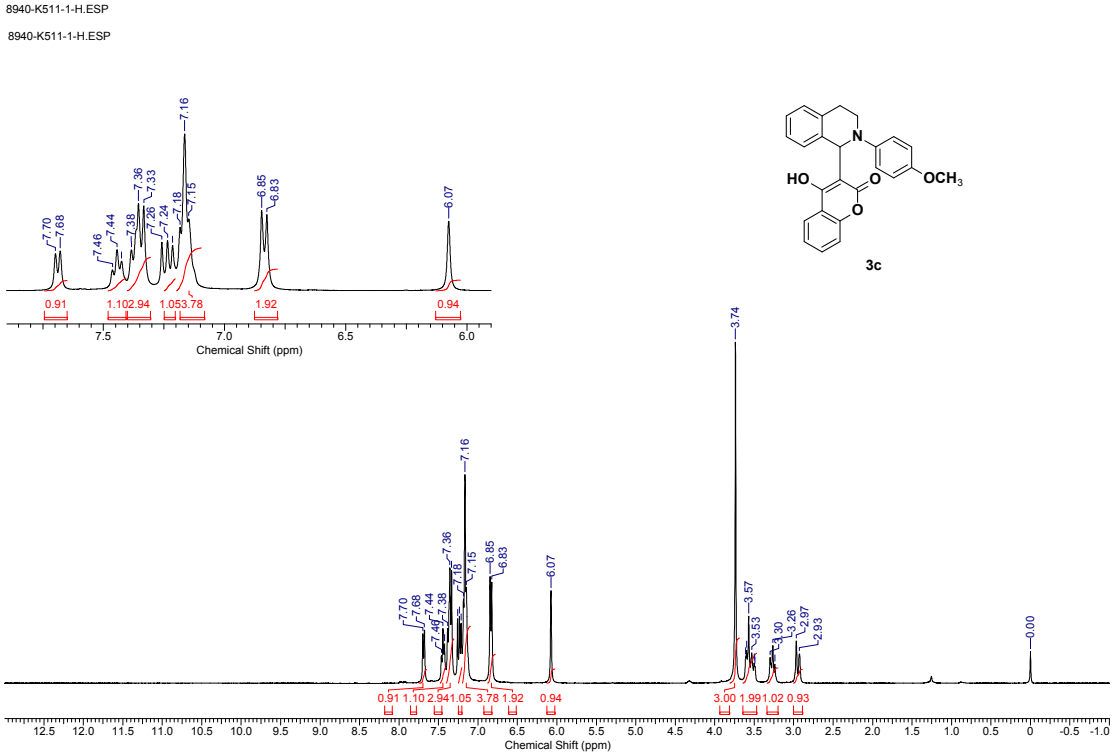


Figure S15. ^{1}H NMR spectrum of compound **3c**

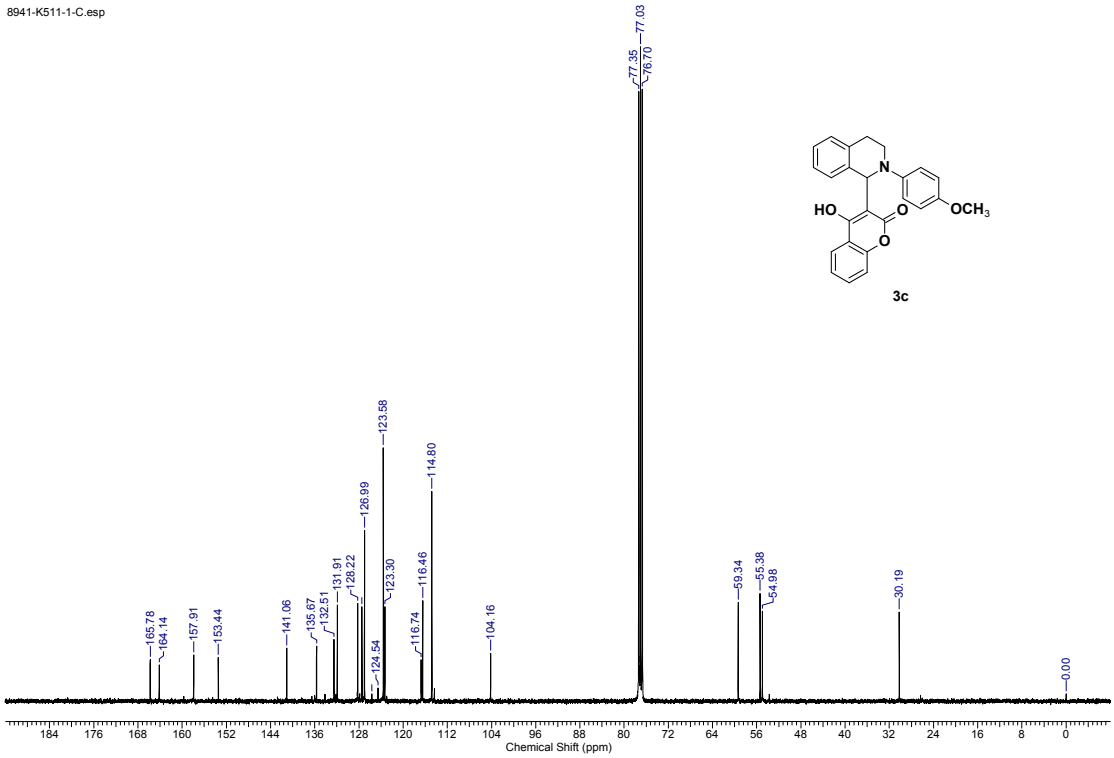


Figure S16. ^{13}C NMR spectrum of compound **3c**

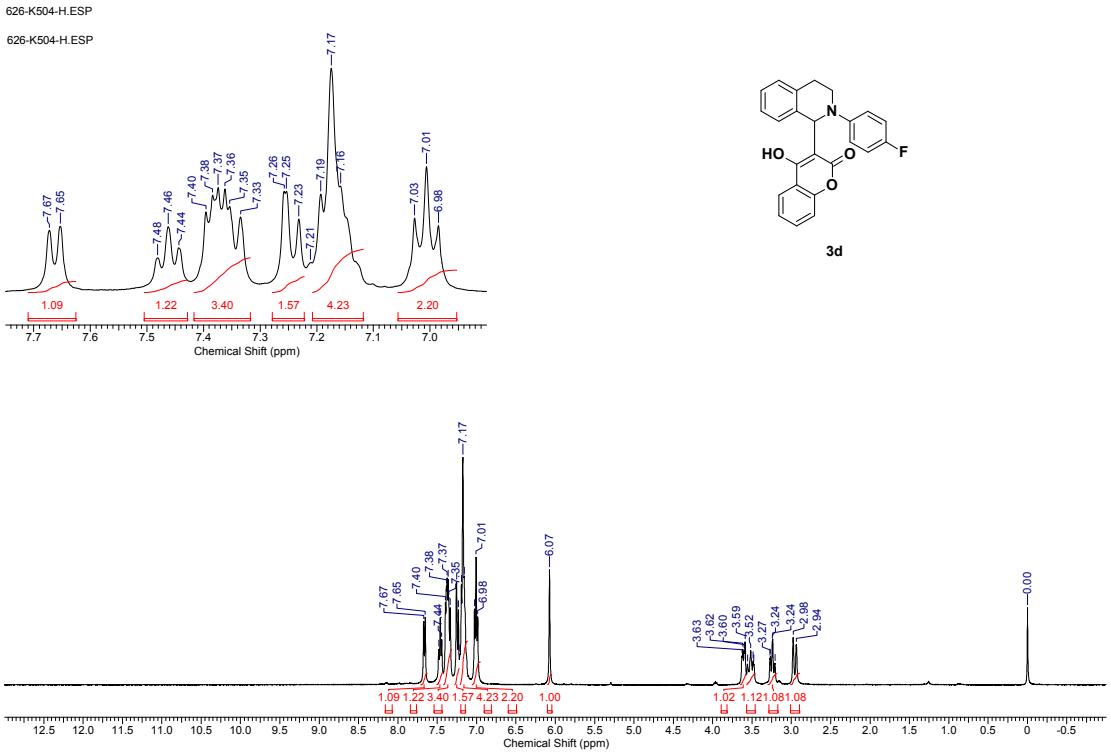


Figure S17. ^{1}H NMR spectrum of compound **3d**

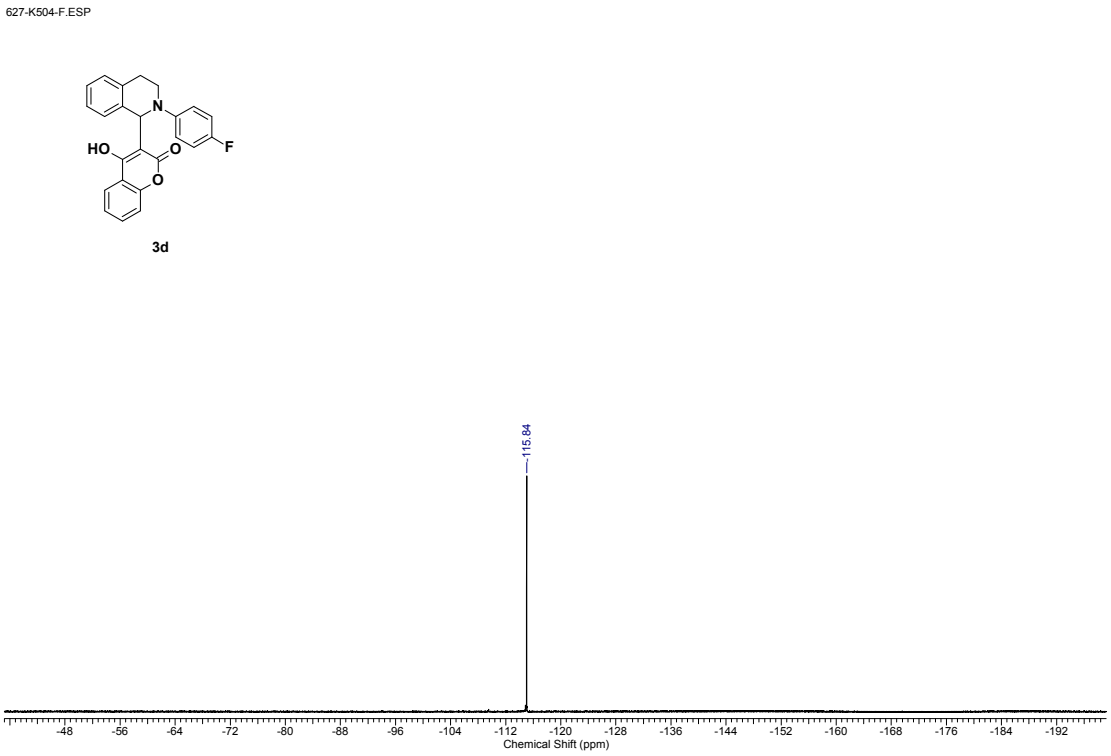


Figure S18. ^{19}F NMR spectrum of compound **3d**

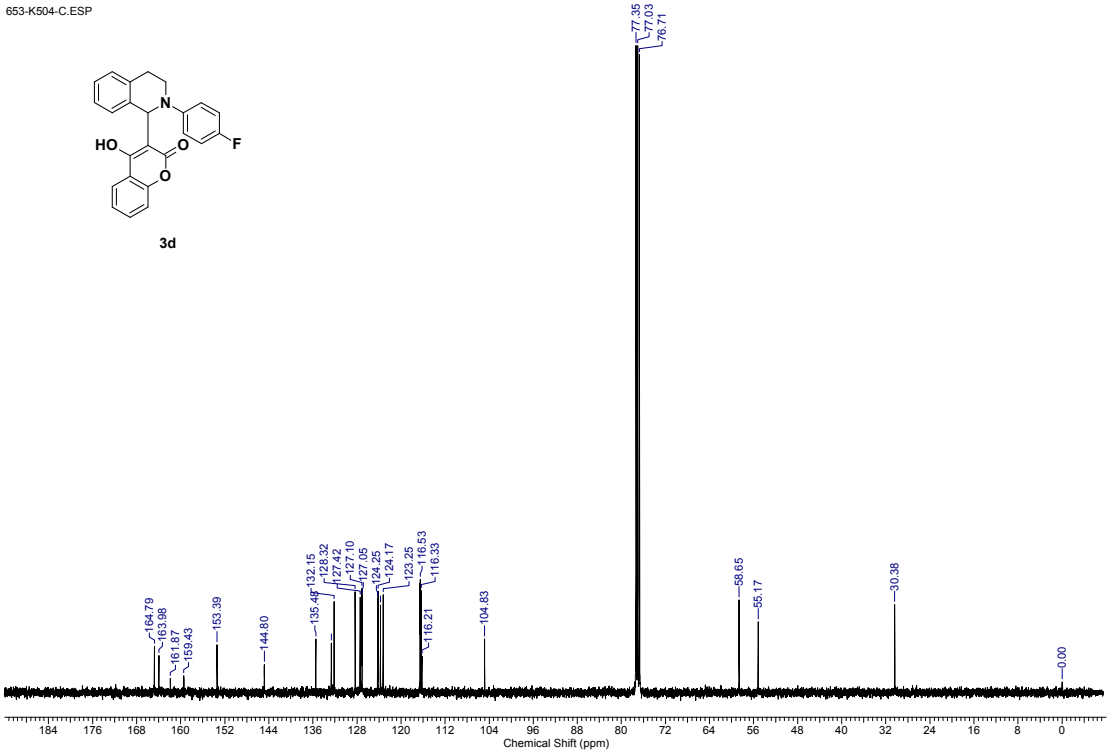


Figure S19. ^{13}C NMR spectrum of compound **3d**

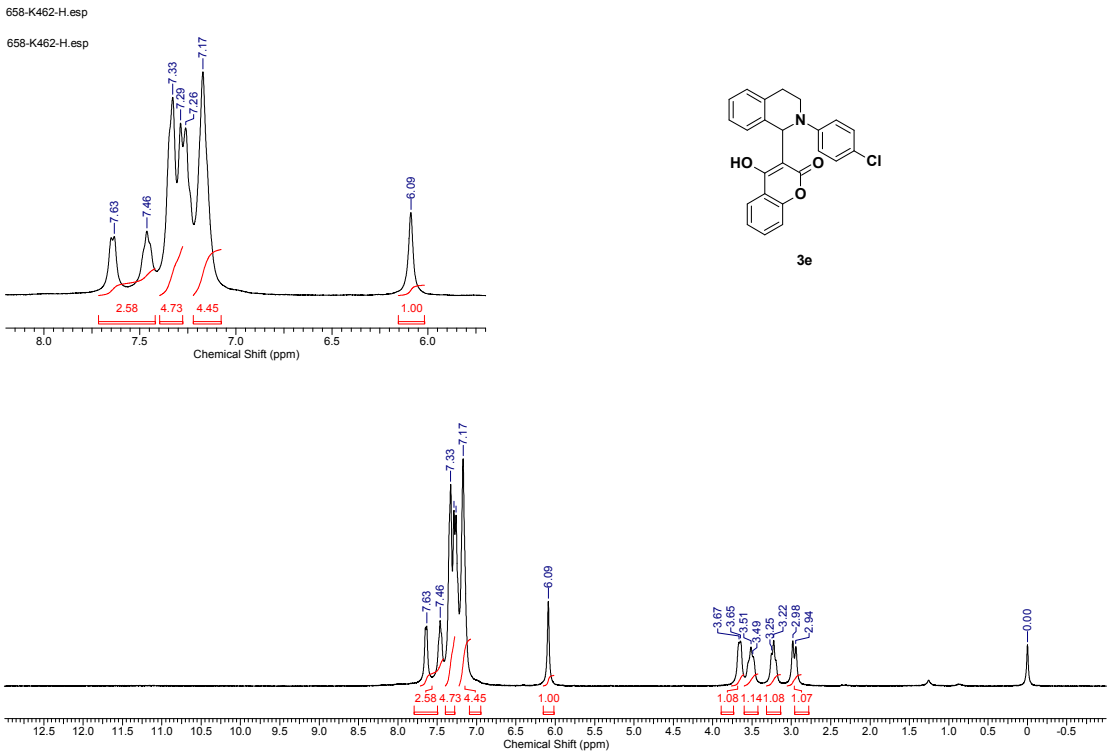


Figure S20. ^{1}H NMR spectrum of compound **3e**

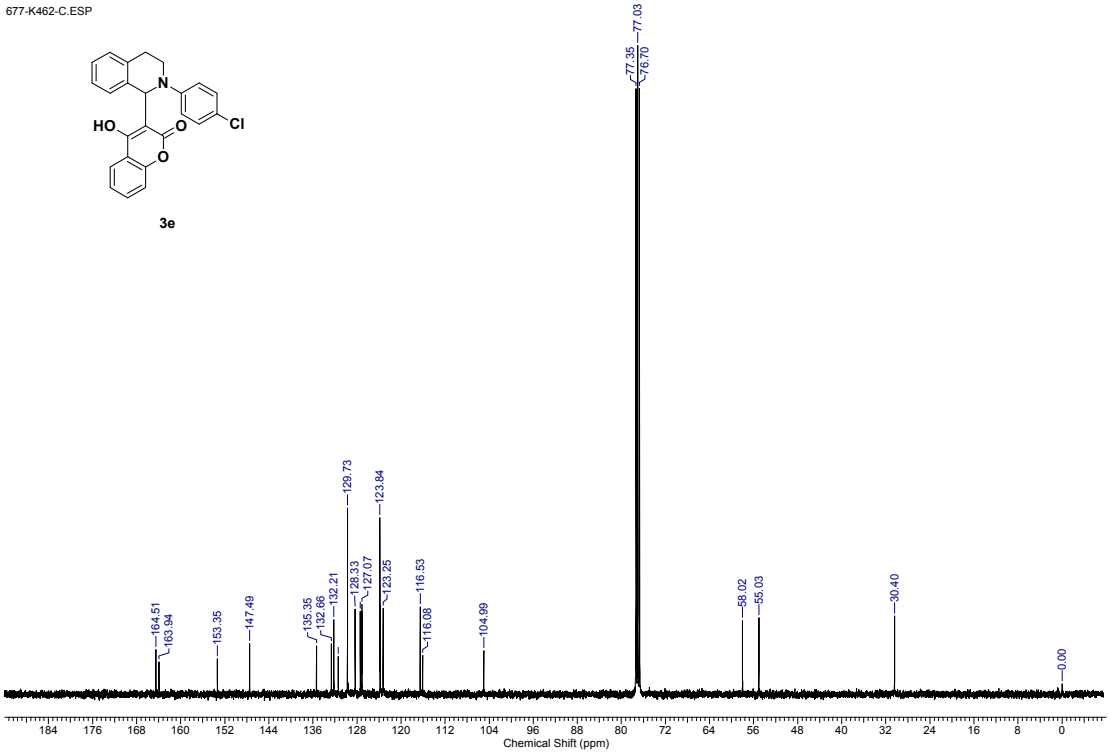


Figure S21. ^{13}C NMR spectrum of compound **3e**

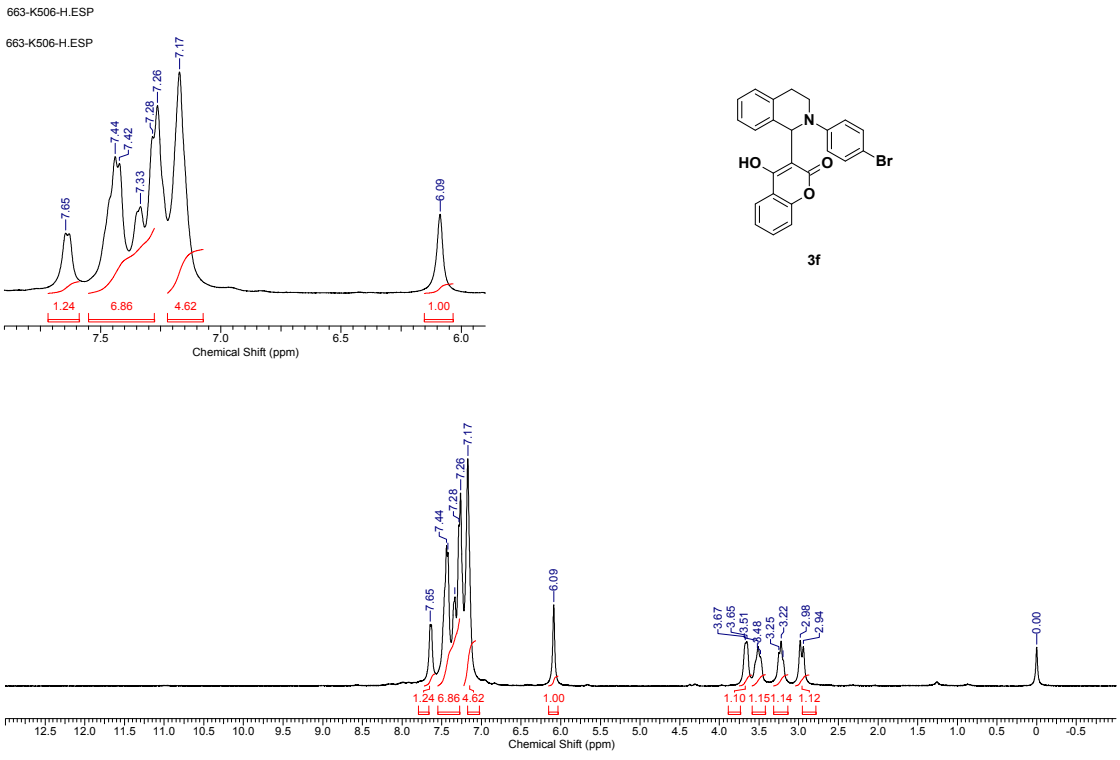


Figure S22. ^{1}H NMR spectrum of compound **3f**

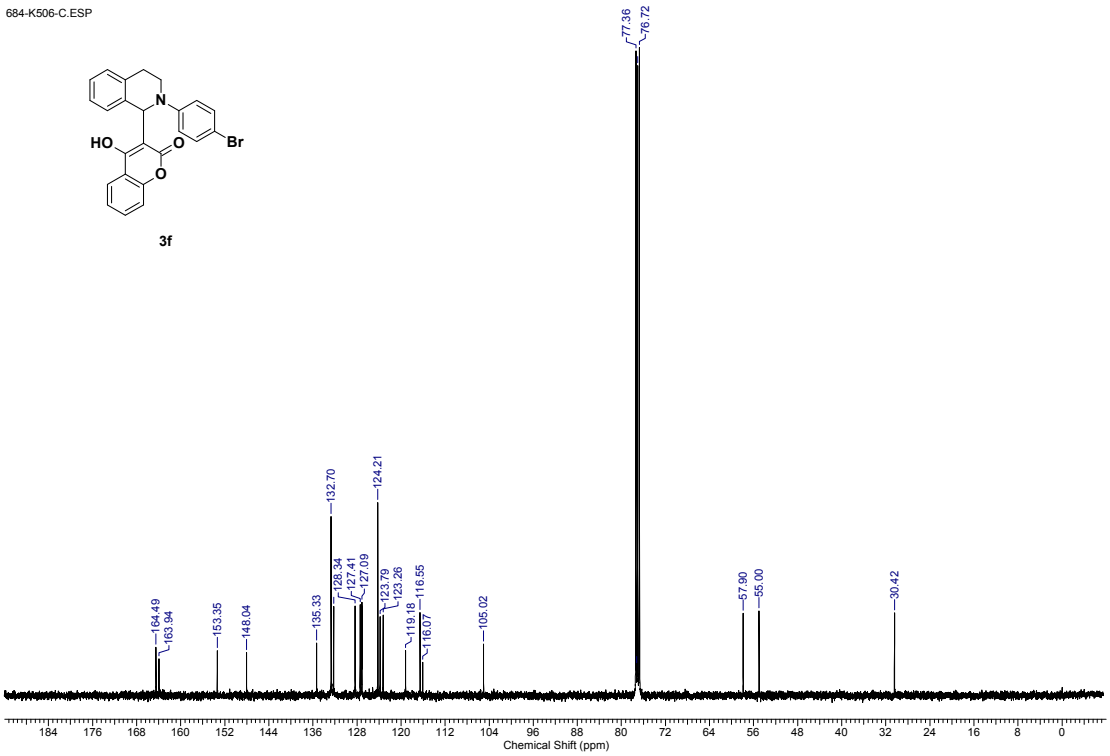


Figure S23. ^{13}C NMR spectrum of compound **3f**

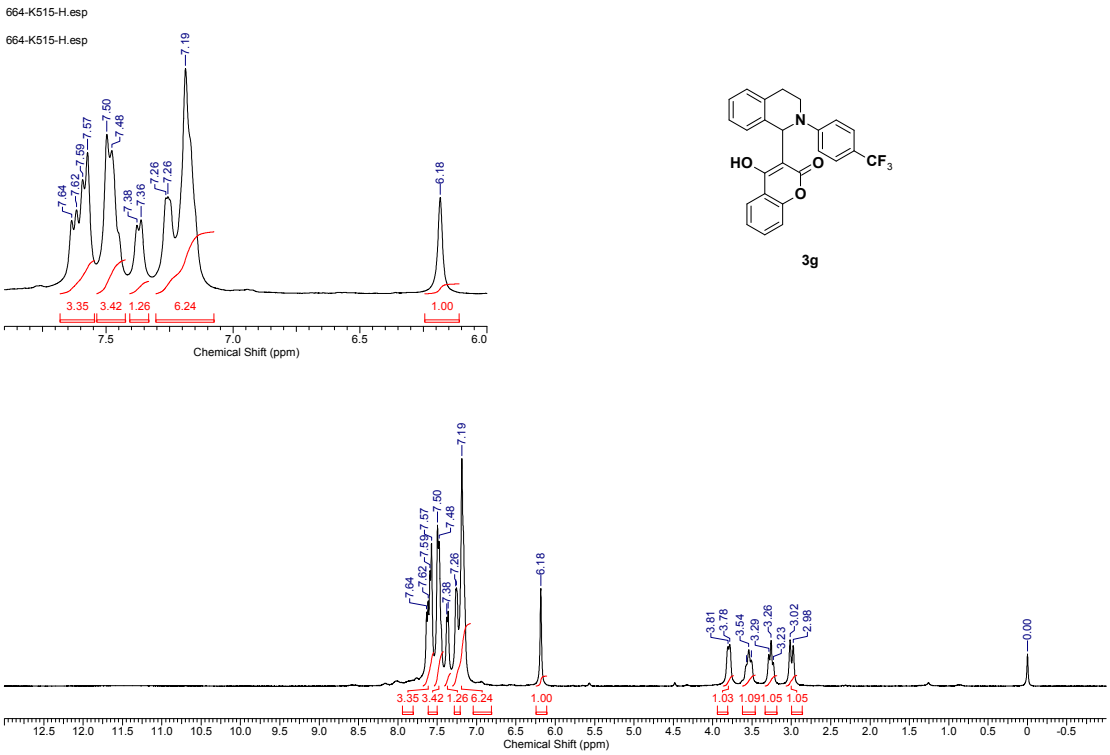
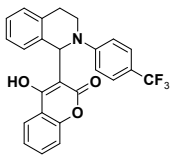


Figure S24. ^{1}H NMR spectrum of compound **3g**

624-K515-F.esp



3g

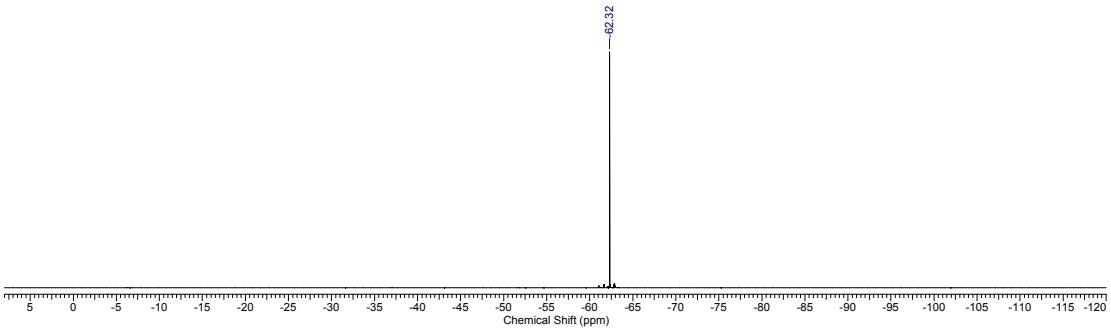


Figure S25. ^{19}F NMR spectrum of compound **3g**

685-K515-C.ESP

3g

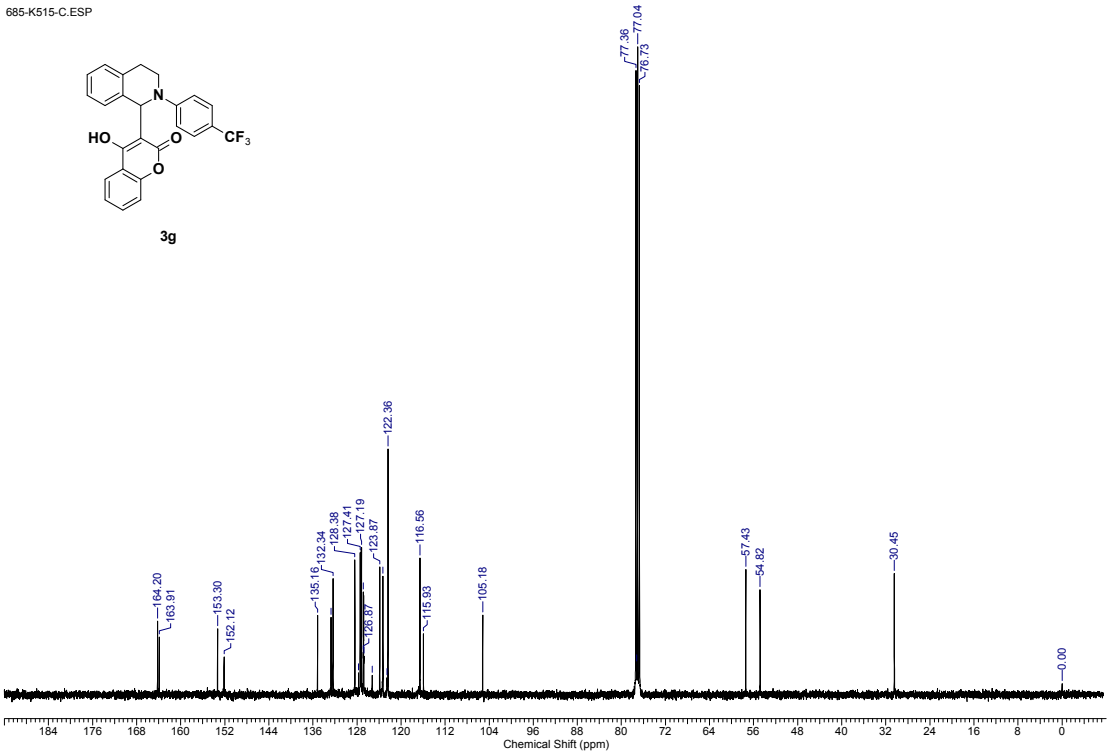


Figure S26. ^{13}C NMR spectrum of compound **3g**

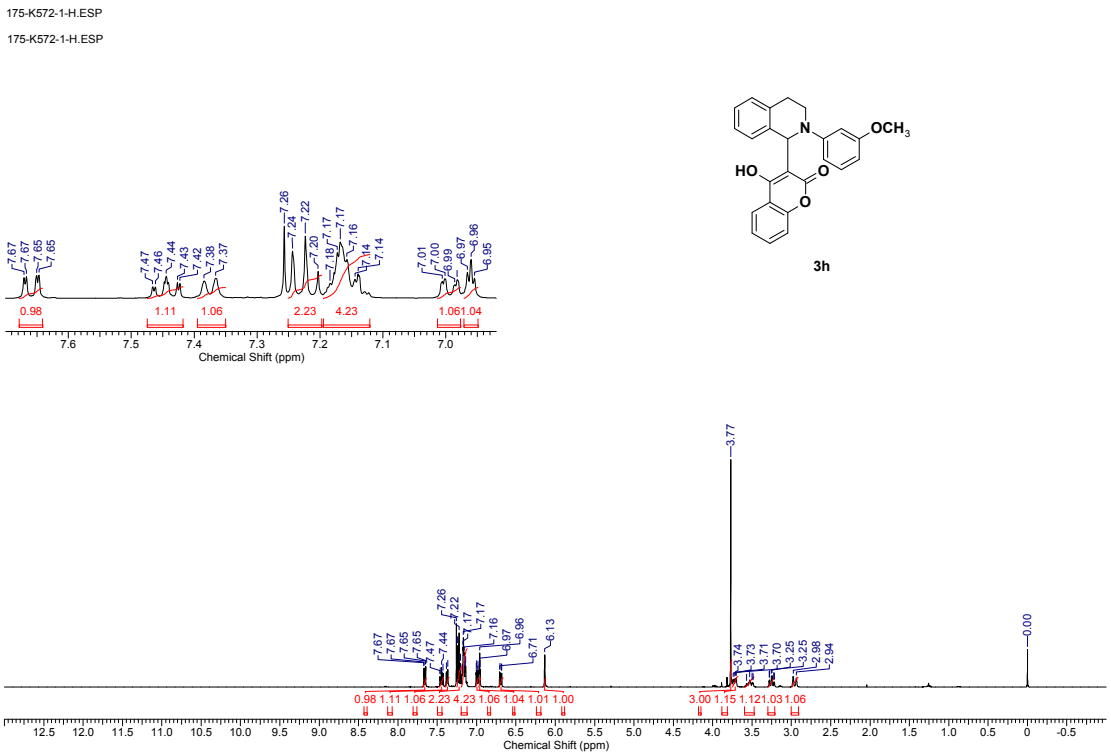


Figure S27. ^{1}H NMR spectrum of compound **3h**

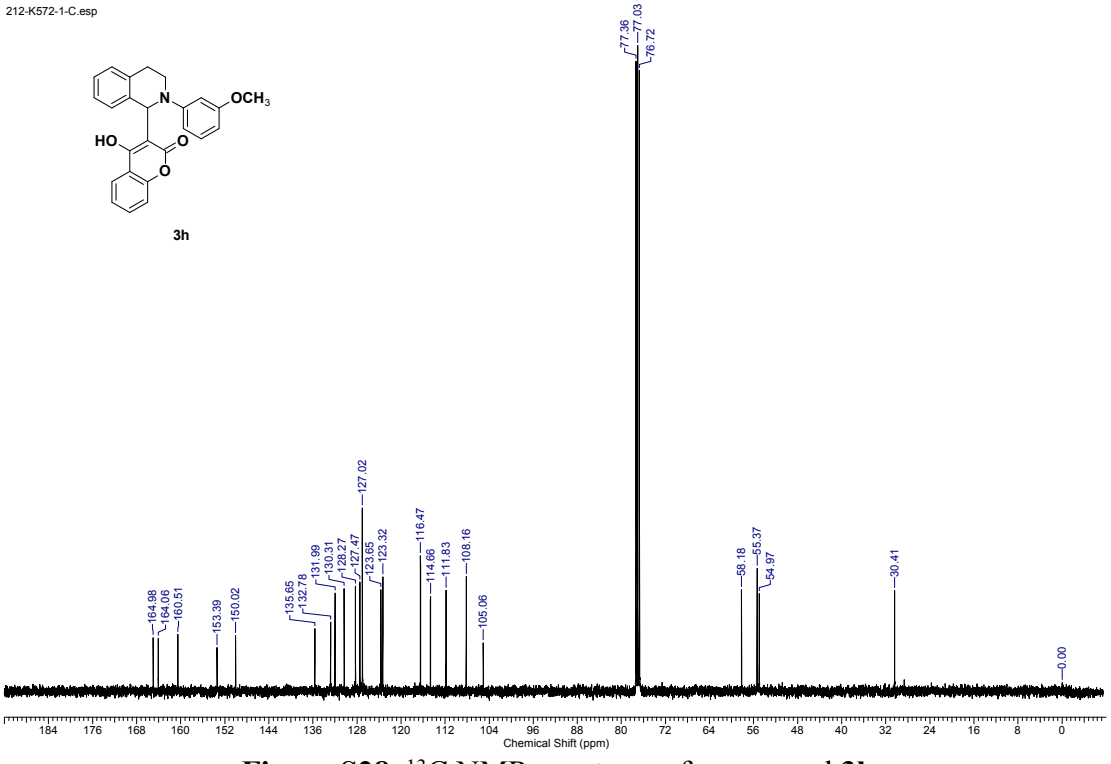


Figure S28. ^{13}C NMR spectrum of compound **3h**

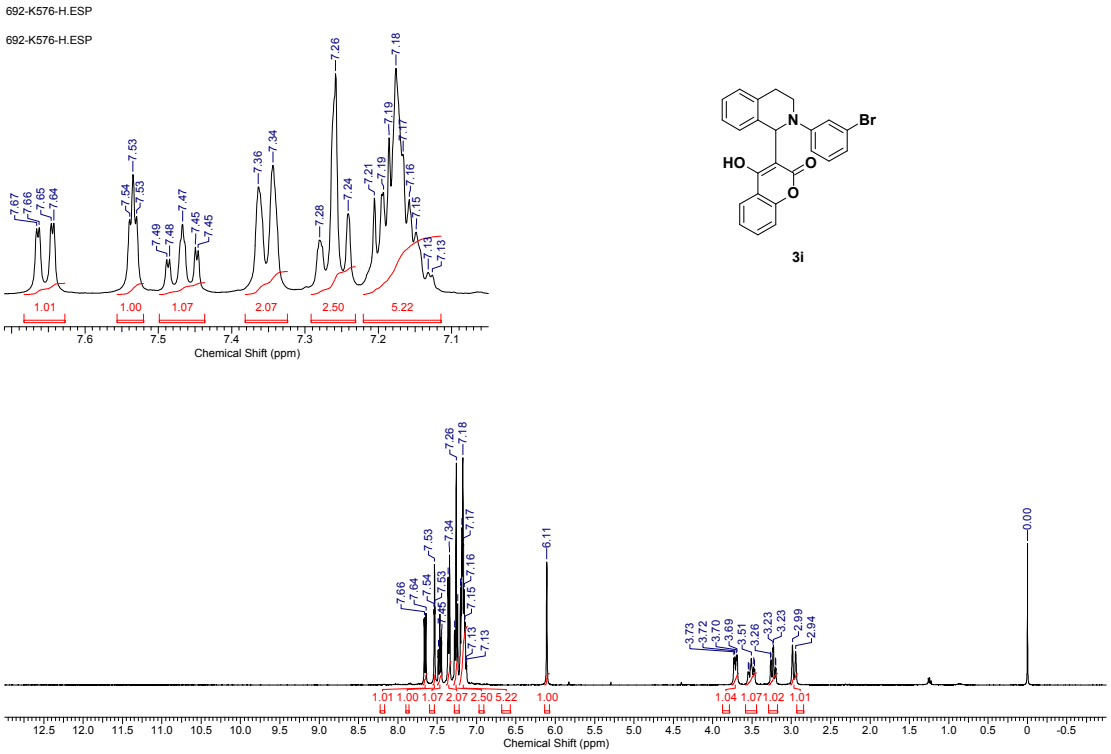


Figure S29. ^{1}H NMR spectrum of compound **3i**

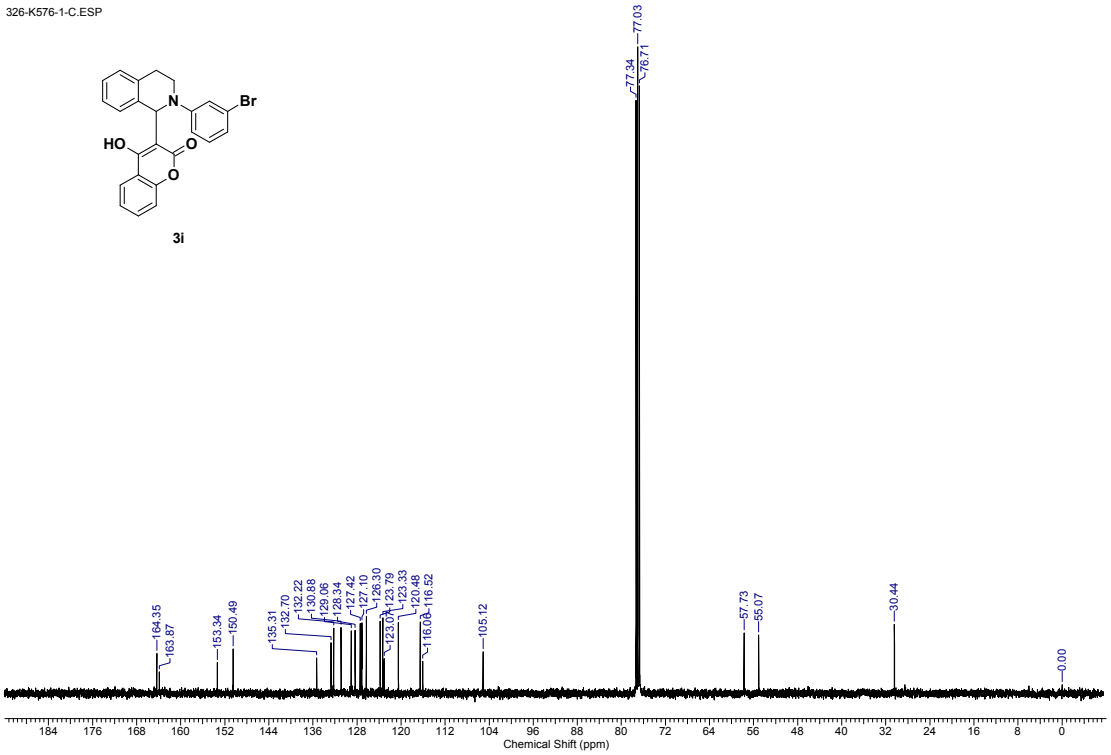


Figure S30. ^{13}C NMR spectrum of compound **3i**

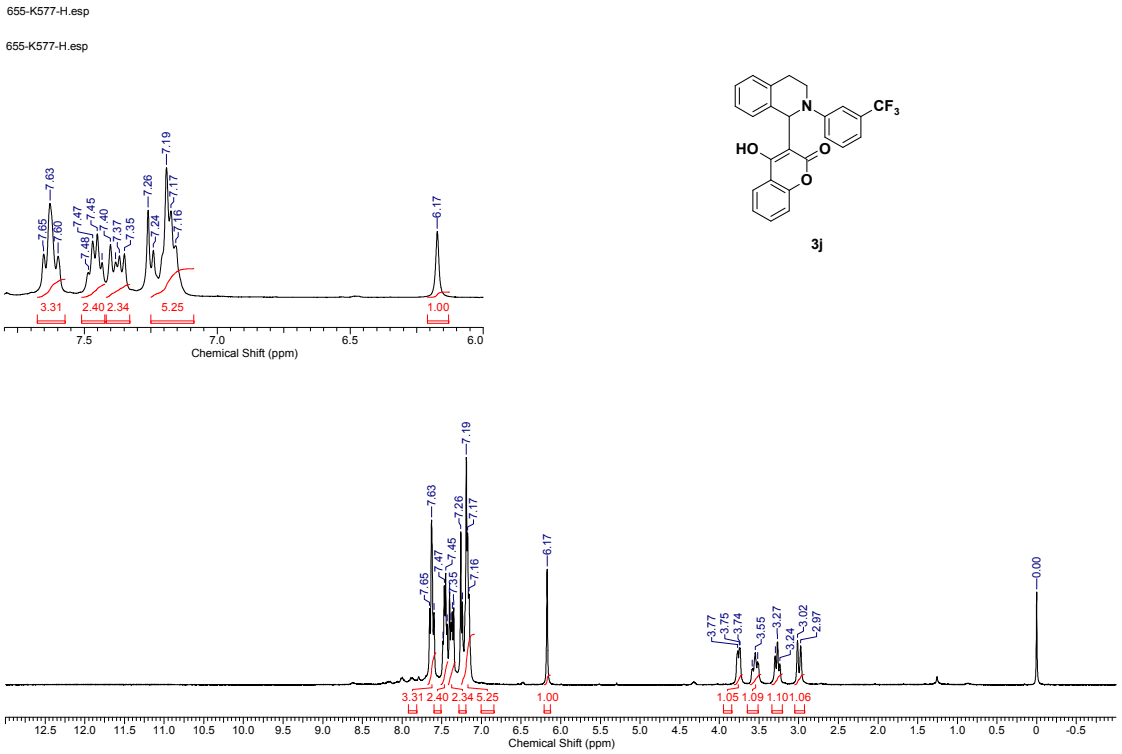


Figure S31. ^{1}H NMR spectrum of compound **3j**

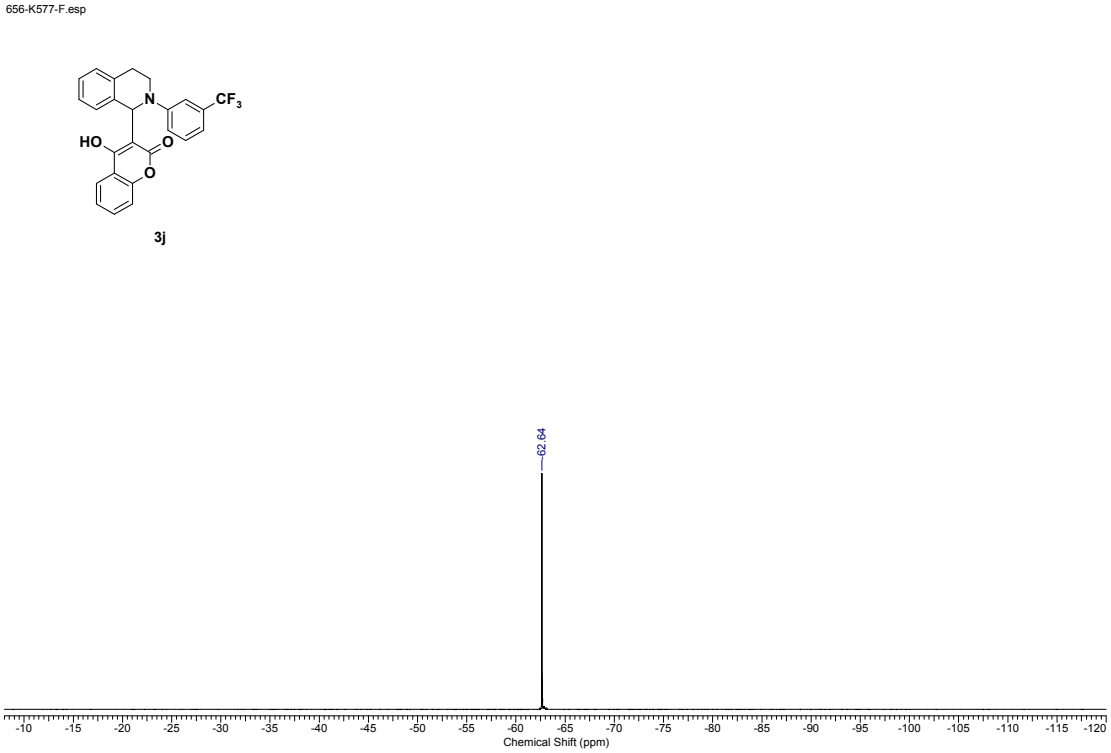


Figure S32. ^{19}F NMR spectrum of compound **3j**

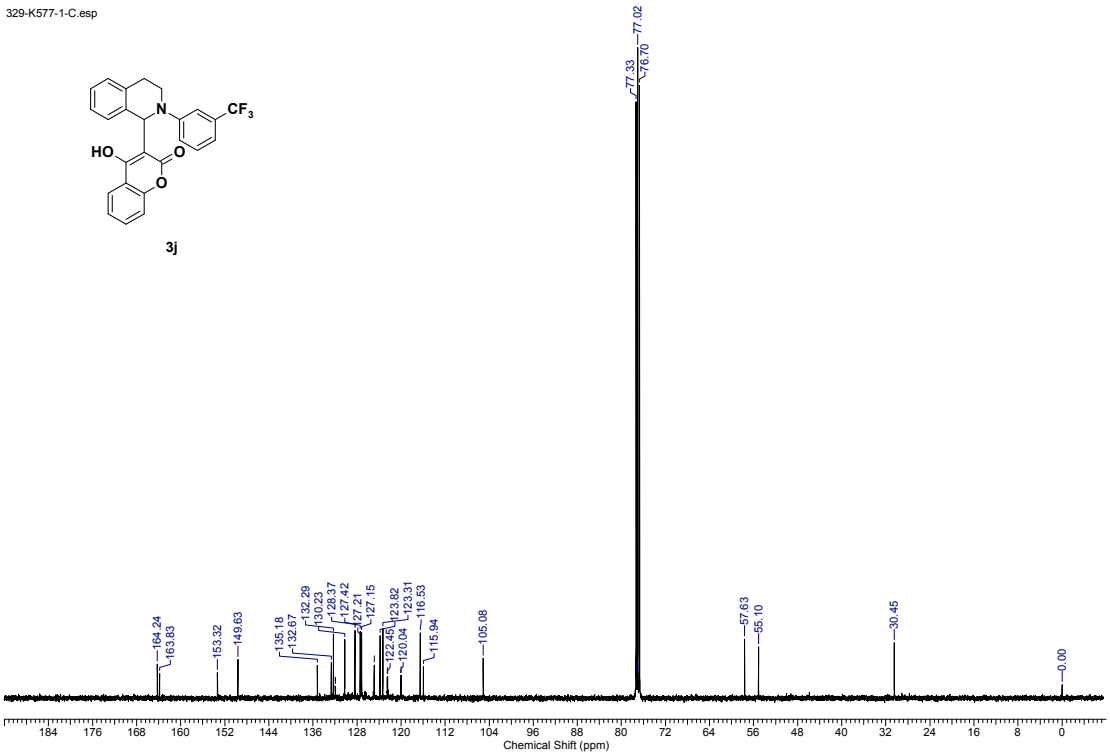


Figure S33. ^{13}C NMR spectrum of compound **3j**

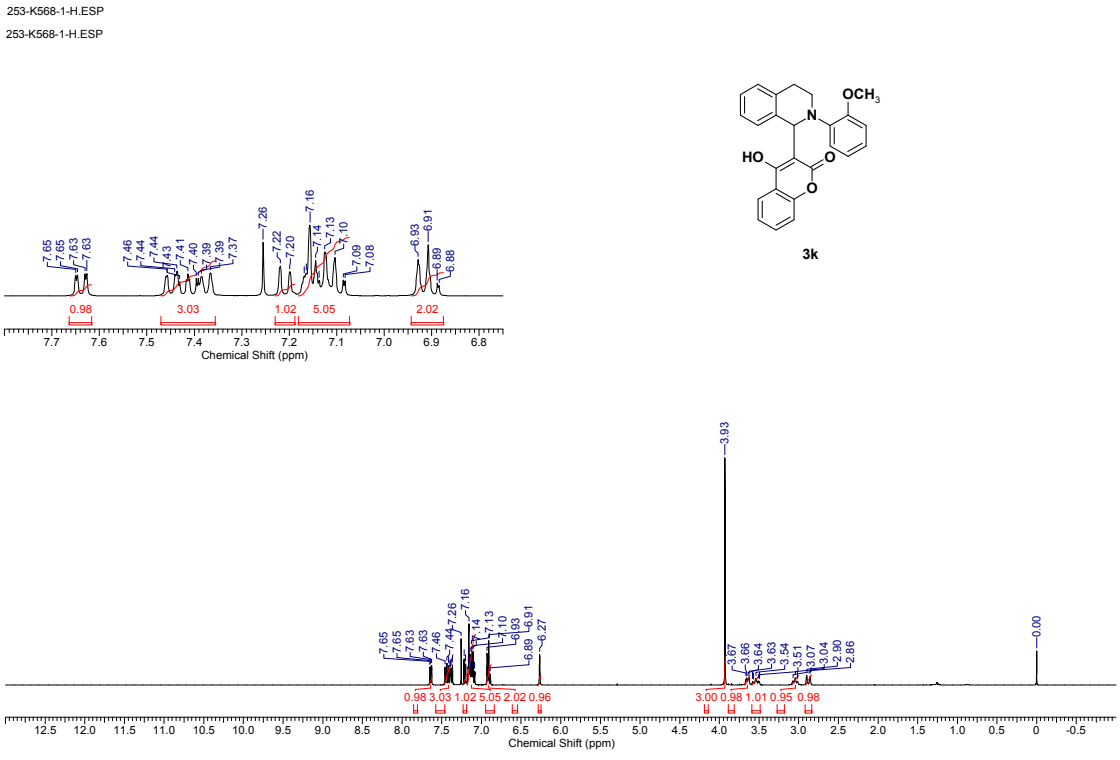


Figure S34. ^{1}H NMR spectrum of compound **3k**

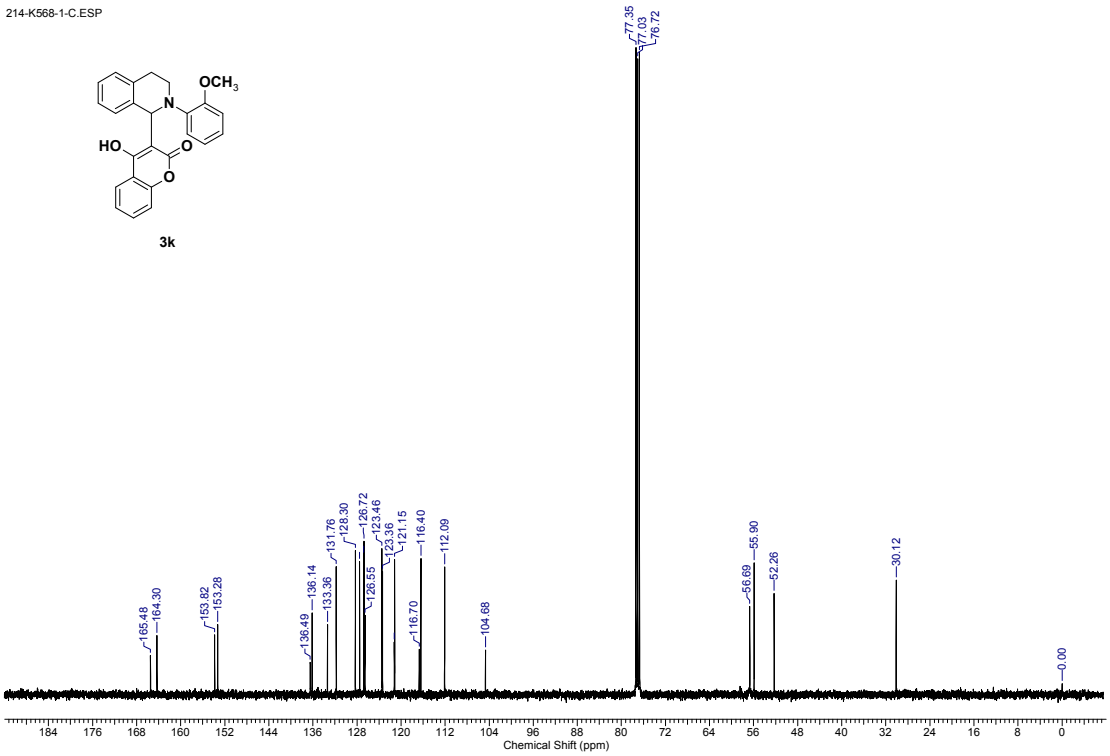


Figure S35. ^{13}C NMR spectrum of compound **3k**

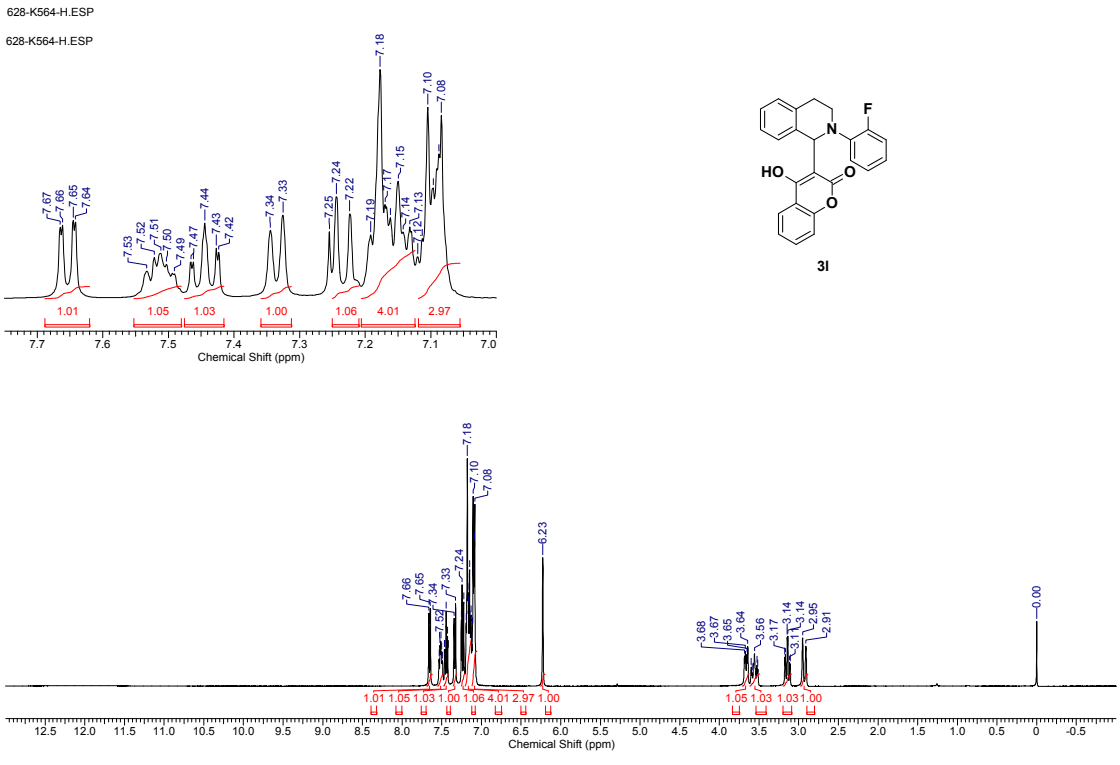


Figure S36. ^{1}H NMR spectrum of compound **3l**

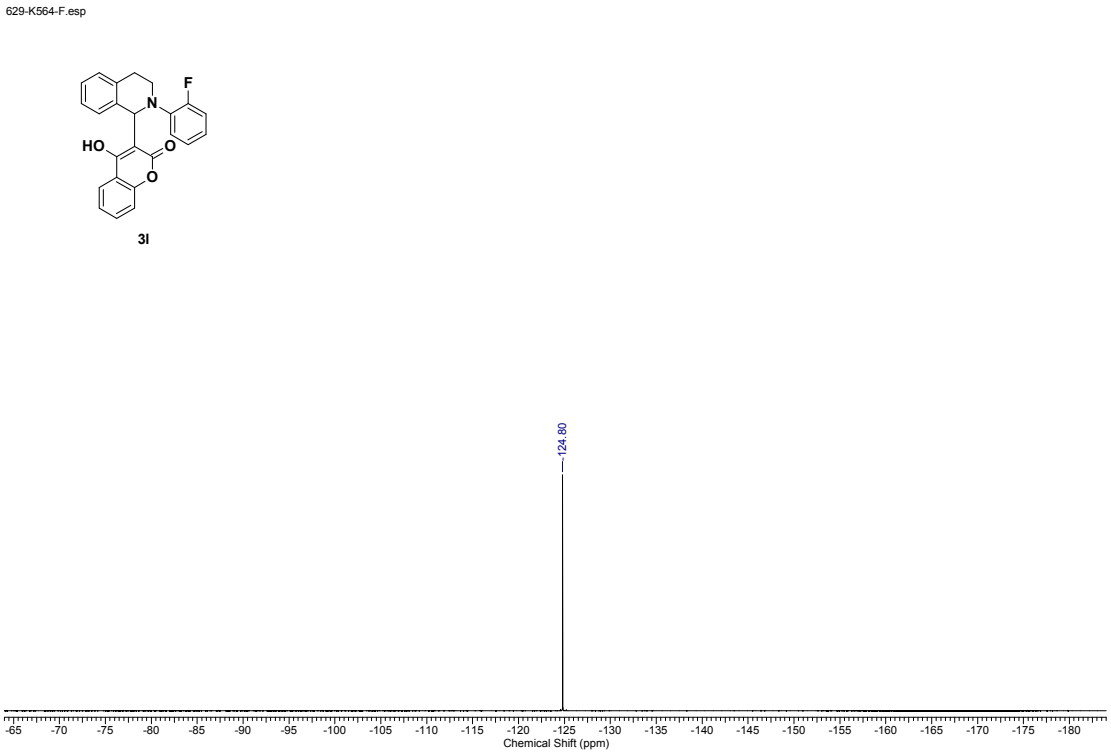


Figure S37. ^{19}F NMR spectrum of compound **3l**

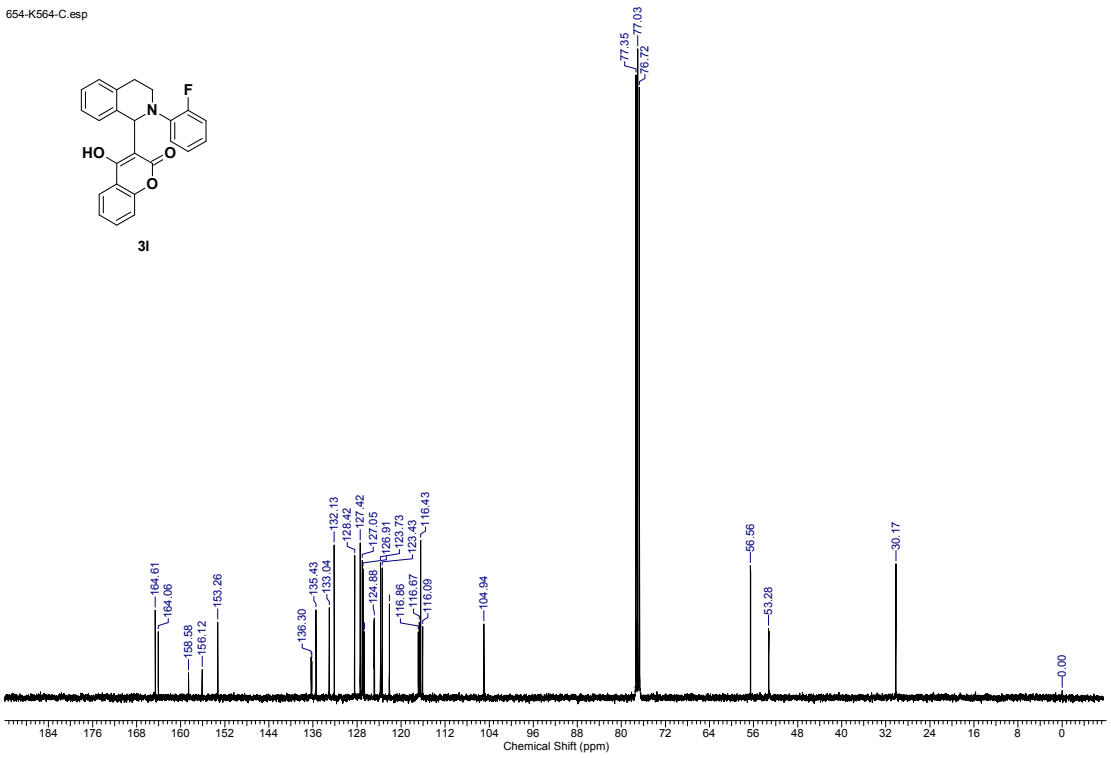


Figure S38. ^{13}C NMR spectrum of compound **3l**

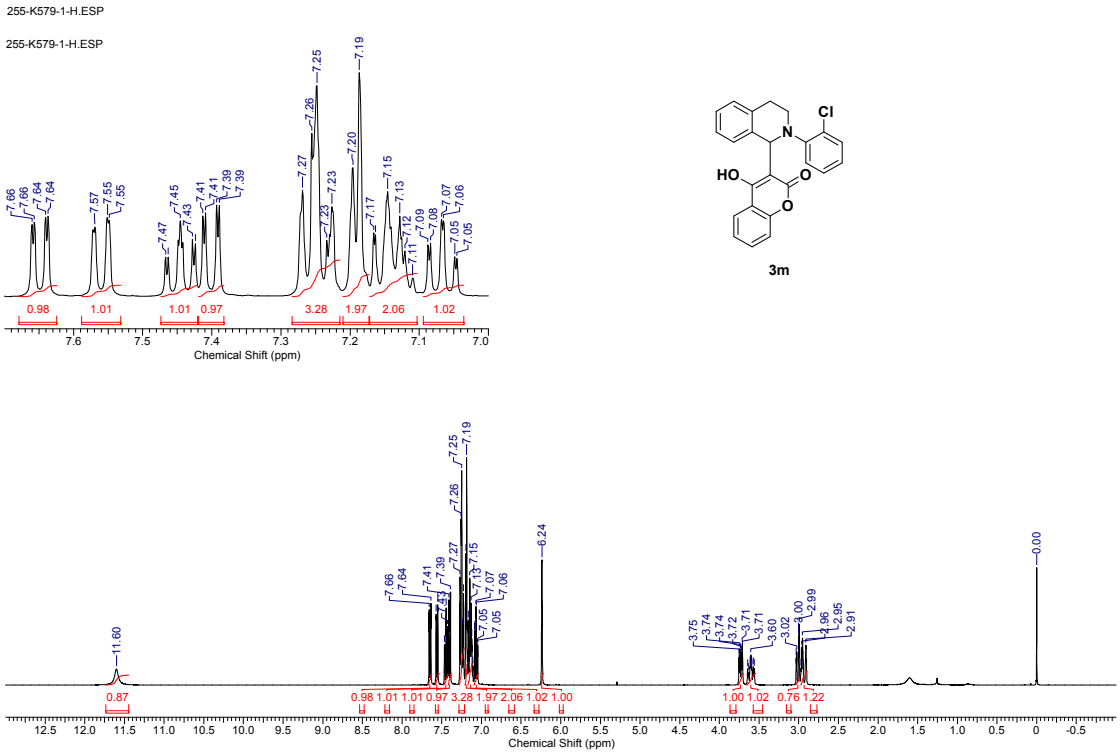


Figure S39. [1]H NMR spectrum of compound **3m**

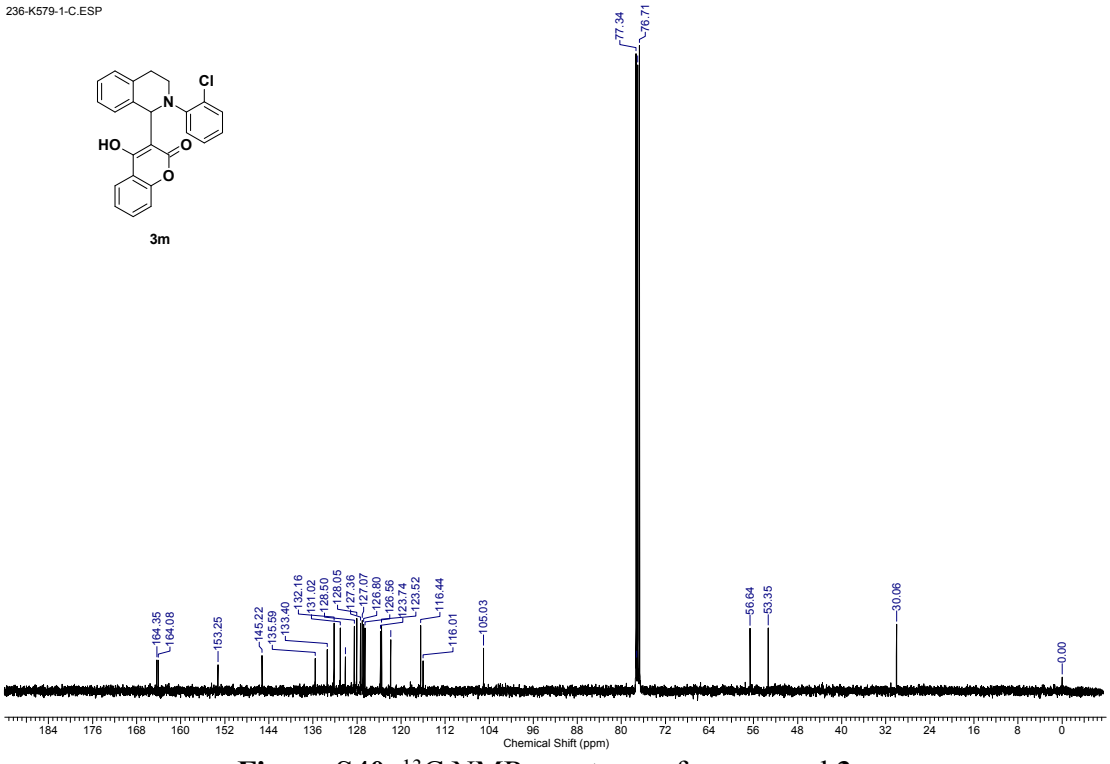


Figure S40. [13]C NMR spectrum of compound **3m**

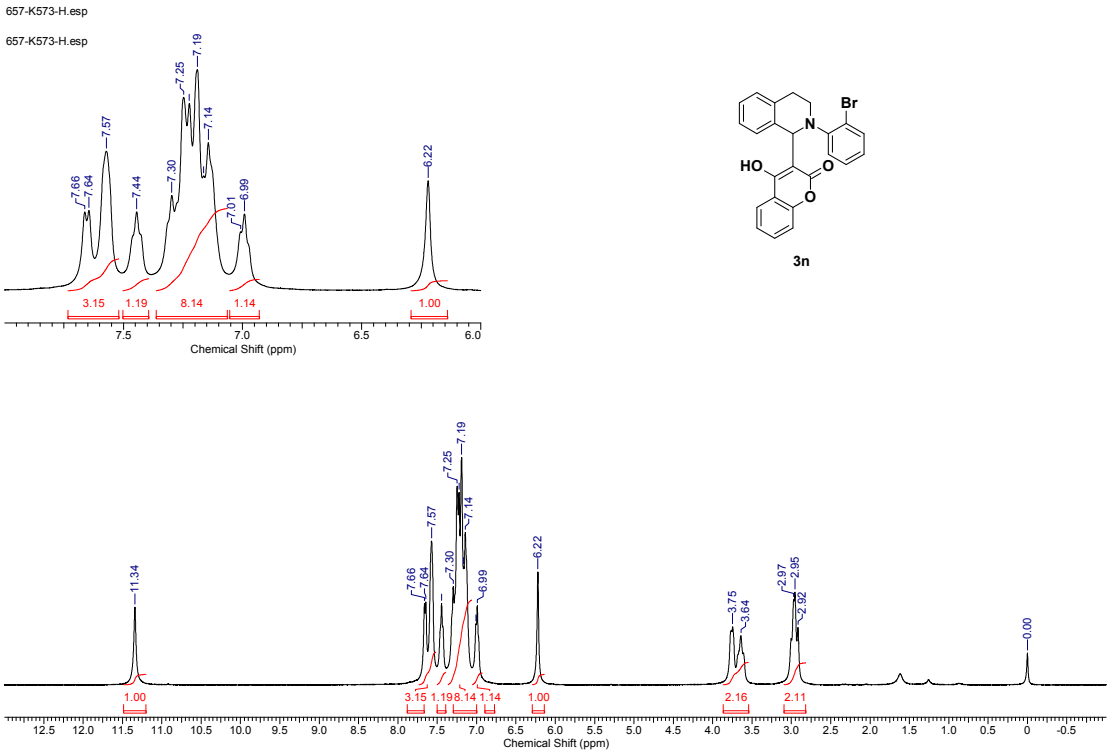


Figure S41. ^{1}H NMR spectrum of compound **3n**

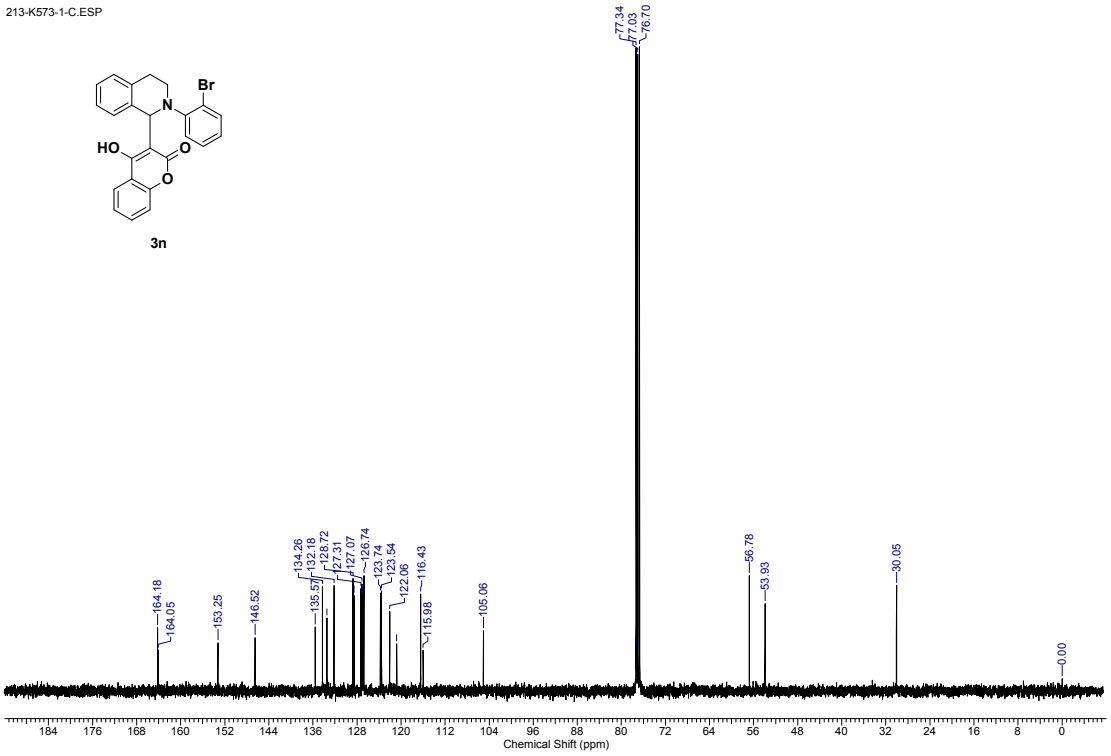


Figure S42. ^{13}C NMR spectrum of compound **3n**

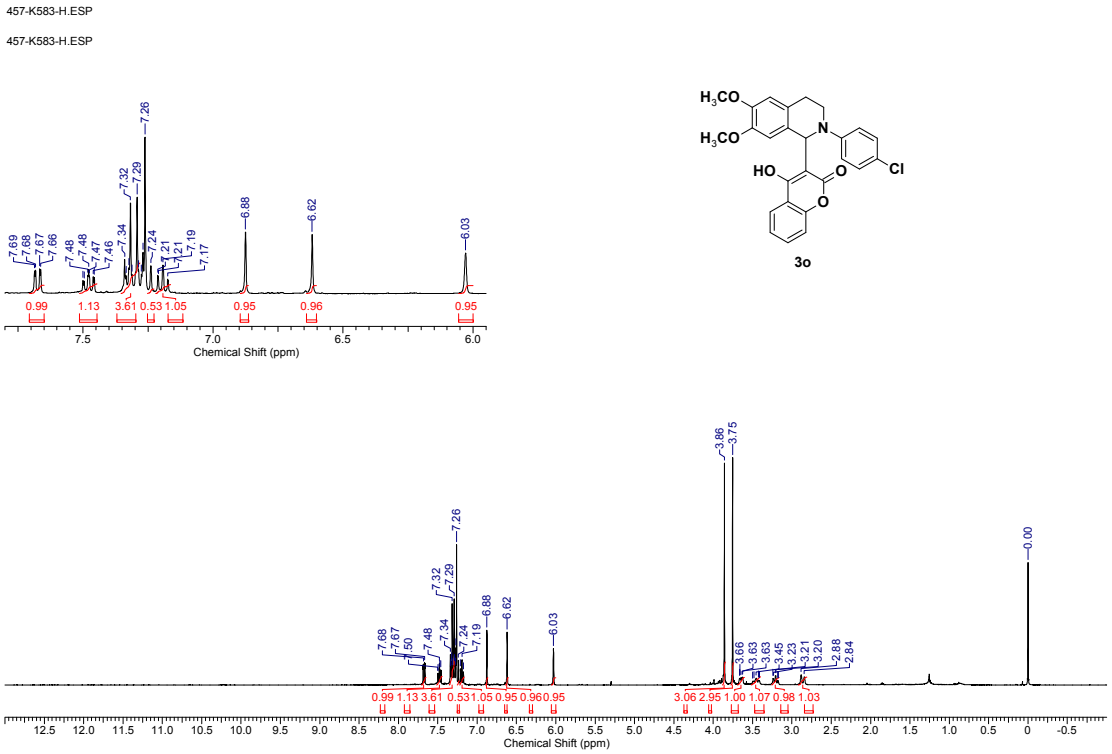


Figure S43. ^{1}H NMR spectrum of compound **3o**

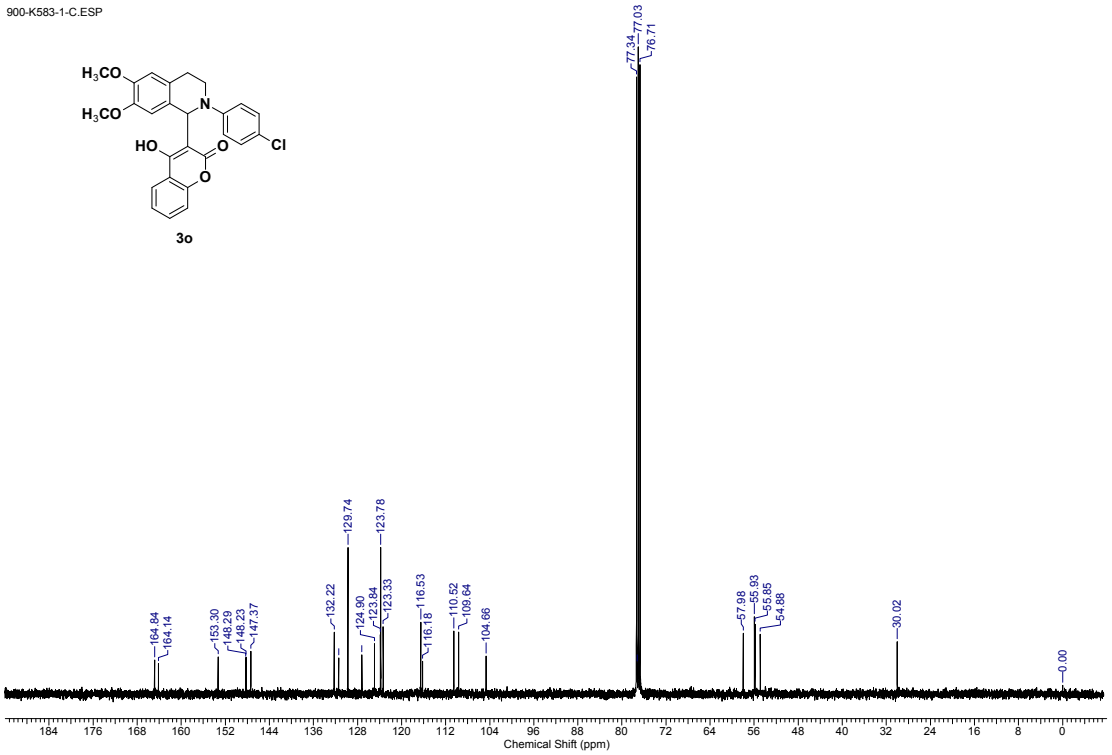


Figure S44. ^{13}C NMR spectrum of compound **3o**

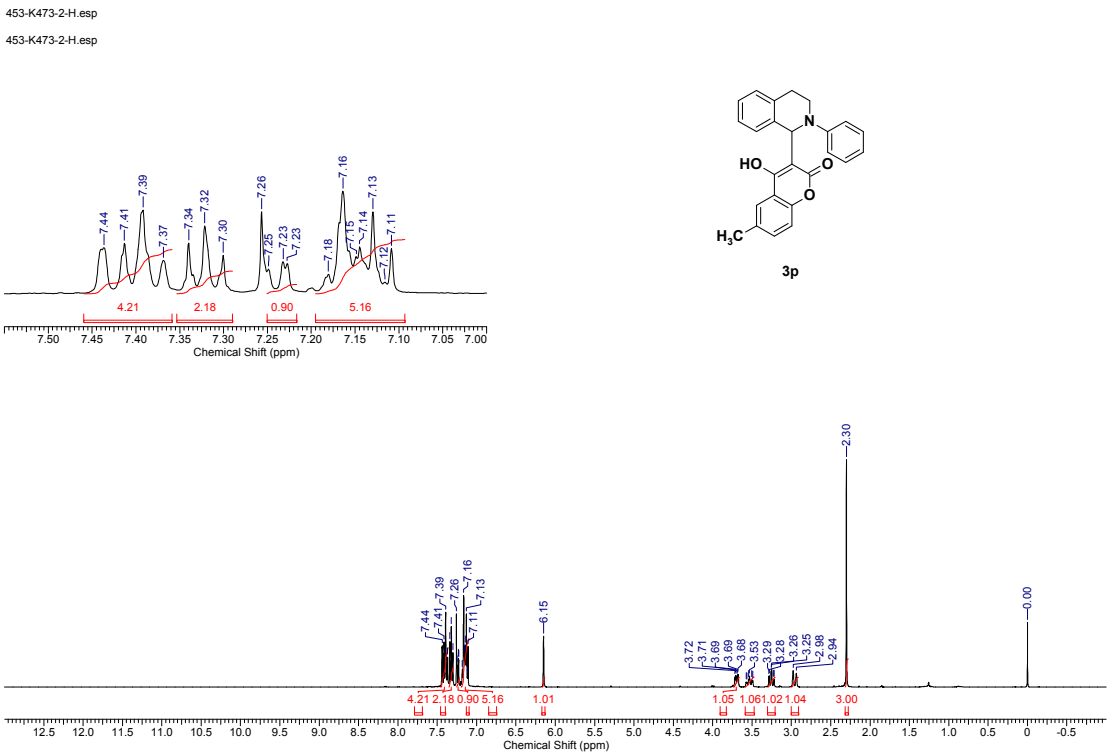


Figure S45. ^{1}H NMR spectrum of compound **3p**

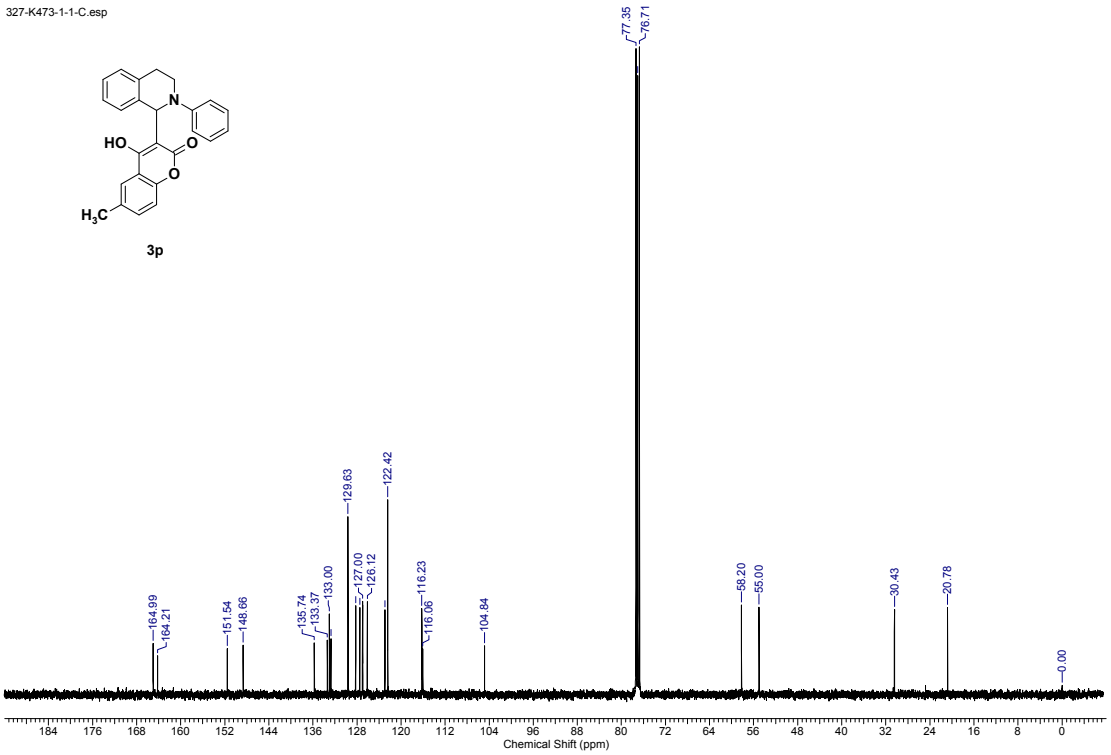


Figure S46. ^{13}C NMR spectrum of compound **3p**

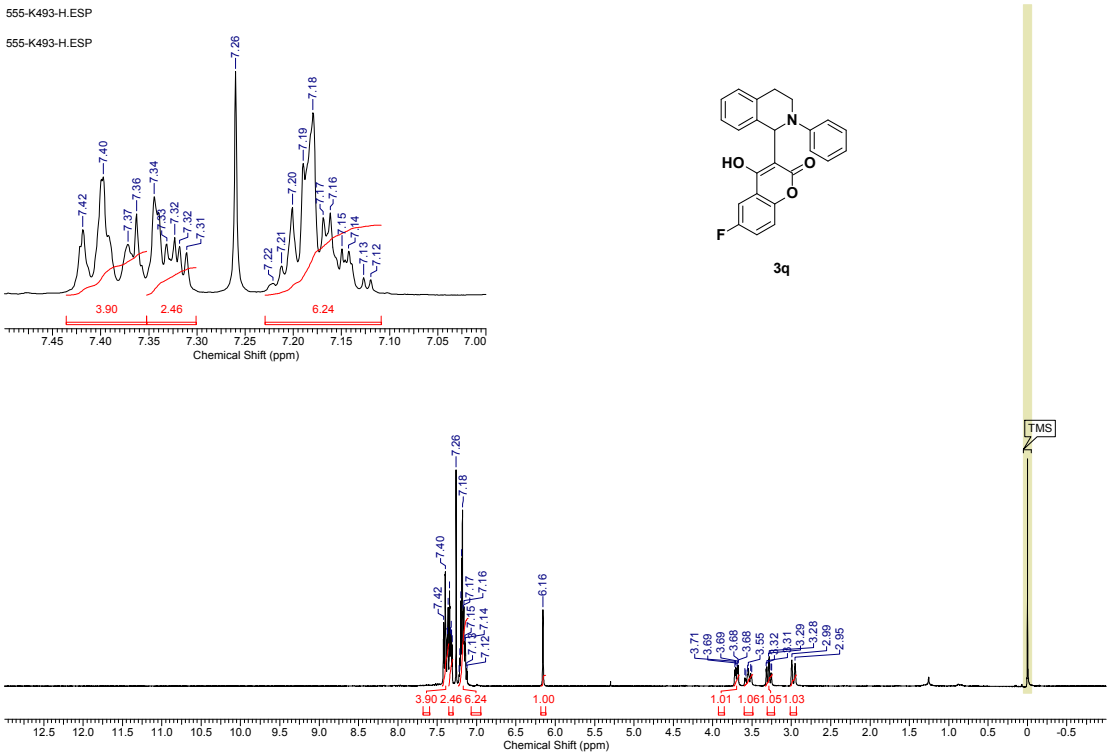


Figure S47. ^{1}H NMR spectrum of compound **3q**

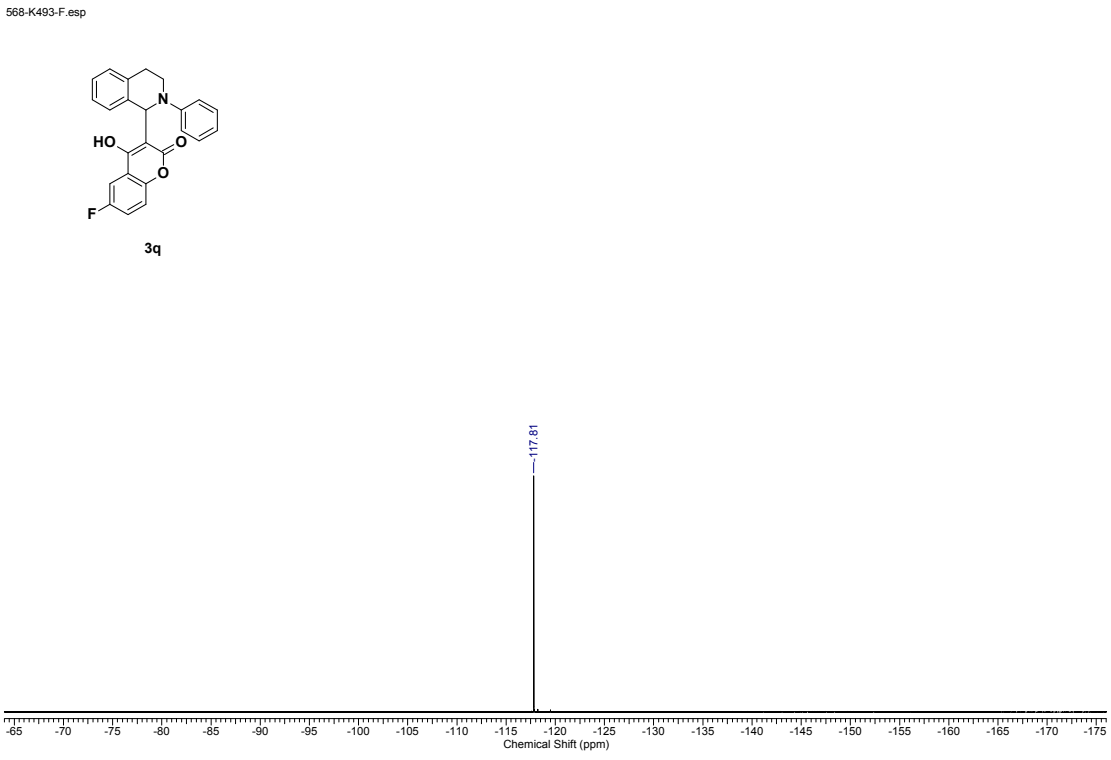


Figure S48. ^{19}F NMR spectrum of compound **3q**

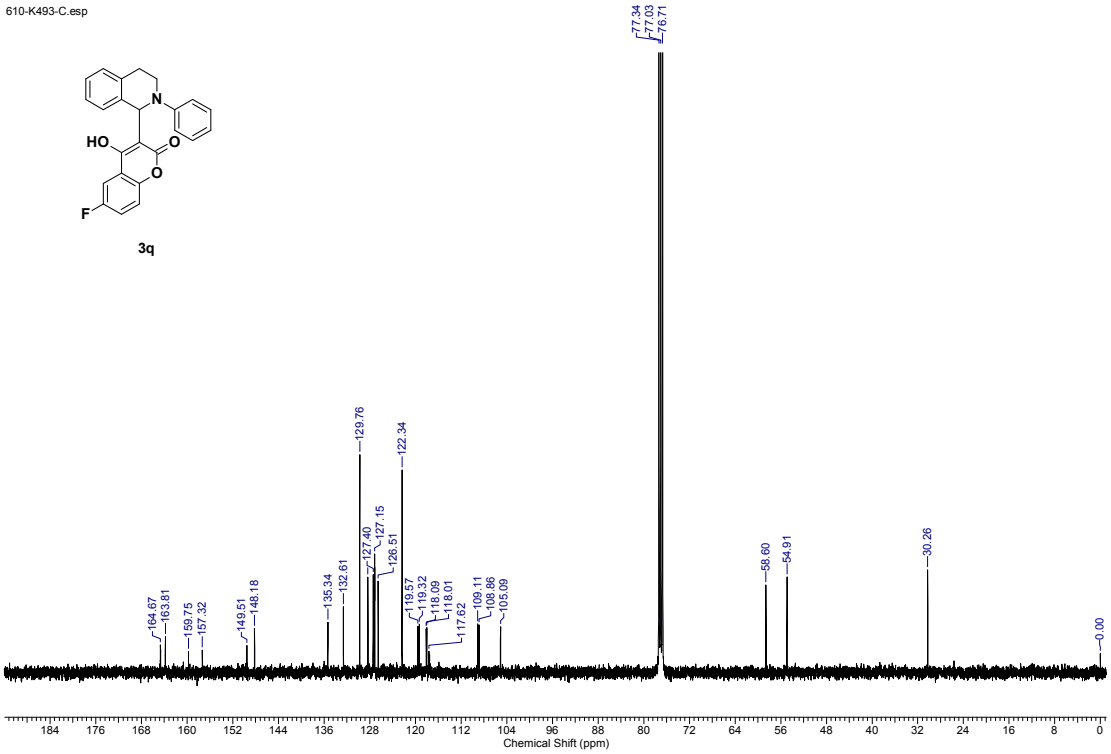


Figure S49. ^{13}C NMR spectrum of compound **3q**

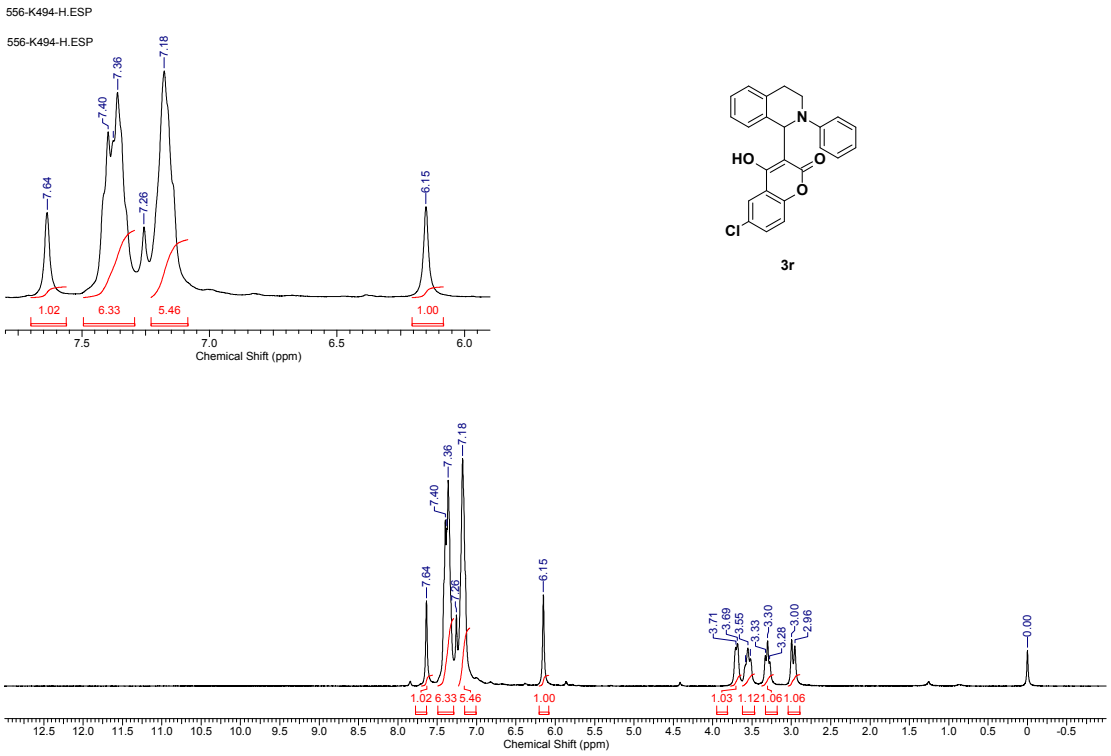


Figure S50. ^{1}H NMR spectrum of compound **3r**

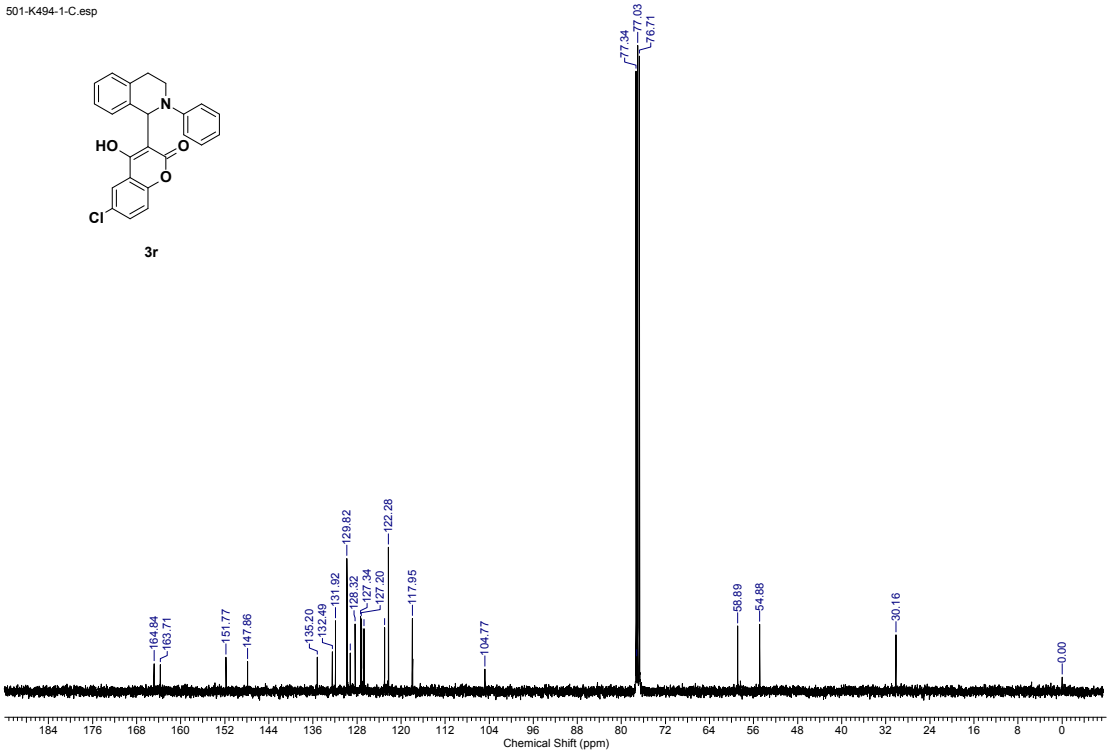


Figure S51. ^{13}C NMR spectrum of compound **3r**

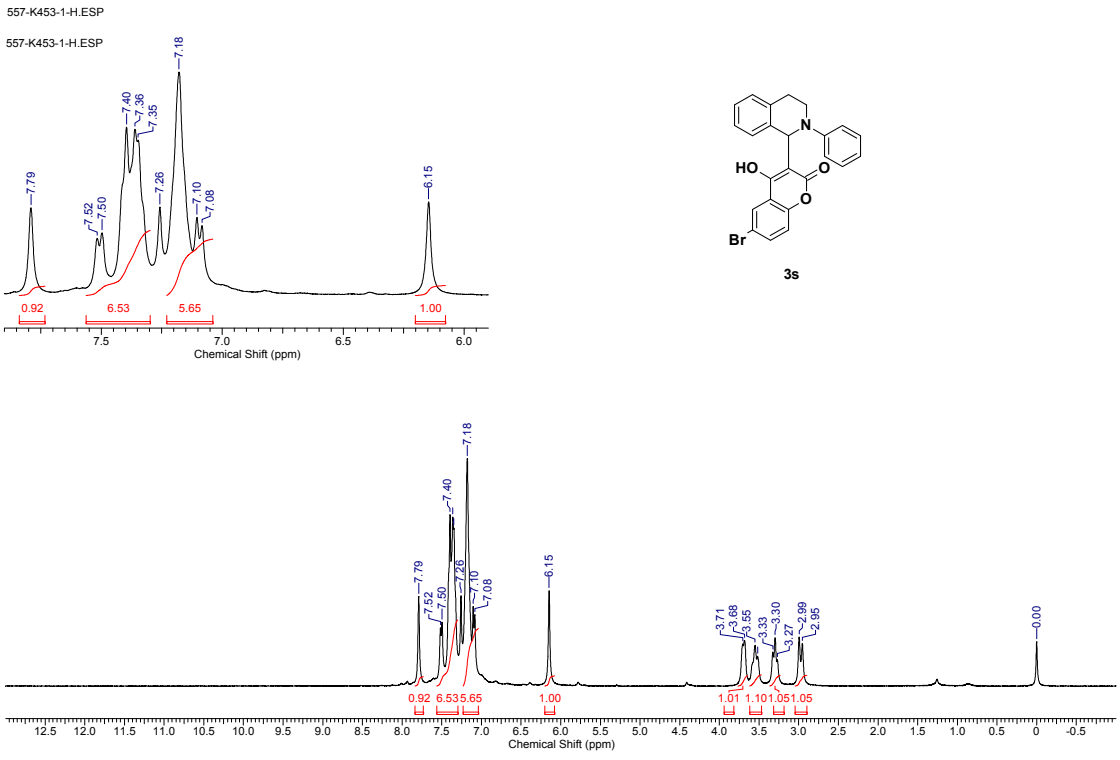


Figure S52. ^{1}H NMR spectrum of compound **3s**

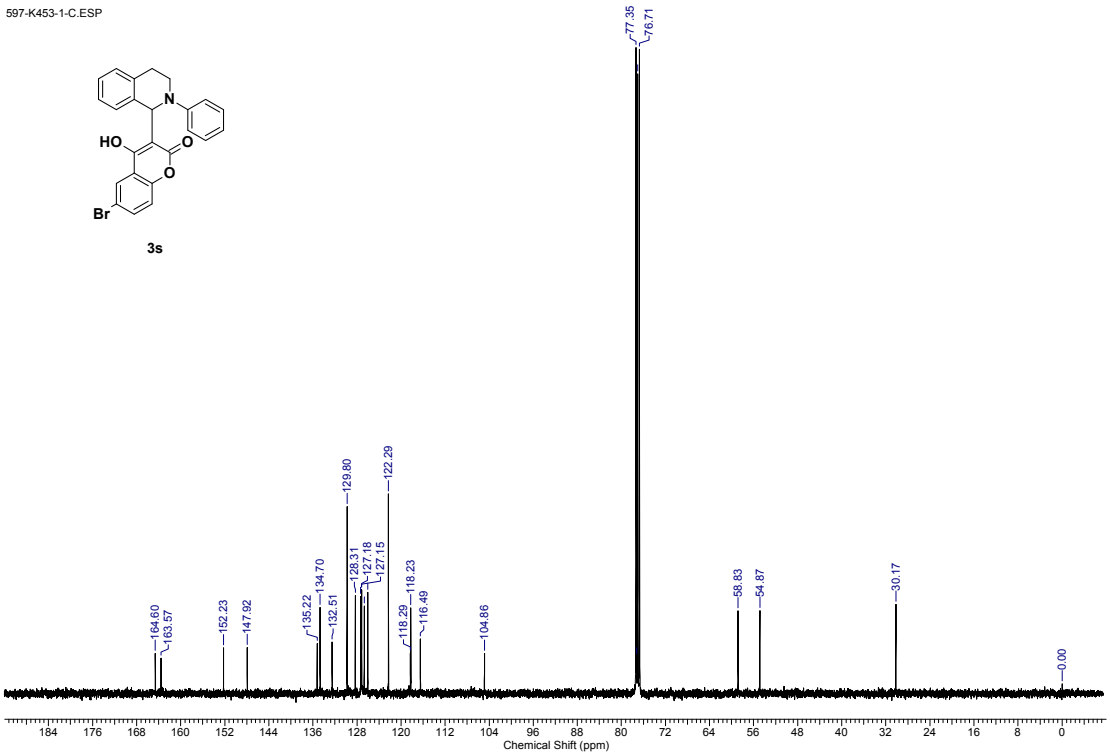


Figure S53. ^{13}C NMR spectrum of compound **3s**

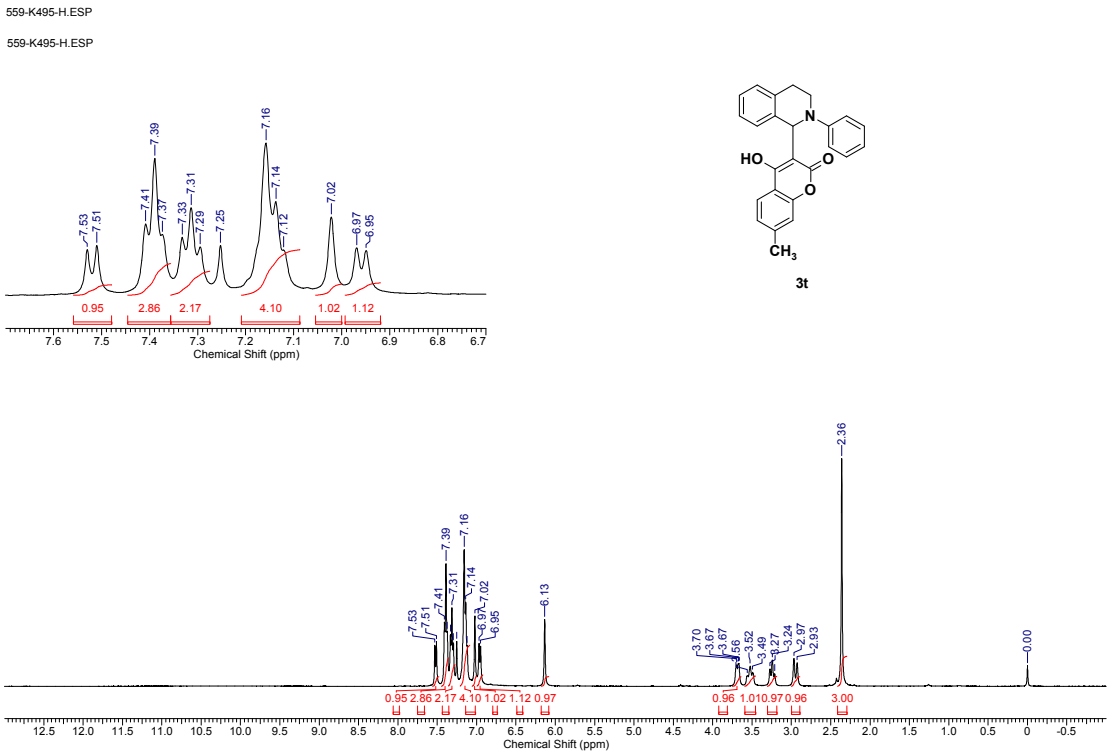


Figure S54. ^{1}H NMR spectrum of compound **3t**

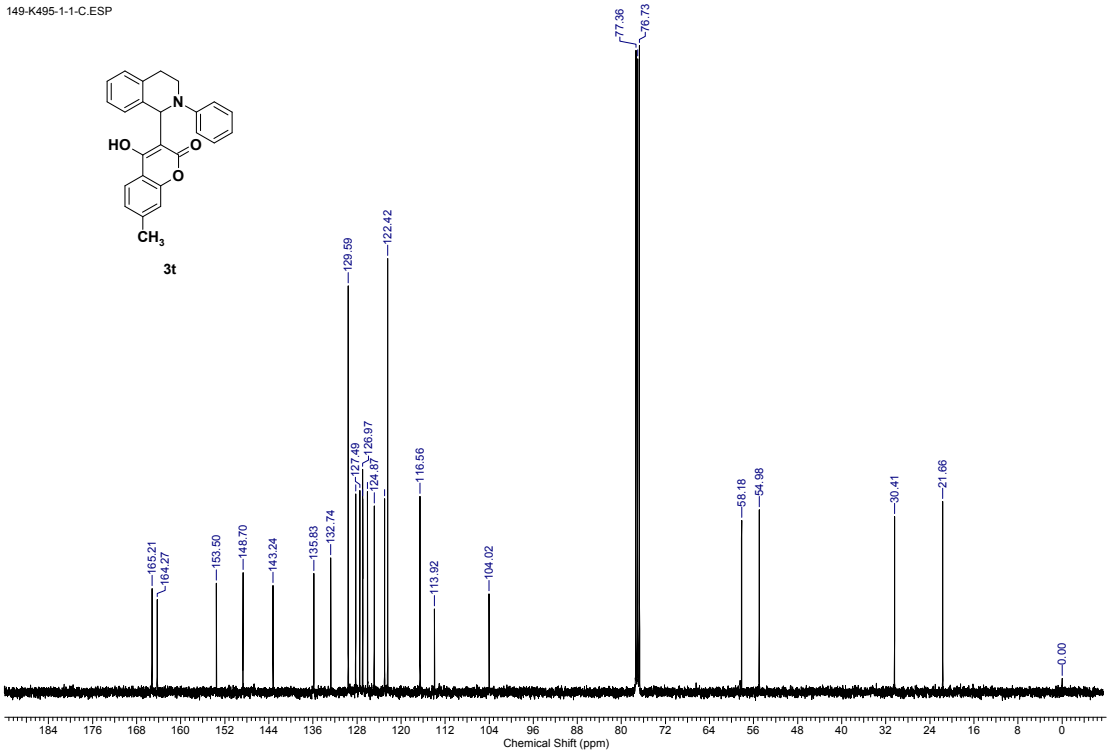


Figure S55. ^{13}C NMR spectrum of compound **3t**

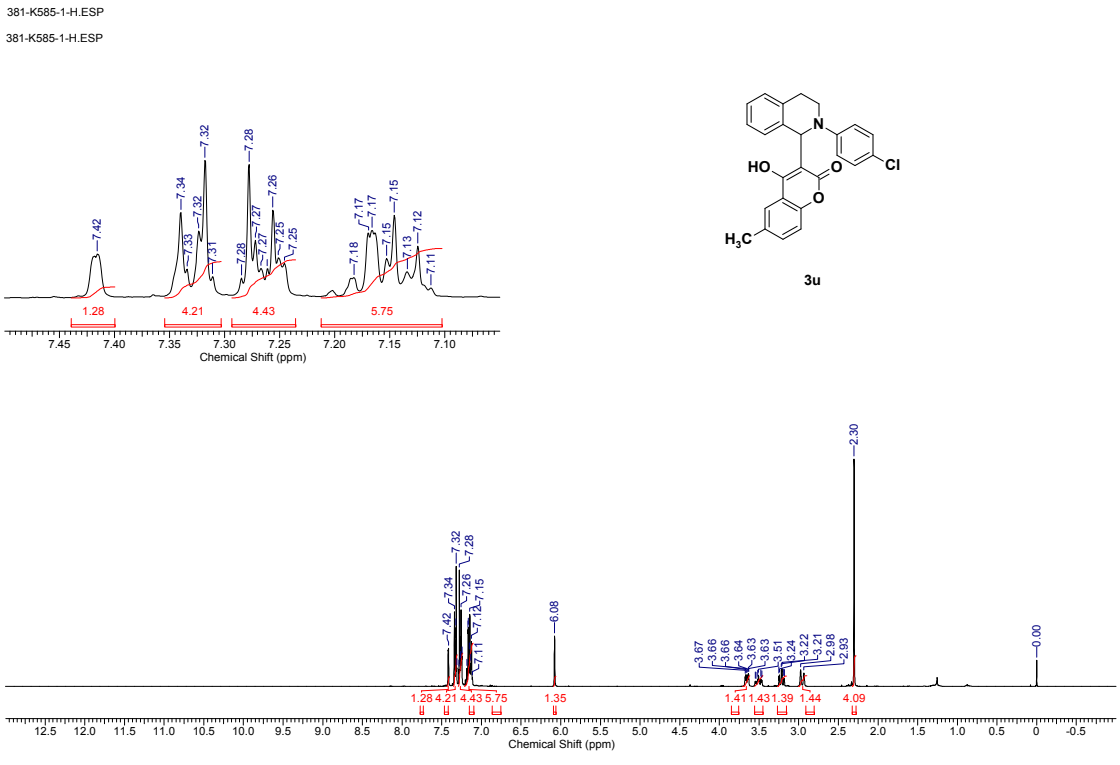


Figure S56. ^{1}H NMR spectrum of compound **3u**

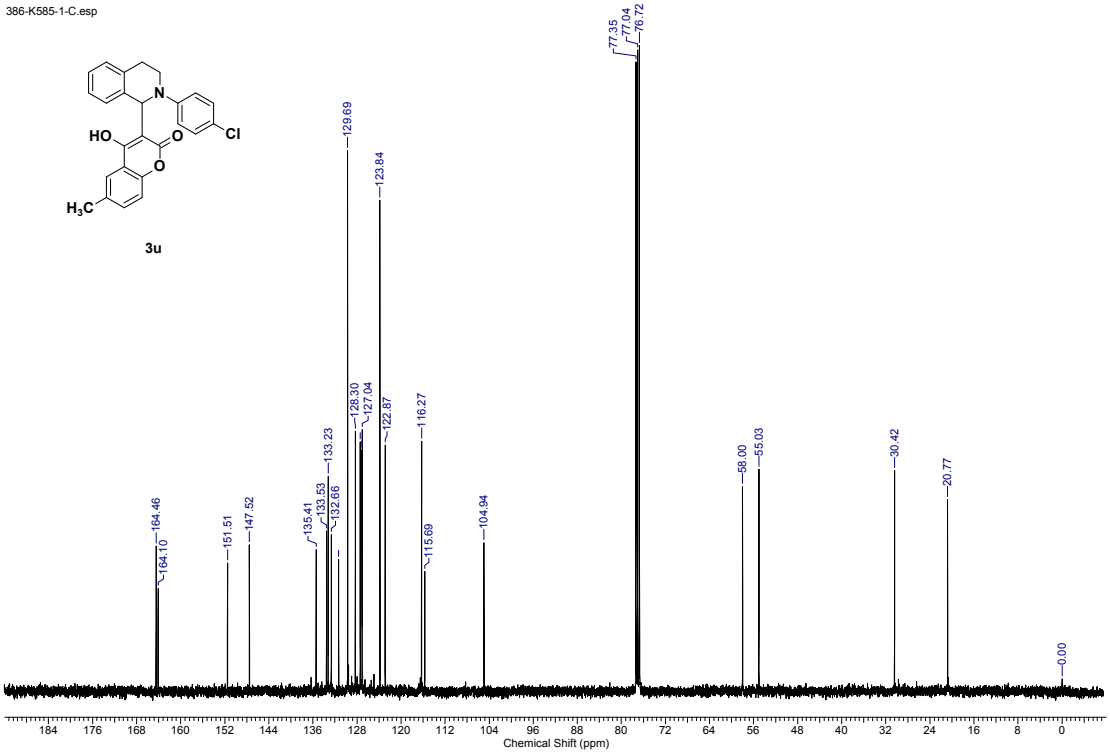


Figure S57. ^{13}C NMR spectrum of compound **3u**

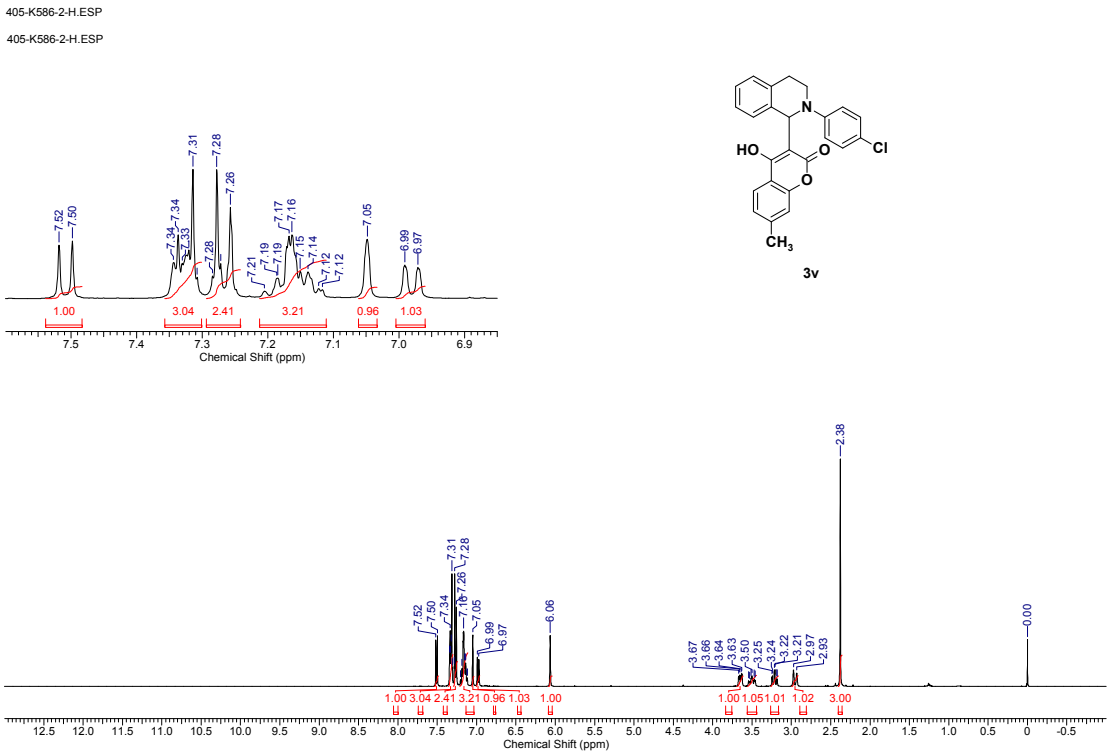


Figure S58. ^{1}H NMR spectrum of compound **3v**

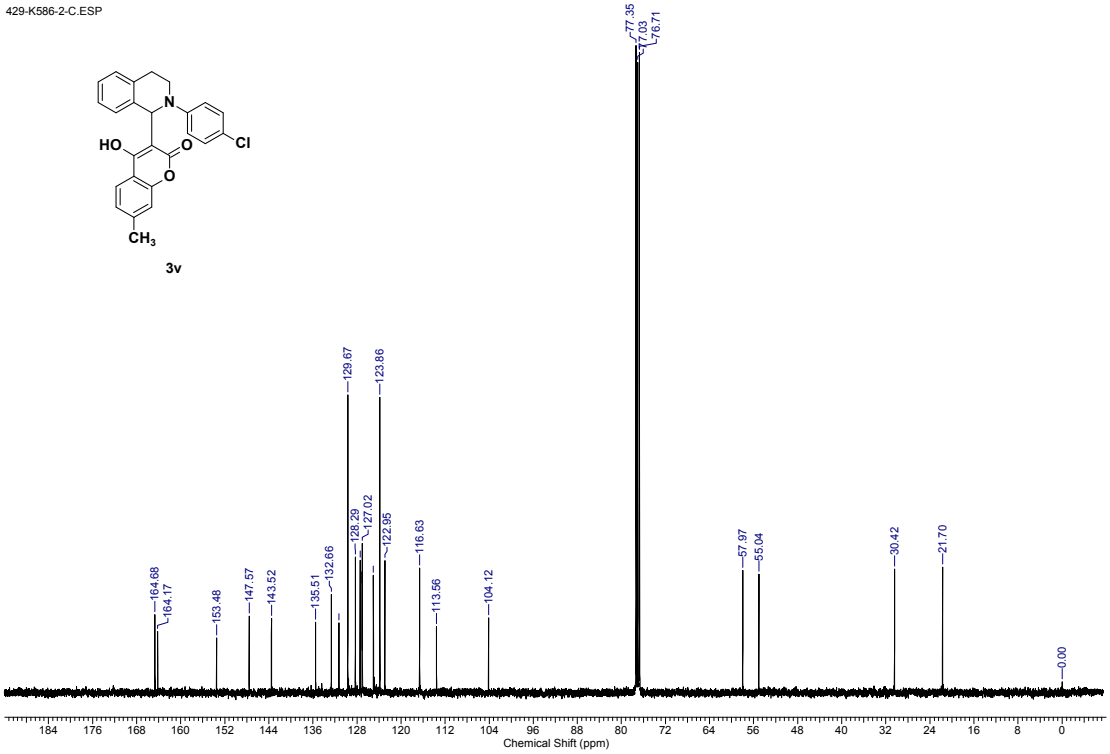


Figure S59. ^{13}C NMR spectrum of compound **3v**

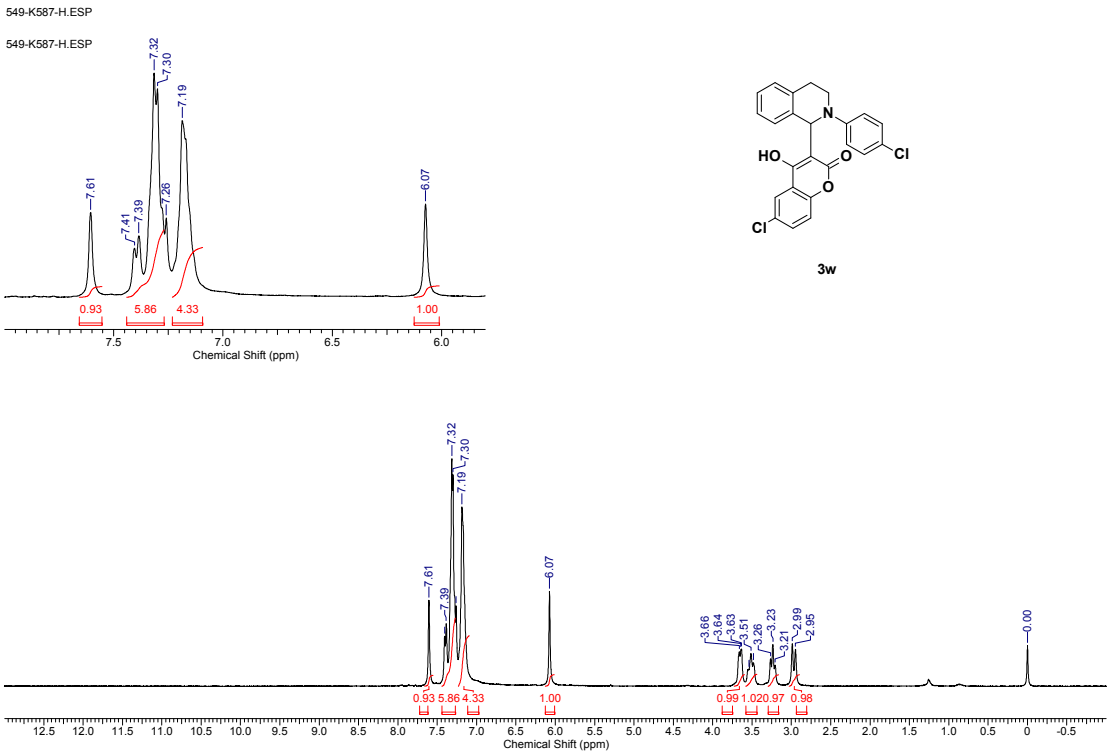


Figure S60. ^{1}H NMR spectrum of compound **3w**

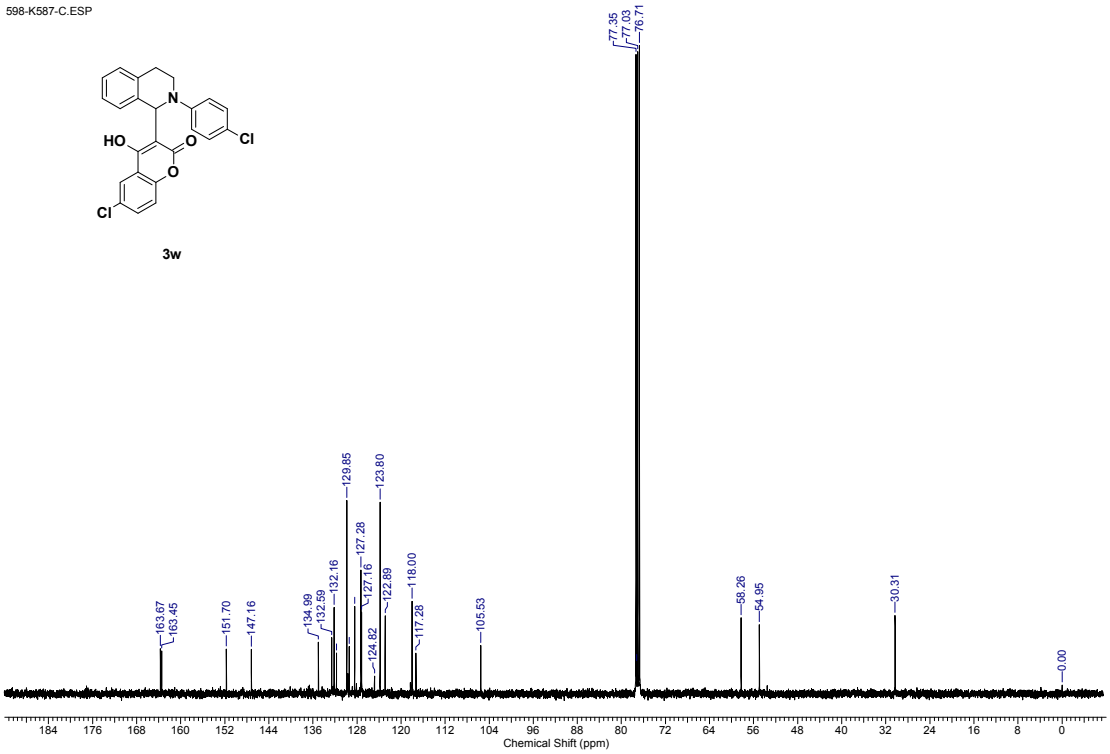


Figure S61. ^{13}C NMR spectrum of compound **3w**

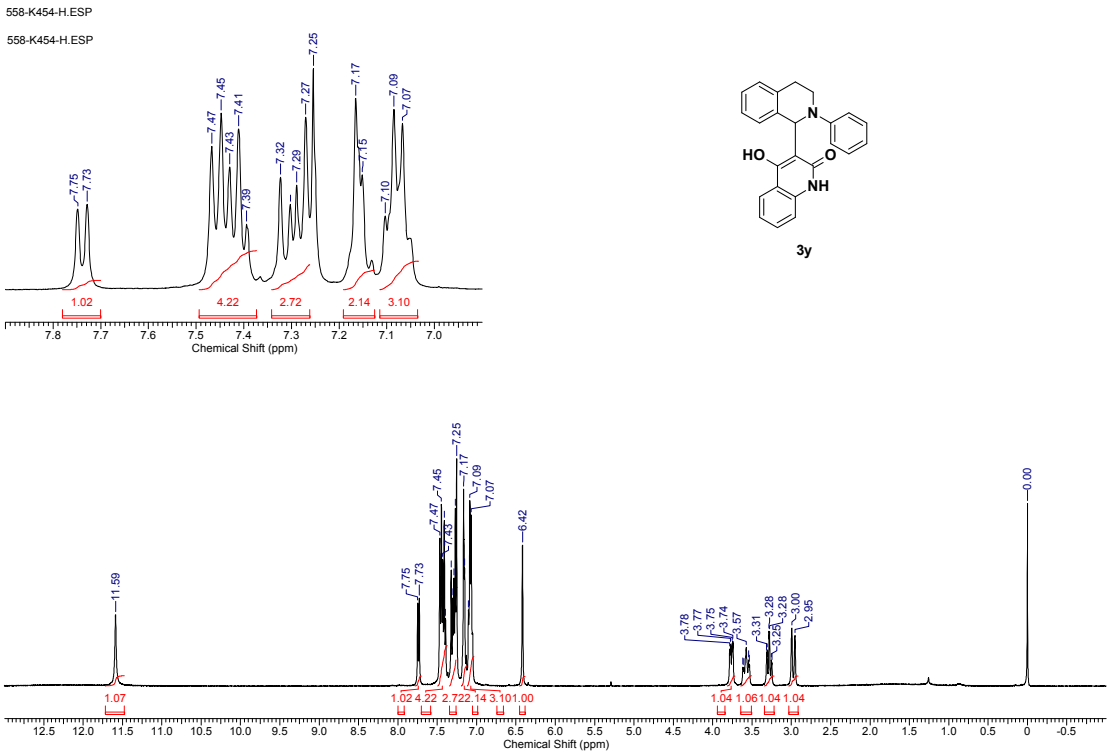


Figure S62. ^{1}H NMR spectrum of compound **3y**

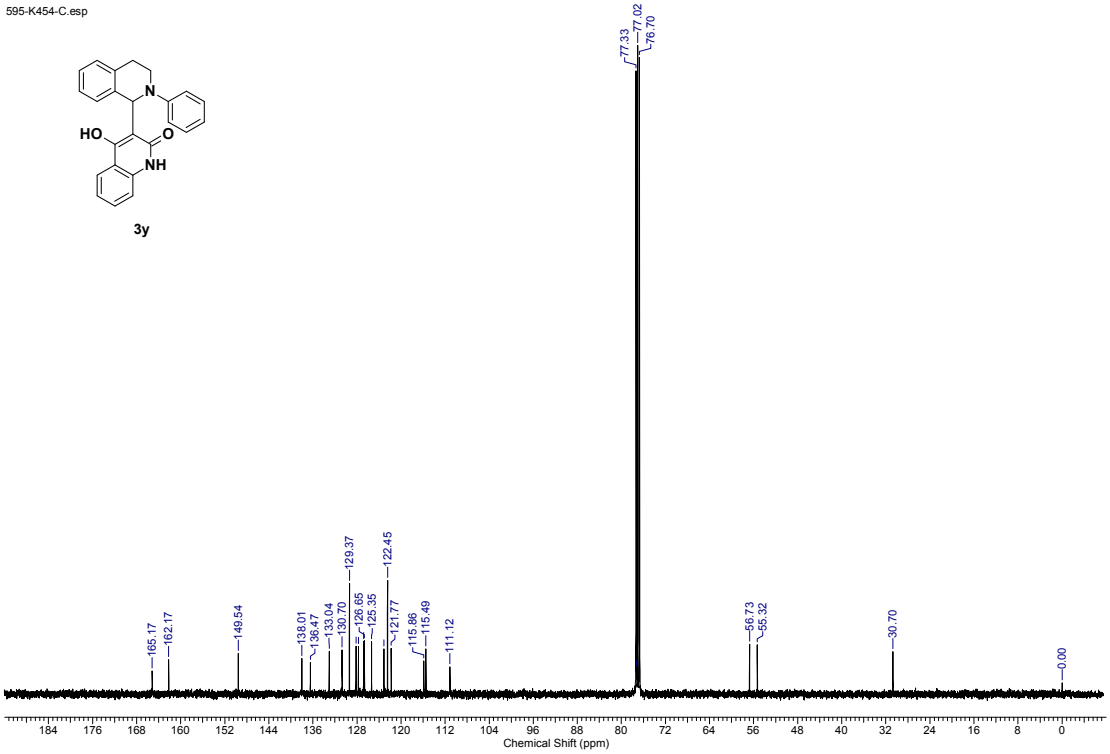


Figure S63. ^{13}C NMR spectrum of compound **3y**

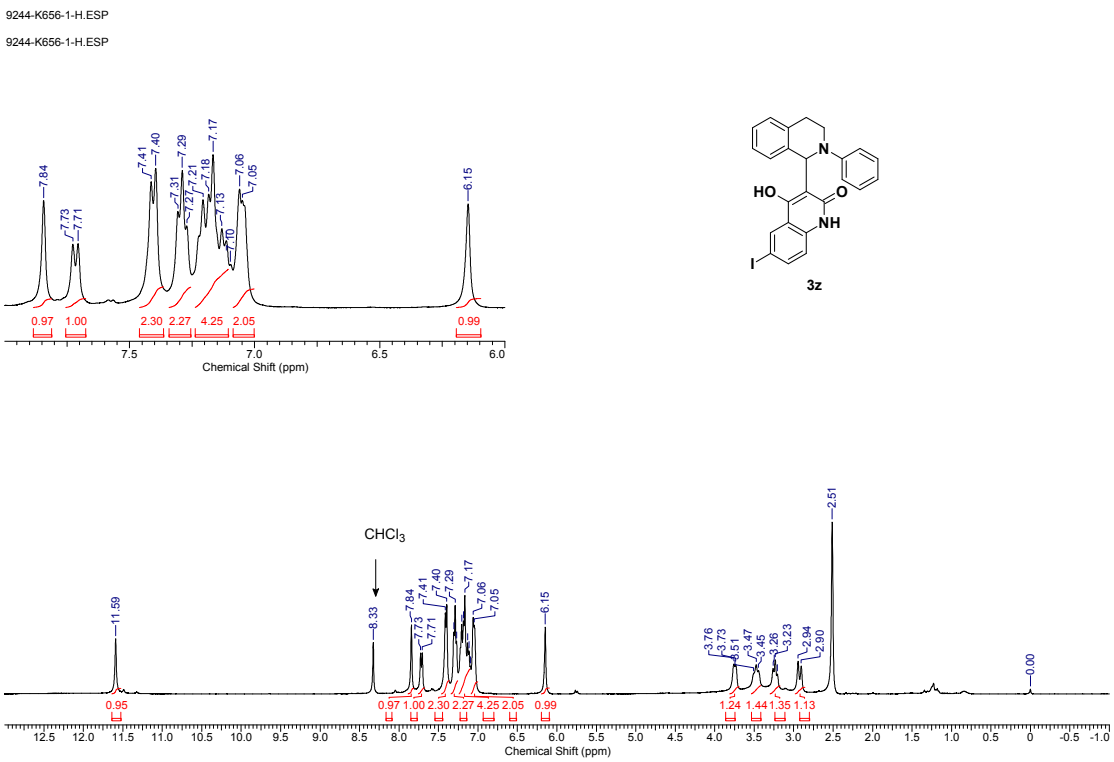


Figure S64. ^{1}H NMR spectrum of compound **3z**

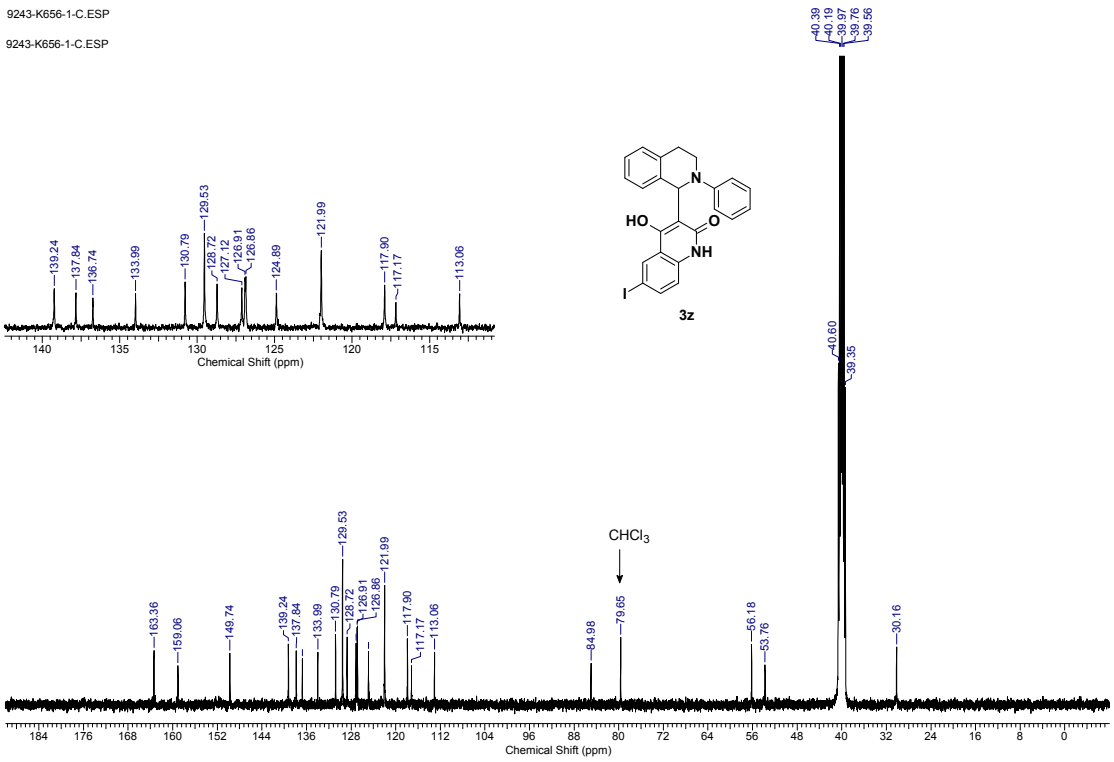


Figure S65. ^{13}C NMR spectrum of compound **3z**

9. Determination of Structure of 3a and 3y

1) Structure determination of **3a**

The structure of **3a** was determined by the X-ray diffraction. Recrystallized from dichloromethane/n-hexane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2032505.

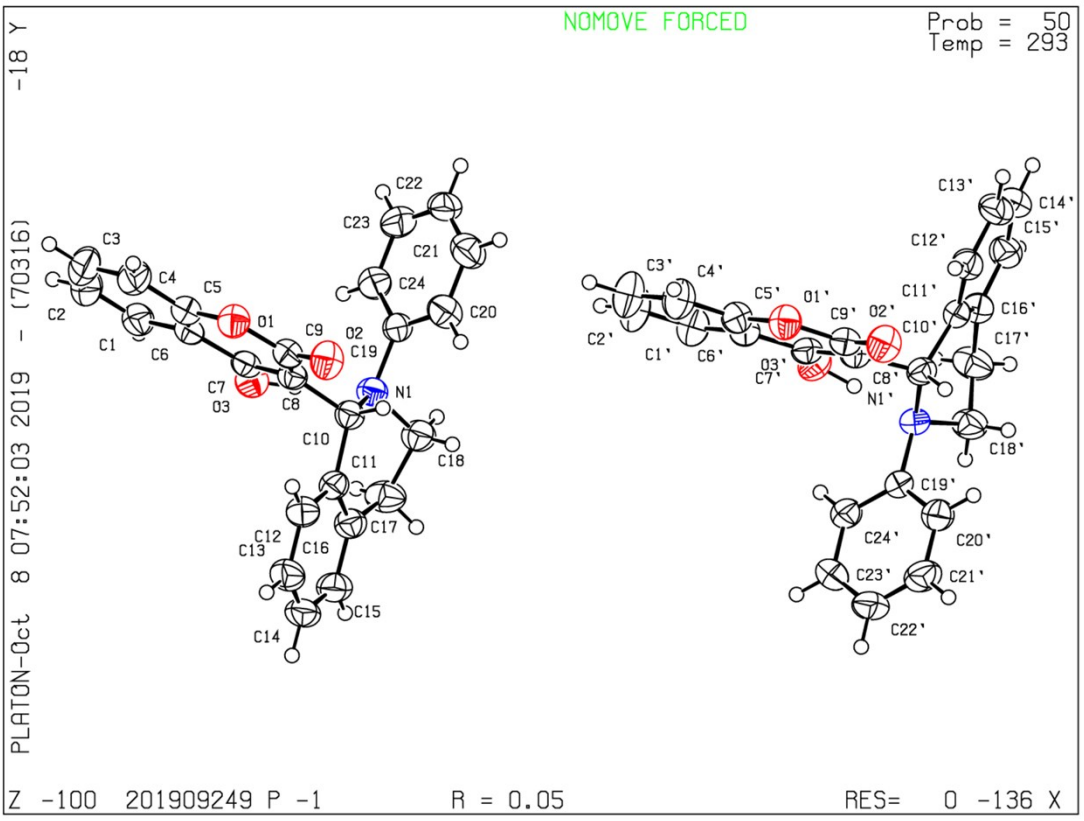


Table S1. Crystal data and structure refinement for 201909249.

Identification code	201909249
Empirical formula	C24H19NO3
Formula weight	369.40
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0990(6)
b/Å	12.6543(9)
c/Å	17.4953(14)
α/°	69.761(7)
β/°	87.356(6)
γ/°	78.198(6)
Volume/Å3	1849.4(2)

Z	4
ρcalcg/cm3	1.327
μ/mm-1	0.704
F(000)	776.0
Crystal size/mm3	0.17 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.602 to 134.14
Index ranges	-10 ≤ h ≤ 7, -15 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	12884
Independent reflections	6584 [Rint = 0.0327, Rsigma = 0.0462]
Data/restraints/parameters	6584/2/513
Goodness-of-fit on F2	1.022
Final R indexes [I>=2σ (I)]	R1 = 0.0512, wR2 = 0.1315
Final R indexes [all data]	R1 = 0.0710, wR2 = 0.1504
Largest diff. peak/hole / e Å-3	0.30/-0.25

2) Structure determination of **3y**

The structure of **3y** was determined by the X-ray diffraction. Recrystallized from dichloromethane/n-hexane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2032506.

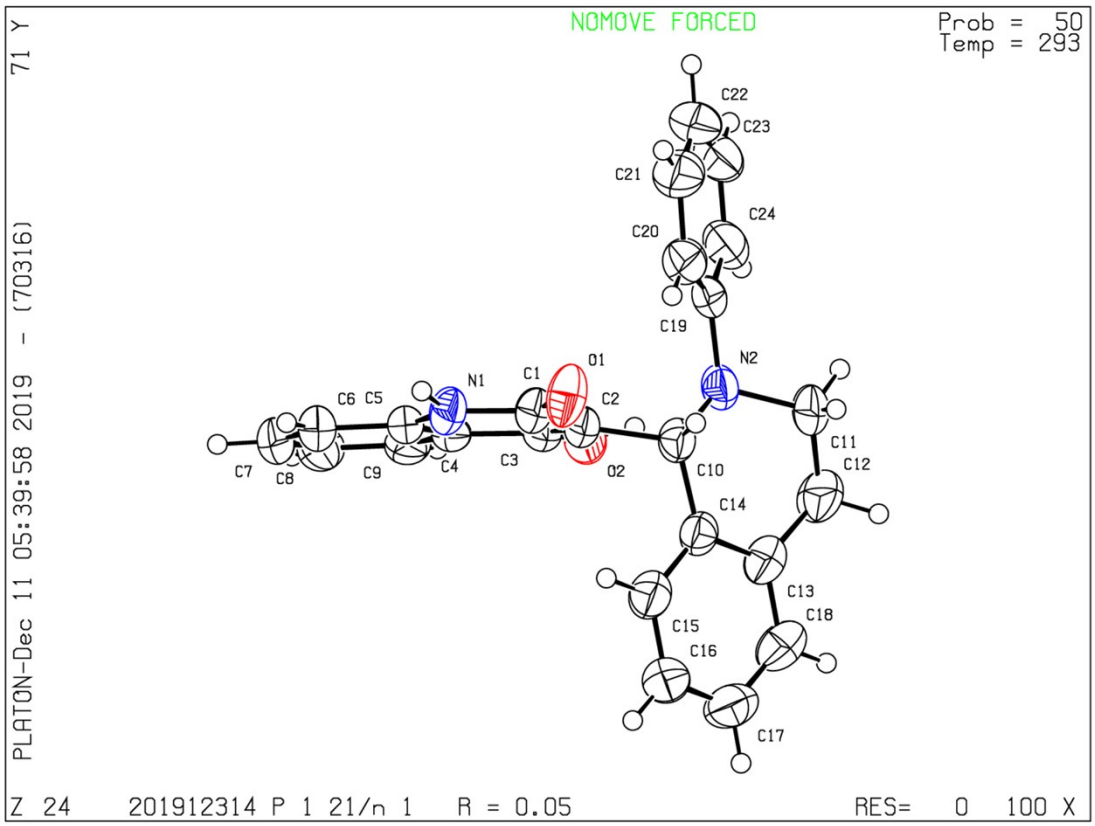


Table S2. Crystal data and structure refinement for 201912314.

Identification code	201912314
Empirical formula	C24H20N2O2
Formula weight	368.42
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	8.6666(5)
b/Å	23.4805(11)
c/Å	9.5853(4)
α/°	90
β/°	102.461(6)
γ/°	90
Volume/Å3	1904.62(18)
Z	4
ρcalcg/cm3	1.285
μ/mm-1	0.656
F(000)	776.0
Crystal size/mm3	0.18 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.53 to 134.086
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 28, -11 ≤ l ≤ 9
Reflections collected	7573
Independent reflections	3403 [Rint = 0.0300, Rsigma = 0.0404]
Data/restraints/parameters	3403/0/258
Goodness-of-fit on F2	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0517, wR2 = 0.1347
Final R indexes [all data]	R1 = 0.0690, wR2 = 0.1502
Largest diff. peak/hole / e Å-3	0.26/-0.19