Supporting information for

Harnessing Visible-light Energy for Unbiased Organic Photoelectrocatalysis: Synthesis of N-Bearing Fused Rings

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Supplemental Experimental Procedures

1. General Information

All reactions were performed using quartz tube. The divided cell used for mechanism study (Fig. 4A, exp.3) is "H-type" cell with a porous glass to separate photoanode and cathode. Commercial grade reagents **2** and EtOH (OCEANPAK, GC ≥ 99.9%) were used without further purification except as indicated below. *N*-aryltetrahydroisoquinolines (**1**) 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. ^{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 UV-Vis absorption spectra were recorded in MeCN on a Perkin Elmer Lambda 35 spectrometer. X-Ray powder diffraction (XRD) patterns were recorded using an X-ray Diffractometer (X' Pert PRO) at a scan rate of 5 ^{o} min^{-1} by using $Cu_{K\alpha}$ radiation. 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. The linear sweep voltammetry (LSV), cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) measurements were performed using a CHI660E Instruments. All reactions were carried out with photoreactor (Serial No: D243V12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD.

2. Experimental Procedures

1) Preparation of the $BiVO_4$

Firstly, Contaminants of the fluorine-doped SnO_2 (FTO) conducting glass (10 mm × 23 mm × 1.1 mm, ≤ 7 ohm/sq, Xiang Science & Technology) were removed by washing with deionized water, acetone and ethanol three times (15 minutes each wash). After drying with Ar, the $BiVO_4$ electrode was prepared by electro-deposition as following steps:[2] (1) $Bi(NO_3)_3 \cdot 5H_2O$ (0.04 M) and KI (0.4 M) were dissolved in 50 mL distilled water to form a clear solution; (2) HNO_3 was used to adjust the pH to 1.7; (3) *p*-benzoquinone ethanol solution (0.23 M, 20 mL) was added to above mixed solution and stirred vigorously for 20 min; (4) The electrodeposition was carried out in three-electrode cell using a constant potential of -0.1 V versus Ag/AgCl for 600 seconds at room temperature (FTO as a working electrode, Pt plate as a counter electrode and Ag/AgCl as a reference electrode); (5) After being taken out and washed with distilled water, the dried BiOI film was covered by dipping 200 μL containing vanadyl acetylacetonate (0.2 M) DMSO solution. $BiVO_4$ film was formed by heating in a muffle furnace at 450 °C for 1 hour; (6) After being cooled down to room temperature, the electrode was soaked in NaOH solution (1.0 M) for 30 min to remove excess V_2O_5. Finally, the $BiVO_4$ electrode was rinsed with distilled water.

2) General procedure for photoelectrocatalytic transformation of malononitrile (2) and *N*-aryl-tetrahydroisoquinolines (1)

N-aryl-tetrahydroisoquinoline (**1**) (0.2 mmol), malononitrile (**2**) (1.5 equiv.), ammonium chloride (0.1 M) and EtOH (5 mL) were added to a quartz-tube with $BiVO_4$/FTO as photoanode and Pt plate as counter electrode at room temperature under 3 W blue LED irradiation. Electrodes were rinsed with DCM (3 mL). The mixture was extracted with dichloromethane (2 × 5 mL) and saturated salt water (2 × 5 mL) and dried over Na_2SO_4. The solvent was removed in vacuum, and the crude reaction mixture was purified by chromatography on silica gel (elute: ethyl acetate/petroleum ether = 1/30-1/10, v/v) to give the desired product **3** and **4**.

3) Reuse of photoanode

The reaction procedure is as mentioned above for the photoelectrocatalysis. After the completion of the reaction, the $BiVO_4$/FTO photoanode was separated from the reaction mixture, and was applied to the next run after cleaning with CH_2Cl_2 (3 x 0.5 mL). The reaction mixture was extracted with dichloromethane and saturated salt water, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Finally, they were purified by chromatography on silica gel (elute: ethyl acetate/petroleum ether = 1/30-1/10, v/v) to give the desired product **3** and **4**.

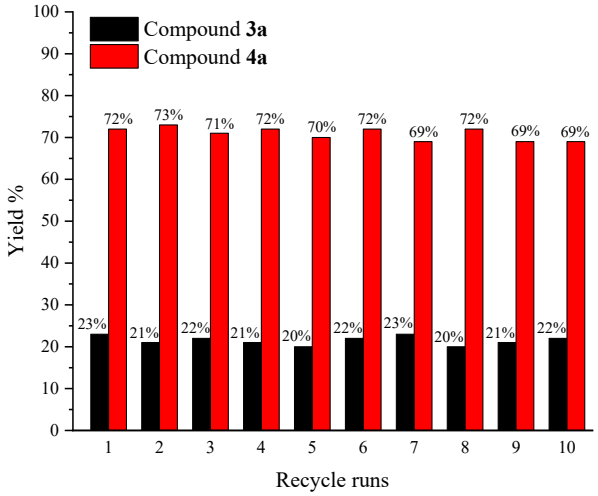


Figure S1. [a]Reaction condition: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**, 0.2 mmol), malononitrile (**2a**, 1.5 equiv.), ammonium chloride (0.1 M), EtOH (5 mL) in a quartz-tube under air at room temperature, 3 W blue LED, for 5 h. Isolated yield.

3. LSV Curves, Photocurrent Density Response and EIS Experiments

1) The linear sweep voltammetry (LSV) curves of $BiVO_4$ photoanode

LSV curves were recorded with a three-electrode configuration using a CHI660E electrochemical workstation. $BiVO_4$/FTO electrode was used as the working electrode with the Ag/AgCl reference electrode and Pt counter electrode. LSV curves were performed at a scan rate of 0.1 V/s without stirring.

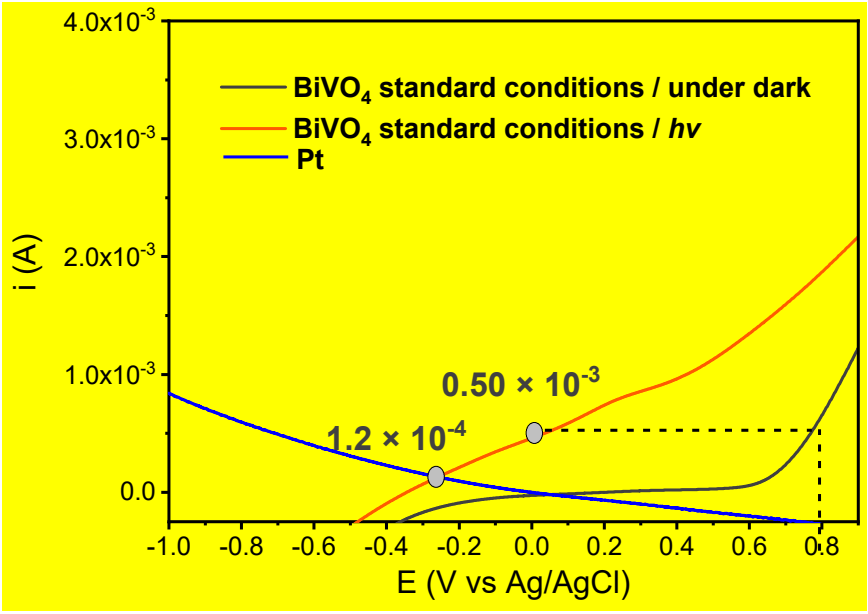


Figure S2. LSVs of a $BiVO_4$ photoanode obtained under blue LED (E = 5.00-5.15 × 10^4 lx, λ_{max} = 450-465 nm) illumination (red) and under dark (black) in EtOH (5 mL) that contained NH_4Cl (0.1 M), **1a** (0.2 mmol) and **2a** (0.3 mmol)

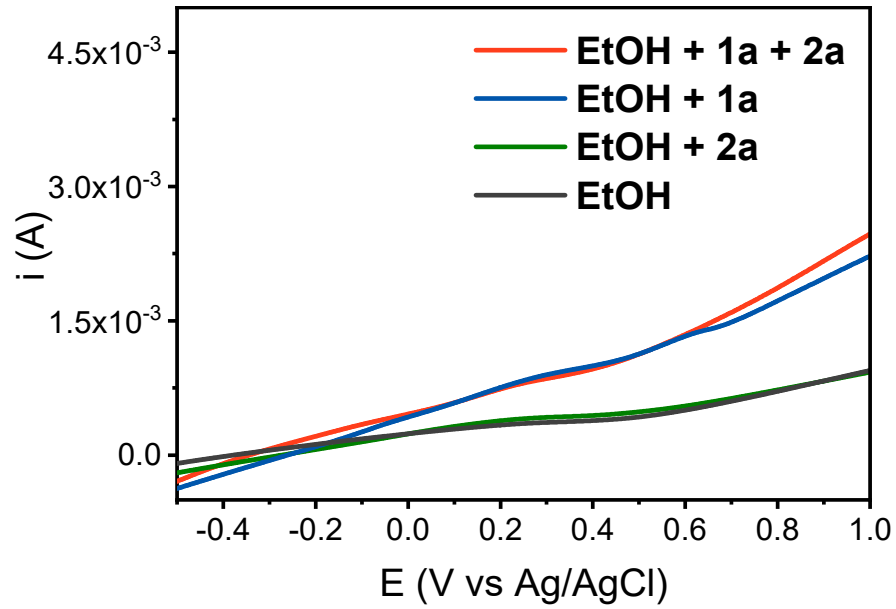


Figure S3. LSVs of PEC oxidation under LED illumination. The electrolyte is 0.1 M NH_4Cl

2) Photocurrent density response test

The measurement was performed by a two-electrode configuration ($BiVO_4$/FTO electrode as the working electrode and Pt as the counter electrode.).

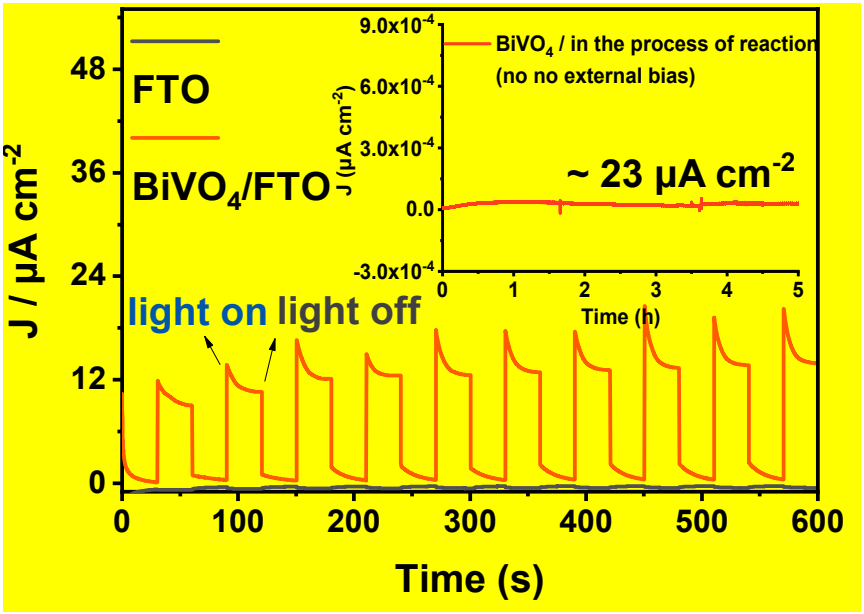


Figure S4. Photocurrent density response for $BiVO_4$/FTO, E_{appl} = 0 V. (Net photocurrent during the 5 hours of operation using $BiVO_4$ photoanode with Pt in reaction mixture (5 mL EtOH, **1a**, **2a** and NH_4Cl (0.1 M)) in a two-electrode configuration (no external bias))

3) Electrochemical impedance spectroscopy (EIS) investigation

EIS measurements were performed by a three-electrode configuration in EtOH using a CHI660E electrochemical workstation with 5 mV amplitude and frequencies that ranged from 100 kHz to 1 Hz. $BiVO_4$/FTO electrode was used as the working electrode with the Ag/AgCl reference electrode and Pt counter electrode. For developing Mott-Schottky plot, the values of capacitance were taken at voltage range between -0.5 V and 0.5 V versus Ag/AgCl.

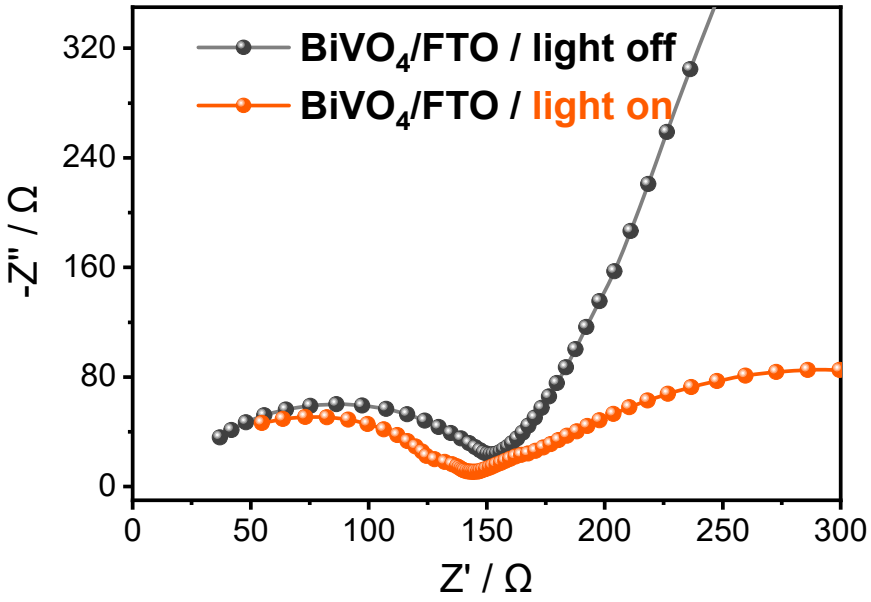


Figure S5. Nyquist plots for $BiVO_4$ photoanode measured in 0.1 M NH_4Cl solution in the dark (black circles) and blue LED (λ = 450-460 nm) illumination (red circles)

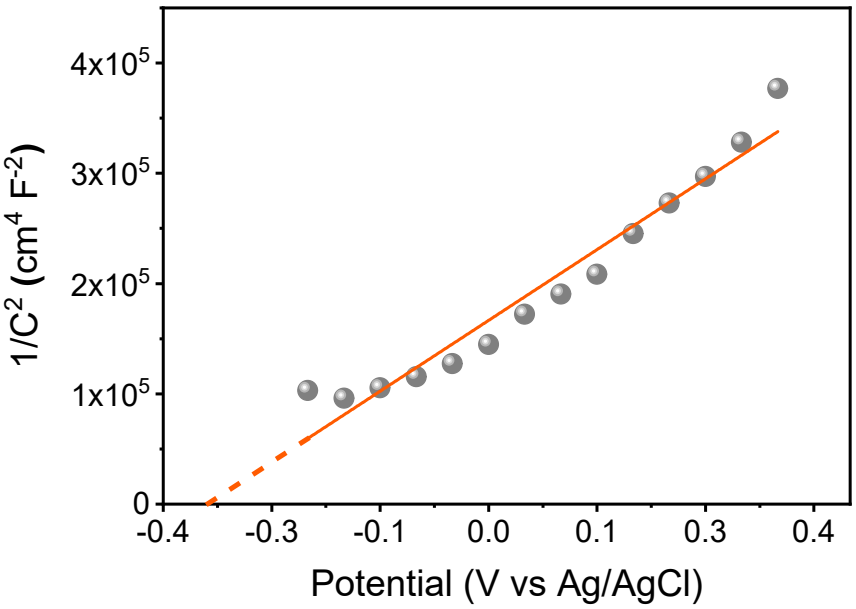


Figure S6. Mott-Schottky plot measured in EtOH

V_{fb} = -0.39 V vs Ag/AgCl;

$E_{Ag/AgCl}$(reference) = 0.1976 V vs NHE at 25 °C

V_{fb} = -0.19 V vs NHE.

4. XRD, UV/VIS Absorption Spectra, Cyclic Voltammetry Experiments

1) The X-ray diffraction (XRD) analysis

The spectra were recorded using a X-ray Diffractometer (X' Pert PRO) at a scan rate of 5 ^{o} min^{-1} by using $Cu_{K\square}$ radiation. The XRD pattern showed strong XRD peaks for $BiVO_4$, which suggests that $BiVO_4$ is monoclinic phase.

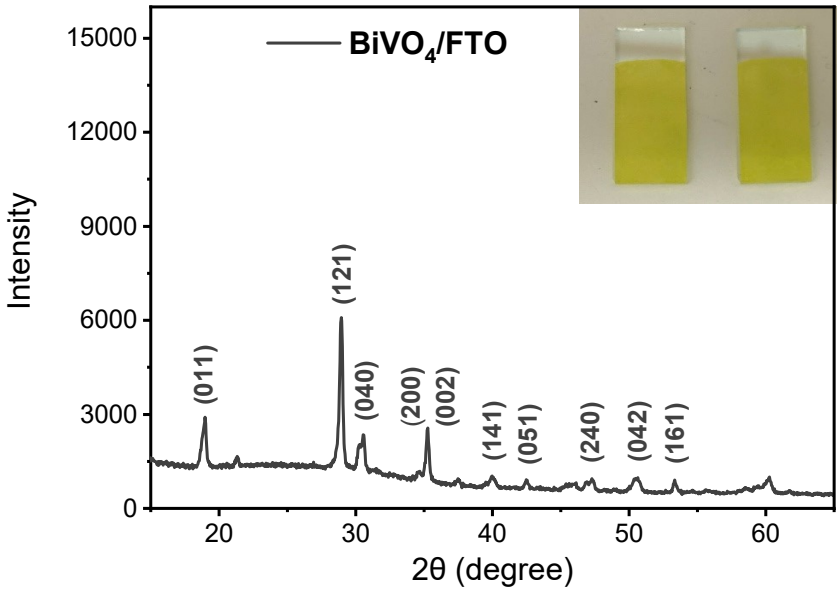


Figure S7. XRD patterns of $BiVO_4$/FTO sample.

2) UV/VIS Absorption spectra

The UV/VIS Absorption spectra were recorded in CH_3CN of a 0.1 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

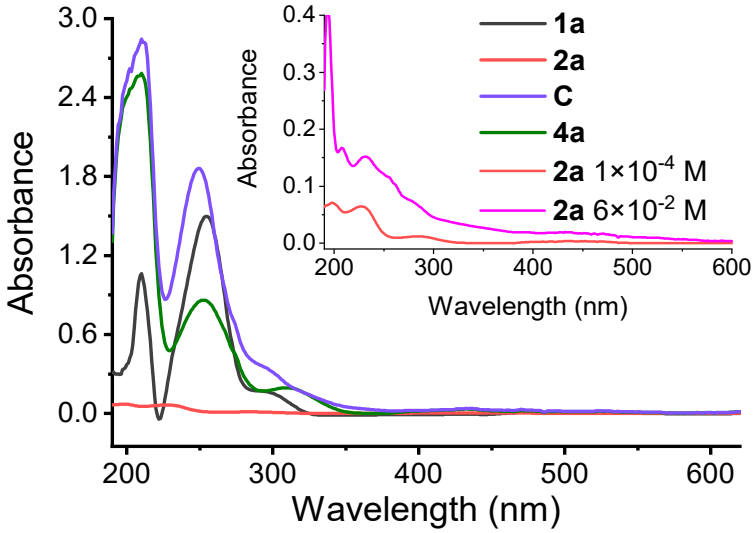


Figure S8. Absorption spectra of *N*-phenyltetrahydroisoquinoline (**1a**), malononitrile (**2a**), 5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (**4a**) and 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malononitrile (**C**) in CH_3CN (0.1 mM).

2) Cyclic Voltammetry Experiments

Cyclic voltammetry was measured in a glass cell with a CHI660E 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. The CV of substrates were measured at the concentration of 5 mM. The scan rate was 0.1 V/s, ranging from 0 V to 2 V.

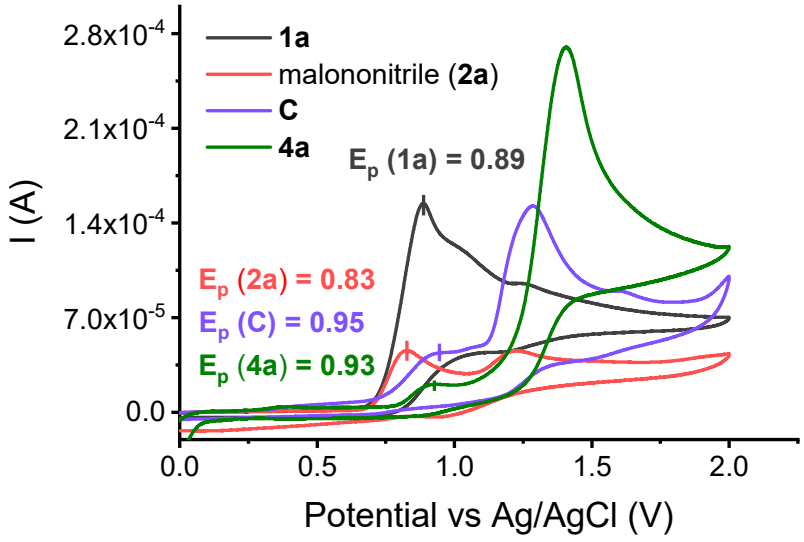


Figure S9. Cyclic voltammograms of compound **1a**, **2a**, **C** and **4a**

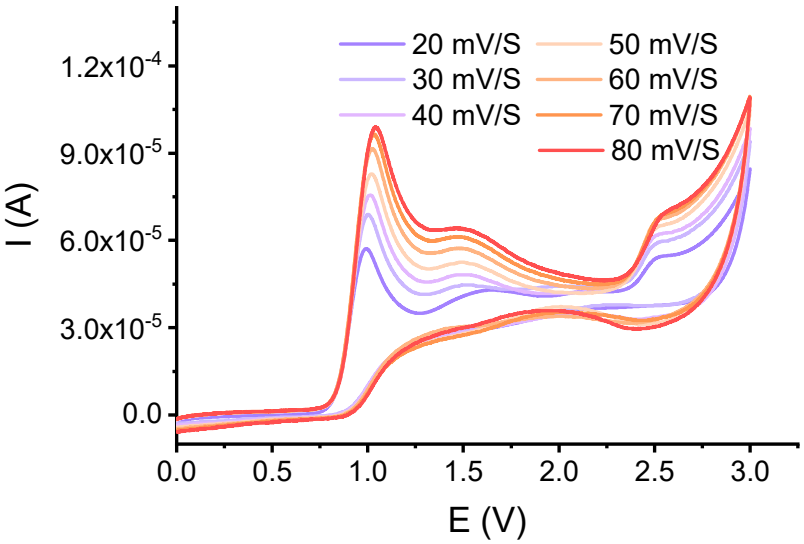


Figure S10. Cyclic voltammetry of compound **1a** (5 mM) in CH_3CN at different scan rates. Curves are obtained at 20, 30, 40, 50, 60, 70 and 80 mV/s, respectively

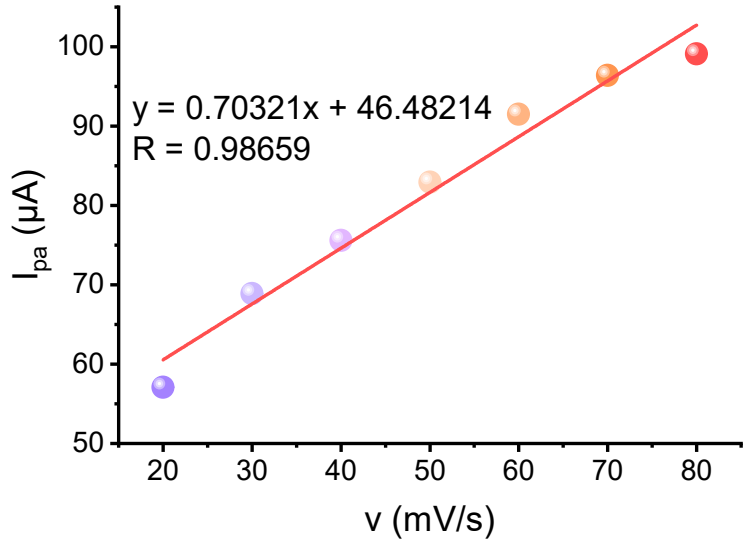


Figure S11. The plot of peak current versus scan rate of **1a**

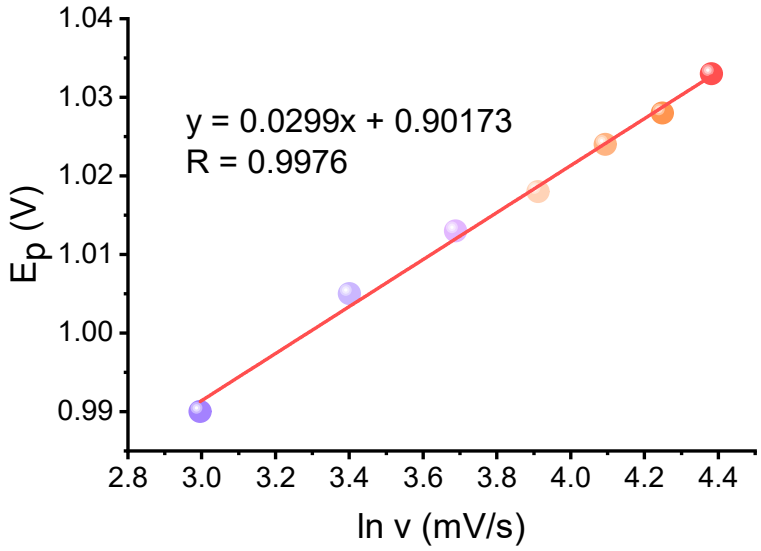


Figure S12. The relationship between E_{pa} of **1a** and ln ν.

The peak current increased linearly with the scan rate in the range of 20-80 mV/s and the equation could be expressed as follows: y = 0.70321 x + 46.48214, R = 0.98659. 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 αn can be easily calculated from the slope of E_{pa}-ln *v*. In this system, the slope is 0.0299. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 2.

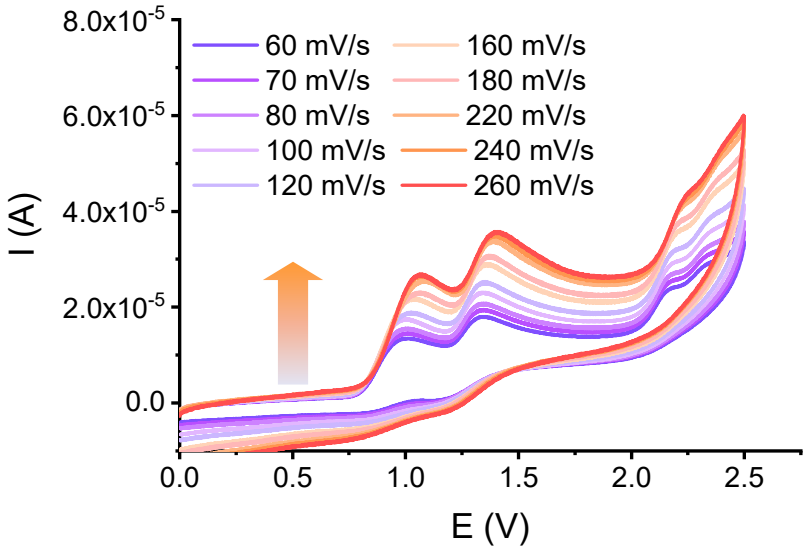


Figure S13. Cyclic voltammetry of compound **2a** (5 mM) in CH_3CN at different scan rates. Curves are obtained at 60, 70, 80, 100, 120, 160, 180, 220, 240 and 260 mV/s, respectively

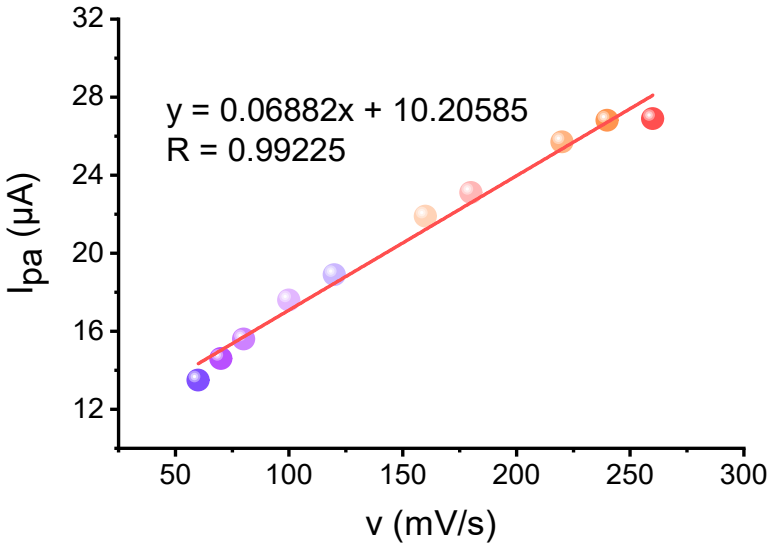


Figure S14. The plot of peak current versus scan rate of **2a**

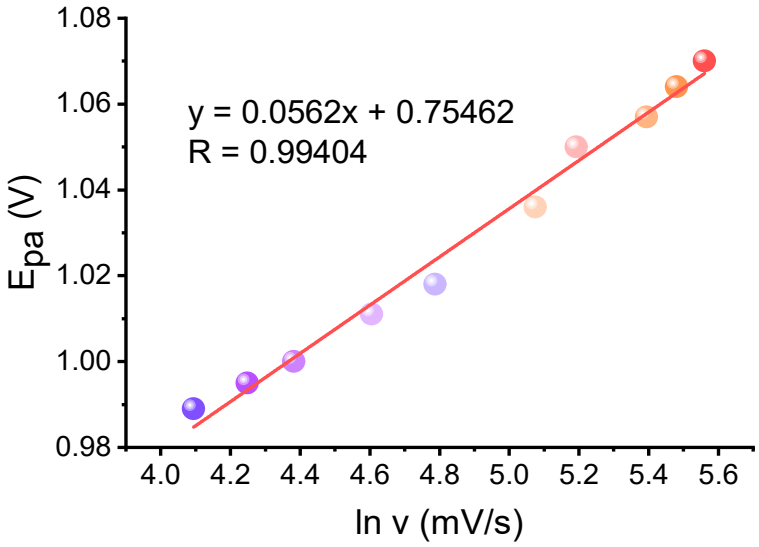


Figure S15. The relationship between E_{pa} of **2a** and ln ν

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}-lnv was 0.0562. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 1.

The cyclic voltammetry of $BiVO_4$ was tested in a three-electrode configuration ($BiVO_4$/FTO electrode as the working electrode, Ag/AgCl as the reference electrode and Pt as the counter electrode) under 3 W blue LED (E = 5.00-5.15 × 10^4 lx, λ_{max} = 450-465 nm).

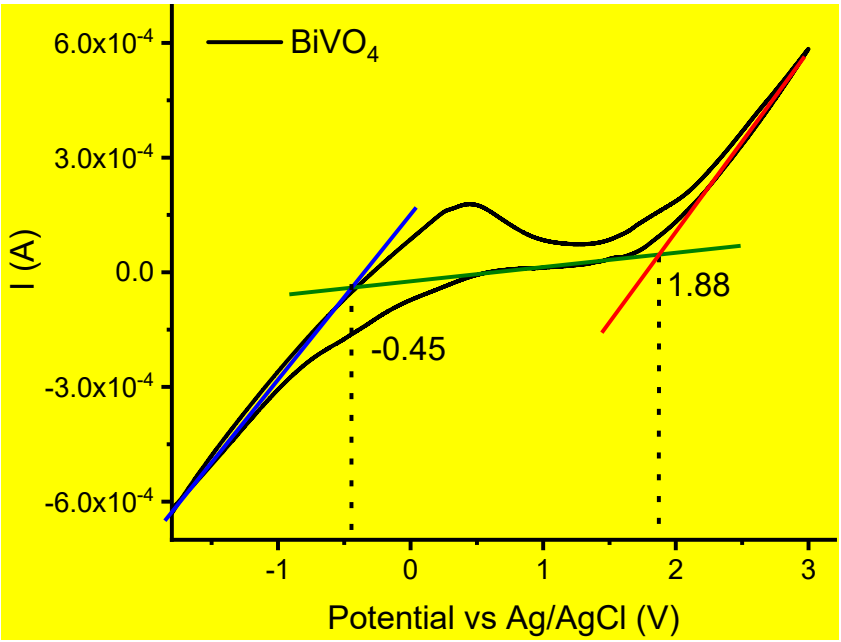


Figure S16. Cyclic voltammetry of $BiVO_4$ in EtOH (5 mL) that contained NH_4Cl (0.1 M), **1a** (0.2 mmol) and **2a** (0.3 mmol)

$E_{Ag/AgCl}$(reference) = 0.1976 V vs NHE at 25 °C

the E_{CB} = -0.25 V vs NHE and E_{VB} = 2.1 V vs NHE.

3) Data processing

With the reversible waves of all the reagents in hand, we calculated the excited redox potential, Eg of different reagents.

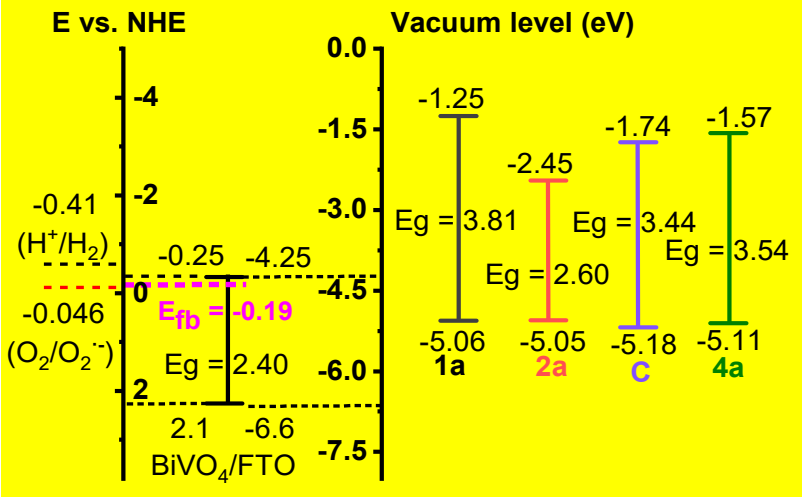


Figure S17. The E_{HOMO}, E_{LUMO} and Eg of different reagents

5. Contorl Experiments

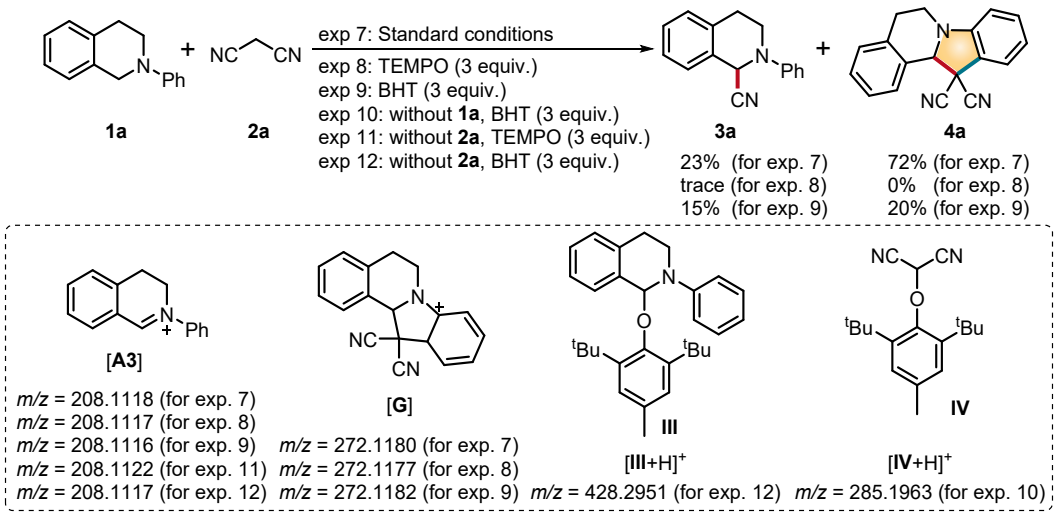


Figure S18. Control experiments

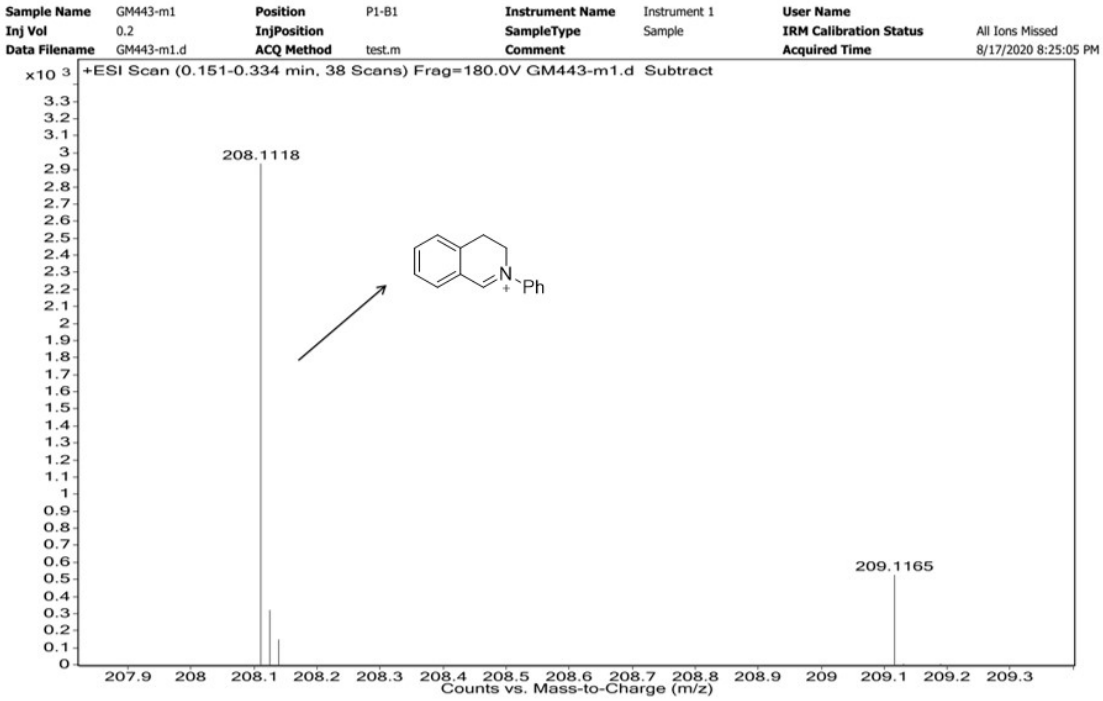


Figure S19. HRMS spectrum of compound **A3** for exp 7

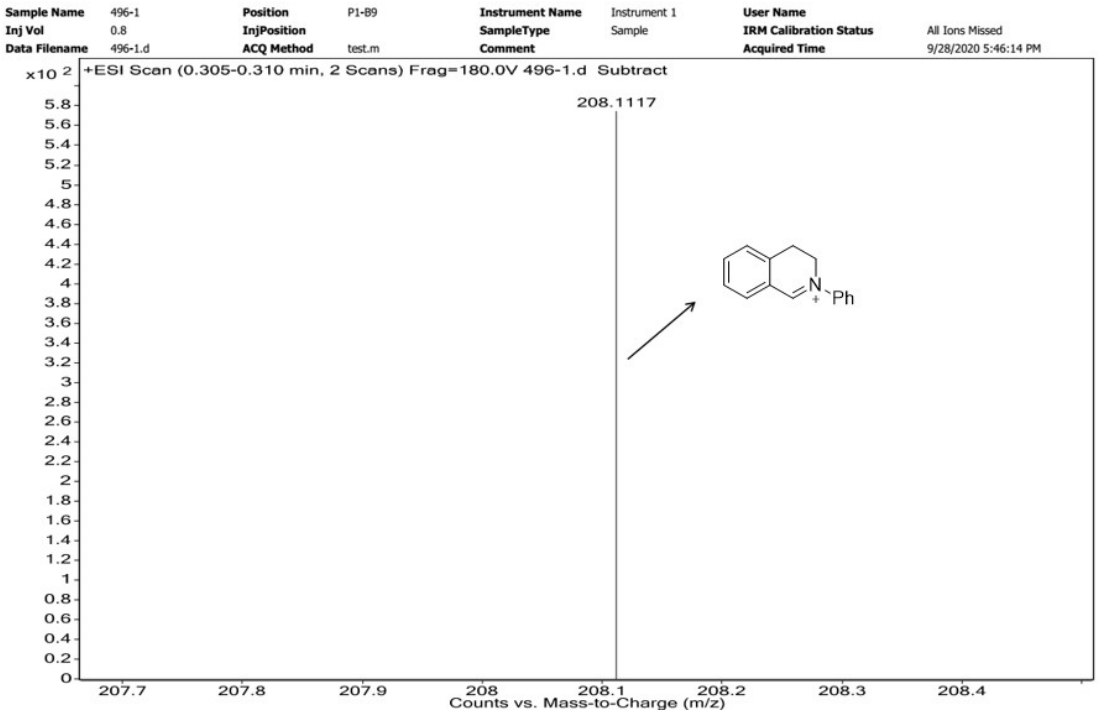


Figure S20. HRMS spectrum of compound **A3** for exp 8

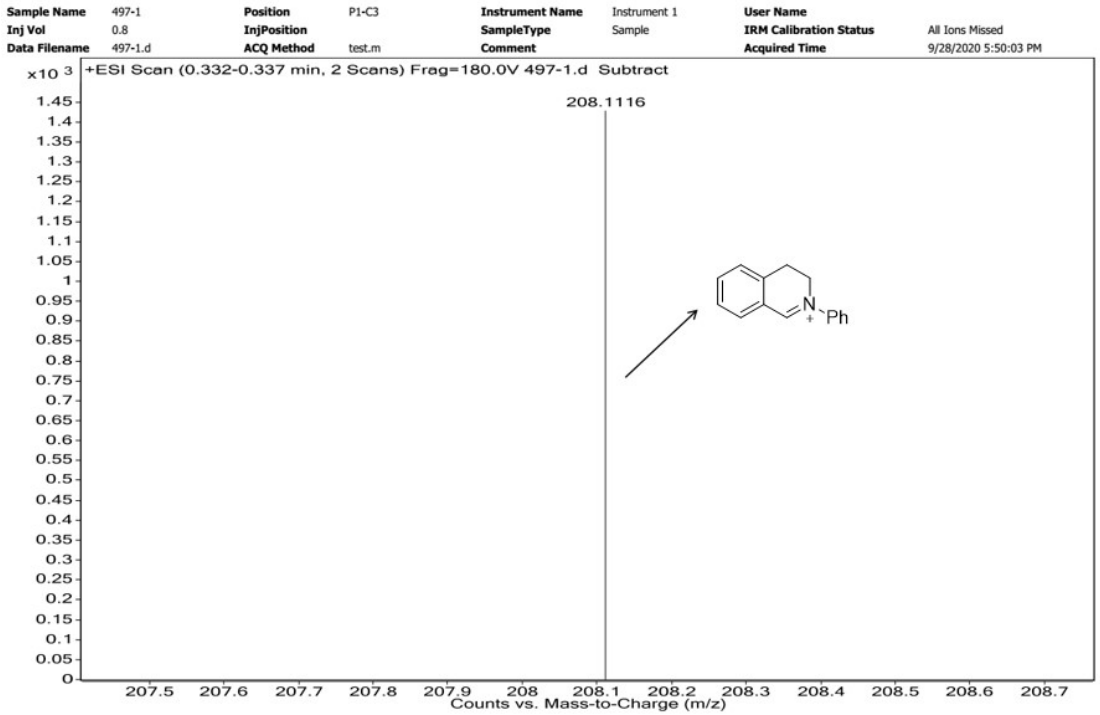


Figure S21. HRMS spectrum of compound **A3** for exp 9

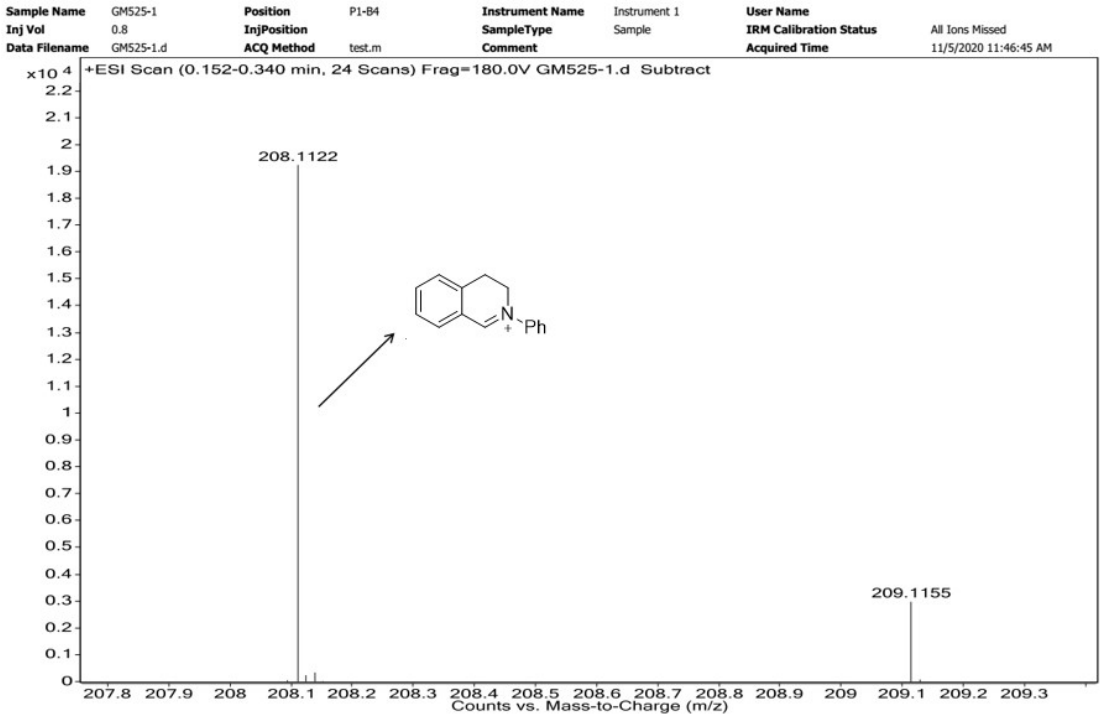


Figure S22. HRMS spectrum of compound **A3** for exp 11

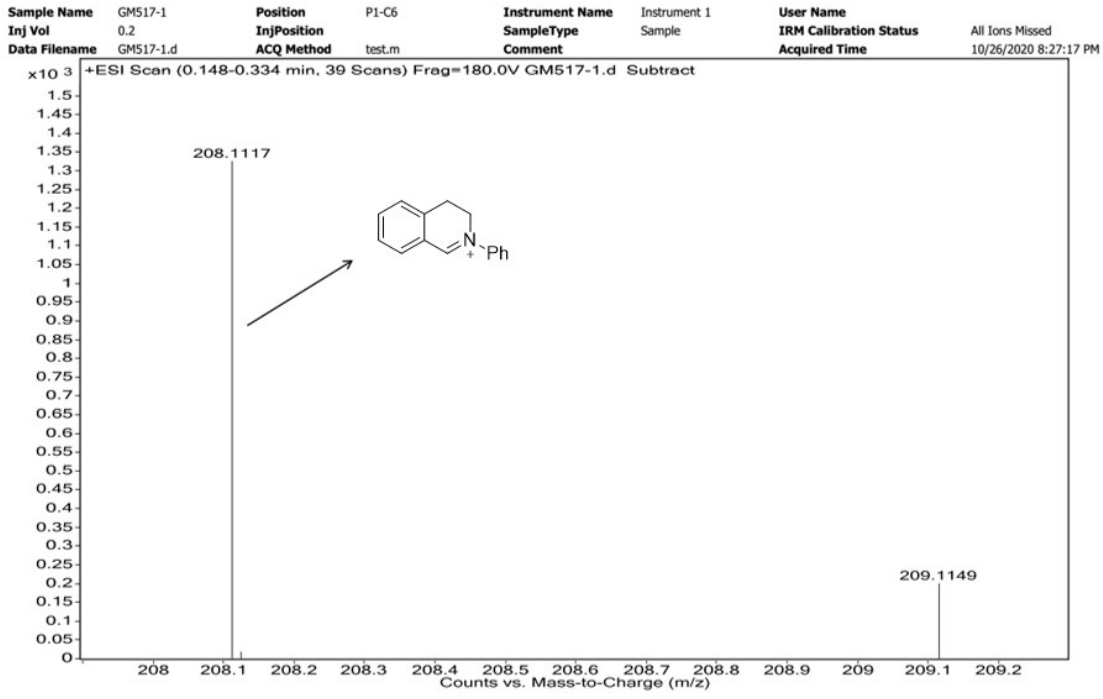


Figure S23. HRMS spectrum of compound A3 for exp 12

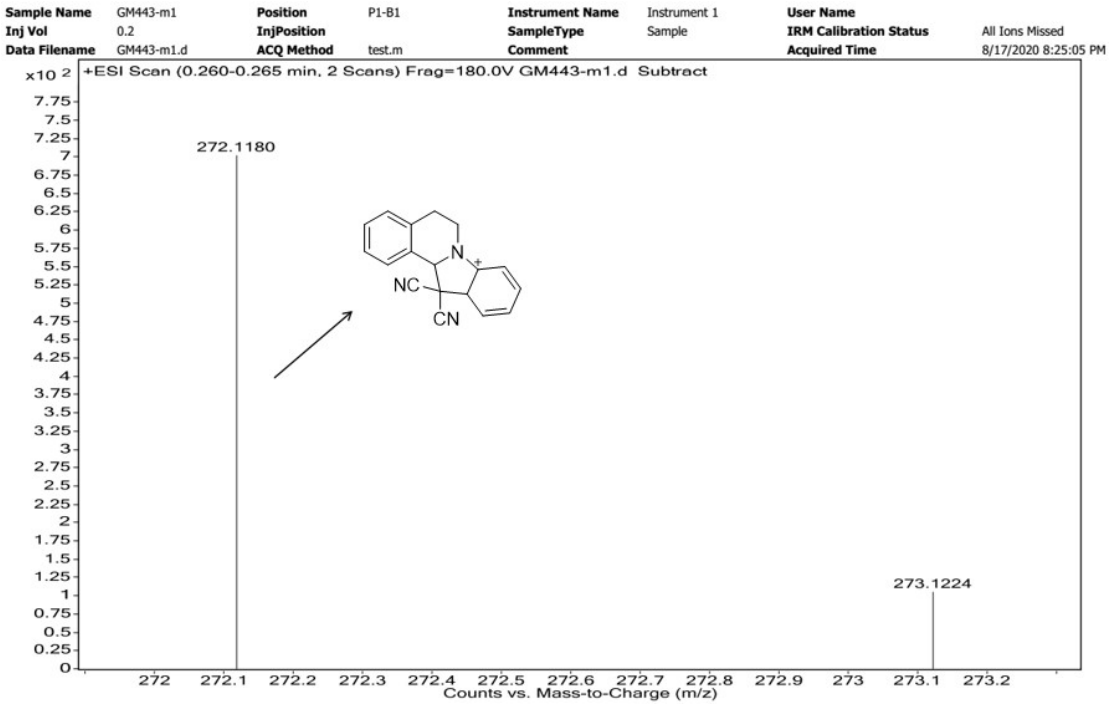


Figure S24. HRMS spectrum of compound **G** for exp 7

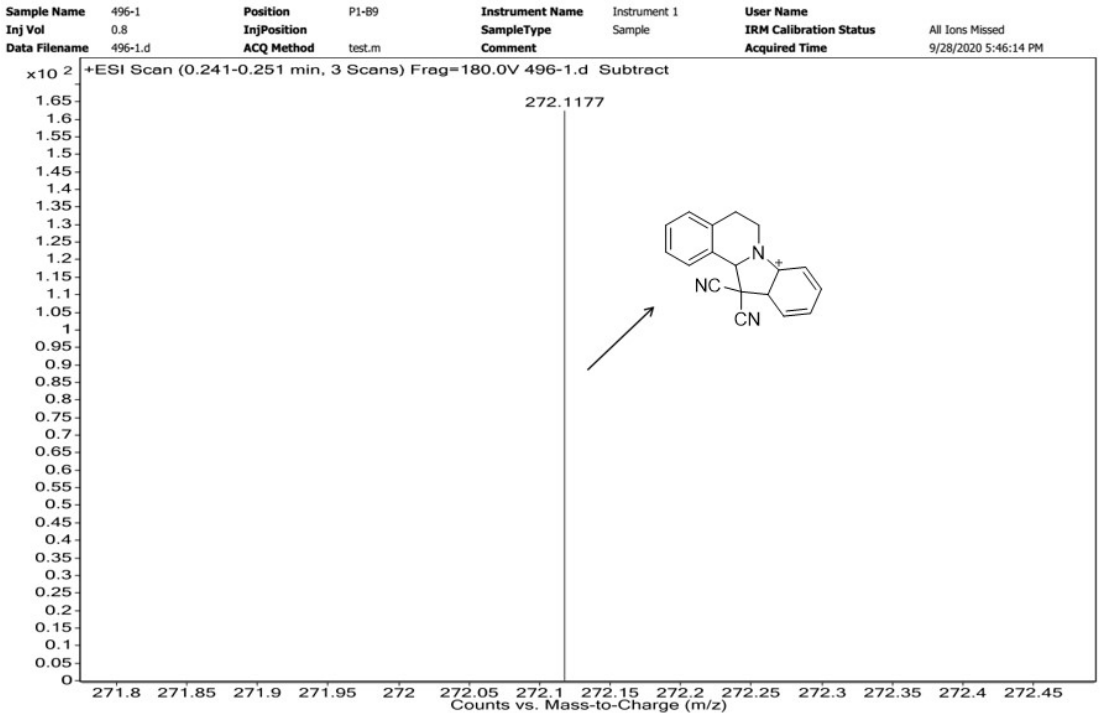


Figure S25. HRMS spectrum of compound **G** for exp 8

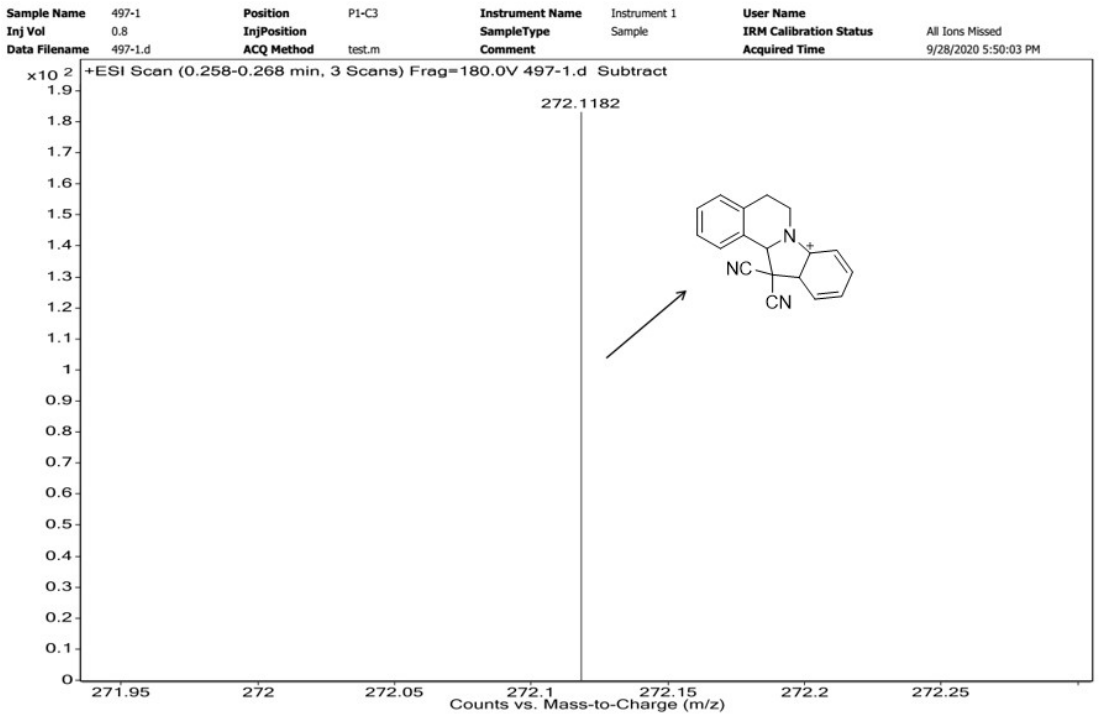


Figure S26. HRMS spectrum of compound **G** for exp 9

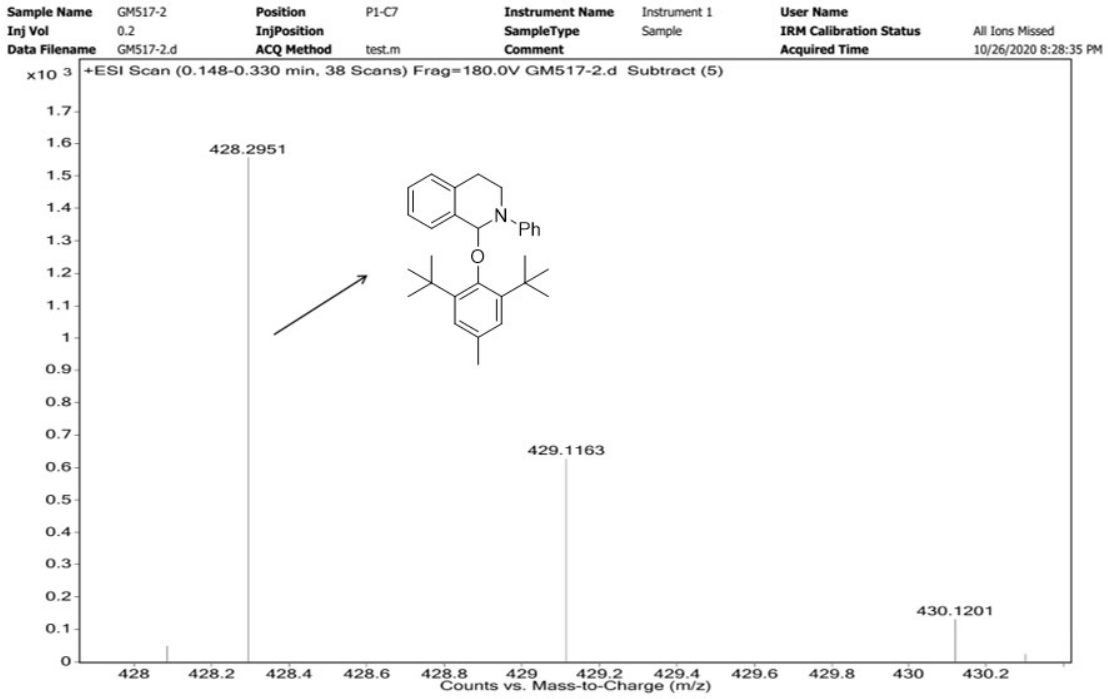


Figure S27. HRMS spectrum of compound [**III**+H]$^+$ for exp 12

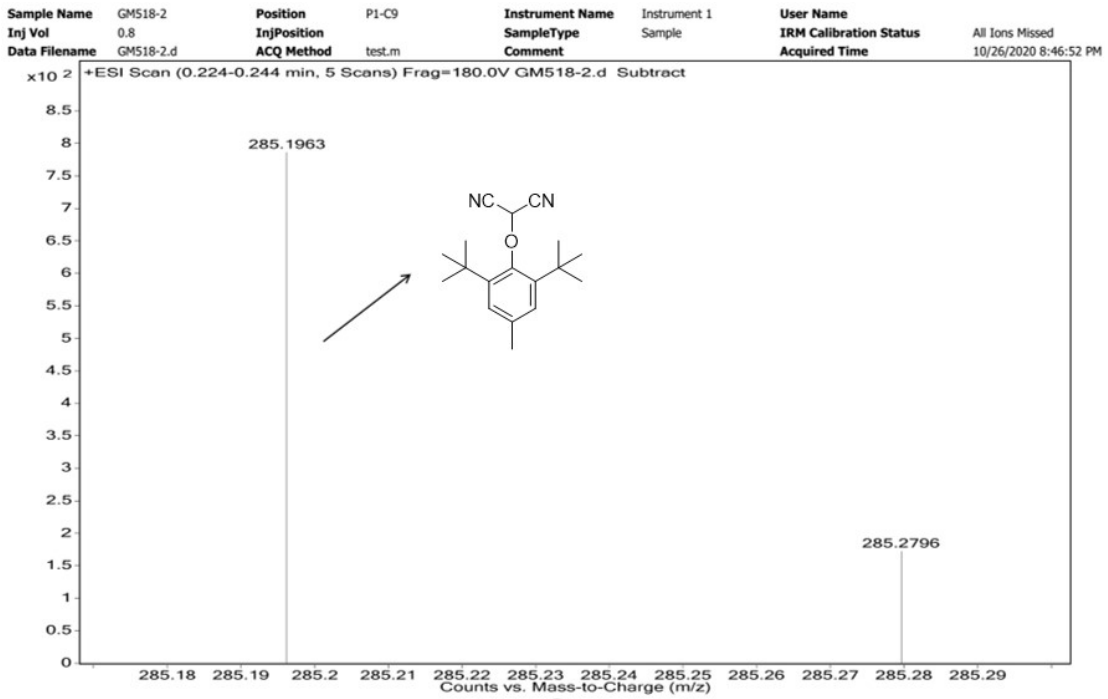


Figure S28. HRMS spectrum of compound [**IV**+H]$^+$ for exp 10

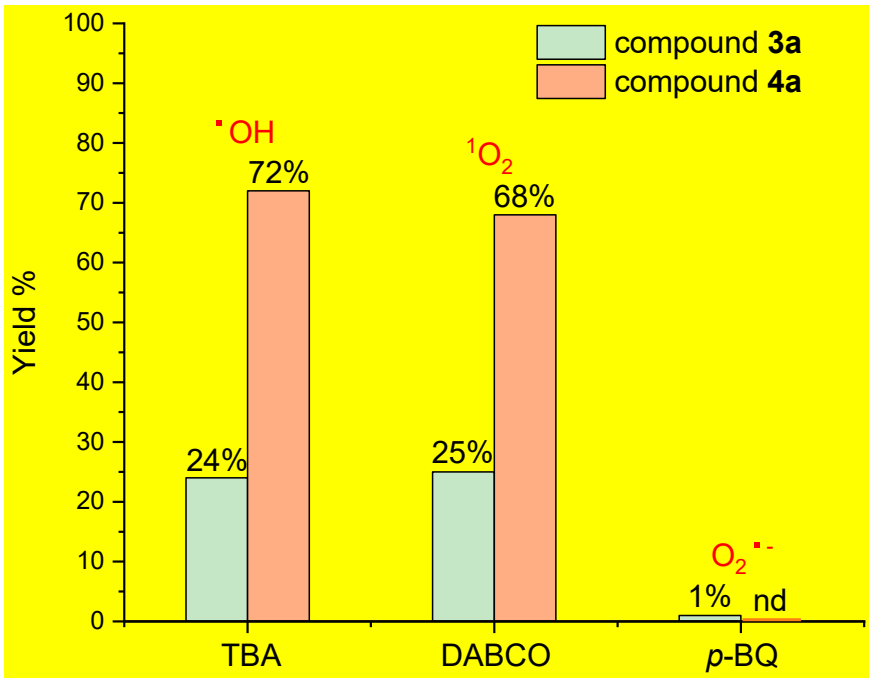


Figure S29. Quenching experiments of reactive oxygen species. Reaction conditions: **1a** (0.2 mmol), malononitrile **2a** (1.5 equiv.), quenching agent, NH_4Cl (0.1 M), EtOH (5 mL) in a quartz-tube under air at room temperature, 3 W blue LED, for 5 h, isolated yield. TBA = tert-butyl alcohol (2 equiv.); DABCO = bicyclo[2.2.2]-1,4-diazaoctane (0.5 equiv.); *p*-BQ = 1,4-benzochinon (0.5 equiv.).

6. Computational Details

All the calculations were conducted by using the Gaussian 16 program package.[3] The Coulomb attenuation method cam-B3LYP functional[4] and the def2-TZVP(D) basis set[5] were used for all the calculations. The polarizable continuum model (PCM)[6] was employed to consider the solvent effect of EtOH. 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[7-8] and VMD VERSION 1.9.3 program[9], we drawn and analyzed **TS1** and **TS2**. **A3**, **I**, **II**, **B3** and **B5** were also analyzed by ADCH[10].

1a

Sum of electronic and zero-point Energies= -635.016488
Sum of electronic and thermal Energies= -635.004258
Sum of electronic and thermal Enthalpies= -635.003313
Sum of electronic and thermal Free Energies= -635.055895

C	-0.30414900	-0.75677800	0.42676400
H	-0.11936200	-0.83100900	1.51069700
C	-1.77392700	-0.52813900	0.20135500
C	-2.66188800	-1.57580000	0.41921700
H	-2.27650800	-2.54217800	0.72265700
H	-4.70001400	-2.22573500	0.42144700
C	-4.50955600	-0.16155300	-0.14020200
H	-5.57274400	-0.01178200	-0.27408300
C	-3.63036900	0.88175800	-0.35643400
H	-4.00794400	1.85136700	-0.65869900
C	-2.25963000	0.71280000	-0.18875700
C	-1.30771900	1.84696700	-0.44200700
H	-1.17429100	1.97104300	-1.51979400
H	-1.73158900	2.78050300	-0.06850600
C	0.05021800	1.61529400	0.19320800
H	0.74896000	2.35523900	-0.18825600
H	-0.01152900	1.75037000	1.28392100
N	0.53057900	0.28958000	-0.14786700
H	-0.03006400	-1.71758700	-0.00025000
C	1.91317300	0.05080200	-0.08171500
C	2.80857900	0.96595000	0.47018700
C	2.43223100	-1.13792700	-0.60540500
C	4.17128600	0.70611200	0.48147800
H	2.45127900	1.88593600	0.90684000
C	3.78792500	-1.39382100	-0.57949300
H	1.76636100	-1.85660500	-1.06217200
C	4.67311000	-0.47211900	-0.03737200
H	4.84183000	1.43684100	0.91514500
H	4.15929700	-2.31955300	-0.99976700
H	5.73572400	-0.67233100	-0.02368400

C	-4.02152800	-1.40047600	0.25077200

2a

Sum of electronic and zero-point Energies=			-224.926028
Sum of electronic and thermal Energies=			-224.921262
Sum of electronic and thermal Enthalpies=			-224.920317
Sum of electronic and thermal Free Energies=			-224.952991
C	0.00000000	1.21130100	0.02711400
N	0.00000000	2.16811800	-0.59660100
C	0.00000000	0.00000000	0.84219400
H	0.88012500	0.00000000	1.48694300
H	-0.88012500	0.00000000	1.48694300
C	0.00000000	-1.21130100	0.02711400
N	0.00000000	-2.16811800	-0.59660100

3a

Sum of electronic and zero-point Energies=			-727.256647
Sum of electronic and thermal Energies=			-727.242717
Sum of electronic and thermal Enthalpies=			-727.241773
Sum of electronic and thermal Free Energies=			-727.298112
N	-0.54482600	-0.37056000	0.10286600
N	0.15261300	2.42771500	1.95195100
C	-2.49434600	1.03040100	-0.37622900
H	-1.90025900	1.93139400	-0.37920800
C	-3.85249300	1.14264700	-0.63193900
H	-4.26654600	2.12144900	-0.83571500
C	-4.67345600	0.03147700	-0.61475100
H	-5.73286400	0.12473000	-0.80928400
C	-4.11007300	-1.20781700	-0.34700500
H	-4.72948600	-2.09518000	-0.34054700
C	-2.75752900	-1.33331100	-0.10266000
H	-2.34479300	-2.31712200	0.06529500
C	-1.92044100	-0.21267200	-0.10744400
C	0.32748100	0.75700200	-0.07618700
H	0.02308400	1.30192900	-0.96935800
C	1.77725100	0.33662900	-0.25613500
C	2.68163200	1.26549100	-0.75467400
H	2.34170700	2.26381900	-1.00274500
C	4.00661400	0.92441200	-0.93848400
H	4.70411400	1.65187400	-1.33055300
C	4.43294000	-0.35708500	-0.61941600
H	5.46917300	-0.63513900	-0.75800600
C	3.53225900	-1.27843300	-0.12221800
H	3.86590200	-2.27755200	0.12979300

C	2.19446800	-0.94692300	0.06859900
C	1.22100300	-1.96292300	0.59783000
H	1.68566600	-2.53899000	1.39890300
H	0.96874100	-2.66798000	-0.19813800
C	-0.04742500	-1.30840600	1.10182900
H	-0.80378300	-2.05439900	1.31198600
H	0.14670600	-0.77839200	2.04387700
C	0.23513900	1.71442100	1.06054700

4a

Sum of electronic and zero-point Energies=			-857.589605
Sum of electronic and thermal Energies=			-857.573678
Sum of electronic and thermal Enthalpies=			-857.572734
Sum of electronic and thermal Free Energies=			-857.633117
N	-0.41175300	-1.17427400	-0.15885100
N	0.05037300	1.59919900	2.49667100
N	-0.66186000	3.34528100	-1.36666400
C	3.71516900	-1.15569900	0.24729900
H	4.21086000	-2.08411000	0.50293700
C	4.44868700	0.01138200	0.15912400
H	5.51361100	-0.00391300	0.34862900
C	3.81730000	1.19784700	-0.18064200
H	4.38187700	2.11677700	-0.25907400
C	2.45835500	1.19989200	-0.42577600
H	1.97546700	2.12710200	-0.70565500
C	1.71492800	0.03021500	-0.31908700
C	2.34452100	-1.16852500	0.01144400
C	1.58220000	-2.46449300	0.13383300
H	1.44328100	-2.69053900	1.19357800
H	2.17350400	-3.27738900	-0.28824500
C	0.21925600	-2.41392900	-0.53516600
H	0.31516000	-2.48641300	-1.62642200
H	-0.39656900	-3.24521600	-0.20078500
C	0.24383700	0.03141200	-0.62272700
H	0.09605000	0.14285000	-1.70803400
C	-0.65503700	1.14203500	0.02073800
C	-2.01029000	0.43411700	0.00130000
C	-1.76780100	-0.93583900	-0.09539300
C	-2.82939900	-1.82552600	-0.08336100
H	-2.67219300	-2.89083300	-0.17032900
C	-4.11251900	-1.30733300	0.03742800
H	-4.95165400	-1.99032000	0.04394100
C	-4.34663300	0.05626000	0.13896300
H	-5.35740100	0.42832400	0.22506200

C	-3.27795100	0.94577000	0.12564900
H	-3.44407100	2.01211300	0.20554900
C	-0.24957000	1.41407600	1.40955200
C	-0.64925700	2.38336100	-0.74972000

A1

Sum of electronic and zero-point Energies= -634.821190

Sum of electronic and thermal Energies= -634.808932

Sum of electronic and thermal Enthalpies= -634.807988

Sum of electronic and thermal Free Energies= -634.861670

C	-0.39497400	-0.91433000	0.84337800
H	-0.47462100	-1.13109200	1.91202200
C	-1.74859200	-0.54985200	0.27425500
C	-2.68278900	-1.56849100	0.13118900
H	-2.42275200	-2.57784100	0.42602900
H	-4.65505700	-2.10224300	-0.49448500
C	-4.25962300	-0.00988300	-0.77136600
H	-5.23748100	0.20680000	-1.17960200
C	-3.33190700	1.00261700	-0.62782000
H	-3.58477000	2.01374600	-0.92140500
C	-2.06993700	0.74683700	-0.10266300
C	-1.06632600	1.85439000	0.05422500
H	-0.60944200	2.09489400	-0.90829200
H	-1.55291800	2.76161300	0.41059900
C	0.01174500	1.46536100	1.04897800
H	0.79164100	2.20916600	1.13014700
H	-0.42398000	1.33354300	2.04088000
N	0.57029400	0.16686400	0.68097800
H	-0.03608600	-1.80541300	0.34600600
C	1.82367700	-0.01361400	0.23438700
C	2.62786200	1.09846500	-0.14364400
C	2.38329400	-1.31828700	0.13091000
C	3.90087000	0.90331800	-0.60159300
H	2.23024700	2.09874500	-0.11279000
C	3.66423200	-1.48415800	-0.31626100
H	1.82196500	-2.18218700	0.44438800
C	4.43383800	-0.38248300	-0.68992000
H	4.49326600	1.75496000	-0.90320700
H	4.08294300	-2.47857500	-0.37119200
H	5.44375000	-0.52528900	-1.04724300
C	-3.93449900	-1.30303400	-0.38717100

A2

Sum of electronic and zero-point Energies= -634.403246

Sum of electronic and thermal Energies= -634.391127

Sum of electronic and thermal Enthalpies= -634.390183

Sum of electronic and thermal Free Energies= -634.442683

C	0.35657500	-0.76814600	-0.14371500
C	1.74647200	-0.56315800	-0.09585400
C	2.65389000	-1.60896200	-0.37151600
H	2.26673800	-2.58843300	-0.62430100
H	4.69219100	-2.20454400	-0.54522200
C	4.51483200	-0.12972400	-0.01523200
H	5.58217400	0.04247900	0.00994700
C	3.63166600	0.90736800	0.26679900
H	4.01770500	1.88862700	0.51745900
C	2.26712400	0.71029700	0.23957000
C	1.27878500	1.77867900	0.59639700
H	1.04972600	1.72460600	1.66544300
H	1.69191100	2.76989600	0.40927900
C	-0.01618100	1.62172000	-0.18364900
H	-0.75733700	2.31893800	0.19540800
H	0.15199600	1.84695700	-1.24220500
N	-0.53720200	0.26635000	-0.04347200
H	-0.04926300	-1.74691100	-0.34459300
C	-1.91330100	0.03160000	-0.01584500
C	-2.81424800	0.96432300	-0.53347900
C	-2.41808500	-1.15168200	0.52986700
C	-4.17497600	0.71616000	-0.50077800
H	-2.45621600	1.87706900	-0.98547100
C	-3.77909000	-1.39115500	0.54718300
H	-1.74384100	-1.87249800	0.96883800
C	-4.67045100	-0.46127200	0.03478800
H	-4.85327700	1.45218500	-0.91220200
H	-4.14621400	-2.31192100	0.98146100
H	-5.73472600	-0.65096900	0.05493600
C	4.01179600	-1.39103800	-0.32861400

A3

Sum of electronic and zero-point Energies= -634.263322

Sum of electronic and thermal Energies= -634.251472

Sum of electronic and thermal Enthalpies= -634.250528

Sum of electronic and thermal Free Energies= -634.302080

C	1.74898700	-0.54039700	-0.11095300
C	2.59209400	-1.60055300	-0.44606200
H	2.16887400	-2.55646600	-0.72430500
H	4.62142900	-2.22173300	-0.69774500
C	4.47279300	-0.17698600	-0.06325700

H	5.54416100	-0.02899200	-0.04794200
C	3.63619500	0.87260800	0.28970900
H	4.05610300	1.82531200	0.58308900
C	2.26719500	0.70484600	0.26560700
C	1.29587400	1.76296400	0.69266200
H	1.11427100	1.66594600	1.76648700
H	1.70577500	2.75721900	0.52732800
C	-0.00968900	1.64666200	-0.06238000
H	-0.77821500	2.27066300	0.38037000
H	0.11420500	1.93118600	-1.10834100
N	-0.50623300	0.25121900	-0.04619900
C	-1.92158900	0.02038200	-0.02289000
C	-2.74541200	0.77500500	-0.84136700
C	-2.43679400	-0.94933200	0.81948500
C	-4.10712300	0.53594800	-0.82421800
H	-2.33267100	1.52759700	-1.49769500
C	-3.80109400	-1.18076900	0.82490800
H	-1.78410800	-1.50014800	1.48247700
C	-4.63593000	-0.44118400	0.00452800
H	-4.75632900	1.11410200	-1.46667800
H	-4.21062600	-1.93339500	1.48391700
H	-5.70195200	-0.62112600	0.01512100
C	3.95722700	-1.41266700	-0.43019800
C	0.33127500	-0.72730200	-0.12230500
H	-0.08132600	-1.72405000	-0.21231200

B1

Sum of electronic and zero-point Energies=	-224.565253
Sum of electronic and thermal Energies=	-224.559710
Sum of electronic and thermal Enthalpies=	-224.558766
Sum of electronic and thermal Free Energies=	-224.593504

C	0.00000000	1.21723000	0.01330800
N	0.00000000	2.23861400	-0.54008400
C	0.00000000	0.00000000	0.73384900
H	0.82583800	0.00000000	1.49918900
H	-0.82583800	0.00000000	1.49918900
C	0.00000000	-1.21723000	0.01330800
N	0.00000000	-2.23861400	-0.54008400

B2

Sum of electronic and zero-point Energies=	-224.992980
Sum of electronic and thermal Energies=	-224.987722
Sum of electronic and thermal Enthalpies=	-224.986778
Sum of electronic and thermal Free Energies=	-225.021911

C	0.04658300	0.99899100	0.00000500
H	0.00544200	1.64419400	0.87635300
H	0.00544100	1.64420300	-0.87633600
C	-1.10791900	0.11349600	0.00000100
C	1.41993800	0.23821000	0.00000100
N	-1.93851900	-0.68035800	-0.00000200
N	1.62959200	-0.94715400	-0.00000700

B3

Sum of electronic and zero-point Energies=			-224.469065
Sum of electronic and thermal Energies=			-224.464397
Sum of electronic and thermal Enthalpies=			-224.463452
Sum of electronic and thermal Free Energies=			-224.496402
C	0.00000000	0.05797500	-1.20845200
N	0.00000000	-0.49530800	-2.22986100
C	0.00000000	0.73707800	0.00000000
H	0.00000000	1.81614000	0.00000000
C	0.00000000	0.05797500	1.20845200
N	0.00000000	-0.49530800	2.22986100

B4

Sum of electronic and zero-point Energies=			-224.290165
Sum of electronic and thermal Energies=			-224.285441
Sum of electronic and thermal Enthalpies=			-224.284496
Sum of electronic and thermal Free Energies=			-224.317545
C	0.00000000	1.21423900	0.05429800
N	0.00000000	2.22882900	-0.49257900
C	0.00000000	0.00000000	0.73755200
H	0.00000000	0.00000000	1.81922800
C	0.00000000	-1.21423900	0.05429800
N	0.00000000	-2.22882900	-0.49257900

B5

Sum of electronic and zero-point Energies=			-92.950860
Sum of electronic and thermal Energies=			-92.948499
Sum of electronic and thermal Enthalpies=			-92.947555
Sum of electronic and thermal Free Energies=			-92.969878
C	0.00000000	0.00000000	-0.62606500
N	0.00000000	0.00000000	0.53662700

C

Sum of electronic and zero-point Energies=			-858.764070
Sum of electronic and thermal Energies=			-858.746967
Sum of electronic and thermal Enthalpies=			-858.746023

Sum of electronic and thermal Free Energies= -858.810444

N	0.56898200	-0.63268900	-0.26557000
C	2.23337500	-0.32958300	1.47599900
H	1.45308000	-0.13914800	2.19907500
C	3.55017300	-0.31675900	1.89430600
H	3.77096700	-0.09571500	2.93042400
C	4.57869000	-0.60256100	1.01002500
H	5.60762600	-0.59695600	1.34212300
C	4.26318500	-0.89767100	-0.30459800
H	5.04948600	-1.11684700	-1.01519800
C	2.94816300	-0.89669600	-0.73717800
H	2.74031100	-1.08982500	-1.77888500
C	1.90837500	-0.61213300	0.14721300
C	-0.35954400	0.35394800	0.20735300
H	-0.03518000	0.72556000	1.17312100
C	-1.75683000	-0.20283600	0.33733800
C	-2.66713600	0.40313300	1.19610500
H	-2.35890700	1.25271200	1.79069800
C	-3.95857500	-0.07396600	1.30734200
H	-4.65636800	0.40548000	1.98015200
C	-4.34850000	-1.17194000	0.55571700
H	-5.35869000	-1.55182200	0.63063000
C	-3.43797100	-1.79193200	-0.27799500
H	-3.73508800	-2.66413700	-0.84734300
C	-2.13370800	-1.32408400	-0.39378300
C	-1.13850700	-2.08032200	-1.22955500
H	-1.58479500	-2.35865700	-2.18506400
H	-0.90615200	-3.01335600	-0.71025900
C	0.15800000	-1.32468100	-1.47270000
H	0.93056500	-2.03344700	-1.74992600
H	0.04951500	-0.63670400	-2.32009000
C	-0.37327000	1.60645800	-0.77104800
H	-0.75140500	1.27343700	-1.73952800
C	-1.24748500	2.68426900	-0.31564700
C	0.97163900	2.14321800	-0.98008600
N	-1.92512600	3.53076500	0.04545200
N	2.01965500	2.56538900	-1.15027800

D

Sum of electronic and zero-point Energies= -858.555512

Sum of electronic and thermal Energies= -858.538478

Sum of electronic and thermal Enthalpies= -858.537534

Sum of electronic and thermal Free Energies= -858.602320

N	-0.67842000	-0.23332900	0.52383400

C	-2.33860700	0.39656000	-1.11461900
H	-1.73598700	1.20440900	-1.49326300
C	-3.57435700	0.19600100	-1.65649100
H	-3.91008500	0.83181100	-2.46251500
C	-4.40867900	-0.81279900	-1.16989400
H	-5.38394500	-0.96533300	-1.60961300
C	-3.98333200	-1.62447000	-0.11613300
H	-4.62370500	-2.41423200	0.24855500
C	-2.75738800	-1.43707600	0.45251600
H	-2.44055500	-2.09846700	1.24060400
C	-1.88754400	-0.41637900	-0.03279200
C	0.38212700	0.54536700	-0.11138100
H	0.04830500	0.86103900	-1.09044200
C	1.62264700	-0.30764300	-0.28963800
C	2.55196300	0.07473800	-1.25089200
H	2.36858200	0.94573700	-1.86483700
C	3.70621500	-0.65820000	-1.43739000
H	4.42469800	-0.35002000	-2.18393700
C	3.93060000	-1.79156800	-0.67090900
H	4.83244900	-2.37190200	-0.81016600
C	2.99267200	-2.19006200	0.26028600
H	3.15669700	-3.08749400	0.84298400
C	1.82704800	-1.46050100	0.46105700
C	0.78915400	-1.96246400	1.42467200
H	1.25421100	-2.29242400	2.35258200
H	0.28707400	-2.83120600	0.99359500
C	-0.23846400	-0.89777000	1.75281000
H	-1.08853500	-1.29023800	2.29203100
H	0.20198500	-0.13368400	2.39095500
C	0.66356400	1.83641400	0.73582800
H	1.16510400	1.55951500	1.66484400
C	1.55491400	2.75357700	0.02676200
C	-0.58224400	2.52504800	1.08148700
N	2.24737300	3.47436900	-0.52492700
N	-1.57724300	3.01894000	1.34637300

E

Sum of electronic and zero-point Energies=	-858.139167
Sum of electronic and thermal Energies=	-858.122052
Sum of electronic and thermal Enthalpies=	-858.121107
Sum of electronic and thermal Free Energies=	-858.186278

N	-0.49046000	-0.74155600	0.09256100
C	-2.40381300	-0.57079600	-1.38448900
H	-1.73727800	-0.52145300	-2.23429600

C	-3.76906500	-0.53483100	-1.58867600
H	-4.15176500	-0.44210100	-2.59632100
C	-4.64520400	-0.63269100	-0.51792700
H	-5.71373100	-0.60847900	-0.68166500
C	-4.13482200	-0.76237100	0.76154400
H	-4.80414600	-0.83271600	1.60866000
C	-2.76677700	-0.78523000	0.97668000
H	-2.38982000	-0.85684700	1.98644100
C	-1.88388900	-0.69458300	-0.09593500
C	0.32646000	0.29494900	-0.51636300
H	-0.02324000	0.46765300	-1.52985100
C	1.78954400	-0.06418500	-0.56485300
C	2.64178100	0.73850600	-1.31510100
H	2.23700700	1.58406600	-1.85816000
C	3.99329900	0.46688400	-1.37211100
H	4.64841500	1.09468400	-1.96042900
C	4.50269400	-0.61663300	-0.66948700
H	5.56128200	-0.83693200	-0.70346400
C	3.65635200	-1.41312300	0.07583500
H	4.05448000	-2.25658200	0.62626300
C	2.29123100	-1.14967300	0.13930600
C	1.37761700	-2.03921500	0.93299500
H	1.87605800	-2.36389200	1.84678300
H	1.16366900	-2.93903100	0.35116000
C	0.06655900	-1.36181800	1.28392500
H	-0.64170700	-2.10373500	1.64025300
H	0.21261000	-0.64074400	2.09571200
C	0.08995100	1.57528300	0.27167800
C	0.84520100	1.86839600	1.41040200
C	-0.99430700	2.39990200	-0.04056500
N	1.49247000	2.09215100	2.33785300
N	-1.88611000	3.06990500	-0.33216200

F

Sum of electronic and zero-point Energies= -858.133075

Sum of electronic and thermal Energies= -858.116792

Sum of electronic and thermal Enthalpies= -858.115847

Sum of electronic and thermal Free Energies= -858.177620

N	-0.46343000	-1.02153500	-0.95019900
N	-0.21353700	0.68542100	2.45758100
N	-0.19999500	3.67060200	-0.64074900
C	3.43063500	-1.23537500	0.65982100
H	3.75210000	-2.15381100	1.13479800
C	4.31273100	-0.17899900	0.53477800

H	5.31957400	-0.26777000	0.92022900
C	3.91092400	0.98513800	-0.10266100
H	4.59959000	1.81046600	-0.22052100
C	2.62588400	1.08152800	-0.59924300
H	2.31693800	1.98266800	-1.11375600
C	1.72762000	0.03175800	-0.44618100
C	2.13081500	-1.14621700	0.17635700
C	1.18405600	-2.30895600	0.27801200
H	0.61587700	-2.25753700	1.21028400
H	1.74402100	-3.24380700	0.29429700
C	0.21652600	-2.29719200	-0.89325300
H	0.75349900	-2.46619300	-1.82902200
H	-0.52726500	-3.08195000	-0.79778700
C	0.31986600	0.20310000	-0.94879500
H	0.34804400	0.64831700	-1.94846600
C	-0.57566900	1.15963800	-0.08015300
C	-1.99685900	0.66480800	-0.51624200
C	-1.76281300	-0.81329500	-0.59467800
C	-2.74241800	-1.71265800	-0.28708700
H	-2.58186000	-2.77351700	-0.41633200
C	-3.94665600	-1.25455400	0.27524100
H	-4.72201600	-1.96463800	0.52324500
C	-4.11159900	0.10845000	0.61027300
H	-5.00806900	0.41107000	1.13622700
C	-3.17913700	1.04284200	0.30224300
H	-3.32011100	2.08551100	0.55340300
C	-0.36352600	0.91269200	1.34784500
C	-0.35460500	2.56869800	-0.37875600
H	-2.10623600	1.06133200	-1.53815800

G

Sum of electronic and zero-point Energies=	-857.977100
Sum of electronic and thermal Energies=	-857.961075
Sum of electronic and thermal Enthalpies=	-857.960131
Sum of electronic and thermal Free Energies=	-858.020570

N	-0.47362700	-1.06283300	-0.78421200
N	-0.16097000	1.02862700	2.43477200
N	-0.32819000	3.62860700	-0.99000300
C	3.47598000	-1.24328000	0.60253000
H	3.84051200	-2.17958900	1.00501000
C	4.30581900	-0.14024700	0.56433600
H	5.31556700	-0.21206800	0.94474100
C	3.84917200	1.05161300	0.02255400
H	4.49737200	1.91526800	-0.02647900

C	2.56108600	1.12926500	-0.46609500
H	2.21301100	2.05542500	-0.90424100
C	1.71658400	0.02708600	-0.39945300
C	2.17309600	-1.17848100	0.12375400
C	1.29251900	-2.39795500	0.15750300
H	0.81654400	-2.49405900	1.13576200
H	1.89209400	-3.29378100	0.00475400
C	0.22144000	-2.33681100	-0.91430100
H	0.65671700	-2.37581600	-1.91280000
H	-0.49732900	-3.14285100	-0.81962300
C	0.30904700	0.17313700	-0.90532600
H	0.30941900	0.47967000	-1.95477100
C	-0.60614200	1.18708100	-0.13280500
C	-2.00924000	0.60778700	-0.45794900
C	-1.72442700	-0.85514300	-0.51695200
C	-2.74663300	-1.79628600	-0.25014800
H	-2.60560200	-2.84812700	-0.44055400
C	-3.86342500	-1.33254300	0.35311800
H	-4.63881500	-2.03879200	0.61802900
C	-4.06750100	0.05477300	0.71131400
H	-4.96317500	0.31619300	1.25493400
C	-3.18495500	0.98997100	0.36392500
H	-3.34019700	2.03706400	0.58344300
C	-0.34701700	1.11935000	1.31207800
C	-0.44158200	2.55989000	-0.60457600
H	-2.23954500	0.90542200	-1.49315100

H

Sum of electronic and zero-point Energies= -375.272485

Sum of electronic and thermal Energies= -375.265418

Sum of electronic and thermal Enthalpies= -375.264473

Sum of electronic and thermal Free Energies= -375.303923

C	1.55899100	-0.25025500	0.08042600
N	2.67108600	-0.36568600	-0.14815400
C	-0.34017000	1.25454000	0.07510700
N	-0.73583100	2.29835700	-0.16473600
C	0.13224500	-0.10741200	0.38785500
H	-0.01835000	-0.29013200	1.45569200
O	-0.54008200	-1.08426900	-0.37585400
O	-1.86602200	-1.14377400	0.13591500
H	-2.38600800	-0.79546200	-0.60627100

J

Sum of electronic and zero-point Energies= -298.934562

Sum of electronic and thermal Energies= -298.929137
Sum of electronic and thermal Enthalpies= -298.928193
Sum of electronic and thermal Free Energies= -298.963040

C	0.00000000	1.23458700	-0.30190900
N	0.00000000	2.20453000	-0.90635400
C	0.00000000	-1.23458700	-0.30190900
N	0.00000000	-2.20453000	-0.90635400
C	0.00000000	0.00000000	0.48429200
O	0.00000000	0.00000000	1.67576400

K

Sum of electronic and zero-point Energies= -93.407486
Sum of electronic and thermal Energies= -93.404975
Sum of electronic and thermal Enthalpies= -93.404030
Sum of electronic and thermal Free Energies= -93.426828

C	0.00000000	0.00000000	-0.49398900
H	0.00000000	0.00000000	-1.56383400
N	0.00000000	0.00000000	0.64682400

L

Sum of electronic and zero-point Energies= -360.520423
Sum of electronic and thermal Energies= -360.512930
Sum of electronic and thermal Enthalpies= -360.511986
Sum of electronic and thermal Free Energies= -360.553116

C	-1.44158300	0.68705900	-0.00039100
N	-1.98113200	1.69446900	-0.00064700
C	-0.81285300	-0.65020700	0.00004700
O	-1.50223700	-1.62734200	-0.00028100
O	0.49546600	-0.68339900	0.00063800
C	1.28582800	0.54181800	0.00211800
H	1.02685100	1.11613000	-0.88576000
H	1.03005800	1.11163800	0.89381400
C	2.73118400	0.13353900	-0.00158600
H	2.96668600	-0.44997900	-0.89027000
H	3.35301500	1.02794100	-0.00055400
H	2.97003000	-0.45434000	0.88332200

M

Sum of electronic and zero-point Energies= -282.420287
Sum of electronic and thermal Energies= -282.415127
Sum of electronic and thermal Enthalpies= -282.414183
Sum of electronic and thermal Free Energies= -282.449509

C	0.00000000	0.63216300	0.00000000
H	0.17033400	1.22972600	0.89358100

H	0.17033400	1.22972600	-0.89358100
C	-1.34639900	0.07908300	0.00000000
N	-2.40700600	-0.34531600	0.00000000
O	0.92355600	-0.48348000	0.00000000
O	2.14978900	-0.05523500	0.00000000

N

Sum of electronic and zero-point Energies= -283.050943
Sum of electronic and thermal Energies= -283.045363
Sum of electronic and thermal Enthalpies= -283.044419
Sum of electronic and thermal Free Energies= -283.079551

C	-0.04403300	0.60347600	0.00268400
H	0.12371000	1.20168600	0.90079100
H	0.11205500	1.22551500	-0.88034000
C	-1.41392400	0.09859400	0.00594500
N	-2.48998700	-0.28639700	0.00997500
O	0.80422600	-0.53162700	-0.02443700
O	2.13270700	-0.02888800	-0.09511800
H	2.44642100	-0.15072700	0.81438500

O_2

Sum of electronic and zero-point Energies= -150.341418
Sum of electronic and thermal Energies= -150.339055
Sum of electronic and thermal Enthalpies= -150.338111
Sum of electronic and thermal Free Energies= -150.361365

O	0.00000000	0.00000000	0.59729800
O	0.00000000	0.00000000	-0.59729800

$O_2^{\cdot-}$

Sum of electronic and zero-point Energies= -150.470802
Sum of electronic and thermal Energies= -150.468428
Sum of electronic and thermal Enthalpies= -150.467484
Sum of electronic and thermal Free Energies= -150.490564

O	0.00000000	0.00000000	0.66233300
O	0.00000000	0.00000000	-0.66233300

HOO^-

Sum of electronic and zero-point Energies= -151.068632
Sum of electronic and thermal Energies= -151.065729
Sum of electronic and thermal Enthalpies= -151.064785
Sum of electronic and thermal Free Energies= -151.090357

O	0.67453500	-0.11946300	-0.00000100
H	0.96529200	0.79786200	0.00000800
O	-0.79519600	0.01973000	0.00000000

$HOO^{\cdot}$

Sum of electronic and zero-point Energies=			-150.920011
Sum of electronic and thermal Energies=			-150.917158
Sum of electronic and thermal Enthalpies=			-150.916214
Sum of electronic and thermal Free Energies=			-150.942161
O	0.59000500	-0.12521500	-0.00000100
H	0.97360600	0.77371200	0.00000800
O	-0.71170600	0.02850100	0.00000000

H_2O_2

Sum of electronic and zero-point Energies=			-151.549171
Sum of electronic and thermal Energies=			-151.545970
Sum of electronic and thermal Enthalpies=			-151.545025
Sum of electronic and thermal Free Energies=			-151.571429
O	-0.70652500	-0.10645100	-0.06599000
H	-1.01649000	0.59192600	0.52790900
O	0.70652500	0.10645000	-0.06598900
H	1.01648800	-0.59191600	0.52792400

HO^{-}

Sum of electronic and zero-point Energies=			-75.926885
Sum of electronic and thermal Energies=			-75.924524
Sum of electronic and thermal Enthalpies=			-75.923580
Sum of electronic and thermal Free Energies=			-75.943132
O	0.00000000	0.00000000	0.10689000
H	0.00000000	0.00000000	-0.85512400

H_2O

Sum of electronic and zero-point Energies=			-76.421167
Sum of electronic and thermal Energies=			-76.418331
Sum of electronic and thermal Enthalpies=			-76.417387
Sum of electronic and thermal Free Energies=			-76.438812
O	0.00000000	0.00000000	0.11720000
H	0.00000000	0.76373500	-0.46880200
H	0.00000000	-0.76373500	-0.46880200

EtOH

Sum of electronic and zero-point Energies=			-154.958297
Sum of electronic and thermal Energies=			-154.953987
Sum of electronic and thermal Enthalpies=			-154.953043
Sum of electronic and thermal Free Energies=			-154.983701
O	1.19658400	-0.22245300	0.00000000
H	1.95066100	0.37479900	0.00000000

C	0.00000000	0.54977600	0.00000000
H	-0.03303100	1.19406700	0.88416400
H	-0.03303100	1.19406700	-0.88416400
C	-1.17345600	-0.39623400	0.00000000
H	-2.10982400	0.16213700	0.00000000
H	-1.15335700	-1.03334900	-0.88472400
H	-1.15335700	-1.03334900	0.88472400

EtO$^{\cdot}$

Sum of electronic and zero-point Energies=			-154.302123
Sum of electronic and thermal Energies=			-154.297682
Sum of electronic and thermal Enthalpies=			-154.296738
Sum of electronic and thermal Free Energies=			-154.328403
O	1.29655900	0.09286000	0.00000000
C	0.00000000	0.50762900	0.00000000
H	-0.11823100	1.18863200	0.86215900
H	-0.11823100	1.18863200	-0.86215900
C	-1.03874600	-0.59287700	0.00000000
H	-2.04364900	-0.16922600	0.00000000
H	-0.92994300	-1.21971700	-0.88503300
H	-0.92994300	-1.21971700	0.88503300

H^{+}

Sum of electronic and zero-point Energies=			-0.159984
Sum of electronic and thermal Energies=			-0.158567
Sum of electronic and thermal Enthalpies=			-0.157623
Sum of electronic and thermal Free Energies=			-0.169983
H	0.00000000	0.00000000	0.00000000

H_2

Sum of electronic and zero-point Energies=			-1.161316
Sum of electronic and thermal Energies=			-1.158956
Sum of electronic and thermal Enthalpies=			-1.158012
Sum of electronic and thermal Free Energies=			-1.172813
H	0.00000000	0.00000000	0.37330900
H	0.00000000	0.00000000	-0.37330900

TS1

Sum of electronic and zero-point Energies=			-858.482145
Sum of electronic and thermal Energies=			-858.464963
Sum of electronic and thermal Enthalpies=			-858.464019
Sum of electronic and thermal Free Energies=			-858.528611
N	0.50645000	-0.66970200	-0.15085400
C	2.17149900	-0.23498200	1.55546200

H	1.40133600	-0.00757100	2.27689500
C	3.48908400	-0.19922500	1.94289700
H	3.73892900	0.09505700	2.95216300
C	4.49280800	-0.56622400	1.05327600
H	5.52704100	-0.53861700	1.36679000
C	4.16870300	-0.97976600	-0.23158400
H	4.94844900	-1.25865000	-0.92561700
C	2.85530800	-1.02569200	-0.63689900
H	2.62339500	-1.31264400	-1.65025700
C	1.83983200	-0.64002600	0.25255500
C	-0.41323800	0.17429400	0.36249000
H	-0.06686200	0.79350500	1.17628400
C	-1.82994400	-0.18140000	0.33870600
C	-2.75656100	0.64338800	0.97717300
H	-2.43149000	1.55587700	1.45769000
C	-4.08870900	0.29070200	1.00468800
H	-4.80679300	0.93096100	1.49717900
C	-4.49881500	-0.89195900	0.40520600
H	-5.54345100	-1.17170900	0.42331200
C	-3.57748000	-1.72354500	-0.20674900
H	-3.90149300	-2.65357500	-0.65523800
C	-2.23681100	-1.37963200	-0.24923100
C	-1.20511400	-2.29887300	-0.82832900
H	-1.59171000	-2.81147000	-1.70785100
H	-0.96073600	-3.07109400	-0.09480200
C	0.05499900	-1.56284600	-1.23623600
H	0.84672500	-2.26629300	-1.45462300
H	-0.11937600	-0.94659700	-2.12046500
C	-0.32414000	1.83683800	-1.00973800
H	-1.08934000	1.46867900	-1.68301300
C	-0.70307900	2.94492200	-0.20526700
C	0.98977700	1.86342800	-1.53737900
N	-1.01626900	3.81263100	0.47659500
N	2.06077000	1.82531800	-1.94927000

TS2

Sum of electronic and zero-point Energies=	-858.072703
Sum of electronic and thermal Energies=	-858.056606
Sum of electronic and thermal Enthalpies=	-858.055662
Sum of electronic and thermal Free Energies=	-858.117346

N	-0.43046700	-0.95522900	-0.86426600
N	-0.51743600	0.60559600	2.58085900
N	-0.31759000	3.74899400	-0.45482200
C	3.54192400	-1.24138800	0.54996800

H	3.88624100	-2.18165400	0.96274600
C	4.41811900	-0.17986800	0.43020900
H	5.44369400	-0.28514300	0.75827100
C	3.98315300	1.01226400	-0.12978800
H	4.66498500	1.84401700	-0.24444600
C	2.67333700	1.13044400	-0.55124900
H	2.33864000	2.05753000	-0.99997900
C	1.78116600	0.07265000	-0.40711900
C	2.21893900	-1.13160400	0.13580600
C	1.28103400	-2.30338400	0.21717400
H	0.75918200	-2.31394900	1.17747400
H	1.84203400	-3.23529500	0.14666700
C	0.26492400	-2.22637200	-0.90690700
H	0.76714600	-2.32681300	-1.87253800
H	-0.46266500	-3.02816600	-0.83931400
C	0.34461200	0.28151700	-0.83582500
H	0.34821400	0.75687100	-1.82281900
C	-0.44070400	1.24033500	0.08903700
C	-2.17999400	0.58140600	-0.71193200
C	-1.75080200	-0.79414400	-0.61487500
C	-2.62931200	-1.76350300	-0.13231900
H	-2.33847300	-2.80232700	-0.08919500
C	-3.85327300	-1.37706600	0.37160300
H	-4.51631300	-2.12899400	0.77728800
C	-4.24241200	-0.02359700	0.40037700
H	-5.20446700	0.24520400	0.81477000
C	-3.44338300	0.93246700	-0.15375300
H	-3.77663800	1.95905000	-0.22497700
C	-0.45381800	0.91272400	1.47612800
C	-0.34601200	2.63188400	-0.18696000
H	-1.89812400	1.11554400	-1.61379600

$BiVO_4$

Sum of electronic and zero-point Energies= -1459.735606

Sum of electronic and thermal Energies= -1459.728887

Sum of electronic and thermal Enthalpies= -1459.727943

Sum of electronic and thermal Free Energies= -1459.769153

Bi	-1.09323200	0.00000000	0.00000000
O	0.42362200	-0.40812400	1.25015800
O	0.42362200	0.40812200	-1.25015900
V	1.78093400	0.00000000	-0.00000100
O	2.68742500	1.25556600	0.40636600
O	2.68743100	-1.25556200	-0.40636400

I

Sum of electronic and zero-point Energies=	-1093.902404		
Sum of electronic and thermal Energies=	-1093.889315		
Sum of electronic and thermal Enthalpies=	-1093.888371		
Sum of electronic and thermal Free Energies=	-1093.943356		
C	2.52810900	-0.56593100	-0.11378300
C	3.32241100	-1.66430300	-0.44662800
H	2.85697700	-2.60005700	-0.72598800
H	5.32150000	-2.37864300	-0.69142600
C	5.26535500	-0.32914800	-0.05709900
H	6.34237200	-0.23101200	-0.03813900
C	4.47738700	0.75808900	0.29406700
H	4.94053300	1.68976400	0.58992100
C	3.10230300	0.65395000	0.26587600
C	2.18027900	1.75473300	0.69421200
H	1.99489800	1.66430500	1.76796600
H	2.63488300	2.72960900	0.53030100
C	0.87027400	1.70033500	-0.06002400
H	0.13133800	2.35635100	0.38683300
H	1.00571600	1.98318000	-1.10498500
N	0.31150900	0.32810400	-0.04895800
C	-1.11089100	0.16218300	-0.02728500
C	-1.90099300	0.96098700	-0.83675000
C	-1.67500000	-0.78876200	0.80475800
C	-3.27131600	0.79318100	-0.82614400
H	-1.45803500	1.70014100	-1.48812100
C	-3.04641000	-0.95943700	0.81338600
H	-1.05561000	-1.38041200	1.46421600
C	-3.83265000	-0.16767000	-0.00295000
H	-3.89937800	1.40235600	-1.45900900
H	-3.49995400	-1.69401600	1.46201000
C	4.69449200	-1.53973300	-0.42612600
C	1.10446800	-0.68755100	-0.12936500
H	0.64712600	-1.66366800	-0.22647900
Cl	-5.55234300	-0.37412800	0.01169100

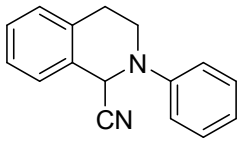
II

Sum of electronic and zero-point Energies=	-726.504113		
Sum of electronic and thermal Energies=	-726.490435		
Sum of electronic and thermal Enthalpies=	-726.489491		
Sum of electronic and thermal Free Energies=	-726.545541		
C	2.37986600	-0.56807500	-0.11156200
C	3.17561600	-1.66640800	-0.44415200
H	2.71112800	-2.60370600	-0.71970000

H	5.17535300	-2.37636200	-0.69366800
C	5.11590900	-0.32532200	-0.06415600
H	6.19276400	-0.22483900	-0.04894000
C	4.32727100	0.76146700	0.28733200
H	4.78981400	1.69443000	0.57982500
C	2.95266200	0.65458200	0.26381800
C	2.02977100	1.75362400	0.69381500
H	1.84737400	1.66358900	1.76806700
H	2.48176700	2.72929700	0.52778500
C	0.71825200	1.69617500	-0.05735800
H	-0.01986800	2.35258300	0.39033800
H	0.85120900	1.97609500	-1.10334200
N	0.16272000	0.32212500	-0.04030500
C	-1.25780800	0.15125700	-0.02239200
C	-2.04680600	0.96519300	-0.81879200
C	-1.81592200	-0.81769600	0.79416700
C	-3.41453800	0.79347900	-0.81131600
H	-1.60329200	1.71616100	-1.45532400
C	-3.18455800	-0.99184700	0.79877300
H	-1.19325500	-1.41670900	1.44316000
C	-3.98383600	-0.18684900	-0.00455600
H	-4.04092500	1.41440400	-1.43457500
H	-3.63269200	-1.74087900	1.43472800
C	4.54696500	-1.53852200	-0.42848800
C	0.95883600	-0.69324100	-0.12171500
H	0.50403400	-1.67075200	-0.21693500
C	-5.40411900	-0.36229500	0.00378200
N	-6.54111400	-0.50304700	0.00964500

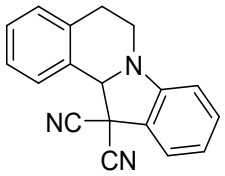
7. Characterization Data

2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3a)[11]



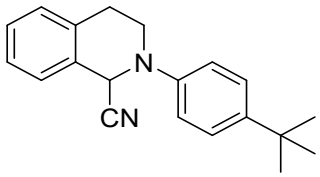
White solid (10.8 mg, 23 %). mp. 96-97 °C (lit.[11] 95-96 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.20 (m, 6H), 7.12-7.05 (m, 2H), 7.01 (t, J = 7.3 Hz, 1H), 5.51 (s, 1H), 3.82-3.71 (m, 1H), 3.53-3.42 (m, 1H), 3.21-3.09 (m, 1H), 2.96 (dt, J = 16.3, 3.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.4, 134.7, 129.7, 129.6, 129.4, 128.8, 127.1, 126.9, 121.9, 117.8, 117.6, 53.2, 44.2, 28.6.

5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4a)



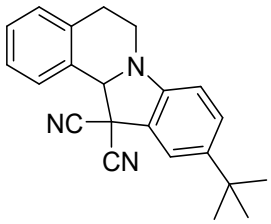
White solid (39.2 mg, 72 %). mp. 125-126 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.28. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.45 (m, 2H), 7.40-7.21 (m, 4H), 6.92 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 5.19 (s, 1H), 3.91-3.76 (m, 1H), 3.27-3.10 (m, 2H), 2.94-2.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 135.6, 132.2, 129.7, 129.6, 128.9, 127.2, 125.6, 124.9, 122.0, 120.5, 115.1, 112.2, 109.6, 72.0, 42.6, 42.5, 28.7. **HRMS** (ESI), calcd. for $C_{18}H_{14}N_3$ $(M+H)^+$: 272.1182, found: 272.1183.

2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3b)[12]



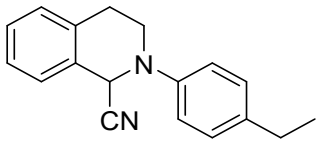
Yellow oil (10.5 mg, 18 %). TLC (PE : EA, 10:1 v/v): R_f = 0.43. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.35 (m, 2H), 7.34-7.21 (m, 4H), 7.07-7.01 (m, 2H), 5.48 (s, 1H), 3.74 (dddd, J = 12.4, 6.0, 2.6, 1.1 Hz, 1H), 3.47 (ddd, J = 12.4, 11.0, 4.0 Hz, 1H), 3.21-3.10 (m, 1H), 2.95 (dt, J = 16.4, 3.3 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.0, 144.9, 134.6, 129.7, 129.4, 128.7, 127.1, 126.8, 126.4, 117.9, 117.6, 53.7, 44.3, 34.2, 31.4, 28.6.

10-(tert-butyl)-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4b)



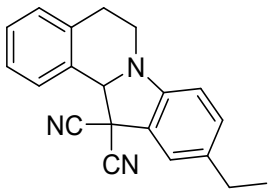
White solid (43.3 mg, 66 %). mp. 145-146 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.32. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62-7.57 (m, 1H), 7.52 (d, J = 1.8 Hz, 1H), 7.43-7.32 (m, 3H), 7.28-7.24 (m, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.19 (s, 1H), 3.86-3.75 (m, 1H), 3.26-3.11 (m, 2H), 2.95-2.84 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.5, 144.6, 135.7, 129.9, 129.6, 129.2, 128.9, 127.2, 125.6, 122.0, 121.6, 115.3, 112.5, 109.8, 72.3, 43.1, 42.9, 34.6, 31.5, 28.8. **HRMS** (ESI), calcd. for $C_{22}H_{22}N_3$ $(M+H)^+$: 328.1808, found: 328.1812.

2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3c)[13]



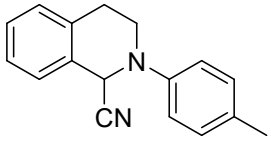
White solid (6.9 mg, 13 %). mp. 133-134 °C (lit.[13] 133-134 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.25 (m, 3H), 7.24-7.16 (m, 3H), 7.06-7.00 (m, 2H), 5.46 (s, 1H), 3.75-3.67 (m, 1H), 3.45 (ddd, J = 12.1, 11.0, 4.0 Hz, 1H), 3.21-3.10 (m, 1H), 2.94 (dt, J = 16.4, 3.3 Hz, 1H), 2.62 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.4, 138.2, 134.6, 129.7, 129.4, 128.9, 128.7, 127.1, 126.8, 118.3, 117.8, 54.0, 44.4, 28.6, 28.0, 15.7.

10-ethyl-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4c)



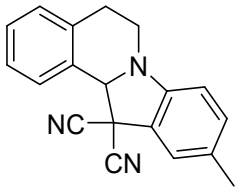
White solid (36.6 mg, 61 %). mp. 105-106 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62-7.56 (m, 1H), 7.40-7.31 (m, 3H), 7.28-7.23 (m, 1H), 7.20 (dd, J = 8.2, 1.5 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 5.18 (s, 1H), 3.85-3.74 (m, 1H), 3.26-3.10 (m, 2H), 2.95-2.84 (m, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.9, 137.4, 135.7, 131.6, 129.9, 129.6, 128.9, 127.2, 125.6, 124.1, 122.3, 115.2, 112.4, 110.1, 72.3, 43.2, 42.7, 28.8, 28.3, 15.8. **HRMS** (ESI), calcd. for $C_{20}H_{18}N_3$ $(M+H)^+$: 300.1495, found: 300.1497.

2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3d)[11]



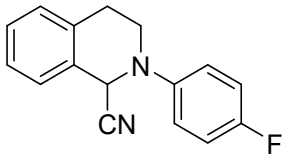
White solid (6.0 mg, 12 %). mp. 96-97 °C (lit.[11] 94-96 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.42. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.20 (m, 4H), 7.16 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 3.75-3.65 (m, 1H), 3.44 (td, J = 11.5, 4.0 Hz, 1H), 3.22-3.10 (m, 1H), 2.94 (dt, J = 16.3, 3.1 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 134.5, 131.8, 130.1, 129.6, 129.4, 128.7, 127.1, 126.8, 118.3, 117.7, 54.1, 44.4, 28.6, 20.6.

10-methyl-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4d)



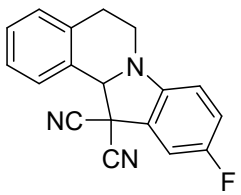
White solid (38.8 mg, 68 %). mp. 135-136 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.32. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62-7.55 (m, 1H), 7.40-7.31 (m, 3H), 7.27-7.23 (m, 1H), 7.20-7.14 (m, 1H), 6.79 (d, J = 8.3 Hz, 1H), 5.17 (s, 1H), 3.83-3.72 (m, 1H), 3.24-3.10 (m, 2H), 2.94-2.84 (m, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7, 135.7, 132.7, 130.8, 129.9, 129.6, 128.9, 127.2, 125.6, 125.3, 122.4, 115.2, 112.4, 110.1, 72.3, 43.3, 42.7, 28.8, 20.8. **HRMS** (ESI), calcd. for $C_{19}H_{16}N_3$ $(M+H)^+$: 286.1339, found: 286.1338.

2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3e)[13]



White solid (9.6 mg, 19 %). mp. 125-126 °C (lit.[13] 124-125 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 4H), 7.10-7.03 (m, 4H), 5.40 (s, 1H), 3.63 (dddd, J = 12.2, 6.1, 2.4, 1.2 Hz, 1H), 3.45 (td, J = 11.6, 4.0 Hz, 1H), 3.22-3.11 (m, 1H), 2.95 (dt, J = 16.4, 2.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.6 (d, J = 242.1 Hz), 145.1 (d, J = 2.9 Hz), 134.3, 129.5, 129.4, 128.8, 127.1, 126.8, 120.5 (d, J = 8.1 Hz), 117.4, 116.2 (d, J = 22.7 Hz), 54.8, 44.8, 28.6. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -120.7.

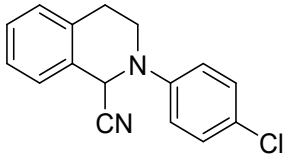
10-fluoro-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4e)



White solid (44.5 mg, 77 %). mp. 140-141 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.24. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63-7.52 (m, 1H), 7.44-7.20 (m, 4H), 7.11 (td, J = 8.7, 2.4 Hz, 1H), 6.74 (dd, J = 8.7, 4.0 Hz, 1H), 5.23 (s, 1H), 3.82-3.70 (m, 1H), 3.28-3.10 (m, 2H), 2.98-2.86 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.2 (d, J = 242.1 Hz), 146.4 (d, J = 1.5 Hz), 135.5, 129.6, 129.4, 129.1, 127.3, 125.6, 123.1 (d, J = 8.8 Hz), 119.1 (d, J = 23.5 Hz), 114.6, 112.5 (d, J = 25.7 Hz), 111.8, 111.0 (d, J = 8.1 Hz), 72.5,

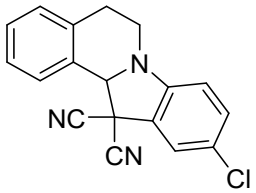
43.4, 42.7, 28.7. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -121.3. HRMS (ESI), calcd. for $C_{18}H_{13}FN_3$ $(M+H)^+$: 290.1088, found: 290.1086.

2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3f)[13]



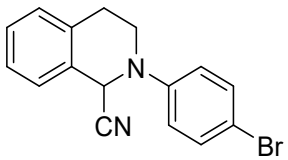
White solid (12.5 mg, 23 %). mp. 152-153 °C (lit.[13] 152-153 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 5H), 7.25-7.23 (m, 1H), 7.05-6.98 (m, 2H), 5.46 (s, 1H), 3.72 (dddd, J = 12.2, 5.9, 3.1, 1.0 Hz, 1H), 3.47 (ddd, J = 12.3, 10.6, 4.1 Hz, 1H), 3.22-3.10 (m, 1H), 2.98 (dt, J = 16.4, 3.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147. 0, 134.4, 129.5, 129.4, 129.2, 128.9, 127.1, 127.1, 127.0, 118.9, 117.5, 53.2, 44.3, 28.4.

10-chloro-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4f)



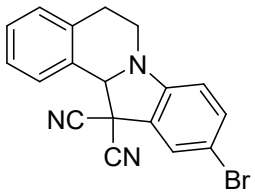
White solid (48.2 mg, 77 %). mp. 152-153 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61-7.45 (m, 2H), 7.43-7.24 (m, 4H), 6.69 (d, J = 8.6 Hz, 1H), 5.24 (s, 1H), 3.88-3.75 (m, 1H), 3.28-3.11 (m, 2H), 2.95-2.84 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.1, 135.4, 132.3, 129.7, 129.3, 129.1, 127.4, 125.6, 125.1, 125.0, 123.1, 114.4, 111.6, 110.4, 72.1, 42.6, 42.5, 28.6. **HRMS** (ESI), calcd. for $C_{18}H_{13}ClN_3$ $(M+H)^+$: 306.0793, found: 306.0791.

2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3g)[13]



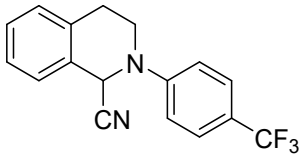
White solid (15.2 mg, 24 %). mp. 156-157 °C (lit.[13] 155-156 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.36. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.42 (m, 2H), 7.35-7.26 (m, 3H), 7.26-7.22 (m, 1H), 6.98-6.91 (m, 2H), 5.46 (s, 1H), 3.72 (dddd, J = 12.3, 5.8, 3.2, 1.0 Hz, 1H), 3.46 (ddd, J = 12.3, 10.5, 4.2 Hz, 1H), 3.20-3.10 (m, 1H), 2.98 (dt, J = 16.4, 3.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147. 4, 134.4, 132.4, 129.4, 129.2, 128.9, 127.1, 127.0, 119.1, 117.5, 114.4, 52.9, 44.2, 28.4.

10-bromo-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4g)



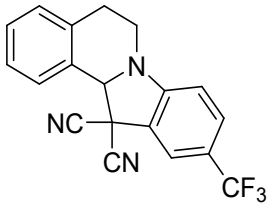
White solid (52.0 mg, 74 %). mp. 161-162 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.24. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.26 (m, 6H), 6.64 (d, J = 8.4 Hz, 1H), 5.24 (s, 1H), 3.94-3.69 (m, 1H), 3.28-3.11 (m, 2H), 2.97-2.80 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.5, 135.4, 135.1, 129.7, 129.2, 129.1, 127.9, 127.4, 125.6, 123.4, 114.4, 111.6, 111.5, 110.8, 72.0, 42.4, 42.4, 28.6. **HRMS** (ESI), calcd. for $C_{18}H_{13}BrN_3$ $(M+H)^+$: 350.0287, found: 350.0291.

2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3h)[13]



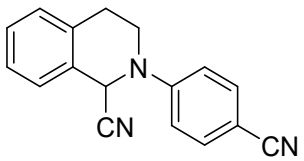
White solid (44.2 mg, 73 %). mp. 101-102 °C (lit.[13] 102-103 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.8 Hz, 2H), 7.38-7.26 (m, 4H), 7.09 (d, J = 8.7 Hz, 2H), 5.58 (s, 1H), 3.86 (dt, J = 12.2, 5.0 Hz, 1H), 3.61-3.52 (m, 1H), 3.22-3.11 (m, 1H), 3.05 (dt, J = 16.3, 4.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.3, 134.6, 129.2, 129.1, 129.0, 127.2, 127.0, 126.9 (q, J = 3.7 Hz), 124.4 (q, J = 271.4 Hz), 122.6 (q, J = 33.0 Hz), 117.5, 115.4, 51.2, 43.9, 28.3. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -61.6.

10-(trifluoromethyl)-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4h)



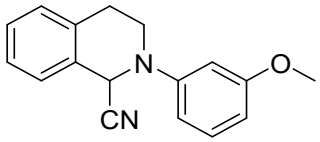
White solid (13.6 mg, 20 %). mp. 157-158 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.16. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.65-7.55 (m, 2H), 7.44-7.35 (m, 2H), 7.32-7.27 (m, 1H), 6.77 (d, J = 8.4 Hz, 1H), 5.37 (s, 1H), 3.98-3.90 (ddd, J = 12.4, 6.0, 2.2 Hz, 1H), 3.35-3.15 (m, 2H), 2.95-2.87 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.4, 135.2, 130.1 (q, J = 3.7 Hz), 129.8, 129.3, 129.0, 127.6, 125.6, 123.9 (d, J = 271.4 Hz), 122.5 (q, J = 3.7 Hz), 122.0 (d, J = 33.8 Hz), 121.7, 114.2, 111.4, 108.4, 71.6, 42.5, 41.7, 28.7. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -61.3. **HRMS** (ESI), calcd. for $C_{19}H_{12}F_3N_3$ $(M+H)^+$: 340.1056, found: 340.1058.

2-(4-cyanophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3i)[13]



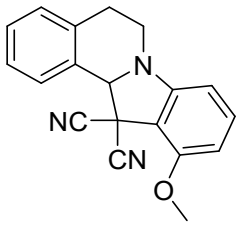
White solid (20.2 mg, 39 %). mp. 153-154 °C (lit.[13] 155-156 °C). TLC (PE : EA, 5:1 v/v): R_f = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.9 Hz, 2H), 7.41-7.27 (m, 4H), 7.03 (d, J = 8.9 Hz, 2H), 5.59 (s, 1H), 3.90-3.80 (m, 1H), 3.67-3.57 (m, 1H), 3.21-3.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.6, 134.7, 133.9, 129.4, 129.1, 128.8, 127.4, 127.0, 119.4, 117.3, 114.7, 102.7, 50.1, 43.8, 28.2.

2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3j)[12]



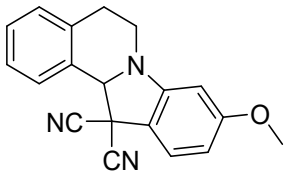
Yellow oil (8.1 mg, 15 %). TLC (PE : EA, 10:1 v/v): R_f = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 5H), 6.68 (dd, J = 8.1, 2.2 Hz, 1H), 6.61 (t, J = 2.3 Hz, 1H), 6.56 (dd, J = 8.2, 2.1 Hz, 1H), 5.51 (s, 1H), 3.82 (s, 3H), 3.77 (dddd, J = 12.4, 5.8, 3.1, 0.9 Hz, 1H), 3.47 (ddd, J = 12.5, 10.6, 4.2 Hz, 1H), 3.20-3.09 (m, 1H), 2.96 (dt, J = 16.4, 3.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.8, 149.7, 134.6, 130.3, 129.5, 129.3, 128.8, 127.1, 126.9, 117.7, 109.9, 106.5, 104.0, 55.3, 52.9, 44.1, 28.5.

11-methoxy-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4j1)



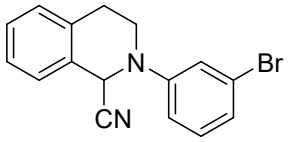
White solid (35.1 mg, 58 %). mp. 129-130 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63-7.59 (m, 1H), 7.41-7.28 (m, 3H), 7.25-7.23 (m, 1H), 6.40 (dd, J = 18.7, 8.3 Hz, 2H), 5.34 (s, 1H), 3.96 (s, 3H), 3.81 (ddd, J = 12.4, 5.6, 2.6 Hz, 1H), 3.25 (td, J = 11.3, 3.7 Hz, 1H), 3.17-3.07 (m, 1H), 2.85 (dt, J = 15.5, 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.0, 151.5, 135.7, 133.8, 130.0, 129.5, 128.9, 127.3, 125.9, 114.9, 111.9, 107.6, 102.9, 102.5, 72.2, 56.0, 43.1, 40.8, 28.9. **HRMS** (ESI), calcd. for $C_{19}H_{16}N_3O$ $(M+H)^+$: 302.1288, found: 302.1293.

9-methoxy-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4j2)



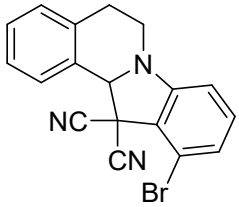
White solid (10.9 mg, 18 %). mp. 135-136 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.12. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60-7.55 (m, 1H), 7.41-7.32 (m, 3H), 7.28-7.24 (m, 1H), 6.44 (dd, J = 8.4, 2.2 Hz, 1H), 6.28 (d, J = 2.2 Hz, 1H), 5.22 (s, 1H), 3.86-3.80 (m, 4H), 3.26-3.13 (m, 2H), 2.94-2.84 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.4, 150.9, 135.5, 129.8, 129.6, 128.9, 127.2, 125.7, 125.5, 115.2, 113.9, 112.4, 105.4, 96.2, 72.4, 55.7, 42.4, 42.2, 28.8. **HRMS** (ESI), calcd. for $C_{19}H_{16}N_3O$ $(M+H)^+$: 302.1288, found: 302.1291.

2-(3-bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3k)[14]



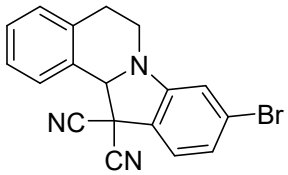
White solid (13.8 mg, 22 %). mp. 93-94 °C (lit.[14] 92-93 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.31. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 3H), 7.25-7.17 (m, 3H), 7.12 (d, *J*= 7.8 Hz, 1H), 6.98 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.49 (s, 1H), 3.80-3.72 (m, 1H), 3.54-3.44 (m, 1H), 3.20-3.09 (m, 1H), 3.00 (dt, *J* = 16.3, 3.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 134.5, 130.8, 129.3, 129.1, 129.0, 127.0, 127.0, 124.4, 123.5, 120.1, 117.5, 115.4, 52.4, 44.1, 28.4.

11-bromo-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4k1)



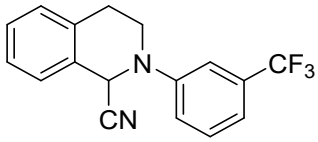
White solid (26.0 mg, 37 %). mp. 183-184 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.12. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.61 (m, 1H), 7.44-7.35 (m, 2H), 7.30-7.27 (m, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 5.44 (s, 1H), 3.82 (ddd, *J* = 12.5, 5.8, 2.3 Hz, 1H), 3.29 (td, *J* = 11.5, 3.7 Hz, 1H), 3.18-3.08 (m, 1H), 2.92-2.83 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.3, 135.5, 133.6, 129.7, 129.3, 129.2, 127.5, 125.9, 123.6, 120.7, 120.4, 114.2, 110.7, 108.3, 71.5, 44.7, 42.8, 28.8. **HRMS** (ESI), calcd. for $C_{18}H_{13}BrN_3$ $(M+H)^+$: 350.0287, found: 350.0284.

9-bromo-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4k2)



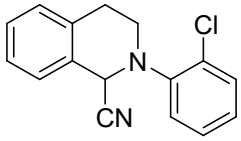
White solid (10.6 mg, 15 %). mp. 84-85 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.28. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 1H), 7.42-7.34 (m, 3H), 7.32-7.27 (m, 1H), 7.04 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.90 (d, *J* = 1.6 Hz, 1H), 5.27 (s, 1H), 3.88-3.81 (m, 1H), 3.29-3.14 (m, 2H), 2.93-2.86 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.3, 135.3, 129.7, 129.2, 129.1, 127.4, 126.6, 126.0, 125.5, 123.1, 120.7, 114.5, 112.6, 111.6, 71.9, 42.3, 42.1, 28.7. **HRMS** (ESI), calcd. for $C_{18}H_{13}BrN_3$ $(M+H)^+$: 350.0287, found: 350.0286.

2-(3-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3l)[14]



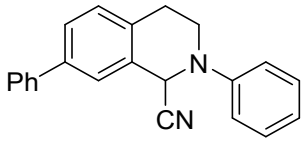
White solid (46.1 mg, 76 %). mp. 101-102 °C (lit.[14] 100-101 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.34. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (t, J = 8.0 Hz, 1H), 7.37-7.29 (m, 3H), 7.29-7.21 (m, 4H), 5.54 (s, 1H), 3.81 (dddd, J = 12.4, 5.6, 3.7, 1.0 Hz, 1H), 3.54 (ddd, J = 12.4, 10.3, 4.2 Hz, 1H), 3.23-3.12 (m, 1H), 3.03 (dt, J = 16.4, 3.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.5, 134.4, 132.0 (q, J = 32.3 Hz), 130.2, 129.3, 129.0, 127.1, 127.0, 124.0 (d, J = 272.2 Hz), 119.8, 118.0 (q, J = 3.7 Hz), 117.4, 113.6 (q, J = 3.7 Hz), 52.4, 44.1, 28.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.7.

2-(2-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3m)[13]



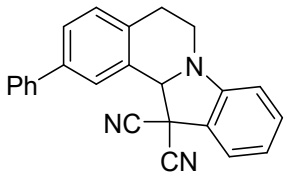
White solid (28.6 mg, 53 %). mp. 115-116 °C (lit.[13] 115-116 °C). TLC (PE : EA, 10:1 v/v): R_f = 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.40 (m, 1H), 7.38-7.20 (m, 6H), 7.17-7.11 (m, 1H), 5.53 (s, 1H), 3.62 (td, J = 12.0, 3.8 Hz, 1H), 3.50-3.41 (m, 1H), 3.31-3.20 (m, 1H), 2.92 (dt, J = 16.5, 2.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.8, 134.1, 130.6, 129.6, 129.5, 129.4, 128.7, 128.2, 127.1, 126.7, 126.0, 123.2, 117.3, 53.8, 45.6, 28.8.

2,7-diphenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3n)



White solid (17.2 mg, 28 %). mp. 133-134 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.36. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61-7.50 (m, 4H), 7.45 (t, J = 7.2 Hz, 2H), 7.41-7.34 (m, 3H), 7.31 (d, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.03 (t, J = 7.3 Hz, 1H), 5.58 (s, 1H), 3.81 (dddd, J = 12.5, 6.0, 2.8, 1.0 Hz, 1H), 3.52 (ddd, J = 12.4, 10.8, 4.0 Hz, 1H), 3.25-3.14 (m, 1H), 3.01 (dt, J = 16.5, 3.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.4, 140.1, 133.6, 130.0, 129.8, 129.6, 128.9, 127.6, 127.6, 127.0, 125.6, 122.0, 117.8, 53.5, 44.3, 28.3. **HRMS** (ESI), calcd. for $C_{22}H_{19}N_2$ $(M+H)^+$: 311.1543, found: 311.1546.

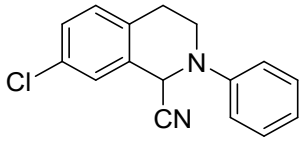
2-phenyl-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4n)



White solid (35.7 mg, 51 %). mp. 157-158 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.24. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.68-7.44 (m, 6H), 7.43-7.29 (m, 3H), 6.94 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 5.27 (s, 1H), 3.96-3.82 (m, 1H), 3.31-3.15 (m, 2H), 2.98-2.86 (m, 1H). **^{13}C NMR** (100 MHz,

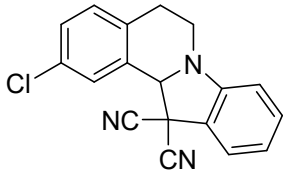
$CDCl_3$): δ 149.5, 140.3, 140.0, 134.6, 132.2, 130.2, 130.1, 129.0, 127.7, 127.7, 127.1, 125.0, 124.1, 121.9, 120.6, 115.0, 112.3, 109.7, 72.2, 42.7, 42.5, 28.4. **HRMS** (ESI), calcd. for $C_{24}H_{18}N_3$ $(M+H)^+$: 348.1495, found: 348.1493.

7-chloro-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3o)[15]



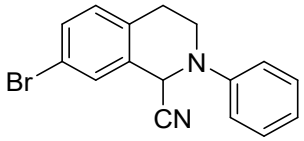
White solid (9.0 mg, 16 %). mp. 108-109 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.33 (m, 2H), 7.32-7.7.26 (m, 2H), 7.18 (d, J = 8.2 Hz, 1H), 7.10-7.01 (m, 3H), 5.46 (s, 1H), 3.77 (dddd, J = 12.5, 5.9, 2.6, 1.0 Hz, 1H), 3.46 (ddd, J = 12.5, 10.9, 4.0 Hz, 1H), 3.16-3.05 (m, 1H), 2.93 (dt, J = 16.4, 3.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.1, 133.1, 132.4, 131.1, 130.8, 129.7, 129.1, 127.0, 122.4, 117.9, 117.2, 53.1, 44.1, 28.0.

2-chloro-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4o)



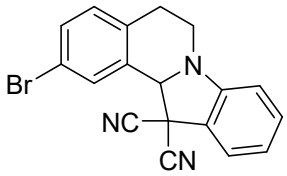
White solid (39.9 mg, 65 %). mp. 152-153 °C. TLC (P E: EA, 10:1 v/v): R_f = 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63-7.46 (m, 2H), 7.44-7.29 (m, 2H), 7.27-7.15 (m, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 5.14 (s, 1H), 3.96-3.77 (m, 1H), 3.25-3.06 (m, 2H), 2.94-2.81 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.2, 134.2, 133.0, 132.3, 131.4, 131.0, 129.3, 125.5, 124.9, 121.8, 120.8, 114.7, 111.9, 109.7, 71.5, 42.5, 42.4, 28.4. **HRMS** (ESI), calcd. for $C_{18}H_{13}ClN_3$ $(M+H)^+$: 306.0793, found: 306.0790.

7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3p)



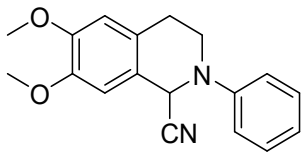
White solid (9.0 mg, 14 %). mp. 90-91 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.31. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48-7.30 (m, 4H), 7.16-6.98 (m, 4H), 5.46 (s, 1H), 3.83-3.71 (m, 1H), 3.45 (td, J = 11.5, 4.0 Hz, 1H), 3.17-3.01 (m, 1H), 2.91 (dt, J = 16.4, 3.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.1, 133.6, 132.0, 131.5, 131.0, 129.9, 129.7, 122.4, 120.2, 117.9, 117.2, 52.9, 44.1, 28.1. **HRMS** (ESI), calcd. for $C_{16}H_{14}BrN_2$ $(M+H)^+$: 313.0335, found: 313.0334.

2-bromo-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4p)



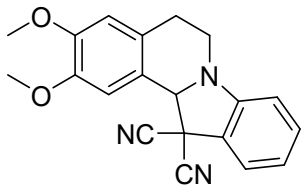
White solid (59.8 mg, 85 %). mp. 158-159 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.56-7.43 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 5.14 (s, 1H), 3.94-3.77 (m, 1H), 3.25-3.01 (m, 2H), 2.84 (d, J = 15.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.2, 137.4, 132.3, 132.1, 131.7, 131.3, 128.4, 124.9, 121.7, 120.8, 120.7, 114.7, 111.9, 109.7, 71.3, 42.5, 42.3, 28.4. **HRMS** (ESI), calcd. for $C_{18}H_{13}BrN_3$ $(M+H)^+$: 350.0287, found: 350.0289.

6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3q)[11]



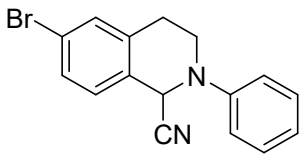
Yellow solid (12.6 mg, 21 %). mp. 136-137 °C (lit.[11] 137-138 °C). TLC (PE : EA, 5:1 v/v): R_f = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (t, J = 8.2 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.02 (t, J = 7.3 Hz, 1H), 6.75 (s, 1H), 6.69 (s, 1H), 5.45 (s, 1H), 3.89 (s, 6H), 3.82-3.74 (m, 1H), 3.45 (td, J = 12.1, 3.9 Hz, 1H), 3.14-3.03 (m, 1H), 2.86 (dt, J = 16.0, 2.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.4, 148.5, 148.1, 129.6, 126.9, 122.0, 121.1, 117.9, 117.8, 111.5, 109.3, 56.1, 56.0, 53.1, 44.2, 28.1.

2,3-dimethoxy-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4q)



Yellow solid (35.7 mg, 54 %). mp. 168-169 °C. TLC (PE : EA, 5:1 v/v): R_f = 0.21. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.3 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.03 (s, 1H), 6.92 (t, J = 7.2 Hz, 1H), 6.80-6.67 (s, 2H), 5.20 (s, 1H), 4.00-3.79 (m, 7H), 3.27-3.04 (m, 2H), 2.78 (d, J = 15.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.6, 149.4, 148.3, 132.2, 128.2, 125.0, 121.9, 121.3, 120.4, 115.3, 112.4, 111.9, 109.7, 108.0, 71.9, 56.1, 55.9, 43.1, 42.6, 28.3. **HRMS** (ESI), calcd. for $C_{20}H_{18}N_3O_2$ $(M+H)^+$: 332.1394, found: 332.1398.

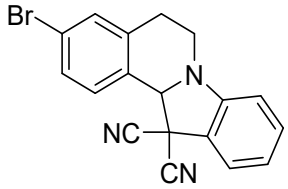
6-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3r)



Colorless oil (11.0 mg, 17 %). TLC (PE : EA, 10:1 v/v): R_f = 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.33 (m, 4H), 7.20-7.14 (m, 1H), 7.10-7.00 (m, 3H), 5.45 (s, 1H), 3.80-3.72 (m, 1H), 3.45 (td, J = 12.4,

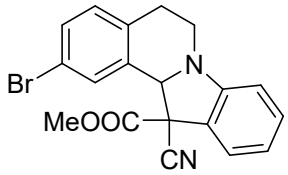
11.0, 4.0 Hz, 1H), 3.20-3.07 (m, 1H), 2.94 (dt, J = 16.5, 3.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.1, 136.8, 132.3, 130.1, 129.6, 128.6, 128.6, 122.7, 122.3, 117.9, 117.2, 53.0, 43.9, 28.4. **HRMS** (ESI), calcd. for $C_{16}H_{14}BrN_2$ $(M+H)^+$: 313.0335, found: 313.0337.

3-bromo-5,12a-dihydroindolo[2,1-*a*]isoquinoline-12,12(6*H*)-dicarbonitrile (4r)



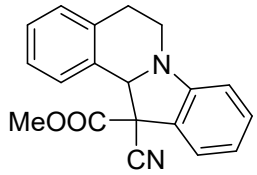
White solid (46.3 mg, 66 %). mp. 160-161 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55-7.32 (m, 5H), 6.95 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 5.12 (s, 1H), 3.94-3.76 (m, 1H), 3.24-3.10 (m, 2H), 2.93-2.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.2, 137.9, 132.6, 132.3, 130.4, 128.7, 127.1, 124.9, 123.0, 121.7, 120.8, 114.8, 112.0, 109.7, 71.6, 42.4, 42.1, 28.5. **HRMS** (ESI), calcd. for $C_{18}H_{13}BrN_3$ $(M+H)^+$: 350.0287, found: 350.0289.

methyl 2-bromo-12-cyano-5,6,12,12a-tetrahydroindolo[2,1-*a*]isoquinoline-12-carboxylate (4s)



Yellow solid (52.8 mg, 68 %). mp. 77-78 °C. TLC (PE : EA, 10:1 v/v): R_f = 0.19. Isolated diastereomeric ratio = 4:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (s, 1H, minor isomer), 7.41-7.26 (m, 4H, mixture of isomers), 7.09-7.03 (m, 1H, mixture of isomers), 6.84-6.77 (m, 1H, mixture of isomers), 6.71 (d, J = 8.1 Hz, 1 H, mixture of isomers), 5.48 (s, 1H, mixture of isomers), 4.06 (s, 3H, major isomer), 3.92-3.78 (m, 1H, mixture of isomers), 3.45 (s, 3H, minor isomer), 3.25-3.15 (m, 1H, mixture of isomers), 3.10-2.98 (m, 1H, mixture of isomers), 2.74 (d, J = 15.9 Hz, 1H, mixture of isomers). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.1 (165.0), 149.5 (150.3), 134.8 (135.1), 133.9 (133.5), 131.3 (131.2), 131.1, 131.0 (130.8), 129.3 (128.6), 124.7 (125.0), 124.3 (124.7), 120.1 (120.0), 119.6 (119.4), 115.5, 109.2 (109.3), 68.5 (70.3), 54.7 (55.9), 53.3, 42.7 (42.7), 28.0 (28.4). **HRMS** (ESI), calcd. for $C_{19}H_{16}BrN_2O_2$ $(M+H)^+$: 383.0390, found: 383.0386.

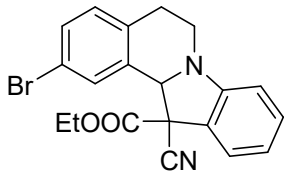
methyl 12-cyano-5,6,12,12a-tetrahydroindolo[2,1-*a*]isoquinoline-12-carboxylate (4t)



Colorless oil (23.5 mg, 38 %). TLC (PE : DCM, 1:1 v/v): R_f = 0.35. Isolated diastereomeric ratio = 4:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 1H, minor isomer), 7.34-7.26 (m, 4H, mixture of isomers), 7.22-7.17 (m, 1H, mixture of isomers), 7.16-7.12 (m, 1H, mixture of isomers), 6.83-6.76 (m, 1H, mixture of isomers), 6.72 (d, J = 8.0 Hz, 1H, mixture of isomers), 5.56 (s, 1H, minor isomer), 5.52 (s, 1H, major

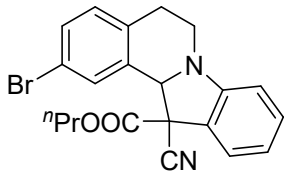
isomer), 4.05 (s, 3H, major isomer), 3.93-3.78 (m, 1H, mixture of isomers), 3.34 (s, 3H, minor isomer), 3.26 (td, *J* = 11.6, 3.4 Hz, 1H, mixture of isomers), 3.20-3.09 (m, 1H, major isomer), 3.08-2.98 (m, 1H, minor isomer), 2.85-2.75 (m, 1H, mixture of isomers). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.6 (165.3), 149.8 (150.7), 135.7 (136.0), 131.8 (131.3), 131.2 (131.1), 129.4 (129.1), 128.0 (127.9), 126.7 (126.6), 126.3 (125.9), 124.6 (124.6), 124.5, 119.4 (119.1), 115.8, 109.0 (109.2), 69.3 (70.9), 54.5 (56.0), 53.1, 42.8 (43.0), 28.3 (28.9). **HRMS** (ESI), calcd. for $C_{19}H_{17}N_2O_2$ $(M+H)^+$: 305.1285, found: 305.1281.

ethyl 2-bromo-12-cyano-5,6,12,12a-tetrahydroindolo[2,1-*a*]isoquinoline-12-carboxylate (4u)



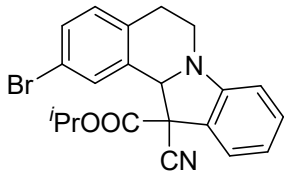
Colorless oil (44.4 mg, 56 %). TLC (PE : EA, 10:1 v/v): R_f = 0.24. Isolated diastereomeric ratio = 4:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 1.7 Hz, 1H, minor isomer), 7.41-7.26 (m, 4H, mixture of isomers), 7.11-7.03 (m, 1H, mixture of isomers), 6.81 (t, *J* = 7.6 Hz, 1H, mixture of isomers), 6.71 (d, *J* = 8.0 Hz, 1H, mixture of isomers), 5.47 (s, 1H, mixture of isomers), 4.58-4.47 (m, 2H, major isomer), 3.97-3.77 (m, 1H, mixture of isomers), 3.21 (td, *J* = 11.9, 3.6 Hz, 1H, mixture of isomers), 3.11-3.96 (m, 1H, mixture of isomers), 2.82-2.70 (m, 1H, mixture of isomers), 1.48 (t, *J* = 7.2 Hz, 3H, major isomer), 0.98 (t, *J* = 7.1 Hz, 3H, minor isomer). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 149.5, 134.8, 133.9, 131.2 (131.2), 131.1, 131.0 (130.7), 129.3 (128.8), 124.6 (124.6), 124.5, 120.1, 119.7, 115.6, 109.1, 68.5 (70.3), 64.1 (62.9), 55.9, 42.7, 28.1 (28.6), 14.2 (13.6). **HRMS** (ESI), calcd. for $C_{20}H_{18}BrN_2O_2$ $(M+H)^+$: 397.0546, found: 397.0542.

propyl 2-bromo-12-cyano-5,6,12,12a-tetrahydroindolo[2,1-*a*]isoquinoline-12-carboxylate (4v)



Colorless oil (49.5 mg, 60 %). TLC (PE : EA, 10:1 v/v): R_f = 0.29. Isolated diastereomeric ratio = 4:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 1.3 Hz, 1H, minor isomer), 7.41-7.26 (m, 4H, mixture of isomers), 7.10-7.03 (m, 1H, mixture of isomers), 6.80 (td, *J* = 7.6, 0.7 Hz, 1H, mixture of isomers), 6.70 (d, *J* = 8.0 Hz, 1H, mixture of isomers), 5.46 (s, 1H, major isomer), 5.44 (s, 1H, minor isomer), 4.50-4.43 (m, 2H, major isomer), 3.90-3.74 (m, 1H, mixture of isomers), 3.26-3.15 (m, 1H, mixture of isomers), 3.10-2.92 (m, 1H, mixture of isomers), 2.75 (d, *J* = 15.8 Hz, 1H, mixture of isomers), 1.93-1.81 (m, 2H, major isomer), 1.47-1.35 (m, 2H, minor isomer), 1.07 (t, *J* = 7.5 Hz, 3H, major isomer), 0.78 (t, *J* = 7.5 Hz, 3H, minor isomer). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7 (164.6), 149.5 (150.3), 134.8 (135.0), 134.0 (133.7), 131.2 (131.1), 131.1 (130.9), 131.0 (130.8), 129.2 (128.6), 124.6 (125.4), 124.5 (124.5), 120.1 (120.0), 119.6 (119.4), 115.5 (115.3), 109.1 (109.2), 69.5 (70.2), 68.5 (68.4), 55.9 (55.7), 42.6, 28.0 (28.5), 22.0 (21.5), 10.4 (10.1). **HRMS** (ESI), calcd. for $C_{21}H_{20}BrN_2O_2$ $(M+H)^+$: 411.0703, found: 411.0702.

isopropyl 2-bromo-12-cyano-5,6,12,12a-tetrahydroindolo[2,1-*a*]isoquinoline-12-carboxylate (4w)



Colorless oil (41.3 mg, 50 %). TLC (PE : EA, 10:1 v/v): R_f = 0.24. Isolated diastereomeric ratio = 3:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, J = 1.3 Hz, 1H, minor isomer), 7.41-7.26 (m, 4H, mixture of isomers), 7.10-7.03 (m, 1H, mixture of isomers), 6.85-6.77 (m, 1H, mixture of isomers), 6.73-6.67 (m, 1H, mixture of isomers), 5.48-5.40 (m, 1H, mixture of isomers), 5.38-5.29 (m, 1H, major isomer), 4.75-4.65 (m, 1H, minor isomer), 3.91-3.83 (m, 1H, major isomer), 3.82-3.74 (m, 1H, minor isomer), 3.28-3.15 (m, 1H, mixture of isomers), 3.10-2.93 (m, 1H, mixture of isomers), 2.77 (d, J = 15.3 Hz, 1H, mixture of isomers), 1.46 (dd, J = 14.8, 6.4 Hz, 6H, major isomer), 1.02 (d, J = 6.2 Hz, 3H, minor isomer), 0.93 (d, J = 6.2 Hz, 3H, minor isomer). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 149.5, 134.8, 134.0, 131.1, 131.0, 131.0, 129.2 (128.8), 124.6, 124.5, 120.1, 119.6 (119.3), 115.6, 109.0 (109.2), 72.4 (71.2), 68.6 (70.1), 55.9, 42.6, 28.2 (28.6), 21.7 (21.1), 21.6 (21.1). **HRMS** (ESI), calcd. for $C_{21}H_{20}BrN_2O_2$ $(M+H)^+$: 411.0703, found: 411.0696.

Supplemental Data

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

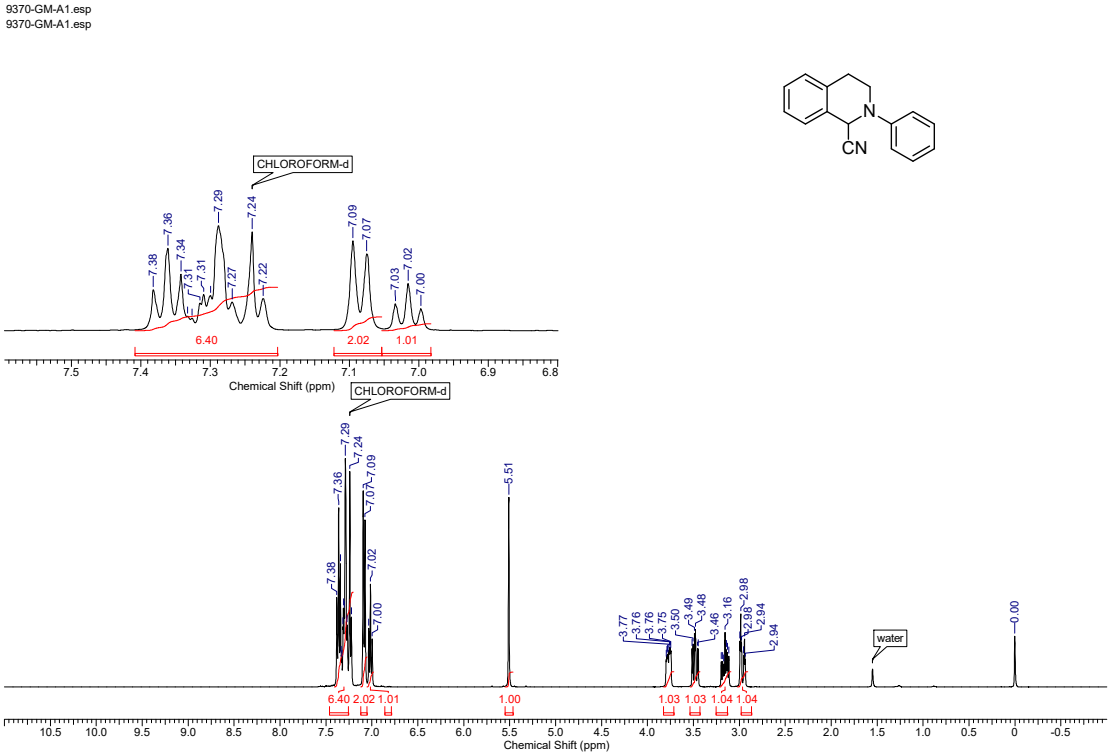


Figure S28. ^{1}H NMR spectrum of compound **3a**

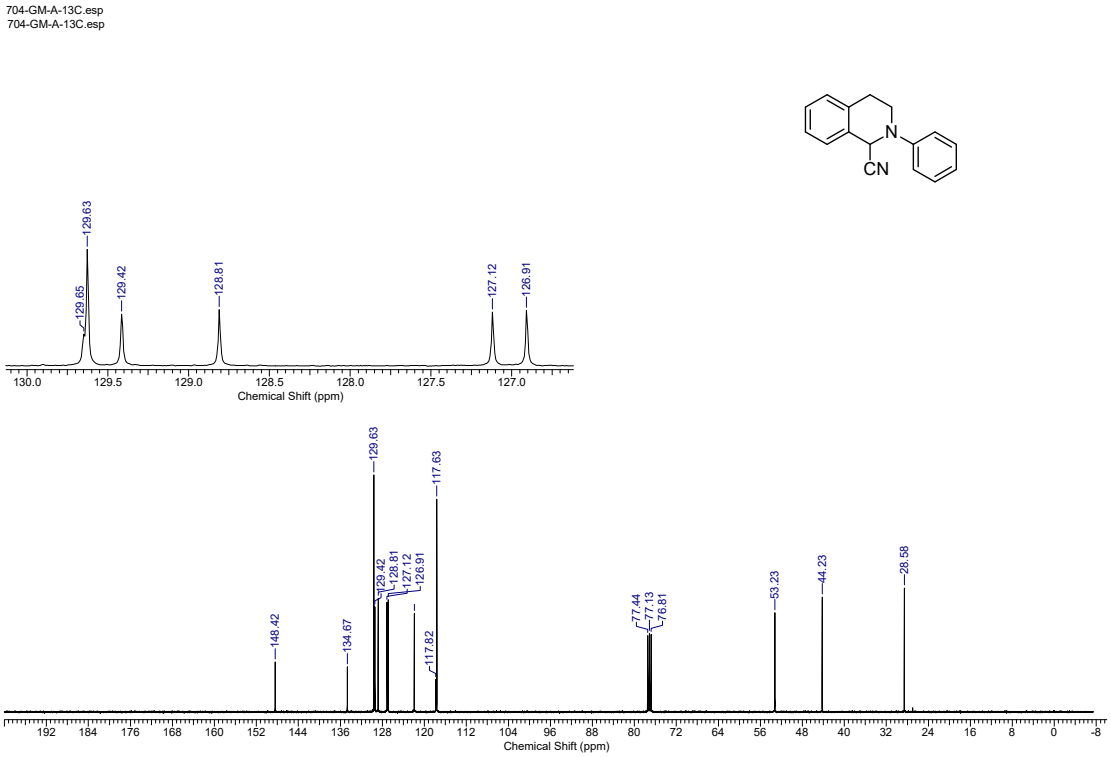


Figure S29 ^{13}C NMR spectrum of compound **3a**

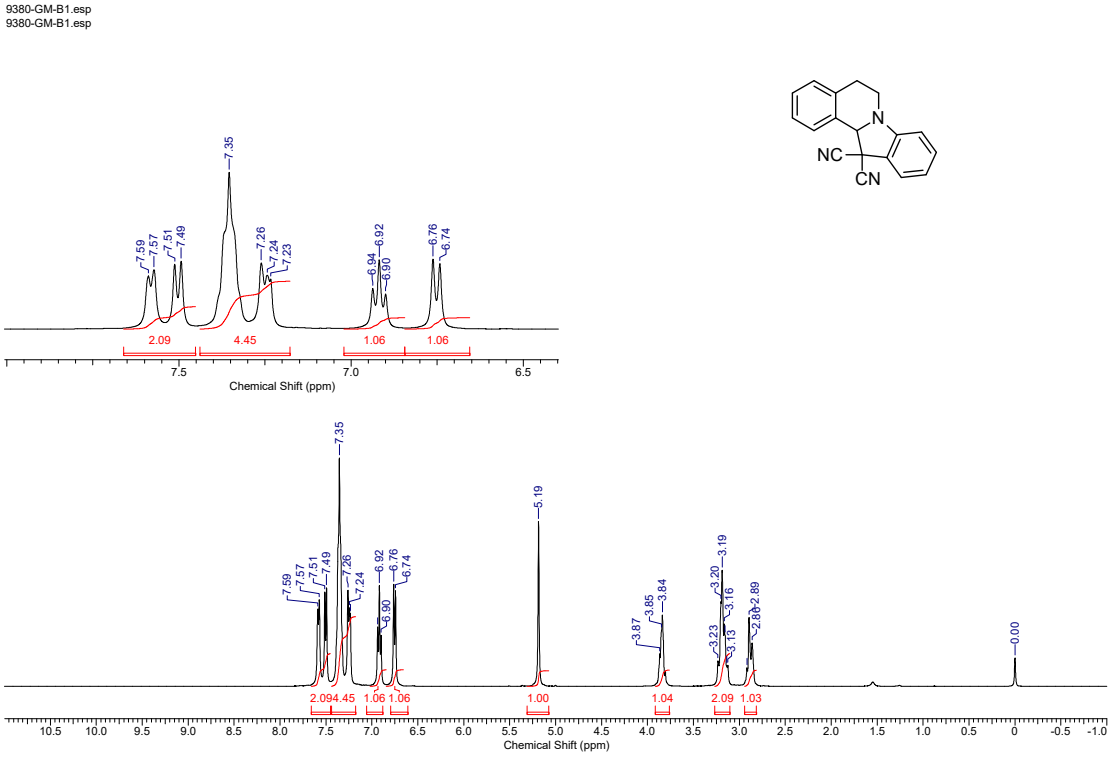


Figure S30. ^{1}H NMR spectrum of compound **4a**

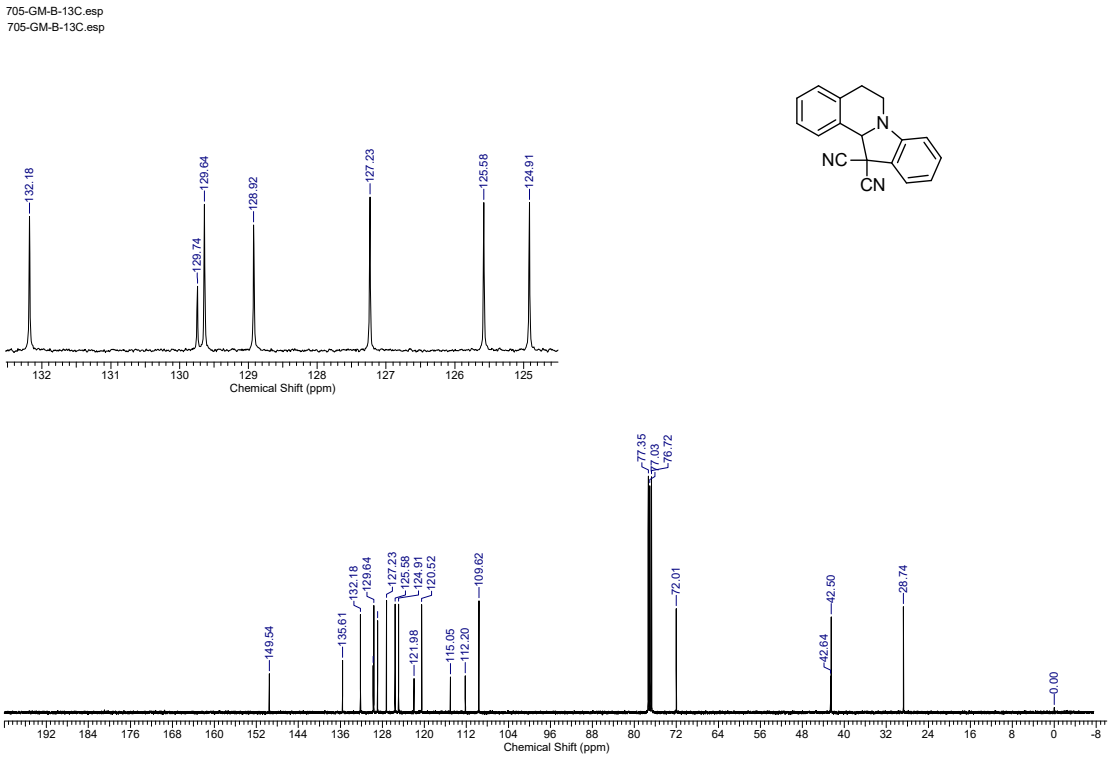


Figure S31. ^{13}C NMR spectrum of compound **4a**

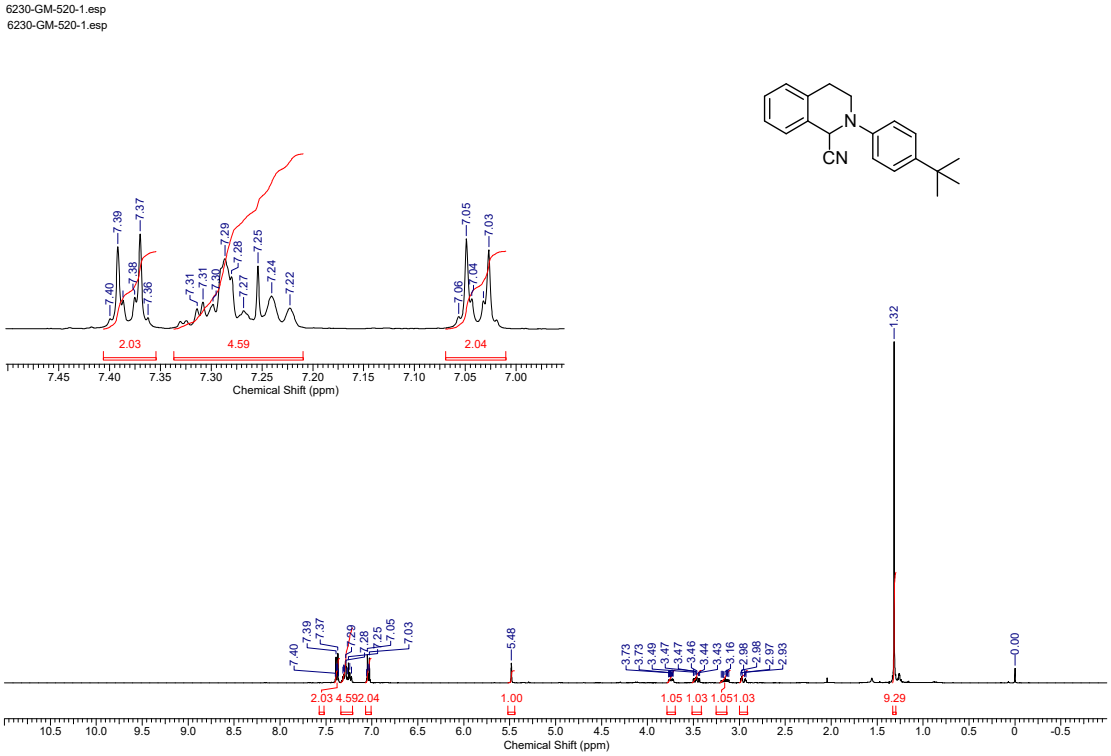


Figure S32. ^{1}H NMR spectrum of compound **3b**

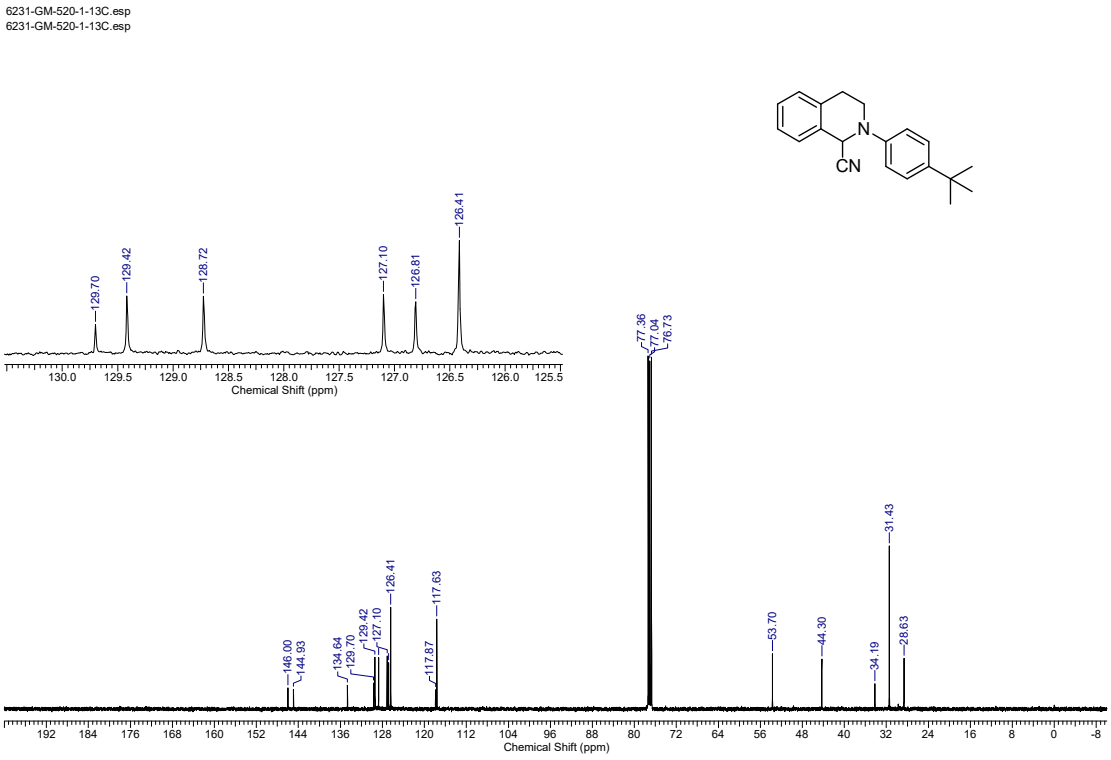


Figure S33. ^{13}C NMR spectrum of compound **3b**

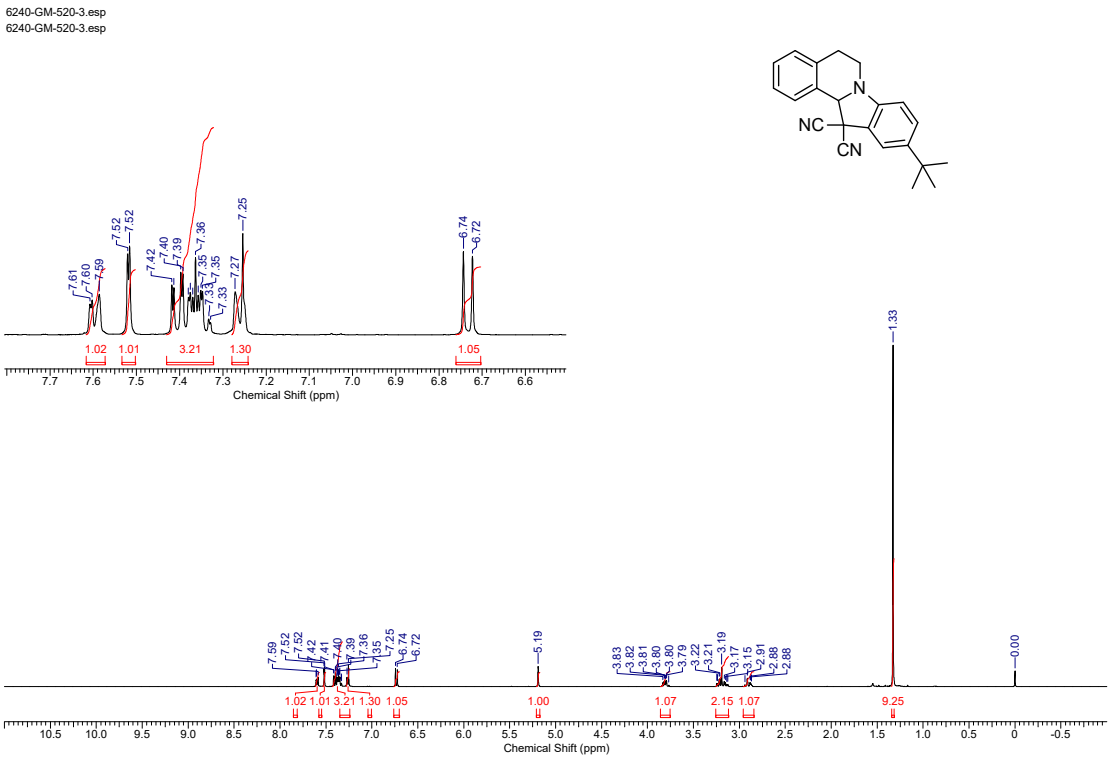


Figure S34.[1]H NMR spectrum of compound **4b**

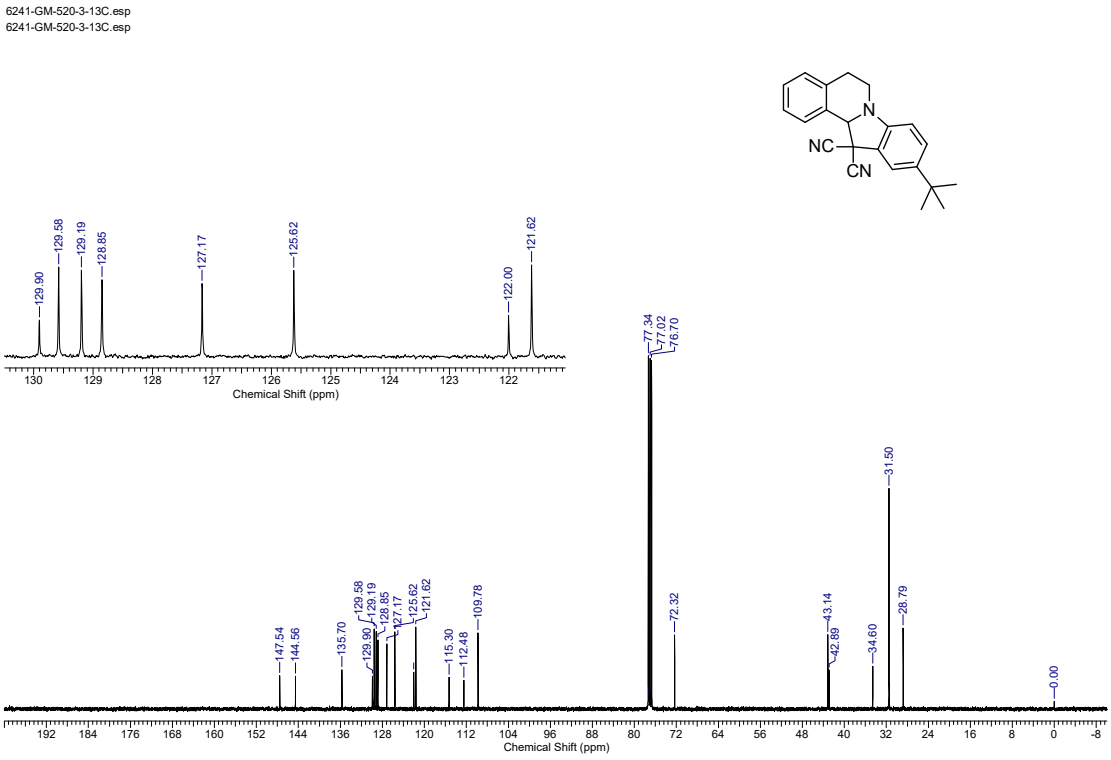


Figure S35.[13]C NMR spectrum of compound **4b**

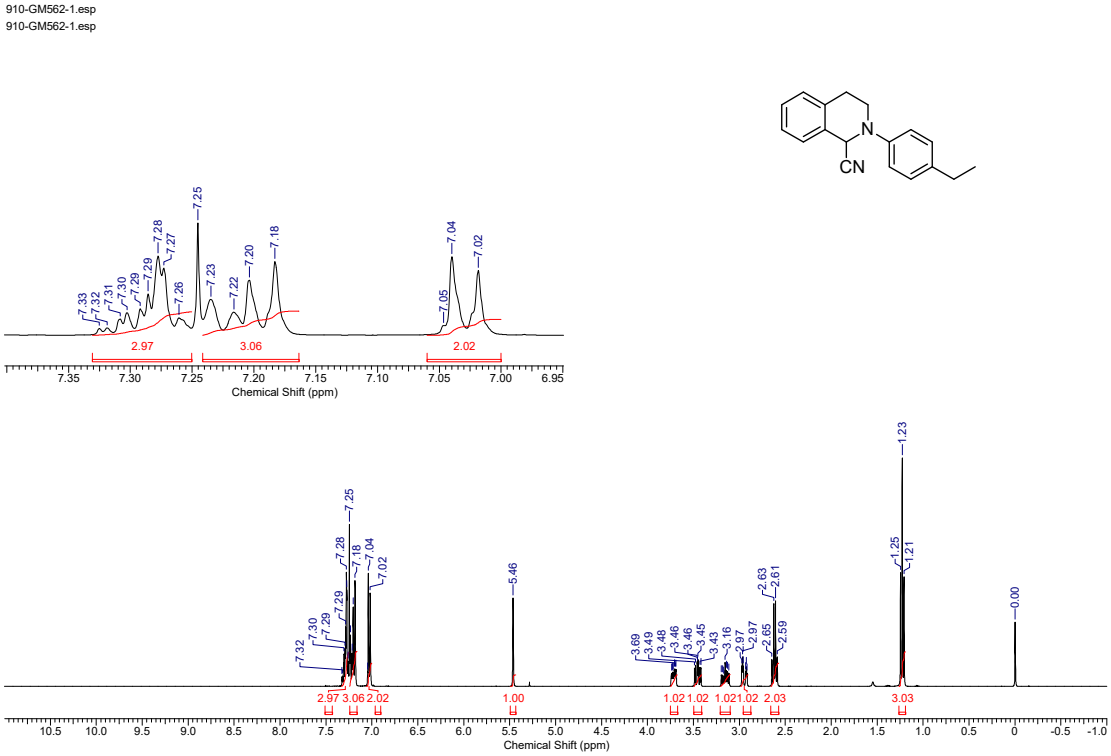


Figure S36. ^{1}H NMR spectrum of compound **3c**

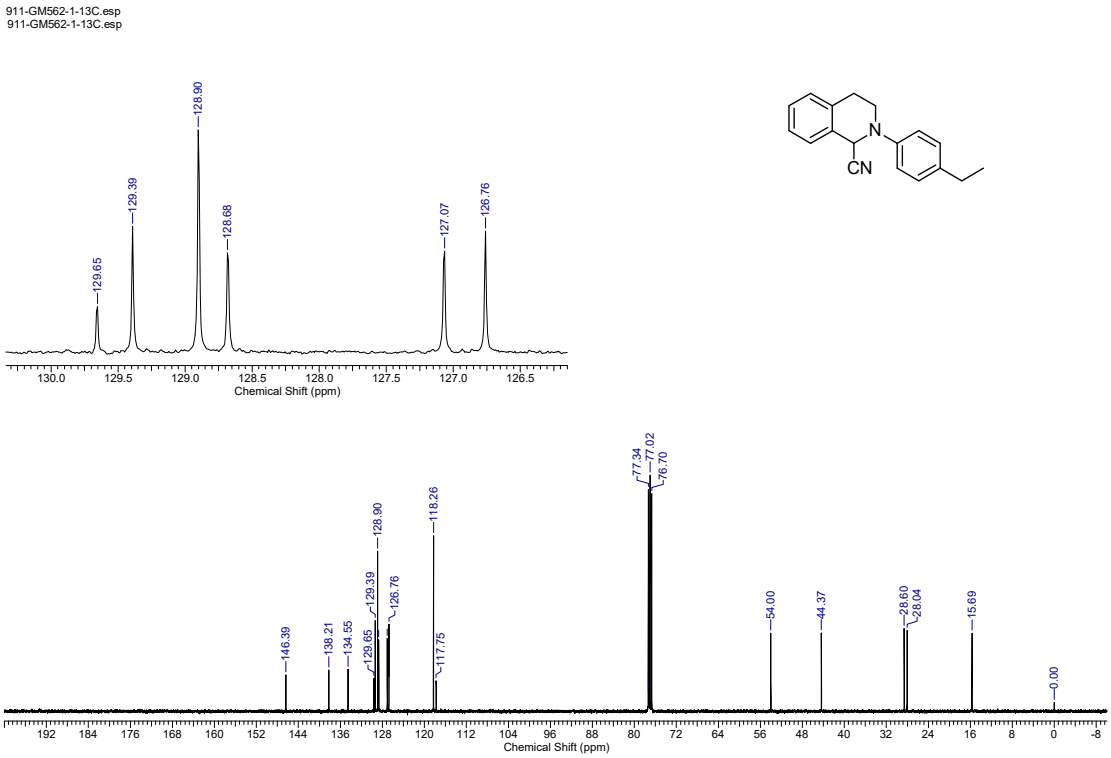


Figure S37. ^{13}C NMR spectrum of compound **3c**

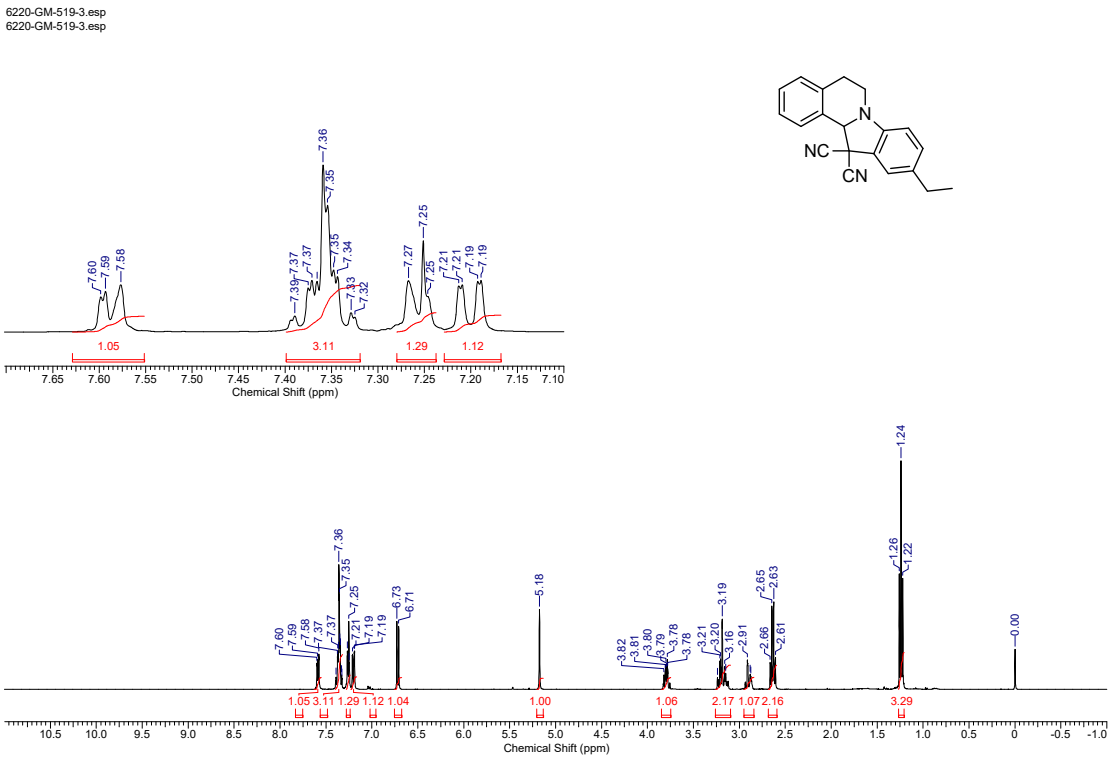


Figure S38. ^{1}H NMR spectrum of compound **4c**

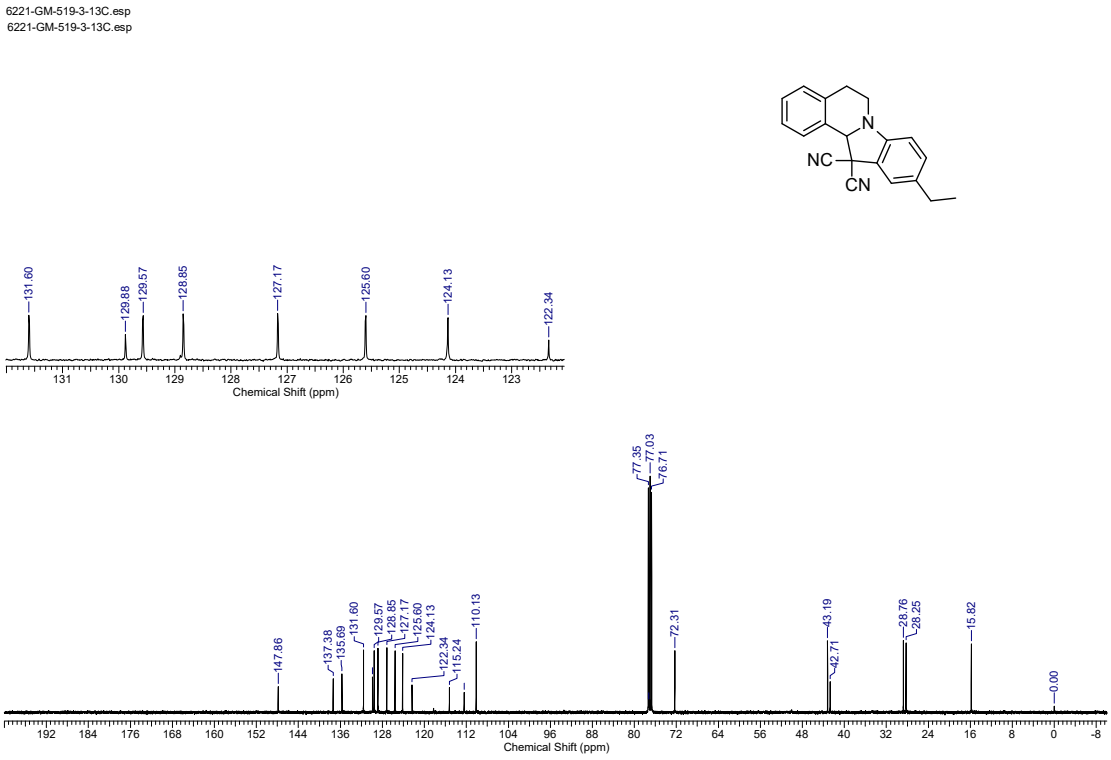


Figure S39. ^{13}C NMR spectrum of compound **4c**

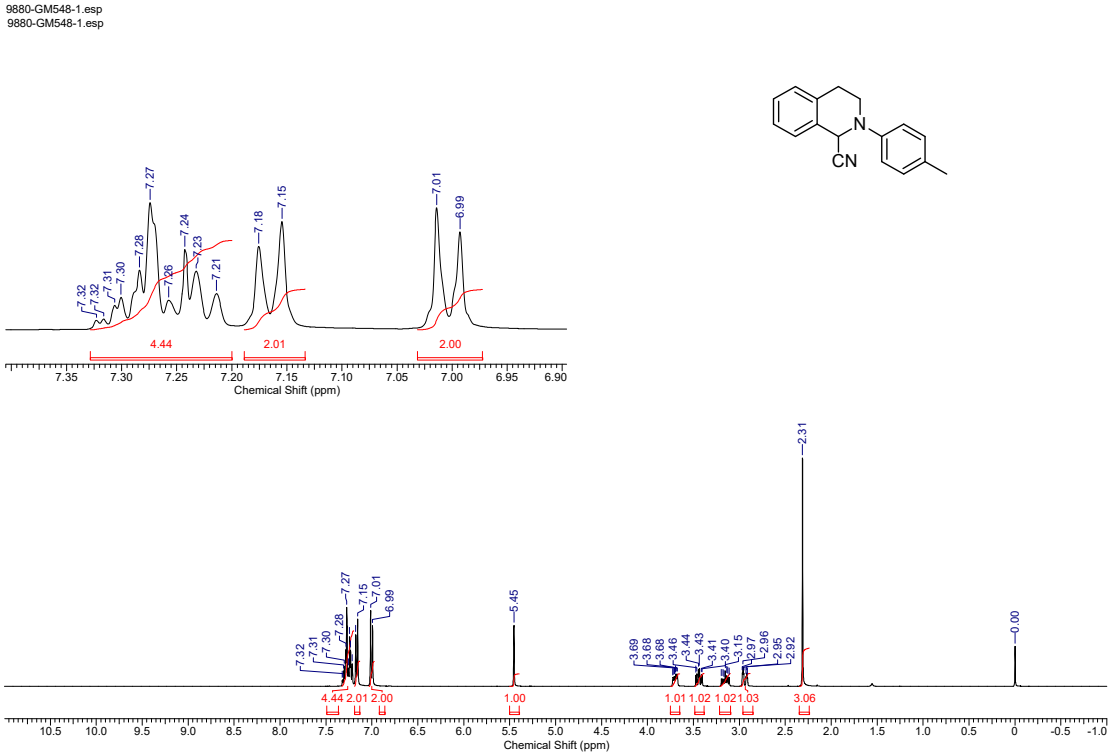


Figure S40. [1]H NMR spectrum of compound **3d**

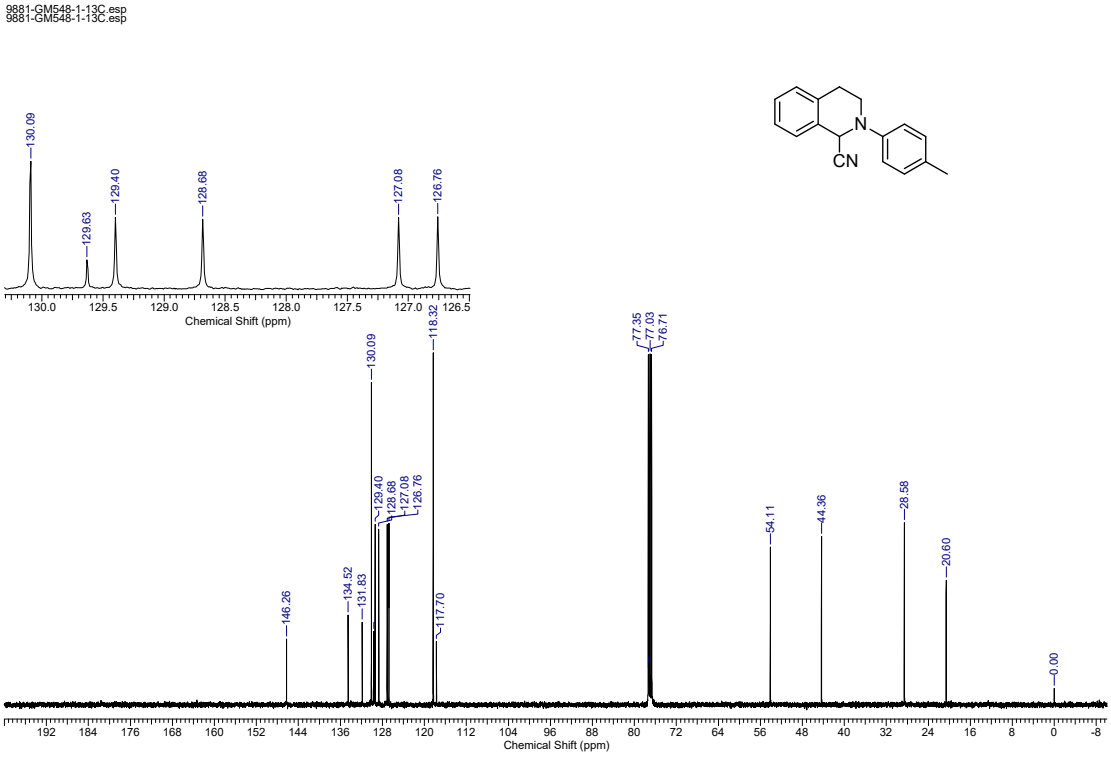


Figure S41. [13]C NMR spectrum of compound **3d**

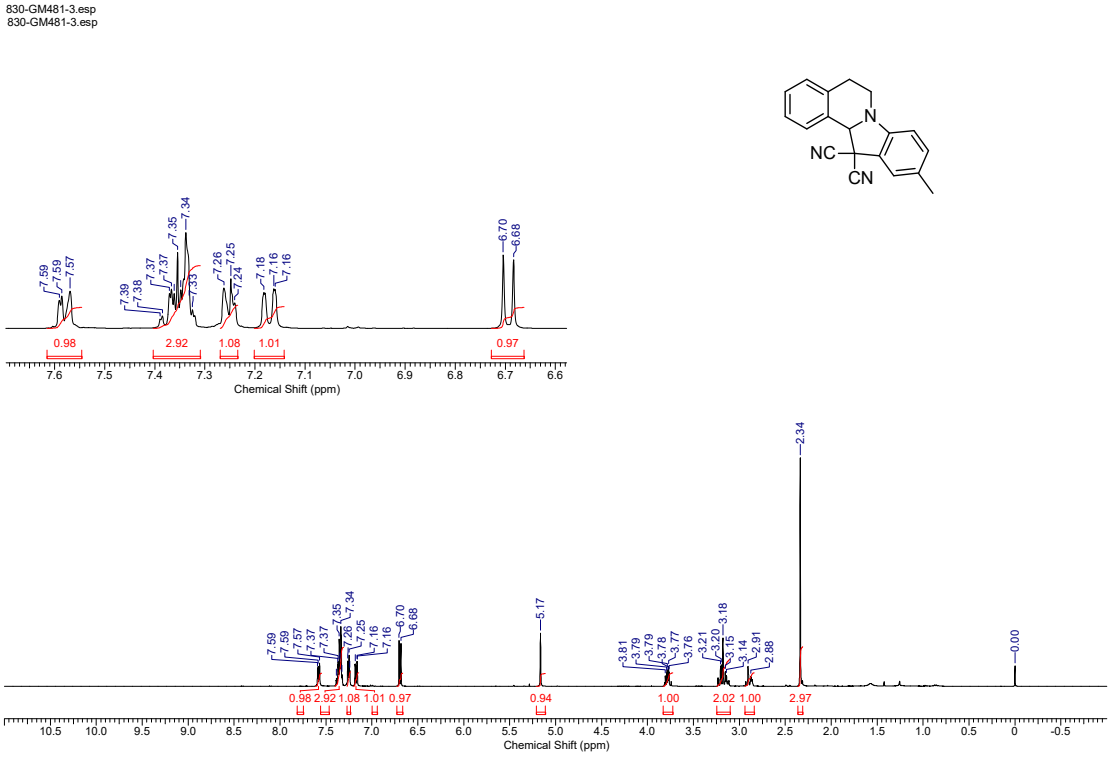


Figure S42. [1]H NMR spectrum of compound **4d**

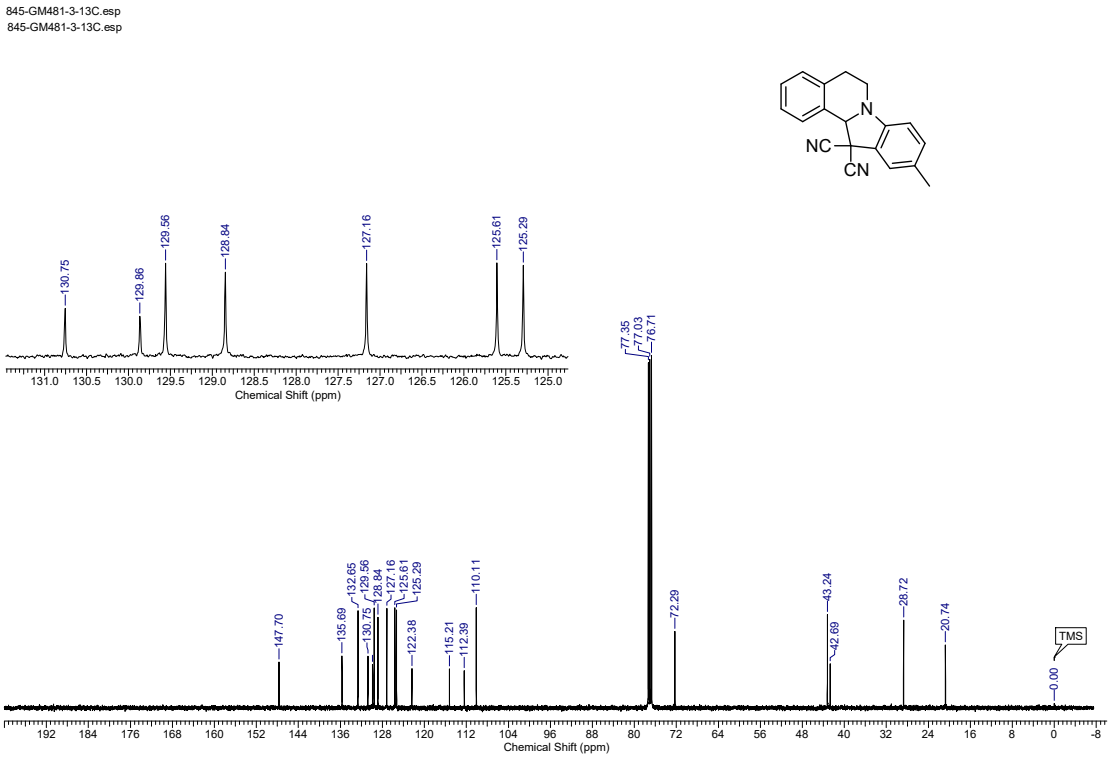


Figure S43. [13]C NMR spectrum of compound **4d**

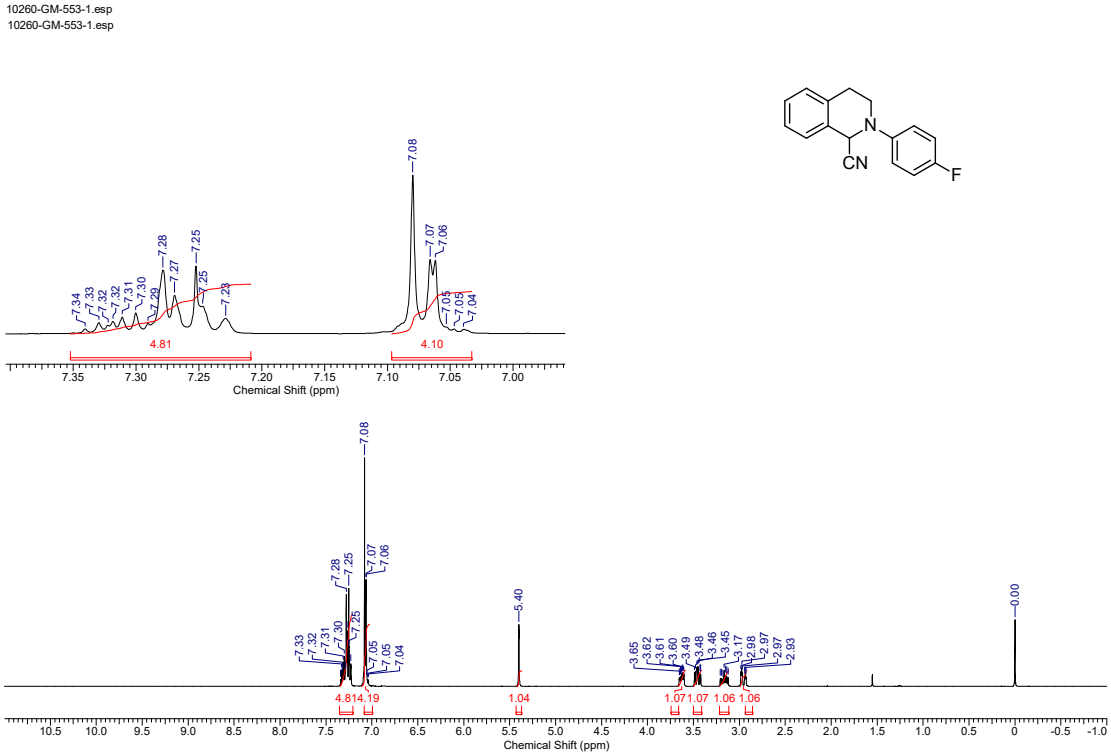


Figure S44. ^{1}H NMR spectrum of compound **3e**

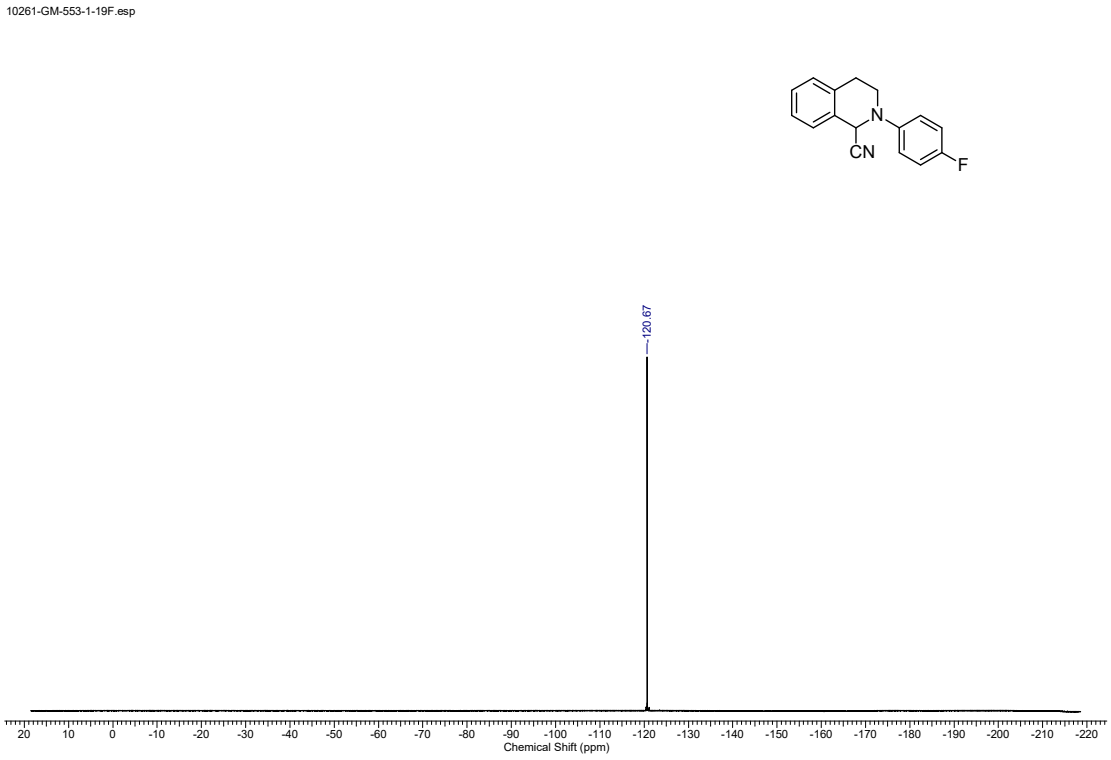


Figure S45. ^{19}F NMR spectrum of compound **3e**

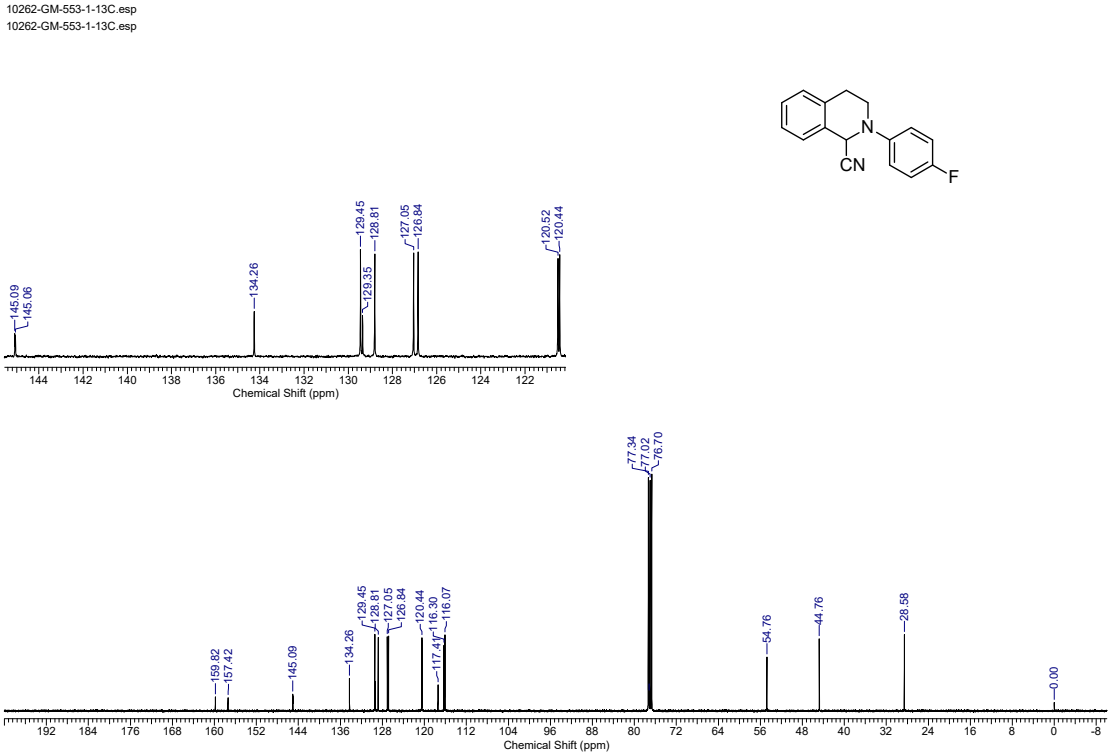


Figure S46. ^{13}C NMR spectrum of compound **3e**

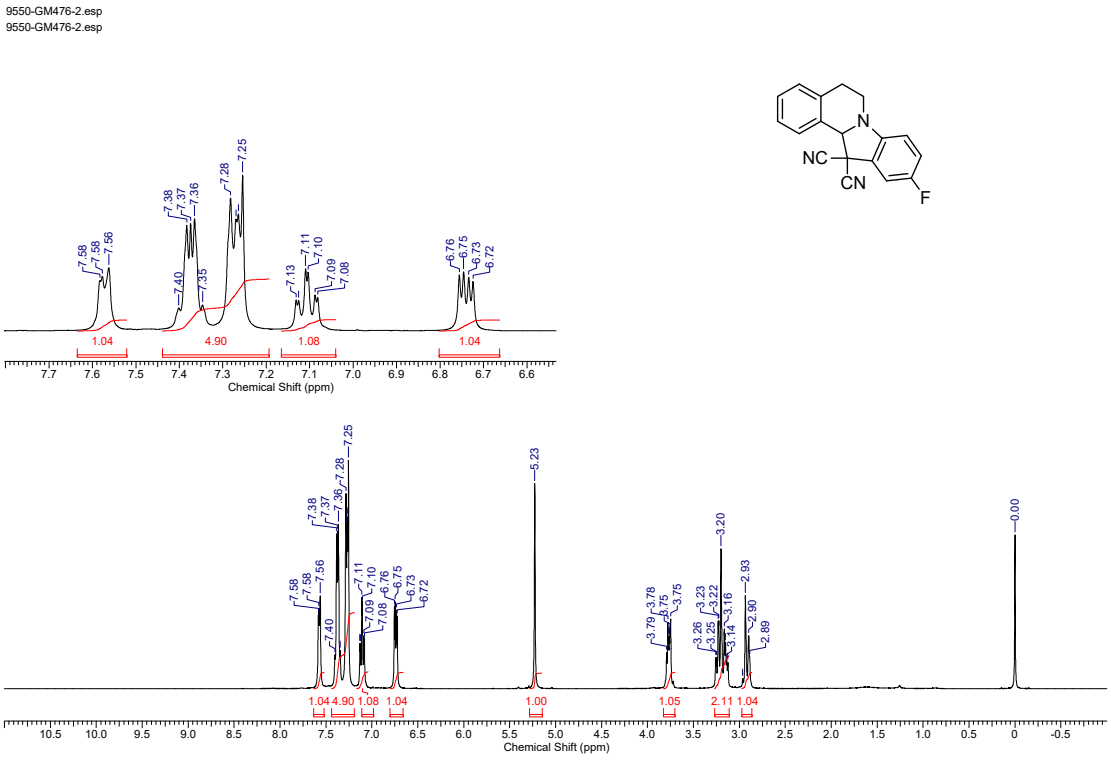


Figure S47. ^{1}H NMR spectrum of compound **4e**

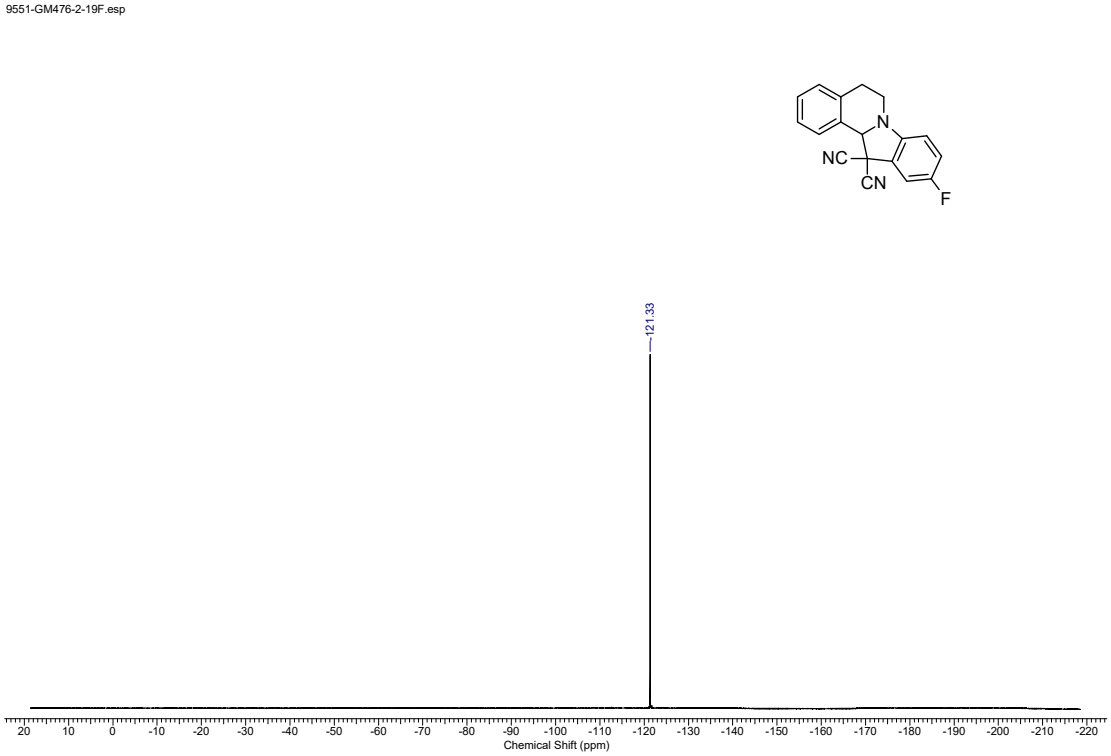


Figure S48. ^{19}F NMR spectrum of compound **4e**

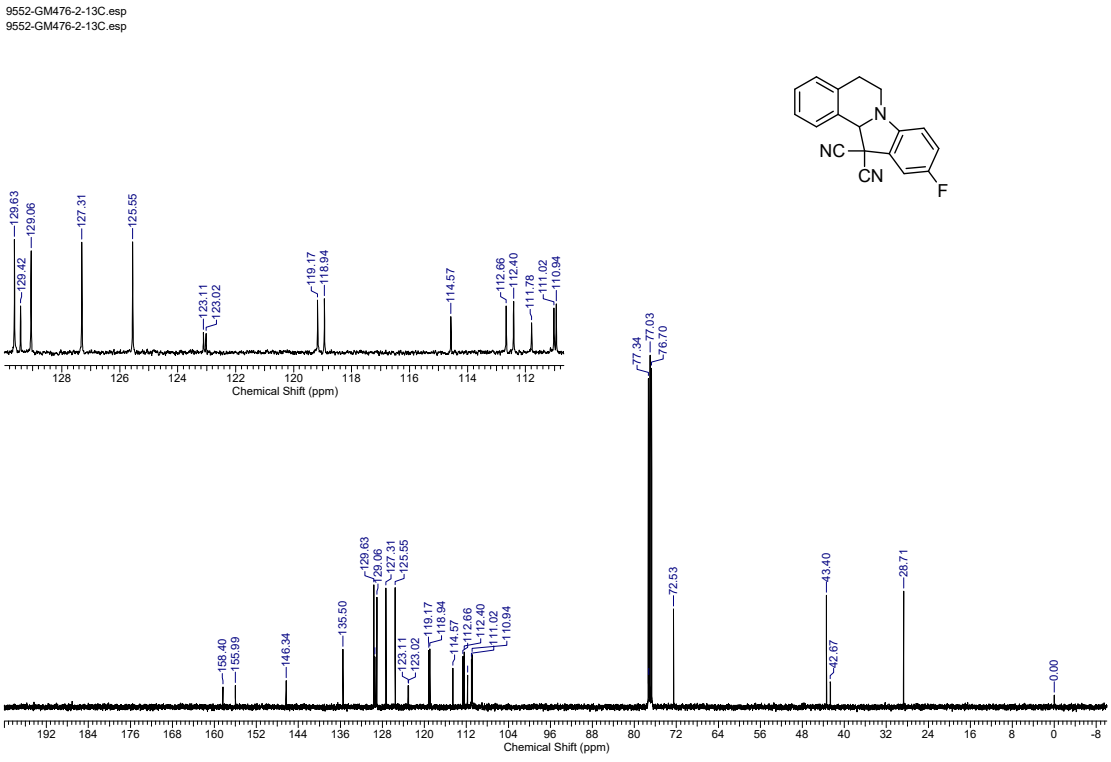


Figure S49. ^{13}C NMR spectrum of compound **4e**

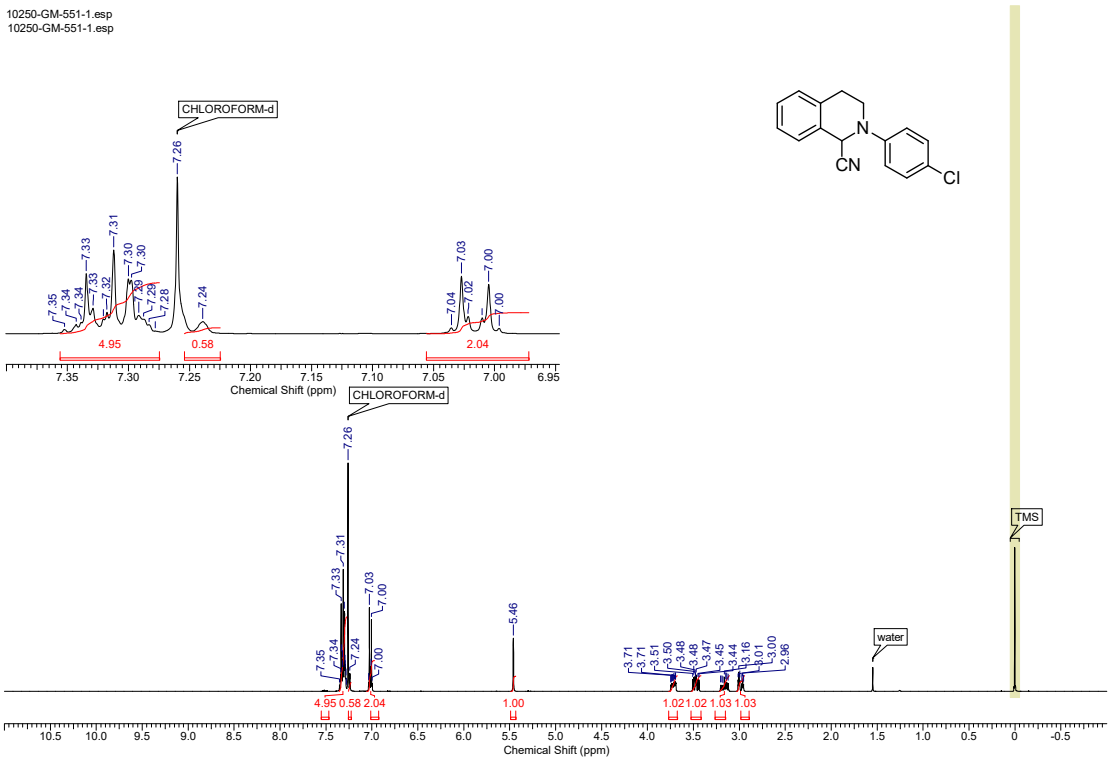


Figure S50. ^{1}H NMR spectrum of compound **3f**

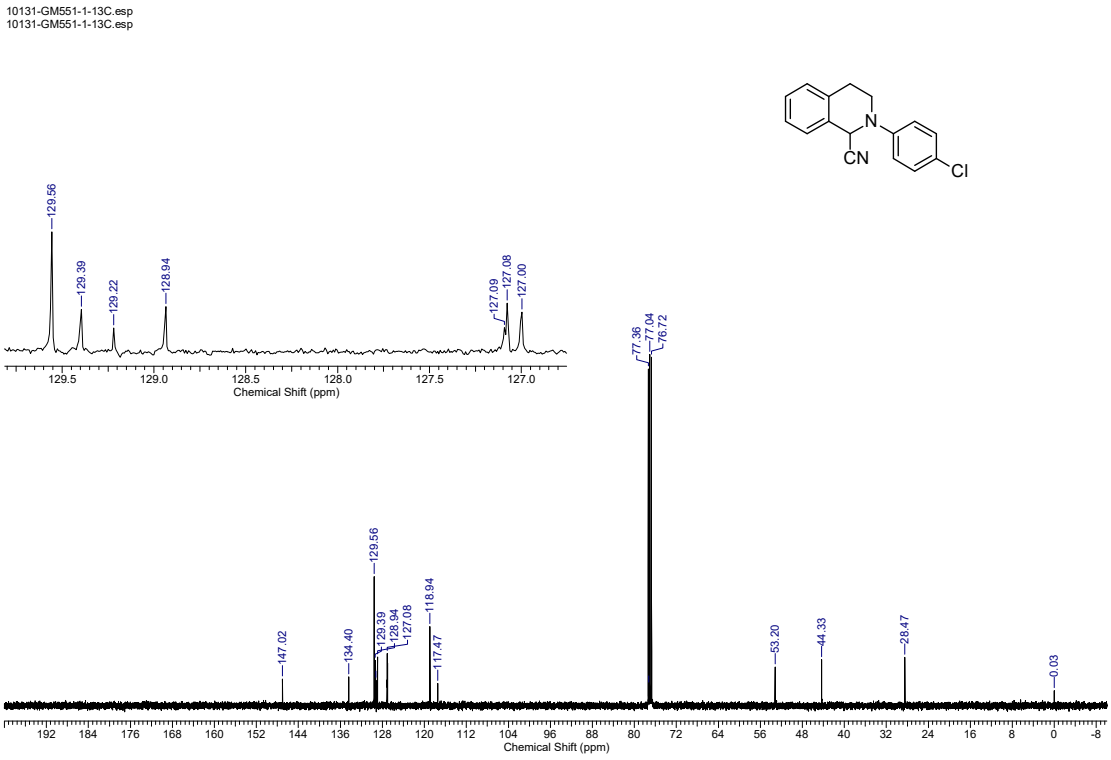


Figure S51. ^{13}C NMR spectrum of compound **3f**

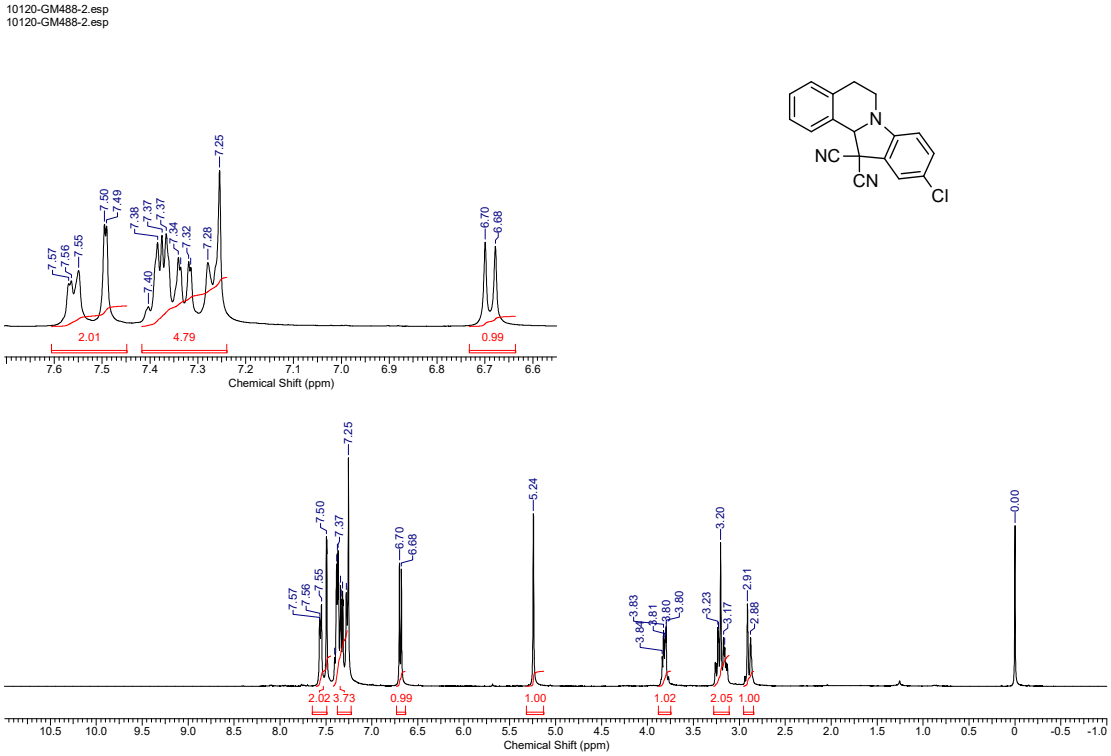


Figure S52. ^{1}H NMR spectrum of compound **4f**

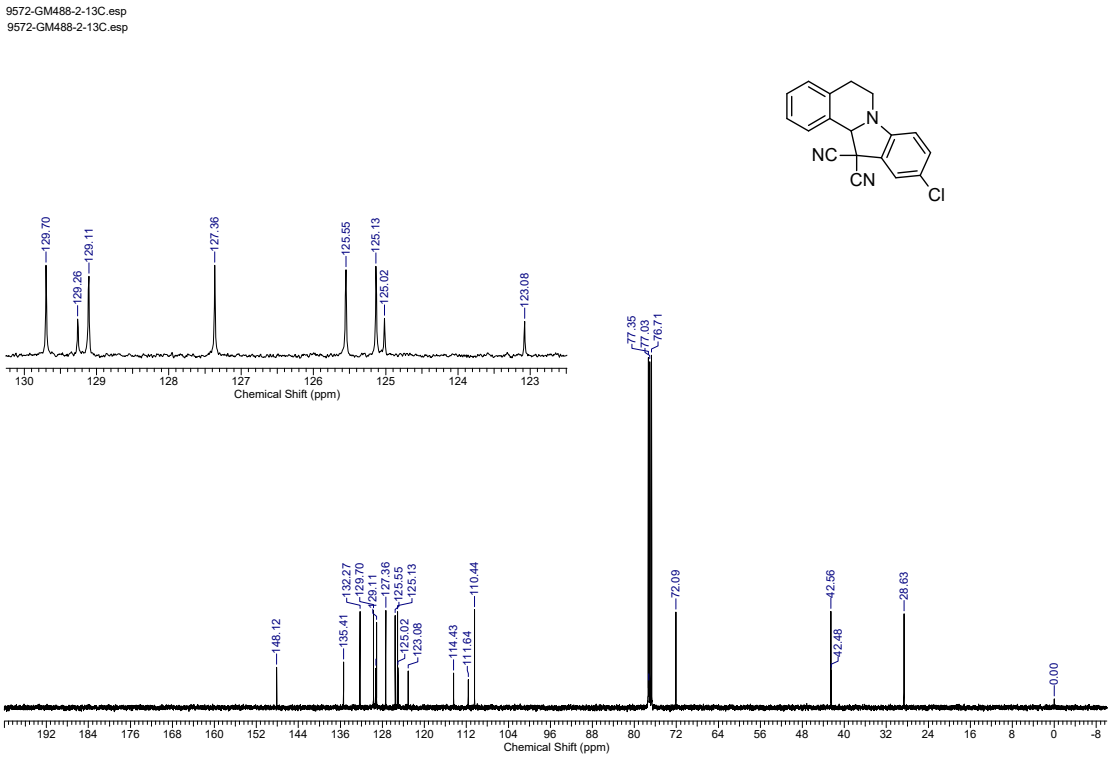


Figure S53. ^{13}C NMR spectrum of compound **4f**

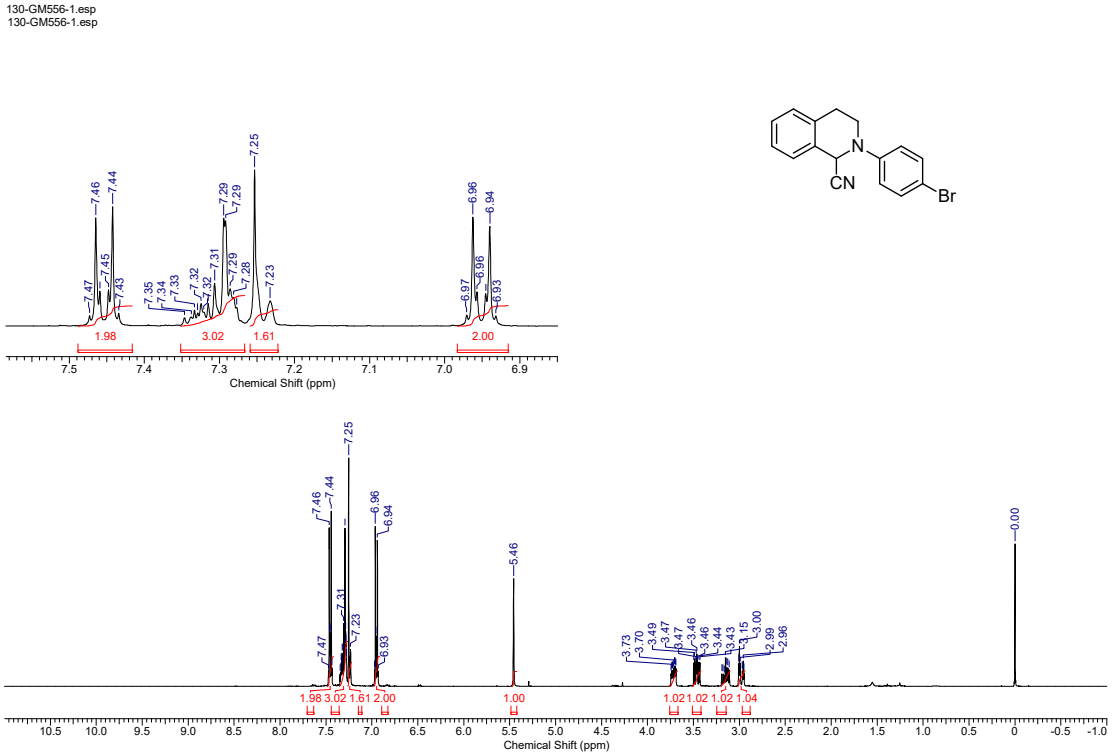


Figure S54. ^{1}H NMR spectrum of compound **3g**

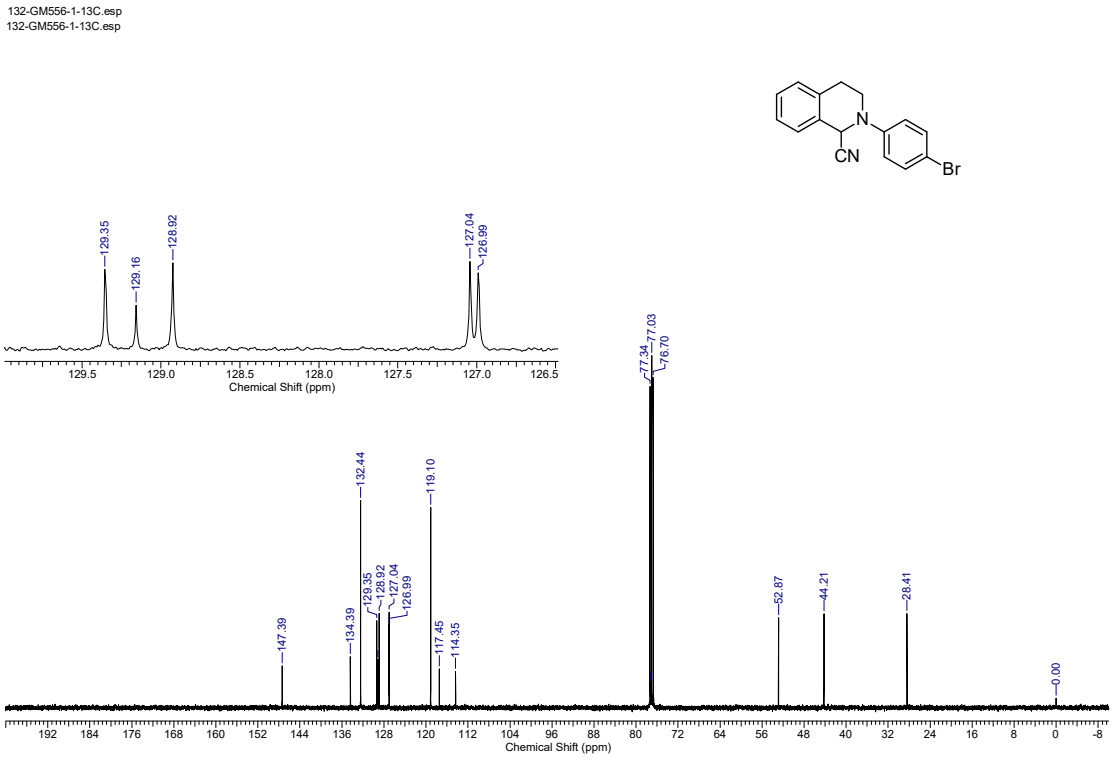


Figure S55. ^{13}C NMR spectrum of compound **3g**

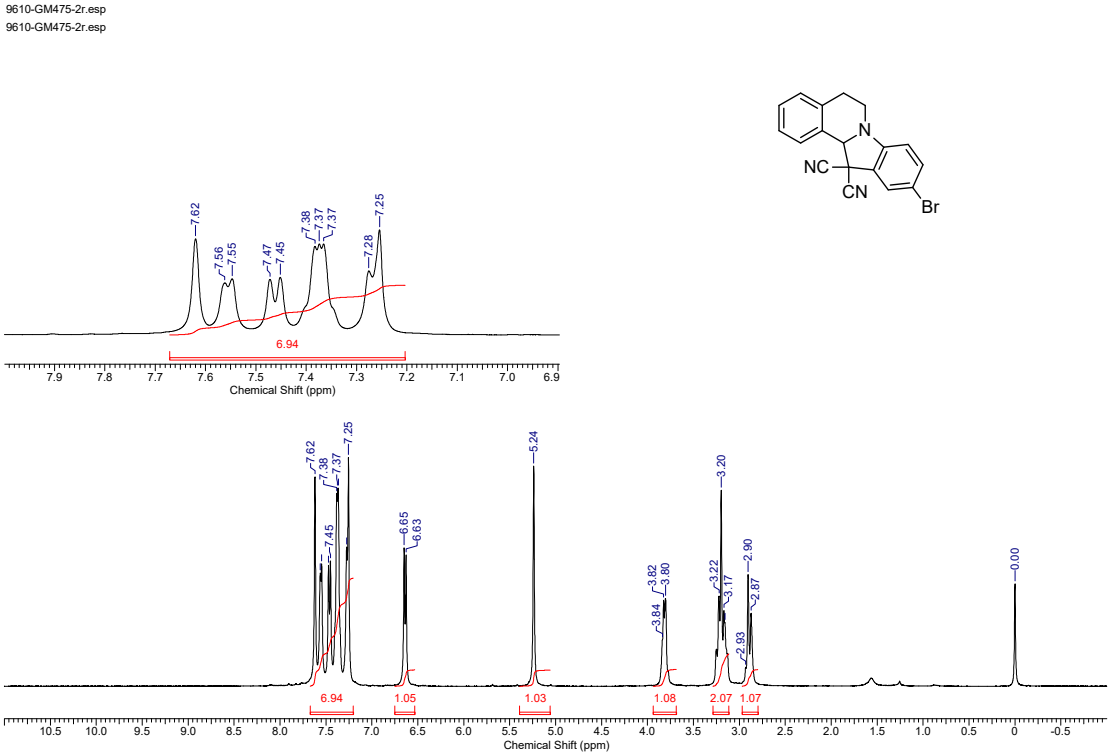


Figure S56. ^{1}H NMR spectrum of compound **4g**

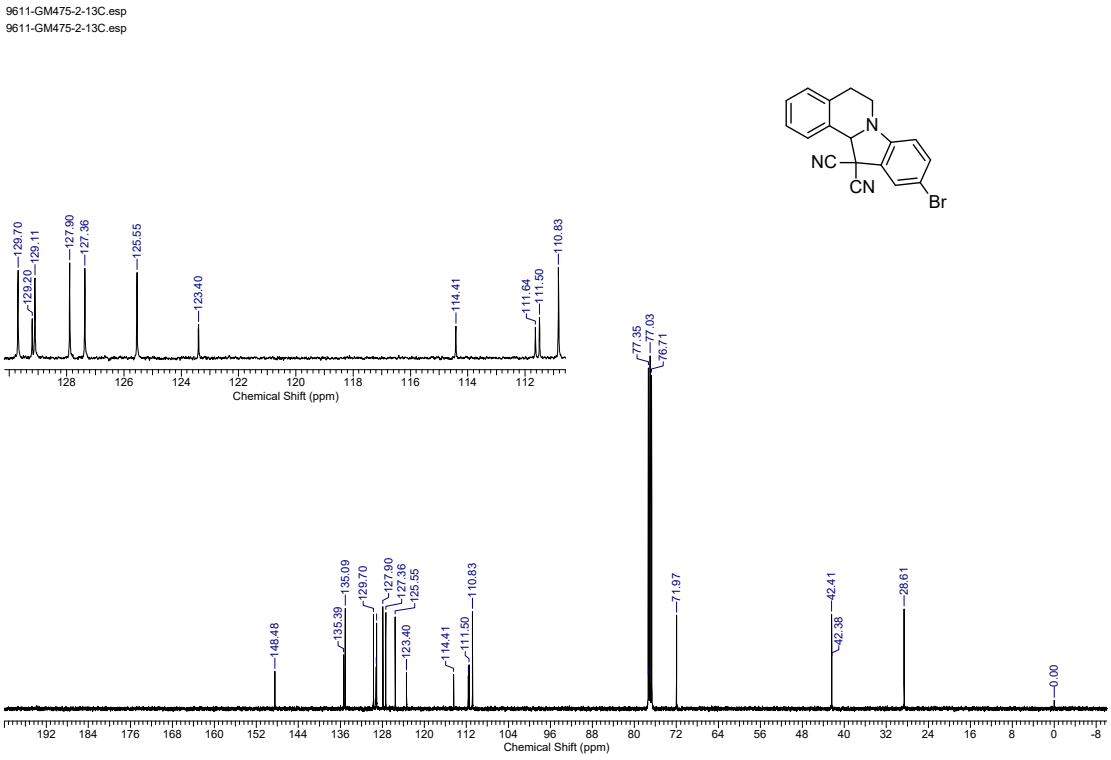


Figure S57. ^{13}C NMR spectrum of compound **4g**

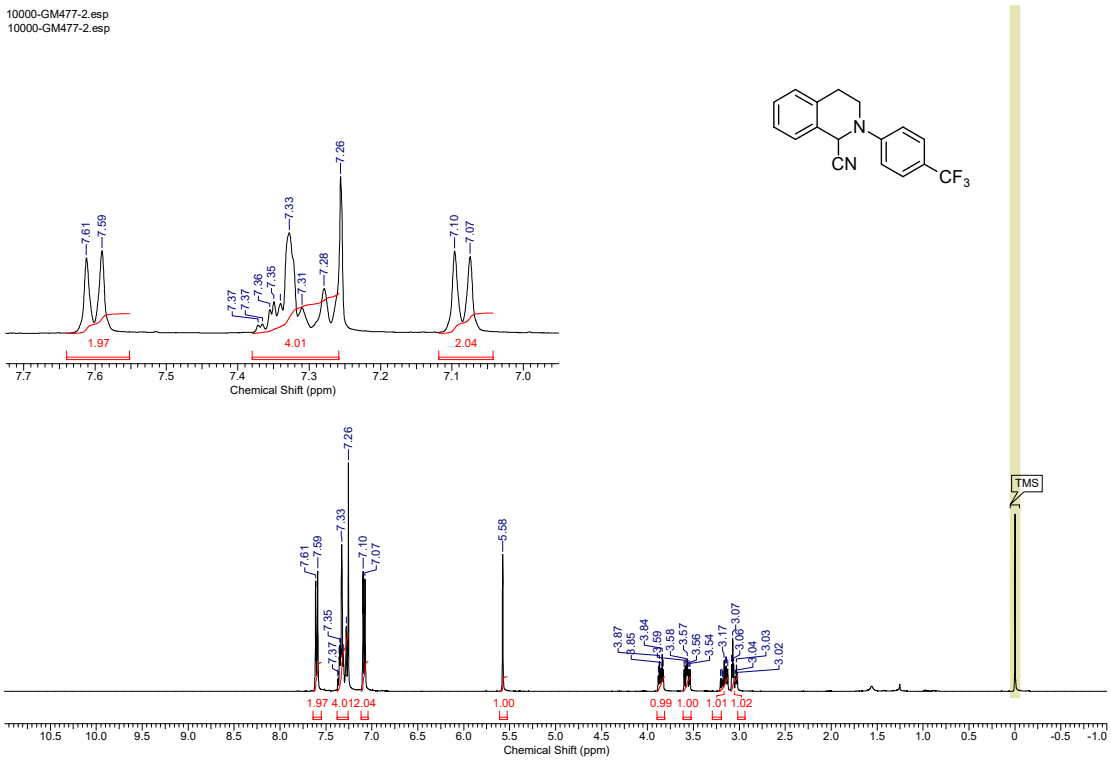


Figure S58. [1]H NMR spectrum of compound **3h**

Figure S59. [19]F NMR spectrum of compound **3h**

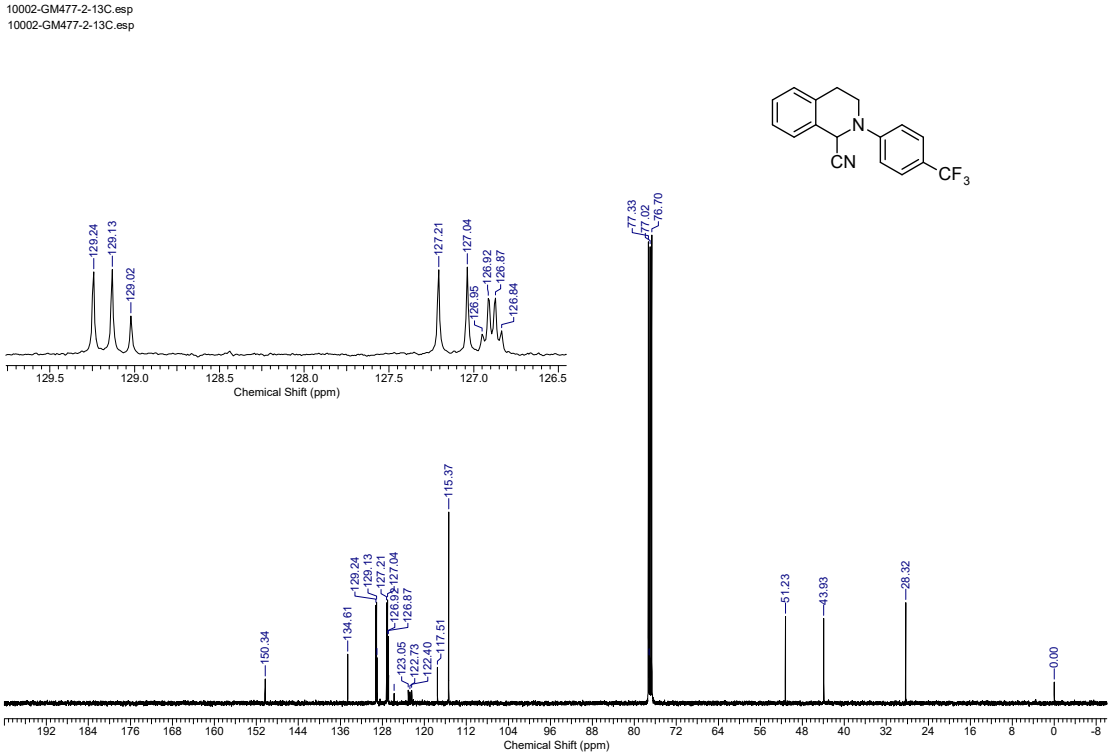


Figure S60. ^{13}C NMR spectrum of compound **3h**

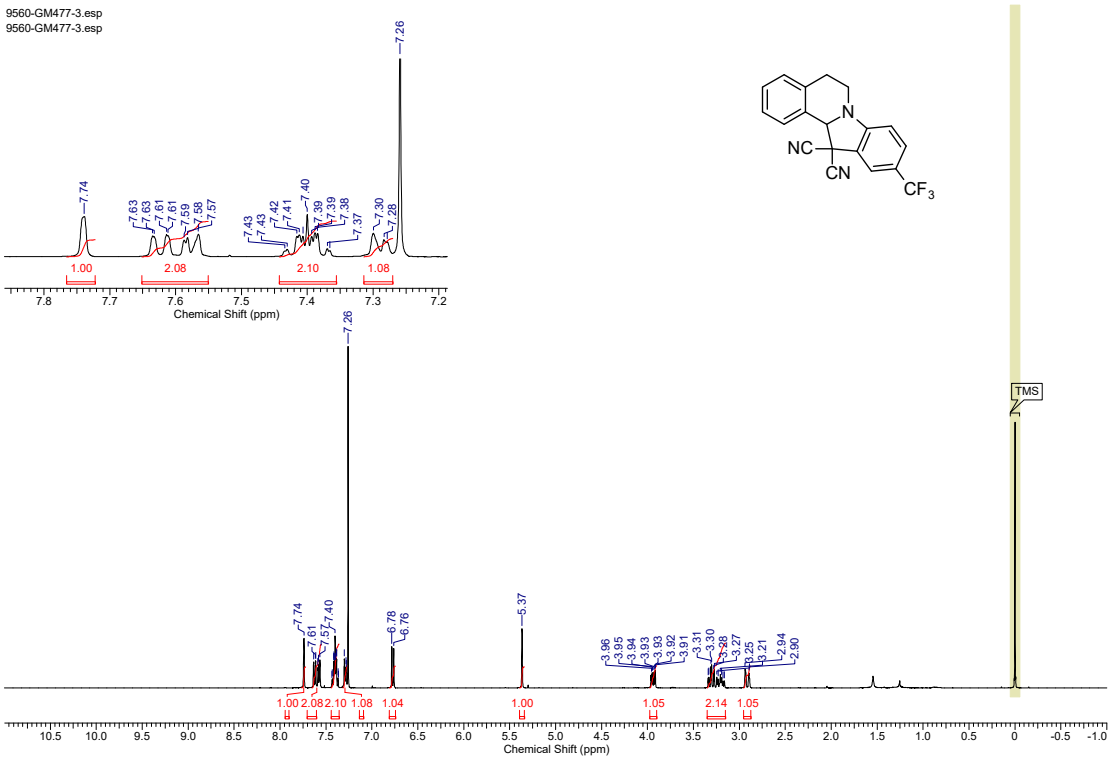


Figure S61. ^{1}H NMR spectrum of compound **4h**

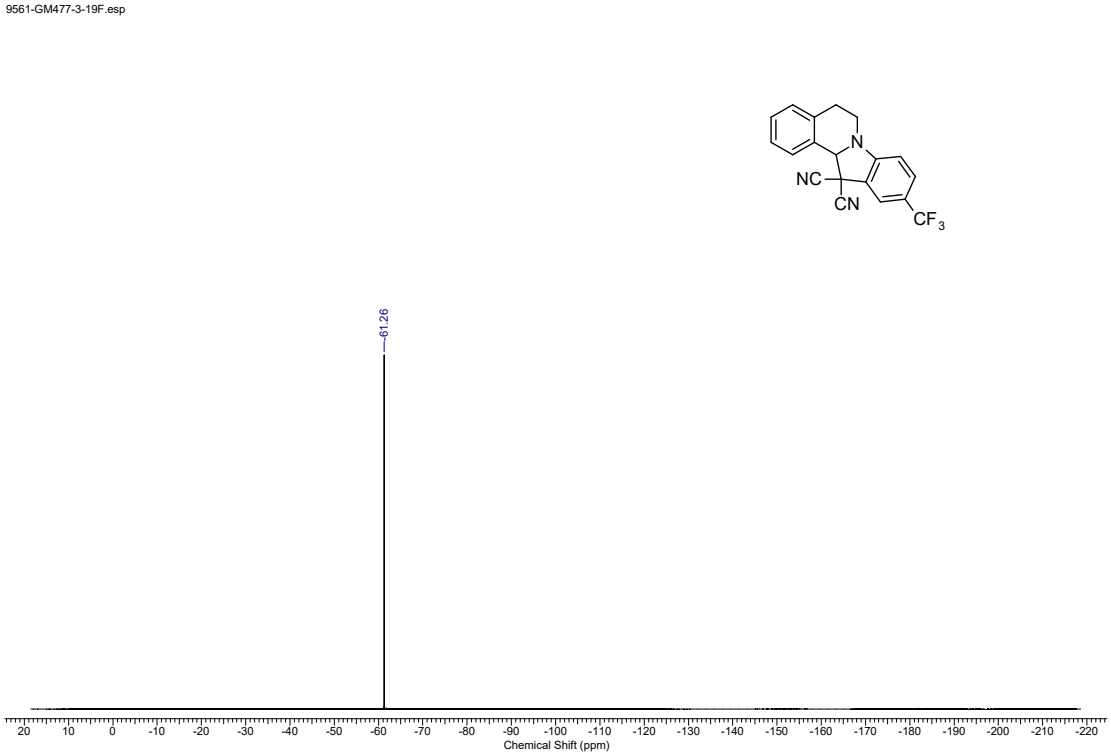


Figure S62. ^{19}F NMR spectrum of compound **4h**

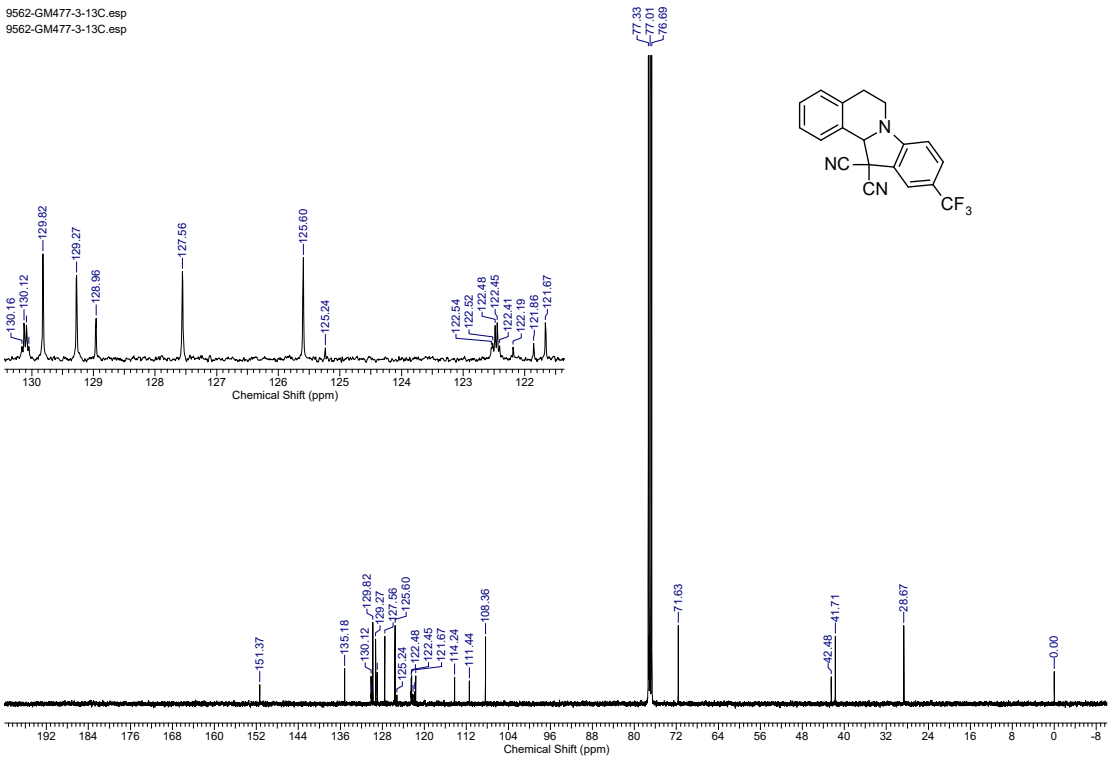


Figure S63. ^{13}C NMR spectrum of compound **4h**

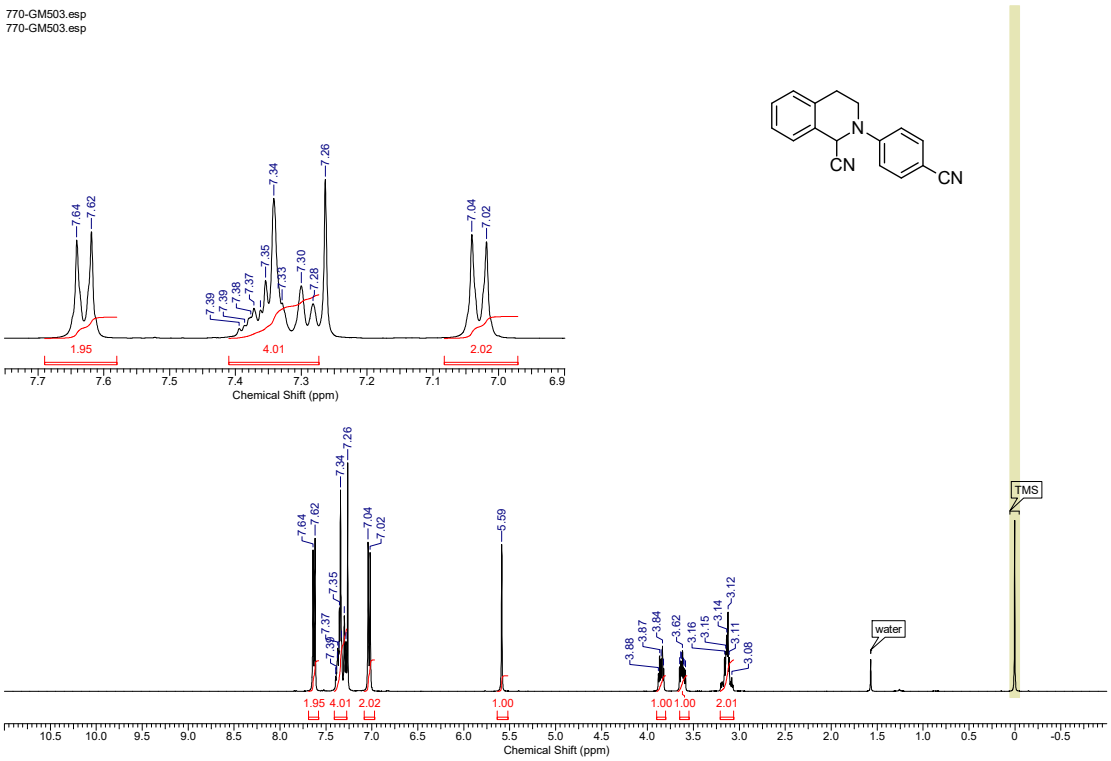


Figure S64. ^{1}H NMR spectrum of compound **3i**

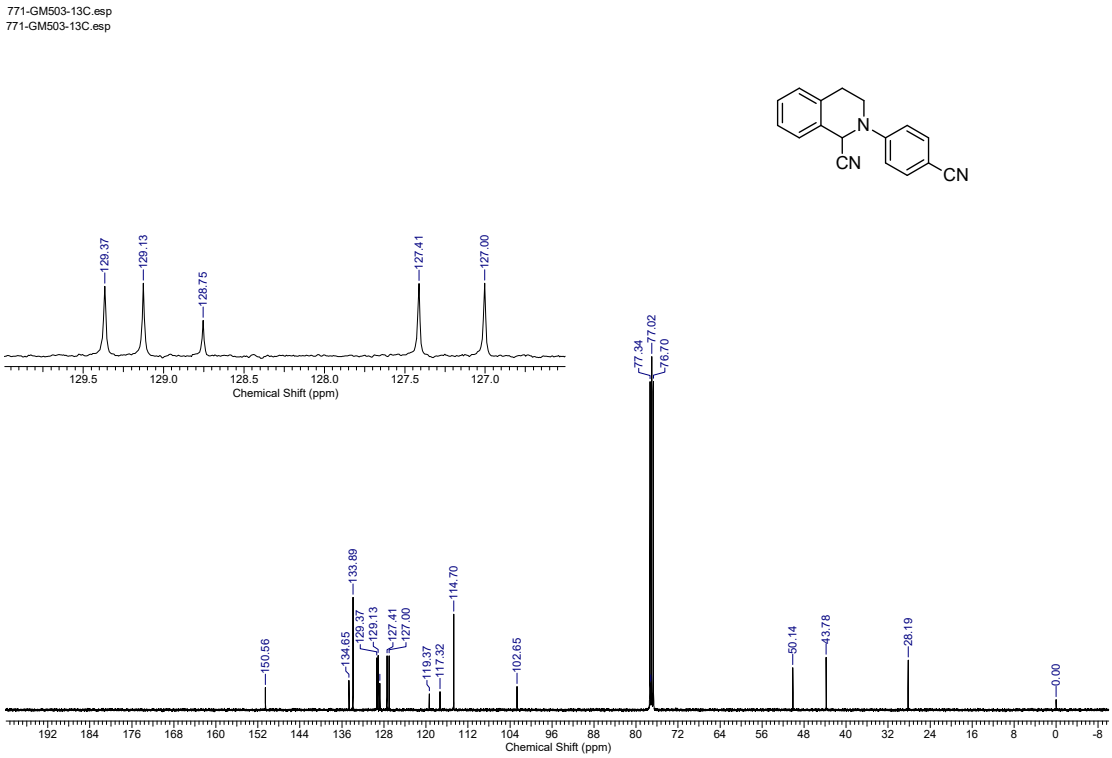


Figure S65. ^{13}C NMR spectrum of compound **3i**

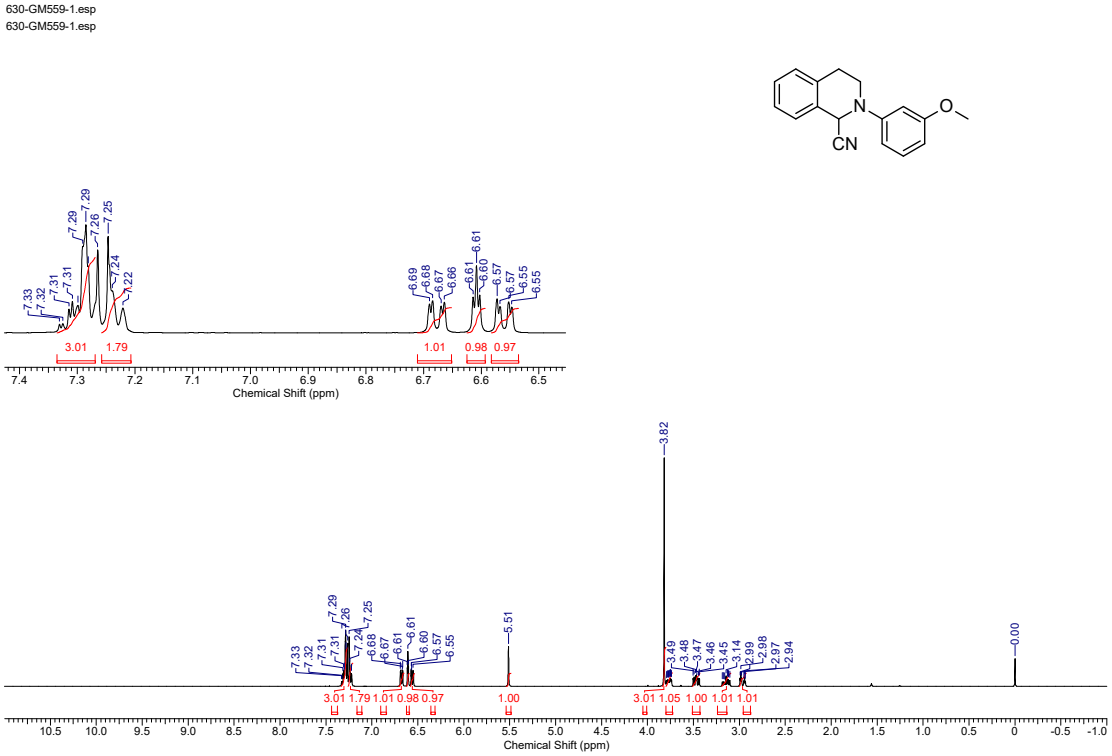


Figure S66. [1]H NMR spectrum of compound **3j**

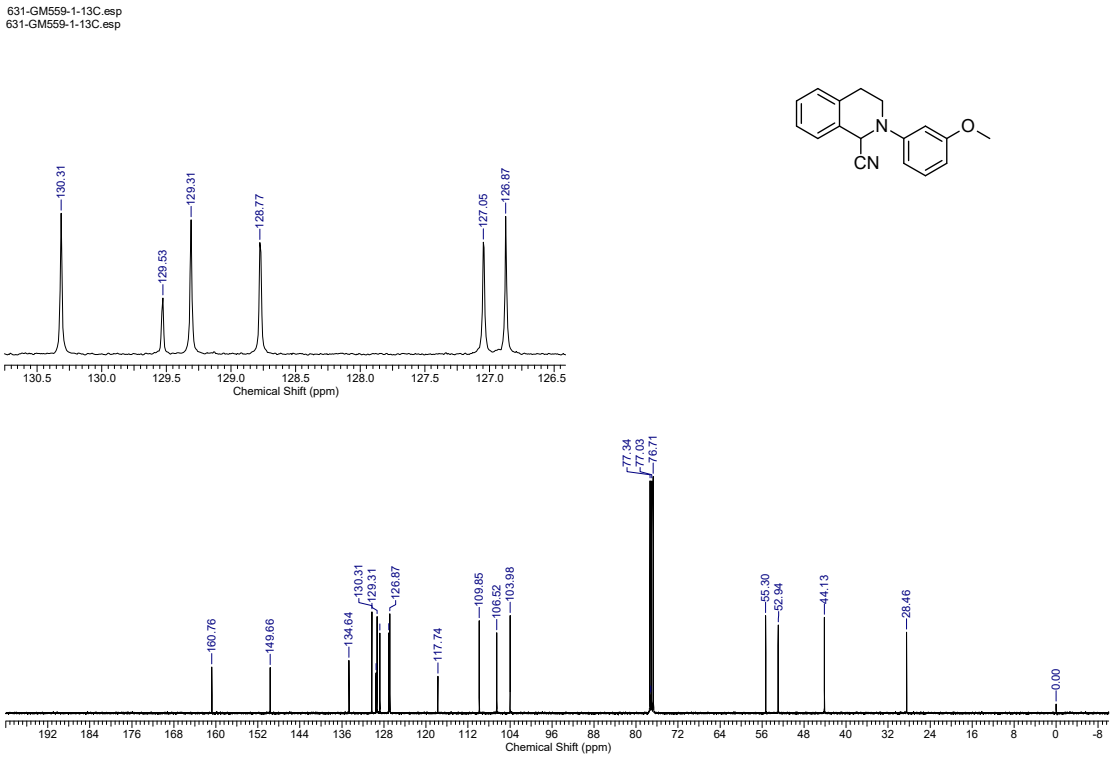


Figure S67. [13]C NMR spectrum of compound **3j**

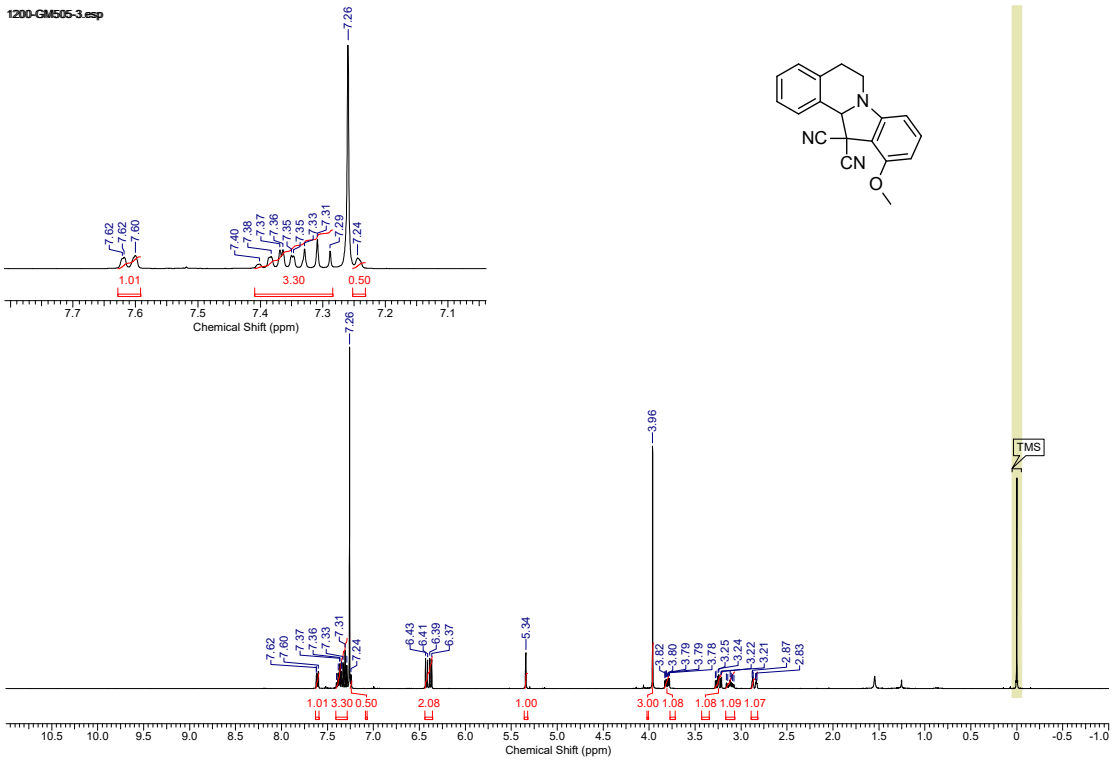


Figure S68. ^{1}H NMR spectrum of compound **4j1**

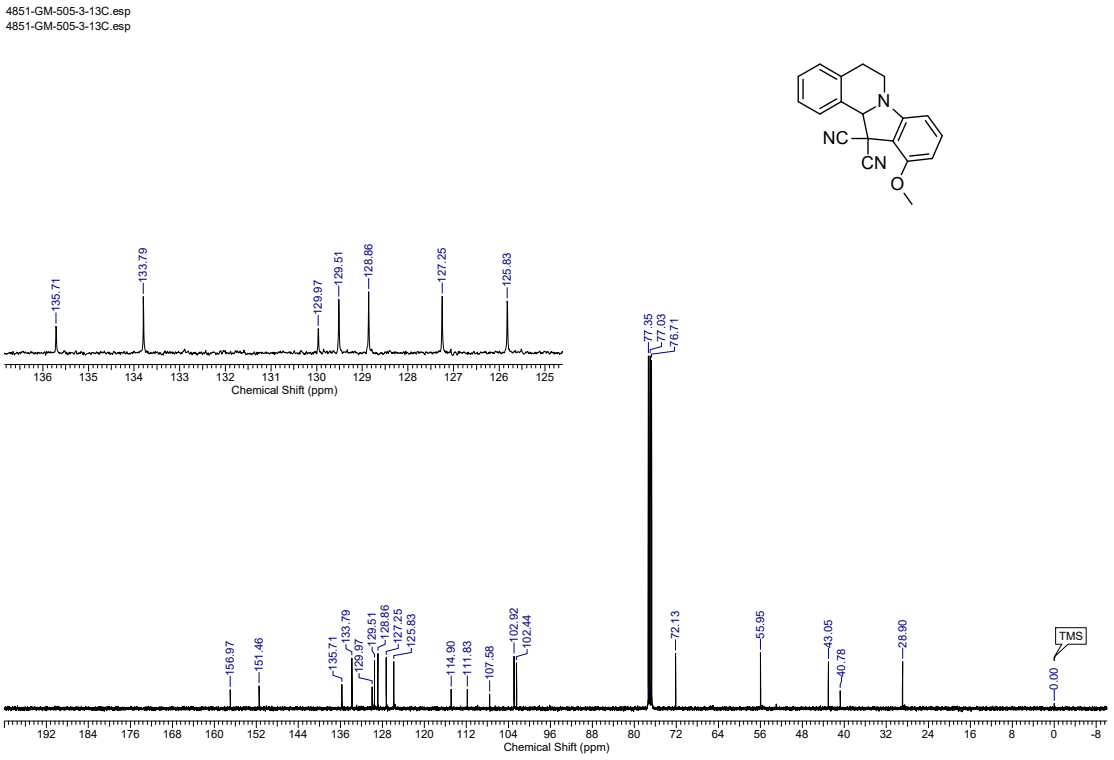


Figure S69. ^{13}C NMR spectrum of compound **4j1**

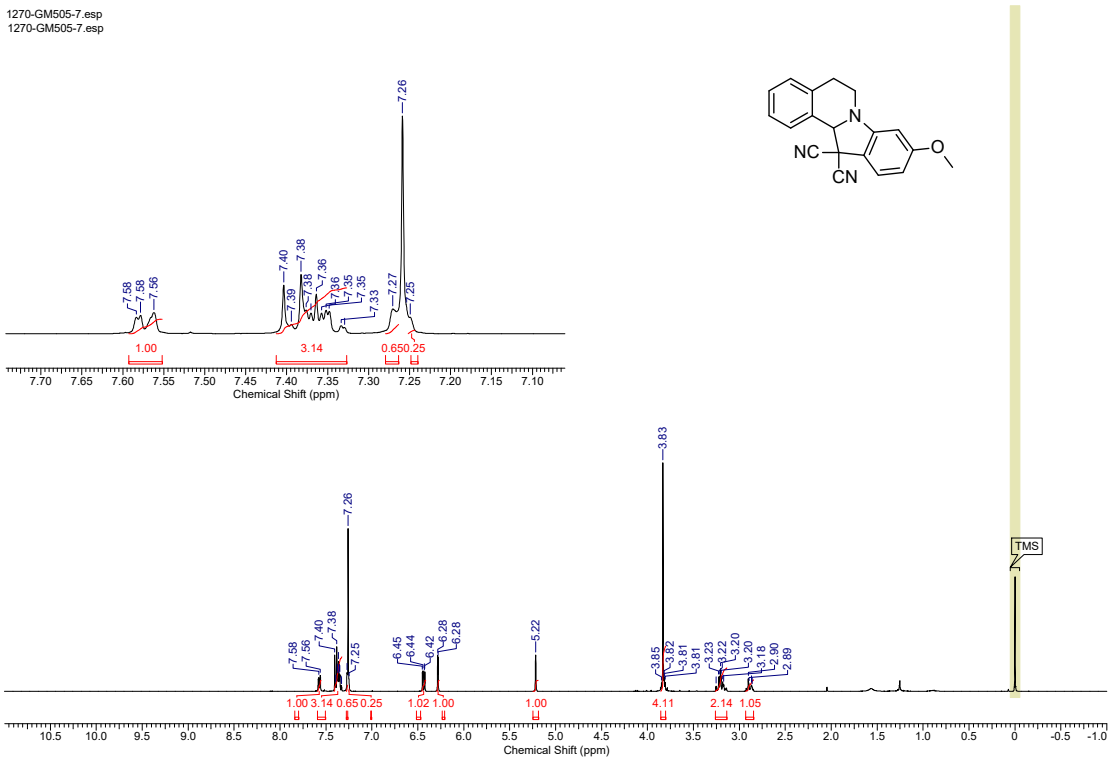


Figure S70. ^{1}H NMR spectrum of compound **4j2**

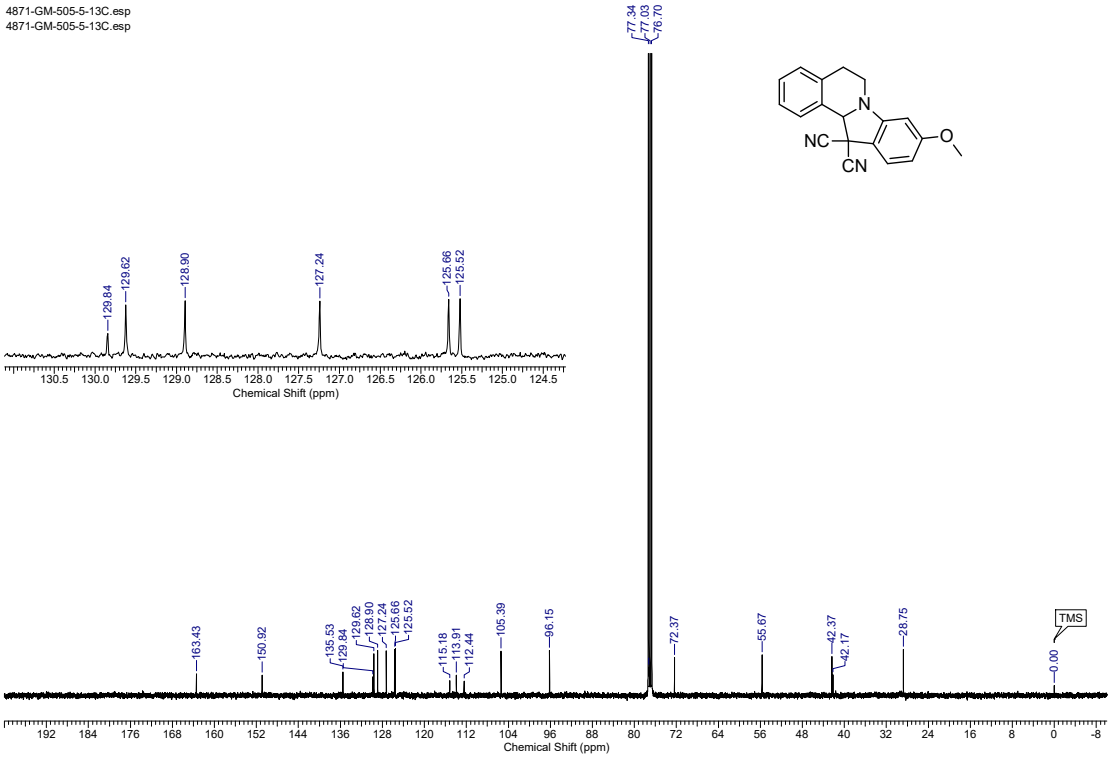


Figure S71. ^{13}C NMR spectrum of compound **4j2**

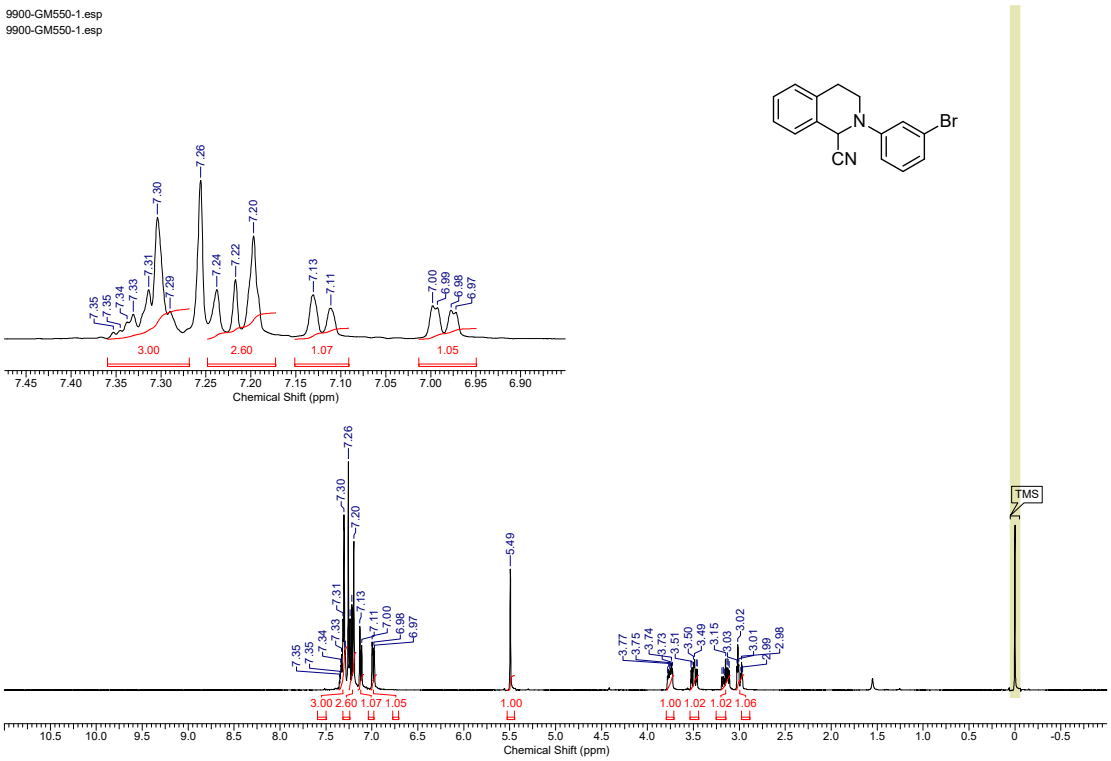


Figure S72. [1]H NMR spectrum of compound **3k**

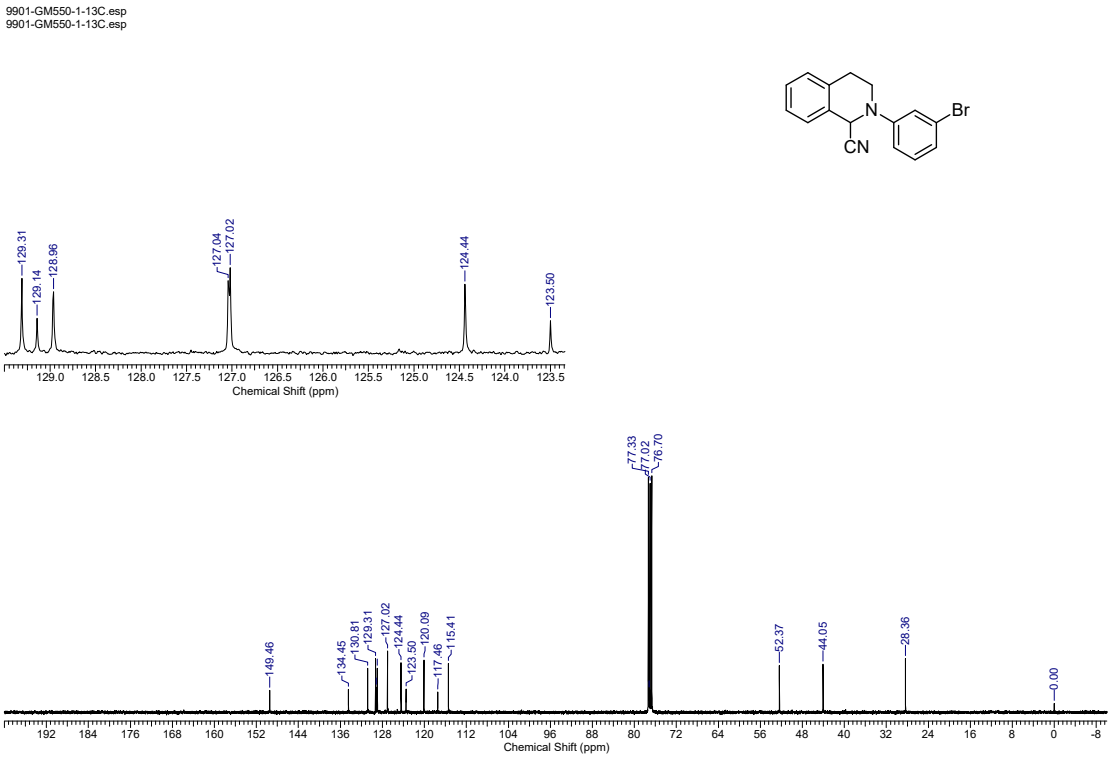


Figure S73. [13]C NMR spectrum of compound **3k**

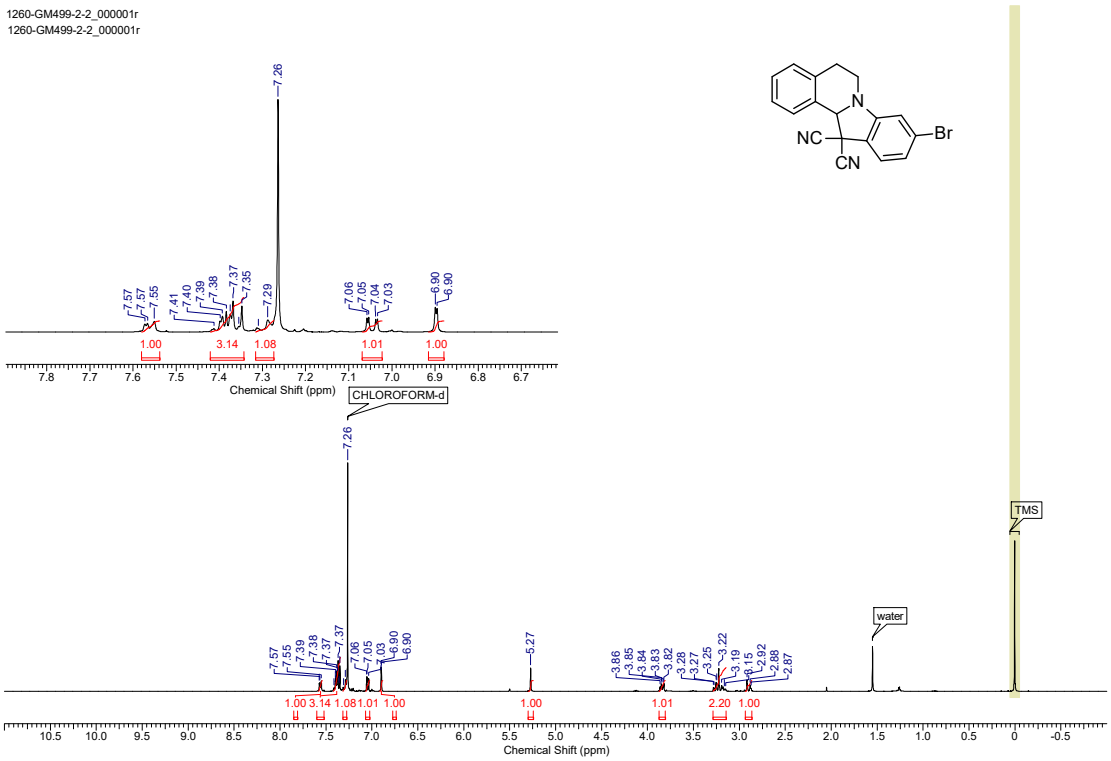


Figure S74. ^{1}H NMR spectrum of compound **4k1**

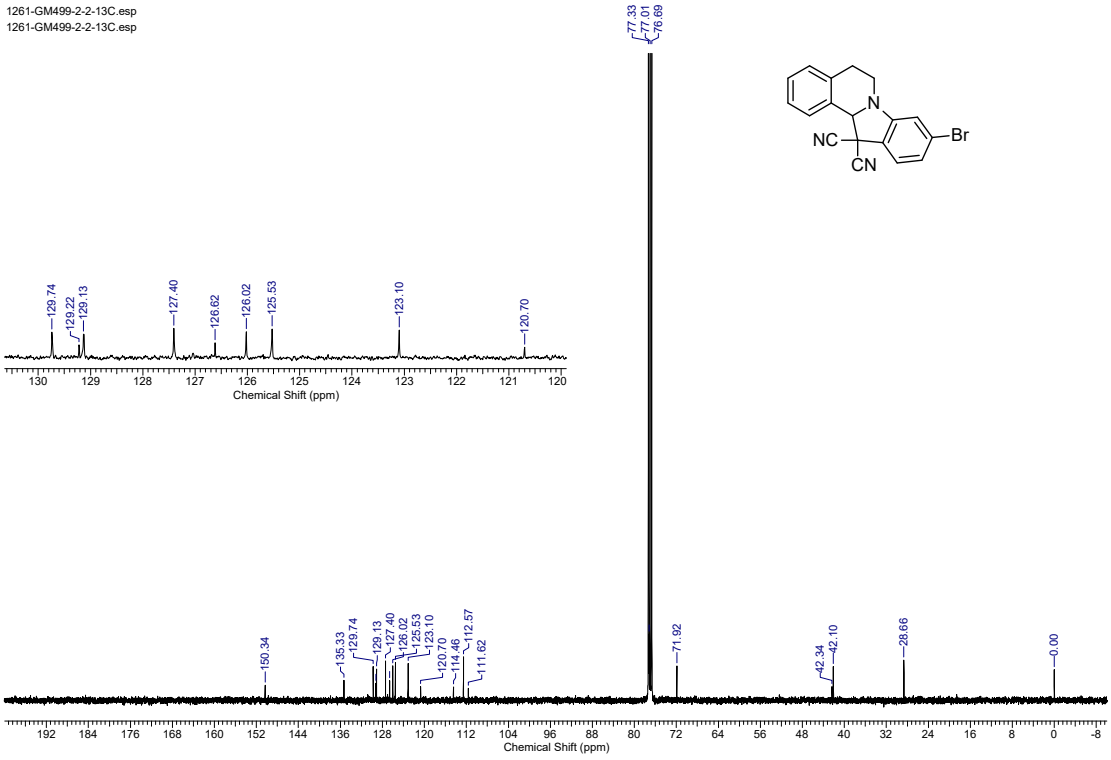


Figure S75. ^{13}C NMR spectrum of compound **4k1**

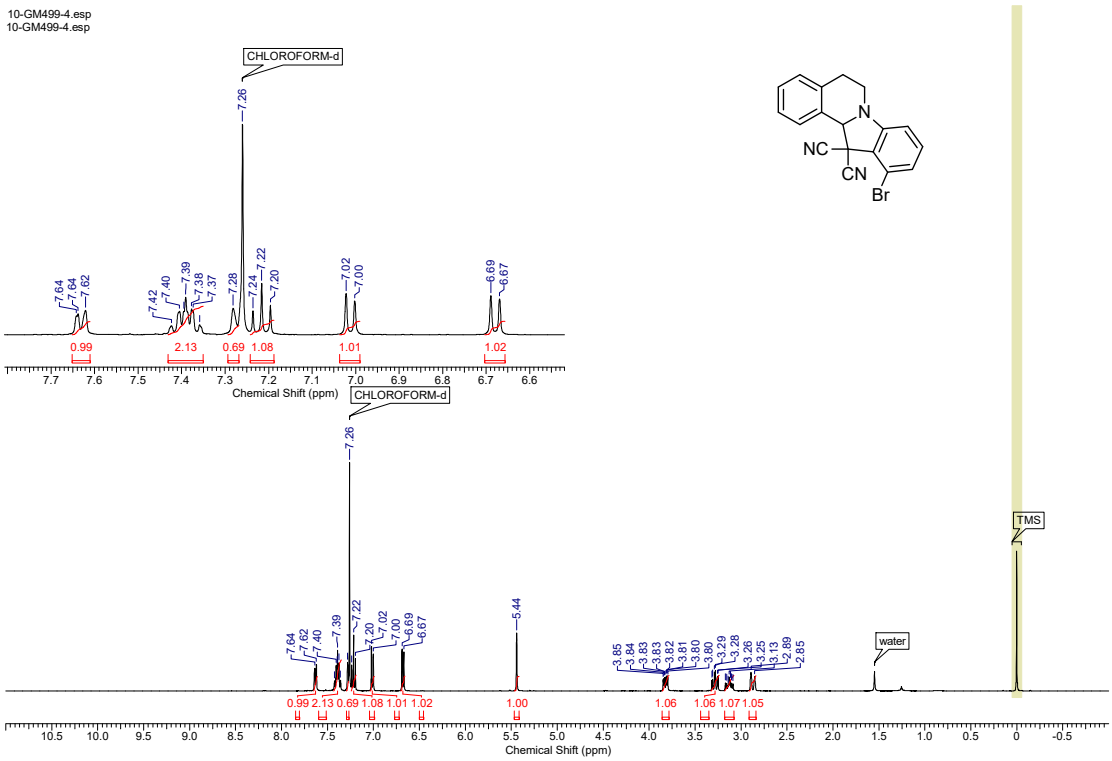


Figure S76. ^{1}H NMR spectrum of compound **4k2**

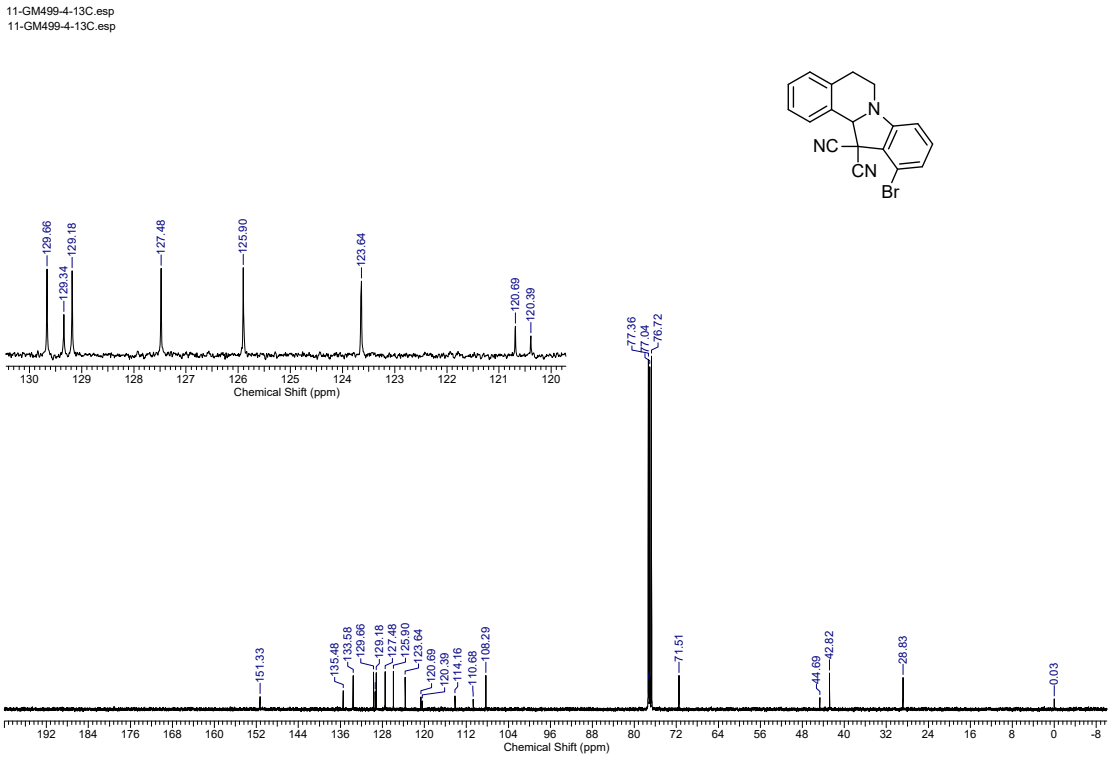


Figure S77. ^{13}C NMR spectrum of compound **4k2**

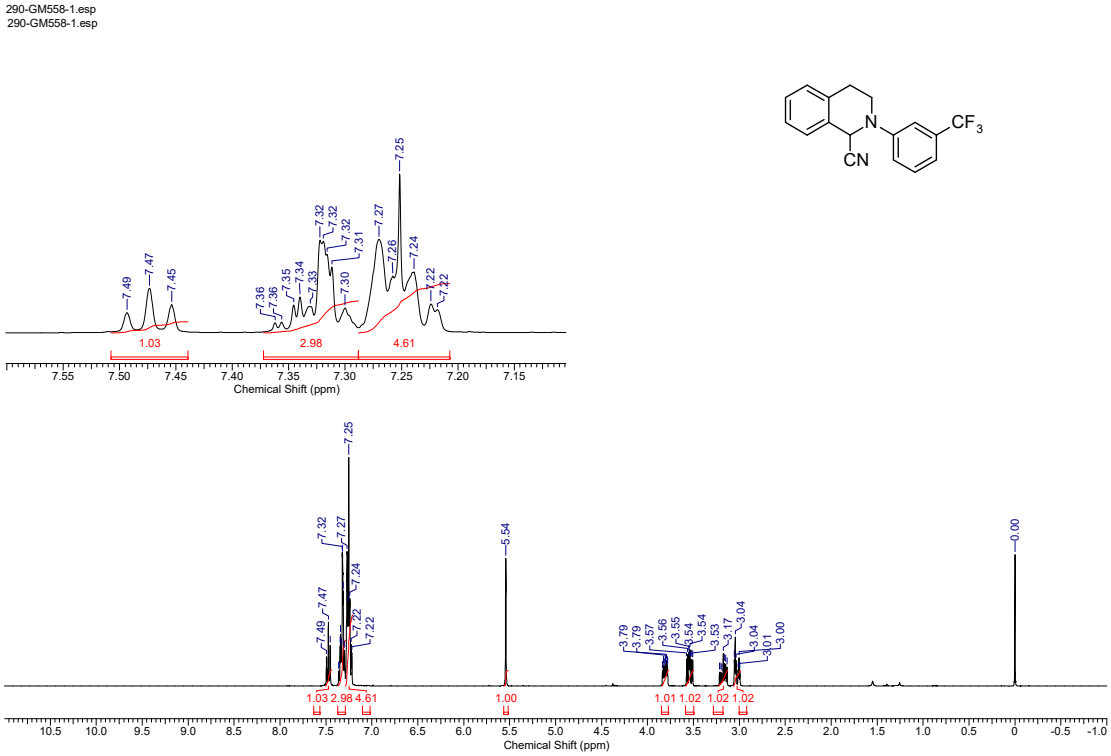


Figure S78. ^{1}H NMR spectrum of compound **3l**

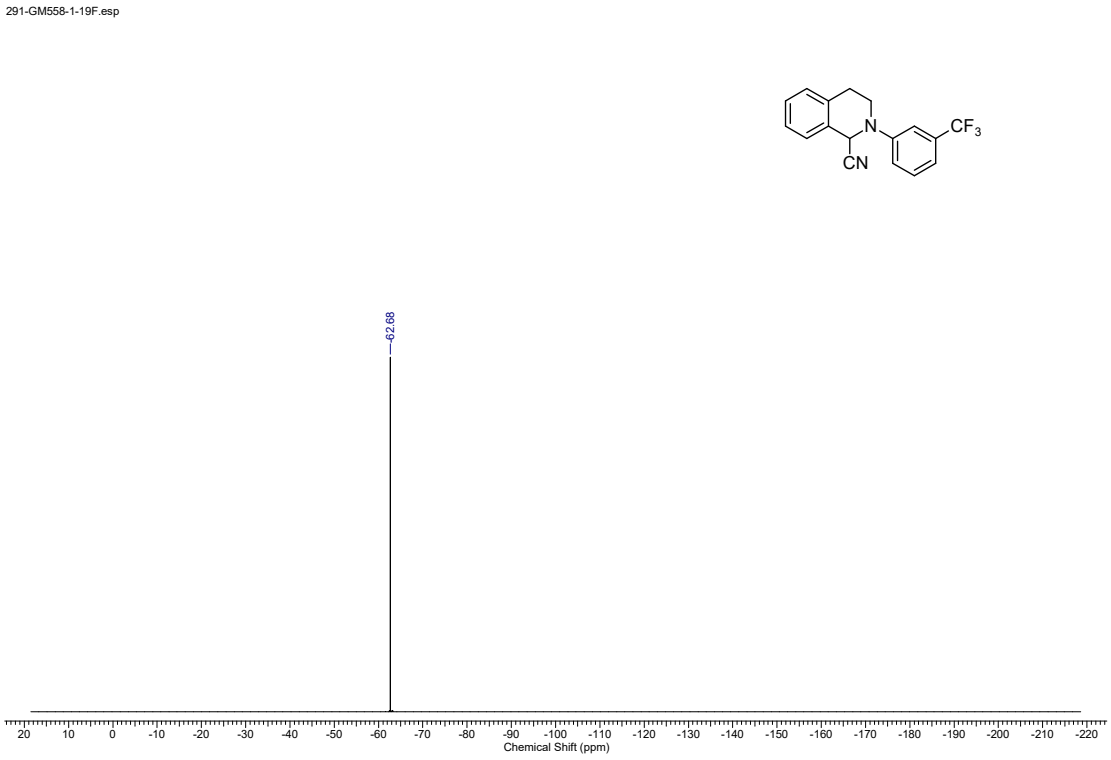


Figure S79. ^{19}F NMR spectrum of compound **3l**

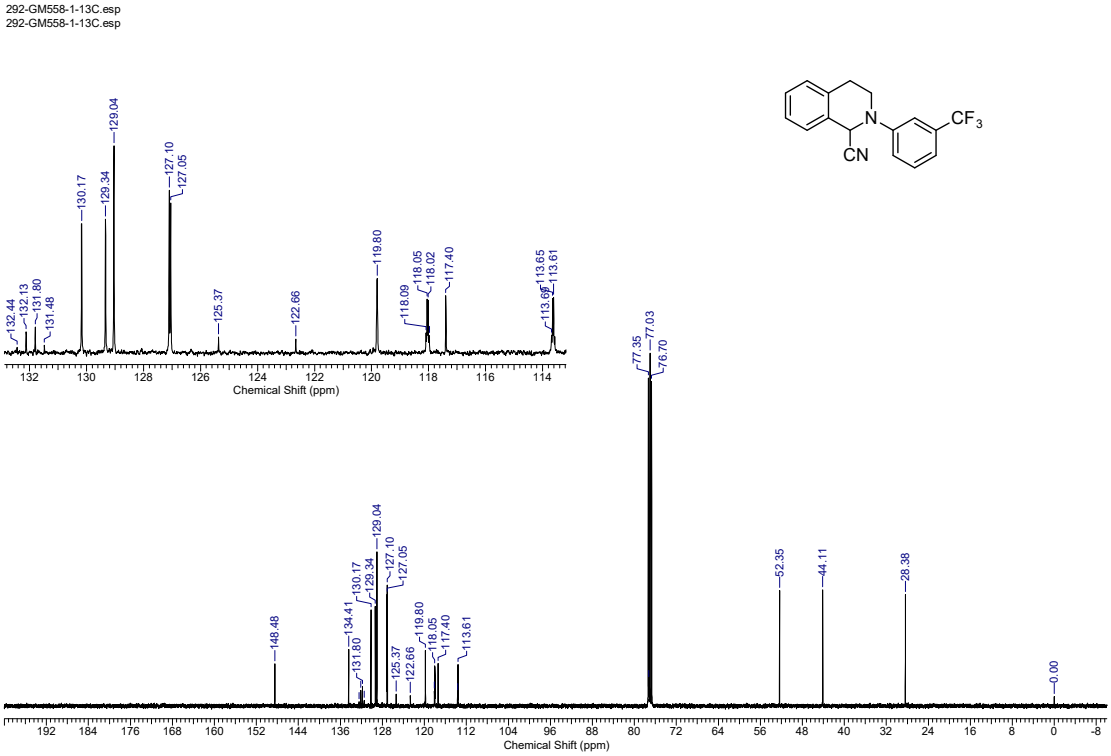


Figure S80. ^{13}C NMR spectrum of compound **3l**

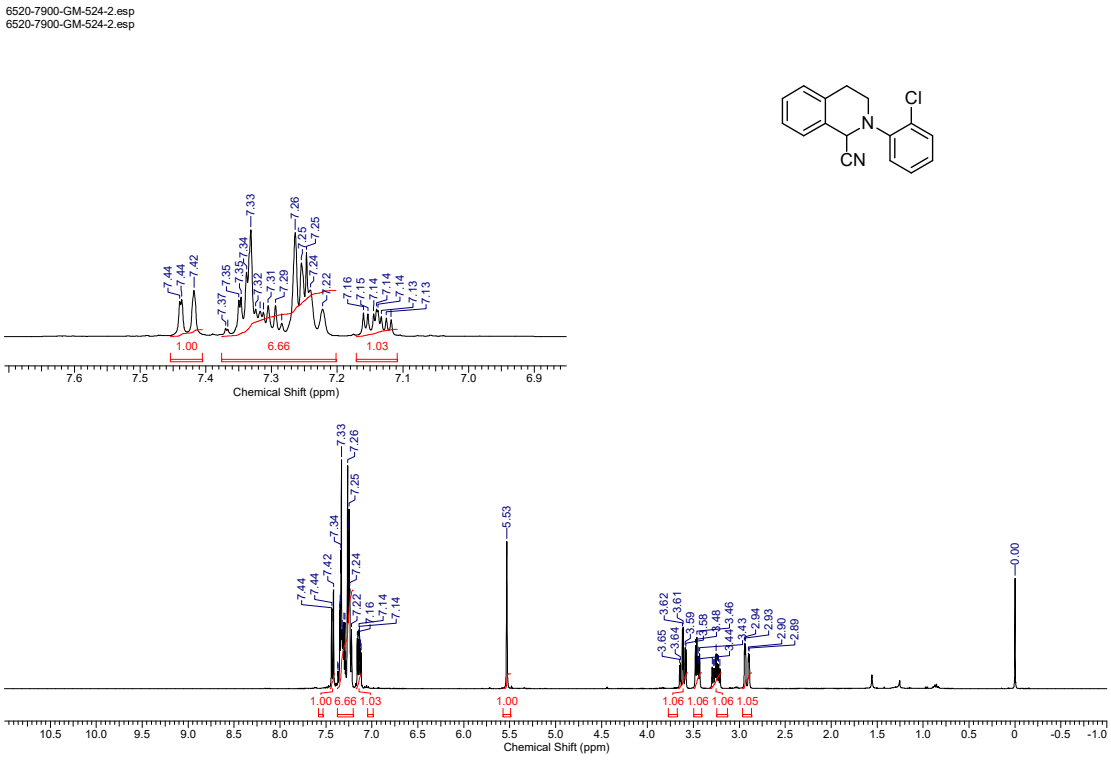


Figure S81. ^{1}H NMR spectrum of compound **3m**

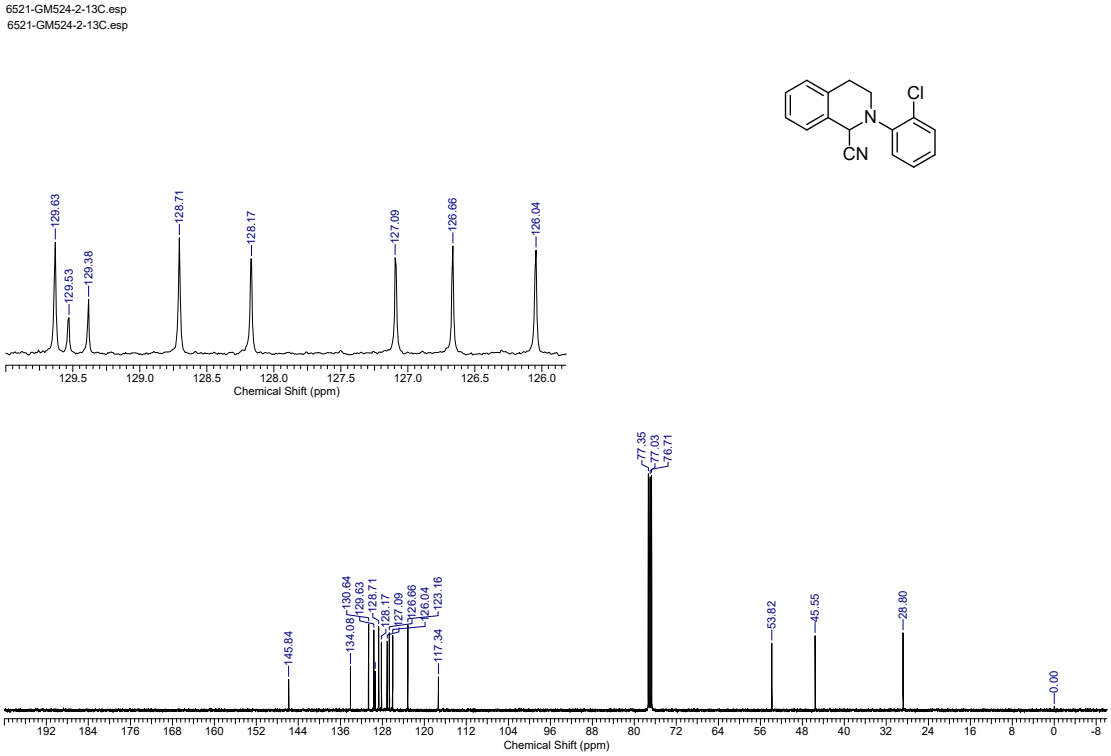


Figure S82. ^{13}C NMR spectrum of compound **3m**

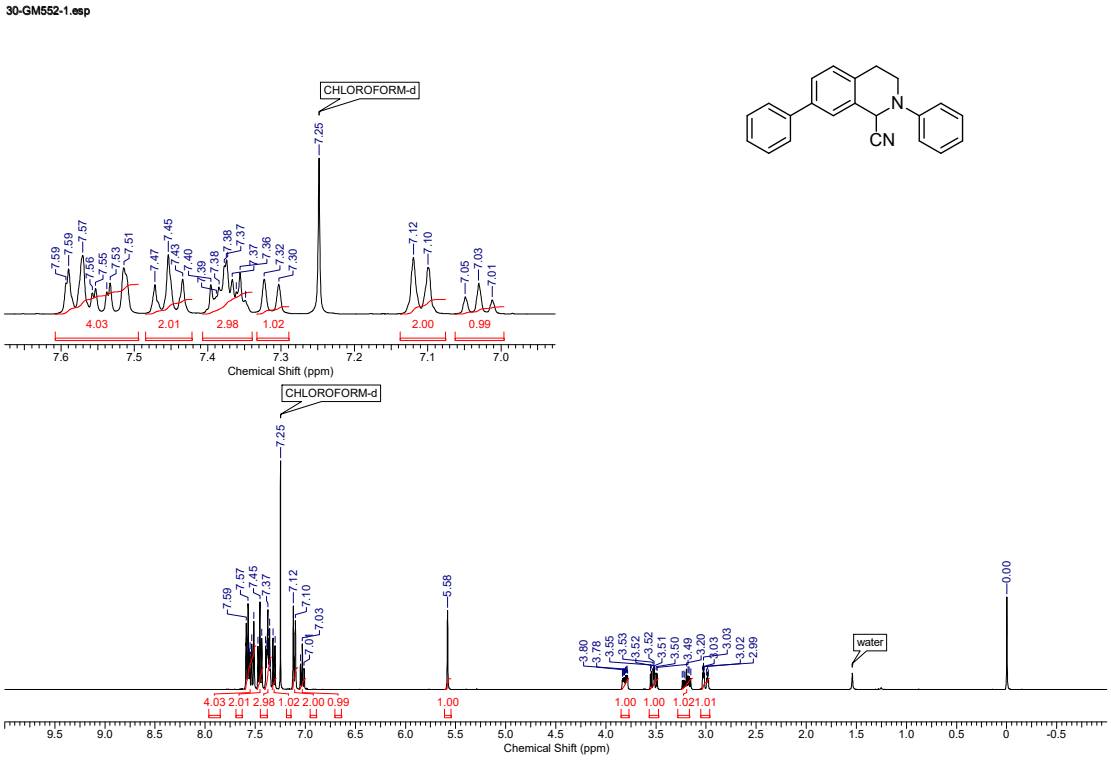


Figure S83. ^{1}H NMR spectrum of compound **3n**

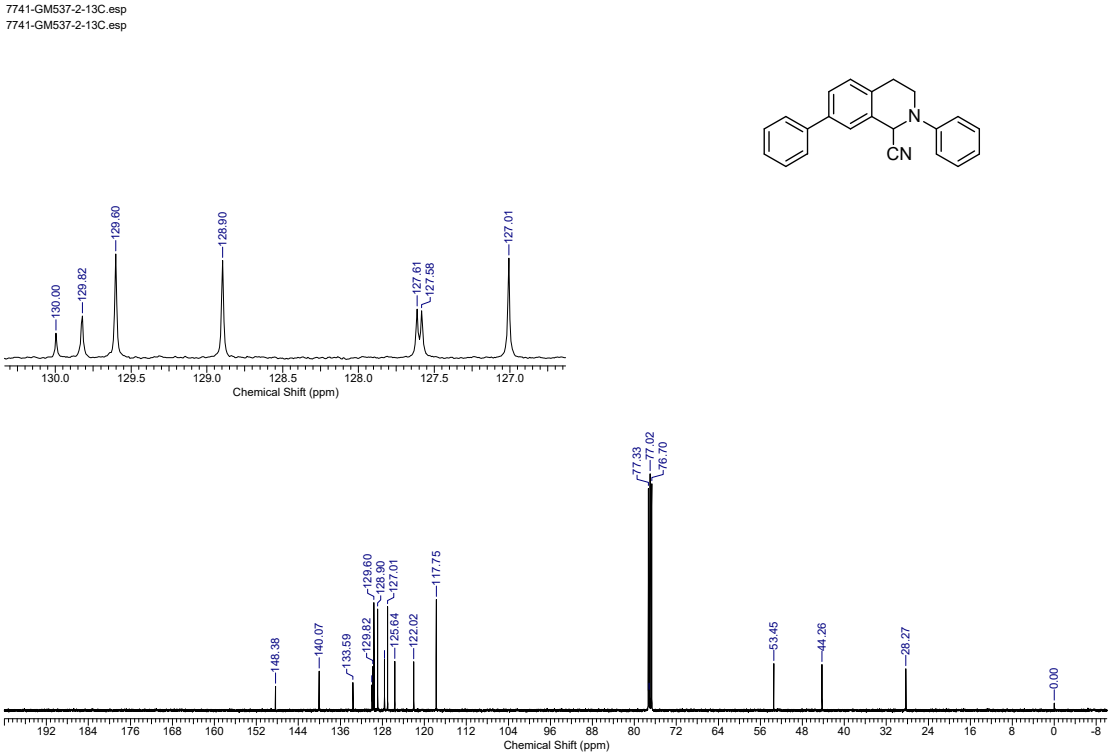


Figure S84. ^{13}C NMR spectrum of compound **3n**

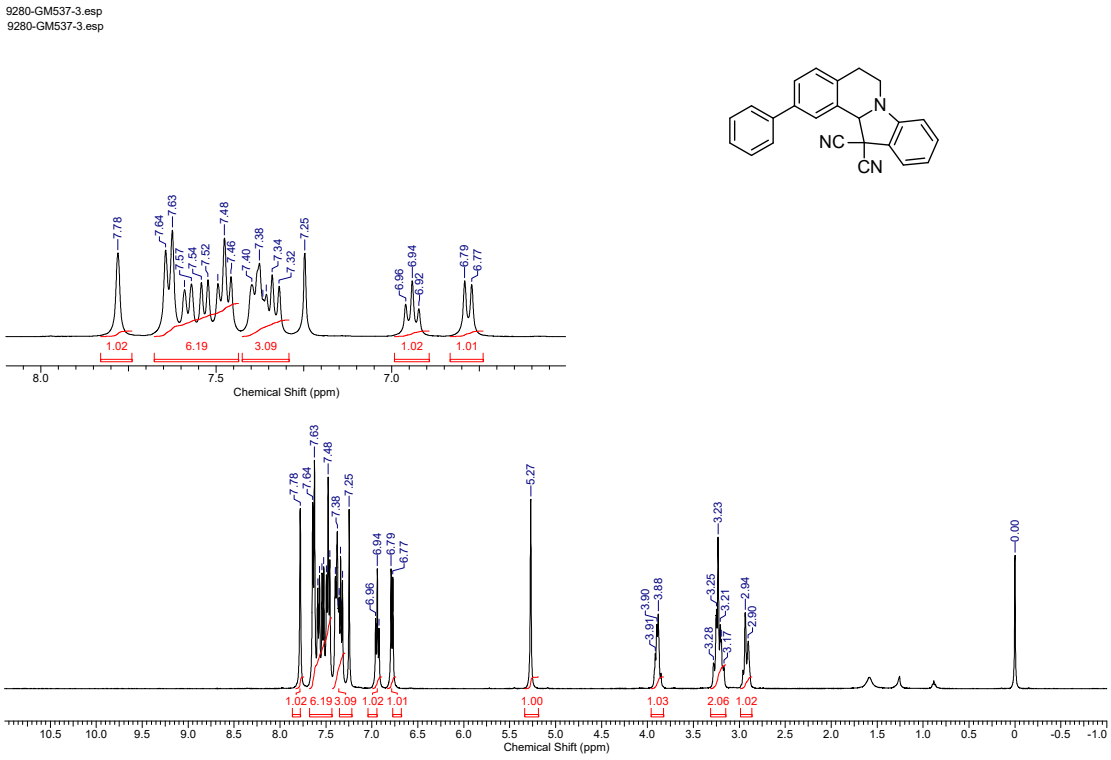


Figure S85. ^{1}H NMR spectrum of compound **4n**

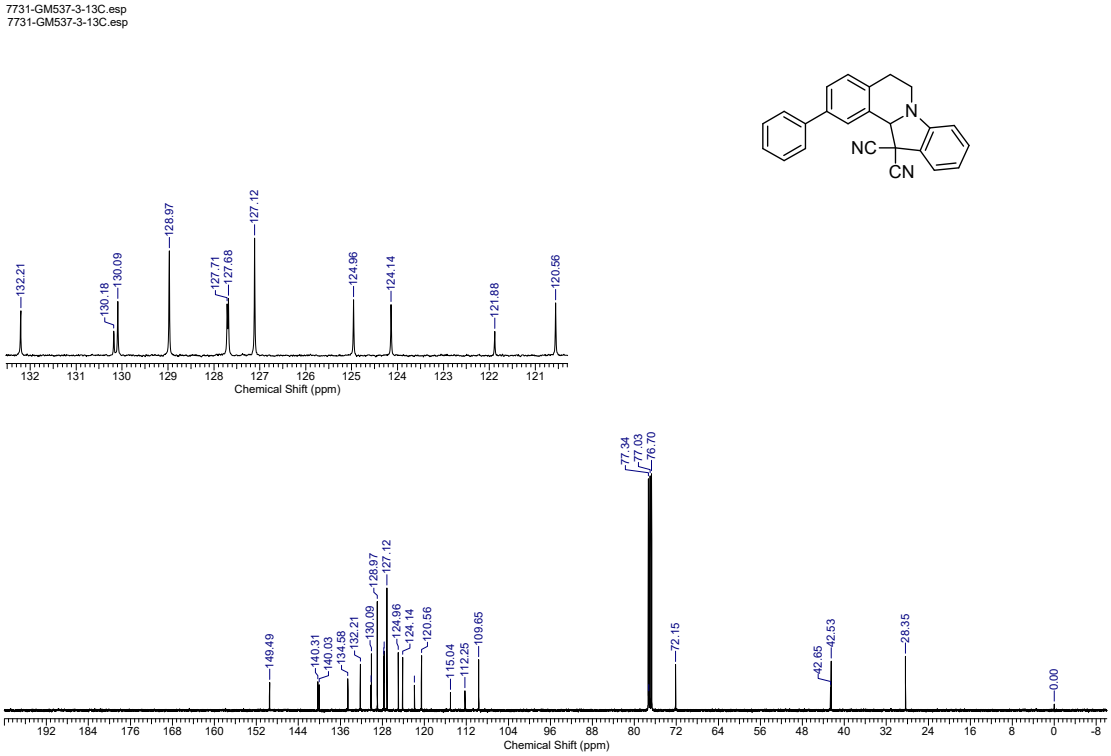


Figure S86. ^{13}C NMR spectrum of compound **4n**

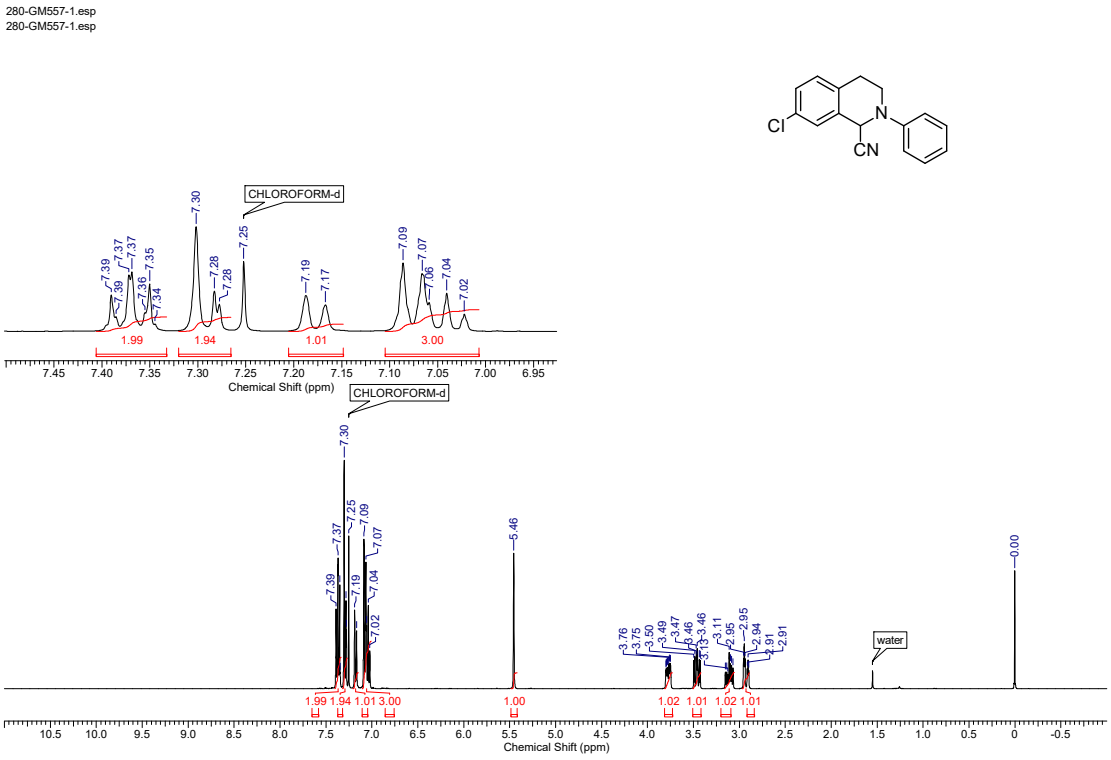


Figure S87. ^{1}H NMR spectrum of compound **3o**

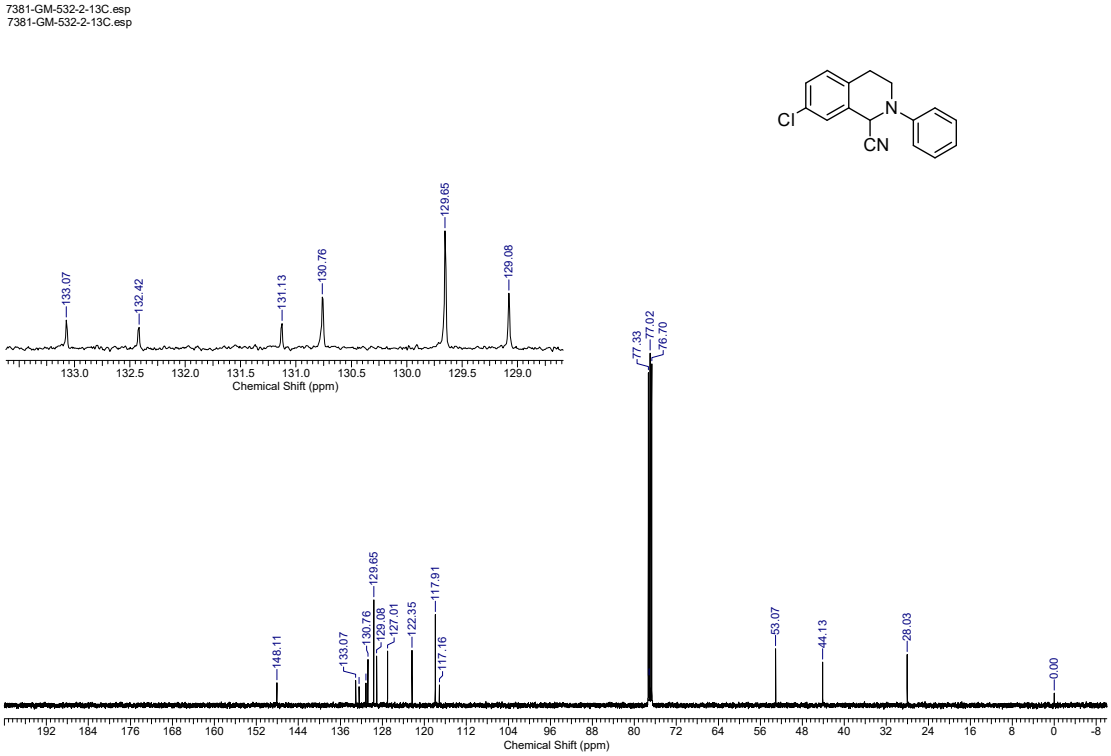


Figure S88. ^{13}C NMR spectrum of compound **3o**

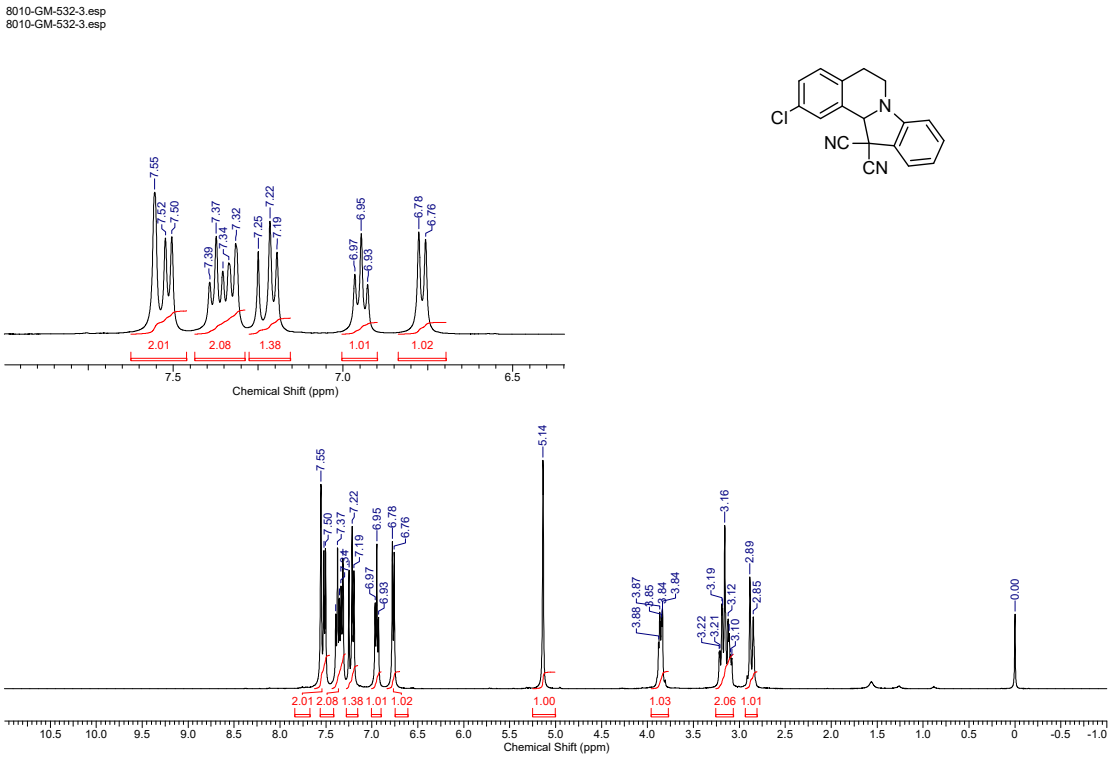


Figure S89. ^{1}H NMR spectrum of compound **4o**

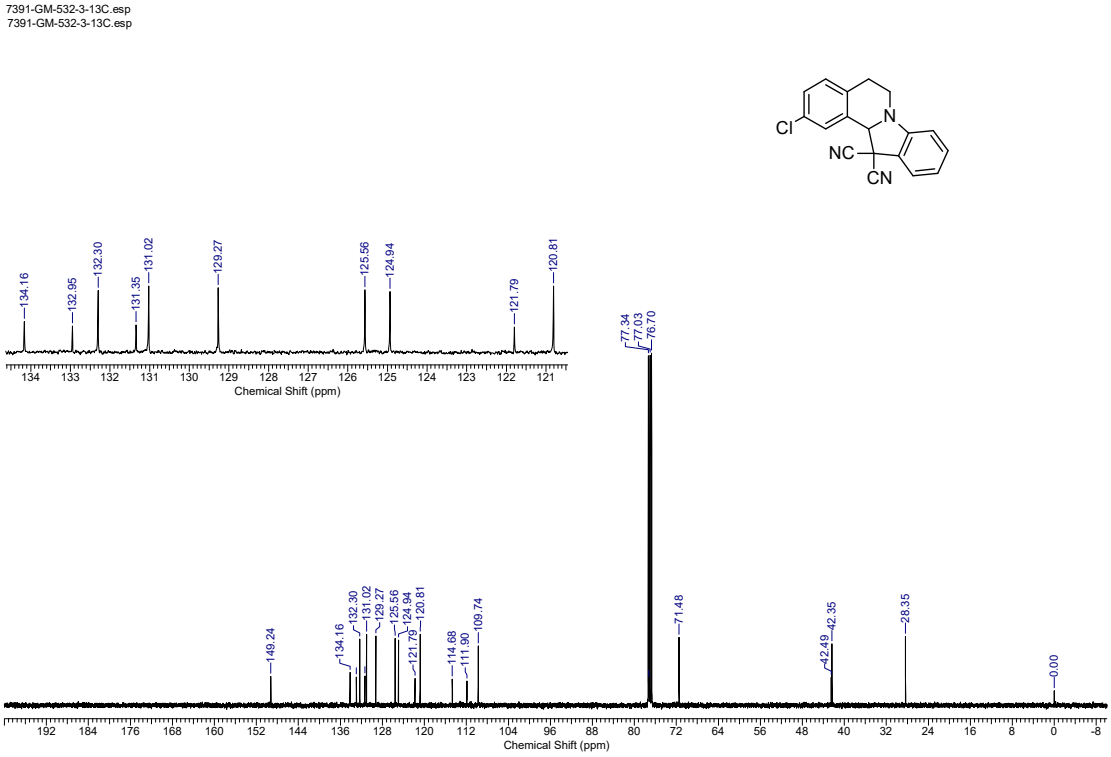


Figure S90. ^{13}C NMR spectrum of compound **4o**

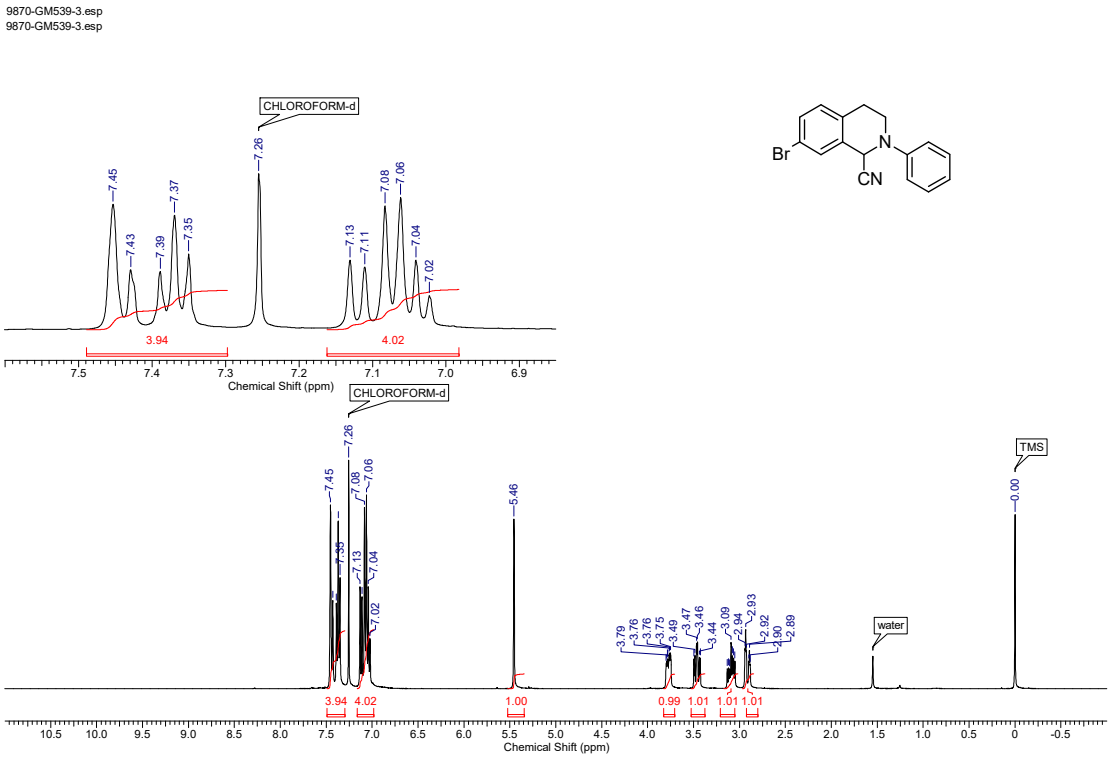


Figure S91. ^{1}H NMR spectrum of compound **3p**

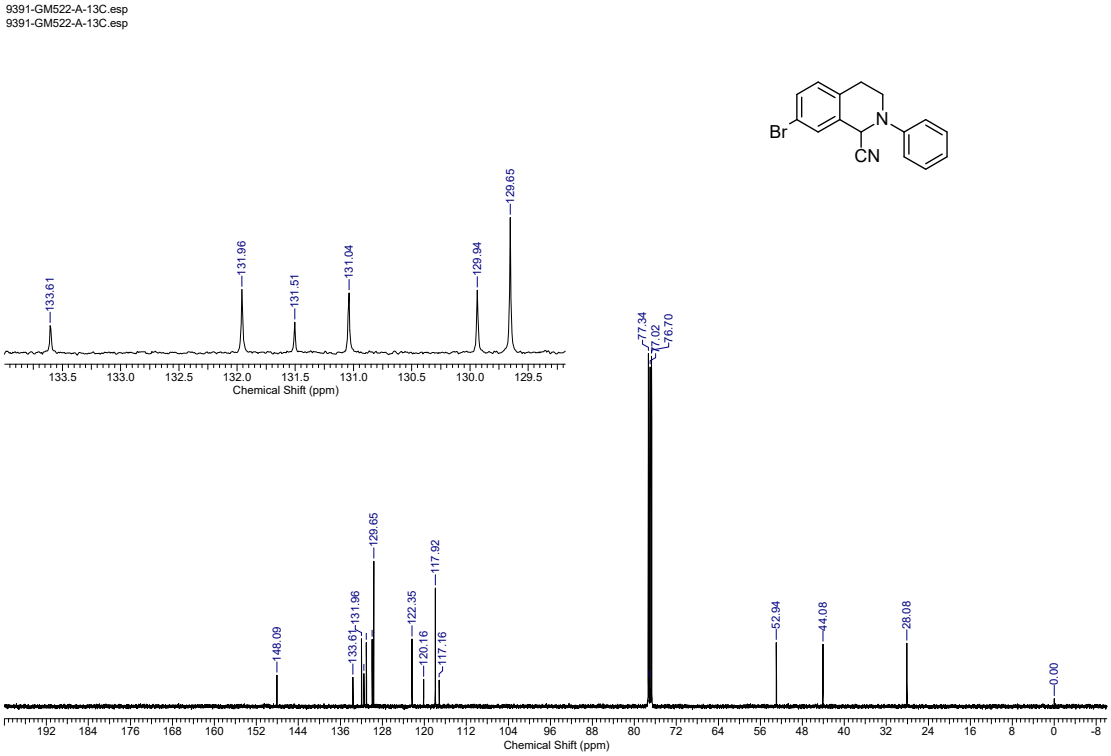


Figure S92. ^{13}C NMR spectrum of compound **3p**

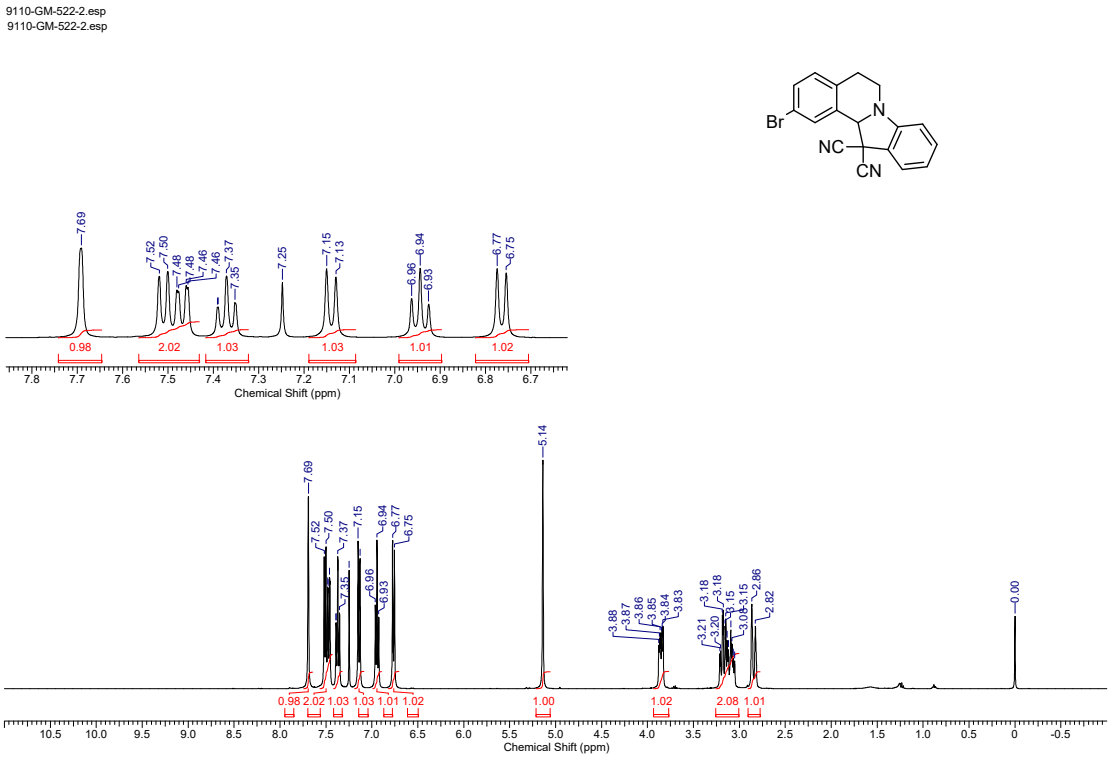


Figure S93. ^{1}H NMR spectrum of compound **4p**

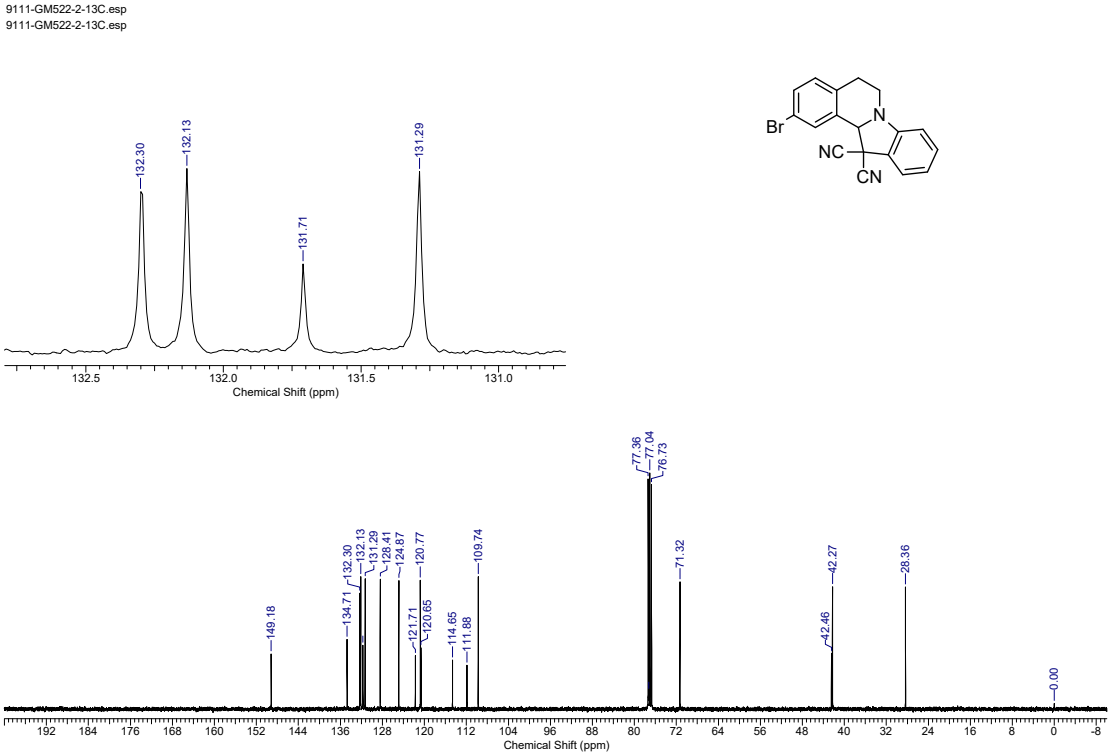


Figure S94. ^{13}C NMR spectrum of compound **4p**

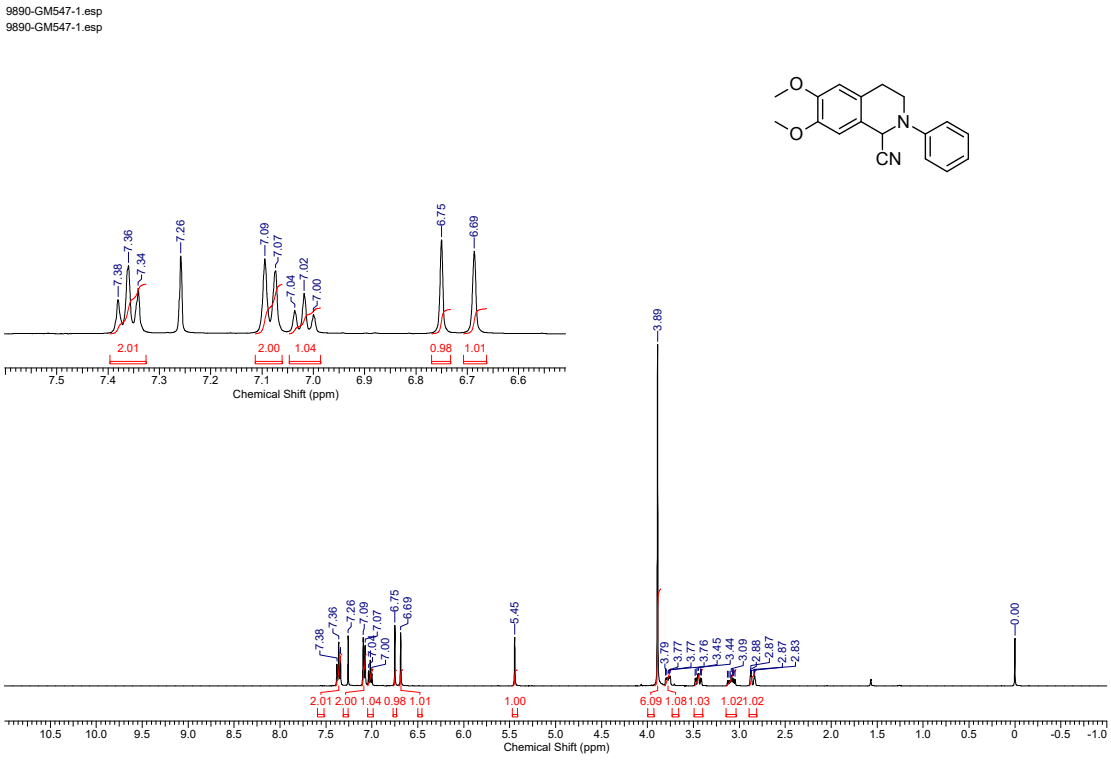


Figure S95. ^{1}H NMR spectrum of compound **3q**

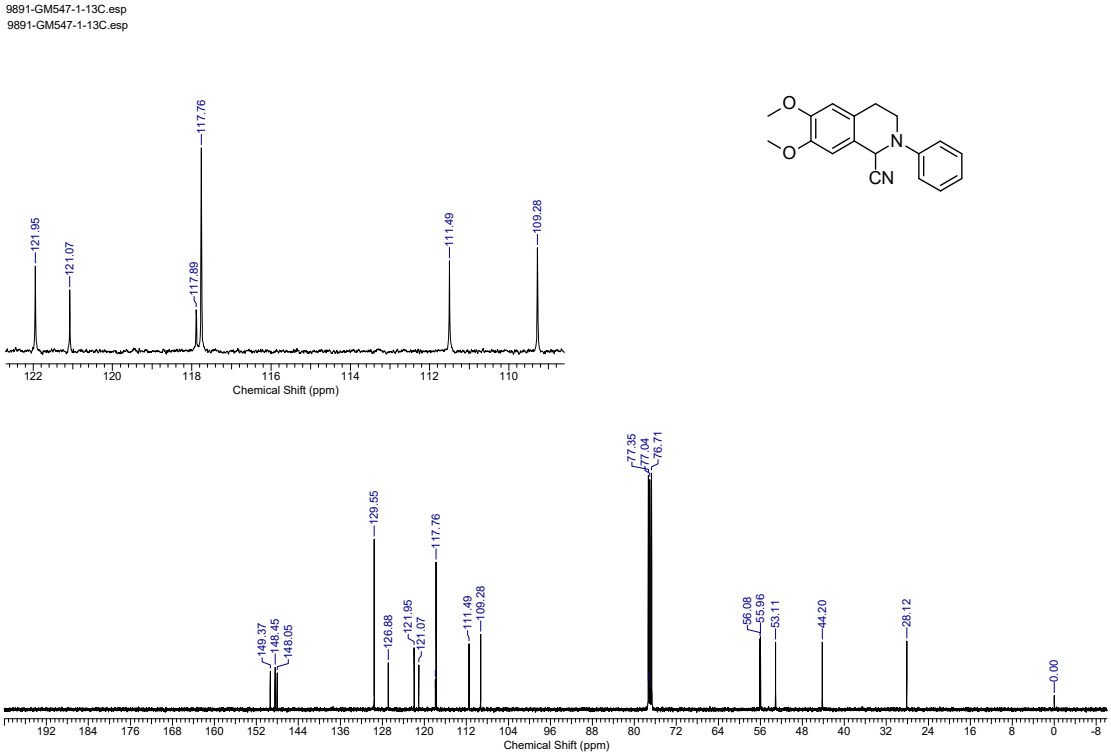


Figure S96. ^{13}C NMR spectrum of compound **3q**

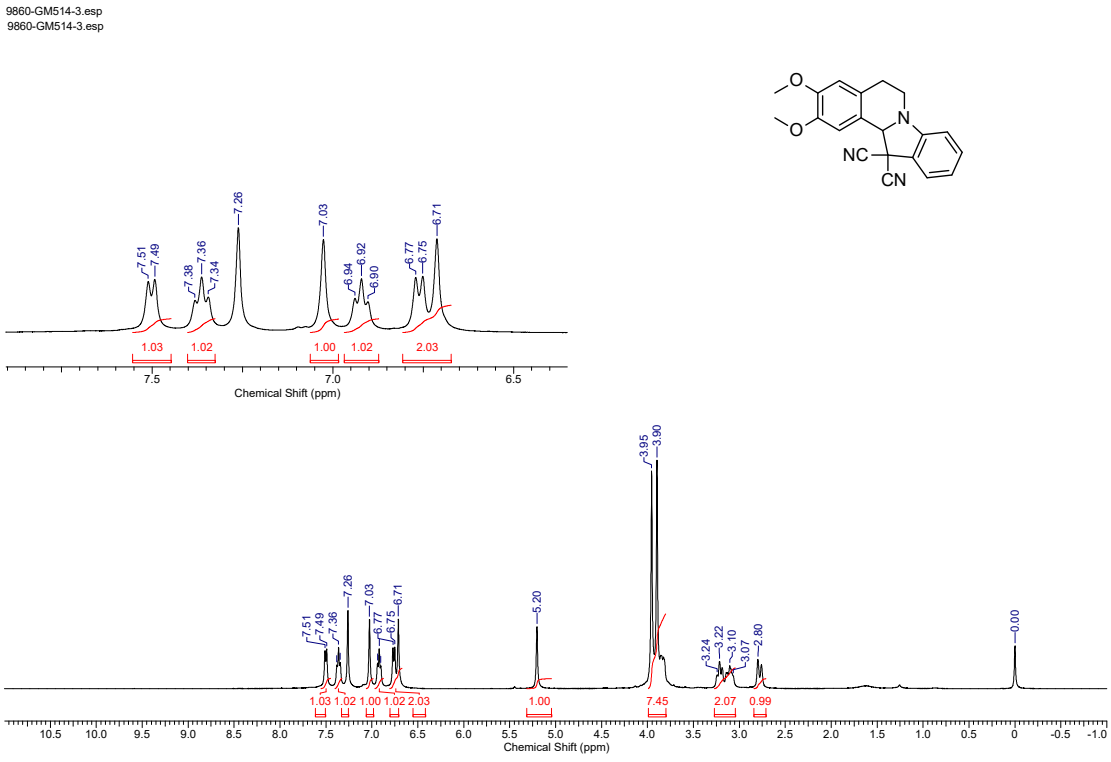


Figure S97. ^{1}H NMR spectrum of compound **4q**

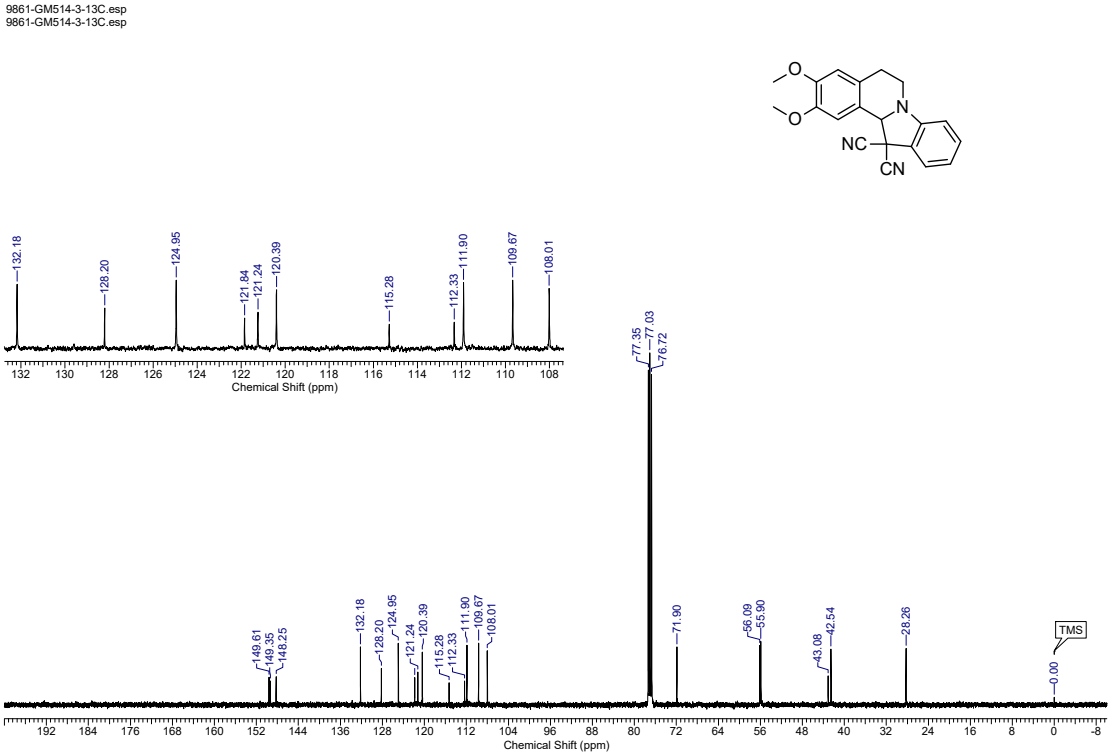


Figure S98. ^{13}C NMR spectrum of compound **4q**

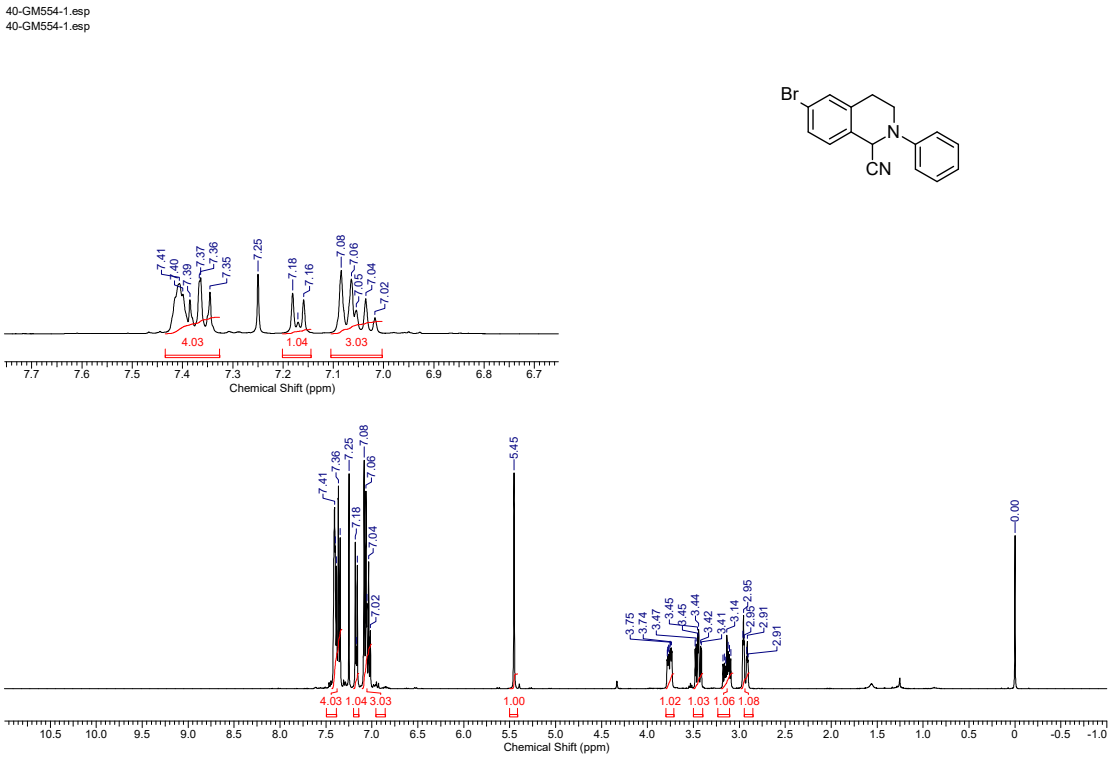


Figure S99. ^{1}H NMR spectrum of compound **3r**

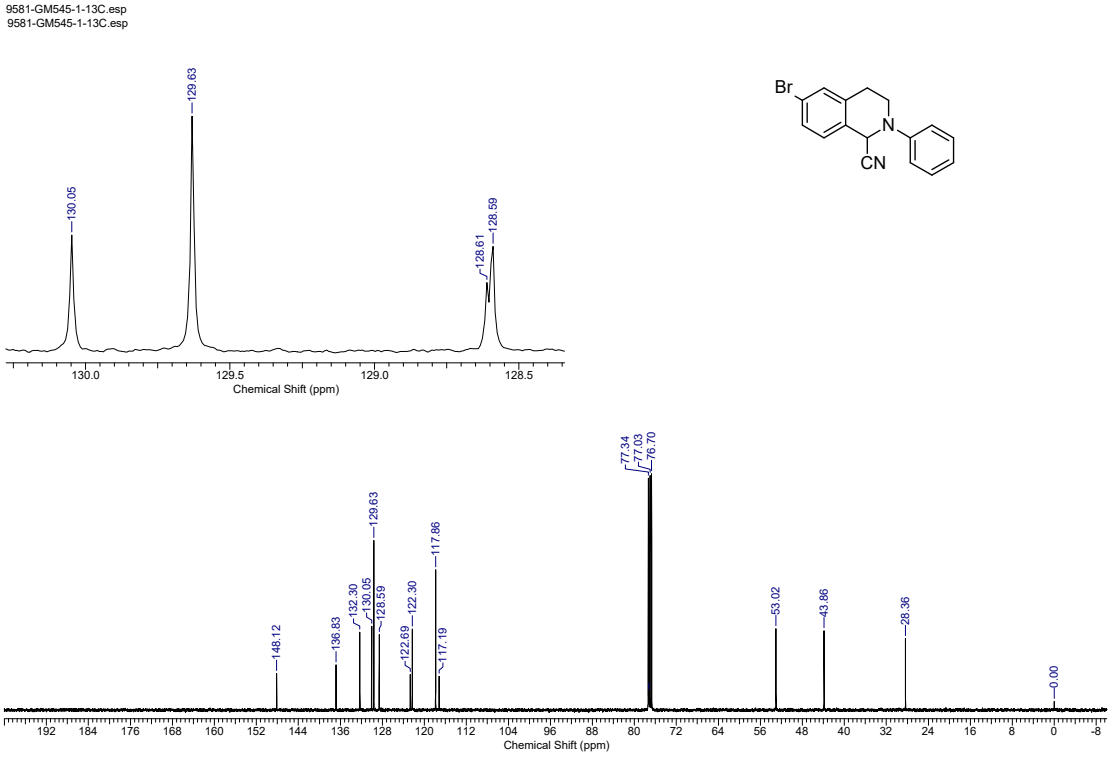


Figure S100. ^{13}C NMR spectrum of compound **3r**

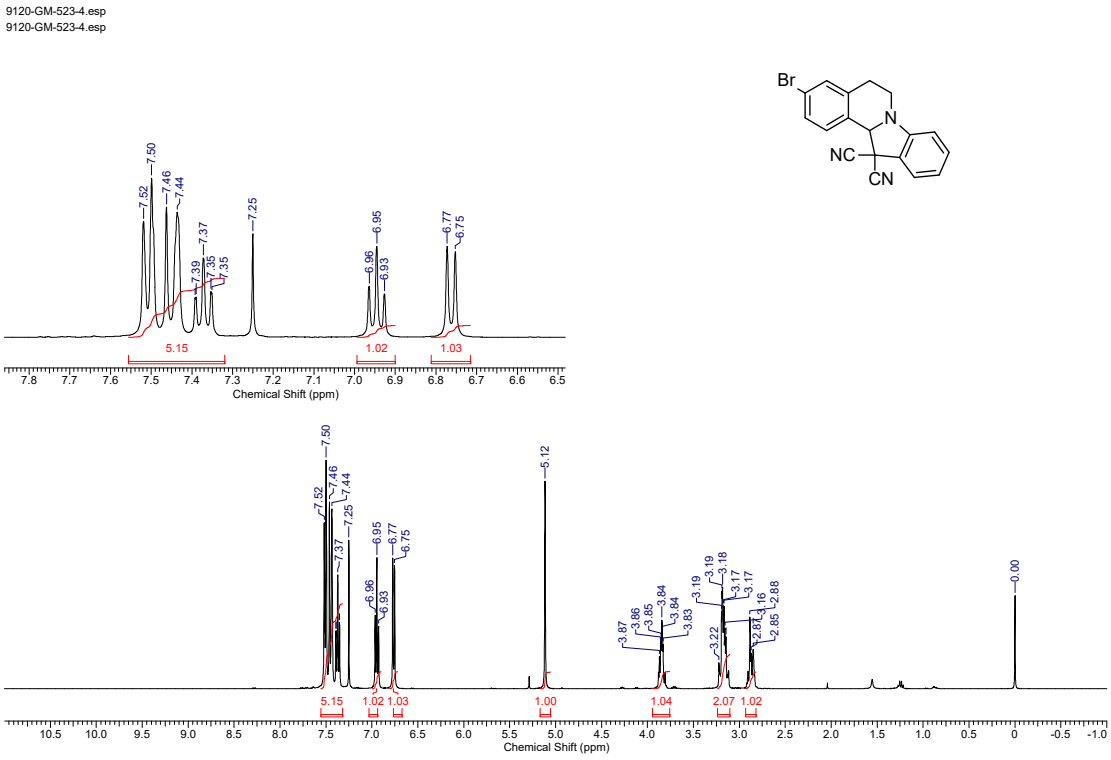


Figure S101. ^{1}H NMR spectrum of compound **4r**

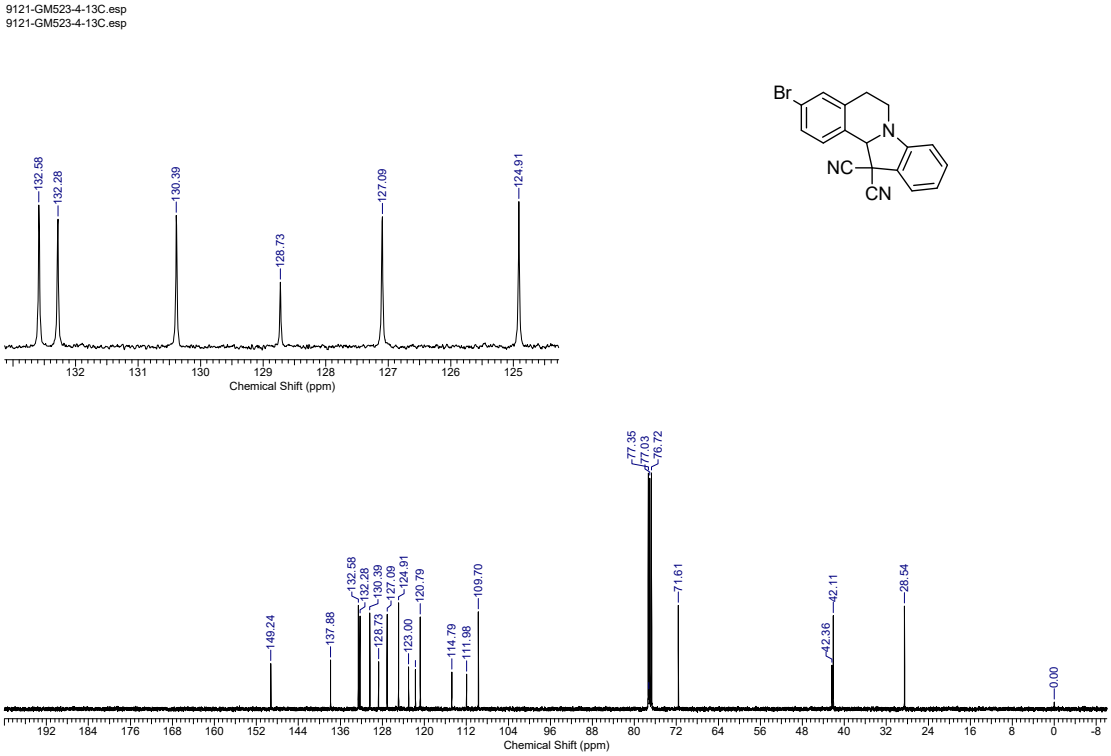


Figure S102. ^{13}C NMR spectrum of compound **4r**

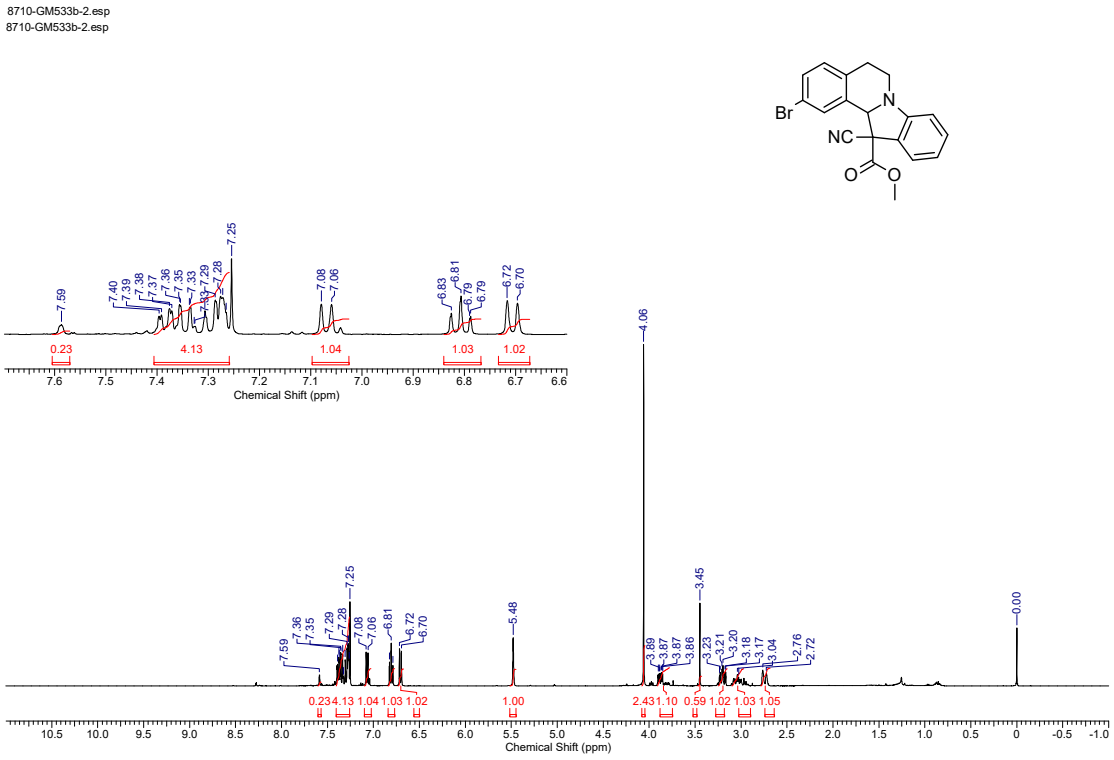


Figure S103. ^{1}H NMR spectrum of compound **4s**

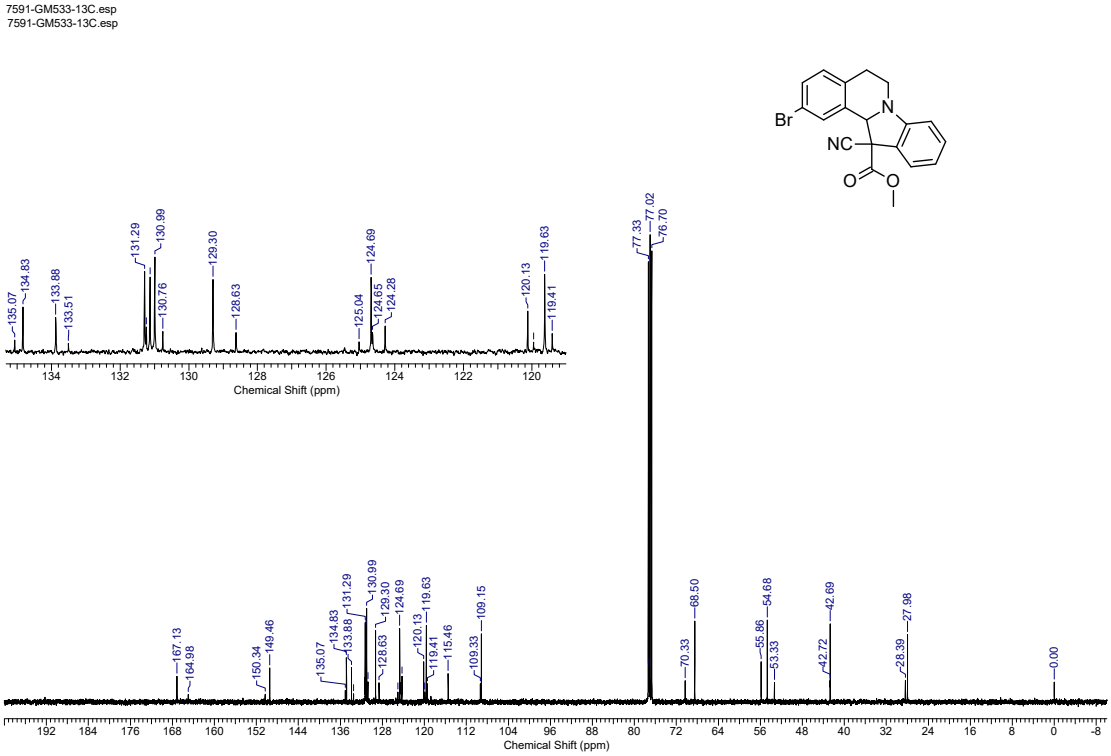


Figure S104. ^{13}C NMR spectrum of compound **4s**

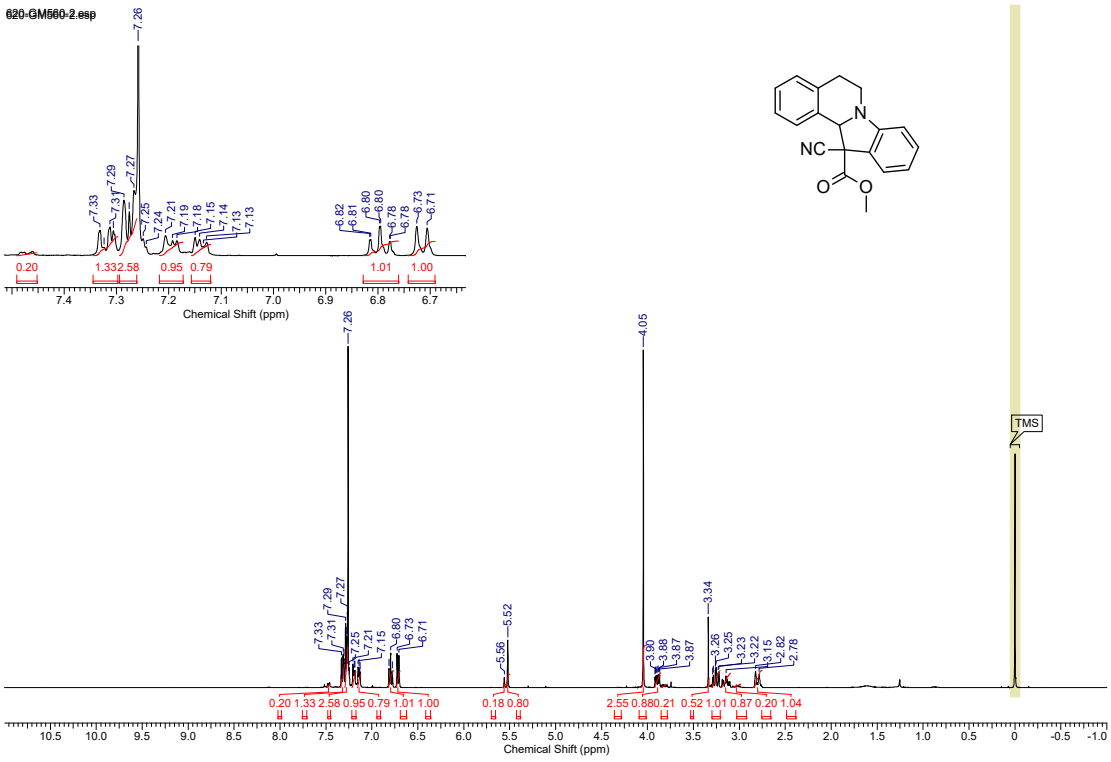


Figure S105. ^{1}H NMR spectrum of compound **4t**

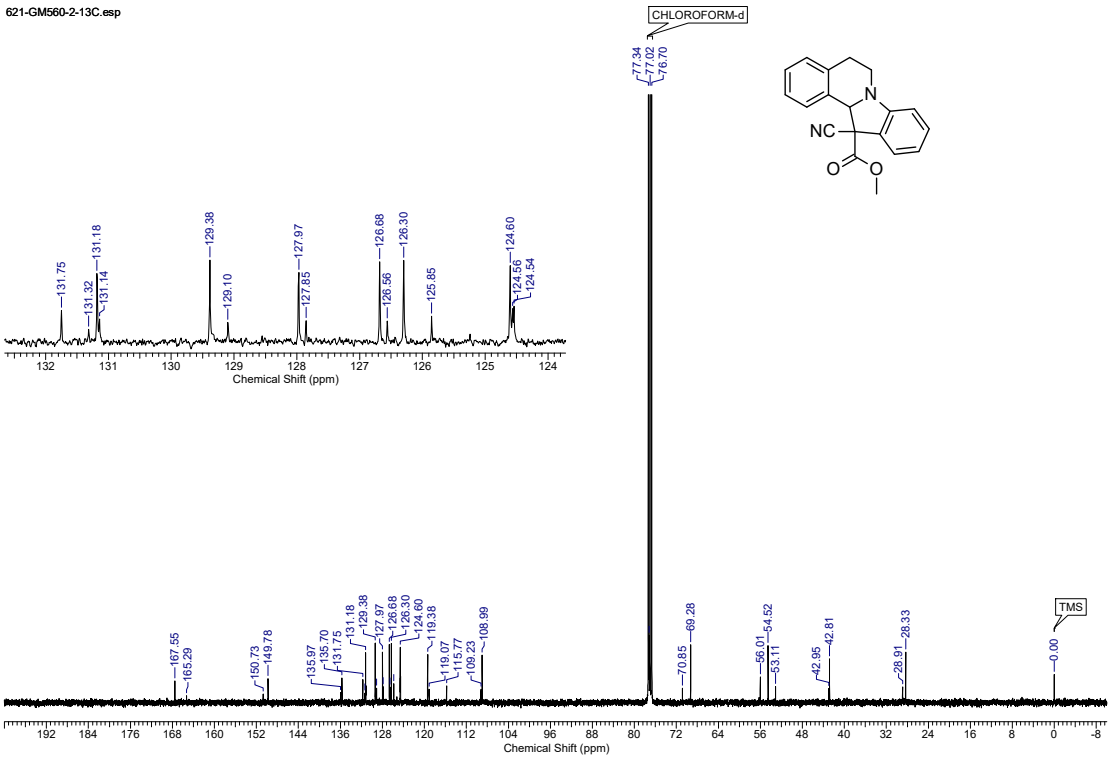


Figure S106. ^{13}C NMR spectrum of compound **4t**

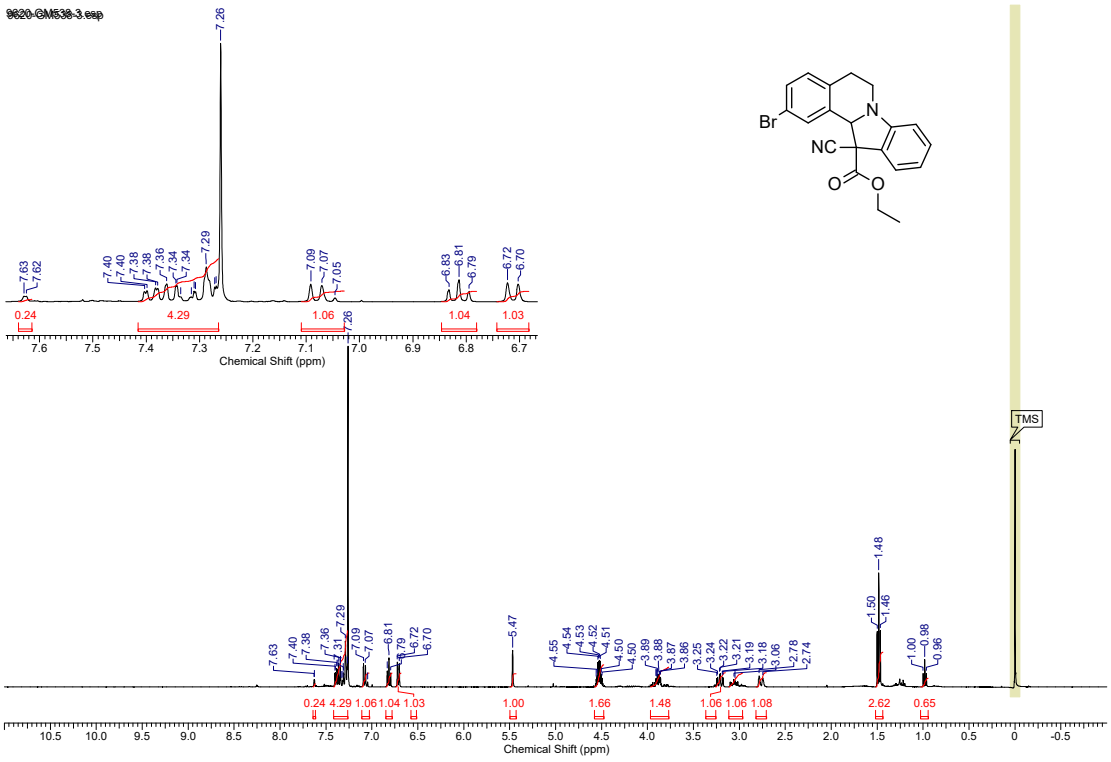


Figure S107. ^{1}H NMR spectrum of compound **4u**

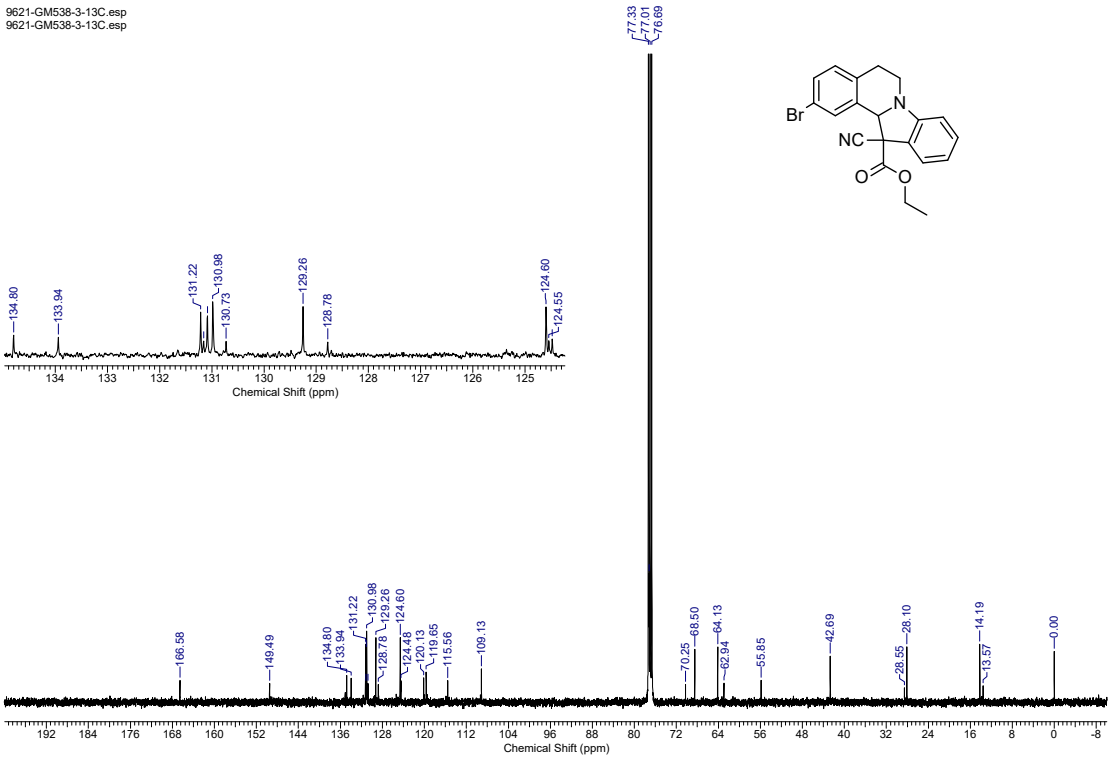


Figure S108. ^{13}C NMR spectrum of compound **4u**

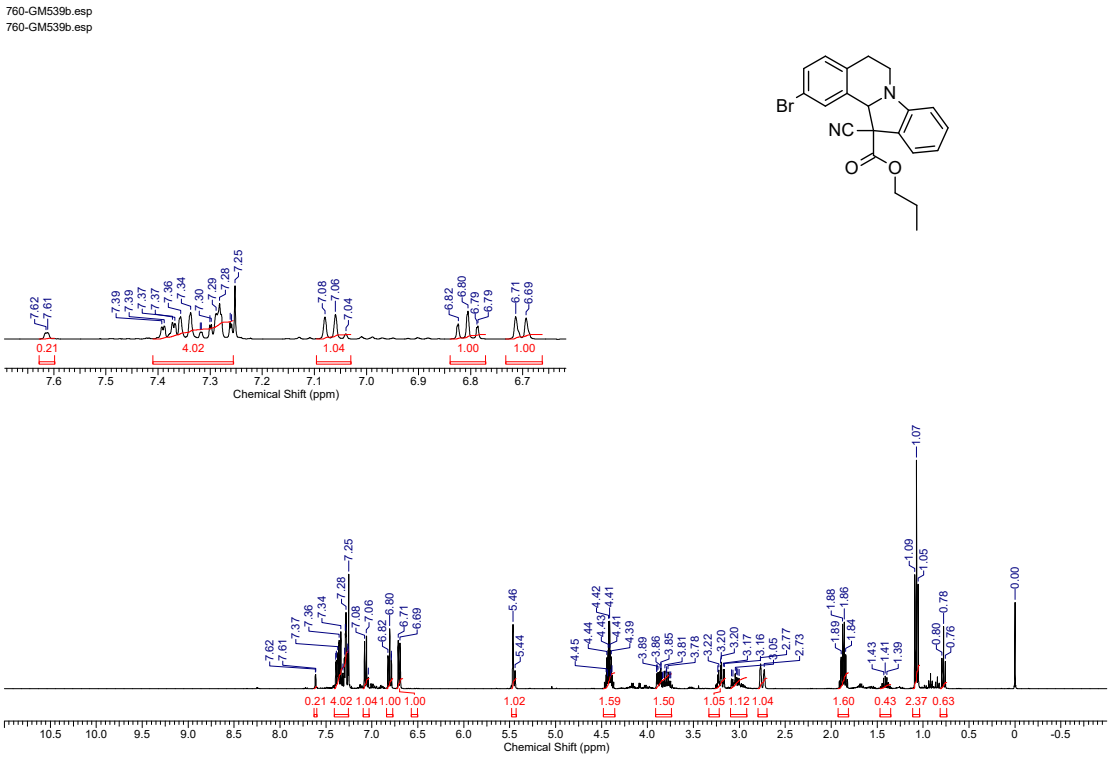


Figure S109. ^{1}H NMR spectrum of compound **4v**

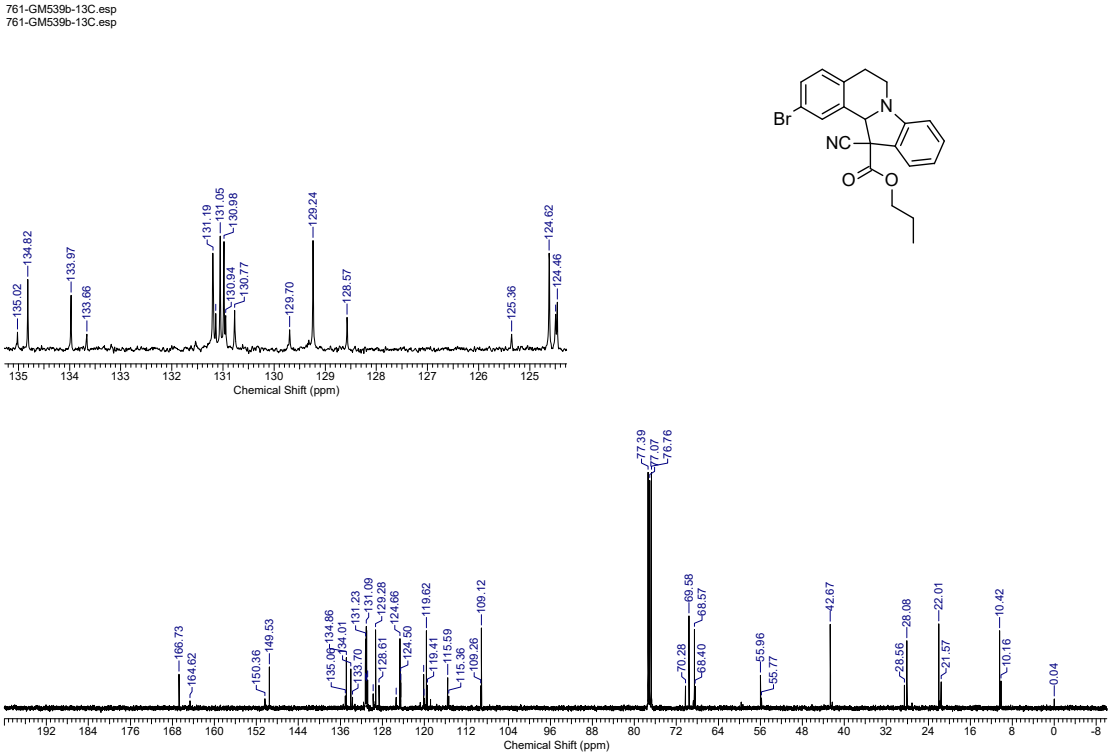


Figure S110. ^{13}C NMR spectrum of compound **4v**

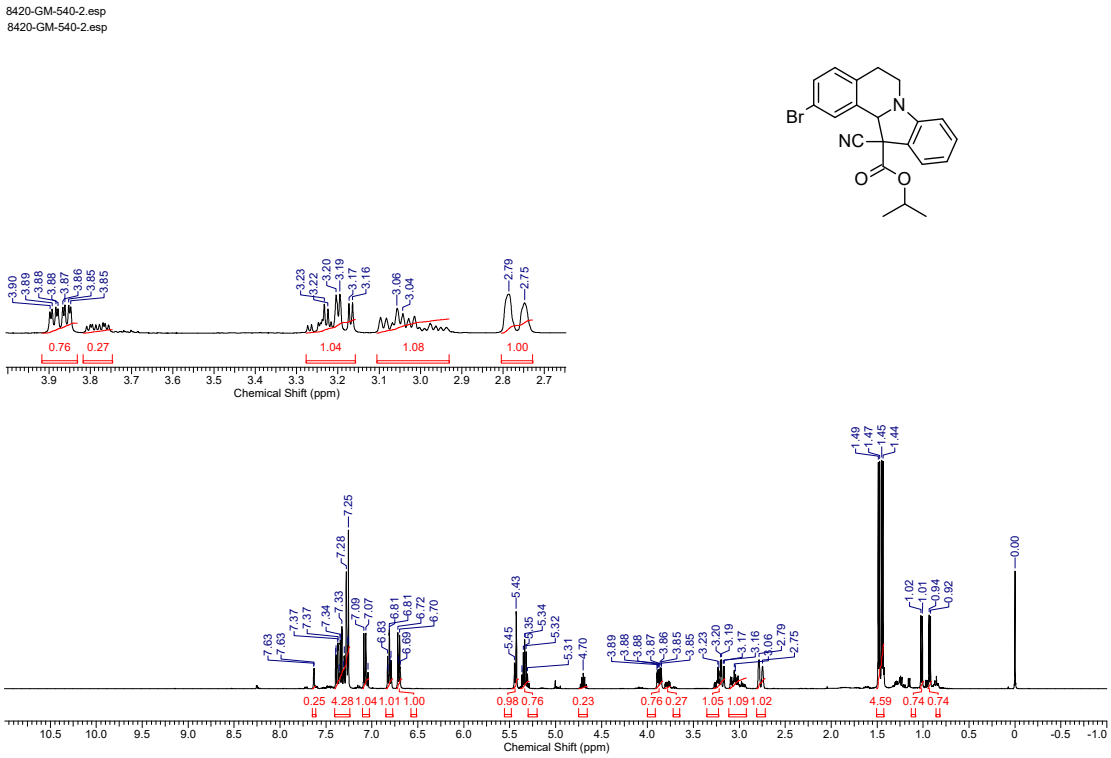


Figure S111. ^{1}H NMR spectrum of compound **4w**

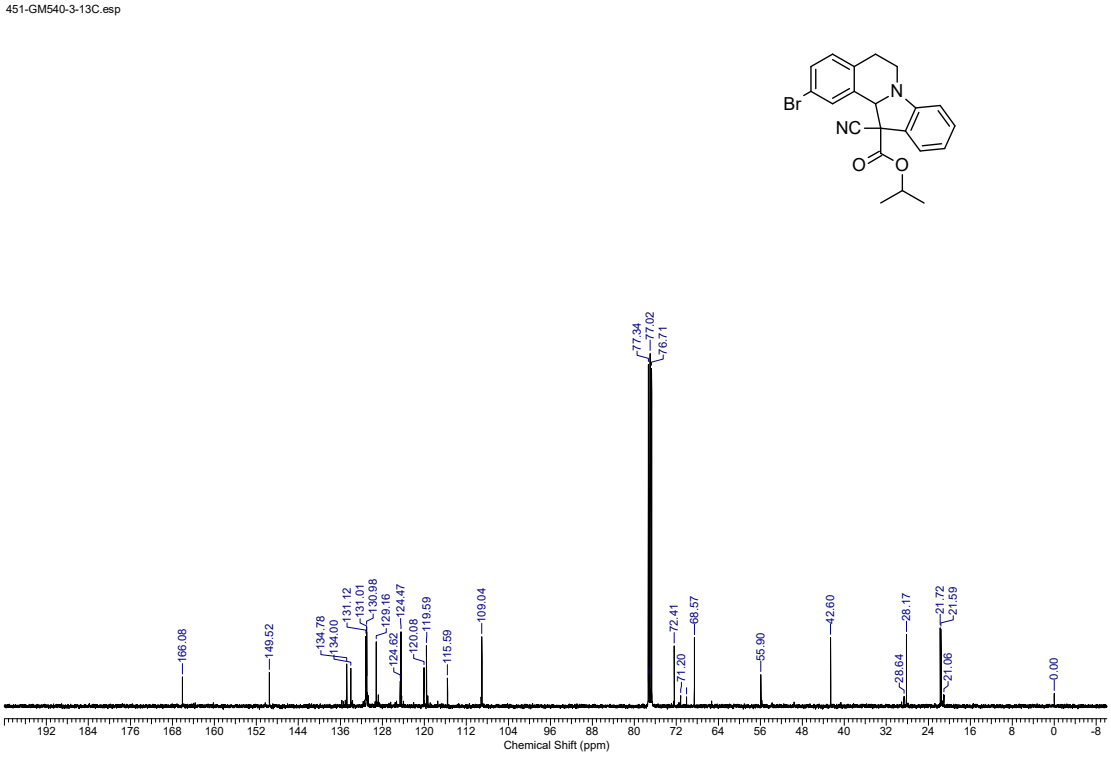


Figure S112. ^{13}C NMR spectrum of compound **4w**

2. Crystallographic Analysis: Determination of Structure of 4a, 4j1 and 4s

1) Structure determination of **4a**

The structure of **4a** was determined by the X-ray diffraction. Recrystallized from dichloromethane/EtOH. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2077460.

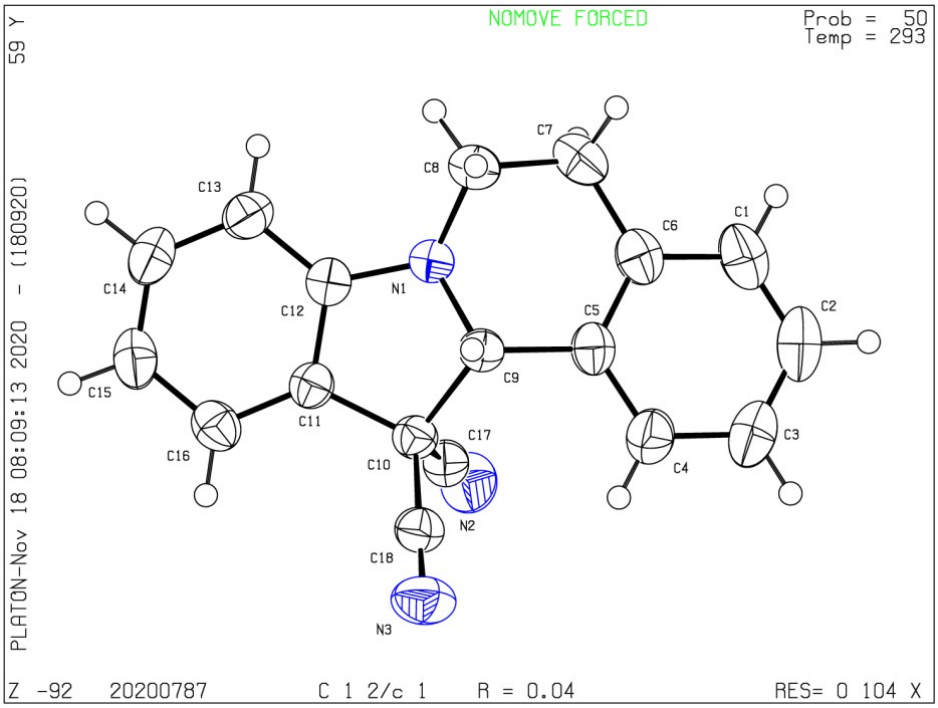


Table S1. Crystal data and structure refinement for 4a.

Identification code	20200787
Empirical formula	C18H13N3
Formula weight	271.31
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	10.9525(3)
b/Å	12.9657(4)
c/Å	20.7069(7)
α/°	90
β/°	103.542(3)
γ/°	90
Volume/Å3	2858.76(16)
Z	8
ρcalcg/cm3	1.261
μ/mm-1	0.600

F(000)	1136.0
Crystal size/mm3	0.18 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.786 to 134.144
Index ranges	-12 ≤ h ≤ 13, -15 ≤ k ≤ 12, -24 ≤ l ≤ 18
Reflections collected	5277
Independent reflections	2555 [Rint = 0.0257, Rsigma = 0.0323]
Data/restraints/parameters	2555/0/190
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0439, wR2 = 0.1125
Final R indexes [all data]	R1 = 0.0544, wR2 = 0.1230
Largest diff. peak/hole / e Å-3	0.13/-0.18

2) Structure determination of **4j1**

The structure of **4j1** was determined by the X-ray diffraction. Recrystallized from dichloromethane/EtOH. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2077464.

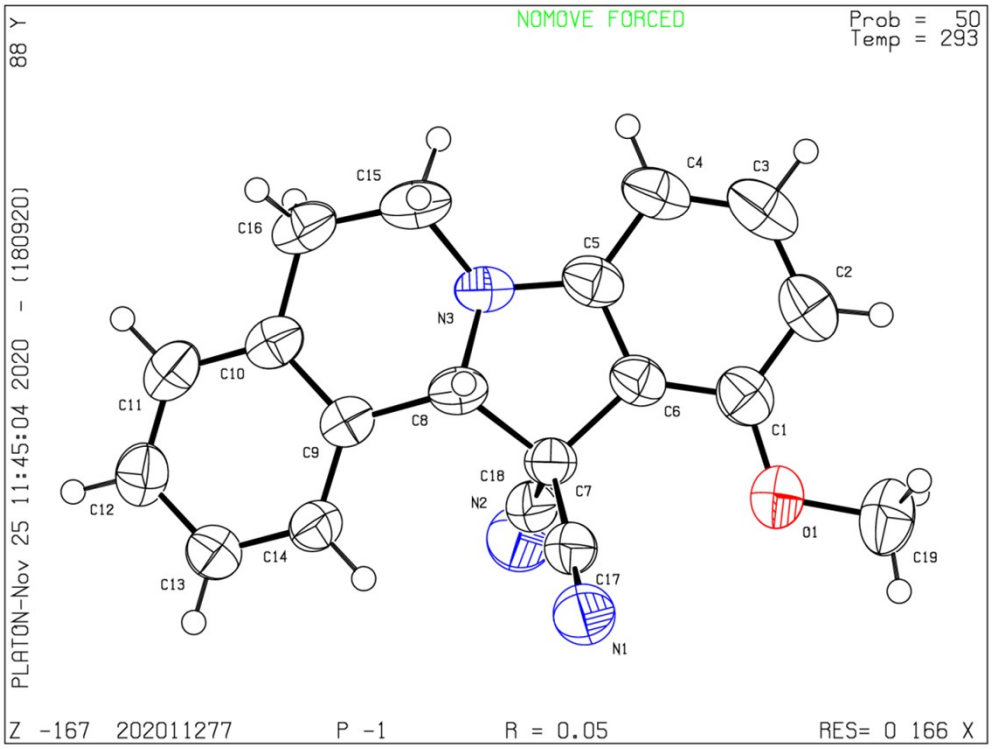


Table S2. Crystal data and structure refinement for 4j1.

Identification code	202011277
Empirical formula	C19H15N3O
Formula weight	301.34
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1

a/Å	7.5372(7)
b/Å	7.8330(5)
c/Å	13.1572(11)
α/°	81.704(6)
β/°	86.697(7)
γ/°	83.076(6)
Volume/Å3	762.42(11)
Z	2
ρcalcg/cm3	1.313
μ/mm-1	0.667
F(000)	316.0
Crystal size/mm3	0.19 × 0.15 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.794 to 134.092
Index ranges	-8 ≤ h ≤ 9, -6 ≤ k ≤ 9, -15 ≤ l ≤ 15
Reflections collected	5367
Independent reflections	2719 [Rint = 0.0216, Rsigma = 0.0347]
Data/restraints/parameters	2719/0/209
Goodness-of-fit on F2	1.061
Final R indexes [I>=2σ (I)]	R1 = 0.0466, wR2 = 0.1078
Final R indexes [all data]	R1 = 0.0660, wR2 = 0.1220
Largest diff. peak/hole / e Å-3	0.13/-0.24

3) Structure determination of **4s**

The structure of **4s** was determined by the X-ray diffraction. Recrystallized from dichloromethane/EtOH. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2077465.

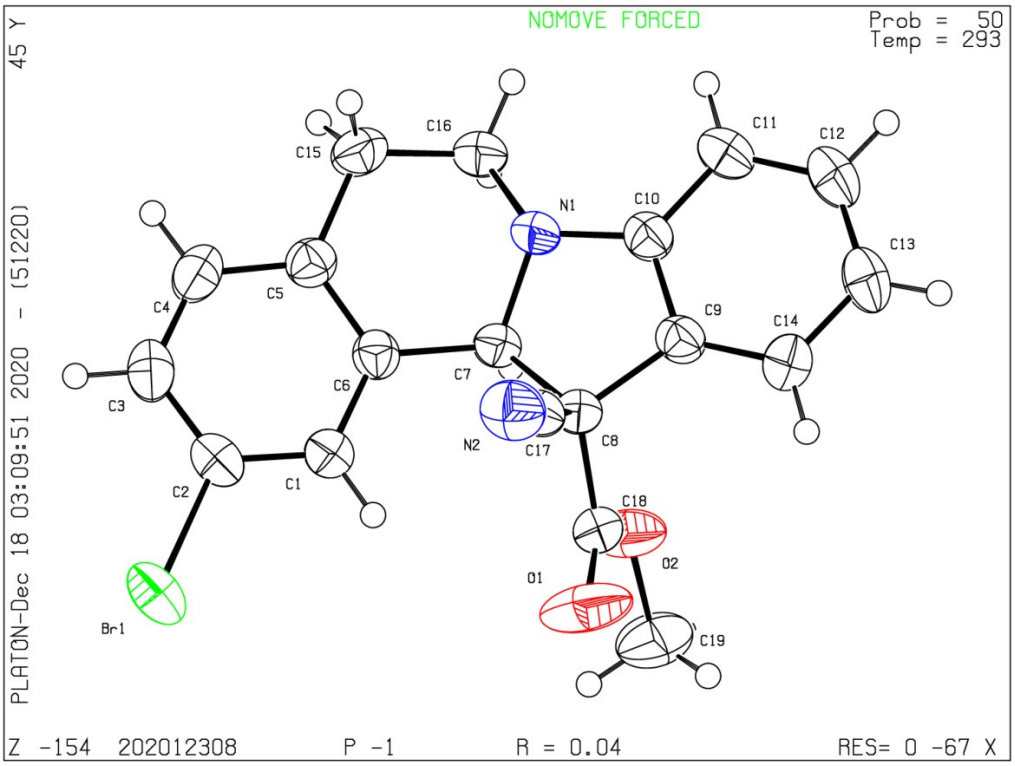


Table S3. Crystal data and structure refinement for 4s.

Identification code	202012308
Empirical formula	C19H15BrN2O2
Formula weight	383.24
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.5331(6)
b/Å	9.1322(6)
c/Å	11.9513(10)
α/°	77.749(6)
β/°	79.907(7)
γ/°	65.413(7)
Volume/Å3	823.62(11)
Z	2
ρcalcg/cm3	1.545
μ/mm-1	3.514
F(000)	388.0
Crystal size/mm3	0.15 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.606 to 134.16
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -13 ≤ l ≤ 14

Reflections collected	11170
Independent reflections	2930 [Rint = 0.0433, Rsigma = 0.0360]
Data/restraints/parameters	2930/0/218
Goodness-of-fit on F2	1.041
Final R indexes [I>=2σ (I)]	R1 = 0.0372, wR2 = 0.0835
Final R indexes [all data]	R1 = 0.0491, wR2 = 0.0907
Largest diff. peak/hole / e Å-3	0.66/-0.51

Supplementary References

1. F. Y. Kwong, A. Klapars and S. L. Buchwald, *Org. Lett.*, 2002, **4**, 581.
2. J.-H. Wang, X.-B. Li, J. Li, T. Lei, H.-L. Wu, X.-L. Nan, C.-H. Tung and L.-Z. Wu, *Chem. Commun.*, 2019, **55**, 10376.
3. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.
4. T. Yanai, D. P. Tew and N. C. Handy, *Chem Phys Lett.*, 2004, **393**, 51
5. F. Weigend and R. Ahlrichs, Phys. *Chem. Chem. Phys.*, 2005, **7**, 3297.
6. M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327.
7. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580;
8. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-Garcia, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498.
9. W. Humphrey, A. Dalke and K. Schulten, *J. Molec. Graphics*, 1996, **14**, 33.
10. T. Lu and F. Chen, *J. Theor. Comput. Chem.*, 2012, **11**, 163.
11. M. R. Patil, N. P. Dedhia, A. R. Kapdi and A. V. Kumar, *J. Org. Chem.*, 2018, **83**, 4477.
12. G. Zhang, Y. Ma, G. Cheng, D. Liu and R. Wang, *Org. Lett.*, 2014, **16**, 656.
13. B. Yi, N. Yan, N. Yi, Y. Xie, X. Wen, C.-T. Au and D. Lan, *RSC Adv.*, 2019, **9**, 29721.
14. R. Yang, Q. Ruan, B.-Y. Zhang, Z.-L. Zheng, F. Miao, L. Zhou and H.-L. Geng, *Molecules*, 2014, **19**, 8051.
15. T. Ide, K. Shimizu, H. Egami and Y. Hamashima, *Tetrahedron Lett.*, 2018, **59**, 3258.