Electronic Supplementary Information for

Tunable C-H Functionalization and Dearomatization Enabled by an Organic Photocatalyst

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1. General methods

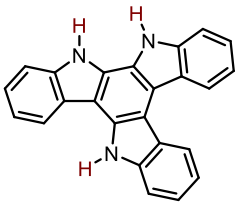
Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Bruker instrument (375 MHz). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). HRMS were obtained on FTICRMS bruker 15T LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Fourier Transform Infrared spectra were recorded on a Nicolet IS50 FT-IR spectrophotometer.

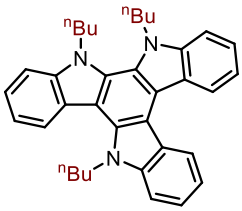
Substrates $^{n}Bu_4NPF_6$ were purchased from Energy-chemical, solvents were purchased from Aladdin, and used without further purification. Substrates **1a-1u** were synthesized according to the literature procedures[1-3].

2. Characterization of ITNs

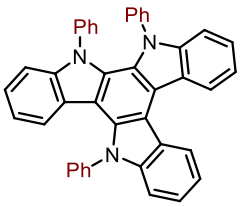
The substrates **ITN-1**, **ITN-2** and **ITN-3** were known compounds. The synthesis of **ITN-1**, **ITN-2** and **ITN-3** were accomplished following the reported procedures[4-6].



ITN-1[4], gray solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.87 (s, 1H), 11.48 (s, 1H), 11.38 (s, 1H), 8.87-8.78 (m, 3H), 7.82 (d, J = 8.0 Hz, 3H), 7.50-7.37 (m, 6H).



ITN-2[5], yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90-8.82 (m, 2H), 8.35 (d, J = 8.4 Hz, 1H), 7.63-7.57 (m, 3H), 7.48-7.29 (m, 6H), 4.90 (t, J = 7.6 Hz, 2H), 4.64 (t, J = 7.6 Hz, 2H), 4.52 (t, J = 7.2 Hz, 2H), 2.05-1.97 (m, 2H), 1.37-1.31 (m, 2H), 1.25-1.15 (m, 4H), 0.86 (t, J = 7.2 Hz, 3H), 0.77-0.71 (m, 4H), 0.52-0.47 (m, 6H).



ITN-3[6], yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06-9.00 (m, 2H), 7.78-7.68 (m, 5H), 7.57-7.48 (m, 4H), 7.45-7.44 (m, 2H), 7.25-7.12 (m, 8H), 6.76-6.66 (m, 5H), 6.08 (d, J = 8.4 Hz, 1H).

2.1 UV/Vis absorption spectra of ITNs

UV/vis absorption spectra of **ITNs** (0.01 mM in DMSO) were recorded in 1 cm path quartz cuvettes using Pgeneral TU-1901 UV/Vis spectrometer.

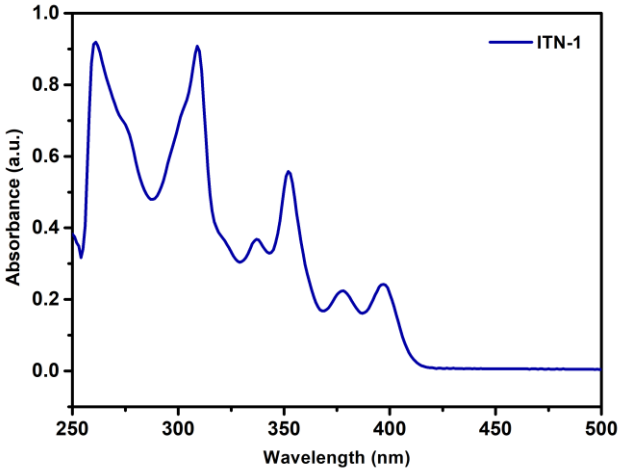


Figure S1. UV/vis absorption spectrum of **ITN-1** in DMSO.

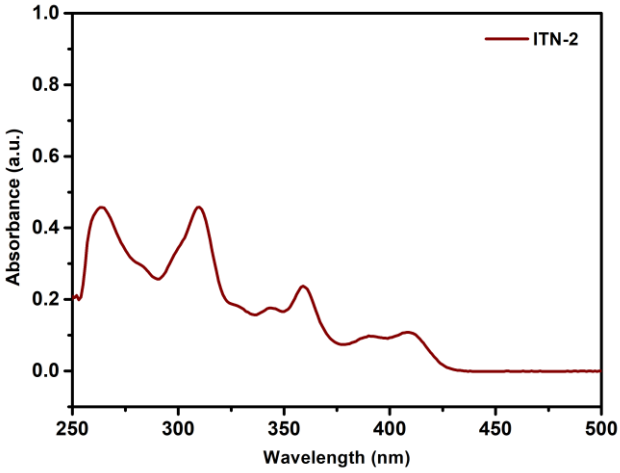


Figure S2. UV/vis absorption spectrum of **ITN-2** in DMSO.

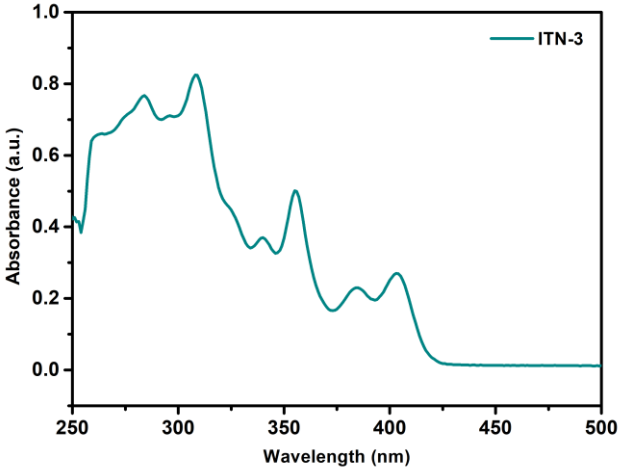


Figure S3. UV/vis absorption spectrum of **ITN-3** in DMSO.

2.2 Emission spectra of ITNs

Fluorescence spectra were recorded on Edinburgh Instruments FS5 Spectrofluorometer in 1 cm quartz cuvettes. **ITN**s were prepared as a 0.01 mM solution in DMSO and used freshly for the measurements.

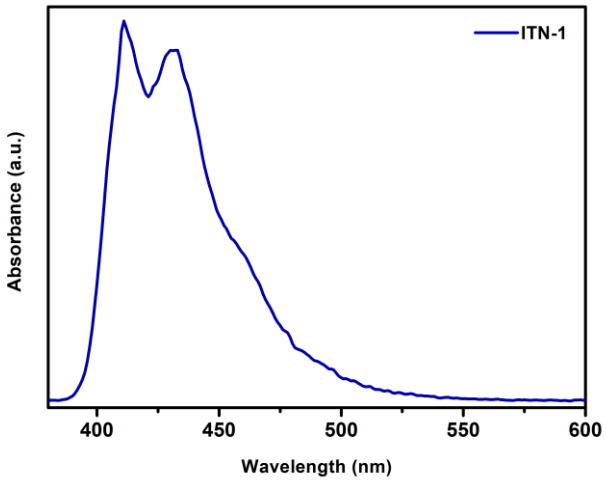


Figure S4. Emission spectrum of **ITN-1** in DMSO.

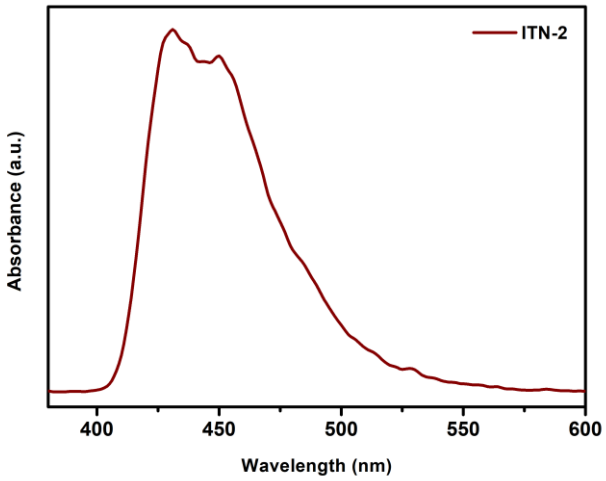


Figure S5. Emission spectrum of **ITN-2** in DMSO.

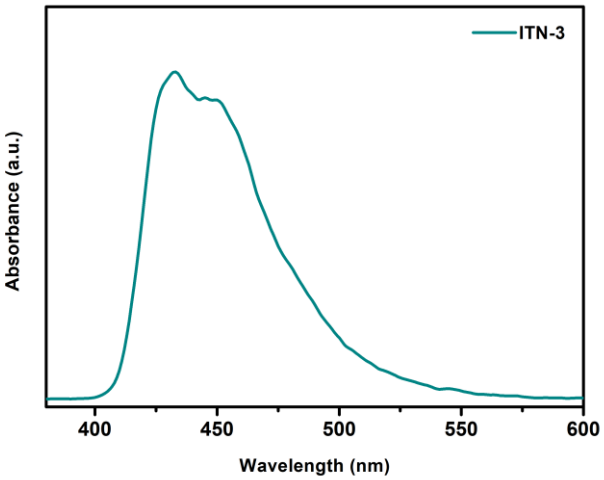


Figure S6. Emission spectrum of **ITN-3** in DMSO.

2.3 Fluorescence decay curves of ITNs

Estimating lifetimes of excited states of **ITN**s were based on the ultrafast transient absorption spectroscopic techniques. The luminescence decays were measured on an Japan horiba Instruments FluoroMax-4 spectrometer. The sample compartment was home-built and designed as 10×10 mm cuvettes in 90° geometry between excitation and detection. The solution of **ITN**s in DMSO (0.01 mM) were excited at 352 nm, 359 nm and 355 nm, respectively. All decay traces were fitted by iterative reconvolution with an experimental instrument response function recorded directly after decay acquisition.

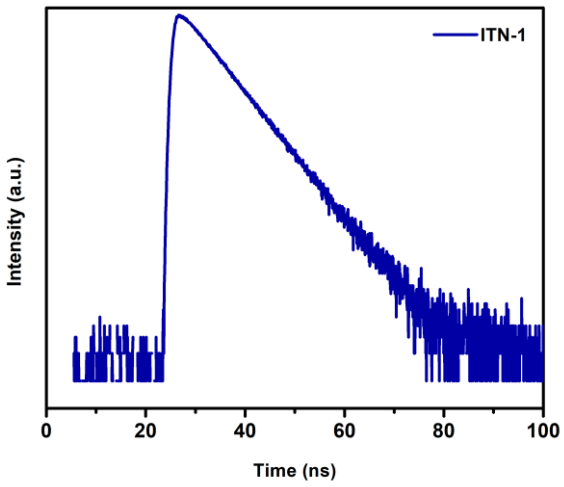


Figure S7. Fluorescence decay curve of **ITN-1** in DMSO.

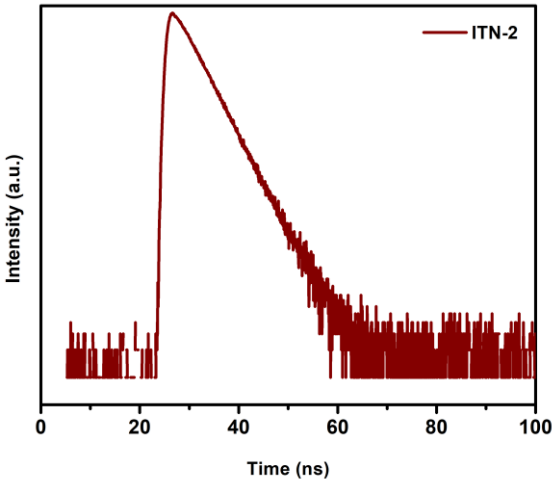


Figure S8. Fluorescence decay curve of **ITN-2** in DMSO.

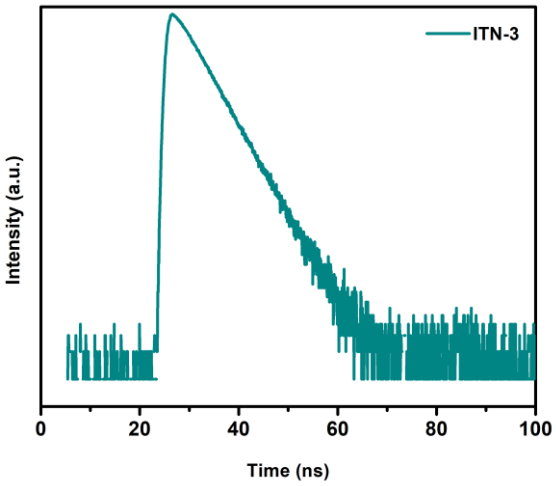


Figure S9. Fluorescence decay curve of **ITN-3** in DMSO.

2.4 UV/Vis absorption and emission spectra of ITNs

The zero-zero vibrational state excitation energy $E_{0,0}$ was estimated by the corresponding energy of the wavelength at which emission and absorption overlap. This wavelength was determined setting the intensity of emission λ_{max} to the absorbance of **ITN**s at excitation wavelength.

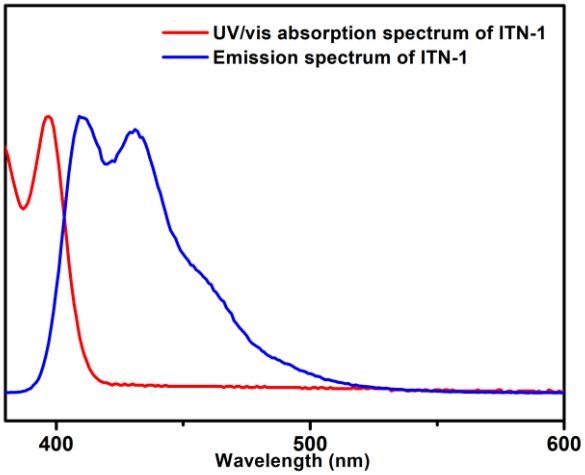


Figure S10. UV/Vis absorption and emission spectra of **ITN-1** in DMSO (0.01 mM). Cross point λ: 403 nm. $E_{0\text{-}0}$: 3.08 eV.

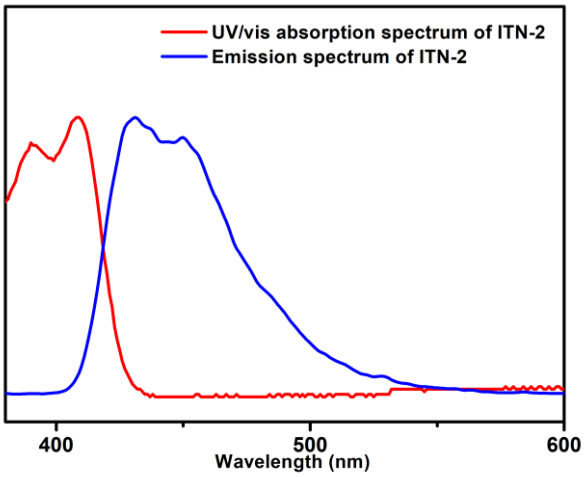


Figure S11. UV/Vis absorption and emission spectra of **ITN-2** in DMSO (0.01 mM). Cross point λ: 419 nm. $E_{0\text{-}0}$: 2.96 eV.

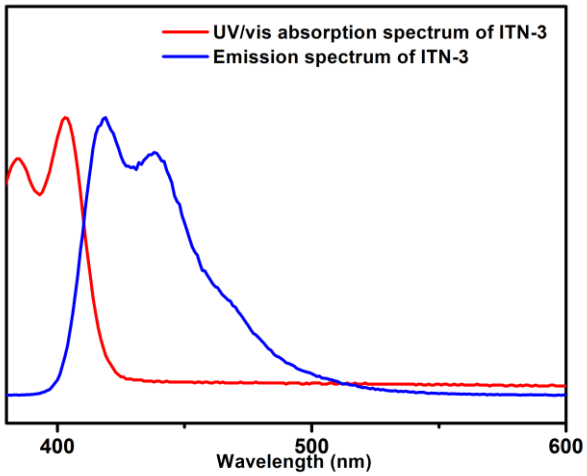


Figure S12. UV/Vis absorption and emission spectra of **ITN-3** in DMSO (0.01 mM). Cross point λ: 410 nm. $E_{0\text{-}0}$: 3.02 eV.

2.5 Cyclic voltammograms of ITNs

Voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI660E containing glassy carbon electrode serving as the working electrode, saturated calomel reference electrode, Pt wire auxiliary electrode.

All solutions used for the voltammetric experiments were deoxygenated by purging with high purity nitrogen gas and measurements were performed in a electrolytic cell at room temperature.

Excited state oxidation and reduction potentials were calculated by the following approximating formulas: $E_{1/2}(PC^{*}/PC^{\bullet-}) = E_{1/2}(PC/PC^{\bullet-}) + E_{0,0}$ and $E_{1/2}(PC^{\bullet+}/PC^{*}) = E_{1/2}(PC^{\bullet+}/PC) - E_{0,0}$.

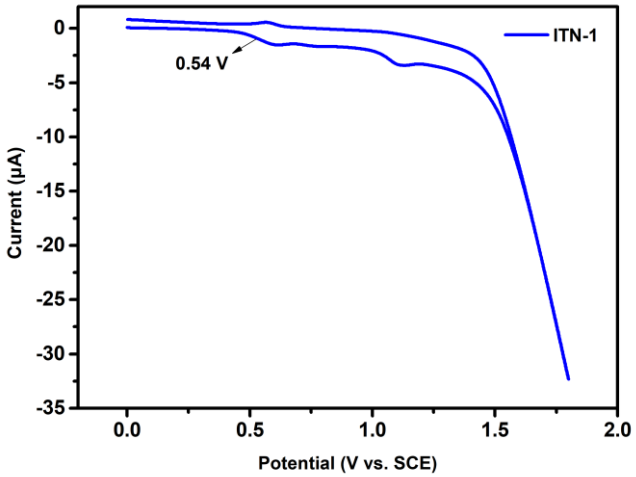


Figure S13. Cyclic voltammogram of **ITN-1** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(PC^{\bullet+}/PC)$ = +0.54 V, $E_{1/2}(PC^{\bullet+}/PC^{*})$ = -2.54 V

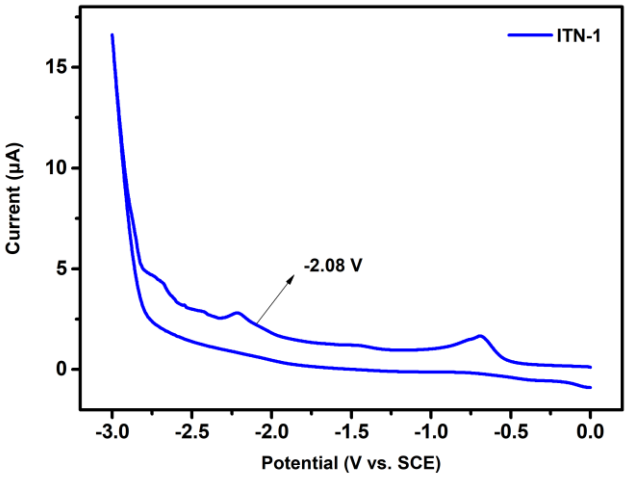


Figure S14. Cyclic voltammogram of **ITN-1** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(PC/PC^{\bullet-})$ = -2.08 V, $E_{1/2}(PC^{*}/PC^{\bullet-})$ = +1.00 V.

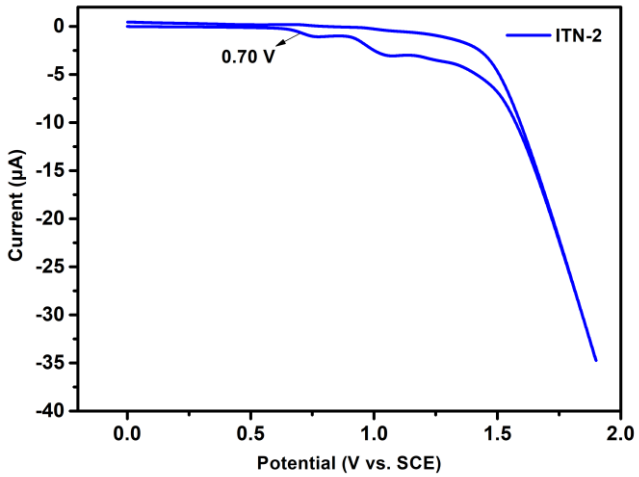


Figure S15. Cyclic voltammogram of **ITN-2** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(PC^{\bullet+}/PC)$ = +0.70 V, $E_{1/2}(PC^{\bullet+}/PC^{*})$ = -2.26 V

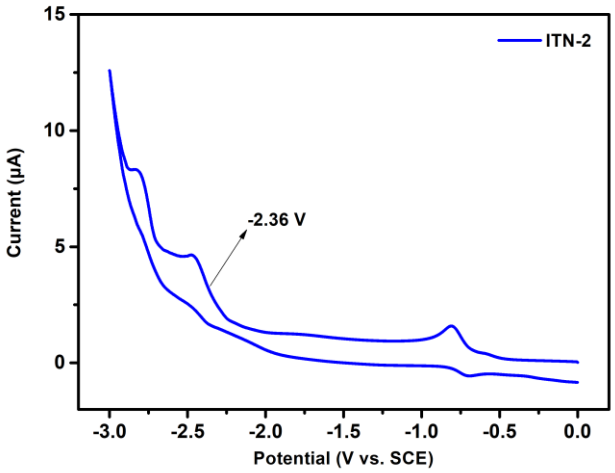


Figure S16. Cyclic voltammogram of **ITN-2** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(PC/PC^{\bullet-})$ = -2.36 V, $E_{1/2}(PC^{*}/PC^{\bullet-})$ = +0.60 V.

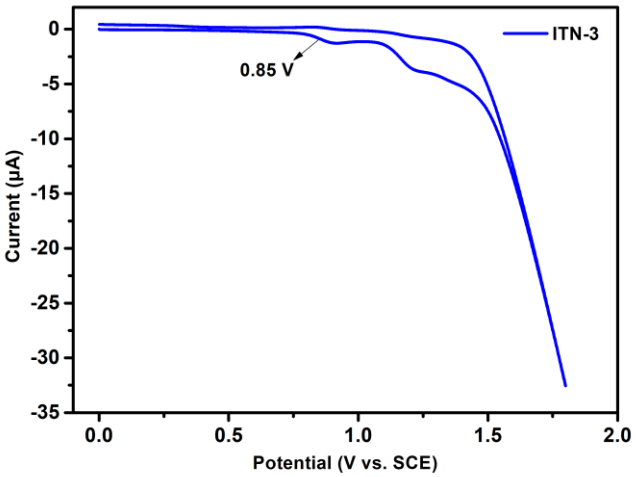


Figure S17. Cyclic voltammogram of **ITN-3** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(PC^{\bullet+}/PC)$ = +0.85 V, $E_{1/2}(PC^{\bullet+}/PC^{*})$ = -2.17 V

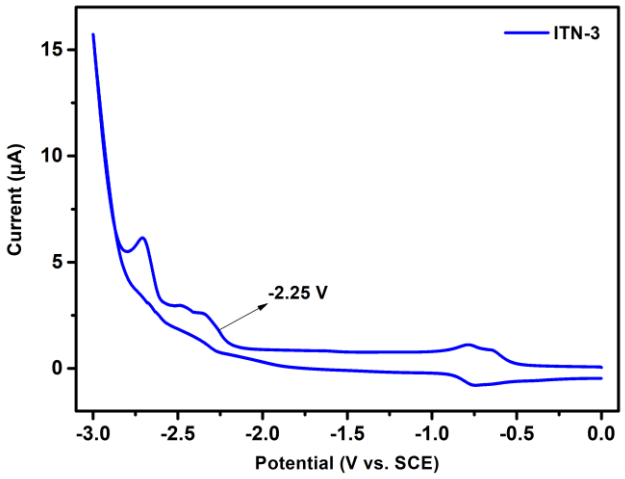


Figure S18. Cyclic voltammogram of **ITN-3** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(PC/PC^{\bullet-})$ = -2.25 V, $E_{1/2}(PC^{*}/PC^{\bullet-})$ = +0.77 V.

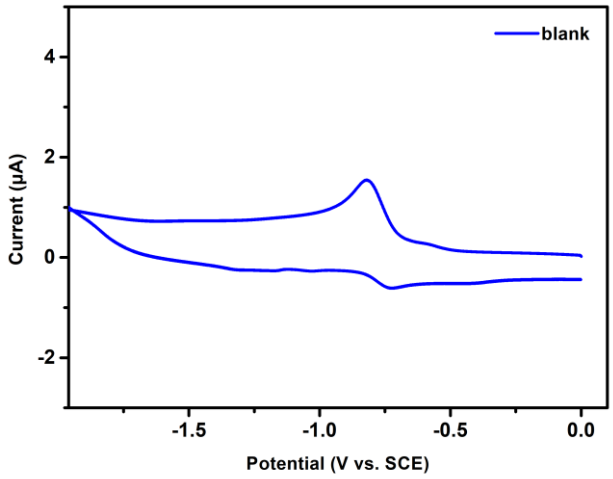


Figure S19. Cyclic voltammogram of DMSO containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s.

3. DFT calculations

Computational Methods

All the calculation in this study were performed with Gaussian16 package.[7] DFT calculations were carried out with the B3LYP functional[8] including the D3 version of Grimme's empirical dispersion correction[9] with Becke−Johnson damping.[10] For the ground-state structures of **ITN-1**, **ITN-2** and **ITN-3**, the standard 6-31G** basis sets were employed for all atoms. Optimizations were conducted without any constraint in the gas phase. Frequency analyses were performed to confirm each structure being a local minimum (no imaginary frequency). In order to obtain the vertical excitation energies of **ITN**s, time-dependent (TD)-DFT calculations were carried using the B3LYP-D3(BJ) functional with the def2-TZVP basis sets of Weigend and Ahlrichs[11] with implicit solvation model (PCM,[12] DMSO, ε = 46.826) on the basis of the ground-state structures optimized at the same level of theory. The keywords "td(nstates=20)" and "iop(9/40=4)" in Gaussian16 were specified in the calculations. The natural transition orbital (NTO) analyses were performed using Multiwfn 3.8 software.[13] By comparing the distributions of the calculated NTOs and MOs, it could be recognized that the S_0-to-S_1 excitation were mainly contributed by one electron transition from the HOMO to LUMO for each **ITN** molecule. The orbital diagrams were prepared using VMD 1.9.3.[14]

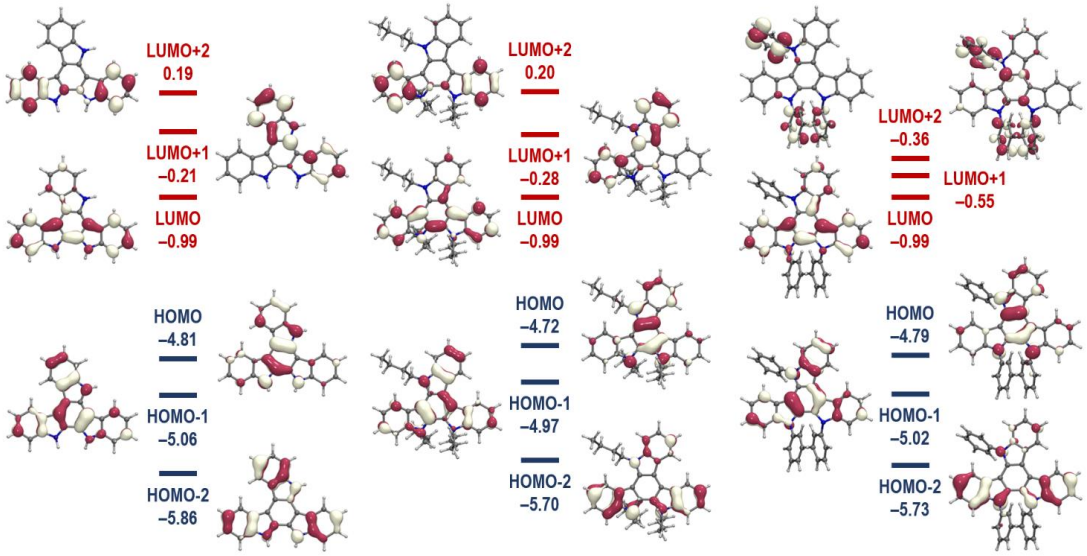


Figure S20. Selected molecular orbitals (HOMO–2 to LUMO+2) and the corresponding energies (in eV) of **ITN-1** (left), **INT-2** (middle) and **INT-3** (right). The isovalues of the orbitals are set as ±0.04.

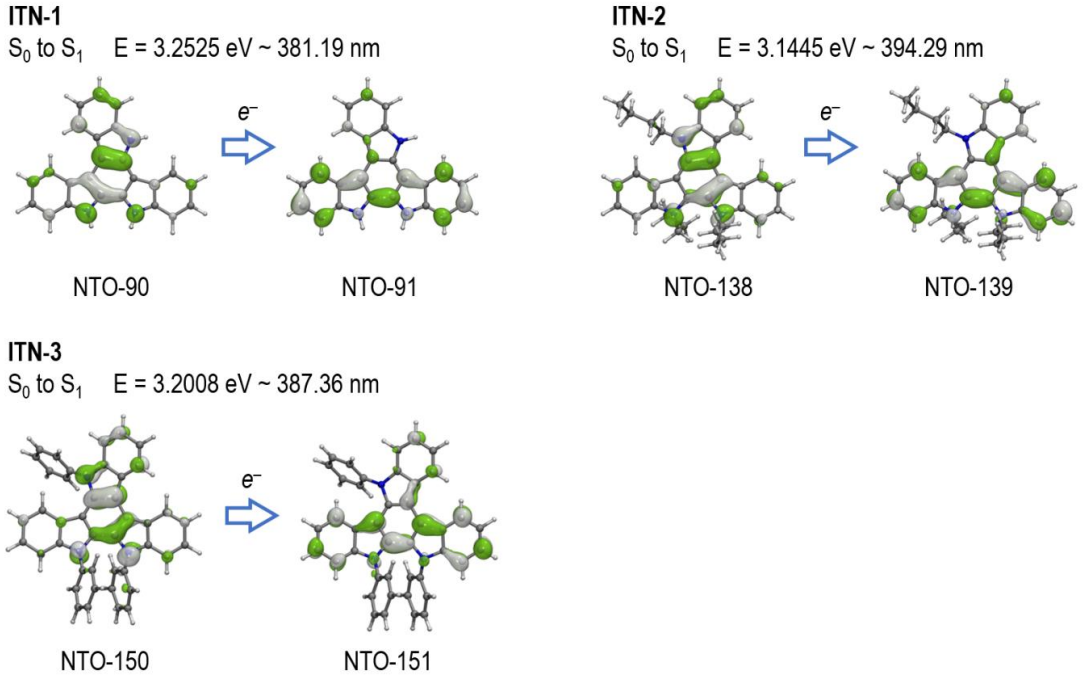


Figure S21. Calculated NTOs, vertical excitation energies and wavelengths of maximum absorptions for the S_0-to-S_1 excitation of **ITN**s. The isovalues of the orbitals are set as ±0.04.

Cartesian Coordinates and Energies for All the Optimized Structures

ITN-1

Opt @ B3LYP-D3(BJ)/6-31G** in gas phase

SCF Done: E(RB3LYP) = -1087.93290855 a.u.

Zero-point correction = 0.328419 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1087.651011 a.u.

C,0,1.2309924048,3.2944294194,9.5959620525

C,0,1.6252743469,2.892034428,8.3134646524

C,0,0.931617209,3.3418556087,7.1711293324

C,0,-0.201955864,4.1550374443,7.3722535501

C,0,-0.6594419477,4.5360114016,8.6597159189

C,0,0.1070032551,4.132555126,9.7958535132

C,0,1.134587219,3.6625380917,11.8170699534

C,0,0.0604915323,4.3882573999,11.2276957227

C,0,-0.7296416592,5.1863675048,12.0716061474

C,0,-0.4627593436,5.227706732,13.4359096241

C,0,0.5926829486,4.4847008611,13.9911784769

C,0,1.4070425768,3.69573892,13.1859007419

C,0,2.6803776993,1.9915137451,6.5261280037

C,0,3.536741752,1.2779156002,5.6871716323

C,0,3.3147591107,1.3563257554,4.314250937

C,0,2.2663101645,2.1321684701,3.7919459142

C,0,1.413574718,2.8403499275,4.6340030677

C,0,1.604246647,2.7746369901,6.0217351118

C,0,-2.0855115891,5.3515919134,7.0330955807

C,0,-3.1779389638,5.997650828,6.4521783511

C,0,-4.1144995525,6.5799393333,7.3000072382

C,0,-3.9631585533,6.504263138,8.69449789

C,0,-2.8679837215,5.8631088664,9.2650384105

C,0,-1.887494392,5.2840662855,8.4425564652

N,0,1.805648647,2.9719844976,10.822633823

N,0,2.6917265941,2.098071195,7.9090799011

N,0,-1.0506981826,4.678063802,6.4141445636

H,0,-1.5219150473,5.8013420238,11.6671179485

H,0,-1.0754973886,5.8504060443,14.0804784022

H,0,0.7811640409,4.5320980092,15.0595336187

H,0,2.2329502235,3.1281520499,13.6053452014

H,0,4.3513014217,0.6827574745,6.0898517675

H,0,3.9660031992,0.8111121836,3.6378923298
H,0,2.1208052488,2.1799623996,2.7172380531
H,0,0.6134653635,3.4376809819,4.2060350606
H,0,-3.2956157915,6.035178054,5.3728258678
H,0,-4.9761913335,7.088260276,6.8778197633
H,0,-4.7165325467,6.9467719208,9.3391231273
H,0,-2.8031919106,5.7858389788,10.3420467527
H,0,2.7464575232,2.6300061996,10.935329644
H,0,3.2389463733,1.508851898,8.5142521512
H,0,-0.9951424316,4.4896982208,5.4279037358

ITN-1

Opt @ B3LYP-D3(BJ)/def2-TZVP in DMSO (PCM)
SCF Done: E(RB3LYP) = -1088.41934541 a.u.
Zero-point correction = 0.327524 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -1088.138910 a.u.
TD-DFT calculations
Sp @ B3LYP-D3(BJ)/def2-TZVP in DMSO (PCM)
Excited State 1: Singlet-A 3.2525 eV 381.19 nm f = 0.1887
<S**2> = 0.000

C,0,-0.1674231528,-1.6254156858,-0.0390159678
C,0,1.1992390991,-1.330615644,-0.0341641292
C,0,1.6432026845,0.00567613,0.0052922596
C,0,0.6745827906,1.0222108676,0.0187580722
C,0,-0.7163977298,0.7584129718,0.0018420712
C,0,-1.1456867484,-0.6017802096,-0.0072506744
C,0,-2.1479227471,-2.6836339254,-0.0207406747
C,0,-2.4241282988,-1.2865870549,0.0159290671
C,0,-3.7663108292,-0.8919351854,0.0853517737
C,0,-4.7693863689,-1.8480646254,0.099967683
C,0,-4.4660486429,-3.2159352499,0.0486844112
C,0,-3.1515493416,-3.6488614342,-0.0092194333
C,0,3.4511237792,-1.4065210872,-0.0240974128
C,0,4.7803225836,-1.8162012708,-0.0268095763
C,0,5.7590036712,-0.8326547463,0.0102094971
C,0,5.4212744989,0.5272586208,0.0496544989

C,0,4.0945840147,0.9330071219,0.0521672245
C,0,3.0853516727,-0.0333876775,0.0138099544
C,0,-0.3316552164,3.0343343823,0.0174045402
C,0,-0.5862578529,4.4017514934,0.0126307197
C,0,-1.9092064126,4.8154126442,-0.0287910964
C,0,-2.9492642913,3.8780931121,-0.0710744937
C,0,-2.6881114183,2.5155685969,-0.0635466648
C,0,-1.3665489322,2.0557767517,-0.0104758964
N,0,-0.7875860988,-2.8606932174,-0.0571252957
N,0,2.2988413523,-2.165666621,-0.0530925733
N,0,0.8798307286,2.3849868337,0.0400194715
H,0,-4.0369002949,0.1484959699,0.1438182652
H,0,-5.8031433888,-1.5329866751,0.1545140196
H,0,-5.2673145903,-3.9433169636,0.0599441285
H,0,-2.9076211608,-4.7027555654,-0.0403679991
H,0,5.0410187448,-2.8661465336,-0.0558390909
H,0,6.8016970185,-1.1222501541,0.0092013704
H,0,6.2074179324,1.2700447418,0.0794290127
H,0,3.8597226748,1.9884559132,0.0870399563
H,0,0.2261620331,5.1167084138,0.0366864932
H,0,-2.1387308898,5.8729964783,-0.0340872031
H,0,-3.9748719008,4.2210915686,-0.1125339193
H,0,-3.515303075,1.8280906574,-0.1148446274
H,0,-0.3279773563,-3.7538058244,-0.0636682204
H,0,2.2788443667,-3.1698252756,-0.0793531198
H,0,1.7740010933,2.8405373572,0.0211995784

ITN-2

Opt @ B3LYP-D3(BJ)/6-31G** in gas phase

SCF Done: E(RB3LYP) = -1559.69930239 a.u.

Zero-point correction = 0.670882 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1559.097092 a.u.

C,0,8.6258615886,16.2539020862,5.3773089157
C,0,8.6133188685,15.4508658482,6.5362783194
C,0,7.4280968181,14.7397360882,6.8652602063
C,0,6.2575854031,14.9072068196,6.0652670391

C,0,6.2531305972,15.7654471747,4.9286435817
C,0,7.4369899084,16.5082006239,4.6749449657
C,0,10.7079924613,16.3673781513,6.2131838436
C,0,12.0541772031,16.6608318133,6.4394900276
C,0,12.6312725583,16.2257119797,7.6296368193
C,0,11.872734189,15.5221474585,8.5770036477
C,0,10.5384084102,15.2085376841,8.3344998808
C,0,9.9406165306,15.5917062029,7.1233803473
C,0,7.1012209387,13.7660673789,7.8875761819
C,0,7.8146578895,13.0964799602,8.8949658568
C,0,7.1573061775,12.2002152893,9.7314920766
C,0,5.7849146451,11.9487458406,9.5799534735
C,0,5.0576926062,12.5616565027,8.5643938226
C,0,5.7305307707,13.4453982893,7.7131115963
C,0,5.9414005946,17.2142512183,3.1498988529
C,0,5.3178331632,17.8552615768,2.0768495134
C,0,4.0584214364,17.4154302495,1.6824180543
C,0,3.4443581119,16.3421411153,2.3414925477
C,0,4.0623217887,15.7169056535,3.4207251035
C,0,5.3150372599,16.16319453,3.8766368203
C,0,10.4938740709,16.7491580714,3.7748390886
C,0,11.0039321453,15.3705354903,3.3292912804
C,0,11.5588987578,15.3932029857,1.8996723167
C,0,12.0744998038,14.0266975768,1.4381442899
C,0,7.7991912796,18.798514189,3.6832667434
C,0,7.443129351,19.6157593792,4.9354842264
C,0,5.9537848453,19.9234039444,5.1299145528
C,0,5.6955673454,20.8052143895,6.3559050495
C,0,3.7978379911,14.1941128374,6.3559390509
C,0,3.2574131899,12.9850978458,5.5765949329
C,0,1.7392423659,13.0513352236,5.3685767851
C,0,1.1860465446,11.8438389979,4.6059891755
N,0,9.9156303257,16.7724551209,5.132676118
N,0,7.2293311073,17.4376125416,3.6435175587
N,0,5.2302246834,14.1327417804,6.6170862527
H,0,12.6299079843,17.2367611782,5.721872489
H,0,13.6729464924,16.4546417269,7.8341538446

H,0,12.3287402019,15.2241479644,9.5162066835
H,0,9.9654922049,14.7043262042,9.1001337635
H,0,8.8797072859,13.241246081,9.0083219053
H,0,7.7158101312,11.6853905935,10.5073234643
H,0,5.2859758003,11.2537740815,10.2488626825
H,0,4.0039117923,12.3408567171,8.4331792898
H,0,5.8114857001,18.6587940894,1.5405716813
H,0,3.5622703541,17.8926543241,0.8427816755
H,0,2.4778356309,15.982691177,2.001561778
H,0,3.5721181209,14.8684632047,3.8730175853
H,0,9.7257904968,17.0800780183,3.0751183606
H,0,11.3040018796,17.4865451618,3.7371702324
H,0,11.7795126691,15.0232469568,4.0217098489
H,0,10.1781219269,14.6512014629,3.3956041575
H,0,12.3713104497,16.1303630125,1.8348097071
H,0,10.7777323622,15.7404479432,1.2096974022
H,0,12.4645254157,14.0717768876,0.4162717968
H,0,11.2765598804,13.2763263924,1.4578462117
H,0,12.8807126246,13.6680706718,2.0875923931
H,0,7.4538083883,19.3125813991,2.7827102053
H,0,8.8847990429,18.7359920101,3.6093193255
H,0,7.8329260474,19.095951812,5.8188997473
H,0,8.0034811853,20.5590676876,4.8664085443
H,0,5.5607368137,20.4177905062,4.2313706313
H,0,6.2128152277,21.7678822445,6.2708120832
H,0,6.0494044738,20.3207134617,7.272780308
H,0,4.6277033847,21.0112109664,6.4799944388
H,0,3.2876510848,14.25934571,7.3249689654
H,0,3.5812127068,15.1287743106,5.8392999362
H,0,3.516612608,12.0669728623,6.1168927831
H,0,3.7697853884,12.9158974261,4.6087920935
H,0,1.242807489,13.1265785802,6.3456905667
H,0,1.4818292538,13.9738654101,4.8300392139
H,0,1.6372534587,11.7631368097,3.6108807743
H,0,0.1018690235,11.917667748,4.4750844014
H,0,1.3946303213,10.9097516361,5.1392556511
H,0,5.3933985616,18.987417081,5.2309908824

ITN-2

Opt @ B3LYP-D3(BJ)/def2-TZVP in DMSO (PCM)

SCF Done: E(RB3LYP) = -1560.39016610 a.u.

Zero-point correction = 0.669184 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1559.790139 a.u.

TD-DFT calculations

Sp @ B3LYP-D3(BJ)/def2-TZVP in DMSO (PCM)

Excited State 1: Singlet-A 3.1445 eV 394.29 nm f = 0.1809

<S**2> = 0.000

C,0,-1.5041690997,0.1631316021,-0.1716434432

C,0,-1.2056490163,-1.1933183648,-0.3990801172

C,0,0.1486729925,-1.6076763746,-0.3666954896

C,0,1.1778210927,-0.6414546381,-0.1584463028

C,0,0.8774493425,0.7342864983,0.0133169

C,0,-0.4841763494,1.1142382077,-0.0943869958

C,0,-3.4856753806,-0.8603145019,-0.3885915111

C,0,-4.8435681018,-1.1525986952,-0.4513278599

C,0,-5.2202495266,-2.4381035249,-0.8126931528

C,0,-4.2562511743,-3.4074408805,-1.1104801142

C,0,-2.9022738088,-3.1198693002,-1.0159777354

C,0,-2.4887426016,-1.8449777098,-0.6143754488

C,0,0.7998695139,-2.8954887045,-0.4562984334

C,0,0.374684247,-4.2250327465,-0.5589415411

C,0,1.3095778872,-5.2481600107,-0.6147030174

C,0,2.6811451295,-4.9725604905,-0.5651731782

C,0,3.1379315424,-3.670027344,-0.4311936696

C,0,2.1927354381,-2.6480259019,-0.3605624239

C,0,0.6621072991,3.030560211,0.1194462397

C,0,1.0176527923,4.370269873,0.2366577354

C,0,2.3367206286,4.6788803378,0.5304805188

C,0,3.2767630744,3.6616208777,0.7167863559

C,0,2.9220057265,2.3280163151,0.579710264

C,0,1.6090678974,1.9789516386,0.240586941

C,0,-3.4822446017,1.2249000436,0.9287685278

C,0,-3.5221575093,0.558771286,2.3019005917

C,0,-4.0856802405,1.4890815271,3.3720156371
C,0,-4.1289197181,0.8403545439,4.7524840712
C,0,-1.5685163107,3.2023324205,-0.9684683764
C,0,-1.4906083731,2.7597337855,-2.4281499645
C,0,-0.1223504792,2.9434015892,-3.0784122995
C,0,-0.1159758013,2.5172208082,-4.5434576453
C,0,3.7406389534,-0.7275211607,-0.2554009778
C,0,4.4695078961,-0.7478703547,1.0858104189
C,0,5.8817632839,-0.1783630535,0.987970183
C,0,6.6094998019,-0.1765368005,2.3286501754
N,0,-2.891582018,0.3681437707,-0.1113606014
N,0,-0.6083749955,2.5049479651,-0.0954494093
N,0,2.4060764124,-1.296289899,-0.1924010044
H,0,-5.5876069647,-0.3955896508,-0.2438865648
H,0,-6.271286117,-2.6864735382,-0.881982925
H,0,-4.569479965,-4.3950306171,-1.4227725549
H,0,-2.1879260579,-3.8805526724,-1.2806474603
H,0,-0.671994373,-4.475483746,-0.5708568383
H,0,0.9721239124,-6.2734526495,-0.6921768737
H,0,3.3950499465,-5.7844283412,-0.6149515287
H,0,4.1970078905,-3.4643701746,-0.364953779
H,0,0.2829361742,5.155288269,0.1261491122
H,0,2.6322942933,5.7143278063,0.6371223056
H,0,4.2958187004,3.9127894063,0.980084337
H,0,3.6720696305,1.5820043803,0.7639148216
H,0,-2.8925754326,2.133045044,0.999463017
H,0,-4.4840725306,1.5127732487,0.6077364516
H,0,-4.1232699385,-0.3524418034,2.2532058827
H,0,-2.5067531473,0.2549353437,2.5738613453
H,0,-5.0938104553,1.802892746,3.0828989298
H,0,-3.4804770526,2.4002364785,3.413956531
H,0,-4.5351554591,1.5236838938,5.500405559
H,0,-3.1282732526,0.5449902527,5.0769418669
H,0,-4.753075061,-0.0563740478,4.7438119798
H,0,-1.3559807468,4.2653590806,-0.8828905065
H,0,-2.5801208202,3.0557827253,-0.6032242265
H,0,-1.7918161242,1.7112424085,-2.4990252847

H,0,-2.241581676,3.3340142163,-2.9799733503
H,0,0.18266145,3.9909866193,-2.9951940969
H,0,-0.8304964069,3.1027678272,-5.127083039
H,0,-0.3900402202,1.464107054,-4.6436952945
H,0,0.8704863544,2.6495099259,-4.9914517193
H,0,4.3085125196,-1.3034561591,-0.9886190007
H,0,3.6672307301,0.277569639,-0.6587099654
H,0,4.5134005319,-1.7776186785,1.4496925619
H,0,3.8876778935,-0.190158329,1.8250459426
H,0,6.4527424703,-0.7608620147,0.2583735956
H,0,5.839667083,0.8423208105,0.593928536
H,0,6.0730884386,0.4290856583,3.0628698814
H,0,7.6180165931,0.2291682302,2.2324788483
H,0,6.6921750252,-1.1892864159,2.7299963765
H,0,0.6235543188,2.3624389293,-2.5310297202

ITN-3

Opt @ B3LYP-D3(BJ)/6-31G** in gas phase
SCF Done: E(RB3LYP) = -1781.07906393 a.u.
Zero-point correction = 0.571184 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -1780.571355 a.u.

C,0,3.1876962918,2.1916124539,19.293854481
C,0,2.867498393,1.3408377141,18.2037017439
C,0,1.4941793075,1.1294777112,17.9134822348
C,0,0.4753891122,1.6176149166,18.7699140384
C,0,0.8154587917,2.5731387638,19.7670042614
C,0,2.1760041408,2.8968062705,19.9791334303
C,0,5.1478980148,1.3387082006,18.5482064843
C,0,4.1300541852,0.7953743534,17.7233668298
C,0,4.5008065217,-0.1384046358,16.7405925826
C,0,5.8385281931,-0.4892548958,16.5931102852
C,0,6.8259728006,0.0636100486,17.421270508
C,0,6.4901183496,0.9772814087,18.4149439937
C,0,0.9826365388,4.252974251,21.3408547493
C,0,0.0491588596,3.4480592686,20.6385306957
C,0,-1.3200247622,3.6928969053,20.8353064834

C,0,-1.7257511067,4.681135923,21.7248599392
C,0,-0.7821276601,5.4545585689,22.417795307
C,0,0.5812819771,5.2584574245,22.2237882412
C,0,-0.4642871707,0.2553533989,17.1674922594
C,0,-1.449179787,-0.4157994029,16.4392590063
C,0,-2.7496091879,-0.4059053925,16.9351971206
C,0,-3.0546891501,0.2477953005,18.1387114166
C,0,-2.0752292594,0.9446572696,18.8383710383
C,0,-0.7639290461,0.998862167,18.3375963777
C,0,5.2166308203,2.4168369983,20.7607887553
C,0,6.3873519932,3.1787112648,20.8216009762
C,0,7.0581121959,3.3259645877,22.0352551065
C,0,6.5566708764,2.7308617564,23.1938099772
C,0,5.3802951141,1.9809910739,23.1325060813
C,0,4.7141747718,1.8133136809,21.9194340471
C,0,3.3324611597,4.8887214457,20.9893716739
C,0,3.801507011,5.4726779844,19.8065343349
C,0,4.7806111193,6.4633828344,19.8624275719
C,0,5.2824178965,6.8913225275,21.0932787072
C,0,4.808563832,6.3115149034,22.2710313588
C,0,3.8434415033,5.3061867439,22.2223549918
C,0,1.4532356792,0.063525688,15.6237172068
C,0,1.9846469754,1.1024362129,14.8504895944
C,0,2.4967769698,0.8321048515,13.5826163086
C,0,2.4632240346,-0.4661952573,13.0696155146
C,0,1.9215029775,-1.4992726114,13.8365937852
C,0,1.4232521978,-1.240280313,15.1139459998
N,0,4.5750795537,2.1999159557,19.4988756855
N,0,2.2871860171,3.9116511284,20.9483871921
N,0,0.9111478358,0.3328785583,16.9134707379
H,0,3.7593093001,-0.6016947719,16.1069884791
H,0,6.1174986729,-1.2095412101,15.8300027797
H,0,7.8640425659,-0.2298354108,17.2961267485
H,0,7.2462610599,1.3846636042,19.0752558736
H,0,-2.0643224244,3.150814614,20.2700200481
H,0,-2.7855804902,4.8642679008,21.8732720636
H,0,-1.1162513491,6.2270171863,23.1040605538

H,0,1.3091393443,5.8802664609,22.731060104
H,0,-1.2085020615,-0.9385546274,15.5208821557
H,0,-3.5307803053,-0.9282158238,16.3910095885
H,0,-4.0656662488,0.2063936575,18.5325102133
H,0,-2.3244343961,1.4055920599,19.7843164924
H,0,6.7509689482,3.6671171705,19.9244017807
H,0,7.9668209538,3.9189656057,22.0758739594
H,0,7.0780140856,2.8513592546,24.1386836558
H,0,4.9862052185,1.5104073845,24.0285029618
H,0,3.8114902557,1.2145846439,21.8618828216
H,0,3.3928374969,5.1520716611,18.8542345296
H,0,5.1398746953,6.912881003,18.9412235177
H,0,6.0382186783,7.6699243924,21.1335913659
H,0,5.2003219931,6.6307618869,23.2321581738
H,0,3.4984642089,4.8248113593,23.1306248626
H,0,1.9979355288,2.1103514258,15.2512467976
H,0,2.9155655436,1.6406060151,12.9909985783
H,0,2.8586869093,-0.6717926623,12.0796483946
H,0,1.8975401675,-2.5128268024,13.4475009228
H,0,1.030196767,-2.0424939838,15.7294734628

ITN-3

Opt @ B3LYP-D3(BJ)/def2-TZVP in DMSO (PCM)
SCF Done: E(RB3LYP) = -1781.88294387 a.u.
Zero-point correction = 0.570923 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -1781.375091 a.u.
TD-DFT calculations
Sp @ B3LYP-D3(BJ)/def2-TZVP in DMSO (PCM)
Excited State 1: Singlet-A 3.2008 eV 387.36 nm f = 0.2301
<S**2> = 0.000

C,0,-0.4563199391,-0.5041219072,-0.1630411949
C,0,0.9263955131,-0.8054065836,-0.1604407853
C,0,1.8308467071,0.2779144422,-0.1758067454
C,0,1.3911180203,1.614350961,-0.3385939157
C,0,0.0047510621,1.8946702938,-0.233578875
C,0,-0.9021409129,0.8224427475,-0.0863708667

C,0,-0.294943016,-2.7511288332,-0.3012946078
C,0,1.0306785383,-2.2525929289,-0.2500052883
C,0,2.0843767018,-3.1668091166,-0.3680424149
C,0,1.8079574385,-4.5180622491,-0.5107752992
C,0,0.4902576051,-4.9842587,-0.5541161725
C,0,-0.576989652,-4.1033712137,-0.4598716172
C,0,-2.1331659763,2.705137029,0.0668450389
C,0,-0.7887550486,3.1063199282,-0.1408364356
C,0,-0.5012148463,4.4757884341,-0.1327326113
C,0,-1.5213191617,5.3947610291,0.0575390218
C,0,-2.8394665967,4.9718065235,0.2594729347
C,0,-3.157816941,3.6222264249,0.2768524345
C,0,3.6912126535,1.5494395554,-0.3783119075
C,0,5.0050646983,2.0017262845,-0.4318802418
C,0,5.2203421348,3.3434379017,-0.7124272202
C,0,4.144568535,4.206892559,-0.9457487564
C,0,2.8362049285,3.7550366845,-0.8580311766
C,0,2.5813028394,2.4180135531,-0.5325845368
C,0,-2.5007137396,-1.7864529763,-0.8049469742
C,0,-3.4581265256,-2.5931741192,-0.2011666523
C,0,-4.7115002894,-2.7252098324,-0.7823101254
C,0,-5.0154332237,-2.0458681897,-1.9567111463
C,0,-4.0553190277,-1.2369421411,-2.5548064587
C,0,-2.7949407979,-1.1122824297,-1.9868698473
C,0,-3.2182615685,0.635818733,0.827924228
C,0,-2.8926759763,-0.0247891015,2.0098457218
C,0,-3.8869989536,-0.6598892348,2.7409684438
C,0,-5.2075697762,-0.622955555,2.3065239682
C,0,-5.5281393053,0.0471323827,1.1312517351
C,0,-4.5364308041,0.6709070137,0.3872272828
C,0,4.0355137016,-0.759060367,0.4119048798
C,0,3.7460909968,-1.2248451208,1.6911783888
C,0,4.5277433574,-2.2249970887,2.2534501055
C,0,5.609037941,-2.7471029422,1.5510183954
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N,0,-2.2018734759,1.3113054503,0.0917351574
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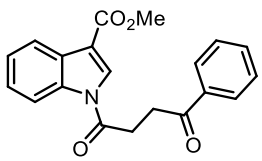
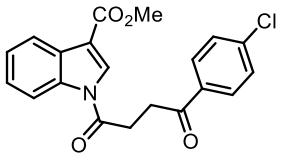
4. General procedure for photocatalytic C-H functionalization

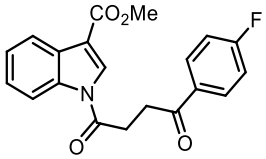
The synthesis of **1a-1u** was accomplished following the reported procedures[1,2].



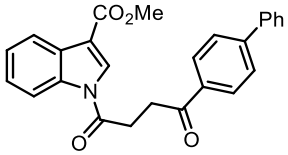
1a, white solid, m.p. = 159.3-162.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.41 (m, 1H), 8.33 (s, 1H), 8.18-8.04 (m, 3H), 7.63-7.38 (m, 5H), 3.96 (s, 3H), 3.56 (t, *J* = 6.4 Hz, 2H), 3.44 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 170.8, 164.6, 136.4, 136.2, 133.7, 130.8, 128.9, 128.3, 127.4, 126.1, 125.0, 121.7, 116.6, 114.0, 51.8, 32.9, 29.9. IR (thin film): νmax (cm^{-1}) = 3151, 2922, 1704, 1682, 1553, 1443, 1387, 1364, 1318, 1255, 1207, 1181, 1145, 1105, 1081, 1045, 1017, 988, 969, 938, 777, 763, 742, 695. HRMS (ESI) calcd for $C_{20}H_{17}NaNO_4$ $[M+Na]^+$: 358.1055. Found: 358.1051.



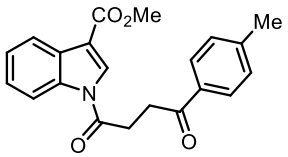
1b, yellow solid, m.p. = 145.7-147.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42-8.40 (m, 1H), 8.32 (s, 1H), 8.17-7.97 (m, 3H), 7.49-7.38 (m, 4H), 3.96 (s, 3H), 3.53-3.50 (m, 2H), 3.45-3.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 170.7, 164.5, 140.1, 136.2, 134.7, 130.7, 129.7, 129.2, 127.4, 126.1, 125.0, 121.7, 116.6, 114.1, 51.8, 32.8, 29.8. IR (thin film): νmax (cm^{-1}) = 3129, 3094, 2945, 1722, 1705, 1686, 1583, 1560, 1446, 1391, 1273, 1251, 1217, 1183, 1151, 1109, 1089, 1037, 1011, 972, 950, 904, 835, 817, 804, 762, 746, 661. HRMS (ESI) calcd for $C_{20}H_{16}ClNaNO_4$ $[M+Na]^+$: 392.0666. Found: 392.0662.



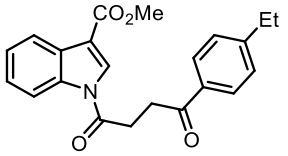
1c, white solid, m.p. = 136.1-139.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.35 (m, 1H), 8.23 (s, 1H), 8.13-8.00 (m, 3H), 7.36-7.34 (m, 2H), 7.15-7.11 (m, 2H), 3.93 (s, 3H), 3.45-3.42 (m, 2H), 3.37-3.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 170.7, 166.0 (d, *J* = 254.0 Hz), 164.4, 136.0, 132.8 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 9.5 Hz), 130.7, 127.3, 126.0, 124.8, 121.6, 116.5, 115.8 (d, *J* = 22.0 Hz), 113.8, 51.7, 32.6, 29.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -104.39 to -104.47 (m). IR (thin film): νmax (cm^{-1}) = 2957, 1708, 1683, 1594, 1556, 1442, 1408, 1382, 1316, 1254, 1227, 1207, 1185, 1174, 1157, 1143, 1104, 1077, 1041, 1017, 992, 963, 939, 930, 876, 835, 763, 738, 671. HRMS (ESI) calcd for $C_{20}H_{16}FNaNO_4$ $[M+Na]^+$: 376.0961. Found: 376.0958.



1d, white solid, m.p. = 199.7-200.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.43 (m, 1H), 8.35 (s, 1H), 8.19-8.11 (m, 3H), 7.74-7.64 (m, 4H), 7.51-7.38 (m, 5H), 3.97 (s, 3H), 3.59 (t, *J* = 6.0 Hz, 2H), 3.47 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 170.9, 164.6, 146.3, 139.9, 136.2, 135.1, 130.9, 129.1, 128.9, 128.5, 127.5, 127.4, 126.1, 125.0, 121.7, 116.7, 114.0, 51.8, 32.9, 29.9. IR (thin film): νmax (cm^{-1}) = 3152, 2922, 2360, 1727, 1704, 1689, 1605, 1553, 1478, 1442, 1382, 1356, 1318, 1214, 1184, 1145, 1106, 1080, 1044, 1016, 998, 987, 968, 954, 932, 896, 836, 777, 764, 742, 723, 698, 673. HRMS (ESI) calcd for $C_{26}H_{21}NaNO_4$ $[M+Na]^+$: 434.1368. Found: 434.1366.

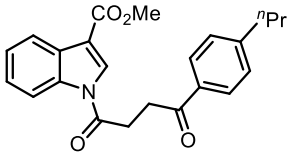


1e, white solid, m.p. = 140.7-142.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42-8.39 (m, 1H), 8.30 (s, 1H), 8.16-7.92 (m, 3H), 7.38-7.27 (m, 4H), 3.95 (s, 3H), 3.50 (t, *J* = 6.8 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 170.9, 164.5, 144.5, 136.1, 133.9, 130.8, 129.5, 128.3, 127.4, 126.0, 124.9, 121.6, 116.6, 113.9, 51.7, 32.7, 29.8, 21.8. IR (thin film): νmax (cm^{-1}) = 3129, 3094, 2921, 2360, 1725, 1704, 1681, 1606, 1558, 1444, 1392, 1357, 1274, 1255, 1218, 1183, 1147, 1107, 1042, 972, 951, 933, 903, 812, 804, 777, 764, 745, 698. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_4$ $[M+Na]^+$: 372.1212. Found: 372.1208.

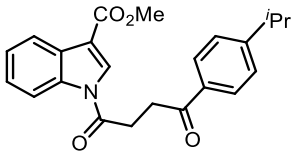


1f, yellow solid, m.p. = 140.8-142.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.40 (m, 1H), 8.32 (s, 1H), 8.17-7.96 (m, 3H), 7.39-7.37 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 3H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 6.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 170.9, 164.5, 150.6, 136.1, 134.1, 130.9, 128.5, 128.3, 127.4, 126.0, 124.9, 121.6, 116.6, 113.9, 51.8, 32.7, 29.9, 29.1, 15.3. IR (thin film): νmax (cm^{-1}) = 3130, 3095, 2965, 2943, 1703, 1678, 1605, 1584, 1560, 1514, 1478, 1447, 1433, 1392, 1368, 1343, 1302, 1273, 1254, 1218,

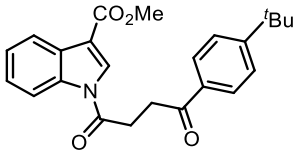
1179, 1153, 1110, 1064, 1038, 973, 955, 904, 829, 804, 777, 761, 746, 724, 662. HRMS (ESI) calcd for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1549. Found: 364.1537.



1g, yellow solid, m.p. = 108.1-109.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.40 (m, 1H), 8.31 (s, 1H), 8.18-7.95 (m, 3H), 7.39-7.28 (m, 4H), 3.95 (s, 3H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.41 (t, *J* = 5.6 Hz, 2H), 2.65 (t, *J* = 8.4 Hz, 2H), 1.68-1.57 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 170.9, 164.5, 149.1, 136.1, 134.1, 130.9, 128.9, 128.4, 127.4, 127.2, 126.0, 124.9, 121.6, 116.6, 113.9, 51.7, 38.1, 32.7, 29.9, 24.3, 13.9. IR (thin film): νmax (cm^{-1}) = 3130, 3095, 2930, 2224, 1704, 1682, 1604, 1583, 1561, 1478, 1447, 1389, 1304, 1273, 1256, 1218, 1198, 1181, 1152, 1109, 1038, 1021, 974, 950, 903, 815, 580, 776, 759, 746, 700, 664, 617. HRMS (ESI) calcd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1705. Found: 378.1700.

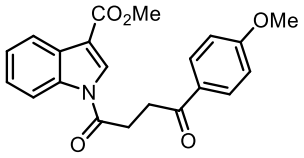


1h, white solid, m.p. = 139.7-141.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (m, 1H), 8.32 (s, 1H), 8.17-7.97 (m, 3H), 7.39-7.33 (m, 4H), 3.95 (s, 3H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 5.6 Hz, 2H), 3.03-2.93 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 170.9, 164.5, 155.2, 136.2, 134.3, 130.9, 128.5, 127.4, 126.9, 126.0, 124.9, 121.7, 116.6, 113.9, 51.7, 34.4, 32.7, 29.9, 23.8. IR (thin film): νmax (cm^{-1}) = 2923, 1706, 1678, 1604, 1557, 1478, 1442, 1387, 1366, 1317, 1253, 1209, 1179, 1143, 1104, 1045, 988, 969, 935, 900, 831, 737, 672. HRMS (ESI) calcd for $C_{23}H_{23}NaNO_4$ $[M+Na]^+$: 400.1525. Found: 400.1519.

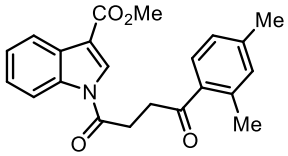


1i, white solid, m.p. = 153.3-154.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (m, 1H), 8.33 (s, 1H), 8.17-8.15 (m, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.40-7.36 (m, 2H), 3.96 (s, 3H), 3.53 (t, *J* = 5.6 Hz, 2H), 3.43 (t, *J* = 5.6 Hz, 2H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 170.9, 164.6, 157.4, 136.2, 133.9, 130.9, 128.2, 127.4, 126.1, 125.8, 124.9, 121.7, 116.6, 113.9, 51.8, 35.3, 32.7, 31.2,

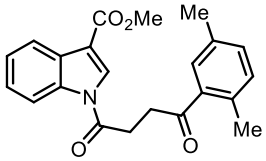
29.9. IR (thin film): νmax (cm^{-1}) = 3131, 3096, 2947, 1717, 1703, 1663, 1603, 1585, 1561, 1514, 1477, 1446, 1433, 1390, 1370, 1342, 1315, 1300, 1251, 1235, 1219, 1200, 1179, 1153, 1111, 1064, 1045, 975, 928, 900, 878, 855, 815, 776, 762, 745, 724, 663, 649. HRMS (ESI) calcd for $C_{24}H_{26}NO_4$ $[M+H]^+$: 392.1862. Found: 392.1852.



1j, white solid, m.p. = 175.3-178.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42-8.40 (m, 1H), 8.31 (s, 1H), 8.16-8.14 (m, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.40-7.35 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 3.48 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 171.0, 164.6, 163.9, 136.2, 130.9, 130.6, 129.5, 127.4, 126.0, 124.9, 121.7, 116.6, 113.9, 55.6, 51.8, 32.5, 29.9. IR (thin film): νmax (cm^{-1}) = 3095, 2927, 2224, 1705, 1678, 1603, 1583, 1561, 1511, 1478, 1445, 1386, 1320, 1273, 1254, 1218, 1197, 1181, 1152, 1106, 1045, 1023, 984, 973, 952, 935, 903, 834, 805, 777, 757, 672. HRMS (ESI) calcd for $C_{21}H_{20}NO_5$ $[M+H]^+$: 366.1341. Found: 366.1333.

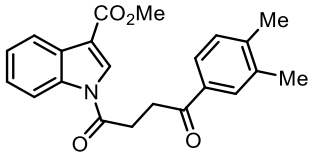


1k, yellow solid, m.p. = 157.3-160.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.41 (m, 1H), 8.34 (s, 1H), 8.18-8.15 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.42-7.36 (m, 2H), 7.13-7.09 (m, 2H), 3.96 (s, 3H), 3.49-3.40 (m, 4H), 2.51 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 170.9, 164.6, 142.7, 139.3, 136.2, 134.0, 133.2, 130.9, 129.5, 127.4, 126.6, 126.1, 124.9, 121.7, 116.7, 113.9, 51.8, 35.0, 30.2, 21.9, 21.6. IR (thin film): νmax (cm^{-1}) = 1703, 1651, 1613, 1586, 1575, 1514, 1479, 1438, 1393, 1376, 1343, 1305, 1276, 1197, 1179, 1154, 1106, 1041, 975, 940, 904, 855, 818, 777, 756, 741, 715, 664, 647. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_4$ $[M+Na]^+$: 386.1368. Found: 386.1363.

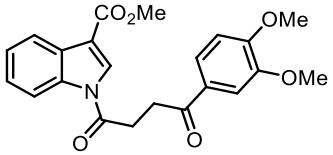


1l, pink solid, m.p. = 146.8-148.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47-8.43 (m, 1H), 8.35 (s, 1H), 8.20-8.16 (m, 1H), 7.66 (s, 1H), 7.43-7.40 (m, 2H), 7.26-7.17 (m,

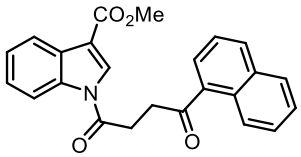
2H), 3.98 (s, 3H), 3.50-3.42 (m, 4H), 2.49 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 170.9, 164.6, 137.0, 136.2, 135.54, 135.46, 132.6, 132.1, 130.8, 129.5, 127.4, 126.0, 124.9, 121.7, 116.6, 113.9, 51.8, 35.3, 30.1, 21.12, 21.08. IR (thin film): νmax (cm^{-1}) = 3131, 3096, 2944, 1703, 1604, 1585, 1561, 1514, 1479, 1447, 1390, 1353, 1343, 1326, 1301, 1272, 1254, 1200, 1185, 1147, 1111, 1064, 1042, 1000, 972, 949, 904, 877, 805, 776, 760, 745, 724, 655, 617. HRMS (ESI) calcd for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1549. Found: 364.1545.



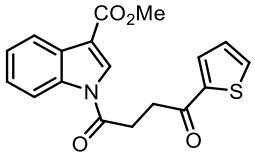
1m, white solid, m.p. = 169.0-170.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.42 (m, 1H), 8.35 (s, 1H), 8.18-8.16 (m, 1H), 7.81 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.40-7.37 (m, 2H), 7.25-7.24 (m, 1H), 3.97 (s, 3H), 3.54 (t, *J* = 6.8 Hz, 2H), 3.44 (t, *J* = 5.6 Hz, 2H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 171.0, 164.6, 143.3, 137.2, 136.2, 134.3, 130.9, 130.1, 129.4, 127.4, 126.1, 126.0, 124.9, 121.7, 116.7, 113.9, 51.8, 32.8, 30.0, 20.3, 20.0. IR (thin film): νmax (cm^{-1}) = 3132. 3097, 2946, 1704, 1680, 1605, 1584, 1559, 1479, 1445, 1387, 1343, 1304, 1273, 1256, 1217, 1180, 1152, 1107, 1041, 1020, 973, 950, 903, 858, 820, 805, 777, 757, 688, 663, 614. HRMS (ESI) calcd for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1549. Found: 364.1540.



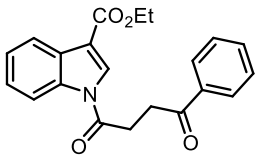
1n, white solid, m.p. = 198.5-199.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.40 (m, 1H), 8.32 (s, 1H), 8.16-8.14 (m, 1H), 7.70-7.67 (m, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.40-7.35 (m, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.96 and 3.95 (s, 6H), 3.93 (s, 3H), 3.51 (t, *J* = 6.0 Hz, 2H), 3.41 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 171.0, 164.5, 153.7, 149.2, 136.2, 130.9, 129.6, 127.4, 126.0, 124.9, 123.0, 121.7, 116.6, 114.0, 110.2, 56.2, 56.1, 51.8, 32.4, 30.0. IR (thin film): νmax (cm^{-1}) = 3009, 2954, 1716, 1668, 1599, 1587, 1558, 1517, 1479, 1432, 1417, 1350, 1326, 1301, 1282, 1264, 1209, 1200, 1185, 1144, 1104, 1037, 1022, 975, 947, 900, 884, 816, 790, 775, 761, 739, 721, 671, 622. HRMS (ESI) calcd for $C_{22}H_{22}NO_6$ $[M+H]^+$: 396.1447. Found: 396.1444.



1o, yellow solid, m.p. = 191.4-192.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.46-8.43 (m, 1H), 8.37 (s, 1H), 8.19-8.17 (m, 1H), 8.10-8.08 (m, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.94-7.89 (m, 2H), 7.65-7.56 (m, 2H), 7.42-7.37 (m, 2H), 3.98 (s, 3H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.51 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 170.9, 164.6, 136.2, 135.9, 133.7, 132.6, 130.9, 130.2, 129.8, 128.8, 128.7, 128.0, 127.4, 127.1, 126.1, 125.0, 123.9, 121.7, 116.7, 114.0, 51.8, 32.9, 30.0. IR (thin film): νmax (cm^{-1}) = 2947, 1706, 1679, 1621, 1605, 1584, 1553, 1479, 1444, 1433, 1386, 1370, 1317, 1273, 1255, 1217, 1194, 1181, 1146, 1106, 1092, 1043, 1019, 973, 941, 902, 858, 829, 818, 777, 758, 687, 671, 623, 613. HRMS (ESI) calcd for $C_{24}H_{19}NaNO_4$ $[M+Na]^+$: 408.1212. Found: 408.1201.

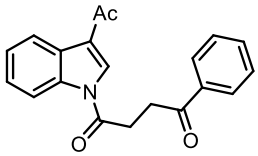


1p, white solid, m.p. = 168.6-170.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.39 (m, 1H), 8.29 (s, 1H), 8.17-8.13 (m, 1H), 7.85-7.84 (m, 1H), 7.69-7.67 (m, 1H), 7.40-7.36 (m, 2H), 7.18-7.16 (m, 1H), 3.95 (s, 3H), 3.51-3.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 170.6, 164.5, 143.4, 136.1, 134.2, 132.5, 130.8, 128.4, 127.4, 126.1, 125.0, 121.7, 116.6, 114.0, 51.8, 33.3, 29.8. IR (thin film): νmax (cm^{-1}) = 3095, 2920, 1705, 1675, 1605, 1583, 1553, 1489, 1479, 1446, 1432, 1387, 1370, 1343, 1312, 1274, 1254, 1219, 1180, 1153, 1126, 1106, 1092, 1042, 1002, 973, 944, 920, 904, 858, 828, 804, 760, 732, 722, 687, 671, 623. HRMS (ESI) calcd for $C_{18}H_{16}NO_4S$ $[M+H]^+$: 342.0800. Found: 342.0791.

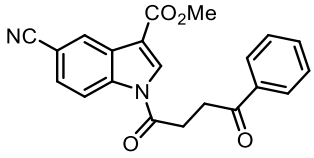


1q, yellow solid, m.p. = 152.8-154.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.42 (m, 1H), 8.33 (s, 1H), 8.19-8.04 (m, 3H), 7.64-7.36 (m, 5H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.57 (t, *J* = 6.8 Hz, 2H), 3.47 (t, *J* = 6.0 Hz, 2H), 1.46 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 170.8, 164.2, 136.4, 136.2, 133.7, 130.7, 128.9, 128.3, 127.5, 126.1, 124.9, 121.8, 116.6, 114.4, 60.7, 32.9, 29.9, 14.6. IR (thin film): νmax

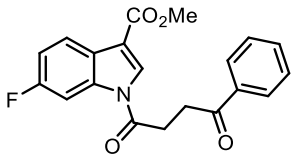
(cm^{-1}) = 2984, 2928, 2852, 1705, 1682, 1646, 1595, 1557, 1480, 1399, 1388, 1367, 1341, 1317, 1254, 1216, 1205, 1185, 1145, 1104, 1045, 1017, 1006, 968, 947, 931, 905, 775, 768, 753, 739, 694, 679. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_4$ $[M+Na]^+$: 372.1212. Found: 372.1207.



1r, yellow solid, m.p. = 167.6-168.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.34 (m, 2H), 8.24 (s, 1H), 8.07-8.04 (m, 2H), 7.64-7.60 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.42-7.37 (m, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.47 (t, *J* = 6.0 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 194.0, 170.8, 136.33, 136.25, 133.8, 130.9, 128.9, 128.3, 127.3, 126.4, 125.3, 122.7, 122.1, 116.3, 32.9, 30.0, 28.1. IR (thin film): νmax (cm^{-1}) = 3096, 2918, 1718, 1682, 1664, 1595, 1584, 1544, 1514, 1476, 1446, 1388, 1365, 1317, 1300, 1271, 1250, 1218, 1185, 1146, 1101, 1064, 1013, 967, 940, 927, 899, 879, 855, 814, 761, 746, 694, 688, 633. HRMS (ESI) calcd for $C_{20}H_{17}NaNO_3$ $[M+Na]^+$: 342.1106. Found: 342.1097.

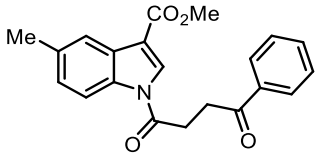


1s, yellow solid, m.p. = 164.1-165.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56-8.53 (m, 2H), 8.47 (s, 1H), 8.06-8.04 (m, 2H), 7.66-7.50 (m, 4H), 4.01 (s, 3H), 3.59 (t, *J* = 5.6 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 170.9, 163.7, 137.9, 136.2, 133.9, 132.6, 129.2, 128.9, 128.3, 127.5, 126.8, 119.4, 117.7, 113.9, 108.6, 52.2, 32.8, 29.9. IR (thin film): νmax (cm^{-1}) = 3103, 2953, 2904, 2225, 1712, 1692, 1609, 1596, 1577, 1563, 1515, 1459, 1446, 1432, 1387, 1364, 1324, 1275, 1208, 1182, 1146, 1114, 1063, 1045, 1000, 976, 964, 919, 901, 882, 819, 775, 762, 744, 709, 693, 656, 630, 616. HRMS (ESI) calcd for $C_{21}H_{17}N_2O_4$ $[M+H]^+$: 361.1188. Found: 361.1183.



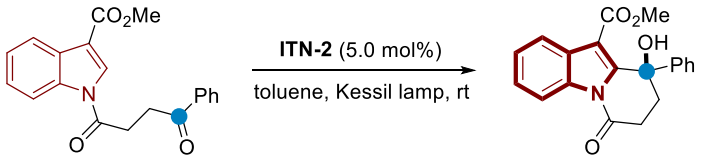
1t, yellow solid, m.p. = 150.7-151.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.17-8.03 (m, 4H), 7.63-7.48 (m, 3H), 7.15-7.10 (m, 1H), 3.95 (s, 3H), 3.55 (t, *J* = 6.0

Hz, 2H), 3.42 (t, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 170.7, 164.1, 161.5 (d, J = 241.0 Hz), 136.2, 136.1 (d, J = 13.0 Hz), 133.6, 130.8 (d, J = 3.0 Hz), 128.8, 128.2, 123.5, 122.4 (d, J =9.0 Hz), 113.6, 113.1 (d, J = 24.0 Hz), 103.9 (d, J = 28.0 Hz), 51.7, 32.7, 29.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.97 to -115.03 (m). IR (thin film): νmax (cm^{-1}) = 2956, 2919, 1710, 1674, 1616, 1596, 1581, 1553, 1489, 1480, 1431, 1405, 1385, 1371, 1342, 1312, 1286, 1244, 1219, 1180, 1160, 1126, 1092, 1078, 1064, 1042, 1002, 972, 943, 933, 921, 858, 837, 828, 800, 767, 750, 732, 687, 671, 623. HRMS (ESI) calcd for $C_{20}H_{16}FNaNO_4$ $[M+Na]^+$: 376.0961. Found: 376.0952.



1u, yellow solid, m.p. = 157.3-160.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.02 (m, 4H), 7.94 (s, 1H), 7.61-7.47 (m, 3H), 7.20-7.17 (m, 1H), 3.95 (s, 3H), 3.52 (t, J = 6.4 Hz, 2H), 3.39 (t, J = 6.4 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 170.6, 164.6, 136.4, 134.7, 134.3, 133.6, 130.8, 128.8, 128.2, 127.6, 127.3, 121.5, 116.2, 113.6, 51.7, 32.8, 29.7, 21.6. IR (thin film): νmax (cm^{-1}) = 2919, 1708, 1688, 1651, 1615, 1595, 1476, 1450, 1394, 1366, 1343, 1316, 1215, 1184, 1138, 1111, 1043, 993, 968, 945, 918, 857, 818, 774, 764, 753, 739, 717, 691, 670, 630. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_4$ $[M+Na]^+$: 372.1212. Found: 372.1208.

4.1 Optimization of the reaction conditions for C-H functionalization[a]

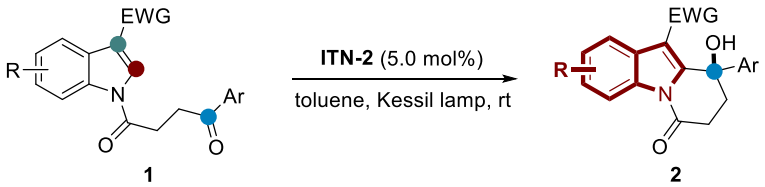


entry	variations from standard conditions	time (h)	yield (%)[b]
1	none	4	90 (89)[c]
2	$Ir(ppy)_3$ instead of **ITN-2**	12	0
3	$Ir(ppy)_2(dtbbpy)PF_6$ instead of **ITN-2**	12	0
4	$Ir[(dFCF_3ppy)_2(dtbbpy)]PF_6$ instead of **ITN-2**	12	0

5	$Ru(bpy)_3Cl_2·6H_2O$ instead of **ITN-2**	12	0
6	4CzIPN instead of **ITN-2**	12	11
7	PTH instead of **ITN-2**	12	13
8	Rhodamine B instead of **ITN-2**	12	0
9	Eosin Y instead of **ITN-2**	12	0
10	Fluorescein instead of **ITN-2**	12	0
11	Rose Bengal instead of **ITN-2**	12	0
12	Methylene Blue instead of **ITN-2**	12	0
13	Thioxanthen-9-one instead of **ITN-2**	12	11
14	**ITN-1** instead of **ITN-2**	12	6
15	**ITN-3** instead of **ITN-2**	12	15
16	CH_3CN instead of toluene	4	trace
17	EtOH instead of toluene	4	33
18	CH_2Cl_2 instead of toluene	4	11
19	no **ITN-2**	4	0
20	no light	4	0

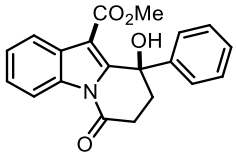
[a]Reaction conditions: a solution of **ITN-2** (2.6 mg, 5.0 mol%) and **1a** (0.1 mmol, 1.0 equiv) in toluene (1.0 mL, 0.1 M) was irradiated by 427 nm Kessil lamp (40 W) at room temperature under nitrogen atmosphere for indicated time. [b]Determined by ^1H NMR yield using CH_2Br_2 as an internal standard. [c]Isolated yield.

4.2 General procedure for photocatalytic C-H functionalization of indole derivatives with ketones

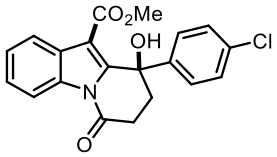


To a flame-dried sealed tube were added **ITN-2** (5.20 mg, 5.0 mol%), **1** (0.20 mmol, 1.0 equiv) and toluene (2.0 mL, 0.1 M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 40 W Kessil lamp. Then the reaction mixture was stirred at room temperature for the indicated time

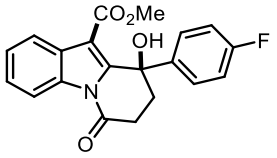
(monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired products **2**. The analytical data of the product **2a**-**2u** were summarized below.



2a, blue solid, 59.7 mg, 89% yield, m.p. = 153.1-154.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65-8.62 (m, 1H), 8.13-8.10 (m, 1H), 7.49-7.41 (m, 2H), 7.34-7.29 (m, 2H), 7.25-7.20 (m, 3H), 3.89 (s, 3H), 2.86-2.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.3, 151.4, 144.1, 134.3, 128.5, 128.3, 126.7, 126.2, 125.6, 125.4, 122.0, 116.8, 110.0, 73.2, 52.5, 37.2, 30.8. IR (thin film): νmax (cm^{-1}) = 3285, 2952, 1731, 1679, 1544, 1506, 1477, 1435, 1356, 1306, 1278, 1153, 1079, 962, 830, 753, 550, 485, 425. HRMS (ESI) calcd for $C_{20}H_{17}NaNO_4$ $[M+Na]^+$: 358.1055. Found: 358.1040.

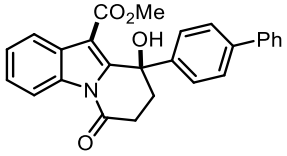


2b, blue solid, 52.5 mg, 71% yield, m.p. = 154.6-156.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63-8.61 (m, 1H), 8.12-8.09 (m, 1H), 7.48-7.40 (m, 2H), 7.28-7.27 (m, 1H), 7.20-7.16 (m, 3H), 3.90 (s, 3H), 2.87-2.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.3, 150.8, 142.8, 134.3, 134.2, 128.8, 127.1, 126.6, 126.4, 125.6, 122.0, 116.9, 110.2, 72.8, 52.7, 37.2, 30.7. IR (thin film): νmax (cm^{-1}) = 3286, 2952, 1731, 1679, 1545, 1451, 1434, 1356, 1329, 1164, 1153, 1116, 1000, 962, 899, 830, 797, 775, 729, 596, 506, 485, 445. HRMS (ESI) calcd for $C_{20}H_{16}ClNaNO_4$ $[M+Na]^+$: 392.0666. Found: 392.0665.

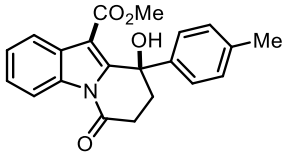


2c, blue solid, 64.5 mg, 91% yield, m.p. = 153.9-155.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63-8.60 (m, 1H), 8.12-8.09 (m, 1H), 7.47-7.39 (m, 2H), 7.23-7.19 (m, 2H), 7.01-6.96 (m, 2H), 3.90 (s, 3H), 2.86-2.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.3, 162.5 (d, J = 246.0 Hz), 151.0, 140.0 (d, J = 3.0 Hz), 134.3, 127.4 (d, J = 8.0 Hz), 126.6, 126.3, 125.5, 122.0, 116.8, 115.4 (d, J = 22.0 Hz), 110.1, 72.7, 52.6, 37.3, 30.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -113.96 to -114.03 (m). IR (thin film):

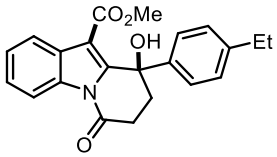
νmax (cm^{-1}) = 3382, 2950, 1732, 1680, 1549, 1507, 1449, 1162, 1148, 1081, 967, 831, 798, 753, 690, 555, 513, 490. HRMS (ESI) calcd for $C_{20}H_{16}FNaNO_4$ $[M+Na]^+$: 376.0961. Found: 376.0956.



2d, blue solid, 68.6 mg, 83% yield, m.p. = 163.7-164.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66-8.64 (m, 1H), 8.14-8.11 (m, 1H), 7.56-7.39 (m, 8H), 7.34-7.28 (m, 3H), 3.90 (s, 3H), 2.87-2.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.4, 151.4, 143.0, 141.1, 140.4, 134.4, 128.9, 127.6, 127.3, 127.2, 126.8, 126.3, 126.1, 125.5, 122.0, 116.9, 110.1, 73.1, 52.6, 37.2, 30.8. IR (thin film): νmax (cm^{-1}) = 3305, 2951, 1730, 1674, 1548, 1356, 1279, 1165, 1151, 1117, 1085, 967, 909, 756, 580, 487. HRMS (ESI) calcd for $C_{26}H_{21}NaNO_4$ $[M+Na]^+$: 434.1368. Found: 434.1364.

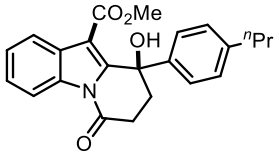


2e, white solid, 64.0 mg, 92% yield, m.p. = 149.7-150.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.61 (m, 1H), 8.12-8.10 (m, 1H), 7.46-7.39 (m, 2H), 7.19 (s, 1H), 7.12-7.09 (m, 3H) 3.89 (s, 3H), 2.83-2.65 (m, 2H), 2.54-2.33 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.3, 151.7, 141.0, 138.0, 134.3, 129.2, 126.8, 126.2, 125.5, 125.4, 122.0, 116.8, 109.9, 73.1, 52.5, 37.2, 30.8, 21.2. IR (thin film): νmax (cm^{-1}) = 3286, 2952, 1731, 1679, 1600, 1545, 1451, 1435, 1356, 1306, 1278, 1164, 1153, 1116, 1079, 962, 830, 797, 753, 728, 550, 485, 444, 428. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_4$ $[M+Na]^+$: 372.1212. Found: 372.1207.

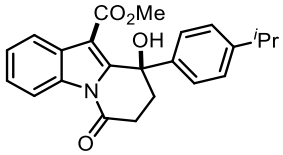


2f, blue solid, 66.1 mg, 91% yield, m.p. = 146.1-146.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.62 (m, 1H), 8.12-8.10 (m, 1H), 7.47-7.40 (m, 2H), 7.20 (s, 1H), 7.14-7.11 (m, 3H), 3.89 (s, 3H), 2.83-2.35 (m, 6H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.3, 151.7, 144.3, 141.2, 134.3, 128.0, 126.8, 126.2, 125.6, 125.4, 122.0, 116.8, 110.0, 73.1, 52.6, 37.2, 30.9, 28.5, 15.4. IR (thin film): νmax (cm^{-1}) = 3286, 2953, 1729, 1679, 1545, 1476, 1451, 1435, 1417, 1356, 1329, 1278,

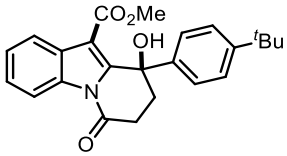
1236, 1164, 1153, 1117, 962, 910, 866, 797, 775, 729, 663, 596, 550, 486. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_4$ $[M+Na]^+$: 386.1368. Found: 386.1361.



2g, blue oil, 64.2 mg, 85% yield, m.p. = 105.1-106.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.57 (m, 1H), 8.15-8.10 (m, 1H), 7.47-7.37 (m, 2H), 7.18-7.06 (m, 3H), 6.93-6.91 (m, 1H), 3.89 and 3.81 (s, 3H), 2.84-2.23 (m, 6H), 1.64-1.56 (m, 2H), 0.94-0.90 m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 164.8, 147.5, 141.5, 137.9, 134.8, 128.9, 127.3, 125.6, 125.2, 121.6, 116.7, 111.2, 51.5, 37.8, 30.0, 28.7, 24.6, 14.0. IR (thin film): νmax (cm^{-1}) = 3286, 2953, 1729, 1679, 1600, 1507, 1477, 1451, 1435, 1356, 1306, 1278, 1164, 1115, 1079, 962, 830, 753, 596, 444. HRMS (ESI) calcd for $C_{23}H_{23}NaNO_4$ $[M+Na]^+$: 400.1525. Found: 400.1526.

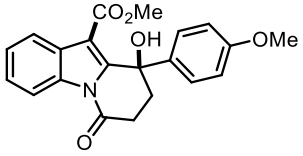


2h, blue solid, 62.1 mg, 82% yield, m.p. = 148.3-149.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.61 (m, 1H), 8.12-8.09 (m, 1H), 7.46-7.39 (m, 2H), 7.20-7.13 (m, 4H), 3.88 (s, 3H), 2.90-2.35 (m, 5H), 1.22-1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.4, 151.8, 148.8, 141.2, 134.3, 126.8, 126.6, 126.2, 125.6, 125.4, 122.0, 116.8, 110.0, 73.1, 52.6, 37.2, 33.8, 30.9, 24.0. IR (thin film): νmax (cm^{-1}) = 3286, 2952, 1729, 1679, 1600, 1544, 1506, 1477, 1356, 1306, 1164, 1079, 961, 866, 753, 690, 596, 550, 485, 429. HRMS (ESI) calcd for $C_{23}H_{23}NaNO_4$ $[M+Na]^+$: 400.1525. Found: 400.1520.

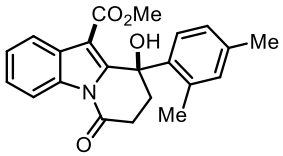


2i, yellow solid, 59.7 mg, 76% yield, m.p. = 168.1-169.4 °C. The NMR spetra appear as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.62 (m, 1H), 8.14-8.10 (m, 1H), 7.47-7.39 (m, 2H), 7.32-7.26 (m, 2H), 7.21-7.12 (m, 2H), 3.89 (s, 3H), 2.83-2.36 (m, 4H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.4, 151.8, 151.1, 140.8, 134.3, 126.8, 126.2, 125.5, 125.4, 125.3, 122.0, 116.8, 110.0, 73.1, 52.6, 37.2, 34.6, 31.4, 30.9. IR (thin film): νmax (cm^{-1}) = 3285, 2952, 1729, 1679, 1544, 1506,

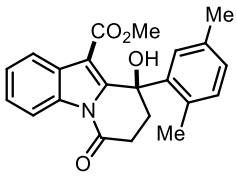
1451, 1434, 1356, 1278, 1188, 1164, 1153, 1079, 962, 866, 830, 753, 729, 690, 646, 596, 550, 486. HRMS (ESI) calcd for $C_{24}H_{25}NaNO_4$ $[M+Na]^+$: 414.1681. Found: 414.1676.



2j, yellow solid, 54.1 mg, 74% yield, m.p. = 166.1-167.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.61 (m, 1H), 8.13-8.10 (m, 1H), 7.47-7.40 (m, 2H), 7.20-7.13 (m, 2H), 6.84-6.80 (m, 2H), 3.91 (s, 3H), 3.77 (s, 3H), 2.84-2.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.3, 159.5, 151.7, 135.9, 134.3, 126.9, 126.8, 126.2, 125.4, 122.0, 116.8, 113.9, 110.0, 72.9, 55.3, 52.6, 37.3, 30.8. IR (thin film): νmax (cm^{-1}) = 3285, 2952, 1731, 1679, 1584, 1544, 1451, 1435, 1356, 1164, 1153, 1079, 962, 866, 830, 797, 550, 485, 414. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_5$ $[M+Na]^+$: 388.1161. Found: 388.1155.

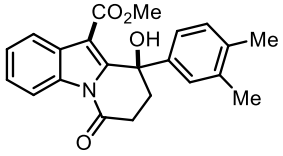


2k, blue solid, 58.2 mg, 80% yield, m.p. = 158.9-160.1 °C. The NMR spectra appear as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63-8.59 (m, 1H), 8.13-8.08 (m, 1H), 7.47-7.38 (m, 2H), 7.07-6.76 (m, 3H), 6.39-5.50 (m, 1H), 3.85 and 3.79 (s, 3H), 2.89-2.39 (m, 7H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 137.7, 134.4, 134.1, 127.0, 126.9, 126.2, 126.1, 125.4, 121.9, 116.9, 116.6, 52.5, 34.8, 34.2, 31.0, 29.9, 21.2, 20.9. IR (thin film): νmax (cm^{-1}) = 3286, 2952, 1728, 1678, 1544, 1451, 1306, 1278, 1166, 1152, 1115, 966, 909, 754, 728, 647, 555, 480. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_4$ $[M+Na]^+$: 386.1368. Found: 386.1364.

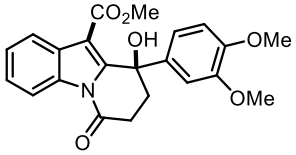


2l, blue solid, 60.3 mg, 83% yield, m.p. = 159.6-160.7 °C. The NMR spectra appear as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.61 (m, 1H), 8.16-8.07 (m, 1H), 7.48-7.40 (m, 2H), 7.25-6.93 (m, 3H), 6.29 and 5.51 (s, 1H), 3.83 and 3.79 (s, 3H), 2.92-2.43 (m, 7H), 2.14-2.06 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 134.8, 134.1, 132.6, 128.8, 127.4, 126.9, 126.2, 125.4, 121.9, 116.9, 52.4, 31.0, 21.2.

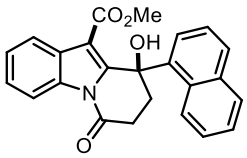
IR (thin film): νmax (cm^{-1}) = 3260, 2950, 1738, 1673, 1534, 1438, 1356, 1309, 1193, 1164, 1148, 1116, 1086, 971, 796, 753, 662, 563, 477, 458. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_4$ $[M+Na]^+$: 386.1368. Found: 386.1364.



2m, yellow solid, 58.9 mg, 81% yield, m.p. = 158.9-160.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65-8.62 (m, 1H), 8.13-8.11 (m, 1H), 7.48-7.40 (m, 2H), 7.20 (s, 1H), 7.08-7.01 (m, 2H), 6.84-6.82 (m, 1H), 3.90 (s, 3H), 2.82-2.34 (m, 4H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.4, 151.9, 141.3, 137.0, 136.8, 134.3, 129.6, 126.83, 126.75, 126.1, 125.4, 123.1, 122.0, 116.8, 109.9, 73.1, 52.6, 37.3, 30.9, 20.2, 19.6. IR (thin film): νmax (cm^{-1}) = 3286, 3054, 2952, 1731, 1679, 1545, 1451, 1306, 1278, 1164, 1153, 1079, 962, 830, 753, 646, 550, 485. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_4$ $[M+Na]^+$: 386.1368. Found: 386.1362.

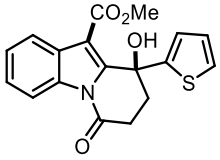


2n, yellow solid, 41.6 mg, 52% yield, m.p. = 168.7-169.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.62 (m, 1H), 8.13-8.11 (m, 1H), 7.48-7.41 (m, 2H), 7.31 (s, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.32-6.29 (m, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 2.85-2.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.4, 151.5, 149.6, 149.1, 136.4, 134.3, 126.7, 126.2, 125.4, 122.0, 118.0, 116.8, 110.0, 108.7, 73.2, 56.1, 55.9, 52.6, 37.2, 30.9. IR (thin film): νmax (cm^{-1}) = 3306, 2951, 1733, 1672, 1542, 1303, 1280, 1256, 1167, 1151, 1089, 1025, 966, 795, 754, 641. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_6$ $[M+Na]^+$: 418.1267. Found: 418.1261.

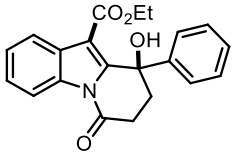


2o, blue solid, 61.7 mg, 80% yield, m.p. = 165.1-166.7 °C. The NMR spectra appear as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69-8.67 (m, 1H), 8.16-8.14 (m, 1H), 7.88-7.81 (m, 2H), 7.69-7.61 (m, 2H), 7.52-7.41 (m, 5H), 3.86 (s, 3H), 2.85-2.46 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.4, 151.5, 141.4, 134.4, 133.2, 132.8, 128.9, 128.4, 127.7, 126.9, 126.5, 126.3, 125.5, 124.6, 123.6, 122.1, 116.9,

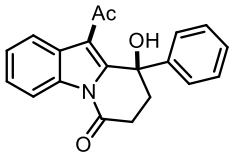
110.2, 73.4, 52.6, 37.1, 30.8. IR (thin film): νmax (cm^{-1}) = 3285, 2953, 1731, 1679, 1545, 1451, 1435, 1329, 1164, 1153, 1079, 962, 830, 753, 596, 550, 506. HRMS (ESI) calcd for $C_{24}H_{19}NaNO_4$ $[M+Na]^+$: 408.1212. Found: 408.1208.



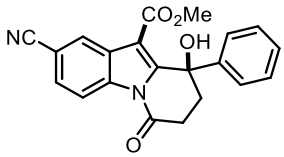
2p, yellow solid, 56.2 mg, 82% yield, m.p. = 158.4-159.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62-8.59 (m, 1H), 8.13-8.11 (m, 1H), 7.82 (s, 1H), 7.47-7.29 (m, 3H), 6.84-6.82 (m, 1H), 6.54-6.52 (m, 1H), 3.97 (s, 3H), 2.90-2.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.5, 150.2, 148.3, 134.3, 126.5, 126.4, 126.1, 125.5, 125.2, 122.1, 116.8, 110.1, 71.2, 52.8, 37.6, 31.0. IR (thin film): νmax (cm^{-1}) = 3286, 2952, 1731, 1679, 1545, 1451, 1279, 1165, 1080, 964, 830, 754, 596, 551, 487. HRMS (ESI) calcd for $C_{18}H_{15}NaNO_4S$ $[M+Na]^+$: 364.0619. Found: 364.0611.



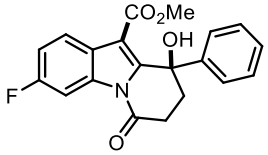
2q, blue solid, 64.0 mg, 87% yield, m.p. = 153.5-154.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.62 (m, 1H), 8.14-8.12 (m, 1H), 7.48-7.40 (m, 2H), 7.32-7.29 (m, 3H), 7.24-7.22 (m, 2H), 4.40-4.25 (m, 2H), 2.85-2.35 (m, 4H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 166.8, 151.3, 144.2, 134.3, 128.5, 128.2, 126.9, 126.2, 125.6, 125.4, 122.0, 116.8, 110.3, 73.1, 61.8, 37.2, 30.8, 14.2. IR (thin film): νmax (cm^{-1}) = 3286, 2952, 1731, 1679, 1544, 1451, 1279, 1165, 1079, 962, 830, 753, 551, 457. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_4$ $[M+Na]^+$: 372.1212. Found: 372.1208.



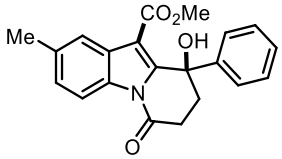
2r, yellow solid, 52.3 mg, 82% yield, m.p. = 143.6-144.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.69 (m, 1H), 7.92-7.89 (m, 1H), 7.51-7.44 (m, 2H), 7.31-7.25 (m, 3H), 7.24-7.15 (m, 2H), 2.91-2.85 (m, 1H), 2.70-2.53 (m, 5H), 2.39-2.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 169.9, 150.8, 144.2, 134.6, 128.4, 128.1, 126.8, 126.1, 125.5, 125.4, 120.5, 118.7, 117.5, 72.9, 37.4, 32.1, 30.8. IR (thin film): νmax (cm^{-1}) = 3262, 2950, 1724, 1673, 1533, 1446, 1307, 1278, 1166, 1149, 1115, 970, 754, 563, 478. HRMS (ESI) calcd for $C_{20}H_{17}NaNO_3$ $[M+Na]^+$: 342.1106. Found: 342.1101.



2s, yellow solid, 54.8 mg, 76% yield, m.p. = 171.6-172.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76-8.73 (m, 1H), 8.48-8.47 (m, 1H), 7.73-7.70 (m, 1H), 7.34-7.32 (m, 2H), 7.21-7.19 (m, 2H), 7.06 (s, 1H), 3.94 (s, 3H), 2.90-2.69 (m, 2H), 2.59-2.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.3, 153.7, 143.4, 136.0, 129.3, 128.8, 128.7, 127.2, 127.0, 125.5, 119.4, 117.8, 109.7, 109.2, 73.3, 53.6, 53.0, 37.1, 30.7. IR (thin film): νmax (cm^{-1}) = 3286, 2951, 1731, 1680, 1546, 1450, 1305, 1278, 1164, 1080, 965, 830, 754, 552, 487. HRMS (ESI) calcd for $C_{21}H_{16}NaN_2O_4$ $[M+Na]^+$: 383.1008. Found: 383.1005.

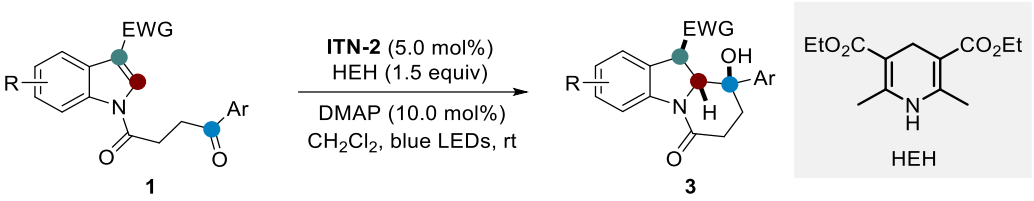


2t, blue solid, 54.4 mg, 77% yield, m.p. = 160.1-161.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37-8.34 (m, 1H), 8.06-8.02 (m, 1H), 7.32-7.29 (m, 2H), 7.23-7.11 (m, 4H), 3.87 (s, 3H), 2.85-2.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.9, 161.6 (d, J = 242.0 Hz), 151.7 (d, J = 3.0 Hz), 144.0, 134.3 (d, J = 13.0 Hz), 128.6, 128.4, 125.6, 123.0 (d, J = 9.0 Hz), 113.7 (d, J = 23.0 Hz), 109.8, 104.1 (d, J = 28.0 Hz), 73.1, 52.6, 37.2, 30.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.63 to -114.70 (m). IR (thin film): νmax (cm^{-1}) = 3261, 2961, 1724, 1681, 1551, 1484, 1426, 1290, 1190, 1163, 1111, 1070, 966, 857, 763, 697, 555, 526, 440. HRMS (ESI) calcd for $C_{20}H_{16}NaFNO_4$ $[M+Na]^+$: 376.0961. Found: 376.0958.

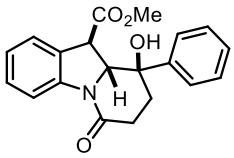


2u, blue solid, 63.0 mg, 90% yield, m.p. = 171.3-172.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 7.88 (s, 1H), 7.33-7.26 (m, 4H), 7.24-7.20 (m, 2H), 3.88 (s, 3H), 2.84-2.34 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.4, 151.4, 144.2, 135.2, 132.5, 128.5, 128.3, 127.5, 126.9, 125.6, 121.8, 116.4, 109.8, 73.2, 52.5, 37.3, 30.7, 21.8. IR (thin film): νmax (cm^{-1}) = 3285, 3055, 2952, 1731, 1679, 1544, 1451, 1356, 1279, 1164, 1153, 1116, 1079, 1042, 962, 866, 830, 798, 753, 729, 550, 486. HRMS (ESI) calcd for $C_{21}H_{19}NaNO_4$ $[M+Na]^+$: 372.1212. Found: 372.1205.

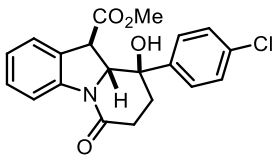
5. General procedure for photocatalytic intramolecular dearomatization of indole derivatives with ketones



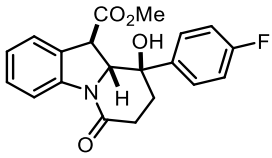
To a flame-dried sealed tube were added **ITN-2** (5.20 mg, 5.0 mol%), **1** (0.20 mmol, 1.0 equiv), HEH (0.30 mmol, 1.5 equiv), DMAP (2.40 mg, 10.0 mol%) and CH_2Cl_2 (2.0 mL, 0.1M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 30 W blue LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Ratios of diastereoisomers were determined by crude ^{1}H NMR analysis. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford the desired products **3**. The analytical data of the product **3a-3u** were summarized below.



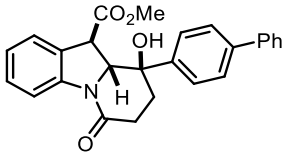
3a, white solid, 61.1 mg, 90% yield, m.p. = 134.0-135.1 °C, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.36-7.28 (m, 6H), 7.26-7.23 (m, 1H), 7.08-7.04 (m, 1H), 4.91 (d, *J* = 9.6 Hz, 1H), 4.14 (d, *J* = 9.6 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 1H), 2.87-2.80 (m, 1H), 2.54-2.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.6, 143.0, 141.7, 129.3, 128.8, 127.2, 126.1, 125.7, 125.3, 124.4, 116.9, 74.4, 69.8, 53.3, 48.6, 38.6, 31.8. IR (thin film): νmax (cm^{-1}) = 3282, 2954, 1744, 1645, 1595, 1541, 1485, 1463, 1424, 1265, 1251, 1231, 1183, 1157, 1108, 1090, 1067, 1029, 1007, 971, 938, 902, 884, 857, 843, 831, 769, 756, 740, 716, 690, 634. HRMS (ESI) calcd for $C_{20}H_{20}NO_4$ $[M+H]^+$: 338.1392. Found: 338.1384.



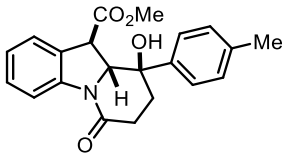
3b, yellow oil, 66.4 mg, 90% yield, 18:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.33-7.27 (m, 4H), 7.24-7.22 (m, 2H), 7.08-7.04 (m, 1H), 4.93 (d, *J* = 8.8 Hz, 1H), 4.17 (s, 1H), 4.06 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 2.89-2.80 (m, 1H), 2.53-2.28 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 169.6, 141.6, 141.5, 133.8, 129.3, 128.9, 127.3, 125.9, 125.3, 124.6, 116.8, 74.2, 69.5, 53.3, 48.5, 38.4, 31.7. IR (thin film): νmax (cm^{-1}) = 3366, 2953, 1737, 1636, 1594, 1483, 1462, 1433, 1399, 1306, 1271, 1228, 1198, 1177, 1094, 1077, 1043, 1012, 967, 933, 908, 831, 754, 736, 699. HRMS (ESI) calcd for $C_{20}H_{19}ClNO_4$ $[M+H]^+$: 372.1003. Found: 372.0997.



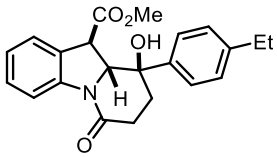
3c, white solid, 67.1 mg, 95% yield, m.p. = 144.9-145.7 °C, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.34-7.27 (m, 4H), 7.08-7.04 (m, 1H), 6.97-6.92 (m, 2H), 4.93 (d, *J* = 9.2 Hz, 1H), 4.09 (d, *J* = 8.8 Hz, 1H), 4.05 (s, 1H), 3.80 (s, 3H), 2.88-2.80 (m, 1H), 2.52-2.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 169.5, 162.1 (d, *J* = 246.0 Hz), 141.5, 138.7 (d, *J* = 3.0 Hz), 129.3, 127.6 (d, *J* = 8.0 Hz), 126.1, 125.2, 124.6, 116.8, 115.6 (d, *J* = 21.0 Hz), 74.1, 69.5, 53.2, 48.4, 38.5, 31.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.31 to -114.38 (m). IR (thin film): νmax (cm^{-1}) = 3469, 2955, 1714, 1686, 1661, 1598, 1507, 1483, 1463, 1442, 1398, 1314, 1277, 1218, 1199, 1180, 1161, 1114, 1073, 1041, 1024, 1007, 967, 940, 908, 841, 816, 753, 731, 687, 637. HRMS (ESI) calcd for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1298. Found: 356.1289.



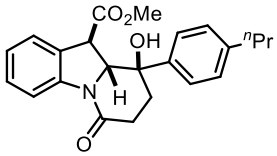
3d, white solid, 72.5 mg, 88% yield, m.p. = 105.1-106.7 °C, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.61-7.48 (m, 4H), 7.42-7.38 (m, 4H), 7.35-7.29 (m, 3H), 7.08-7.04 (m, 1H), 4.95 (d, *J* = 9.2 Hz, 1H), 4.21 (d, *J* = 9.6 Hz, 1H), 3.95 (s, 1H), 3.80 (s, 3H), 2.89-2.80 (m, 1H), 2.57-2.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.6, 141.9, 141.7, 140.5, 140.2, 129.3, 128.9, 127.6, 127.4, 127.0, 126.2, 126.1, 125.3, 124.5, 116.9, 74.3, 69.8, 53.3, 48.7, 38.5, 31.7. IR (thin film): νmax (cm^{-1}) = 3367, 2953, 1739, 1640, 1594, 1482, 1462, 1433, 1399, 1302, 1267, 1231, 1197, 1166, 1075, 1006, 968, 933, 908, 845, 756, 735, 696. HRMS (ESI) calcd for $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1705. Found: 414.1699.



3e, yellow oil, 68.5 mg, 98% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.32-7.20 (m, 4H), 7.07-7.03 (m, 3H), 4.92 (d, *J* = 9.2 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.92 (s, 1H), 3.78 (s, 3H), 2.85-2.76 (m, 1H), 2.51-2.30 (m, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.6, 141.7, 139.9, 137.6, 129.5, 129.2, 126.2, 125.6, 125.2, 124.4, 116.9, 74.3, 69.8, 53.2, 48.6, 38.5, 31.7, 21.0. IR (thin film): νmax (cm^{-1}) = 3368, 2951, 1739, 1640, 1594, 1513, 1482, 1462, 1433, 1401, 1303, 1272, 1231, 1195, 1165, 1076, 1043, 1020, 1007, 968, 908, 842, 819, 755, 728, 646, 617. HRMS (ESI) calcd for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1549. Found: 352.1540.

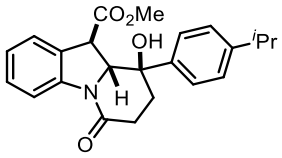


3f, yellow oil, 71.8 mg, 98% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.33-7.23 (m, 4H), 7.10-7.04 (m, 3H), 4.92 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.6 Hz, 1H), 3.85 (s, 1H), 3.79 (s, 3H), 2.84-2.75 (m, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.50-2.29 (m, 3H), 1.17 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.6, 143.8, 141.7, 140.0, 129.2, 128.3, 126.3, 125.7, 125.2, 124.4, 116.9, 74.2, 69.8, 53.2, 48.6, 38.5, 31.7, 28.4, 15.4. IR (thin film): νmax (cm^{-1}) = 3367, 2962, 1740, 1640, 1594, 1511, 1482, 1462, 1433, 1401, 1304, 1273, 1231, 1196, 1177, 1165, 1079, 1045, 1019, 1007, 968, 908, 833, 755, 729, 646, 618. HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M+H]^+$: 366.1705. Found: 366.1692.

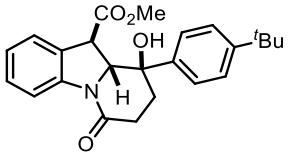


3g, yellow oil, 54.3 mg, 75% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.33-7.28 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.08-7.04 (m, 3H), 4.91 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 1H), 2.84-2.75 (m, 1H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.44-2.29 (m, 3H), 1.61-1.52 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.5, 142.3, 141.7, 139.9, 129.2, 128.9, 126.3, 125.6, 125.2, 124.4, 116.9, 74.2, 69.8, 53.2, 48.6, 38.5, 37.5, 31.7, 24.4, 13.9.

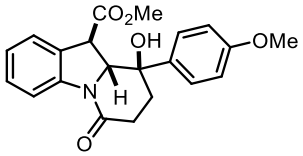
IR (thin film): νmax (cm^{-1}) = 3369, 2955, 2871, 1740, 1644, 1595, 1510, 1482, 1462, 1434, 1401, 1304, 1273, 1231, 1197, 1166, 1076, 1018, 968, 908, 844, 807, 755, 729, 646. HRMS (ESI) calcd for $C_{23}H_{26}NO_4$ $[M+H]^+$: 380.1862. Found: 380.1850.



3h, yellow oil, 61.6 mg, 82% yield, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.34-7.28 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.13-7.04 (m, 3H), 4.92 (d, *J* = 9.6 Hz, 1H), 4.22 (d, *J* = 9.2 Hz, 1H), 3.80 (s, 1H), 3.79 (s, 3H), 2.86-2.74 (m, 2H), 2.49-2.28 (m, 3H), 1.18 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.5, 148.4, 141.7, 139.9, 129.2, 126.8, 126.3, 125.7, 125.2, 124.4, 117.0, 74.1, 69.9, 53.2, 48.6, 38.5, 33.7, 31.6, 23.92, 23.88. IR (thin film): νmax (cm^{-1}) = 3368, 2957, 2871, 1741, 1640, 1594, 1510, 1482, 1462, 1433, 1401, 1301, 1272, 1231, 1197, 1165, 1077, 1017, 968, 934, 908, 832, 754, 717. HRMS (ESI) calcd for $C_{23}H_{26}NO_4$ $[M+H]^+$: 380.1862. Found: 380.1847.

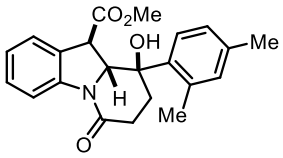


3i, white solid, 61.9 mg, 79% yield, m.p. = 180.1-180.7 °C, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.33-7.24 (m, 6H), 7.08-7.04 (m, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 3.78 (s, 3H), 2.81-2.73 (m, 1H), 2.45-2.29 (m, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 169.4, 150.7, 141.8, 139.4, 129.2, 126.5, 125.7, 125.4, 125.1, 124.4, 117.0, 74.0, 69.9, 53.1, 48.6, 38.4, 34.5, 31.6, 31.3. IR (thin film): νmax (cm^{-1}) = 3507, 2954, 2868, 1718, 1659, 1599, 1512, 1481, 1463, 1429, 1397, 1375, 1363, 1312, 1283, 1255, 1212, 1198, 1163, 1150, 1112, 1081, 1042, 1025, 1015, 967, 940, 912, 847, 829, 810, 771, 754, 723, 698, 614. HRMS (ESI) calcd for $C_{24}H_{28}NO_4$ $[M+H]^+$: 394.2018. Found: 394.2006.

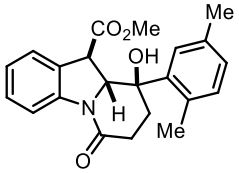


3j, yellow oil, 60.2 mg, 85% yield, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.31-7.23 (m, 4H), 7.06-7.02 (m, 1H), 6.78-6.76 (m, 2H), 4.92 (d, *J* = 8.8 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 2.84-

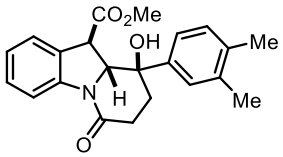
2.77 (m, 1H), 2.50-2.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 169.5, 158.9, 141.6, 134.7, 129.1, 126.9, 126.3, 125.0, 124.3, 116.8, 114.0, 74.0, 69.8, 55.2, 53.1, 48.5, 38.4, 31.7. IR (thin film): νmax (cm^{-1}) = 3369, 2953, 1739, 1640, 1610, 1594, 1511, 1482, 1462, 1433, 1401, 1249, 1178, 1075, 1028, 967, 932, 907, 834, 806, 756, 734, 701. HRMS (ESI) calcd for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1498. Found: 368.1486.



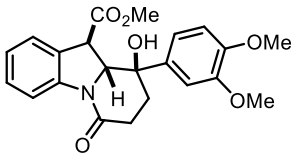
3k, yellow solid, 55.1 mg, 76% yield, m.p. = 140.8-142.3 °C, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.42-7.32 (m, 2H), 7.15-7.11 (m, 1H), 7.02-6.78 (m, 3H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.49 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 3.44 (s, 1H), 2.75-2.66 (m, 1H), 2.58-2.52 (m, 1H), 2.46 (s, 3H), 2.33-2.26 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 168.7, 141.6, 137.5, 134.7, 129.4, 126.5, 126.2, 126.0, 125.2, 124.6, 117.5, 75.5, 71.3, 53.2, 48.6, 35.7, 31.6, 22.2, 20.8. IR (thin film): νmax (cm^{-1}) = 3131, 3096, 2947, 1717, 1703, 1663, 1603, 1585, 1561, 1514, 1477, 1446, 1433, 1390, 1370, 1342, 1315, 1300, 1251, 1235, 1219, 1200, 1179, 1153, 1111, 1064, 1045, 975, 955, 928, 900, 878, 855, 830, 815, 804, 776, 762, 745, 724, 663, 649, 617. HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M+H]^+$: 366.1705. Found: 366.1691.



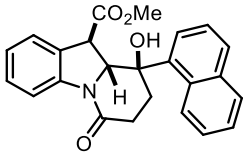
3l, yellow solid, 70.1 mg, 96% yield, m.p. = 140.8-142.3 °C, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.43-7.32 (m, 2H), 7.13-6.94 (m, 4H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.41-4.40 (m, 1H), 3.78 (s, 3H), 3.60 (s, 1H), 2.78-2.71 (m, 1H), 2.59-2.51 (m, 1H), 2.38 (s, 3H), 2.32-2.24 (m, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 169.3, 141.5, 135.2, 133.6, 129.4, 128.6, 127.0, 126.0, 125.3, 124.5, 117.3, 76.0, 71.1, 53.6, 53.3, 48.8, 35.7, 31.8, 21.7, 21.3. IR (thin film): νmax (cm^{-1}) = 3219, 2955, 2224, 1716, 1668, 1594, 1532, 1483, 1437, 1398, 1367, 1281, 1254, 1222, 1205, 1107, 1042, 1025, 920, 887, 866, 836, 806, 771, 755, 700, 628. HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M+H]^+$: 366.1705. Found: 366.1700.



3m, white solid, 69.2 mg, 95% yield, m.p. = 147.6-149.3 °C, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.32-7.26 (m, 2H), 7.17 (s, 1H), 7.07-6.93 (m, 3H), 4.91 (d, *J* = 9.2 Hz, 1H), 4.17 (d, *J* = 9.2 Hz, 1H), 3.87 (s, 1H), 3.79 (s, 3H), 2.84-2.77 (m, 1H), 2.52-2.30 (m, 3H), 2.17 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.7, 141.7, 140.3, 137.1, 136.2, 129.9, 129.2, 127.0, 126.3, 125.2, 124.3, 122.8, 116.8, 74.3, 69.8, 53.2, 48.6, 38.5, 31.8, 20.1, 19.4. IR (thin film): νmax (cm^{-1}) = 3341, 2972, 1741, 1644, 1595, 1483, 1462, 1402, 1269, 1230, 1182, 1165, 1082, 1067, 1047, 1026, 969, 940, 868, 818, 758, 703. HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M+H]^+$: 366.1705. Found: 366.1692.

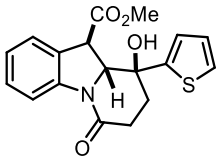


3n, yellow oil, 71.3 mg, 90% yield, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.6 Hz, 1H), 7.33-7.26 (m, 2H), 7.07-7.03 (m, 1H), 6.84-6.71 (m, 3H), 4.94 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.61 (s, 3H), 2.88-2.79 (m, 1H), 2.54-2.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 169.7, 148.9, 148.3, 141.7, 135.4, 129.2, 126.3, 125.2, 124.4, 117.7, 116.6, 110.8, 108.8, 74.3, 69.5, 55.8, 55.6, 53.1, 48.5, 38.4, 31.8. IR (thin film): νmax (cm^{-1}) = 3263, 3000, 2937, 2838, 1746, 1647, 1594, 1518, 1484, 1460, 1422, 1326, 1240, 1222, 1199, 1168, 1137, 1105, 1083, 1059, 1048, 1025, 1007, 941, 913, 866, 852, 832, 813, 796, 767, 753, 729, 715, 696, 646. HRMS (ESI) calcd for $C_{22}H_{24}NO_6$ $[M+H]^+$: 398.1604. Found: 398.1590.

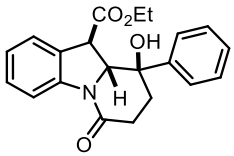


3o, white solid, 67.4 mg, 87% yield, m.p. = 108.5-110.2 °C, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.75-7.67 (m, 3H), 7.45-7.43 (m, 2H), 7.31-7.25 (m, 3H), 7.06-7.01 (m, 1H), 4.98 (d, *J* = 9.2 Hz, 1H), 4.24 (s, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 2.92-2.84 (m, 1H), 2.59-2.45 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 170.1, 141.6, 140.8, 133.0, 132.6, 129.2, 128.8,

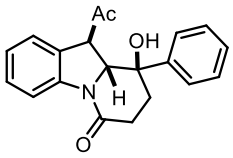
128.5, 127.5, 126.53, 126.48, 126.0, 125.4, 124.9, 124.4, 123.4, 116.7, 74.9, 69.8, 53.3, 48.8, 38.4, 32.0. IR (thin film): νmax (cm^{-1}) = 3343, 2938, 1737, 1643, 1594, 1506, 1464, 1435, 1418, 1357, 1339, 1269, 1250, 1228, 1195, 1180, 1123, 1098, 1076, 1043, 1020, 1007, 991, 969, 940, 934, 909, 895, 866, 859, 846, 819, 798, 772, 762, 752, 714, 694, 648, 624. HRMS (ESI) calcd for $C_{24}H_{22}NO_4$ $[M+H]^+$: 388.1549. Found: 388.1536.



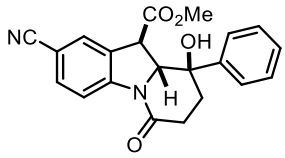
3p, yellow solid, 57.7 mg, 85% yield, m.p. = 167.8-170.2 ºC, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.36-7.28 (m, 2H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.90-6.88 (m, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 4.32 (s, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 2.85-2.78 (m, 1H), 2.67-2.58 (m, 1H), 2.49-2.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 168.4, 145.7, 142.0, 129.2, 127.5, 126.1, 125.3, 125.1, 124.6, 123.8, 117.2, 73.8, 69.5, 53.4, 48.6, 38.0, 31.1. IR (thin film): νmax (cm^{-1}) = 3276, 3104, 2951, 1743, 1627, 1591, 1482, 1462, 1434, 1399, 1367, 1327, 1293, 1259, 1236, 1200, 1104, 1091, 1075, 1051, 1019, 1007, 961, 945, 930, 908, 852, 835, 809, 759, 722, 706, 696, 626. HRMS (ESI) calcd for $C_{18}H_{18}NO_4S$ $[M+H]^+$: 344.0957. Found: 344.0947.



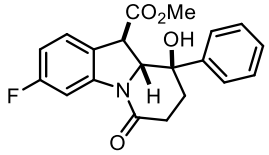
3q, yellow oil, 59.2 mg, 85% yield, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.35-7.20 (m, 7H), 7.05 (t, *J* = 7.6 Hz, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 4.31-4.17 (m, 2H), 4.12 (d, *J* = 9.6 Hz, 1H), 4.04 (s, 1H), 2.86-2.78 (m, 1H), 2.52-2.31 (m, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 169.7, 143.0, 141.6, 129.1, 128.7, 127.8, 126.3, 125.7, 125.1, 124.4, 116.8, 74.3, 69.6, 62.4, 48.6, 38.5, 31.7, 14.2. IR (thin film): νmax (cm^{-1}) = 3368, 2956, 1735, 1640, 1594, 1482, 1462, 1402, 1302, 1271, 1229, 1182, 1158, 1093, 1066, 1026, 912, 888, 867, 754, 702. HRMS (ESI) calcd for $C_{21}H_{21}NO_4Na$ $[M+Na]^+$: 374.1368. Found: 374.1354.



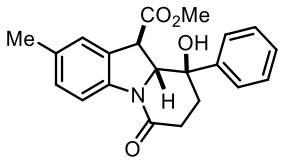
3r, yellow oil, 48.3 mg, 73% yield, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.31-7.20 (m, 6H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.86 (d, *J* = 8.4 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 1H), 2.88-2.80 (m, 1H), 2.52-2.35 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 169.6, 142.9, 142.2, 129.2, 128.8, 127.9, 126.9, 125.7, 124.5, 124.4, 117.1, 74.6, 69.2, 56.8, 38.5, 31.9, 29.6. IR (thin film): νmax (cm^{-1}) = 3369, 2955, 1713, 1640, 1593, 1481, 1461, 1400, 1354, 1267, 1202, 1160, 1092, 1064, 1027, 1001, 934, 869, 840, 754, 731, 702. HRMS (ESI) calcd for $C_{20}H_{20}NO_3$ $[M+H]^+$: 322.1443. Found: 322.1432.



3s, white oil, 62.4 mg, 87% yield, 18:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 1H), 7.33-7.22 (m, 6H), 6.76-6.71 (m, 1H), 4.95 (d, *J* = 9.2 Hz, 1H), 4.06 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 1H), 3.80 (s, 3H), 2.88-2.80 (m, 1H), 2.55-2.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.6, 145.1, 142.8, 134.1, 129.4, 129.0, 128.2, 127.1, 125.5, 119.0, 116.8, 112.8, 107.3, 74.5, 69.9, 53.7, 48.1, 38.3, 32.0. IR (thin film): νmax (cm^{-1}) = 3116, 2954, 2223, 1738, 1675, 1603, 1584, 1528, 1483, 1444, 1388, 1365, 1326, 1245, 1206, 1181, 1140, 1115, 1066, 1039, 920, 887, 776, 743, 703, 627. HRMS (ESI) calcd for $C_{21}H_{19}N_2O_4$ $[M+H]^+$: 363.1345. Found: 363.1339.



3t, white solid, 68.2 mg, 96% yield, m.p. = 108.5-110.2 °C, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 1H), 7.33-7.26 (m, 5H), 7.24-7.22 (m, 1H), 6.76-6.71 (m, 1H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.06 (d, *J* = 9.2 Hz, 1H), 3.86 (s, 1H), 3.80 (s, 3H), 2.88-2.80 (m, 1H), 2.55-2.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 169.9, 163.3 (d, *J* = 244.0 Hz), 142.9, 142.8 (d, *J* = 12.0 Hz), 128.8, 128.0, 126.1 (d, *J* = 10.0 Hz), 125.6, 121.6 (d, *J* = 3.0 Hz), 111.1 (d, *J* = 23.0 Hz), 104.8 (d, *J* = 29.0 Hz), 74.4, 70.4, 53.3, 47.9, 38.4, 31.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -111.47 to -111.53 (m). IR (thin film): νmax (cm^{-1}) = 3311, 2954, 1743, 1647, 1595, 1486, 1435, 1417, 1357, 1268, 1252, 1230, 1206, 1170, 1123, 1098, 1068, 1029, 1007, 969, 933, 909, 895, 880, 856, 846, 818, 797, 771, 752, 739, 703, 694, 670, 613. HRMS (ESI) calcd for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1298. Found: 356.1286.



3u, white solid, 60.2 mg, 86% yield, m.p. = 160.1-162.4 ºC, > 20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 1H), 7.37-7.28 (m, 4H), 7.26-7.23 (m, 1H), 7.12 (d, *J* = 6.4 Hz, 2H), 4.93 (d, *J* = 9.2 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.85 (s, 1H), 3.82 (s, 3H), 2.85-2.77 (m, 1H), 2.51-2.35 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 169.2, 142.9, 139.4, 134.2, 129.8, 128.8, 127.8, 126.3, 125.7, 125.6, 116.6, 74.3, 69.9, 53.2, 48.5, 38.5, 31.6, 21.3. IR (thin film): νmax (cm^{-1}) = 3237, 2952, 1733, 1632, 1608, 1589, 1489, 1435, 1399, 1346, 1302, 1274, 1245, 1194, 1174, 1151, 1116, 1086, 1071, 1030, 1006, 966, 929, 897, 833, 802, 767, 752, 701. HRMS (ESI) calcd for $C_{21}H_{21}NaNO_4$ $[M+Na]^+$: 374.1368. Found: 374.1353.

6. X-Ray crystal data of ITN-1, ITN-2, ITN-3, 2a and 3k

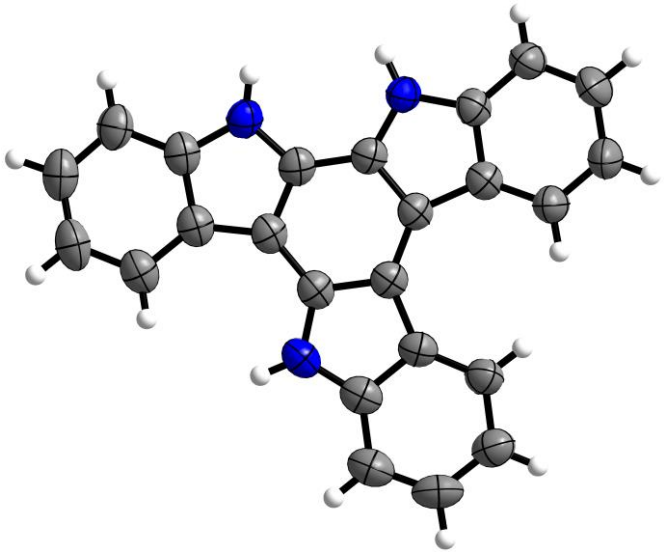


Figure S22. X-Ray crystal structure of ITN-1 (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC: 2271792)

Table S2 Crystal data and structure refinement for ITN-1.

Identification code	**ITN-1**
Empirical formula	$C_{26}H_{18}ClN_3O_2$
Formula weight	439.88
Temperature/K	261 K
Crystal system	Monoclinic
Space group	C 2/c
a/Å	30.8340(15)

b/Å	7.8320(2)
c/Å	22.5177(11)
α/°	90
β/°	132.054(8)
γ/°	90
Volume/Å^3	4037.7(5)
Z	8
ρcalcg/cm^3	1.447
μ/mm^{-1}	1.925
F(000)	1824
Crystal size/mm^3	0.32 x 0.25 x 0.13
Radiation	CuK\a (λ = 1.54184)
2Θ range for data collection/°	5.686 to 153.072
Index ranges	-38<=h<=37, -9<=k<=9, -28<=l<=28
Reflections collected	21560
Independent reflections	4262 [R(int) = 0.09]
Data/restraints/parameters	4262 / 0 / 289
Goodness-of-fit on F2	1.075
Final R indexes [I>=2σ (I)]	R1 = 0.0873, wR2 = 0.2537
Final R indexes [all data]	R1 = 0.0965, wR2 = 0.2661
Largest diff. peak/hole / e Å-3	0.581 / -0.691

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ITN-1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C(1)	3208(1)	4252(3)	5737(1)	43(1)
C(2)	2957(1)	3743(3)	4961(1)	45(1)
C(3)	2394(1)	4268(3)	4283(1)	45(1)
C(4)	2074(1)	5256(3)	4399(2)	45(1)
C(5)	2316(1)	5789(3)	5177(1)	43(1)
C(6)	2896(1)	5297(3)	5852(1)	43(1)
C(7)	3819(1)	4715(3)	7047(2)	47(1)
C(8)	3298(1)	5615(3)	6706(1)	45(1)
C(9)	3286(1)	6564(4)	7216(2)	56(1)
C(10)	3766(1)	6585(5)	8026(2)	68(1)

C(11)	4274(1)	5676(5)	8349(2)	66(1)
C(12)	4309(1)	4741(4)	7864(2)	58(1)
C(13)	2788(1)	2613(3)	3907(2)	50(1)
C(14)	2823(1)	1688(4)	3420(2)	58(1)
C(15)	2346(2)	1731(4)	2604(2)	65(1)
C(16)	1851(2)	2696(4)	2288(2)	66(1)
C(17)	1812(1)	3610(4)	2774(2)	58(1)
C(18)	2282(1)	3561(3)	3601(2)	49(1)
C(19)	1373(1)	6744(3)	4214(2)	50(1)
C(20)	852(1)	7600(4)	3867(2)	63(1)
C(21)	822(1)	8435(4)	4373(2)	66(1)
C(22)	1281(1)	8401(4)	5201(2)	64(1)
C(23)	1796(1)	7553(4)	5539(2)	55(1)
C(24)	1855(1)	6732(3)	5050(2)	45(1)
C(25)	4816(1)	1053(4)	6446(2)	56(1)
C(26)	4981(2)	629(6)	5961(2)	76(1)
N(1)	3747(1)	3879(3)	6449(1)	47(1)
N(2)	3191(1)	2754(3)	4738(1)	49(1)
N(3)	1515(1)	5824(3)	3842(1)	52(1)
Cl(1)	4544(1)	1683(3)	5039(1)	134(1)
O(5)	4384(1)	1863(3)	6174(1)	65(1)
O(4)	5187(1)	453(3)	7154(1)	68(1)

Table S4 Anisotropic Displacement Parameters ($Å^2×10^3$) for ITN-1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
C(1)	48(1)	33(1)	45(1)	1(1)	30(1)	-1(1)
C(2)	53(1)	34(1)	48(1)	0(1)	34(1)	-4(1)
C(3)	51(1)	36(1)	44(1)	-2(1)	31(1)	-6(1)
C(4)	50(1)	34(1)	45(1)	2(1)	30(1)	-4(1)
C(5)	48(1)	33(1)	48(1)	0(1)	32(1)	-3(1)
C(6)	48(1)	33(1)	45(1)	-1(1)	30(1)	-3(1)

C(7)	49(1)	41(1)	48(1)	-6(1)	31(1)	-5(1)
C(8)	48(1)	37(1)	47(1)	-2(1)	30(1)	-4(1)
C(9)	50(1)	61(2)	51(1)	-9(1)	31(1)	1(1)
C(10)	58(2)	84(2)	53(2)	-21(2)	34(1)	-2(2)
C(11)	50(1)	81(2)	47(1)	-14(1)	23(1)	-4(1)
C(12)	48(1)	61(2)	52(1)	-7(1)	28(1)	1(1)
C(13)	61(1)	42(1)	47(1)	-2(1)	36(1)	-10(1)
C(14)	73(2)	52(2)	61(2)	-3(1)	49(2)	-6(1)
C(15)	88(2)	62(2)	56(2)	-11(1)	53(2)	-13(2)
C(16)	83(2)	65(2)	46(1)	-6(1)	42(1)	-16(2)
C(17)	63(2)	53(2)	48(1)	-1(1)	34(1)	-7(1)
C(18)	60(1)	38(1)	48(1)	-2(1)	37(1)	-8(1)
C(19)	49(1)	45(1)	52(1)	5(1)	31(1)	-4(1)
C(20)	48(1)	64(2)	58(2)	11(1)	28(1)	0(1)
C(21)	51(1)	65(2)	78(2)	15(2)	42(2)	13(1)
C(22)	61(2)	64(2)	71(2)	10(1)	47(2)	12(1)
C(23)	53(1)	55(2)	53(1)	5(1)	34(1)	6(1)
C(24)	49(1)	35(1)	48(1)	5(1)	31(1)	-1(1)
C(25)	65(2)	49(2)	57(1)	1(1)	42(1)	1(1)
C(26)	82(2)	92(2)	61(2)	11(2)	50(2)	21(2)
N(1)	48(1)	40(1)	49(1)	-4(1)	31(1)	1(1)
N(2)	56(1)	42(1)	48(1)	-1(1)	34(1)	0(1)
N(3)	49(1)	52(1)	43(1)	1(1)	25(1)	-4(1)
Cl(1)	134(1)	208(2)	76(1)	55(1)	77(1)	70(1)
O(5)	68(1)	66(1)	66(1)	5(1)	47(1)	13(1)
O(4)	71(1)	78(2)	52(1)	6(1)	39(1)	10(1)

Table S5 Bond Lengths for ITN-1.

Bond	**Angle/°**	**Bond**	**Angle/°**
C(1)-N(1)	1.359(3)	C(15)-C(16)	1.397(5)
C(1)-C(6)	1.413(4)	C(15)-H(15)	0.9300
C(1)-C(2)	1.414(3)	C(16)-C(17)	1.378(5)
C(2)-N(2)	1.365(3)	C(16)-H(16)	0.9300

C(2)-C(3)	1.402(4)	C(17)-C(18)	1.398(4)
C(3)-C(4)	1.410(4)	C(17)-H(17)	0.9300
C(3)-C(18)	1.441(3)	C(19)-N(3)	1.379(4)
C(4)-N(3)	1.358(3)	C(19)-C(20)	1.400(4)
C(4)-C(5)	1.430(3)	C(19)-C(24)	1.415(3)
C(5)-C(6)	1.419(3)	C(20)-C(21)	1.371(5)
C(5)-C(24)	1.452(4)	C(20)-H(20)	0.9300
C(6)-C(8)	1.450(3)	C(21)-C(22)	1.395(5)
C(7)-N(1)	1.375(3)	C(21)-H(21)	0.9300
C(7)-C(12)	1.395(4)	C(22)-C(23)	1.385(4)
C(7)-C(8)	1.419(4)	C(22)-H(22)	0.9300
C(8)-C(9)	1.389(4)	C(23)-C(24)	1.389(4)
C(9)-C(10)	1.379(4)	C(23)-H(23)	0.9300
C(9)-H(9)	0.9300	C(25)-O(5)	1.207(4)
C(10)-C(11)	1.399(5)	C(25)-O(4)	1.277(4)
C(10)-H(10)	0.9300	C(25)-C(26)	1.517(4)
C(11)-C(12)	1.379(4)	C(26)-Cl(1)	1.750(4)
C(11)-H(11)	0.9300	C(26)-H(26A)	0.9700
C(12)-H(12)	0.9300	C(26)-H(26B)	0.9700
C(13)-C(14)	1.379(4)	N(1)-H(1)	0.8600
C(13)-N(2)	1.393(3)	N(2)-H(2)	0.8600
C(13)-C(18)	1.420(4)	N(3)-H(3)	0.8600
C(14)-C(15)	1.386(4)	O(4)-H(4)	0.8200
C(14)-H(14)	0.9300		

Table S6 Bond Angles for ITN-1.

Bond	**Angle/°**	**Bond**	**Angle/°**
N(1)-C(1)-C(6)	110.7(2)	C(17)-C(16)-H(16)	119.2
N(1)-C(1)-C(2)	128.4(2)	C(15)-C(16)-H(16)	119.2
C(6)-C(1)-C(2)	120.9(2)	C(16)-C(17)-C(18)	118.6(3)
N(2)-C(2)-C(3)	109.9(2)	C(16)-C(17)-H(17)	120.7
N(2)-C(2)-C(1)	129.0(2)	C(18)-C(17)-H(17)	120.7
C(3)-C(2)-C(1)	121.1(2)	C(17)-C(18)-C(13)	118.9(2)

C(2)-C(3)-C(4)	118.0(2)	C(17)-C(18)-C(3)	134.7(3)
C(2)-C(3)-C(18)	106.6(2)	C(13)-C(18)-C(3)	106.4(2)
C(4)-C(3)-C(18)	135.4(2)	N(3)-C(19)-C(20)	128.5(3)
N(3)-C(4)-C(3)	128.4(2)	N(3)-C(19)-C(24)	109.1(2)
N(3)-C(4)-C(5)	109.6(2)	C(20)-C(19)-C(24)	122.3(3)
C(3)-C(4)-C(5)	122.0(2)	C(21)-C(20)-C(19)	117.1(3)
C(6)-C(5)-C(4)	118.9(2)	C(21)-C(20)-H(20)	121.4
C(6)-C(5)-C(24)	135.6(2)	C(19)-C(20)-H(20)	121.4
C(4)-C(5)-C(24)	105.5(2)	C(20)-C(21)-C(22)	121.9(3)
C(1)-C(6)-C(5)	119.0(2)	C(20)-C(21)-H(21)	119.0
C(1)-C(6)-C(8)	105.1(2)	C(22)-C(21)-H(21)	119.0
C(5)-C(6)-C(8)	135.9(2)	C(23)-C(22)-C(21)	120.5(3)
N(1)-C(7)-C(12)	128.3(2)	C(23)-C(22)-H(22)	119.7
N(1)-C(7)-C(8)	109.0(2)	C(21)-C(22)-H(22)	119.7
C(12)-C(7)-C(8)	122.7(2)	C(22)-C(23)-C(24)	119.7(3)
C(9)-C(8)-C(7)	117.7(2)	C(22)-C(23)-H(23)	120.1
C(9)-C(8)-C(6)	135.7(2)	C(24)-C(23)-H(23)	120.1
C(7)-C(8)-C(6)	106.5(2)	C(23)-C(24)-C(19)	118.3(2)
C(10)-C(9)-C(8)	120.1(3)	C(23)-C(24)-C(5)	135.3(2)
C(10)-C(9)-H(9)	120.0	C(19)-C(24)-C(5)	106.4(2)
C(8)-C(9)-H(9)	120.0	O(5)-C(25)-O(4)	126.0(3)
C(9)-C(10)-C(11)	121.1(3)	O(5)-C(25)-C(26)	122.6(3)
C(9)-C(10)-H(10)	119.4	O(4)-C(25)-C(26)	111.5(3)
C(11)-C(10)-H(10)	119.4	C(25)-C(26)-Cl(1)	112.8(2)
C(12)-C(11)-C(10)	120.9(3)	C(25)-C(26)-H(26A)	109.0
C(12)-C(11)-H(11)	119.6	Cl(1)-C(26)-H(26A)	109.0
C(10)-C(11)-H(11)	119.6	C(25)-C(26)-H(26B)	109.0
C(11)-C(12)-C(7)	117.5(3)	Cl(1)-C(26)-H(26B)	109.0
C(11)-C(12)-H(12)	121.3	H(26A)-C(26)-H(26B)	107.8
C(7)-C(12)-H(12)	121.3	C(1)-N(1)-C(7)	108.7(2)
C(14)-C(13)-N(2)	129.3(3)	C(1)-N(1)-H(1)	125.7
C(14)-C(13)-C(18)	122.3(3)	C(7)-N(1)-H(1)	125.7
N(2)-C(13)-C(18)	108.3(2)	C(2)-N(2)-C(13)	108.8(2)

C(13)-C(14)-C(15)	117.5(3)	C(2)-N(2)-H(2)	125.6
C(13)-C(14)-H(14)	121.2	C(13)-N(2)-H(2)	125.6
C(15)-C(14)-H(14)	121.2	C(4)-N(3)-C(19)	109.4(2)
C(14)-C(15)-C(16)	121.0(3)	C(4)-N(3)-H(3)	125.3
C(14)-C(15)-H(15)	119.5	C(19)-N(3)-H(3)	125.3
C(16)-C(15)-H(15)	119.5	C(25)-O(4)-H(4)	109.5
C(17)-C(16)-C(15)	121.6(3)		

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ITN-1.

Atom	x	y	z	U(eq)
H(9)	2954	7186	7011	67
H(10)	3753	7214	8363	81
H(11)	4591	5703	8897	80
H(12)	4648	4151	8074	70
H(14)	3155	1058	3631	70
H(15)	2355	1108	2261	78
H(16)	1540	2722	1737	80
H(17)	1480	4247	2556	69
H(20)	540	7603	3316	75
H(21)	485	9042	4158	79
H(22)	1242	8952	5528	76
H(23)	2100	7534	6092	65
H(26A)	4946	-593	5870	92
H(26B)	5386	941	6268	92
H(1)	4001	3229	6514	57
H(2)	3532	2292	5057	59
H(3)	1285	5639	3336	62
H(4)	5339	1240	7477	103

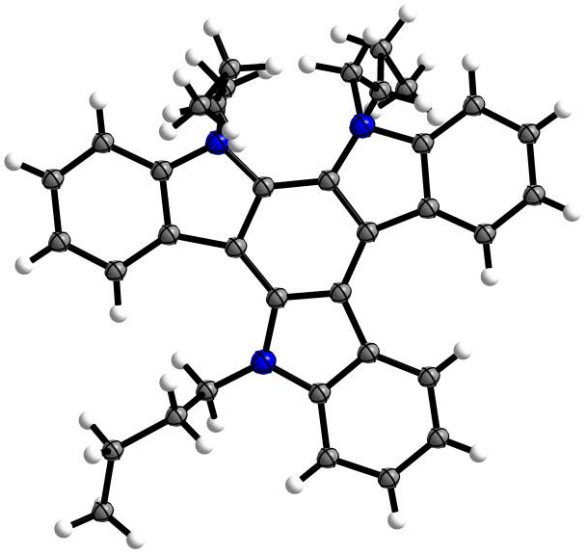


Figure S23. X-Ray crystal structure of ITN-2 (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC: 2271797)

Table S8 Crystal data and structure refinement for ITN-2.

Identification code	**ITN-2**
Empirical formula	$C_{36}H_{29}N_3$
Formula weight	513.70
Temperature/K	300 K
Crystal system	Monoclinic
Space group	C 2/c
a/Å	12.4937(2)
b/Å	24.0509(4)
c/Å	10.0306(2)
α/°	90
β/°	104.017(2)
γ/°	90
Volume/$Å^3$	2924.29(9)
Z	4
ρcalcg/cm^3	1.167
μ/mm^{-1}	0.517
F(000)	1104
Crystal size/mm^3	0.30 x 0.25 x 0.13
Radiation	CuK\a (λ = 1.54184)
2Θ range for data collection/°	7.30 to 156.08
Index ranges	-15<=h<=15, -30<=k<=29, -12<=l<=10
Reflections collected	39094

Independent reflections	6232 [R(int) = 0.0369]
Data/restraints/parameters	6232 / 78 / 451
Goodness-of-fit on F2	1.059
Final R indexes [I>=2σ (I)]	R1 = 0.0741, wR2 = 0.2096
Final R indexes [all data]	R1 = 0.0869, wR2 = 0.2211
Largest diff. peak/hole / e Å-3	0.385 / -0.358

Table S9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for ITN-2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C(29')	6838(2)	7782(1)	3680(3)	88(1)
C(25')	9130(2)	7091(2)	3926(3)	94(1)
C(1)	7915(2)	6746(1)	5418(2)	61(1)
C(2)	8163(2)	6386(1)	6540(2)	63(1)
C(3)	7325(2)	6027(1)	6777(2)	62(1)
C(4)	6242(2)	6073(1)	5951(2)	63(1)
C(5)	5955(2)	6480(1)	4891(2)	61(1)
C(6)	6817(2)	6822(1)	4679(2)	59(1)
C(7)	9702(2)	6875(1)	6401(3)	71(1)
C(8)	10782(2)	7070(1)	6751(3)	88(1)
C(9)	11458(2)	6897(2)	7972(4)	104(1)
C(10)	11073(3)	6542(2)	8829(4)	108(1)
C(11)	10012(2)	6337(1)	8480(3)	92(1)
C(12)	9304(2)	6492(1)	7224(2)	71(1)
C(13)	7331(2)	5570(1)	7714(2)	71(1)
C(14)	8135(3)	5299(1)	8708(3)	93(1)
C(15)	7828(3)	4870(1)	9445(4)	109(1)
C(16)	6754(3)	4695(1)	9196(4)	111(1)
C(17)	5947(3)	4936(1)	8189(3)	102(1)
C(18)	6250(2)	5375(1)	7450(3)	77(1)
C(19)	5286(2)	7122(1)	3202(2)	66(1)
C(20)	4555(2)	7409(1)	2154(3)	81(1)
C(21)	3484(3)	7234(2)	1797(3)	99(1)

C(22)	3137(3)	6798(2)	2478(4)	110(1)
C(23)	3854(2)	6517(1)	3515(3)	92(1)
C(24)	4964(2)	6672(1)	3907(2)	66(1)
C(25)	9130(2)	7091(2)	3926(3)	94(1)
C(26)	9840(5)	6721(3)	3370(7)	97(2)
C(27)	9390(7)	6136(3)	3281(9)	106(2)
C(28)	9984(17)	5745(4)	2519(19)	135(4)
C(26')	9471(9)	6458(4)	3673(9)	114(3)
C(27')	9894(7)	6389(4)	2422(8)	123(3)
C(28')	10240(20)	5816(5)	2121(19)	150(6)
C(29)	6838(2)	7782(1)	3680(3)	88(1)
C(30)	6198(7)	8186(4)	4426(11)	118(3)
C(31)	6752(7)	8613(4)	5325(10)	128(3)
C(32)	6195(14)	8899(7)	6287(18)	111(4)
C(30')	6883(8)	8123(3)	4899(7)	157(5)
C(31')	5883(9)	8414(5)	4912(11)	180(5)
C(32')	6022(17)	8911(7)	5900(20)	157(8)
C(33)	4469(3)	5497(2)	5745(4)	85(1)
C(34)	3653(4)	5775(3)	6426(6)	122(2)
C(35)	2450(5)	5634(4)	5804(10)	151(3)
C(36)	1980(10)	5151(6)	6225(13)	235(6)
C(33')	4381(8)	5835(4)	6524(10)	83(3)
C(34')	3581(7)	5385(4)	5908(12)	90(3)
C(35')	2437(9)	5446(7)	6160(20)	222(17)
C(36')	1607(14)	5035(11)	5450(20)	310(30)
N(1)	8866(2)	7030(1)	5275(2)	69(1)
N(2)	6406(2)	7220(1)	3675(2)	64(1)
N(3)	5588(2)	5674(1)	6384(2)	77(1)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for ITN-2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12

C(29')	83(2)	71(2)	104(2)	13(1)	13(2)	-1(1)
C(25')	70(2)	135(3)	80(2)	6(2)	24(1)	-2(2)
C(1)	57(1)	63(1)	60(1)	0(1)	10(1)	2(1)
C(2)	63(1)	61(1)	61(1)	1(1)	9(1)	4(1)
C(3)	67(1)	59(1)	57(1)	-1(1)	9(1)	2(1)
C(4)	69(1)	61(1)	58(1)	-5(1)	12(1)	-7(1)
C(5)	60(1)	63(1)	55(1)	-4(1)	8(1)	-1(1)
C(6)	60(1)	62(1)	53(1)	1(1)	9(1)	3(1)
C(7)	58(1)	76(1)	75(1)	3(1)	5(1)	2(1)
C(8)	64(1)	95(2)	98(2)	7(2)	7(1)	-6(1)
C(9)	67(2)	116(2)	112(2)	10(2)	-9(2)	-10(2)
C(10)	86(2)	117(2)	98(2)	18(2)	-25(2)	-7(2)
C(11)	85(2)	95(2)	82(2)	18(2)	-8(1)	-6(1)
C(12)	66(1)	72(1)	69(1)	4(1)	4(1)	4(1)
C(13)	84(2)	60(1)	64(1)	2(1)	12(1)	-1(1)
C(14)	96(2)	77(2)	99(2)	24(1)	9(2)	5(1)
C(15)	122(3)	86(2)	109(2)	35(2)	7(2)	2(2)
C(16)	136(3)	85(2)	107(2)	34(2)	20(2)	-13(2)
C(17)	112(2)	86(2)	101(2)	22(2)	13(2)	-25(2)
C(18)	93(2)	65(1)	69(1)	2(1)	14(1)	-11(1)
C(19)	62(1)	73(1)	58(1)	-4(1)	6(1)	10(1)
C(20)	76(2)	89(2)	73(2)	8(1)	8(1)	20(1)
C(21)	73(2)	126(3)	88(2)	10(2)	-3(1)	24(2)
C(22)	65(2)	143(3)	107(2)	9(2)	-7(2)	-1(2)
C(23)	65(1)	110(2)	92(2)	6(2)	1(1)	-9(1)
C(24)	61(1)	74(1)	60(1)	-7(1)	8(1)	2(1)
C(25)	70(2)	135(3)	80(2)	6(2)	24(1)	-2(2)
C(26)	88(3)	130(5)	84(4)	14(3)	42(3)	-6(3)
C(27)	106(4)	119(5)	100(5)	4(4)	38(4)	11(4)
C(28)	143(9)	155(9)	115(10)	-29(6)	45(7)	10(7)
C(26')	132(7)	130(9)	91(5)	-3(5)	50(5)	-5(7)
C(27')	121(6)	159(9)	100(5)	8(5)	48(5)	23(5)
C(28')	171(17)	173(12)	112(11)	-13(8)	44(8)	43(10)

C(29)	83(2)	71(2)	104(2)	13(1)	13(2)	-1(1)
C(30)	77(4)	107(5)	161(6)	-51(5)	10(4)	-10(4)
C(31)	99(5)	153(7)	141(6)	-64(5)	46(5)	-14(5)
C(32)	121(8)	114(9)	103(11)	14(5)	38(6)	24(6)
C(30')	186(9)	70(4)	145(7)	10(4)	-95(6)	11(4)
C(31')	215(13)	198(12)	170(9)	-49(9)	129(10)	-47(10)
C(32')	240(19)	151(12)	101(9)	-8(8)	82(11)	29(10)
C(33)	87(3)	87(3)	75(2)	-4(2)	9(2)	-30(2)
C(34)	90(3)	163(5)	112(4)	0(4)	26(3)	-20(4)
C(35)	98(4)	216(8)	142(5)	25(6)	37(4)	-25(5)
C(36)	217(10)	297(14)	179(10)	60(10)	23(8)	-123(10)
C(33')	88(6)	82(6)	78(5)	-9(4)	18(5)	-18(5)
C(34')	73(6)	85(6)	112(7)	14(5)	23(5)	-18(5)
C(35')	151(17)	250(30)	220(30)	140(20)	-42(15)	-118(17)
C(36')	610(80)	170(20)	129(18)	18(15)	70(30)	90(30)
N(1)	58(1)	77(1)	69(1)	10(1)	11(1)	-1(1)
N(2)	63(1)	66(1)	61(1)	6(1)	9(1)	6(1)
N(3)	77(1)	76(1)	72(1)	5(1)	7(1)	-18(1)

Table S11 Bond Lengths for ITN-2.

Bond	**Angle/°**	**Bond**	**Angle/°**
C(29')-N(2)	1.456(3)	C(27)-H(27B)	0.9700
C(29')-C(30')	1.462(7)	C(28)-H(28A)	0.9600
C(29')-H(29A)	0.9700	C(28)-H(28B)	0.9600
C(29')-H(29B)	0.9700	C(28)-H(28C)	0.9600
C(25')-N(1)	1.476(3)	C(26')-C(27')	1.485(8)
C(25')-C(26')	1.615(8)	C(26')-H(26C)	0.9700
C(25')-H(25A)	0.9700	C(26')-H(26D)	0.9700
C(25')-H(25B)	0.9700	C(27')-C(28')	1.498(9)
C(1)-C(2)	1.394(3)	C(27')-H(27C)	0.9700
C(1)-C(6)	1.405(3)	C(27')-H(27D)	0.9700
C(1)-N(1)	1.407(3)	C(28')-H(28D)	0.9600
C(2)-C(3)	1.421(3)	C(28')-H(28E)	0.9600

C(2)-C(12)	1.448(3)	C(28')-H(28F)	0.9600
C(3)-C(4)	1.409(3)	C(30)-C(31)	1.430(8)
C(3)-C(13)	1.444(3)	C(30)-H(30A)	0.9700
C(4)-N(3)	1.395(3)	C(30)-H(30B)	0.9700
C(4)-C(5)	1.426(3)	C(31)-C(32)	1.488(9)
C(5)-C(6)	1.411(3)	C(31)-H(31A)	0.9700
C(5)-C(24)	1.458(3)	C(31)-H(31B)	0.9700
C(6)-N(2)	1.395(3)	C(32)-H(32A)	0.9600
C(7)-C(8)	1.390(3)	C(32)-H(32B)	0.9600
C(7)-N(1)	1.391(3)	C(32)-H(32C)	0.9600
C(7)-C(12)	1.405(4)	C(30')-C(31')	1.434(9)
C(8)-C(9)	1.373(4)	C(30')-H(30D)	0.9700
C(8)-H(8)	0.9300	C(30')-H(30C)	0.9700
C(9)-C(10)	1.379(5)	C(31')-C(32')	1.533(10)
C(9)-H(9)	0.9300	C(31')-H(31C)	0.9700
C(10)-C(11)	1.377(4)	C(31')-H(31D)	0.9700
C(10)-H(10)	0.9300	C(32')-H(32D)	0.9600
C(11)-C(12)	1.403(3)	C(32')-H(32E)	0.9600
C(11)-H(11)	0.9300	C(32')-H(32F)	0.9600
C(13)-C(18)	1.394(4)	C(33)-N(3)	1.453(4)
C(13)-C(14)	1.394(4)	C(33)-C(34)	1.514(7)
C(14)-C(15)	1.377(4)	C(33)-H(33A)	0.9700
C(14)-H(14)	0.9300	C(33)-H(33B)	0.9700
C(15)-C(16)	1.369(5)	C(34)-C(35)	1.520(7)
C(15)-H(15)	0.9300	C(34)-H(34A)	0.9700
C(16)-C(17)	1.370(5)	C(34)-H(34B)	0.9700
C(16)-H(16)	0.9300	C(35)-C(36)	1.411(9)
C(17)-C(18)	1.394(4)	C(35)-H(35A)	0.9700
C(17)-H(17)	0.9300	C(35)-H(35B)	0.9700
C(18)-N(3)	1.385(3)	C(36)-H(36A)	0.9600
C(19)-N(2)	1.384(3)	C(36)-H(36B)	0.9600
C(19)-C(20)	1.396(3)	C(36)-H(36C)	0.9600
C(19)-C(24)	1.405(3)	C(33')-C(34')	1.502(9)

C(20)-C(21)	1.365(4)	C(33')-N(3)	1.595(10)
C(20)-H(20)	0.9300	C(33')-H(33C)	0.9700
C(21)-C(22)	1.378(5)	C(33')-H(33D)	0.9700
C(21)-H(21)	0.9300	C(34')-C(35')	1.518(10)
C(22)-C(23)	1.375(4)	C(34')-H(34C)	0.9700
C(22)-H(22)	0.9300	C(34')-H(34D)	0.9700
C(23)-C(24)	1.398(3)	C(35')-C(36')	1.485(10)
C(23)-H(23)	0.9300	C(35')-H(35C)	0.9700
C(26)-C(27)	1.512(8)	C(35')-H(35D)	0.9700
C(26)-H(26A)	0.9700	C(36')-H(36D)	0.9600
C(26)-H(26B)	0.9700	C(36')-H(36E)	0.9600
C(27)-C(28)	1.514(8)	C(36')-H(36F)	0.9600
C(27)-H(27A)	0.9700		

Table S12 Bond Angles for ITN-2.

Bond	**Angle/°**	**Bond**	**Angle/°**
N(2)-C(29')-C(30')	117.6(4)	C(27')-C(26')-H(26D)	108.9
N(2)-C(29')-H(29A)	107.9	C(25')-C(26')-H(26D)	108.9
C(30')-C(29')-H(29A)	107.9	H(26C)-C(26')-H(26D)	107.7
N(2)-C(29')-H(29B)	107.9	C(26')-C(27')-C(28')	117.1(8)
C(30')-C(29')-H(29B)	107.9	C(26')-C(27')-H(27C)	108.0
H(29A)-C(29')-H(29B)	107.2	C(28')-C(27')-H(27C)	108.0
N(1)-C(25')-C(26')	100.2(4)	C(26')-C(27')-H(27D)	108.0
N(1)-C(25')-H(25A)	111.7	C(28')-C(27')-H(27D)	108.0
C(26')-C(25')-H(25A)	111.7	H(27C)-C(27')-H(27D)	107.3
N(1)-C(25')-H(25B)	111.7	C(27')-C(28')-H(28D)	109.5
C(26')-C(25')-H(25B)	111.7	C(27')-C(28')-H(28E)	109.5
H(25A)-C(25')-H(25B)	109.5	H(28D)-C(28')-H(28E)	109.5
C(2)-C(1)-C(6)	120.3(2)	C(27')-C(28')-H(28F)	109.5
C(2)-C(1)-N(1)	110.87(19)	H(28D)-C(28')-H(28F)	109.5
C(6)-C(1)-N(1)	128.6(2)	H(28E)-C(28')-H(28F)	109.5
C(1)-C(2)-C(3)	118.9(2)	C(31)-C(30)-H(30A)	106.9
C(1)-C(2)-C(12)	105.8(2)	C(31)-C(30)-H(30B)	106.9

C(3)-C(2)-C(12)	135.2(2)	H(30A)-C(30)-H(30B)	106.7
C(4)-C(3)-C(2)	119.7(2)	C(30)-C(31)-C(32)	120.7(9)
C(4)-C(3)-C(13)	107.2(2)	C(30)-C(31)-H(31A)	107.2
C(2)-C(3)-C(13)	133.0(2)	C(32)-C(31)-H(31A)	107.2
N(3)-C(4)-C(3)	108.34(19)	C(30)-C(31)-H(31B)	107.2
N(3)-C(4)-C(5)	130.0(2)	C(32)-C(31)-H(31B)	107.2
C(3)-C(4)-C(5)	121.6(2)	H(31A)-C(31)-H(31B)	106.8
C(6)-C(5)-C(4)	116.70(19)	C(31')-C(30')-C(29')	115.1(6)
C(6)-C(5)-C(24)	105.49(19)	C(31')-C(30')-H(30D)	108.5
C(4)-C(5)-C(24)	137.8(2)	C(29')-C(30')-H(30D)	108.5
N(2)-C(6)-C(1)	127.7(2)	C(31')-C(30')-H(30C)	108.5
N(2)-C(6)-C(5)	110.38(18)	C(29')-C(30')-H(30C)	108.5
C(1)-C(6)-C(5)	121.88(19)	H(30D)-C(30')-H(30C)	107.5
C(8)-C(7)-N(1)	127.4(2)	C(30')-C(31')-C(32')	115.0(9)
C(8)-C(7)-C(12)	122.2(2)	C(30')-C(31')-H(31C)	108.5
N(1)-C(7)-C(12)	110.4(2)	C(32')-C(31')-H(31C)	108.5
C(9)-C(8)-C(7)	118.2(3)	C(30')-C(31')-H(31D)	108.5
C(9)-C(8)-H(8)	120.9	C(32')-C(31')-H(31D)	108.5
C(7)-C(8)-H(8)	120.9	H(31C)-C(31')-H(31D)	107.5
C(8)-C(9)-C(10)	120.8(3)	C(31')-C(32')-H(32D)	109.5
C(8)-C(9)-H(9)	119.6	C(31')-C(32')-H(32E)	109.5
C(10)-C(9)-H(9)	119.6	H(32D)-C(32')-H(32E)	109.5
C(11)-C(10)-C(9)	121.5(3)	C(31')-C(32')-H(32F)	109.5
C(11)-C(10)-H(10)	119.2	H(32D)-C(32')-H(32F)	109.5
C(9)-C(10)-H(10)	119.2	H(32E)-C(32')-H(32F)	109.5
C(10)-C(11)-C(12)	119.4(3)	N(3)-C(33)-C(34)	110.6(4)
C(10)-C(11)-H(11)	120.3	N(3)-C(33)-H(33A)	109.5
C(12)-C(11)-H(11)	120.3	C(34)-C(33)-H(33A)	109.5
C(11)-C(12)-C(7)	117.8(2)	N(3)-C(33)-H(33B)	109.5
C(11)-C(12)-C(2)	135.4(3)	C(34)-C(33)-H(33B)	109.5
C(7)-C(12)-C(2)	106.60(19)	H(33A)-C(33)-H(33B)	108.1
C(18)-C(13)-C(14)	118.3(2)	C(33)-C(34)-C(35)	115.1(6)
C(18)-C(13)-C(3)	106.3(2)	C(33)-C(34)-H(34A)	108.5

C(14)-C(13)-C(3)	135.4(3)	C(35)-C(34)-H(34A)	108.5
C(15)-C(14)-C(13)	119.3(3)	C(33)-C(34)-H(34B)	108.5
C(15)-C(14)-H(14)	120.3	C(35)-C(34)-H(34B)	108.5
C(13)-C(14)-H(14)	120.3	H(34A)-C(34)-H(34B)	107.5
C(16)-C(15)-C(14)	121.3(3)	C(36)-C(35)-C(34)	120.1(8)
C(16)-C(15)-H(15)	119.4	C(36)-C(35)-H(35A)	107.3
C(14)-C(15)-H(15)	119.4	C(34)-C(35)-H(35A)	107.3
C(15)-C(16)-C(17)	121.3(3)	C(36)-C(35)-H(35B)	107.3
C(15)-C(16)-H(16)	119.4	C(34)-C(35)-H(35B)	107.3
C(17)-C(16)-H(16)	119.4	H(35A)-C(35)-H(35B)	106.9
C(16)-C(17)-C(18)	117.7(3)	C(34')-C(33')-N(3)	109.8(7)
C(16)-C(17)-H(17)	121.1	C(34')-C(33')-H(33C)	109.7
C(18)-C(17)-H(17)	121.1	N(3)-C(33')-H(33C)	109.7
N(3)-C(18)-C(13)	110.0(2)	C(34')-C(33')-H(33D)	109.7
N(3)-C(18)-C(17)	128.0(3)	N(3)-C(33')-H(33D)	109.7
C(13)-C(18)-C(17)	122.0(3)	H(33C)-C(33')-H(33D)	108.2
N(2)-C(19)-C(20)	126.7(2)	C(33')-C(34')-C(35')	114.9(9)
N(2)-C(19)-C(24)	110.34(19)	C(33')-C(34')-H(34C)	108.5
C(20)-C(19)-C(24)	123.0(2)	C(35')-C(34')-H(34C)	108.5
C(21)-C(20)-C(19)	117.8(3)	C(33')-C(34')-H(34D)	108.5
C(21)-C(20)-H(20)	121.1	C(35')-C(34')-H(34D)	108.5
C(19)-C(20)-H(20)	121.1	H(34C)-C(34')-H(34D)	107.5
C(20)-C(21)-C(22)	120.7(3)	C(36')-C(35')-C(34')	15.5(12)
C(20)-C(21)-H(21)	119.6	C(36')-C(35')-H(35C)	108.4
C(22)-C(21)-H(21)	119.6	C(34')-C(35')-H(35C)	108.4
C(23)-C(22)-C(21)	121.5(3)	C(36')-C(35')-H(35D)	108.4
C(23)-C(22)-H(22)	119.2	C(34')-C(35')-H(35D)	108.4
C(21)-C(22)-H(22)	119.2	H(35C)-C(35')-H(35D)	107.5
C(22)-C(23)-C(24)	120.2(3)	C(35')-C(36')-H(36D)	109.5
C(22)-C(23)-H(23)	119.9	C(35')-C(36')-H(36E)	109.5
C(24)-C(23)-H(23)	119.9	H(36D)-C(36')-H(36E)	109.5
C(23)-C(24)-C(19)	116.7(2)	C(35')-C(36')-H(36F)	109.5
C(23)-C(24)-C(5)	136.7(2)	H(36D)-C(36')-H(36F)	109.5

C(19)-C(24)-C(5)	106.57(19)	H(36E)-C(36')-H(36F)	109.5
C(27)-C(26)-H(26A)	109.7	C(7)-N(1)-C(1)	105.88(19)
C(27)-C(26)-H(26B)	109.7	C(7)-N(1)-C(25')	118.7(2)
H(26A)-C(26)-H(26B)	108.2	C(1)-N(1)-C(25')	121.6(2)
C(26)-C(27)-C(28)	112.7(7)	C(19)-N(2)-C(6)	107.16(18)
C(26)-C(27)-H(27A)	109.0	C(19)-N(2)-C(29')	120.21(19)
C(28)-C(27)-H(27A)	109.0	C(6)-N(2)-C(29')	124.4(2)
C(26)-C(27)-H(27B)	109.0	C(18)-N(3)-C(4)	108.2(2)
C(28)-C(27)-H(27B)	109.0	C(18)-N(3)-C(33)	121.2(2)
H(27A)-C(27)-H(27B)	107.8	C(4)-N(3)-C(33)	129.6(2)
C(27')-C(26')-C(25')	113.6(7)	C(18)-N(3)-C(33')	117.3(4)
C(27')-C(26')-H(26C)	108.9	C(4)-N(3)-C(33')	119.9(4)
C(25')-C(26')-H(26C)	108.9	C(33)-N(3)-C(33')	44.1(3)

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ITN-2.

Atom	x	y	z	U(eq)
H(29A)	6393	7978	2893	105
H(29B)	7580	7757	3546	105
H(25A)	9738	7346	3967	113
H(25B)	8495	7212	3224	113
H(8)	11039	7310	6173	105
H(9)	12184	7021	8223	124
H(10)	11540	6438	9662	130
H(11)	9767	6098	9072	111
H(14)	8870	5406	8871	112
H(15)	8360	4695	10126	131
H(16)	6570	4408	9719	133
H(17)	5222	4811	8006	122
H(20)	4789	7709	1714	97
H(21)	2983	7411	1087	119
H(22)	2400	6691	2229	132
H(23)	3600	6223	3958	110

H(25C)	8427	7096	3252	113
H(25D)	9441	7460	3921	113
H(26A)	10581	6728	3957	117
H(26B)	9875	6848	2463	117
H(27A)	8612	6143	2818	127
H(27B)	9454	5995	4203	127
H(28A)	9729	5807	1549	202
H(28B)	9837	5368	2729	202
H(28C)	10763	5814	2798	202
H(26C)	10033	6336	4466	136
H(26D)	8831	6221	3598	136
H(27C)	10520	6636	2498	148
H(27D)	9324	6512	1638	148
H(28D)	10578	5831	1354	225
H(28E)	9612	5577	1904	225
H(28F)	10768	5675	2912	225
H(29C)	6766	7907	2743	105
H(29D)	7615	7785	4145	105
H(30A)	5638	8367	3719	142
H(30B)	5811	7957	4955	142
H(31A)	6966	8897	4755	154
H(31B)	7428	8452	5875	154
H(32A)	5421	8816	6036	166
H(32B)	6300	9293	6239	166
H(32C)	6505	8773	7207	166
H(30D)	7072	7885	5703	188
H(30C)	7471	8393	4977	188
H(31C)	5371	8153	5160	217
H(31D)	5554	8544	3989	217
H(32D)	5979	9250	5380	236
H(32E)	6727	8889	6541	236
H(32F)	5448	8906	6381	236
H(33A)	4415	5096	5823	102

H(33B)	4293	5591	4776	102
H(34A)	3745	6175	6382	146
H(34B)	3832	5671	7389	146
H(35A)	2013	5948	5973	181
H(35B)	2354	5610	4817	181
H(36A)	1782	4897	5466	353
H(36B)	1334	5250	6528	353
H(36C)	2506	4977	6965	353
H(33C)	4387	5882	7486	99
H(33D)	4155	6184	6054	99
H(34C)	3884	5030	6277	108
H(34D)	3512	5377	4924	108
H(35C)	2499	5416	7142	266
H(35D)	2167	5816	5880	266
H(36D)	1606	5024	4489	458
H(36E)	889	5142	5542	458
H(36F)	1788	4674	5844	458

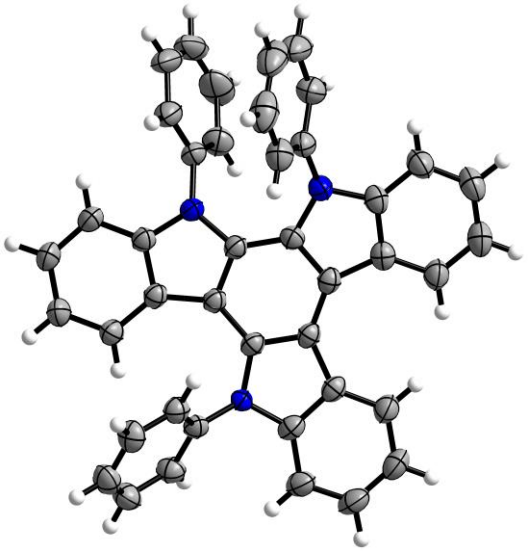


Figure S24. X-Ray crystal structure of ITN-3 (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC: 2271798)

Table S14 Crystal data and structure refinement for ITN-3.

Identification code	**ITN-3**
Empirical formula	$C_{24}H_{27}N_3$

Formula weight	573.67
Temperature/K	236(2) K
Crystal system	Monoclinic
Space group	P21/n
a/Å	16.36722(18)
b/Å	9.18575(9)
c/Å	19.55340(19)
α/°	90
β/°	91.7495(9)
γ/°	90
Volume/Å^3	2938.39(5)
Z	4
ρcalcg/cm^3	1.297
μ/mm^{-1}	0.587
F(000)	1200
Crystal size/mm^3	0.32 x 0.25 x 0.13
Radiation	CuK\a (λ = 1.54184)
2Θ range for data collection/°	6.94 to 156.12
Index ranges	-20<=h<=19, -10<=k<=11, -24<=l<=24
Reflections collected	35966
Independent reflections	6265 [R(int) = 0.0408]
Data/restraints/parameters	6265 / 1 / 407
Goodness-of-fit on F2	1.054
Final R indexes [I>=2σ (I)]	R1 = 0.0411, wR2 = 0.1138
Final R indexes [all data]	R1 = 0.0453, wR2 = 0.1179
Largest diff. peak/hole / e Å-3	0.202 / -0.176

Table S15 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ITN-3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C(1)	2279(1)	2381(1)	9863(1)	37(1)
C(2)	2062(1)	1411(1)	9332(1)	36(1)
C(3)	1220(1)	1210(1)	9177(1)	36(1)
C(4)	612(1)	1774(1)	9594(1)	37(1)
C(5)	847(1)	2757(1)	10128(1)	38(1)
C(6)	1677(1)	3125(1)	10222(1)	38(1)

C(7)	3452(1)	1402(1)	9498(1)	39(1)
C(8)	2816(1)	765(1)	9101(1)	37(1)
C(9)	3020(1)	-320(1)	8633(1)	43(1)
C(10)	3829(1)	-709(2)	8566(1)	49(1)
C(11)	4445(1)	-61(2)	8965(1)	52(1)
C(12)	4267(1)	993(2)	9439(1)	48(1)
C(13)	993(1)	4480(1)	10976(1)	44(1)
C(14)	412(1)	3608(1)	10625(1)	41(1)
C(15)	-405(1)	3756(2)	10805(1)	53(1)
C(16)	-619(1)	4734(2)	11300(1)	59(1)
C(17)	-36(1)	5598(2)	11628(1)	60(1)
C(18)	777(1)	5494(2)	11466(1)	56(1)
C(19)	16(1)	373(1)	8744(1)	41(1)
C(20)	-589(1)	-262(2)	8325(1)	53(1)
C(21)	-1388(1)	-76(2)	8505(1)	59(1)
C(22)	-1582(1)	690(2)	9087(1)	58(1)
C(23)	-982(1)	1324(2)	9494(1)	51(1)
C(24)	-162(1)	1208(1)	9322(1)	40(1)
C(25)	3582(1)	2768(1)	10569(1)	42(1)
C(26)	4267(1)	3639(2)	10537(1)	57(1)
C(27)	4729(1)	3909(2)	11127(1)	78(1)
C(28)	4509(1)	3345(3)	11734(1)	88(1)
C(29)	3825(1)	2480(3)	11768(1)	83(1)
C(30)	3356(1)	2174(2)	11180(1)	57(1)
C(31)	2398(1)	5275(1)	10747(1)	46(1)
C(32)	2629(1)	5923(2)	10144(1)	56(1)
C(33)	3223(1)	7006(2)	10163(1)	78(1)
C(34)	3571(1)	7442(2)	10781(1)	87(1)
C(35)	3336(1)	6798(2)	11378(1)	79(1)
C(36)	2754(1)	5707(2)	11366(1)	60(1)
C(37)	1205(1)	32(1)	8017(1)	39(1)
C(38)	1629(1)	1080(1)	7663(1)	43(1)
C(39)	1963(1)	728(2)	7040(1)	52(1)

C(40)	1862(1)	-642(2)	6766(1)	57(1)
C(41)	1430(1)	-1679(2)	7115(1)	56(1)
C(42)	1107(1)	-1352(1)	7741(1)	48(1)
N(1)	3134(1)	2412(1)	9951(1)	40(1)
N(2)	1774(1)	4181(1)	10736(1)	45(1)
N(3)	862(1)	356(1)	8659(1)	41(1)

Table S16 Anisotropic Displacement Parameters ($Å^2×10^3$) for ITN-3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
C(1)	32(1)	43(1)	35(1)	1(1)	-1(1)	0(1)
C(2)	33(1)	40(1)	34(1)	2(1)	-1(1)	2(1)
C(3)	33(1)	39(1)	35(1)	3(1)	-2(1)	0(1)
C(4)	33(1)	39(1)	38(1)	5(1)	-1(1)	2(1)
C(5)	36(1)	40(1)	37(1)	5(1)	2(1)	4(1)
C(6)	38(1)	42(1)	36(1)	-1(1)	1(1)	1(1)
C(7)	35(1)	45(1)	35(1)	1(1)	-1(1)	3(1)
C(8)	34(1)	40(1)	36(1)	3(1)	0(1)	3(1)
C(9)	40(1)	43(1)	45(1)	-3(1)	-4(1)	5(1)
C(10)	45(1)	51(1)	52(1)	-9(1)	1(1)	10(1)
C(11)	36(1)	63(1)	57(1)	-7(1)	0(1)	11(1)
C(12)	33(1)	61(1)	49(1)	-5(1)	-3(1)	3(1)
C(13)	46(1)	45(1)	42(1)	1(1)	10(1)	2(1)
C(14)	43(1)	40(1)	39(1)	5(1)	6(1)	5(1)
C(15)	43(1)	59(1)	56(1)	-2(1)	11(1)	4(1)
C(16)	52(1)	63(1)	65(1)	-1(1)	19(1)	9(1)
C(17)	68(1)	55(1)	59(1)	-8(1)	24(1)	6(1)
C(18)	60(1)	56(1)	54(1)	-11(1)	14(1)	-3(1)
C(19)	34(1)	47(1)	42(1)	6(1)	-1(1)	-4(1)
C(20)	43(1)	68(1)	47(1)	-1(1)	-2(1)	-12(1)
C(21)	39(1)	77(1)	61(1)	4(1)	-7(1)	-13(1)
C(22)	33(1)	66(1)	74(1)	3(1)	2(1)	-2(1)

C(23)	38(1)	55(1)	62(1)	-2(1)	5(1)	1(1)
C(24)	35(1)	41(1)	43(1)	8(1)	-1(1)	1(1)
C(25)	37(1)	47(1)	41(1)	-6(1)	-6(1)	3(1)
C(26)	41(1)	59(1)	71(1)	-11(1)	-5(1)	-4(1)
C(27)	49(1)	80(1)	104(1)	-37(1)	-26(1)	3(1)
C(28)	77(1)	106(2)	79(1)	-46(1)	-42(1)	35(1)
C(29)	97(1)	109(2)	42(1)	-3(1)	-14(1)	34(1)
C(30)	60(1)	67(1)	45(1)	2(1)	-3(1)	3(1)
C(31)	41(1)	45(1)	53(1)	-7(1)	3(1)	1(1)
C(32)	53(1)	53(1)	64(1)	3(1)	11(1)	5(1)
C(33)	64(1)	58(1)	112(2)	11(1)	30(1)	0(1)
C(34)	53(1)	60(1)	148(2)	-19(1)	13(1)	-12(1)
C(35)	56(1)	71(1)	108(2)	-33(1)	-12(1)	-4(1)
C(36)	56(1)	61(1)	63(1)	-14(1)	-4(1)	0(1)
C(37)	35(1)	45(1)	36(1)	0(1)	-4(1)	1(1)
C(38)	42(1)	41(1)	45(1)	1(1)	-1(1)	2(1)
C(39)	53(1)	55(1)	47(1)	9(1)	8(1)	2(1)
C(40)	62(1)	65(1)	43(1)	-6(1)	8(1)	6(1)
C(41)	64(1)	52(1)	52(1)	-13(1)	0(1)	0(1)
C(42)	50(1)	45(1)	48(1)	-1(1)	1(1)	-6(1)
N(1)	31(1)	52(1)	38(1)	-5(1)	-2(1)	1(1)
N(2)	43(1)	50(1)	44(1)	-10(1)	7(1)	-3(1)
N(3)	35(1)	51(1)	38(1)	-2(1)	-1(1)	-4(1)

Table S17 Bond Lengths for ITN-3.

Bond	**Angle/°**	**Bond**	**Angle/°**
C(1)-N(1)	1.4039(14)	C(19)-N(3)	1.4002(15)
C(1)-C(6)	1.4053(16)	C(19)-C(24)	1.4024(17)
C(1)-C(2)	1.4054(15)	C(20)-C(21)	1.375(2)
C(2)-C(3)	1.4146(15)	C(21)-C(22)	1.384(2)
C(2)-C(8)	1.4537(15)	C(22)-C(23)	1.375(2)
C(3)-N(3)	1.3966(14)	C(23)-C(24)	1.3973(17)
C(3)-C(4)	1.4044(16)	C(25)-C(30)	1.3748(19)

C(4)-C(5)	1.4238(16)	C(25)-C(26)	1.3805(19)
C(4)-C(24)	1.4558(15)	C(25)-N(1)	1.4313(14)
C(5)-C(6)	1.4067(16)	C(26)-C(27)	1.383(2)
C(5)-C(14)	1.4508(16)	C(27)-C(28)	1.354(3)
C(6)-N(2)	1.4027(15)	C(28)-C(29)	1.376(3)
C(7)-C(12)	1.3941(16)	C(29)-C(30)	1.390(2)
C(7)-N(1)	1.3949(15)	C(31)-C(32)	1.384(2)
C(7)-C(8)	1.4075(16)	C(31)-C(36)	1.386(2)
C(8)-C(9)	1.3996(16)	C(31)-N(2)	1.4321(16)
C(9)-C(10)	1.3828(17)	C(32)-C(33)	1.391(2)
C(10)-C(11)	1.3897(19)	C(33)-C(34)	1.378(3)
C(11)-C(12)	1.3781(19)	C(34)-C(35)	1.375(3)
C(13)-C(18)	1.3909(18)	C(35)-C(36)	1.383(2)
C(13)-N(2)	1.4017(16)	C(37)-C(38)	1.3837(17)
C(13)-C(14)	1.4061(18)	C(37)-C(42)	1.3878(17)
C(14)-C(15)	1.4000(17)	C(37)-N(3)	1.4227(15)
C(15)-C(16)	1.374(2)	C(38)-C(39)	1.3888(18)
C(16)-C(17)	1.384(2)	C(39)-C(40)	1.377(2)
C(17)-C(18)	1.379(2)	C(40)-C(41)	1.380(2)
C(19)-C(20)	1.3929(17)	C(41)-C(42)	1.3811(19)

Table S18 Bond Angles for ITN-3.

Bond	**Angle/°**	**Bond**	**Angle/°**
N(1)-C(1)-C(6)	129.80(10)	C(21)-C(20)-C(19)	117.54(13)
N(1)-C(1)-C(2)	109.41(9)	C(20)-C(21)-C(22)	121.10(13)
C(6)-C(1)-C(2)	120.78(10)	C(23)-C(22)-C(21)	120.97(13)
C(1)-C(2)-C(3)	117.62(10)	C(22)-C(23)-C(24)	120.10(13)
C(1)-C(2)-C(8)	106.91(9)	C(23)-C(24)-C(19)	117.44(11)
C(3)-C(2)-C(8)	135.32(10)	C(23)-C(24)-C(4)	135.68(12)
N(3)-C(3)-C(4)	109.82(10)	C(19)-C(24)-C(4)	106.87(10)
N(3)-C(3)-C(2)	127.85(10)	C(30)-C(25)-C(26)	120.65(13)
C(4)-C(3)-C(2)	122.07(10)	C(30)-C(25)-N(1)	119.90(12)
C(3)-C(4)-C(5)	118.62(10)	C(26)-C(25)-N(1)	119.34(12)

C(3)-C(4)-C(24)	106.27(10)	C(25)-C(26)-C(27)	119.36(17)
C(5)-C(4)-C(24)	135.02(11)	C(28)-C(27)-C(26)	120.59(18)
C(6)-C(5)-C(4)	119.11(10)	C(27)-C(28)-C(29)	120.14(15)
C(6)-C(5)-C(14)	105.91(10)	C(28)-C(29)-C(30)	120.40(18)
C(4)-C(5)-C(14)	134.89(11)	C(25)-C(30)-C(29)	118.85(17)
N(2)-C(6)-C(1)	128.94(11)	C(32)-C(31)-C(36)	120.19(14)
N(2)-C(6)-C(5)	110.37(10)	C(32)-C(31)-N(2)	120.17(12)
C(1)-C(6)-C(5)	120.48(10)	C(36)-C(31)-N(2)	119.62(13)
C(12)-C(7)-N(1)	127.53(11)	C(31)-C(32)-C(33)	119.57(16)
C(12)-C(7)-C(8)	122.37(11)	C(34)-C(33)-C(32)	120.10(18)
N(1)-C(7)-C(8)	110.06(10)	C(35)-C(34)-C(33)	120.05(16)
C(9)-C(8)-C(7)	118.05(10)	C(34)-C(35)-C(36)	120.51(18)
C(9)-C(8)-C(2)	135.65(10)	C(35)-C(36)-C(31)	119.58(17)
C(7)-C(8)-C(2)	106.19(10)	C(38)-C(37)-C(42)	119.83(11)
C(10)-C(9)-C(8)	119.62(11)	C(38)-C(37)-N(3)	120.83(11)
C(9)-C(10)-C(11)	121.09(12)	C(42)-C(37)-N(3)	119.34(11)
C(12)-C(11)-C(10)	120.96(12)	C(37)-C(38)-C(39)	119.55(12)
C(11)-C(12)-C(7)	117.89(11)	C(40)-C(39)-C(38)	120.60(13)
C(18)-C(13)-N(2)	127.99(12)	C(39)-C(40)-C(41)	119.67(13)
C(18)-C(13)-C(14)	122.37(12)	C(40)-C(41)-C(42)	120.32(13)
N(2)-C(13)-C(14)	109.61(10)	C(41)-C(42)-C(37)	120.01(12)
C(15)-C(14)-C(13)	117.33(11)	C(7)-N(1)-C(1)	107.35(9)
C(15)-C(14)-C(5)	135.47(12)	C(7)-N(1)-C(25)	119.72(9)
C(13)-C(14)-C(5)	107.19(10)	C(1)-N(1)-C(25)	126.26(10)
C(16)-C(15)-C(14)	120.45(14)	C(13)-N(2)-C(6)	106.87(10)
C(15)-C(16)-C(17)	120.93(14)	C(13)-N(2)-C(31)	121.00(10)
C(18)-C(17)-C(16)	120.75(13)	C(6)-N(2)-C(31)	124.11(10)
C(17)-C(18)-C(13)	118.13(14)	C(3)-N(3)-C(19)	107.58(9)
C(20)-C(19)-N(3)	127.79(12)	C(3)-N(3)-C(37)	126.13(10)
C(20)-C(19)-C(24)	122.74(11)	C(19)-N(3)-C(37)	121.78(9)
N(3)-C(19)-C(24)	109.42(10)		

Table S19 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ITN-3.

Atom	x	y	z	U(eq)
H(9)	2608	-782	8366	51
H(10)	3966	-1424	8244	59
H(11)	4991	-346	8910	62
H(12)	4682	1423	9714	57
H(15)	-810	3183	10585	63
H(16)	-1170	4817	11418	71
H(17)	-195	6263	11964	72
H(18)	1173	6092	11682	68
H(20)	-456	-797	7935	63
H(21)	-1810	-476	8227	71
H(22)	-2132	779	9206	69
H(23)	-1123	1836	9890	61
H(26)	4418	4045	10118	69
H(27)	5201	4490	11107	94
H(28)	4823	3546	12133	106
H(29)	3673	2093	12190	100
H(30)	2894	1571	11201	69
H(32)	2387	5632	9724	67
H(33)	3387	7443	9755	93
H(34)	3969	8179	10793	104
H(35)	3573	7103	11798	95
H(36)	2600	5261	11775	72
H(38)	1690	2023	7844	51
H(39)	2262	1432	6804	62
H(40)	2086	-871	6342	68
H(41)	1354	-2612	6926	67
H(42)	820	-2067	7981	57

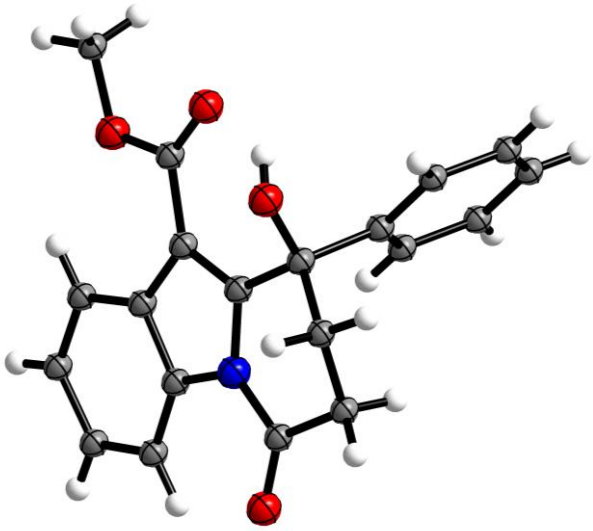


Figure S25. X-Ray crystal structure of 2a (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC: 2309597)

Table S20 Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_{40}H_{34}N_2O_8$
Formula weight	668.68
Temperature/K	301(2) K
Crystal system	triclinic
Space group	P -1
a/Å	6.01120(10)
b/Å	15.7452(2)
c/Å	19.7395(2)
α/°	83.7750(10)
β/°	82.4220(10)
γ/°	80.2710(10)
Volume/Å^3	1818.23(4)
Z	4
ρcalcg/cm^3	1.221
μ/mm^{-1}	0.703
F(000)	700
Crystal size/mm^3	0.32 x 0.25 x 0.13
Radiation	CuK\a (λ = 0.714)
2Θ range for data collection/°	3.19 to 78.12
Index ranges	-7<=h<=6, -19<=k<=19, -24<=l<=25
Reflections collected	33979
Independent reflections	7682 [R(int) = 0.0485]

Data/restraints/parameters	7682 / 0 / 456
Goodness-of-fit on F2	1.495
Final R indexes [I>=2σ (I)]	R1 = 0.1029, wR2 = 0.3149
Final R indexes [all data]	R1 = 0.1094, wR2 = 0.3290
Largest diff. peak/hole / e Å-3	1.690 / -0.296

Table S21 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(20)	12131(2)	6885(1)	3779(1)	63(1)
O(45)	9450(3)	2676(1)	2778(1)	67(1)
O(46)	980(3)	4302(1)	3387(1)	65(1)
O(21)	5484(3)	5140(1)	3591(1)	68(1)
N(1)	7204(3)	6314(1)	3202(1)	48(1)
N(26)	3697(3)	3722(1)	2577(1)	47(1)
O(25)	11528(4)	8285(2)	2904(1)	77(1)
O(23)	9984(5)	8552(2)	1929(1)	88(1)
O(48)	8181(5)	3207(2)	592(1)	94(1)
O(50)	9810(4)	2431(2)	1467(1)	96(1)
C(2)	8702(3)	6881(1)	3262(1)	47(1)
C(27)	5790(3)	3233(1)	2379(1)	48(1)
C(34)	2796(3)	4163(1)	1994(1)	51(1)
C(14)	8585(3)	7608(1)	4337(1)	47(1)
C(3)	8880(3)	7414(1)	2665(1)	52(1)
C(35)	7081(3)	2650(1)	2912(1)	50(1)
C(13)	6558(3)	5671(1)	3713(1)	52(1)
C(10)	9757(3)	6857(1)	3923(1)	49(1)
C(4)	7424(4)	7178(2)	2209(1)	55(1)
C(38)	2676(3)	3789(1)	3257(1)	50(1)
C(28)	6263(4)	3364(2)	1681(1)	55(1)
C(9)	6410(3)	6490(2)	2559(1)	52(1)
C(39)	6621(4)	1717(1)	2936(1)	53(1)
C(19)	6339(4)	7982(2)	4306(1)	57(1)

C(29)	4374(4)	3958(2)	1426(1)	56(1)
C(11)	9606(4)	5988(2)	4348(1)	58(1)
C(22)	10290(4)	8104(2)	2530(1)	62(1)
C(36)	6375(4)	3002(2)	3612(1)	60(1)
C(12)	7253(4)	5738(2)	4403(1)	61(1)
C(37)	3829(5)	3174(2)	3781(1)	63(1)
C(33)	698(4)	4694(2)	1941(2)	65(1)
C(18)	5340(4)	8635(2)	4723(2)	68(1)
C(15)	9794(4)	7914(2)	4787(1)	63(1)
C(47)	8271(5)	2949(2)	1261(2)	70(1)
C(17)	6555(6)	8922(2)	5165(1)	71(1)
C(44)	8124(5)	1051(2)	3232(1)	68(1)
C(5)	6867(5)	7491(2)	1553(1)	70(1)
C(8)	4818(4)	6121(2)	2281(2)	66(1)
C(30)	3875(5)	4324(2)	772(1)	73(1)
C(16)	8791(6)	8568(2)	5191(2)	74(1)
C(6)	5314(6)	7122(3)	1276(2)	81(1)
C(32)	258(5)	5035(2)	1283(2)	79(1)
C(7)	4301(5)	6454(2)	1634(2)	78(1)
C(31)	1828(6)	4864(2)	715(2)	81(1)
C(40)	4748(5)	1509(2)	2691(2)	78(1)
C(43)	7701(7)	202(2)	3290(2)	88(1)
C(42)	5834(7)	8(2)	3059(2)	92(1)
C(41)	4365(6)	651(2)	2761(3)	101(1)
C(24)	11344(10)	9238(3)	1750(3)	117(2)
C(49)	10105(10)	2866(4)	134(2)	123(2)

Table S22 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
O(20)	37(1)	76(1)	77(1)	-23(1)	-5(1)	-3(1)
O(45)	42(1)	70(1)	87(1)	-4(1)	-9(1)	-9(1)

O(46)	51(1)	66(1)	75(1)	-26(1)	2(1)	1(1)
O(21)	60(1)	48(1)	98(1)	-8(1)	-13(1)	-14(1)
N(1)	42(1)	46(1)	57(1)	-13(1)	-4(1)	-6(1)
N(26)	43(1)	46(1)	52(1)	-8(1)	-2(1)	-5(1)
O(25)	75(1)	78(1)	87(1)	-15(1)	-4(1)	-36(1)
O(23)	111(2)	82(1)	77(1)	6(1)	-5(1)	-45(1)
O(48)	108(2)	97(2)	62(1)	-11(1)	24(1)	3(1)
O(50)	77(1)	104(2)	88(2)	-16(1)	17(1)	22(1)
C(2)	40(1)	47(1)	55(1)	-16(1)	0(1)	-4(1)
C(27)	42(1)	45(1)	54(1)	-8(1)	-2(1)	-6(1)
C(34)	48(1)	48(1)	59(1)	-6(1)	-9(1)	-9(1)
C(14)	46(1)	44(1)	49(1)	-9(1)	-1(1)	-6(1)
C(3)	49(1)	54(1)	53(1)	-15(1)	3(1)	-10(1)
C(35)	42(1)	48(1)	60(1)	-7(1)	-5(1)	-5(1)
C(13)	44(1)	40(1)	71(1)	-8(1)	-4(1)	-2(1)
C(10)	38(1)	51(1)	58(1)	-15(1)	-5(1)	-2(1)
C(4)	52(1)	59(1)	54(1)	-16(1)	1(1)	-6(1)
C(38)	49(1)	48(1)	56(1)	-15(1)	3(1)	-10(1)
C(28)	52(1)	56(1)	55(1)	-8(1)	1(1)	-6(1)
C(9)	45(1)	56(1)	55(1)	-17(1)	-3(1)	-5(1)
C(39)	50(1)	47(1)	59(1)	-11(1)	4(1)	-2(1)
C(19)	46(1)	50(1)	75(1)	-16(1)	-3(1)	-4(1)
C(29)	57(1)	58(1)	55(1)	-5(1)	-8(1)	-11(1)
C(11)	58(1)	49(1)	68(1)	-10(1)	-17(1)	4(1)
C(22)	64(1)	59(1)	64(1)	-13(1)	8(1)	-19(1)
C(36)	69(1)	54(1)	59(1)	-9(1)	-18(1)	-4(1)
C(12)	67(1)	48(1)	64(1)	1(1)	-7(1)	-7(1)
C(37)	75(1)	59(1)	52(1)	-7(1)	4(1)	-4(1)
C(33)	51(1)	61(1)	83(2)	-2(1)	-15(1)	-3(1)
C(18)	59(1)	52(1)	88(2)	-15(1)	6(1)	2(1)
C(15)	61(1)	72(1)	60(1)	-19(1)	-14(1)	-6(1)
C(47)	68(1)	70(2)	65(1)	-13(1)	12(1)	-4(1)
C(17)	97(2)	51(1)	61(1)	-18(1)	14(1)	-7(1)

C(44)	80(2)	55(1)	65(1)	-7(1)	-11(1)	5(1)
C(5)	74(2)	82(2)	54(1)	-9(1)	-4(1)	-12(1)
C(8)	58(1)	72(2)	74(2)	-24(1)	-11(1)	-14(1)
C(30)	83(2)	83(2)	56(1)	1(1)	-15(1)	-19(1)
C(16)	91(2)	75(2)	60(1)	-25(1)	-13(1)	-11(1)
C(6)	82(2)	102(2)	60(1)	-19(1)	-18(1)	-5(2)
C(32)	66(2)	76(2)	97(2)	8(2)	-32(2)	-7(1)
C(7)	70(2)	99(2)	73(2)	-25(2)	-20(1)	-15(1)
C(31)	87(2)	86(2)	75(2)	10(1)	-35(2)	-19(2)
C(40)	54(1)	57(1)	126(3)	-18(2)	-13(1)	-8(1)
C(43)	124(3)	51(1)	77(2)	-4(1)	-3(2)	9(2)
C(42)	114(3)	48(1)	107(2)	-19(1)	22(2)	-13(2)
C(41)	79(2)	70(2)	160(4)	-37(2)	-2(2)	-25(2)
C(24)	154(4)	99(3)	106(3)	8(2)	8(3)	-70(3)
C(49)	145(4)	118(3)	86(2)	-26(2)	52(3)	-1(3)

Table S23 Bond Lengths for 2a.

Bond	**Angle/°**	**Bond**	**Angle/°**
O(20)-C(10)	1.426(2)	C(35)-C(39)	1.534(3)
O(45)-C(35)	1.421(2)	C(13)-C(12)	1.494(4)
O(46)-C(38)	1.206(3)	C(10)-C(11)	1.535(3)
O(21)-C(13)	1.201(3)	C(4)-C(5)	1.398(4)
N(1)-C(2)	1.394(2)	C(4)-C(9)	1.403(3)
N(1)-C(9)	1.398(3)	C(38)-C(37)	1.496(3)
N(1)-C(13)	1.416(3)	C(28)-C(29)	1.452(3)
N(26)-C(27)	1.392(3)	C(28)-C(47)	1.469(3)
N(26)-C(34)	1.401(3)	C(9)-C(8)	1.396(3)
N(26)-C(38)	1.408(3)	C(39)-C(40)	1.383(4)
O(25)-C(22)	1.201(3)	C(39)-C(44)	1.394(3)
O(23)-C(22)	1.331(4)	C(19)-C(18)	1.393(3)
O(23)-C(24)	1.449(4)	C(29)-C(30)	1.404(3)
O(48)-C(47)	1.343(4)	C(11)-C(12)	1.519(3)
O(48)-C(49)	1.436(4)	C(36)-C(37)	1.507(4)

O(50)-C(47)	1.209(4)	C(33)-C(32)	1.391(4)
C(2)-C(3)	1.373(3)	C(18)-C(17)	1.366(4)
C(2)-C(10)	1.519(3)	C(15)-C(16)	1.379(4)
C(27)-C(28)	1.369(3)	C(17)-C(16)	1.371(5)
C(27)-C(35)	1.523(3)	C(44)-C(43)	1.392(5)
C(34)-C(29)	1.399(3)	C(5)-C(6)	1.377(4)
C(34)-C(33)	1.400(3)	C(8)-C(7)	1.381(4)
C(14)-C(19)	1.385(3)	C(30)-C(31)	1.383(5)
C(14)-C(15)	1.390(3)	C(6)-C(7)	1.386(5)
C(14)-C(10)	1.529(3)	C(32)-C(31)	1.385(5)
C(3)-C(4)	1.450(3)	C(40)-C(41)	1.398(4)
C(3)-C(22)	1.469(3)	C(43)-C(42)	1.357(6)
C(35)-C(36)	1.525(3)	C(42)-C(41)	1.363(6)

Table S24 Bond Angles for 2a.

Bond	**Angle/°**	**Bond**	**Angle/°**
C(2)-N(1)-C(9)	109.18(18)	O(46)-C(38)-C(37)	124.2(2)
C(2)-N(1)-C(13)	125.53(18)	N(26)-C(38)-C(37)	114.84(18)
C(9)-N(1)-C(13)	125.28(17)	C(27)-C(28)-C(29)	107.77(19)
C(27)-N(26)-C(34)	109.32(17)	C(27)-C(28)-C(47)	126.3(2)
C(27)-N(26)-C(38)	125.55(18)	C(29)-C(28)-C(47)	125.9(2)
C(34)-N(26)-C(38)	125.10(17)	C(8)-C(9)-N(1)	129.8(2)
C(22)-O(23)-C(24)	114.8(3)	C(8)-C(9)-C(4)	122.3(2)
C(47)-O(48)-C(49)	115.8(3)	N(1)-C(9)-C(4)	107.74(18)
C(3)-C(2)-N(1)	108.50(18)	C(40)-C(39)-C(44)	118.4(2)
C(3)-C(2)-C(10)	131.01(18)	C(40)-C(39)-C(35)	122.8(2)
N(1)-C(2)-C(10)	120.45(18)	C(44)-C(39)-C(35)	118.7(2)
C(28)-C(27)-N(26)	108.58(18)	C(14)-C(19)-C(18)	120.3(2)
C(28)-C(27)-C(35)	131.35(19)	C(34)-C(29)-C(30)	118.7(2)
N(26)-C(27)-C(35)	120.02(18)	C(34)-C(29)-C(28)	106.97(19)
C(29)-C(34)-C(33)	123.1(2)	C(30)-C(29)-C(28)	134.3(2)
C(29)-C(34)-N(26)	107.36(18)	C(12)-C(11)-C(10)	112.15(18)
C(33)-C(34)-N(26)	129.5(2)	O(25)-C(22)-O(23)	121.9(2)

C(19)-C(14)-C(15)	117.9(2)	O(25)-C(22)-C(3)	126.8(3)
C(19)-C(14)-C(10)	123.28(18)	O(23)-C(22)-C(3)	111.2(2)
C(15)-C(14)-C(10)	118.79(19)	C(37)-C(36)-C(35)	112.05(19)
C(2)-C(3)-C(4)	107.91(19)	C(13)-C(12)-C(11)	111.9(2)
C(2)-C(3)-C(22)	125.0(2)	C(38)-C(37)-C(36)	112.9(2)
C(4)-C(3)-C(22)	127.1(2)	C(32)-C(33)-C(34)	116.3(3)
O(45)-C(35)-C(27)	110.96(17)	C(17)-C(18)-C(19)	120.8(2)
O(45)-C(35)-C(36)	104.76(18)	C(16)-C(15)-C(14)	121.1(2)
C(27)-C(35)-C(36)	109.18(17)	O(50)-C(47)-O(48)	122.7(3)
O(45)-C(35)-C(39)	110.45(17)	O(50)-C(47)-C(28)	126.3(3)
C(27)-C(35)-C(39)	110.73(17)	O(48)-C(47)-C(28)	111.0(2)
C(36)-C(35)-C(39)	110.61(18)	C(18)-C(17)-C(16)	119.3(2)
O(21)-C(13)-N(1)	121.2(2)	C(43)-C(44)-C(39)	120.2(3)
O(21)-C(13)-C(12)	124.4(2)	C(6)-C(5)-C(4)	118.8(3)
N(1)-C(13)-C(12)	114.43(18)	C(7)-C(8)-C(9)	116.9(3)
O(20)-C(10)-C(2)	110.46(17)	C(31)-C(30)-C(29)	118.5(3)
O(20)-C(10)-C(14)	110.34(16)	C(17)-C(16)-C(15)	120.5(3)
C(2)-C(10)-C(14)	110.57(16)	C(5)-C(6)-C(7)	121.4(3)
O(20)-C(10)-C(11)	104.63(17)	C(31)-C(32)-C(33)	121.6(3)
C(2)-C(10)-C(11)	110.11(17)	C(8)-C(7)-C(6)	121.7(3)
C(14)-C(10)-C(11)	110.58(18)	C(30)-C(31)-C(32)	121.7(3)
C(5)-C(4)-C(9)	119.0(2)	C(39)-C(40)-C(41)	119.9(3)
C(5)-C(4)-C(3)	134.3(2)	C(42)-C(43)-C(44)	120.8(3)
C(9)-C(4)-C(3)	106.7(2)	C(43)-C(42)-C(41)	119.6(3)
O(46)-C(38)-N(26)	121.0(2)	C(42)-C(41)-C(40)	121.0(3)

Table S25 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	x	y	z	U(eq)
H(20)	12329	7341	3553	94
H(45)	9990	2396	2452	100
H(19)	5493	7795	4005	68
H(11A)	10709	5540	4138	70

H(11B)	9989	6025	4805	70
H(36A)	7024	2588	3962	72
H(36B)	6979	3535	3615	72
H(12A)	7240	5187	4674	73
H(12B)	6162	6168	4638	73
H(37A)	3245	2631	3818	76
H(37B)	3464	3410	4224	76
H(33)	-344	4813	2324	78
H(18)	3828	8878	4700	81
H(15)	11305	7673	4817	76
H(17)	5872	9354	5445	86
H(44)	9413	1174	3391	81
H(5)	7533	7941	1308	84
H(8)	4139	5672	2521	79
H(30)	4900	4206	385	88
H(16)	9638	8770	5483	89
H(6)	4937	7326	839	97
H(32)	-1122	5386	1223	95
H(7)	3245	6224	1434	93
H(31)	1496	5118	285	97
H(40)	3744	1940	2479	94
H(43)	8711	-238	3490	106
H(42)	5559	-560	3104	110
H(41)	3087	517	2603	121
H(24A)	11678	9317	1260	176
H(24B)	12738	9086	1954	176
H(24C)	10518	9765	1917	176
H(49A)	10045	3178	-310	185
H(49B)	10077	2265	97	185
H(49C)	11480	2926	310	185

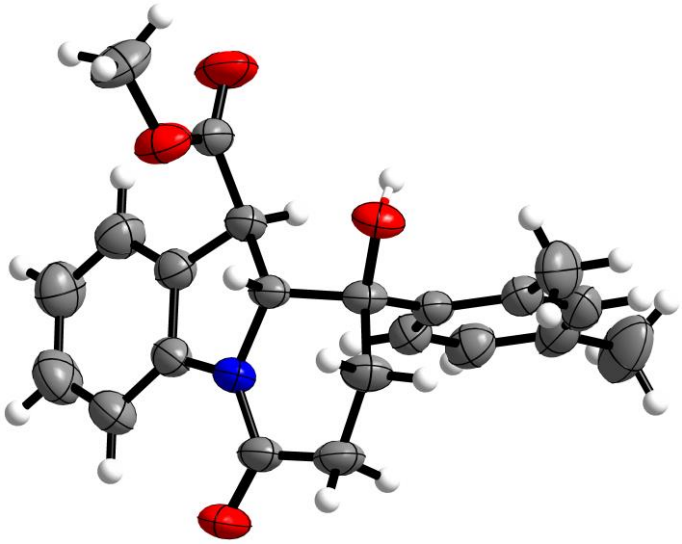


Figure S26. X-Ray crystal structure of 3k (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC: 2271810)

Table S26 Crystal data and structure refinement for 3k.

Identification code	**3k**
Empirical formula	$C_{22}H_{23}NO_4$
Formula weight	365.41
Temperature/K	278 K
Crystal system	Orthorhombic
Space group	Pna21
a/Å	27.5274(3)
b/Å	9.94060(10)
c/Å	27.6836(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7575.31(14)
Z	16
ρcalcg/cm^3	1.282
μ/mm^{-1}	0.714
F(000)	3104
Crystal size/mm^3	0.32 x 0.25 x 0.13
Radiation	CuK\a (λ = 0.714)
2Θ range for data collection/°	6.38 to 156.24
Index ranges	-34<=h<=34, -11<=k<=12, -35<=l<=35
Reflections collected	97642

Independent reflections	15892 [R(int) = 0.0566]
Data/restraints/parameters	3017 / 0 / 238
Goodness-of-fit on F2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0369, wR2 = 0.0978
Final R indexes [all data]	R1 = 0.0409, wR2 = 0.1010
Largest diff. peak/hole / e Å-3	0.195 / -0.149

Table S27 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3k. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O(22)	3974(1)	2378(1)	5420(1)	51(1)
O(53)	3253(1)	2955(2)	6059(1)	61(1)
O(54)	1330(1)	4453(1)	5950(1)	54(1)
O(25)	4079(1)	5934(2)	5231(1)	65(1)
O(80)	9676(1)	2734(1)	4078(1)	60(1)
N(82)	6257(1)	3843(1)	3584(1)	41(1)
N(28)	2533(1)	3410(1)	6408(1)	39(1)
O(103)	5051(1)	4880(1)	4041(1)	54(1)
O(50)	1171(1)	5009(2)	7252(1)	70(1)
O(81)	7718(1)	2297(2)	4389(1)	59(1)
O(77)	7571(1)	6487(2)	4205(1)	64(1)
O(23)	5910(1)	3103(2)	5803(1)	70(1)
O(104)	6986(1)	3562(2)	3929(1)	75(1)
N(1)	5140(1)	3898(1)	5789(1)	45(1)
O(106)	4899(1)	5277(2)	2691(1)	73(1)
C(95)	5710(1)	6418(2)	4063(1)	39(1)
C(29)	2674(1)	3284(2)	6900(1)	43(1)
O(79)	7946(1)	5581(2)	4831(1)	100(1)
C(36)	2825(1)	3292(2)	6017(1)	44(1)
C(68)	8108(1)	1891(2)	3600(1)	44(1)
C(90)	5729(1)	4138(2)	3600(1)	38(1)
O(27)	3615(1)	6089(2)	5878(1)	81(1)
N(55)	8930(1)	3693(1)	4102(1)	45(1)

C(14)	4364(1)	1718(2)	6180(1)	43(1)
C(32)	2008(1)	3732(2)	6390(1)	39(1)
C(96)	5475(1)	7334(2)	4376(1)	45(1)
O(108)	4973(1)	3144(2)	2935(1)	85(1)
C(46)	2400(1)	6460(2)	6168(1)	44(1)
O(52)	1237(1)	2851(2)	7057(1)	92(1)
C(83)	6398(1)	3707(2)	3091(1)	44(1)
C(94)	5568(1)	4933(2)	4047(1)	41(1)
C(35)	2611(1)	3656(2)	5535(1)	50(1)
C(45)	2544(1)	7793(2)	6160(1)	49(1)
C(33)	1846(1)	4516(2)	5940(1)	40(1)
C(41)	1987(1)	6003(2)	5927(1)	39(1)
C(88)	6032(1)	4200(2)	2798(1)	46(1)
C(73)	8352(1)	2573(2)	3236(1)	48(1)
C(24)	3971(1)	5674(2)	5686(1)	48(1)
C(100)	6082(1)	6917(2)	3770(1)	41(1)
C(30)	2308(1)	3804(2)	7192(1)	46(1)
C(15)	4585(1)	2290(2)	6586(1)	48(1)
C(76)	7889(1)	5668(2)	4406(1)	56(1)
C(91)	6552(1)	3797(2)	3972(1)	48(1)
C(89)	5612(1)	4724(2)	3099(1)	43(1)
C(19)	4094(1)	528(2)	6256(1)	52(1)
C(31)	1899(1)	4354(2)	6885(1)	43(1)
C(9)	4618(1)	3770(2)	5649(1)	41(1)
C(99)	6206(1)	8256(2)	3761(1)	49(1)
C(7)	4771(1)	5774(2)	6101(1)	46(1)
C(59)	8410(1)	3630(2)	4242(1)	44(1)
C(98)	5962(1)	9181(2)	4047(1)	52(1)
C(2)	5217(1)	5170(2)	6005(1)	46(1)
C(93)	5779(1)	4168(2)	4481(1)	52(1)
C(69)	7834(1)	751(2)	3464(1)	58(1)
C(63)	9235(1)	2627(2)	4137(1)	46(1)
C(42)	1719(1)	6958(2)	5662(1)	47(1)

C(97)	5607(1)	8686(2)	4349(1)	52(1)
C(87)	6088(1)	4193(2)	2302(1)	62(1)
C(13)	4423(1)	2329(2)	5676(1)	41(1)
C(60)	8168(1)	2277(2)	4135(1)	44(1)
C(34)	2061(1)	3758(2)	5506(1)	47(1)
C(105)	5125(1)	4268(2)	2907(1)	53(1)
C(10)	5474(1)	2920(2)	5721(1)	49(1)
C(49)	1400(1)	3958(2)	7071(1)	52(1)
C(84)	6825(1)	3183(2)	2902(1)	60(1)
C(43)	1862(1)	8299(2)	5679(1)	53(1)
C(40)	2363(1)	3815(2)	7686(1)	61(1)
C(37)	3101(1)	2776(2)	7092(1)	57(1)
C(18)	4058(1)	13(2)	6721(1)	61(1)
C(17)	4281(1)	587(2)	7120(1)	64(1)
C(6)	4752(1)	7027(2)	6308(1)	60(1)
C(47)	1296(1)	6628(3)	5336(1)	69(1)
C(72)	8347(1)	2150(2)	2758(1)	61(1)
C(38)	3149(1)	2807(3)	7590(1)	71(1)
C(16)	4544(1)	1746(2)	7044(1)	58(1)
C(12)	4775(1)	1500(2)	5365(1)	52(1)
C(8)	4355(1)	4868(2)	5946(1)	43(1)
C(70)	7841(1)	350(2)	2982(1)	70(1)
C(44)	2271(1)	8746(2)	5923(1)	52(1)
C(61)	8486(1)	1236(2)	4394(1)	52(1)
C(58)	8179(1)	4906(2)	4029(1)	47(1)
C(57)	8612(1)	5727(2)	3869(1)	49(1)
C(3)	5650(1)	5812(2)	6122(1)	61(1)
C(11)	5292(1)	1562(2)	5563(1)	56(1)
C(71)	8097(1)	1006(2)	2625(1)	67(1)
C(62)	9008(1)	1275(2)	4217(1)	51(1)
C(86)	6513(1)	3676(3)	2107(1)	73(1)
C(92)	6331(1)	4094(2)	4458(1)	56(1)
C(56)	9042(1)	4996(2)	3931(1)	49(1)

C(39)	2790(1)	3309(3)	7885(1)	72(1)
C(101)	5089(1)	6969(3)	4740(1)	67(1)
C(67)	8631(1)	7017(2)	3682(1)	62(1)
C(65)	9499(1)	6838(2)	3632(1)	73(1)
C(64)	9490(1)	5541(2)	3812(1)	64(1)
C(85)	6872(1)	3188(3)	2404(1)	73(1)
C(20)	3837(1)	-240(2)	5857(1)	77(1)
C(78)	7275(1)	7234(3)	4539(1)	75(1)
C(66)	9079(1)	7567(2)	3564(1)	74(1)
C(48)	2407(1)	10208(2)	5924(1)	77(1)
C(26)	3752(1)	6850(3)	4985(1)	74(1)
C(74)	7528(1)	-65(3)	3804(1)	87(1)
C(102)	6078(1)	10653(2)	4032(1)	86(1)
C(5)	5179(1)	7685(2)	6420(1)	72(1)
C(21)	4244(1)	-48(3)	7615(1)	98(1)
C(4)	5621(1)	7069(3)	6329(1)	75(1)
C(75)	8106(2)	477(4)	2116(1)	108(1)
C(107)	4434(1)	4976(4)	2474(1)	108(1)
C(51)	692(1)	4797(4)	7445(1)	100(1)

Table S28 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3k. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
O(22)	34(1)	68(1)	51(1)	-5(1)	-7(1)	6(1)
O(53)	35(1)	77(1)	70(1)	-3(1)	6(1)	12(1)
O(54)	30(1)	54(1)	79(1)	1(1)	-8(1)	-7(1)
O(25)	61(1)	76(1)	58(1)	11(1)	-4(1)	26(1)
O(80)	35(1)	64(1)	81(1)	0(1)	3(1)	6(1)
N(82)	34(1)	37(1)	52(1)	2(1)	-5(1)	4(1)
N(28)	31(1)	39(1)	47(1)	0(1)	1(1)	3(1)
O(103)	32(1)	50(1)	79(1)	-4(1)	8(1)	-7(1)
O(50)	48(1)	77(1)	85(1)	-12(1)	21(1)	3(1)

O(81)	36(1)	84(1)	57(1)	20(1)	4(1)	8(1)
O(77)	62(1)	64(1)	65(1)	8(1)	9(1)	23(1)
O(23)	31(1)	69(1)	110(1)	3(1)	-4(1)	9(1)
O(104)	42(1)	104(1)	81(1)	8(1)	-14(1)	19(1)
N(1)	30(1)	49(1)	55(1)	4(1)	3(1)	4(1)
O(106)	57(1)	75(1)	88(1)	4(1)	-30(1)	14(1)
C(95)	31(1)	39(1)	46(1)	0(1)	-4(1)	-1(1)
C(29)	42(1)	37(1)	51(1)	2(1)	-3(1)	-3(1)
O(79)	116(2)	131(2)	53(1)	-15(1)	-8(1)	65(1)
C(36)	37(1)	40(1)	54(1)	-4(1)	5(1)	-1(1)
C(68)	35(1)	42(1)	56(1)	7(1)	-7(1)	1(1)
C(90)	30(1)	33(1)	52(1)	1(1)	-3(1)	-1(1)
O(27)	57(1)	91(1)	93(1)	11(1)	17(1)	37(1)
N(55)	34(1)	47(1)	53(1)	-2(1)	-6(1)	1(1)
C(14)	34(1)	40(1)	55(1)	-2(1)	1(1)	7(1)
C(32)	30(1)	36(1)	50(1)	1(1)	1(1)	-3(1)
C(96)	40(1)	48(1)	47(1)	-6(1)	-3(1)	4(1)
O(108)	72(1)	70(1)	113(2)	5(1)	-34(1)	-23(1)
C(46)	35(1)	38(1)	58(1)	5(1)	-5(1)	-2(1)
O(52)	74(1)	66(1)	137(2)	1(1)	41(1)	-25(1)
C(83)	40(1)	39(1)	54(1)	-2(1)	2(1)	-3(1)
C(94)	32(1)	40(1)	51(1)	2(1)	1(1)	-4(1)
C(35)	48(1)	53(1)	48(1)	-3(1)	6(1)	-1(1)
C(45)	44(1)	41(1)	63(1)	-1(1)	3(1)	-7(1)
C(33)	29(1)	40(1)	52(1)	-2(1)	-4(1)	-3(1)
C(41)	31(1)	39(1)	46(1)	2(1)	1(1)	0(1)
C(88)	42(1)	44(1)	51(1)	-1(1)	-1(1)	-6(1)
C(73)	51(1)	46(1)	48(1)	3(1)	-5(1)	-4(1)
C(24)	37(1)	42(1)	64(1)	-1(1)	1(1)	5(1)
C(100)	36(1)	38(1)	50(1)	-1(1)	0(1)	-2(1)
C(30)	46(1)	44(1)	47(1)	0(1)	1(1)	-8(1)
C(15)	47(1)	46(1)	51(1)	4(1)	-3(1)	2(1)
C(76)	52(1)	60(1)	55(1)	-1(1)	0(1)	13(1)

C(91)	40(1)	45(1)	61(1)	7(1)	-10(1)	4(1)
C(89)	38(1)	39(1)	51(1)	1(1)	-7(1)	1(1)
C(19)	43(1)	42(1)	72(1)	0(1)	4(1)	3(1)
C(31)	39(1)	38(1)	53(1)	0(1)	7(1)	-2(1)
C(9)	30(1)	47(1)	45(1)	4(1)	2(1)	8(1)
C(99)	48(1)	41(1)	59(1)	4(1)	-1(1)	-7(1)
C(7)	45(1)	47(1)	47(1)	4(1)	1(1)	4(1)
C(59)	37(1)	53(1)	41(1)	0(1)	-3(1)	8(1)
C(98)	54(1)	38(1)	65(1)	-2(1)	-13(1)	0(1)
C(2)	39(1)	51(1)	48(1)	7(1)	1(1)	-1(1)
C(93)	60(1)	46(1)	49(1)	8(1)	4(1)	-3(1)
C(69)	45(1)	47(1)	80(1)	4(1)	-13(1)	-5(1)
C(63)	35(1)	56(1)	46(1)	0(1)	-5(1)	6(1)
C(42)	43(1)	53(1)	46(1)	5(1)	-1(1)	7(1)
C(97)	53(1)	44(1)	58(1)	-11(1)	-7(1)	9(1)
C(87)	66(1)	68(1)	53(1)	0(1)	-1(1)	-9(1)
C(13)	31(1)	47(1)	46(1)	-4(1)	-3(1)	7(1)
C(60)	33(1)	51(1)	49(1)	10(1)	0(1)	3(1)
C(34)	48(1)	46(1)	48(1)	-5(1)	-7(1)	-3(1)
C(105)	40(1)	59(1)	58(1)	-4(1)	-9(1)	3(1)
C(10)	34(1)	56(1)	58(1)	7(1)	5(1)	11(1)
C(49)	44(1)	56(1)	57(1)	0(1)	9(1)	-5(1)
C(84)	47(1)	60(1)	73(1)	-5(1)	4(1)	5(1)
C(43)	62(1)	46(1)	51(1)	9(1)	4(1)	14(1)
C(40)	66(1)	68(1)	48(1)	-3(1)	4(1)	-11(1)
C(37)	51(1)	55(1)	66(1)	6(1)	-9(1)	5(1)
C(18)	60(1)	41(1)	80(2)	8(1)	17(1)	5(1)
C(17)	71(1)	54(1)	67(1)	17(1)	16(1)	18(1)
C(6)	61(1)	54(1)	64(1)	-6(1)	-3(1)	7(1)
C(47)	64(1)	73(1)	70(1)	7(1)	-24(1)	10(1)
C(72)	75(1)	58(1)	50(1)	2(1)	-7(1)	3(1)
C(38)	70(1)	74(1)	70(1)	16(1)	-24(1)	-3(1)
C(16)	62(1)	60(1)	51(1)	4(1)	-2(1)	9(1)

C(12)	42(1)	59(1)	54(1)	-10(1)	1(1)	11(1)
C(8)	35(1)	45(1)	50(1)	3(1)	5(1)	5(1)
C(70)	65(1)	55(1)	89(2)	-11(1)	-26(1)	-6(1)
C(44)	65(1)	39(1)	54(1)	3(1)	14(1)	-1(1)
C(61)	39(1)	60(1)	56(1)	18(1)	-4(1)	5(1)
C(58)	44(1)	50(1)	45(1)	-4(1)	-7(1)	9(1)
C(57)	58(1)	45(1)	44(1)	-5(1)	-6(1)	1(1)
C(3)	43(1)	67(1)	73(1)	5(1)	-1(1)	-7(1)
C(11)	39(1)	58(1)	69(1)	-3(1)	3(1)	17(1)
C(71)	79(1)	60(1)	63(1)	-10(1)	-24(1)	11(1)
C(62)	40(1)	50(1)	63(1)	10(1)	-3(1)	9(1)
C(86)	76(1)	88(2)	56(1)	-10(1)	16(1)	-11(1)
C(92)	60(1)	55(1)	52(1)	7(1)	-14(1)	3(1)
C(56)	49(1)	51(1)	47(1)	-7(1)	-8(1)	-5(1)
C(39)	83(2)	81(2)	53(1)	12(1)	-16(1)	-14(1)
C(101)	65(1)	71(1)	66(1)	-8(1)	18(1)	2(1)
C(67)	81(1)	50(1)	56(1)	-2(1)	-3(1)	6(1)
C(65)	76(1)	69(1)	75(2)	0(1)	-5(1)	-26(1)
C(64)	56(1)	66(1)	70(1)	-1(1)	-13(1)	-15(1)
C(85)	60(1)	83(2)	76(2)	-16(1)	21(1)	0(1)
C(20)	77(1)	54(1)	98(2)	-9(1)	-7(1)	-15(1)
C(78)	68(1)	73(1)	85(2)	7(1)	22(1)	26(1)
C(66)	105(2)	50(1)	67(1)	2(1)	1(1)	-18(1)
C(48)	107(2)	39(1)	86(2)	5(1)	18(1)	-5(1)
C(26)	84(2)	67(1)	71(1)	0(1)	-27(1)	25(1)
C(74)	66(1)	72(2)	124(2)	10(2)	2(1)	-28(1)
C(102)	105(2)	39(1)	114(2)	-5(1)	-1(2)	-6(1)
C(5)	76(1)	59(1)	82(2)	-11(1)	-8(1)	-8(1)
C(21)	138(3)	79(2)	76(2)	29(1)	28(2)	20(2)
C(4)	63(1)	75(2)	87(2)	0(1)	-10(1)	-21(1)
C(75)	148(3)	99(2)	75(2)	-29(2)	-43(2)	21(2)
C(107)	71(2)	129(3)	124(3)	-18(2)	-53(2)	19(2)
C(51)	58(1)	133(3)	109(2)	6(2)	33(2)	11(2)

Table S29 Bond Lengths for 3k.

Bond	Angle/°	Bond	Angle/°
O(22)-C(13)	1.4275(19)	C(88)-C(87)	1.382(3)
O(53)-C(36)	1.230(2)	C(88)-C(89)	1.518(2)
O(54)-C(33)	1.4219(17)	C(73)-C(72)	1.389(3)
O(25)-C(24)	1.319(2)	C(24)-C(8)	1.509(2)
O(25)-C(26)	1.450(2)	C(100)-C(99)	1.375(2)
O(80)-C(63)	1.232(2)	C(30)-C(40)	1.377(3)
N(82)-C(91)	1.350(2)	C(30)-C(31)	1.514(3)
N(82)-C(83)	1.425(2)	C(15)-C(16)	1.384(3)
N(82)-C(90)	1.4814(18)	C(76)-C(58)	1.518(3)
N(28)-C(36)	1.355(2)	C(91)-C(92)	1.506(3)
N(28)-C(29)	1.420(2)	C(89)-C(105)	1.513(2)
N(28)-C(32)	1.4814(18)	C(19)-C(18)	1.389(3)
O(103)-C(94)	1.4240(18)	C(19)-C(20)	1.518(3)
O(50)-C(49)	1.319(2)	C(31)-C(49)	1.518(2)
O(50)-C(51)	1.438(3)	C(9)-C(13)	1.533(2)
O(81)-C(60)	1.423(2)	C(9)-C(8)	1.546(2)
O(77)-C(76)	1.319(2)	C(99)-C(98)	1.386(3)
O(77)-C(78)	1.440(3)	C(7)-C(6)	1.372(3)
O(23)-C(10)	1.232(2)	C(7)-C(2)	1.392(2)
O(104)-C(91)	1.222(2)	C(7)-C(8)	1.520(2)
N(1)-C(10)	1.351(2)	C(59)-C(60)	1.531(3)
N(1)-C(2)	1.415(2)	C(59)-C(58)	1.537(2)
N(1)-C(9)	1.4934(19)	C(98)-C(97)	1.378(3)
O(106)-C(105)	1.323(3)	C(98)-C(102)	1.498(3)
O(106)-C(107)	1.446(3)	C(2)-C(3)	1.390(3)
C(95)-C(100)	1.397(2)	C(93)-C(92)	1.524(3)
C(95)-C(96)	1.413(2)	C(69)-C(70)	1.394(4)
C(95)-C(94)	1.527(2)	C(69)-C(74)	1.501(3)
C(29)-C(37)	1.386(3)	C(63)-C(62)	1.498(3)

C(29)-C(30)	1.389(2)	C(42)-C(43)	1.391(3)
O(79)-C(76)	1.190(3)	C(42)-C(47)	1.508(3)
C(36)-C(35)	1.503(3)	C(87)-C(86)	1.386(3)
C(68)-C(73)	1.388(3)	C(13)-C(12)	1.535(2)
C(68)-C(69)	1.412(3)	C(60)-C(61)	1.534(2)
C(68)-C(60)	1.538(3)	C(10)-C(11)	1.505(3)
C(90)-C(94)	1.534(2)	C(84)-C(85)	1.385(4)
C(90)-C(89)	1.539(2)	C(43)-C(44)	1.385(3)
O(27)-C(24)	1.188(2)	C(40)-C(39)	1.390(3)
N(55)-C(63)	1.355(2)	C(37)-C(38)	1.386(3)
N(55)-C(56)	1.413(2)	C(18)-C(17)	1.385(4)
N(55)-C(59)	1.484(2)	C(17)-C(16)	1.376(3)
C(14)-C(15)	1.399(3)	C(17)-C(21)	1.513(3)
C(14)-C(19)	1.412(2)	C(6)-C(5)	1.381(3)
C(14)-C(13)	1.530(3)	C(72)-C(71)	1.378(3)
C(32)-C(31)	1.533(2)	C(38)-C(39)	1.376(4)
C(32)-C(33)	1.534(2)	C(12)-C(11)	1.527(3)
C(96)-C(97)	1.394(3)	C(70)-C(71)	1.378(4)
C(96)-C(101)	1.509(3)	C(44)-C(48)	1.500(3)
O(108)-C(105)	1.196(3)	C(61)-C(62)	1.519(2)
C(46)-C(45)	1.384(2)	C(58)-C(57)	1.512(3)
C(46)-C(41)	1.393(2)	C(57)-C(67)	1.384(3)
O(52)-C(49)	1.189(3)	C(57)-C(56)	1.398(3)
C(83)-C(88)	1.384(3)	C(3)-C(4)	1.376(4)
C(83)-C(84)	1.388(3)	C(71)-C(75)	1.506(4)
C(94)-C(93)	1.537(3)	C(86)-C(85)	1.376(4)
C(35)-C(34)	1.519(2)	C(56)-C(64)	1.387(3)
C(45)-C(44)	1.377(3)	C(67)-C(66)	1.390(4)
C(33)-C(41)	1.529(2)	C(65)-C(66)	1.378(4)
C(33)-C(34)	1.538(2)	C(65)-C(64)	1.381(3)
C(41)-C(42)	1.410(2)	C(5)-C(4)	1.385(4)

Table S30 Bond Angles for 3k.

Bond	Angle/°	Bond	Angle/°
C(24)-O(25)-C(26)	115.58(16)	C(6)-C(7)-C(2)	120.43(18)
C(91)-N(82)-C(83)	126.43(14)	C(6)-C(7)-C(8)	128.78(17)
C(91)-N(82)-C(90)	125.00(15)	C(2)-C(7)-C(8)	110.79(15)
C(83)-N(82)-C(90)	108.46(13)	N(55)-C(59)-C(60)	114.02(14)
C(36)-N(28)-C(29)	126.72(13)	N(55)-C(59)-C(58)	105.28(14)
C(36)-N(28)-C(32)	124.69(14)	C(60)-C(59)-C(58)	118.02(14)
C(29)-N(28)-C(32)	108.57(13)	C(97)-C(98)-C(99)	116.92(16)
C(49)-O(50)-C(51)	117.6(2)	C(97)-C(98)-C(102)	121.1(2)
C(76)-O(77)-C(78)	114.96(18)	C(99)-C(98)-C(102)	121.9(2)
C(10)-N(1)-C(2)	126.92(15)	C(3)-C(2)-C(7)	120.86(18)
C(10)-N(1)-C(9)	123.91(15)	C(3)-C(2)-N(1)	129.54(17)
C(2)-N(1)-C(9)	109.16(13)	C(7)-C(2)-N(1)	109.60(14)
C(105)-O(106)-C(107)	116.6(2)	C(92)-C(93)-C(94)	111.65(15)
C(100)-C(95)-C(96)	117.52(14)	C(70)-C(69)-C(68)	118.5(2)
C(100)-C(95)-C(94)	120.95(14)	C(70)-C(69)-C(74)	117.0(2)
C(96)-C(95)-C(94)	121.54(15)	C(68)-C(69)-C(74)	124.5(2)
C(37)-C(29)-C(30)	121.85(18)	O(80)-C(63)-N(55)	122.27(17)
C(37)-C(29)-N(28)	129.02(17)	O(80)-C(63)-C(62)	120.56(16)
C(30)-C(29)-N(28)	109.10(14)	N(55)-C(63)-C(62)	117.04(14)
O(53)-C(36)-N(28)	121.01(17)	C(43)-C(42)-C(41)	118.54(16)
O(53)-C(36)-C(35)	121.73(16)	C(43)-C(42)-C(47)	116.66(17)
N(28)-C(36)-C(35)	117.20(14)	C(41)-C(42)-C(47)	124.73(17)
C(73)-C(68)-C(69)	117.18(18)	C(98)-C(97)-C(96)	124.16(17)
C(73)-C(68)-C(60)	121.73(15)	C(88)-C(87)-C(86)	118.8(2)
C(69)-C(68)-C(60)	120.87(17)	O(22)-C(13)-C(14)	112.00(13)
N(82)-C(90)-C(94)	114.25(13)	O(22)-C(13)-C(9)	104.32(13)
N(82)-C(90)-C(89)	104.61(13)	C(14)-C(13)-C(9)	116.92(14)
C(94)-C(90)-C(89)	118.15(13)	O(22)-C(13)-C(12)	106.62(13)
C(63)-N(55)-C(56)	127.31(15)	C(14)-C(13)-C(12)	111.48(14)
C(63)-N(55)-C(59)	123.00(15)	C(9)-C(13)-C(12)	104.67(14)
C(56)-N(55)-C(59)	109.68(13)	O(81)-C(60)-C(59)	105.71(14)
C(15)-C(14)-C(19)	116.71(18)	O(81)-C(60)-C(61)	105.96(13)

C(15)-C(14)-C(13)	121.59(15)	C(59)-C(60)-C(61)	104.62(14)
C(19)-C(14)-C(13)	121.67(16)	O(81)-C(60)-C(68)	112.71(14)
N(28)-C(32)-C(31)	104.31(12)	C(59)-C(60)-C(68)	116.92(14)
N(28)-C(32)-C(33)	115.02(13)	C(61)-C(60)-C(68)	110.08(15)
C(31)-C(32)-C(33)	117.55(13)	C(35)-C(34)-C(33)	112.06(14)
C(97)-C(96)-C(95)	118.03(16)	O(108)-C(105)-O(106)	125.01(18)
C(97)-C(96)-C(101)	116.78(17)	O(108)-C(105)-C(89)	124.51(18)
C(95)-C(96)-C(101)	125.19(17)	O(106)-C(105)-C(89)	110.45(17)
C(45)-C(46)-C(41)	122.60(16)	O(23)-C(10)-N(1)	122.00(18)
C(88)-C(83)-C(84)	121.83(18)	O(23)-C(10)-C(11)	120.61(16)
C(88)-C(83)-N(82)	109.18(14)	N(1)-C(10)-C(11)	117.31(15)
C(84)-C(83)-N(82)	128.99(17)	O(52)-C(49)-O(50)	124.37(18)
O(103)-C(94)-C(95)	107.01(12)	O(52)-C(49)-C(31)	124.78(18)
O(103)-C(94)-C(90)	105.09(13)	O(50)-C(49)-C(31)	110.85(16)
C(95)-C(94)-C(90)	116.52(13)	C(85)-C(84)-C(83)	117.0(2)
O(103)-C(94)-C(93)	111.70(14)	C(44)-C(43)-C(42)	123.76(16)
C(95)-C(94)-C(93)	111.00(14)	C(30)-C(40)-C(39)	118.8(2)
C(90)-C(94)-C(93)	105.45(13)	C(29)-C(37)-C(38)	116.9(2)
C(36)-C(35)-C(34)	116.97(15)	C(17)-C(18)-C(19)	123.64(19)
C(44)-C(45)-C(46)	120.61(17)	C(16)-C(17)-C(18)	117.2(2)
O(54)-C(33)-C(41)	107.26(12)	C(16)-C(17)-C(21)	121.6(3)
O(54)-C(33)-C(32)	104.70(13)	C(18)-C(17)-C(21)	121.3(2)
C(41)-C(33)-C(32)	115.86(13)	C(7)-C(6)-C(5)	119.3(2)
O(54)-C(33)-C(34)	112.21(13)	C(71)-C(72)-C(73)	120.5(2)
C(41)-C(33)-C(34)	110.94(14)	C(39)-C(38)-C(37)	122.0(2)
C(32)-C(33)-C(34)	105.82(13)	C(17)-C(16)-C(15)	120.7(2)
C(46)-C(41)-C(42)	117.25(15)	C(11)-C(12)-C(13)	111.45(15)
C(46)-C(41)-C(33)	120.72(14)	C(24)-C(8)-C(7)	110.39(14)
C(42)-C(41)-C(33)	122.00(14)	C(24)-C(8)-C(9)	116.77(15)
C(87)-C(88)-C(83)	120.07(18)	C(7)-C(8)-C(9)	102.37(12)
C(87)-C(88)-C(89)	129.18(18)	C(71)-C(70)-C(69)	123.88(19)
C(83)-C(88)-C(89)	110.72(16)	C(45)-C(44)-C(43)	117.09(16)
C(68)-C(73)-C(72)	122.70(18)	C(45)-C(44)-C(48)	121.9(2)

O(27)-C(24)-O(25)	122.93(17)	C(43)-C(44)-C(48)	121.02(19)
O(27)-C(24)-C(8)	123.32(19)	C(62)-C(61)-C(60)	111.83(14)
O(25)-C(24)-C(8)	113.67(14)	C(57)-C(58)-C(76)	110.33(15)
C(99)-C(100)-C(95)	122.42(16)	C(57)-C(58)-C(59)	103.35(14)
C(40)-C(30)-C(29)	120.10(18)	C(76)-C(58)-C(59)	111.39(15)
C(40)-C(30)-C(31)	129.54(18)	C(67)-C(57)-C(56)	119.79(19)
C(29)-C(30)-C(31)	110.29(15)	C(67)-C(57)-C(58)	129.64(18)
C(16)-C(15)-C(14)	122.75(18)	C(56)-C(57)-C(58)	110.57(16)
O(79)-C(76)-O(77)	123.41(19)	C(4)-C(3)-C(2)	117.6(2)
O(79)-C(76)-C(58)	125.09(18)	C(10)-C(11)-C(12)	116.78(15)
O(77)-C(76)-C(58)	111.47(17)	C(70)-C(71)-C(72)	117.2(2)
O(104)-C(91)-N(82)	121.14(19)	C(70)-C(71)-C(75)	120.9(2)
O(104)-C(91)-C(92)	121.34(17)	C(72)-C(71)-C(75)	121.9(3)
N(82)-C(91)-C(92)	117.49(15)	C(63)-C(62)-C(61)	117.69(15)
C(105)-C(89)-C(88)	112.30(15)	C(85)-C(86)-C(87)	120.3(2)
C(105)-C(89)-C(90)	112.93(14)	C(91)-C(92)-C(93)	116.75(16)
C(88)-C(89)-C(90)	101.88(13)	C(64)-C(56)-C(57)	121.31(19)
C(18)-C(19)-C(14)	119.03(19)	C(64)-C(56)-N(55)	129.18(18)
C(18)-C(19)-C(20)	117.10(19)	C(57)-C(56)-N(55)	109.45(15)
C(14)-C(19)-C(20)	123.9(2)	C(38)-C(39)-C(40)	120.3(2)
C(30)-C(31)-C(49)	112.85(15)	C(57)-C(67)-C(66)	119.0(2)
C(30)-C(31)-C(32)	102.13(13)	C(66)-C(65)-C(64)	121.7(2)
C(49)-C(31)-C(32)	112.14(14)	C(65)-C(64)-C(56)	117.8(2)
N(1)-C(9)-C(13)	113.83(12)	C(86)-C(85)-C(84)	121.9(2)
N(1)-C(9)-C(8)	104.74(13)	C(65)-C(66)-C(67)	120.4(2)
C(13)-C(9)-C(8)	118.00(13)	C(6)-C(5)-C(4)	119.9(2)
C(100)-C(99)-C(98)	120.82(17)	C(3)-C(4)-C(5)	121.9(2)

Table S31 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3k.

Atom	x	y	z	U(eq)
H(22)	3756	2616	5603	76
H(54)	1242	3671	5914	81

H(103)	4962	4097	4070	81
H(81)	7516	2717	4231	88
H(90)	5564	3267	3618	46
H(32)	1836	2869	6380	46
H(46)	2585	5844	6342	53
H(35A)	2717	2990	5301	60
H(35B)	2746	4514	5436	60
H(45)	2829	8047	6317	59
H(73)	8525	3344	3315	58
H(100)	6251	6322	3573	50
H(15)	4769	3068	6546	57
H(89)	5623	5709	3112	51
H(31)	1923	5336	6865	52
H(9)	4596	4044	5310	49
H(99)	6457	8545	3562	59
H(59)	8401	3739	4594	52
H(93A)	5683	4617	4778	62
H(93B)	5647	3264	4488	62
H(97)	5445	9292	4548	62
H(87)	5844	4528	2102	74
H(34A)	1924	2860	5494	57
H(34B)	1972	4220	5211	57
H(84)	7069	2845	3100	72
H(43)	1673	8931	5518	63
H(40)	2119	4156	7884	73
H(37)	3345	2430	6895	68
H(18)	3875	-762	6768	73
H(6)	4454	7429	6373	72
H(47A)	1024	6346	5529	103
H(47B)	1386	5917	5120	103
H(47C)	1208	7412	5153	103
H(72)	8514	2642	2525	73
H(38)	3432	2479	7729	85

H(16)	4695	2168	7303	69
H(12A)	4667	572	5357	62
H(12B)	4771	1842	5037	62
H(8)	4210	4454	6233	52
H(70)	7661	-405	2895	84
H(61A)	8480	1411	4739	62
H(61B)	8353	345	4340	62
H(58)	7973	4680	3751	56
H(3)	5949	5406	6063	73
H(11A)	5313	956	5837	67
H(11B)	5510	1221	5316	67
H(62A)	9206	792	4448	61
H(62B)	9023	783	3915	61
H(86)	6554	3660	1773	88
H(92A)	6461	4945	4571	67
H(92B)	6439	3405	4682	67
H(39)	2832	3310	8218	87
H(10A)	4820	6553	4577	101
H(10B)	4980	7767	4902	101
H(10C)	5221	6353	4972	101
H(67)	8347	7508	3635	75
H(65)	9797	7228	3556	88
H(64)	9775	5051	3852	77
H(85)	7155	2850	2266	87
H(20A)	4073	-596	5636	115
H(20B)	3622	355	5688	115
H(20C)	3654	-966	5995	115
H(78A)	7033	7731	4365	113
H(78B)	7475	7846	4718	113
H(78C)	7118	6622	4758	113
H(66)	9096	8433	3437	88
H(48A)	2628	10380	6185	116
H(48B)	2120	10745	5965	116

H(48C)	2560	10433	5623	116
H(26A)	3786	6741	4642	111
H(26B)	3829	7759	5073	111
H(26C)	3423	6655	5078	111
H(74A)	7412	-855	3641	131
H(74B)	7256	464	3910	131
H(74C)	7719	-325	4078	131
H(10D)	6350	10835	4238	129
H(10E)	5801	11158	4141	129
H(10F)	6155	10909	3706	129
H(5)	5170	8540	6555	87
H(21A)	3912	-299	7676	147
H(21B)	4348	585	7855	147
H(21C)	4446	-834	7628	147
H(4)	5906	7517	6410	90
H(75A)	8190	1192	1898	161
H(75B)	7791	130	2034	161
H(75C)	8343	-228	2091	161
H(10G)	4478	4349	2214	162
H(10H)	4291	5789	2351	162
H(10I)	4222	4590	2712	162
H(51A)	486	4435	7198	151
H(51B)	562	5639	7556	151
H(51C)	709	4177	7710	151

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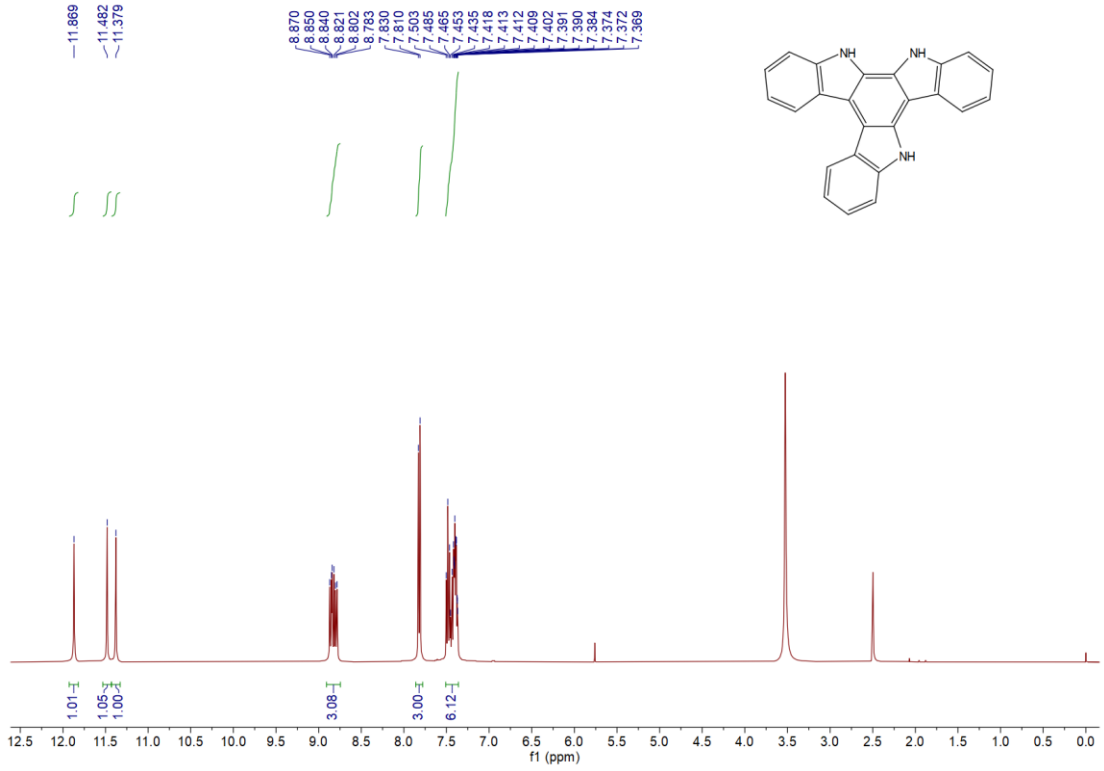
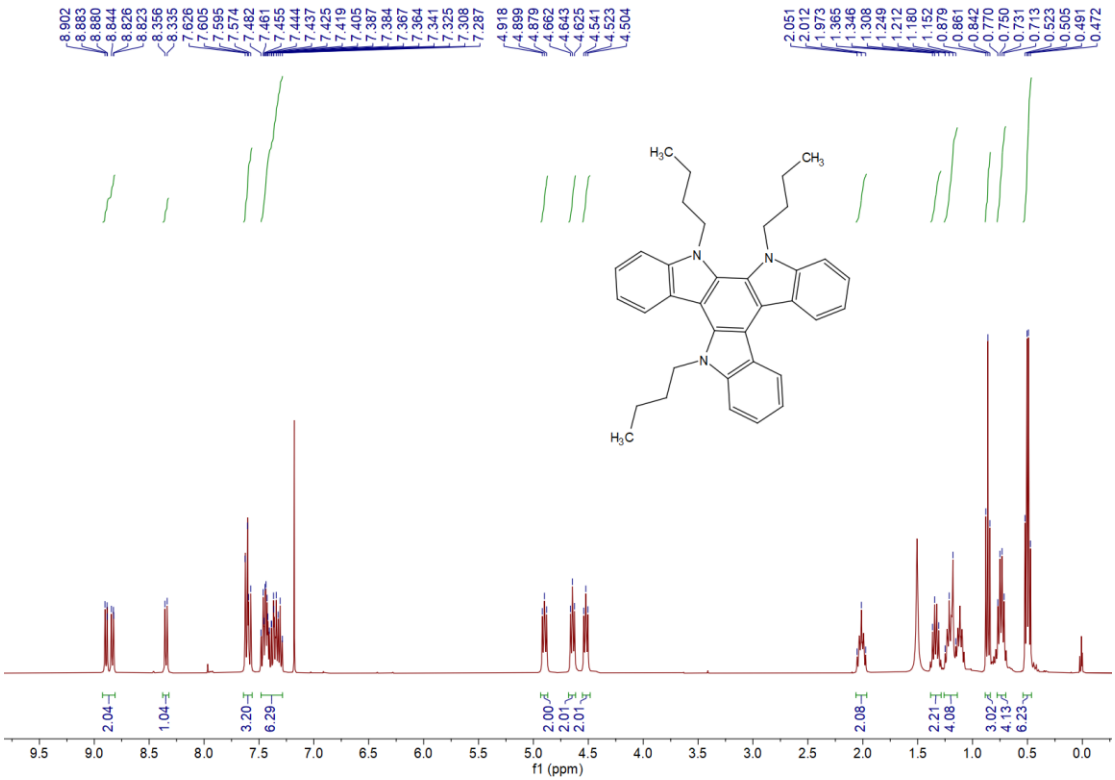
8. Copies of NMR spectra

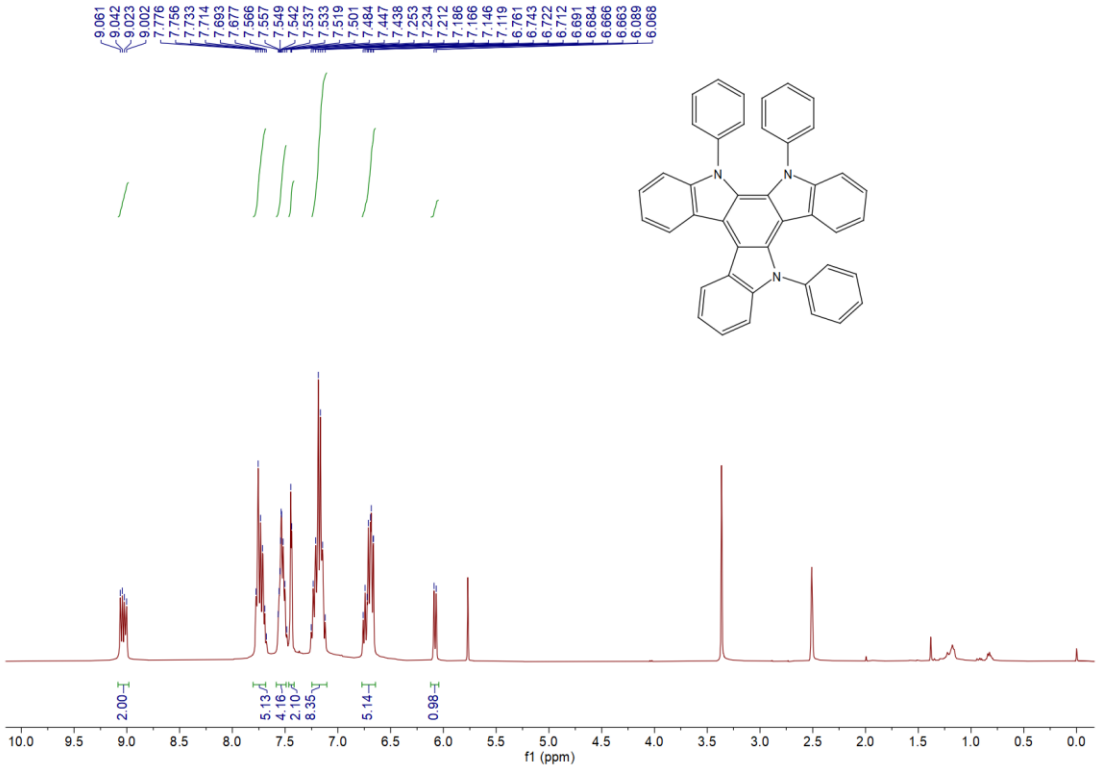
^{1}H NMR Spectrum of **ITN-1**



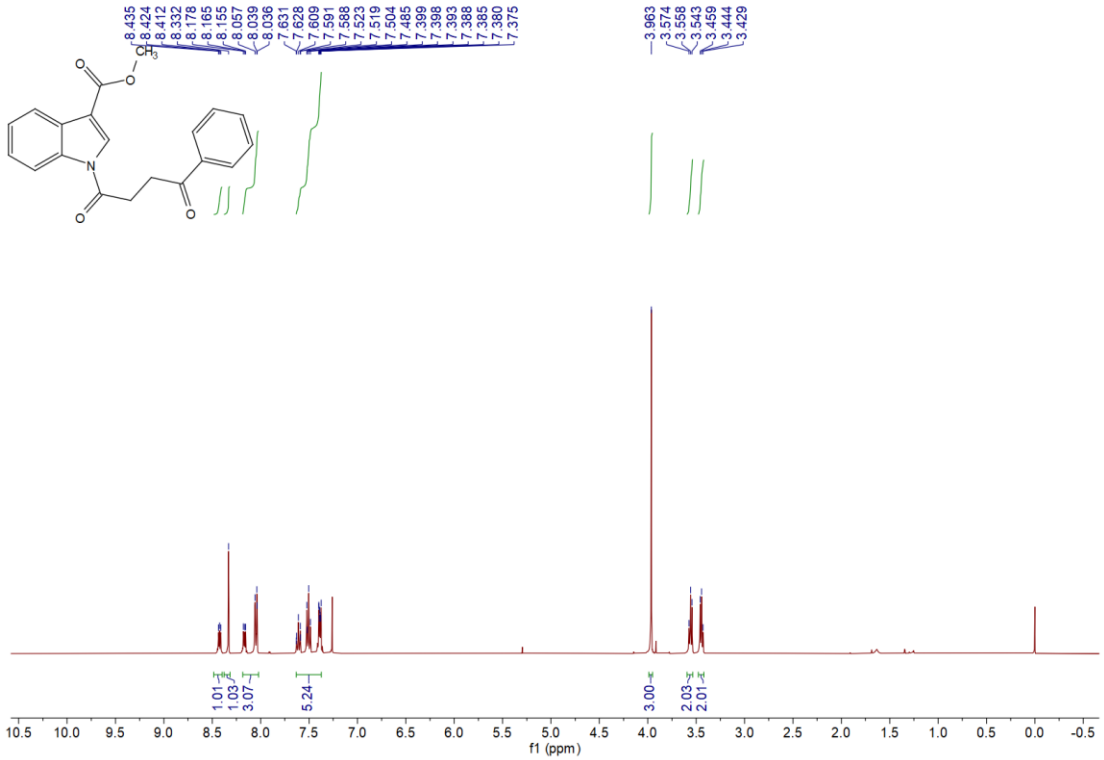
^{1}H NMR Spectrum of **ITN-2**



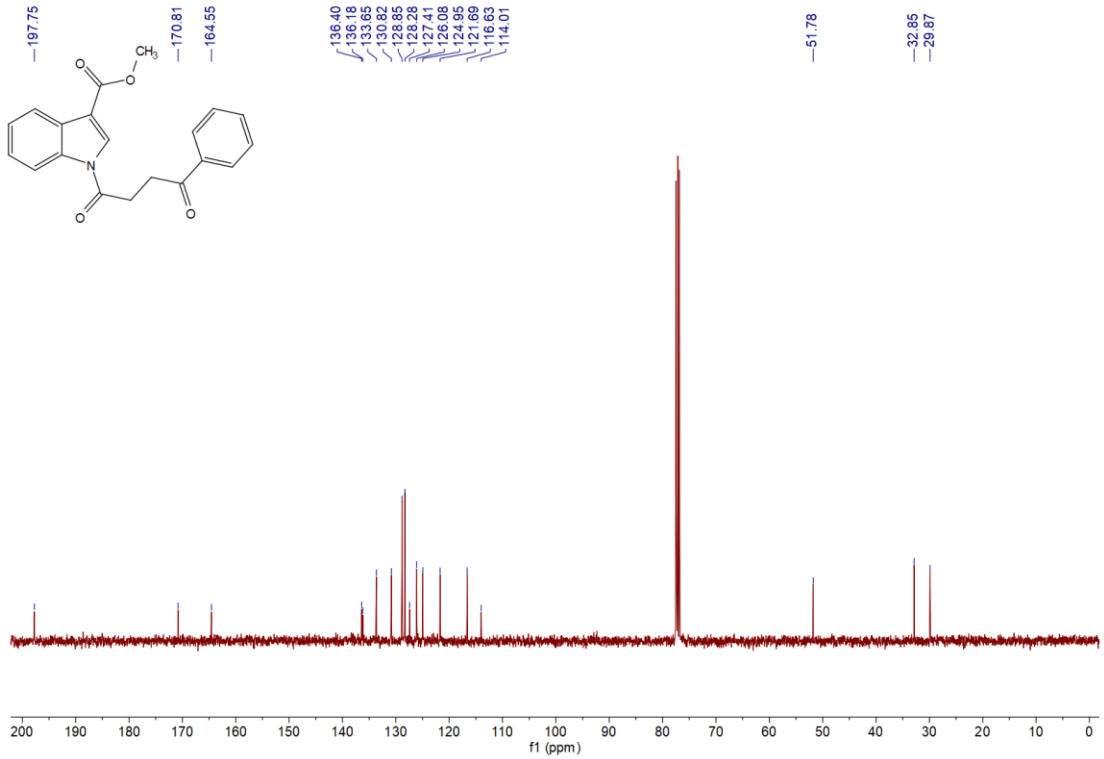
^{1}H NMR Spectrum of **ITN-3**



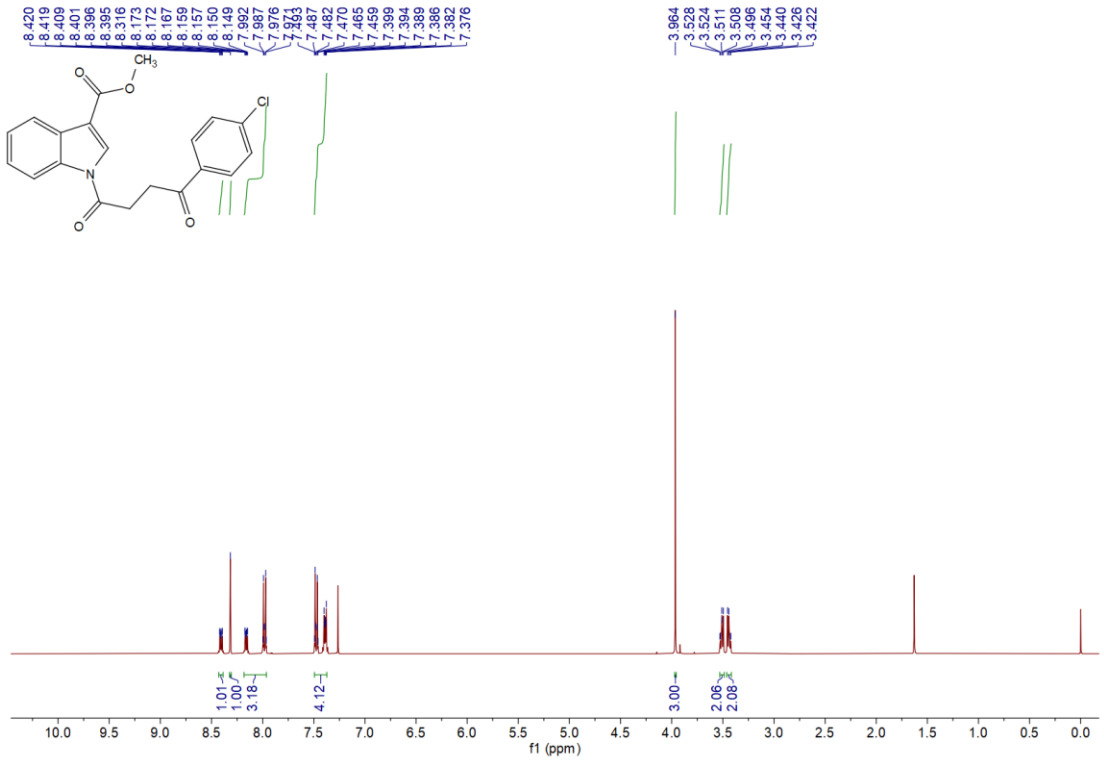
^{1}H NMR Spectrum of **1a**



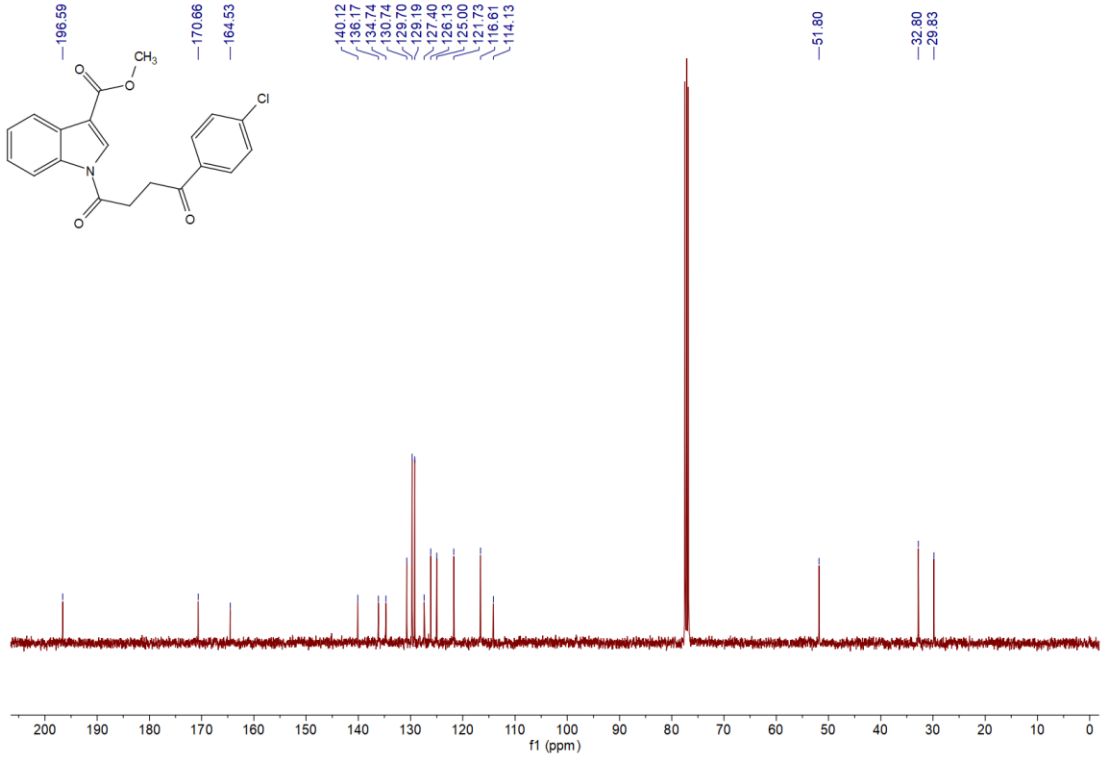
^{13}C NMR Spectrum of **1a**



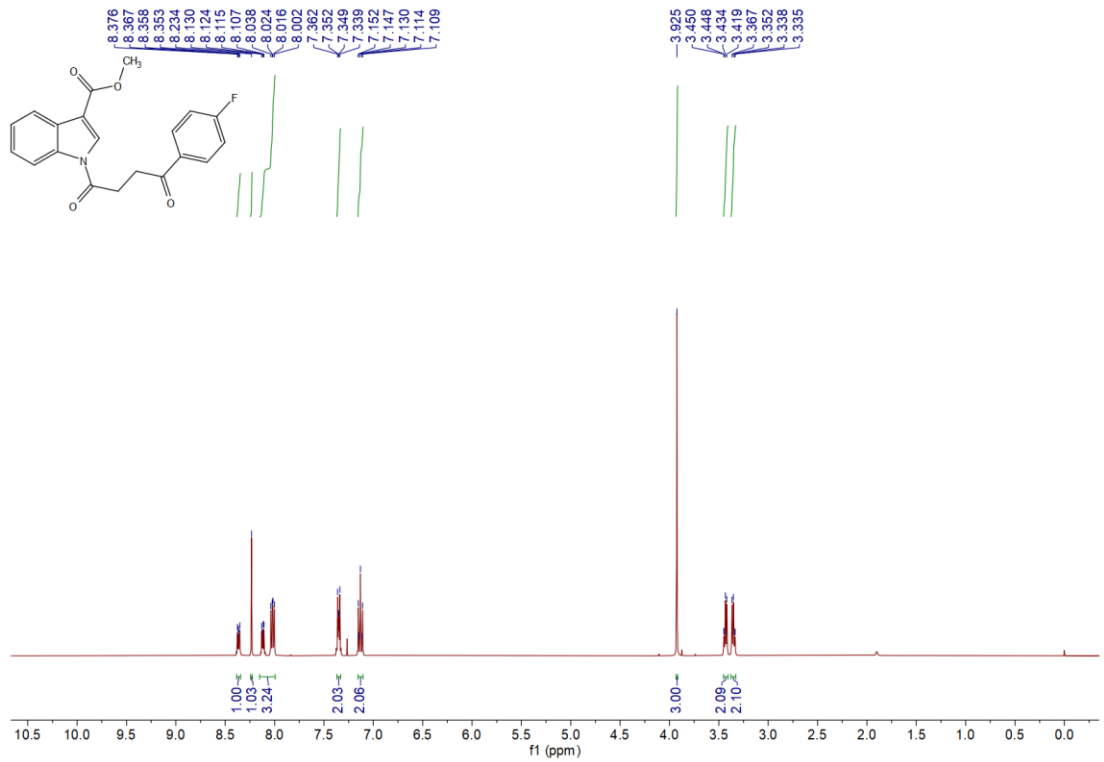
^{1}H NMR Spectrum of **1b**



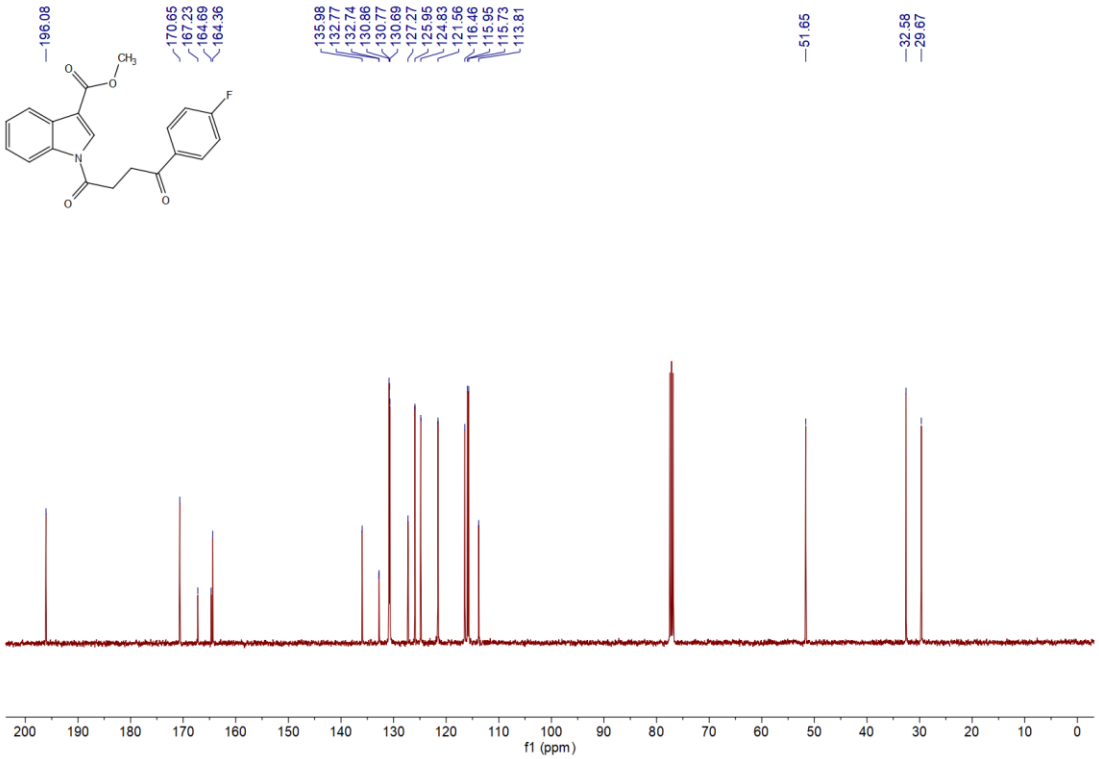
^{13}C NMR Spectrum of **1b**



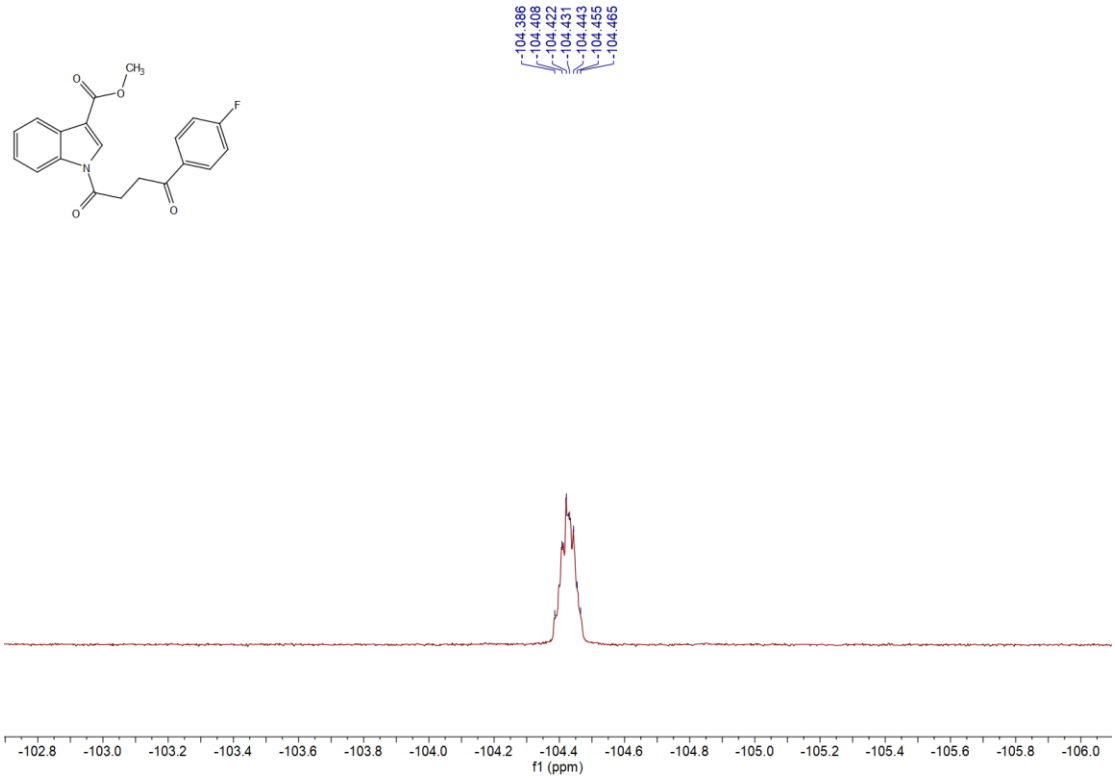
^{1}H NMR Spectrum of **1c**



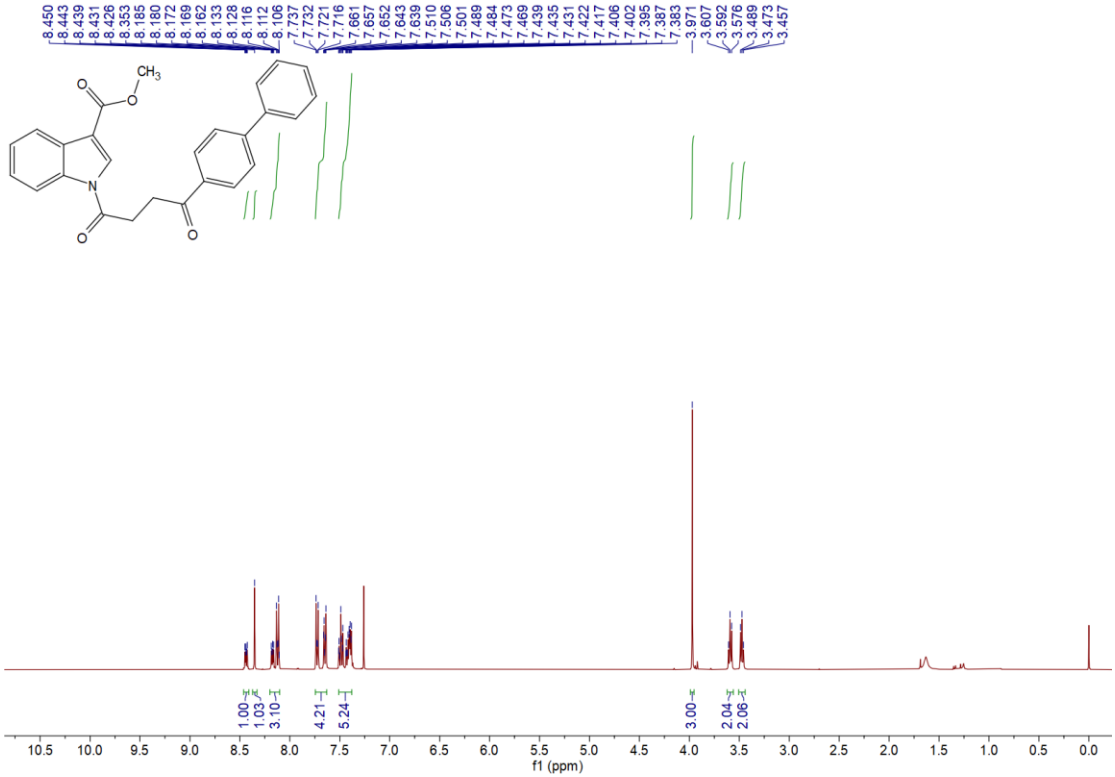
^{13}C NMR Spectrum of **1c**



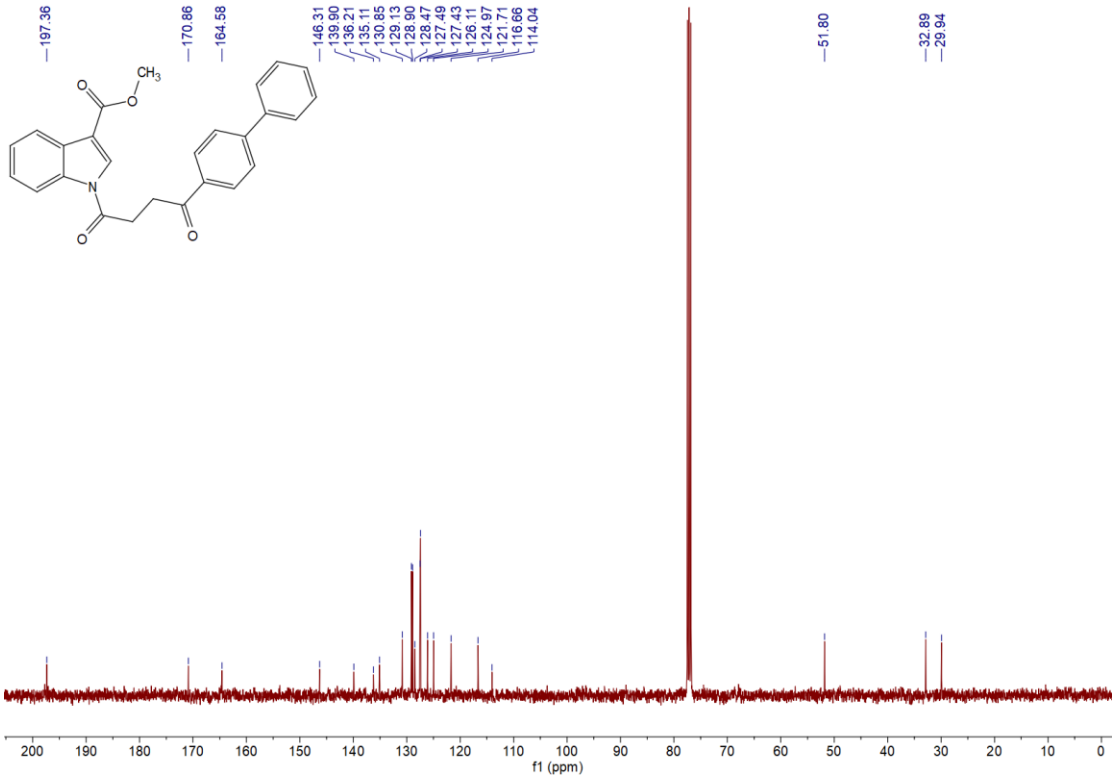
^{19}F NMR Spectrum of **1c**



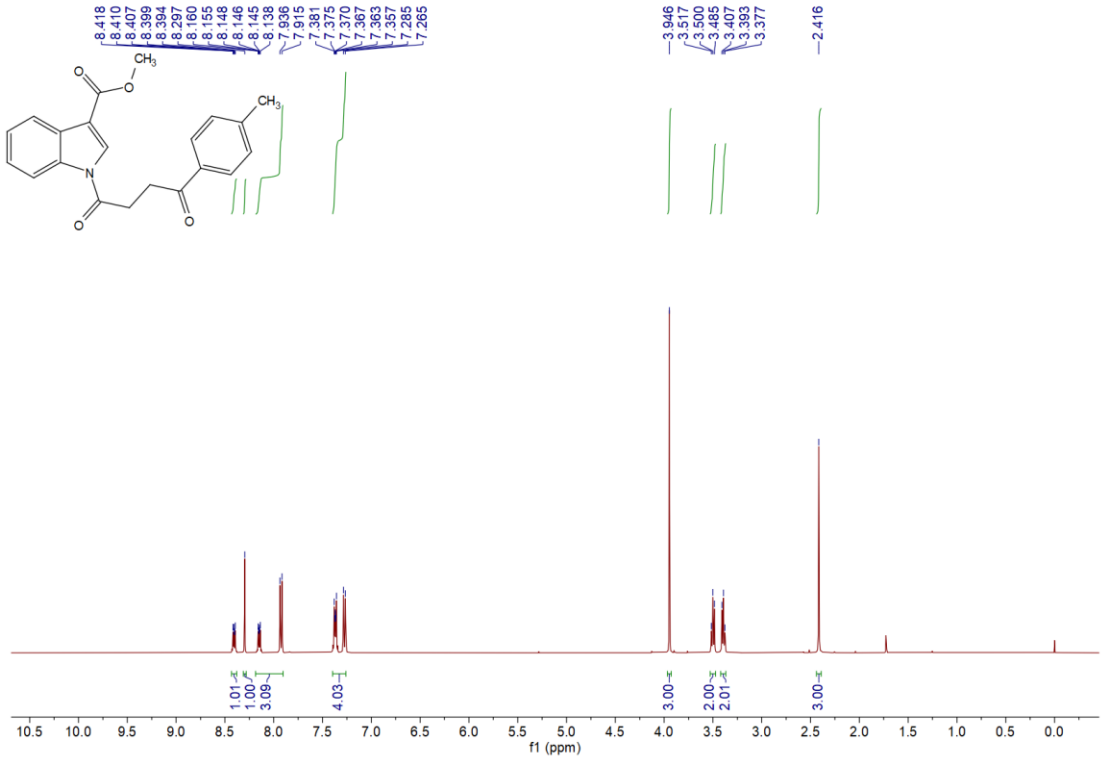
^{1}H NMR Spectrum of **1d**



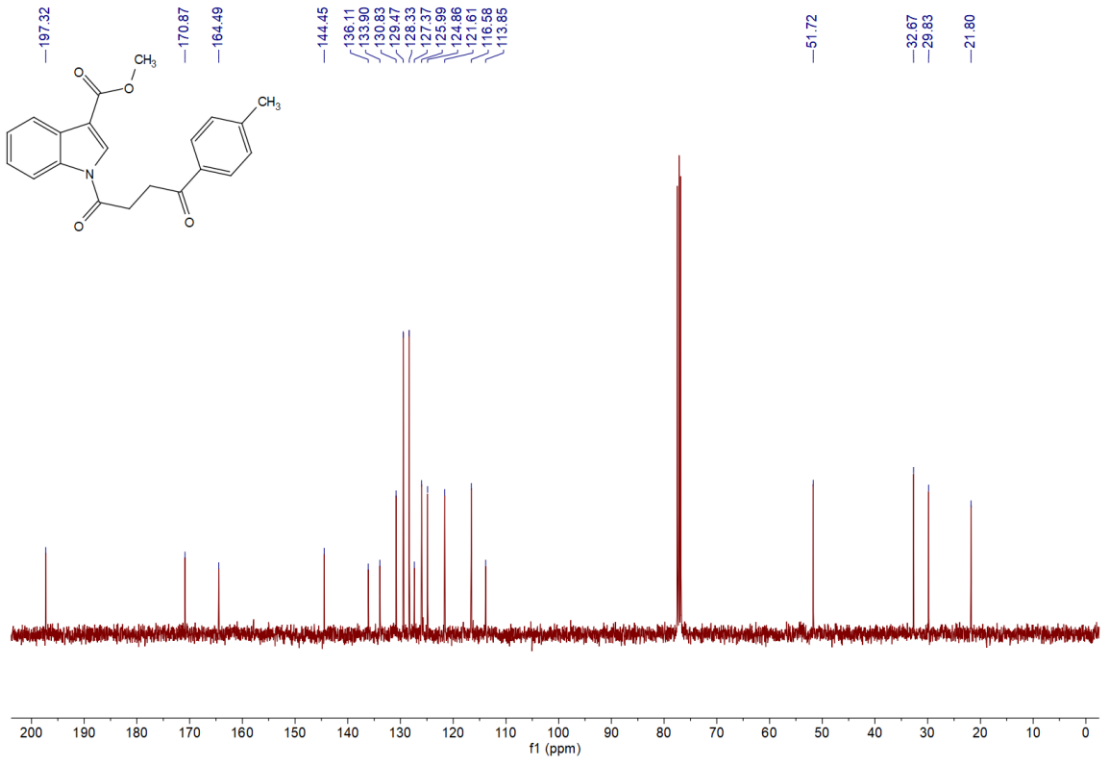
^{13}C NMR Spectrum of **1d**



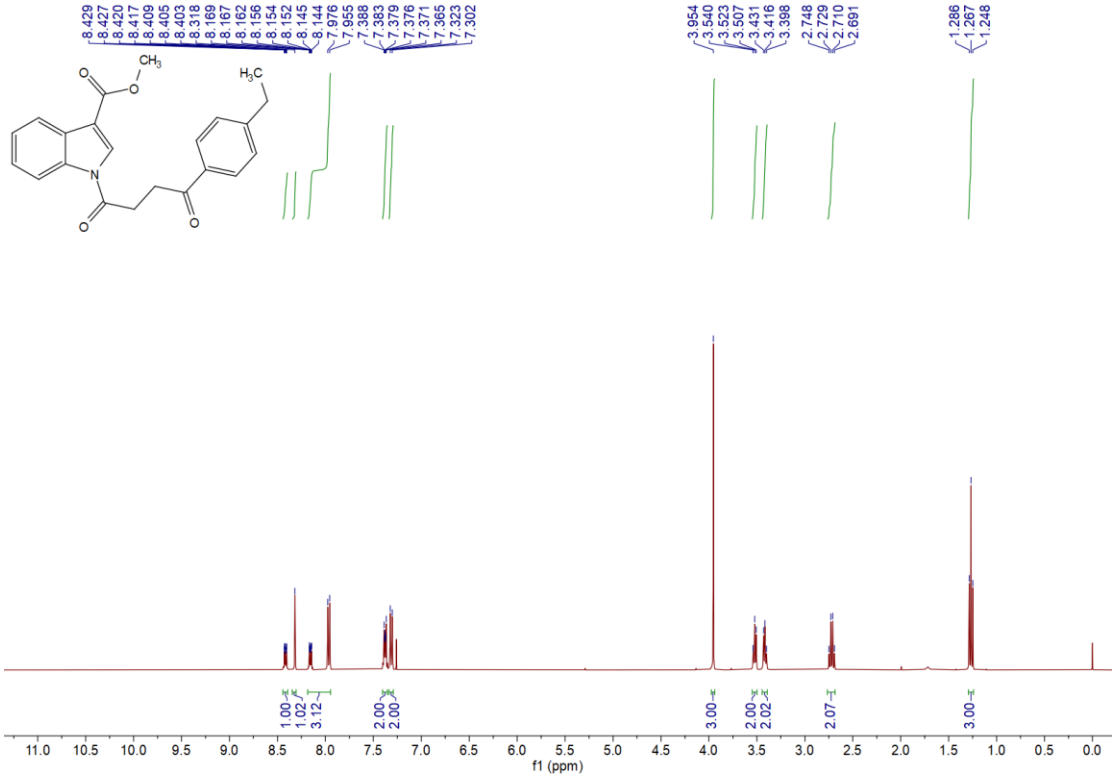
^{1}H NMR Spectrum of **1e**



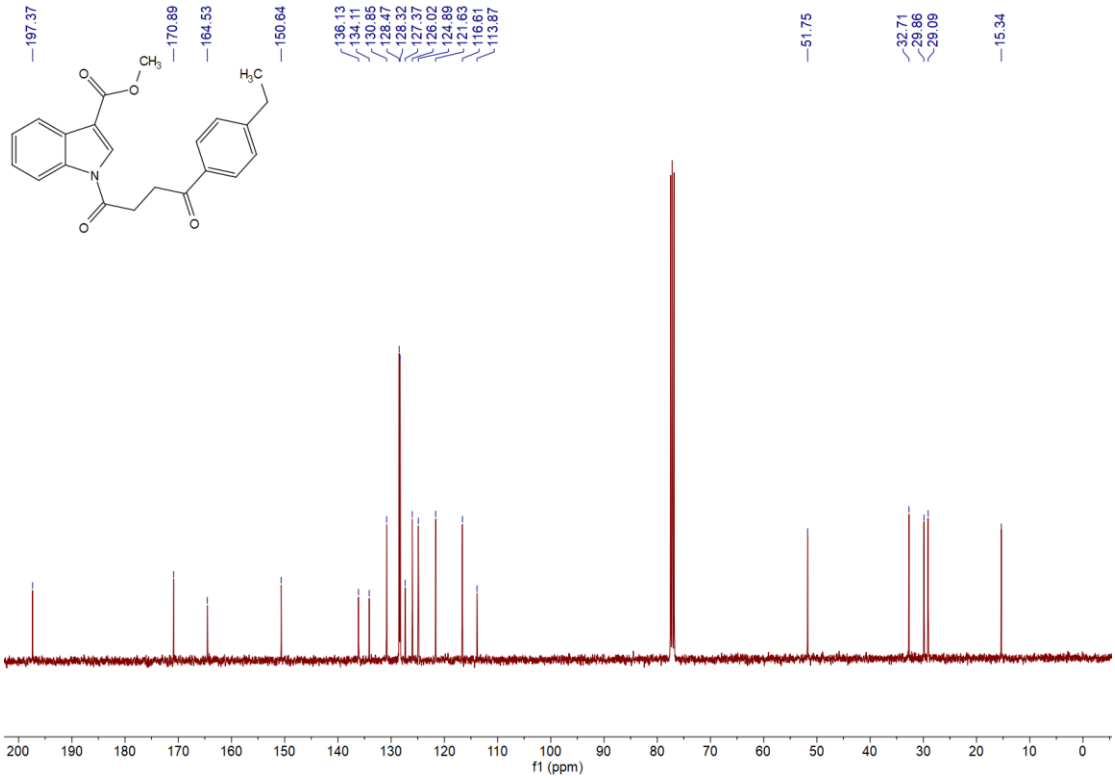
^{13}C NMR Spectrum of **1e**



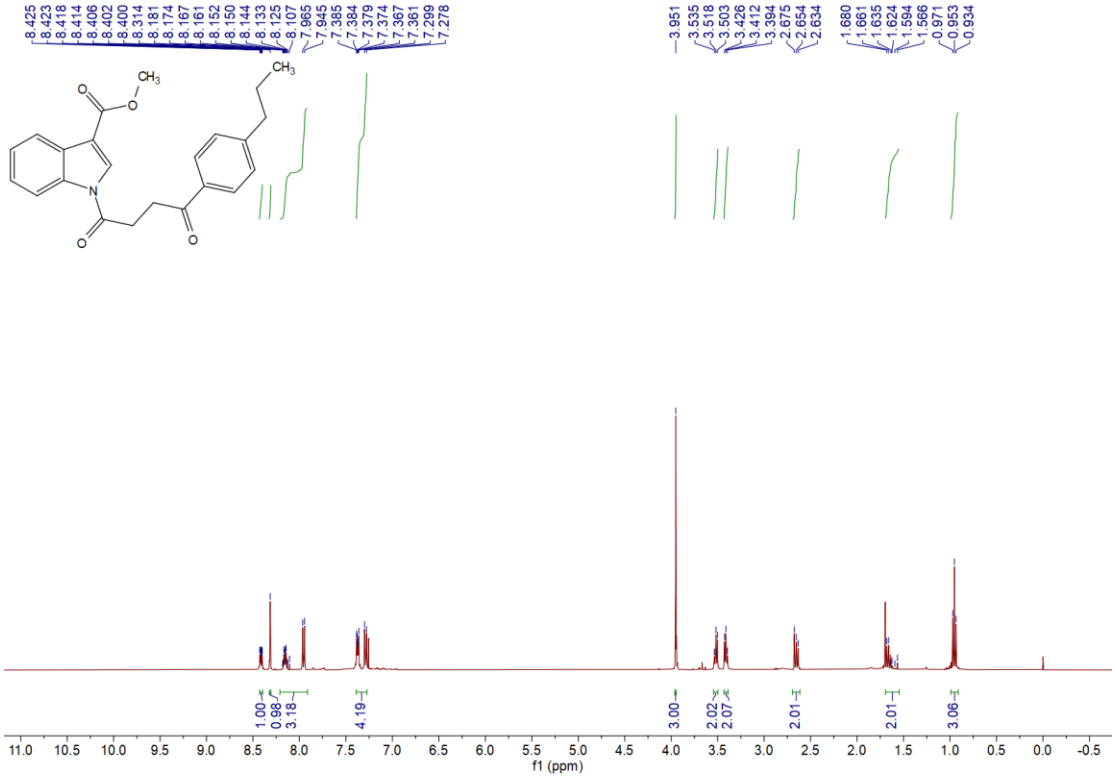
^{1}H NMR Spectrum of **1f**



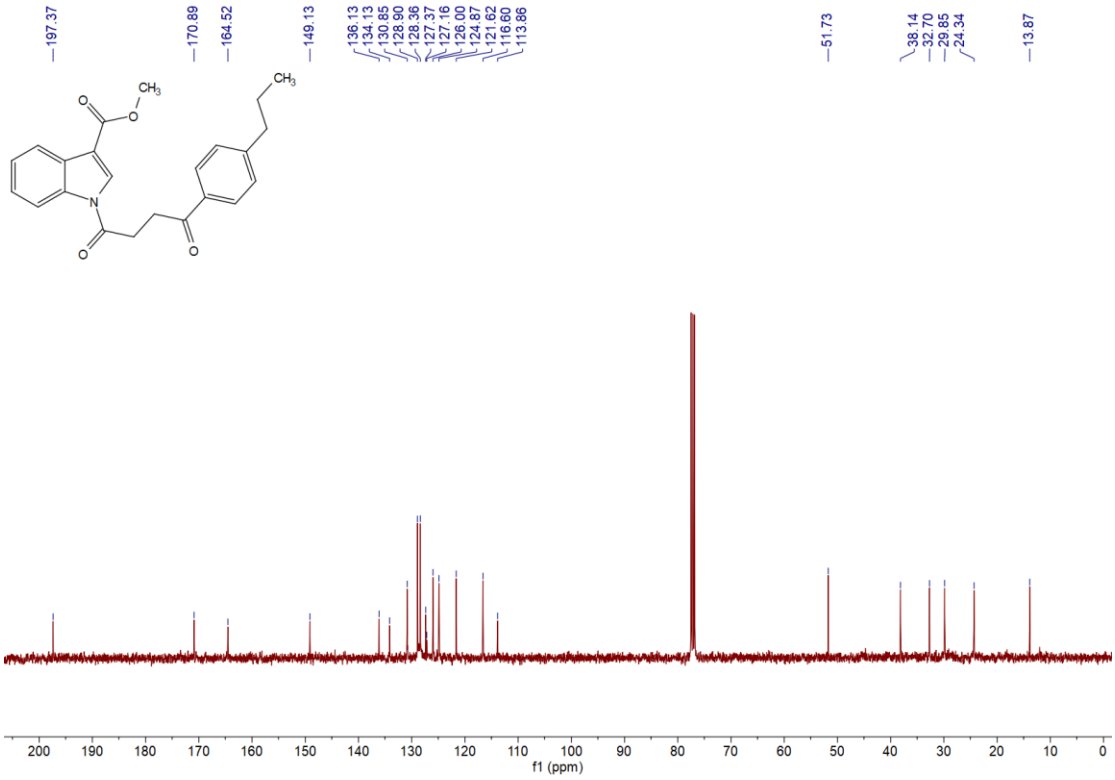
^{13}C NMR Spectrum of **1f**



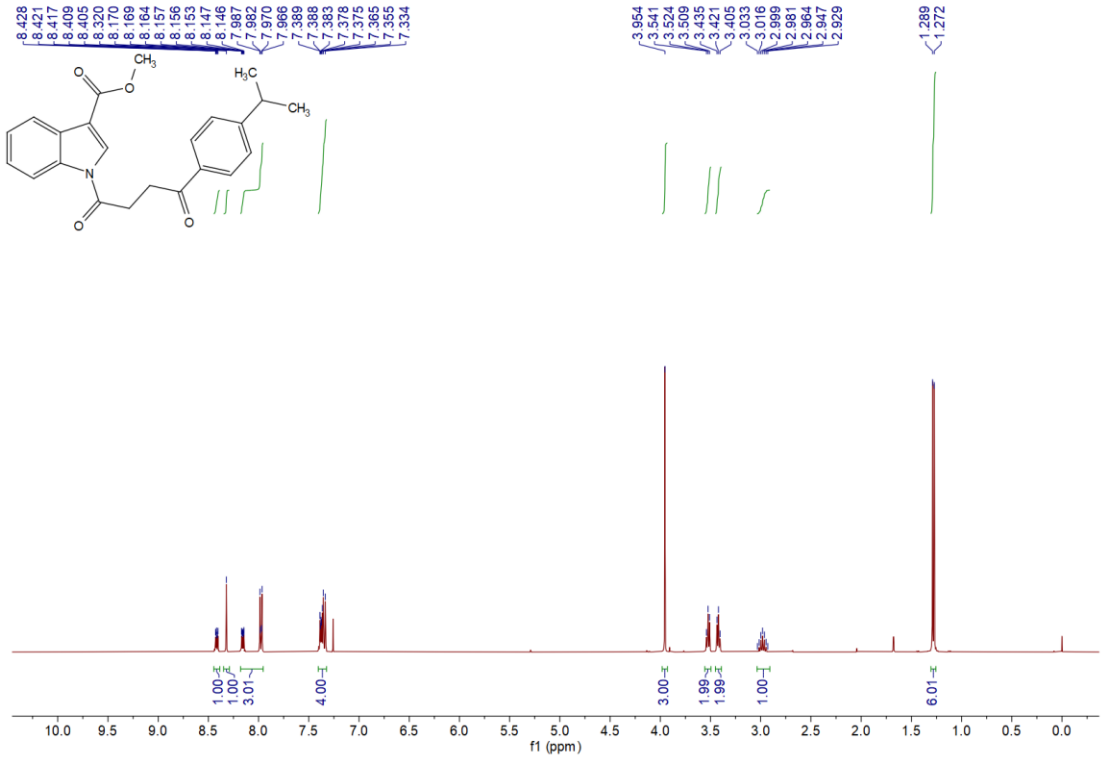
^{1}H NMR Spectrum of **1g**



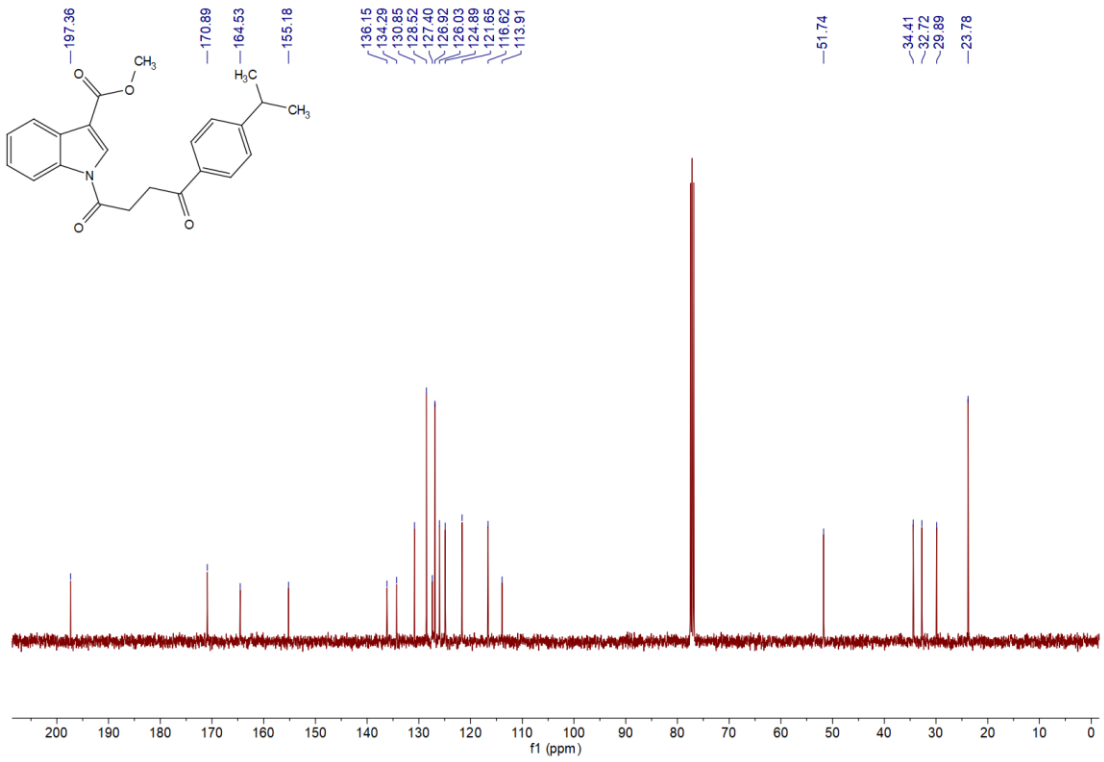
^{13}C NMR Spectrum of **1g**



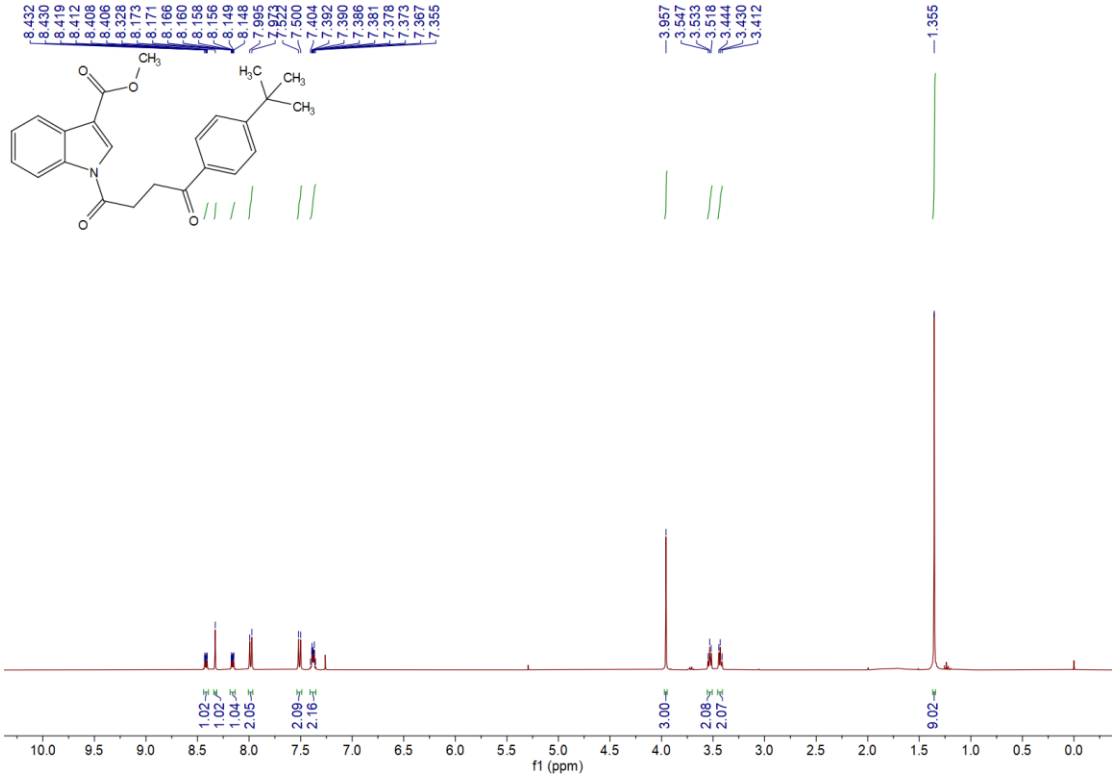
^{1}H NMR Spectrum of **1h**



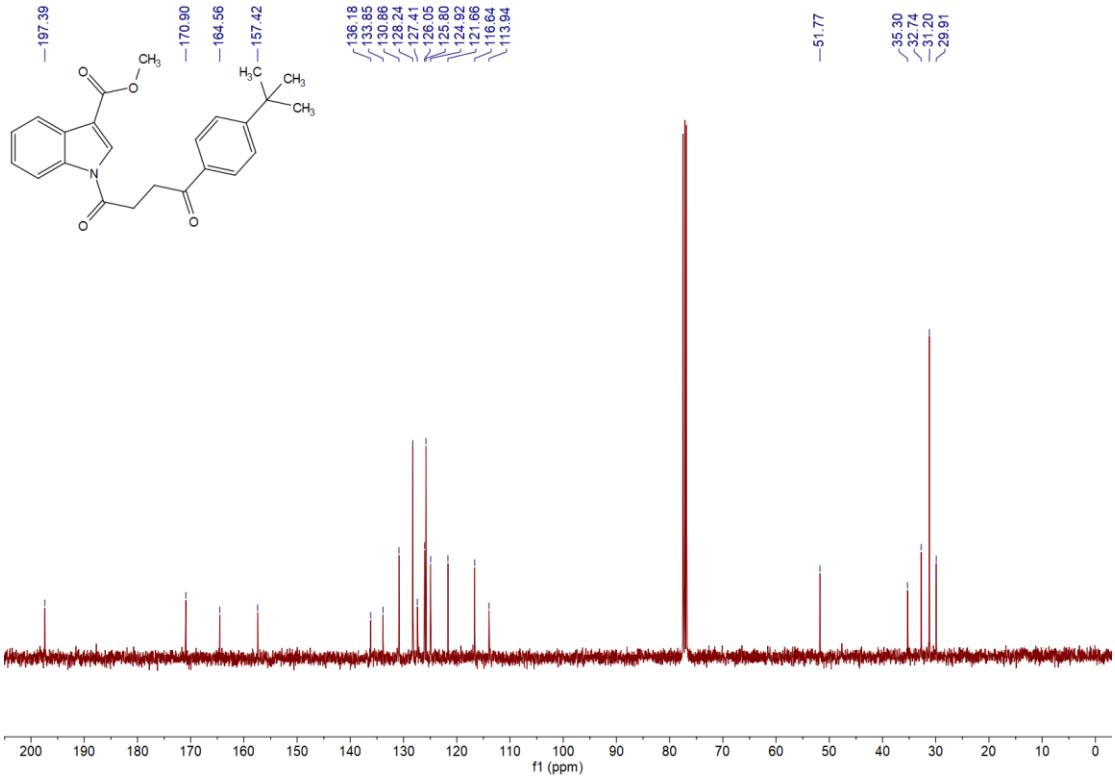
^{13}C NMR Spectrum of **1h**



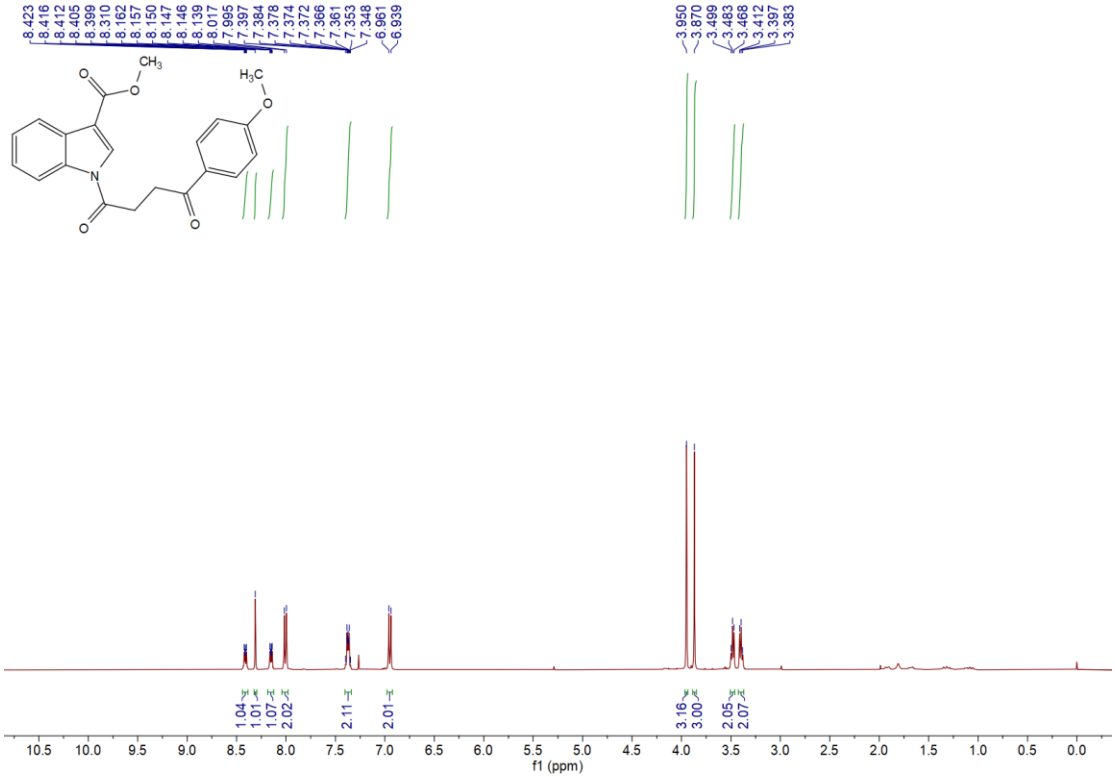
^{1}H NMR Spectrum of **1i**



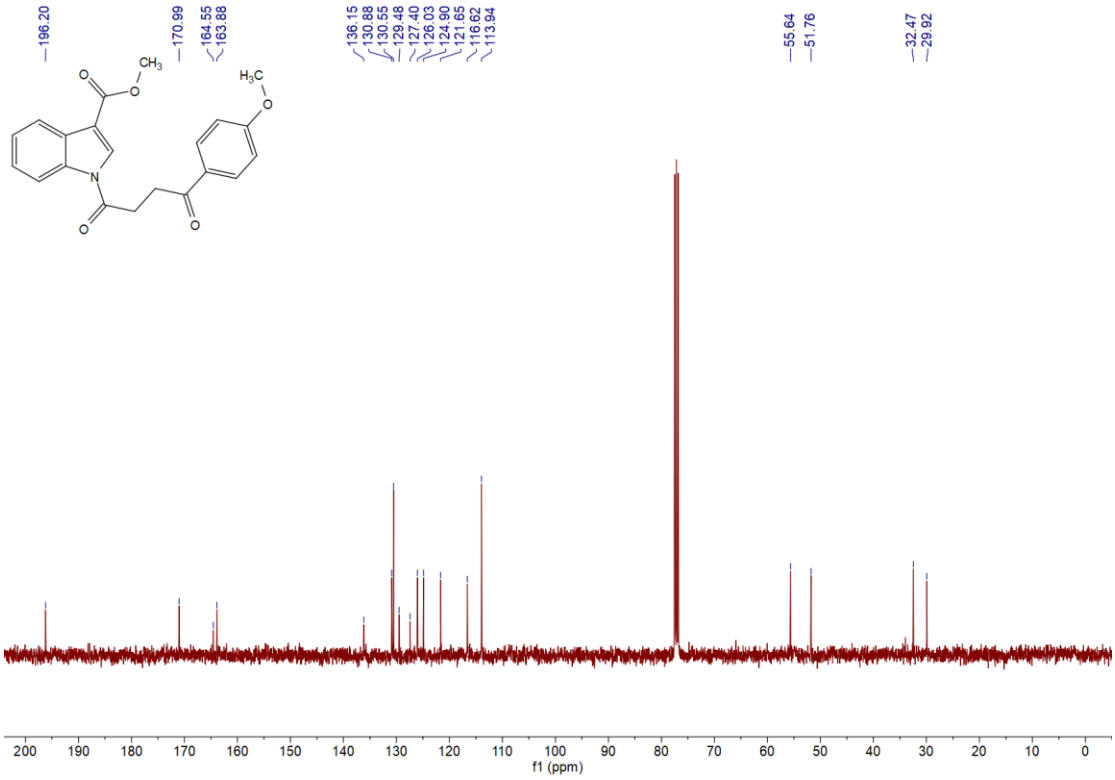
^{13}C NMR Spectrum of **1i**



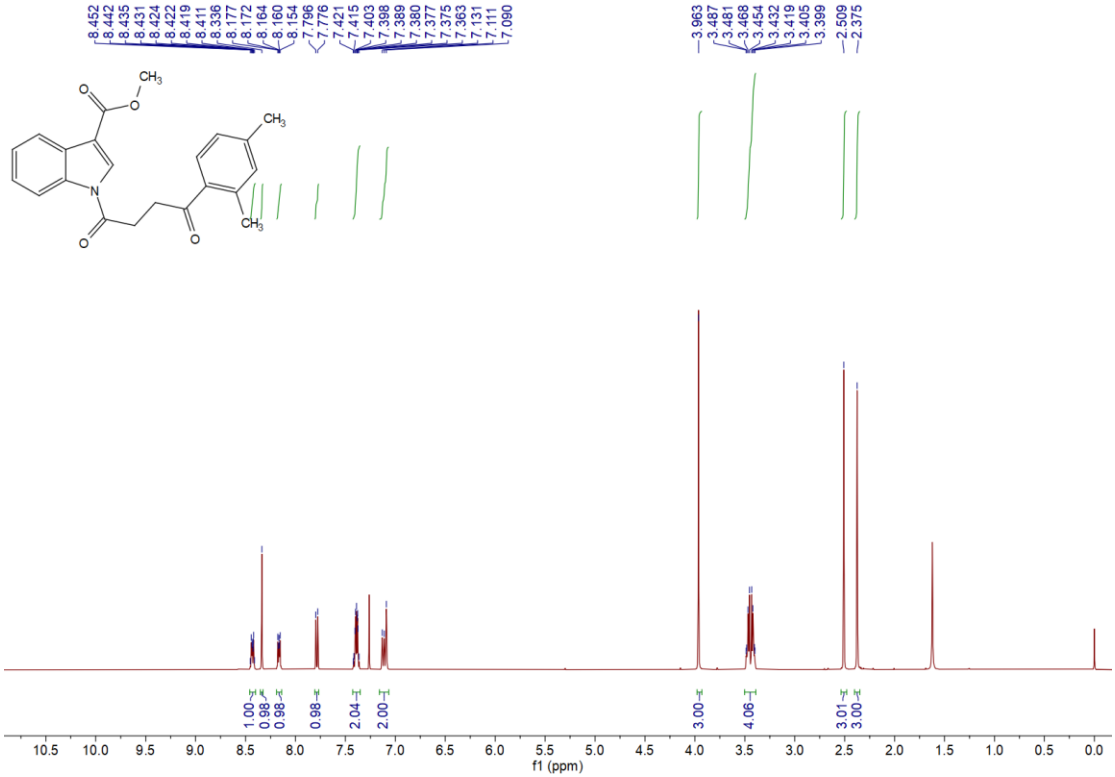
^{1}H NMR Spectrum of **1j**



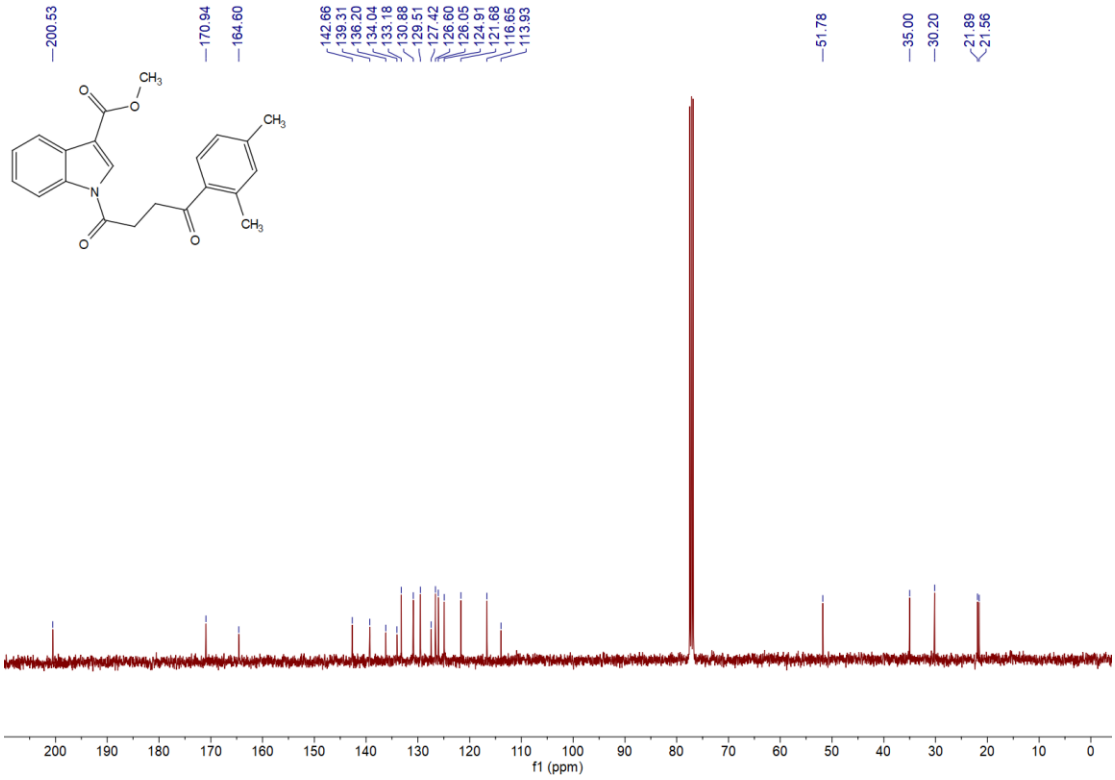
^{13}C NMR Spectrum of **1j**



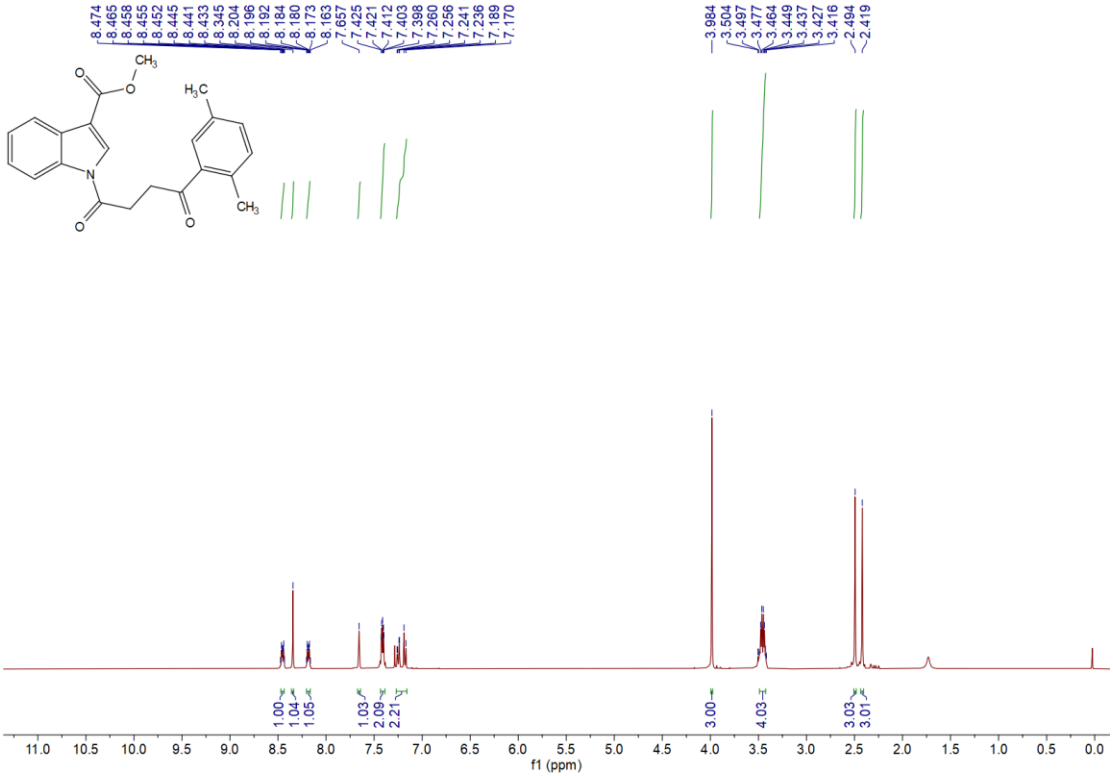
^{1}H NMR Spectrum of **1k**



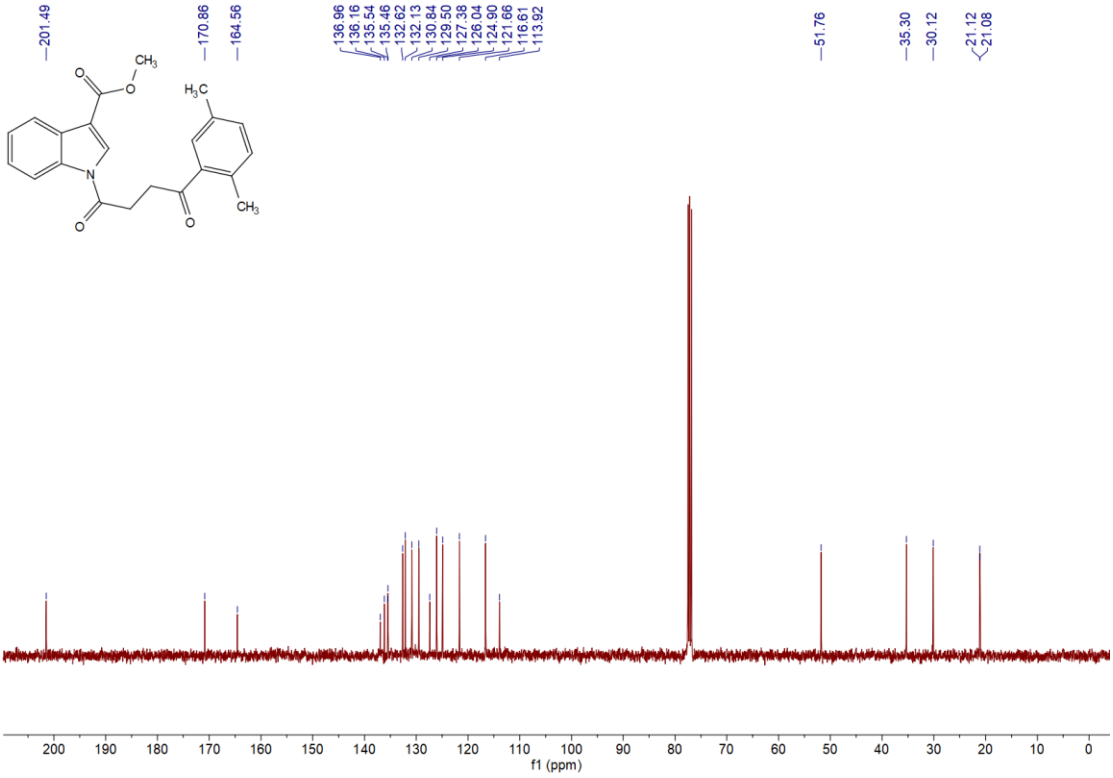
^{13}C NMR Spectrum of **1k**



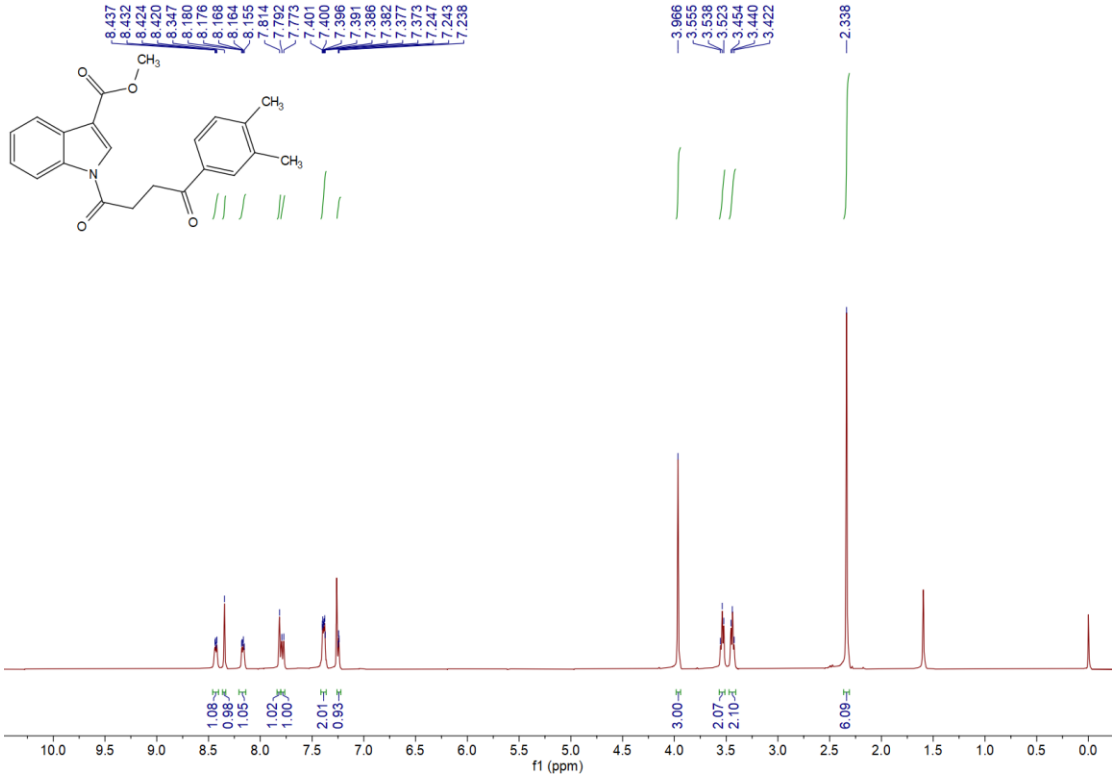
^{1}H NMR Spectrum of **1l**



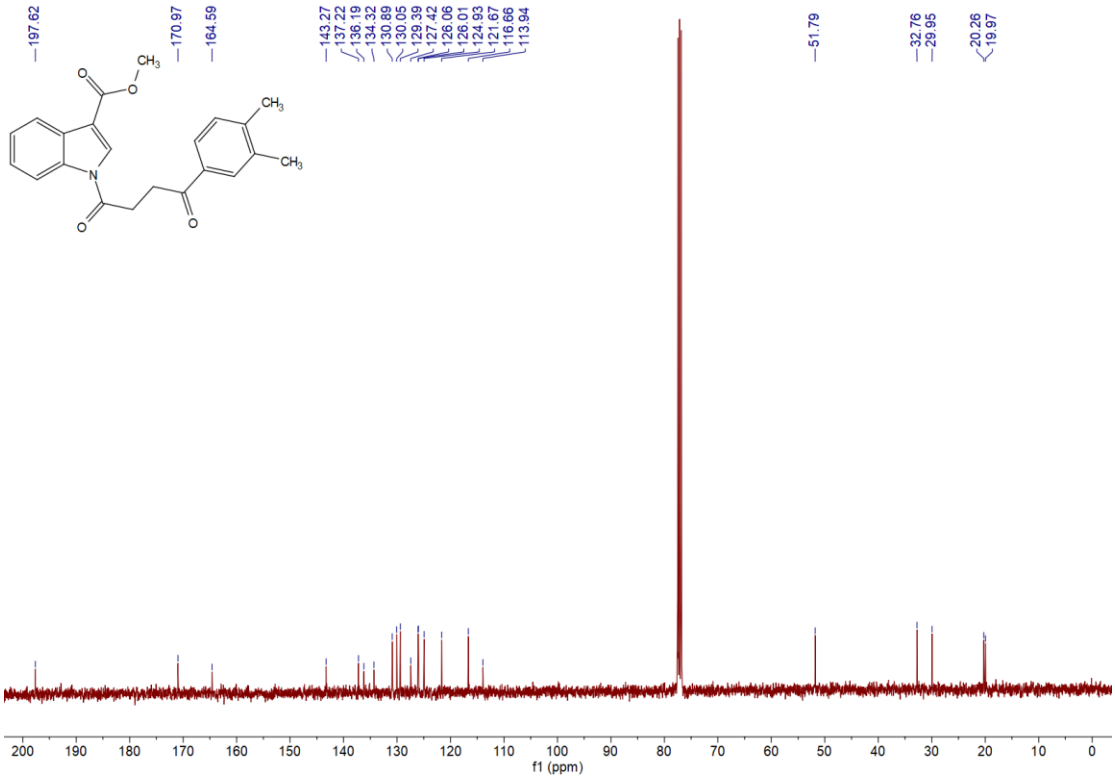
^{13}C NMR Spectrum of **1l**



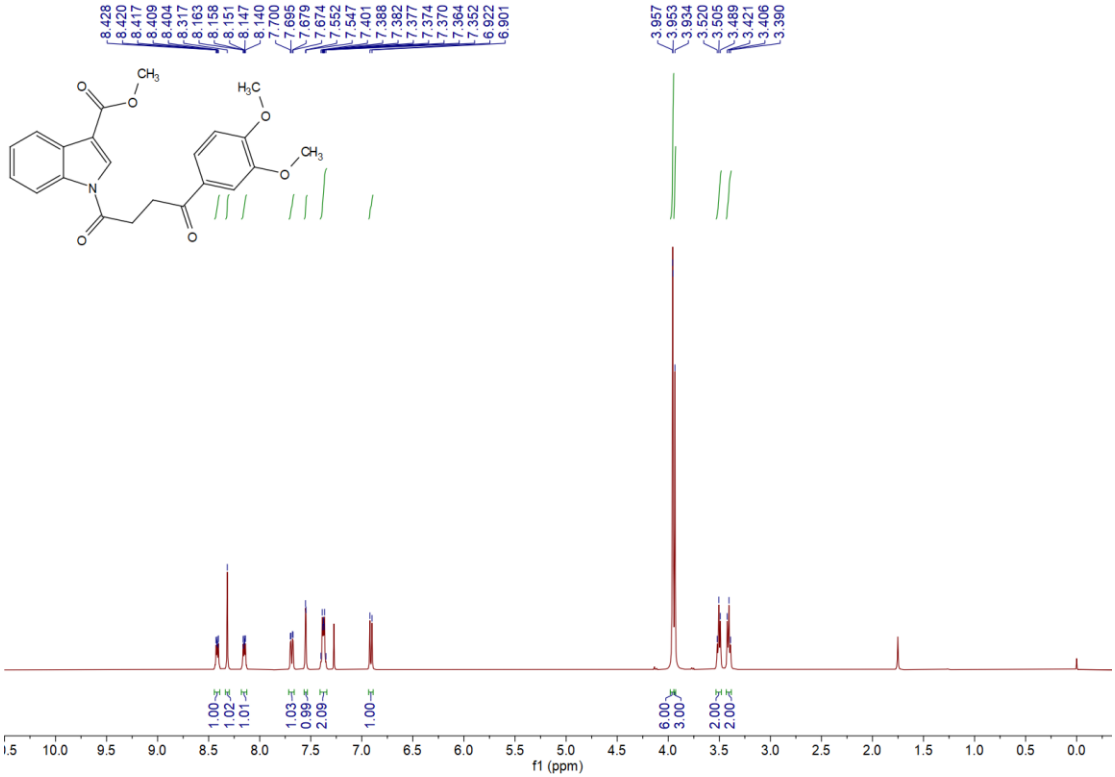
^{1}H NMR Spectrum of **1m**



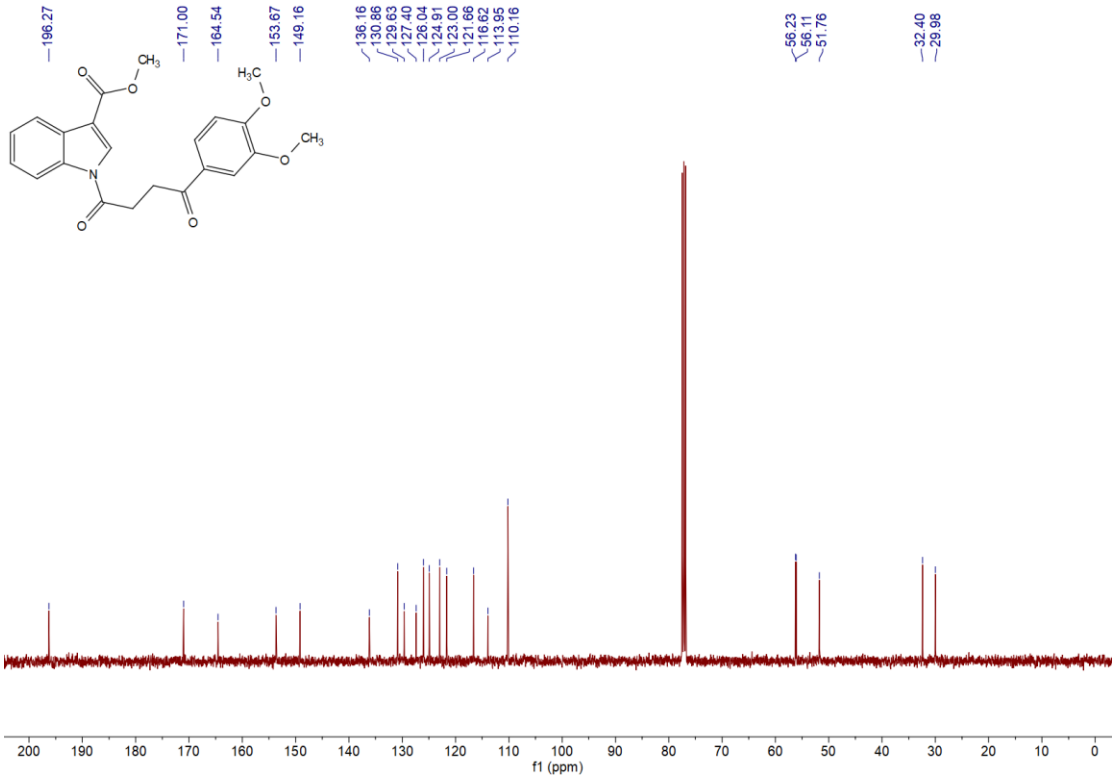
^{13}C NMR Spectrum of **1m**



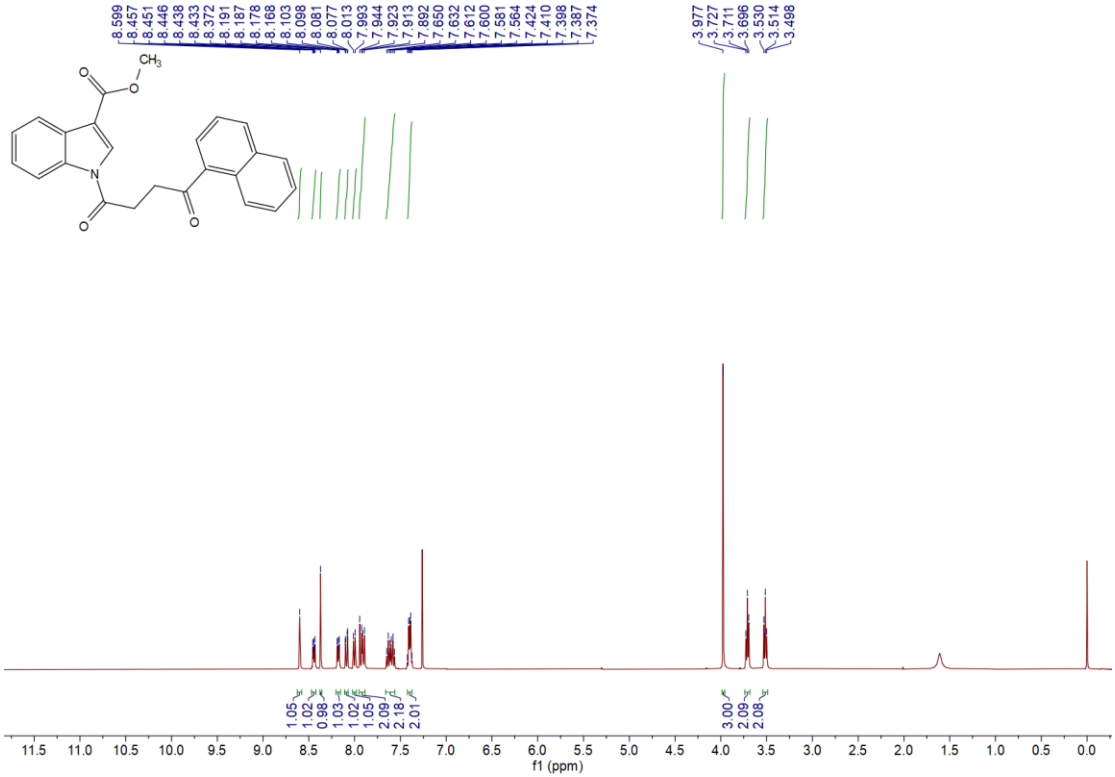
^{1}H NMR Spectrum of **1n**



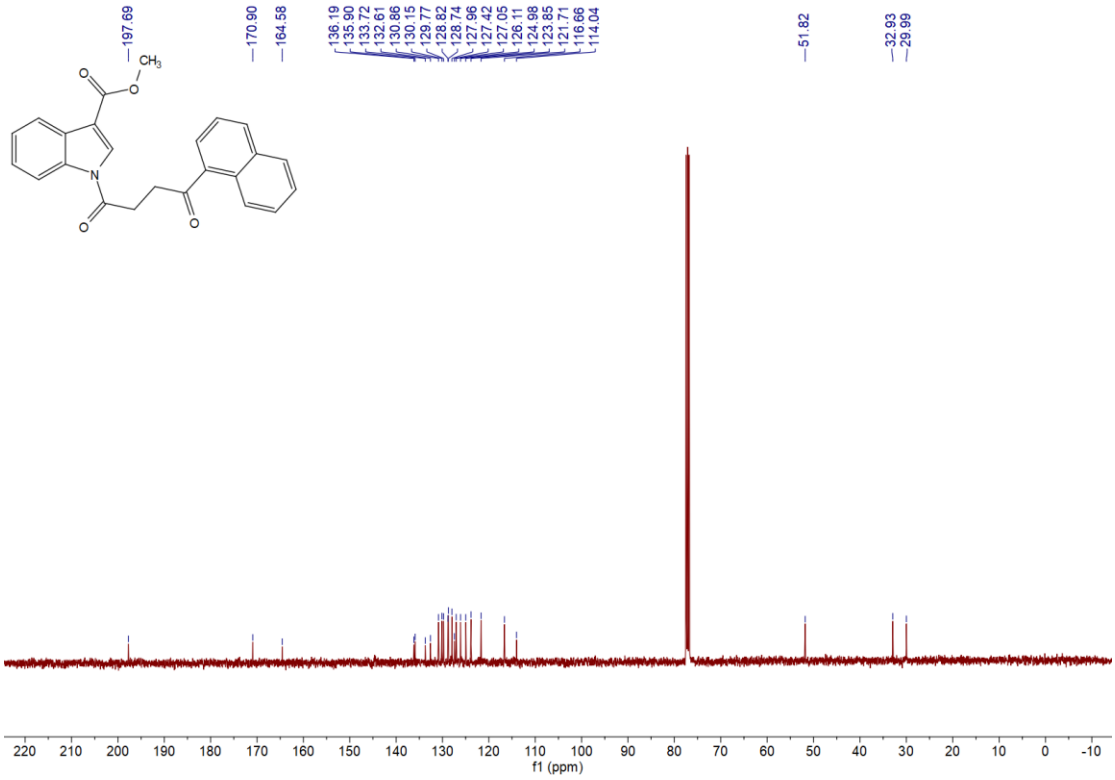
^{13}C NMR Spectrum of **1n**



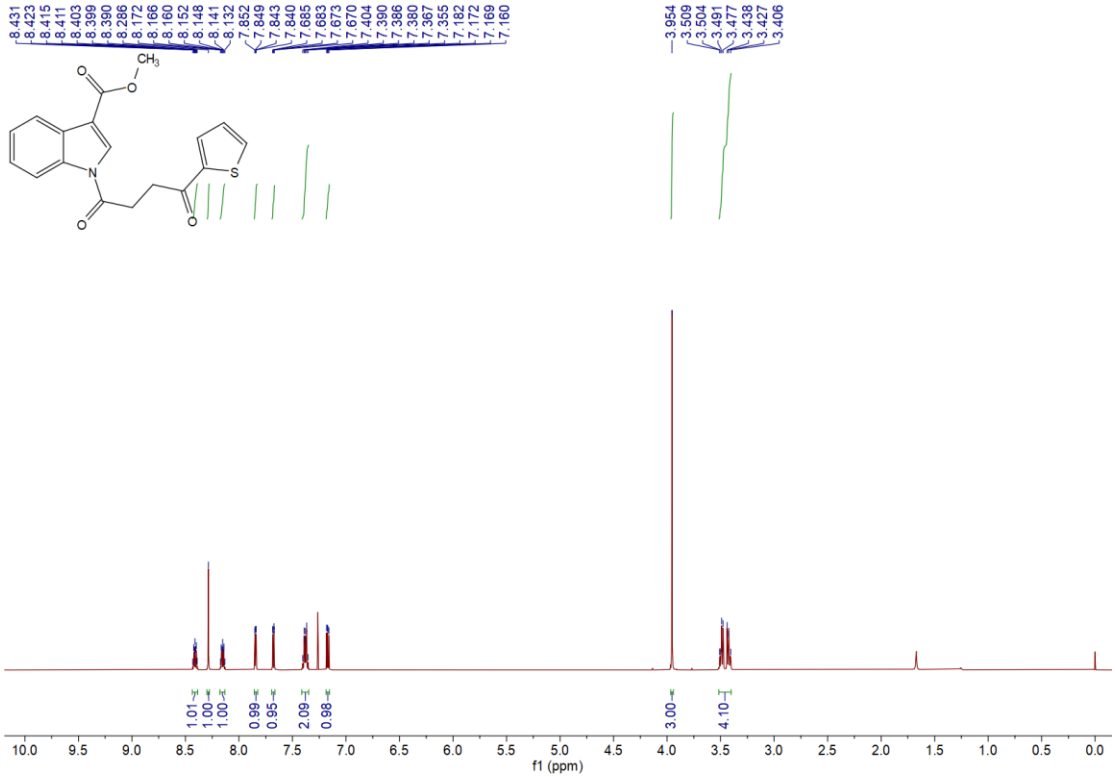
^{1}H NMR Spectrum of **1o**



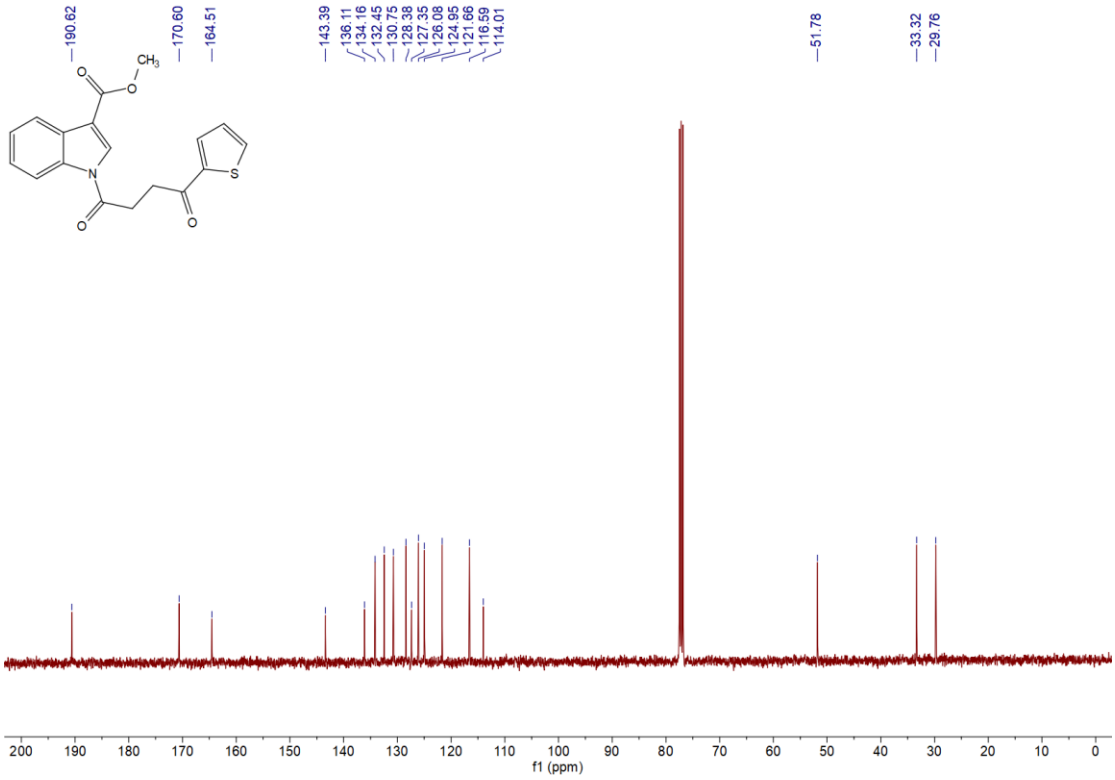
^{13}C NMR Spectrum of **1o**



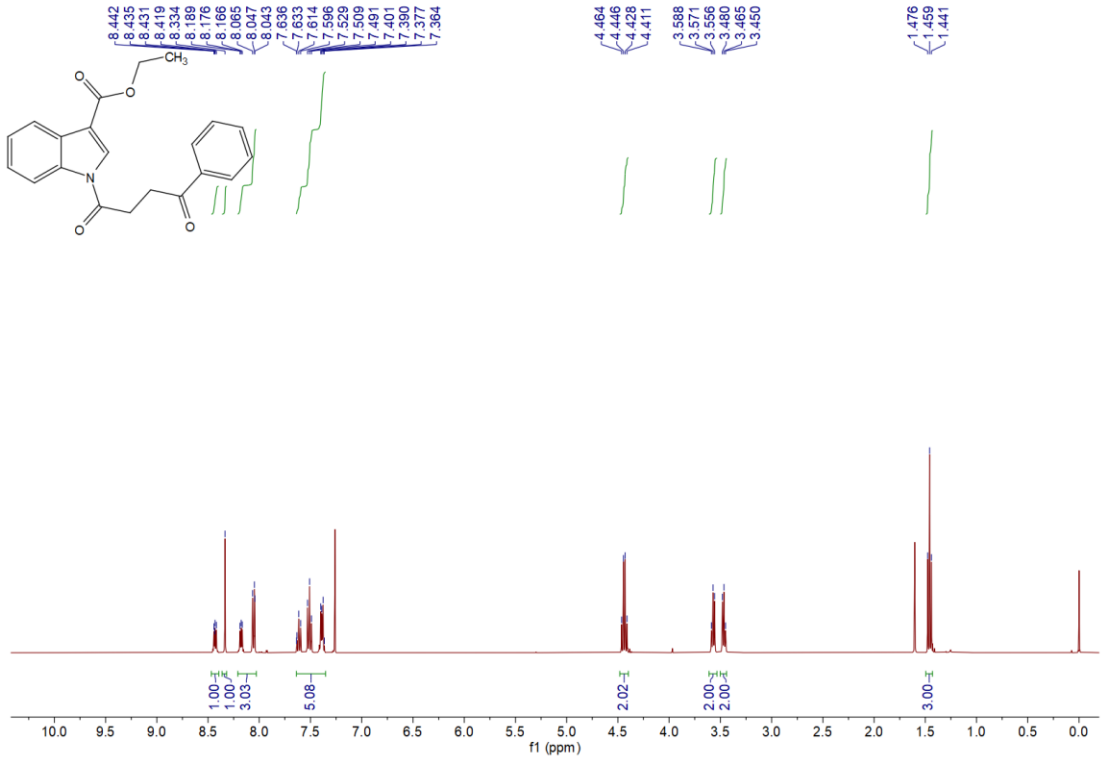
^{1}H NMR Spectrum of **1p**



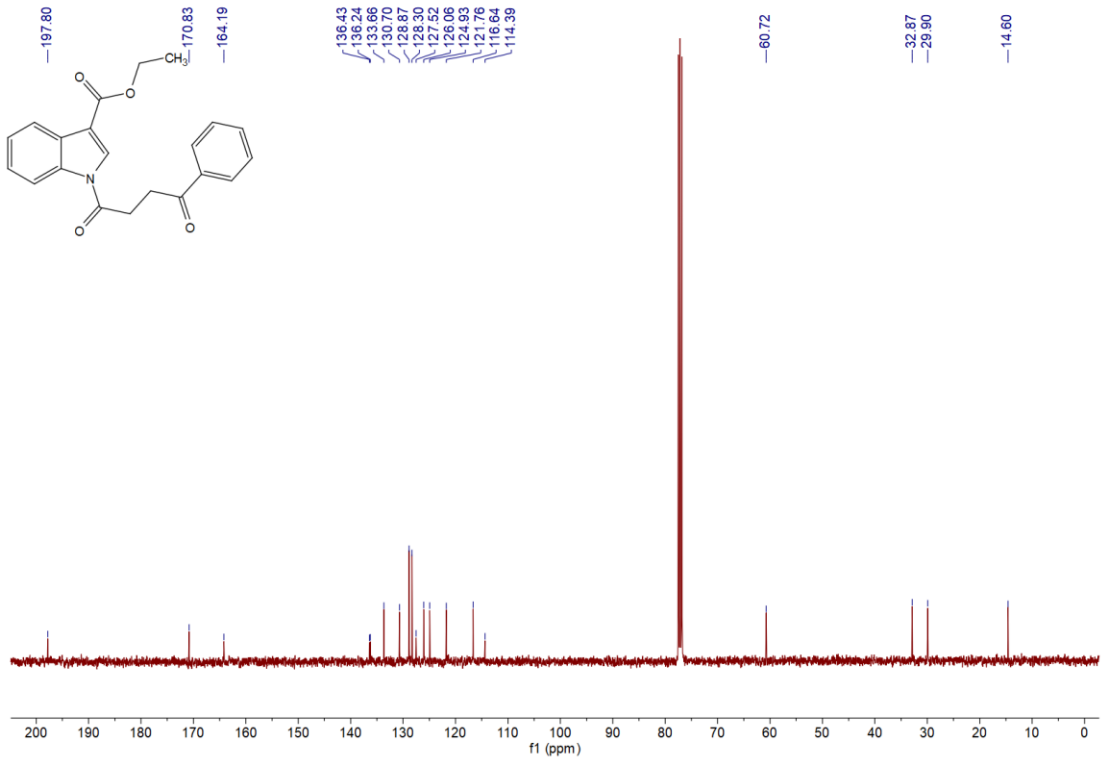
^{13}C NMR Spectrum of **1p**



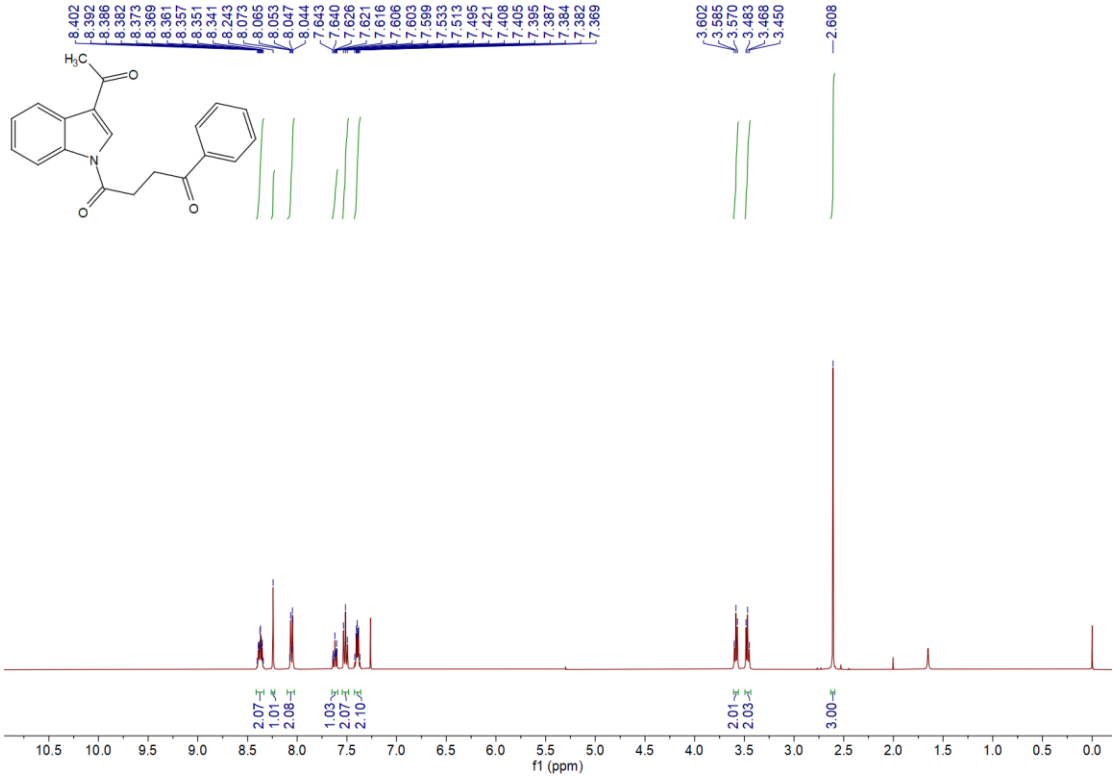
^{1}H NMR Spectrum of **1q**



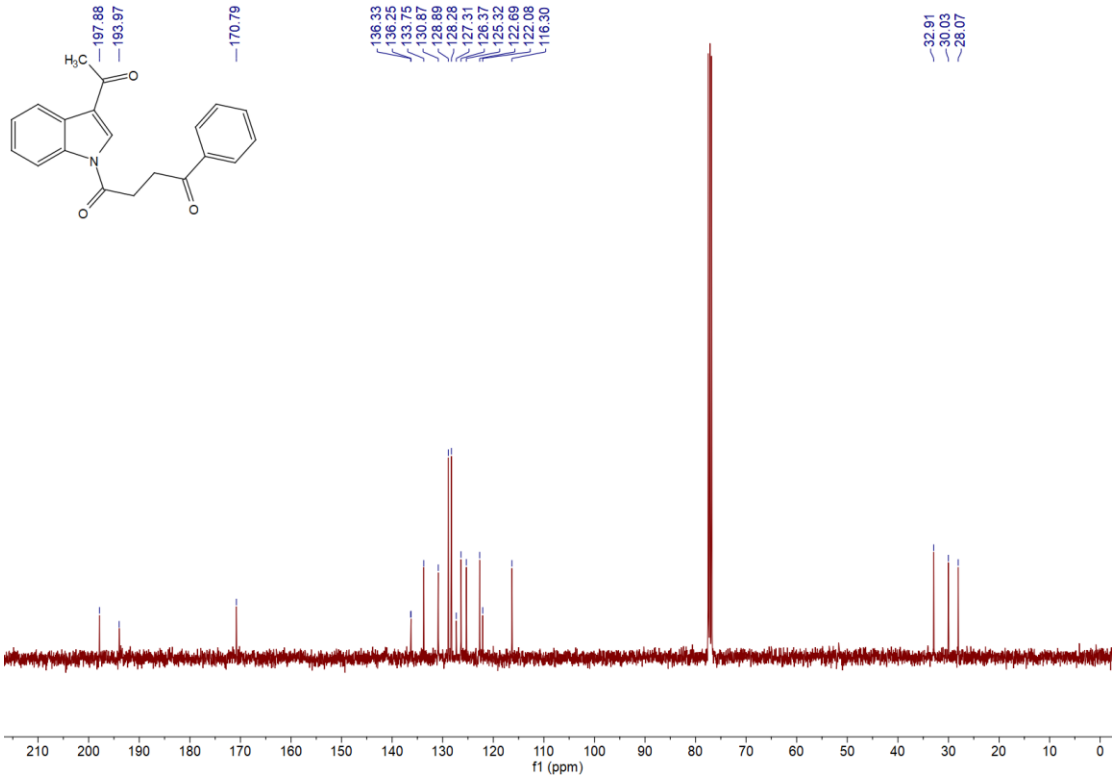
^{13}C NMR Spectrum of **1q**



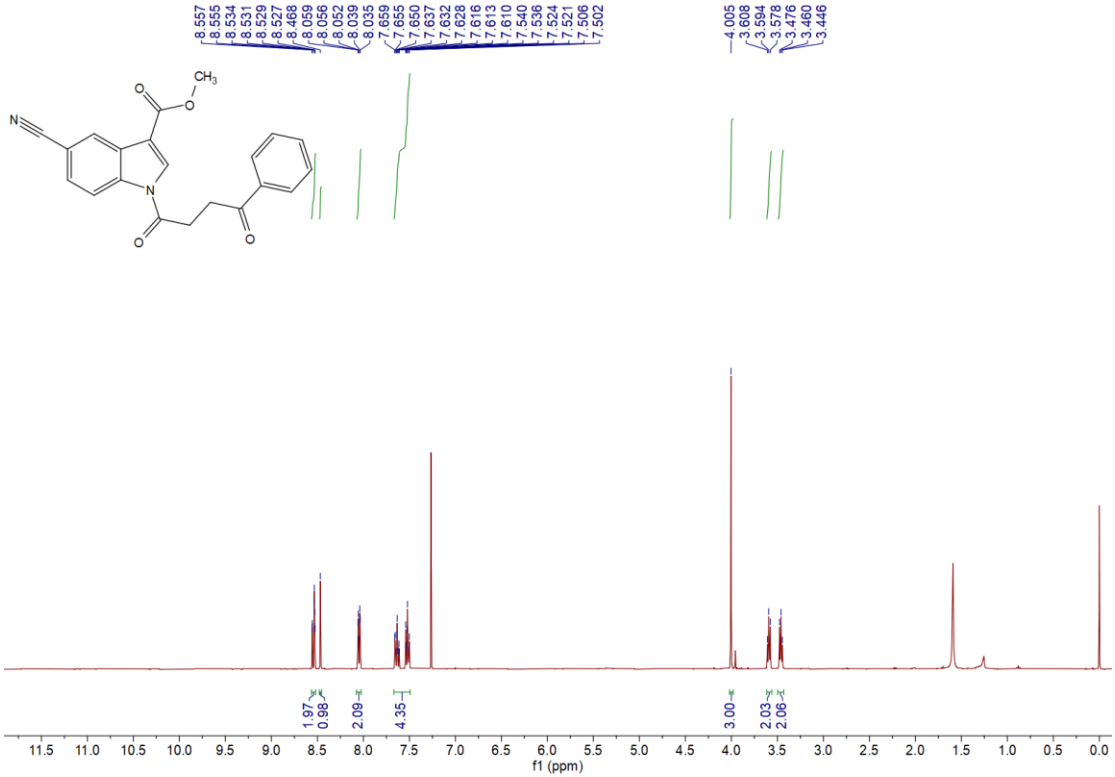
^{1}H NMR Spectrum of **1r**



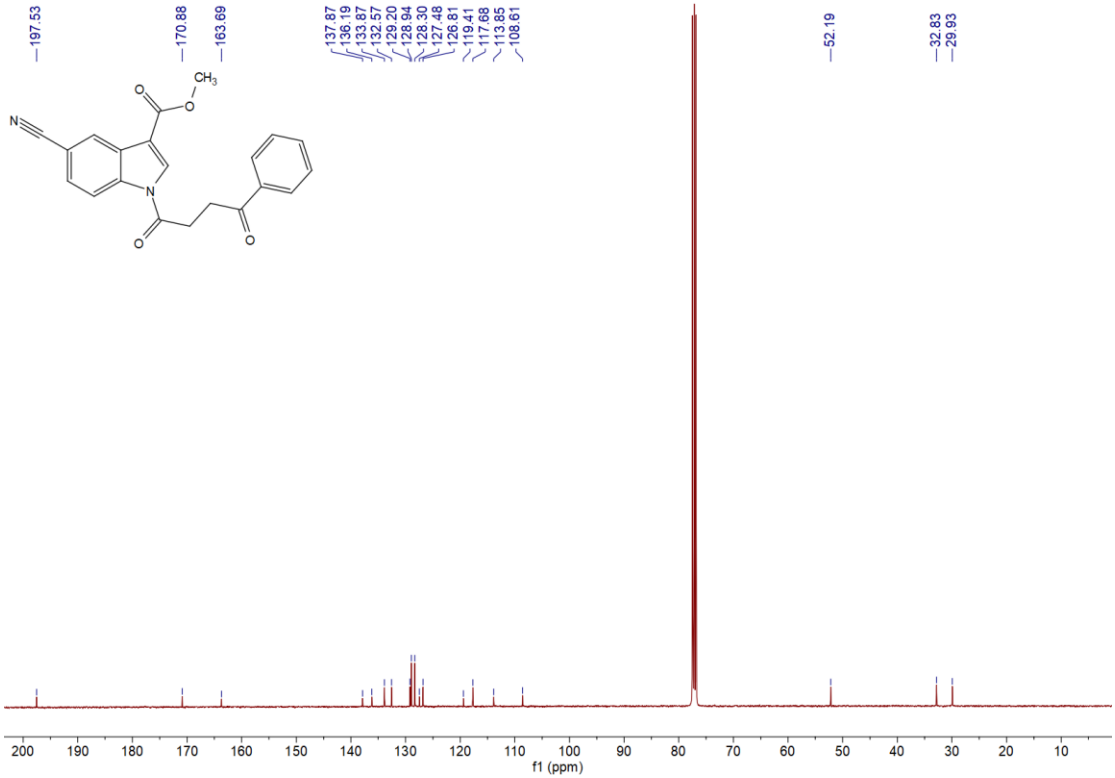
^{13}C NMR Spectrum of **1r**



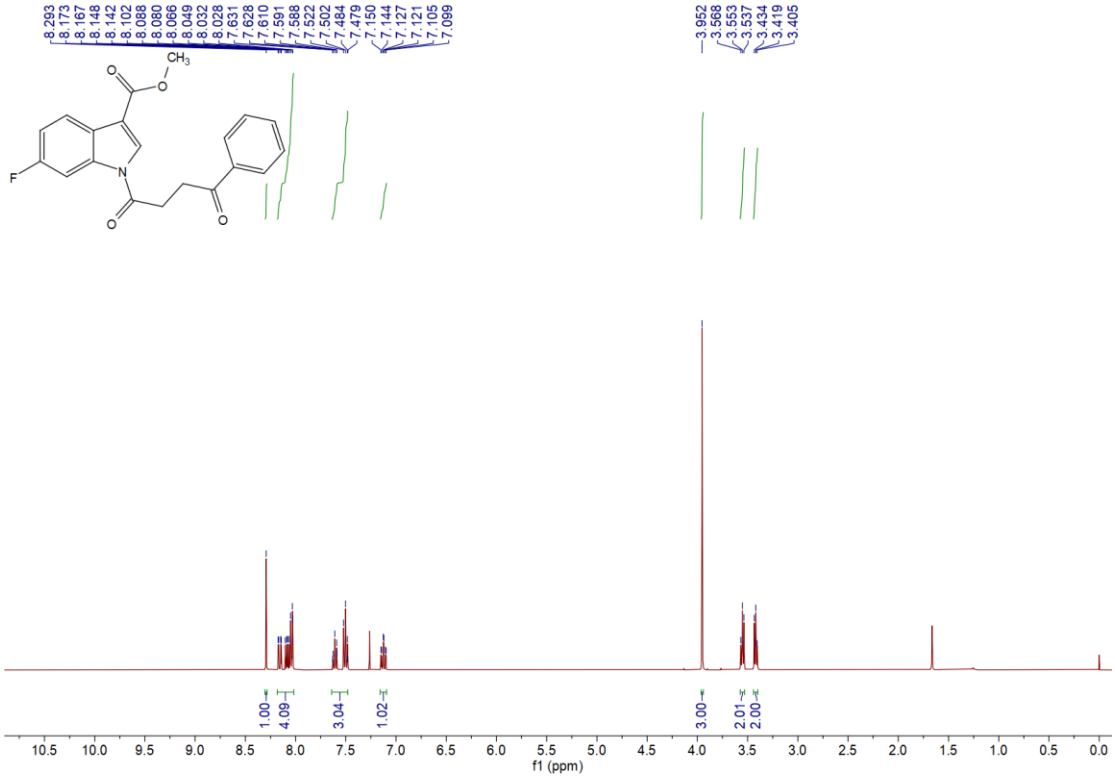
^{1}H NMR Spectrum of **1s**



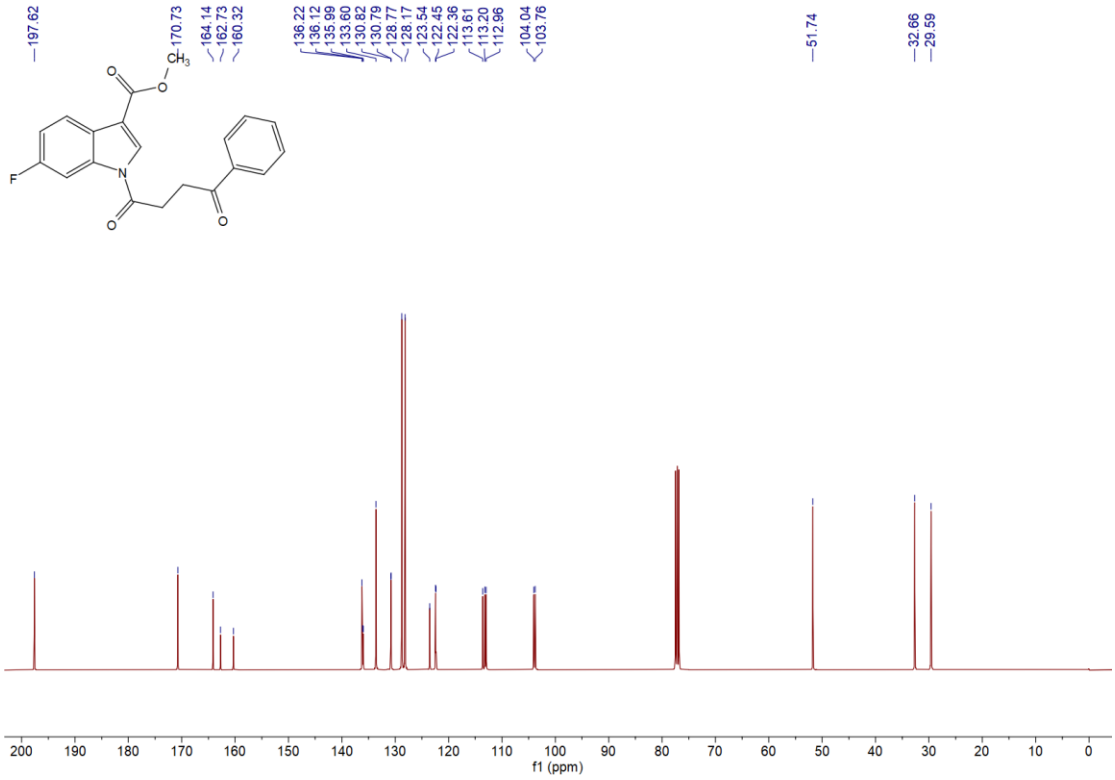
^{13}C NMR Spectrum of **1s**



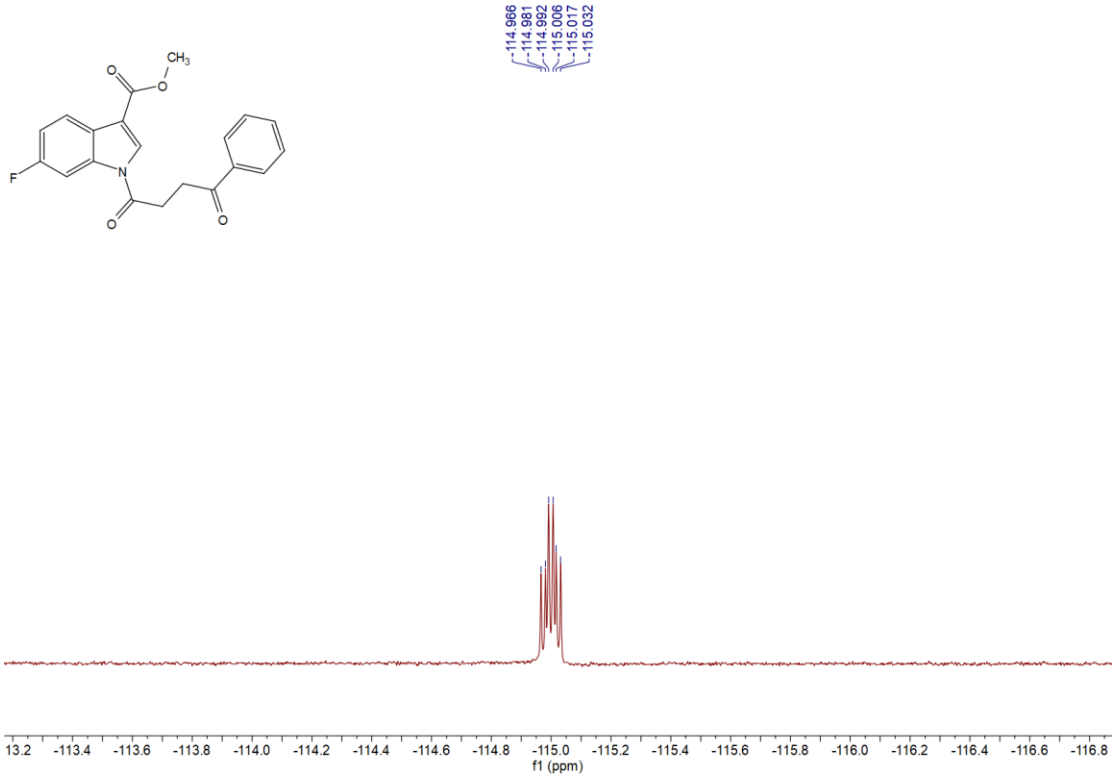
^{1}H NMR Spectrum of **1t**



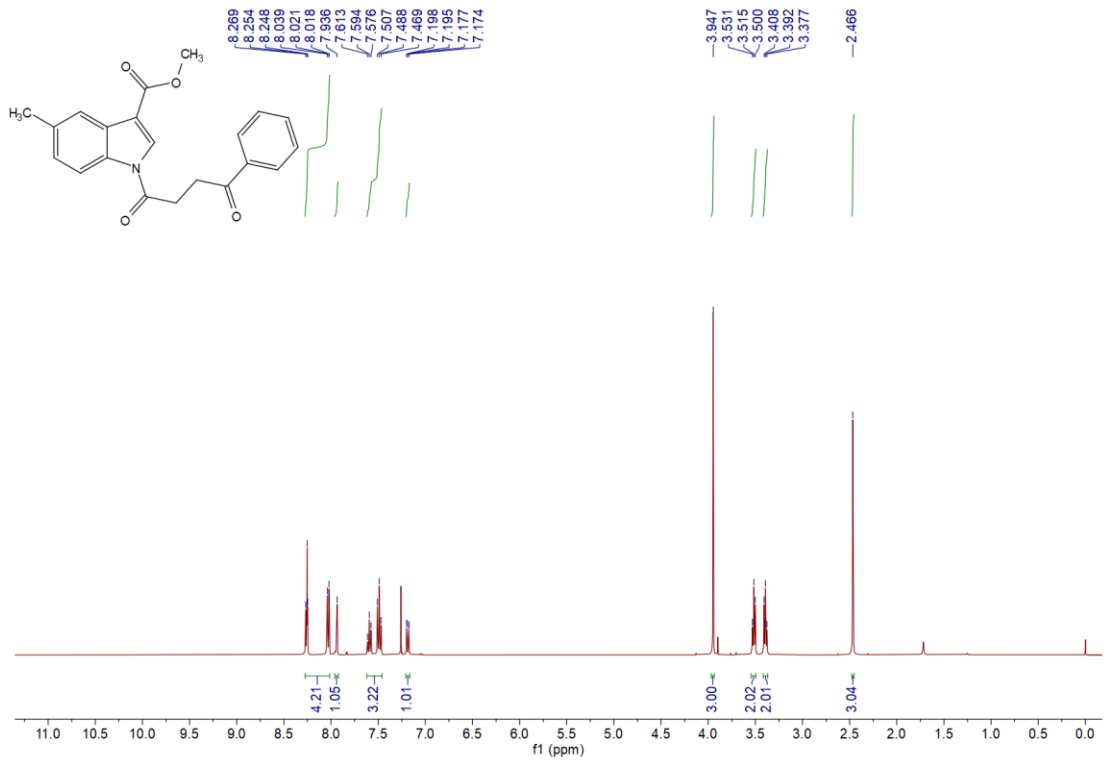
^{13}C NMR Spectrum of **1t**



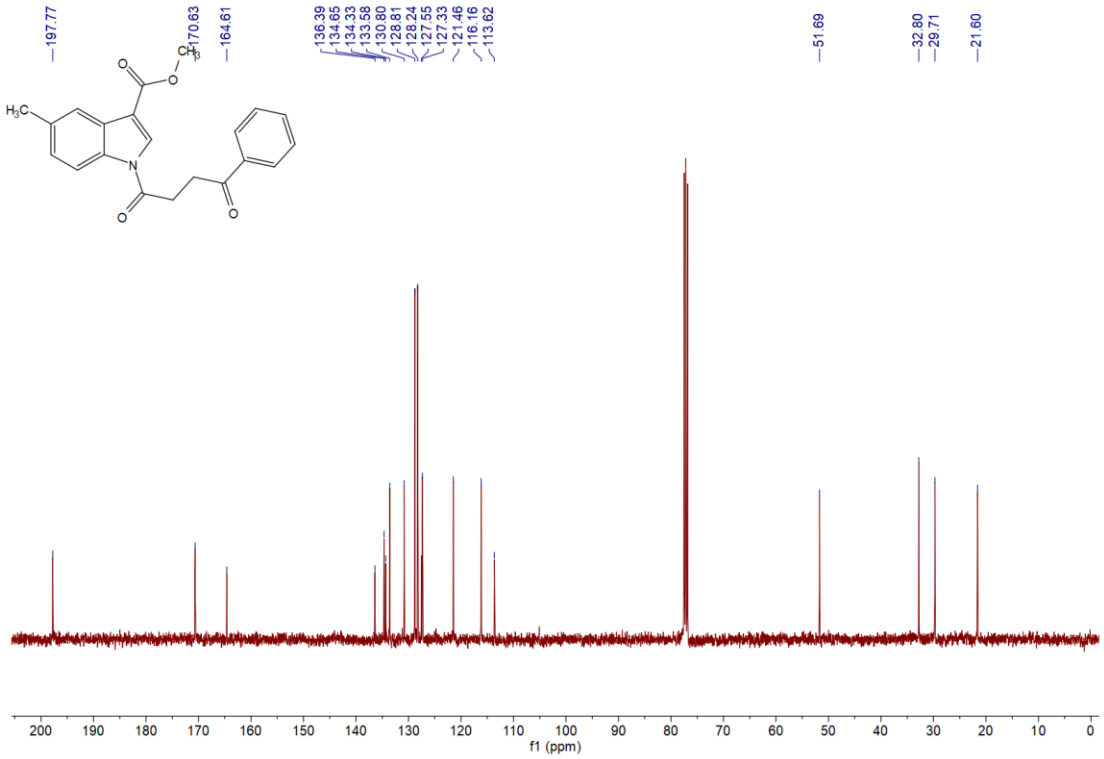
^{19}F NMR Spectrum of **1t**



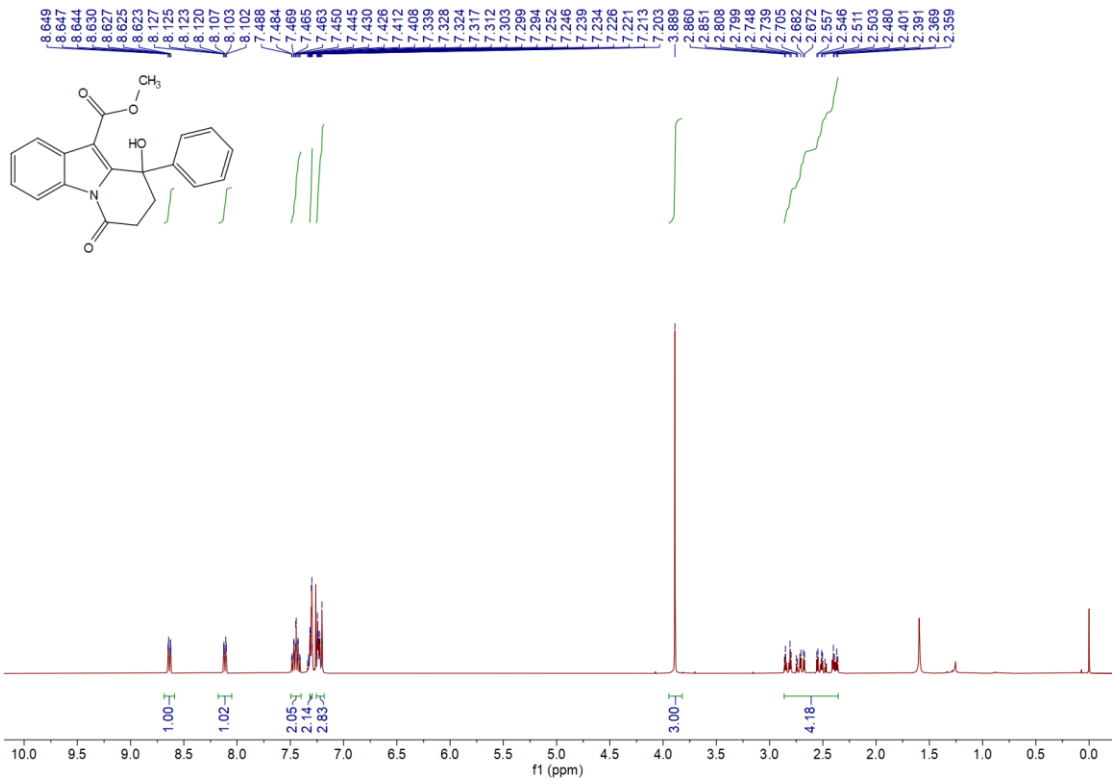
^{1}H NMR Spectrum of **1u**



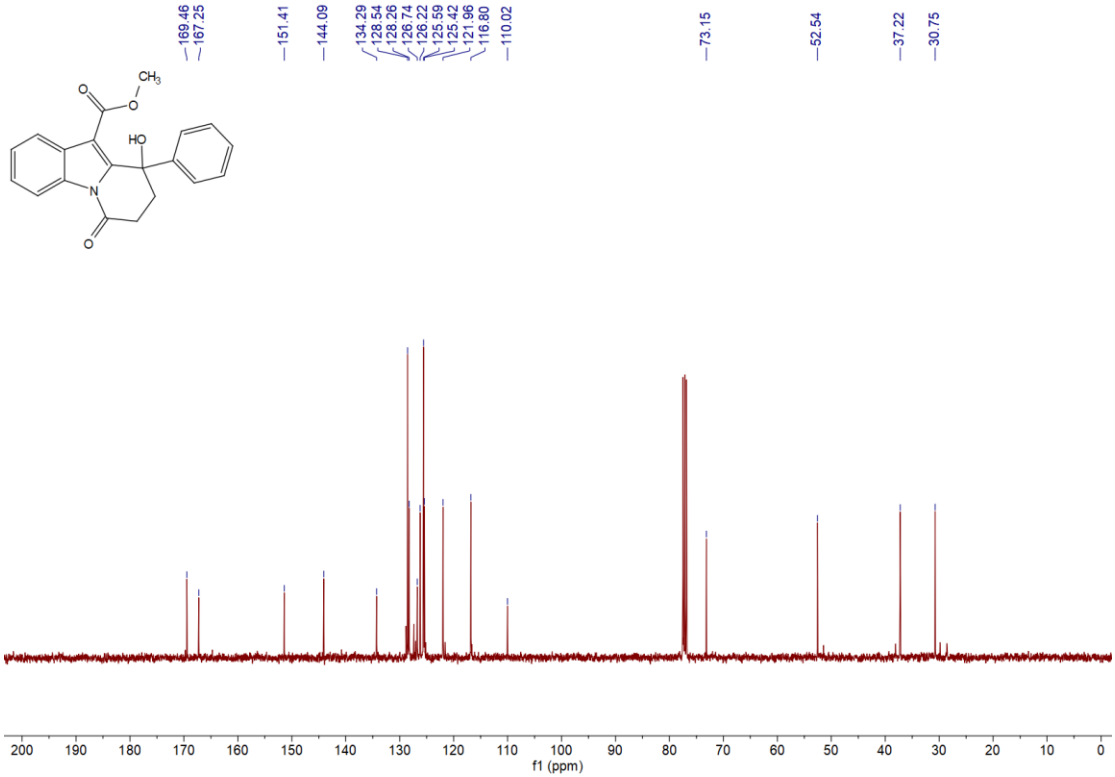
^{13}C NMR Spectrum of **1u**



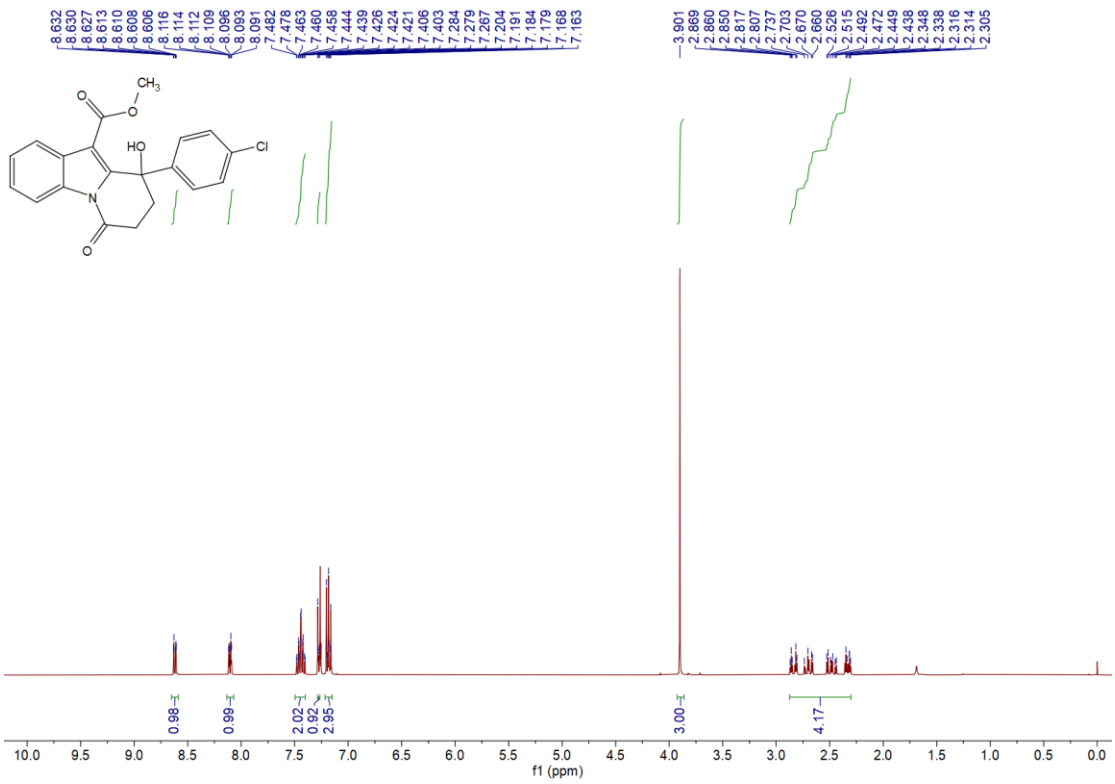
^{1}H NMR Spectrum of **2a**



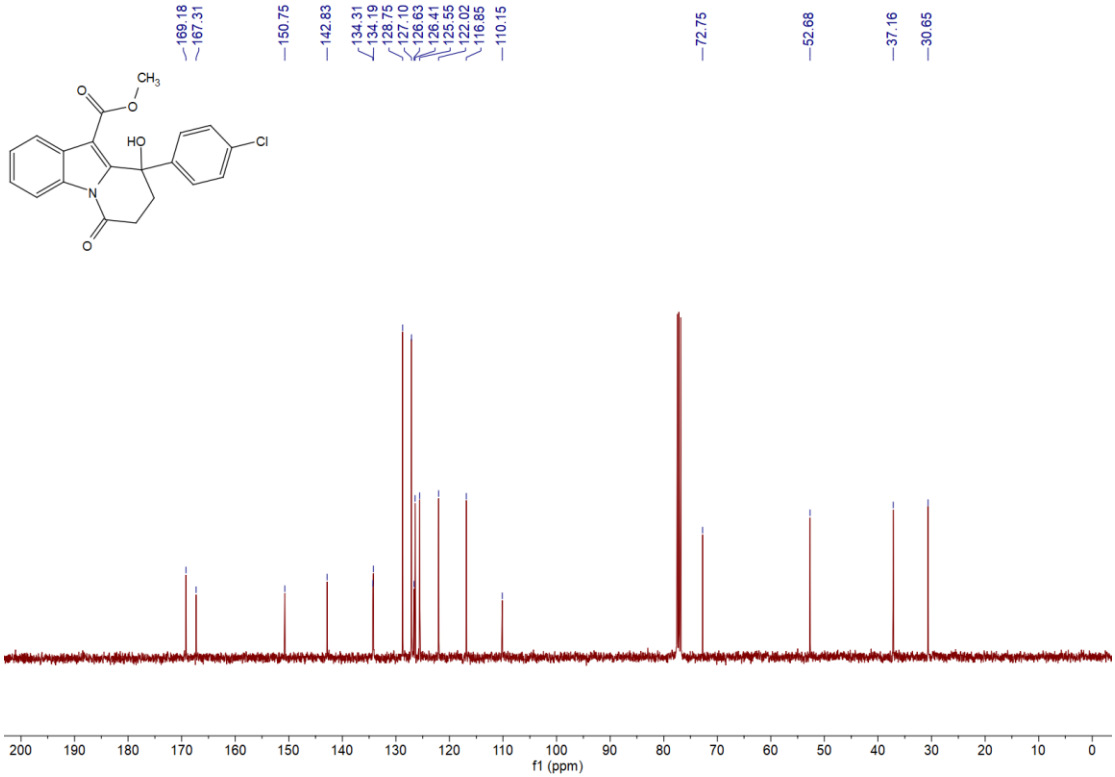
^{13}C NMR Spectrum of **2a**



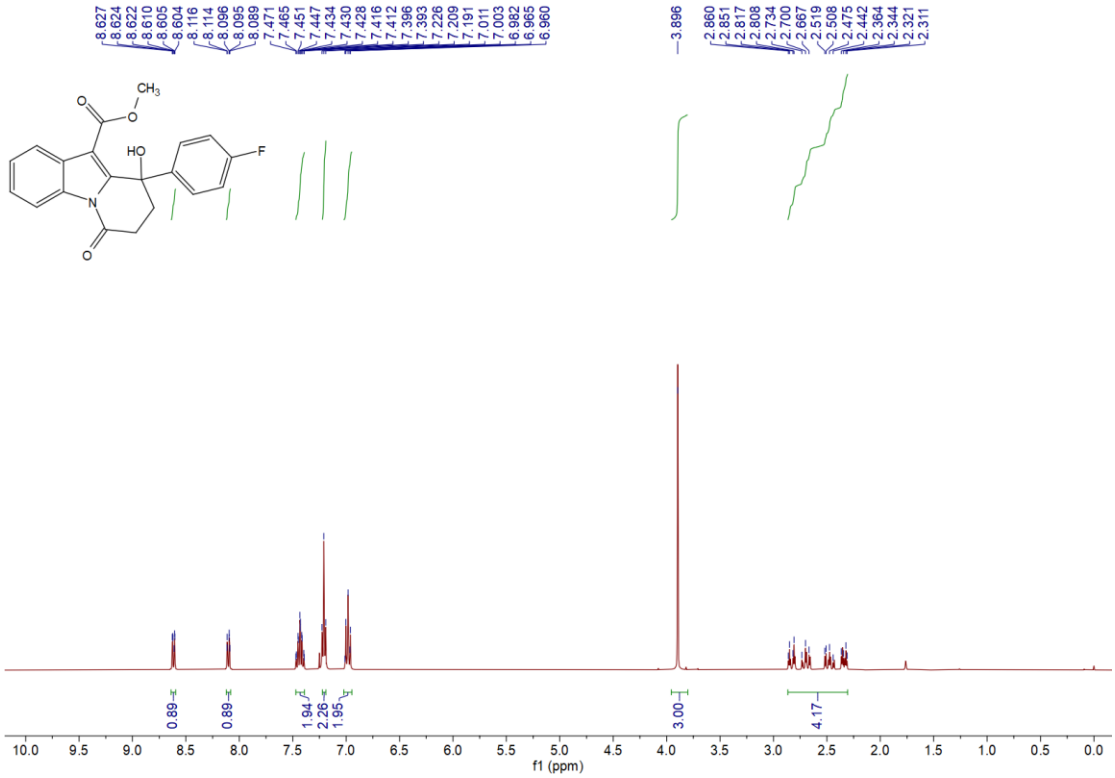
^{1}H NMR Spectrum of **2b**



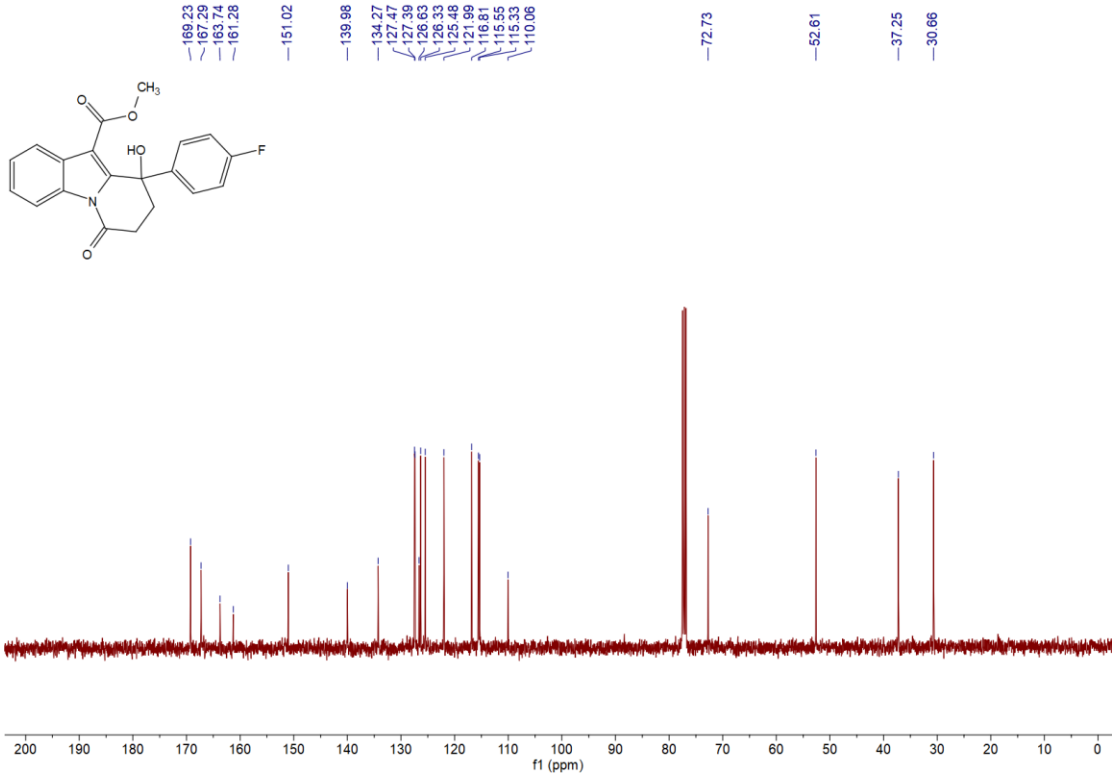
^{13}C NMR Spectrum of **2b**



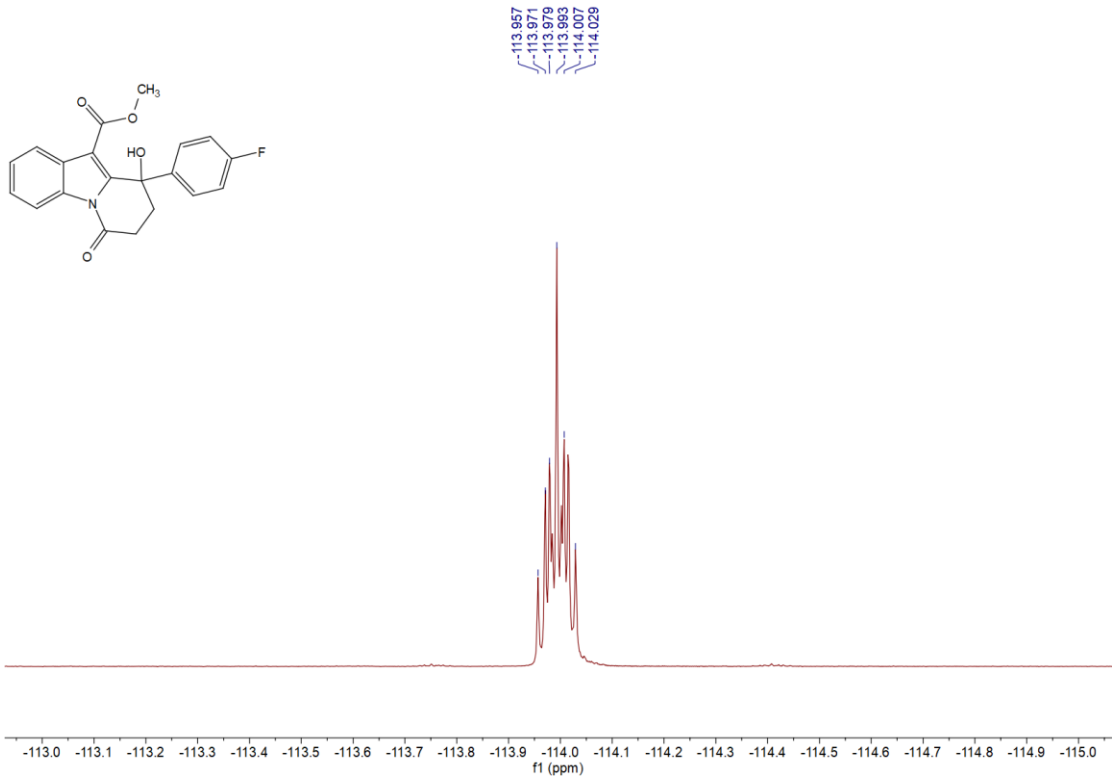
^{1}H NMR Spectrum of **2c**



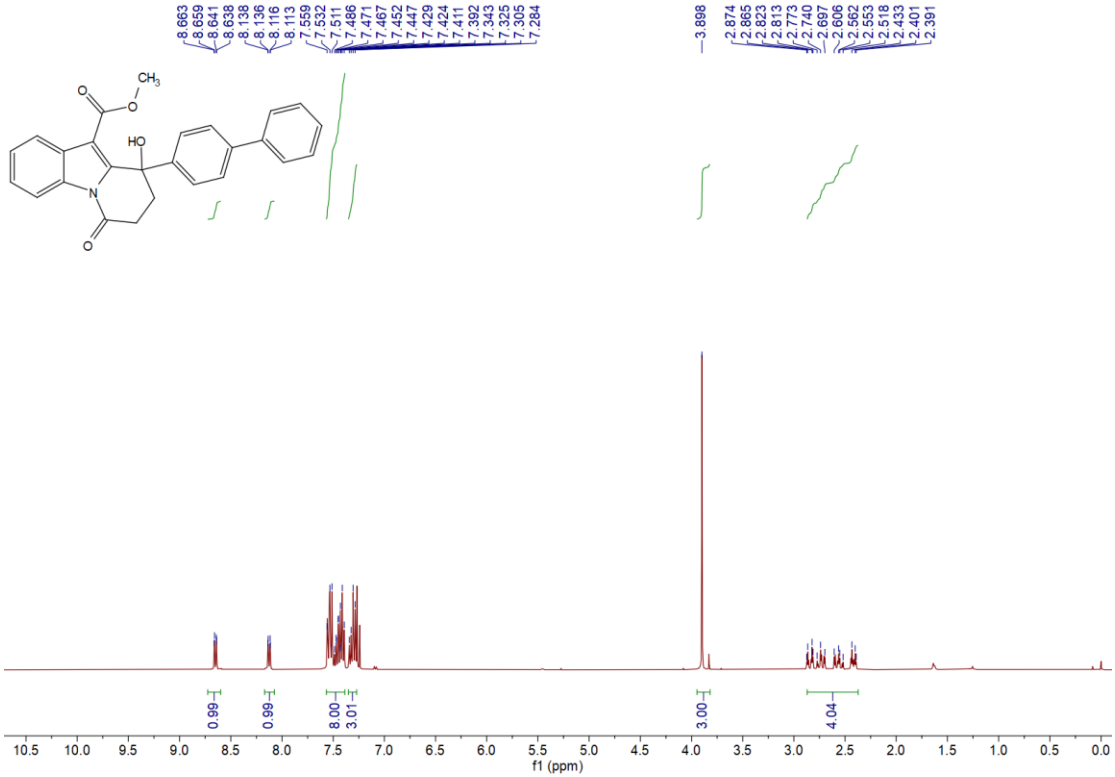
^{13}C NMR Spectrum of **2c**



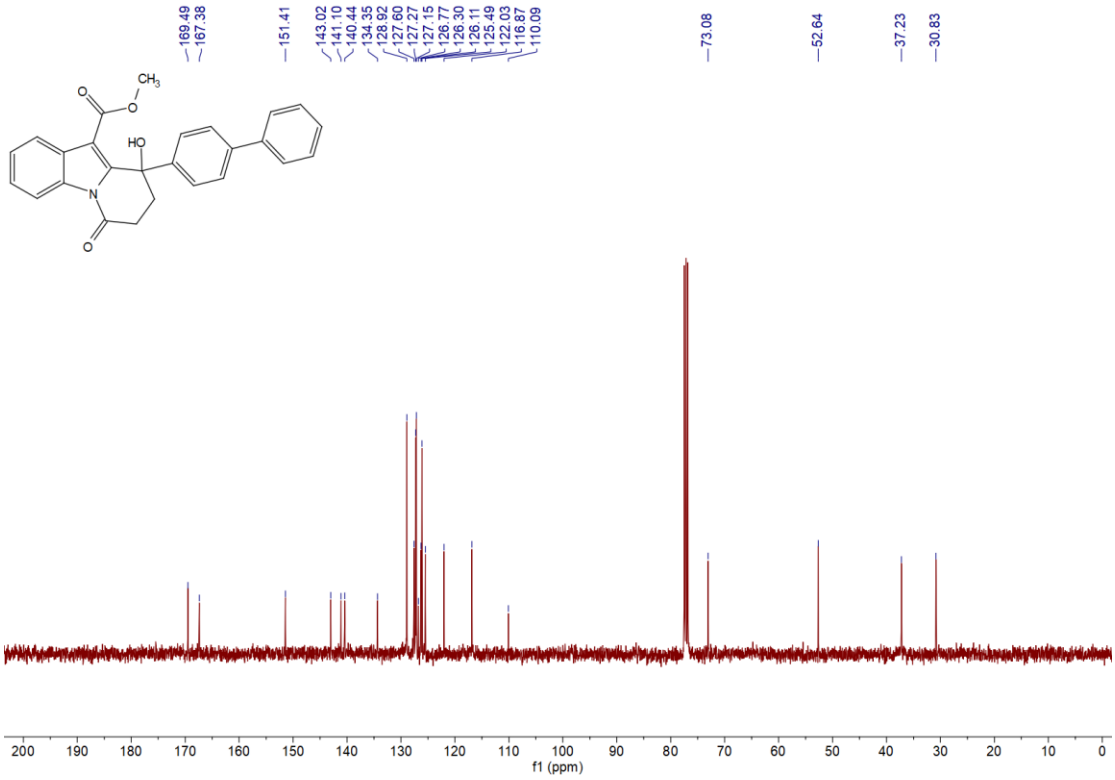
^{19}F NMR Spectrum of **2c**



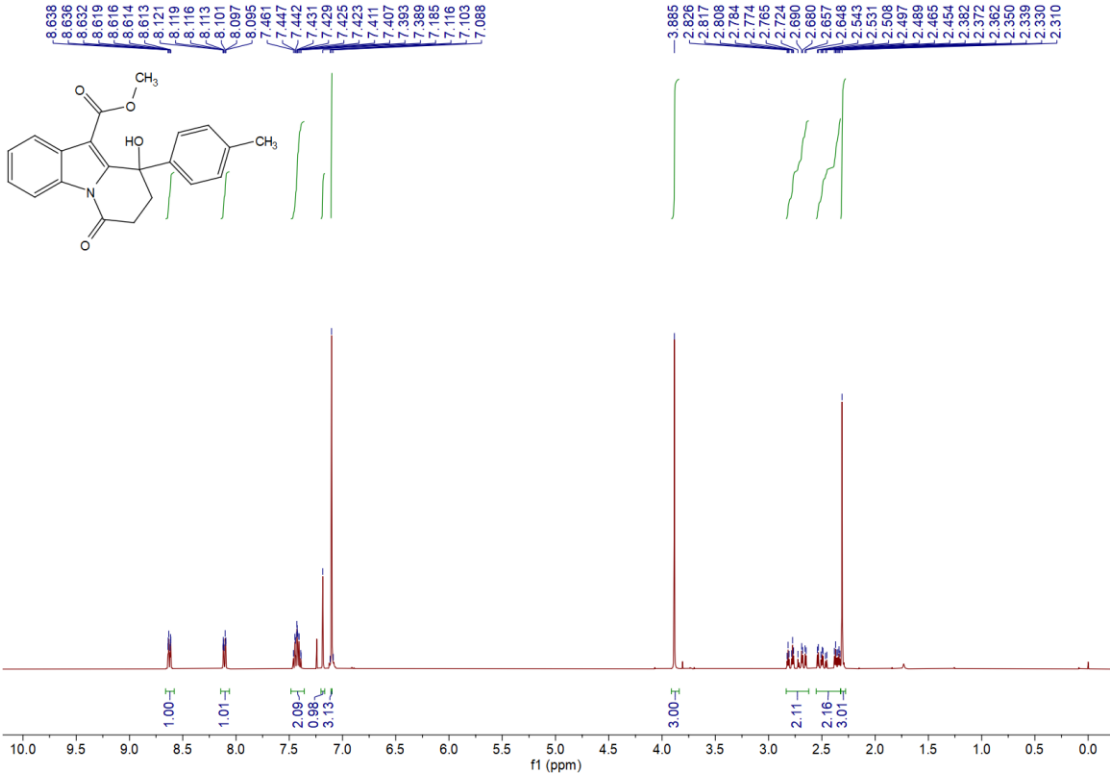
^{1}H NMR Spectrum of **2d**



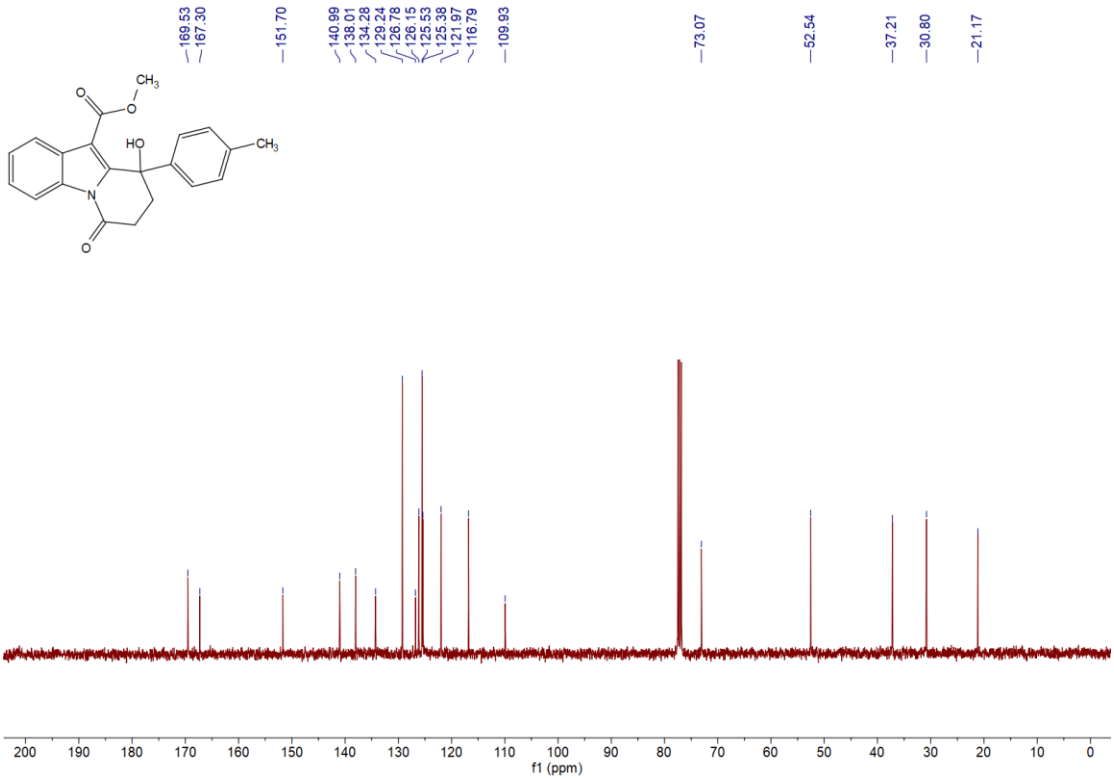
^{13}C NMR Spectrum of **2d**



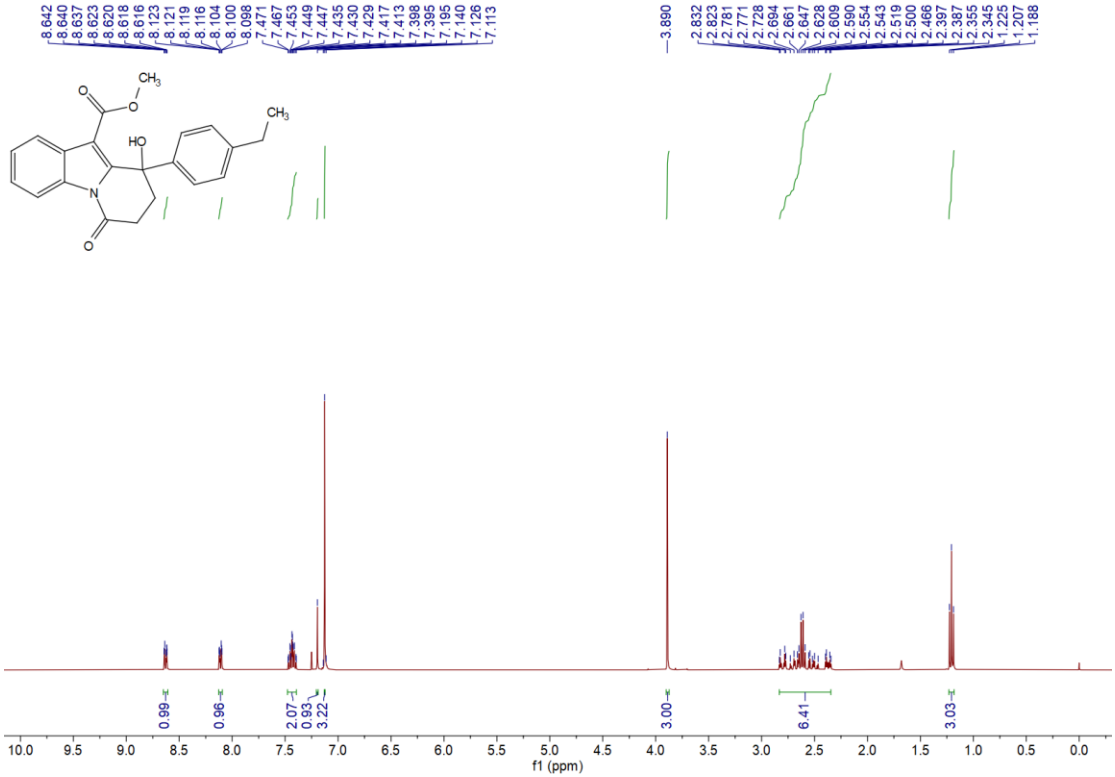
^{1}H NMR Spectrum of **2e**



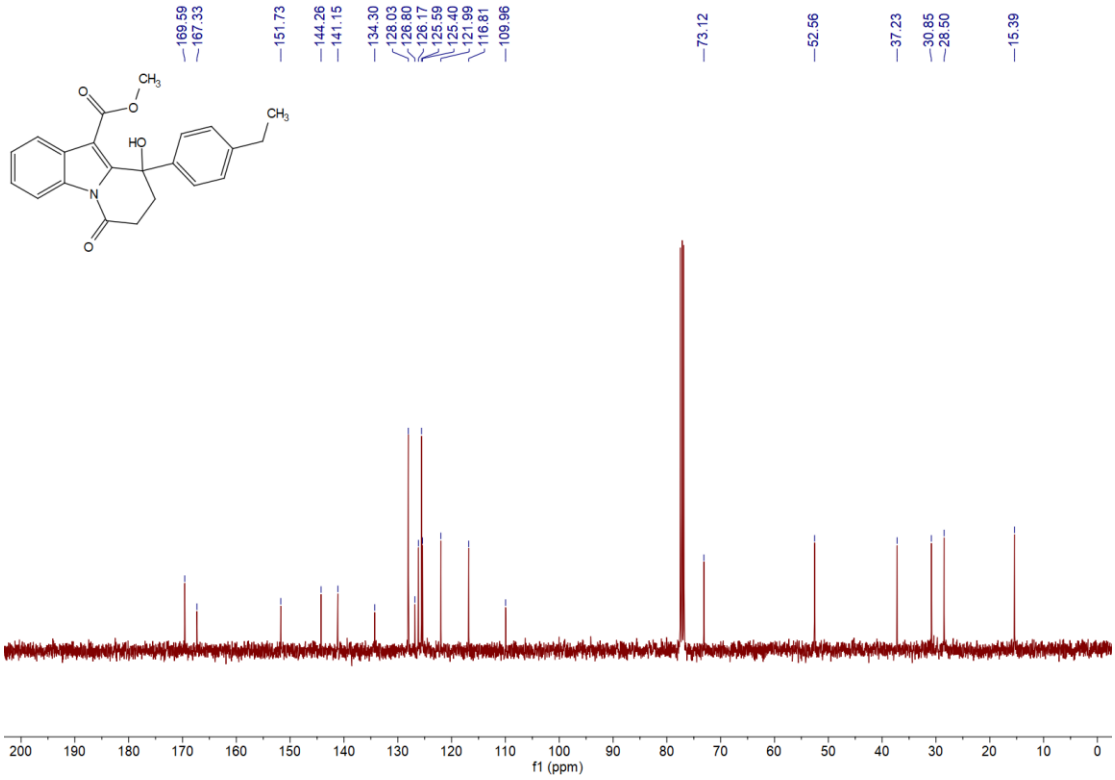
^{13}C NMR Spectrum of **2e**



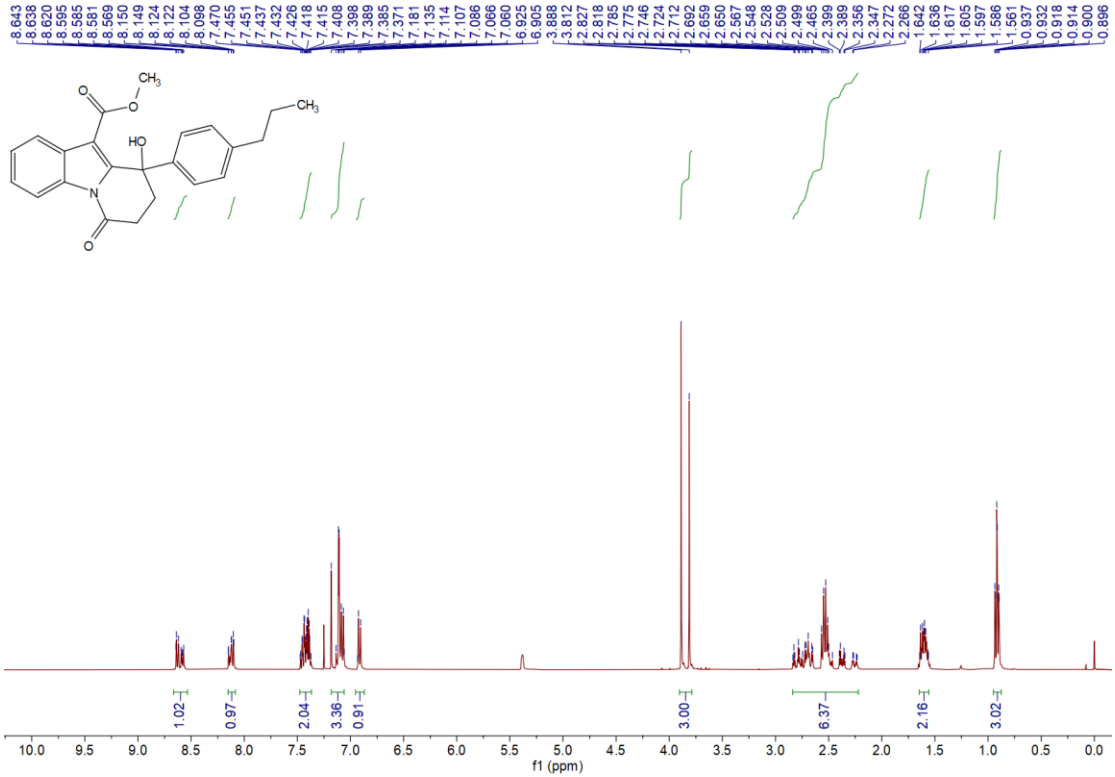
^{1}H NMR Spectrum of **2f**



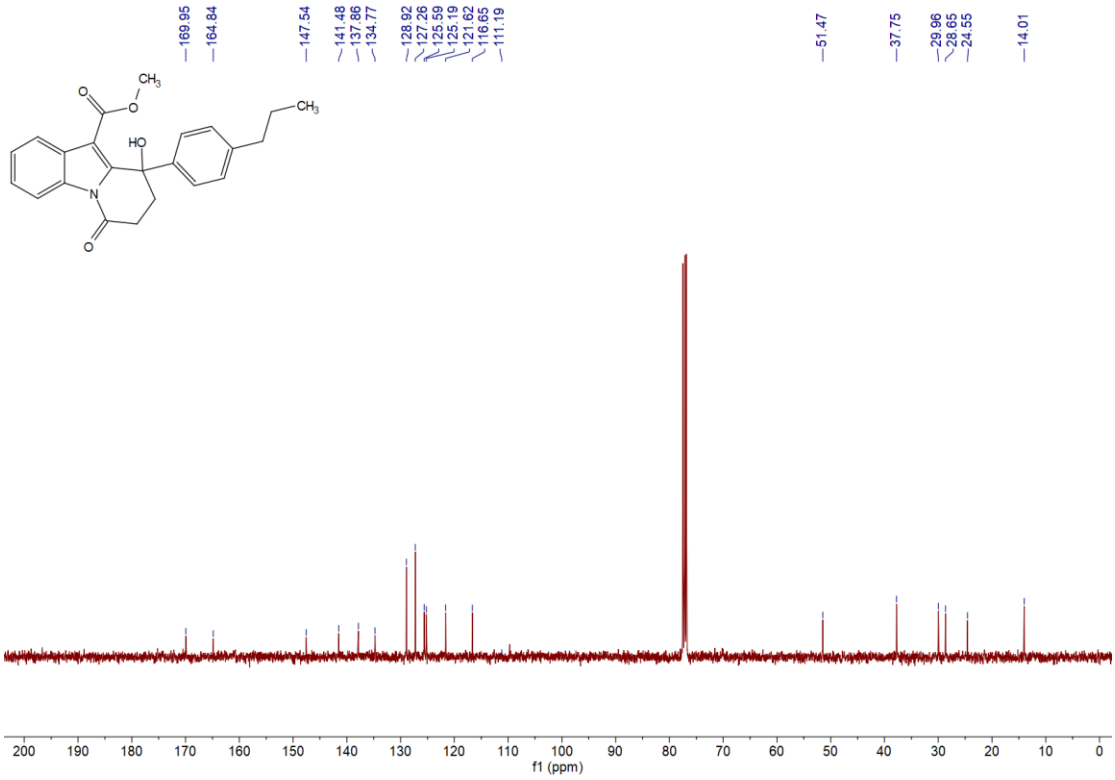
^{13}C NMR Spectrum of **2f**



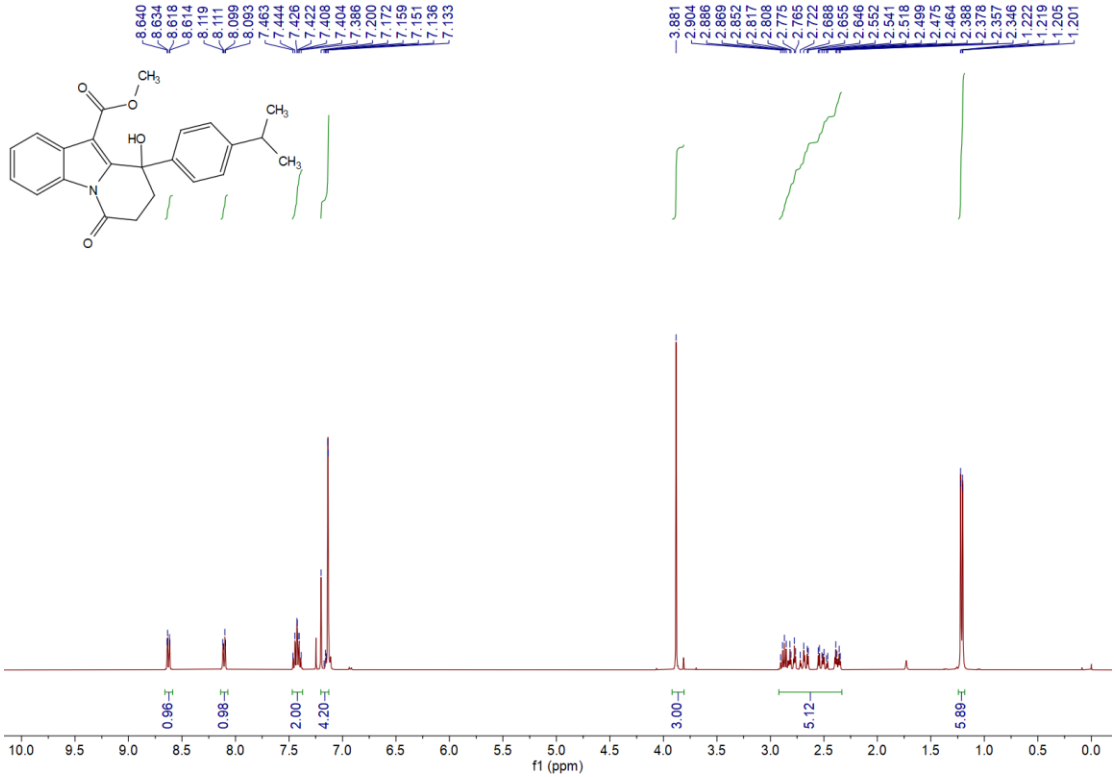
^{1}H NMR Spectrum of **2g**



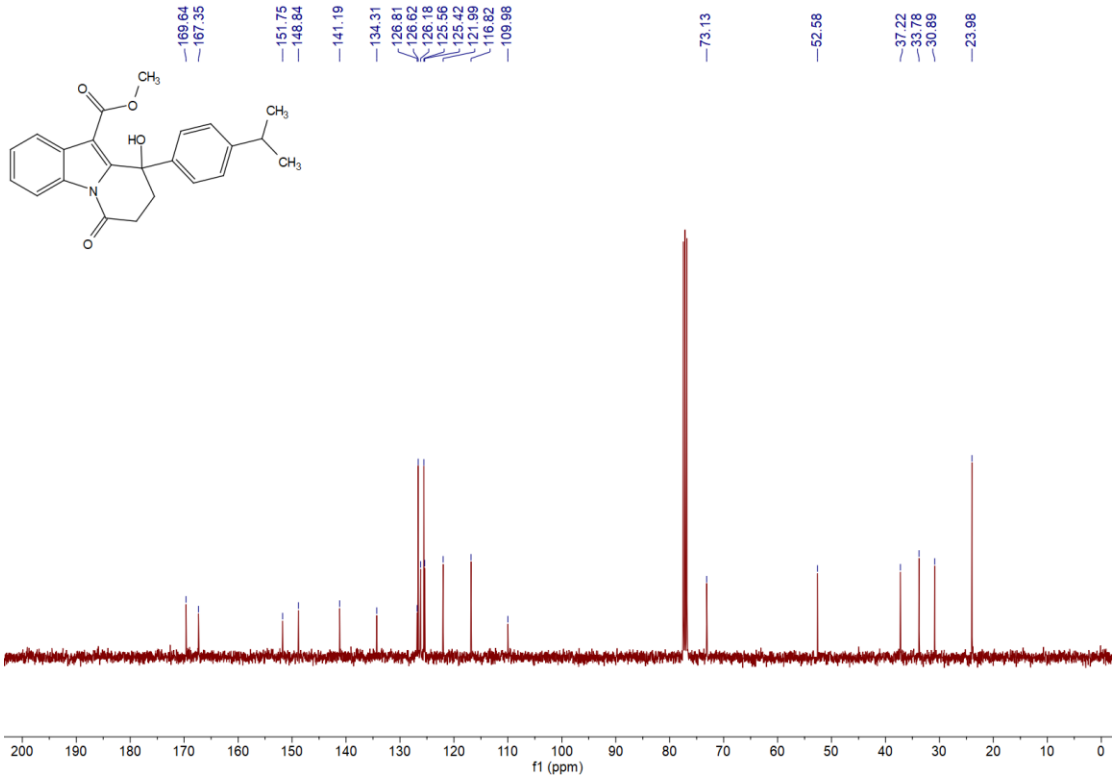
^{13}C NMR Spectrum of **2g**



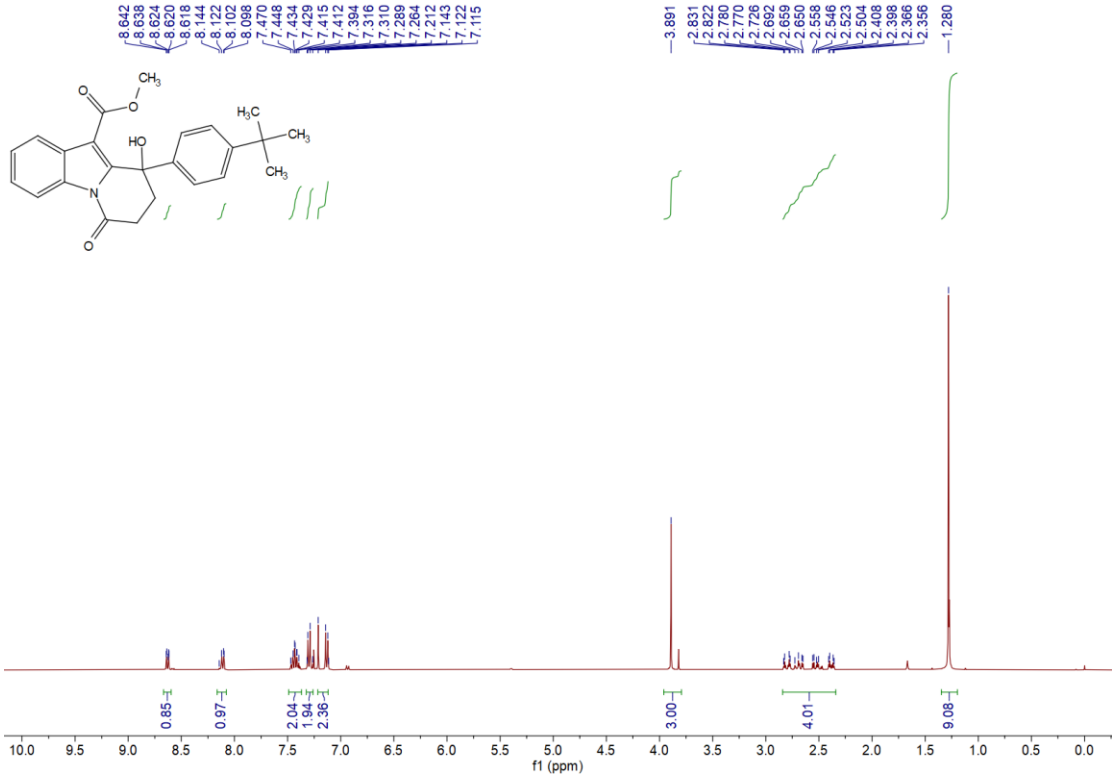
^{1}H NMR Spectrum of **2h**



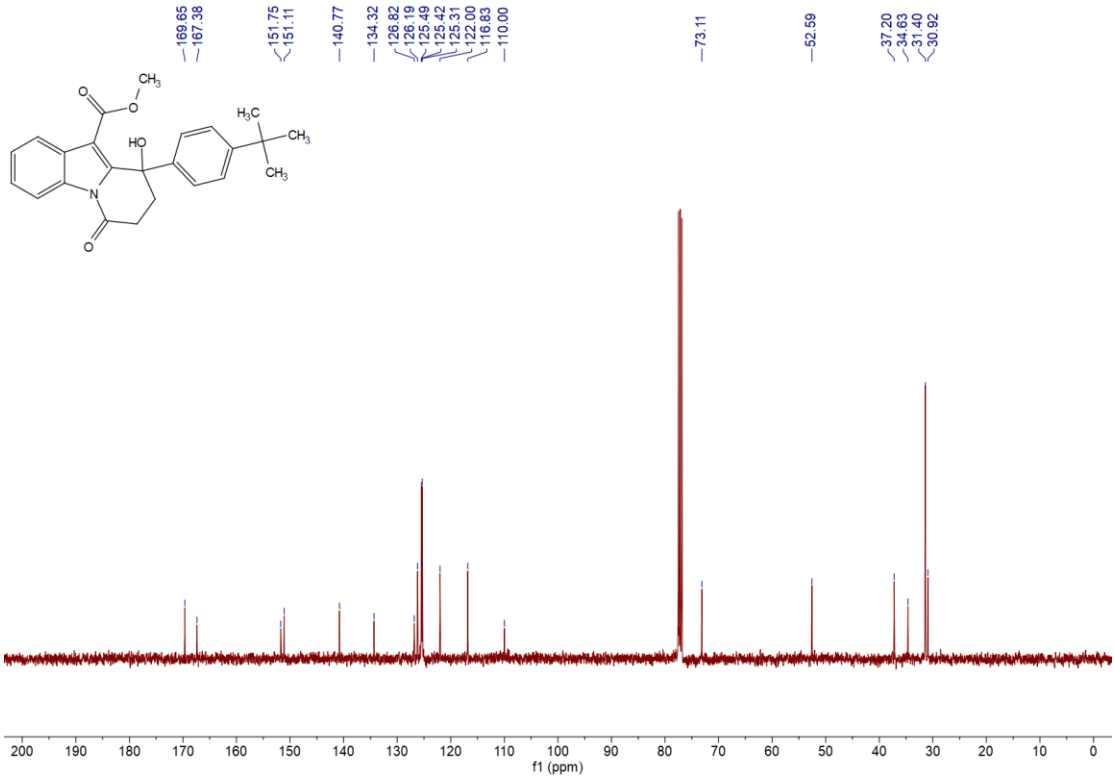
^{13}C NMR Spectrum of **2h**



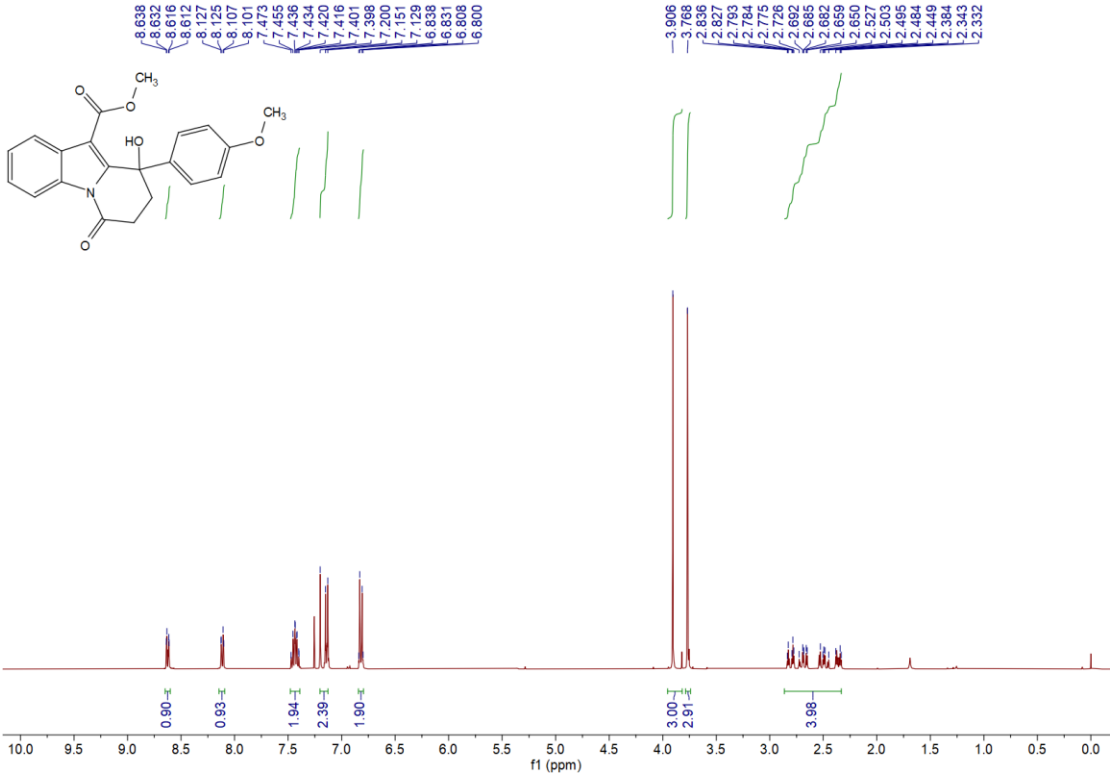
^{1}H NMR Spectrum of **2i**



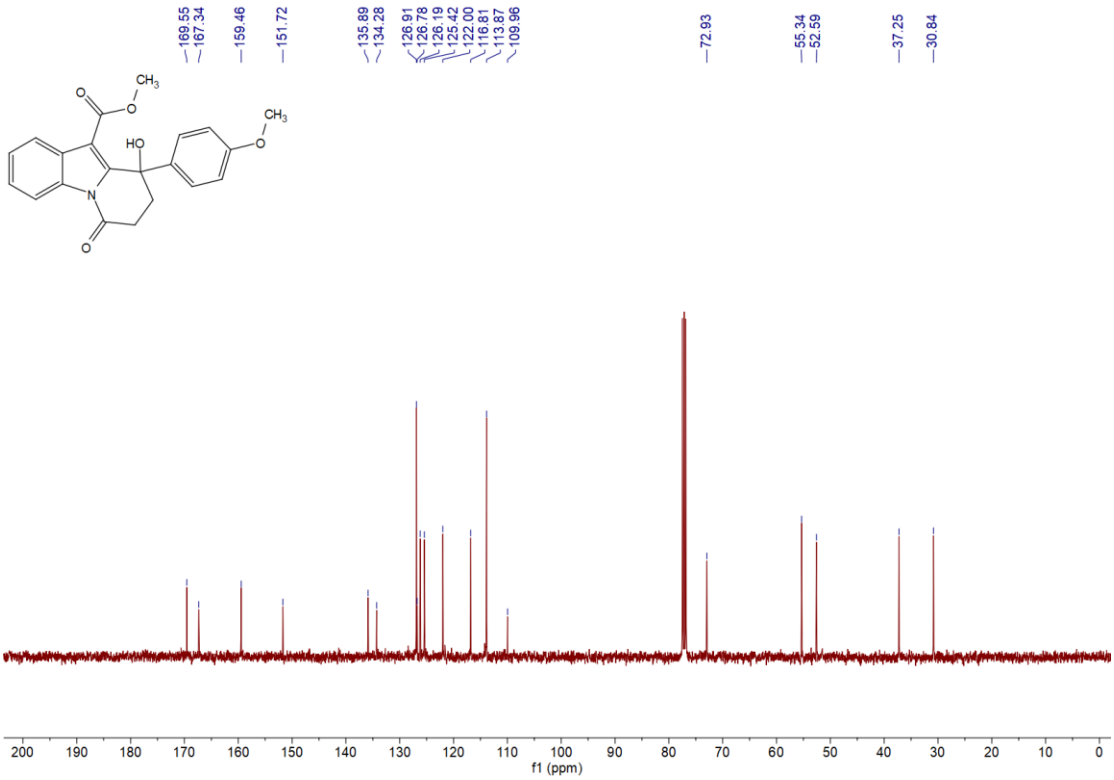
^{13}C NMR Spectrum of **2i**



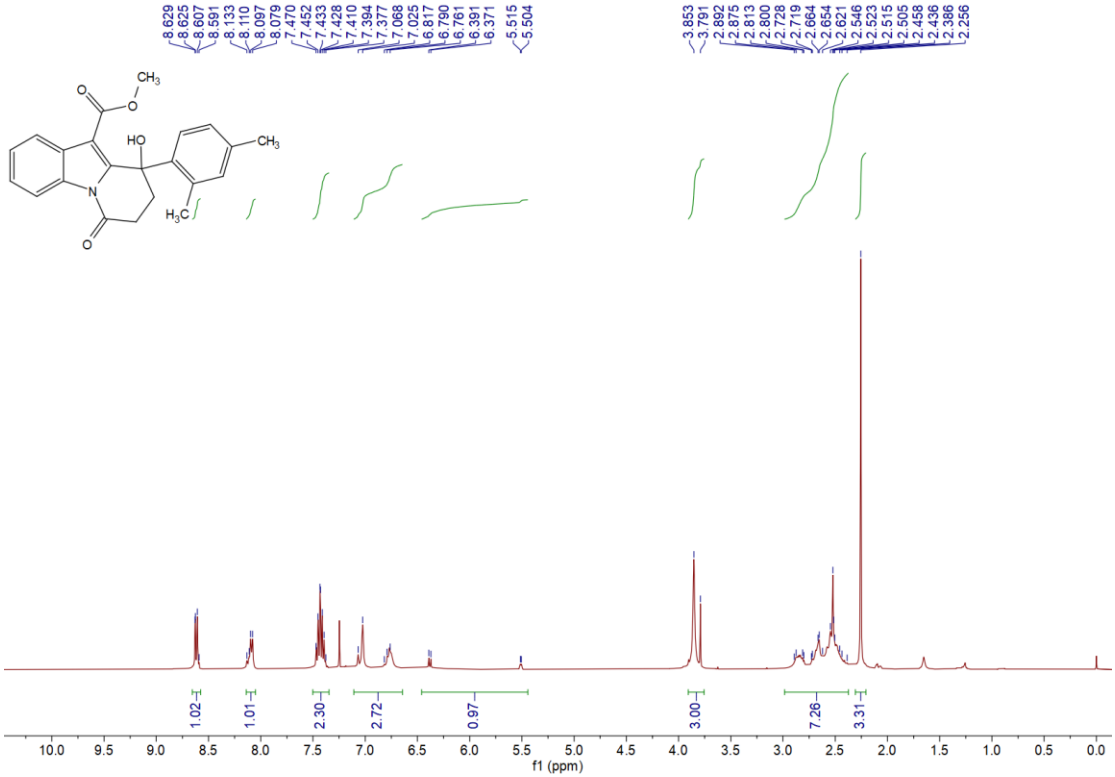
^{1}H NMR Spectrum of **2j**



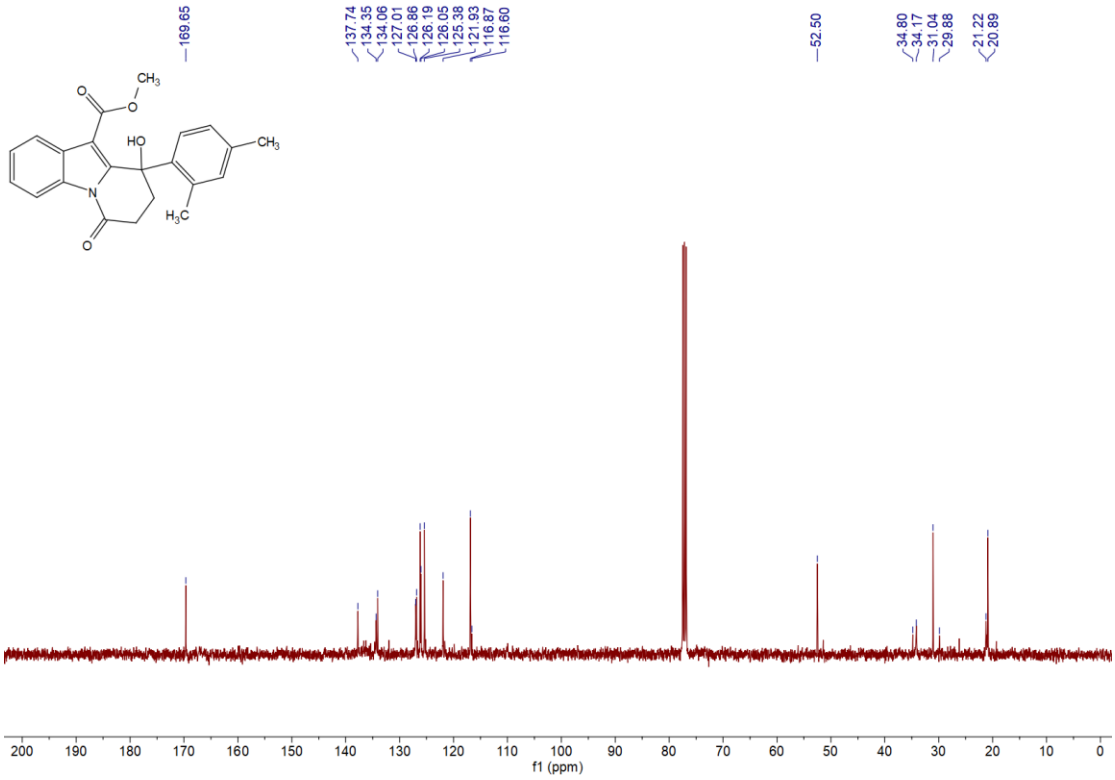
^{13}C NMR Spectrum of **2j**



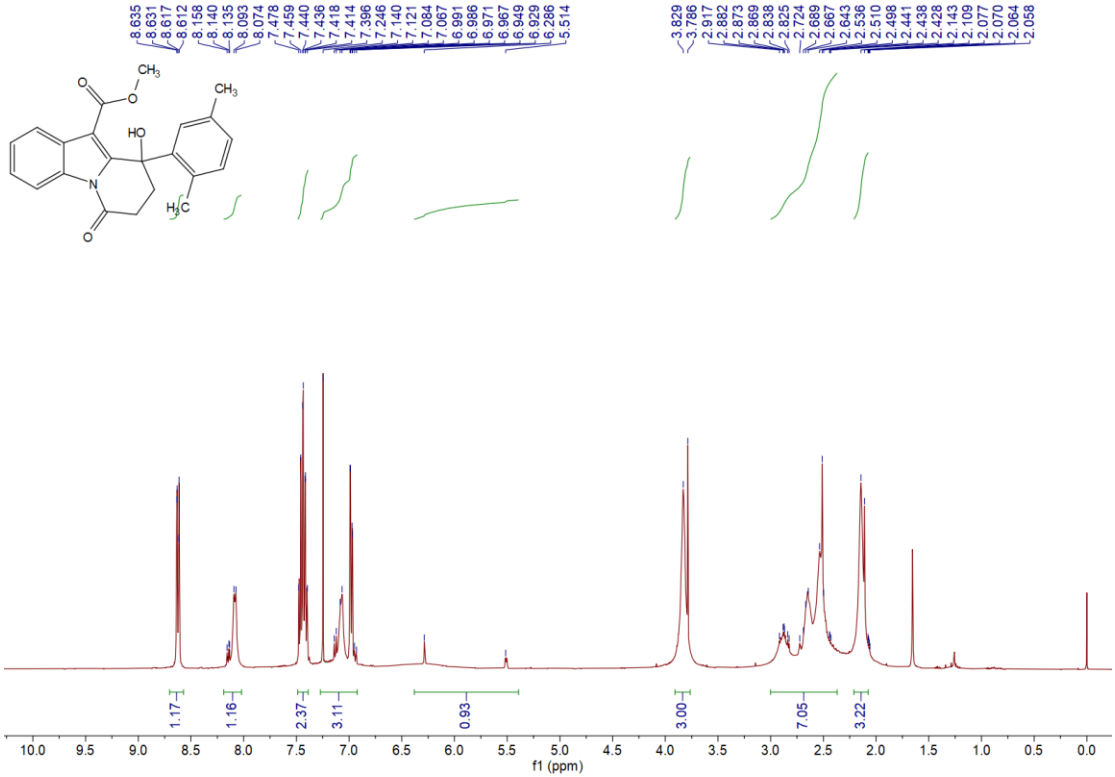
^{1}H NMR Spectrum of **2k**



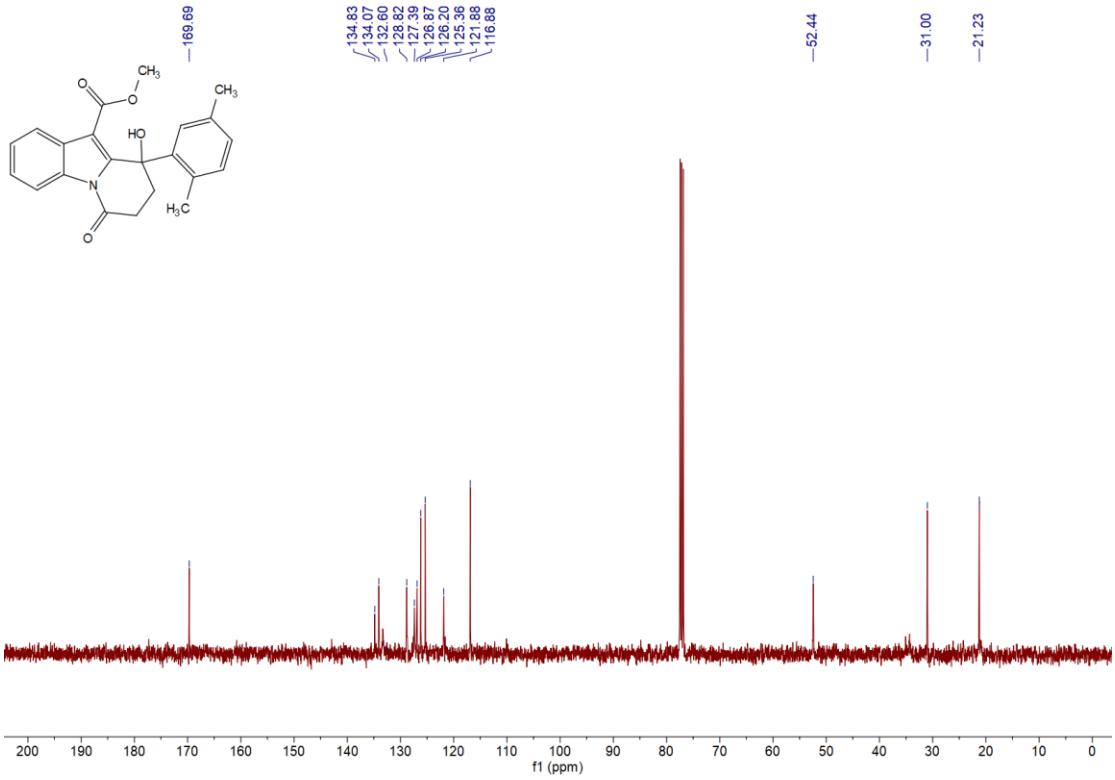
^{13}C NMR Spectrum of **2k**



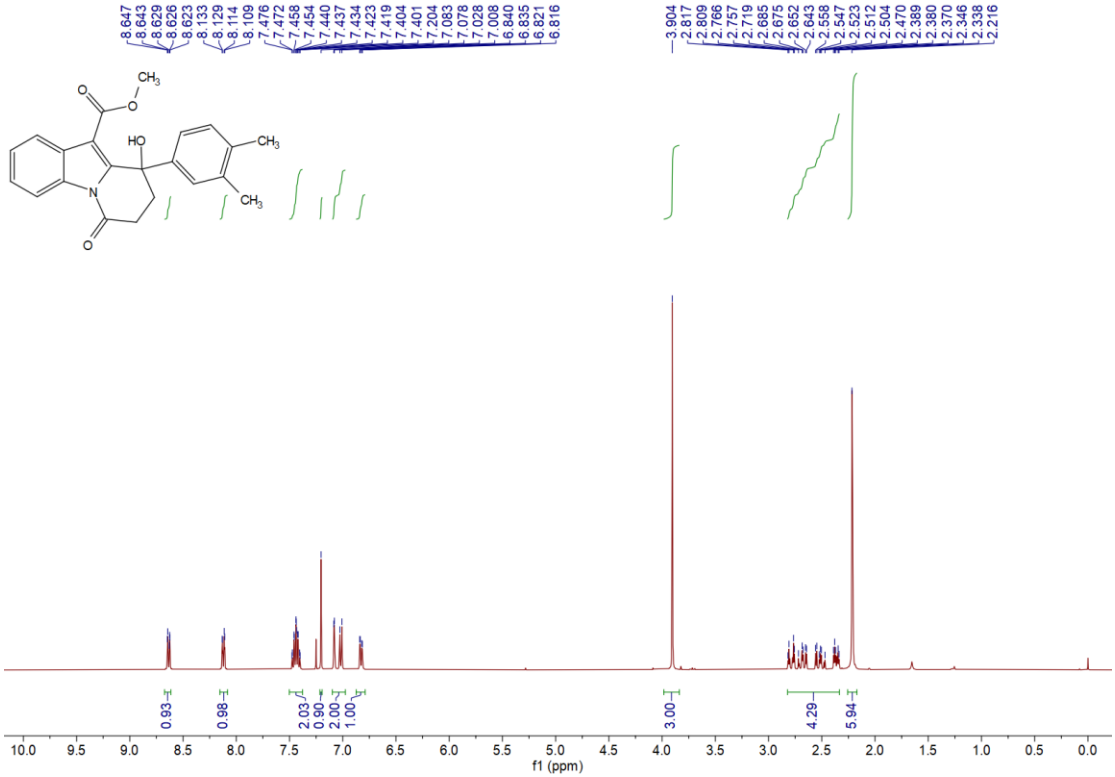
^{1}H NMR Spectrum of **2l**



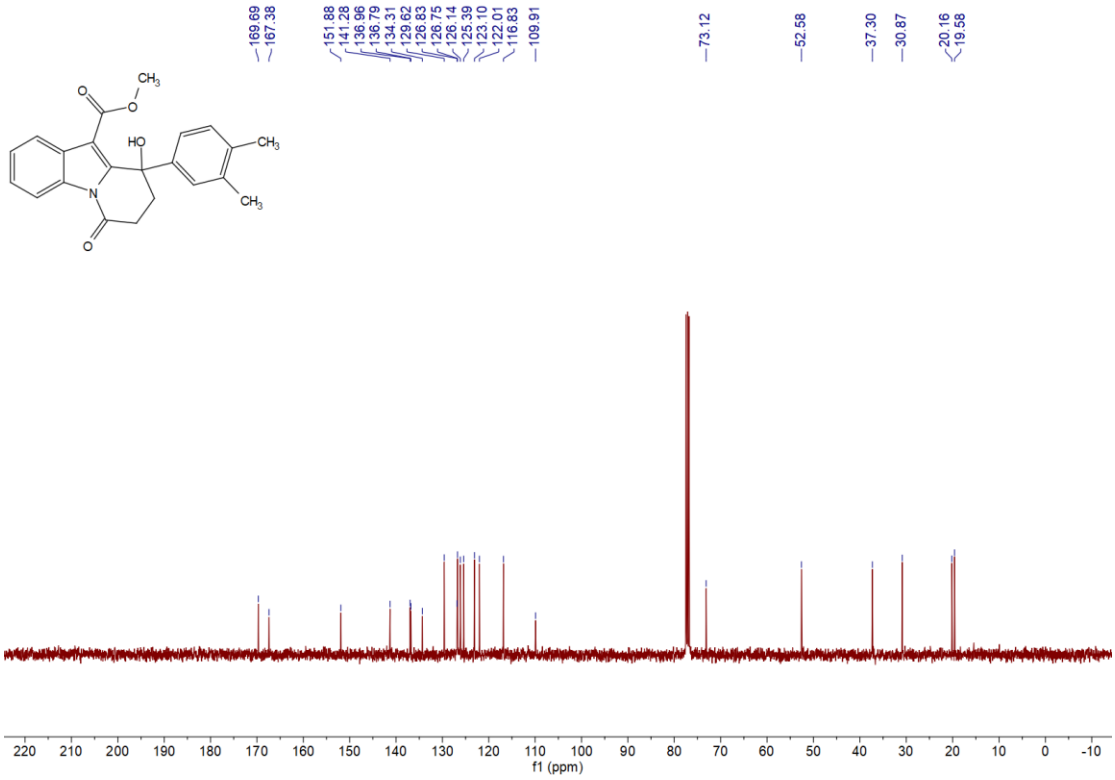
^{13}C NMR Spectrum of **2l**



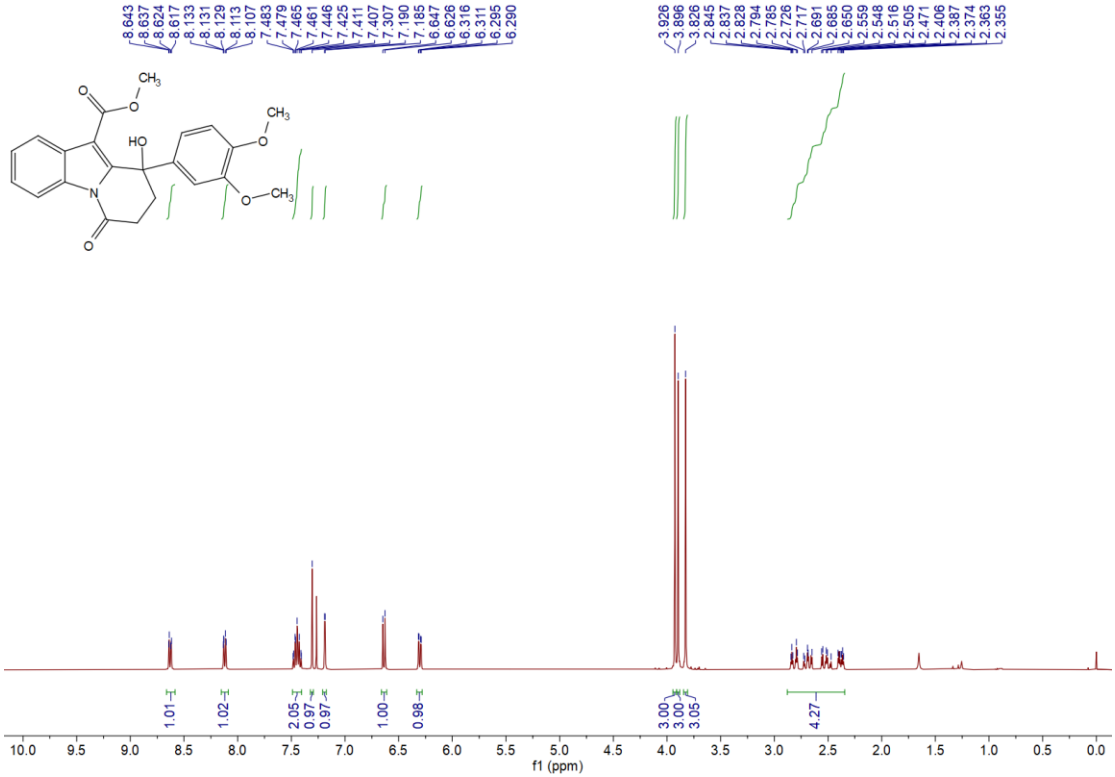
^{1}H NMR Spectrum of **2m**



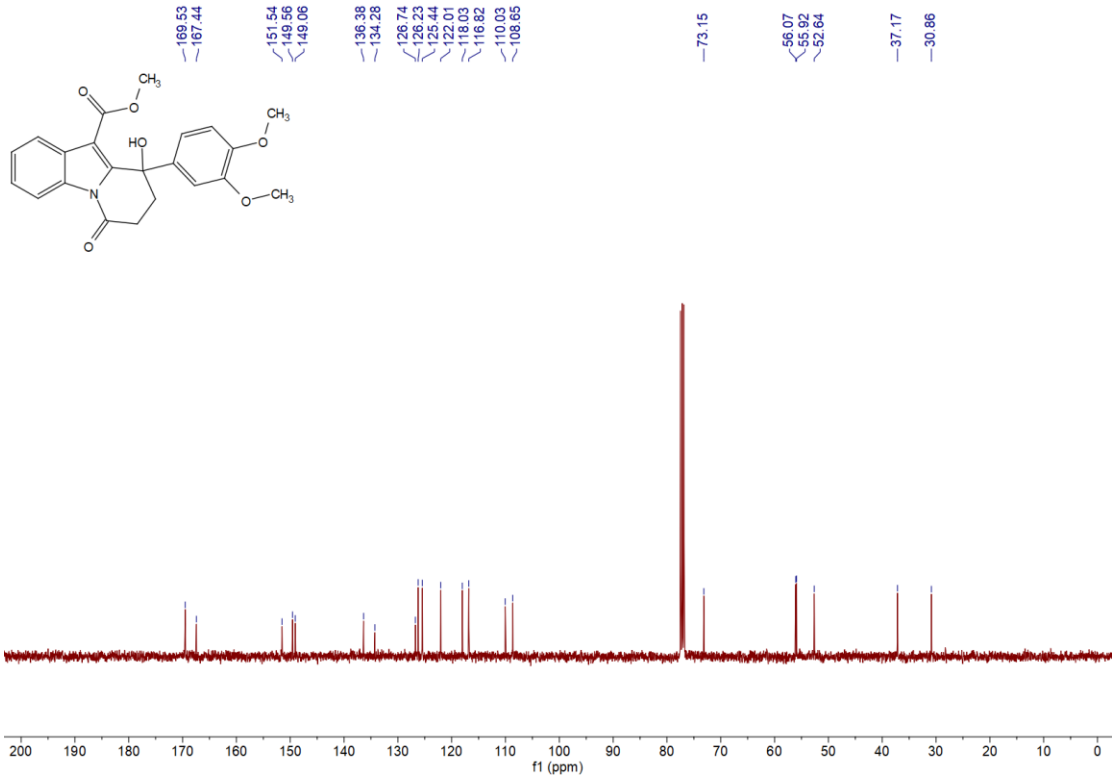
^{13}C NMR Spectrum of **2m**



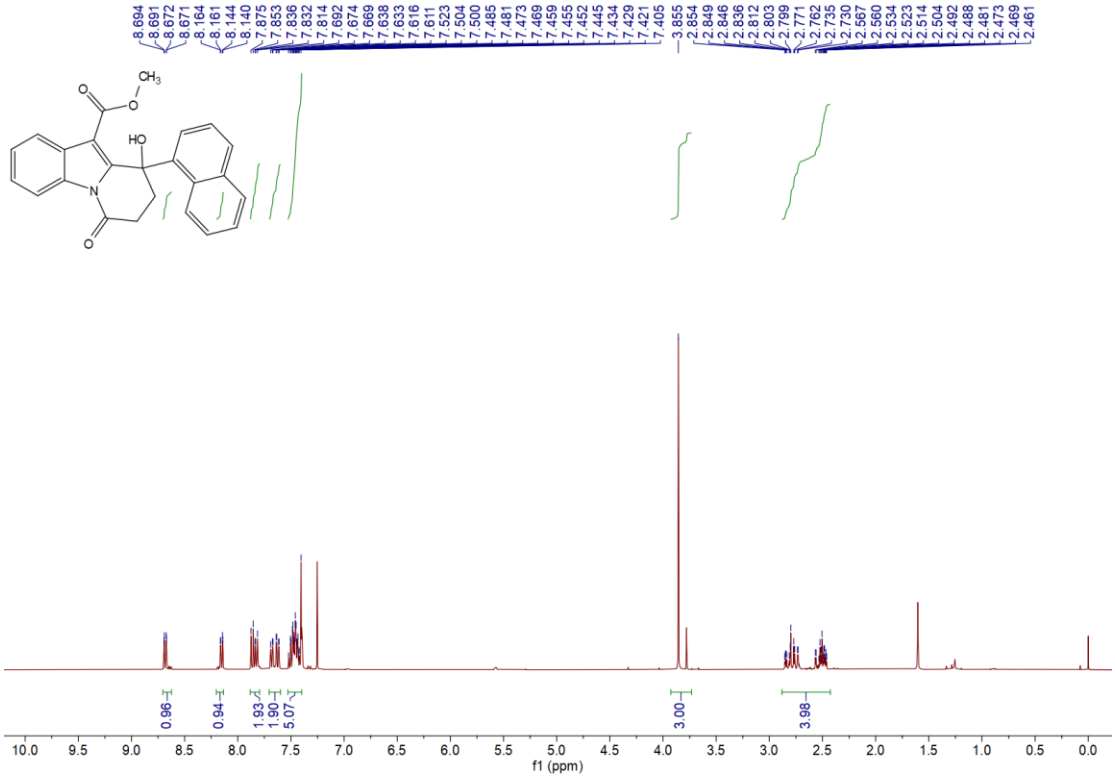
^{1}H NMR Spectrum of **2n**



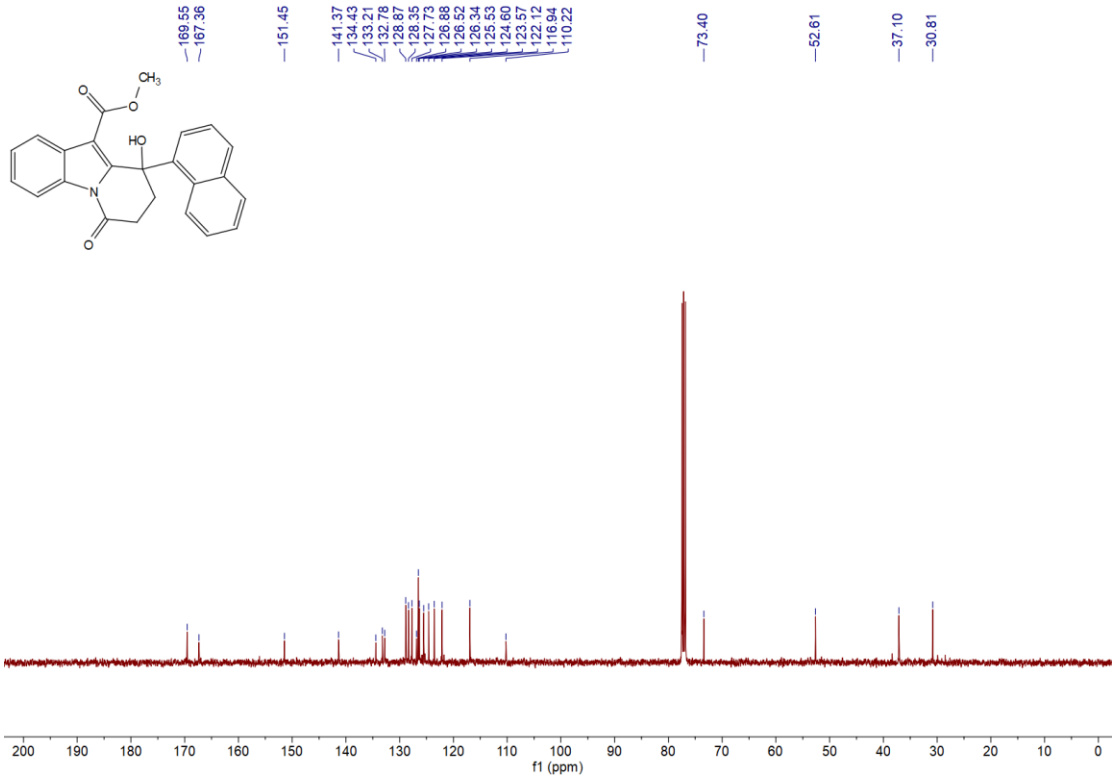
^{13}C NMR Spectrum of **2n**



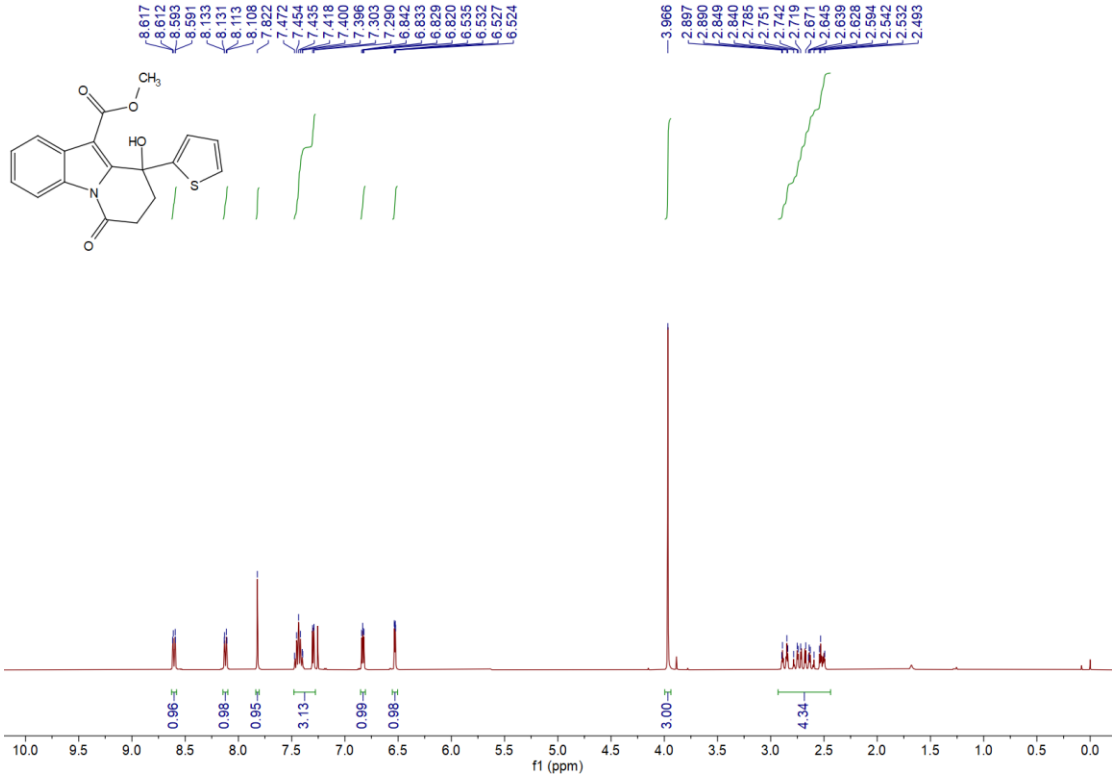
^{1}H NMR Spectrum of **2o**



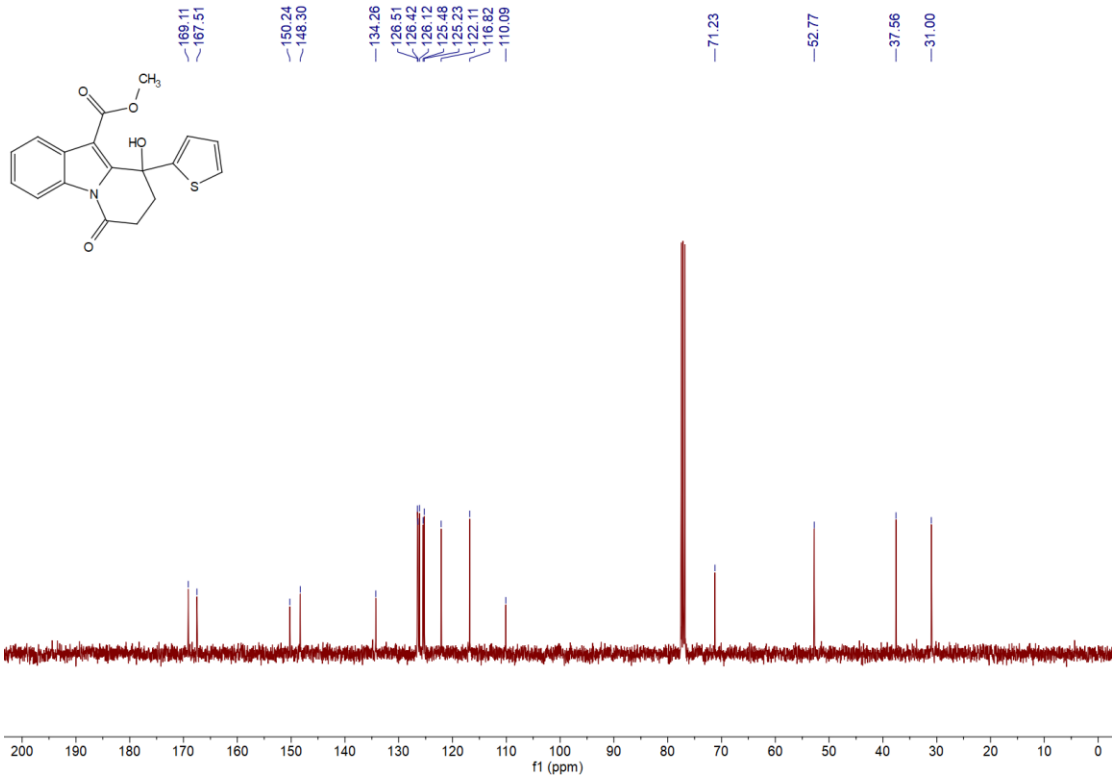
^{13}C NMR Spectrum of **2o**



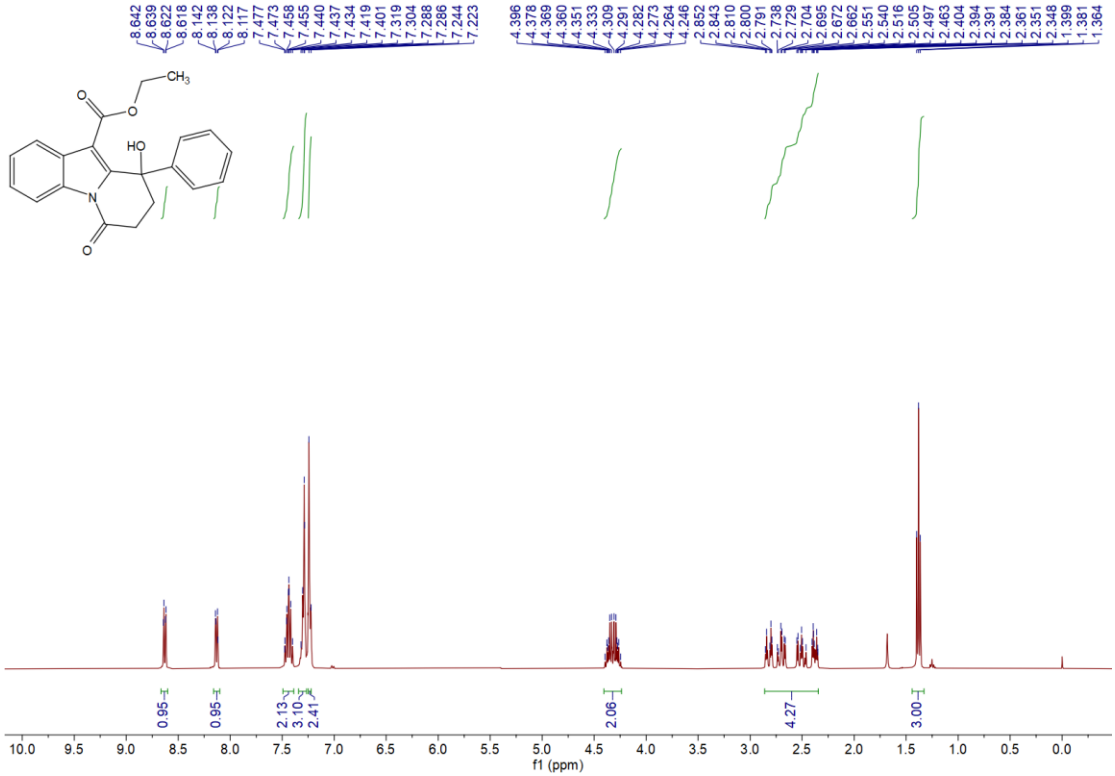
^{1}H NMR Spectrum of **2p**



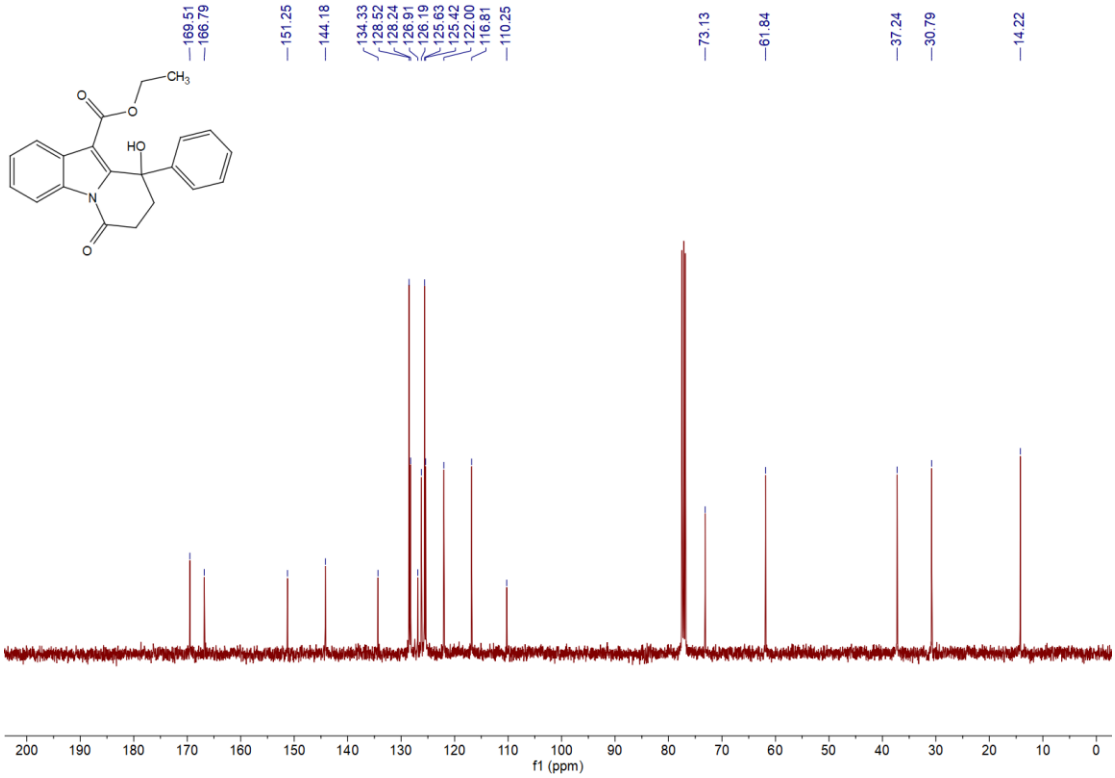
^{13}C NMR Spectrum of **2p**



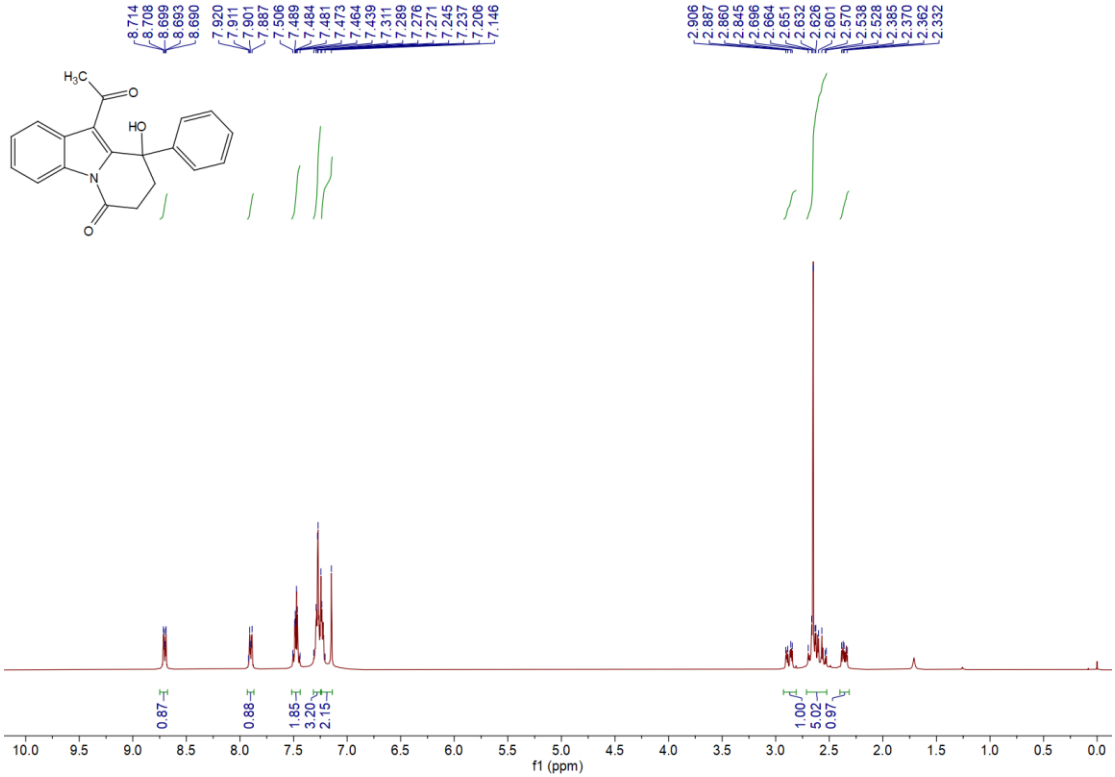
^{1}H NMR Spectrum of **2q**



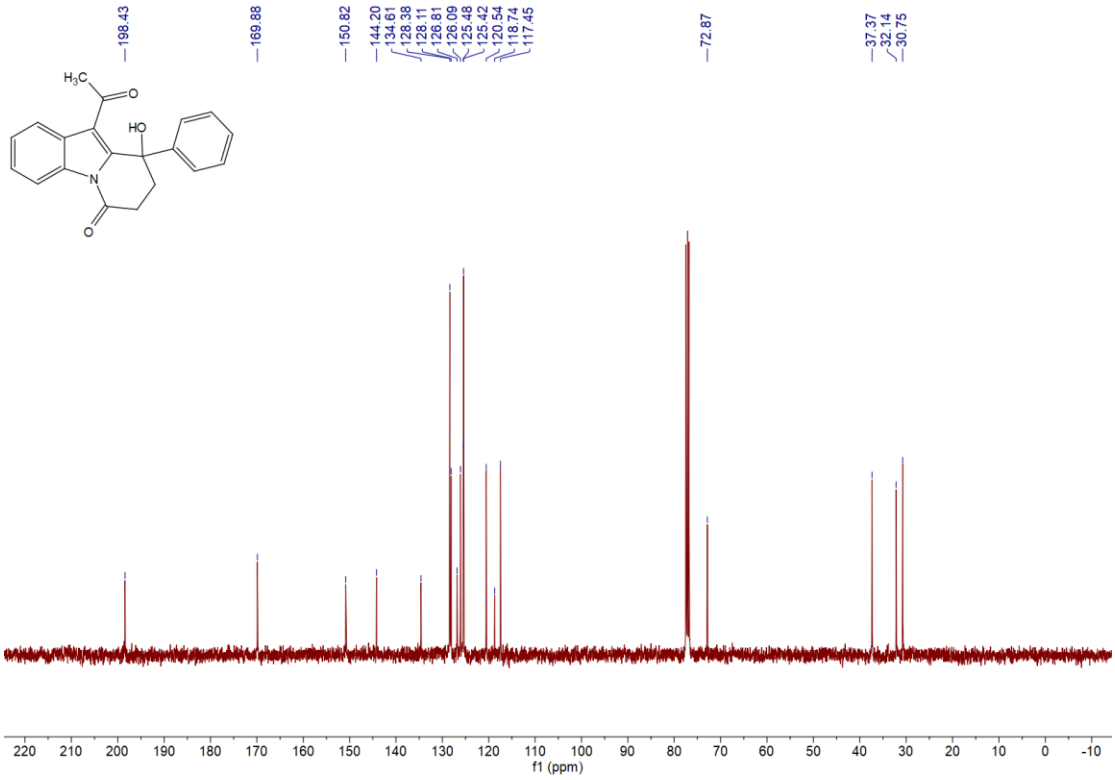
^{13}C NMR Spectrum of **2q**



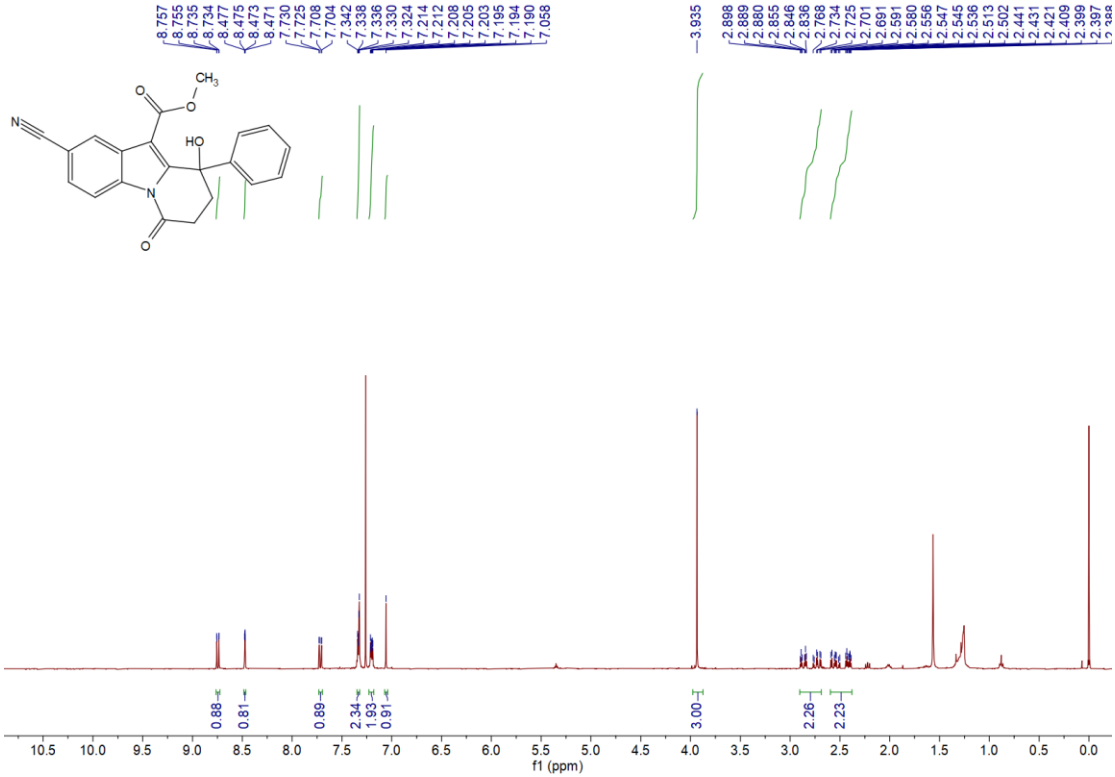
^{1}H NMR Spectrum of **2r**



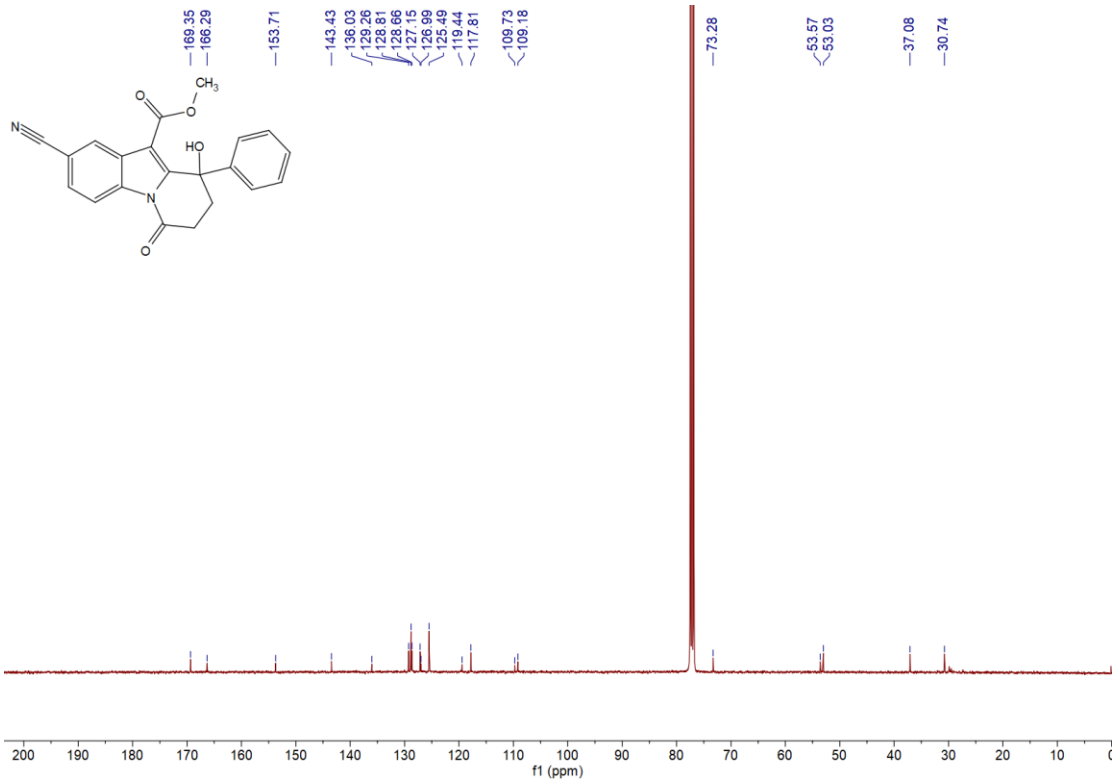
^{13}C NMR Spectrum of **2r**



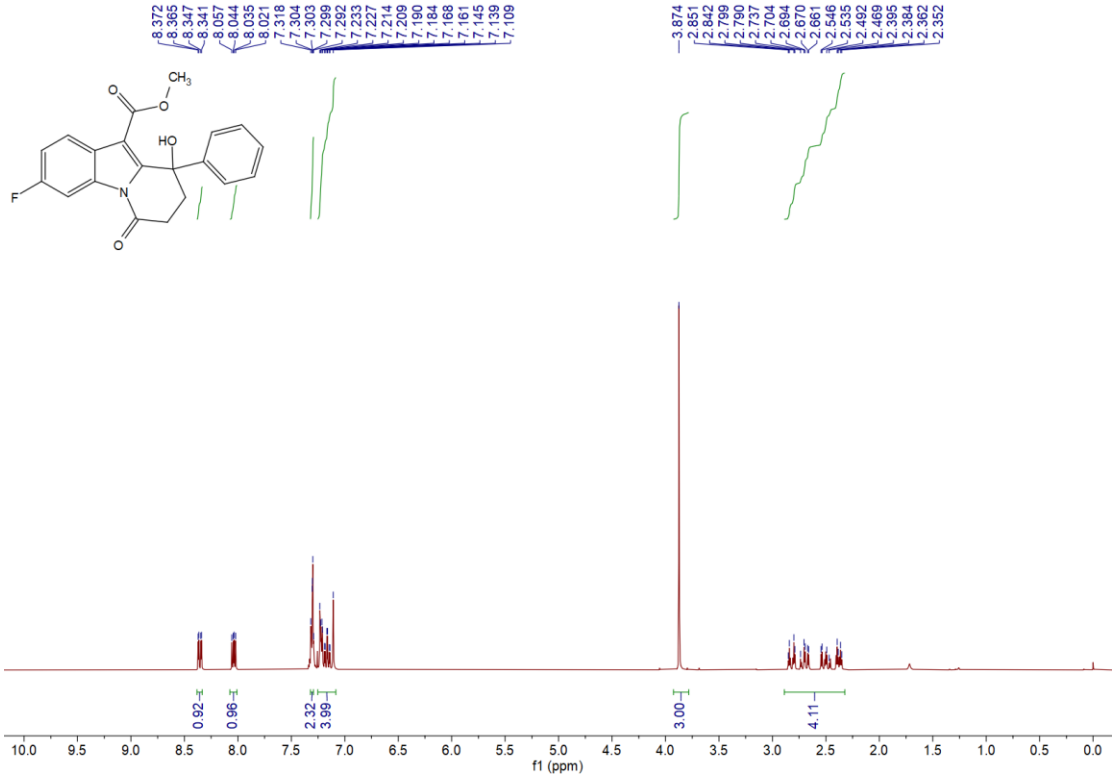
^{1}H NMR Spectrum of **2s**



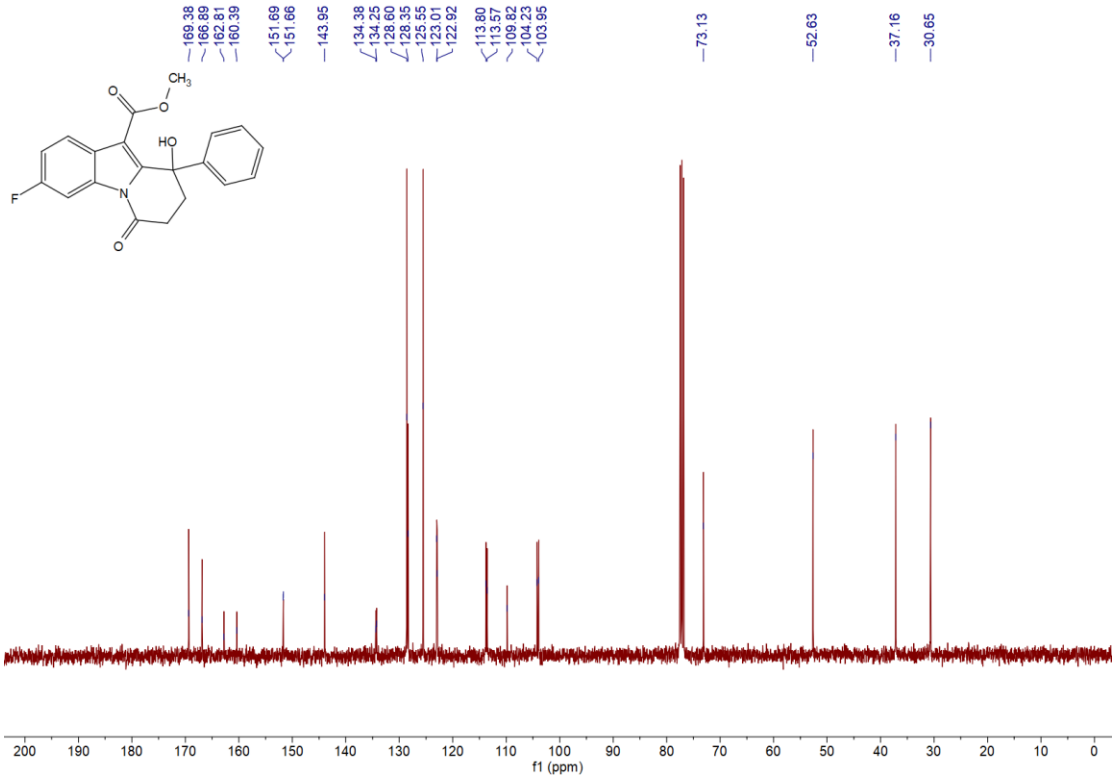
^{13}C NMR Spectrum of **2s**



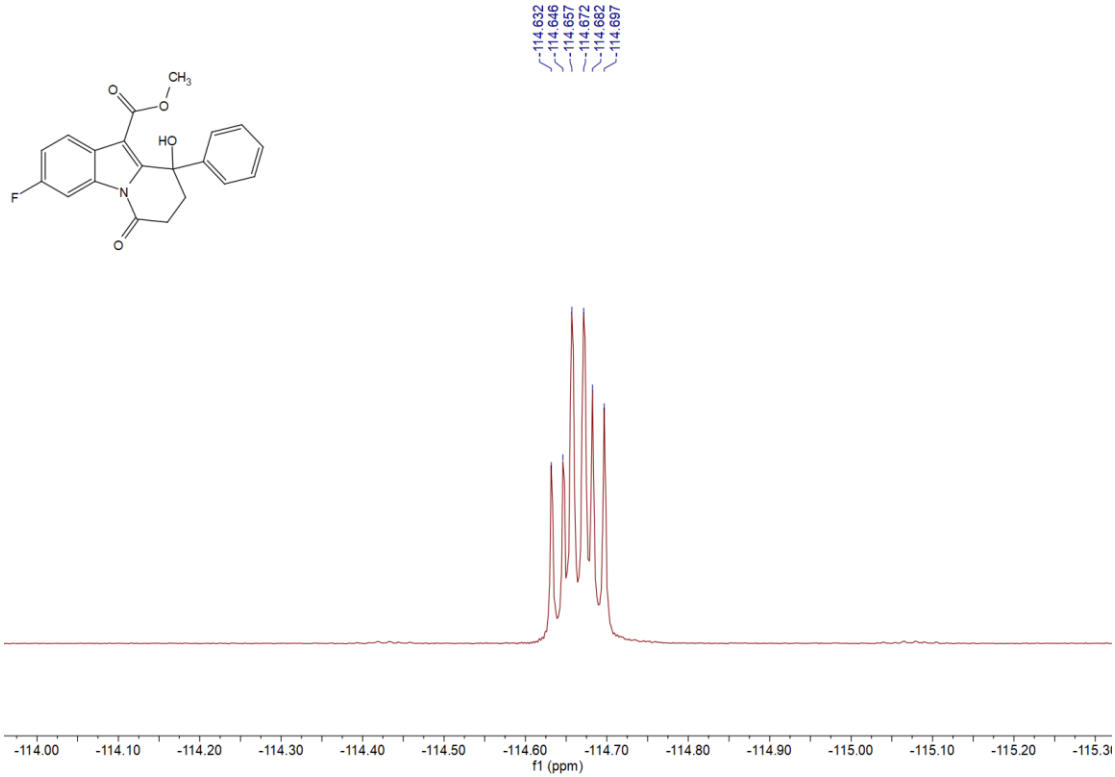
^{1}H NMR Spectrum of **2t**



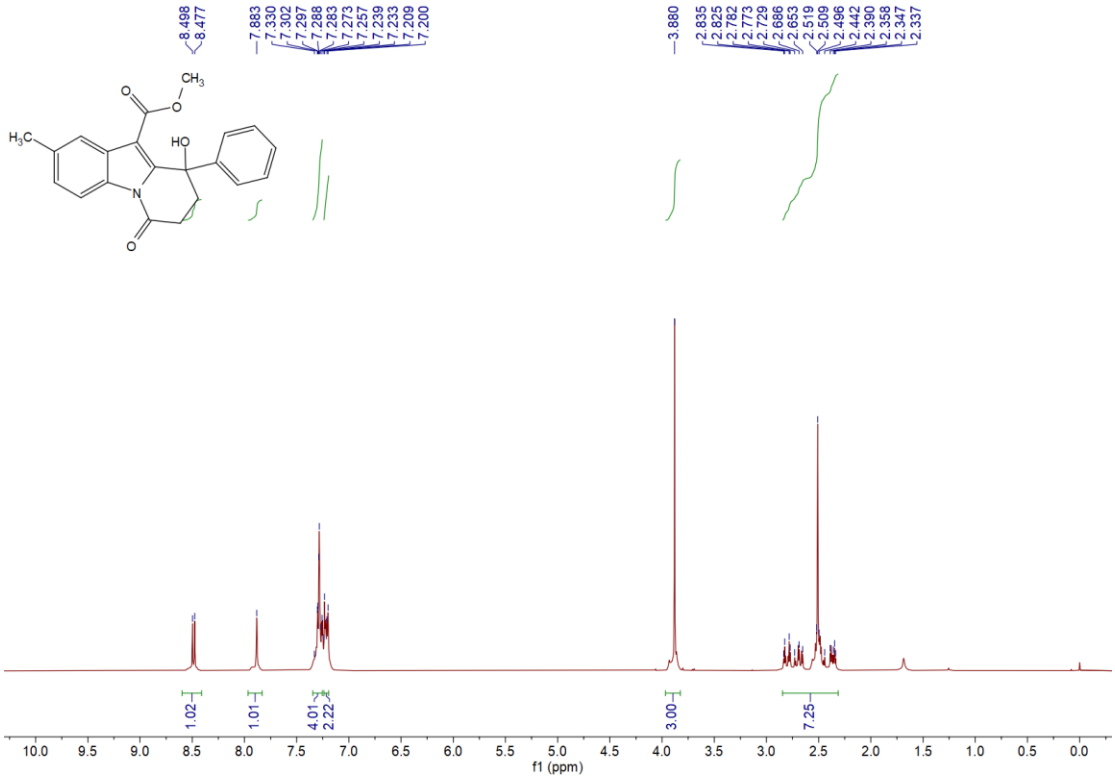
^{13}C NMR Spectrum of **2t**



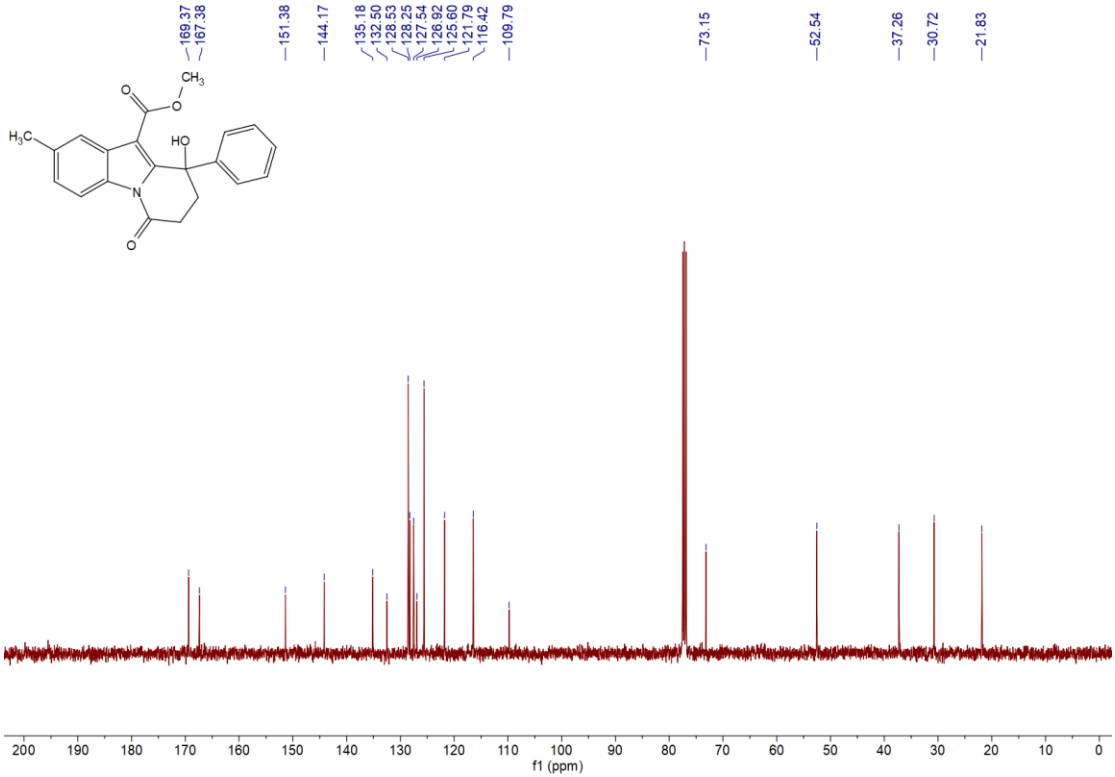
^{19}F NMR Spectrum of **2t**



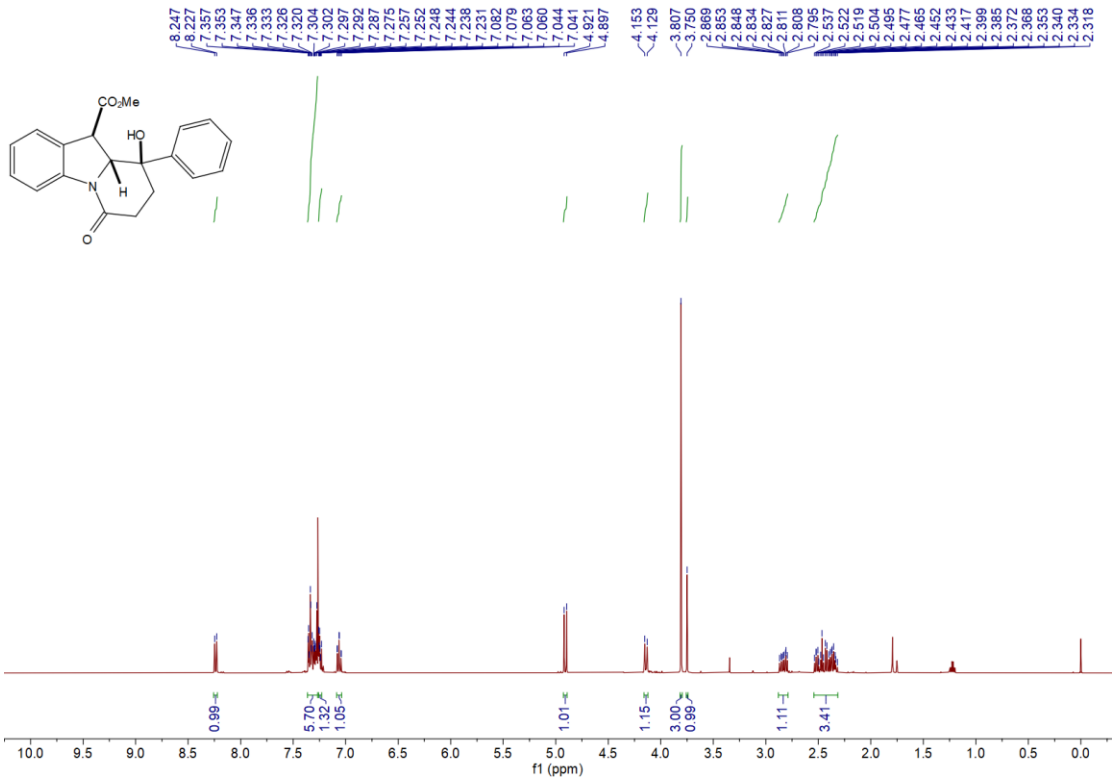
^{1}H NMR Spectrum of **2u**



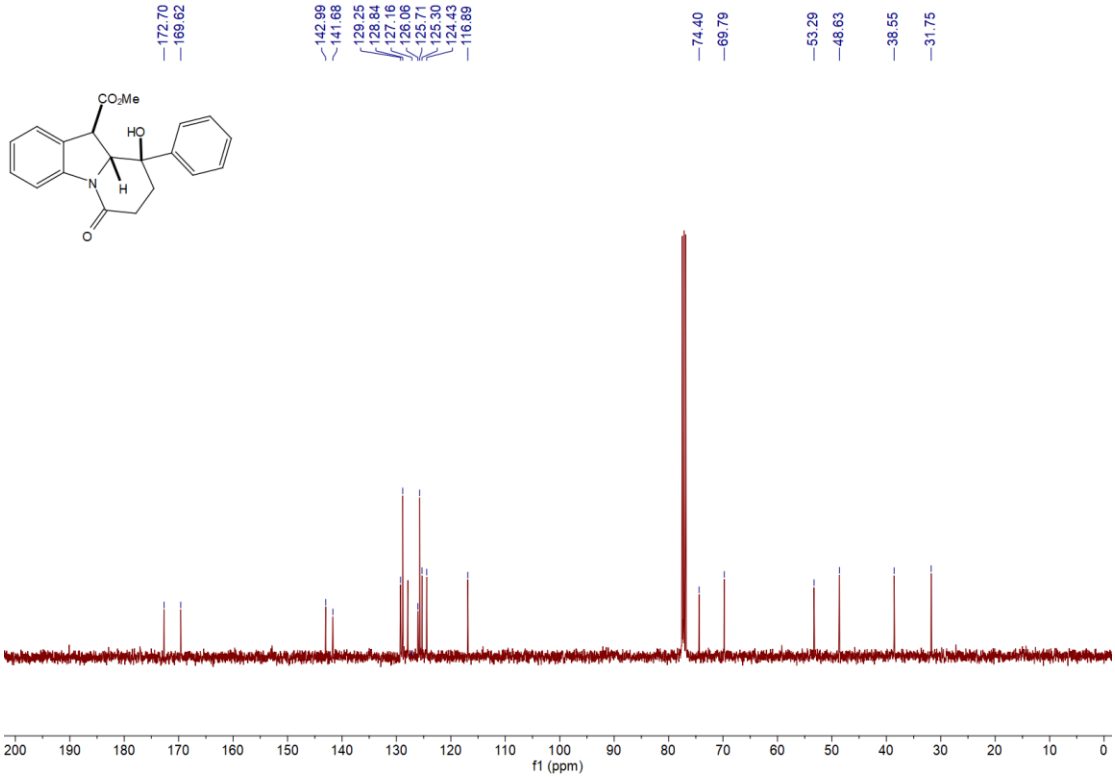
^{13}C NMR Spectrum of **2u**



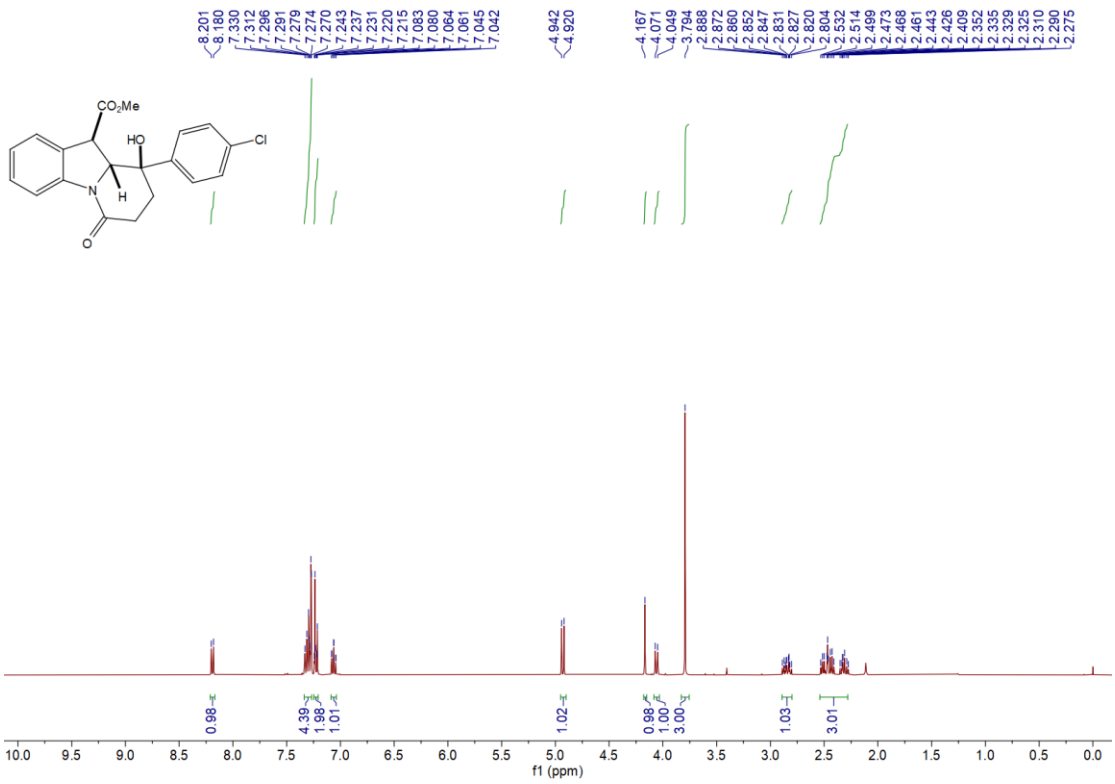
^{1}H NMR Spectrum of **3a**



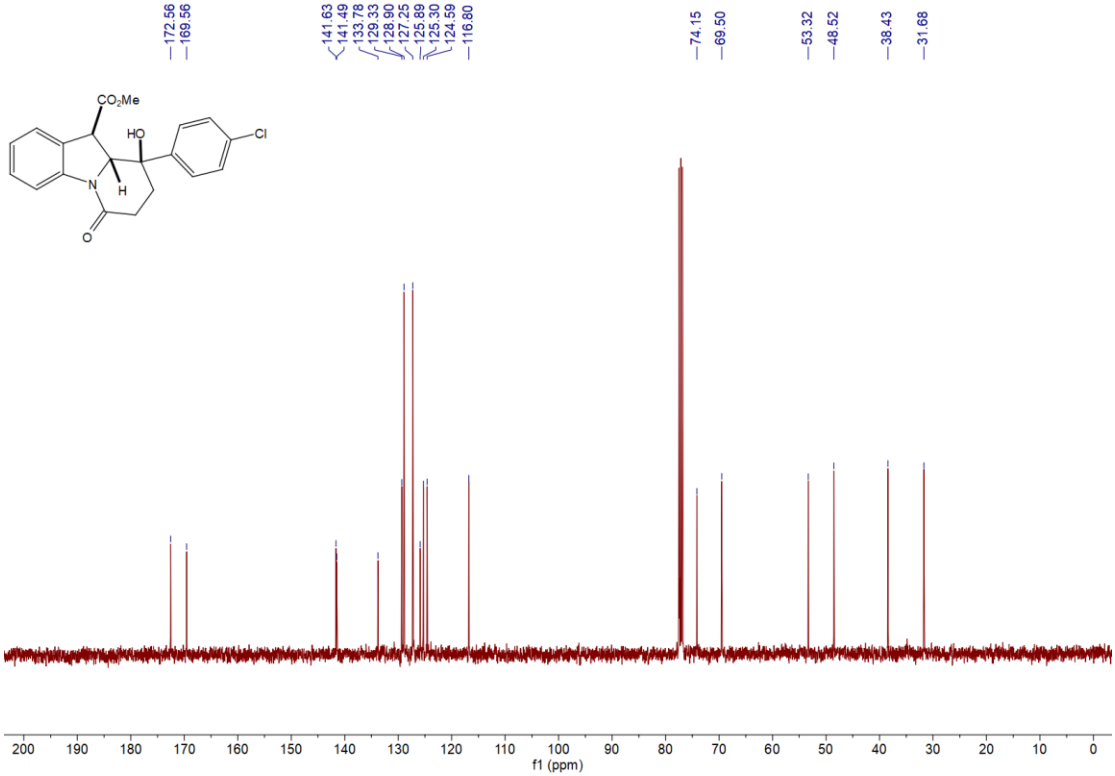
^{13}C NMR Spectrum of **3a**



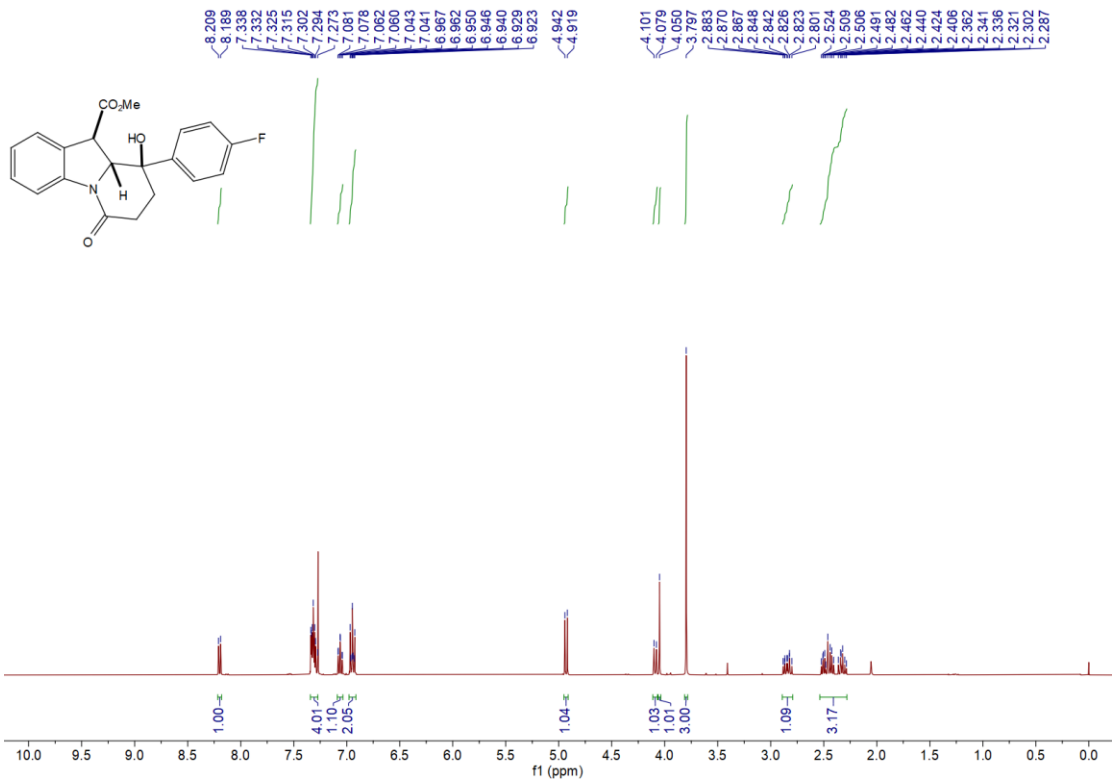
^{1}H NMR Spectrum of **3b**



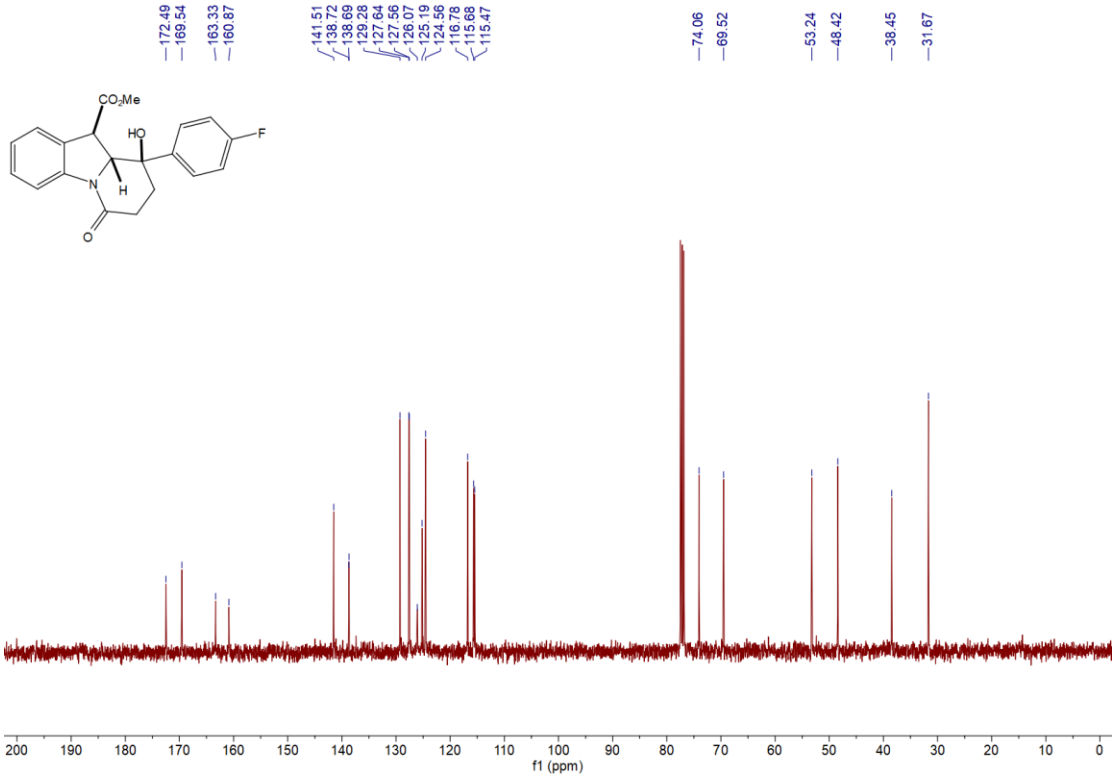
^{13}C NMR Spectrum of **3b**



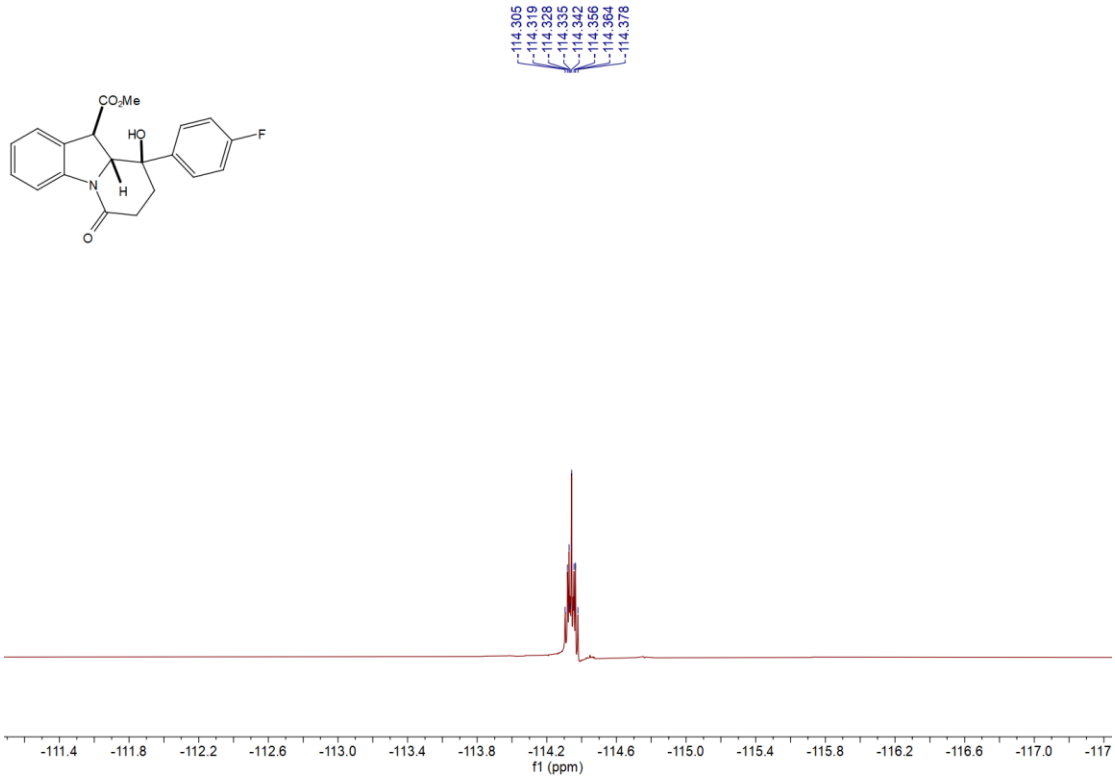
^{1}H NMR Spectrum of **3c**



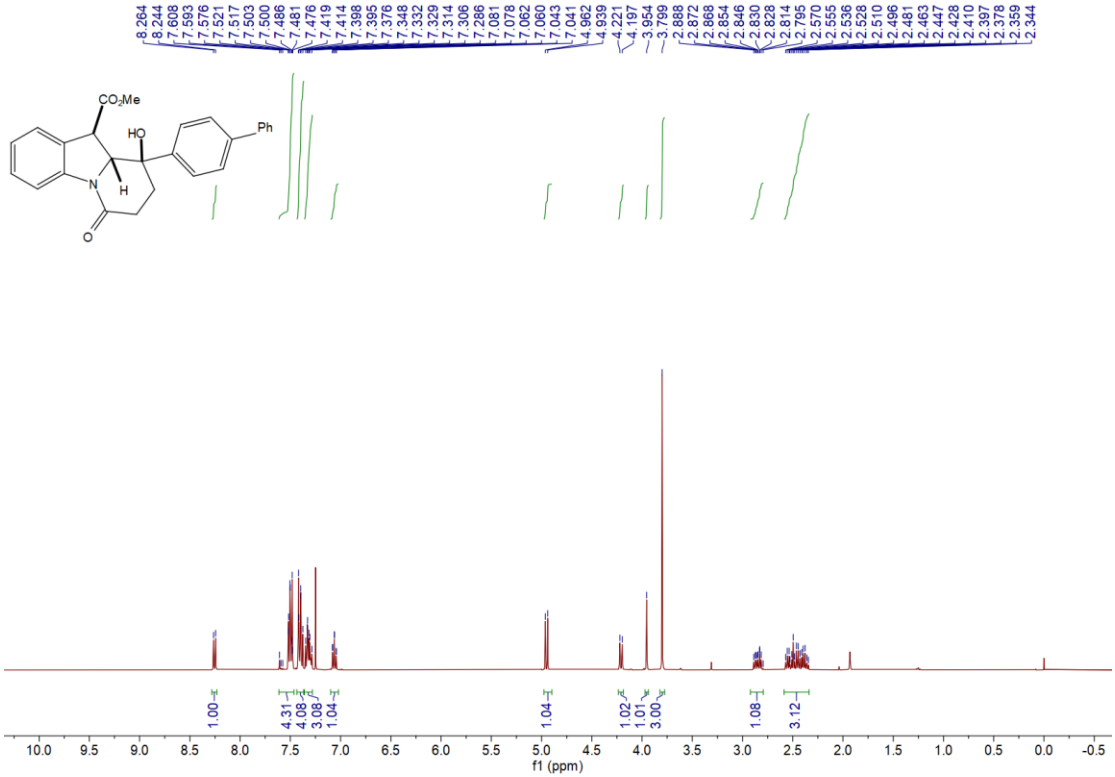
^{13}C NMR Spectrum of **3c**



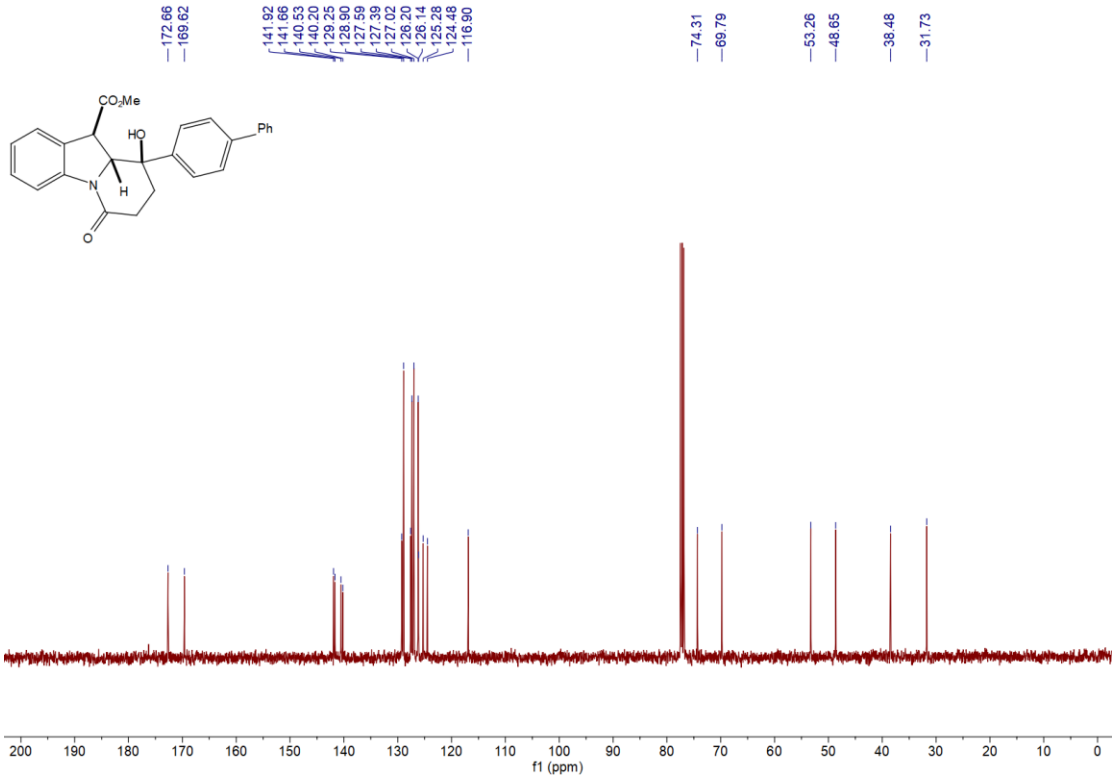
^{19}F NMR Spectrum of **3c**



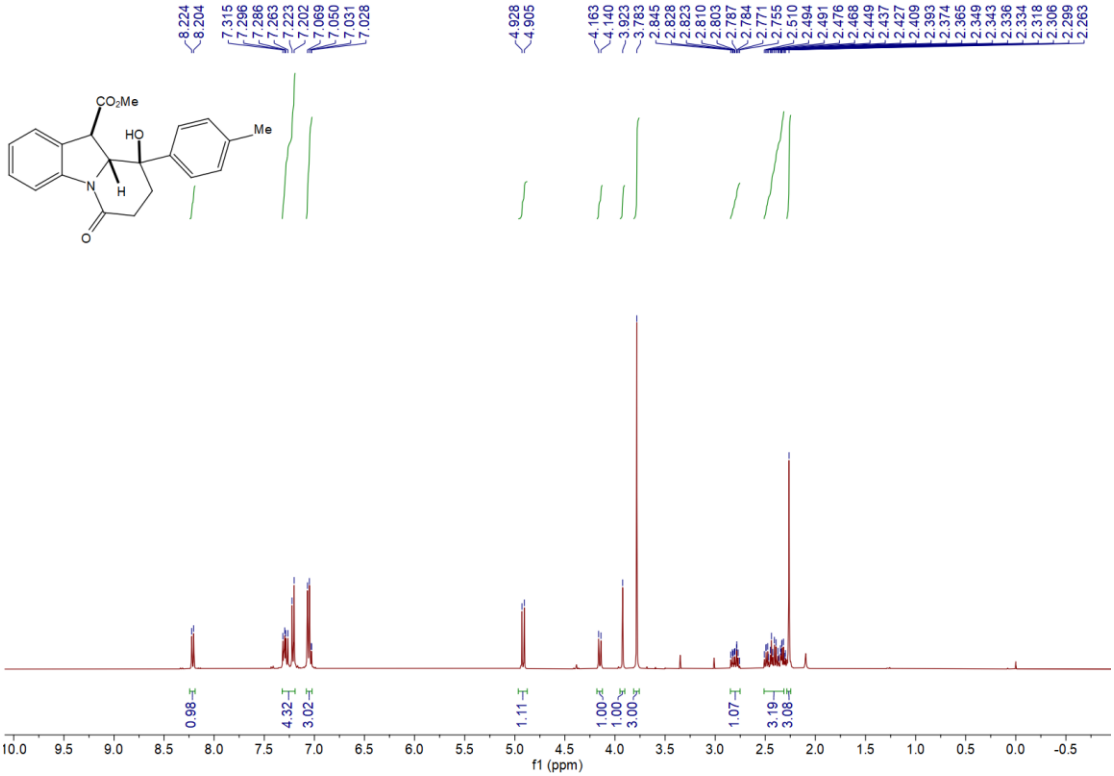
^{1}H NMR Spectrum of **3d**



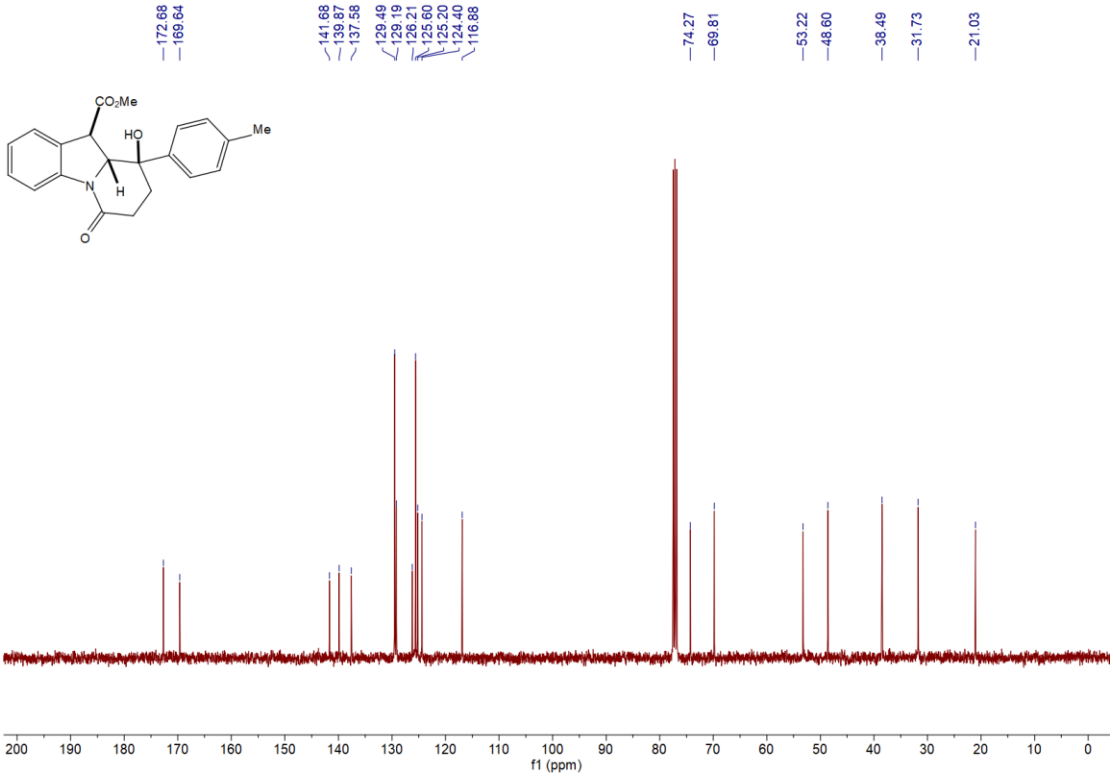
^{13}C NMR Spectrum of **3d**



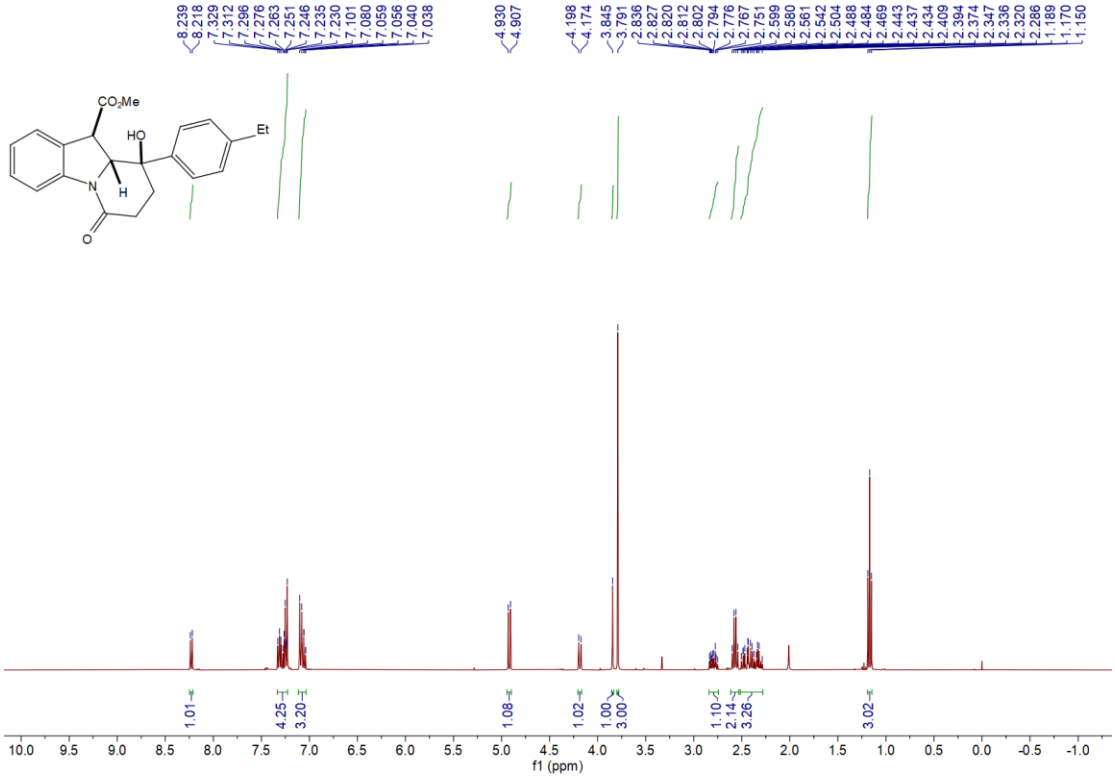
^{1}H NMR Spectrum of **3e**



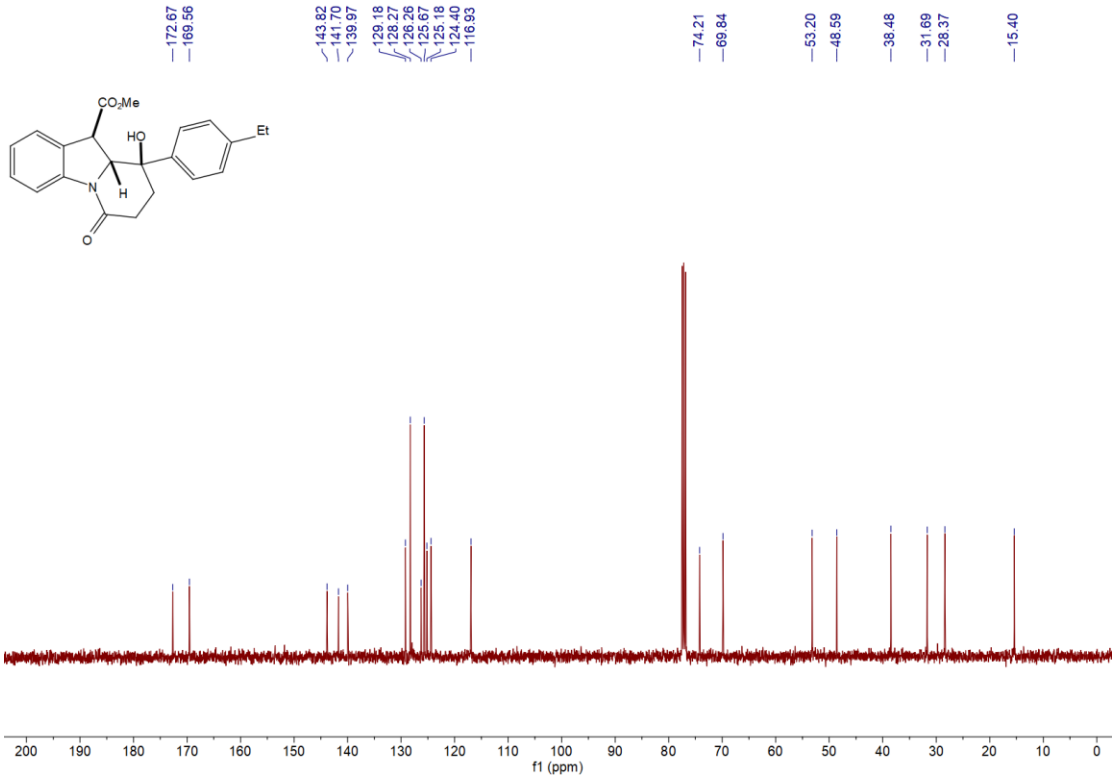
^{13}C NMR Spectrum of **3e**



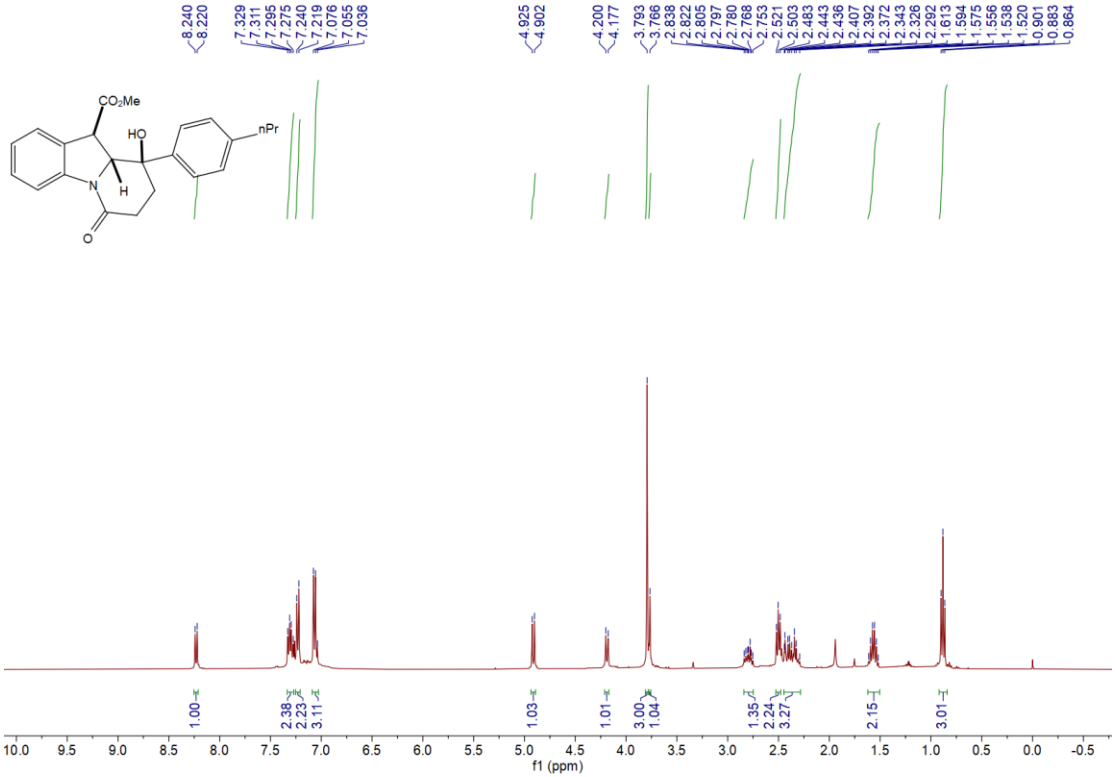
^{1}H NMR Spectrum of **3f**



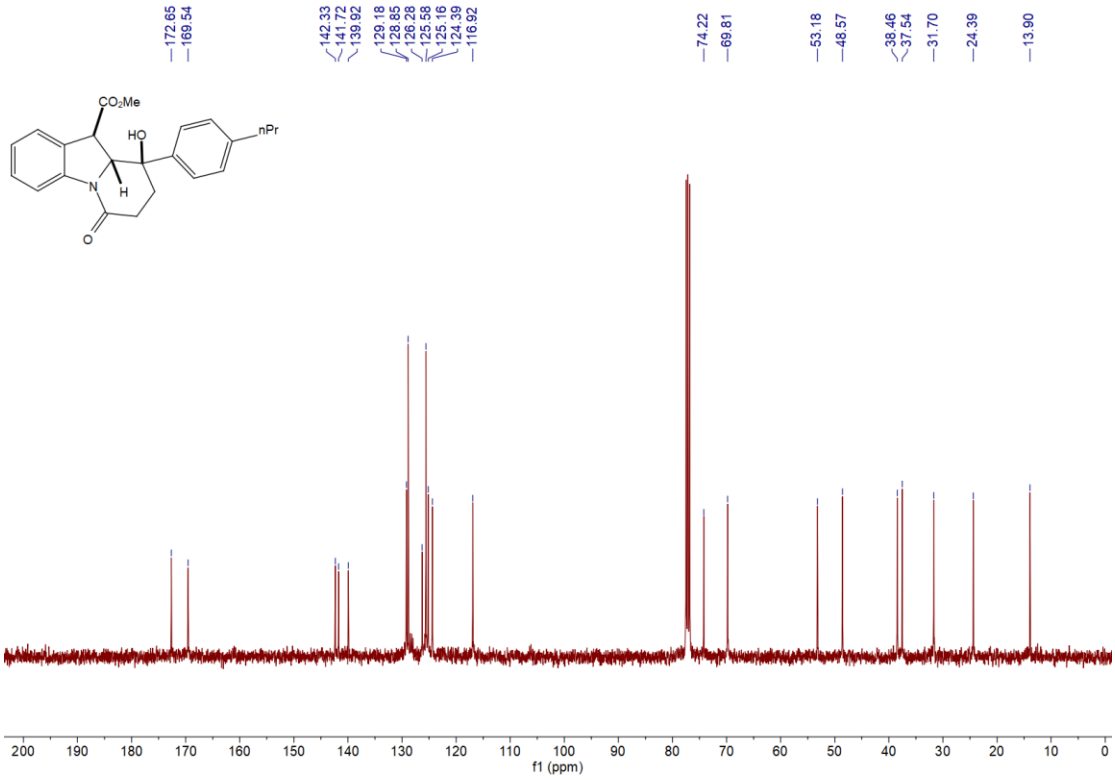
^{13}C NMR Spectrum of **3f**



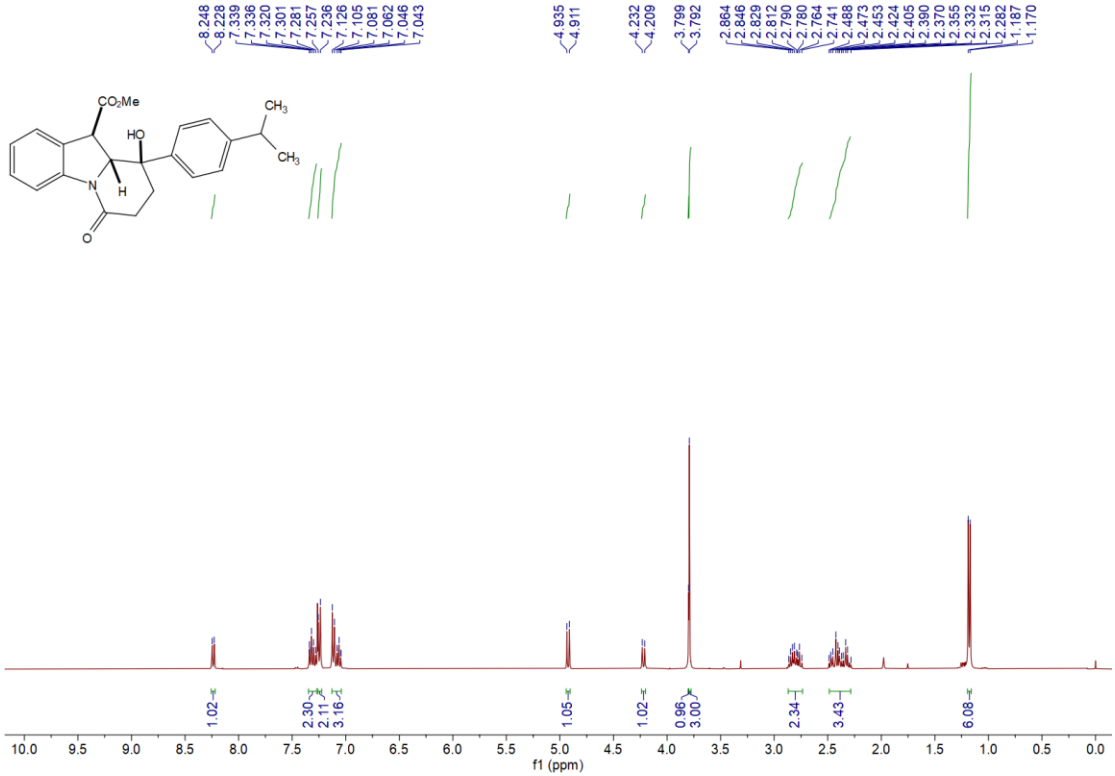
^{1}H NMR Spectrum of **3g**



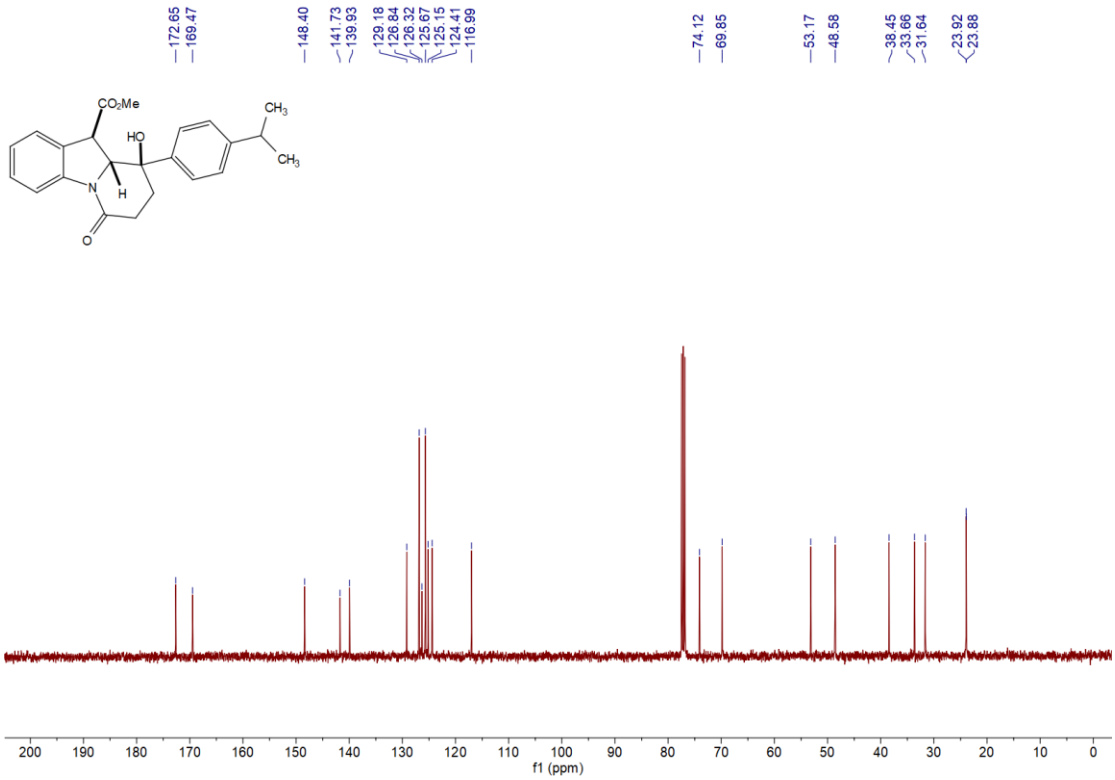
^{13}C NMR Spectrum of **3g**



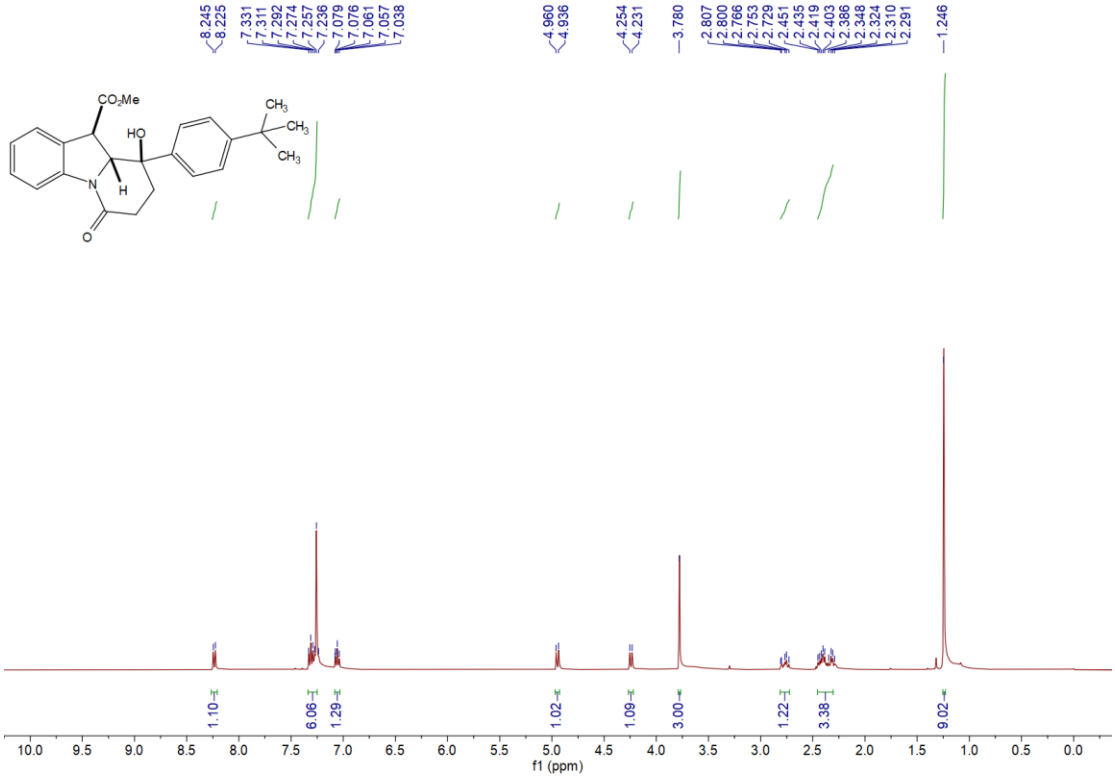
^{1}H NMR Spectrum of **3h**



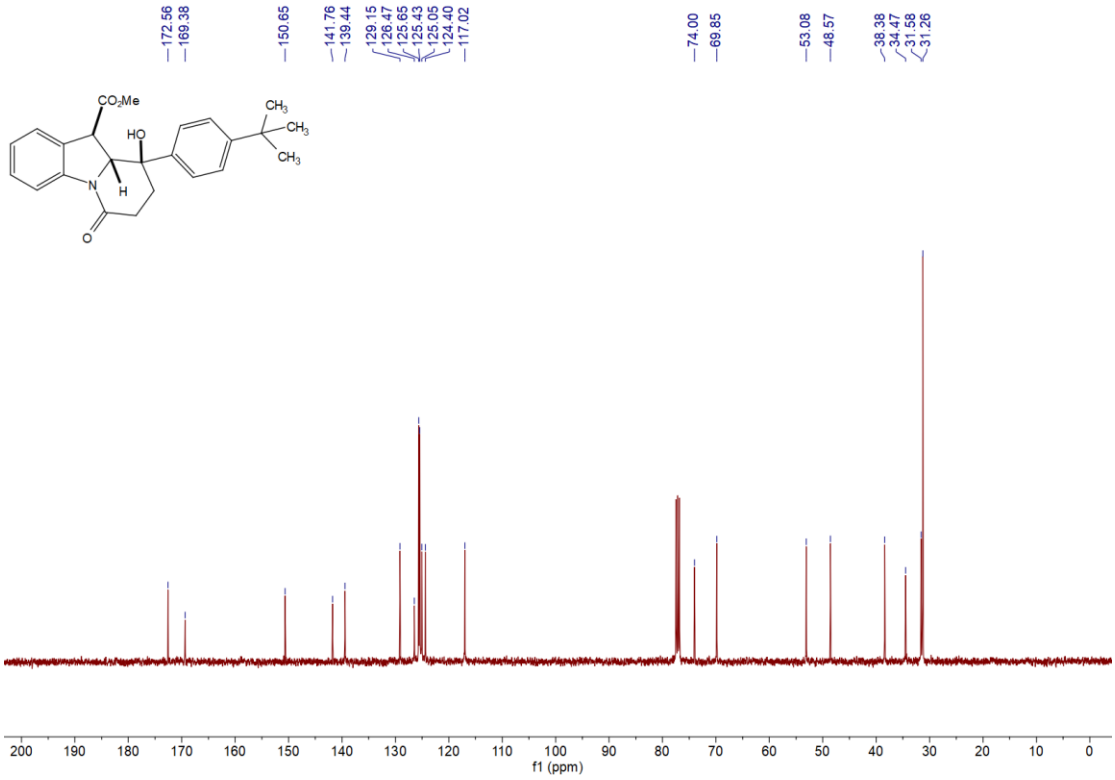
^{13}C NMR Spectrum of **3h**



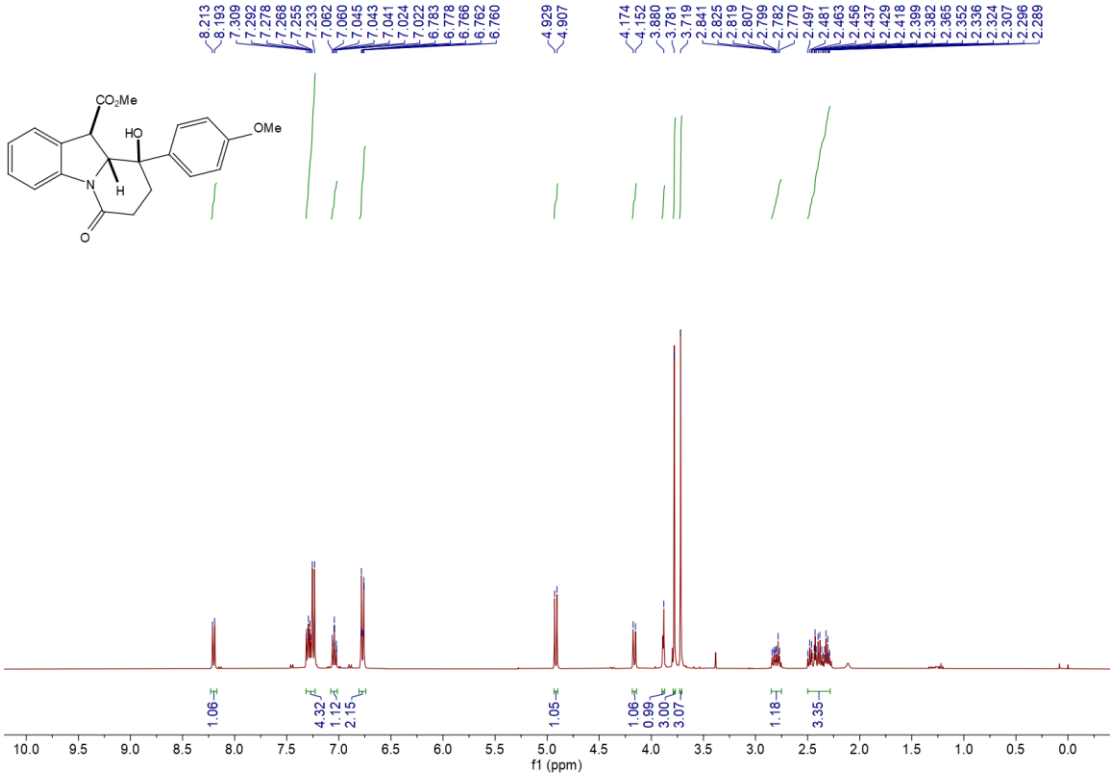
^{1}H NMR Spectrum of **3i**



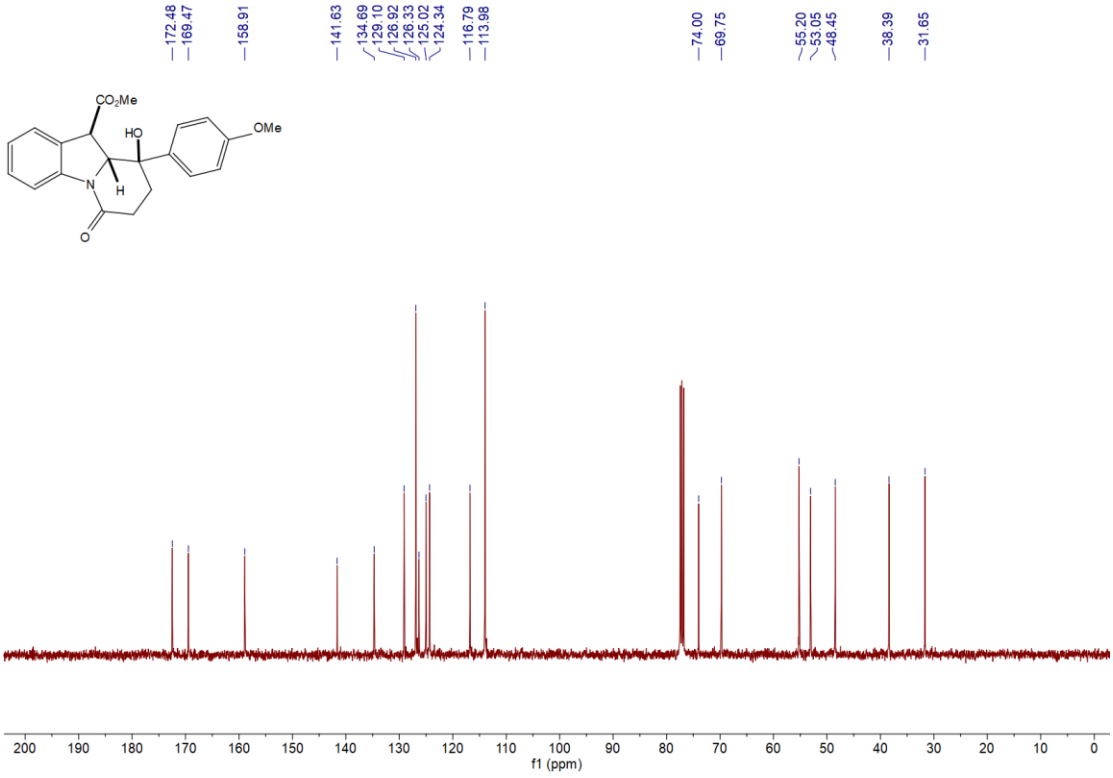
^{13}C NMR Spectrum of **3i**



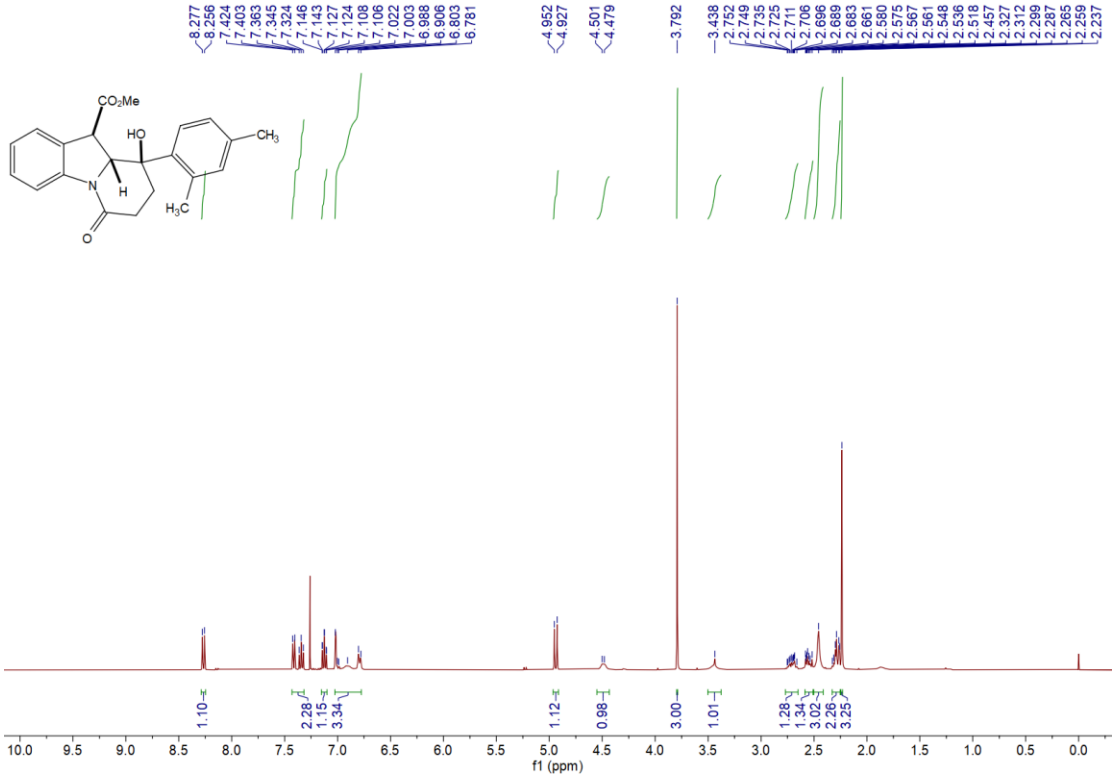
^{1}H NMR Spectrum of **3j**



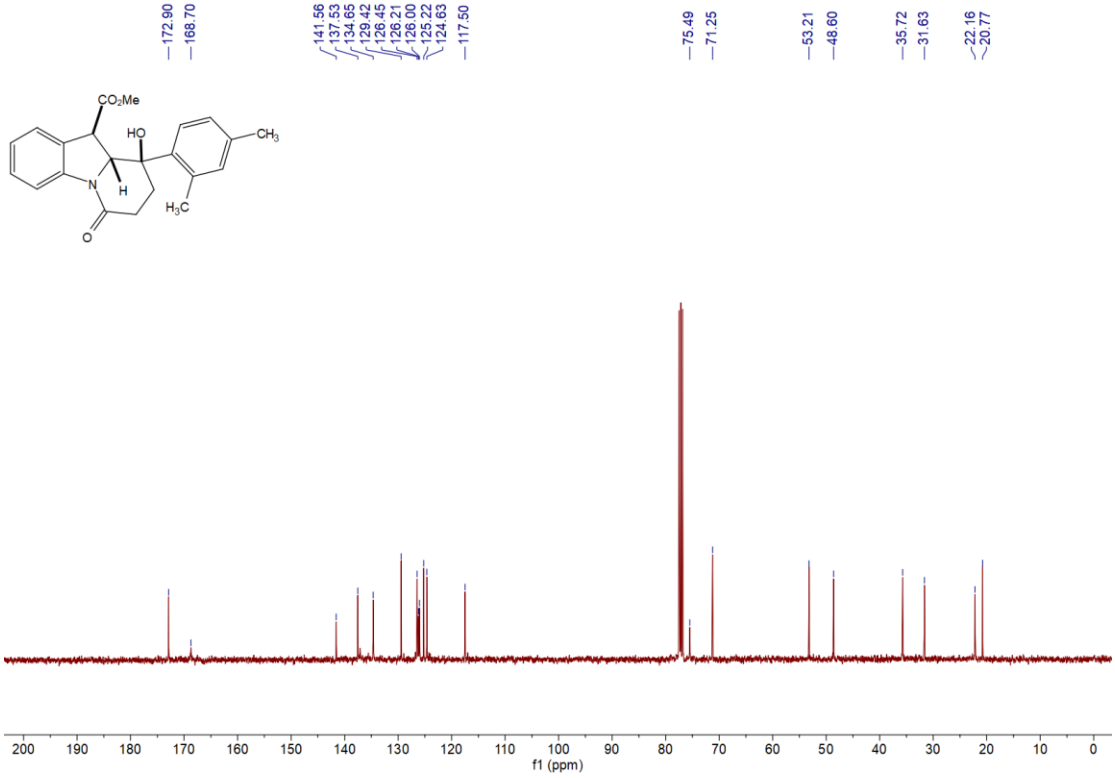
^{13}C NMR Spectrum of **3j**



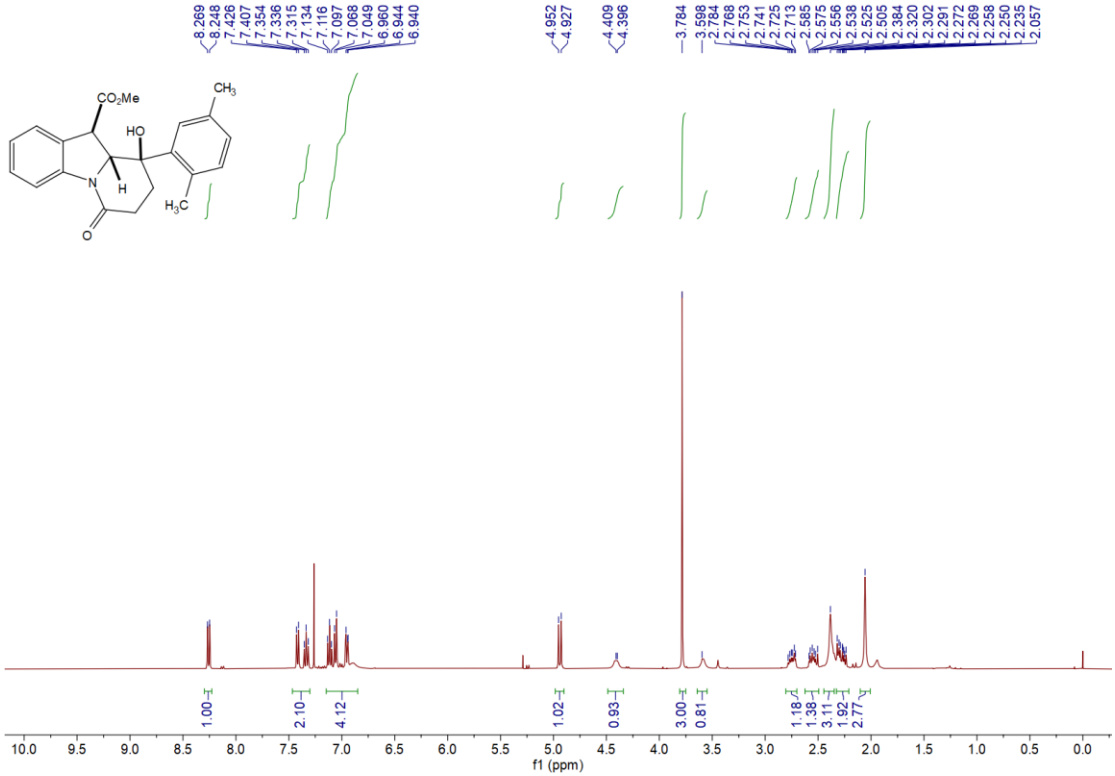
^{1}H NMR Spectrum of **3k**



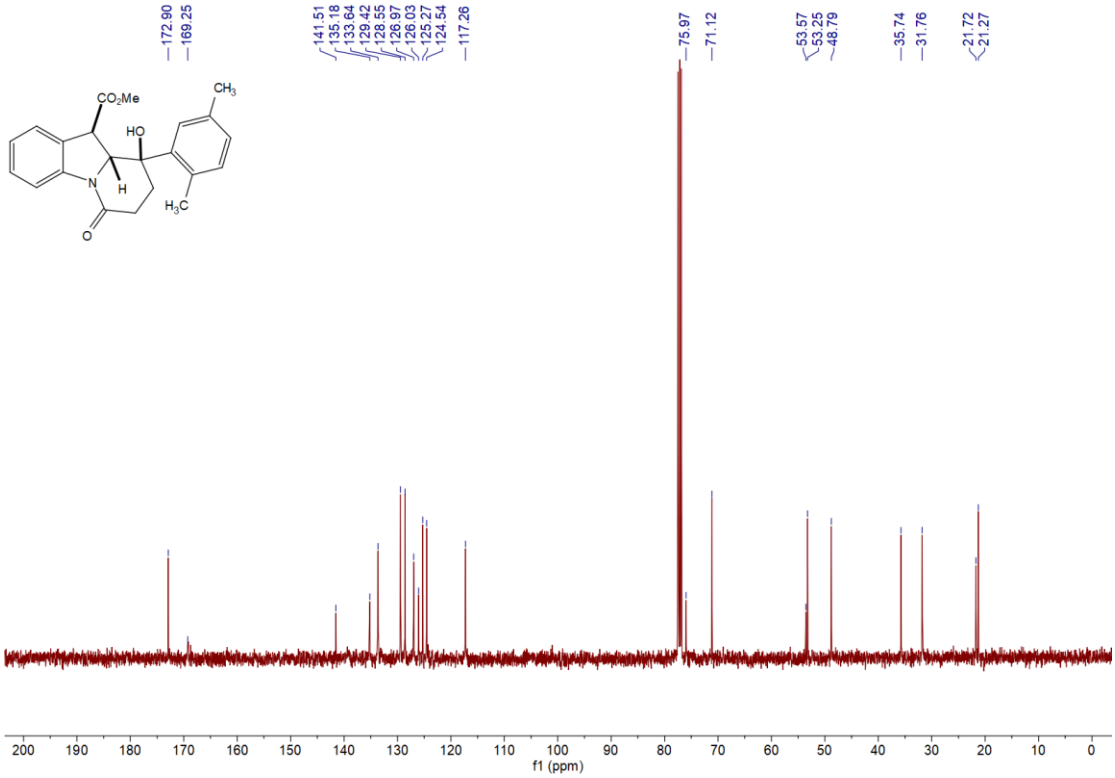
^{13}C NMR Spectrum of **3k**



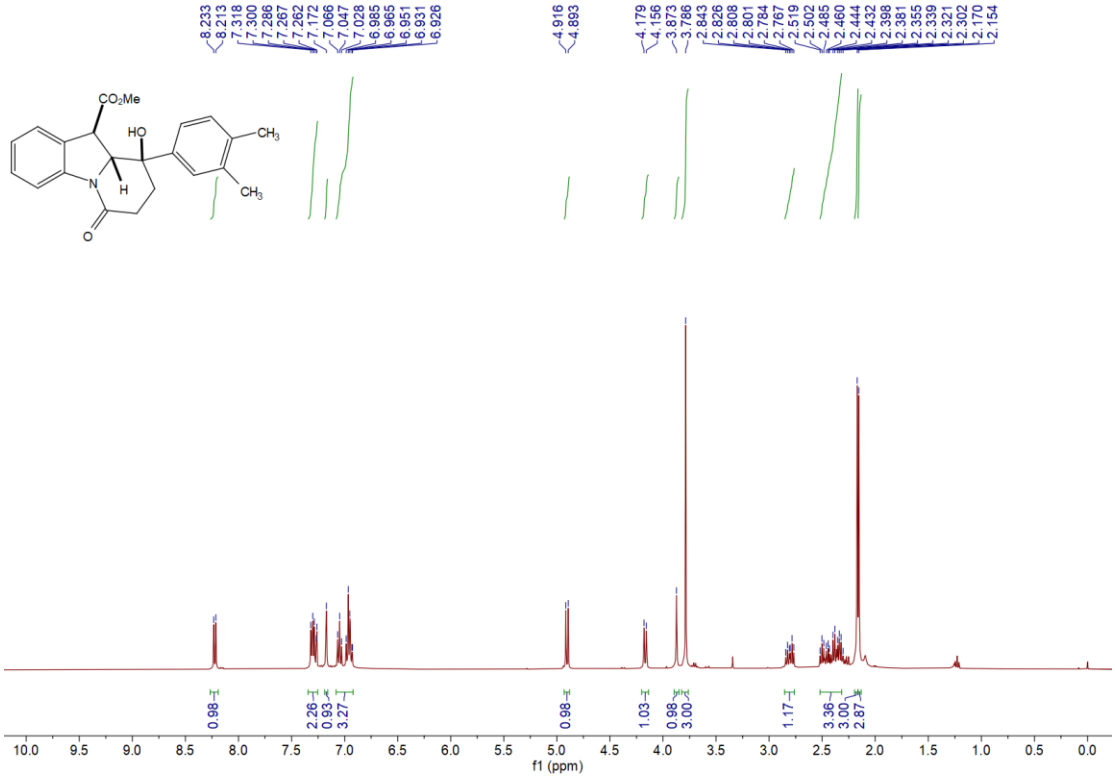
^{1}H NMR Spectrum of **3l**



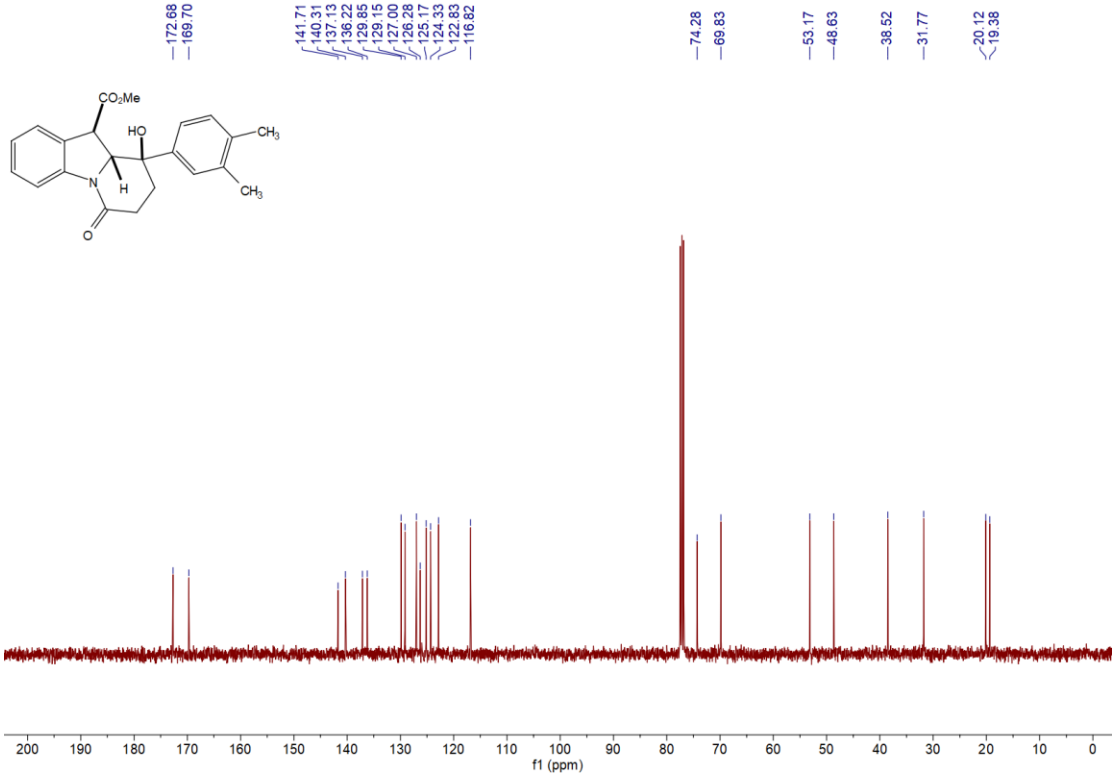
^{13}C NMR Spectrum of **3l**



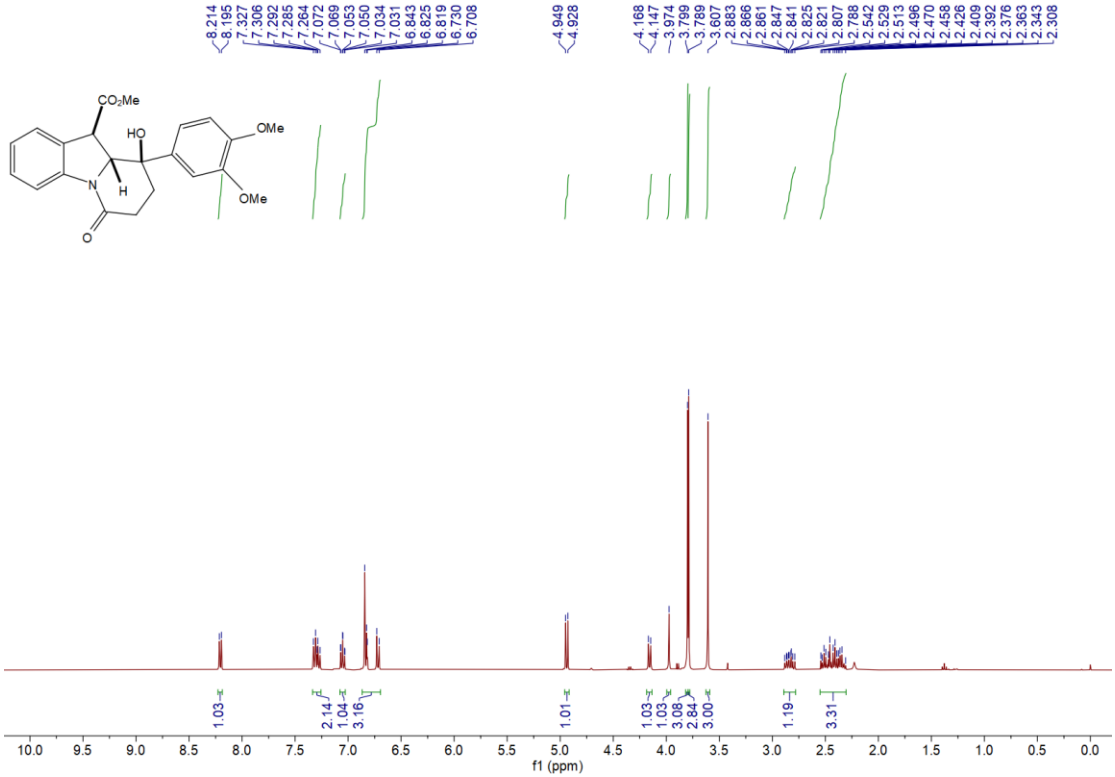
^{1}H NMR Spectrum of **3m**



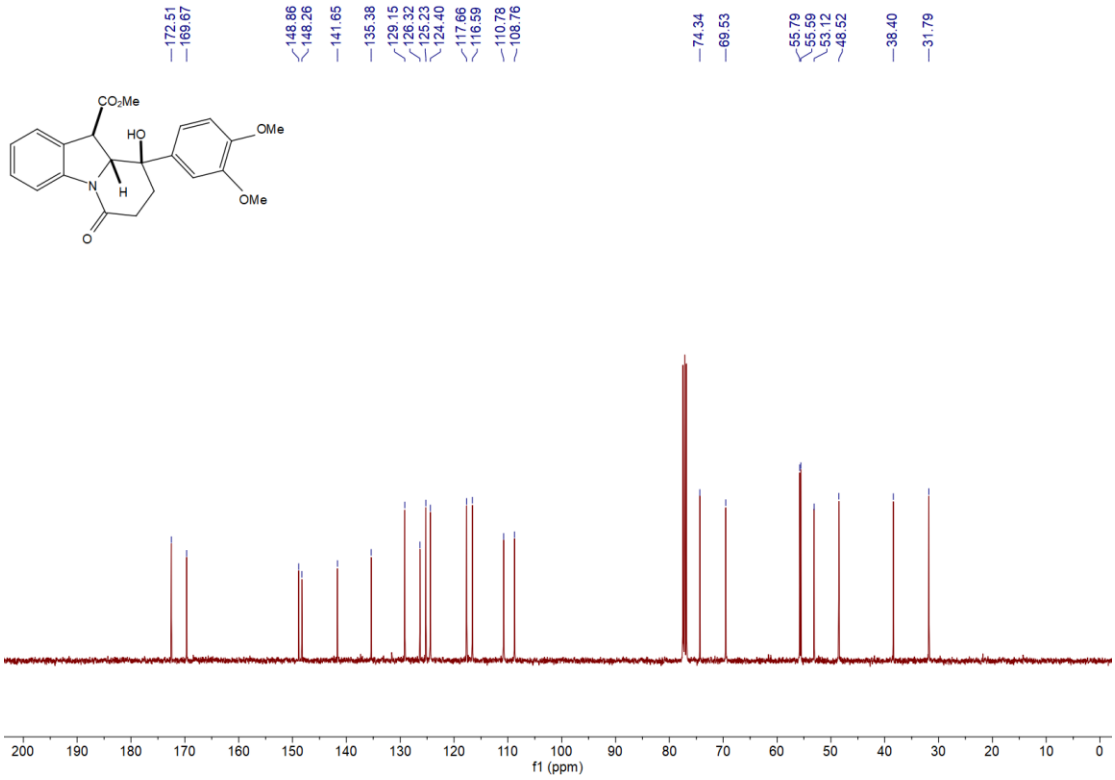
^{13}C NMR Spectrum of **3m**



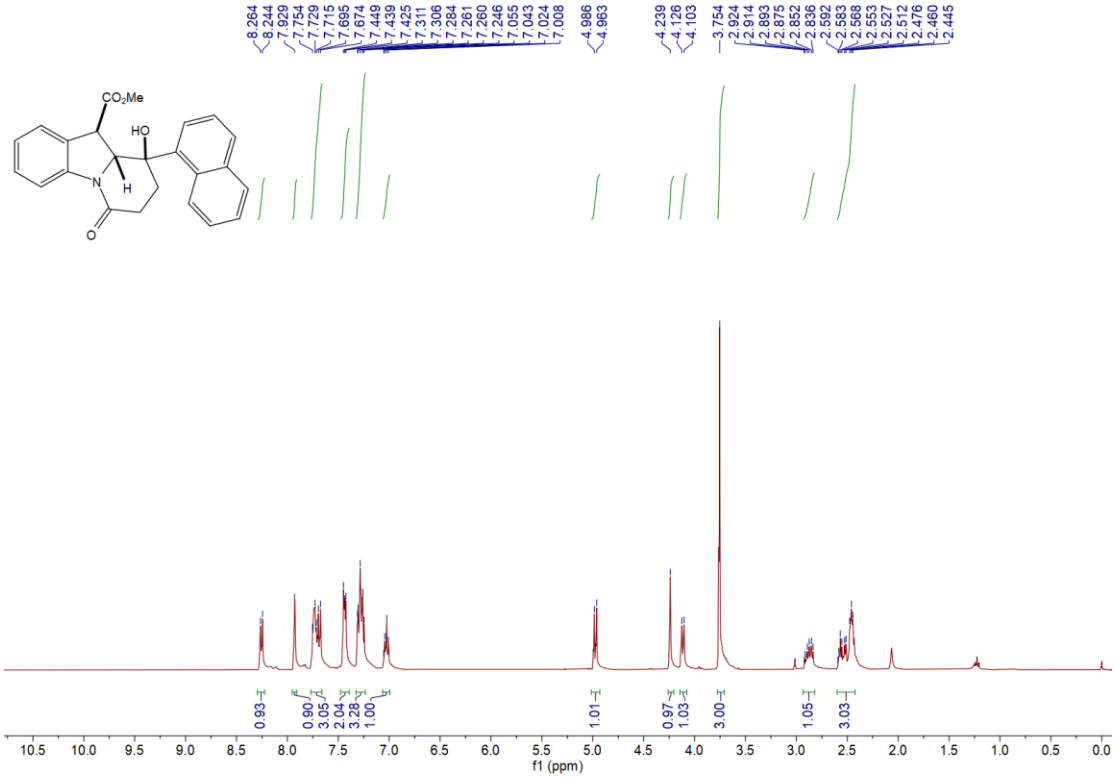
^{1}H NMR Spectrum of **3n**



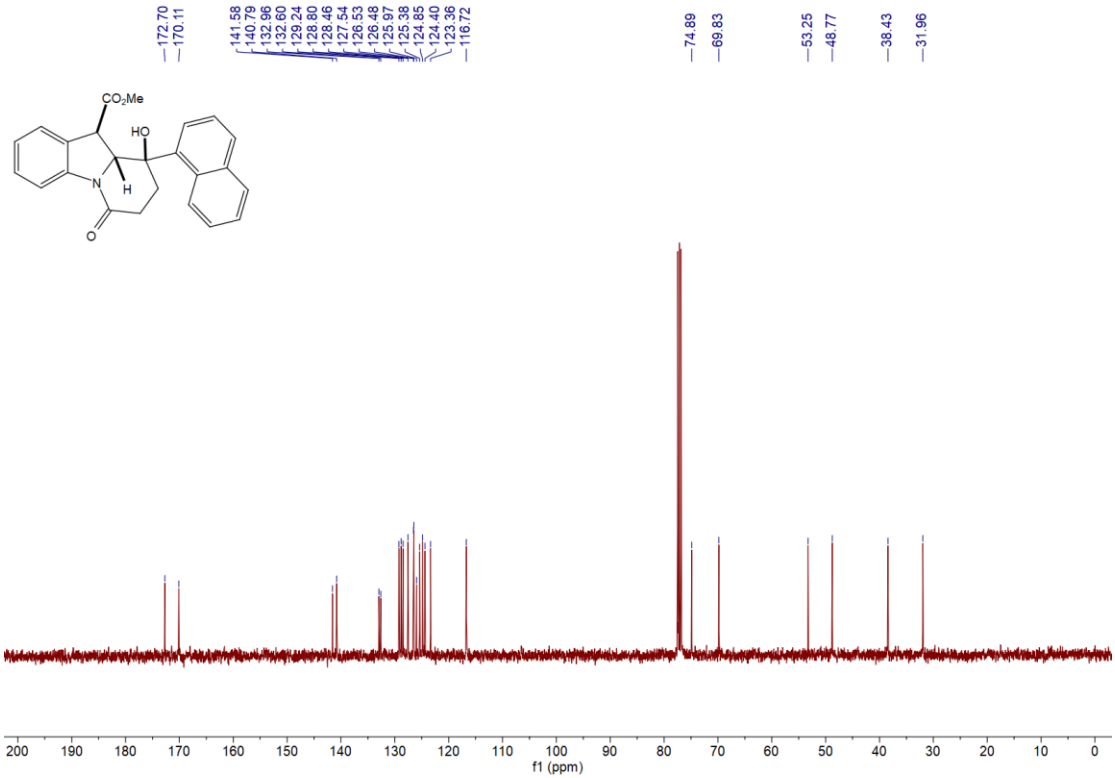
^{13}C NMR Spectrum of **3n**



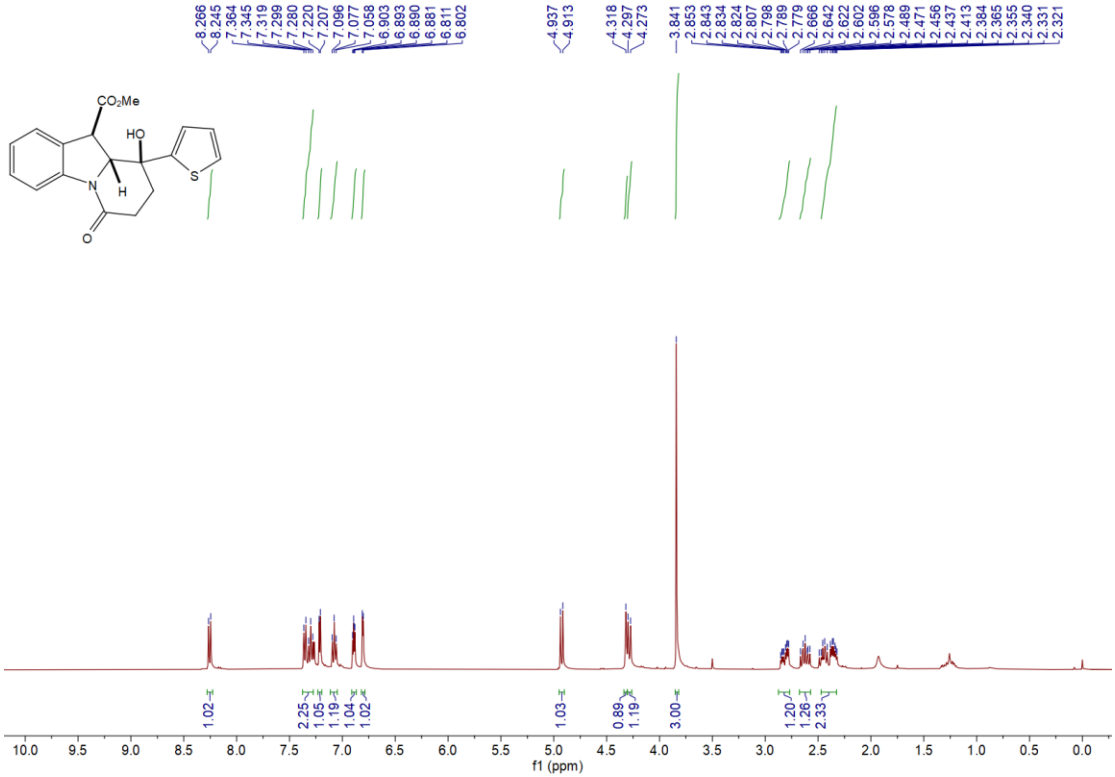
^{1}H NMR Spectrum of **3o**



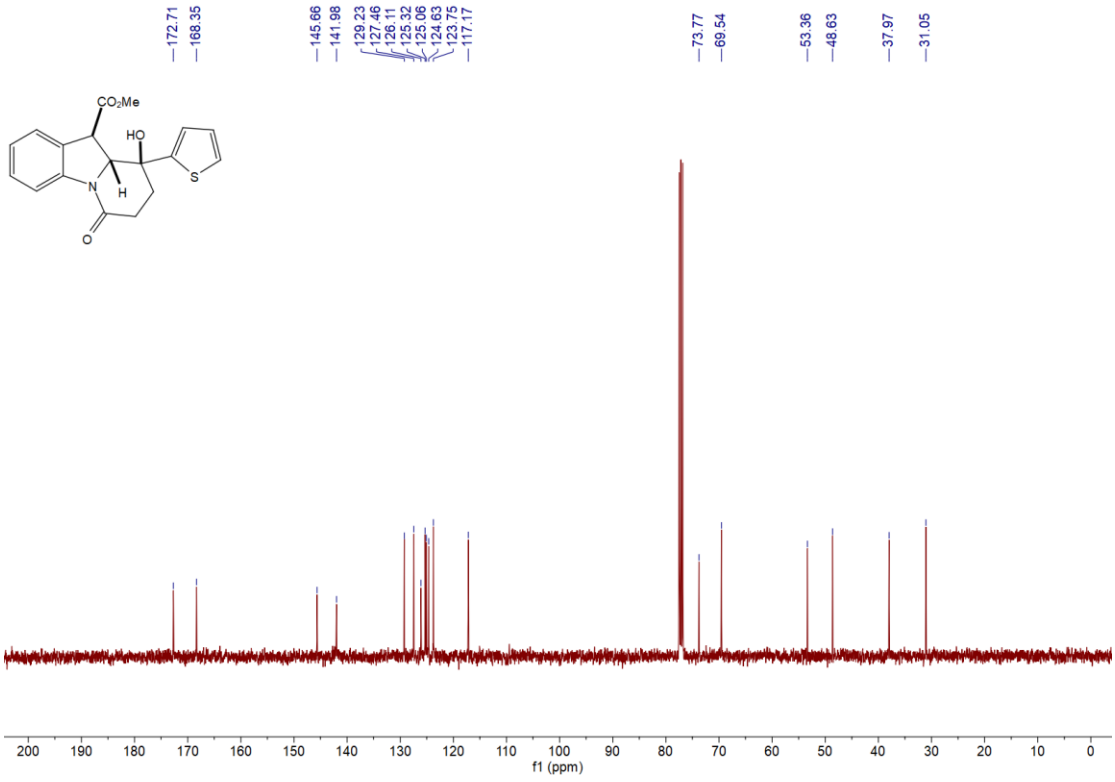
^{13}C NMR Spectrum of **3o**



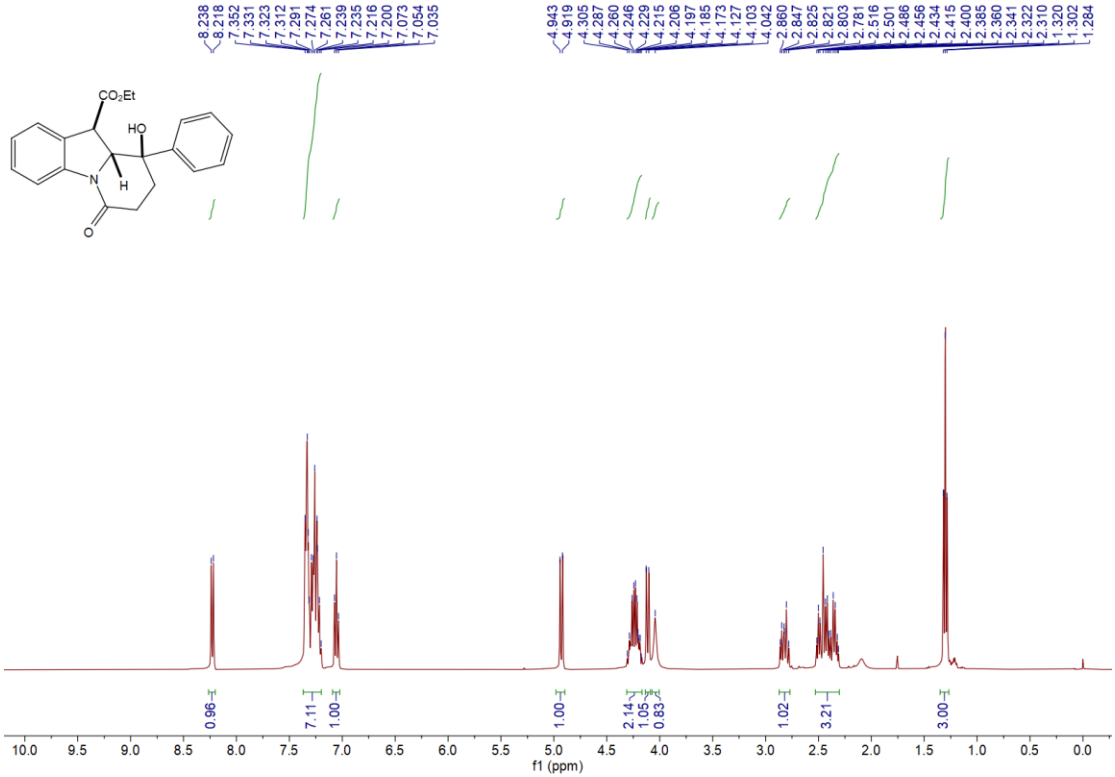
^{1}H NMR Spectrum of **3p**



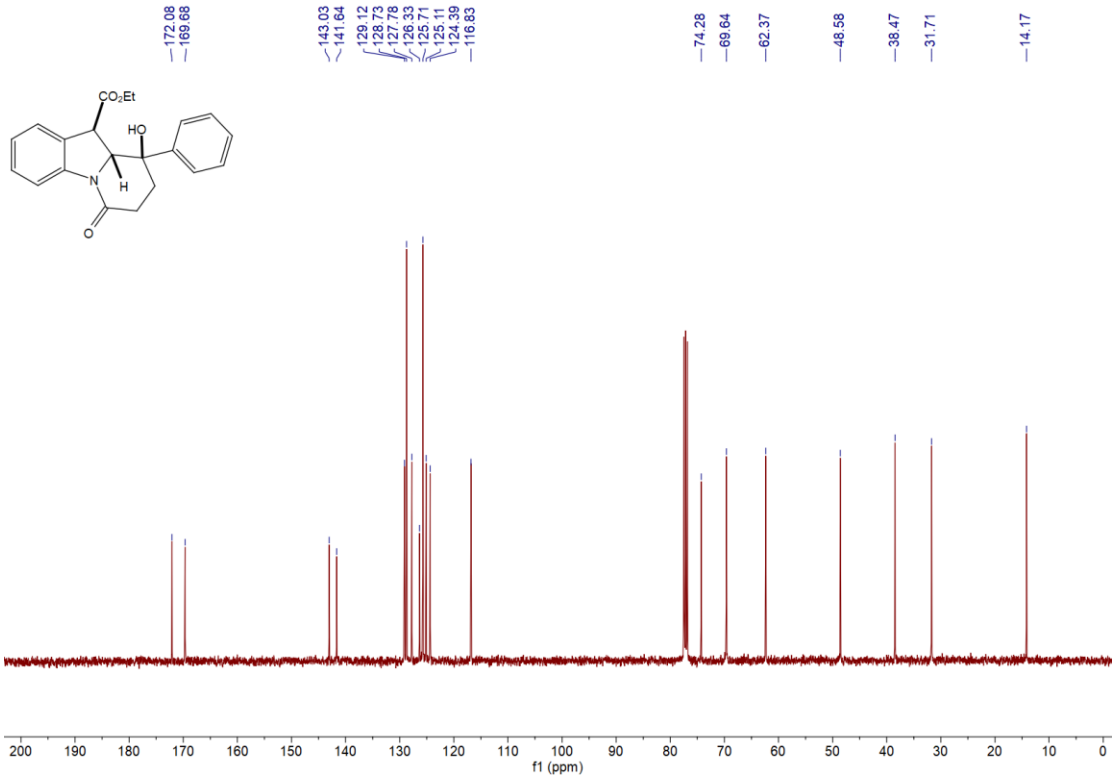
^{13}C NMR Spectrum of **3p**



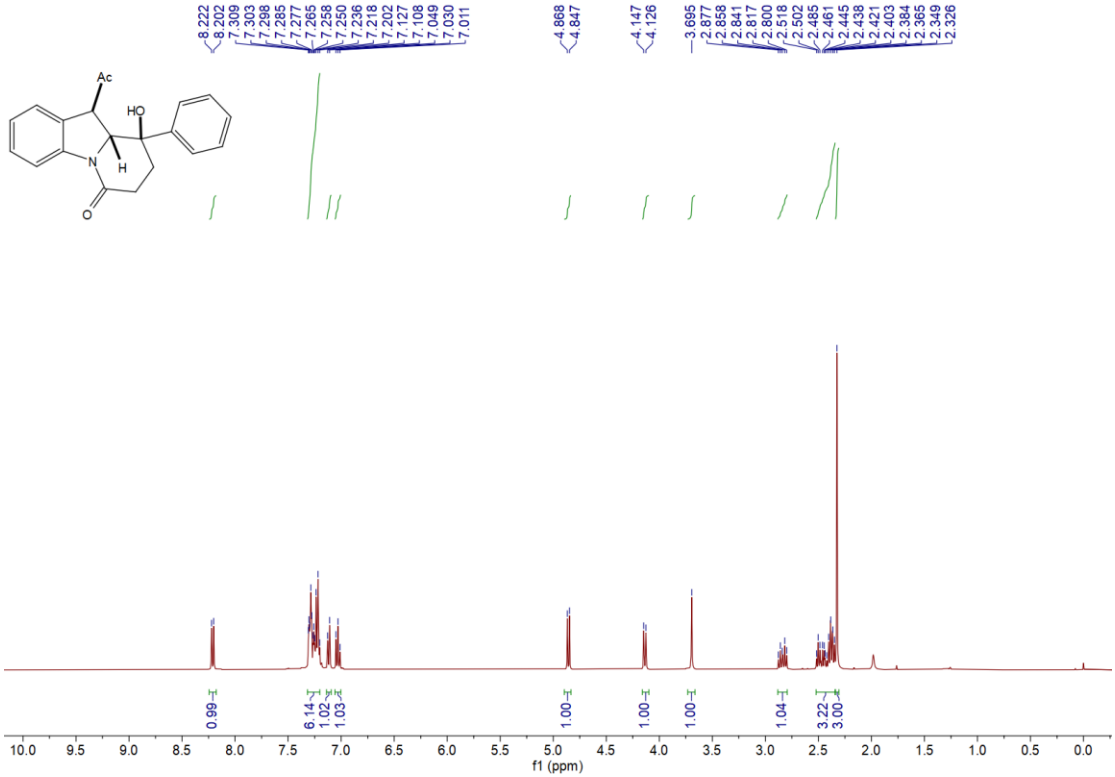
^{1}H NMR Spectrum of **3q**



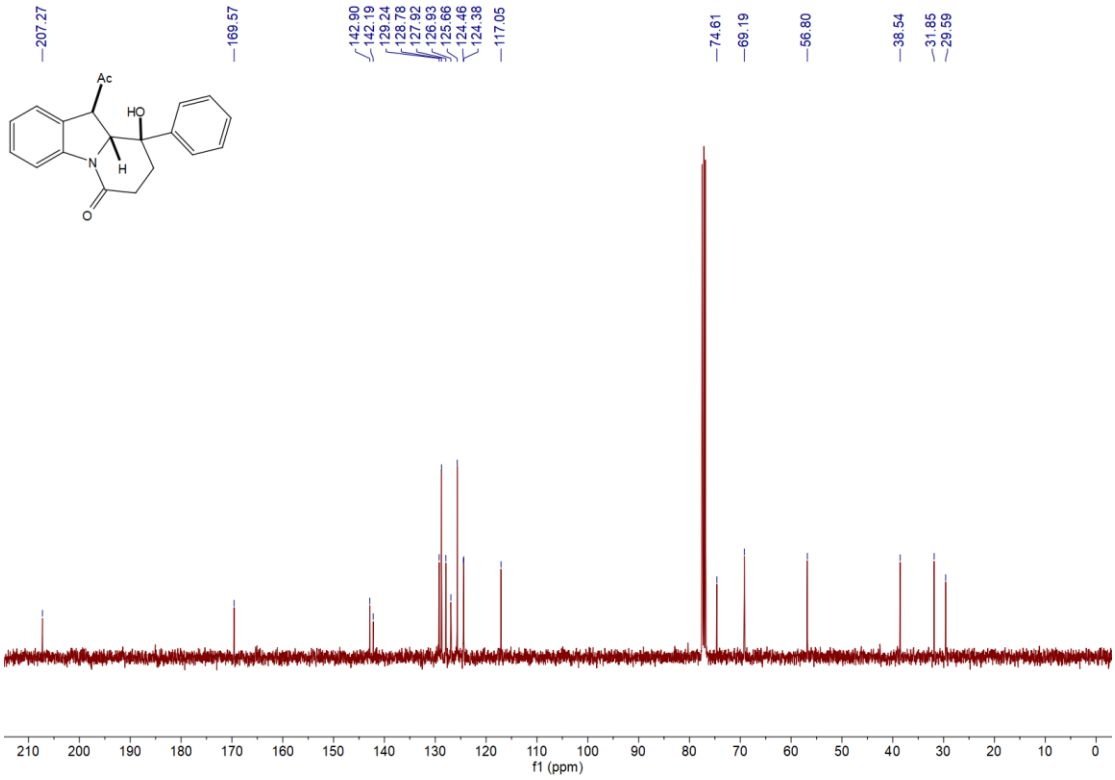
^{13}C NMR Spectrum of **3q**



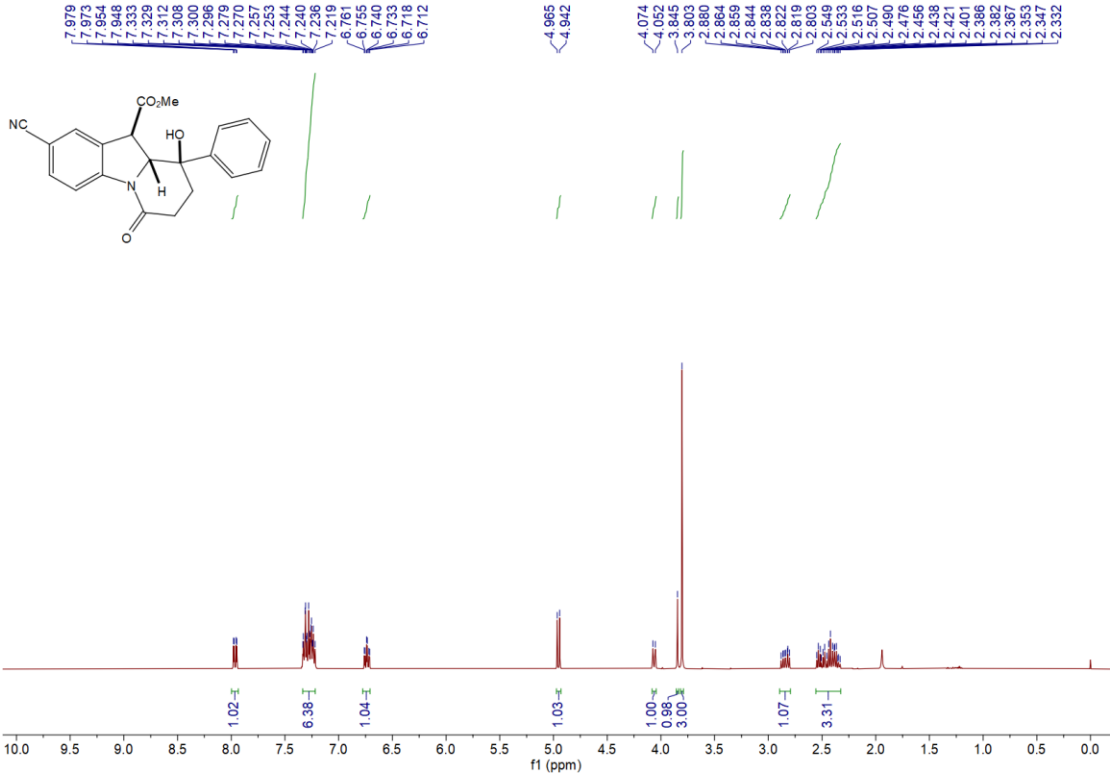
^{1}H NMR Spectrum of **3r**



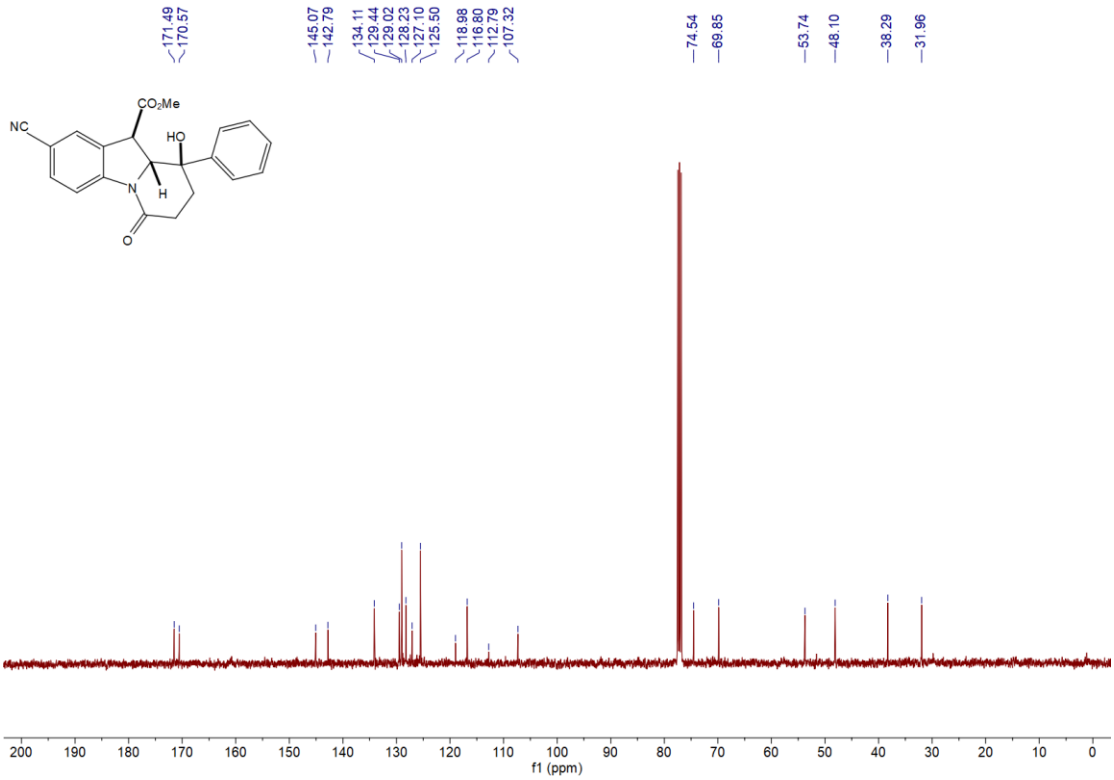
^{13}C NMR Spectrum of **3r**



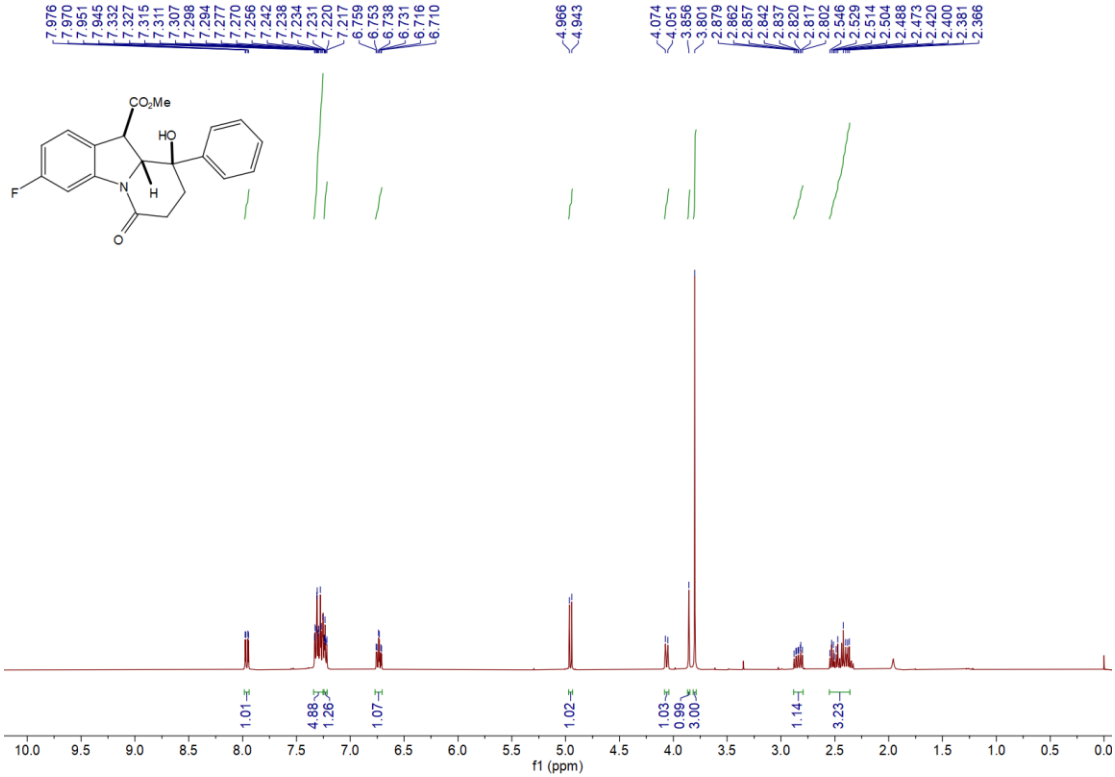
^{1}H NMR Spectrum of **3s**



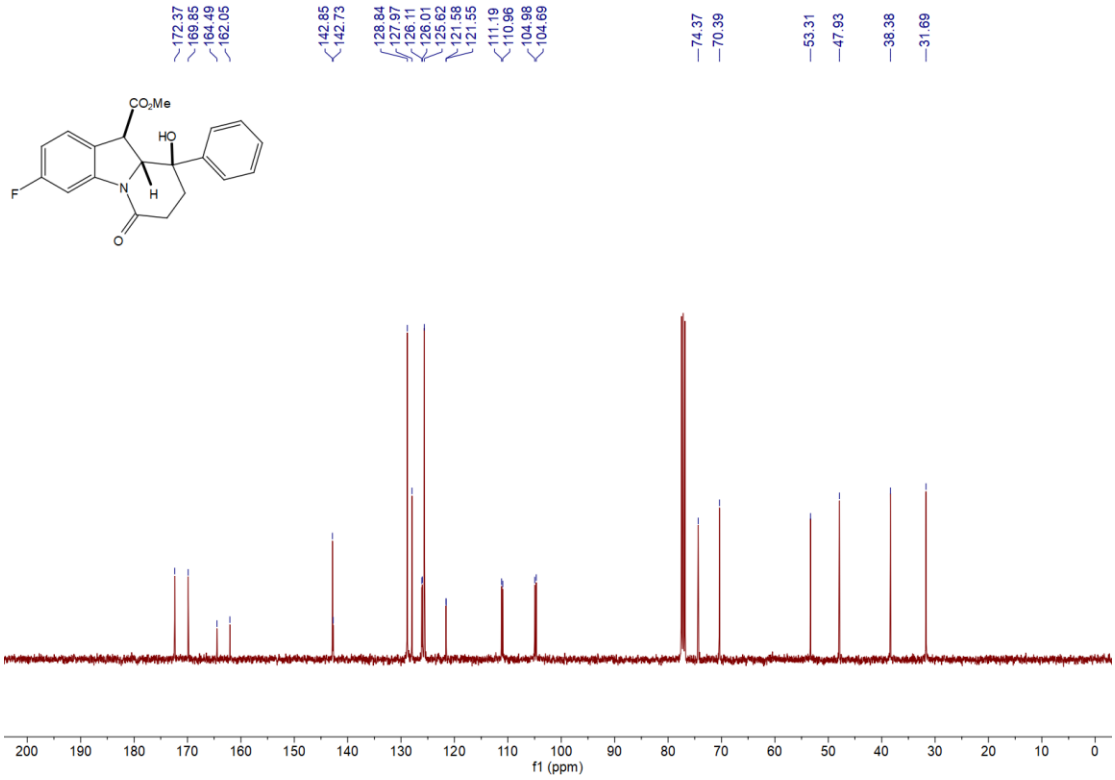
^{13}C NMR Spectrum of **3s**



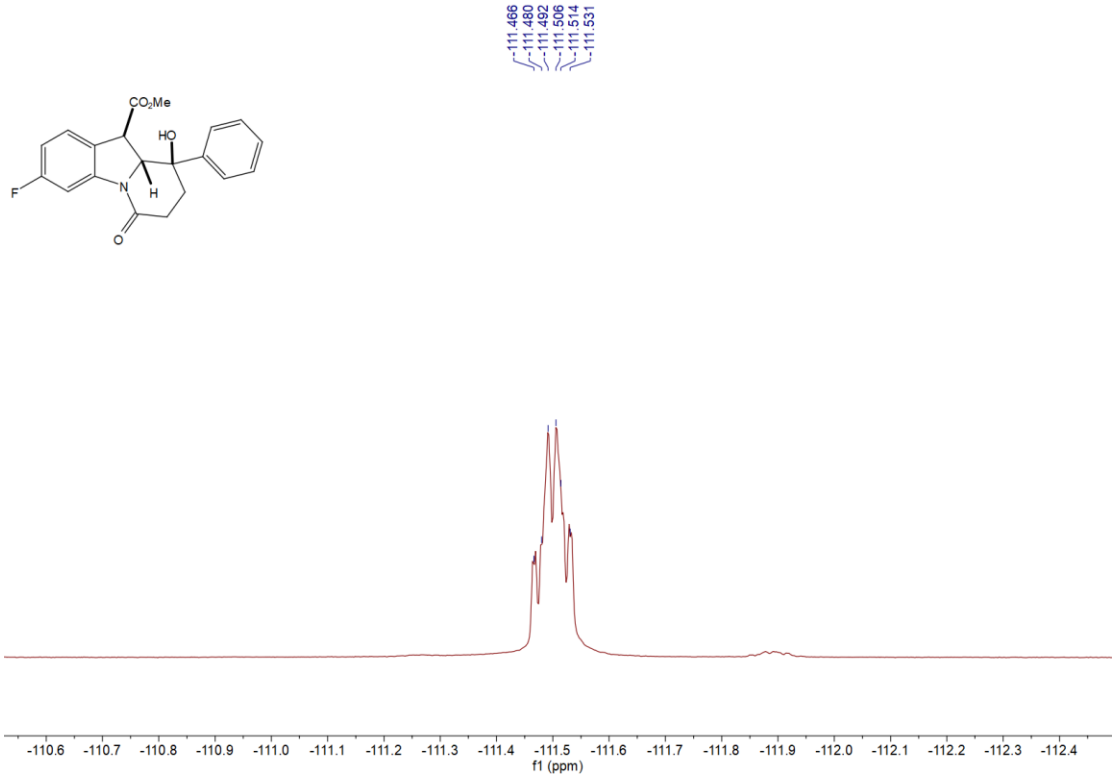
^{1}H NMR Spectrum of **3t**



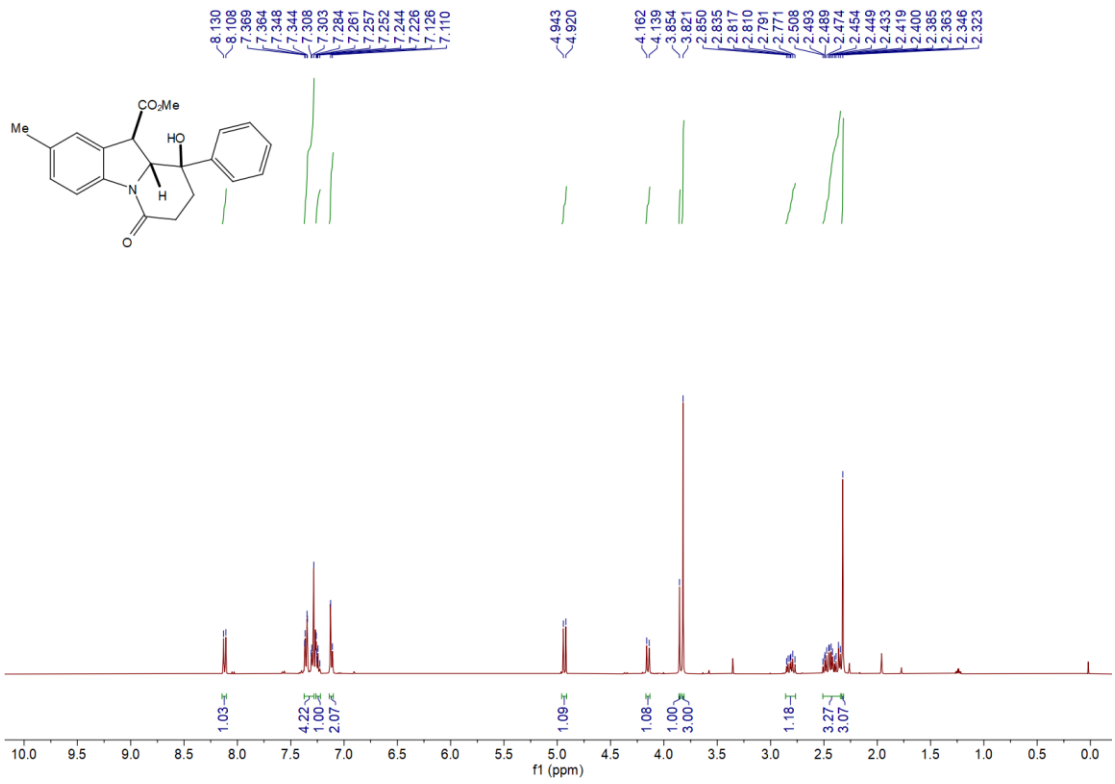
^{13}C NMR Spectrum of **3t**



^{19}F NMR Spectrum of **3t**



^{1}H NMR Spectrum of **3u**



^{13}C NMR Spectrum of **3u**