Sustainable Preparation of Photoactive Indole-fused Tetracyclic Molecules: A New Class of Organophotocatalysts

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Supporting Information

General Considerations

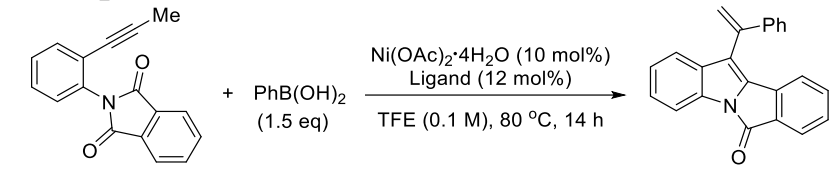
General reagent information

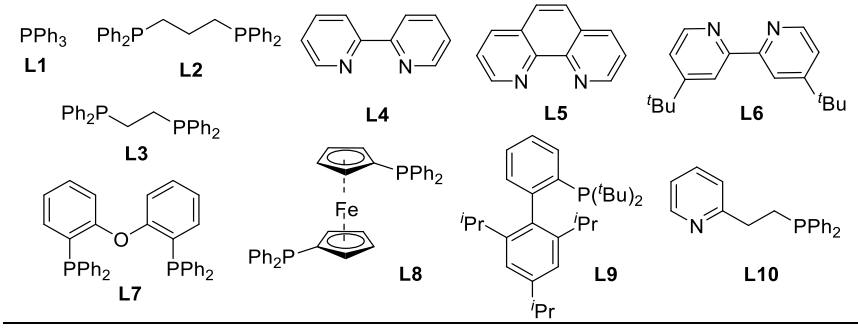
All commercially available reagents including nickel acetate tetrahydrate, arylboronic acids, 2-iodoanilines, phthalic anhydrides, and 2,2,2-trifluoroethanol were purchased from Sigma-Aldrich, Alfa Aesar, Combi blocks or TCI chemical companies and used without further purification. 2-(2-(Diphenylphosphino)ethyl)pyridine (PyPhos) was synthesized according to the known procedure.[S1] Flash column chromatography was performed using ZEOCHEM ZEOprep silica gel 60 (60-200 mesh).

General analytical information

The synthesized phthalimide substrates (**1**) and indole-fused polycylic products (**3**, **5)** were characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR, and 151 MHz for ^{13}C NMR). Copies of ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet 6700 Thermo Scientific FT-IR spectrometer. Reactions were monitored by GC-MS of the crude reaction mixture using dodecane as internal standard and products were detected by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector. Mass spectral data of all unknown compounds were acquired at the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high-resolution mass spectrometer. A quadrupole mass analyzer was used for HRMS measurements. Melting points of unknown compounds were recorded on a Stuart SMP30 apparatus. Single crystal X-ray diffraction data were collected in Bruker-AXS SMART BREEZE X-ray diffractometers. The structures were solved with direct methods using the SHELXL programs. UV−Vis spectra were recorded on a Scinco S-3100 spectrophotometer equipped with a Peltier temperature controller. UV-Vis spectra for Stern-Volmer quenching studies were recorded using PerkinElmer Lamda 25 UV-Vis spectroscopy. Fluorescence spectra were obtained on a PTI QuantaMaster steady-state spectrofluorometer.

Table S1: Full Optimization Table[a]

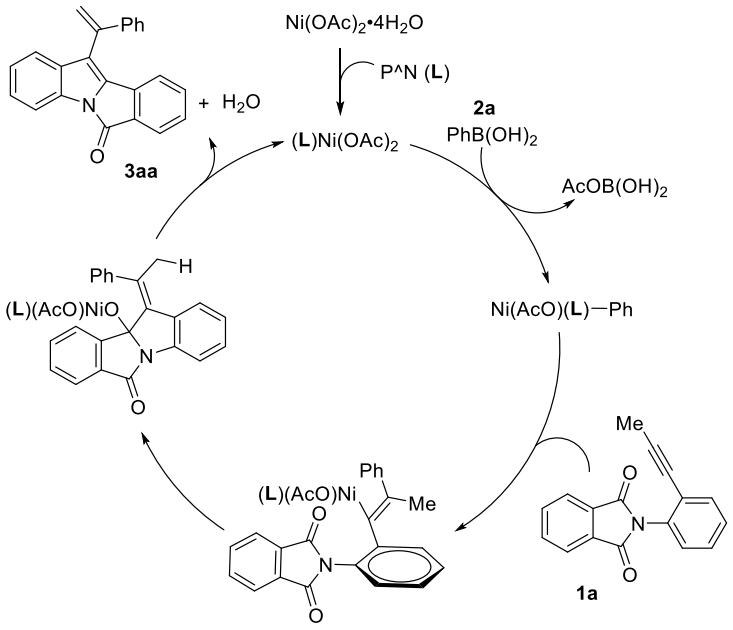




Entry	$Ni(OAc)_2 \cdot 4H_2O$ (X mol%)	Solvent	Ligand	Variations[b]	Yield[c]
1	10 mol%	TFE	L1	-	trace
2	10 mol%	TFE	L2	-	trace
3	10 mol%	TFE	L3	-	trace
4	10 mol%	TFE	L4	-	trace
5	10 mol%	TFE	L5	-	trace
6	10 mol%	TFE	L6	-	trace
7	10 mol%	TFE	L7	-	trace
8	10 mol%	TFE	L8	-	18
9	10 mol%	TFE	L9		N.R
10	10 mol%	TFE	L10	-	91
11	10 mol%	MeCN	L10	-	21
12	10 mol%	DMF	L10	-	10
13	10 mol%	Dioxane	L10	-	9
14	10 mol%	THF	L10	-	17
15	10 mol%	EtOH	L10	-	trace
16	-	TFE	L10	$Cu(OAc)_2$	N.R
17	-	TFE	L10	$Pd(OAc)_2$	N.R
18	-	TFE	L10	$Ni(Cp)_2$	trace
19	-	TFE	L10	$Ni(acac)_2$	41
20	-	TFE	L10	$NiBr_2$	52
21	-	TFE	L10	$Ni(COD)_2$	90
22	10 mol%	TFE	L10	23 °C	7
23	10 mol%	TFE	L10	40 °C	15
24	10 mol%	TFE	L10	60 °C	55
25	5 mol%	TFE	L10	-	91
26	3 mol%	TFE	L10	-	77
27	-	TFE	L10	-	N.R
28	5 mol%	TFE	-	-	N.R
29	5 mol%	TFE	L10	Under air	43

[a]All reactions were carried out at 0.1 mmol scale. [b]Varied catalysts in 10 mol% loading. [c]GC yield using dodecane as an internal standard. N.R: no reaction.

Proposed Mechanism



Scheme S1. Proposed mechanism

Computational Details

All calculations were performed by using the density functional theory (DFT) and time dependent-density functional theory (TD-DFT) with the GAUSSIAN 09 program package.[S2] For the calculation of geometry optimizations, CAM-B3LYP[S3] functional with 6-31G* basis set was used. Frequency calculation was performed for all stationary points to confirm the local minima, thermodynamic parameters including Gibbs free energies at 298 K. After geometry optimization, TD-DFT calculation was conducted using same functional and basis set. For TD calculation, solvent effects were considered at the polarizable continuum model (PCM) method[S4] in acetonitrile solvent (ε = 35.7). All optimized structures, molecular orbitals and electrostatic potential were visualized by CYLview [S5] and GaussView.[S2]

HOMO/LUMO orbital

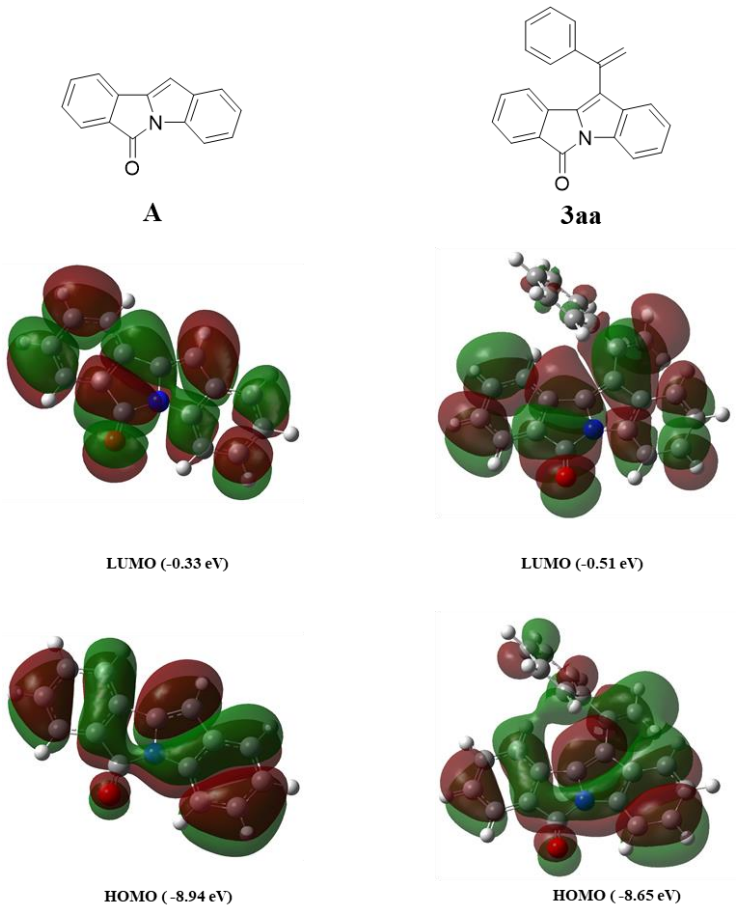
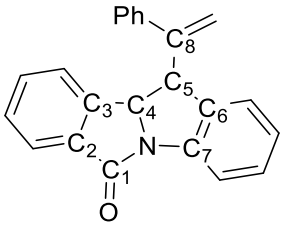


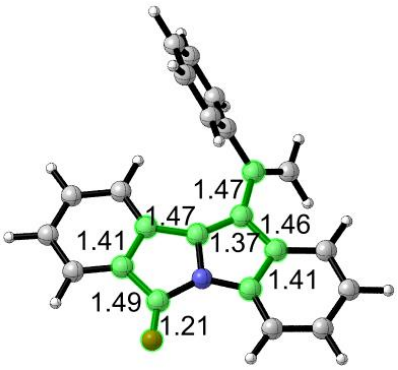
Figure S1. Comparison of HOMO/LUMO of **A** and **3aa**

Excited states and oscillator strengths of 3aa



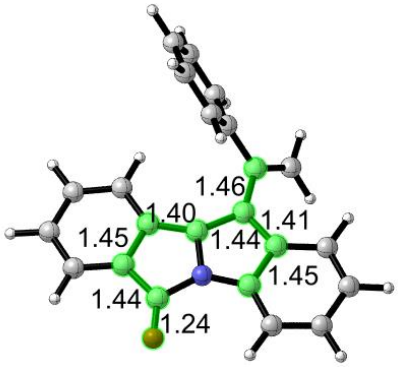
Bonds	Ground state	Excited state
C_1–O	1.21	1.24
C_1–C_2	1.49	1.44
C_2–C_3	1.41	1.45
C_3–C_4	1.47	1.40
C_4–C_5	1.37	1.44
C_5–C_6	1.46	1.41
C_6–C_7	1.41	1.45
C_5–C_8	1.47	1.46

Figure S2. Bond length changes of ground state & excited state **3aa**.



Optimized ground state structure

3.4674 eV (357.57 nm) f=0.4638
HOMO-1 → LUMO 0.25028
HOMO → LUMO 0.65200



Optimized excited state structure

2.5715 eV (482.14 nm) f=0.3155
HOMO-1 → LUMO 0.20413
HOMO → LUMO 0.67037

Figure S3. Results of TD-DFT calculation for **3aa**.

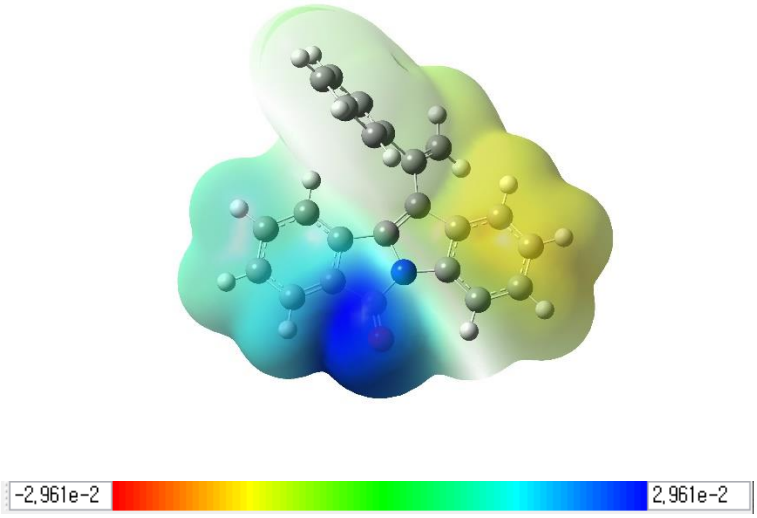
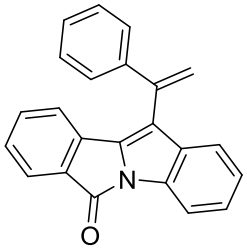


Figure S4. Isosurface of the ground state electron density, color mapped using the value of the difference density between the excited state and ground state. Isosurface of 0.0004 was used. The blue region indicates that the electron density in the excited state is larger than it is in the ground state.

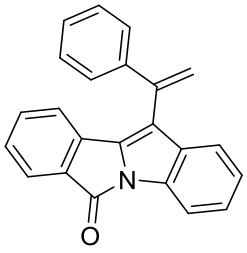
Cartesian coordinates and energies of all optimized geometries



3aa

E(CAM-B3LYP/6-31G(d)) = -1014.92030655 a.u.

O	-2.52297900	3.06272900	0.33381300
N	-1.64790300	0.93694000	0.01347500
C	2.98308300	-2.07446600	-0.77234500
H	2.88401100	-2.43574300	-1.79766000
C	1.82733800	-1.80335600	-0.02727900
C	-0.40988600	0.34960200	-0.23775200
C	2.55493400	2.76036200	-0.57570500
H	3.62795200	2.81731700	-0.76495100
C	1.96732800	-1.30423300	1.27539800
H	1.07353900	-1.08273000	1.86187100
C	0.46095400	3.88719400	-0.10932500
H	-0.13014500	4.78735500	0.06691800
C	4.24706900	-1.84734400	-0.23087600
C	0.47613300	-2.02059300	-0.61493500
C	3.23034500	-1.08306000	1.81834900
H	3.32222100	-0.69561900	2.83412400
C	0.21339200	-3.09501400	-1.37804900
H	-0.75985800	-3.22488400	-1.85368500
C	4.37441900	-1.34884500	1.06570300
H	5.36360700	-1.16631600	1.48841500
C	1.83686400	3.93727300	-0.34945100
H	2.35435800	4.89716800	-0.36401900
C	-1.59485300	2.33320900	0.11858400
C	1.93754300	1.50490900	-0.56701000
H	2.52203000	0.60376300	-0.74849400
C	-0.56220900	-1.01353900	-0.33362600
C	0.56688800	1.44920100	-0.32179600
C	-2.62896400	-0.03294500	0.09897900
C	-0.14749400	2.64374000	-0.10105300
H	5.13685000	-2.05273900	-0.82825400
H	0.97238800	-3.86128300	-1.54588400
C	-2.74912200	-2.44903500	-0.02918500
C	-3.99345600	0.08787400	0.35446100
C	-1.98528100	-1.27666300	-0.11113500
C	-4.11221800	-2.34329900	0.22633100
C	-4.72699100	-1.09287200	0.40819300
H	-4.44478800	1.06758400	0.50691000
H	-5.79922700	-1.04728300	0.60371500
H	-4.71683800	-3.24892100	0.28965400
H	-2.28183800	-3.42667400	-0.15233300



3aa*

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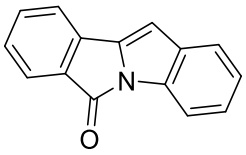
C	5.53084306	-4.32672452	-1.22569900
H	5.49341006	-4.60685652	-2.27363200
C	4.33732306	-4.18197652	-0.51076100
C	1.90816906	-2.15829452	-0.68067300
C	4.53619706	0.50074448	-1.09193200
H	5.58060306	0.68935848	-1.31560400
C	4.40338406	-3.78712152	0.82931300
H	3.48592506	-3.67274052	1.39813800
C	2.33688006	1.41883448	-0.53632300
H	1.68660906	2.26432448	-0.33613000
C	6.75700606	-4.08912952	-0.61553800
C	3.02347606	-4.45393352	-1.15708000
C	5.62887106	-3.55155452	1.44020000
H	5.66120206	-3.25129652	2.48287500
C	2.87744106	-5.47982552	-2.01265700
H	1.94615406	-5.65426352	-2.53984900
C	6.81000106	-3.70060452	0.71959700
H	7.76711106	-3.51058752	1.19499300
C	3.67768606	1.60211348	-0.82487400
H	4.08934406	2.60599848	-0.84953700
C	0.48087306	-0.33026752	-0.25701300
C	4.06781906	-0.78963352	-1.06793900
H	4.72922306	-1.62446152	-1.26741600
C	1.89189306	-3.58924552	-0.82073000
C	2.69853906	-1.01096552	-0.77497800
C	-0.23522494	-2.79871352	-0.32099300
C	1.82888706	0.12253148	-0.50906600
H	7.67282406	-4.19945352	-1.18783900
H	3.69383206	-6.16507152	-2.21436100
H	-0.65705200	-2.89663000	-0.00075900
C	-0.09186194	-5.23992952	-0.54794000
C	-1.60658694	-2.85478052	-0.04875900
C	0.55865206	-3.97603252	-0.59516000
C	-1.43202694	-5.28390552	-0.27570300
C	-2.19096394	-4.09960352	-0.03589300
H	-2.16149794	-1.94536952	0.14337900
H	-3.25195994	-4.19104552	0.17096100
H	-1.93910394	-6.24201652	-0.23299800
H	0.47351906	-6.14892952	-0.71560900



A

E(CAM-B3LYP/6-31G(d)) = -706.63853669 a.u.

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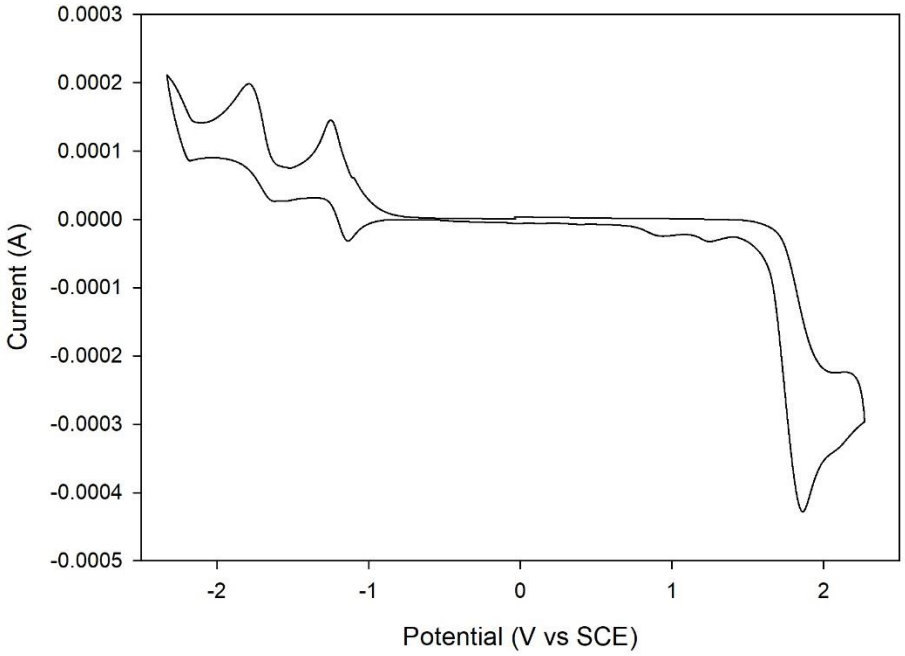
N	-0.32370100	0.38576600	0.00191500
C	0.22039900	-0.89218100	0.00126700
C	4.03996900	-1.13479500	-0.00037000
H	4.87913000	-1.82735900	-0.00046900
C	3.23435900	1.15564900	-0.00090700
H	3.40135700	2.23098000	-0.00141300
C	4.29010700	0.23909900	-0.00103800
H	5.31701900	0.59760800	-0.00164100
C	0.63957500	1.39817300	0.00034300
C	2.73623100	-1.64112000	0.00045800
H	2.55004500	-2.71254100	0.00103100
C	-0.77178000	-1.81889500	0.00007700
C	1.68996200	-0.73030300	0.00056200
C	-1.70323400	0.30528900	0.00086600
C	1.94909000	0.64618900	-0.00013400
C	-3.37383700	-1.45081000	-0.00094800
C	-2.66966700	1.31229300	0.00069600
C	-2.02503800	-1.07095600	0.00006600
C	-4.34396300	-0.46043900	-0.00123400
C	-3.99477600	0.90339100	-0.00039000
H	-2.37783900	2.35894800	0.00128600
H	-4.78286700	1.65343500	-0.00062700
H	-5.39548900	-0.73917800	-0.00215900
H	-3.65175600	-2.50298000	-0.00160000

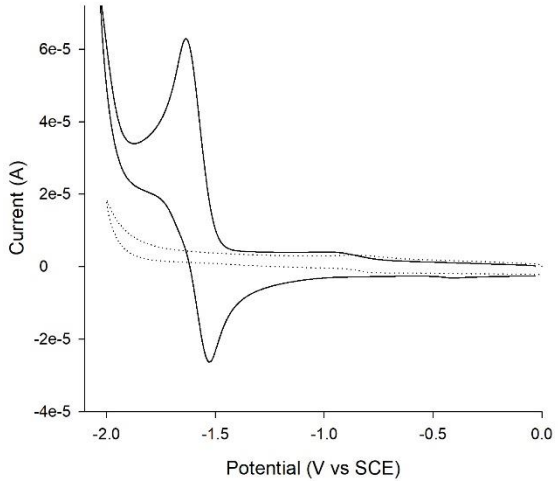
Electrochemical and Photochemical Properties

Cyclic voltammetry studies

The ground-state oxidation (E_{ox}) and reduction (E_{red}) potentials of products were determined by cyclic voltammetry. 2.0 mM of sample was dissolved in 5 mL of dry and degassed acetonitrile (MeCN) solution containing 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The solution was delivered to a three-electrode cell assembly and deaerated. A glassy carbon working electrode, a coiled Pt wire counter electrode, and 1.0 M KCl Ag/AgCl pseudo reference electrode were employed for the voltammetric measurements. Voltammograms were measured at a scan rate of 100 $mV \cdot s^{-1}$. Reductions were measured by scanning potentials in negative direction. The obtained value was referenced to Ag/AgCl and converted to SCE by subtracting 0.03 V.



3aa



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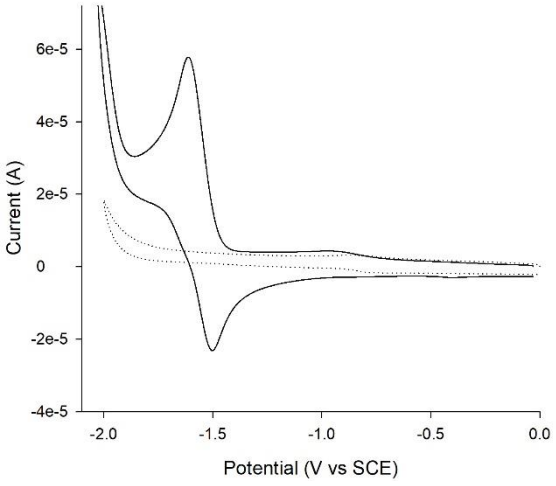

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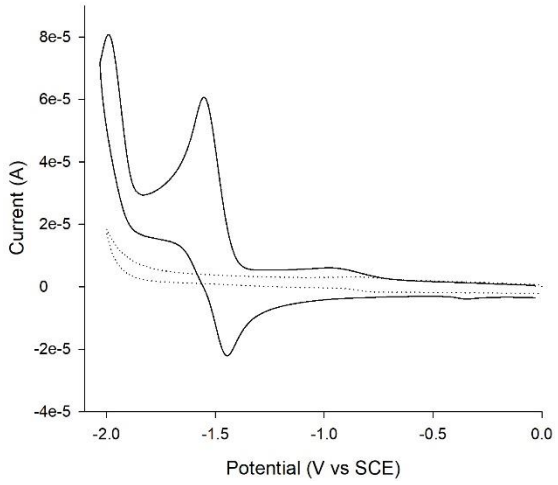

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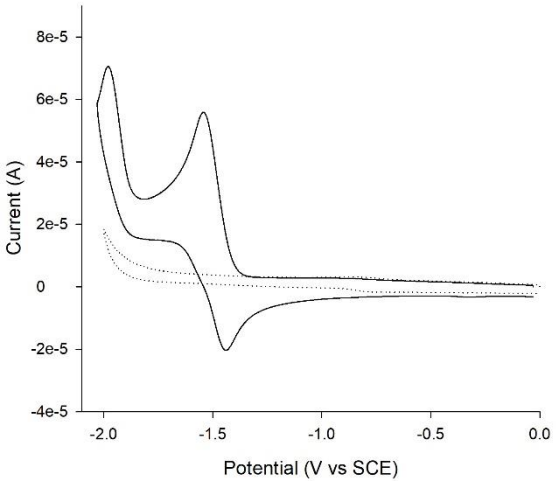

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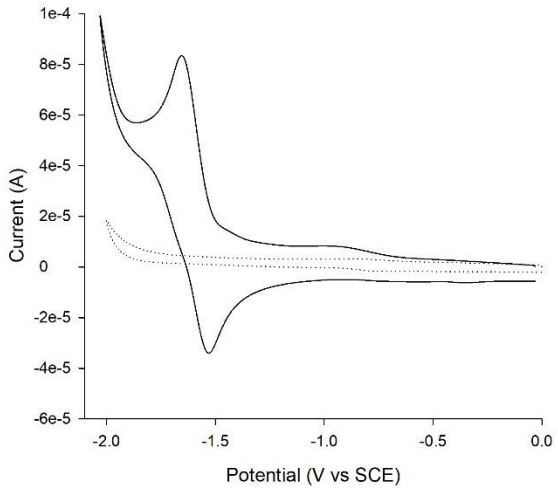

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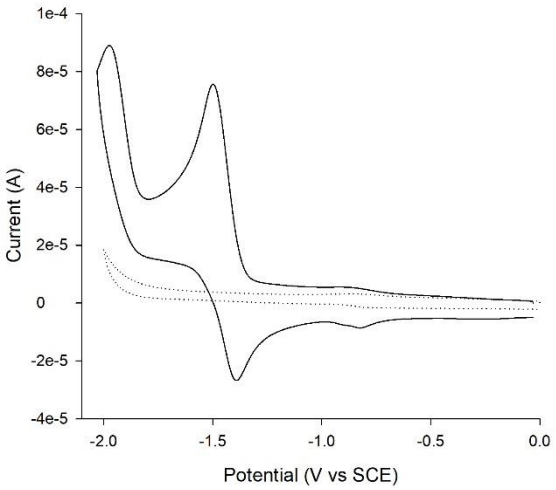

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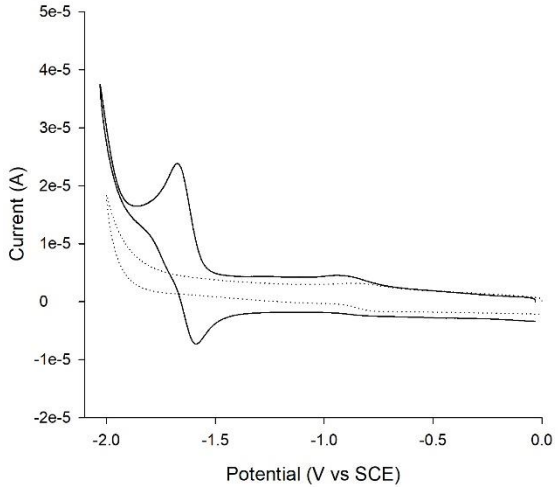

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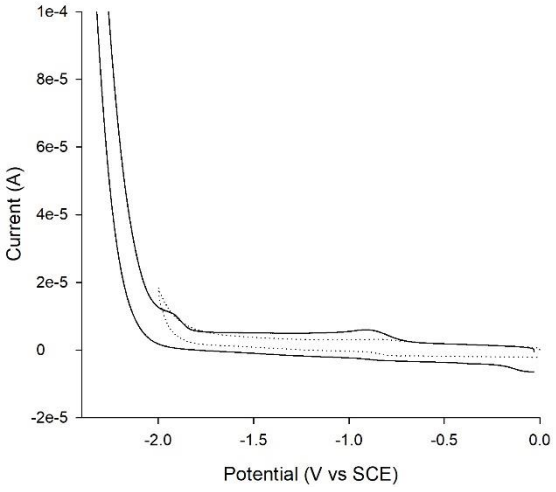

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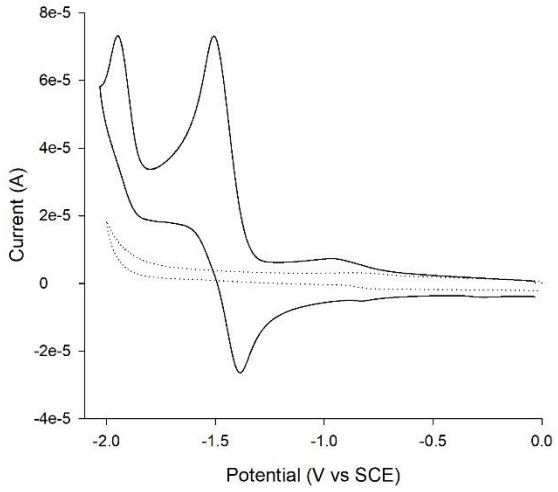

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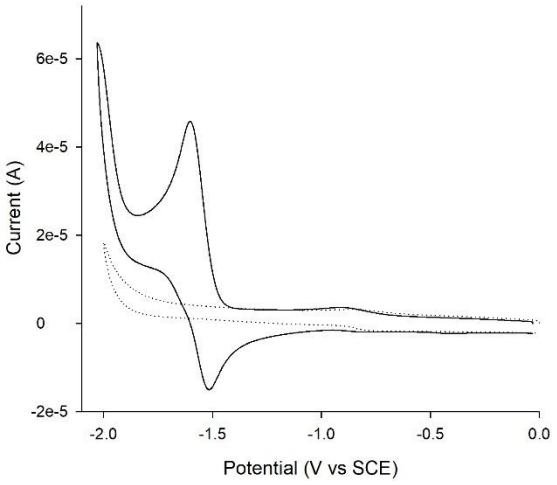

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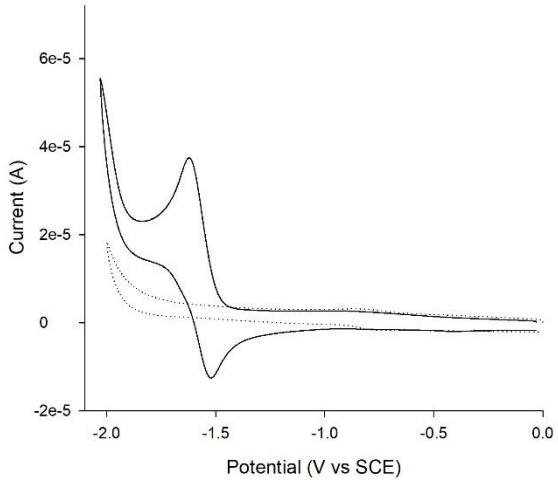

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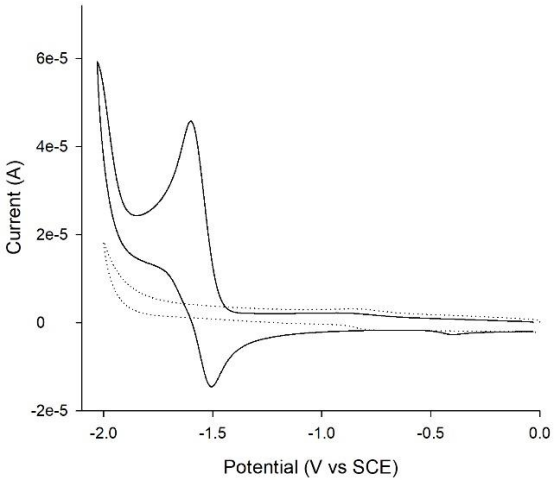

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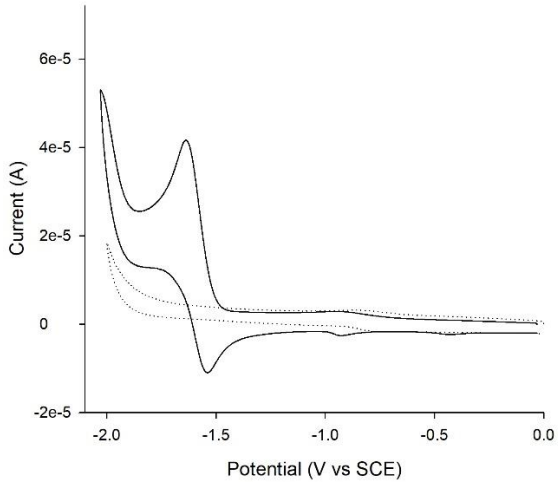

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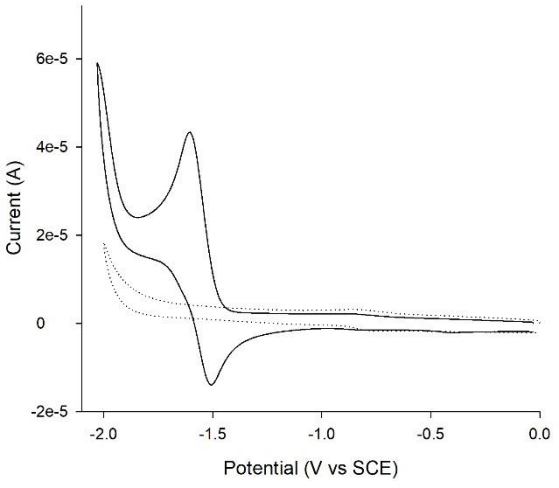

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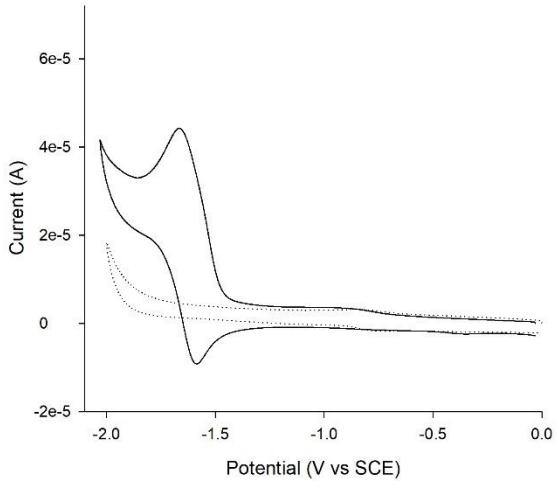

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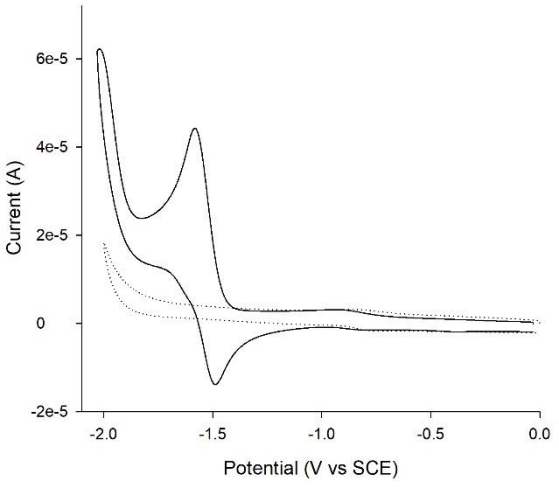

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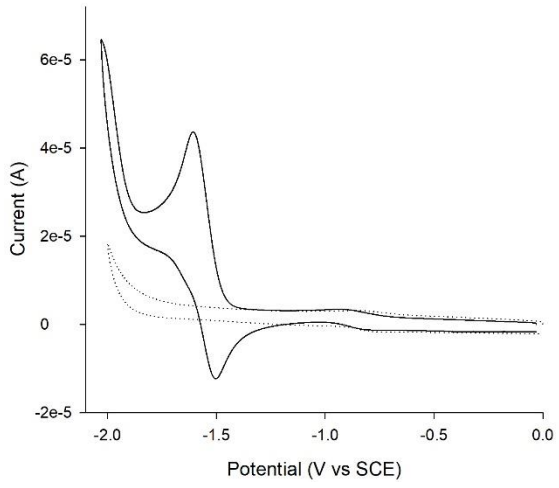

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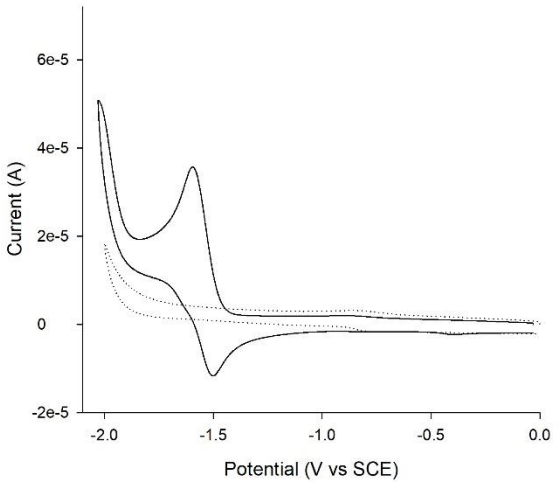

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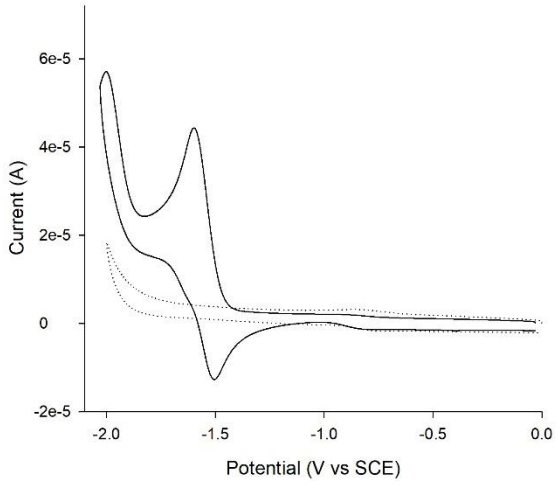

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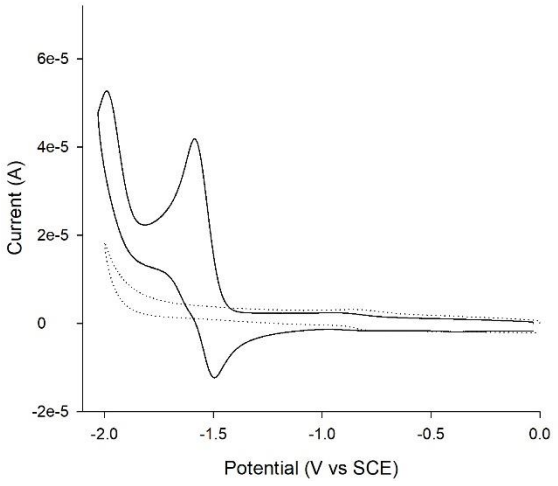

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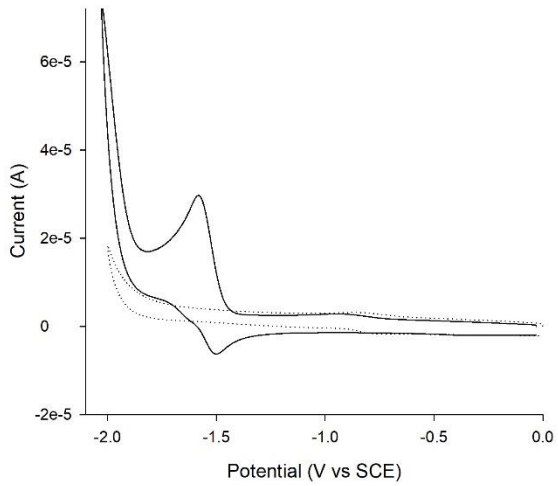

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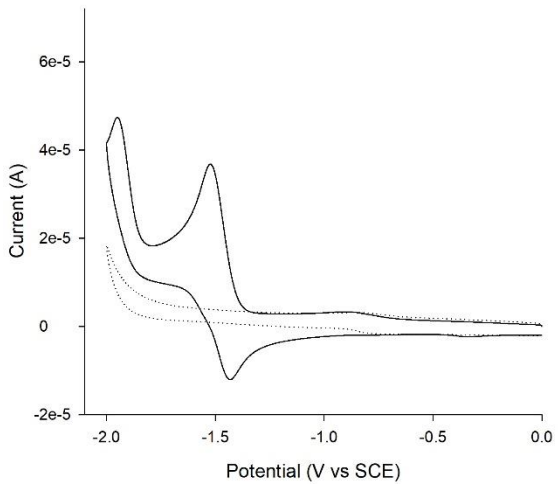

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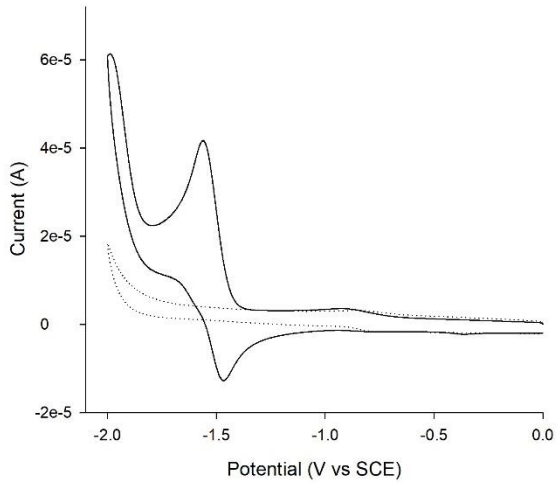

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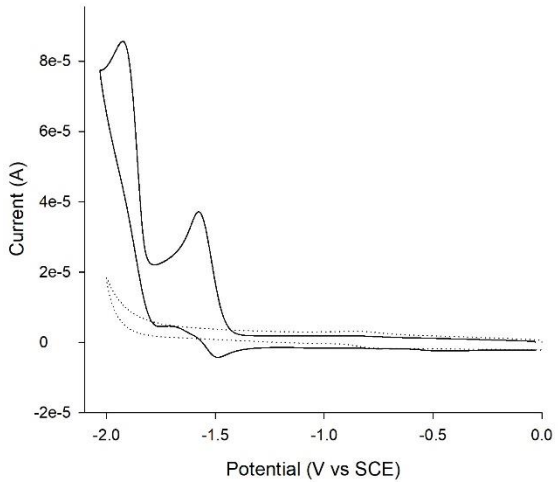

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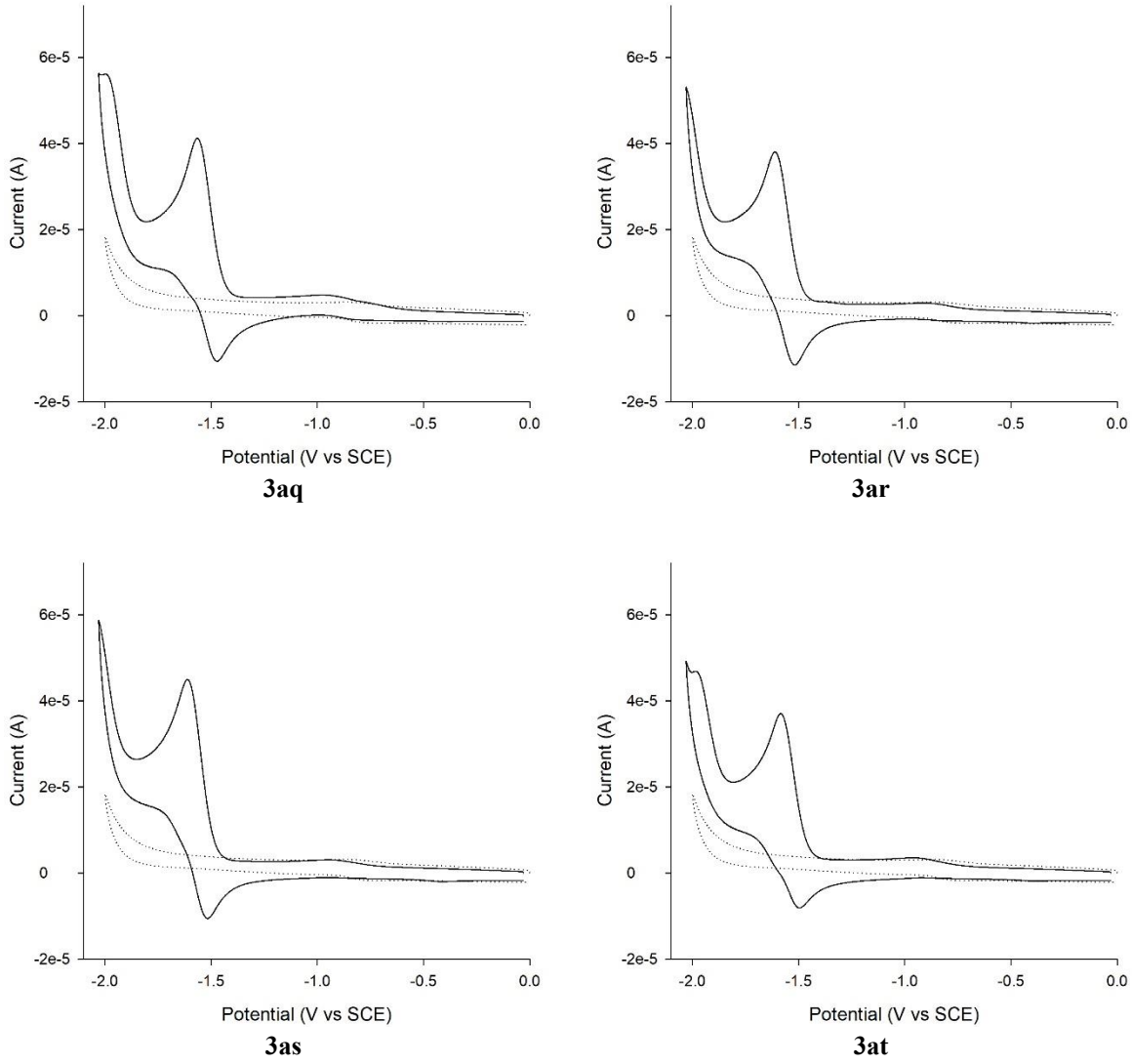
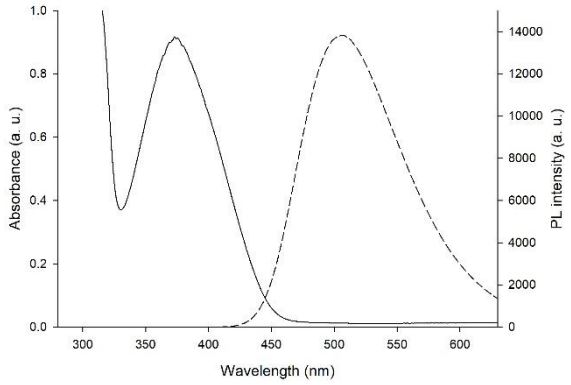


Figure S5. Cyclic voltammograms of synthesized molecules shown in Figure 1 & Scheme 2. (dotted line: blank)

Steady-state UV-Vis absorption & photoluminescence spectroscopy

UV-Vis absorption spectra were collected on a Scinco S-3100 spectrophotometer with a Peltier temperature controller at 298 K. 50 μM CH_3CN solutions of the synthesized products were used for the measurements unless otherwise mentioned. Phosphorescence spectra were obtained using a PTI QuantaMaster steady-state spectrofluorometer at room temperature. The 50 μM solutions were thoroughly deaerated by bubbling argon prior to performing the measurements. The excited state energy ($E_{0.0}$) is the energy corresponding to the wavelength at which the absorption and emission spectra intersect.



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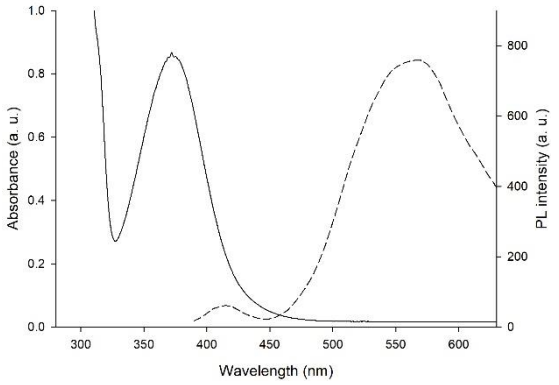

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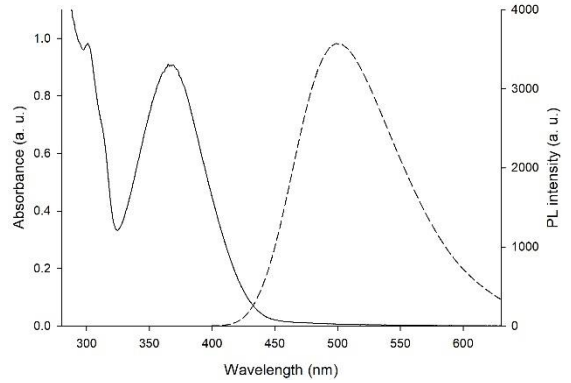

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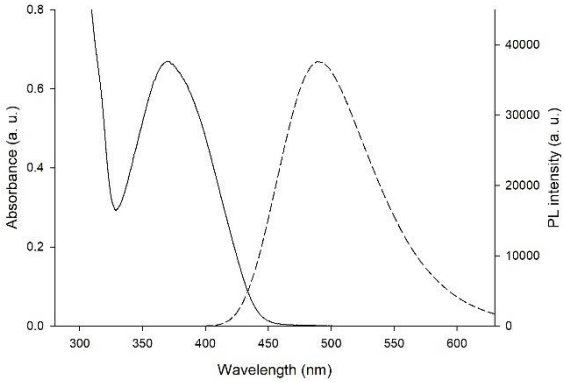

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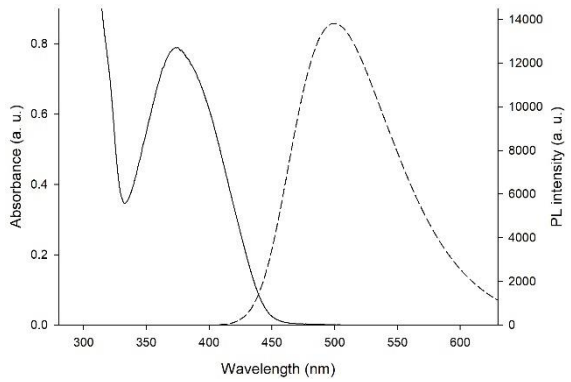

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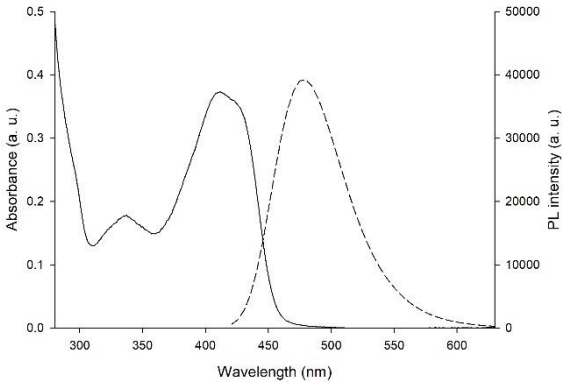

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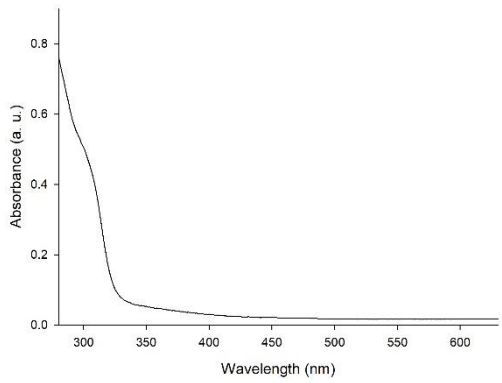

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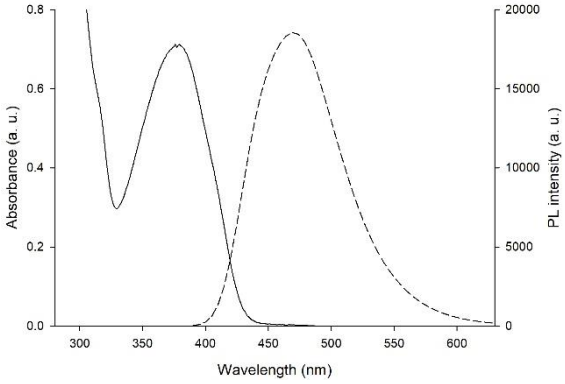

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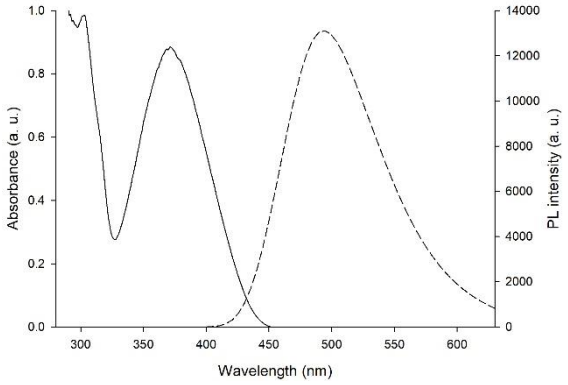

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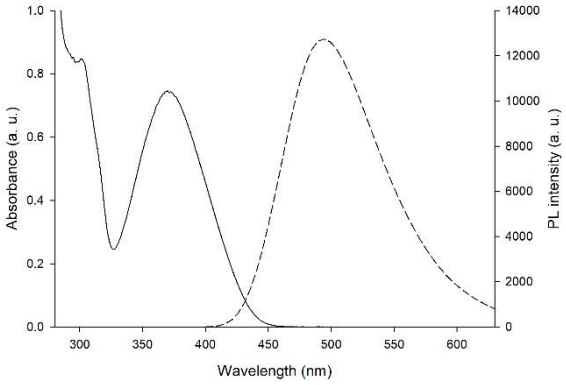

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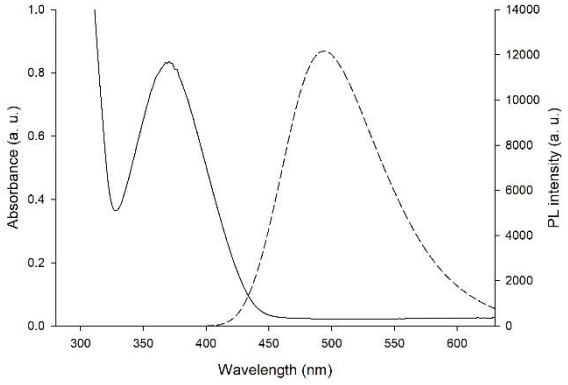

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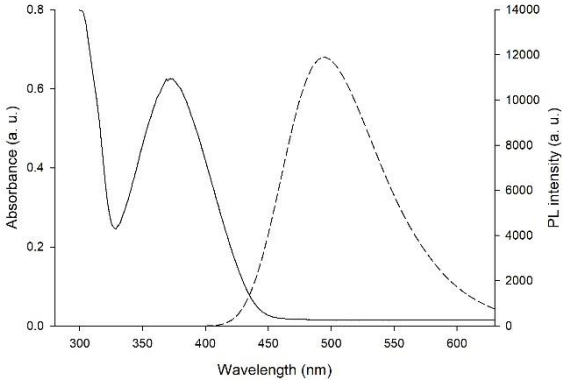

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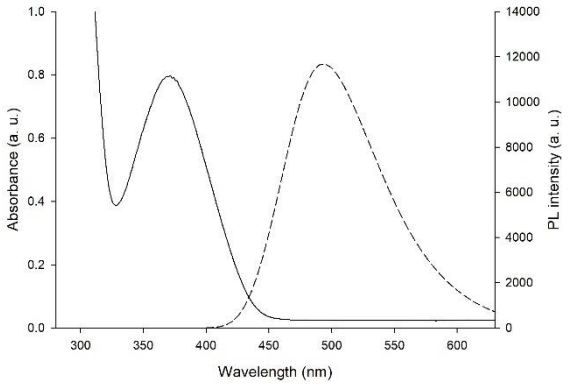

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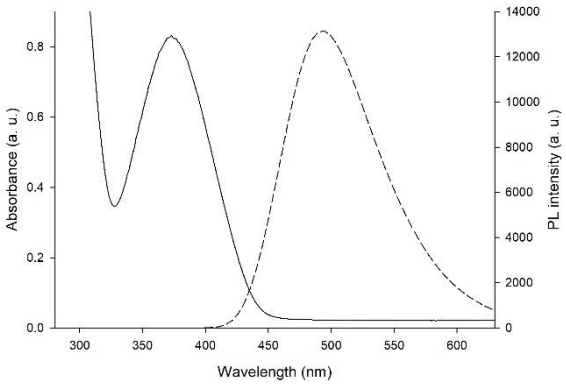

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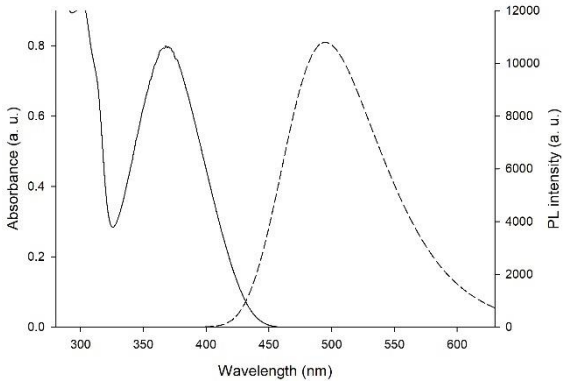

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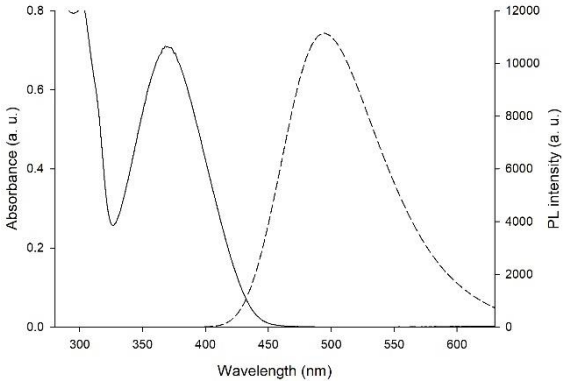

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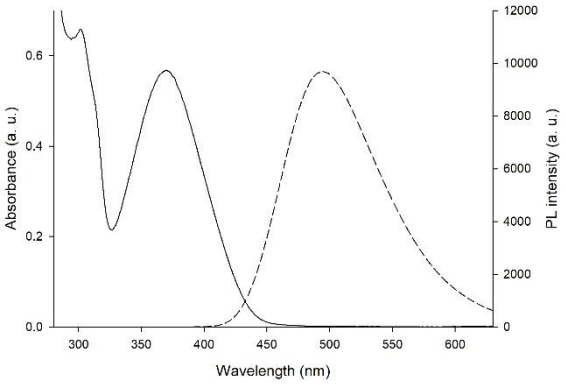

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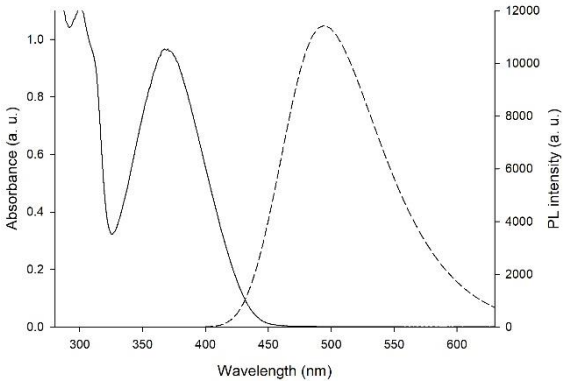

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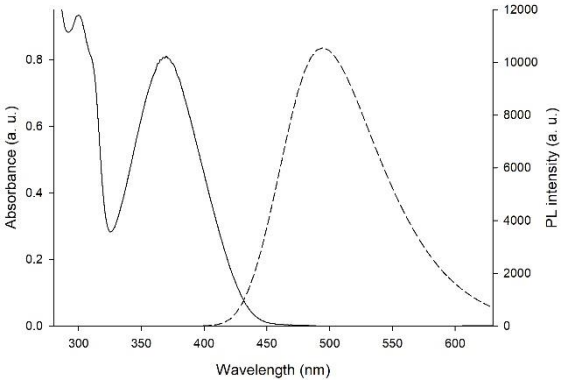

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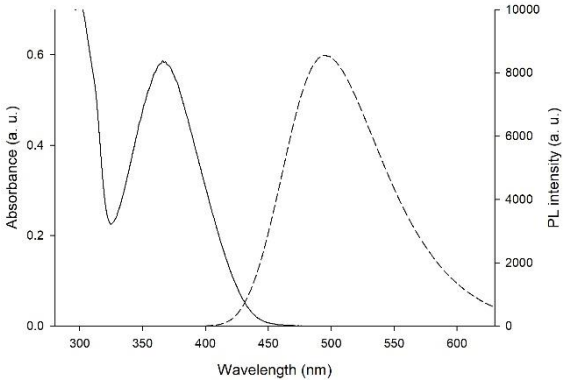

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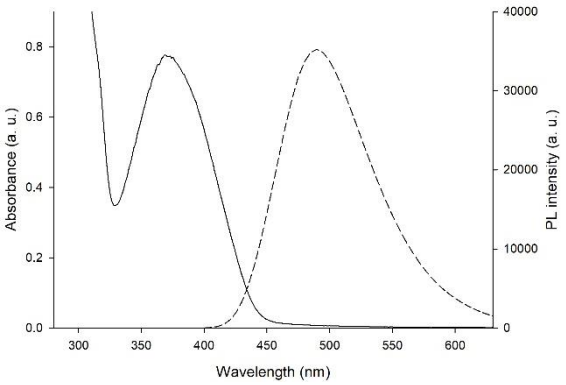

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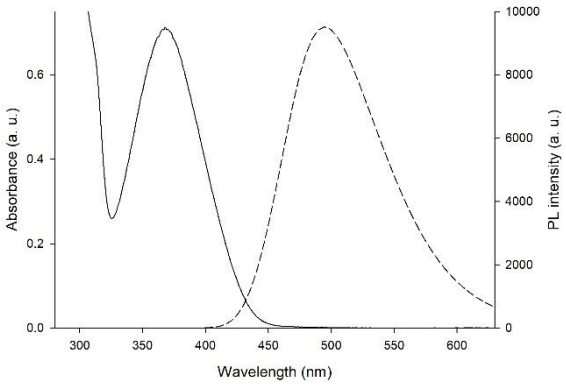

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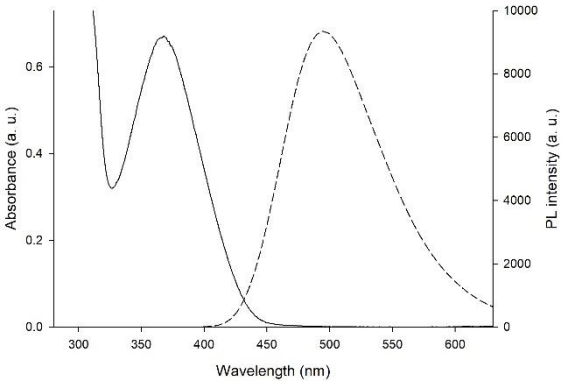

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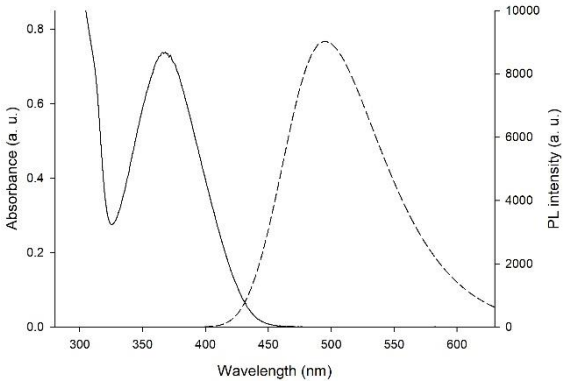

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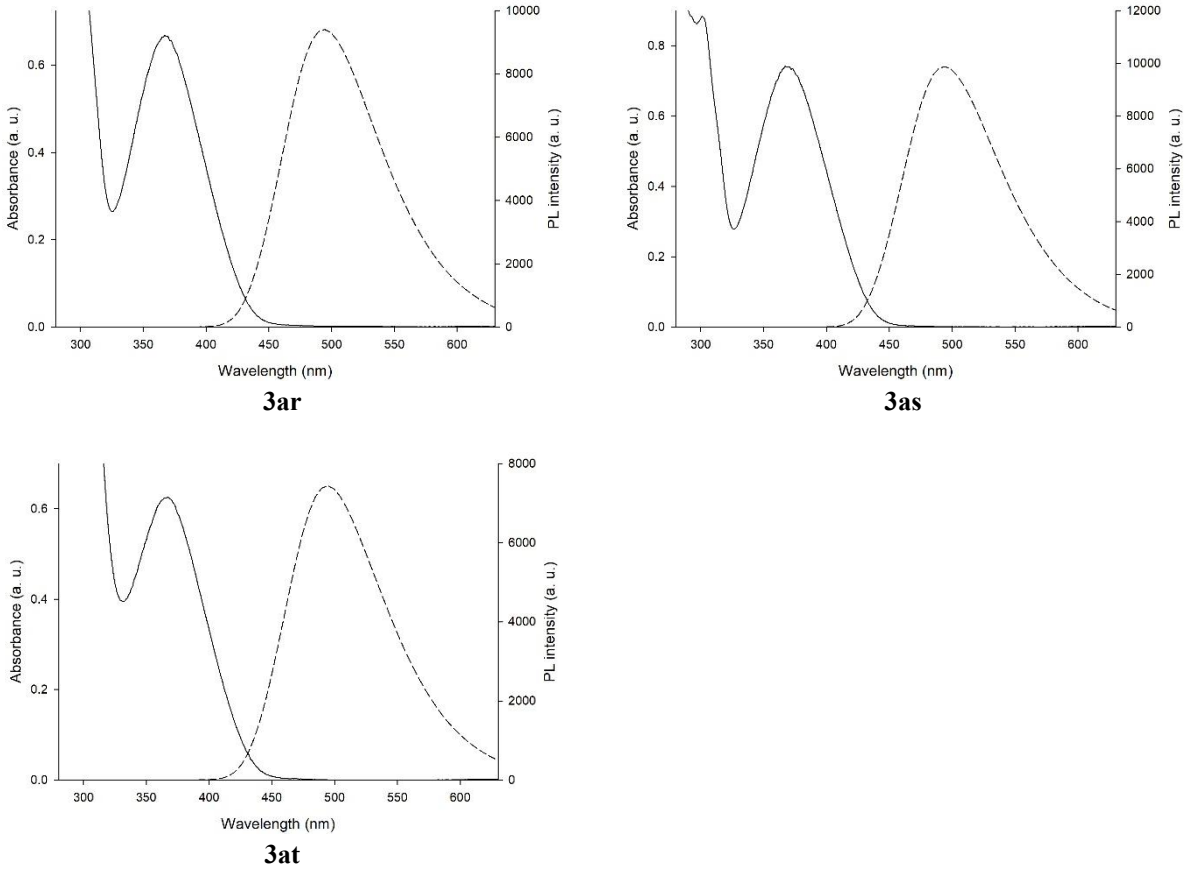


Figure S6. UV-Vis spectra and photoluminescence spectra of synthesized molecules shown in Figure 1 & Scheme 2.

Calculation of the excited state energy ($E_{0.0}$) and excited state reduction potential (E^*_{red})

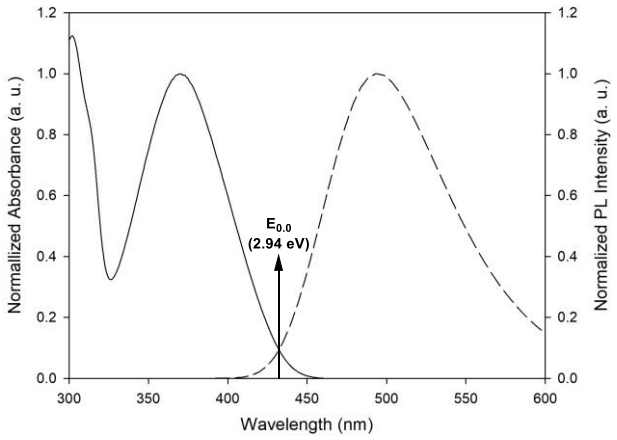


Figure S7. Steady state absorbance spectrum (solid line) and emission spectrum (dashed line) for **3aa**. Excitation energy $E_{0.0}$ is determined to be 2.94 eV at the intersection of absorption and photoluminescence spectra normalized to 1.

The excited-state reduction potential is estimated according to the following relationship:

$$E^*_{red} = E_{red} + E_{0.0}$$

E_{red} is the ground-state reduction potential and $E_{0.0}$ is the excited state energy determined by Figure S7.[S7]

For example,

$$E^*_{red}\,(\mathbf{3aa}) = E_{red}\,(= -1.55) + E_{0.0}\,(= 2.94) = 1.39\ V$$

Photoluminescence quantum yield (Φ_{PL}) measurement

The photoluminescence quantum yields (PLQYs, $\mathbf{\Phi_{PL}}$) were relatively determined according to following standard equation:

$$\Phi_{PL} = \Phi_{st} \cdot \frac{I}{I_{st}} \cdot \frac{A_{st}}{A} \cdot \frac{\eta^2}{\eta_{st}^2}$$

Where I, A, and η are the integrated photoluminescence intensity, absorbance at the excitation wavelength and the refractive index of the solvent, respectively. All samples were prepared at 50 μM concentration in degassed CH_3CN. Fluorescein (aqueous 0.1 N NaOH solution) was used as the external standard (= 0.79). [S6] The refractive index of the 0.1 N NaOH solution was assumed to be identical to the value for pure water.

Summary of photo & electrochemical properties

sample	$E_{1/2}$ (V vs SCE)	λ_{max} (nm)	Em_{max} (nm)	$E_{0,0}$ (nm)
3ba	1.56	373	508	443
3ca	1.53	372	566	455
3da	1.47	365	499	434
3ea	1.46	371	489	430
3fa	1.56	372	496	433
3ga	1.41	373	497	434
3ha	1.60	411	480	446
3ja	1.42	379	469	421

sample	$E_{1/2}$ (V vs SCE)	λ_{max} (nm)	Em_{max} (nm)	$E_{0,0}$ (nm)
3ab	1.53	370	494	431
3ac	1.54	370	494	431
3ad	1.53	370	494	431
3ae	1.56	370	494	431
3af	1.53	370	494	431
3ag	1.60	373	494	433
3ah	1.51	368	495	432
3ai	1.53	370	494	431
3aj	1.52	370	494	431
3ak	1.52	370	494	431
3al	1.52	370	494	431
3am	1.52	366	495	434
3an	1.48	369	490	429
3ao	1.51	368	495	432
3ap	1.51	368	495	432
3aq	1.49	364	495	428
3ar	1.54	367	494	431
3as	1.54	367	494	431
3at	1.52	368	494	431

Photophysical and electrochemical properties of 5

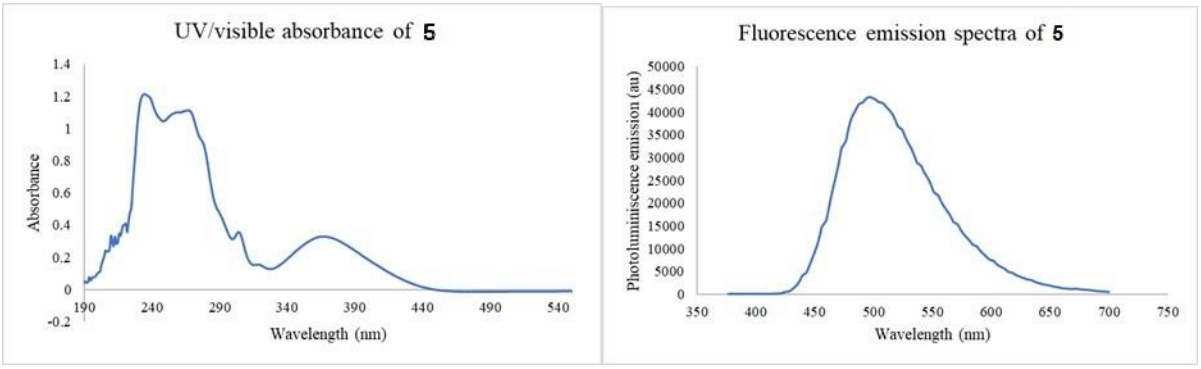


Figure S8. UV-vis absorption (left), and photoluminescence (right) spectra for 50 μM of the compound **5** in MeCN.

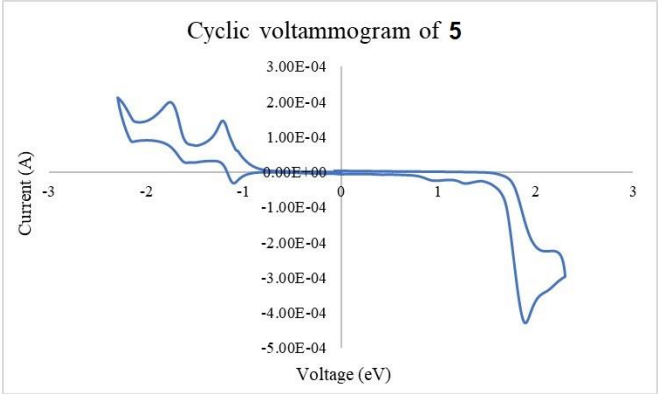


Figure S9. CV Diagram of **5** (10 mM) in MeCN/DCM (10:1), Ag/AgCl as a Reference Electrode, Bu_4NPF_6 as an electrolyte.

Determination of quantum yield with 3aa and 3ja for singlet oxygen generation

Air-equilibrated DMSO solutions containing substrate (10 μM), 1,3-diphenylisobenzofuran (DPBF), were photoexcited using a hand-held blue light lamp (240 mW, 450 nm, LEDC2-Collimated LED lamp by Thorlabs). The absorbance of DPBF at 418 nm was recorded during the photoillumination.

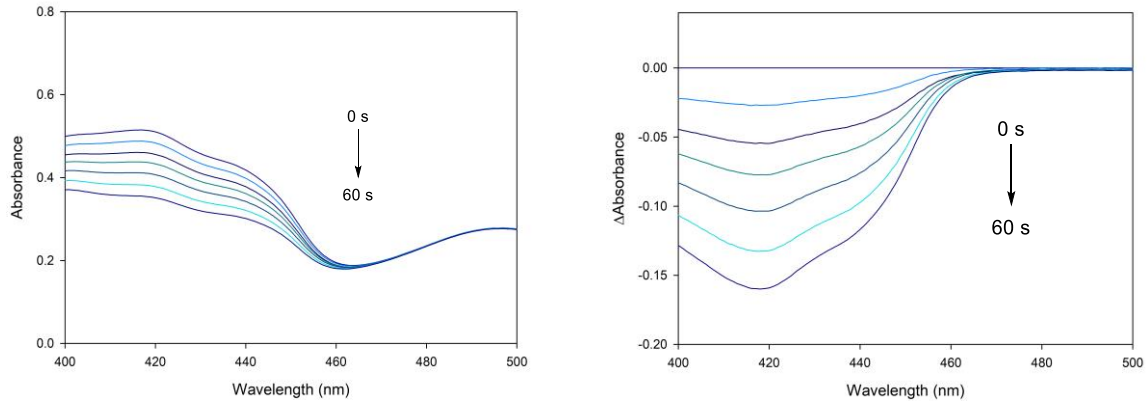


Figure S10. Changes in the UV–Vis absorption spectra of an O_2-saturated DMSO containing 10 μM 1,3-diphenylisobenzofuran (DPBF) and 100 μM methylene blue upon photoexcitation at 450 nm.

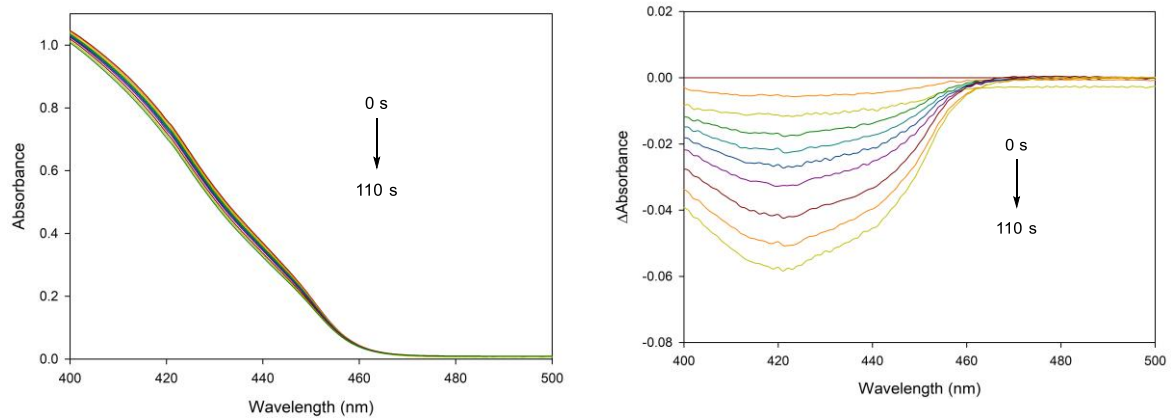


Figure S11. Changes in the UV–Vis absorption spectra of an O_2-saturated DMSO containing 10 μM 1,3-diphenylisobenzofuran (DPBF) and 100 μM **3aa** upon photoexcitation at 450 nm.

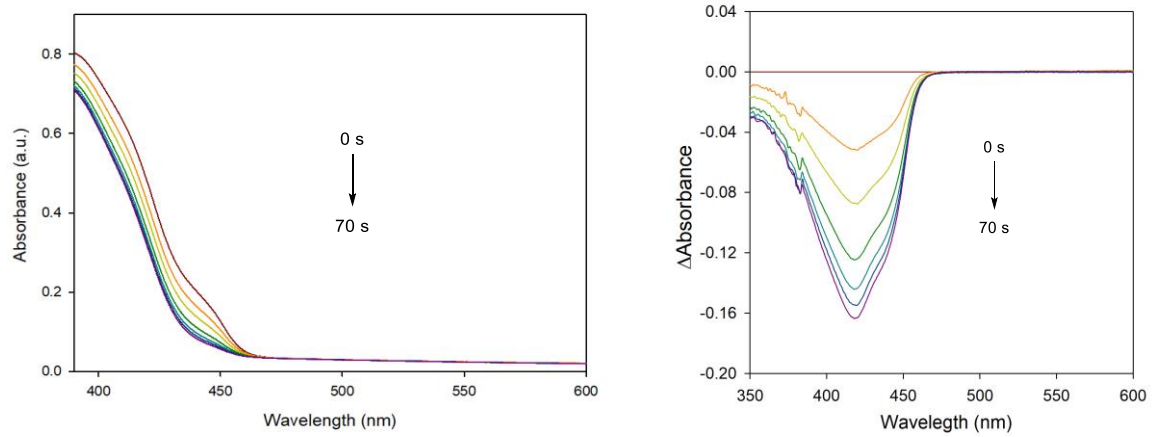


Figure S12. Changes in the UV–Vis absorption spectra of an O_2-saturated DMSO containing 10 μM 1,3-diphenylisobenzofuran (DPBF) and 100 μM **3ja** upon photoexcitation at 450 nm.

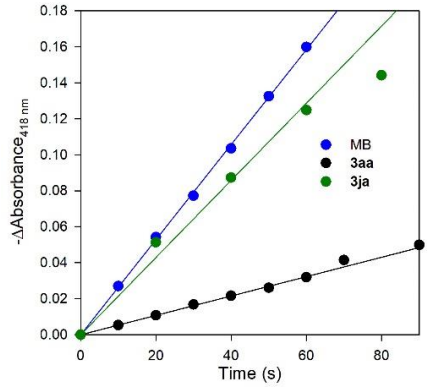


Figure S13. Changes at the 418 nm absorption bands ($-\Delta Absorbance_{418\ nm}$) of the MB/DPBF standard solution (blue), **3aa**/DPBF solution (black) and **3ja**/DPBF solution (green) as a function of photoirradiation time.

The Φ_Δ was calculated by the following relationship:

$$\Phi_\Delta = \Phi_\Delta(\mathrm{MB}) \times (m/m(\mathrm{MB})).$$

Φ_Δ(MB) is the reference methylene blue quantum yield (0.52), *m* is the slope of a linear fit to the data shown in Figure S13.

Photoluminescence quenching experiment of 3aa

Photoluminescence quenching experiments were performed in combination of **3aa** with DBU. Stern-Volmer analysis supports that the DBU quenched the excited state of **3aa**. A Stern-Volmer constants, K_{SV} (DBU) = 69.0 M^{-1} were obtained.

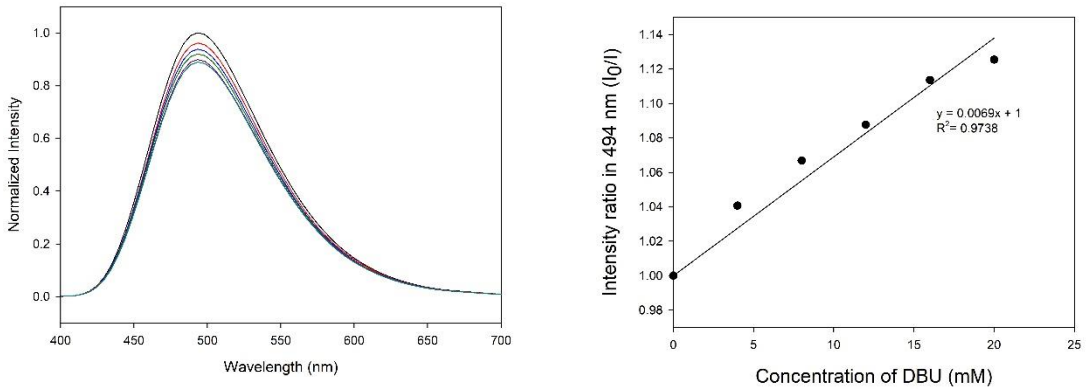


Figure S14. Photoluminescence spectra (excitation wavelength = 370 nm) of 100 μM **3aa** (Ar-saturated MeCN) obtained with increasing the concentration of DBU (0-20 mM). (left) Stern-Volmer plots for 100 μM **3aa** solution upon adding 0-20 mM DBU.

Photographs of Preparation Process

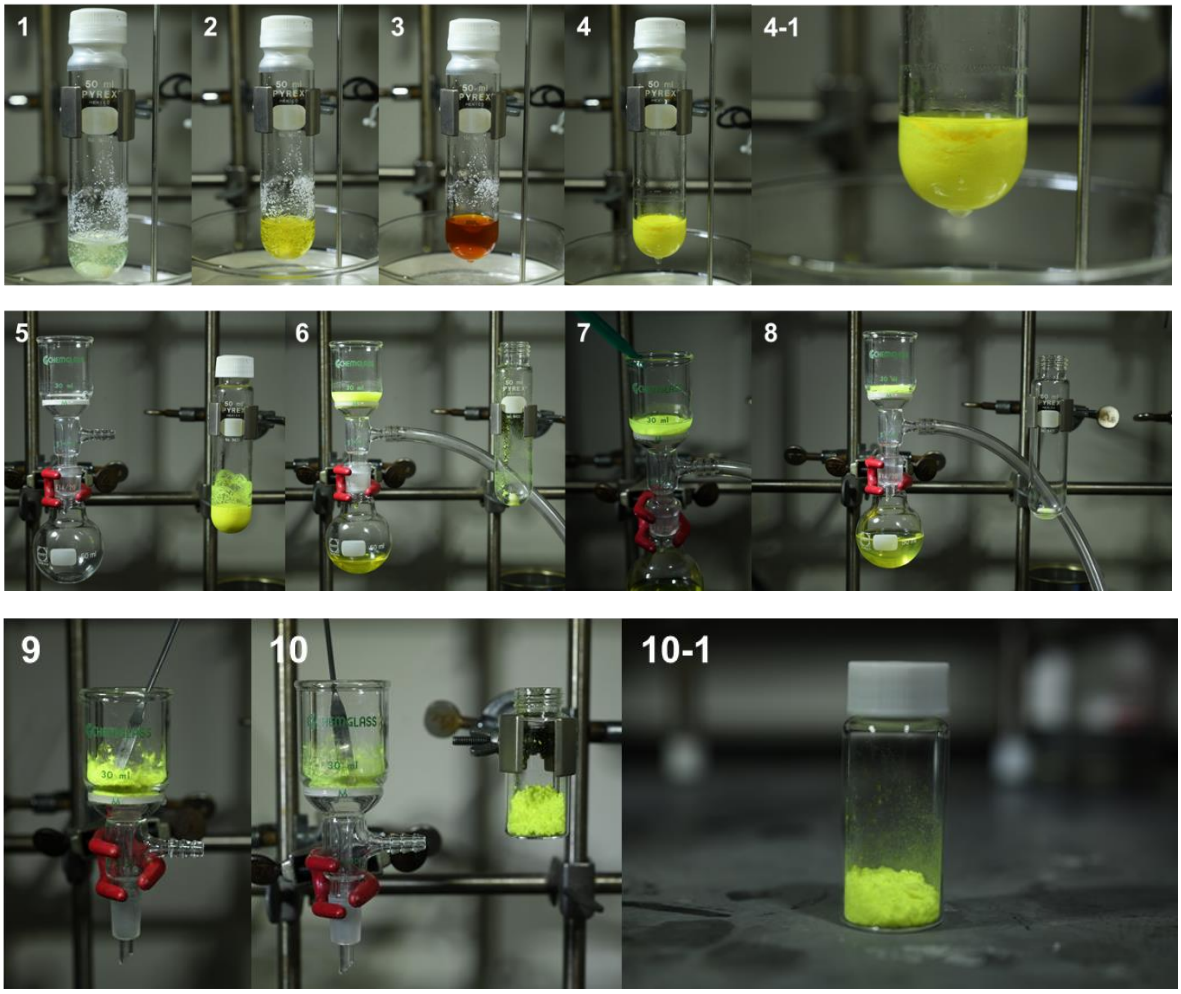


Figure S15. Photographs of preparation process of 3aa in 0.5 mmol scale. (1) Reaction mixture before heating; (2) t = 10 min at 80 °C (3) t = 30 min at 80 °C; (4) t = 14 h. Reaction completed; (4-1) Close photographs of precipitated products; (5) Filtration set-up; (6) Filtering the reaction mixture; (7) Washing the crude precipitates with cold methanol for three times; (8) Drying filtered cakes; (9) Dried product; (10) Collected products; (10-1) Final products in glass vial.

Structure Determination by NMR spectra

1D NOESY Spectrum of 3fa

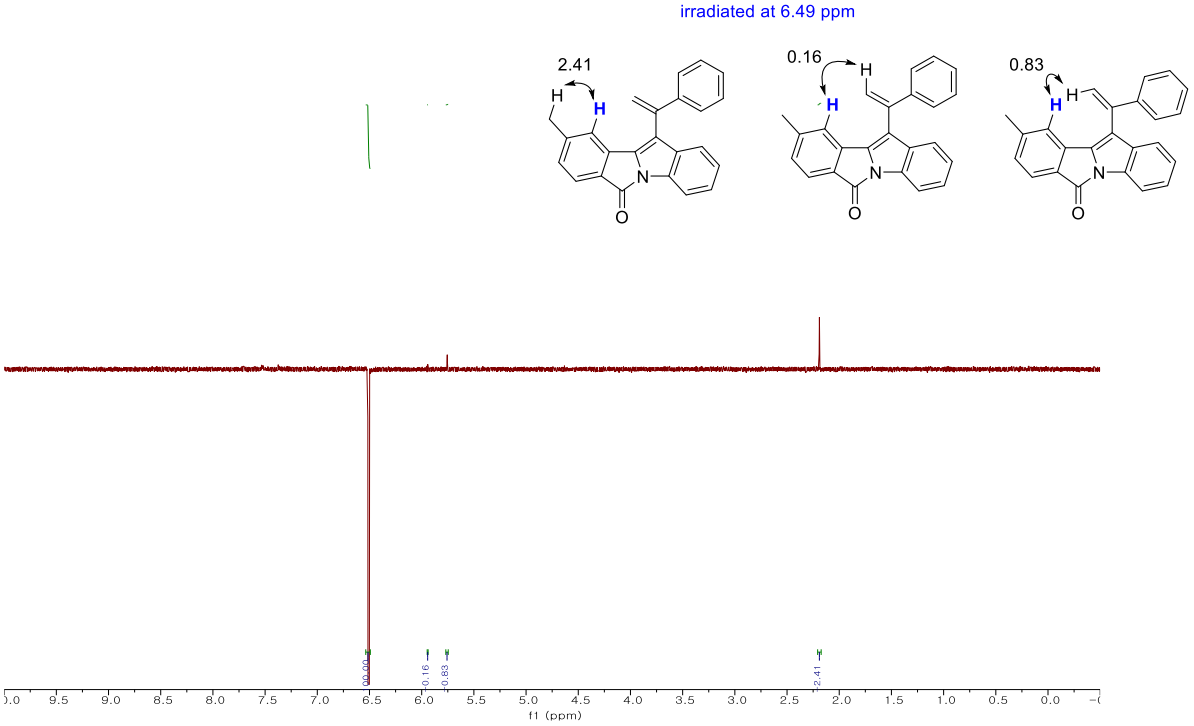
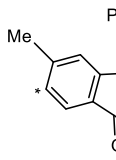


Figure S16. 1D NOESY spectrum of **3fa**.

^{1}H-^{1}H COSY Spectrum of 3fa



3fa COSY
(mixture in 10:1 ratio)*

* Major isomer enriched by recrystallization, from 2.4:1 mixture.

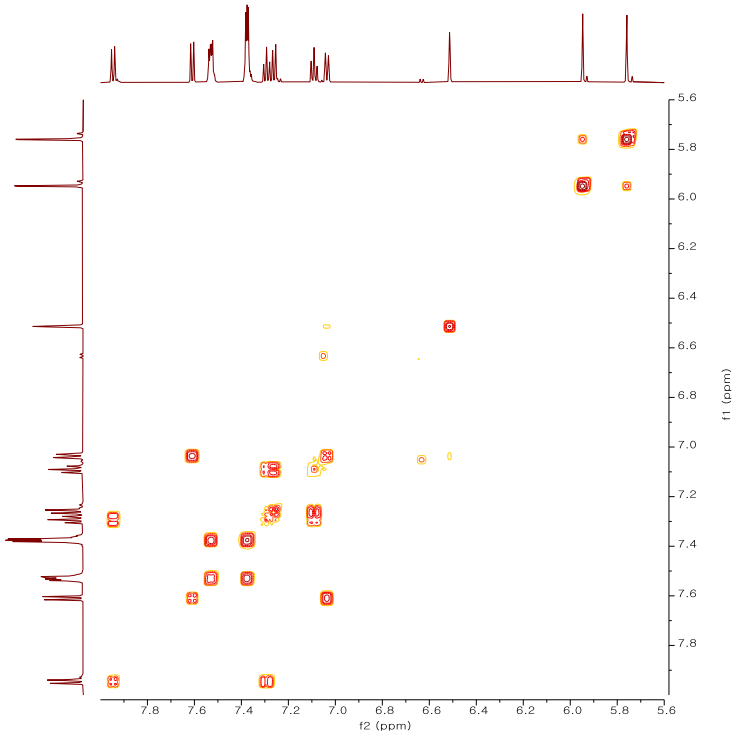


Figure S17. ^{1}H-^{1}H COSY Spectrum of **3fa**.

1D NOESY Spectrum of 3ga

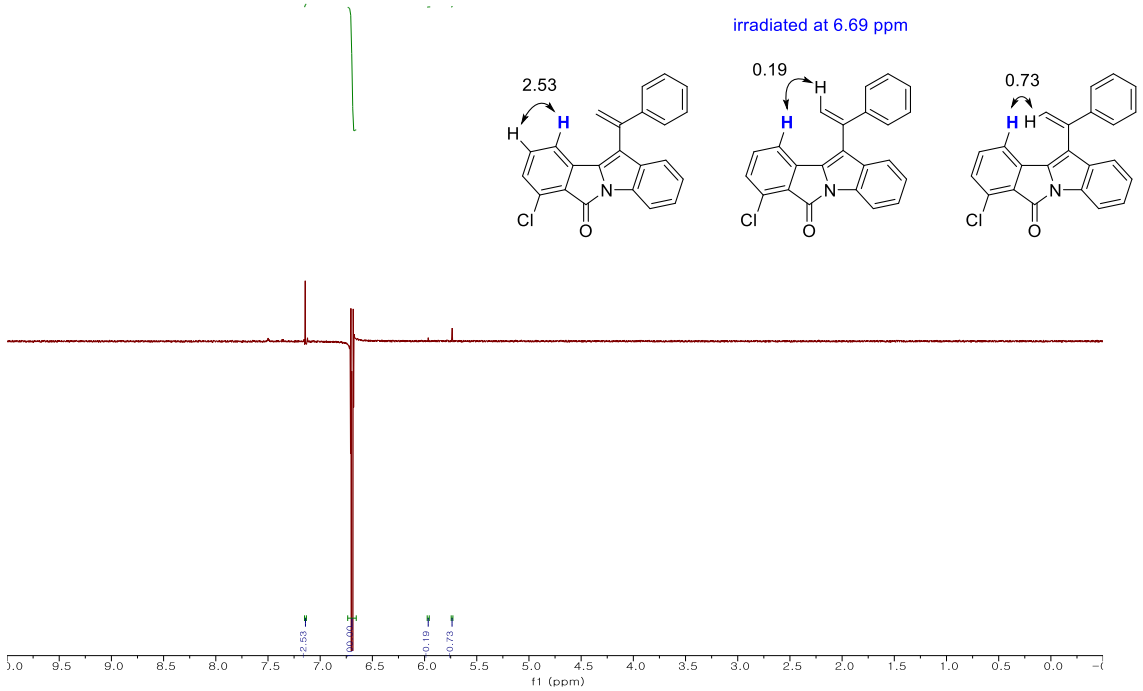
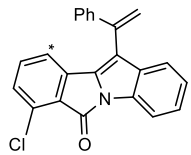


Figure S18. 1D NOESY spectrum of **3ga**.

^{1}H-^{1}H COSY Spectrum of 3ga



3ga COSY
(mixture in 8:1 ratio)

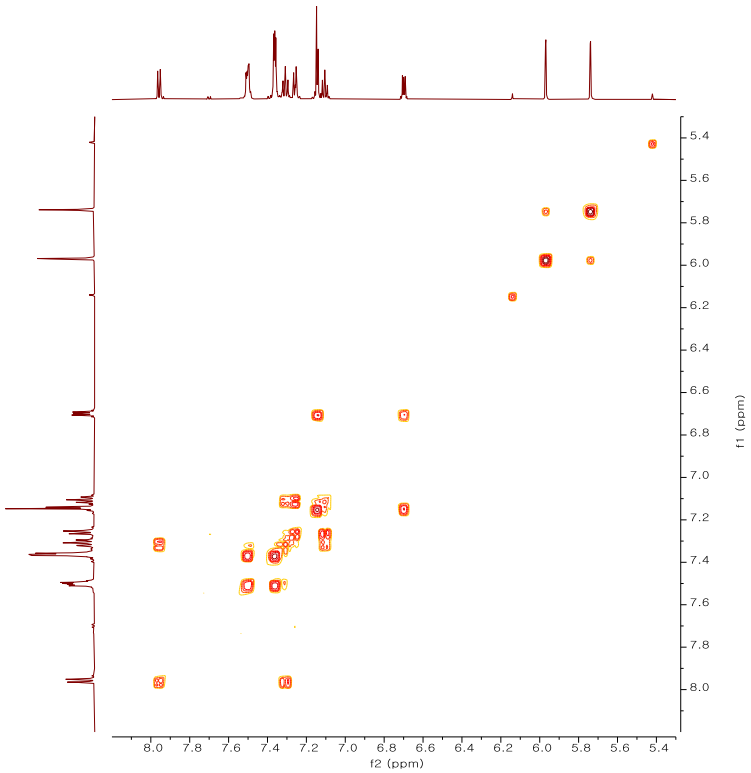


Figure S19. ^{1}H-^{1}H COSY Spectrum of **3ga**.

^{1}H-^{1}H COSY Spectrum of 3ha

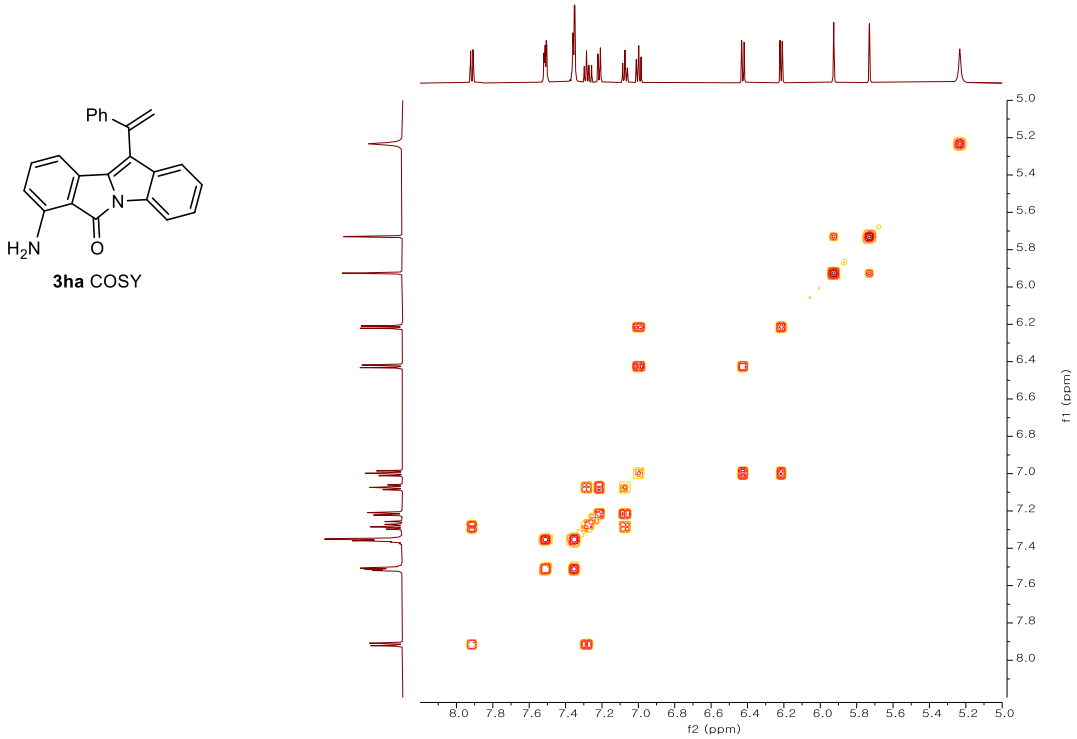


Figure S20. ^{1}H-^{1}H COSY Spectrum of **3ha**.

1D NOESY Spectrum of 3na

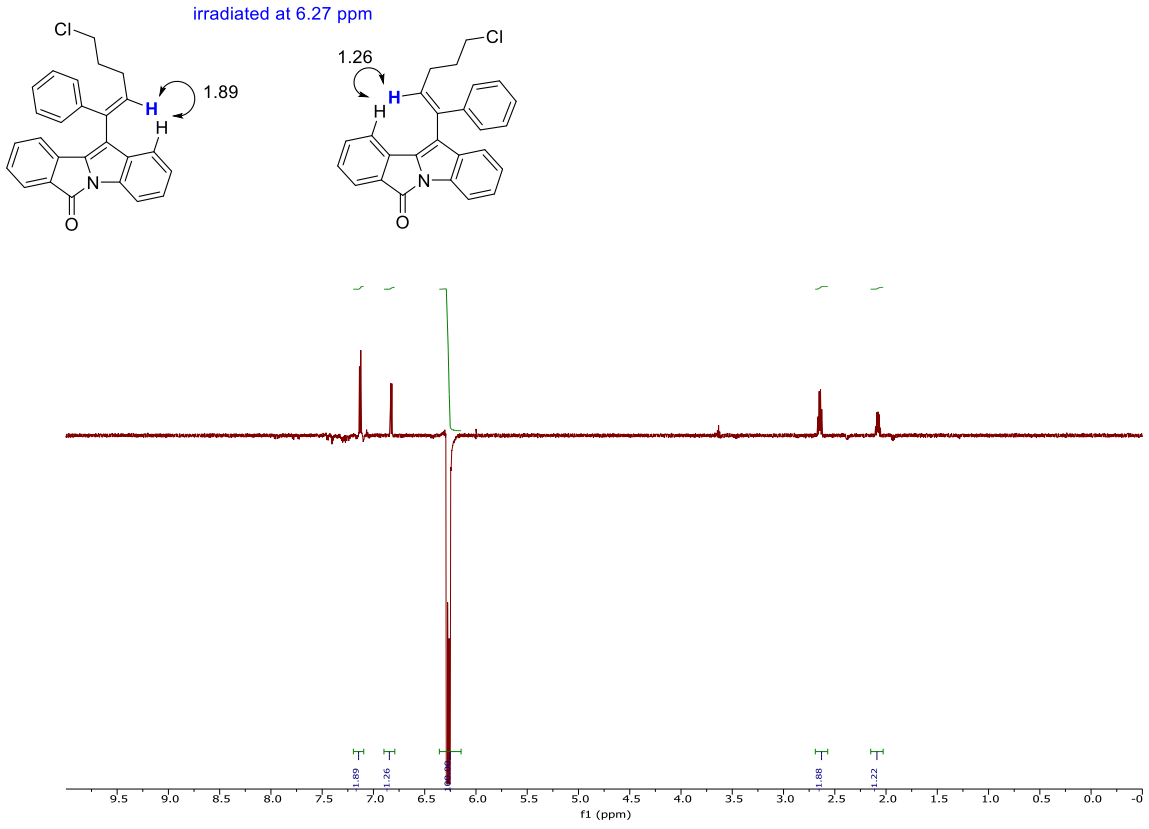
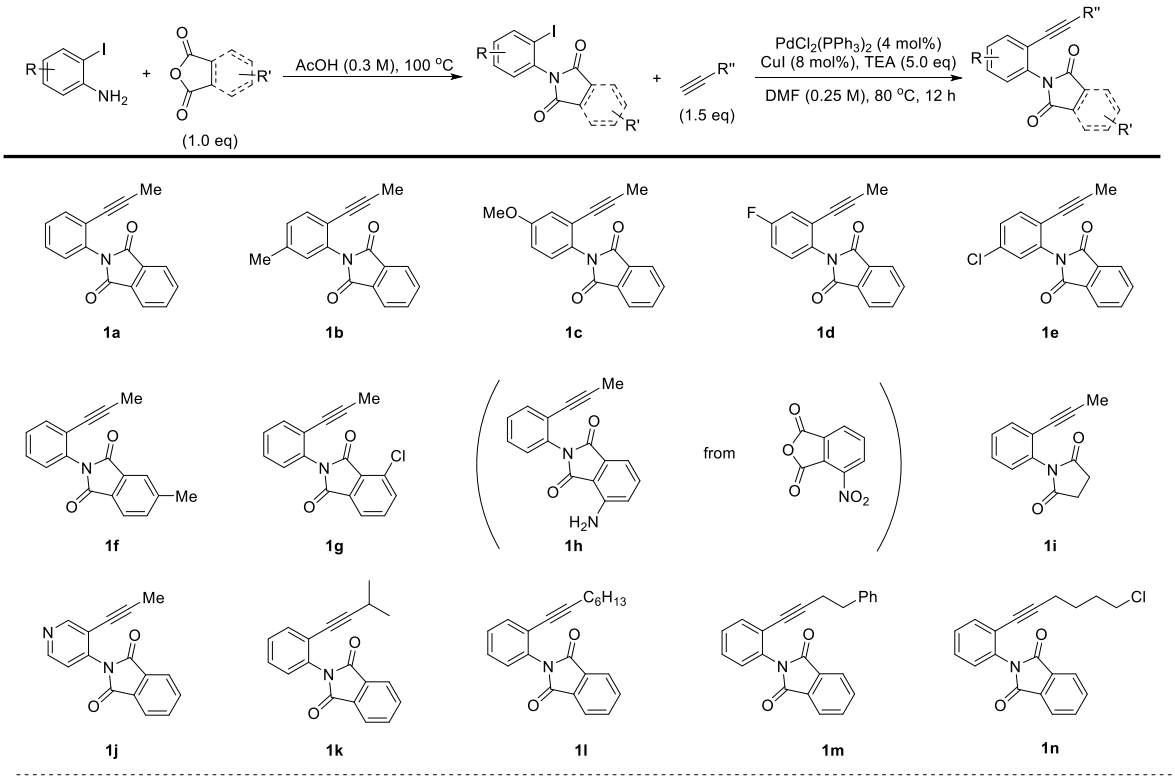


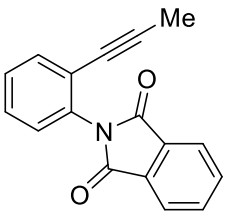
Figure S21. 1D NOESY spectrum of **3na**.

Synthesis of Substrates

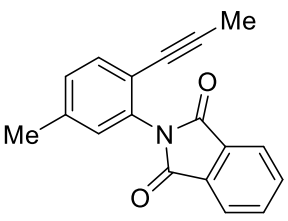
Scheme S2: General synthetic strategy for the preparation of phthalimide derivatives



Analytic Data for Substrates

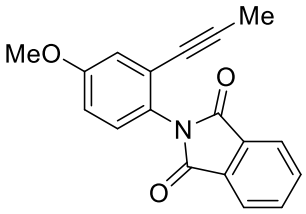


2-(2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1a**: colorless solid; melting point 134~136 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.56 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.41 (td, *J* = 7.5, 1.6 Hz, 1H), 7.38 (td, *J* = 7.5, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.5 Hz, 1H), 1.83 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.13, 134.39, 133.36, 133.20, 132.19, 129.15, 129.06, 128.53, 124.08, 123.85, 91.55, 75.92, 4.50; **IR (neat)**: ν_{max} = 2988, 2901, 2338, 1720, 1382, 1079, 718 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{17}H_{11}NO_2$ [M^+] 261.0790, found 261.0789; ***R_f*** 0.31 (Hexane:EA, 4:1).

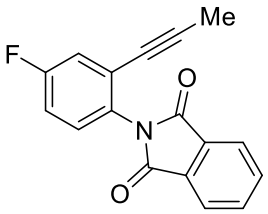


2-(5-methyl-2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1b**: colorless solid; melting point 156~158 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 2.39 (s, 3H), 1.82 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.31, 139.00, 134.38, 133.19, 132.97, 132.27,

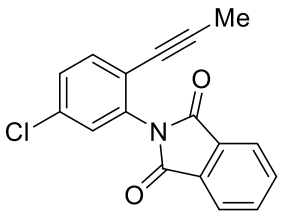
130.15, 129.65, 123.87, 121.07, 90.62, 75.88, 21.45, 4.53. **IR (neat)**: ν_{max} = 2987, 2323, 1721, 1372, 1082, 718 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{13}NO_2$ [M^+] 275.0946, found 275.0945; $\boldsymbol{R_f}$ 0.31 (Hexane:EA, 4:1).



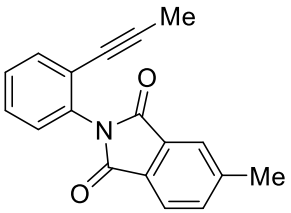
2-(4-methoxy-2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1c**: colorless solid; melting point 144~146 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.82 (s, 3H), 1.83 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.55, 159.90, 134.35, 132.27, 130.07, 126.05, 125.08, 123.85, 117.82, 115.03, 91.33, 75.91, 55.76, 4.54. **IR (neat)**: ν_{max} = 2972, 2358, 1723, 1504, 1385, 1082, 720 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{13}NO_3$ [M^+] 291.0895, found 291.0898; $\boldsymbol{R_f}$ 0.24 (Hexane:EA, 4:1).



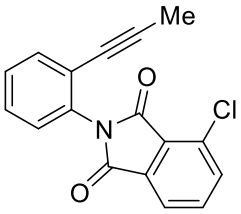
2-(4-fluoro-2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1d**: colorless solid; melting point 162~164 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.24 (t, *J* = 9.1 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.10 (td, *J* = 8.2, 2.9 Hz, 1H), 1.83 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.10, 162.45 (d, *J* = 249.2 Hz), 134.51, 132.11, 130.79 (d, *J* = 9.6 Hz), 129.45, 126.07 (d, *J* = 10.6 Hz), 123.94, 119.92 (d, *J* = 24.2 Hz), 115.94 (d, *J* = 23.0 Hz) 92.90, 75.11, 4.50; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -112.14; **IR (neat)**: ν_{max} = 2987, 2322, 1728, 1499, 1385, 1172, 718 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{17}H_{10}FNO_2$ [M^+] 279.0696, found 279.0694; $\boldsymbol{R_f}$ 0.33 (Hexane:EA, 4:1).



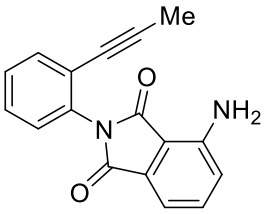
2-(5-chloro-2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1e**: yellow solid; melting point 168~170 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 1.83 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.75, 134.62, 134.38, 134.05, 133.91, 132.08, 129.54, 129.46, 124.06, 122.78, 92.73, 75.16, 4.59; **IR (neat)**: ν_{max} = 2988, 2355, 1723, 1489, 1369, 1077, 718 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{17}H_{10}ClNO_2$ [M^+] 295.0400, found 295.0398; $\boldsymbol{R_f}$ 0.31 (Hexane:EA, 4:1).



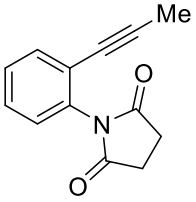
5-methyl-2-(2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1f**: colorless solid; melting point 148~150 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.40 (ddd, *J* = 7.6, 7.6, 1.9 Hz, 1H), 7.37 (ddd, *J* = 7.6, 7.6, 1.9 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.4 Hz, 1H), 2.54 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.36, 167.26, 145.72, 134.98, 133.50, 133.22, 132.62, 129.65, 129.11, 129.10, 128.53, 124.39, 124.13, 123.81, 91.47, 75.98, 22.21, 4.55; **IR (neat)**: ν_{max} = 2917, 2355, 1718, 1493, 1374, 1104, 740 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{13}NO_2$ [M^+] 275.0946, found 275.0948 $\boldsymbol{R_f}$ 0.36 (Hexane:EA, 4:1).



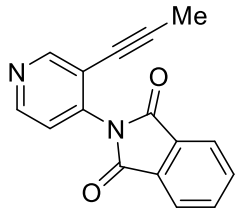
4-chloro-2-(2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1g**: yellow solid; melting point 190~192 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.88 (dd, *J* = 5.2, 3.0 Hz, 1H), 7.73-7.68 (m, 2H), 7.56 (dd, *J* = 6.6, 2.4 Hz, 1H), 7.45-7.37 (m, 2H), 7.27 (dd, *J* = 7.3, 1.8 Hz, 1H), 1.86 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.62, 164.68, 136.18, 135.34, 134.26, 133.28, 132.96, 131.95, 129.34, 129.01, 128.57, 127.90, 124.06, 122.39, 91.79, 75.89, 4.60; **IR (neat)**: ν_{max} = 2917, 2241, 1719, 1374, 1114, 900, 737 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{17}H_{10}ClNO_2$ [M^+] 295.0400, found 295.0401; $\boldsymbol{R_f}$ 0.32 (Hexane:EA, 4:1).



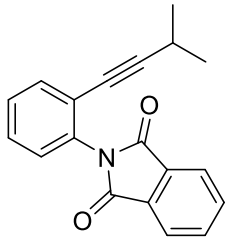
4-amino-2-(2-(prop-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1h:** yellow solid; melting point 210~212 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.55 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.46 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.40 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.37 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.33 (s, 2H), 1.88 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.13, 167.43, 145.91, 135.55, 133.50, 133.24, 132.90, 129.21, 129.01, 128.53, 124.21, 121.36, 113.21, 111.46, 91.48, 76.09, 4.65. **IR (neat)**: ν_{max} = 3369, 2987, 2355, 1700, 1493, 1371, 738 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{17}H_{12}N_2O_2$ [M^+] 276.0899, found 276.0896; $\boldsymbol{R_f}$ 0.54 (Hexane:EA, 1:1).



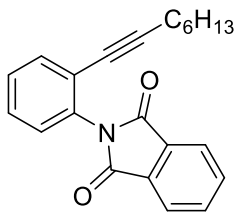
1-(2-(prop-1-yn-1-yl)phenyl)pyrrolidine-2,5-dione, **1i**: brown solid; melting point 154~156 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.53 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.39-7.34 (m, 2H), 7.15 (dd, *J* = 7.0, 2.0 Hz, 1H), 2.88 (s, 4H), 1.99 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.93, 133.67, 133.28, 129.31, 128.66, 128.26, 123.25, 91.29, 75.61, 28.85, 4.59; **IR (neat)**: ν_{max} = 2987, 2355, 1712, 1385, 1183, 764 cm^{-1}; $\boldsymbol{R_f}$ 0.48 (Hexane:EA, 2:1).



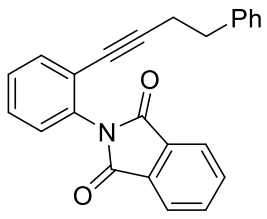
2-(3-(prop-1-yn-1-yl)pyridin-4-yl)isoindoline-1,3-dione, **1j**: colorless solid; melting point 142~144 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.79 (s, 1H), 8.61 (d, *J* = 5.2 Hz, 1H), 7.97 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.81 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.24 (d, *J* = 5.2 Hz, 1H), 1.92 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.88, 154.51, 149.01, 140.56, 134.81, 131.98, 124.24, 122.93, 120.41, 95.31, 73.45, 4.76; **IR (neat)**: ν_{max} = 2987, 2245, 1723, 1372, 1082, 717 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{16}H_{10}N_2O_2$ [M^+] 262.0742, found 262.0739; ***R*$_f$** 0.40 (Hexane:EA, 1:1).



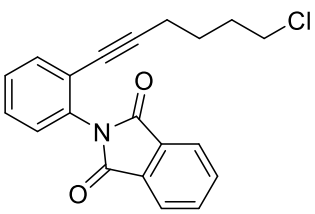
2-(2-(3-methylbut-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1k**: colorless solid; melting point 142~144 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.54 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 (td, *J* = 7.6, 1.7 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.5 Hz, 1H), 2.53 (hept, *J* = 6.8 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.15, 134.39, 133.76, 132.68, 132.30, 129.20, 129.13, 128.51, 124.03, 123.75, 101.57, 76.04, 22.66, 21.13; **IR (neat)**: ν_{max} = 2971, 2355, 1724, 1379, 1104, 718 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{19}H_{15}NO_2$ [M^+] 289.1103, found 289.1104; ***R*$_f$** 0.41 (Hexane:EA, 4:1).



2-(2-(oct-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1l**: yellow solid; melting point 56~58 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.55 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.43-7.35 (m, 2H), 7.29 (dd, *J* = 7.5, 1.6 Hz, 1H), 2.19 (t, *J* = 7.0 Hz, 2H), 1.23 (tt, *J* = 7.5, 7.3 Hz, 2H), 1.18-1.08 (m, 4H), 1.02 (qt, *J* = 7.3, 6.9 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.08, 134.33, 133.50, 132.92, 132.23, 129.16, 129.08, 128.45, 124.14, 123.76, 96.22, 76.79, 31.32, 28.47, 28.39, 22.47, 19.44, 14.15; **IR (neat)**: ν_{max} = 2929, 2229, 1719, 1493, 1378, 888, 717 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{21}NO_2$ [M^+] 331.1572, found 331.1576; ***R*$_f$** 0.45 (Hexane:EA, 4:1).

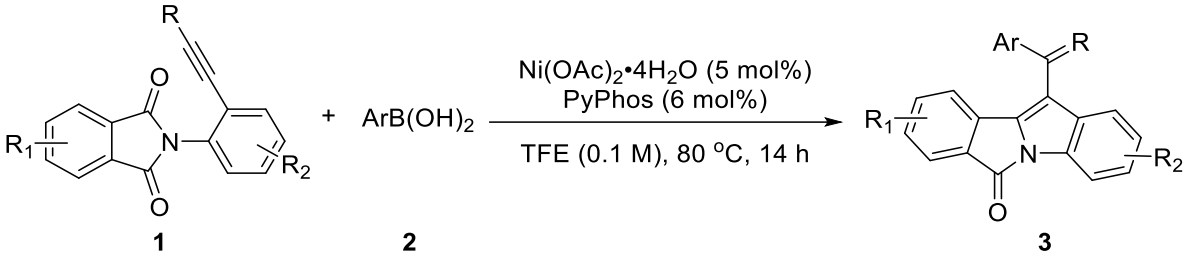


2-(2-(4-phenylbut-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1m**: colorless solid; melting point 142~144 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.56 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.44 (td, *J* = 7.6, 1.6 Hz, 1H), 7.41 (td, *J* = 7.6, 1.6 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.10, 140.40, 134.39, 133.50, 133.48, 133.11, 132.22, 129.18, 129.09, 128.67, 128.42, 128.28, 126.36, 123.84, 95.29, 77.48, 34.91, 21.61; **IR (neat)**: ν_{max} = 2987, 2355, 1720, 1379, 1264, 733, 701 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NO_2$ [M^+] 351.1259, found 351.1256; ***R*$_f$** 0.35 (Hexane:EA, 4:1).



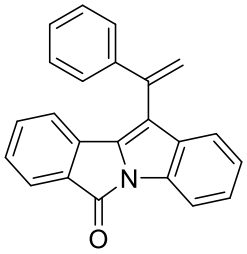
2-(2-(6-chlorohex-1-yn-1-yl)phenyl)isoindoline-1,3-dione, **1n**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.55 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.42 (td, *J* = 7.6, 1.9 Hz, 1H), 7.39 (td, *J* = 7.6, 1.6 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.30 (t, *J* = 6.5 Hz, 2H), 2.25 (t, *J* = 6.9 Hz, 2H), 1.63 (tt, *J* = 8.0, 6.5 Hz, 2H), 1.42 (tt, *J* = 8.0, 6.9 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.02, 134.47, 133.44, 133.00, 132.13, 129.19, 129.11, 128.68, 123.81, 123.79, 94.97, 77.42, 44.42, 31.26, 25.62, 18.70.; **IR (neat)**: ν_{max} = 3674, 2957, 2355, 1720, 1378, 1081, 718 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{16}ClNO_2$ [M^+] 337.0870, found 337.0869; R_f 0.31 (Hexane:EA, 4:1).

Synthesis of 11-Arylvinyl-6*H*-Isoindolo[2,1-a]indol-6-ones

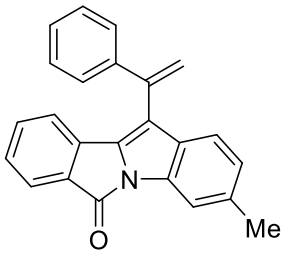


An oven-dried 25 mL reaction tube with rubber septum, equipped with a magnetic stirrer bar, was charged with **1** (0.5 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (5 mol%), Pyphos (6 mol%), and **2** (0.75 mmol). The tube was purged with nitrogen gas before the addition of 2,2,2-trifluoroethanol (5 mL) and allowed to stir at 80 °C for 14 h. The reaction progress was monitored using thin layer chromatography or gas chromatography. After the completion, the reaction mixture was cooled to room temperature and filtered. The filter cake was washed with cold methanol with three times to give the corresponding 11-arylvinyl-6*H*-Isoindolo[2,1-*a*]indol-6-ones product **3**.

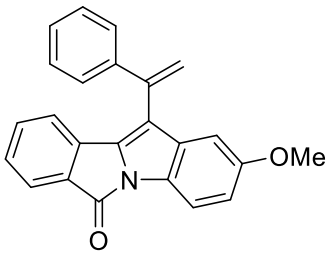
Analytic Data for 11-Arylvinyl-6*H*-Isoindolo[2,1-a]indol-6-ones



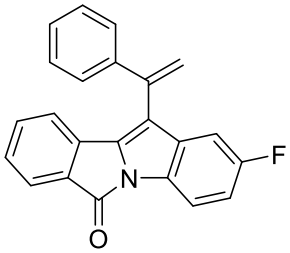
11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3aa**: yellow solid (146 mg, 91% yield); melting point 163~165 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 6.4 Hz, 1H), 7.54 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.41-7.34 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.28-7.23 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 6.8 Hz, 1H), 5.96 (d, *J* = 1.1 Hz, 1H), 5.76 (d, *J* = 1.1 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.72, 140.59, 140.20, 135.85, 134.68, 134.52, 133.96, 133.77, 133.66, 128.92, 128.66, 128.61, 127.58, 126.80, 125.27, 124.02, 122.62, 122.15, 120.20, 117.83, 113.51; **IR (neat)**: ν_{max} = 2927, 1719, 1443, 1361, 916, 744, 701 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{15}NO$ [M^+] 321.1154, found 321.1155; ***R*$_f$** 0.62 (Hexane:EA, 4:1).



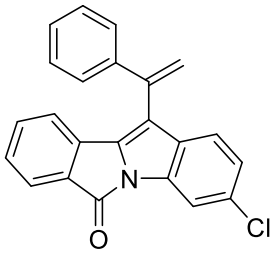
3-methyl-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ba**: yellow solid (149 mg, 89% yield); melting point 175~177 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79 (s, 1H), 7.74 (dd, *J* = 6.5, 2.2 Hz, 1H), 7.52 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.39-7.34 (m, 3H), 7.27-7.21 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.78 (dd, *J* = 6.2, 1.7 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 1H), 5.74 (d, *J* = 1.1 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.81, 140.73, 140.28, 137.41, 135.28, 134.83, 134.14, 133.91, 133.59, 132.24, 128.91, 128.58, 128.42, 127.62, 125.34, 125.25, 122.45, 121.80, 120.39, 117.70, 113.94, 21.90; **IR (neat)**: ν_{max} = 2970, 1739, 1437, 1366, 1229, 890, 528 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NO$ [M^+] 335.1310, found 335.1307; ***R*$_f$** 0.63 (Hexane:EA, 4:1).



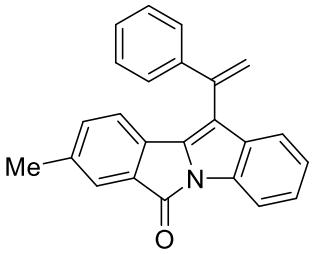
2-methoxy-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ca**: yellow solid (126 mg, 72% yield); melting point 189~191 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.7 Hz, 1H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 1H), 7.53 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.39-7.35 (m, 3H), 7.26-7.20 (m, 2H), 6.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.78 (dd, *J* = 5.5, 2.6 Hz, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 5.95 (s, 1H), 5.74 (s, 1H), 3.72 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.43, 156.92, 140.62, 140.11, 136.71, 135.54, 134.66, 134.04, 133.50, 128.92, 128.62, 128.62, 128.40, 127.59, 125.15, 122.45, 120.02, 117.68, 114.40, 114.02, 105.97, 55.82; **IR (neat)**: ν_{max} = 2970, 1739, 1367, 1217, 918, 702, 541 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NO_2$ [M^+] 351.1259, found 351.1260; ***R*$_f$** 0.54 (Hexane:EA, 4:1).



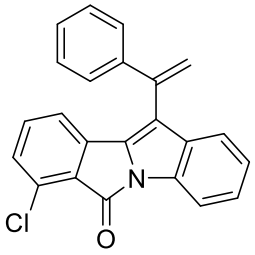
2-fluoro-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3da**: yellow solid (137 mg, 81% yield); melting point 183~185 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 8.8, 4.5 Hz, 1H), 7.76-7.72 (m, 1H), 7.54-7.49 (m, 2H), 7.39-7.35 (m, 3H), 7.30-7.25 (m, 2H), 7.02 (td, *J* = 8.8, 2.5 Hz, 1H), 6.90 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.84-6.79 (m, 1H), 5.95 (d, *J* = 0.9 Hz, 1H), 5.72 (d, *J* = 0.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.51, 160.11 (d, *J* = 240.5 Hz), 140.34, 139.88, 137.39, 135.64 (d, *J* = 9.6 Hz), 134.53, 133.82, 130.12 (d, *J* = 1.0 Hz), 129.04, 129.03, 128.82, 127.57, 125.43, 122.78, 119.77 (d, *J* = 4.0 Hz), 117.95, 114.28 (d, *J* = 25.4 Hz), 114.21, 114.14 (d, *J* = 9.3 Hz), 108.39 (d, *J* = 25.1 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -118.35; **IR (neat)**: ν_{max} = 3461, 2970, 1738, 1366, 1217, 765, 705, 530 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}FNO$ [M^+] 339.1050, found 339.1057; ***R*$_f$** 0.61 (Hexane:EA, 4:1).



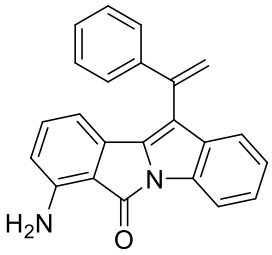
3-chloro-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ea**: yellow solid (149 mg, 84% yield); melting point 182~184 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.75 (dd, *J* = 6.2, 2.0 Hz, 1H), 7.50 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.39-7.35 (m, 3H), 7.32-7.27 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.85 (dd, *J* = 6.2, 1.8 Hz, 1H), 5.95 (s, 1H), 5.72 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.57, 140.31, 139.94, 136.21, 134.60, 134.04, 133.98, 133.61, 133.01, 132.84, 129.01, 128.96, 128.79, 127.58, 125.56, 124.50, 122.89, 122.76, 119.82, 118.03, 113.82; **IR (neat)**: ν_{max} = 2970, 1739, 1440, 1366, 1229, 1217, 900, 528 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}ClNO$ [M^+] 355.0764, found 355.0760; ***R*$_f$** 0.63 (Hexane:EA, 4:1).



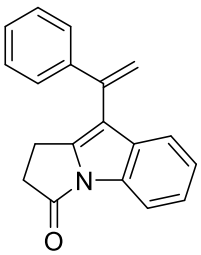
8-methyl-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3fa**: yellow solid (147 mg, 88% yield); melting point 168~170 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 4.2, 2.8 Hz, 2H), 7.40-7.37 (m, 3H), 7.31-7.28 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.10 (t, *J* = 8.2 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.52 (s, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 5.77 (d, *J* = 1.1 Hz, 1H) 2.20 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.84, 144.56, 140.75, 140.43, 135.91, 134.92, 134.35, 133.80, 131.35, 129.39, 128.90, 128.49, 127.74, 126.66, 125.09, 123.84, 123.48, 122.07, 119.86, 117.76, 113.41, 22.09; **IR (neat)**: ν_{max} = 3057, 1731, 1451, 1128, 777, 690 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NO$ [M^+] 335.1316, found 335.1308; ***R*$_f$** 0.63 (Hexane:EA, 4:1).



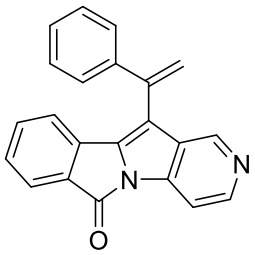
7-chloro-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ga**: yellow solid (149 mg, 84% yield); melting point 181~183 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.39-7.34 (m, 3H), 7.31 (dt, *J* = 7.7, 0.8 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.17-7.13 (m, 2H), 7.11 (dt, *J* = 7.7, 0.8 Hz, 1H), 6.70 (dd, *J* = 5.2, 3.3 Hz, 1H), 5.97 (d, *J* = 0.9 Hz, 1H), 5.74 (d, *J* = 0.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 160.23, 140.32, 140.02, 136.78, 134.44, 134.36, 133.80, 133.72, 133.09, 130.29, 129.36, 128.97, 128.70, 127.51, 127.20, 124.27, 122.24, 121.05, 120.88, 118.21, 113.63; **IR (neat)**: ν_{max} = 3060, 2970, 1739, 1380, 1217, 912, 737, 704 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}ClNO$ [M^+] 355.0764, found 355.0766; $\boldsymbol{R_f}$ 0.61 (Hexane:EA, 4:1).



10-amino-11-(1-phenylvinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ha**: yellow solid (126 mg, 75% yield); melting point 193~195 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.51 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.38-7.34 (m, 3H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 6.22 (d, *J* = 7.4 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 1H), 5.73 (d, *J* = 1.1 Hz, 1H), 5.23 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 164.78, 147.32, 140.78, 140.24, 136.02, 135.23, 134.96, 134.32, 133.43, 128.82, 128.47, 127.57, 126.36, 123.49, 122.03, 119.54, 117.64, 116.08, 114.16, 113.07, 112.26; **HRMS** m/z (EI) calc. for $C_{23}H_{16}N_2O$ [M^+] 336.1263, found 336.1264; **IR (neat)**: ν_{max} = 3451, 3016, 2970, 1739, 1366, 1229, 528 cm^{-1}; $\boldsymbol{R_f}$ 0.39 (Hexane:EA, 4:1).

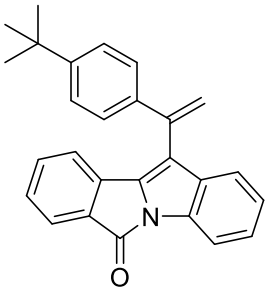


9-(1-phenylvinyl)-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one, **3ia**: colorless solid (104 mg 76% yield), ; melting point 110~112 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.43-7.38 (m, 3H), 7.38-7.34 (m, 3H), 7.32-7.29 (m, 1H), 7.26-7.23 (m, 1H), 5.65 (d, *J* = 1.2 Hz, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 3.03-2.99 (m, 2H), 2.82-2.79 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.79, 141.94, 141.50, 140.98, 134.37, 130.80, 128.56, 128.15, 127.85, 124.31, 123.73, 120.70, 115.25, 114.74, 113.85, 34.78, 20.16; **IR (neat)**: ν_{max} = 3053, 2937, 1739, 1453, 1179, 751, 703 cm^{-1}; $\boldsymbol{R_f}$ 0.47 (Hexane:EA, 4:1).

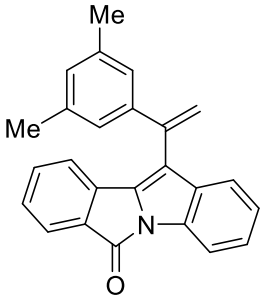


11-(1-phenylvinyl)-6*H*-pyrido[3',4':4,5]pyrrolo[2,1-*a*]isoindol-6-one, **3ja**: pale yellow solid (85 mg, 53% yield); melting point 178~180 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 8.49 (d, *J* = 5.3 Hz, 1H), 7.83 (d, *J* = 5.3 Hz, 1H), 7.82-7.76 (m, 1H), 7.51 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.40-7.35 (m, 3H), 7.35-7.30 (m, 2H), 6.82-6.79 (m, 1H), 5.98 (d, *J* = 0.8 Hz, 1H), 5.80 (d, *J* = 0.8 Hz,1H);

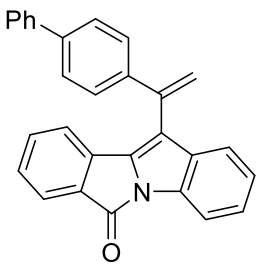
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.69, 146.69, 144.44, 139.98, 139.87, 138.01, 136.11, 134.41, 134.33, 133.45, 130.66, 129.40, 129.13, 128.95, 127.62, 125.77, 123.28, 118.83, 118.53, 108.36; **IR (neat)**: ν_{max} = 2927, 1721, 1368, 1181, 1000, 764, 701 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{14}N_2O$ [M^+] 322.1106, found 322.1107; $\boldsymbol{R_f}$ 0.54 (Hexane:EA, 1:1).



11-(1-(4-(tert-butyl)phenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ab**: yellow solid (143 mg, 76% yield); melting point 201~203 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.74 (dd, *J* = 6.2, 1.9 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 6.9 Hz, 2H), 7.24 (td, *J* = 7.3, 1.1 Hz, 1H), 7.22 (td, *J* = 7.3, 1.4 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 6.3, 1.7 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 1H), 5.71 (d, *J* = 1.1 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.78, 151.85, 140.36, 137.39, 135.82, 134.77, 134.60, 133.99, 133.81, 133.55, 128.62, 127.34, 126.80, 125.84, 125.22, 124.04, 122.82, 122.25, 120.54, 117.07, 113.53, 34.85, 31.52; **IR (neat)**: ν_{max} = 2969, 1721, 1443, 1365, 1217, 748 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{27}H_{23}NO$ [M^+] 377.1780, found 377.1777; $\boldsymbol{R_f}$ 0.62 (Hexane:EA, 4/1).

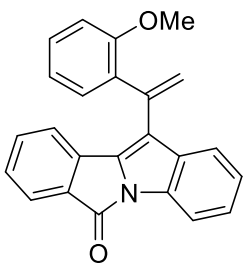


11-(1-(3,5-dimethylphenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ac**: yellow solid (141 mg, 81% yield); melting point 195~197 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.32-7.28 (m, 2H), 7.28-7.23 (m, 2H), 7.14 (s, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 5.92 (d, *J* = 1.2 Hz, 1H), 5.70 (d, *J* = 1.2 Hz, 1H), 2.30 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.78, 140.79, 140.08, 138.40, 135.78, 134.82, 134.67, 134.02, 133.79, 133.68, 130.26, 128.62, 126.74, 125.38, 125.25, 124.01, 122.69, 122.28, 120.55, 117.50, 113.48, 21.53; **IR (neat)**: ν_{max} = 3016, 1737, 1441, 1365, 1229, 751 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{25}H_{19}NO$ [M^+] 349.1467, found 349.1464; $\boldsymbol{R_f}$ 0.60 (Hexane:EA, 4:1).

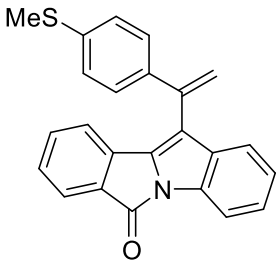


11-(1-([1,1'-biphenyl]-4-yl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ad**: yellow solid (168 mg, 85% yield); melting point 187~189 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 6.5 Hz, 1H), 7.67-7.57 (m, 6H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.30-7.24 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.02 (s, 1H), 5.77 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.77, 141.36, 140.57, 140.11, 138.96, 135.94, 134.71, 134.55, 134.00, 133.80, 133.72, 129.04, 128.75, 127.99, 127.74, 127.55, 127.17, 126.86, 125.35, 124.08, 122.67, 122.21, 120.13, 117.74, 113.56; **IR (neat)**: ν_{max} = 2969, 1721,

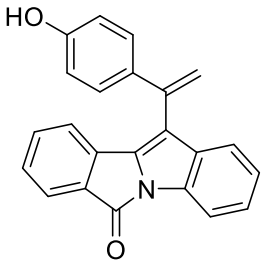
1443, 1365, 1217, 748 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{29}H_{19}NO$ [M^+] 397.1467, found 397.1465; $\boldsymbol{R_f}$ 0.56 (Hexane:EA, 4:1).



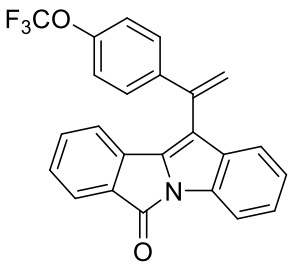
11-(1-(2-methoxyphenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ae**: yellow-orange solid (163 mg, 93% yield); melting point 152~154 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.35 (td, *J* = 8.0, 1.7 Hz, 1H), 7.30-7.25 (m, 2H), 7.26-7.22 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 2H), 5.89 (s, 2H), 3.59 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.82, 157.68, 138.27, 134.98, 134.60, 134.51, 134.02, 133.74, 133.61, 130.87, 130.21, 129.90, 128.38, 126.57, 125.18, 123.92, 122.50, 122.06, 121.99, 121.15, 120.67, 113.41, 111.89, 55.95; **IR (neat)**: ν_{max} = 2838, 1709, 1362, 1016, 758, 740 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NO_2$ [M^+] 351.1259, found 351.1257; $\boldsymbol{R_f}$ 0.50 (Hexane:EA, 4:1).



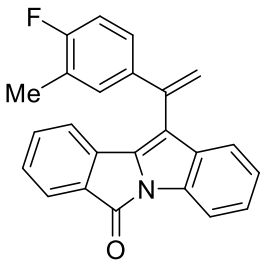
11-(1-(4-(methylthio)phenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3af**: yellow solid (167 mg, 91% yield); melting point 167~169 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.25-7.20 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.93 (s, 1H), 5.69 (s, 1H), 2.49 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.64, 139.81, 139.29, 136.61, 135.84, 134.62, 134.45, 133.92, 133.70(2C), 128.69, 127.86, 126.78, 126.54, 125.28, 124.00, 122.57, 122.14, 119.98, 117.14, 113.48, 15.73; **IR (neat)**: ν_{max} = 2970, 1738, 1366, 1217, 748, 541 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NOS$ [M^+] 367.1031, found 367.1034; $\boldsymbol{R_f}$ 0.53 (Hexane:EA, 4/1).



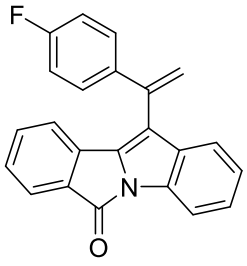
11-(1-(4-hydroxyphenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ag**: orange solid (128 mg, 76% yield); melting point 246~248 °C; **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.67 (bs, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.35-7.30 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 2H), 5.87 (s, 1H), 5.56 (s, 1H); **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.71, 157.80, 138.92, 135.03, 134.05, 133.86, 133.80, 132.94, 132.87, 130.10, 129.02, 128.35, 126.69, 124.98, 123.93, 122.27, 121.84, 119.78, 115.49, 115.43, 112.61; **IR (neat)**: ν_{max} = 3459, 3016, 2970, 1739, 1367, 1217, 756 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{15}NO_2$ [M^+] 337.1103, found 337.1101; $\boldsymbol{R_f}$ 0.38 (Hexane:EA, 2:1).



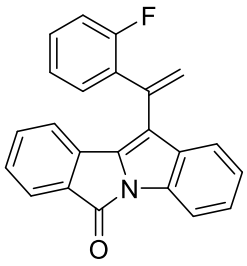
11-(1-(4-(trifluoromethoxy)phenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ah**: yellow solid (176 mg, 87% yield); melting point 149~151 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.31 (td, *J* = 7.8, 0.8 Hz, 1H), 7.29-7.26 (m, 2H), 7.24-7.21 (m, 3H), 7.11 (td, *J* = 8.3, 7.8, 0.8 Hz, 1H), 6.81 (dd, *J* = 5.9, 2.7 Hz, 1H), 5.96 (d, *J* = 1.3 Hz, 1H), 5.78 (d, *J* = 1.3 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.70, 149.49, 139.39, 138.89, 135.99, 134.53, 134.26, 133.99, 133.77, 133.75, 129.06, 128.93, 126.98, 125.47, 124.16, 122.46, 121.98, 121.39, 120.67 (q, *J* = 257.5 Hz), 119.51, 118.58, 113.63; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -60.38; **IR (neat)**: ν_{max} = 3460, 2970, 1738, 1366, 1217, 742 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{14}F_3NO_2$ [M^+] 405.0977, found 405.0977; ***R*$_f$** 0.57 (Hexane:EA, 4:1).



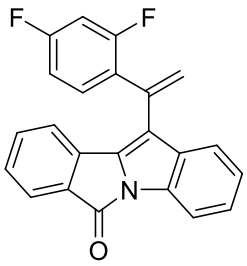
11-(1-(4-fluoro-3-methylphenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ai**: yellow solid (153 mg, 87% yield); melting point 175~177 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.33-7.28 (m, 3H), 7.28-7.25 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 8.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 5.70 (s, 1H), 2.27 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.67, 161.66 (d, *J* = 246.9 Hz), 139.71, 135.94 (d, *J* = 3.6 Hz), 135.83, 134.64, 134.43, 133.97, 133.75, 133.72, 130.57 (d, *J* = 5.3 Hz), 128.75, 126.82, 126.62 (d, *J* = 8.1 Hz), 125.34, 125.32 (d, *J* = 17.6 Hz), 124.03, 122.52, 122.12, 120.06, 117.42, 115.42 (d, *J* = 22.6 Hz), 113.52, 14.81 (d, *J* = 3.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -117.51; **IR (neat)**: ν_{max} = 2970, 1739, 1366, 1217, 899, 528 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{16}FNO$ [M^+] 353.1216, found 353.1217; ***R*$_f$** 0.62 (Hexane:EA, 4:1).



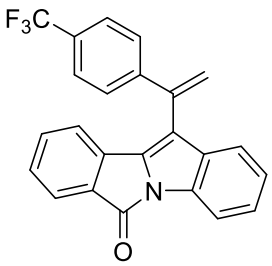
11-(1-(4-fluorophenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3aj**: yellow solid (152 mg, 90% yield); melting point 175~177 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.30-7.24 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 7.4 Hz, 1H), 5.90 (s, 1H), 5.72 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 163.10 (d, *J* = 248.3 Hz), 162.72, 139.55, 136.26 (d, *J* = 3.3 Hz), 135.91, 134.61, 134.38, 134.00, 133.78, 129.30 (d, *J* = 8.1 Hz), 128.84, 126.92, 125.43, 124.10, 122.51, 122.08, 119.92, 117.67 (d *J* = 1.1 Hz), 115.95, 115.81, 113.59; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -113.24; **IR (neat)**: ν_{max} = 2970, 1737, 1366, 1217, 752, 578 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}FNO$ [M^+] 339.1059, found 339.1057; ***R*$_f$** 0.45 (Hexane:EA, 4:1).



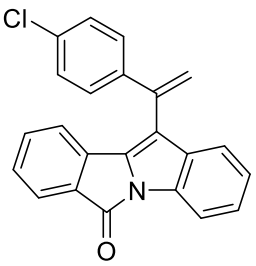
11-(1-(2-fluorophenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ak**: yellow solid (120 mg, 71% yield); melting point 161~163 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.44 (td, *J* = 7.7, 1.7 Hz, 1H), 7.34 (dtd, *J* = 9.4, 5.0, 1.7 Hz, 1H), 7.32-7.28 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.15 (td, *J* = 7.5, 0.8 Hz, 1H), 7.11 (dd, *J* = 10.7, 8.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 5.99 (s, 1H), 5.98 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.72, 160.55 (d, *J* = 250.5 Hz), 135.30, 135.15, 134.70, 134.17, 134.05, 133.76, 133.73, 130.99 (d, *J* = 3.0 Hz), 130.18 (d, *J* = 8.4 Hz), 128.75, 128.26 (d, *J* = 12.1 Hz), 126.84, 125.41, 124.62 (d, *J* = 3.7 Hz), 124.09, 122.23, 121.96 (d, *J* = 4.4 Hz), 121.79, 120.42, 116.50 (d, *J* = 22.4 Hz), 113.57; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -116.41; **IR (neat)**: ν_{max} = 2970, 1737, 1366, 1217, 752, 562 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}FNO$ [M^+] 339.1059, found 339.1058; $\boldsymbol{R_f}$ 0.52 (Hexane:EA, 4:1).



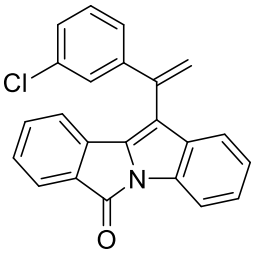
11-(1-(2,4-difluorophenyl)vinyl)-6H-isoindolo[2,1-*a*]indol-6-one, **3al**: yellow solid (105 mg, 59% yield); melting point 197~199 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.40 (td, *J* = 8.8, 6.6 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (tdd, *J* = 7.4, 2.8, 1.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.92-6.83 (m, 2H), 5.96 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.94 (dd, *J* = 251.1, 12.1 Hz), 162.67, 160.71 (dd, *J* = 254.1, 12.4 Hz), 135.40, 134.63, 134.28, 134.07, 134.04, 133.85, 133.72, 131.83 (dd, *J* = 9.4, 4.5 Hz), 128.90, 126.93, 125.54, 124.45 (dd, *J* = 12.3, 4.0 Hz), 124.14, 122.09, 121.89 (d, *J* = 4.4 Hz), 121.67, 120.08, 113.63, 111.86 (dd, *J* = 20.7, 4.2 Hz), 104.89 (dd, *J* = 26.1, 25.5 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -111.89, -111.97; **IR (neat)**: ν_{max} = 2970, 1739, 1366, 1217, 754, 561 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{13}F_2NO$ [M^+] 357.0965, found 357.0962; $\boldsymbol{R_f}$ 0.55 (Hexane:EA, 4:1).



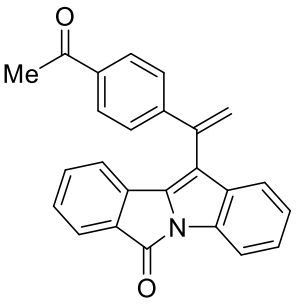
11-(1-(4-(trifluoromethyl)phenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3am**: yellow solid (171 mg, 88% yield); melting point 177~179 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.69-7.58 (m, 4H), 7.31 (td, *J* = 8.0, 1.4 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.05 (s, 1H), 5.86 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.62, 143.50, 139.54, 136.07, 134.46, 134.15, 133.97, 133.80, 133.72, 130.60 (q, *J* = 32.6 Hz), 128.99, 127.85, 126.99, 125.92 (q, *J* = 3.8 Hz), 125.50, 125.16 (q, *J* = 272.5 Hz), 124.16, 122.27, 121.90, 119.77, 119.06, 113.63; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -113.22; **IR (neat)**: ν_{max} = 2970, 1737, 1366, 1217, 1111, 745, 529 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{14}F_3NO$ [M^+] 389.1027, found 389.1025; $\boldsymbol{R_f}$ 0.58 (Hexane:EA, 4:1).



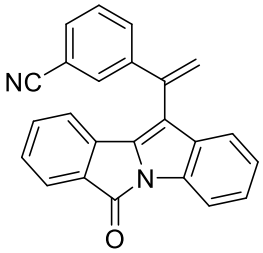
11-(1-(4-chlorophenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3an**: pale yellow solid (153 mg, 86% yield); melting point 198~200 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 1.6 Hz, 1H), 7.75 (dd, *J* = 6.1, 1.8 Hz, 1H), 7.50 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.41-7.34 (m, 3H), 7.32-7.26 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.84 (dd, *J* = 6.1, 1.6 Hz, 1H), 5.95 (s, 1H), 5.72 (s, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.56, 140.31, 139.94, 136.21, 134.59, 134.04, 133.97, 133.60, 133.00, 132.84, 129.01, 128.95, 128.78, 127.58, 125.55, 124.50, 122.89, 122.76, 119.81, 118.03, 113.81; **IR (neat)**: ν_{max} = 2970, 1739, 1440, 1366, 1217, 703 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}ClNO$ [M$^+$] 355.0764, found 355.0761; ***R*$_f$** 0.58 (Hexane:EA, 4:1).



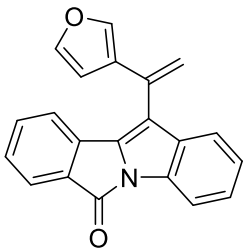
11-(1-(3-chlorophenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ao**: yellow solid (151 mg, 85% yield); melting point 162~164 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 1.7 Hz, 1H), 7.38 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.34 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.33-7.27 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.97 (d, *J* = 0.9 Hz, 1H), 5.78 (d, *J* = 0.9 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.71, 141.95, 139.50, 136.03, 134.96, 134.56, 134.30, 134.02, 133.83, 133.76, 130.20, 128.93, 128.71, 127.48, 126.96, 125.85, 125.49, 124.16, 122.42, 121.99, 119.31, 118.96, 113.62; **IR (neat)**: ν_{max} = 2970, 1737, 1367, 1217, 915, 739, cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{14}ClNO$ [M$^+$] 355.0764, found 355.0765; ***R*$_f$** 0.57 (Hexane:EA, 4:1).



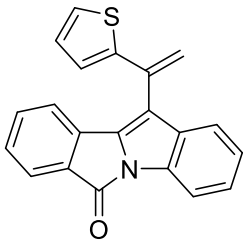
11-(1-(4-acetylphenyl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ap**: yellow solid (149 mg, 82% yield); melting point 190~192 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.94 (t, *J* = 8.7 Hz, 3H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.31-7.23 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 6.9 Hz, 1H), 6.05 (s, 1H), 5.85 (s, 1H), 2.60 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 197.65, 162.57, 144.46, 139.70, 136.94, 135.98, 134.42, 134.20, 133.90, 133.77, 133.66, 128.97, 128.88, 127.66, 126.91, 125.41, 124.08, 122.30, 121.88, 119.83, 119.13, 113.55, 26.82; **IR (neat)**: ν_{max} = 2970, 1738, 1366, 1229, 1217, 737 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{17}NO_2$ [M$^+$] 363.1259, found 363.1261; ***R*$_f$** 0.33 (Hexane:EA, 4:1).



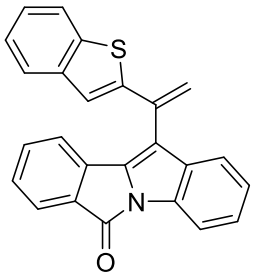
3-(1-(6-oxo-6*H*-isoindolo[2,1-*a*]indol-11-yl)vinyl)benzonitrile, **3aq**: yellow solid (81 mg, 47% yield); melting point 201~203 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.35-7.28 (m, 3H), 7.12-7.07 (m, 2H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.02 (s, 1H), 5.86 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.56, 141.26, 138.80, 136.17, 134.33, 133.98, 133.96, 133.86, 133.70, 132.02, 131.84, 130.91, 129.83, 129.12, 127.08, 125.63, 124.22, 122.11, 121.71, 119.90, 118.68, 118.44, 113.69, 113.26; **IR (neat)**: ν_{max} = 2970, 1728, 1366, 1217, 913, 741 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{14}N_2O$ [M$^+$] 346.1106, found 346.1103; $\boldsymbol{R_f}$ 0.54 (Hexane:EA, 2:1).



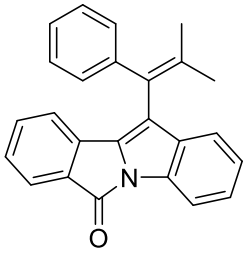
11-(1-(furan-3-yl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ar**: yellow solid (135 mg, 87% yield); melting point 138~140 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.39-7.36 (m, 2H), 7.31 (t, *J* = 6.5 Hz, 1H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 1.8, 0.9 Hz, 1H), 5.85 (d, *J* = 0.9 Hz, 1H), 5.53 (d, *J* = 0.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.74, 143.95, 141.67, 135.41, 134.69, 134.32, 133.99, 133.78, 133.69, 131.32, 128.79, 126.92, 125.81, 125.40, 124.04, 122.83, 122.00, 119.51, 115.84, 113.56, 108.85; **IR (neat)**: ν_{max} = 2970, 1737, 1374, 1229, 904, 730, 597 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H1_3NO_2$ [M$^+$] 311.0946, found 311.0947; $\boldsymbol{R_f}$ 0.50 (Hexane:EA, 4:1).



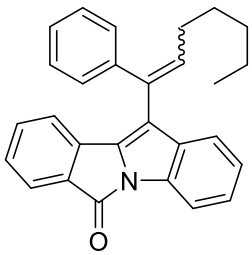
11-(1-(thiophen-2-yl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3as**: yellow solid (114 mg, 70% yield); melting point 162~164 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.37-7.33 (m, 2H), 7.34-7.30 (m, 3H), 7.28 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.28-7.25 (m, 1H), 7.16-7.11 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 5.63 (d, *J* = 1.1 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.78, 141.60, 135.65, 135.03, 134.73, 134.43, 133.98, 133.76, 133.75, 128.75, 126.90, 126.59, 126.54, 125.34, 124.08, 123.84, 122.82, 122.06, 120.12, 116.50, 113.57; **IR (neat)**: ν_{max} = 2970, 1738, 1366, 1217, 884, 751, cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H_{13}NOS$ [M$^+$] 327.0718, found 327.0720; $\boldsymbol{R_f}$ 0.58 (Hexane:EA, 4:1).



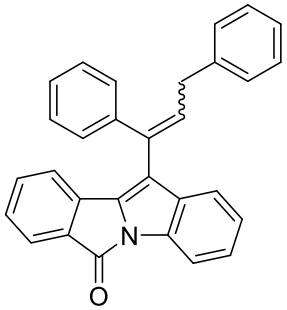
11-(1-(benzo[b]thiophen-2-yl)vinyl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3at**: yellow solid (130 mg, 69% yield); melting point 197~199 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.36-7.31 (m, 3H), 7.31-7.27 (m, 2H), 7.22 (s, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14 (td, *J* = 7.9, 1.0 Hz, 1H), 6.10 (s, 1H), 5.68 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.79, 143.03, 140.26, 139.61, 136.05, 134.58, 134.44, 134.35, 133.98, 133.94, 133.65, 128.96, 127.00, 125.48, 125.36, 124.78, 124.26, 124.20, 124.00, 122.72, 122.41, 121.92, 118.59, 118.45, 113.62; **IR (neat)**: ν_{max} = 2970, 1739, 1366, 1229, 1217, 528 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{25}H_{15}NOS$ [M^+] 377.0874, found 377.0871; ***R*$_f$** 0.57 (Hexane:EA, 4:1).



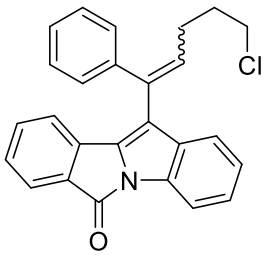
11-(2-methyl-1-phenylprop-1-en-1-yl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ka**: yellow solid (148 mg, 85% yield); melting point 158~160 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (dd, *J* = 7.8, 5.6 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.1 Hz, 1H), 7.37 (t, *J* = 6.5 Hz, 2H), 7.36-7.30 (m, 4H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 6.5 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 2.08 (s, 3H), 1.93 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.53, 140.85, 136.36, 135.15, 135.00, 134.99 134.89, 134.13, 133.78, 133.70, 129.75, 128.48, 128.18, 126.88, 126.41, 125.28, 123.85, 122.02, 121.71, 121.07, 113.34, 23.09, 22.30; **IR (neat)**: ν_{max} = 2971, 1724, 1442, 1356, 744, 702 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{25}H_{19}NO$ [M^+] 349.1467, found 349.1469; ***R*$_f$** 0.61 (Hexane:EA, 4:1).



(*E*,*Z*)-11-(1-phenylhept-1-en-1-yl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3la**: yellow oil (182 mg, 93% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.00(*Z*) (dd, *J* = 7.6, 4.5 Hz, 1H), 7.96(*E*) (dd, *J* = 7.9, 2.5 Hz, 1H), 7.81(*Z*) (d, *J* = 7.5 Hz, 1H), 7.75(*E*) (d, *J* = 7.5 Hz, 1H), 7.52-7.46(*Z*) (m, 2H), 7.46-7.38(*E*/*Z*) (m, 3+3H), 7.38-7.19(*E*/*Z*) (m, 5+5H), 7.16(*E*/*Z*) (td, *J* = 7.5, 4.7 Hz, 1+1H), 7.11(*Z*) (t, *J* = 7.5 Hz, 1H), 7.07(*E*) (t, *J* = 7.6 Hz, 1H), 6.91(*E*) (d, *J* = 7.6 Hz, 1H), 6.49(*Z*) (t, *J* = 7.4 Hz, 1H), 6.35(*E*) (t, *J* = 7.5 Hz, 1H), 2.51(*E*) (dt, *J* = 7.5, 7.5 Hz, 2H), 2.32-2.19(*Z*) (m, 2H), 1.64(*E*) (tt, *J* = 7.7, 7.7 Hz, 2H), 1.55-1.48(*Z*) (m, 1H), 1.35-1.46(*E*) (m, 4H), 1.30-1.18(Z) (m, 4H), 0.97(*E*) (t, *J* = 7.1 Hz, 3H), 0.82(*Z*) (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$) (***E*/*Z* mixtures**)** δ 162.57, 162.53, 140.64, 139.22, 139.21, 135.92, 135.13, 135.10, 134.90, 134.70, 134.67, 134.65, 134.42, 134.02, 133.89, 133.73, 133.69, 133.44, 132.25, 131.33, 129.84, 128.62, 128.59, 128.52, 128.28, 127.65, 127.50, 126.72, 126.58, 126.52, 125.26, 125.11, 123.93, 123.79, 123.07, 122.16, 122.04, 122.00, 121.91, 117.71, 113.42, 113.34, 31.82, 31.45, 30.28, 29.87, 29.78, 29.27, 22.68, 22.55, 14.19, 14.04; **IR (neat)**: ν_{max} = 2927, 1736, 1444, 1360, 753, 700 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{28}H_{25}NO$ [M^+] 391.1936, found 391.1939; ***R*$_f$** 0.58 (*E*/*Z*-overlapping, Hexane:EA, 4:1) .

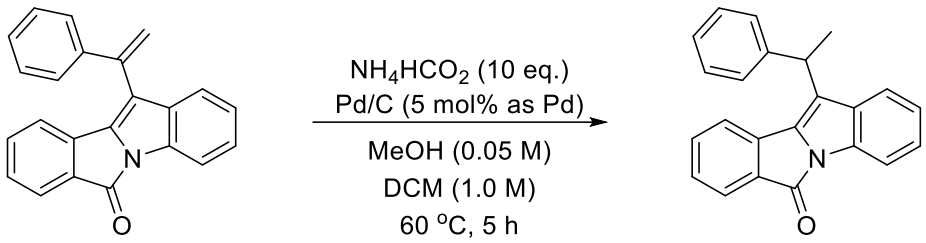


(*E*/*Z*)-11-(1,3-diphenylprop-1-en-1-yl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3ma**: yellow oil (181 mg, 88% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.06(*Z*) (d, *J* = 8.0 Hz, 1H), 7.98(*E*) (d, *J* = 8.0 Hz, 1H), 7.85(*Z*) (d, *J* = 8.1 Hz, 1H), 7.75(*E*) (d, *J* = 7.5 Hz, 1H), 7.56-7.51(*E*/*Z*) (m, 2+2H), 7.48(*E*/*Z*) (t, *J* = 7.5 Hz, 1+1H), 7.46-7.38(*E*/*Z*) (m, 2+2H), 7.34(*E*/*Z*) (p, *J* = 8.2, 7.3 Hz, 4+4H), 7.30-7.19(*E*/*Z*) (m, 4+4H), 7.16(*E*/*Z*) (dt, *J* = 15.2, 7.7 Hz, 1+1H), 7.04(*E*/*Z*) (dt, *J* = 15.0, 7.6 Hz, 1+1H), 6.73(*E*) (d, *J* = 7.6 Hz, 1H), 6.69(*Z*) (t, *J* = 7.4 Hz, 1H), 6.51(*E*) (t, *J* = 7.7 Hz, 1H), 3.87(*E*) (d, *J* = 7.7 Hz, 2H), 3.68(*Z*) (dd, *J* = 15.7, 8.1 Hz, 1H), 3.58(*Z*) (dd, *J* = 15.7, 6.7 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** (*E*/*Z* mixtures) δ 162.55 (2C), 140.22, 139.99, 138.62, 138.61, 136.28, 135.04, 135.00, 134.72, 134.59, 134.44, 134.03, 133.87, 133.84, 133.82, 133.70, 133.51, 133.07, 132.56, 132.20, 132.17, 129.88, 128.88, 128.76, 128.73, 128.70 (2C), 128.62, 128.57, 128.36, 128.04, 127.83, 126.88, 126.76, 126.53, 126.46, 126.29, 125.37, 125.10, 124.10, 123.83, 122.58, 122.20, 122.11, 122.02, 121.88, 117.11, 113.53, 113.34, 36.62, 36.02; **IR (neat)**: ν_{max} = 3030, 1717, 1442, 1360, 741, 699, 497 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{30}H_{21}NO$ [M^+] 411.1623, found 411.1621; ***R*$_f$** 0.59 (*E*/*Z*-overlapping, Hexane:EA, 4:1).



(*E*/*Z*)-11-(5-chloro-1-phenylpent-1-en-1-yl)-6*H*-isoindolo[2,1-*a*]indol-6-one, **3na**: yellow oil (171 mg, 86% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.97(*Z*) (d, *J* = 8.0 Hz, 1H), 7.93(*E*) (d, *J* = 8.0 Hz, 1H), 7.79(*Z*) (d, *J* = 7.5 Hz, 1H), 7.73(*E*) (d, *J* = 7.4 Hz, 1H), 7.45(*Z*) (dd, *J* = 7.2, 2.9 Hz, 2H), 7.43-7.39(*E*/*Z*) (m, 3+3H), 7.32-7.20(*E*/*Z*) (m, 4+4H), 7.17(*Z*) (d, *J* = 7.5 Hz, 1H), 7.14(*E*) (d, *J* = 7.9 Hz, 1H), 7.12-7.08(*Z*) (m, 2H), 7.06(*E*) (t, *J* = 7.6 Hz, 1H), 6.83(*E*) (d, *J* = 7.6 Hz, 1H), 6.43(*Z*) (td, *J* = 7.7, 2.2 Hz, 1H), 6.27(*E*) (t, *J* = 7.5 Hz, 1H), 3.63(*E*) (t, *J* = 6.6 Hz, 2H), 3.52-3.42(*Z*) (m, 2H), 2.65(*E*) (q, *J* = 7.6 Hz, 2H), 2.45-2.32(*Z*) (m, 2H), 2.08(*E*) (dt, *J* = 14.1, 6.6 Hz, 2H), 1.94(*Z*) (p, *J* = 7.2 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** (*E*/*Z* mixtures) δ 162.59, 162.57, 140.25, 138.87, 136.07, 134.93, 134.89, 134.82, 134.60, 134.52, 134.14, 134.05, 133.90, 133.77, 133.72, 133.61, 133.29, 132.90, 132.63, 131.89, 129.78, 128.81, 128.74, 128.73, 128.49, 128.00, 127.86, 126.79, 126.75, 126.67, 125.43, 125.24, 124.09, 123.92, 122.64, 122.04, 122.03, 121.90, 121.77, 117.16, 113.53, 113.43, 44.59, 44.32, 33.04, 32.54, 27.77, 27.25; **IR (neat)**: ν_{max} = 3031, 1736, 1442, 1360, 753, 700, 497 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{26}H_{20}ClNO$ [M^+] 397.1233, found 397.1236; ***R*$_f$** 0.49 (*E*/*Z*-overlapping, Hexane:EA, 4:1).

Synthesis of B; alkenyl reduction of 3aa



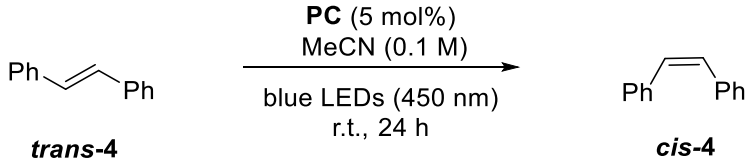
3aa **B**

In an oven-dried 100 ml schlenk flask, **3aa** (0.481 g, 1.5 mmol), ammonium formate (15 mmol, 0.945 g), and Pd/C (0.16 g, 5 mol% as Pd) were added, and the reaction flask was evacuated and backfilled with nitrogen for 3 times. Then, dichloromethane (1.0 M, 1.5 mL) was added and stirred until **3aa** completely dissolved. 30 mL of methanol (0.05 M) was added and the mixture was allowed to warm up to 60 °C for 5 hours. The reaction progress was monitored by gas chromatography. After completion, the mixture was filtered through plug of celite and the filterate was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give **B** in 97% yield.

B: yellow solid (485 mg, 97% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** 7.92 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.33 (dd, J = 7.7 Hz, 2H), 7.29 (dd, J = 8.1 Hz, 2H), 7.27-7.22 (m, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 4.70 (q, J = 7.3 Hz, 1H), 1.86 (d, J = 7.3 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.61, 143.46, 135.04, 134.46, 134.28, 134.08, 133.72, 128.84, 128.44, 127.54, 126.80, 126.67, 125.49, 125.01, 123.77, 122.20, 121.83, 113.67, 35.66, 19.94; R_f 0.65 (Hexane:EA, 4:1)

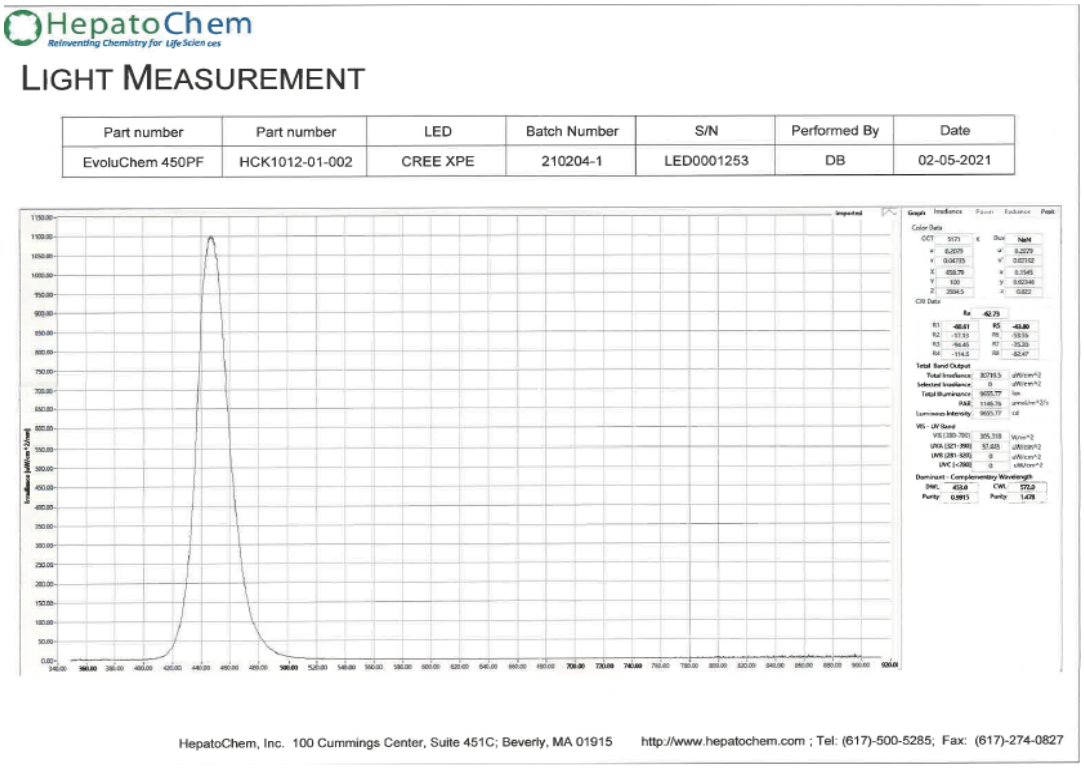
Applications

E/Z isomerization of 4[S8]



***trans*-4** **cis-4**

An oven-dried resealable test tube equipped with a magnetic stir bar was charged with ***trans*-4** (0.5 mmol), appropriate photocatalyst (5 mol%) and degassed MeCN (0.1 M, 5.0 mL) under argon. The reaction test tube was placed under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature. The reaction was stirred for 24 h, and the ratio of **4** was checked by gas chromatography.


HepatoChem
Reinventing Chemistry for Life Sciences

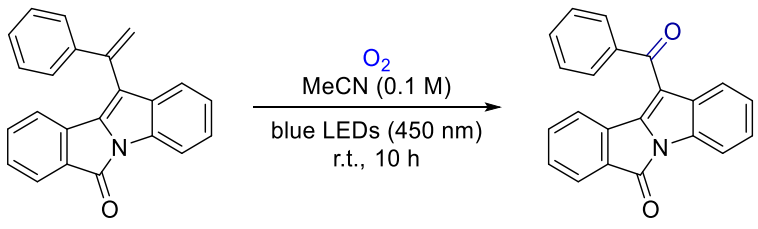
LIGHT MEASUREMENT

Part number	Part number	LED	Batch Number	S/N	Performed By	Date
EvoluChem 450PF	HCK1012-01-002	CREE XPE	210204-1	LED0001253	DB	02-05-2021

HepatoChem, Inc. 100 Cummings Center, Suite 451C; Beverly, MA 01915 http://www.hepatochem.com ; Tel: (617)-500-5285; Fax: (617)-274-0827

EvoluChem LED light spectrum (Sourced by www.hepatochem.com)

Aerobic oxidation of 3aa

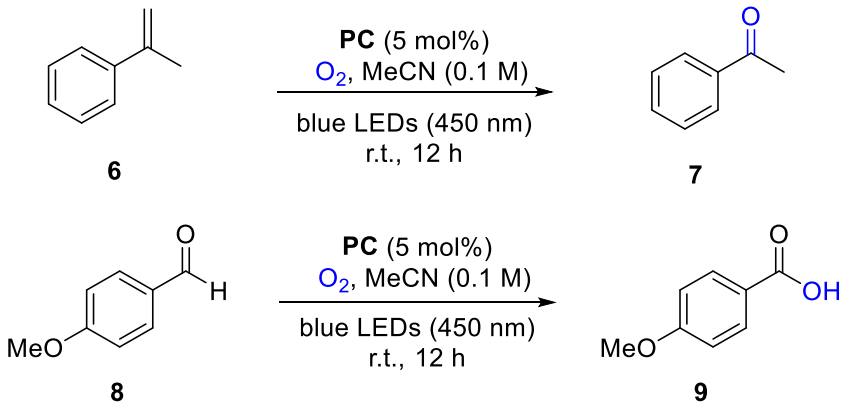


3aa **5: 92%**

An oven-dried resealable test tube equipped with a magnetic stir bar was charged with **3aa** (0.5 mmol) and MeCN (0.1 M, 5.0 mL). Molecular oxygen was then bubbled through the reaction mixture, and the tube was sealed with a silicone septa screw-cap. A balloon filled with oxygen was attached to the tube by needle, and the reaction tube was placed under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature. The reaction was allowed to proceed for 12 h, and reaction progress was checked by gas chromatography. The solvent was removed under vacuum, and the corresponding oxidized product was purified by flash silica gel chromatography to give **5** in 92% yield.

5: orange solid (148 mg, 92% yield); melting point 161~163 ºC; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.76 (dd, *J* = 5.1, 3.4 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.38-7.31 (m, 3H), 7.17-7.10 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 191.68, 163.04, 142.42, 139.36, 134.46, 133.90, 133.72, 133.35, 133.11, 132.46, 130.37, 129.54, 128.98, 127.17, 125.58, 124.91, 124.74, 123.16, 117.04, 113.45; **IR (neat)**: ν_{max} = 3023, 1737, 1444, 1360, 1043, 727, 698 cm^{-1}; ***R*$_f$** 0.51 (Hexane:EA, 4:1)

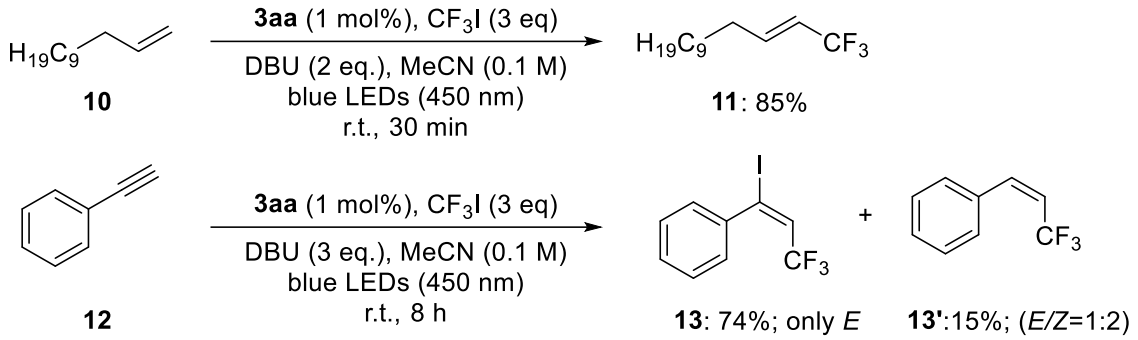
Aerobic oxidation of 6 and 8[S9]



An oven-dried resealable test tube equipped with a magnetic stir bar was charged with appropriate substrate (0.5 mmol), photocatalyst (5 mol%), and MeCN (0.1 M, 5.0 mL). Molecular oxygen was then bubbled through the reaction mixture, and the tube was sealed with a silicone septa screw-cap. A balloon filled with oxygen was attached to the tube by needle, and the reaction tube was placed under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature. The reaction was allowed to proceed for 12 h, and reaction progress was checked

by gas chromatography. The solvent was removed under vacuum, and the corresponding oxidized product was purified by flash silica gel chromatography.

Trifluoromethylation of 10 and 12[S10]



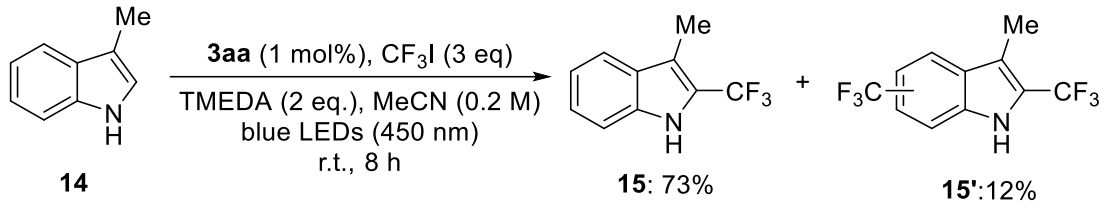
An oven-dried resealable test tube equipped with a magnetic stir bar was charged with the substrate (**10** or **12**, 0.50 mmol) and sealed with a silicone septa screw-cap. A solution of **3aa** (1.0 mol %) in MeCN (5.0 mL, 0.1 M) and DBU (1.0 mmol) were then added to the tube under argon. CF_3I (1.5 mmol) was then delivered into the reaction mixture using a gastight syringe. The test tube was placed and stirred under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature (30 min for **10**; 8 h for **12**), and the progress of the reaction was monitored by gas chromatography. The reaction mixture was diluted in diethyl ether and washed with water and brine. The organic layers were dried over $MgSO_4$, concentrated in vacuo, and purified by flash column chromatography on silica gel to give **11** or **13**/**13′**.

11: Colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.37 (dtq, *J* = 16.0, 6.8, 2.4 Hz, 1H), 5.60 (dqt, *J* = 16.0, 6.4, 1.6 Hz, 2H), 2.19-2.09 (m, 2H), 1.48-1.38 (m, 2H), 1.36-1.20 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.06 (q, *J* = 6.6 Hz), 123.38 (q, *J* = 270.1 Hz), 118.49 (q, *J* = 33.2 Hz), 32.15, 31.70, 29.83, 29.77, 29.61, 29.57, 29.28, 28.19, 22.93, 14.33; ***R*$_f$** 0.51 (hexane).

13: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40-7.30 (m, 5H), 6.64 (q, *J* = 7.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.91, 129.78 (q, *J* = 34.8 Hz), 129.70, 128.37, 127.44, 121.49 (q, *J* = 274.9 Hz), 111.37 (q, *J* = 6.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -57.67 ***R*$_f$** 0.71 (hexane).

13′ (*E*/*Z* = 1:2): colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ *(E)*- : 7.49-7.34 (m, 5H), 7.17 (d, *J* = 16.2, 1H), 6.22 (dq, *J* = 16.2, 6.4 Hz, 1H) *(Z)*- : 7.49-7.34 (m, 5H), 6.94 (d, *J* = 12.8 Hz, 1H), 5.78 (dq, *J* = 12.8, 9.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ *(E)*139.89 (q, *J* = 5.9 Hz), *(Z)*137.88 (q, *J* = 6.9 Hz), *(E)*133.642, *(Z)*132.354, 130.23, 129.15, 128.54, *(Z)*123.85 (q, *J* = 270.0 Hz), *(E)*123.02 (q, *J* = 272.3 Hz), *(E)*118.24 (q, *J* = 34.8 Hz), *(Z)*116.10 (q, *J* = 33.9 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ *(E)*- : -57.55, *(Z)*- : -63.34; **IR (neat)**: ν_{max} = 2922, 2851, 1648, 1459 cm^{-1}; ***R*$_f$** 0.60 (hexane).

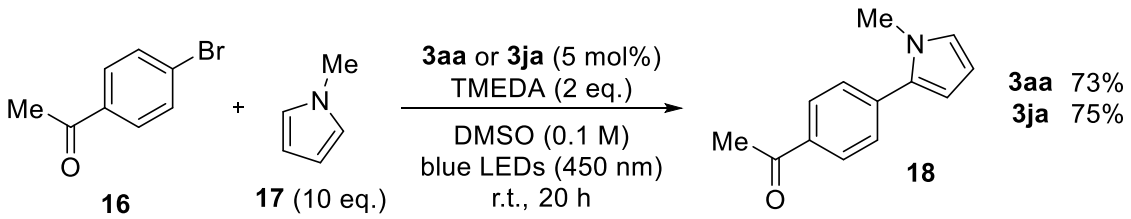
Trifluoromethylation of 14[S11]



A flame-dried tube equipped with a magnetic stirring bar was charged with argon. The substrate **14** (0.5 mmol), **3aa** (1 mol %), TMEDA (1.0 mmol), and MeCN (2.5 mL, 0.2 M) were added to the tube. CF_3I (1.5 mmol, 37.5 mL) was then delivered into the reaction mixture using a gastight syringe. The reaction tube was placed and stirred under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature for 8 h. The reaction progress was monitored by gas chromatography. After 8 h, the mixture was diluted with diethyl ether and washed with brine. The layers were separated, and the organic layer was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give **15** and **15′**.

15: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.20 (dd, *J* = 8.2, 7.8 Hz, 1H), 2.45 (q, *J* = 1.8 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 135.4, 128.3, 124.9, 122.3 (q, *J* = 269.6 Hz), 121.7 (q, *J* = 36.8 Hz), 120.6, 120.3, 114.3 (q, *J* = 3.0 Hz), 111.8, 8.5; **^{19}F NMR (564 MHz, $CDCl_3$)** δ −58.69; ***R*$_f$** 0.71 (Hexane:EA, 10:1).

C-C coupling reaction of 16 and 17[S12]

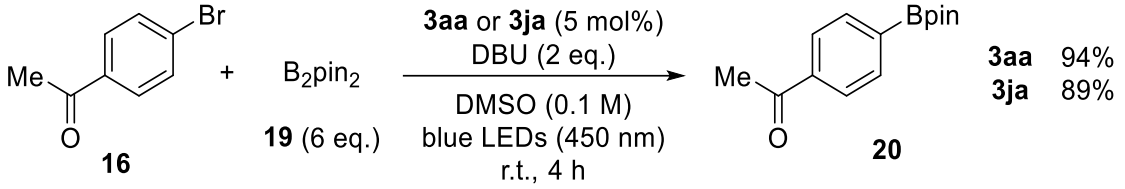


An oven-dried reaction flask equipped with a magnetic stir bar was charged with **16** (0.5 mmol), **17** (5 mmol), 1 mmol of TMEDA, and 5 mol% of **3aa** or **3ja** in degassed DMSO (0.1 M, 5 mL). Then, argon was bubbled through the reaction mixture for 2 min, and the reaction mixture tube was placed and stirred under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature. The reaction progress was monitored by gas chromatography. After 20 h, the mixture was diluted with methylene chloride and washed with brine. The layers were separated, and the organic layer was dried with MgSO4, filtered, and concentrated in vacuo to give a crude residue

that was purified by silica gel column chromatography to give the corresponding C-C coupled **18**.

18: pale-green oil; **1H NMR (600 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.77 (dd, *J* = 2.6, 1.9 Hz, 1H), 6.35 (dd, *J* = 3.6, 1.9 Hz, 1H), 6.23 (dd, *J* = 3.6, 2.6 Hz, 1H), 3.72 (s, 3H), 2.62 (s, 3H); **13C NMR (151 MHz, $CDCl_3$)** δ 197.77, 138.14, 135.18, 133.64, 128.80, 128.18, 125.52, 110.45, 108.58, 35.66, 26.79; $\boldsymbol{R_f}$ 0.37 (Hexane:EA, 4:1).

C-B coupling reaction of 16 and 19[S12]

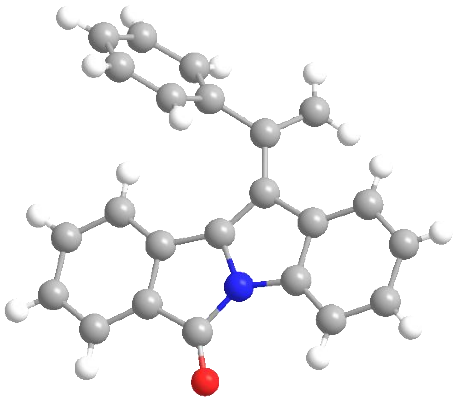


An oven-dried reaction flask equipped with a magnetic stir bar was charged with **16** (0.5 mmol), bis(pinacolato)diboron (**19**, 3 mmol), 1 mmol of DBU, and 5 mol% of **3aa** or **3ja** in degassed DMSO (0.1 M, 5 mL). Then, argon was bubbled through the reaction mixture for 2 min, and the reaction mixture tube was placed and stirred under blue LEDs (450 nm, 18 W, Hepatochem) at room temperature. The reaction progress was monitored by gas chromatography. Upon completion of the reaction, the mixture was diluted with methylene chloride and washed with brine. The layers were separated, and the organic layer was dried with MgSO4, filtered, and concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding C-B coupled product, **20**.

20: pale-green solid; **1H NMR (600 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 2.61 (s, 3H), 1.35 (s, 12H); **13C NMR (151 MHz, $CDCl_3$)** δ 198.72, 139.21, 135.13, 127.50, 110.15, 84.44, 29.92, 25.09; $\boldsymbol{R_f}$ 0.55 (Hexane:EA, 9:1).

Crystal Structure Data

Formula weight: 321.36; Crystal system: Monoclinic; Space group: P2(1)/m; Unit cell dimensions: a = 5.6444(4) Å, b = 15.047(10) Å, c = 9.888(7) Å, α = 90.00°, β = 105.229(9)°, γ = 90.00°; Cell volume = 810.3(16) $Å^3$, Z = 2; Density calculated = 1.337 g/cm^3; R_{All} = 0.154. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (CCDC 2054405).



X-Ray Structure of 3aa

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department of chemistryChung-Ang University, 84 Heukseok-ro, Heukseok-dong, Dongjak-gu, Seoul;
'Dr Naeem Iqbal';
department of chemistryChung-Ang University, 84 Heukseok-ro, Heukseok-dong, Dongjak-gu, Seoul

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They are only intended as comments.
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_atom_sites_solution_primary           ?
_atom_sites_solution_secondary         ?
_atom_sites_solution_hydrogens         geom
_refine_ls_hydrogen_treatment          constr
```

```
_refine_ls_extinction_method          none
_refine_ls_extinction_coef            .
_refine_ls_abs_structure_details
;
 Flack x determined using 455 quotients [(I+)-(I-)]/[(I+)+(I-)]
 (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
;
_refine_ls_abs_structure_Flack       -1.8(10)
_chemical_absolute_configuration   ?
_refine_ls_number_reflns              2845
_refine_ls_number_parameters          226
_refine_ls_number_restraints          1
_refine_ls_R_factor_all               0.1539
_refine_ls_R_factor_gt                0.0707
_refine_ls_wR_factor_ref              0.2623
_refine_ls_wR_factor_gt               0.2264
_refine_ls_goodness_of_fit_ref       0.993
_refine_ls_restrained_S_all          0.993
_refine_ls_shift/su_max               0.000
_refine_ls_shift/su_mean              0.000

loop_
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 _atom_site_U_iso_or_equiv
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 _atom_site_occupancy
 _atom_site_site_symmetry_order
 _atom_site_calc_flag
 _atom_site_refinement_flags_posn
 _atom_site_refinement_flags_adp
 _atom_site_refinement_flags_occupancy
 _atom_site_disorder_assembly
 _atom_site_disorder_group
O001 O 0.8999(14) 0.4210(5) 0.7782(7) 0.076(2) Uani 1 1 d . . . . .
N002 N 0.8027(14) 0.4302(5) 0.5359(8) 0.0491(19) Uani 1 1 d . . . . .
C00A C 0.1365(17) 0.5558(7) 0.0547(9) 0.055(3) Uani 1 1 d . . . . .
H00A H 0.052376 0.504115 0.017535 0.066 Uiso 1 1 calc R U . . .
C00B C 0.3811(16) 0.5505(7) 0.1314(8) 0.048(2) Uani 1 1 d . . . . .
C00C C 0.6264(16) 0.4704(7) 0.4258(9) 0.049(2) Uani 1 1 d . . . . .
C00D C 0.155(2) 0.6130(8) 0.5407(12) 0.067(3) Uani 1 1 d . . . . .
H00D H 0.015534 0.648250 0.507875 0.080 Uiso 1 1 calc R U . . .
C00E C 0.5014(17) 0.6285(7) 0.1828(9) 0.054(2) Uani 1 1 d . . . . .
H00E H 0.666149 0.626914 0.234167 0.065 Uiso 1 1 calc R U . . .
C00F C 0.454(2) 0.5503(8) 0.7338(10) 0.066(3) Uani 1 1 d . . . . .
H00F H 0.518300 0.541975 0.829999 0.079 Uiso 1 1 calc R U . . .
C00G C 0.0161(19) 0.6370(9) 0.0329(10) 0.067(3) Uani 1 1 d . . . . .
H00G H -0.148547 0.639450 -0.018580 0.080 Uiso 1 1 calc R U . . .
C00H C 0.5067(16) 0.4627(7) 0.1592(9) 0.051(2) Uani 1 1 d . . . . .
C00I C 1.0103(18) 0.3402(8) 0.2557(12) 0.064(3) Uani 1 1 d . . . . .
H00I H 0.962433 0.343262 0.158043 0.076 Uiso 1 1 calc R U . . .
C00J C 0.378(2) 0.7093(8) 0.1581(11) 0.069(3) Uani 1 1 d . . . . .
H00J H 0.462023 0.761657 0.191748 0.083 Uiso 1 1 calc R U . . .
C00K C 1.163(2) 0.3294(7) 0.5489(13) 0.067(3) Uani 1 1 d . . . . .
H00K H 1.213697 0.326820 0.646602 0.080 Uiso 1 1 calc R U . . .
C00L C 1.289(2) 0.2853(8) 0.4693(15) 0.077(3) Uani 1 1 d . . . . .
```

H00L H 1.426105 0.250852 0.512650 0.093 Uiso 1 1 calc R U . . .
C00M C 1.216(2) 0.2911(8) 0.3238(15) 0.076(3) Uani 1 1 d . . . . .
H00M H 1.306837 0.261468 0.271011 0.092 Uiso 1 1 calc R U . . .
C00N C 0.471(2) 0.4007(8) 0.0581(10) 0.072(3) Uani 1 1 d . . . . .
H00B H 0.544424 0.344895 0.077277 0.086 Uiso 1 1 calc R U . . .
H00C H 0.371659 0.413424 -0.031370 0.086 Uiso 1 1 calc R U . . .
C00O C 0.136(2) 0.7137(7) 0.0857(10) 0.067(3) Uani 1 1 d . . . . .
H00O H 0.052896 0.768095 0.072400 0.080 Uiso 1 1 calc R U . . .
C00P C 0.249(2) 0.6029(8) 0.6828(12) 0.074(4) Uani 1 1 d . . . . .
H00P H 0.173709 0.631456 0.744624 0.089 Uiso 1 1 calc R U . . .
C003 C 0.7742(19) 0.4502(7) 0.6690(10) 0.056(3) Uani 1 1 d . . . . .
C004 C 0.2617(17) 0.5727(6) 0.4438(10) 0.052(2) Uani 1 1 d . . . . .
H004 H 0.194107 0.580037 0.347629 0.063 Uiso 1 1 calc R U . . .
C005 C 0.8761(17) 0.3847(6) 0.3351(10) 0.051(2) Uani 1 1 d . . . . .
C006 C 0.6625(15) 0.4429(6) 0.3002(9) 0.047(2) Uani 1 1 d . . . . .
C007 C 0.4698(16) 0.5217(6) 0.4943(9) 0.045(2) Uani 1 1 d . . . . .
C008 C 0.9600(18) 0.3779(7) 0.4812(10) 0.053(2) Uani 1 1 d . . . . .
C009 C 0.5619(19) 0.5107(6) 0.6394(9) 0.052(2) Uani 1 1 d . . . . .

loop_
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 _atom_site_aniso_U_23
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O001 0.097(5) 0.075(6) 0.042(4) 0.008(4) -0.005(4) -0.008(4)
N002 0.056(4) 0.042(5) 0.047(4) 0.005(4) 0.008(3) -0.005(4)
C00A 0.061(6) 0.059(7) 0.043(5) -0.006(5) 0.010(4) -0.009(5)
C00B 0.054(5) 0.057(7) 0.032(5) 0.006(4) 0.010(4) -0.002(5)
C00C 0.051(5) 0.052(6) 0.042(5) 0.004(4) 0.010(4) -0.011(5)
C00D 0.070(7) 0.056(8) 0.085(8) -0.004(6) 0.039(6) 0.002(5)
C00E 0.060(6) 0.057(7) 0.044(5) 0.001(5) 0.009(4) -0.014(6)
C00F 0.091(8) 0.069(8) 0.045(6) -0.010(5) 0.029(6) -0.025(7)
C00G 0.065(6) 0.077(8) 0.052(6) 0.002(6) 0.005(5) 0.006(7)
C00H 0.058(5) 0.063(7) 0.035(5) 0.004(5) 0.016(4) -0.005(5)
C00I 0.061(6) 0.052(7) 0.086(8) -0.002(6) 0.034(6) -0.004(5)
C00J 0.090(8) 0.052(8) 0.057(6) 0.005(5) 0.007(6) -0.015(6)
C00K 0.055(6) 0.052(7) 0.086(7) 0.012(6) 0.004(6) -0.003(5)
C00L 0.054(7) 0.057(8) 0.117(11) 0.016(7) 0.017(7) 0.010(6)
C00M 0.065(7) 0.054(8) 0.122(11) 0.002(7) 0.047(7) 0.005(6)
C00N 0.095(8) 0.080(9) 0.040(5) -0.004(5) 0.018(5) 0.000(6)
C00O 0.087(8) 0.054(8) 0.054(6) 0.005(5) 0.009(5) 0.005(6)
C00P 0.102(9) 0.069(9) 0.067(8) -0.021(6) 0.048(7) -0.012(7)
C003 0.080(7) 0.045(7) 0.039(5) -0.003(4) 0.006(5) -0.030(6)
C004 0.059(6) 0.047(7) 0.056(6) 0.000(5) 0.025(5) -0.002(5)
C005 0.055(6) 0.041(6) 0.062(6) 0.005(5) 0.022(5) -0.004(5)
C006 0.051(5) 0.051(7) 0.042(5) -0.001(4) 0.015(4) -0.007(4)
C007 0.052(5) 0.047(6) 0.037(5) -0.003(4) 0.014(4) -0.010(5)
C008 0.051(6) 0.044(6) 0.060(6) 0.008(5) 0.010(5) -0.004(5)
C009 0.065(6) 0.047(6) 0.044(6) 0.000(4) 0.014(5) -0.009(5)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only

```
  used when they are defined by crystal symmetry.    An approximate (isotropic)
  treatment of cell esds is used for estimating esds involving l.s. planes.
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loop_
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O001 C003 1.203(11) . ?
N002 C008 1.389(13) . ?
N002 C003 1.394(13) . ?
N002 C00C 1.398(11) . ?
C00A C00G 1.381(15) . ?
C00A C00B 1.383(12) . ?
C00A H00A 0.9300 . ?
C00B C00E 1.378(13) . ?
C00B C00H 1.483(14) . ?
C00C C006 1.369(13) . ?
C00C C007 1.457(13) . ?
C00D C00P 1.368(15) . ?
C00D C004 1.389(13) . ?
C00D H00D 0.9300 . ?
C00E C00J 1.384(15) . ?
C00E H00E 0.9300 . ?
C00F C009 1.369(14) . ?
C00F C00P 1.377(17) . ?
C00F H00F 0.9300 . ?
C00G C00O 1.362(15) . ?
C00G H00G 0.9300 . ?
C00H C00N 1.338(13) . ?
C00H C006 1.465(13) . ?
C00I C00M 1.383(16) . ?
C00I C005 1.389(14) . ?
C00I H00I 0.9300 . ?
C00J C00O 1.359(15) . ?
C00J H00J 0.9300 . ?
C00K C00L 1.356(17) . ?
C00K C008 1.368(14) . ?
C00K H00K 0.9300 . ?
C00L C00M 1.387(19) . ?
C00L H00L 0.9300 . ?
C00M H00M 0.9300 . ?
C00N H00B 0.9300 . ?
C00N H00C 0.9300 . ?
C00O H00O 0.9300 . ?
C00P H00P 0.9300 . ?
C003 C009 1.462(15) . ?
C004 C007 1.374(13) . ?
C004 H004 0.9300 . ?
C005 C008 1.396(14) . ?
C005 C006 1.448(13) . ?
C007 C009 1.398(14) . ?

loop_
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C008 N002 C003 136.6(8) . . ?
C008 N002 C00C 109.5(8) . . ?
C003 N002 C00C 113.9(8) . . ?
C00G C00A C00B 120.6(9) . . ?
C00G C00A H00A 119.7 . . ?
C00B C00A H00A 119.7 . . ?
C00E C00B C00A 118.1(9) . . ?
C00E C00B C00H 121.5(9) . . ?
C00A C00B C00H 120.4(8) . . ?
C006 C00C N002 109.3(8) . . ?
C006 C00C C007 145.7(9) . . ?
N002 C00C C007 104.9(7) . . ?
C00P C00D C004 122.5(11) . . ?
C00P C00D H00D 118.7 . . ?
C004 C00D H00D 118.7 . . ?
C00B C00E C00J 120.2(9) . . ?
C00B C00E H00E 119.9 . . ?
C00J C00E H00E 119.9 . . ?
C009 C00F C00P 118.4(10) . . ?
C009 C00F H00F 120.8 . . ?
C00P C00F H00F 120.8 . . ?
C00O C00G C00A 120.8(10) . . ?
C00O C00G H00G 119.6 . . ?
C00A C00G H00G 119.6 . . ?
C00N C00H C006 120.1(10) . . ?
C00N C00H C00B 120.4(9) . . ?
C006 C00H C00B 119.4(8) . . ?
C00M C00I C005 119.1(11) . . ?
C00M C00I H00I 120.4 . . ?
C005 C00I H00I 120.4 . . ?
C00O C00J C00E 121.2(10) . . ?
C00O C00J H00J 119.4 . . ?
C00E C00J H00J 119.4 . . ?
C00L C00K C008 118.0(11) . . ?
C00L C00K H00K 121.0 . . ?
C008 C00K H00K 121.0 . . ?
C00K C00L C00M 120.6(11) . . ?
C00K C00L H00L 119.7 . . ?
C00M C00L H00L 119.7 . . ?
C00I C00M C00L 121.2(11) . . ?
C00I C00M H00M 119.4 . . ?
C00L C00M H00M 119.4 . . ?
C00H C00N H00B 120.0 . . ?
C00H C00N H00C 120.0 . . ?
H00B C00N H00C 120.0 . . ?
C00J C00O C00G 118.9(11) . . ?
C00J C00O H00O 120.5 . . ?
C00G C00O H00O 120.5 . . ?
C00D C00P C00F 119.8(10) . . ?
C00D C00P H00P 120.1 . . ?
C00F C00P H00P 120.1 . . ?
O001 C003 N002 125.3(11) . . ?
O001 C003 C009 131.2(9) . . ?
N002 C003 C009 103.5(8) . . ?
C007 C004 C00D 117.9(10) . . ?
C007 C004 H004 121.0 . . ?
```

```
C00D C004 H004 121.0 . . ?
C00I C005 C008 117.4(9) . . ?
C00I C005 C006 133.7(9) . . ?
C008 C005 C006 108.9(8) . . ?
C00C C006 C005 105.9(8) . . ?
C00C C006 C00H 127.2(9) . . ?
C005 C006 C00H 126.8(8) . . ?
C004 C007 C009 119.2(9) . . ?
C004 C007 C00C 133.0(9) . . ?
C009 C007 C00C 107.7(8) . . ?
C00K C008 N002 129.9(10) . . ?
C00K C008 C005 123.7(10) . . ?
N002 C008 C005 106.4(8) . . ?
C00F C009 C007 122.2(10) . . ?
C00F C009 C003 127.8(9) . . ?
C007 C009 C003 109.9(8) . . ?

_refine_diff_density_max        0.150
_refine_diff_density_min       -0.179
_refine_diff_density_rms        0.039

_shelx_res_file
;
TITL Integration of BJH
      200331BJHF_0m.res
      created by SHELXL-2017/1 at 11:58:13 on 01-Apr-2020
CELL    0.71073      5.6019    14.9798      9.8511      90.000    105.147      90.000
ZERR       2.000      0.0198      0.0521      0.0366       0.000       0.039       0.000
LATT -1
SYMM -X, 1/2+Y, -Z
SFAC C    H    N    O
UNIT 46    30    2    2
L.S. 10
ACTA
BOND $H
FMAP 2
PLAN 20
TEMP 0.000
WGHT       0.102300       1.147900
FVAR            1.13008
O001    4      0.899924       0.421046       0.778190       11.00000       0.09730       0.07467 =
             0.04238       0.00815      -0.00482      -0.00761
N002    3      0.802745       0.430216       0.535946       11.00000       0.05598       0.04158 =
             0.04672       0.00476       0.00810      -0.00500
C00A    1    0.136525       0.555769       0.054727       11.00000       0.06067       0.05944 =
             0.04261      -0.00575       0.01017      -0.00913
AFIX    43
H00A    2    0.052376       0.504115       0.017535       11.00000      -1.20000
AFIX     0
C00B    1      0.381132       0.550483       0.131448       11.00000       0.05401       0.05688 =
             0.03183       0.00637       0.00971      -0.00184
C00C    1      0.626359       0.470411       0.425832       11.00000       0.05087       0.05182 =
             0.04175       0.00437       0.01005      -0.01129
C00D    1    0.155467       0.613038       0.540738       11.00000       0.07025       0.05637 =
             0.08456      -0.00409       0.03934       0.00189
AFIX    43
H00D    2    0.015534       0.648250       0.507875       11.00000      -1.20000
AFIX     0
C00E    1      0.501356       0.628534       0.182769       11.00000       0.05996       0.05679 =
```

```
          0.04398       0.00061       0.00874      -0.01447
AFIX   43
H00E   2     0.666149       0.626914       0.234167       11.00000      -1.20000
AFIX    0
C00F   1     0.454242       0.550336       0.733795       11.00000       0.09076       0.06904 =
          0.04461      -0.01012       0.02937      -0.02505
AFIX   43
H00F   2     0.518300       0.541975       0.829999       11.00000      -1.20000
AFIX    0
C00G   1     0.016143       0.637029       0.032853       11.00000       0.06545       0.07736 =
          0.05212       0.00163       0.00545       0.00591
AFIX   43
H00G   2    -0.148547       0.639450      -0.018580       11.00000      -1.20000
AFIX    0
C00H   1     0.506740       0.462712       0.159200       11.00000       0.05827       0.06267 =
          0.03467       0.00429       0.01611      -0.00516
C00I   1     1.010274       0.340151       0.255708       11.00000       0.06090       0.05217 =
          0.08574      -0.00166       0.03376      -0.00439
AFIX   43
H00I   2     0.962433       0.343262       0.158043       11.00000      -1.20000
AFIX    0
C00J   1     0.377795       0.709339       0.158119       11.00000       0.09024       0.05250 =
          0.05704       0.00469       0.00740      -0.01545
AFIX   43
H00J   2     0.462023       0.761657       0.191748       11.00000      -1.20000
AFIX    0
C00K   1     1.163375       0.329416       0.548937       11.00000       0.05472       0.05230 =
          0.08620       0.01192       0.00438      -0.00289
AFIX   43
H00K   2     1.213697       0.326820       0.646602       11.00000      -1.20000
AFIX    0
C00L   1     1.289320       0.285305       0.469294       11.00000       0.05400       0.05674 =
          0.11727       0.01641       0.01651       0.00991
AFIX   43
H00L   2     1.426105       0.250852       0.512650       11.00000      -1.20000
AFIX    0
C00M   1     1.215999       0.291107       0.323808       11.00000       0.06550       0.05369 =
          0.12243       0.00234       0.04715       0.00451
AFIX   43
H00M   2     1.306837       0.261468       0.271011       11.00000      -1.20000
AFIX    0
C00N   1     0.470601       0.400707       0.058091       11.00000       0.09548       0.08021 =
          0.03964      -0.00417       0.01826       0.00017
AFIX   93
H00B   2     0.544424       0.344895       0.077277       11.00000      -1.20000
H00C   2     0.371659       0.413424      -0.031370       11.00000      -1.20000
AFIX    0
C00O   1     0.135641       0.713672       0.085678       11.00000       0.08697       0.05409 =
          0.05380       0.00484       0.00857       0.00518
AFIX   43
H00O   2     0.052896       0.768095       0.072400       11.00000      -1.20000
AFIX    0
C00P   1     0.248787       0.602918       0.682766       11.00000       0.10167       0.06934 =
          0.06701      -0.02057       0.04818      -0.01225
AFIX   43
H00P   2     0.173709       0.631456       0.744624       11.00000      -1.20000
AFIX    0
C003   1     0.774151       0.450206       0.669013       11.00000       0.07976       0.04530 =
          0.03867      -0.00296       0.00633      -0.03024
```

```
C004    1    0.261734       0.572732       0.443766       11.00000       0.05937       0.04725 =
             0.05575       0.00002       0.02457      -0.00246
AFIX   43
H004    2    0.194107       0.580037       0.347629       11.00000      -1.20000
AFIX    0
C005    1    0.876117       0.384686       0.335140       11.00000       0.05535       0.04109 =
             0.06173       0.00519       0.02209      -0.00446
C006    1    0.662452       0.442876       0.300175       11.00000       0.05095       0.05106 =
             0.04175      -0.00147       0.01466      -0.00732
C007    1    0.469827       0.521742       0.494258       11.00000       0.05167       0.04703 =
             0.03685      -0.00254       0.01428      -0.00950
C008    1    0.959999       0.377859       0.481215       11.00000       0.05105       0.04387 =
             0.06012       0.00842       0.00967      -0.00398
C009    1    0.561936       0.510656       0.639430       11.00000       0.06493       0.04699 =
             0.04394      -0.00041       0.01401      -0.00863
HKLF 4

REM    Integration of BJH
REM R1 =    0.0707 for        1399 Fo > 4sig(Fo)    and    0.1539 for all        2845 data
REM        226 parameters refined using           1 restraints

END

WGHT          0.0368          0.2920

REM Highest difference peak    0.150,    deepest hole -0.179,    1-sigma level    0.039
Q1        1     0.5132    0.4608    0.3179    11.00000    0.05        0.15
Q2        1     1.0040    0.3970    0.4170    11.00000    0.05        0.15
Q3        1     1.0764    0.3193    0.7626    11.00000    0.05        0.14
Q4        1     0.6624    0.7509    0.0836    11.00000    0.05        0.14
Q5        1     1.0908    0.2508    0.6610    11.00000    0.05        0.14
Q6        1     0.0463    0.4574    0.0580    11.00000    0.05        0.14
Q7        1     1.0461    0.3884    0.7630    11.00000    0.05        0.13
Q8        1     1.0876    0.3196    0.6952    11.00000    0.05        0.13
Q9        1     0.0614    0.6304    0.1372    11.00000    0.05        0.13
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Q11       1     0.4554    0.7892    0.2588    11.00000    0.05        0.13
Q12       1     0.6944    0.3964    0.5875    11.00000    0.05        0.12
Q13       1     0.9469    0.6066    0.1991    11.00000    0.05        0.12
Q14       1    -0.0284    0.5955    0.6848    11.00000    0.05        0.12
Q15       1     0.4052    0.4330    0.4065    11.00000    0.05        0.12
Q16       1     0.3446    0.5726    0.2080    11.00000    0.05        0.12
Q17       1     0.9002    0.4347    0.6356    11.00000    0.05        0.12
Q18       1     0.2969    0.5402    0.0239    11.00000    0.05        0.12
Q19       1     0.2740    0.5799    0.5889    11.00000    0.05        0.12
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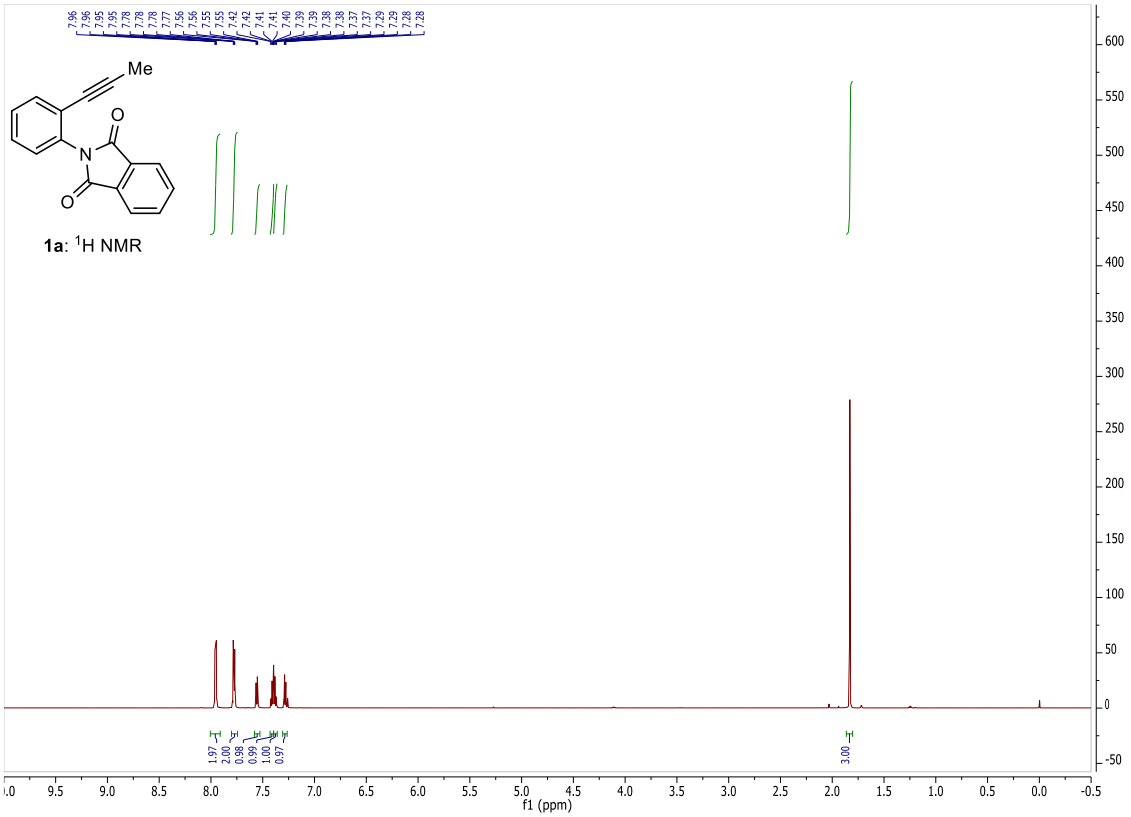
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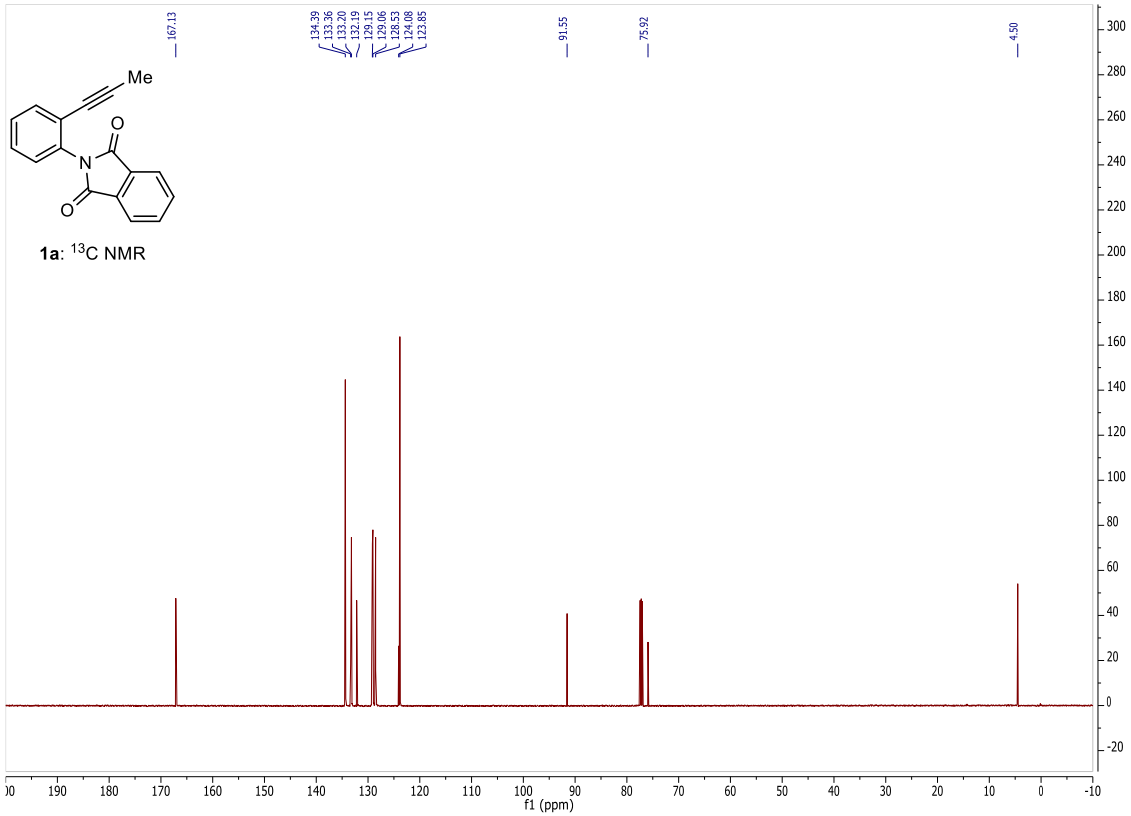
f1 (ppm)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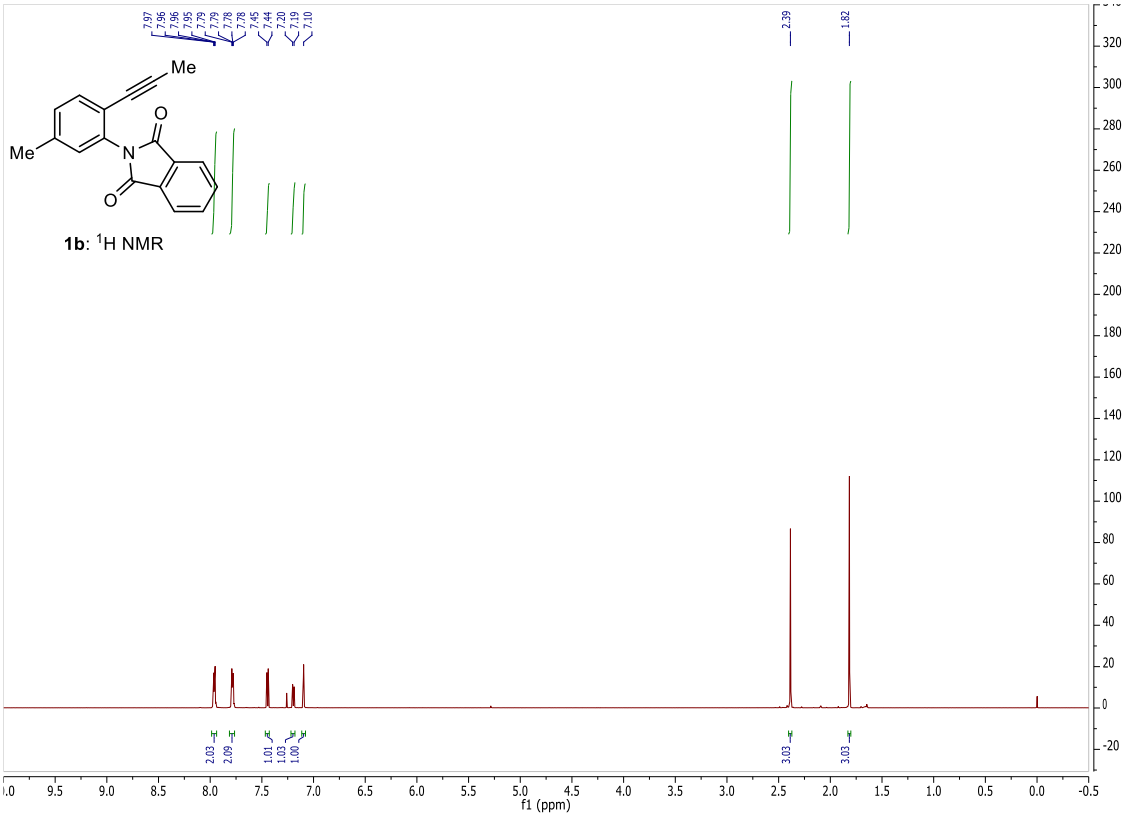

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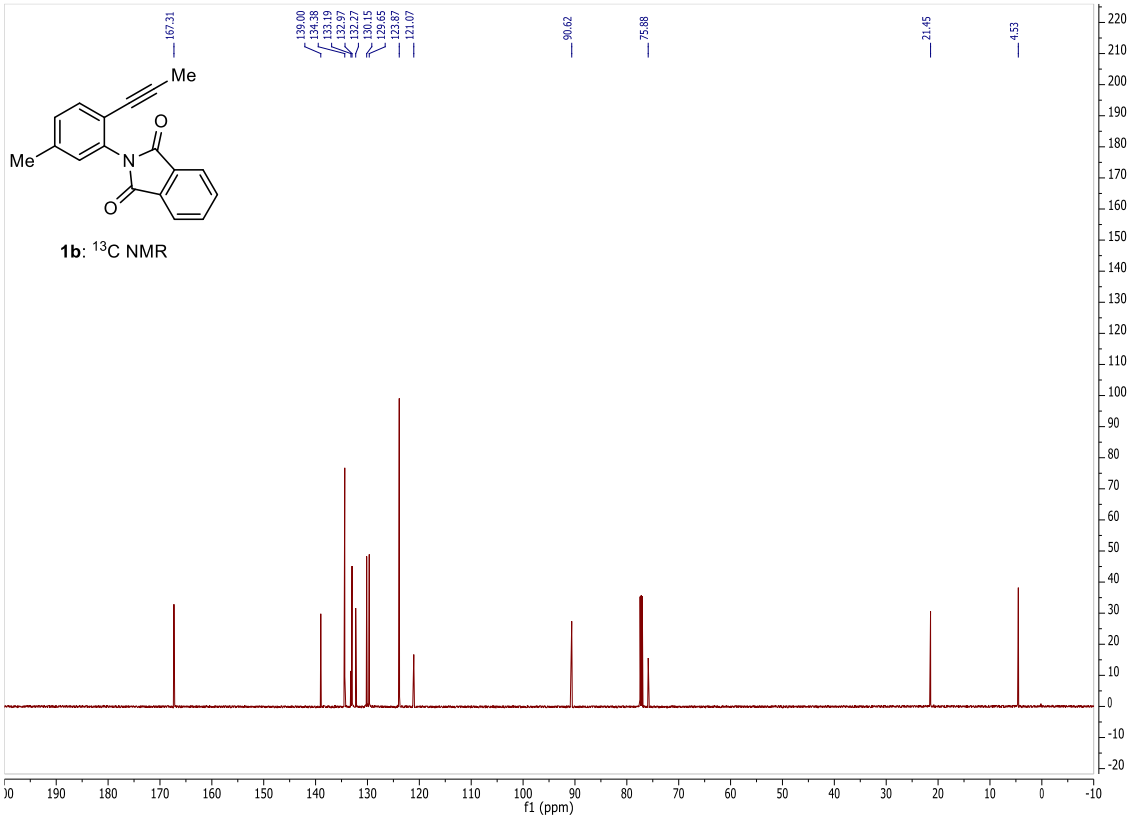

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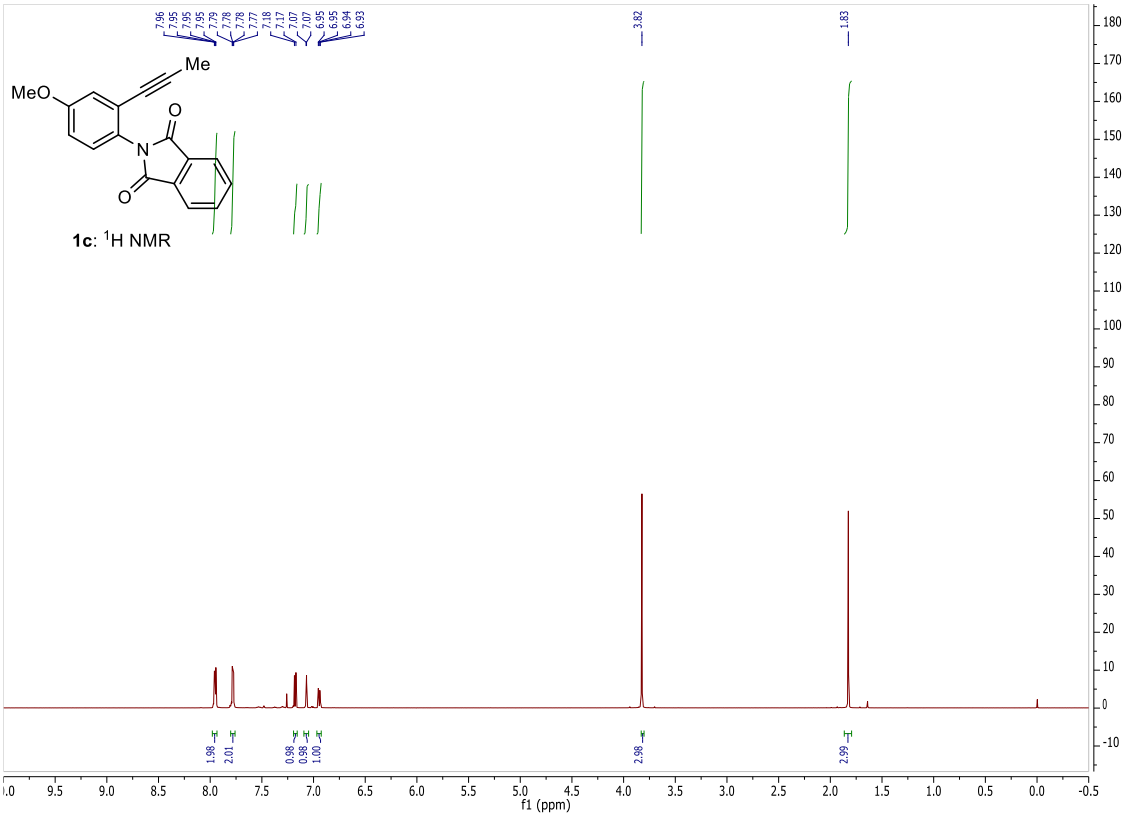
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6.95
6.94
6.93
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1.83
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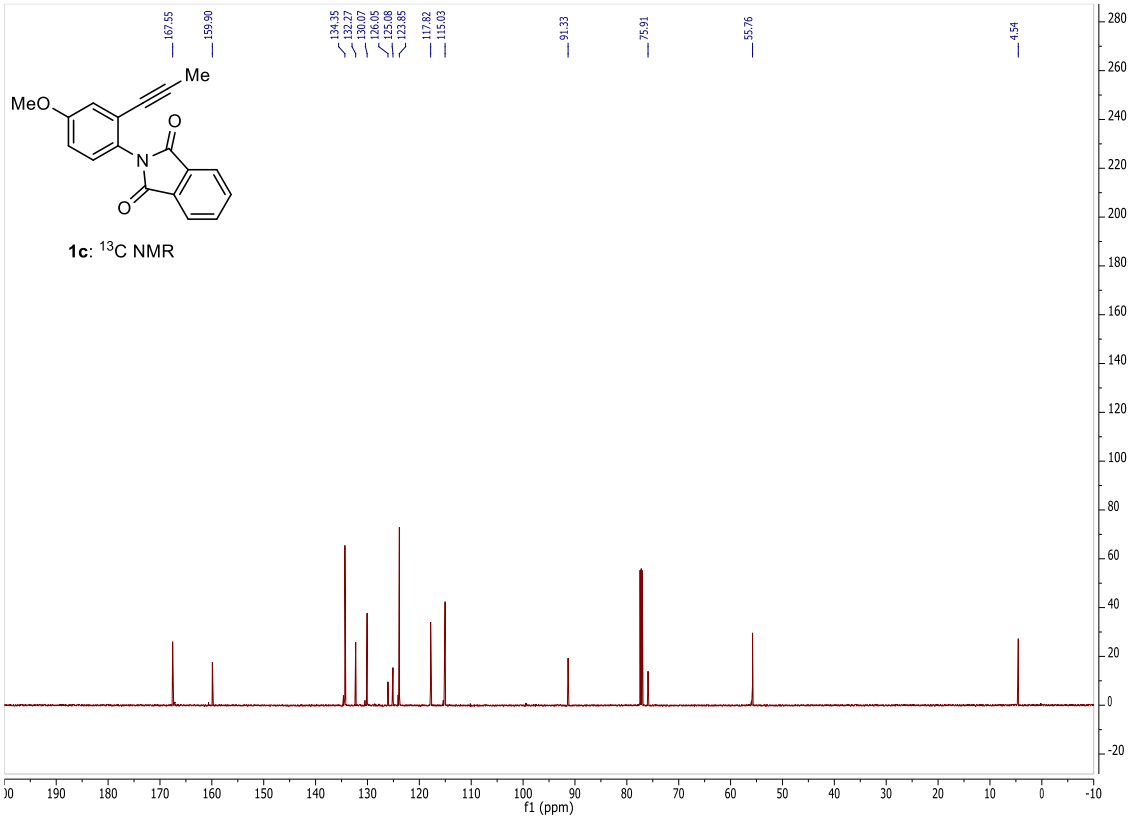
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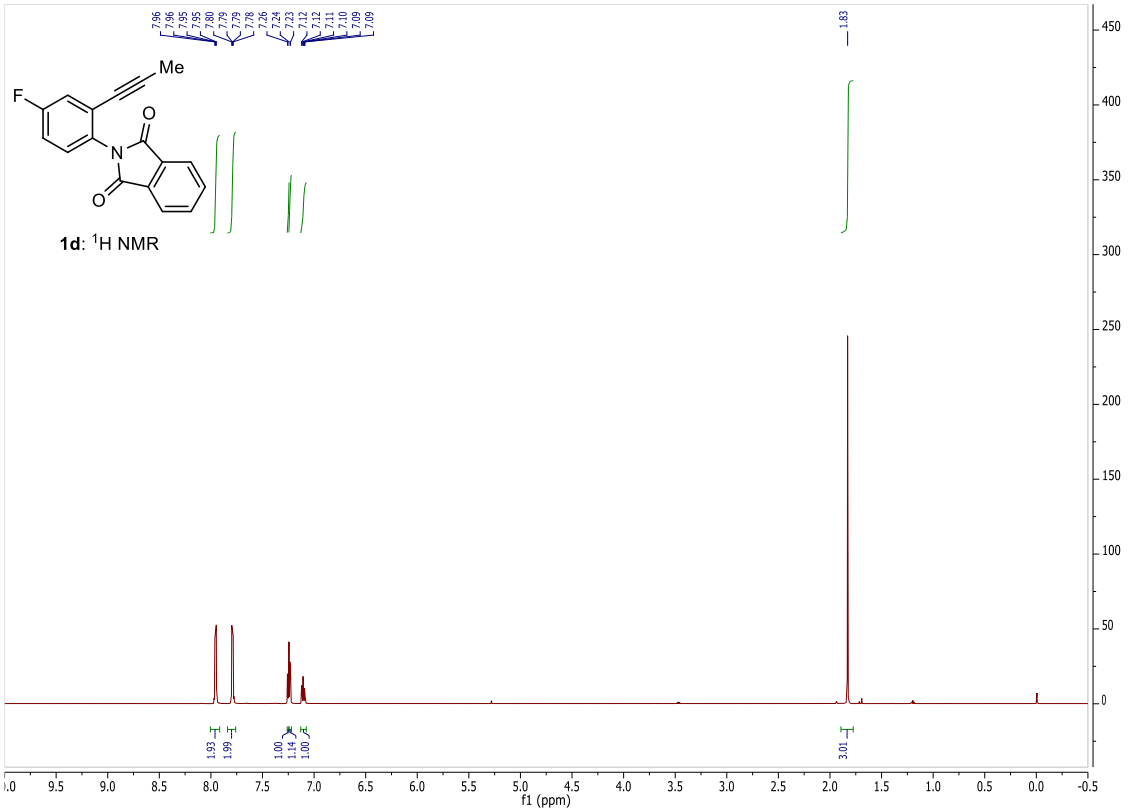
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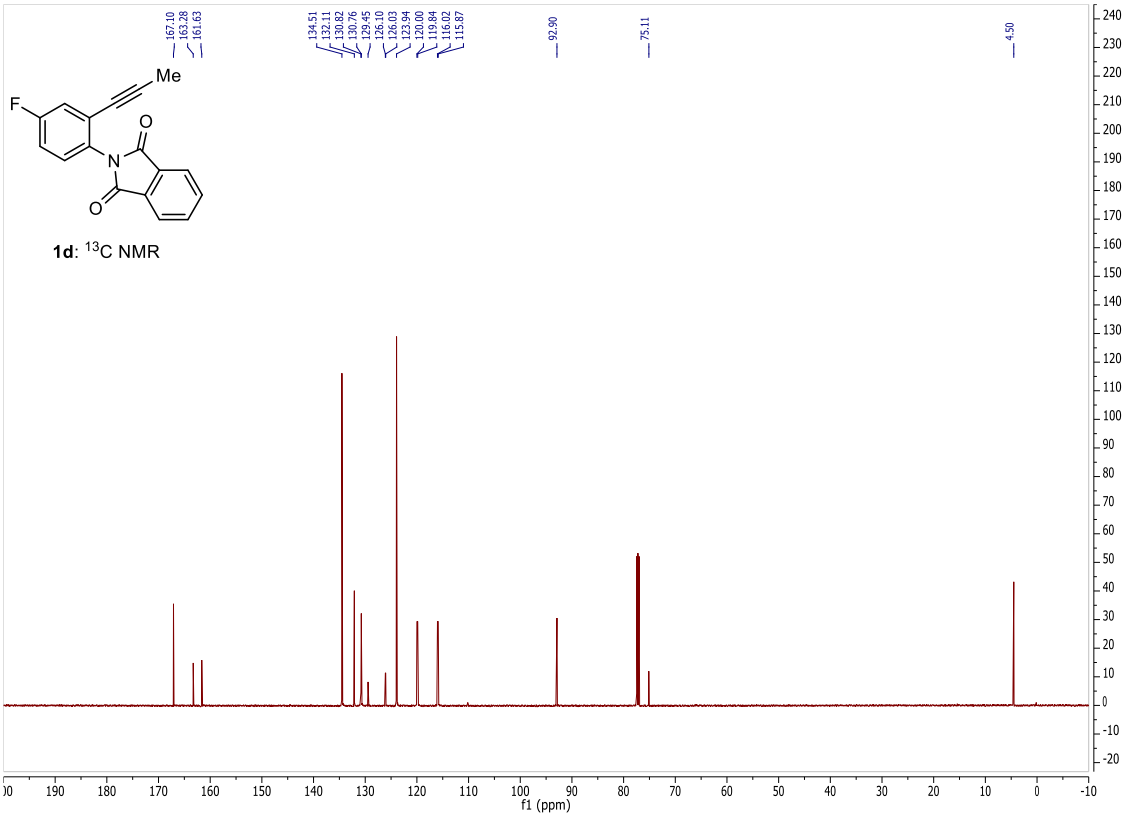
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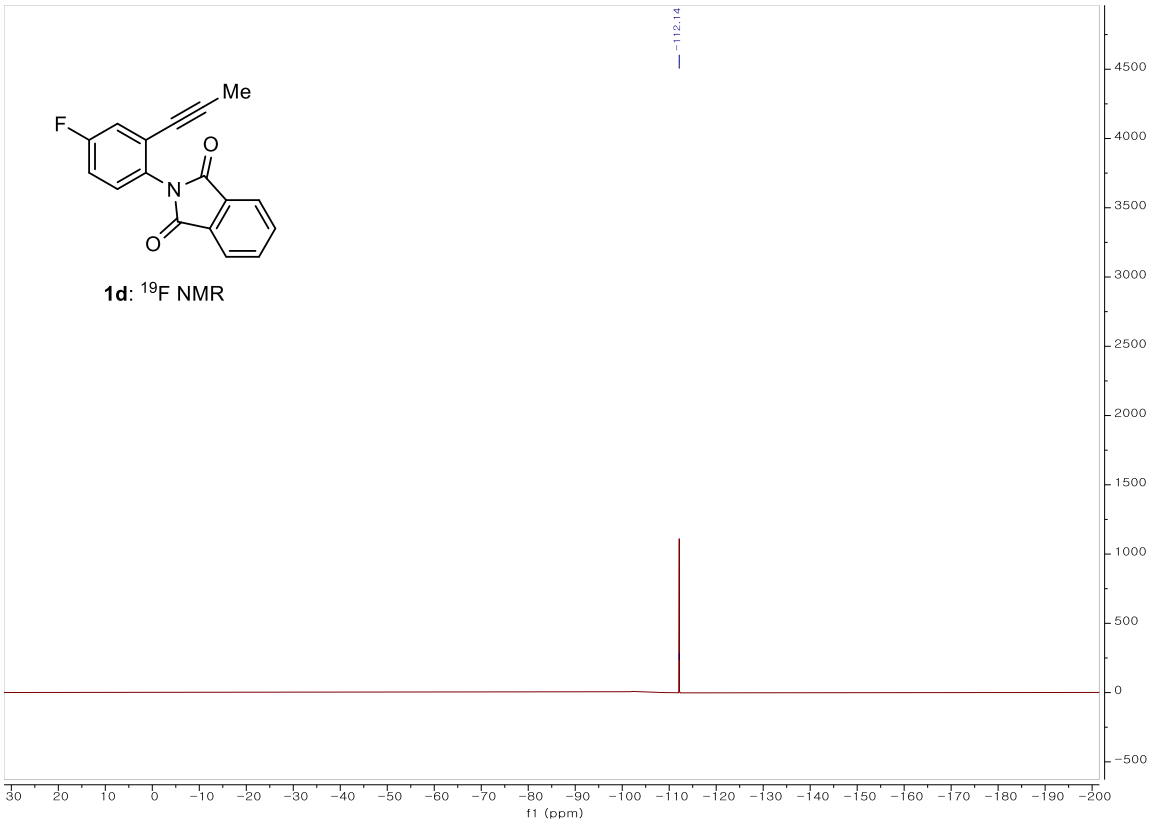

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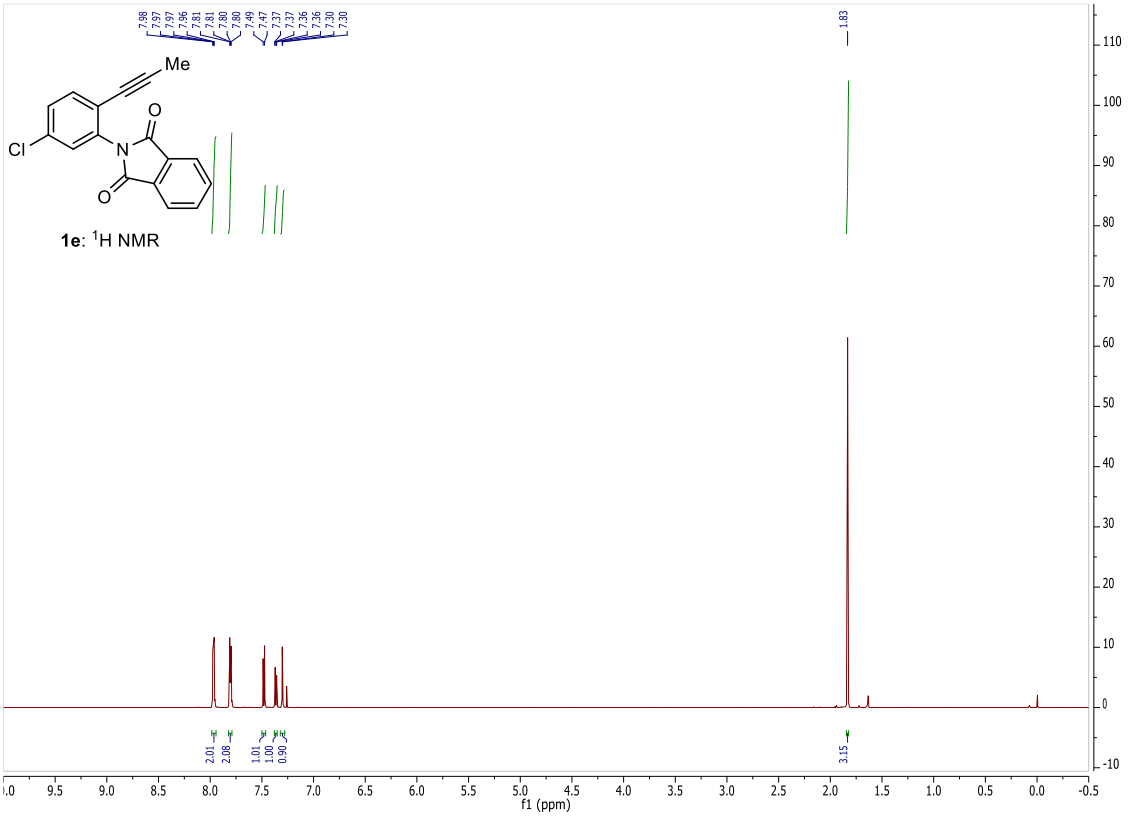

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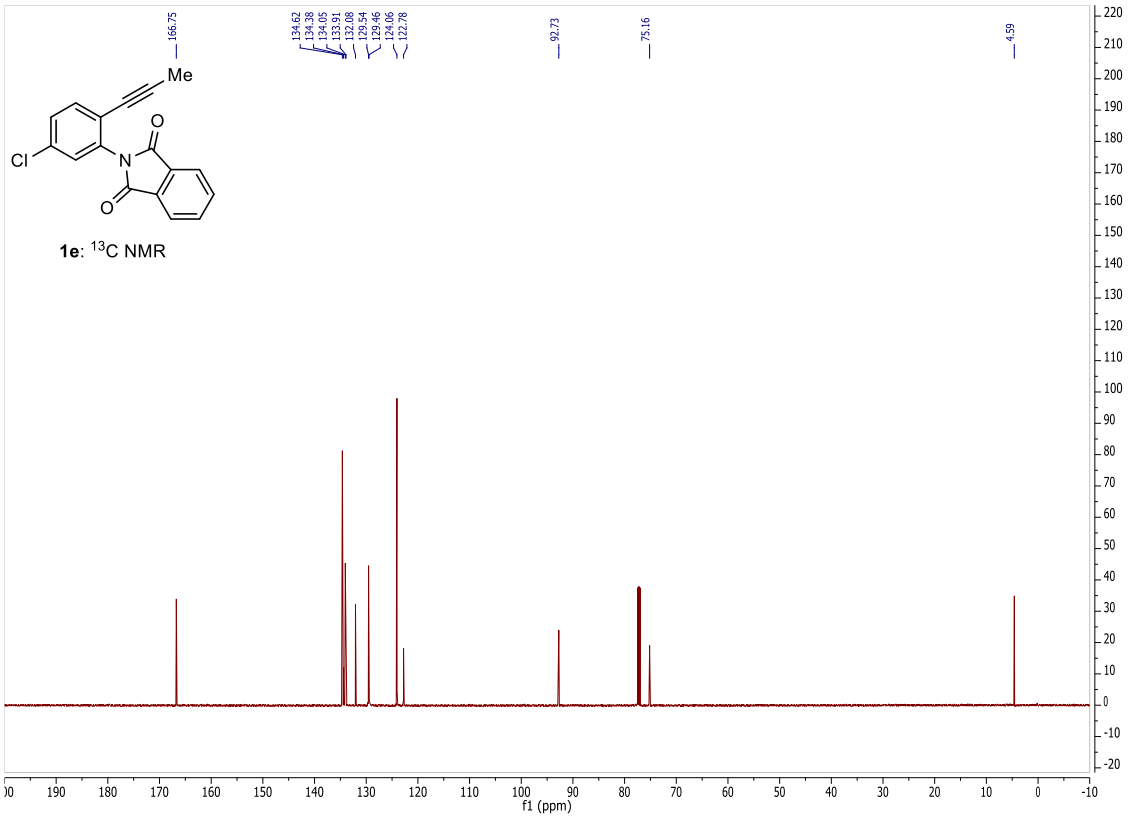

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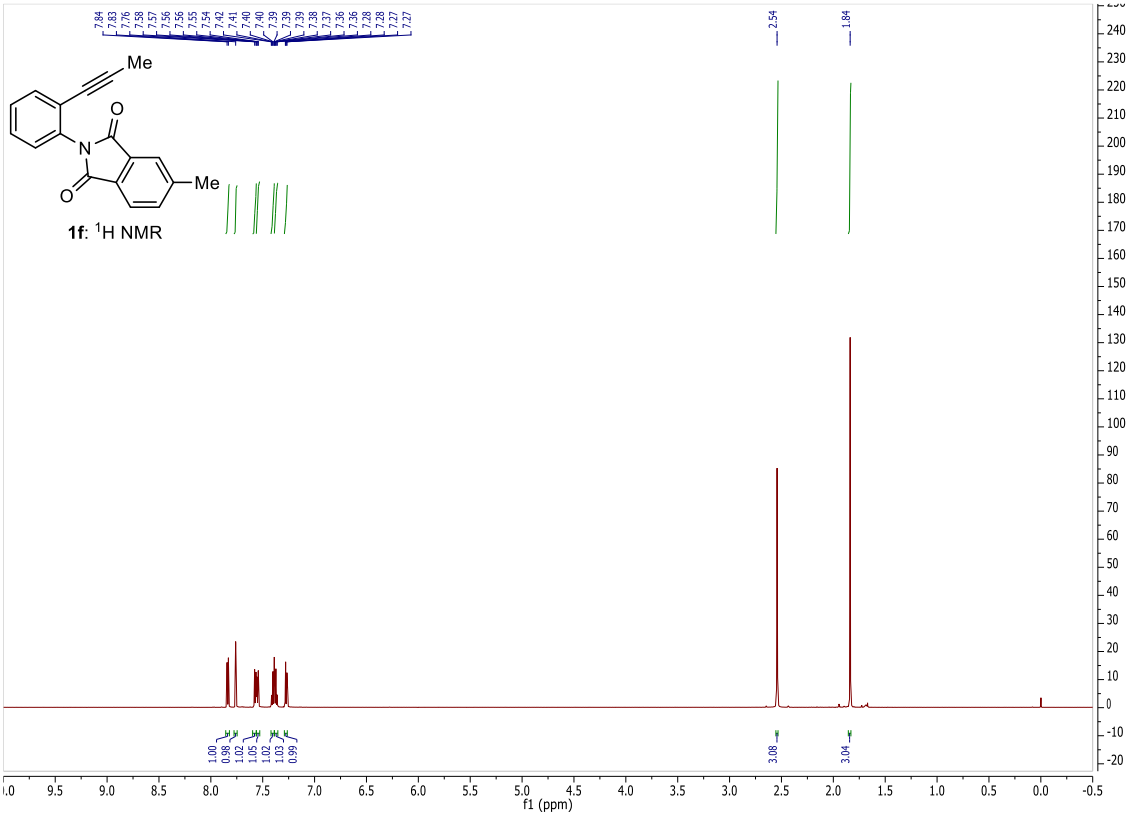

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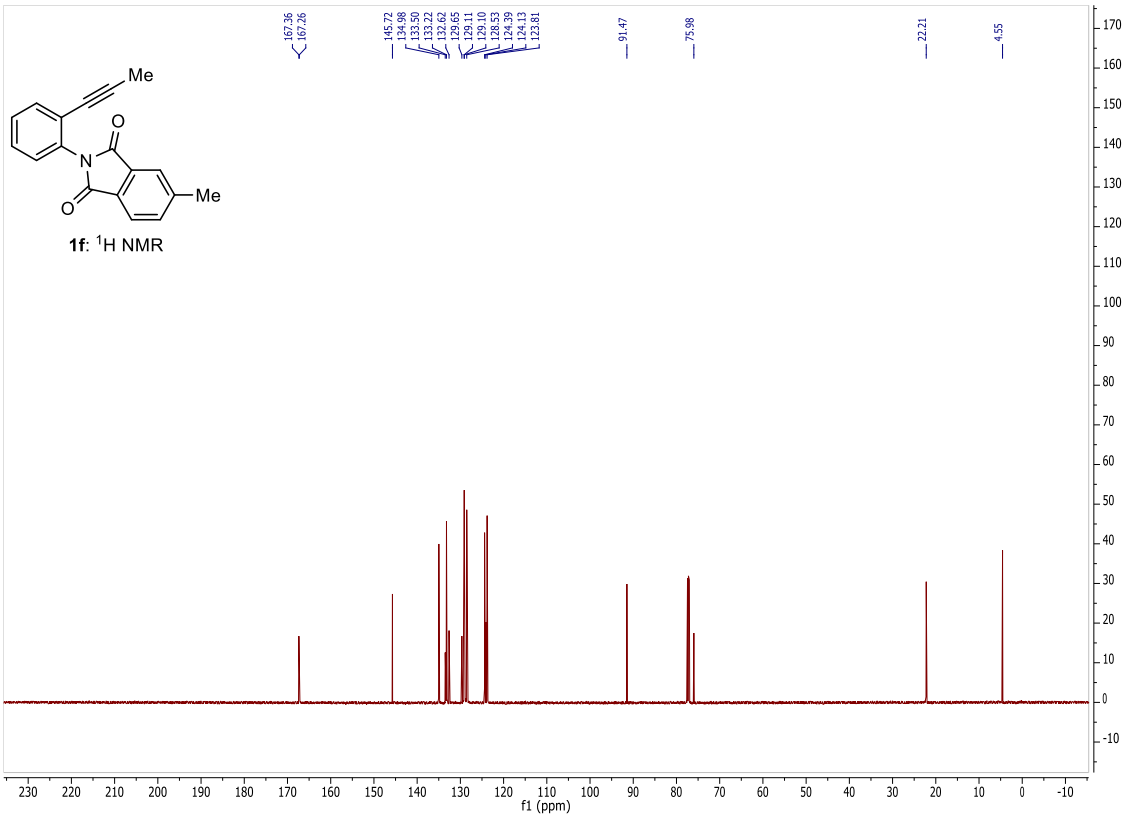

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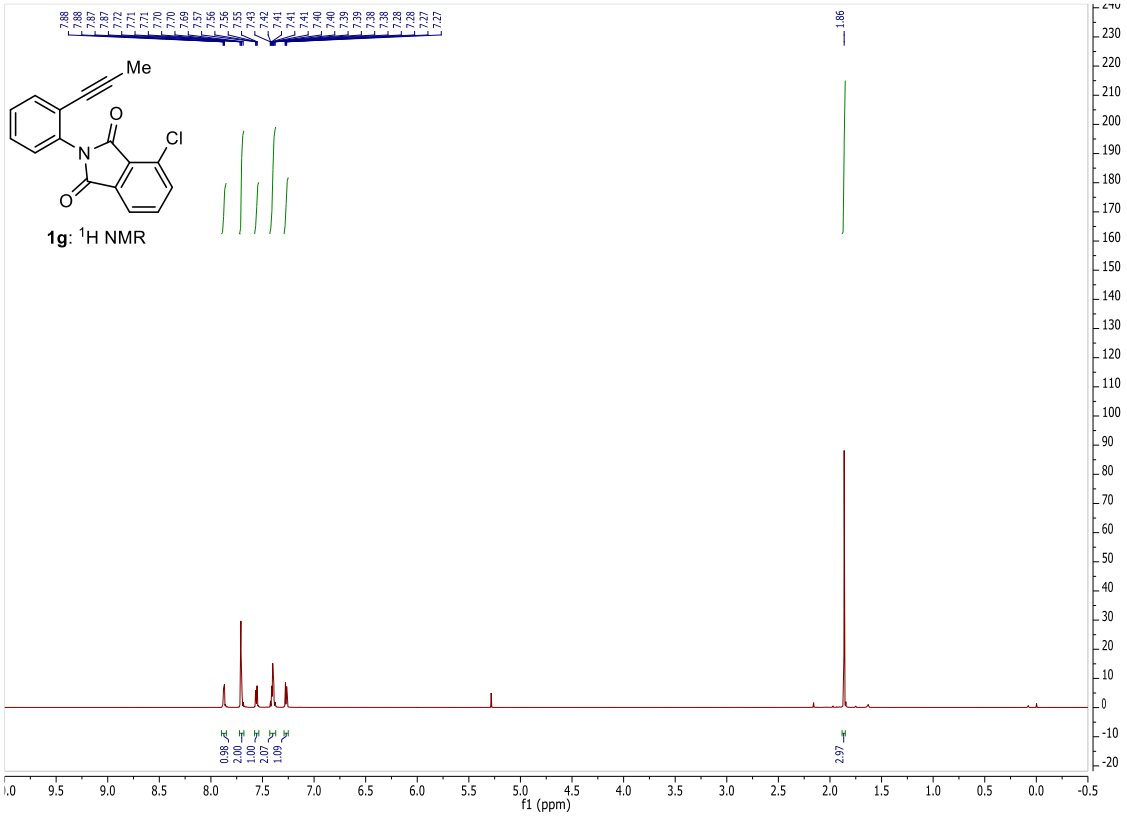

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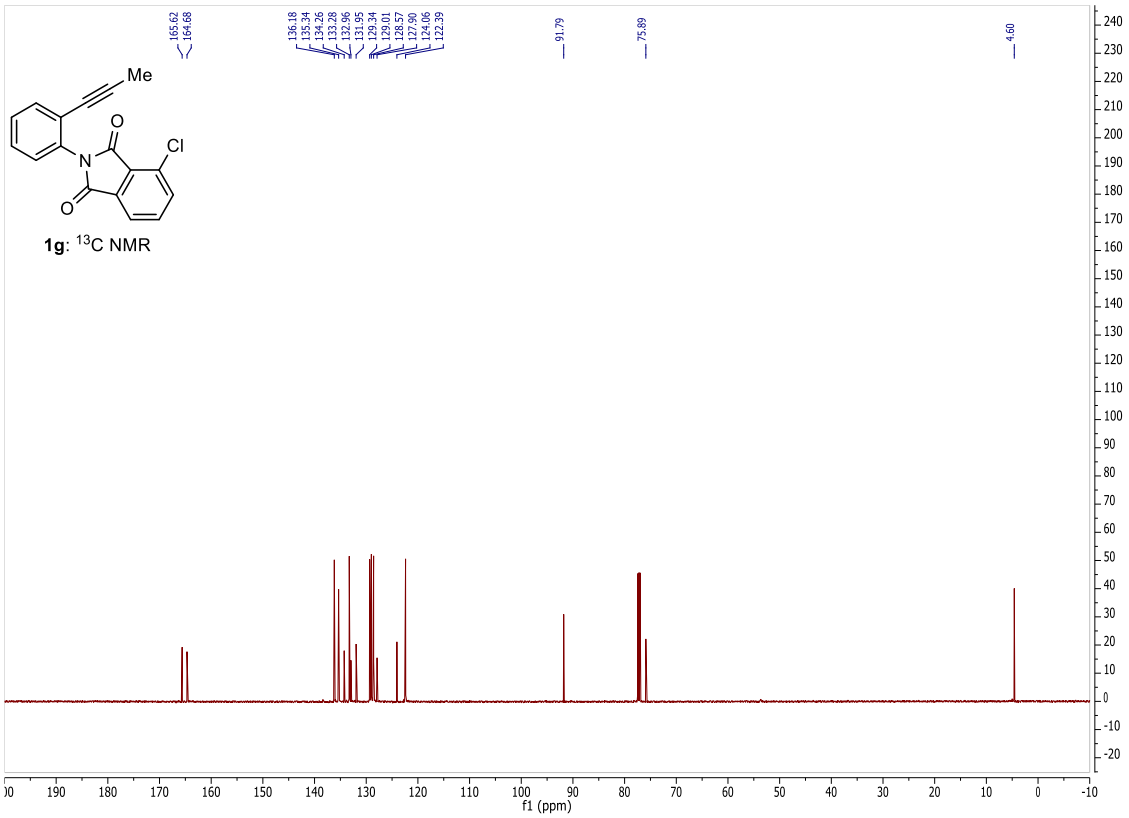

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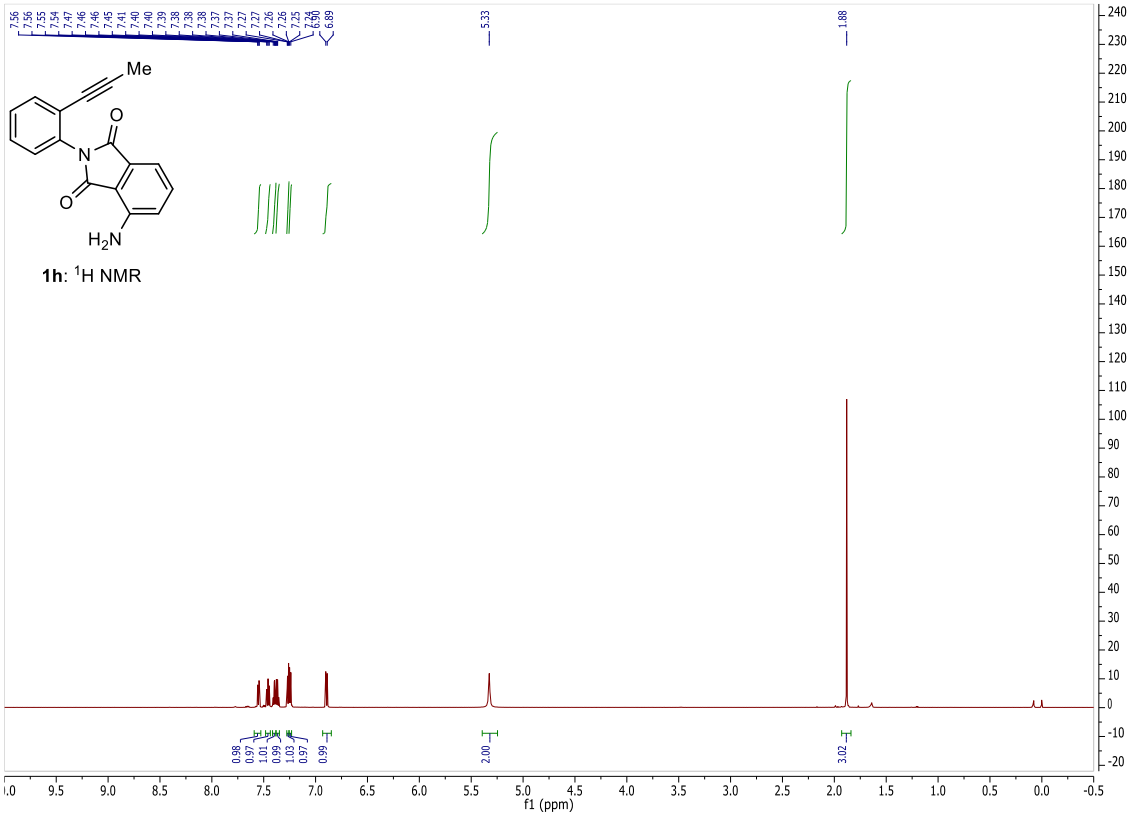

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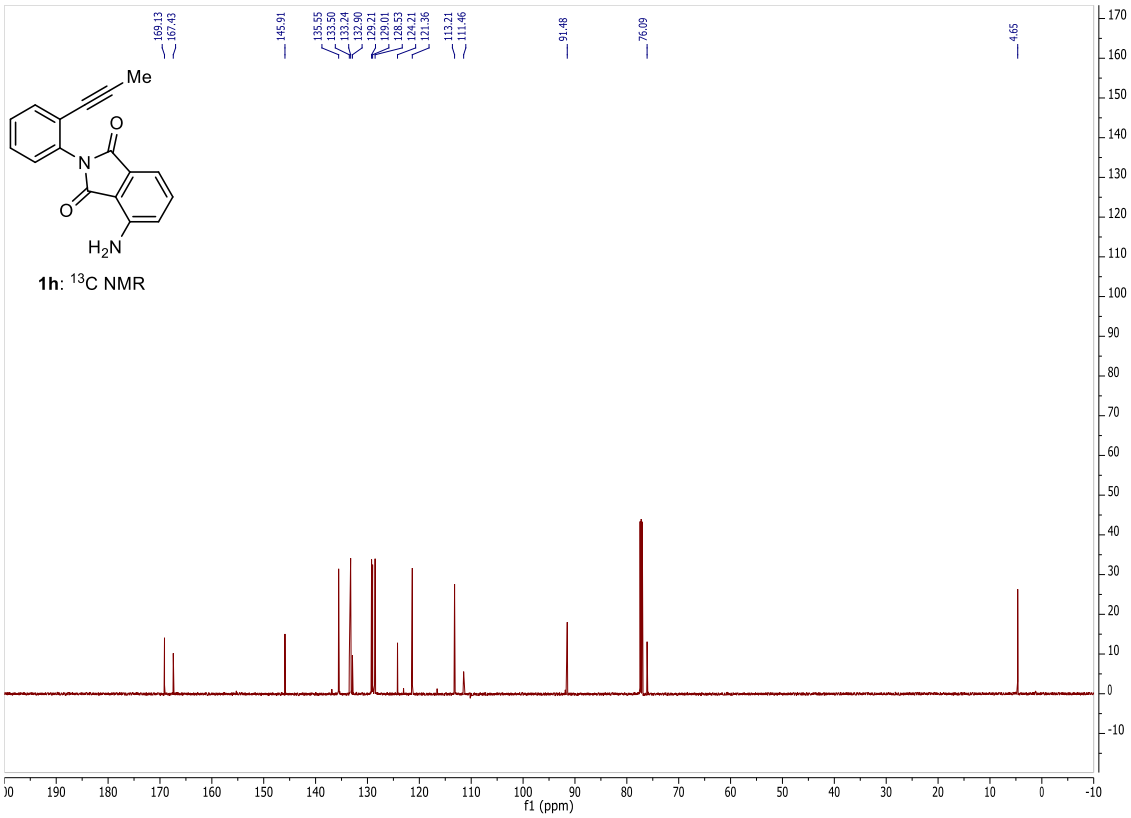

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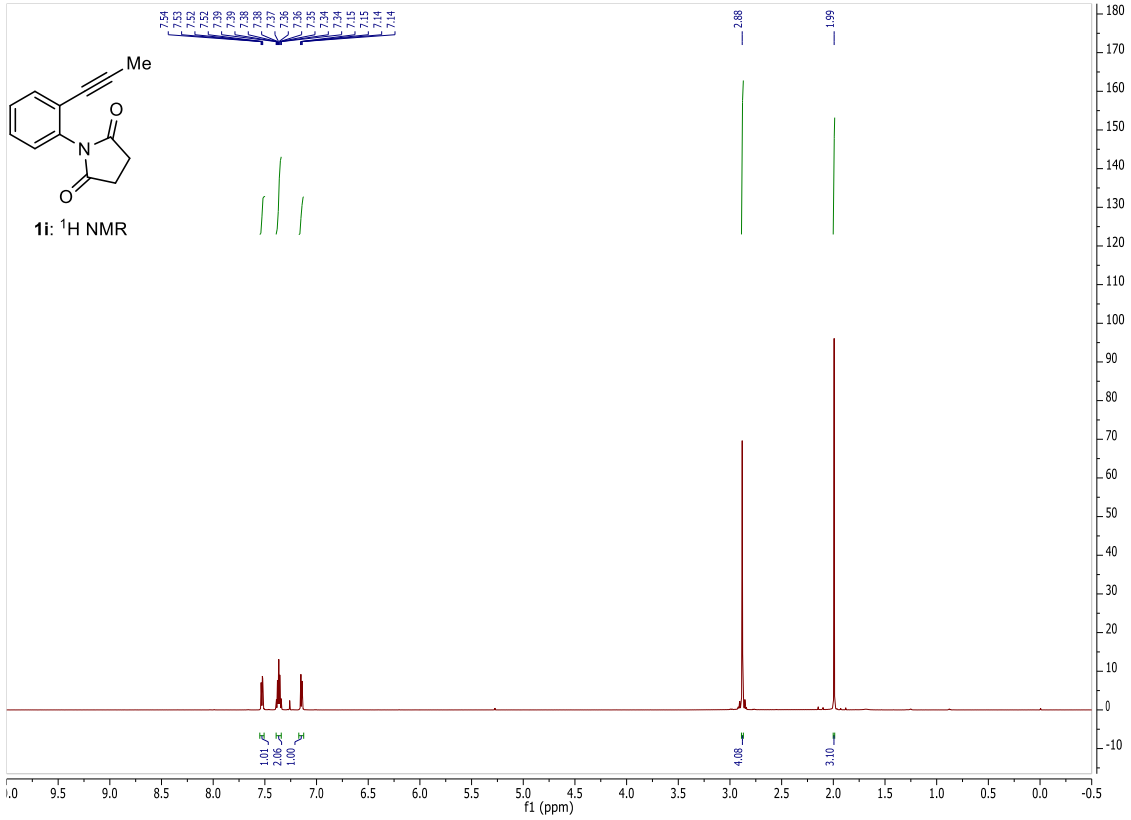

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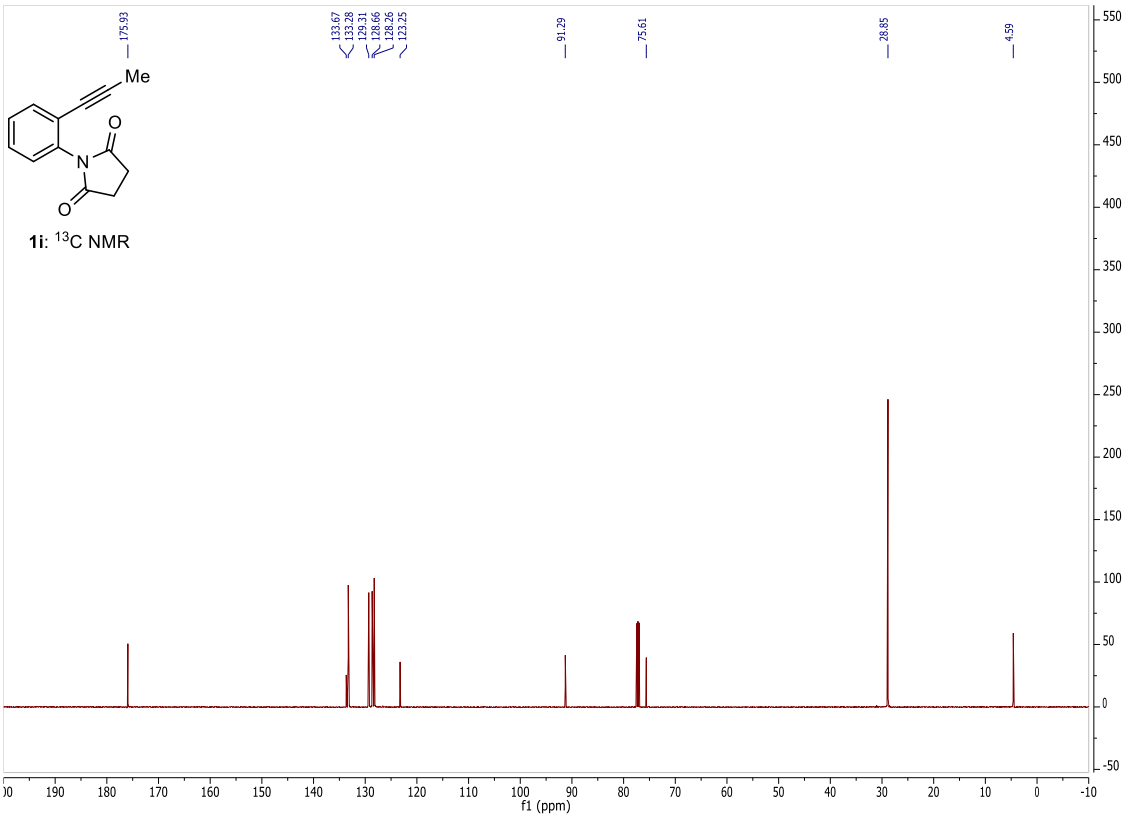
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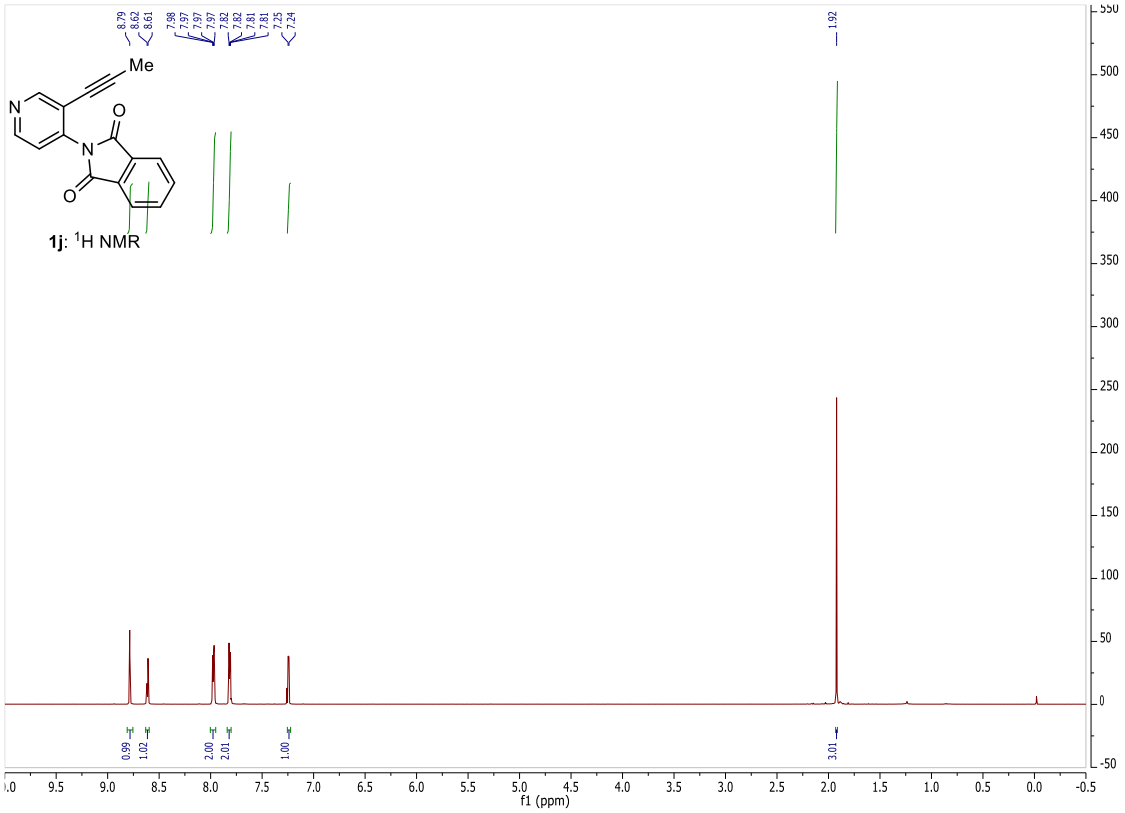
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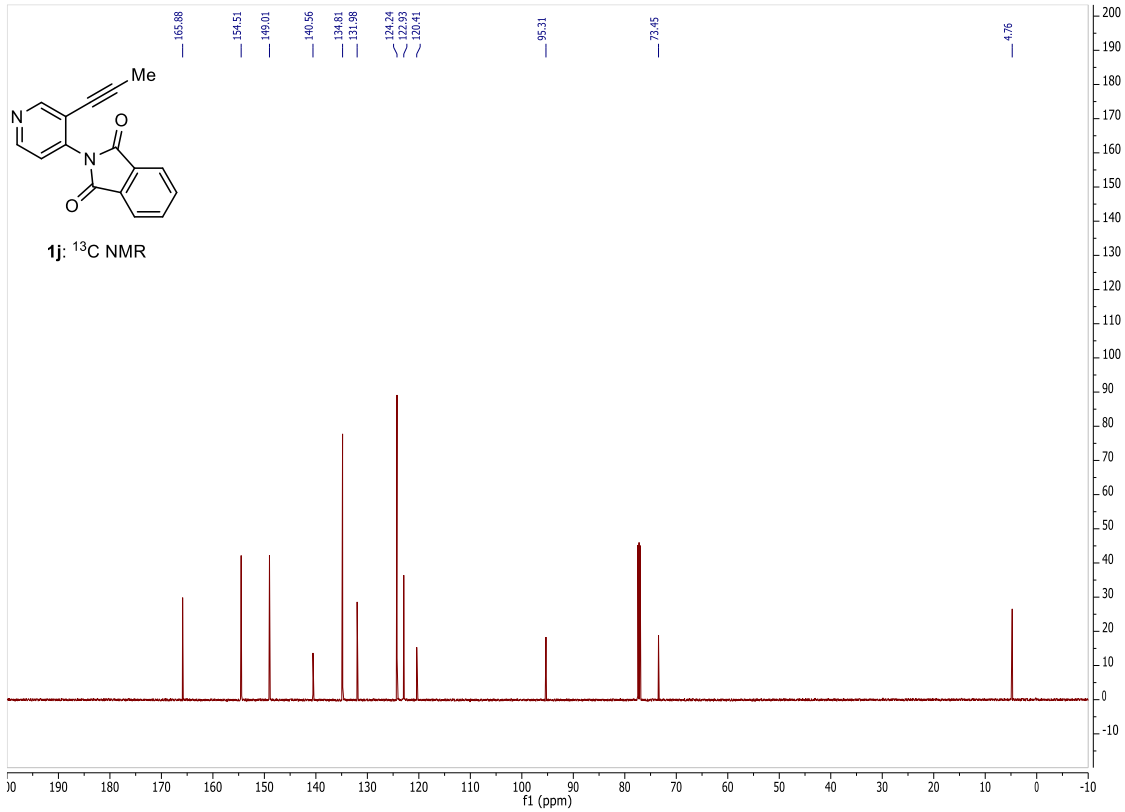
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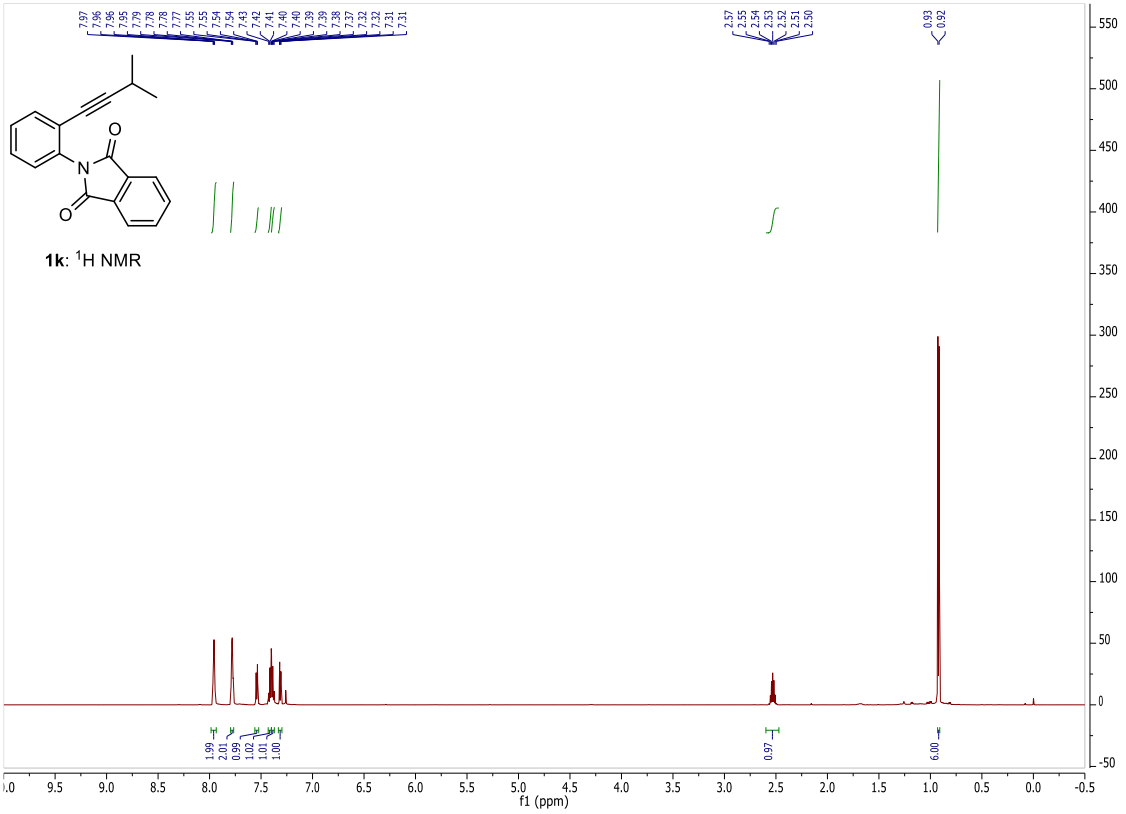
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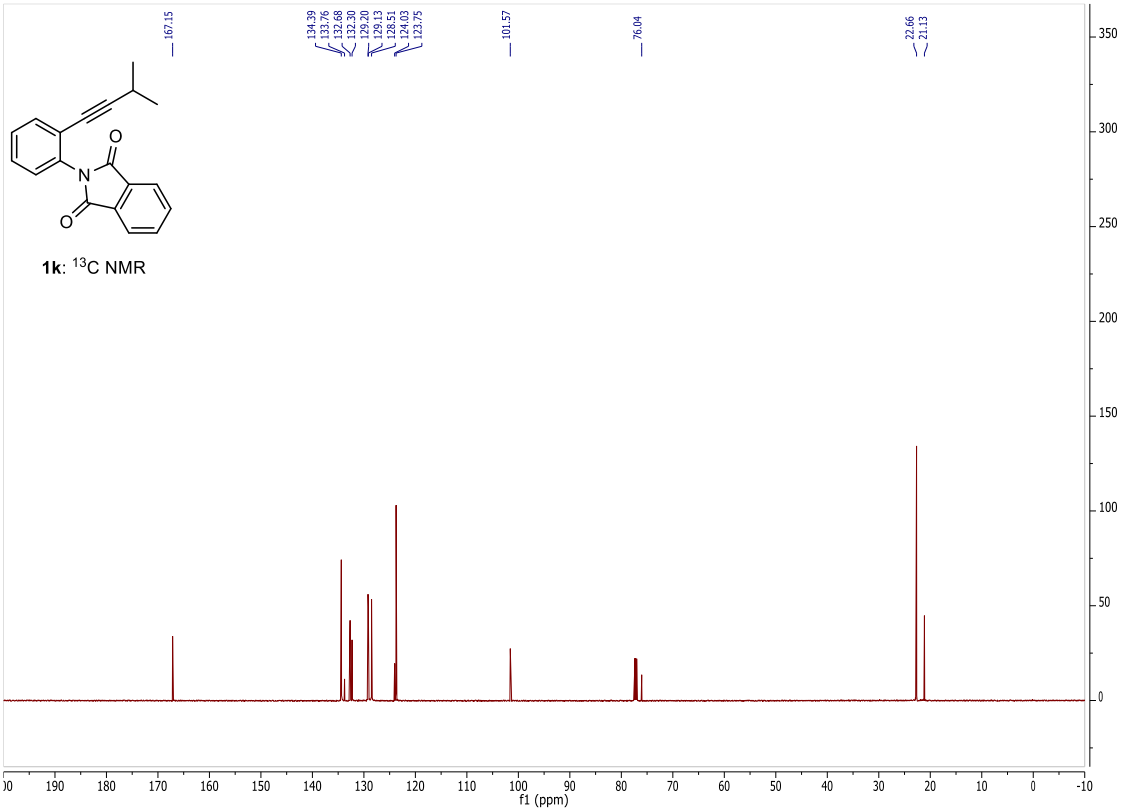
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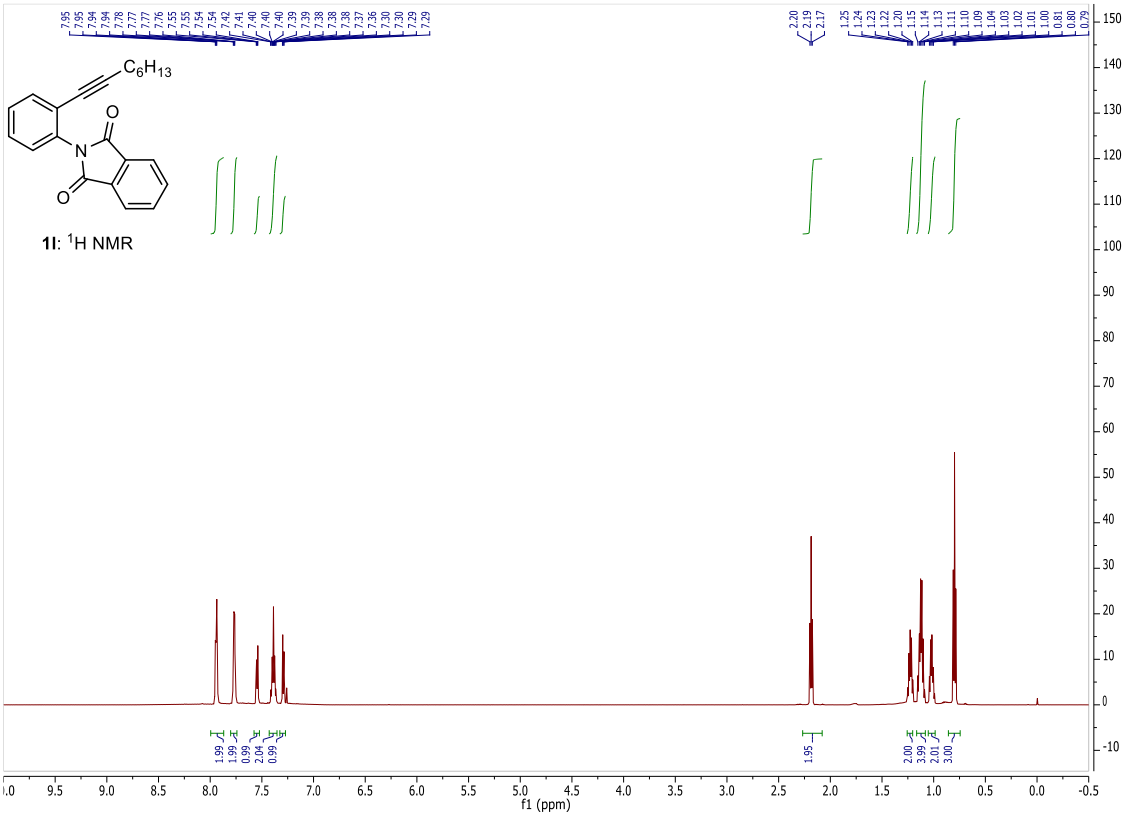
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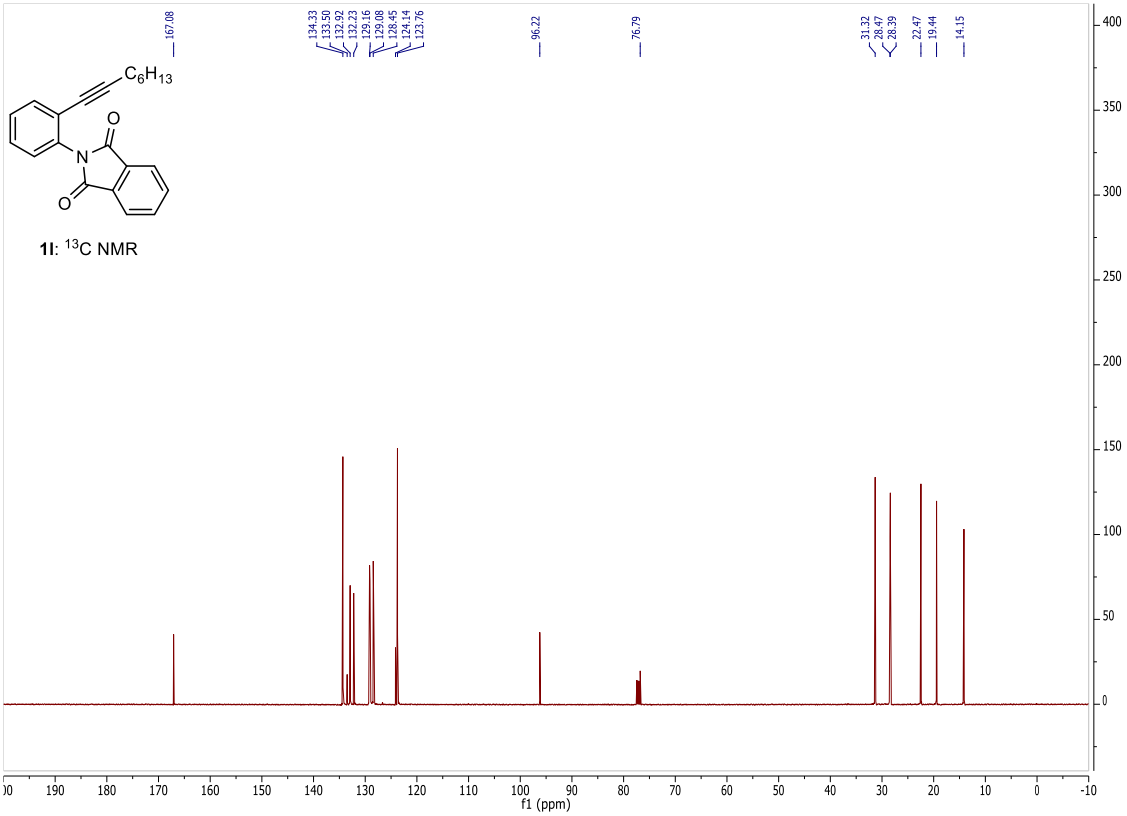
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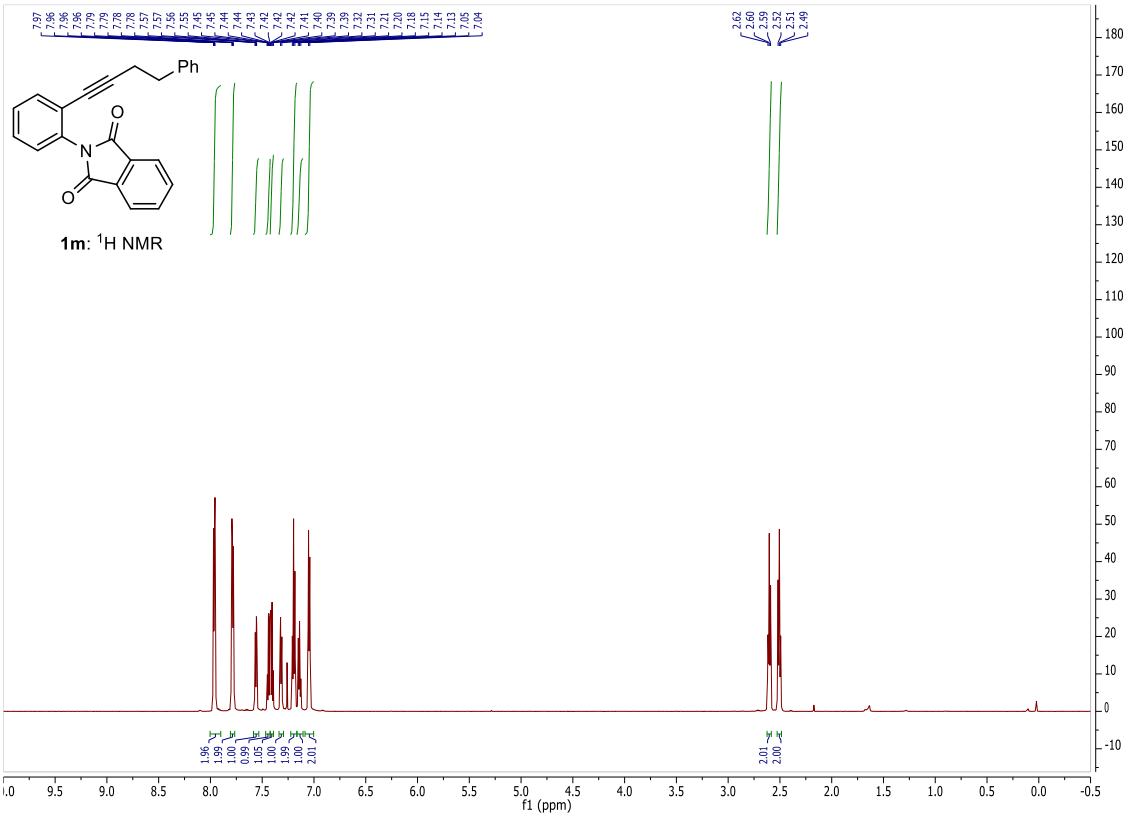
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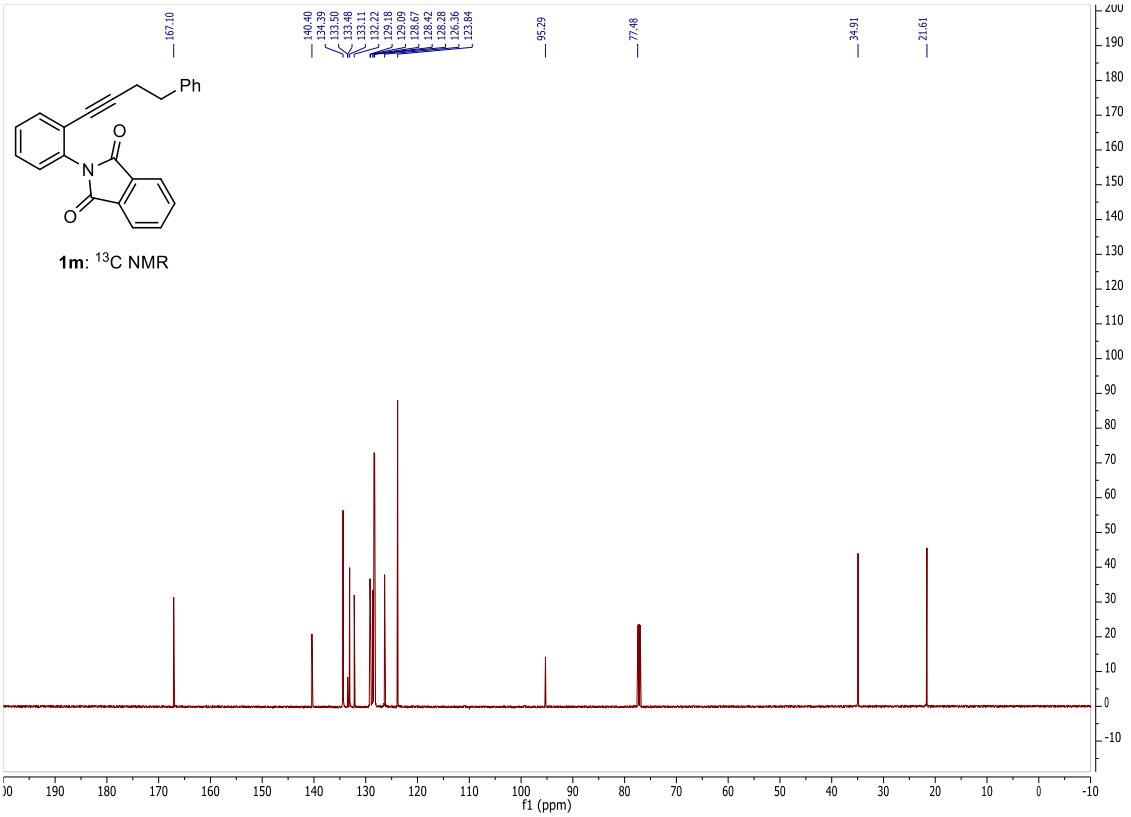
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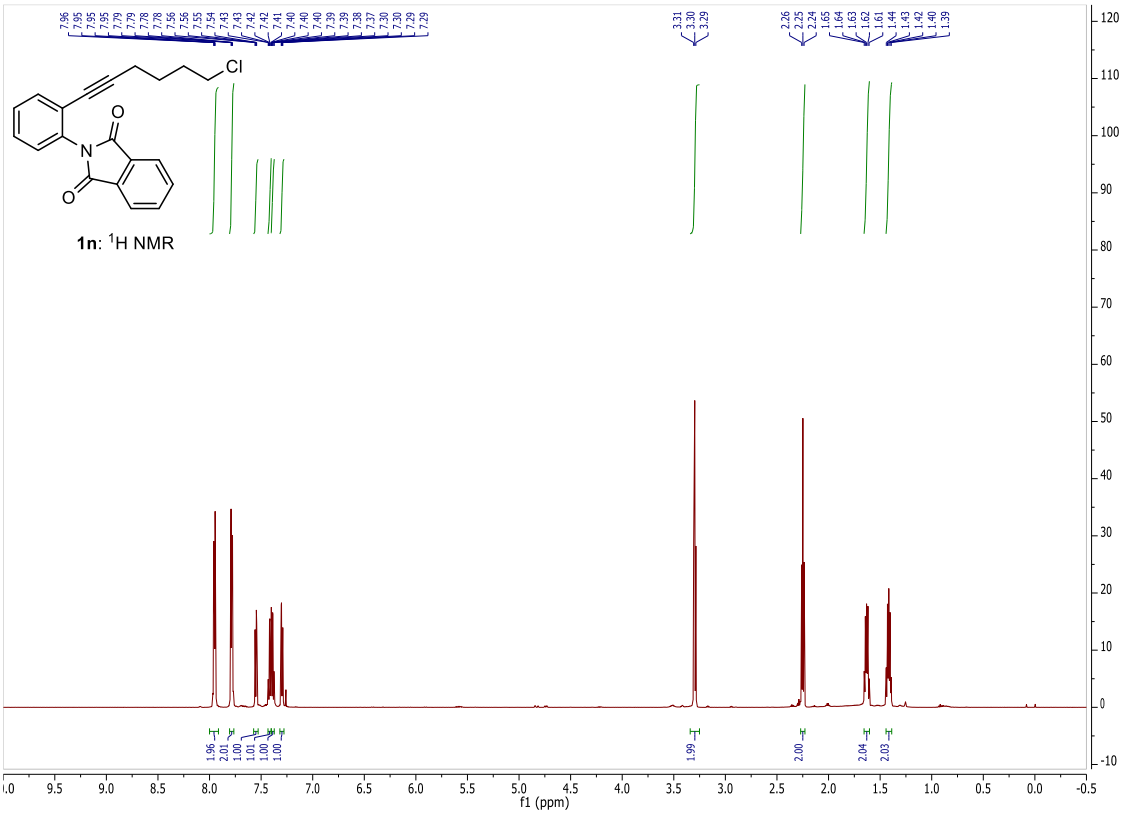
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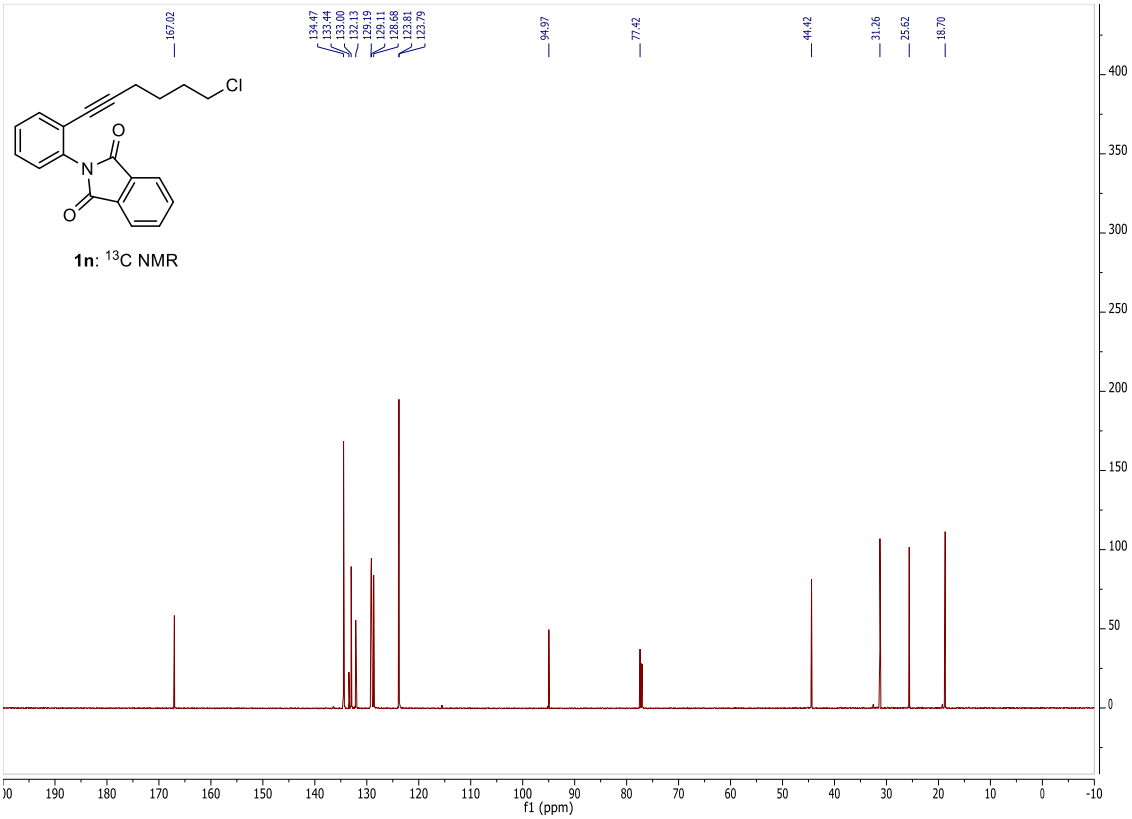
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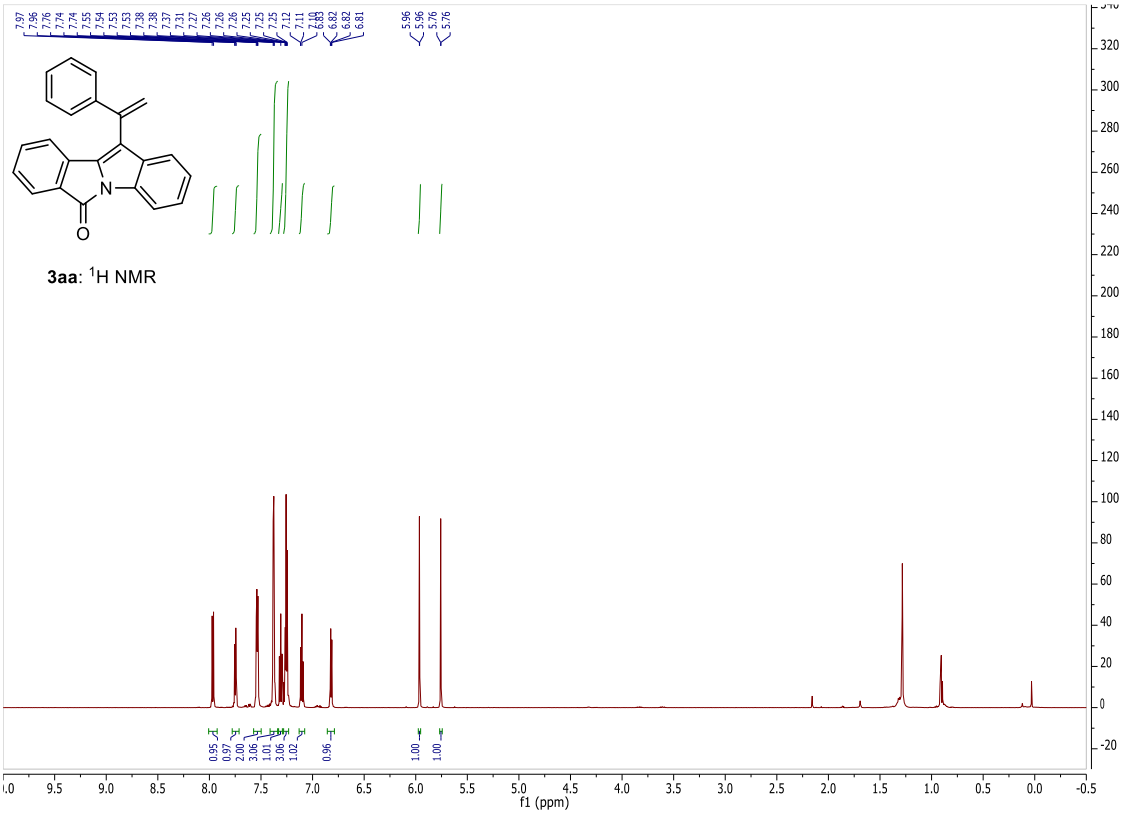
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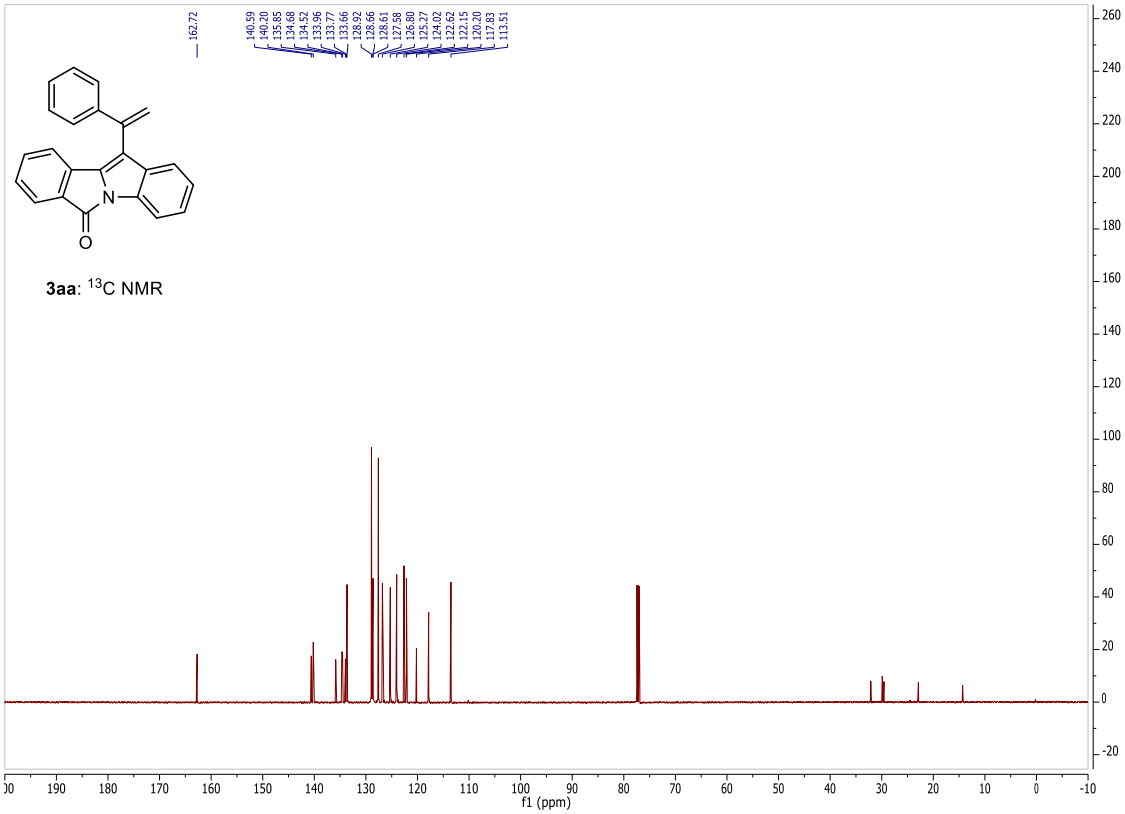
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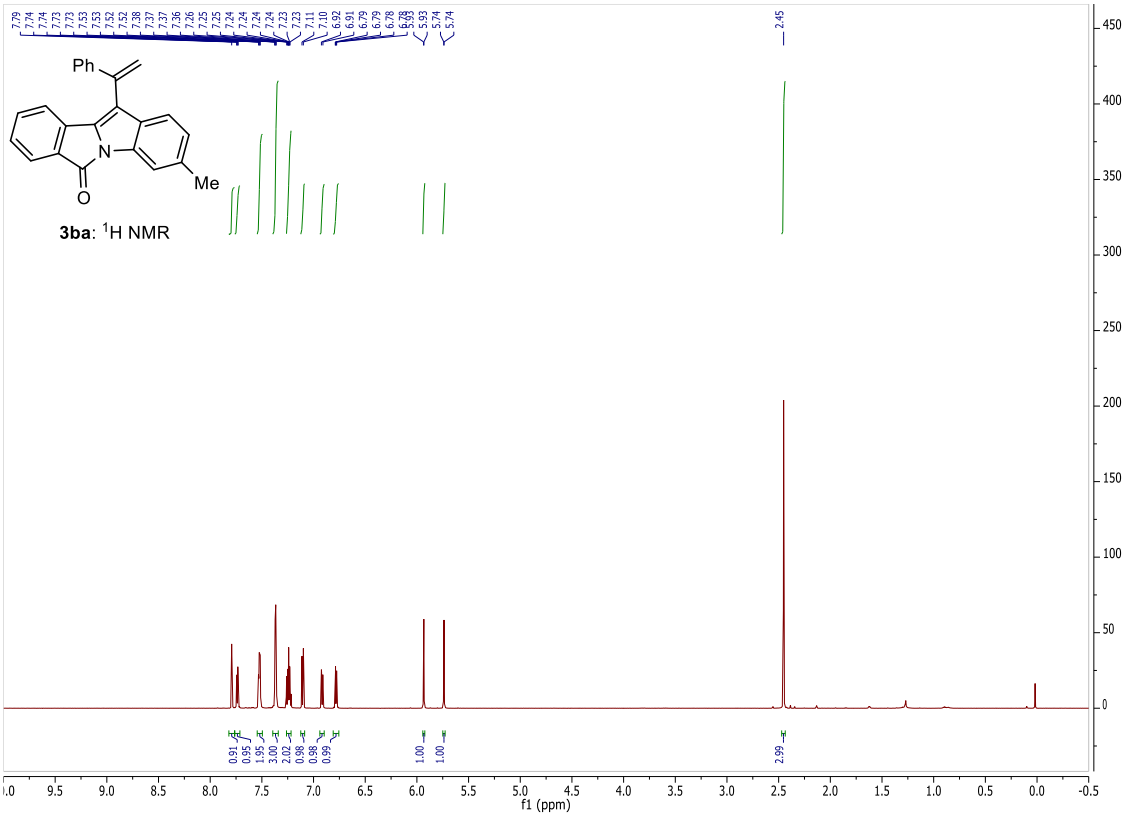
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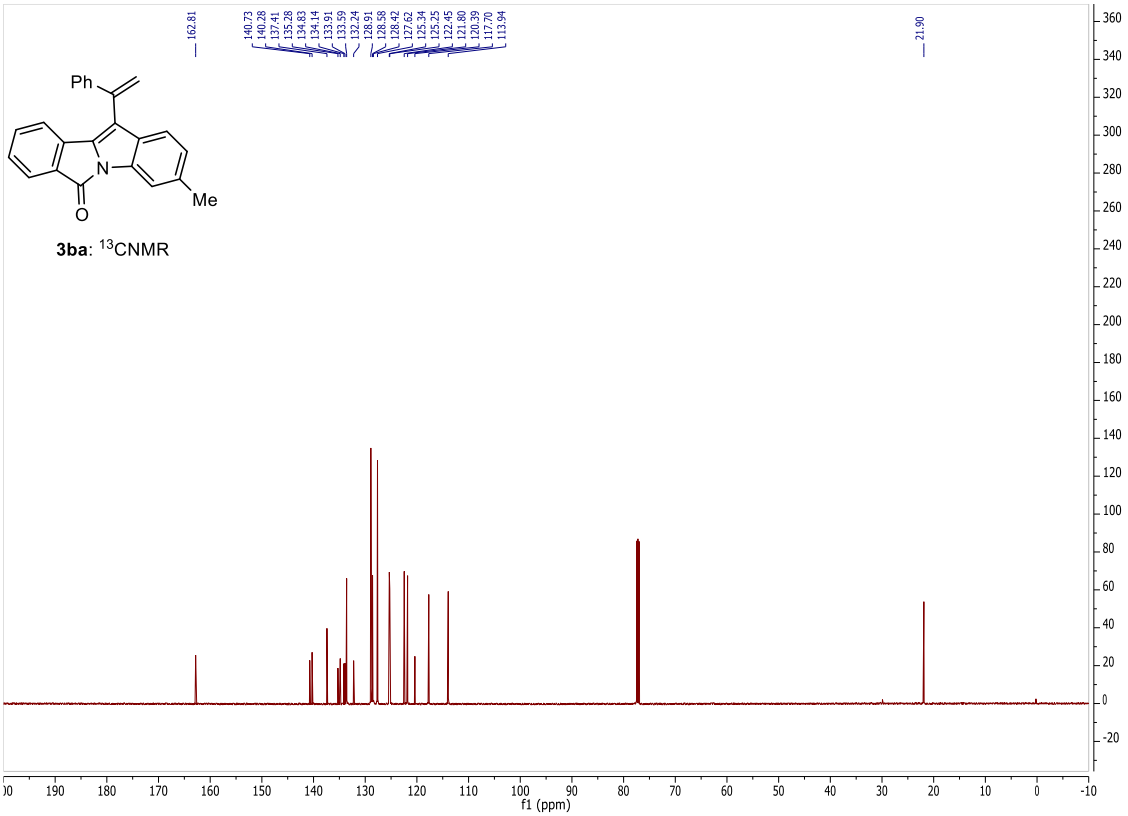
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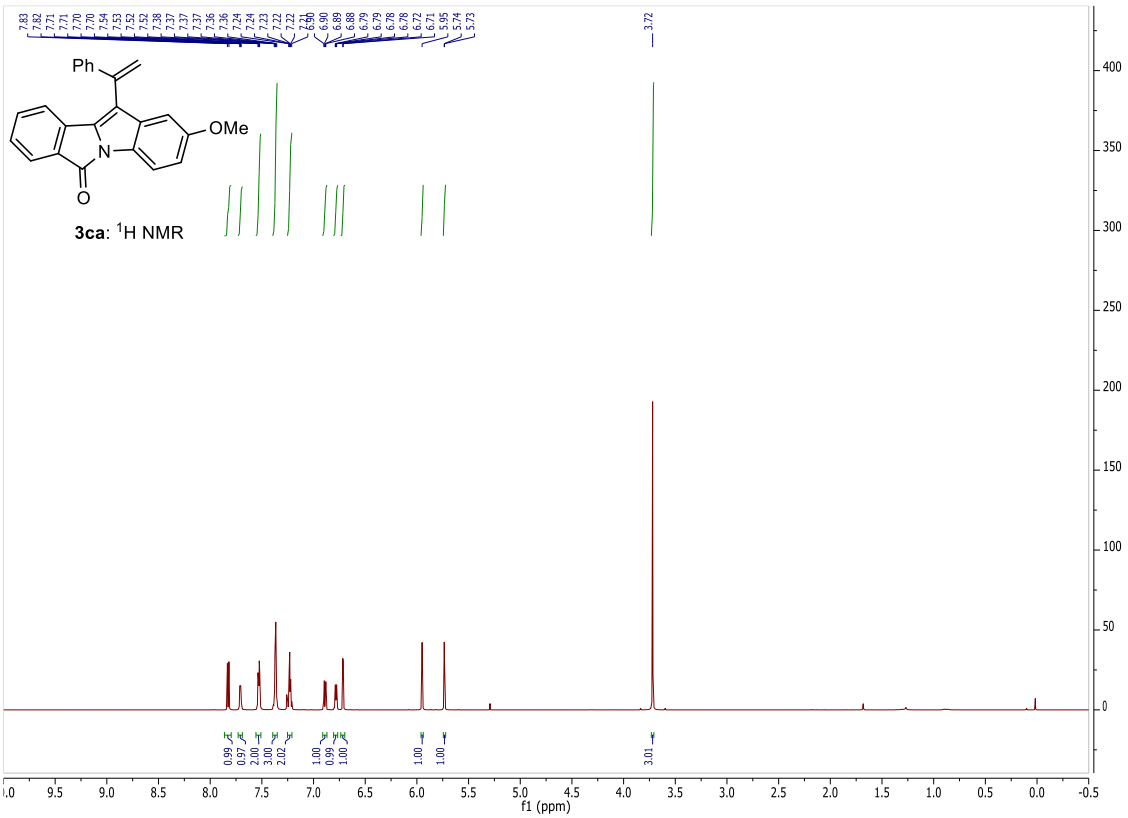
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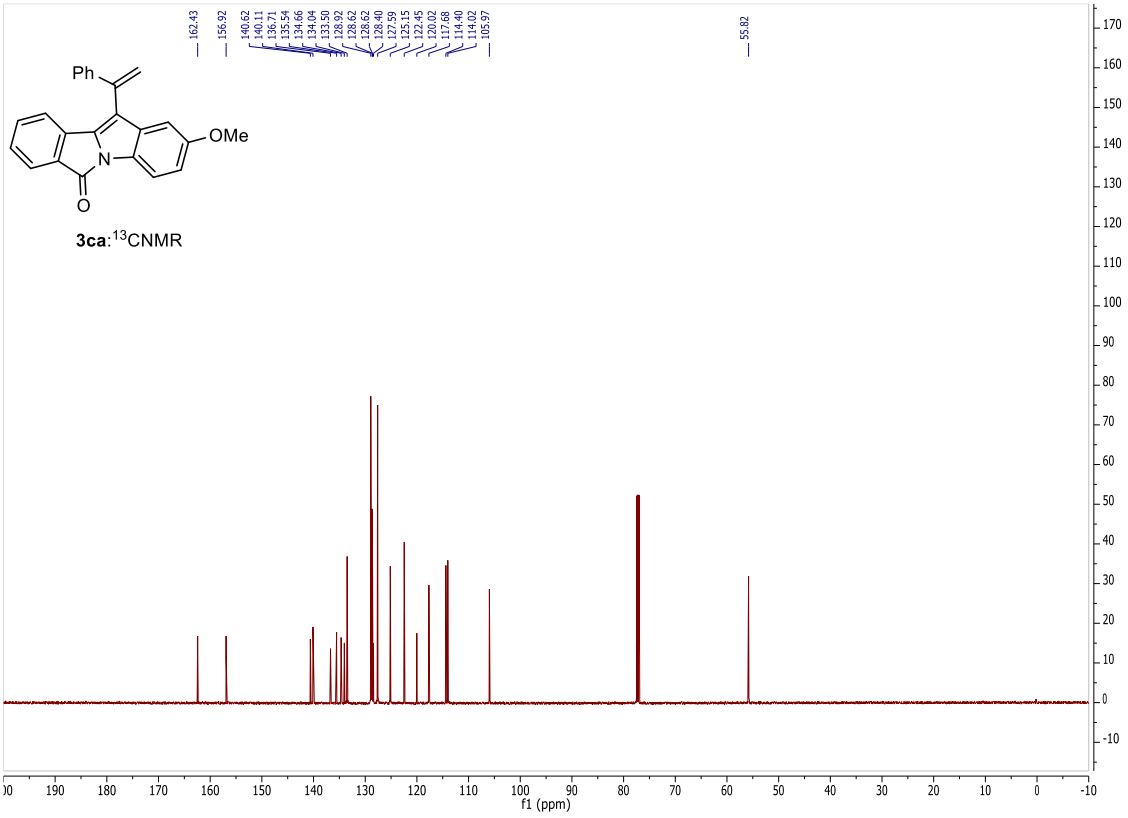
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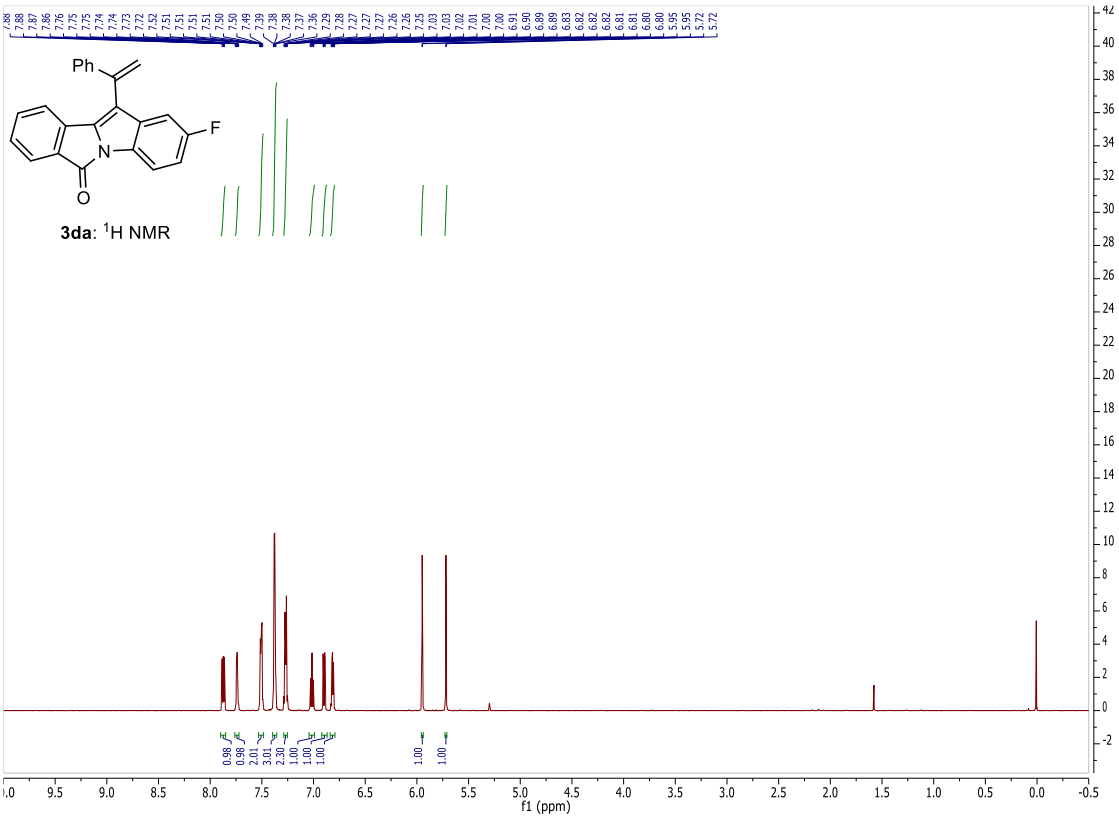
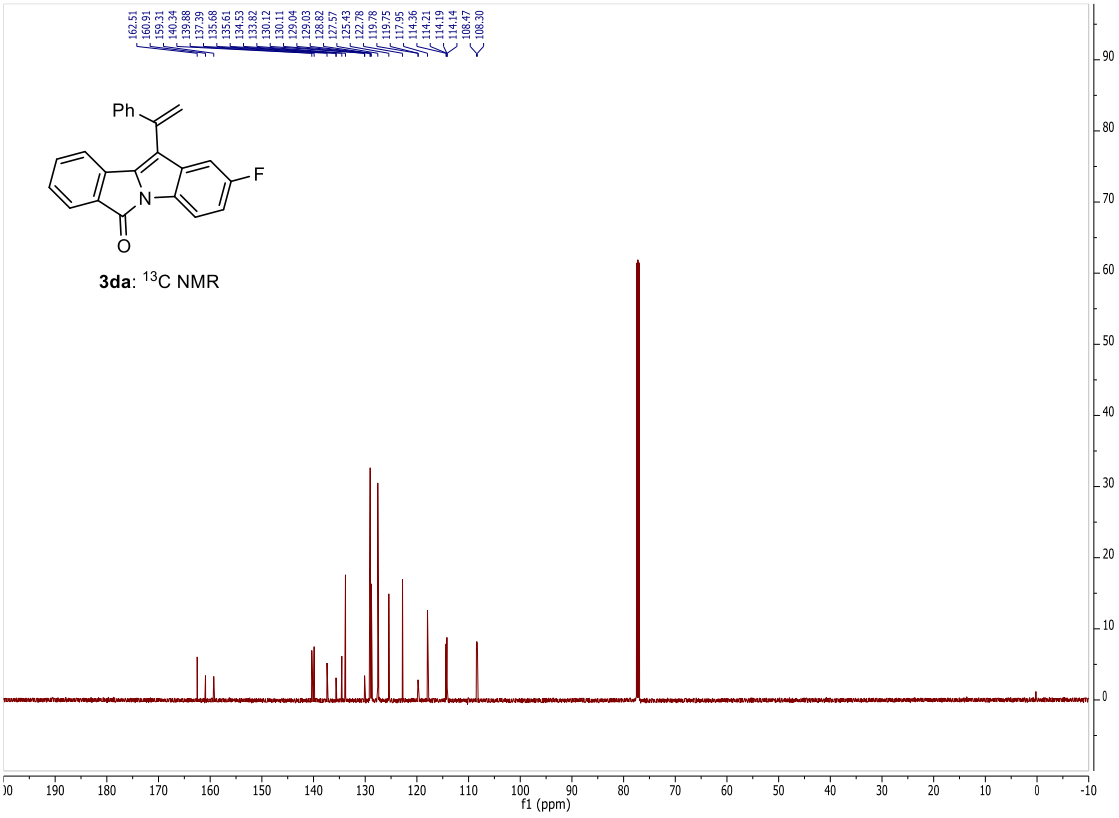
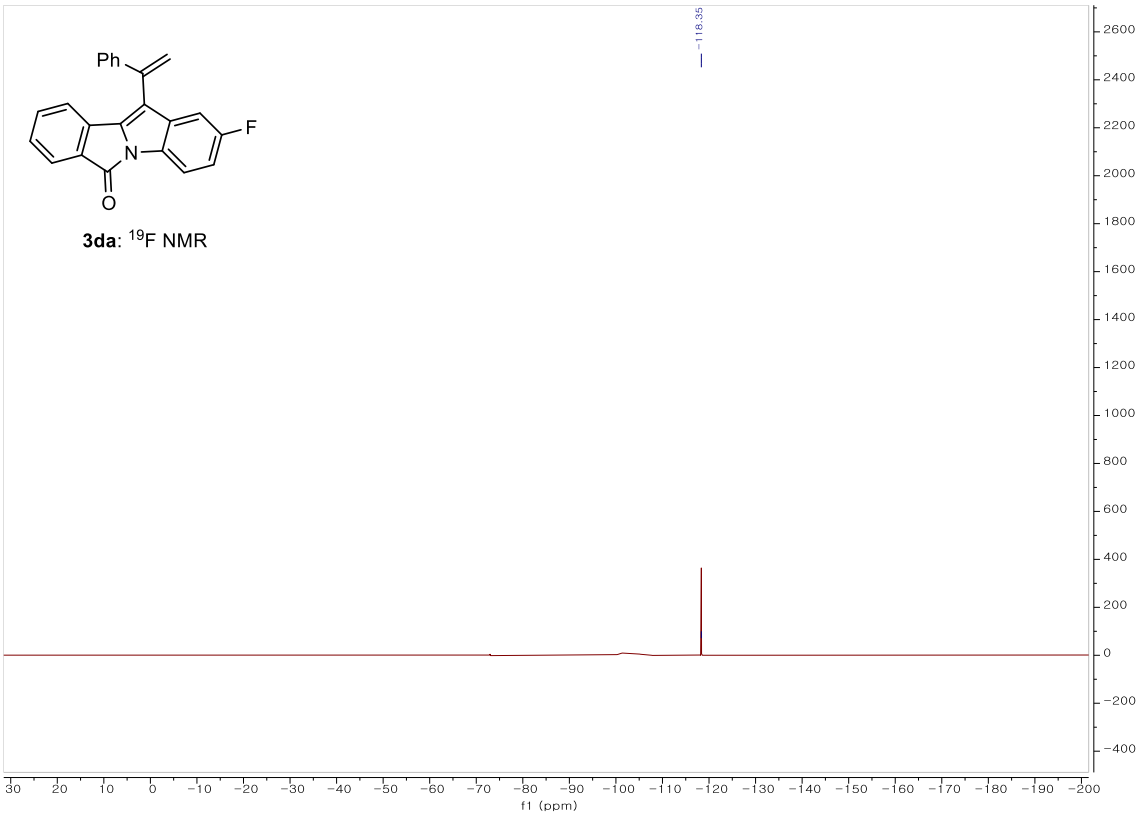
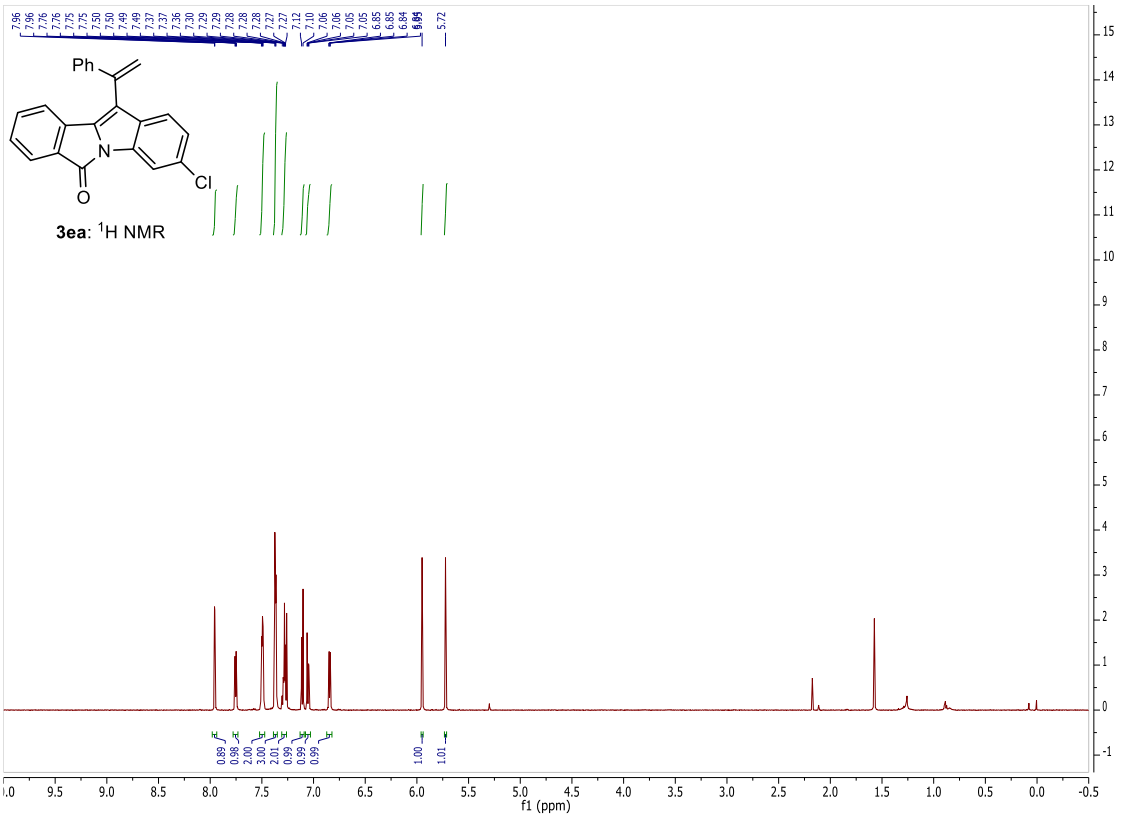
3ca:13CNMR
f1 (ppm)

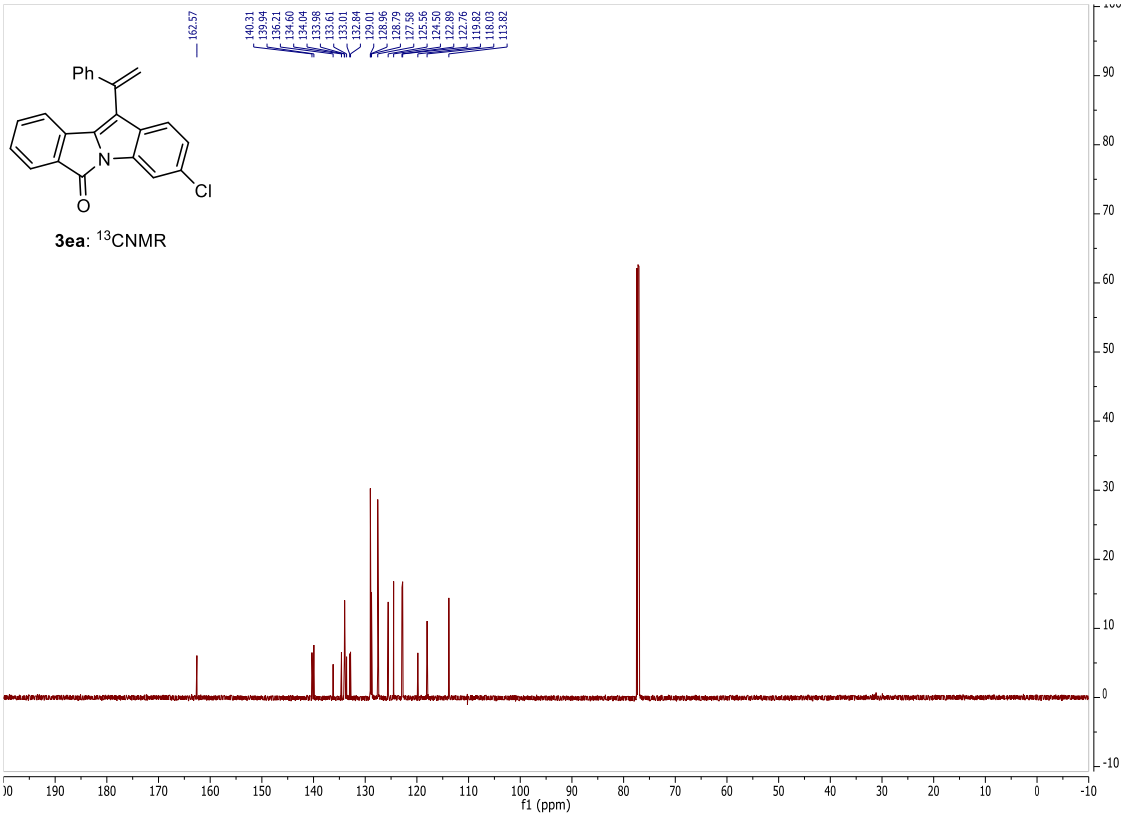

Ph
F
N
O
3da: 1H NMR
f1 (ppm)

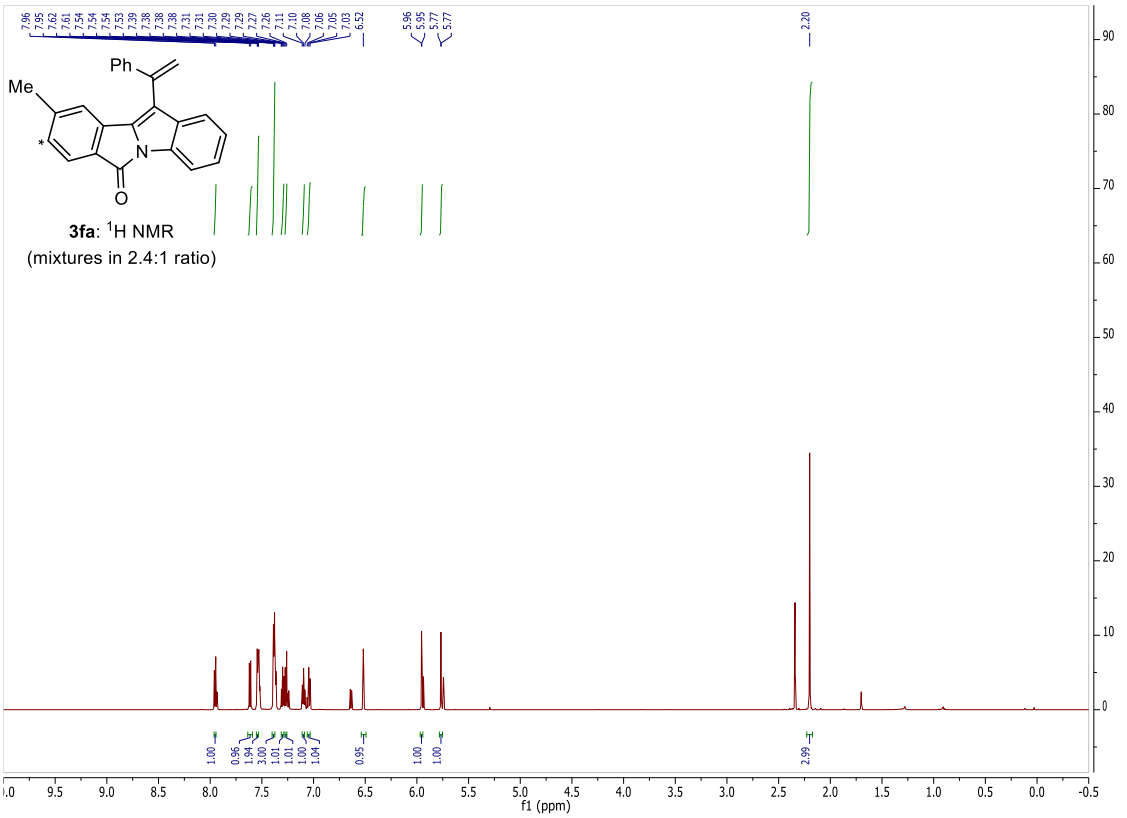

Ph
F
N
O
3da: 13C NMR
f1 (ppm)


Ph
F
N
O
−118.35
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
−400
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

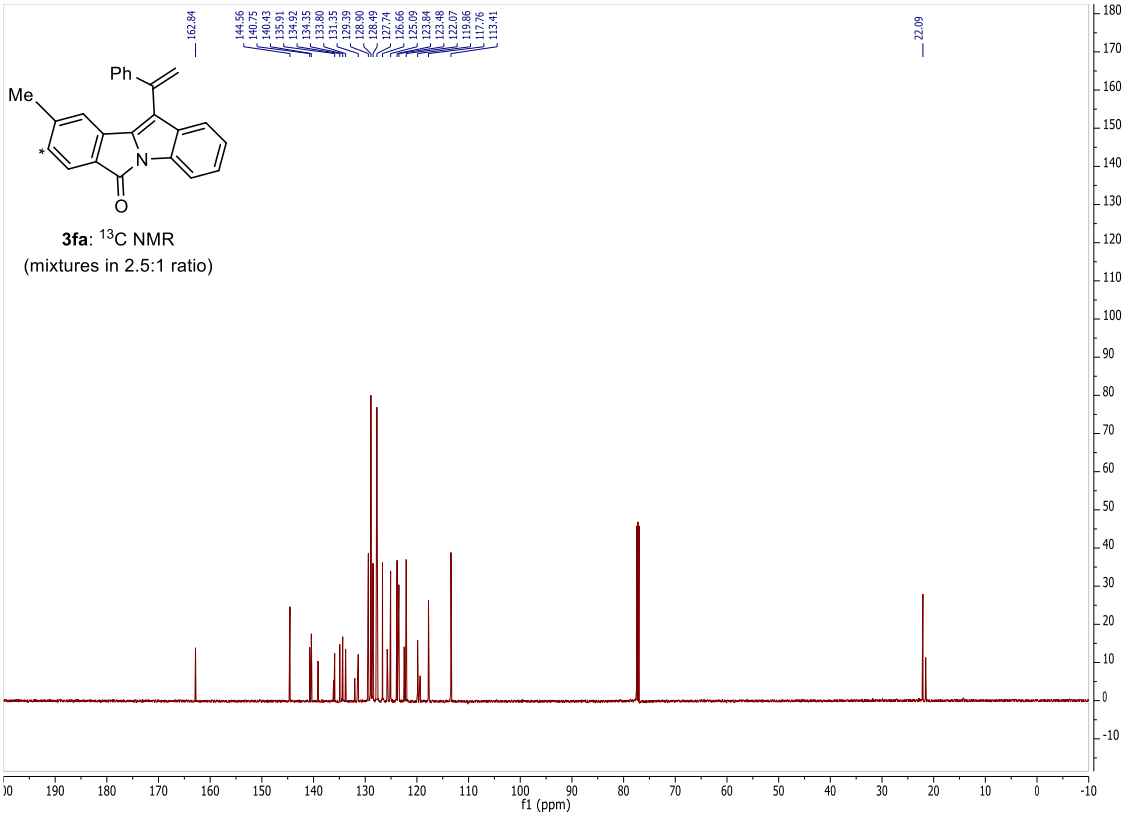
3da: ^{19}F NMR


Ph
N
O
Cl
3ea: 1H NMR
f1 (ppm)

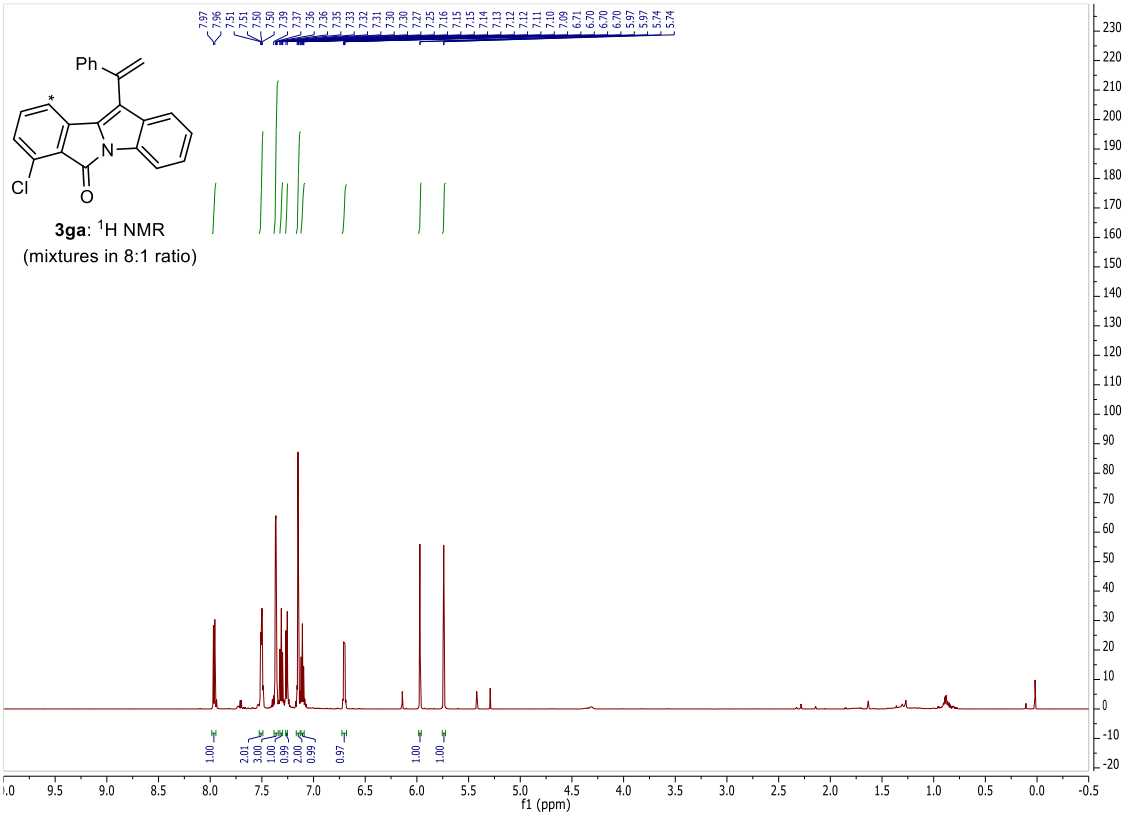

Ph
N
O
Cl
3ea: 13CNMR
f1 (ppm)

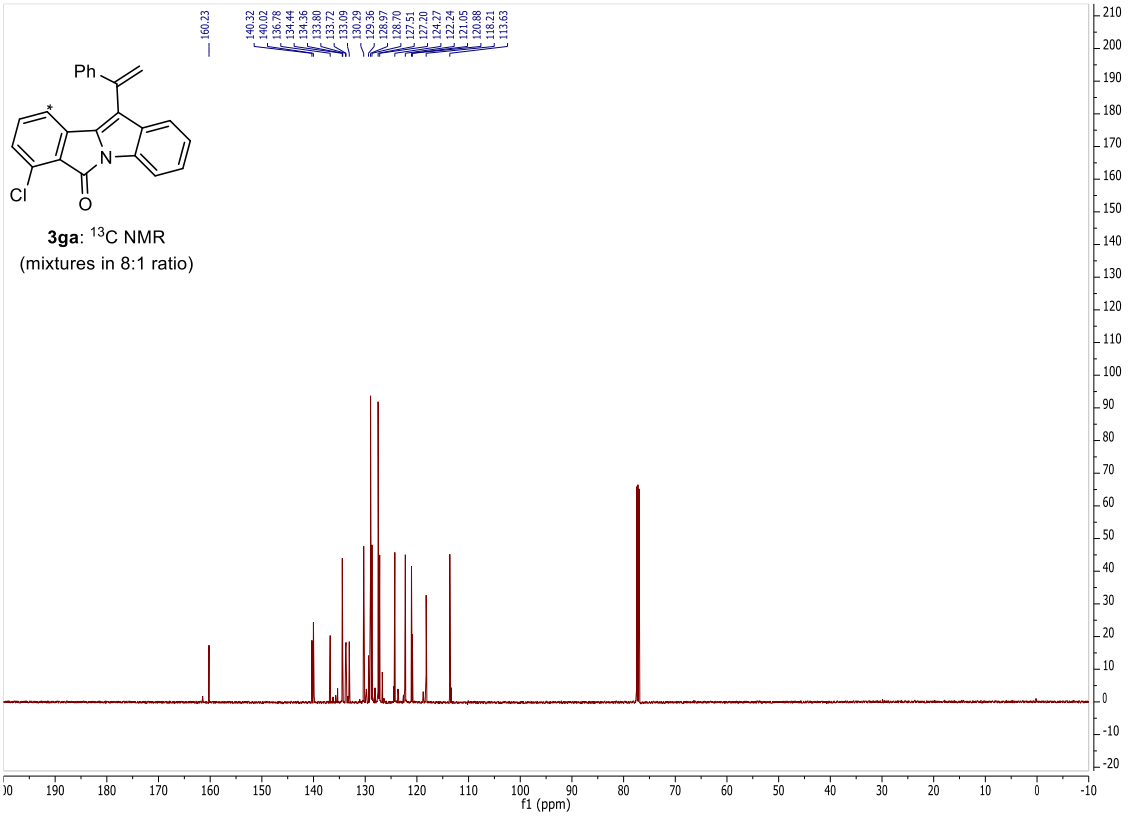


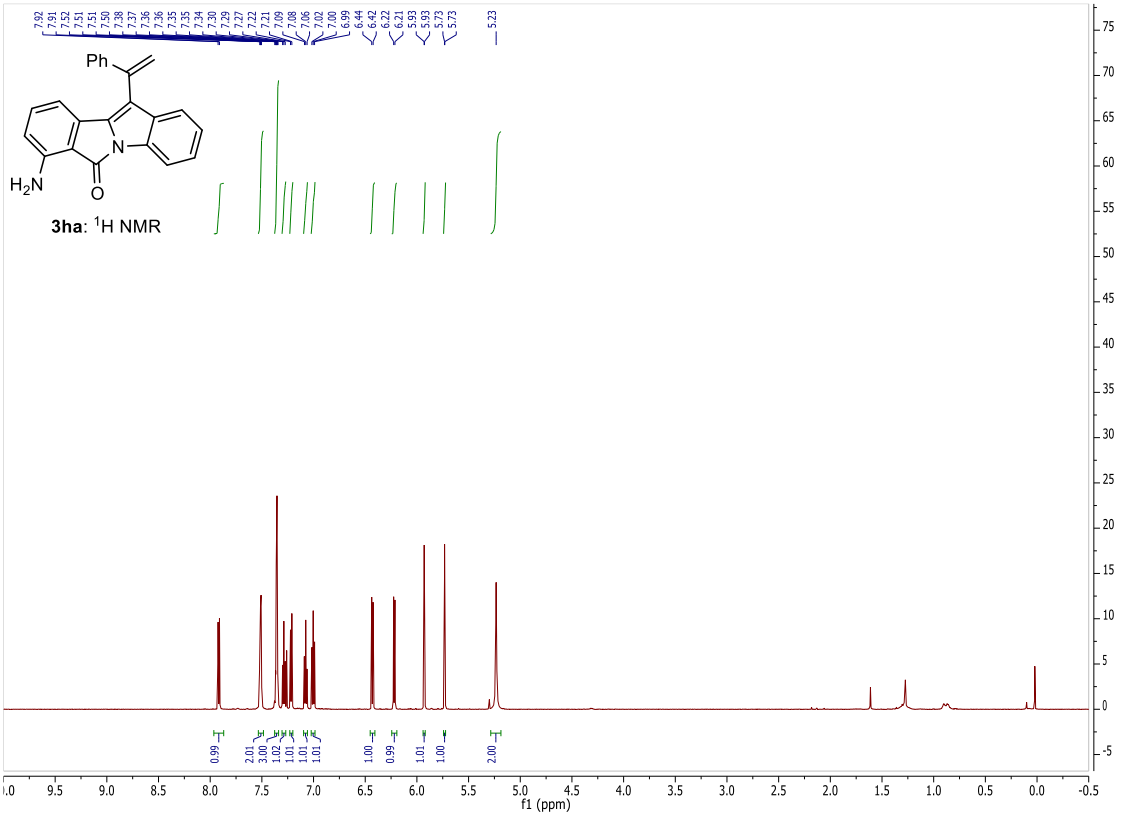
3fa: ^{1}H NMR
(mixtures in 2.4:1 ratio)

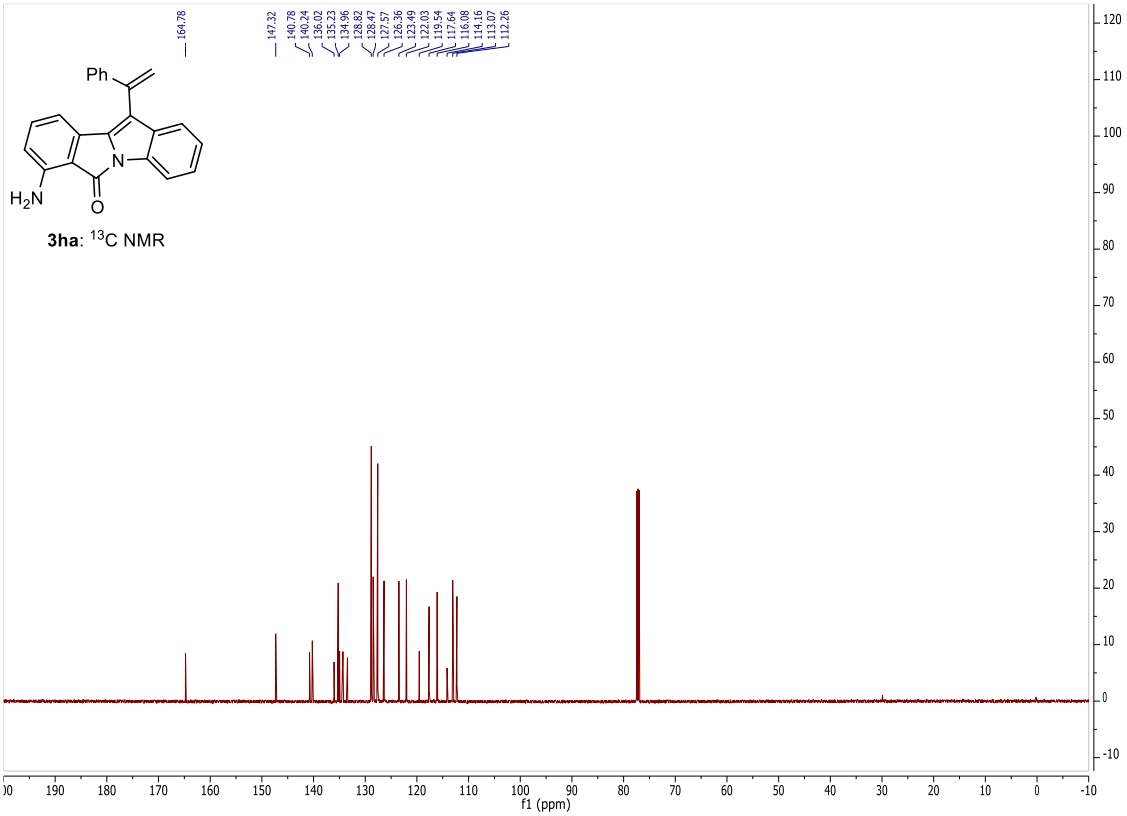


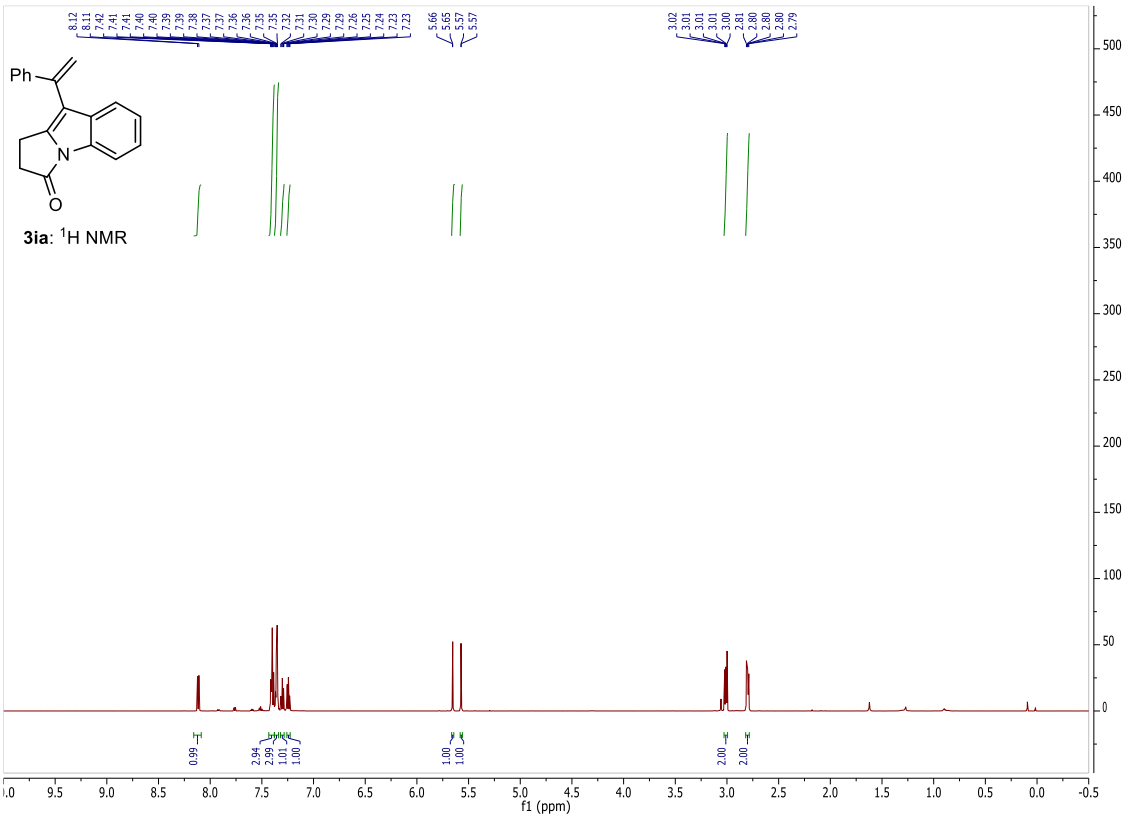
3fa: ^{13}C NMR
(mixtures in 2.5:1 ratio)

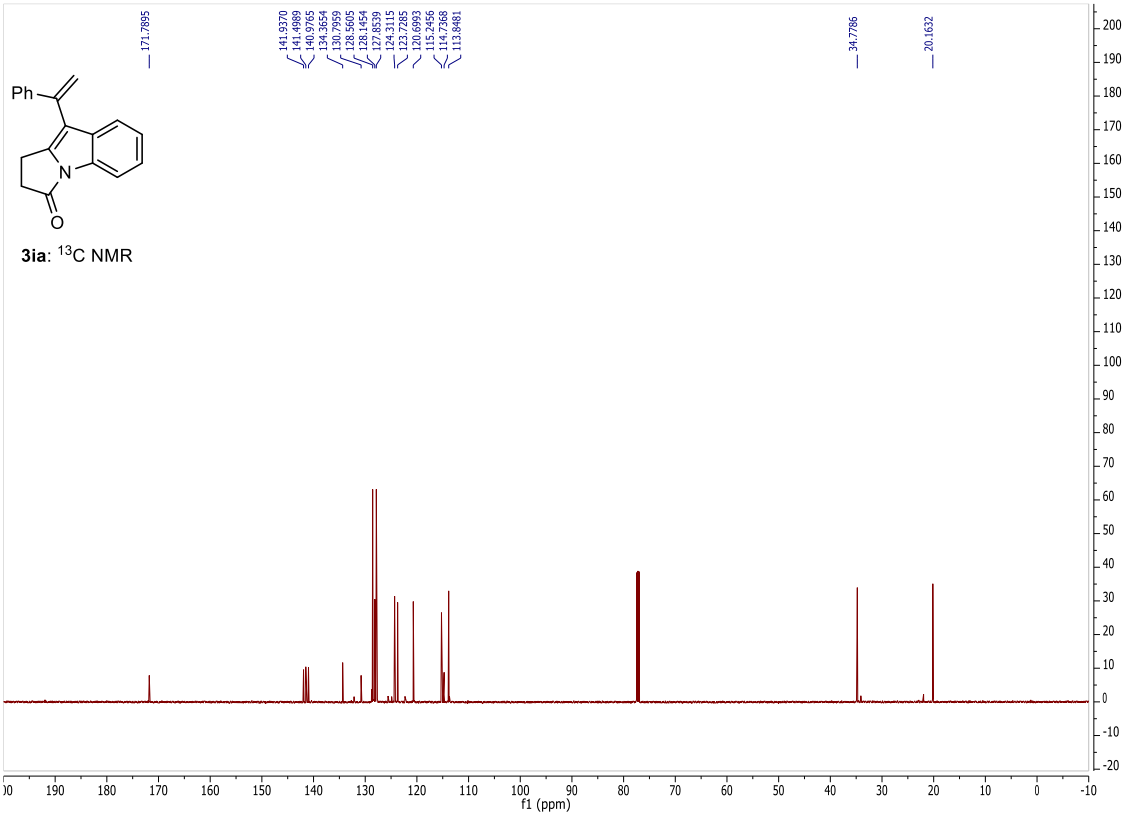

Ph
Cl
O
N
*
3ga: 1H NMR
(mixtures in 8:1 ratio)
f1 (ppm)

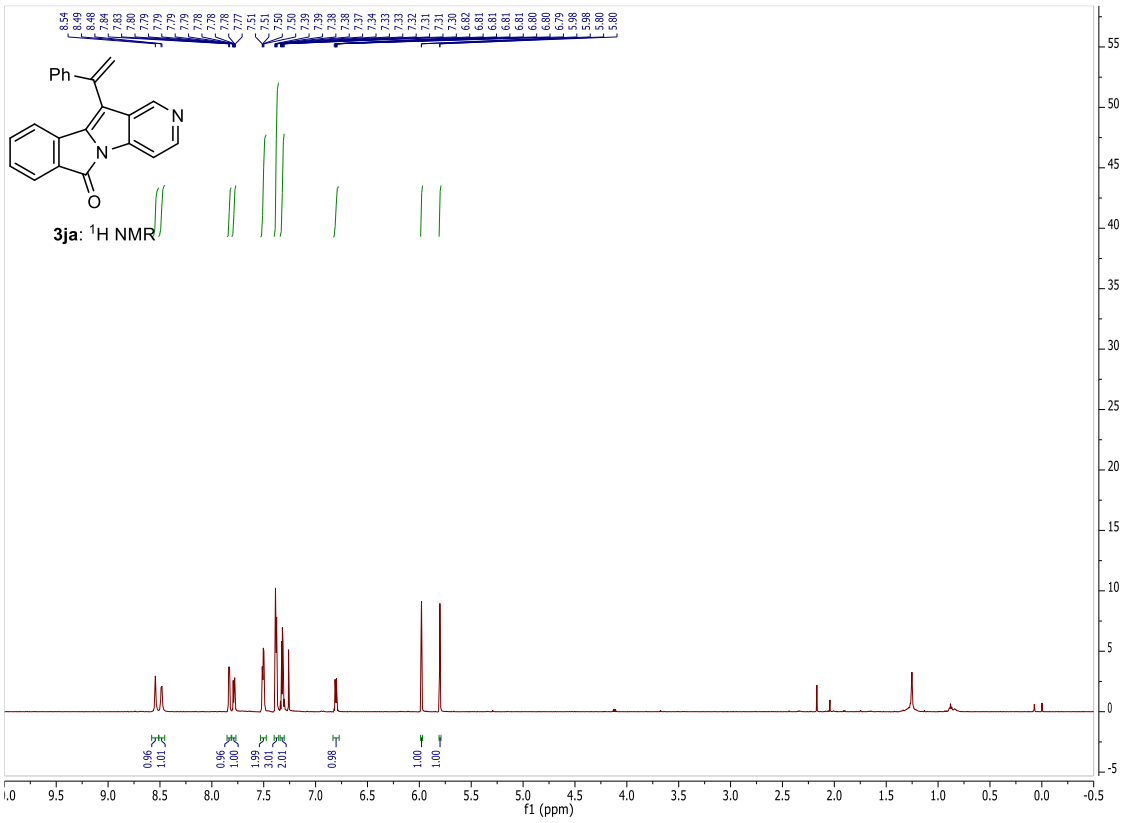

Ph
Cl
O
N
*
3ga: 13C NMR
(mixtures in 8:1 ratio)
f1 (ppm)

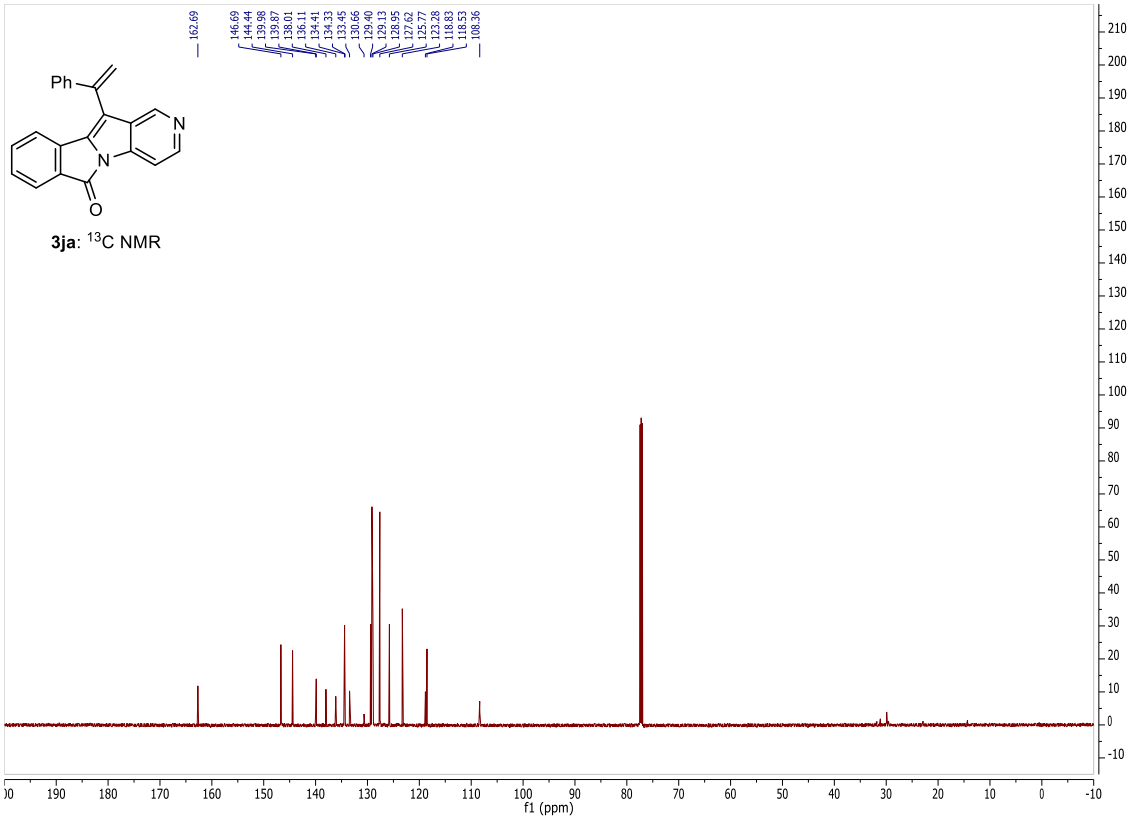

Ph
N
O
H_2N
3ha: ^{1}H NMR
f1 (ppm)

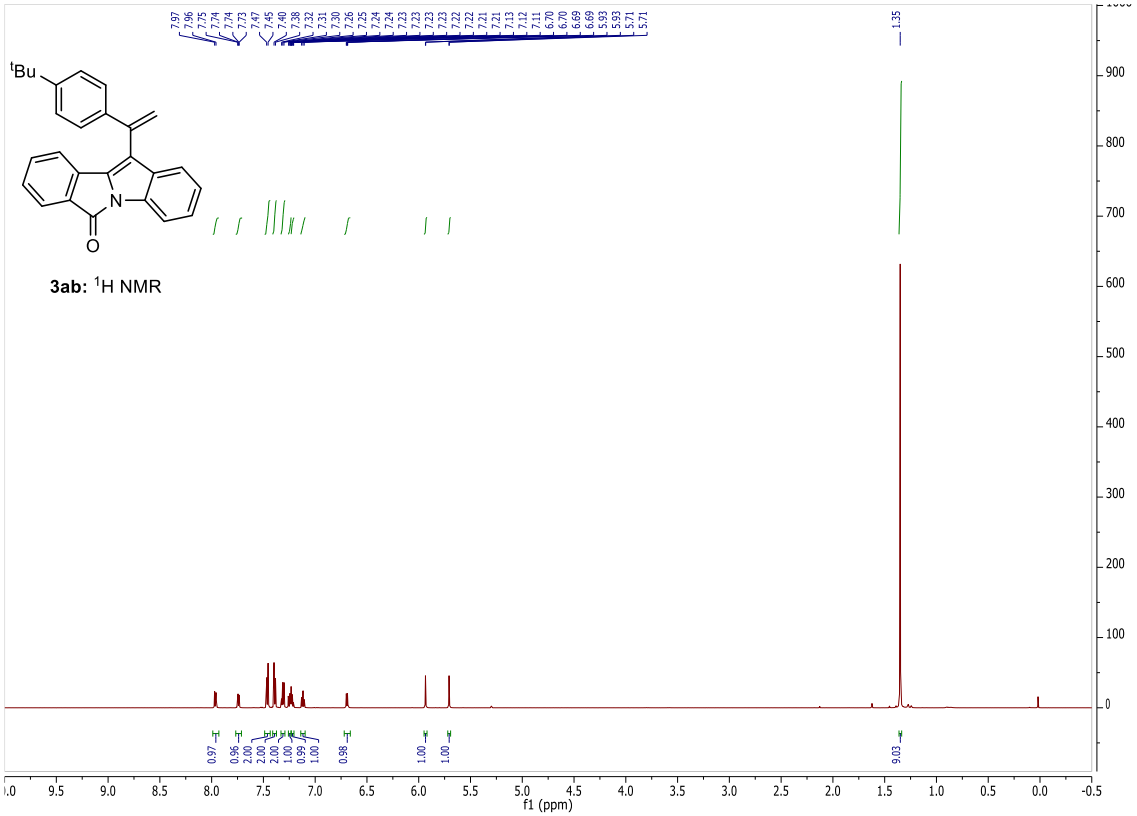

Ph
N
O
H_2N
3ha: ^{13}C NMR
f1 (ppm)


Ph
N
O
3ia: 1H NMR
f1 (ppm)

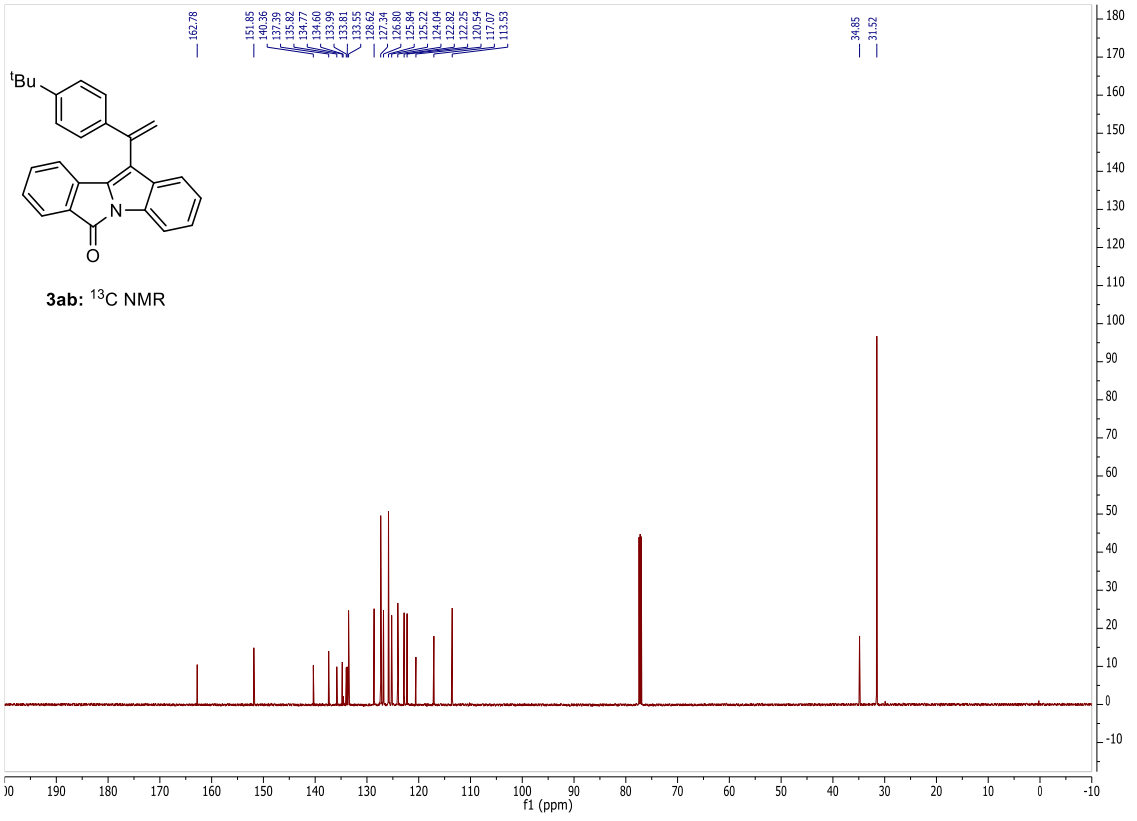

Ph
N
O
3ia: 13C NMR
f1 (ppm)


Ph
N
N
O
3ja: 1H NMR
f1 (ppm)

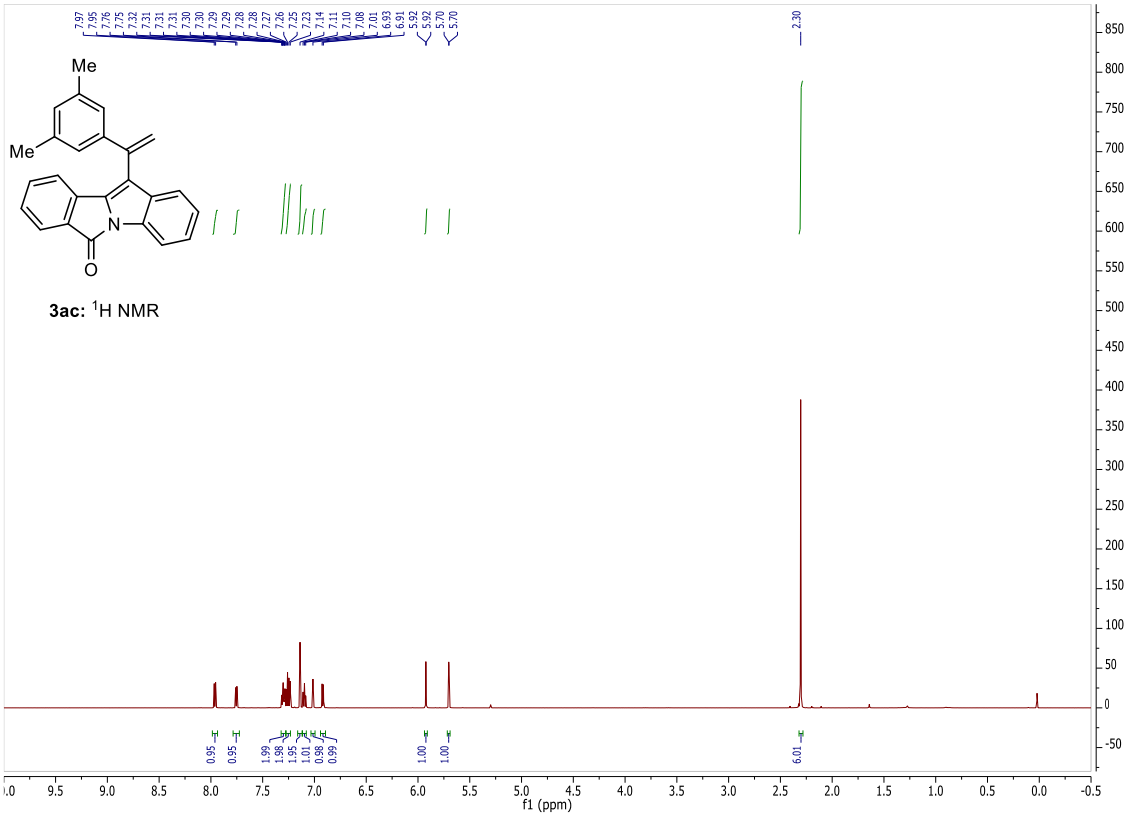

Ph
N
N
O
3ja: 13C NMR
f1 (ppm)



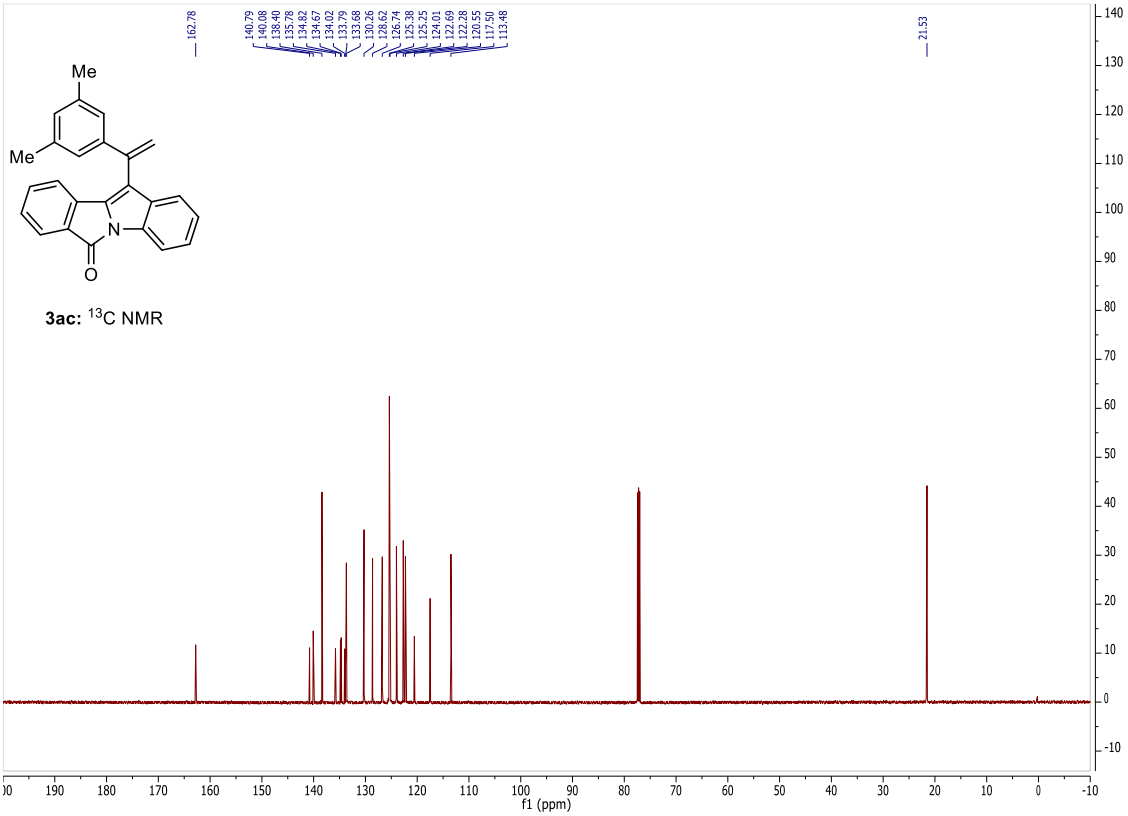
3ab: ^{1}H NMR



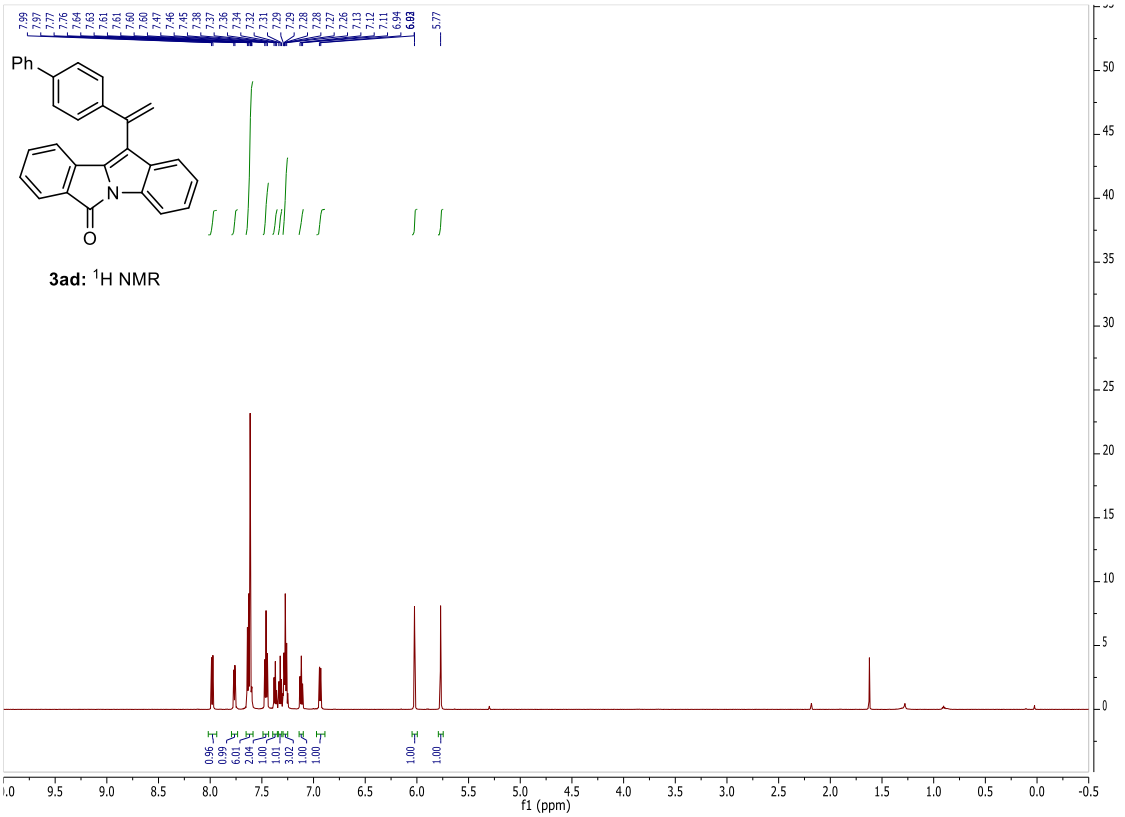
3ab: ^{13}C NMR



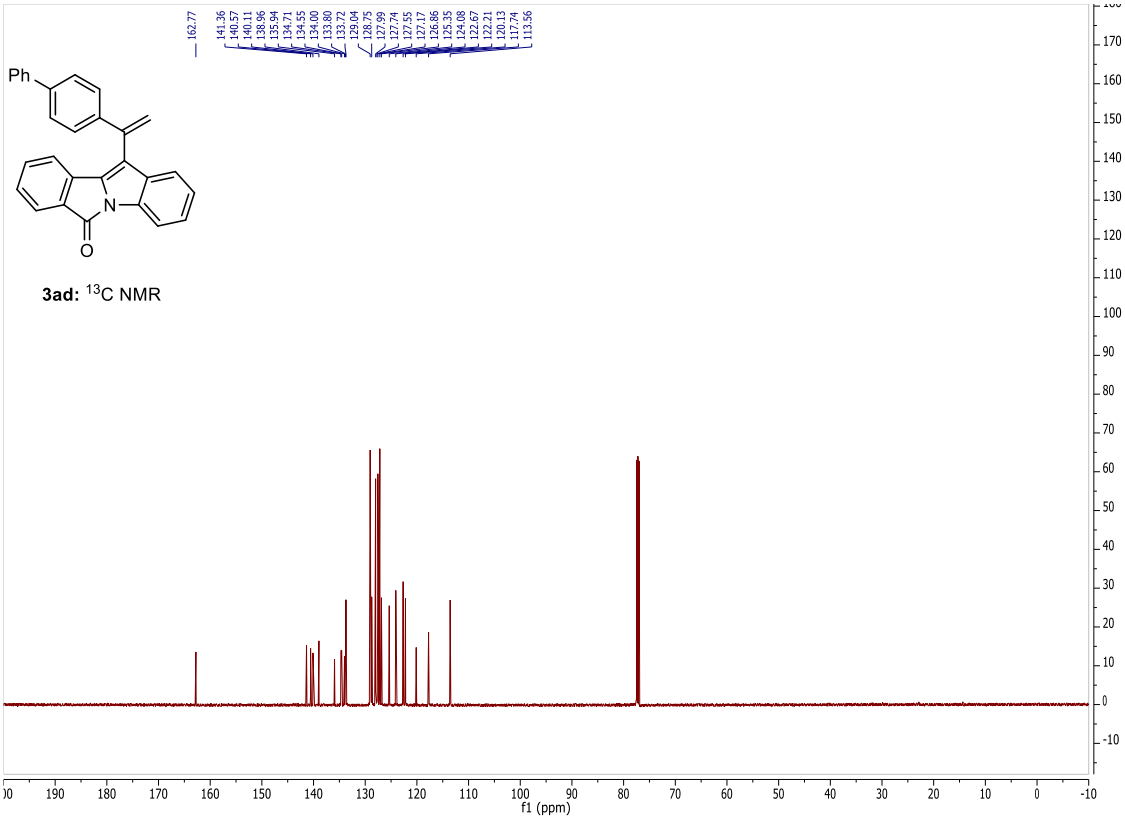
3ac: ^{1}H NMR



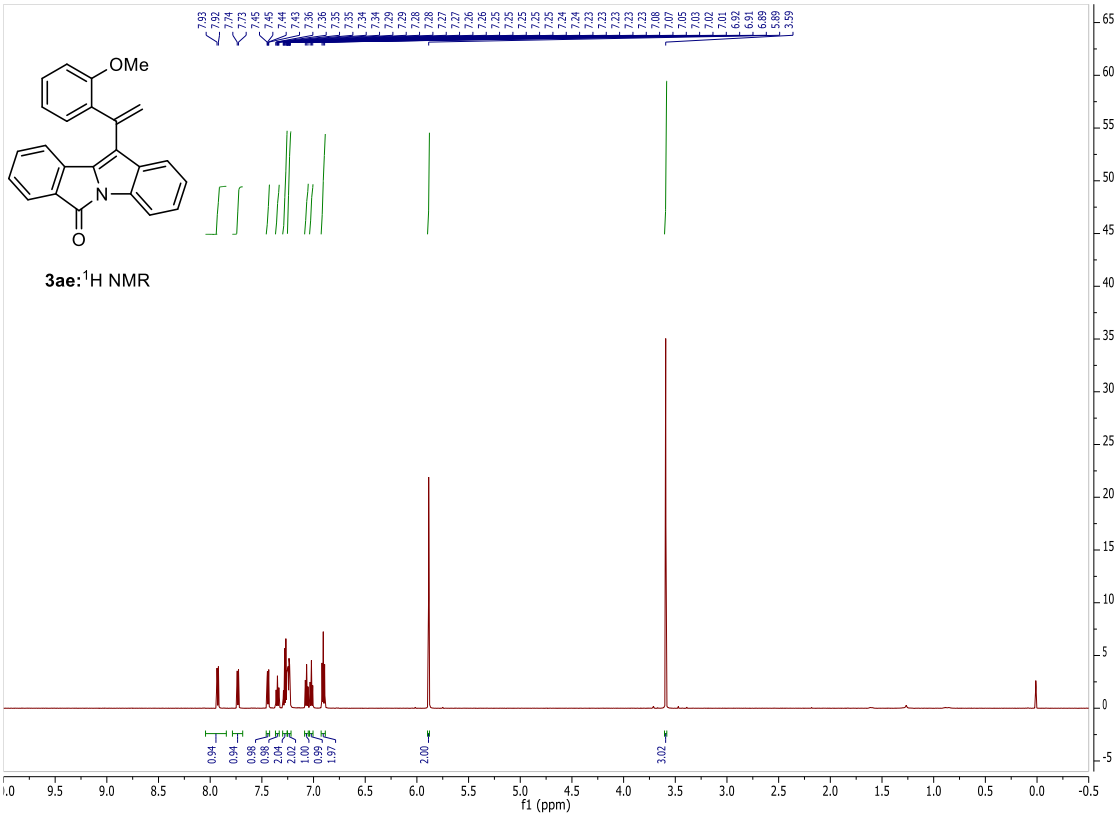
3ac: ^{13}C NMR

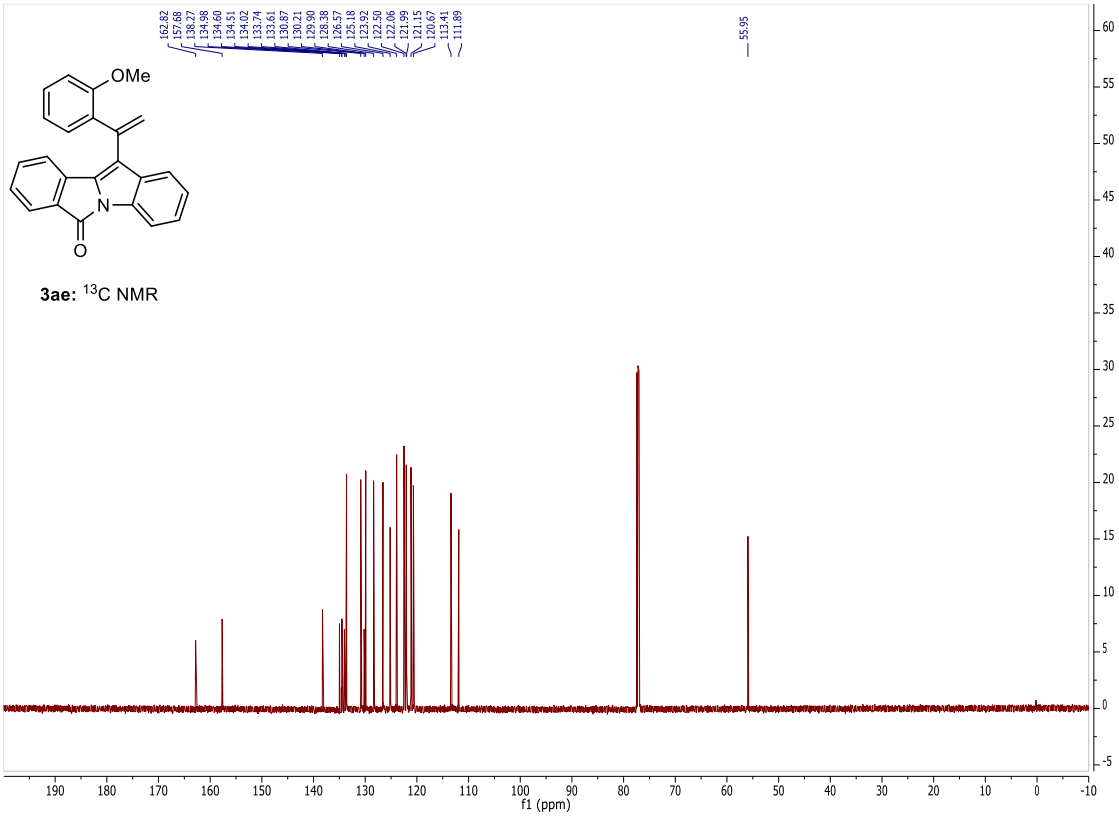


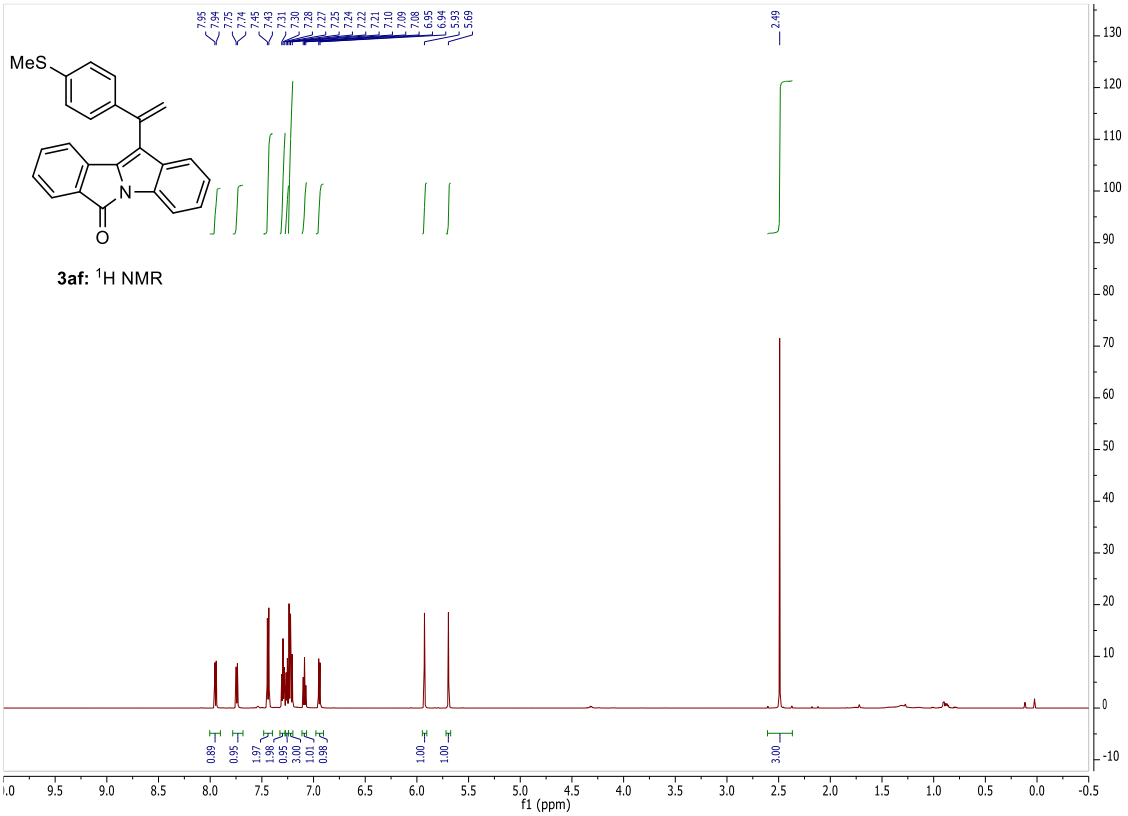
3ad: ^{1}H NMR



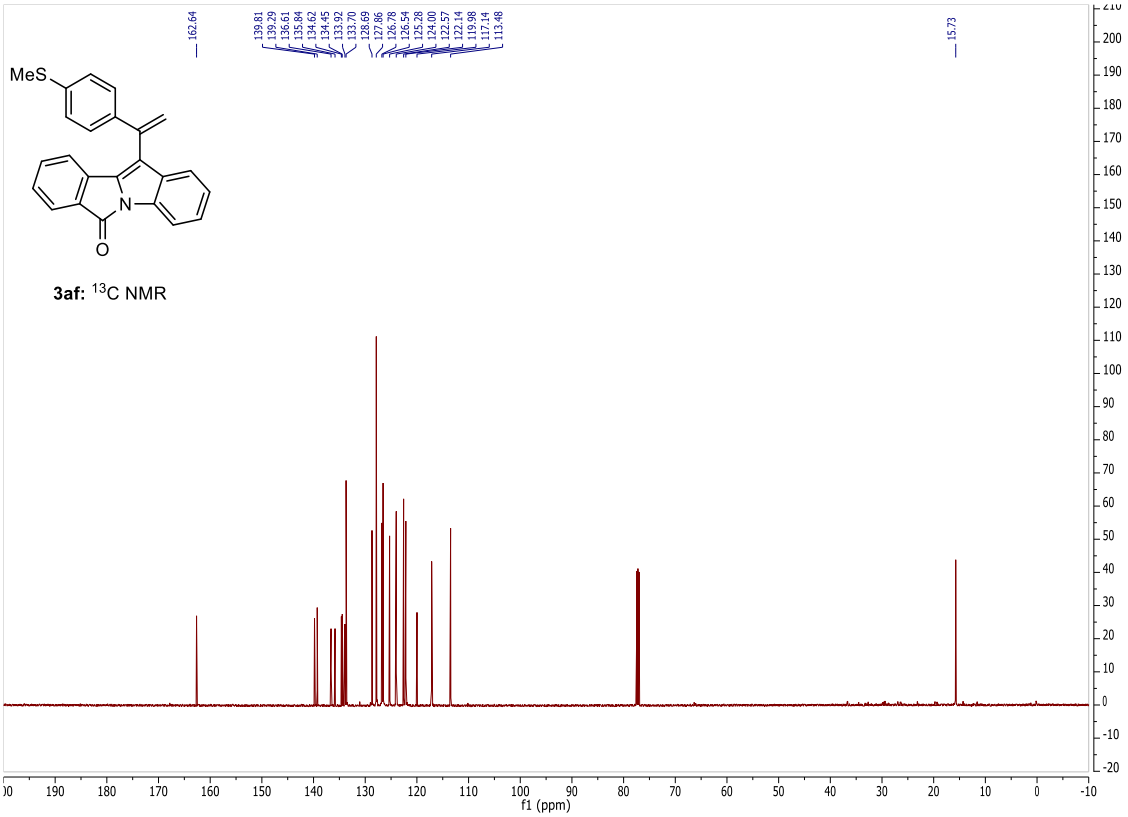
3ad: ^{13}C NMR


OMe
N
O
3ae:1H NMR
f1 (ppm)

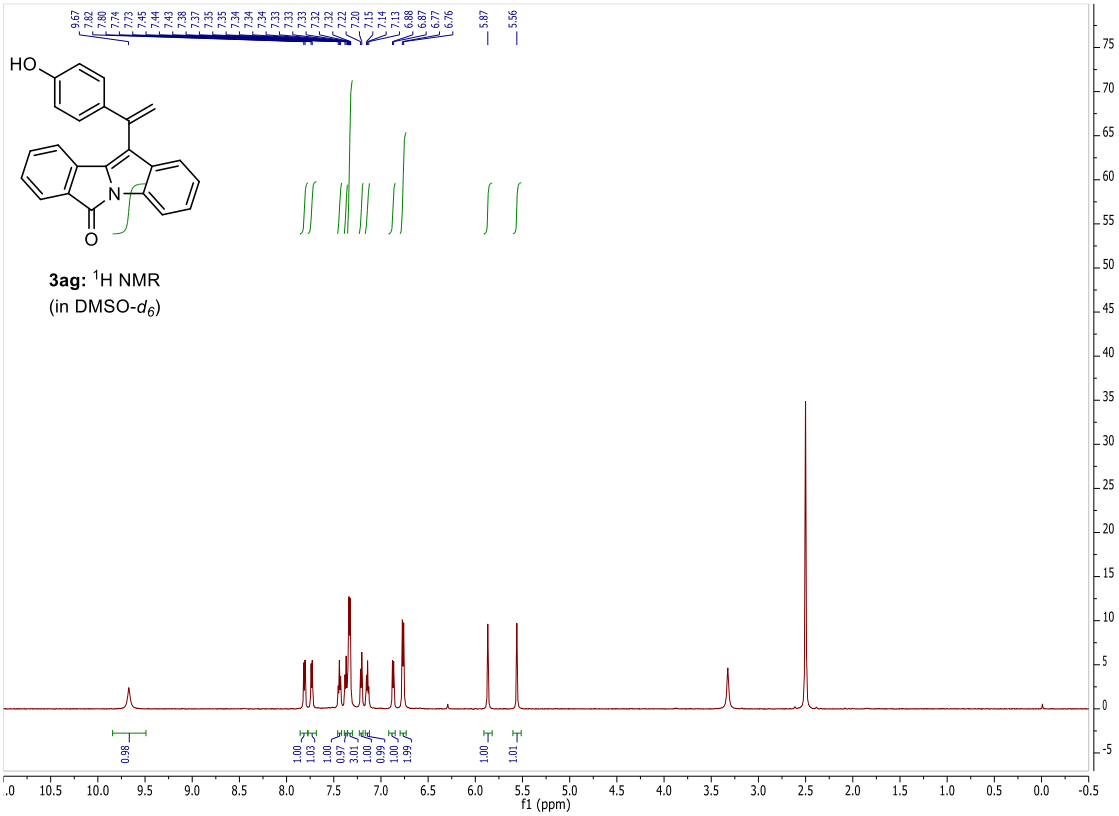

OMe
N
O
3ae: 13C NMR
f1 (ppm)



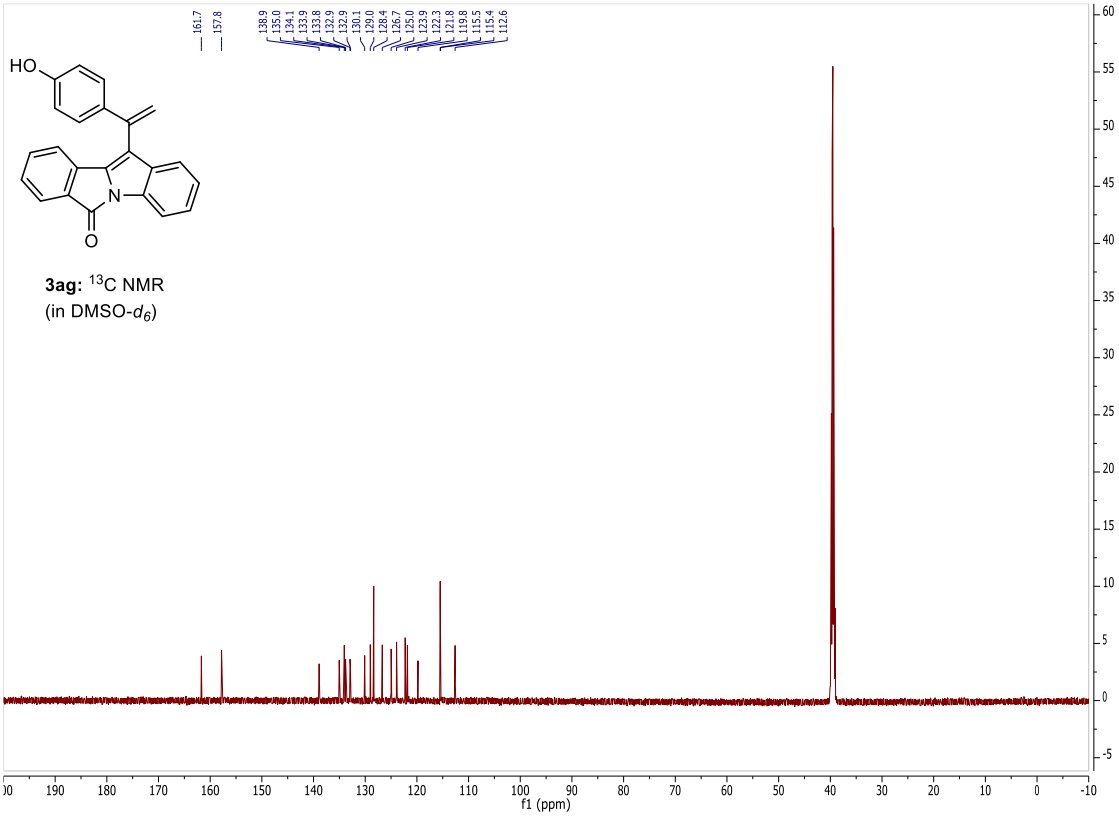
3af: ^{1}H NMR



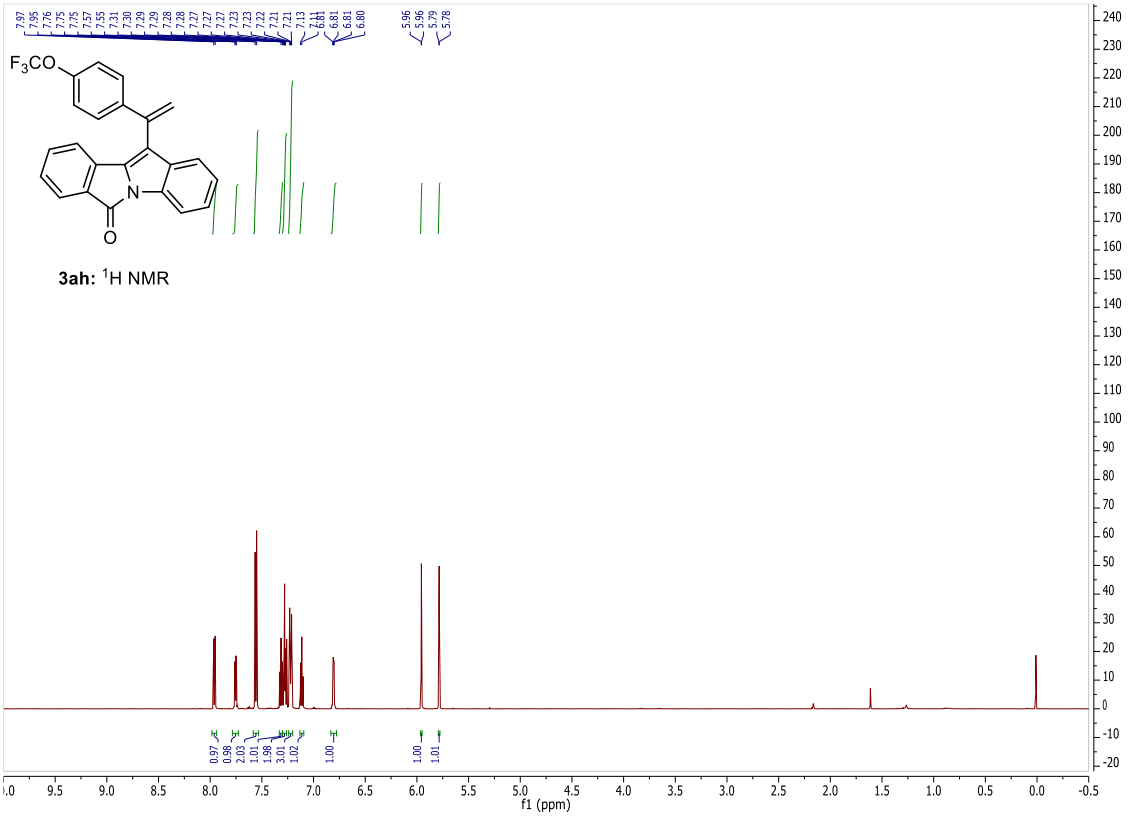
3af: ^{13}C NMR



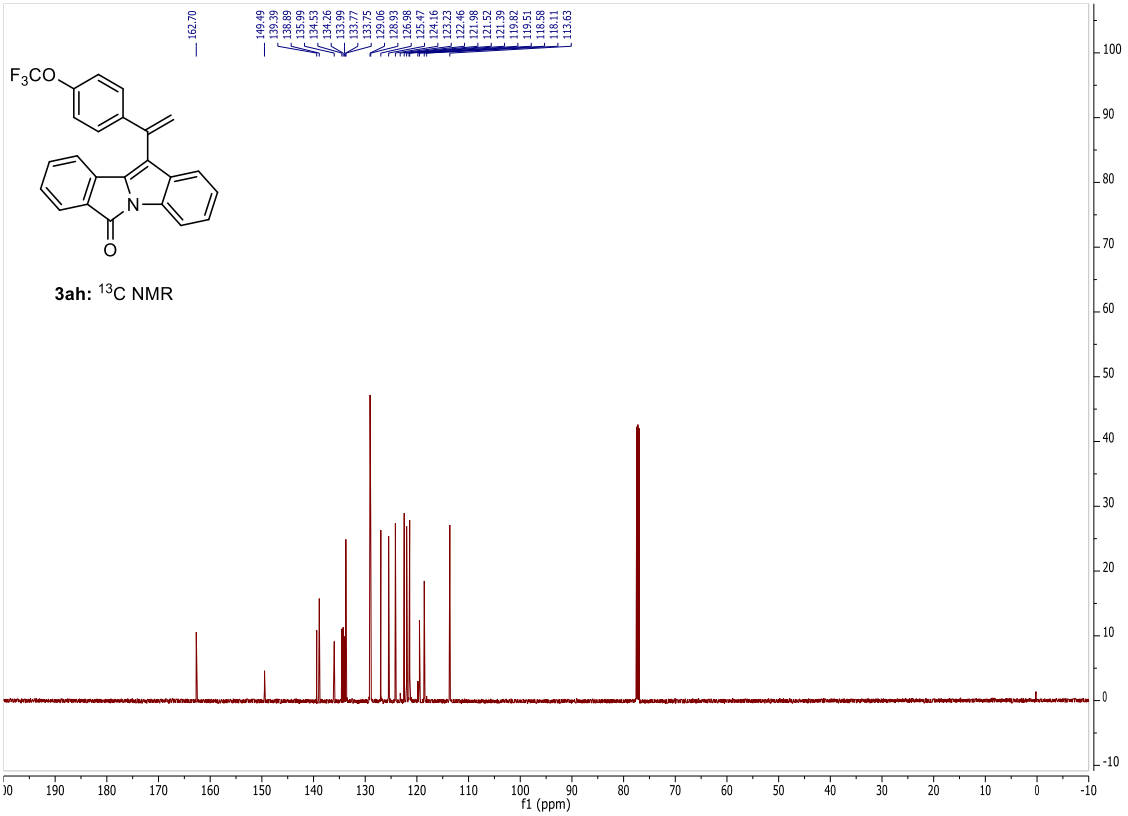
3ag: ^{1}H NMR
(in DMSO-d_6)



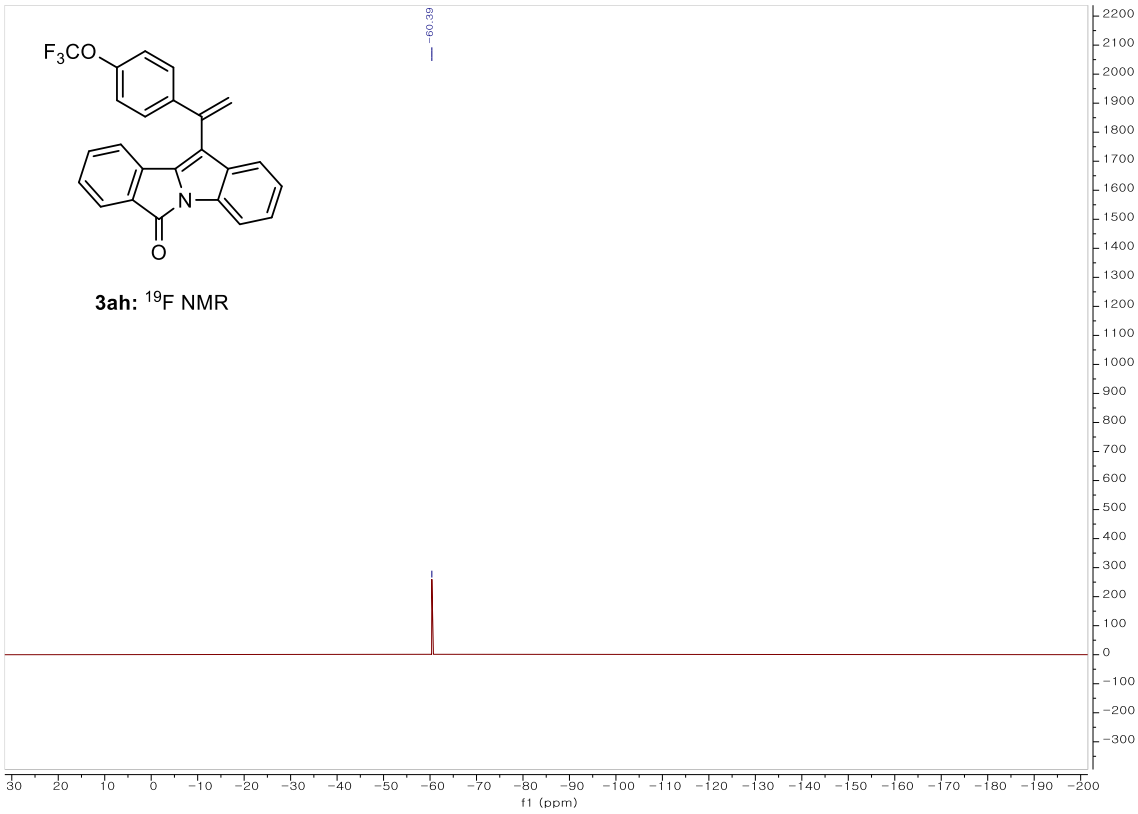
3ag: ^{13}C NMR
(in DMSO-d_6)



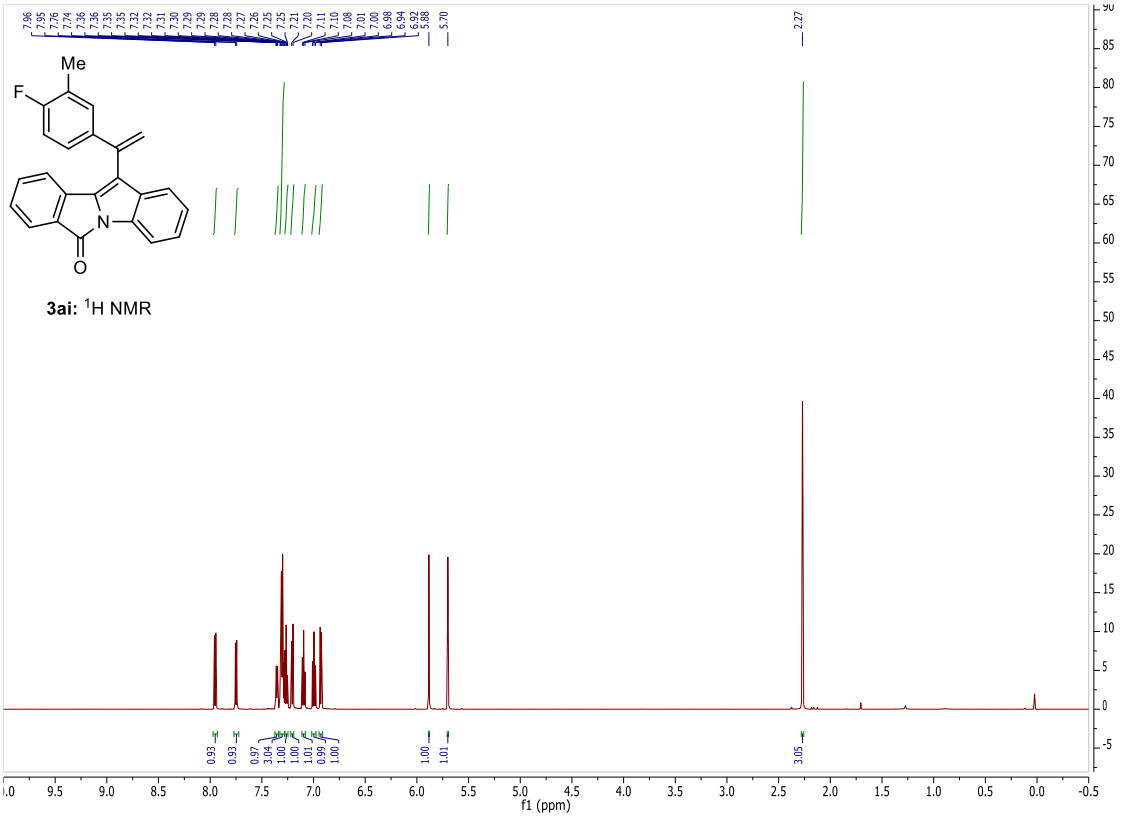
3ah: ^{1}H NMR

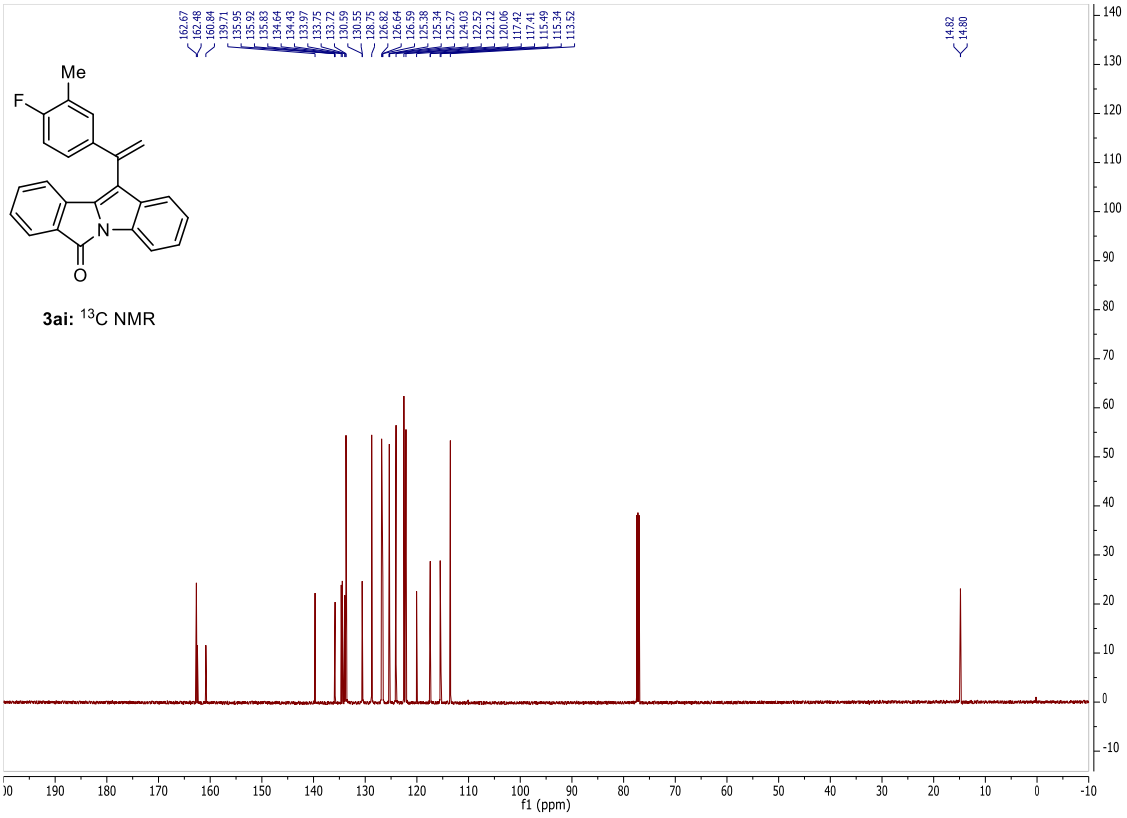


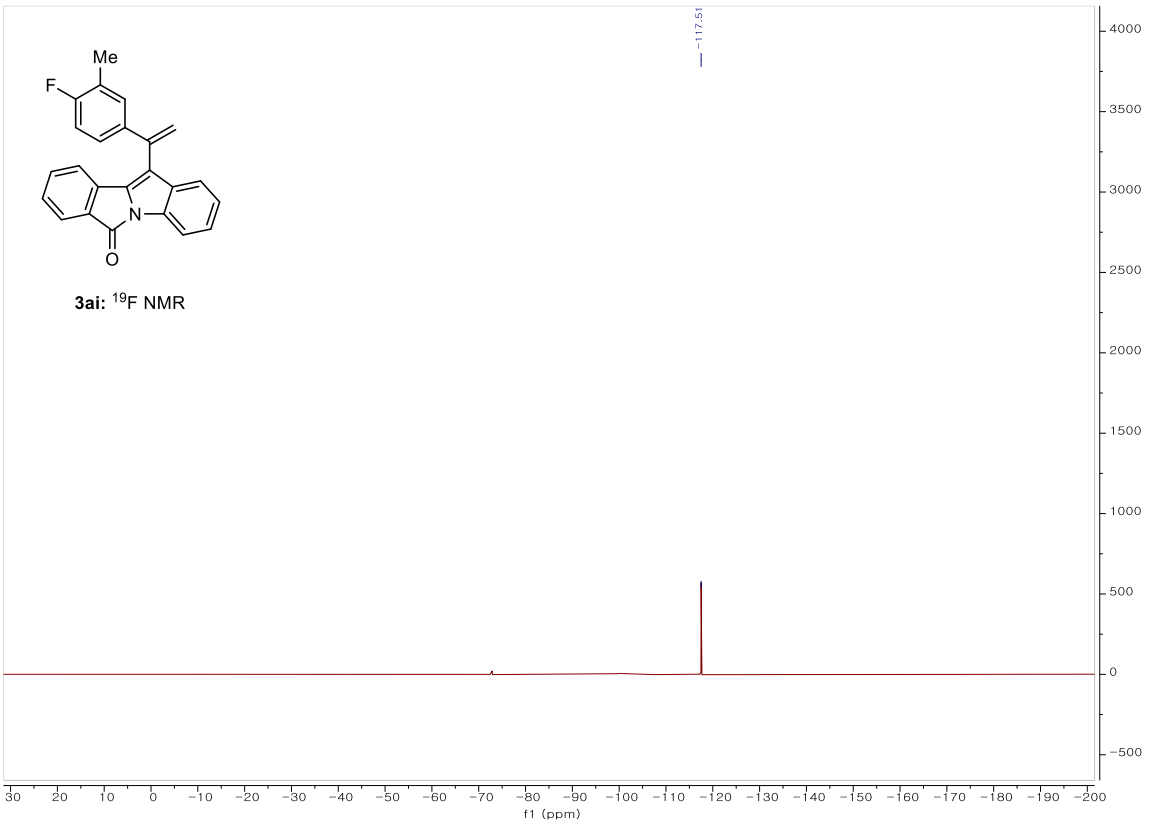
3ah: ^{13}C NMR


F3CO
N
O
−60.39
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
−300
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

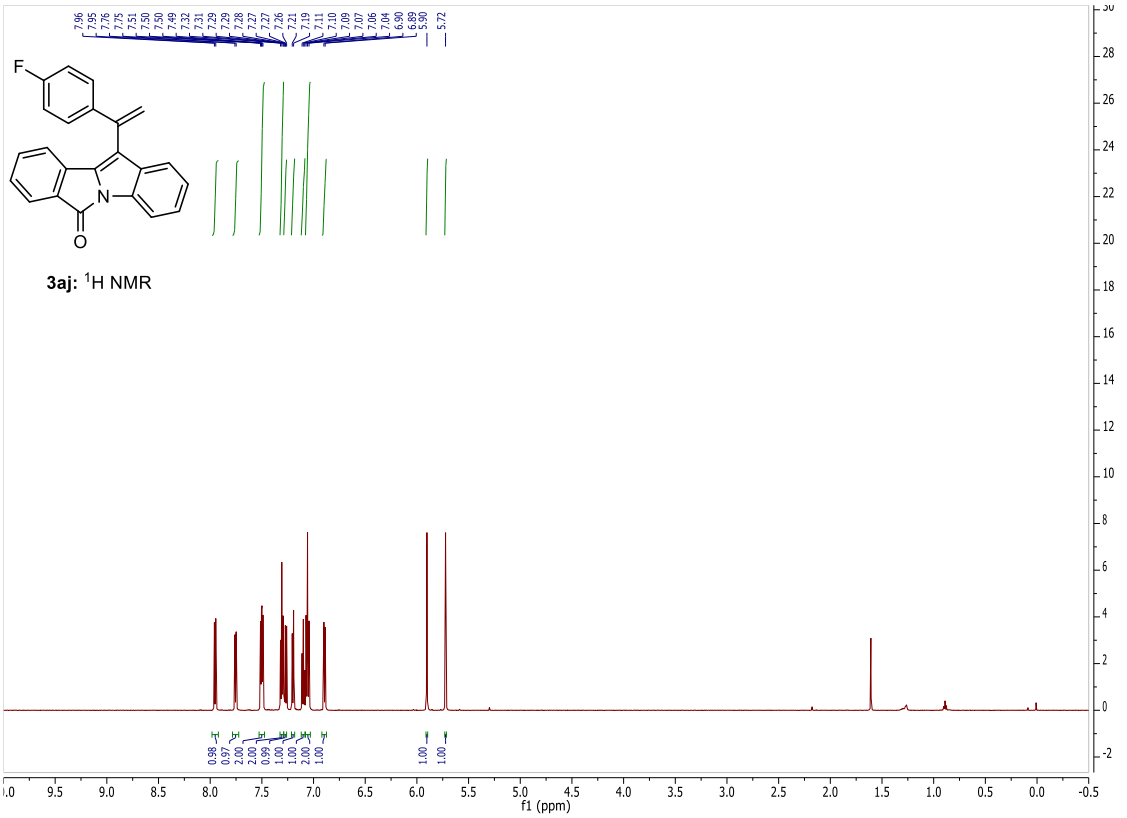
3ah: ^{19}F NMR


Me
F
N
O
3ai: 1H NMR
f1 (ppm)

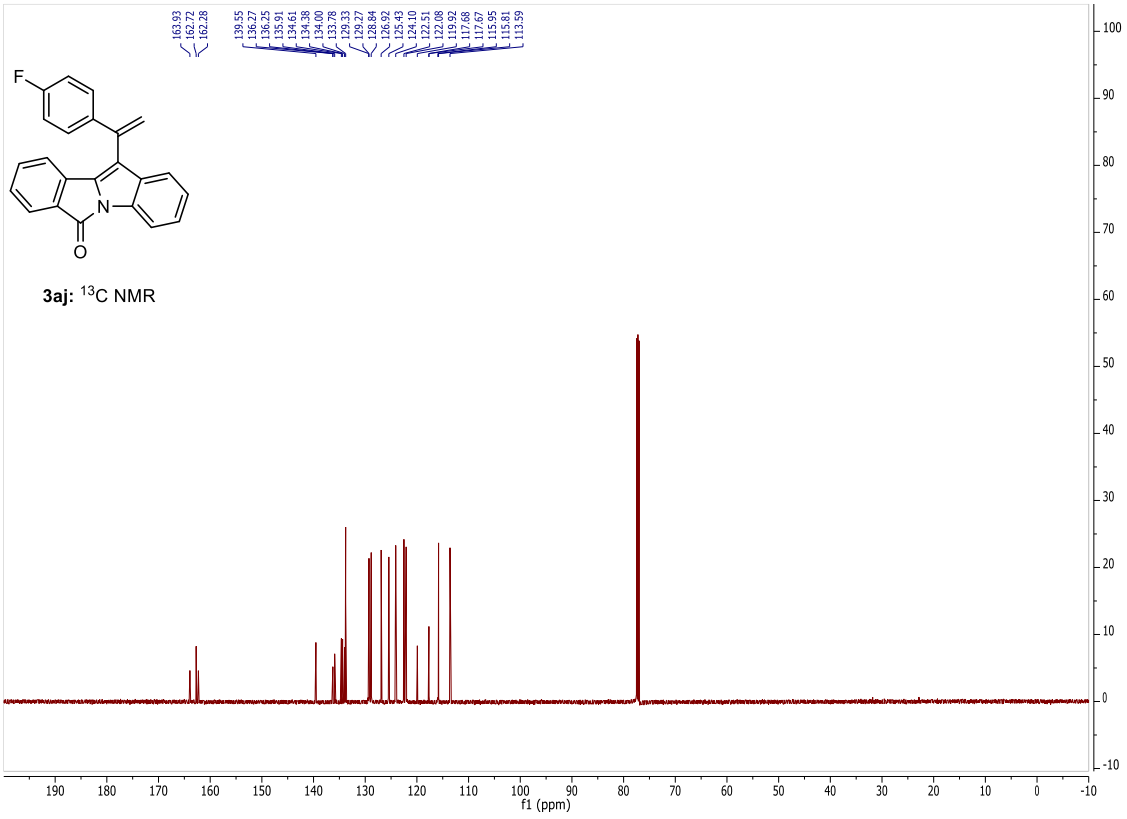

Me
F
N
O
3ai: 13C NMR
f1 (ppm)


Me
F
N
O
−117.51
4000
3500
3000
2500
2000
1500
1000
500
0
−500
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

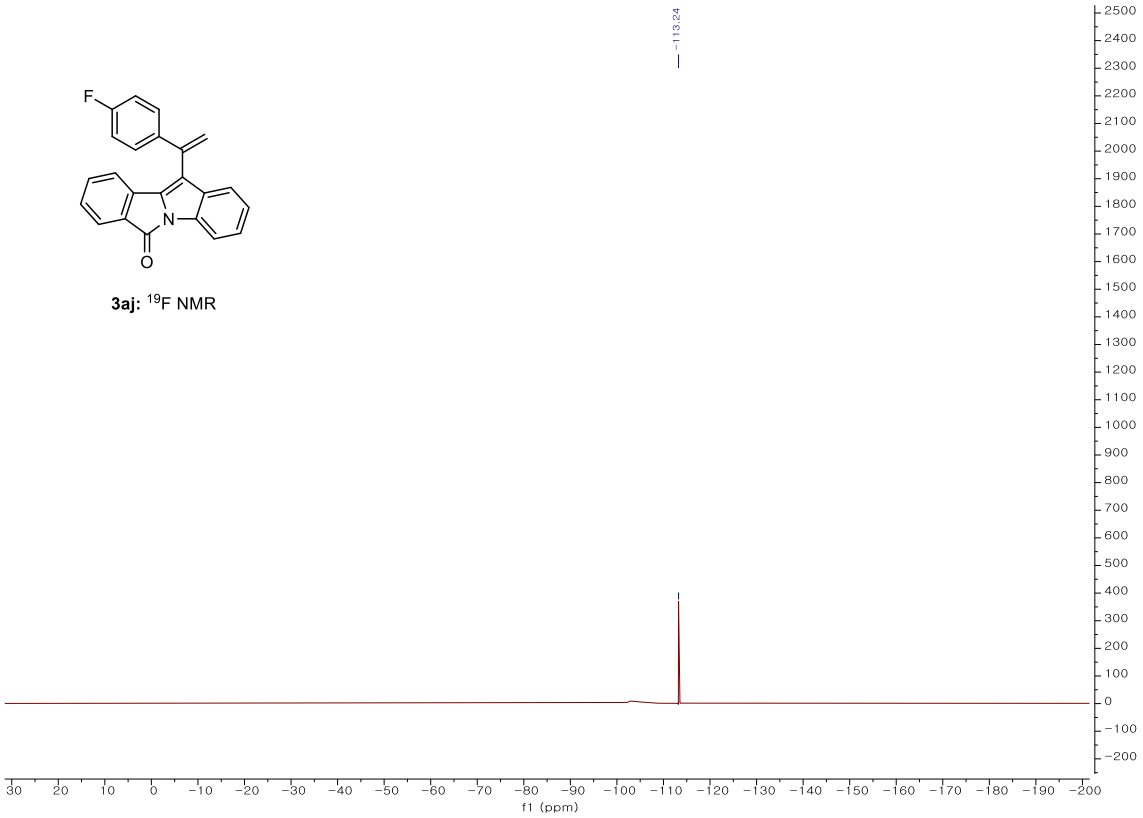
3ai: ^{19}F NMR



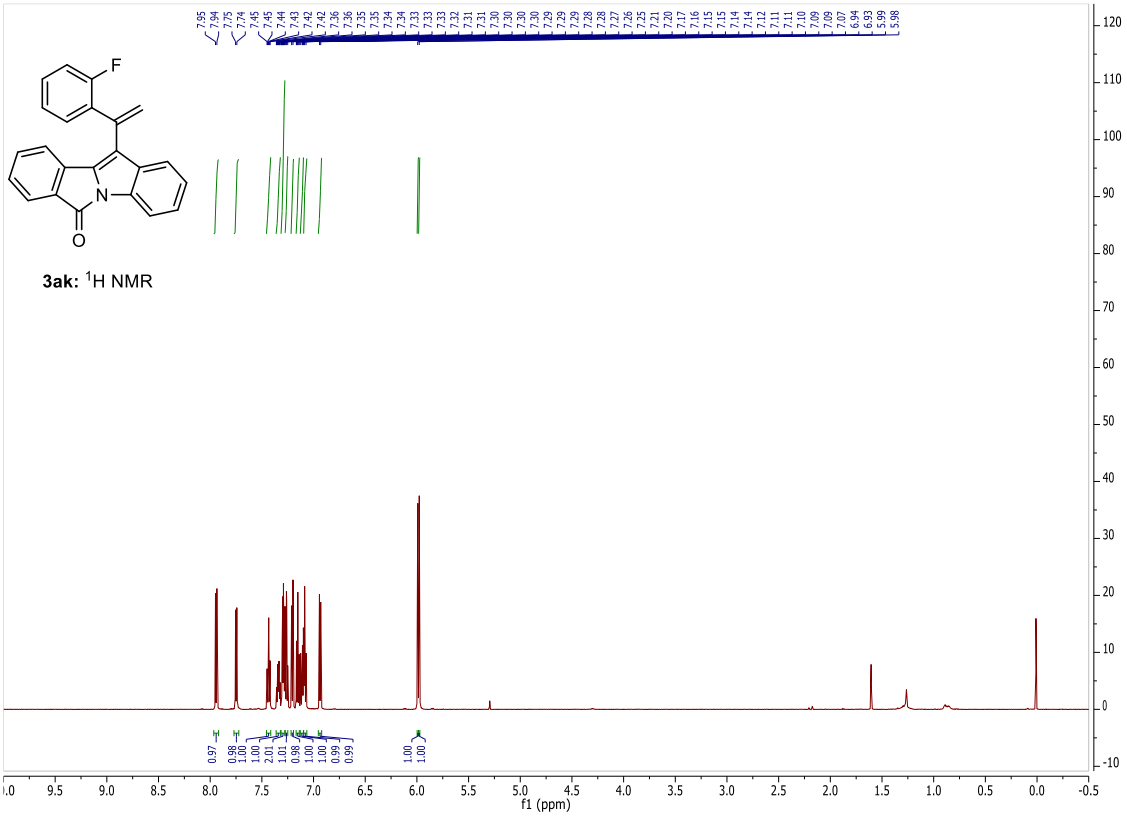
3aj: ^{1}H NMR

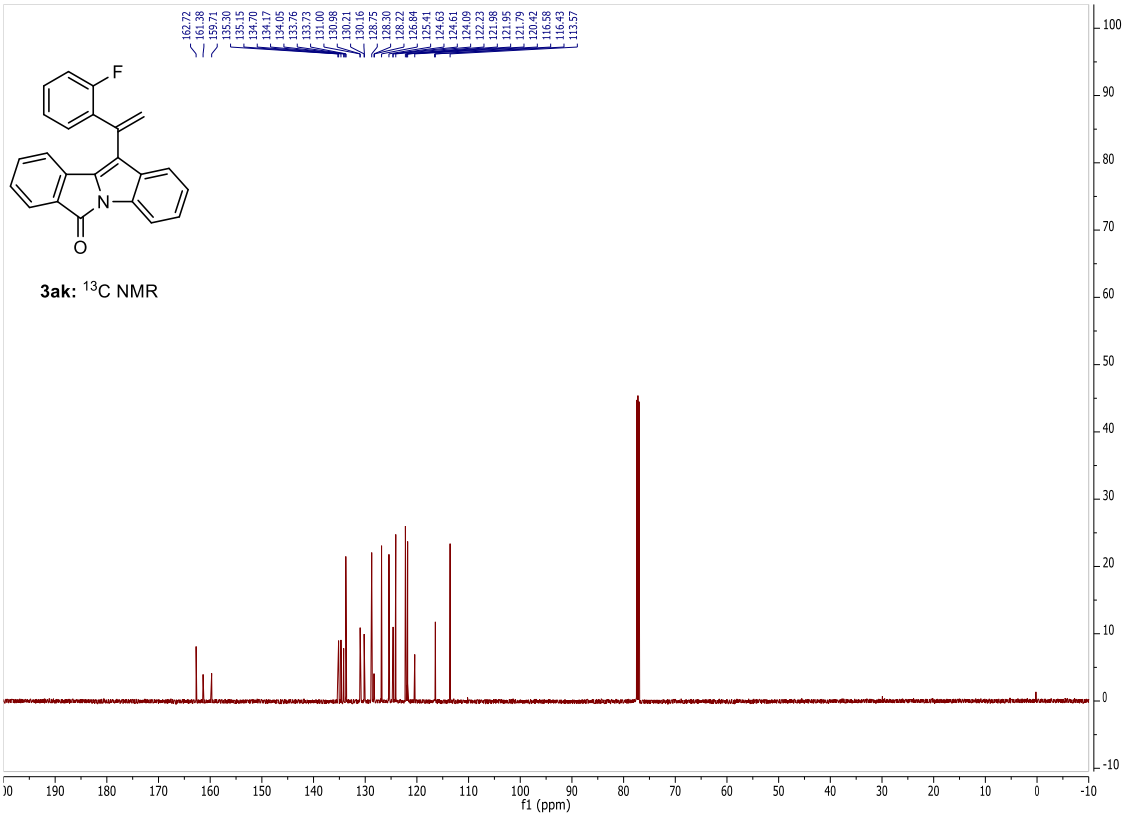


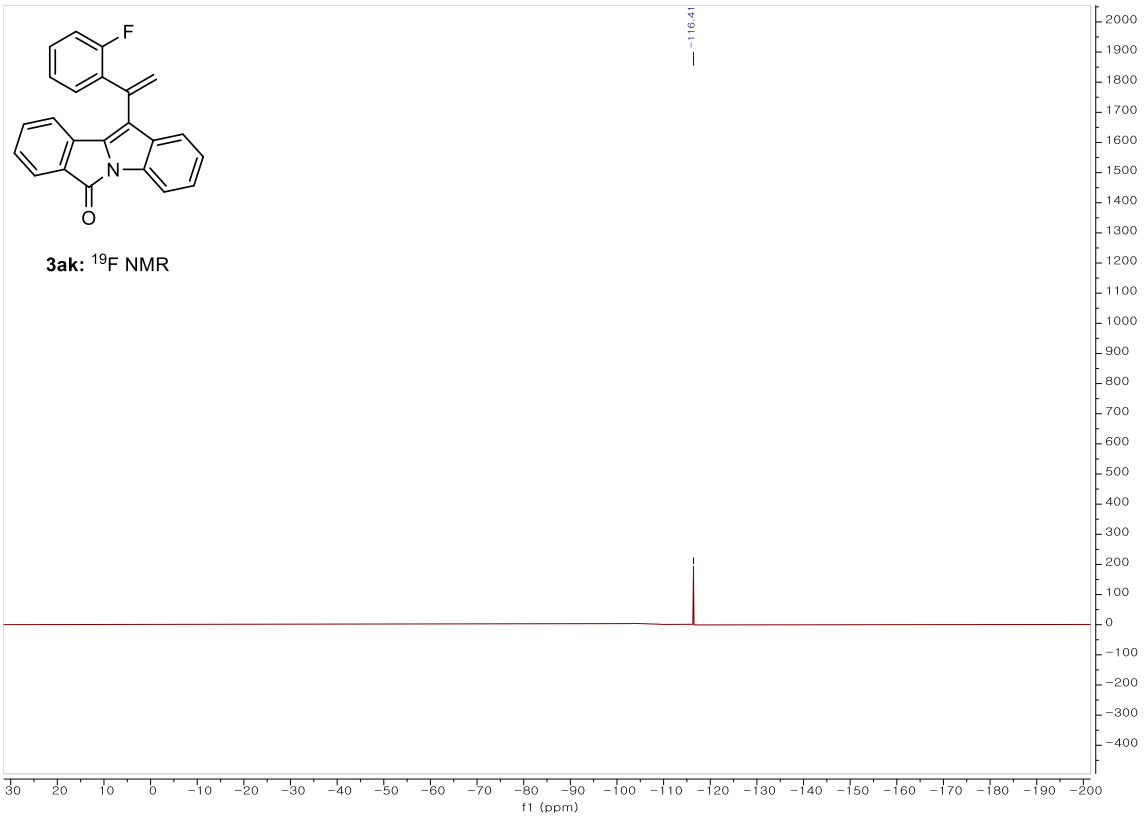
3aj: ^{13}C NMR


F
N
O
-113.24
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

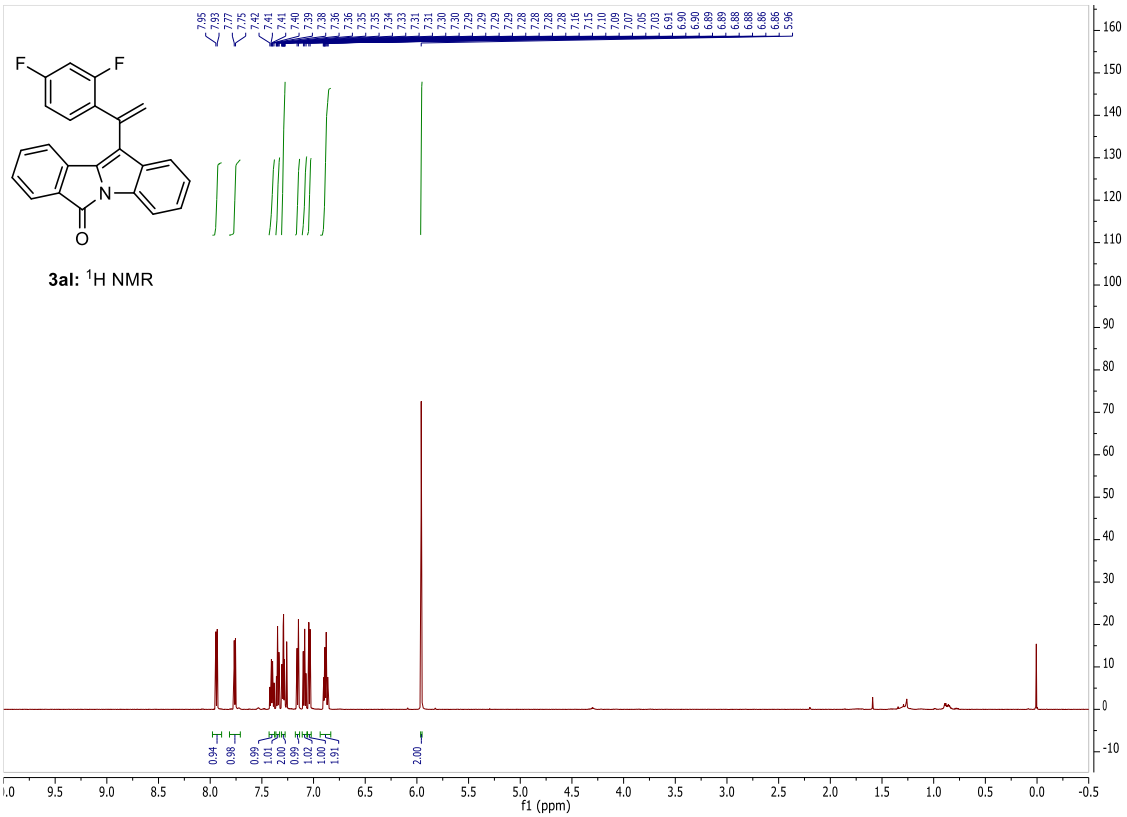
3aj: ^{19}F NMR


F
N
O
3ak: 1H NMR
f1 (ppm)

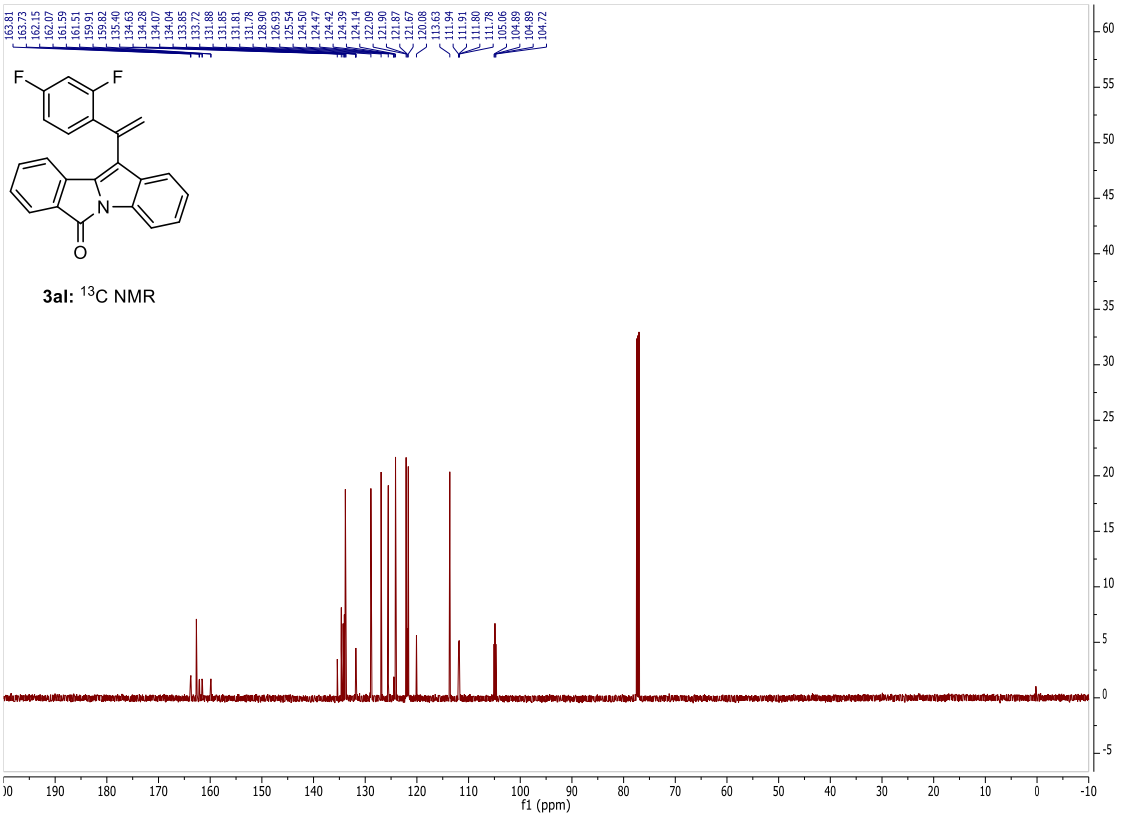

F
N
O
3ak: 13C NMR
f1 (ppm)


F
N
O
−116.41
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
−300
−400
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

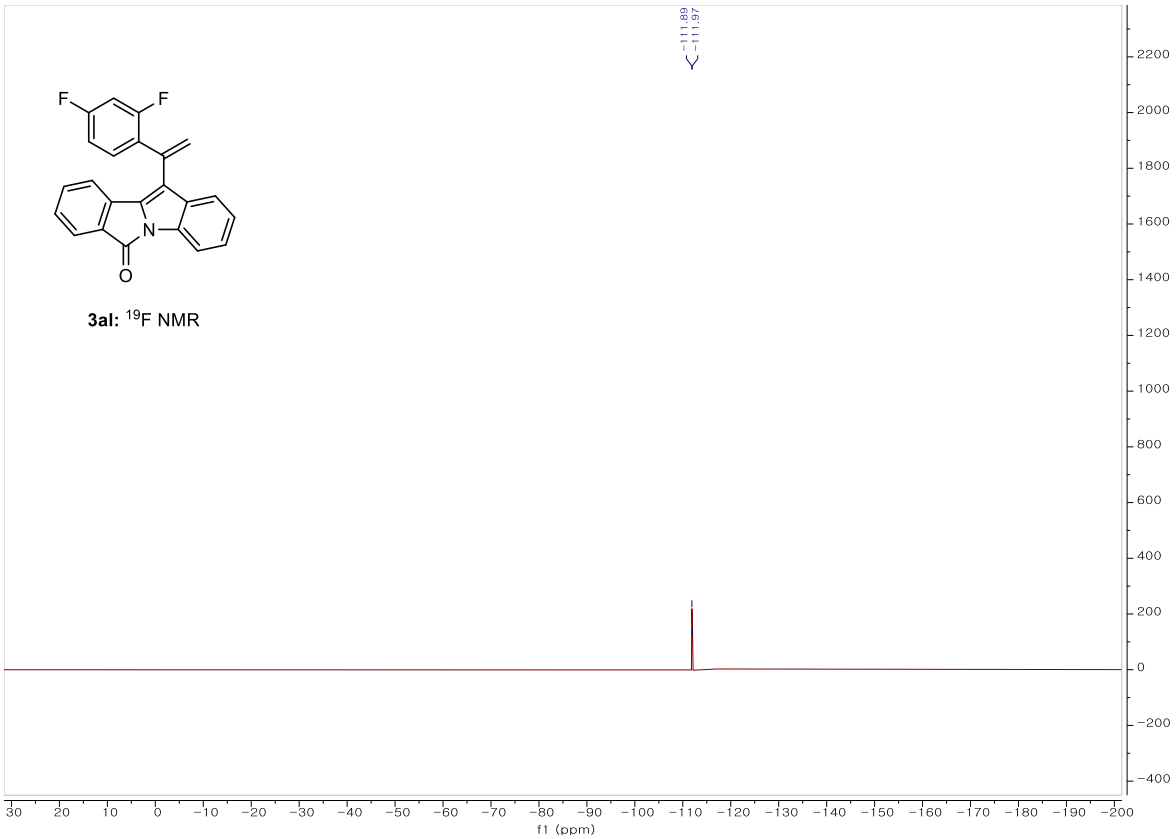
3ak: ^{19}F NMR



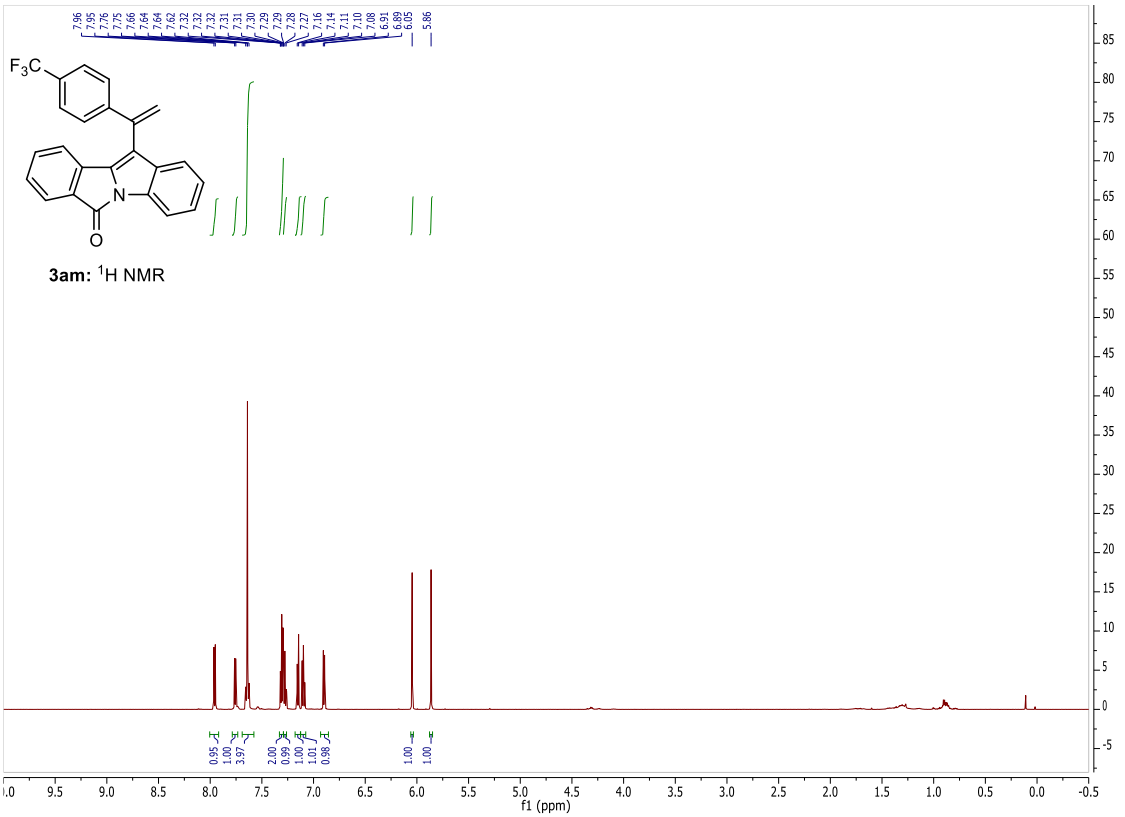
3al: ^{1}H NMR

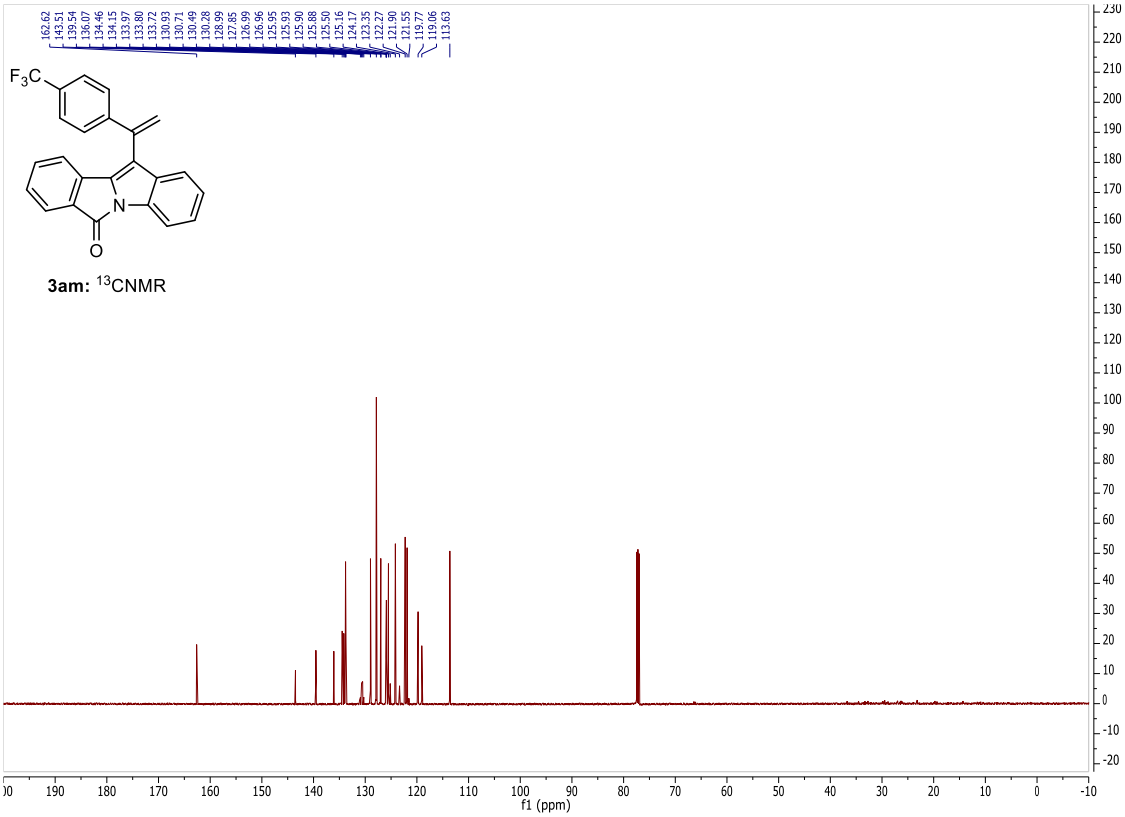


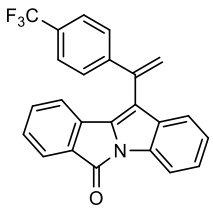
3al: ^{13}C NMR


F
F
N
O
-111.99
-111.97
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

3al: ^{19}F NMR

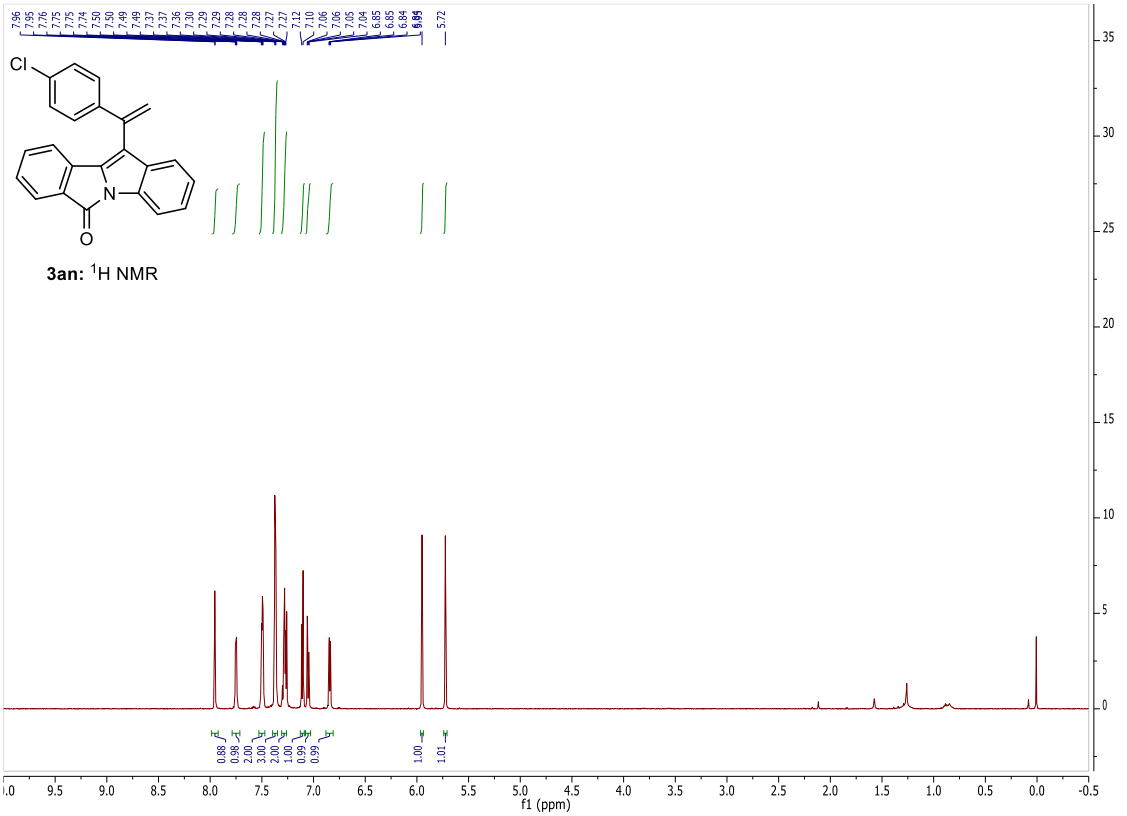

F3C
N
O
3am: 1H NMR
f1 (ppm)


F3C
N
O
3am: 13CNMR
f1 (ppm)

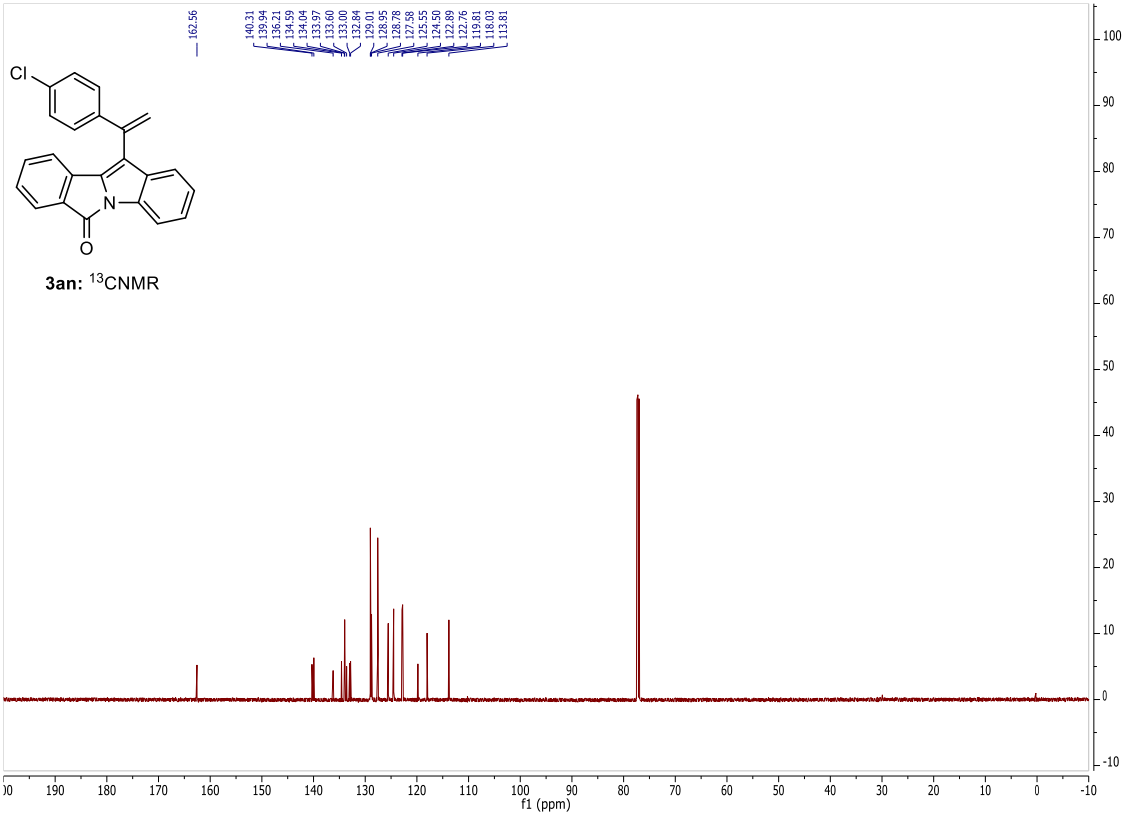

F3C
N
O

3am: ^{19}F NMR

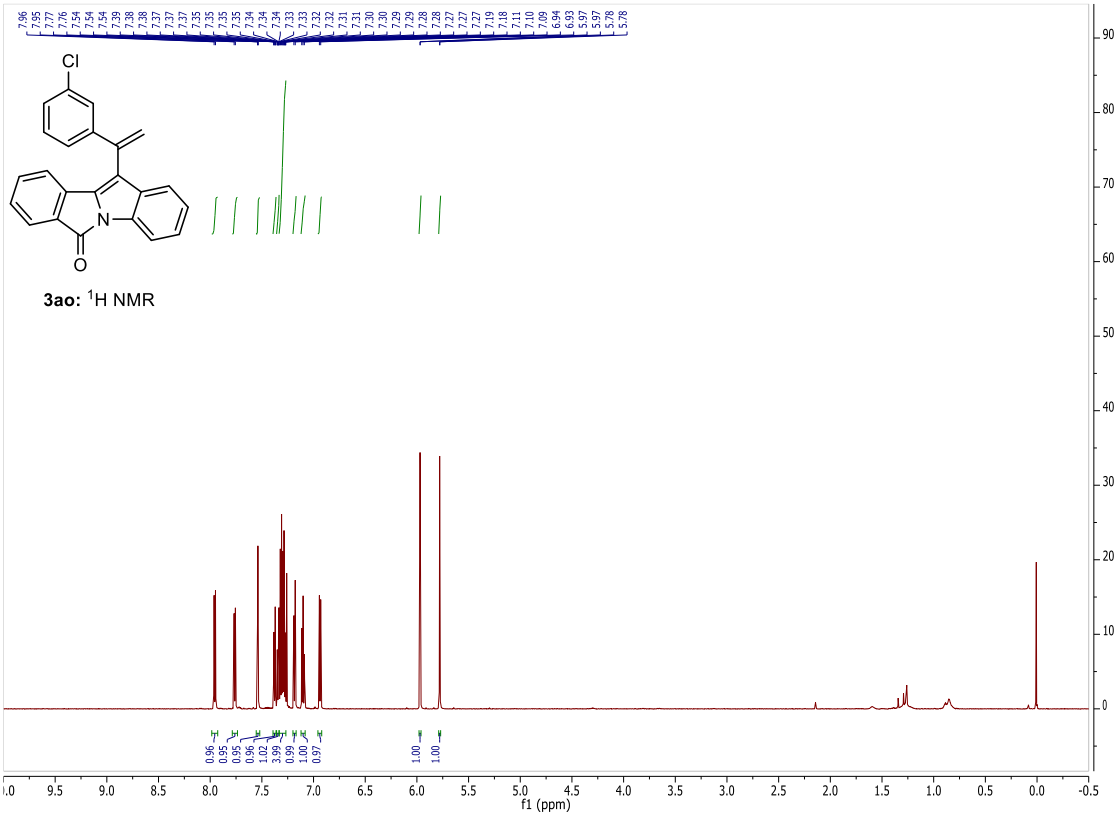
-113.22
1000
900
800
700
600
500
400
300
200
100
0
-100
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

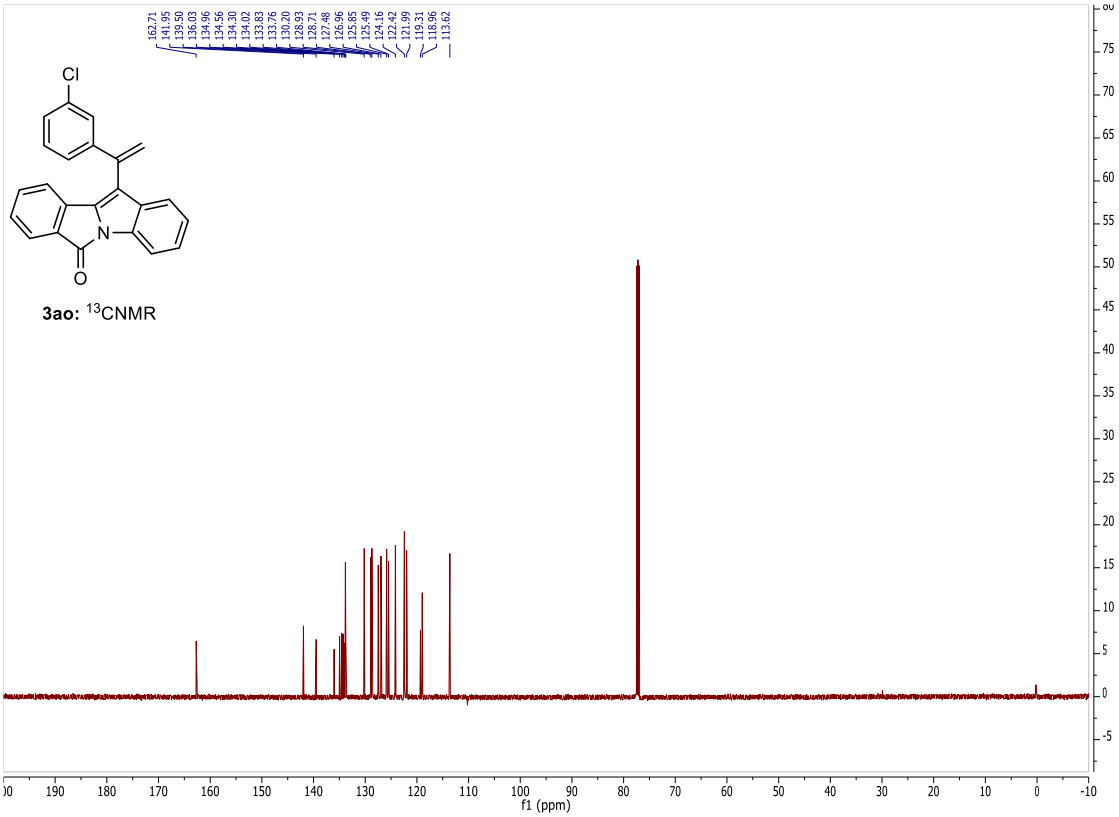


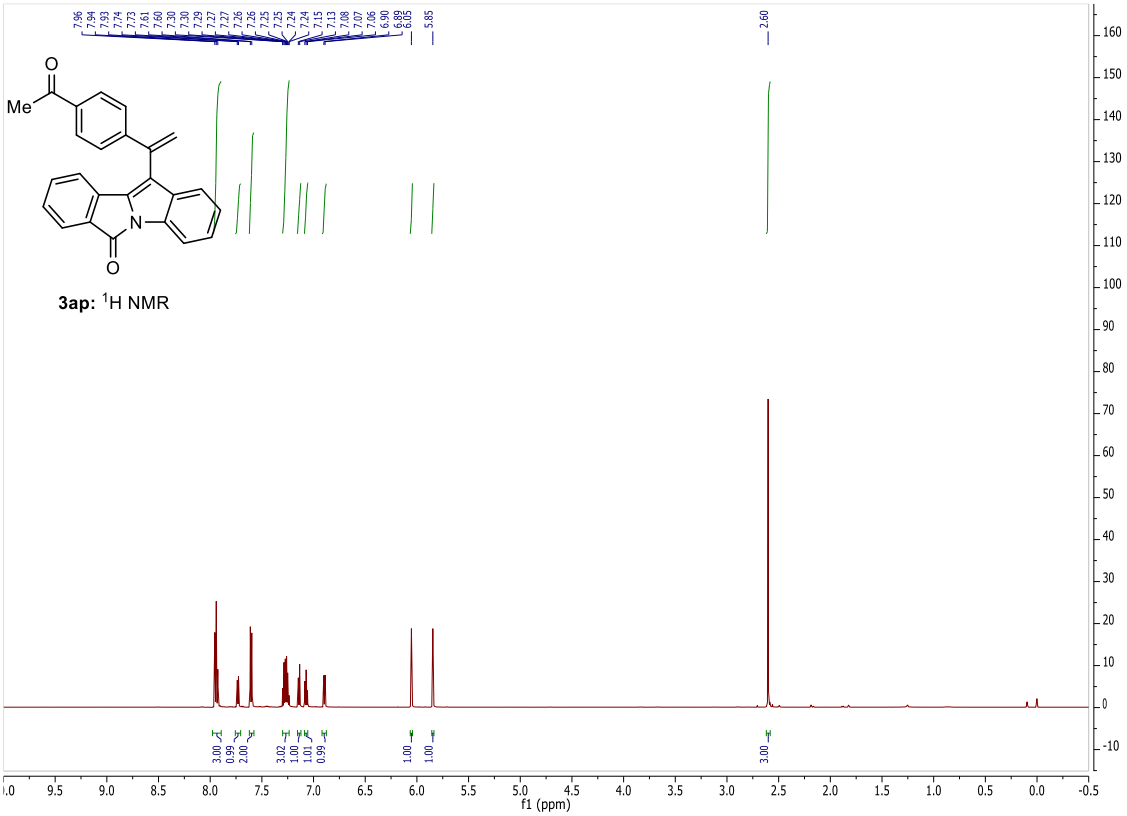
3an: ^{1}H NMR



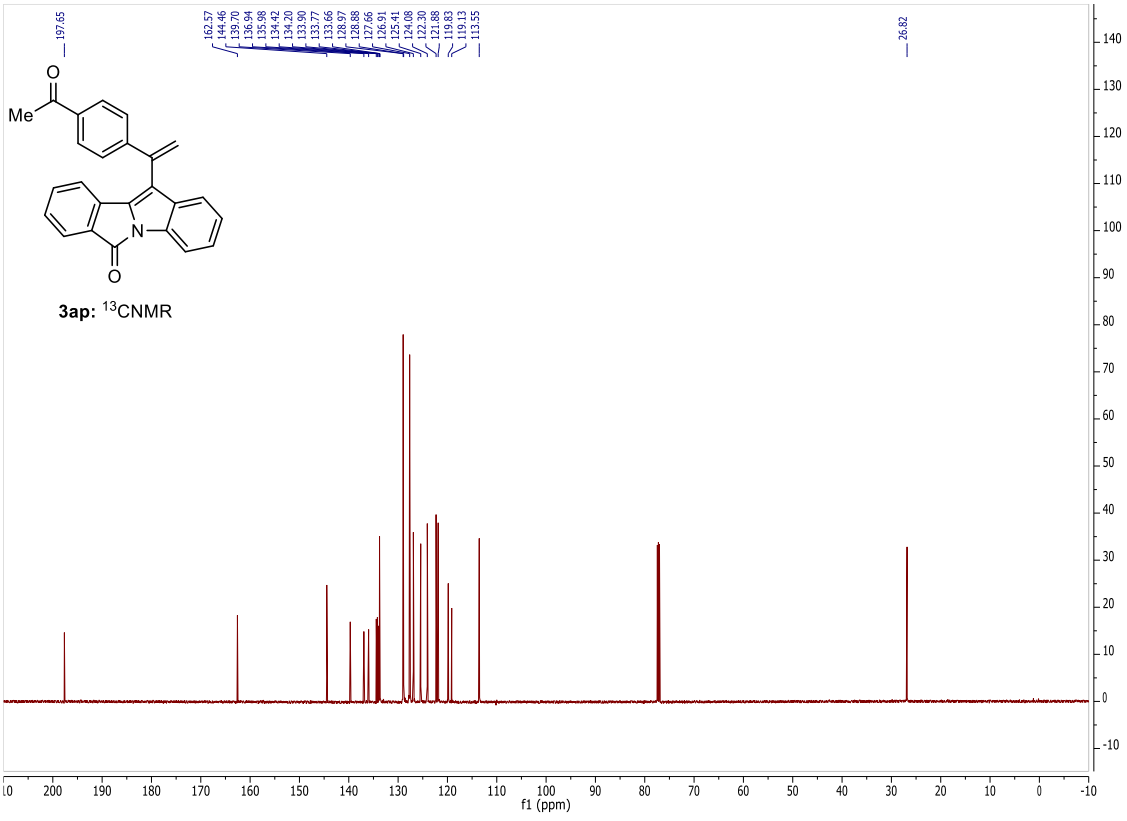
3an: ^{13}CNMR


Cl
N
O
3ao: 1H NMR
f1 (ppm)

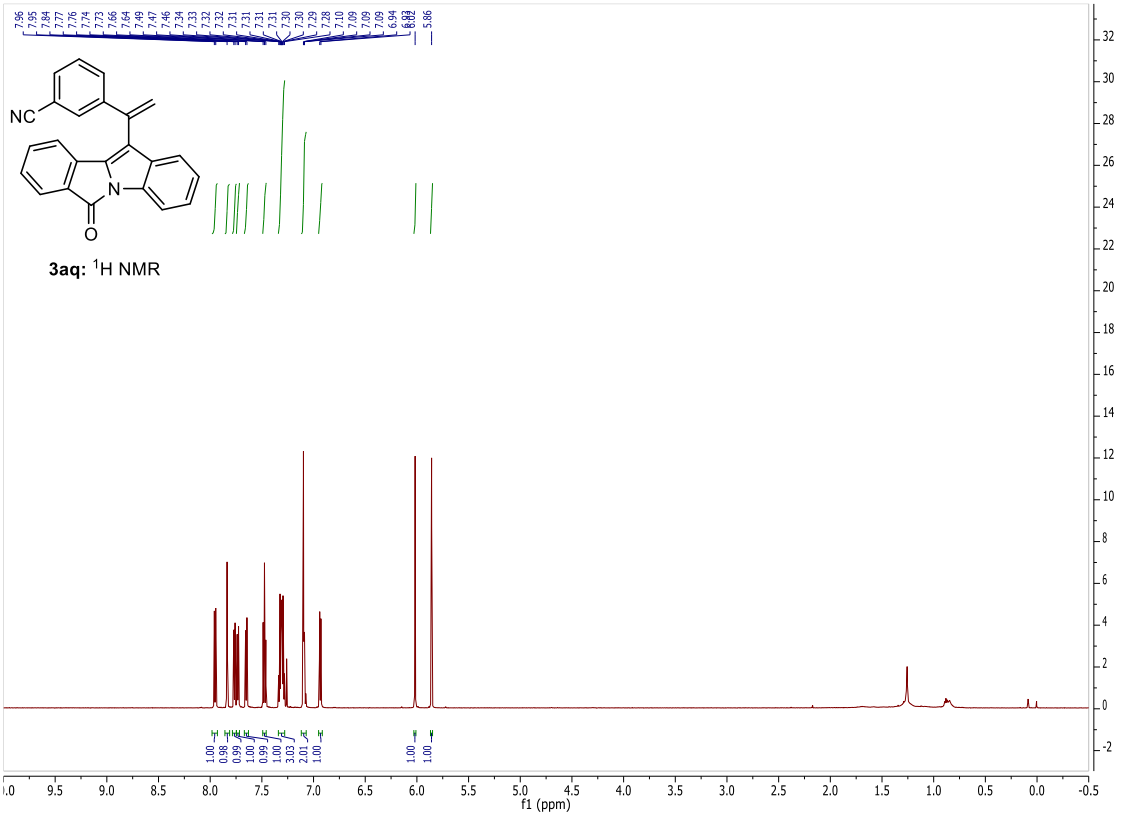

Cl
N
O
3ao: 13CNMR
f1 (ppm)



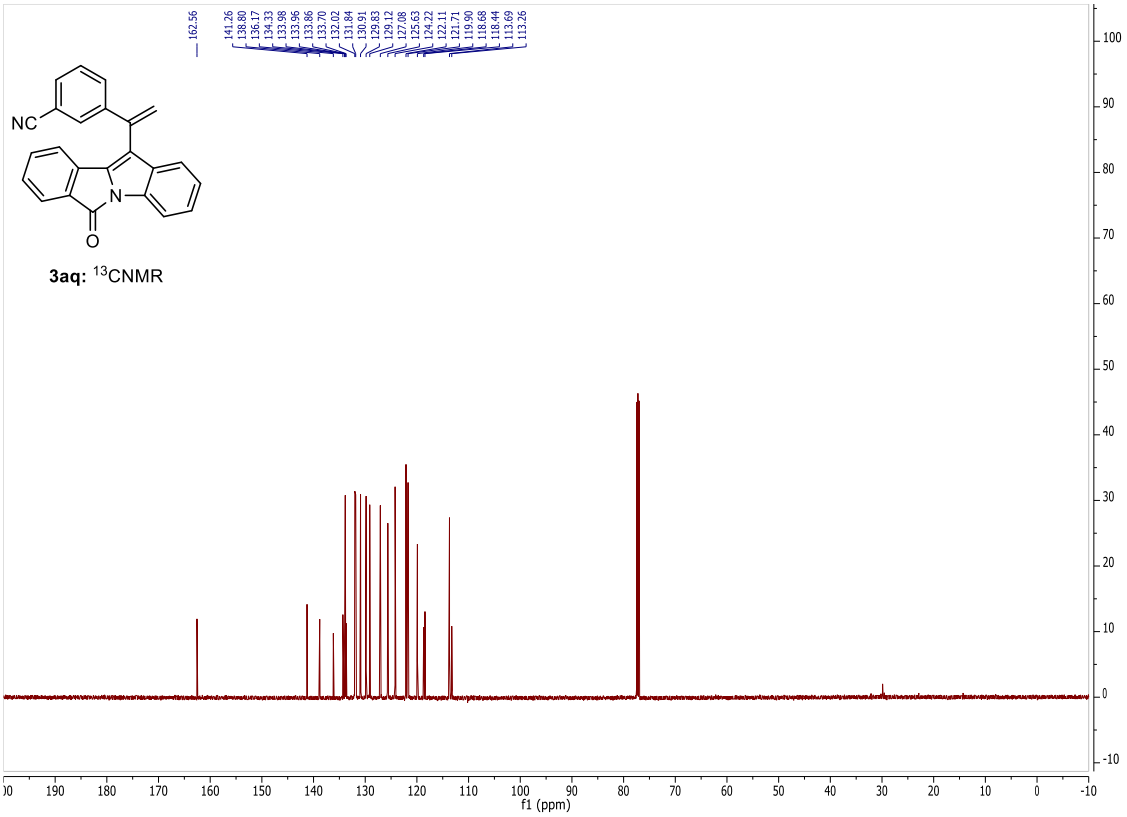
3ap: ^{1}H NMR



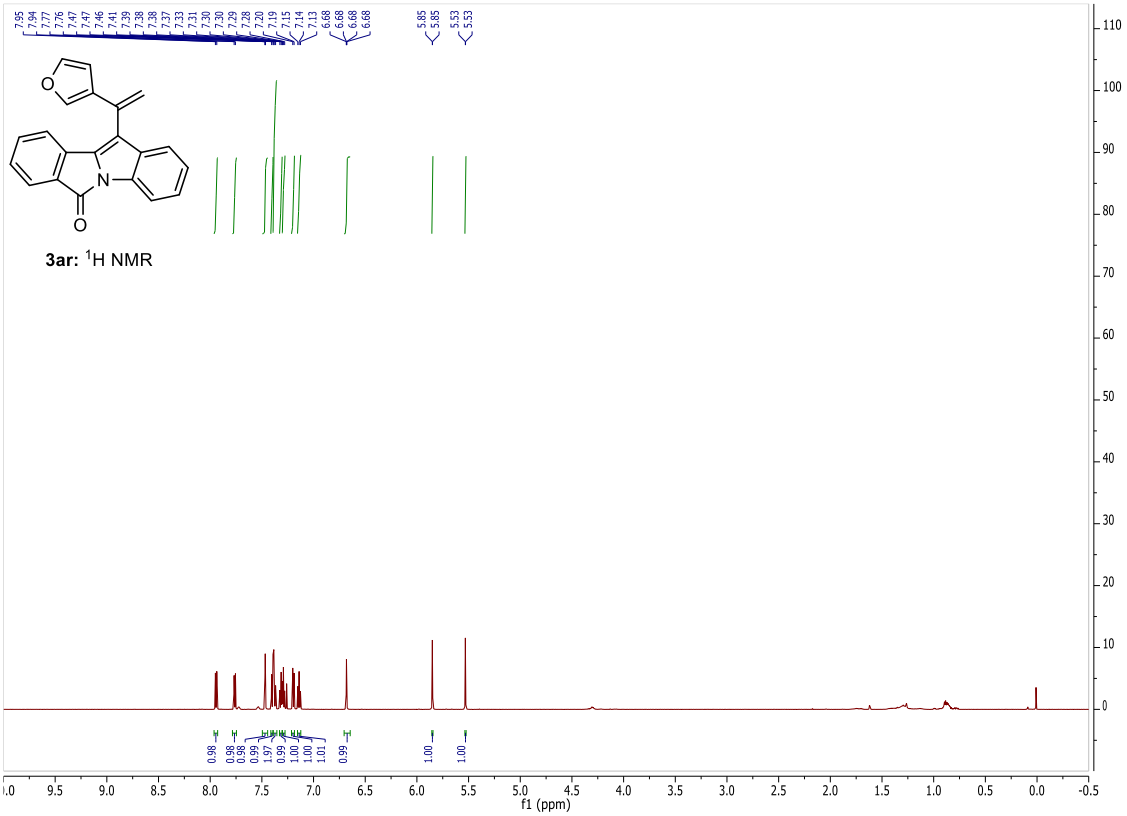
3ap: ^{13}CNMR

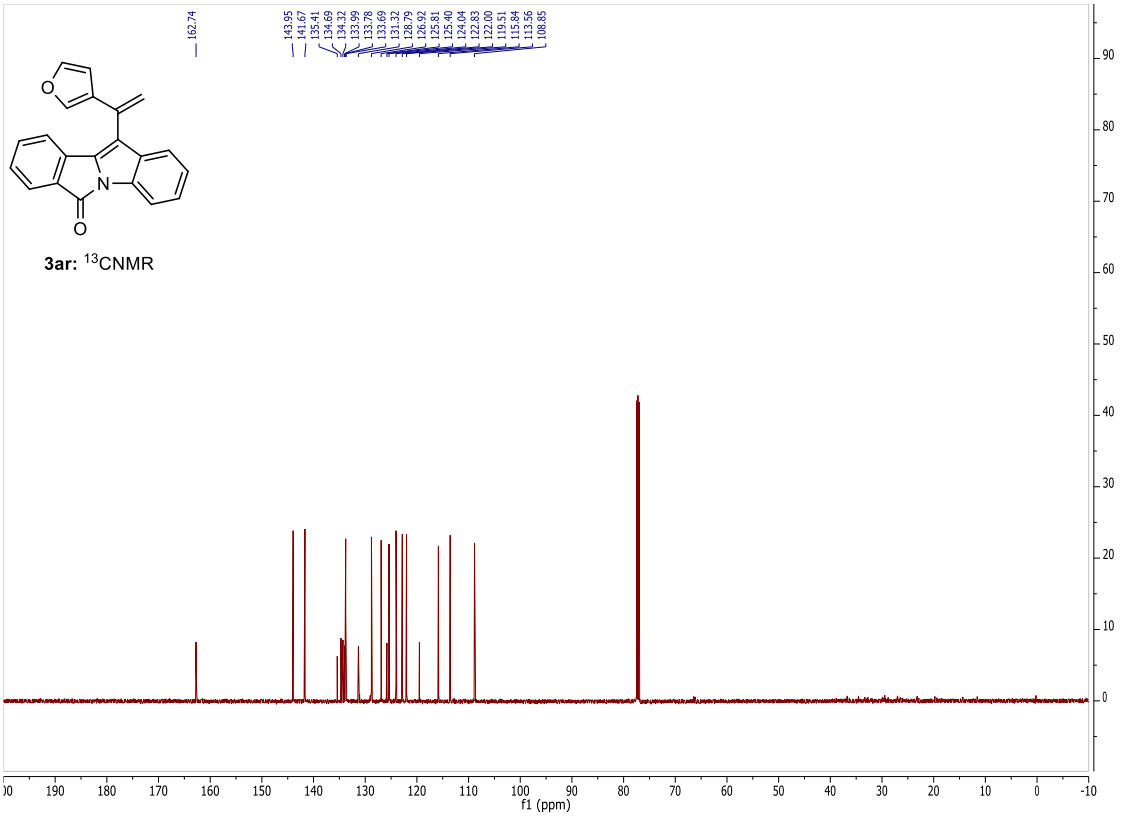


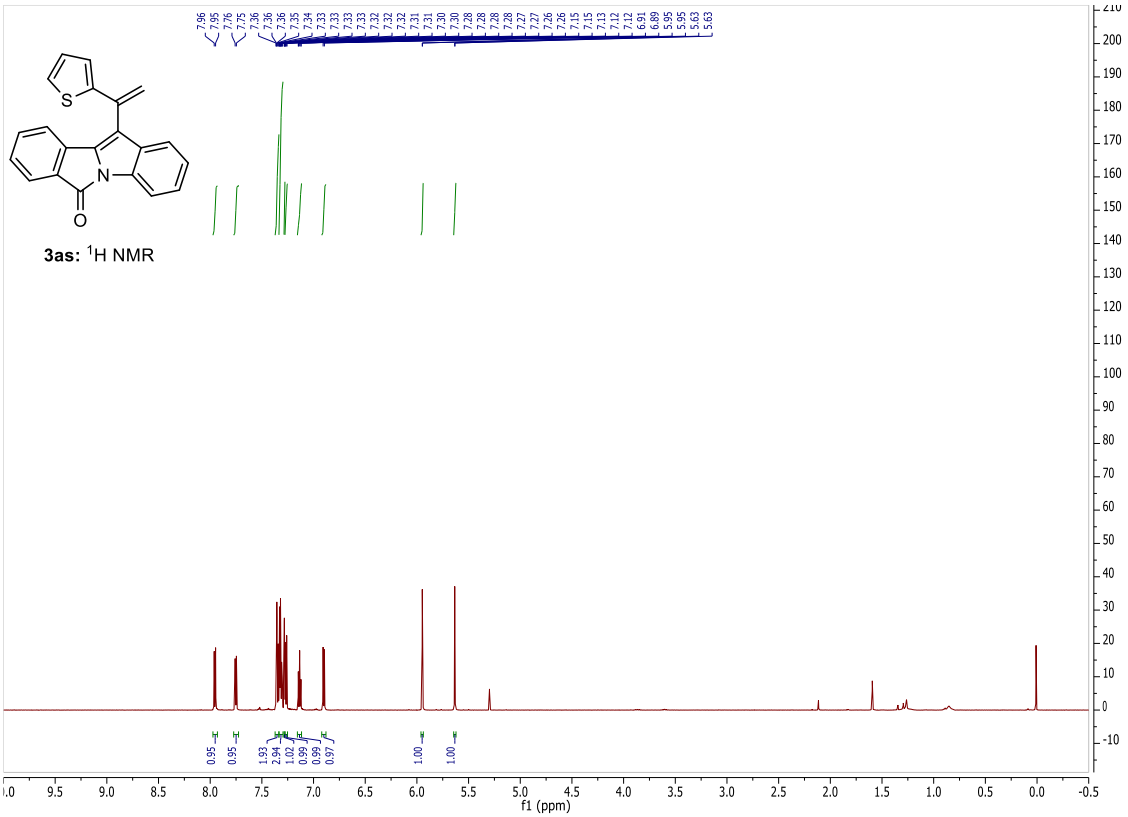
3aq: ^{1}H NMR

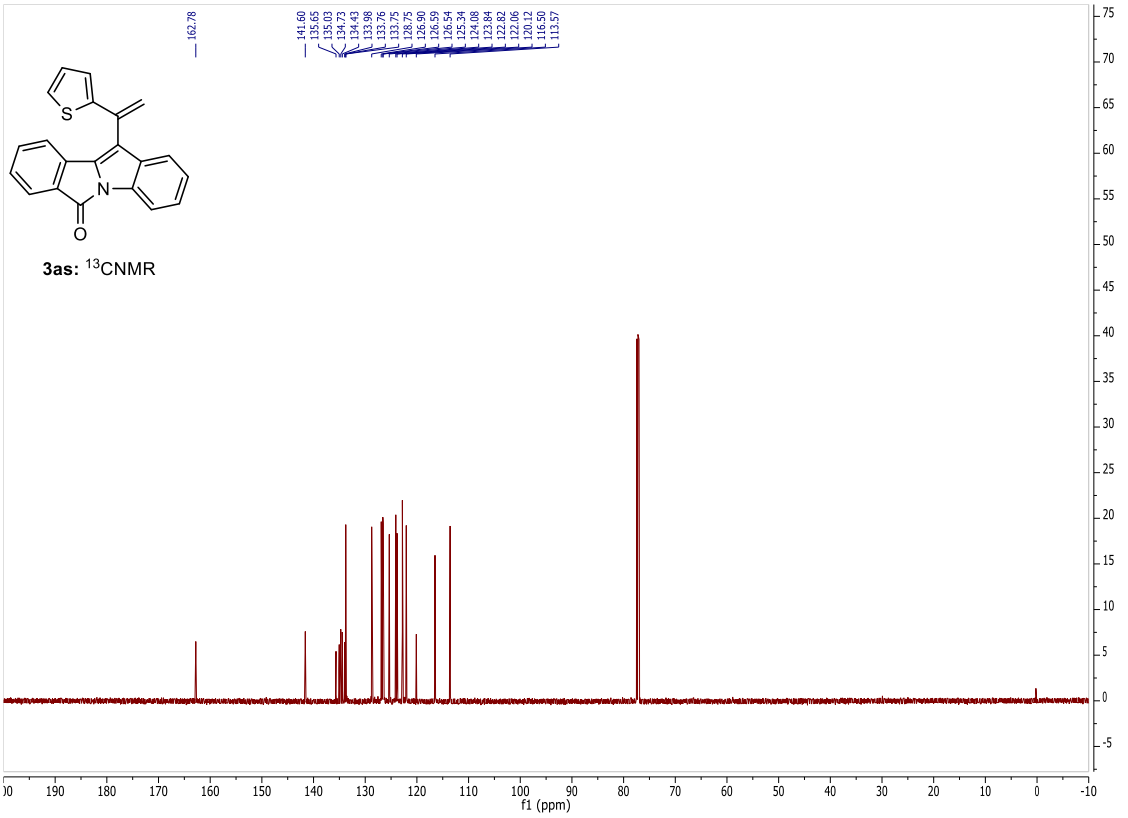


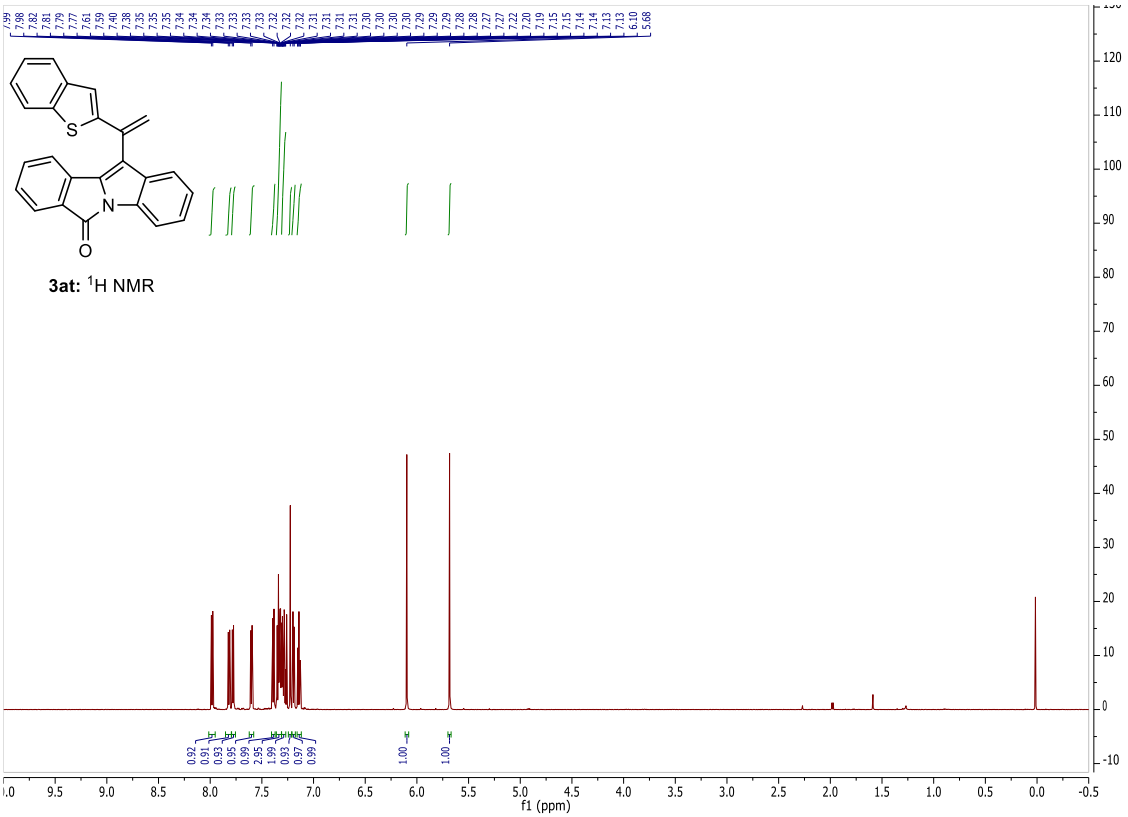
3aq: ^{13}CNMR


7.95
7.94
7.77
7.76
7.47
7.47
7.46
7.41
7.39
7.38
7.38
7.37
7.33
7.31
7.30
7.30
7.29
7.28
7.20
7.19
7.15
7.14
7.13
6.68
6.68
6.68
6.68
5.85
5.85
5.53
5.53
O
N
O
3ar: 1H NMR
0.98
0.98
0.98
0.99
1.97
0.99
1.00
1.00
1.01
0.99
1.00
1.00
f1 (ppm)

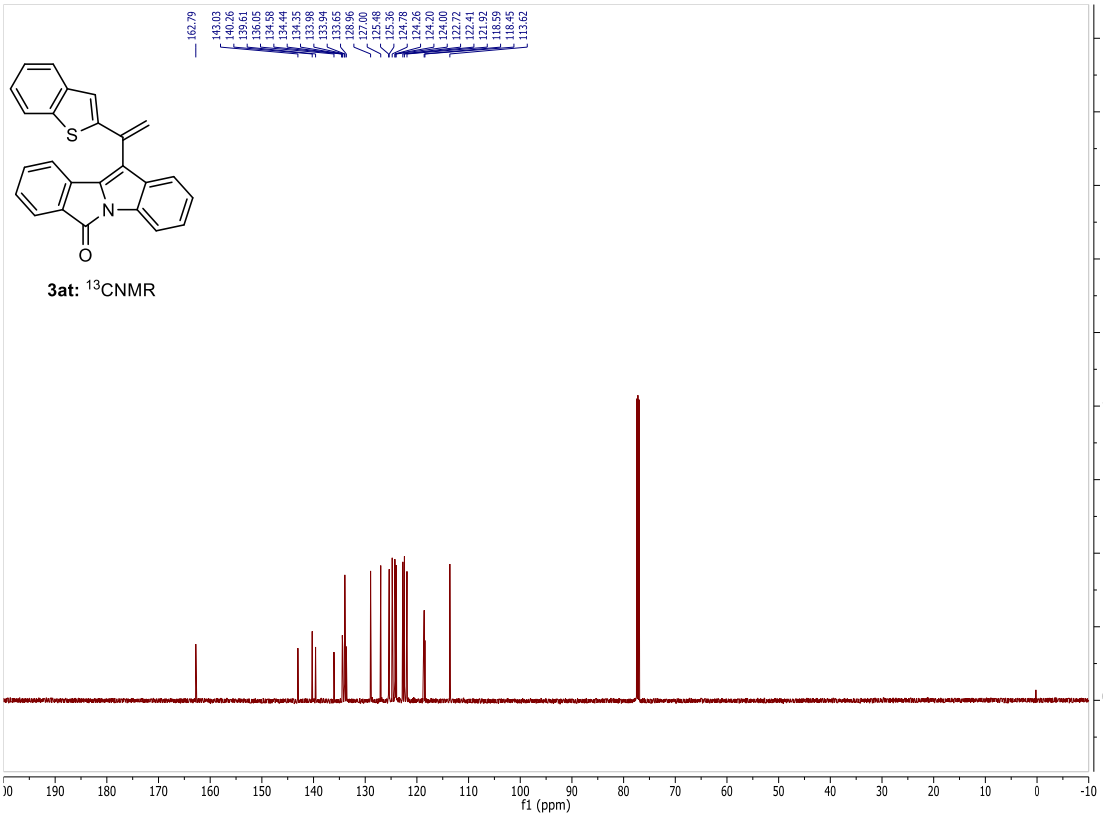

162.74
143.95
141.67
135.41
134.69
134.32
133.99
133.78
133.69
131.32
128.79
126.92
125.81
125.40
124.04
122.83
122.00
119.51
115.84
113.56
108.85
O
N
O
3ar: 13CNMR
f1 (ppm)


3as: 1H NMR
f1 (ppm)

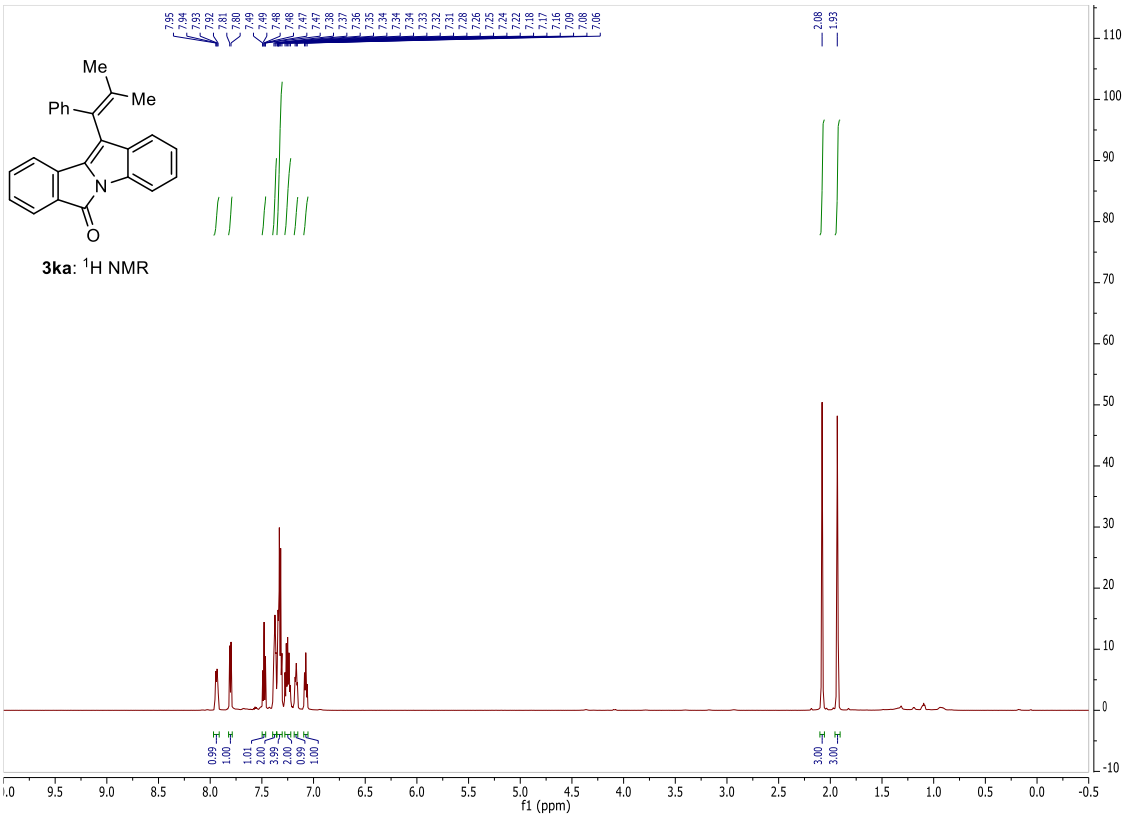

3as: 13CNMR
f1 (ppm)

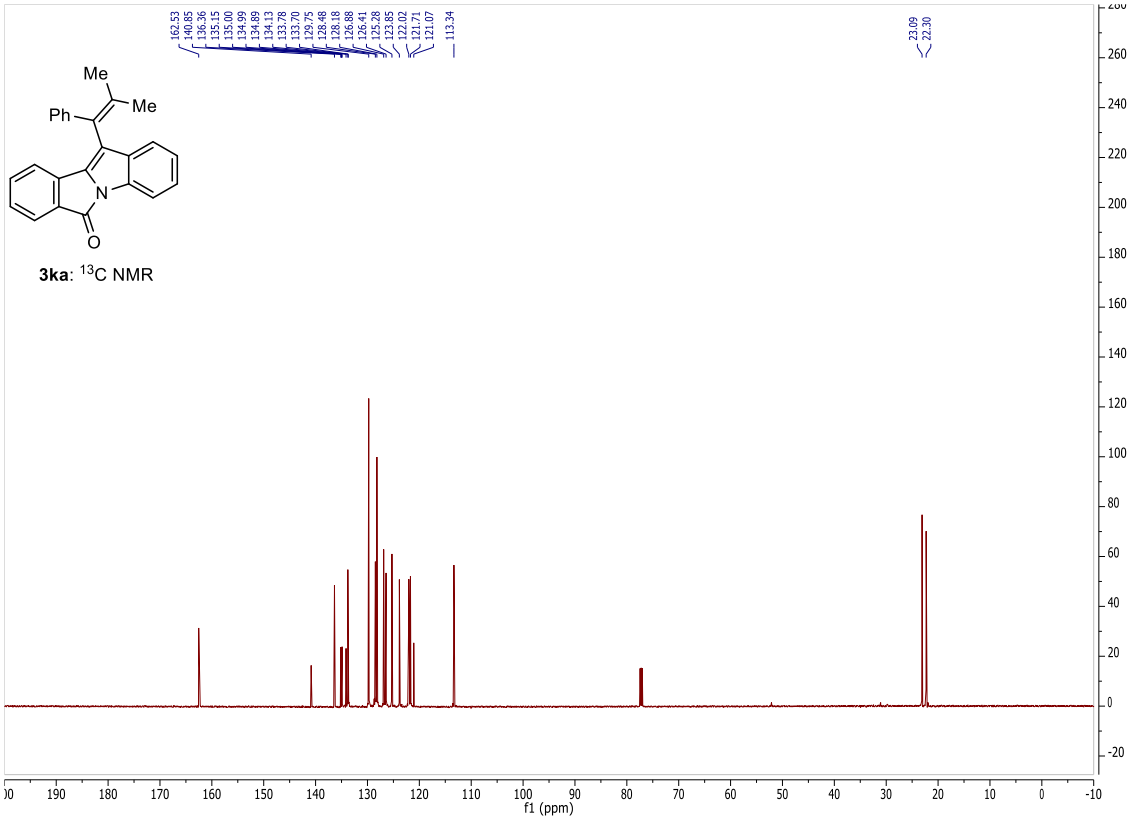


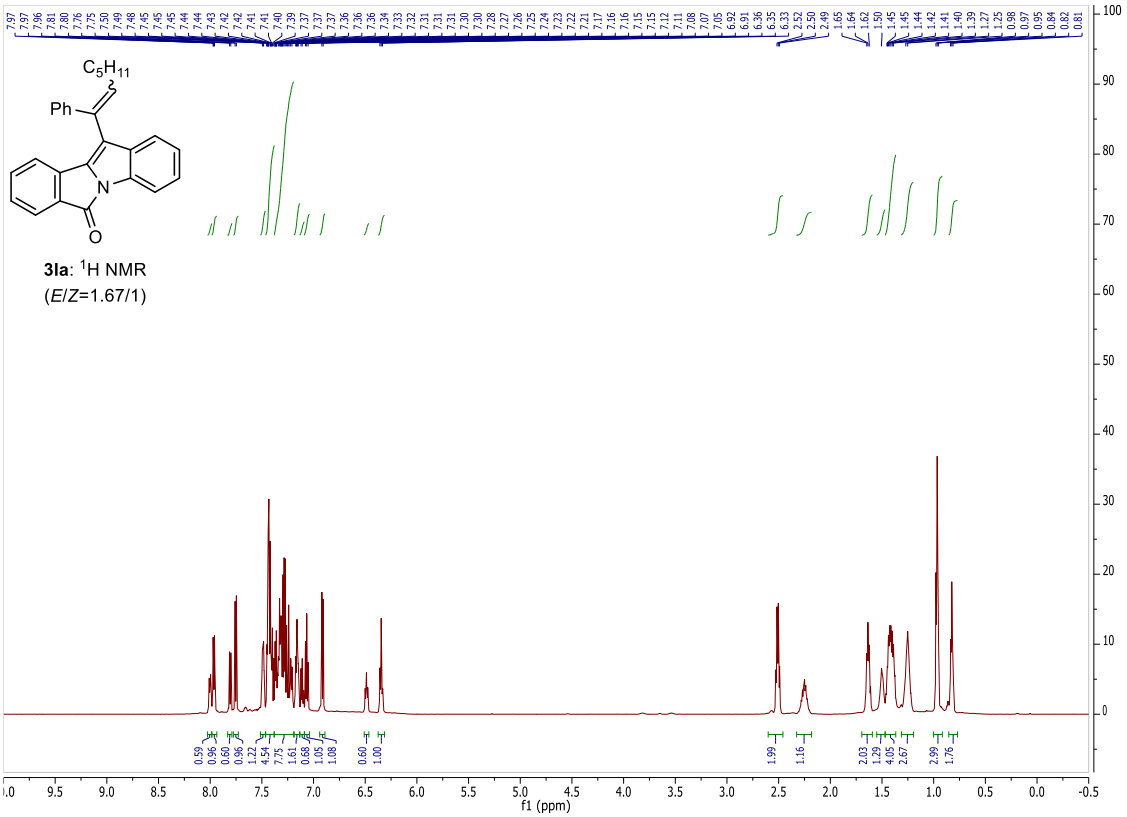
3at: ^{1}H NMR

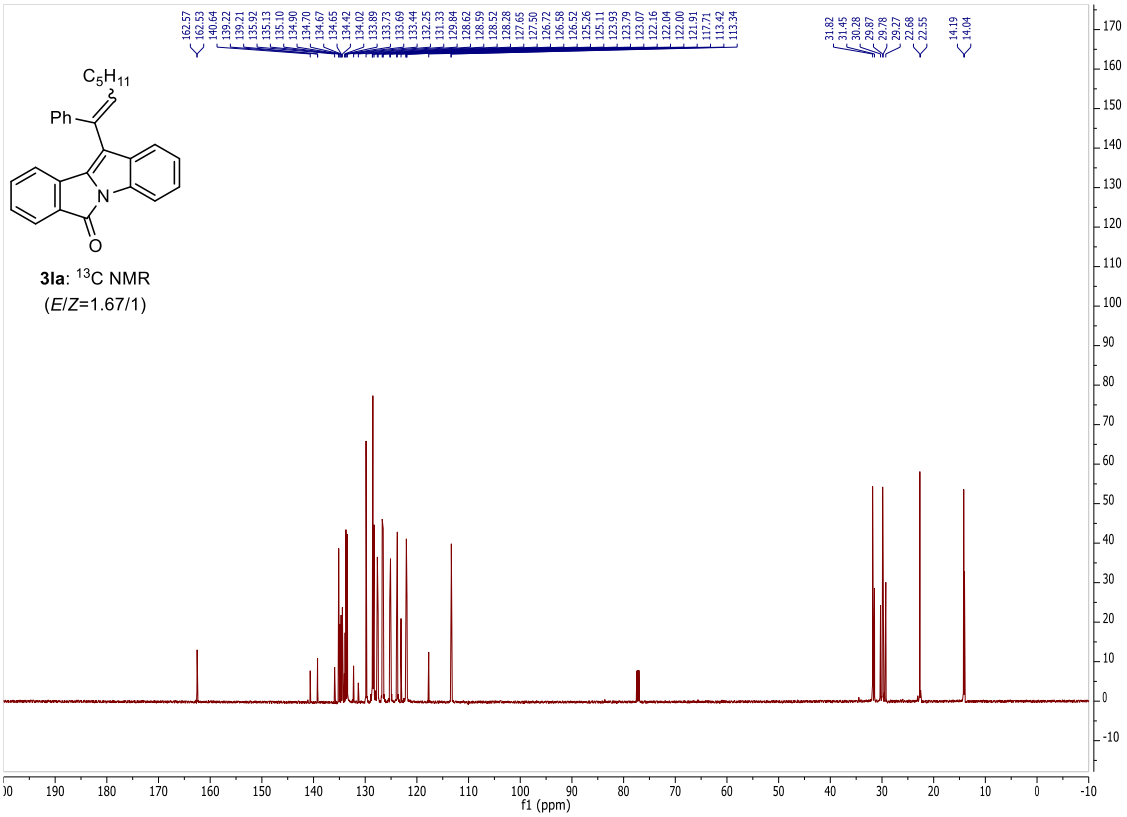


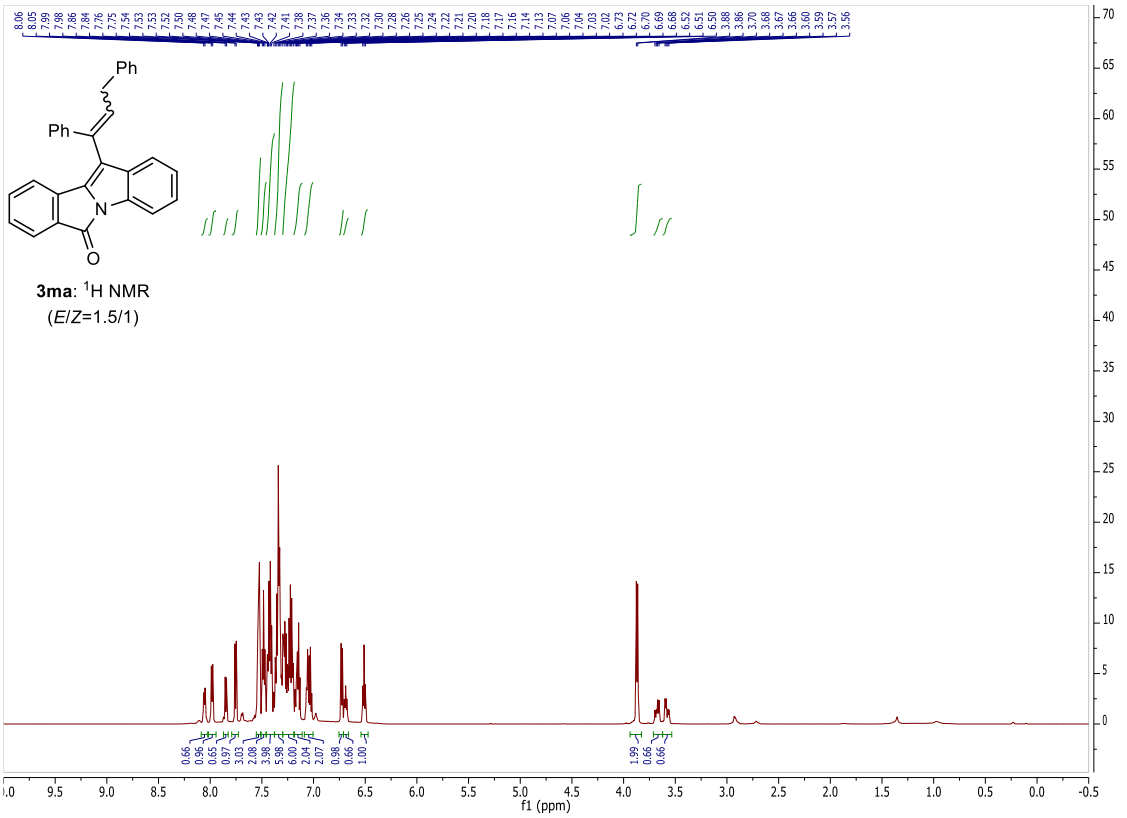
3at: ^{13}CNMR


Me
Ph
Me
N
O
3ka: 1H NMR
f1 (ppm)

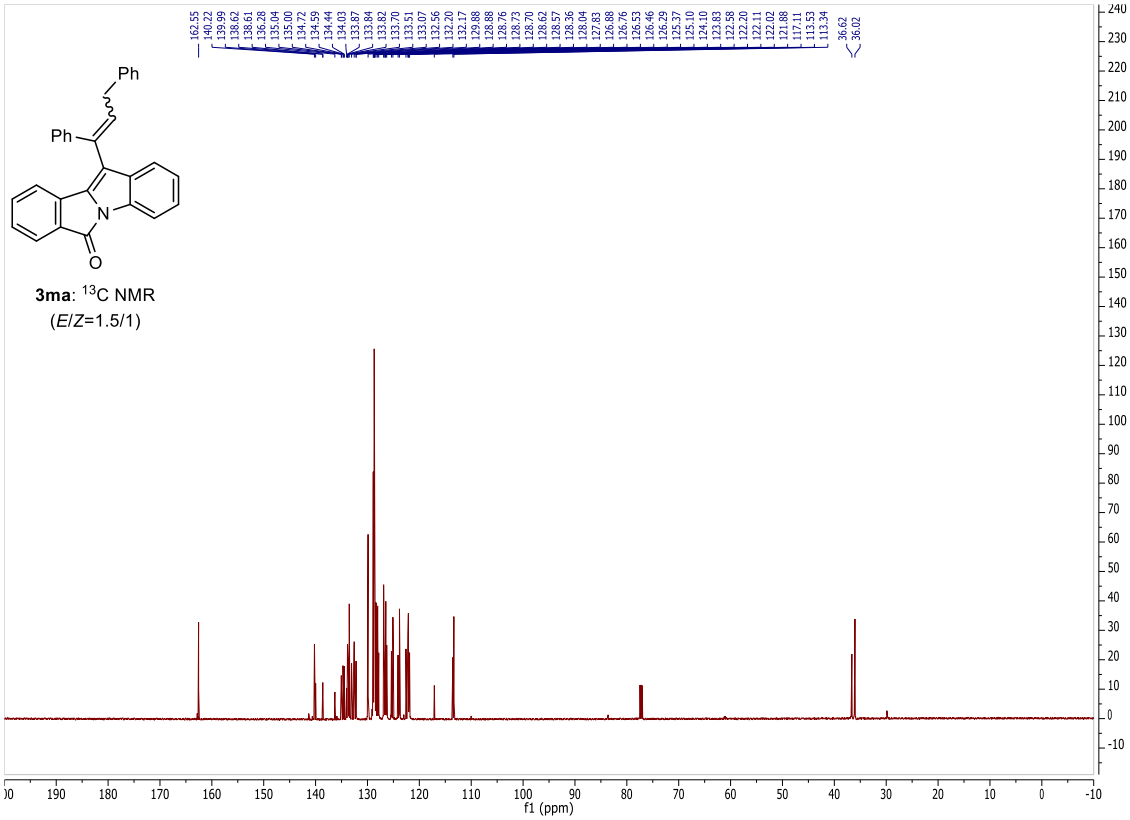

Me
Ph
Me
N
O
3ka: 13C NMR
f1 (ppm)


C5H11
Ph
N
O
3la: 1H NMR
(E/Z=1.67/1)
f1 (ppm)

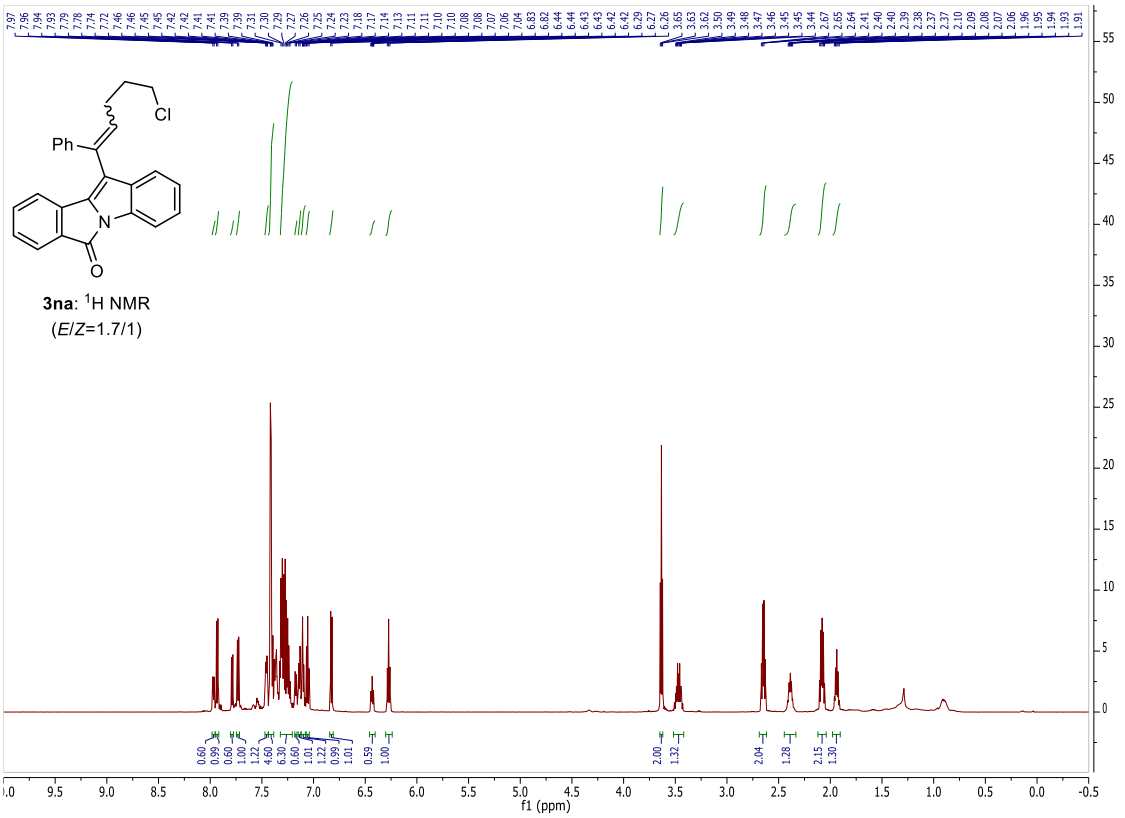

C5H11
Ph
N
O
3la: 13C NMR
(E/Z=1.67/1)
f1 (ppm)



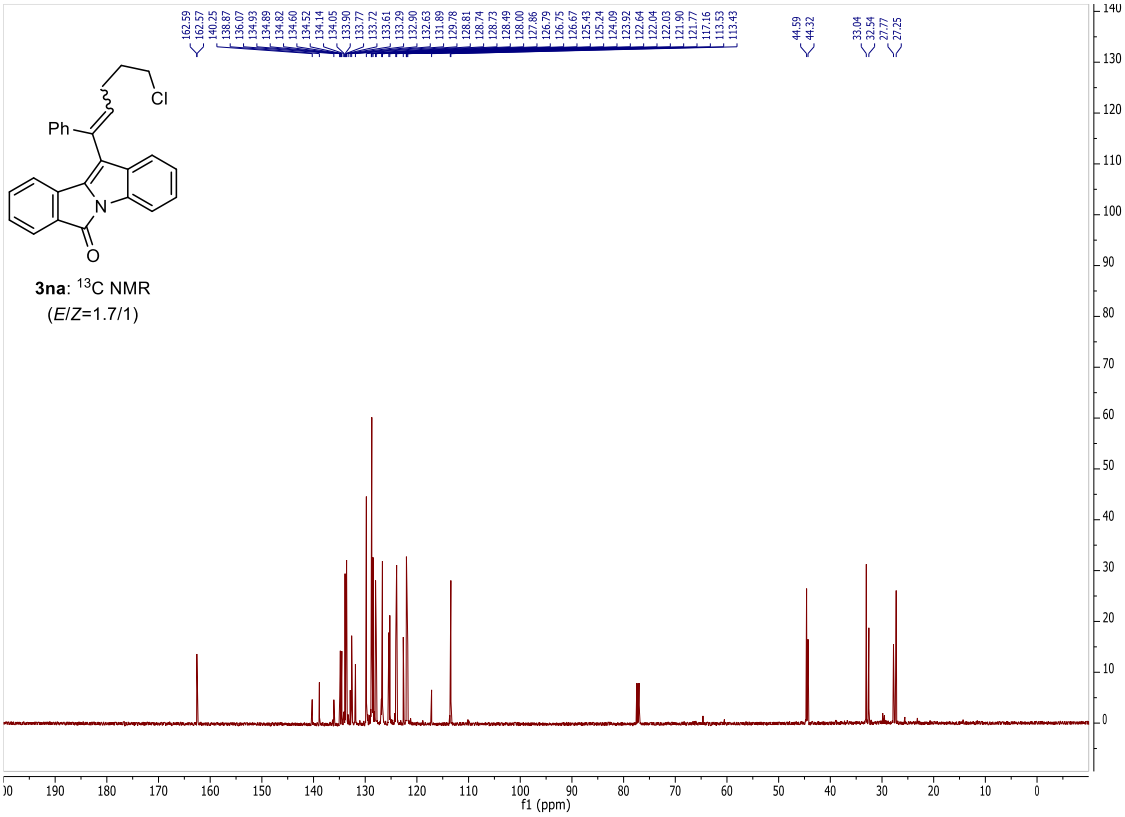
3ma: ^{1}H NMR
(*E*/*Z*=1.5/1)



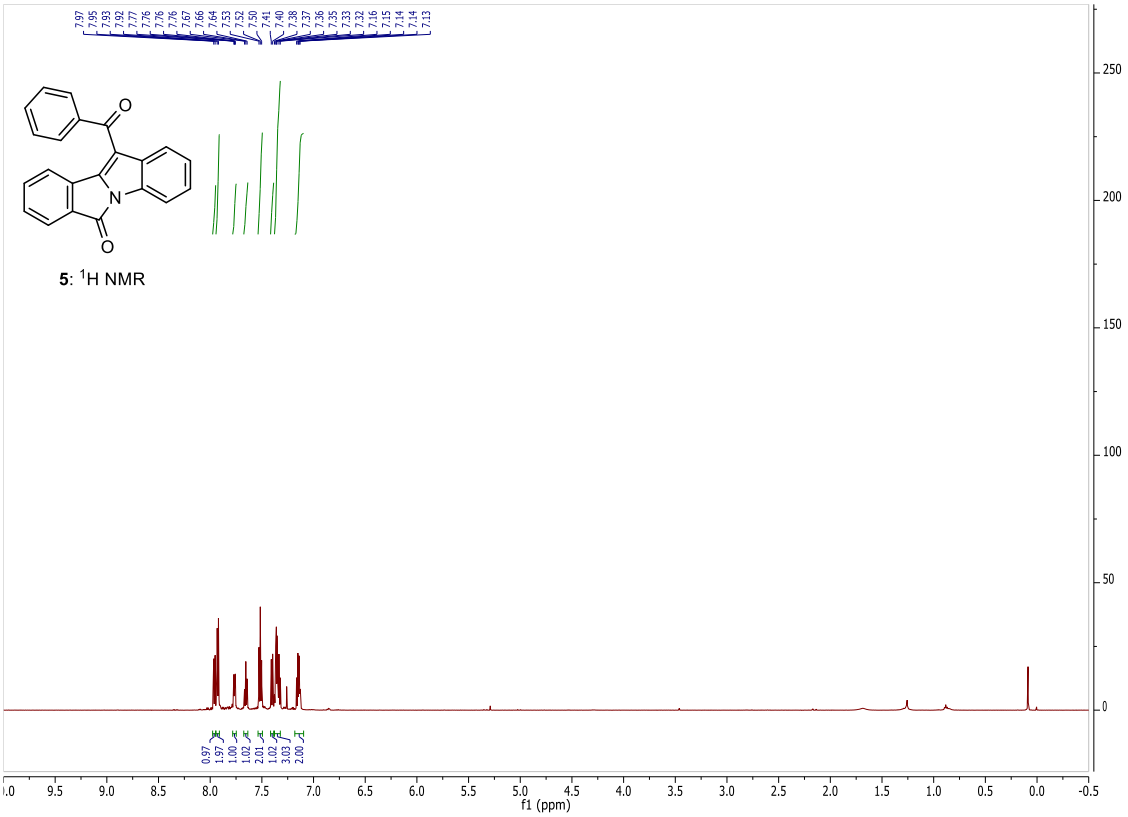
3ma: ^{13}C NMR
(*E*/*Z*=1.5/1)



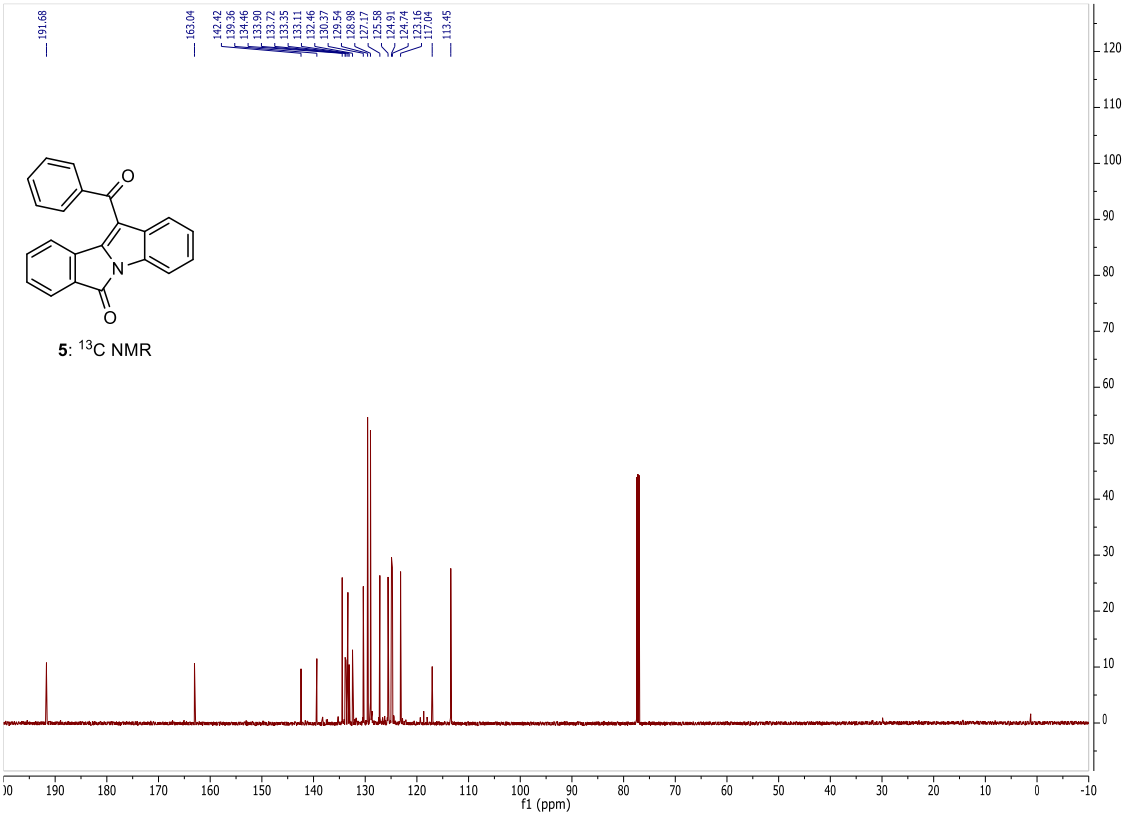
3na: ^{1}H NMR
(*E*/*Z*=1.7/1)



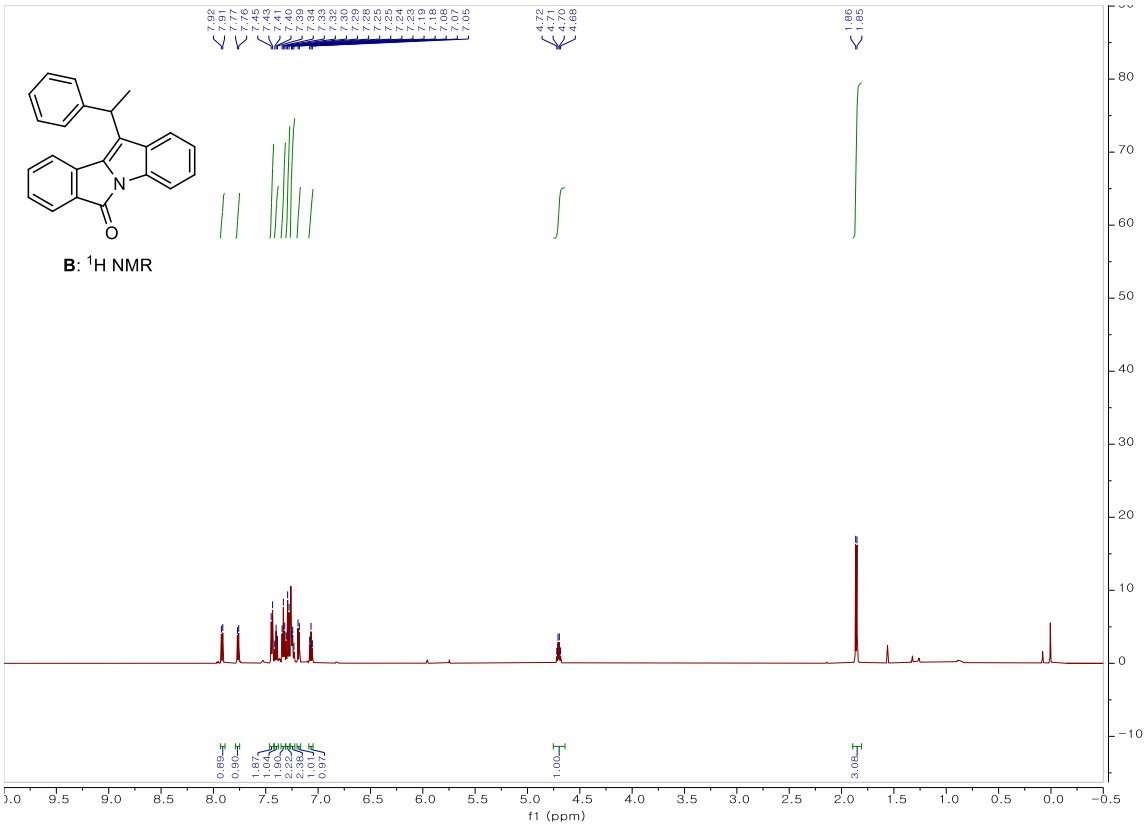
3na: ^{13}C NMR
(*E*/*Z*=1.7/1)



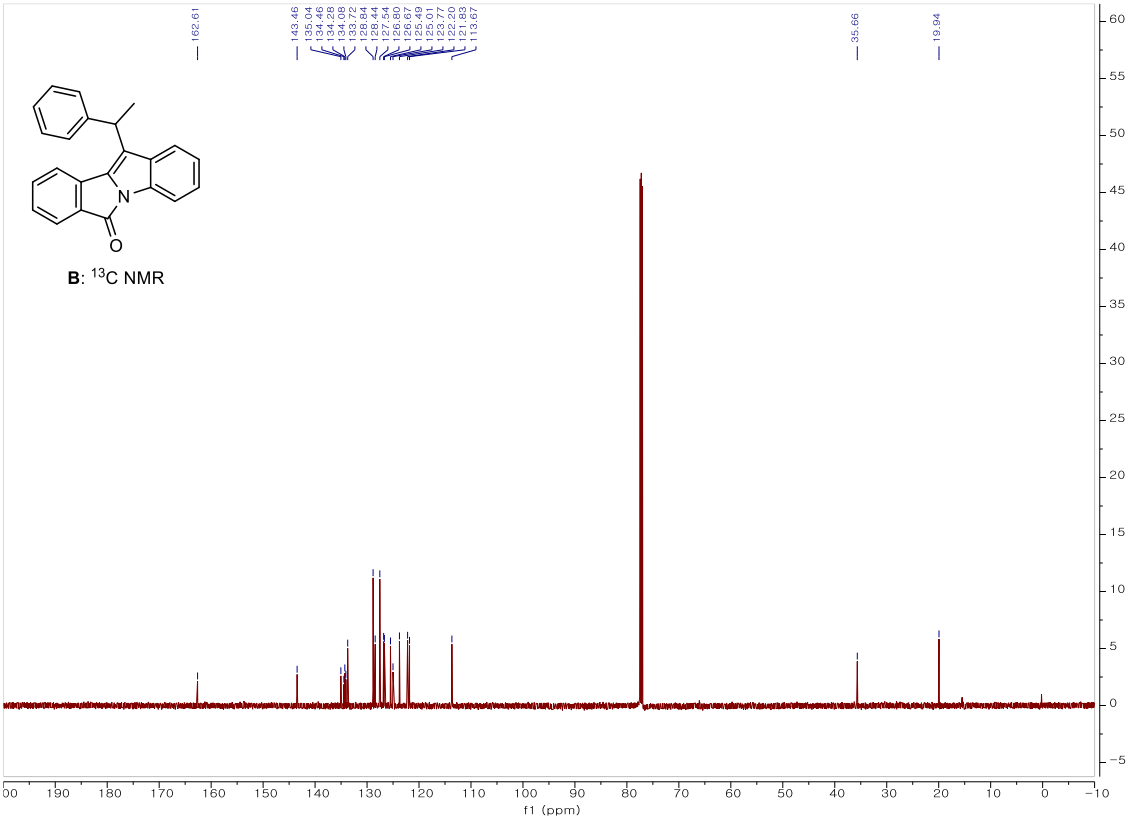
5: ^{1}H NMR



5: ^{13}C NMR



B: ^{1}H NMR



B: ^{13}C NMR