Unorthodox cascade reaction of arynes and *N*-nitrosamides leading to indazole scaffolds

Popuri Sureshbabu,[a] Vinod Bhajammanavar,[a] Venkata Surya Kumar Choutipalli,[b] Venkatesan Subramanian[b] and Mahiuddin Baidya[a]*

[a]Department of Chemistry, Indian Institute of Technology Madras,
Chennai 600 036, Tamil Nadu, India.
[b]Inorganic and Physical Chemistry Laboratory, CSIR-Central Leather Research Institute,
Chennai 600 020, Tamil Nadu, India.
E-mail: mbaidya@iitm.ac.in

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General Information

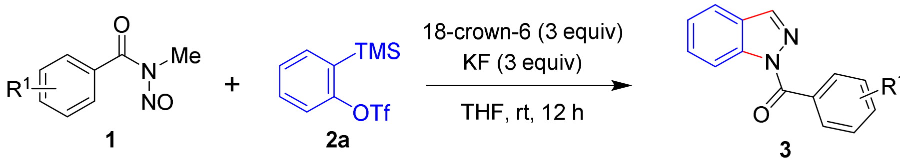
Benzoic acids, $MeNH_2$ (aq), benzyne precursor, 18-crown-6, *tert*-butyl nitrite, potassium fluoride and cesium fluoride were purchased from Aldrich company. All reactions were carried out using anhydrous solvent unless otherwise noted. Dry toluene, xylene, mesitylene, tetrahydrofuran and chlorobenzene were prepared by distilling over sodium ketyl. Dry DCE and CH_3CN were prepared by distilling over calcium hydride.

All reactions were monitored by thin layer chromatography (TLC) on WhatmanPartisil® K6F TLC plates (silica gel 60 Å, 0.25 mm thickness) and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 10 g phosphomolybdic acid/ 100 mL ethanol, $KMnO_4$: 0.75 g potassium permanganate, 5 g K_2CO_3 / 100mL water. Products were isolated by column chromatography (Merck silica gel 100-200μm). Yields refer to chromatographically and spectroscopically homogenous materials unless noted otherwise. ^{13}C and ^1H NMR spectra were recorded on a Bruker 400 or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak $CDCl_3$ δ = 7.260 ppm for ^1H and δ = 77.160 ppm for ^{13}C calibrated to tetramethylsilane (δ = 0.00). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; ddd, doublet of doublet of doublet; br, broad; app, apparent.

Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source. X-ray data of the crystals were collected and integrated using a Bruker Axs (Kappa Apex 2) CCD diffractometer equipped with graphite monochromatic Mo (Kα) radiation. The crystal sample was prepared through solvent evaporation method in ethyl acetate: hexane (9:1) solvent mixture at room temperature.

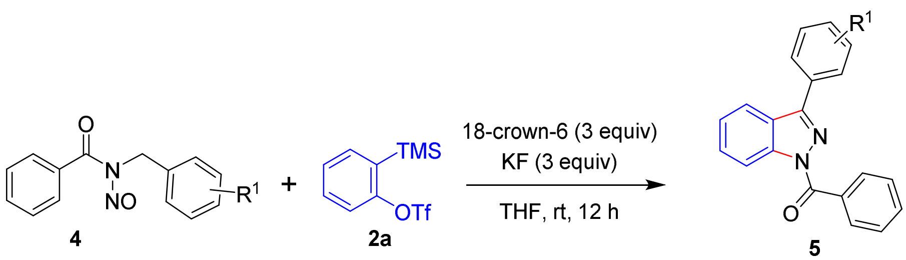
The *N*-nitrosobenzamide derivatives **1** and **4** were synthesized by following literature procedures (*Org. Biomol. Chem.*, **2019**, *17*, 845–850; *J. Org. Chem.* **2017**, *82*, 5769-5781).

General Procedure for the Synthesis of Indazoles 3:



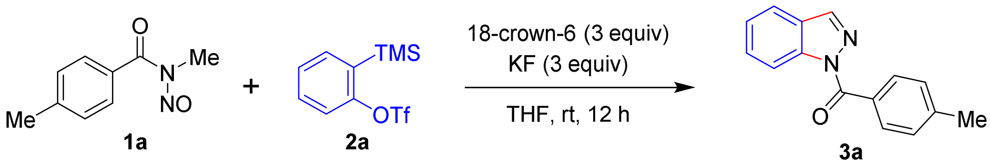
To an oven dried reaction tube (16×100 mm) equipped with a magnetic stir bar, corresponding *N*-methyl *N*-nitrosobenzamide **1** (0.2 mmol, 1.0 equiv), benzyne precursor **2a** (0.4 mmol, 2.0 equiv), 18-crown-6 (0.6 mmol, 3 equiv), and KF (0.6 mmol, 3 equiv) were taken under nitrogen atmosphere. The reaction tube was capped and dry THF (0.25 mL) was added *via* a syringe under the positive pressure of nitrogen (balloon). The reaction mixture was then stirred at room temperature for 12 h. After that the volatiles were evaporated under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (1→5% EtOAc : hexane) to give pure indazole product **3**.

General Procedure for the Synthesis of 3-Substituted Indazoles 5:



To an oven dried reaction tube (16×100 mm) equipped with a magnetic stir bar, corresponding *N*-benzyl *N*-nitrosobenzamide **4** (0.2 mmol, 1.0 equiv), benzyne precursor **2a** (0.4 mmol, 2.0 equiv), 18-crown-6 (0.6 mmol, 3 equiv), and KF (0.6 mmol, 3 equiv) were taken under nitrogen atmosphere. The reaction tube was capped and dry THF (0.25 mL) was added *via* a syringe under the positive pressure of nitrogen (balloon).The reaction mixture was then stirred at room temperature for 12 h. After that the volatiles were evaporated under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (1→5% EtOAc : hexane) to give pure 3-substituted indazole product **5**.

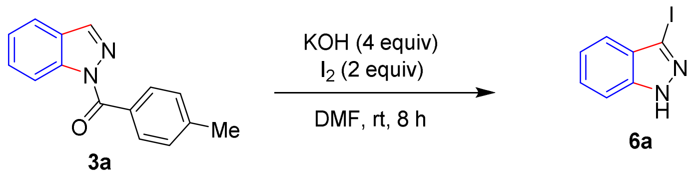
Experimental Procedure for the Gram Scale Synthesis of Indazole 3a:



To an oven dried pear shaped flask (25 mL) equipped with a magnetic stir bar, *N*-methyl-*N*-nitrosobenzamide **1a** (1.25 g, 7 mmol, 1.0 equiv), benzyne precursor **2a** (14 mmol, 2.0 equiv), 18-crown-6 (21 mmol, 3 equiv), and KF (21 mmol, 3 equiv) were taken under nitrogen atmosphere. The flask was capped with a rubber septum and dry THF (1.5 mL) was added *via* syringe under the positive pressure of nitrogen (balloon). The reaction mixture was then stirred at room temperature for 12 h under nitrogen atmosphere. After that the volatiles were evaporated under reduced pressure and the resulting crude residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (1→5% EtOAc : hexane) to get the pure product **3a** (1.09 g, 66%).

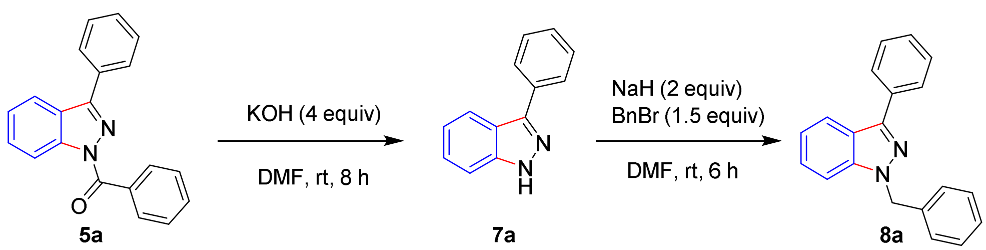
Post-Functionalization:

Synthesis of 3-Iodo-1*H*-indazole 6a:



To an oven dried reaction tube (16×100 mm) equipped with a magnetic stir bar, indazole product **3a** (60 mg, 0.25 mmol, 1 equiv), iodine (127 mg, 0.5 mmol, 2 equiv) and potassium hydroxide (56 mg, 1.0 mmol, 4 equiv) were taken. Then, DMF (2 mL) was added and the reaction mixture was stirred for 8 h at room temperature. The reaction was quenched by cold sodium bisulfite saturated solution (8 mL), and extracted with ethyl acetate (3×10 mL). The combined organic fractions were dried over Na_2SO_4. Volatiles were removed under reduced pressure and the crude residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (10→15% EtOAc : hexane) to afford **6a** in 81% yield (49 mg).

Synthesis of YD-3 Analogue 8a:

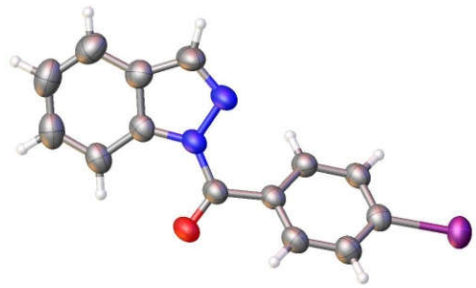


*Procedure for **7a:*** To an oven dried reaction tube (16×100 mm) equipped with a magnetic stir bar, indazole product **5a** (75 mg, 0.25 mmol), potassium hydroxide (56 mg, 1.0 mmol, 4 equiv) and DMF (2 mL) were taken and the mixture was stirred for 8 h at room temperature. The reaction was diluted with cold water, extracted with ethyl acetate (3×10 mL) and the combined organic fractions were dried over Na_2SO_4. After removal of volatiles under reduced pressure, the crude residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (10→15% EtOAc : hexane) to afford 3-phenyl 1*H*-indazole (**7a**) in 79% yield (38 mg).

*Procedure for **8a:*** To an oven dried reaction tube (16×100 mm) equipped with a magnetic stir bar, 3-phenyl 1*H*-indazole **7a** (39 mg, 0.2 mmol, 1 equiv) and sodium hydride (60% dispersion on oil, 17 mg, 0.4 mmol) were taken under nitrogen atmosphere. The tube was capped with a rubber septum and benzylbromide (52 mg, 0.3 mmol) in DMF (1 mL) was added *via* syringe under nitrogen (balloon). The mixture was then stirred for 6 h at room temperature. The reaction was carefully quenched with dilute HCl (1N, 5 mL) and extracted with ethyl acetate (3×10 mL). The combined organic fractions were dried over Na_2SO_4. After removal of the volatiles under reduced pressure, the crude residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (5→10% EtOAc : hexane) to afford the **8a** in 85% yield (48 mg).

Crystallographic Experimental Section:

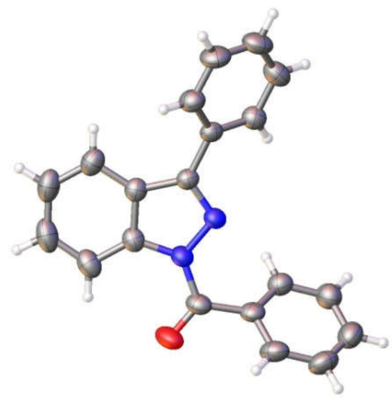
Table S1. Crystal data and structure refinement for compound **3h** (CCDC number: 2110972), Ellipsoid Probability 50):



Identification code	**3h**	
Empirical formula	$C_{14}H_9IN_2O$	
Formula weight	348.13	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 4.3661(4) Å	a= 90°.
	b = 23.242(2) Å	b= 95.256(3)°.
	c = 12.7698(12) Å	g = 90°.
Volume	1290.4(2) $Å^3$	
Z	4	
Density (calculated)	1.792 Mg/m^3	
Absorption coefficient	2.470 mm^{-1}	
F(000)	672	
Crystal size	0.300 x 0.250 x 0.150 mm^3	
Theta range for data collection	3.506 to 30.490°.	
Index ranges	-6<=h<=6, -30<=k<=32, -17<=l<=18	
Reflections collected	20496	
Independent reflections	3837 [R(int) = 0.0214]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5964 and 0.4959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3837 / 2 / 163	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0179, wR2 = 0.0455	

R indices (all data)	R1 = 0.0196, wR2 = 0.0459
Absolute structure parameter	0.008(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.452 and -0.550 e.Å^{-3}

Table S2. Crystal data and structure refinement for compound **5a** (CCDC number: 2110971), Ellipsoid Probability 50):



Identification code	**5a**
Empirical formula	$C_{20}H_{14}N_2O$
Formula weight	298.33
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	8.0248(3)
b/Å	9.5325(5)
c/Å	10.9187(5)
α/°	82.054(2)
β/°	77.986(2)
γ/°	69.701(2)
Volume/Å^3	764.22(6)
Z	2
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.081
F(000)	312.0
Crystal size/mm^3	0.300 x 0.220 x 0.150 mm3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.824 to 49.992
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-12 \le l \le 12$
Reflections collected	9743
Independent reflections	2672 [R_{int} = 0.0223, R_{sigma} = 0.0220]
Data/restraints/parameters	2672/0/209

Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0817
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.0910
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.12

Note: Compounds **3h** and **5a** were dissolved in mixture of hexane: ethyl acetate (9:1) and allowed to evaporate slowly at room temperature for obtaining crystals.

Computational Details

Quantum chemical computations were carried out with (U)M06-2X[1] functional in conjunction with the 6-31G(d,p) basis set.[2] M06-2X functional based calculations yielded all the transition states successfully andit is well known that, the accuracy in reproducing the free energies of such organic systems is better in the case of M06-2X functional when compared to other functionals. In addition, it accounts for the non-covalent interactions.[3] Standard convergence criteria and an ultrafine integration grid were used. All the thermodynamic data is computed at 298.15 K and 1 atm. All the optimized geometries were verified as minima or first order saddle points by the harmonic vibrational frequency analysis and thermal and zero point energy (ZPE) corrections were also included. As in the standard practice, the presence of one imaginary frequency criteria was used for the characterization of transition states (TS). Further, intrinsic reaction coordinate (IRC) calculations confirmed the nature of the transition states and provided the information that, they were connected to the respective minima (reactant and product). All the calculations were performed using G09RevC.01 suite of program.[4]

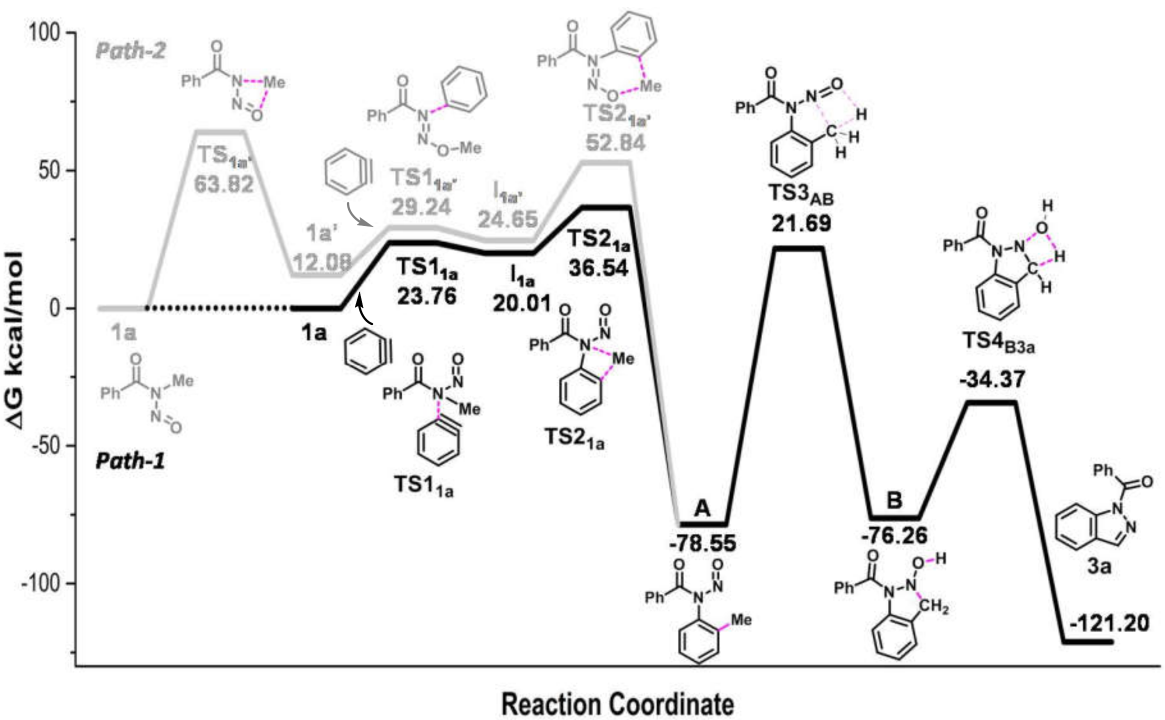


Figure S1. Gibbs free energy profile for the formation of **3a** from **1a** and benzyne computed at UM06-2X/6-31G (d,p) level of theory.

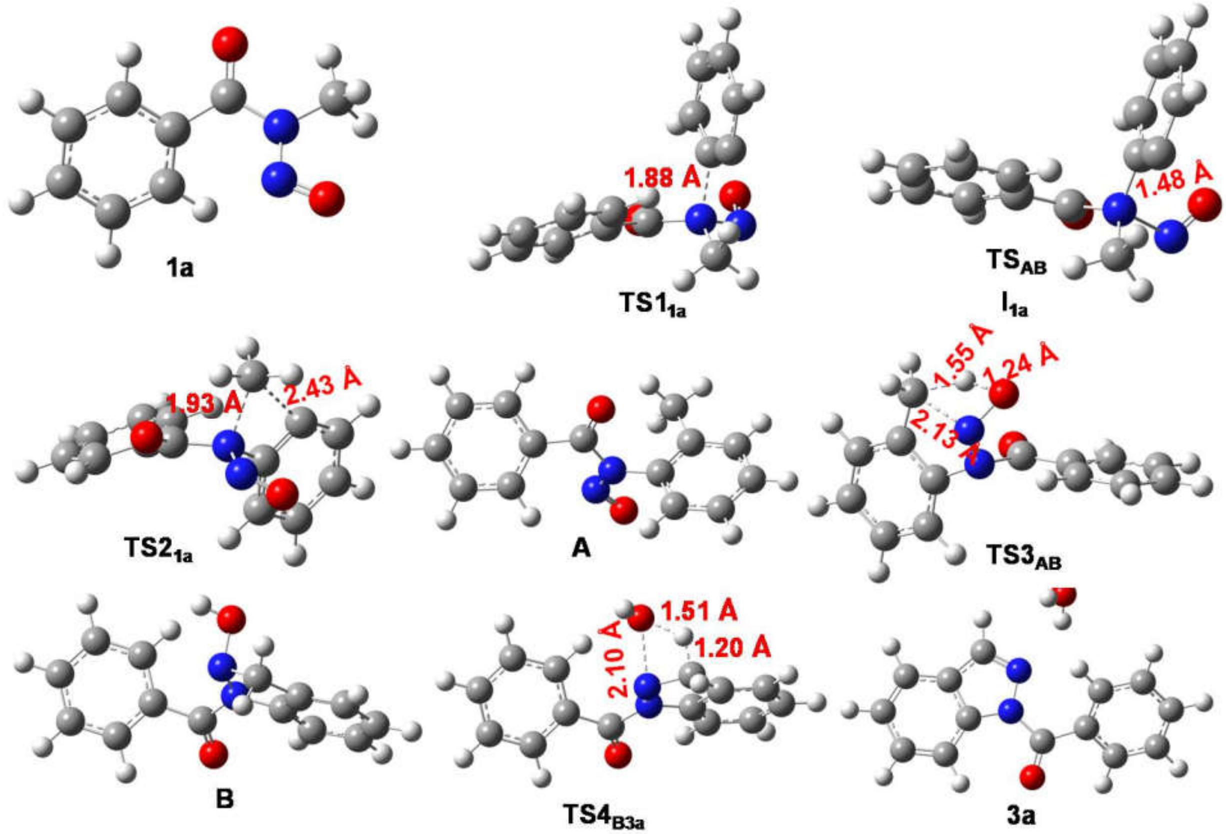


Figure S2. Optimized geometries of intermediates involved in pathway-1 calculated at M06-2X/6-31G (d,p) level of theory.

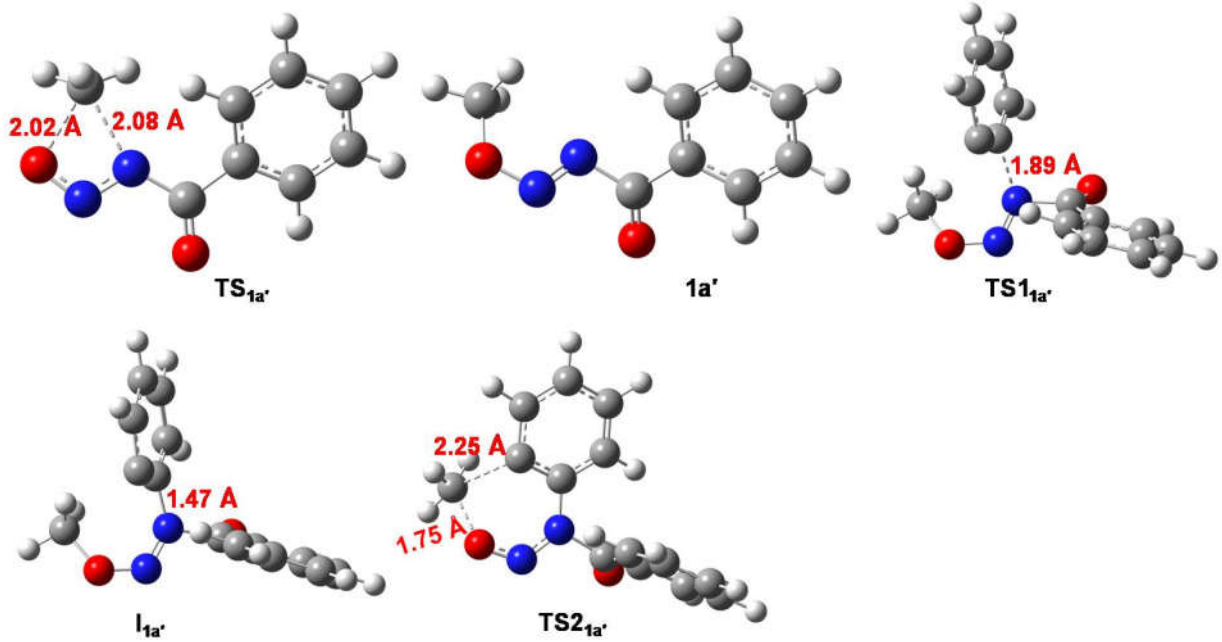


Figure S3. Optimized geometries of intermediates involved in pathway-2 calculated at M06-2X/6-31G (d,p) level of theory.

Table S3. Cartesian coordinates of intermediates calculated at UM06-2X/6-31G(d,p) level of theory.

1a

C	3.33856200	-0.58613600	-0.00805100
C	2.34539100	-1.38823600	0.54801400
C	1.02703400	-0.94836400	0.58110600
C	0.70299100	0.30842900	0.06423800
C	1.70631000	1.12332900	-0.46648000
C	3.01855000	0.67088900	-0.51577000
H	4.36450100	-0.93889700	-0.03980800
H	2.59673800	-2.36079500	0.95767000
H	0.26029600	-1.57646700	1.01806300
H	1.43777900	2.10875400	-0.83203400
H	3.79183000	1.30057000	-0.94286600
C	-0.65929900	0.91534300	0.14021900
N	-1.79098200	0.06838000	0.08064000
N	-1.64815900	-1.15907300	-0.47586000
O	-2.69314100	-1.74404100	-0.61509900
C	-3.12607900	0.58416300	0.34860200
H	-3.70007700	0.62630800	-0.57990500
H	-3.63561400	-0.08861100	1.03977300
H	-3.01328000	1.57792500	0.77215900
O	-0.82547800	2.10773700	0.26787800

$TS1_{1a}$

C	3.83152300	-1.54594600	-0.06180200
C	3.96127300	-0.32754000	-0.72588500
C	2.89437100	0.55928600	-0.75513100
C	1.69755200	0.23742700	-0.10516700
C	1.56500600	-0.98679500	0.55964800
C	2.63550400	-1.87440200	0.57134100
H	4.66324300	-2.24306600	-0.04261900
H	4.89046600	-0.07261600	-1.22408700
H	2.96539400	1.50605700	-1.27959900
H	0.62817200	-1.26258600	1.03492400
H	2.52971000	-2.82972500	1.07399100
C	0.60716000	1.24726700	-0.23622000
N	-0.50336500	1.16478600	0.72691600
N	-1.42251900	2.37787800	0.67862400
O	-1.84309500	2.59701400	-0.38544800
C	-0.15366800	0.97887400	2.14550800
H	0.92468200	0.92963900	2.27888400
H	-0.56126700	1.82744700	2.69628600
H	-0.64701600	0.04444000	2.46473900
O	0.60027800	2.09690600	-1.08618300
C	-3.09804000	-2.22263500	-0.68011700
C	-2.68989300	-2.17618000	0.65430700
C	-1.87209900	-1.12026000	1.10752700
C	-1.58663100	-0.26443900	0.16304100
C	-1.88010300	-0.18384900	-1.18551200
C	-2.69343900	-1.24177700	-1.59619200
H	-3.72859400	-3.03799000	-1.02505900
H	-3.01048200	-2.97125900	1.32654600
H	-1.53770700	0.58671800	-1.86727500
H	-3.00397700	-1.30126100	-2.63453200

I_{1a}

C	3.98746800	1.31827700	-0.03680800
C	4.03795000	0.11974400	0.67352700
C	2.90996700	-0.68499200	0.74833200
C	1.73132700	-0.29417000	0.10386900
C	1.67617500	0.91191000	-0.60693600
C	2.81093100	1.71232100	-0.67052900
H	4.86852000	1.94983000	-0.09238500
H	4.95387400	-0.18295000	1.16957200
H	2.91844400	-1.61817800	1.30150000
H	0.75323700	1.23437500	-1.08410900
H	2.77252000	2.65052800	-1.21322300
C	0.56675000	-1.20337400	0.24267300
N	-0.59873300	-0.93336900	-0.60809800
N	-1.61609900	-2.42403100	-0.31032900
O	-2.57358300	-2.12661200	0.20664200
C	-0.33274900	-1.05601200	-2.05908100
H	0.73514300	-0.96972300	-2.25820200
H	-0.68018500	-2.03773100	-2.39659000
H	-0.91228900	-0.22739000	-2.50465100
O	0.50970400	-2.13263200	1.00932300
C	-2.92075000	2.28969800	0.70079600
C	-2.68142100	2.10613800	-0.66004600
C	-1.89870600	1.05694100	-1.18970600
C	-1.40799000	0.23397800	-0.18506800
C	-1.60190800	0.35048500	1.20385200
C	-2.37839400	1.40912500	1.64464300
H	-3.52606700	3.12673900	1.04257600

$TS2_{1a}$

C	3.78309300	-1.38627400	0.12398700
C	3.93071800	-0.16365500	-0.52815300
C	2.87454500	0.73648200	-0.55374300
C	1.65365200	0.40580600	0.04479900
C	1.50832600	-0.81867000	0.70726200
C	2.58023800	-1.70401400	0.74900500
H	4.60916500	-2.08990700	0.15005600
H	4.86962900	0.08954300	-1.00896300
H	2.97559900	1.70527700	-1.03149800
H	0.57402000	-1.07745000	1.19283800
H	2.47016700	-2.64951700	1.26915900
C	0.61436700	1.47567900	0.00389200
N	-0.78088800	1.11530000	0.08091600
N	-1.61528500	2.22533000	-0.67226100
O	-2.61963700	1.78931100	-1.05170100
C	-1.33581500	1.54493500	1.88942500
H	-0.87488000	0.90710400	2.63149200
H	-0.81248900	2.49164300	1.74754000
H	-2.40532500	1.64507400	2.01161300
O	0.89092600	2.65178100	-0.02525700
C	-2.39379200	-2.68051900	-0.22317800
C	-2.58669500	-1.88985700	0.91220300
C	-2.02732300	-0.60845000	1.00142500
C	-1.29576700	-0.20184400	-0.09968800
C	-1.10267800	-0.93423000	-1.27279500
C	-1.66062600	-2.20615000	-1.31525300
H	-2.82029200	-3.67979300	-0.26712700

H	-3.12529100	2.83241300	-1.34324500
H	-1.17366000	-0.35112800	1.91788900
H	-2.56129200	1.54854400	2.70504700

H	-3.17692700	-2.29543700	1.73264100
H	-0.53024000	-0.54802500	-2.11253800
H	-1.52898900	-2.82709900	-2.19527000

A

C	4.82991600	-0.21504600	-0.15975400
C	3.95487700	-1.29709100	-0.10395700
C	2.58101600	-1.08782700	-0.14263800
C	2.08102000	0.21235900	-0.24899400
C	2.96162200	1.29380900	-0.33253500
C	4.33288900	1.08145700	-0.27493500
H	5.90138000	-0.38356500	-0.11967000
H	4.34281800	-2.30737100	-0.02913200
H	1.90394000	-1.93303500	-0.10289900
H	2.55062000	2.29132700	-0.44550500
H	5.01391900	1.92435800	-0.32537000
C	0.62987300	0.53359000	-0.38682200
N	-0.31719600	-0.34236100	0.20376700
N	0.07758100	-1.04005600	1.31766600
O	-0.81805700	-1.60310800	1.88316300
O	0.23367400	1.50021000	-0.99611000
C	-1.71023800	-0.23208600	-0.14396900
C	-2.21114000	-1.06984800	-1.13017900
C	-2.51126800	0.70061800	0.52030800
C	-3.55435900	-0.98579300	-1.48291000
H	-1.54496000	-1.77808100	-1.61228200
C	-3.85387900	0.76610400	0.15201900
C	-4.37292700	-0.06530900	-0.83781300
H	-3.95542300	-1.63508500	-2.25339200
H	-4.50037200	1.48352100	0.64923900
H	-5.42224000	0.00835200	-1.10498200
C	-1.92662000	1.59277600	1.57998300
H	-1.50470200	1.00056900	2.39810200
H	-1.12756500	2.20974600	1.15727300
H	-2.68973900	2.25310000	1.99535900

TS3$_{AB}$

C	-4.68634800	-0.42562700	-0.36452700
C	-3.81120100	0.12137100	-1.30058600
C	-2.45314500	0.20589400	-1.01914600
C	-1.97424600	-0.26076700	0.20723000
C	-2.85190200	-0.81041800	1.14612400
C	-4.20747400	-0.89154300	0.85899400
H	-5.74650800	-0.48791900	-0.58898300
H	-4.18814900	0.48637800	-2.24982900
H	-1.77204900	0.63525500	-1.74508100
H	-2.45154100	-1.16451700	2.09014200
H	-4.89182500	-1.31521200	1.58621100
C	-0.54262700	-0.21895700	0.57330600
N	0.38455800	0.29443300	-0.48023100
N	0.44440900	1.58985700	-0.67049500
O	-0.48821500	2.25226600	0.09184500
O	-0.06475800	-0.64755800	1.58487400
C	1.71904900	-0.22427000	-0.45984200
C	2.03199100	-1.51664300	-0.85528400
C	2.63640400	0.65656200	0.14752300
C	3.32641000	-1.97214800	-0.64271500
H	1.27543100	-2.14480000	-1.31358800
C	3.92239000	0.15174300	0.36413700
C	4.26307300	-1.13843400	-0.03026900
H	3.60391300	-2.97567000	-0.94597900
H	4.66457600	0.78747000	0.83679300
H	5.27214700	-1.50068700	0.13899200
C	2.16689300	2.02402200	0.51870900
H	0.66060300	2.38787200	0.55028300
H	2.39616800	2.26546700	1.56557200
H	2.56265500	2.79395400	-0.14513300

B

C	4.70146700	0.20703500	-0.04289600
C	3.83311000	0.84211800	0.84184500
C	2.48582800	0.49715400	0.86276200
C	2.00864500	-0.49446300	0.00414400
C	2.88616600	-1.15818700	-0.85182200
C	4.22791400	-0.79446400	-0.88751600
H	5.75094200	0.48310200	-0.06423200
H	4.20861900	1.60023600	1.52165600
H	1.80362200	0.96154700	1.56770100
H	2.50405300	-1.95595500	-1.48045800
H	4.90721700	-1.29925900	-1.56667800
C	0.59073500	-0.97019500	0.05354400
N	-0.40062600	-0.00297600	0.13045200
N	-0.17254400	1.32190900	-0.30438500
O	-0.19810400	2.15184200	0.86176100
O	0.30761500	-2.15215700	0.06291900
C	-1.78881700	-0.28773400	0.14627500
C	-2.45945200	-1.36772800	0.70069200
C	-2.45640600	0.74054400	-0.51383900
C	-3.85122000	-1.37176200	0.59253900
H	-1.91864700	-2.17119900	1.18210600
C	-3.83612600	0.72817900	-0.61581400
C	-4.53491100	-0.34000900	-0.04810900
H	-4.40923900	-2.19815500	1.02068800
H	-4.36406900	1.52632900	-1.12839100

TS4$_{B3a}$

C	-4.70432300	0.23407200	-0.17922000
C	-3.70923800	1.07033200	-0.67807600
C	-2.36689000	0.72332400	-0.55606400
C	-2.03900800	-0.48680900	0.05990800
C	-3.03605100	-1.34567500	0.53453400
C	-4.36886300	-0.97575600	0.42852800
H	-5.74757600	0.52059800	-0.26985800
H	-3.97803300	2.00072600	-1.16744800
H	-1.57945200	1.36835500	-0.94431100
H	-2.74830700	-2.29344900	0.97779500
H	-5.14554400	-1.63055800	0.80898200
C	-0.65035700	-0.99452500	0.12642200
N	0.43290000	-0.04398600	0.23984400
N	0.25923600	1.13227800	0.76583200
O	0.10888900	2.48797700	-0.83592200
O	-0.35161500	-2.16204700	0.09362900
C	1.79632200	-0.36680900	-0.01240000
C	2.36975100	-1.48400700	-0.60928000
C	2.53763600	0.71043100	0.46766300
C	3.75739600	-1.48852600	-0.70157100
H	1.76806200	-2.31068000	-0.96089000
C	3.92436000	0.69099700	0.36181800
C	4.52390800	-0.42121300	-0.21999400
H	4.25289400	-2.34083100	-1.15361300
H	4.52124700	1.52278800	0.72033700

H	-5.61743900	-0.36932600	-0.11127000
C	-1.40473800	1.67088400	-1.05989100
H	0.66739300	2.57845400	0.82145000
H	-1.21352000	1.47328700	-2.12021700
H	-1.59599400	2.73270600	-0.91375600

H	5.60476600	-0.46228300	-0.30557500
C	1.56685500	1.72107100	0.92846200
H	-0.46803800	3.17017100	-0.46168000
H	1.67495700	2.20395300	1.89884700
H	1.33289600	2.50428100	0.05164800

3a

C	4.62219500	-0.12203400	0.05905000
C	3.71729800	0.77508400	0.62085800
C	2.35648000	0.49020400	0.61866100
C	1.89569800	-0.69951700	0.04739200
C	2.81037600	-1.61097700	-0.48895000
C	4.16802100	-1.31799000	-0.49249700
H	5.68254900	0.10963200	0.05470200
H	4.06549900	1.70573900	1.05606700
H	1.66202600	1.19505000	1.05544500
H	2.43625100	-2.54330400	-0.89808500
H	4.87190900	-2.02253900	-0.92273100
C	0.46880500	-1.14042900	0.03239300
N	-0.54562700	-0.16814500	-0.05609600
N	-0.28772100	1.14230600	-0.33983800
O	1.15800500	3.61849700	-0.03158700
O	0.15137600	-2.30903300	0.07885300
C	-1.91370400	-0.40019600	0.02315800
C	-2.65581200	-1.56059600	0.27997300
C	-2.52848300	0.84270800	-0.20408900
C	-4.03201100	-1.41772100	0.30265800
H	-2.16923200	-2.51156500	0.44242100
C	-3.92477900	0.95997300	-0.17717500
C	-4.66472000	-0.17792500	0.07779000
H	-4.64473700	-2.29175900	0.49877900
H	-4.40475600	1.91722300	-0.35110100
H	-5.74760000	-0.12318900	0.10591900
C	-1.43888000	1.74974700	-0.42345700
H	1.11555600	2.74796800	-0.44871600
H	-1.46097300	2.81010900	-0.64119100
H	0.66899300	3.48980000	0.78729700

1a′

C	3.44764500	-0.93883700	-0.09318500
C	2.28869800	-1.71115000	-0.08105800
C	1.04370000	-1.09641100	0.00074800
C	0.96273100	0.29639400	0.06722700
C	2.12697600	1.06989400	0.05407500
C	3.36711000	0.45187100	-0.02460700
H	4.41775100	-1.42176800	-0.15670600
H	2.35536200	-2.79273600	-0.13405400
H	0.13575100	-1.68908200	0.01847200
H	2.03193000	2.14940800	0.10623100
H	4.27208500	1.05009400	-0.03338100
C	-0.33817000	1.01232500	0.13494800
N	-1.48924700	0.13809100	0.19225400
N	-2.38087200	0.51145800	-0.57536100
O	-3.50376300	-0.22347600	-0.50183000
O	-0.45042900	2.20912000	0.20609800
C	-3.53462300	-1.27283900	0.46741000
H	-2.76360400	-2.01847100	0.25776900
H	-3.38002600	-0.87506100	1.47295700
H	-4.52928000	-1.70184800	0.36296500

$TS_{1a'}$

C	3.35700900	-0.79859400	-0.01060600
C	2.24265100	-1.57577200	-0.31568600
C	0.97673300	-0.99907800	-0.33123400
C	0.82786800	0.35936700	-0.04432200
C	1.94911700	1.13974900	0.24785500
C	3.21027400	0.55968800	0.26941300
H	4.34367100	-1.25074300	0.00501200
H	2.36060600	-2.62939000	-0.54604300
H	0.10850000	-1.59545000	-0.59105300
H	1.80390700	2.19513700	0.45365400
H	4.08082000	1.16316900	0.50391900
C	-0.49835000	1.03822800	-0.06330100
N	-1.60062800	0.13023700	-0.01524300
N	-2.75637500	0.57180700	-0.28250100
O	-3.59784200	-0.30802800	-0.07946300
O	-0.63155500	2.23729200	-0.07230300
C	-2.31702200	-1.75097300	0.53106500
H	-1.38906900	-1.81042000	1.08900000
H	-3.18298900	-2.02225700	1.12444700
H	-2.28092900	-2.23416100	-0.43970300

$TS1_{1a'}$

C	4.04004600	-0.99164900	-0.93908600
C	2.84893400	-0.77361700	-1.62644300
C	1.74693800	-0.23871600	-0.96785100
C	1.85055000	0.06415400	0.39341900
C	3.03971000	-0.17360600	1.09077300
C	4.13674200	-0.69409600	0.42058500
H	4.89773400	-1.40237100	-1.46275400
H	2.77503800	-1.02313900	-2.67938100
H	0.80134200	-0.11155900	-1.49215200
H	3.08125700	0.06090900	2.14935000
H	5.06530800	-0.87098900	0.95266900
C	0.71791900	0.61749900	1.16706000
N	-0.42460800	1.13249600	0.39777100
N	-0.08304300	2.03736600	-0.38252800
O	-1.04461900	2.62672500	-1.07434300
O	0.62522500	0.65199700	2.36388100
C	-2.42760600	2.44717500	-0.70471400
H	-2.82817600	1.54195600	-1.15569300
H	-2.51606600	2.39841300	0.38327800
H	-2.91307500	3.33942000	-1.09680200
C	-3.06643900	-1.75231600	1.09177500
C	-2.25068100	-0.63313800	1.27141000
C	-1.63164400	-0.29223200	0.08905400

				C	-1.62169400	-0.74323100	-1.12812700
				C	-2.44816100	-1.88111600	-1.26785800
				C	-3.16241100	-2.36349000	-0.16840400
				H	-3.61932300	-2.15151700	1.93624300
				H	-2.11128200	-0.12694300	2.22018800
				H	-2.55063400	-2.39122500	-2.22472700
				H	-3.80664700	-3.23147800	-0.28277000
$I_{1a'}$				**$TS2_{1a'}$**			
C	-4.03039000	0.81464400	-1.05852100	C	4.01661000	-0.88463400	-1.04444500
C	-2.80677200	0.65044300	-1.70340900	C	2.77373600	-0.87254800	-1.67321000
C	-1.70051300	0.17968000	-1.00476000	C	1.69340600	-0.23868900	-1.07124000
C	-1.84289000	-0.11699400	0.35617000	C	1.86931000	0.38843900	0.16637200
C	-3.06757300	0.05819500	1.01189100	C	3.11812200	0.38226400	0.79505800
C	-4.16282800	0.52086700	0.29940400	C	4.19030000	-0.25779300	0.18921000
H	-4.88845600	1.17796200	-1.61560900	H	4.85531400	-1.38441100	-1.51861100
H	-2.70953000	0.89346000	-2.75585800	H	2.64430900	-1.35837100	-2.63410700
H	-0.73026400	0.09045600	-1.49781600	H	0.72263300	-0.23615300	-1.55703500
H	-3.13762900	-0.17767500	2.06872300	H	3.22545000	0.88407800	1.75106800
H	-5.11801400	0.65369000	0.79566100	H	5.16038700	-0.26813400	0.67440600
C	-0.72356100	-0.62154700	1.16636700	C	0.77229900	1.11354000	0.84535100
N	0.51945400	-0.92603300	0.37210300	N	-0.55418800	0.97173600	0.19738300
N	0.40642000	-2.03109300	-0.20602100	N	-0.91200500	2.10203400	-0.31509200
O	1.38906800	-2.54501200	-0.89345500	O	-1.98928400	2.19187300	-0.97404600
O	-0.67956500	-0.79705900	2.34711300	O	0.87576400	1.79957200	1.81945200
C	2.77184600	-2.12883400	-0.76401100	C	-3.53142200	1.49896100	-0.51116500
H	2.94229300	-1.26237300	-1.40293600	H	-4.00549000	1.07998600	-1.38752800
H	2.99605600	-1.89356200	0.27716200	H	-3.73404700	0.96543400	0.41203200
H	3.31311900	-3.01640000	-1.08828300	H	-3.78629700	2.55807700	-0.37948300
C	2.64928200	1.97694000	1.16686400	C	-1.39032000	-2.48608200	1.10717700
C	1.87818000	0.84098200	1.33932100	C	-0.76681100	-1.25371700	1.12557900
C	1.44248700	0.20745000	0.16621900	C	-1.24235600	-0.26923400	0.23290300
C	1.63725500	0.55451500	-1.17015600	C	-2.34165000	-0.41534900	-0.61391400
C	2.42478600	1.73295700	-1.24088100	C	-2.99801000	-1.65316600	-0.50008700
C	2.91733100	2.42129700	-0.13592000	C	-2.49983000	-2.69454200	0.27305500
H	3.03412400	2.51345000	2.02776300	H	-1.04019600	-3.27810500	1.76069800
H	1.63527700	0.45817500	2.32694000	H	0.03726400	-1.05795500	1.83083200
H	2.67039600	2.13641300	-2.22448900	H	-3.91411700	-1.82437100	-1.06834200
H	3.51565400	3.31929300	-0.27456400	H	-2.97399300	-3.67272700	0.25291900

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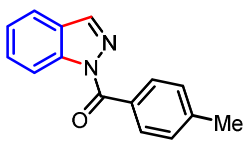
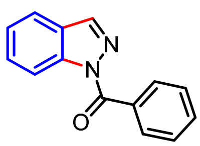
4. Frisch, M. J. *et. al,* Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, USA, 2010.

NMR Spectroscopic Data of Synthesized Compounds:



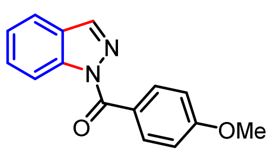
3a

(1*H*-indazol-1-yl)(*p*-tolyl)methanone 3a: White solid; melting point (M.p.) 88-90 °C; yield = 35 mg (73%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 143.1, 140.3, 140.2, 131.2, 130.5, 129.5, 128.9, 126.2, 124.8, 121.0, 116.0, 21.8 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{12}N_2ONa$ 259.0847; Found 259.0844.



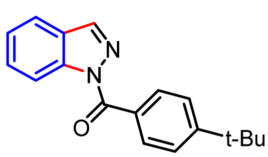
3b

(1*H*-indazol-1-yl)(phenyl)methanone 3b: White solid; M.p. 80-83 °C; yield = 28 mg (68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.65-7.59 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 140.4, 140.3, 133.4, 132.4, 131.1, 129.6, 128.1, 126.3, 125.0, 121.1, 116.0 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{10}N_2ONa$ 245.0691; Found 245.0686.



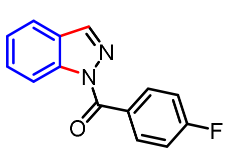
3c

(1*H*-indazol-1-yl)(4-methoxyphenyl)methanone 3c: White solid; M.p. 97-99 °C; yield = 38 mg (75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 163.1, 140.4, 140.0, 133.7, 129.5, 126.1, 125.4, 124.7, 121.0, 116.0, 113.5, 55.6 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{12}N_2O_2Na$ 275.0796; Found 275.0790.



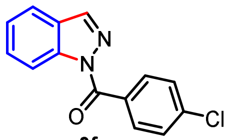
3d

(4-(tert-butyl)phenyl)(1*H*-indazol-1-yl)methanone 3d: White solid; M.p. 78-80 °C; yield = 40 mg (72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 1.38 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 156.0, 140.2, 131.1 (2×C), 130.5, 129.6, 126.2, 125.2, 124.8, 121.0, 116.1, 35.2, 31.3. ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{18}N_2ONa$ 301.1317; Found 301.1322.



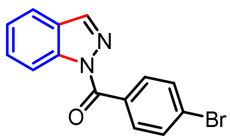
3e

(4-fluorophenyl)(1*H*-indazol-1-yl)methanone 3e: White solid; M.p. 118-120 °C; yield = 34 mg (71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 8.18 – 8.13 (m, 2H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 165.3 (d, J = 254.1 Hz), 140.5, 140.3, 133.9 (d, J = 9.1 Hz), 129.7, 129.4 (d, J = 3.4 Hz), 126.2, 125.0, 121.1, 116.0, 115.3 (d, J = 21.9 Hz) ppm; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -106.2 ppm. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_9FN_2ONa$ 263.0597; Found 263.0591.



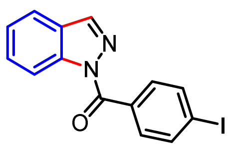
3f

(4-chlorophenyl)(1*H*-indazol-1-yl)methanone 3f: White solid; M.p. 96-98 °C; yield = 35 mg (69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 8.07 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.80–7.78 (m, 1H), 7.65–7.61 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.47-7.41 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 140.7, 140.3, 138.9, 132.6, 131.7, 129.8, 128.5, 126.3, 125.1, 121.2, 116.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_9ClN_2ONa$ 279.0301; Found 279.0299.



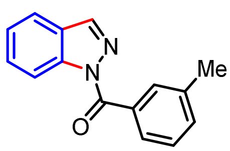
3g

(4-bromophenyl)(1*H*-indazol-1-yl)methanone 3g: White solid; M.p. 91-93 °C; yield = 42 mg (70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.19 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 5.9 Hz, 1H), 7.66–7.60 (m, 3H), 7.43–7.40 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 140.7, 140.2, 132.7, 132.2, 131.4, 129.8, 127.5, 126.3, 125.2, 121.2, 116.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_9BrN_2ONa$ 322.9796; Found 322.9792.



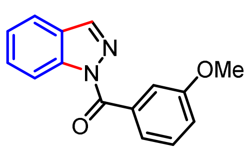
3h

(1*H*-indazol-1-yl)(4-iodophenyl)methanone 3h: White solid; M.p. 97-99 °C; yield = 61 mg (72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.2 Hz, 1H), 8.20 (s, 1H), 7.89–7.87 (m, 2H), 7.81–7.78 (m, 3H), 7.63 (dd, *J* = 7.2, 6.0 Hz, 1H), 7.42 (t, *J* = 5.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 140.7, 140.2, 137.4, 132.8, 132.6, 129.8, 126.3, 125.2, 121.2, 116.0, 100.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_9IN_2ONa$ 370.9657; Found 370.9653.



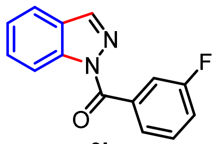
3i

(1*H*-indazol-1-yl)(m-tolyl)methanone 3i: White solid; M.p. 61-63 °C; yield = 32 mg (67%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 7.86 (s, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 6.3 Hz, 3H), 2.46 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 140.3 (2×C), 137.9, 133.4, 133.1, 131.4, 129.6, 128.2, 128.0, 126.2, 124.9, 121.0, 116.0, 21.5 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{12}N_2ONa$ 259.0847; Found 259.0846.



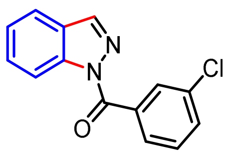
3j

(1*H*-indazol-1-yl)(3-methoxyphenyl)methanone 3j: Colorless liquid; yield = 33 mg (66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.67–7.60 (m, 3H), 7.42 (dd, *J* = 17.8, 8.0 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 159.2, 140.5, 140.2, 134.6, 129.6, 129.1, 126.2, 124.9, 123.5, 121.0, 118.5, 116.0, 115.9, 55.5 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{12}N_2O_2Na$ 275.0796; Found 275.0791.



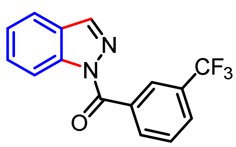
3k

(3-fluorophenyl)(1*H*-indazol-1-yl)methanone 3k: White solid; M.p. 95-97 °C; yield = 33 mg (69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.80 (dd, *J* = 14.1, 8.7 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.52-7.47 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.32-7.28 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 162.1 (d, J = 246.8 Hz), 140.8, 140.2, 135.3 (d, J = 7.4 Hz), 129.8, 129.7 (d, J = 7.8 Hz), 126.9 (d, J = 3.2 Hz), 126.3, 125.2, 121.1, 119.4 (d, J = 21.2 Hz), 118.2 (d, J = 23.8 Hz), 116.0, ppm; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -112.4 ppm. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_9FN_2ONa$ 263.0597; Found 263.0592.



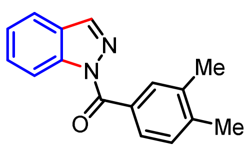
3l

(3-chlorophenyl)(1*H*-indazol-1-yl)methanone 3l: White solid; M.p. 99-101 °C; yield = 33 mg (65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 8.07 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.80–7.78 (m, 1H), 7.65–7.61 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.47–7.41 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 140.9, 140.2, 135.0, 134.2, 132.3, 131.1, 129.8, 129.4, 129.2, 126.3, 125.2, 121.2, 116.0 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_9ClN_2ONa$ 279.0301; Found 279.0295.



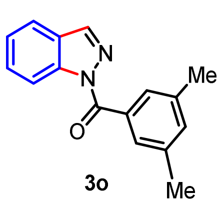
3m

(1*H*-indazol-1-yl)(3-(trifluoromethyl)phenyl)methanone 3m: White solid; M.p. 72-74 °C; yield = 36 mg (63%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.22 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.67-7.62 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 141.0, 140.2, 134.4, 134.2, 130.7 (d, *J* = 33.1 Hz), 129.9, 128.8 (q, J = 3.7 Hz), 128.7, 128.2 (q, J = 3.8 Hz), 126.3, 125.3, 121.8 (q, J = 272.3 Hz), 121.2, 116.0 ppm; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.6 ppm. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_9F_3N_2ONa$ 313.2350; Found 313.0563.



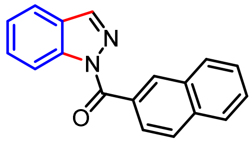
3n

(3,4-dimethylphenyl)(1*H*-indazol-1-yl)methanone 3n: White solid; M.p. 76-78 °C; yield = 33 mg (66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 7.84-7.81 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 2.36 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 141.8, 140.3, 140.1, 136.5, 132.0, 130.9, 129.5, 129.4, 128.8, 126.2, 124.8, 121.0, 116.0, 20.1, 19.9 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{14}N_2ONa$ 273.1004; Found 273.1002.



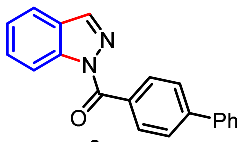
3o

(3,5-dimethylphenyl)(1*H*-indazol-1-yl)methanone 3o: Semisolid; yield = 34 mg (68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.4 Hz, 1H), 8.20 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.63-7.60 (m, 3H), 7.41 (t, J = 7.5 Hz, 1H), 7.23 (s, 1H), 2.42 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 140.3, 137.8 (2×C), 134.1, 133.5, 129.5, 128.5, 126.3, 124.9, 121.0, 116.0, 21.4 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{14}N_2ONa$ 273.1004; Found 273.0999.



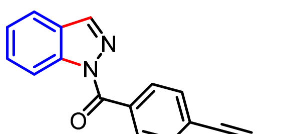
3p

(1*H*-indazol-1-yl)(naphthalen-2-yl)methanone 3p: White solid; M.p. 96-98 °C; yield = 38 mg (70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.01-7.96 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.67-7.55 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 140.5, 140.4, 135.2, 132.7, 132.4, 130.6, 129.7, 129.6, 128.4, 127.9, 127.7, 126.8 (2×C), 126.3, 125.0, 121.1, 116.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{12}N_2ONa$ 295.0847; Found 295.0845.



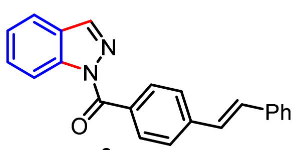
3q

[1,1'-biphenyl]-4-yl(1H-indazol-1-yl)methanone 3q: White solid; M.p. 136-138 °C; yield = 44 mg (74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.69-7.63 (m, 3H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.45-7.40 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 145.2, 140.4, 140.3, 140.2, 132.1, 131.7, 129.7, 129.1, 128.2, 127.5, 126.8, 126.2, 125.0, 121.1, 116.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{14}N_2ONa$ 321.1004; Found 321.1001.



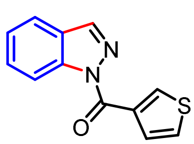
3r

(1*H*-indazol-1-yl)(4-(phenylethynyl)phenyl)methanone 3r: White solid; M.p. 140-142 °C; yield = 42 mg (65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.68-7.62 (m, 3H), 7.58 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.39–7.37 (m, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 140.6, 140.3, 132.7, 131.9, 131.2 (2×C), 129.7, 128.9, 128.6, 127.6, 126.3, 125.1, 122.9, 121.1, 116.1, 92.4, 88.9 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{14}N_2ONa$ 345.1004; Found 345.1005.



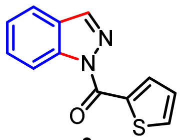
3s

(E)-(1*H*-indazol-1-yl)(4-styrylphenyl)methanone 3s: White solid; M.p. 170-172 °C; yield = 43 mg (67%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.22 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.66-7.62 (m, 3H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.44-7.38 (m, 3H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 16.3 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 141.5, 140.3, 136.9, 132.0, 131.8, 131.5, 129.6, 128.9 (2×C), 128.4, 127.7, 127.0, 126.2, 126.1, 124.9, 121.1, 116.1 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. for $C_{22}H_{16}N_2ONa$ 347.1160; Found 347.1161.

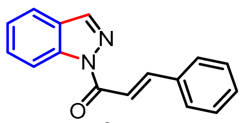


3t

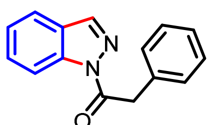
(1*H*-indazol-1-yl)(thiophen-3-yl)methanone 3t: White solid; M.p. 95-97 °C; yield = 30 mg (65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 1.3 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 7.95 (d, *J* = 5.0 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.40-7.36 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 140.4, 140.2, 136.0, 134.6, 130.4, 129.6, 126.0, 125.0, 124.8, 121.0, 116.1 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_9N_2OS$ 229.0436; Found 229.0446.


3u

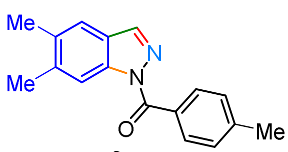
(1*H*-indazol-1-yl)(thiophen-2-yl)methanone 3u: White solid; M.p. 108-110 °C; yield = 29 mg (63%); **^{1}H NMR** (400 MHz, CDCl3) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 3.6 Hz, 1H), 8.24 (s, 1H), 7.78 (d, J = 7.0 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 3.7 Hz, 1H).ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 140.2, 140.0, 137.6, 136.4, 134.0, 129.8, 127.3, 126.3, 124.9, 121.2, 116.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{12}H_8N_2OSNa$ 251.0255; Found 251.0252.


3v

(E)-1-(1*H*-indazol-1-yl)-3-phenylprop-2-en-1-one 3v: White solid; M.p. 98-100 °C; yield = 35 mg (71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 8.03 (s, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.73–7.71 (m, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.44-7.43 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 146.3, 139.8, 139.5, 134.9, 130.8, 129.6, 129.1, 128.8, 126.6, 124.8, 121.1, 117.5, 116.1 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{12}N_2ONa$ 271.0847; Found 271.0845.

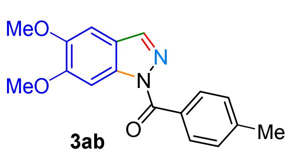

3w

1-(1*H*-indazol-1-yl)-2-phenylethan-1-one 3w: White solid; M.p. 62-64 °C; yield = 30 mg (65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.18 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.38-7.34 (m, 3H), 7.30 (d, *J* = 6.9 Hz, 1H), 4.56 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 140.1, 139.4, 134.1, 129.9, 129.7, 128.7, 127.3, 126.6, 124.8, 121.0, 115.8, 41.8 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{12}N_2ONa$ 259.0847; Found 259.0846.



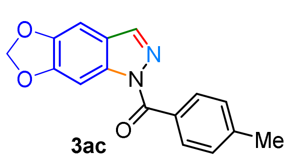
3aa

(5,6-dimethyl-1H-indazol-1-yl)(p-tolyl)methanone 3aa: White solid; M.p. 123-125 °C; yield = 37 mg (70%); **^{1}H NMR** (400 MHz, CDCl3) δ 8.39 (s, 1H), 8.08-8.02 (m, 3H), 7.49 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 2.47 (s, 6H), 2.41 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 168.2, 142.7, 139.8, 139.5, 139.3, 134.0, 131.1, 130.7, 128.7, 124.7, 120.5, 116.0, 21.7, 21.0, 20.2 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{16}N_2ONa$ 287.1160; Found 287.1158.



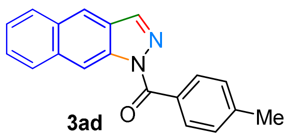
3ab

(5,6-dimethoxy-1H-indazol-1-yl)(p-tolyl)methanone 3ab: White solid; M.p. 115-117 °C; yield = 38 mg (65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.02 (s, 1H), 7.98 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.07 (s, 1H), 4.02 (s, 3H), 3.94 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR** δ 168.4, 152.1, 148.2, 142.9, 139.8, 135.8, 131.1, 130.5, 128.7, 119.0, 100.4, 98.0, 56.4, 56.2, 21.7 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{16}N_2O_3Na$ 319.1059; Found 319.1047.



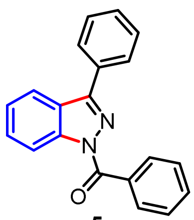
3ac

(1H-[1,3]dioxolo[4,5-f]indazol-1-yl)(p-tolyl)methanone 3ac: White solid; M.p. 111-113 °C; yield = 36 mg (64%); **^{1}H NMR** (400 MHz, CDCl3) δ 8.00 (d, J = 2.4 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.03 (s, 1H), 6.10 (s, 2H), 2.44 (s, 3H), ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 150.8, 146.6, 143.1, 139.8, 137.0, 131.2, 130.5, 128.8, 120.7, 102.3, 98.2, 96.6, 21.8 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{12}N_2O_3Na$ 303.0746; Found 303.0738.



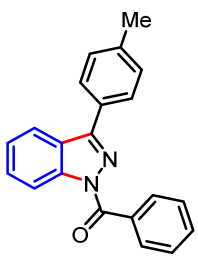
3ad

(1H-benzo[f]indazol-1-yl)(p-tolyl)methanone 3ad: White solid; M.p. 118-120 °C; yield = 31 mg (59%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 2H), 7.93 – 7.82 (m, 3H), 7.69 (d, J = 2.3 Hz, 1H), 7.50-7.49 (m, 2H), 7.48-7.33 (m, 3H), 2.47 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 148.8, 144.6, 134.0, 131.6, 130.4, 129.6, 129.5 (2×C), 127.9, 127.8, 127.0, 126.7, 125.8, 121.5, 118.9, 21.9 ppm; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{14}N_2ONa$ 309.1004; Found 309.1155.



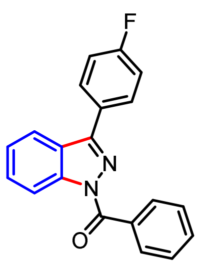
5a

Phenyl(3-phenyl-1*H*-indazol-1-yl)methanone 5a: White solid; M.p. 148-150 °C; yield = 47 mg (79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 7.7 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.55-7.46 (m, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 150.5, 141.9, 133.6, 132.3, 132.0, 131.5, 129.7, 129.6, 129.1, 128.4, 128.1, 125.2, 124.7, 121.4, 116.5 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{15}N_2O$ 299.1184; Found 299.1176.



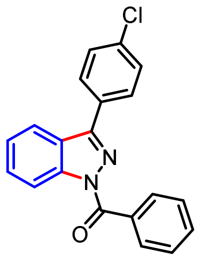
5b

Phenyl(3-(p-tolyl)-1*H*-indazol-1-yl)methanone 5b: White solid; M.p. 97-99 °C; yield = 47 mg (76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.49–7.45 (m, 1H), 7.34 (d, *J* = 7.4 Hz, 2H), 2.45 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 150.5, 141.9, 139.8, 133.6, 132.3, 131.5, 129.8, 129.5, 129.2, 128.2, 128.0, 125.1, 124.8, 121.5, 116.5, 21.6 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{17}N_2O$ 313.1341; Found 313.1335.



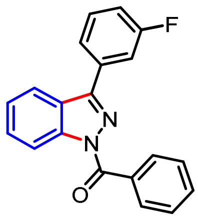
5c

(3-(4-fluorophenyl)-1*H*-indazol-1-yl)(phenyl)methanone 5c: White solid; M.p. 98-100 °C; yield = 54 mg (85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 2H), 8.01–7.95 (m, 3H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 8.4 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 163.8 (d, *J* = 249.5 Hz), 149.4, 141.8, 133.5, 132.4, 131.4, 130.1 (d, *J* = 8.4 Hz), 129.6, 128.1, 128.0 (d, *J* = 2.9 Hz), 125.3, 124.5, 121.2, 116.5, 116.2 (d, *J* = 21.7 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.1 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{14}FN_2O$ 317.1090; Found 317.1084.



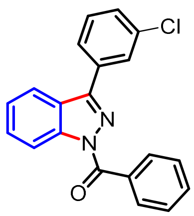
5d

(3-(4-chlorophenyl)-1*H*-indazol-1-yl)(phenyl)methanone 5d: White solid; M.p. 162-164 °C; yield = 54 mg (82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.68–7.60 (m, 2H), 7.56–7.46 (m, 5H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 149.2, 141.9, 135.7, 133.4, 132.4, 131.5, 130.5, 129.6, 129.5, 129.3, 128.1, 125.4, 124.4, 121.1, 116.5 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{14}ClN_2O$ 333.0795; Found 333.0785.



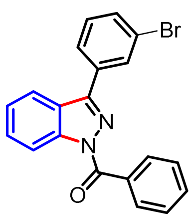
5e

(3-(3-fluorophenyl)-1*H*-indazol-1-yl)(phenyl)methanone 5e: White solid; M.p. 90-92 °C; yield = 52 mg (83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70–7.61 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 8.2 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 163.2 (d, *J* = 246.5 Hz), 149.1, 141.9, 134.1 (d, *J* = 8.1 Hz), 133.3, 132.5, 131.5, 130.7 (d, *J* = 8.4 Hz), 129.7, 128.1, 125.4, 124.3, 124.0 (d, *J* = 3.1 Hz), 121.1, 116.6 (d, *J* = 21.1 Hz), 116.5, 115.2 (d, J = 22.8 Hz) ppm; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -112.0 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{14}FN_2O$ 317.1090; Found 317.1084.



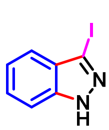
5f

(3-(3-chlorophenyl)-1*H*-indazol-1-yl)(phenyl)methanone 5f: White solid; M.p. 116-118 °C; yield = 55 mg (83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 2H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.96 (s, 1H), 7.87 (s, 1H), 7.69–7.61 (m, 2H), 7.57–7.46 (m, 5H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 149.0, 141.9, 135.1, 133.8, 133.3, 132.5, 131.5, 130.4, 129.7 (2×C), 128.3, 128.1, 126.5, 125.4, 124.4, 121.1, 116.6 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{14}ClN_2O$ 333.0795; Found 333.0786.



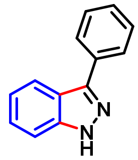
5g

(3-(3-bromophenyl)-1*H*-indazol-1-yl)(phenyl)methanone 5g: White solid; M.p. 140-142 °C; yield = 60 mg (80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 7.4 Hz, 2H), 8.11 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.4 Hz 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 148.8, 141.9, 134.0, 133.3, 132.6, 132.5, 131.5, 131.1, 130.6, 129.7, 128.1, 126.9, 125.4, 124.3, 123.1, 121.1, 116.5 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{14}BrN_2O$ 377.0290; Found 377.0275.



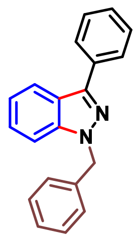
6a

3-iodo-1*H*-indazole 6a: White solid; M.p. 126-128 °C; yield = 49 mg (81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 128.2, 127.5, 122.0, 121.4, 110.8, 93.6 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_7H_6IN_2$ 244.9576; Found 244.9569.



7a

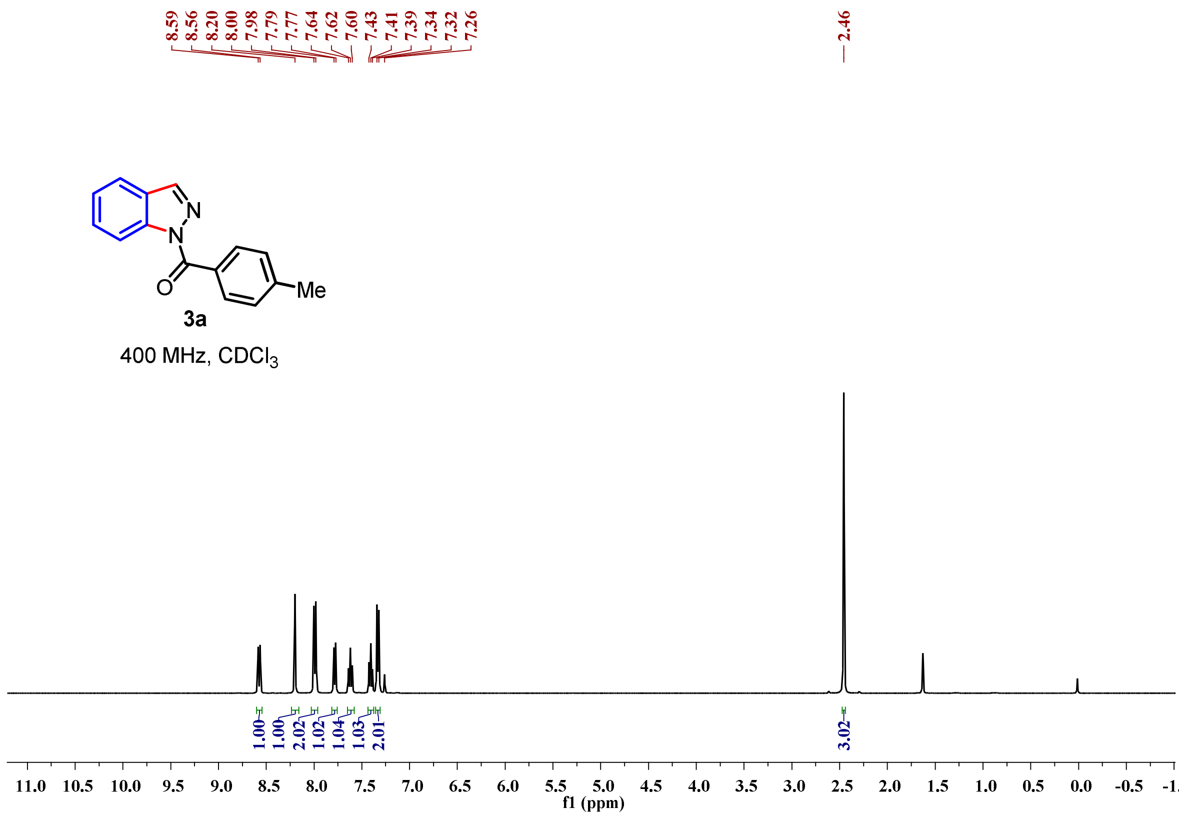
3-phenyl-1H-indazole 7a: White solid; M.p. 86-88 °C; yield = 38 mg (79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 2H), 8.16 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 6.6 Hz, 2H), 7.64–7.61 (m, 1H), 7.43–7.39 (m, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3, 141.6, 133.5, 129.0, 128.1, 127.8, 126.6, 121.1, 120.8, 120.7, 110.5 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{11}N_2$ 195.0922; Found 195.0916.

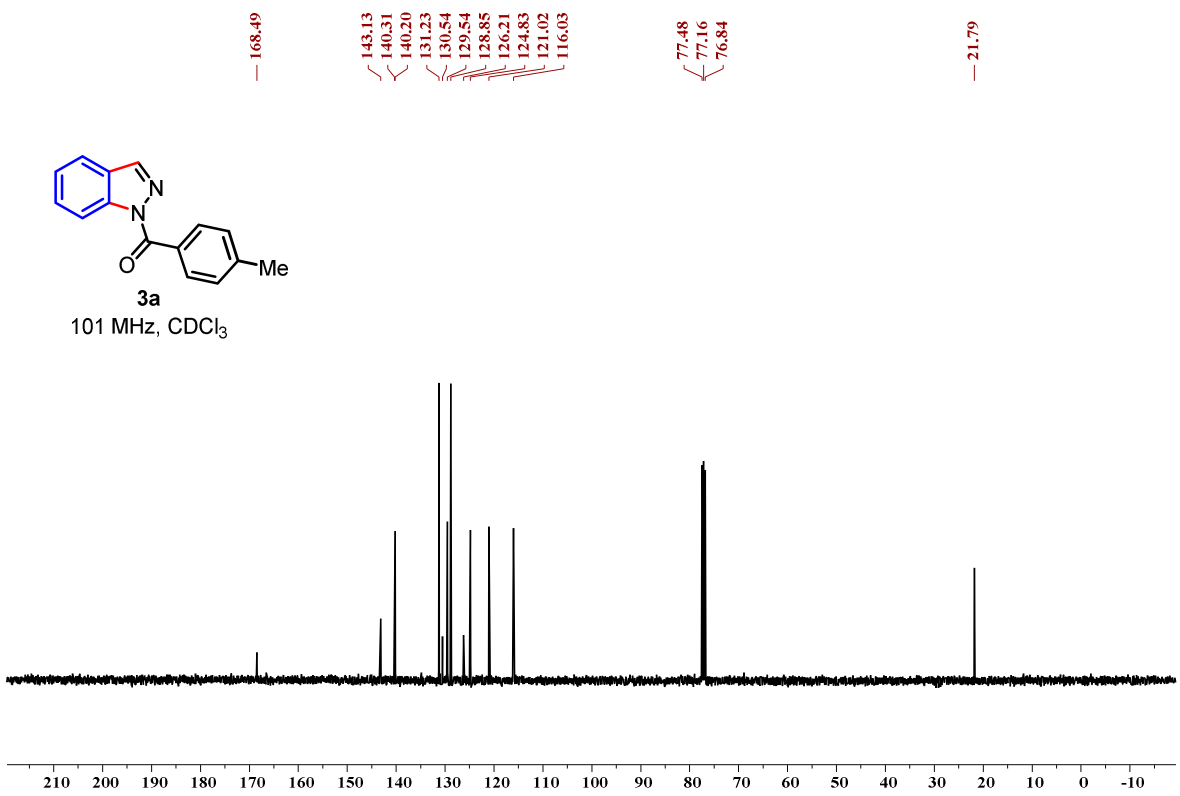


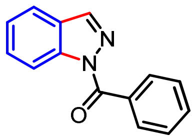
8a

1-benzyl-3-phenyl-1H-indazole 8a: liquid; yield = 48 mg (85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04–7.98 (m, 3H), 7.53-7.46 (m, 2H), 7.40-7.36 (m, 1H), 7.30 (d, *J* = 4.4 Hz, 2H), 7.25-7.20 (m, 5H), 7.18–7.14 (m, 1H), 5.61 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 141.2, 137.0, 133.8, 128.9, 128.8, 128.0, 127.8, 127.6, 127.2, 126.5, 122.2, 121.5, 121.2, 109.7, 53.1 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}N_2$ 285.1392; Found 285.1385.

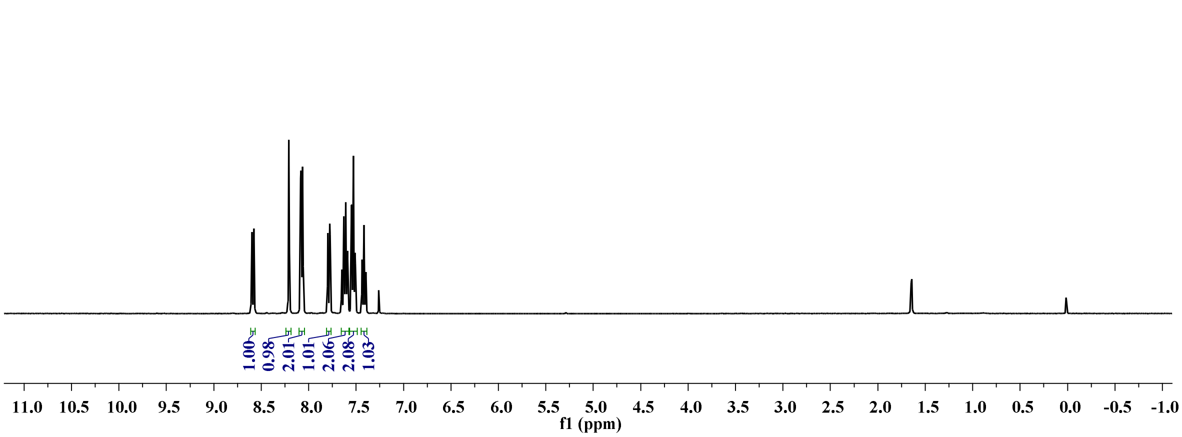
NMR Spectra of Synthesized Compounds

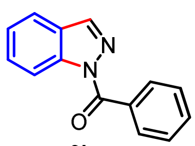

8.59
8.56
8.20
8.00
7.98
7.79
7.77
7.64
7.62
7.60
7.43
7.41
7.39
7.34
7.32
7.26
2.46
N
N
O
Me
3a
400 MHz, CDCl3
1.00
1.00
2.02
1.02
1.04
1.03
2.01
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.49
143.13
140.31
140.20
131.23
130.54
129.54
128.85
126.21
124.83
121.02
116.03
77.48
77.16
76.84
21.79
N
N
O
Me
3a
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

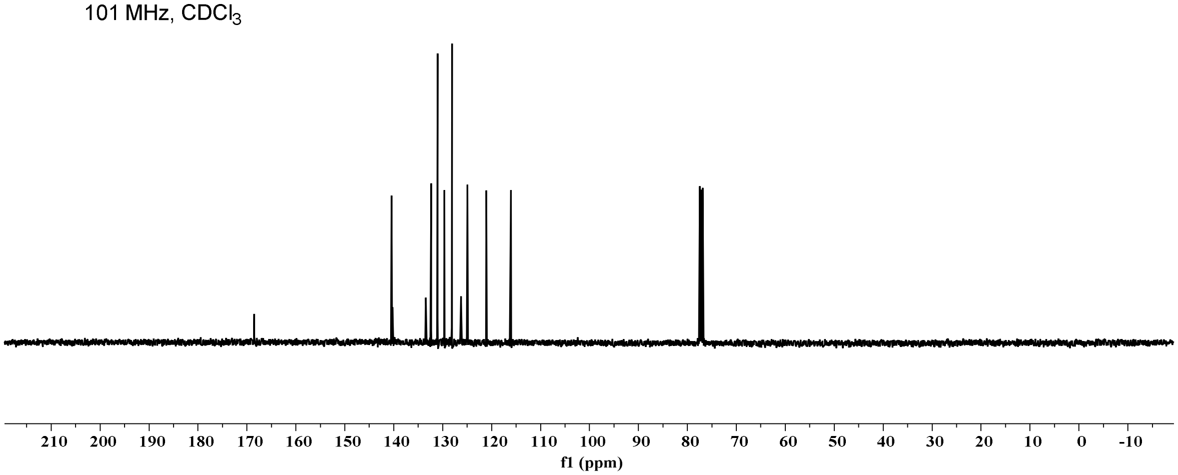


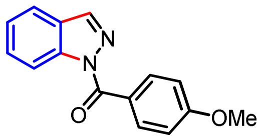
3b
400 MHz, $CDCl_3$





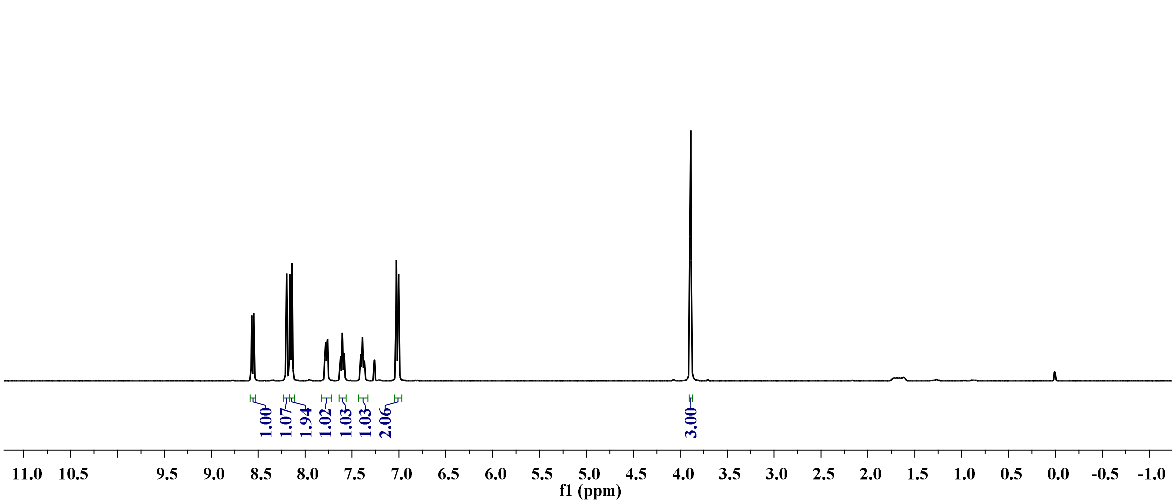
3b
101 MHz, $CDCl_3$

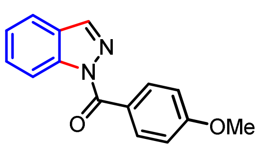




3c

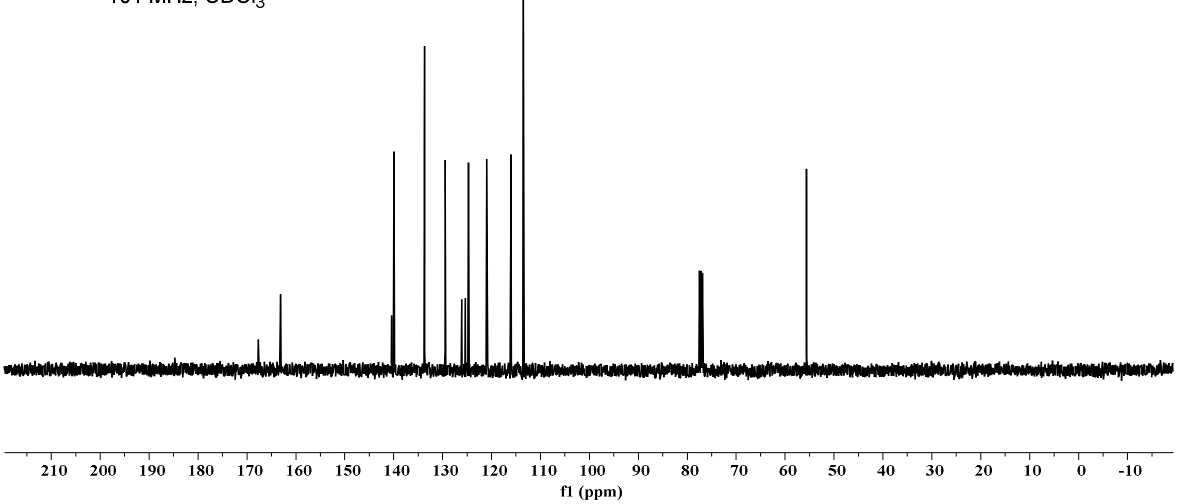
400 MHz, $CDCl_3$

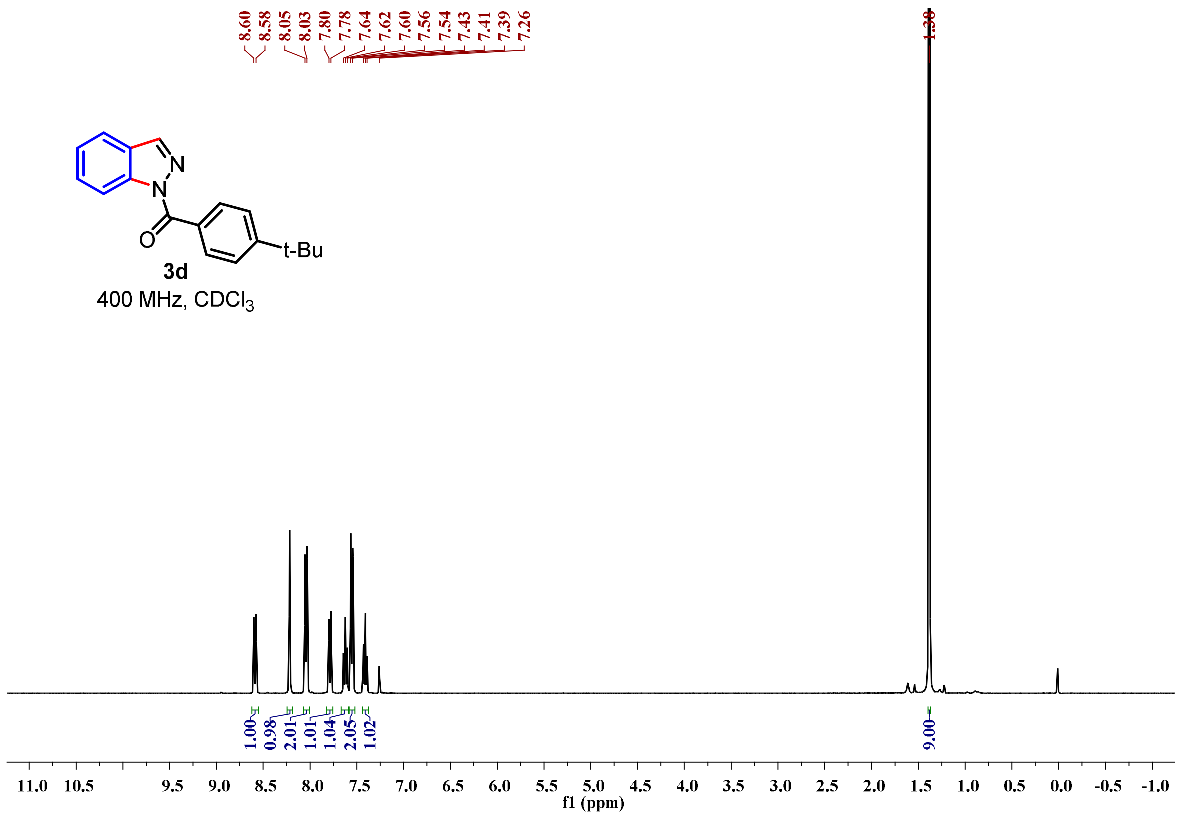


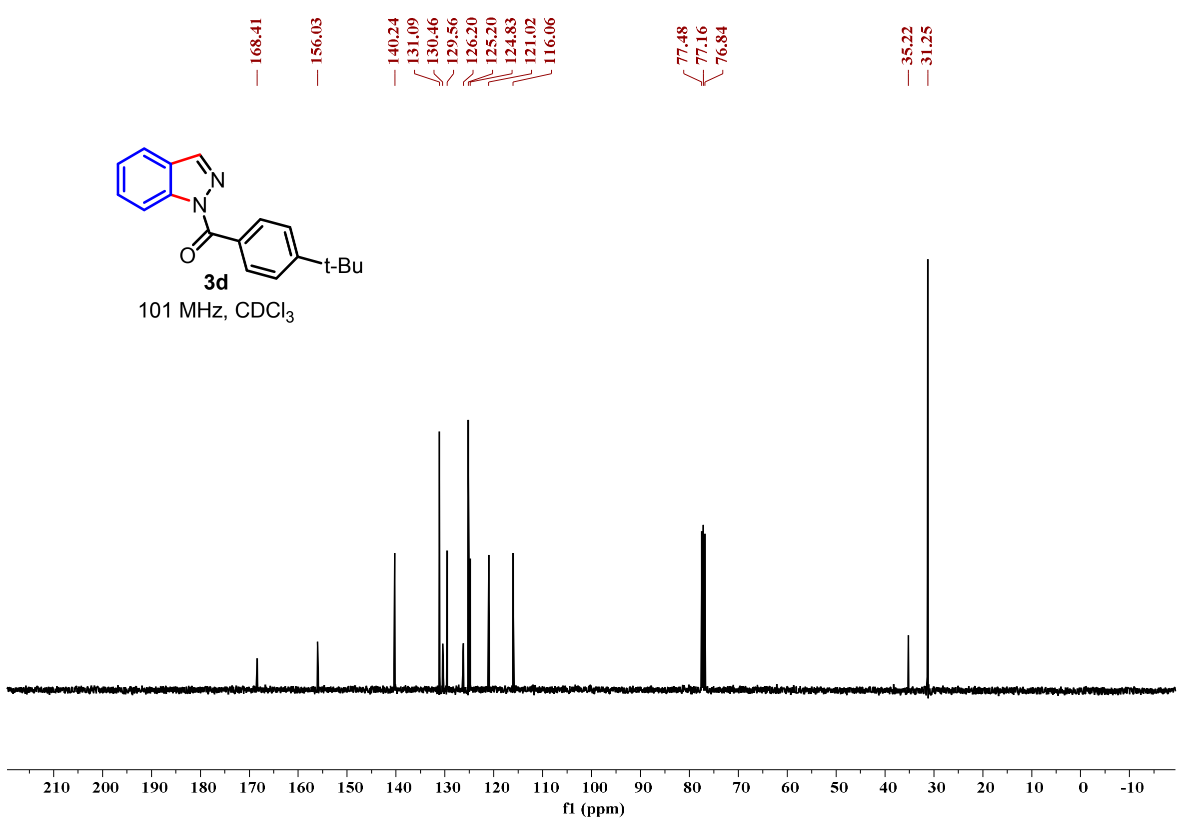


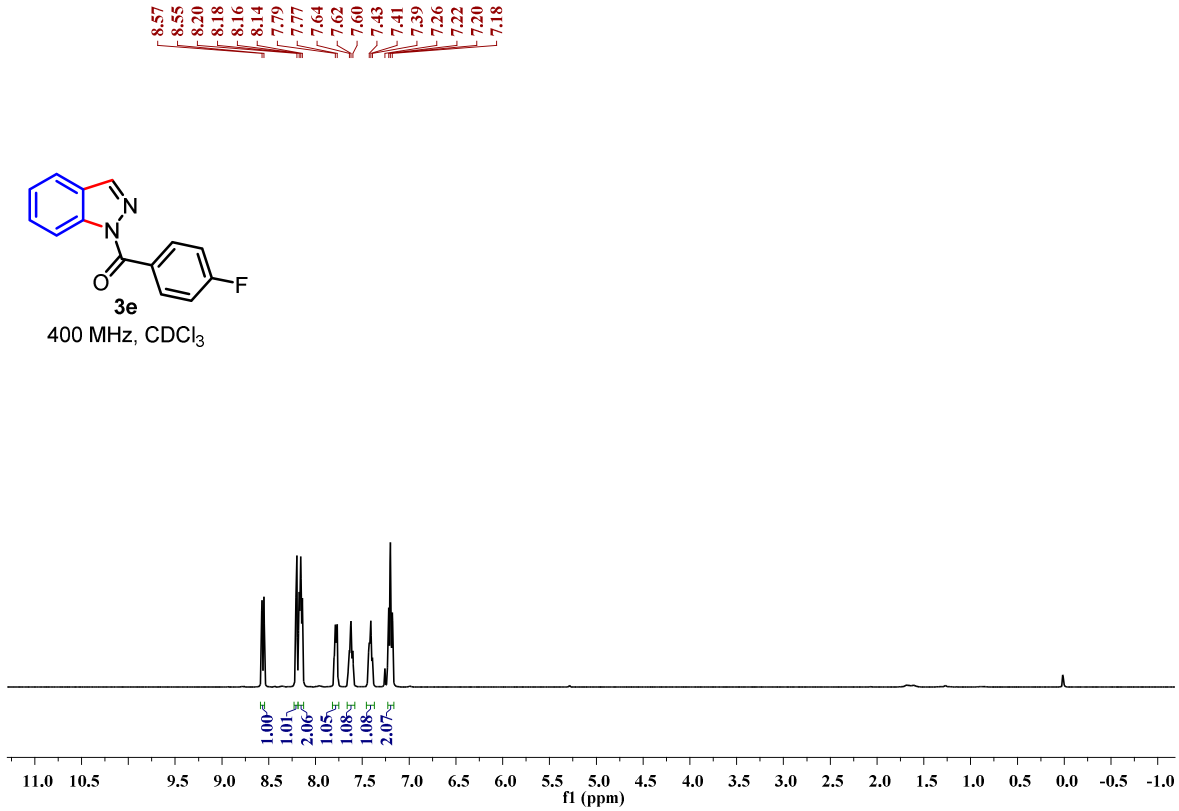
3c

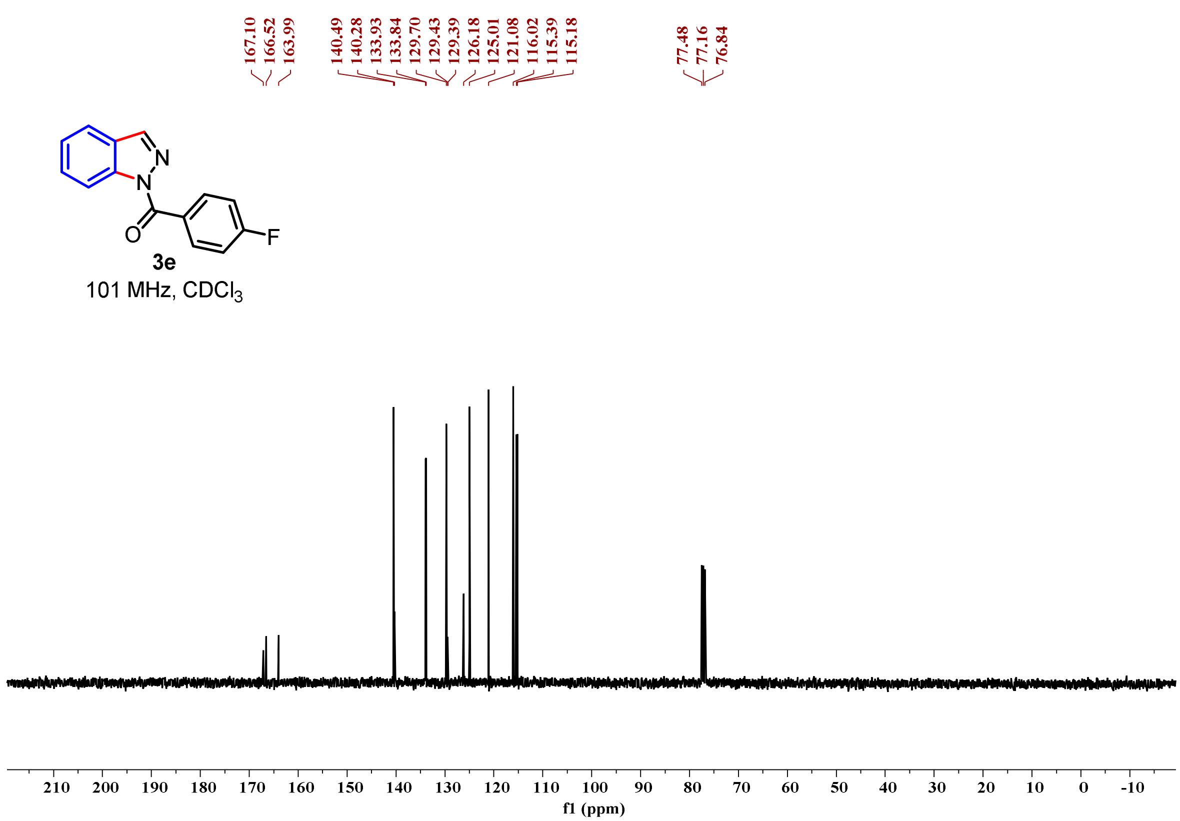
101 MHz, $CDCl_3$

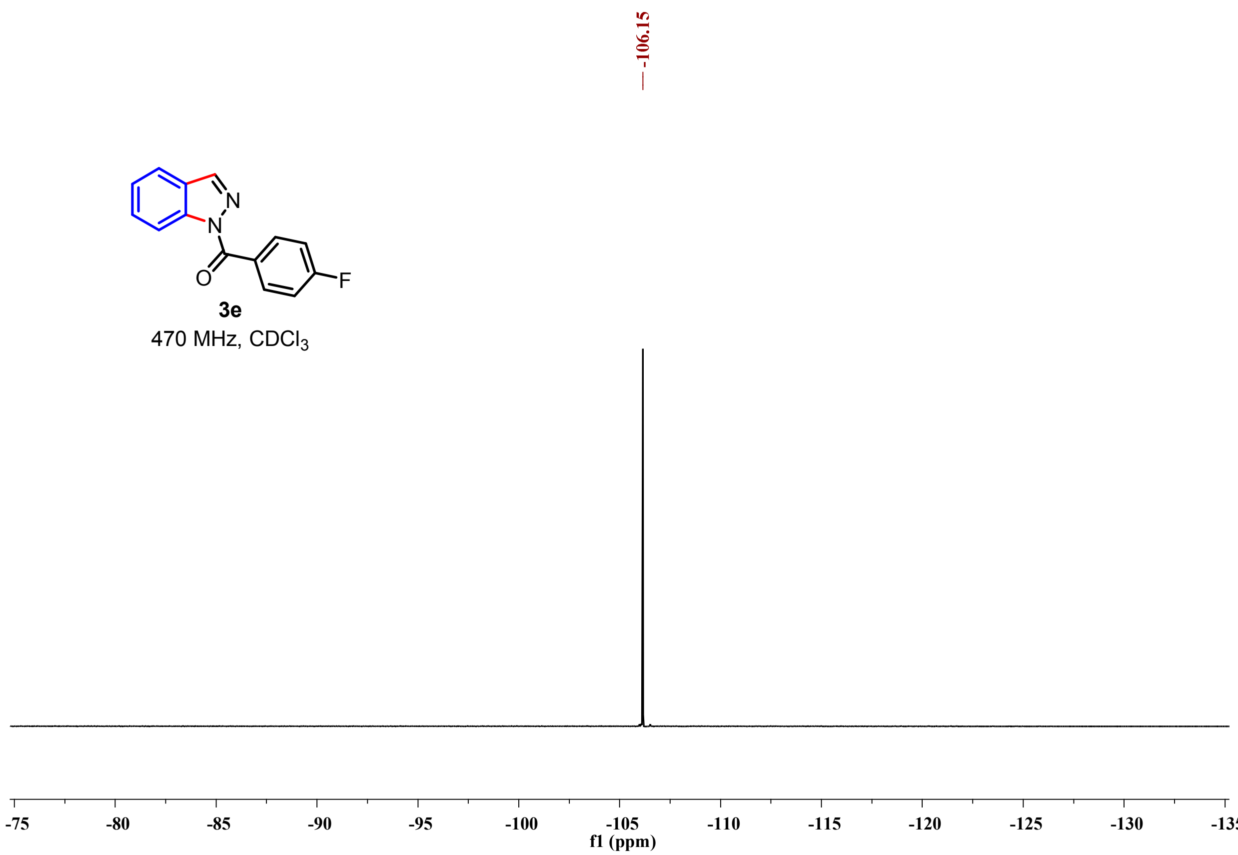


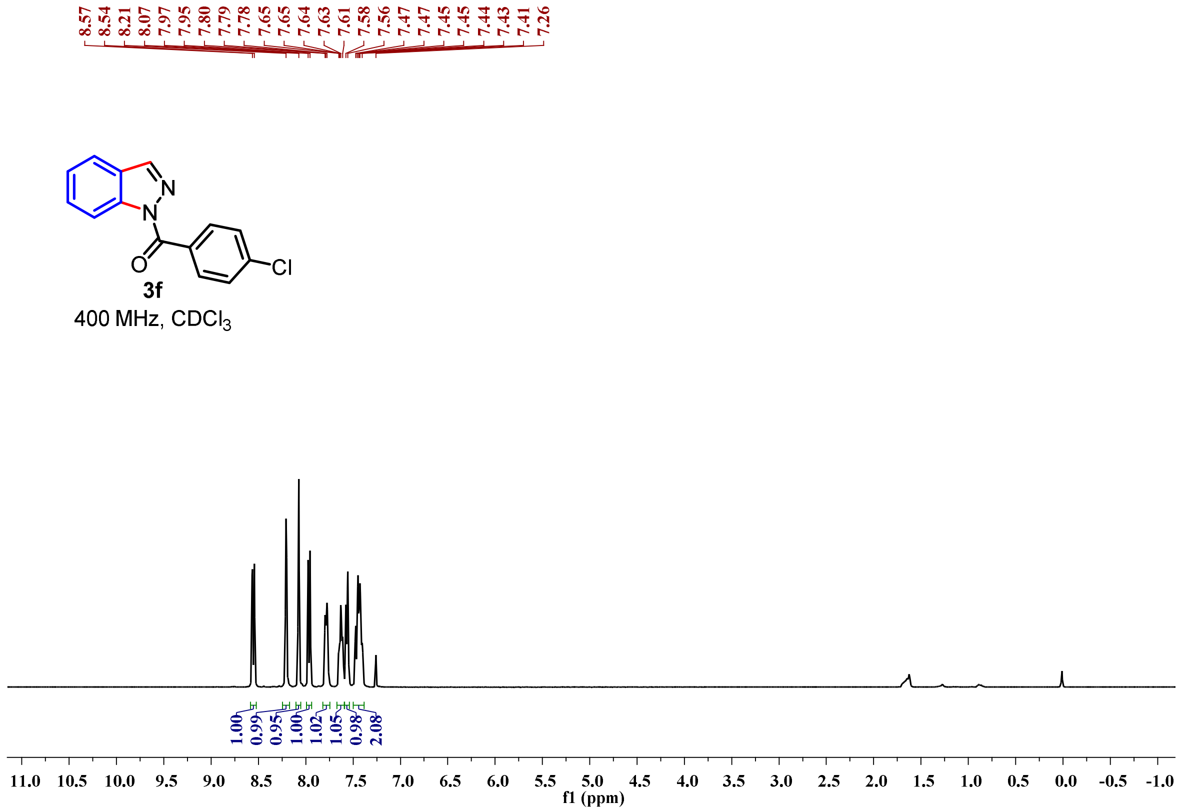

8.60
8.58
8.05
8.03
7.80
7.78
7.64
7.62
7.60
7.56
7.54
7.43
7.41
7.39
7.26
1.38
N
N
O
t-Bu
3d
400 MHz, CDCl3
1.00
0.98
2.01
1.01
1.04
2.05
1.02
9.00
f1 (ppm)

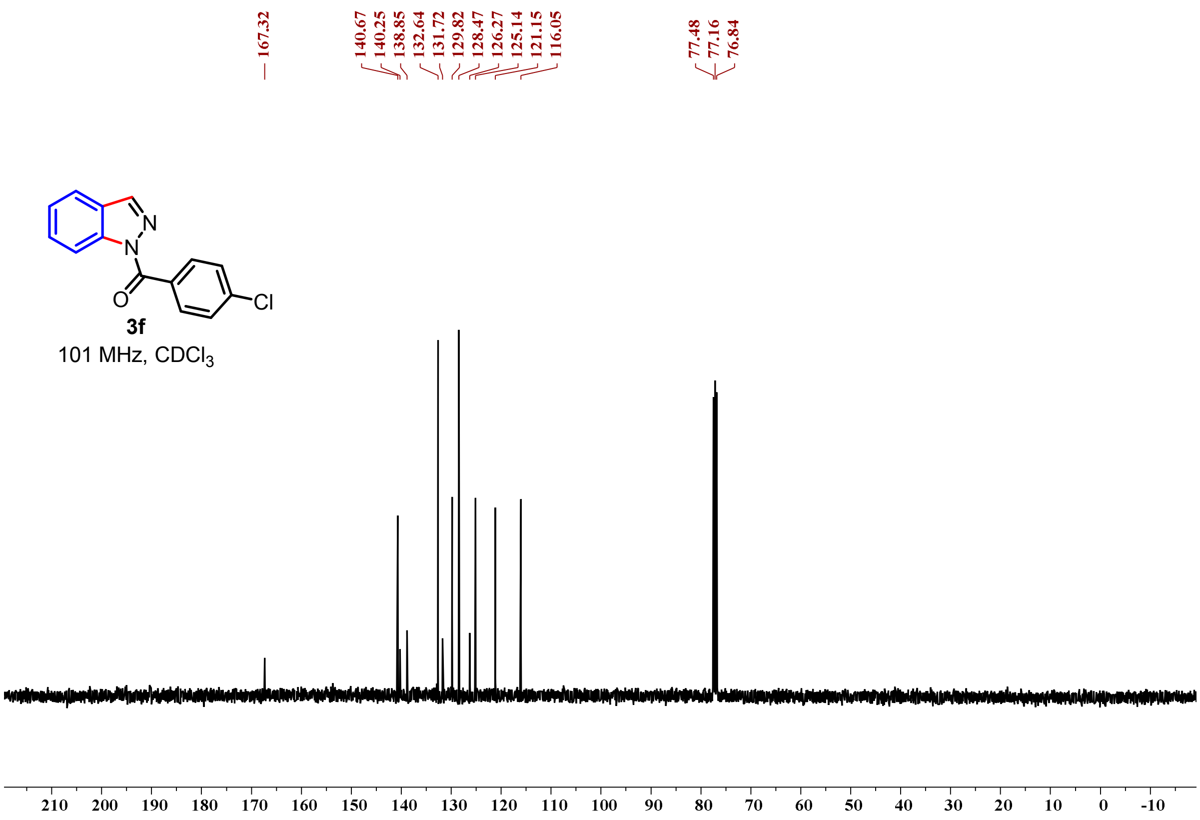

168.41
156.03
140.24
131.09
130.46
129.56
126.20
125.20
124.83
121.02
116.06
77.48
77.16
76.84
35.22
31.25
N
N
O
t-Bu
3d
101 MHz, CDCl3
f1 (ppm)


8.57
8.55
8.20
8.18
8.16
8.14
7.79
7.77
7.64
7.62
7.60
7.43
7.41
7.39
7.26
7.22
7.20
7.18
N
N
O
F
3e
400 MHz, $CDCl_3$
1.00
1.01
2.06
1.05
1.08
1.08
2.07
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.10
166.52
163.99
140.49
140.28
133.93
133.84
129.70
129.43
129.39
126.18
125.01
121.08
116.02
115.39
115.18
77.48
77.16
76.84
N
N
O
F
3e
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-106.15
N
N
O
F
3e
470 MHz, CDCl3
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)


8.57
8.54
8.21
8.07
7.97
7.95
7.80
7.79
7.78
7.65
7.65
7.64
7.63
7.61
7.58
7.56
7.47
7.47
7.45
7.45
7.44
7.43
7.41
7.26
N
N
O
Cl
3f
400 MHz, $CDCl_3$
1.00
0.99
0.95
1.00
1.02
1.05
0.98
2.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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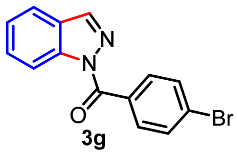
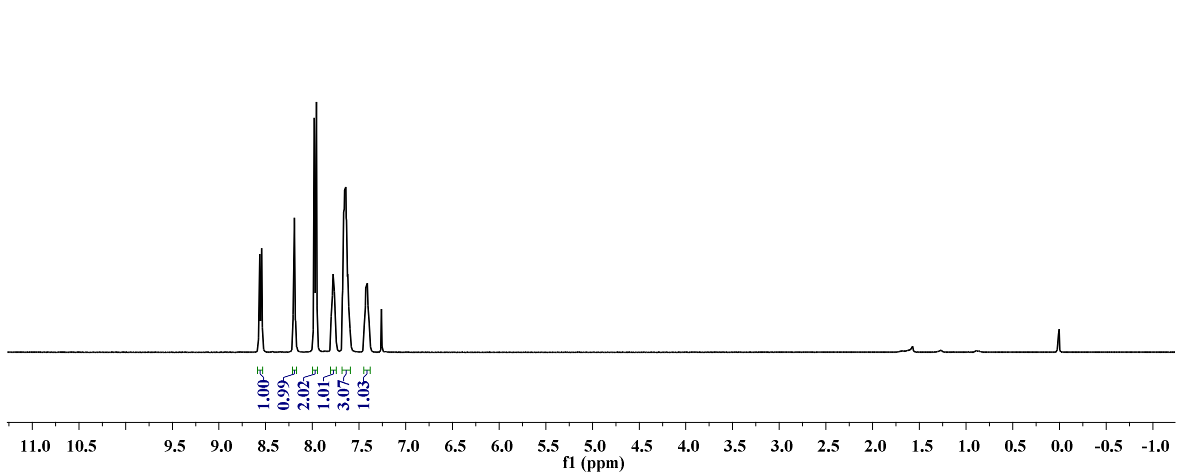
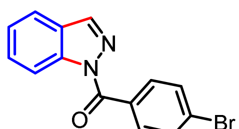
140.67
140.25
138.85
132.64
131.72
129.82
128.47
126.27
125.14
121.15
116.05
77.48
77.16
76.84
N
N
O
Cl
3f
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3g

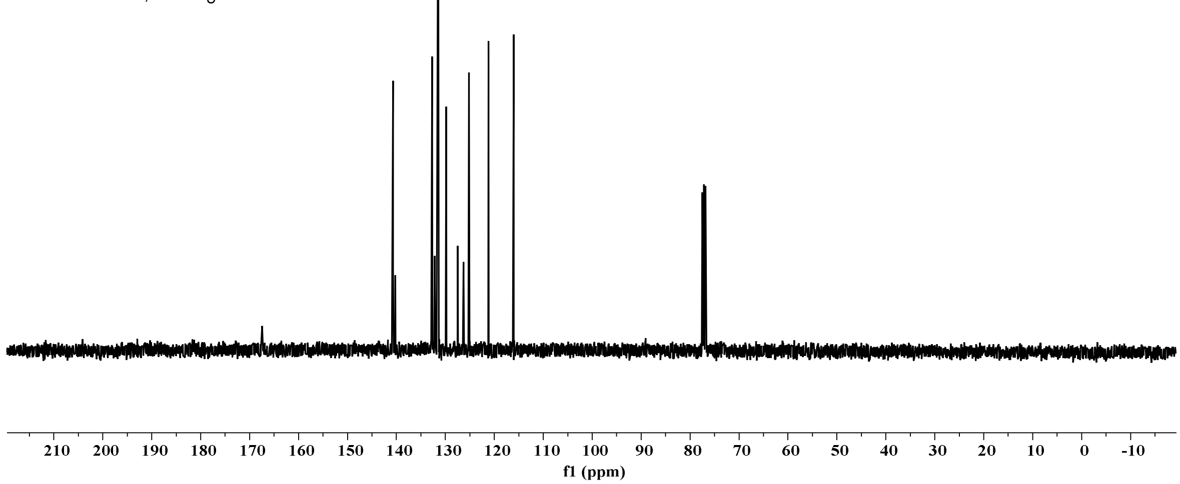
400 MHz, $CDCl_3$

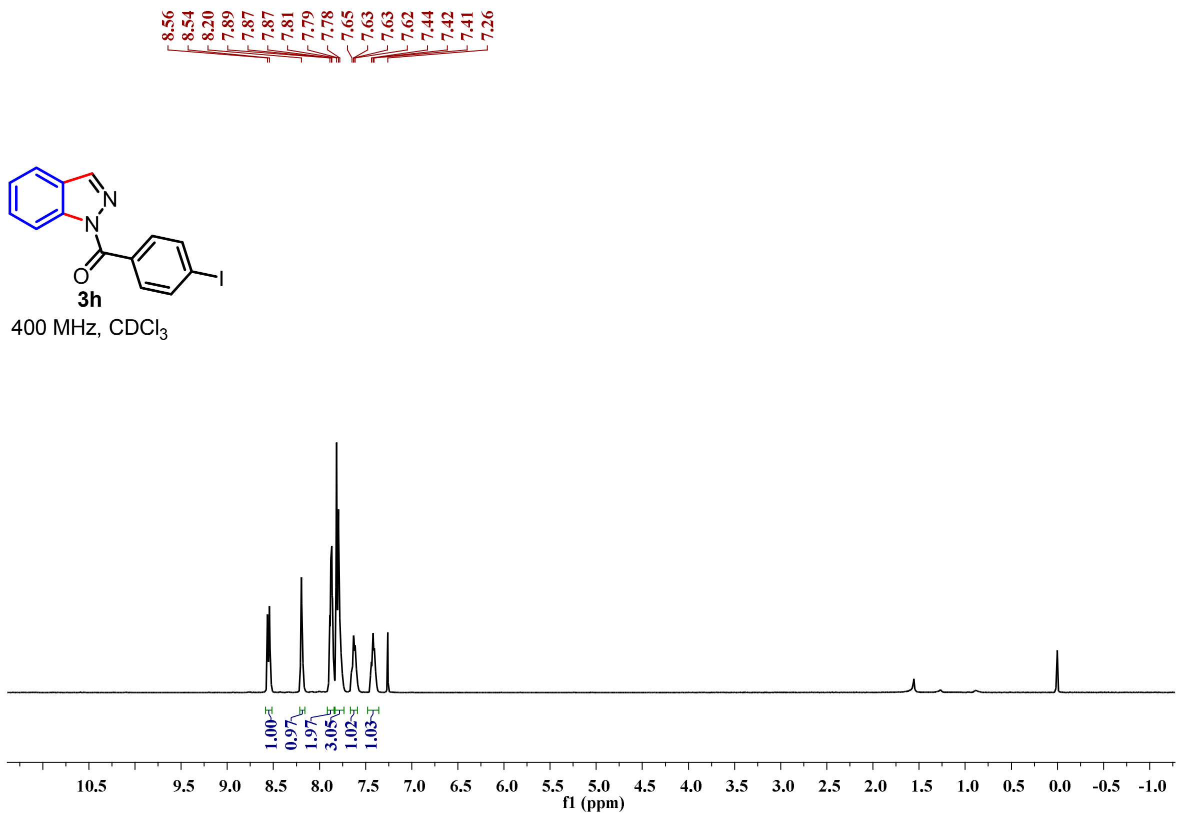


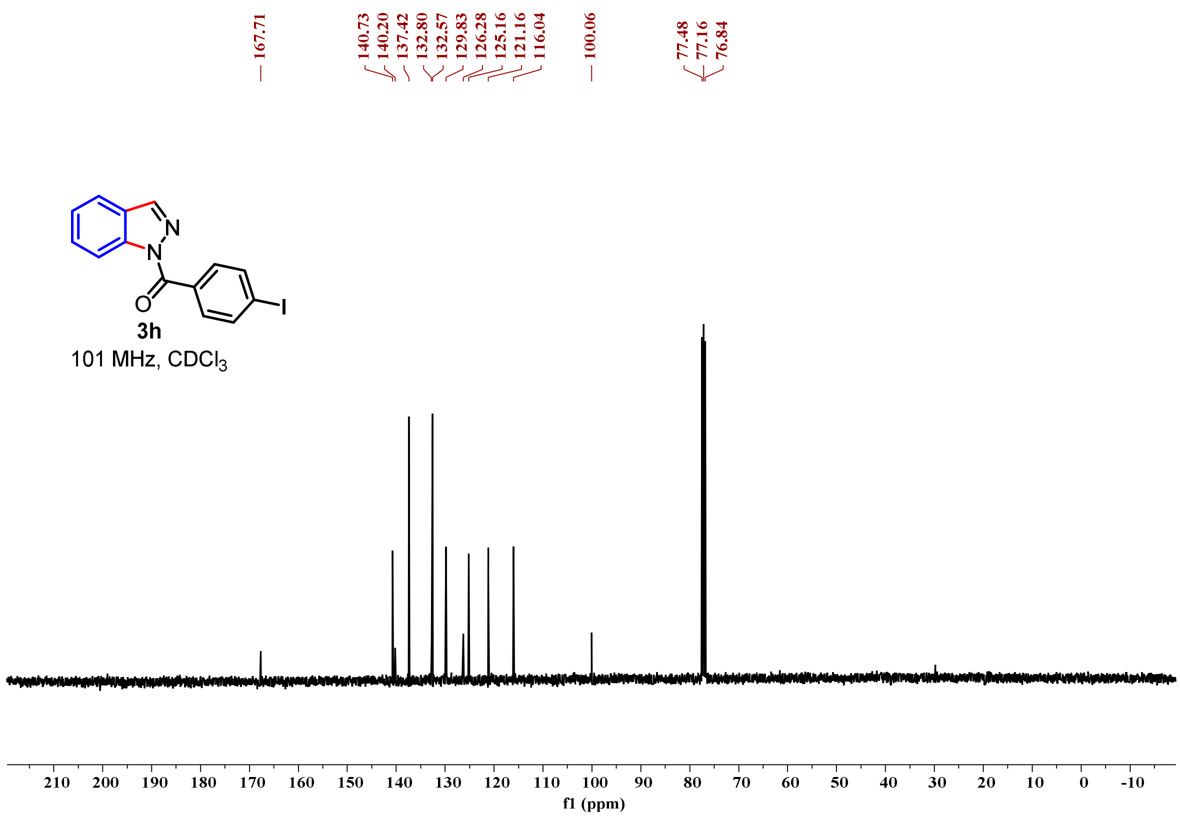


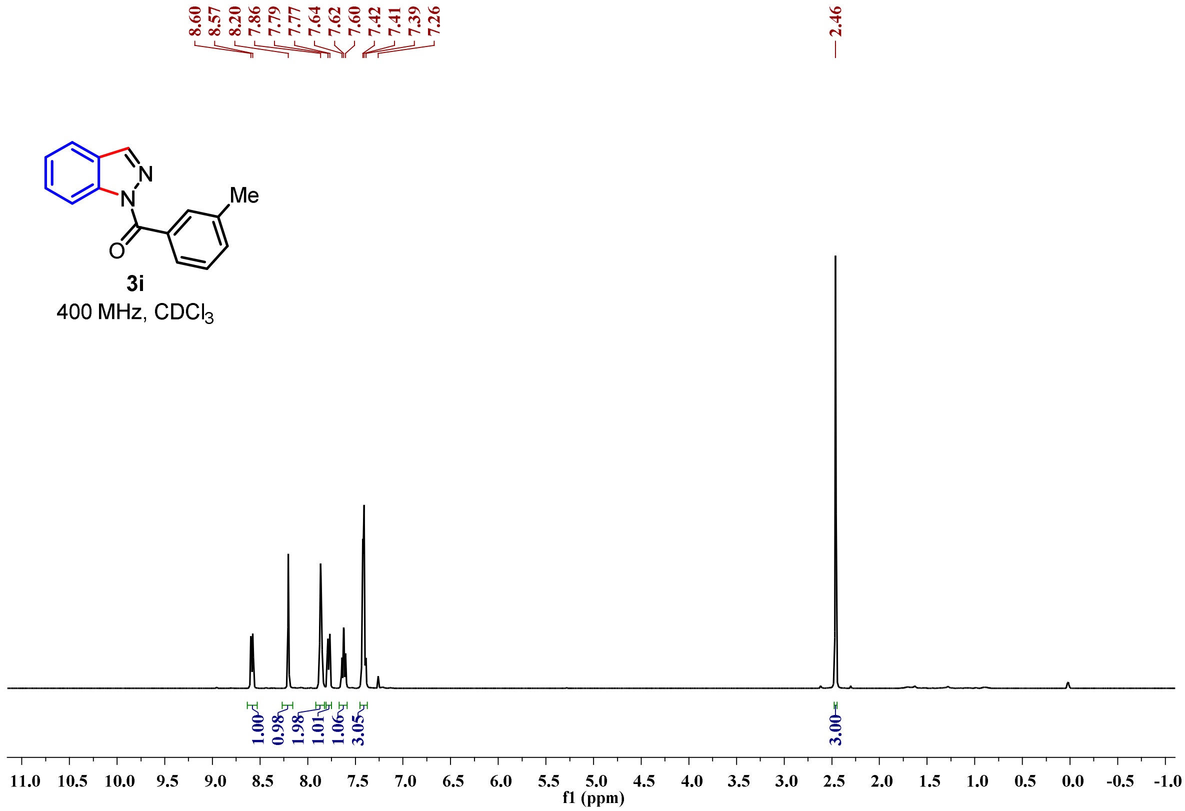
3g

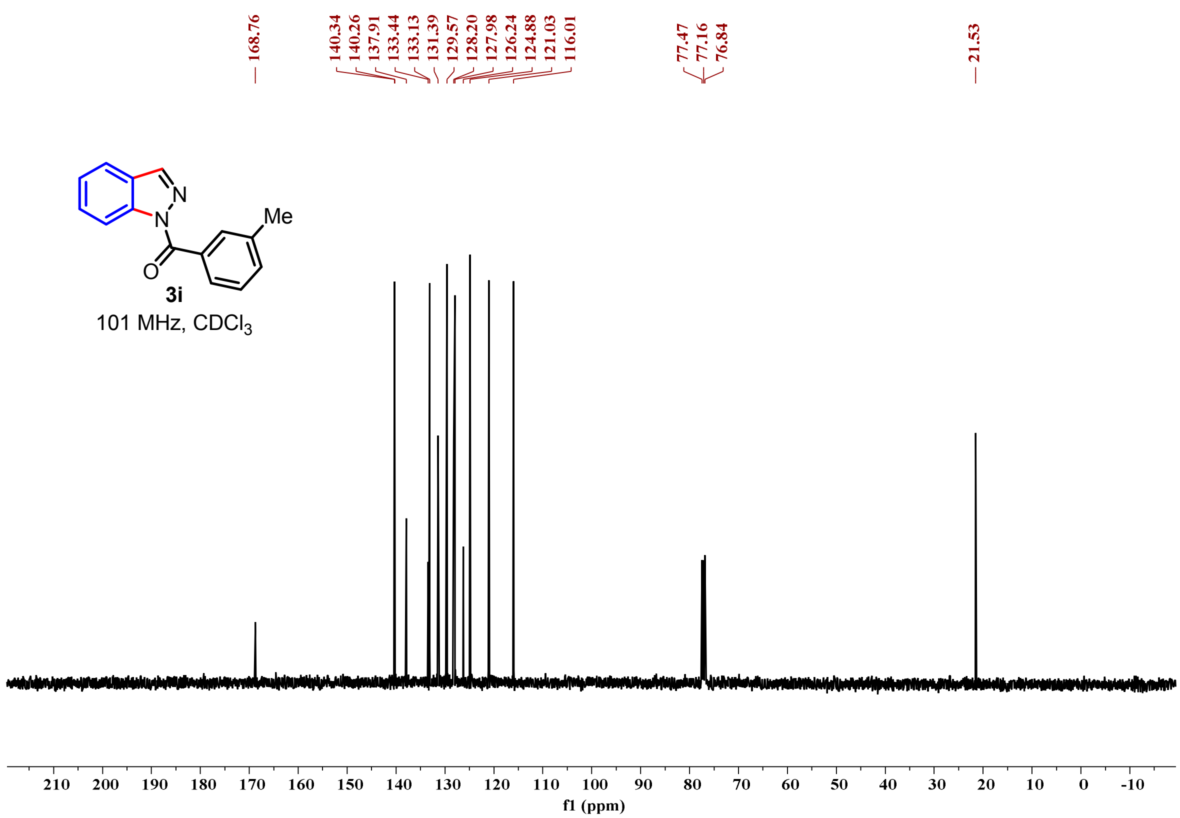
101 MHz, $CDCl_3$

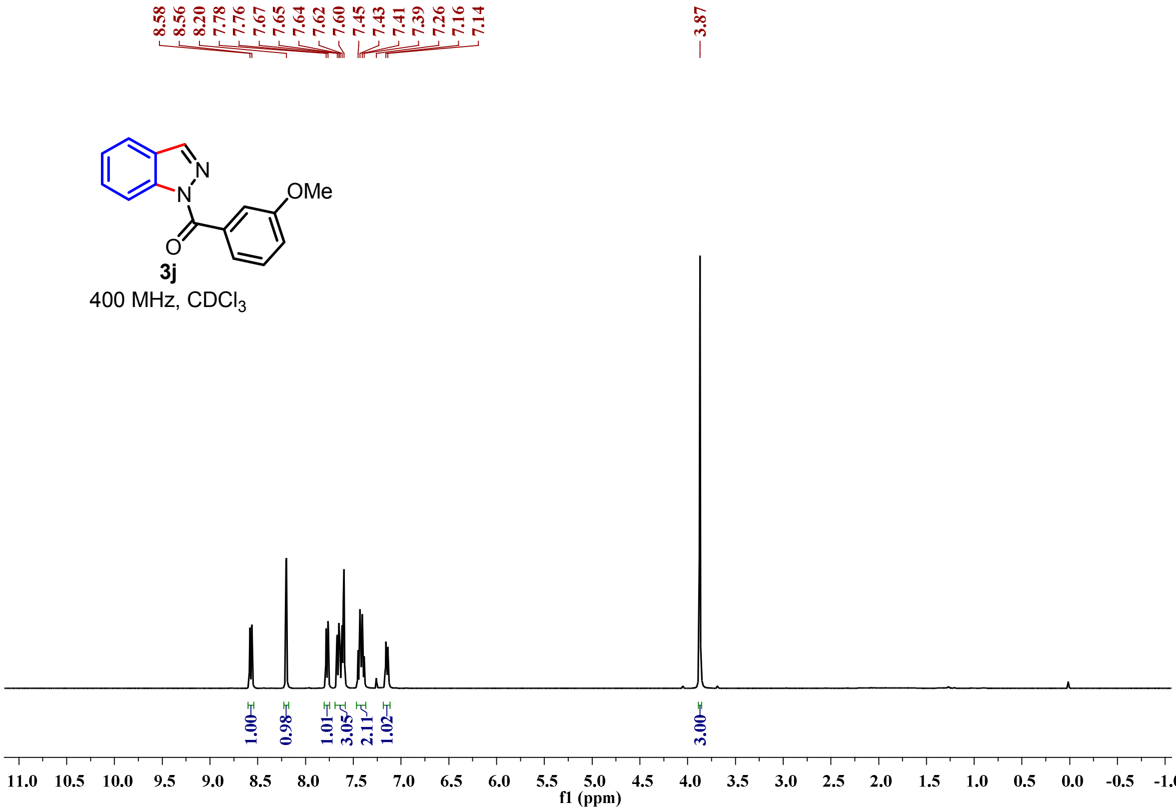


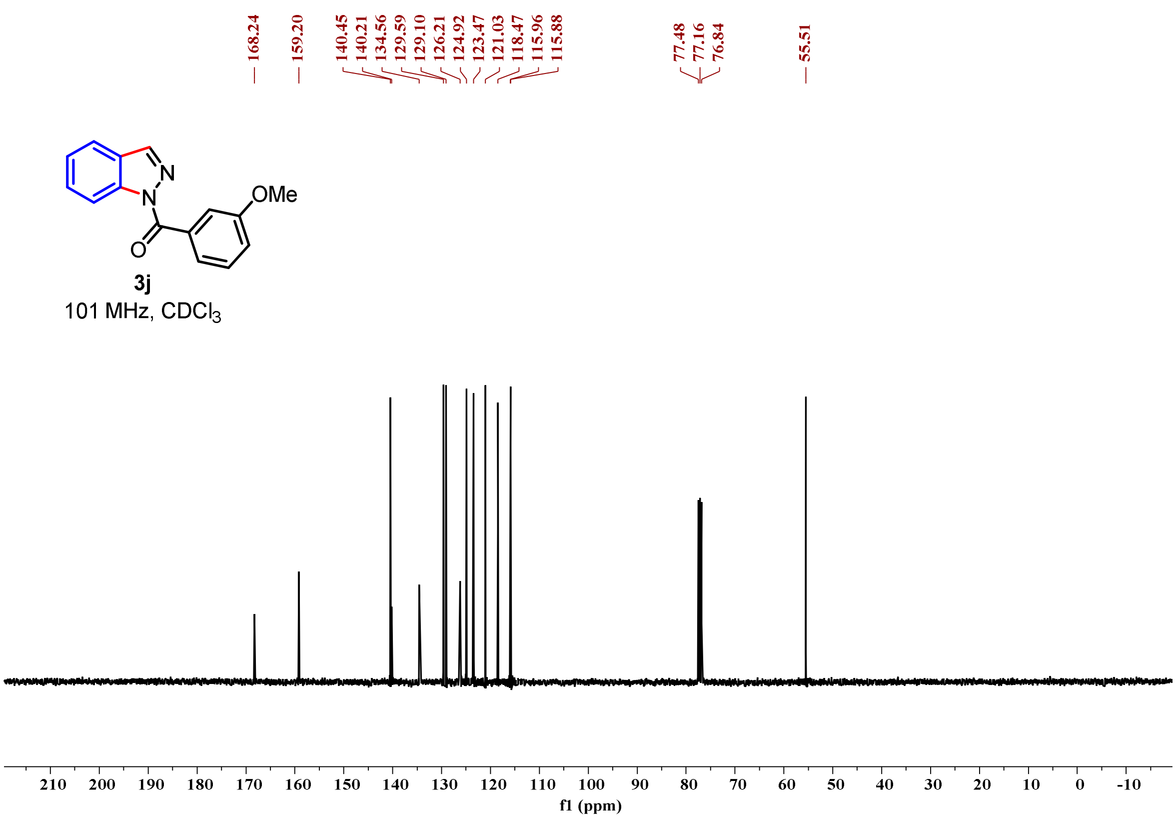

8.56 8.54 8.20 7.89 7.87 7.87 7.81 7.79 7.78 7.65 7.63 7.63 7.62 7.44 7.42 7.41 7.26
N
N
O
I
3h
400 MHz, CDCl3
1.00 0.97 1.97 3.05 1.02 1.03
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

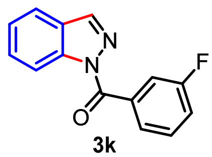

167.71
140.73 140.20 137.42 132.80 132.57 129.83 126.28 125.16 121.16 116.04
100.06
77.48 77.16 76.84
N
N
O
I
3h
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.60
8.57
8.20
7.86
7.79
7.77
7.64
7.62
7.60
7.42
7.41
7.39
7.26
2.46
Me
N
N
O
3i
400 MHz, CDCl3
1.00
0.98
1.98
1.01
1.06
3.05
3.00
f1 (ppm)


168.76
140.34
140.26
137.91
133.44
133.13
131.39
129.57
128.20
127.98
126.24
124.88
121.03
116.01
77.47
77.16
76.84
21.53
Me
N
N
O
3i
101 MHz, CDCl3
f1 (ppm)

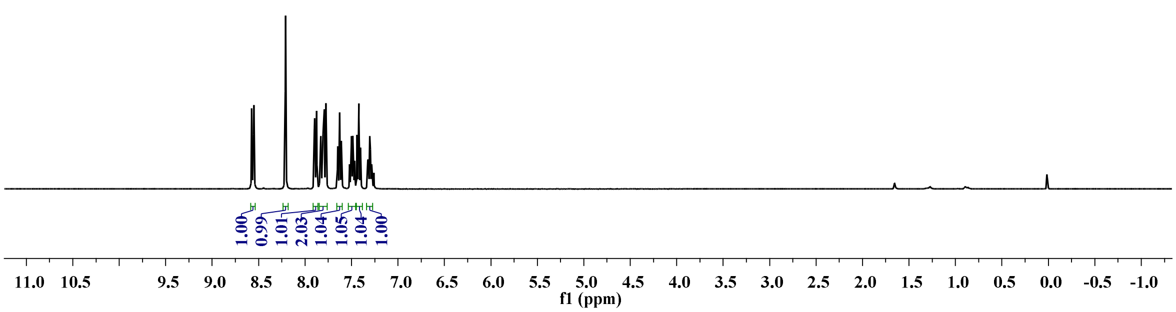

8.58
8.56
8.20
7.78
7.76
7.67
7.65
7.64
7.62
7.60
7.45
7.43
7.41
7.39
7.26
7.16
7.14
3.87
OMe
3j
400 MHz, CDCl3
1.00
0.98
1.01
3.05
2.11
1.02
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

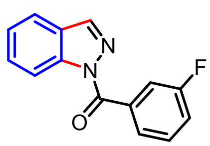

168.24
159.20
140.45
140.21
134.56
129.59
129.10
126.21
124.92
123.47
121.03
118.47
115.96
115.88
77.48
77.16
76.84
55.51
OMe
3j
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3k

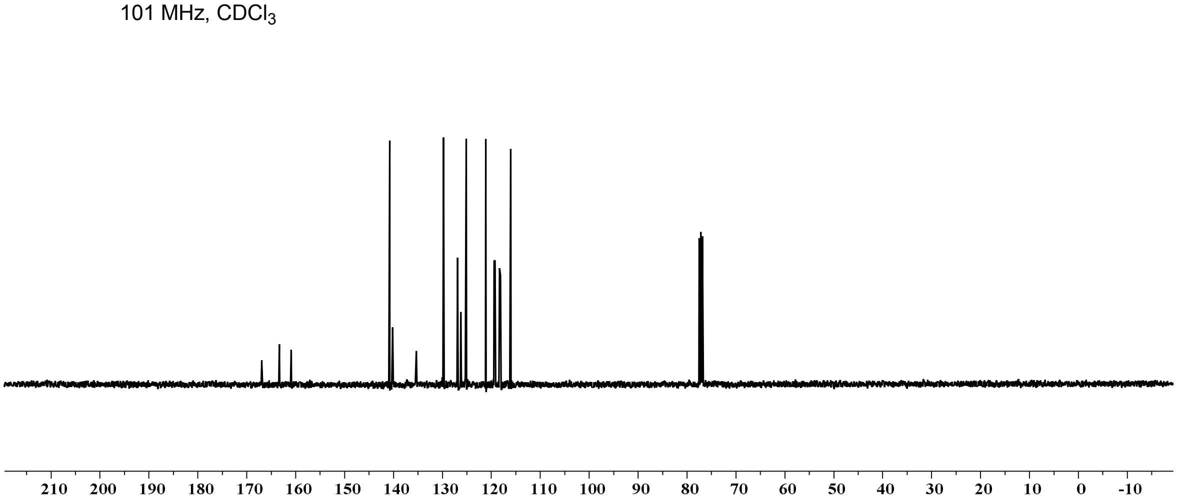
400 MHz, $CDCl_3$

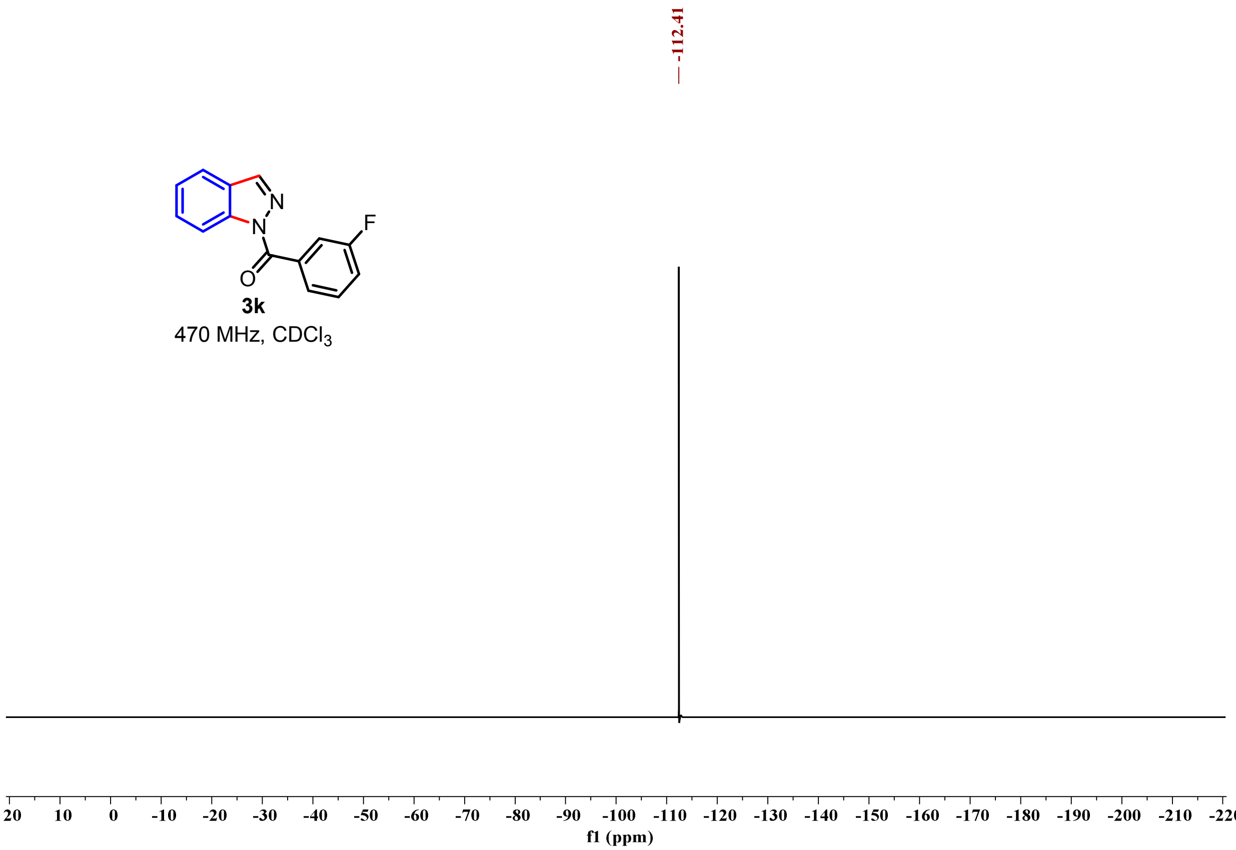




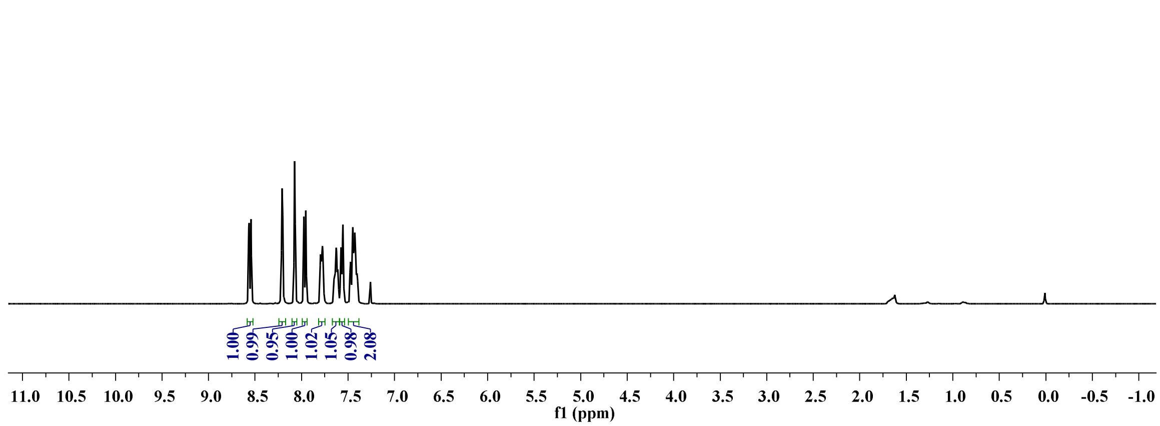
3k

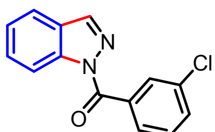
101 MHz, $CDCl_3$





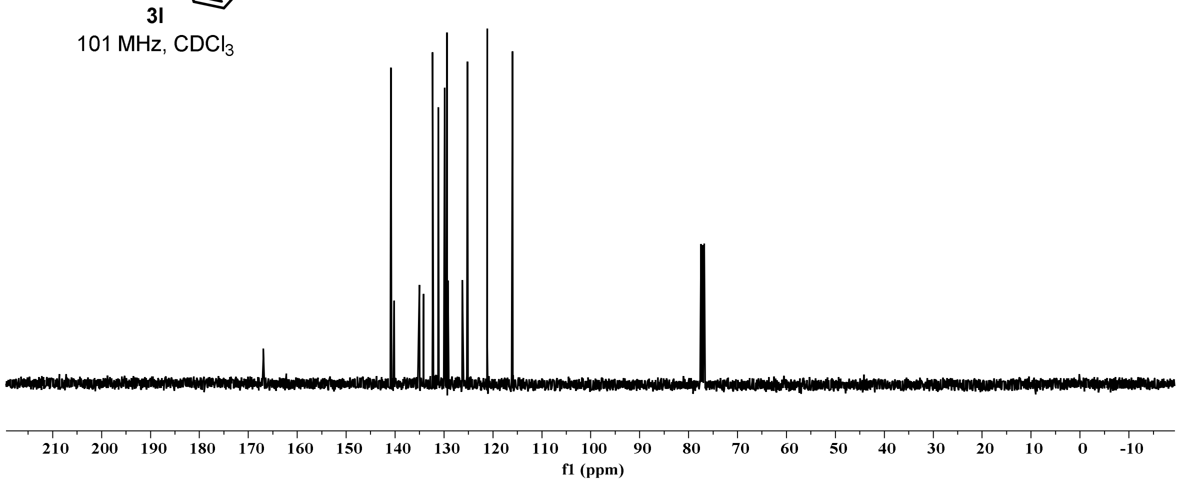
-112.41
N
N
F
O
3k
470 MHz, CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

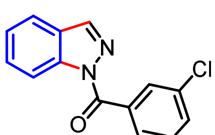




3l

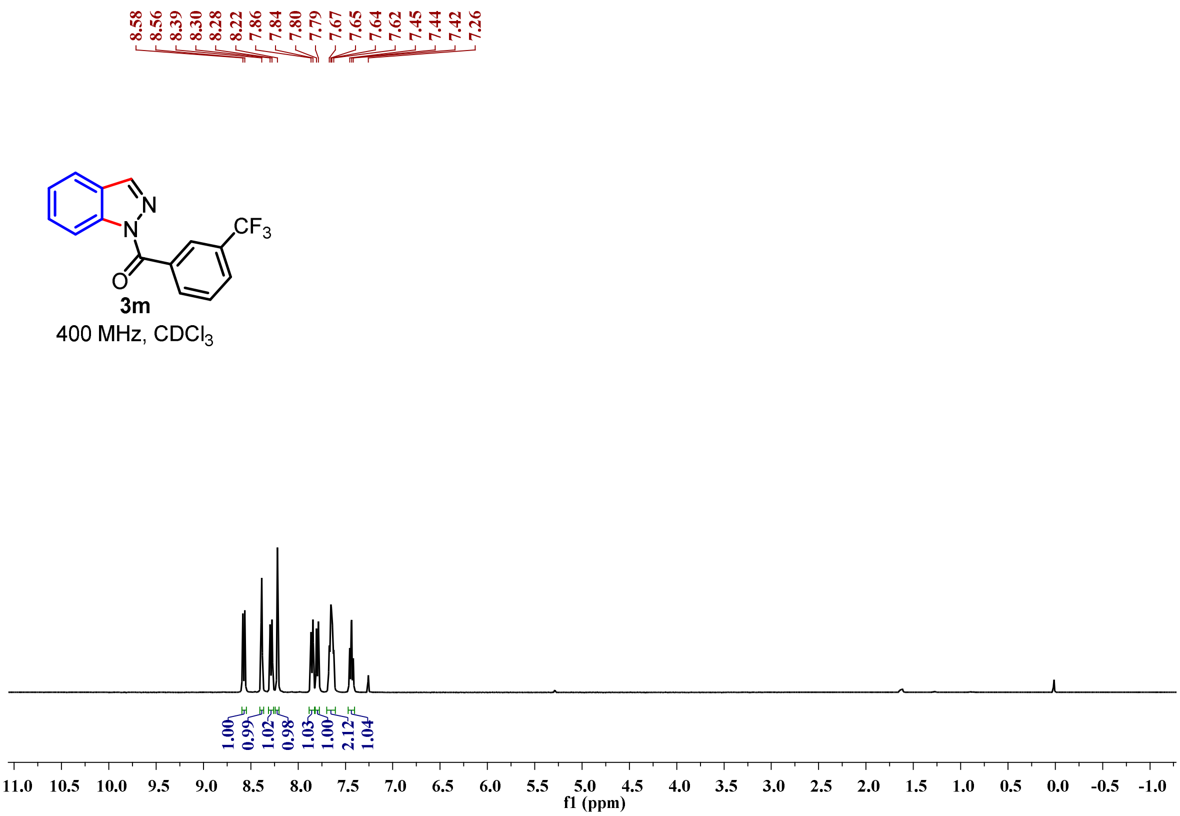
400 MHz, $CDCl_3$

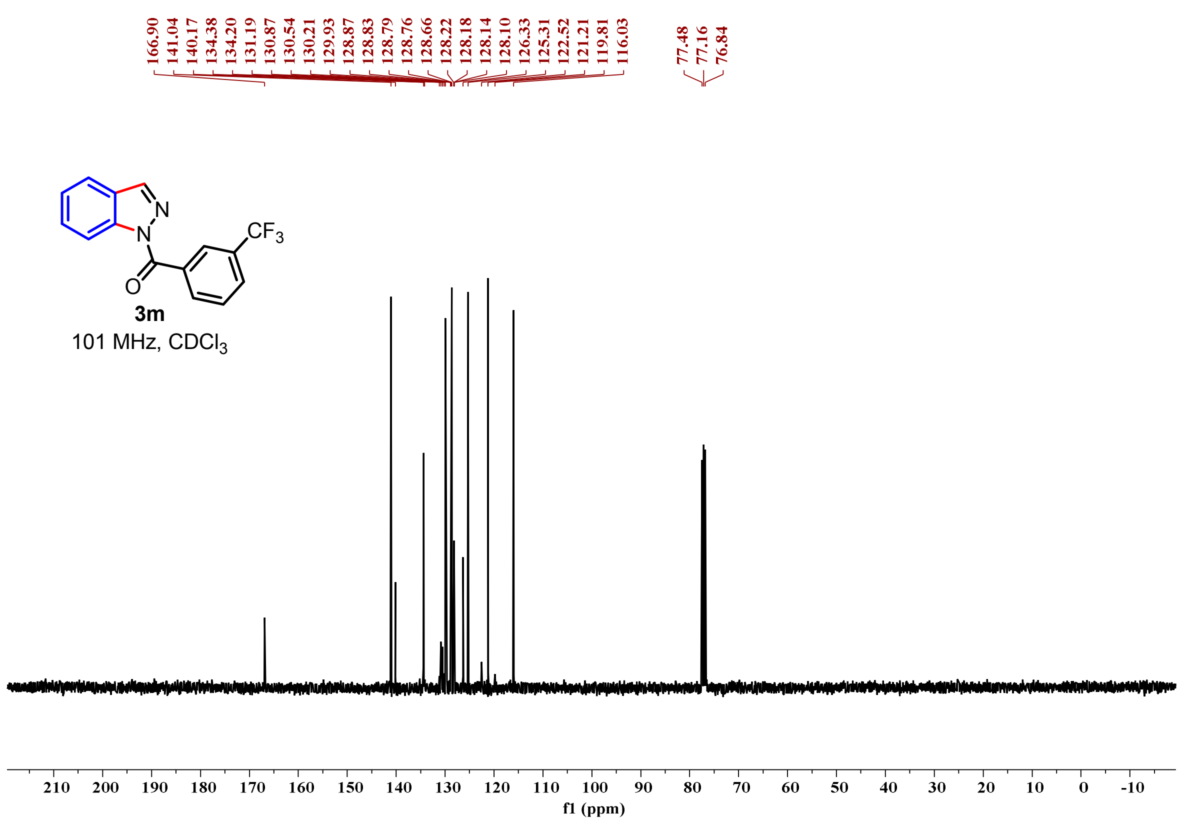


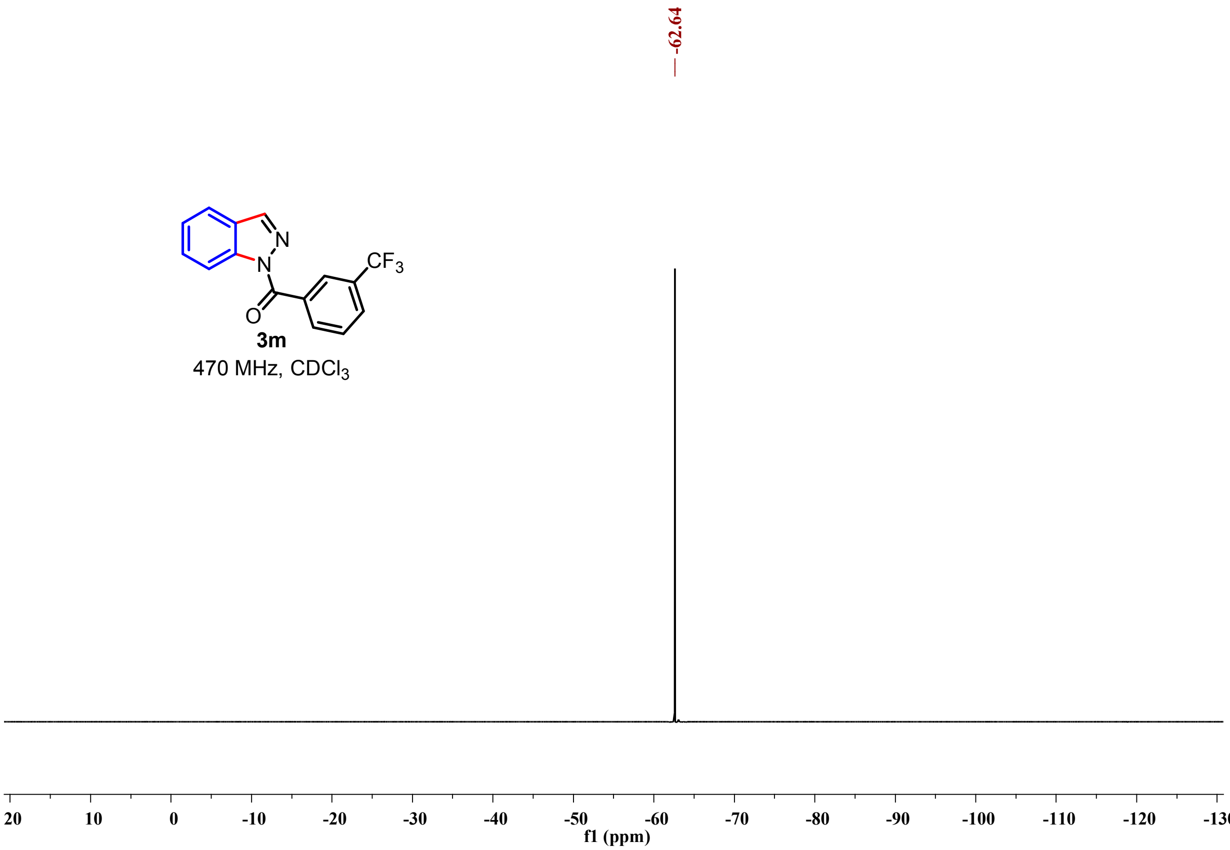


3l

101 MHz, $CDCl_3$

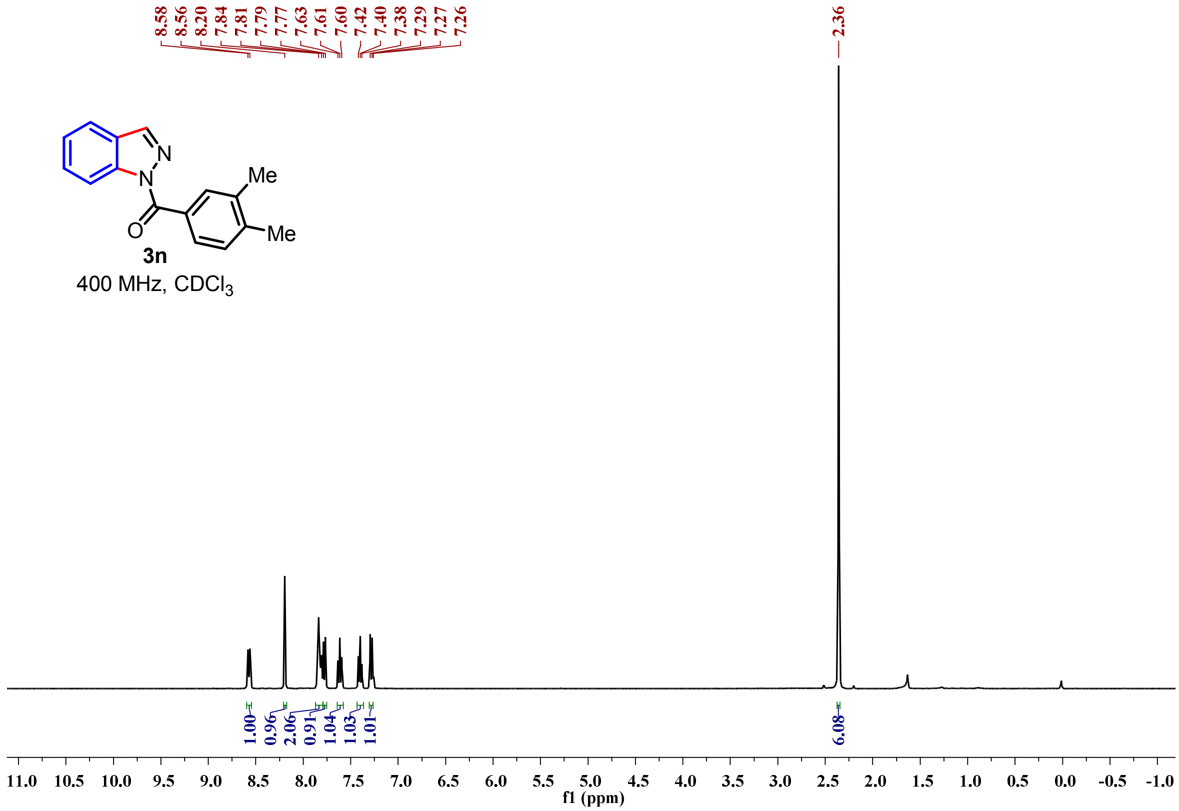

8.58 8.56 8.39 8.30 8.28 8.22 7.86 7.84 7.80 7.79 7.67 7.65 7.64 7.62 7.45 7.44 7.42 7.26
CF3
N
N
O
3m
400 MHz, CDCl3
1.00 0.99 1.02 0.98 1.03 1.00 2.12 1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

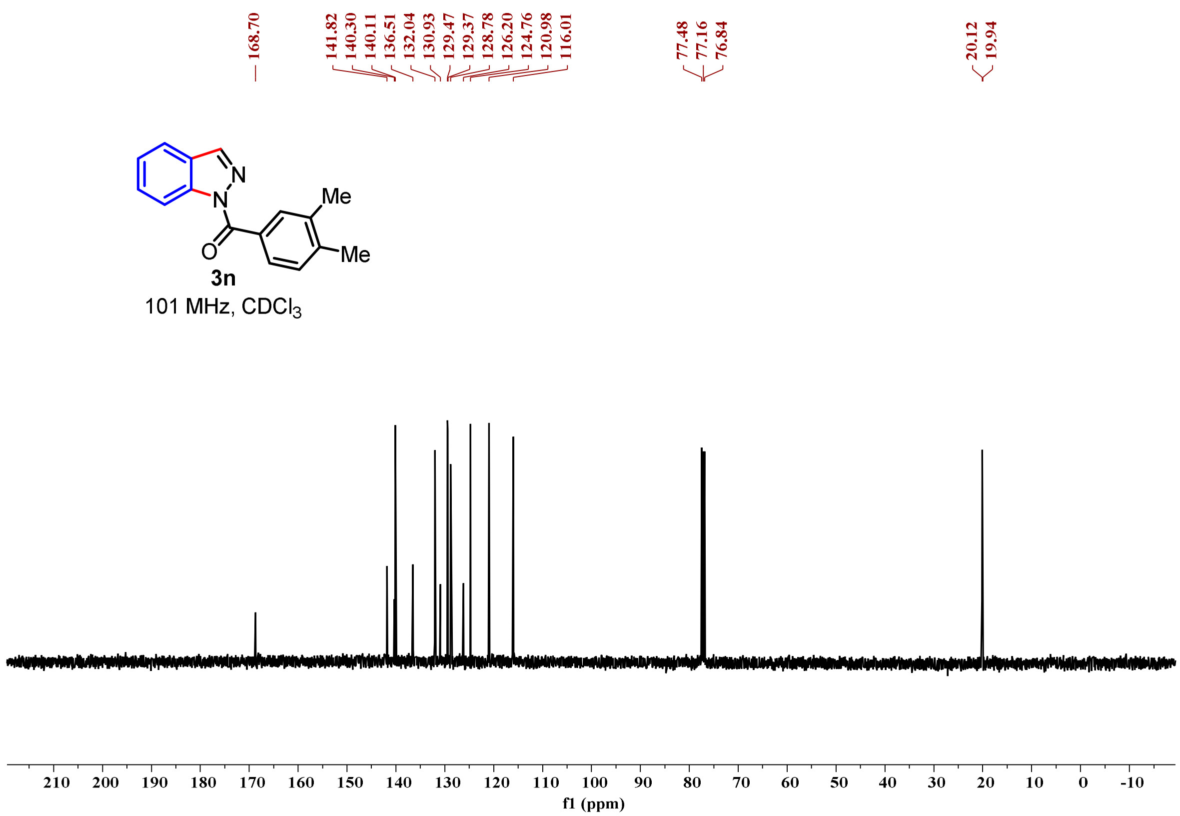

166.90 141.04 140.17 134.38 134.20 131.19 130.87 130.54 130.21 129.93 128.87 128.83 128.79 128.76 128.66 128.22 128.18 128.14 128.10 126.33 125.31 122.52 121.21 119.81 116.03
77.48 77.16 76.84
CF3
N
N
O
3m
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

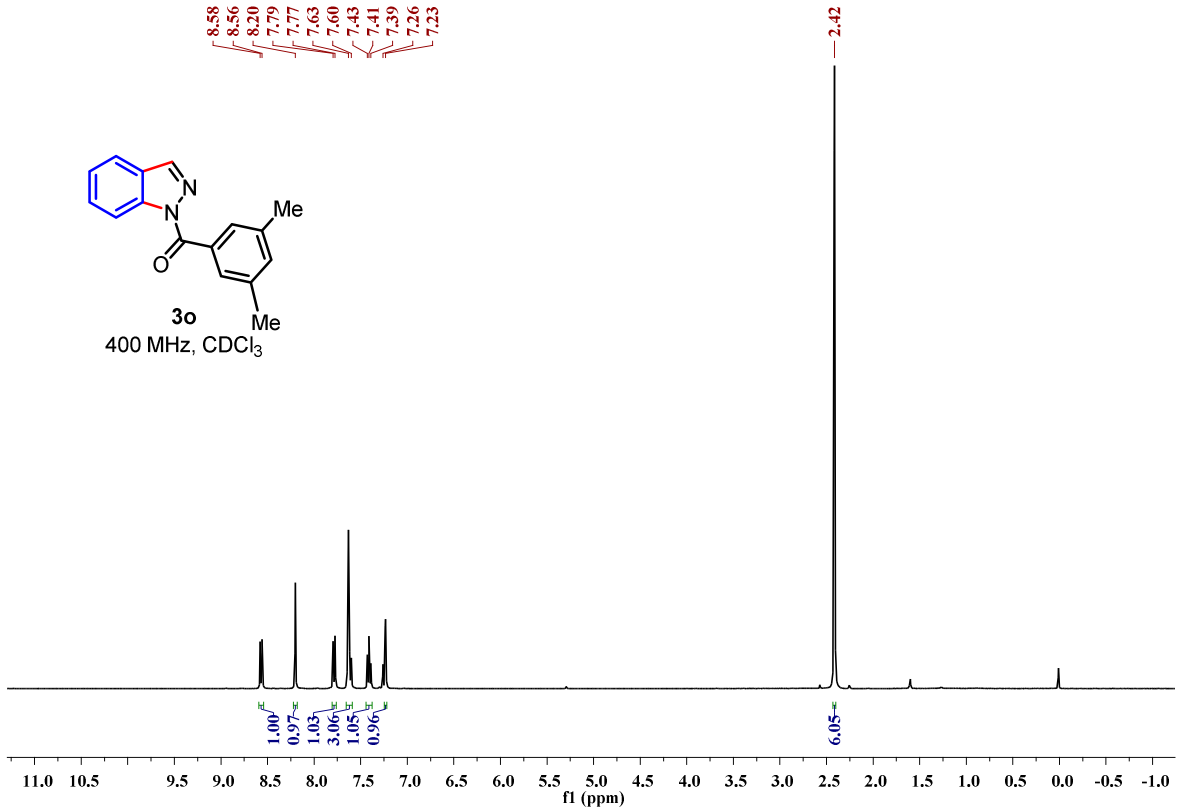


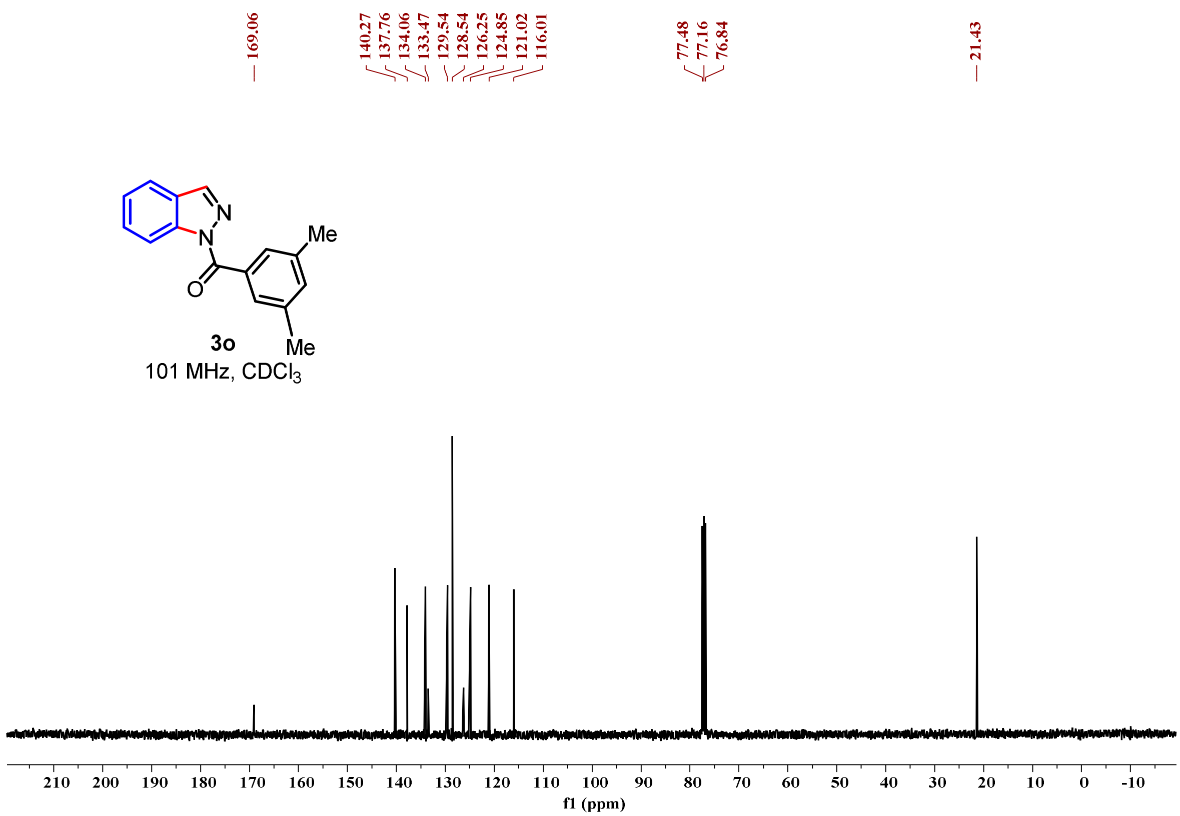
3m

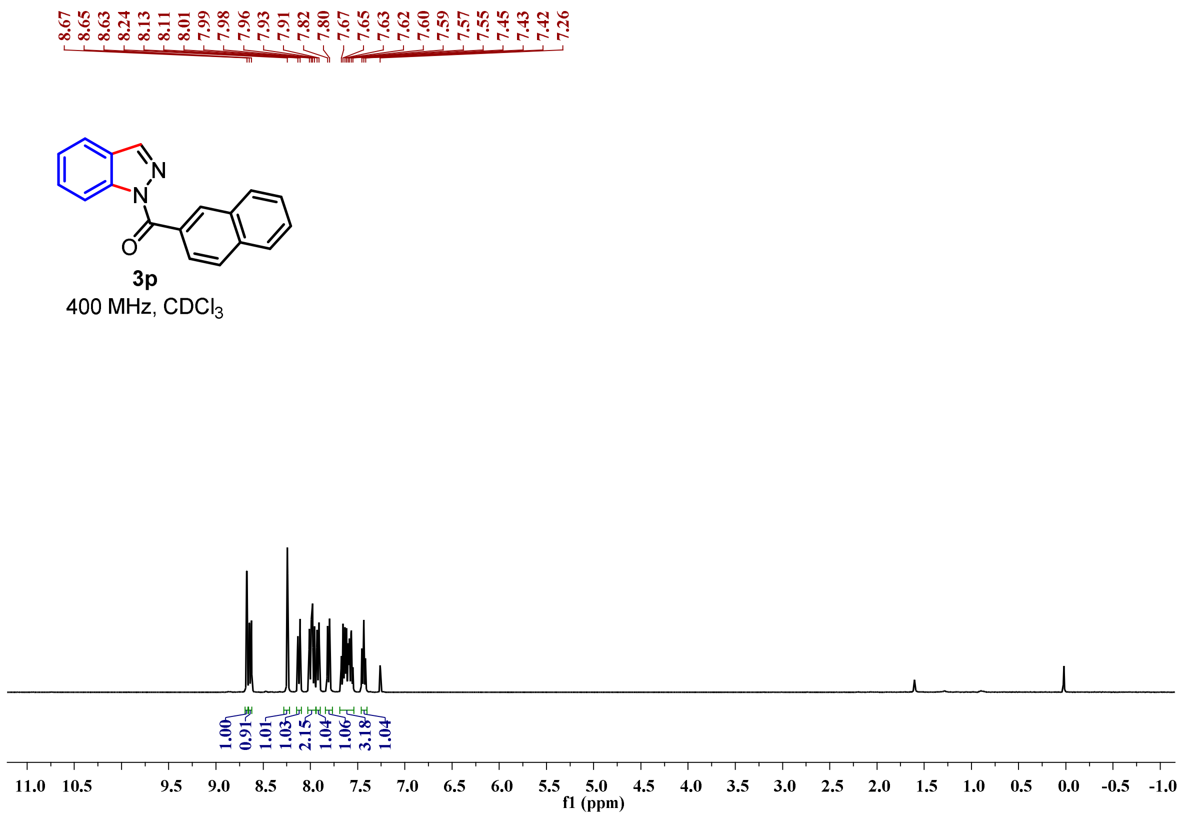
470 MHz, $CDCl_3$

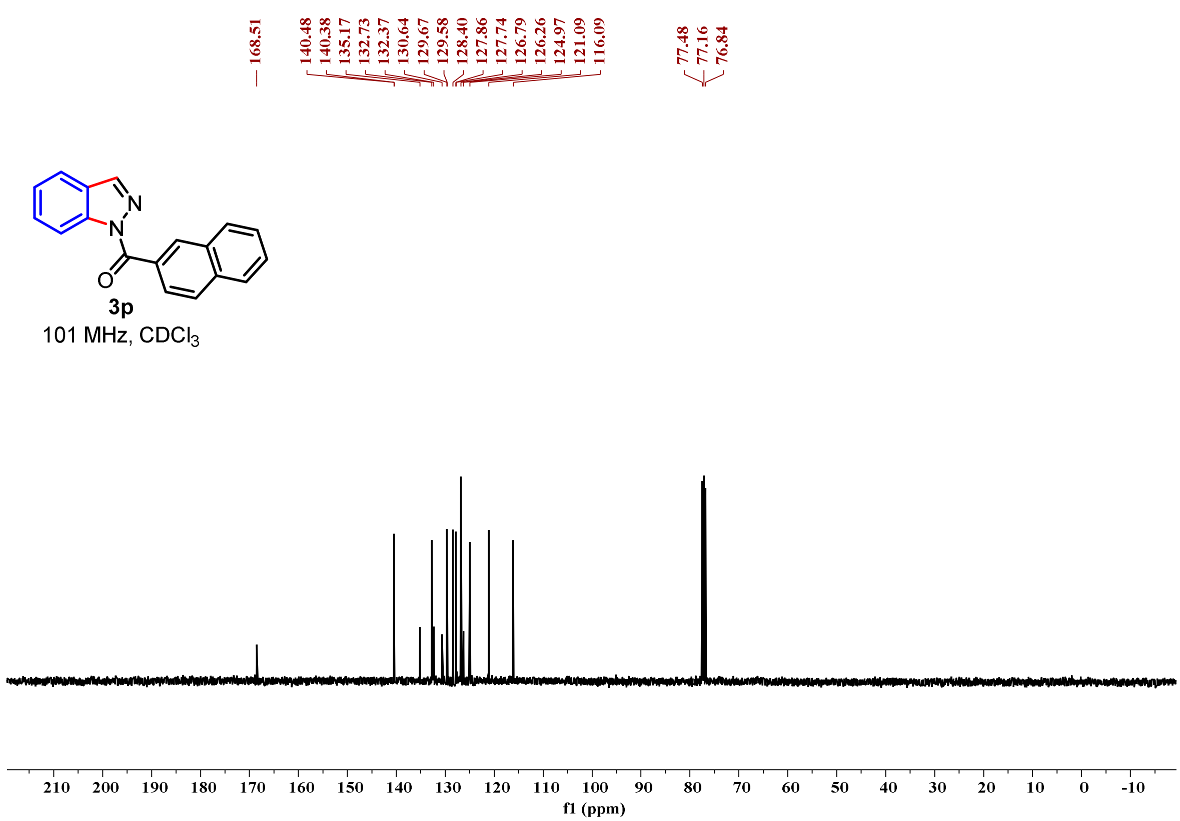

8.58
8.56
8.20
7.84
7.81
7.79
7.77
7.63
7.61
7.60
7.42
7.40
7.38
7.29
7.27
7.26
2.36
Me
Me
N
N
O
3n
400 MHz, $CDCl_3$
1.00
0.96
2.06
0.91
1.04
1.03
1.01
6.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

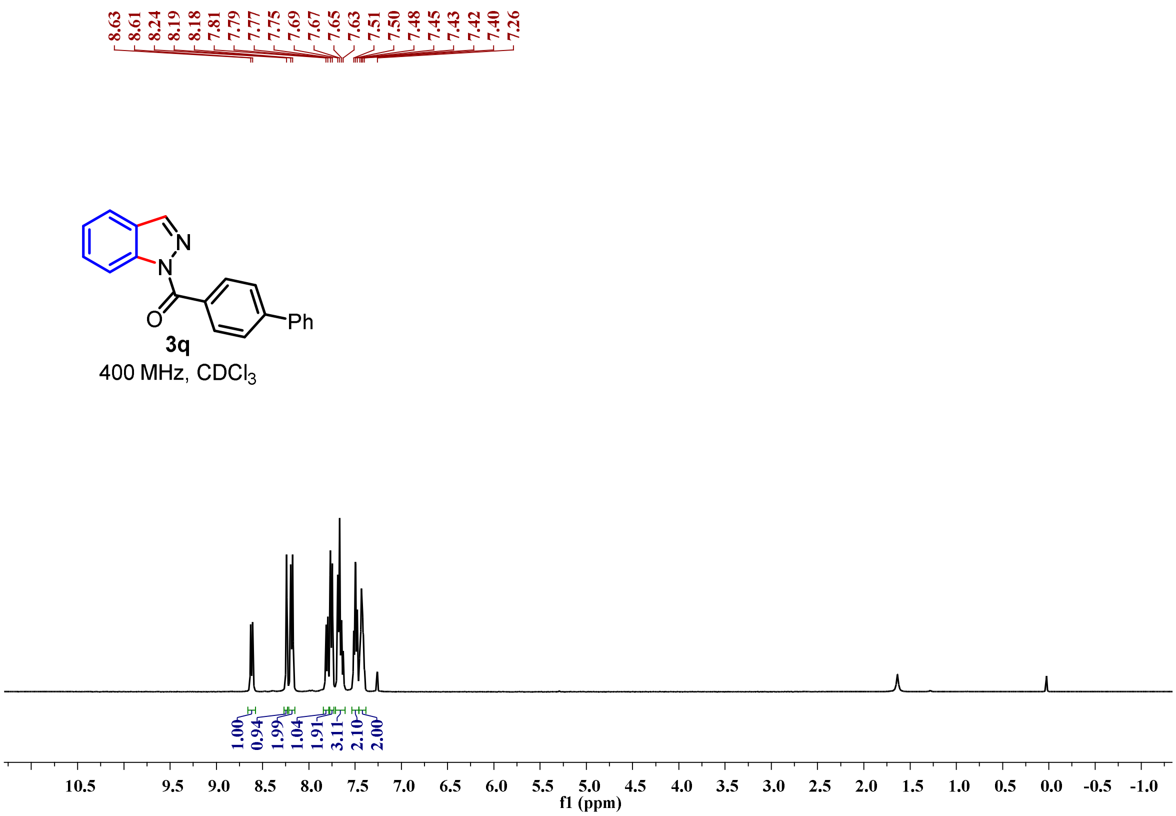

168.70
141.82
140.30
140.11
136.51
132.04
130.93
129.47
129.37
128.78
126.20
124.76
120.98
116.01
77.48
77.16
76.84
20.12
19.94
Me
Me
N
N
O
3n
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

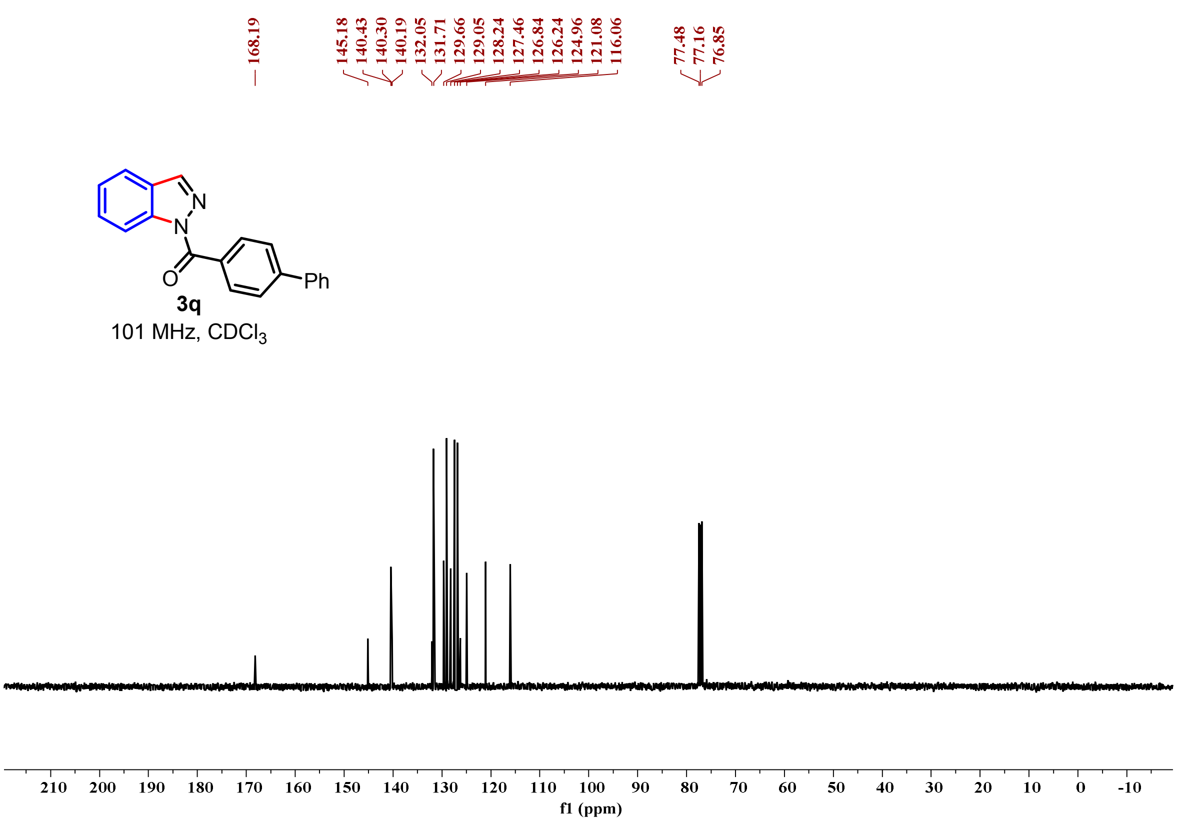

8.58
8.56
8.20
7.79
7.77
7.63
7.60
7.43
7.41
7.39
7.26
7.23
2.42
Me
Me
3o
400 MHz, CDCl3
f1 (ppm)

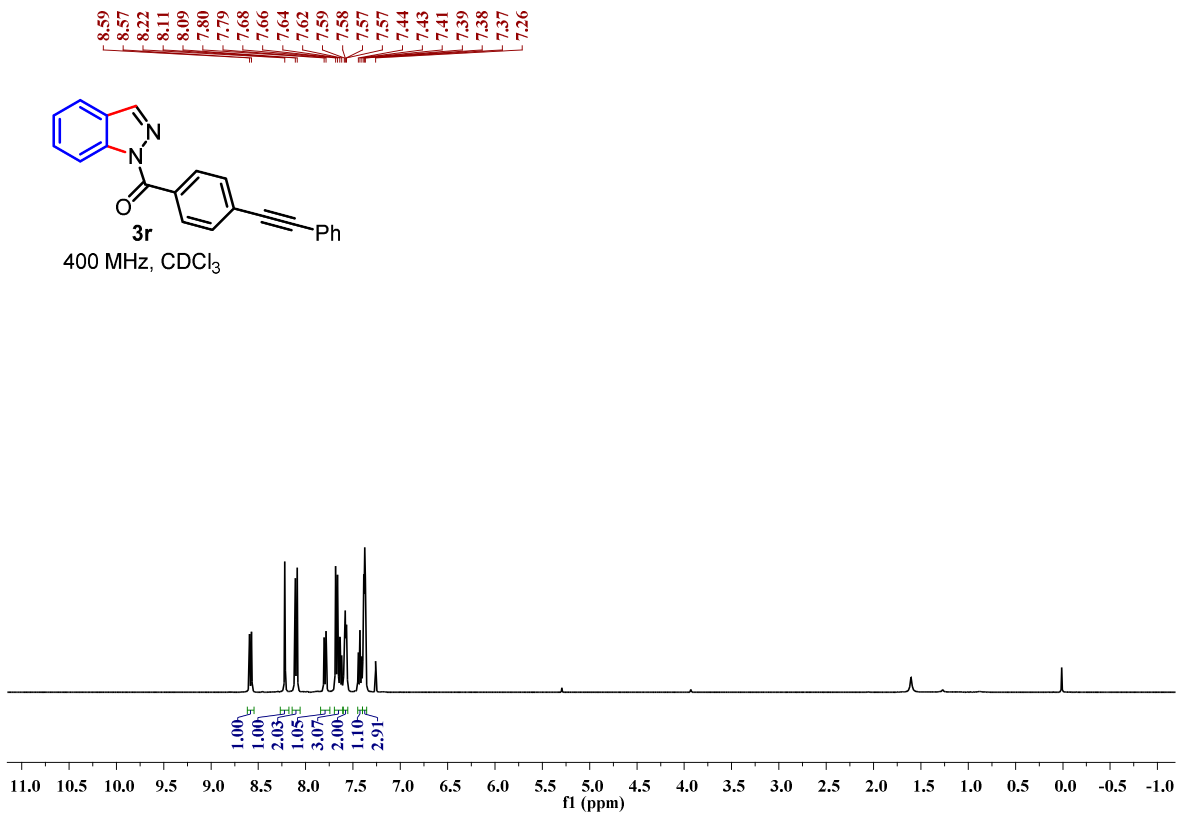

169.06
140.27
137.76
134.06
133.47
129.54
128.54
126.25
124.85
121.02
116.01
77.48
77.16
76.84
21.43
Me
Me
3o
101 MHz, CDCl3
f1 (ppm)

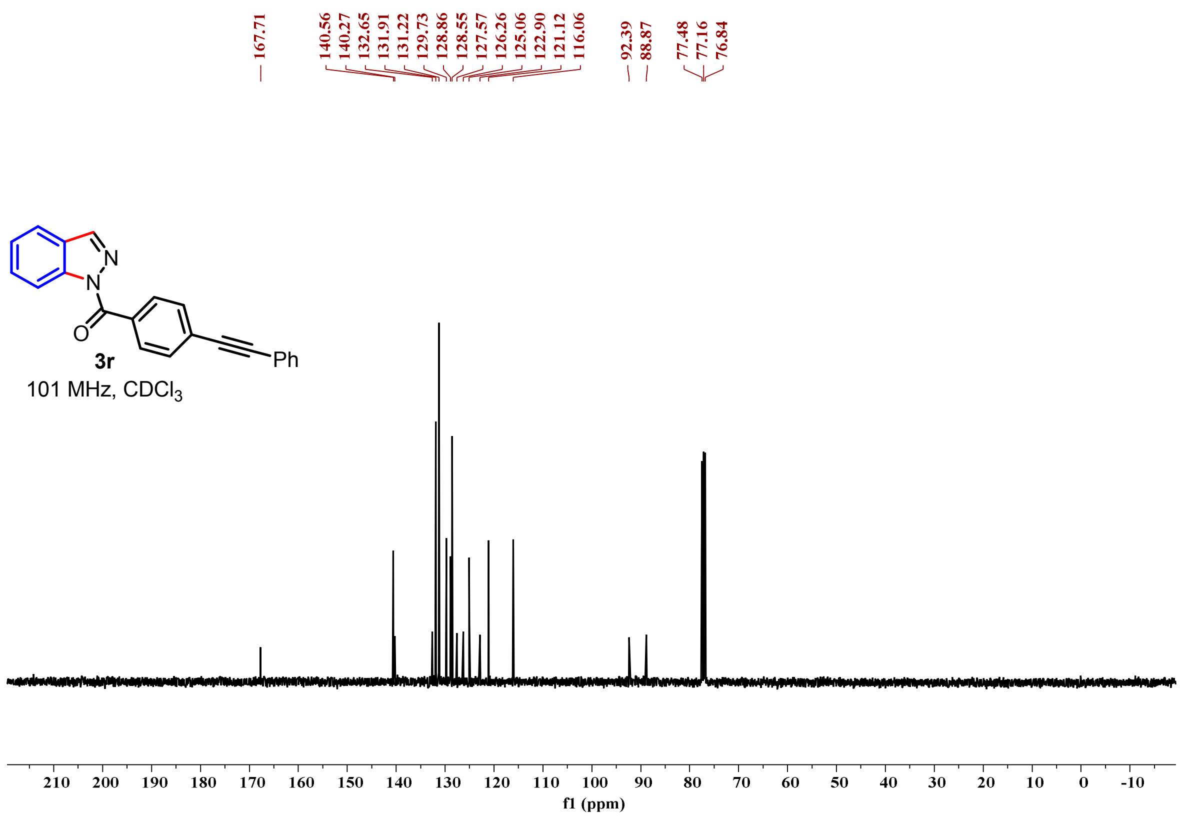

8.67
8.65
8.63
8.24
8.13
8.11
8.01
7.99
7.98
7.96
7.93
7.91
7.82
7.80
7.67
7.65
7.63
7.62
7.60
7.59
7.57
7.55
7.45
7.43
7.42
7.26
N
N
O
3p
400 MHz, $CDCl_3$
1.00
0.91
1.01
1.03
2.15
1.04
1.06
3.18
1.04
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

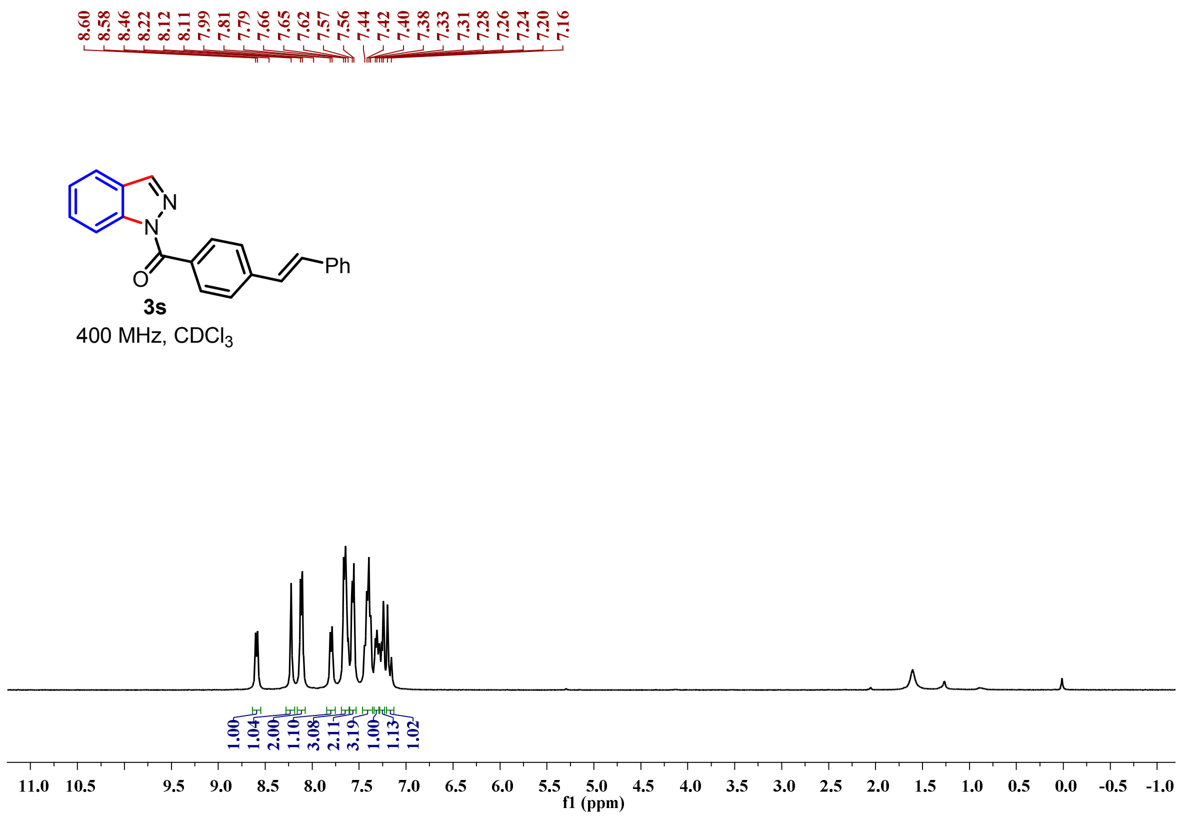

168.51
140.48
140.38
135.17
132.73
132.37
130.64
129.67
129.58
128.40
127.86
127.74
126.79
126.26
124.97
121.09
116.09
77.48
77.16
76.84
N
N
O
3p
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

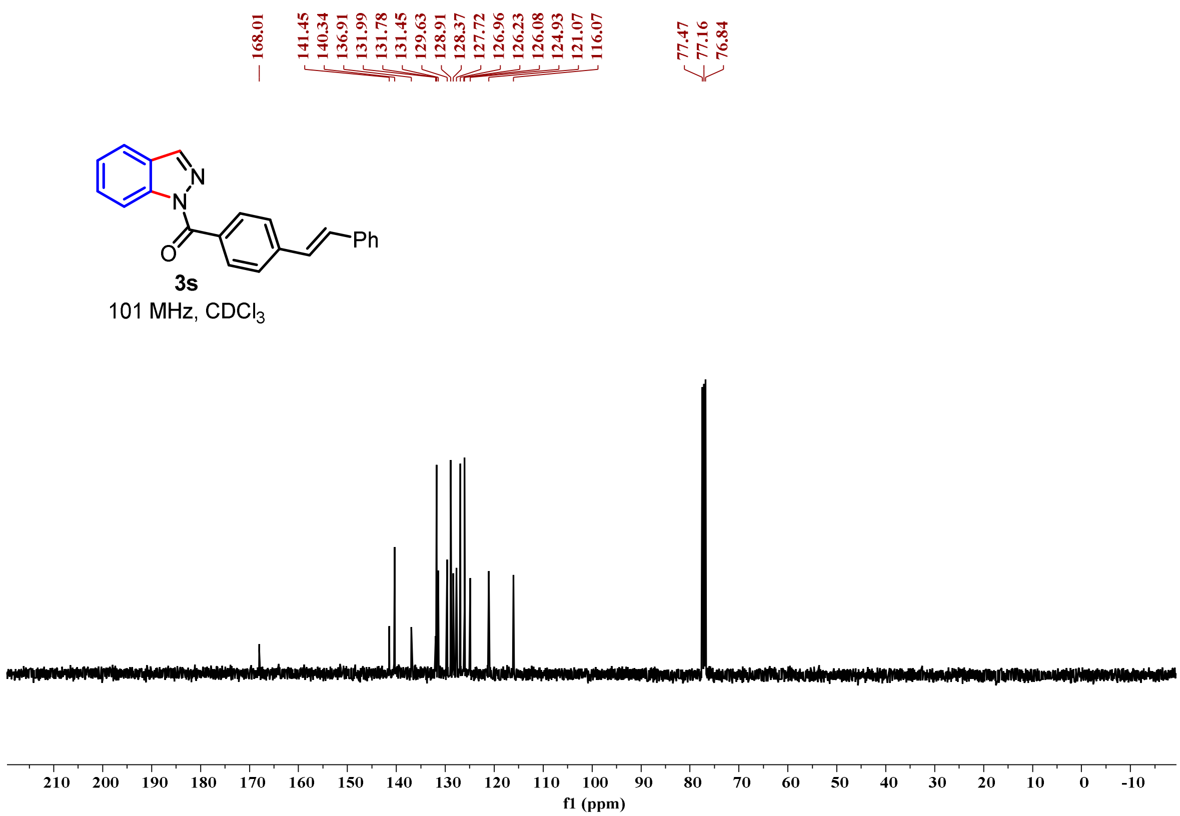

8.63 8.61 8.24 8.19 8.18 7.81 7.79 7.77 7.75 7.69 7.67 7.65 7.63 7.51 7.50 7.48 7.45 7.43 7.42 7.40 7.26
N
N
O
Ph
3q
400 MHz, CDCl3
1.00 0.94 1.99 1.04 1.91 3.11 2.10 2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

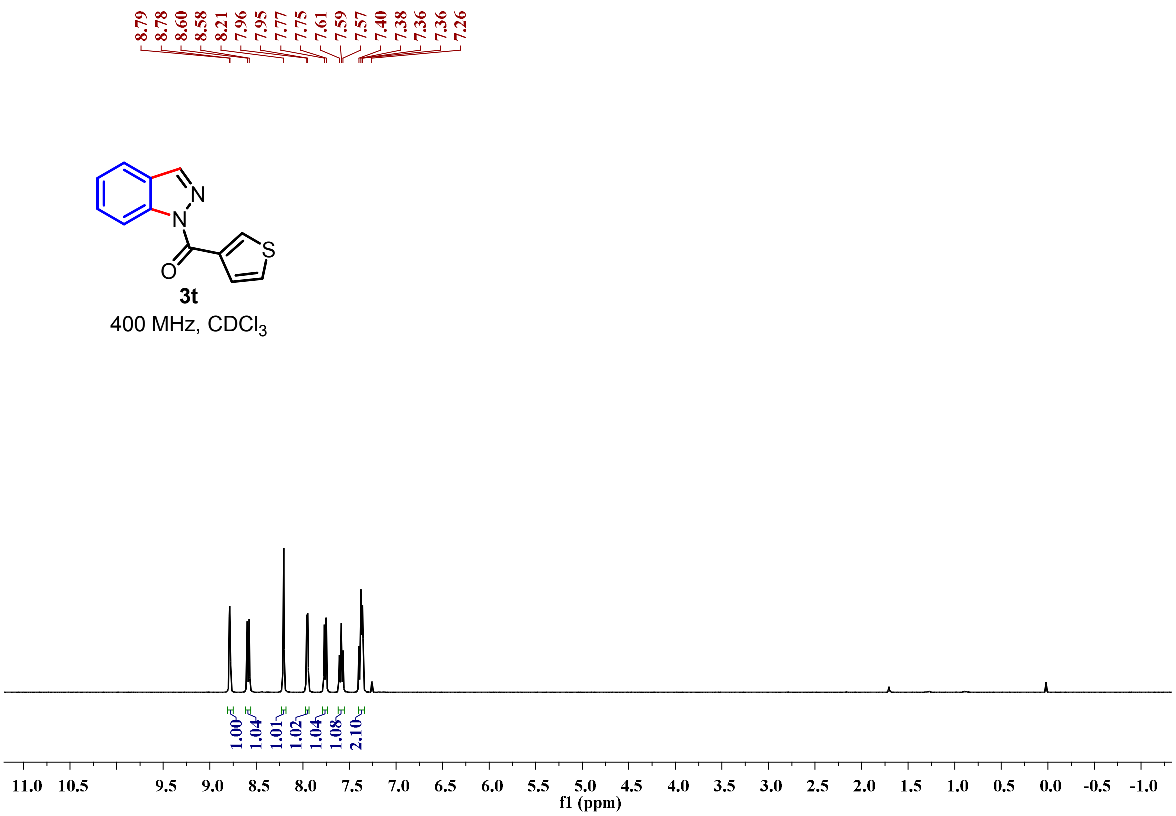

168.19
145.18 140.43 140.30 140.19 132.05 131.71 129.66 129.05 128.24 127.46 126.84 126.24 124.96 121.08 116.06
77.48 77.16 76.85
N
N
O
Ph
3q
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

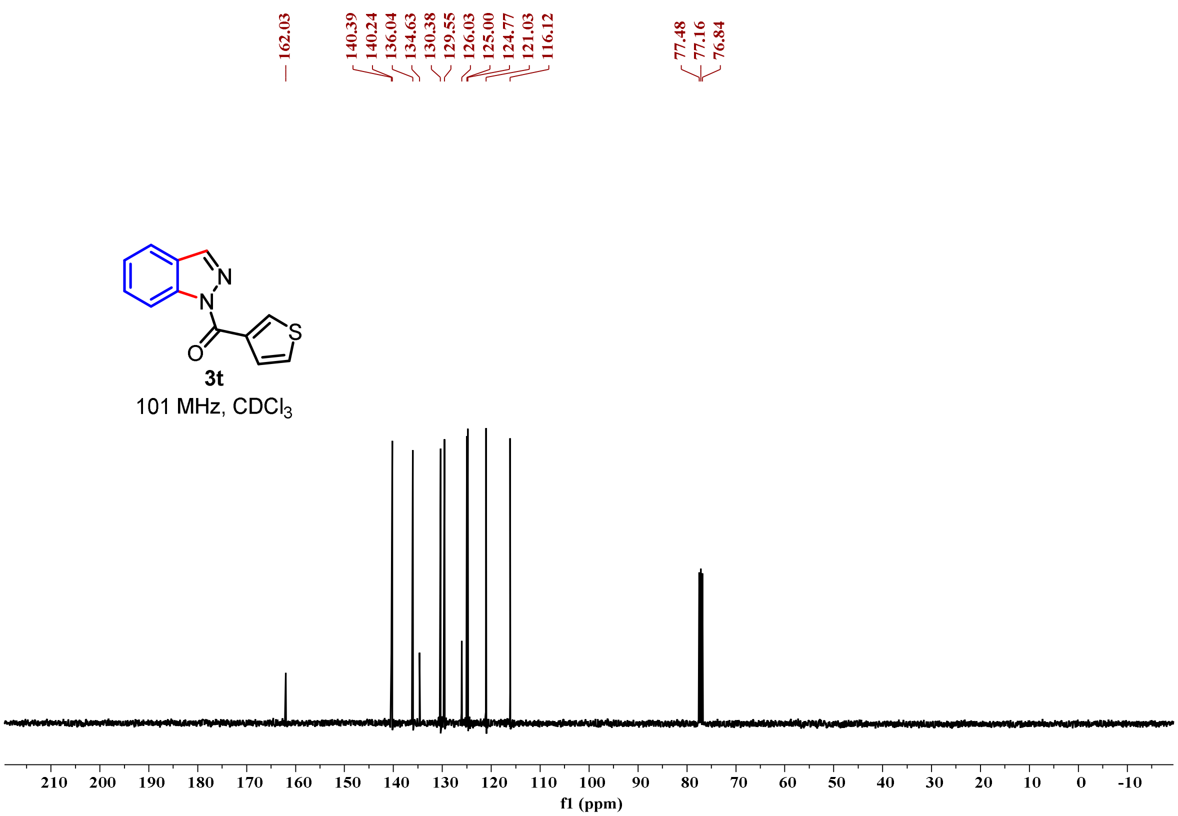

8.59
8.57
8.22
8.11
8.09
7.80
7.79
7.68
7.66
7.64
7.62
7.59
7.58
7.57
7.57
7.44
7.43
7.41
7.39
7.38
7.37
7.26
N
N
O
Ph
3r
400 MHz, CDCl3
1.00
1.00
2.03
1.05
3.07
2.00
1.10
2.91
f1 (ppm)

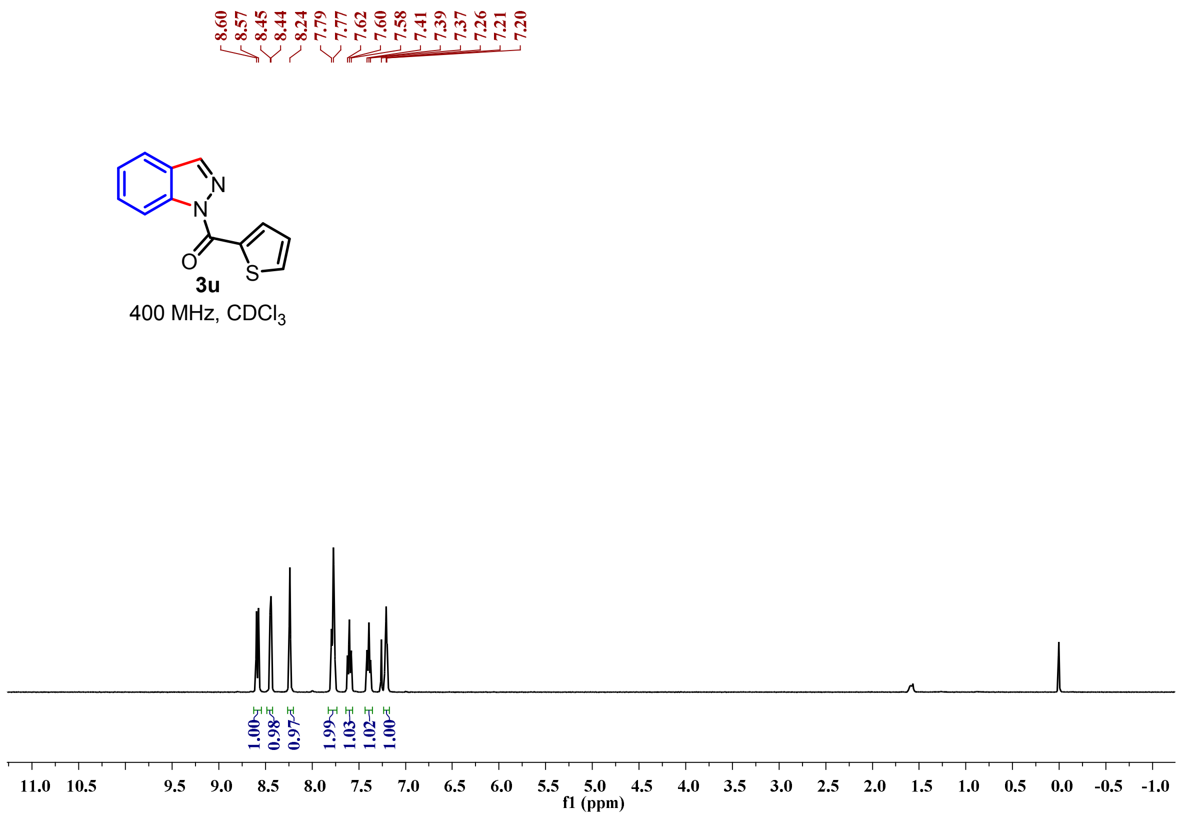

167.71
140.56
140.27
132.65
131.91
131.22
129.73
128.86
128.55
127.57
126.26
125.06
122.90
121.12
116.06
92.39
88.87
77.48
77.16
76.84
N
N
O
Ph
3r
101 MHz, CDCl3
f1 (ppm)

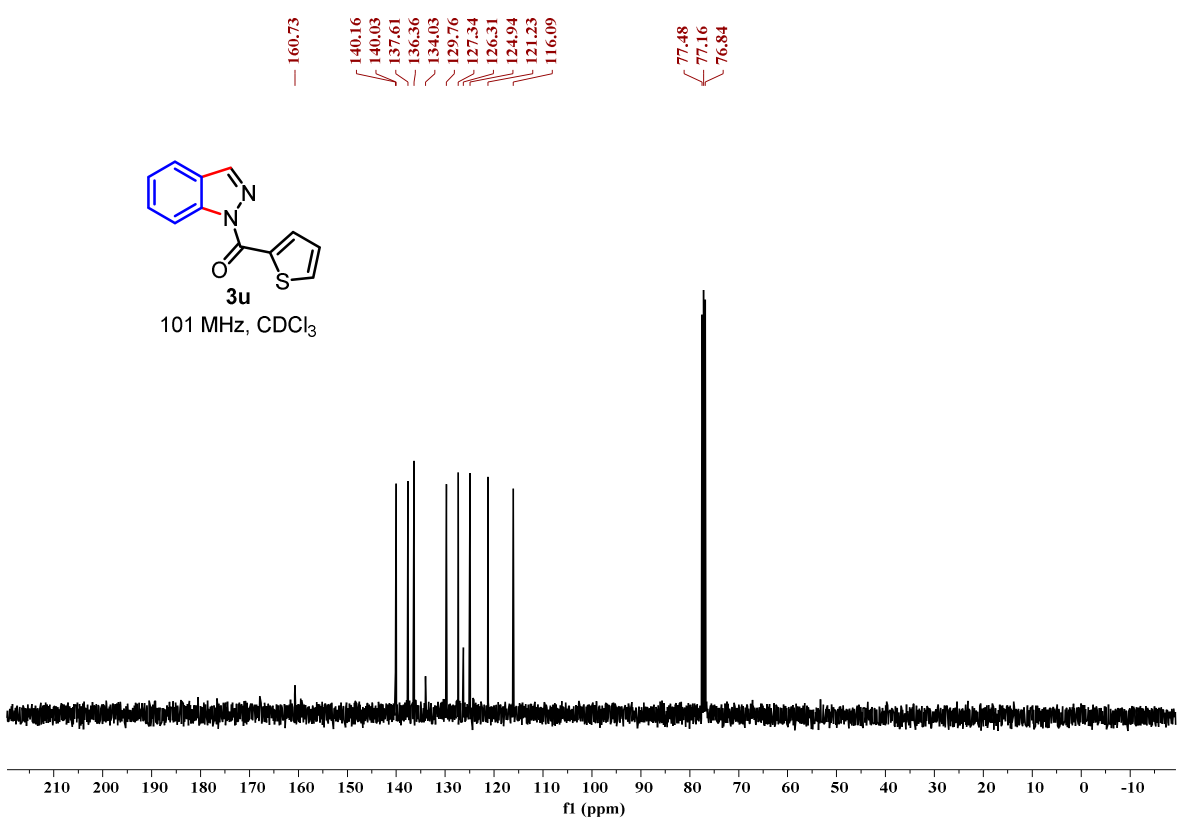

8.60
8.58
8.46
8.22
8.12
8.11
7.99
7.81
7.79
7.66
7.65
7.62
7.57
7.56
7.44
7.42
7.40
7.38
7.33
7.31
7.28
7.26
7.24
7.20
7.16
N
N
O
Ph
3s
400 MHz, CDCl3
1.00
1.04
2.00
1.10
3.08
2.11
3.19
1.00
1.13
1.02
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

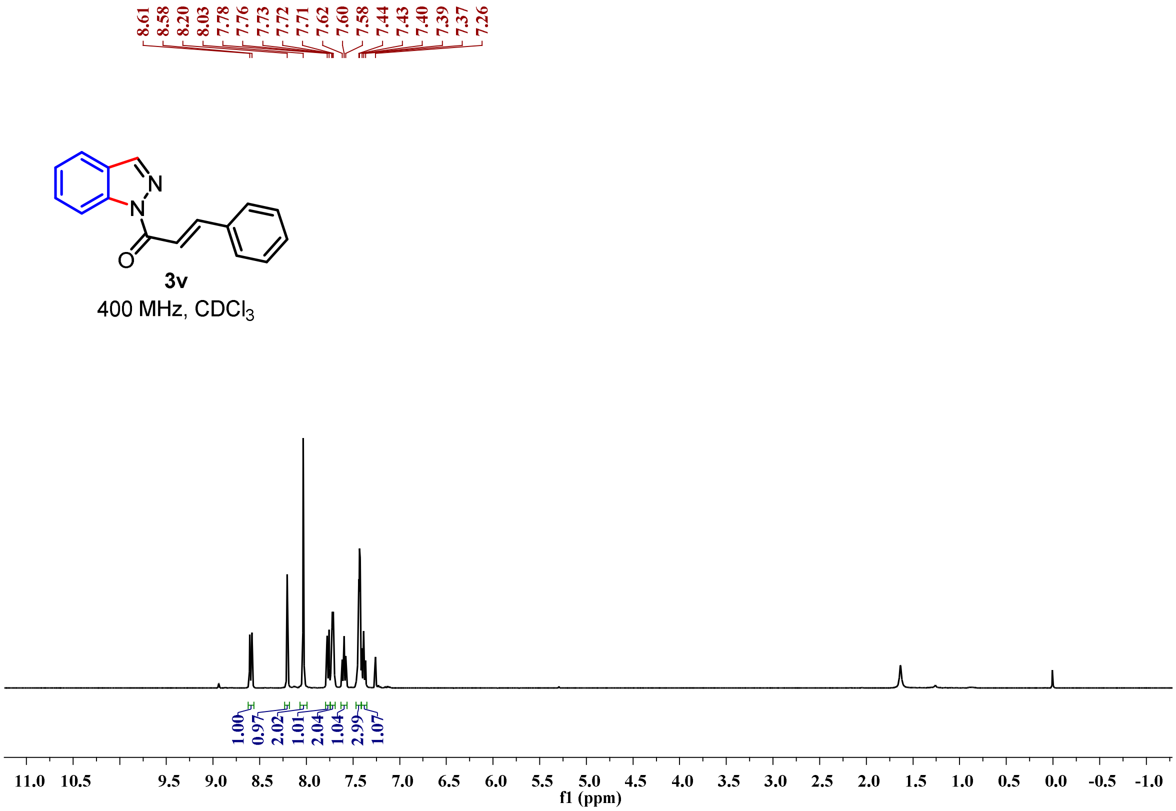

168.01
141.45
140.34
136.91
131.99
131.78
131.45
129.63
128.91
128.37
127.72
126.96
126.23
126.08
124.93
121.07
116.07
77.47
77.16
76.84
N
N
O
Ph
3s
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

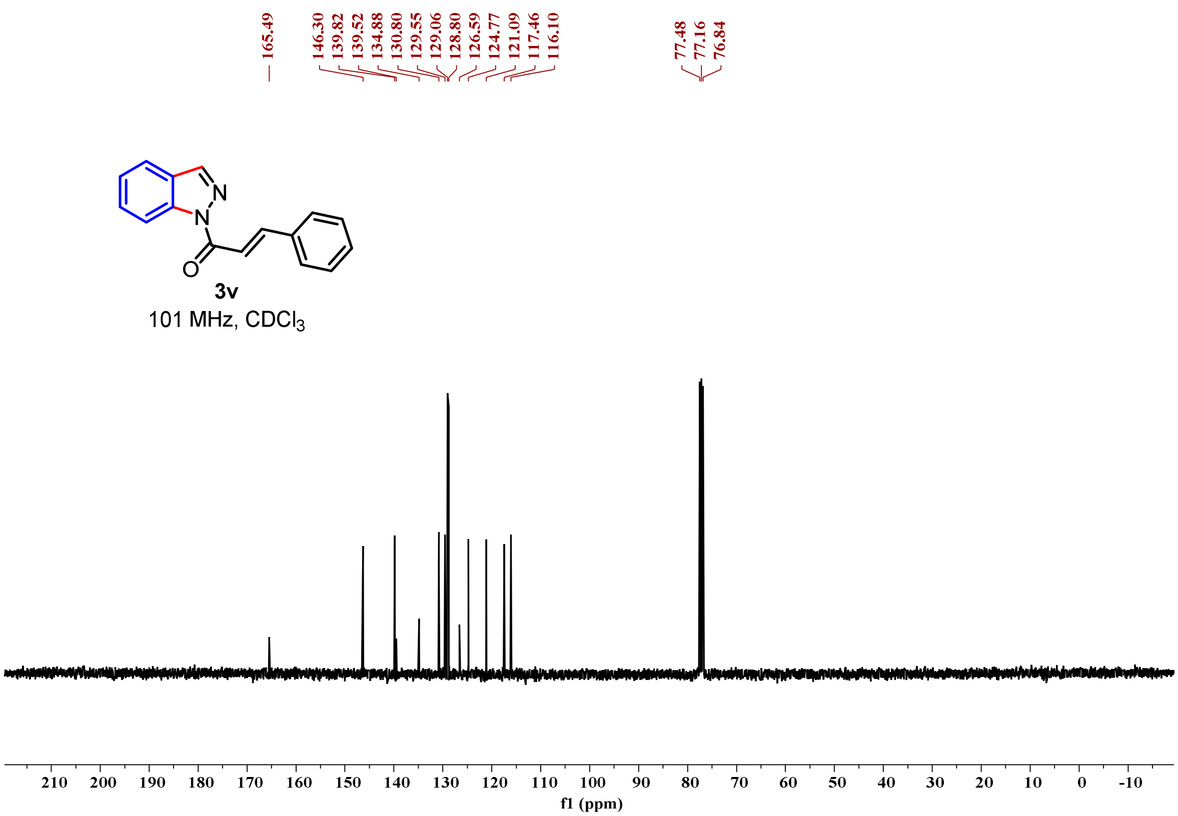

8.79
8.78
8.60
8.58
8.21
7.96
7.95
7.77
7.75
7.61
7.59
7.57
7.40
7.38
7.36
7.36
7.26
N
N
O
S
3t
400 MHz, $CDCl_3$
1.00
1.04
1.01
1.02
1.04
1.08
2.10
f1 (ppm)

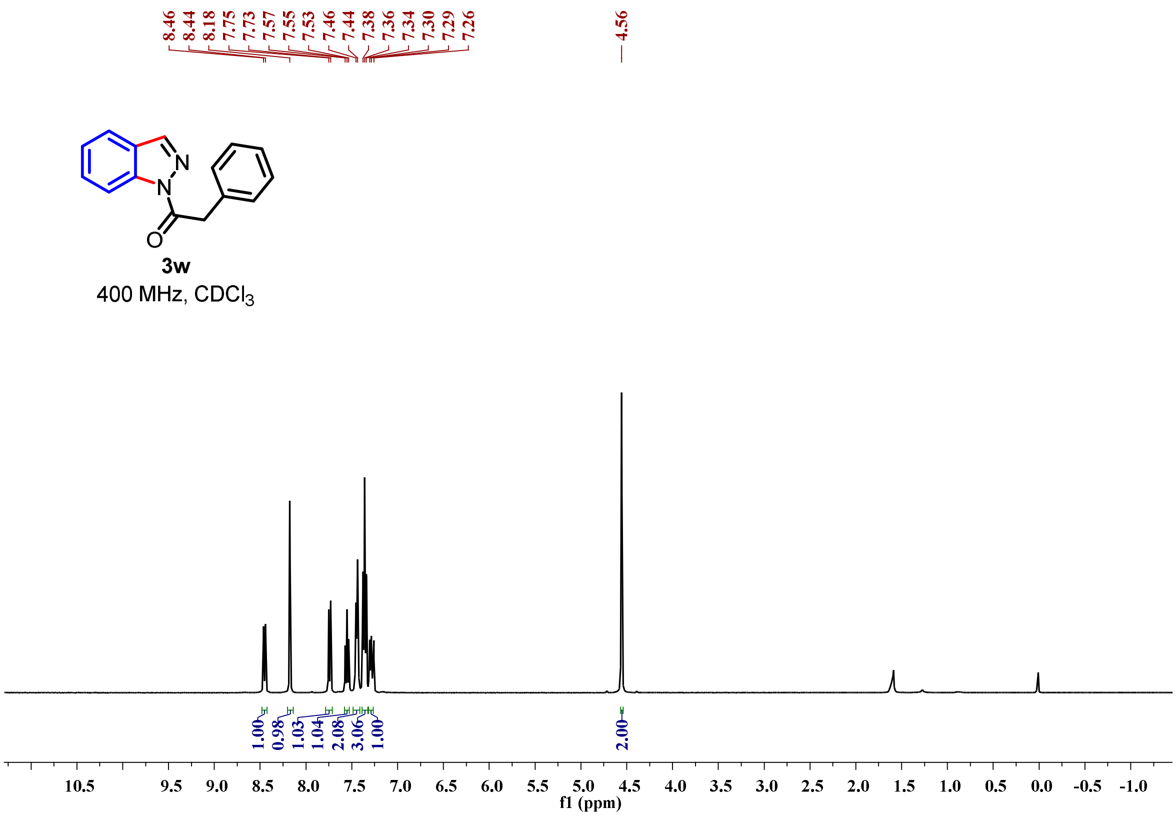

162.03
140.39
140.24
136.04
134.63
130.38
129.55
126.03
125.00
124.77
121.03
116.12
77.48
77.16
76.84
N
N
O
S
3t
101 MHz, $CDCl_3$
f1 (ppm)

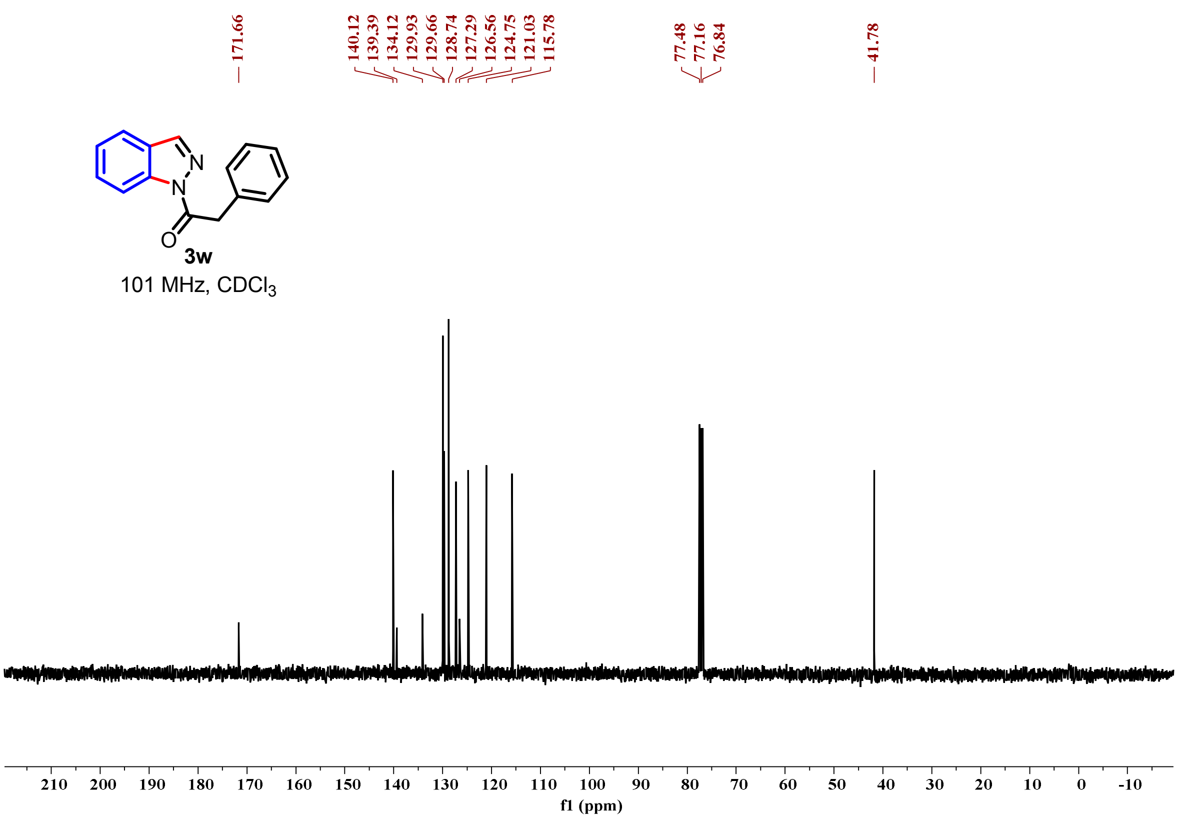

8.60
8.57
8.45
8.44
8.24
7.79
7.77
7.62
7.60
7.58
7.41
7.39
7.37
7.26
7.21
7.20
3u
400 MHz, CDCl3
1.00
0.98
0.97
1.99
1.03
1.02
1.00
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

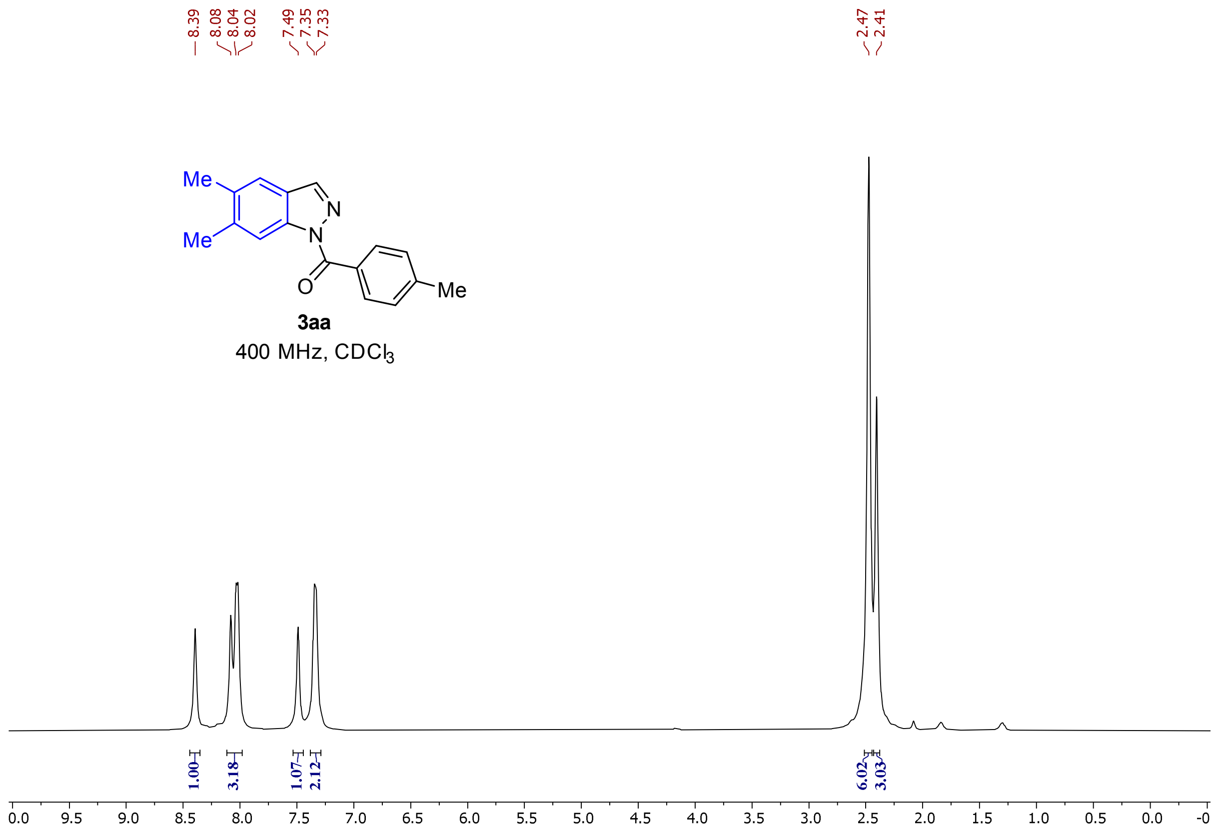

160.73
140.16
140.03
137.61
136.36
134.03
129.76
127.34
126.31
124.94
121.23
116.09
77.48
77.16
76.84
3u
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

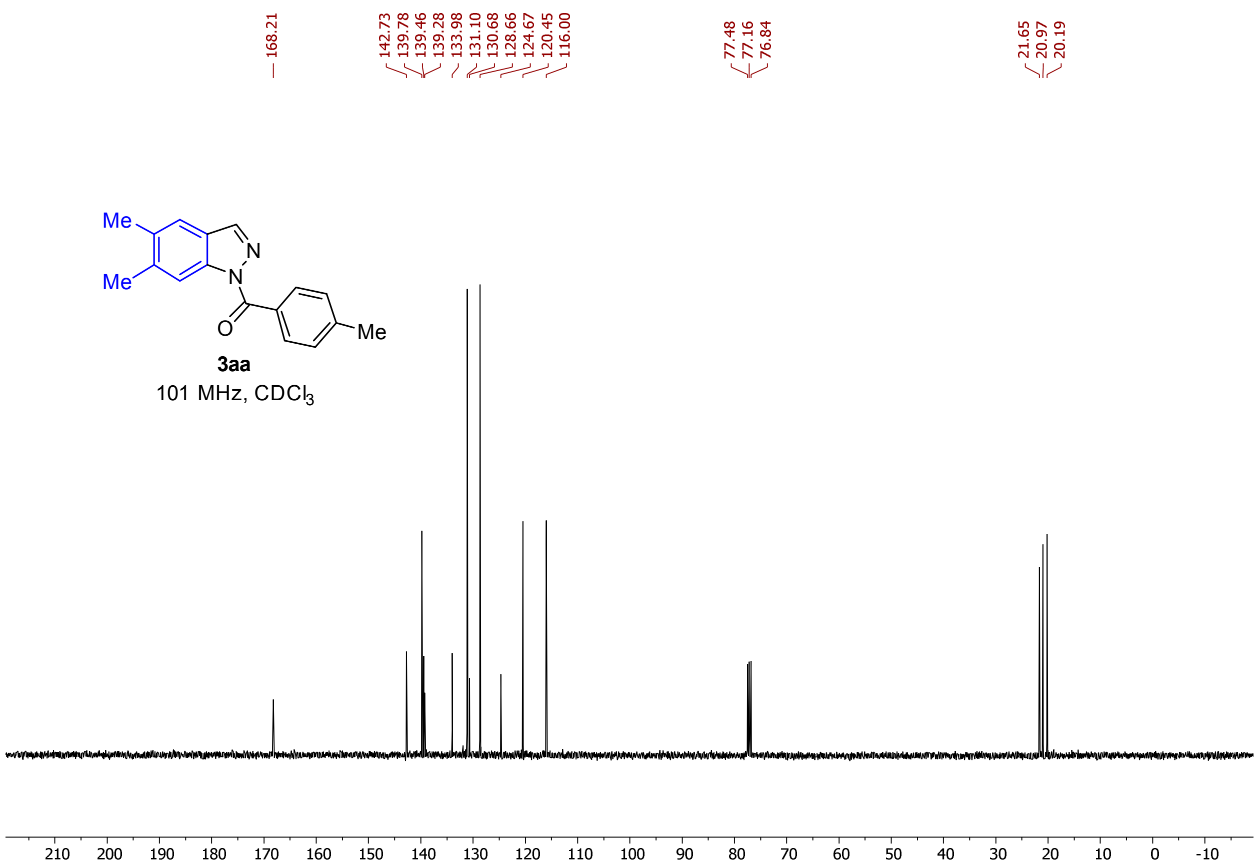

8.61
8.58
8.20
8.03
7.78
7.76
7.73
7.72
7.71
7.62
7.60
7.58
7.44
7.43
7.40
7.39
7.37
7.26
N
N
O
3v
400 MHz, $CDCl_3$
1.00
0.97
2.02
1.01
2.04
1.04
2.99
1.07
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

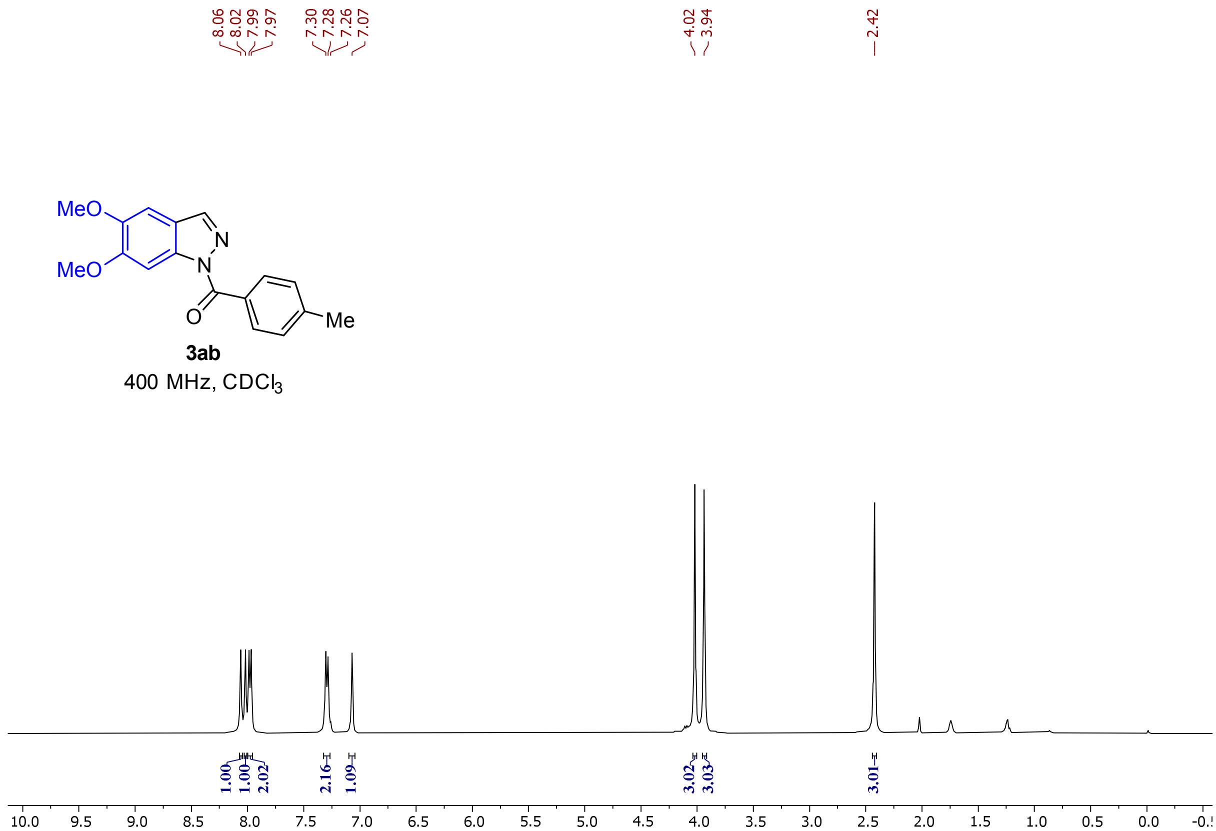

165.49
146.30
139.82
139.52
134.88
130.80
129.55
129.06
128.80
126.59
124.77
121.09
117.46
116.10
77.48
77.16
76.84
N
N
O
3v
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.46
8.44
8.18
7.75
7.73
7.57
7.55
7.53
7.46
7.44
7.38
7.36
7.34
7.30
7.29
7.26
4.56
N
N
O
3w
400 MHz, CDCl3
1.00
0.98
1.03
1.04
2.08
3.06
1.00
2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

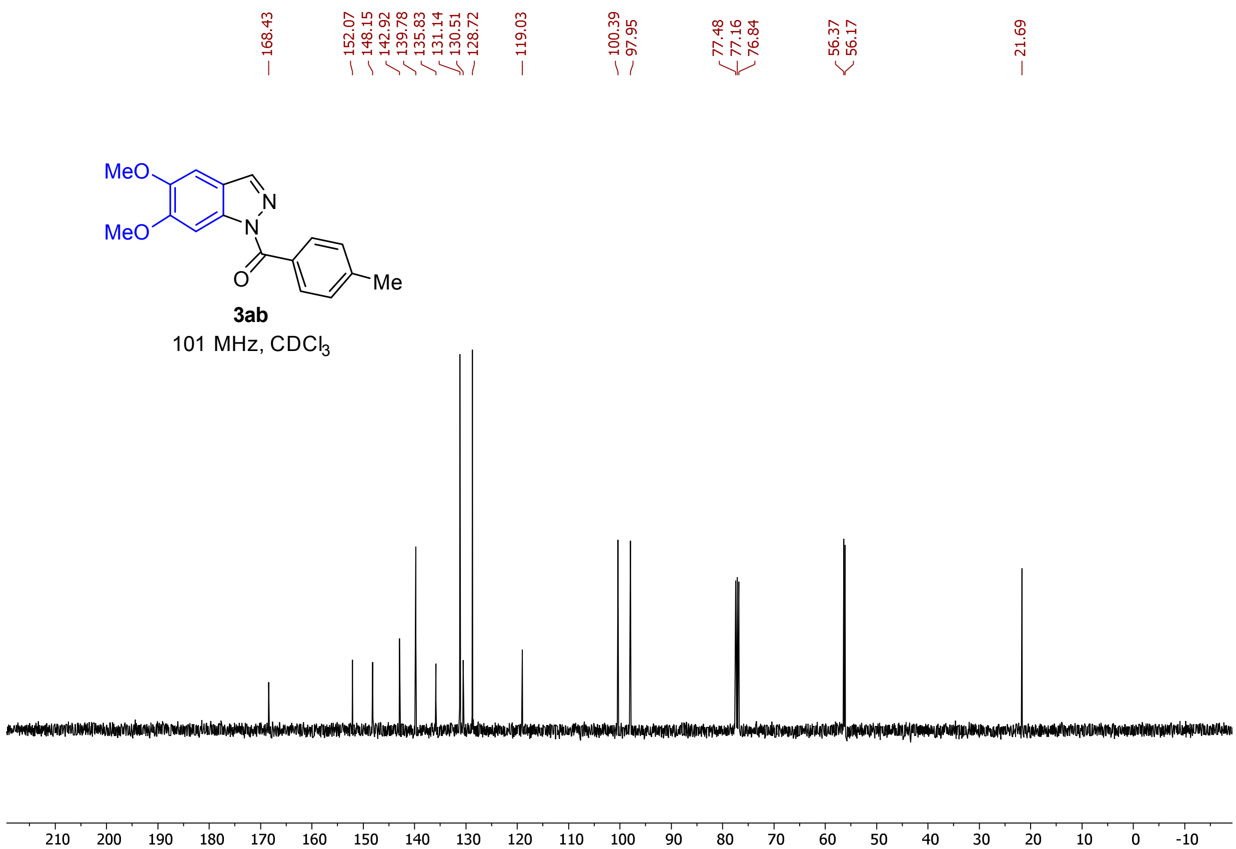

171.66
140.12
139.39
134.12
129.93
129.66
128.74
127.29
126.56
124.75
121.03
115.78
77.48
77.16
76.84
41.78
N
N
O
3w
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.39
8.08
8.04
8.02
7.49
7.35
7.33
2.47
2.41
Me
Me
N
N
O
Me
3aa
400 MHz, CDCl3
1.00
3.18
1.07
2.12
6.02
3.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

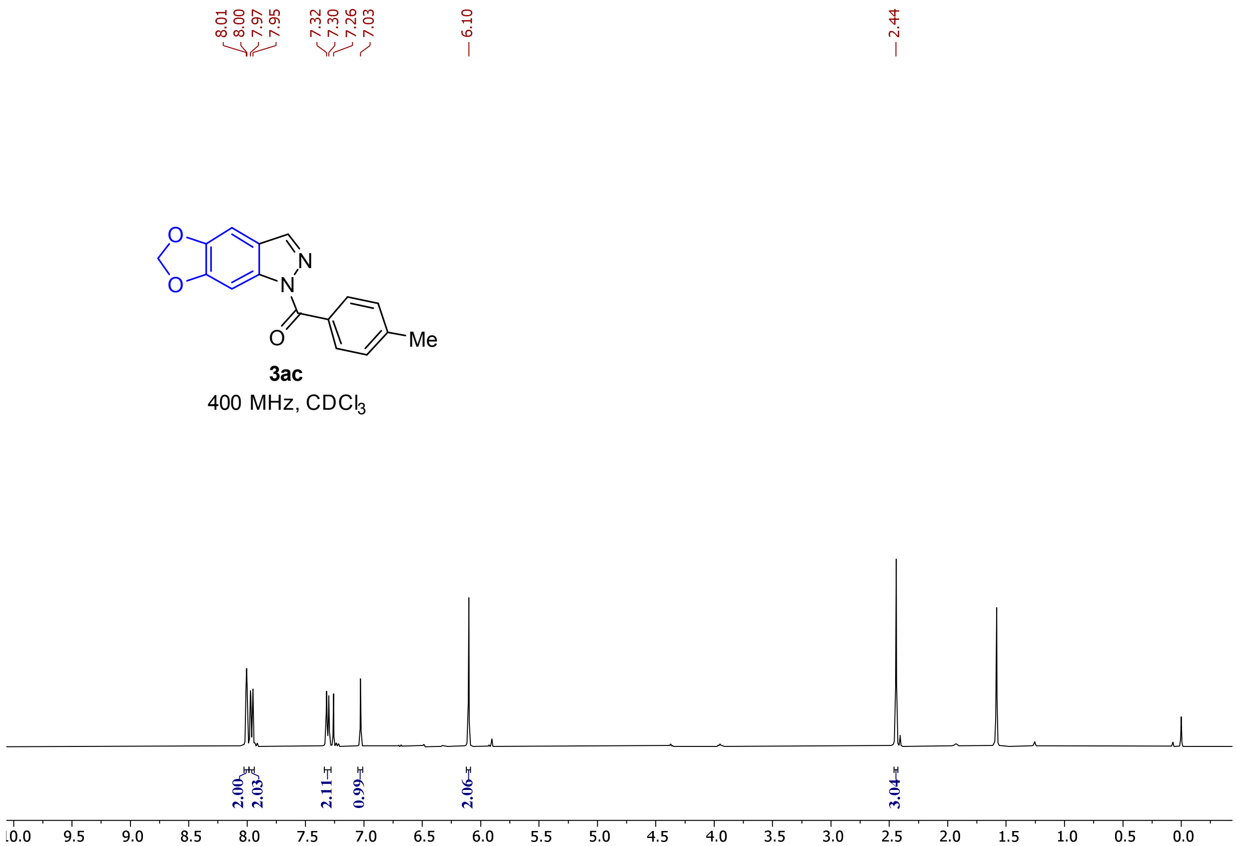

168.21
142.73
139.78
139.46
139.28
133.98
131.10
130.68
128.66
124.67
120.45
116.00
77.48
77.16
76.84
21.65
20.97
20.19
Me
Me
N
N
O
Me
3aa
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

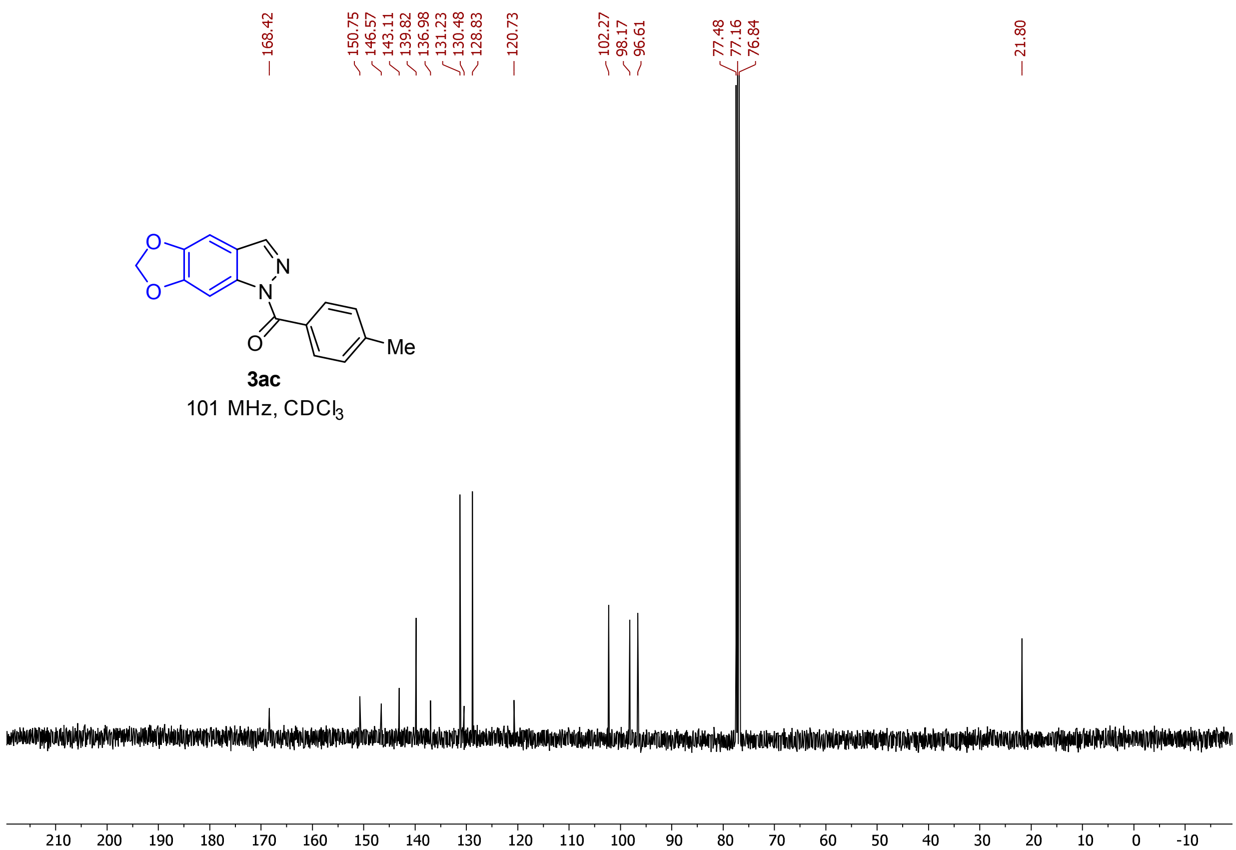


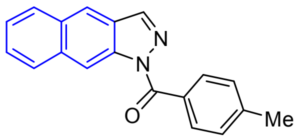
8.06
8.02
7.99
7.97
7.30
7.28
7.26
7.07
4.02
3.94
2.42
MeO
MeO
N
N
O
Me
3ab
400 MHz, CDCl3
1.00
1.00
2.02
2.16
1.09
3.02
3.03
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



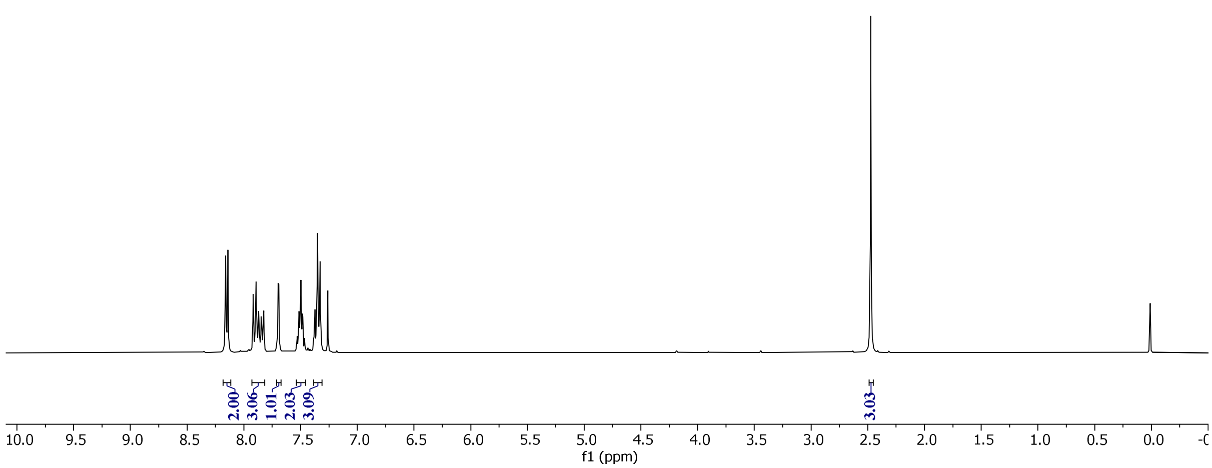
168.43
152.07
148.15
142.92
139.78
135.83
131.14
130.51
128.72
119.03
100.39
97.95
77.48
77.16
76.84
56.37
56.17
21.69
MeO
MeO
N
N
O
Me
3ab
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

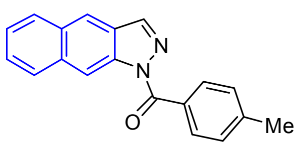

8.01
8.00
7.97
7.95
7.32
7.30
7.26
7.03
6.10
2.44
Me
O
N
3ac
400 MHz, $CDCl_3$
2.00
2.03
2.11
0.99
2.06
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


168.42
150.75
146.57
143.11
139.82
136.98
131.23
130.48
128.83
120.73
102.27
98.17
96.61
77.48
77.16
76.84
21.80
Me
O
N
3ac
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

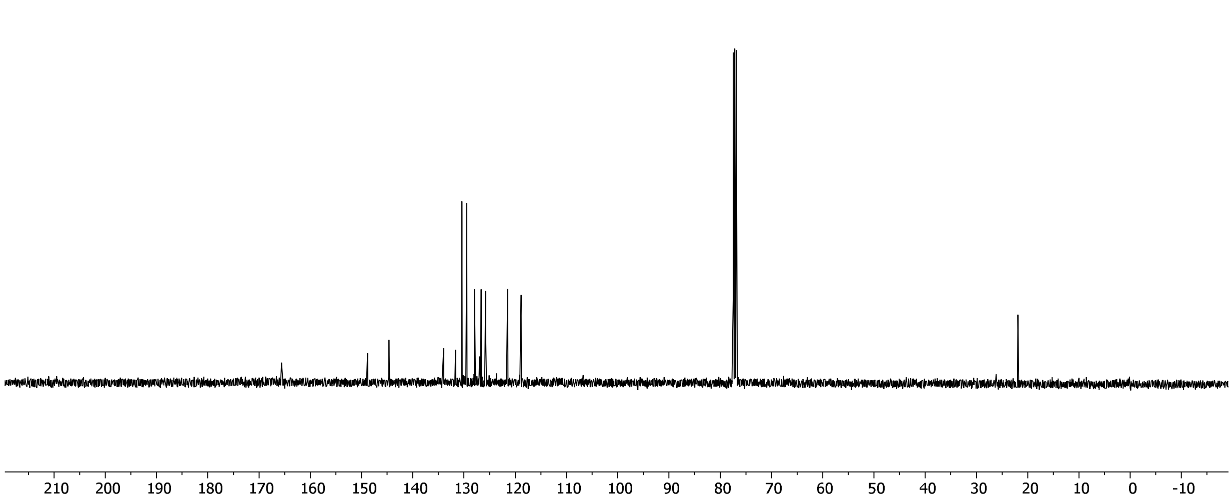


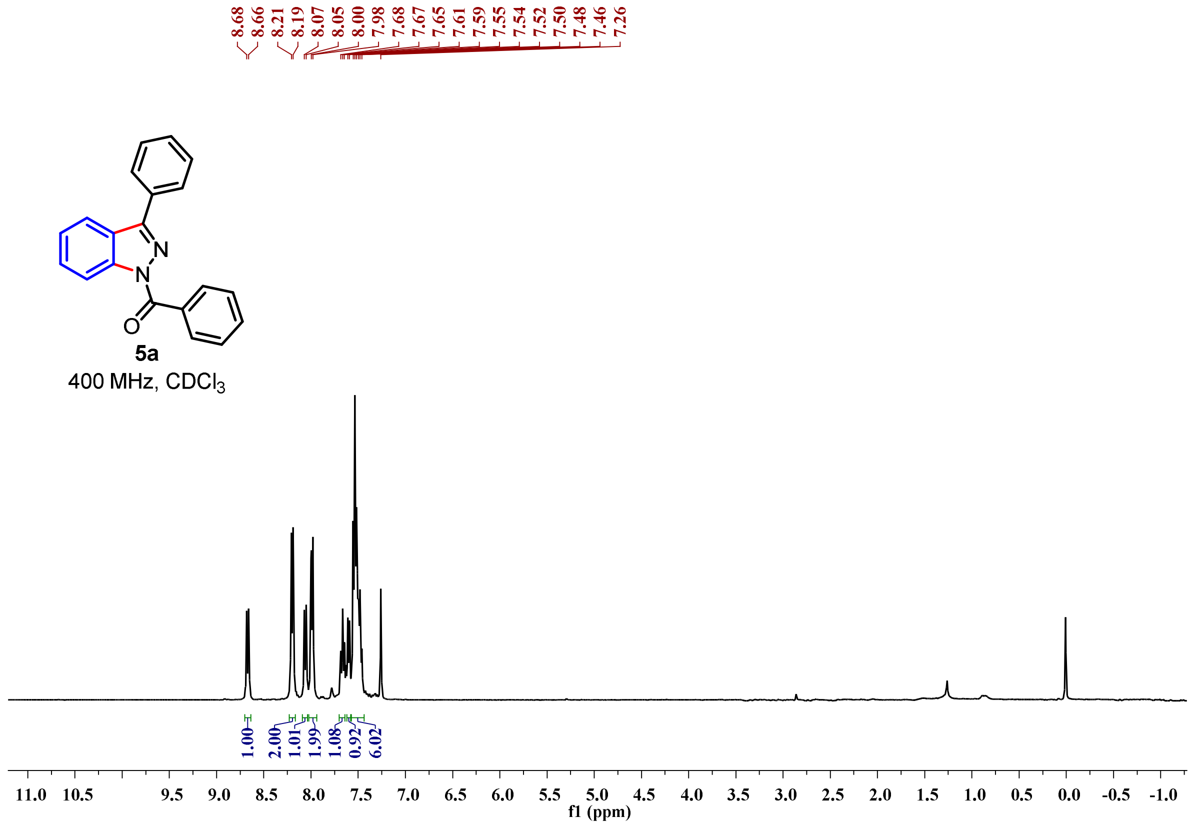
3ad
400 MHz, $CDCl_3$

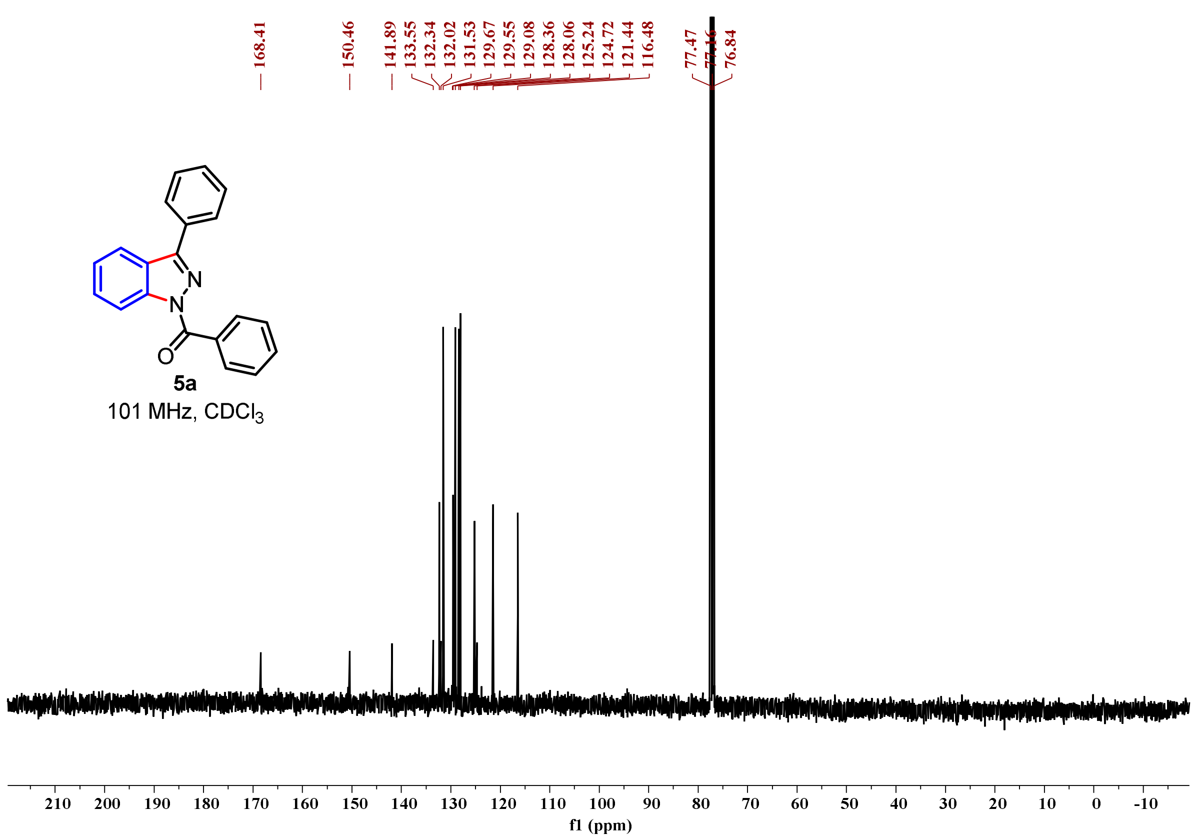


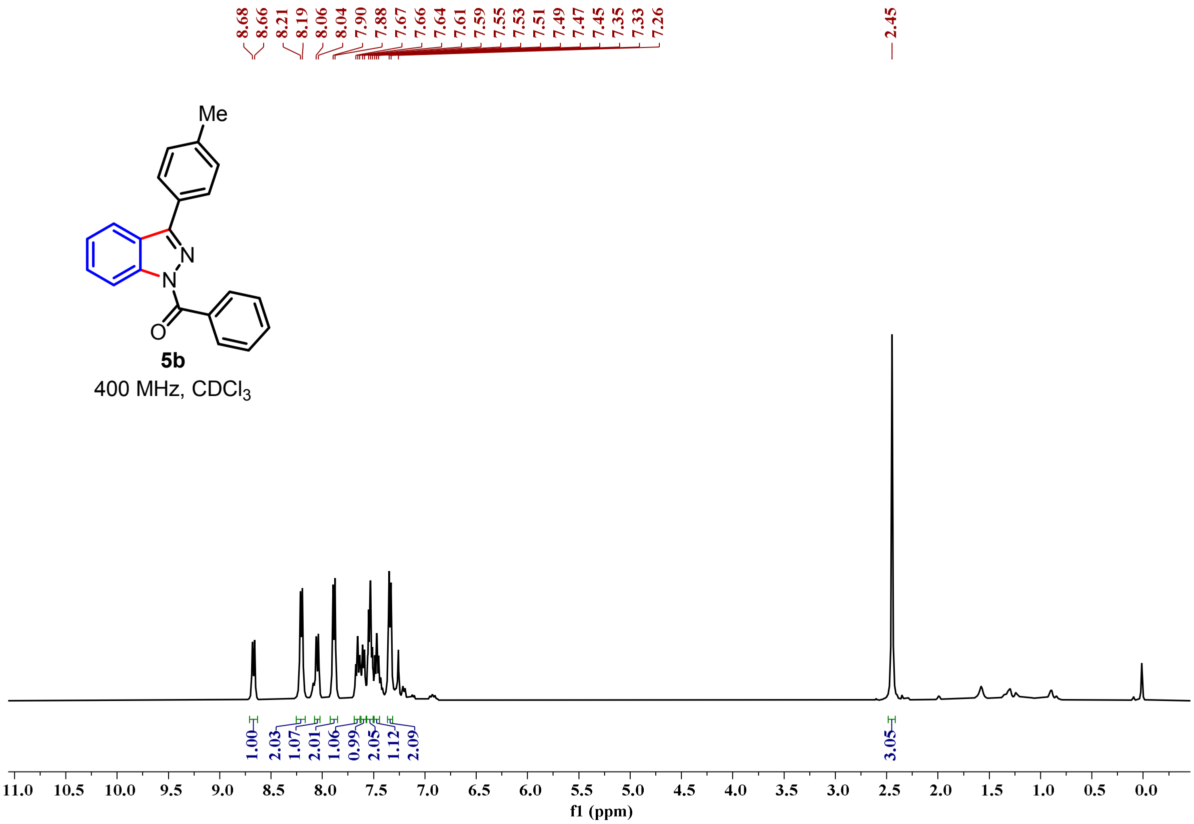


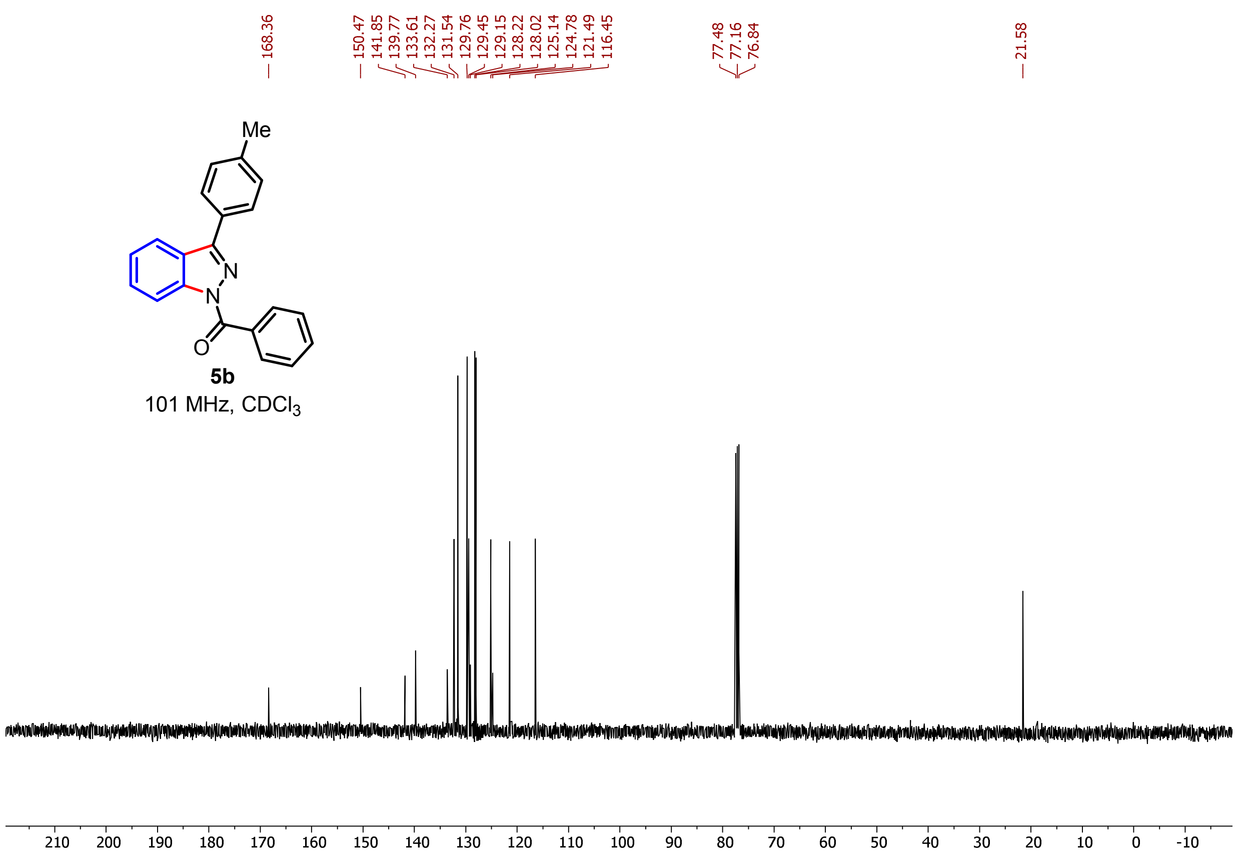
3ad
101 MHz, $CDCl_3$




8.68
8.66
8.21
8.19
8.07
8.05
8.00
7.98
7.68
7.67
7.65
7.61
7.59
7.55
7.54
7.52
7.50
7.48
7.46
7.26
N
N
O
5a
400 MHz, CDCl3
1.00
2.00
1.01
1.99
1.08
0.92
6.02
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.41
150.46
141.89
133.55
132.34
132.02
131.53
129.67
129.55
129.08
128.36
128.06
125.24
124.72
121.44
116.48
77.47
77.16
76.84
N
N
O
5a
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.68
8.66
8.21
8.19
8.06
8.04
7.90
7.88
7.67
7.66
7.64
7.61
7.59
7.55
7.53
7.51
7.49
7.47
7.45
7.35
7.33
7.26
2.45
Me
N
N
O
5b
400 MHz, CDCl3
1.00
2.03
1.07
2.01
1.06
0.99
2.05
1.12
2.09
3.05
f1 (ppm)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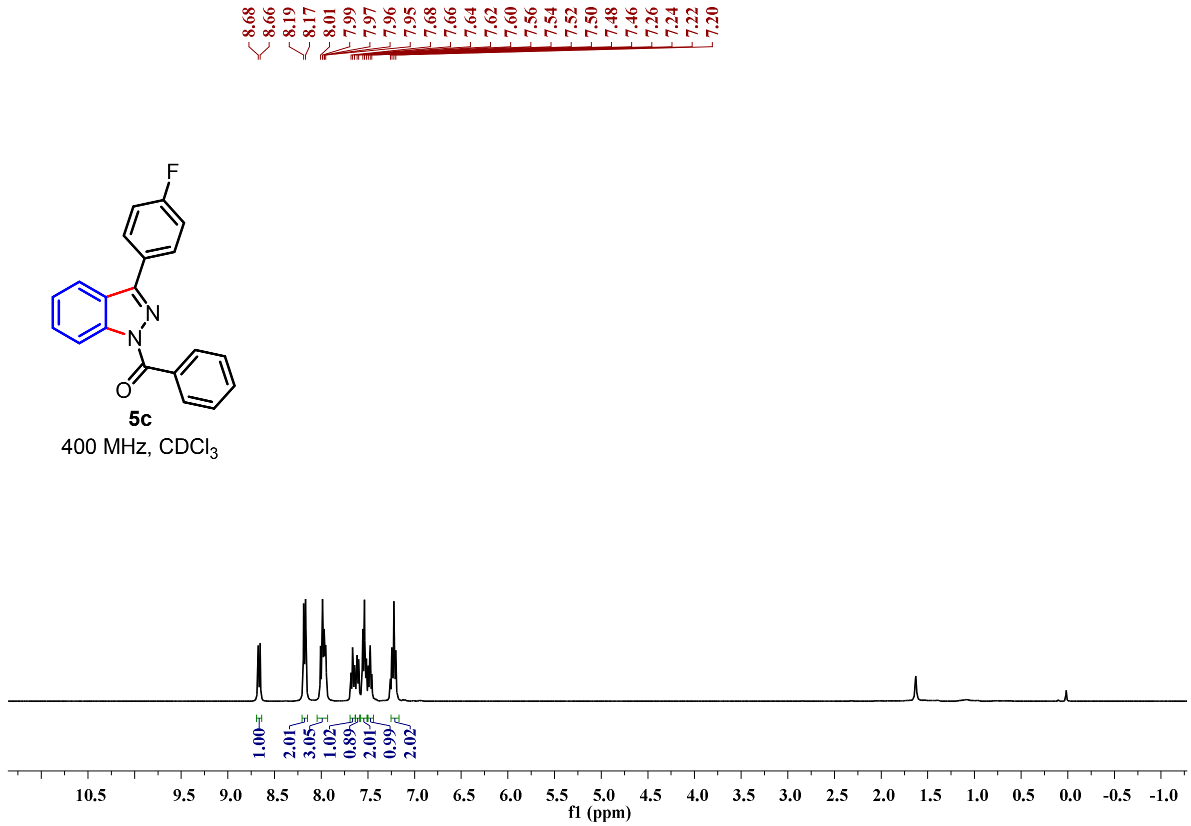
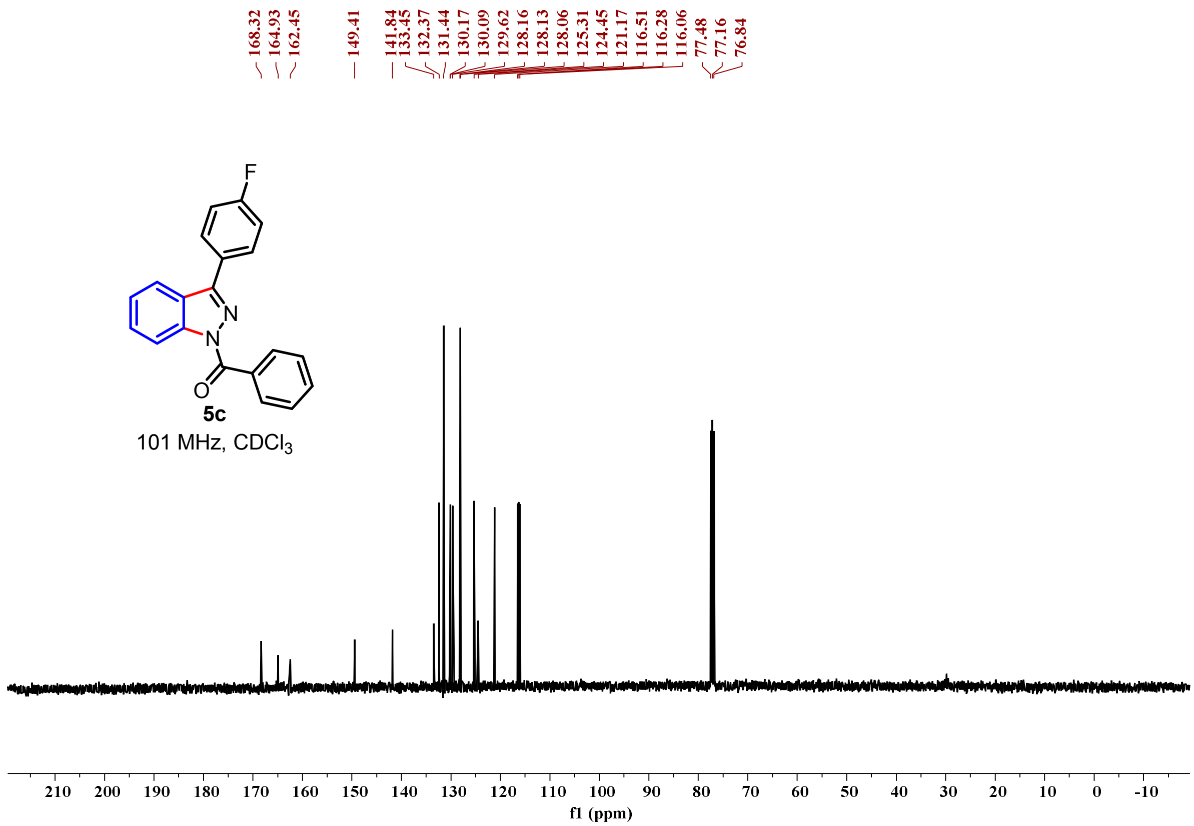
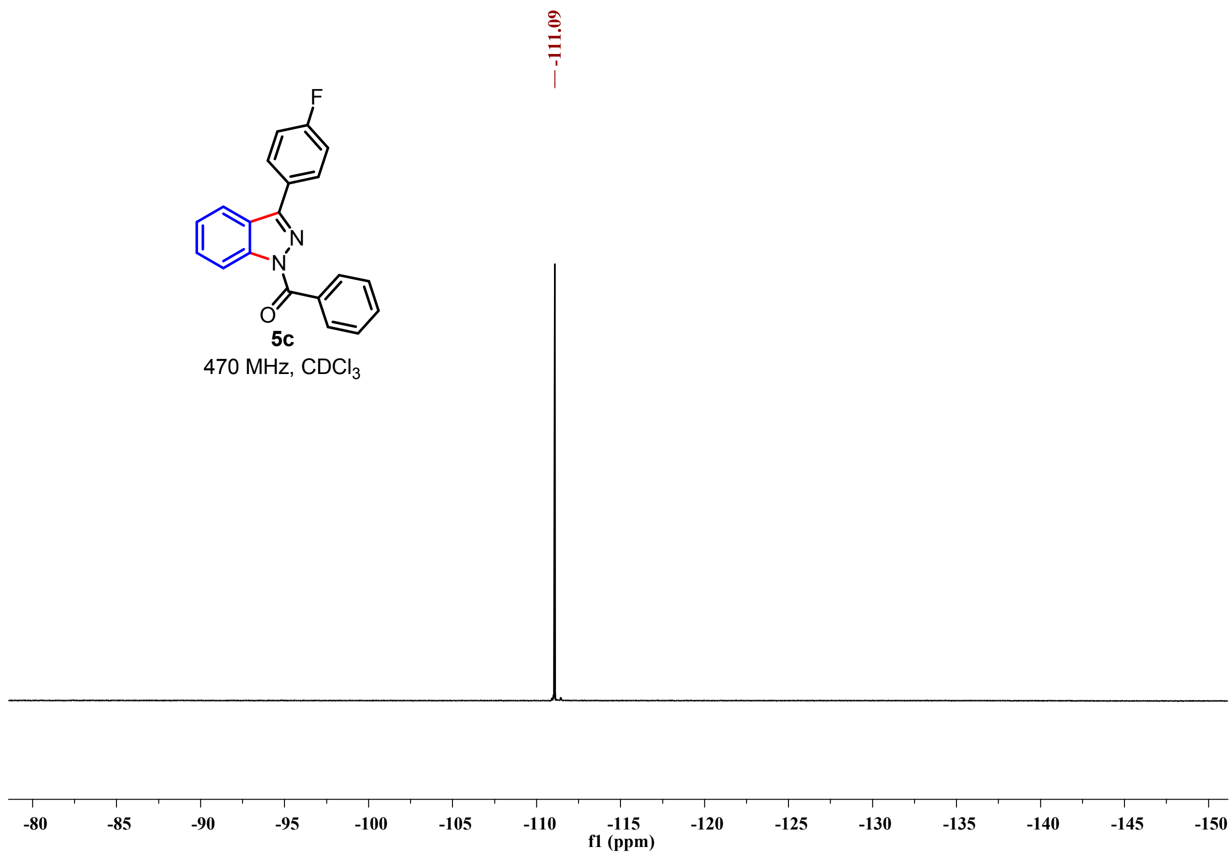
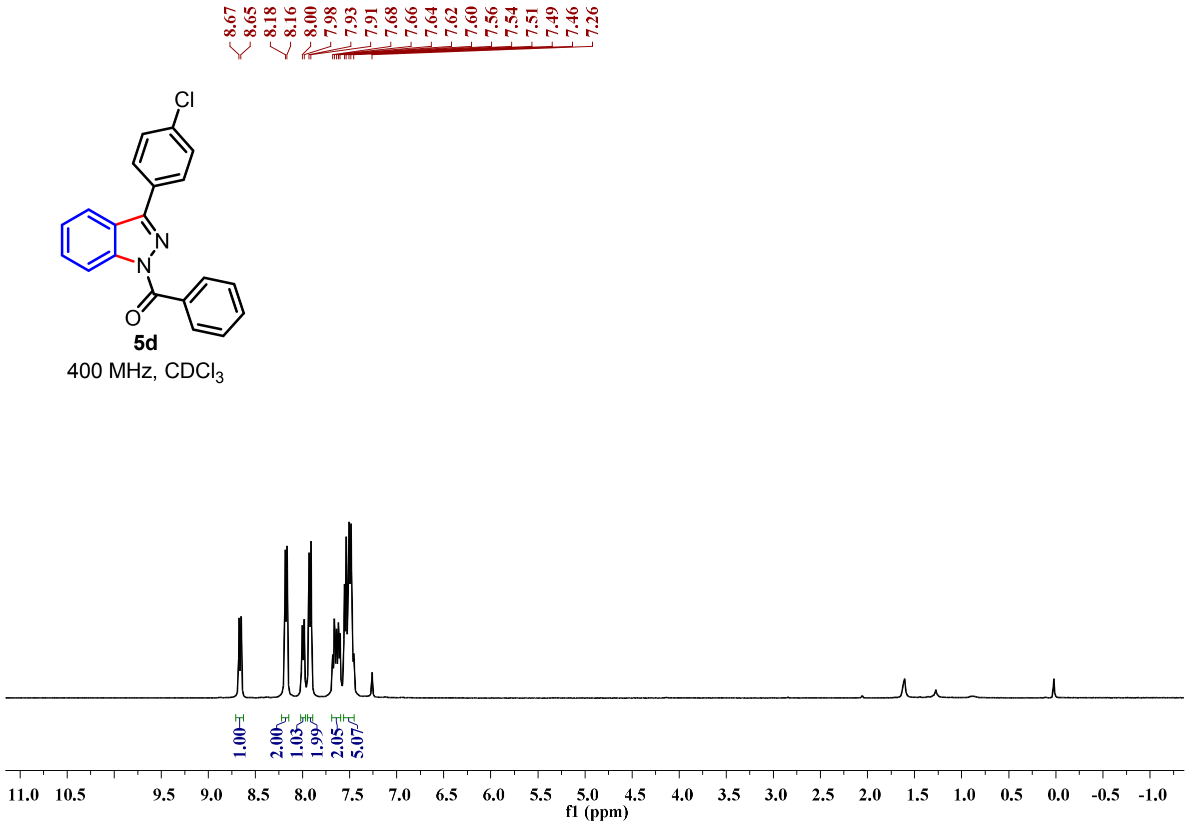
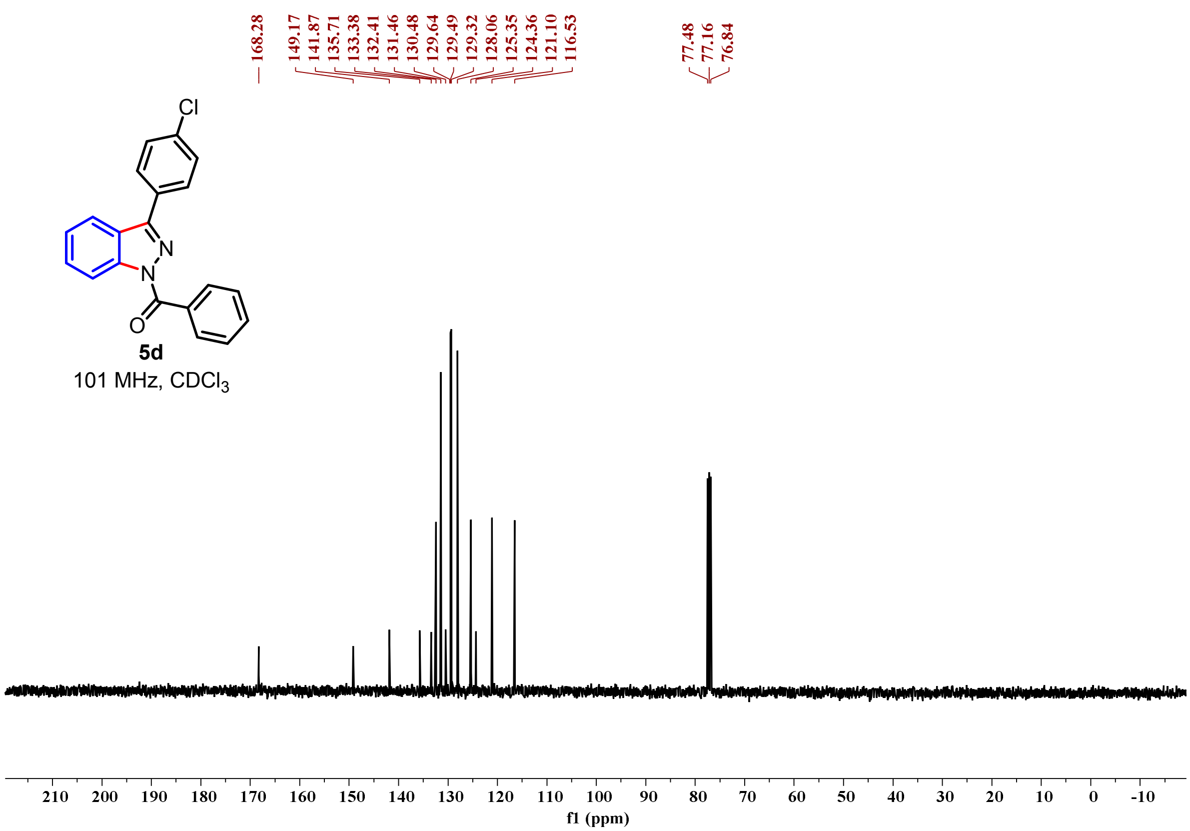
150.47
141.85
139.77
133.61
132.27
131.54
129.76
129.45
129.15
128.22
128.02
125.14
124.78
121.49
116.45
77.48
77.16
76.84
21.58
Me
N
N
O
5b
101 MHz, CDCl3

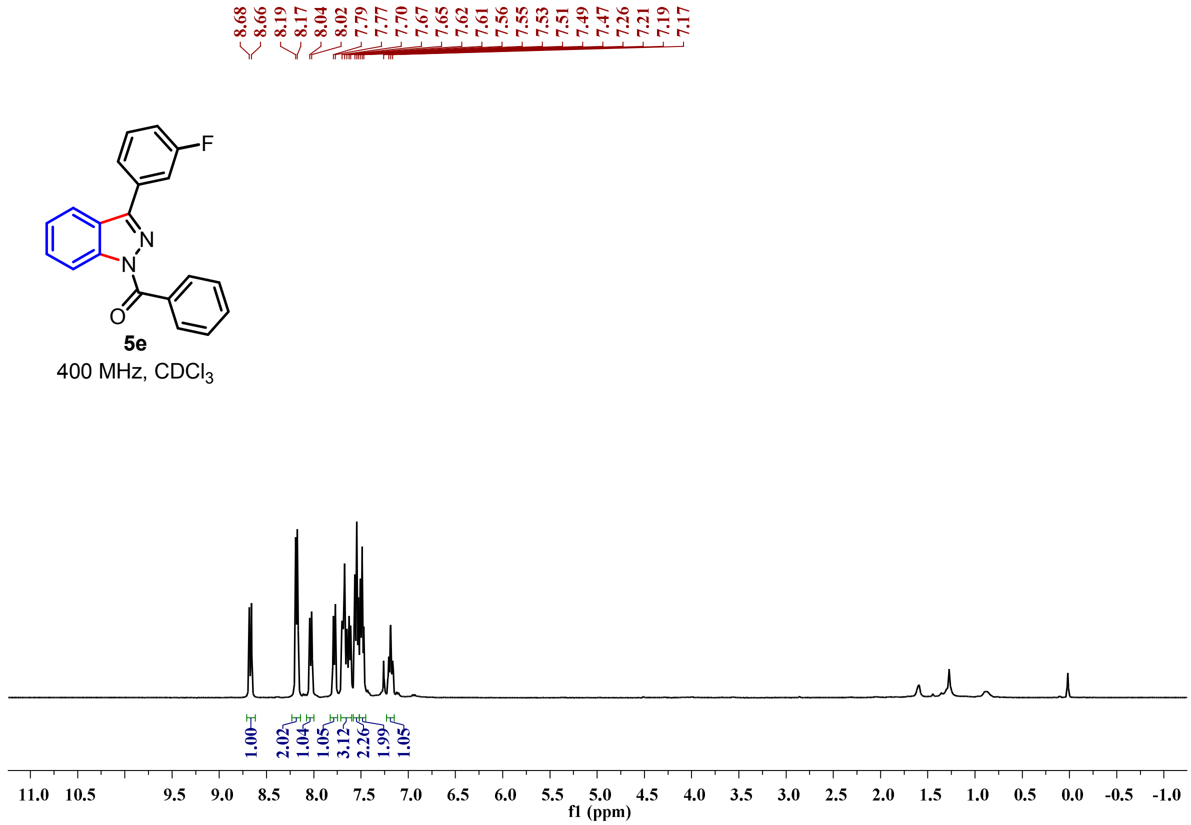

8.68
8.66
8.19
8.17
8.01
7.99
7.97
7.96
7.95
7.68
7.66
7.64
7.62
7.60
7.56
7.54
7.52
7.50
7.48
7.46
7.26
7.24
7.22
7.20
F
N
N
O
5c
400 MHz, $CDCl_3$
1.00
2.01
3.05
1.02
0.89
2.01
0.99
2.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

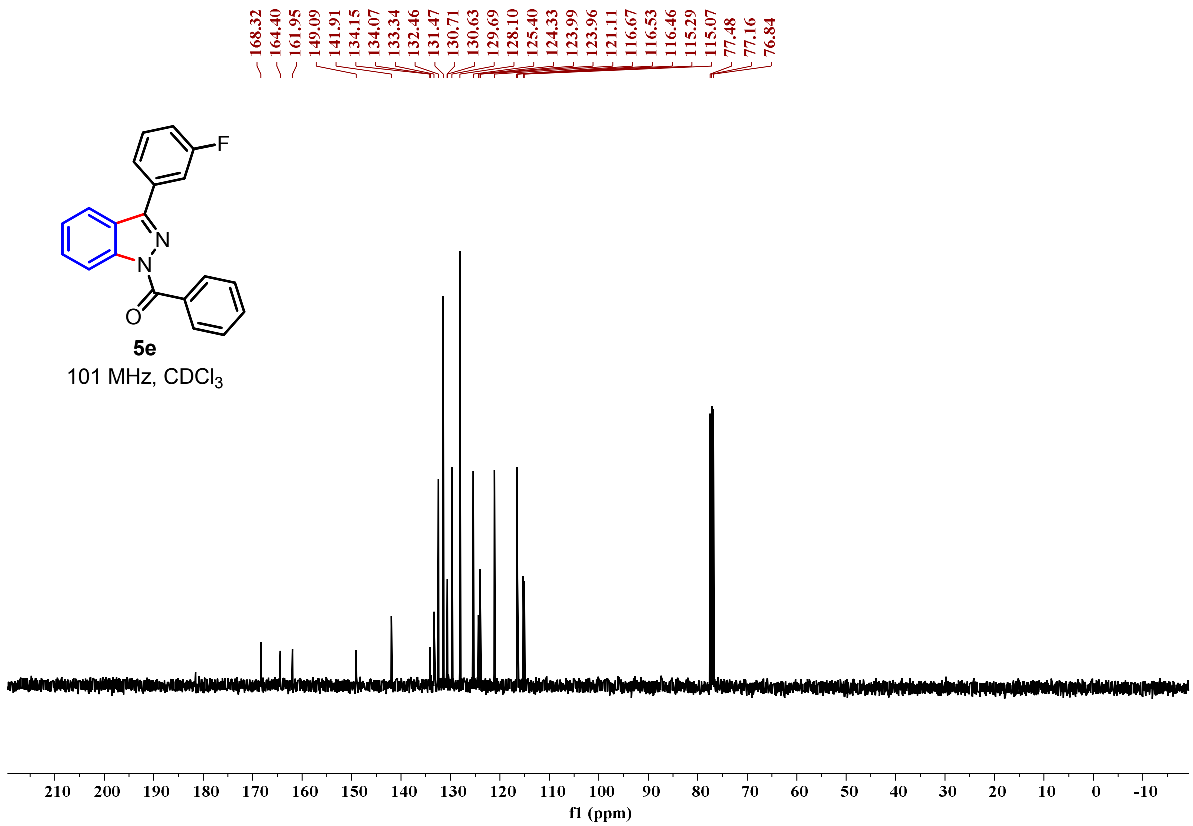

168.32
164.93
162.45
149.41
141.84
133.45
132.37
131.44
130.17
130.09
129.62
128.16
128.13
128.06
125.31
124.45
121.17
116.51
116.28
116.06
77.48
77.16
76.84
F
N
N
O
5c
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

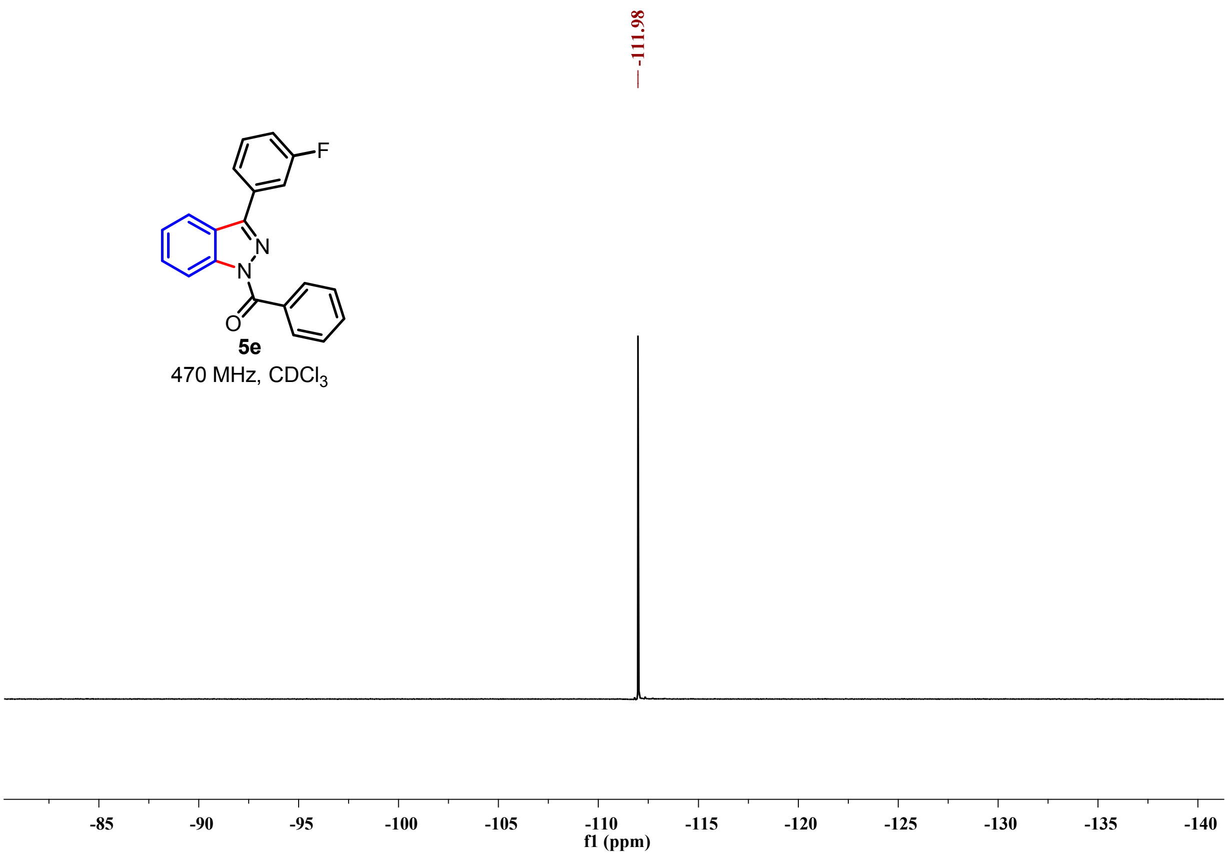

F
N
N
O
5c
470 MHz, CDCl3
-111.09
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

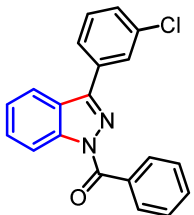

8.67
8.65
8.18
8.16
8.00
7.98
7.93
7.91
7.68
7.66
7.64
7.62
7.60
7.56
7.54
7.51
7.49
7.46
7.26
Cl
N
N
O
5d
400 MHz, CDCl3
1.00
2.00
1.03
1.99
2.05
5.07
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.28
149.17
141.87
135.71
133.38
132.41
131.46
130.48
129.64
129.49
129.32
128.06
125.35
124.36
121.10
116.53
77.48
77.16
76.84
Cl
N
N
O
5d
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.68 8.66 8.19 8.17 8.04 8.02 7.79 7.77 7.70 7.67 7.65 7.62 7.61 7.56 7.55 7.53 7.51 7.49 7.47 7.26 7.21 7.19 7.17
F
N
N
O
5e
400 MHz, CDCl3
1.00 2.02 1.04 1.05 3.12 2.26 1.99 1.05
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

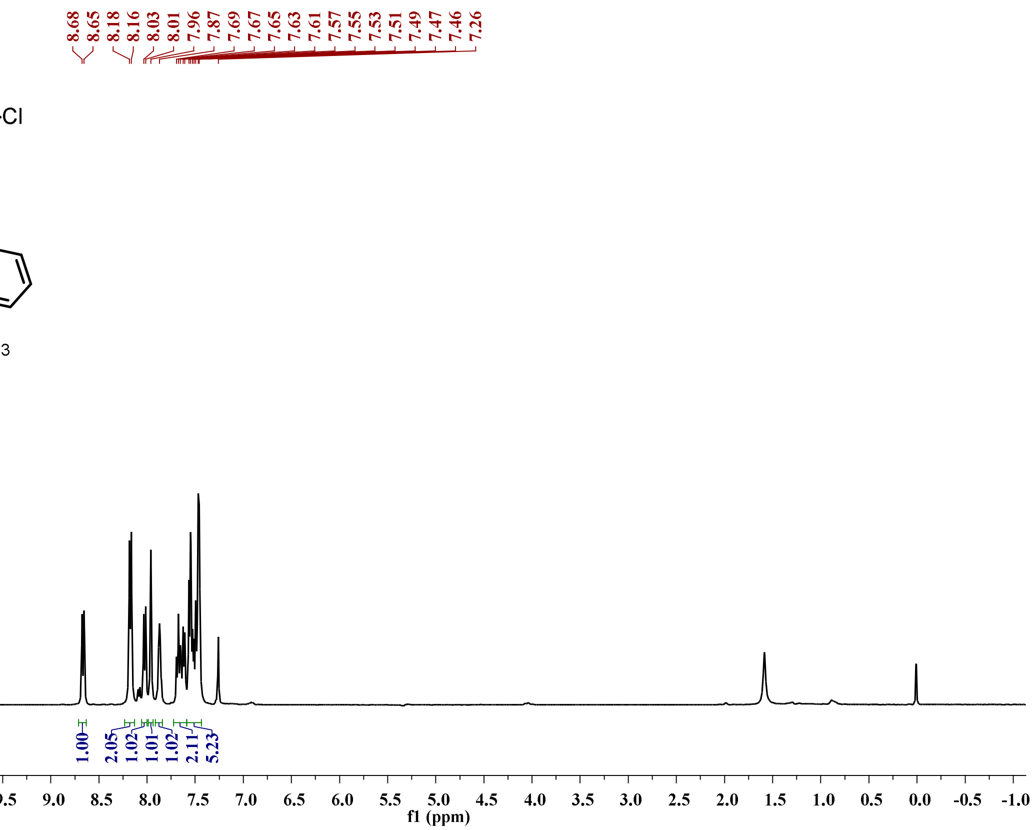

168.32 164.40 161.95 149.09 141.91 134.15 134.07 133.34 132.46 131.47 130.71 130.63 129.69 128.10 125.40 124.33 123.99 123.96 121.11 116.67 116.53 116.46 115.29 115.07 77.48 77.16 76.84
F
N
N
O
5e
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

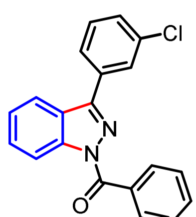

-111.98
F
N
N
O
5e
470 MHz, CDCl3
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)



5f

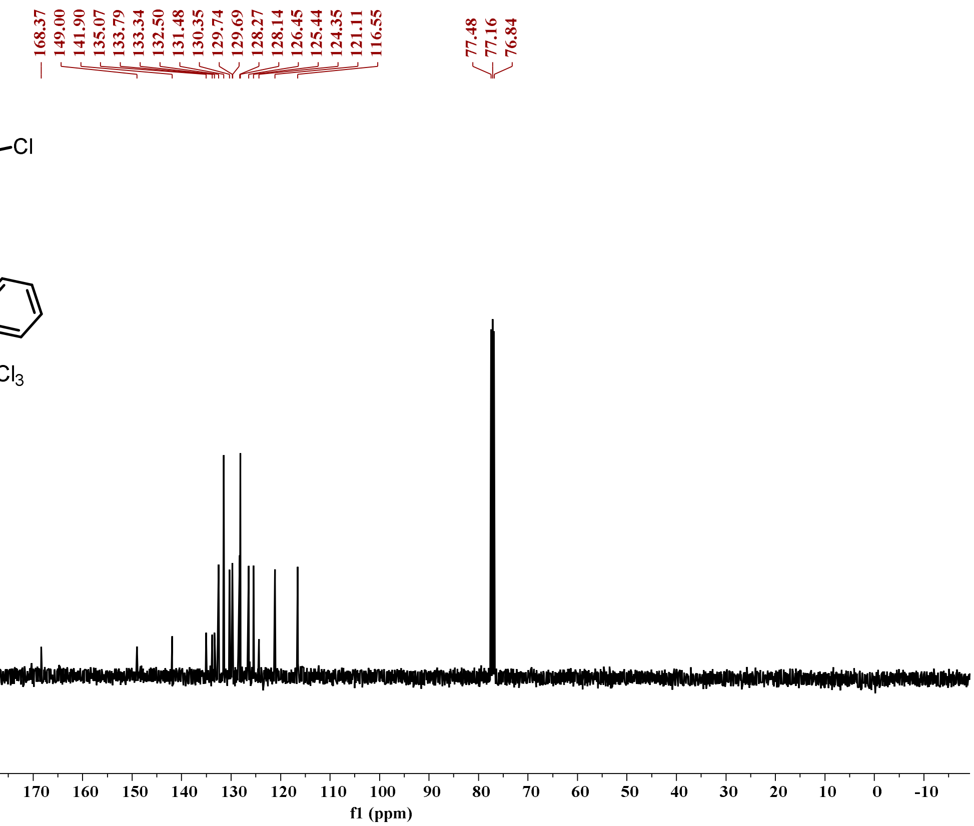
400 MHz, $CDCl_3$

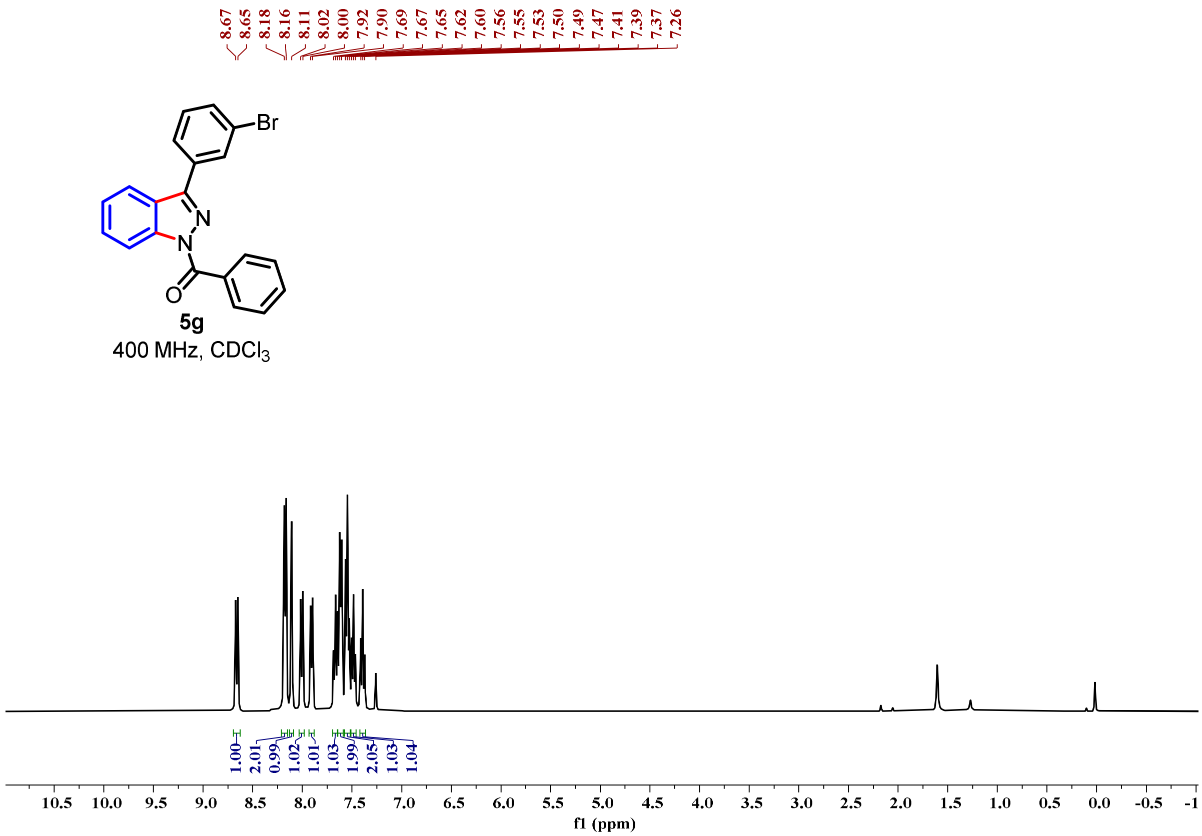


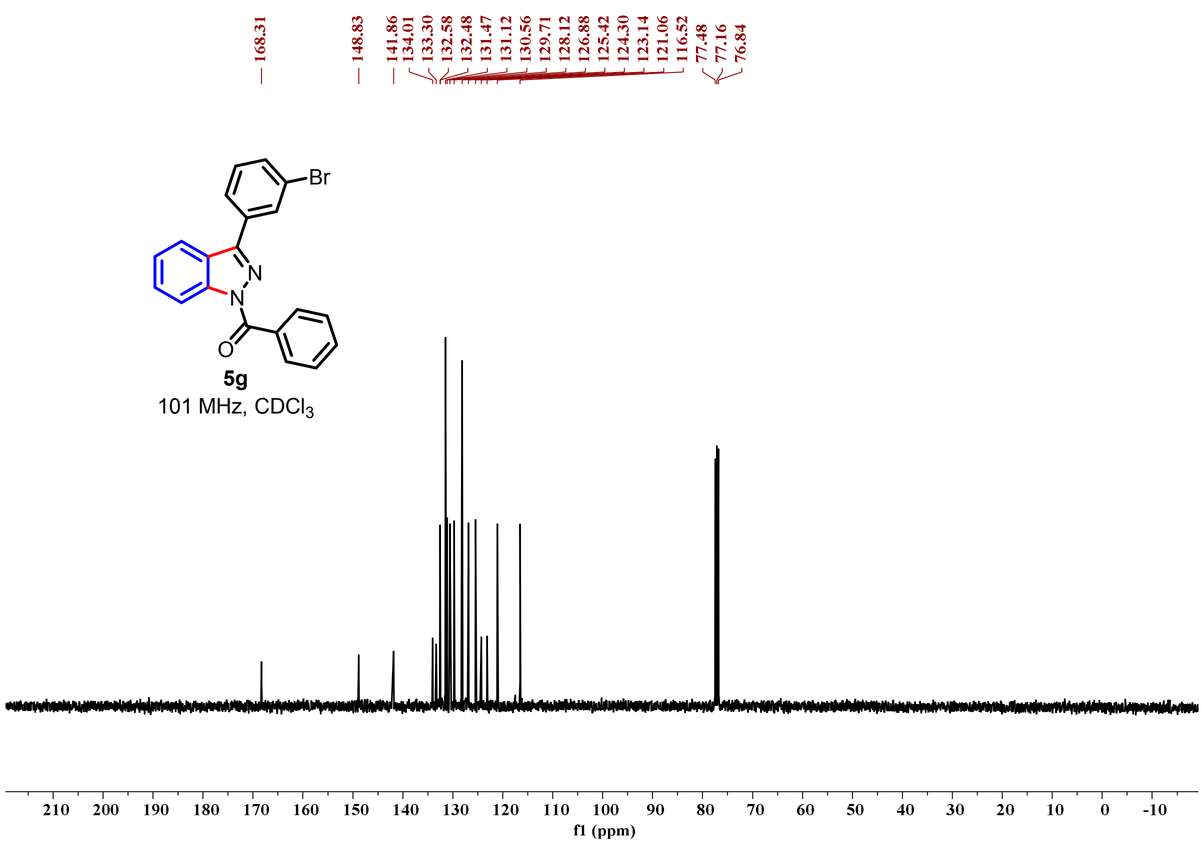


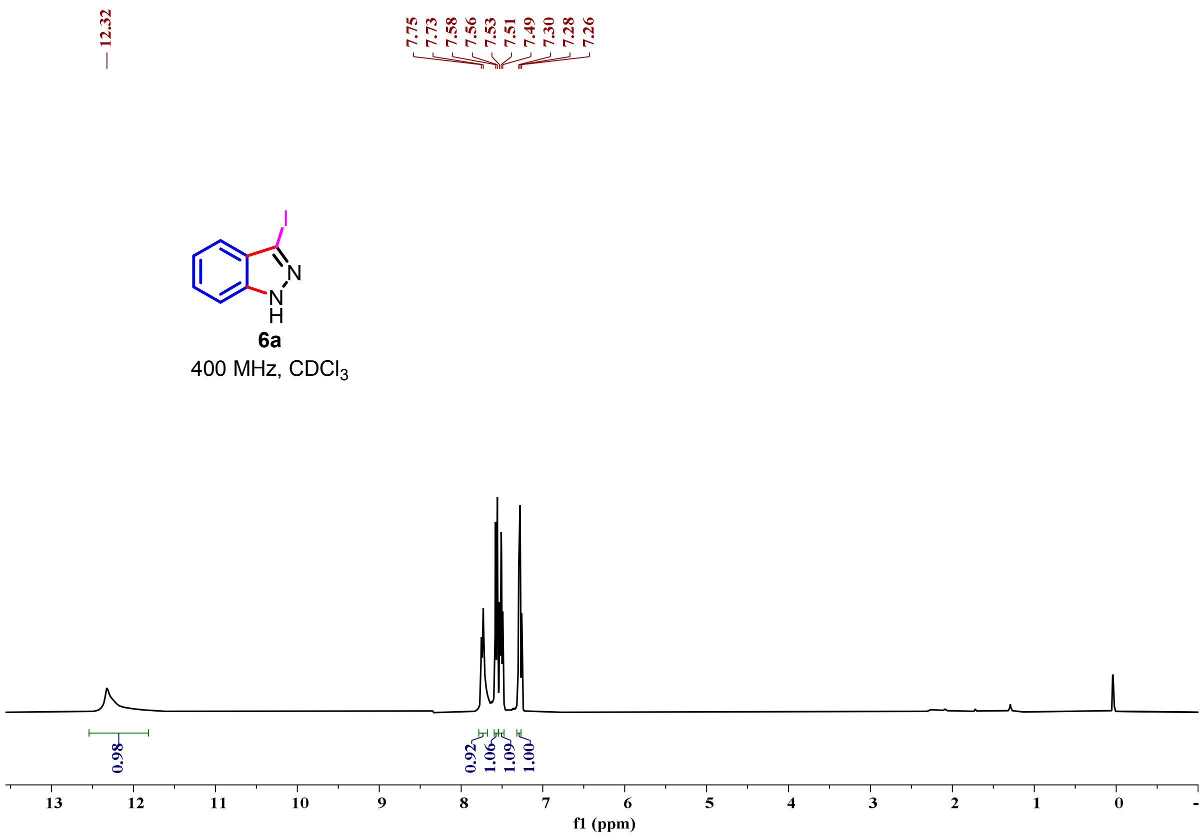
5f

101 MHz, $CDCl_3$

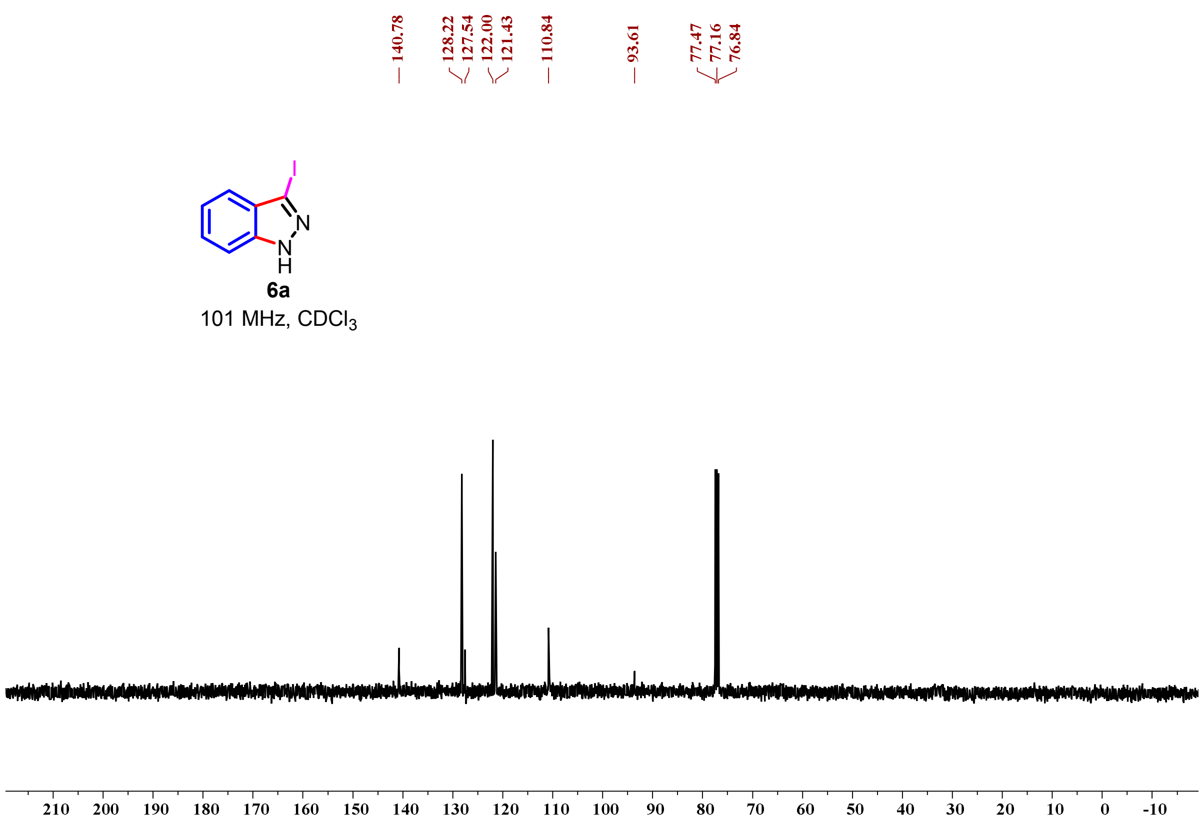



8.67
8.65
8.18
8.16
8.11
8.02
8.00
7.92
7.90
7.69
7.67
7.65
7.62
7.60
7.56
7.55
7.53
7.50
7.49
7.47
7.41
7.39
7.37
7.26
Br
N
N
O
5g
400 MHz, CDCl3
1.00
2.01
0.99
1.02
1.01
1.03
1.99
2.05
1.03
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

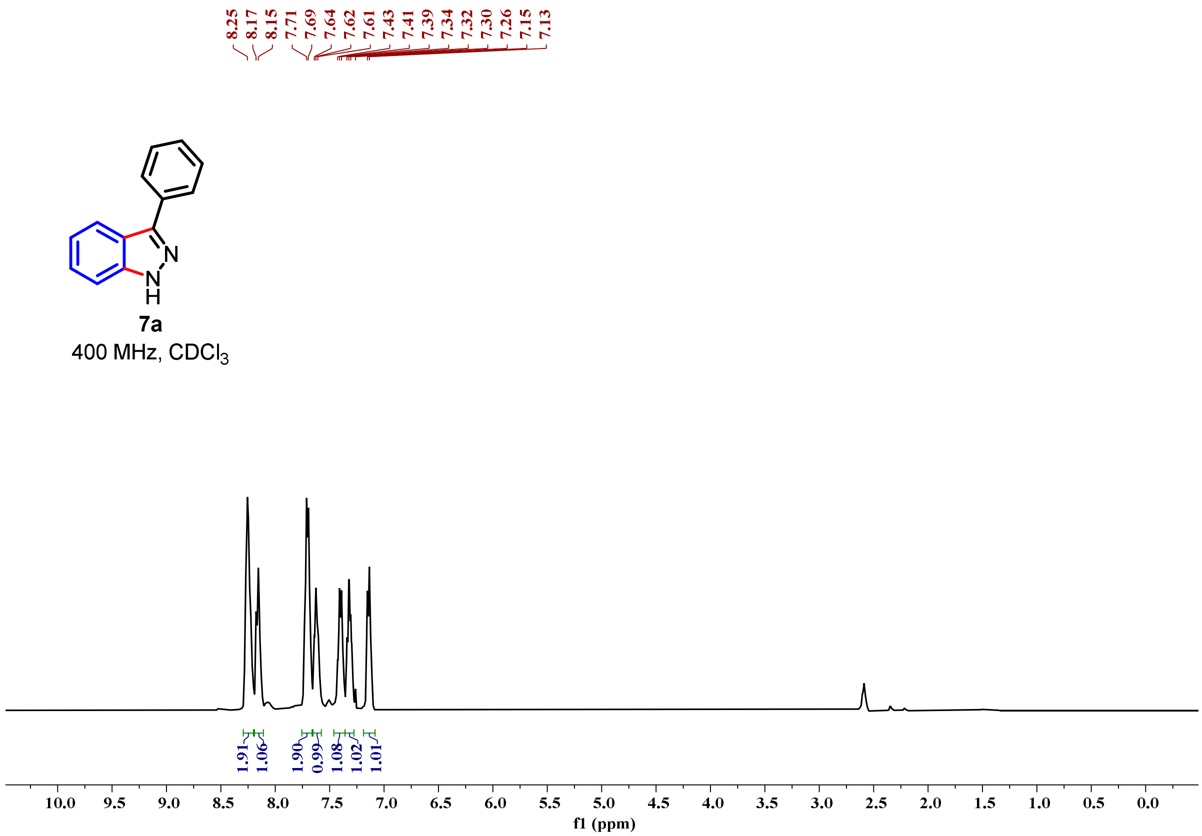

168.31
148.83
141.86
134.01
133.30
132.58
132.48
131.47
131.12
130.56
129.71
128.12
126.88
125.42
124.30
123.14
121.06
116.52
77.48
77.16
76.84
Br
N
N
O
5g
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



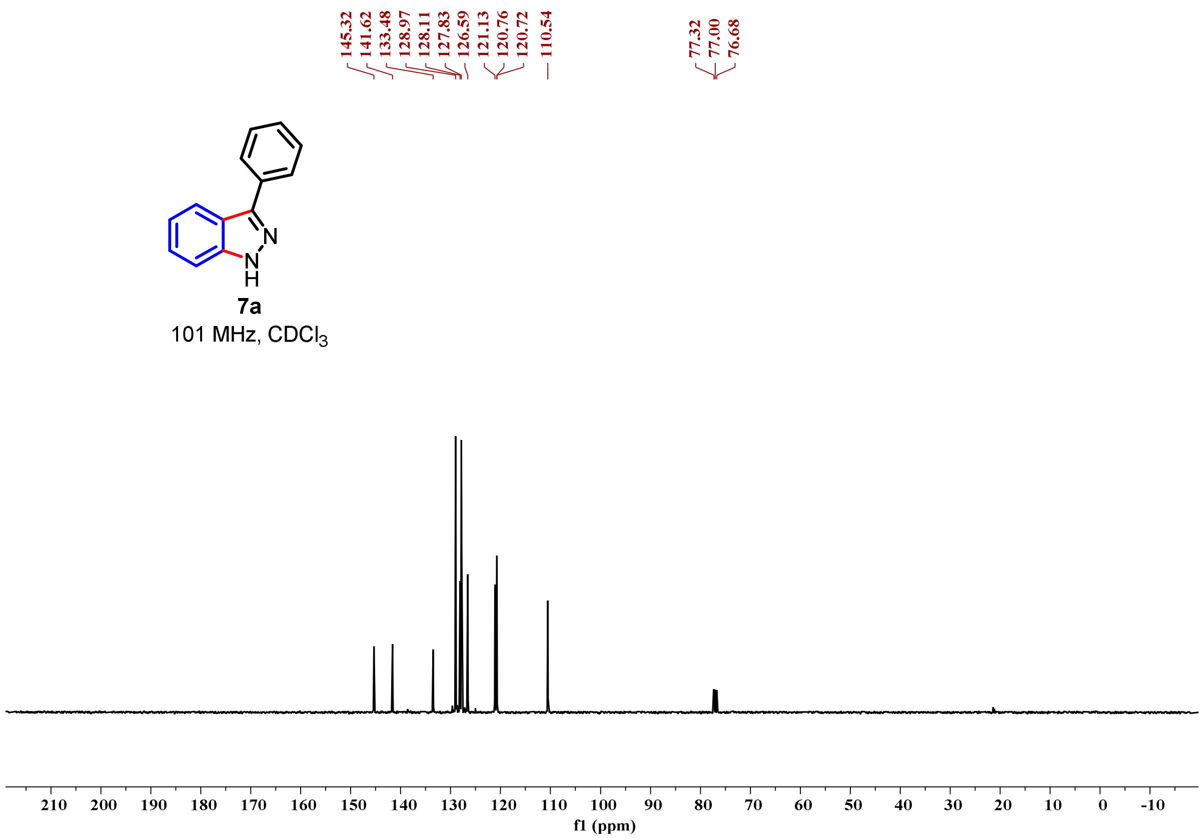
12.32
7.75
7.73
7.58
7.56
7.53
7.51
7.49
7.30
7.28
7.26
I
N
N
H
6a
400 MHz, $CDCl_3$
0.98
0.92
1.06
1.09
1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)



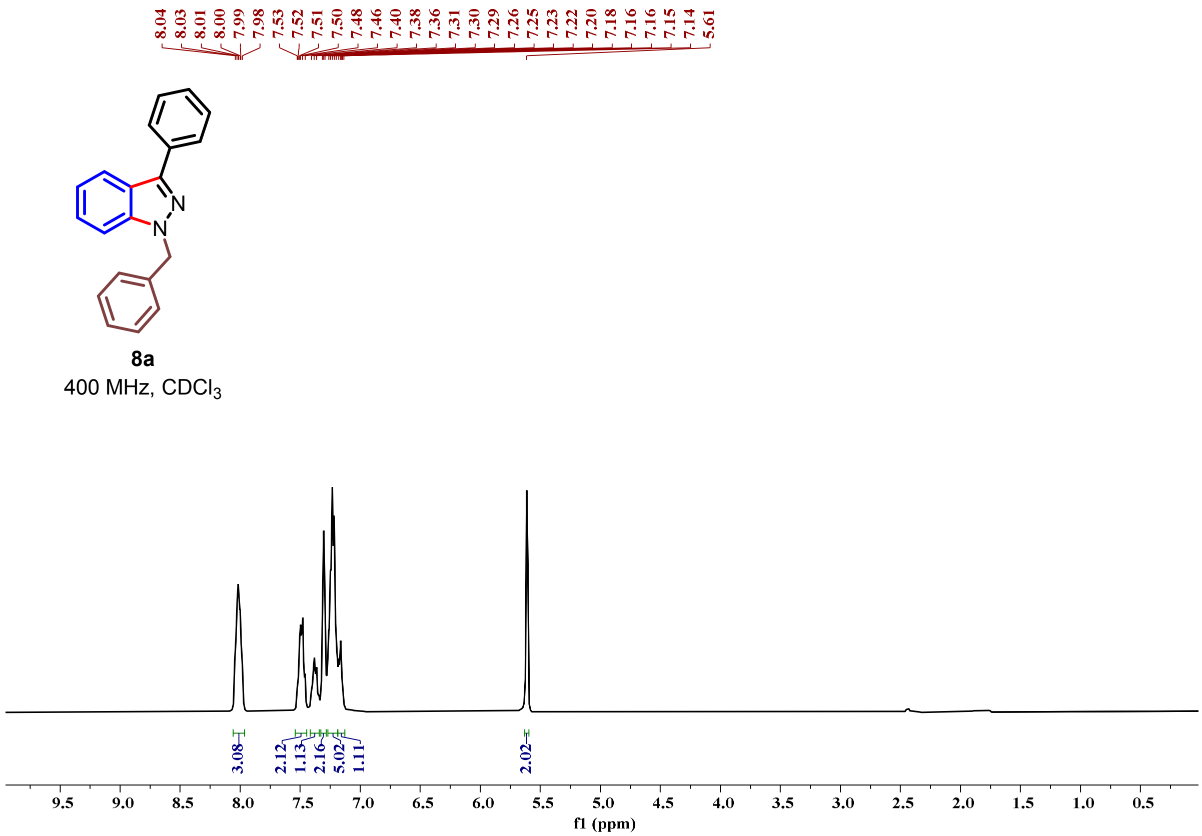
140.78
128.22
127.54
122.00
121.43
110.84
93.61
77.47
77.16
76.84
I
N
N
H
6a
101 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

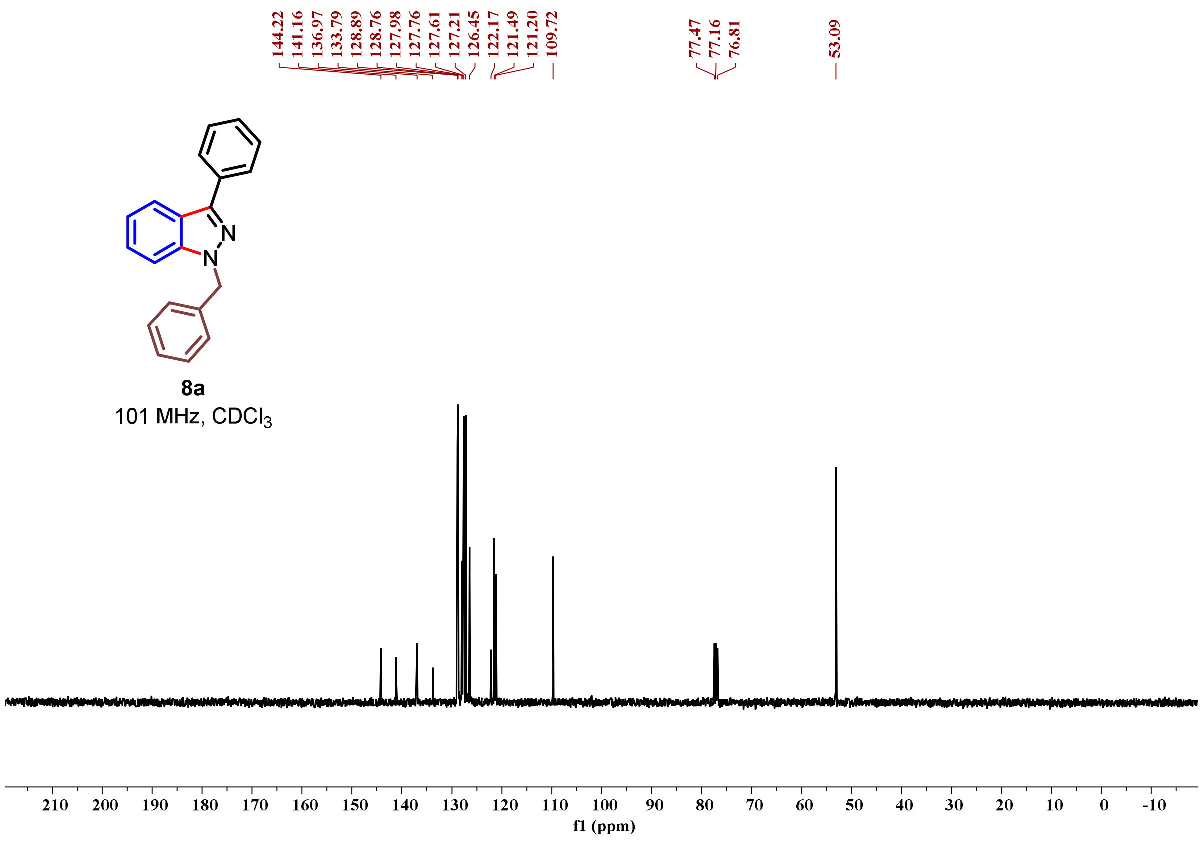


7a
400 MHz, $CDCl_3$



7a
101 MHz, $CDCl_3$


8.04
8.03
8.01
8.00
7.99
7.98
7.53
7.52
7.51
7.50
7.48
7.46
7.40
7.38
7.36
7.31
7.30
7.29
7.26
7.25
7.23
7.22
7.20
7.18
7.16
7.16
7.15
7.14
5.61
8a
400 MHz, $CDCl_3$
3.08
2.12
1.13
2.16
5.02
1.11
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


144.22
141.16
136.97
133.79
128.89
128.76
127.98
127.76
127.61
127.21
126.45
122.17
121.49
121.20
109.72
77.47
77.16
76.81
53.09
8a
101 MHz, $CDCl_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)