Supporting Information

Rhodium(III)-catalysed cascade [3 + 2] annulation of *N*-aryloxyacetamides with 3-(hetero)arylpropiolic acids: synthesis of benzofuran-2(3*H*)-ones

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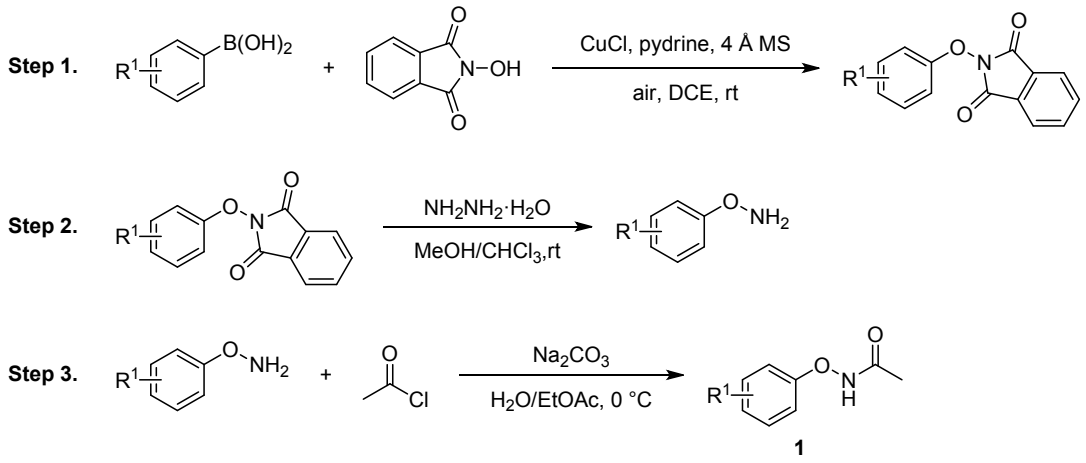
Contents

1. Preparation of the Substrates

1.1 Preparation of *N*-aryloxyacetamides

N-Aryloxyacetamides **1** were prepared according to the following procedures[1]:

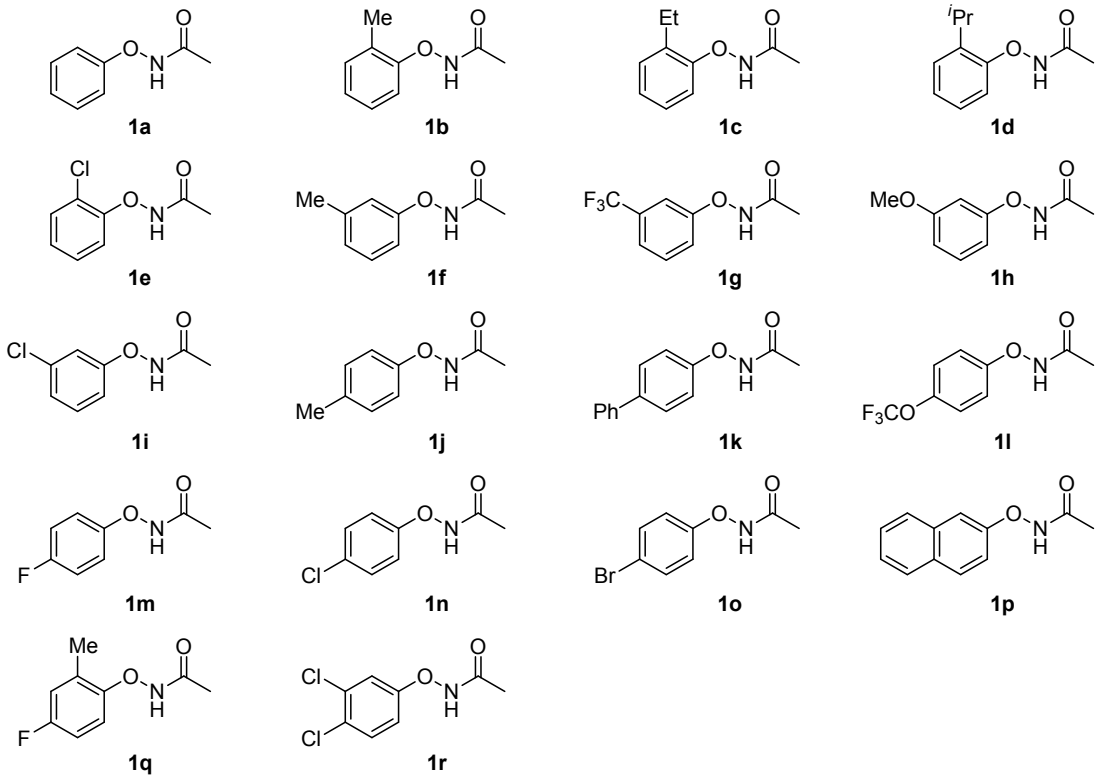


Step 1: To a round-bottom flask equipped with a magnetic stir bar was added *N*-hydroxyphthalimide (1.0 equiv), CuCl (1.0 equiv), freshly activated 4 Å molecular sieves (250 mg/mmol), arylboronic acid (2.0 equiv), pydrine (1.1 equiv) and 1,2-dichloroethane (0.2 M). The reaction flask was open to the atmosphere. The reaction mixture was stirred at ambient temperature until the reaction mixture became green. The reaction mixture was filtered off under reduced pressure, and the filter cake was washed with CH_2Cl_2. The obtained filtrate was concentrated under vacuum, and the residue was purified by flash column chromatograph on silica gel (PE/EtOAc 4:1) to afford the desired *N*-aryloxyphthalimide which was used directly in the next step. This step was typically carried out on a ~5 gram scale (arylboronic acid).

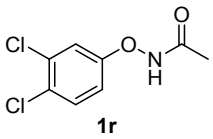
Step 2: To a solution of *N*-aryloxyphthalimide (1.0 equiv) in a mixture of MeOH and $CHCl_3$ (v/v 1:7, 0.2 M) was added hydrazinr monohydrate (3.0 equiv, 80%). The reaction mixture was allowed to stir at room temperature under air. Upon completion (TLC monitoring), the precipitate was filtered off under reduced pressure, and the filter cake was washed with CH_2Cl_2. The obtained filtrate was concentrated under vacuum, and the residue was purified by flash column chromatograph on silica gel (PE/EtOAc 10:1) to afford the desired *N*-aryloxyamide which was directly used in the next step.

Step 3: A solution of *N*-aryloxyamide (1.0 equiv) in EtOAc was added to an aqueous solution of Na_2CO_3 (2.2 equiv) (H_2O/EtOAc 1:2, 0.3 M). The reaction mixture was cooled to 0 °C followed by dropwise addition of acyl ahloride (2.0 equiv). After stirring at 0 °C for 3 h, the reaction was quenched with saturated $NaHCO_3$ aqueous solution. The organic phase was separated and the aqueous phase was

extracted with EtOAc. The combined organic phase was washed with brine, separated, dried over anhydrous Na_2SO_4, filtered, concentrated. The crude product was purified by recrystallization from EtOAc/PE to afford the desired *N*-aryloxyacetamide **1** as a white solid. Except **1r**, all the *N*-aryloxyacetamides used in this manuscript are known.



Scheme S1. List of *N*-aryloxyacetamides used in this manuscript

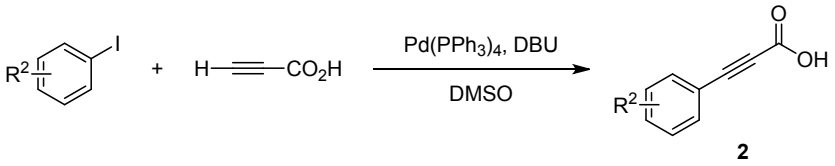


***N*-(3,4-dichlorophenoxy)acetamide (1r)**

39% yield for 3 steps, white crystal. **mp** 157 – 158 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.84 (brs, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.31 (d, J = 2.6 Hz, 1H), 7.05 (dd, J = 8.9, 2.6 Hz, 1H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.7, 159.0, 131.7, 131.1, 124.1, 115.0, 113.8, 19.4. **HRMS** (ESI) *m/z* calculated for $C_8H_8Cl_2NO_2^+$ [M+H$^+$] 219.9927, found 219.9927.

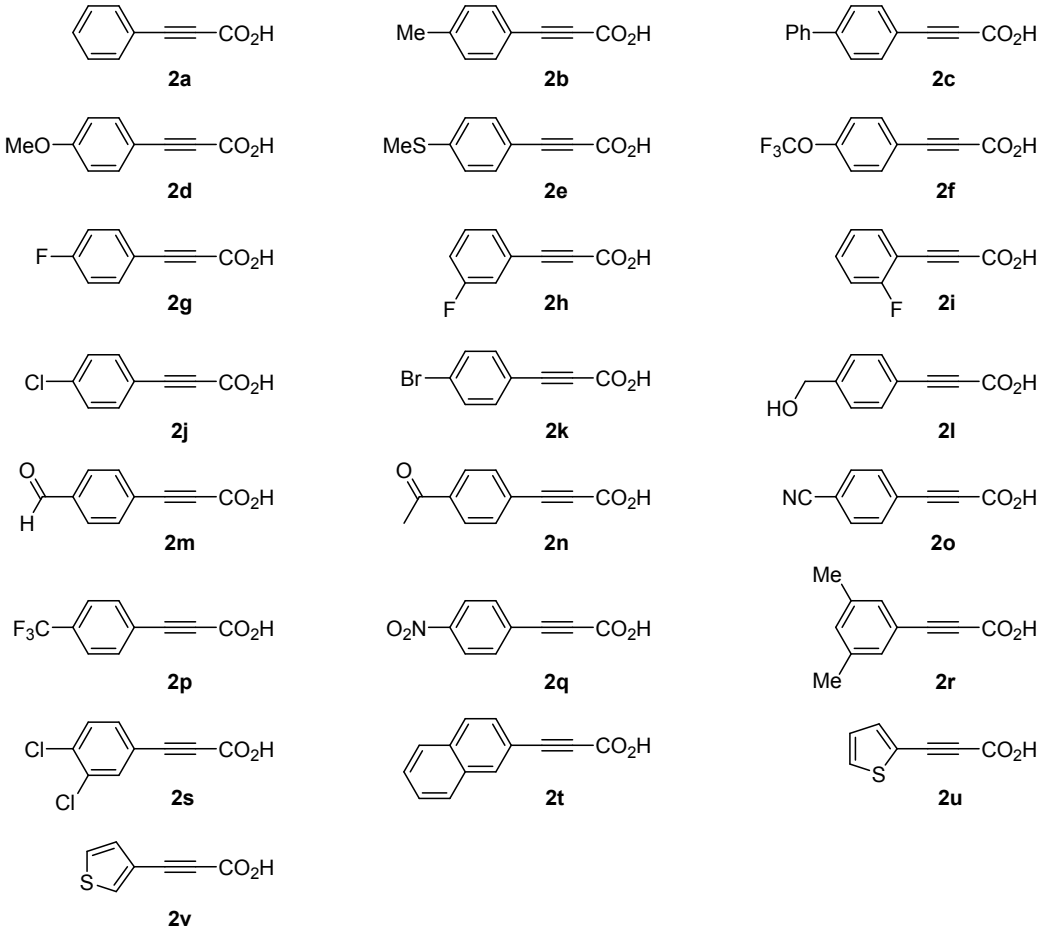
1.2 Preparation of 3-arylpropiolic acids

3-Phenylpropiolic acid **2a** (98%) was purchased from TCI, and other 3-arylpropiolic acid were prepared according to the following procedure[2].



2

A 25-mL round bottom flask equipped with a magnetic stir bar was sequentially charged with aryl iodide (5.0 mmol), DBU (1.80 mL, 12 mmol), $Pd(PPh_3)_4$ (144.4 mg, 2.5 mol %) and DMSO (6 mL). A solution of propiolic acid (420 mg, 6.0 mmol) in DMSO (6 mL) was added into the flask. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (20 mL) was poured into the reaction mixture. The reaction mixture was extracted with saturated aqueous $NaHCO_3$ solution. The aqueous layer was separated, acidified to pH 2.0 by addition of cold HCl aqueous solution (1 N), and extracted with DCM. The combined organic layers were dried with anhydrous Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1, with 1% v/v HOAc) to afford 3-arylpropiolic acids **2**.



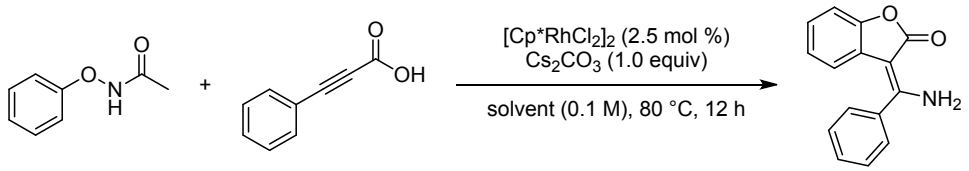
Scheme S2. List of 3-arylpropiolic acids used in this manuscript

2. Optimization of the Reaction Conditions

General procedure for optimization of the reaction conditions:

An oven-dried 15-mL test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with *N*-phenoxyacetamide **1a** (30.2 mg, 0.2 mmol), 3-phenylpropiolic acid **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), catalyst, base (0.2 mmol, 1.0 equiv) and solvent (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA 8:1→5:1) to provide the desired product **3**.

Table S1. Screening of solvent[a]

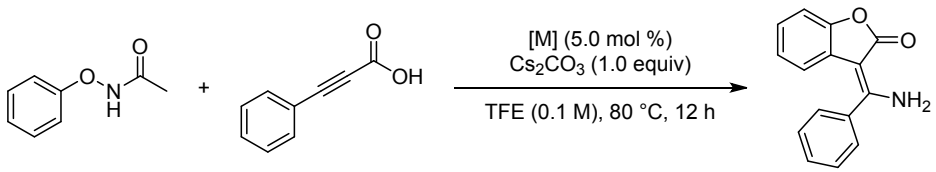


1a **2a** **3aa**

Entry	Solvent	Yield[b] (%)
1	MeOH	9
2	DCM	<2
3	DCE	<2
4	toluene	<2
5	MeCN	<2
6	1,4-dioxane	<2
7	DMF	<2
8	DMSO	<2
9	EtOH	11
10	*i*-PrOH	<2
11	**TFE**	**53**
12	HFIP	<2

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), and Cs_2CO_3 (0.2 mmol) in solvent (2.0 mL) at 80 °C under argon for 12 h. Cp* = pentamethylcyclopentadienyl; DCM = dichloromethane; DCE = 1,2-dichloroethane; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide; TFE = 2,2,2-trifluoroethanol; HFIP = hexafluoroisopropanol. [b]Isolated yield.

Table S2. Screening of Cp*TM-type catalyst[a]

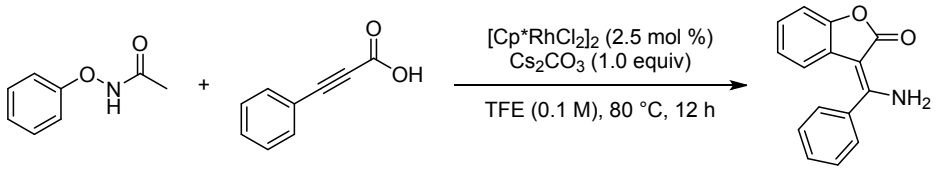


1a **2a** **3aa**

Entry	Catalyst	Yield[b] (%)
1	**$[Cp^*RhCl_2]_2$**	**53**
2	$[Cp^*Rh(OAc)_2]_2$	48
3	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	48
4	$[Cp^*IrCl_2]_2$	0
5	$[Cp^*RuCl_2]_n$	0
6	$[Cp^*CoI_2(CO)]_2$	0
7	$[Cp^*Co(MeCN)_3](SbF_6)_2$	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [Cp*TM] (5 mol %), and Cs_2CO_3 (0.2 mmol) in TFE (2.0 mL) at 80 °C under argon for 12 h. [b]Isolated yield.

Table S3. Screening of atmosphere and moisture[a]

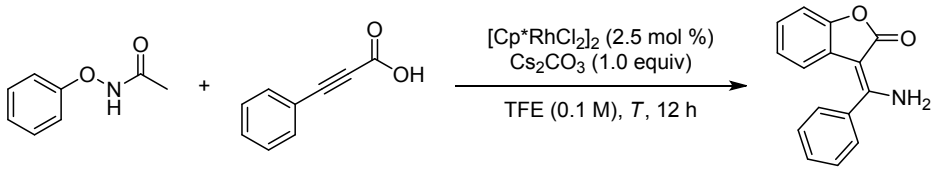


1a **2a** **3aa**

Entry	Atmosphere	Yield[b] (%)
1	**Ar**	**53**
2	air	39
3	O_2 (1 atm)	35
4[c]	Ar	46

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), and Cs_2CO_3 (0.2 mmol) in TFE (2.0 mL) at 80 °C under indicated atmosphere for 12 h. [b]Isolated yield. [c]H_2O (5.0 equiv) was added.

Table S4. Screening of reaction temperature[a]

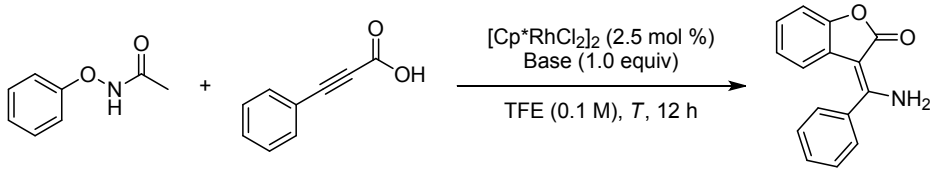


1a **2a** **3aa**

Entry	Temperature (°C)	Yield[b] (%)
1	100	49
2	**80**	**53**
3	60	48
4	40	11
5	25	<2

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), and Cs_2CO_3 (0.2 mmol) in TFE (2.0 mL) at indicated temperature under argon for 12 h. [b]Isolated yield.

Table S5. Screening of base[a]



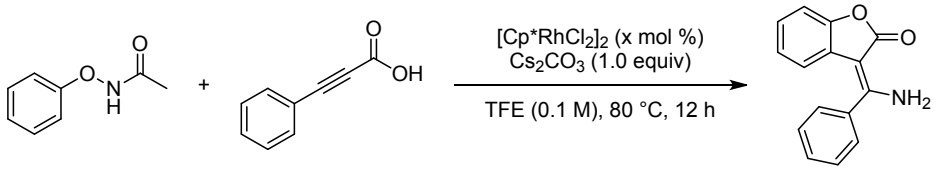
1a **2a** **3aa**

Entry	Base	Yield[b] (%)
1	-	<2
2	Na_2CO_3	30
3	K_2CO_3	44
4	**Cs_2CO_3**	**53**
5	$NaHCO_3$	<2
6	$KHCO_3$	32
7	$CsHCO_3$	46
8	NaOH	37
9	KOH	46
10	Na_3PO_4	11
11	K_3PO_4	45
12	NaOAc	<2
13	KOAc	<2
14	CsOAc	<2
15	**Et_3N**	52
16	**DIPEA**	50
17	**DBU**	51
18	**DBN**	52

19	**TMG**	51
20	DABCO	<2
21	DMAP	<2

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), and base (0.2 mmol) in TFE (2.0 mL) at 80 °C under argon for 12 h. DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene; DBN = 1,5-diazabicyclo[4.3.0]non-5-ene; TMG = 1,1,3,3-tetramethylguanidine; DABCO = 1,4-diazabicyclo[2.2.2]octane; DMAP = 4-dimethylaminopyridine. [b]Isolated yield.

Table S6. Screening of loading of Catalyst[a]



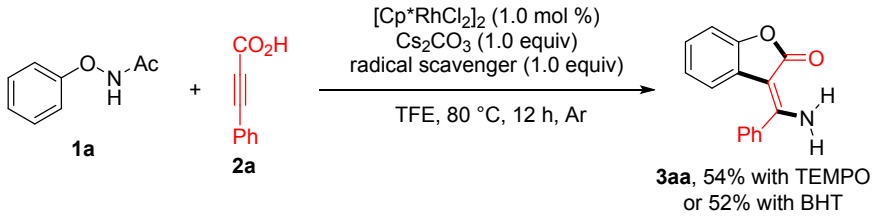
1a **2a** **3aa**

Entry	Loading (mol %)	Yield[b] (%)
1	2.5	53
2	1.5	53
3	**1.0**	**53**
4	0.5	47

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$, and Cs_2CO_3 (0.2 mmol) in TFE (2.0 mL) at 80 °C under argon for 12 h. [b]Isolated yield.

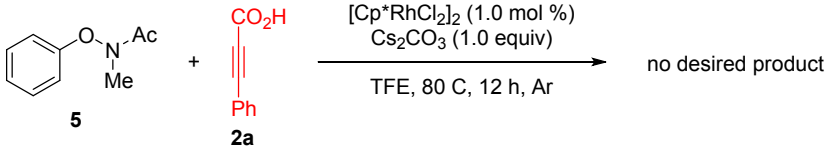
3. Experimental Mechanistic Studies

a) Radical trapping experiments



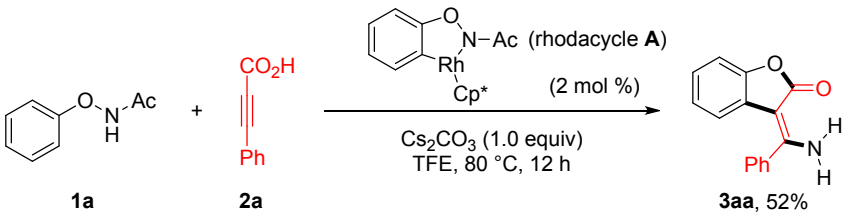
An oven-dried 15-mL test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with *N*-phenoxyacetamide **1a** (30.2 mg, 0.2 mmol, 1.0 equiv), 3-phenylpropiolic acid **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 2 μmol, 1.0 mol %), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO; 31.2 mg, 0.2 mmol, 1.0 equiv) or butylated hydroxytoluene (BHT; 44.1 mg, 0.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the desired product **3** (54% yield with TEMPO, or 52% yield with BHT, respectively).

b) The essential role of N−H bond



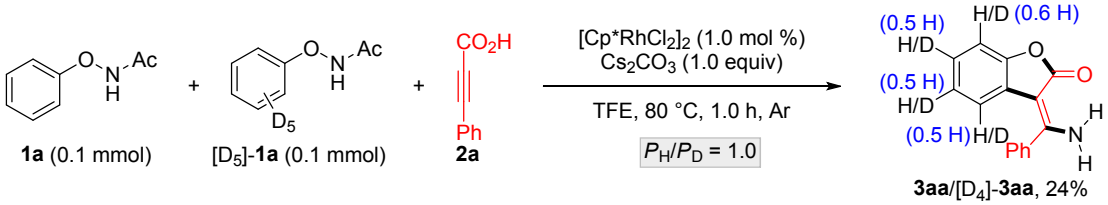
An oven-dried 15-mL test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with *N*-methyl-*N*-phenoxyacetamide **5** (33.0 mg, 0.2 mmol, 1.0 equiv), 3-phenylpropiolic acid **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 2 μmol, 1.0 mol %), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. No desired product was detected.

c) The rhodacycle A



An oven-dried 15-mL test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with *N*-phenoxyacetamide **1a** (30.2 mg, 0.2 mmol, 1.0 equiv), 3-phenylpropiolic acid **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), rhodacycle **A**[3] (1.5 mg, 4 μmol, 2.0 mol %), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the desired product **3** (52%).

d) Intermolecular competition experiment for the KIE studies



An oven-dried 15-mL test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with **1a** (15.1 mg, 0.1 mmol, 0.5 equiv), [D_5]-**1a** (15.6 mg, 0.1 mmol, 0.5 equiv), **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 2 μmol, 1.0 mol %), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 1.0 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the mixed products **3aa**/[D_4]-**3aa** (24%). According to the ^{1}H NMR spectrum of the mixed products (Figure S1), P_H/P_D = 1.0.

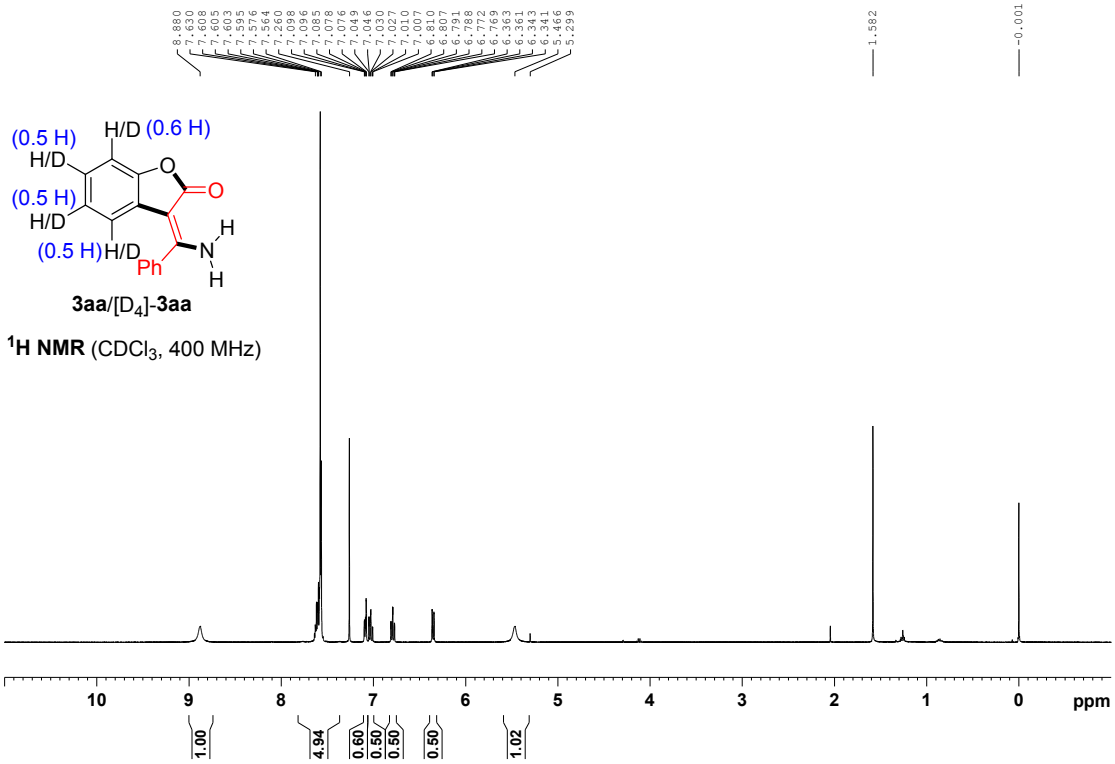
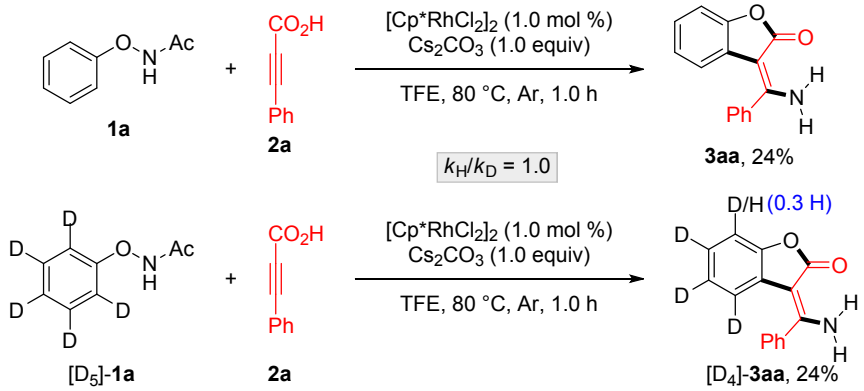


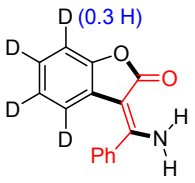
Figure S1. ^{1}H NMR spectrum of the mixed products of the intermolecular competition experiment

e) Parallel experiments for KIE studies



An oven-dried 15-mL test tubes equipped with a Teflon-coated magnetic stir bar was sequentially charged with **1a** (30.2 mg, 0.2 mmol, 1.0 equiv), **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 2 μmol, 1.0 mol %), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (2.0 mL) under a positive pressure of argon. Simultaneously, another parallel experiment was carried out with $[D_5]$-**1a** (31.2 mg, 0.2 mmol, 1.0 equiv). After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 1.0 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was

evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the products **3aa** (24%) and [D_4]-**3aa** (24%), respectively. Thus, k_H/k_D = 1.0.

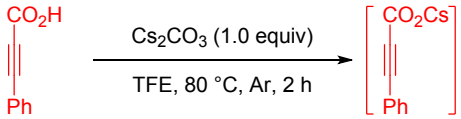


[D_4]-**3aa**

(*Z*)-3-(Amino(phenyl)methylene)-*d*$_4$-benzofuran-2(3*H*)-one ([D_4]-3aa)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.64 – 7.54 (m, 5H), 7.08 (s, 0.3H), 5.53 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 161.1, 149.9 (d, J = 4.8 Hz), 135.0, 131.2, 129.5, 127.7, 125.2, 123.9 (t, J = 24.4 Hz), 122.3 (t, J = 24.2 Hz), 118.1 (t, J = 24.1 Hz), 109.8 (major) (t, J = 24.5 Hz), 110.1 (minor), 90.9. **HRMS** (ESI) *m/z* calculated for $C_{15}H_8D_4NO_2^+$ [M+H$^+$] 242.1114, found 242.1124.

f) Cesium 3-phenylpropiolate



2a **2a'**

A solution of **2a** (29.2 mg, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) in TFE (2.0 equiv) was heated at 80 °C for 2 h. The reaction was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The residue **2a'** was characterized by NMR in CD_3OD.

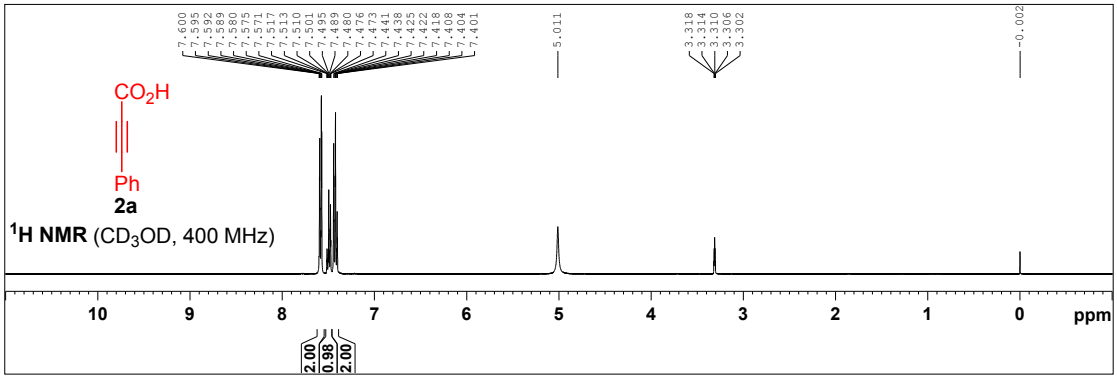


Figure S2. ^{1}H NMR spectrum of **2a**

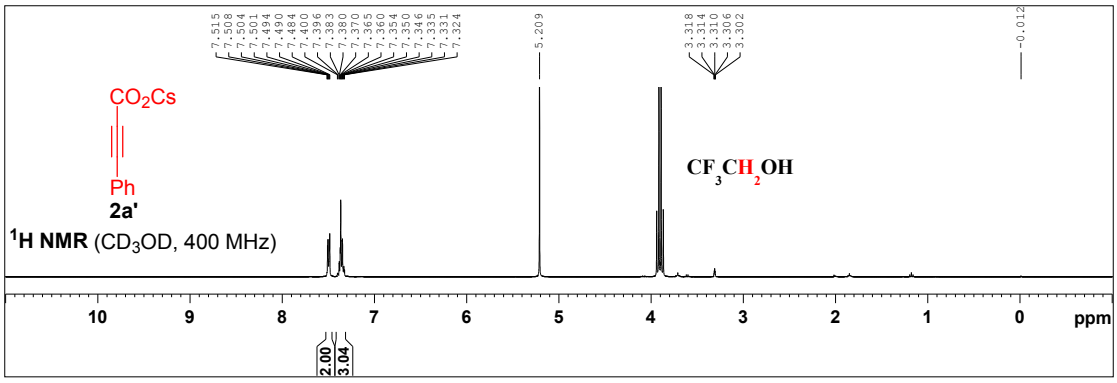


Figure S3. ^{1}H NMR spectrum of **2a'**

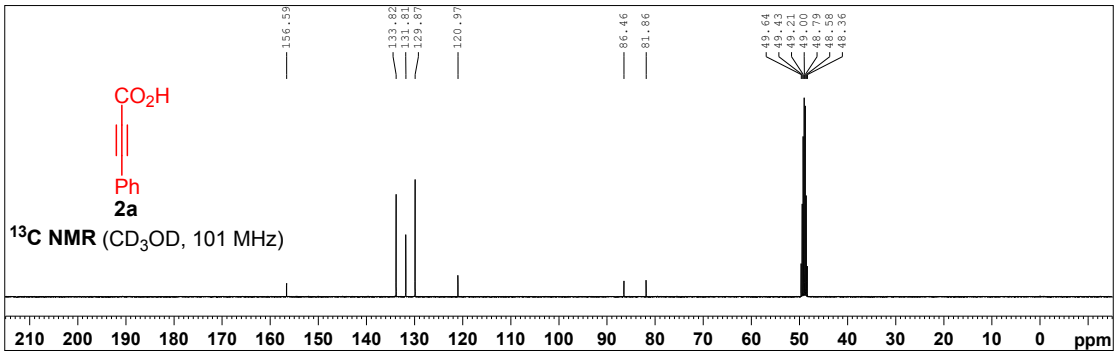


Figure S4. ^{13}C NMR spectrum of **2a**

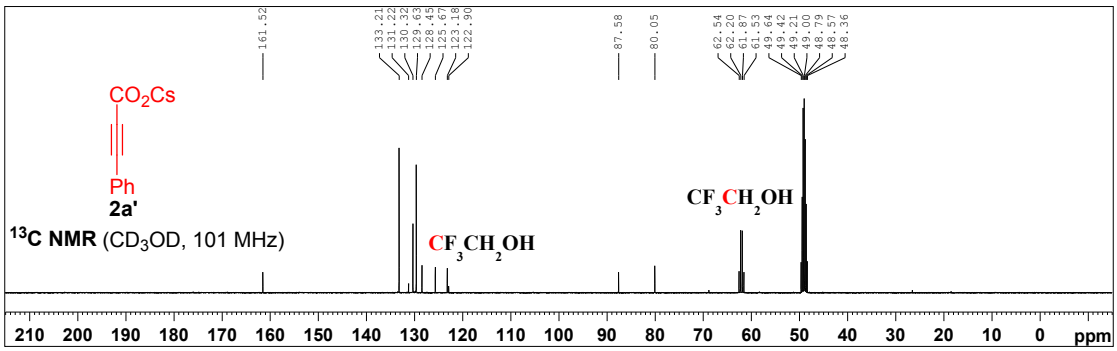
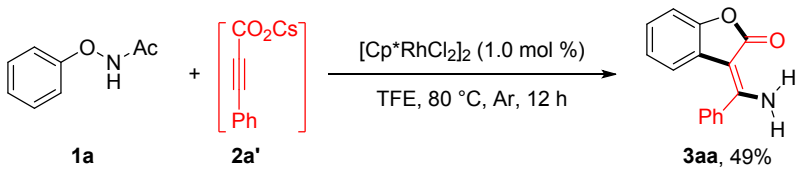


Figure S5. ^{13}C NMR spectrum of **2a'**

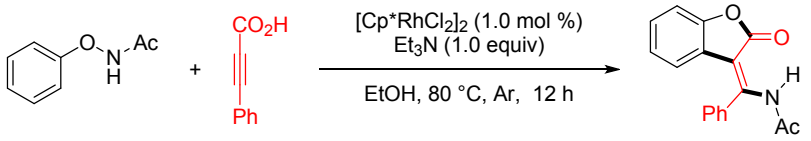


1a **2a'** **3aa**, 49%

To the above reaction solution was added with **1a** (30.2 mg, 0.2 mmol, 1.0 equiv) and $[Cp^*RhCl_2]_2$ (1.2 mg, 2 μmol, 1.0 mol %) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent

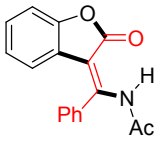
was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the products **3aa** (49%).

g) Synthesis of **3aa-Ac** and further transformations



1a **2a** **3aa-Ac**, 34%

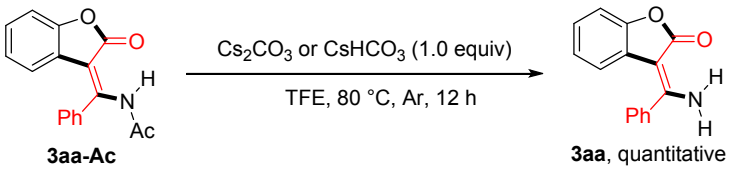
An oven-dried 15-mL test tubes equipped with a Teflon-coated magnetic stir bar was sequentially charged with **1a** (30.2 mg, 0.2 mmol, 1.0 equiv), **2a** (29.2 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 2 μmol, 1.0 mol %), Et_3N (28 μL, 0.2 mmol, 1.0 equiv) and absolute ethanol (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the products **3aa-Ac** (34%).



3aa-Ac

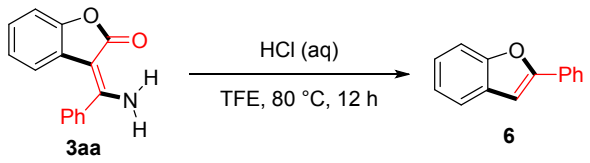
(*Z*)-*N*-((2-Oxobenzofuran-3(2*H*)-ylidene)(phenyl)methyl)acetamide (3aa-Ac)[4]

Yellow solid, **mp** 155 – 156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.11 (brs, 1H), 7.59 – 7.51 (m, 3H), 7.42 – 7.37 (m, 2H), 7.16 – 7.12 (m, 1H), 7.09 – 7.07 (m, 1H), 6.78 (td, J = 7.6, 1.2 Hz, 1H), 5.97 (dd, J = 7.8, 0.7 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 168.1, 153.0, 151.5, 133.3, 130.0, 129.3, 127.8, 127.1, 123.8, 123.2, 121.2, 110.6, 102.1, 25.3. **HRMS** (ESI) *m/z* calculated for $C_{17}H_{14}NO_3^+$ $[M+H^+]$ 280.0968, found 280.0963.



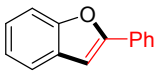
3aa-Ac **3aa**, quantitative

To a solution of **3aa-Ac** (27.9 mg, 0.1 mmol) in TFE (1 mL) was added Cs_2CO_3 (32.6 mg, 0.1 mmol) or $CsHCO_3$ (19.4 mg, 0.1 mmol) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH_2Cl_2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the products **3aa** (quantitative).



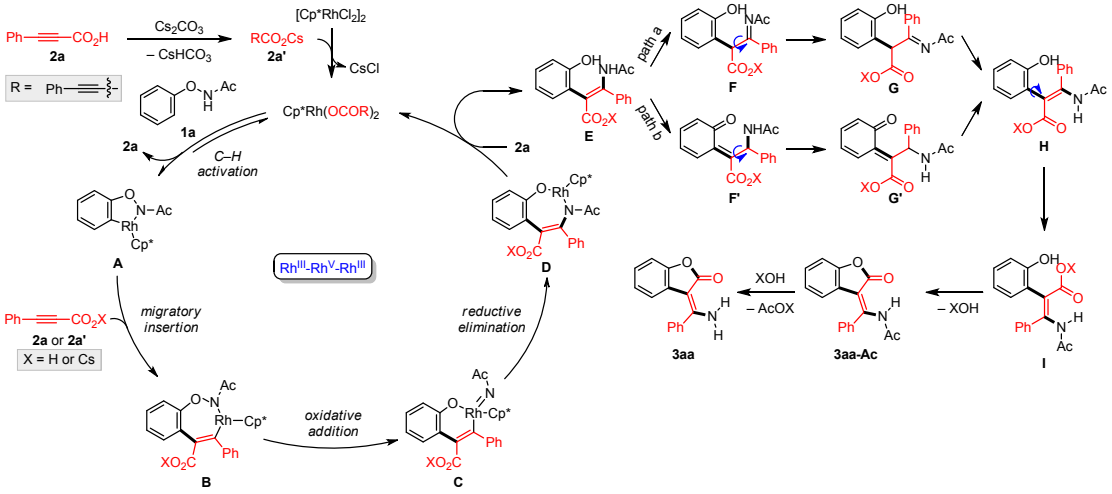
3aa **6**

To a solution of **3aa** (47.5 mg, 0.2 mmol) in TFE (2 mL) was added diluted hydrochloric acid (10%, 1.0 mL), and the reaction was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, quenched with saturated Na_2CO_3 aqueous solution (pH 8-9), extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the products **6**[5] (76%).



6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.30 – 7.21 (m, 2H), 7.02 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 155.0, 130.6, 129.3, 128.9, 128.7, 125.1, 124.4, 123.1, 121.0, 111.3, 101.4.



Scheme S3. Proposed catalytic pathway for the synthesis of **3aa**

Based on the aforementioned experimental results, together with precedent literature[4,6], we have proposed a plausible mechanism for the Cp*Rh(III)-catalyzed redox-neutral cascade [3 + 2] annulation, as depicted in Scheme S3. Initially, the reversible N−H deprotonation and C−H activation of **1a** generated rhodacycle **A**. The regioselective migratory insertion of **2a** into the C−Rh bond gave **B**. The formation of **D** was quite facile through oxidative addition of Rh into the O−N bond via Rh(V) nitrenoid **C** followed by reductive elimination. The protonation was involved to facilitate the generation of **E**. The isomerizaiton of C−C double bond was achieved through enamine-imine (path a)[4] or phenol-semiquinone (path b) tautomerization with promotion of the N−H···O type intramolecular interaction. The consecutive C−C single bond rotation, lactonization and hydrolysis afforded benzofuran-2-one derivative **3aa**.

4. Spectral Behavior Investigations of 3aa

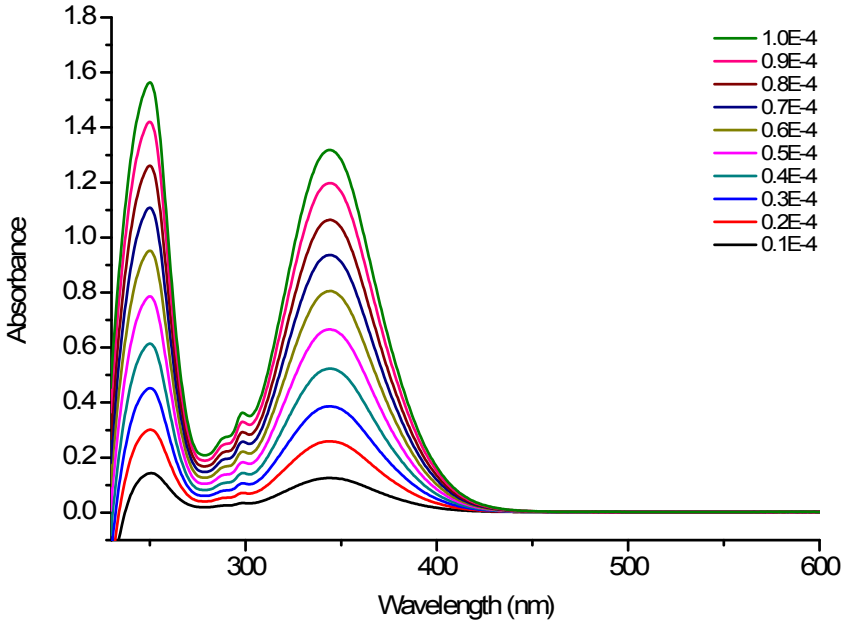


Figure S6. Variation of absorbance intensity of **3aa** in MeOH at different concentrations ranging from 1.0×10^{-5} to 1.0×10^{-4} M

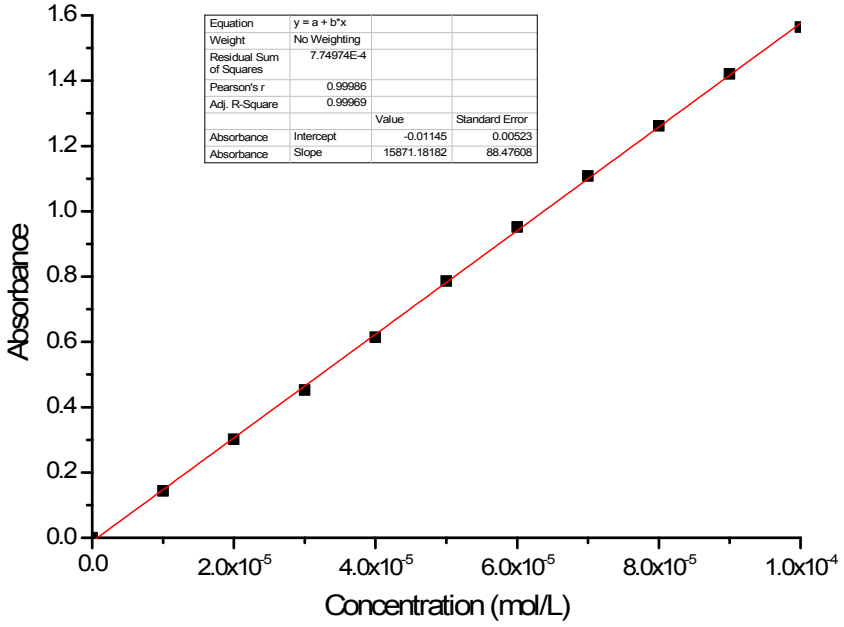


Figure S7. The linearity of the absorbance intensity (λ_{abs} = 250 nm) towards different concentrations of **3aa** in MeOH

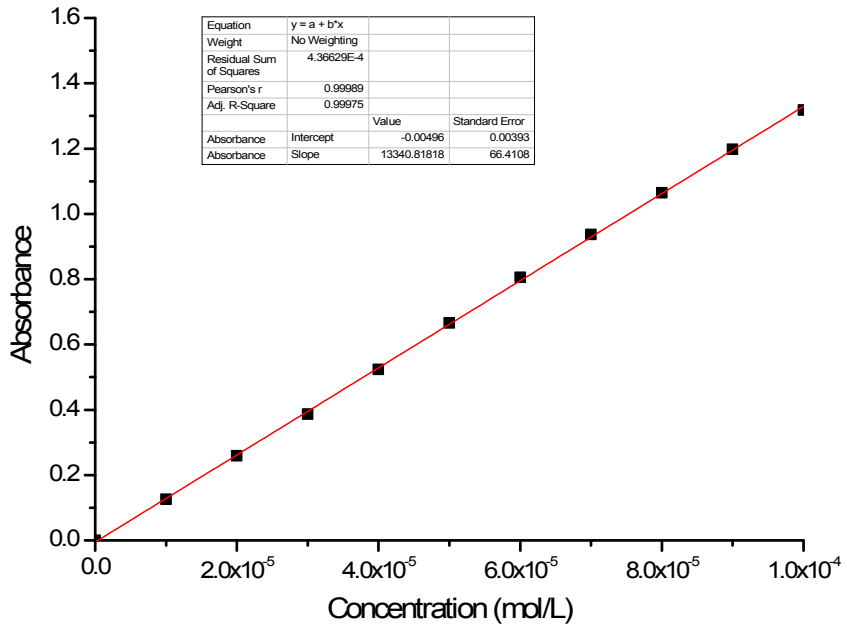


Figure S8. The linearity of the absorbance intensity (λ_{abs} = 344 nm) towards different concentrations of **3aa** in MeOH

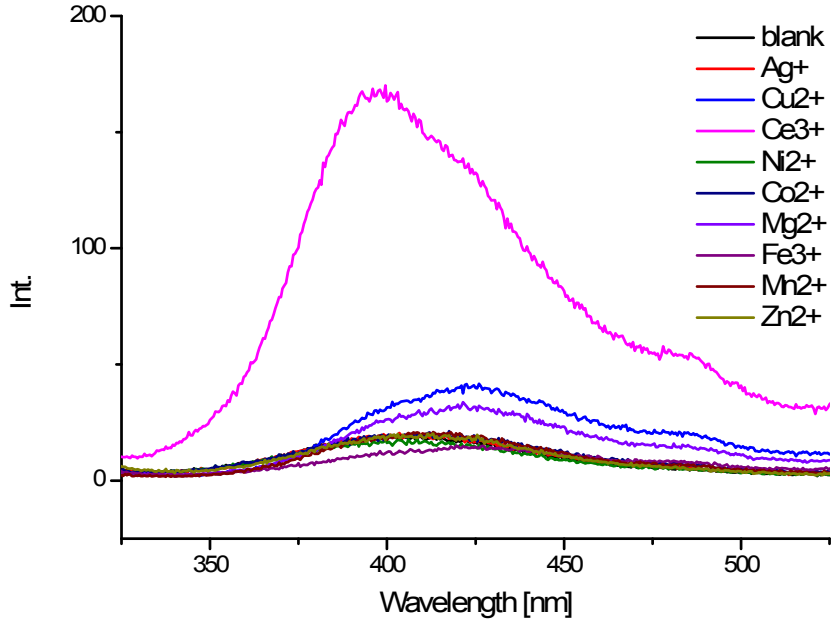


Figure S9. The fluorescence emission spectra of **3aa** in MeOH (1.0×10^{-4} M) upon excitation at 285 nm in the absence and presence of different metal cations

5. X-Ray Crystallography Analysis of 3aa

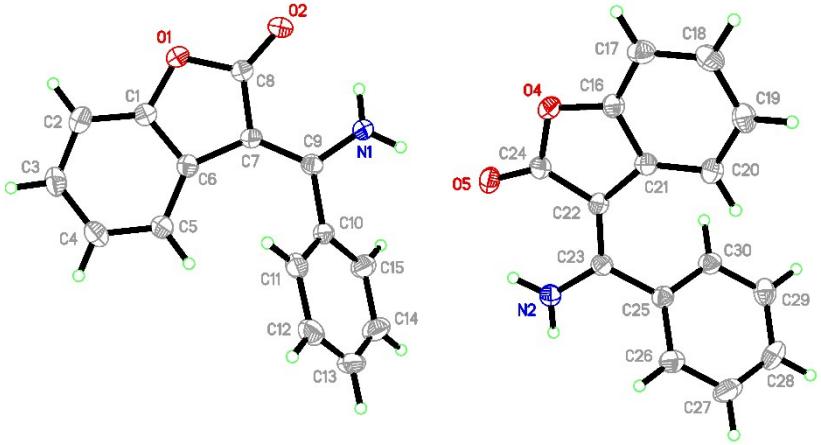


Figure S10. ORTEP diagram of **3aa** with thermal ellipsoids shown at the 50% probability level

A yellow block shaped crystal of **3aa** ($C_{15}H_{11}NO_2$) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 173(2) K, on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochrmator Cu-Kα radiation (λ = 1.54178 Å). The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1918362 for **3aa**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

Table S7. Crystal data and structure refinement for **3aa**

Empirical formula	$C_{15}H_{11}NO_2$	
Formula weight	237.25	
Temperature	173 K	
Wavelength	1.54178 Å	
Crystal habit	Yellow block	
Crystal system, space group,	Monoclinic, P 21/c	
Unit cell dimensions	a = 10.4160(16) Å	α = 90°
	b = 20.705(3) Å	β = 98.861(13)°
	c = 10.7592(19) Å	γ = 90°
Volume	2292.6(6) $Å^3$	
Z, Calculated density	8, 1.375 g/cm^3	
Absorption coefficient	0.746 mm^{-1}	
F(000)	992	
Crystal size	0.22 x 0.20 x 0.17 mm^3	
Theta range for data collection	4.270 to 68.298°	
Limiting indices	$-12 \le h \le 12$, $-24 \le k \le 24$, $-12 \le l \le 12$	
Data/restraints/parameters	4198/0/326	

Goodness-of-fit on F^2	0.678
Final R indices [I > 2 sigma(I)]	R1 = 0.0338, wR2 = 0.0872
R indices (all data)	R1 = 0.0309, wR2 = 0.0836
Extinction coefficient	0.0028(2)
Largest diff. peak and hole	0.231 and -0.161 e·Å^{-3}

6. Reference

(1) (a) H. M. Petrassi, K. B. Sharpless and J. W. Kelly. *Org. Lett.,* 2001, **3**, 139; (b) G. Liu, Y. Shen, Z. Zhou, and X. Lu. *Angew. Chem., Int. Ed.,* 2013, **52**, 6033.

(2) K. Park, Y. Heo and S. Lee. *Org. Lett.,* 2013, **15**, 3322.

(3) (a) Q. Wu, Y. Chen, D. Yan, M. Zhang, Y. Lu, W.-Y. Sun and J. Zhao, *Chem. Sci.*, 2017, **8**, 169; (b) X. Wang, T. Gensch, A. Lerchen, C. G. Daniliuc and F. Glorius, *J. Am. Chem. Soc.*, 2017, **139**, 6506.

(4) J.-L. Pan, P. Xie, C. Chen, Y. Hao, C. Liu, H.-Y. Bai, J. Ding, L.-R. Wang, Y. Xia and S.-Y. Zhang, *Org. Lett.*, 2018, **20**, 7131.

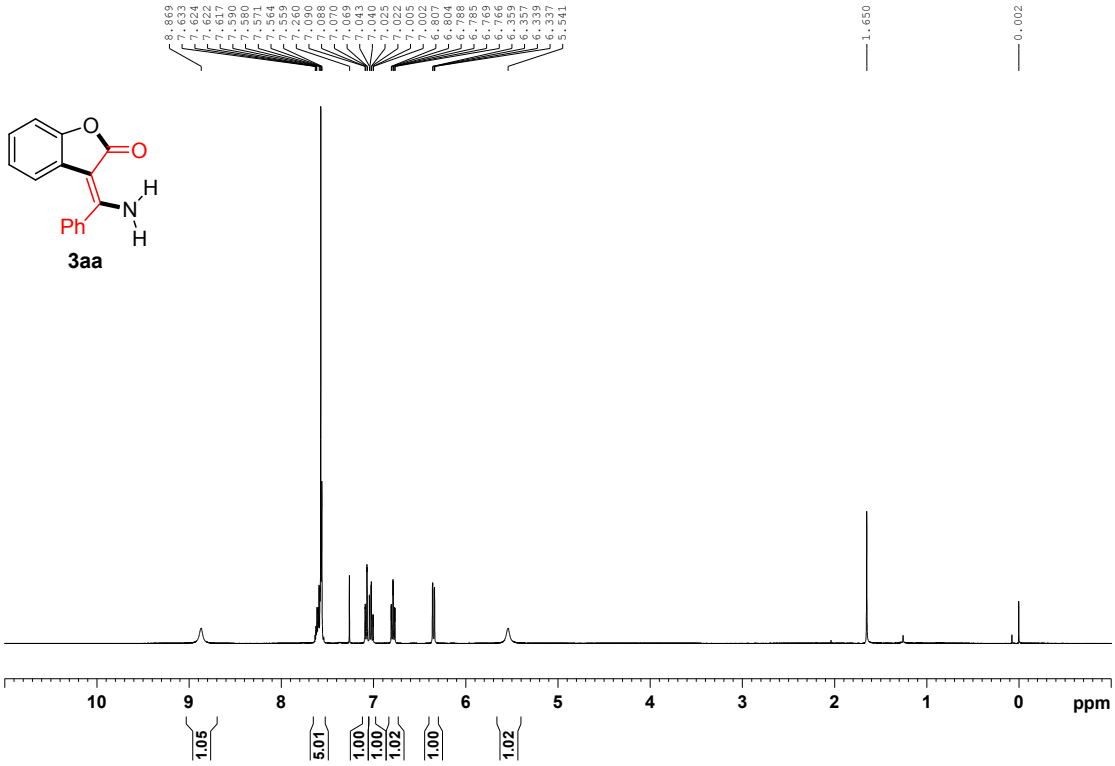
(5) Z.-P. Chen, Y. Zhou, M.-Z. Shui and F. Liu, *Tetrahedron Lett.,* 2019, **60**, 133.

(6) (a) Y.-F. Yang, K. N. Houk and Y.-D. Wu, *J. Am. Chem. Soc.*, 2016, **138**, 6861; (b) J.-L. Yu, S.-Q. Zhang and X. Hong, *J. Am. Chem. Soc.*, 2017, **139**, 7224.

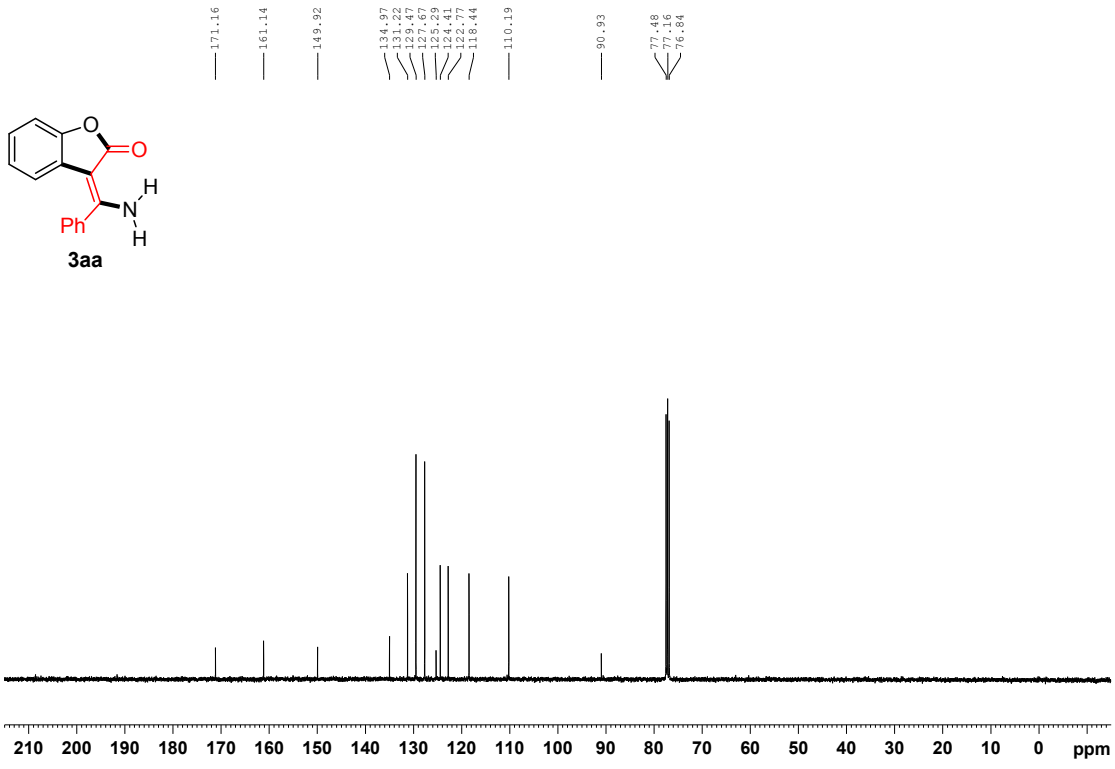
7. Copies of NMR Spectra

(*Z*)-3-(Amino(phenyl)methylene)benzofuran-2(3*H*)-one (3aa)

^{1}H NMR ($CDCl_3$, 400 MHz)

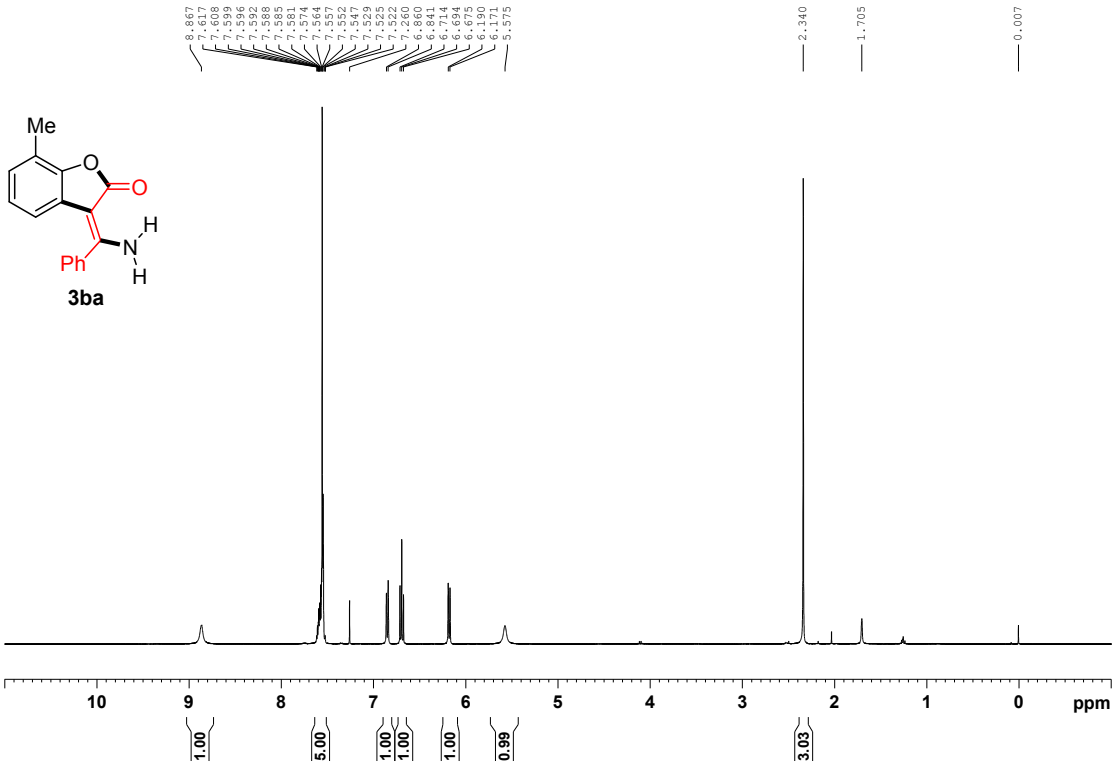


^{13}C NMR ($CDCl_3$, 101 MHz)

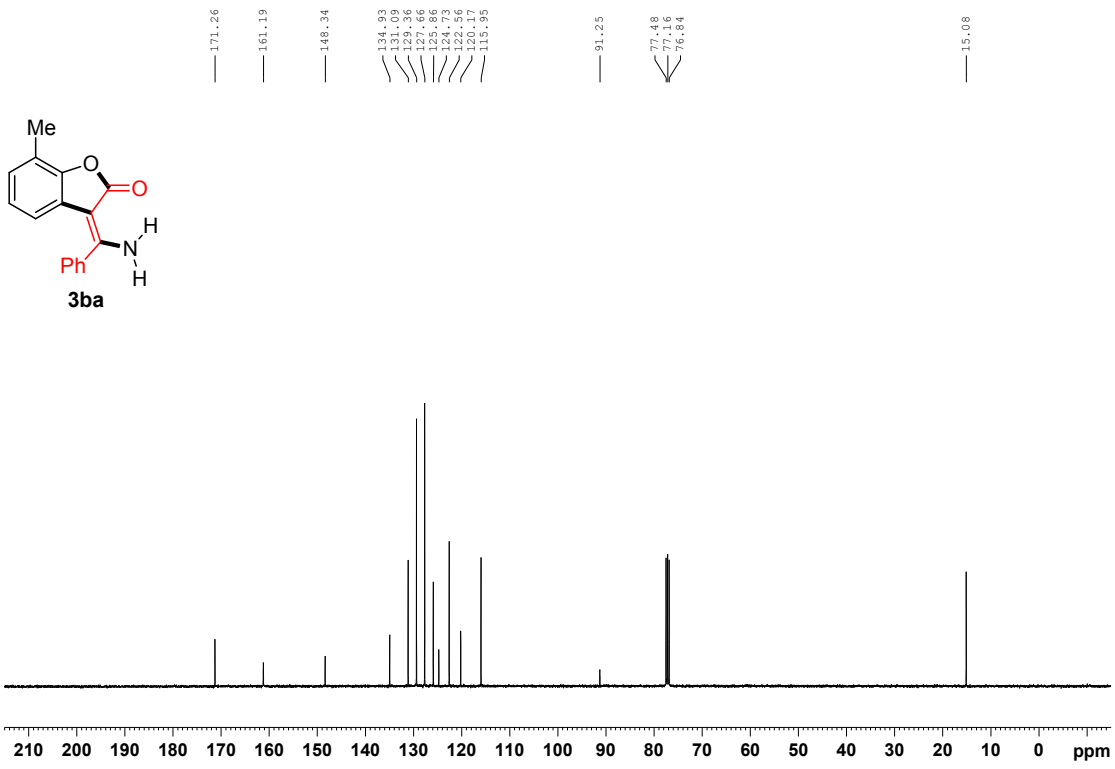


(*Z*)-3-(Amino(phenyl)methylene)-7-methylbenzofuran-2(3*H*)-one (3ba)

^{1}H NMR ($CDCl_3$, 400 MHz)

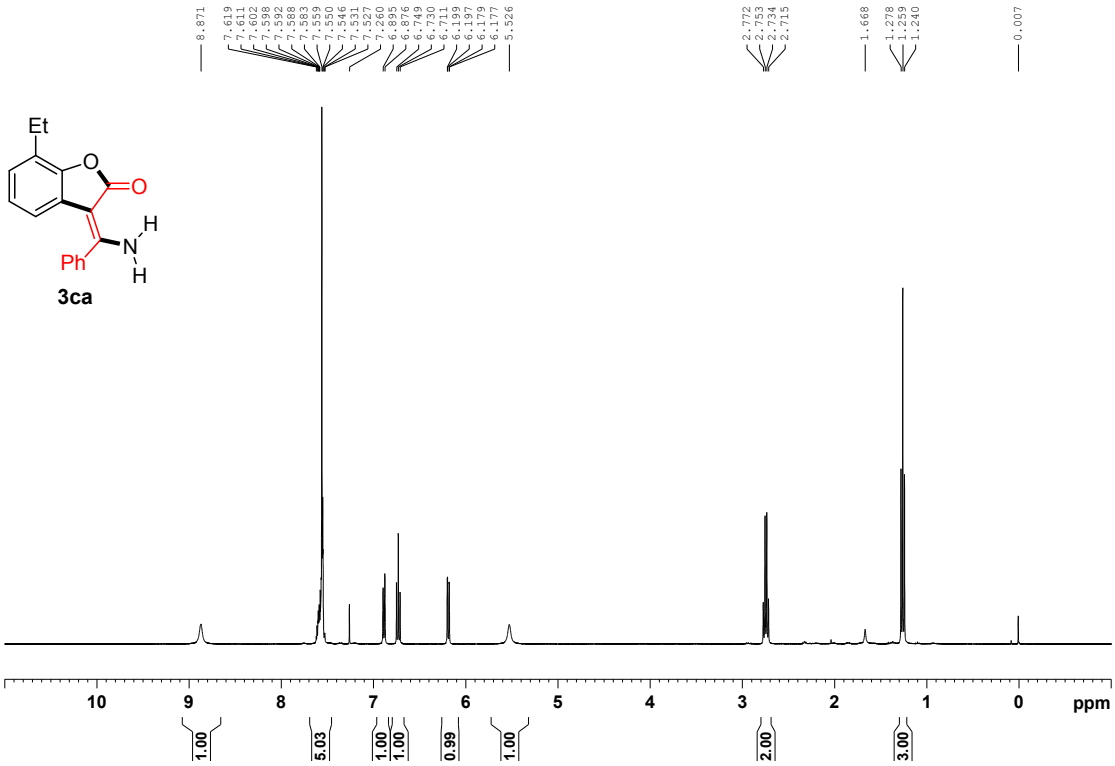


^{13}C NMR ($CDCl_3$, 101 MHz)

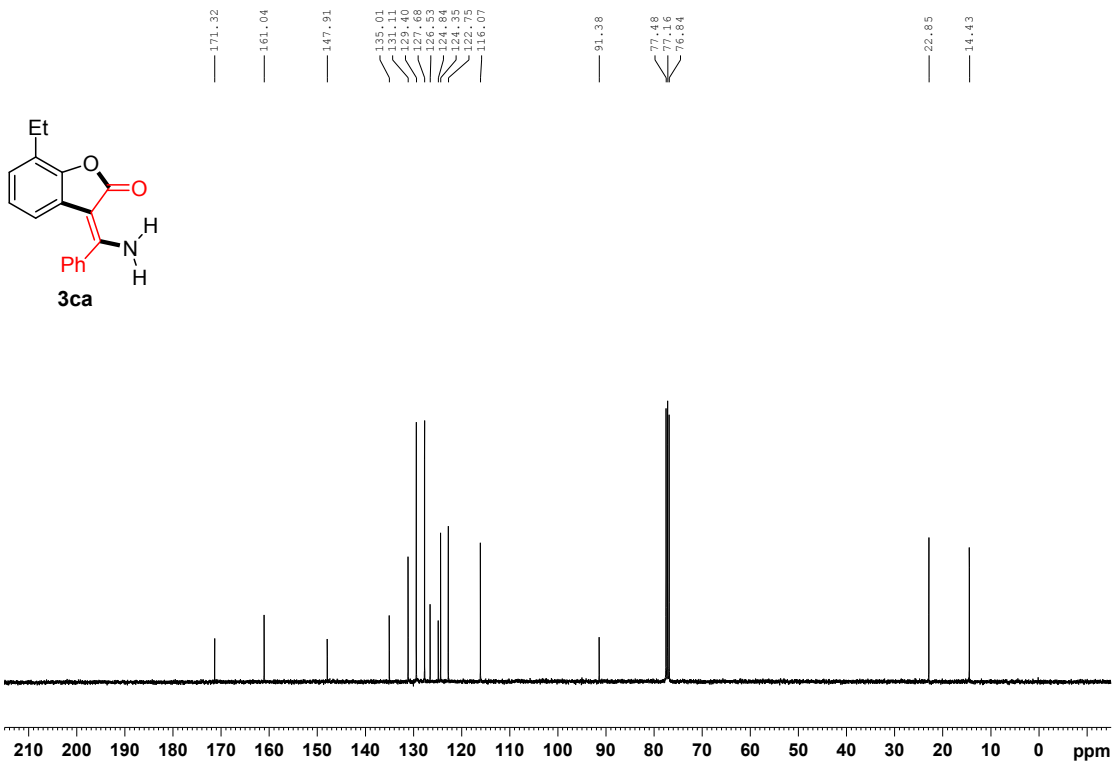


(*Z*)-3-(Amino(phenyl)methylene)-7-ethylbenzofuran-2(3*H*)-one (3ca)

^{1}H NMR ($CDCl_3$, 400 MHz)

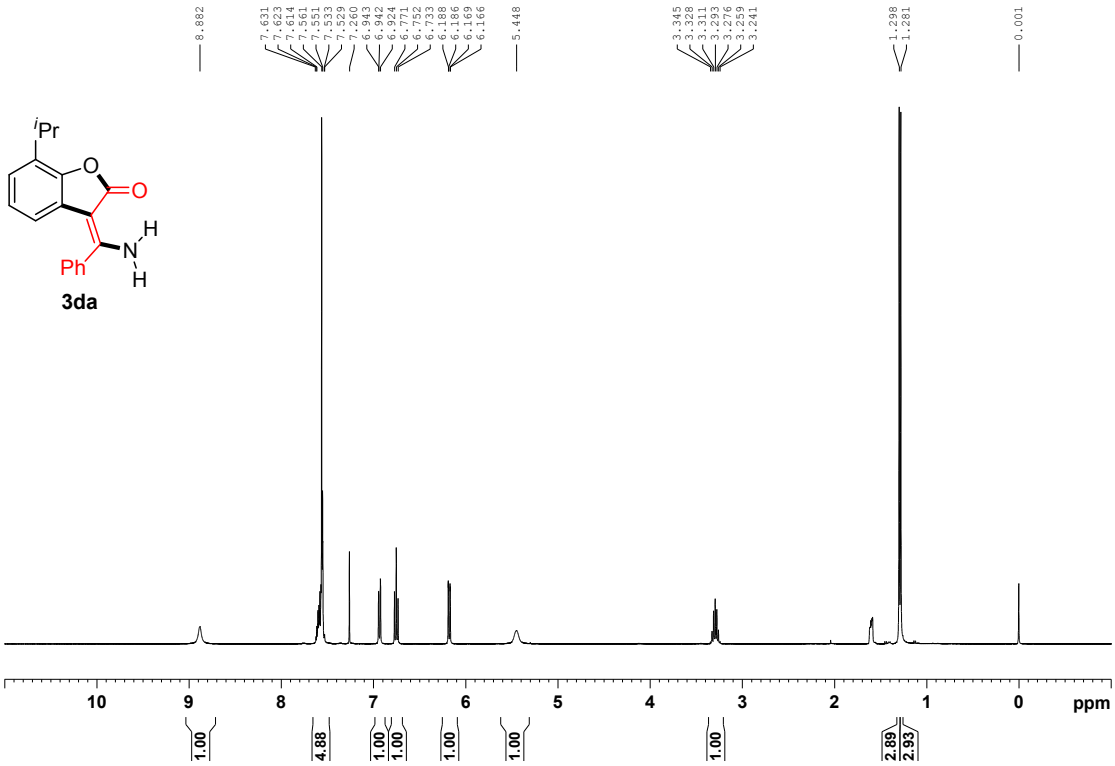


^{13}C NMR ($CDCl_3$, 101 MHz)

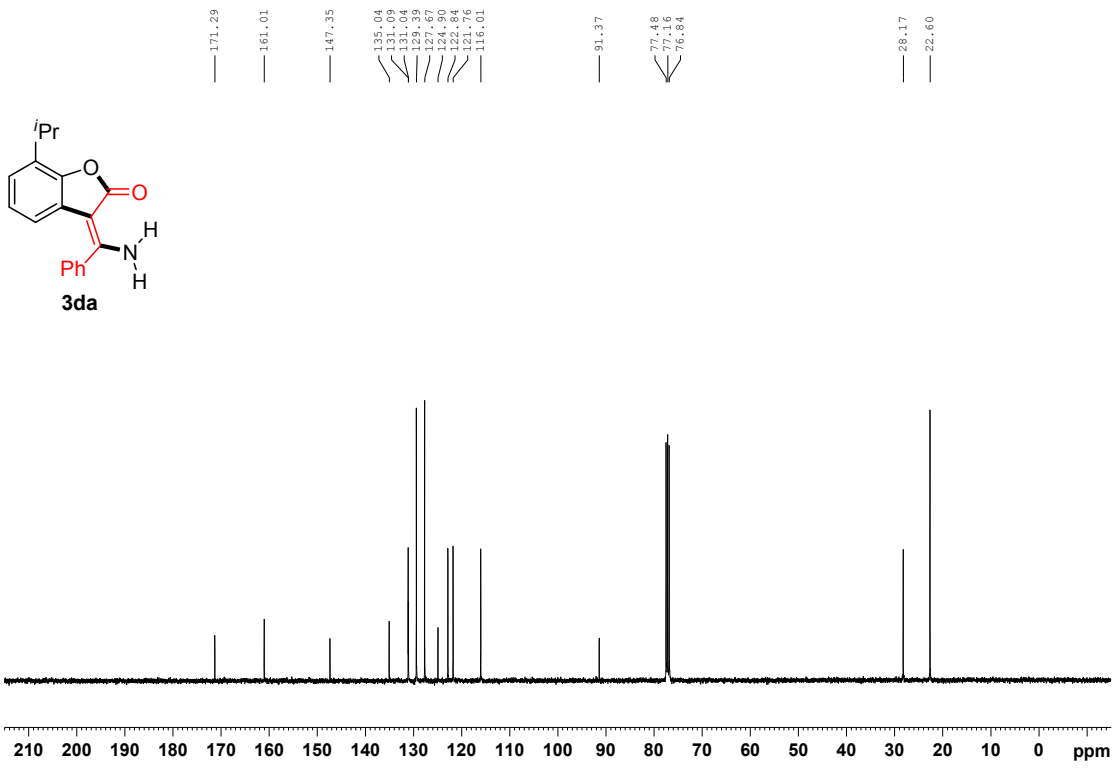


(*Z*)-3-(Amino(phenyl)methylene)-7-isopropylbenzofuran-2(3*H*)-one (3da)

^{1}H NMR ($CDCl_3$, 400 MHz)

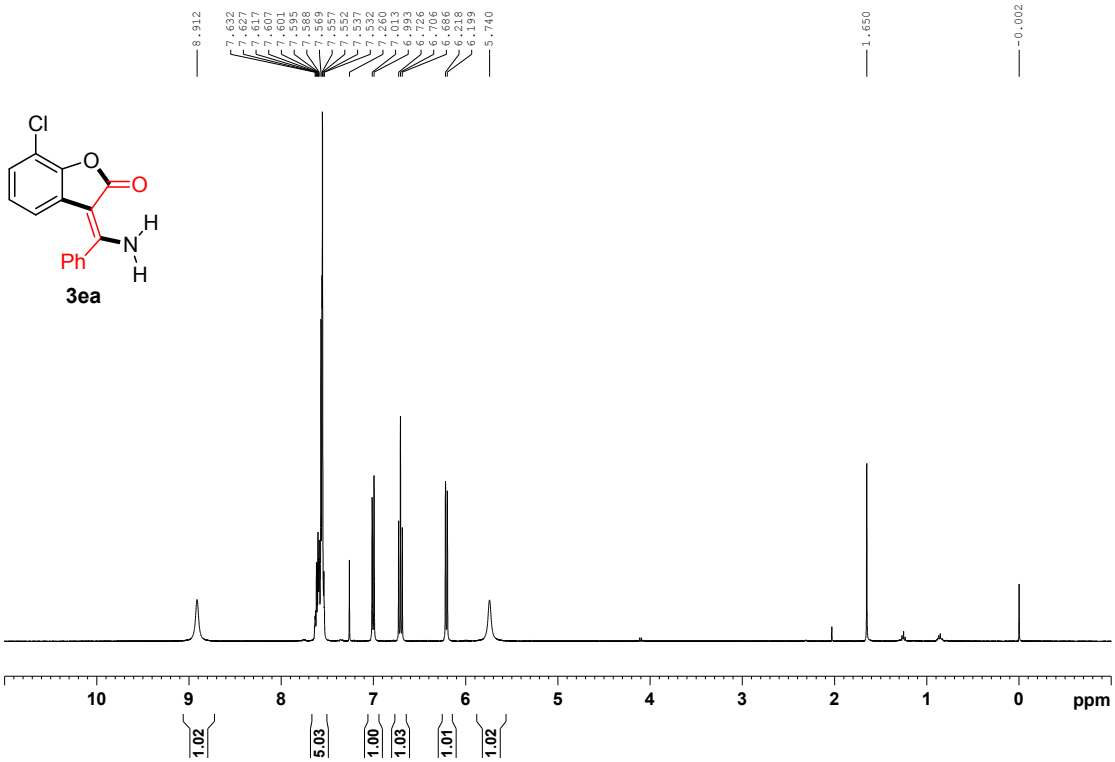


^{13}C NMR ($CDCl_3$, 101 MHz)

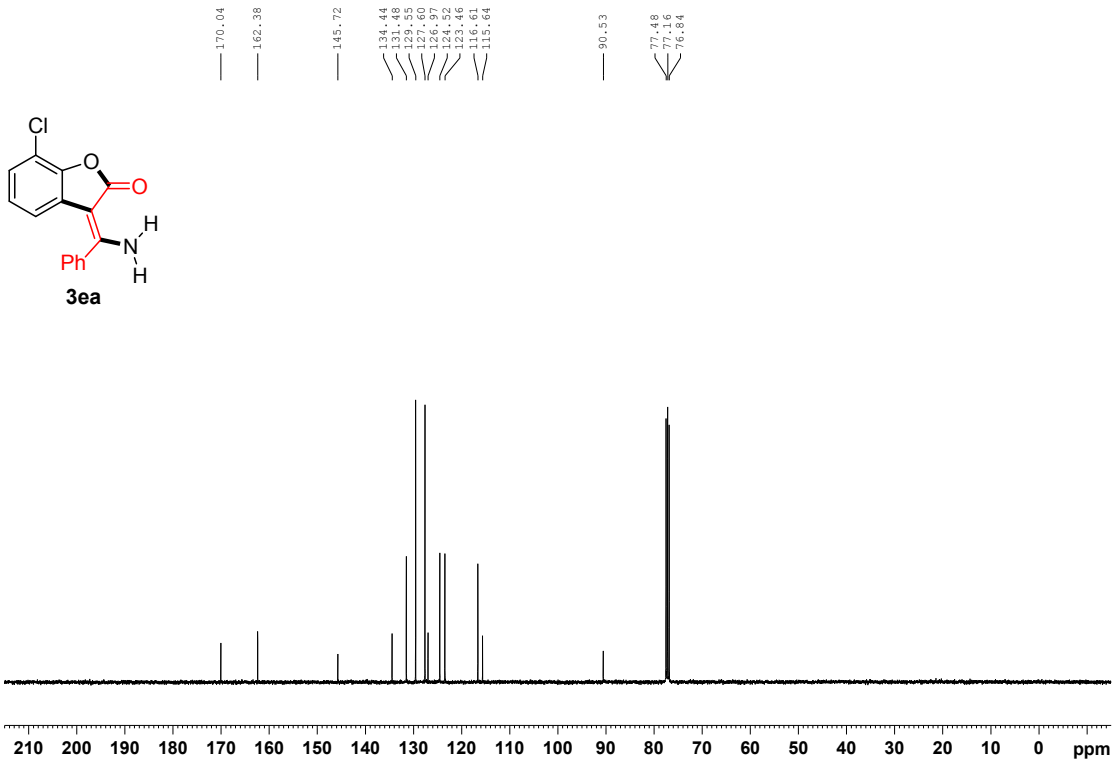


(*Z*)-3-(Amino(phenyl)methylene)-7-chlorobenzofuran-2(3*H*)-one (3ea)

^{1}H NMR ($CDCl_3$, 400 MHz)

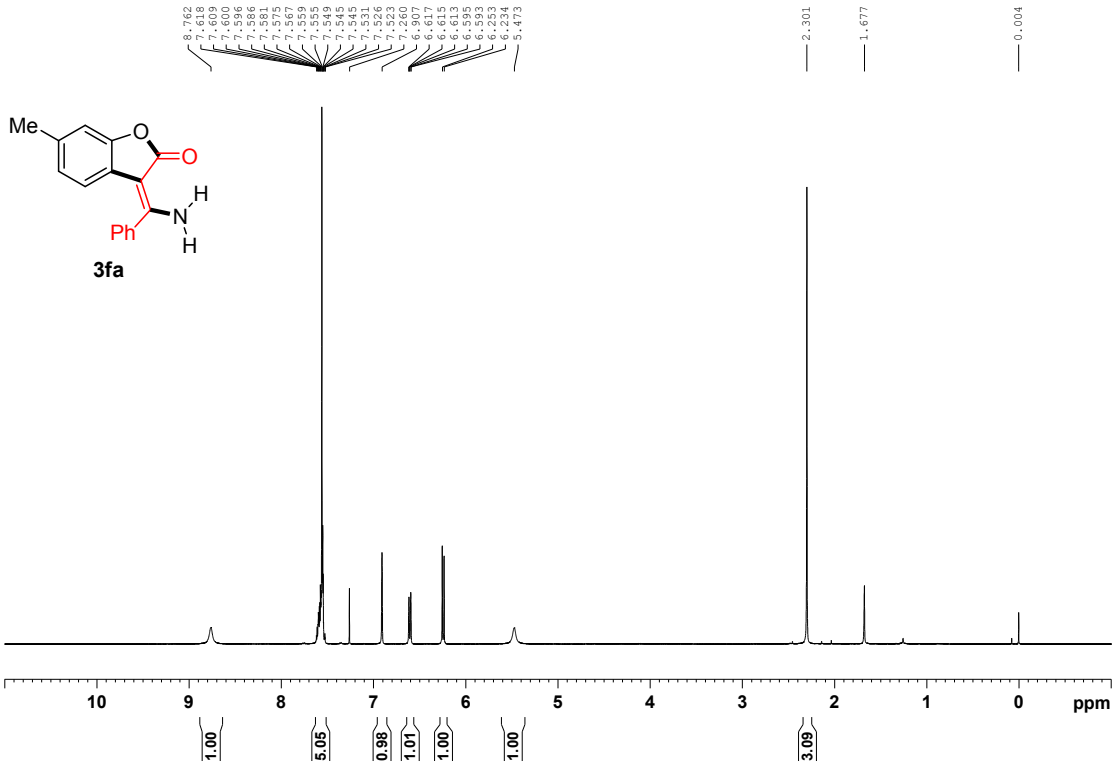


^{13}C NMR ($CDCl_3$, 101 MHz)

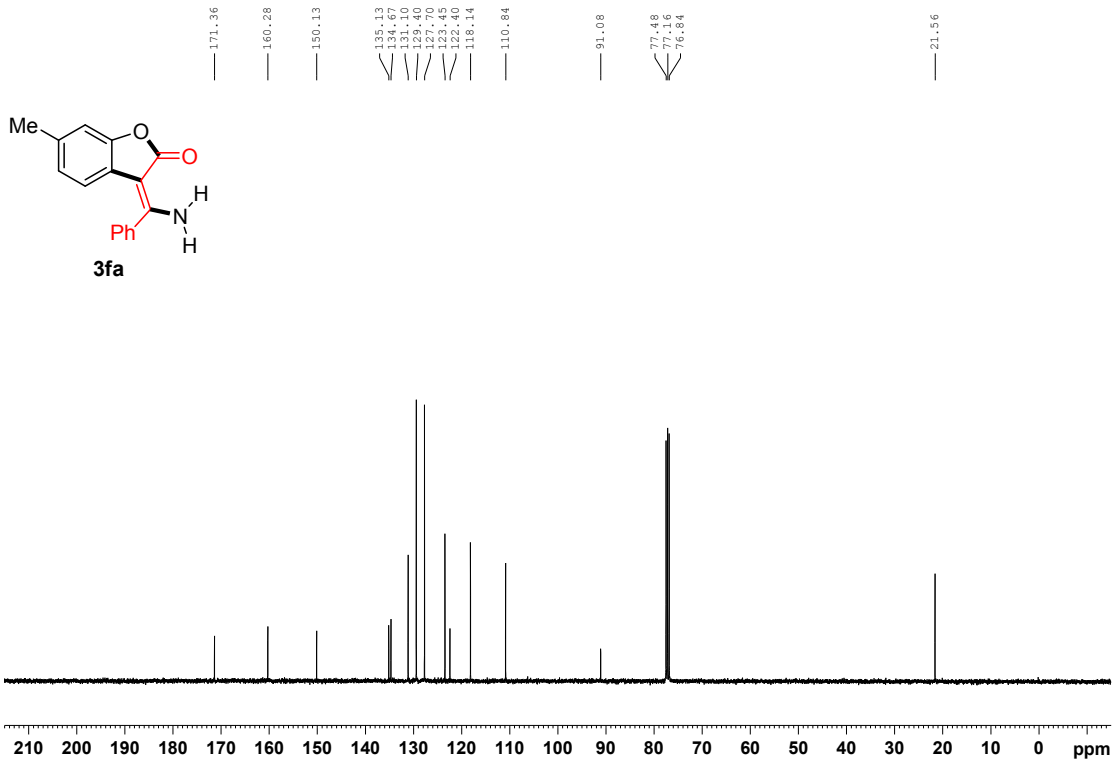


(*Z*)-3-(Amino(phenyl)methylene)-6-methylbenzofuran-2(3*H*)-one (3fa)

^{1}H NMR ($CDCl_3$, 400 MHz)

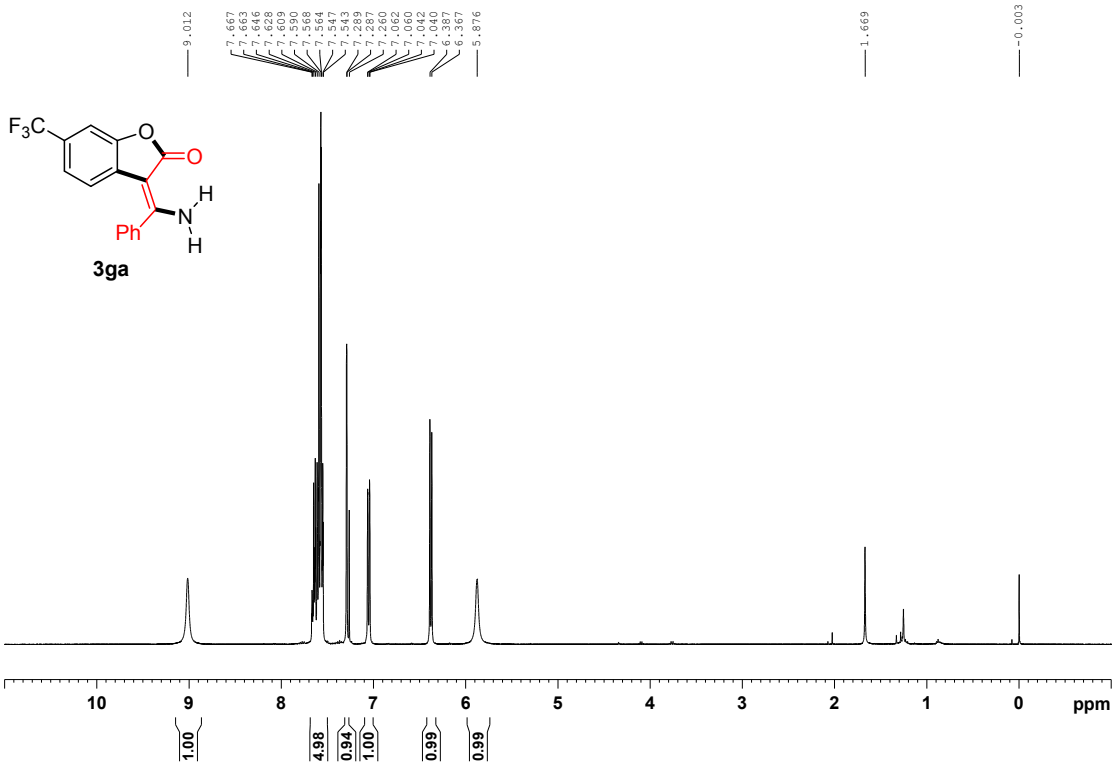


^{13}C NMR ($CDCl_3$, 101 MHz)

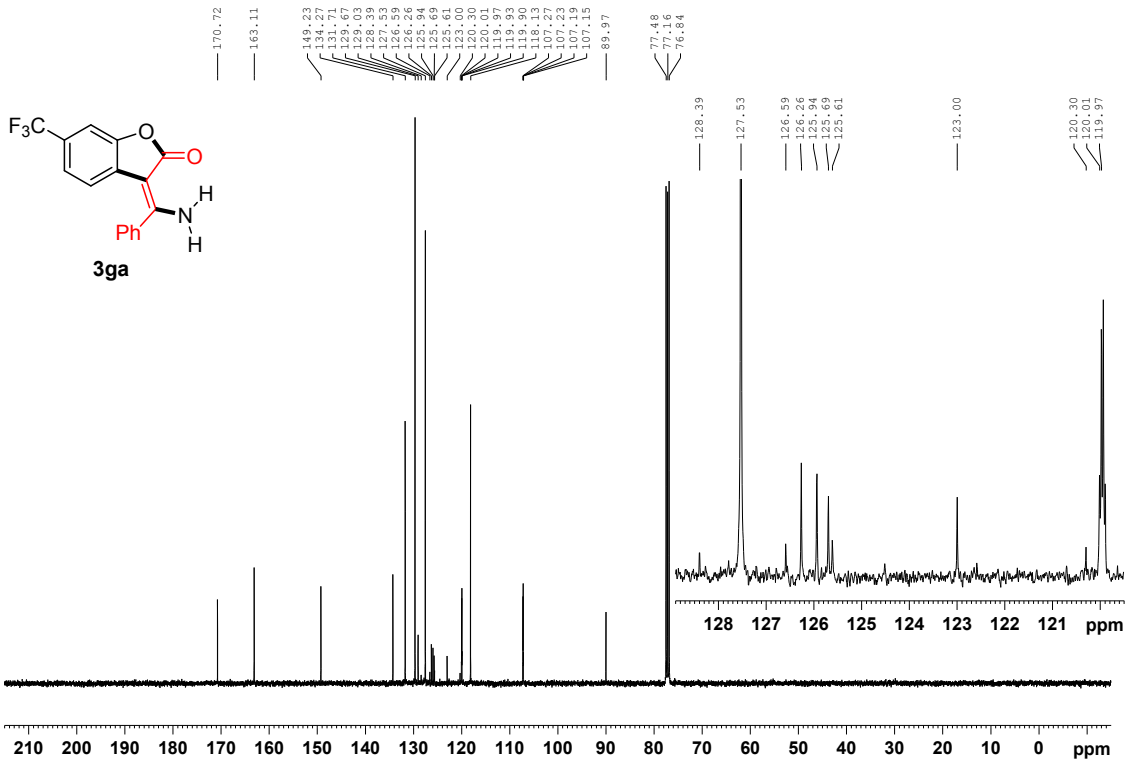


(*Z*)-3-(Amino(phenyl)methylene)-6-(trifluoromethyl)benzofuran-2(3*H*)-one (3ga)

^{1}H NMR ($CDCl_3$, 400 MHz)

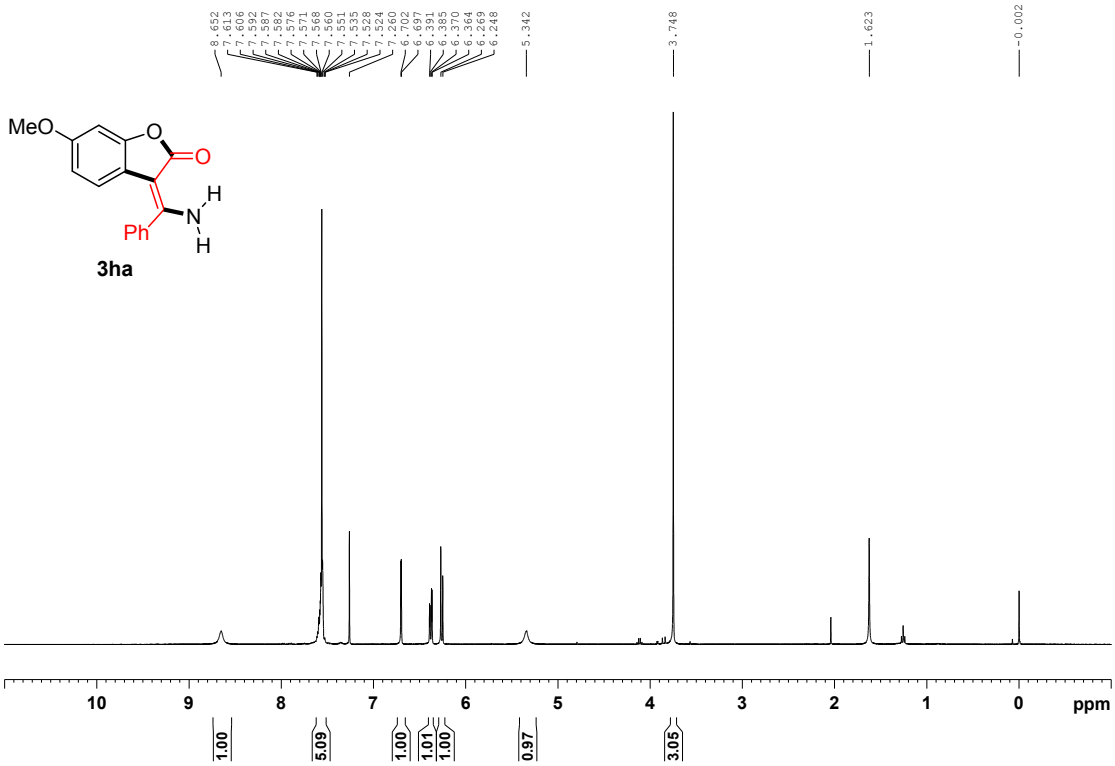


^{13}C NMR ($CDCl_3$, 101 MHz)

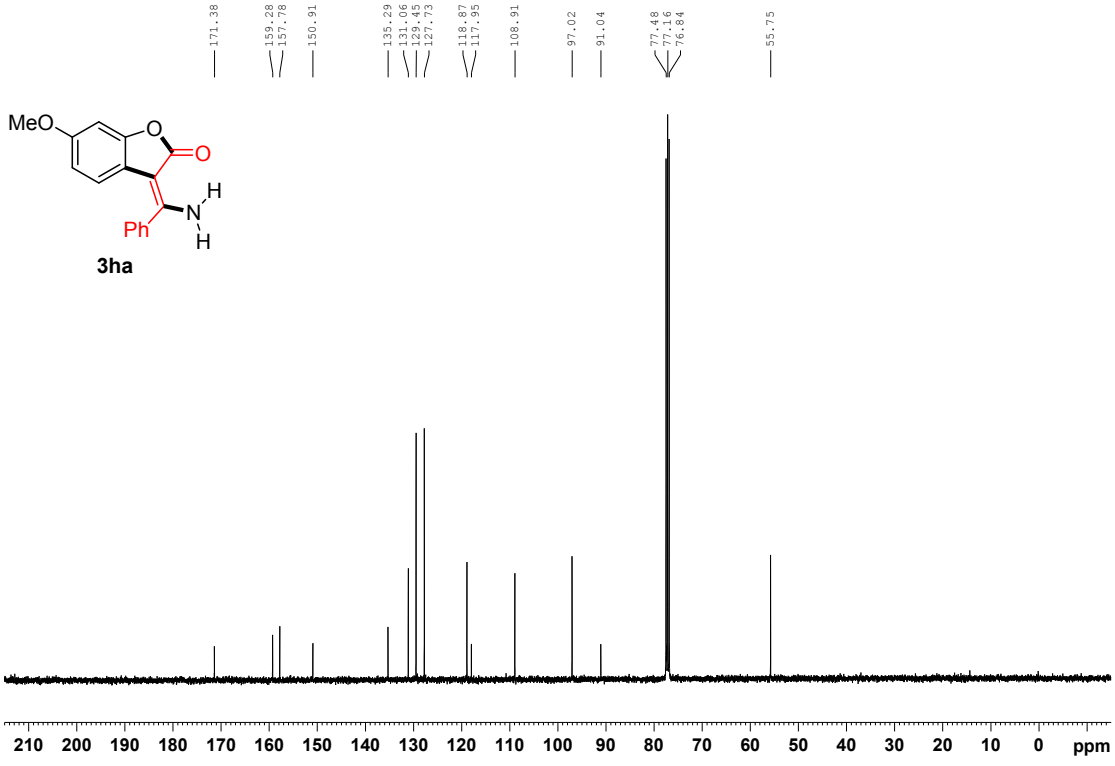


(*Z*)-3-(Amino(phenyl)methylene)-6-methoxybenzofuran-2(3*H*)-one (3ha)

^{1}H NMR ($CDCl_3$, 400 MHz)

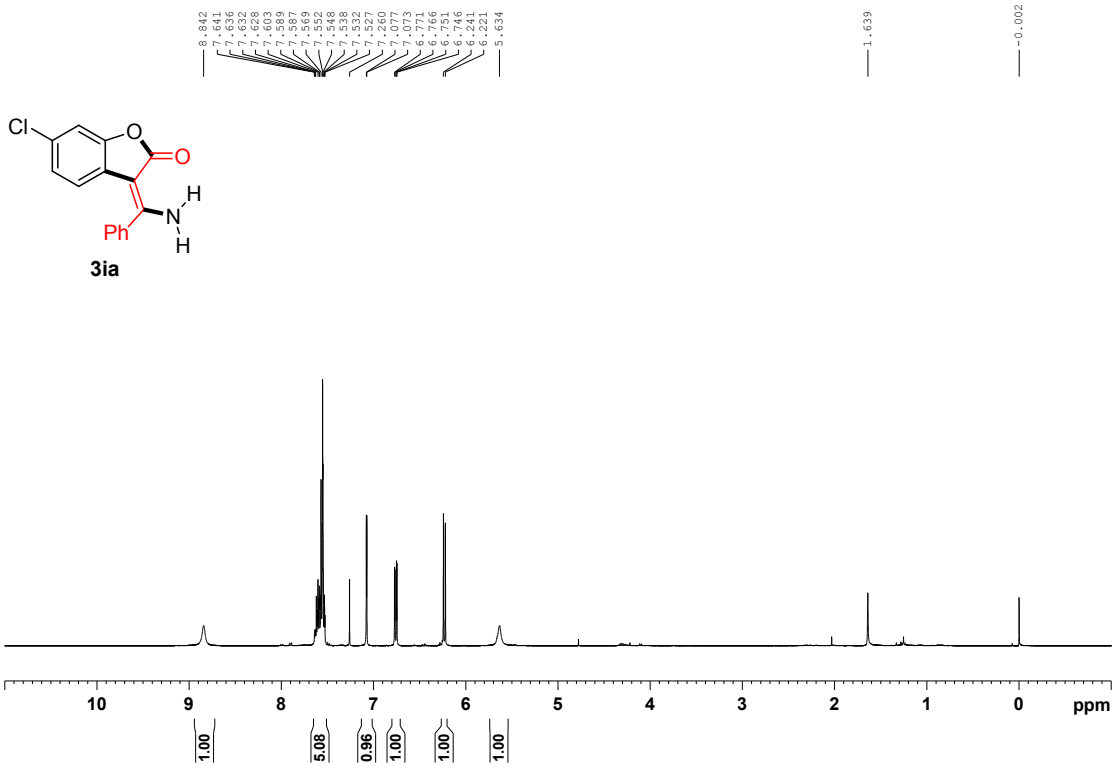


^{13}C NMR ($CDCl_3$, 101 MHz)

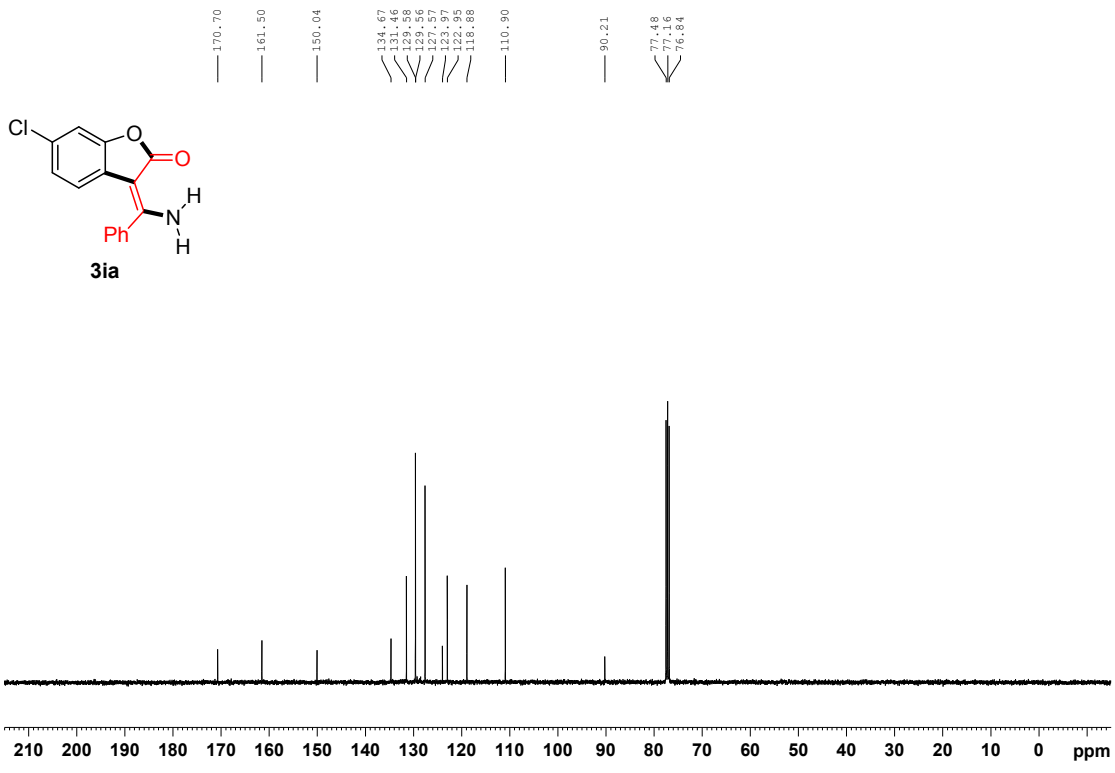


(*Z*)-3-(Amino(phenyl)methylene)-6-chlorobenzofuran-2(3*H*)-one (3ia)

^{1}H NMR ($CDCl_3$, 400 MHz)

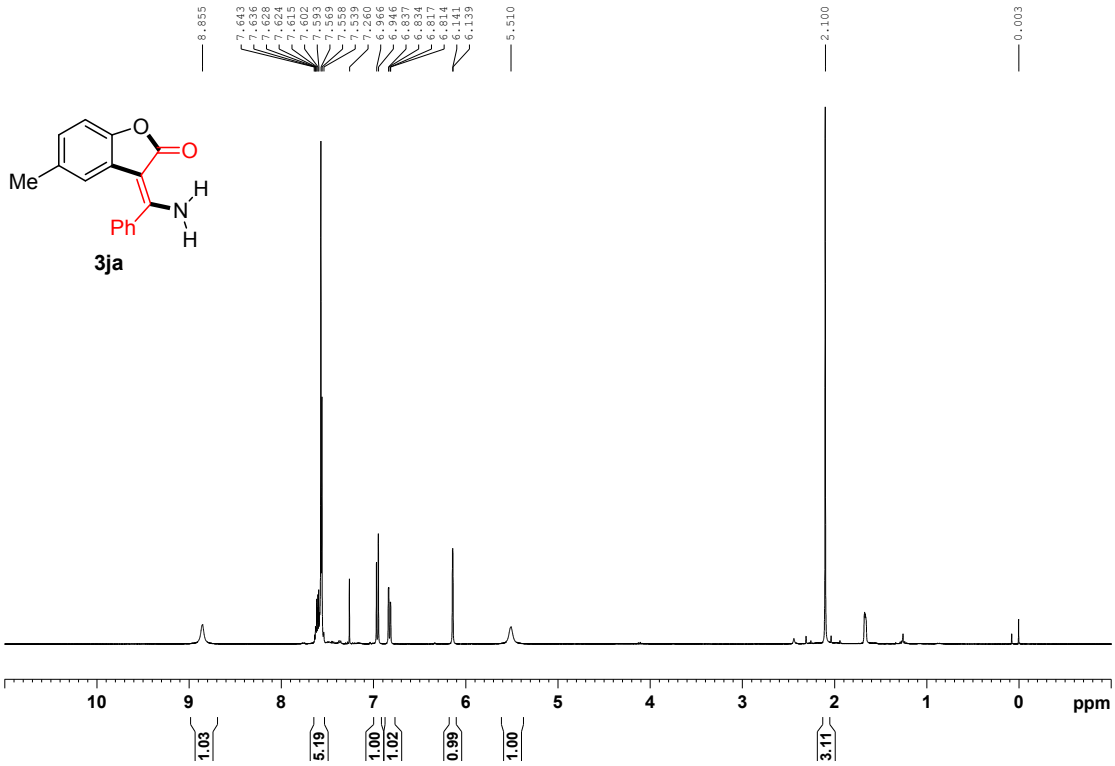


^{13}C NMR ($CDCl_3$, 101 MHz)

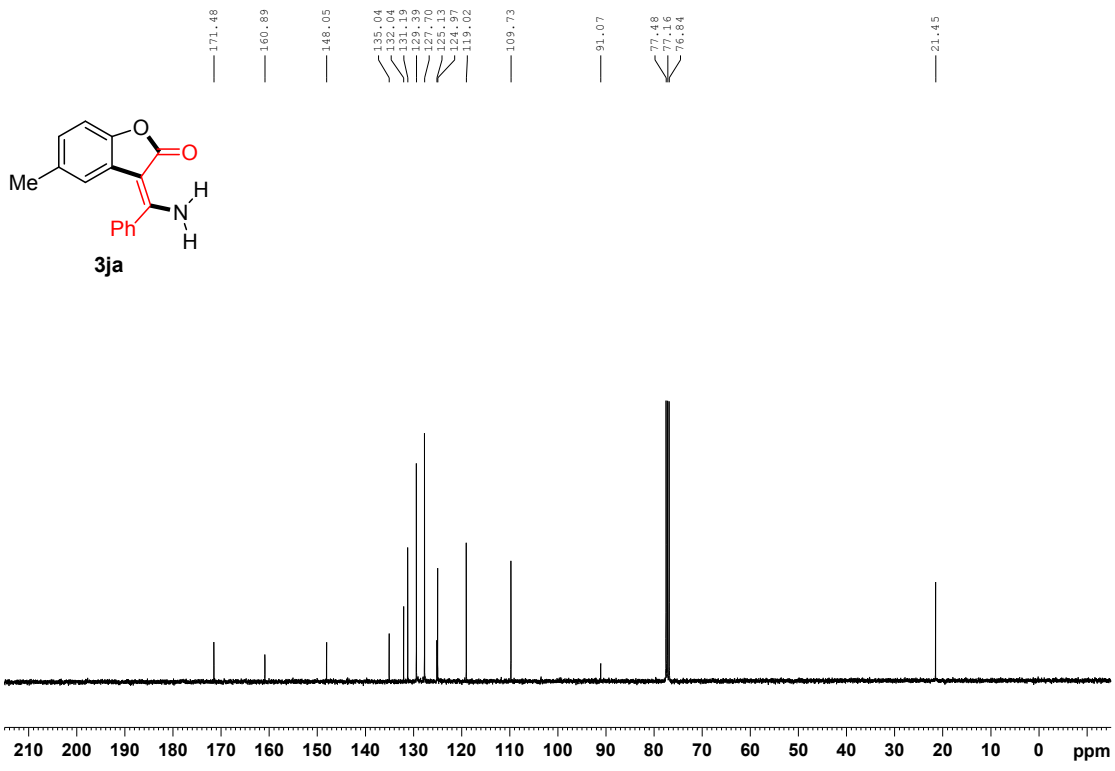


(*Z*)-3-(Amino(phenyl)methylene)-5-methylbenzofuran-2(3*H*)-one (3ja)

^{1}H NMR ($CDCl_3$, 400 MHz)

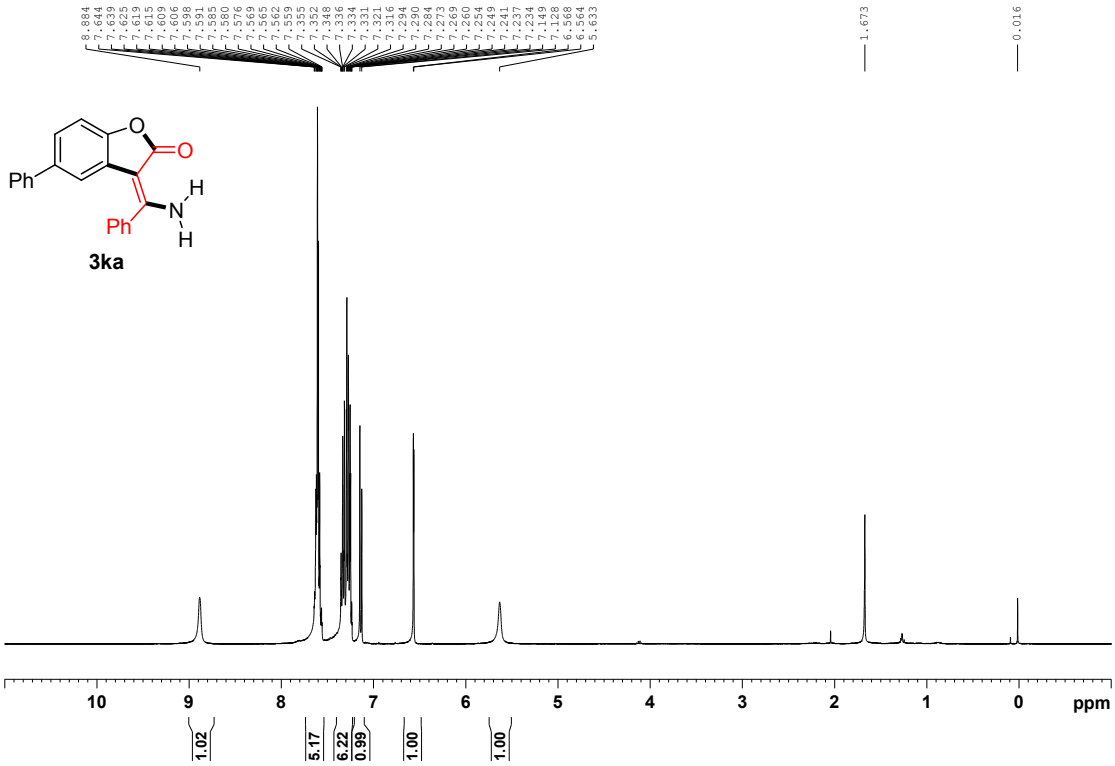


^{13}C NMR ($CDCl_3$, 101 MHz)

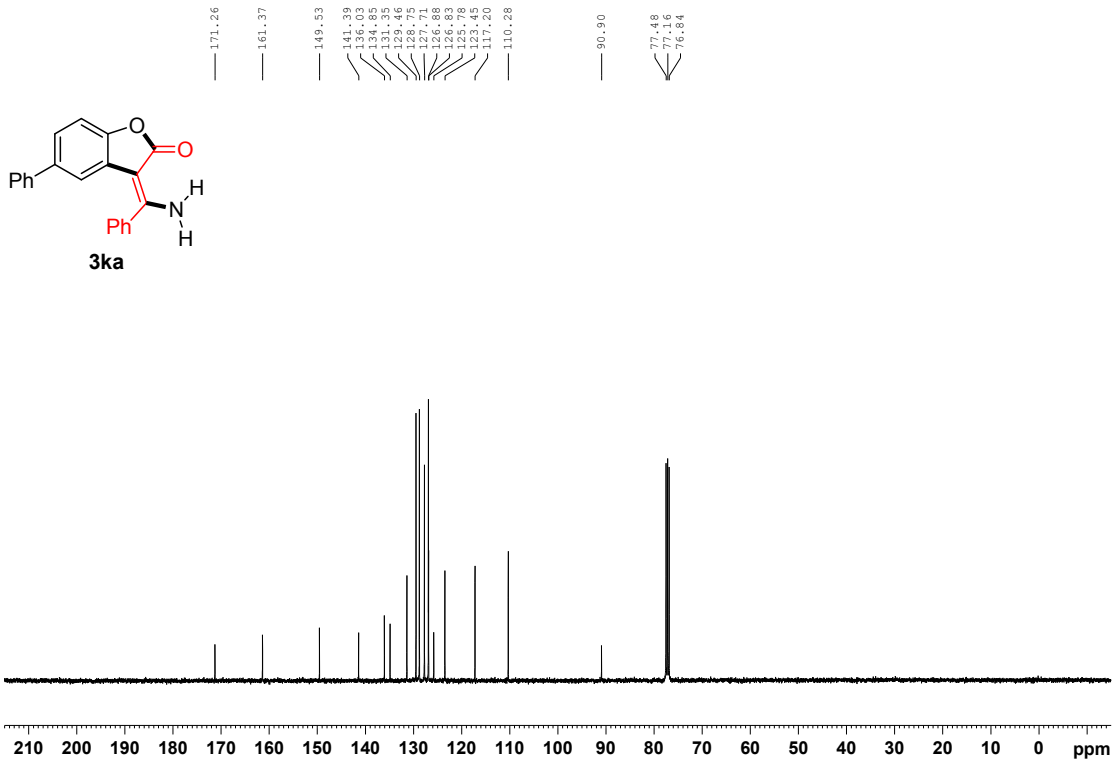


(*Z*)-3-(Amino(phenyl)methylene)-5-phenylbenzofuran-2(3*H*)-one (3ka)

^{1}H NMR ($CDCl_3$, 400 MHz)

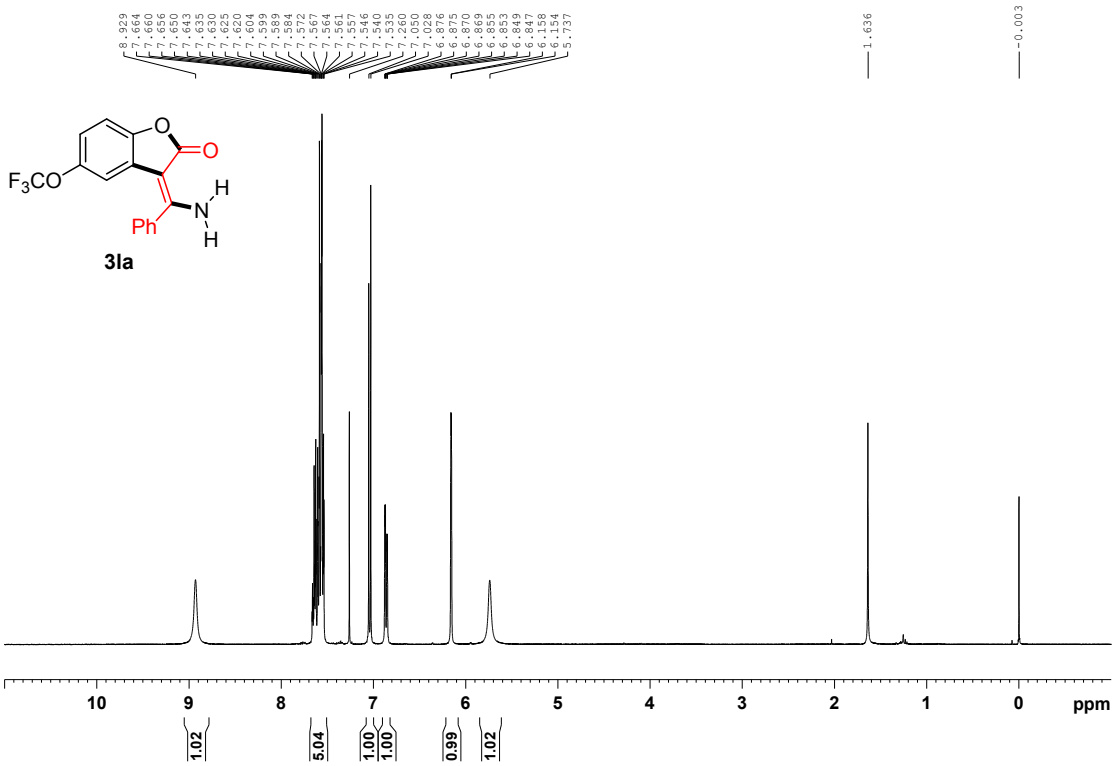


^{13}C NMR ($CDCl_3$, 101 MHz)

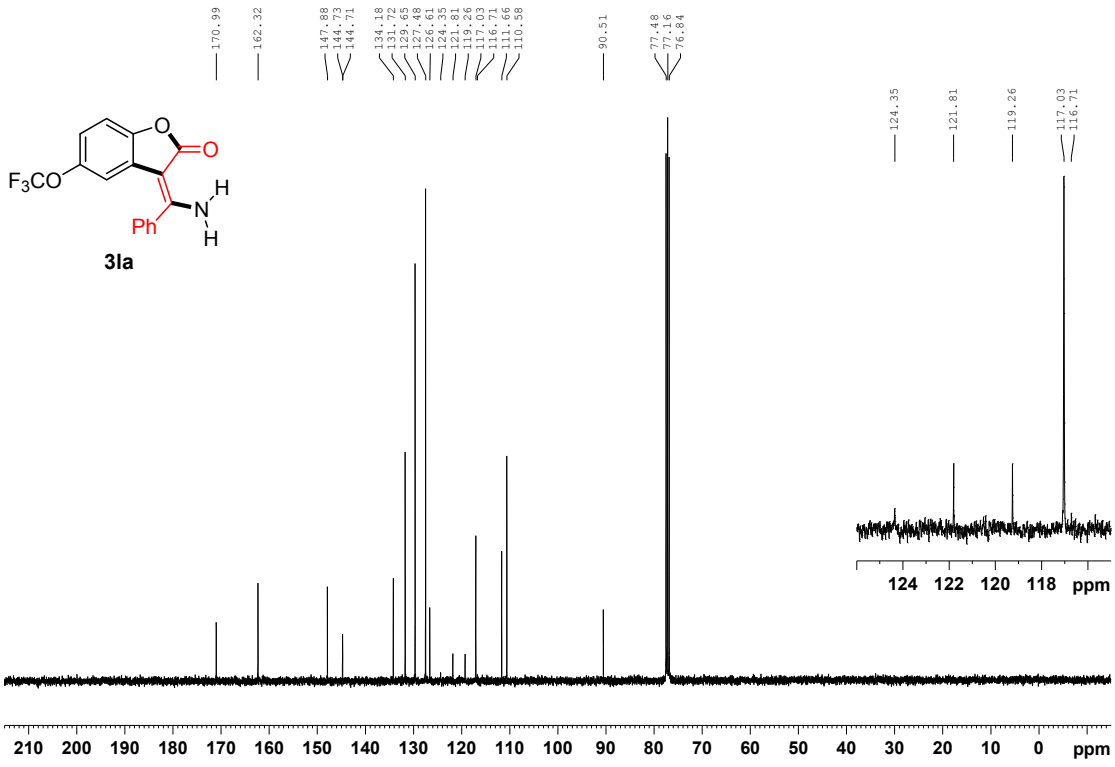


(*Z*)-3-(Amino(phenyl)methylene)-5-(trifluoromethoxy)benzofuran-2(3*H*)-one (3la)

^{1}H NMR ($CDCl_3$, 400 MHz)

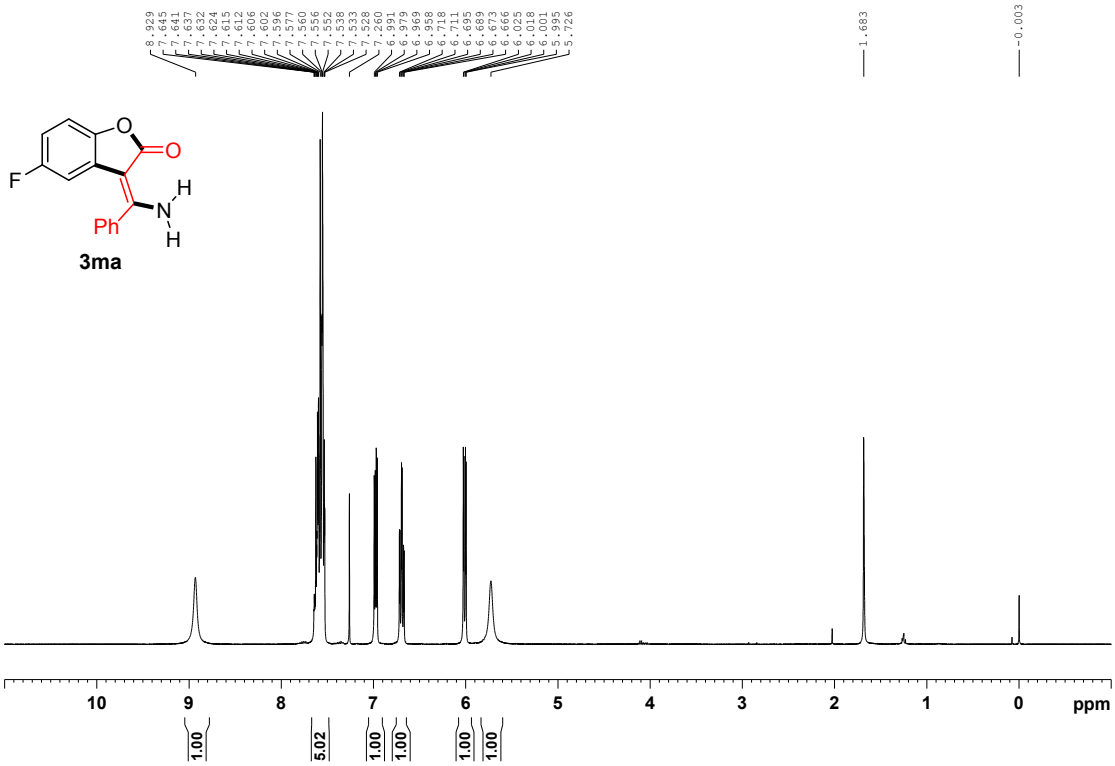


^{13}C NMR ($CDCl_3$, 101 MHz)

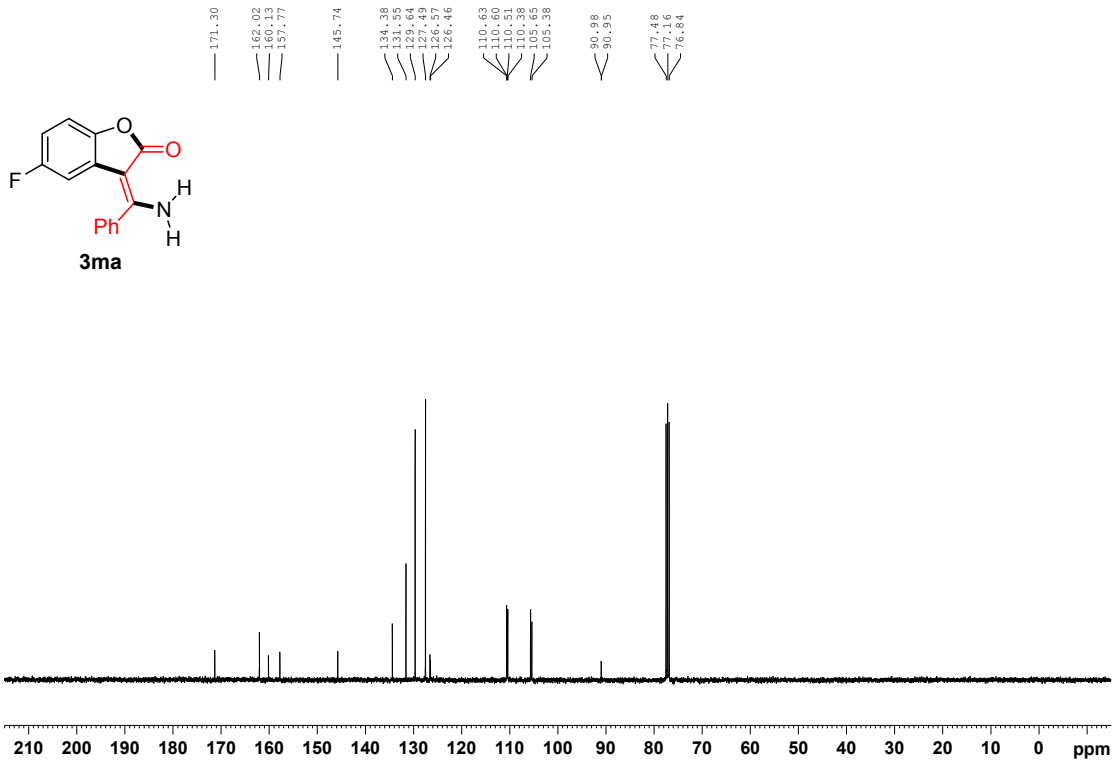


(*Z*)-3-(Amino(phenyl)methylene)-5-fluorobenzofuran-2(3*H*)-one (3ma)

^{1}H NMR ($CDCl_3$, 400 MHz)

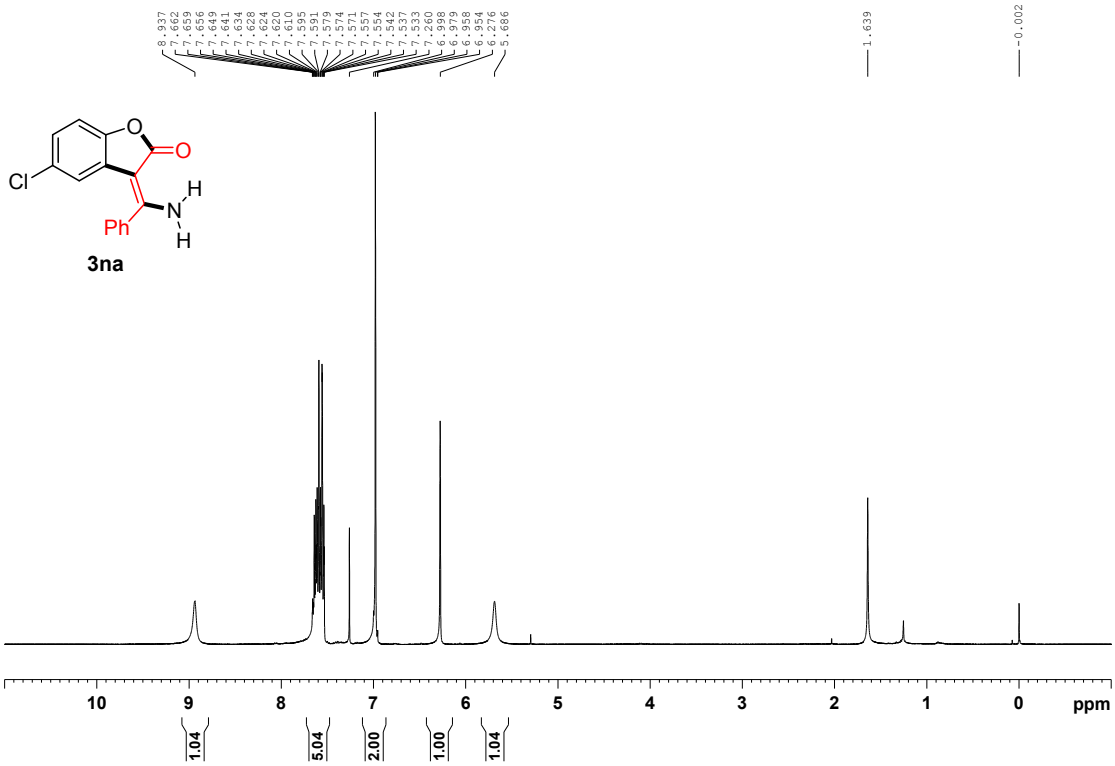


^{13}C NMR ($CDCl_3$, 101 MHz)

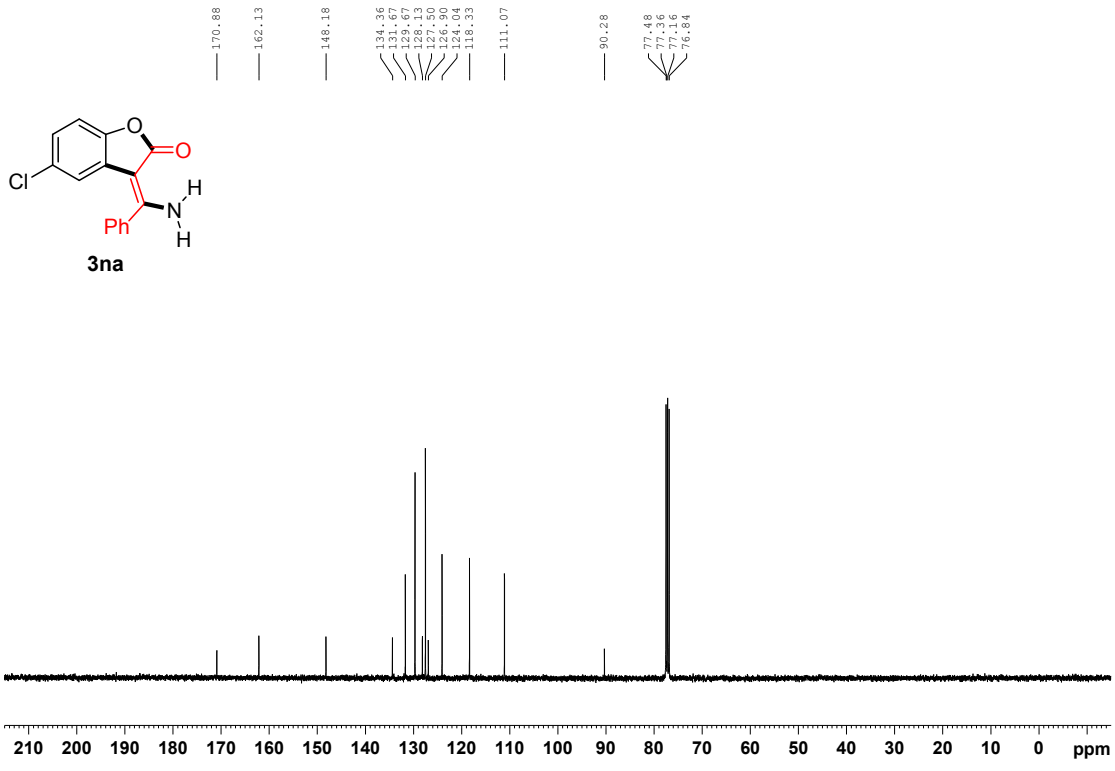


(*Z*)-3-(Amino(phenyl)methylene)-5-chlorobenzofuran-2(3*H*)-one (3na)

^{1}H NMR ($CDCl_3$, 400 MHz)

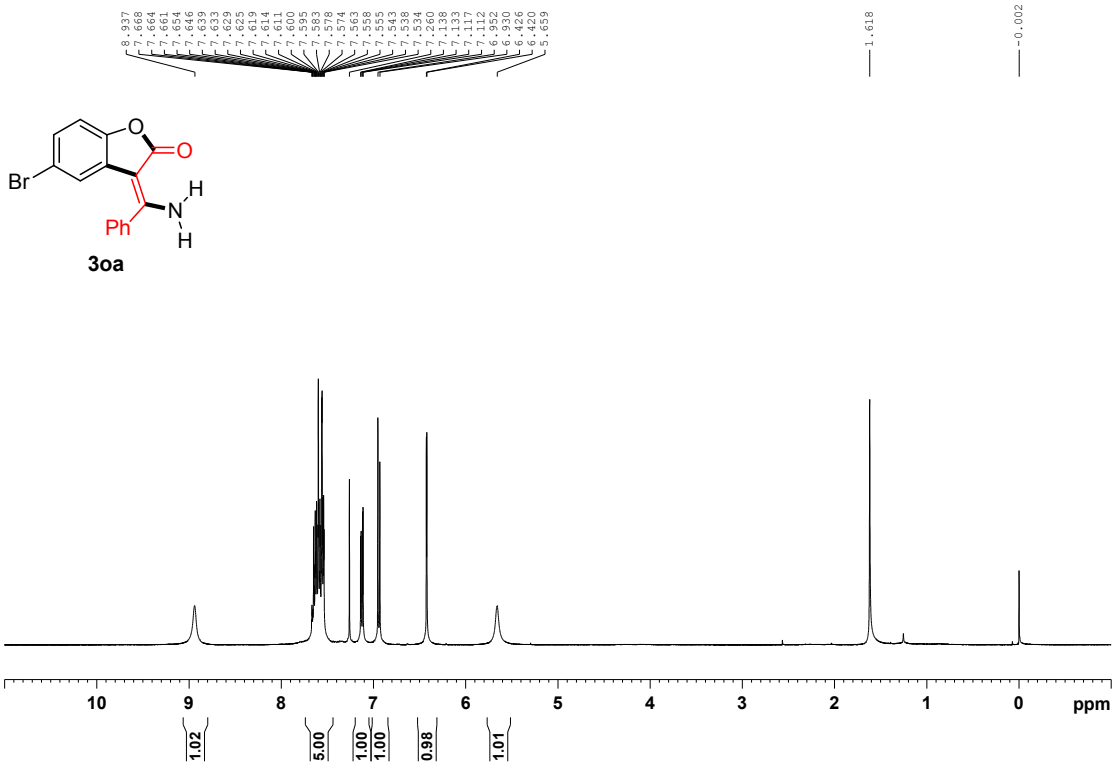


^{13}C NMR ($CDCl_3$, 101 MHz)

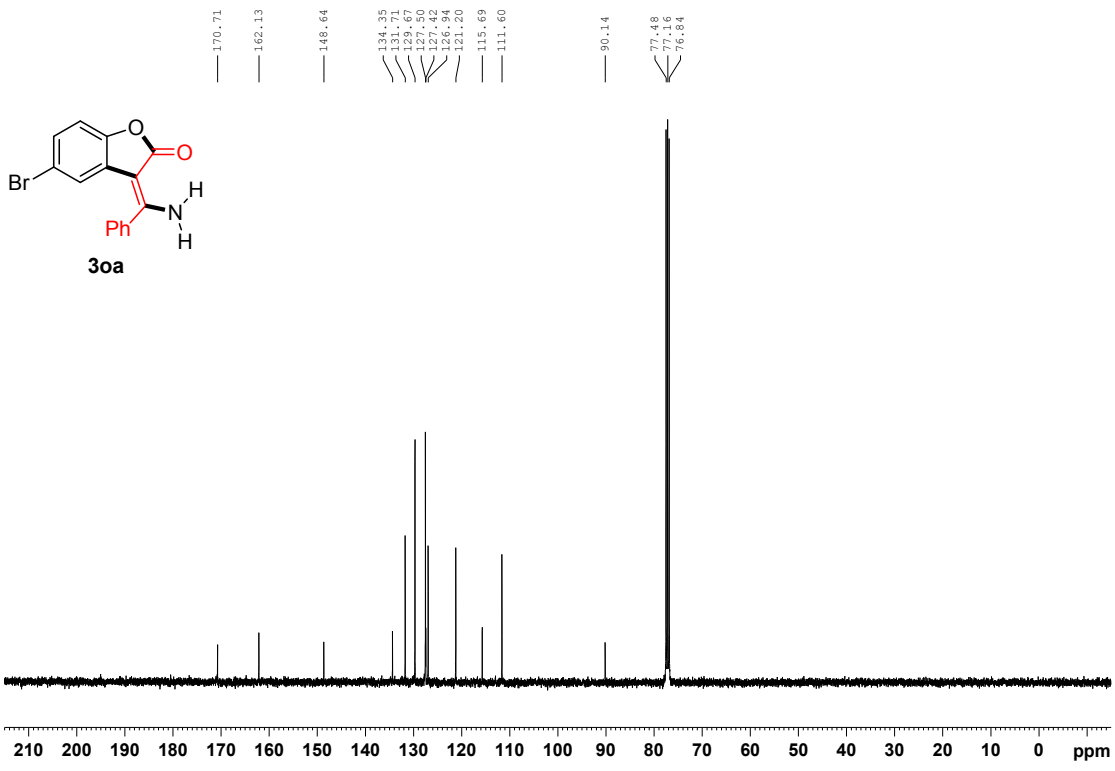


(*Z*)-3-(Amino(phenyl)methylene)-5-bromobenzofuran-2(3*H*)-one (3oa)

^{1}H NMR ($CDCl_3$, 400 MHz)

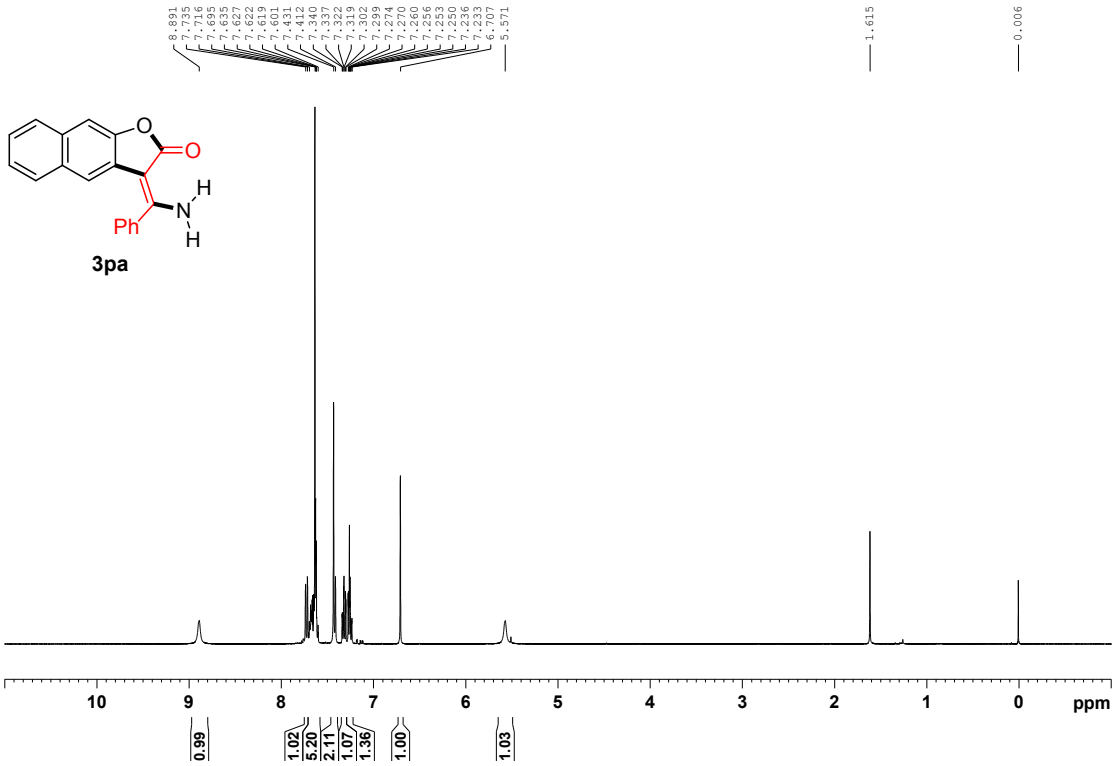


^{13}C NMR ($CDCl_3$, 101 MHz)

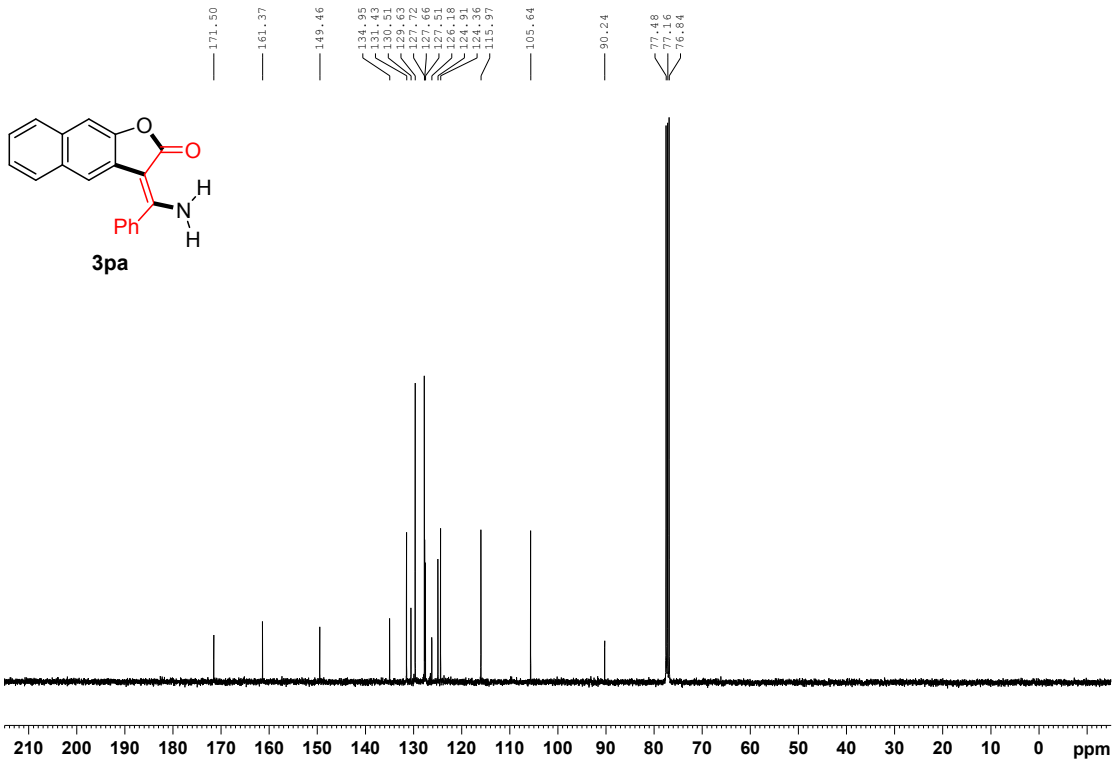


(*Z*)-3-(Amino(phenyl)methylene)naphtho[2,3-*b*]furan-2(3*H*)-one (3pa)

^{1}H NMR ($CDCl_3$, 400 MHz)

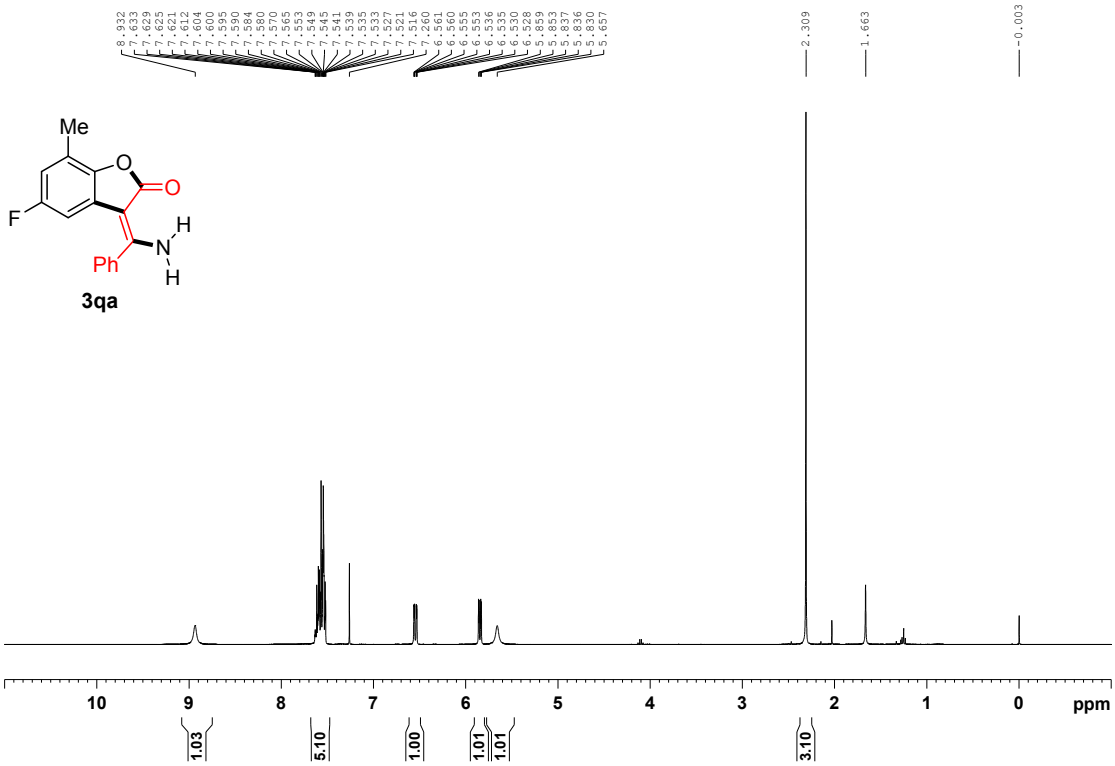


^{13}C NMR ($CDCl_3$, 101 MHz)

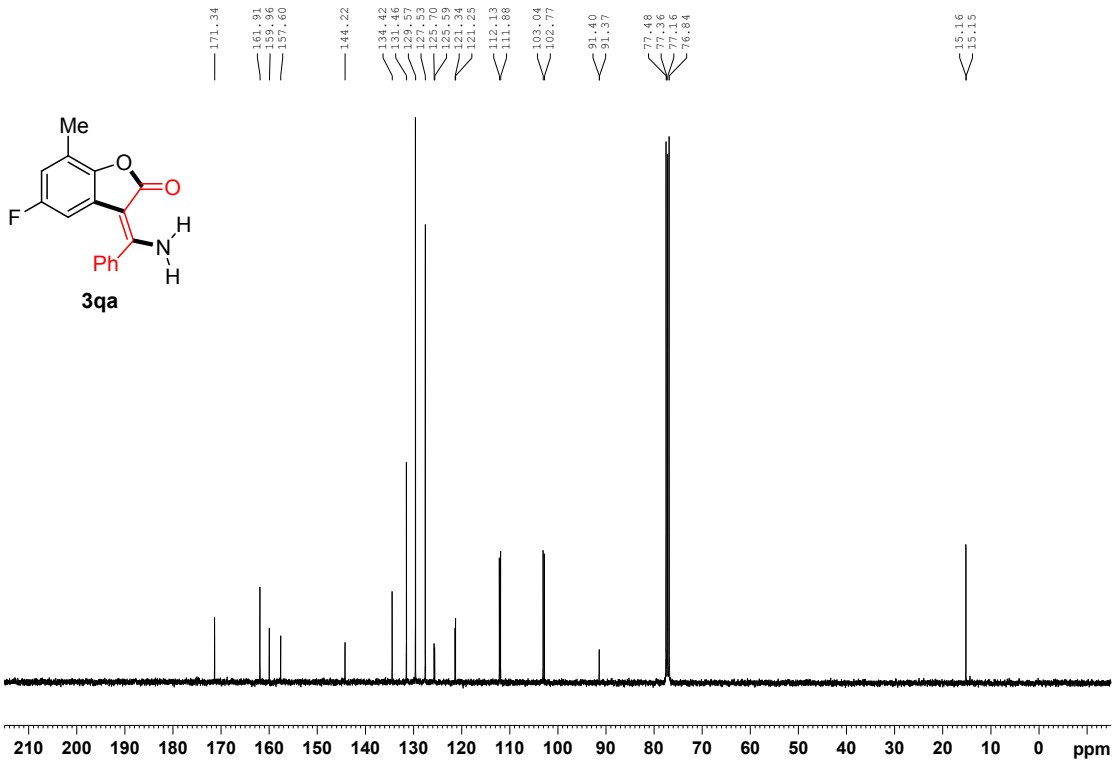


(*Z*)-3-(Amino(phenyl)methylene)-5-fluoro-7-methylbenzofuran-2(3*H*)-one (3qa)

^{1}H NMR ($CDCl_3$, 400 MHz)

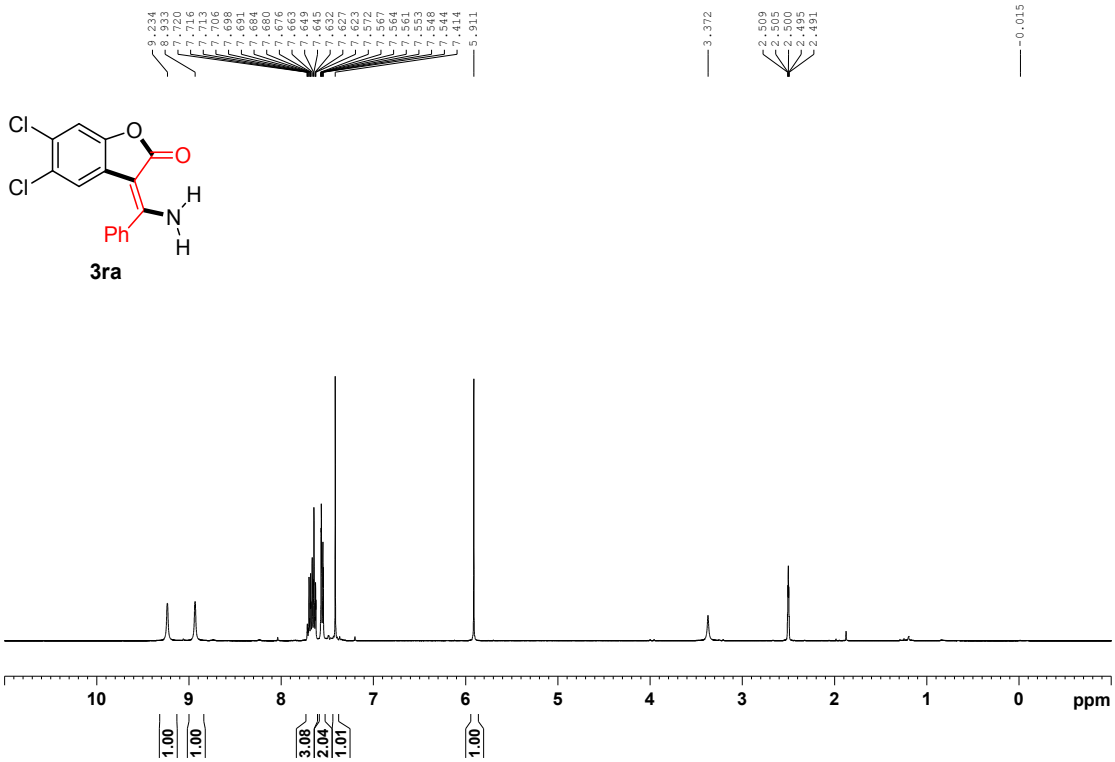


^{13}C NMR ($CDCl_3$, 101 MHz)

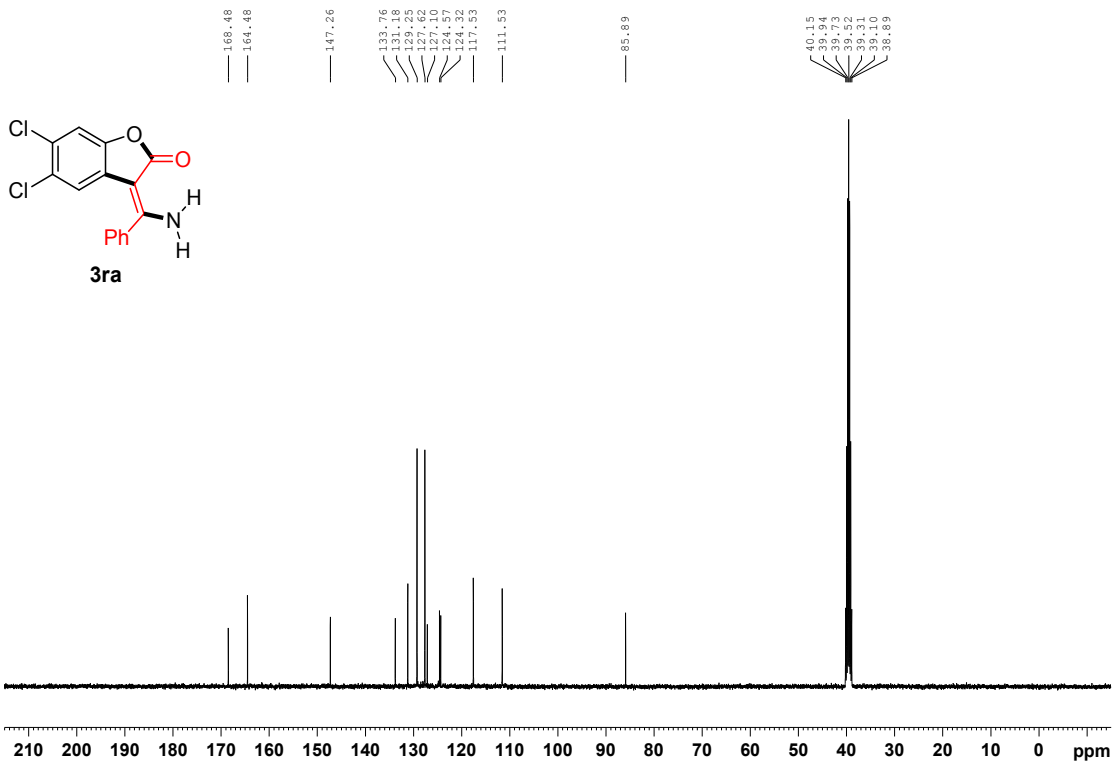


(*Z*)-3-(Amino(phenyl)methylene)-5,6-dichlorobenzofuran-2(3*H*)-one (3ra)

^{1}H NMR (DMSO-d_6, 400 MHz)

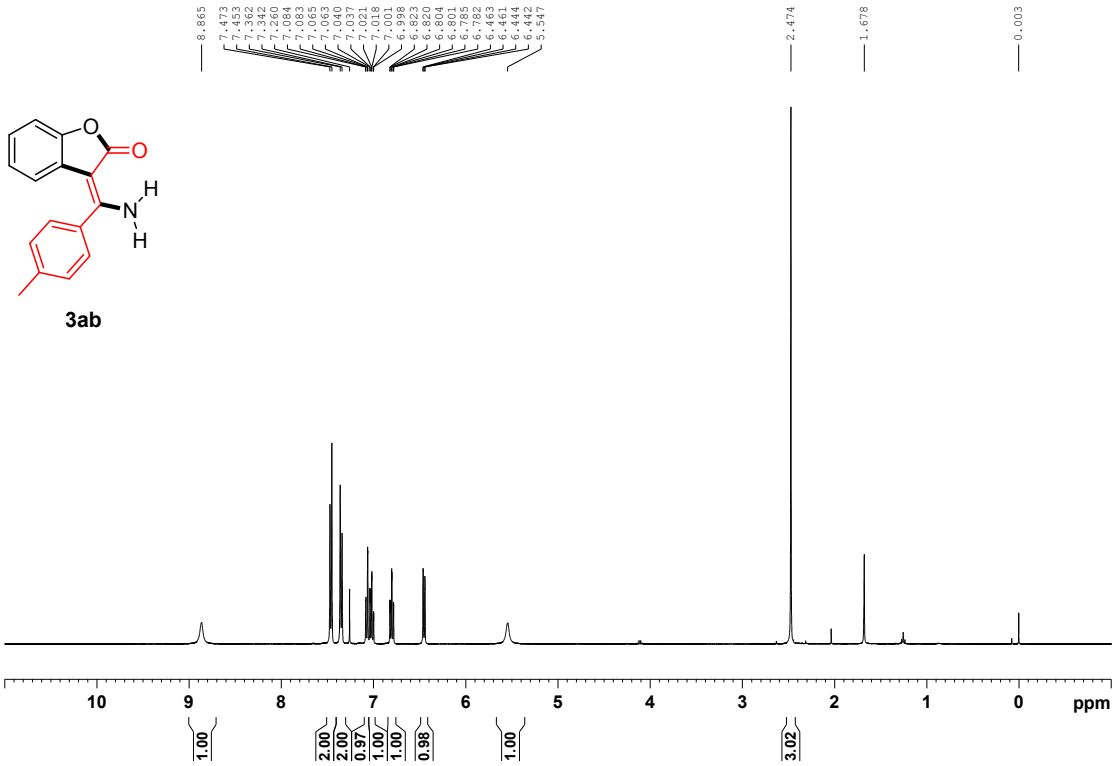


^{13}C NMR (DMSO-d_6, 101 MHz)

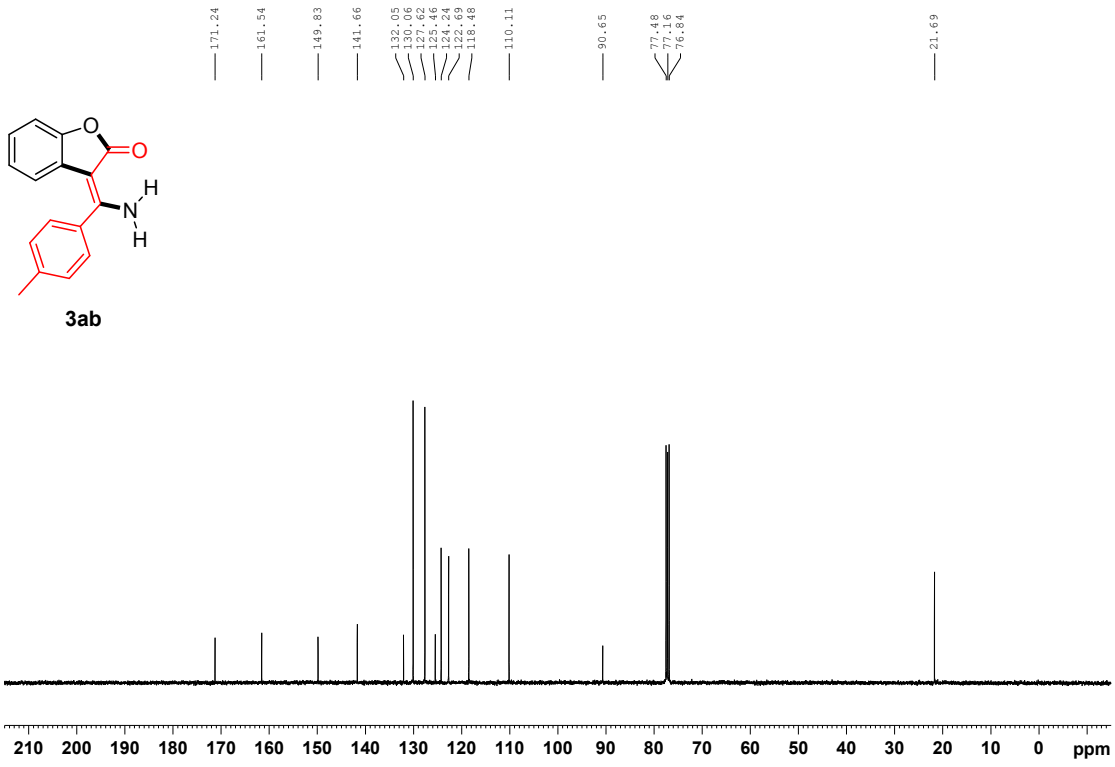


(*Z*)-3-(Amino(p-tolyl)methylene)benzofuran-2(3*H*)-one (3ab)

^{1}H NMR ($CDCl_3$, 400 MHz)

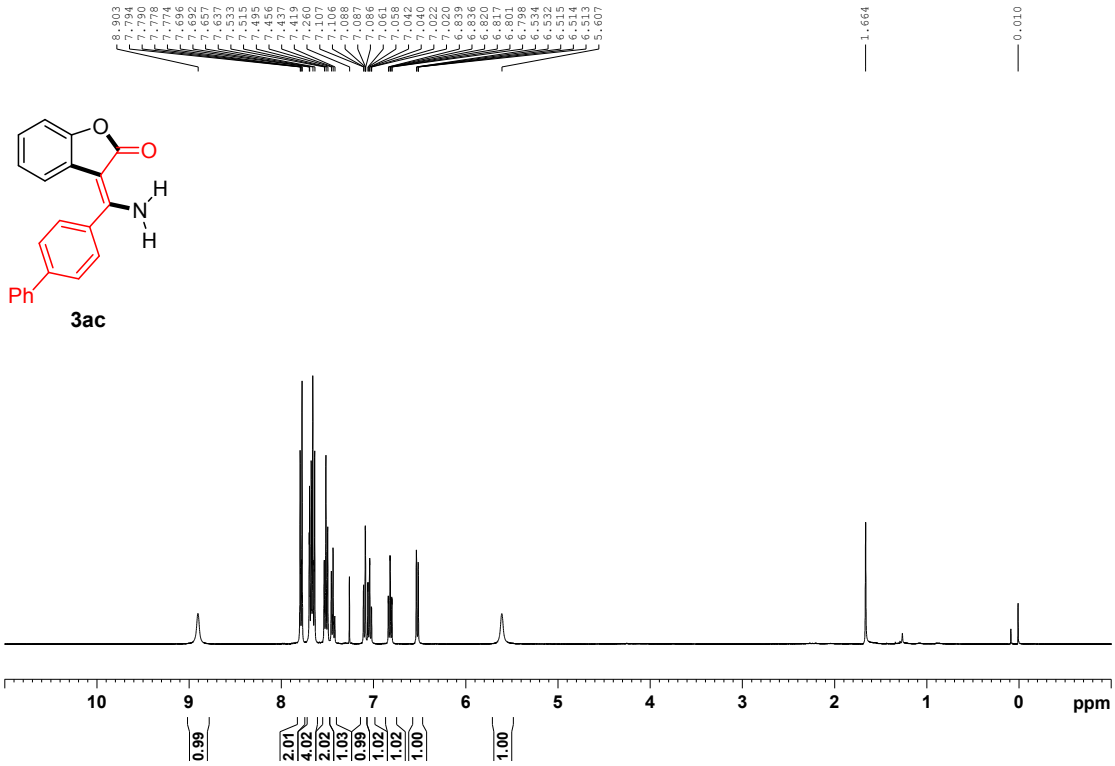


^{13}C NMR ($CDCl_3$, 101 MHz)

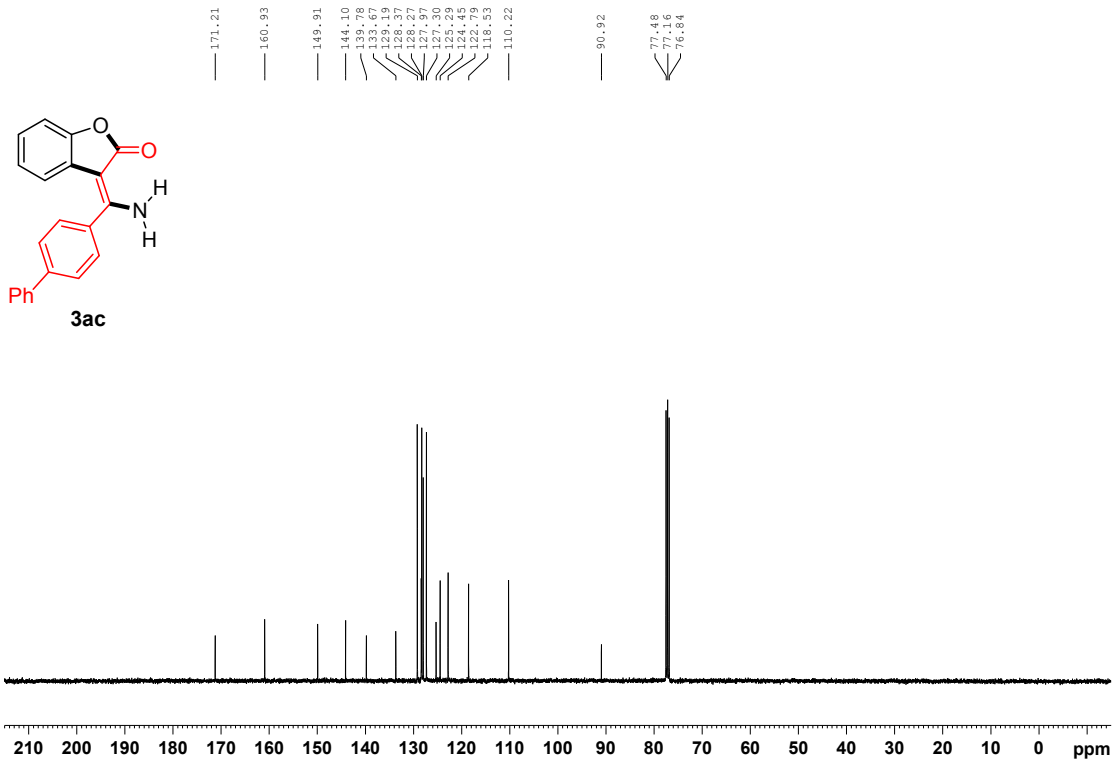


(*Z*)-3-([1,1'-Biphenyl]-4-yl(amino)methylene)benzofuran-2(3*H*)-one (3ac)

^{1}H NMR ($CDCl_3$, 400 MHz)

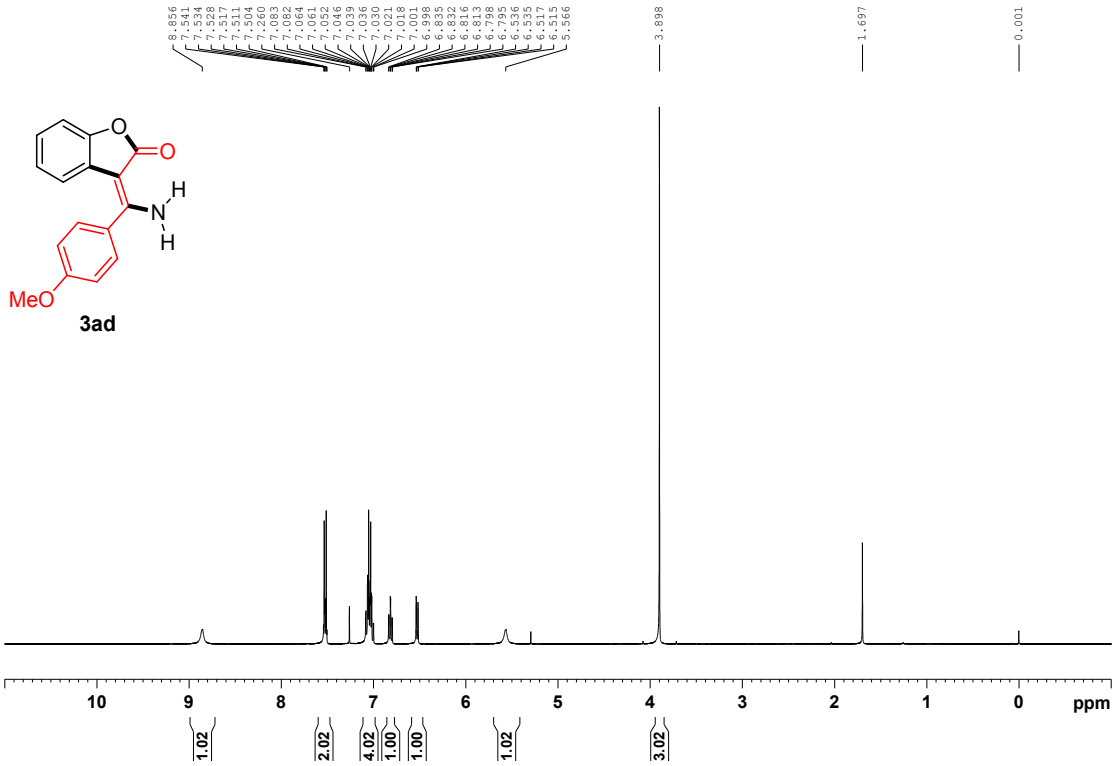


^{13}C NMR ($CDCl_3$, 101 MHz)

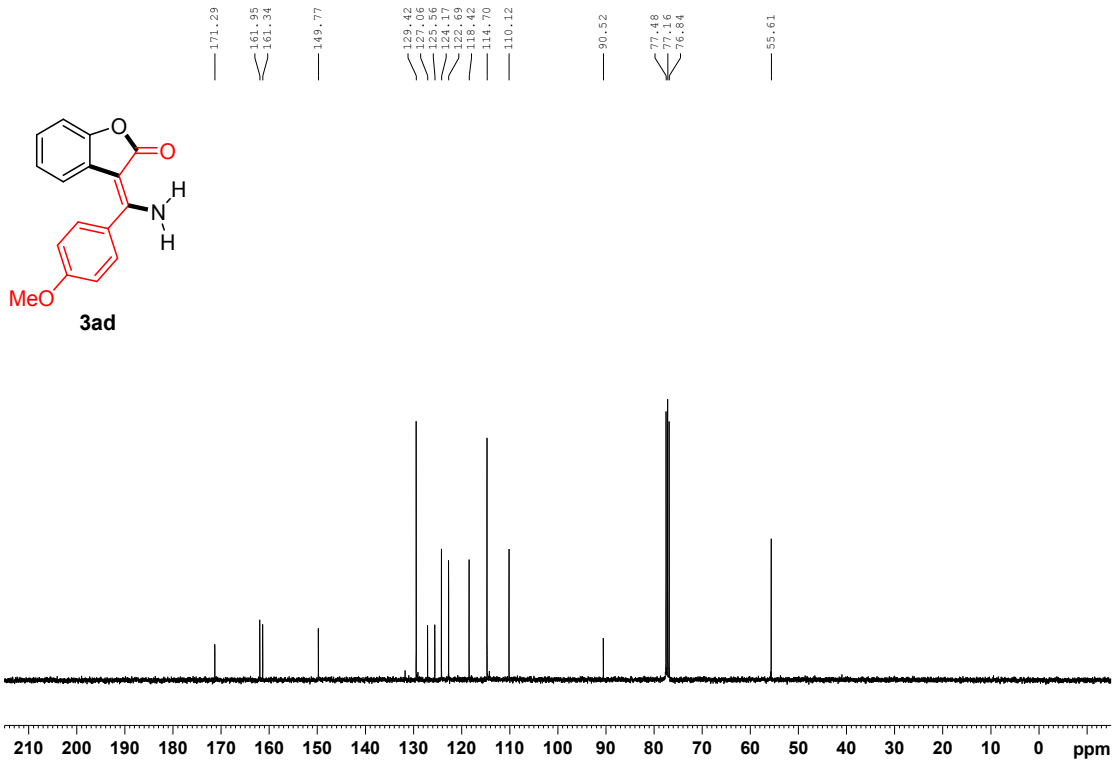


(*Z*)-3-(Amino(4-methoxyphenyl)methylene)benzofuran-2(3*H*)-one (3ad)

^{1}H NMR ($CDCl_3$, 400 MHz)

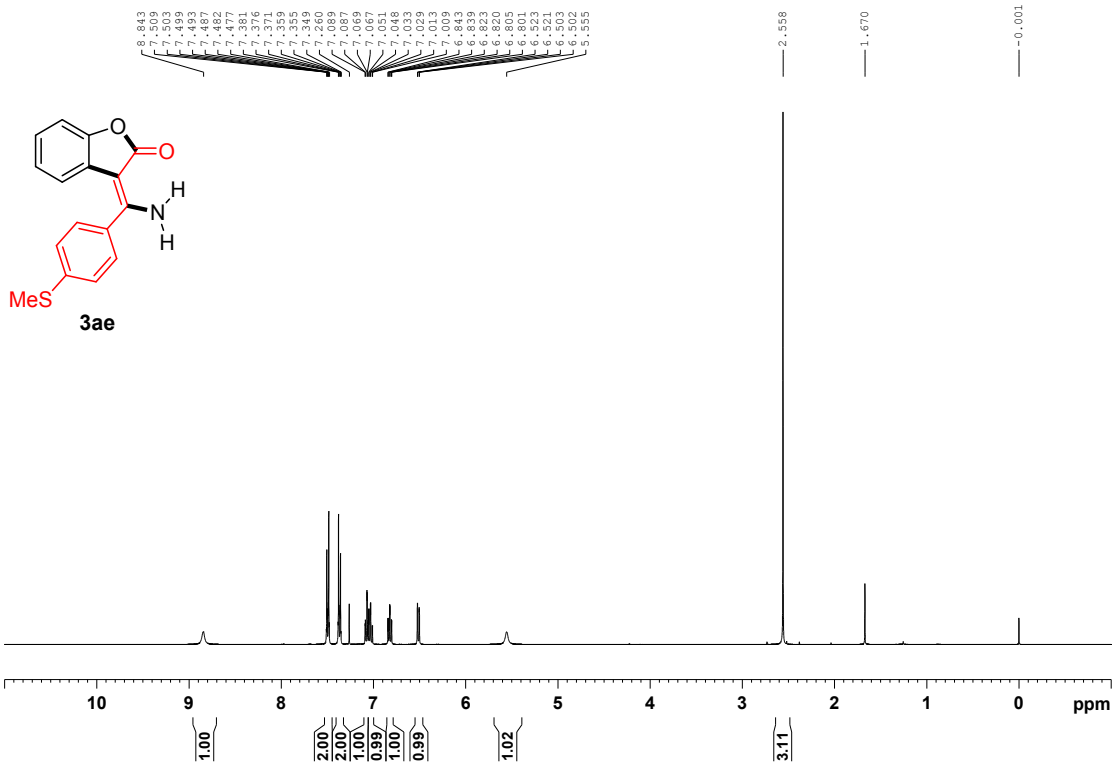


^{13}C NMR ($CDCl_3$, 101 MHz)

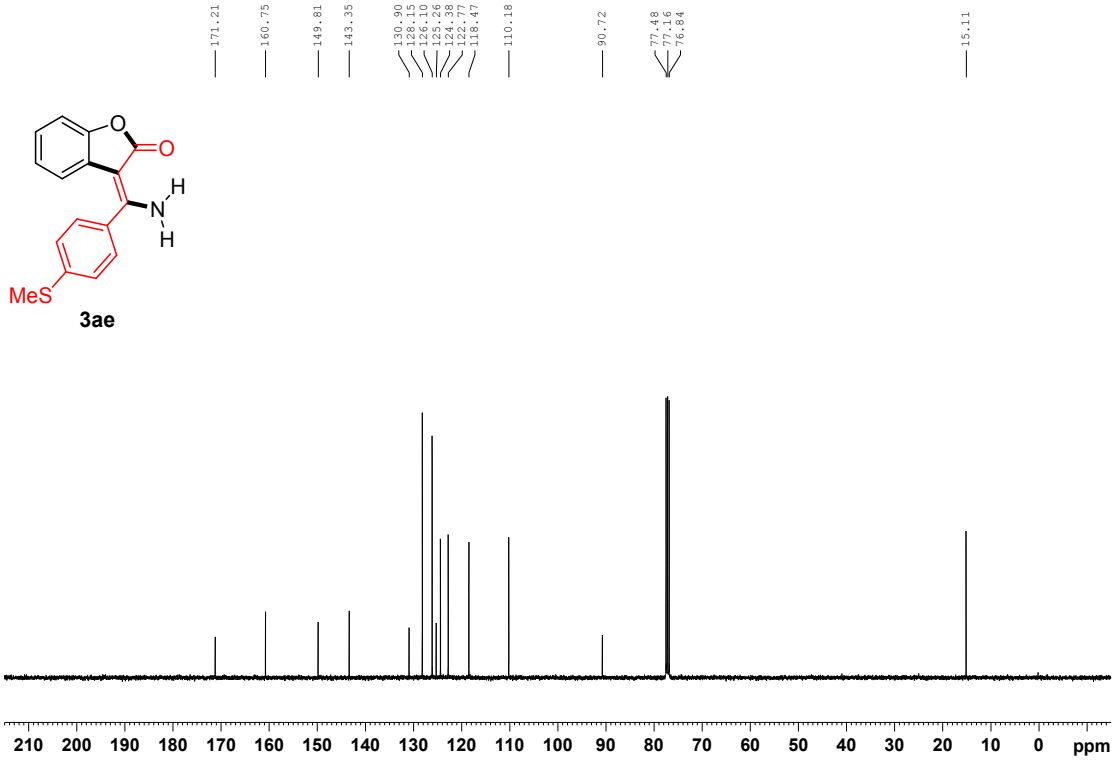


(*Z*)-3-(Amino(4-(methylthio)phenyl)methylene)benzofuran-2(3*H*)-one (3ae)

^{1}H NMR ($CDCl_3$, 400 MHz)

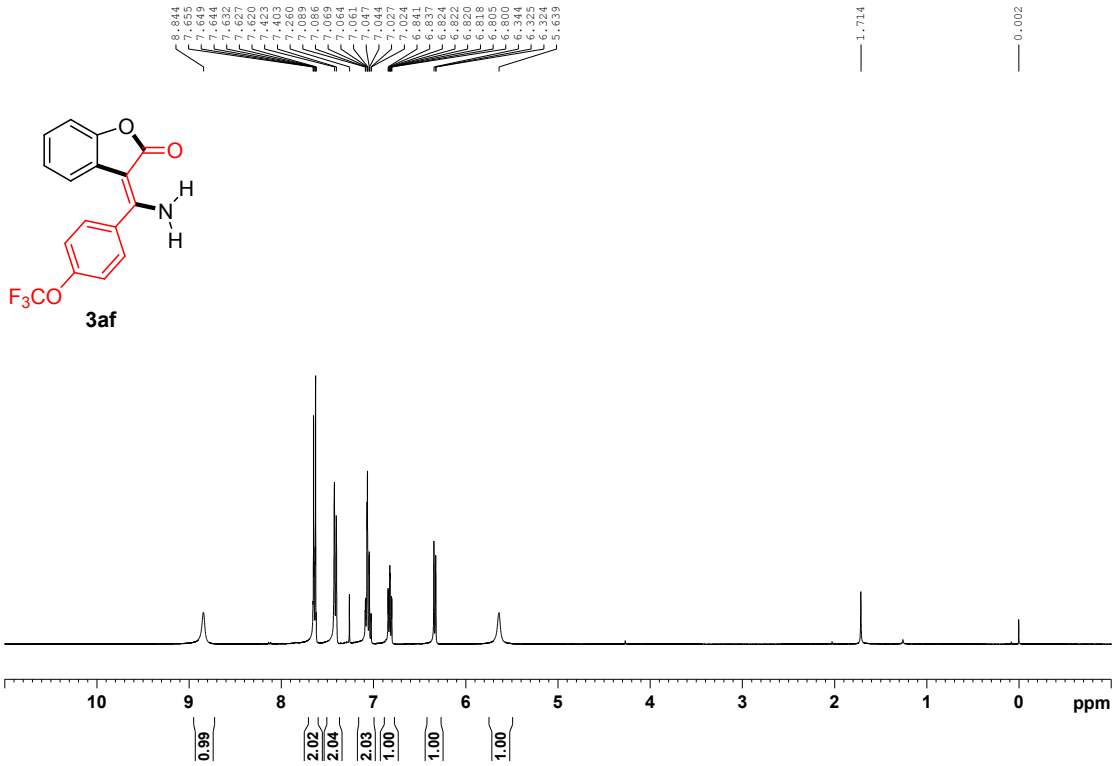


^{13}C NMR ($CDCl_3$, 101 MHz)

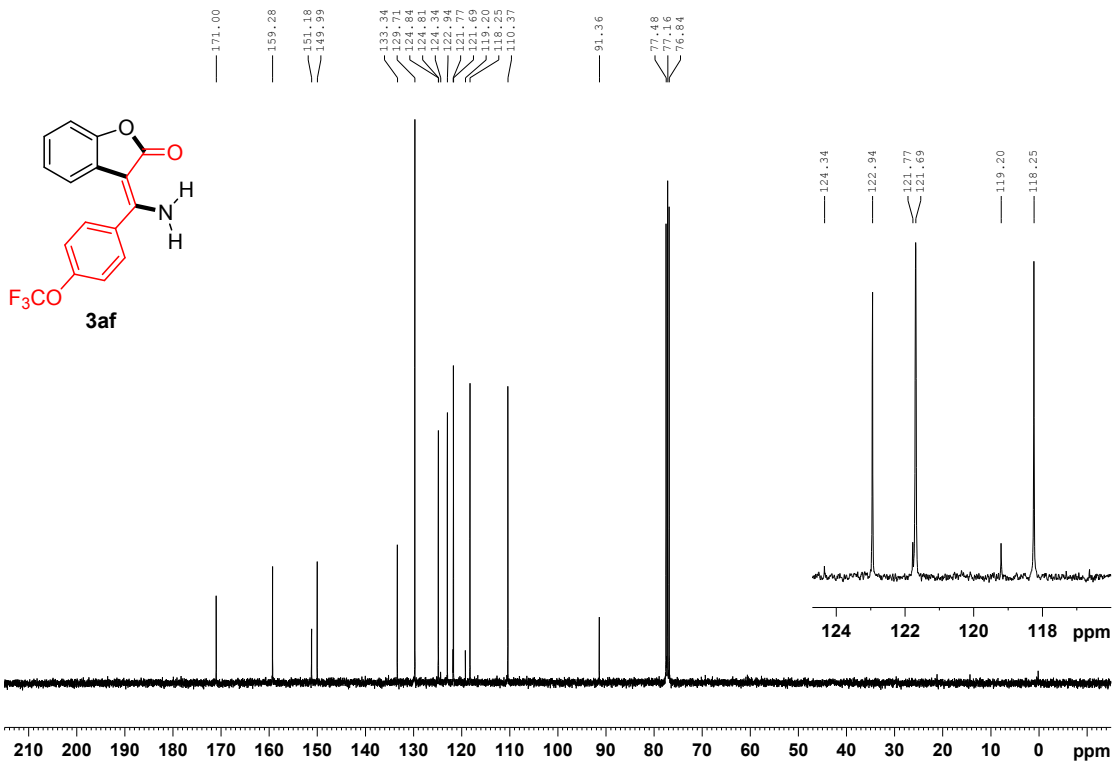


(*Z*)-3-(Amino(4-(trifluoromethoxy)phenyl)methylene)benzofuran-2(3*H*)-one (3af)

^{1}H NMR ($CDCl_3$, 400 MHz)

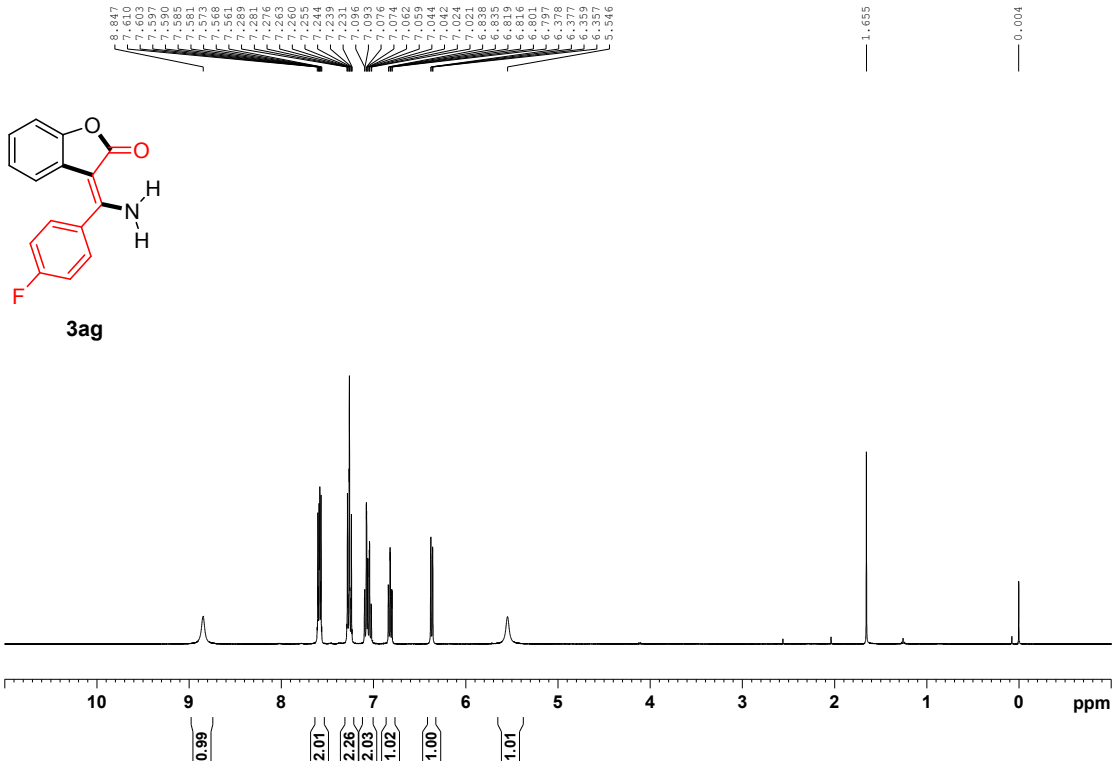


^{13}C NMR ($CDCl_3$, 101 MHz)

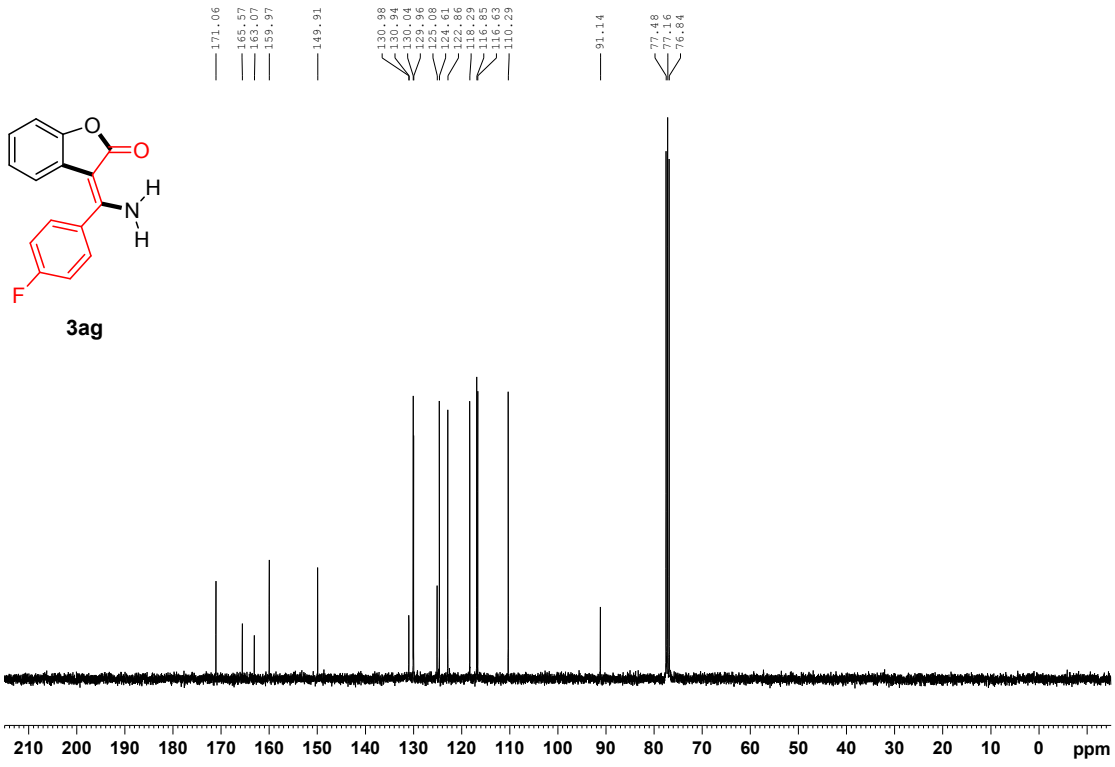


(*Z*)-3-(Amino(4-fluorophenyl)methylene)benzofuran-2(3*H*)-one (3ag)

^{1}H NMR ($CDCl_3$, 400 MHz)

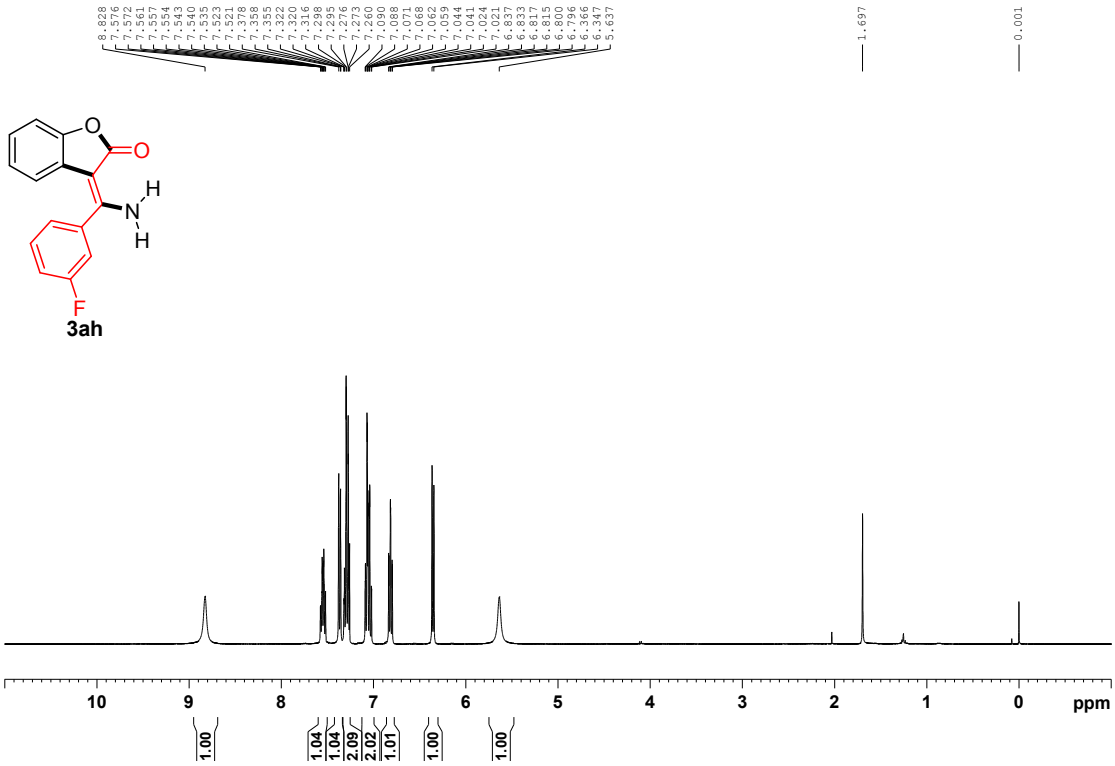


^{13}C NMR ($CDCl_3$, 101 MHz)

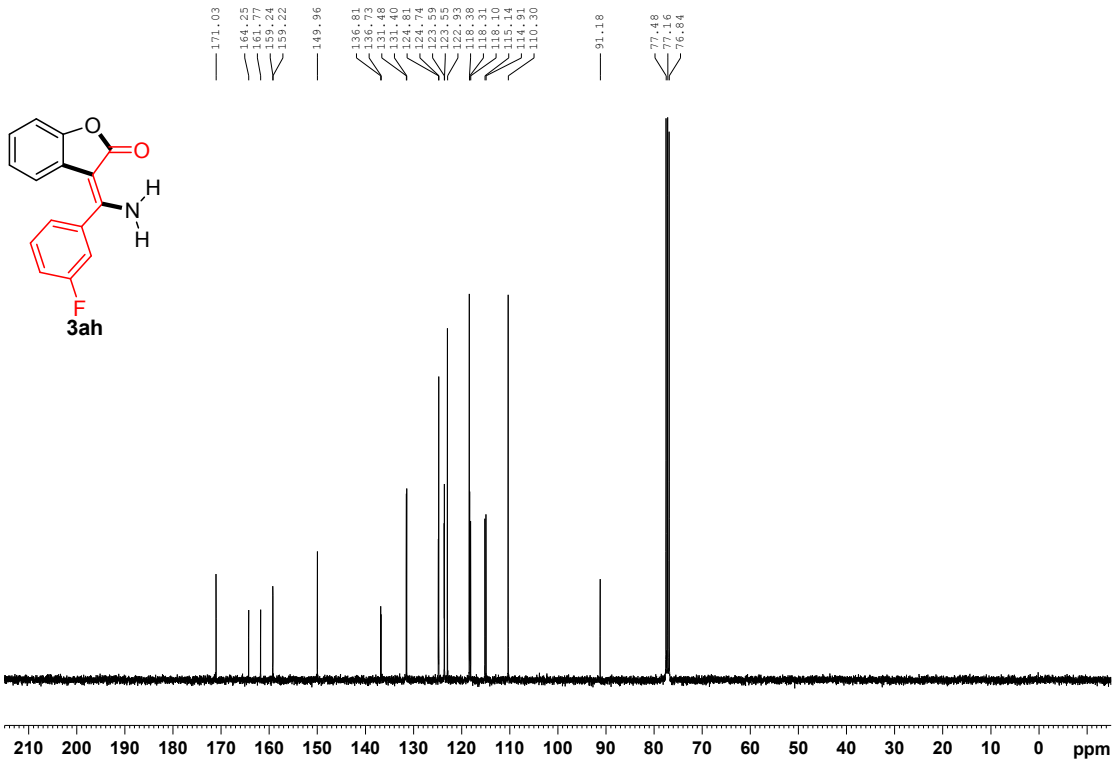


(*Z*)-3-(Amino(3-fluorophenyl)methylene)benzofuran-2(3*H*)-one (3ah)

^{1}H NMR ($CDCl_3$, 400 MHz)

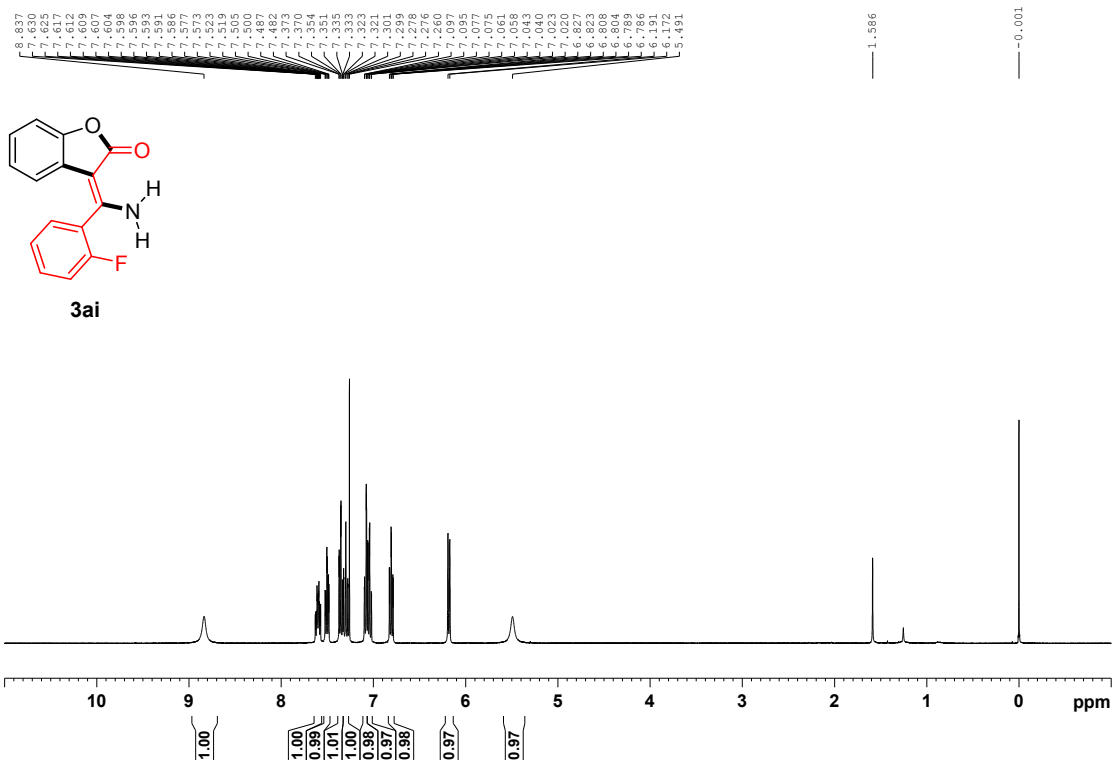


^{13}C NMR ($CDCl_3$, 101 MHz)

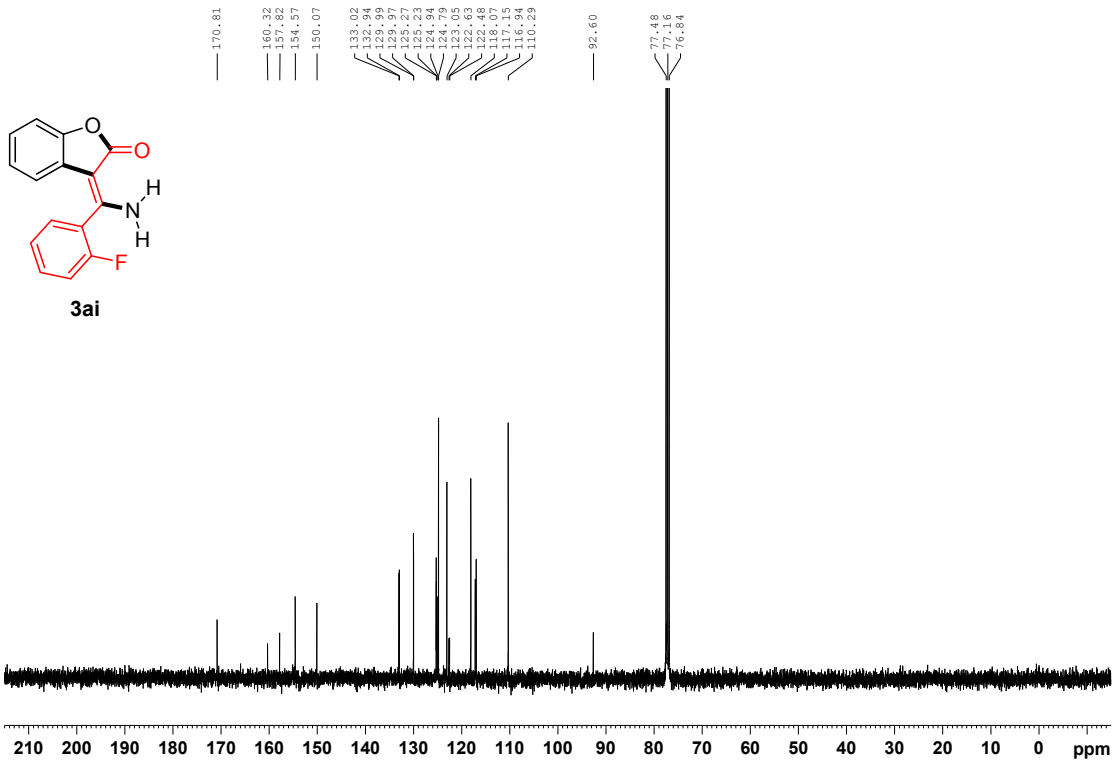


(*Z*)-3-(Amino(2-fluorophenyl)methylene)benzofuran-2(3*H*)-one (3ai)

^{1}H NMR ($CDCl_3$, 400 MHz)

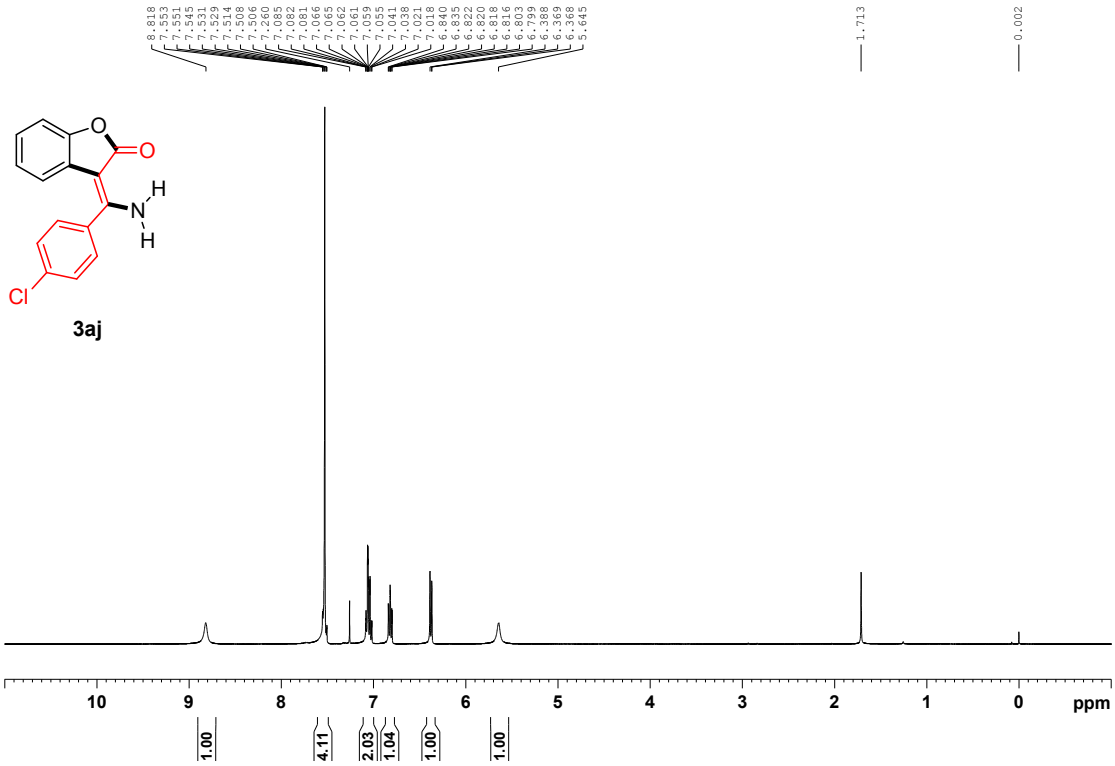


^{13}C NMR ($CDCl_3$, 101 MHz)

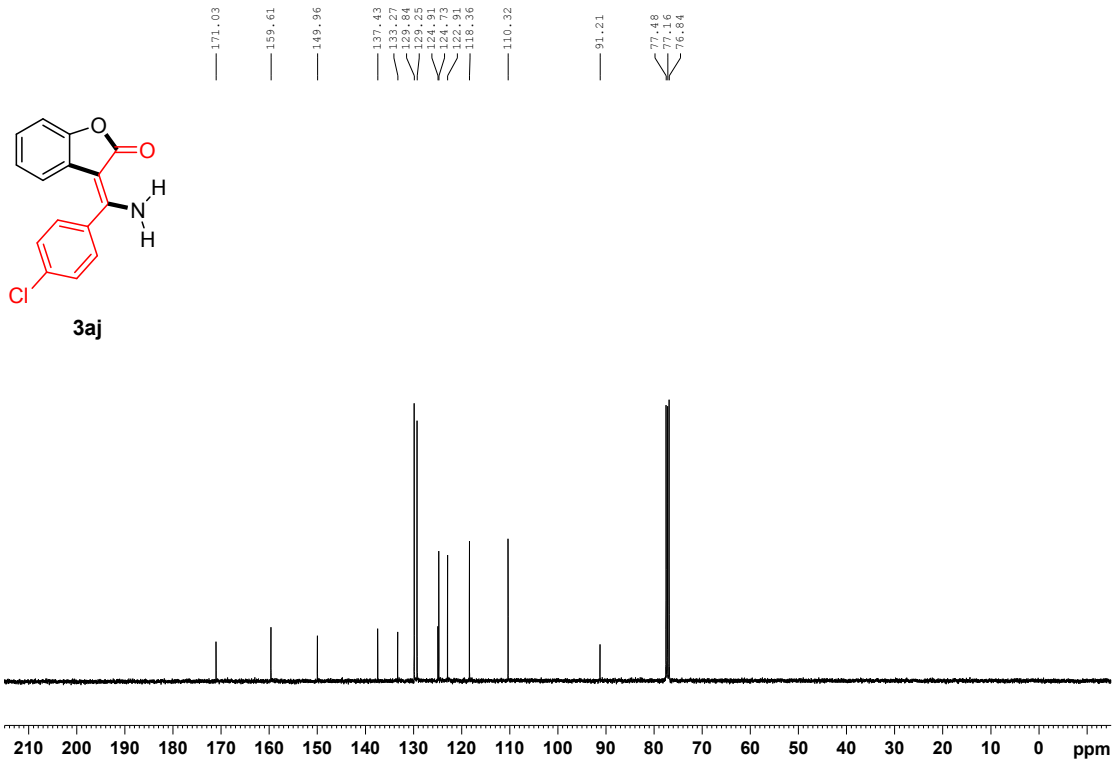


(*Z*)-3-(Amino(4-chlorophenyl)methylene)benzofuran-2(3*H*)-one (3aj)

^{1}H NMR ($CDCl_3$, 400 MHz)

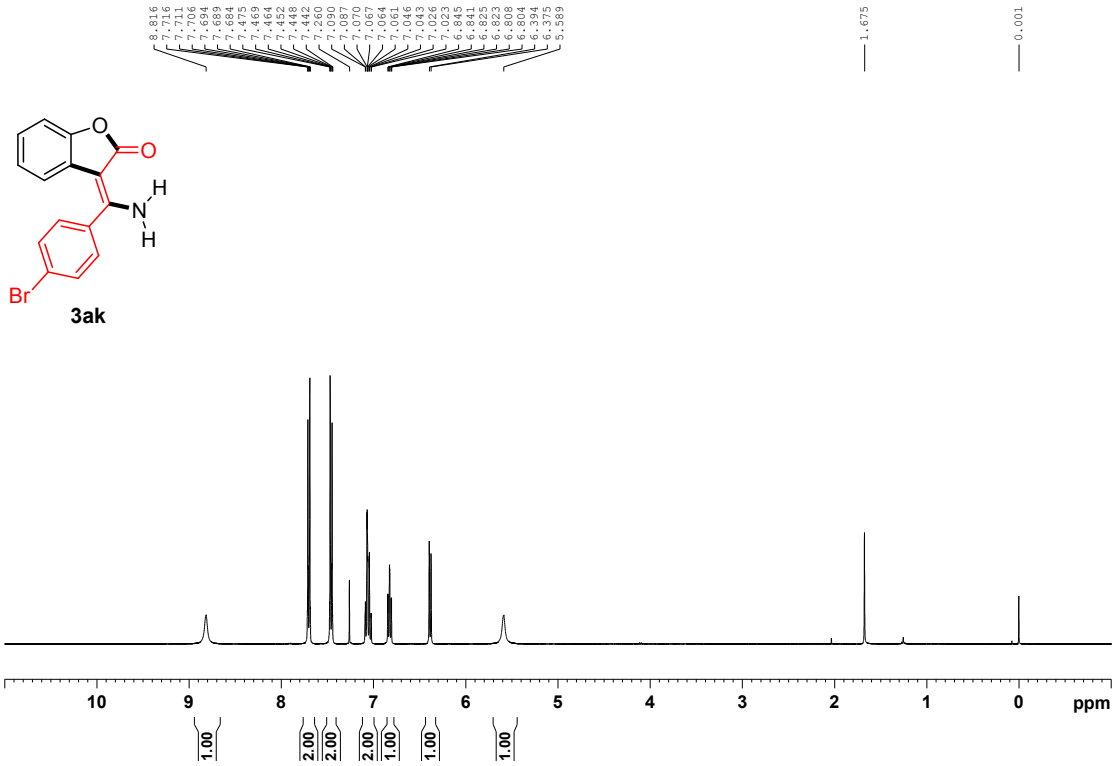


^{13}C NMR ($CDCl_3$, 101 MHz)

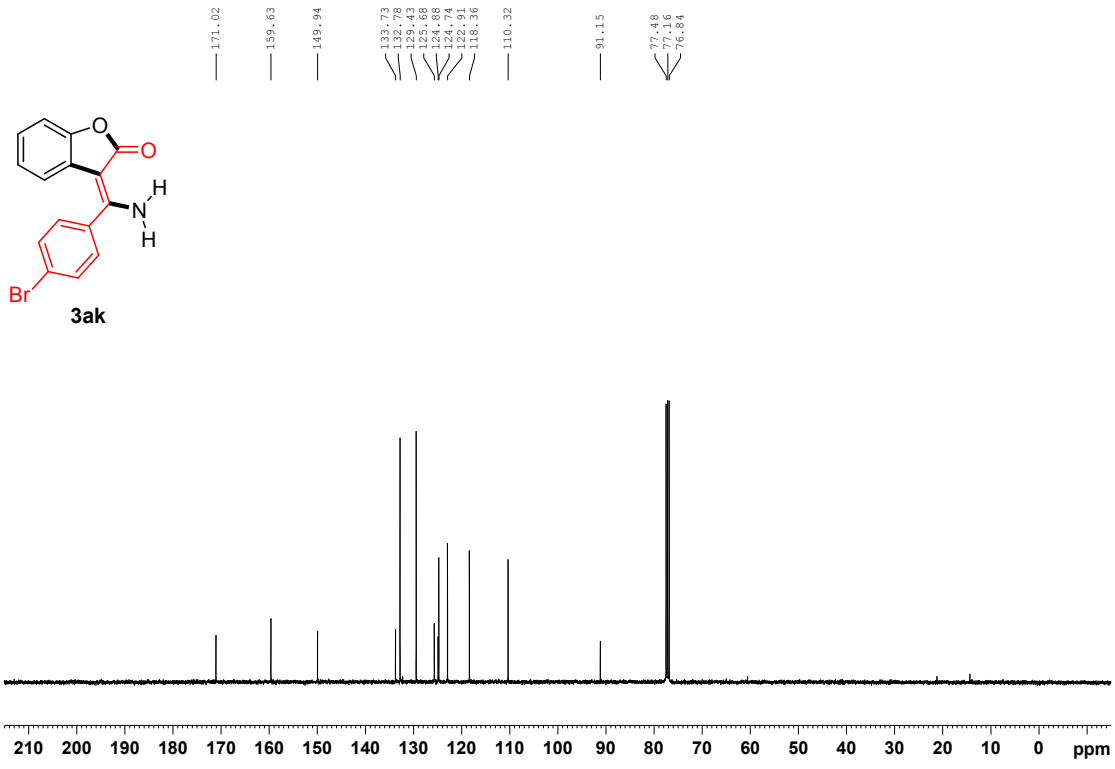


(*Z*)-3-(Amino(4-bromophenyl)methylene)benzofuran-2(3*H*)-one (3ak)

^{1}H NMR ($CDCl_3$, 400 MHz)

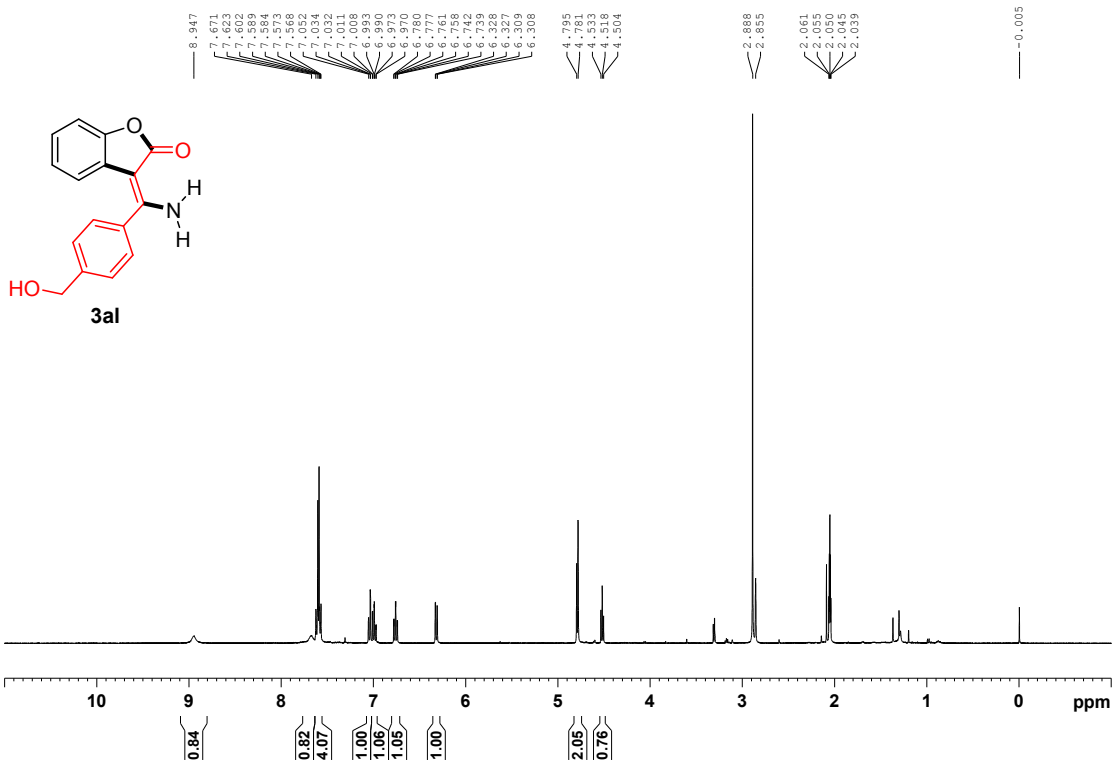


^{13}C NMR ($CDCl_3$, 101 MHz)

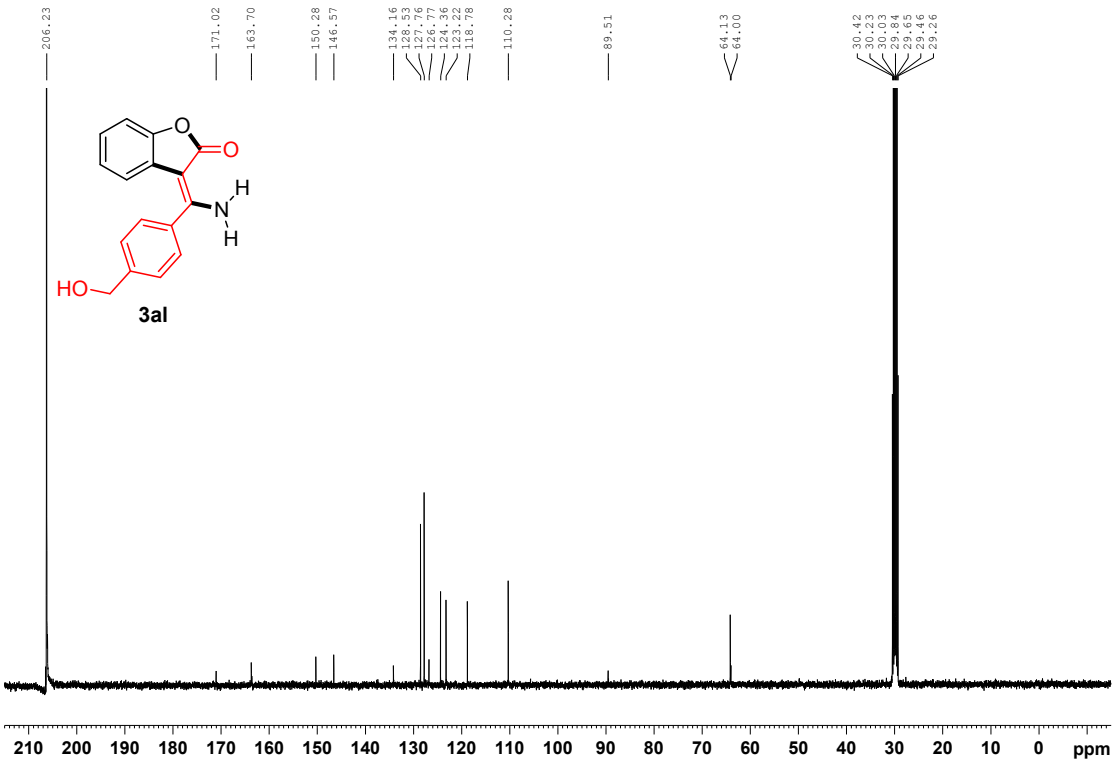


(*Z*)-3-(Amino(4-(hydroxymethyl)phenyl)methylene)benzofuran-2(3*H*)-one (3al)

^{1}H NMR (acetone-d_6, 400 MHz)

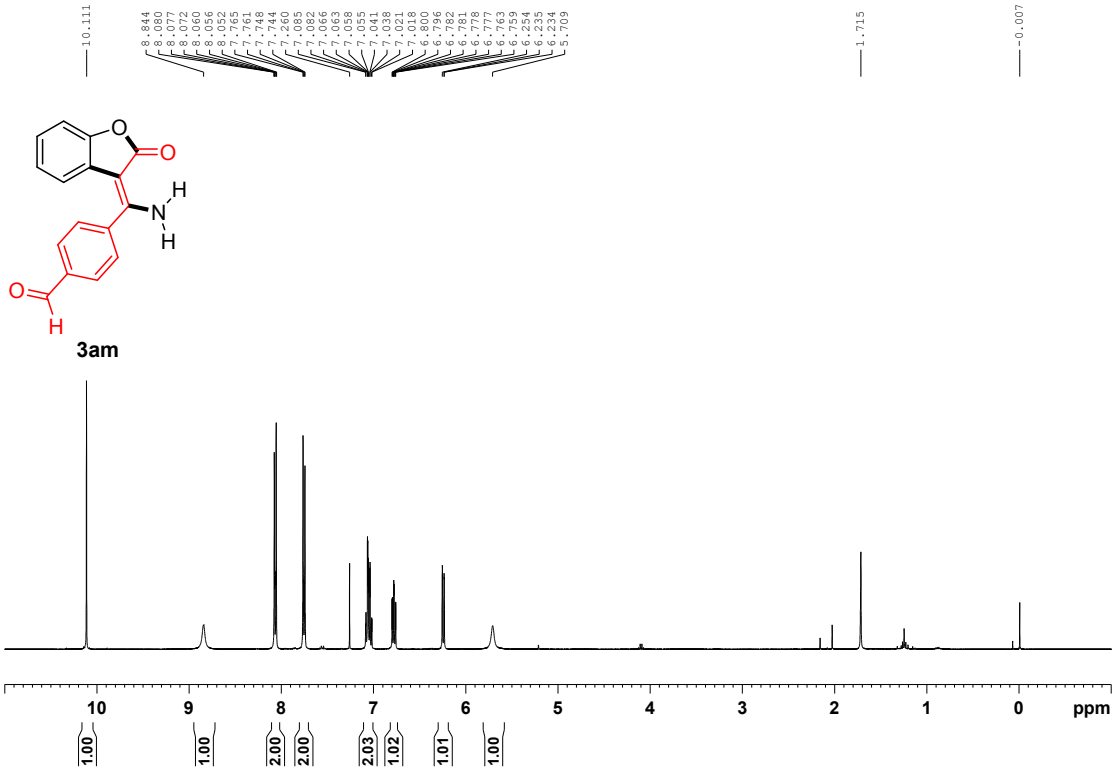


^{13}C NMR (acetone-d_6, 101 MHz)

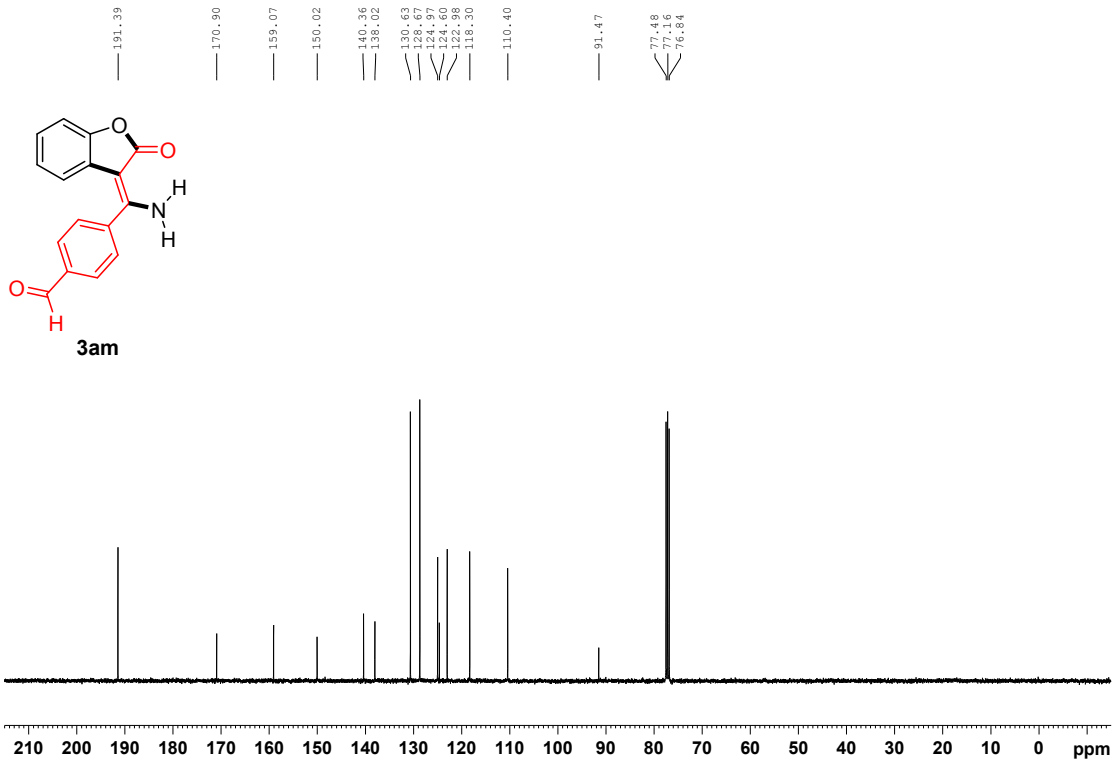


(*Z*)-4-(Amino(2-oxobenzofuran-3(2*H*)-ylidene)methyl)benzaldehyde (3am)

^{1}H NMR ($CDCl_3$, 400 MHz)

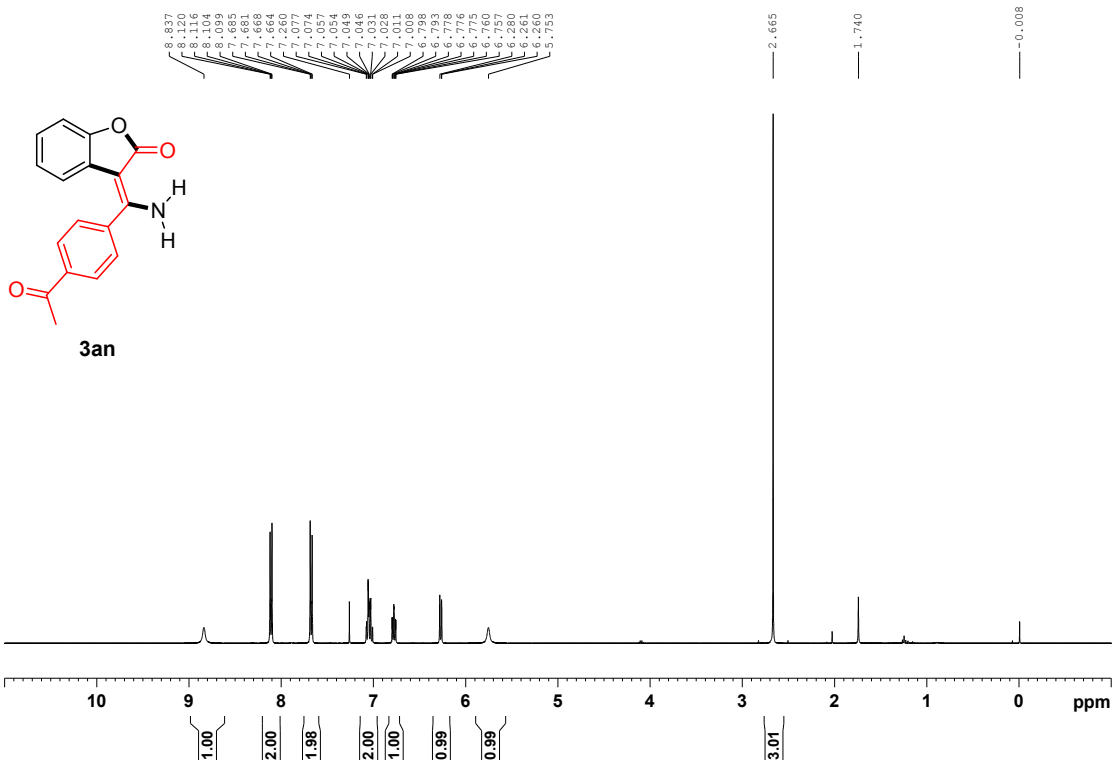


^{13}C NMR ($CDCl_3$, 101 MHz)

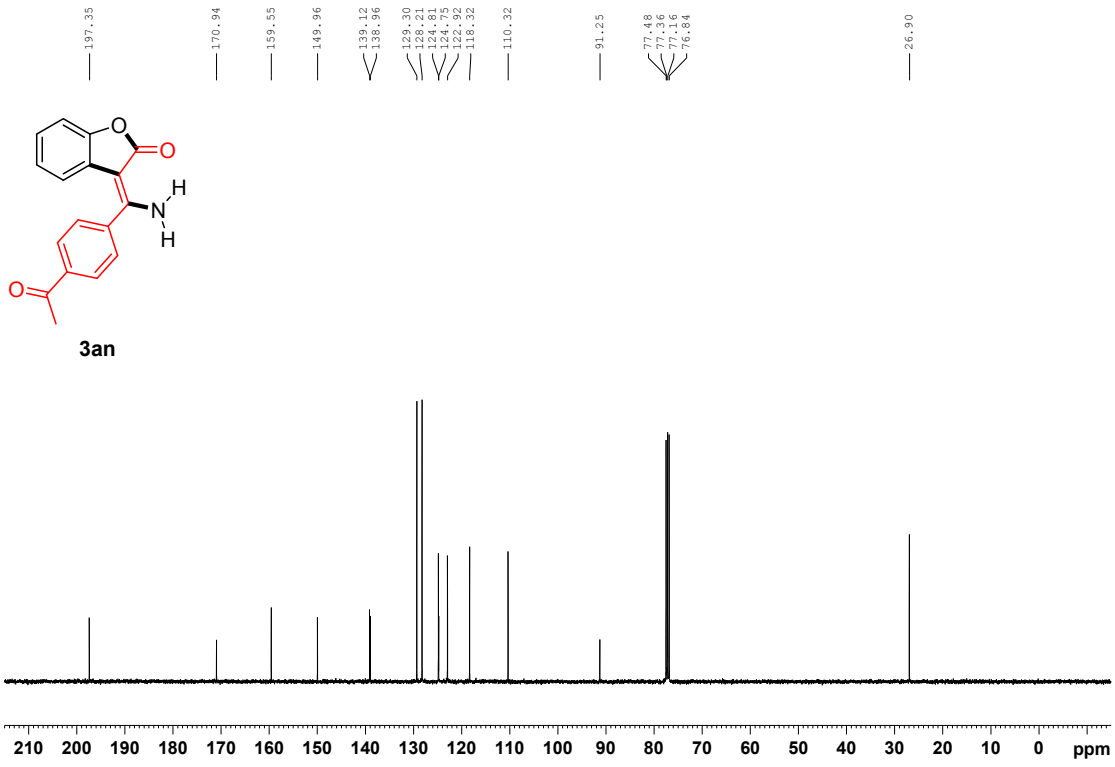


(*Z*)-3-((4-Acetylphenyl)(amino)methylene)benzofuran-2(3*H*)-one (3an)

^{1}H NMR ($CDCl_3$, 400 MHz)

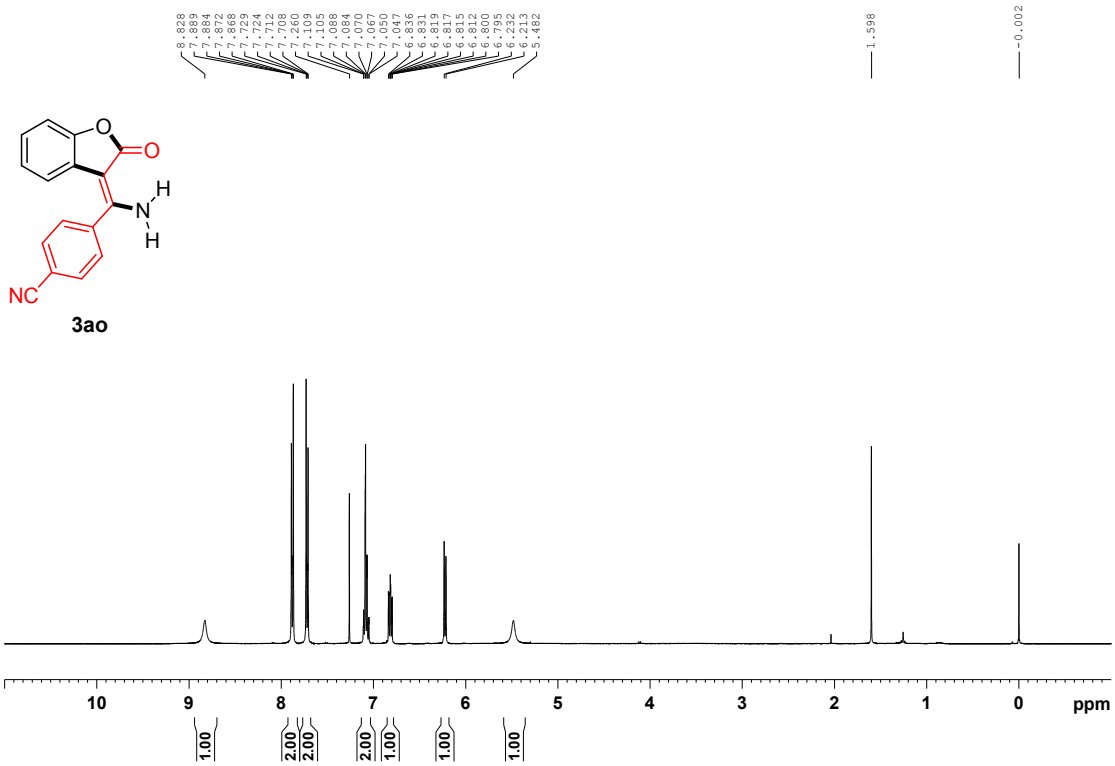


^{13}C NMR ($CDCl_3$, 101 MHz)

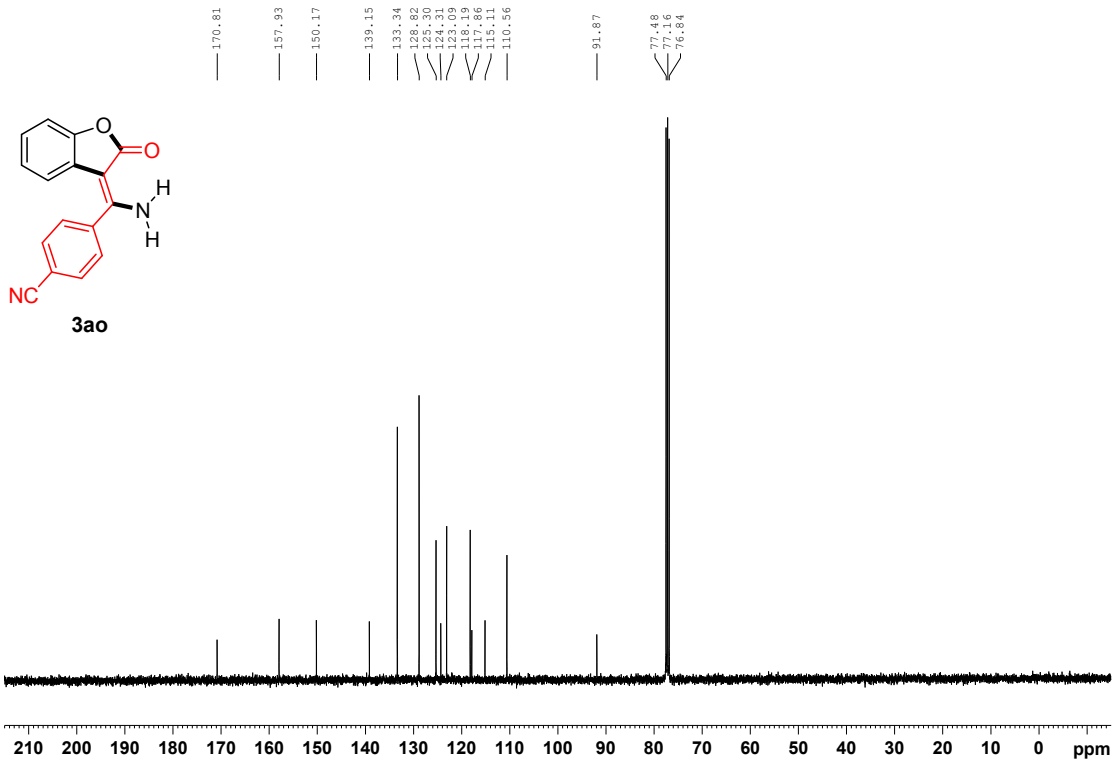


(*Z*)-4-(Amino(2-oxobenzofuran-3(2*H*)-ylidene)methyl)benzonitrile (3ao)

^{1}H NMR ($CDCl_3$, 400 MHz)

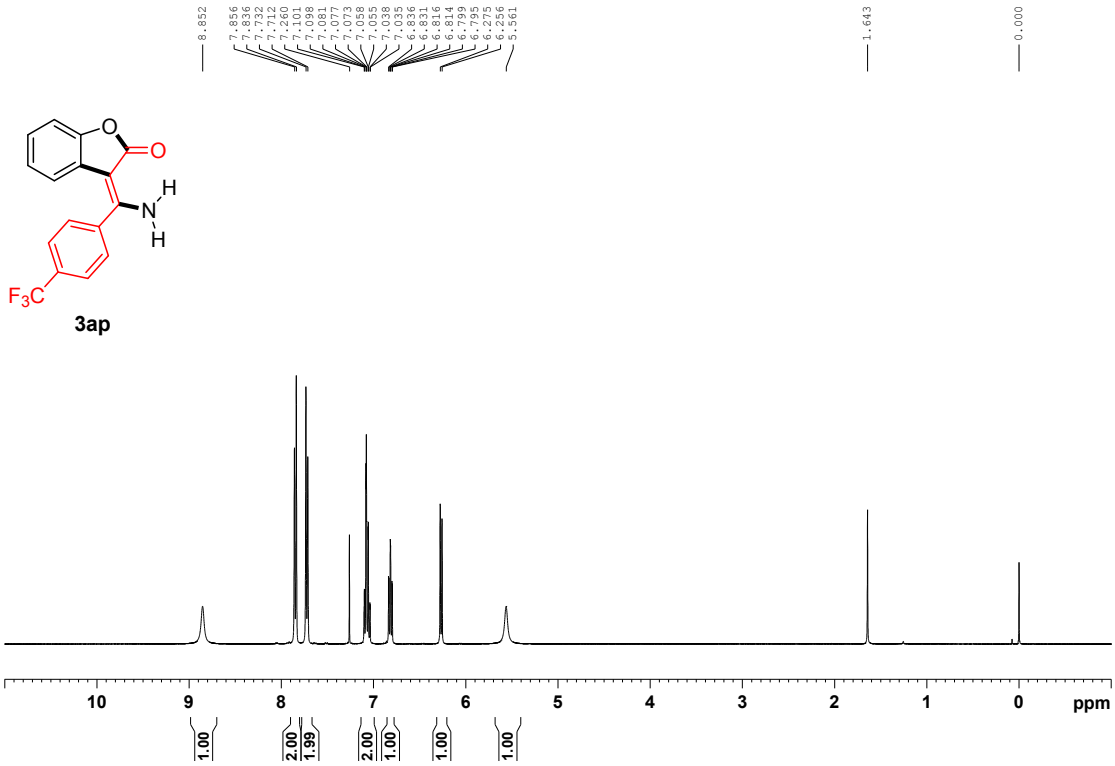


^{13}C NMR ($CDCl_3$, 101 MHz)

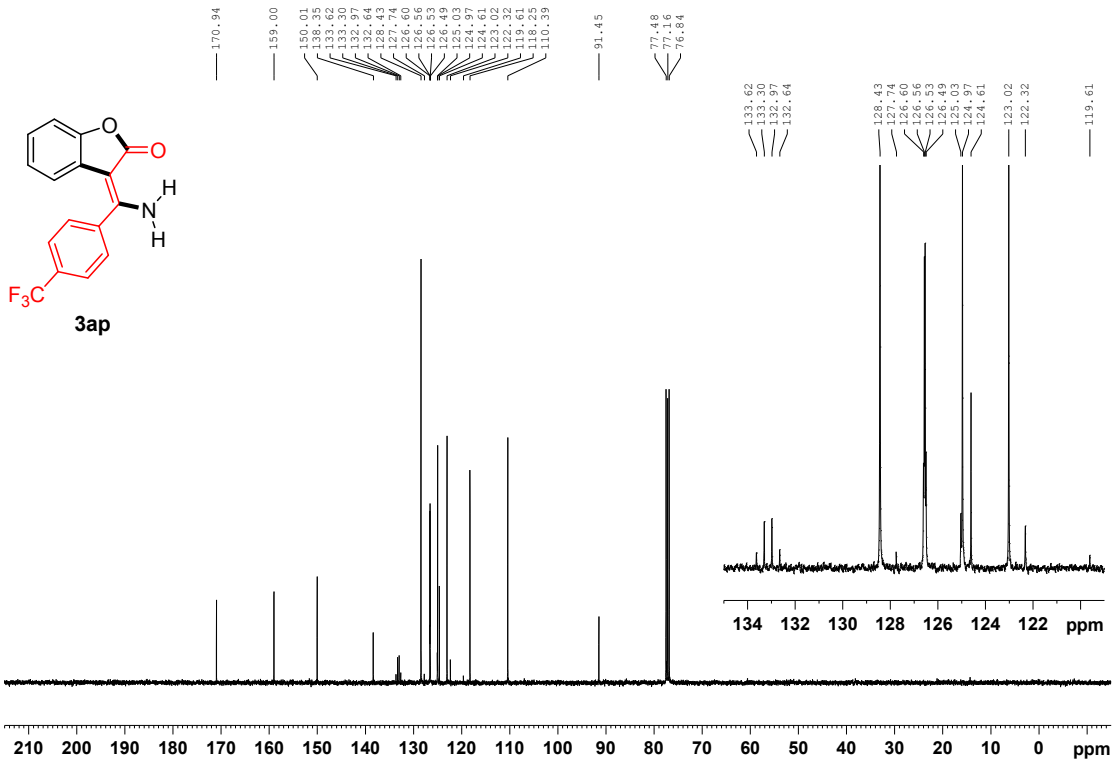


(*Z*)-3-(Amino(4-(trifluoromethyl)phenyl)methylene)benzofuran-2(3*H*)-one (3ap)

^{1}H NMR ($CDCl_3$, 400 MHz)

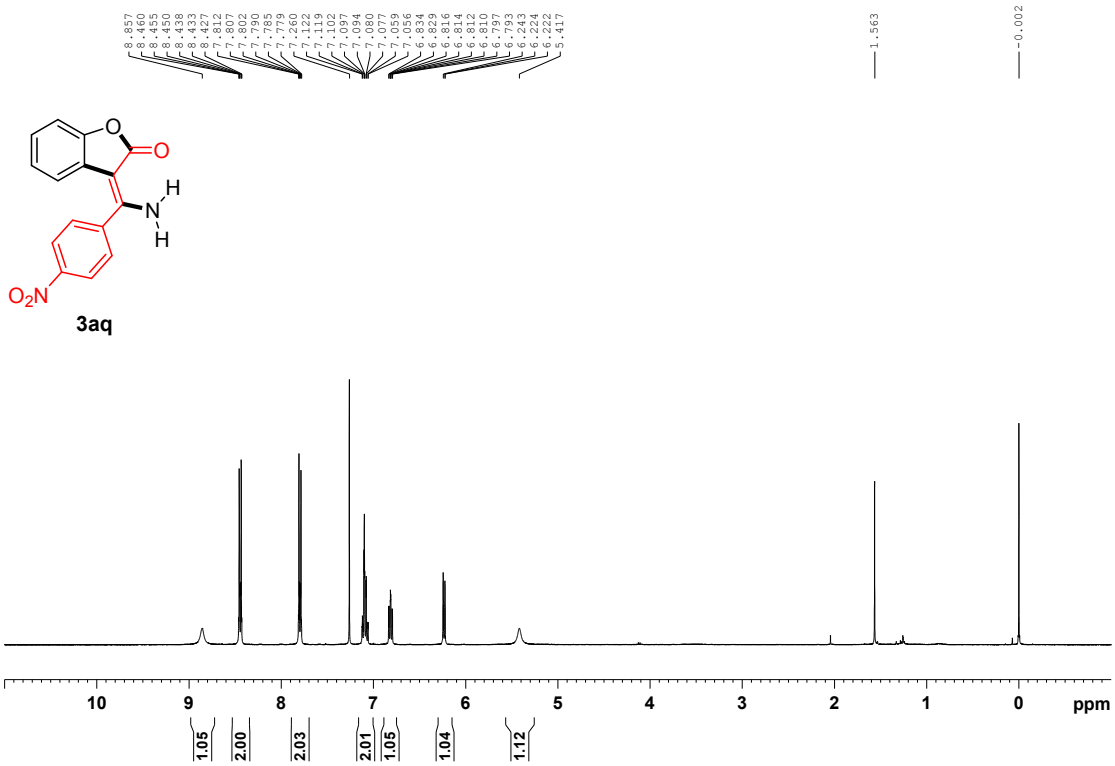


^{13}C NMR ($CDCl_3$, 101 MHz)

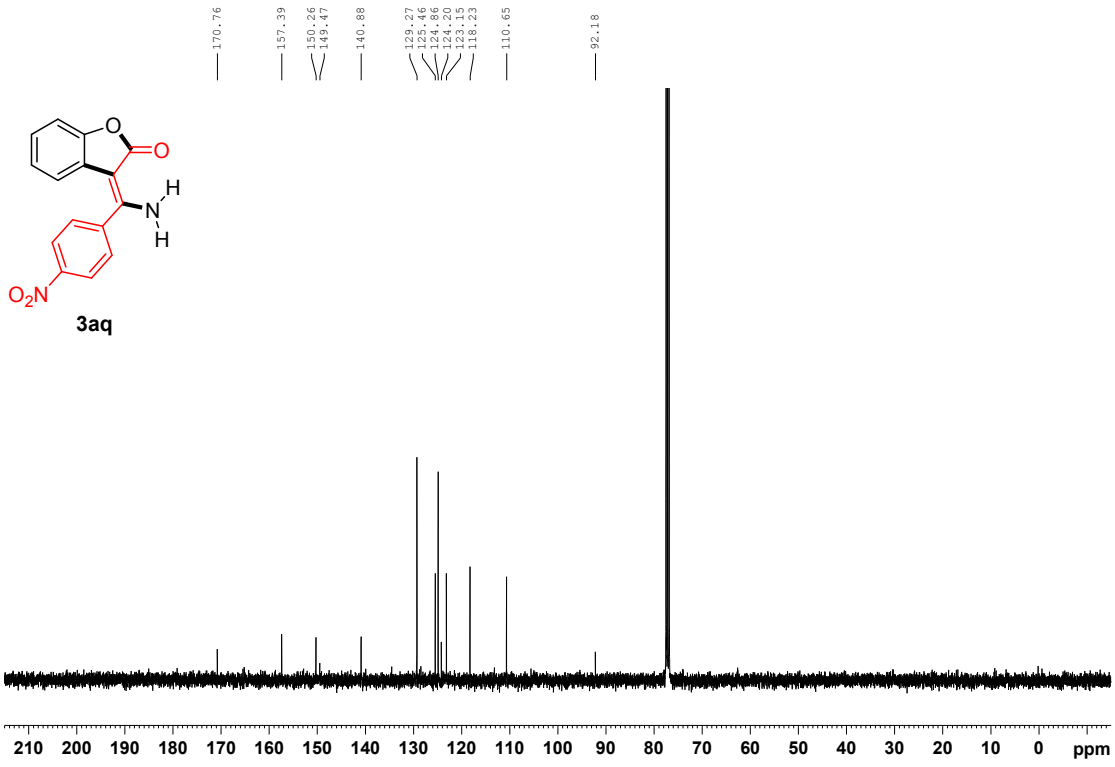


(*Z*)-3-(Amino(4-nitrophenyl)methylene)benzofuran-2(3*H*)-one (3aq)

^{1}H NMR ($CDCl_3$, 400 MHz)

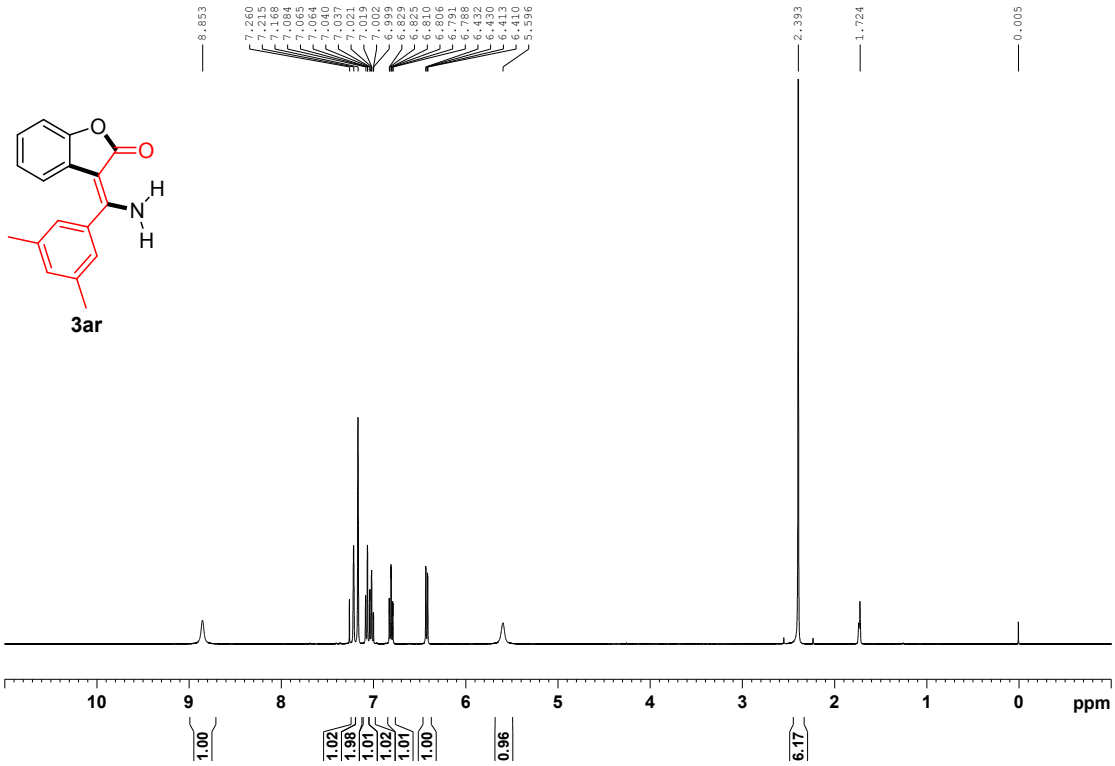


^{13}C NMR ($CDCl_3$, 101 MHz)

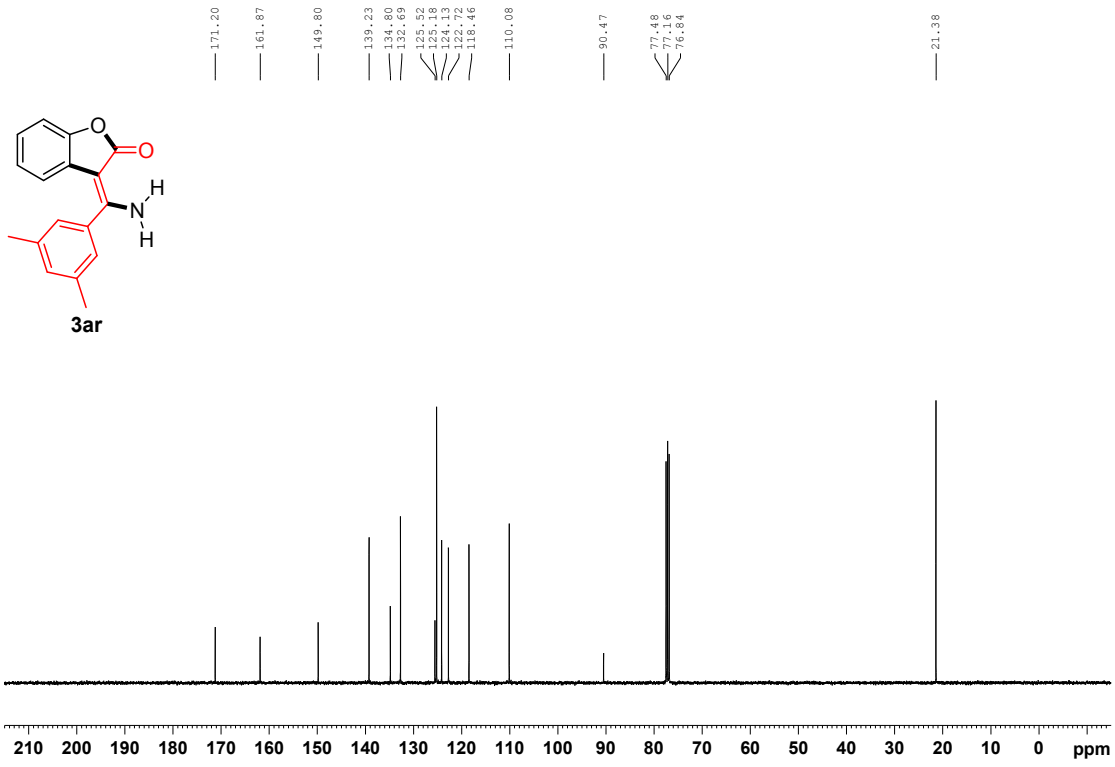


(*Z*)-3-(Amino(3,5-dimethylphenyl)methylene)benzofuran-2(3*H*)-one (3ar)

^{1}H NMR ($CDCl_3$, 400 MHz)

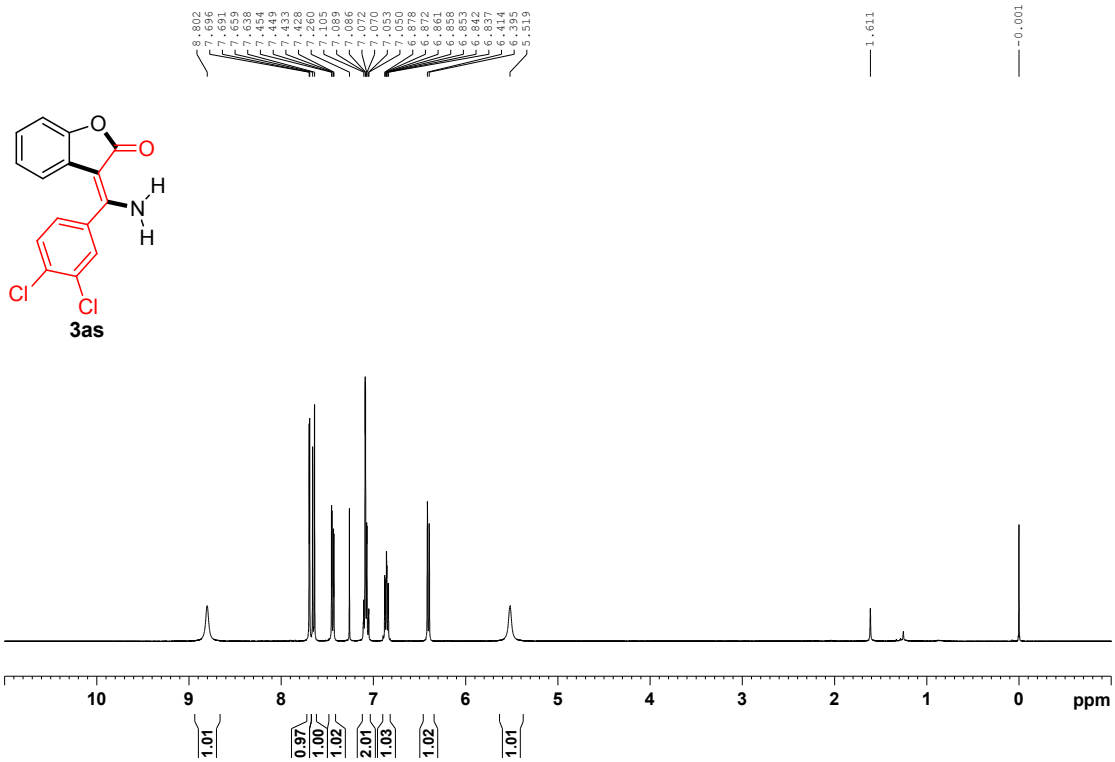


^{13}C NMR ($CDCl_3$, 101 MHz)

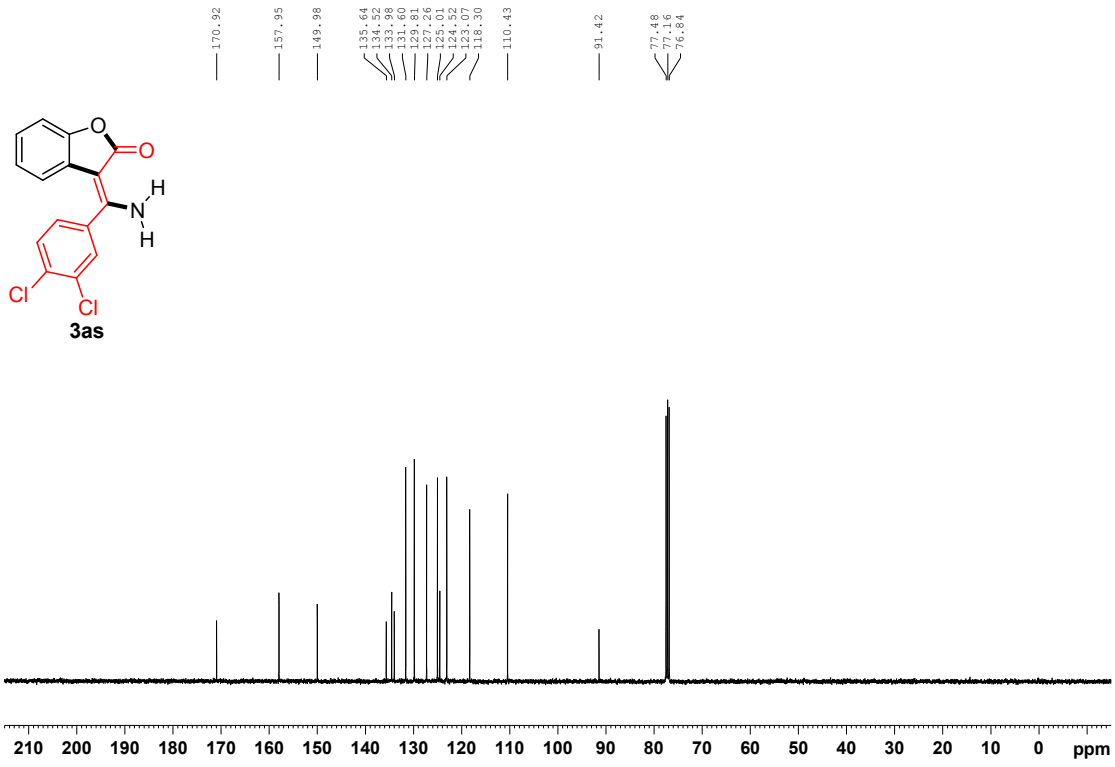


(*Z*)-3-(Amino(3,4-dichlorophenyl)methylene)benzofuran-2(3*H*)-one (3as)

^{1}H NMR ($CDCl_3$, 400 MHz)

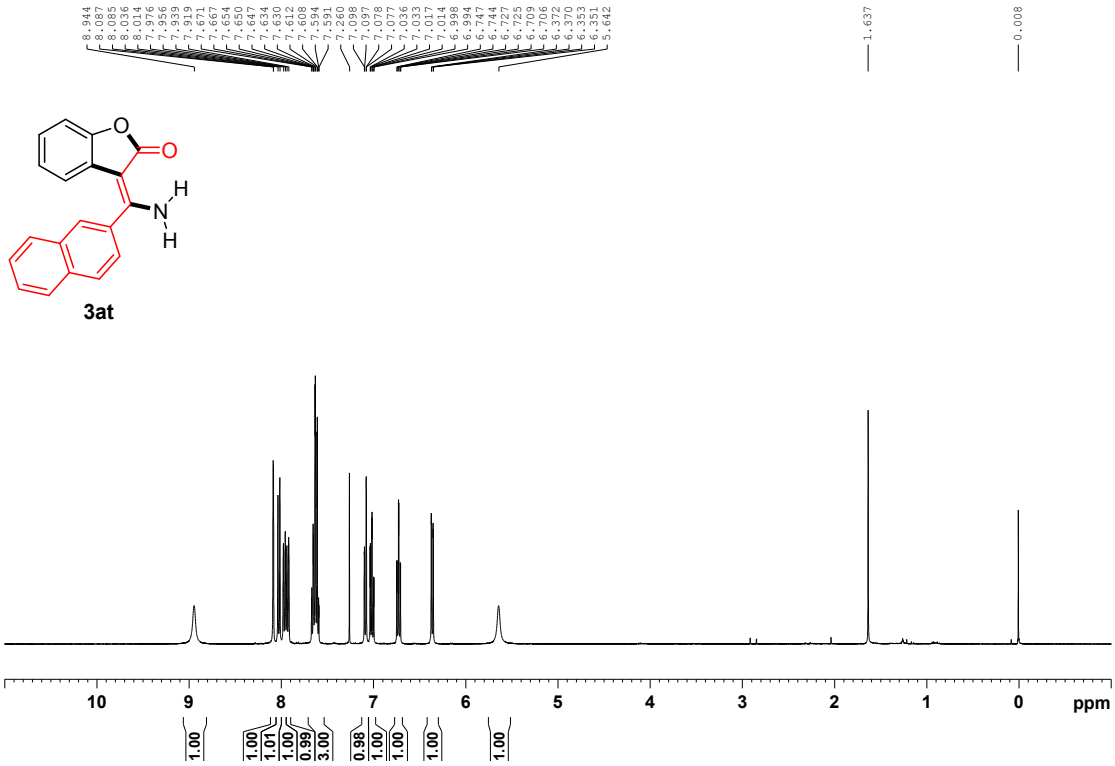


^{13}C NMR ($CDCl_3$, 101 MHz)

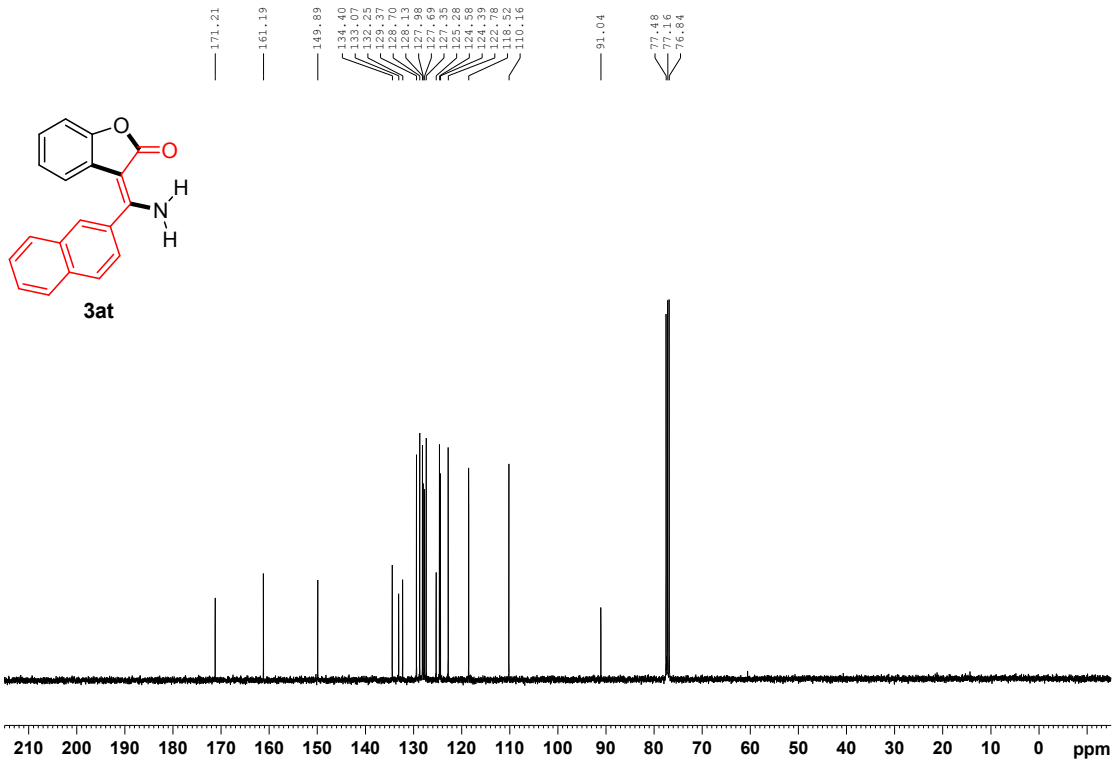


(*Z*)-3-(Amino(naphthalen-2-yl)methylene)benzofuran-2(3*H*)-one (3at)

^{1}H NMR ($CDCl_3$, 400 MHz)

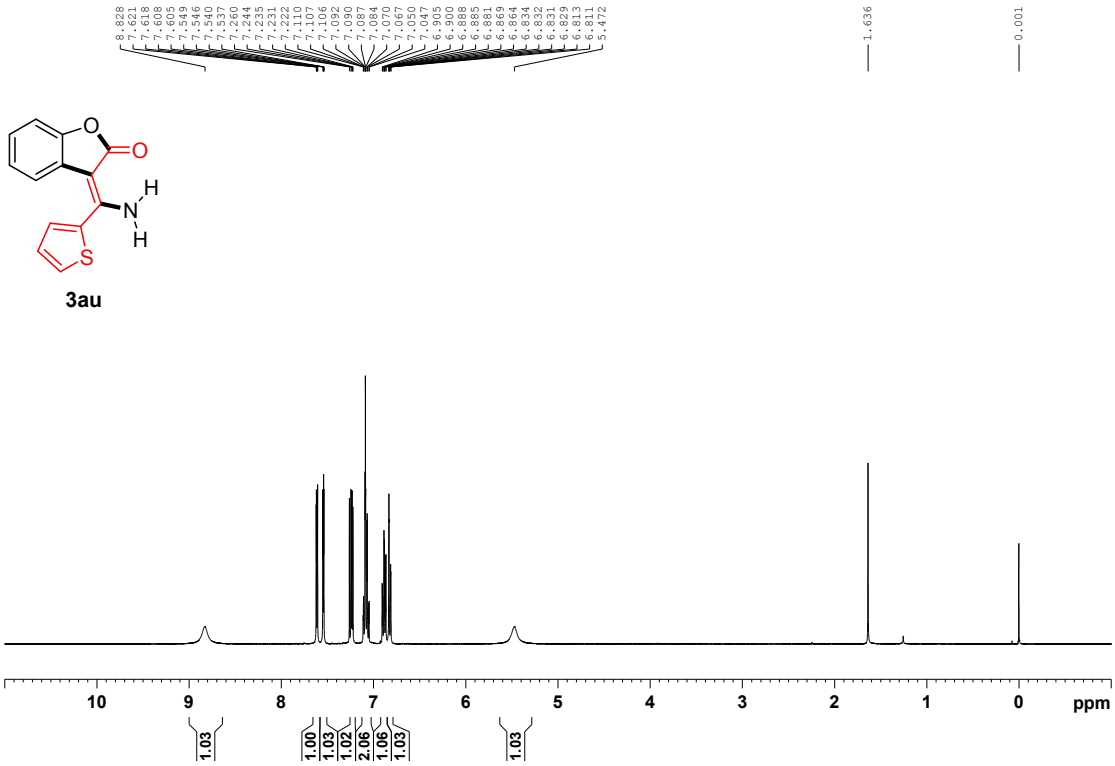


^{13}C NMR ($CDCl_3$, 101 MHz)

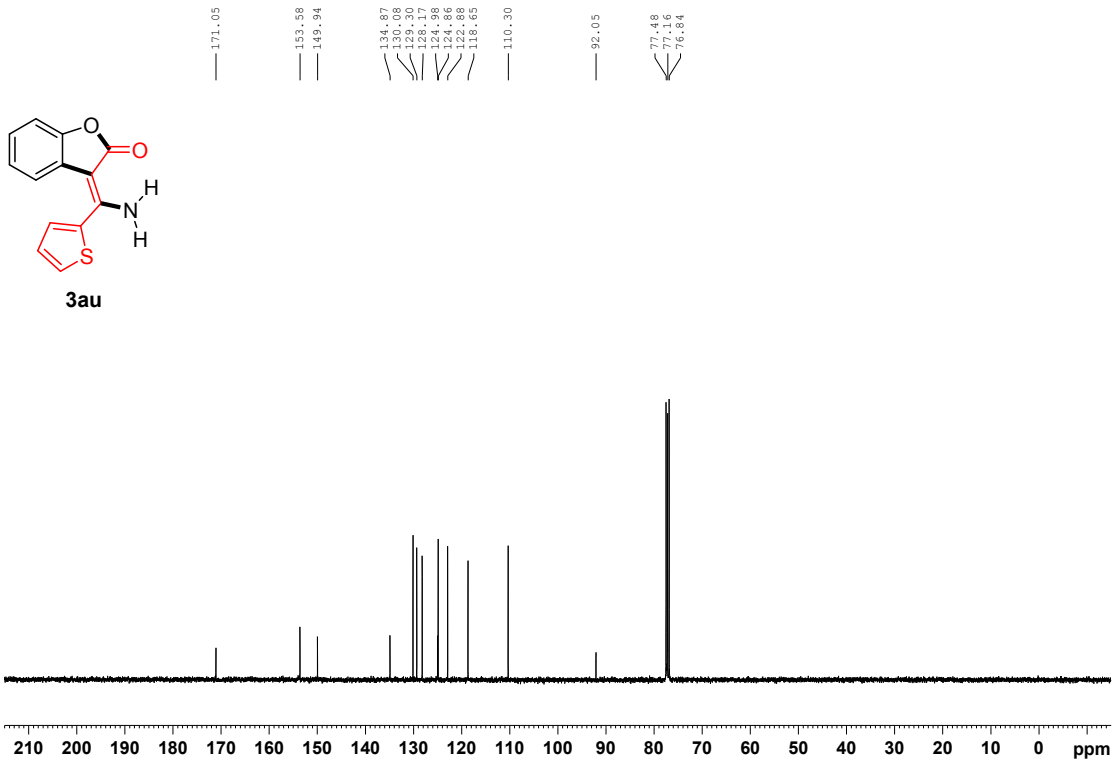


(*Z*)-3-(Amino(thiophen-2-yl)methylene)benzofuran-2(3*H*)-one (3au)

^{1}H NMR ($CDCl_3$, 400 MHz)

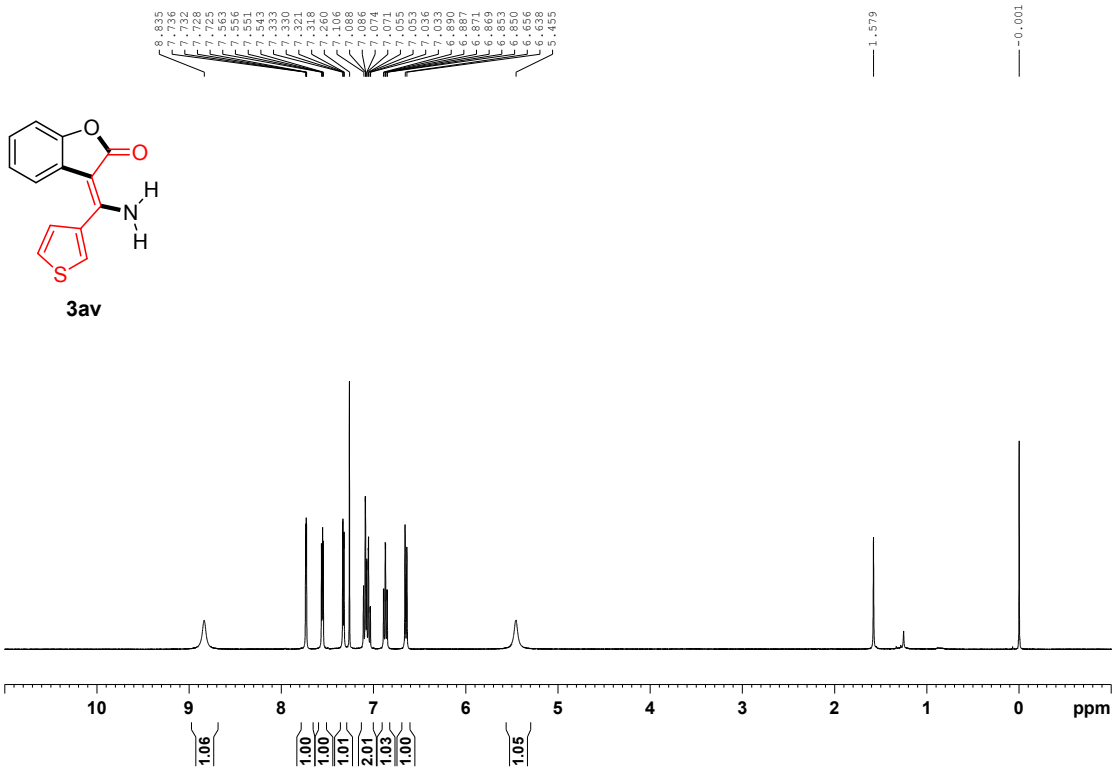


^{13}C NMR ($CDCl_3$, 101 MHz)

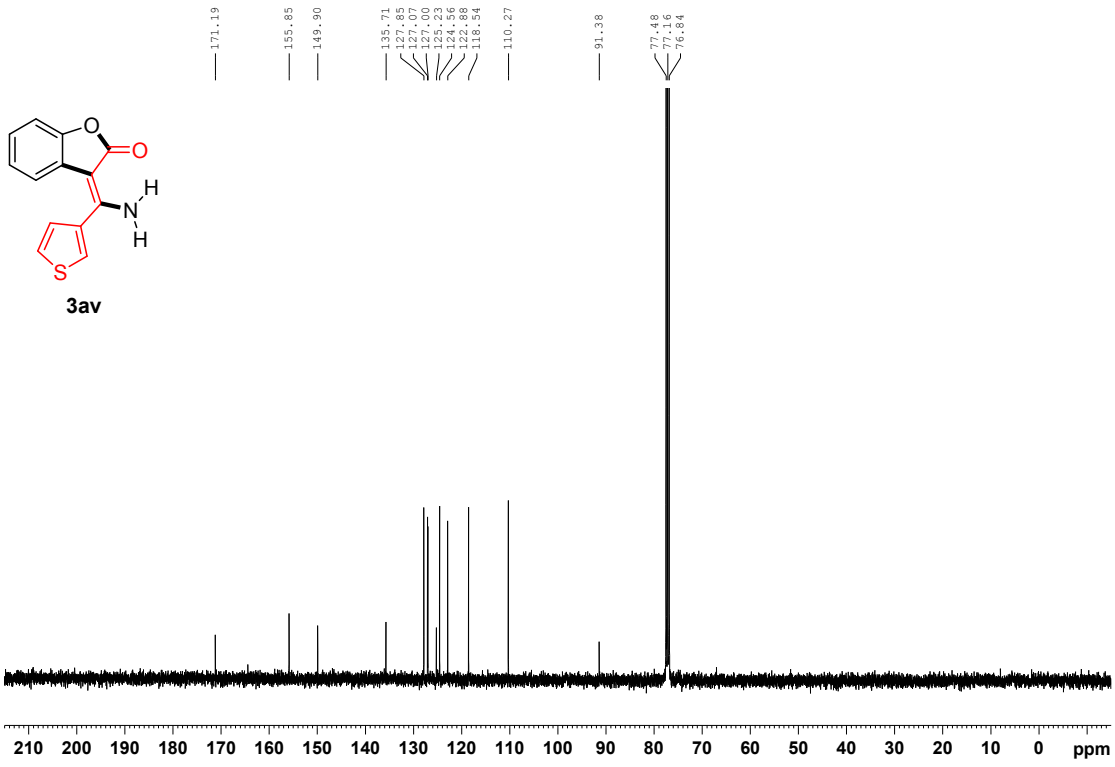


(*Z*)-3-(Amino(thiophen-3-yl)methylene)benzofuran-2(3*H*)-one (3av)

^{1}H NMR ($CDCl_3$, 400 MHz)

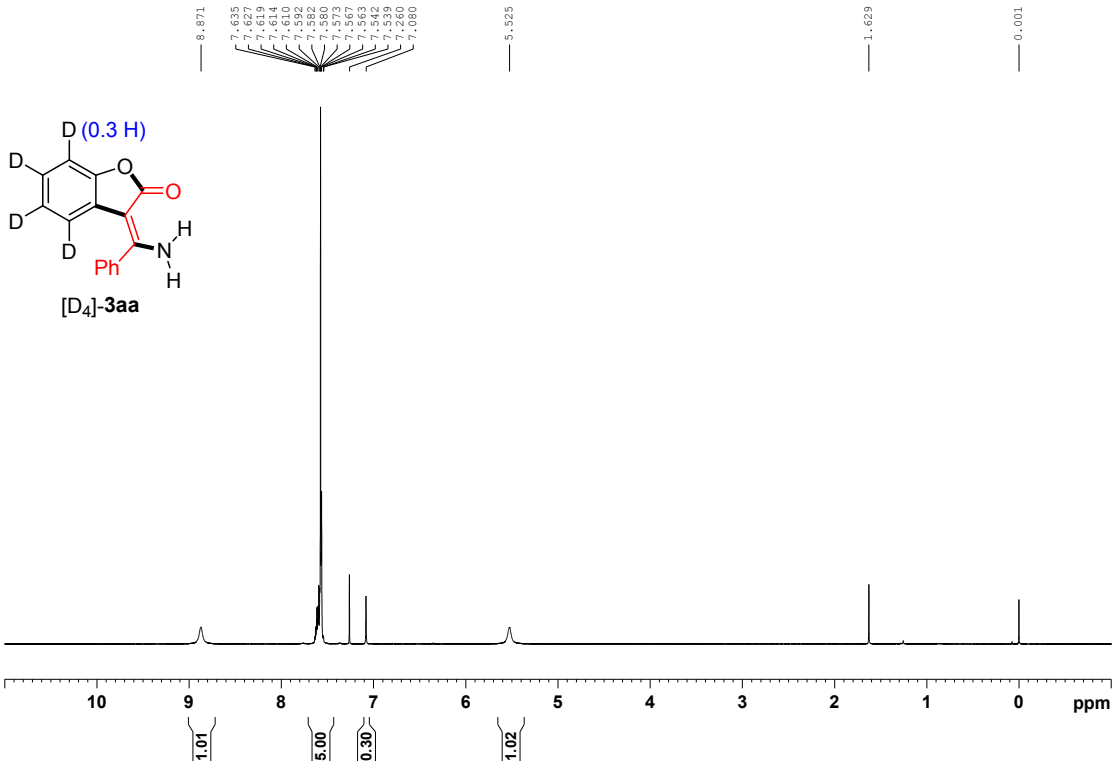


^{13}C NMR ($CDCl_3$, 101 MHz)



(*Z*)-3-(Amino(phenyl)methylene)-d_4-benzofuran-2(3*H*)-one ([D_4]-3aa)

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)