Diastereodivergent Access of Spiro (Pyrroloquinoline-Pyrazolone) and Oxa-azabicyclo[3.2.1]octane Scaffolds *via* Cascade Approaches

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Supporting Information

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1. General Information

1.1 Solvents, Reagents, Glassware and Reaction Setup

Unless otherwise noted, all reactions were performed in oven-dried glassware with magnetic stirring, whereas air and moisture-sensitive reactions were performed in an inert environment (nitrogen) using freshly distilled anhydrous solvent. All solvents were dried with activated 4Å molecular sieves and stored under nitrogen. All reagents and solvents were of analytical grade purity. All chemicals were obtained from AVRA, GLR, and BLD Pharma and were utilized without further purification. All workup and purification were carried out using reagent-grade solvents in air. For reactions that required heating, we used a silicone oil bath as the heat source.

1.2 Analytical Methods

Chromatography: Analytical thin-layer chromatography (TLC) was used to monitor the progress of the reactions by using 0.2 mm commercial silica gel plates (silica gel 60, F_{254}). UV light was used to visualize the spots on the TLC plate. Column chromatography was performed on silica gel (100–200 mesh) using hexanes and ethyl acetate as eluent.

NMR: All compounds were fully characterized. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired using JEOL ECZ500R/S1 (500 MHz for ^{1}H; 126 MHz for ^{13}C; 471 MHz for ^{19}F) at ambient temperature. Chemical shifts were indicated in parts per million (δ), and signals were recorded as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet), q (quartet), and coupling constants (*J*) were given in Hz. Chemical shifts were referenced to $CDCl_3$ (residual $CHCl_3$ δ = 7.26 for ^{1}H NMR, δ = 77.16 for $^{13}C\{^{1}H\}$ NMR as internal standard, and TMS (0 for ^{1}H), δ 1.56 is related to the moisture present in $CDCl_3$. 1D nOe, ^{1}H and ^{13}C NMR experiments of few compounds were performed using a Bruker AVANCE NEO Ascend 700 MHz NMR instrument.

NMR yields: Following workup or/and solvent evaporation, dibromoethane (relative to the limiting starting material) was added to the crude residue. The resultant mixture was dissolved in $CDCl_3$, and a 0.5 mL sample of the resultant solution was taken for ^{1}H NMR analysis. Yields were calculated based on the integrals of known product resonances relative to dibromoethane (2H, at 4.94 ppm in $CDCl_3$).

HRMS: High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time-of-flight (TOF) mass spectrometer.

Melting Point: Melting points were determined using a digital melting point device.

2. Preparation of Starting Materials

2.1. Substrates studied in this report

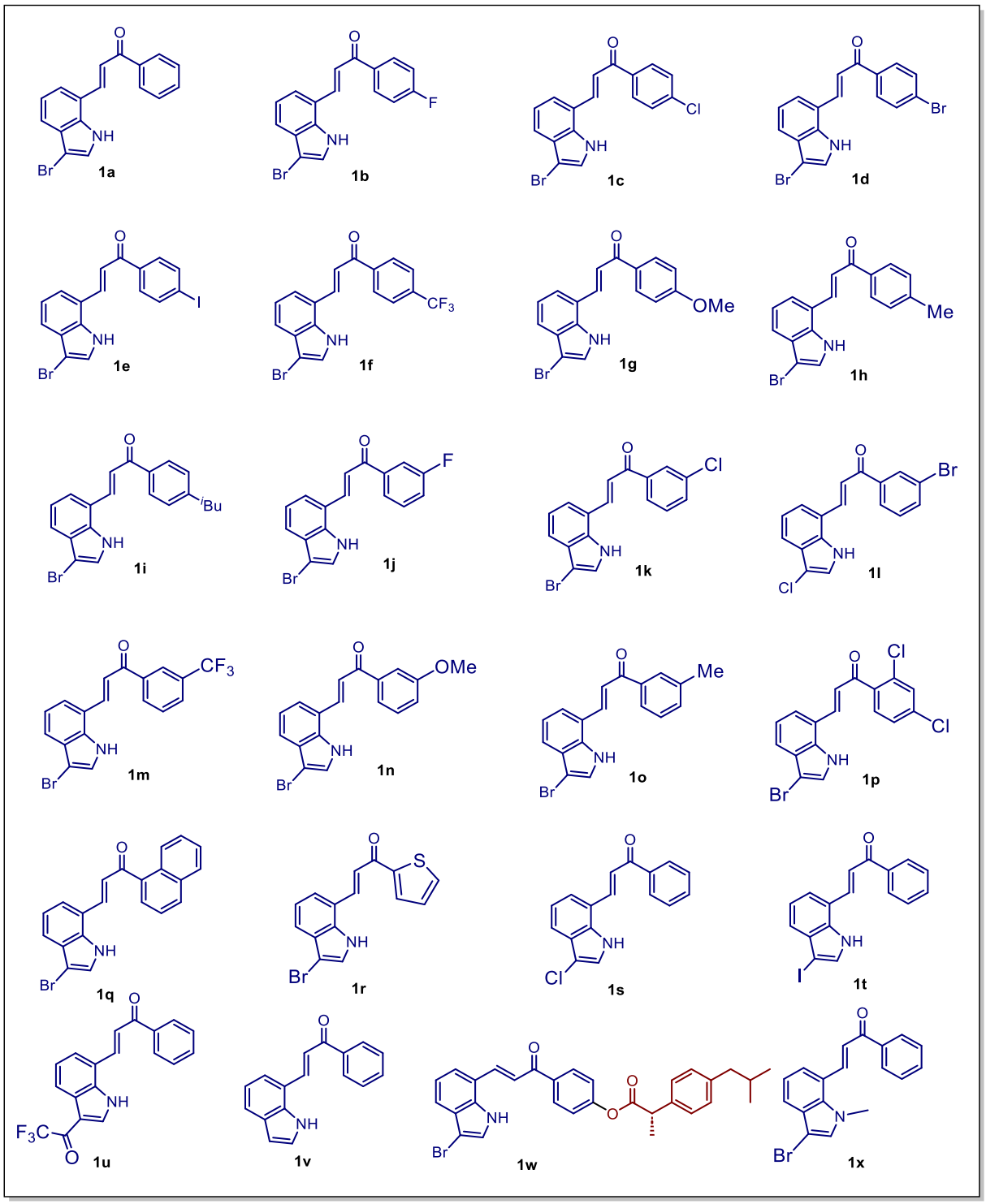


Figure S1: Structures of Indole-Substituted Michael Acceptors **1**

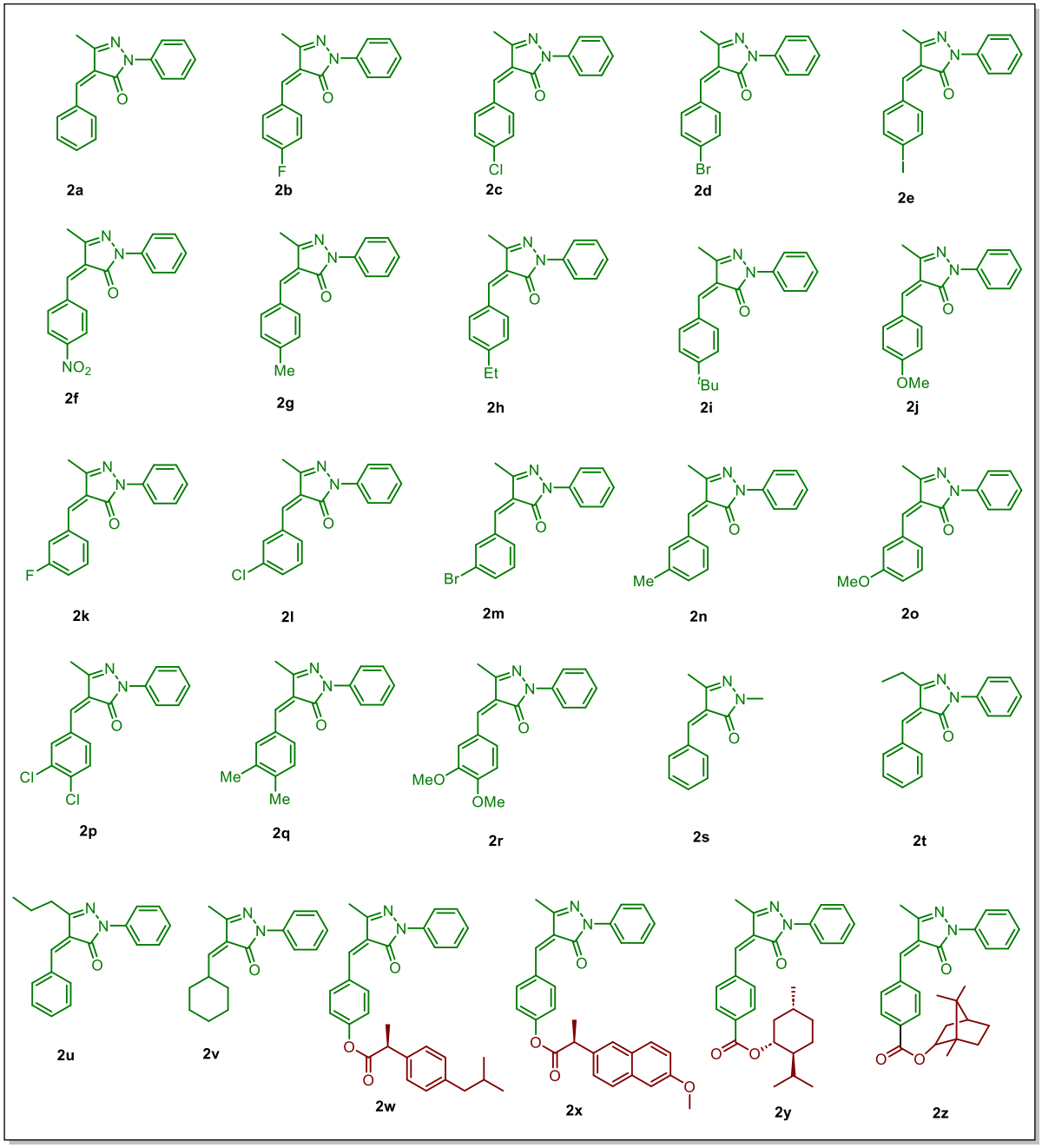


Figure S2: Structures of Alkylidene Pyrazolones **2**

2.2. General procedure for the synthesis of indole-substituted Michael acceptors 1

1*H*-Indole-7-carbaldehyde **S1** was purchased from BLD Pharma, while indole-substituted Michael acceptors **1a**–**1x** were known compounds and were prepared according to the literature procedure (Figure S3).[1]

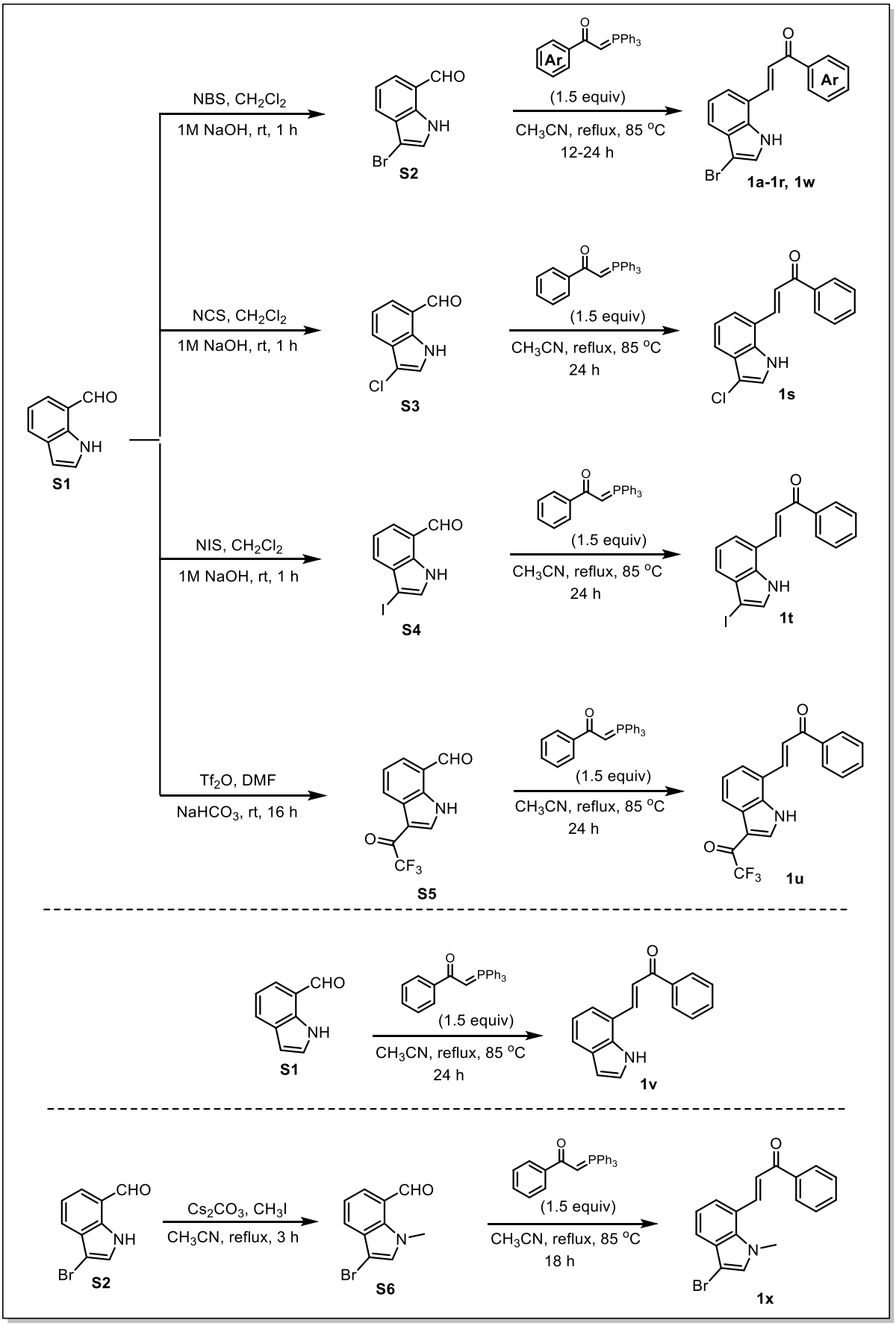


Figure S3: Procedure for Indole-substituted Michael Acceptors **1a**–**1x**

Procedure for the synthesis of 3-bromo-1*H*-indole-7-carbaldehyde (S2)

To a solution of compound **S1** (1.0 g, 6.89 mmol) in dichloromethane CH_2Cl_2 (10 mL), *N*-bromosuccinimide (1.23 g, 6.89 mmol) was added slowly and stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), 1N NaOH (5 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to get the crude product, which was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product **S2** in good yield as an off white solid.

Procedure for the synthesis of 3-chloro-1*H*-indole-7-carbaldehyde (S3)

To a solution of compound **S1** (1.0 g, 6.89 mmol) in dichloromethane CH_2Cl_2 (10 mL), *N*-chlorosuccinimide (0.916 g, 6.89 mmol) was added slowly and stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), 1N NaOH (5 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to get the crude product, which was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product **S3** in good yield as an off-white solid.

Procedure for 3-iodo-1*H*-indole-7-carbaldehyde (S4)

To a solution of compound **S1** (1.0 g, 6.89 mmol) in dichloromethane CH_2Cl_2 (10 mL), *N*-iodosuccinimide (1.55 g, 6.89 mmol) was added slowly and stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), 1N NaOH (5 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to get the crude product, which was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product **S4** in good yield as an off-white solid.

Procedure for 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (S5)

To a solution of compound **S1** (0.406 g, 2.8 mmol) in DMF (5 mL), trifluoroacetic anhydride (1 mL, 7.18 mmol) was added slowly at 0 °C, and stirred at room temperature for 16 h. After completion of the reaction (monitored by TLC), saturated aqueous $NaHCO_3$ solution was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted

with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to get the crude product, which was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product **S4** in good yield as an off-white solid

Procedure for the synthesis of *N*-protected-3-bromo-1*H*-indole-7-carbaldehyde (S6)

To a solution of compound **S2** (1.12 g, 5 mmol) in CH_3CN (25 mL), Cs_2CO_3 (3.25 g, 10 mmol) was added, and stirred under reflux for 2 h. To this, methyl iodide (0.34 mL, 5.5 mmol) was added slowly, and the solution was stirred under reflux for 1 h. After completion of the reaction (as monitored by TLC), the organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to get the crude product, which was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product **S4** in good yield.

Procedure for indole-substituted Michael acceptors 1a-1x

(1a as an example)

A solution of **S2** (1.0 g, 4.48 mmol, 1 equiv) and 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (2.55 g, 6.72 mmol, 1.5 equiv) in acetonitrile (30 mL) was refluxed for 18 h at 85 °C. After completion of the reaction (as monitored by TLC), the solvent was evaporated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product **1a** as a light green solid.

2.3. General procedure for synthesis of alkylidene pyrazolones 2

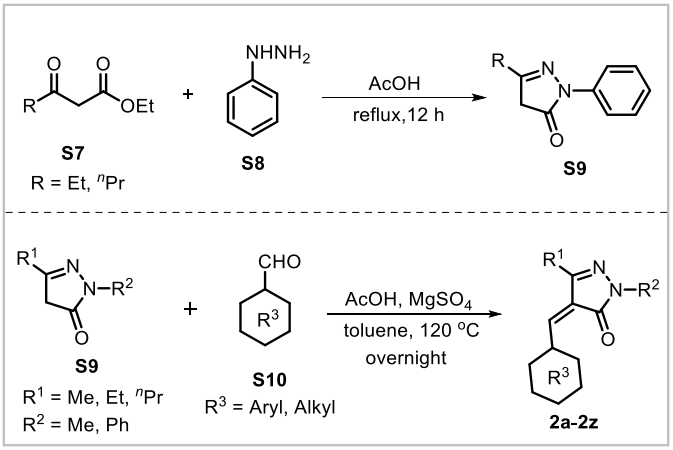


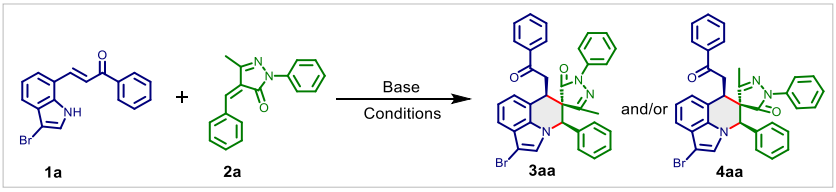
Figure S4: Synthesis of alkylidene pyrazolones **2a**–**2z**

Compounds **S7**, **S8** and **S10** were purchased from AVRA, TCI and BLD Pharma, while all alkylidene pyrazolones **2a**–**2z** were known compounds and were synthesized as described in the literature (Figure S4).[2]

Procedure for alkylidene pyrazolones 2a–2z

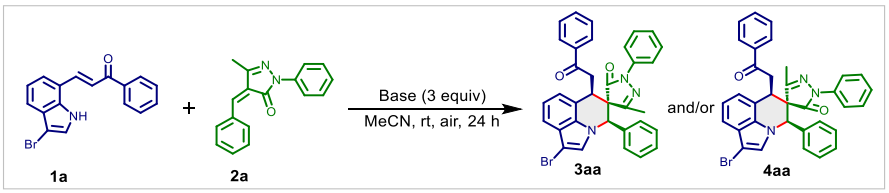
To a solution of pyrazolone **S5** (5 mmol, 1 equiv) and aromatic aldehyde **S6** (5 mmol, 1 equiv) in toluene (50 mL) was added $MgSO_4$ (1 g) and AcOH (1 mL), and the resultant mixture was stirred at reflux temperature for 12 h. The reaction mixture was then cooled to room temperature and filtered with a sand core funnel. The filtrate was concentrated under reduced pressure, and the resulting crude mixture was purified by silica gel column chromatography (EtOAc/hexanes) to afford the desired product (**2a**–**2z**) as an orange solid.

3. General Procedure for Optimization of the Reaction Conditions



An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole acceptor **1a**, alkylidene pyrazolone **2a,** and base. To this, an appropriate solvent was added under an air atmosphere. The reaction mixture was stirred at room temperature for the required reaction time. After completion of the reaction (as monitored by TLC), the solvent was removed using a rotatory evaporator under reduced pressure, and the crude mixture was filtered through a pad of silica gel and eluted with EtOAc. The reaction mixture was concentrated under reduced pressure, and then the yield was determined by the ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard.

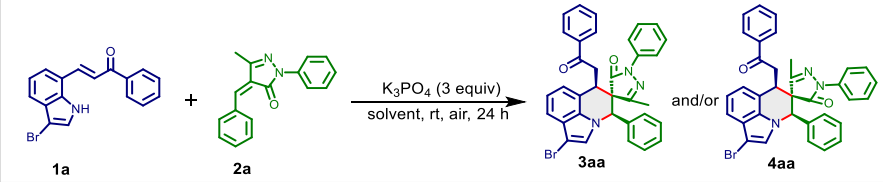
Table S1. Optimization of base[a]



entry	base	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	Na_2CO_3	nr	nr
2	K_2CO_3	40	38
3	Cs_2CO_3	21	8
4	NaO^{t}Bu	nr	nr
5	KO^{t}Bu	nr	nr
6	K_3PO_4	23(20)[c]	53(51)[c]
7	NaOAc	nr	nr
8	NaOH	nr	nr
9	KOH	nr	nr
10	Et_3N	16	34
11	DABCO	nr	nr
12	DBU	nr	nr

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.1 mmol, 1 equiv), **2a** (0.1 mmol, 1 equiv), and base (3 equiv) in MeCN (1 mL) at rt (25 °C) under air for 24 h. [b] Yields are of ^{1}H NMR yield. [c] Isolated yield. nr = no reaction.

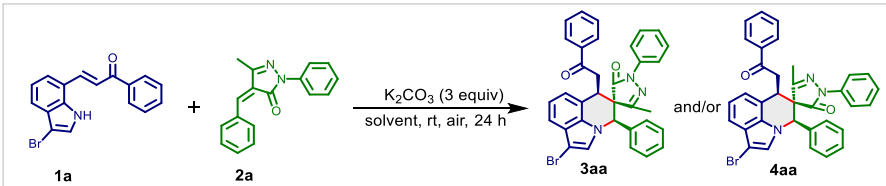
Table S2. Optimization of solvent with K_3PO_4[a]



entry	solvent	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	DCM	83	-
2	DCE	58	-
3	Toluene	64	-
4	THF	54	-
5	Dioxane	nr	nr
6	DMF	nr	nr
7	MeOH	nr	nr
8	Ether	81	11
9	Acetone	53	27
10	EtOAc	78	13

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.1 mmol, 1 equiv), **2a** (0.1 mmol, 1 equiv), and K_3PO_4 (3 equiv) in solvent (1 mL) at rt (25 °C) under air for 24 h. [b] Yields are of ^{1}H NMR yield. nr = no reaction.

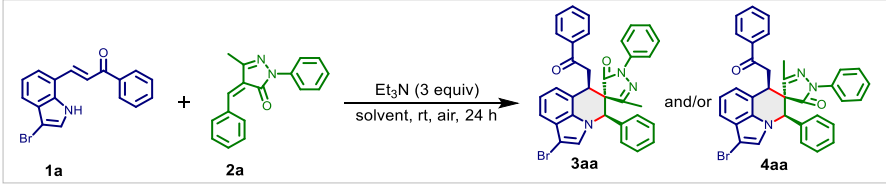
Table S3. Optimization of solvent with K_2CO_3[a]



entry	solvent	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	DCM	nr	nr
2	DCE	nr	nr
3	Toluene	nr	nr
4	THF	nr	nr
5	Dioxane	nr	nr
6	DMF	nr	nr
7	MeOH	nr	nr
8	Ether	nr	nr
9	Acetone	60	22
10	EtOAc	86	<5

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.1 mmol, 1 equiv), **2a** (0.1 mmol, 1 equiv), and K_2CO_3 (3 equiv) in solvent (1 mL) at rt (25 °C) under air for 24 h. [b] Yields are of ^{1}H NMR yield. nr = no reaction.

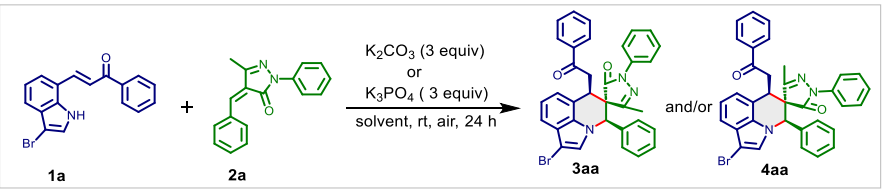
Table S4. Optimization of solvent with Et_3N[a]



entry	solvent	yield (%) of **3aa**	yield (%) of **4aa**
1	DCM	nr	nr
2	DCE	nr	nr
3	Toluene	nr	nr
4	THF	nr	nr
5	Dioxane	nr	nr
6	DMF	nr	nr
7	MeOH	nr	nr
8	Ether	nr	nr
9	Acetone	nr	nr
10	EtOAc	nr	nr

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.1 mmol, 1 equiv), **2a** (0.1 mmol, 1 equiv), and Et_3N (3 equiv) in solvent (1 mL) at rt (25 °C) under air for 24 h. nr = no reaction.

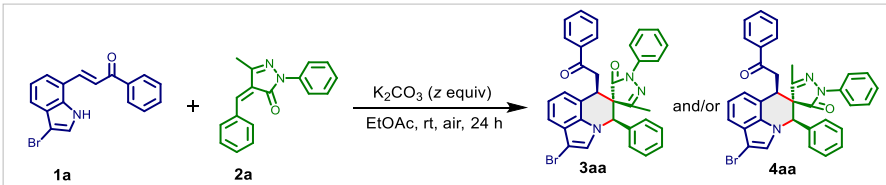
Table S5. Optimization of reactant equivalents[a]



entry	base	solvent	equiv of **1a**	equiv of **2a**	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	K_2CO_3	EtOAc	1	1.25	79	-
2	K_2CO_3	EtOAc	1	1.5	74	-
3	K_2CO_3	EtOAc	1.25	1	98 (94) [c]	-
4	K_2CO_3	EtOAc	1.5	1	81	9
5	K_2CO_3	MeCN	1	1.25	54	28
6	K_2CO_3	MeCN	1	1.5	44	41
7	K_2CO_3	MeCN	1.25	1	74	23
8	K_2CO_3	MeCN	1.5	1	67	27
9	K_3PO_4	MeCN	1	1.25	57	29
10	K_3PO_4	MeCN	1	1.5	68	20
11	K_3PO_4	MeCN	1.25	1	65	24
12	K_3PO_4	Ether	1	1.25	88	-
13	K_3PO_4	Ether	1	1.5	83	-
14	K_3PO_4	Ether	1.25	1	91	-
15	K_3PO_4	Ether	1.5	1	85	-

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (x equiv), **2a** (y equiv), and base (3 equiv) in solvent (1 mL) at rt (25 °C) under air for 24 h. [b] Yields are of ^{1}H NMR yield. [c] Isolated yield.

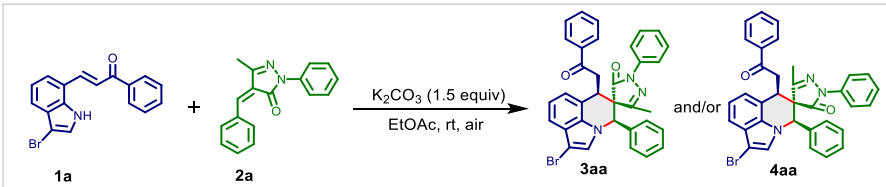
Table S6. Optimization of base equivalents[a]



entry	base (equiv)	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	2	97	-
2	1.5	97 (94) [c]	-
3	1	89	-
4	0.5	86	-

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.125 mmol, 1.25 equiv), **2a** (0.1 mmol, 1 equiv), and K_2CO_3 (*z* equiv) in EtOAc (1 mL) at rt (25 °C) under air for 24 h. [b] Yields are of ^{1}H NMR yield. [c] Isolated yield.

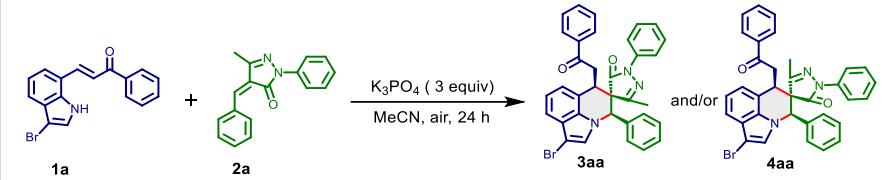
Table S7. Optimization of reaction time[a]



entry	time (h)	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	3	73	-
2	6	85	-
3	12	97	-
4	36	96	-

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.125 mmol, 1.25 equiv), **2a** (0.1 mmol, 1 equiv), and K_2CO_3 (1.5 equiv) in EtOAc (1 mL) at rt (25 °C) under air. [b] Yields are of ^{1}H NMR yield.

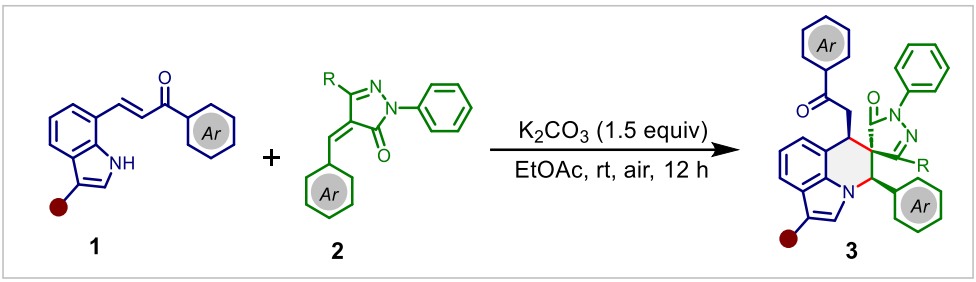
Table S8. Optimization of temperature[a]



entry	time (h)	yield (%) of **3aa** [b]	yield (%) of **4aa** [b]
1	40	45	17
2	60	cm	cm
3	85	cm	cm

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.1 mmol, 1.0 equiv), **2a** (0.1 mmol, 1 equiv), and K_3PO_4 (3 equiv) in MeCN (1 mL) under air for 24 h. [b] Yields are of ^{1}H NMR yield. cm = complex mixture.

4. General Procedure for the K_2CO_3-promoted (4+2) Annulation of Indole-based Acceptors with Alkylidene Pyrazolones for the Synthesis of 3



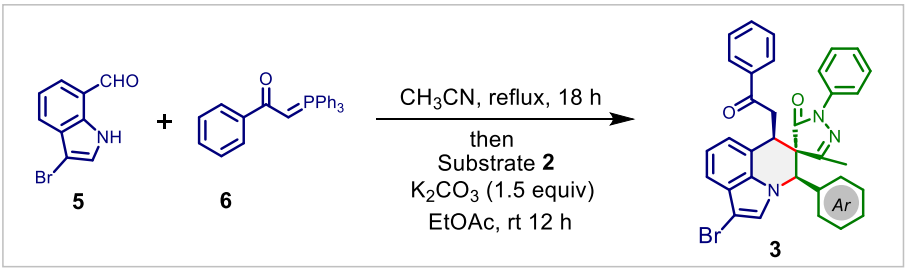
An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1** (0.312 mmol, 1.25 equiv), alkylidene pyrazolone **2** (0.25 mmol, 1.0 equiv) and K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv). To this, ethyl acetate (3 mL) was added under air. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (as monitored by TLC), the solvent was removed using a

rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding spiro pyrroloquinoline **3**.

5. General Procedure for the K_3PO_4-promoted (4+2) Annulation of Indole-based Acceptor with Alkylidene Pyrazolones for the Synthesis of 4

An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (81.6 mg, 0.25 mmol, 1.0 equiv), alkylidene pyrazolone **2** (0.25 mmol, 1.0 equiv) and K_3PO_4 (159.2 mg, 0.75 mmol, 3.0 equiv). To this, acetonitrile (3 mL) was added under air. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed using a rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding spiro pyrroloquinoline **4** along with the product **3**.

6. General Procedure for One-pot Synthesis of Pyrroloquinolines 3



An oven-dried round-bottom flask (25 mL) equipped with a magnetic stir bar was charged with indole **5** (67.2 mg, 0.3 mmol, 1 equiv) and 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)-ethan-1-one (**6**, 171.2 mg, 0.45 mmol, 1.5 equiv). To this, CH_3CN (5 mL) was added under an air atmosphere. The reaction mixture was stirred under reflux at 85 °C using a silicon oil bath as a heating source for 18 h. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was removed under reduced

pressure. Then substrate **2** (0.24 mmol) and K_2CO_3 (50.0 mg, 0.36 mmol) were added with ethyl acetate. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (as monitored by TLC), the solvent was removed using a rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding spiro pyrroloquinoline **3**.

7. General Procedure for Optimization of the Reaction Conditions for 8

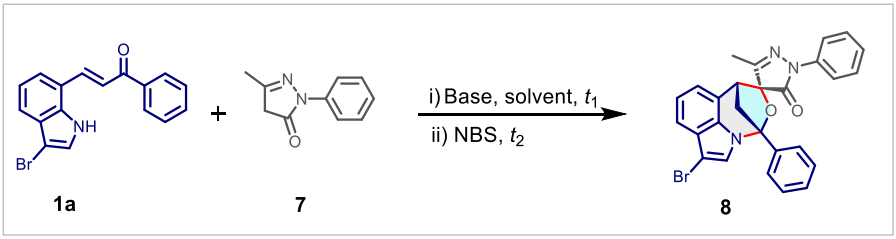
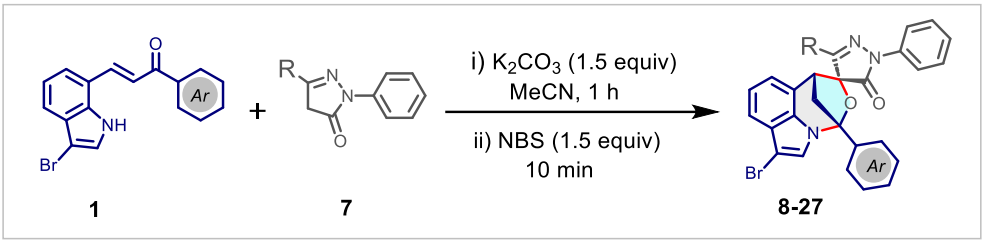


Table S9. Optimization studies[a]

entry	base	solvent	Yield (%) [b] of **8**
1	Na_2CO_3	MeCN	nr
2	K_2CO_3	MeCN	93
3	Cs_2CO_3	MeCN	78
4	K_3PO_4	MeCN	66
5	NaO^{t}Bu	MeCN	<5
6	KO^{t}Bu	MeCN	<5
7	DMAP	MeCN	nr
8	DABCO	MeCN	nr
6	K_2CO_3	DCM	trace
7	K_2CO_3	DCE	trace
8	K_2CO_3	DMF	trace
9	K_2CO_3	1,4-Dioxane	trace
9	K_2CO_3	EtOAc	trace
9	K_2CO_3	Ether	trace
9	K_2CO_3	Acetone	trace
9	K_2CO_3	Toluene	trace
9	K_2CO_3	EtOH	trace
10[c]	K_2CO_3	MeCN	65

[a] Reaction conditions: Unless otherwise noted, all the reactions were performed using **1a** (0.1 mmol, 1.0 equiv), **7** (1.5 equiv), base (1.5 equiv) and NBS (1.5 equiv) in solvent (1 mL) at rt (25 °C) under air for 1 h (t_1) and 10 min (t_2). [b] Isolated yield. [c] NCS was used. nr = no reaction.

8. General Procedure for the Base-promoted Annulation of Indole-based Acceptors with Pyrazolone for the Synthesis of 8–27



An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1** (0.25 mmol, 1.0), pyrazolone **7** (0.312 mmol, 1.25 equiv) and K_2CO_3 (1.5 equiv). To this, acetonitrile (3 mL) was added under air. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), NBS (1.5 equiv) was added, and the reaction mixture was further stirred for up to 10 min. After that, the solvent was removed using a rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding bicyclic scaffold (**8–27**).

9. Two-dimensional NMR Studies of Compounds 3aa and 3al:

The structure of pyrroloquinoline **3aa** was confirmed by the analysis of its ^{1}H and ^{13}C NMR and HRMS spectral data. Further to gain a deeper understanding, the structure of the product **3aa** was corroborated by two-dimensional (2D) NMR experiments such as COSY, HSQC, HMBC, and NOESY. The correlation between protons is clearly visible from the ^{1}H–^{1}H COSY spectrum. The CH connectivity is revealed by the HSQC spectrum. The HMBC analysis provides diagnostic proton–carbon correlations over multiple bonds, which were found to be extremely helpful in the conformation of the structure of the product. We performed a NOESY experiment to determine the spatial correlation between H_c and H_d protons.

The COSY experiment of **3aa** revealed that protons H_a (2.83 ppm), H_b (3.49 ppm), and H_c (4.87 ppm) show correlations with each other.

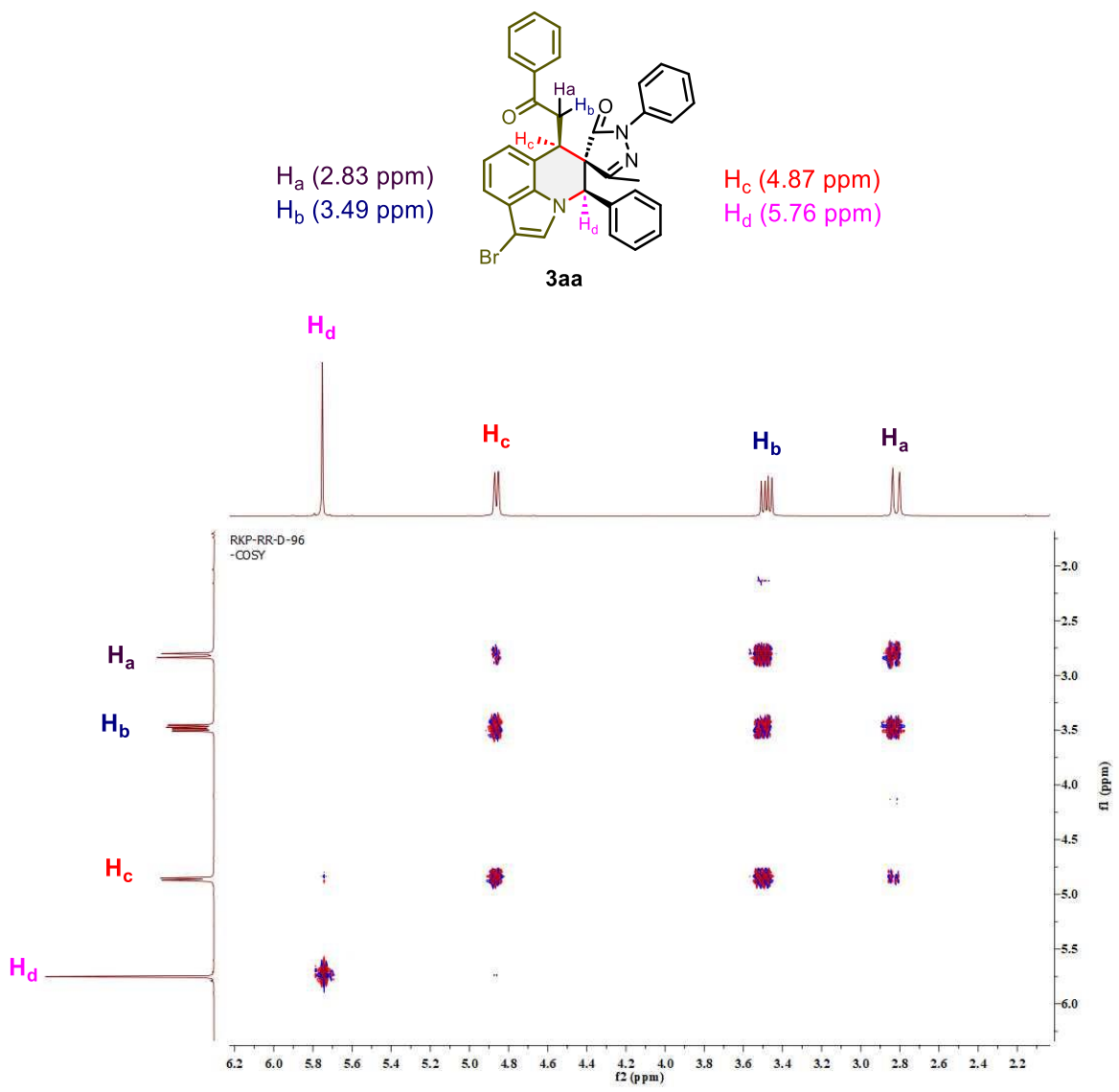


Figure S5: ^1H–^1H COSY spectrum of **3aa**

The HSQC experiment of **3aa** revealed the connectivity between protons H_a (2.83 ppm) and H_b (3.49 ppm) and carbon C_a, having a chemical shift at 38.3 ppm. Similarly, it disclosed that the proton H_c (4.87 ppm) is directly bonded to carbon C_c at 37.0 ppm, and the proton H_d (5.76 ppm) is connected directly to carbon C_d, having a chemical shift at 65.7 ppm.

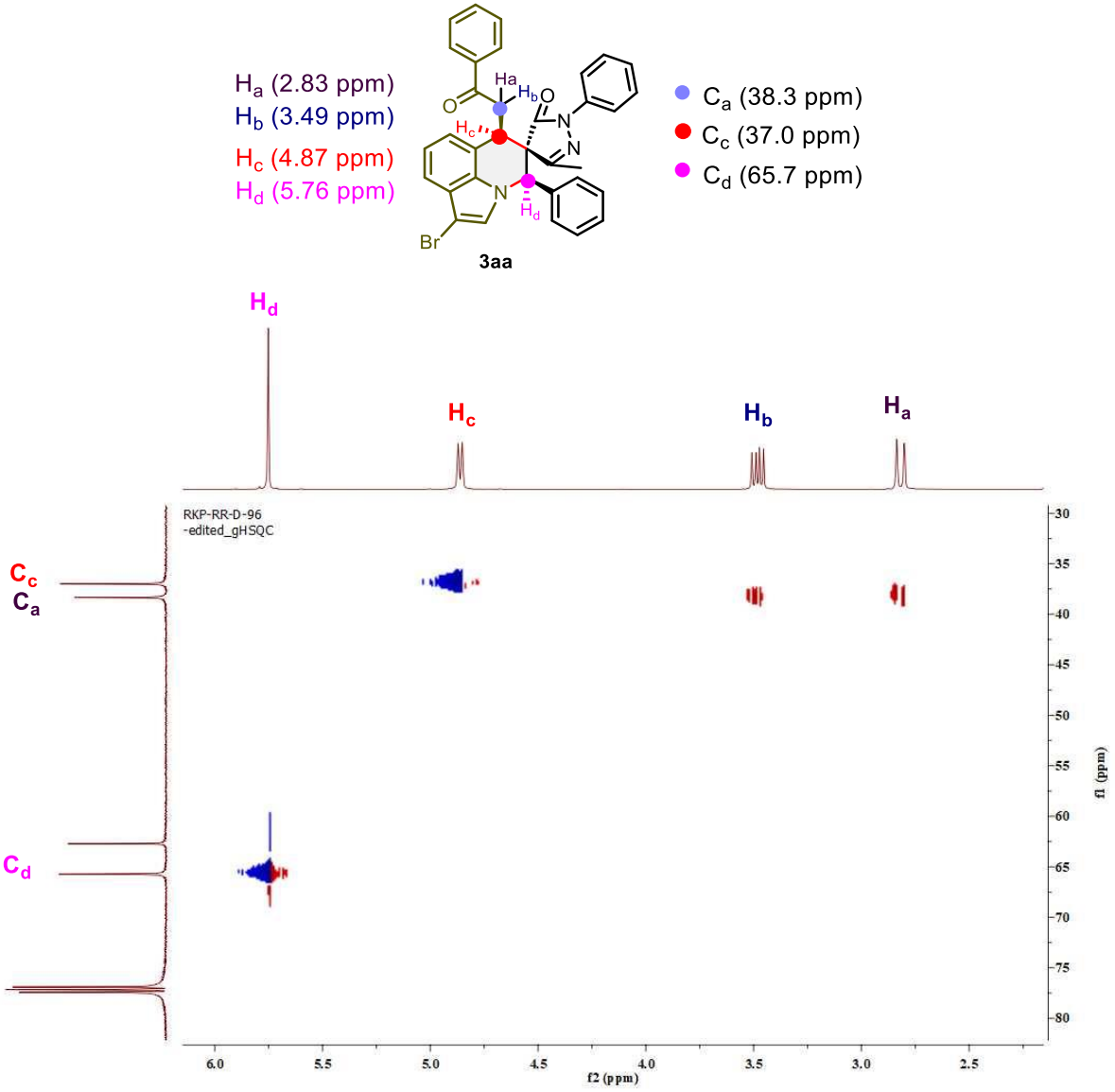


Figure S6: ^{1}H–^{13}C HSQC spectrum of **3aa**

The HMBC experiment of **3aa** revealed the correlation between protons and carbonyl carbon C_a'. It shows that protons H_a (2.83 ppm), H_b (3.49 ppm) and H_c (4.87 ppm) are correlated with carbonyl carbon C_a'(196.5 ppm).

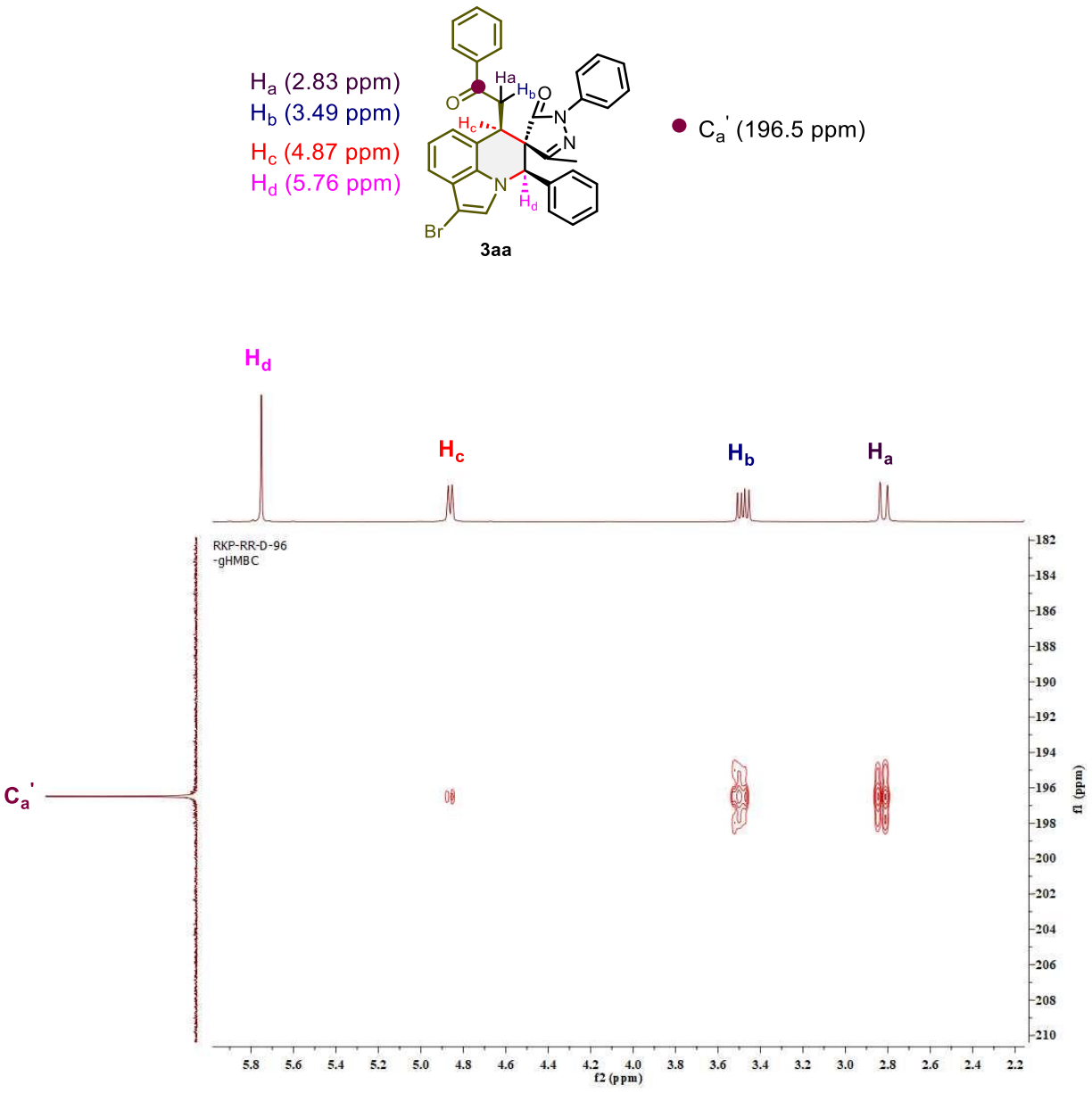
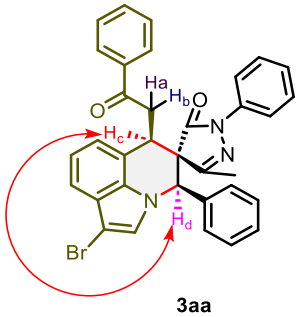


Figure S7: ^{1}H–^{13}C HMBC spectrum of **3aa**

The NOESY experiment of **3aa** revealed that the proton H_c (4.87 ppm) is spatially correlated strongly with proton H_d (5.76 ppm). From the NOESY experiment, we found that protons H_c and H_d are on the same side of pyrroloquinoline ring.



3aa

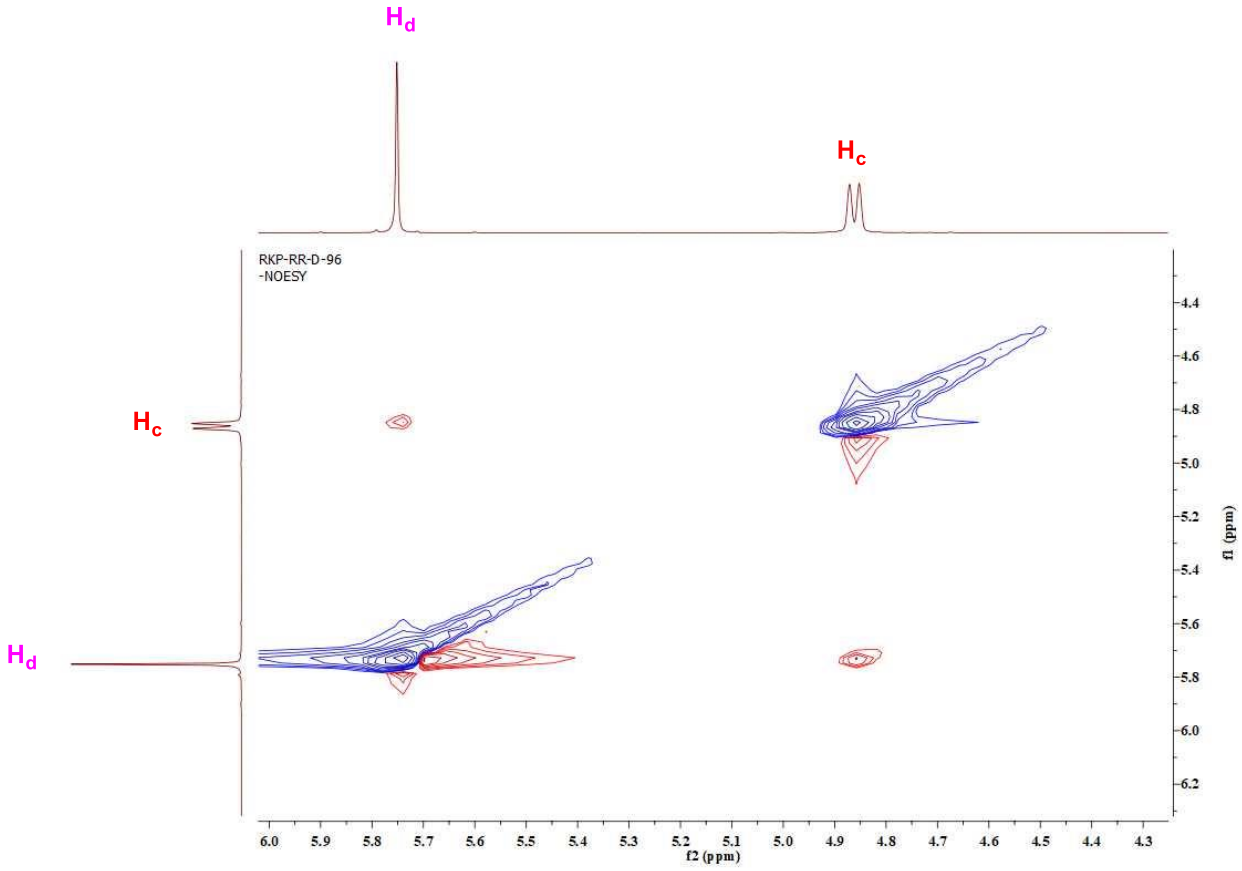
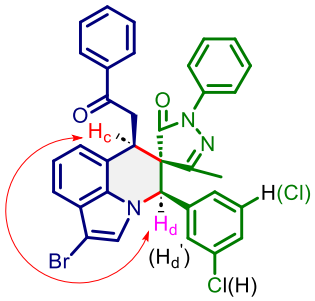


Figure S8: ^{1}H–^{1}H NOESY spectrum of **3aa**

2D NOESY experiment of **3al** revealed that the protons H_c and H_d/H_d' are spatially connected to each other.



3al

^{1}H-^{1}H NOESY correlations

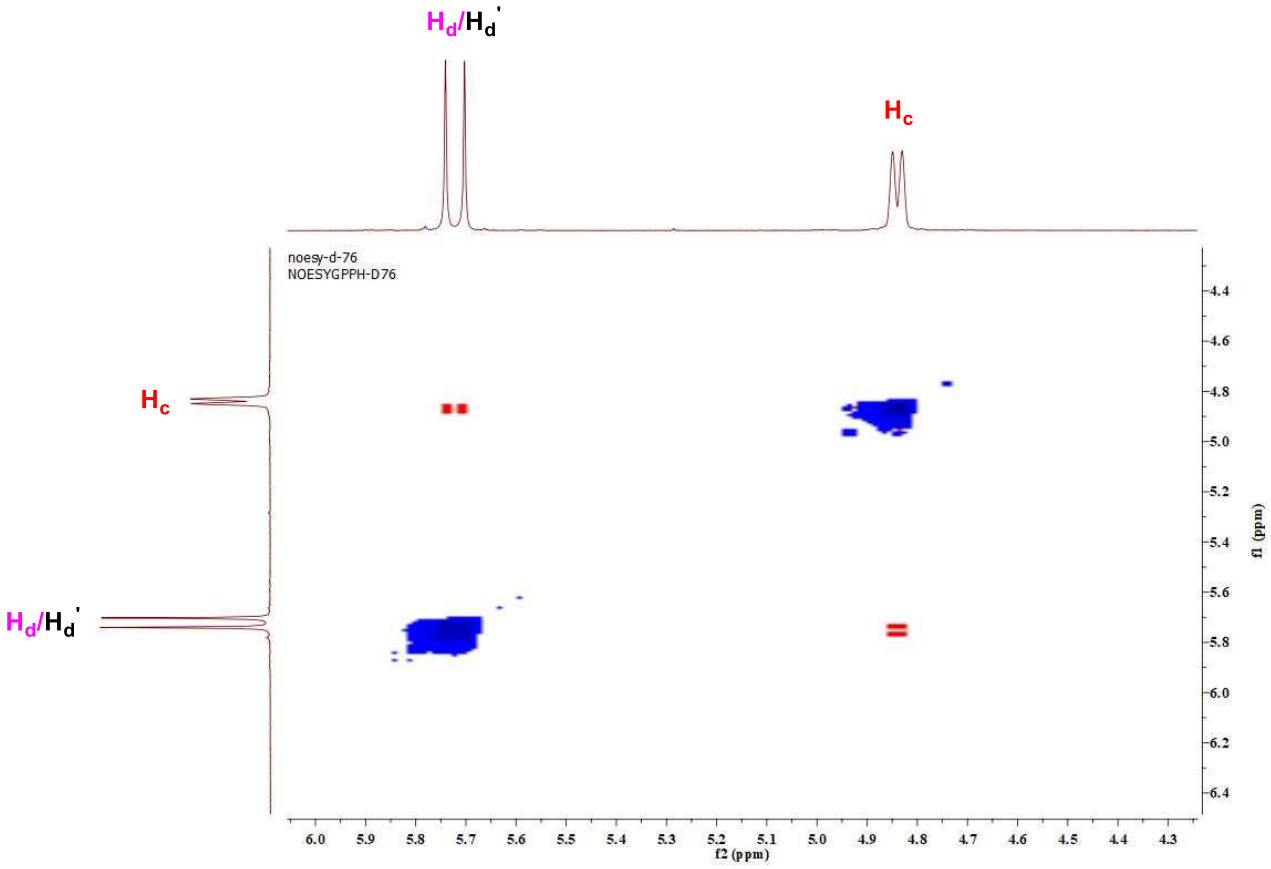


Figure S9: ^{1}H–^{1}H NOESY spectrum of **3al**

10. 1D nOe spectra of 3aa, 3al and 3ao

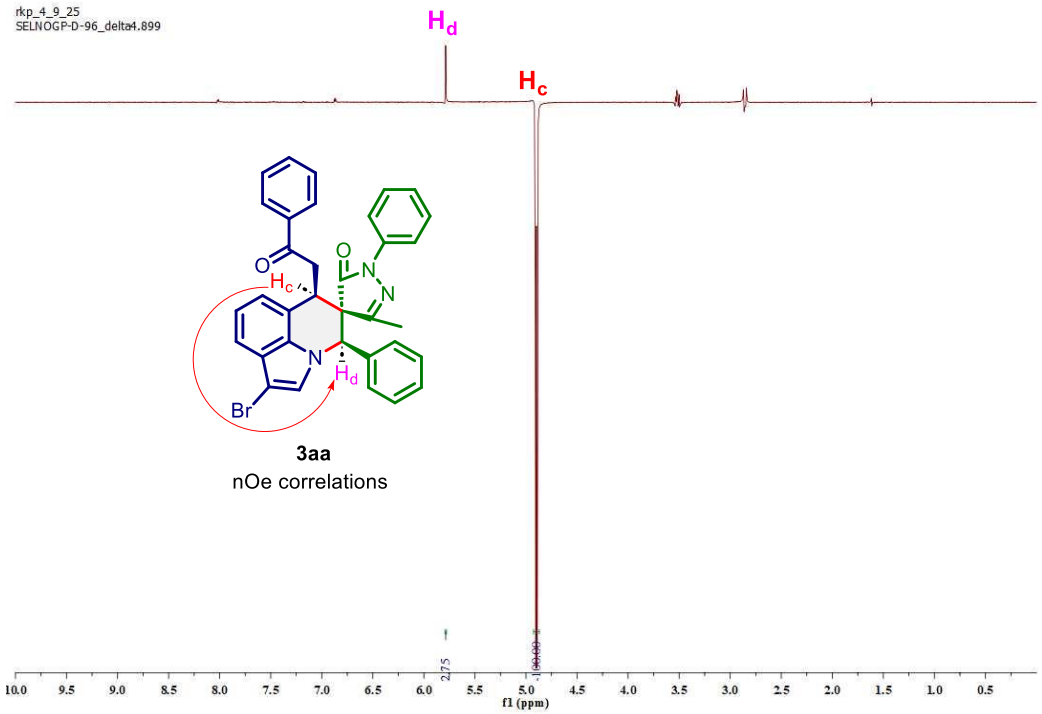


Figure S10: 1D nOe spectrum of **3aa**

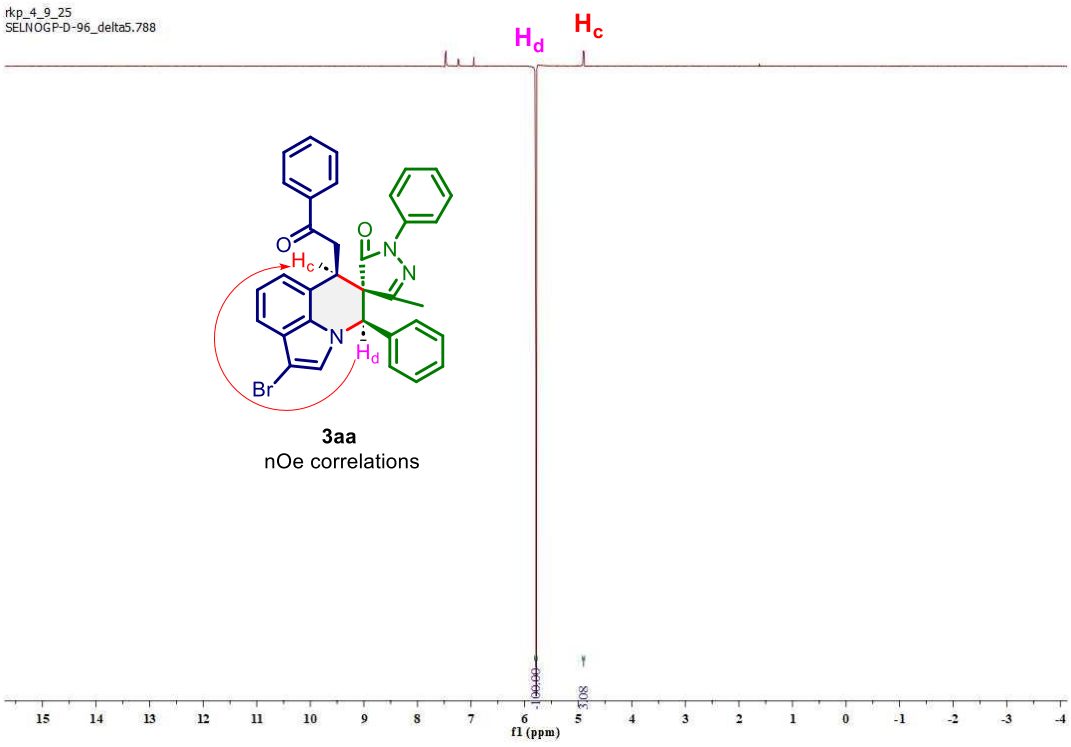


Figure S11: 1D nOe spectrum of **3aa**

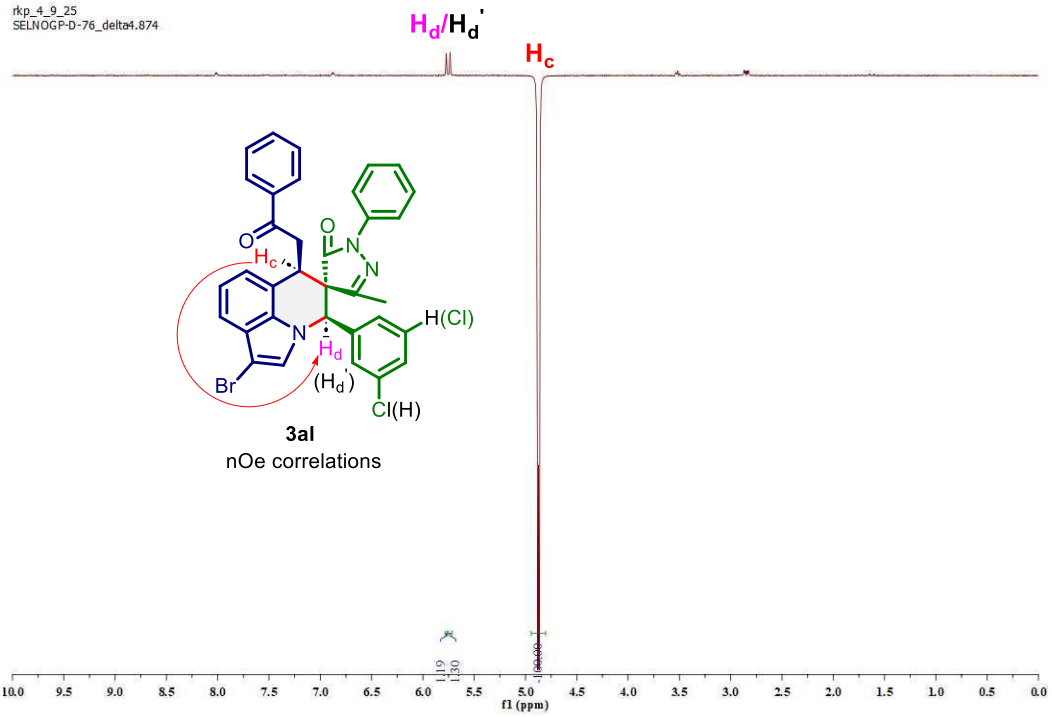


Figure S11: 1D nOe spectrum of **3al**

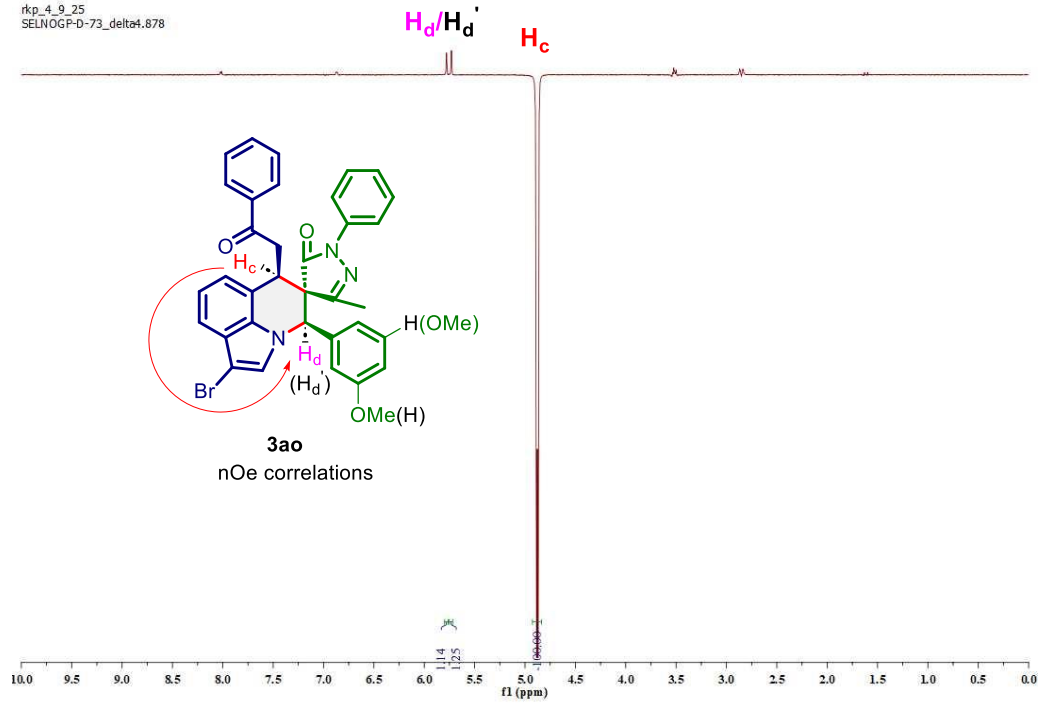
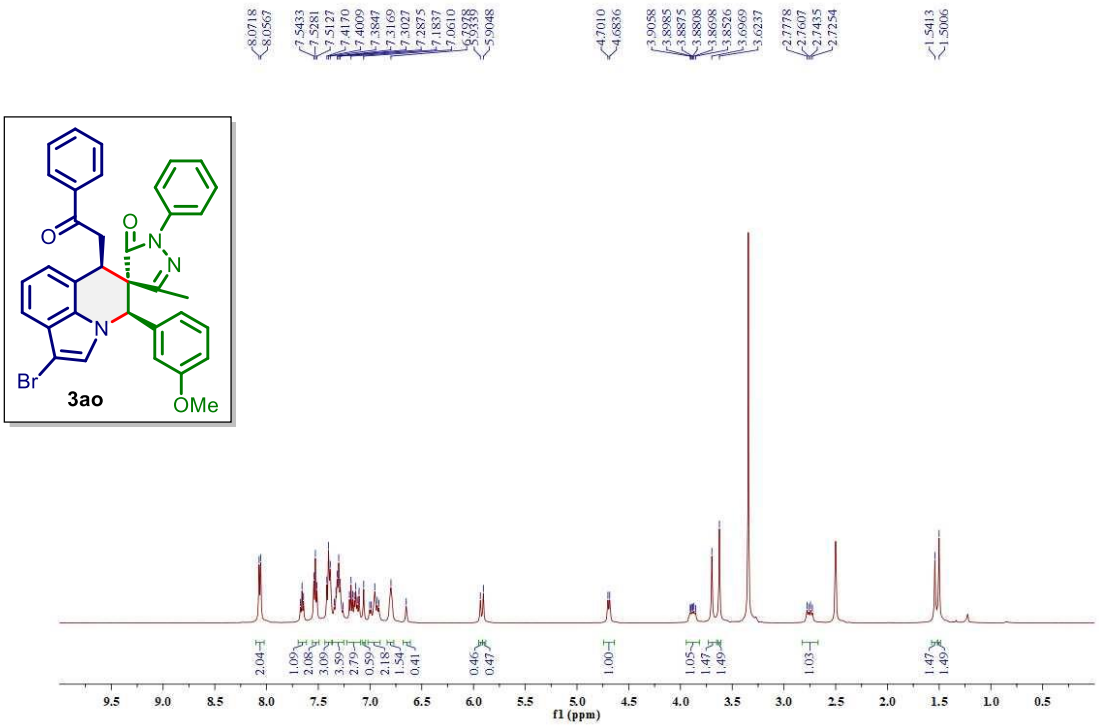


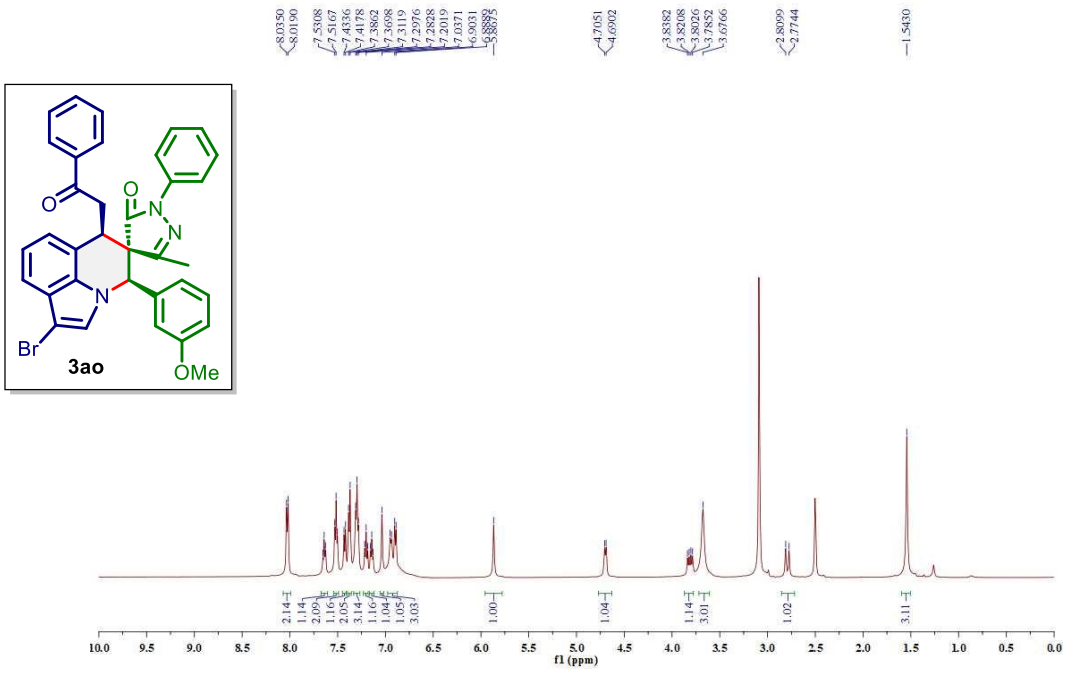
Figure S12: 1D nOe spectrum of **3ao**

11. Variable temperature ^{1}H NMR studies of Compound 3ao

^{1}H NMR Spectrum of 3ao (500 MHz, DMSO-d_6) at 25 °C

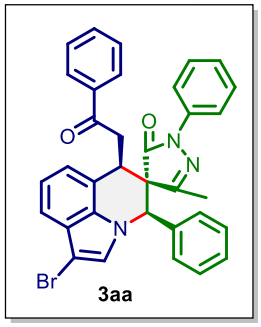


^{1}H NMR Spectrum of 3ao (500 MHz, DMSO-d_6) at 80 °C



12. Experimental Details for Synthesized Compounds (3, 4 and 8–27)

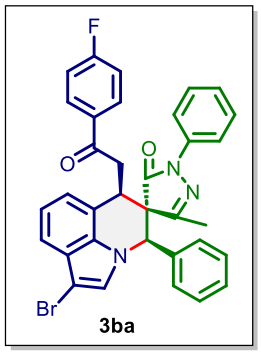
1'-Bromo-3-methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3aa)



3aa

3aa was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (138.3 mg, 94%), **MP**: 209.9–210.2 °C; **R_f** = 0.33 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50–7.43 (m, 6H), 7.40–7.27 (m, 4H), 7.26–7.18 (m, 2H), 7.17–7.10 (m, 2H), 6.92 (s, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.87 (d, *J* = 9.4 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.83 (d, *J* = 17.3 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.6, 159.1, 136.9, 136.2, 133.7, 133.6, 132.0, 131.0, 130.0, 129.2, 128.9, 128.8, 128.5, 128.4, 126.3, 125.8, 125.7, 124.2, 121.8, 121.6, 119.5, 119.4, 119.4, 118.3, 91.2, 65.7, 62.7, 38.3, 37.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{27}BrN_3O_2$ 588.1281, Found 588.1278.

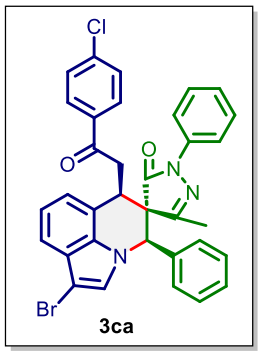
1'-Bromo-6'-(2-(4-fluorophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ba)



3ba

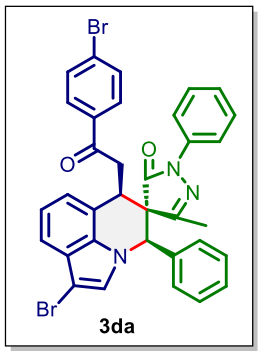
3ba was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-fluorophenyl)prop-2-en-1-one **1b** (107.6 mg, 0.312 mmol, 1.25 euqiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (130.4 mg, 86%), **MP**: 210.2–210.8 °C; **R_f** = 0.33 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03–8.00 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 3H), 7.39–7.26 (m, 5H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.18–7.11 (m, 4H), 6.93 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.85 (d, *J* = 9.1 Hz, 1H), 3.44 (dd, *J* = 17.4, 9.5 Hz, 1H), 2.81 (dd, *J* = 17.4, 2.1 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 194.9, 171.6, 166.1 (d, J_{C-F} = 256.4 Hz), 159.1, 136.9, 133.6, 132.6 (d, J_{C-F} = 3.3 Hz), 131.9, 131.1 (d, J_{C-F} = 9.7 Hz), 131.0, 130.1, 129.3, 128.9, 128.6, 126.3, 125.8, 125.7, 124.2, 121.8, 121.5, 119.4, 118.4, 116.1 (d, J_{C-F} = 22.1 Hz), 91.3, 65.7, 62.7, 38.2, 37.1, 18.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –103.95; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrFN_3O_2$ 606.1187, Found 606.1184.

1'-Bromo-6'-(2-(4-chlorophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ca)



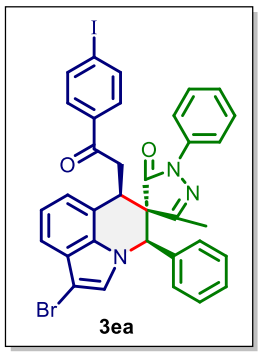
3ca was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-chlorophenyl)prop-2-en-1-one **1c** (112.7 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (135.5 mg, 87%), **MP**: 216.1–216.9 °C; **R_f** = 0.33 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 5H), 7.37–7.27 (m, 4H), 7.25 (s, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.18–7.11 (m, 2H), 6.93 (s, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 5.75 (s, 1H), 4.84 (d, *J* = 8.8 Hz, 1H), 3.44 (dd, *J* = 17.4, 9.5 Hz, 1H), 2.80 (dd, *J* = 17.4, 2.0 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.40, 171.60, 159.07, 140.31, 136.87, 134.52, 133.61, 131.91, 130.99, 130.12, 129.85, 129.81, 129.30, 129.26, 128.88, 128.84, 128.60, 126.34, 125.88, 125.78, 124.25, 121.84, 121.41, 119.40, 119.37, 118.42, 91.31, 65.77, 62.70, 38.29, 37.08, 18.05; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrClN_3O_2$ 622.0891, Found 622.0884.

1'-Bromo-6'-(2-(4-bromophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3da)



3da was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-bromophenyl)prop-2-en-1-one **1d** (126.6 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (163.5 mg, 98%), **MP**: 195.9–196.3 °C; **R_f** = 0.43 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 3H), 7.39–7.26 (m, 4.55H), 7.26–7.24 (m, 0.53H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.18–7.11 (m, 2H), 6.93 (s, 1H), 6.82 (d, *J* = 7.4 Hz, 1H), 5.75 (s, 1H), 4.84 (d, *J* = 8.9 Hz, 1H), 3.43 (dd, *J* = 17.4, 9.4 Hz, 1H), 2.80 (dd, *J* = 17.4, 2.3 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.6, 171.6, 159.0, 136.8, 134.9, 133.6, 132.2, 131.9, 131.0, 130.1, 129.9, 129.3, 129.0, 128.8, 128.6, 126.3, 125.8, 125.8, 124.2, 121.8, 121.4, 119.4, 119.4, 118.4, 91.3, 65.7, 62.7, 38.2, 37.1, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}Br_2N_3O_2$ 666.0386, Found 666.0383.

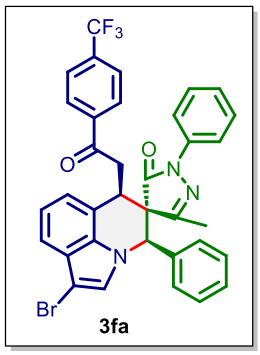
1'-Bromo-6'-(2-(4-iodophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ea)



3ea

3ea was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-iodophenyl)prop-2-en-1-one **1e** (141.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (100.0 mg, 56%), **MP**: 218.9–219.3 °C; $\mathbf{R_f}$ = 0.38 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 3H), 7.40–7.26 (m, 5H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.14 (dt, *J* = 17.4, 7.4 Hz, 2H), 6.92 (s, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 5.75 (s, 1H), 4.83 (d, *J* = 8.8 Hz, 1H), 3.42 (dd, *J* = 17.4, 9.4 Hz, 1H), 2.79 (dd, *J* = 17.4, 2.3 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.9, 171.6, 159.0, 138.2, 136.9, 135.4, 133.6, 131.9, 131.0, 130.1, 129.8, 129.3, 128.9, 128.6, 126.3, 125.9, 125.8, 124.2, 121.8, 121.4, 119.4, 119.4, 118.4, 101.9, 91.3, 65.7, 62.7, 38.2, 37.1, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrIN_3O_2$ 714.0248, Found 714.0240.

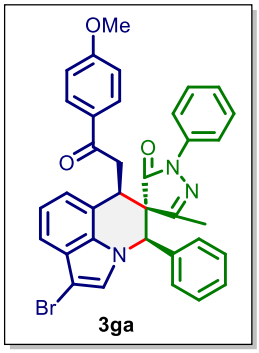
1'-Bromo-3-methyl-6'-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3fa)



3fa

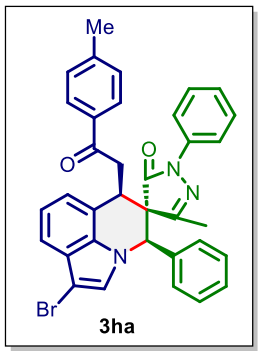
3fa was prepared by following general procedure, treatment of (*E*) 3-(3-bromo-1*H*-indol-7-yl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one **1f** (123.2 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (149.3 mg, 91%), **MP**: 198.2–199.0 °C; $\mathbf{R_f}$ = 0.31 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 3H), 7.40–7.27 (m, 4H), 7.25 (s, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.93 (s, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.85 (d, *J* = 8.6 Hz, 1H), 3.48 (dd, *J* = 17.5, 9.3 Hz, 1H), 2.86 (dd, *J* = 17.5, 2.4 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.8, 171.6, 159.0, 138.8, 136.8, 135.2, 134.9, 133.6, 131.9, 131.0, 130.2, 129.3, 128.9, 128.8, 128.6, 126.3, 126.0 (q, $J_{C–F}$ = 4.0 Hz), 125.9, 124.3, 123.6 (q, $J_{C–F}$ = 273.3 Hz), 121.8, 121.2, 119.4, 119.3, 118.6, 91.4, 65.8, 62.7, 38.6, 37.1, 18.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –63.07; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{26}BrF_3N_3O_2$ 656.1155, Found 656.1154.

1'-Bromo-6'-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ga)



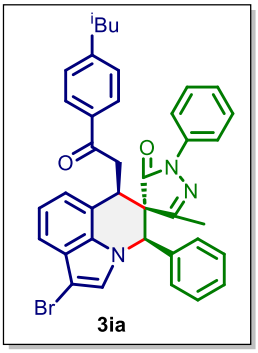
3ga was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-methoxyphenyl)prop-2-en-1-one **1g** (111.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (116.0 mg, 75%), **MP**: 197.8–198.1 °C; $\mathbf{R_f}$ = 0.21 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.49–7.44 (m, 4H), 7.37–7.29 (m, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.17–7.10 (m, 2H), 6.94 (s, 1H), 6.92 (s, 2H), 6.87 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.86 (d, *J* = 9.3 Hz, 1H), 3.86 (s, 3H), 3.44 (dd, *J* = 17.2, 9.6 Hz, 1H), 2.78 (dd, *J* = 17.2, 1.9 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 194.9, 171.6, 164.0, 159.1, 136.9, 133.6, 132.0, 131.0, 130.7, 130.0, 129.3, 129.2, 128.8, 128.5, 126.3, 125.7, 125.6, 124.1, 121.8, 121.8, 119.6, 119.4, 118.2, 114.0, 91.2, 65.7, 62.7, 55.6, 37.9, 37.1, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_3$ 618.1387, Found 618.1384.

1'-Bromo-3-methyl-6'-(2-oxo-2-(*p*-tolyl)ethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ha)



3ha was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(*p*-tolyl)prop-2-en-1-one **1h** (106.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (125.0 mg, 83%), **MP**: 194.9–195.2 °C; $\mathbf{R_f}$ = 0.22 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.47 (dd, *J* = 15.3, 8.1 Hz, 4H), 7.40–7.26 (m, 6H), 7.25 (s, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18–7.09 (m, 2H), 6.92 (s, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.87 (d, *J* = 9.3 Hz, 1H), 3.47 (dd, *J* = 17.4, 9.7 Hz, 1H), 2.80 (dd, *J* = 17.4, 2.0 Hz, 1H), 2.41 (s, 3H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.0, 171.6, 159.1, 144.6, 136.9, 133.8, 133.6, 132.0, 131.0, 130.0, 129.6, 129.2, 128.8, 128.5, 126.3, 125.8, 125.6, 124.1, 121.8, 121.7, 119.6, 119.4, 119.4, 118.2, 91.2, 65.7, 62.7, 38.2, 37.0, 21.8, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_2$ 602.1438, Found 602.1432.

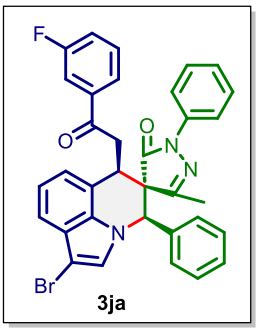
1'-Bromo-6'-(2-(4-isobutylphenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ia)



3ia

3ia was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-isobutylphenyl)prop-2-en-1-one **1i** (119.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (130.5 mg, 81%), **MP**: 204.1–204.5 °C; **R_f** = 0.27 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.49–7.49 (m, 4H), 7.39–7.27 (m. 4H), 7.25–7.19 (m, 4H), 7.13 (dt, *J* = 19.5, 7.5 Hz, 2H), 6.92 (s, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 5.76 (s, 1H), 4.87 (d, *J* = 9.4 Hz, 1H), 3.47 (dd, *J* = 17.4, 9.7 Hz, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 2.53 (d, *J* = 7.1 Hz, 2H), 1.93–1.85 (m, 1H), 1.59 (s, 3H), 0.90 (d, *J* = 6.5 Hz, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.1, 171.6, 159.1, 148.3, 136.9, 134.0, 133.6, 132.0, 131.0, 130.0, 129.6, 129.2, 128.8, 128.5, 128.4, 126.3, 125.7, 125.6, 124.1, 121.8, 121.7, 119.6, 119.4, 118.2, 91.2, 65.7, 62.7, 45.5, 38.2, 37.0, 30.2, 22.4, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{38}H_{35}BrN_3O_2$ 644.1907, Found 644.1901.

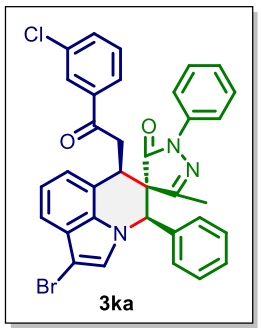
1'-Bromo-6'-(2-(3-fluorophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ja)



3ja

3ja was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-fluorophenyl)prop-2-en-1-one **1j** (107.6 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (122.8 mg, 81%), **MP**: 186.1–186.9 °C; **R_f** = 0.26 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.48–7.42 (m, 4H), 7.36 (dd, *J* = 16.5, 8.5 Hz, 2H), 7.32–7.27 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.86 (d, *J* = 9.2 Hz, 1H), 3.45 (dd, *J* = 17.6, 9.5 Hz, 1H), 2.80 (d, *J* = 17.4 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.3, 171.6, 163.0 (d, J_{C-F} = 249.4 Hz), 159.0, 138.3 (d, J_{C-F} = 6.7 Hz), 136.9, 133.6, 131.9, 131.0, 130.6 (d, J_{C-F} = 8.2 Hz), 130.1, 129.3, 128.9, 128.6, 126.3, 125.9, 125.8, 124.3, 124.2, 124.1, 121.8, 121.4, 120.8 (d, J_{C-F} = 21.7 Hz), 119.4, 119.4, 118.4, 115.2 (d, J_{C-F} = 22.7 Hz), 91.3, 65.8, 62.7, 38.5, 37.0, 18.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –111.07; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrFN_3O_2$ 606.1187, Found 606.1184.

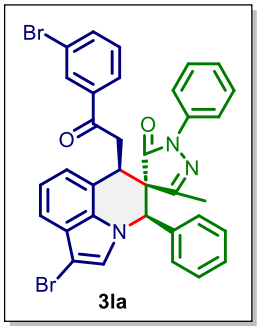
1'-Bromo-6'-(2-(3-chlorophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ka)



3ka

3ka was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-chlorophenyl)prop-2-en-1-one **1k** (112.7 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (143.3 mg, 92%), **MP**: 196.1–196.4 °C; $\mathbf{R_f}$ = 0.26 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (t, *J* = 1.8 Hz, 1H), 7.90–7.83 (m, 1H), 7.58–7.53 (m, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.47–7.44 (m, 3H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.34–7.33 (m, 2H), 7.32–7.27 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.19–7.15 (m, 1H), 7.15–7.10 (m, 1H), 6.93 (s, 1H), 6.80 (d, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 4.85 (d, *J* = 9.5 Hz, 1H), 3.45 (dd, *J* = 17.6, 9.5 Hz, 1H), 2.79 (dd, *J* = 17.5, 2.2 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.3, 171.6, 159.0, 137.7, 136.9, 135.3, 133.7, 133.6, 131.9, 131.0, 130.3, 130.1, 129.3, 128.9, 128.6, 128.5, 126.5, 126.3, 125.9, 125.8, 124.3, 121.8, 121.3, 119.4, 119.4, 118.4, 91.3, 65.8, 62.7, 38.4, 37.0, 18.1; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrClN_3O_2$ 622.0891, Found 622.0894.

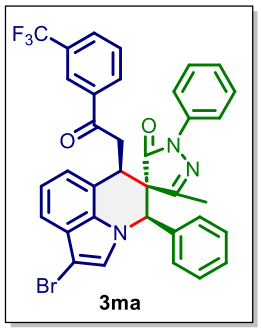
1'-Bromo-6'-(2-(3-bromophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3la)



3la

3la was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-bromophenyl)prop-2-en-1-one **1l** (126.6 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (155.2 mg, 93%), **MP**: 194.3–195.1 °C; °C; $\mathbf{R_f}$ = 0.18 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 (t, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.73–7.67 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.48–7.43 (m, 3H), 7.40–7.33 (m, 3H), 7.33–7.26 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.15–7.10 (m, 1H), 6.93 (s, 1H), 6.80 (d, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 4.85 (d, *J* = 8.9 Hz, 1H), 3.44 (dd, *J* = 17.5, 9.5 Hz, 1H), 2.79 (dd, *J* = 17.5, 2.2 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.2, 171.6, 159.0, 137.9, 136.9, 136.6, 133.6, 131.9, 131.4, 131.0, 130.5, 130.1, 129.3, 128.9, 128.6, 127.0, 126.3, 125.9, 125.8, 124.3, 123.3, 121.8, 121.3, 119.4, 119.3, 118.4, 91.3, 65.8, 62.7, 38.4, 37.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}Br_2N_3O_2$ 666.0386, Found 666.0388.

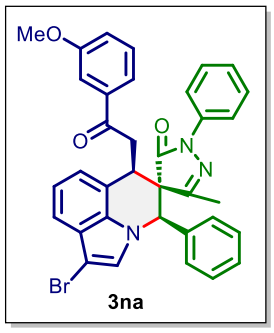
1'-Bromo-3-methyl-6'-(2-oxo-2-(3-(trifluoromethyl)phenyl)ethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ma)



3ma

3ma was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one **1m** (123.2 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (144.4 mg, 88%), **MP**: 203.3–204.0 °C; °C; **R_f** = 0.24 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 3H), 7.40–7.27 (m, 4H), 7.23 (dd, *J* = 13.2, 4.8 Hz, 2H), 7.20–7.15 (m, 1H), 7.12 (dd, *J* = 11.0, 3.8 Hz, 1H), 6.94 (s, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 5.77 (s, 1H), 4.87 (d, *J* = 8.7 Hz, 1H), 3.49 (dd, *J* = 17.6, 9.3 Hz, 1H), 2.86 (dd, *J* = 17.6, 2.2 Hz, 1H), 1.60 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.3, 171.6, 159.0, 136.8, 136.7, 133.6, 131.8, 131.6, 131.0, 130.2, 130.1, 129.6, 129.3, 128.9, 128.6, 126.3, 125.9, 125.8, 125.2 (q, $J_{C–F}$ = 4.4 Hz), 124.3, 123.7 (q, $J_{C–F}$ = 273.0 Hz), 121.8, 121.3, 119.4, 119.3, 118.5, 91.4, 65.8, 62.7, 38.4, 37.0, 30.4, 18.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –62.62; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{26}BrF_3N_3O_2$ 656.1155, Found 656.1150.

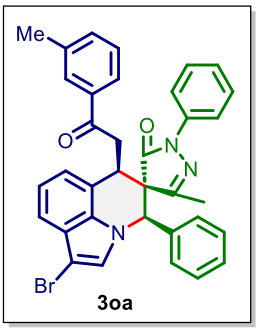
1'-Bromo-6'-(2-(3-methoxyphenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3na)



3na

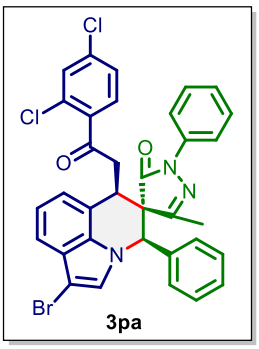
3na was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-methoxyphenyl)prop-2-en-1-one **1n** (111.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (134.5 mg, 87%), **MP**: 185.9–186.2 °C; **R_f** = 0.22 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55–7.53 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.46–7.44 (m, 3H), 7.39–7.27 (m, 5H), 7.25 (d, *J* = 1.7 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.18–7.10 (m, 3H), 6.93 (s, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 4.87 (d, *J* = 9.5 Hz, 1H), 3.85 (s, 3H), 3.48 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.82 (dd, *J* = 17.5, 2.1 Hz, 1H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.3, 171.6, 160.0, 159.1, 137.6, 136.9, 133.6, 132.0, 131.0, 130.0, 129.9, 129.2, 128.8, 128.5, 126.3, 125.8, 125.7, 124.2, 121.8, 121.6, 120.9, 120.2, 119.5, 119.4, 118.3, 112.7, 91.2, 65.7, 62.7, 55.6, 38.4, 37.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_3$ 618.1387, Found 618.1381.

1'-Bromo-3-methyl-6'-(2-oxo-2-(*m*-tolyl)ethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3oa)



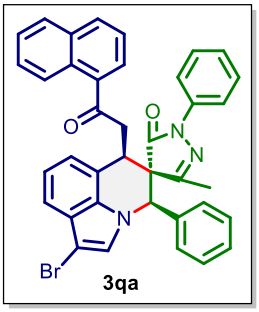
3oa was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(*m*-tolyl)prop-2-en-1-one **1o** (106.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (137.1 mg, 91%), **MP**: 174.9–175.2 °C; **R_f** = 0.25 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79–7.77 (m, 2H), 7.49–7.47 (m, 1H), 7.46–7.44 (m, 3H), 7.41–7.26 (m, 7H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18–7.10 (m, 2H), 6.92 (s, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 4.87 (d, *J* = 9.8 Hz, 1H), 3.47 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.81 (dd, *J* = 17.5, 2.1 Hz, 1H), 2.40 (s, 3H), 1.59 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.7, 171.6, 159.2, 138.8, 136.9, 136.3, 134.5, 133.6, 132.0, 131.0, 130.1, 129.3, 128.9, 128.8, 128.8, 128.6, 126.4, 125.8, 125.7, 125.6, 124.2, 121.8, 121.7, 119.6, 119.5, 119.4, 118.3, 91.2, 65.8, 62.7, 38.4, 37.0, 21.5, 18.1; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_2$ 602.1438, Found 602.1434.

1'-Bromo-6'-(2-(2,4-dichlorophenyl)-2-oxoethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3pa)



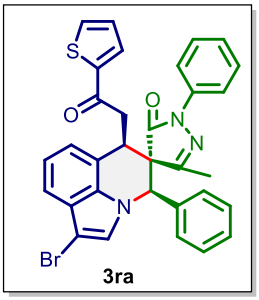
3pa was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(2,4-dichlorophenyl)prop-2-en-1-one **1p** (123.5 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (118.3 mg, 72%), **MP**: 158.2–158.9 °C; **R_f** = 0.25 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58–7.52 (m, 2H), 7.40 (s, 2H), 7.37–7.27 (m, 9H), 7.24–7.12 (m, 3H), 6.91 (s, 1H), 5.52 (s, 1H), 4.42–4.24 (m, 2H), 3.25 (d, *J* = 16.6 Hz, 1H), 1.55 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 198.2, 171.6, 160.4, 137.6, 137.0, 136.9, 133.2, 132.1, 132.0, 131.1, 130.5, 130.0, 128.8, 127.5, 126.2, 126.1, 124.8, 122.4, 122.1, 120.9, 120.5, 118.4, 91.6, 60.9, 59.0, 46.8, 35.3, 17.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{25}BrCl_2N_3O_2$ 656.0502, Found 656.0506.

1'-Bromo-3-methyl-6'-(2-(naphthalen-1-yl)-2-oxoethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3qa)



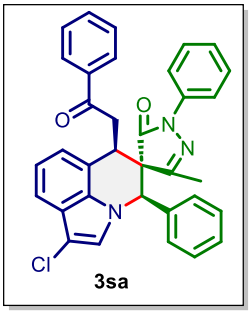
3qa was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(naphthalen-1-yl)prop-2-en-1-one **1q** (117.6 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (156.4 mg, 98%), **MP**: 143.2–143.9 °C; **R_f** = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 8.07 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 17.5, 8.4 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50–7.46 (m, 4H), 7.41–7.26 (m, 4H), 7.25–7.21 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 5.77 (s, 1H), 4.94 (d, *J* = 9.3 Hz, 1H), 3.62 (dd, *J* = 17.2, 9.6 Hz, 1H), 2.97 (dd, *J* = 17.2, 2.0 Hz, 1H), 1.63 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.7, 159.2, 136.9, 135.9, 133.6, 133.5, 132.5, 132.0, 131.0, 130.1, 130.0, 129.8, 129.3, 128.9, 128.8, 128.5, 127.9, 127.0, 126.3, 125.8, 125.7, 124.2, 124.0, 121.9, 121.6, 119.6, 119.5, 119.4, 118.3, 91.2, 65.7, 62.8, 38.4, 37.2, 18.1; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{38}H_{29}BrN_3O_2$ 638.1438, Found 638.1436.

1'-Bromo-3-methyl-6'-(2-oxo-2-(thiophen-2-yl)ethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ra)



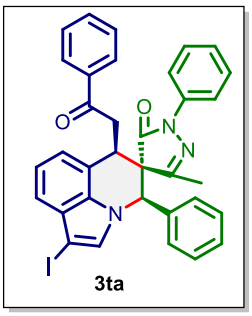
3ra was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(thiophen-2-yl)prop-2-en-1-one **1r** (103.6 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (93.6 mg, 63%), **MP**: 201.9–202.2 °C; **R_f** = 0.22 (10% ethyl acetate in hexanes);); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.67 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.47–7.41 (m, 3H), 7.38–7.28 (m, 4H), 7.25 (s, 1H), 7.19 (dd, *J* = 16.0, 8.3 Hz, 2H), 7.14–7.09 (m, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.92 (s, 1H), 5.75 (s, 1H), 4.83 (d, *J* = 9.4 Hz, 1H), 3.38 (dd, *J* = 16.9, 9.6 Hz, 1H), 2.82 (dd, *J* = 16.9, 2.3 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 189.34, 171.60, 159.00, 143.35, 136.91, 134.66, 133.62, 132.55, 131.97, 131.02, 130.10, 129.29, 128.86, 128.59, 128.45, 126.36, 125.85, 125.75, 124.22, 121.91, 121.49, 119.60, 119.48, 118.40, 91.30, 65.74, 62.71, 39.07, 37.25, 18.03; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{25}BrN_3O_2S$ 594.0845, Found 594.0841.

1'-Chloro-3-methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3sa)



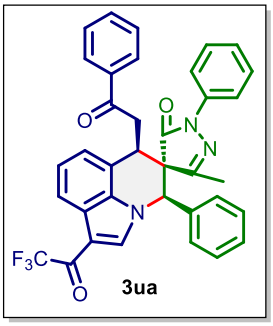
3sa was prepared by following general procedure, treatment of (*E*)-3-(3-chloro-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1s** (88.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (130.6 mg, 96%), **MP**: 220.2–220.8 °C; $\mathbf{R_f}$ = 0.32 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.01–7.99 (m, 2H), 7.61–7.57 (m, 1H), 7.55–7.54 (m, 1H), 7.49–7.44 (m, 5H), 7.40–7.26 (m, 5H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.17–7.10 (m, 2H), 6.88 (s, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 4.87 (d, *J* = 9.2 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.83 (dd, *J* = 17.5, 2.1 Hz, 1H), 1.60 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.6, 159.1, 136.9, 136.2, 133.7, 133.2, 132.0, 130.9, 130.0, 129.2, 128.9, 128.8, 128.5, 128.4, 126.3, 125.8, 124.1, 121.9, 121.7, 121.6, 119.5, 119.4, 117.4, 106.3, 65.6, 62.7, 38.3, 36.9, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{27}ClN_3O_2$ 544.1786, Found 544.1793.

1'-Iodo-3-methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ta)



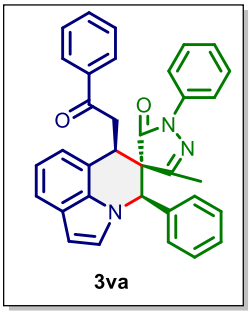
3ta was prepared by following general procedure, treatment of (*E*)-3-(3-iodo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1t** (116.4 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (136.6 mg, 86%), **MP**: 217.1–217.5 °C; $\mathbf{R_f}$ = 0.33 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00–7.97 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49–7.44 (m, 5H), 7.40–7.26 (m, 6H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.18–7.10 (m, 2H), 6.98 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.80 (s, 1H), 4.88 (d, *J* = 9.3 Hz, 1H), 3.50 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.83 (dd, *J* = 17.5, 1.9 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.6, 159.1, 136.9, 136.2, 134.1, 133.7, 132.0, 131.0, 130.1, 129.3, 129.0, 128.9, 128.8, 128.6, 128.4, 126.4, 125.8, 121.9, 121.6, 120.0, 119.5, 119.5, 65.8, 62.8, 56.7, 38.3, 37.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{27}IN_3O_2$ 636.1142, Found 636.1117.

3-Methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-1'-(2,2,2-trifluoroacetyl)-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ua)



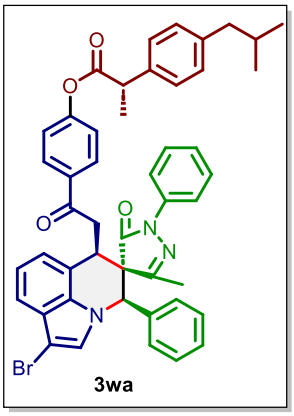
3ua was prepared by following general procedure, treatment of (*E*)-1-phenyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one **1u** (77.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (87.8 mg, 58%), **MP**: 227.3–227.8 °C; $\mathbf{R}_f$ = 0.20 (10% ethyl acetate in hexanes); **^{1}H NMR (700 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.1 Hz, 2H), 7.70 (s, 1H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.53–7.47 (m, 3H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.43–7.34 (m, 4H), 7.28 (d, *J* = 6.9 Hz, 2H), 7.14 (d, *J* = 6.3 Hz, 2H), 6.96 (d, *J* = 6.9 Hz, 1H), 5.86 (s, 1H), 4.91 (d, *J* = 9.2 Hz, 1H), 3.49 (dd, *J* = 17.3, 9.7 Hz, 1H), 2.85 (d, *J* = 17.6 Hz, 1H), 1.57 (s, 3H); **^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$)** δ 196.1, 175.4, 171.1, 158.2, 136.8, 136.1, 134.4, 134.2, 134.0, 131.4, 130.8, 130.7, 129.8, 129.0, 128.9, 128.4, 126.1, 125.8, 125.5, 125.1, 122.4, 121.6, 119.5, 111.0, 66.2, 62.9, 38.2, 36.9, 18.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –72.47; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{27}F_3N_3O_3$ 606.1999, Found 606.1979.

3-Methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3va)



3va was prepared by following general procedure, treatment of (*E*)-3-(1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1v** (77.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (79.0 mg, 62%), **MP**: 153.9–154.2 °C; $\mathbf{R}_f$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.60–7.55 (m, 2H), 7.47 (t, *J* = 7.9 Hz, 5H), 7.38–7.27 (m, 4H), 7.25–7.20 (m, 2H), 7.15–7.03 (m, 2H), 6.89 (s, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 5.81 (s, 1H), 4.90 (d, *J* = 9.4 Hz, 1H), 3.51 (dd, *J* = 17.4, 9.7 Hz, 1H), 2.83 (d, *J* = 17.4 Hz, 1H), 1.55 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.8, 172.0, 159.5, 137.0, 136.4, 134.2, 133.7, 132.7, 131.0, 129.8, 129.1, 128.9, 128.8, 128.4, 128.4, 126.6, 126.6, 125.7, 125.2, 121.3, 121.1, 119.8, 119.5, 118.4, 102.4, 65.7, 63.0, 38.5, 37.4, 17.9; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{28}N_3O_2$ 510.2176, Found 510.2185.

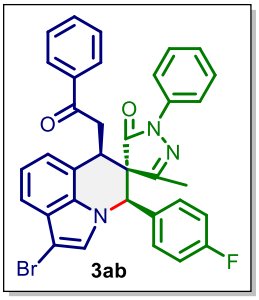
4-(2-(1'-Bromo-3-methyl-5-oxo-1,4'-diphenyl-1,5-dihydro-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-6'-yl)acetyl)phenyl (2*S*)-2-(4-isobutylphenyl)propanoate (3wa)



3wa

3wa was prepared by following general procedure, treatment of (*E*)-4-(3-(3-bromo-1*H*-indol-7-yl)acryloyl)phenyl 2-(4-isobutylphenyl)propanoate **1w** (165.8 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (172.4 mg, 87%), **MP**: 130.2–130.6 °C; $\mathbf{R_f}$ = 0.34 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 6.5 Hz, 3H), 7.38–7.33 (m, 2H), 7.32–7.28 (m, 4H), 7.25–7.18 (m, 2H), 7.16–7.09 (m, 6H), 6.92 (s, 1H), 6.80 (d, *J* = 7.3 Hz, 1H), 5.75 (s, 1H), 4.85 (d, *J* = 9.4 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 1H), 3.44 (dd, *J* = 17.4, 9.7 Hz, 1H), 2.79 (d, *J* = 17.4 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.90–1.82 (m, 4H), 1.61 (d, *J* = 7.1 Hz, 3H), 1.57 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 195.3, 172.7, 171.6, 159.1, 155.1, 141.2, 136.9, 133.7, 133.6, 132.0, 131.0, 130.1, 130.0, 129.7, 129.3, 128.9, 128.6, 127.3, 126.3, 125.8, 125.7, 124.2, 122.0, 121.9, 121.5, 119.5, 118.3, 91.3, 65.7, 62.7, 45.4, 45.1, 38.3, 37.0, 30.3, 22.5, 18.6, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{47}H_{43}BrN_3O_4$ 792.2431, Found 792.2444.

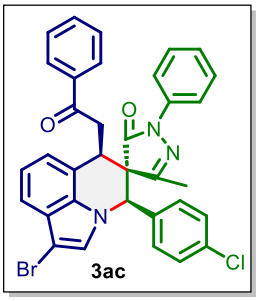
1'-Bromo-4'-(4-fluorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ab)



3ab

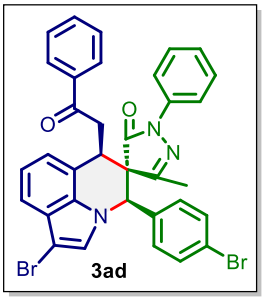
3ab was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-fluorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2b** (70.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (148.6 mg, 98%), **MP**: 224.1–224.4 °C; $\mathbf{R_f}$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.60–7.57 (m, 1H), 7.51–7.43 (m, 6H), 7.31–7.27 (m, 2H), 7.22–7.19 (m, 1H), 7.18–7.12 (m, 2H), 7.08 (dt, *J* = 11.2, 5.6 Hz, 1H), 6.99 (td, *J* = 8.4, 2.7 Hz, 1H), 6.88 (s, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 4.86 (d, *J* = 9.6 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.82 (dd, *J* = 17.5, 2.1 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 171.6, 163.4 (d, J_{C-F} = 250.5 Hz), 158.9, 136.9, 136.2, 133.8, 133.6, 133.0 (d, J_{C-F} = 8.7 Hz), 128.9, 128.4, 128.2, 128.2, 127.9 (d, J_{C-F} = 3.7 Hz), 125.9, 125.8, 123.9, 122.0, 121.5, 119.7, 119.3, 118.4, 116.3, 116.1, 115.9 (d, J_{C-F} = 22.1 Hz), 91.6, 65.0, 62.8, 38.3, 37.0, 18.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –110.33; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrFN_3O_2$ 606.1187, Found 606.1192.

1'-Bromo-4'-(4-chlorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ac)



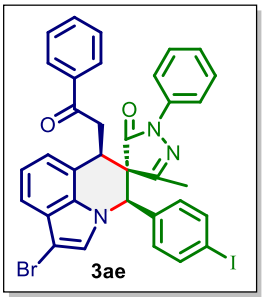
3ac was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-chlorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2c** (74.2 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (149.5 mg, 96%), **MP**: 208.9–209.0 °C; $\mathbf{R_f}$ = 0.20 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.49–7.46 (m, 5H), 7.40–7.35 (m, 2H), 7.32–7.27 (m, 3H), 7.16 (d, *J* = 6.9 Hz, 3H), 6.88 (s, 1H), 6.84 (d, *J* = 7.1 Hz, 1H), 5.75 (s, 1H), 4.86 (d, *J* = 9.2 Hz, 1H), 3.49 (dd, *J* = 17.4, 9.5 Hz, 1H), 2.82 (d, *J* = 17.4 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 171.5, 158.9, 136.8, 136.2, 136.1, 133.8, 133.6, 132.4, 130.7, 129.0, 128.9, 128.4, 127.7, 126.0, 125.8, 123.9, 122.0, 121.5, 119.7, 119.4, 118.4, 91.7, 65.1, 62.6, 38.2, 37.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrClN_3O_2$ 622.0891, Found 622.0898.

1'-Bromo-4'-(4-bromophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ad)



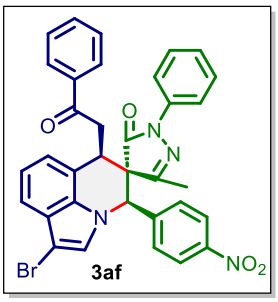
3ad was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-bromobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2d** (85.3 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (140.1 mg, 84%), **MP**: 213.9–214.4 °C; $\mathbf{R_f}$ = 0.33 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00–7.98 (m, 2H) 7.61–7.57 (m, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.49–7.46 (m, 5H), 7.43 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.35–7.28 (m, 3H), 7.19–7.13 (m, 2H), 7.10 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.88 (s, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 5.73 (s, 1H), 4.85 (d, *J* = 9.4 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.82 (dd, *J* = 17.5, 2.1 Hz, 1H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.3, 171.5, 158.9, 136.8, 136.2, 133.8, 133.6, 132.6, 132.4, 131.9, 131.2, 129.0, 128.9, 128.4, 128.0, 126.0, 125.7, 124.3, 123.9, 122.0, 121.5, 119.7, 119.4, 118.4, 91.7, 65.1, 62.6, 38.2, 37.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}Br_2N_3O_2$ 666.0386, Found 666.0392.

1'-Bromo-4'-(4-iodophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ae)



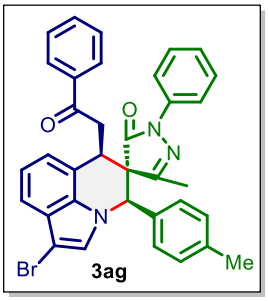
3ae was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-iodobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2e** (97.0 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (175.0 mg, 98%), **MP**: 203.9–204.2 °C; **R_f** = 0.31 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.72 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.65–7.57 (m, 2H), 7.50–7.45 (m, 5H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.18–7.14 (m, 3H), 6.96 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.88 (s, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.71 (s, 1H), 4.85 (d, *J* = 9.2 Hz, 1H), 3.52–3.46 (m, 1H), 2.82 (dd, *J* = 17.5, 2.0 Hz, 1H), 1.57 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.3, 171.5, 158.9, 138.4, 137.8, 136.8, 136.2, 133.8, 133.6, 132.7, 131.9, 129.0, 128.9, 128.4, 128.1, 126.0, 125.7, 123.9, 122.0, 121.4, 119.7, 119.5, 119.5, 118.4, 96.1, 91.7, 65.2, 62.5, 38.2, 36.9, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrIN_3O_2$ 714.0248, Found 714.0239.

1'-Bromo-3-methyl-4'-(4-nitrophenyl)-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3af)



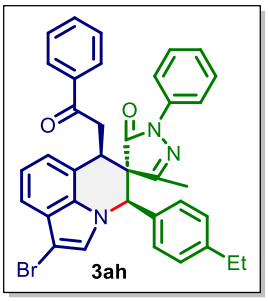
3af was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-5-methyl-4-(4-nitrobenzylidene)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2f** (76.8 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (129.9 mg, 82%), **MP**: 228.6–228.9 °C; **R_f** = 0.23 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.25 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.15 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.66 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.51–7.46 (m, 5H), 7.43 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 11.0, 3.8 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.84 (s, 1H), 5.89 (s, 1H), 4.88 (d, *J* = 9.1 Hz, 1H), 3.51 (dd, *J* = 17.5, 9.5 Hz, 1H), 2.82 (dd, *J* = 17.5, 2.1 Hz, 1H), 1.62 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.1, 171.1, 158.5, 148.7, 139.5, 136.6, 136.1, 133.9, 133.6, 132.1, 129.0, 128.4, 127.5, 126.1, 125.7, 124.2, 123.8, 123.6, 122.2, 121.3, 119.9, 119.0, 118.6, 92.3, 64.9, 62.5, 38.0, 36.9, 18.1; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrN_4O_4$ 633.1132, Found 633.1124.

1'-Bromo-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'-(*p*-tolyl)-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ag)



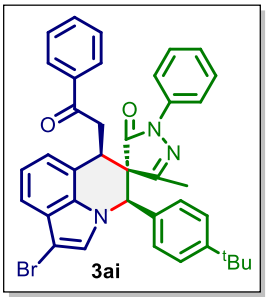
3ag was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-5-methyl-4-(4-methylbenzylidene)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2g** (69.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (120.5 mg, 80%), **MP**: 219.0–219.3 °C; $\mathbf{R_f}$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.49 (s, 2H), 7.46 (d, *J* = 7.3 Hz, 3H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.18–7.07 (m, 5H), 6.92 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.73 (s, 1H), 4.86 (d, *J* = 9.4 Hz, 1H), 3.48 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.82 (dd, *J* = 17.5, 2.0 Hz, 1H), 2.29 (s, 3H), 1.58 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.7, 159.2, 140.0, 137.0, 136.3, 133.7, 133.6, 130.9, 129.8, 129.3, 128.9, 128.8, 128.4, 126.2, 125.7, 124.2, 121.8, 119.5, 119.4, 118.2, 91.1, 65.5, 62.7, 38.3, 37.1, 21.3, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_2$ 602.1438, Found 602.1442.

1'-Bromo-4'-(4-ethylphenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ah)



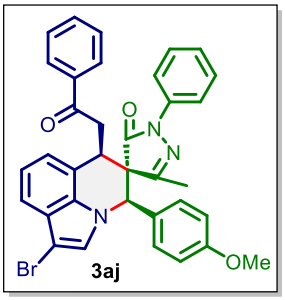
3ah was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-ethylbenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2h** (72.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (118.7 mg, 77%), **MP**: 206.3–206.9 °C; $\mathbf{R_f}$ = 0.32 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51–7.45 (m, 3H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.28 (s,1H), 7.24 (s, 1H), 7.19–7.09 (m, 5H) 6.95 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.73 (s, 1H), 4.87 (d, *J* = 9.2 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.84 (dd, *J* = 17.5, 2.0 Hz, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.57 (s, 3H), 1.14 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.7, 159.2, 146.3, 136.9, 136.3, 133.7, 133.6, 131.0, 129.0, 128.9, 128.8, 128.6, 128.4, 128.1, 126.3, 125.8, 125.7, 124.2, 121.8, 121.7, 119.7, 119.5, 118.2, 91.1, 65.6, 62.8, 38.4, 36.9, 28.6, 18.0, 15.5; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{31}BrN_3O_2$ 616.1594, Found 616.1593.

1'-Bromo-4'-(4-(*tert*-butyl)phenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ai)



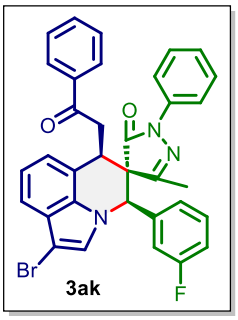
3ai was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-(*tert*-butyl)benzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2i** (79.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (117.6 mg, 73%), **MP**: 234.2–234.8 °C; $\mathbf{R_f}$ = 0.38 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.02–8.00 (m, 2H), 7.62–7.57 (m, 1H), 7.51–7.46 (m, 3H), 7.39–7.26 (m, 5H), 7.24 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.17–7.09 (m, 3H), 6.98 (s, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.72 (s, 1H), 4.88 (d, *J* = 9.8 Hz, 1H), 3.50 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.87 (dd, *J* = 17.5, 2.1 Hz, 1H), 1.57 (s, 3H), 1.23 (s, 9H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 171.7, 159.2, 153.2, 136.8, 136.3, 133.7, 133.6, 130.7, 128.9, 128.7, 128.7, 128.4, 126.1, 126.0, 125.9, 125.7, 125.3, 124.2, 121.8, 121.7, 120.0, 119.5, 118.2, 91.1, 65.6, 62.9, 38.6, 36.7, 34.8, 31.2, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{38}H_{35}BrN_3O_2$ 644.1907, Found 644.1923.

1'-Bromo-4'-(4-methoxyphenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3aj)



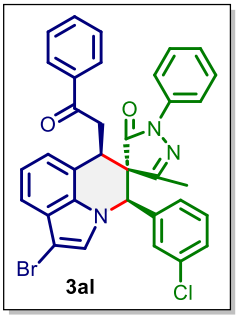
3aj was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(4-methoxybenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2j** (73.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (105.1 mg, 68%), **MP**: 223.9–224.2 °C; $\mathbf{R_f}$ = 0.24 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51–7.46 (m, 5H), 7.37 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.30–7.26 (m, 2H), 7.17–7.10 (m, 3H), 6.91 (s, 1H), 6.88 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.85–6.78 (m, 2H), 5.72 (s, 1H), 4.86 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 3.49 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.82 (dd, *J* = 17.5, 2.0 Hz, 1H), 1.57 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.8, 160.6, 159.2, 137.0, 136.2, 133.7, 133.6, 132.4, 128.9, 128.8, 128.4, 127.5, 125.8, 125.7, 124.1, 123.7, 121.8, 121.6, 119.4, 118.2, 114.5, 114.0, 91.0, 65.2, 62.8, 55.4, 38.3, 37.1, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_3$ 618.1387, Found 618.1393.

1'-Bromo-4'-(3-fluorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ak)



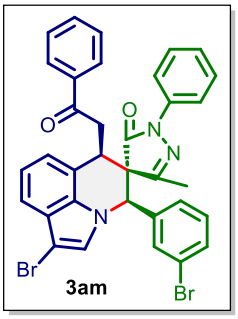
3ak was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3-fluorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2k** (70.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (138.0 mg, 91%), **MP**: 208.1–208.6 °C; $\mathbf{R_f}$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52–7.46 (m, 5H), 7.38–7.27 (m, 3.60H), 7.25–7.21 (m, 0.54H), 7.19–7.11 (m, 2H), 7.08–6.99 (m, 1.41H), 6.91 (d, *J* = 15.1 Hz, 1.46H), 6.84 (d, *J* = 7.0 Hz, 1H), 5.79 (s, 0.52H), 5.73 (s, 0.40H), 4.86 (d, *J* = 9.4 Hz, 1H), 3.56–3.45 (m, 1H), 2.82 (d, *J* = 17.5 Hz, 1H), 1.60 (s, 1.47H), 1.58 (s, 1.46H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 171.5, 162.8 (d, $J_{C–F}$ = 246.6 Hz), 162.4 (d, $J_{C–F}$ = 247.9 Hz), 161.9, 161.5, 158.9, 136.9 (d, $J_{C–F}$ = 4.4 Hz), 136.2, 134.6, 133.8, 133.6, 130.9 (d, $J_{C–F}$ = 8.8 Hz), 130.4 (d, $J_{C–F}$ = 8.3 Hz), 129.0, 128.9, 128.4, 126.6 (d, $J_{C–F}$ = 3.2 Hz), 126.0, 125.9, 125.8 (d, $J_{C–F}$ = 3.4 Hz), 124.0, 123.9, 122.2 (d, $J_{C–F}$ = 3.7 Hz), 122.0, 121.5, 119.7, 119.3, 118.4 (d, $J_{C–F}$ = 4.1 Hz), 118.2, 118.0, 117.4 (d, $J_{C–F}$ = 20.7 Hz), 117.0 (d, $J_{C–F}$ = 20.6 Hz), 113.7, 113.5, 91.8, 91.7, 65.3, 65.1, 62.6, 62.5, 38.3, 38.2, 37.1, 37.0, 18.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –110.29, –111.11; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrFN_3O_2$ 606.1187, Found 606.1183.

1'-Bromo-4'-(3-chlorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3al)



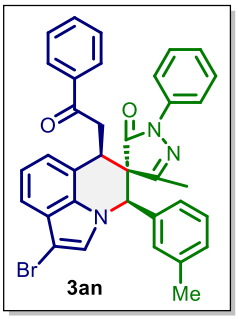
3al was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3-chlorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2l** (74.2 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (138.6 mg, 89%), **MP**: 206.9–207.2 °C; $\mathbf{R_f}$ = 0.28 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.52–7.46 (m, 5.58H), 7.35–7.27 (m, 4H), 7.23 (dd, *J* = 10.7, 5.0 Hz, 0.59H), 7.20–7.08 (m, 3H), 6.93 (s, 0.48H), 6.89 (s, 0.50H), 6.84 (t, *J* = 7.1 Hz, 1H), 5.75 (s, 0.50H), 5.72 (s, 0.50H), 4.85 (d, *J* = 9.4 Hz, 1H), 3.55–3.45 (m, 1H), 2.82 (ddd, *J* = 17.5, 6.7, 1.7 Hz, 1H), 1.62 (s, 1.41H), 1.57 (s, 1.58H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 196.3, 171.4, 158.8, 136.8, 136.8, 136.2, 135.1, 134.5, 134.2, 134.2, 133.8, 133.6, 130.9, 130.5, 130.4, 130.2, 129.9, 129.1, 128.9, 128.4, 126.5, 126.0, 125.9, 125.8, 125.7, 124.5, 123.9, 123.8, 122.0, 121.4, 121.4, 119.7, 119.7, 119.4, 119.4, 118.4, 91.9, 91.7, 65.2, 65.0, 62.6, 62.5, 38.3, 38.2, 36.9, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{34}H_{25}BrClN_3NaO_2$ 644.0711, Found 644.0710.

1'-Bromo-4'-(3-bromophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3am)



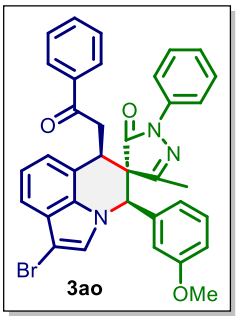
3am was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3-bromobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2m** (85.3 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (138.5 mg, 83%), **MP**: 234.9–235.4 °C; $\mathbf{R_f}$ = 0.24 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.66 (s, 0.60H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52–7.46 (m, 6H), 7.39–7.27 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 0.51H), 7.18–7.13 (m, 3H), 6.93 (s, 0.46H), 6.90 (s, 0.54H), 6.85 (t, *J* = 7.8 Hz, 1H), 5.73 (s, 0.48H), 5.71 (s, 0.49H), 4.85 (d, *J* = 9.2 Hz, 1H), 3.56–3.43 (m, 1H), 2.82 (dd, *J* = 17.4, 7.8 Hz, 1H), 1.62 (s, 1.40H), 1.57 (s, 1.61H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 196.3, 171.4, 158.8, 136.9, 136.8, 136.2, 134.5, 134.4, 133.8, 133.7, 133.6, 133.3, 133.2, 130.8, 130.2, 129.6, 129.4, 129.0, 128.9, 128.4, 126.0, 125.9, 125.0, 123.9, 123.8, 123.2, 122.6, 122.0, 121.5, 121.4, 119.7, 119.7, 119.5, 119.4, 118.4, 92.0, 91.7, 65.1, 65.0, 63.0, 62.6, 38.4, 38.2, 36.9, 36.8, 18.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}Br_2N_3O_2$ 666.0386, Found 666.0379.

1'-Bromo-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'-(*m*-tolyl)-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3an)



3an was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-5-methyl-4-(3-methylbenzylidene)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2n** (69.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (106.9 mg, 71%), **MP**: 203.2–203.6 °C; $\mathbf{R_f}$ = 0.25 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49–7.45 (m, 5H), 7.28 (d, *J* = 7.7 Hz, 1.80H), 7.25 (d, *J* = 9.7 Hz, 1.37H), 7.19–7.11 (m, 3.60H), 7.02–6.97 (m, 1H), 6.94 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.74 (s, 0.41H), 5.71 (s, 0.59H), 4.86 (d, *J* = 9.5 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.83 (dd, *J* = 17.1, 5.5 Hz, 1H), 2.33 (s, 1.20H), 2.21 (s, 1.80H), 1.60 (s, 1.20H), 1.57 (s, 1.80H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.55, 171.78, 171.68, 159.27, 139.10, 138.14, 136.99, 136.93, 136.21, 133.73, 133.57, 131.90, 131.39, 130.87, 130.60, 129.05, 128.89, 128.83, 128.78, 128.40, 128.09, 126.73, 125.79, 125.71, 125.64, 124.29, 124.23, 123.37, 121.77, 121.55, 119.54, 119.47, 119.36, 118.20, 91.11, 65.74, 62.71, 38.43, 38.31, 37.00, 36.77, 21.86, 21.18, 18.02, 17.98; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_2$ 602.1438, Found 602.1439.

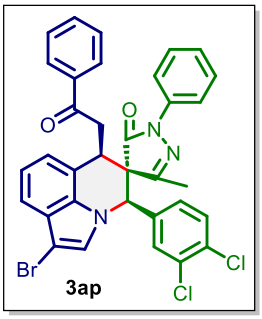
1'-Bromo-4'-(3-methoxyphenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ao)



3ao

3ao was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3-methoxybenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2o** (73.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (99.0 mg, 64%), **MP**: 148.6–149.1 °C; $\mathbf{R_f}$ = 0.27 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52–7.46 (m, 5H), 7.28 (t, *J* = 8.0 Hz, 2.40H), 7.22 (t, *J* = 7.9 Hz, 0.61H), 7.14 (dd, *J* = 16.9, 8.0 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 0.44H), 6.98 (s, 1.47H), 6.85 (dd, *J* = 12.7, 6.6 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 0.52H), 6.73 (s, 0.42H), 5.76 (s, 0.47H), 5.71 (s, 0.49H), 4.86 (d, *J* = 9.4 Hz, 1H), 3.75 (s, 1.44H), 3.65 (s, 1.48H), 3.50 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.83 (dd, *J* = 17.3, 4.0 Hz, 1H), 1.61 (s, 1.47H), 1.58 (s, 1.48H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.7, 171.6, 160.0, 159.4, 159.3, 159.1, 137.0, 137.0, 136.2, 133.8, 133.6, 133.5, 133.5, 130.3, 129.6, 128.9, 128.8, 128.4, 125.8, 125.7, 125.7, 124.4, 124.2, 123.1, 121.8, 121.5, 121.5, 119.5, 119.3, 118.5, 118.2, 116.0, 115.8, 115.0, 112.6, 91.2, 65.7, 65.4, 62.7, 62.6, 55.4, 55.4, 38.3, 38.3, 37.0, 36.9, 18.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_3$ 618.1387, Found 618.1384.

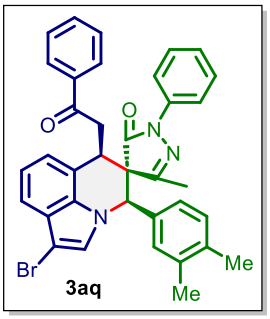
1'-Bromo-4'-(3,4-dichlorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ap)



3ap

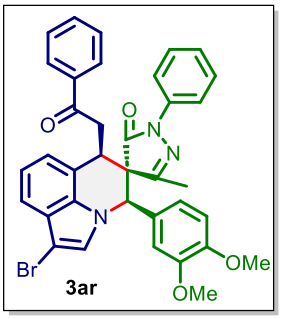
3ap was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3,4-dichlorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2p** (82.8 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (134.8 mg, 82%), **MP**: 130.2–130.9 °C; $\mathbf{R_f}$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1.53H), 7.54–7.44 (m, 5.72H), 7.37–7.28 (m, 3.69H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 0.49H), 6.90 (s, 0.47H), 6.88–6.81 (m, 1.50H), 5.73 (s, 0.47H), 5.71 (s, 0.49H), 4.84 (d, *J* = 9.3 Hz, 1H), 3.55–3.44 (m, 1H), 2.81 (dd, *J* = 17.4, 6.8 Hz, 1H), 1.61 (s, 1.42H), 1.58 (s, 1.57H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.3, 196.2, 171.4, 158.7, 136.8, 136.7, 136.2, 133.9, 133.6, 132.7, 131.2, 130.8, 130.2, 129.1, 129.0, 128.4, 126.2, 126.1, 125.6, 123.7, 123.6, 122.1, 121.3, 119.8, 119.4, 119.3, 118.5, 92.1, 64.6, 64.5, 62.6, 62.5, 38.2, 36.9, 36.9, 18.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{25}BrCl_2N_3O_2$ 656.0502, Found 656.0487.

1'-Bromo-4'-(3,4-dimethylphenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3aq)



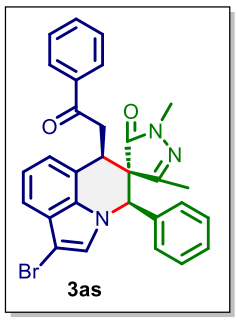
3aq was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3,4-dimethylbenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2q** (72.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (90.9 mg, 59%), **MP**: 194.3–194.7 °C; $\mathbf{R}_f$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03–7.98 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51–7.45 (m, 5H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.21–7.08 (m, 3.75H), 7.04 (d, *J* = 7.7 Hz, 0.36H), 6.93 (dd, *J* = 10.1, 4.7 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.70 (s, 0.38H), 5.69 (s, 0.59H), 4.85 (d, *J* = 9.5 Hz, 1H), 3.49 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.82 (ddd, *J* = 17.4, 8.9, 1.9 Hz, 1H), 2.23 (s, 1.20H), 2.19 (d, *J* = 5.0 Hz, 3H), 2.11 (s, 1.82H), 1.60 (s, 1.21H), 1.57 (s, 1.79H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 171.9, 171.8, 159.4, 159.3, 138.7, 138.5, 137.6, 137.1, 137.0, 136.8, 136.2, 133.7, 133.6, 131.9, 130.2, 129.8, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 127.2, 125.7, 125.7, 124.3, 124.3, 123.7, 121.7, 121.6, 119.6, 119.4, 118.2, 91.0, 65.5, 65.4, 62.8, 62.7, 38.5, 38.3, 37.1, 36.9, 20.4, 19.7, 19.6, 19.5, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{31}BrN_3O_2$ 616.1594, Found 616.1588.

1'-Bromo-4'-(3,4-dimethoxyphenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3ar)



3ar was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(3,4-dimethoxybenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2r** (80.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (90.8 mg, 56%), **MP**: 127.9–128.2 °C; $\mathbf{R}_f$ = 0.20 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.60–7.53 (m, 2H), 7.51–7.45 (m, 3H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.17–7.11 (m, 2H), 7.05 (dd, *J* = 8.2, 1.9 Hz, 0.41H), 7.01 (s, 0.53H), 6.92 (s, 1H), 6.84 (dd, *J* = 7.9, 4.7 Hz, 1.55H), 6.80–6.73 (m, 1H), 6.65 (d, *J* = 1.9 Hz, 0.39H), 5.70 (s, 1H), 4.84 (d, *J* = 9.4 Hz, 1H), 3.85 (s, 1.68H), 3.81 (s, 1.23H), 3.78 (s, 1.30H), 3.72 (s, 1.68H), 3.49 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.86–2.78 (m, 1H), 1.61 (s, 1.20H), 1.57 (s, 1.73H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 171.9, 171.7, 159.4, 159.1, 150.3, 149.8, 149.1, 148.7, 137.0, 136.2, 133.7, 133.6, 128.9, 128.8, 128.4, 125.7, 125.7, 124.4, 124.3, 124.0, 123.9, 121.8, 121.7, 121.5, 119.5, 119.4, 119.3, 119.0, 118.9, 118.2, 113.7, 111.1, 111.0, 109.2, 91.1, 65.6, 65.2, 62.9, 56.0, 38.2, 37.1, 36.9, 17.9; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{31}BrN_3O_4$ 648.1492, Found 648.1489.

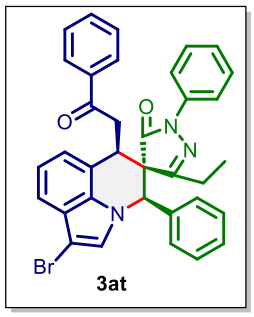
1'-Bromo-1,3-dimethyl-6'-(2-oxo-2-phenylethyl)-4'-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3as)



3as

3as was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-2,5-dimethyl-2,4-dihydro-3*H*-pyrazol-3-one **2s** (50.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (113.2 mg, 86%), **MP**: 213.7–213.9 °C; $\mathbf{R}_f$ = 0.20 (10% ethyl acetate in hexanes); **^{1}H NMR (700 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 4.9 Hz, 2H), 7.62 (s, 1H), 7.51 (s, 2H), 7.46 (d, *J* = 6.5 Hz, 1H), 7.41 (s, 4H), 7.14 (d, *J* = 10.8 Hz, 2H), 6.89 (s, 1H), 6.82 (s, 1H), 5.65 (s, 1H), 4.75 (d, *J* = 7.9 Hz, 1H), 3.42 (dd, *J* = 16.7, 9.5 Hz, 1H), 2.88 (s, 3H), 2.70 (d, *J* = 17.4 Hz, 1H), 1.48 (s, 3H); **^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$)** δ 196.5, 173.0, 158.4, 136.3, 133.7, 133.7, 132.2, 131.0, 129.9, 129.1, 128.9, 128.5, 128.4, 126.4, 125.7, 124.2, 121.8, 121.7, 119.3, 118.2, 91.1, 65.4, 61.5, 38.4, 36.4, 30.9, 17.9; **HRMS (ESI/Q-TOF)** m/z: [M+H] + Calcd for $C_{29}H_{25}BrN_3O_2$ 526.1125, Found 526.1105.

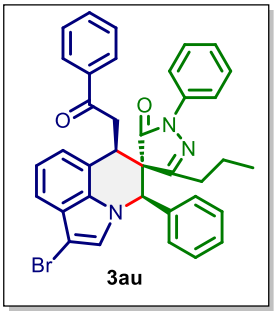
1'-Bromo-3-ethyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3at)



3at

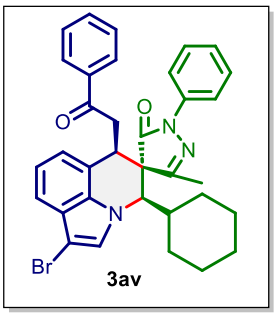
3at was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-ethyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2t** (69.0 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (137.1 mg, 91%), **MP**: 193.9–194.2 °C; $\mathbf{R}_f$ = 0.28 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53–7.45 (m, 5H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.37–7.26 (m, 4H), 7.25 (s, 1H), 7.17–7.10 (m, 3H), 6.92 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.75 (s, 1H), 4.85 (d, *J* = 9.3 Hz, 1H), 3.46 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.81 (dd, *J* = 17.5, 2.0 Hz, 1H), 1.74–1.61 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 171.9, 162.7, 137.2, 136.3, 133.7, 133.6, 132.1, 130.9, 130.0, 129.2, 128.9, 128.8, 128.5, 128.4, 126.3, 125.7, 124.2, 121.8, 121.7, 119.5, 119.5, 118.3, 65.8, 62.8, 38.3, 37.1, 24.9, 8.6; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_2$ 602.1438, Found 602.1417.

1'-Bromo-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-3-propyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3au)



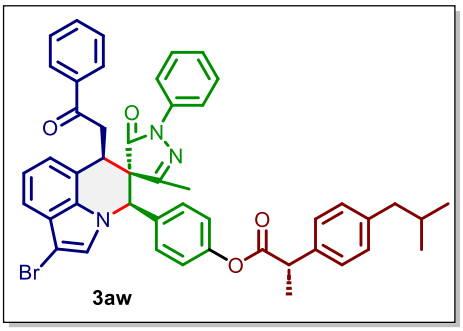
3au was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-2-phenyl-5-propyl-2,4-dihydro-3*H*-pyrazol-3-one **2u** (69.0 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (135.6 mg, 88%), **MP**: 204.2–204.7 °C; **R_f** = 0.43 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52–7.46 (m, 5H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.38–7.27 (m, 4H), 7.25 (s, 1H), 7.21–7.09 (m, 3H), 6.93 (s, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 5.74 (s, 1H), 4.84 (d, *J* = 9.3 Hz, 1H), 3.48 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.81 (dd, *J* = 17.5, 2.0 Hz, 1H), 1.69–1.58 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 171.8, 161.6, 137.2, 136.3, 133.7, 133.7, 132.1, 130.9, 130.0, 129.2, 128.9, 128.1, 128.4, 126.5, 125.7, 125.7, 124.2, 121.8, 121.7, 119.5, 119.4, 118.2, 91.2, 65.8, 62.8, 38.3, 37.1, 33.1, 17.6, 13.8; **HRMS (ESI/Q-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{36}H_{30}BrN_3NaO_2$ 638.1414, Found 638.1491.

1'-Bromo-4'-cyclohexyl-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (3av)



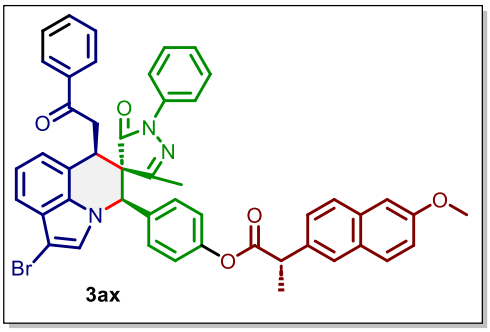
3av was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-(cyclohexylmethylene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2v** (67.1 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (93.6 mg, 63%), **MP**: 182.3–182.8 °C; **R_f** = 0.38 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.49–7.41 (m, 5H), 7.40 (s, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.2 Hz, 1H), 4.78 (d, *J* = 2.1 Hz, 1H), 4.69 (d, *J* = 9.2 Hz, 1H), 3.36 (dd, *J* = 17.6, 9.7 Hz, 1H), 2.73 (d, *J* = 17.4 Hz, 1H), 2.20 (t, *J* = 11.2 Hz, 1H), 1.81 (d, *J* = 11.1 Hz, 4H), 1.69 (d, *J* = 12.6 Hz, 1H), 1.50–1.41 (m, 1H), 1.37 (s, 3H), 1.34–1.19 (m, 3H), 1.18–1.09 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 172.6, 162.0, 137.5, 136.3, 133.7, 133.6, 129.3, 128.9, 128.4, 125.8, 125.2, 123.3, 121.6, 121.5, 119.2, 119.1, 117.9, 91.3, 65.5, 59.6, 41.3, 39.5, 37.0, 30.2, 27.4, 27.3, 26.3, 17.7; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{33}BrN_3O_2$ 594.1751, Found 594.1743.

4-(1'-Bromo-3-methyl-5-oxo-6'-(2-oxo-2-phenylethyl)-1-phenyl-1,5-dihydro-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-4'-yl)phenyl (2*S*)-2-(4-isobutylphenyl)propanoate (3aw)



3aw was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-((3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)methyl)-phenyl 2-(4-isobutylphenyl)propanoate **2w** (116.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (164.5 mg, 83%), **MP**: 135.2–136.0 °C; $\mathbf{R_f}$ = 0.16 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52–7.40 (m, 7H), 7.32–7.27 (m, 2H), 7.22–7.16 (m, 2H), 7.16–7.11 (m, 4H), 7.09–6.93 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 5.75 (d, *J* = 2.4 Hz, 1H), 4.85 (d, *J* = 9.2 Hz, 1H), 3.90 (q, *J* = 6.8 Hz, 1H), 3.48 (dd, *J* = 17.4, 9.6 Hz, 1H), 2.82 (d, *J* = 17.5 Hz), 2.47 (d, *J* = 7.1 Hz, 2H), 1.89–1.83 (m, 1H), 1.59–1.56 (m, 6H), 0.91 (d, *J* = 6.6 Hz, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 172.8, 171.6, 158.9, 152.0, 141.0, 137.1, 137.0, 136.8, 136.2, 133.8, 133.6, 132.1, 132.1, 129.7, 129.5, 129.5, 128.9, 128.4, 127.3, 127.3, 126.0, 125.7, 124.0, 122.3, 122.2, 121.9, 121.5, 119.9, 119.8, 119.5, 118.3, 91.5, 65.0, 62.6, 45.3, 45.1, 38.3, 37.0, 36.9, 30.3, 22.5, 18.6, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{47}H_{43}BrN_3O_4$ 792.2431, Found 792.2430.

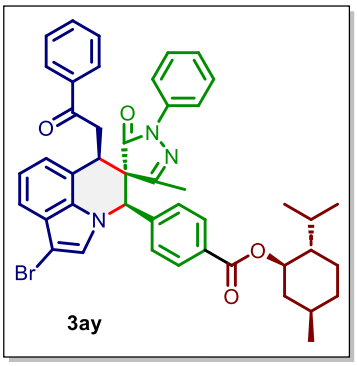
4-(1'-Bromo-3-methyl-5-oxo-6'-(2-oxo-2-phenylethyl)-1-phenyl-1,5-dihydro-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-4'-yl)phenyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (3ax)



3ax was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenyl-prop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-((3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)methyl)phenyl (*S*)-2-(6-methoxynaph-thalen-2-yl)propanoate **2x** (122.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (157.2 mg, 77%), **MP**: 132.5–132.9 °C; $\mathbf{R_f}$ = 0.19 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 9.4 Hz, 3H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49–7.39 (m, 7H), 7.26–7.21 (m, 2H), 7.19–7.05 (m, 6H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.91–6.88 (m, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 5.74 (d, *J* = 3.6 Hz, 1H), 4.84 (d, *J* = 9.3 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 3.48 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.81 (d, *J* = 17.5 Hz, 1H), 1.67 (dd, *J* = 7.0, 2.8 Hz, 3H), 1.55 (d, *J* = 8.8 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 172.8, 172.8, 171.6, 158.9, 157.9, 152.0, 151.9, 136.7,

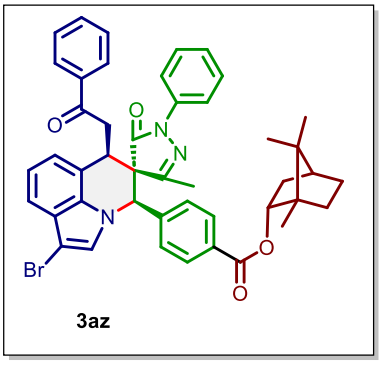
136.2, 135.0, 134.9, 133.9, 133.8, 133.6, 132.14 132.1, 129.5, 129.5, 129.4, 129.1, 128.9, 128.4, 127.6, 127.3, 126.2, 126.1, 125.9, 125.7, 124.1, 122.2, 122.1, 121.9, 121.5, 119.8, 119.8, 119.5, 119.3, 118.3, 105.7, 91.4, 65.0, 62.6, 62.6, 55.4, 45.6, 38.2, 36.9, 18.6, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{47}H_{39}BrN_3O_5$ 816.2068, Found 816.2094.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-(1'-bromo-3-methyl-5-oxo-6'-(2-oxo-2-phenylethyl)-1-phenyl-1,5-dihydro-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-4'-yl)benzoate (3ay)



3ay was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-((*Z*)-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)me thyl)benzoate **2y** (111.2 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (136.8 mg, 71%), **MP**: 210.8–211.4 °C; **R_f** = 0.23 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.08–7.93 (m, 4H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.53–7.42 (m, 6H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.24–7.11 (m, 3H), 6.92–6.83 (m, 2H), 5.83 (s, 1H), 4.88 (d, *J* = 10.1 Hz, 2H), 3.50 (dd, *J* = 17.5, 9.5 Hz, 1H), 2.83 (d, *J* = 17.5 Hz, 1H), 2.10 (d, *J* = 11.5 Hz, 1H), 1.91–1.81 (m, 1H), 1.72 (d, *J* = 11.4 Hz, 2H), 1.60 (s, 3H), 1.54–1.41 (m, 2H),), 1.29–1.26 (m, 1H), 1.15–1.03 (m, 2H), 0.91 (dd, *J* = 11.0, 6.8 Hz, 6H), 0.75 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.4, 171.5, 165.3, 158.9, 136.8, 136.8, 136.2, 133.8, 133.6, 132.4 131.0, 130.4, 129.8, 129.0, 128.9, 128.4, 126.4, 126.0, 125.7, 124.0, 122.0, 121.5, 119.7, 119.5, 118.5, 91.8, 75.4, 65.4, 62.6, 47.3, 41.0, 38.2, 37.0, 34.4, 31.5, 26.6, 23.7, 22.2, 20.9, 18.1, 16.6; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{45}H_{45}BrN_3O_4$ 770.2588, Found 770.2595.

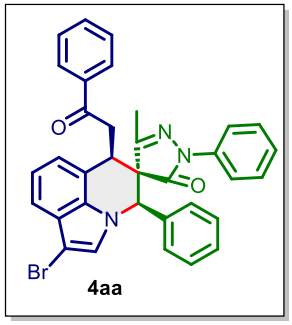
(1*R*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(1'-bromo-3-methyl-5-oxo-6'-(2-oxo-2-phenylethyl)-1-phenyl-1,5-dihydro-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-4'-yl)benzoate (3az)



3az was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (102.0 mg, 0.312 mmol, 1.25 equiv) and (1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((*Z*)-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)methyl)benzoate **2z** (110.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (132.6 mg, 69%), **MP**: 205.8–206.2 °C; **R_f** = 0.36 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ

8.07 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 3H), 7.61–7.53 (m, 2H), 7.50–7.46 (m, 5H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 7.8 Hz), 7.18–7.11 (m, 2H), 6.89–6.83 (m, 2H), 5.84 (s, 1H), 5.14–5.01 (m, 1H), 4.88 (d, *J* = 9.3 Hz, 1H), 3.50 (dd, *J* = 17.5, 9.6 Hz, 1H), 2.83 (d, *J* = 17.4 Hz, 1H), 2.52–2.39 (m, 1H), 2.10–2.02 (m, 1H), 1.81 (ddd, *J* = 11.9, 8.0, 4.0 Hz, 1H), 1.74 (t, *J* = 4.3 Hz, 1H), 1.61 (s, 3H), 1.39 (dd, *J* = 16.2, 8.5 Hz, 1H), 1.33–1.24 (m, 2H), 1.13–1.05 (m, 1H), 0.96 (s, 3H), 0.91 (s, 3H), 0.89 (d, *J* = 9.5 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.3, 171.4, 165.9, 165.9, 158.9, 136.9, 136.8, 136.8, 136.2, 133.8, 133.6, 132.4, 132.4, 131.1, 130.3, 129.7, 128.9, 128.4, 126.5, 126.0, 125.9, 125.7, 123.9, 122.0, 121.4, 119.7, 119.4, 119.3, 118.4, 91.7, 81.1, 81.0, 65.3, 62.5, 49.2, 49.2, 48.0, 45.0, 38.2, 37.1, 37.0, 36.9, 28.1, 27.5, 19.8, 19.0, 18.0, 13.7; **HRMS (ESI/Q-TOF)** *m/z*: [M+H]$^+$ Calcd for $C_{45}H_{43}BrN_3O_4$ 768.2431, Found 768.2438.

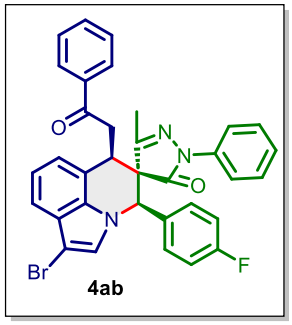
1'-Bromo-3-methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (4aa)



4aa

4aa was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_3PO_4 (159.2 mg, 0.75 mmol, 3.0 equiv) in MeCN (3.0 mL) at rt for 24 h followed by column chromatography (EtOAc/Hexanes). White solid (75.0 mg, 51%), **MP**: 209.6–209.9 °C; **R$_f$** = 0.22 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.62–7.46 (m, 7H), 7.38–7.28 (m, 6H), 7.12 (d, *J* = 4.1 Hz, 2H), 6.74 (d, *J* = 7.1 Hz, 1H), 6.71 (s, 1H), 5.61 (s, 1H), 4.77 (d, *J* = 8.1 Hz, 1H), 3.76 (dd, *J* = 17.8, 8.4 Hz, 1H), 2.68 (d, *J* = 17.9 Hz, 1H), 2.29 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 197.2, 170.4, 158.7, 137.3, 136.1, 134.2, 134.0, 132.6, 130.3, 129.0, 128.8, 128.5, 125.4, 124.5, 121.5, 120.3, 119.5, 118.9, 118.0, 91.3, 62.8, 60.6, 38.1, 35.7, 14.6; **HRMS (ESI/Q-TOF)** *m/z*: [M+H]$^+$ Calcd for $C_{34}H_{27}BrN_3O_2$ 588.1281, Found 588.1277.

1'-Bromo-4'-(4-fluorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (4ab)

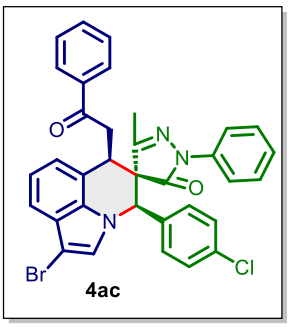


4ab

4ab was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv) and (*Z*)-4-(4-fluorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2b** (70.1 mg, 0.25 mmol, 1.0 equiv) with K_3PO_4 (159.2 mg, 0.75 mmol, 3.0 equiv) in MeCN (3.0 mL) at rt for 24 h followed by column chromatography (EtOAc/Hexanes). White solid (69.7 mg, 46%), **MP**: 228.6–228.9 °C; **R$_f$** = 0.27 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.64–7.56 (m, 3H), 7.48 (t, *J* = 7.9 Hz, 3H), 7.42–7.35 (m, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.16–7.11 (m, 2H), 7.07–6.87 (m, 2H), 6.75 (d, *J* = 7.3 Hz, 1H), 6.68

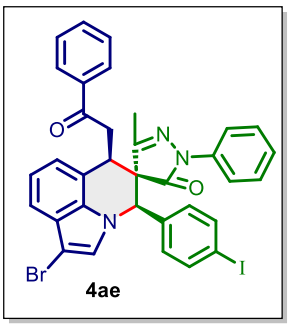
(s, 1H), 5.60 (s, 1H), 4.76 (d, *J* = 8.2 Hz, 1H), 3.76 (dd, *J* = 17.9, 8.6 Hz, 1H), 2.67 (dd, *J* = 17.9, 2.3 Hz, 1H), 2.28 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 197.1, 170.3, 163.6 (d, J_{C-F} = 251.1 Hz), 158.6, 137.2, 136.1, 134.1 (d, J_{C-F} = 8.4 Hz), 129.1, 128.9, 128.5, 125.6, 125.5, 124.2, 121.6, 120.2, 119.6, 118.8, 118.1, 91.6, 61.9, 60.7, 38.1, 35.6, 14.6; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –110.10; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrFN_3O_2$ 606.1187, Found 606.1201.

1'-Bromo-4'-(4-chlorophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (4ac)



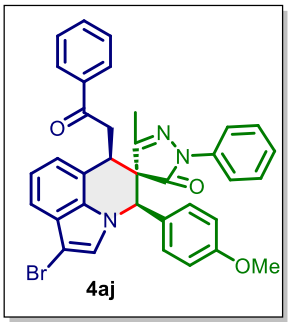
4ac was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv) and (*Z*)-4-(4-chlorobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2c** (74.2 mg, 0.25 mmol, 1.0 equiv) with K_3PO_4 (159.2 mg, 0.75 mmol, 3.0 equiv) in MeCN (3.0 mL) at rt for 24 h followed by column chromatography (EtOAc/Hexanes). White solid (65.4 mg, 42%), **MP**: 242.2–242.5 °C; **R_f** = 0.22 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04–7.97 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.59–7.55 (m, 2H), 7.49–7.42 (m, 3H), 7.43–7.35 (m, 1H), 7.36–7.28 (m, 5H), 7.17–7.11 (m, 2H), 6.74 (d, *J* = 7.3 Hz, 1H), 6.67 (s, 1H), 5.59 (s, 1H), 4.75 (d, *J* = 8.3 Hz, 1H), 3.75 (dd, *J* = 17.9, 8.6 Hz, 1H), 2.67 (dd, *J* = 17.9, 2.3 Hz, 1H), 2.28 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 197.1, 170.2, 158.6, 137.2, 136.3, 136.1, 134.1, 131.3, 129.0, 128.9, 128.5, 125.6, 125.4, 124.2, 121.6, 120.1, 119.7, 118.9, 118.1, 91.7, 62.0, 60.5, 38.0, 35.6, 14.6; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrClN_3O_2$ 622.0891, Found 622.0882.

1'-Bromo-4'-(4-iodophenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (4ae)



4ae was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv) and (*Z*)-4-(4-iodobenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2e** (97.0 mg, 0.25 mmol, 1.0 equiv) with K_3PO_4 (159.2 mg, 0.75 mmol, 3.0 equiv) in MeCN (3.0 mL) at rt for 24 h followed by column chromatography (EtOAc/Hexanes). White solid (76.8 mg, 43%), **MP**: 258.2–258.6 °C; **R_f** = 0.22 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.73 (s, 1H), 7.61 (t, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.51–7.44 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.17–7.10 (m, 4H), 6.74 (d, *J* = 7.3 Hz, 1H), 6.67 (s, 1H), 5.55 (s, 1H), 4.75 (d, *J* = 8.1 Hz, 1H), 3.74 (dd, *J* = 17.9, 8.6 Hz, 1H), 2.66 (d, *J* = 17.8 Hz, 1H), 2.27 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 197.1, 170.2, 158.5, 137.1, 136.1, 134.1, 132.4, 129.0, 128.9, 128.5, 125.6, 125.4, 124.2, 121.6, 120.1, 119.7, 118.9, 118.1, 96.4, 91.7, 62.2, 60.4, 38.0, 35.6, 14.6; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrIN_3O_2$ 714.0248, Found 714.0238.

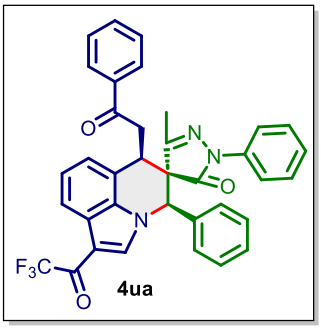
1'-Bromo-4'-(4-methoxyphenyl)-3-methyl-6'-(2-oxo-2-phenylethyl)-1-phenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (4aj)



4aj

4aj was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv) and (*Z*)-4-(4-methoxybenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2j** (73.1 mg, 0.25 mmol, 1.0 equiv) with K_3PO_4 (159.2 mg, 0.75 mmol, 3.0 equiv) in MeCN (3.0 mL) at rt for 24 h followed by column chromatography (EtOAc/Hexanes). White solid (89.7 mg, 58%), **MP**: 214.9–215.2 °C; $\mathbf{R_f}$ = 0.21 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 8.2 Hz, 3H), 7.47 (dd, *J* = 13.6, 7.4 Hz, 3H), 7.29 (t, *J* = 8.3 Hz, 4H), 7.16–7.09 (m, 2H), 6.88 (s, 1H), 6.79–6.69 (m, 3H), 5.57 (s, 1H), 4.76 (d, *J* = 8.2 Hz, 1H), 3.81–3.76 (m, 0.46H), 3.75 (s, 3H), 3.71 (d, *J* = 12.4 Hz, 0.52H), 2.67 (d, *J* = 17.9 Hz, 1H), 2.27 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 197.3, 170.6, 160.8, 158.9, 137.4, 136.1, 134.2, 134.0, 129.0, 128.8, 128.5, 125.5, 125.4, 124.4, 124.3, 121.5, 120.3, 119.5, 118.9, 118.0, 91.2, 62.3, 60.7, 55.4, 38.1, 35.8, 14.6; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{29}BrN_3O_3$ 618.1387, Found 618.1385.

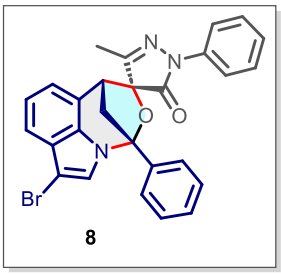
3-Methyl-6'-(2-oxo-2-phenylethyl)-1,4'-diphenyl-1'-(2,2,2-trifluoroacetyl)-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (4ua)



4ua

4ua was prepared by following general procedure, treatment of (*E*)-1-phenyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one **1u** (77.3 mg, 0.312 mmol, 1.25 equiv) and (*Z*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **2a** (65.6 mg, 0.25 mmol, 1.0 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in EtOAc (3.0 mL) at rt for 12 h followed by column chromatography (EtOAc/Hexanes). White solid (50.0 mg, 33%), **MP**: 213.9–214.4 °C; $\mathbf{R_f}$ = 0.13 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.53–7.43 (m, 6H), 7.36–7.27 (m, 5H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.70 (s, 1H), 4.81 (d, *J* = 8.3 Hz, 1H), 3.75 (dd, *J* = 18.0, 8.7 Hz, 1H), 2.68 (dd, *J* = 18.0, 1.8 Hz, 1H), 2.30 (s, 3H); **^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$)** δ 196.9, 175.2 (d, J_{C-F} = 34.7 Hz), 170.2, 158.3, 137.1, 135.9, 134.9, 134.2, 131.1, 130.9, 130.3, 129.8, 129.4, 129.1, 128.9, 128.5, 127.0, 125.8, 125.1, 124.8, 121.6, 121.3, 121.1, 119.0, 116.9 (d, J_{C-F} = 291.1 Hz), 111.0, 63.3, 60.5, 38.0, 35.7, 14.6; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –72.41; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{27}F_3N_3O_3$ 606.1999, Found 606.1977.

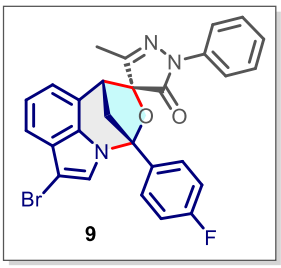
7'-Bromo-3-methyl-1,4'-diphenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (8)



8

8 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (115.8 mg, 93%), **MP**: 172.9–173.2 °C; $\mathbf{R_f}$ = 0.47 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.73–7.66 (m, 2H), 7.51 (dd, *J* = 6.5, 2.8 Hz, 3H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.21–7.14 (m, 2H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.79 (s, 1H), 3.95 (d, *J* = 4.5 Hz, 1H), 3.80 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.05 (d, *J* = 11.6 Hz, 1H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 160.4, 137.9, 134.9, 134.5, 129.8, 129.0, 126.7, 126.1, 125.3, 123.3, 123.0, 121.9, 119.2, 118.6, 118.6, 97.7, 93.5, 90.5, 47.6, 40.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{20}BrN_3NaO_2$ 520.0631, Found 520.0624.

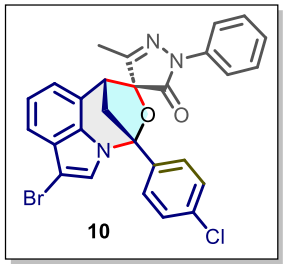
7'-Bromo-4'-(4-fluorophenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (9)



9

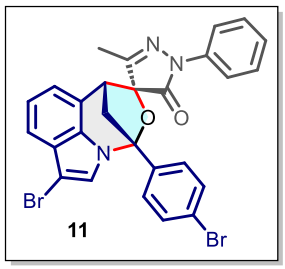
9 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-fluorophenyl)prop-2-en-1-one **1b** (86.0 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (117.5 mg, 91%), **MP**: 153.9–154.2 °C; $\mathbf{R_f}$ = 0.44 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.69 (s, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.24–7.13 (m, 4H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.78 (s, 1H), 3.95 (s, 1H), 3.79 (dd, *J* = 6.9, 4.4 Hz, 1H), 3.03 (d, *J* = 11.5 Hz, 1H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 163.5 (d, J_{C-F} = 249.9 Hz), 160.3, 137.8, 134.5, 130.9 (d, J_{C-F} = 4.0 Hz), 129.0, 128.8 (d, J_{C-F} = 8.9 Hz), 126.1, 125.4, 123.1, 122.9, 122.0, 119.3, 118.7, 118.6, 116.0 (d, J_{C-F} = 22.0 Hz), 97.2, 93.6, 90.8, 47.6, 40.5, 13.4; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –111.19; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{20}BrFN_3O_2$ 516.0717, Found 516.0716.

7'-Bromo-4'-(4-chlorophenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (10)



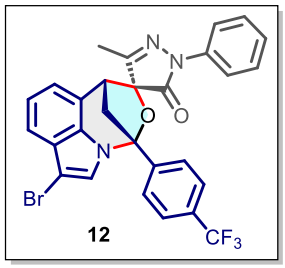
10 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-chlorophenyl)prop-2-en-1-one **1c** (90.2 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (117.2 mg, 88%), **MP**: 199.2–199.9 °C; $\mathbf{R_f}$ = 0.44 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 16.5, 8.3 Hz, 3H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.21–7.15 (m, 2H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.78 (s. 1H), 3.95 (d, *J* = 4.5 Hz, 1H), 3.78 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.02 (d, *J* = 11.6 Hz, 1H), 0.83 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.3, 160.2, 137.8, 135.8, 134.5, 133.5, 129.2, 129.1, 129.0, 128.2, 126.1, 125.4, 123.0, 122.8, 122.0, 119.3, 118.7, 118.6, 97.1, 93.6, 90.9, 47.5, 40.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{20}BrClN_3O_2$ 532.0422, Found 532.0420.

7'-Bromo-4'-(4-bromophenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (11)



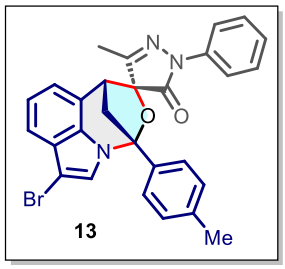
11 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-bromophenyl)prop-2-en-1-one **1d** (101.3 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (134.2 mg, 93%), **MP**: 198.6–199.0 °C; $\mathbf{R_f}$ = 0.44 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.24–7.13 (m, 2H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.78 (s, 1H), 3.95 (d, *J* = 4.1 Hz, 1H), 3.77 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.02 (d, *J* = 11.5 Hz, 1H), 0.83 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.3, 160.2, 137.8, 134.5, 134.0, 132.2, 129.0, 128.5, 126.1, 125.4, 124.1, 123.0, 122.8, 122.0, 119.4, 118.8, 118.6, 97.2, 93.6, 90.9, 47.5, 40.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{20}Br_2N_3O_2$ 575.9917, Found 575.9911.

7'-Bromo-3-methyl-1-phenyl-4'-(4-(trifluoromethyl)phenyl)-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (12)



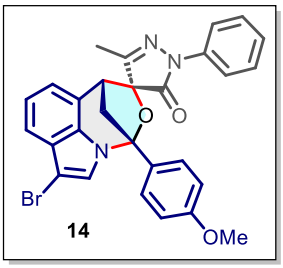
12 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one **1e** (98.6 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (117.5 mg, 83%), **MP**: 177.6–177.9 °C; $\mathbf{R_f}$ = 0.47 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.90–7.83 (m, 4H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.22–7.17 (m, 2H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.76 (s, 1H), 3.98 (d, *J* = 4.4 Hz, 1H), 3.80 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.07 (d, *J* = 11.6 Hz, 1H), 0.85 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.2, 160.1, 138.8, 137.8, 134.6, 132.2, 129.1, 127.3, 126.2, 126.1 (q, $J_{C–F}$ = 4.5 Hz), 125.5, 123.9 (q, $J_{C–F}$ = 273.4 Hz), 122.9, 122.7, 122.2, 119.5, 118.9, 118.6, 97.1, 93.7, 91.2, 47.5, 40.5, 13.4; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –62.65; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{20}BrF_3N_3O_2$ 566.0686, Found 566.0695.

7'-Bromo-3-methyl-1-phenyl-4'-(*p*-tolyl)-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]-oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (13)



13 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(*p*-tolyl)prop-2-en-1-one **1h** (85.1 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (103.8 mg, 81%), **MP**: 185.9–186.2 °C; $\mathbf{R_f}$ = 0.46 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.20–7.13 (m, 2H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.81 (s, 1H), 3.94 (d, *J* = 4.4 Hz, 1H), 3.78 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.03 (d, *J* = 11.6 Hz, 1H), 2.44 (s, 3H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.5, 160.5, 139.7, 137.9, 134.5, 132.0, 129.6, 129.0, 126.6, 126.0, 125.3, 123.4, 123.0, 121.8, 119.2, 118.6, 118.5, 97.7, 93.4, 90.4, 47.6, 40.4, 21.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}BrN_3O_2$ 512.0968, Found 512.0968.

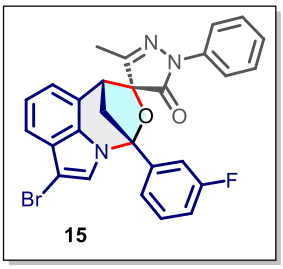
7'-Bromo-4'-(4-methoxyphenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (14)



14

14 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(4-methoxyphenyl)prop-2-en-1-one **1g** (89.1 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/ Hexanes). White solid (95.1 mg, 72%), **MP**: 175.2–175.7 °C; $\mathbf{R_f}$ = 0.38 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.20–7.13 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.81 (s, 1H), 3.94 (d, *J* = 4.5 Hz, 1H), 3.88 (s, 3H), 3.77 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.02 (d, *J* = 11.6 Hz, 1H), 0.83 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.5, 160.6, 160.5, 137.9, 134.5, 129.0, 128.1, 127.1, 126.1, 125.3, 123.3, 123.0, 121.8, 119.2, 118.6, 118.5, 114.3, 97.6, 93.5, 90.4, 55.6, 47.7, 40.5, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}BrN_3O_3$ 528.0917, Found 528.0919.

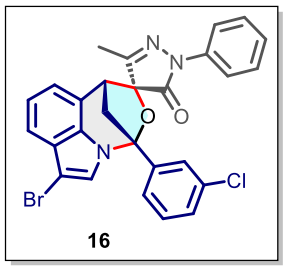
7'-Bromo-4'-(3-fluorophenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (15)



15

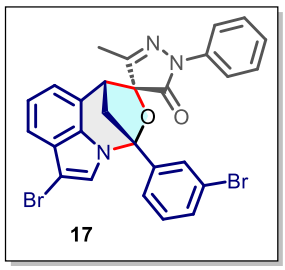
15 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-fluorophenyl)prop-2-en-1-one **1j** (86.1 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (116.2 mg, 90%), **MP**: 184.9–185.2 °C; $\mathbf{R_f}$ = 0.49 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.51–7.43 (m, 4H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.24–7.13 (m, 3H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.79 (s, 1H), 3.96 (d, *J* = 4.5 Hz, 1H), 3.80 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.03 (d, *J* = 11.6 Hz, 1H), 0.83 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.3, 163.0 (d, J_{C-F} = 248.0 Hz), 160.2, 137.8, 137.3 (d, J_{C-F} = 7.9 Hz), 134.5, 130.8 (d, J_{C-F} = 8.5 Hz), 129.1, 126.1, 125.4, 123.1, 122.8, 122.4 (d, J_{C-F} = 4.3 Hz), 122.0, 119.4, 118.8, 118.6, 116.9 (d, J_{C-F} = 21.3 Hz), 114.3 (d, J_{C-F} = 23.7 Hz), 97.0, 93.6, 90.9, 47.5, 40.4, 13.4; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –110.90; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{20}BrFN_3O_2$ 516.0717, Found 516.0702.

7'-Bromo-4'-(3-chlorophenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (16)



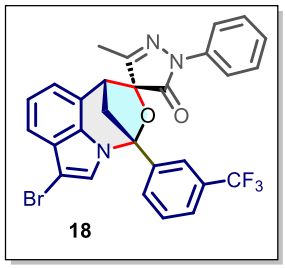
16 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-chlorophenyl)prop-2-en-1-one **1k** (90.2 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (115.9 mg, 87%), **MP**: 198.2–198.9 °C; $\mathbf{R_f}$ = 0.51 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.72 (s, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.50–7.39 (m, 5H), 7.23–7.13 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.77 (s, 1H), 3.96 (d, *J* = 4.3 Hz, 1H), 3.79 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.04 (d, *J* = 11.6 Hz, 1H), 0.83 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.2, 160.2, 137.8, 136.9, 135.1, 134.5, 130.4, 130.1, 129.0, 127.1, 126.1, 125.4, 125.0, 123.0, 122.8, 122.0, 119.4, 118.8, 118.6, 96.9, 93.6, 91.0, 47.5, 40.3, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{19}BrClN_3NaO_2$ 554.0241, Found 554.0231.

7'-Bromo-4'-(3-bromophenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (17)



17 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-bromophenyl)prop-2-en-1-one **1l** (101.3 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (112.6 mg, 78%), **MP**: 161.9–162.2 °C; $\mathbf{R_f}$ = 0.50 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 7.9 Hz, 3H), 7.63 (dd, *J* = 17.4, 7.8 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.42–7.37 (m, 3H), 7.24–7.13 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.77 (s, 1H), 3.96 (d, *J* = 4.3 Hz, 1H), 3.79 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.04 (d, *J* = 11.5 Hz, 1H), 0.83 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.2, 160.2, 137.8, 137.1, 134.5, 133.0, 130.6, 129.9, 129.1, 126.1, 125.4, 123.2, 123.0, 122.8, 122.1, 119.4, 118.8, 118.6, 96.8, 93.6, 91.0, 47.5, 40.3, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{20}Br_2N_3O_2$ 575.9917, Found 575.9915.

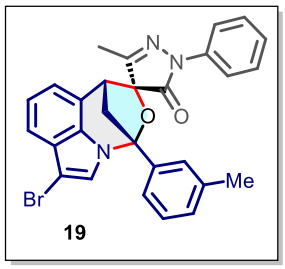
7'-Bromo-3-methyl-1-phenyl-4'-(3-(trifluoromethyl)phenyl)-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (18)



18

18 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one **1m** (98.6 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (106.2 mg, 75%), **MP**: 165.1–165.5 °C; $\mathbf{R_f}$ = 0.49 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.88 (t, *J* = 8.6 Hz, 3H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.25–7.13 (m, 2H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.70 (s, 1H), 3.98 (d, *J* = 4.0 Hz, 1H), 3.82 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.09 (d, *J* = 11.5 Hz, 1H), 0.85 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.2, 160.1, 137.8, 136.1, 134.5, 131.6 (q, $J_{C–F}$ = 33.0 Hz), 130.2, 129.7, 129.1, 126.8 (q, $J_{C–F}$ = 4.5 Hz), 126.2, 125.4, 123.7 (q, $J_{C–F}$ = 4.4 Hz), 124.1 (q, $J_{C–F}$ = 274.5 Hz), 122.8, 122.1, 119.4, 118.9, 118.6, 97.0, 93.7, 91.2, 47.5, 40.3, 13.4; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –62.37; **HRMS (ESI/Q-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{19}BrF_3NaN_3O_2$ 588.0505, Found 588.0501.

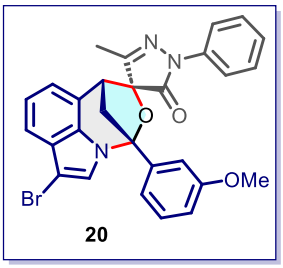
7'-Bromo-3-methyl-1-phenyl-4'-(*m*-tolyl)-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (19)



19

19 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(*m*-tolyl)prop-2-en-1-one **1o** (85.1 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (88.4 mg, 69%), **MP**: 168.2–168.6 °C; $\mathbf{R_f}$ = 0.50 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.52 (s, 1H), 7.48–7.37 (m, 5H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.21–7.14 (m, 2H), 6.97 (d, *J* = 6.8 Hz, 1H), 6.79 (s, 1H), 3.95 (s, 1H), 3.79 (d, *J* = 9.7 Hz, 1H), 3.05 (d, *J* = 11.5 Hz, 1H), 2.44 (s, 3H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 160.5, 138.8, 137.9, 134.8, 134.5, 130.5, 129.0, 128.8, 127.3, 126.0, 125.3, 123.8, 123.4, 123.0, 121.8, 119.2, 118.6, 118.5, 97.7, 93.4, 90.4, 47.6, 40.3, 21.7, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}BrN_3O_2$ 512.0968, Found 512.0983.

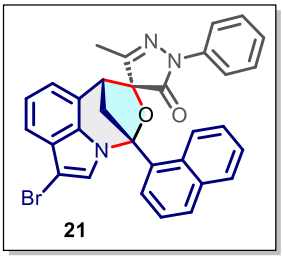
7'-Bromo-4'-(3-methoxyphenyl)-3-methyl-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (20)



20

20 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(3-methoxyphenyl)prop-2-en-1-one **1n** (89.1 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/ Hexanes). White solid (80.6 mg, 61%), **MP**: 191.9–192.3 °C; $\mathbf{R_f}$ = 0.38 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.41 (q, *J* = 7.7 Hz, 3H), 7.25–7.12 (m, 4H), 7.06–7.00 (m, 1H), 6.97 (d, *J* = 7.0 Hz. 1H), 6.83 (s, 1H), 3.94 (d, *J* = 4.5 Hz, 1H), 3.85 (s, 3H), 3.80 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.04 (d, *J* = 11.6 Hz, 1H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 160.4, 160.0, 137.9, 136.3, 134.5, 130.1, 129.1, 129.0, 126.1, 125.3, 123.4, 122.9, 121.9, 119.2, 118.9, 118.6, 115.3, 112.4, 97.5, 93.5, 90.5, 55.6, 47.6, 40.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}BrN_3O_3$ 528.0917, Found 528.0932.

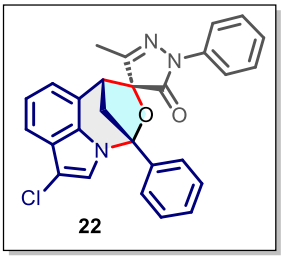
7'-Bromo-3-methyl-4'-(naphthalen-1-yl)-1-phenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (21)



21

21 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-(naphthalen-2-yl)prop-2-en-1-one **1q** (94.1 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (96.0 mg, 70%), **MP**: 210.7–211.2 °C; $\mathbf{R_f}$ = 0.39 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.91 (dd, *J* = 17.1, 7.9 Hz, 4H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.64–7.54 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.23–7.14 (m, 2H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.78 (s, 1H), 4.00 (d, *J* = 4.1 Hz, 1H), 3.88 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.16 (d, *J* = 11.5 Hz, 1H), 0.88 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 160.4, 137.9, 134.6, 133.8, 133.1, 132.1, 129.0, 128.9, 128.8, 127.9, 127.2, 126.9, 126.5, 126.1, 125.3, 123.8, 123.4, 123.0, 121.9, 119.3, 118.6, 97.8, 93.6, 90.6, 47.6, 40.5, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{23}BrN_3O_2$ 548.0968, Found 548.0972.

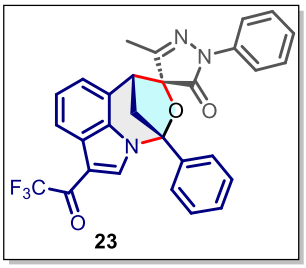
7'-Chloro-3-methyl-1,4'-diphenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (22)



22

22 was prepared by following general procedure, treatment of (*E*)-3-(3-chloro-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1s** (70.4 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (99.9 mg, 88%), **MP**: 165.1–165.5 °C; $\mathbf{R_f}$ = 0.54 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.69 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.51 (dd, *J* = 7.2, 3.5 Hz, 4H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.75 (s, 1H), 3.95 (d, *J* = 4.5 Hz, 1H), 3.80 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.06 (d, *J* = 11.6 Hz, 1H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 160.4, 137.9, 134.9, 134.2, 129.7, 129.0, 126.7, 126.6, 125.3, 124.5, 123.0, 121.7, 121.0, 118.6, 118.5, 105.8, 97.6, 93.5, 47.5, 40.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{21}ClN_3O_2$ 454.1317, Found 454.1328.

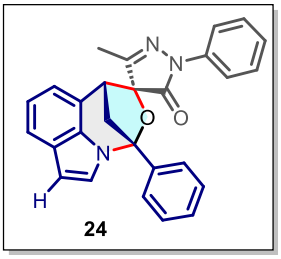
3-Methyl-1,4'-diphenyl-7'-(2,2,2-trifluoroacetyl)-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (23)



23

23 was prepared by following general procedure, treatment of (*E*)-1-phenyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one **1u** (85.8 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (116.0 mg, 90%), **MP**: 217.3–217.9 °C; $\mathbf{R_f}$ = 0.31 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.74–7.66 (m, 2H), 7.60–7.55 (m, 3H), 7.50 (d, *J* = 1.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.38–7.33 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 1H), 4.03 (d, *J* = 4.3 Hz, 1H), 3.93 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.06 (d, *J* = 11.9 Hz, 1H), 0.91 (s); **^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$)** δ 175.5 (d, J_{C-F} = 35.3 Hz), 170.1, 159.4, 137.8, 135.2, 133.4, 132.8, 130.5, 129.4, 129.1, 126.6, 125.6, 125.5, 125.1, 123.4, 122.7, 120.8, 118.6, 116.8 (d, J_{C-F} = 290.4 Hz), 110.8, 98.3, 93.3, 48.0, 40.9, 13.6; **^{19}F NMR (471 MHz, $CDCl_3$)** δ –72.66; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{21}F_3N_3O_3$ 516.1530, Found 516.1517.

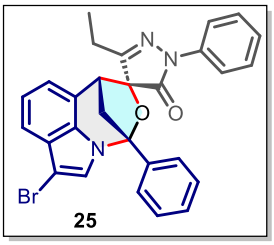
3-Methyl-1,4'-diphenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (24)



24

24 was prepared by following general procedure, treatment of (*E*)-3-(1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1v** (61.8 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (53.5 mg, 51%), **MP**: 193.9–194.2 °C; $\mathbf{R_f}$ = 0.54 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.73–7.67 (m, 2H), 7.51 (dd, *J* = 6.6, 2.9 Hz, 3H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.23–7.13 (m, 2H), 6.97 (d, *J* = 7.0 Hz,1H), 6.79 (s, 1H), 3.95 (d, *J* = 4.5 Hz, 1H), 3.80 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.05 (d, *J* = 11.6 Hz, 1H), 0.84 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.4, 160.4, 137.9, 134.9, 134.5, 129.8, 129.0, 126.7, 126.7, 126.1, 125.3, 123.3, 123.0, 121.9, 119.2, 118.6, 97.6, 93.5, 90.5, 47.6, 40.4, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{21}NaN_3O_2$ 442.1526, Found 442.1531.

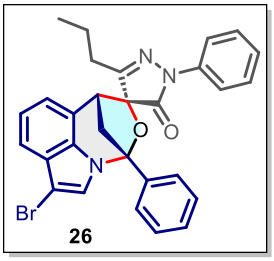
7'-Bromo-3-ethyl-1,4'-diphenyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (25)



25

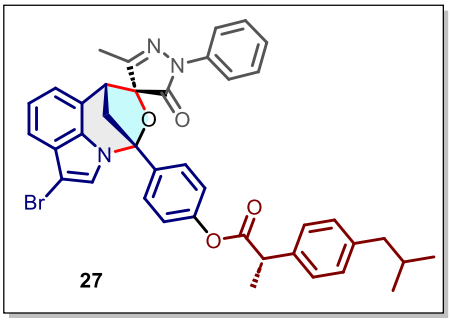
25 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv), 5-ethyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (70.6 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (115.3 mg, 90%), **MP**: 178.8–179.0 °C; $\mathbf{R_f}$ = 0.51 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.70–7.68 (m, 2H), 7.50 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.17–7.12 (m, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.78 (s, 1H), 3.94 (d, *J* = 4.3 Hz, 1H), 3.83 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.03 (d, *J* = 11.6 Hz, 1H), 1.17–1.10 (m, 1H), 0.82 (t, *J* = 7.2 Hz, 3H), 0.72–0.64 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.8, 164.0, 138.1, 135.0, 134.4, 129.7, 129.0, 126.7, 126.0, 125.2, 123.3, 123.1, 121.8, 119.2, 118.6, 97.6, 94.0, 90.5, 47.7, 40.3, 20.8, 9.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}BrN_3O_2$ 512.0968, Found 512.0953.

7'-Bromo-1,4'-diphenyl-3-propyl-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-5(1*H*)-one (26)



26 was prepared by following general procedure, treatment of (*E*)-3-(3-bromo-1*H*-indol-7-yl)-1-phenylprop-2-en-1-one **1a** (81.6 mg, 0.25 mmol, 1.0 equiv), 2-phenyl-5-propyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (75.8 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (110.6 mg, 84%), **MP**: 179.3–180.0 °C; $\mathbf{R_f}$ = 0.46 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93–7.86 (m, 2H), 7.70 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.54–7.49 (m, 3H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.23–7.12 (m, 2H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.78 (s, 1H), 3.94 (d, *J* = 4.3 Hz, 1H), 3.83 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.04 (d, *J* = 11.6 Hz, 1H), 1.29–1.18 (m, 2H), 0.90–0.84 (m, 2H), 0.59 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 170.8, 163.0, 138.0, 135.0, 134.5, 129.7, 129.0, 128.9, 126.7, 126.1, 125.2, 123.3, 123.1, 121.9, 119.2, 118.7, 118.6, 97.6, 94.0, 90.5, 47.8, 40.2, 29.9, 18.6, 13.7; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{25}BrN_3O_2$ 526.1125, Found 526.1114.

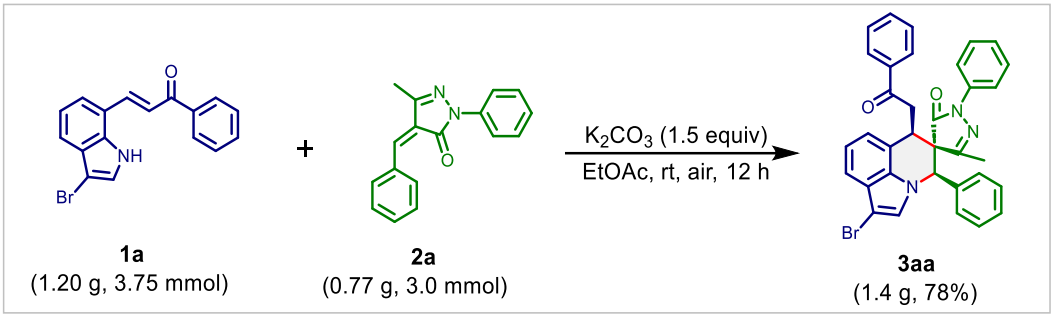
4-(7'-Bromo-3-methyl-5-oxo-1-phenyl-1,5-dihydro-1'*H*,4'*H*-spiro[pyrazole-4,2'-[1,4]methano[1,3]oxazepino[5,4,3-*hi*]indol]-4'-yl)phenyl (2*S*)-2-(4-isobutylphenyl)propanoate (27)



27 was prepared by following general procedure, treatment of (*E*)-4-(3-(3-bromo-1*H*-indol-7-yl)acryloyl)phenyl 2-(4-isobutylphenyl)propanoate **1w** (132.6 mg, 0.25 mmol, 1.0 equiv), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **7** (65.3 mg, 0.375 mmol, 1.5 equiv) and *N*-bromosuccinimide (66.7 mg, 0.375 mmol, 1.5 equiv) with K_2CO_3 (51.8 mg, 0.375 mmol, 1.5 equiv) in CH_3CN (3.0 mL) at rt for 70 min followed by column chromatography (EtOAc/Hexanes). White solid (149.3 mg, 85%), **MP**: 161.3–161.6 °C; $\mathbf{R_f}$ = 0.30 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20–7.13 (m, 6H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 4.9 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 1H), 3.93 (d, *J* = 4.4 Hz, 1H), 3.78–3.74 (m, 1H), 3.01 (d, *J* = 11.6 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.91–1.85 (m, 1H), 1.64 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H), 0.82 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.2, 170.3, 160.3, 151.9, 141.1, 137.9, 137.2, 134.5, 132.4, 129.7, 129.0, 127.9, 127.4, 126.1, 125.3, 123.2, 122.9, 122.0, 121.9, 119.3, 118.6, 97.3, 93.6, 90.8, 47.6, 45.4, 45.2, 40.6, 30.3, 22.5, 18.6, 13.4; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{40}H_{37}BrN_3O_4$ 702.1962, Found 702.1971.

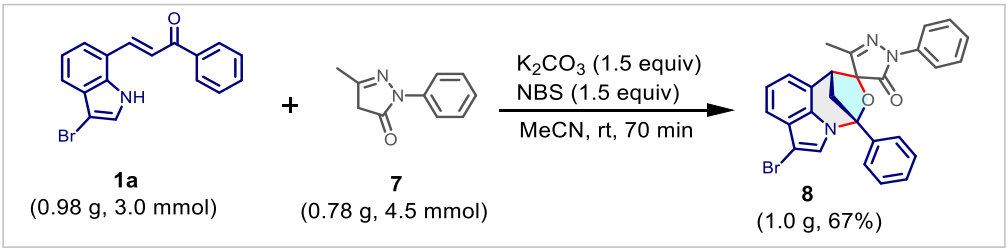
13. General Procedure for Gram-scale Synthesis of 3aa and 8

for 3aa



An oven-dried round-bottom flask (100 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (1.20 g, 3.75 mmol, 1.25 equiv), alkylidene pyrazolone **2a** (0.77 g, 3.0 mmol, 1.0 equiv) and K_2CO_3 (0.62 g, 4.5 mmol, 1.5 equiv). To this, EtOAc (40 mL) was added under air atmosphere. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (as monitored by TLC), the solvent was removed using a rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding pyrroloquinoline **3aa** in 78% yield.

For 8

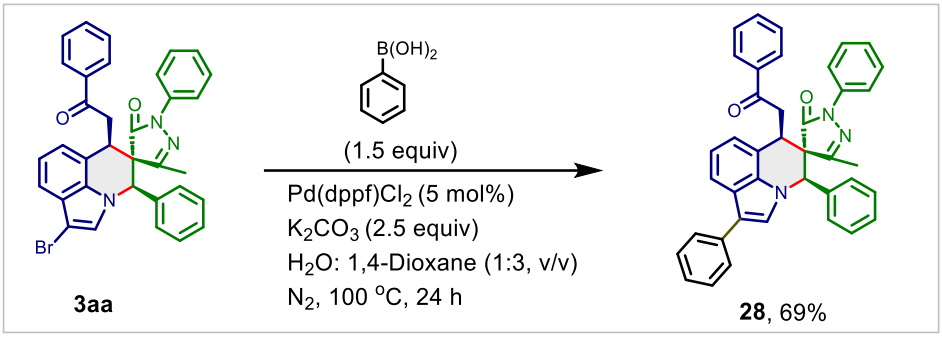


An oven-dried round-bottom flask (100 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (0.98 g, 3.0 mmol, 1.0 equiv), pyrazolone **7** (0.78 g, 4.5 mmol, 1.5 equiv) and K_2CO_3 (0.62 g, 4.5 mmol, 1.5 equiv). To this, acetonitrile (40 mL) was added under air. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), NBS (1.5 equiv) was added, and the reaction mixture was further stirred for up to 10 min. After that, the solvent was removed using a rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding bicyclic scaffold **8** in 67% yield.

14. General Procedures and Experimental Details of Synthetic Transformations

14.1. The Suzuki cross-coupling reaction

3-Methyl-6'-(2-oxo-2-phenylethyl)-1,1',4'-triphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (28)

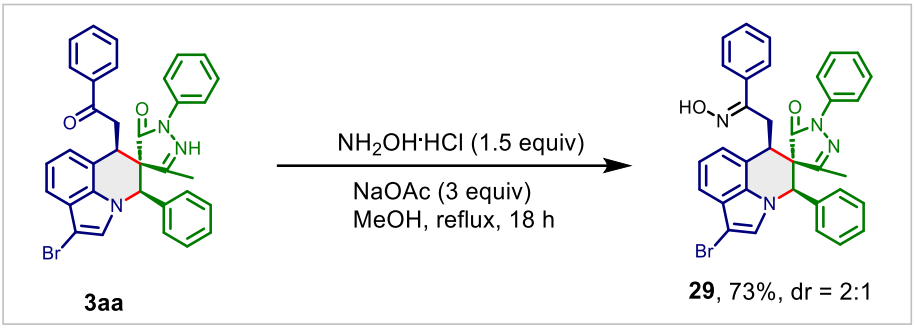


Compound **28** was prepared using the literature procedure.[3] An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with bromo compound **3aa** (58.8 mg, 0.1 mmol, 1 equiv), phenylboronic acid (18.3 mg, 1.5 equiv) and K_2CO_3 (34.6 mg, 2.5 equiv). To this, 2 mL mixture of water and 1,4-dioxane (1:3) was added under a nitrogen atmosphere. Then, the reaction mixture was purged with nitrogen for 5 min. Then, Pd(dppf)Cl_2 (3.7 mg, 5 mol%) was added and purged again with nitrogen for 5 min, and the reaction mixture was stirred for 24 h at 100 °C in an oil bath. After completion of the reaction (as monitored by TLC), the reaction mixture was filtered through a plug of Celite pad and washed with ethyl acetate. The solvents were removed under reduced pressure, and the resulting crude product was purified by silica gel column chromatography using hexanes and ethyl acetate to afford the corresponding coupled product **28**.

White solid (40.4 mg, 69%), **MP**: 221.9–222.4 °C; $\mathbf{R_f}$ = 0.20 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.47–7.42 (m, 1H), 7.39–7.31 (m, 5H), 7.19 (s, 3H), 7.12–7.11 (m, 6H), 7.04–6.93 (m, 3H), 6.70 (d, *J* = 7.0 Hz, 1H), 5.70 (s, 1H), 4.77 (d, *J* = 8.9 Hz, 1H), 3.39 (dd, *J* = 17.3, 9.7 Hz, 1H), 2.70 (d, *J* = 17.3 Hz, 1H), 1.48 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.7, 171.9, 159.5, 137.0, 136.4, 135.4, 135.0, 133.7, 132.5, 131.1, 129.9, 129.2, 128.9, 128.5, 127.2, 126.6, 126.2, 125.8, 124.5, 122.7, 121.6, 119.5, 119.2, 119.0, 118.2, 65.7, 62.9, 38.5, 37.2, 18.1; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{40}H_{32}N_3O_2$ 586.2489, Found 586.2498.

14.2. Synthesis of aryl oxime

1'-Bromo-6'-((*Z*)-2-(hydroxyimino)-2-phenylethyl)-3-methyl-1,4'-diphenyl-4'*H*,6'*H*-spiro[pyrazole-4,5'-pyrrolo[3,2,1-*ij*]quinolin]-5(1*H*)-one (29)

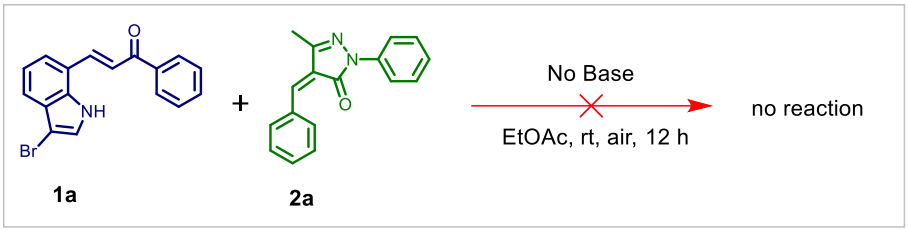


Compound **29** was prepared using the literature procedure.[4] An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with ketone **3aa** (58.8 mg, 0.1 mmol, 1 equiv), NH_2OH•HCl (10.4 mg, 0.15 mmol, 1.5 equiv) and NaOAc (24.6 mg, 0.3 mmol, 3.0 equiv), To this methanol (3 ml) was added under air atmosphere. The reaction mixture was stirred at 65 °C using a silicon oil bath as a heating source with a reflux condenser for 18 h. After completion of the reaction (as monitored by TLC), cooling to room temperature, the reaction was quenched with water (5 mL) and the resultant mixture was extracted with EtOAc. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding aryl oxime product **29**.

White solid (44.1 mg, 73%), **MP**: 122.1–122.5 °C; **R_f** = 0.17 (10% ethyl acetate in hexanes); **^{1}H NMR (700 MHz, $CDCl_3$)** δ 8.43 (s, 0.54H), 7.66 (s, 0.42H), 7.56 (d, *J* = 5.7 Hz, 1.33H), 7.49 (d, *J* = 5.1 Hz, 2.67H), 7.44 (d, *J* = 7.0 Hz, 2.62H), 7.41–7.28 (m, 8H), 7.25–7.21 (m, 1H), 7.19–7.11 (m, 2.28H), 6.84 (d, *J* = 11.9 Hz, 1H), 5.53 (s, 1H), 4.28 (s, 0.65H), 4.20 (s, 0.34H), 3.74 (dd, *J* = 14.7, 8.6 Hz, 0.68H), 3.13 (dd, *J* = 15.4, 7.9 Hz, 0.32H), 2.68 (d, *J* = 15.0 Hz, 0.67H), 2.60 (d, *J* = 15.6 Hz, 0.30H), 1.59 (s, 2H), 1.54 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 171.8, 171.7, 158.8, 158.6, 156.4, 137.1, 137.0, 134.1, 133.5, 131.9, 131.0, 130.9, 130.0, 129.7, 129.1, 129.1, 128.8, 128.8, 128.5, 128.3, 127.2, 126.5, 125.7, 124.2, 124.1, 121.9, 121.8, 121.5, 119.6, 119.5, 119.5, 119.4, 118.8, 118.4, 118.3, 91.2, 65.9, 65.7, 62.9, 62.8, 38.5, 37.7, 35.4, 24.5, 18.0, 18.0; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{28}BrN_4O_2$ 603.1390, Found 603.1401.

15. Control Experiments

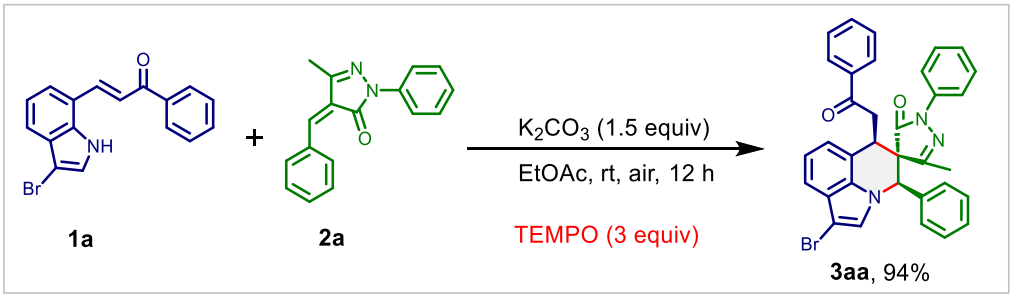
15.1. Reaction without base



An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (40.8 mg, 0.125 mmol, 1.25 equiv) and alkylidene pyrazolone **2a** (26.2 mg, 0.1 mmol, 1.0 equiv). To this EtOAc (1 mL) was added under air atmosphere. The reaction mixture was stirred at rt for 12 h. After 12 h, we observed that (as monitored by TLC) both starting materials were unreacted and no product **3aa** was observed.

"The above result suggested that a base is necessary for this transformation"

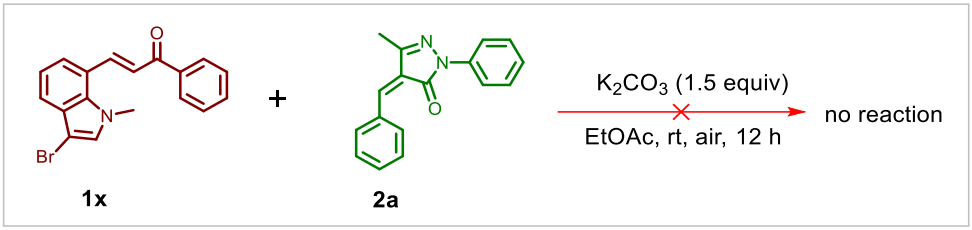
15.2. Radical trapping experiment



An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (40.8 mg, 0.125 mmol, 1.25 equiv) and alkylidene pyrazolone **2a** (26.2 mg, 0.1 mmol, 1.0 equiv), K_2CO_3 (20.7 mg, 0.15 mmol, 1.5 equiv) and TEMPO (0.9 mmol, 3 equiv). To this EtOAc (1 mL) was added under air atmosphere. The reaction mixture was stirred at rt for 12 h. After completion of the reaction (as monitored by TLC), the solvent was removed using a rotatory evaporator under reduced pressure and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding pyrroloquinoline **3aa** in 94% yield.

"The above result demonstrated that a radical reaction pathway was not involved in this transformation"

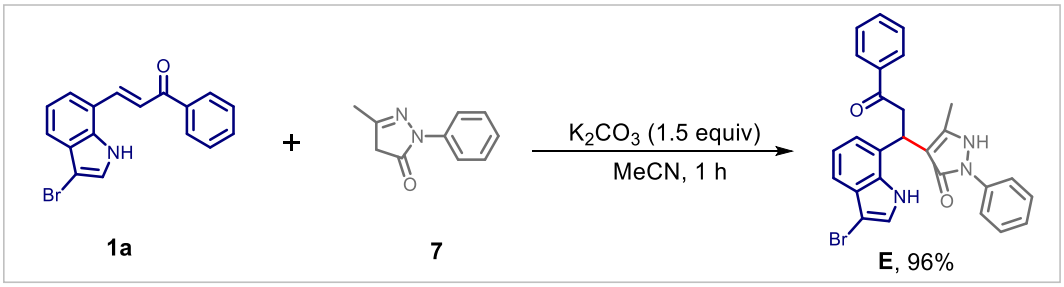
15.3. Reaction with *N*-substituted indole-Michael acceptor 1v



An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with *N*-substituted indole-Michael acceptor **1x** (42.5 mg, 0.125 mmol, 1.25 equiv), alkylidene pyrazolone **2a** (26.2 mg, 0.1 mmol, 1.0 equiv), K_2CO_3 (20.7 mg, 0.15 mmol, 1.5 equiv). To this, EtOAc (1 mL) was added under air atmosphere. The reaction mixture was stirred at room temperature for 12 h. After 12 h, we observed that (as monitored by TLC) both starting materials were unreacted and no product was observed.

"The above result demonstrated that the N-alkylation is the initiation step for this annulation process"

15.4. Isolation of intermediate E



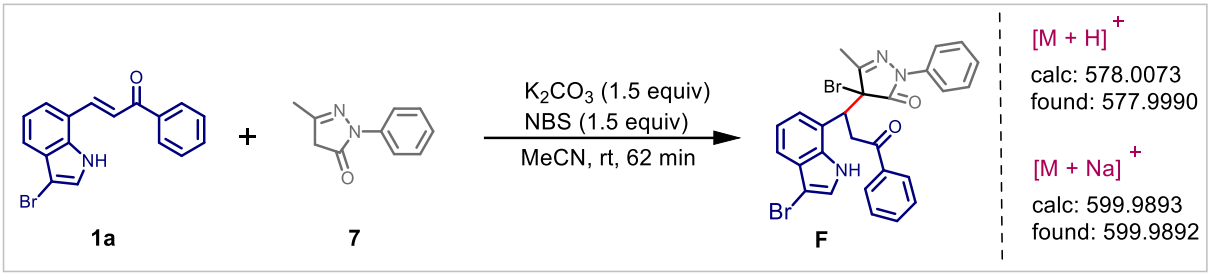
An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (81.6 mg, 0.25 mmol, 1 equiv), pyrazolone **7** (66.7 mg, 0.375 mmol, 1.5 equiv) and K_2CO_3 (1.5 equiv). To this, acetonitrile (3 mL) was added under air. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), the solvent was removed using a rotatory evaporator under reduced pressure, and the residue was purified by column chromatography using hexanes and ethyl acetate to afford the corresponding intermediate **E**.

White solid (120.1 mg, 96%), **MP**: 126.9–127.2 °C; $\mathbf{R_f}$ = 0.18 (10% ethyl acetate in hexanes); **^{1}H NMR (500 MHz, DMSO-d_6)** δ 12.08 (s, 1H), 11.52 (s, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.63–7.57 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 6.7 Hz, 1H), 7.26 (d,

J = 7.9 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 4.79 (s, 1H), 4.51–4.33 (m, 1H), 3.73 (dd, J = 17.7, 5.4 Hz, 1H), 2.21 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6)** δ 198.1, 163.0, 147.4, 136.7, 136.4, 133.6, 133.1, 129.0, 128.7, 128.4, 127.8, 126.6, 125.1, 124.8, 121.0, 120.1, 119.2, 116.3, 106.1, 89.3, 32.4, 10.9; **HRMS (ESI/Q-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{23}BrN_3O_2$ 500.0968, Found 500.0964.

*"The above result demonstrated that the intermediate **E** was formed during the bicyclic scaffold formation"*

15.5. HRMS study of intermediate F



An oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar was charged with indole-substituted Michael acceptor **1a** (32.6 mg, 0.1 mmol, 1 equiv), pyrazolone **7** (26.7 mg, 0.15 mmol, 1.5 equiv) and K_2CO_3 (1.5 equiv). To this, acetonitrile (1 mL) was added under air. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), NBS (1.5 equiv) was added. After that crude mixture was analysed by HRMS and intermediate **F** was characterized.

*"The above result demonstrated that the intermediate **F** was formed during the bicyclic scaffold formation"*

Compound Details

Cpd. 1: C27 H21 Br2 N3 O2

Formula	Mass	Score	Algorithm	Diff (Tgt, ppm)	Polarity
C27 H21 Br2 N3 O2	576.9991	98.57	FBF	-1.60225123161742	Positive

Compound Spectra (overlaid)

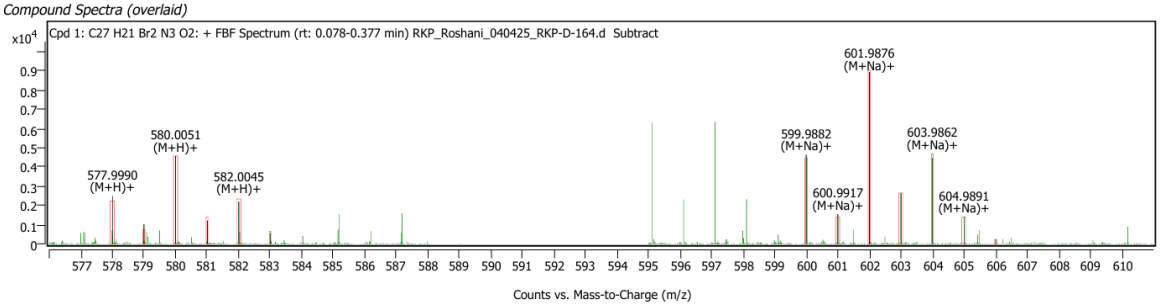


Figure S12: HRMS spectrum of intermediate **F**

16. X-Ray Crystallographic Analysis

Crystals of compounds **3aa**/**4ae**/**8**/**intermediate E** were obtained by dissolving the compound in acetonitrile solvent and allowing the solvent to slowly evaporate at 25 ºC. A suitable crystal was picked and placed on a glass fiber sheet using paraffin oil for mounting. The data were collected on a Bruker Kappa (D8 QUEST) Apex-II CCD diffractometer by using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal structure was solved by using Olex2 software and refined using least-squares minimization. The crystal structure details are deposited at the Cambridge Crystallographic Data Centre with the deposition number.

16.1. Compound 3aa

Crystals of compound **3aa** were obtained by dissolving the compound in acetonitrile solvent and allowing the solvent to slowly evaporate at 25 ºC.

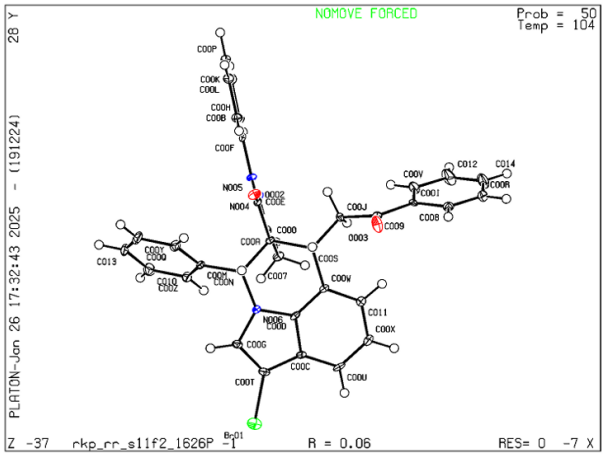


Figure S13: Structure refinement for **3aa** (Thermal ellipsoids are shown at the 50% level).

Table S10: X-Ray crystallographic data of **3aa**.

CCDC	**2432958**
Formula	$C_{34}H_{26}BrN_3O_2$
Formula weight	588.49
Crystal system	Triclinic
Space group	*P*-1
a (Å)	9.5740(5)
b (Å)	11.5688(6)
c (Å)	13.1776(7)
α (º)	109.523(2)
β (º)	95.932(2)
γ (º)	96.091(2)
Volume (Å^3)	1352.78(12)

Z	2
Crystal size, mm^3	0.204× 0.097× 0.054
Density (g/cm^3)	1.445
Absorption coefficient (mm^{-1})	1.557
Temp. (K)	104
Total reflns.	46110
Indepnt. reflns.	4756
Final R indices [I > 2σ(I)]	R1 = 0.0566, wR2 = 0.1735
R indices (all data)	R1 = 0.0584, wR2 = 0.1753

16.2. Compound 4ae

Crystals of compound **4ae** were obtained by dissolving the compound in acetonitrile solvent and allowing the solvent to slowly evaporate at 25 ºC.

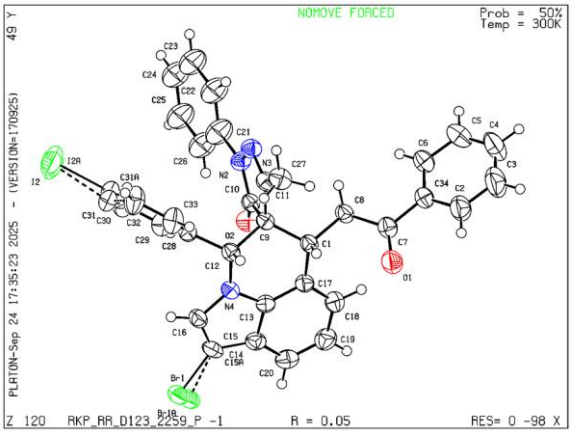


Figure S14: Structure refinement for **4ae** (Thermal ellipsoids are shown at the 50% level).

Table S11: X-Ray crystallographic data of **4ae**.

CCDC	**2491349**
Formula	$C_{34}H_{25}BrIN_3O_2$
Formula weight	714.38
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.3392(17)
b (Å)	11.4509(19)
c (Å)	14.151(2)
α (º)	95.267(4)
β (º)	90.302(4)
γ (º)	116.301(4)

Volume ($Å^3$)	1493.6(4)
Z	2
Crystal size, mm^3	0.2× 0.06× 0.02
Density (g/cm^3)	1.588
Absorption coefficient (mm^{-1})	2.445
Temp. (K)	300(2)
Total reflns.	40439
Indepnt. reflns.	5281
Final R indices [I > 2σ(I)]	R1 = 0.0471, wR2 = 0.1251
R indices (all data)	R1 = 0.0523, wR2 = 0.1308

16.3. Compound 8

Crystals of compound **8** were obtained by dissolving the compound in acetonitrile solvent and allowing the solvent to slowly evaporate at 25 ºC.

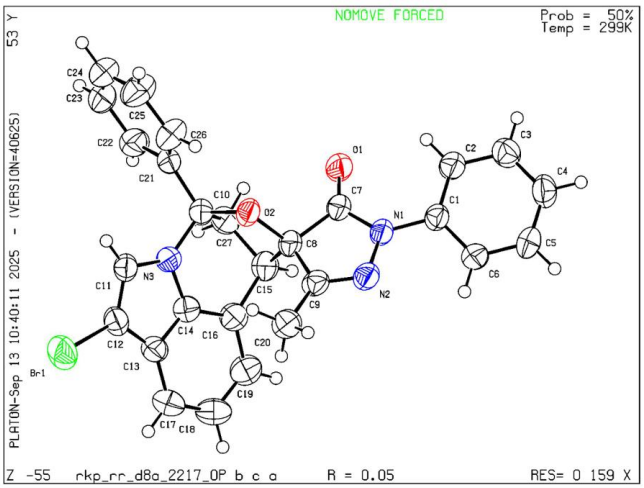


Figure S15: Structure refinement for **8** (Thermal ellipsoids are shown at the 50% level).

Table S12: X-Ray crystallographic data of **8**.

CCDC	**2488040**
Formula	$C_{27}H_{20}BrN_3O_2$
Formula weight	498.37
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	14.676(5)
b (Å)	16.567(6)
c (Å)	18.169(6)
α (º)	90
β (º)	90
γ (º)	90

Volume (Å^3)	4418(3)
Z	8
Density (g/cm^3)	1.499
Absorption coefficient (mm^{-1})	1.892
Temp. (K)	299(2)
Total reflns.	80413
Indepnt. reflns.	4300
Final R indices [I > 2σ(I)]	R1 = 0.0535, wR2 = 0.1292
R indices (all data)	R1 = 0.0957, wR2 = 0.1490

16.4. Intermediate E

Crystals of intermediate **E** were obtained by dissolving the compound in acetonitrile solvent and allowing the solvent to slowly evaporate at 25 ºC.

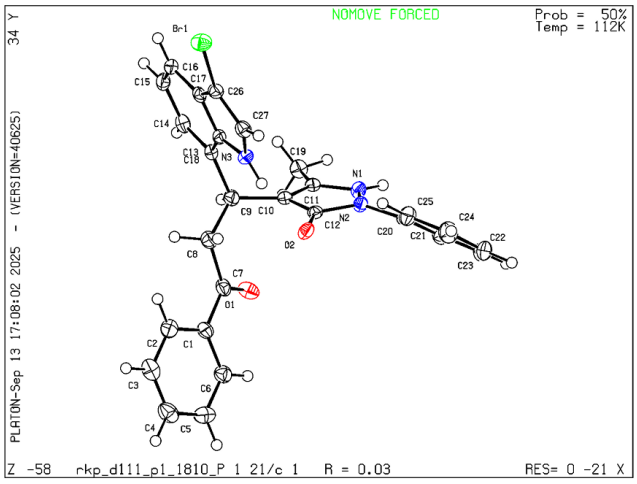


Figure S16: Structure refinement for **E** (Thermal ellipsoids are shown at the 50% level).

Table S13: X-Ray crystallographic data of **E**.

CCDC	**2488041**
Formula	$C_{27}H_{22}BrN_3O_2$
Formula weight	500.38
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.2227(9)
b (Å)	26.033(3)
c (Å)	9.7619(9)
α (º)	90
β (º)	102.821(3)
γ (º)	90
Volume (Å^3)	2285.4(4)

Z	4
Density (g/cm^3)	1.454
Absorption coefficient (mm^{-1})	1.829
Temp. (K)	112.0
Total reflns.	53379
Indepnt. reflns.	4028
Final R indices [I > 2σ(I)]	R1 = 0.0342, wR2 = 0.0906
R indices (all data)	R1 = 0.0479, wR2 = 0.1099

17. References

1 (a) G. Hazra, S. Kundu, R. Dandela and B. Thirupathi, *J. Org. Chem.,* 2023, **88**, 8493; (b) M. S. Raza, K. Roshani and R. K. Peddinti, *Chem. Commun.,* 2025, **61**, 12522.

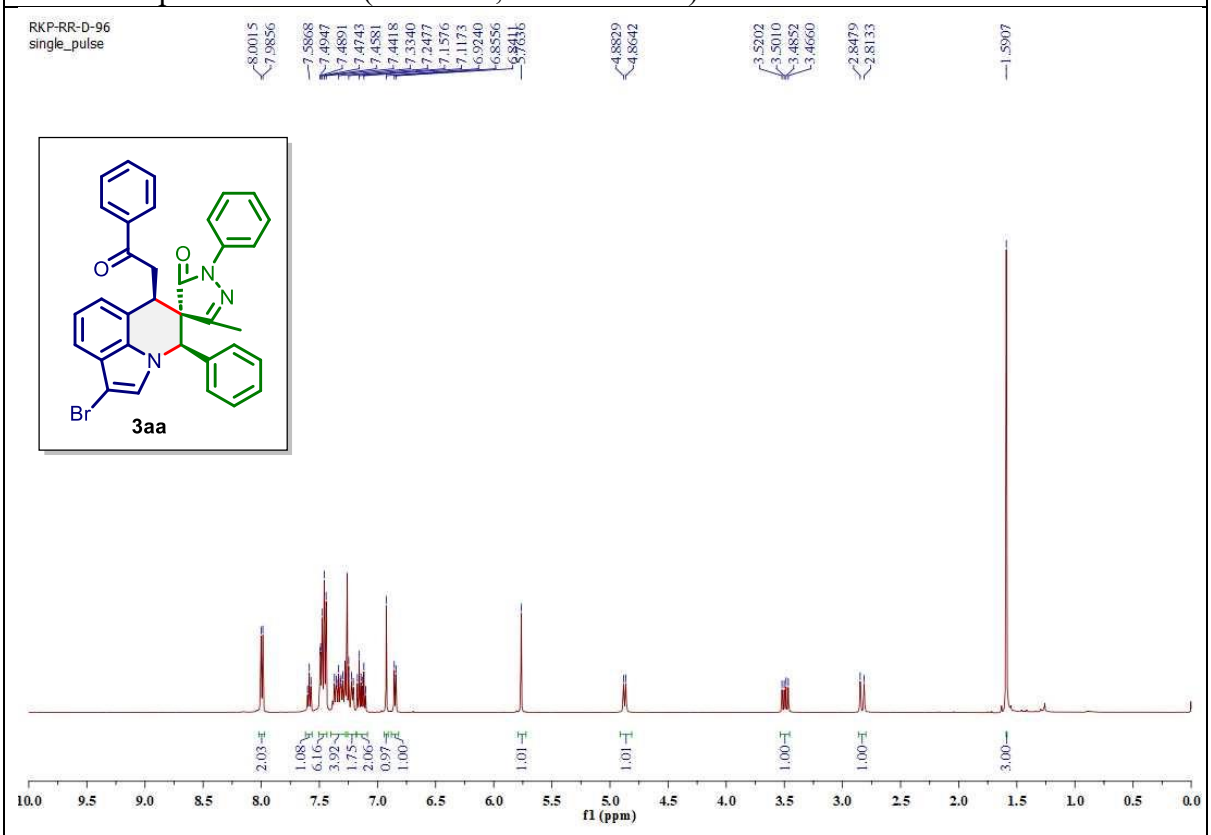
2 (a) D. S. Ji, X. Zhang, P. Zhang, X. Bao, Y. Yuan, C. Huo and P. F. Xu, *Org. Lett.,* 2025, **27**, 709; (b) Y. Feng, Y. Ren, D. Tang, K. Wang, J. Wang, D. Huang, X. Lv and Y. Hu, *Org. Biomol. Chem.,* 2024, **22**, 2797.

3 S. Wen, Y. Zhang, Q. Tian, Y. Chen and G. Cheng, *Org. Chem. Front.,* 2022, **9***,* 4388.

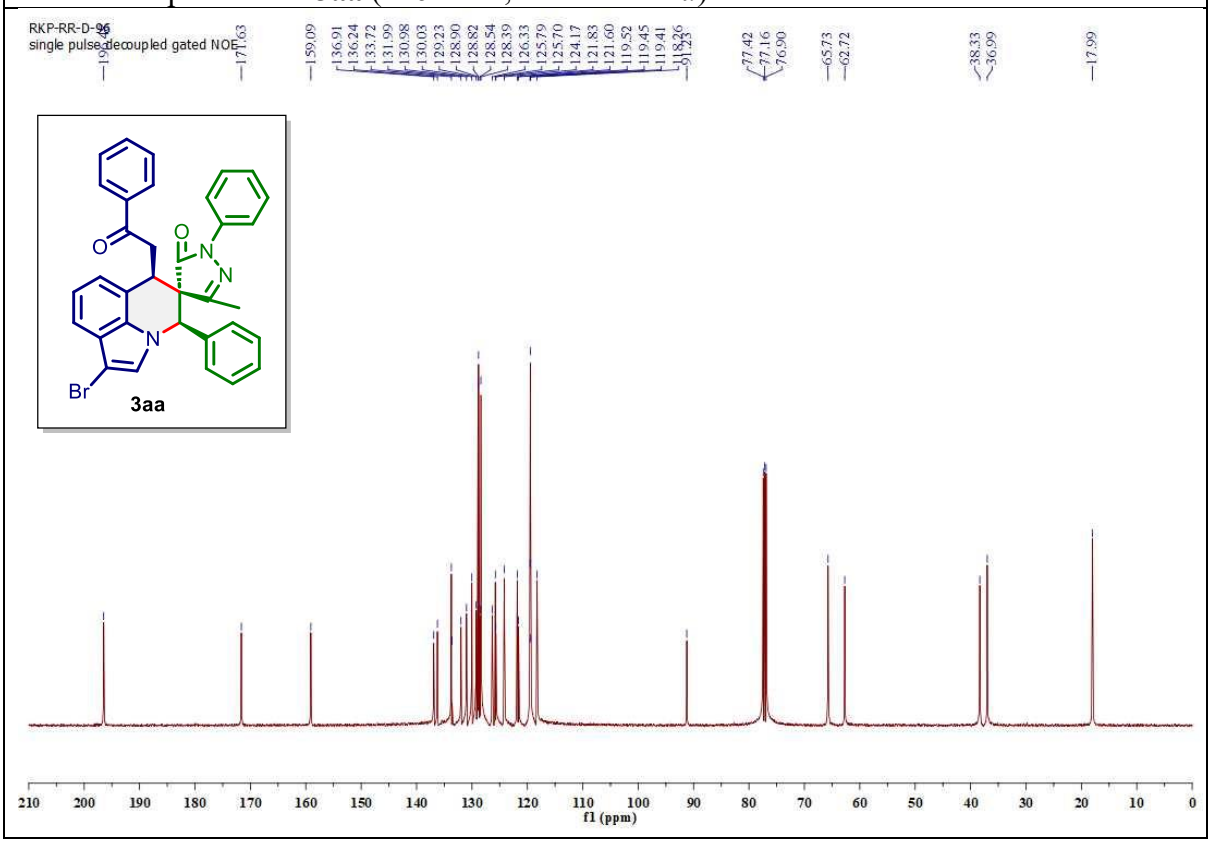
4 J. Liu, Z. Yang, H. Long, J. Xian, L. Zheng and Z. Q. Liu, *Asian J. Org. Chem.,* 2024, **13**, e202300562.

18. Copies of NMR Spectra of Products

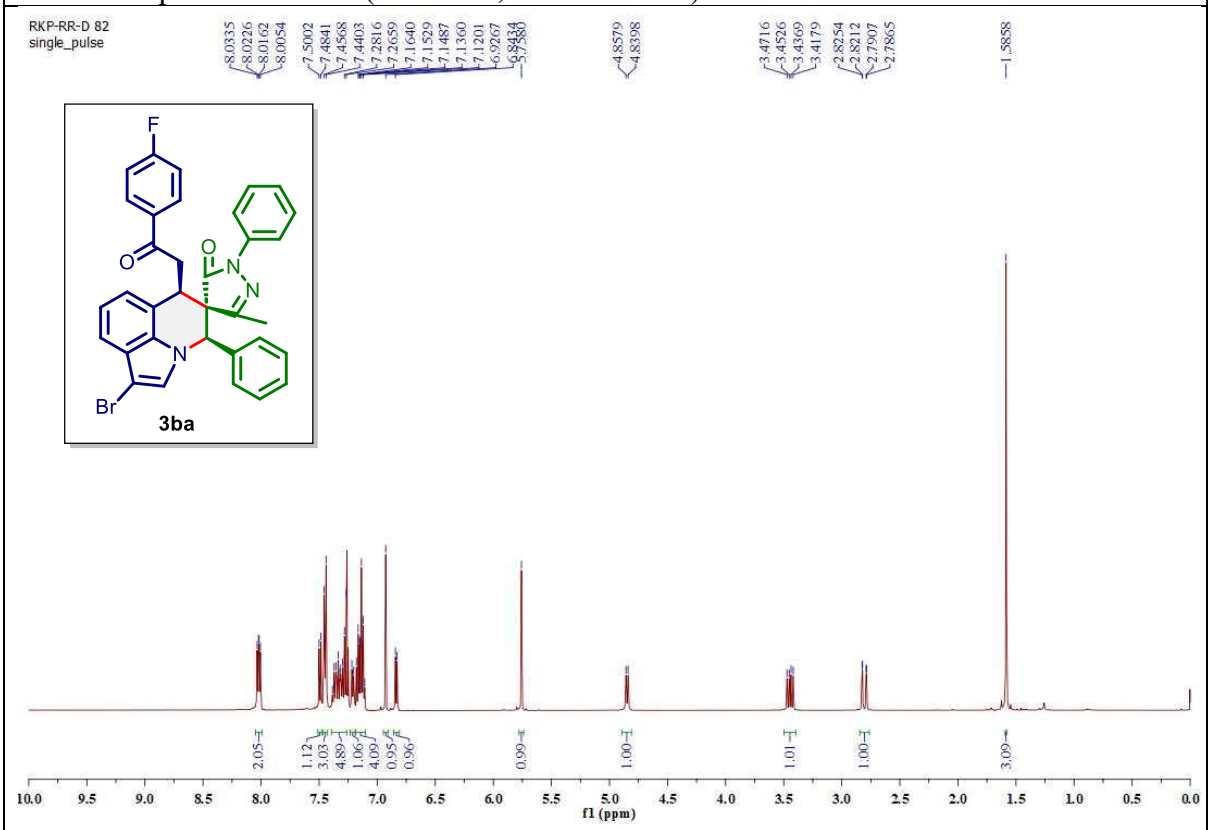
^{1}H NMR Spectrum of **3aa** (500 MHz, Chloroform-*d*)



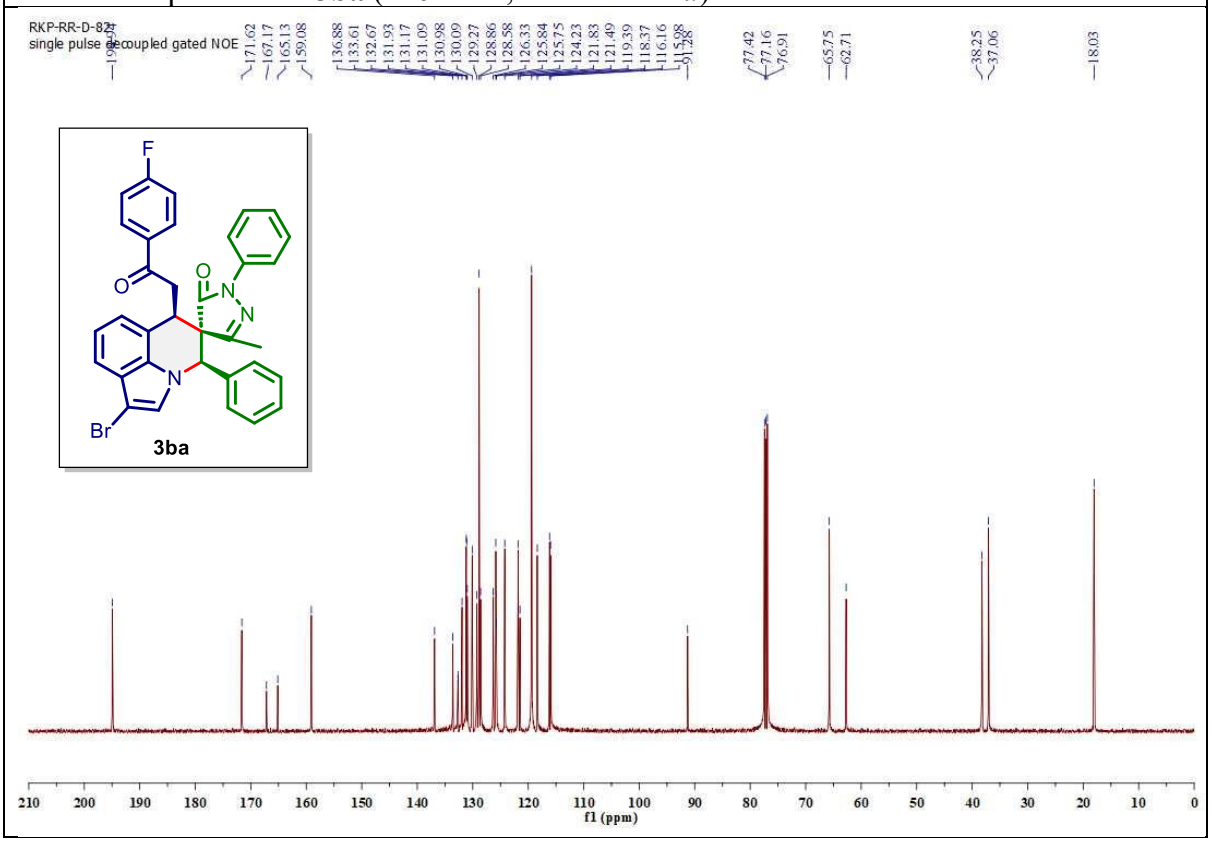
^{13}C NMR Spectrum of **3aa** (126 MHz, Chloroform-*d*)



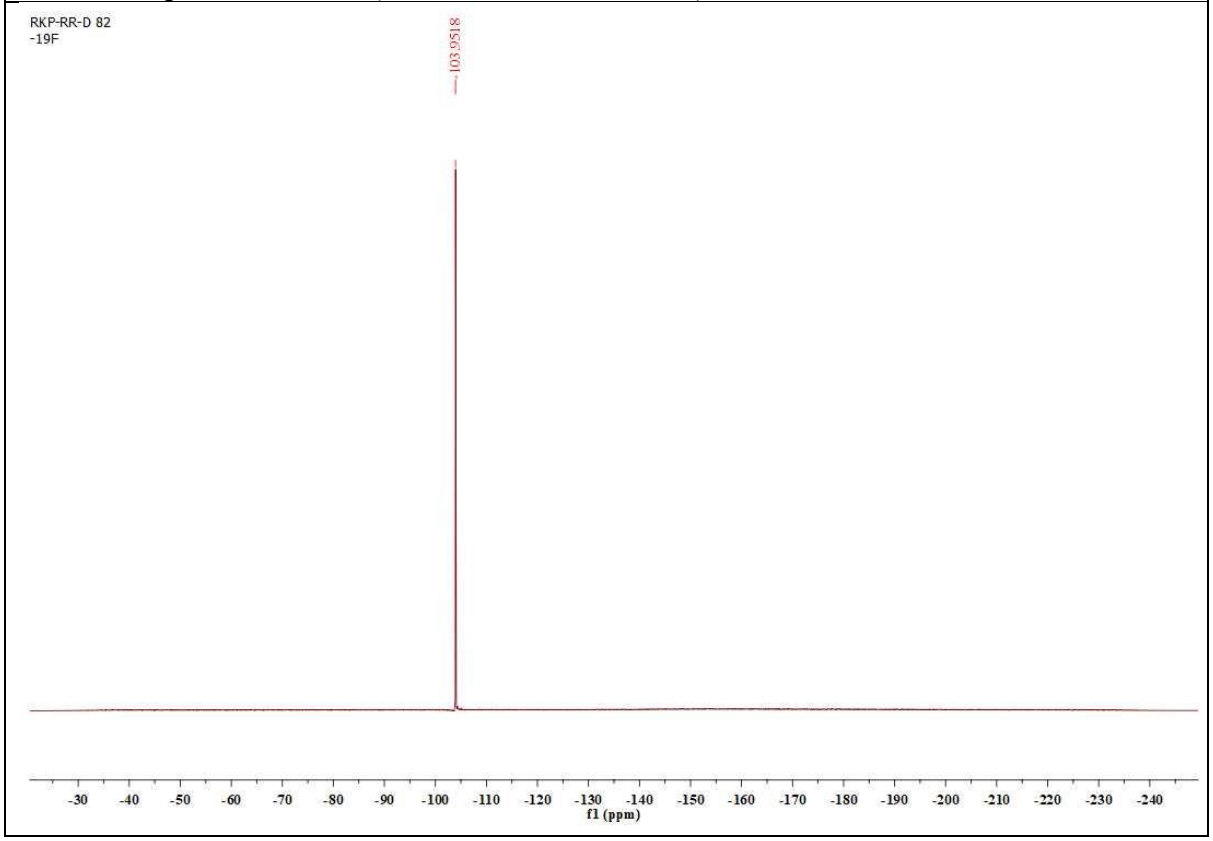
^{1}H NMR Spectrum of **3ba** (500 MHz, Chloroform-*d*)



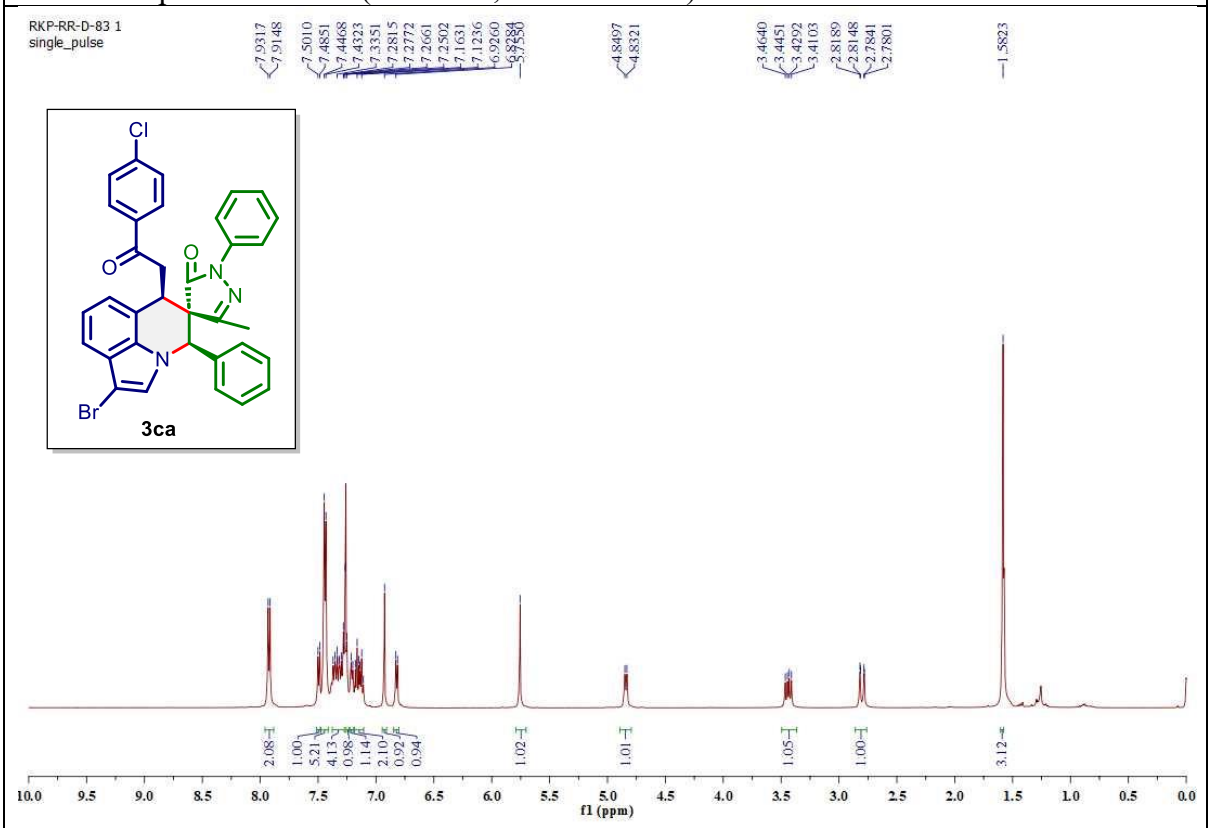
^{13}C NMR Spectrum of **3ba** (126 MHz, Chloroform-*d*)



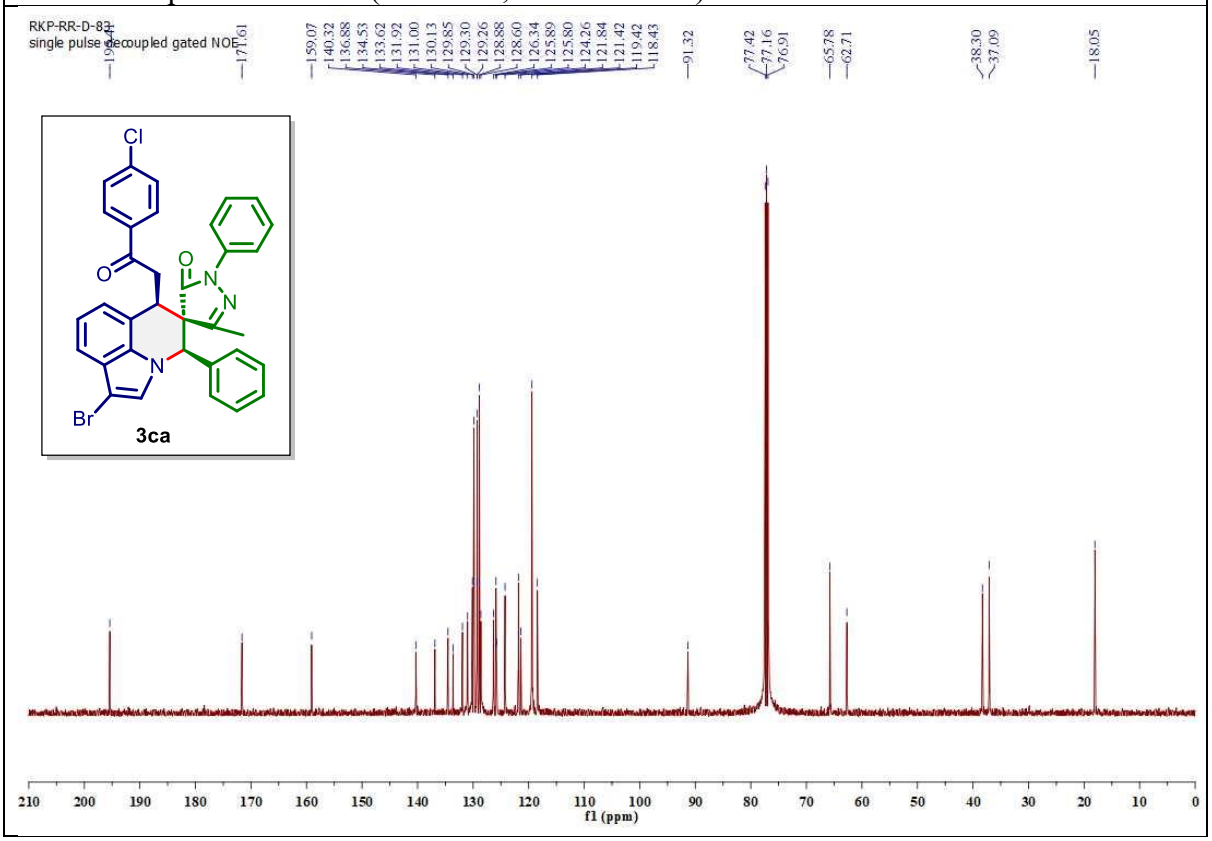
^{19}F NMR Spectrum of **3ba** (471 MHz, Chloroform-*d*)



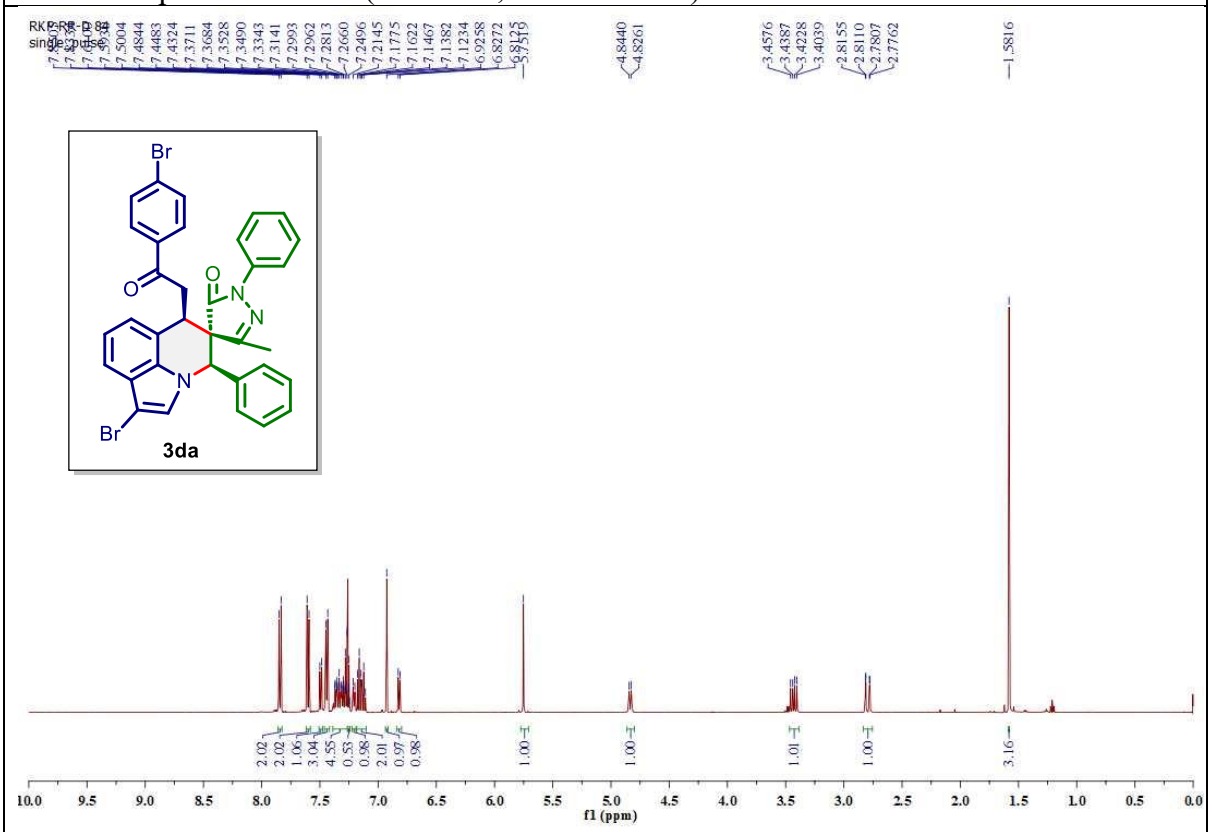
^{1}H NMR Spectrum of **3ca** (500 MHz, Chloroform-*d*)



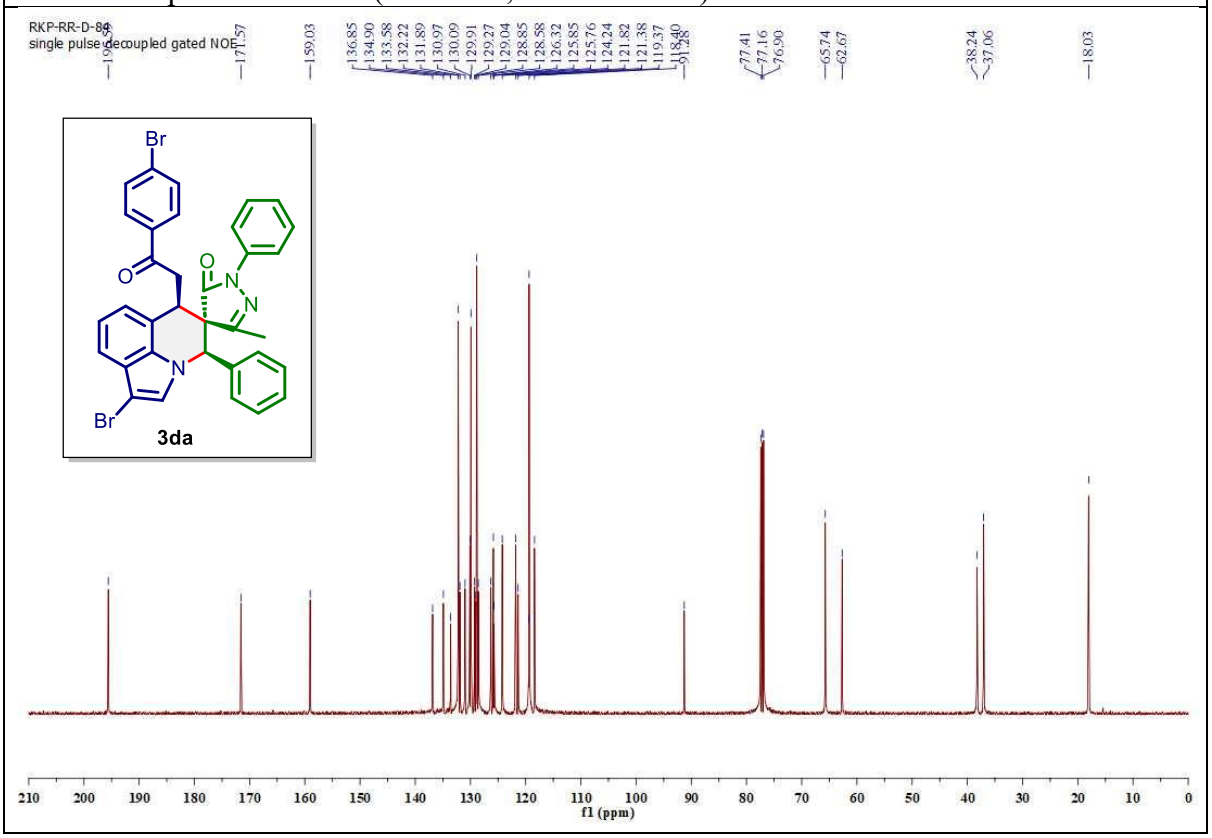
^{13}C NMR Spectrum of **3ca** (126 MHz, Chloroform-*d*)



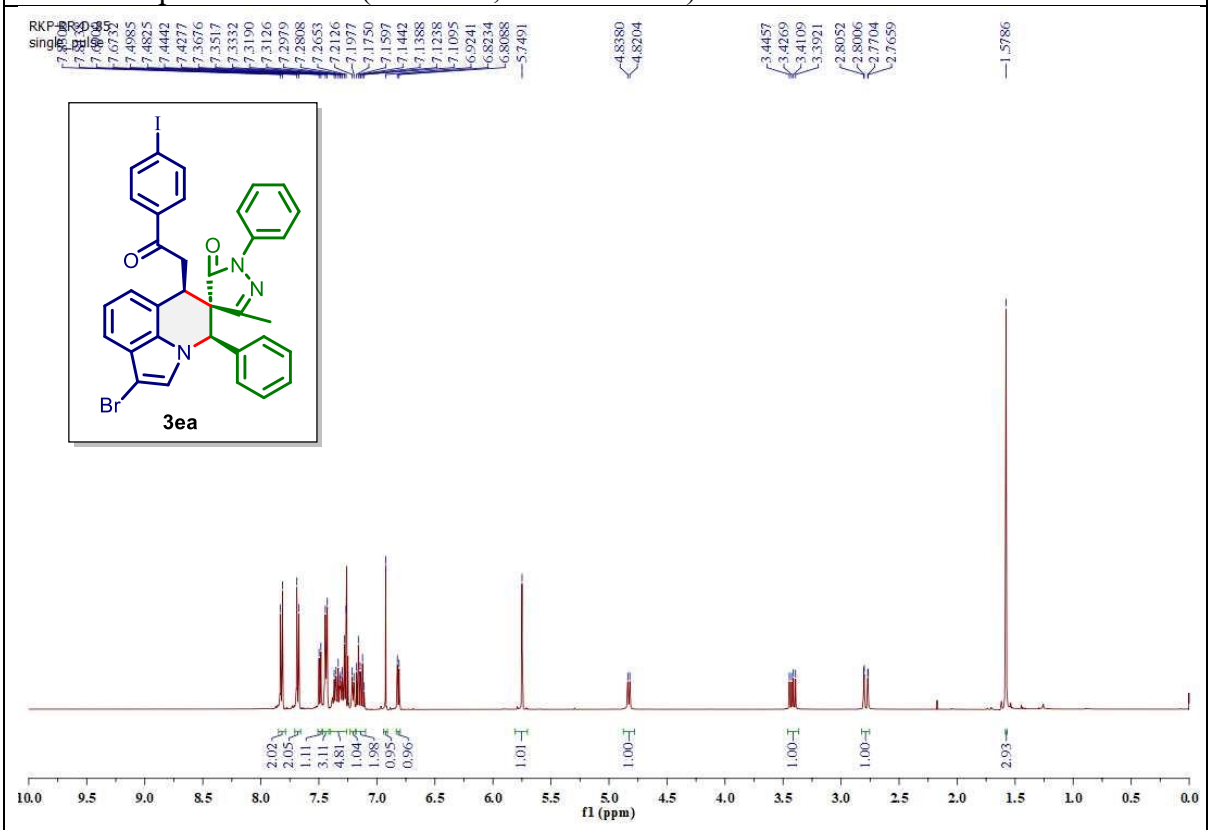
^{1}H NMR Spectrum of **3da** (500 MHz, Chloroform-*d*)



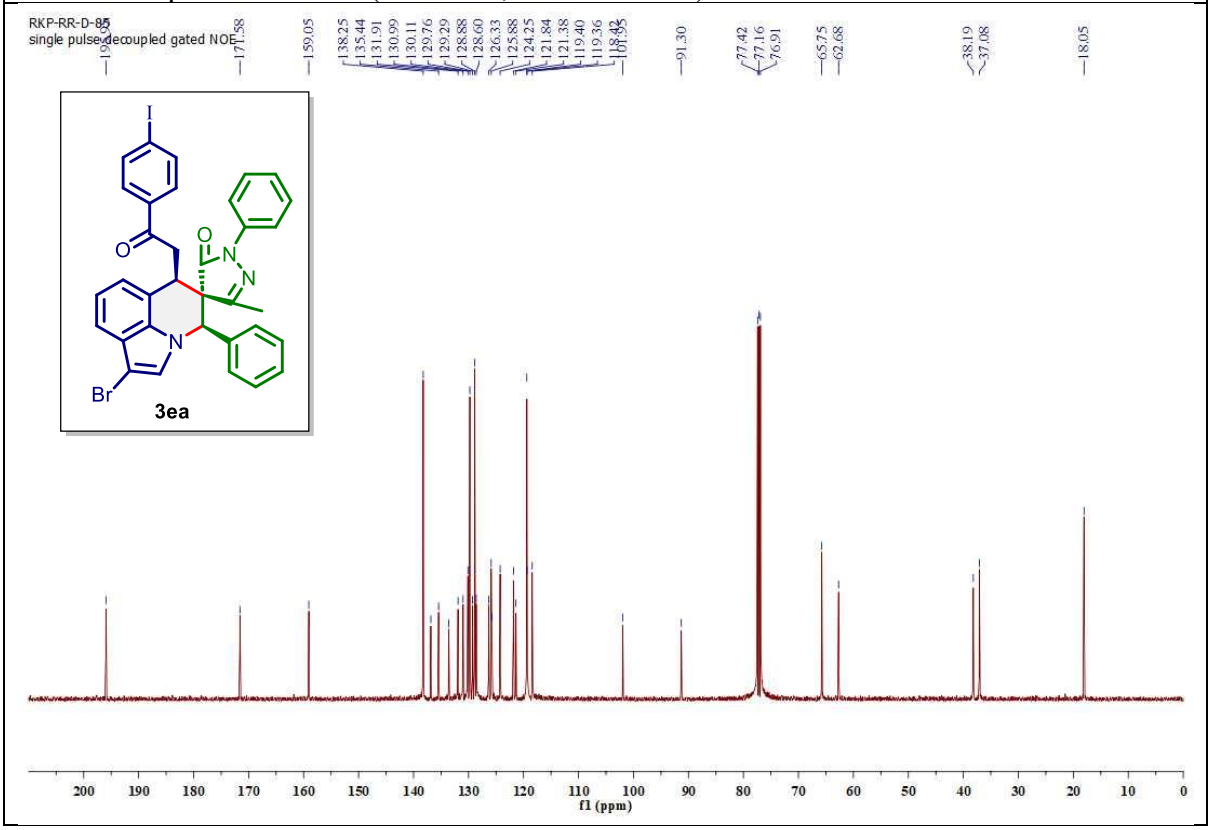
^{13}C NMR Spectrum of **3da** (126 MHz, Chloroform-*d*)



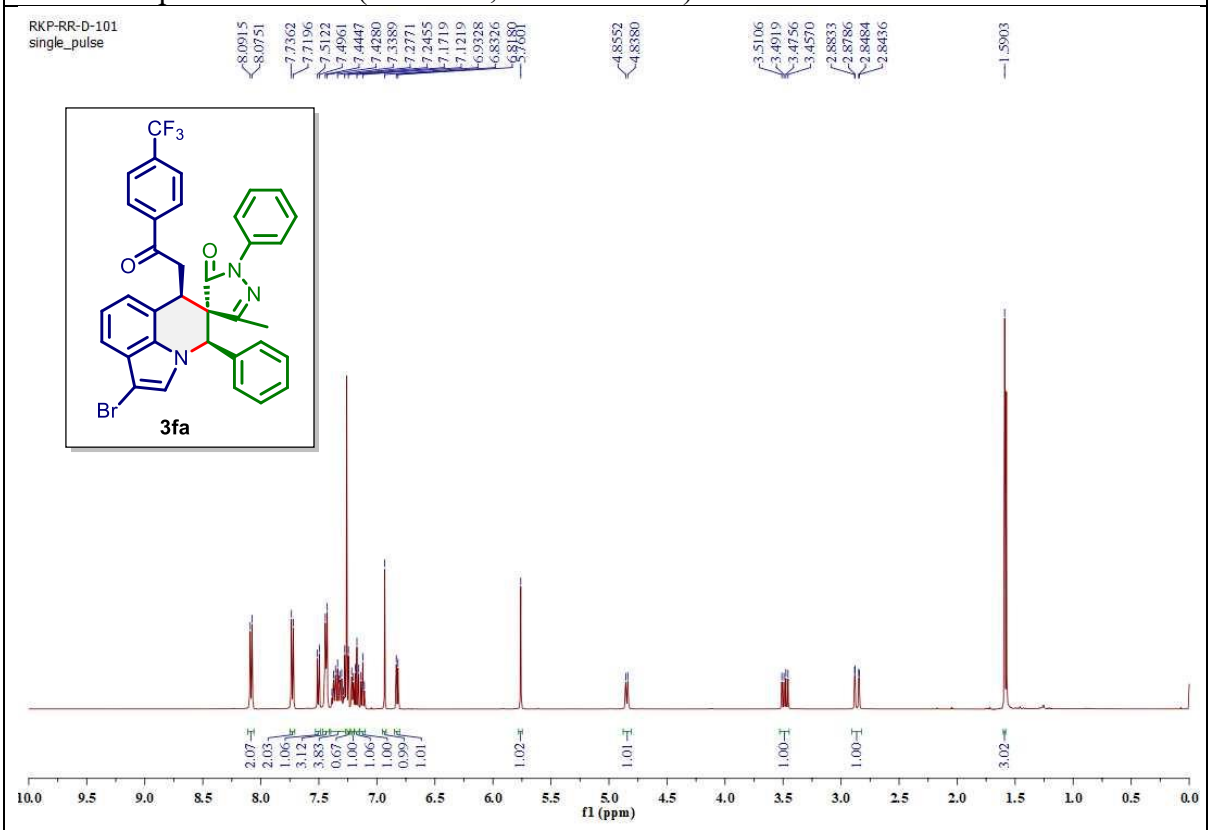
^{1}H NMR Spectrum of **3ea** (500 MHz, Chloroform-*d*)



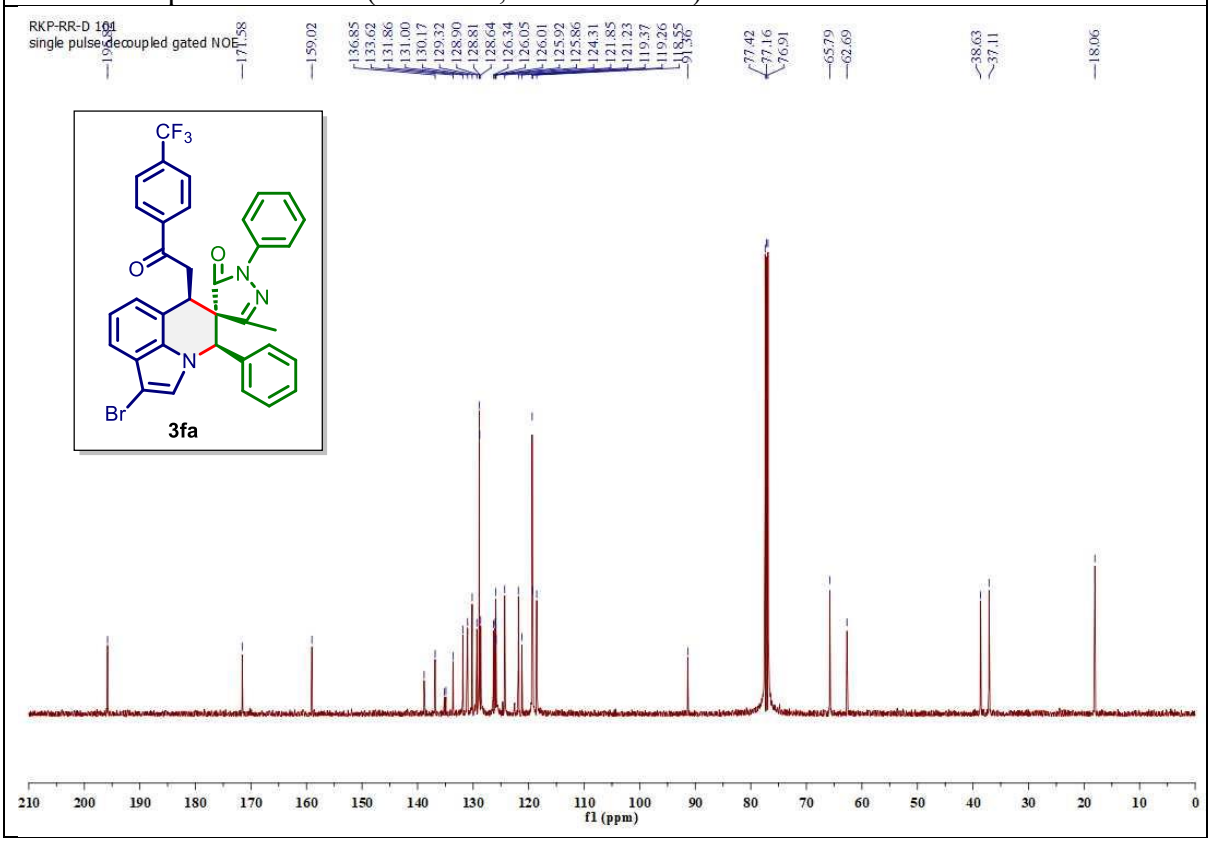
^{13}C NMR Spectrum of **3ea** (126 MHz, Chloroform-*d*)



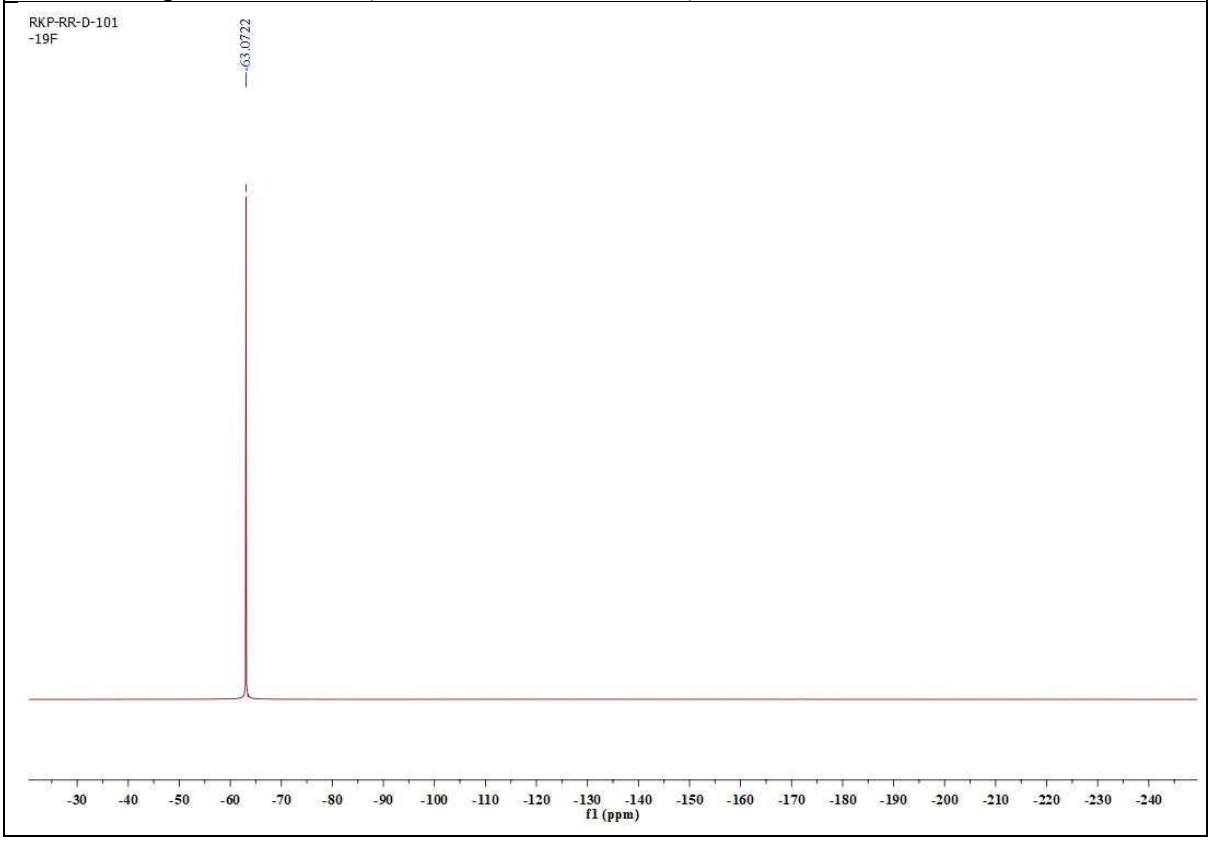
^{1}H NMR Spectrum of **3fa** (500 MHz, Chloroform-*d*)



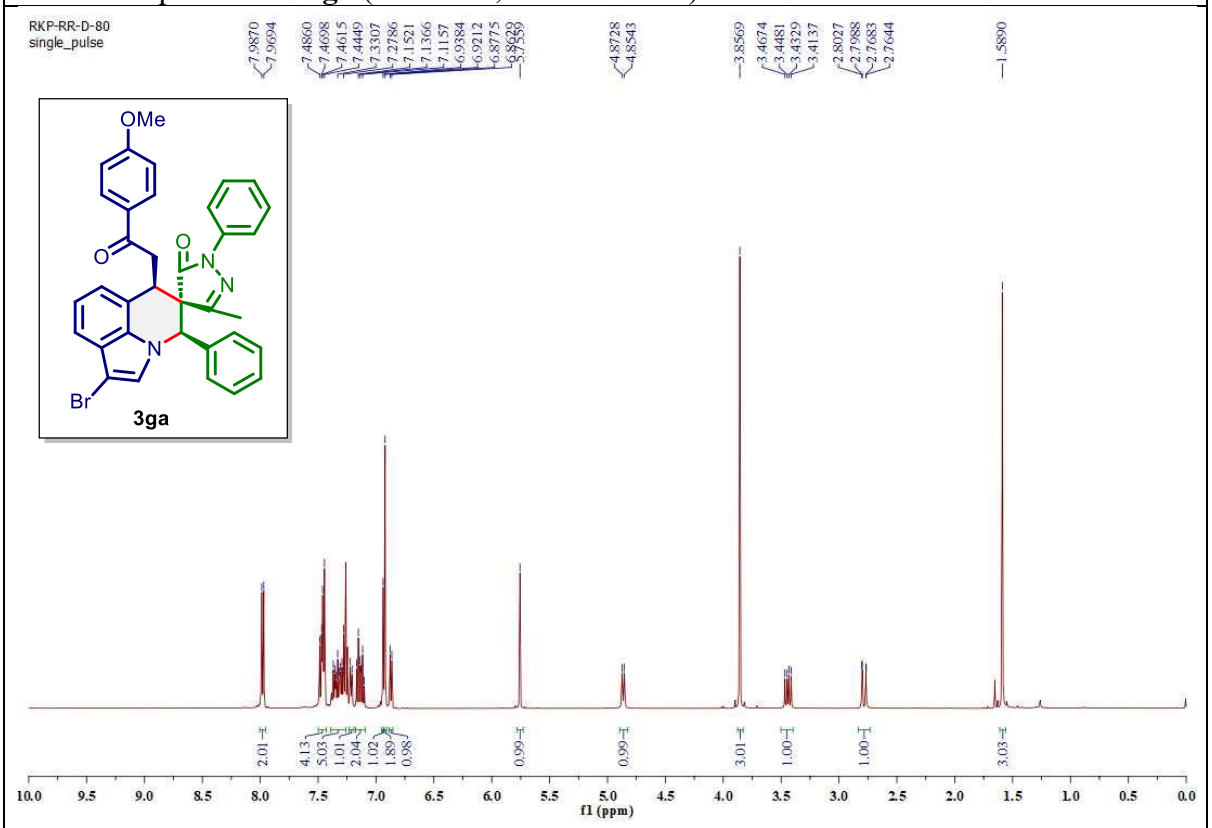
^{13}C NMR Spectrum of **3fa** (126 MHz, Chloroform-*d*)



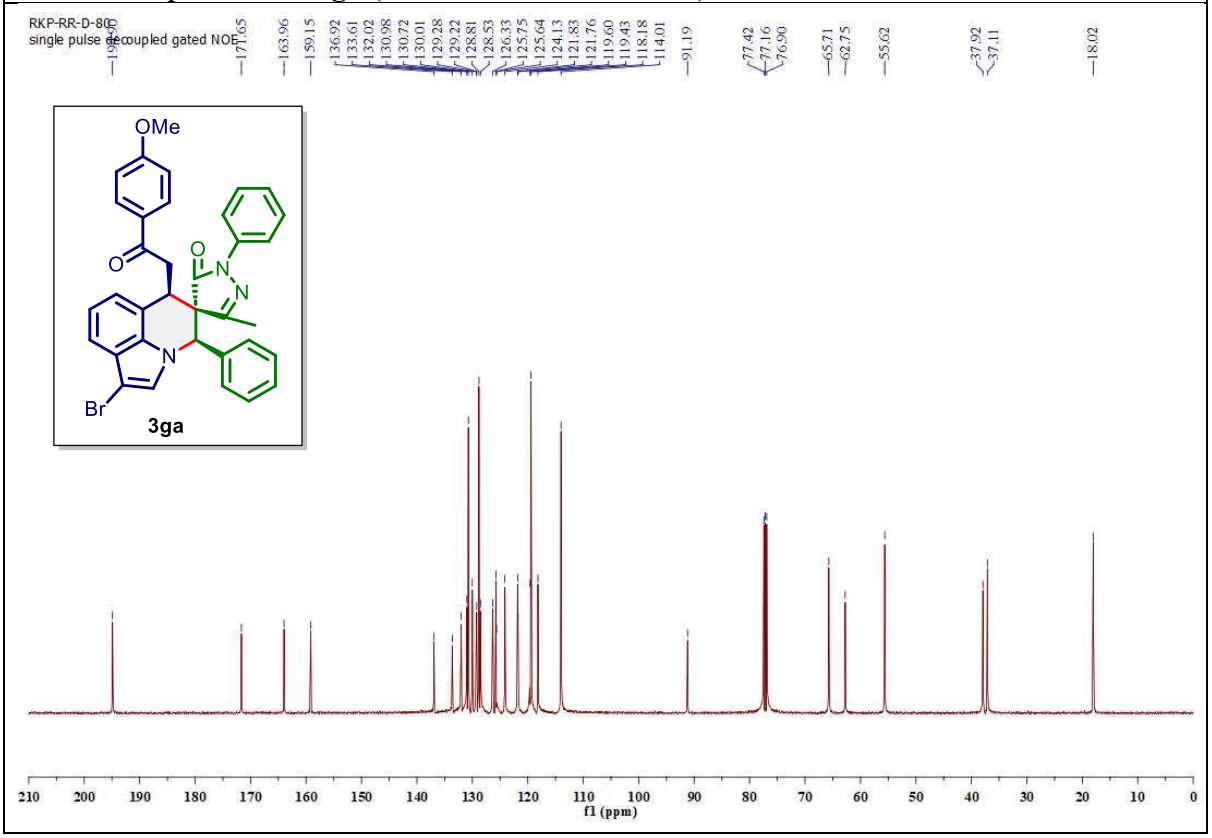
^{19}F NMR Spectrum of **3fa** (471 MHz, Chloroform-*d*)



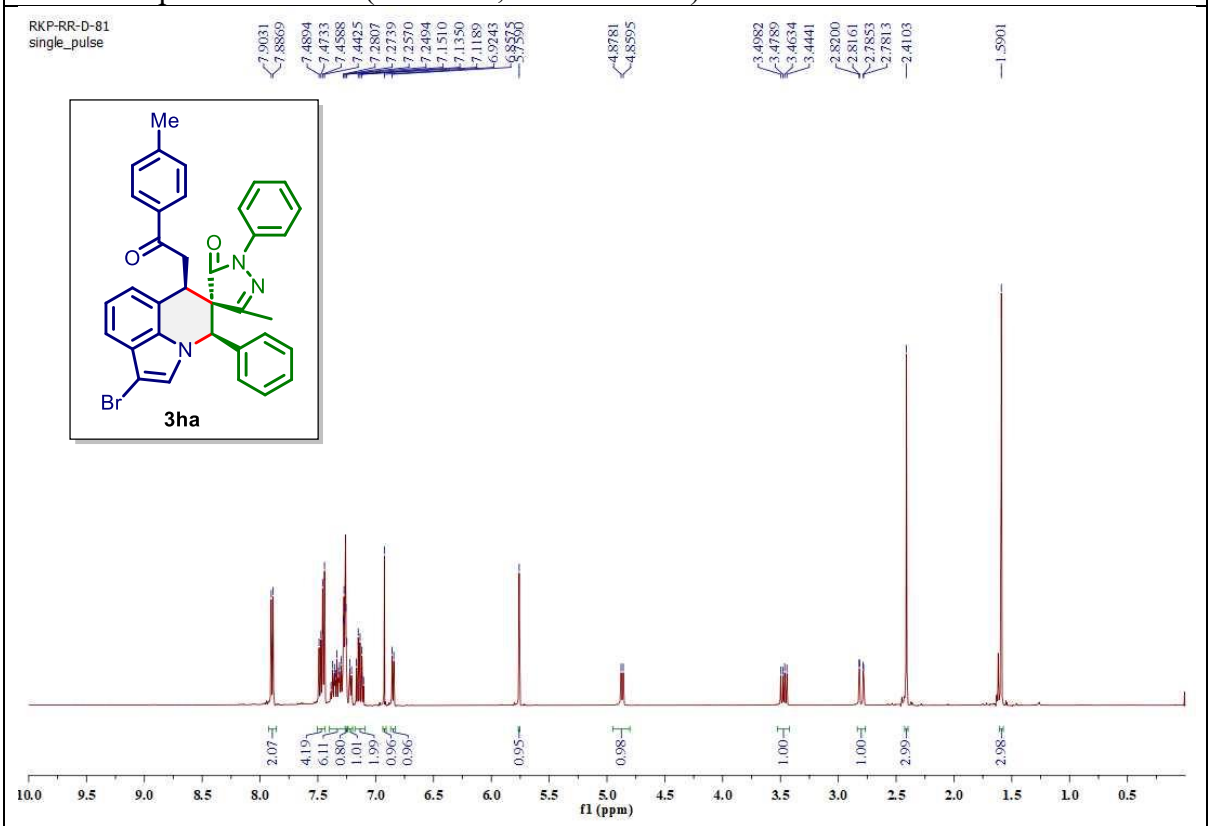
^{1}H NMR Spectrum of **3ga** (500 MHz, Chloroform-*d*)



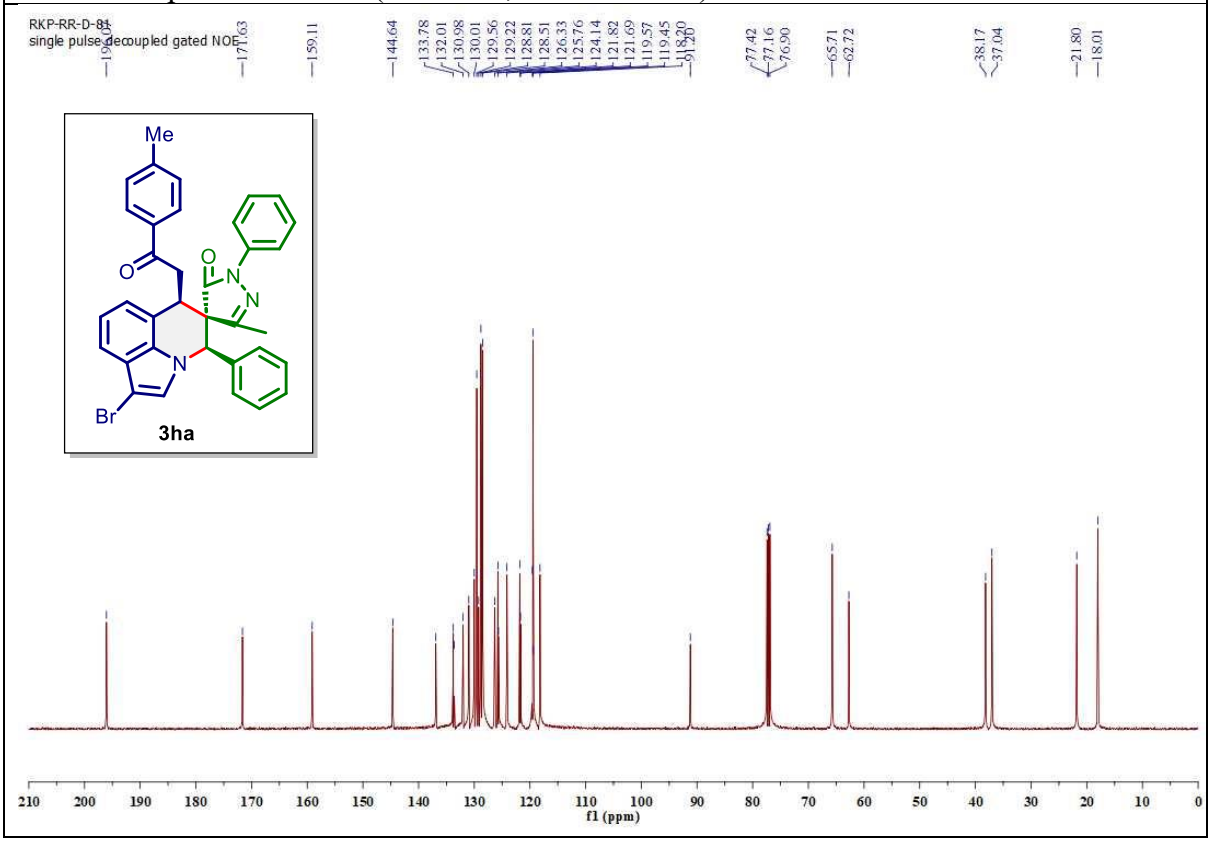
^{13}C NMR Spectrum of **3ga** (126 MHz, Chloroform-*d*)



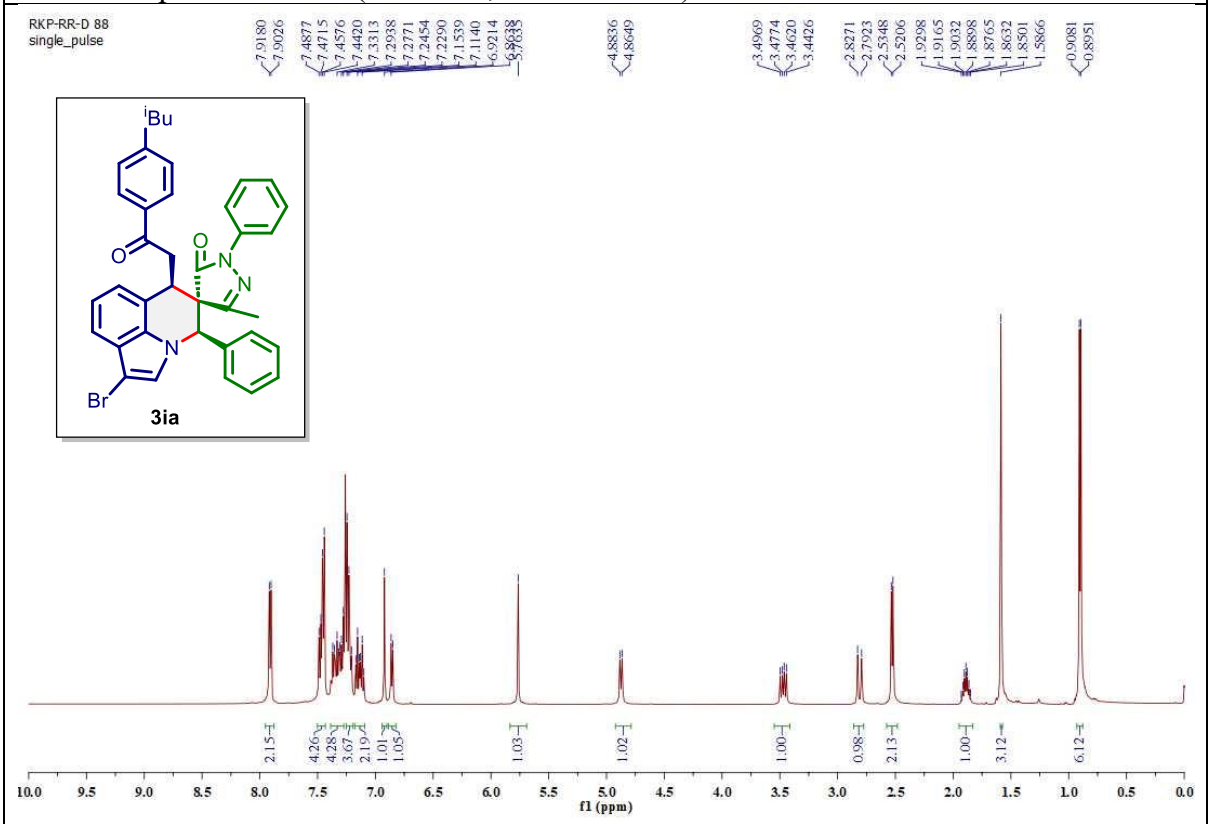
^{1}H NMR Spectrum of **3ha** (500 MHz, Chloroform-*d*)



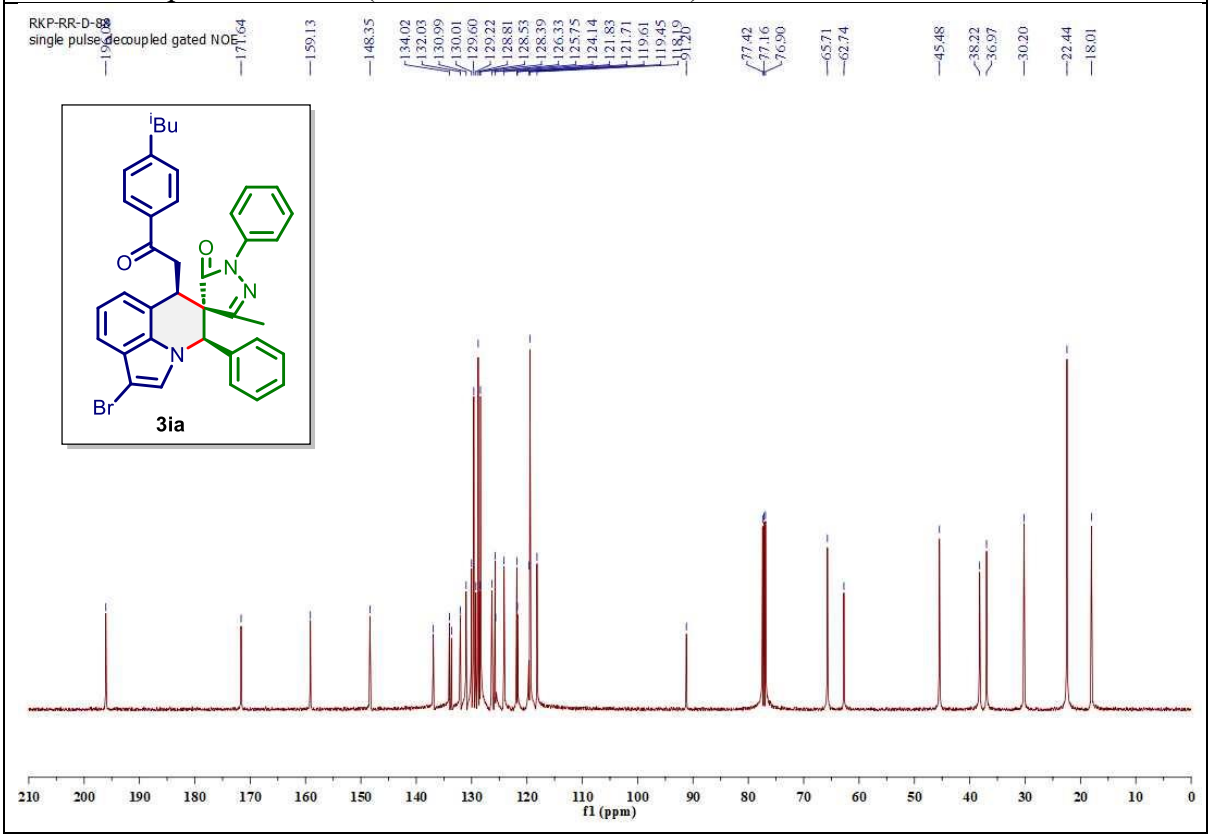
^{13}C NMR Spectrum of **3ha** (126 MHz, Chloroform-*d*)



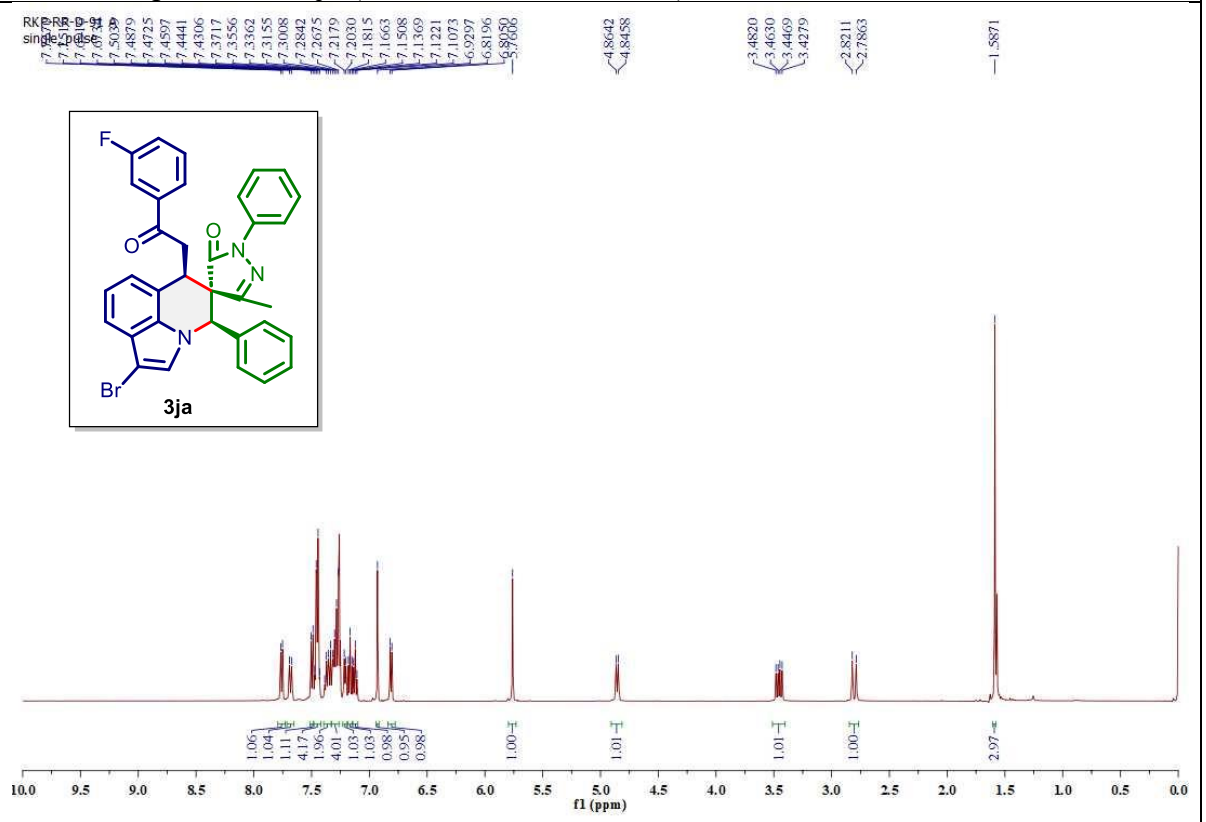
^{1}H NMR Spectrum of **3ia** (500 MHz, Chloroform-*d*)



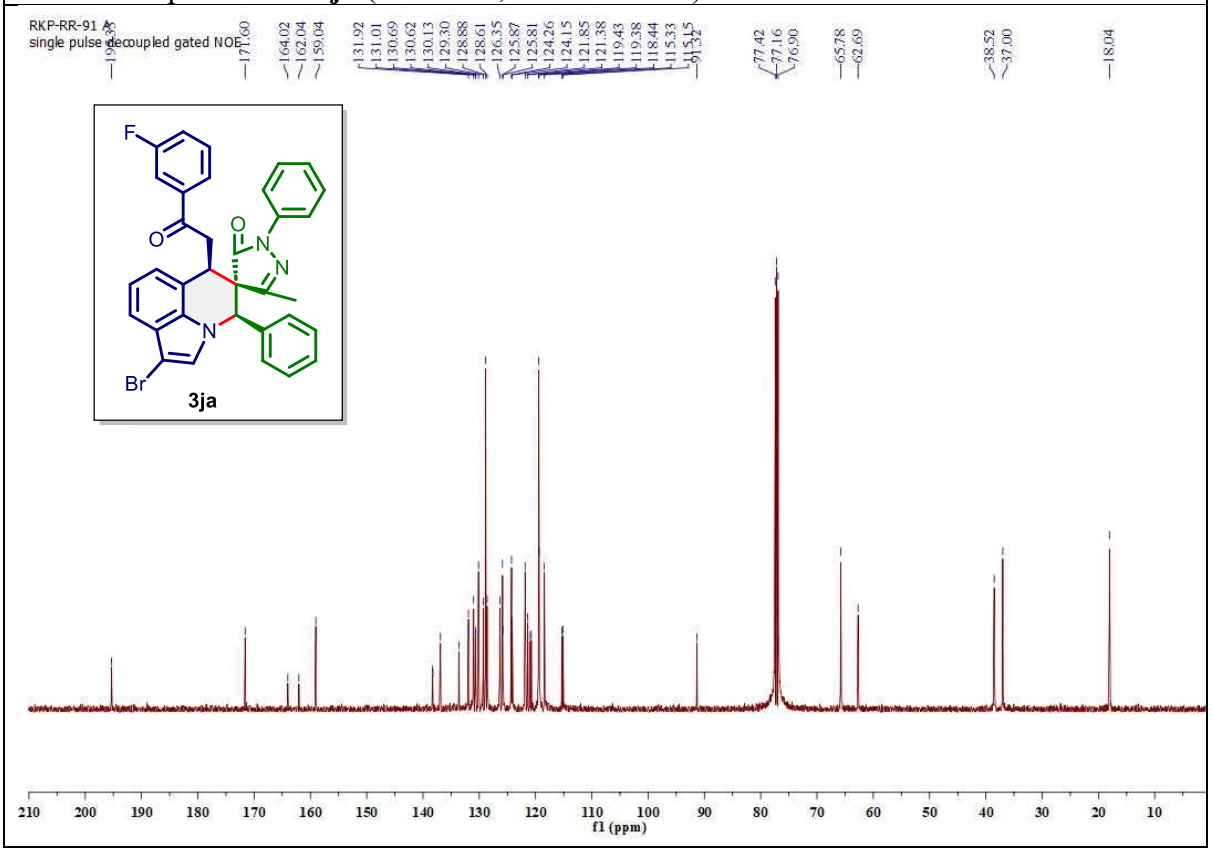
^{13}C NMR Spectrum of **3ia** (126 MHz, Chloroform-*d*)



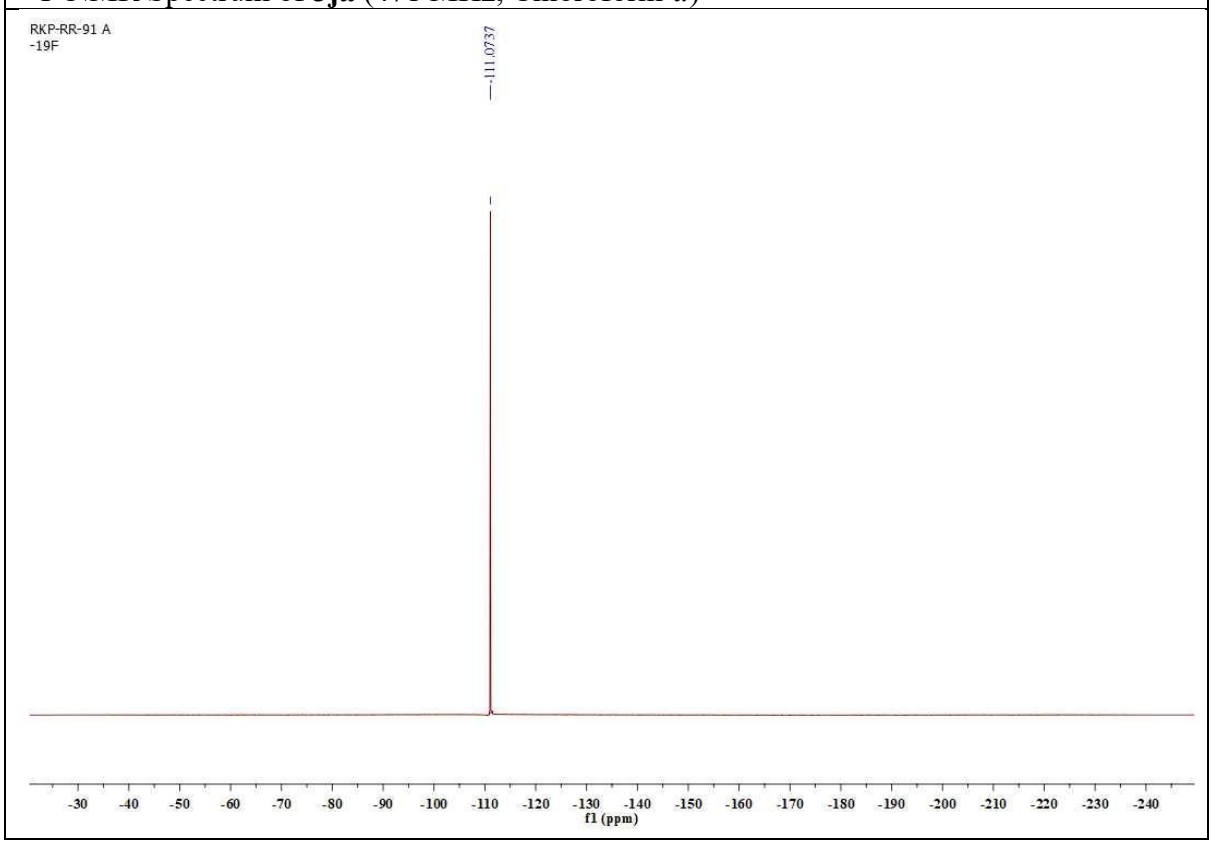
^{1}H NMR Spectrum of **3ja** (500 MHz, Chloroform-*d*)



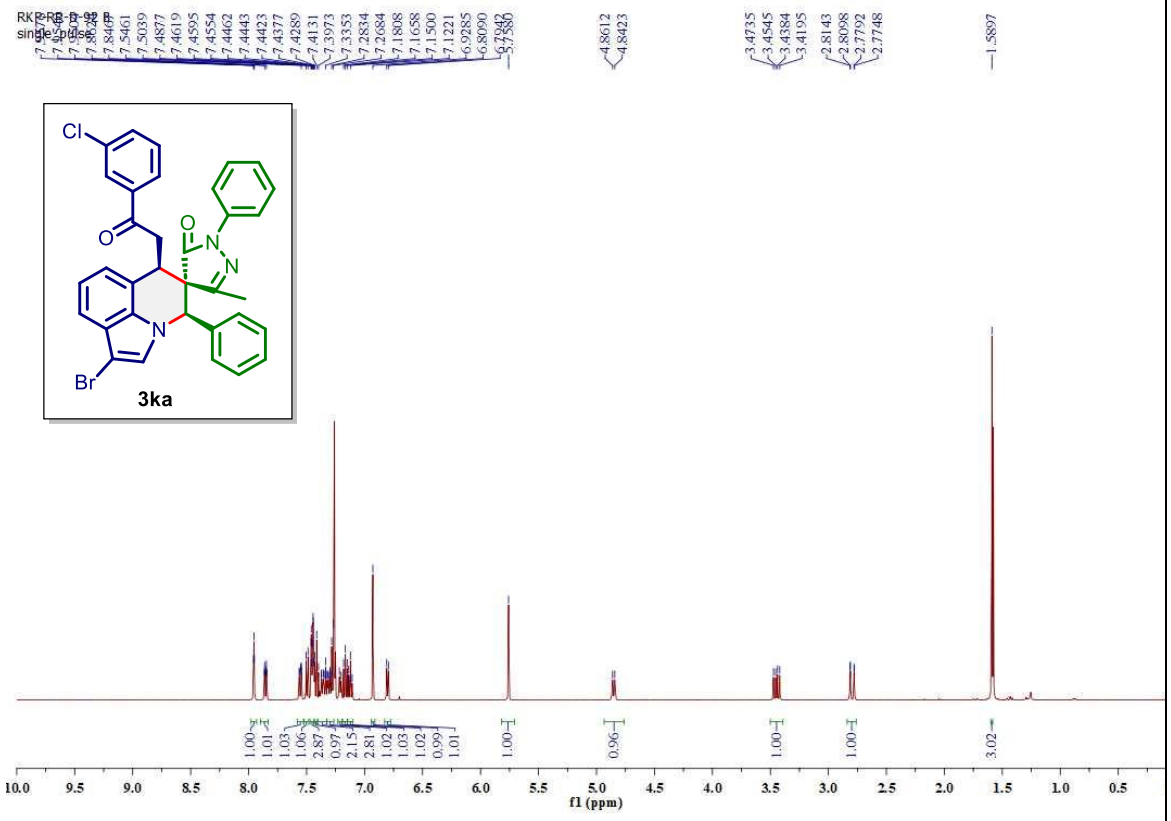
^{13}C NMR Spectrum of **3ja** (126 MHz, Chloroform-*d*)



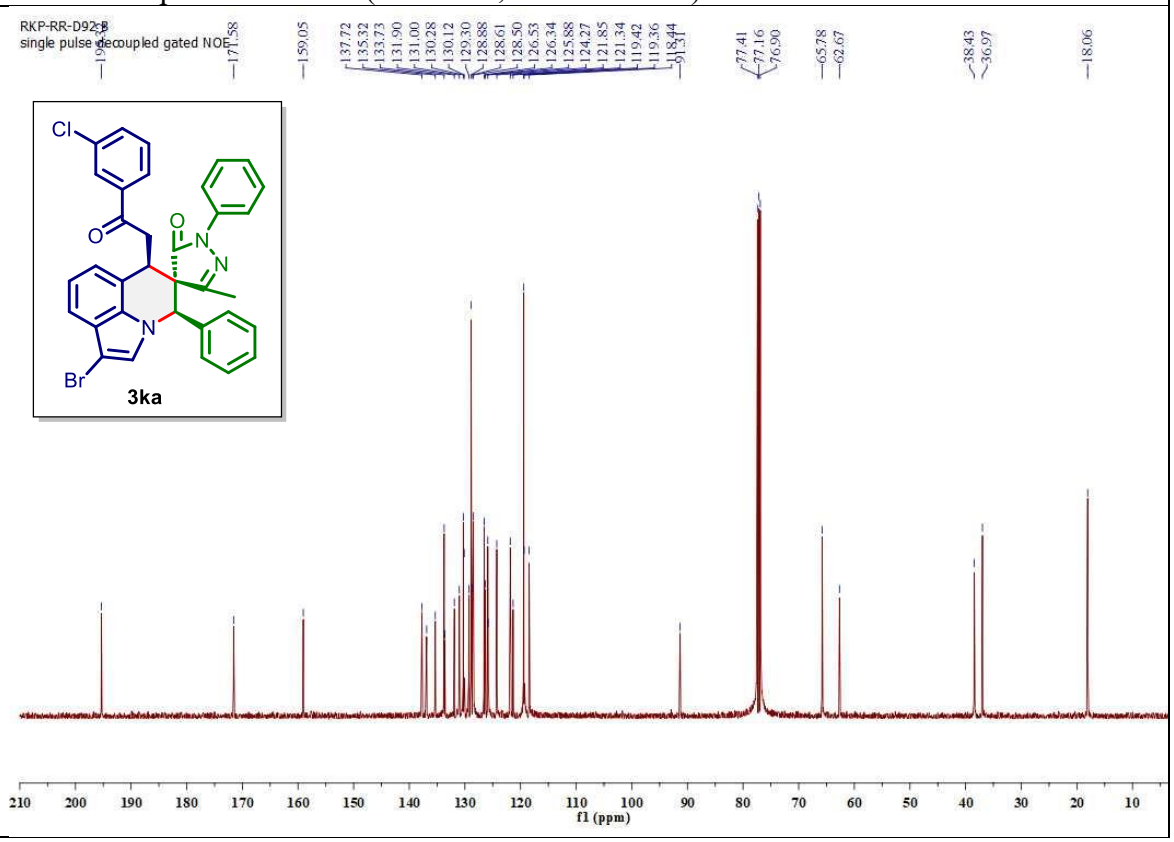
^{19}F NMR Spectrum of **3ja** (471 MHz, Chloroform-*d*)



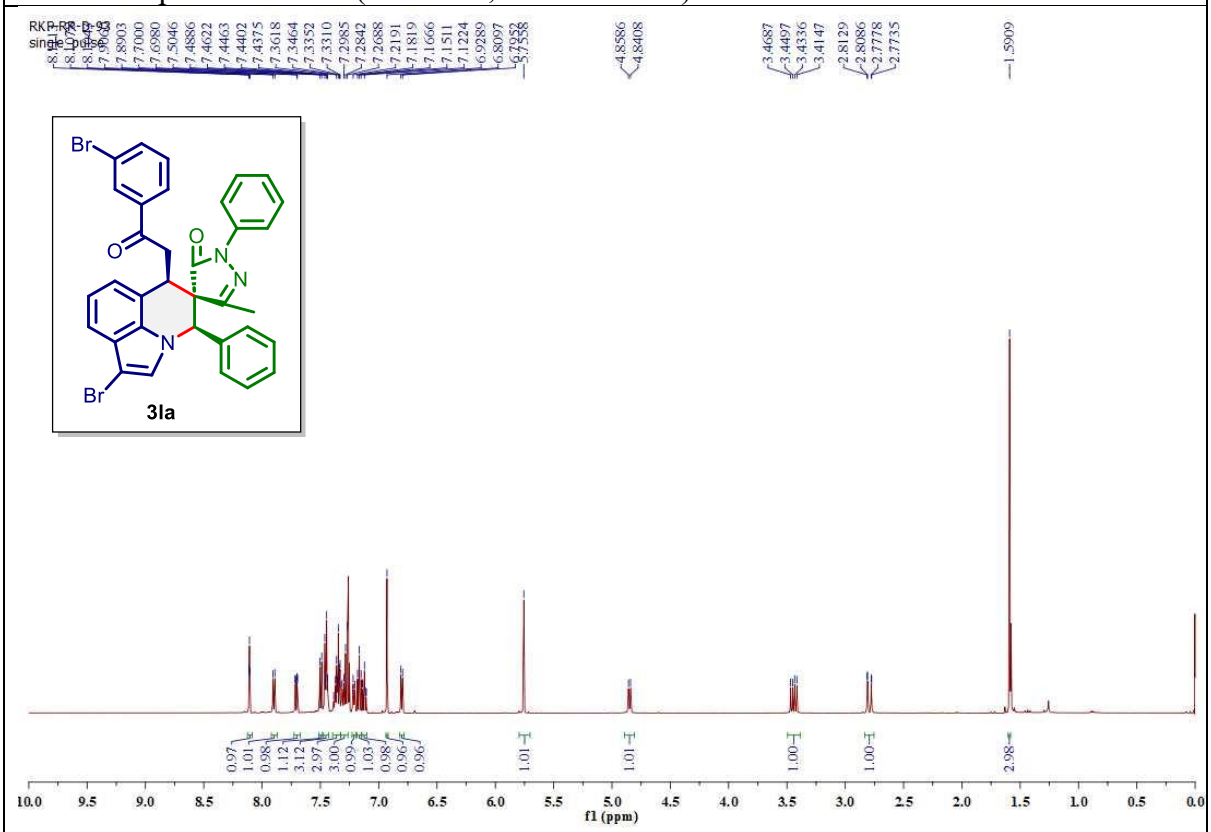
^{1}H NMR Spectrum of **3ka** (500 MHz, Chloroform-*d*)



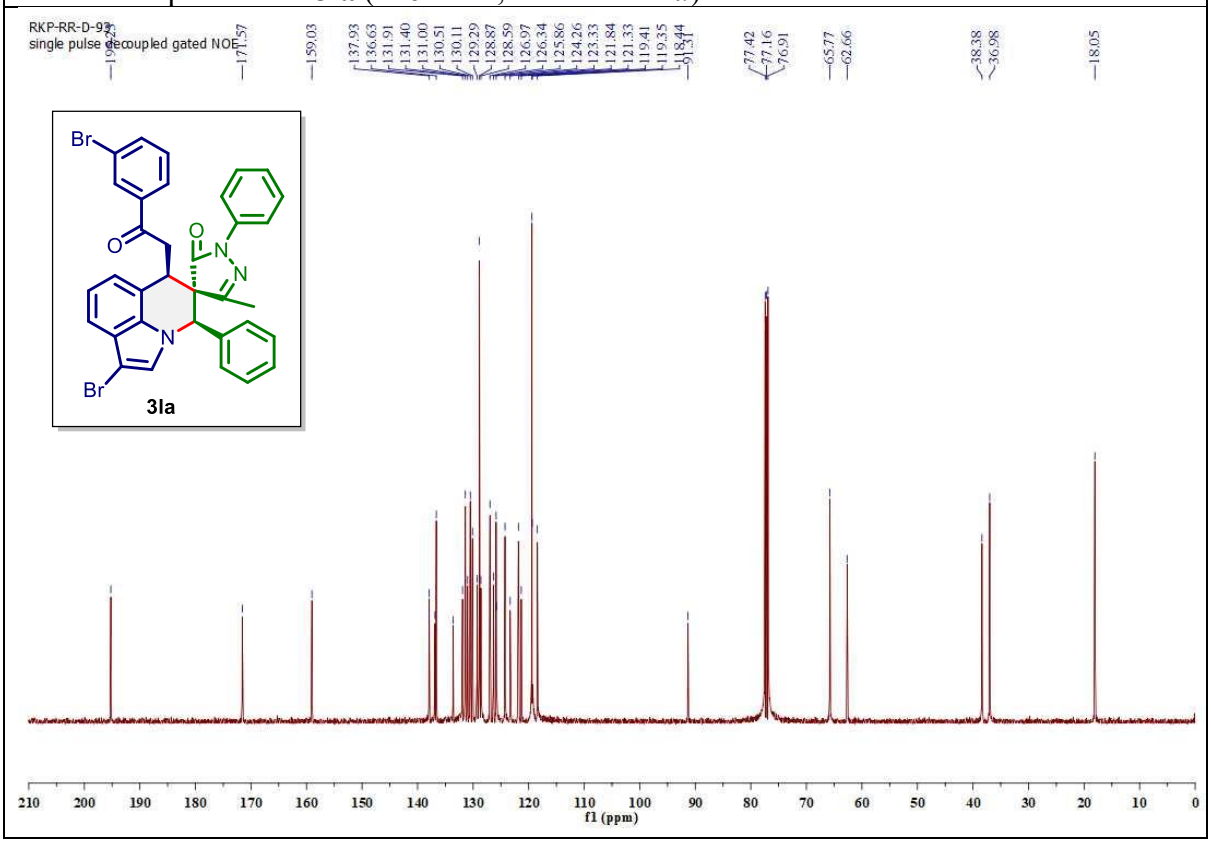
^{13}C NMR Spectrum of **3ka** (126 MHz, Chloroform-*d*)



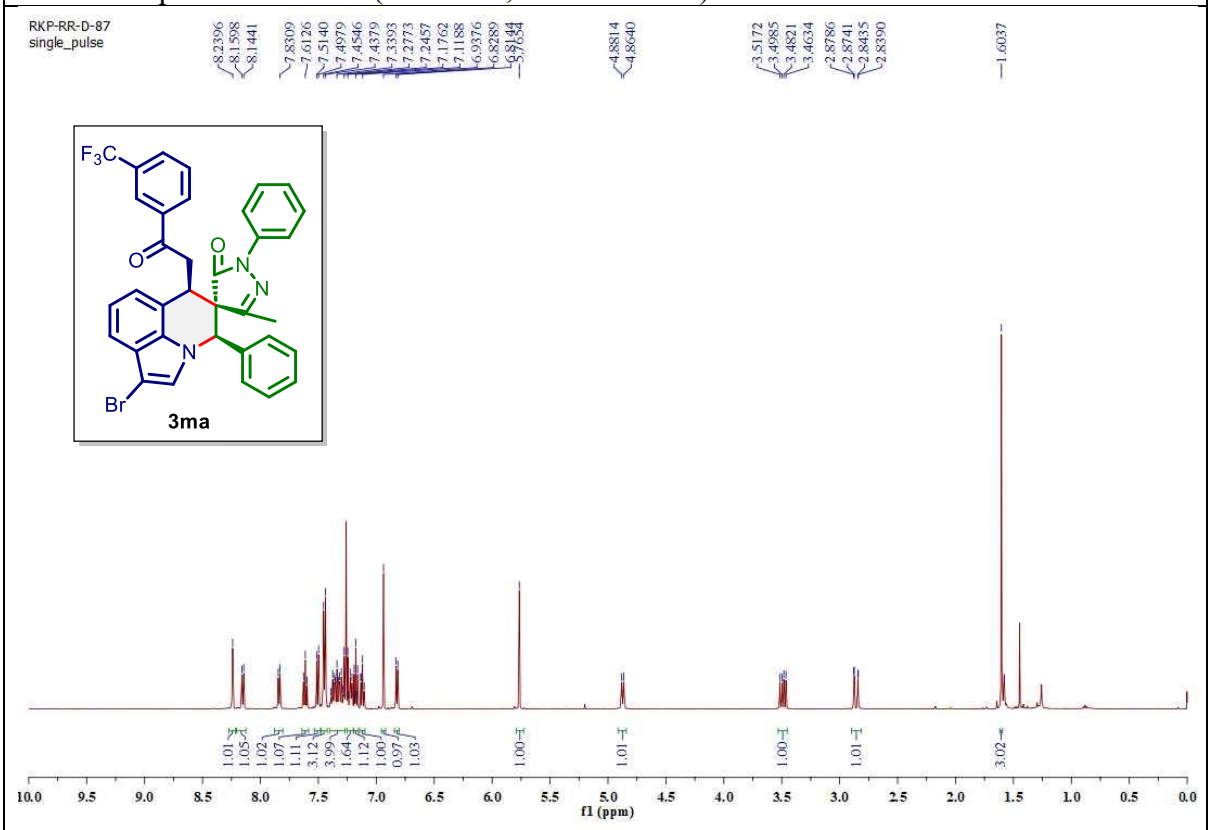
^{1}H NMR Spectrum of **3la** (500 MHz, Chloroform-*d*)



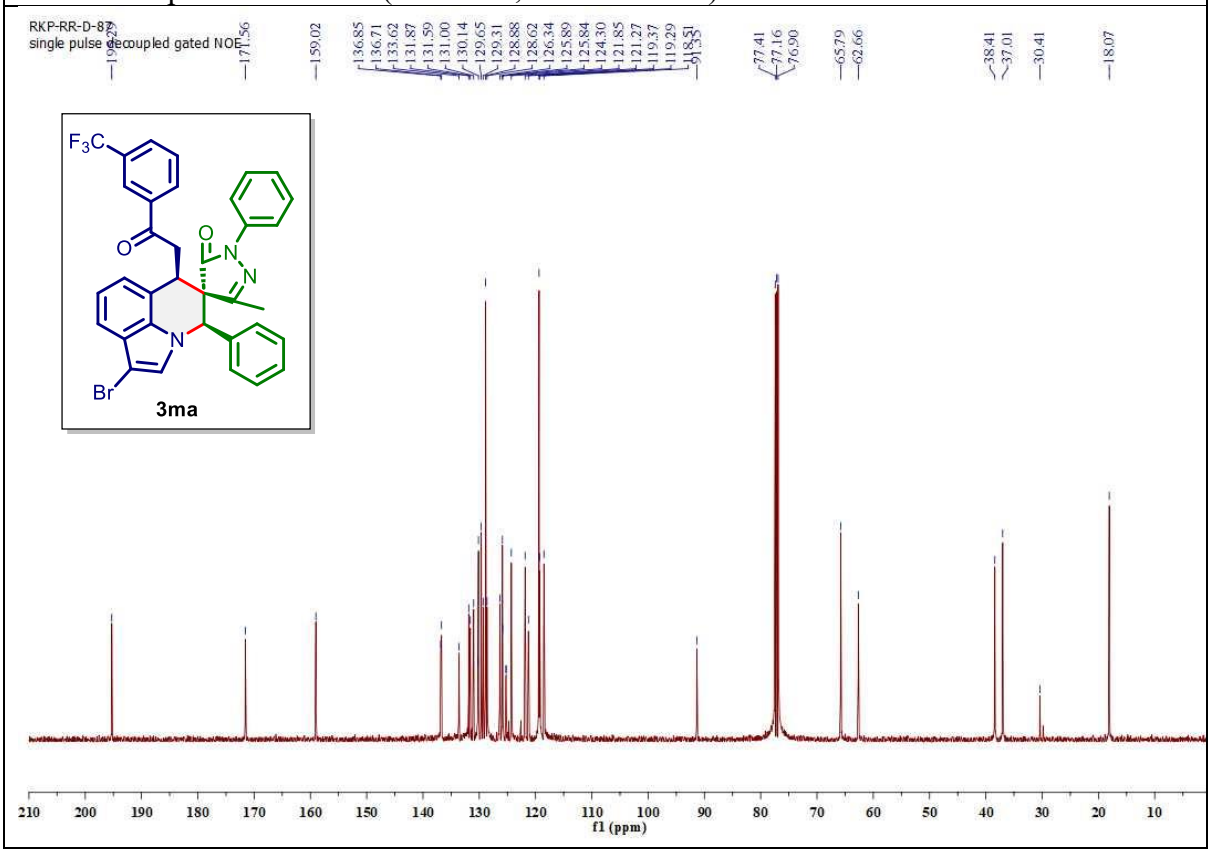
^{13}C NMR Spectrum of **3la** (126 MHz, Chloroform-*d*)



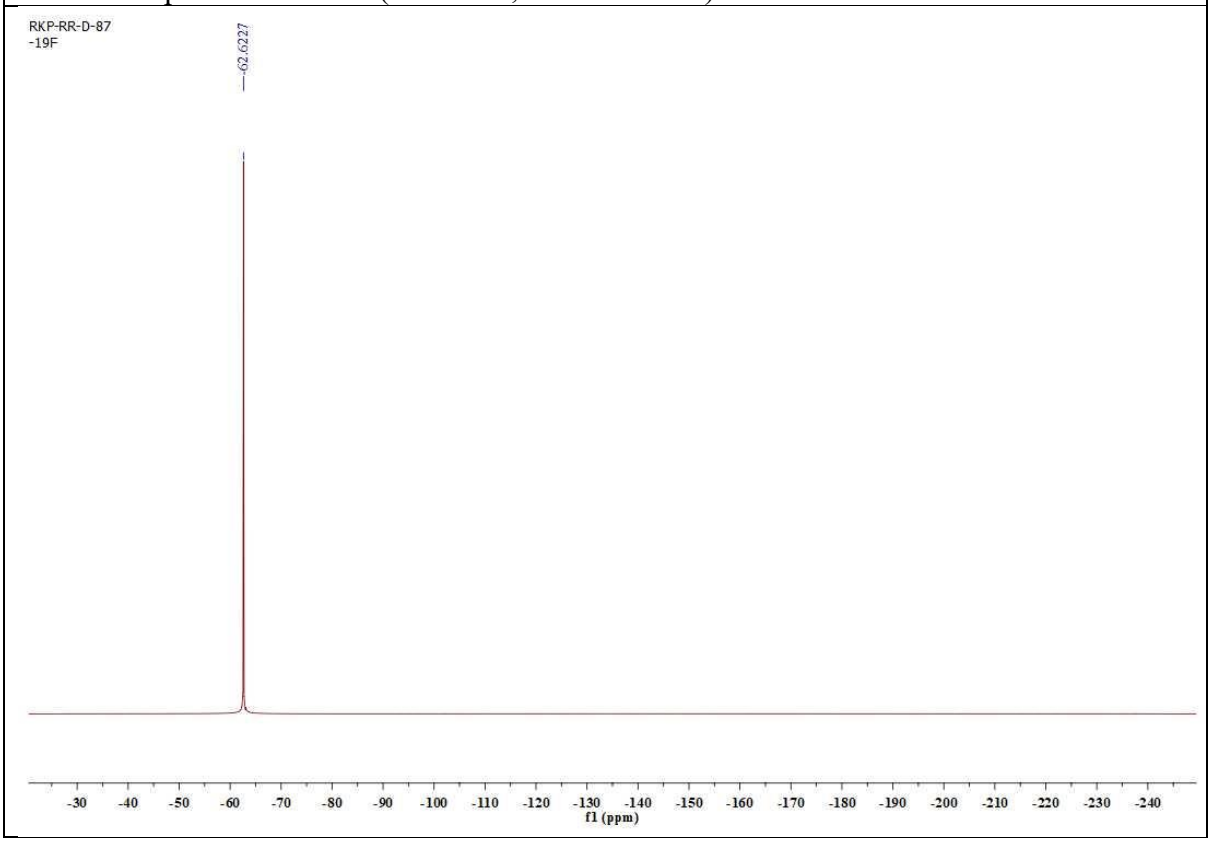
^{1}H NMR Spectrum of **3ma** (500 MHz, Chloroform-*d*)



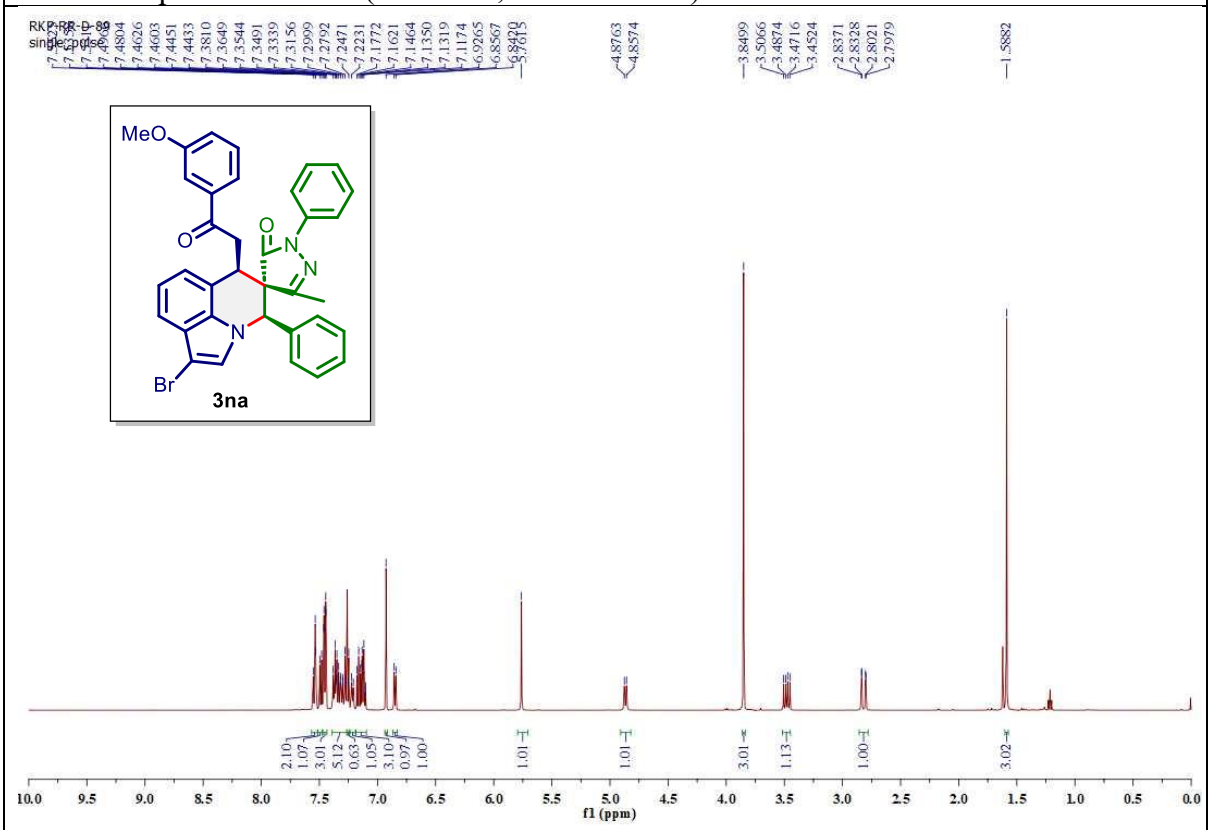
^{13}C NMR Spectrum of **3ma** (126 MHz, Chloroform-*d*)



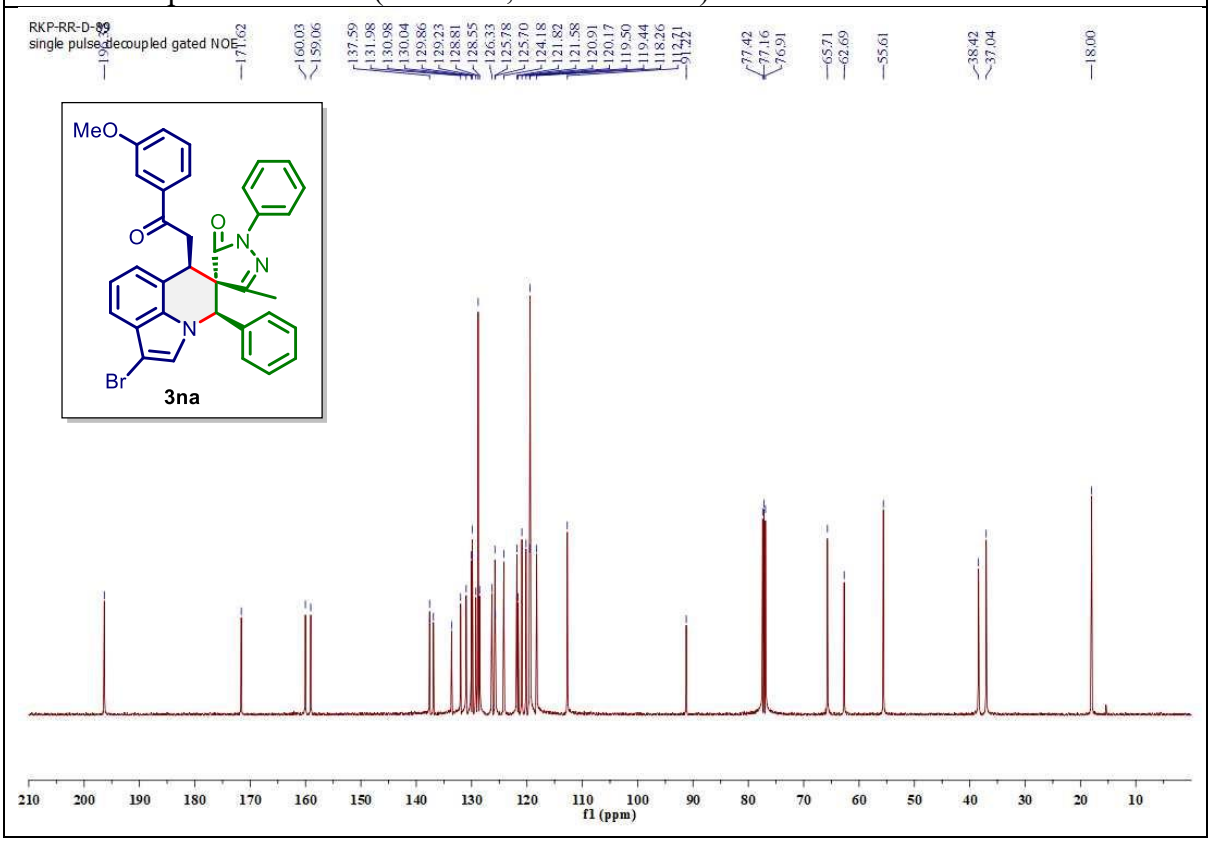
^{19}F NMR Spectrum of **3ma** (471 MHz, Chloroform-*d*)



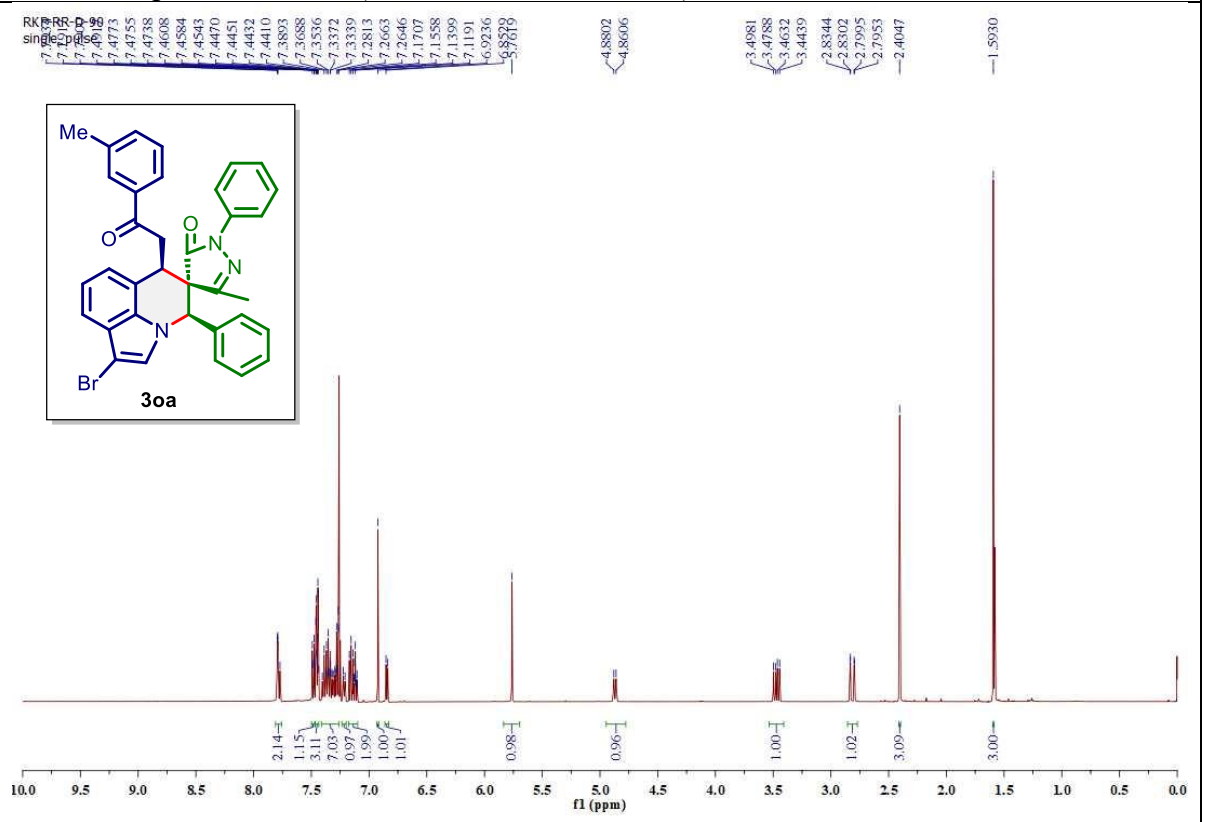
^{1}H NMR Spectrum of **3na** (500 MHz, Chloroform-*d*)



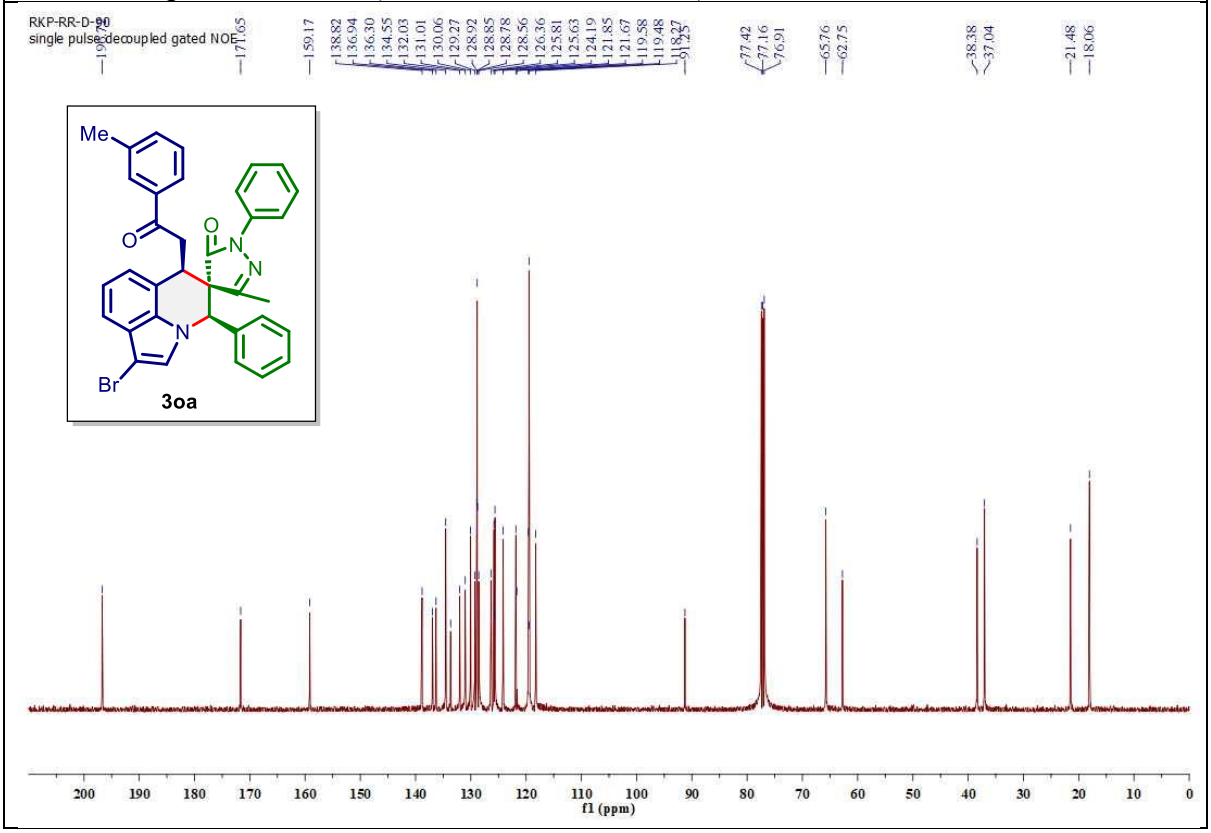
^{13}C NMR Spectrum of **3na** (126 MHz, Chloroform-*d*)



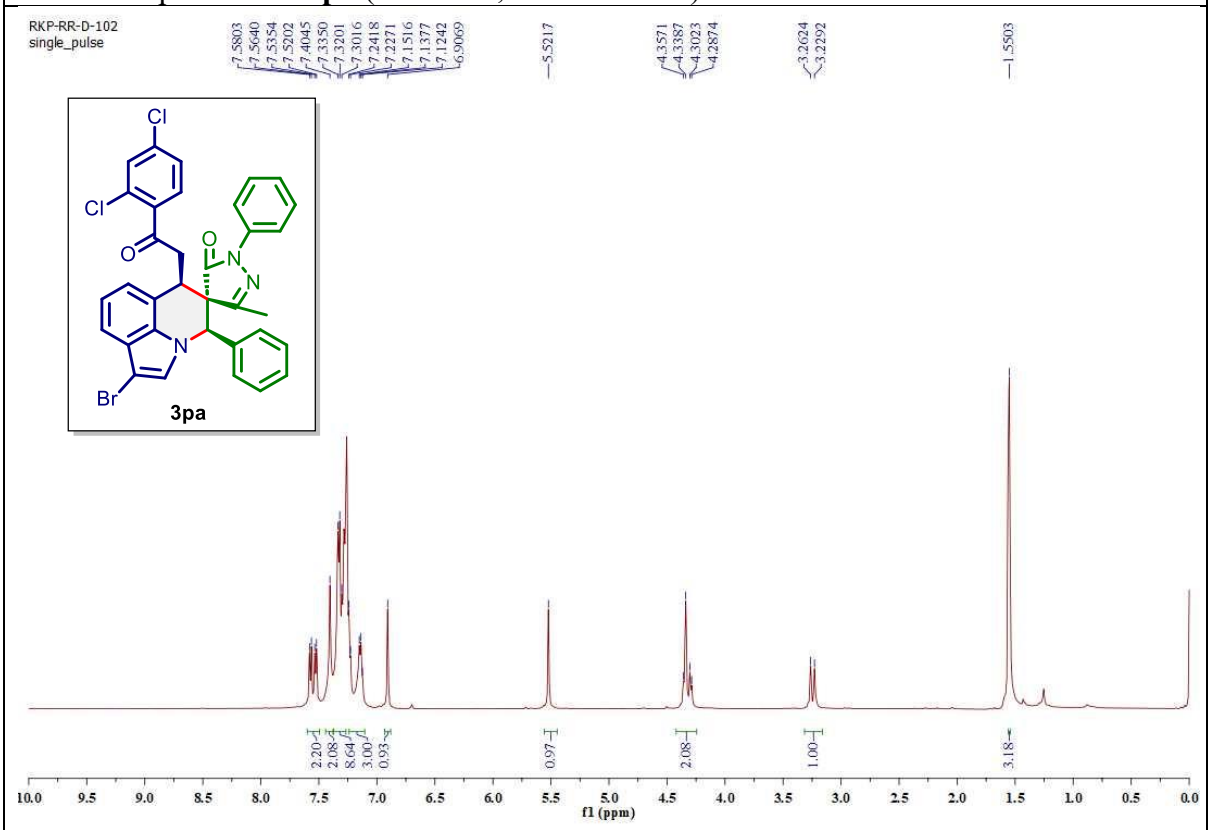
^{1}H NMR Spectrum of **3oa** (500 MHz, Chloroform-*d*)



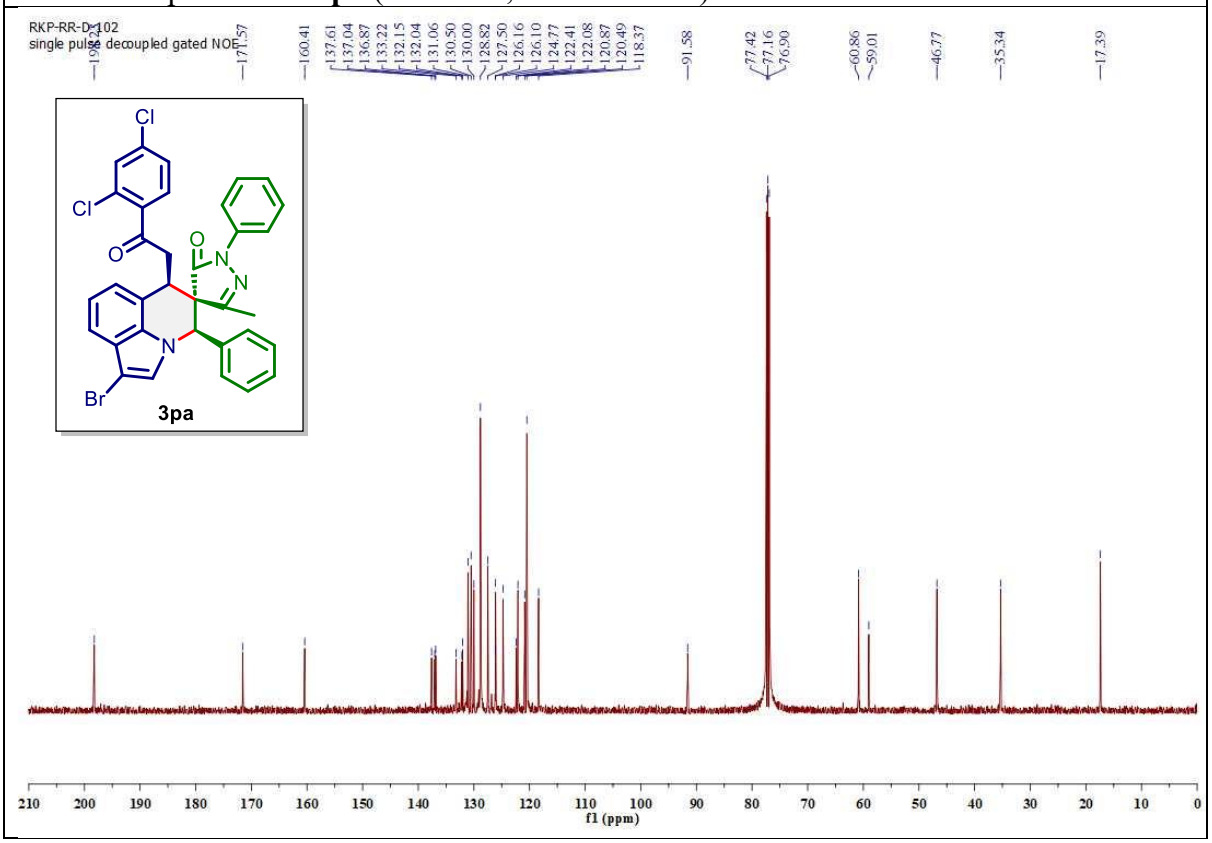
^{13}C NMR Spectrum of **3oa** (126 MHz, Chloroform-*d*)



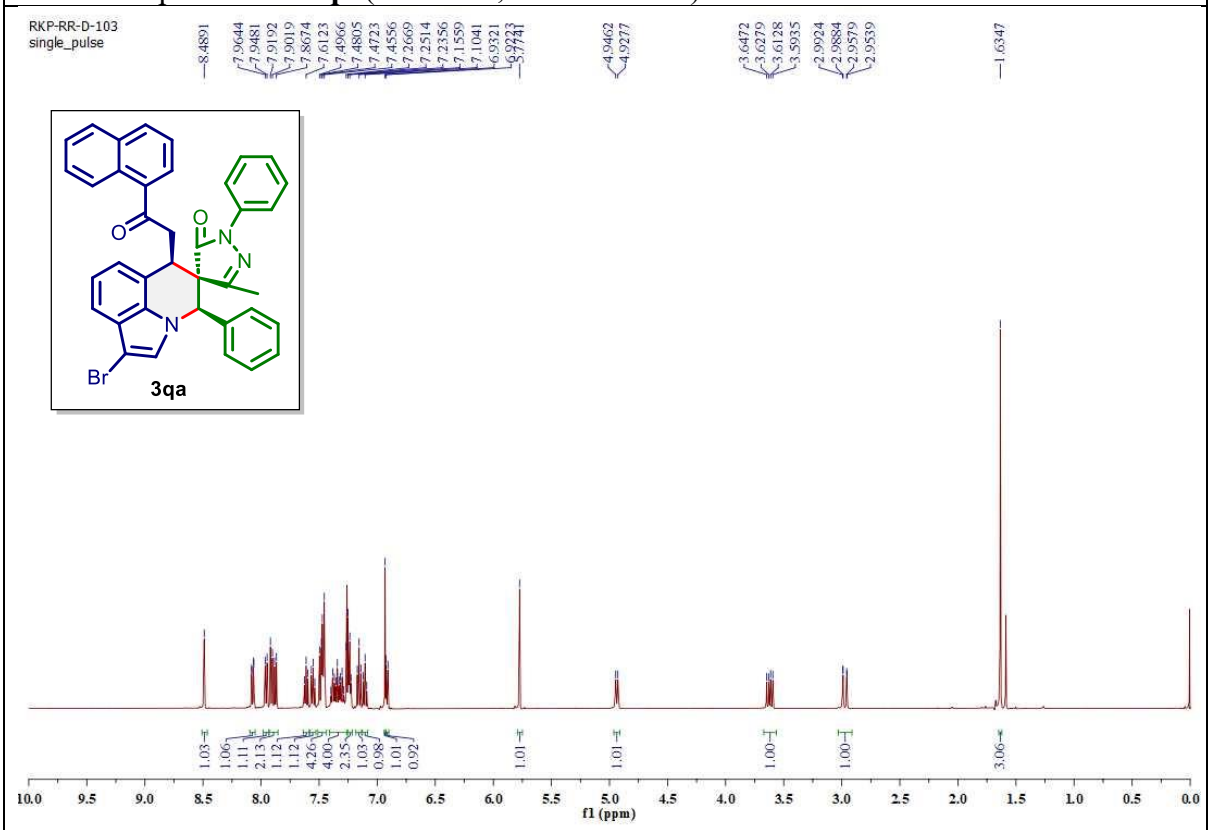
^{1}H NMR Spectrum of **3pa** (500 MHz, Chloroform-*d*)



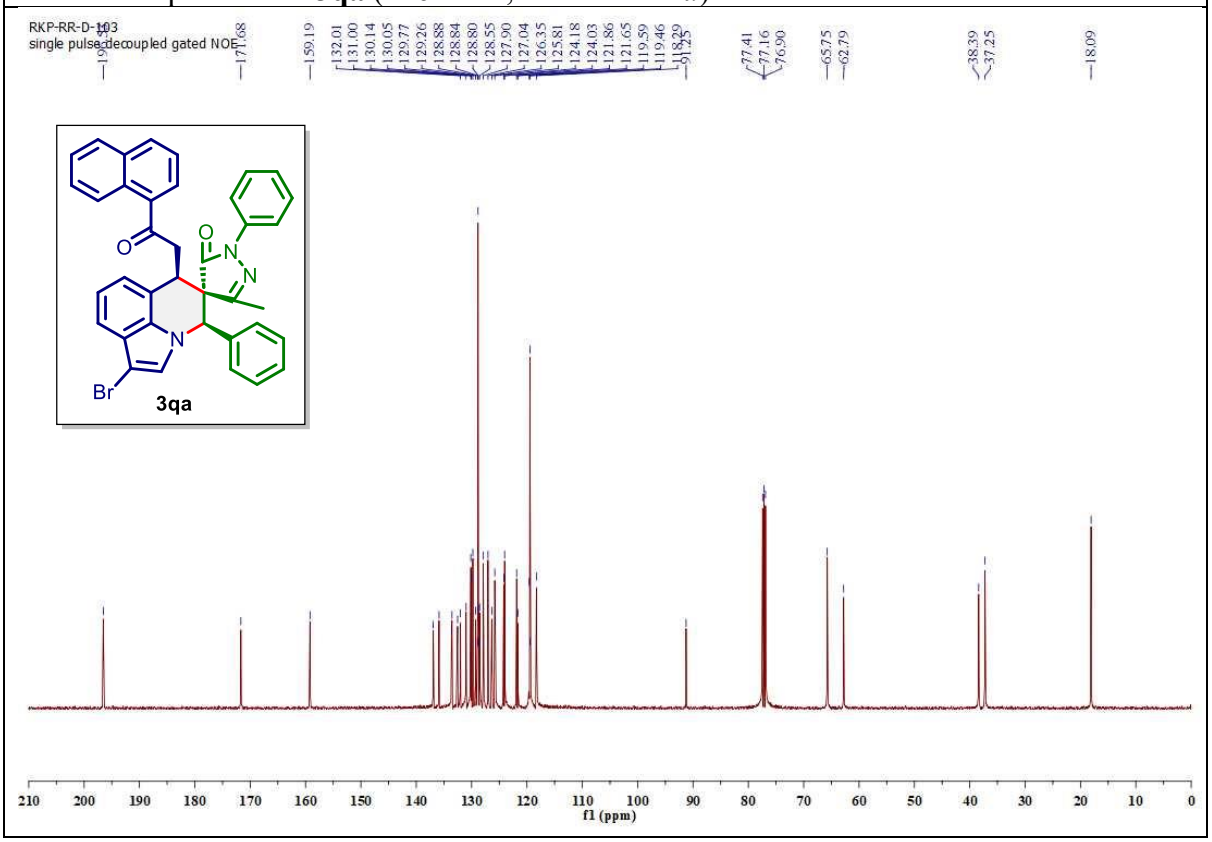
^{13}C NMR Spectrum of **3pa** (126 MHz, Chloroform-*d*)



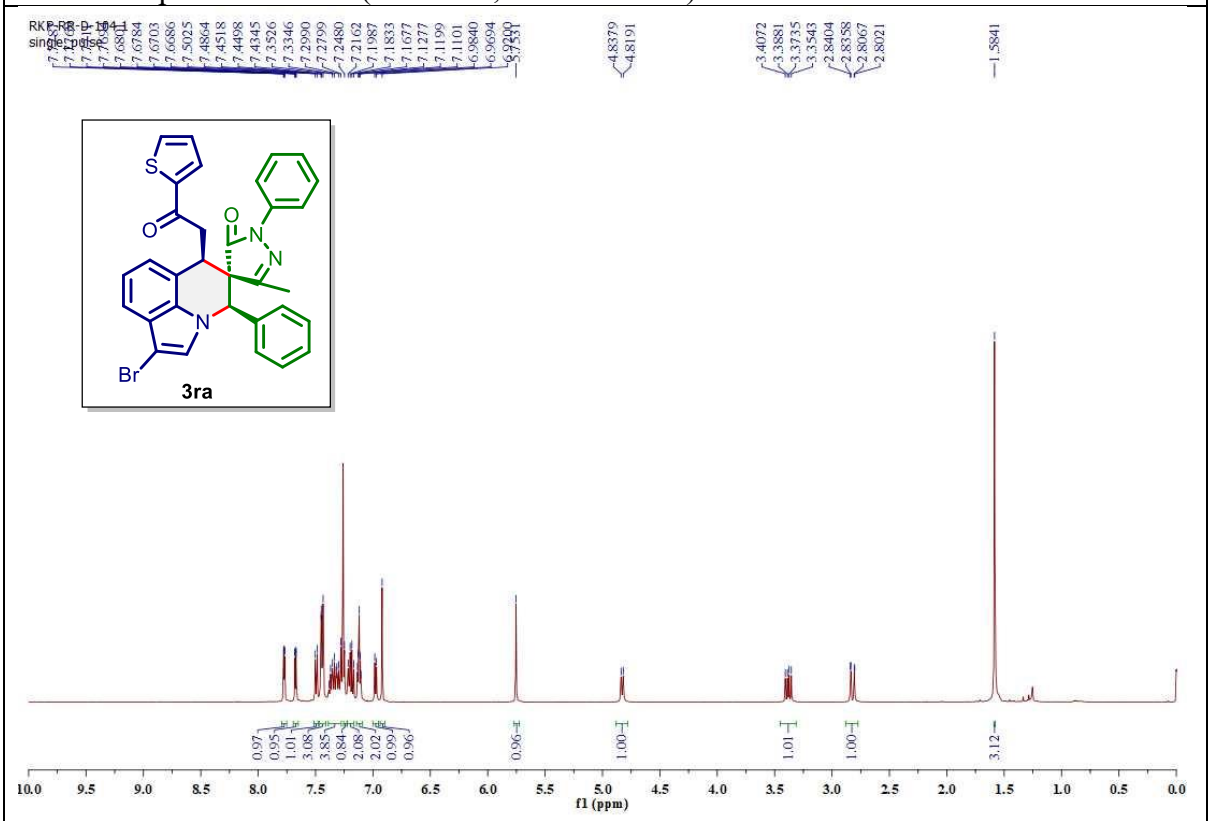
^{1}H NMR Spectrum of **3qa** (500 MHz, Chloroform-*d*)



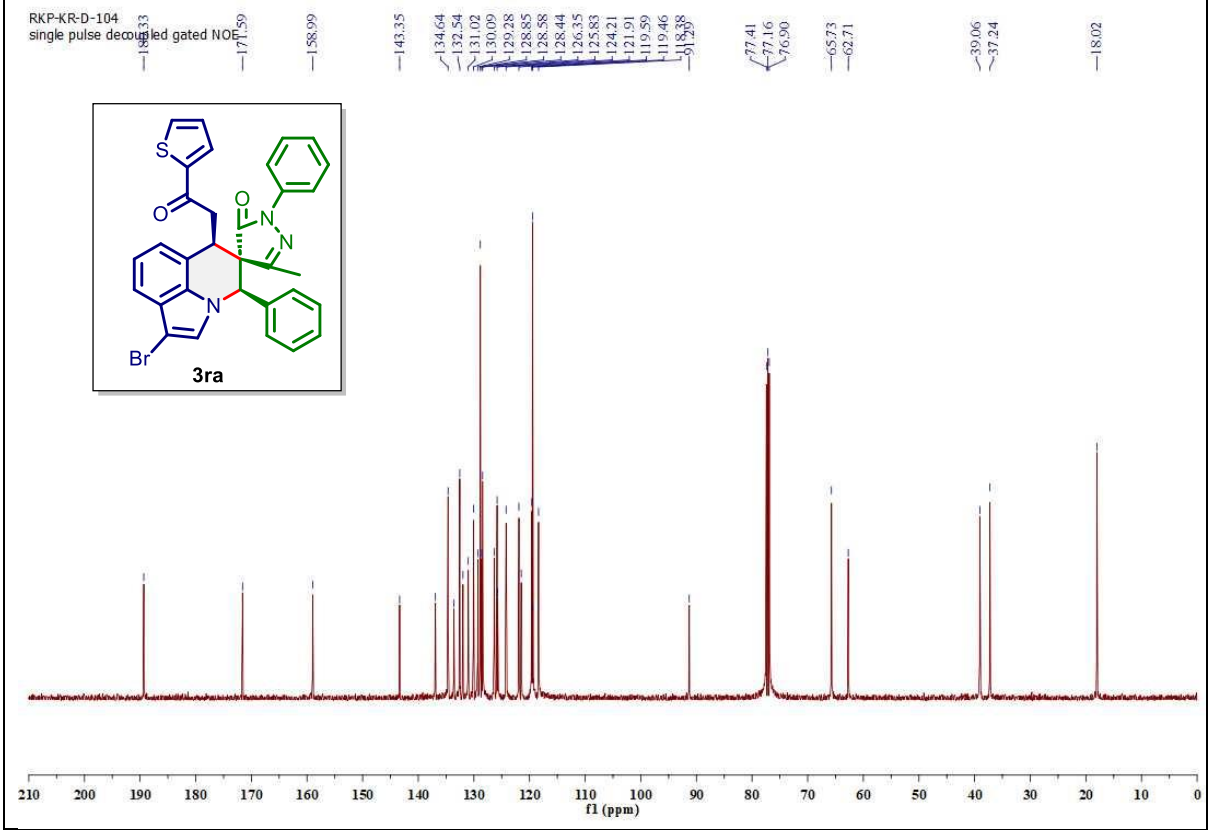
^{13}C NMR Spectrum of **3qa** (126 MHz, Chloroform-*d*)



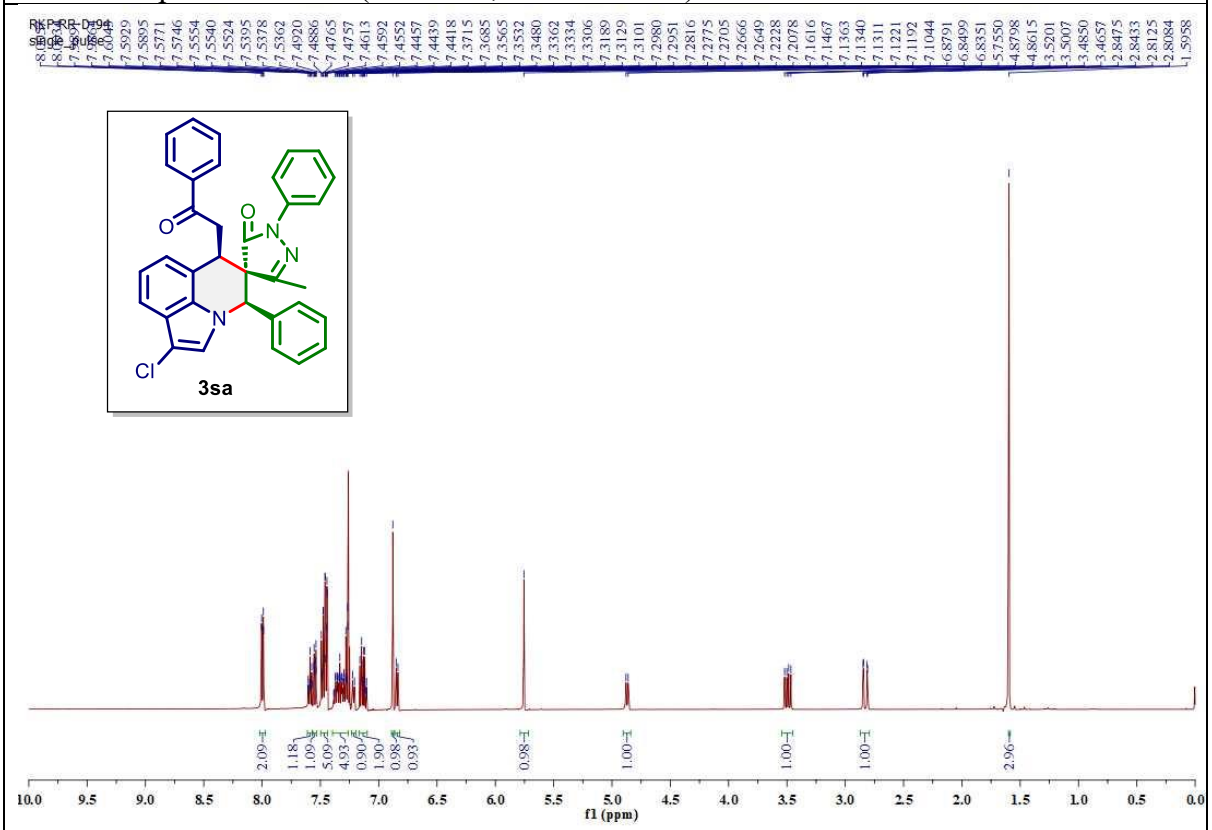
^{1}H NMR Spectrum of **3ra** (500 MHz, Chloroform-*d*)



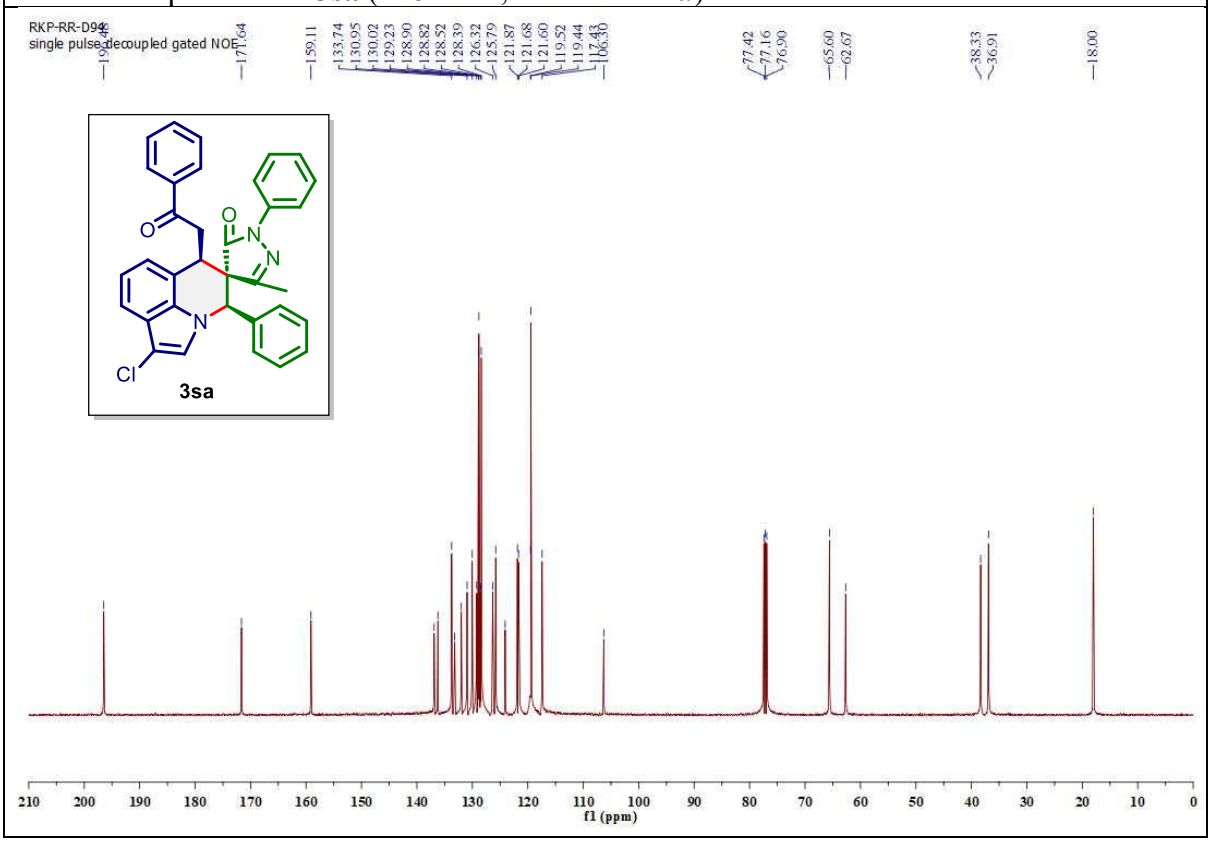
^{13}C NMR Spectrum of **3ra** (126 MHz, Chloroform-*d*)



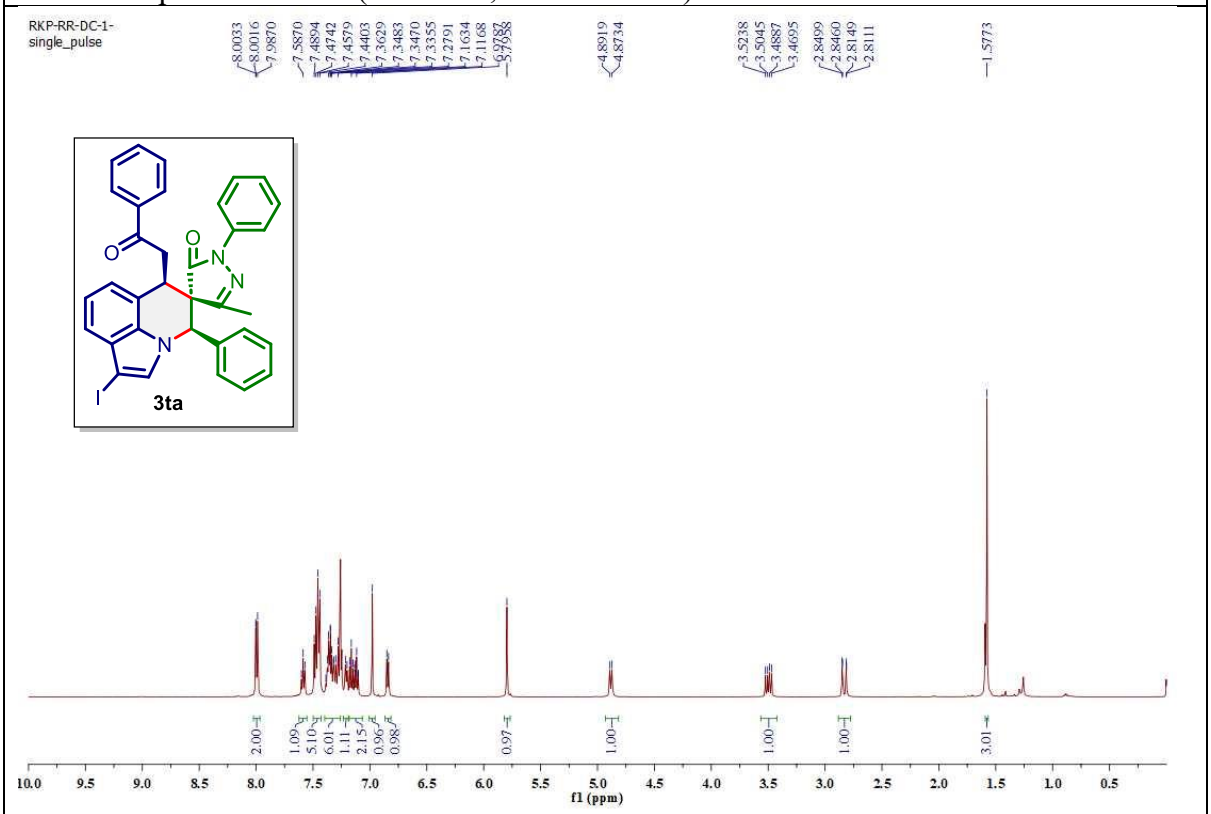
^{1}H NMR Spectrum of **3sa** (500 MHz, Chloroform-*d*)



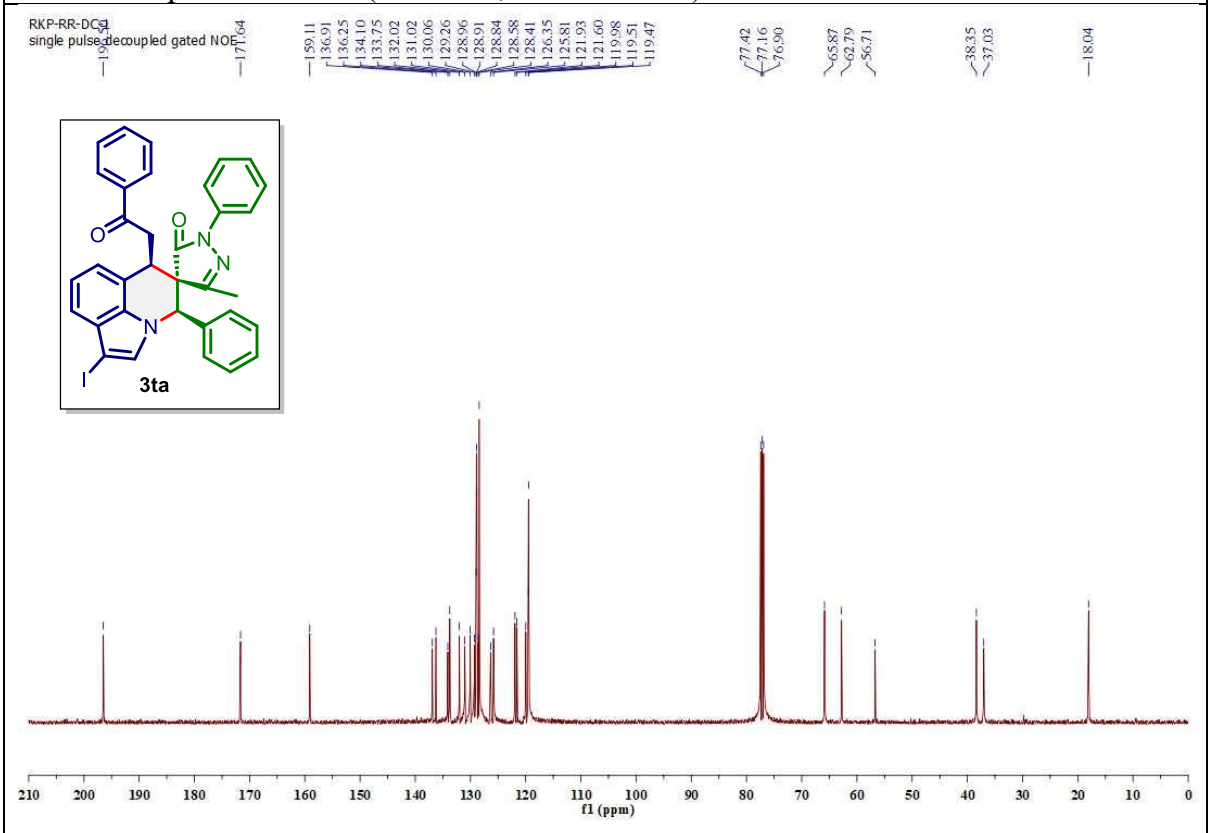
^{13}C NMR Spectrum of **3sa** (126 MHz, Chloroform-*d*)



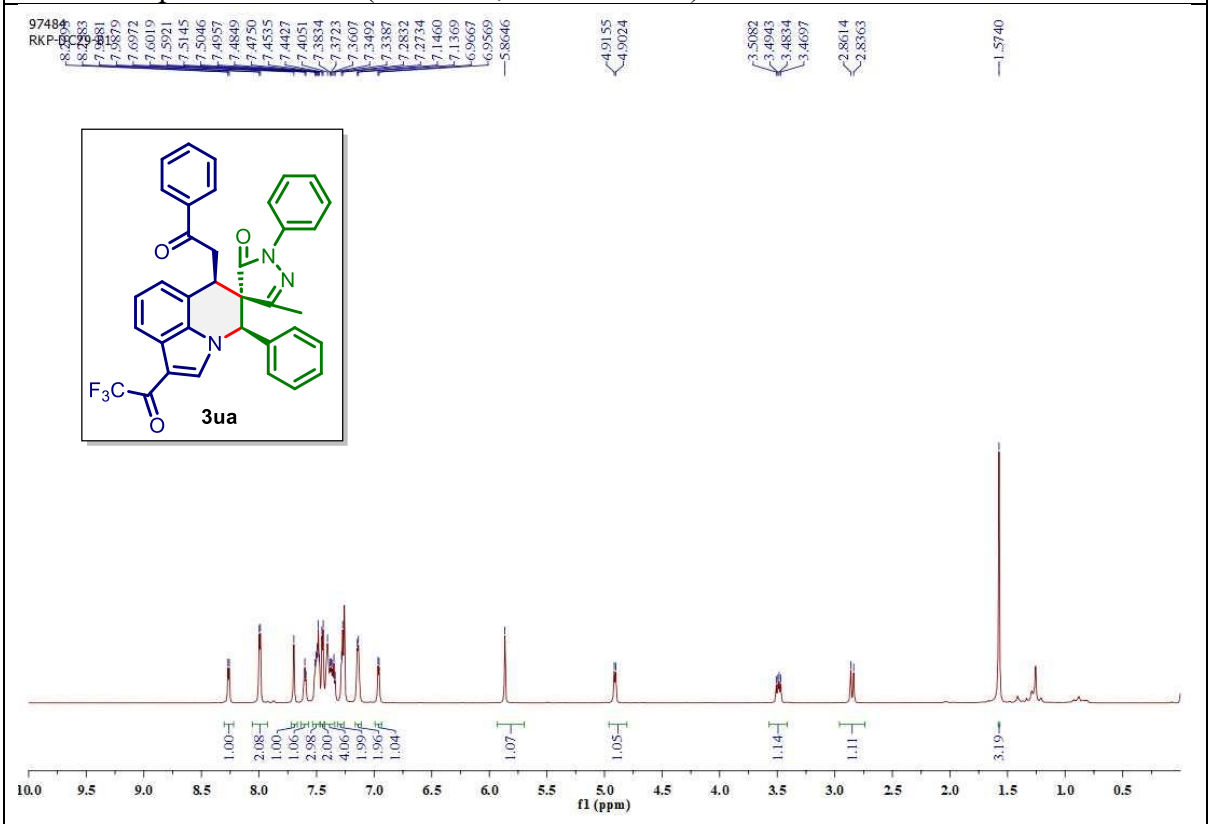
^{1}H NMR Spectrum of **3ta** (500 MHz, Chloroform-*d*)



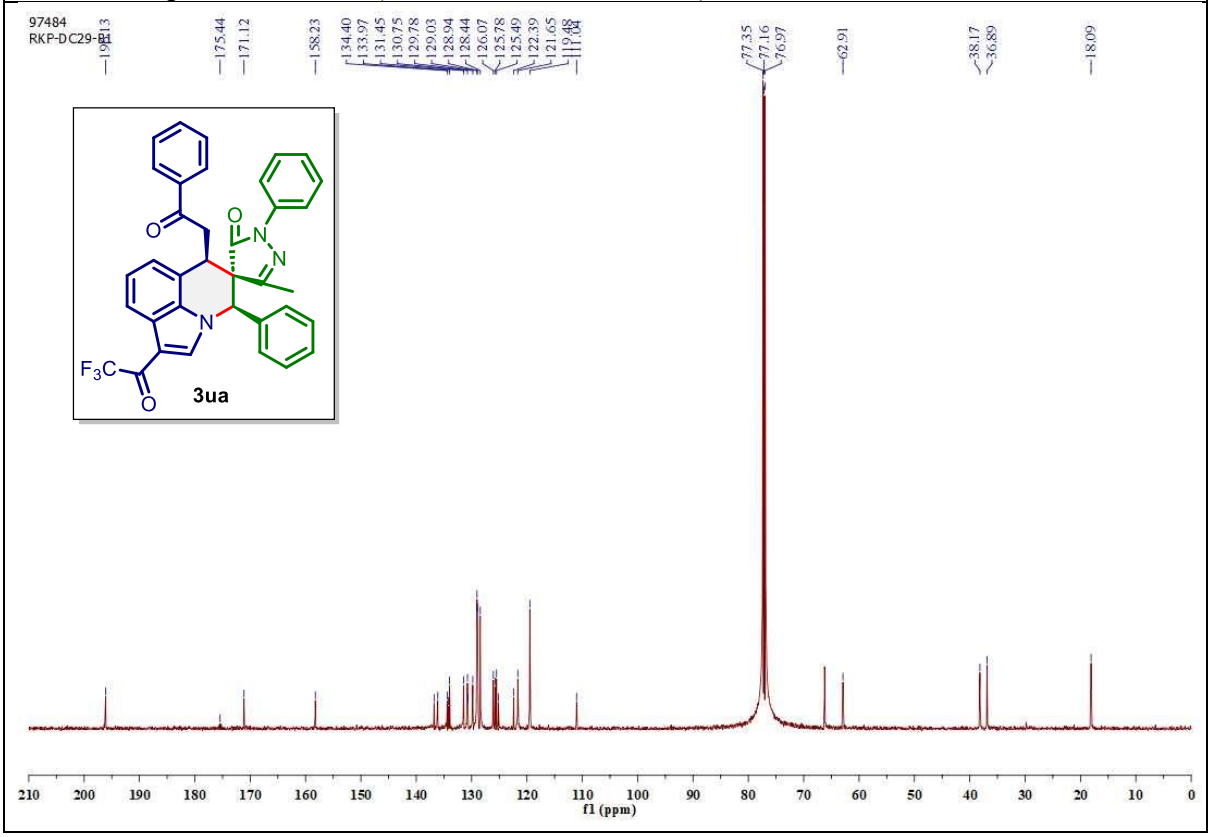
^{13}C NMR Spectrum of **3ta** (126 MHz, Chloroform-*d*)



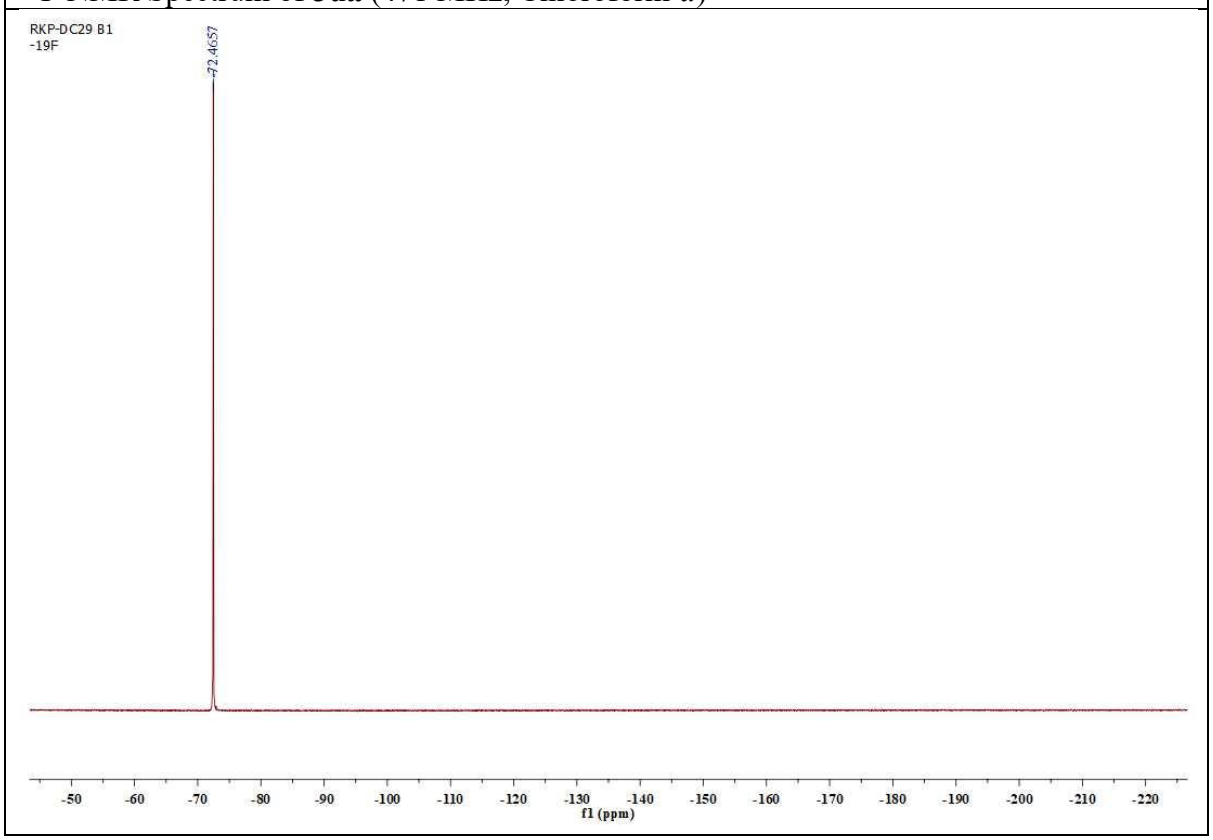
^{1}H NMR Spectrum of **3ua** (700 MHz, Chloroform-*d*)



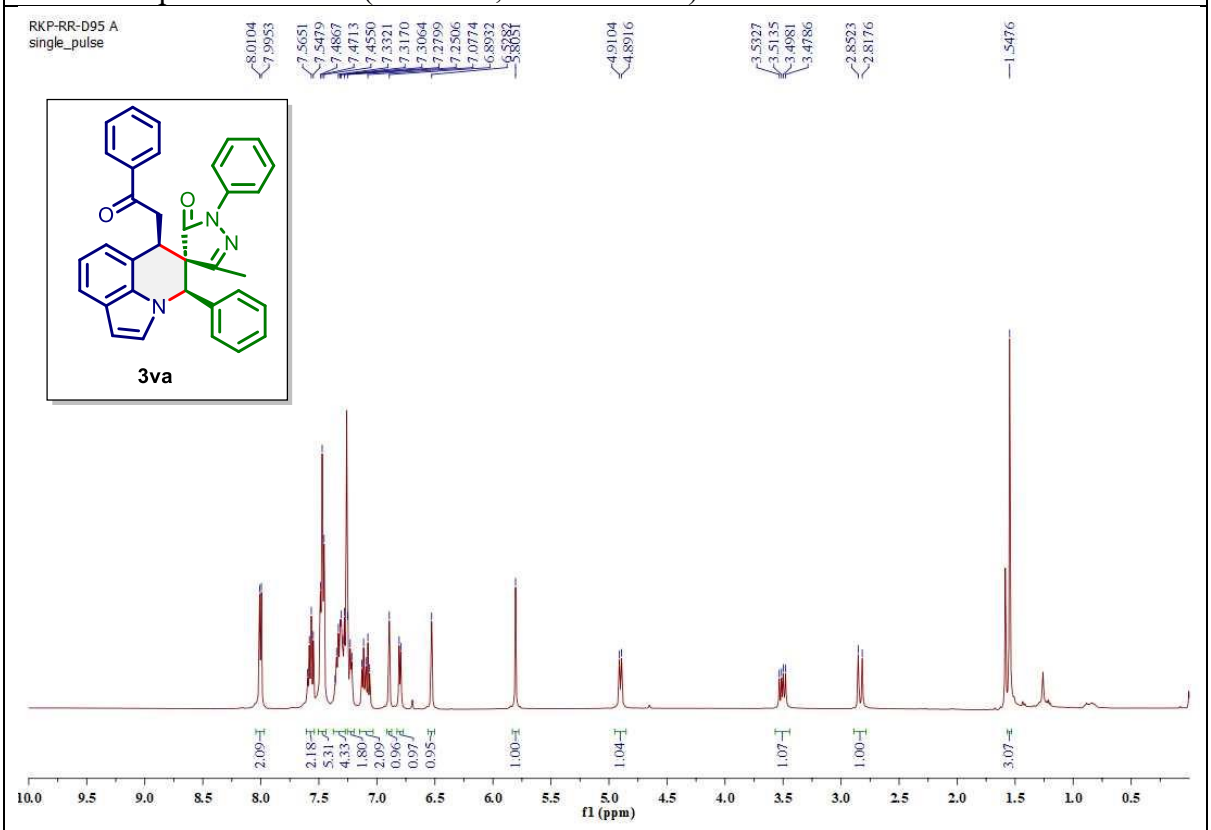
^{13}C NMR Spectrum of **3ua** (176 MHz, Chloroform-*d*)



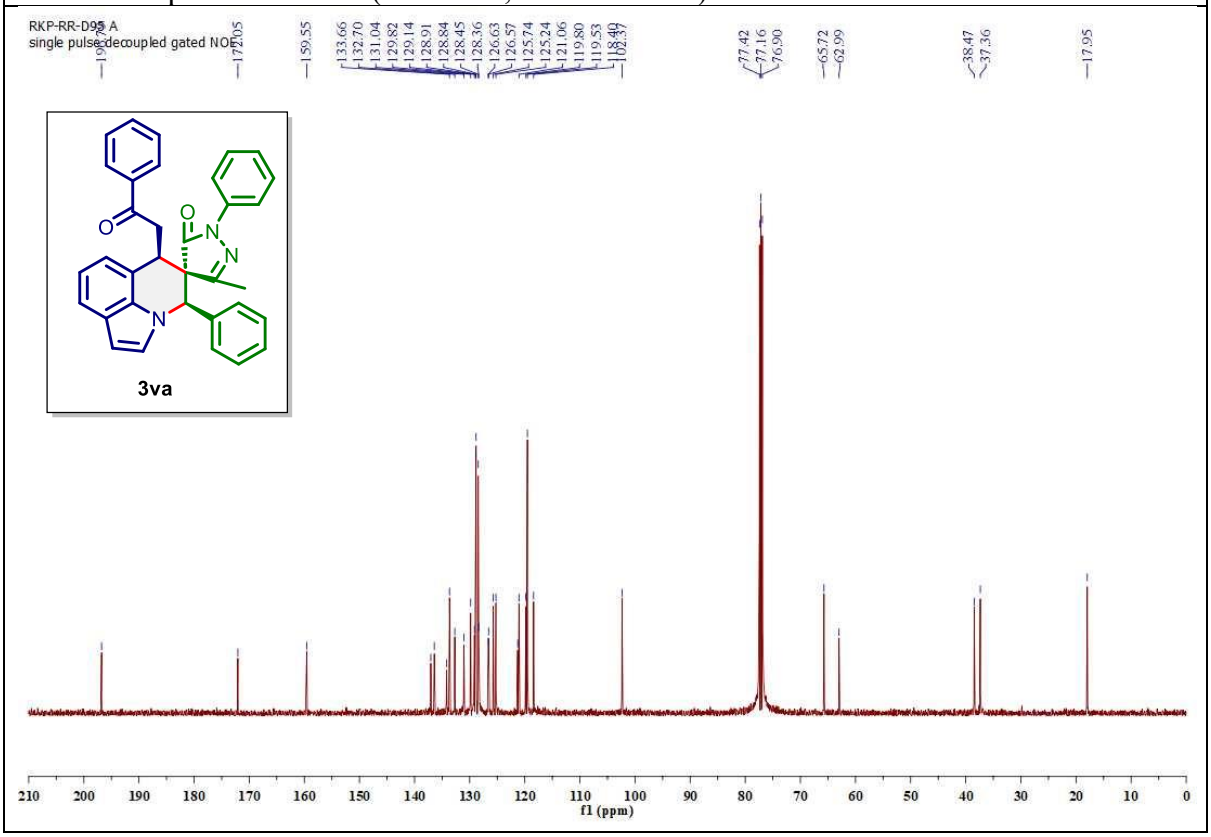
^{19}F NMR Spectrum of **3ua** (471 MHz, Chloroform-*d*)



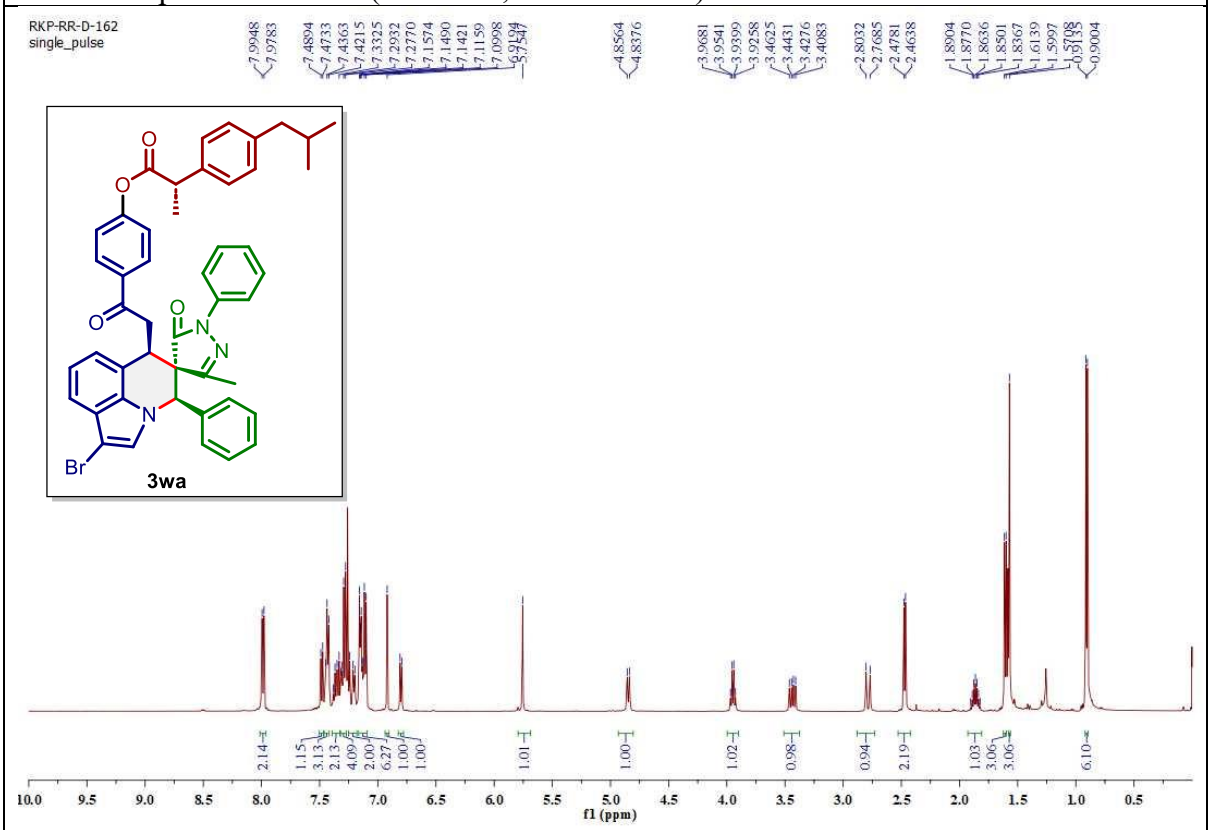
^{1}H NMR Spectrum of **3va** (500 MHz, Chloroform-*d*)



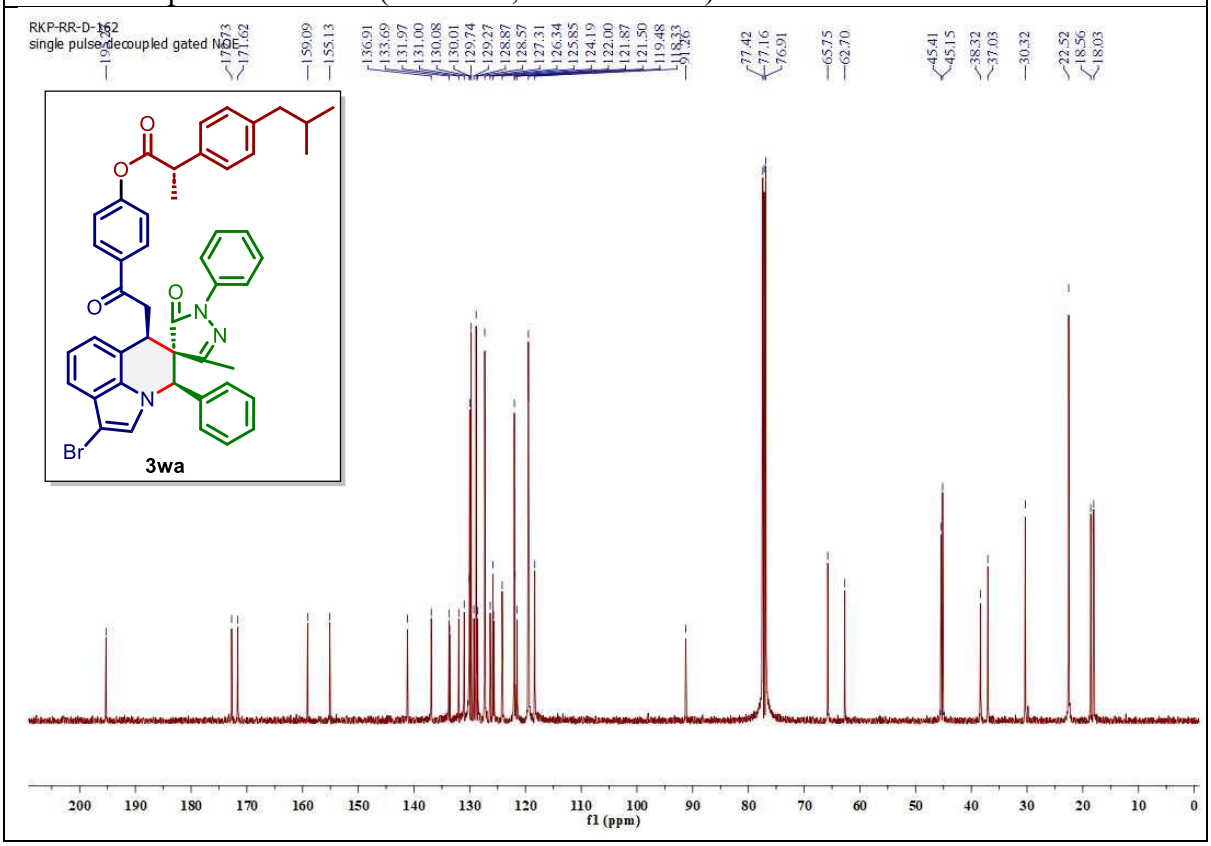
^{13}C NMR Spectrum of **3va** (126 MHz, Chloroform-*d*)



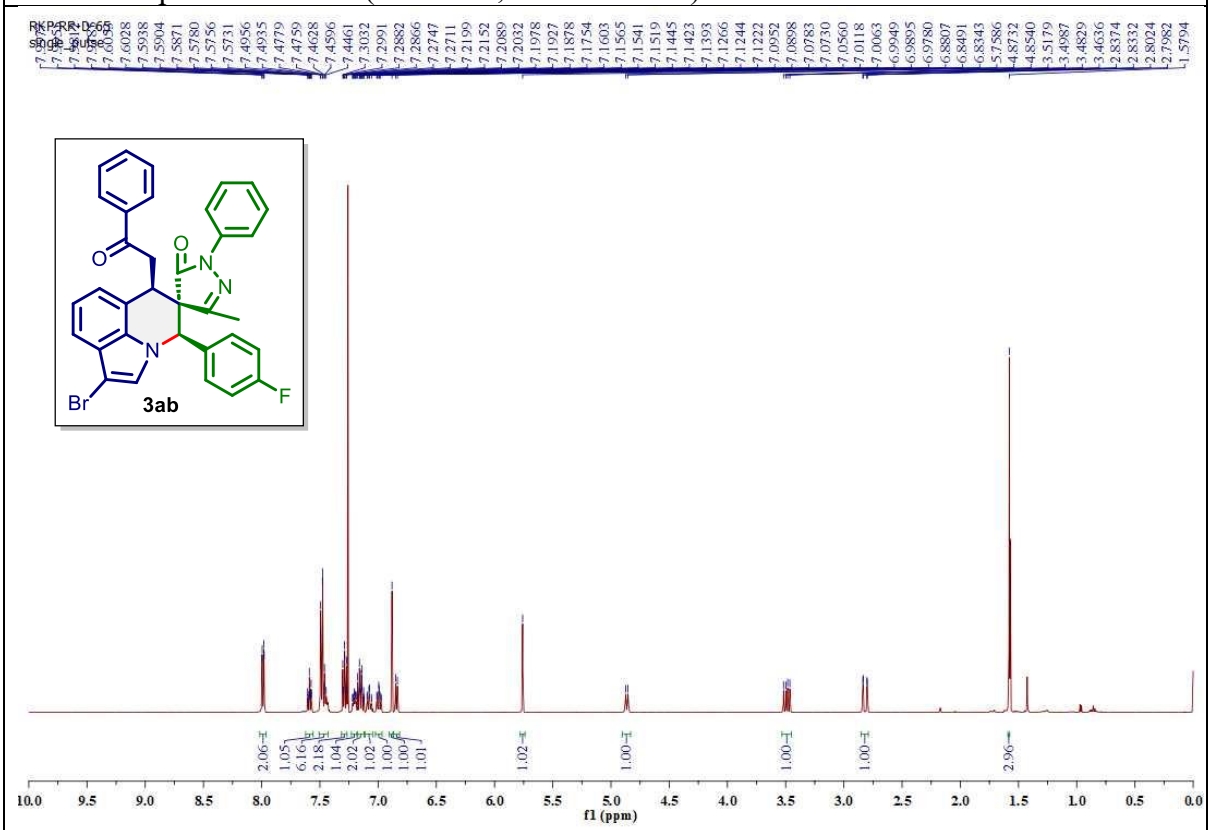
^{1}H NMR Spectrum of **3wa** (500 MHz, Chloroform-*d*)



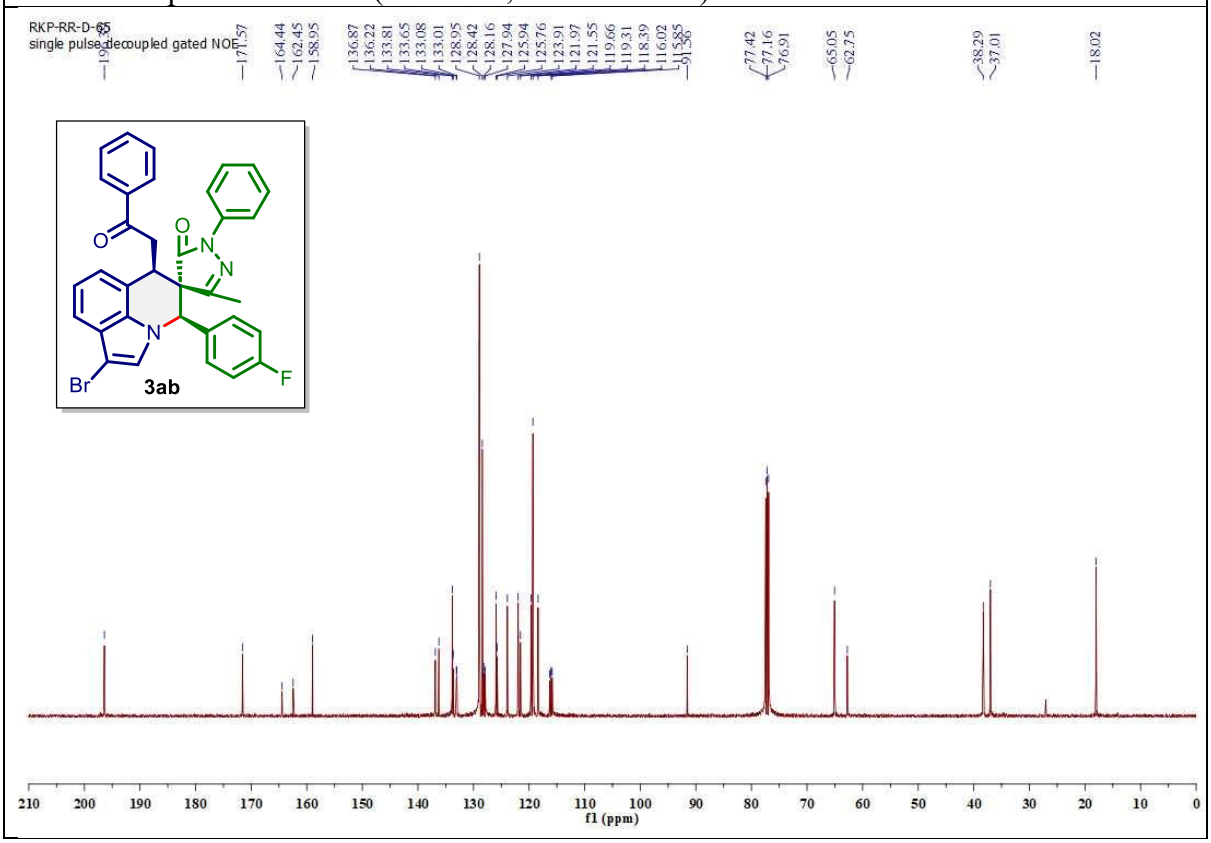
^{13}C NMR Spectrum of **3wa** (126 MHz, Chloroform-*d*)



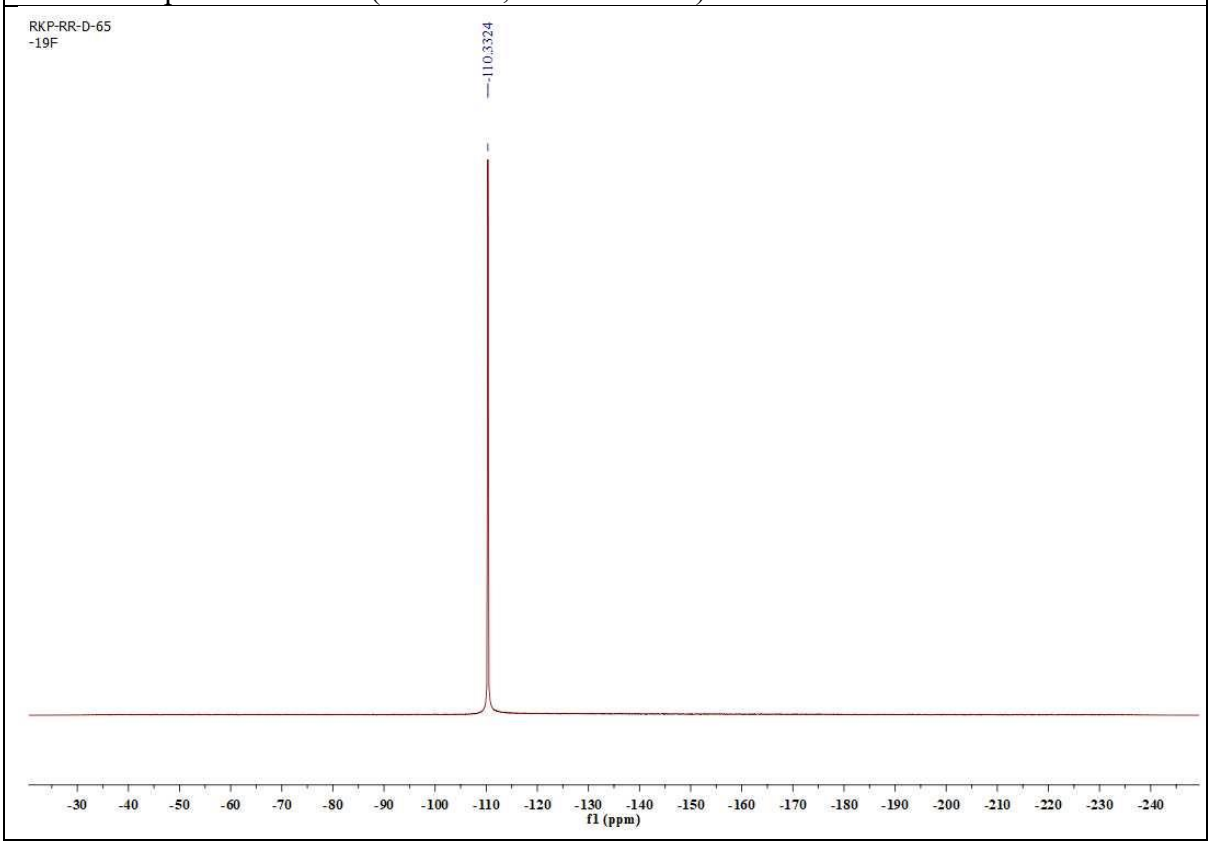
^{1}H NMR Spectrum of **3ab** (500 MHz, Chloroform-*d*)



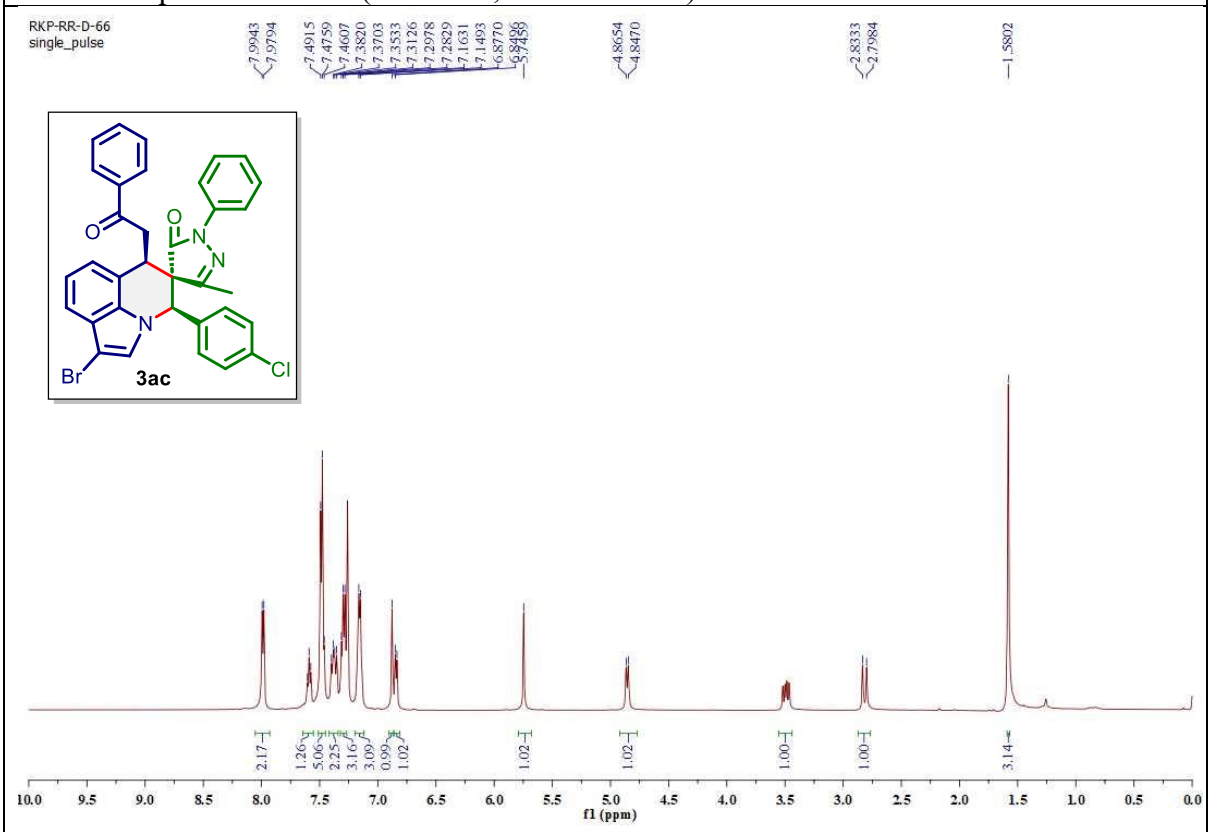
^{13}C NMR Spectrum of **3ab** (126 MHz, Chloroform-*d*)



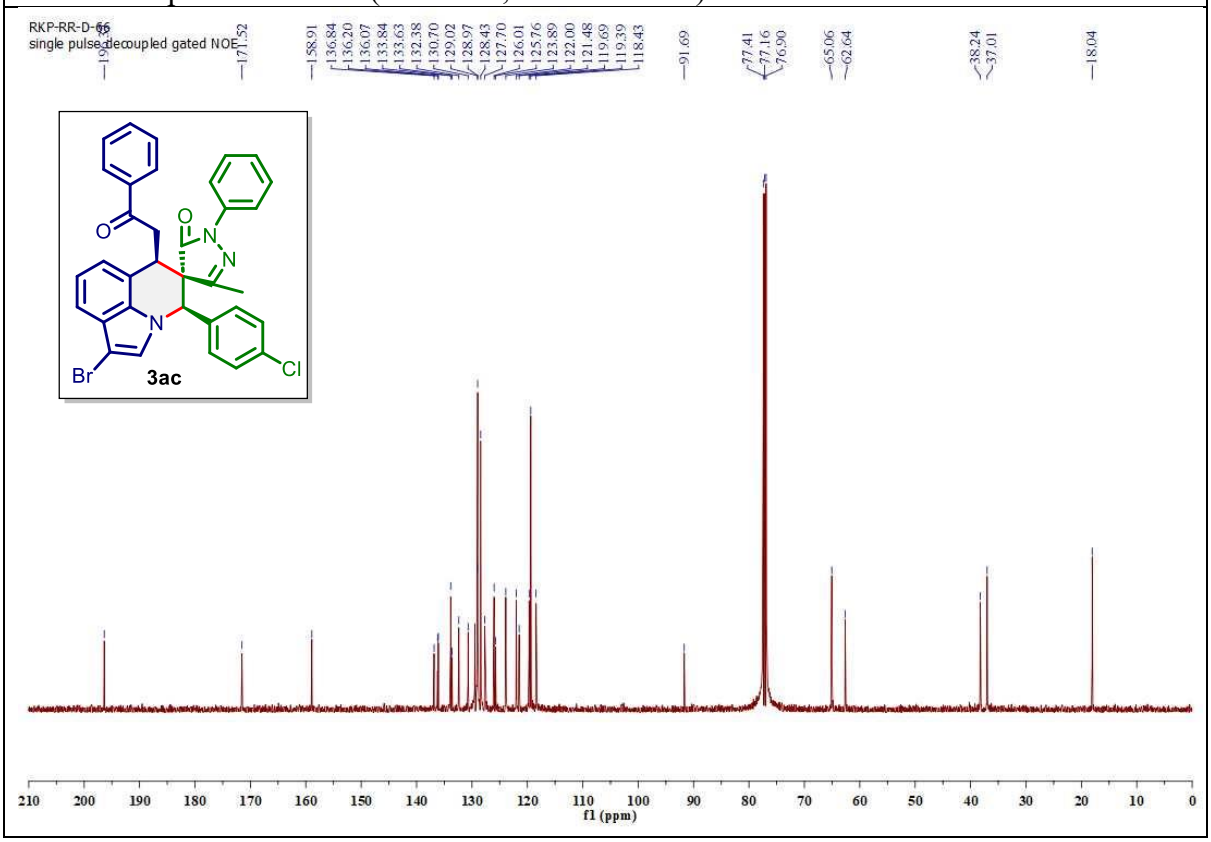
^{19}F NMR Spectrum of **3ab** (471 MHz, Chloroform-*d*)



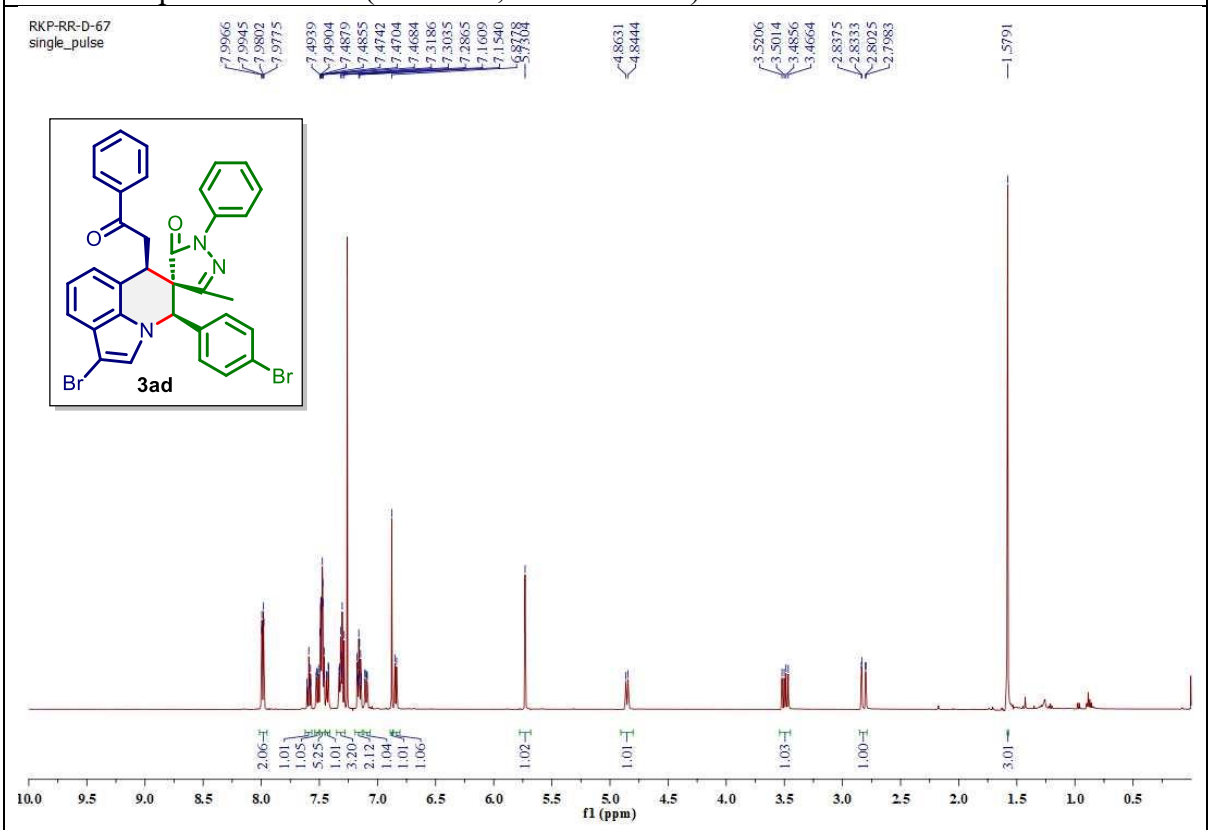
^{1}H NMR Spectrum of **3ac** (500 MHz, Chloroform-*d*)



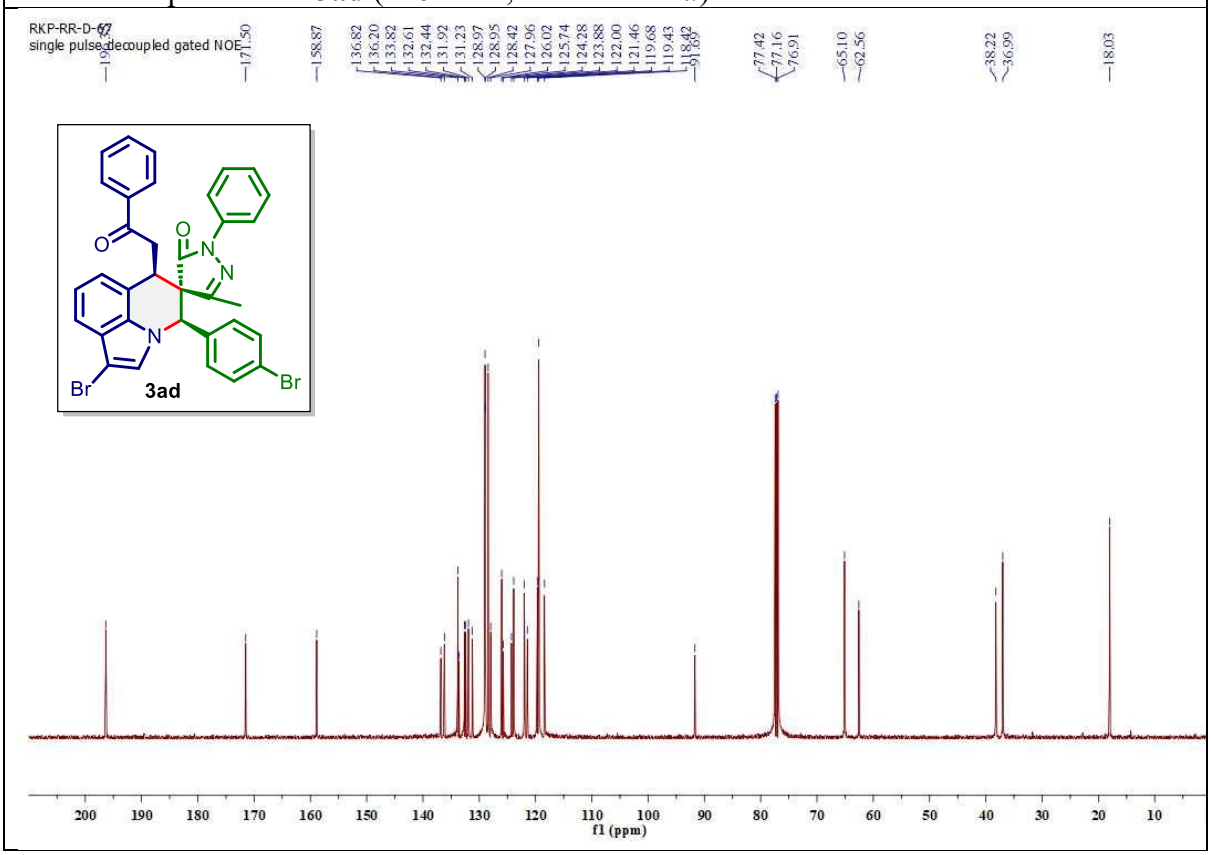
^{13}C NMR Spectrum of **3ac** (126 MHz, Chloroform-*d*)



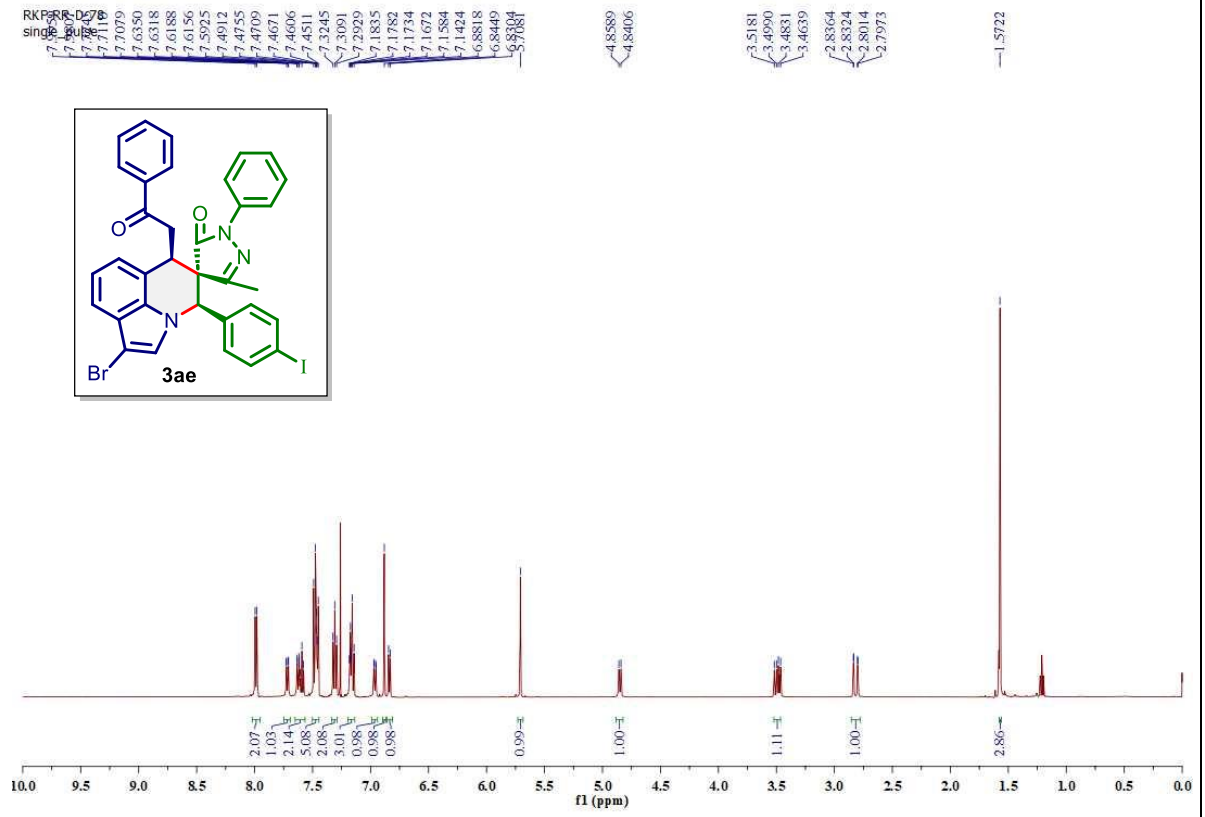
^{1}H NMR Spectrum of **3ad** (500 MHz, Chloroform-*d*)



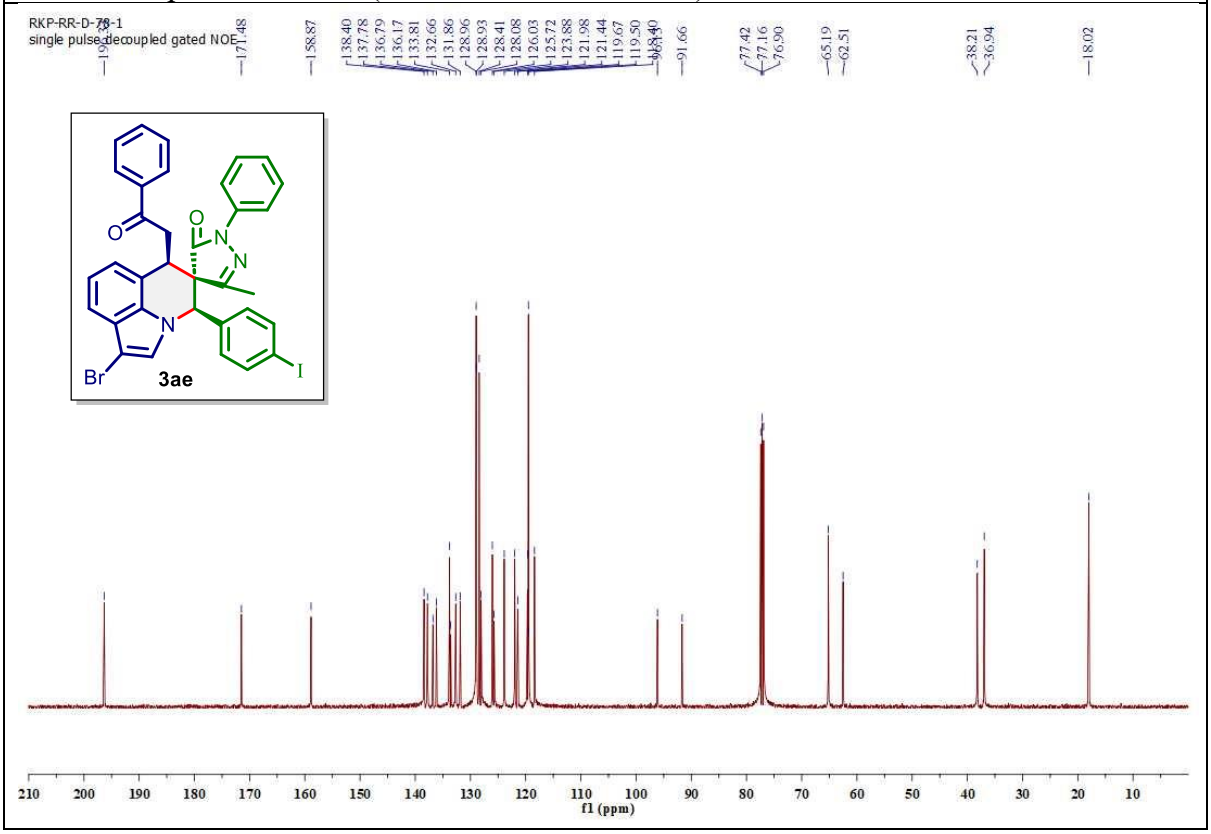
^{13}C NMR Spectrum of **3ad** (126 MHz, Chloroform-*d*)



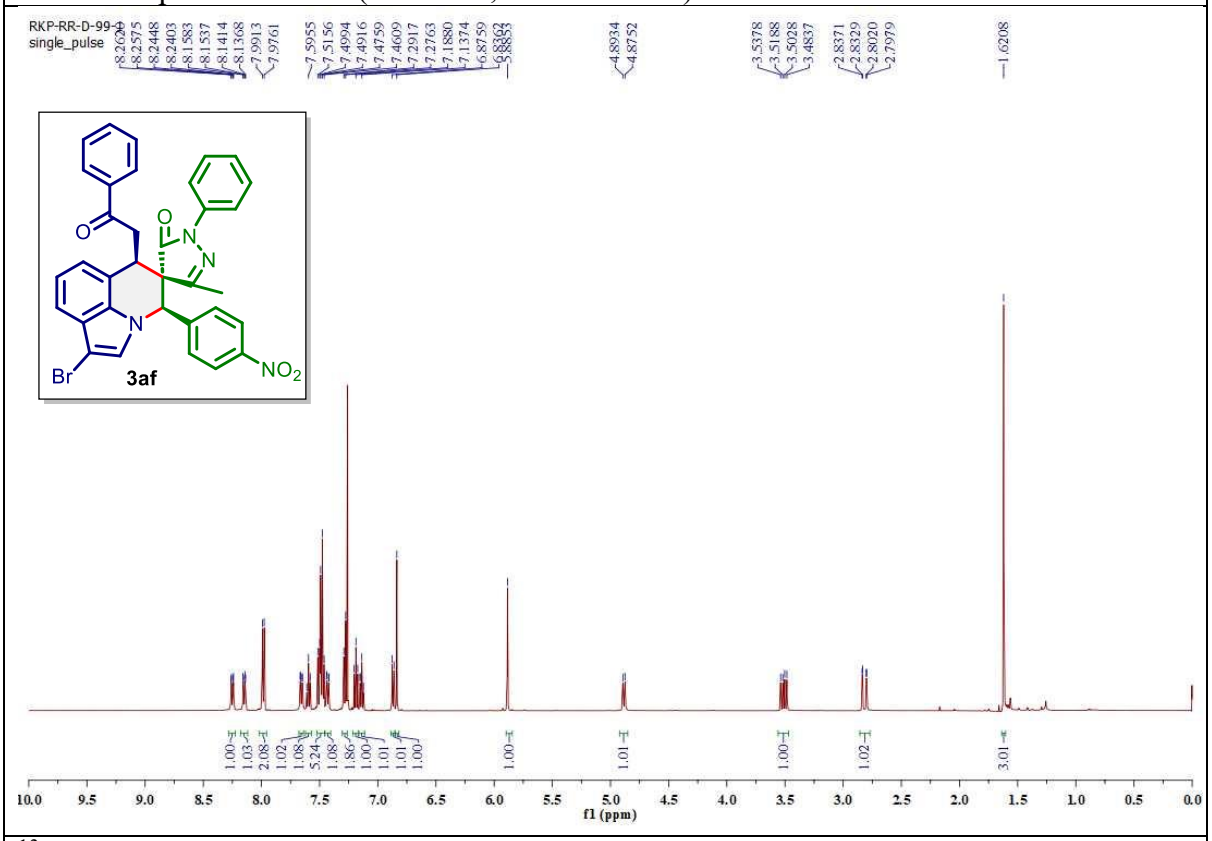
^{1}H NMR Spectrum of **3ae** (500 MHz, Chloroform-*d*)



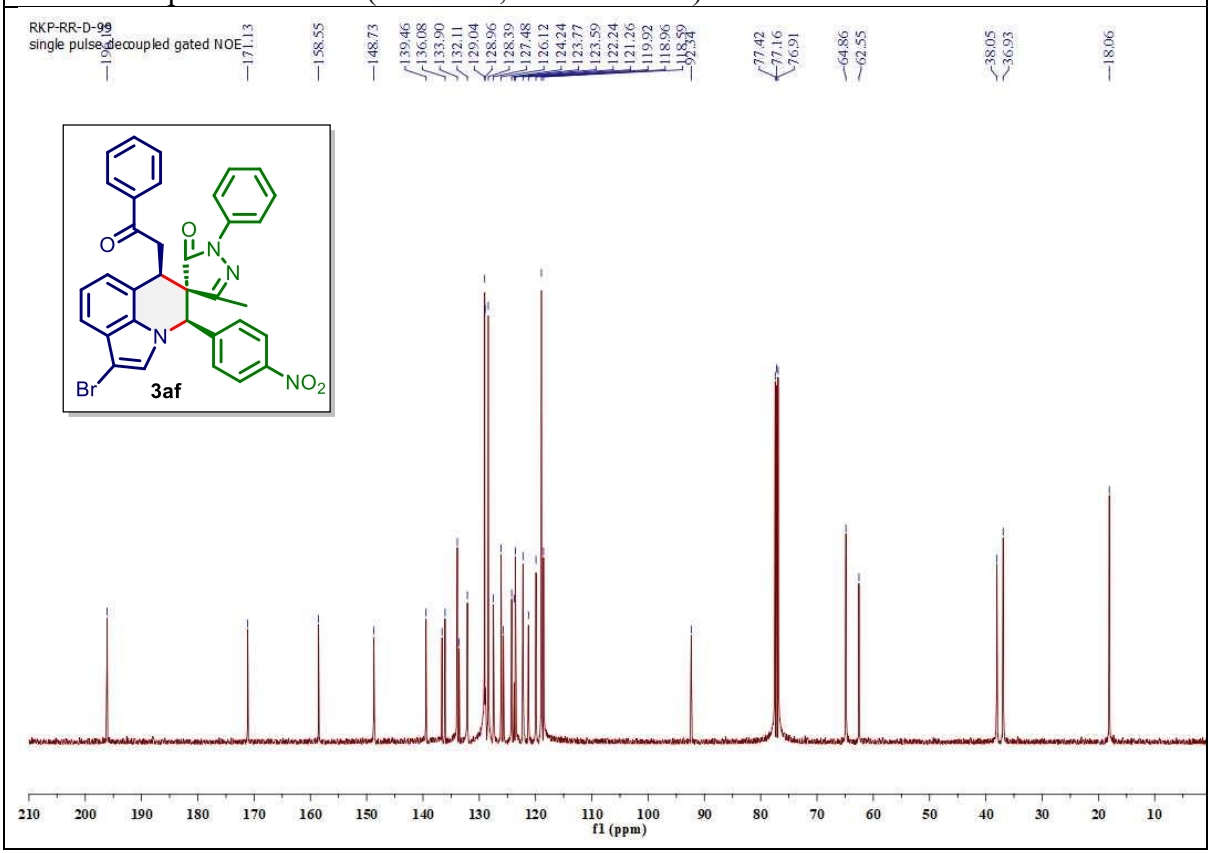
^{13}C NMR Spectrum of **3ae** (126 MHz, Chloroform-*d*)



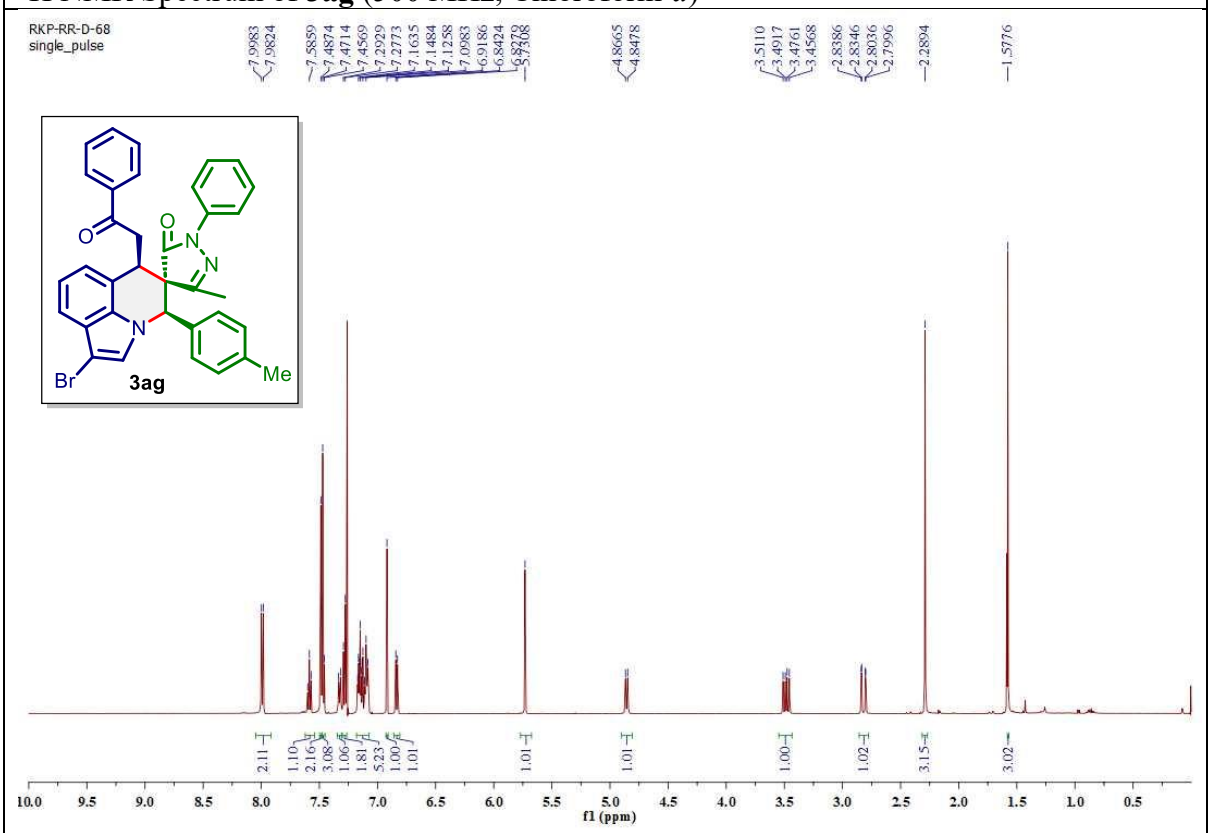
^{1}H NMR Spectrum of **3af** (500 MHz, Chloroform-*d*)



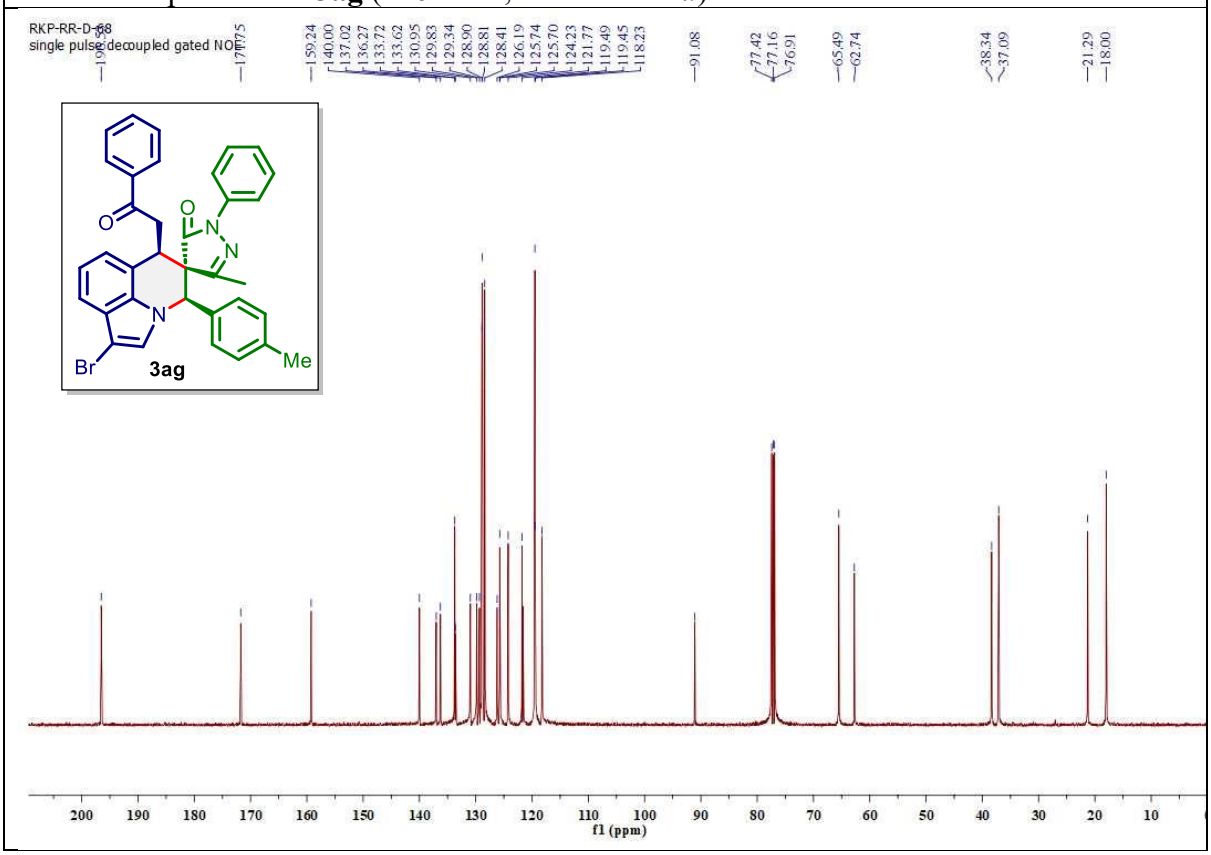
^{13}C NMR Spectrum of **3af** (126 MHz, Chloroform-*d*)



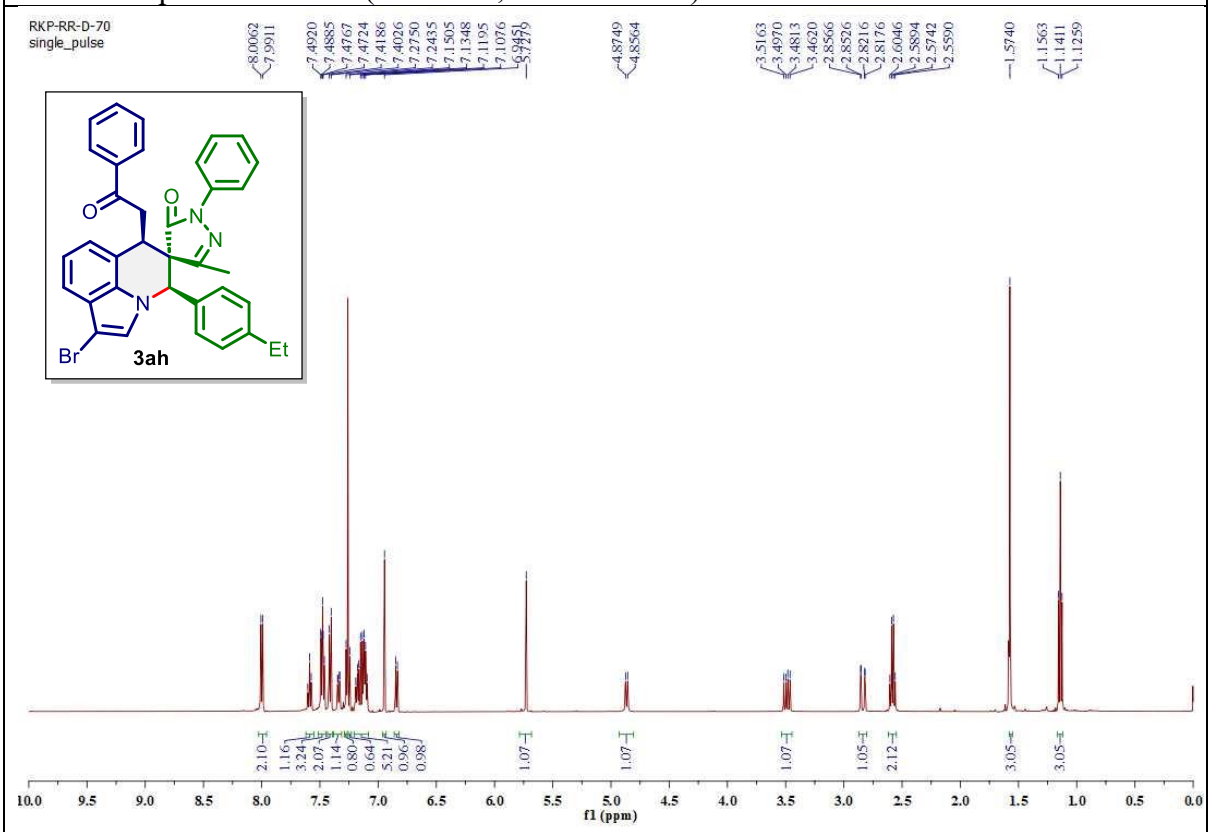
^{1}H NMR Spectrum of **3ag** (500 MHz, Chloroform-*d*)



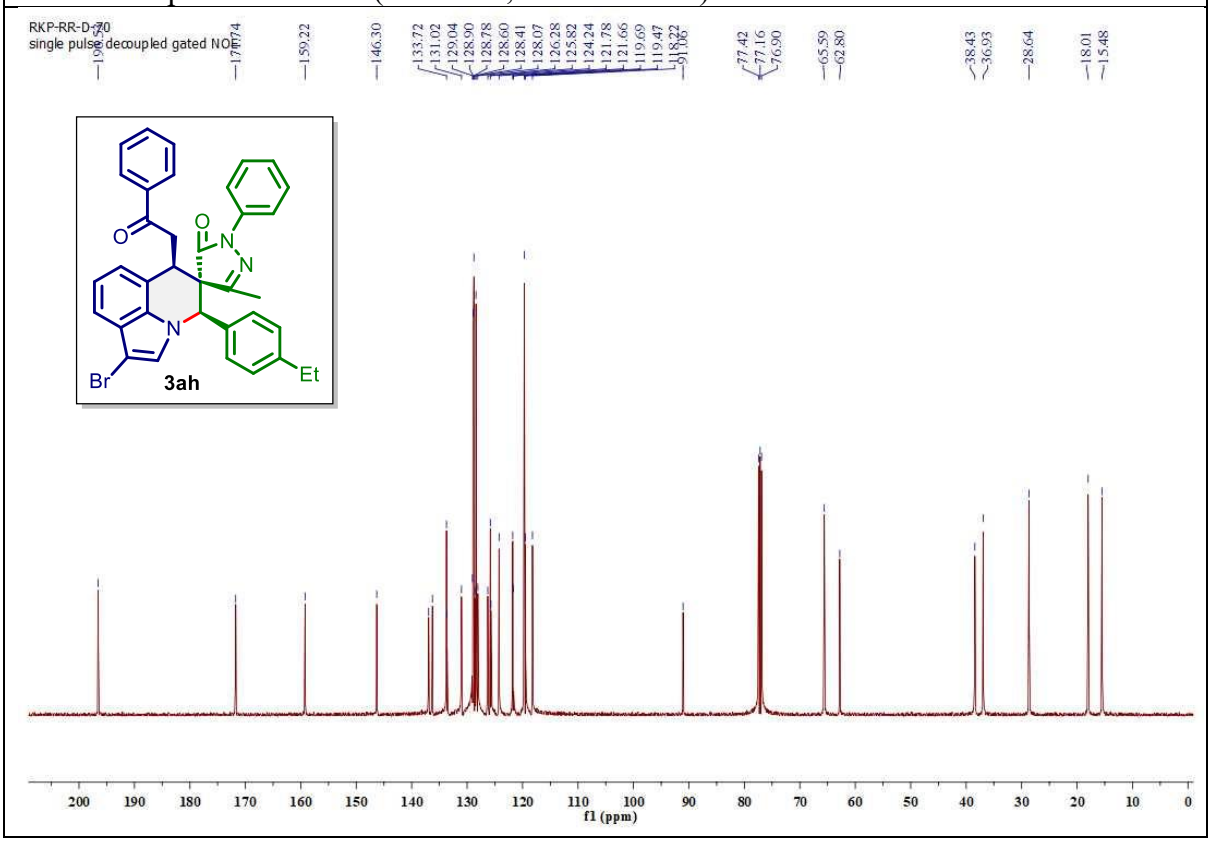
^{13}C NMR Spectrum of **3ag** (126 MHz, Chloroform-*d*)



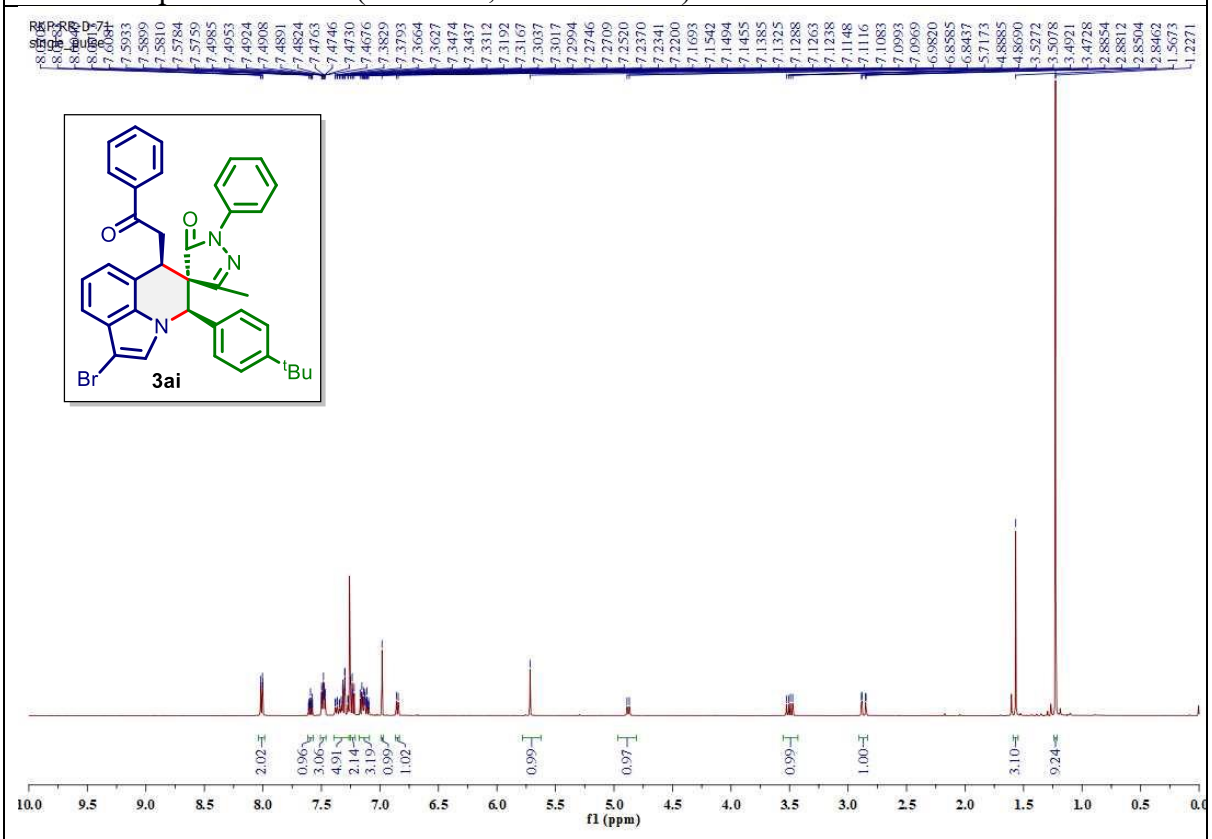
^{1}H NMR Spectrum of **3ah** (500 MHz, Chloroform-*d*)



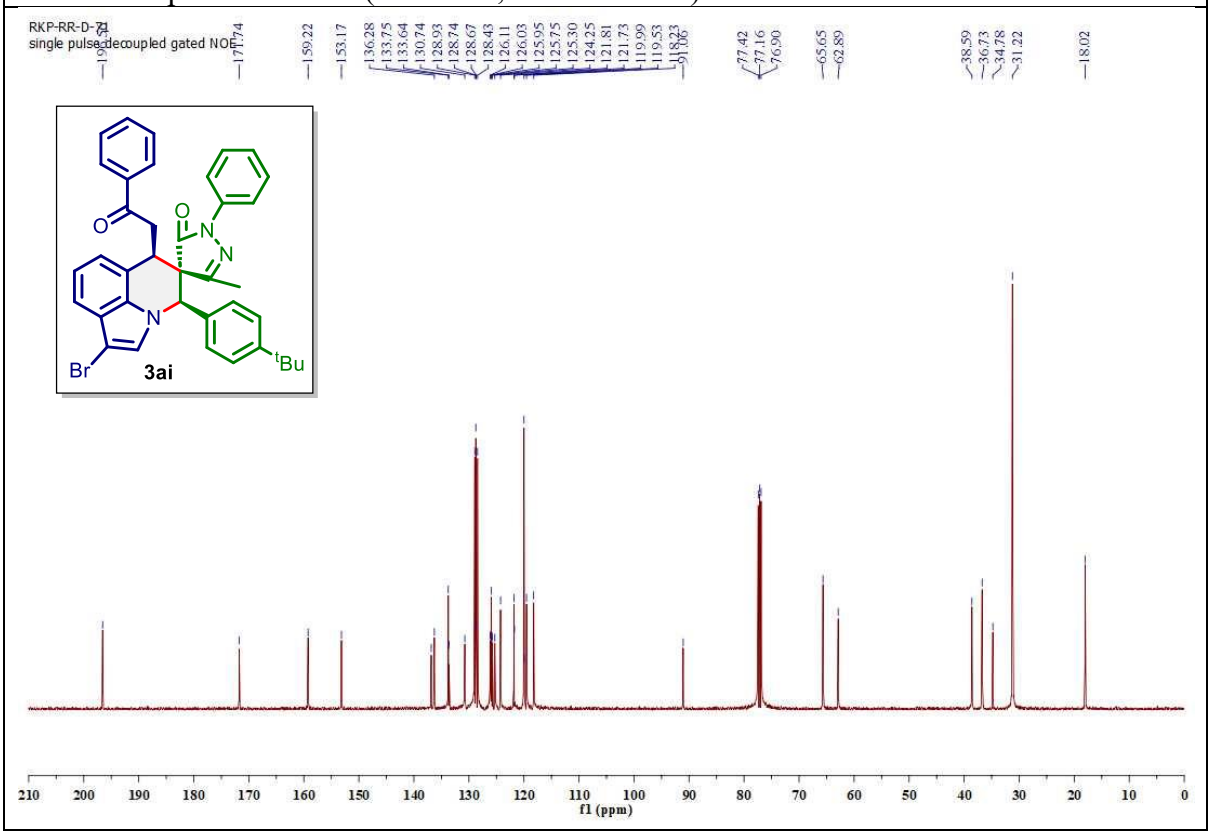
^{13}C NMR Spectrum of **3ah** (126 MHz, Chloroform-*d*)



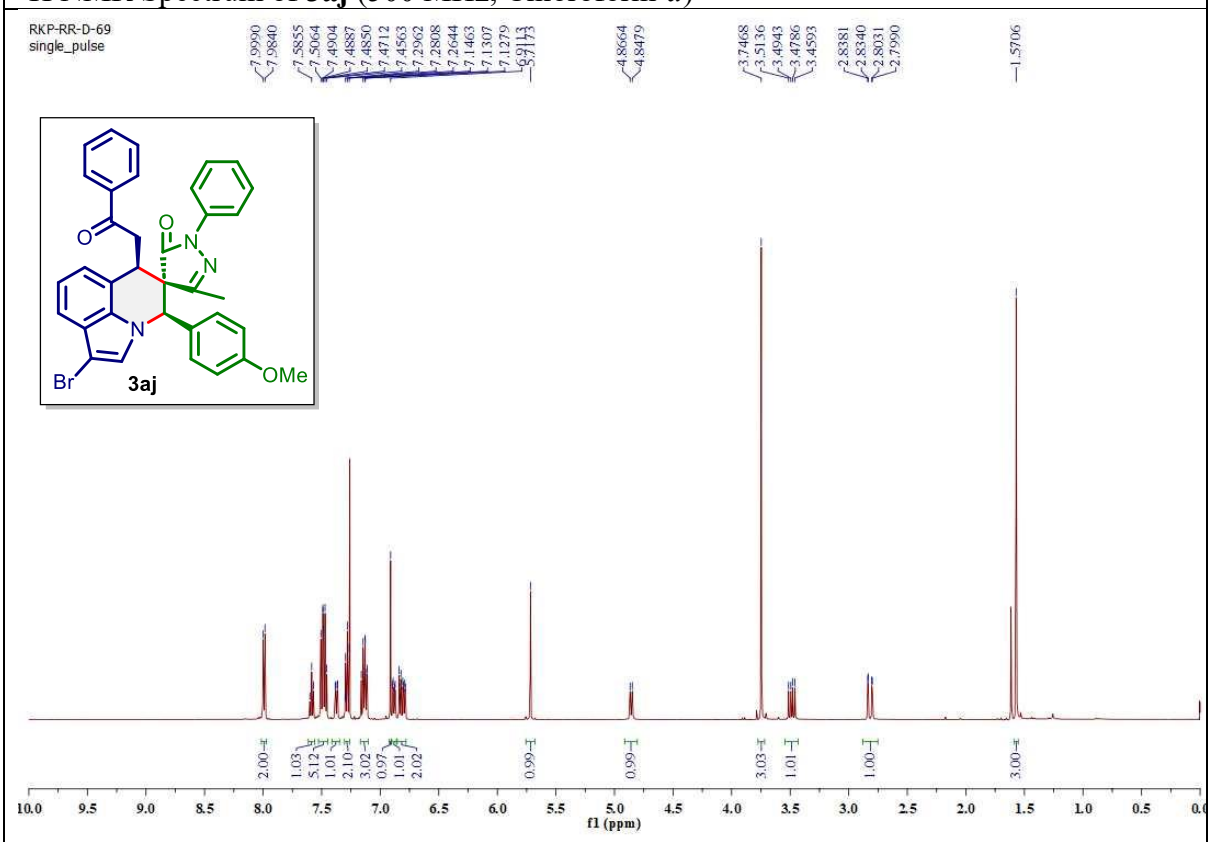
^{1}H NMR Spectrum of **3ai** (500 MHz, Chloroform-*d*)



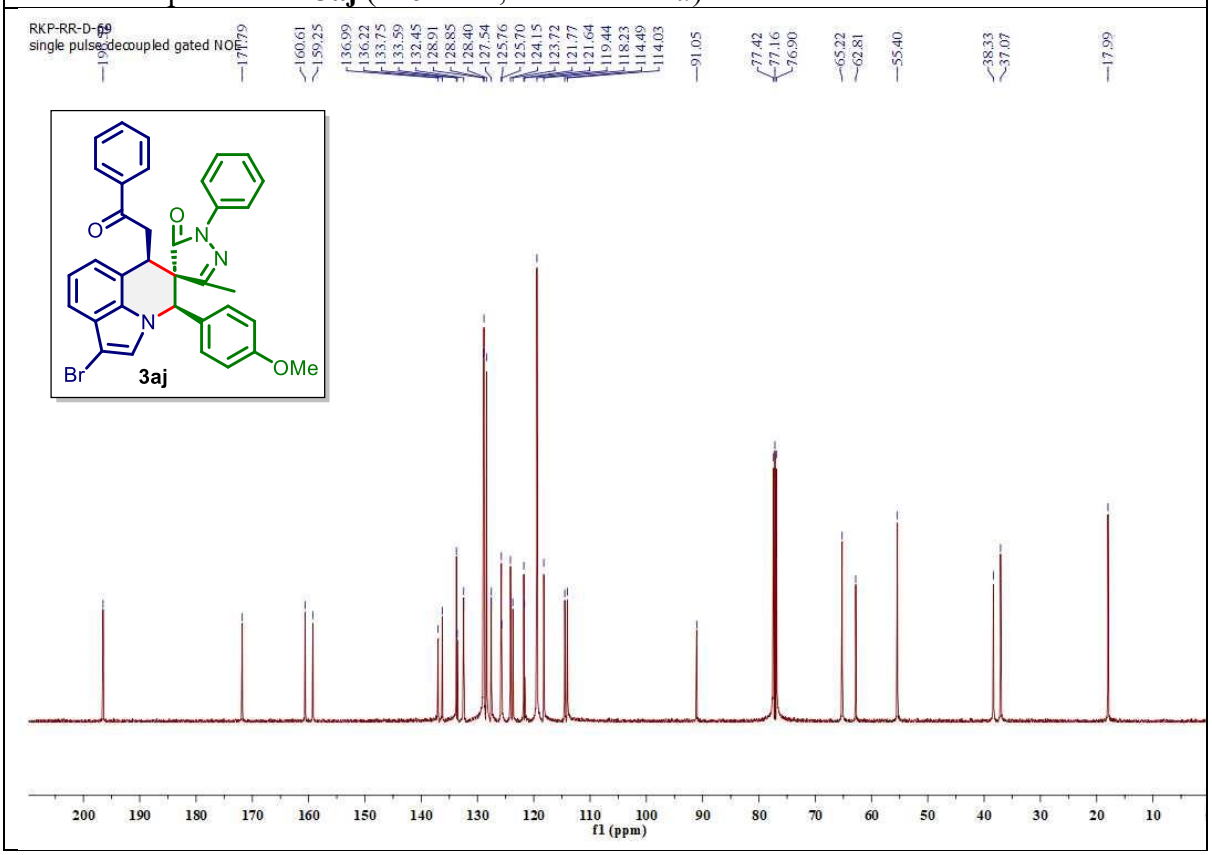
^{13}C NMR Spectrum of **3ai** (126 MHz, Chloroform-*d*)



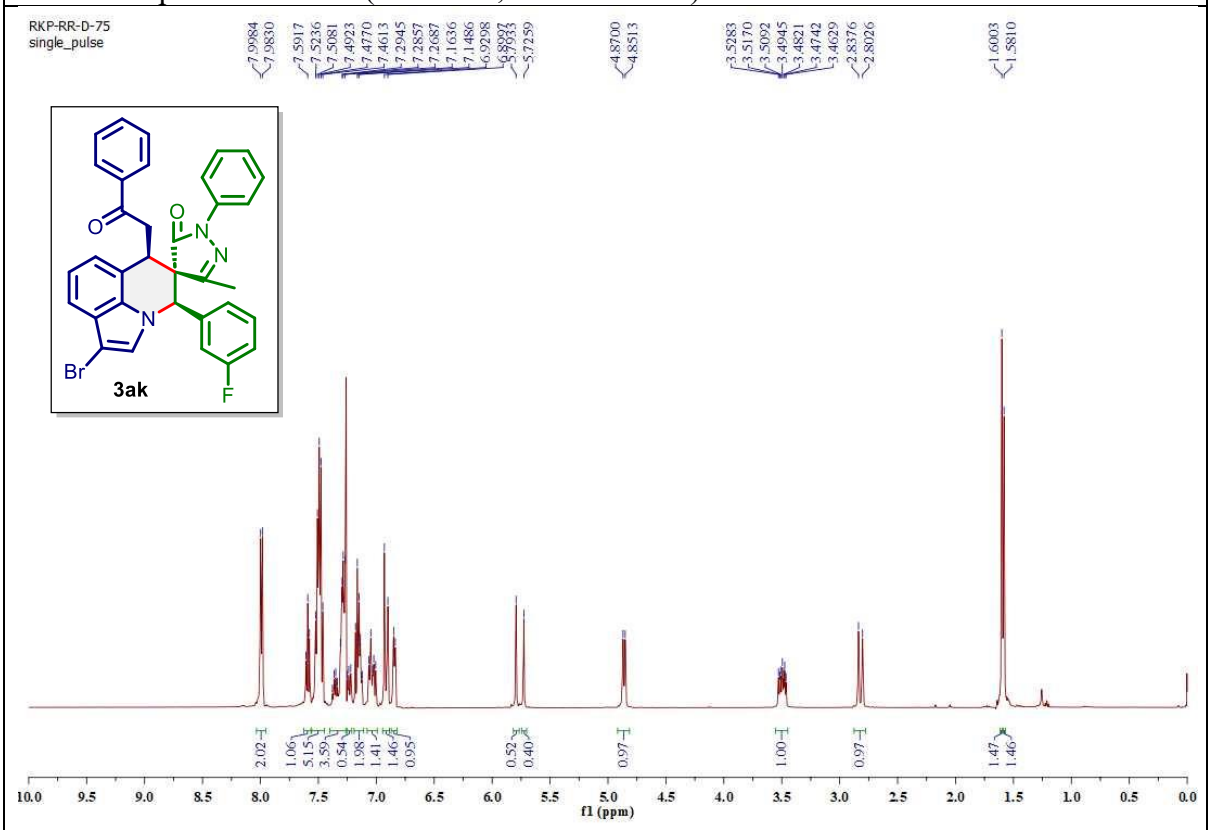
^{1}H NMR Spectrum of **3aj** (500 MHz, Chloroform-*d*)



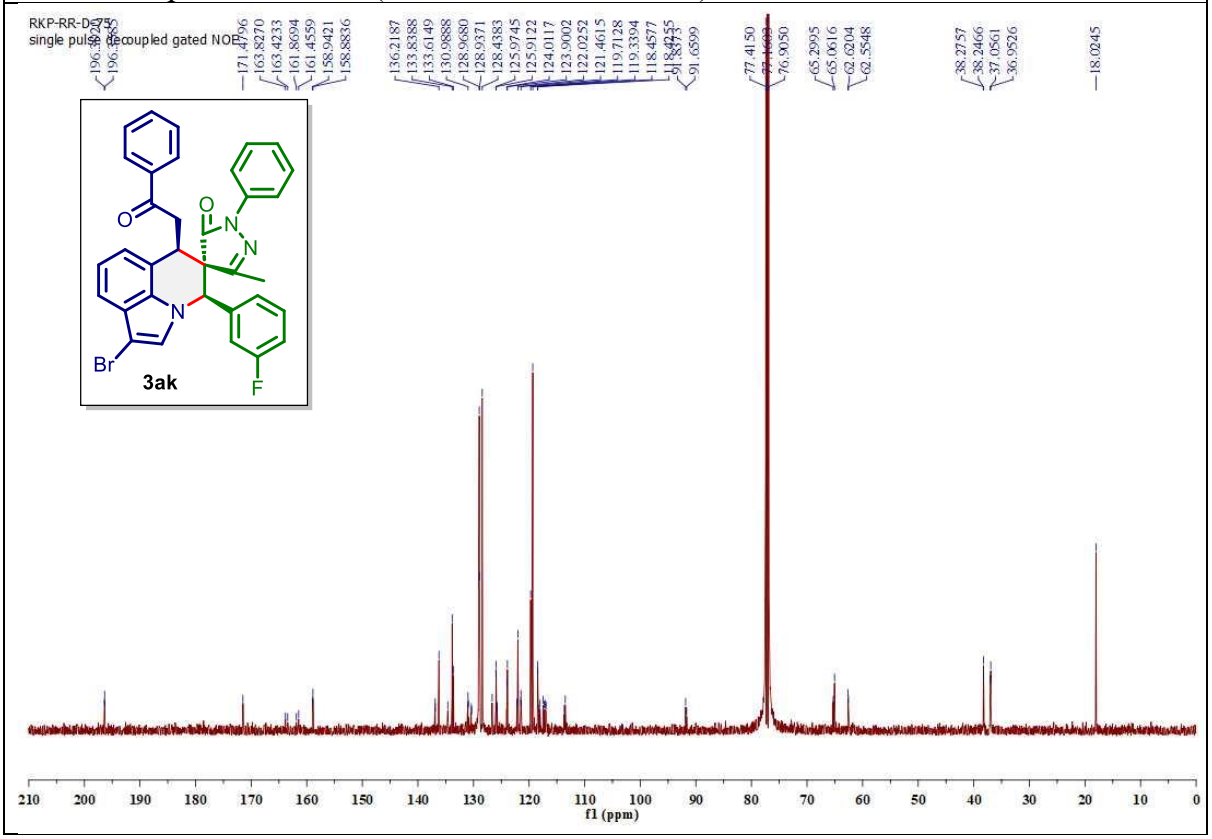
^{13}C NMR Spectrum of **3aj** (126 MHz, Chloroform-*d*)



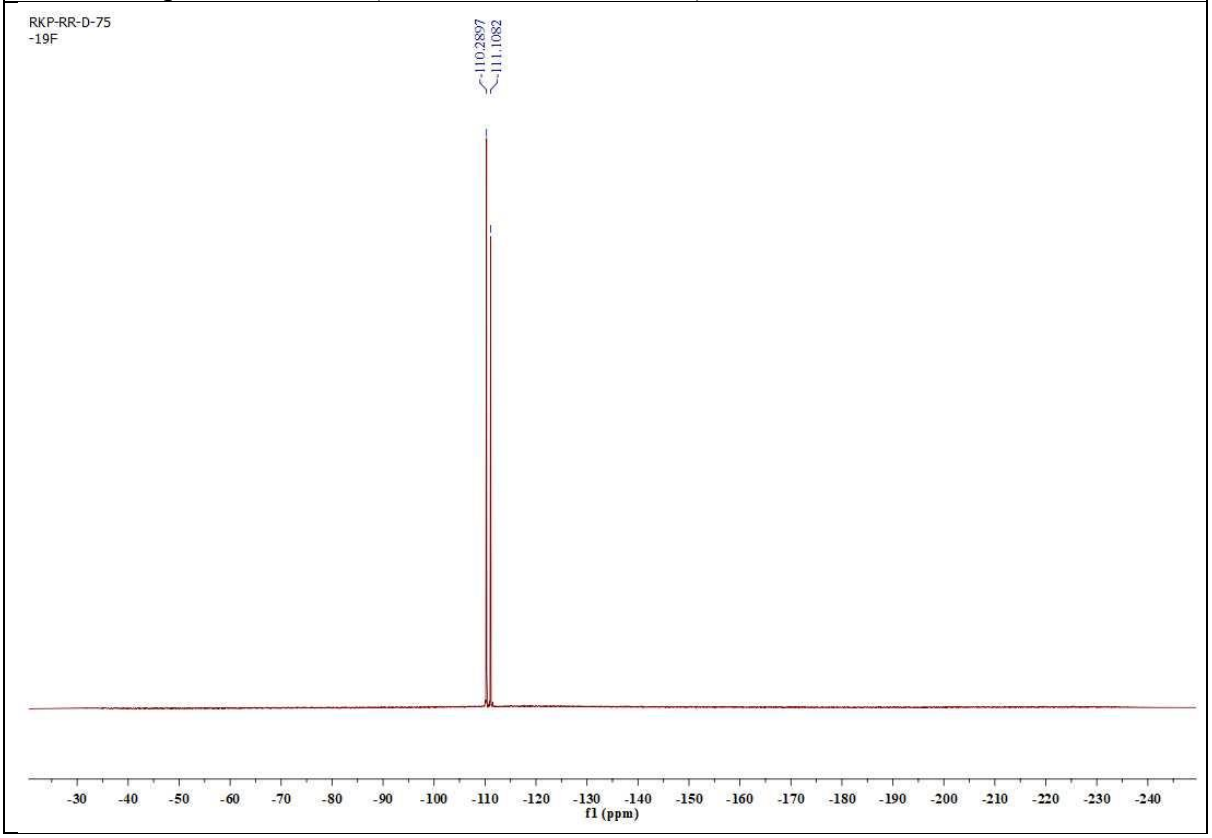
^{1}H NMR Spectrum of **3ak** (500 MHz, Chloroform-*d*)



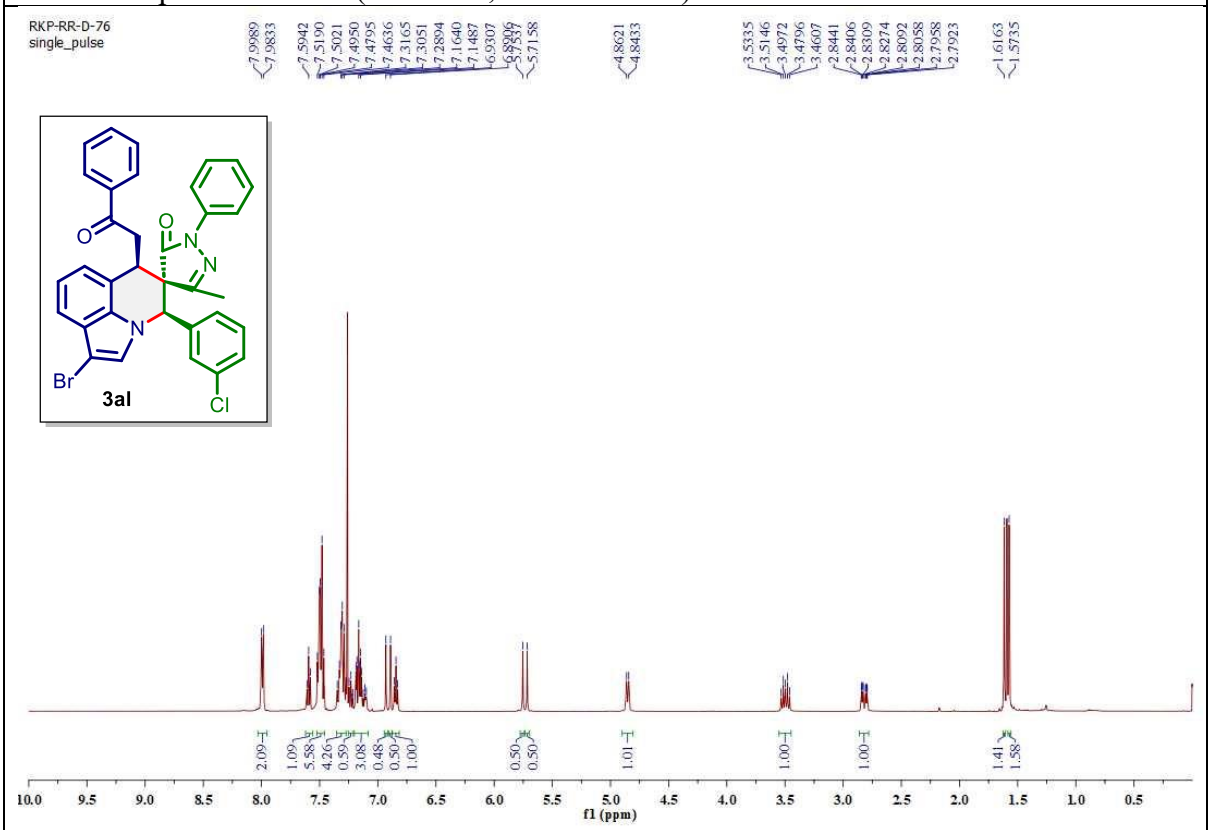
^{13}C NMR Spectrum of **3ak** (126 MHz, Chloroform-*d*)



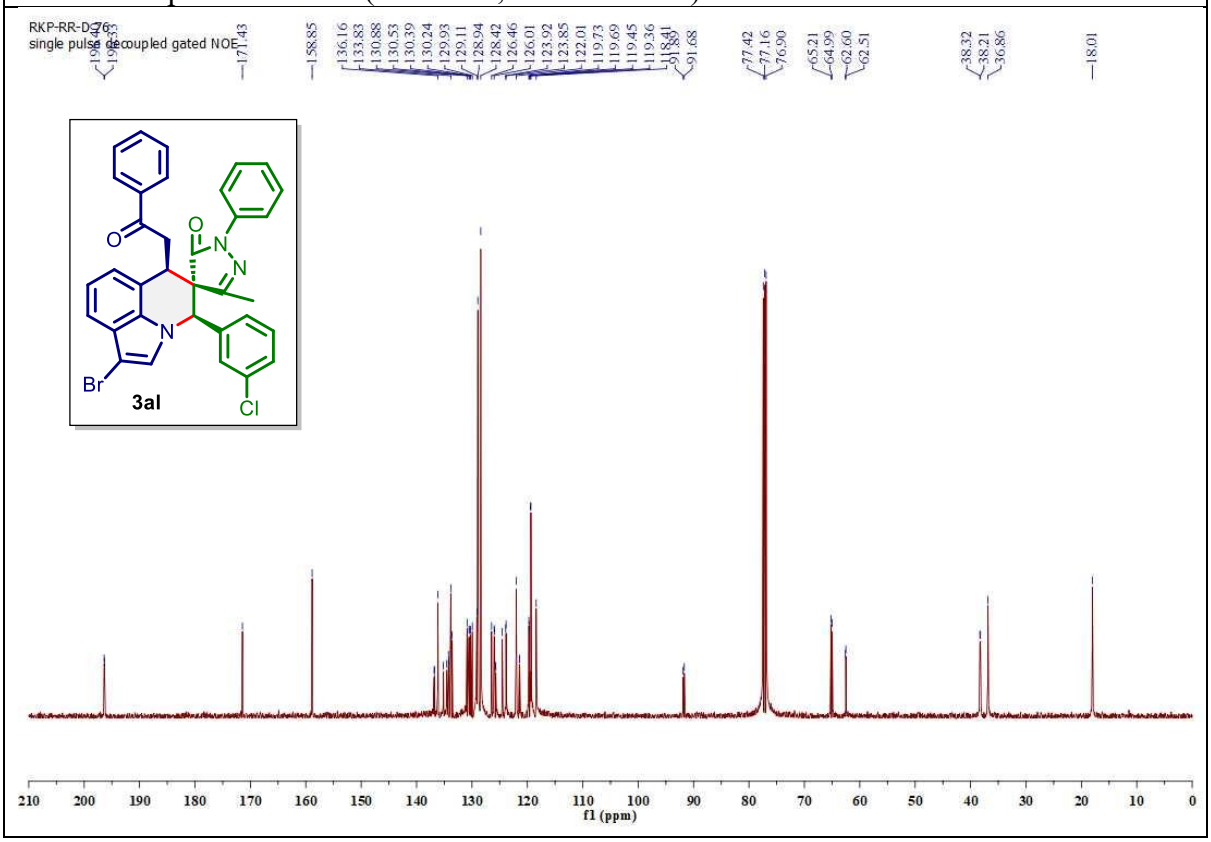
^{19}F NMR Spectrum of **3ak** (471 MHz, Chloroform-*d*)



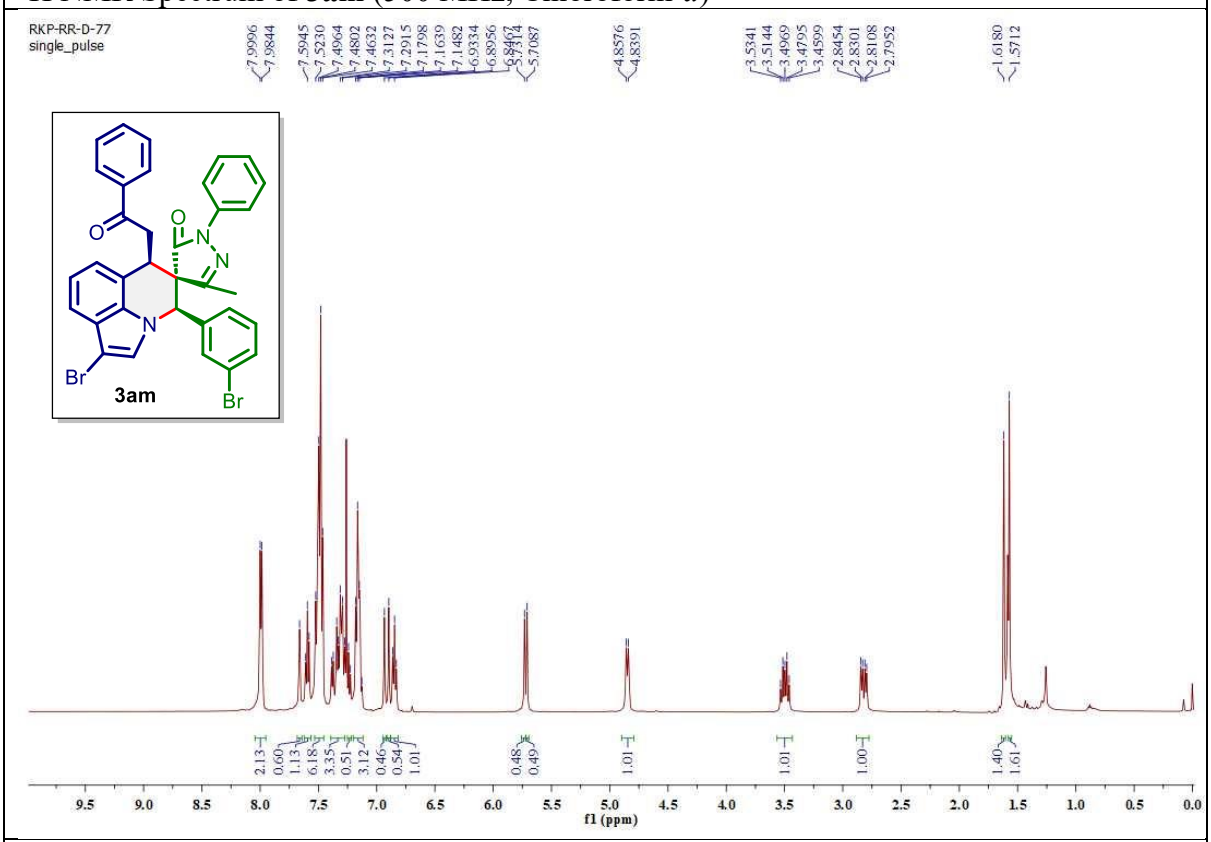
^{1}H NMR Spectrum of **3al** (500 MHz, Chloroform-*d*)



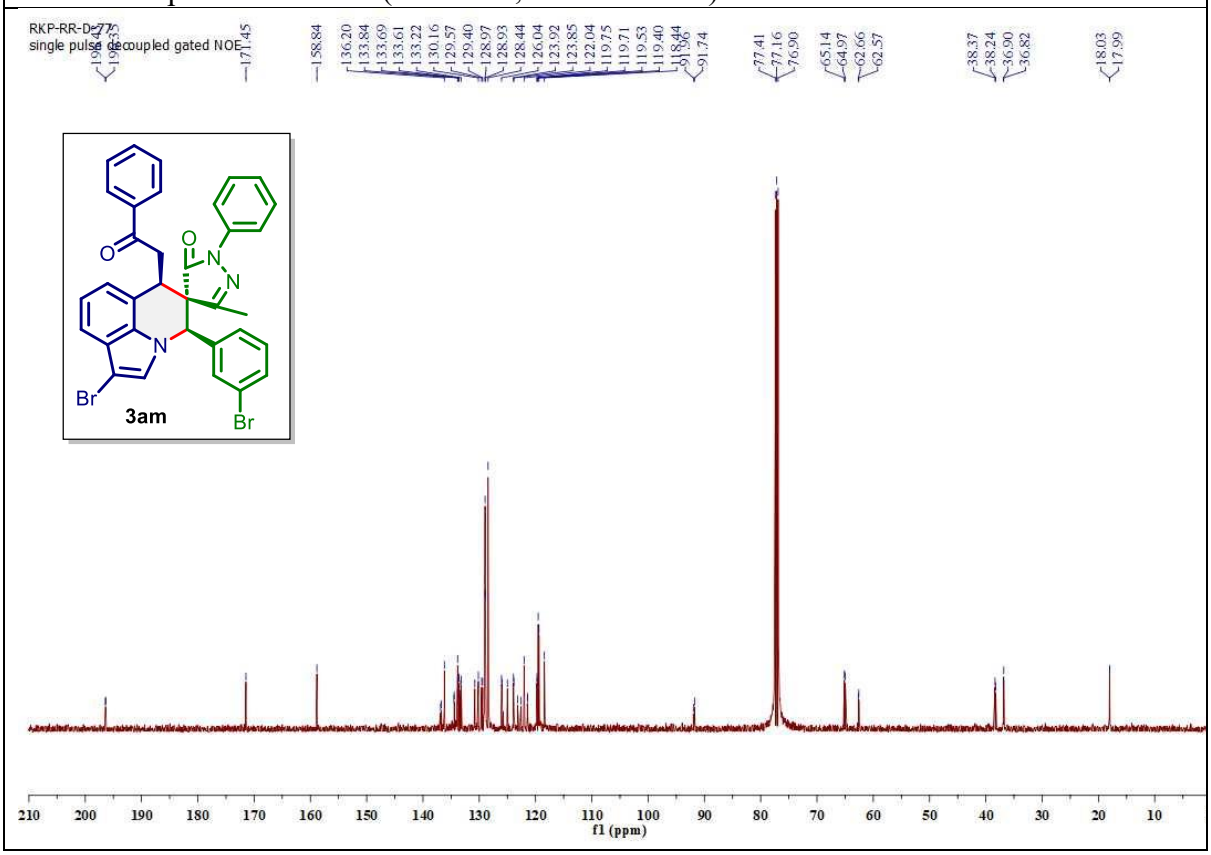
^{13}C NMR Spectrum of **3al** (126 MHz, Chloroform-*d*)



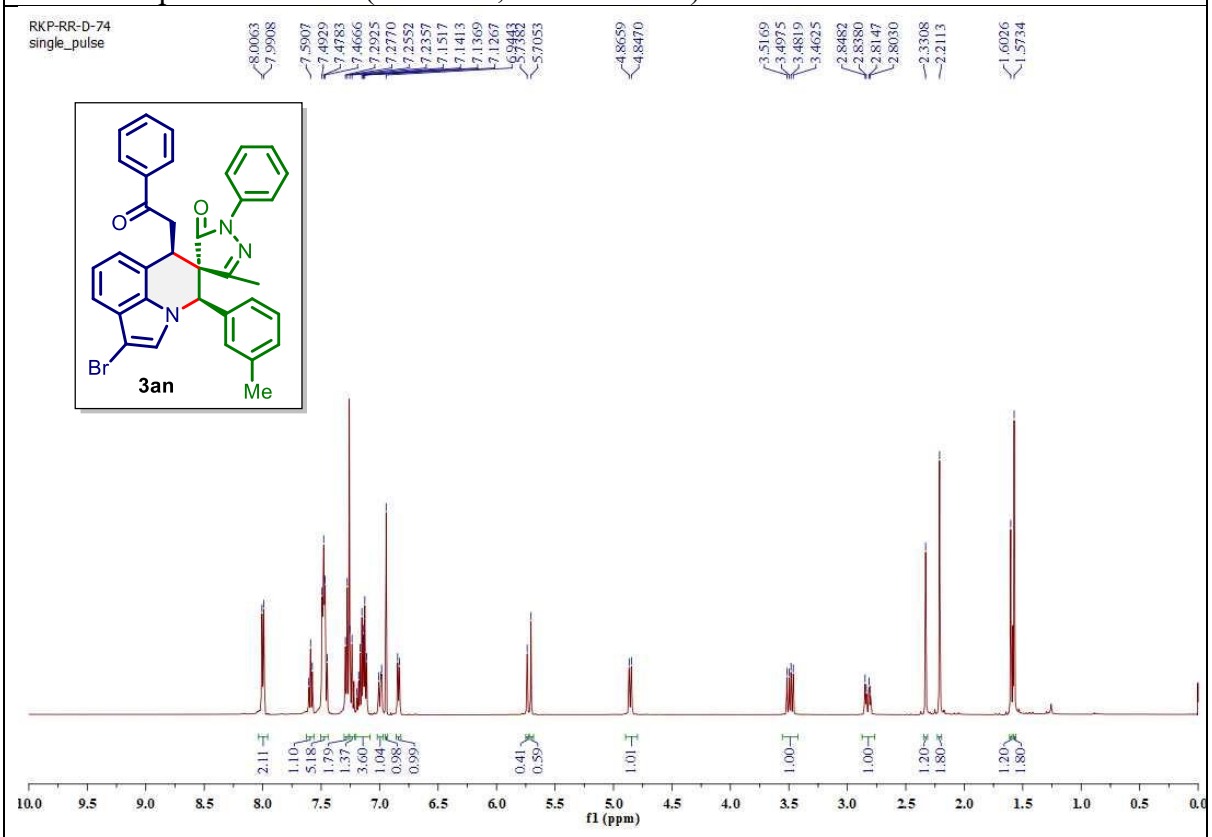
^{1}H NMR Spectrum of **3am** (500 MHz, Chloroform-*d*)



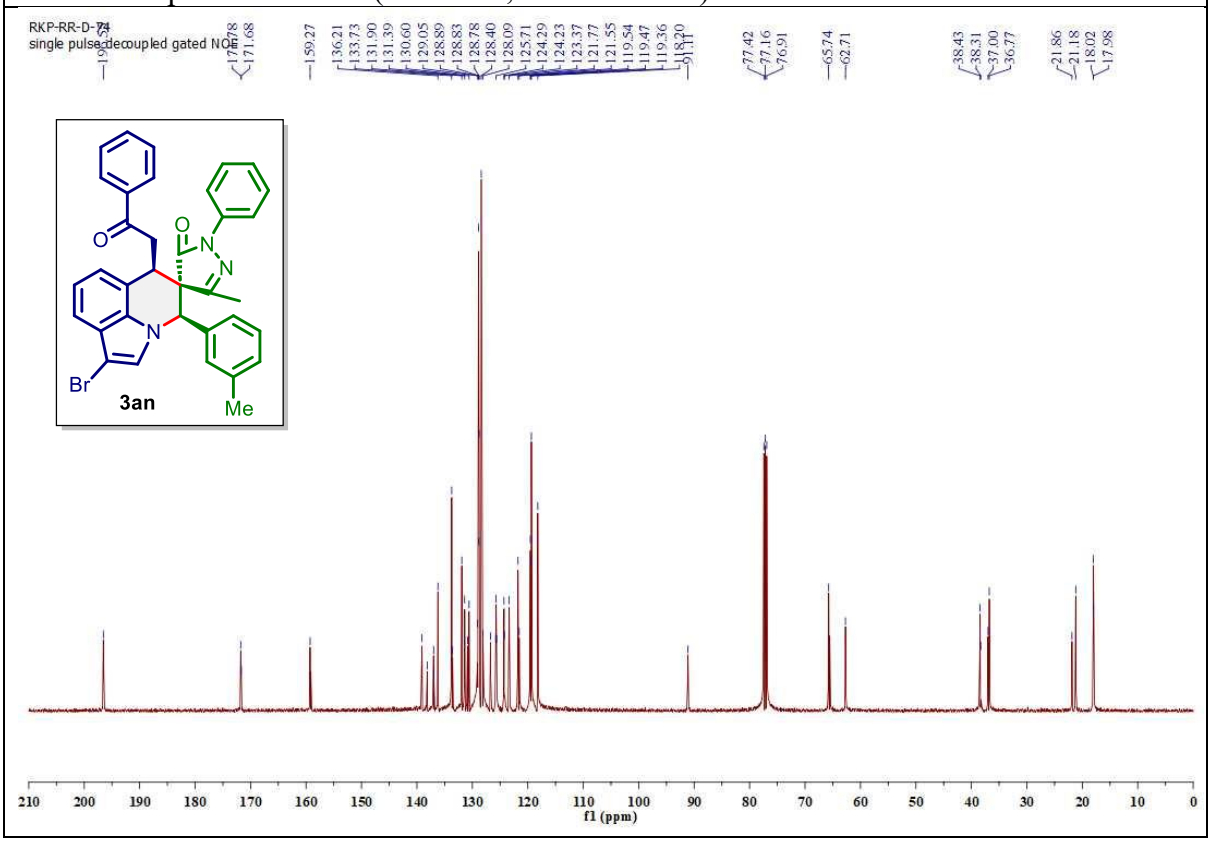
^{13}C NMR Spectrum of **3am** (126 MHz, Chloroform-*d*)



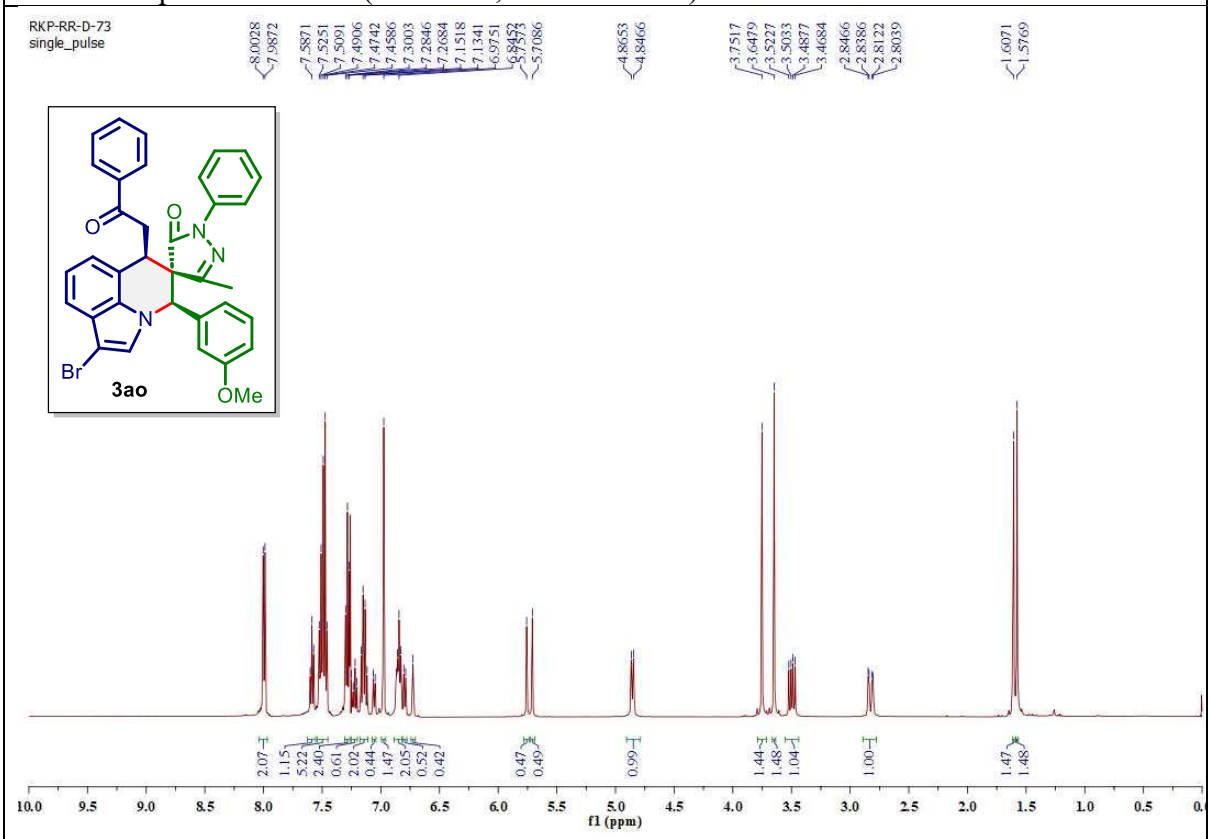
^{1}H NMR Spectrum of **3an** (500 MHz, Chloroform-*d*)



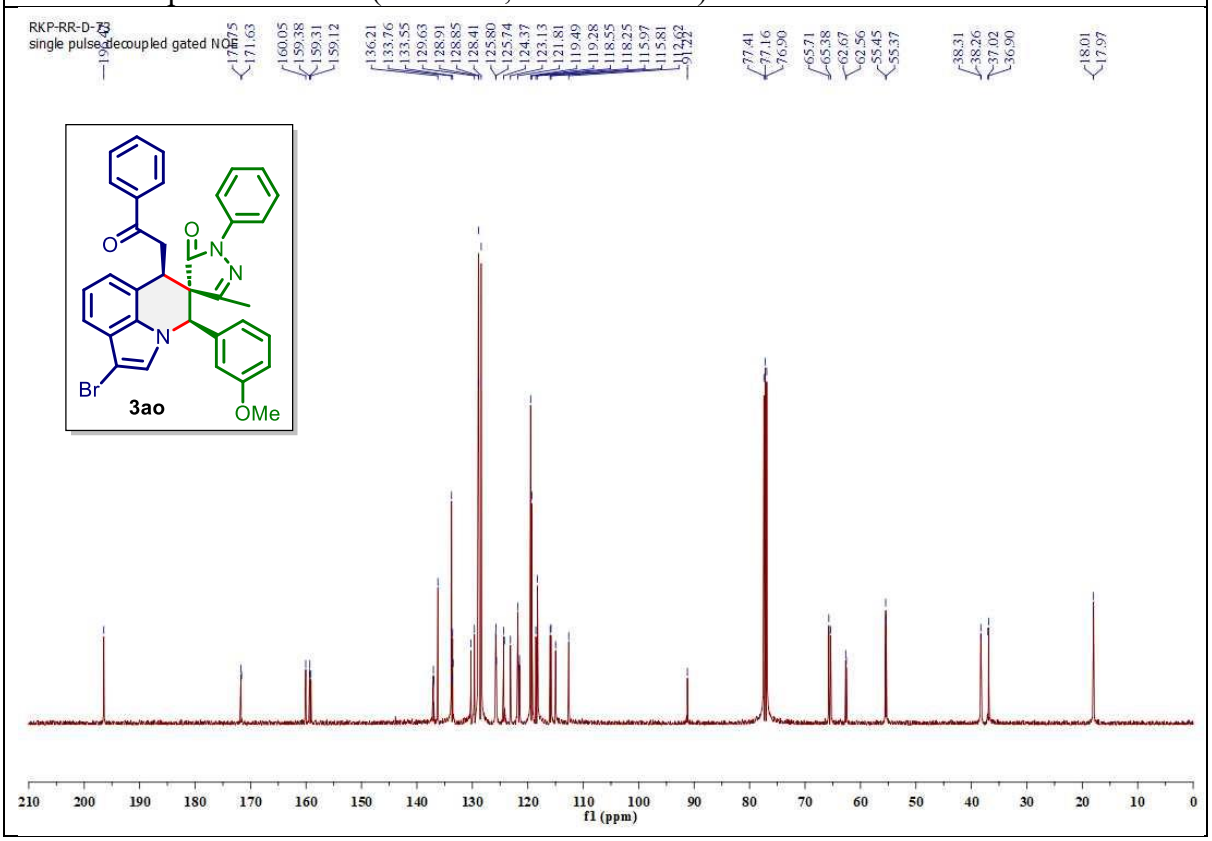
^{13}C NMR Spectrum of **3an** (126 MHz, Chloroform-*d*)



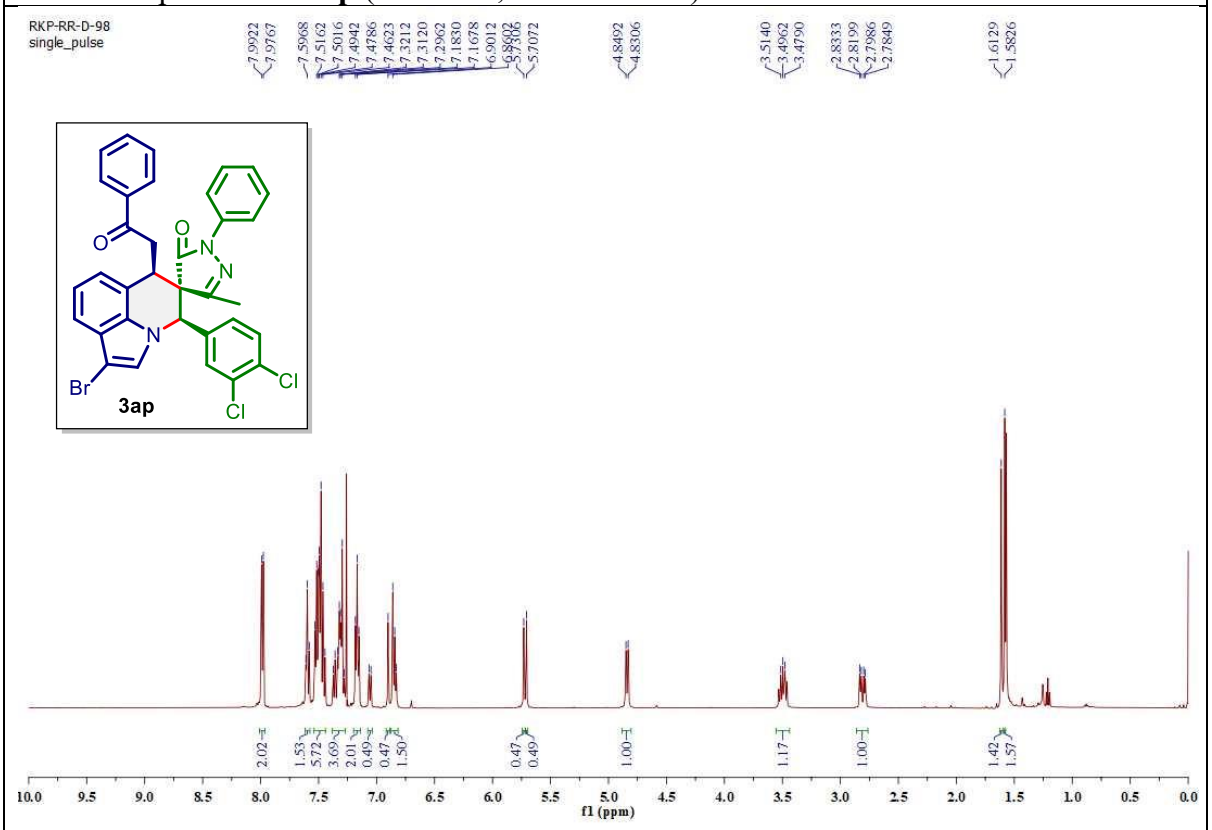
^{1}H NMR Spectrum of **3ao** (500 MHz, Chloroform-*d*)



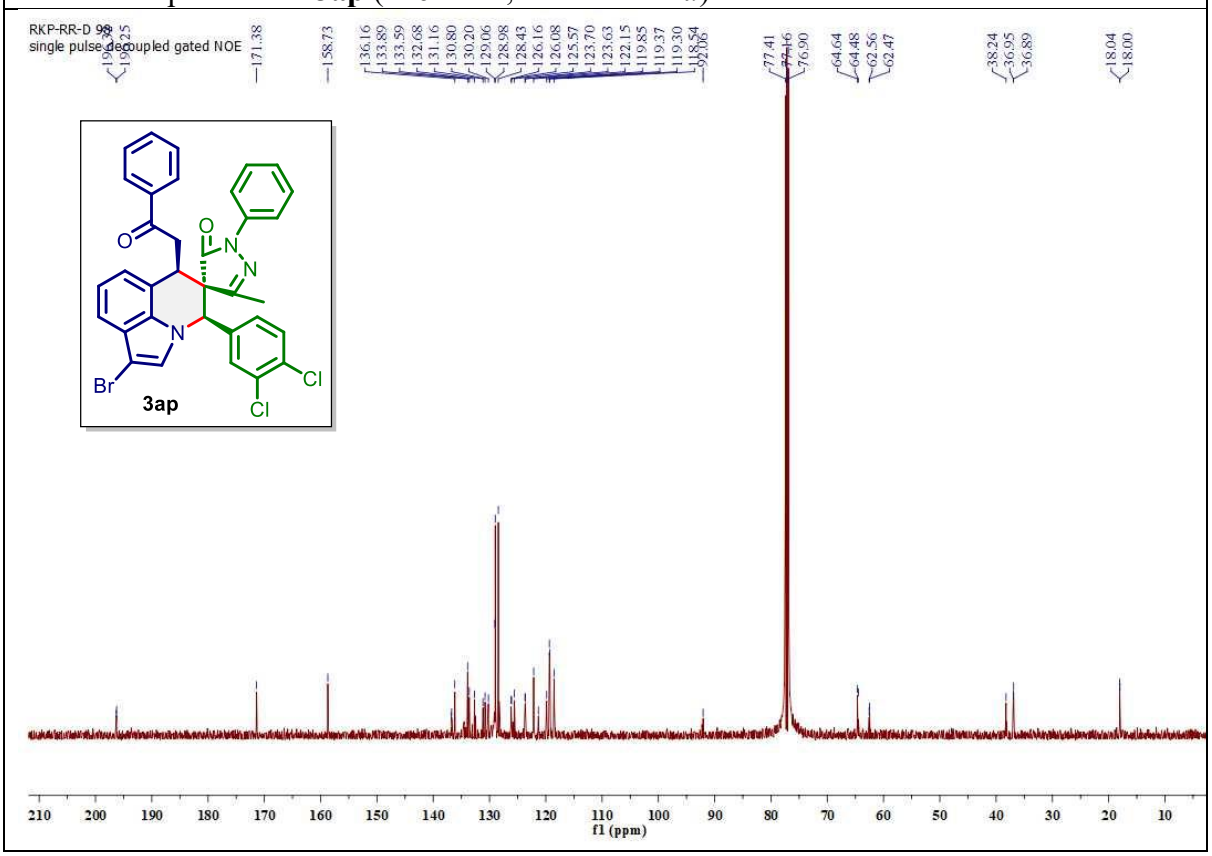
^{13}C NMR Spectrum of **3ao** (126 MHz, Chloroform-*d*)



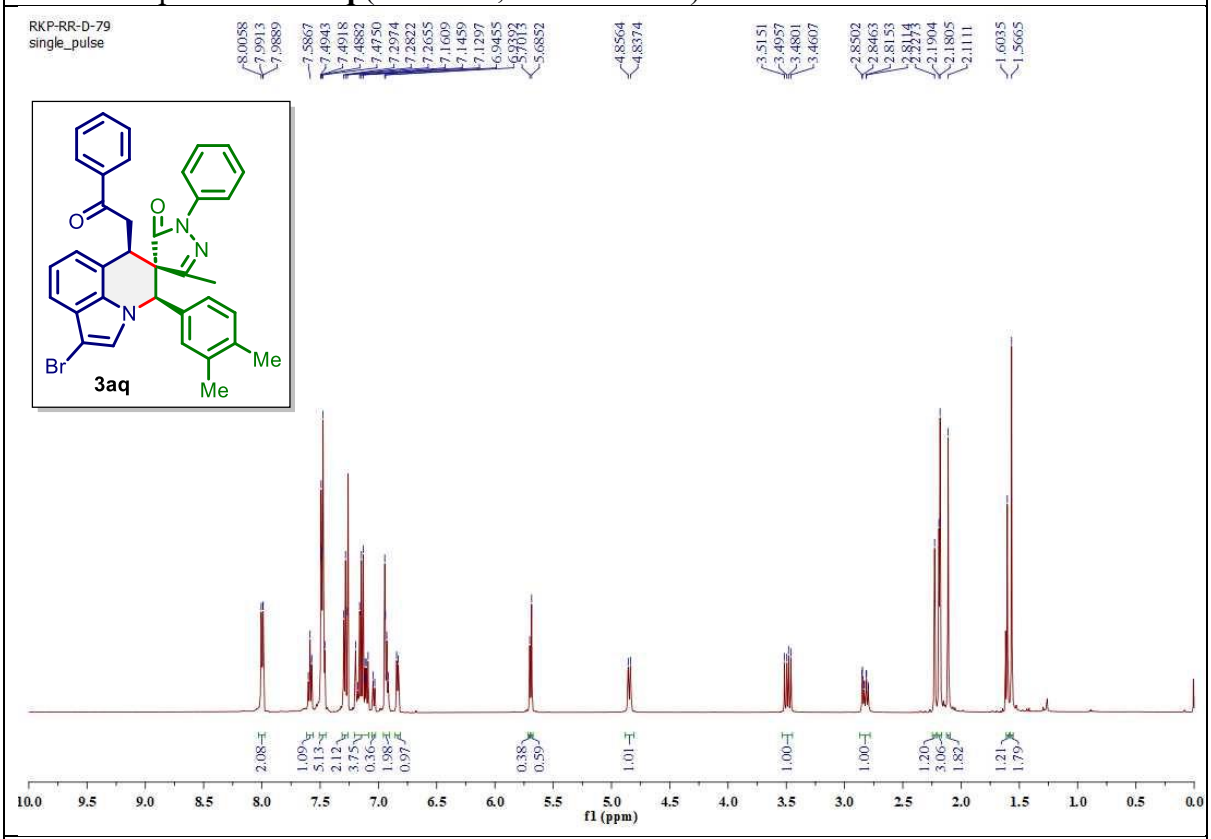
^{1}H NMR Spectrum of **3ap** (500 MHz, Chloroform-*d*)



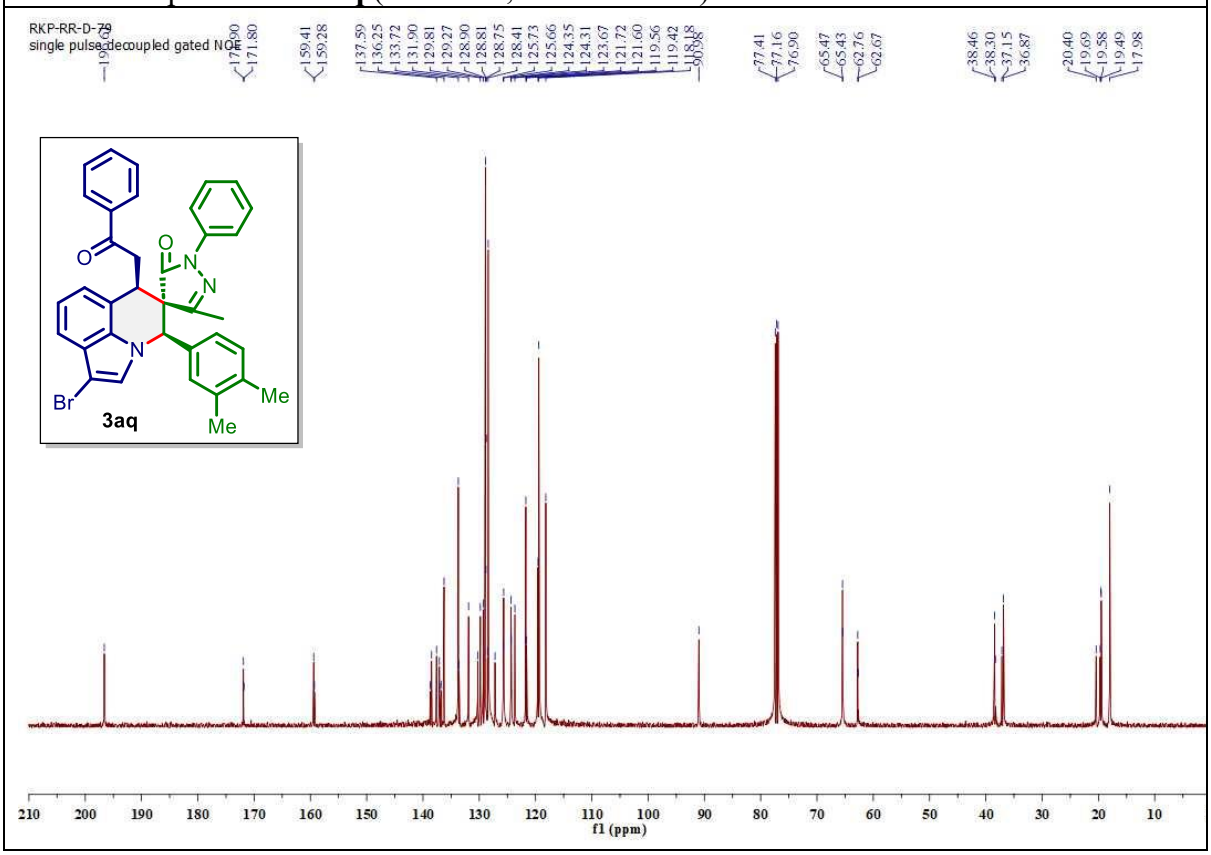
^{13}C NMR Spectrum of **3ap** (126 MHz, Chloroform-*d*)



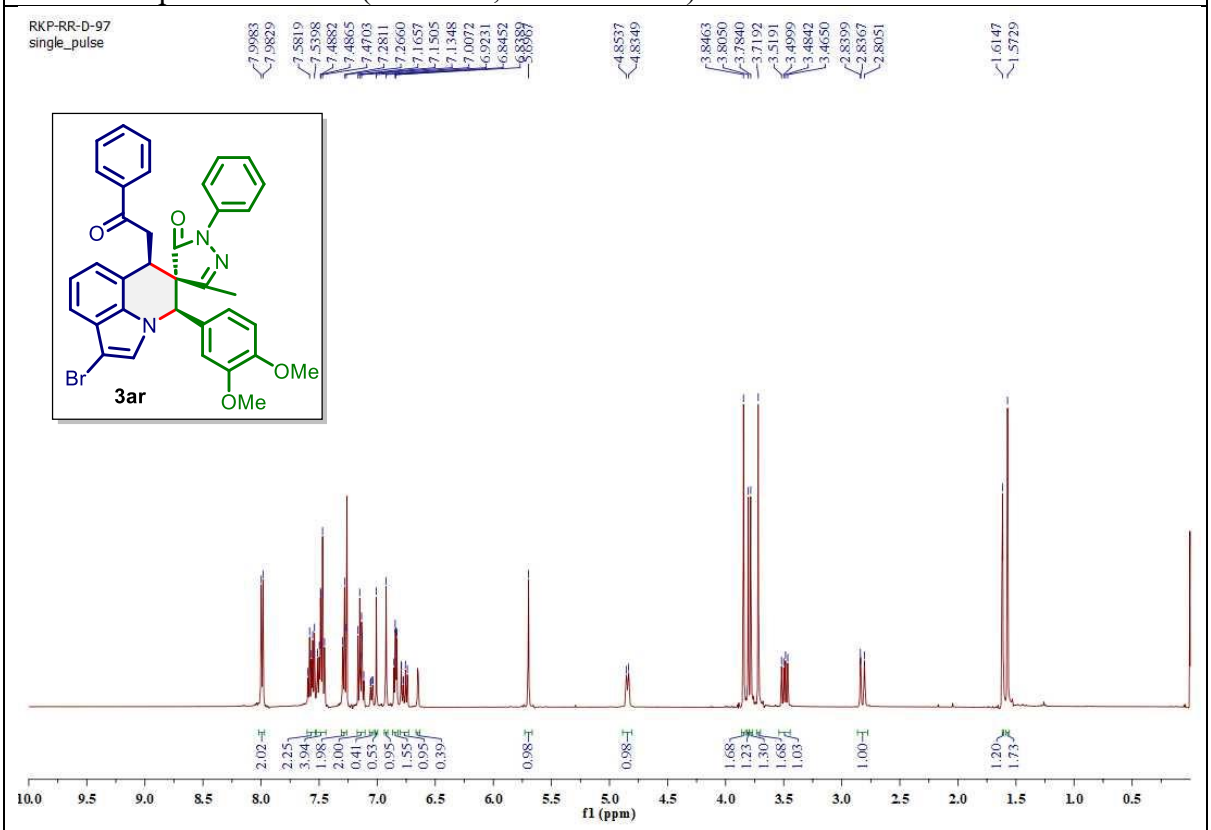
^{1}H NMR Spectrum of **3aq** (500 MHz, Chloroform-*d*)



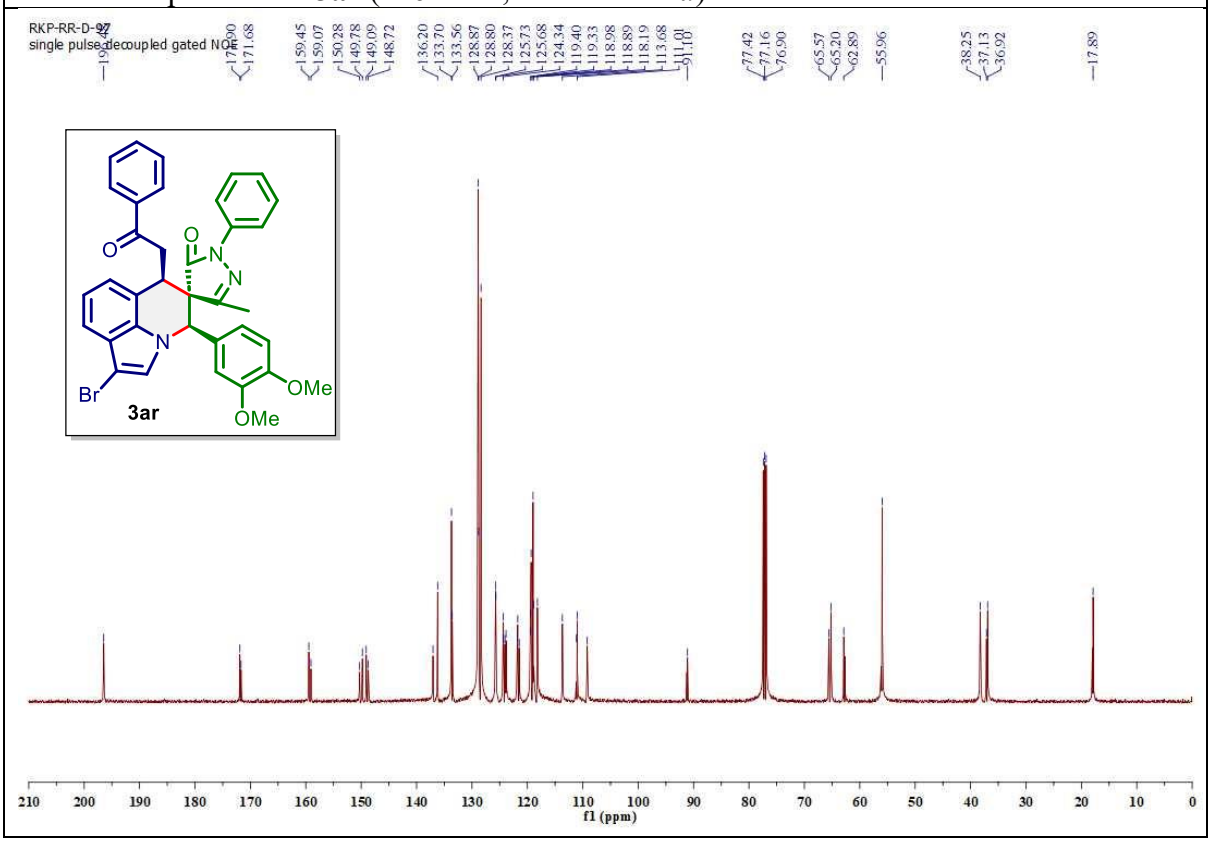
^{13}C NMR Spectrum of **3aq** (126 MHz, Chloroform-*d*)



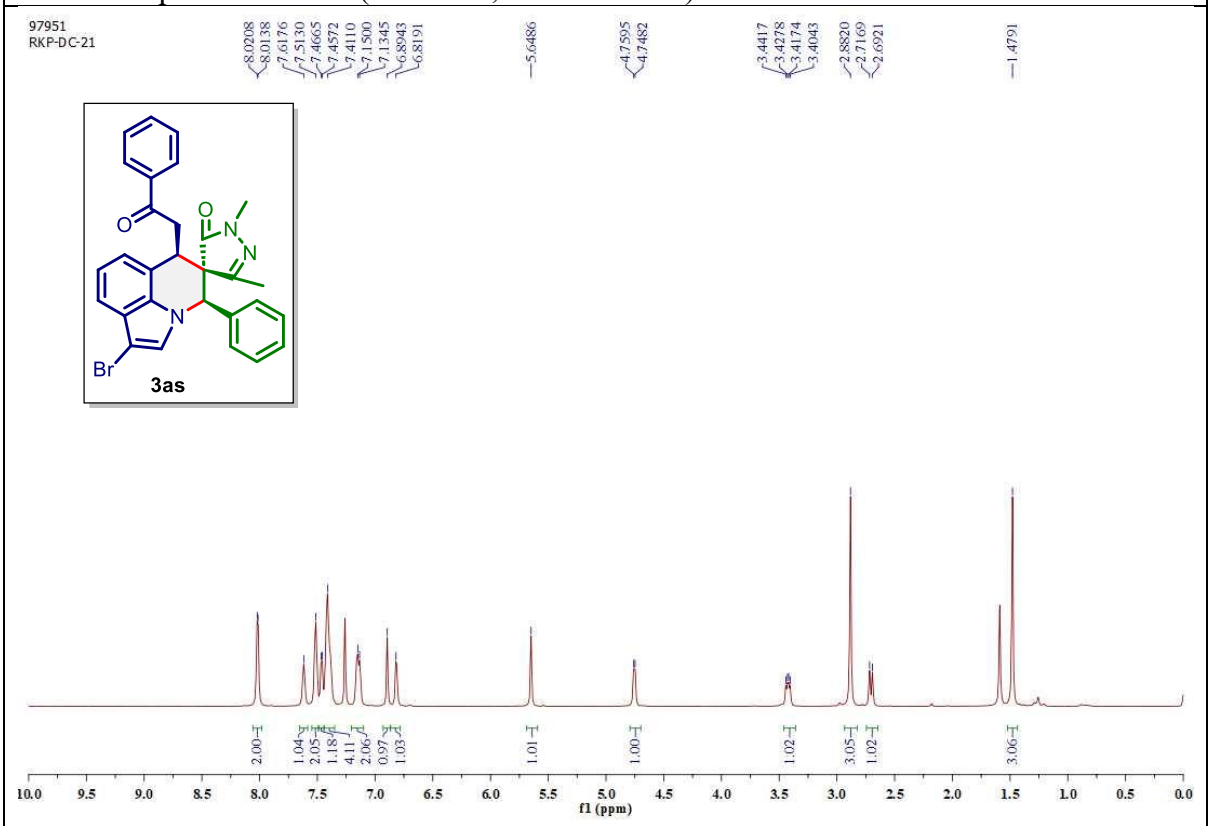
^{1}H NMR Spectrum of **3ar** (500 MHz, Chloroform-*d*)



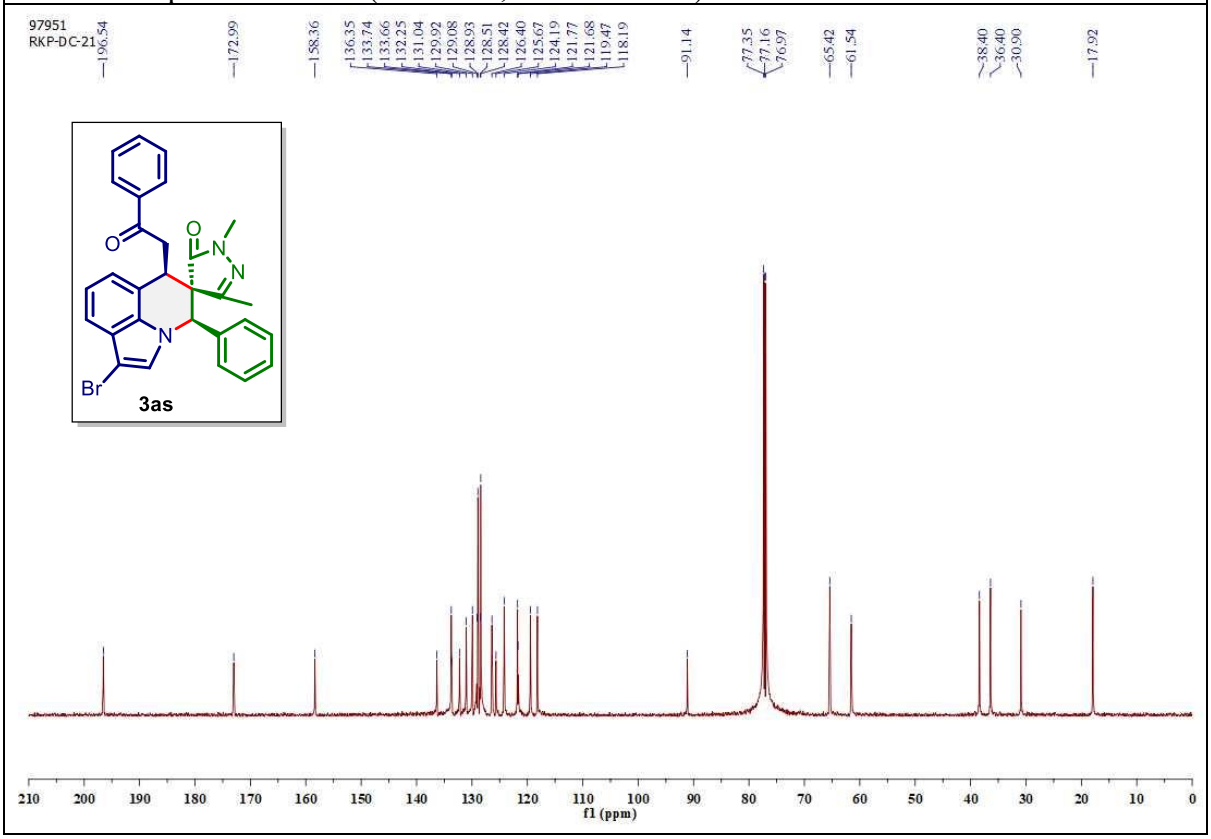
^{13}C NMR Spectrum of **3ar** (126 MHz, Chloroform-*d*)



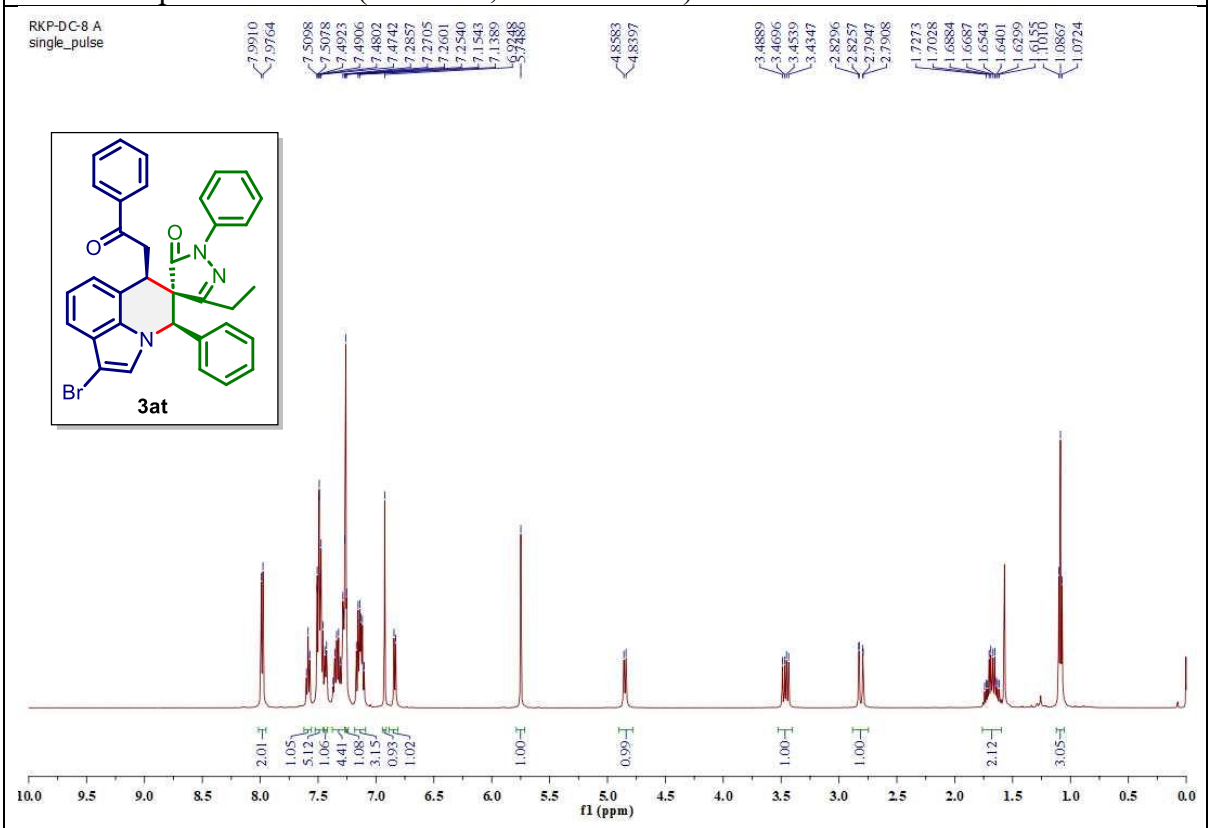
^{1}H NMR Spectrum of **3as** (700 MHz, Chloroform-*d*)



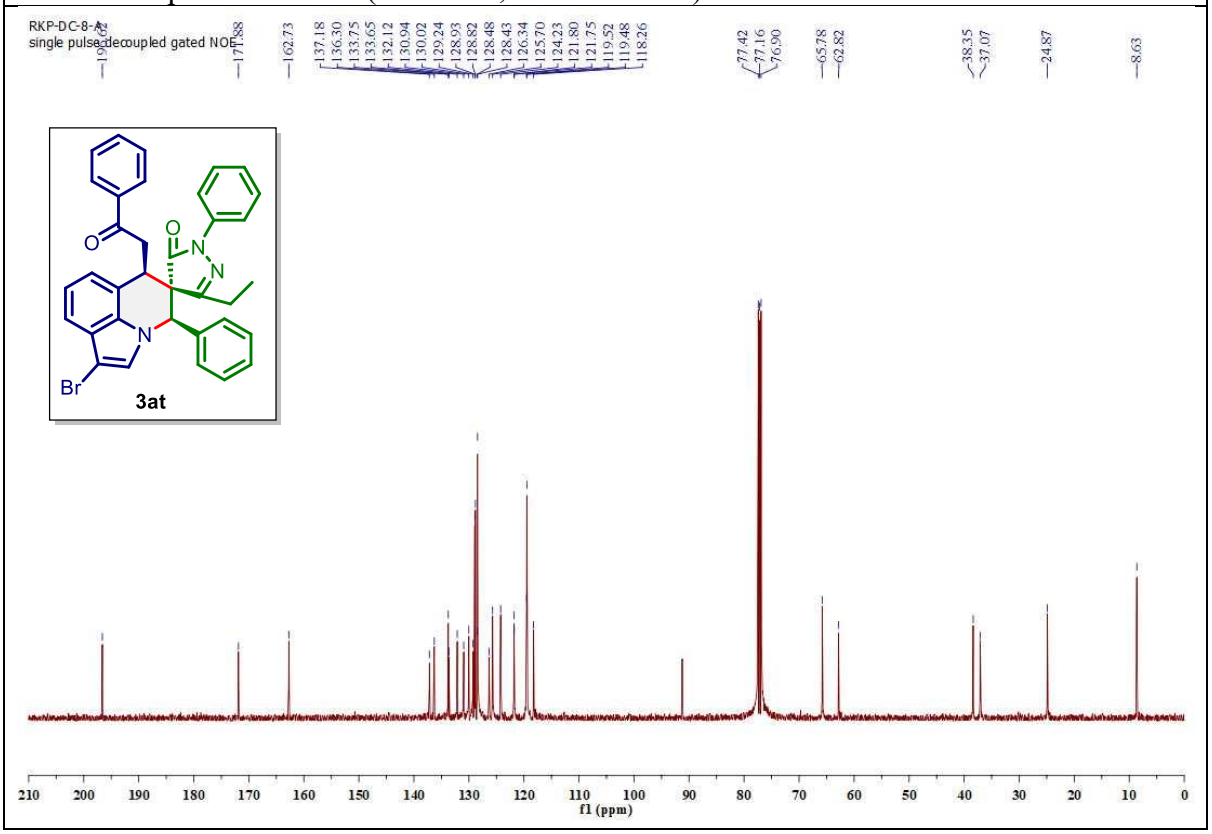
^{13}C NMR Spectrum of **3as** (176 MHz, Chloroform-*d*)



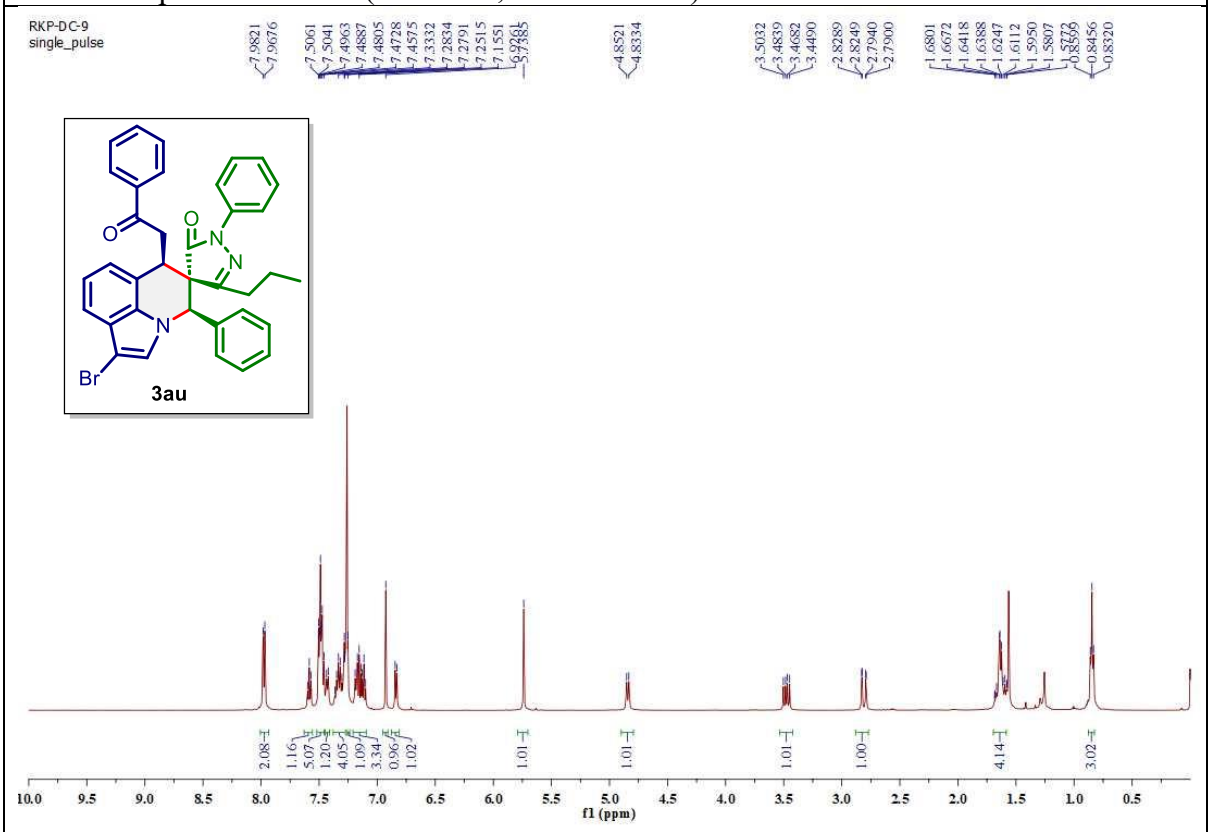
^{1}H NMR Spectrum of **3at** (500 MHz, Chloroform-*d*)



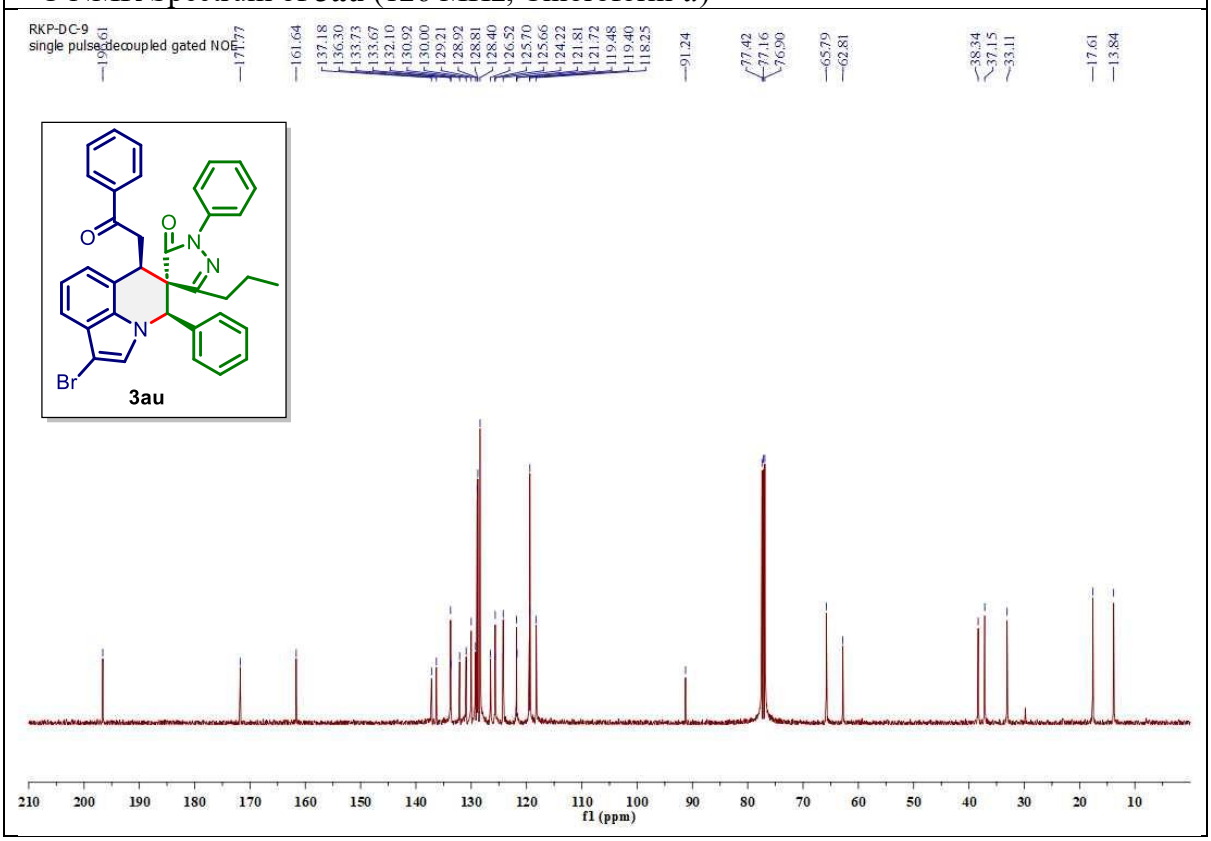
^{13}C NMR Spectrum of **3at** (126 MHz, Chloroform-*d*)



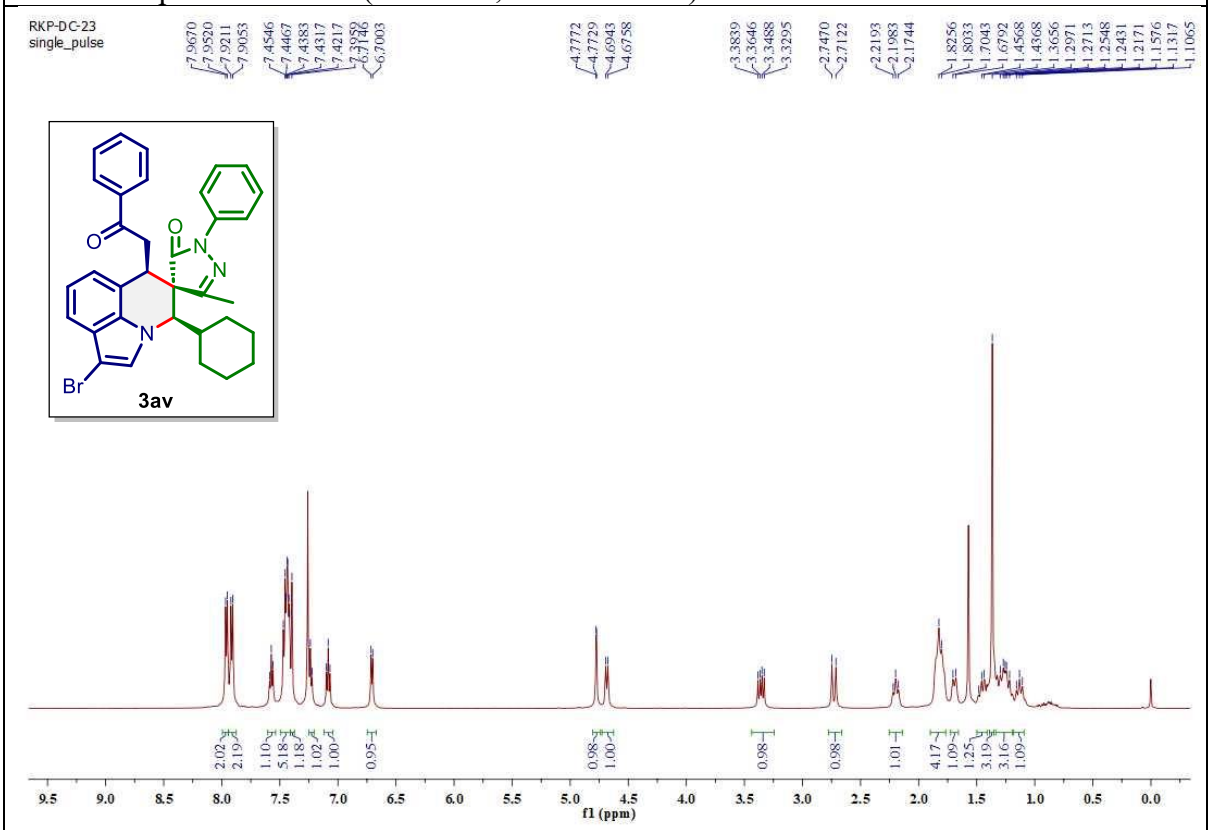
^{1}H NMR Spectrum of **3au** (500 MHz, Chloroform-*d*)



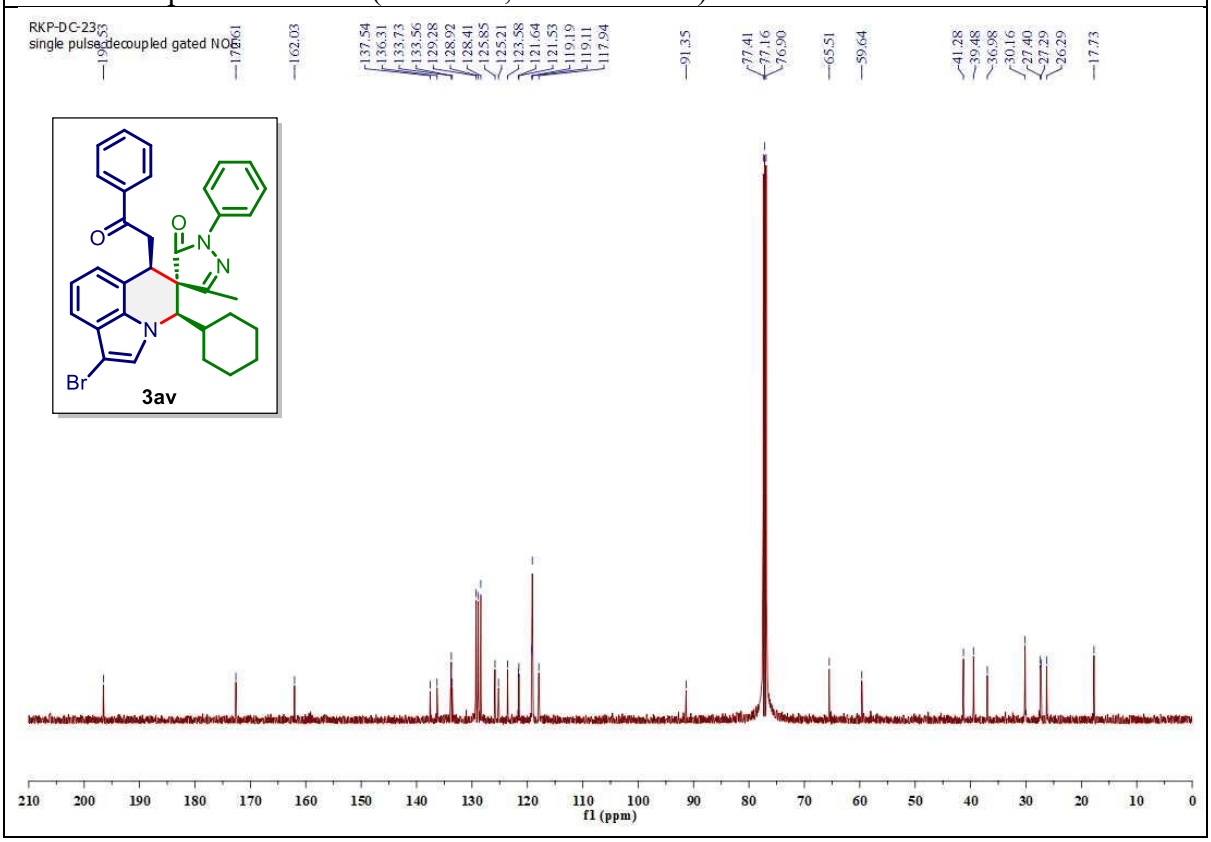
^{13}C NMR Spectrum of **3au** (126 MHz, Chloroform-*d*)



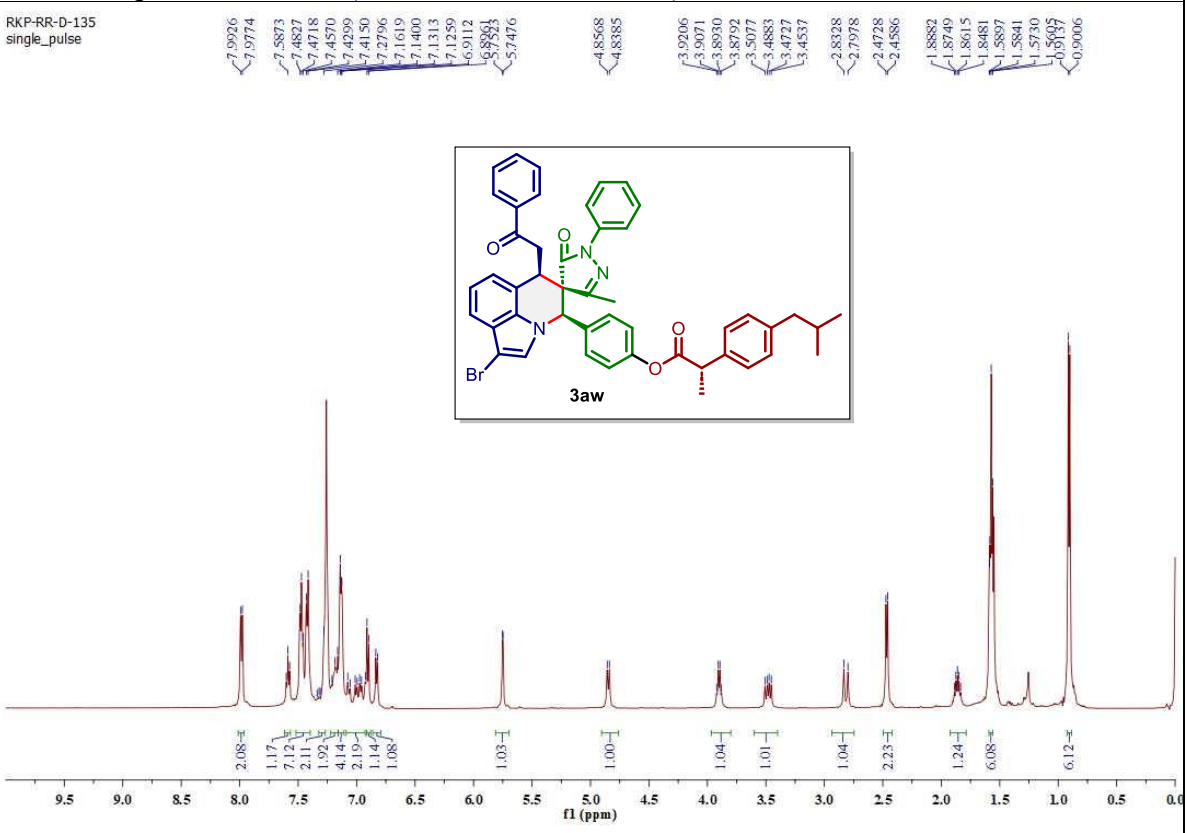
^{1}H NMR Spectrum of **3av** (500 MHz, Chloroform-*d*)



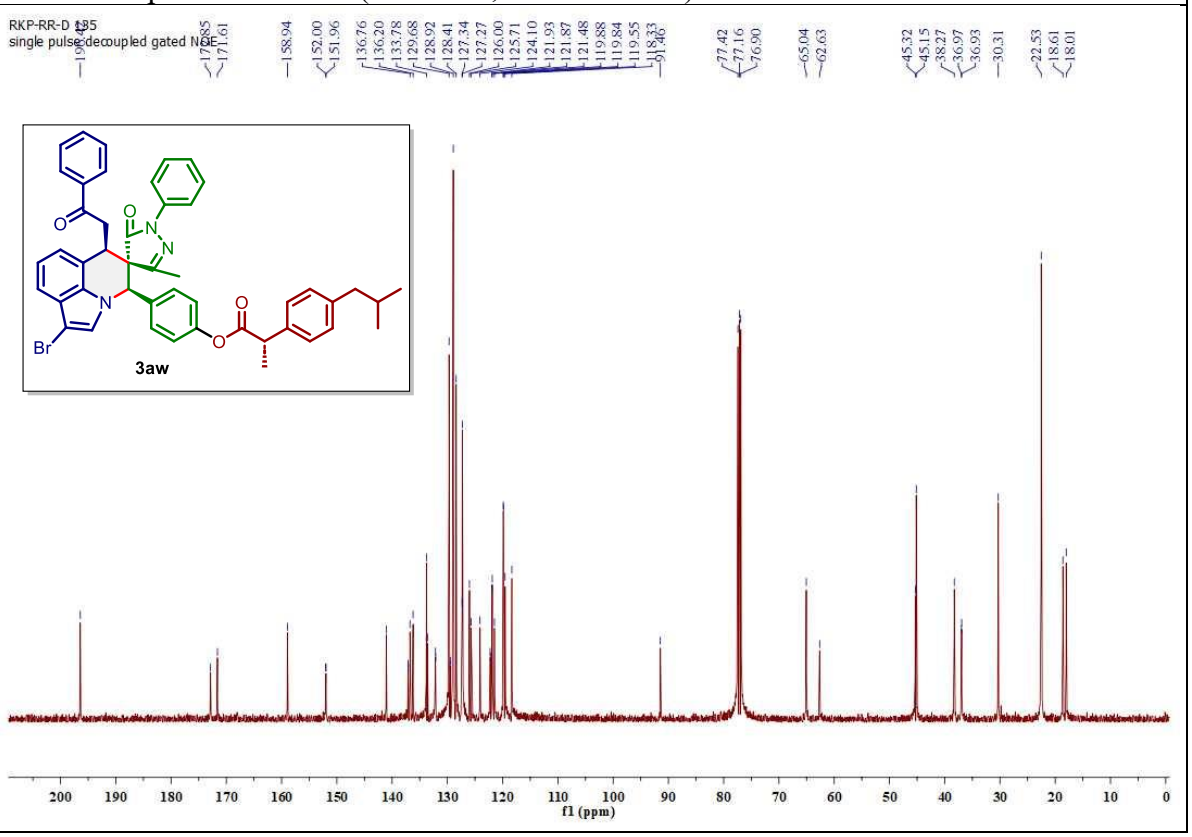
^{13}C NMR Spectrum of **3av** (126 MHz, Chloroform-*d*)



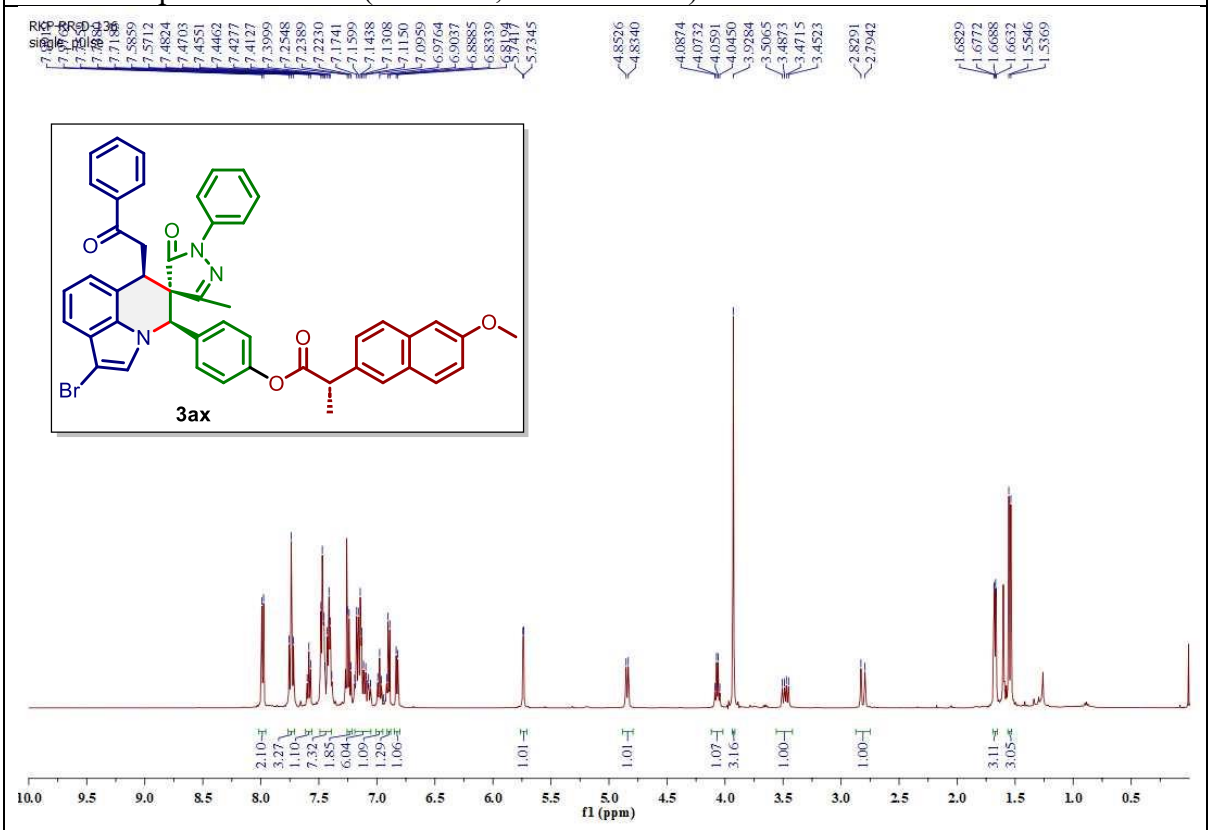
^{1}H NMR Spectrum of **3aw** (500 MHz, Chloroform-*d*)



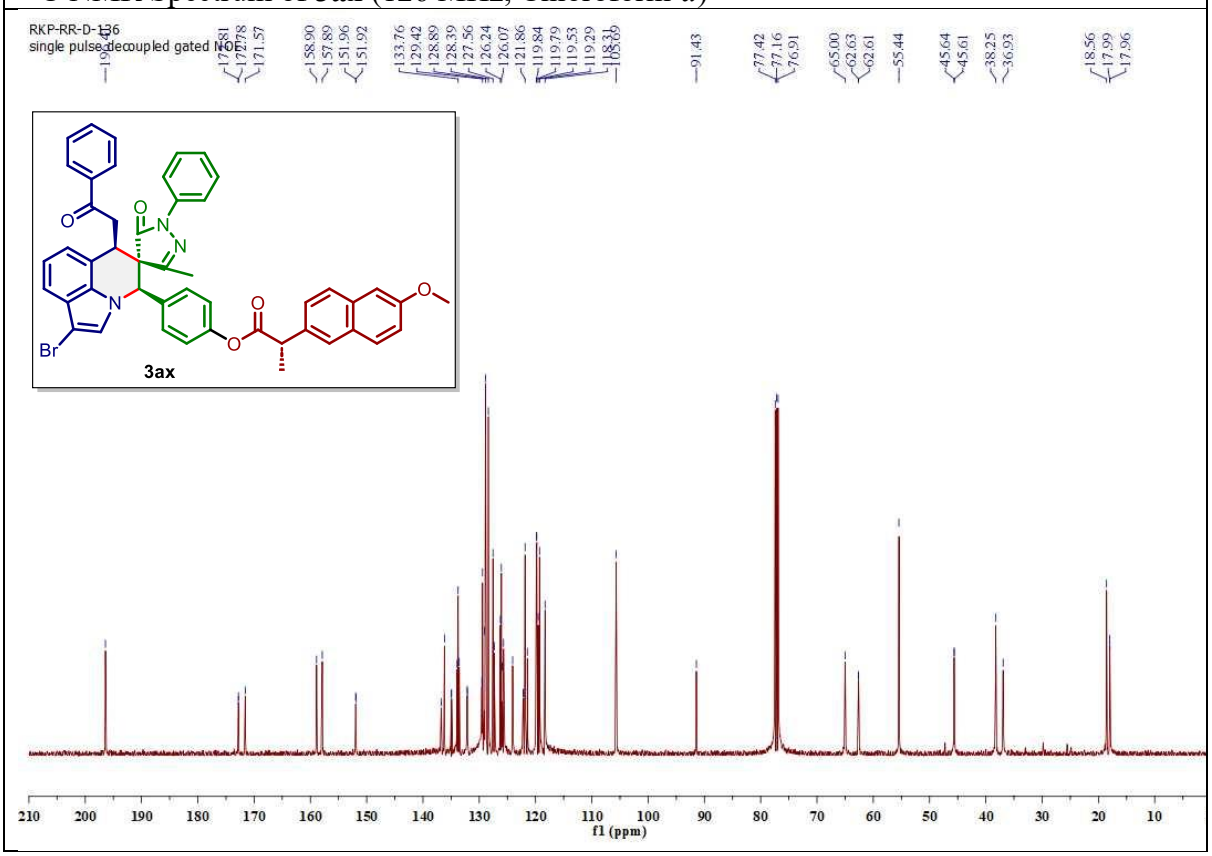
^{13}C NMR Spectrum of **3aw** (126 MHz, Chloroform-*d*)



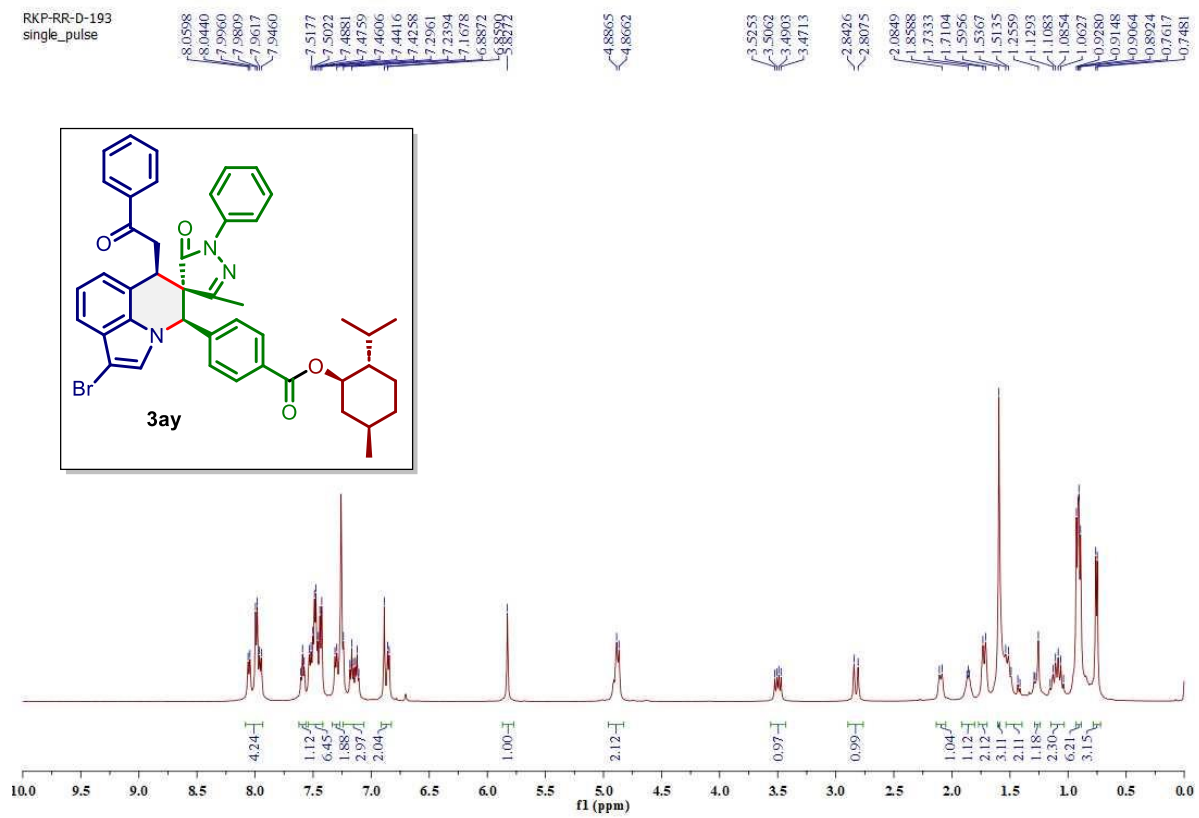
^{1}H NMR Spectrum of **3ax** (500 MHz, Chloroform-*d*)



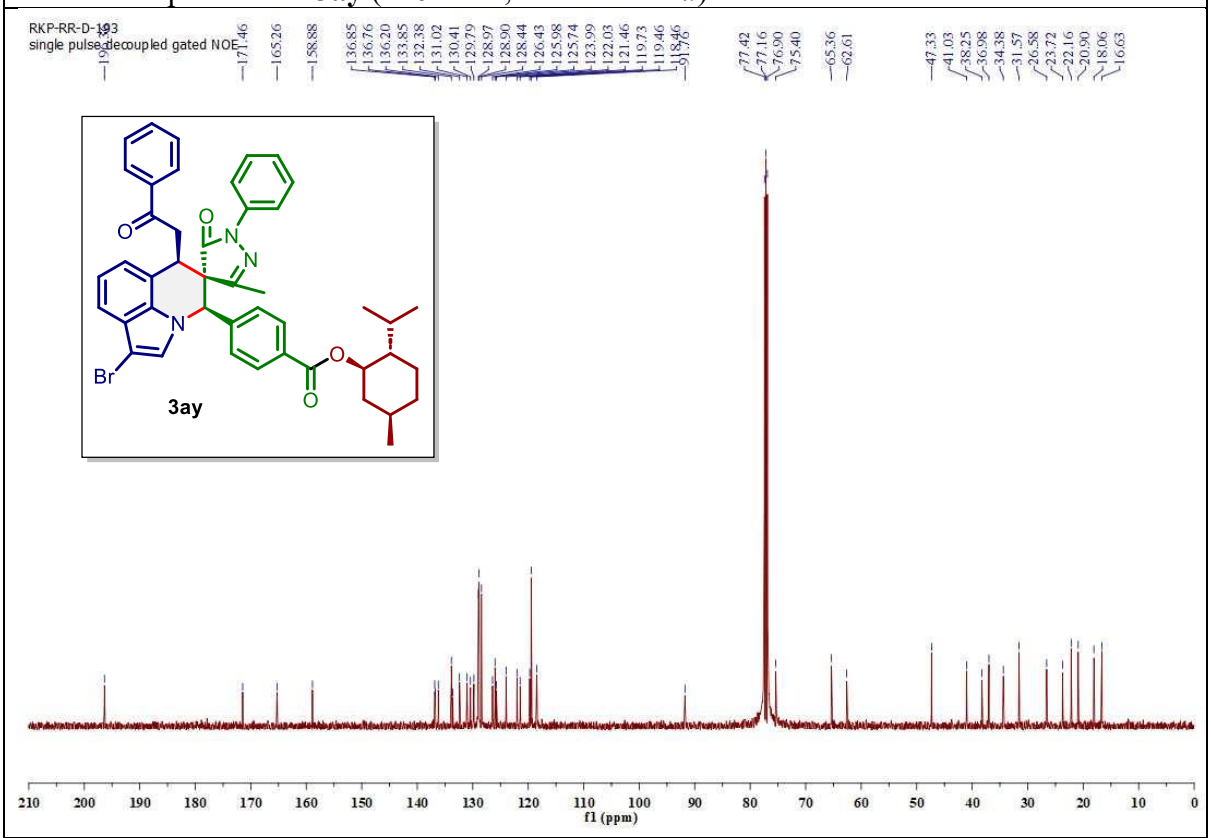
^{13}C NMR Spectrum of **3ax** (126 MHz, Chloroform-*d*)



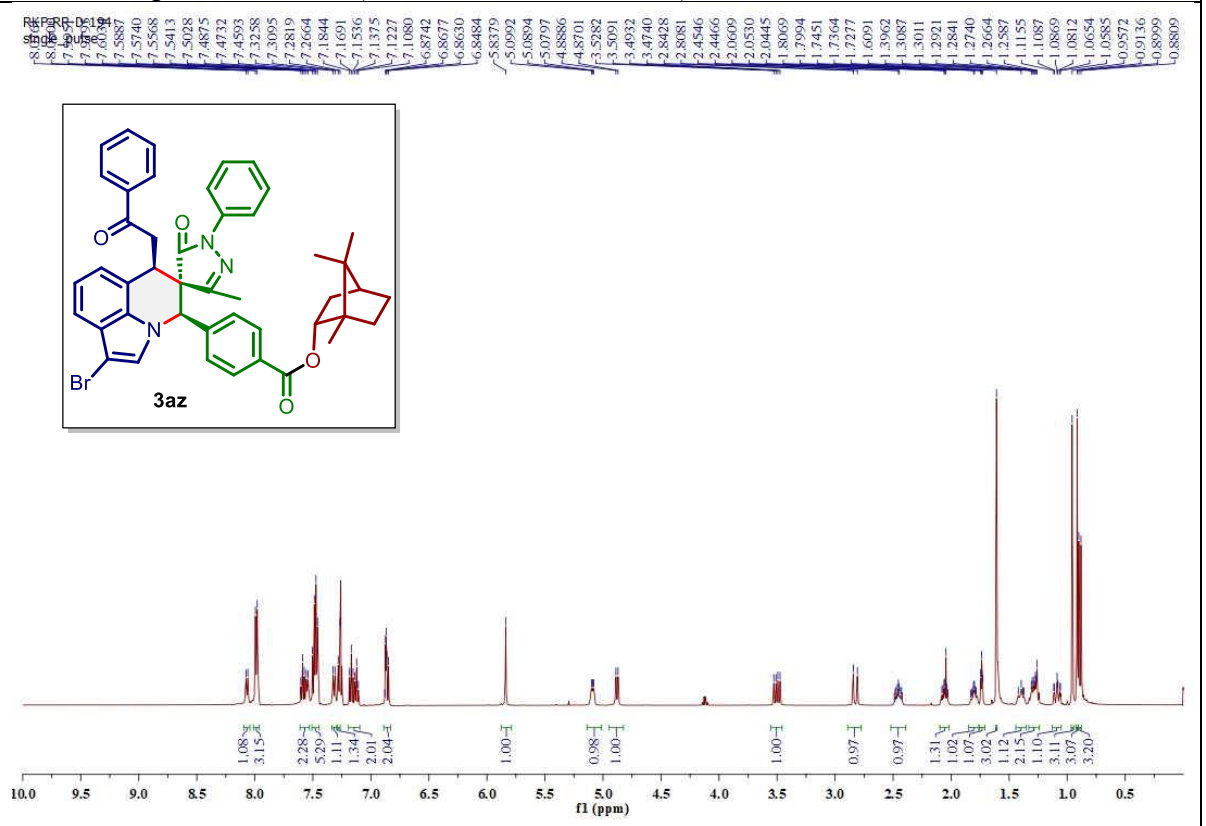
^{1}H NMR Spectrum of **3ay** (500 MHz, Chloroform-*d*)



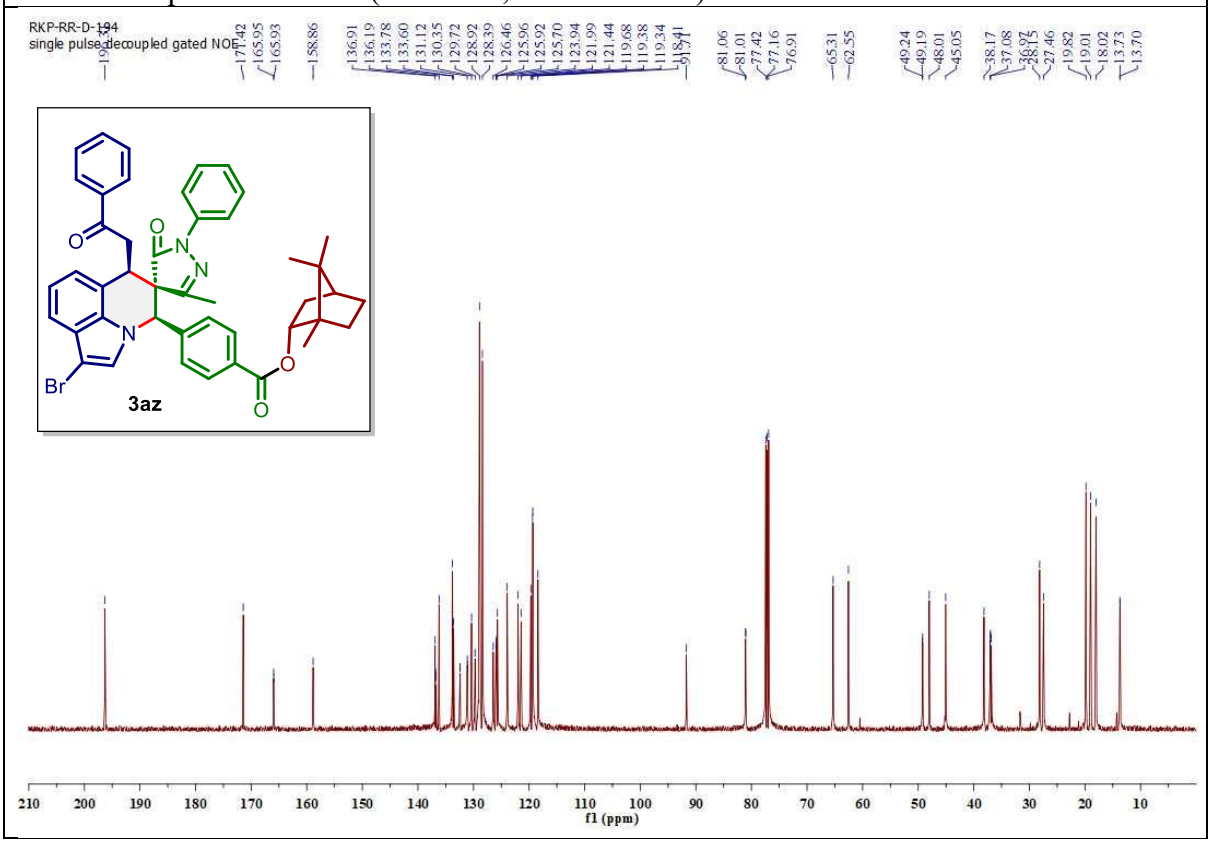
^{13}C NMR Spectrum of **3ay** (126 MHz, Chloroform-*d*)



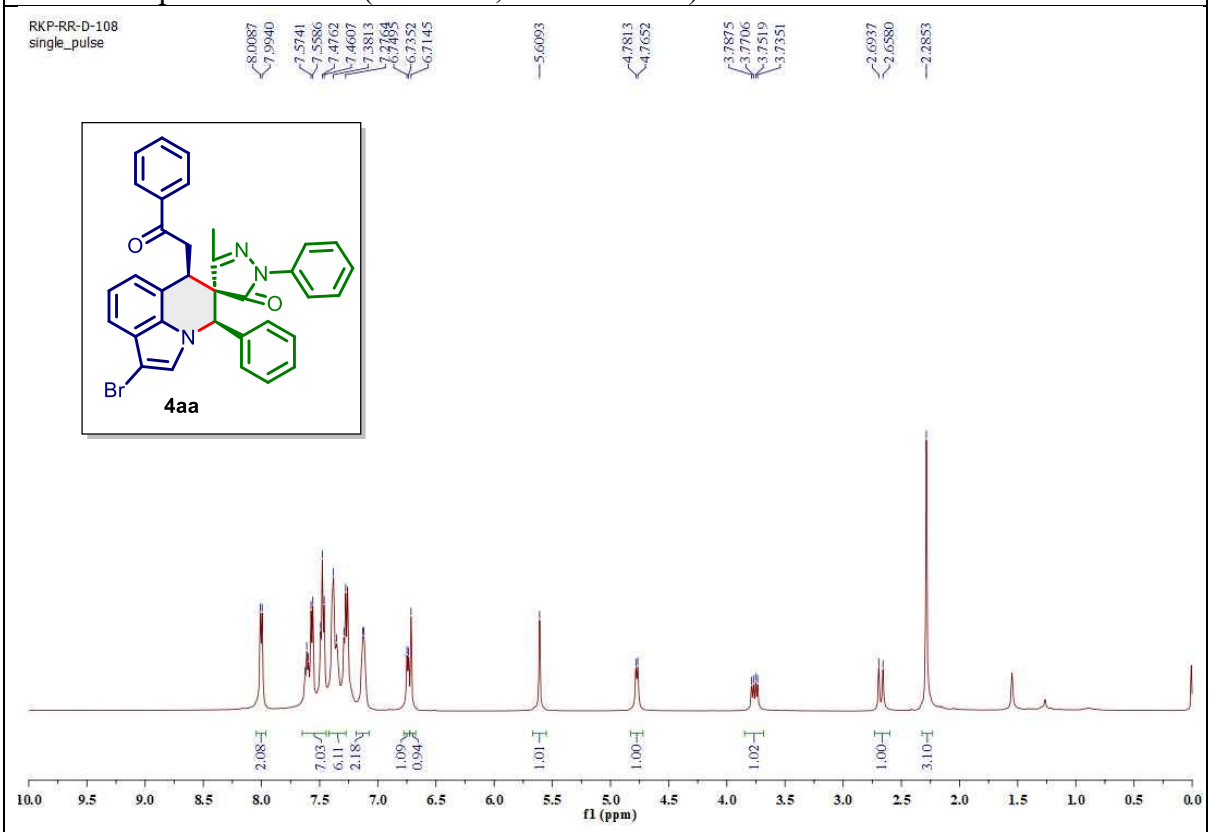
^{1}H NMR Spectrum of **3az** (500 MHz, Chloroform-*d*)



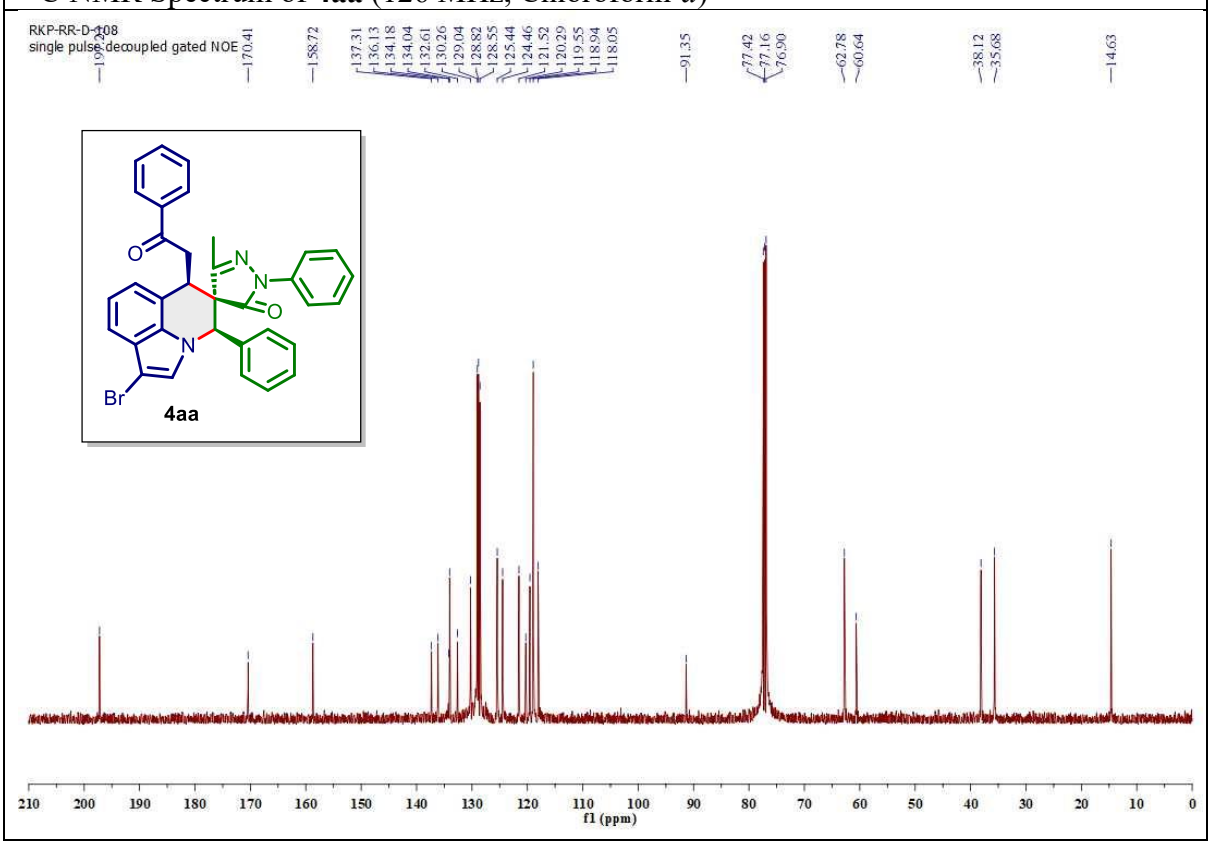
^{13}C NMR Spectrum of **3az** (126 MHz, Chloroform-*d*)



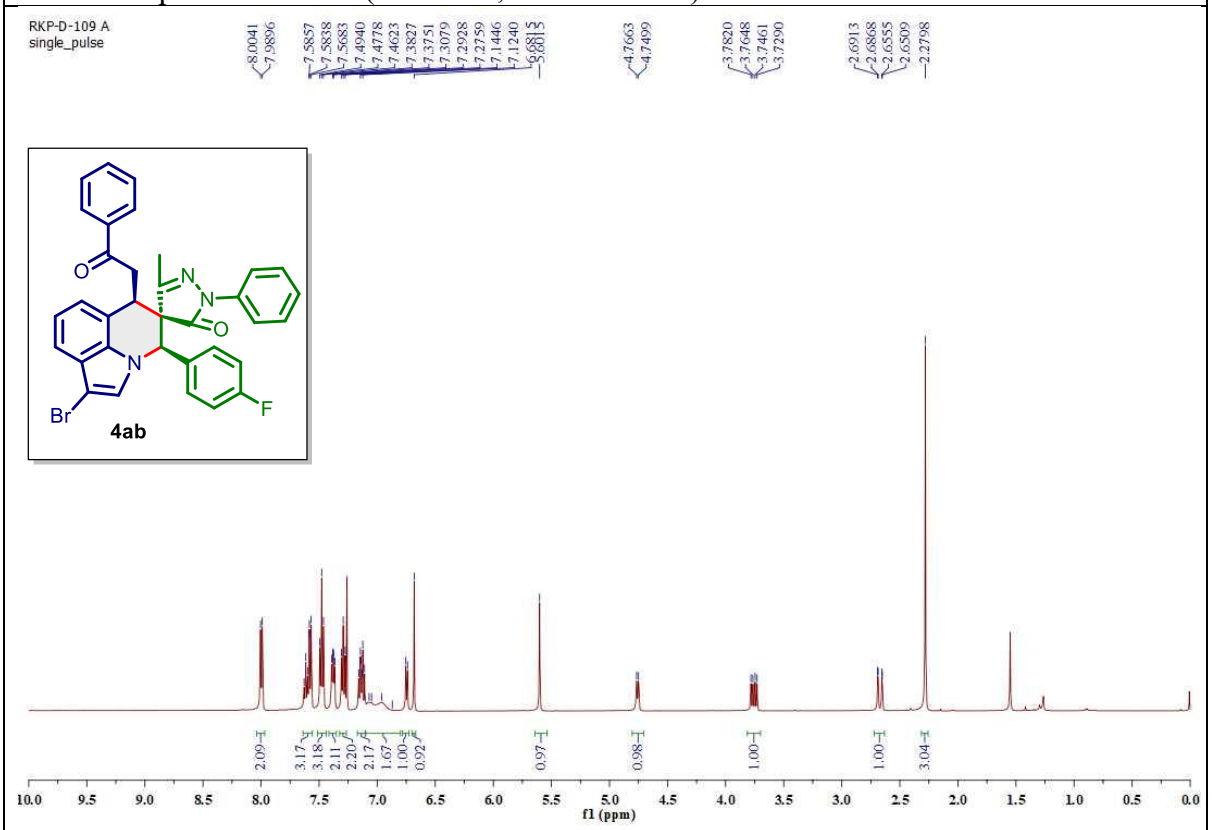
^{1}H NMR Spectrum of **4aa** (500 MHz, Chloroform-*d*)



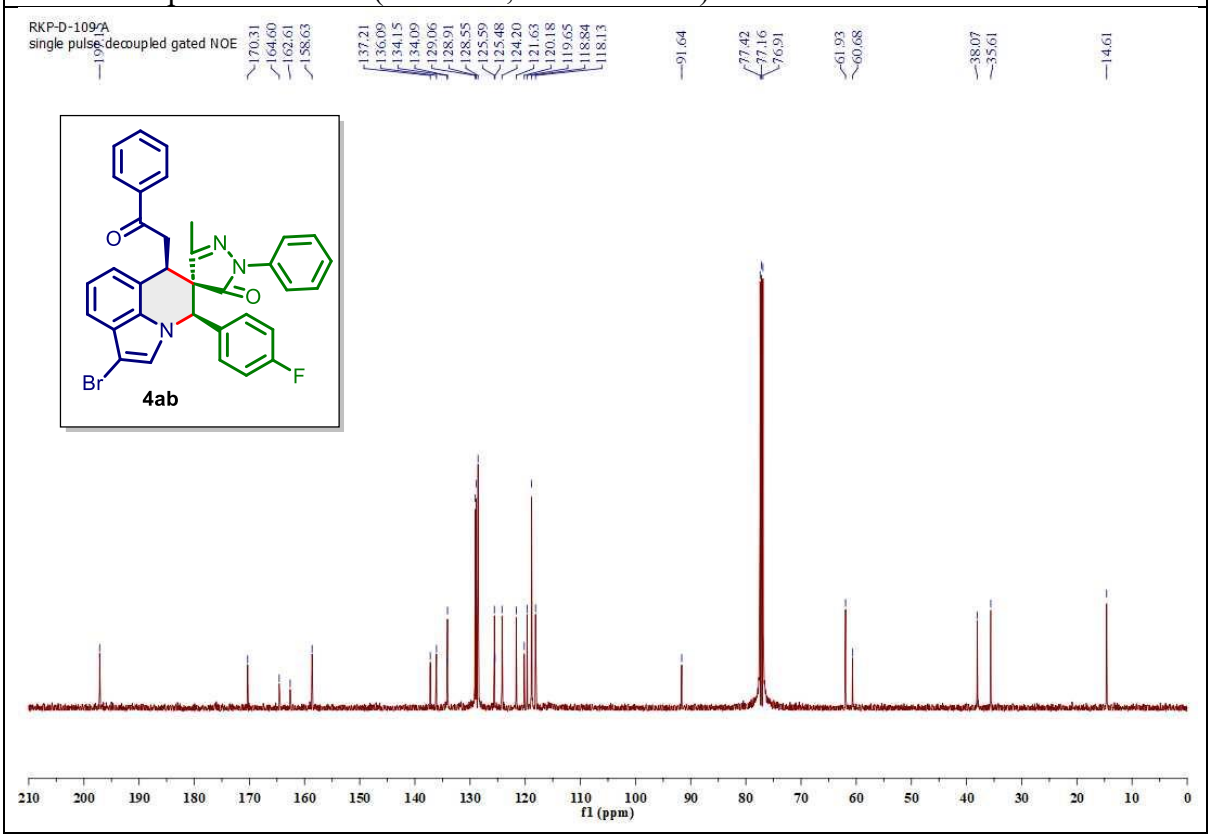
^{13}C NMR Spectrum of **4aa** (126 MHz, Chloroform-*d*)



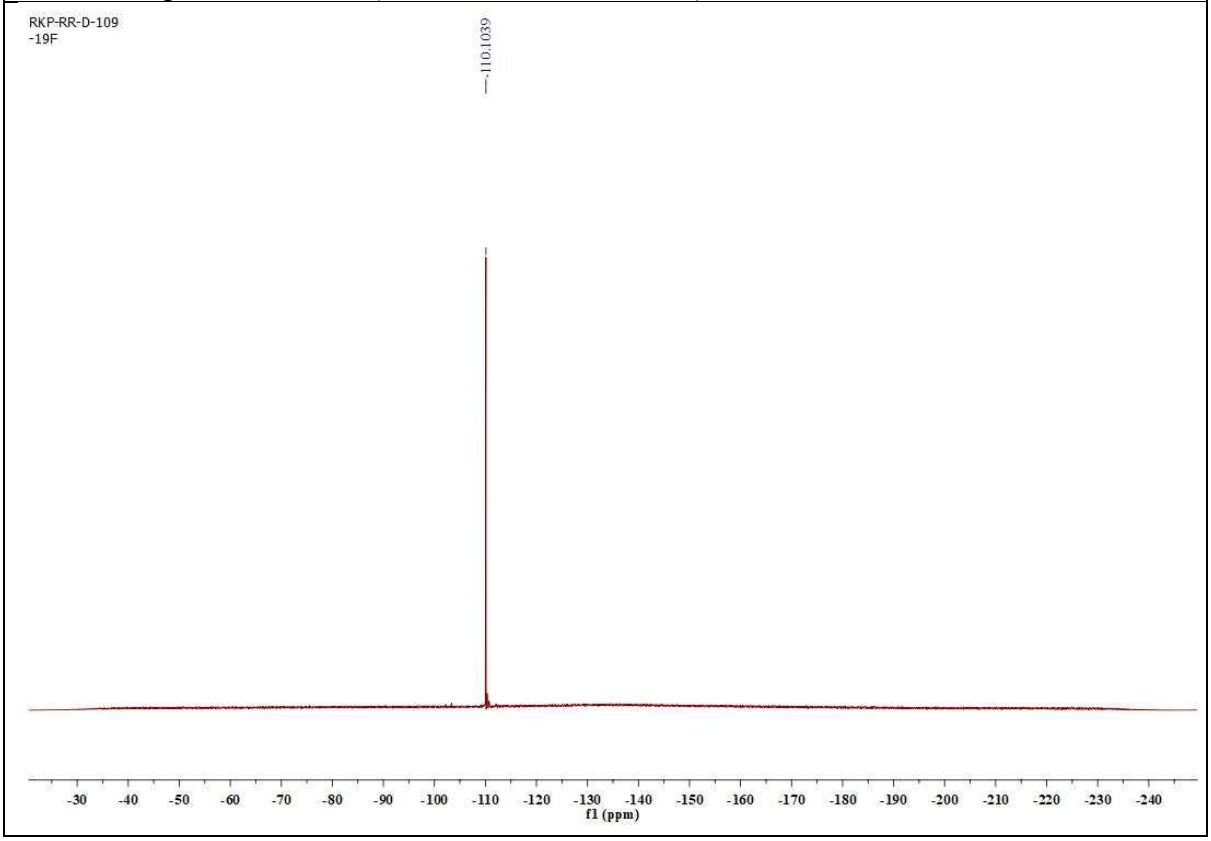
^{1}H NMR Spectrum of **4ab** (500 MHz, Chloroform-*d*)



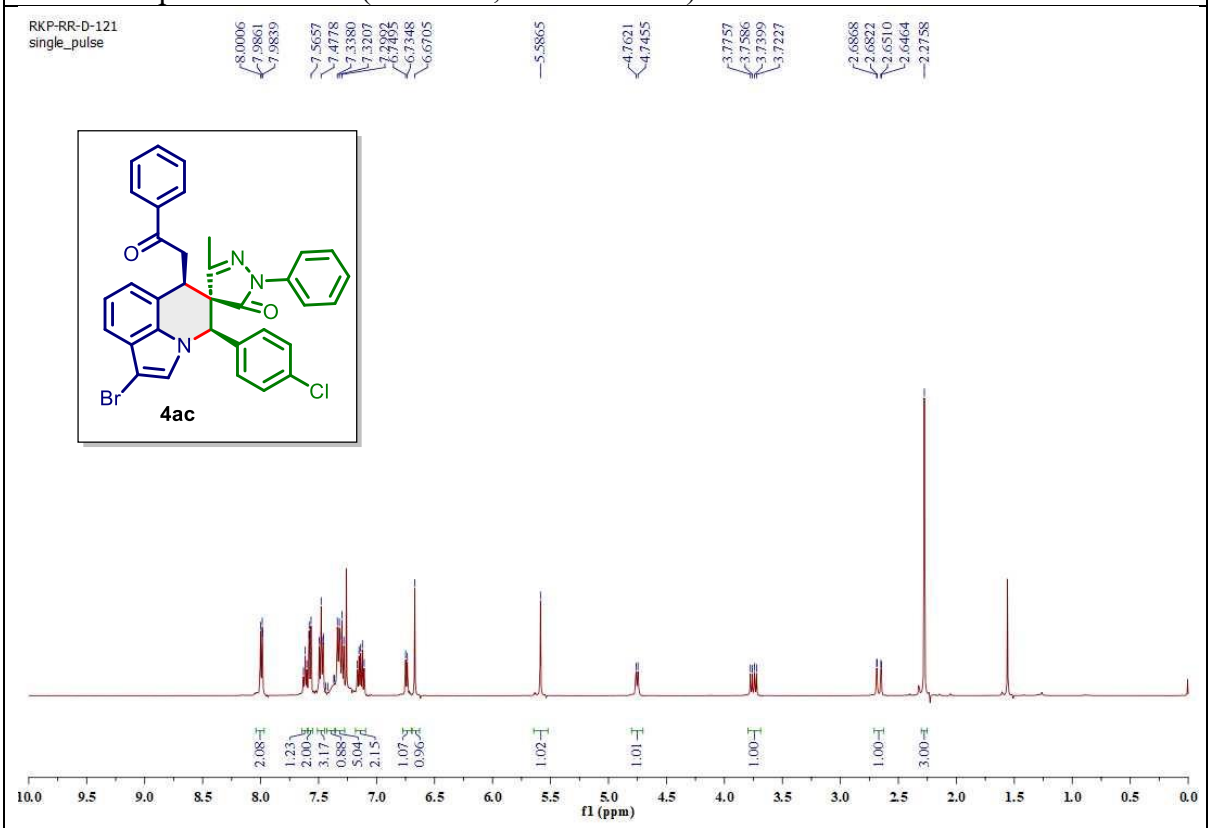
^{13}C NMR Spectrum of **4ab** (126 MHz, Chloroform-*d*)



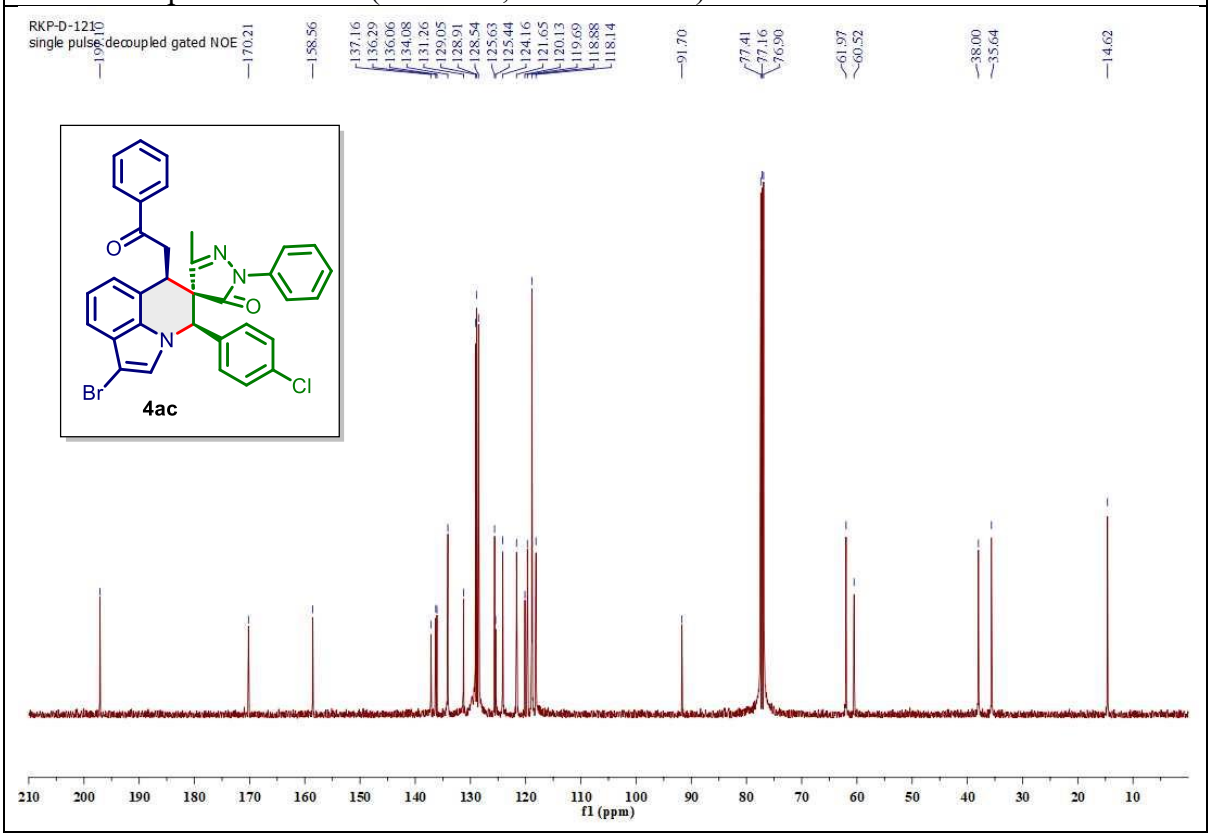
^{19}F NMR Spectrum of **4ab** (471 MHz, Chloroform-*d*)



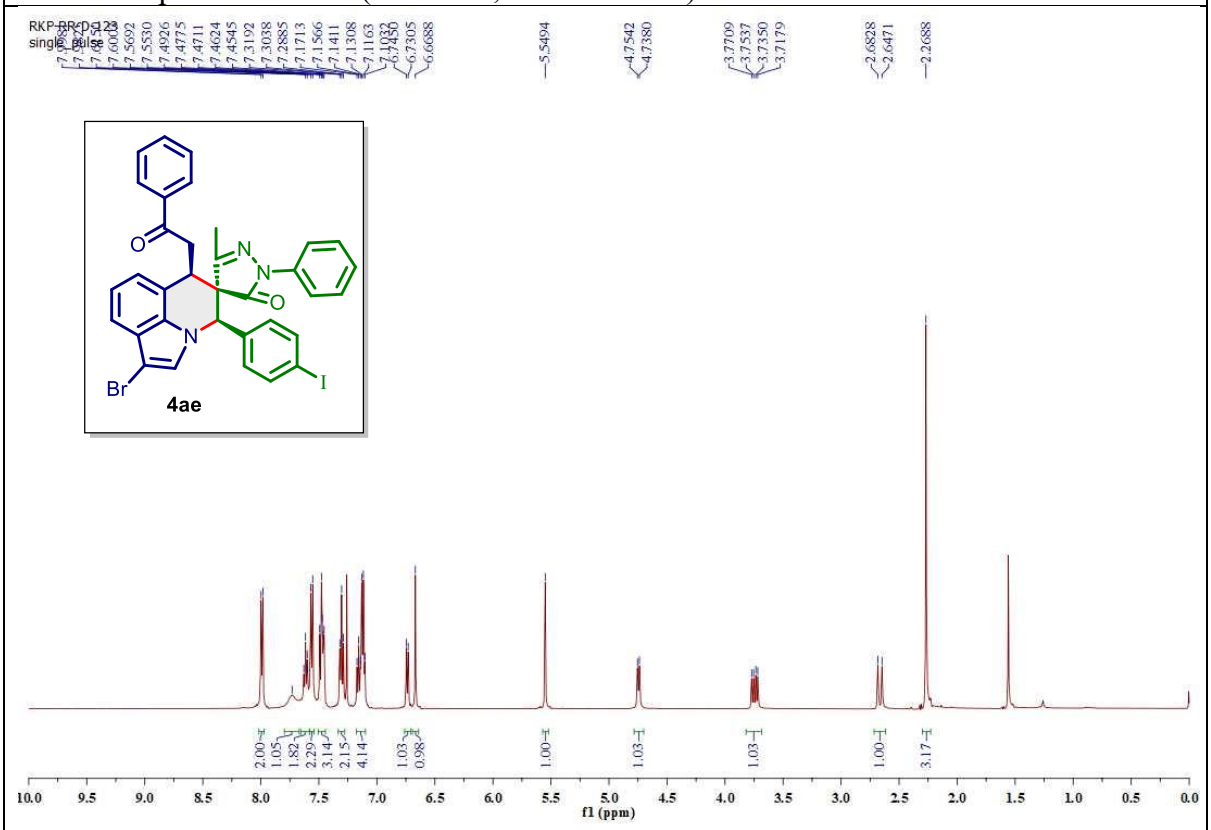
^{1}H NMR Spectrum of **4ac** (500 MHz, Chloroform-*d*)



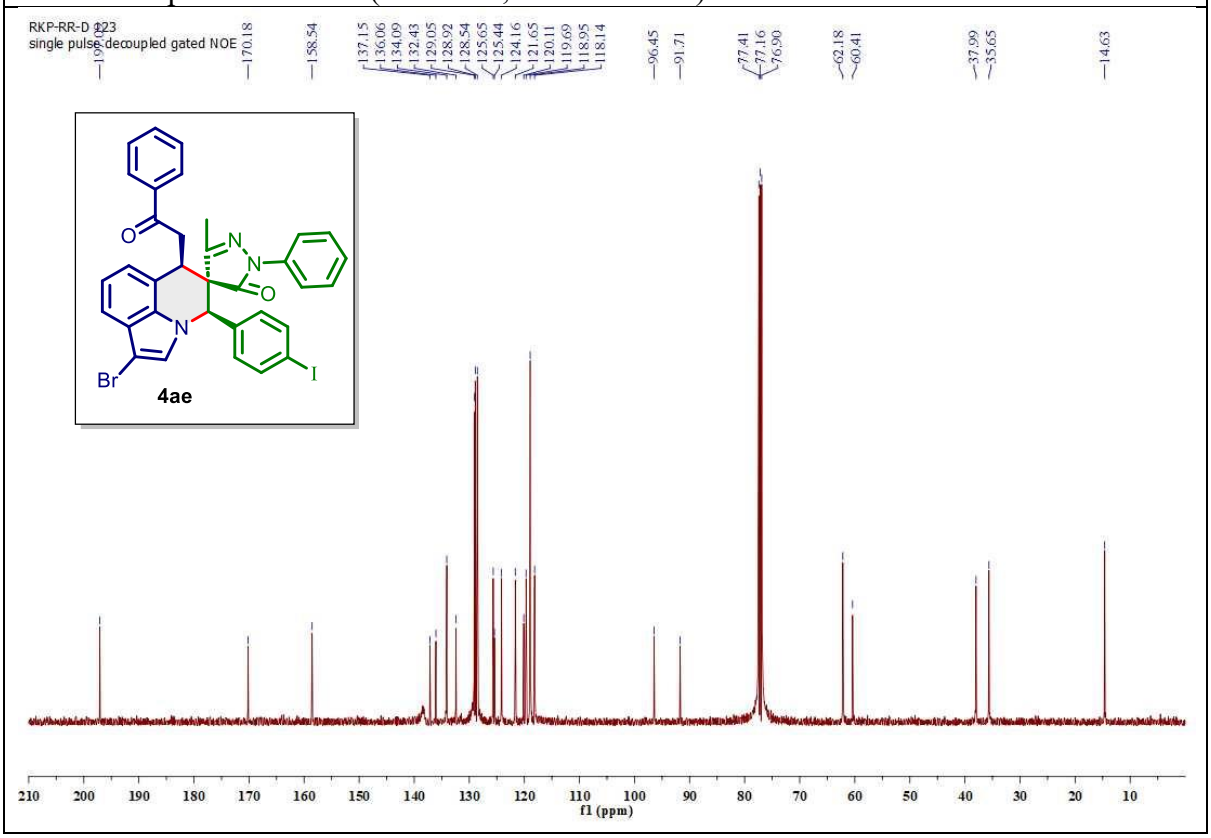
^{13}C NMR Spectrum of **4ac** (126 MHz, Chloroform-*d*)



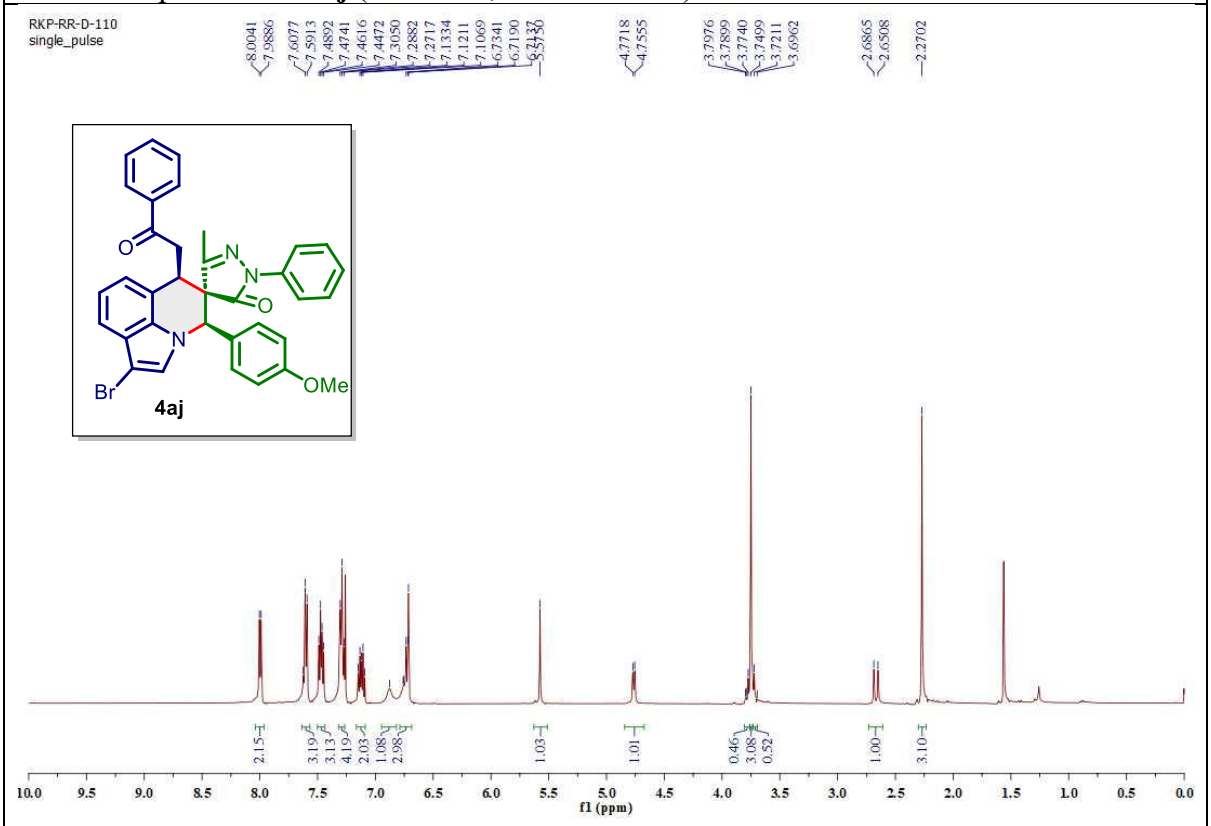
^{1}H NMR Spectrum of **4ae** (500 MHz, Chloroform-*d*)



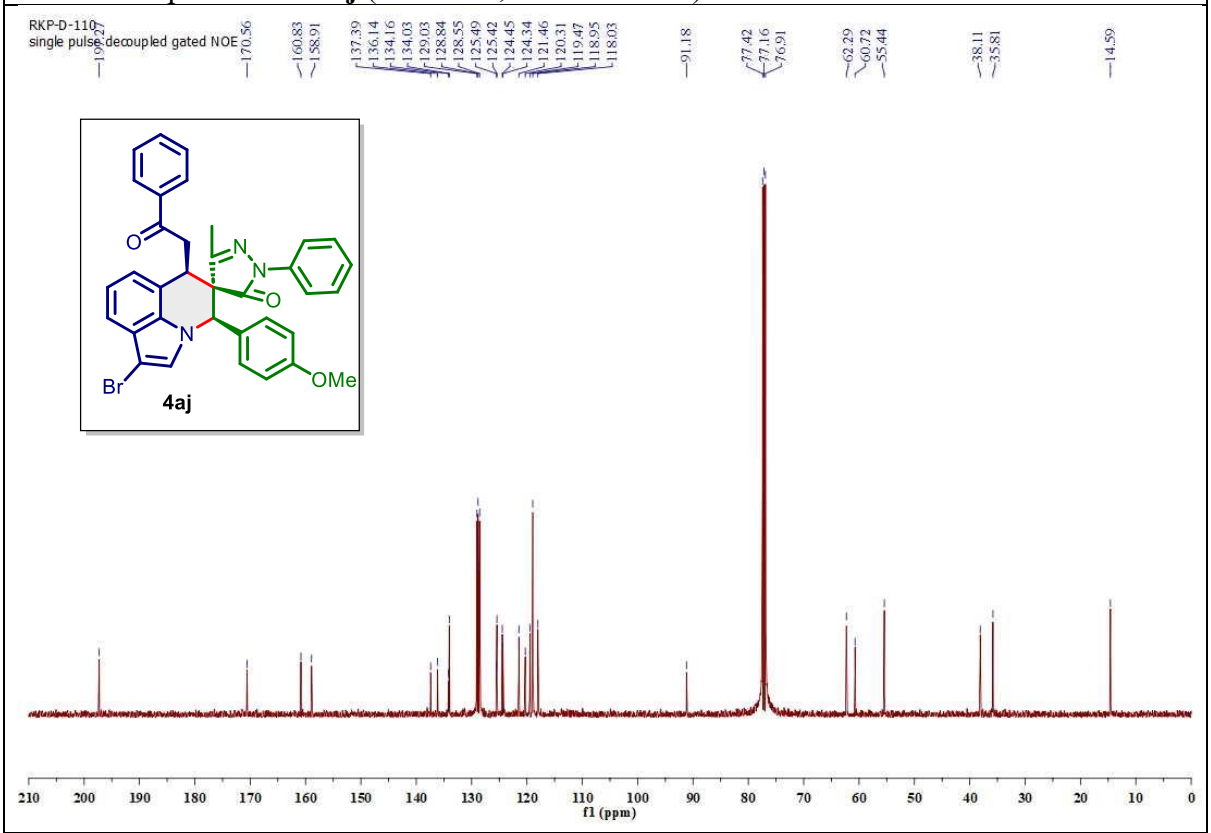
^{13}C NMR Spectrum of **4ae** (126 MHz, Chloroform-*d*)



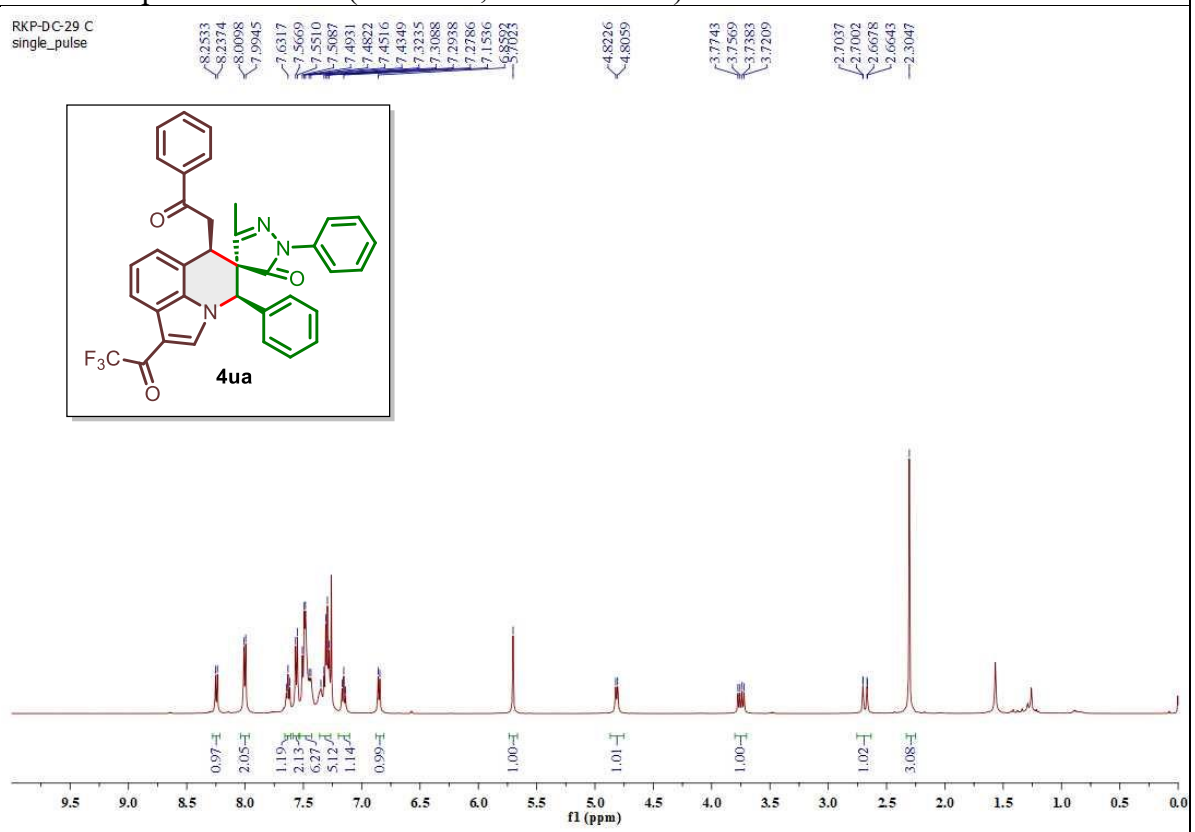
^{1}H NMR Spectrum of **4aj** (500 MHz, Chloroform-*d*)



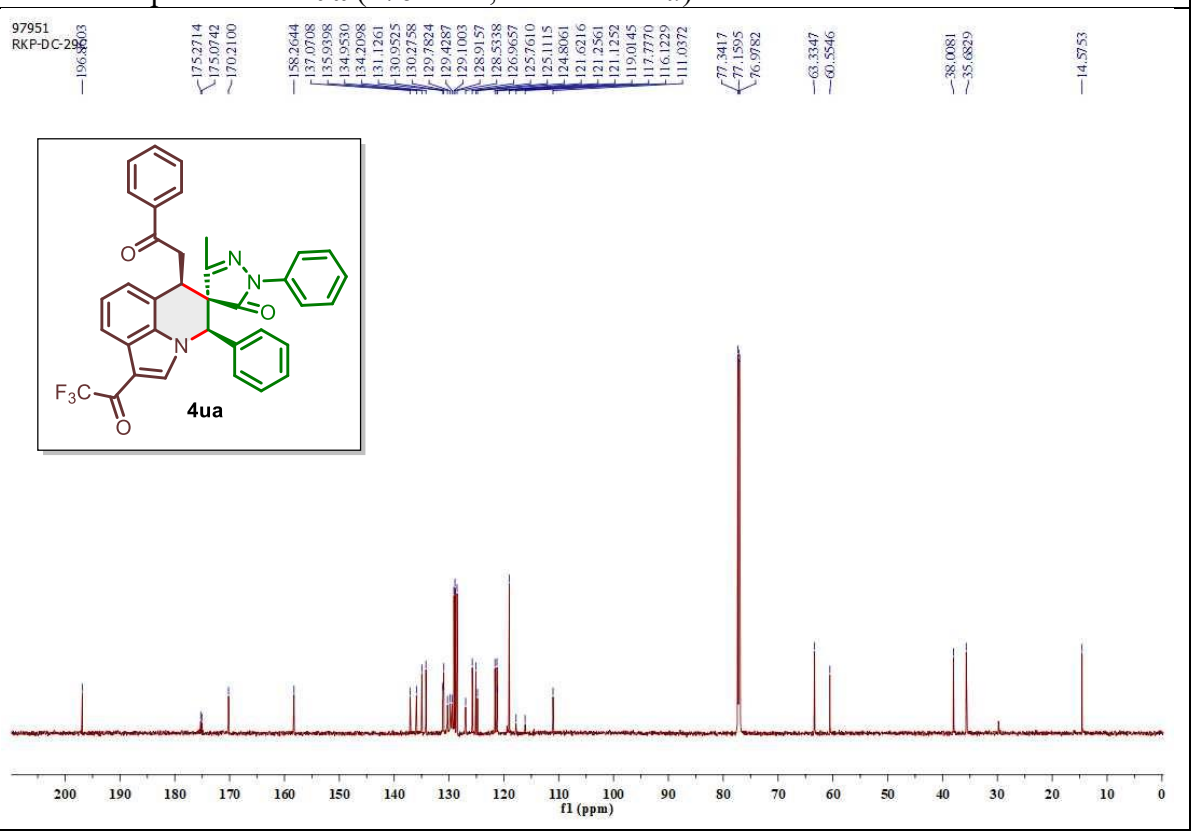
^{13}C NMR Spectrum of **4aj** (126 MHz, Chloroform-*d*)



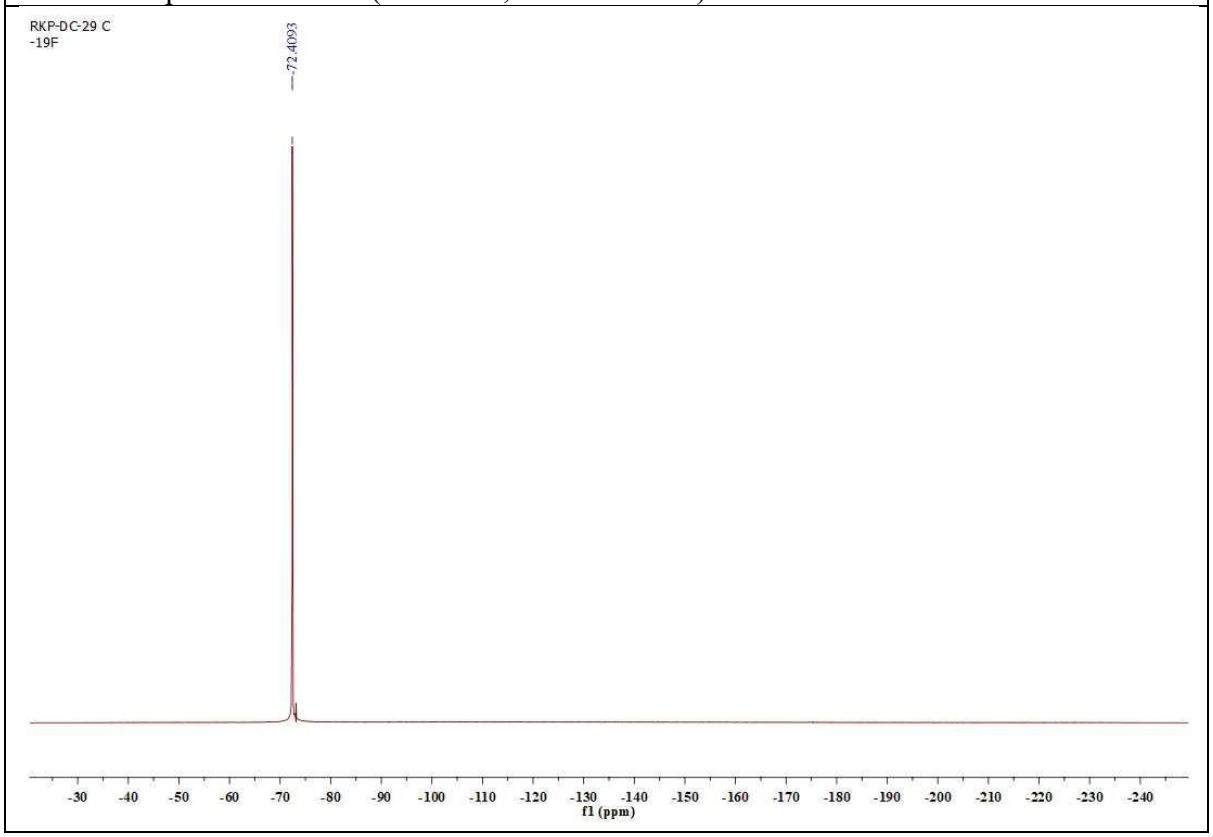
^{1}H NMR Spectrum of **4ua** (500 MHz, Chloroform-*d*)



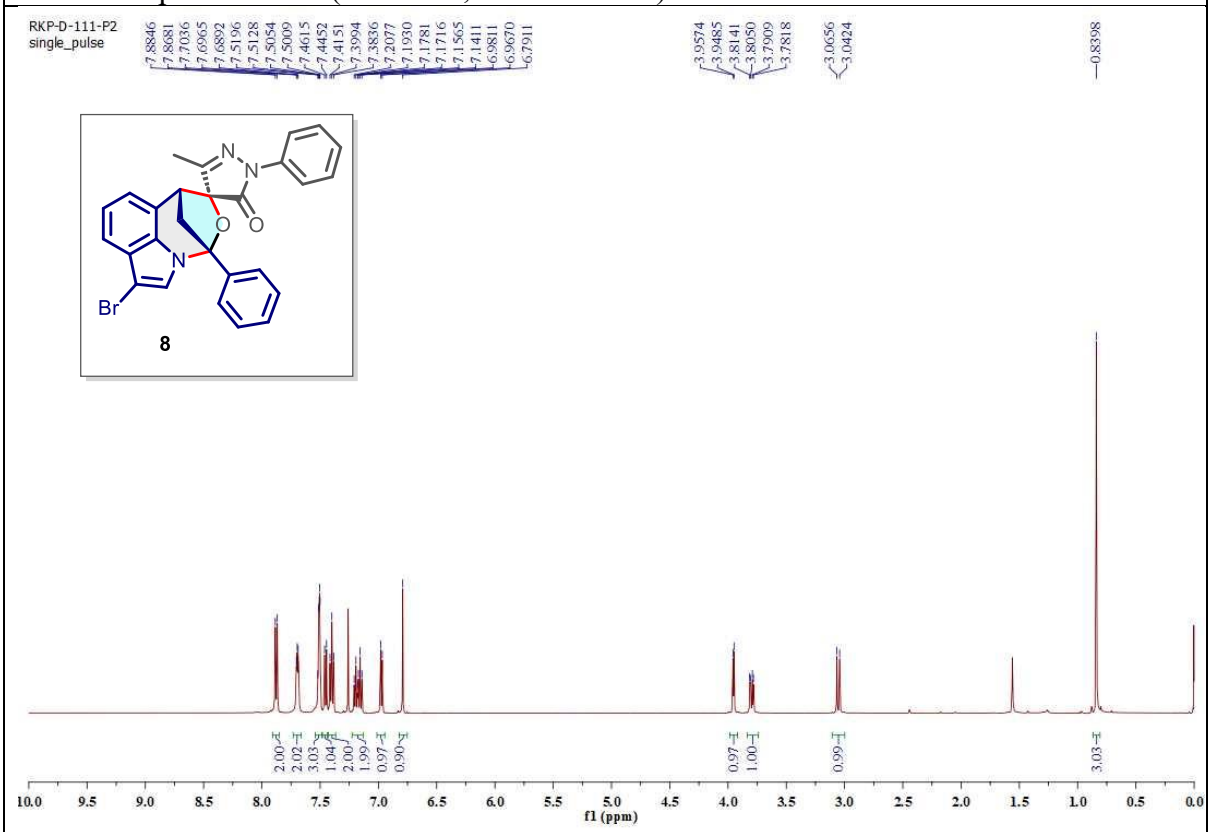
^{13}C NMR Spectrum of **4ua** (176 MHz, Chloroform-*d*)



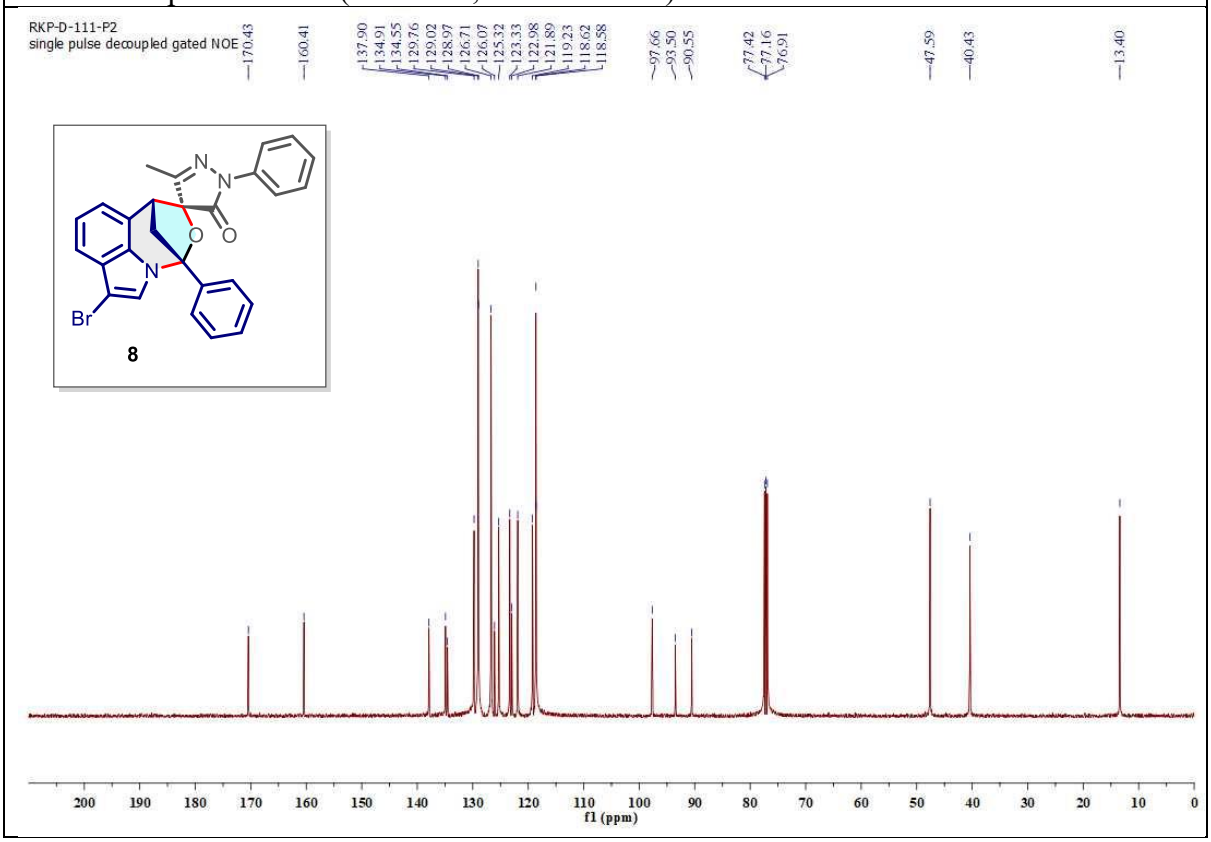
^{19}F NMR Spectrum of **4ua** (471 MHz, Chloroform-*d*)



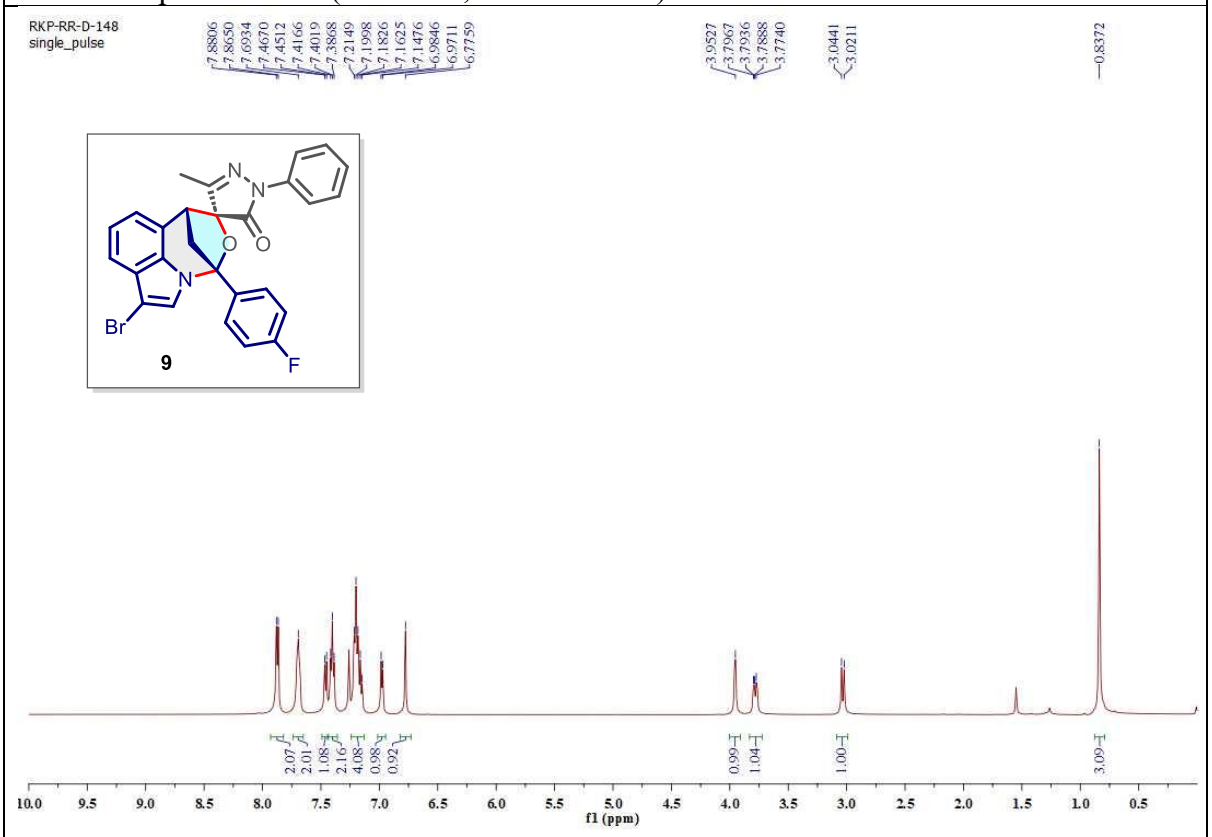
^{1}H NMR Spectrum of **8** (500 MHz, Chloroform-*d*)



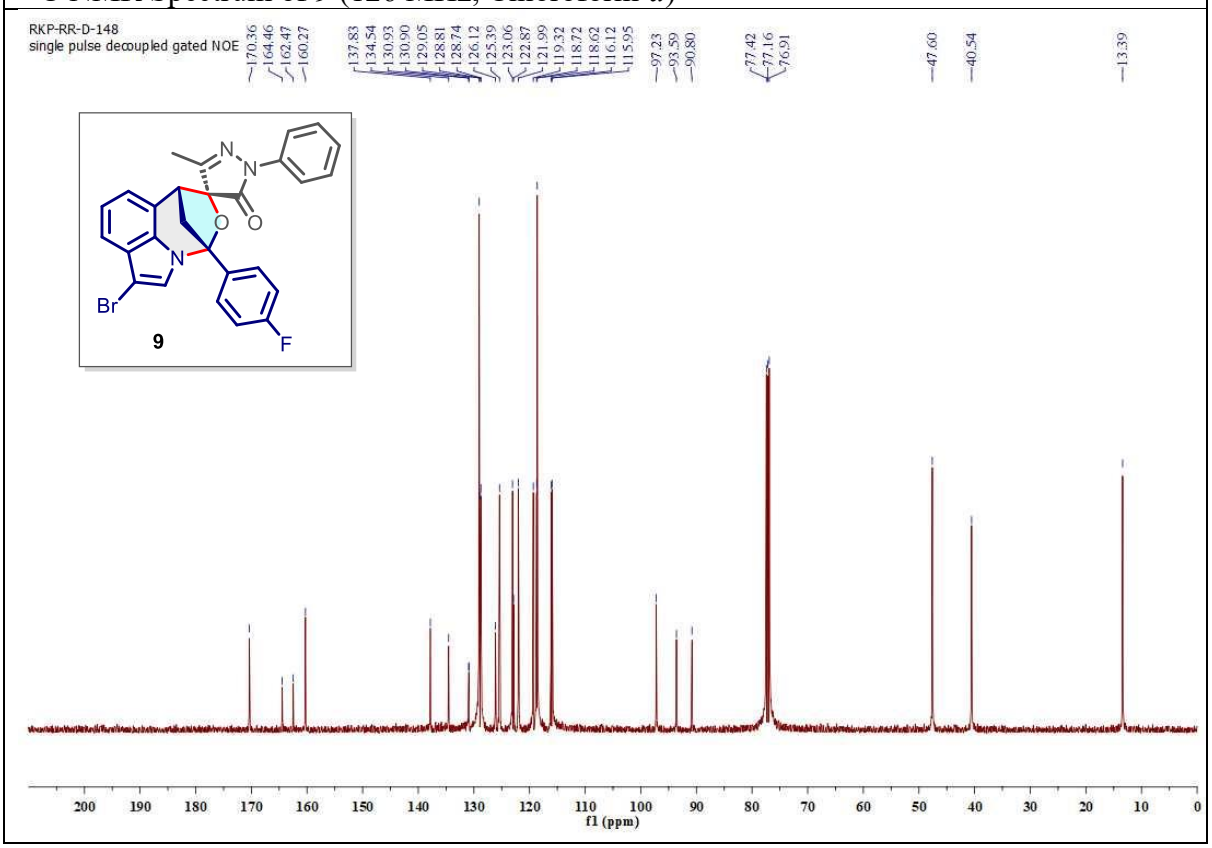
^{13}C NMR Spectrum of **8** (126 MHz, Chloroform-*d*)



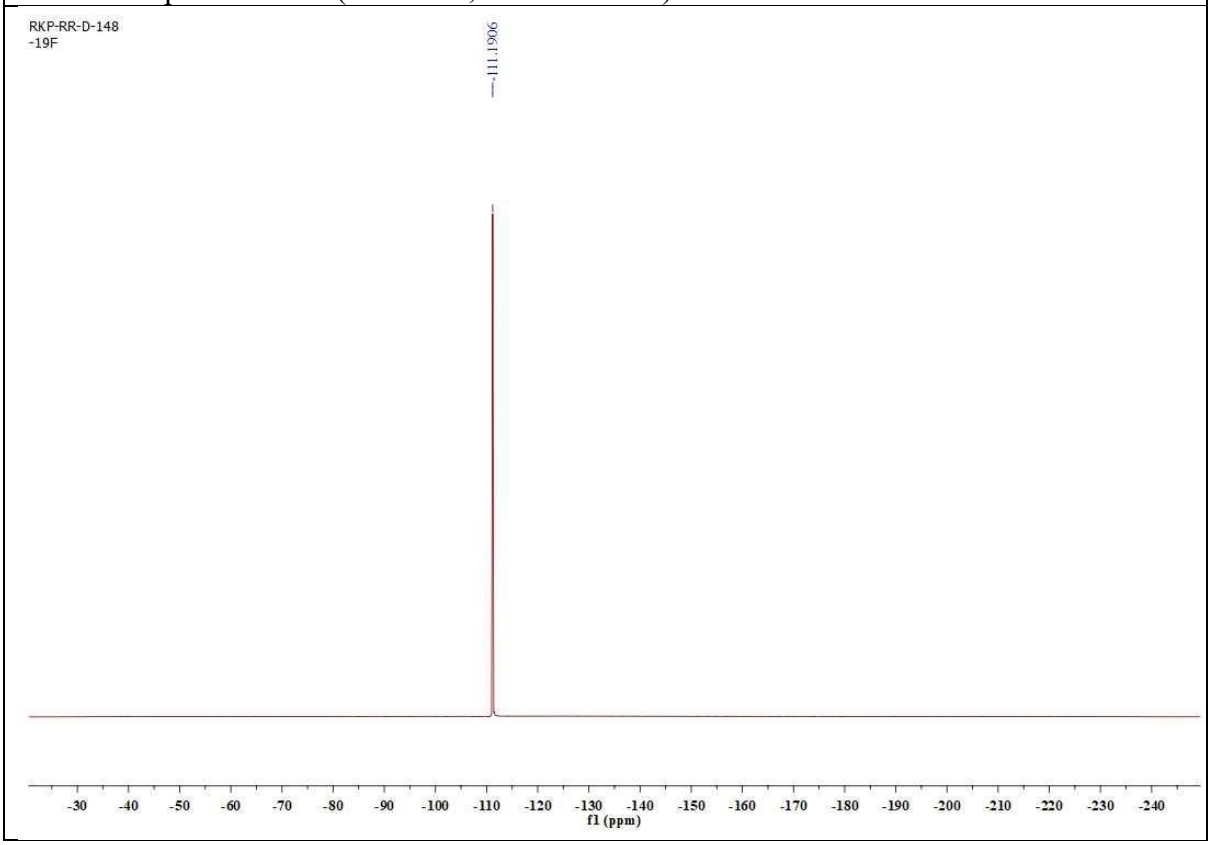
^{1}H NMR Spectrum of **9** (500 MHz, Chloroform-*d*)



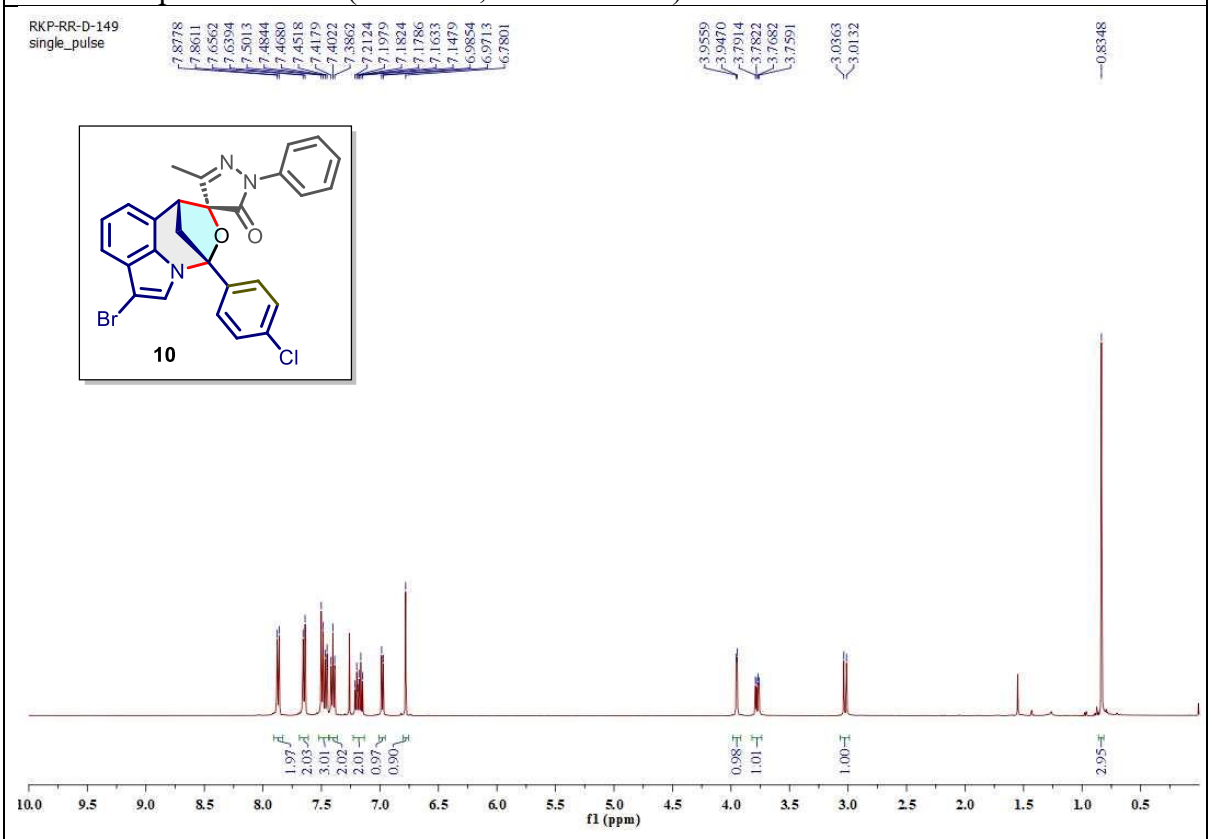
^{13}C NMR Spectrum of **9** (126 MHz, Chloroform-*d*)



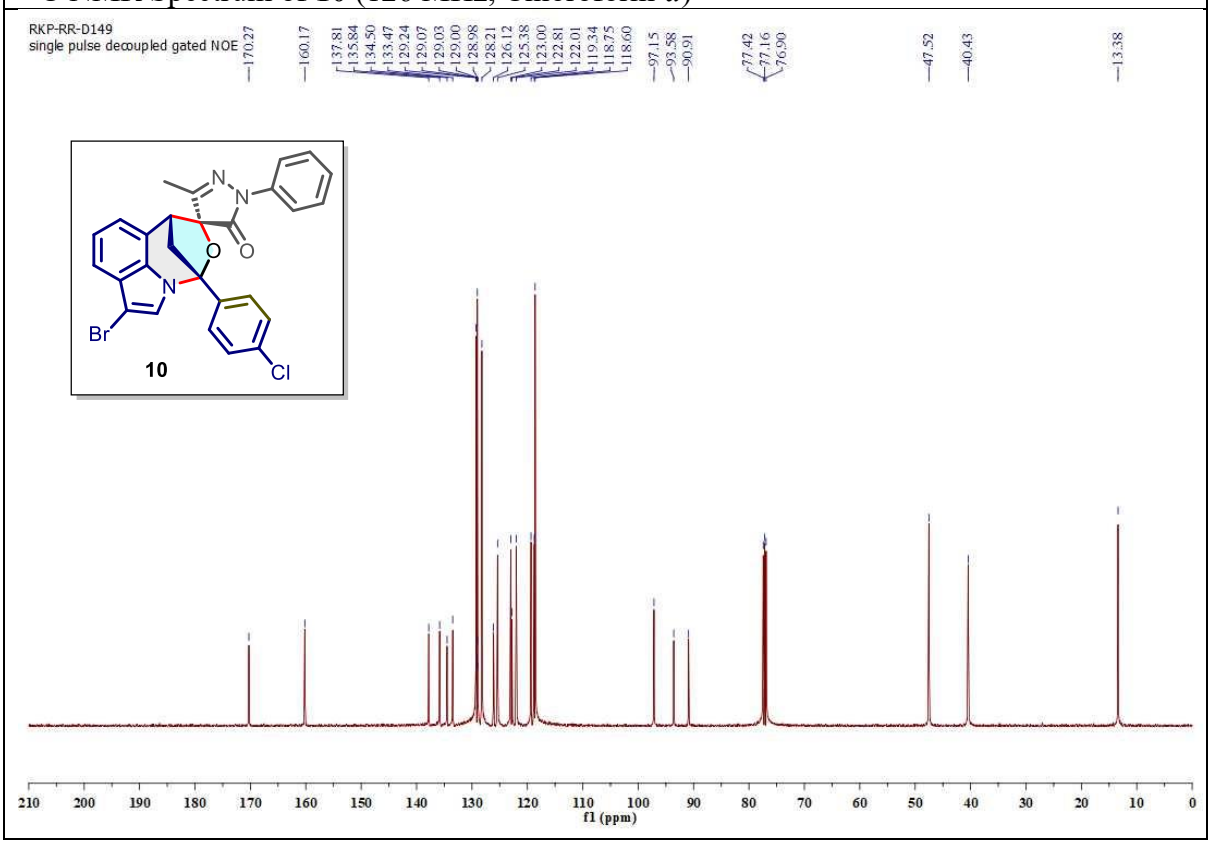
^{19}F NMR Spectrum of **9** (471 MHz, Chloroform-*d*)



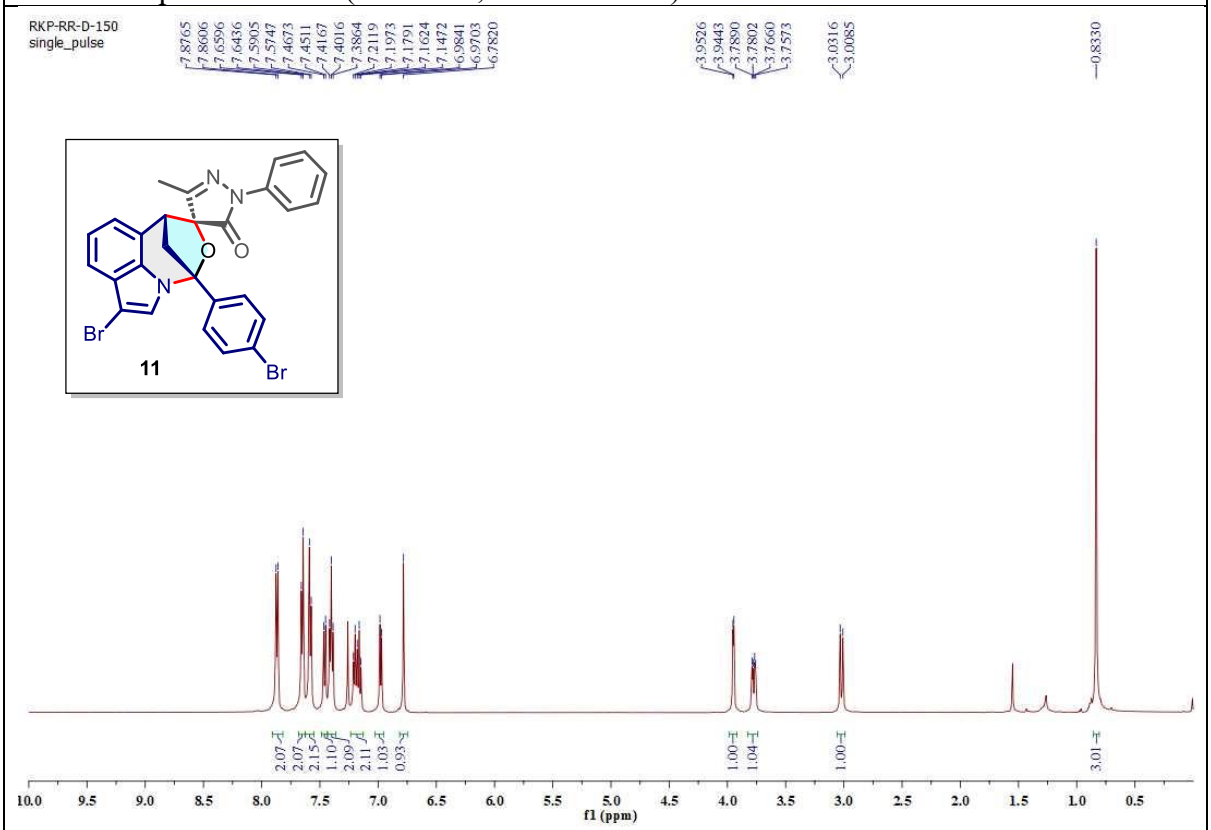
^{1}H NMR Spectrum of **10** (500 MHz, Chloroform-*d*)



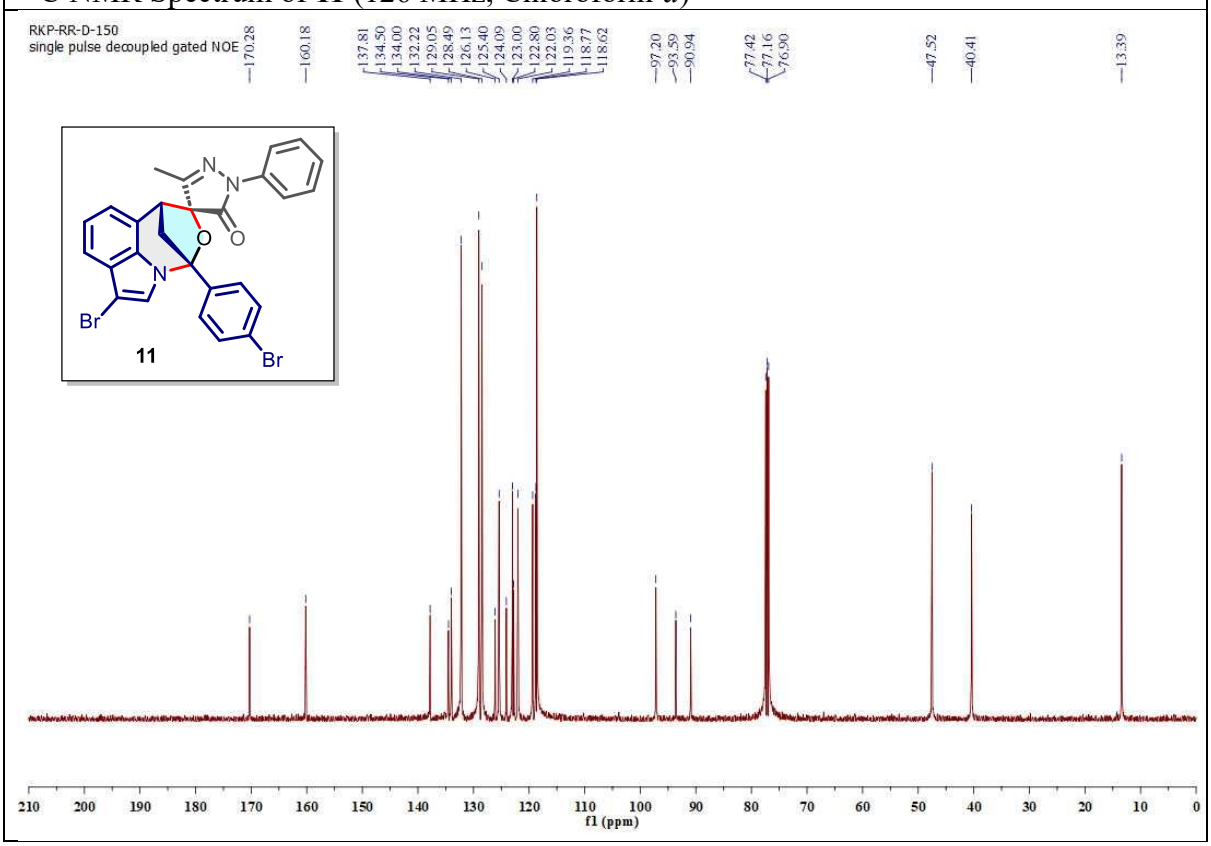
^{13}C NMR Spectrum of **10** (126 MHz, Chloroform-*d*)



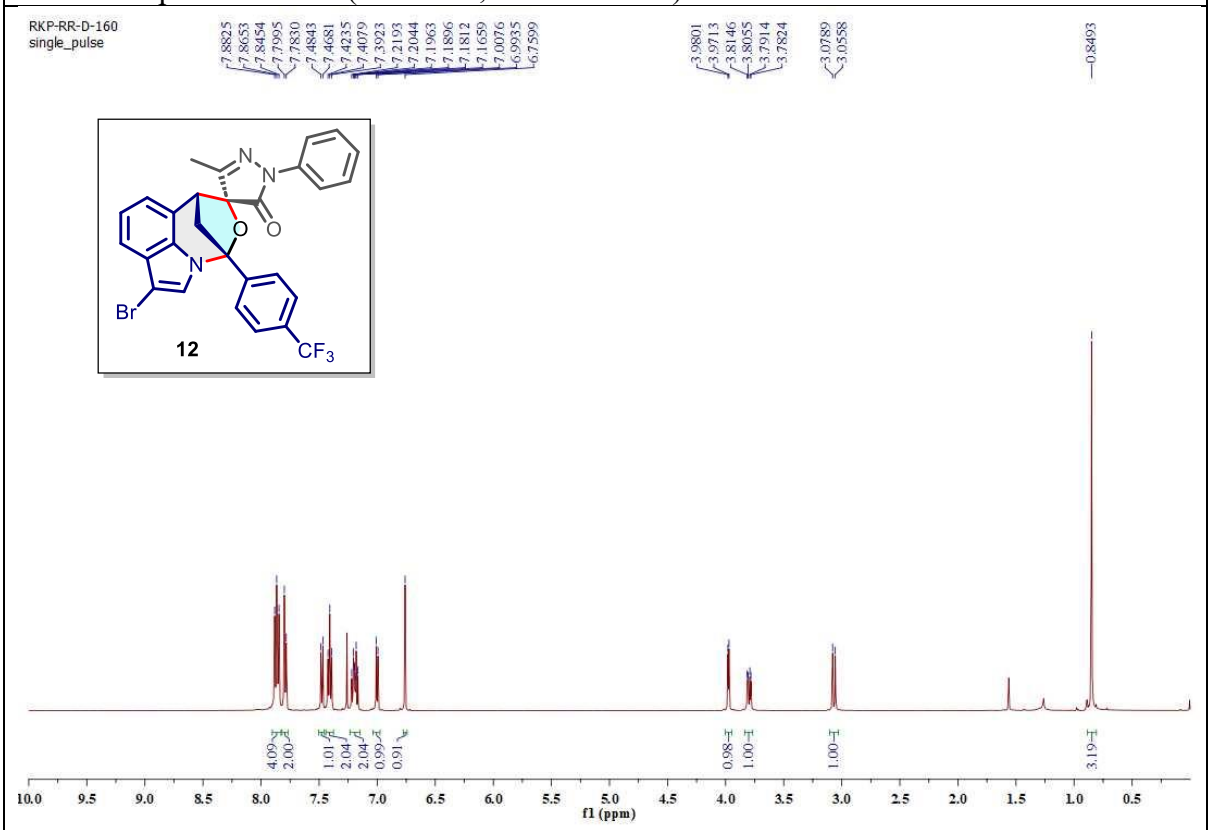
^{1}H NMR Spectrum of **11** (500 MHz, Chloroform-*d*)



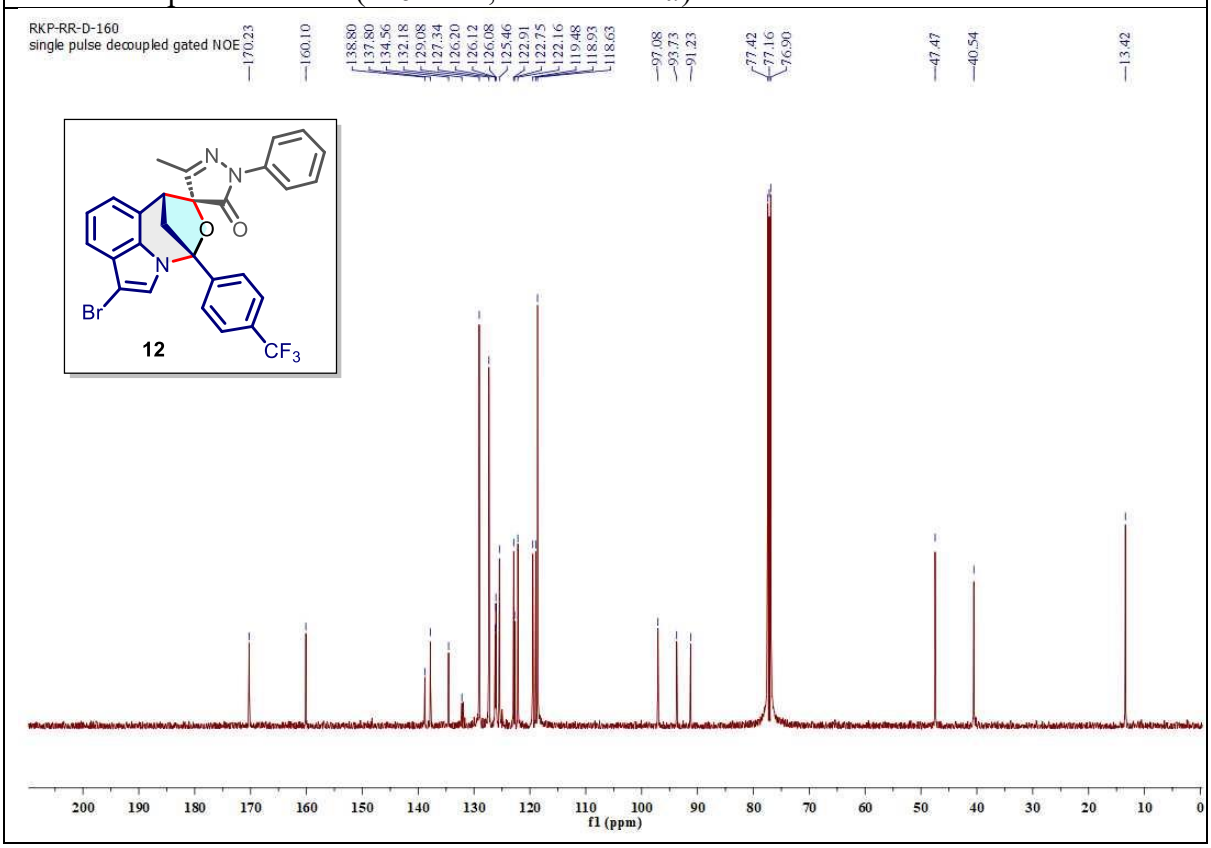
^{13}C NMR Spectrum of **11** (126 MHz, Chloroform-*d*)



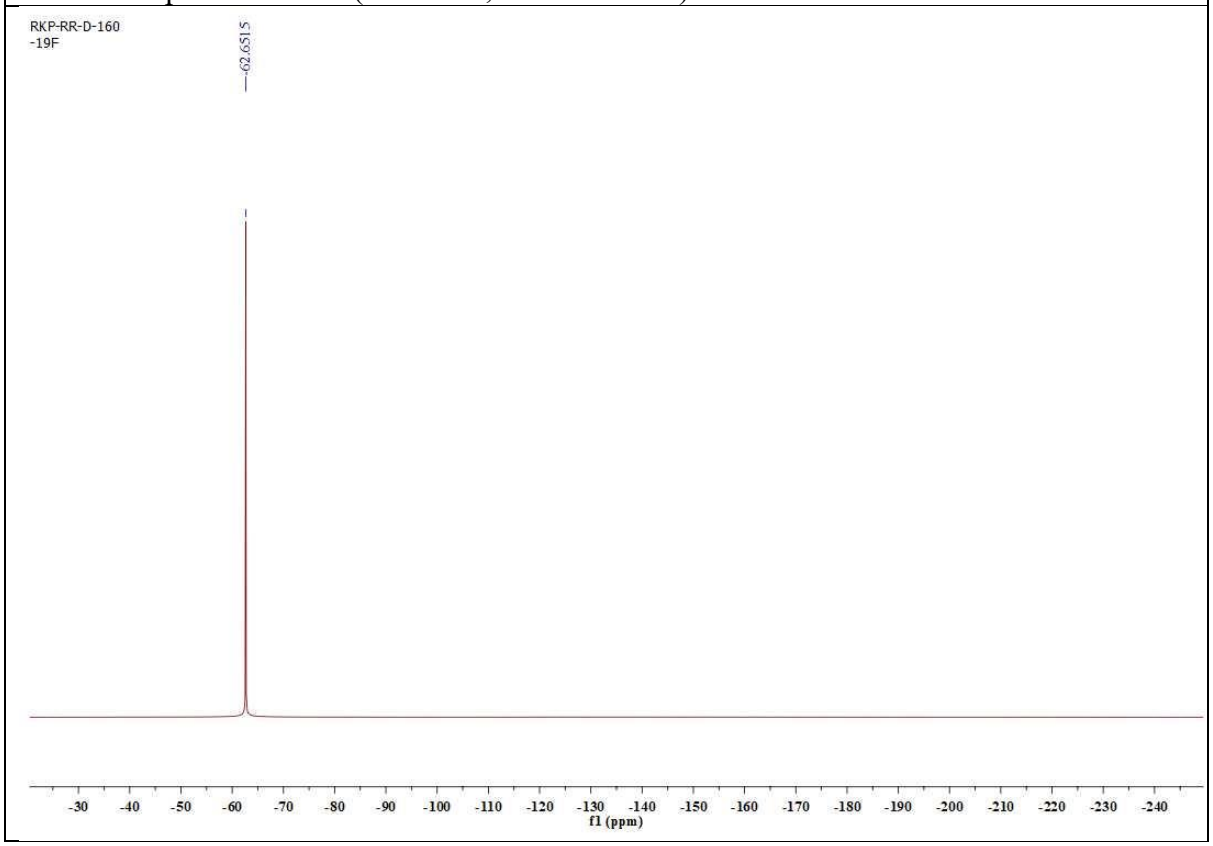
^{1}H NMR Spectrum of **12** (500 MHz, Chloroform-*d*)



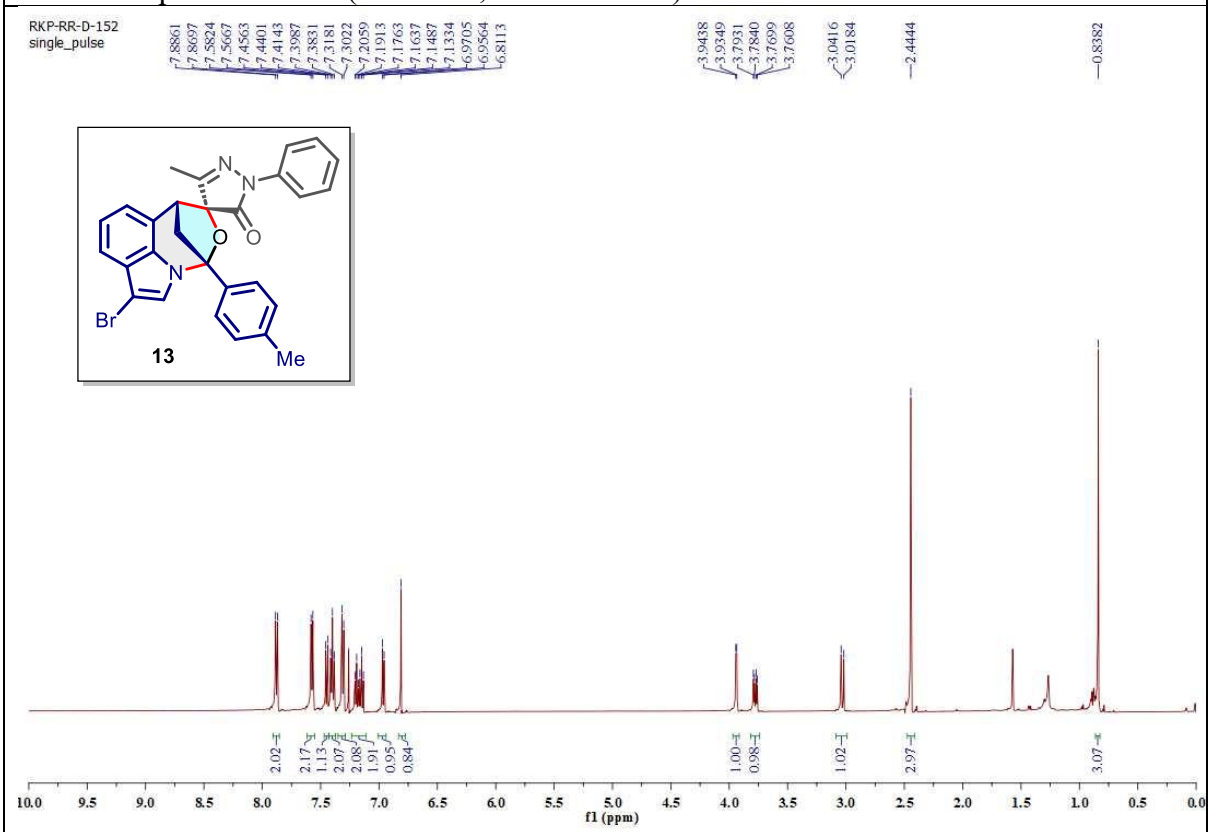
^{13}C NMR Spectrum of **12** (126 MHz, Chloroform-*d*)



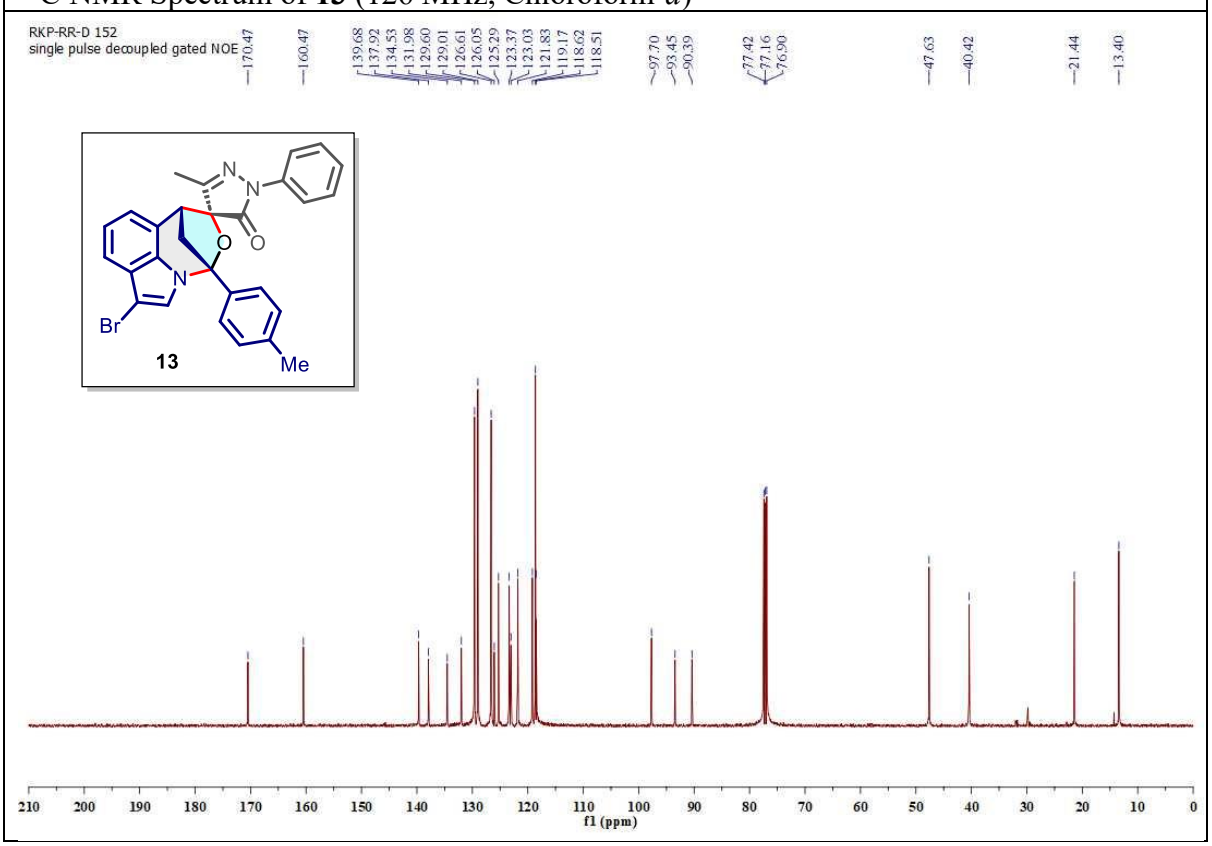
^{19}F NMR Spectrum of **12** (471 MHz, Chloroform-*d*)



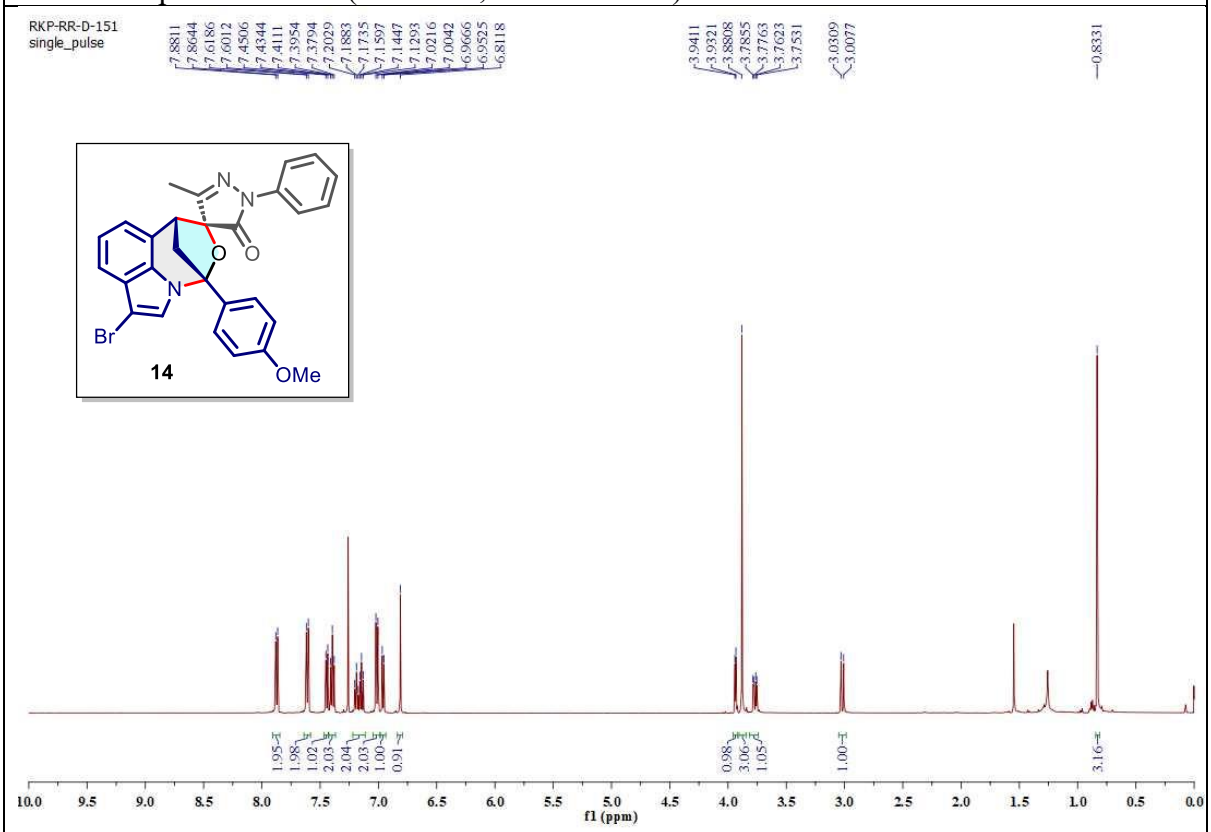
^{1}H NMR Spectrum of **13** (500 MHz, Chloroform-*d*)



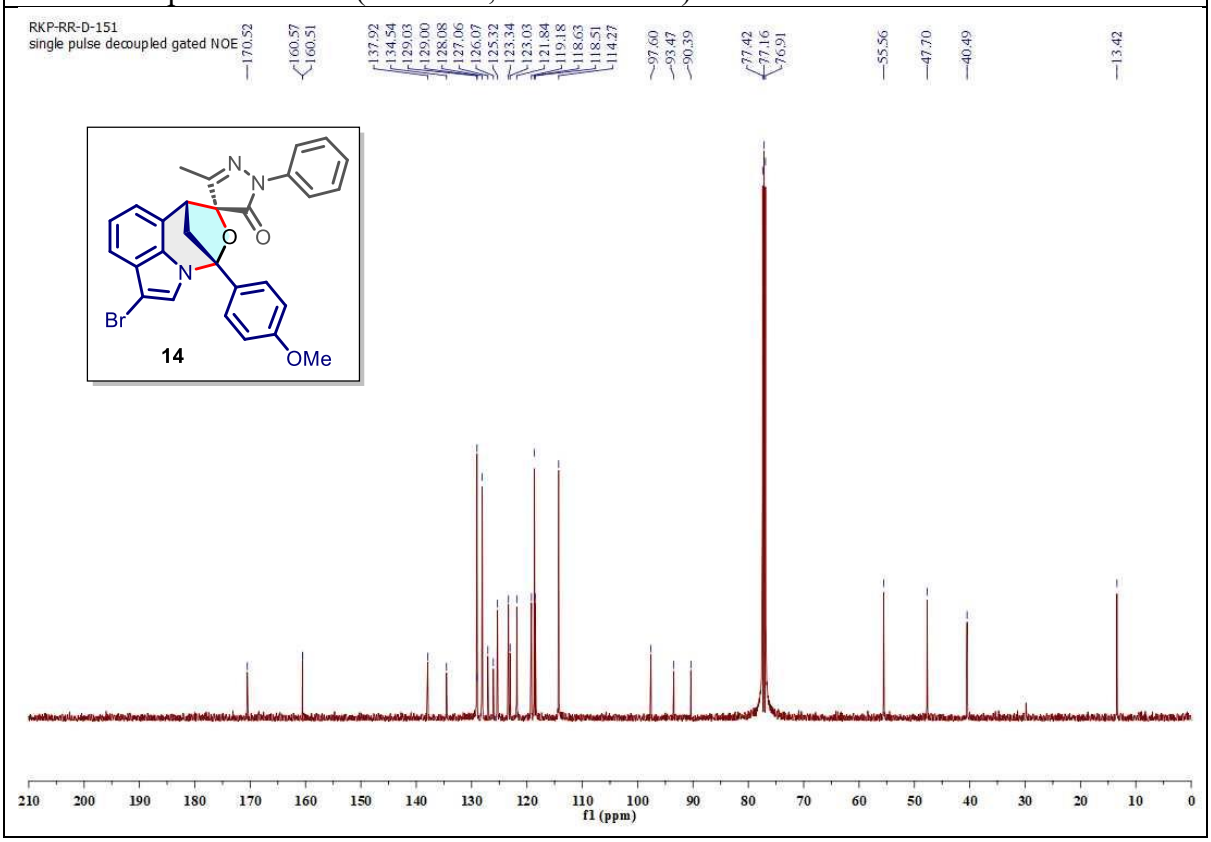
^{13}C NMR Spectrum of **13** (126 MHz, Chloroform-*d*)



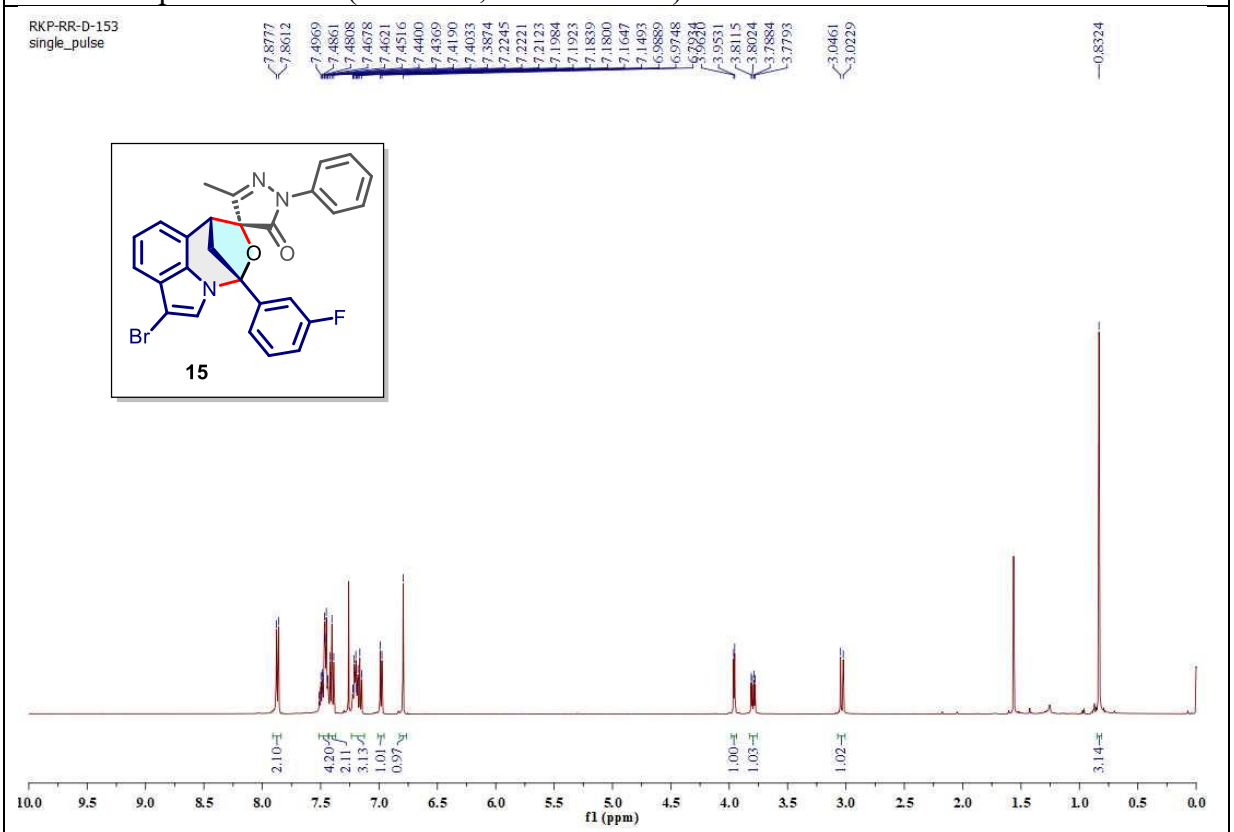
^{1}H NMR Spectrum of **14** (500 MHz, Chloroform-*d*)



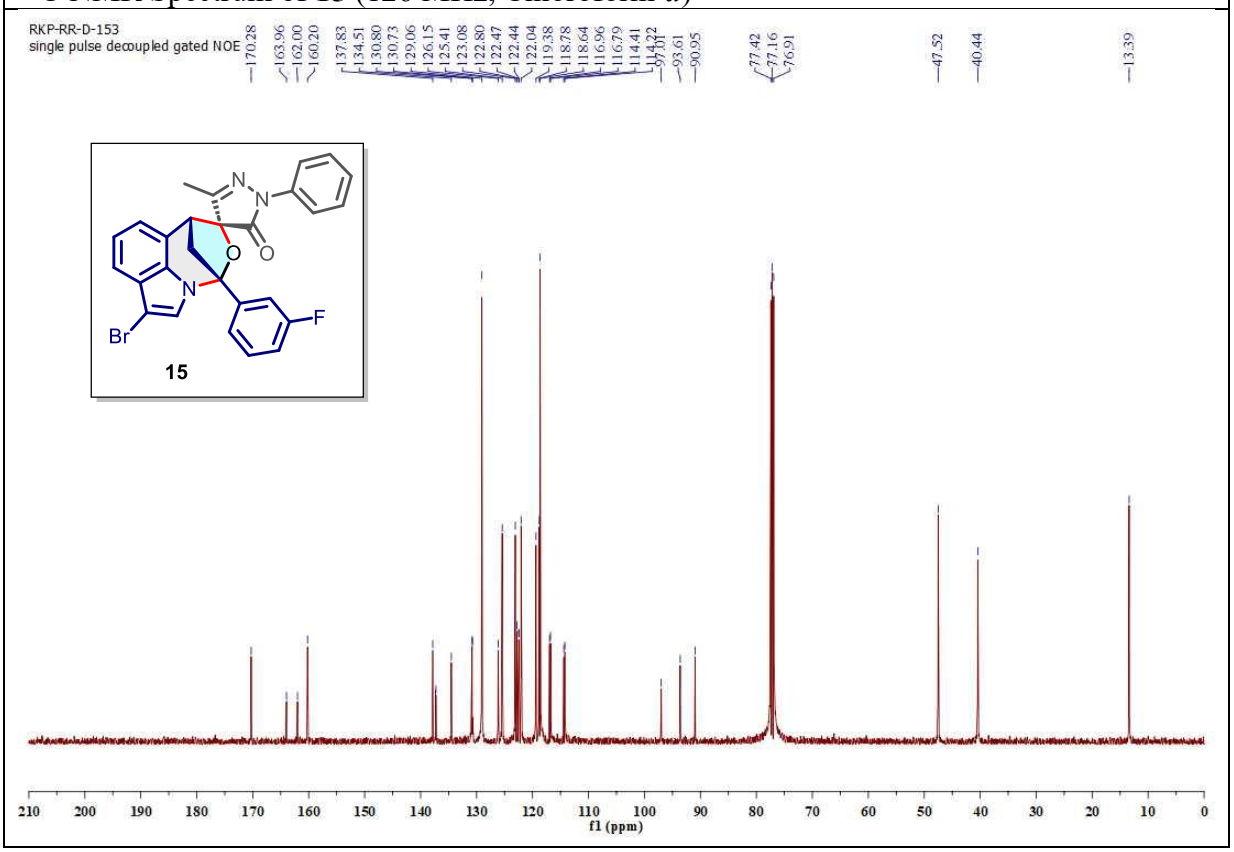
^{13}C NMR Spectrum of **14** (126 MHz, Chloroform-*d*)



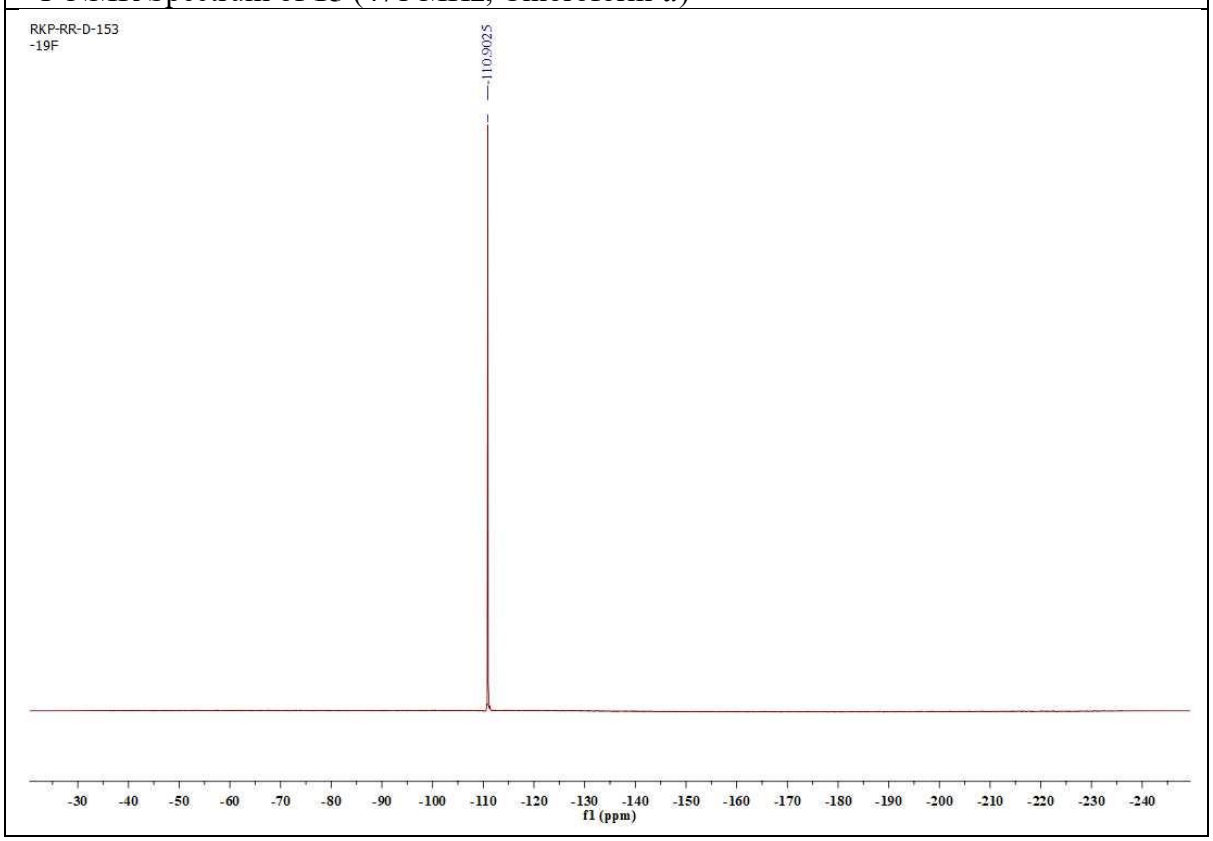
^{1}H NMR Spectrum of **15** (500 MHz, Chloroform-*d*)



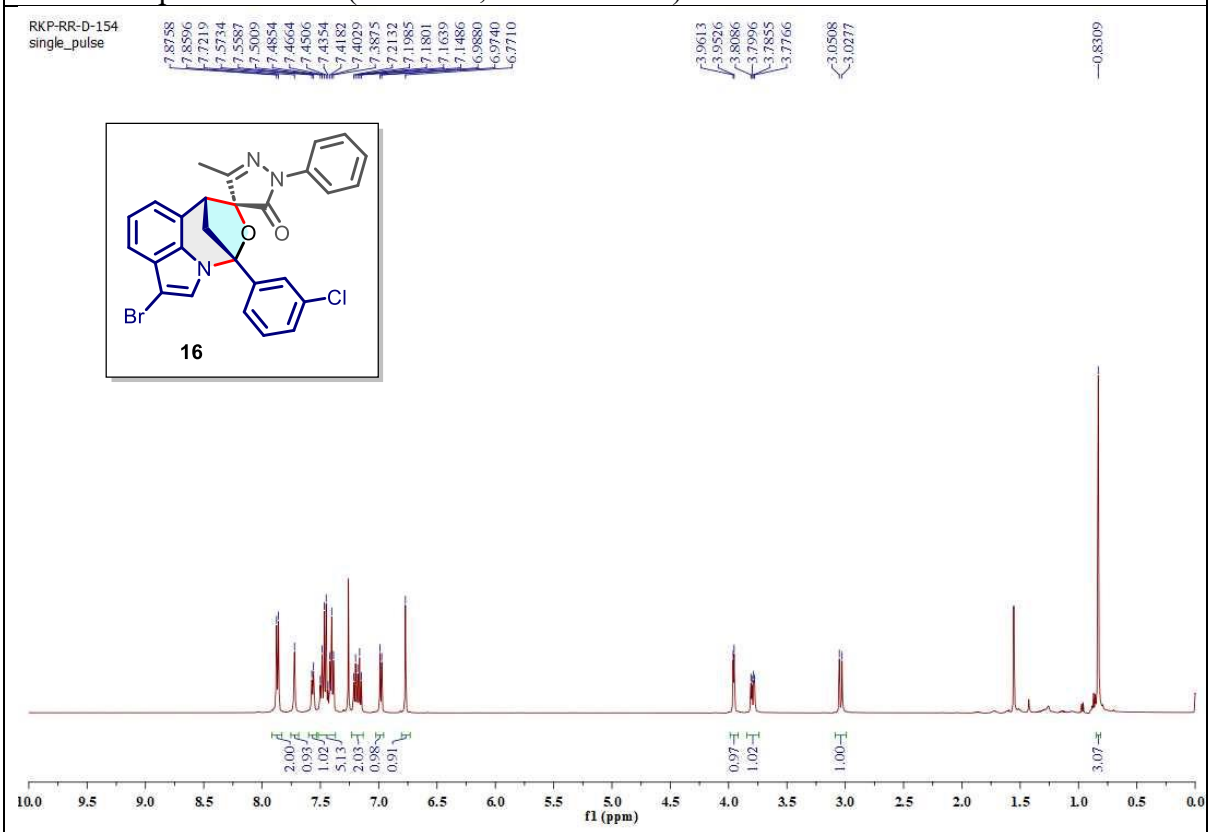
^{13}C NMR Spectrum of **15** (126 MHz, Chloroform-*d*)



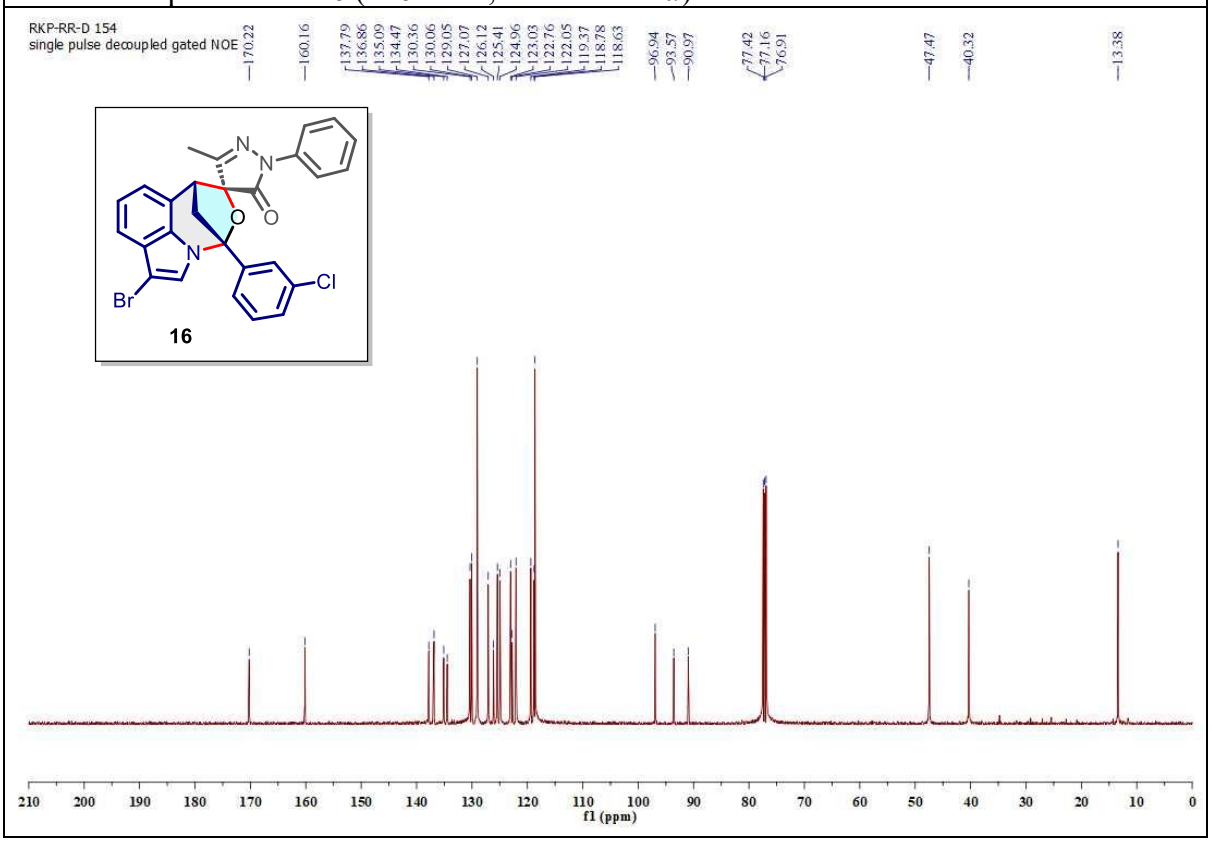
^{19}F NMR Spectrum of **15** (471 MHz, Chloroform-*d*)



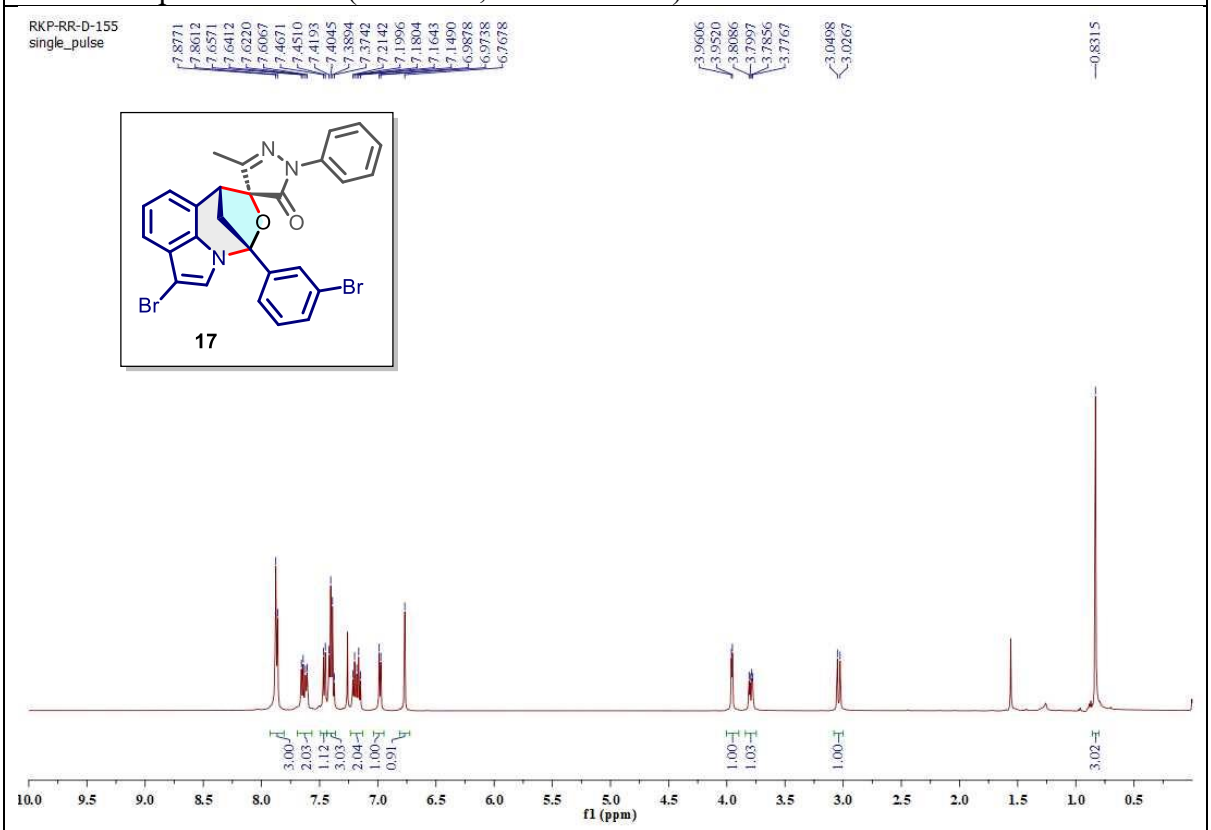
^{1}H NMR Spectrum of **16** (500 MHz, Chloroform-*d*)



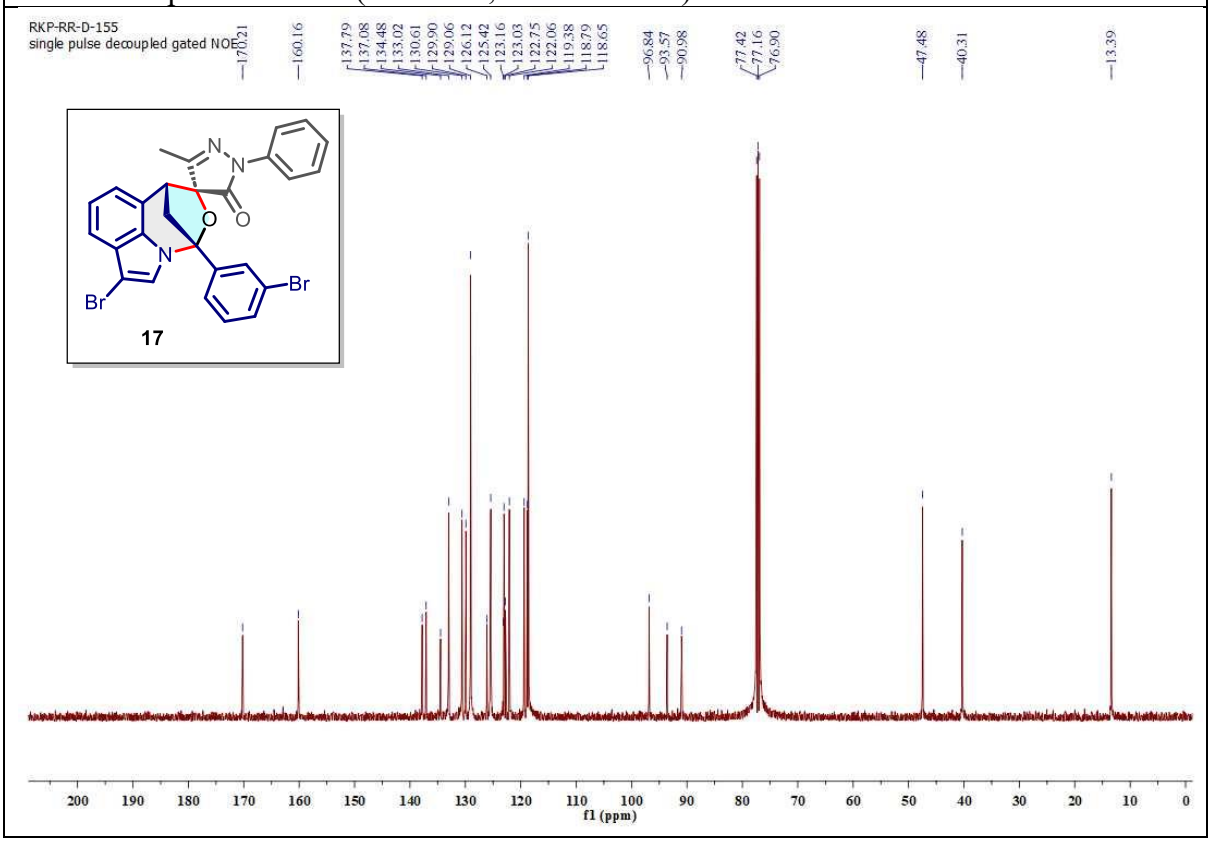
^{13}C NMR Spectrum of **16** (126 MHz, Chloroform-*d*)



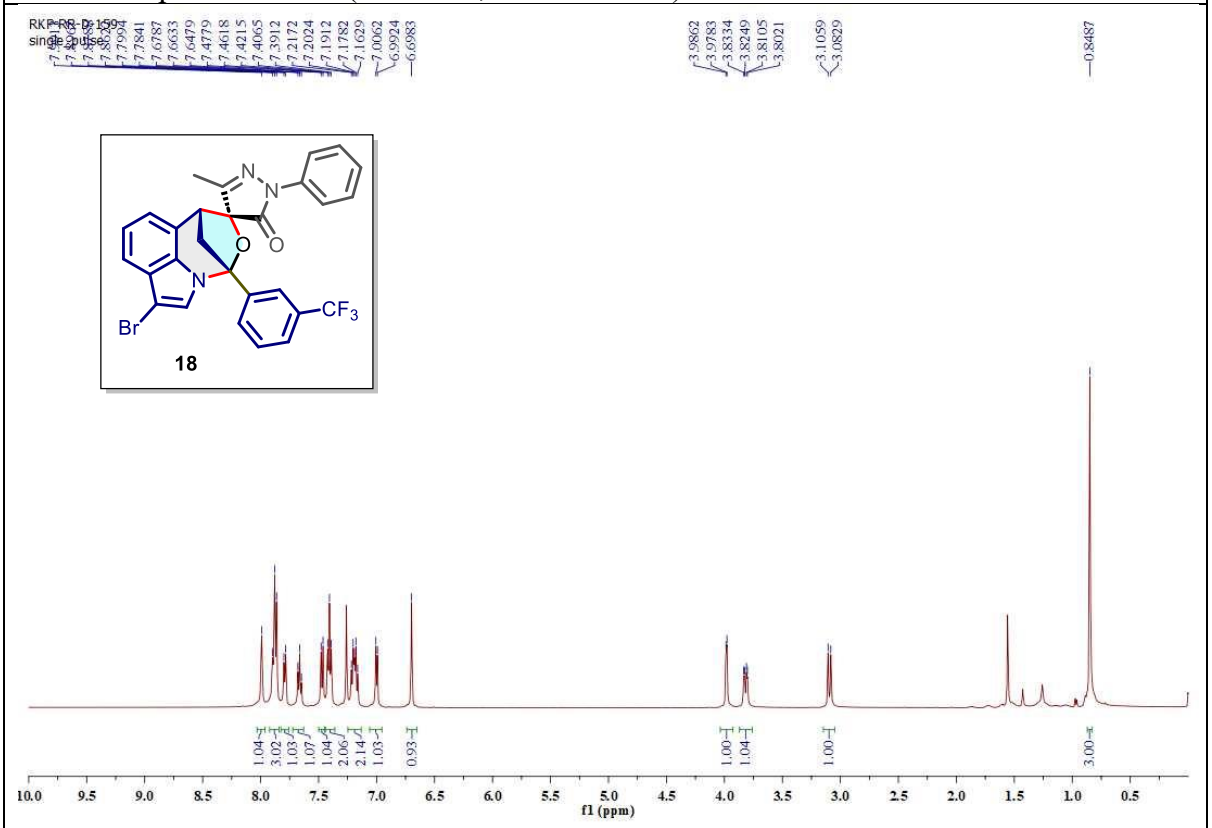
^{1}H NMR Spectrum of **17** (500 MHz, Chloroform-*d*)



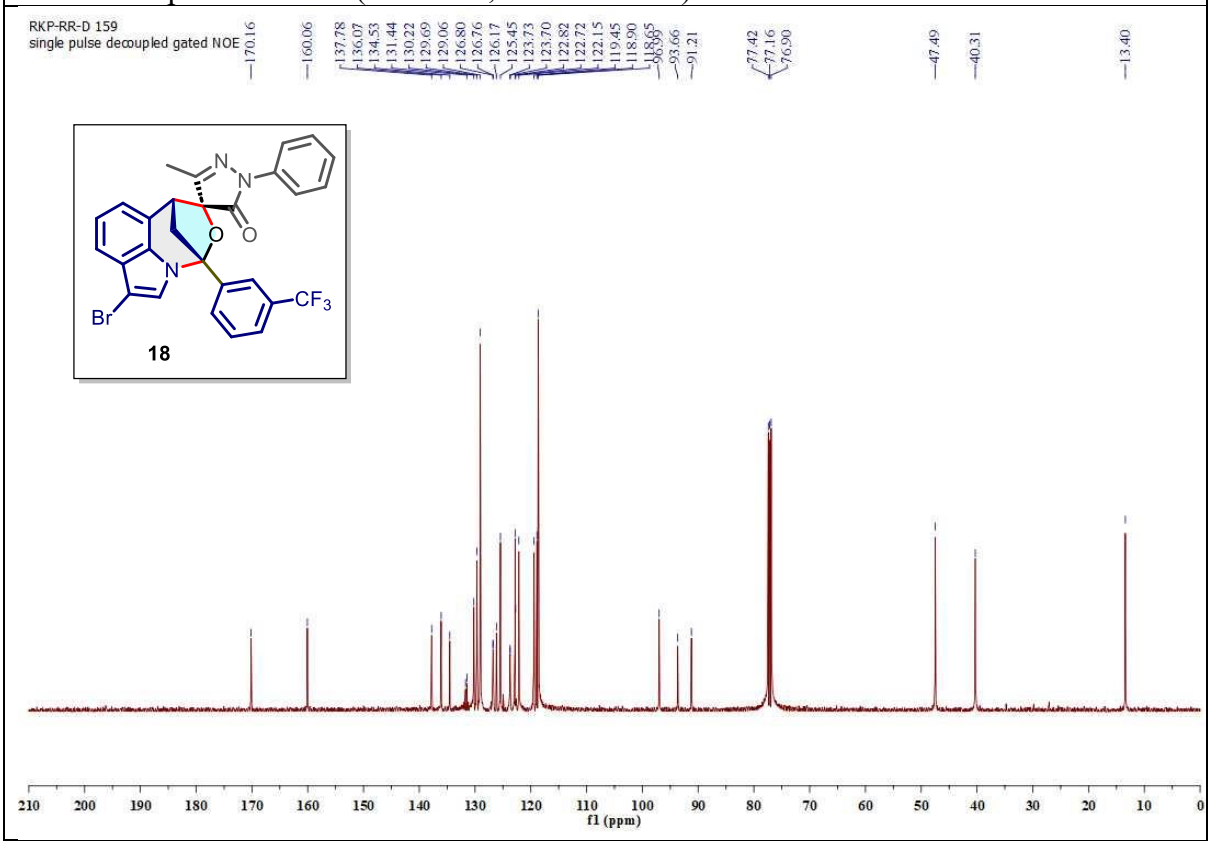
^{13}C NMR Spectrum of **17** (126 MHz, Chloroform-*d*)



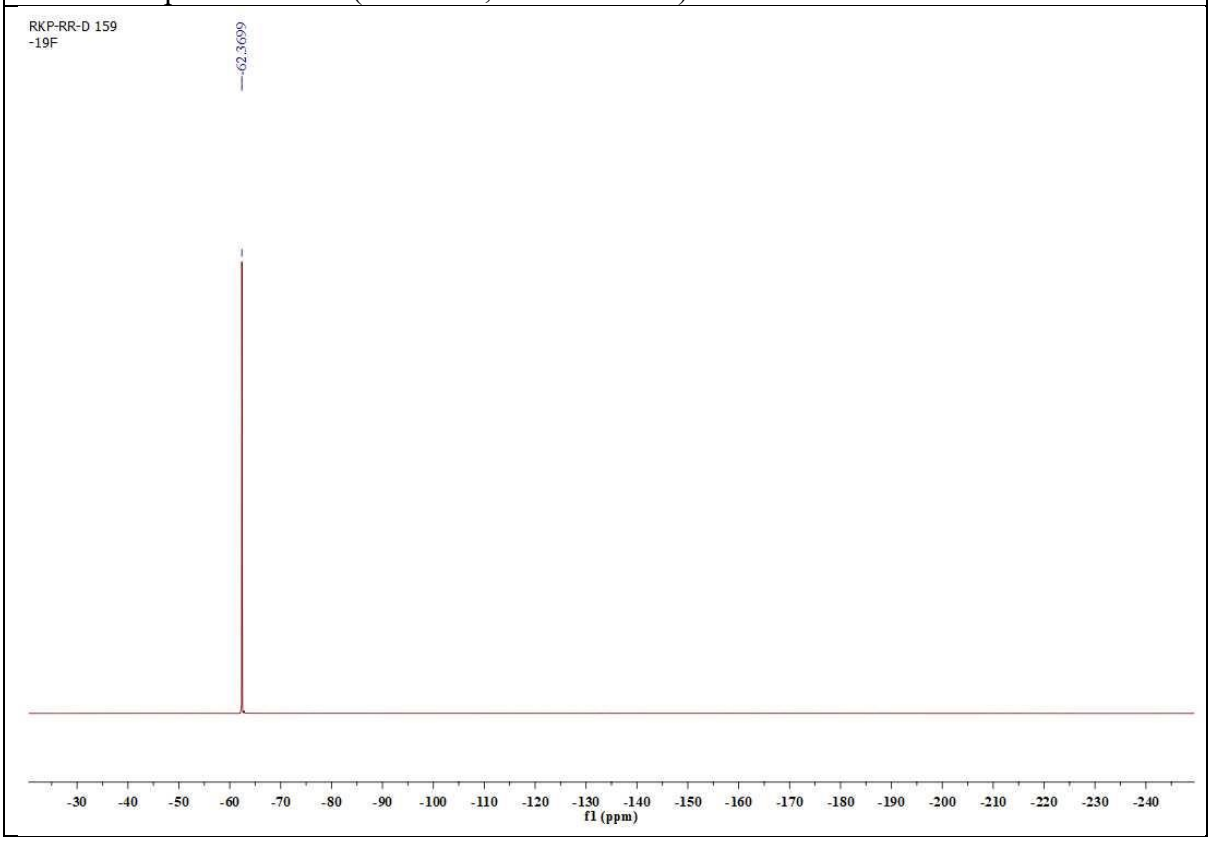
^{1}H NMR Spectrum of **18** (500 MHz, Chloroform-*d*)



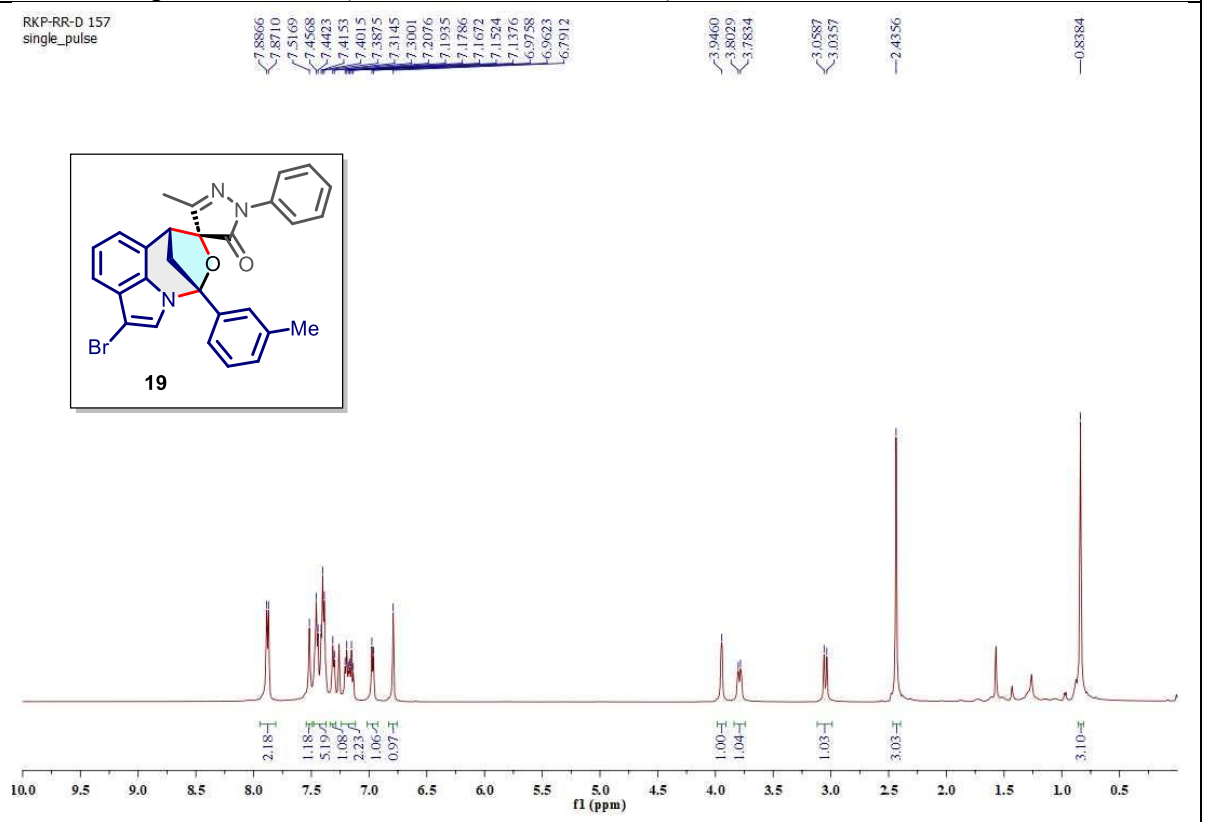
^{13}C NMR Spectrum of **18** (126 MHz, Chloroform-*d*)



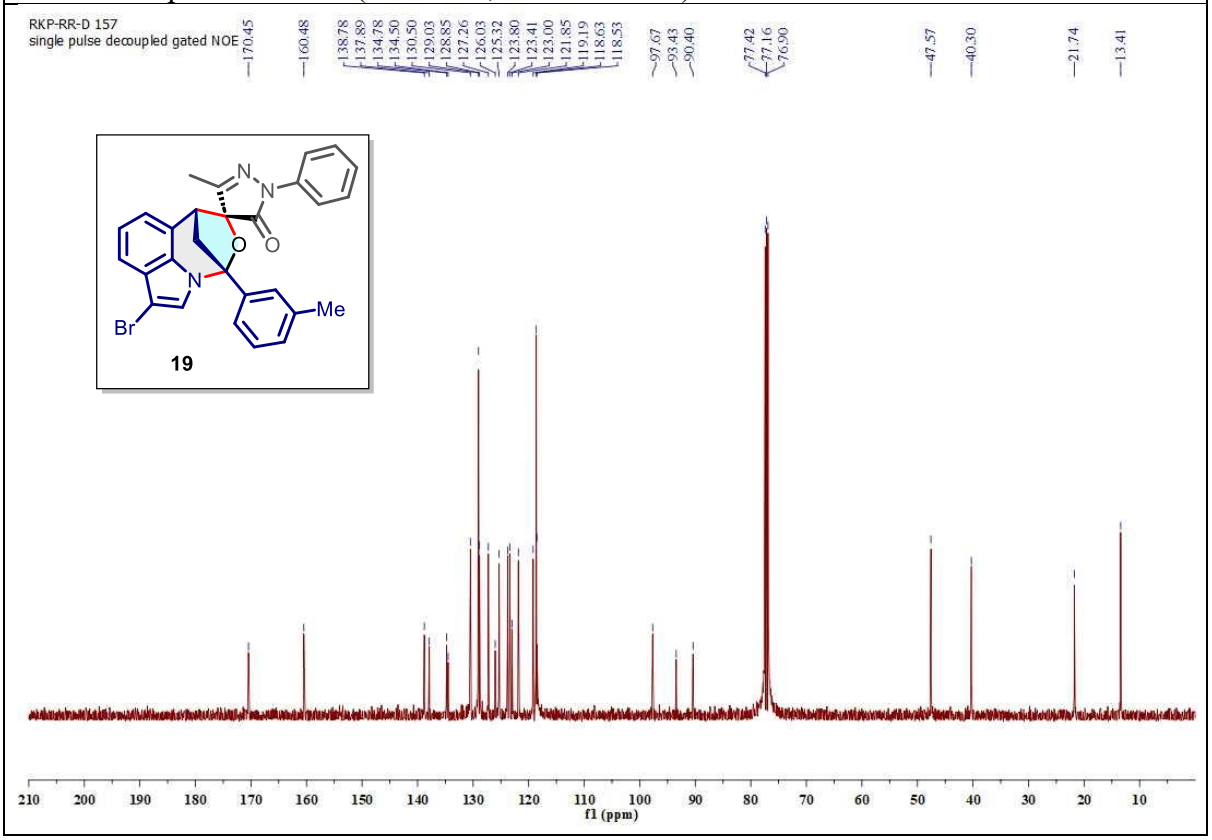
^{19}F NMR Spectrum of **18** (471 MHz, Chloroform-*d*)



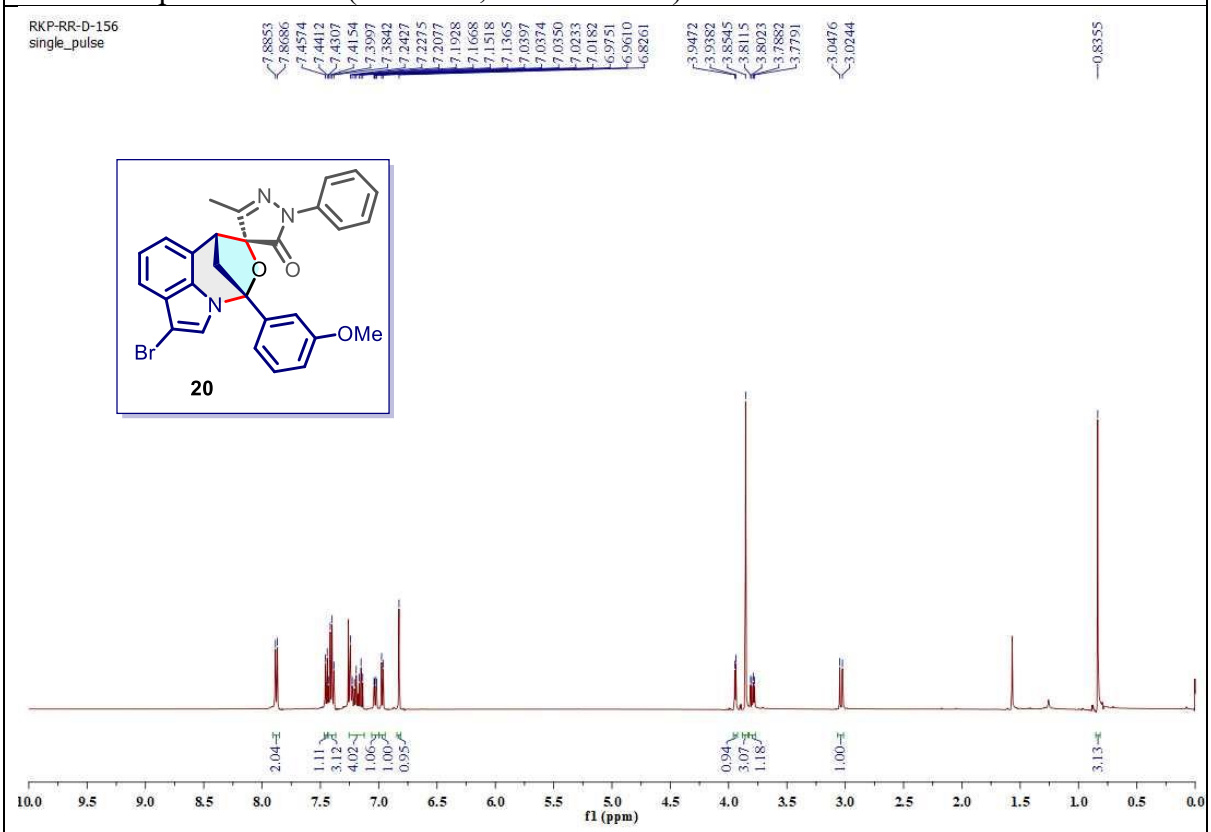
^{1}H NMR Spectrum of **19** (500 MHz, Chloroform-*d*)



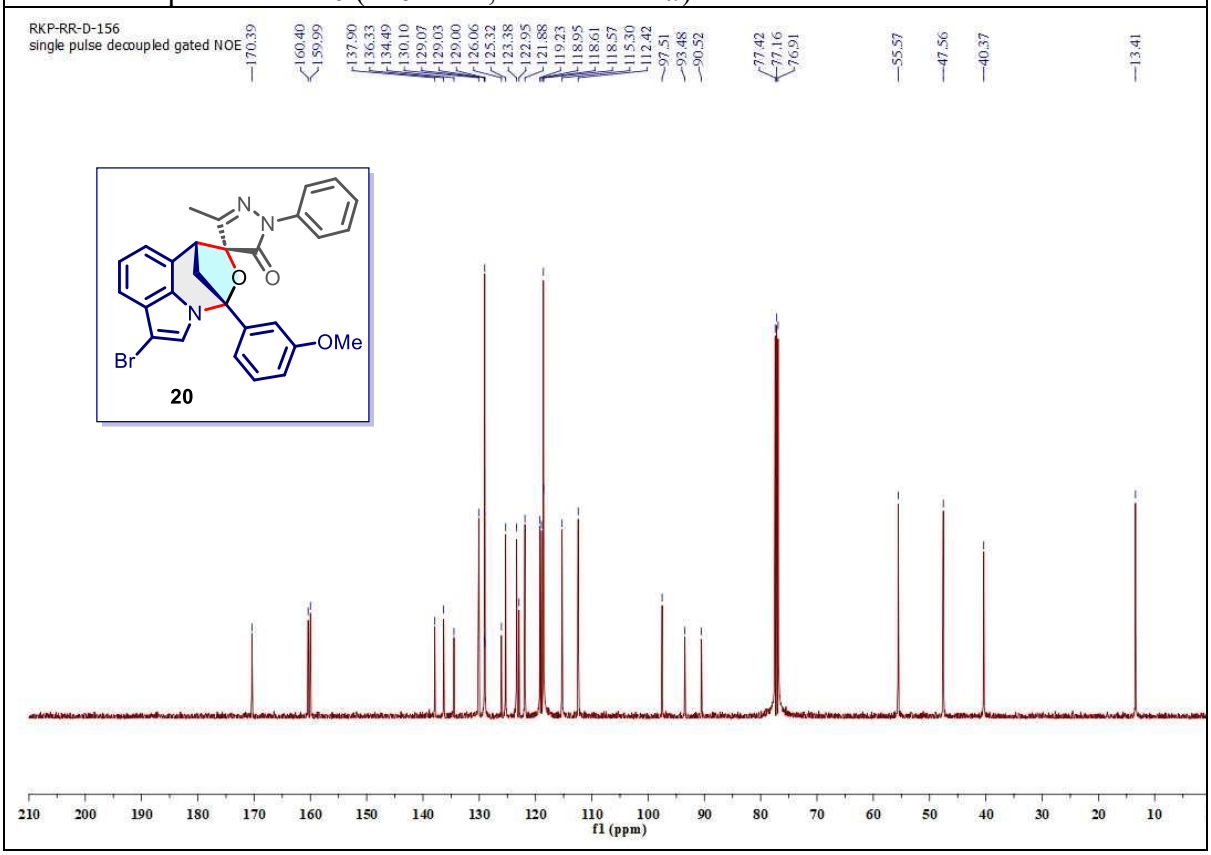
^{13}C NMR Spectrum of **19** (126 MHz, Chloroform-*d*)



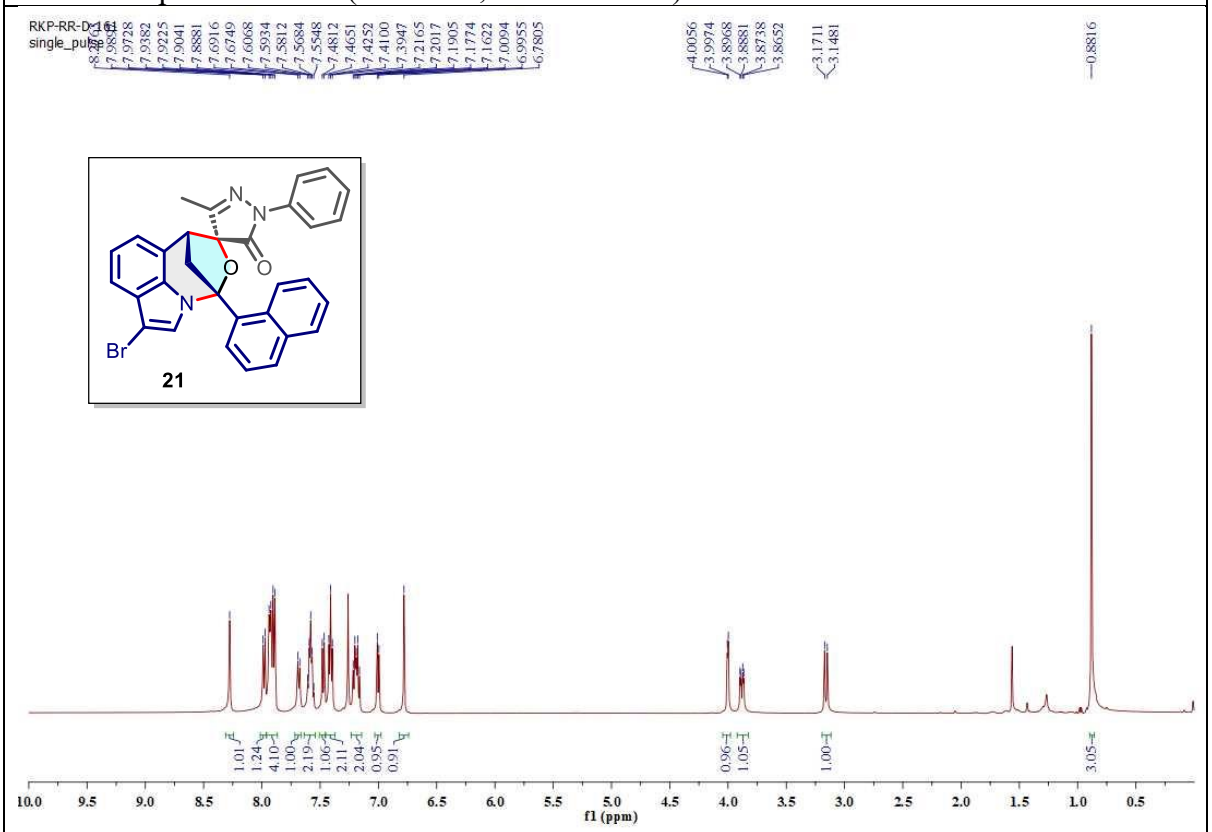
^{1}H NMR Spectrum of **20** (500 MHz, Chloroform-*d*)



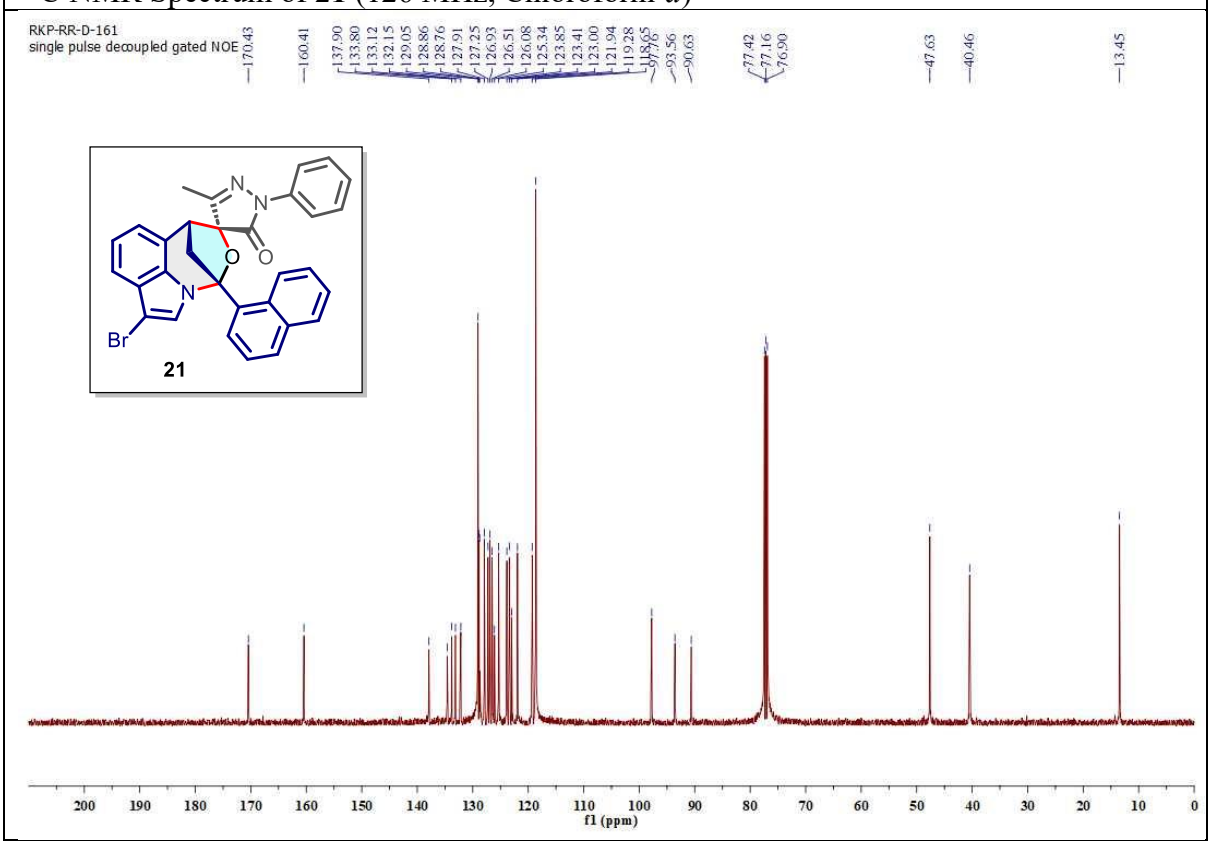
^{13}C NMR Spectrum of **20** (126 MHz, Chloroform-*d*)



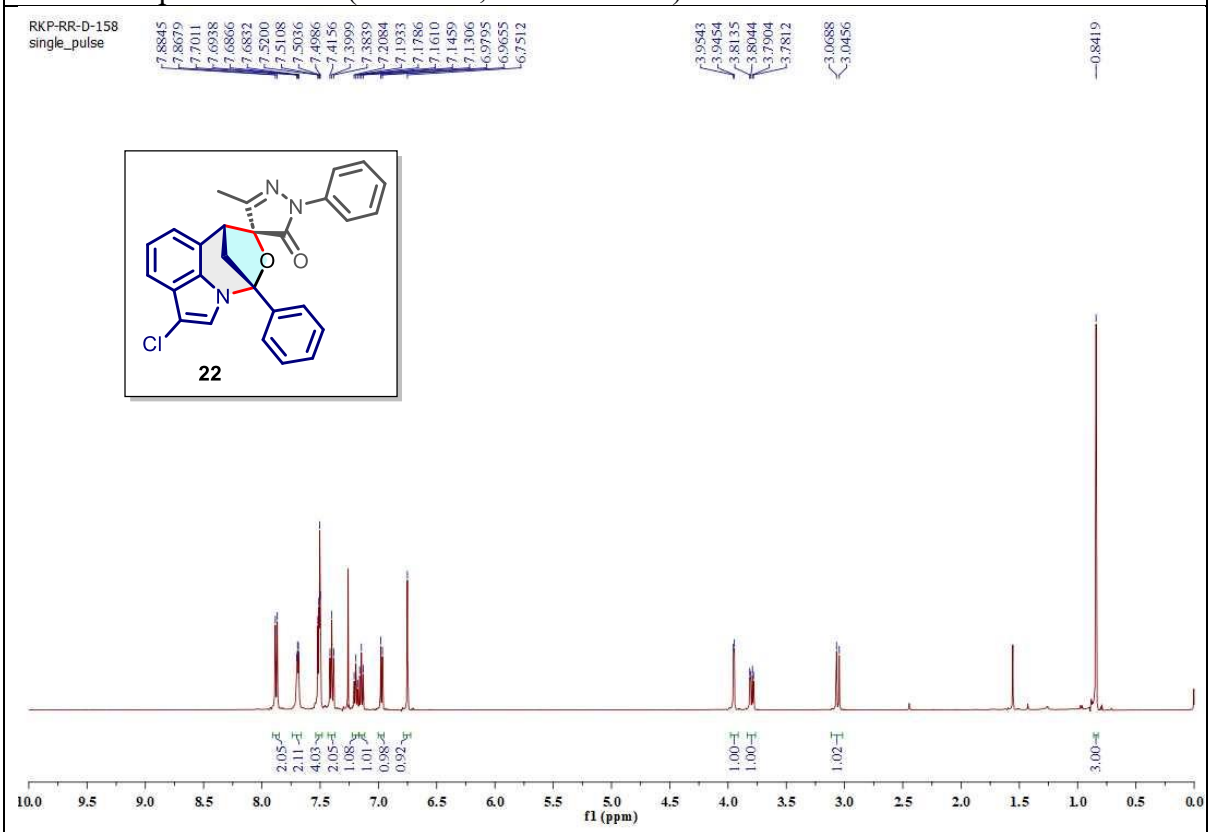
^{1}H NMR Spectrum of **21** (500 MHz, Chloroform-*d*)



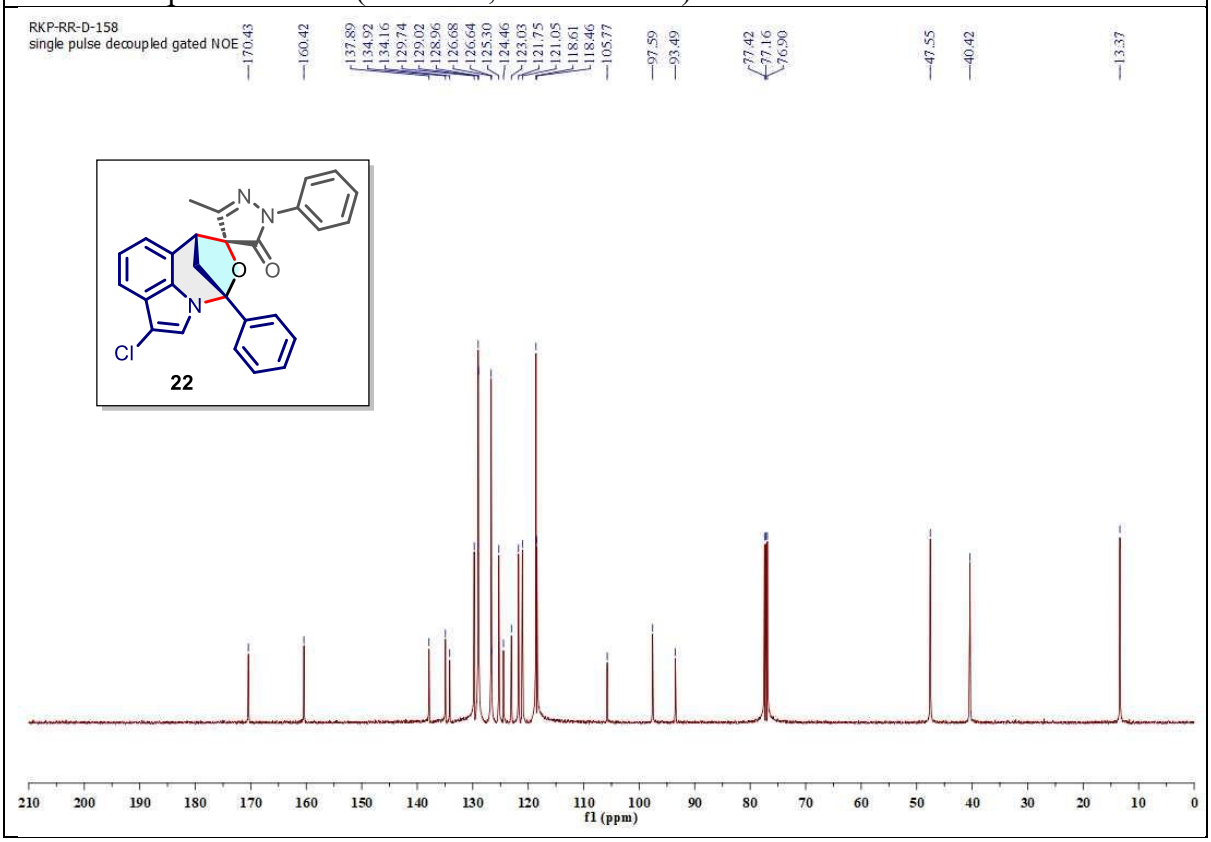
^{13}C NMR Spectrum of **21** (126 MHz, Chloroform-*d*)



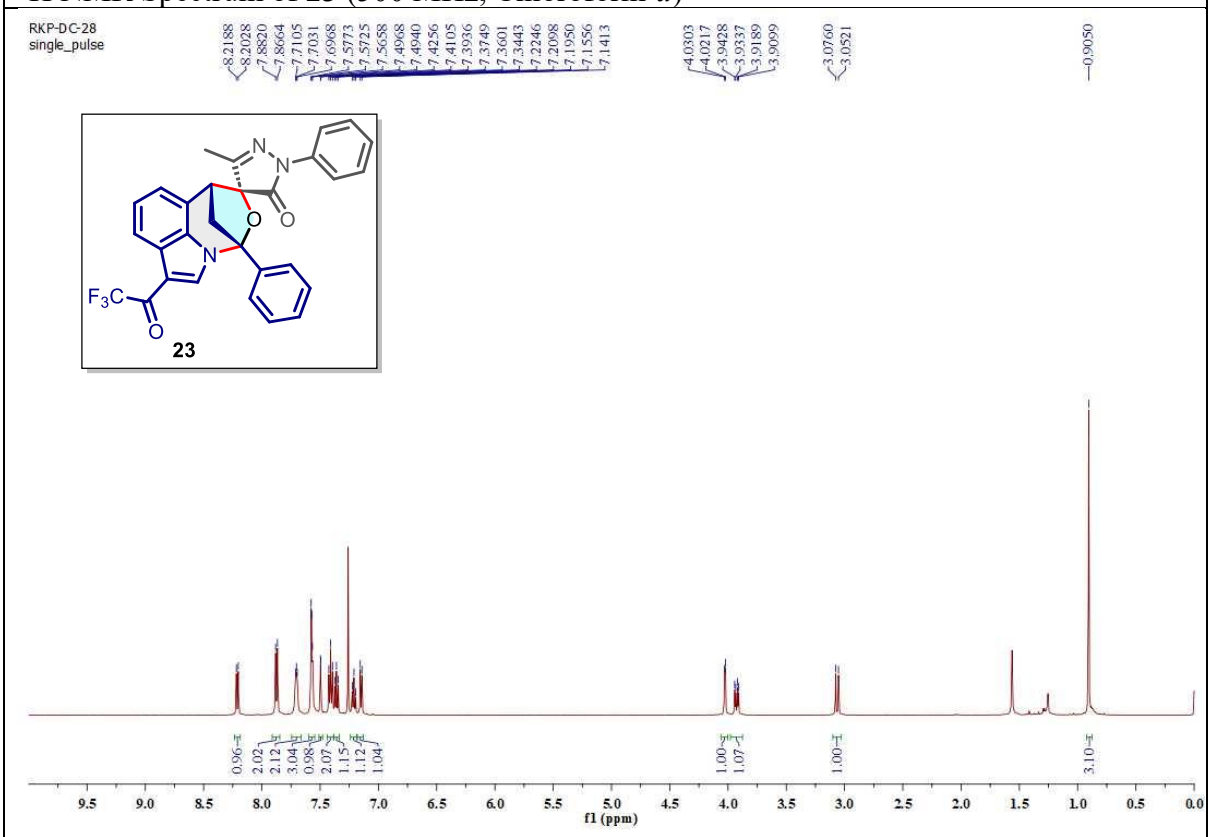
^{1}H NMR Spectrum of **22** (500 MHz, Chloroform-*d*)



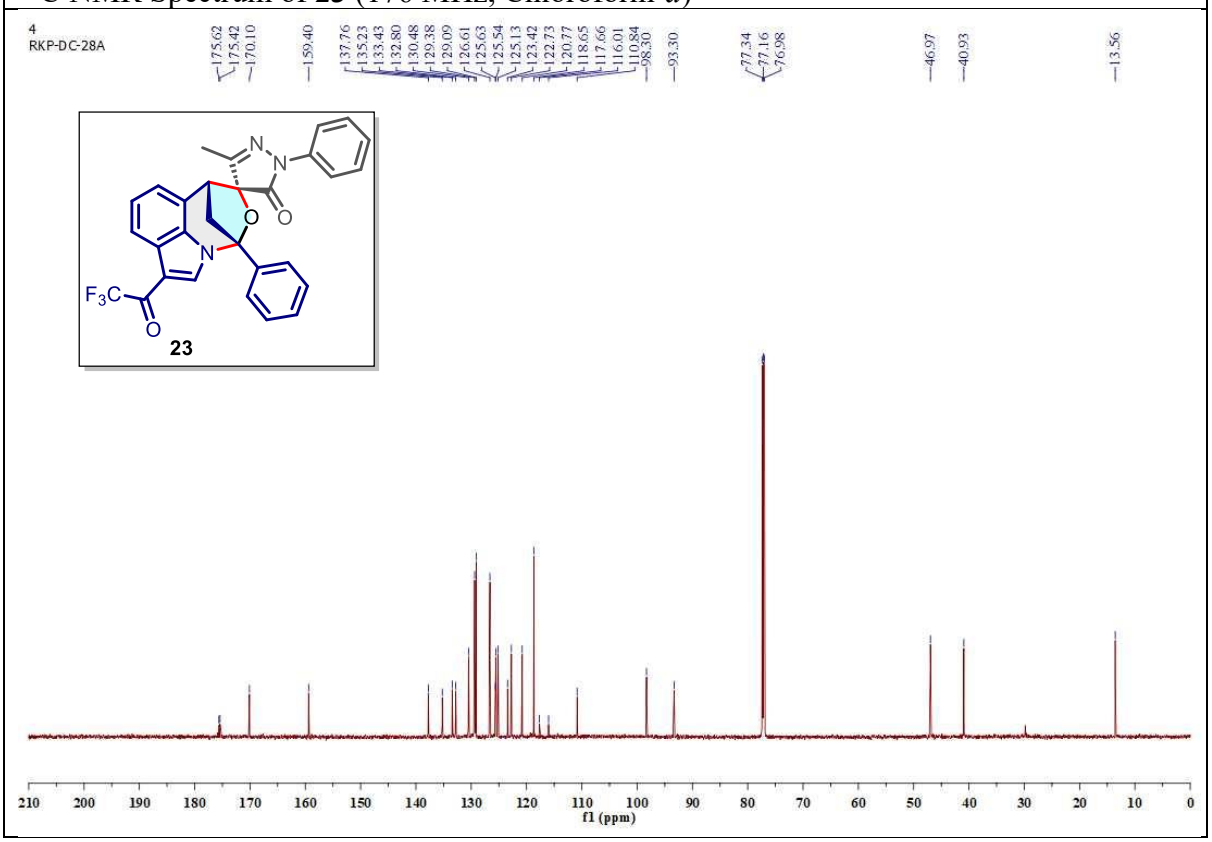
^{13}C NMR Spectrum of **22** (126 MHz, Chloroform-*d*)



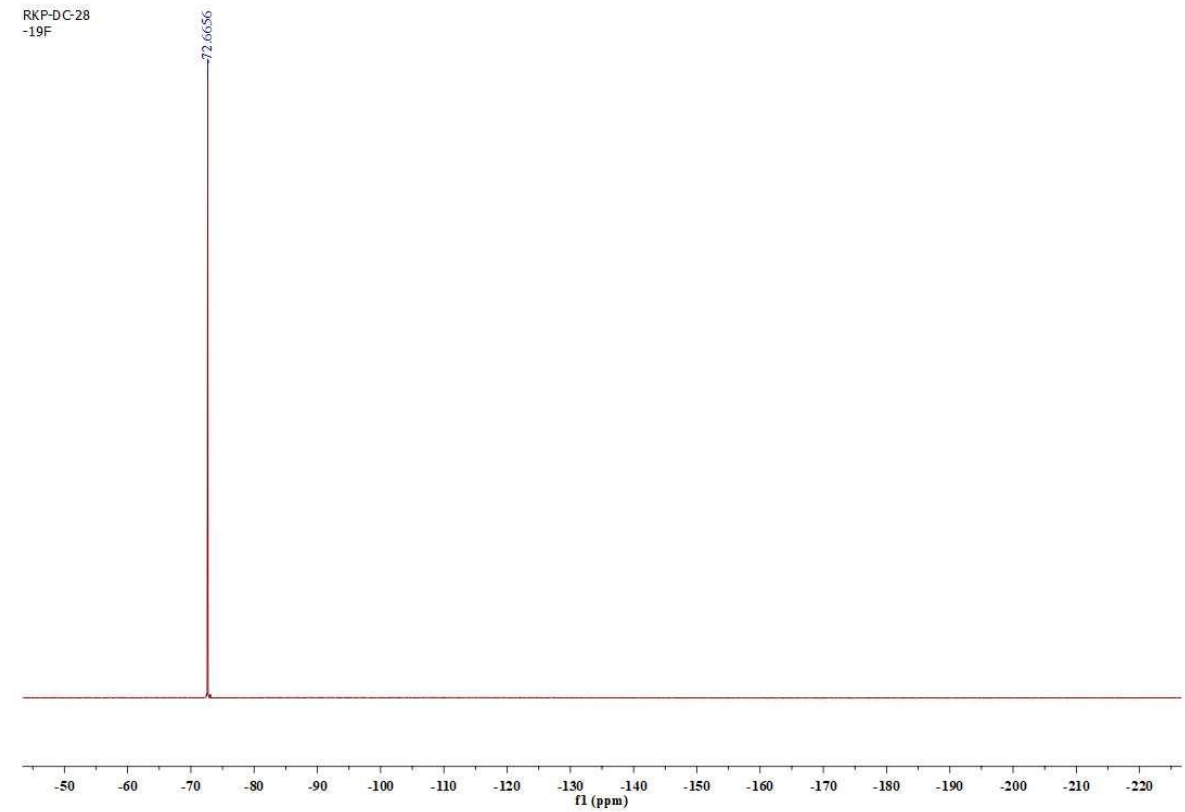
^{1}H NMR Spectrum of **23** (500 MHz, Chloroform-*d*)



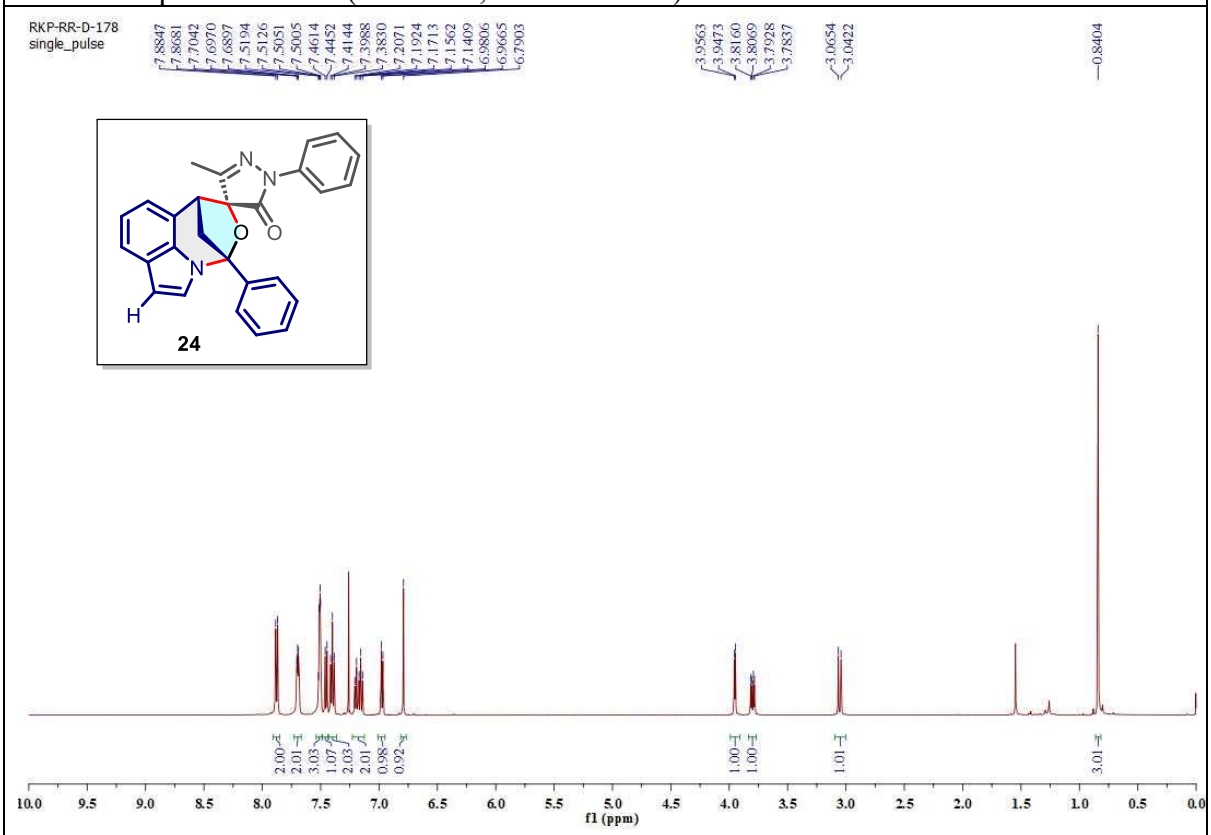
^{13}C NMR Spectrum of **23** (176 MHz, Chloroform-*d*)



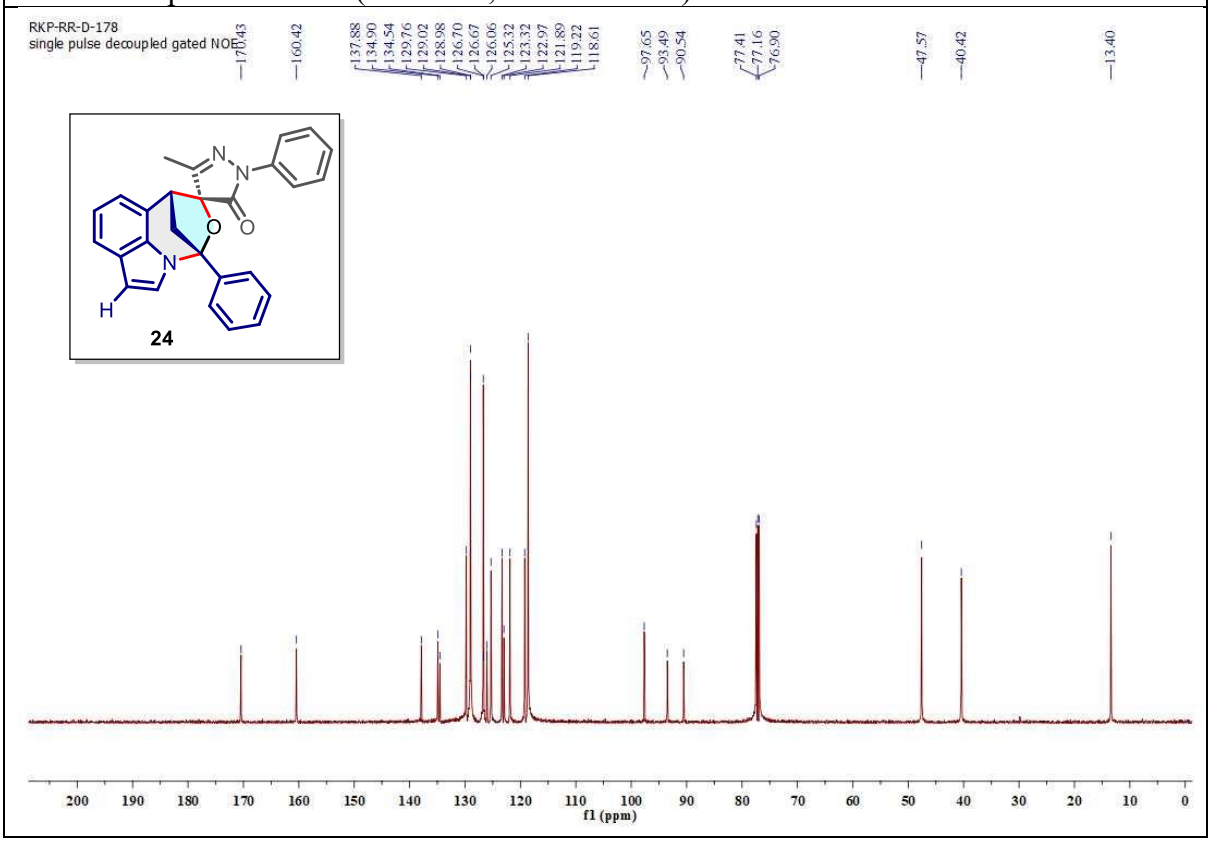
^{19}F NMR Spectrum of **23** (471 MHz, Chloroform-*d*)



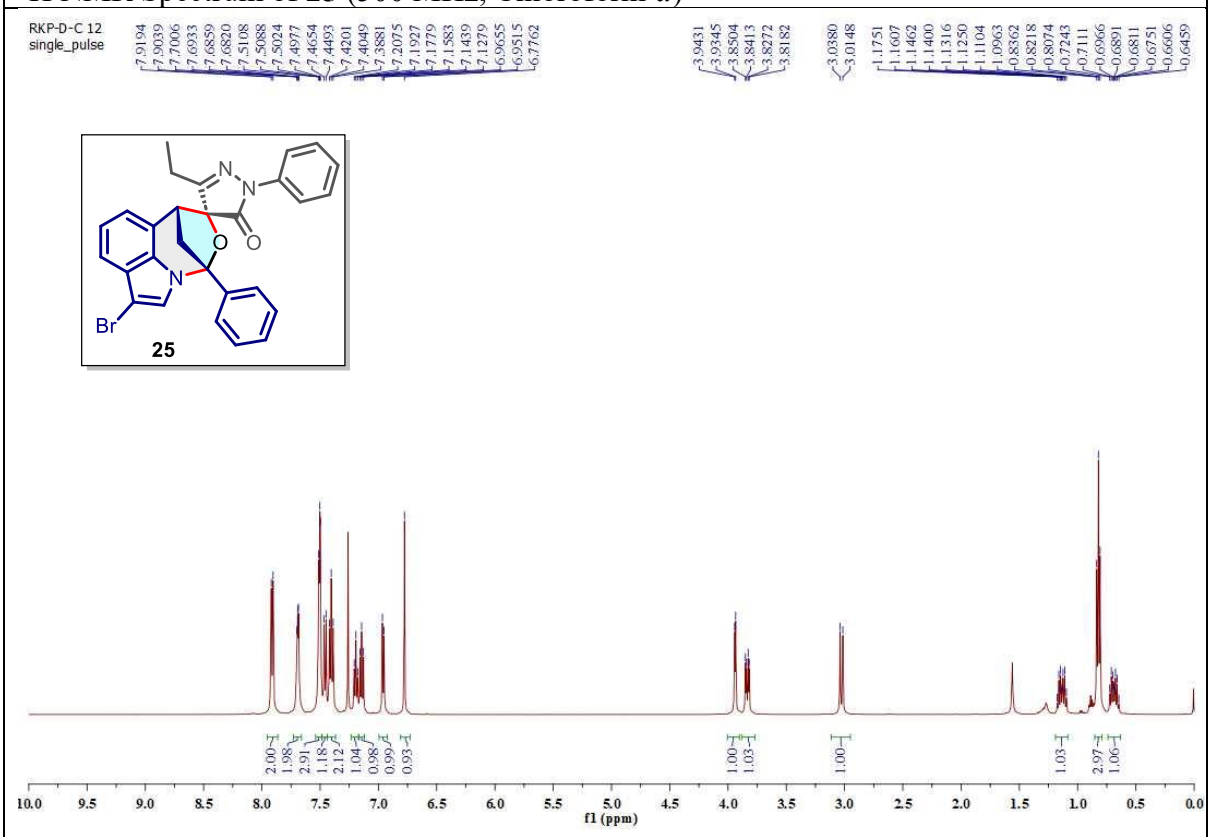
^{1}H NMR Spectrum of **24** (500 MHz, Chloroform-*d*)



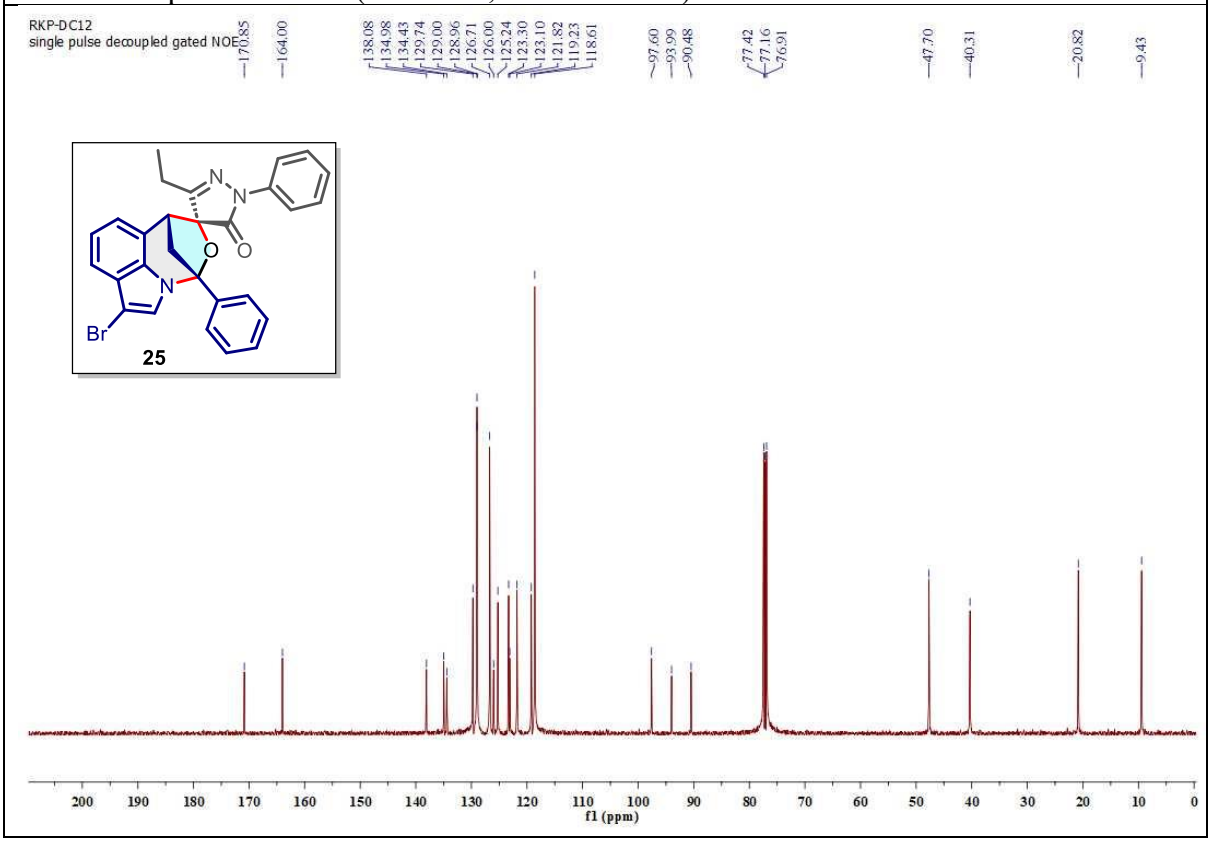
^{13}C NMR Spectrum of **24** (126 MHz, Chloroform-*d*)



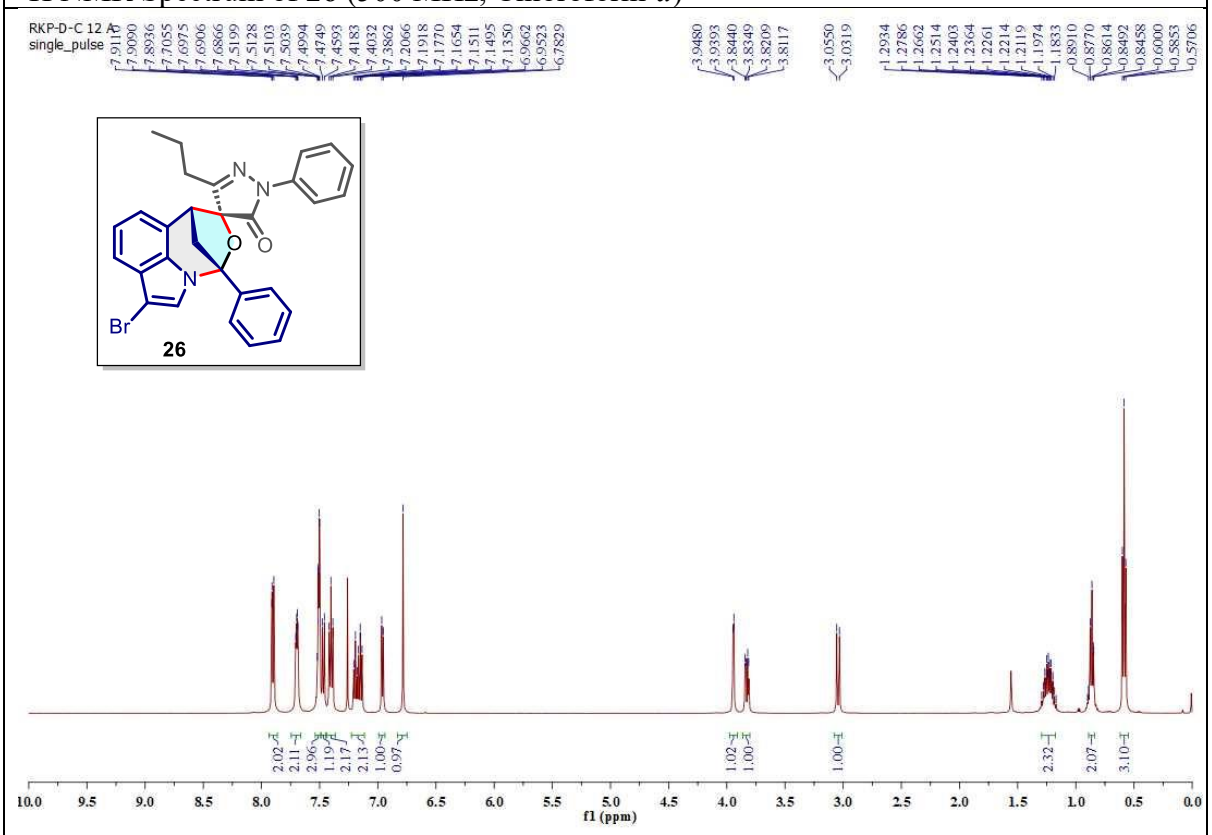
^{1}H NMR Spectrum of **25** (500 MHz, Chloroform-*d*)



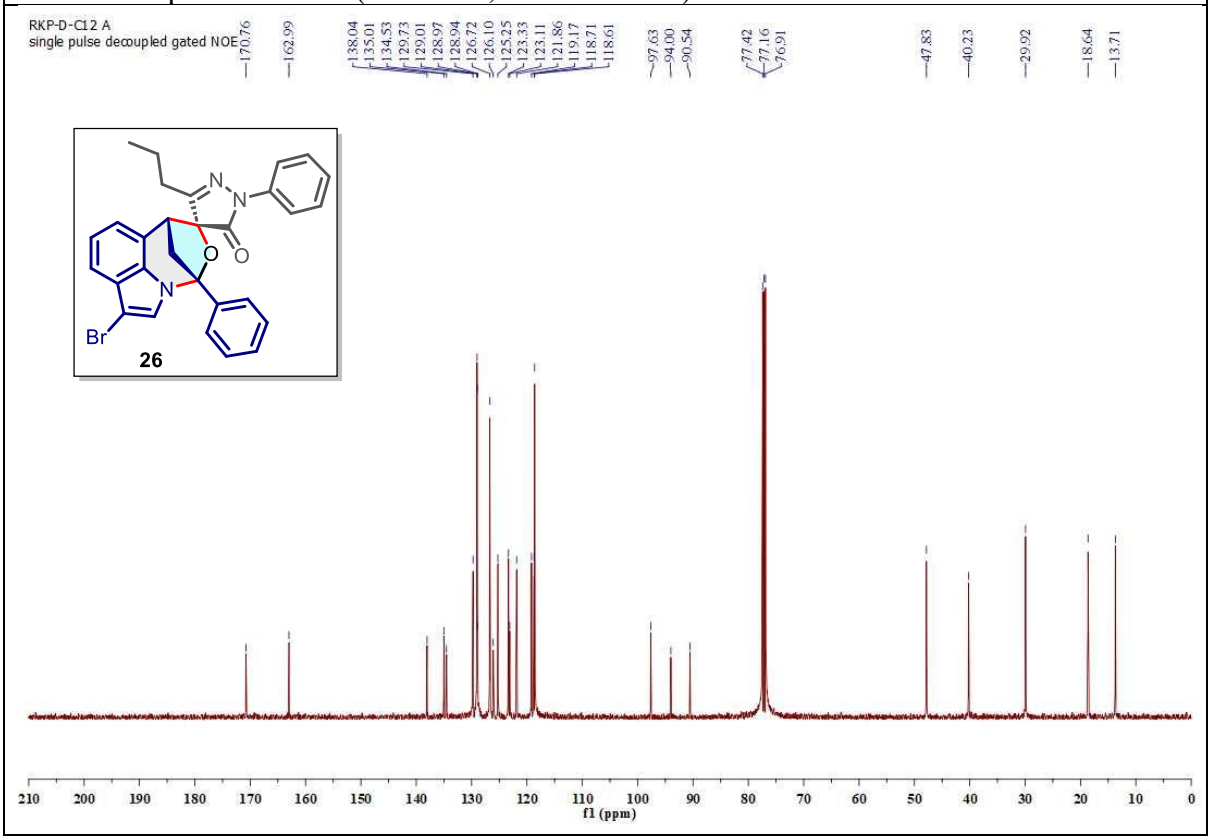
^{13}C NMR Spectrum of **25** (126 MHz, Chloroform-*d*)



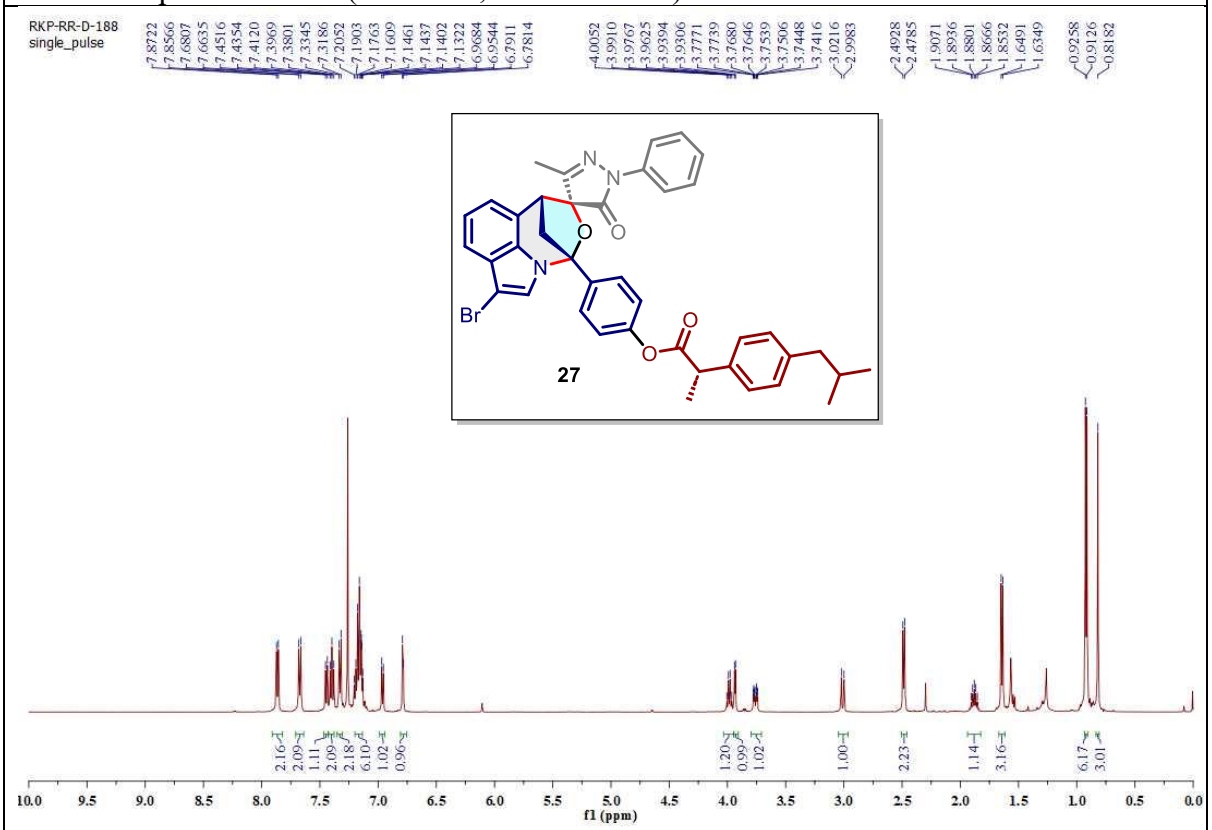
^{1}H NMR Spectrum of **26** (500 MHz, Chloroform-*d*)



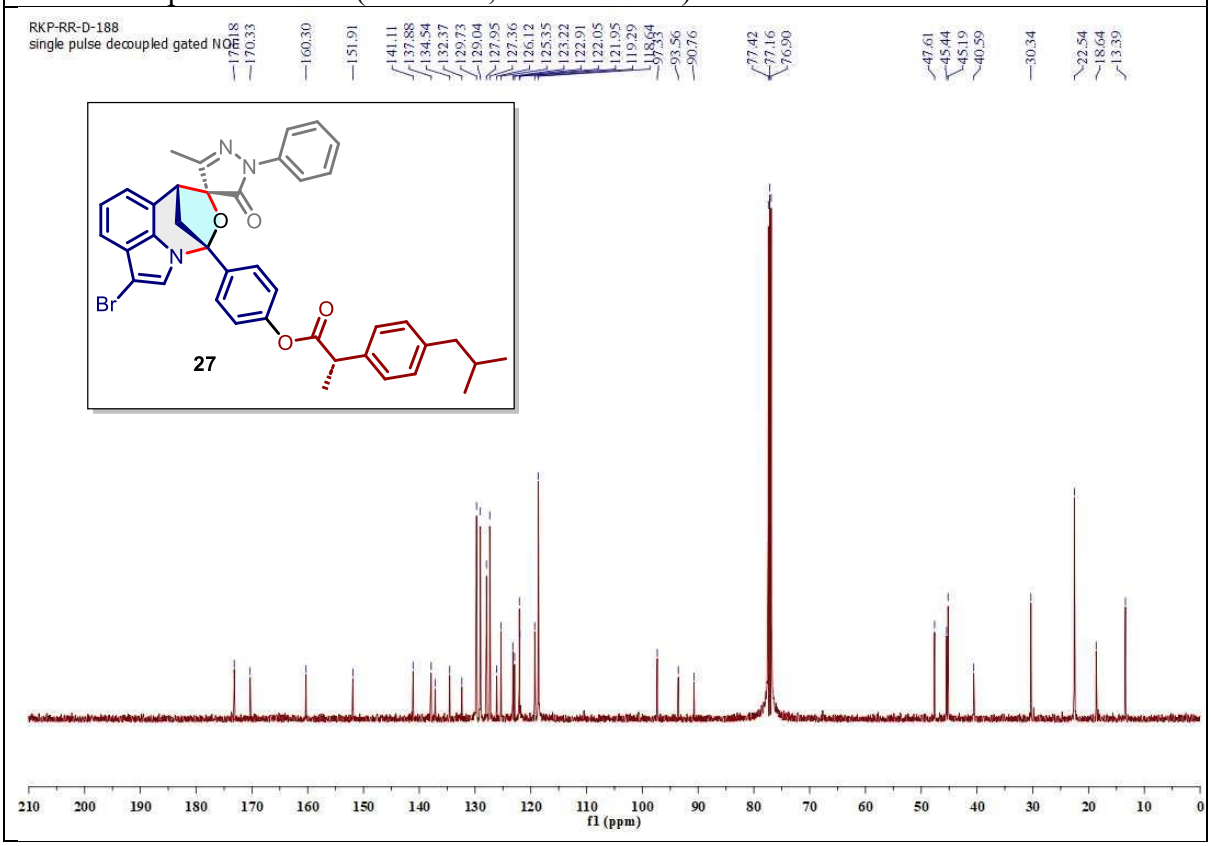
^{13}C NMR Spectrum of **26** (126 MHz, Chloroform-*d*)



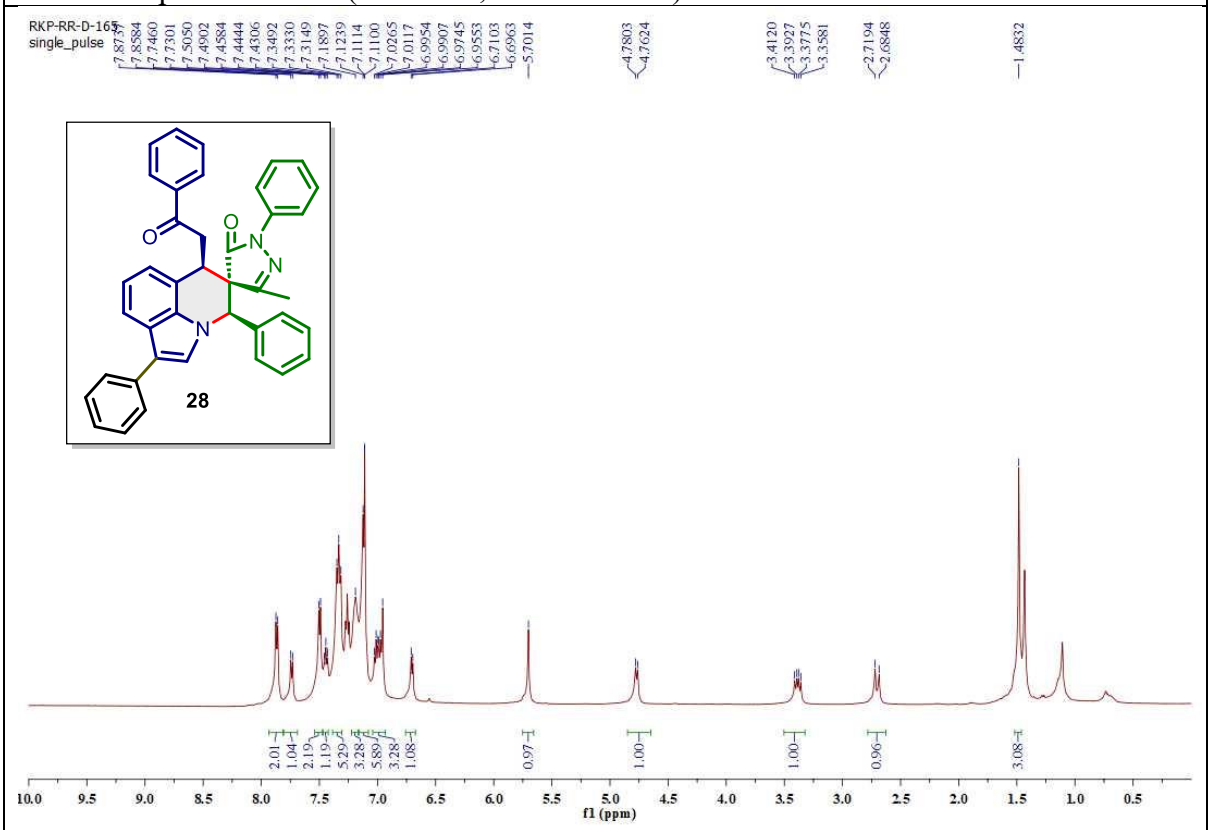
^{1}H NMR Spectrum of **27** (500 MHz, Chloroform-*d*)



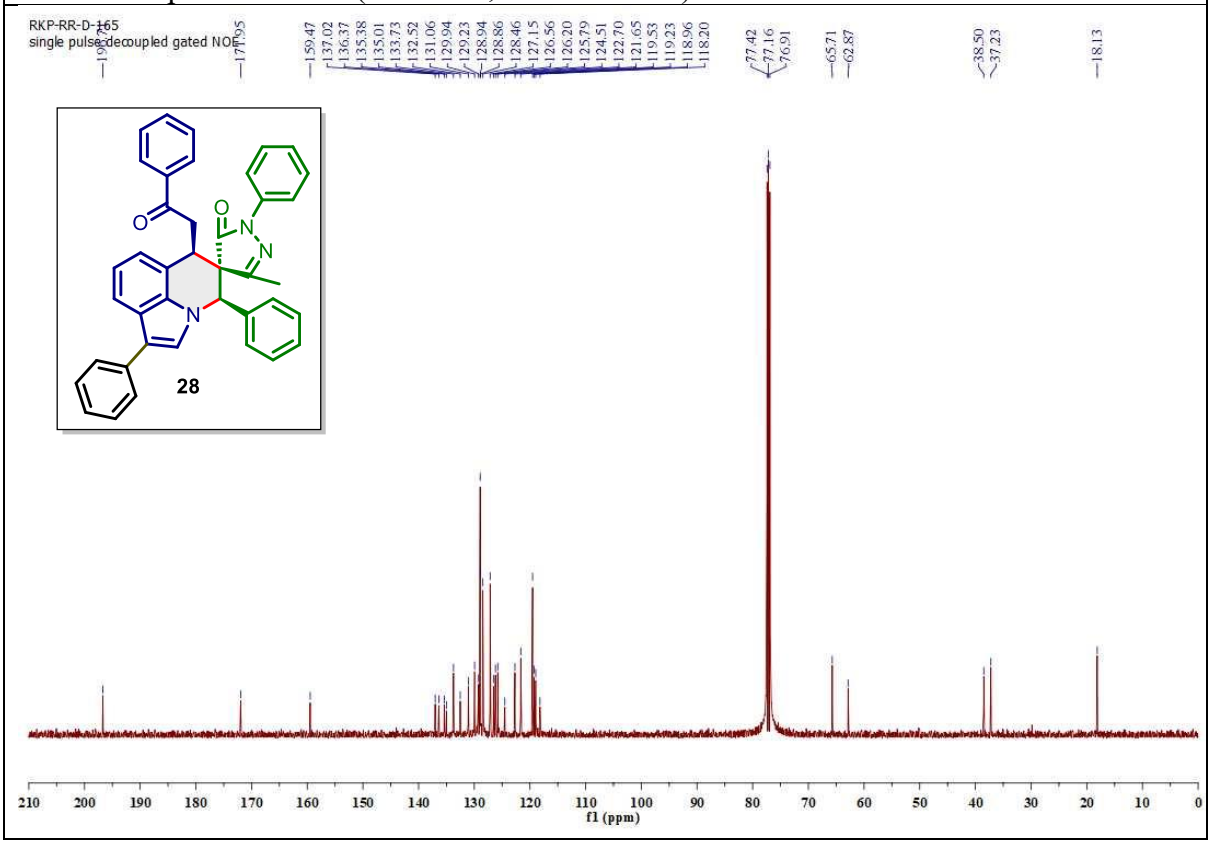
^{13}C NMR Spectrum of **27** (126 MHz, Chloroform-*d*)



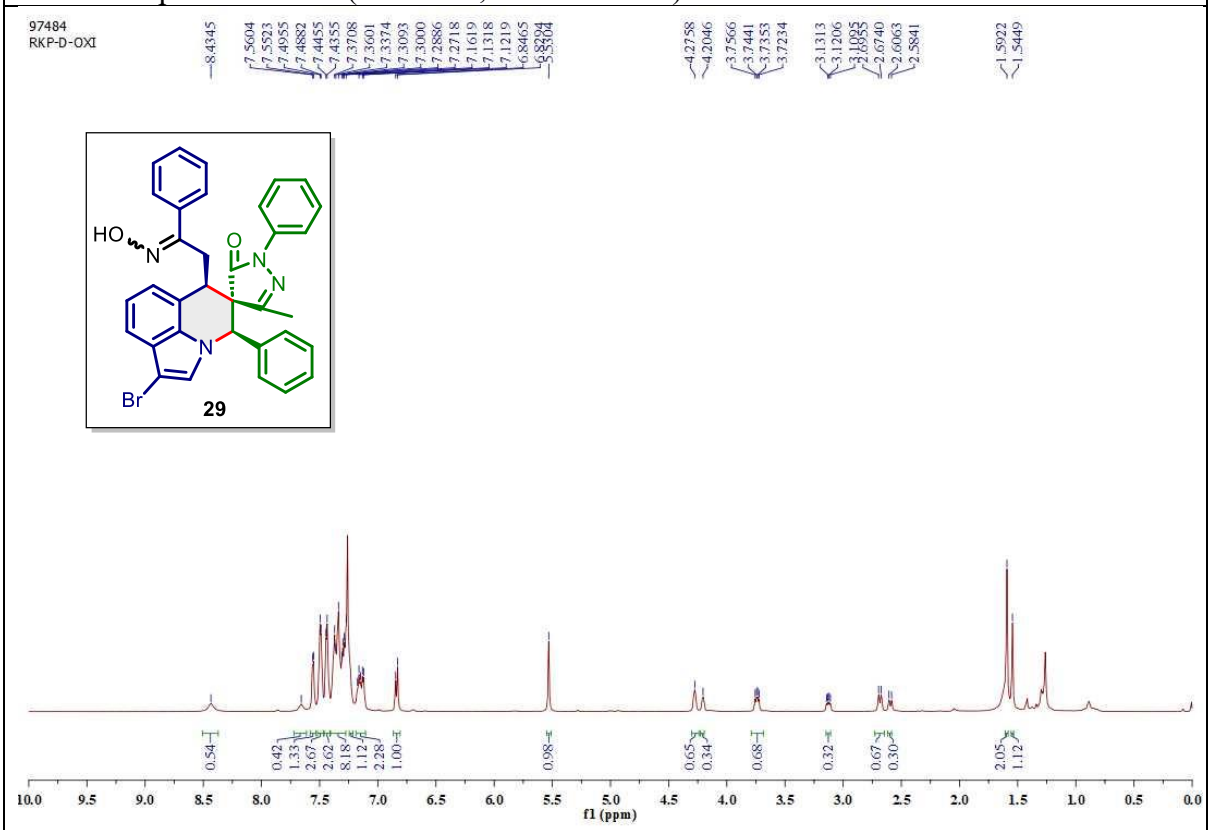
^{1}H NMR Spectrum of **28** (500 MHz, Chloroform-*d*)



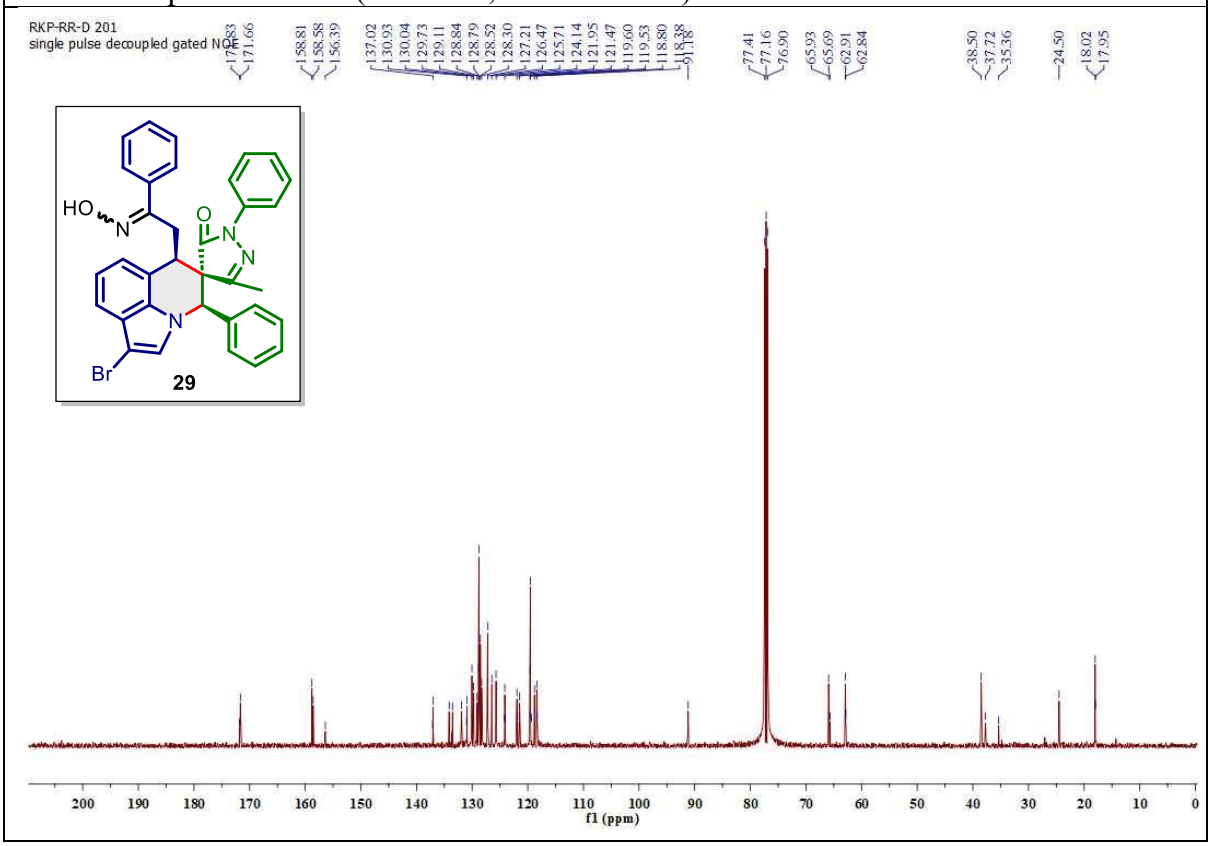
^{13}C NMR Spectrum of **28** (126 MHz, Chloroform-*d*)



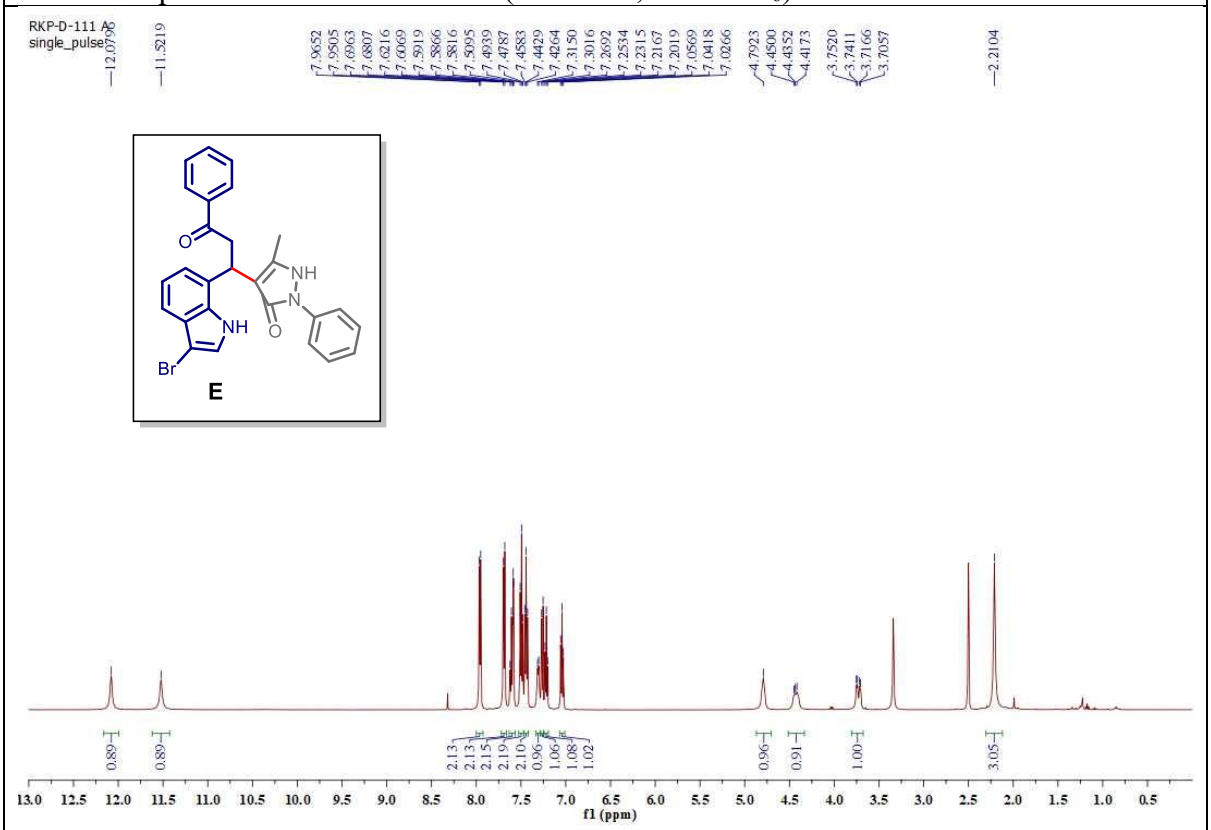
^{1}H NMR Spectrum of **29** (700 MHz, Chloroform-*d*)



^{13}C NMR Spectrum of **29** (126 MHz, Chloroform-*d*)



^{1}H NMR Spectrum of intermediate **E** (500 MHz, DMSO-d_6)



^{13}C NMR Spectrum of intermediate **E** (126 MHz, DMSO-d_6)