Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Highly Diastereoselective Cascade Dearomatization of 3-(2-Isocyanoethyl)indoles with Nitrile Imines: A Facile Access to Unexpected Polycyclic Indolines

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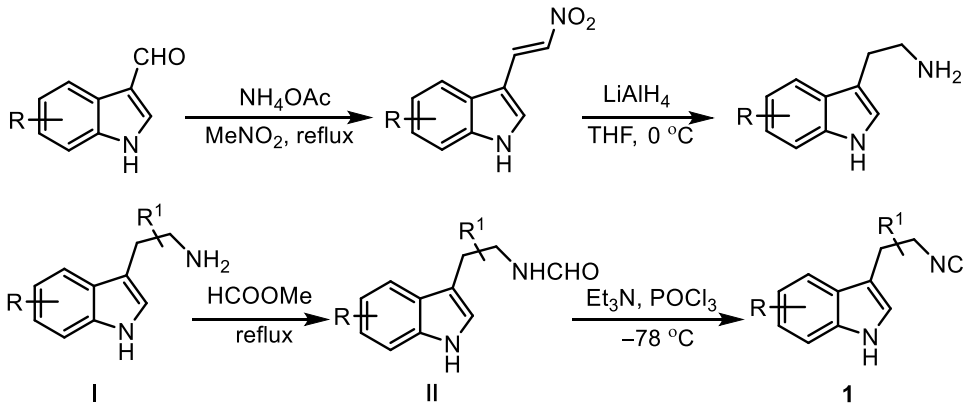
1. General experimental details

All NMR spectra were acquired on Bruker 400 MHz NMR spectrometers. ^{1}HNMR chemical shifts were recorded relative to TMS (δ 0.00) or residual protiated solvents ($CDCl_3$: δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at 101 MHz on 400 MHz NMR instrument and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). ^{19}F NMR spectra were recorded at 376 MHz on 400 MHz NMR spectrometers without any external standard. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C and ^{19}F NMR spectra. HRMS was recorded on a commercial apparatus (ESI Source). Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Anhydrous Methanol (Adamas), 1,4-dioxane (Adamas) and CH_3CN (Adamas) were used without further purification. Other solvents used in the solvent optimization were dried and purified according to the procedure from "Purification of Laboratory chemicals book". Dry THF, toluene were distilled from sodium under nitrogen. Dry DCM was distilled from calcium hydride under nitrogen. Unless noted otherwise, commercially available chemicals were used as received without purification. The NMR internal standard, CH_2Br_2 was used to determine the yield of product. DBU = 1,8-Dizabicyclo[5.4.0]undec-7-ene. DMAP = 4-Dimethylaminopyridine; triethylenediamine. Et_3N = Triethylamine. DIPEA = Diisopropylethylamine.

2. General procedure for the synthesis of substrates:

2.1 Preparation of the compound 3-(2-isocyanoethyl)indoles 1



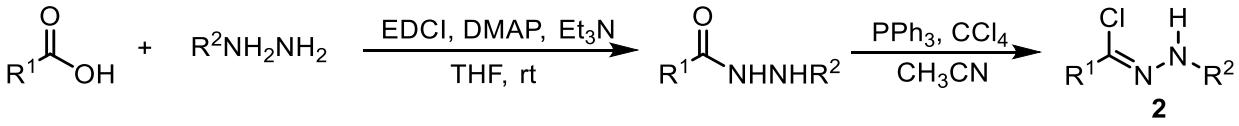
The compound 3-(2-Isocyanoethyl)indoles derivatives **1** were synthesized by the reported procedure in the literature.[1]

The preparation of tryptamine derivatives I: To a solution of indole-3-carbaldehyde derivatives (1.0 equiv) and ammonium acetate (3.0 equiv) were added nitromethane or nitroethane (20 mL/g of aldehyde) at refluxed for 2 hour. The solvent was removed under reduce pressure. After the completion of the reaction, and the mixtures were washed with water for three times, filtered and concentrated under reduce pressure to give the desired nitro olefin without

further purification. Under nitrogen atmosphere, a tetrahydrofuran solution of nitroolefin (1.0 equiv) was added to a stirred slurry of lithium aluminium hydride powder (6.0 equiv) in tetrahydrofuran (2.0 mL/mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 36 hours. The reaction was quenched by dropwise addition of ice water until effervescence ceased. The mixture was then diluted with diethyl ether before addition of a saturated aqueous solution of Rochelle's salt. Then the organic layer was extracted with 1.0 M HCl (aq). The aqueous phase was basified with 3.0 M KOH (aq), extracted with diethyl ether, dried over Na_2SO_4, filtered and concentrated to deliver the desired tryptamine without further purification.

The preparation of 3-(2-isocyanoethyl)indole derivatives 1: The tryptamine derivatives **I** were dissolved in HCO_2Me (6 mL per 10 mol), and the mixture was heat to 60 °C for 4 hours. After the completion of the reaction, it was concentrated under reduce pressure and purified by column chromatography (eluent: ethyl acetate/methol = 20/1) to give intermediate **II**, then a solution of the intermediate **II** (1.0 equiv) and Et_3N (5.0 equiv) in anhydrous dichloromethane (2 mL/mmol) was treated with $POCl_3$ (1.5 equiv) at -78 °C. After being stirred at -78 °C for 3-5 hours. After the completion of the reaction (detected by TLC), ice water was added to the mixture carefully, extracted with CH_2Cl_2 (3x), then the combined organic layer was dried over Na_2SO_4, concentrated under reduce pressure and purified by column chromatography (ethyl acetate/ ethyl acetate = 1/6-1/4) to give 3-(2-isocyanoethyl)indole derivatives **1**.

2.2 Preparation of the compound hydrazonyl chlorides 2.



The compound hydrazonyl chlorides **2** were synthesized by the same procedure in the literature. [2]

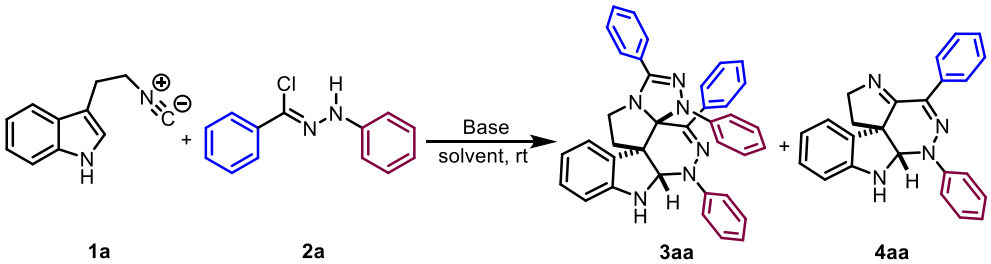
Preparation of the acylhydrazunes: The corresponding acid (1.0 equiv) was dissolved in THF (1.0 mL/mmol), and then EDCI (1.1 equiv), DMAP (0.2 equiv), Et_3N (2.0 equiv), and hydrazine (1.1 equiv) were added at 0 °C. The resulting mixture was heated to room temperature and stirred for 24 h. The crude reaction mixture was washed with dilute HCl (aq) and saturated $NaHCO_3$ (aq), extracted with DCM (3x), the mixture was concentrated to give the acylhydrazunes under reduce pressure and used in the next step without further purification.

Preparation of the hydrazonyl chlorides 2:To a solution of acylhydrazines (1.0 equiv) in CH_3CN (1 mL/mmol) was added triphenylphosphine (1.2 equiv), and carbon tetrachloride (1.3 equiv) at room temperature. The mixture was stirred at room teamperature for 3-8 h, After the completion of the reaction (detected by TLC), The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph directly to afford the corresponding hydrazonyl chlorides (eluent: petroleum ether/ethyl acetate = 100/1-50/1).

3. Reaction optimization between 3-(2-isocyanoethyl)indole 1a and hydrazonyl chloride 2a.

A general procedure: 3-(2-Isocyanoethyl)indole **1a** (8.5 mg, 0.05 mmol, 1.0 equiv), hydrazonyl chloride **2a** (11.5 mg, 0.05 mmol, 1.0 equiv), base (0.05 mmol, 1.0 equiv) and dry solvent (0.5 mL, 0.1 M) were added to a 10-mL sealed tube under N_2. Then the reaction was stirred at room temperature (25 °C) for 20 h. after removal of the solvent, the filtrate was subjected to ^{1}HNMR analysis of the crude reaction mixture to determine the yield of the product.

Table S1. Optimization of reaction conditions



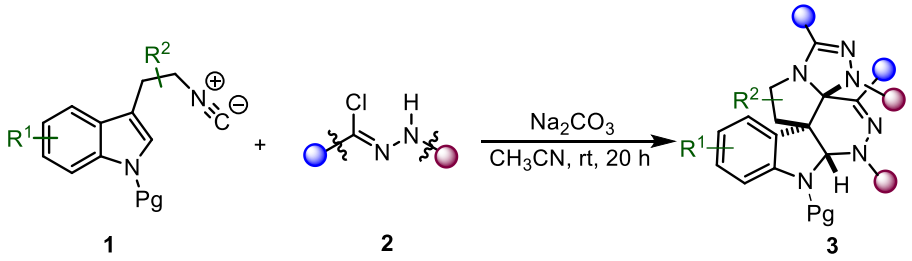
1a **2a** **3aa** **4aa**

Entry[a]	Solvent	Base	Yield [%][b]	D.r.[c]
1	DCM	Et_3N	25	>19:1
2	EtOAc	Et_3N	16	>19:1
3	1,4-Dioxane	Et_3N	5	>19:1
4	THF	Et_3N	6	>19:1
5	Toluene	Et_3N	20	>19:1
6	Et_2O	Et_3N	11	>19:1
7	Hexane	Et_3N	5	>19:1
8	CH_3CN	Et_3N	38	>19:1
9	CH_3CH_2CN	Et_3N	22	>19:1
10	CH_3CN	DIPEA	34	>19:1
11	CH_3CN	DMAP	<5	>19:1
12	CH_3CN	DBU	7	>19:1
13	CH_3CN	Li_2CO_3	Trace	---
14	**CH_3CN**	**Na_2CO_3**	**46**	**>19:1**
15	CH_3CN	K_2CO_3	29	>19:1
16	CH_3CN	Cs_2CO_3	17	>19:1
17	CH_3CN	^{t}BuOK	24	>19:1
18	CH_3CN	$NaHCO_3$	15	>19:1
19	CH_3CN	NaOH	<5	>19:1
20[d]	CH_3CN	Na_2CO_3	86	>19:1
21[e]	**CH_3CN**	**Na_2CO_3**	**95[f]**	**>19:1**
22[g]	CH_3CN	Na_2CO_3	30 (12)[h]	>19:1
23[i]	CH_3CN	--	nr[j]	--

[a]Unless otherwise specified, the reactions were carried by using **1a** (0.05 mmol), **2a** (0.05 mmol), base (0.05 mmol, 1.0 equiv) and solvent (0.5 mL, 0.1 M) under N_2 at rt (25 °C) for 20 h. [b]Yield were determined by ^{1}H NMR (CH_2Br_2 as internal

standard) of the crude reaction mixture. [c]D.r. was determined by ^{1}H NMR. [d]2.0 equiv of **2a** was used. [e]**1a** (0.1 mmol), **2a** (0.3 mmol, 3.0 equiv) and base (0.3 mmol, 3.0 equiv) was used. [f]Isolated yield. [g]**1a**/**2a** = 2:1. [h]Data in parentheses is yield of **4aa**. [i]Without base. [j]nr = no reaction.

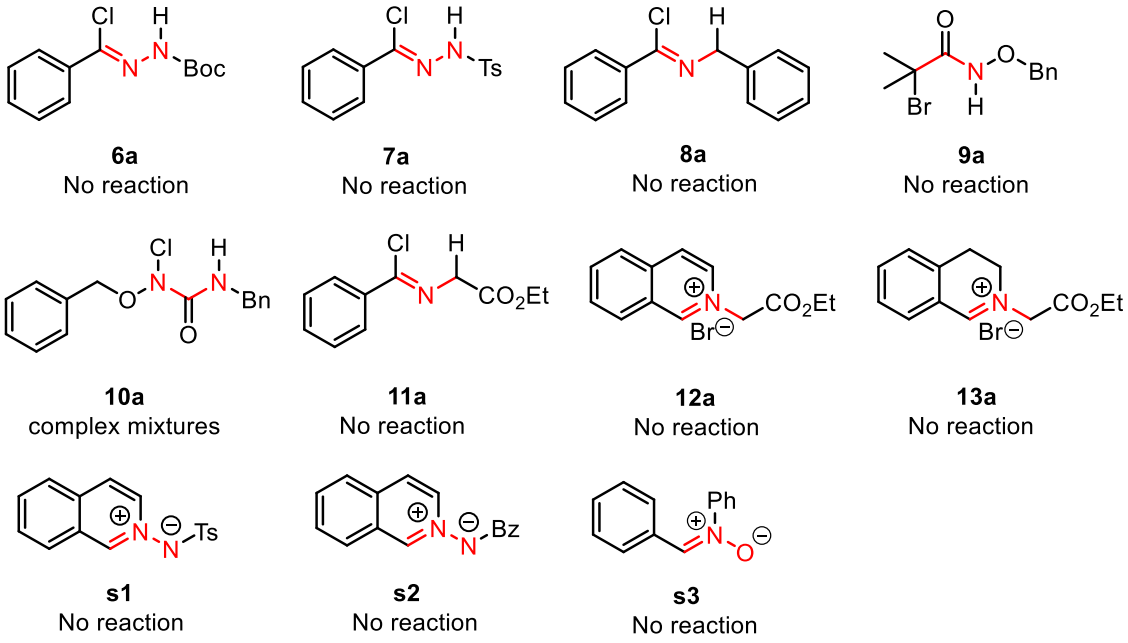
4. General procedure for reaction between 3-(2-isocyanoethyl)indoles and hydrazonyl chlorides



1 **2** **3**

A general procedure: 3-(2-Isocyanoethyl)indoles **1** (0.1 mmol, 1.0 equiv), hydrazonyl chlorides **2** (0.3 mmol, 3.0 equiv), Na_2CO_3 (0.3 mmol, 3.0 equiv) and dry CH_3CN (1.0 mL, 0.1 M) were added to a 10-mL sealed tube under N_2. Then the reaction was stirred at room temperature (25 °C) for 20 h. After completion of the reaction (detected by TLC), the solvent was removed under reduced pressure and the crude product was purified by flash chromatograph directly (eluent: petroleum ether/ethyl acetate = 7/1-4/1).

5. Some unsuccessful representive types of 1,3-dipoles and 1,3-dipolar precursors.



6a No reaction

7a No reaction

8a No reaction

9a No reaction

10a complex mixtures

11a No reaction

12a No reaction

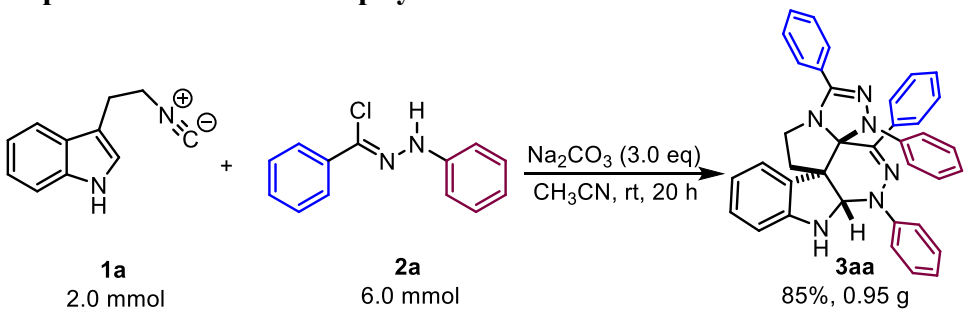
13a No reaction

s1 No reaction

s2 No reaction

s3 No reaction

6. Experimental procedure for a scale-up synthesis of 3aa.



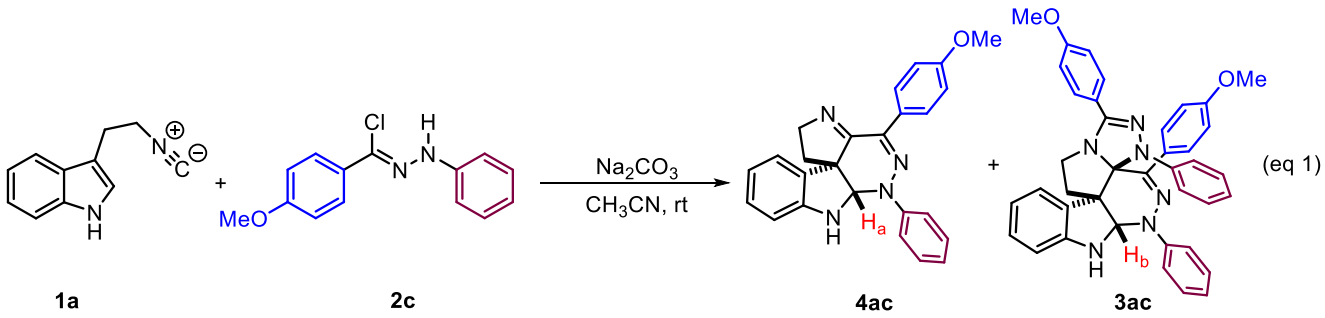
1a 2.0 mmol

2a 6.0 mmol

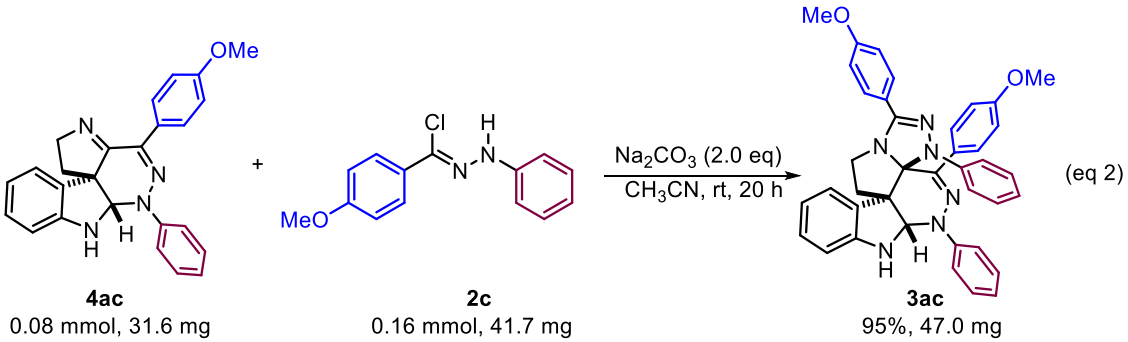
3aa 85%, 0.95 g

A scale-up synthesis of 3aa: The scale-up reaction was carried out according to the similar procedure: 3-(2-isocyanoethyl)indole **1a** (340 mg, 2.0 mmol, 1.0 equiv), hydrazonyl chloride **2a** (1.38 g, 6.0 mmol, 3.0 equiv), Na_2CO_3 (6.0 mmol, 3.0 equiv) and dry CH_3CN (20.0 mL, 0.1 M) were added to a 100-mL round bottom flask under N_2. Then the reaction was stirred at room temperature (25 °C) for 20 h. After completion of the reaction (detected by TLC), the solvent was removed under reduced pressure and the crude product was purified by flash chromatograph directly on silica gel (eluent: petroleum ether/ethyl acetate = 8/1-6/1) to afford the desired product **3aa** (85% yield, 0.95 g).

7. Control experiments and reaction mechanistic investigations



1a **2c** **4ac** **3ac**

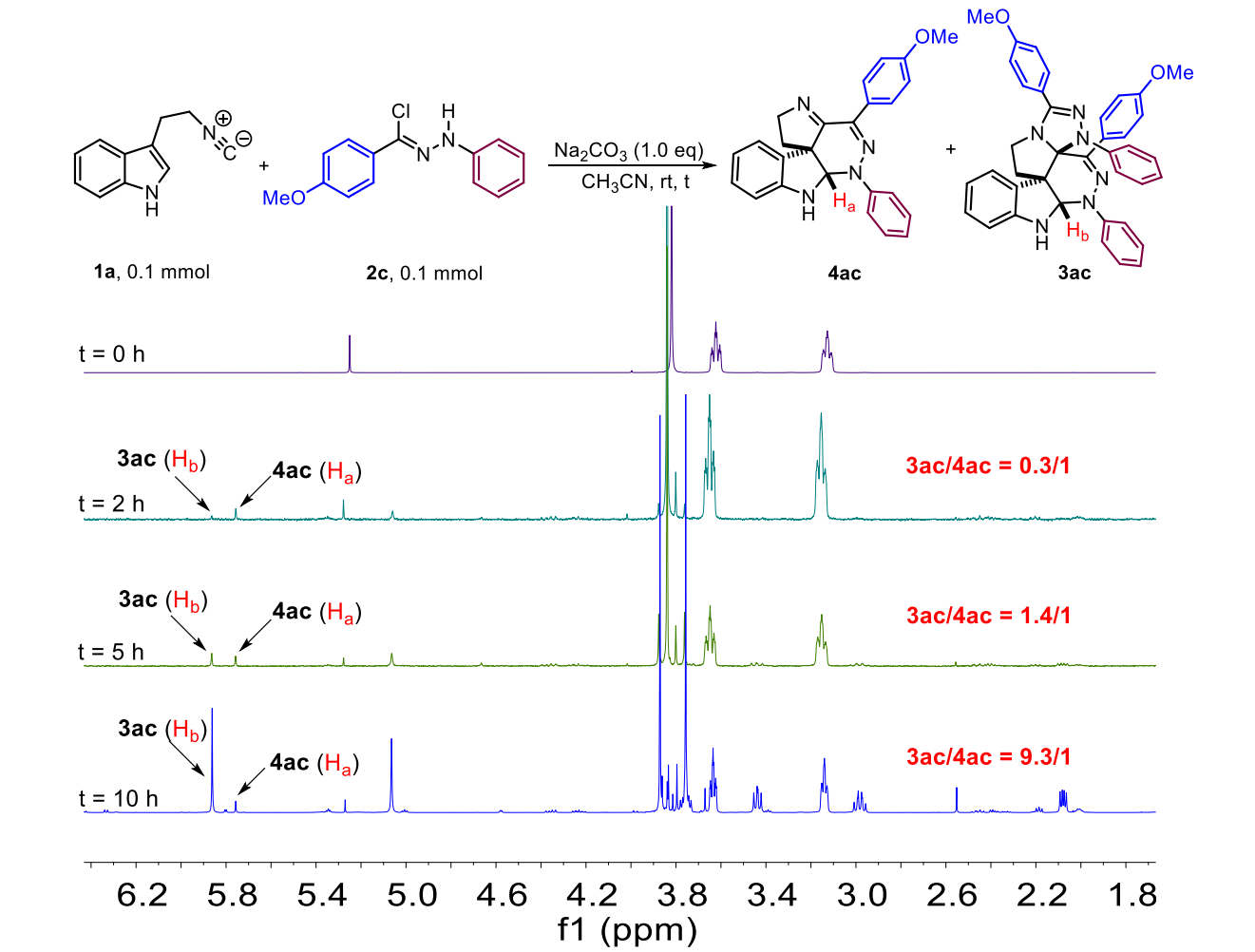


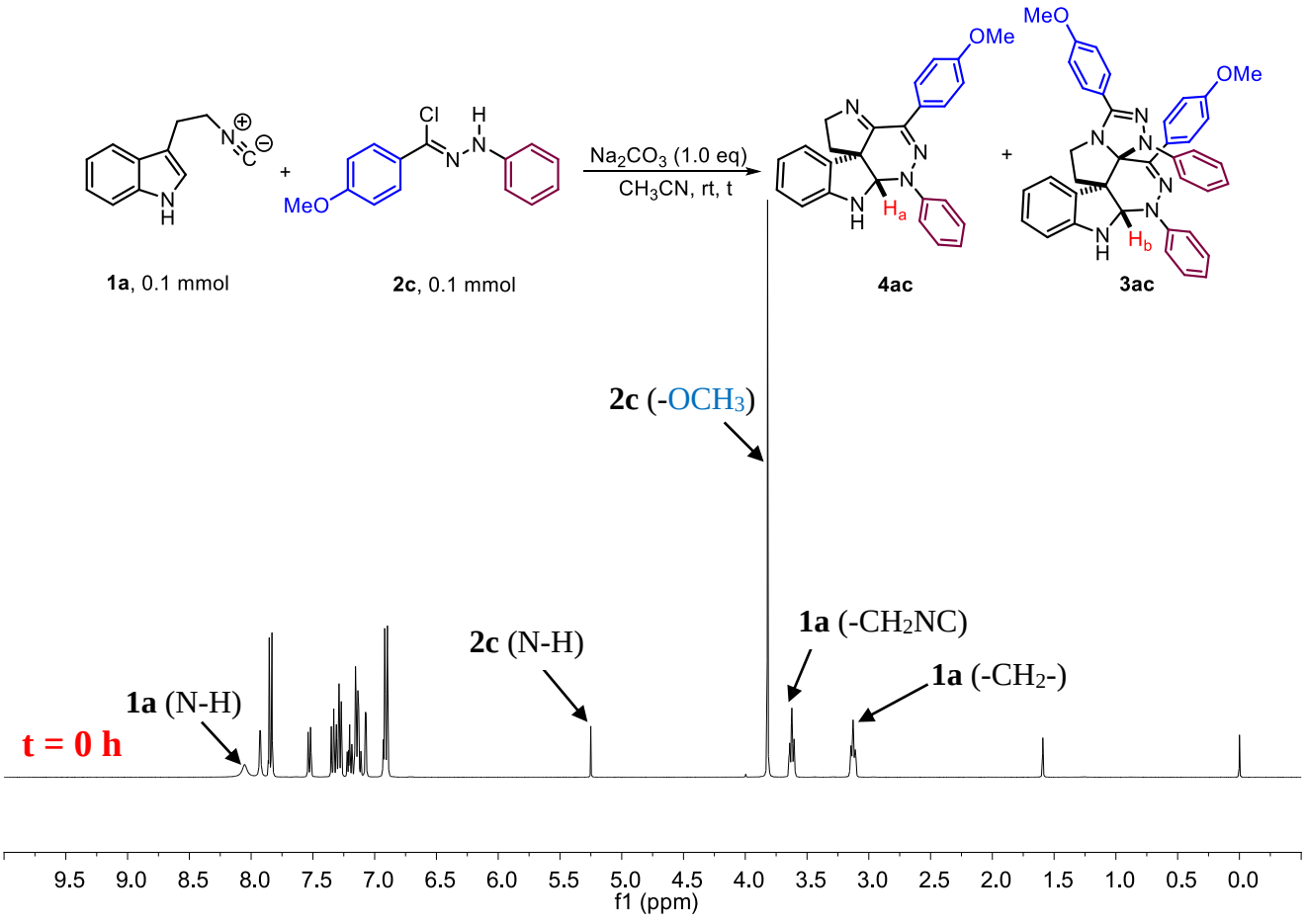
4ac 0.08 mmol, 31.6 mg

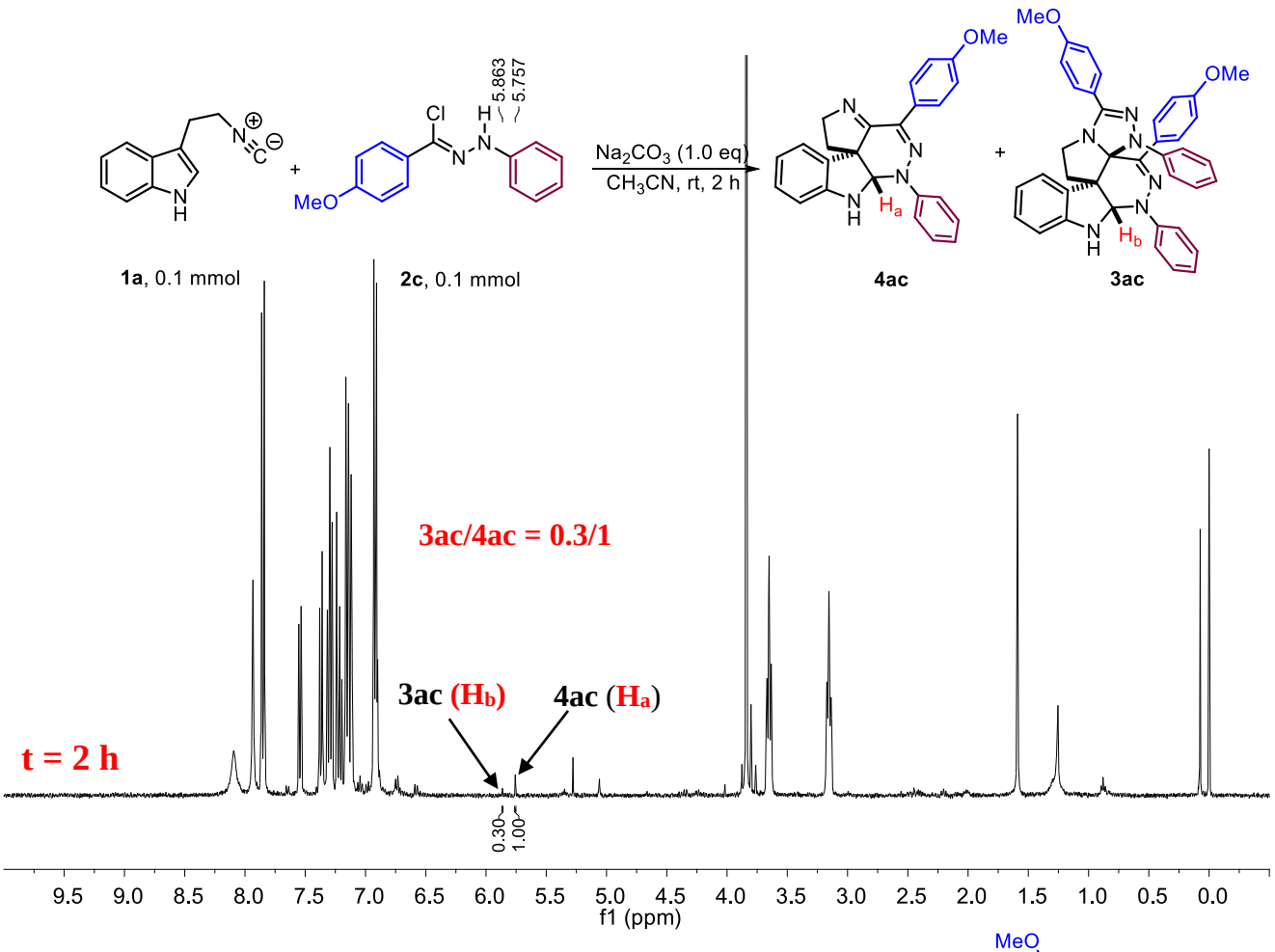
2c 0.16 mmol, 41.7 mg

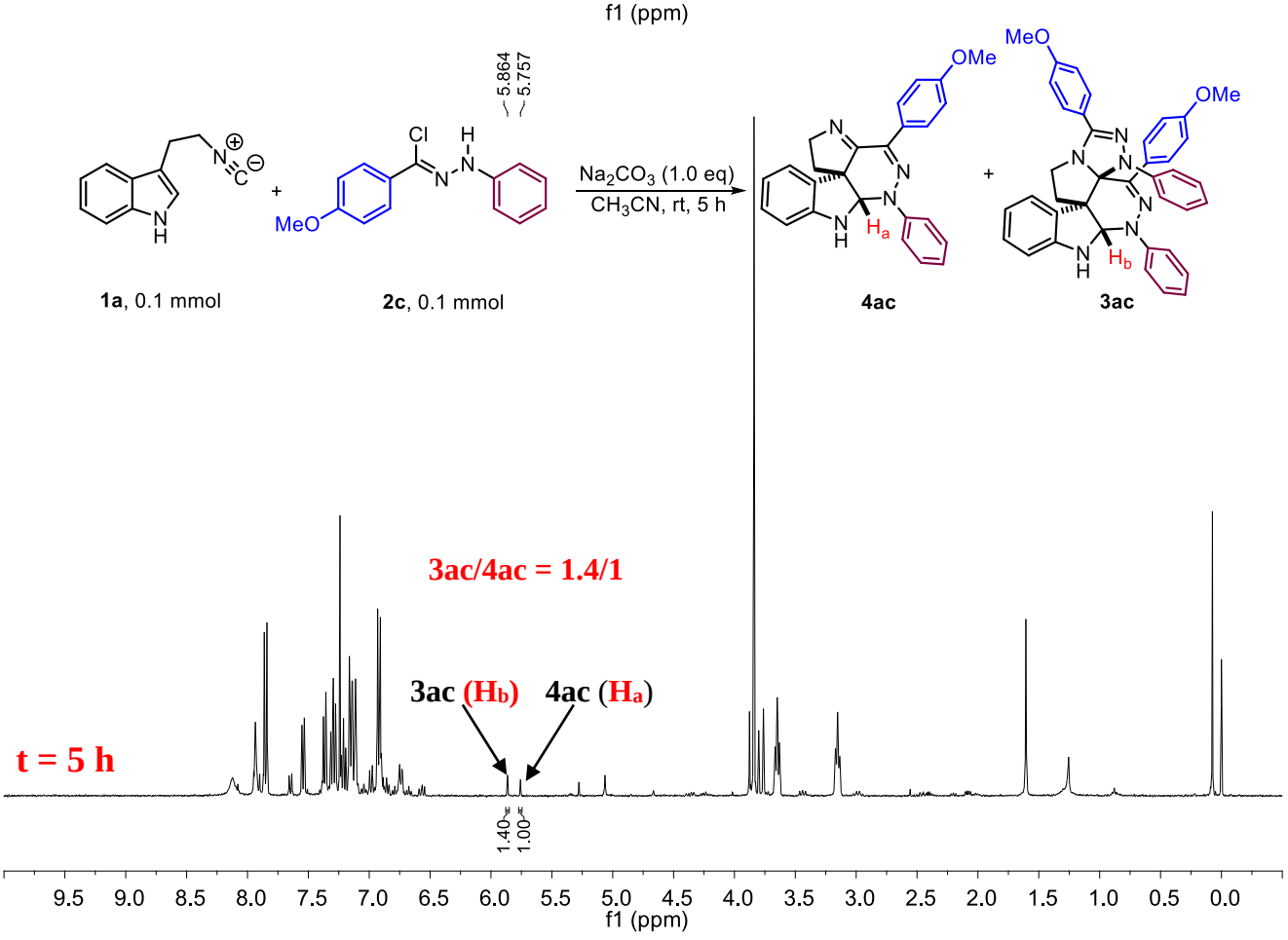
3ac 95%, 47.0 mg

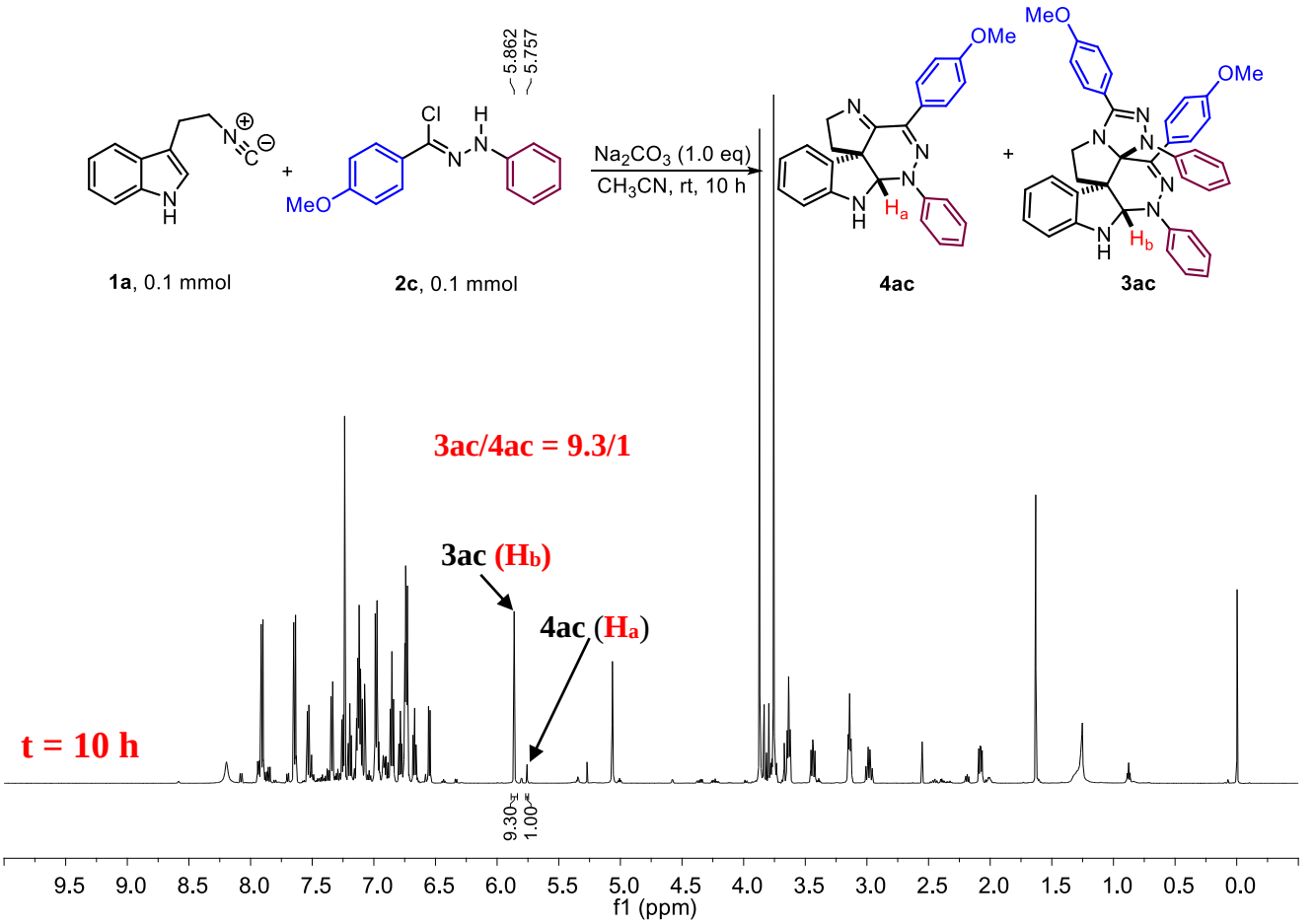
When the cascade process was extended to the reaction between hydrazonyl chloride **2c** and 3-(2-isocyanoethyl)indole **1a** under the optimal conditions, the mixture of polycyclic compound **3ac** and **4ac** were observed (eq. 1). Afterwards, the compound **4ac** can be readily isolated by flash chromatography directly on silica gel (eluent: petroleum ether/ethyl acetate = 4/1-3/1), and control experiment was conducted by subjecting the compound **4ac** and **2c** in the presence of Na_2CO_3 (2 equiv), and CH_3CN as the solvent at room temperature (25 °C) for 20 h. Remarkably, the compound **4ac** could be converted smoothly into the desired polycyclic product **3ac** with 95% yield. (eq. 2). Moreover, *in-situ* ^1H NMR spectra was acquired for the mixture of the cascade reaction between 3-(2-isocyanoethyl)indole **1a** (0.1 mmol) and hydrazonyl chloride **2c** (0.1 mmol) in the presence of Na_2CO_3 (0.1 mmol, 1.0 equiv), CH_3CN (1.0 mL, 0.1M) as solvent for 2, 5 and 10 h at room temperature, respectively. The ratios of **3ac** and **4ac** were measured to be 0.3/1, 1.4/1 and 9.3/1 via ^{1}HNMR analysis of the characteristic peaks (black arrows) from hydrogen (H_a and H_b) on two compounds at 2, 5 and 10 h, respectively. Additionally, when 2.0 equiv of **1a** was employed under optimal condition, the ratio of **3aa** and **4aa** was determined to be 2.5/1. The detailed results are as follows.

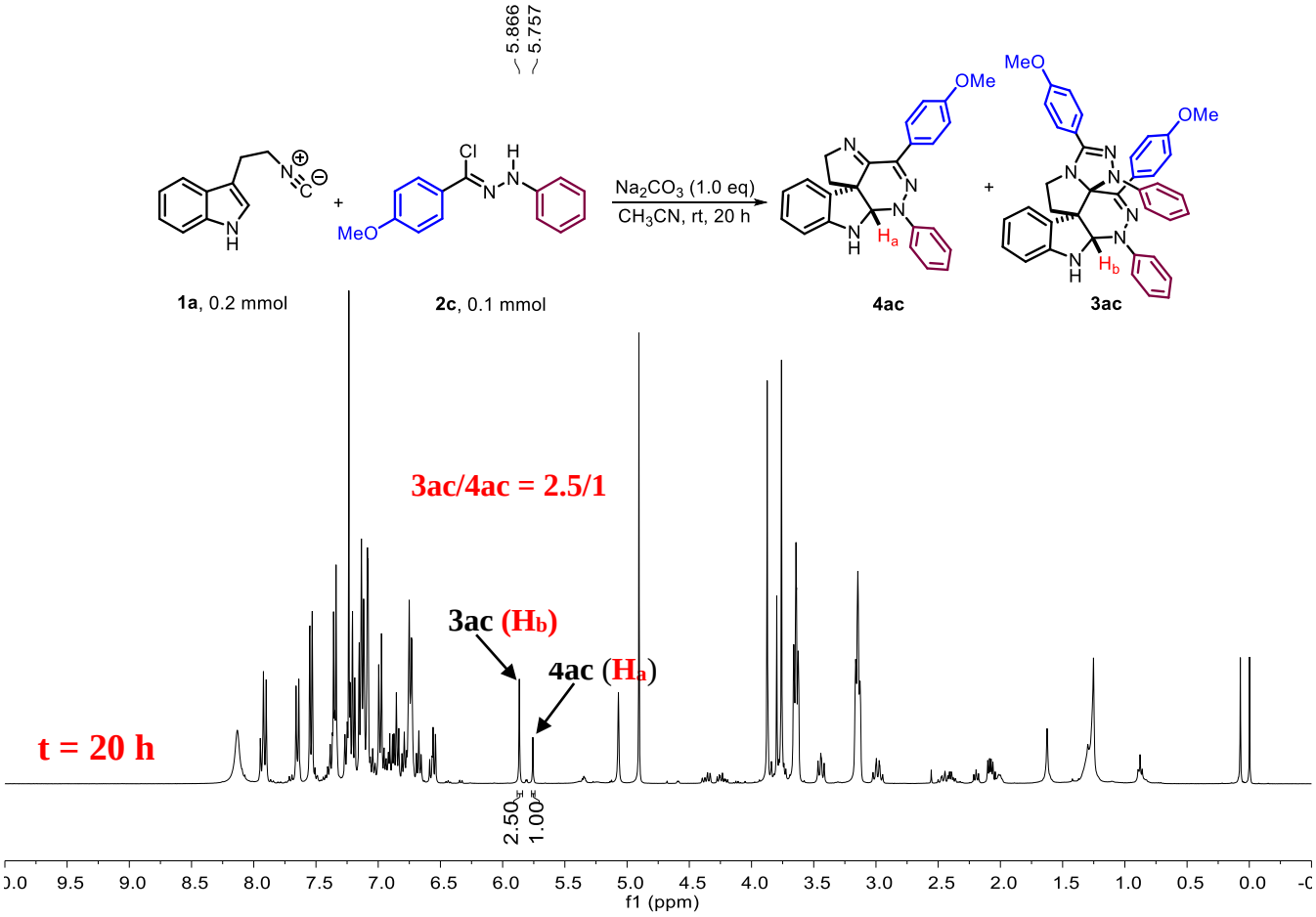

Na2CO3 (1.0 eq)
CH3CN, rt, t
1a, 0.1 mmol
2c, 0.1 mmol
4ac
3ac
t = 0 h
3ac (Hb)
4ac (Ha)
t = 2 h
3ac/4ac = 0.3/1
t = 5 h
3ac/4ac = 1.4/1
t = 10 h
3ac/4ac = 9.3/1
f1 (ppm)


Na2CO3 (1.0 eq)
CH3CN, rt, t
1a, 0.1 mmol
2c, 0.1 mmol
4ac
3ac
2c (-OCH3)
1a (-CH2NC)
2c (N-H)
1a (-CH2-)
1a (N-H)
t = 0 h
f1 (ppm)

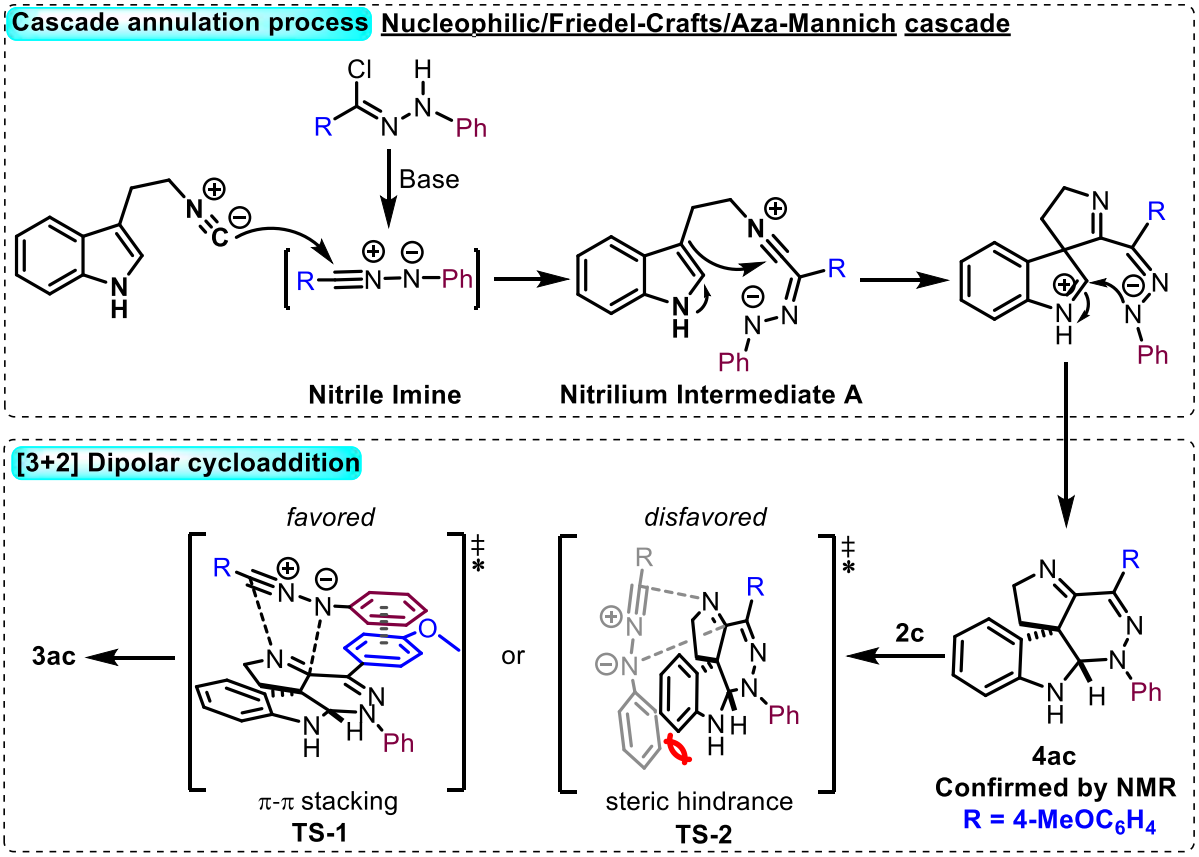

1a, 0.1 mmol
2c, 0.1 mmol
Na2CO3 (1.0 eq)
CH3CN, rt, 2 h
4ac
3ac
5.863
5.757
3ac/4ac = 0.3/1
3ac (Hb)
4ac (Ha)
t = 2 h
0.30
1.00
f1 (ppm)


1a, 0.1 mmol
2c, 0.1 mmol
Na2CO3 (1.0 eq)
CH3CN, rt, 5 h
4ac
3ac
5.864
5.757
3ac/4ac = 1.4/1
3ac (Hb)
4ac (Ha)
t = 5 h
1.40
1.00
f1 (ppm)


5.862
5.757
Cl
H
N
MeO
Na2CO3 (1.0 eq)
CH3CN, rt, 10 h
OMe
MeO
OMe
Ha
Hb
1a, 0.1 mmol
2c, 0.1 mmol
4ac
3ac
3ac/4ac = 9.3/1
3ac (Hb)
4ac (Ha)
t = 10 h
9.30
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


5.866
5.757
Cl
H
N
MeO
Na2CO3 (1.0 eq)
CH3CN, rt, 20 h
OMe
MeO
OMe
Ha
Hb
1a, 0.2 mmol
2c, 0.1 mmol
4ac
3ac
3ac/4ac = 2.5/1
3ac (Hb)
4ac (Ha)
t = 20 h
2.50
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

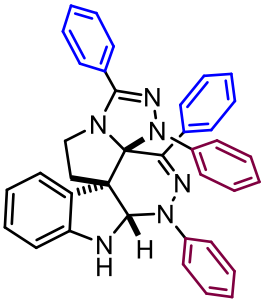
8. Proposed mechanism of the cascade process.



Based on the X-ray crystal structure of the product and the previous reports,[3] a possible model has been proposed to explain the cascade process.

9. The analytical and spectral characterization data of products 3.

1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole (3aa)

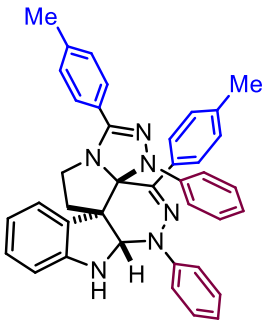


The compound **3aa** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 53.0 mg, 95% yield, >19:1 d.r. was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, Chloroform-d) δ = 8.05 – 7.93 (m, 2H), 7.79 – 7.67 (m, 2H), 7.52 – 7.42 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.19 – 7.11 (m, 4H), 7.01(td, J = 7.6, 1.6 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.87– 6.75(m, 4H), 6.71 (td, *J* = .7.6, 1,2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.92 (s, 1H), 5.09 (s, 1H), 3.89 – 3.73 (m, 1H), 3.48 (dd, *J* = 11.2, 8.4, 1H), 3.01 (td, *J* = 11.2, 8.8 Hz, 1H), 2.12 (dd, *J* =10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ = 156.52, 147.78, 144.41, 144.33, 143.32, 136.70, 132.70, 129.94, 129.00, 128.90, 128.72, 128.12, 128.05, 127.88, 127.58, 127.27, 127.05, 124.72, 120.36, 120.30, 113.91, 111.62, 94.39, 77.48, 62.33, 54.32, 33.66.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{30}N_6$ ([M+H$^+$]) = 559.2605, Found 559.2602.

3,6-diphenyl-1,4-di-p-tolyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino [3,4-b]indole (3ab)



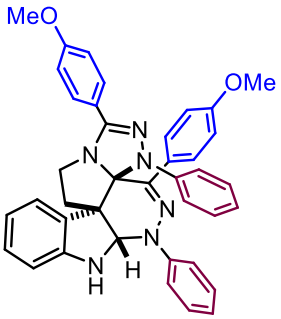
The compound **3ab** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 55.1 mg, 94% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.56 (m, 2H), 7.33 – 7.27 (m, 3H), 7.19 – 7.09 (m, 4H), 7.08 – 6.97 (m, 3H), 6.93 – 6.85 (m, 2H), 6.84 – 6.74 (s, 4H),6.70 (td, *J* = .7.2, 1.0 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 5.08 (s, 1H), 3.86 – 3.72 (m, 1H), 3.46 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.00 (td, *J* = 11.2, 8.8, 1H), 2.45 (s, 3H), 2.31 (m, 3H), 2.10 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.67, 147.84, 144.85, 144.59, 143.37, 140.14, 138.03, 133.99, 132.82, 129.63, 128.95, 128.89, 128.63, 128.06, 127.81, 127.52, 127.30, 126.93, 126.23, 124.75, 120.30, 120.04, 113.71, 111.58, 94.22, 62.43, 54.29, 33.62, 21.69, 21.36.

HRMS (ESI$^+$) m/z calcd for $C_{39}H_{34}N_6$ ([M+H$^+$]) = 587.2918, Found 587.1922.

1,4-bis(4-methoxyphenyl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ac)



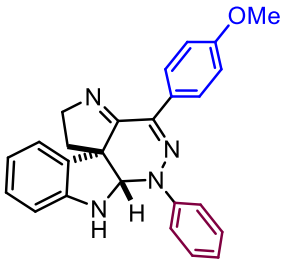
The compound **3ac** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:4); light yellow solid; 49.4 mg, 80% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 – 7.86 (m, 2H), 7.71 – 7.62 (m, 2H), 7.30 – 7.27 (m, 1H), 7.17 – 7.09 (m, 4H), 7.04 – 6.97 (m, 3H), 6.91 – 6.85 (m, 2H), 6.84 – 6.80 (s, 1H), 6.79-6.73 (m, 5H), 6.69 (td, *J* = 7.6, 1.2 Hz, 1H), 5.58 (d, *J* = 7.6 Hz, 1H), 5.89 (s, 1H), 5.09 (s, 1H), 3.89 (s, 3H), 3.82 – 3.72 (m, 4H), 3.46 (dd, *J* = 11.2, 8.8 Hz, 1H), 3.01 (td, *J* = 10.8, 8.4 Hz, 1H), 2.10 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.25, 161.11, 159.75, 156.42, 147.90, 144.73, 143.39, 132.83, 129.61, 129.02, 128.94, 128.87, 128.63, 127.99, 127.76, 126.85, 124.69, 121.59, 120.21, 119.87, 114.36, 113.56, 113.53, 111.56, 94.12, 77.48, 62.44, 55.52, 55.32, 54.25, 33.56.

HRMS (ESI$^+$) m/z calcd for $C_{39}H_{34}N_6O_2$ ([M+H$^+$]) = 619.2816, Found 619.2813

4-(4-methoxyphenyl)-6-phenyl-2,6,6a,7-tetrahydro-1H-pyrrolo[3',2':4,5]pyridazino[3,4-b]indole (4ac)



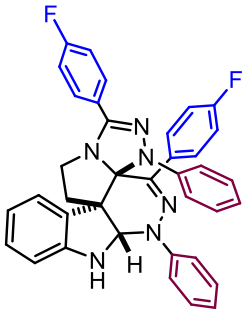
The compound **4ac** was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:4); light yellow solid, 4.1 mg, 1.0% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 7.89 (m, 2H), 7.43 – 7.33 (m, 4H), 7.09 – 7.02 (m, 2H), 6.95 – 6.88 (m, 3H), 6.75 (td, *J* = 5.2, 0.8 Hz, 1H), 6.59 (d, *J* = 5.2 Hz, 1H), 5.77 (s, 1H), 5.09 (s, 1H), 4.41 – 4.34 (m, 1H), 4.29 – 4.20 (m, 1H), 3.81 (s, 3H), 2.51 – 2.44 (m, 1H), 2.43 – 2.37 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.97, 159.88, 147.76, 144.60, 136.07, 130.42, 129.62, 129.23, 128.58, 128.05, 122.28, 122.12, 120.24, 116.31, 113.74, 110.48, 80.87, 61.50, 59.50, 55.43, 39.93.

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{22}N_4O$ ([M+H$^+$]) = 395.1866, Found 395.1863.

1,4-bis(4-fluorophenyl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ad)



The compound **3ad** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 53.5 mg, 90% yield, >19:1 d.r. was determined by ^{1}H NMR.

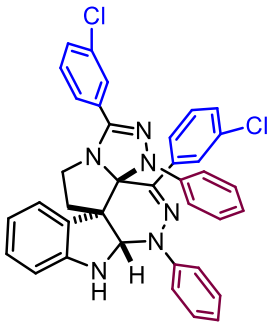
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.91 (m, 2H), 7.73 – 7.63 (m, 2H), 7.25 – 7.23 (m, 1H), 7.20 – 7.10 (m, 6H), 7.02 (td, *J* = 7.6, 1.2 Hz, 1H),6.95 – 6.88 (m, 4H), 6.87 – 6.75 (m, 4H), 6.71 (td, *J* = 7.2, 1.0 Hz, 1H), 5.59 (d, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 5.07 (s, 1H), 3.87 – 3.70 (m, 1H), 3.45 (dd, *J* = 11.2, 8.8 Hz, 1H), 3.00 (td, *J* = 10.8, 8.8, 1H), 2.13 (dd, *J* = 10.8, 6.0, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.91 (d, *J* = 250.6 Hz), 162.95 (d, *J* =248.4 Hz), 155.51, 147.77, 144.26, 143.21, 143.12, 132.96 (d, *J* = 3.1 Hz), 132.53, 129.30 (d, *J* = 8.0 Hz), 129.07 (d, *J* = 8.0 Hz), 129.05, 128.86, 127.94, 127.91, 127.17, 125.12 (d, *J* = 3.2 Hz) , 124.52, 120.47, 120.35, 116.18 (d, *J* = 21.9 Hz), 115.15 (d, *J* = 21.3 Hz) , 113.95, 111.70, 94.44, 77.48, 62.26, 54.32, 33.65.

^{19}F NMR (376 MHz, CDCl3) δ = -110.02, -113.60.

HRMS (ESI^+) m/z calcd for $C_{37}H_{28}F_2N_6$ ([M+H^+]) = 595.2416, Found 595.2419.

1,4-bis(3-chlorophenyl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']Pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ae)



The compound **3ae** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 57.1 mg, 91% yield, >19:1 d.r. was determined by ^{1}H NMR.

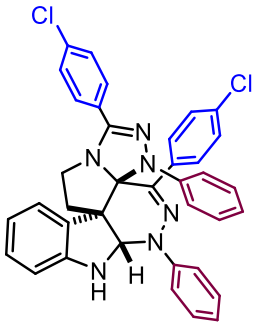
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.95 (m, 1H), 7.90 – 7.85 (m, 1H), 7.84 – 7.81 (m, 1H), 7.63 – 7.58 (m, 1H), 7.45 – 7.38 (m, 2H), 7.31(dd, *J* = 7.6, 1.2 Hz, 1H), 7.23 – 7.10 (m, 6H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H),6.98 – 6.91 (m, 2H), 6.90 – 6.74 (m, 5H), 6.58 (d, *J* = 7.6 Hz, 1H), 5.92 (s, 1H), 5.06 (s, 1H), 3.89 – 3.77 (m, 1H), 3.46 (dd, *J* = 11.2, 8.8 Hz, 1H), 2.98 (td, *J* = 10.8, 8.4 Hz, 1H), 2.15 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.12, 147.56, 143.91, 143.07, 141.18, 138.51, 135.05, 134.24, 132.31, 130.56, 130.27, 130.00, 129.48, 129.11, 128.98, 128.11, 128.03, 127.96, 127.37, 127.31, 126.93, 125.28, 125.20, 124.44, 120.91, 120.61, 114.32, 111.72, 94.79, 77.65, 61.95, 54.37, 33.74.

HRMS (ESI^+) m/z calcd for $C_{37}H_{28}{}^{34.9689}Cl_2N_6$ ([M+H^+]) = 627.1825, Found 627.1824.

HRMS (ESI^+) m/z calcd for $C_{37}H_{28}{}^{36.9659}Cl_2N_6$ ([M+H^+]) = 629.1796, Found 629.1800.

1,4-bis(4-chlorophenyl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3af)



The compound **3af** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 57.7 mg, 92% yield, >19:1 d.r. was determined by ^{1}H NMR.

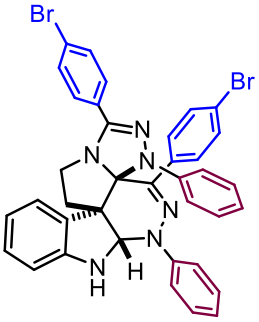
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.84 (m, 2H), 7.67 – 7.57 (m, 2H), 7.49 – 7.38 (m, 2H), 7.23(dd, *J* = 7.6, 1.2 Hz, 1H), 7.21 – 7.09 (m, 6H), 7.01 (td, J = 7.6, 1.2 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.88 – 6.75 (m, 4H), 6.70 (td, *J* = 7.2, 1.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 5.06 (s, 1H), 3.87 – 3.72 (m, 1H), 3.43 (dd, *J* = 10.8, 8.4 Hz, 1H), 2.98 (td, *J* = 10.8, 8.4Hz, 1H), 2.13 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.40, 147.67, 144.05, 143.12, 142.55, 135.97, 135.20, 134.20, 132.44, 129.34, 129.09, 128.91, 128.63, 128.43, 128.29, 127.99, 127.92, 127.33, 127.30, 124.48, 120.71, 120.44, 114.10, 111.73, 94.54, 77.53, 62.20, 54.39, 33.65.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{28}{}^{34.9689}Cl_2N_6$ ([M+H$^+$]) = 627.1825, Found 627.1830.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{28}{}^{36.9659}Cl_2N_6$ ([M+H$^+$]) = 629.1796, Found 629.1801.

1,4-bis(4-bromophenyl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ag)



The compound **3ag** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 64.5 mg, 90% yield, >19:1 d.r. was determined by ^{1}H NMR.

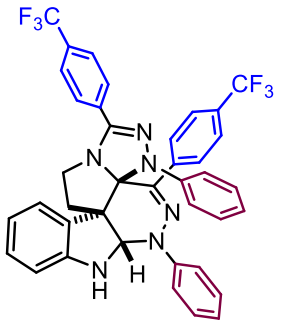
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.79 (m, 2H),7.65 – 7.60 (m, 2H), 7.59 – 7.53 (m, 2H), 7.38 – 7.31 (m, 2H), 7.23(dd, *J* = 7.6, 1.2 Hz, 1H), 7.19 – 7.09 (m, 4H), 7.01 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.88 – 6.76 (m, 4H), 6.71 (td, *J* = 7.6, 1.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 5.06 (s, 1H), 3.86 – 3.74 (m, 1H), 3.43 (dd, *J* = 11.2, 8.8 Hz, 1H), 2.97 (td, *J* = 11.2, 8.4 Hz, 1H), 2.13 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.43, 147.63, 143.99, 143.09, 142.53, 135.61, 132.40, 132.27, 131.36, 129.08, 128.90, 128.88, 128.49, 127.99, 127.90, 127.74, 127.31, 124.45, 124.29, 122.57, 120.74, 120.44, 114.11, 111.72, 94.51, 77.54, 62.19, 54.39, 33.62.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{28}{}^{78.9183}Br_2N_6$ ([M+H$^+$]) = 715.0815, Found 715.0809.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{28}{}^{80.9163}Br_2N_6$ ([M+H$^+$]) = 717.0794, Found 717.0793.

3,6-diphenyl-1,4-bis(4-(trifluoromethyl)phenyl)-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo [3',2':4,5]pyridazino[3,4-b]indole (3ah)



The compound **3ah** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 64.6 mg, 93% yield, >19:1 d.r. was determined by ^{1}H NMR.

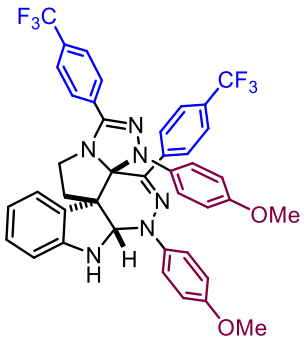
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 1H),7.20 – 7.11 (m, 4H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.91 – 6.77 (m, 4H), 6.73 (td, *J* = 7.6, 0.8 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 1H), 5.07 (s, 1H), 3.94 – 3.70 (m, 1H), 3.46 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.98 (td, *J* = 11.2, 8.4 Hz, 1H), 2.16 (dd, *J* = 11.2, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.91, 147.54, 143.69, 142.99, 141.60, 139.96, 139.95, 132.26, 129.17, 129.04, 128.14, 127.96,127.77 (q, *J* = 269.5 Hz), 127.58, 127.52 (q, *J* = 272.1 Hz), 127.27, 127.13, 126.09 (q, *J* = 3.7 Hz), 125.23 (q, *J* = 3.7 Hz), 124.40, 121.22, 120.57, 114.48, 111.83, 94.74, 77.80, 62.19, 54.55, 33.64.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.47, -62.65.

HRMS (ESI$^+$) m/z calcd for $C_{39}H_{28}F_6N_6$ ([M+H$^+$]) = 695.2352, Found 695.2350.

3,6-bis(4-methoxyphenyl)-1,4-bis(4-(trifluoromethyl)phenyl)-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo [4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole (3ai)



The compound **3ai** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:4); light yellow solid; 67.8 mg, 90% yield, >19:1 d.r. was determined by ^{1}H NMR.

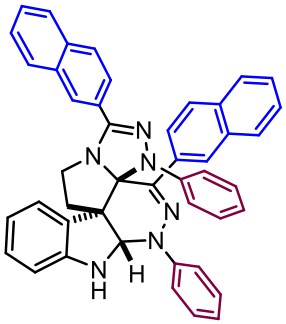
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 7.6 Hz, 2H), 7.82 – 7.70 (m, 4H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.12 – 7.01 (m, 3H), 6.79 – 6.68 (m, 5H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.54 – 6.48 (m, 2H), 5.82 (s, 1H), 4.93 (s, 1H), 3.85 – 3.78 (m, 1H), 3.77 (s, 3H), 3.51 (s, 3H), 3.42 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.93 (td, *J* = 11.2, 8.8 Hz, 1H), 2.11 (dd, *J* = 11.2, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.94, 154.89, 154.45, 147.50, 140.42, 140.09, 137.22, 136.47, 132.50, 132.26, 129.21, 128.96, 127.64 (q, *J* = 271.8 Hz), 127.07, 127.02 (q, *J* = 272.0 Hz), 127.03, 126.05 (q, *J* = 3.8 Hz), 125.21 (q, *J* = 3.8 Hz), 124.43, 120.56, 116.79, 114.51, 113.47, 111.77, 94.44, 78.42, 62.01, 55.72, 55.39, 54.57, 33.55.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.44, -62.64.

HRMS (ESI$^+$) m/z calcd for $C_{41}H_{32}F_6N_6O_2$ ([M+H$^+$]) = 755.2564, Found 755.2560.

1,4-di(naphthalen-2-yl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3aj)



The compound **3aj** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 59.9 mg, 91% yield, >19:1 d.r. was determined by ^{1}H NMR.

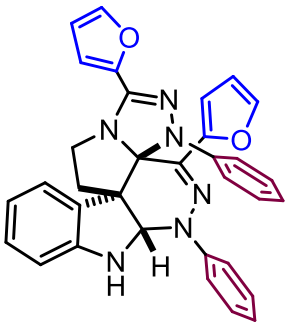
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 12.8 Hz, 2H), 8.16 (dd, *J* = 8.4, 1.6 Hz , 1H), 8.07 – 8.00 (m, 1H), 7.98 – 7.89 (m, 2H), 7.79 (dd, *J* = 8.8, 6.0 Hz, 1H),7.73 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.45 – 7.34 (m, 3H), 7.25 – 7.24 (m, 1H), 7.22 – 7.15 (m, 4H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 – 6.85 (m, 5H), 6.84 – 6.78(m, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.62(d, *J* = 7.6 Hz, 1H), 5.99 (s, 1H), 5.13 (s, 1H), 4.00 – 3.87 (m, 1H), 3.62 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.07 (td, *J* = 11.2, 8.8 Hz, 1H), 2.19 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.66, 147.74, 144.37, 143.39, 143.34, 134.27, 134.24, 133.51, 133.32, 133.09, 132.76, 129.07, 128.79, 128.69, 128.62, 128.16, 128.08, 127.92, 127.75, 127.51, 127.17, 127.09, 126.83, 126.77, 126.54, 126.21, 126.08, 124.85, 124.68, 124.49, 120.47, 114.02, 111.68, 94.88, 77.70, 62.43, 54.55, 33.60.

HRMS (ESI$^+$) m/z calcd for $C_{45}H_{34}N_6$ ([M+H$^+$]) = 659.2918, Found 659.2914.

1,4-di(furan-2-yl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]

pyridazino[3,4-b]indole (3ak)



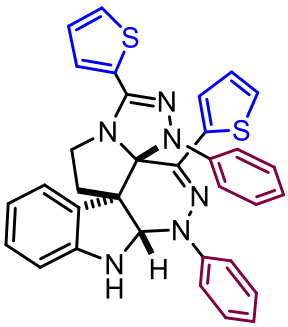
The compound **3ak** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 32.8 mg, 61% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 7.57 (m, 1H),7.38 – 7.35 (m, 1H), 7.32 (d, *J* = 6.4 Hz, 1H), 7.16 – 7.06 (m, 4H), 7.03 – 6.96 (m, 3H), 6.95 – 6.88 (m, 2H), 6.86 – 6.75 (m, 4H), 6.71 (td, *J* = 7.6, 0.8 Hz, 1H), 6.60 (dd, *J* = 3.6, 2.0 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.37 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.86 (s, 1H), 5.02 (s, 1H), 3.90 – 3.78 (m, 1H), 3.54 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.97 (td, *J* = 11.2, 8.4 Hz, 1H), 2.10 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.08, 149.12, 147.60, 144.83, 144.69, 143.81, 143.12, 134.95, 132.34, 129.02, 128.89, 128.03, 128.00, 127.23, 124.46, 120.57, 114.17, 111.89, 111.82, 111.65, 111.59, 111.19, 92.99, 77.62, 61.29, 54.92, 33.68.

HRMS (ESI$^+$) m/z calcd for $C_{33}H_{26}N_6O_2$ ([M+H$^+$]) = 539.2190, Found 539.2188.

3,6-diphenyl-1,4-di(thiophen-2-yl)-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3al)



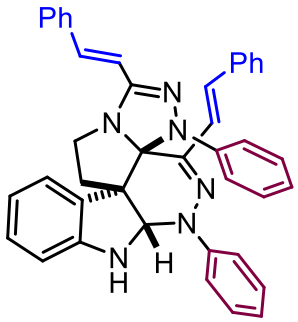
The compound **3al** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 49.0 mg, 86% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 – 7.65 (m, 2H), 7.44 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.38 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.14 – 7.11 (m, 2H), 7.08 (dd, *J* = 5.6, 0.8 Hz, 2H), 7.00 (td, *J* = 4.8, 0.8 Hz, 1H), 6.92 (dd, *J* = 3.6, 2.4 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.81 (t, *J* = 4.8 Hz, 1H), 6.79 – 6.70 (m, 4H), 6.57 (d, *J* = 4.8 Hz, 1H), 5.86 (s, 1H), 5.05 (s, 1H), 3.91 – 3.81 (m, 1H), 3.62 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.00 (td, *J* = 7.6, 6.0 Hz, 1H), 2.11 (dd, *J* = 6.8, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.36, 147.61, 144.03, 142.97, 141.94, 138.76, 132.44, 132.30, 129.03, 128.86, 128.09, 128.02, 127.91, 127.63, 127.19, 126.45, 126.36, 124.46, 120.61, 120.29, 113.67, 111.70, 94.23, 61.84, 54.90, 33.54.

HRMS (ESI$^+$) m/z calcd for $C_{33}H_{26}N_6S_2$ ([M+H$^+$]) = 571.1733, Found 571.1733.

3,6-diphenyl-1,4-di((E)-styryl)-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3am)



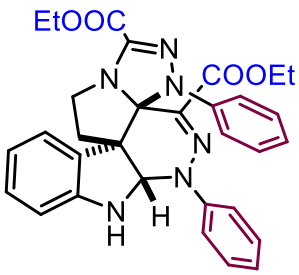
The compound **3am** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 36.6 mg, 60% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 – 7.60 (m, 2H), 7.48 – 7.43 (m, 4H), 7.42- 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 7.25 – 7.23 (m, 2H), 7.20 – 7.16 (m, 3H), 7.14 – 7.11 (m, 2H), 7.03 (td, *J* = 5.2, 0.8 Hz, 1H), 7.00 (d, *J* = 10.8 Hz, 1H), 6.94 (t, *J* = 5.6 Hz, 2H), 6.84 – 6.75 (m, 6H), 6.58 (d, *J* = 5.2 Hz, 1H), 5.82 (s, 1H), 5.01 (s, 1H), 3.92 – 3.83 (m, 1H), 3.59 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.96 (td, *J* = 7.6, 6.0 Hz, 1H), 2.11 (dd, *J* = 6.8, 4.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.92, 147.58, 143.96, 143.02, 142.79, 137.62, 136.38, 134.86, 132.57, 131.97, 129.12, 129.00, 128.89, 128.78, 128.05, 127.82, 127.24, 127.19, 126.81, 126.22, 124.65, 120.63, 116.96, 114.08, 111.59, 94.73, 77.57, 61.37, 54.77, 33.50.

HRMS (ESI$^+$) m/z calcd for $C_{41}H_{34}N_6$ ([M+H$^+$]) = 611.2918, Found 611.2913.

diethyl 3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole-1,4-dicarboxylate (3an)



The compound **3an** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow solid; 34.1 mg, 62% yield, >19:1 d.r. was determined by ^{1}H NMR.

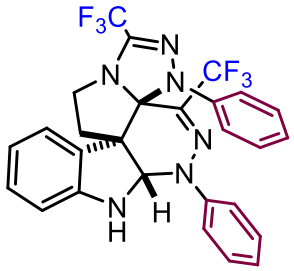
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 – 7.40 (m, 4H), 7.19 – 7.15 (m, 1H), 7.04 – 6.97 (m, 3H), 6.94 – 6.85 (m, 3H), 6.69 – 6.58 (m, 2H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.85 (d, *J* = 3.6 Hz, 1H), 4.75 (d, *J* = 4.0 Hz, 1H), 4.51 – 4.43 (m, 1H),

4.41 – 4.35 (m, 1H), 4.21 – 4.15 (m, 1H), 4.13 – 4.05 (m, 1H), 3.99 – 3.88 (m, 1H), 3.56 – 3.40 (m, 1H), 2.50 – 2.19 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.44, 159.35, 147.28, 145.29, 141.37, 140.33, 135.00, 129.81, 129.66, 128.76, 128.05, 125.21, 124.18, 120.72, 120.58, 116.83, 115.30, 109.99, 85.80, 76.49, 61.99, 61.24, 60.06, 49.04, 40.16, 14.45, 13.87.

HRMS (ESI$^+$) m/z calcd for $C_{31}H_{30}N_6O_4$ ([M+H$^+$]) = 551.2401, Found 551.2405.

3,6-diphenyl-1,4-bis(trifluoromethyl)-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ao)



The compound **3ao** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 29.3 mg, 54% yield, >19:1 d.r. was determined by ^{1}H NMR.

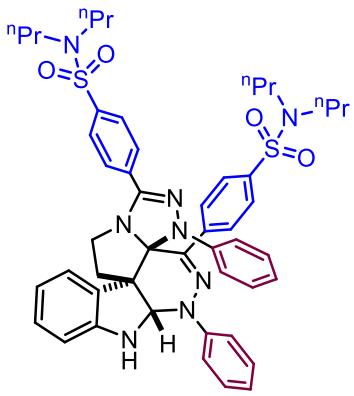
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.20 – 7.11 (m, 4H), 7.07(td, *J* = 7.6, 1.2 Hz, 1H), 7.02 – 6.93 (m, 2H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.72 (dd, *J* = 8.8, 1.2 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.84 (s, 1H), 4.82 (s, 1H), 3.85 – 3.72 (m, 1H), 3.57 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.86 (td, *J* = 11.6, 9.2 Hz, 1H), 2.14 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.48, 146.11, 145.73, 142.09, 141.61, 130.76, 129.52, 129.33, 128.79, 128.59, 127.96, 124.95, 123.44, 121.14, 120.55 (q, *J* = 271.5 Hz), 118.83 (q, *J* = 270.3 Hz), 116.65, 111.67, 94.38, 78.60, 60.51, 55.42, 34.43.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -64.95, -66.52.

HRMS (ESI$^+$) m/z calcd for $C_{27}H_{20}F_6N_6$ ([M+H$^+$]) = 543.1726, Found 543.1724.

4,4'-(3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole-1,4-diyl)bis(N,N-dipropylbenzenesulfonamide) (3ap)



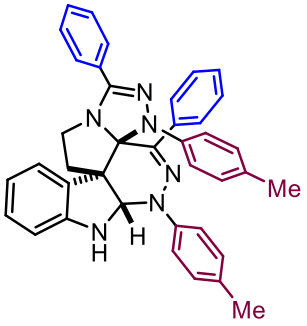
The compound **3ap** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:3); yellow solid; 82.2 mg, 93% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.21 – 7.14 (m, 2H), 7.13 – 7.08 (m, 2H), 7.02 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.91 – 6.84 (m, 2H), 6.82 (dd, *J* = 8.8, 1.2 Hz, 2H), 6.72 (td, *J* = 7.6, 1.2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.95 (s, 1H), 5.07 (s, 1H), 3.91 – 3.77 (m, 1H), 3.43 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.24 – 3.12 (m, 4H), 3.09 – 3.00 (m, 4H), 2.95 (td, *J* = 11.2, 8.8 Hz, 1H), 2.15 (dd, *J* = 10.8, 6.0 Hz, 1H), 1.67 – 1.59 (m, 4H), 1.58 – 1.49 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 6H), 0.85 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.66, 147.41, 143.54, 142.91, 141.17, 140.45, 140.38, 138.96, 132.27, 132.10, 129.18, 129.06, 128.07, 127.90, 127.79, 127.57, 127.40, 127.14, 126.99, 124.28, 121.45, 120.54, 114.71, 111.77, 94.84, 77.87, 61.90, 54.55, 50.23, 50.21, 33.57, 22.22, 11.32, 11.28.

HRMS (ESI$^+$) m/z calcd for $C_{49}H_{56}N_8O_4S_2$ ([M+H$^+$]) = 885.3939, Found 885.3936.

1,4-diphenyl-3,6-di-p-tolyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]Pyridazino[3,4-b]indole (3aq)



The compound **3aq** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 49.8 mg, 85% yield, >19:1 d.r. was determined by ^{1}H NMR.

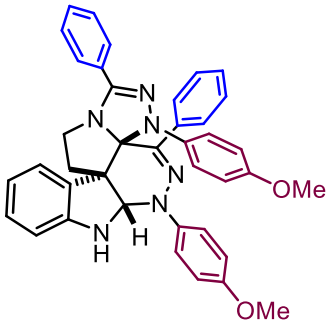
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.93 (m, 2H),7.79 – 7.64 (m, 2H), 7.49 – 7.41 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.00 (td, *J* = 7.6, 1.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.74 – 6.64

(m, 5H), 6.58 (d, *J* = 7.6 Hz, 1H), 5.83 (s, 1H), 5.02 (s, 1H), 3.84 – 3.73 (m, 1H), 3.45 (dd, *J* = 11.2, 8.8 Hz, 1H), 2.99 (td, *J* = 11.2, 8.8 Hz, 1H), 2.26 (s, 3H), 2.10 (dd, *J* = 10.8, 6.0 Hz, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.19, 147.88, 144.00, 141.66, 141.12, 137.00, 136.81, 132.88, 129.78, 129.47, 129.38, 129.11, 128.85, 128.64, 128.54, 128.08, 127.93, 127.76, 127.53, 127.21, 124.74, 120.31, 114.07, 111.59, 94.34, 77.53, 62.34, 54.30, 33.74, 20.88, 20.53.

HRMS (ESI$^+$) m/z calcd for $C_{39}H_{34}N_6$ ([M+H$^+$]) = 587.2918, Found 587.2915.

3,6-bis(4-methoxyphenyl)-1,4-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole (3ar)



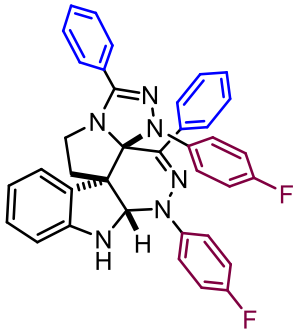
The compound **3ar** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:4); yellow solid; 49.5 mg, 80% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.94 (m, 2H),7.70 – 7.64 (m, 2H), 7.45 – 7.42 (m, 3H), 7.23-7.18 (m, 3H), 7.13 – 7-08 (m, 2H), 7.05 – 6.96 (m, 2H), 6.76 – 6-71 (m, 4H), 6.69 (td, *J* = 7.2, 0.8 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.46 (dd, *J* = 6.4, 2.0 Hz, 2H),5.80 (s, 1H), 4.95 (s, 1H), 3.79 – 3.71 (m, 4H), 3.48 (s, 3H), 3.44 (dd, *J* = 11.2, 8.8 Hz, 1H), 2.96 (td, *J* = 11.2, 8.8 Hz, 1H), 2.07 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.58, 156.12, 154.23, 147.78, 137.69, 137.29, 136.80, 132.95, 129.83, 129.22, 129.10, 128.87, 128.70, 128.65, 128.12, 127.86, 127.42, 127.24, 126.48, 124.78, 120.37, 115.93, 114.71, 114.42, 113.25, 111.59, 94.13, 78.00, 62.26, 55.75, 55.34, 54.35, 33.60.

HRMS (ESI$^+$) m/z calcd for $C_{39}H_{34}N_6O_2$ ([M+H$^+$]) = 619.2816, Found 619.2815.

3,6-bis(4-fluorophenyl)-1,4-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole (3as)



The compound **3as** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 54.6 mg, 92% yield, >19:1 d.r. was determined by ^{1}H NMR.

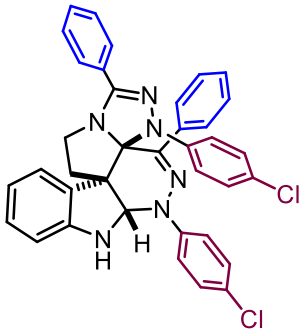
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 – 7.89 (m, 2H),7.76 – 7.62 (m, 2H), 7.53 – 7.43 (m, 3H), 7.25 – 7.19 (m, 4H), 7.18 – 7.09 (m, 2H), 7.02 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 – 6.85 (m, 2H), 6.80 – 6.68 (m, 3H), 6.67 – 6.53 (m, 3H), 5.81 (s, 1H), 4.99 (s, 1H), 3.89 – 3.71 (m, 1H), 3.47 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.95 (td, *J* = 11.2, 8.8 Hz, 1H), 2.12 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.50 (d, *J* = 246.34 Hz), 157.70 (d, *J* = 239.81 Hz), 156.74, 147.60, 144.68, 140.59, 140.57 (d, *J* = 3.1 Hz), 139.73 (d, *J* = 2.1 Hz), 136.35, 132.49, 130.17, 129.74 (d, *J* = 8.6 Hz), 128.97, 128.85, 128.74, 128.31, 128.24, 127.44, 127.33, 124.74, 120.49, 115.78 (d, *J* = 22.4 Hz), 115.15 (d, *J* = 7.6 Hz), 114.62 (d, *J* = 22.7 Hz), 111.60, 94.33, 77.78, 62.47, 54.31, 33.57.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.69, -123.85.

HRMS (ESI^+) m/z calcd for $C_{37}H_{28}F_2N_6$ ([M+H$^+$]) = 595.2416, Found 595.2415.

3,6-bis(4-chlorophenyl)-1,4-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3at)



The compound **3at** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 58.2 mg, 93% yield, >19:1 d.r. was determined by ^{1}H NMR.

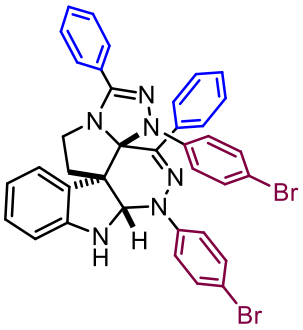
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 7.87 (m, 2H), 7.73 – 7.61 (m, 2H), 7.53 – 7.43 (m, 3H), 7.25 – 7.19 (m, 4H), 7.18 – 7.12 (m, 2H), 7.07 – 7.98 (m, 3H), 6.89 – 6.81 (m, 2H), 6.74 – 6.65 (m, 3H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.77 (s, 1H), 5.00 (s, 1H), 3.86 – 3.71 (m, 1H), 3.46 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.94 (td, *J* = 11.2, 8.8 Hz, 1H), 2.12 (dd, *J* = 10.8, 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.06, 147.63, 145.93, 143.12, 141.80, 136.12, 132.74, 132.24, 130.28, 129.31, 129.12, 129.00, 128.95, 128.62, 128.58, 128.28, 128.01, 127.54, 127.35, 125.65, 124.73, 120.55, 114.60, 111.66, 94.61, 77.48, 62.64, 54.27, 33.66.

HRMS (ESI^+) m/z calcd for $C_{37}H_{28}{}^{34.9689}Cl_2N_6$ ([M+H$^+$]) = 627.1825, Found 627.1823.

HRMS (ESI^+) m/z calcd for $C_{37}H_{28}{}^{36.9659}Cl_2N_6$ ([M+H$^+$]) = 629.1796, Found 629.1808.

3,6-bis(4-bromophenyl)-1,4-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3au)



The compound **3au** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 67.8 mg, 95% yield, >19:1 d.r. was determined by ^{1}H NMR.

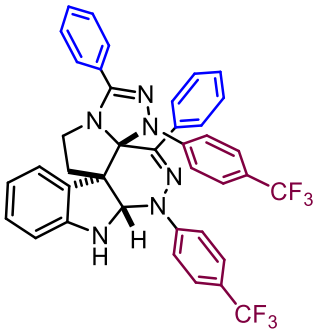
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.89 (m, 2H), 7.74 – 7.61 (m, 2H), 7.52 – 7.42 (m, 3H), 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 4H), 7.08 – 7.95 (m, 5H), 6.70 (td, *J* = 7.6, 1.2 Hz, 1H), 6.67 – 6.57 (m, 3H), 5.75 (s, 1H), 4.99 (s, 1H), 3.90 – 3.70 (m, 1H), 3.46 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.95 (td, *J* = 11.2, 8.8 Hz, 1H), 2.13 (dd, *J* = 10.8, 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.09, 147.65, 146.27, 143.59, 142.18, 136.05, 132.18, 132.03, 131.01, 130.29, 129.63, 128.99, 128.96, 128.63, 128.58, 128.28, 127.54, 127.34, 124.71, 120.73, 120.55, 114.85, 113.11, 111.67, 94.64, 77.48, 62.67, 54.24, 33.71.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{28}{}^{78.9183}Br_2N_6$ ([M+H$^+$]) = 715.0815, Found 715.0811.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{28}{}^{80.9163}Br_2N_6$ ([M+H$^+$]) = 717.0794, Found 717.0794

1,4-diphenyl-3,6-bis(4-(trifluoromethyl)phenyl)-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo [3',2':4,5]pyridazino[3,4-b]indole (3av)



The compound **3av** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 65.2 mg, 94% yield, >19:1 d.r. was determined by ^{1}H NMR.

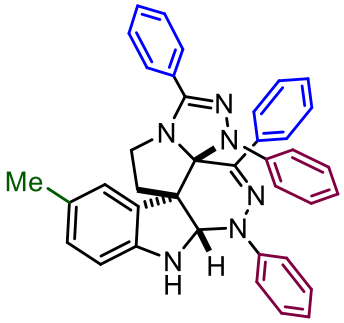
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 – 7.92 (m, 2H),7.72 – 7.62 (m, 2H), 7.54 – 7.46 (m, 3H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (td, *J* = 8.0,1.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.72 (td, *J* = 7.6,1.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 5.83 (s, 1H), 5.02(s, 1H), 3.90 – 3.77 (m, 1H), 3.51 (dd, *J* = 11.2, 8.8 Hz, 1H), 3.01(td, *J* = 11.2, 8.8 Hz, 1H), 2.19 (dd, *J* = 10.8, 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.55, 147.98, 147.88, 147.62, 145.34, 135.70, 131.85, 130.52, 129.13, 129.07, 128.39, 128.35, 127.71, 127.43, 126.51 (q, *J* = 3,7 Hz), 125.05 (q, *J* = 3,7 Hz), 124.73, 124.65 (q, *J* = 270.9 Hz), 123.60 (q, *J* = 272.4 Hz), 120.69, 112.23, 111.74, 94.99, 62.81, 54.22, 33.85.

^{19}F NMR (376 MHz, $CDCl_3$) *δ* = -61.71, -62.84.

HRMS (ESI^+) m/z calcd for $C_{39}H_{28}F_6N_6$ ([M+H^+]) = 695.2352, Found 695.2344.

10-methyl-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ba)



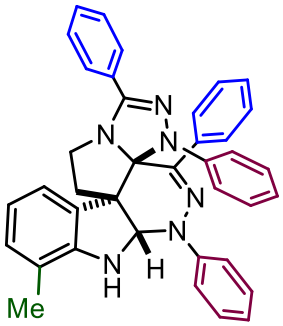
The compound **3ba** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 54.9 mg, 96% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.02 – 7.94 (m, 2H), 7.76 – 7.67 (m, 2H), 7.51 – 7.43 (m, 3H), 7.25 – 7.21 (m, 3H), 7.18 (dd, *J* = 5.6, 0.8 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.04 (d, *J* = 1.2 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.85 – 6.77 (m, 5H), 6.48 (d, *J* = 5.2 Hz, 1H), 5.91 (s, 1H), 4.95 (s, 1H), 3.84 – 3.74 (m, 1H), 3.47 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.98 (td, *J* = 7.2, 5.6 Hz, 1H), 2.17 (s, 3H), 2.11 (dd, *J* = 7.2, 4.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* = 156.46, 145.42, 144.50, 144.38, 143.36, 136.86, 133.02, 129.90, 129.58, 129.10, 129.06, 128.98, 128.89, 128.10, 128.06, 127.87, 127.64, 127.27, 127.04, 125.43, 120.26, 114.01, 111.45, 94.48, 77.88, 62.38, 54.32, 33.61, 21.20.

HRMS (ESI^+) m/z calcd for $C_{38}H_{32}N_6$ ([M+H^+]) = 573.2761, Found 573.2768.

8-methyl-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ca)



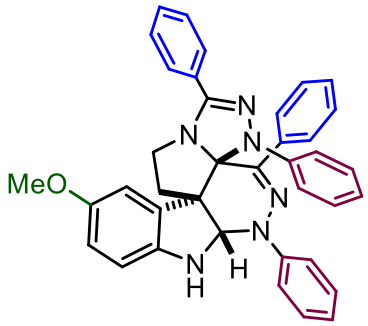
The compound **3ca** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); yellow solid; 51.5 mg, 90% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 – 7.89 (m, 2H), 7.77 – 7.67 (m, 2H), 7.51 – 7.40 (m, 3H), 7.25 – 7.19 (m, 3H), 7.18 – 7.17 (m, 2H), 7.16 – 7.10 (m, 3H), 6.95 – 6.88 (m, 2H), 6.86 – 6.75 (m, 5H), 6.64 (t, *J* = 5.2 Hz, 1H), 5.92 (s, 1H), 4.86 (s, 1H), 3.86 – 3.74 (m, 1H), 3.46 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.00 (td, *J* = 7.2, 5.6 Hz, 1H), 2.12 (dd, *J* = 7.2, 4.0 Hz, 1H), 1.96 (s, 3H),

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.53, 146.29, 144.52, 144.48, 143.33, 136.74, 132.18, 129.91, 129.84, 129.04, 129.00, 128.89, 128.12, 128.11, 127.90, 127.60, 127.28, 127.07, 122.30, 120.75, 120.47, 114.16, 94.44, 77.52, 62.66, 54.37, 33.71, 16.55.

HRMS (ESI$^+$) m/z calcd for $C_{38}H_{32}N_6$ ([M+H$^+$]) = 573.2761, Found 573.2766.

10-methoxy-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3da)



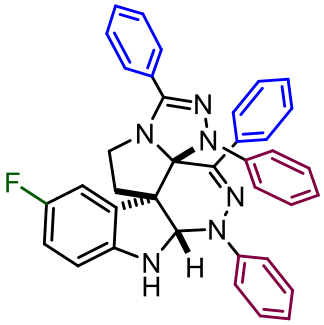
The compound **3da** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:4); light yellow solid; 47.6 mg, 81% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.91 (m, 2H), 7.79 – 7.71 (m, 2H), 7.50- 7.41 (m, 3H), 7.24 – 7.19 (m, 3H), 7.17 – 7.11 (m, 4H), 6.94 (d, *J* = 1.6 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.85 – 6.76 (m, 4H), 6.56 (dd, *J* = 5.6, 2.0 Hz, 1H), 6.50 (d, *J* = 5.6 Hz, 1H), 5.90 (s, 1H), 4.85 (s, 1H), 3.85 – 3.75 (m, 1H), 3.60 (s, 3H), 3.46 (dd, *J* = 7.6, 6.0 Hz, 1H), 2.99 (td, *J* = 7.6, 5.6 Hz, 1H), 2.13 (dd, *J* = 7.2, 4.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.48, 154.17, 144.38, 143.88, 143.30, 141.40, 136.78, 134.29, 129.97, 129.01, 128.92, 128.17, 128.14, 128.07, 127.87, 127.61, 127.26, 127.08, 120.31, 113.97, 113.22, 112.28, 111.97, 94.36, 78.11, 62.54, 56.01, 54.32, 33.57.

HRMS (ESI$^+$) m/z calcd for $C_{38}H_{32}N_6O$ ([M+H$^+$]) = 589.2710, Found 589.2711.

10-fluoro-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]Pyrid azino[3,4-b]indole (3ea)



The compound **3ea** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 54.2 mg, 94% yield, >19:1 d.r. was determined by ^{1}H NMR.

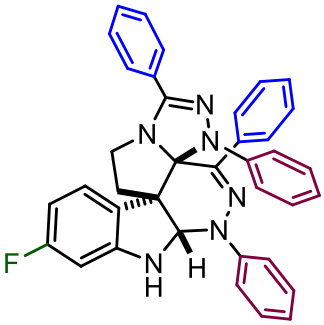
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.88 (m, 2H), 7.81 – 7.66 (m, 2H), 7.52 – 7.42 (m, 3H), 7.25 – 7.20 (m, 3H), 7.19 – 7.10 (m, 4H), 7.05 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.87 – 6.76 (m, 4H), 6.71 (td, *J* = 8.8, 2.8 Hz, 1H), 6.49 (dd, *J* = 8.4, 4.0 Hz, 1H), 5.92 (s, 1H), 4.96 (s, 1H), 3.83 – 3.70 (m, 1H), 3.48 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.01 (td, *J* = 11.2, 8.8 Hz, 1H), 2.13 (dd, *J* = 11.2, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.16 (d, *J* = 248.3 Hz), 156.48, 144.25, 143.95, 143.73 (d, *J* = 1.2 Hz) , 143.18, 136.59, 134.35 (d, *J* = 7.9 Hz), 130.05, 129.07, 128.95, 128.79, 128.33, 128.27, 128.02, 127.93, 127.50, 127.28, 127.15, 120.48, 114.96 (d, *J* = 23.4 Hz), 113.95, 112.36 (d, *J* = 25.3 Hz), 111.91 (d, *J* = 8.2 Hz), 94.11, 77.99, 62.59, 62.57, 54.22, 33.53.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -123.95.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{29}FN_6$ ([M+H$^+$]) = 577.2510, Found 577.2515.

9-fluoro-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]Pyridazino[3,4-b]indole (3fa)



The compound **3fa** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 50.7 mg, 88% yield, >19:1 d.r. was determined by ^{1}H NMR.

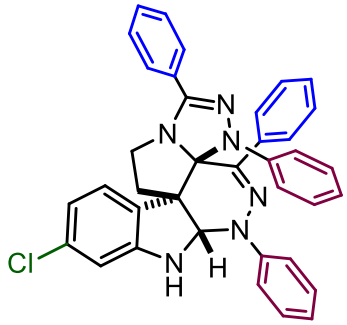
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 – 7.89 (m, 2H), 7.75 – 7.62 (m, 2H), 7.49 – 7.40 (m, 3H), 7.25 – 7.17 (m, 4H), 7.16 – 7.10 (m, 4H), 6.95 – 6.87 (m, 2H), 6.86 – 6.74 (m, 4H), 6.41 – 6.33 (m, 1H), 6.29 (dd, *J* = 9.2, 2.4 Hz, 1H), 5.92 (s, 1H), 5.15 (s, 1H), 3.86 – 3.67 (m, 1H), 3.47 (dd, *J* = 10.8, 8.4 Hz, 1H), 2.99 (td, *J* = 11.2, 8.4 Hz, 1H), 2.10 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.55 (d, J = 244.2 Hz), 156.46, 149.49 (d, J = 11.7 Hz), 144.62, 144.33, 143.19, 136.53, 130.02, 129.09, 128.93, 128.88, 128.36 (d, J = 2.3 Hz), 128.28, 128.21, 128.01, 127.94, 127.57, 127.26, 127.14, 125.44 (d, J = 10.2 Hz), 120.53, 113.92, 106.52 (d, J = 22.7 Hz), 99.66 (d, J = 26.4 Hz), 94.26, 77.76, 61.72, 54.27, 33.68.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.43.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{29}FN_6$ ([M+H$^+$]) = 577.2510, Found 577.2507.

9-chloro-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]Pyrid azino[3,4-b]indole (3ga)



The compound **3ga** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 56.2 mg, 95% yield, >19:1 d.r. was determined by ^{1}H NMR.

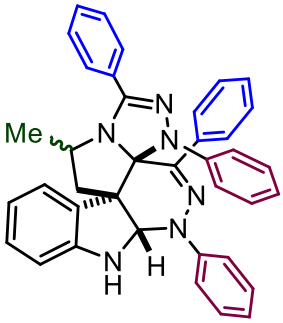
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.91 (m, 2H), 7.77 – 7.65 (m, 2H), 7.51 – 7.42 (m, 3H), 7.25 – 7.21 (m, 3H), 7.20 – 7.11 (m, 5H), 6.95 – 6.88 (m, 2H), 6.87 – 6.75 (m, 4H), 6.66 (dd, J = 8.0, 1.6 Hz, 1H), 6.56 (d, J = 1.6 Hz, 1H), 5.92 (s, 1H), 5.15 (s, 1H), 3.82 – 3.64 (m, 1H), 3.48 (dd, J = 11.2, 8.4 Hz, 1H), 3.00 (td, J = 11.2, 8.8 Hz, 1H), 2.10 (dd, J = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.42, 149.10, 144.44, 144.27, 143.12, 136.48, 134.31, 131.40, 130.03, 129.10, 128.93, 128.82, 128.29, 128.23, 128.00, 127.93, 127.53, 127.25, 127.16, 125.42, 120.57, 120.18, 113.91, 111.91, 94.13, 77.54, 61.94, 54.23, 33.57.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{29}{}^{34.9689}ClN_6$ ([M+H$^+$]) = 593.2215, Found 593.2214.

HRMS (ESI$^+$) m/z calcd for $C_{37}H_{29}{}^{36.9659}ClN_6$ ([M+H$^+$]) = 594.2249, Found 594.2241.

13-methyl-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyrid azino[3,4-b]indole (3ha)



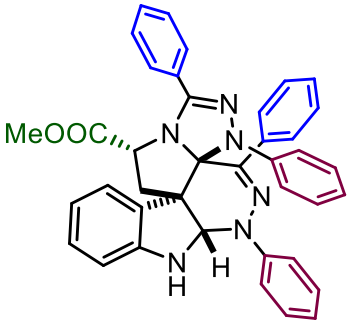
The compound **3ha** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 45.8 mg, 80% yield, 3.9:1 d.r. was determined by ^{1}H NMR of the crude reaction mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.90 (m, 2H), 7.80 – 7.73 (m, 2H), 7.50 – 7.38 (m, 4H), 7.24 – 7.16 (m, 4H), 7.15 – 7.09 (m, 3H), 7.01 – 6.91 (m, 3H), 6.82 – 6.70 (m, 5H), 6.56 (d, *J* = 7.6 Hz, 1H), 5.82 (s, 1H), 5.03 (s, 1H), 4.34 – 4.19 (m, 1H), 2.75 (t, *J* = 10.8 Hz, 1H), 2.35 (dd, *J* = 10.8, 6.0 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.23, 147.78, 144.66, 143.64, 143.17, 137.06, 133.13, 131.42, 129.50, 128.91, 128.74, 128.72, 128.13, 127.99, 127.76, 126.85, 126.81, 124.85, 120.43, 120.19, 113.76, 111.54, 96.84, 60.05, 60.03, 43.86, 19.30.

HRMS (ESI$^+$) m/z calcd for $C_{38}H_{32}N_6$ ([M+H$^+$]) = 573.2761, Found 573.2759.

methyl (13R)-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole-13-carboxylate (3ia)



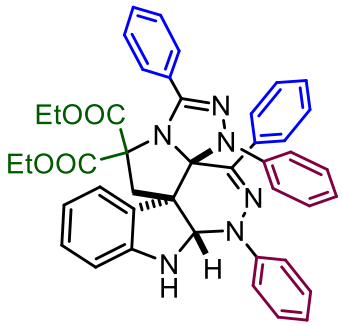
The compound **3ia** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid; 57.3 mg, 93% yield, 2.7:1 d.r. was determined by ^{1}H NMR of the crude reaction mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.87 (m, 2H), 7.77 – 7.68 (m, 2H), 7.44 – 7.38 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.17 (m, 5H), 7.12 (td, *J* = 7.2, 2.0 Hz, 2H), 7.01 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.85 – 6.70 (m, 5H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 1H), 5.05 (s, 1H), 4.61 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.35 (t, *J* = 10.8 Hz, 1H), 3.09 (s, 3H), 2.38 (dd, *J* = 10.8, 5.6 Hz, 1H),

^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.93, 152.82, 147.67, 144.27, 143.50, 143.10, 136.61, 132.42, 129.88, 129.17, 129.05, 128.99, 128.49, 128.29, 128.18, 128.05, 128.01, 127.70, 127.51, 127.09, 124.51, 120.54, 120.52, 114.05, 111.83, 95.06, 77.37, 65.98, 60.86, 52.14, 39.09.

HRMS (ESI$^+$) m/z calcd for $C_{39}H_{32}N_6O_2$ ([M+H$^+$]) = 617.2660, Found 617.2663.

Diethyl 1,3,4,6-tetraphenyl-6a,7-dihydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]pyridazino[3,4-b]indole-13,13(12H)-dicarboxylate (3ja)



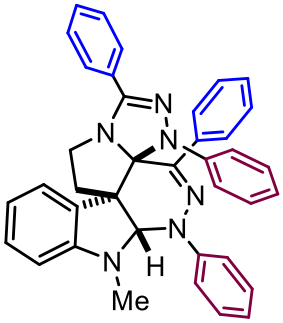
The compound **3ja** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid; 50.6 mg, 72% yield, >19:1 d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 – 8.25 (m, 2H), 8.11 – 8.02 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 7.13 – 7.07 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.94 (td, *J* = 7.6,1.2 Hz, 1H), 6.04 – 6.74 (m, 4H), 6.66 (td, *J* = 7.6,1.2 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 5.87 (s, 1H), 4,96 (s, 1H), 4.17 – 4.07 (m, 2H), 3.99 (d, *J* = 12.0 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.44 – 3.33 (m, 1H), 3.14 (d, *J* = 12.0 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.17, 166.78, 152.22, 147.30, 144.06, 142.83, 140.14, 136.84, 132.35, 129.51, 128.89, 128.83, 128.29, 128.20, 128.12, 128.09, 127.87, 127.66, 127.14, 124.77, 120.54, 120.12, 114.23, 111.52, 98.07, 79.83, 78.60, 62.82, 62.13, 58.77, 44.28, 13.90, 13.00.

HRMS (ESI$^+$) m/z calcd for $C_{43}H_{38}N_6O_4$ ([M+H$^+$]) = 703.3027, Found 703.3019.

7-methyl-1,3,4,6-tetraphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5]Pyridazino[3,4-b]indole (3ka)



The compound **3ka** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 22.9 mg, 40% yield, >19:1 d.r. was determined by ^{1}H NMR.

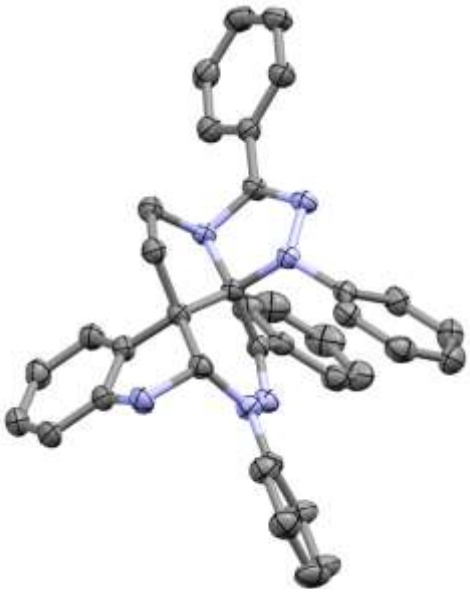
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 – 7.90 (m, 2H), 7.70 – 7.61 (m, 2H), 7.49 – 7.41 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.15 (m, 4H), 7.11 – 7.02 (m, 5H), 6.94 – 6.81 (m, 4H), 6.64 (td, *J* = 7.2, 0.8 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 5.91 (s, 1H), 3.82 – 3.62 (m, 1H), 3.41 (dd, *J* = 10.8, 8.4 Hz, 1H), 2.98 (td, *J* = 11.2, 8.8 Hz, 1H), 2.63 (s, 3H), 2.01 (dd, *J* = 10.8, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.44, 149.39, 146.50, 144.74, 144.13, 136.77, 133.88, 129.83, 129.07, 128.86, 128.37, 128.34, 128.25, 128.09, 127.82, 127.48, 127.27, 127.23, 124.50, 121.86, 118.93, 118.82, 108.49, 93.73, 83.98, 62.68, 53.88, 35.41, 34.03.

HRMS (ESI$^+$) m/z calcd for $C_{38}H_{32}N_6$ ([M+H$^+$]) = 573.2761, Found 573.2757.

10. The X-ray data for 3aa.

The X-ray data for 3aa: The **3aa** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at rt. CCDC-2022402 (**3aa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif. The yellow crystal in block-shape, with approximate dimensions of 0.255 × 0.104 × 0.071 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 171(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.[4]



X-ray structure of **3aa**

Crystallographic Data for **3aa**.

Formula	C_{37} H_{30} N_6

Formula mass (amu)	558.6777
Space group	P 21/c
a (Å)	14.0564(9)
b (Å)	11.0498(8)
c (Å)	18.7354(15)
α (deg)	90
β (deg)	105.202(2)
γ (deg)	90
V (Å^3)	2808.2(4)
Z	4
λ (Å)	0.71073
T (K)	171K
ρ_{calcd} (g cm^{-3})	1.321
μ (mm^{-1})	0.080
Transmission factors	0.920,1.000
θ_{max} (deg)	27.701
No. of unique data, including $F_o^2 < 0$	6481
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3443
No. of variables	392
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0574
$R_w(F_o^2)$ [b]	0.1817
Goodness of fit	1.092

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

11. References

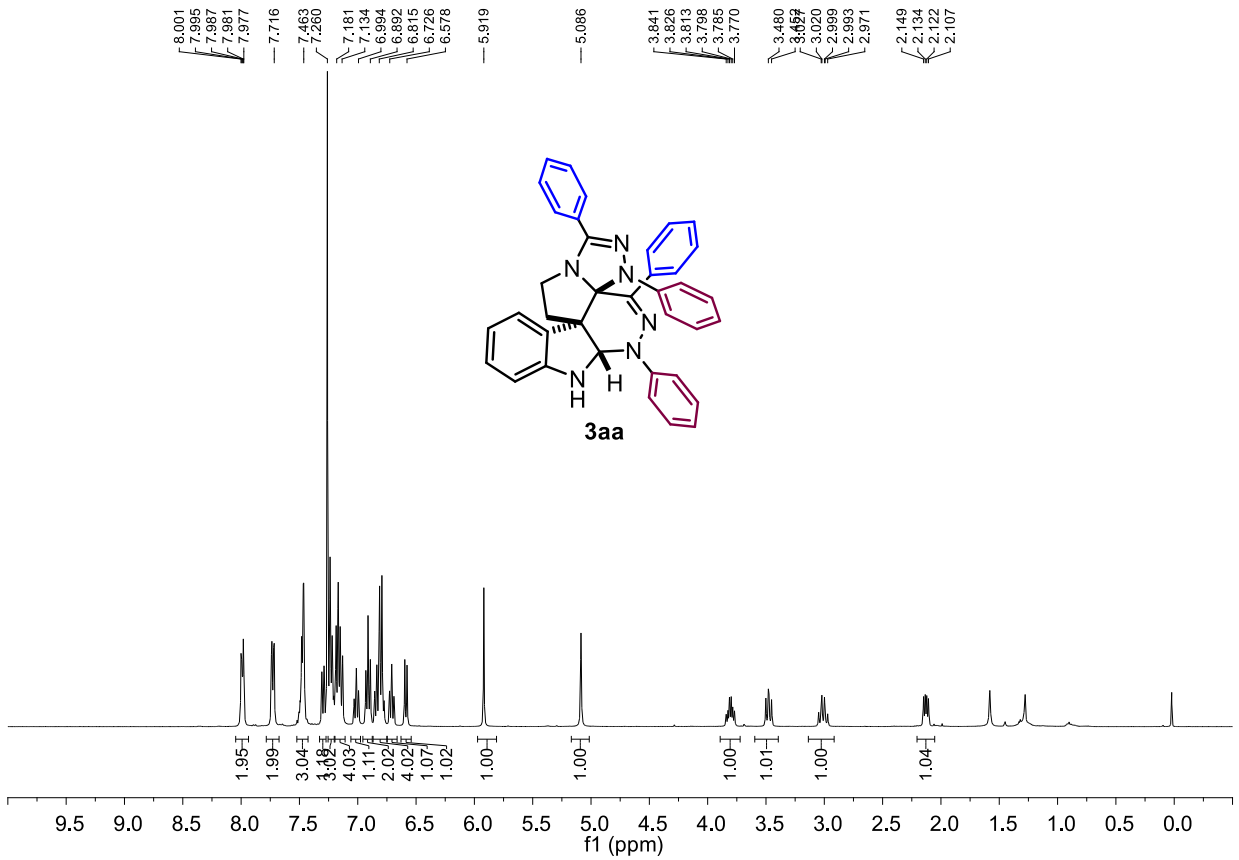
1. (a) H. Liu and A. Dömling, Efficient and Diverse Synthesis of Indole Derivatives, *J. Org. Chem*., 2009, **74**, 6895–6898; (b) W. Wang, E. Herdtweck and A. Dömling, Polycyclic Indole Alkaloid-type Compounds by MCR, *Chem. Commun*., 2010, **46**, 770–772; (c) X. H. Zhao, X. H. Liu, H. J. Mei, J. Guo, L. L. Lin and X. M. Feng, Asymmetric Dearomatization of Indoles through Michael/Friedel–Crafts-Type Cascade to Construct Polycyclic Spiroindolines, *Angew. Chem. Int. Ed*., 2015, **54**, 4032–4035.

2. (a) M. Giustiniano, V. Mercalli, J. Amato, E. Novellino and G. C. Tron, Exploiting the Electrophilic and Nucleophilic Dual Role of Nitrile Imines: One-Pot, Three-Component Synthesis of Furo[2,3-*d*]pyridazin-4(5*H*)-ones, *Org. Lett*., 2015, **17**, 3964−3967; (b) L. K. B. Garve, M. Petzold, P. G. Jones and D. B. Werz, [3 + 3]-Cycloaddition of Donor–Acceptor Cyclopropanes with Nitrile Imines Generated in Situ: Access to Tetrahydropyridazines, *Org. Lett*., 2016, **18**, 564−567.

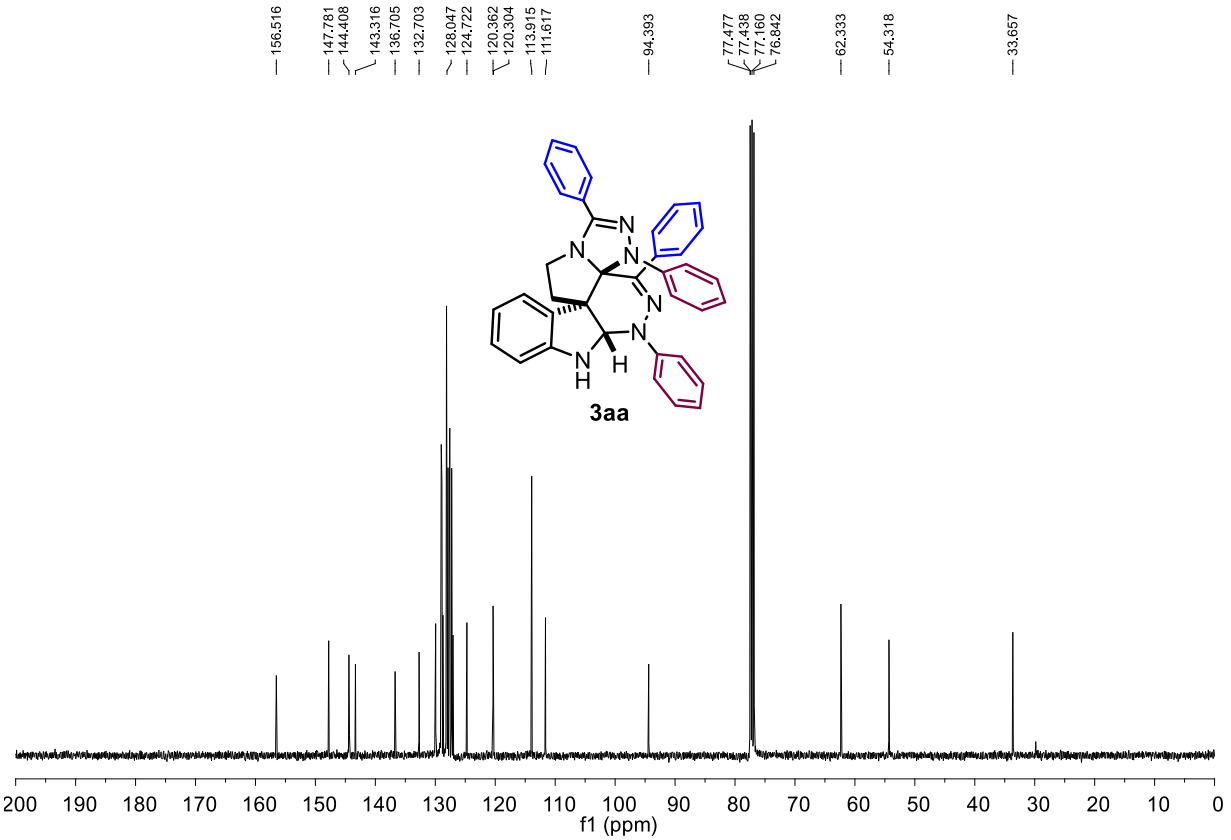
3. (a) C. J. A. Ribeiro, R. C. Nunes, J. D. Amaral, L. M. Goncalves, C. M. P. Rodrigues, R. Moreira and M. M. M. Santos, Spirotriazoline Oxindoles: A Novel Chemical Scaffold with in Vitro Anticancer Properties, *Eur. J. Med. Chem*., 2017, **140**, 494−509; (b) L. Li, J. Liu and M. Shi, A Highly Regio- and Diastereoselective Four-Component Reaction to Construct Polycyclic Bispiroindolines from 2-Isocyanoethylindoles and Isocyanates, *Org. Lett*., 2018, **20**, 7076–7079; (c) W.-B. Cao, S. Li, M.-M. Xu, H. Li, X.-P. Xu, Y. Lan and S.-J. Ji, Hydrogen-Bonding-Promoted Cascade Rearrangement Involving the Enlargement of Two Rings: Efficient Access to Polycyclic Quinoline Derivatives, *Angew. Chem. Int. Ed.*, 2020, **59**, 21425–21430.

4. (a) G. M. Sheldrick, A Short History of SHELX, *Acta Cryst.*, 2008, **A64**, 112–122; (b) G. M. Sheldrick, SHELXT – Integrated Space-group and Crystal-structure Determination, *Acta Cryst.*, 2015, **A71**, 3–8; (c) G. M. Sheldrick, Crystal Structure Refinement with SHELXL, *Acta Cryst*., 2015, **C71**, 3–8.

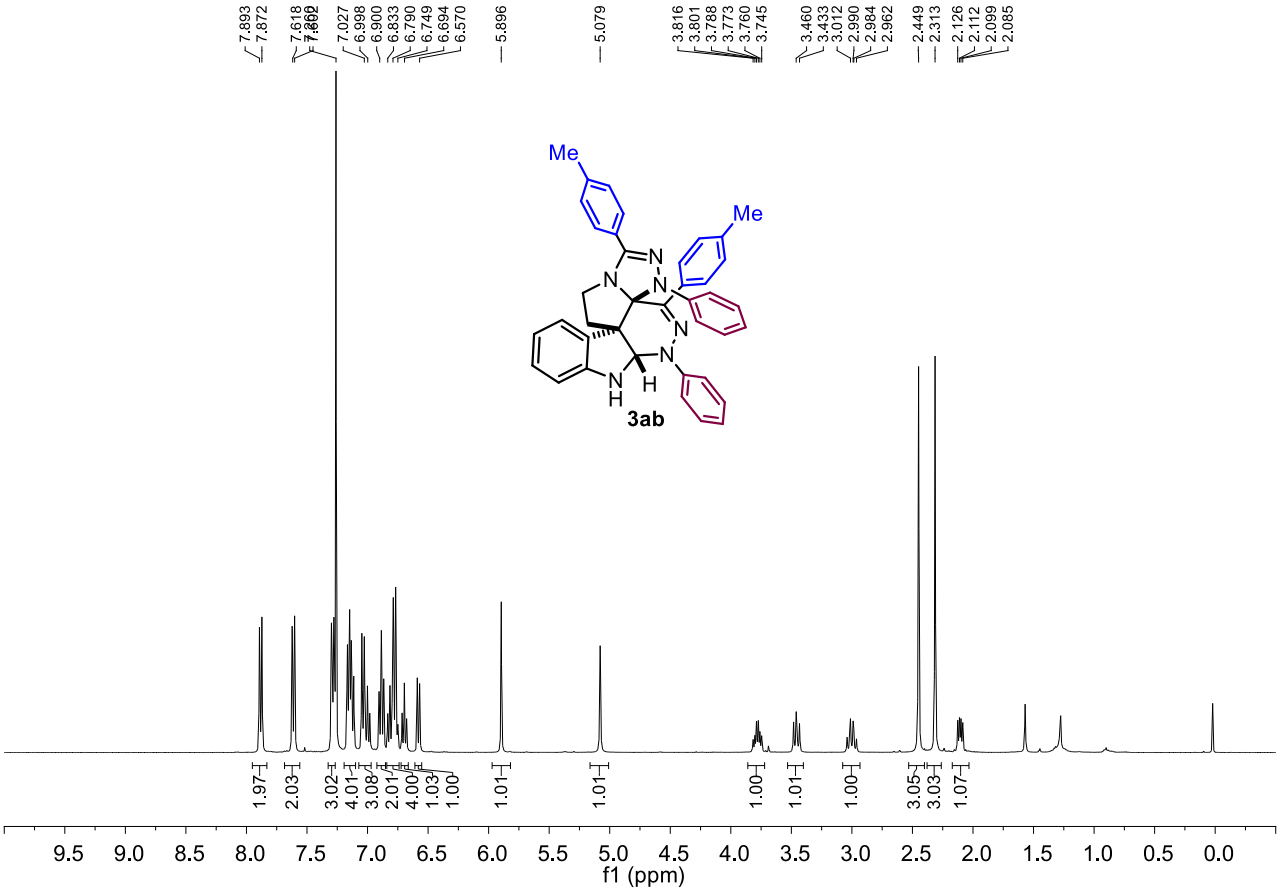
12. Copies of NMR spectra for the reaction products



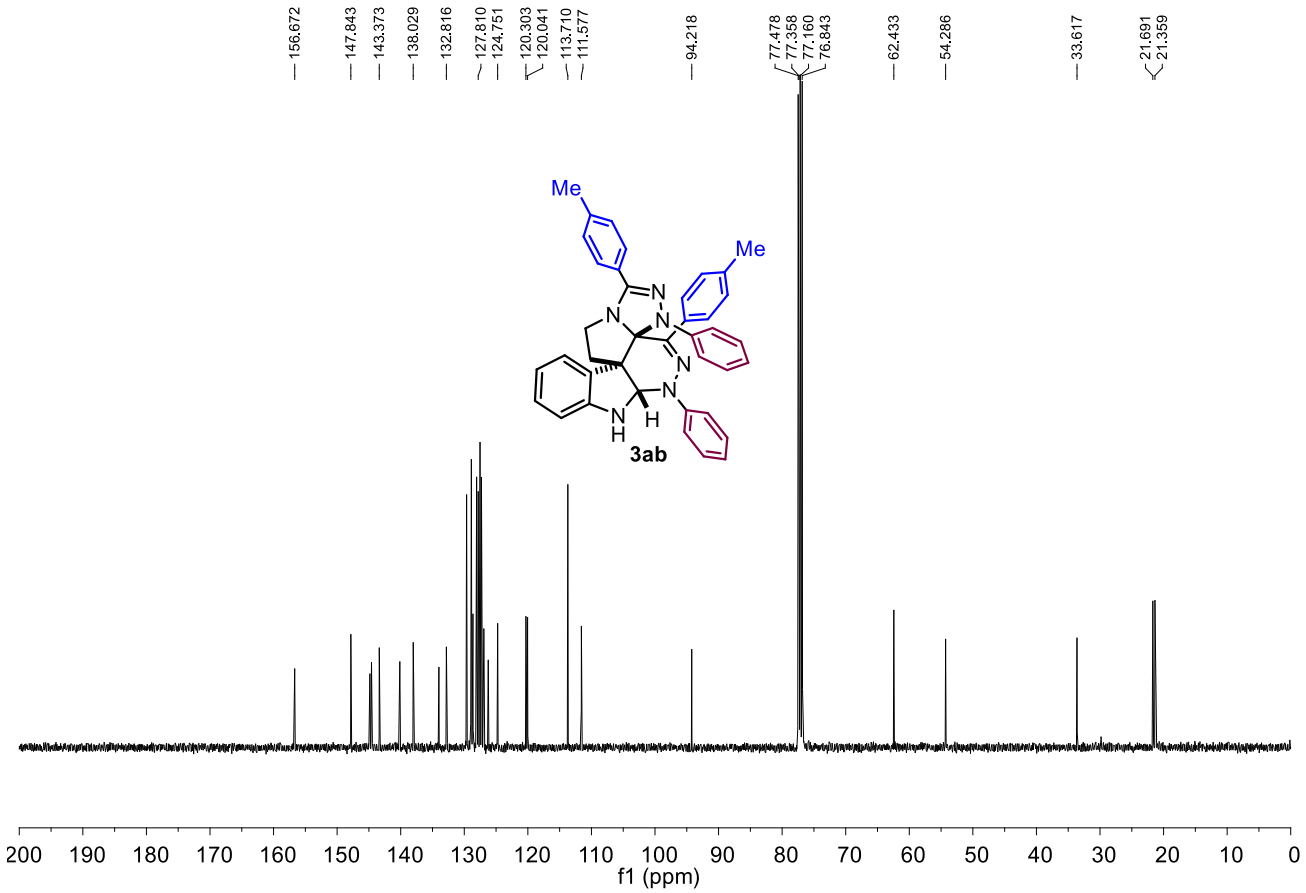
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



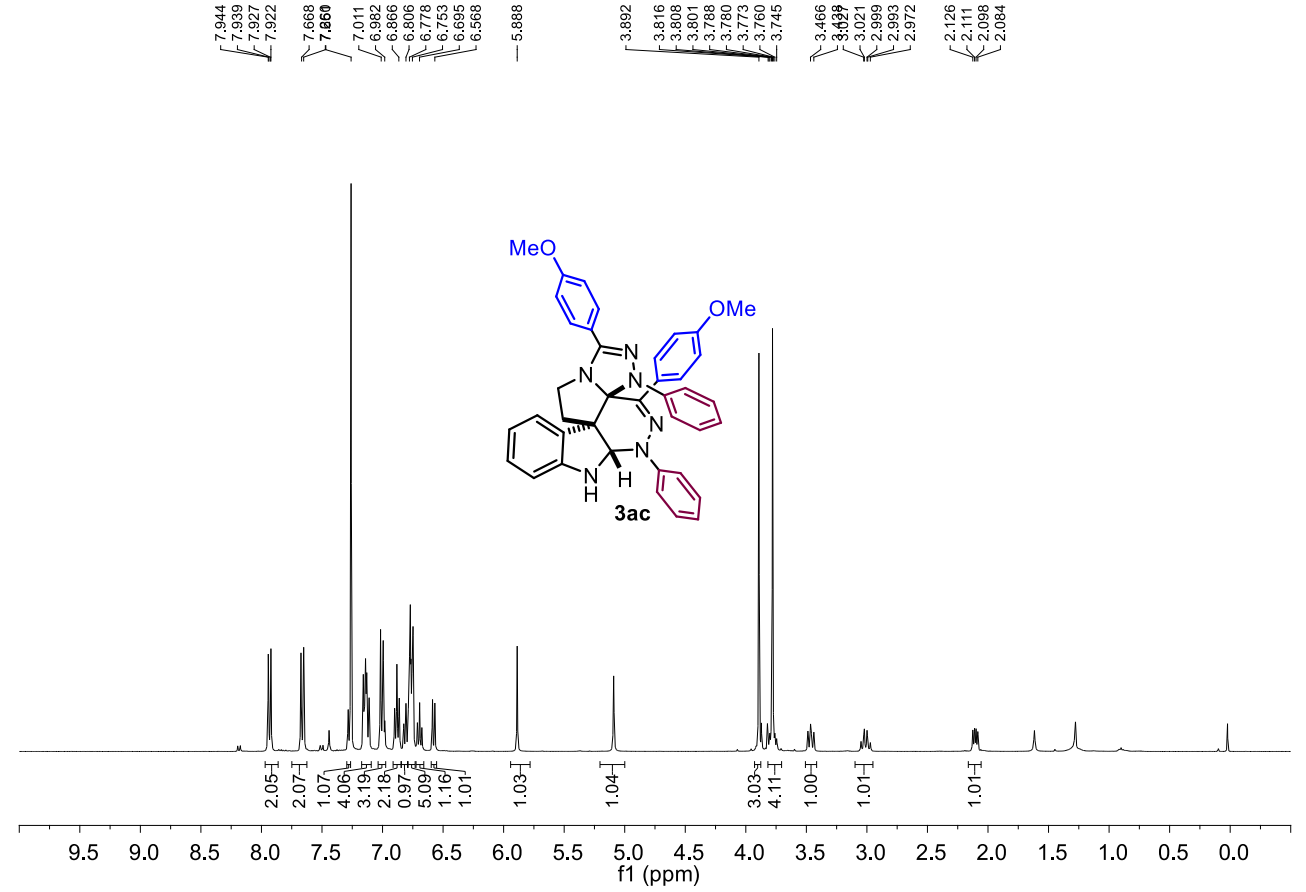
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



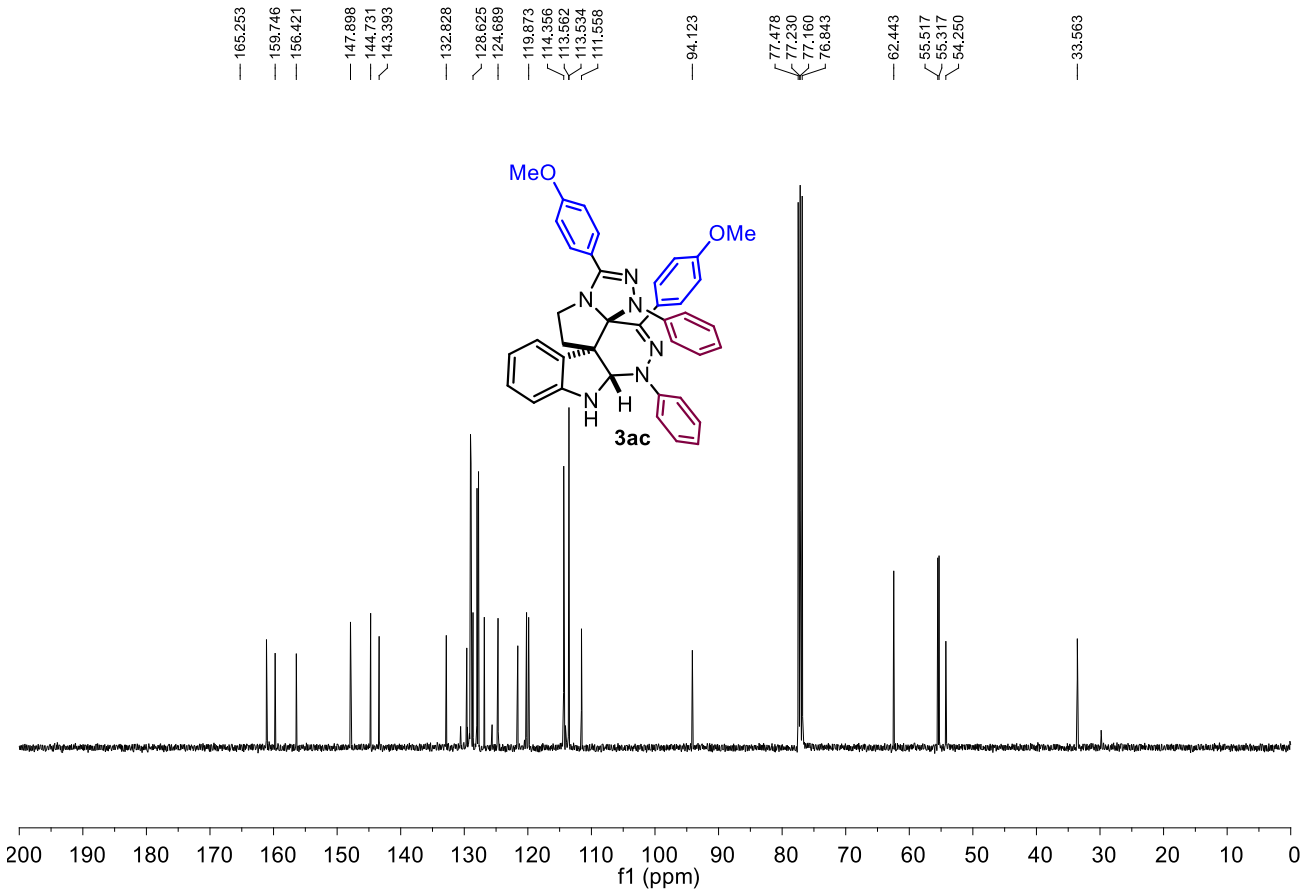
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



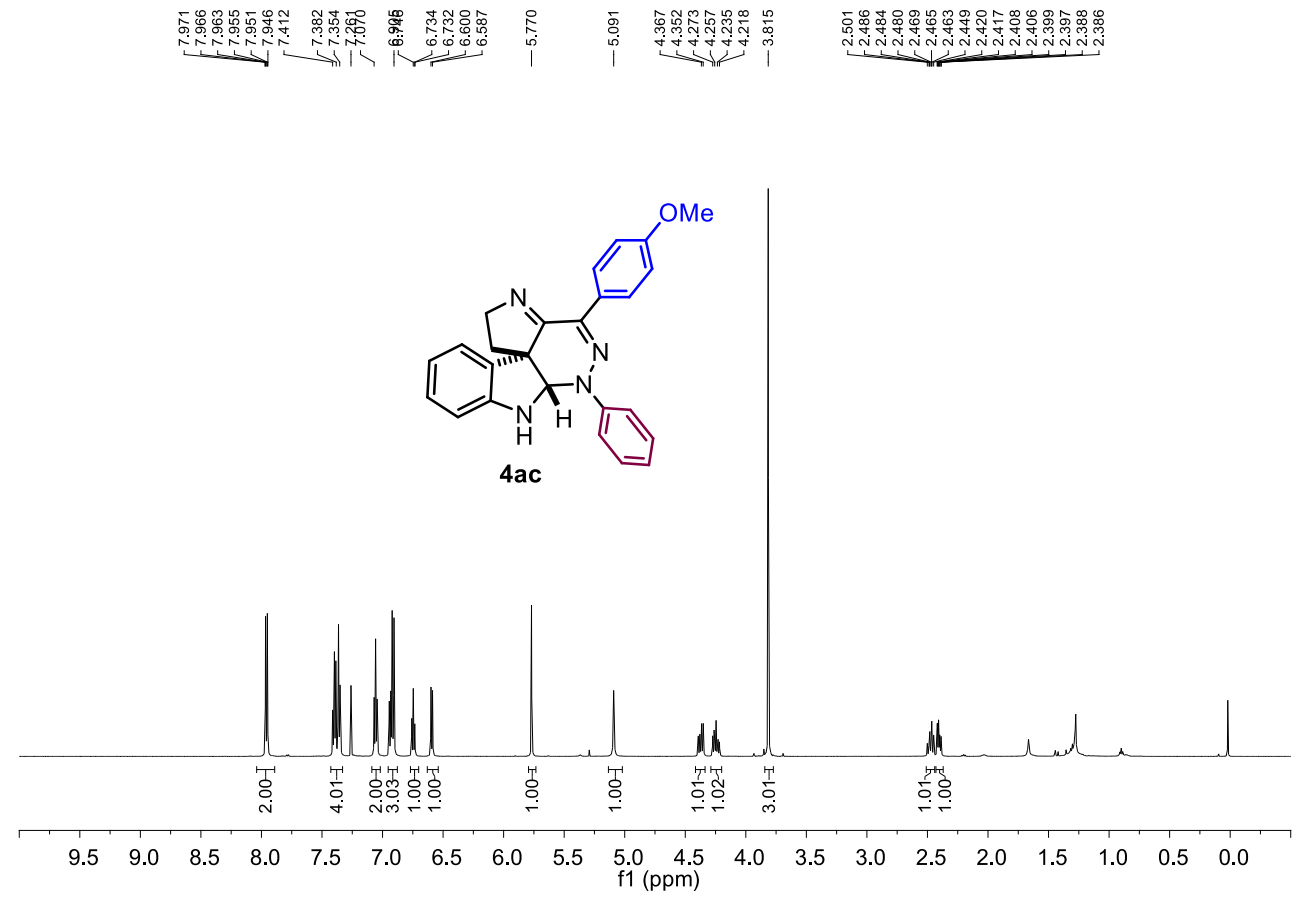
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



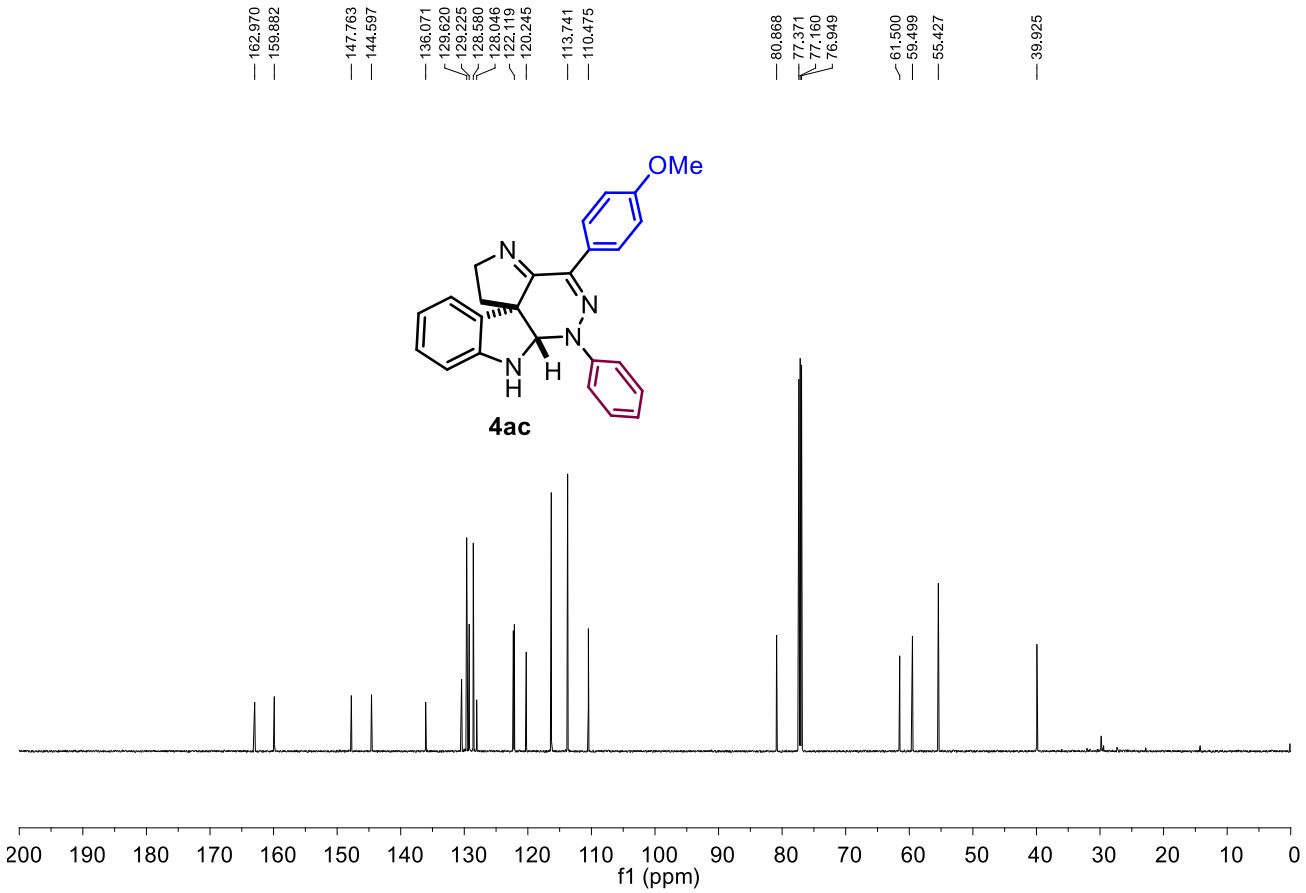
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



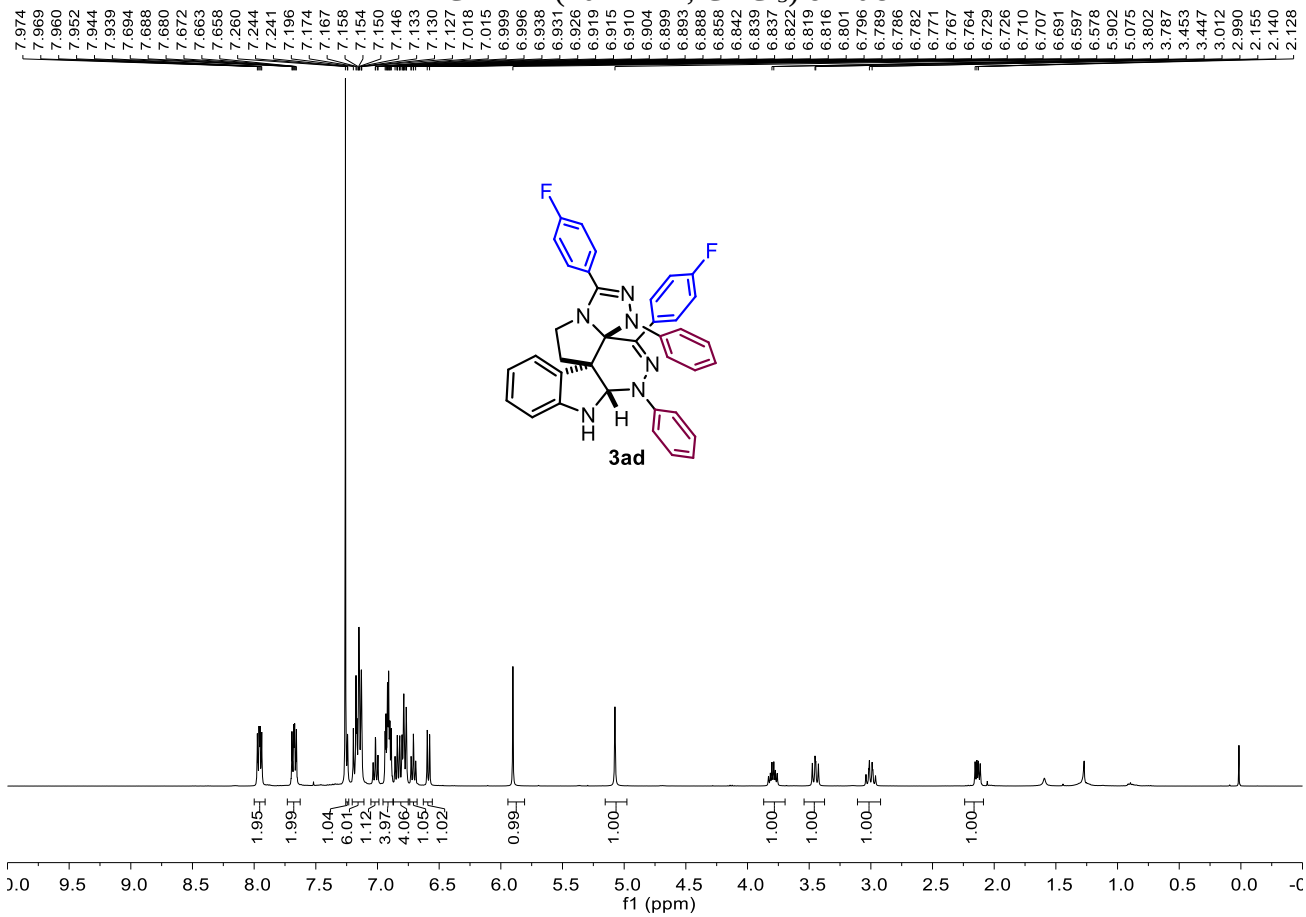
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



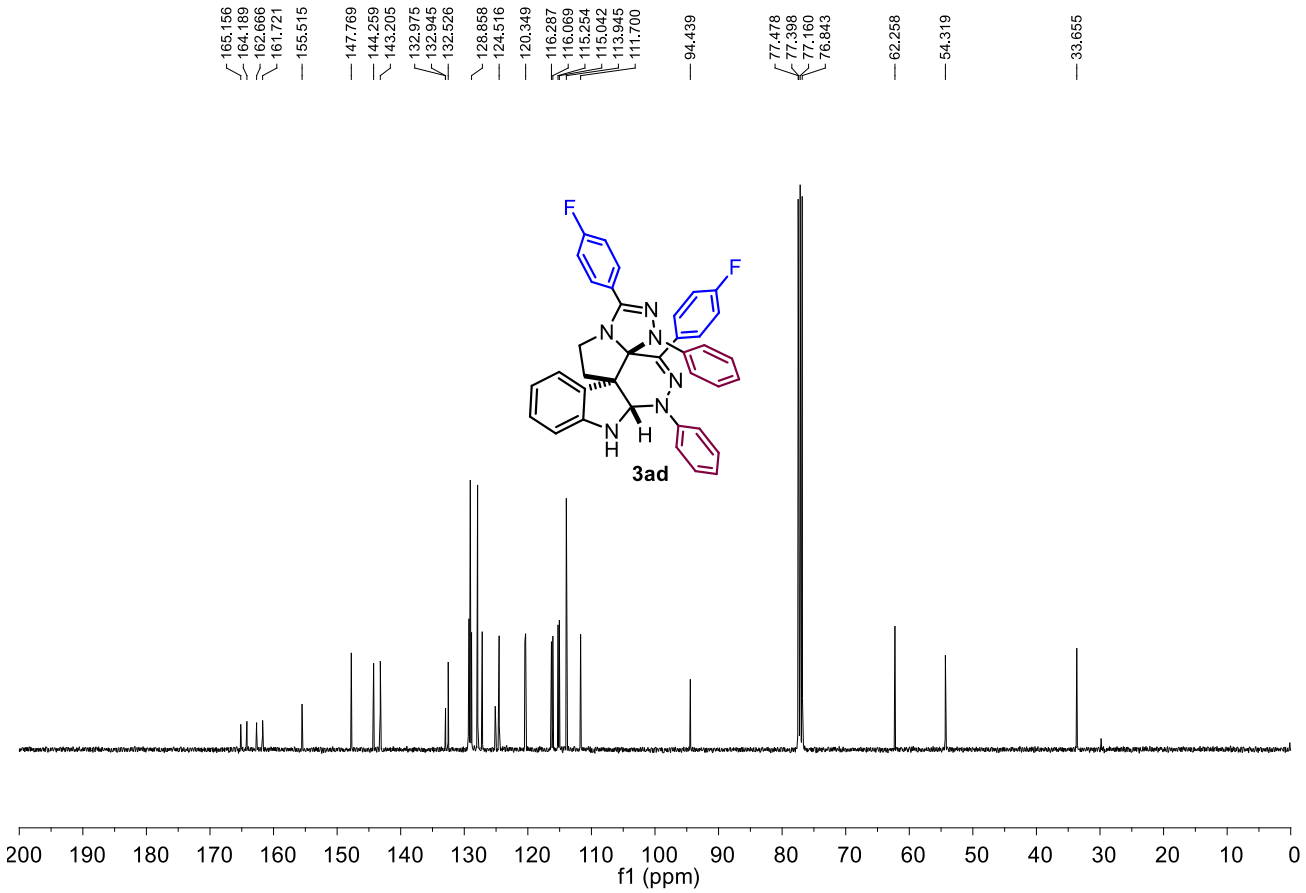
^{1}H NMR (400 MHz, $CDCl_3$) of **4ac**



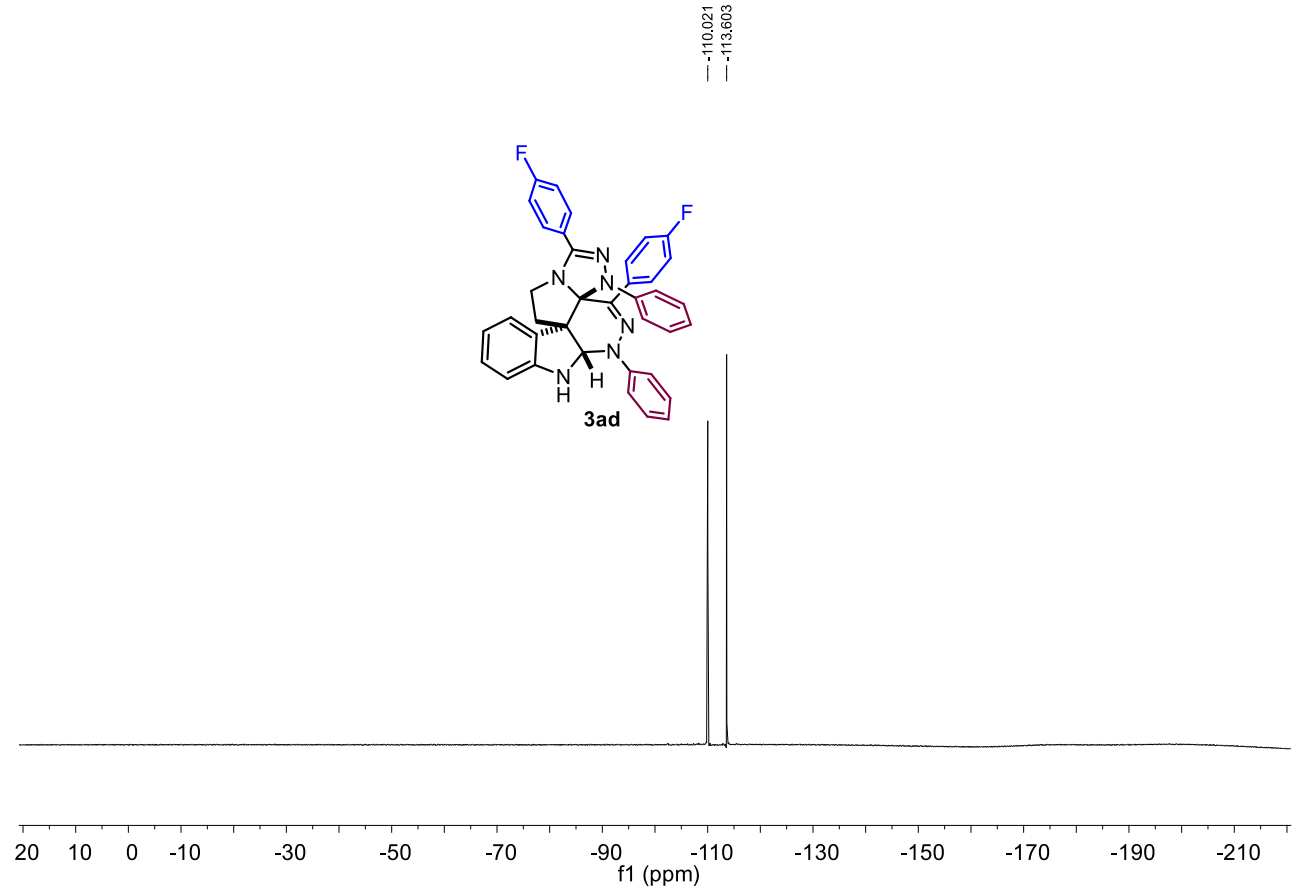
^{13}C NMR (101 MHz, $CDCl_3$) of **4ac**



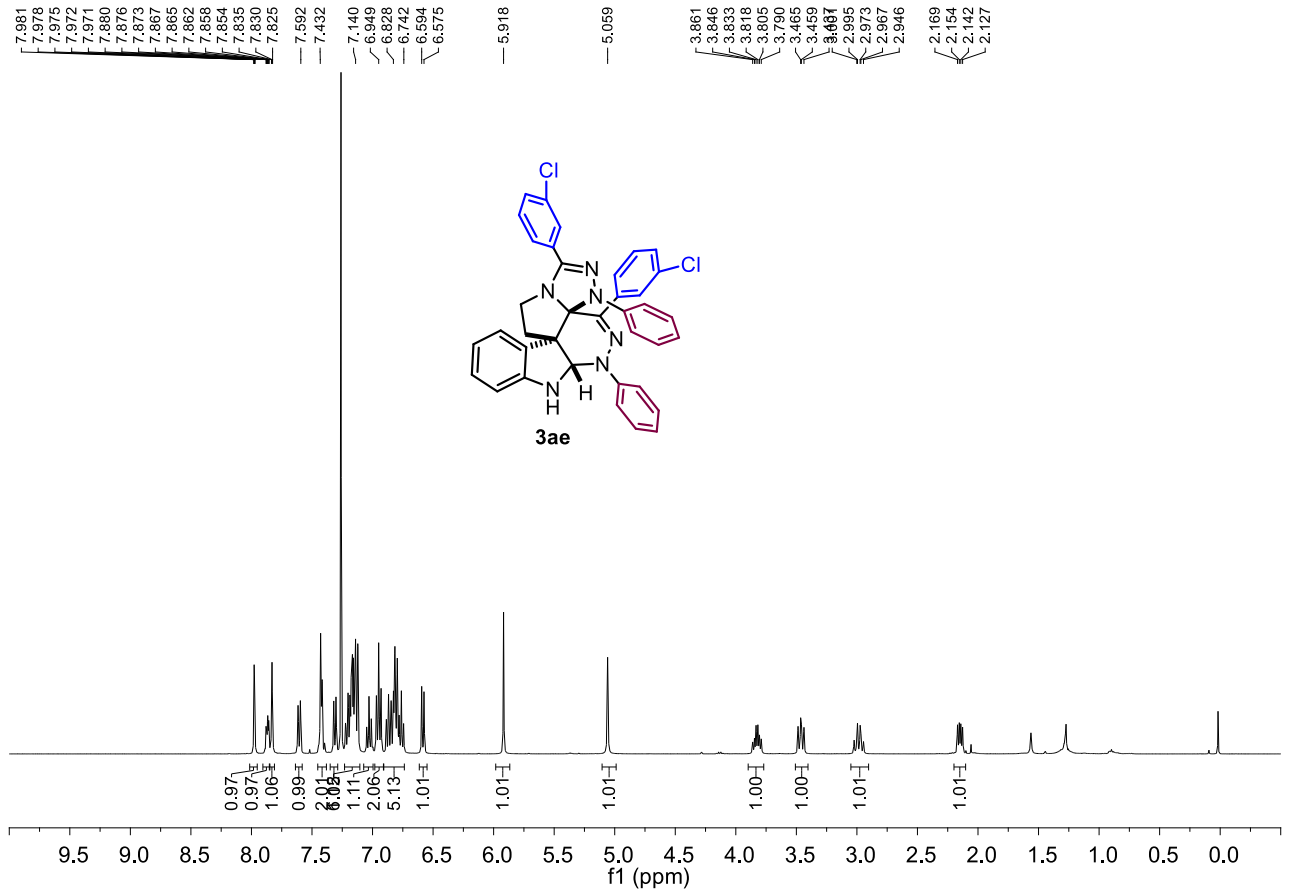
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



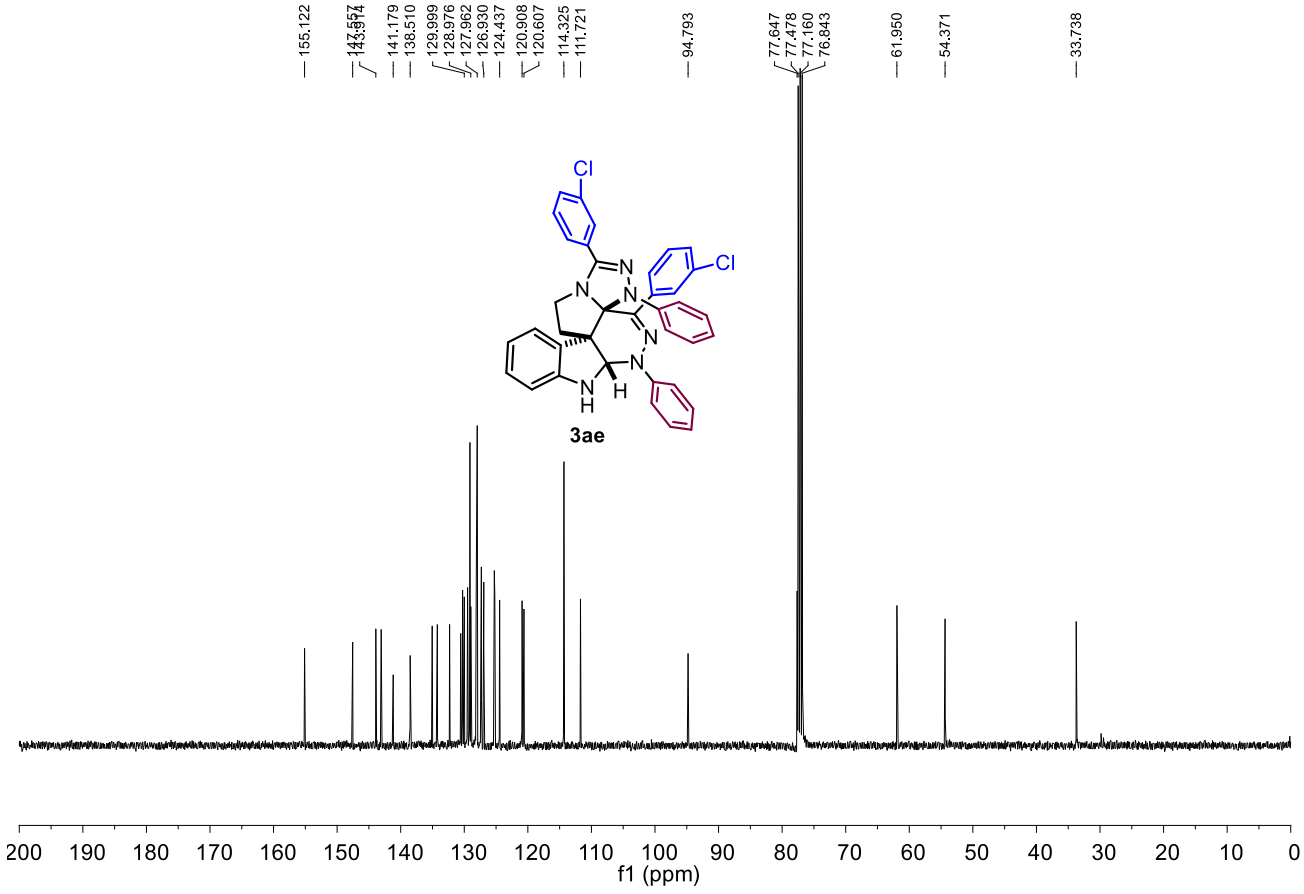
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



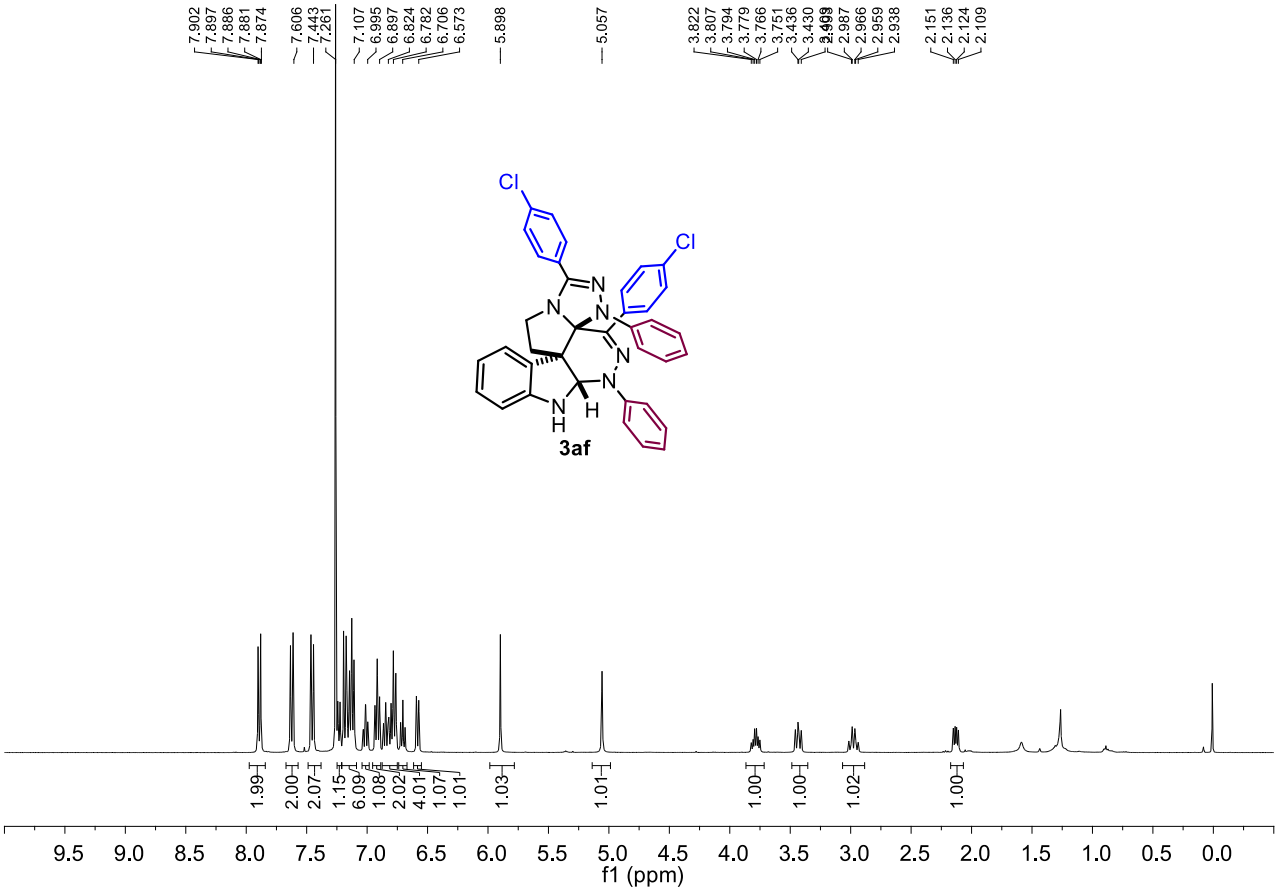
^{19}F NMR (376 MHz, $CDCl_3$) of **3ad**



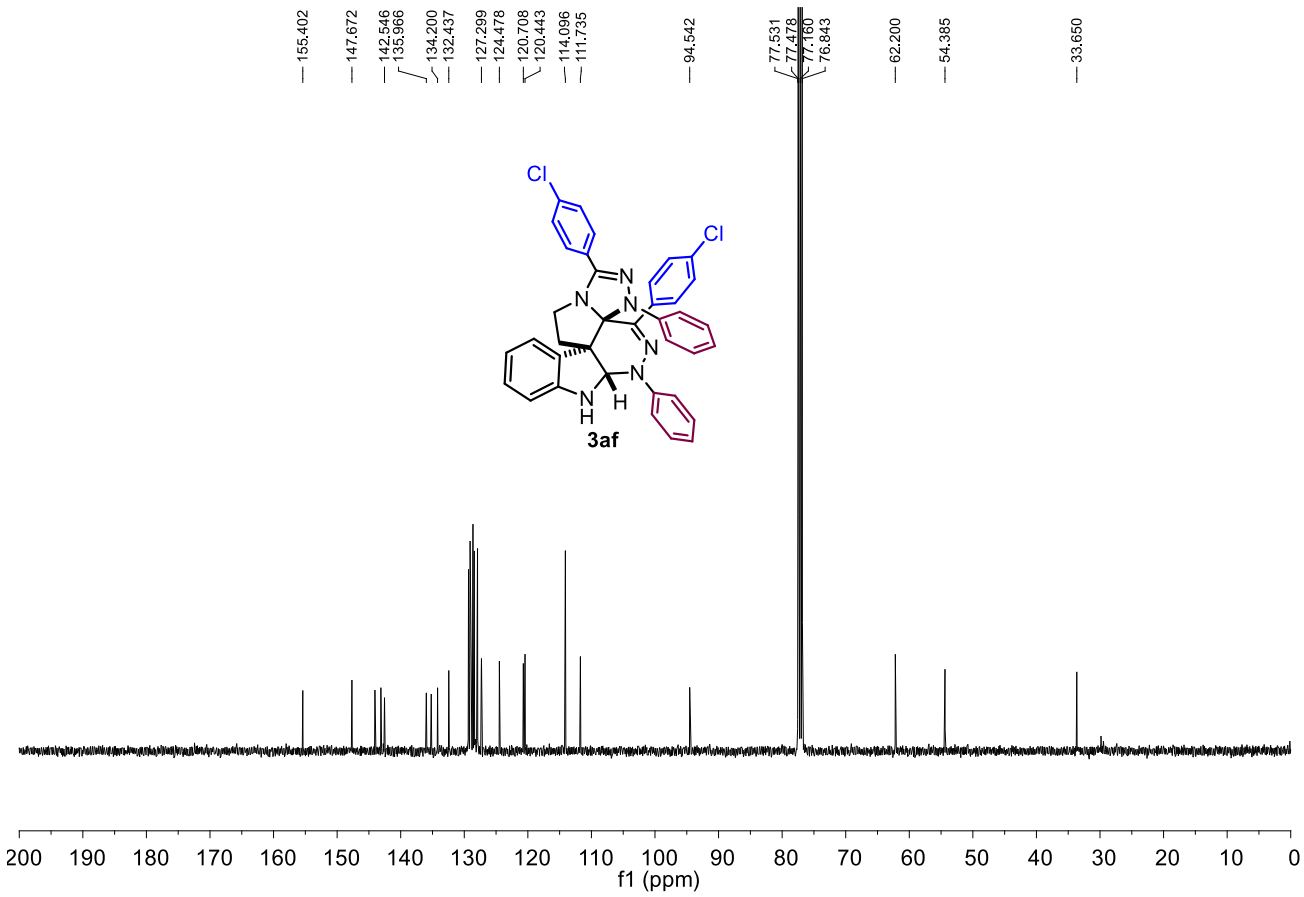
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



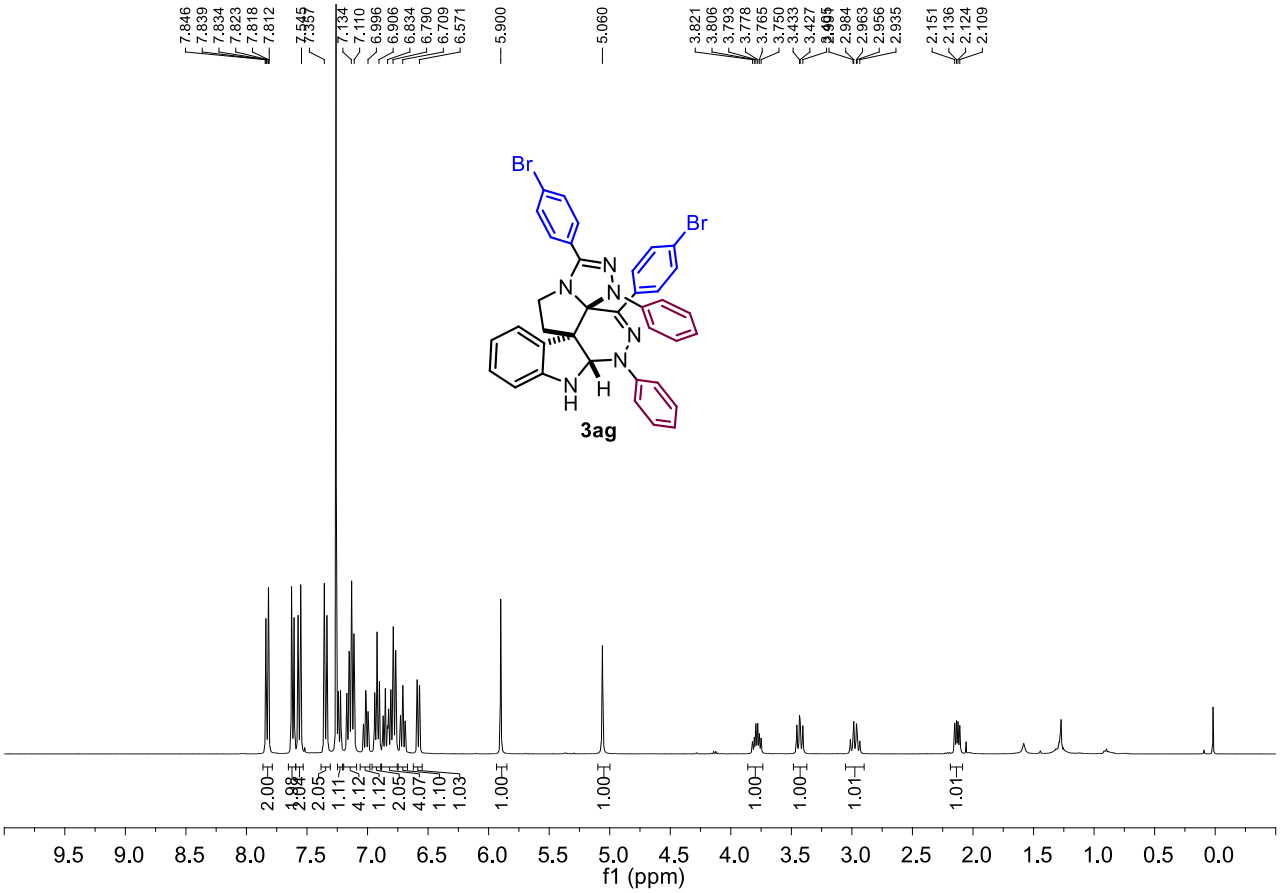
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



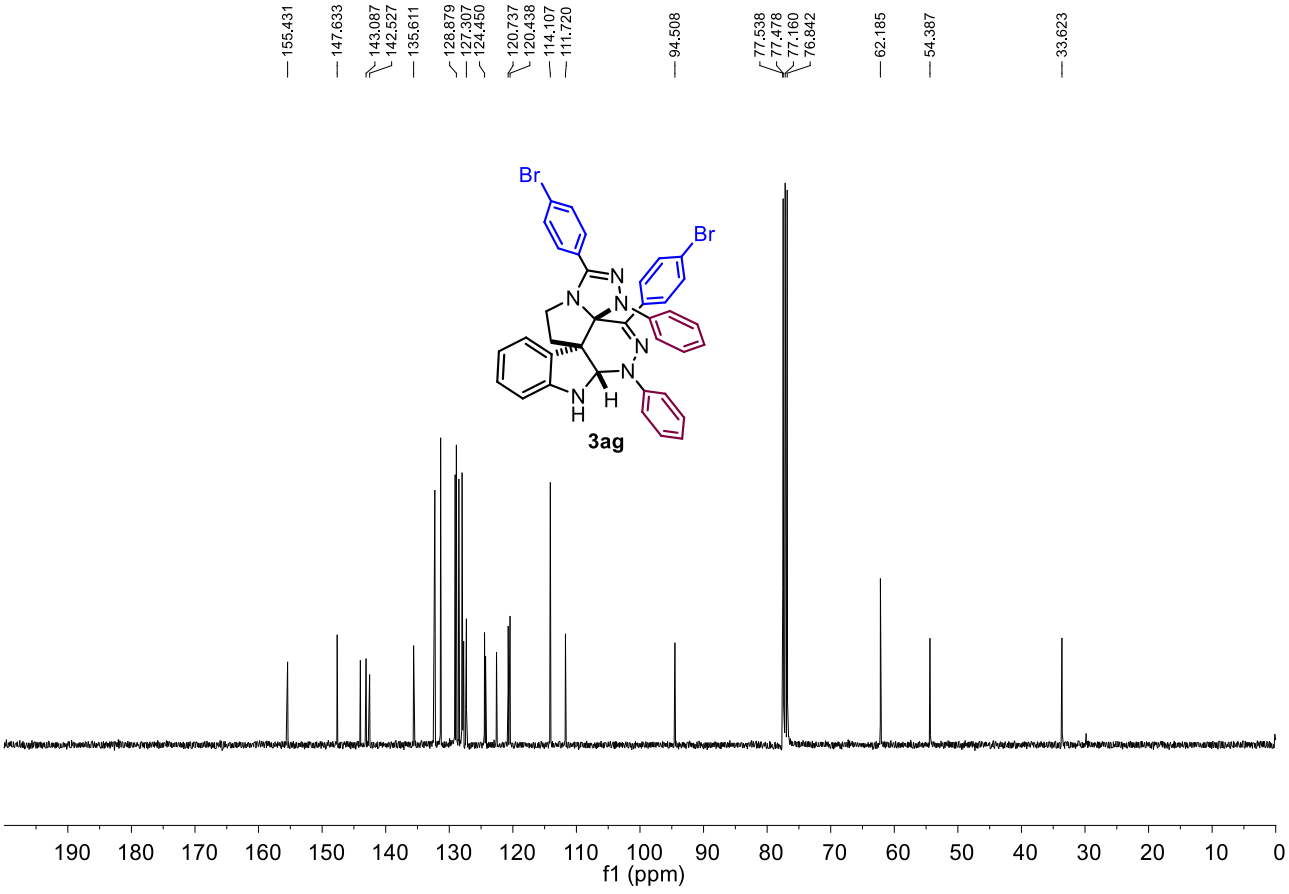
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



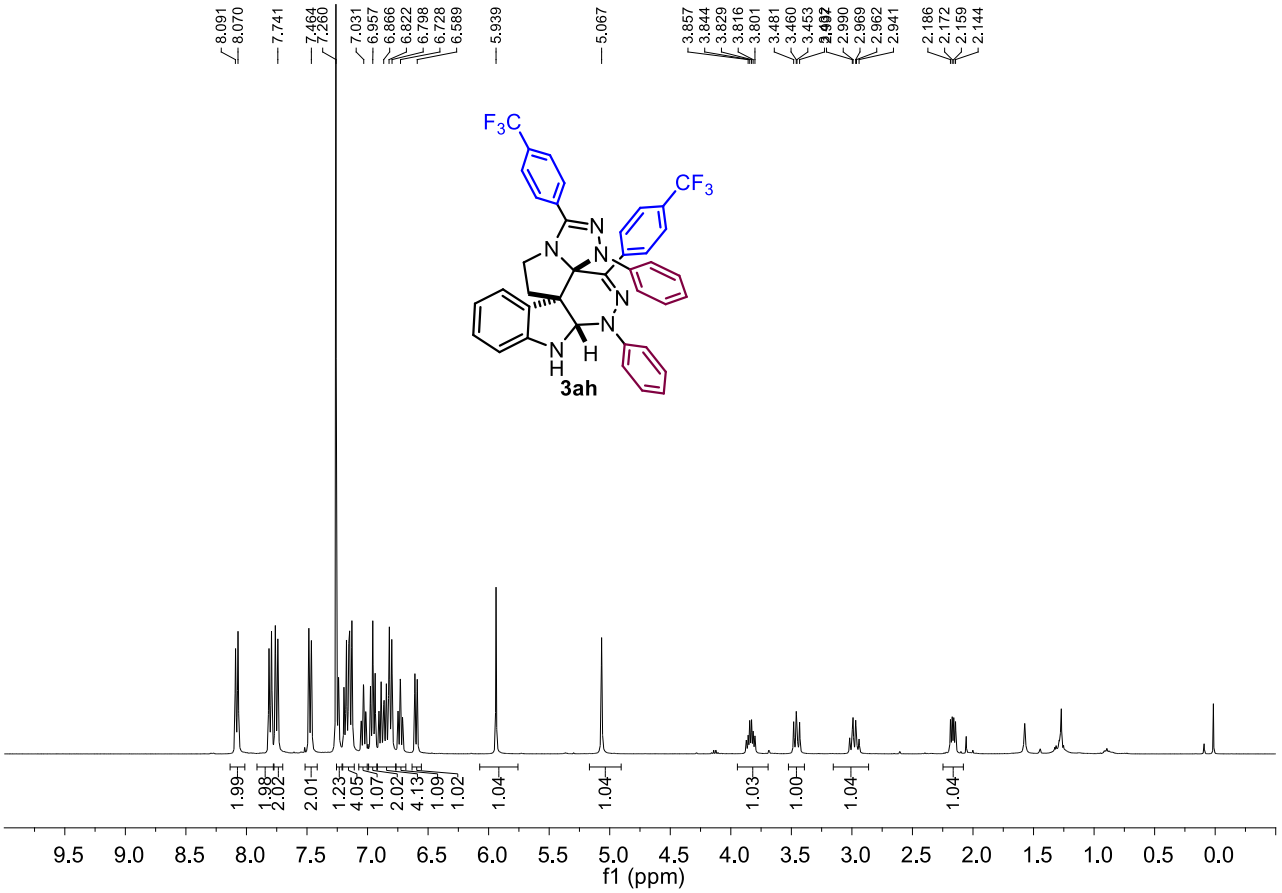
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



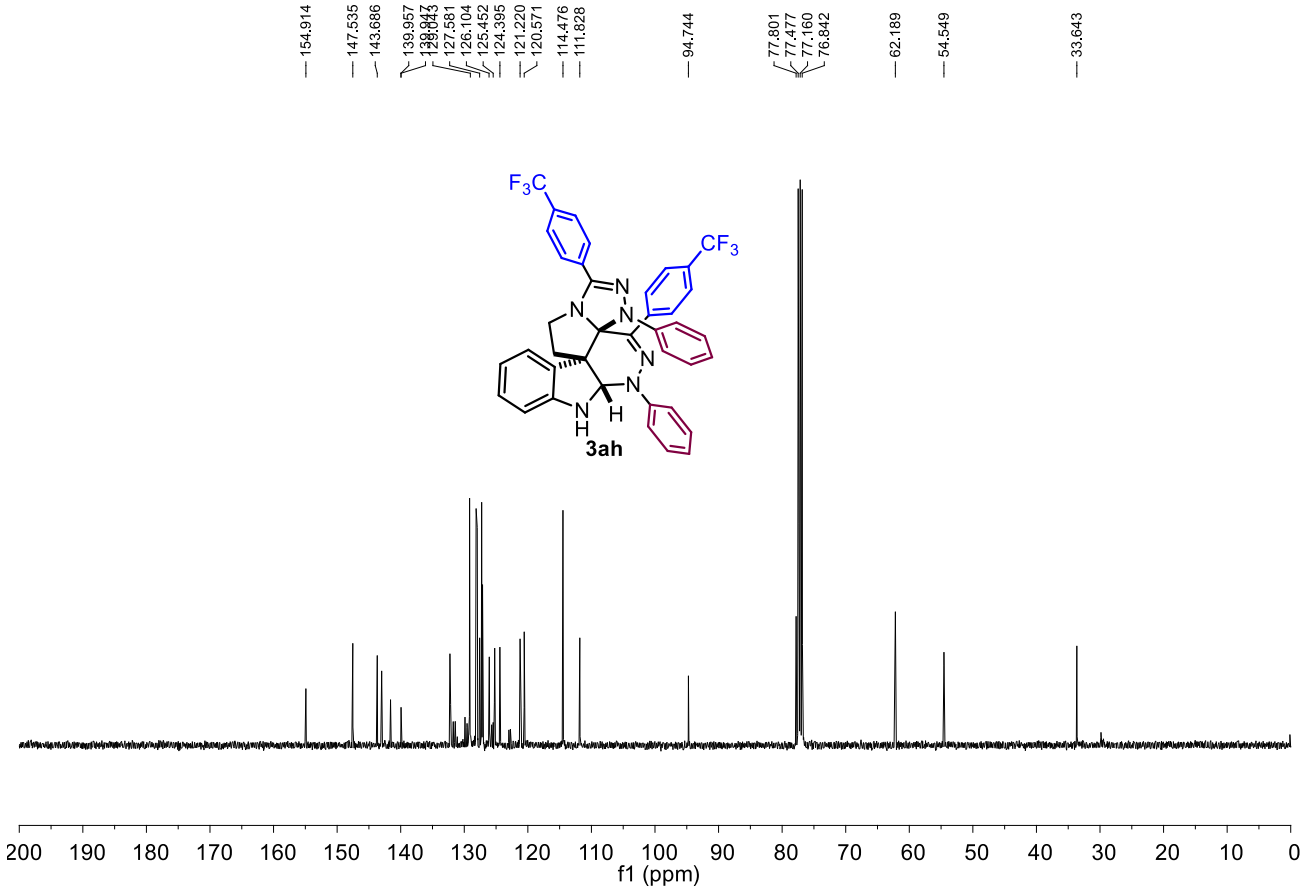
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



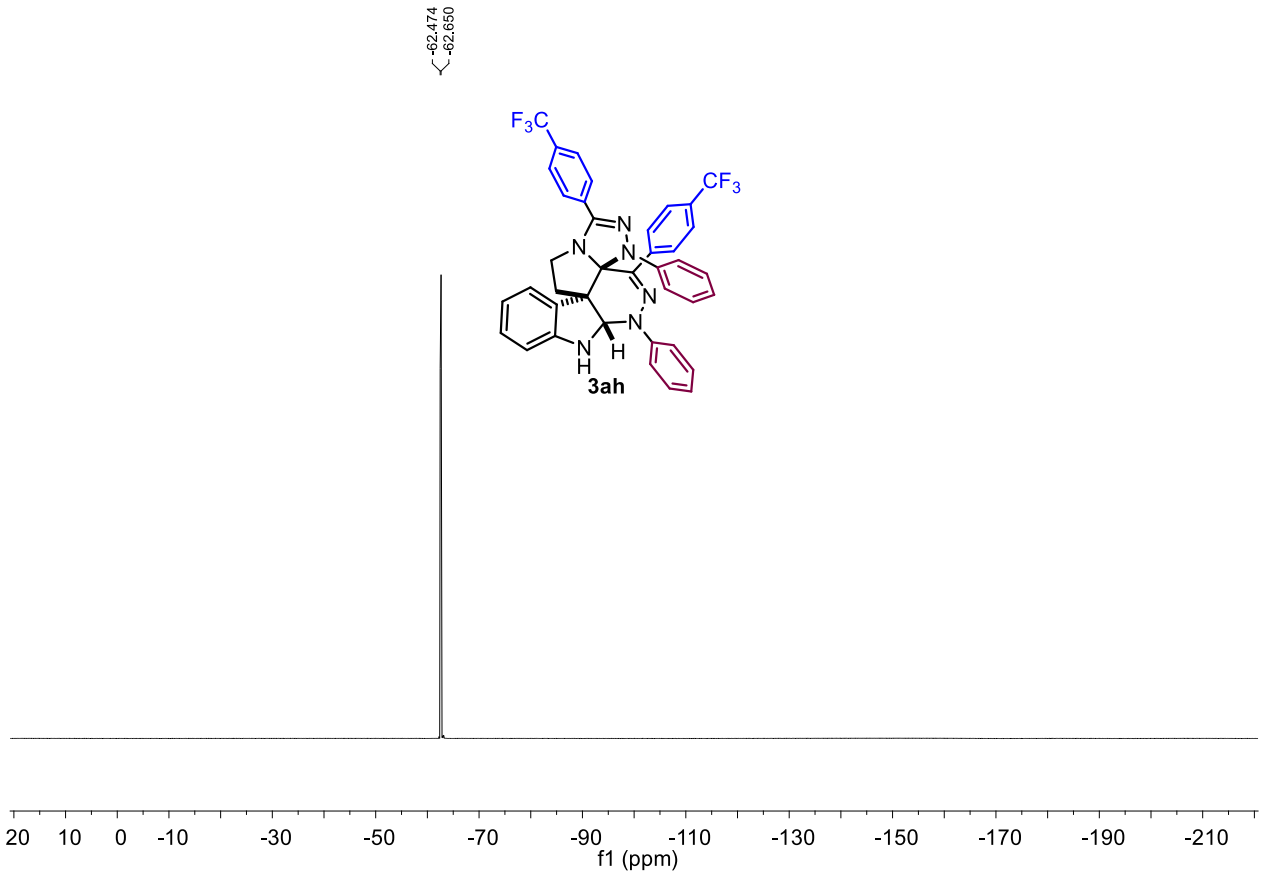
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



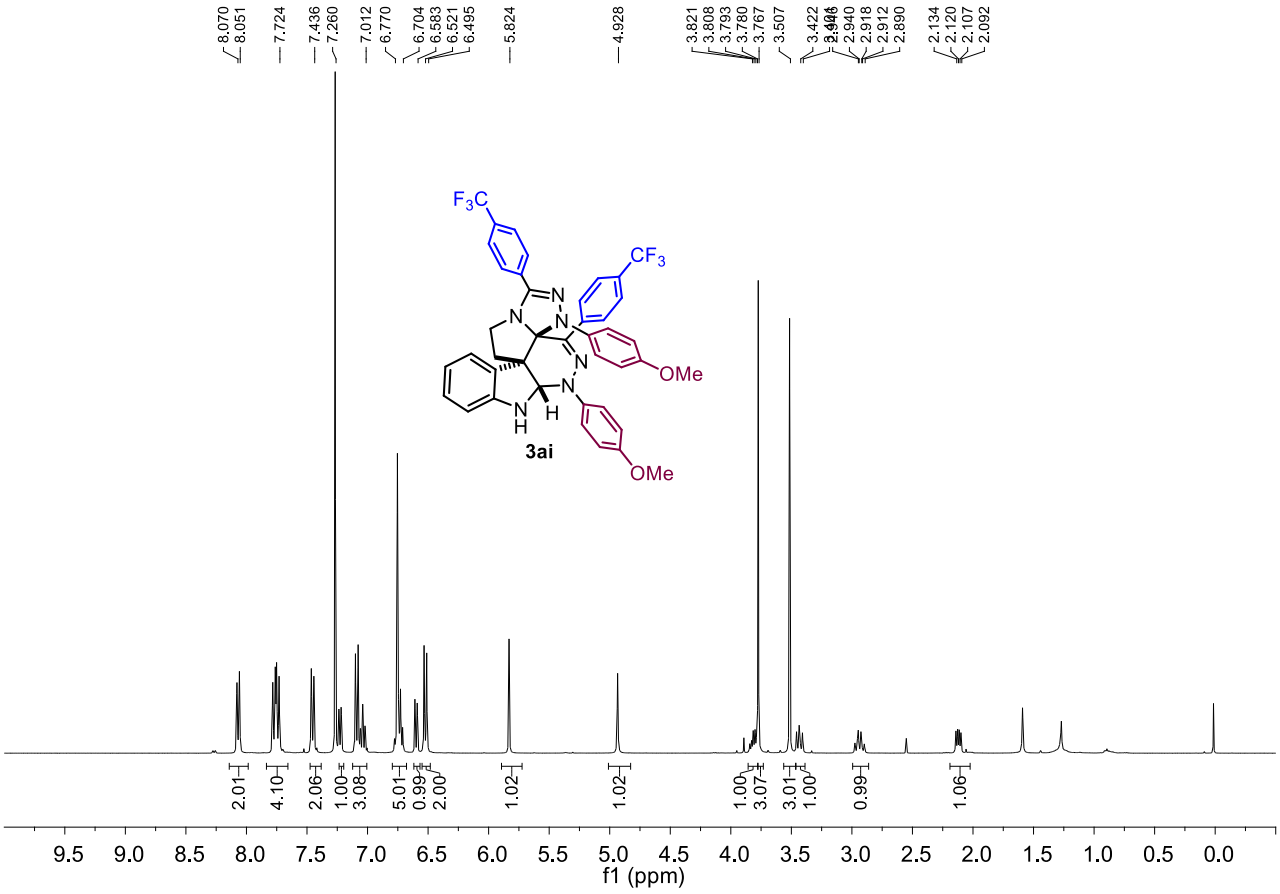
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



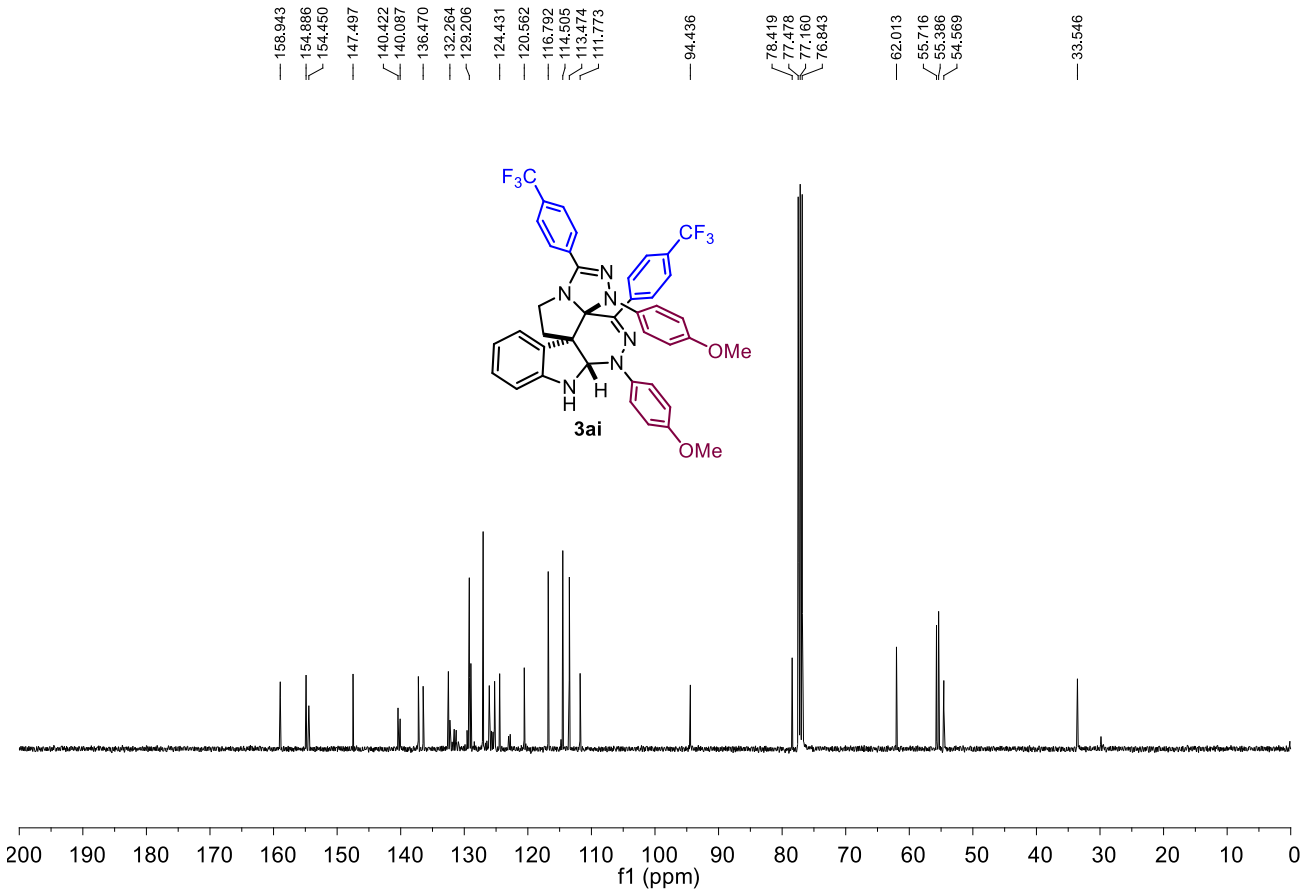
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**



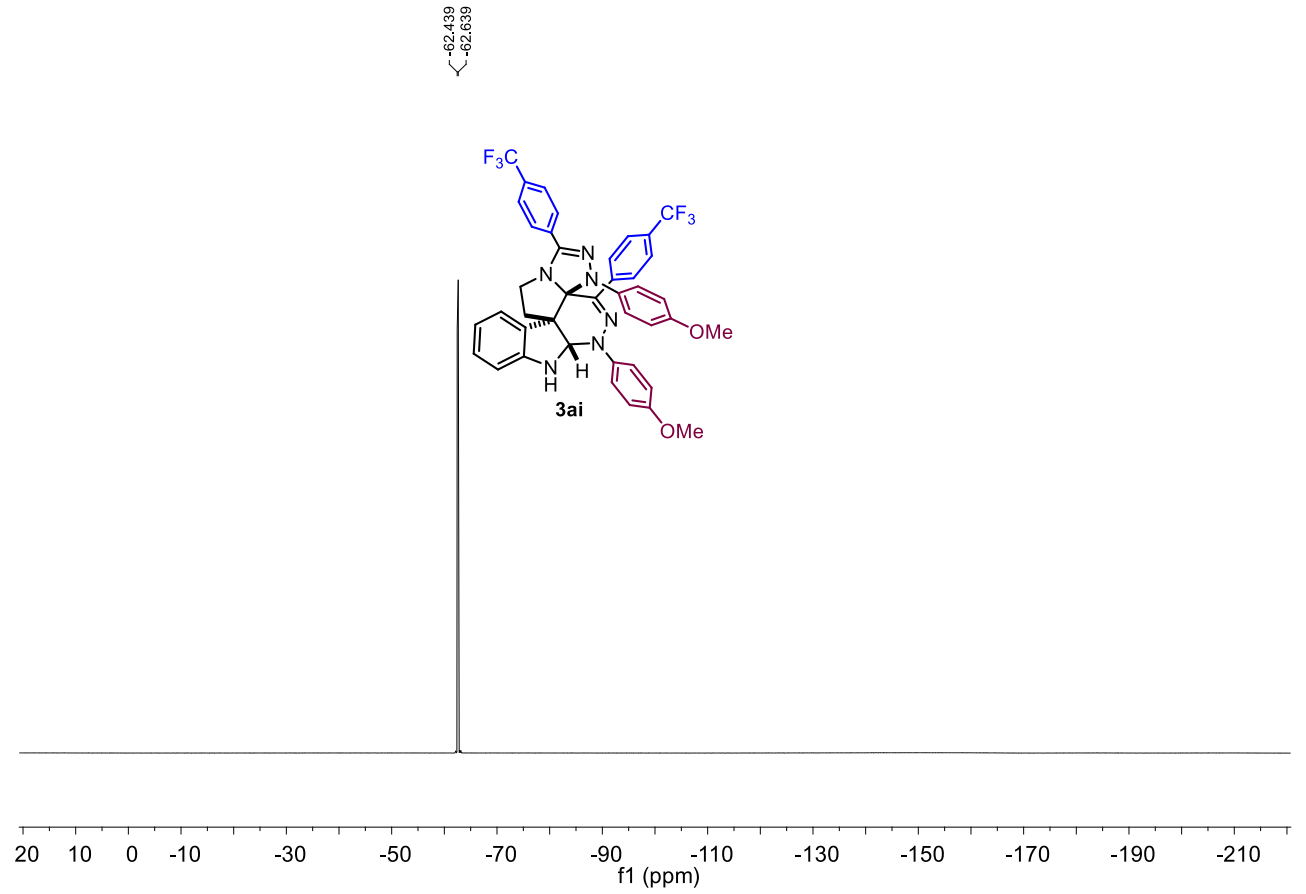
^{19}F NMR (376 MHz, $CDCl_3$) of **3ah**



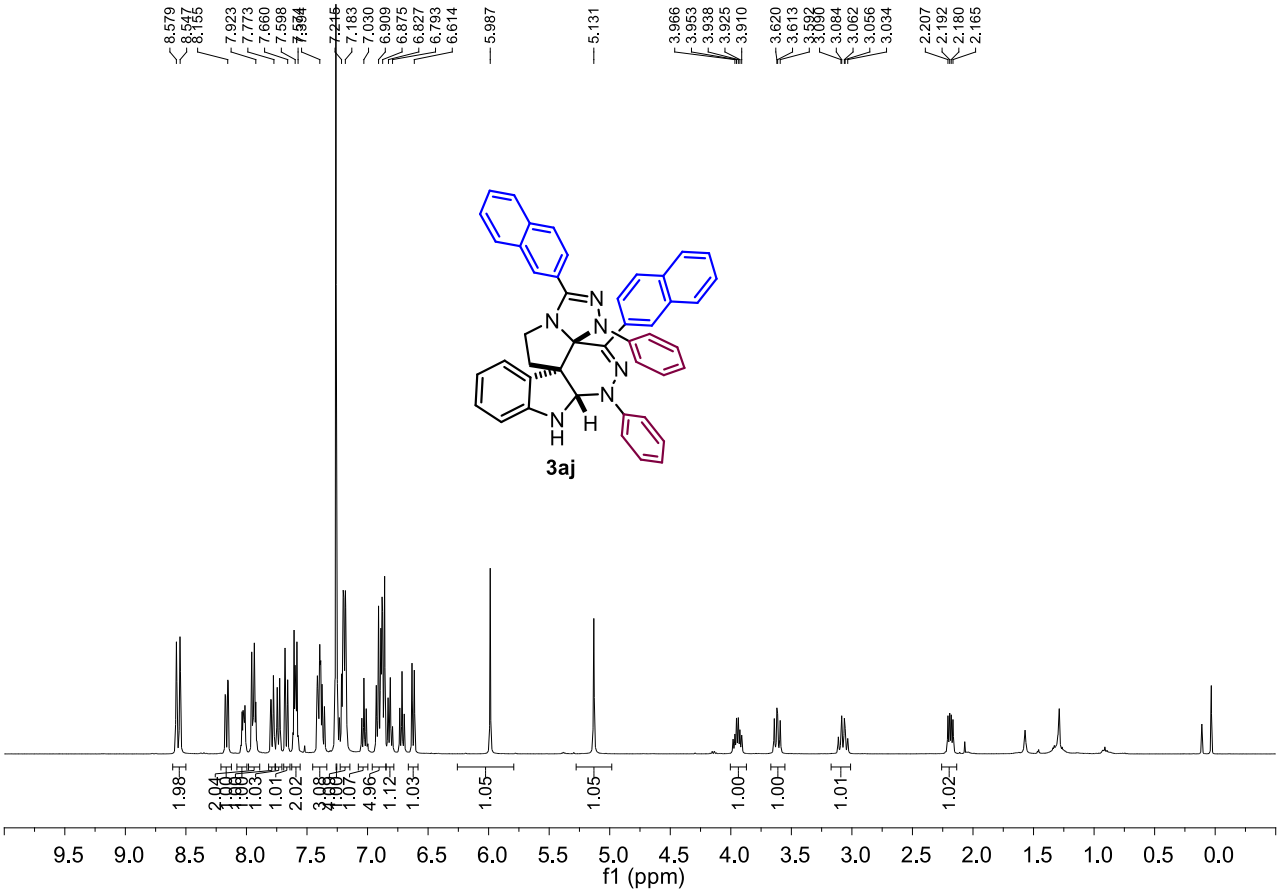
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



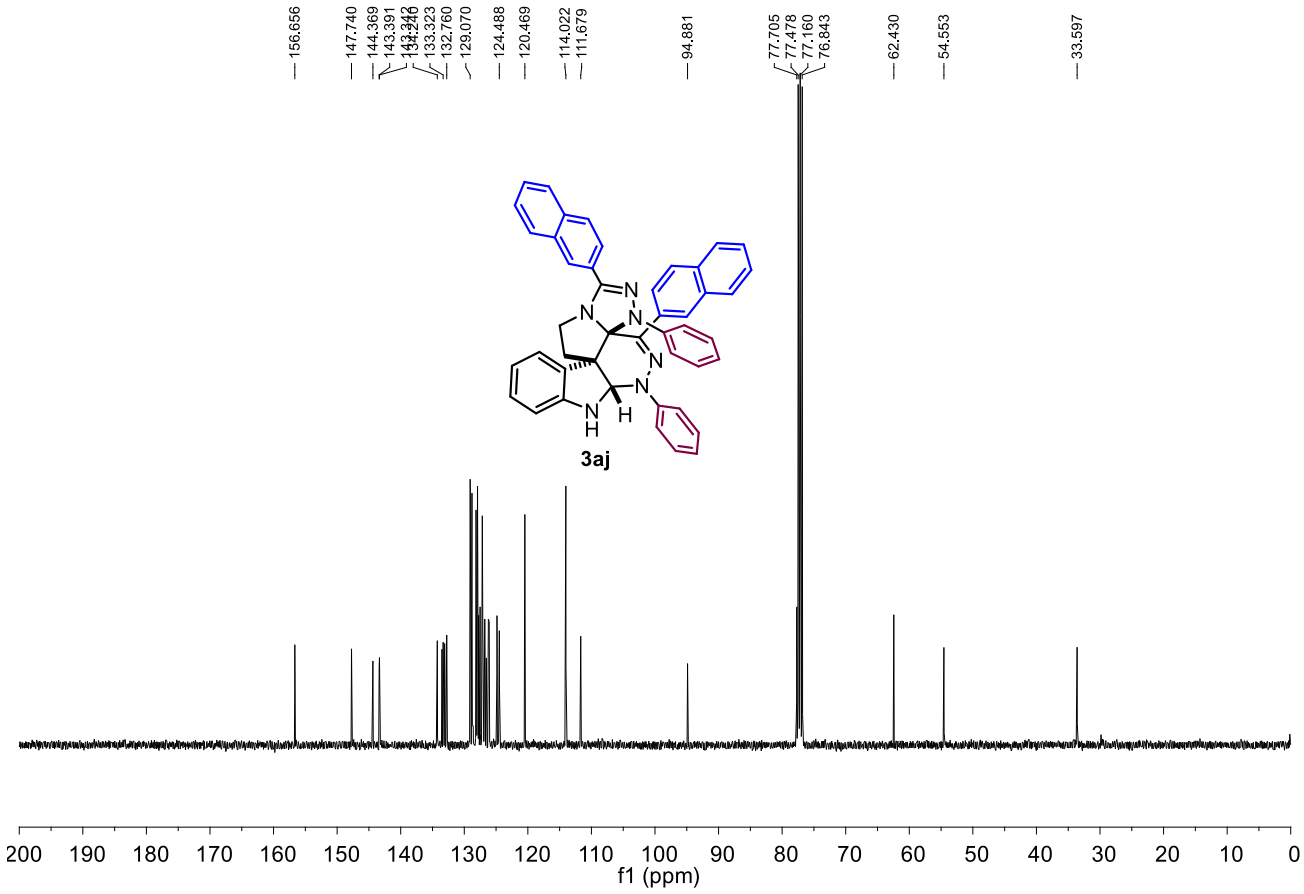
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



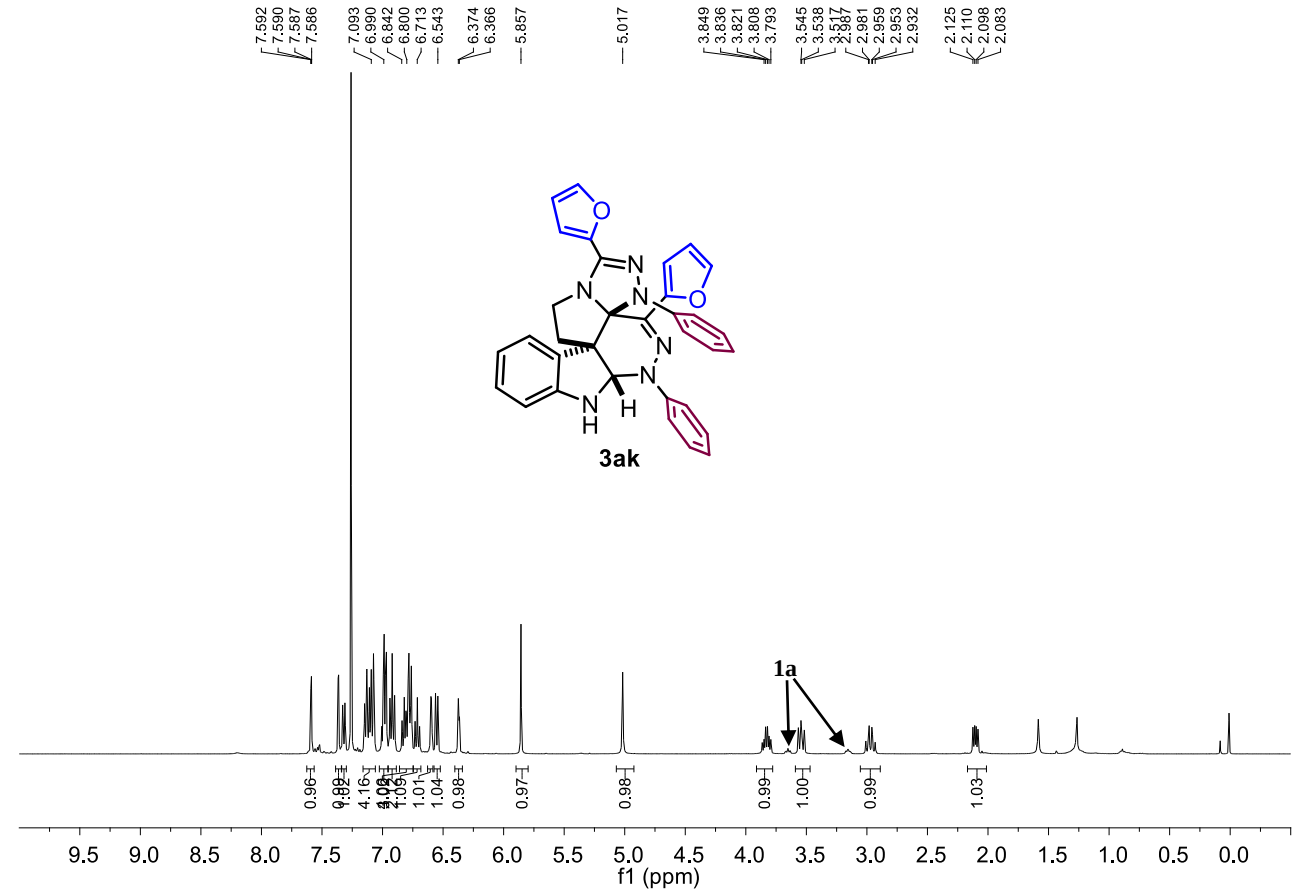
^{19}F NMR (376 MHz, $CDCl_3$) of **3ai**



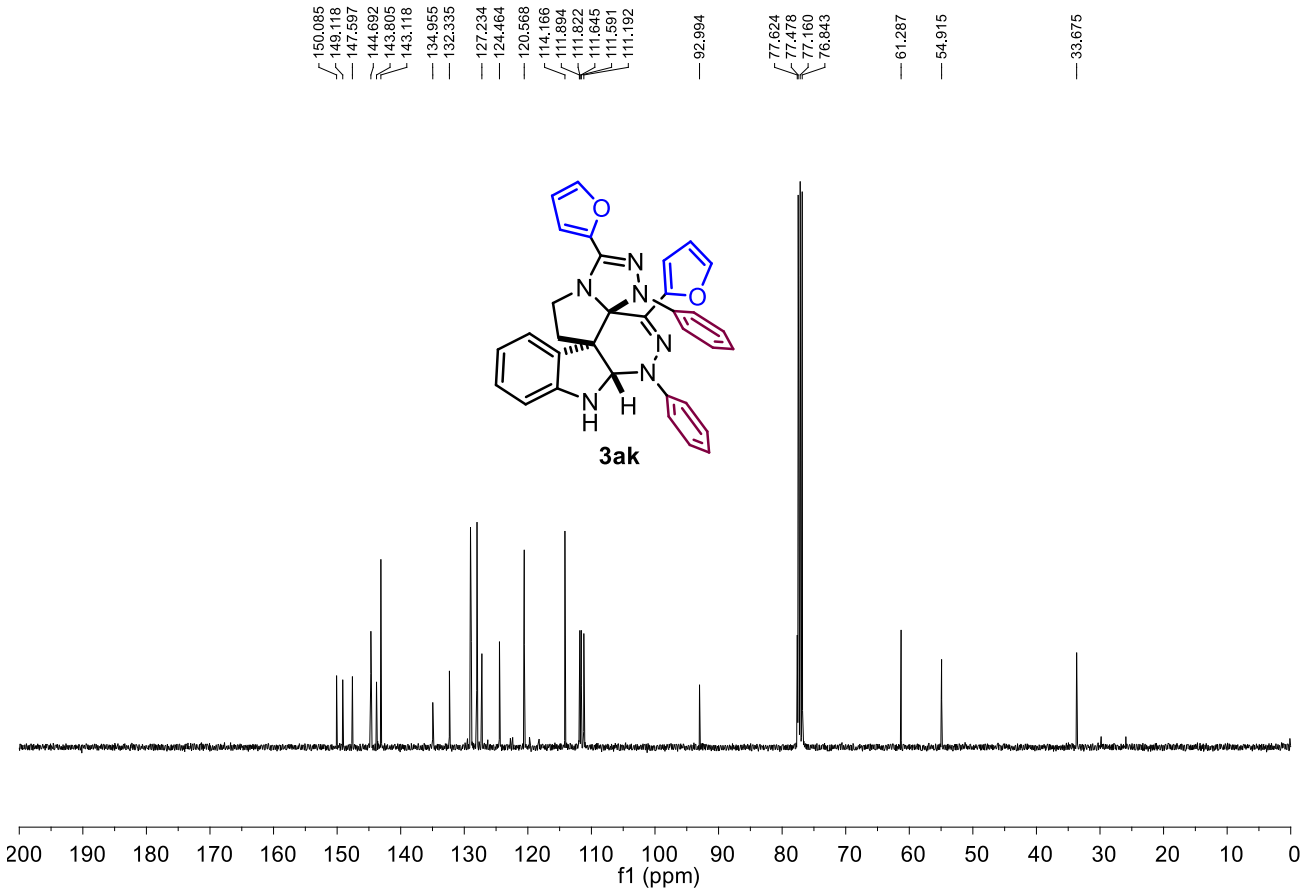
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



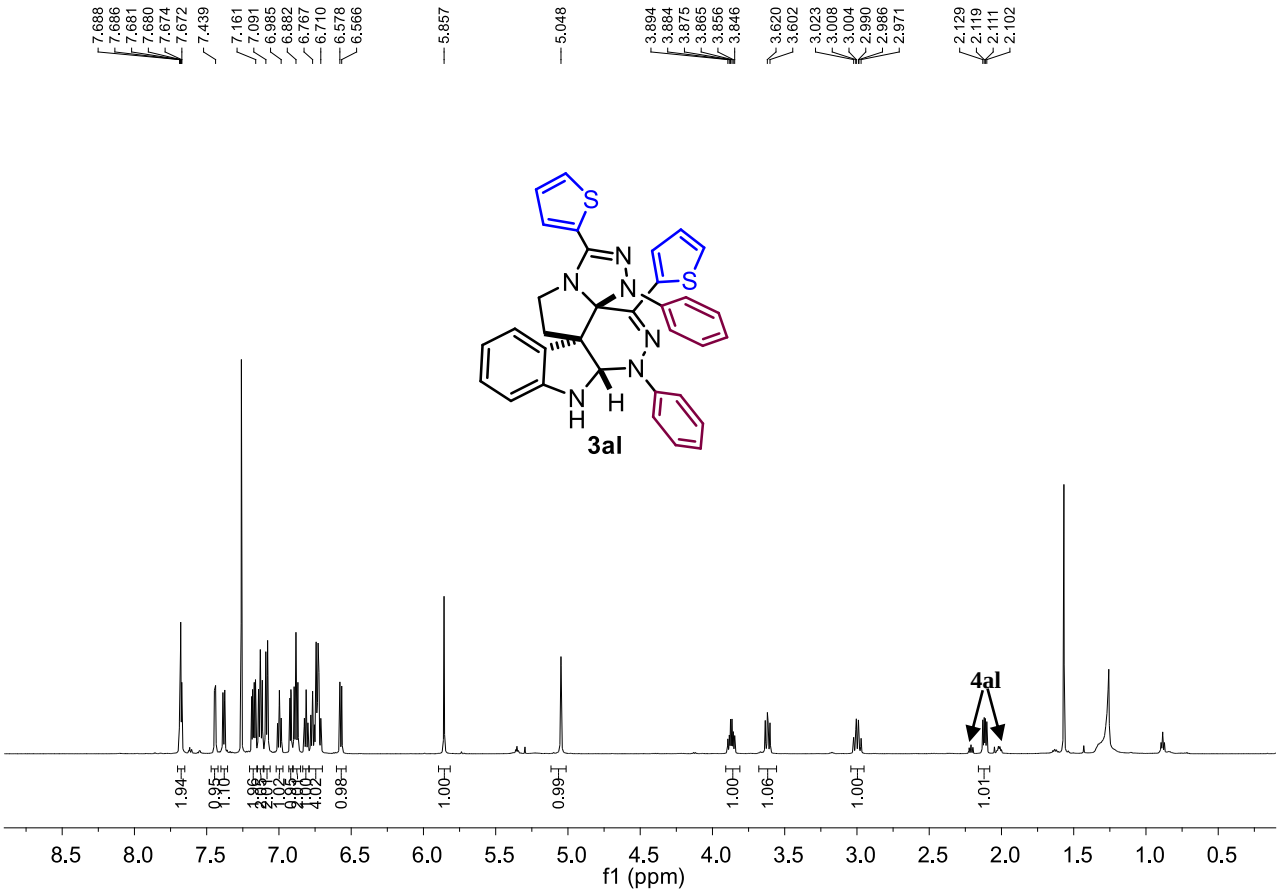
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



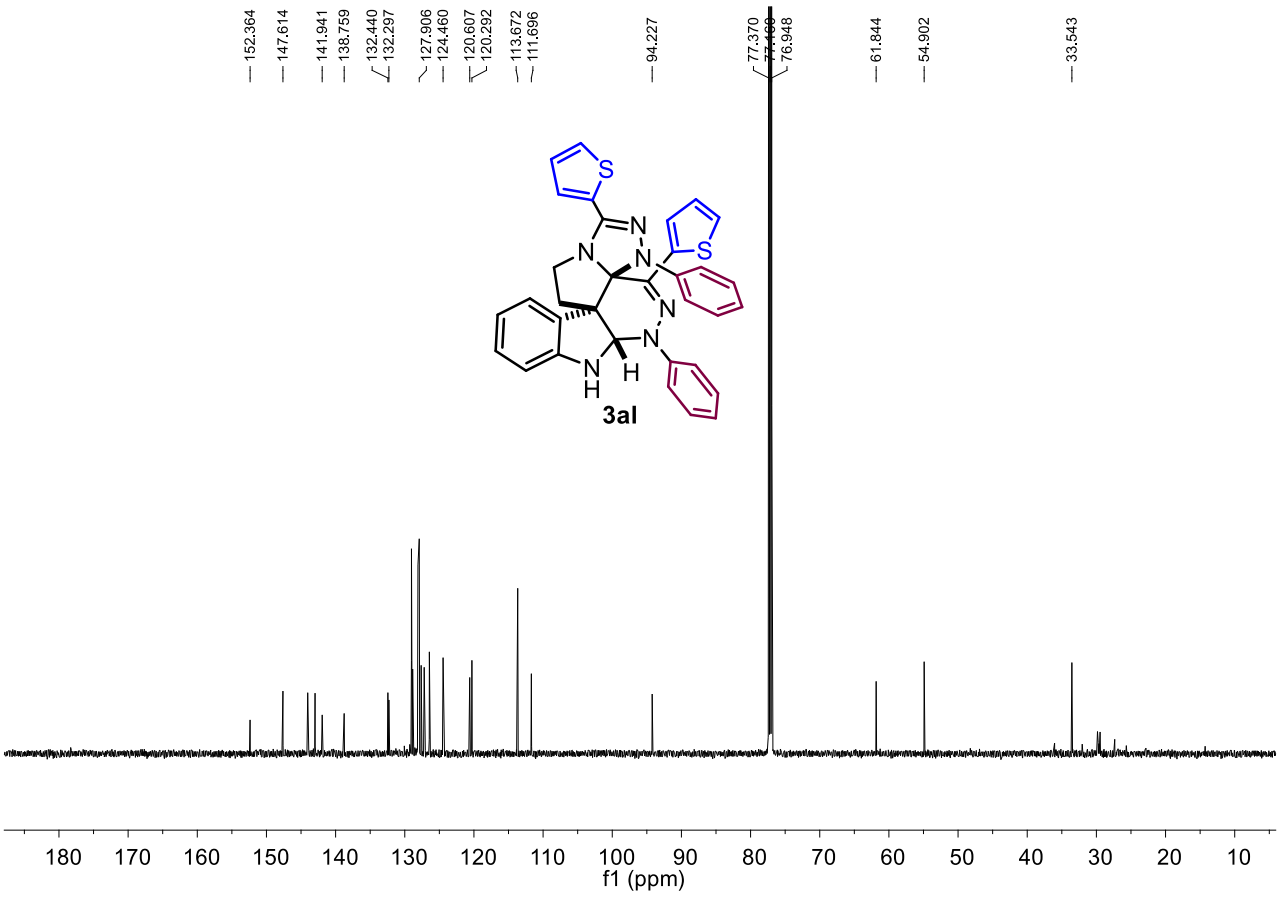
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



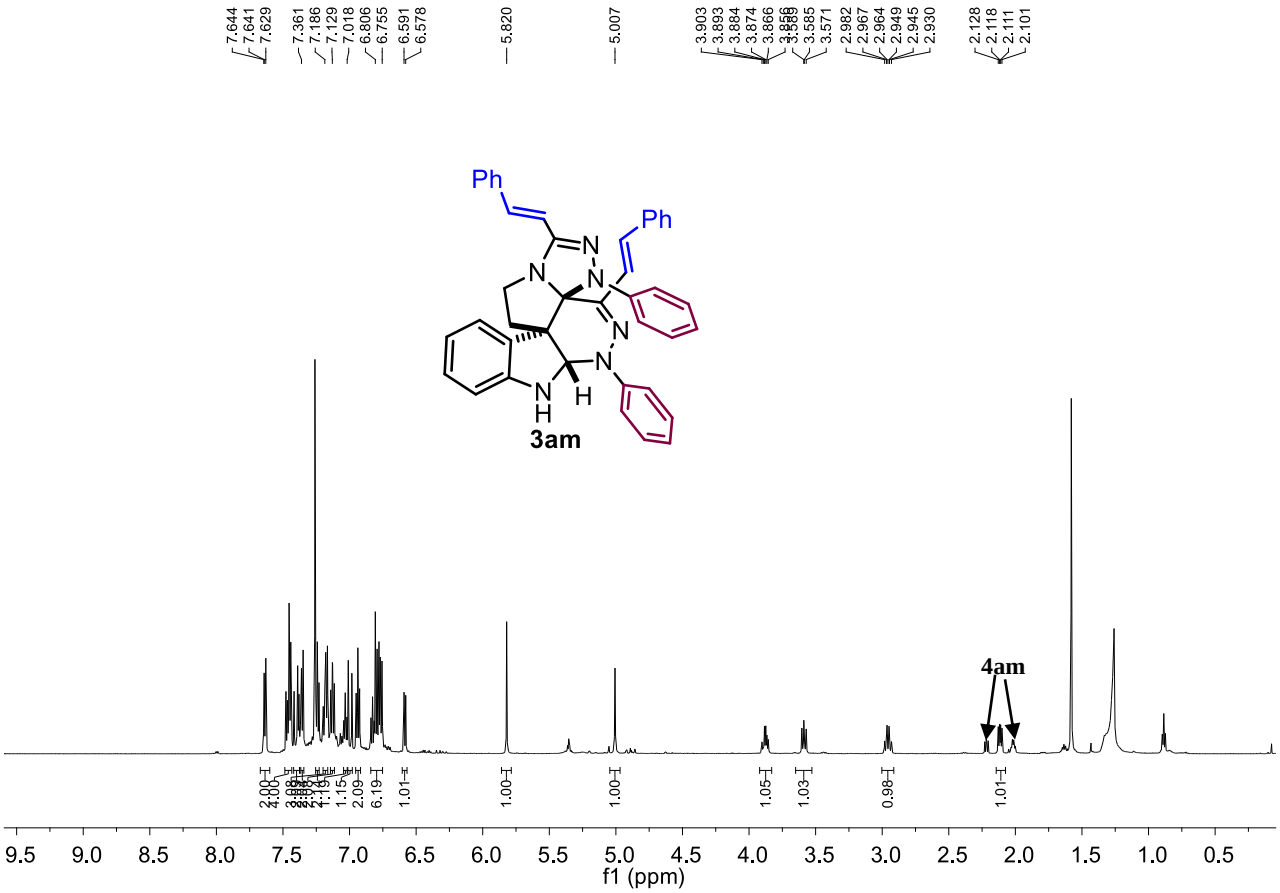
^{13}C NMR (101 MHz, $CDCl_3$) of **3ak**



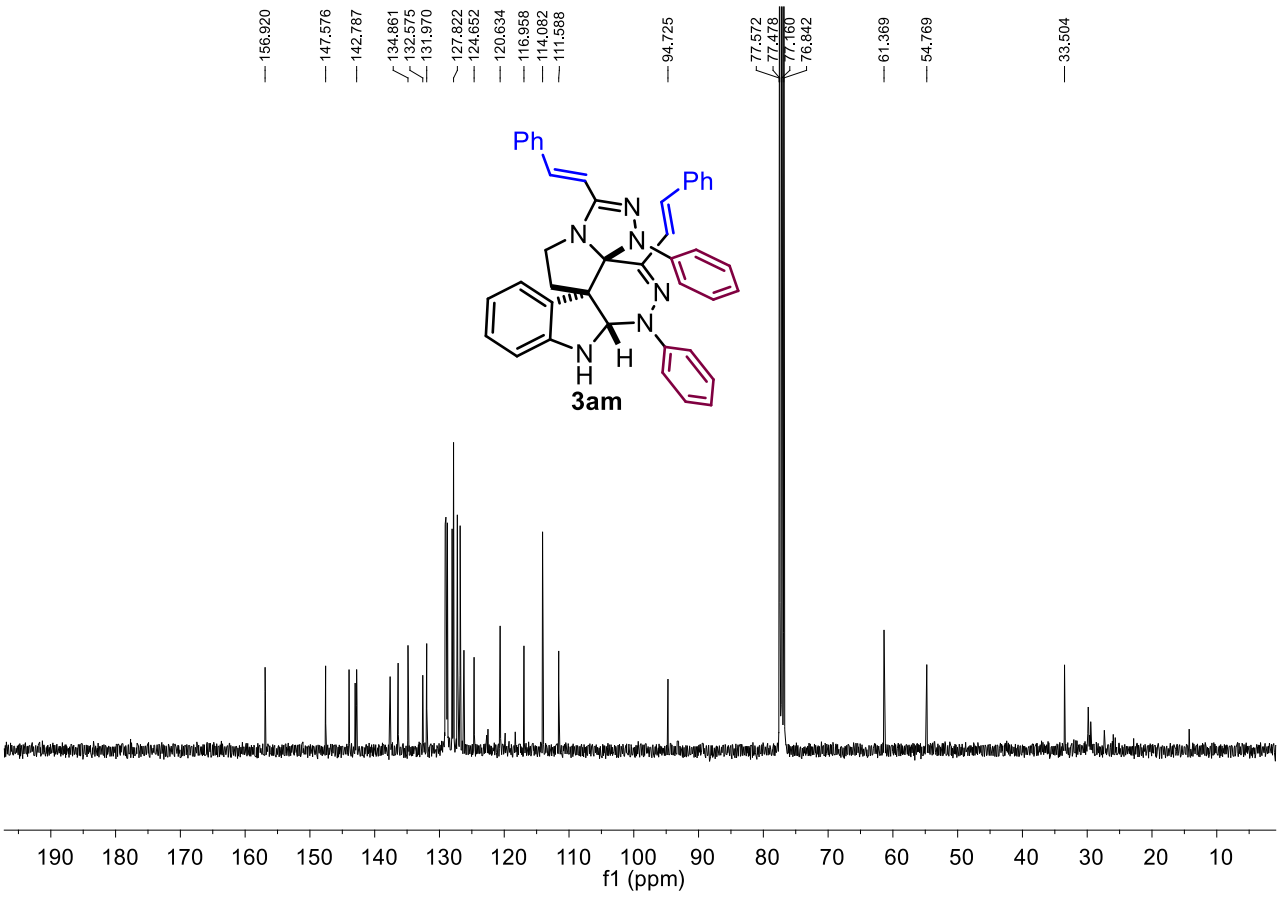
^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



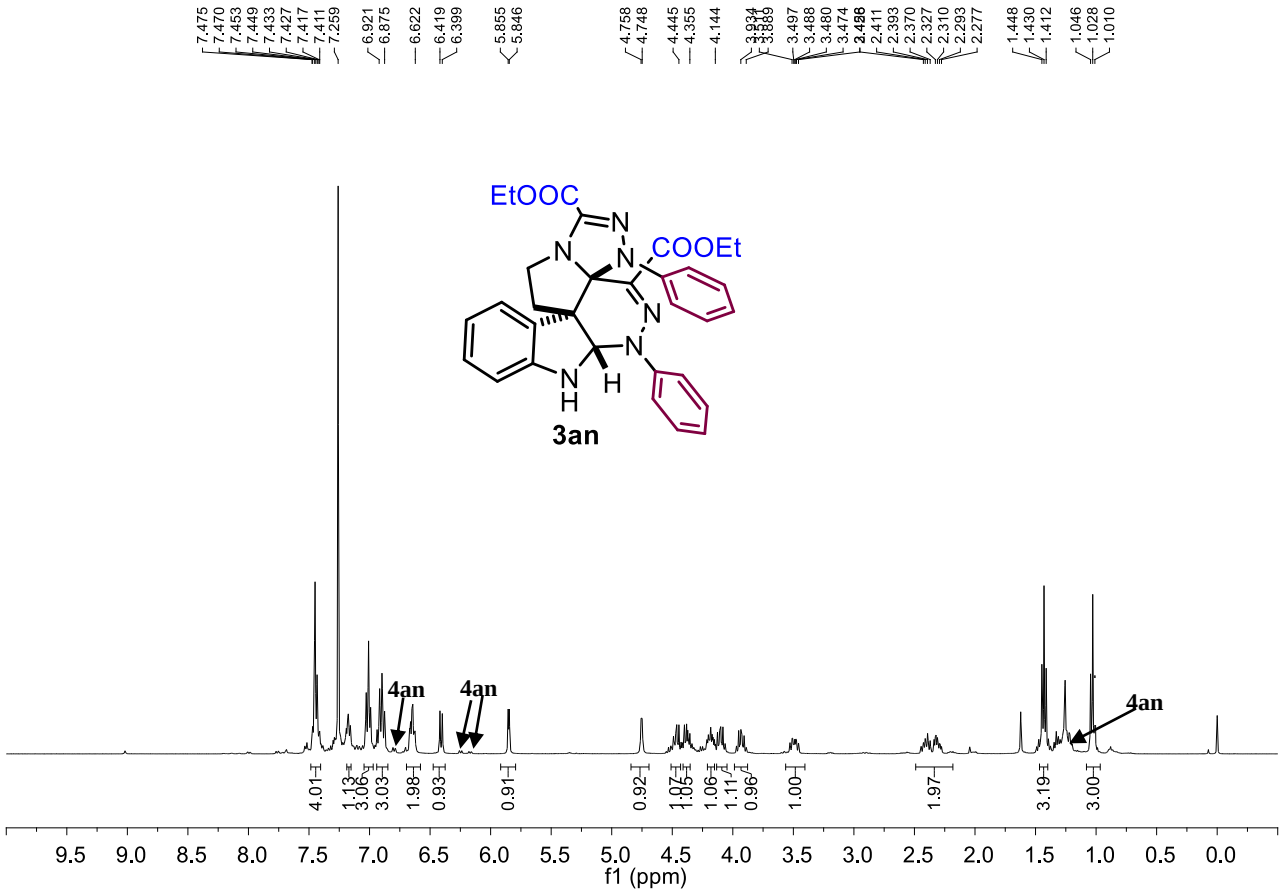
^{13}C NMR (101 MHz, $CDCl_3$) of **3al**



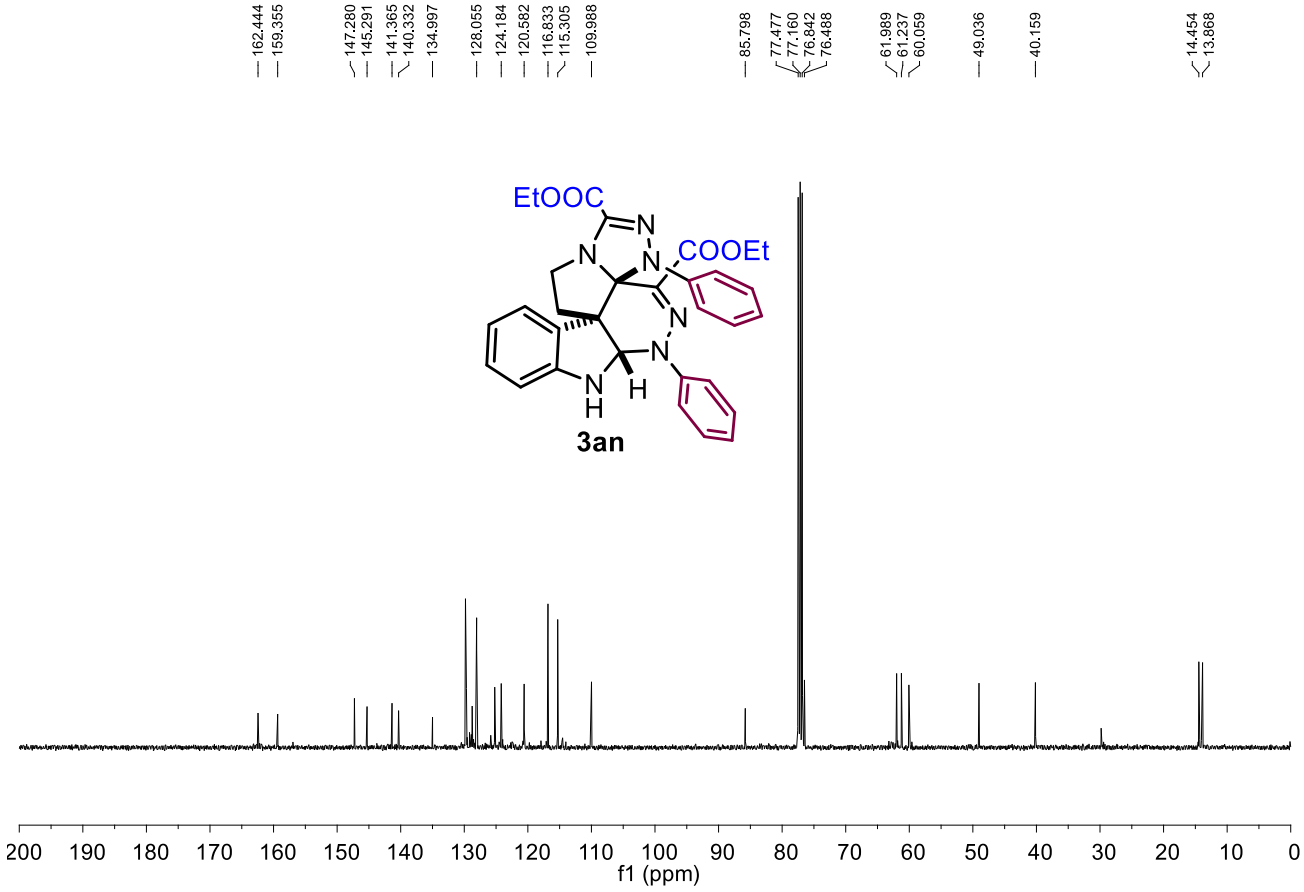
^{1}H NMR (400 MHz, $CDCl_3$) of **3am**



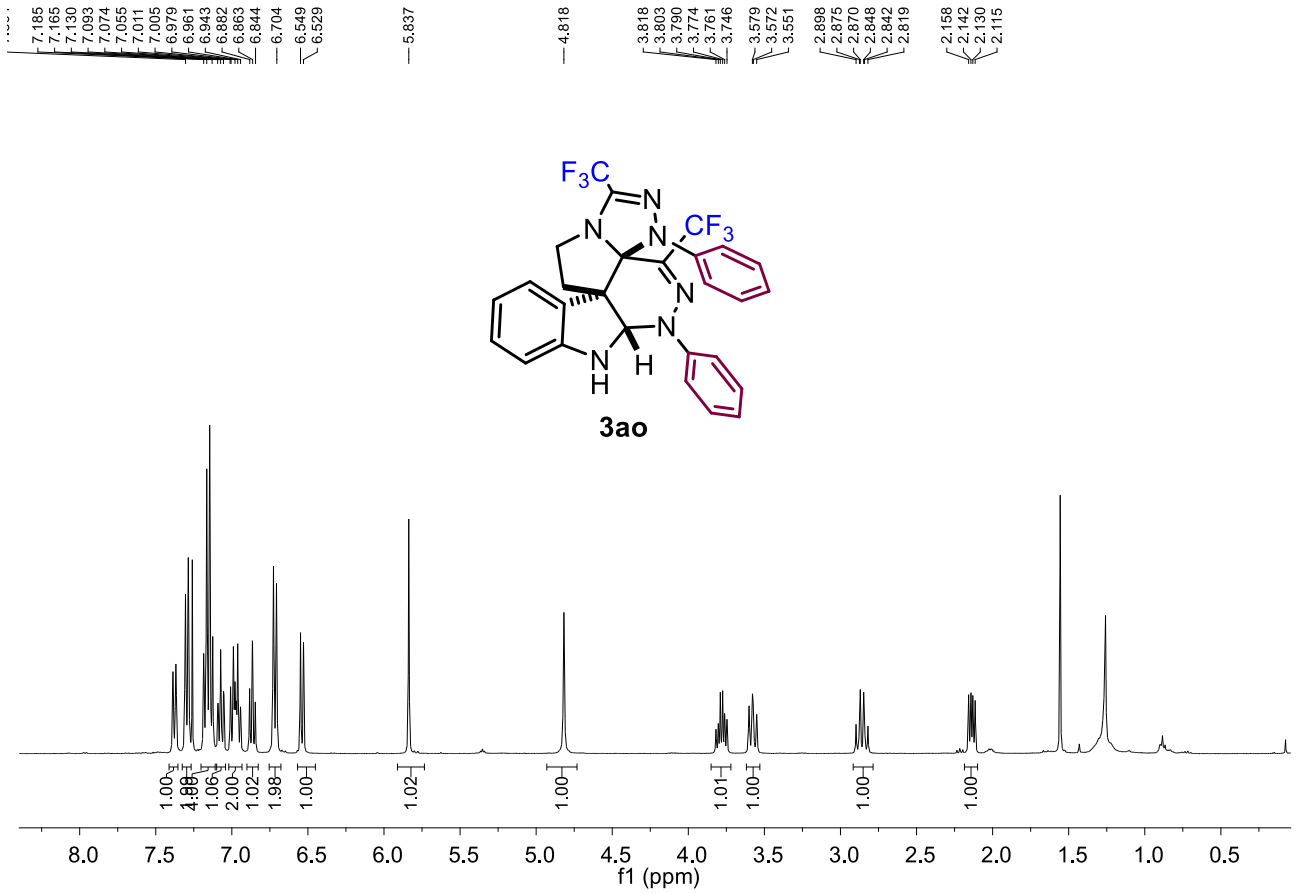
^{13}C NMR (101 MHz, $CDCl_3$) of **3am**



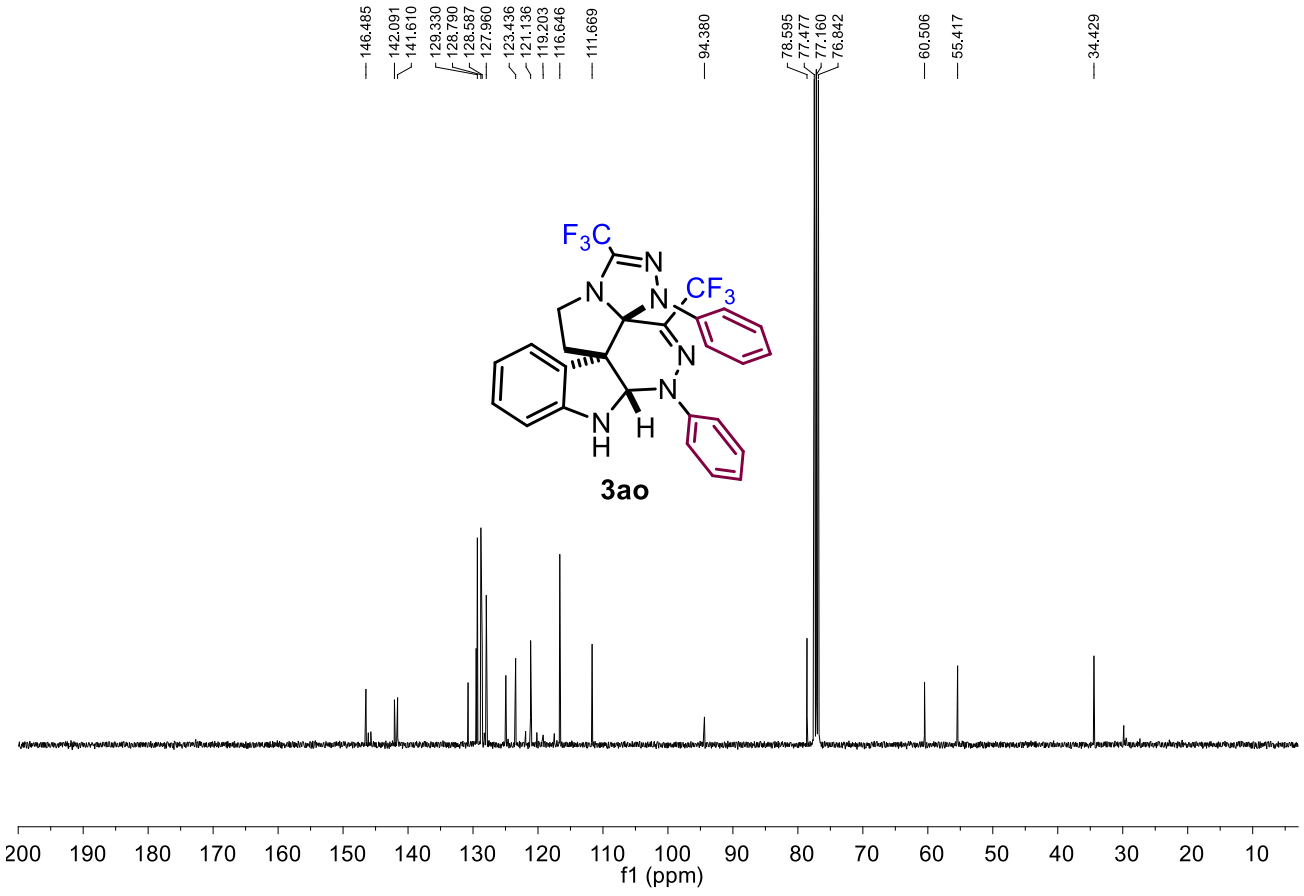
^{1}H NMR (400 MHz, $CDCl_3$) of **3an**



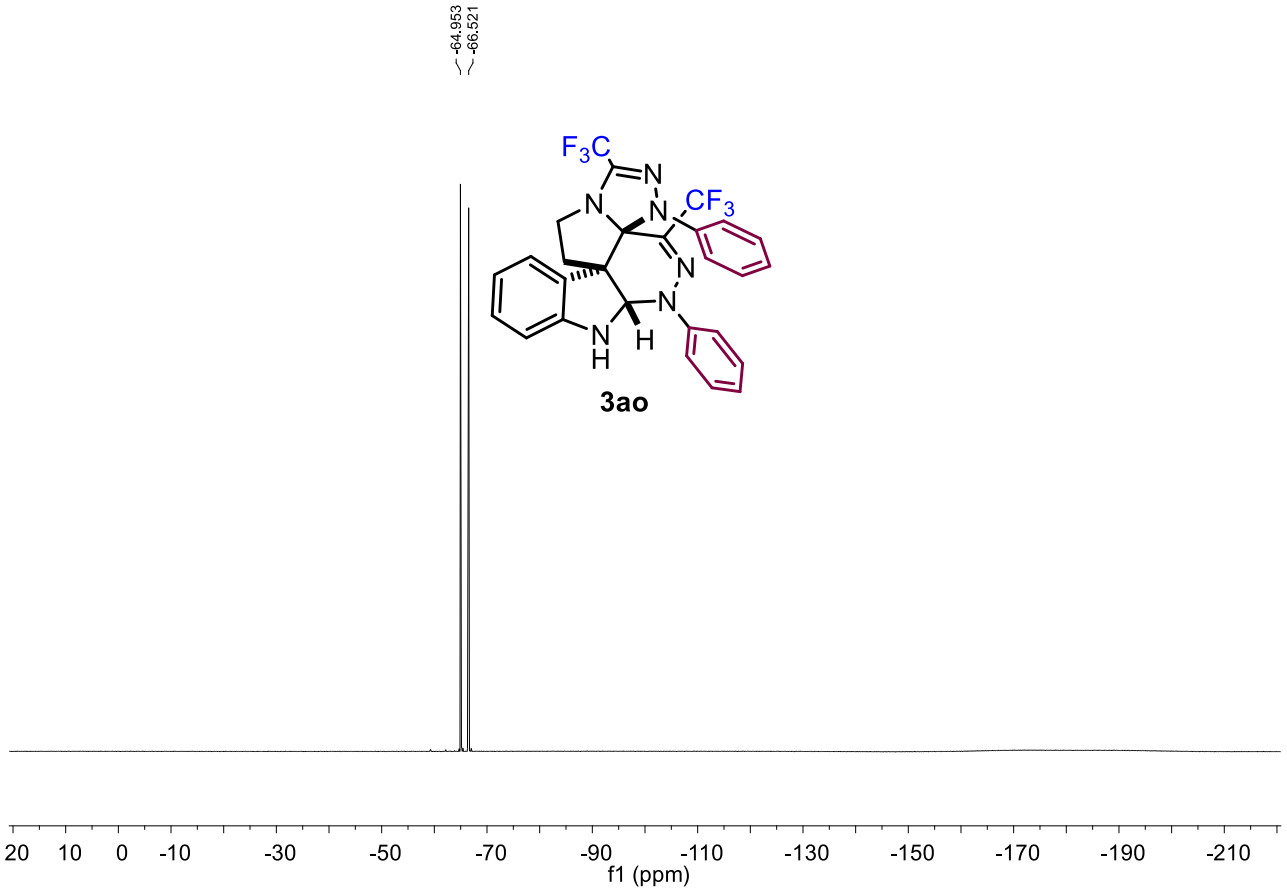
^{13}C NMR (101 MHz, $CDCl_3$) of **3an**



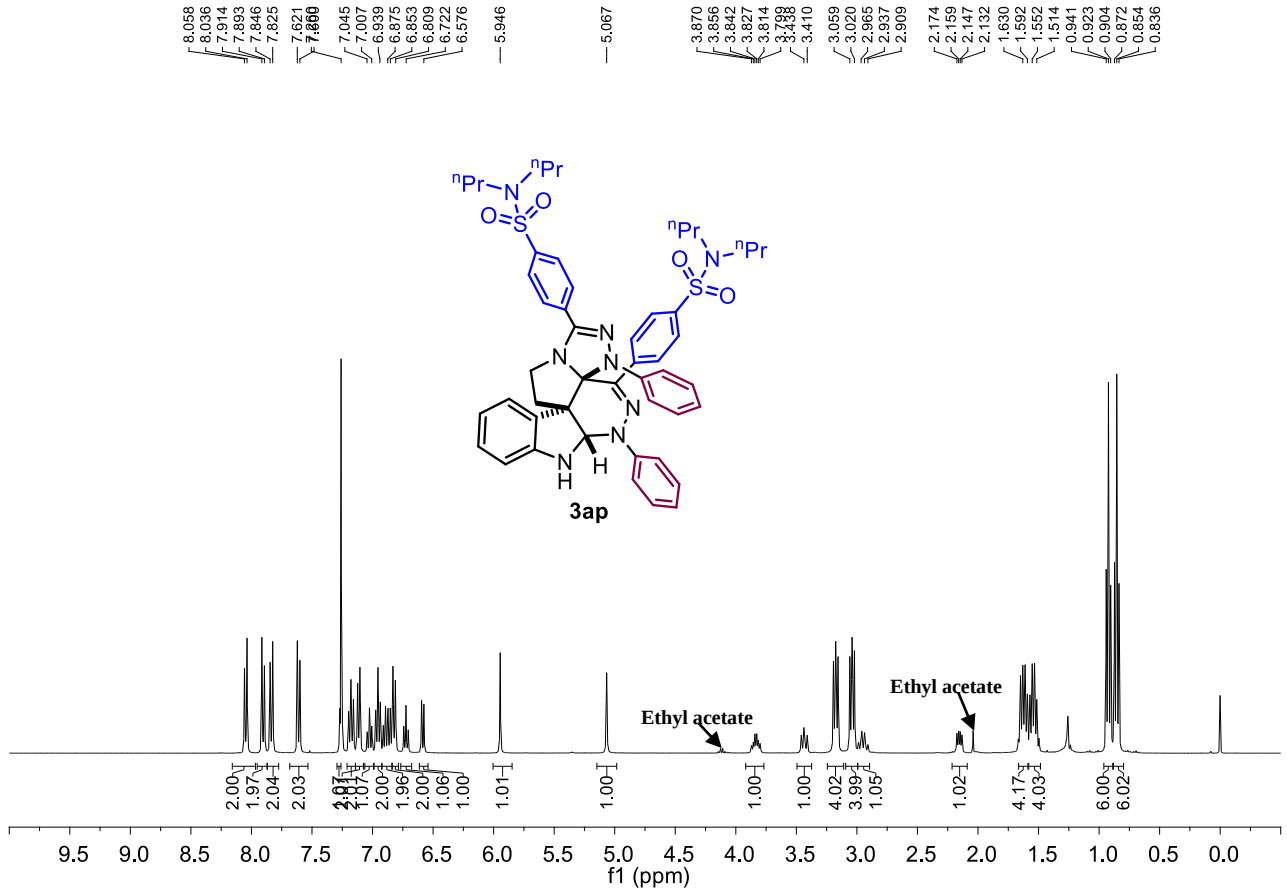
^{1}H NMR (400 MHz, $CDCl_3$) of **3ao**



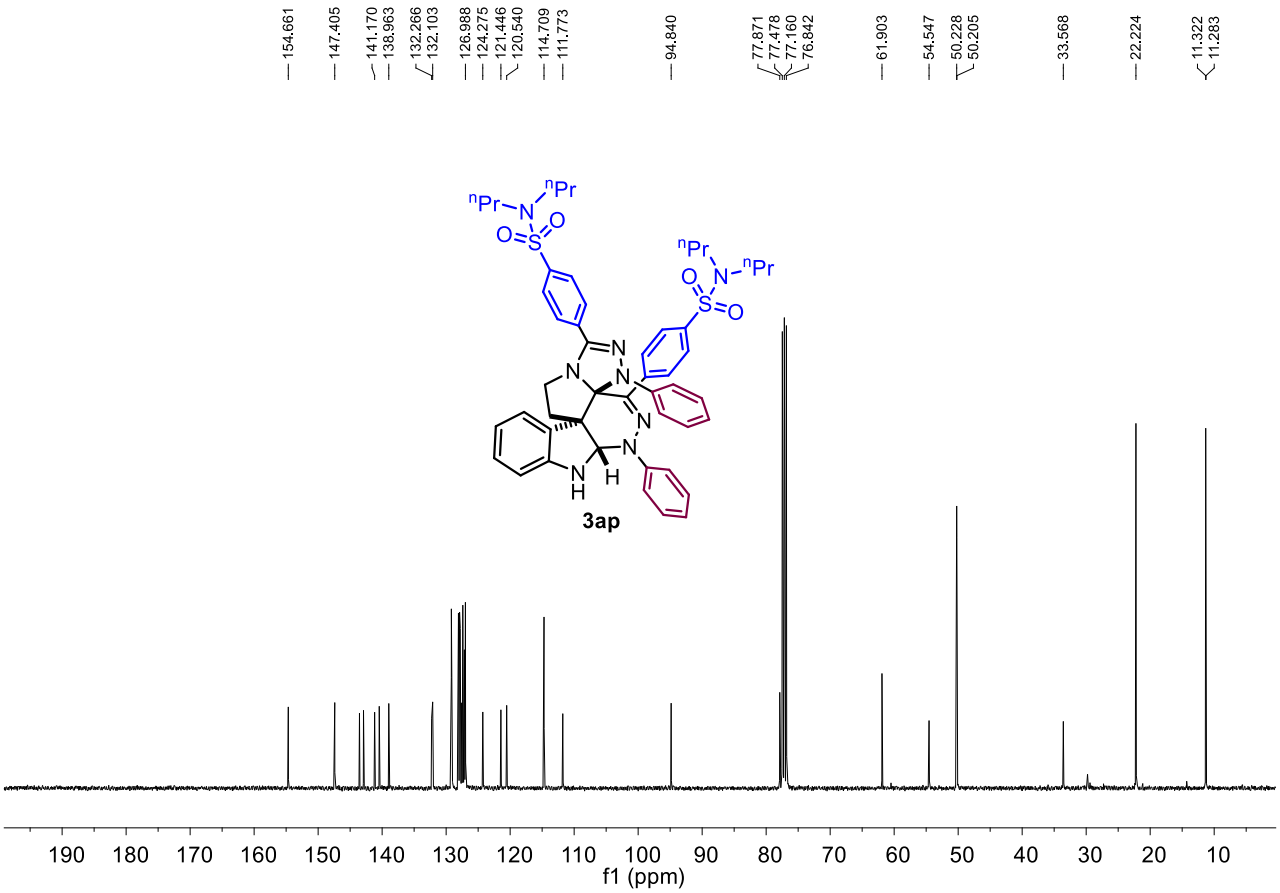
^{13}C NMR (101 MHz, $CDCl_3$) of **3ao**



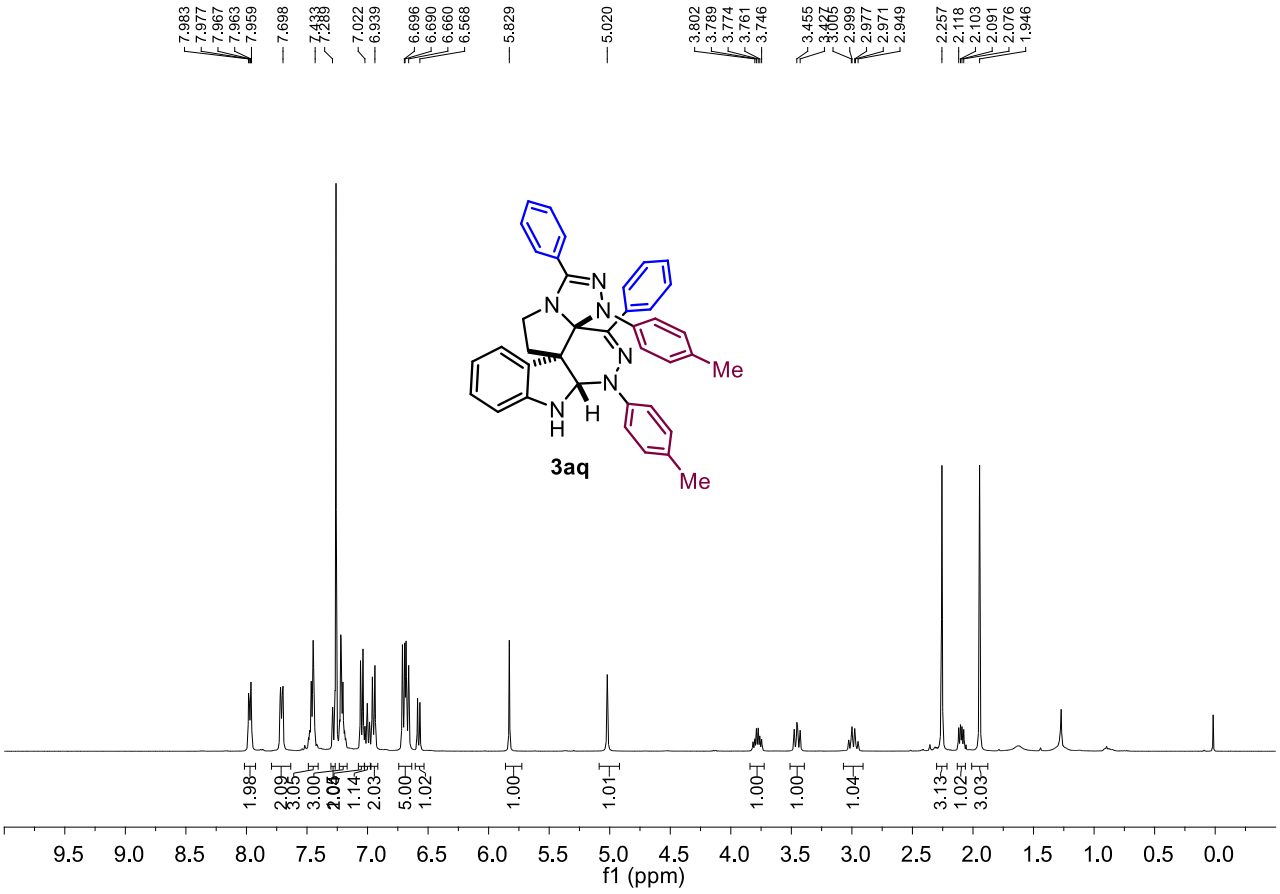
^{19}F NMR (376 MHz, $CDCl_3$) of **3ao**



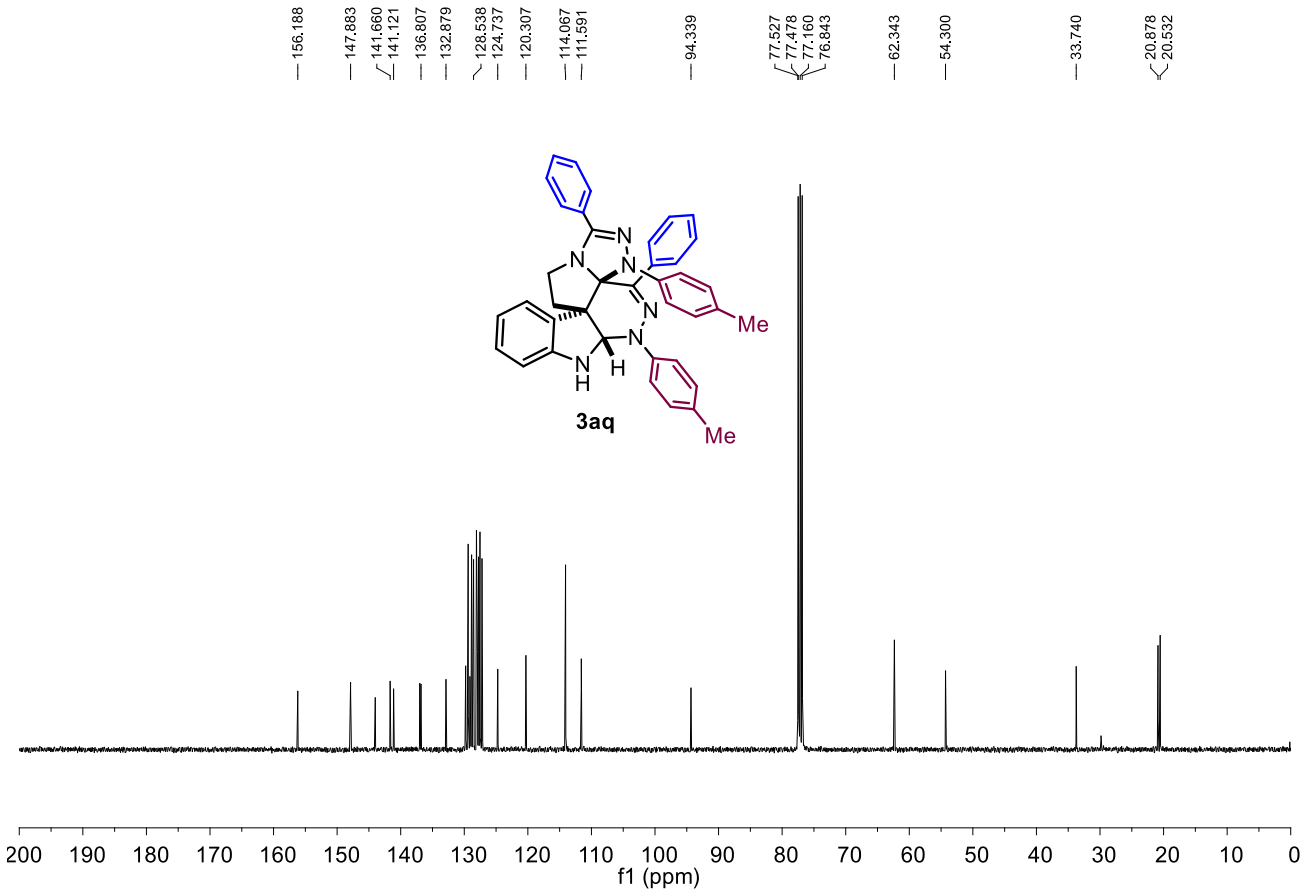
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap**



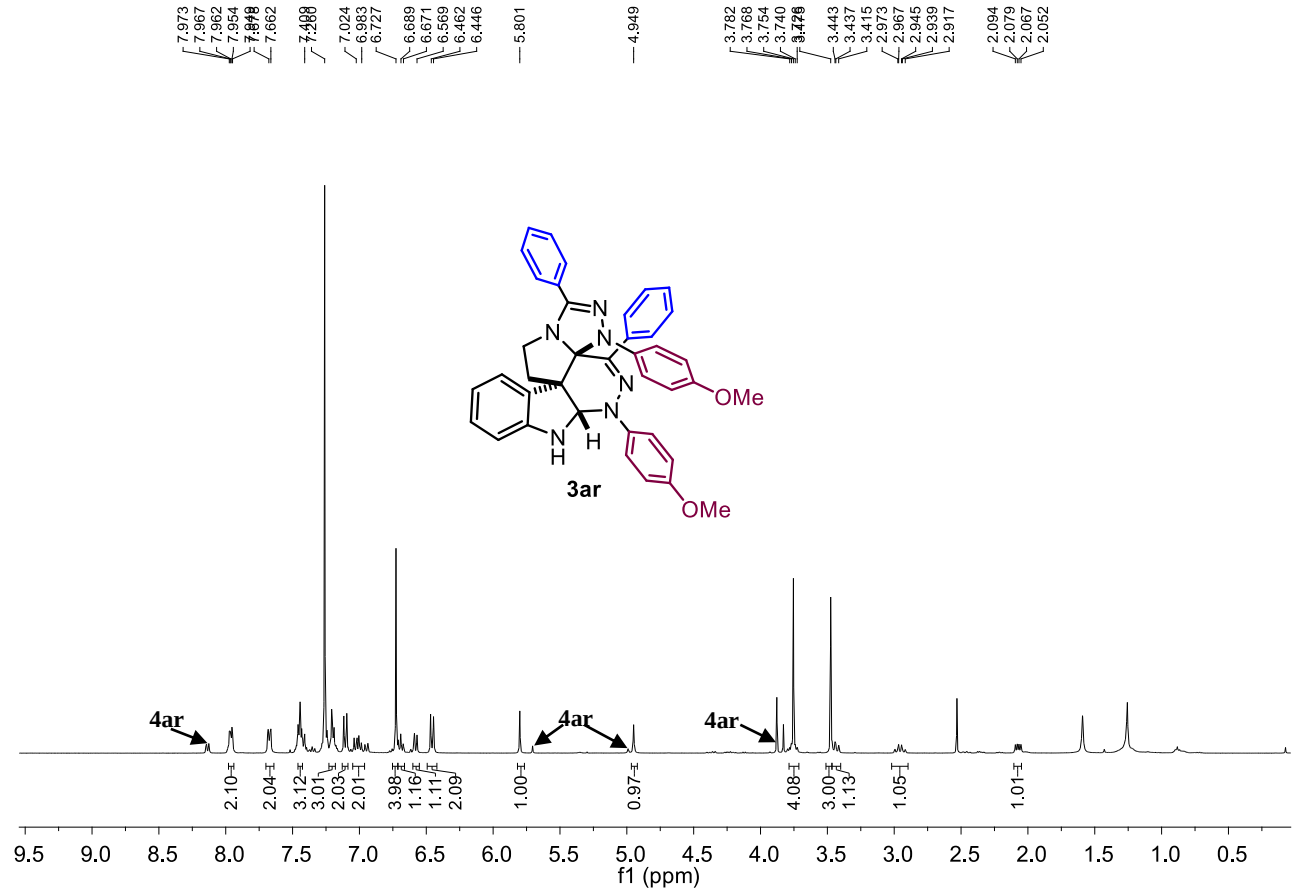
^{13}C NMR (101 MHz, $CDCl_3$) of **3ap**



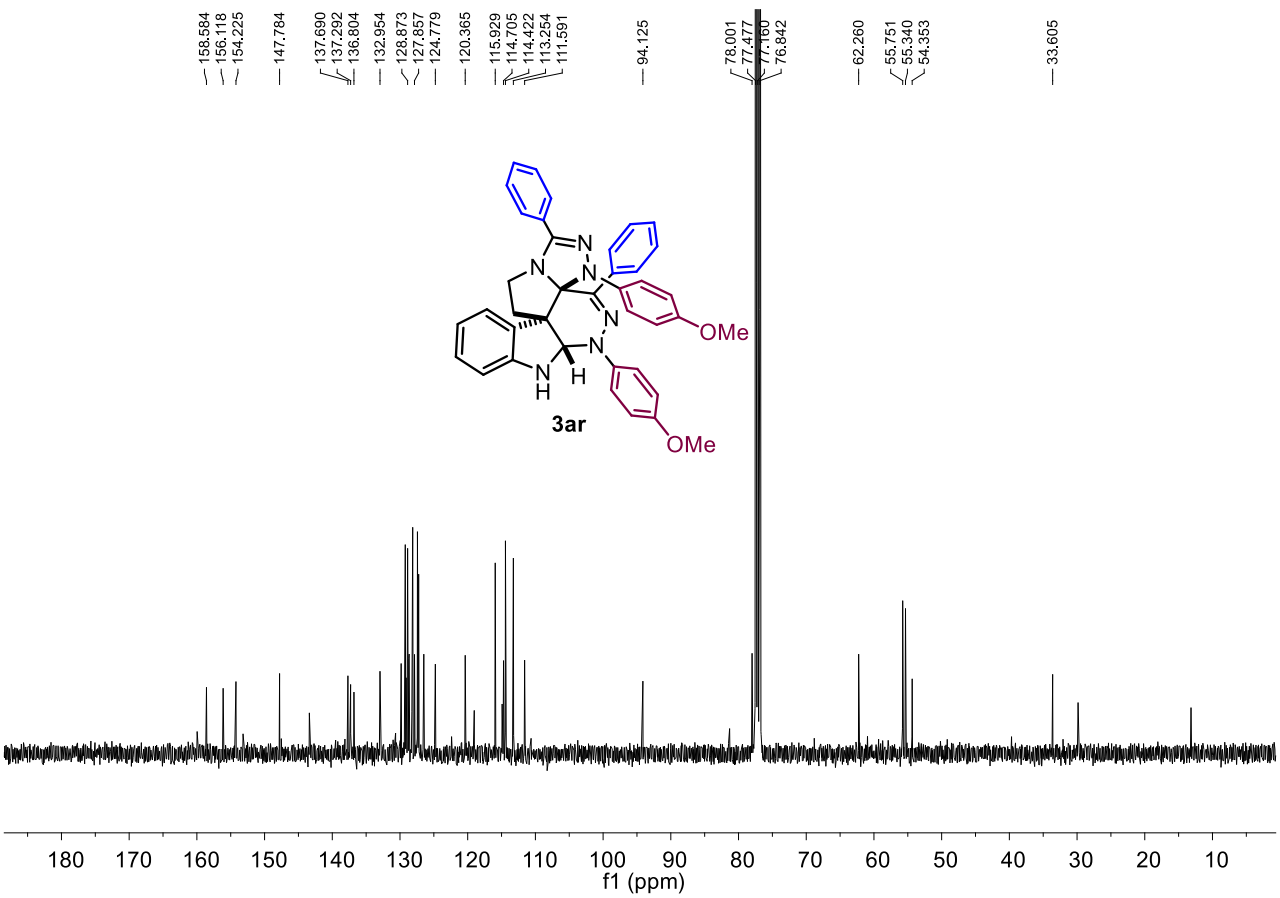
^{1}H NMR (400 MHz, $CDCl_3$) of **3aq**



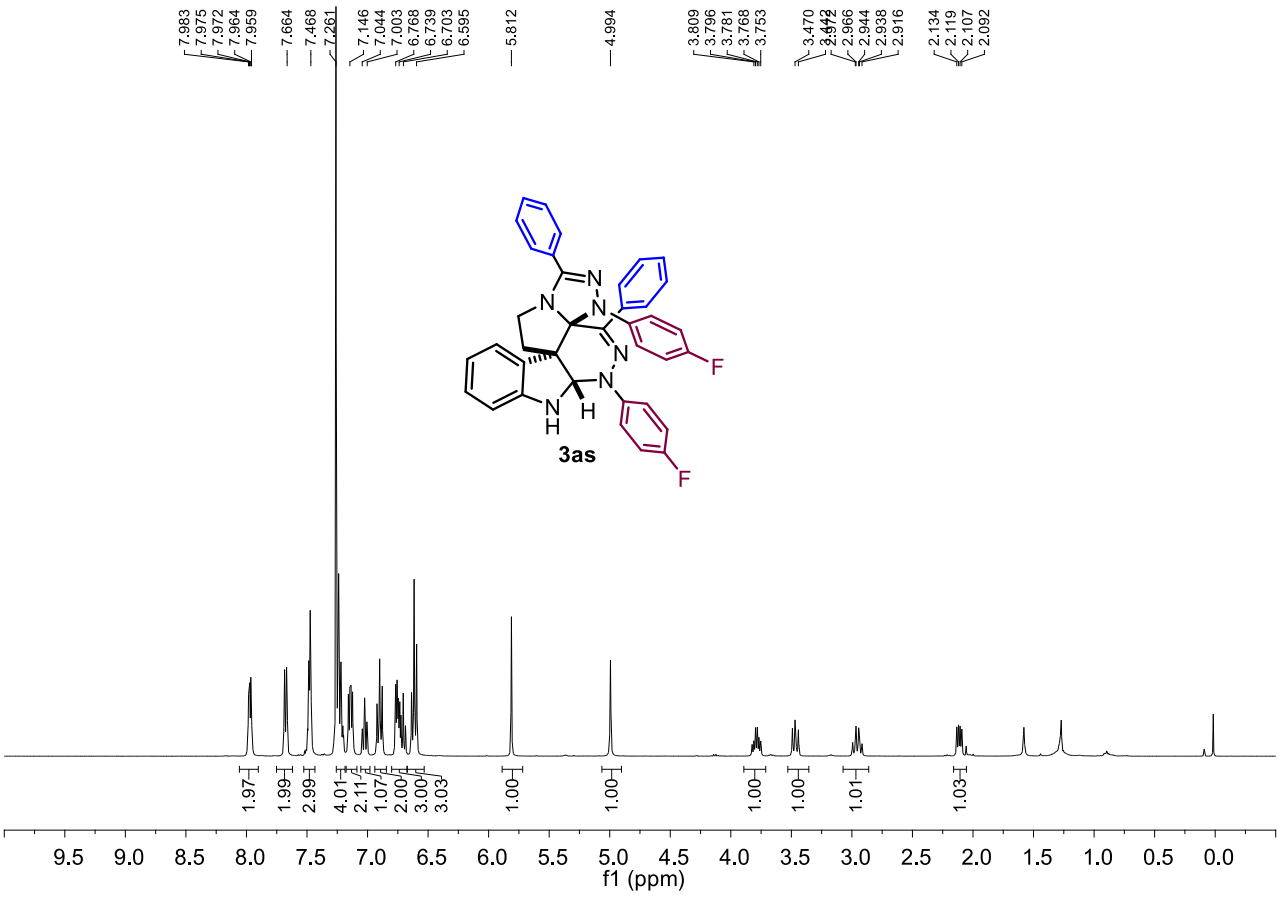
^{13}C NMR (101 MHz, $CDCl_3$) of **3aq**



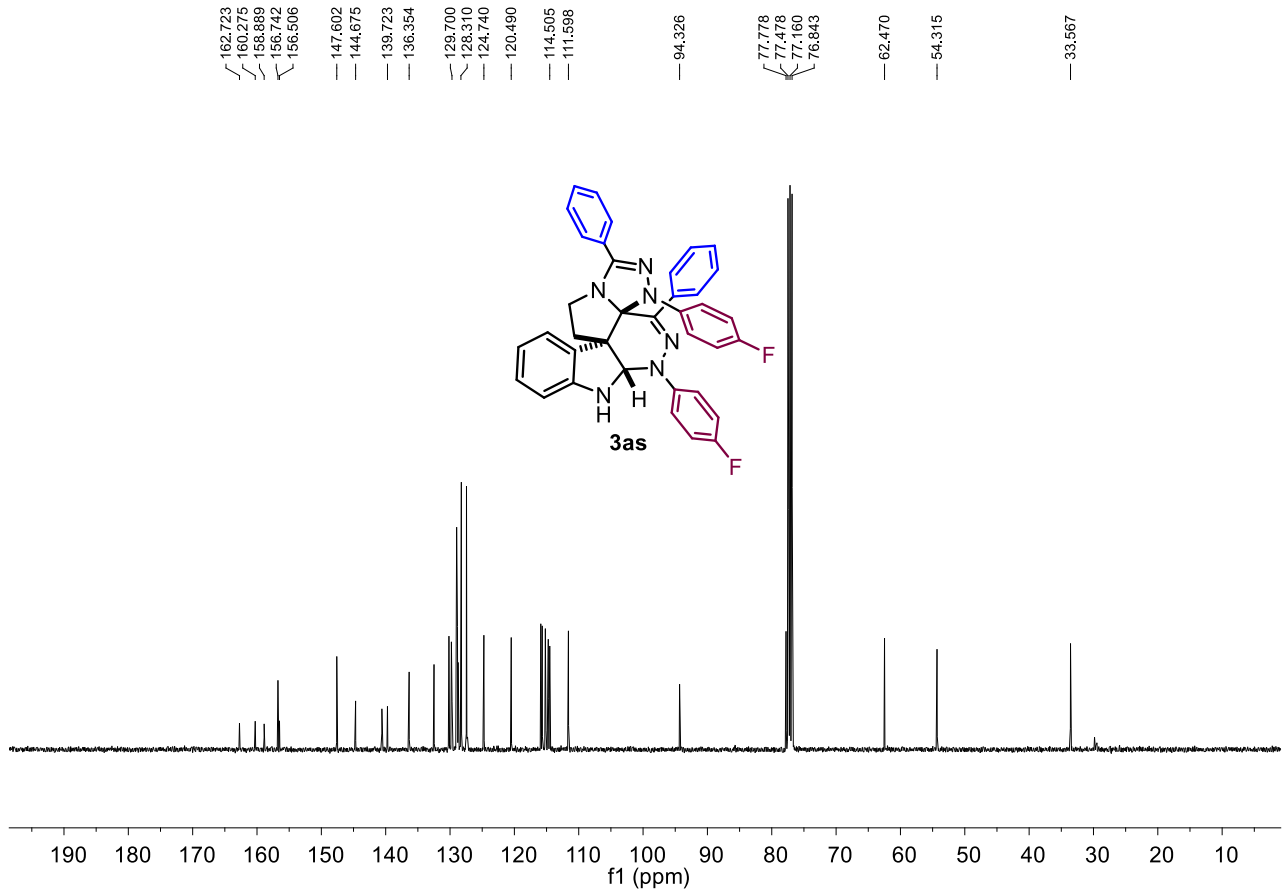
^{1}H NMR (400 MHz, $CDCl_3$) of **3ar**



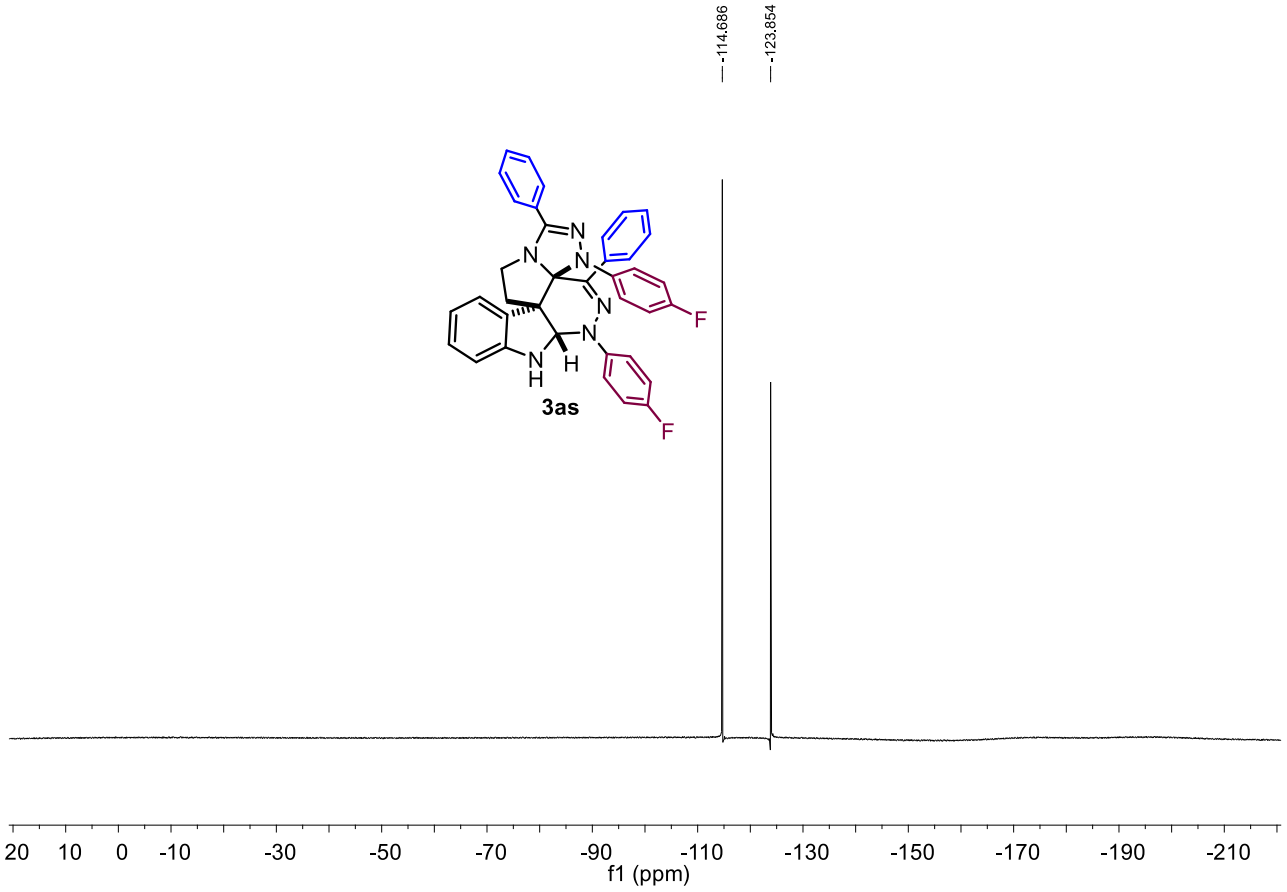
^{13}C NMR (101 MHz, $CDCl_3$) of **3ar**



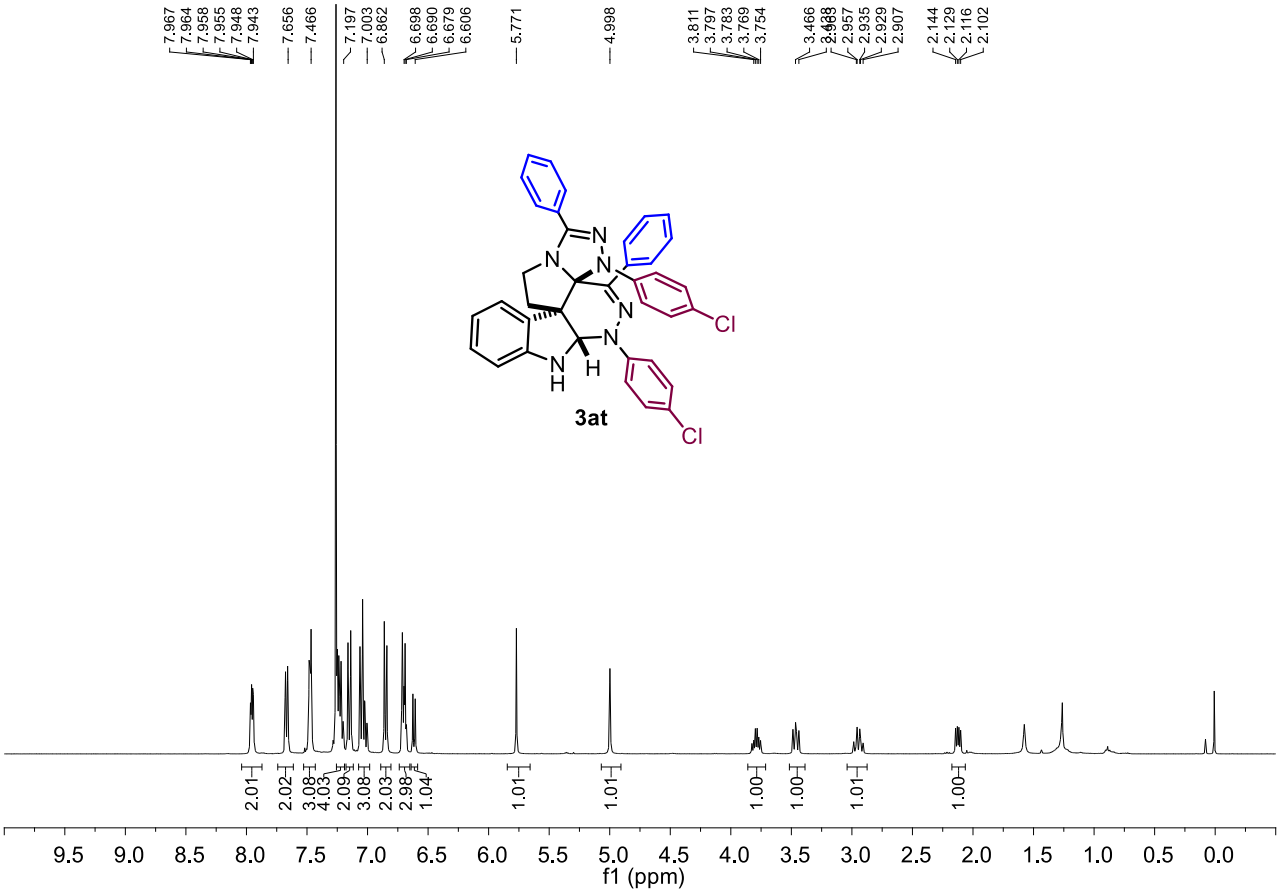
^{1}H NMR (400 MHz, $CDCl_3$) of **3as**



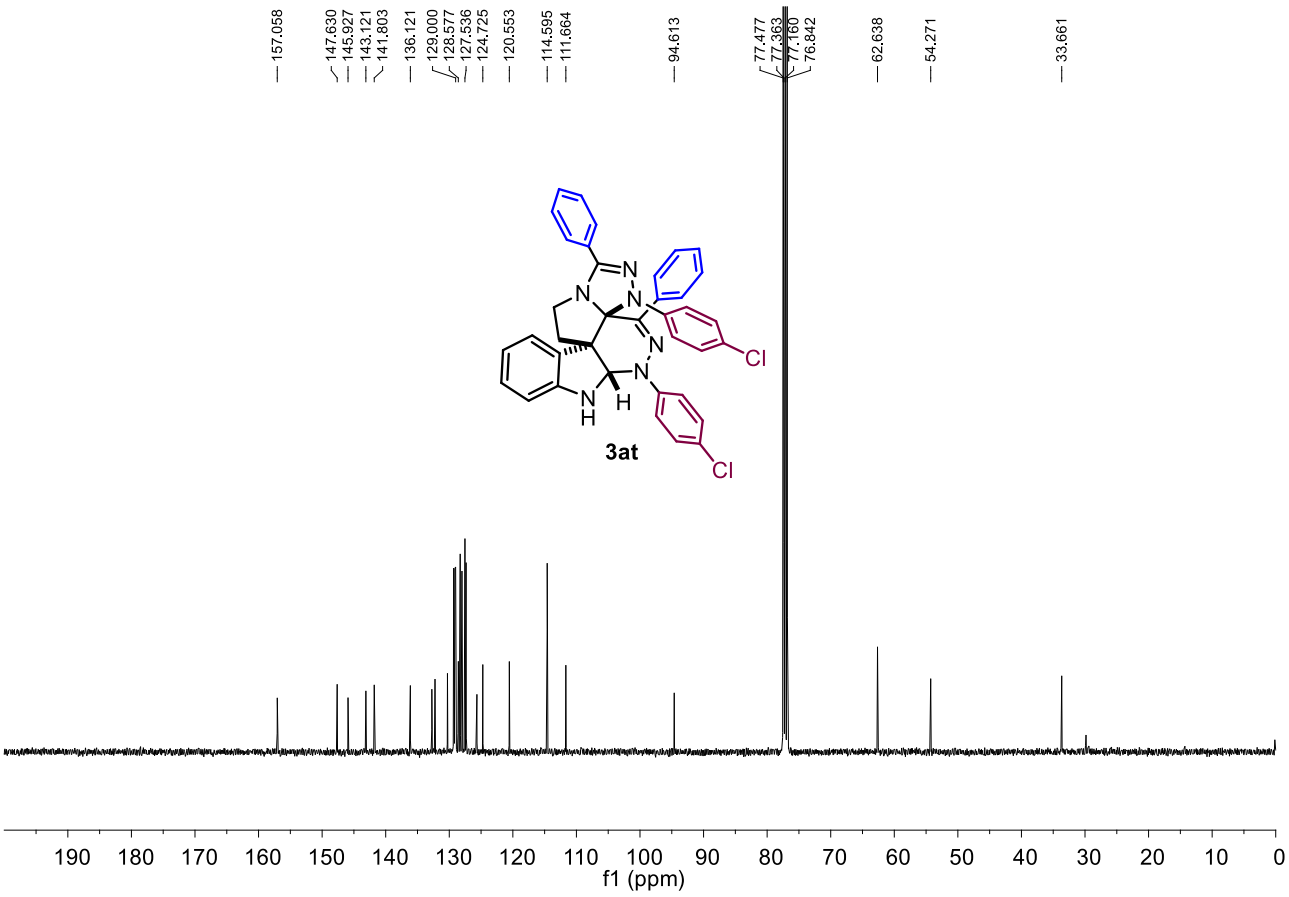
^{13}C NMR (101 MHz, $CDCl_3$) of **3as**



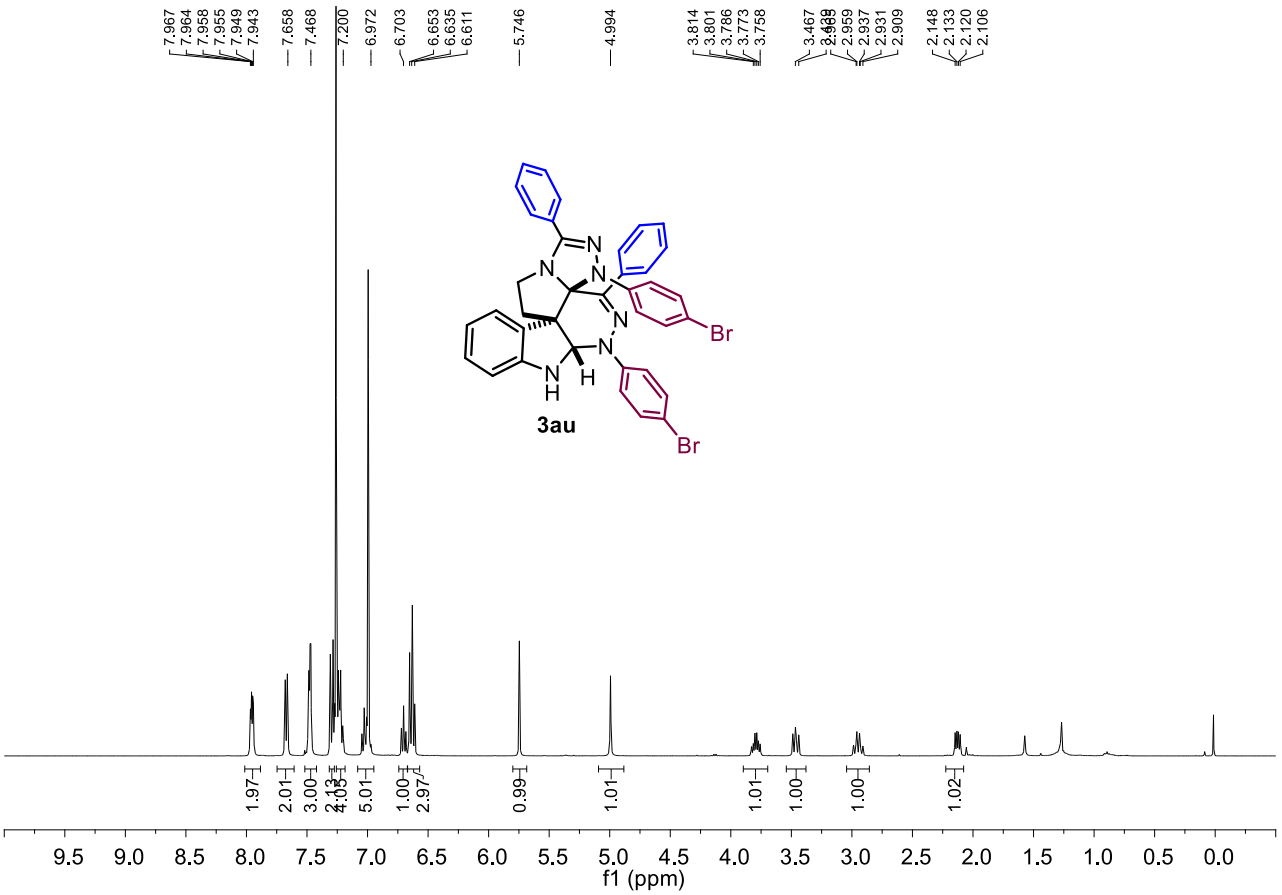
^{19}F NMR (376 MHz, $CDCl_3$) of **3as**



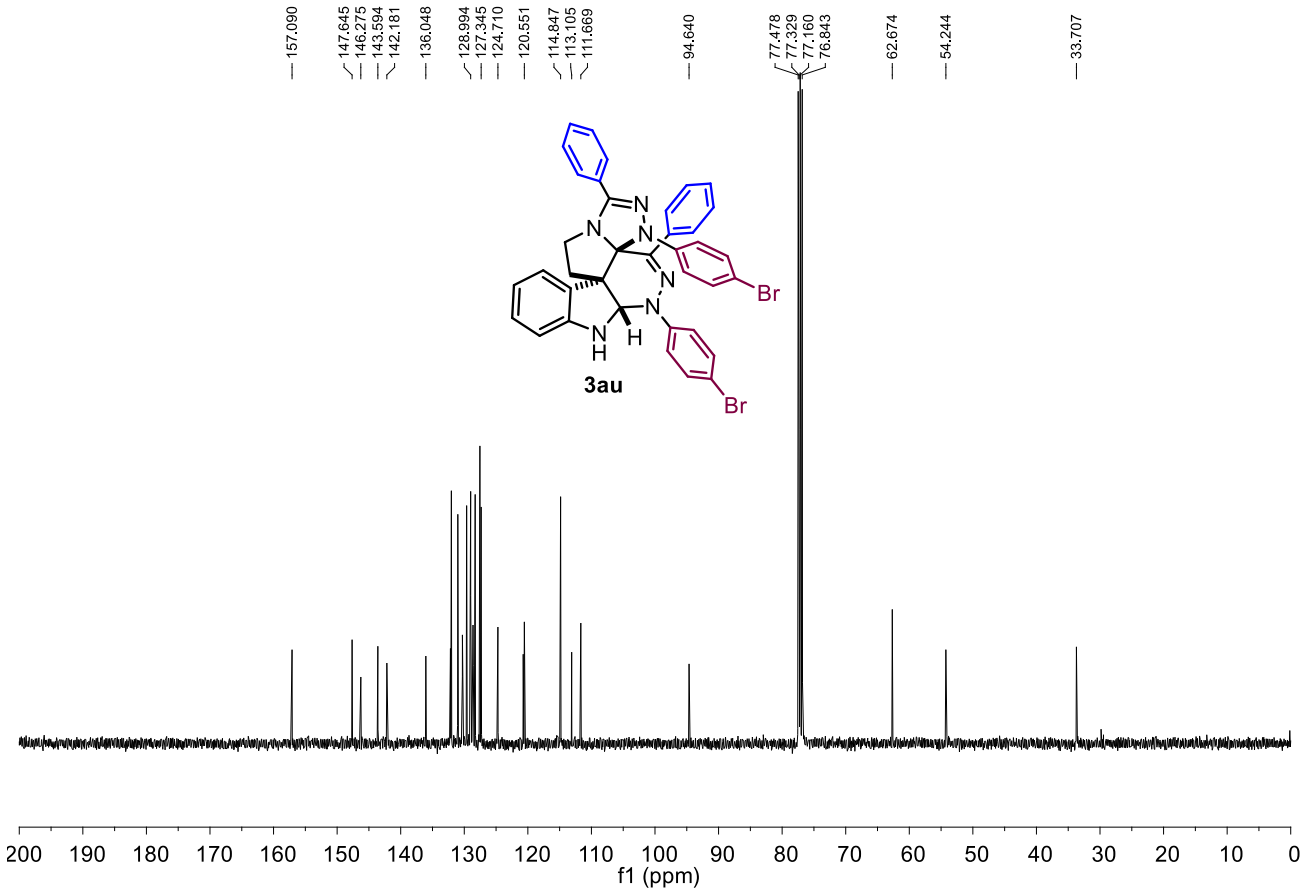
^{1}H NMR (400 MHz, $CDCl_3$) of **3at**



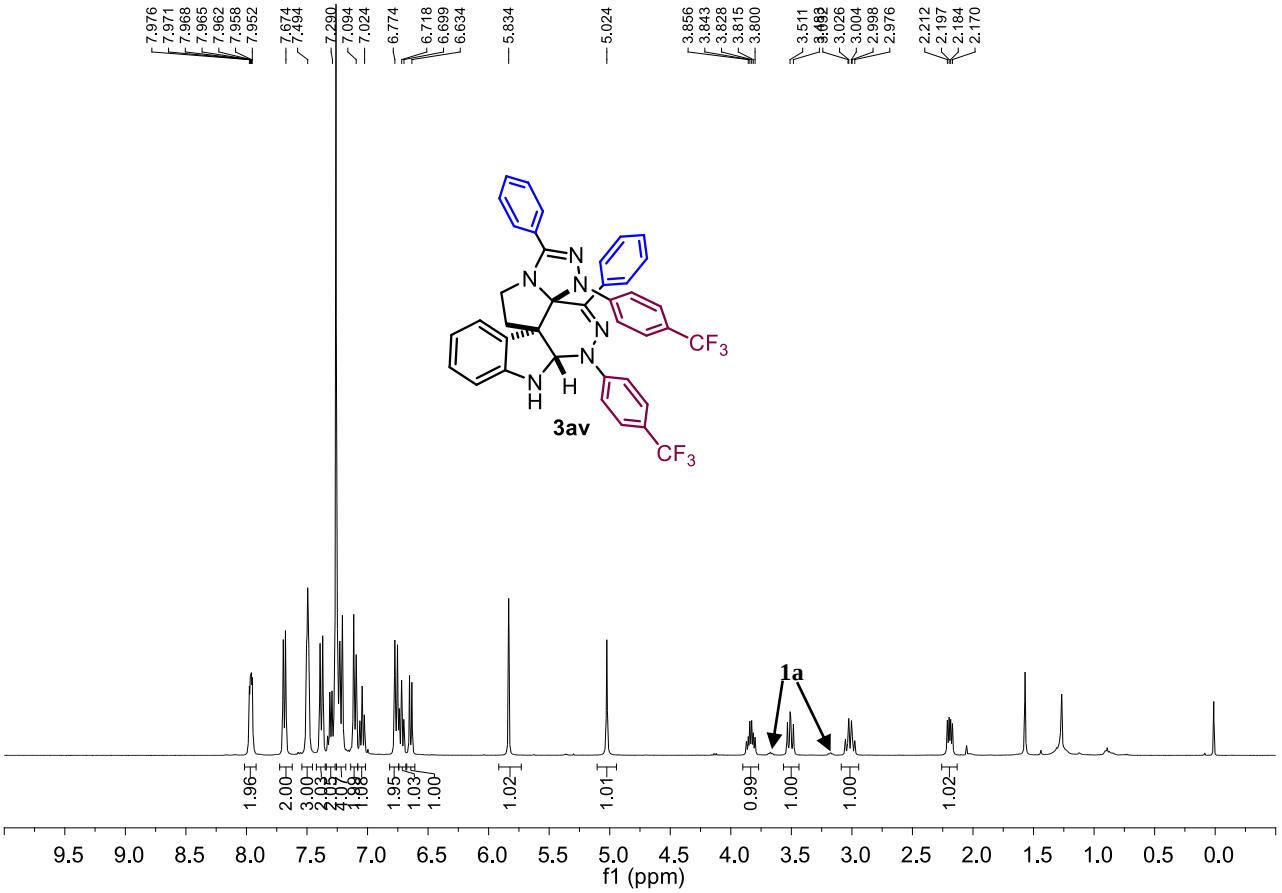
^{13}C NMR (101 MHz, $CDCl_3$) of **3at**



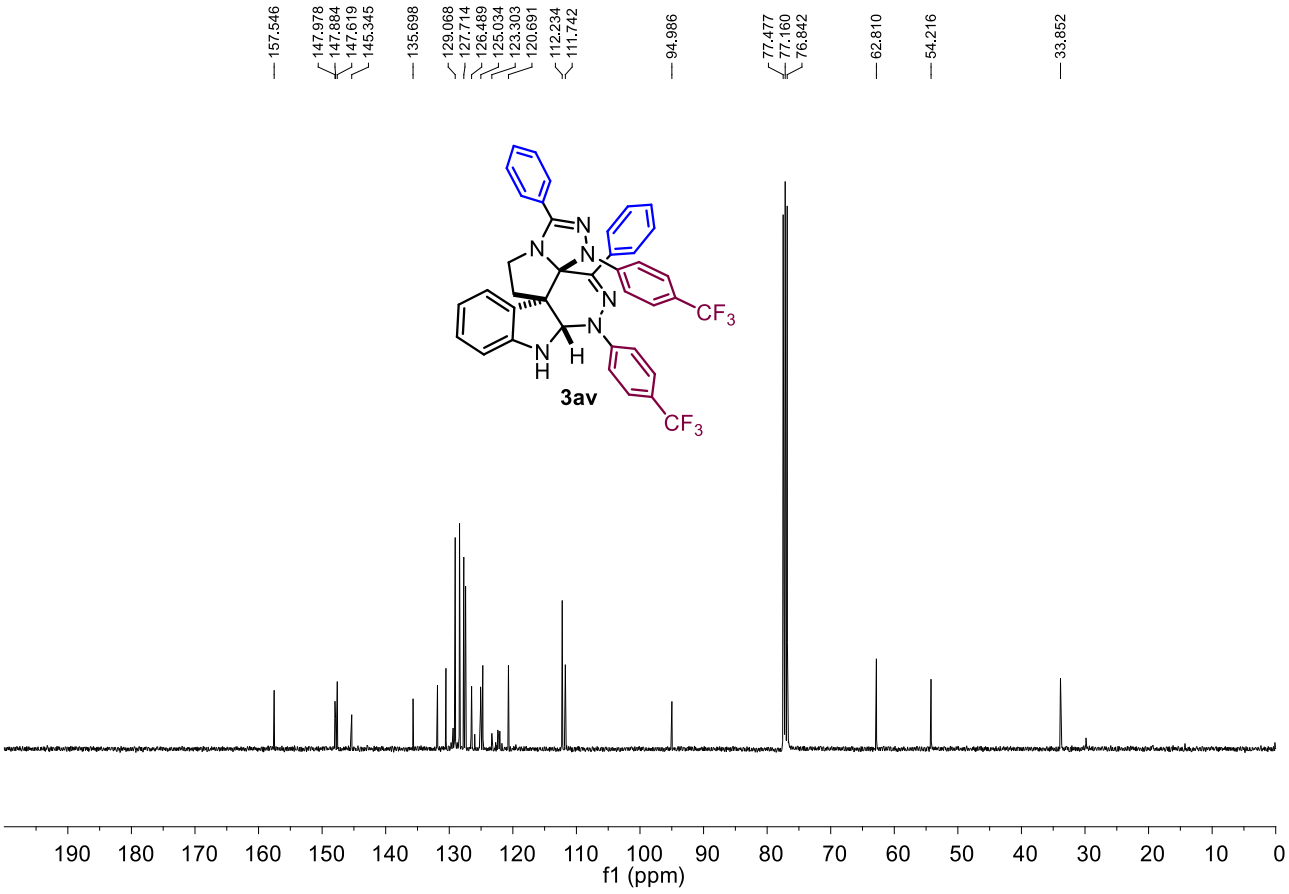
^{1}H NMR (400 MHz, $CDCl_3$) of **3au**



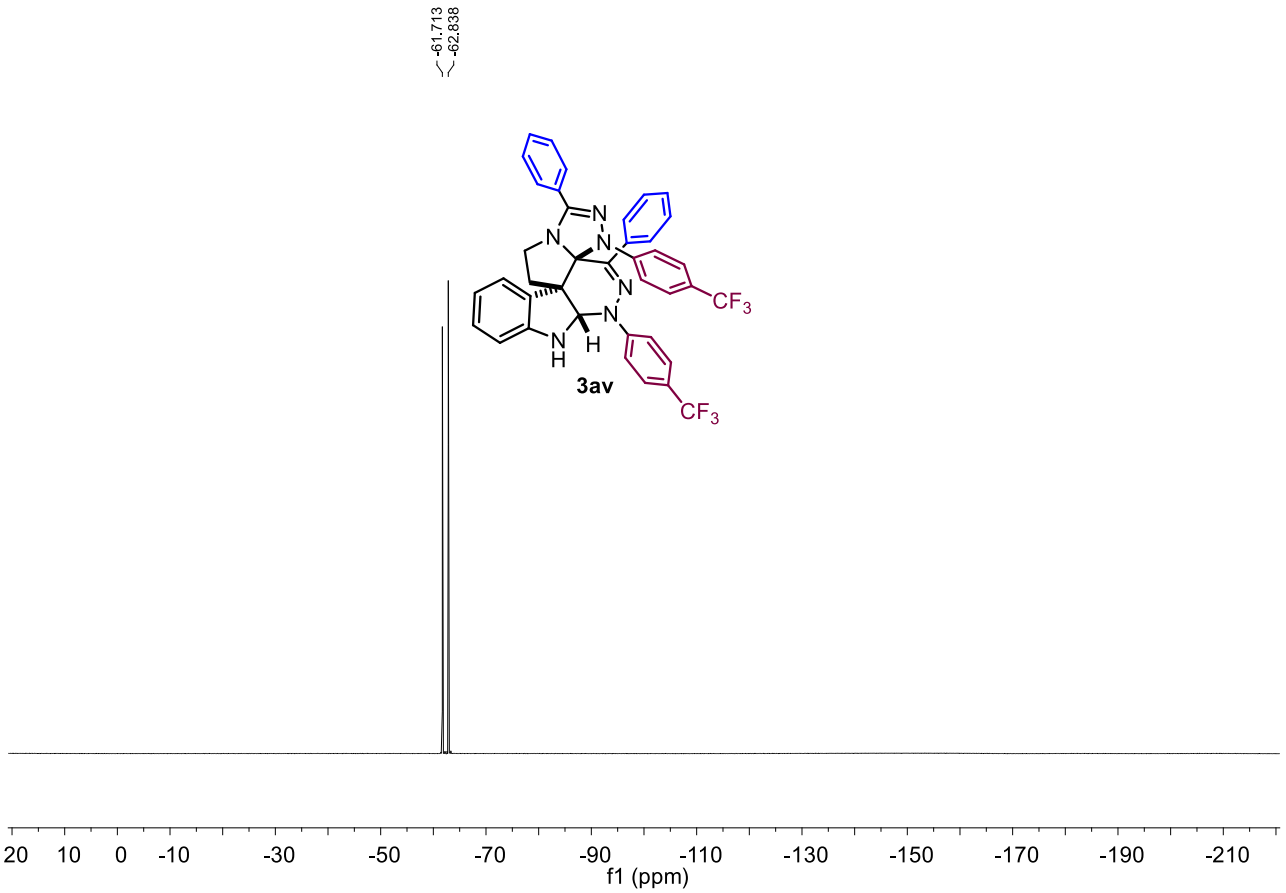
^{13}C NMR (101 MHz, $CDCl_3$) of **3au**



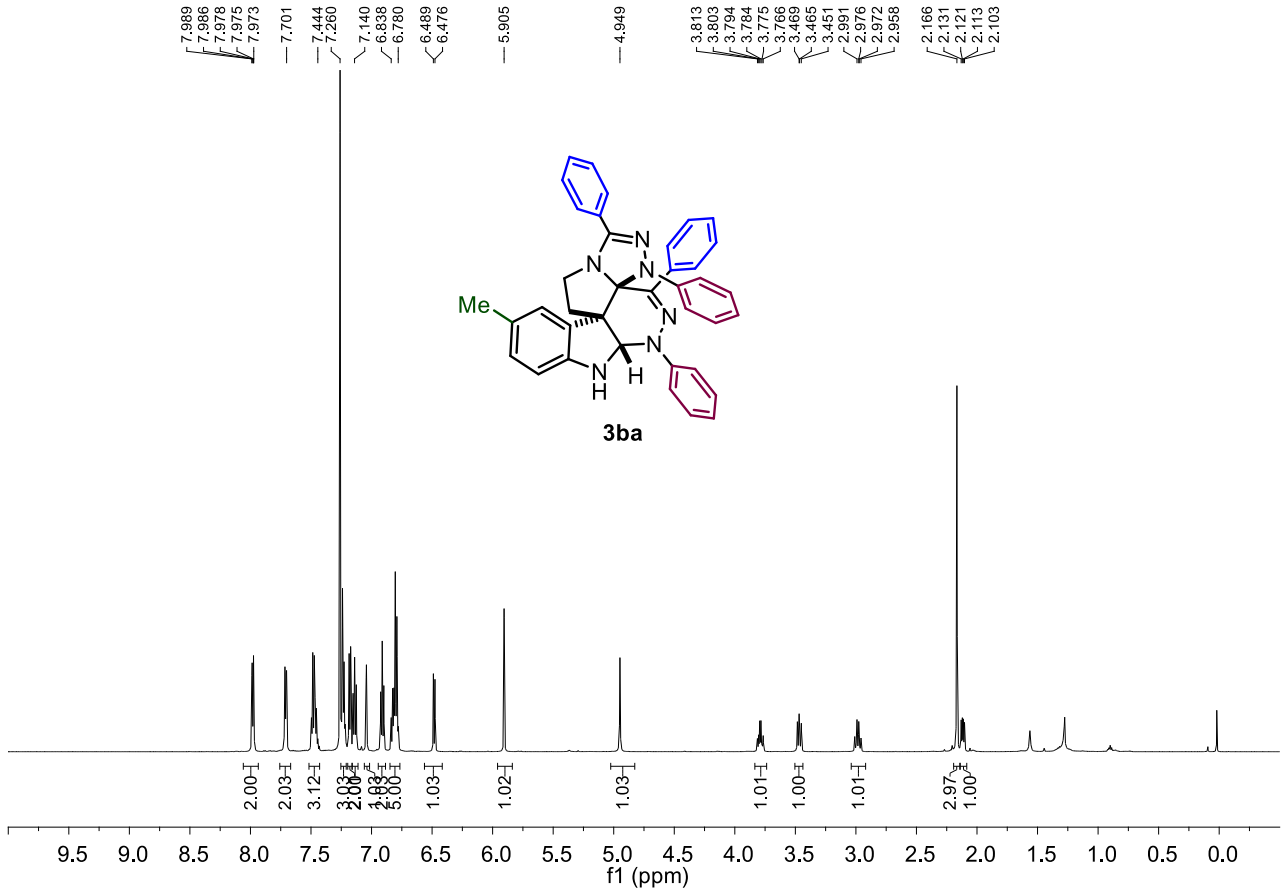
^{1}H NMR (400 MHz, $CDCl_3$) of **3av**



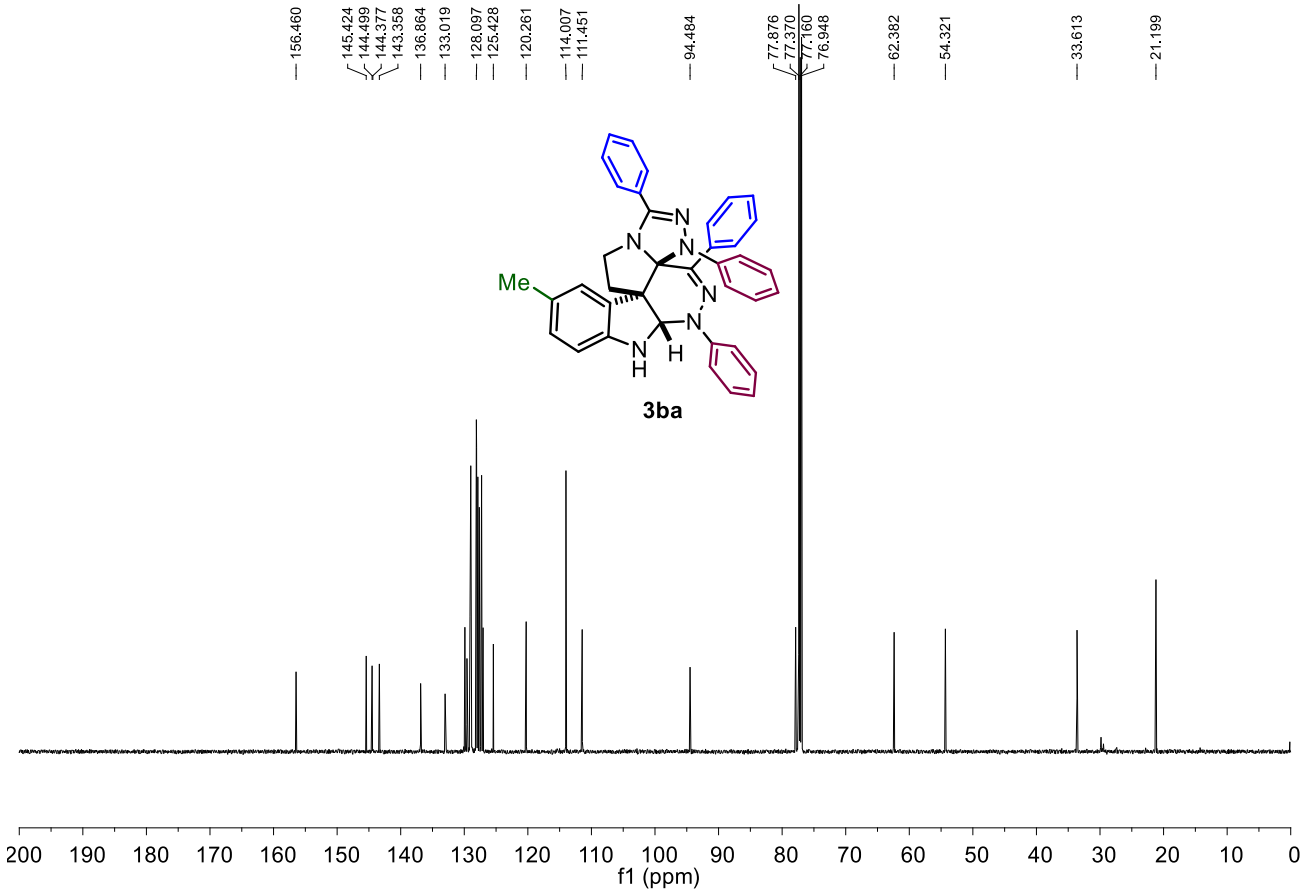
^{13}C NMR (101 MHz, $CDCl_3$) of **3av**



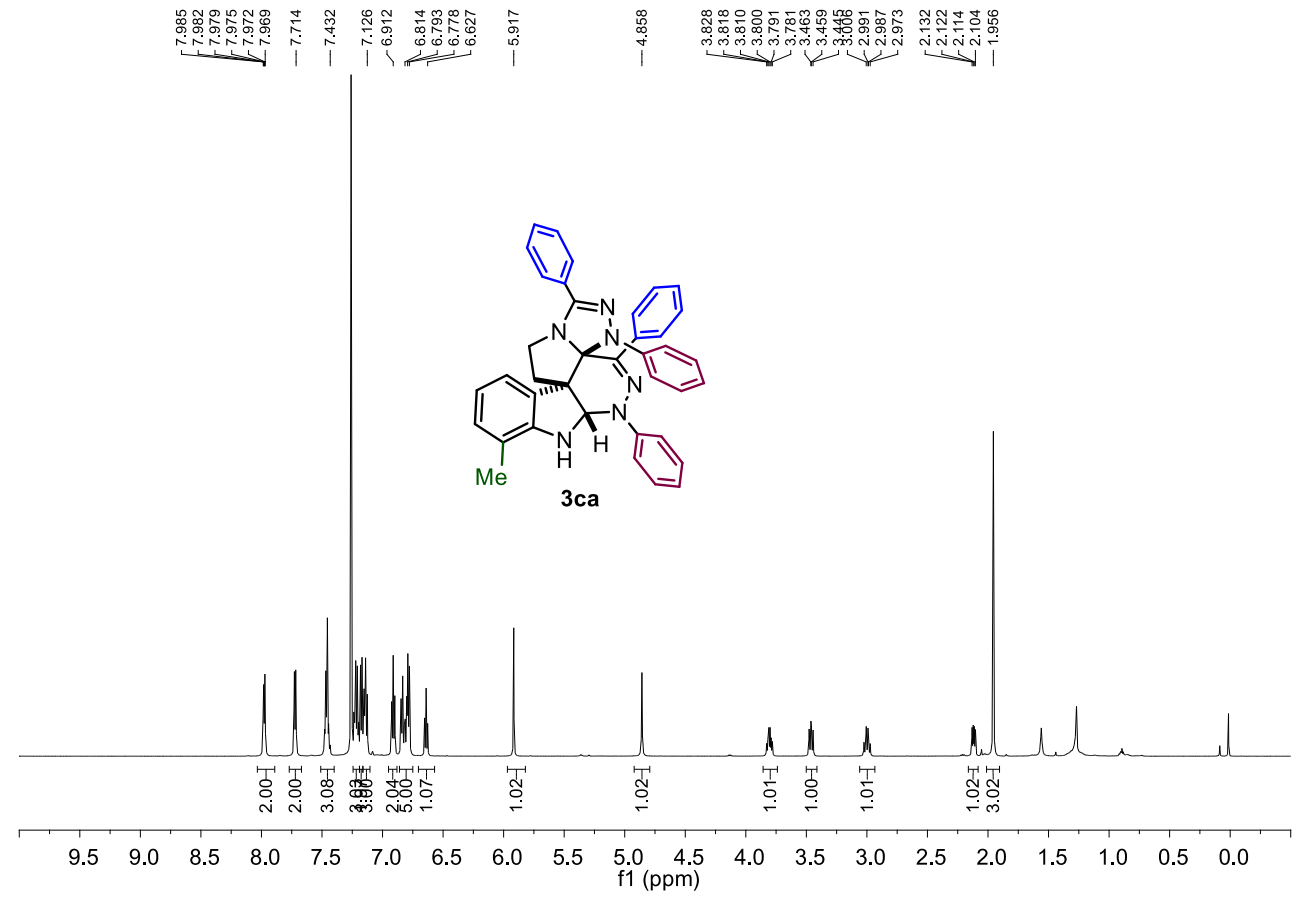
^{19}F NMR (376 MHz, $CDCl_3$) of **3av**



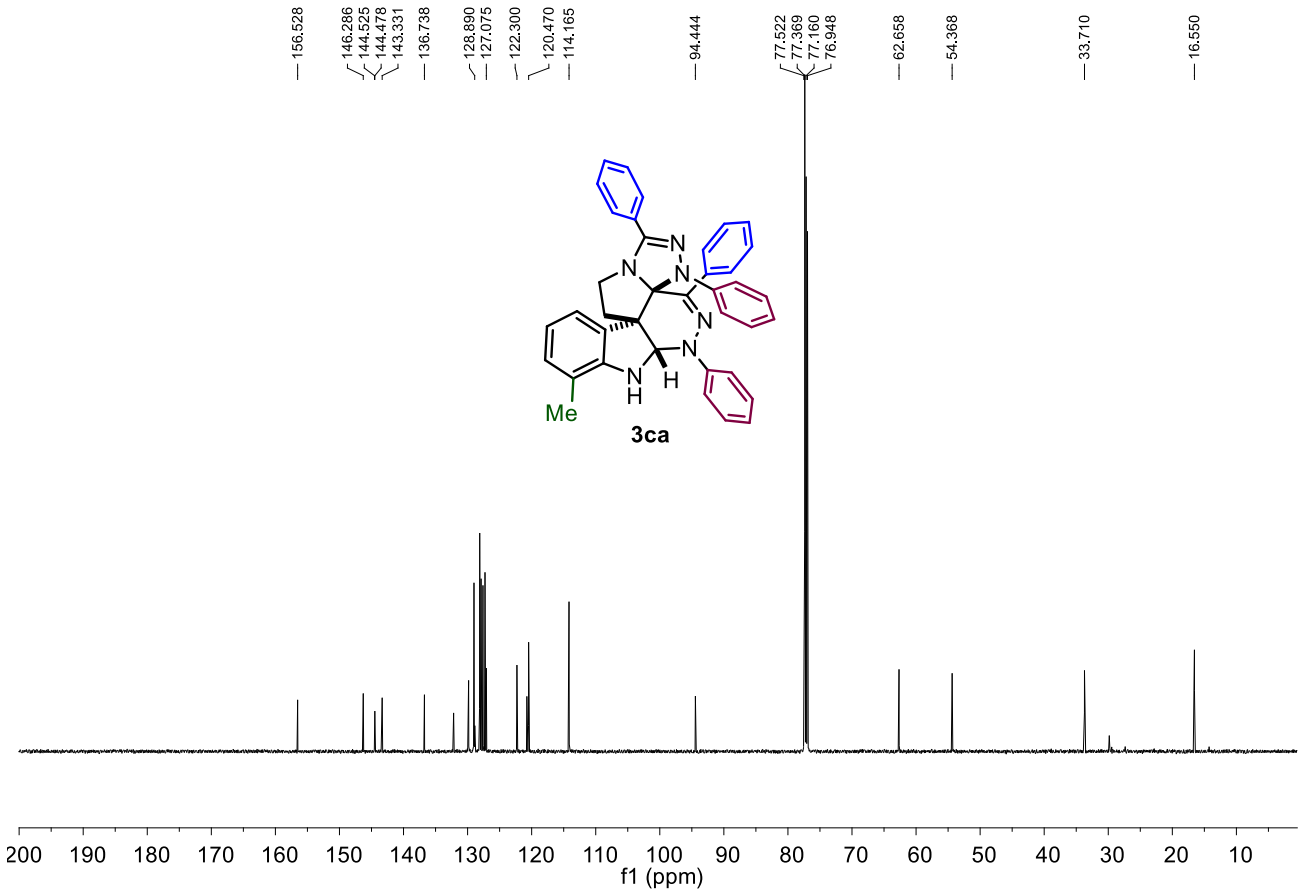
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



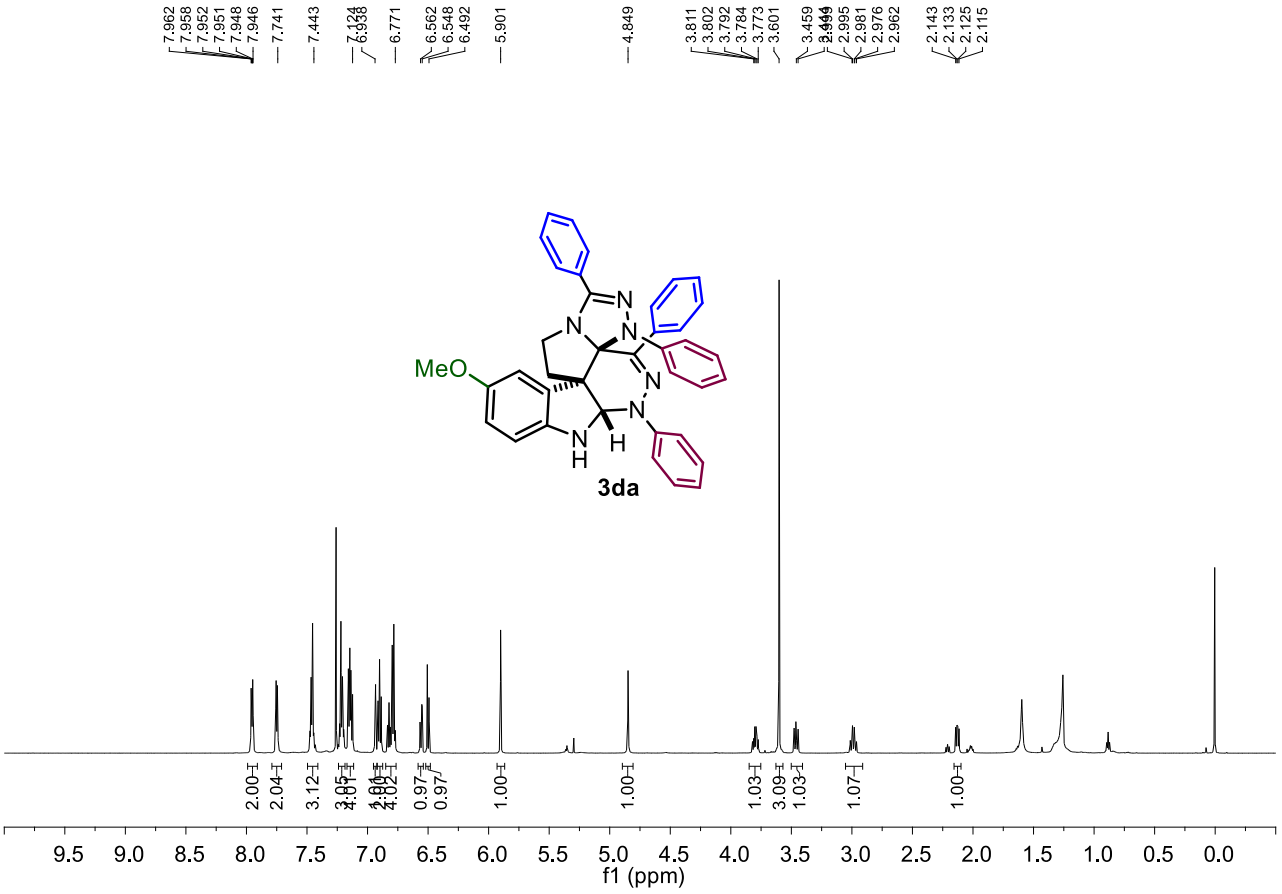
^{13}C NMR (101 MHz, $CDCl_3$) of **3ba**



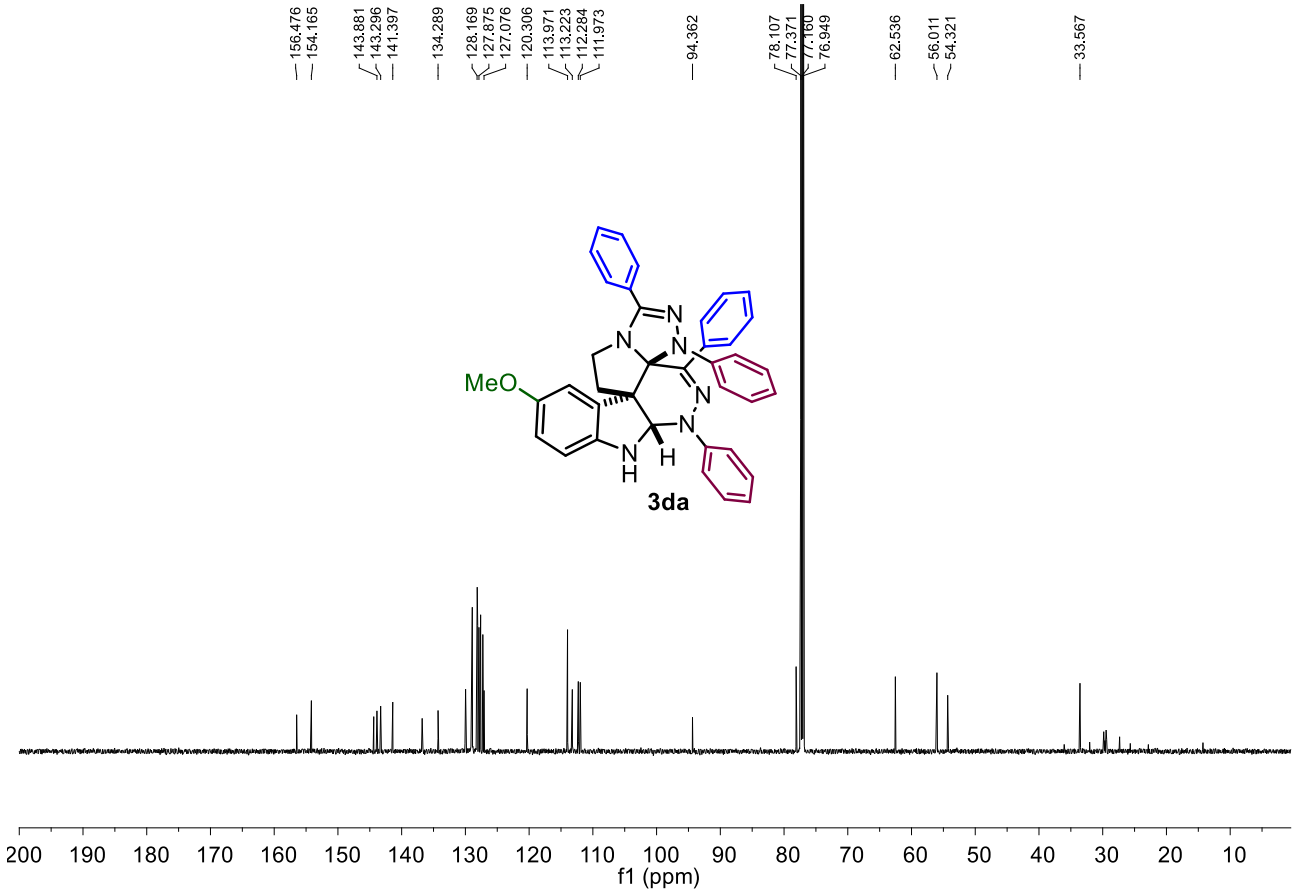
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



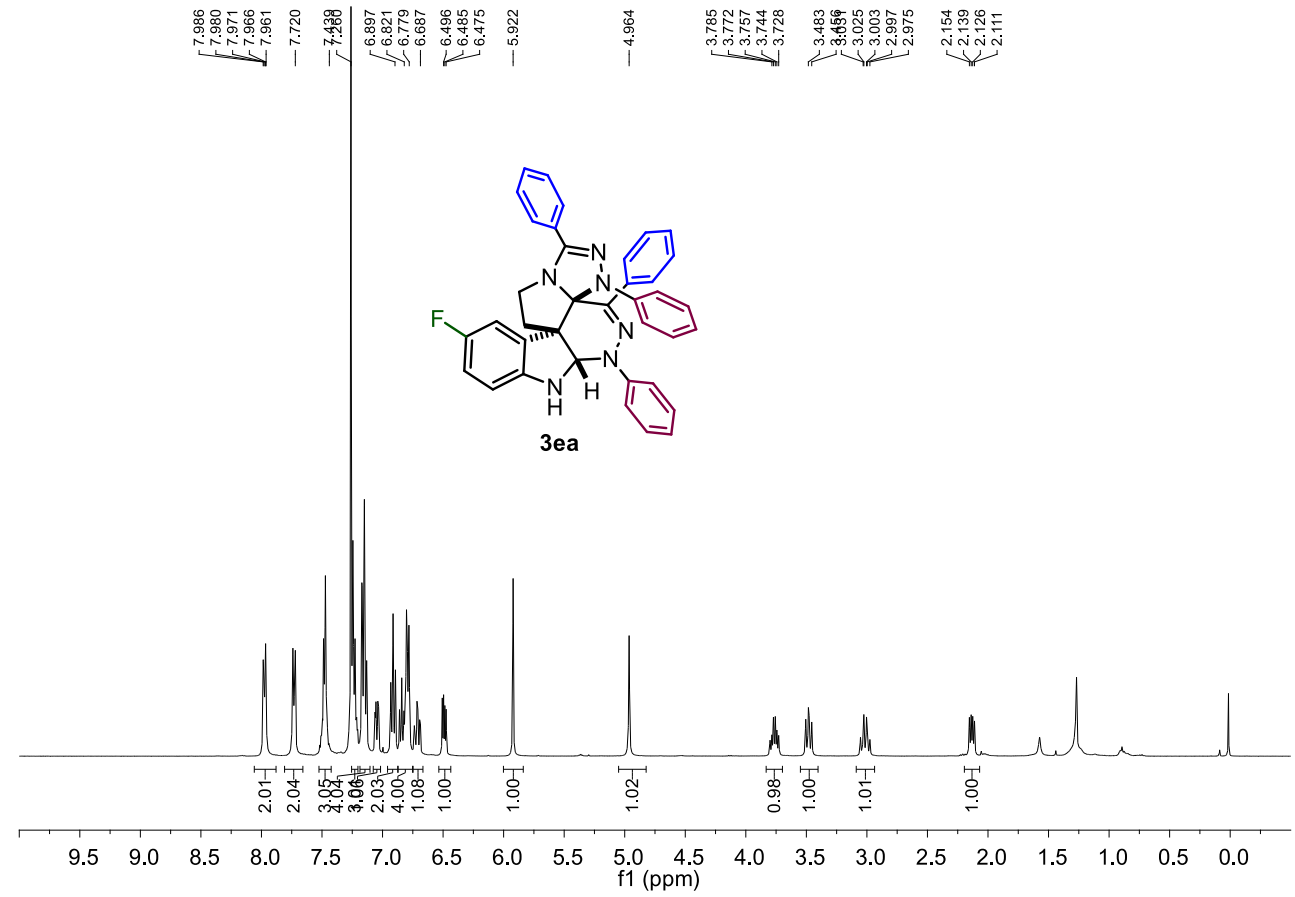
^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**



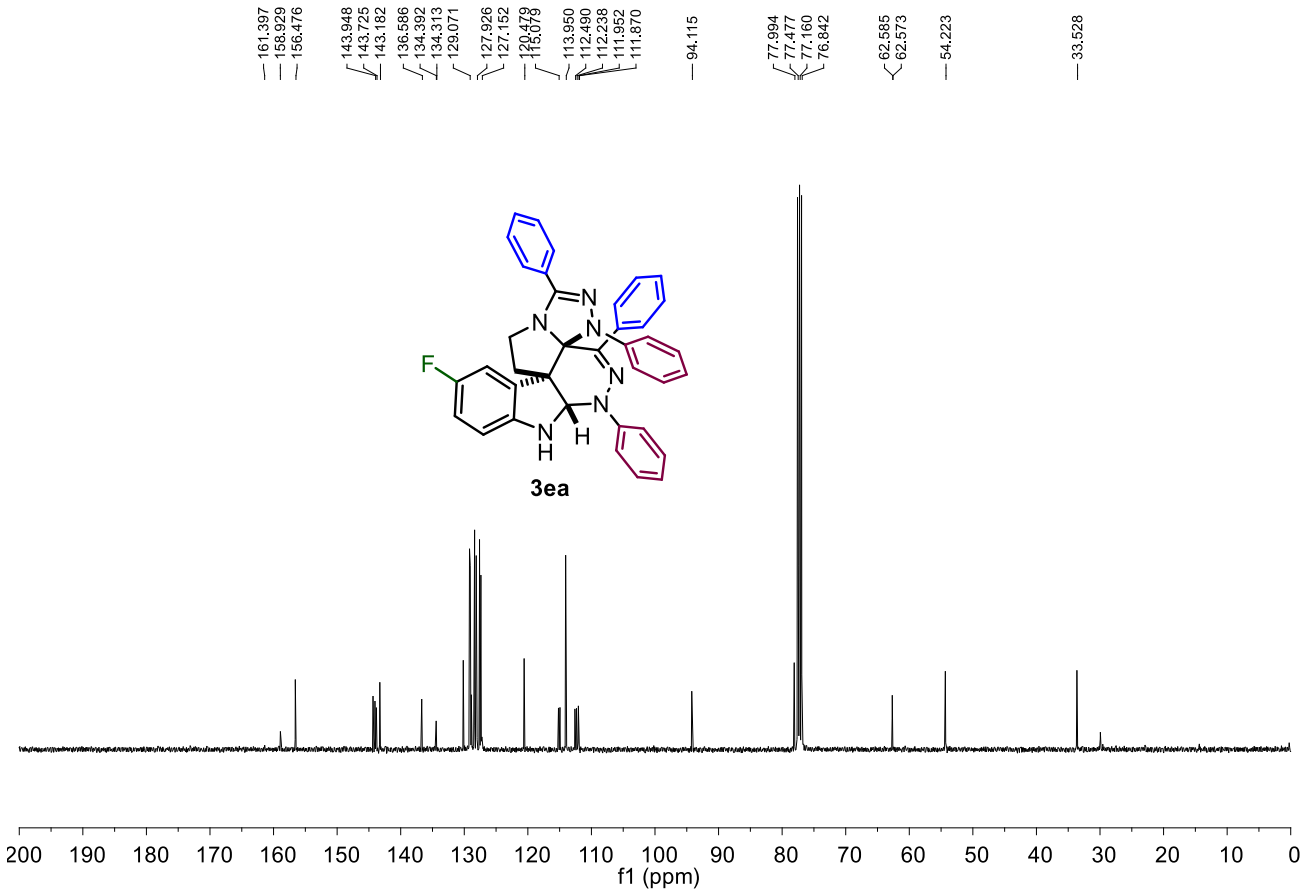
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



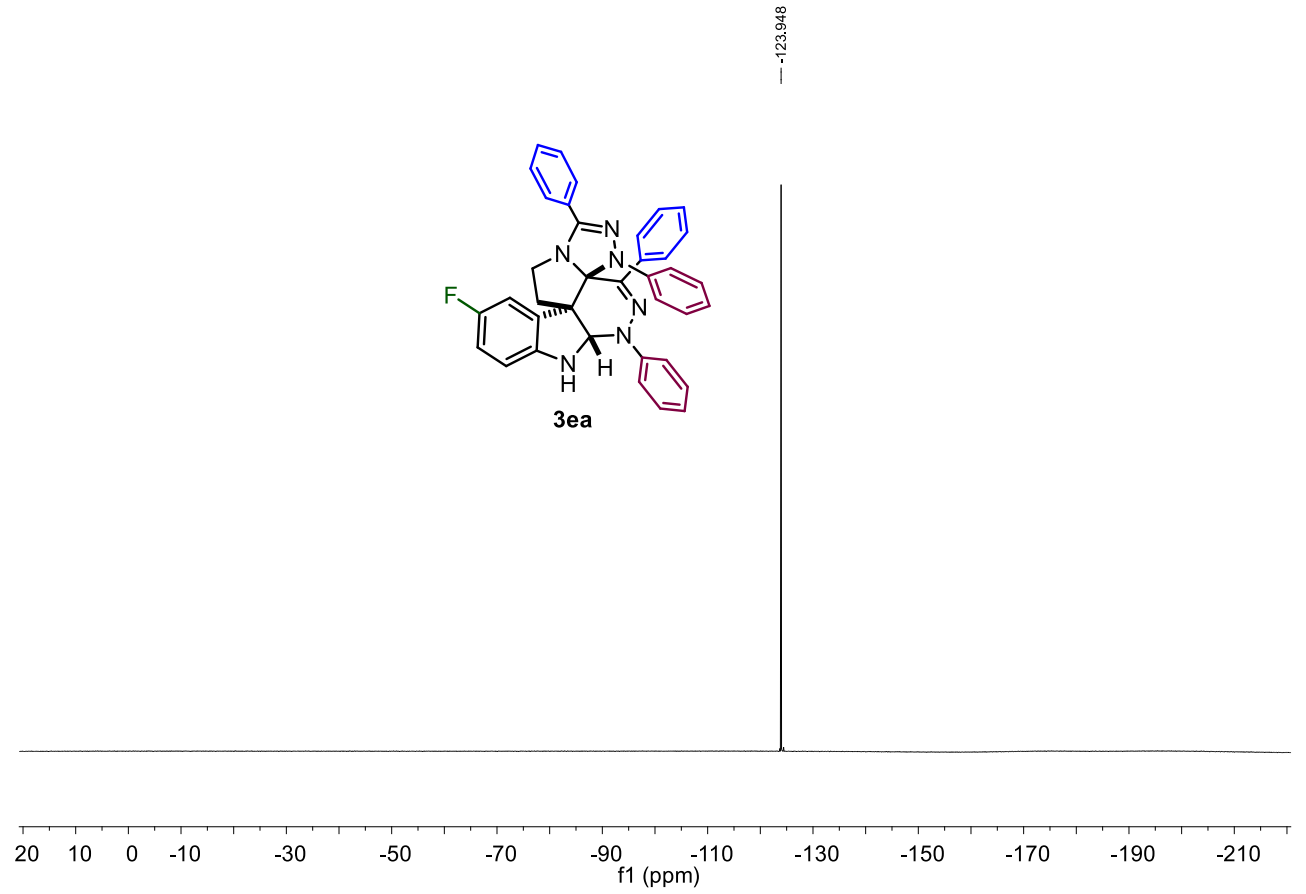
^{13}C NMR (101 MHz, $CDCl_3$) of **3da**



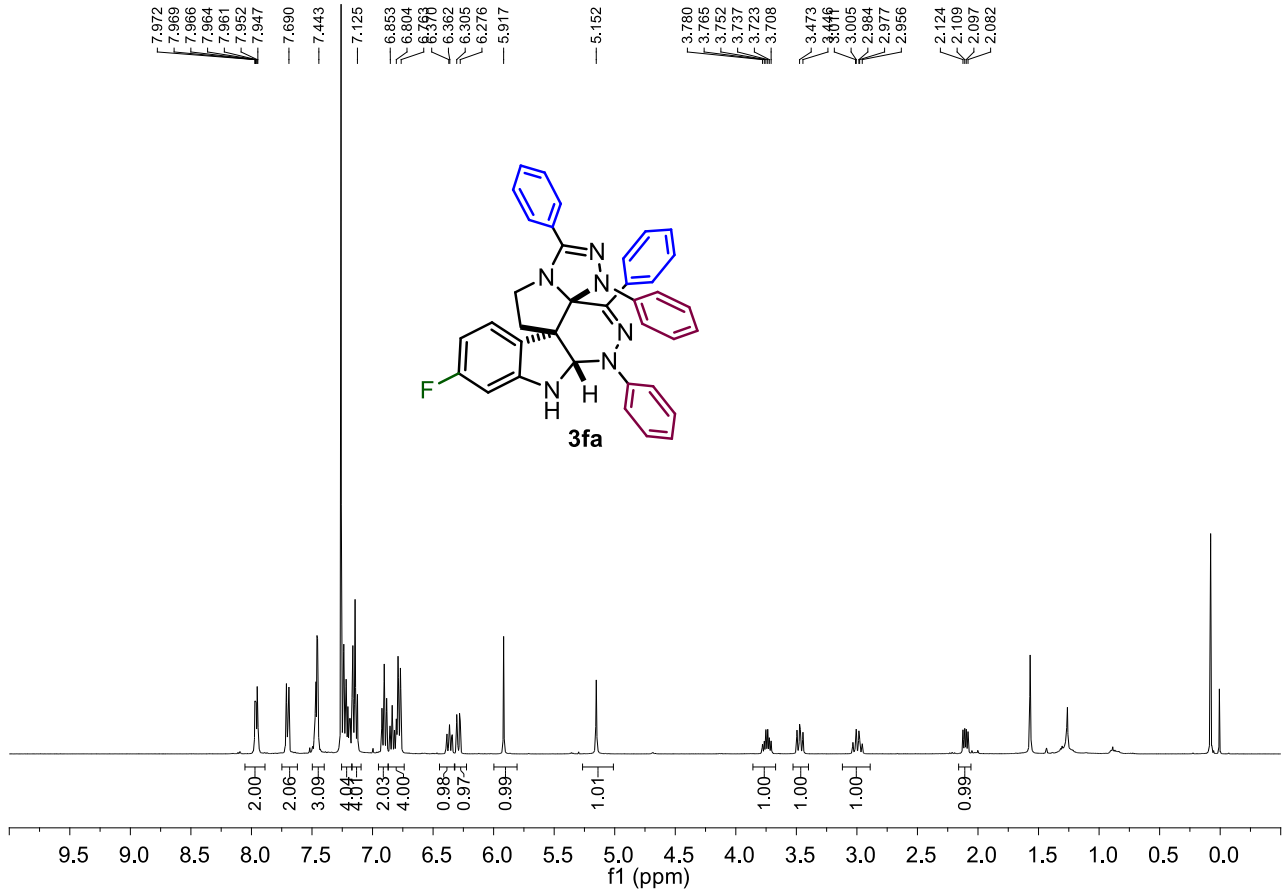
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



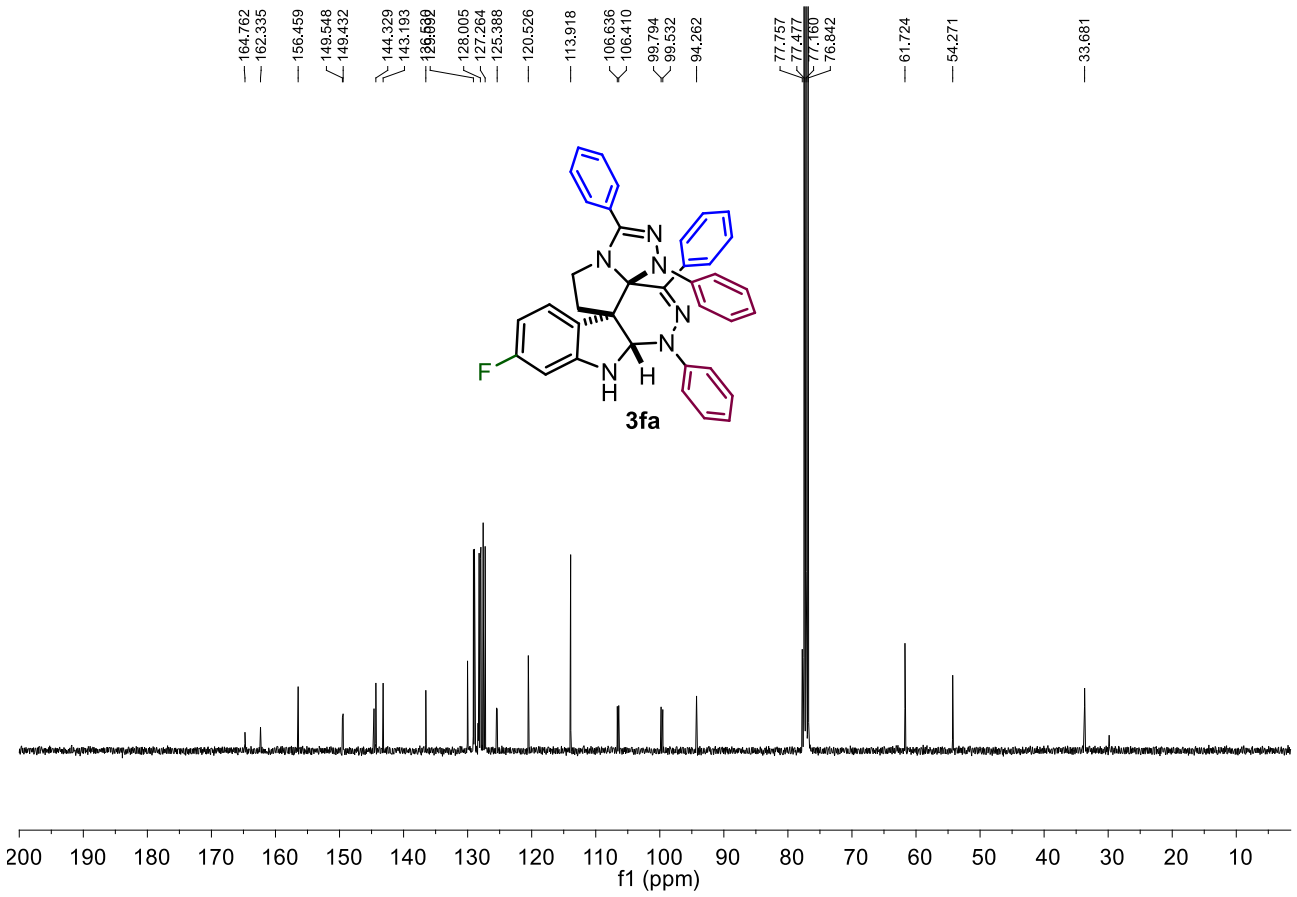
^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**



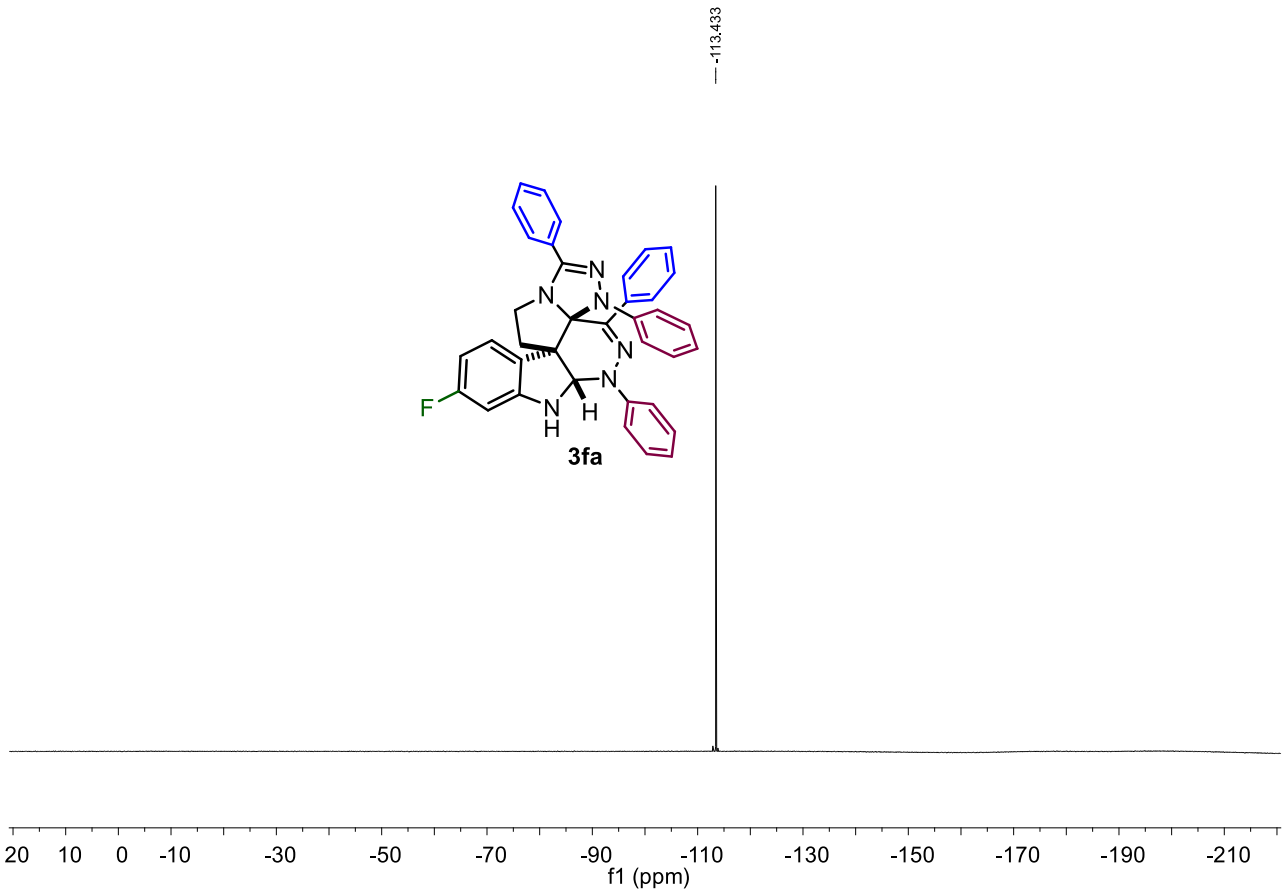
^{19}F NMR (376 MHz, $CDCl_3$) of **3ea**



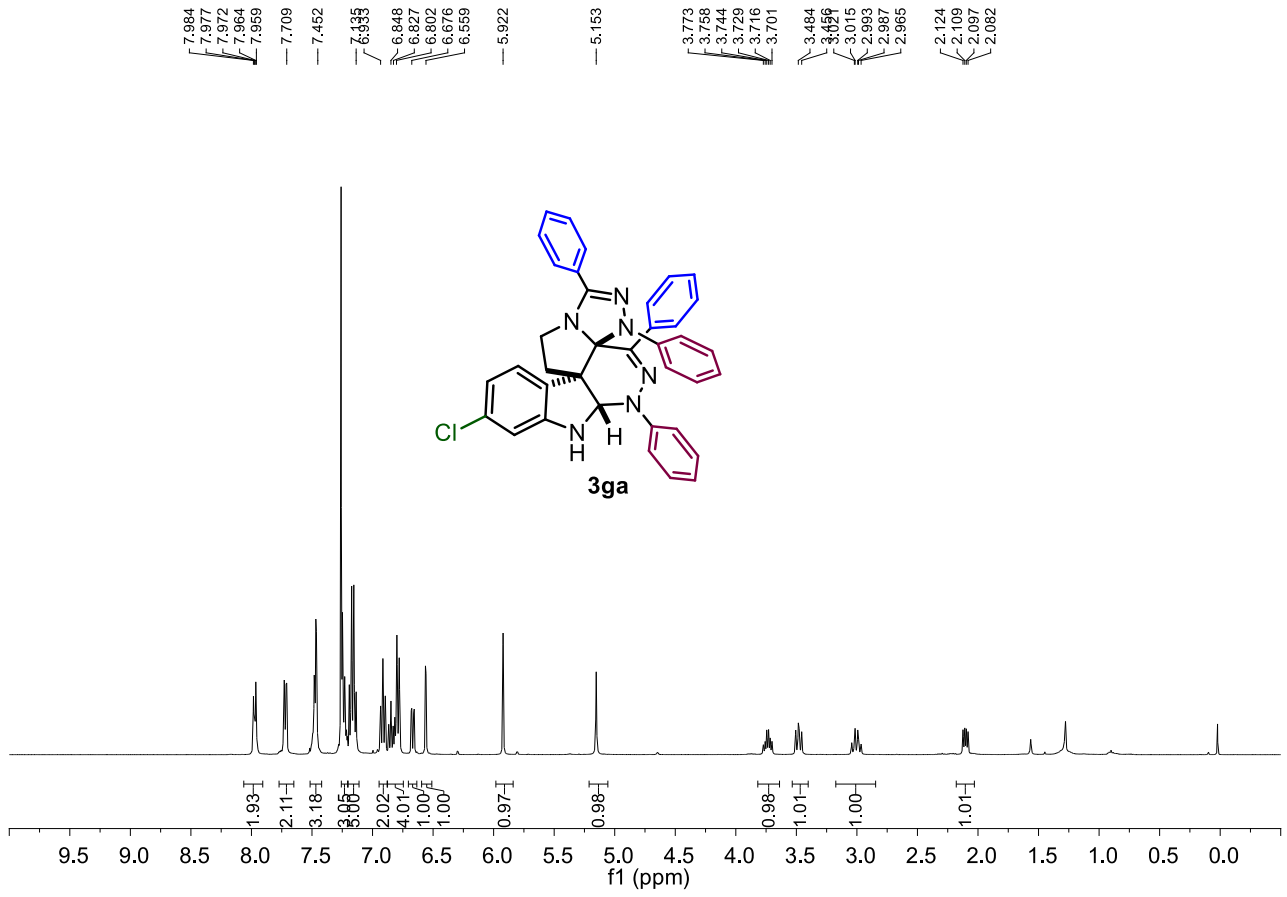
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



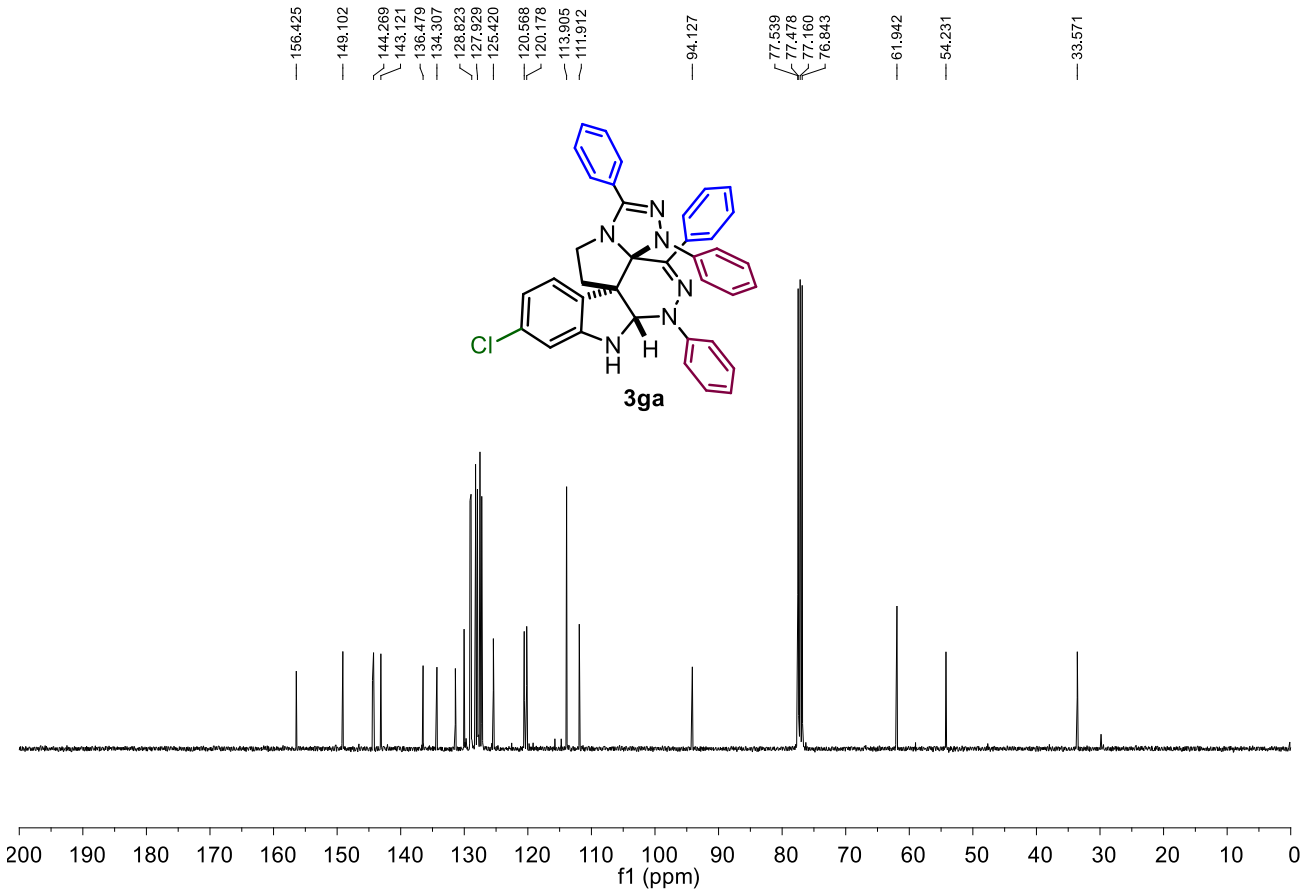
^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**



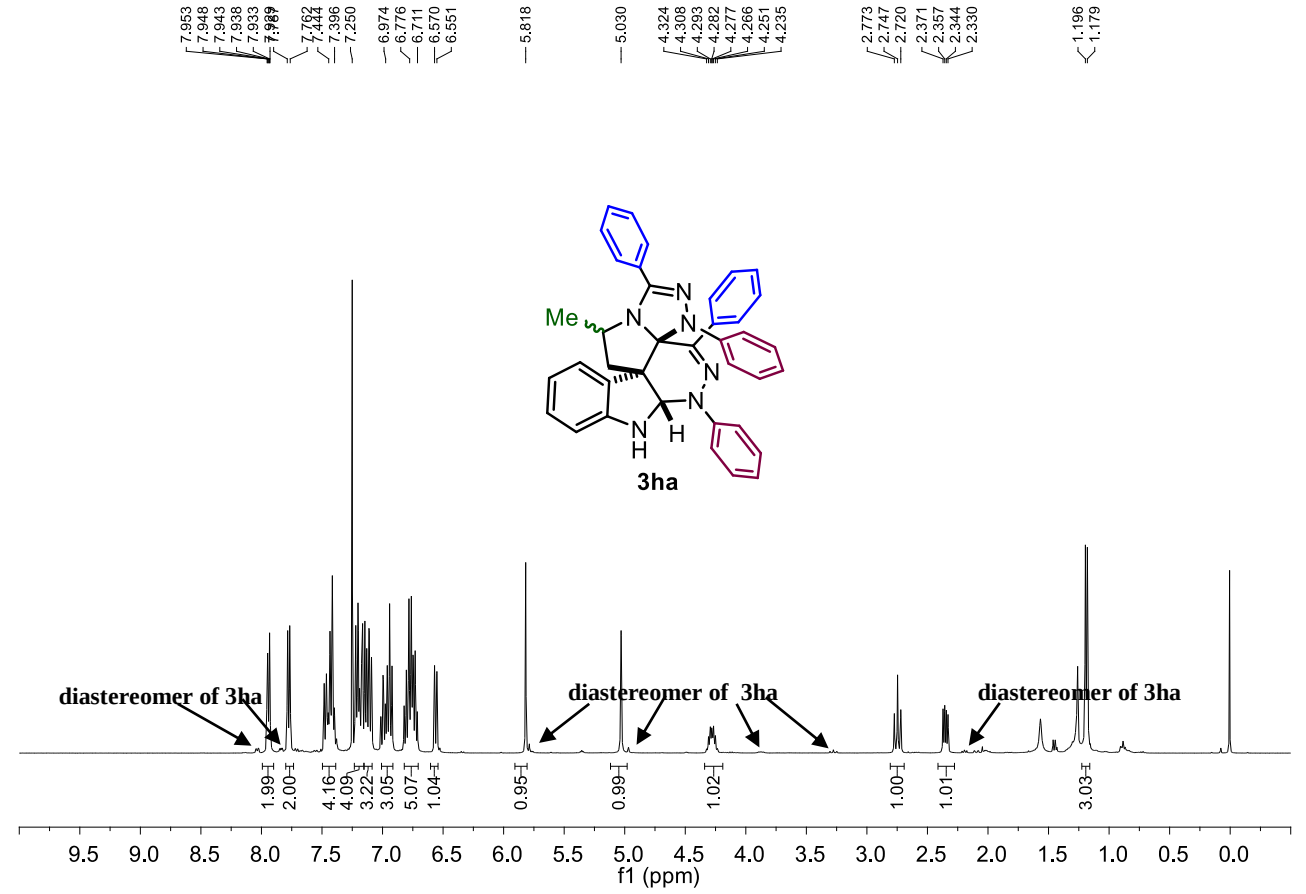
^{19}F NMR (376 MHz, $CDCl_3$) of **3fa**



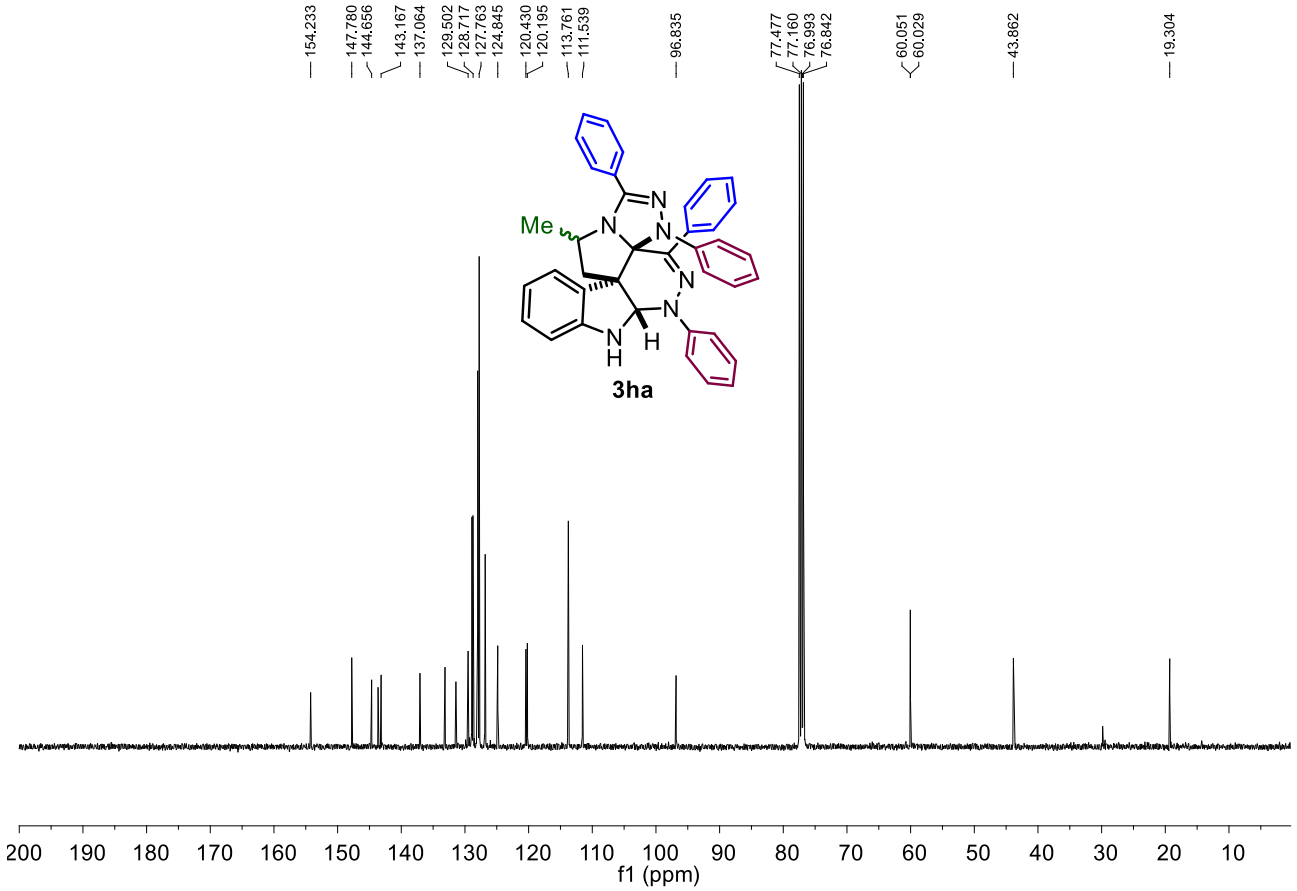
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



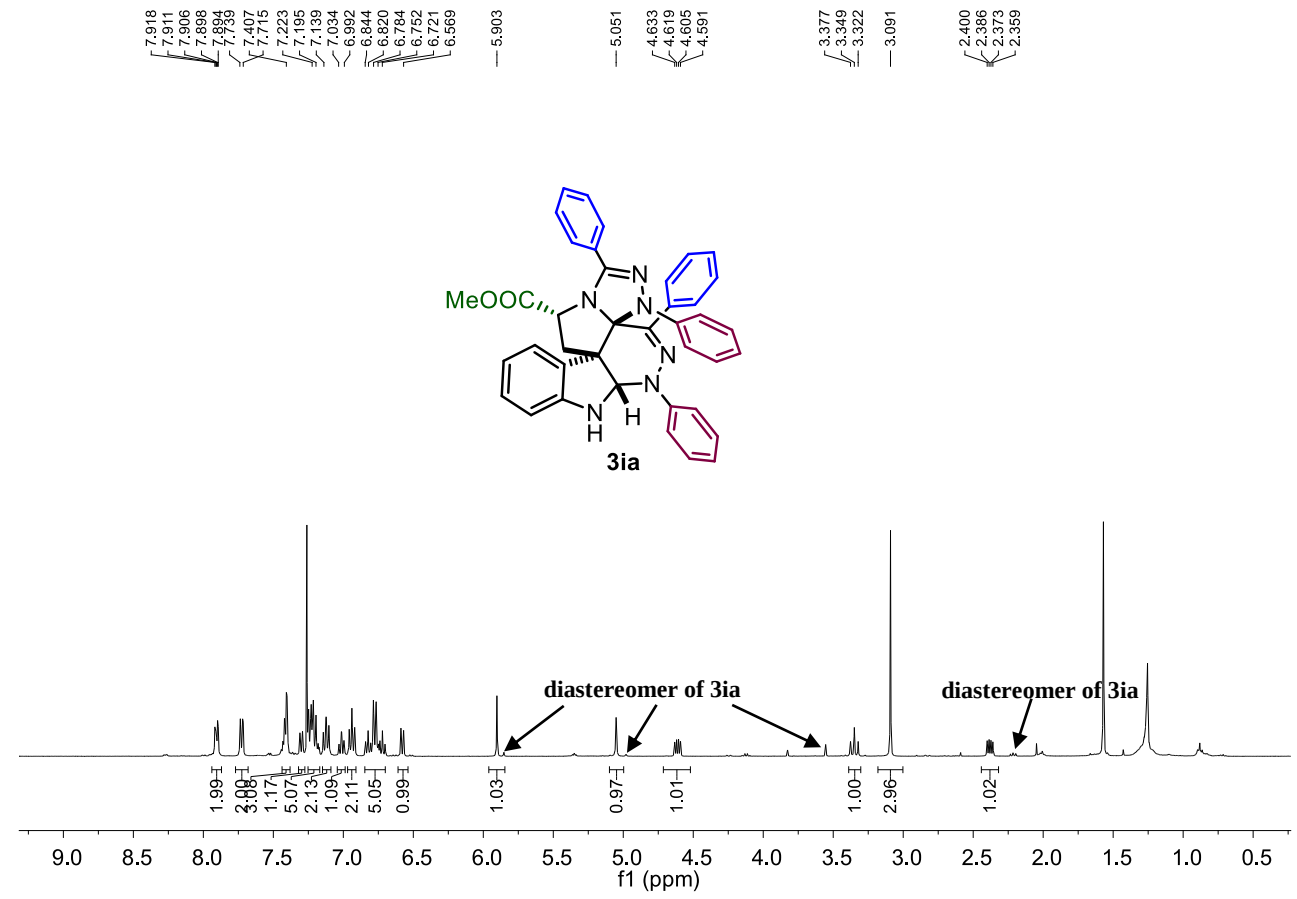
^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



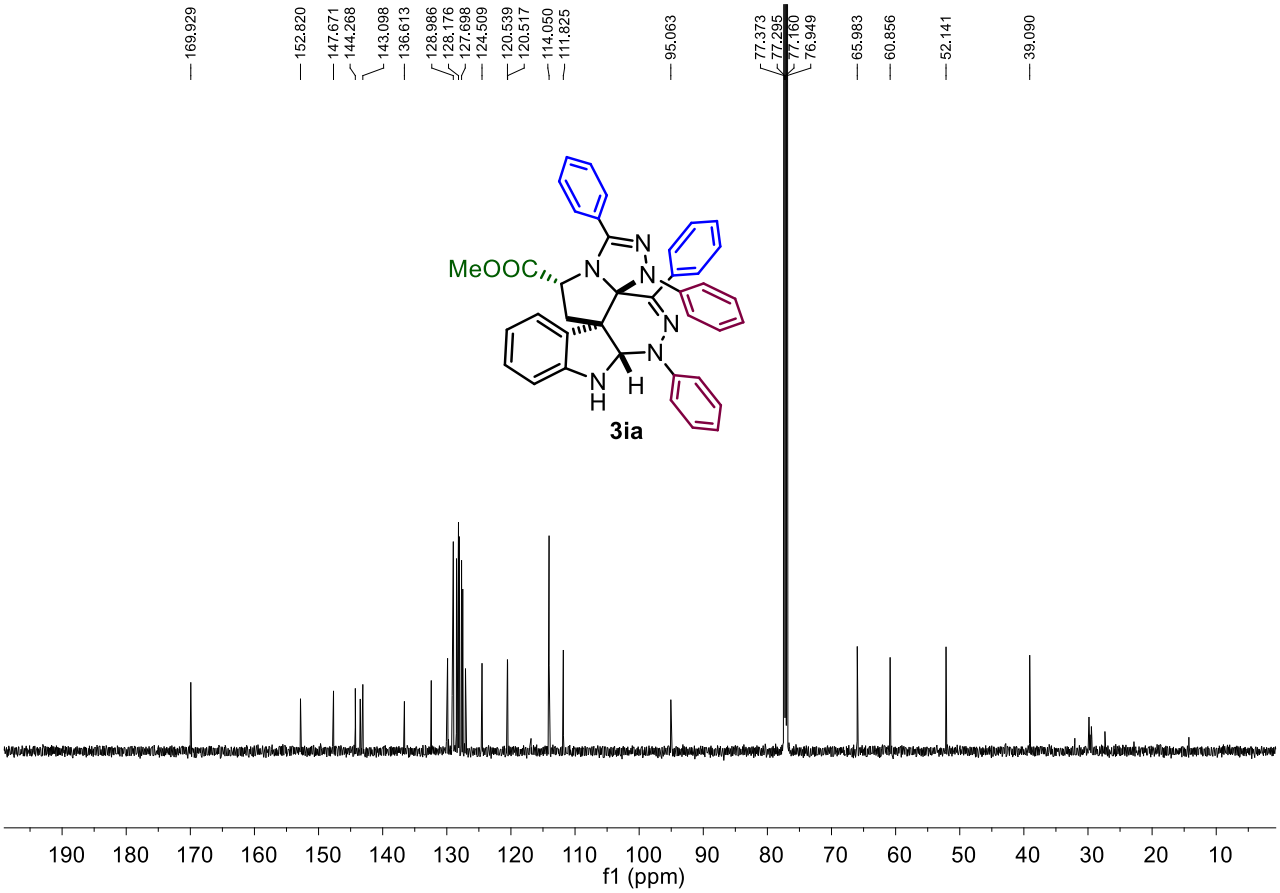
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



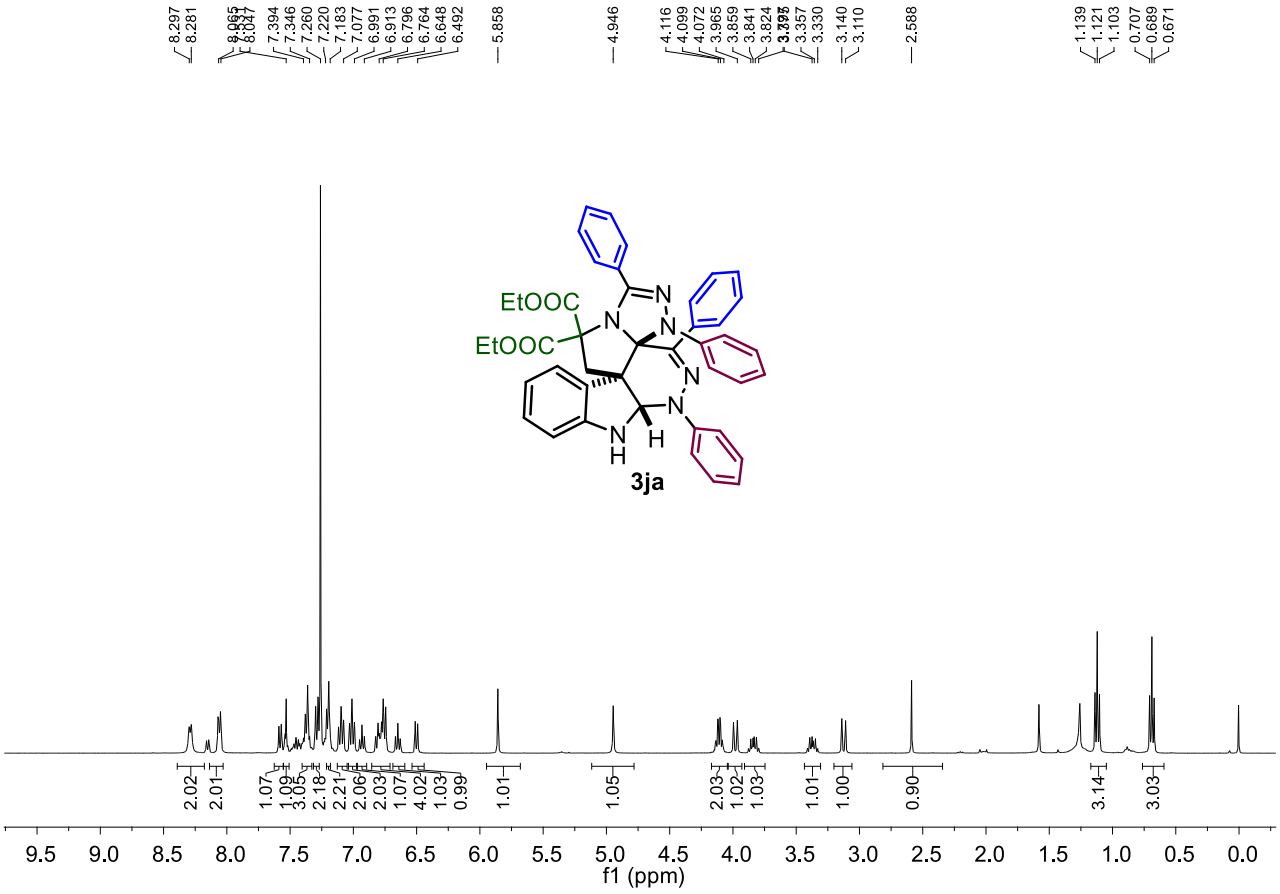
^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**



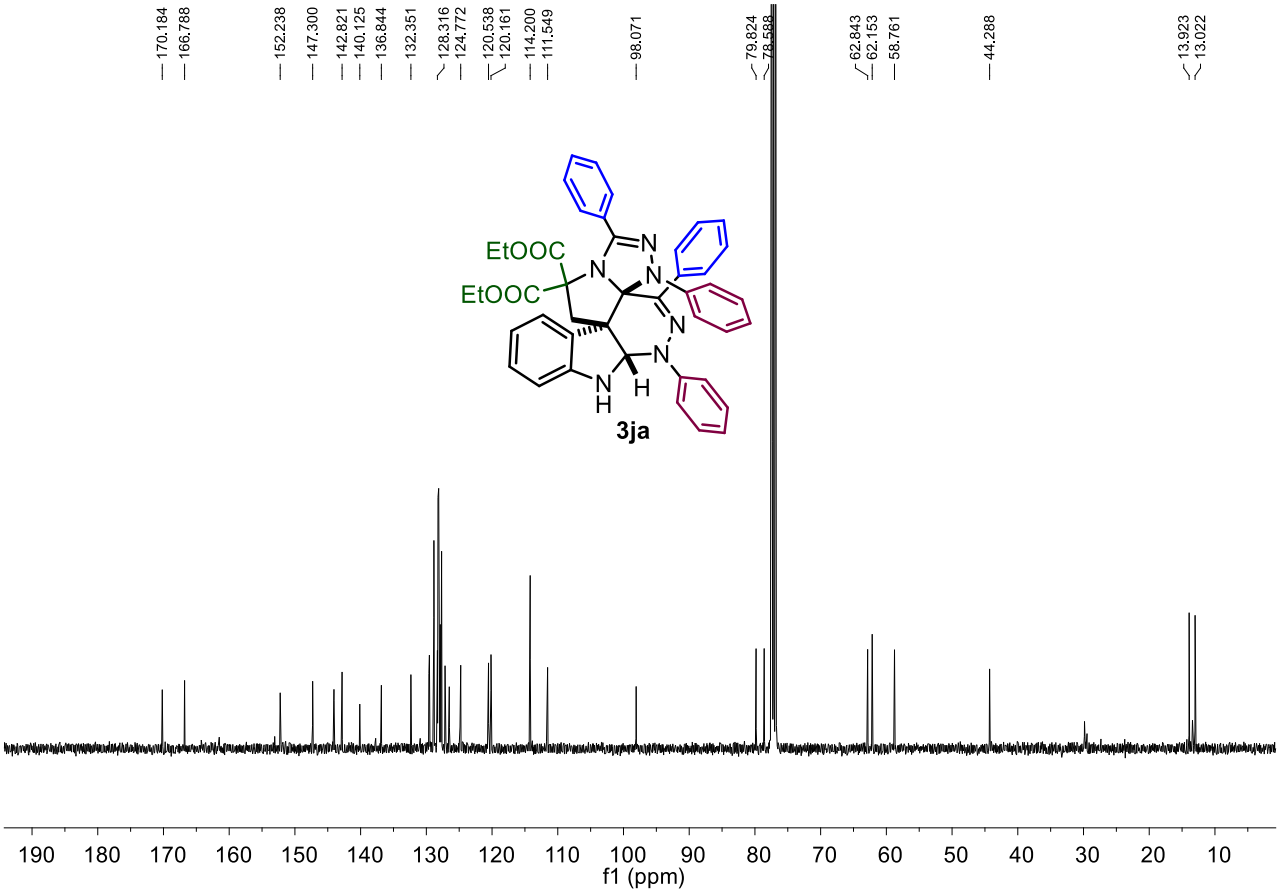
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



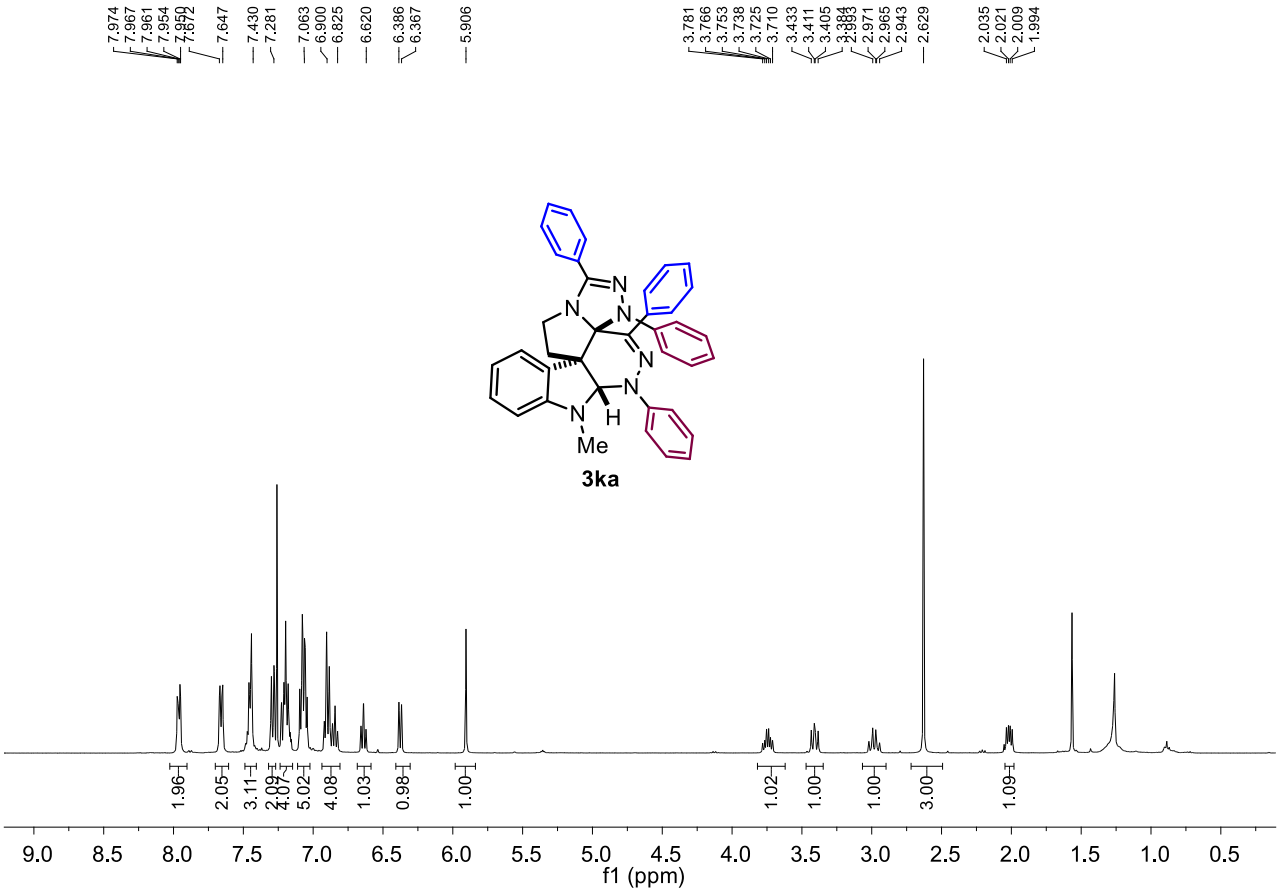
^{13}C NMR (101 MHz, $CDCl_3$) of **3ia**



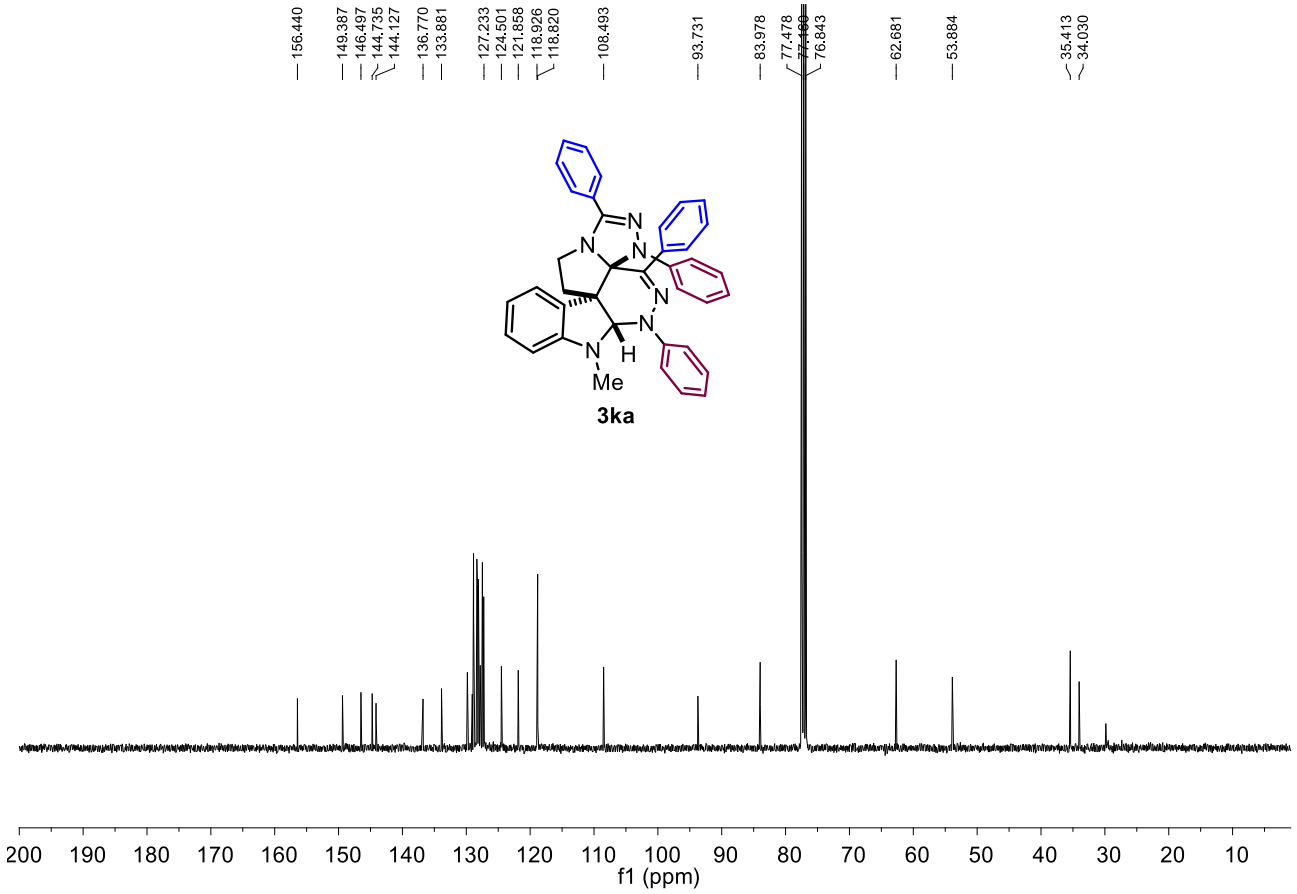
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ja**



^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ka**