Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Tandem Isonitrile Insertion/Azacyclopropylidene-Annulated Cyclohexenone-Tropone Rearrangement of *p*-QMs and TosMIC: De Novo Synthesis of Pyrrolotropones with Anti-Cancer Activity

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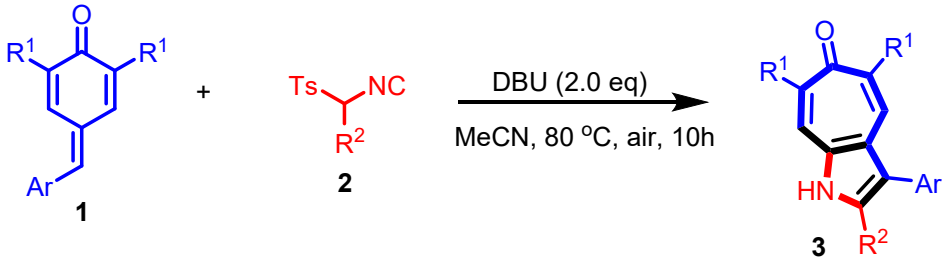
1. General Information

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were measured on 400 MHz spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. HRMS were obtained in the ESI mode. The products were purified by Biotage Isolera™ Spektra Systems and Petroleum Ether/EtOAc solvent systems. Unless otherwise noted, all reagents and solvents were obtained from commercial sources and used without further purification. Melting points (m.p.) were determined on a micro melting point apparatus (WRX-4) and were uncorrected.

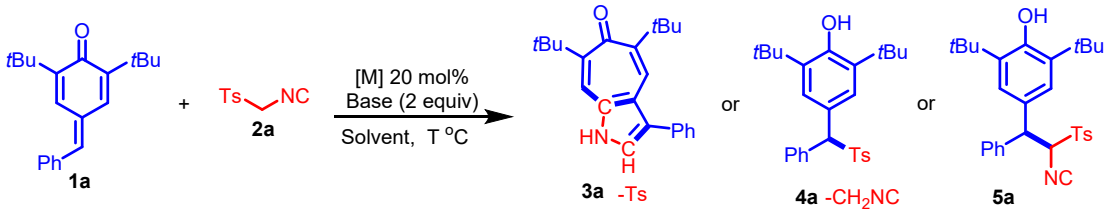
2. General Procedure for Synthesis of 5,7-di-*tert*-butyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one 3a



In an oven-dried glass tubes *p*-QM[1] **1** (0.2 mmol, 1.0 eq.), *p*-toluenesulfonyl isonitrile **2** (0.4 mmol, 2.0 eq.), DBU (60 uL, 0.4 mmol, 2.0 eq) were dissolved in MeCN (1 mL) and the reaction mixture was stirred at 80 °C for 10 h and monitored by TLC. Then the reaction mixture was concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 10/1~5/1 as eluent to afford the desired product **3**.

3. Optimization of Reaction Conditions

Table S1: Optimization of Reaction Conditions

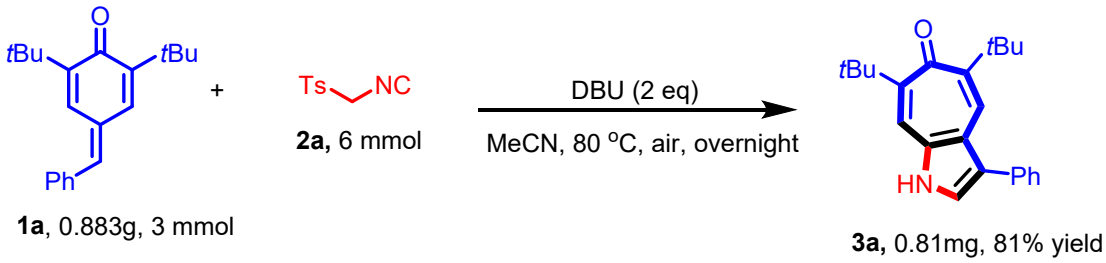


Entry	[M] (20mol%)	Solvent	Base	Temp. (℃)	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]	Yield of **5a** (%)[b]
1	$Cu(OAc)_2$	THF	Cs_2CO_3	MW 90 10 min	-	trace	-
2	Ag_2CO_3	THF	Cs_2CO_3	MW 90 10 min	-	36	-
3	ZnI_2	THF	Cs_2CO_3	MW 90 10 min	-	94	-
4	ZnI_2	THF	CH_3ONa	MW 90 10 min	-	61	-
5	ZnI_2	THF	*t*BuONa	MW 90 10 min	-	50	-
6	Ag_2CO_3	$CHCl_3$	DBU	MW 90	70	-	-

				10 min			
7	Ag_2CO_3	MeCN	DBU	MW 90 10 min	76	-	-
8	Ag_2CO_3	DMF	DBU	MW 90 10 min	54	-	-
9	Ag_2CO_3	THF	DBU	MW 90 10 min	62		
10	Ag_2CO_3	MeCN	DBU	R.T	NR		
11[c]	Ag_2CO_3	MeCN	DBU	80	82	-	-
12[c]	**-**	**MeCN**	**DBU**	**80**	**88**	**-**	**-**
13[c,d]	**-**	**MeCN**	**DBU**	**80**	**-**	**-**	**81 (dr: 1/1)**

[a]Reaction were performed on a 0.2 mmol scale using 2.0 eq. of **2a**, 20 mol% [M], and 2.0 eq. of base, MW, 90 °C, 10 min. [b]Yield are those of products isolated by column chromatography. [c] 80 °C oil bath was used. [d]0.3 eq. DBU was used.

4. Gram Scale-up Experiment



1a, 0.883g, 3 mmol

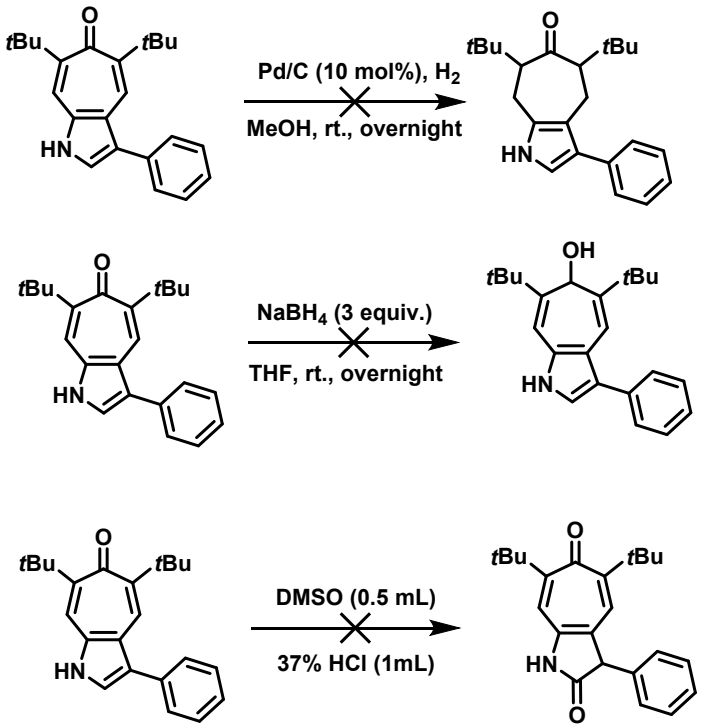
3a, 0.81mg, 81% yield

An oven-dried glass tube (25 mL) was equipped with a magnetic stir bar, **1a** (3 mmol, 0.883 g), **2a** (2.0 eq., 6.0 mmol, 1.20 g), DBU (2.0 eq., 6 mmol, 0.90 mL), 15 ml MeCN was added with syringe. and the resulting solution was stirred at 80 °C for 10 h and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove MeCN, and the residue was purified by chromatography on silica gel (EA/PE = 1/10) to afford the **3a** 0.81 g, yellow solid.

5. Follow-up Experiment

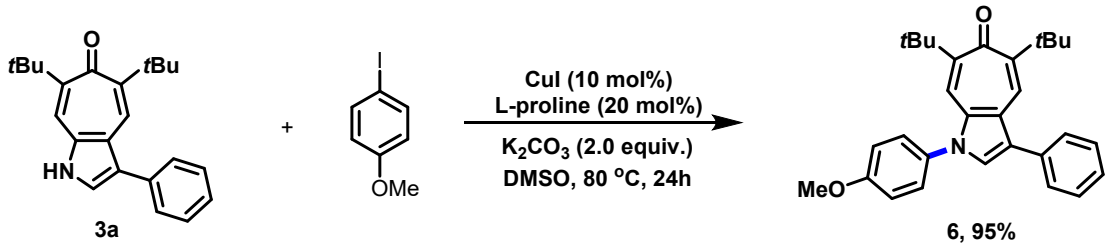
5.1 Unsuccessful follow-up experiments

In the initial derivatization attempt of **3a** (Scheme S1), we found that the double bond or carbonyl group in its structure cannot be reduced under conventional reducing conditions such as Pd/C and sodium borohydride reduction conditions. In addition, **3a** cannot be generated amide under DMSO/concentrated hydrochloric acid conditions.[2] these reaction attempts to further prove the aromatic nature of **3a**.



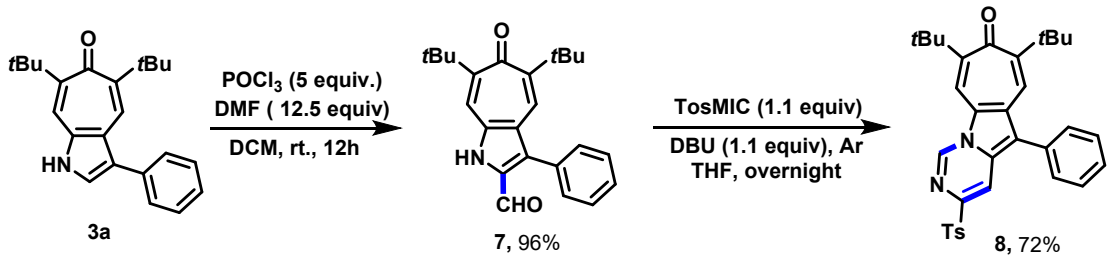
Scheme S1. Failed transformation of **3a**

5.2 Successful follow-up experiments



Scheme S2. Ullmann reaction of **3a**

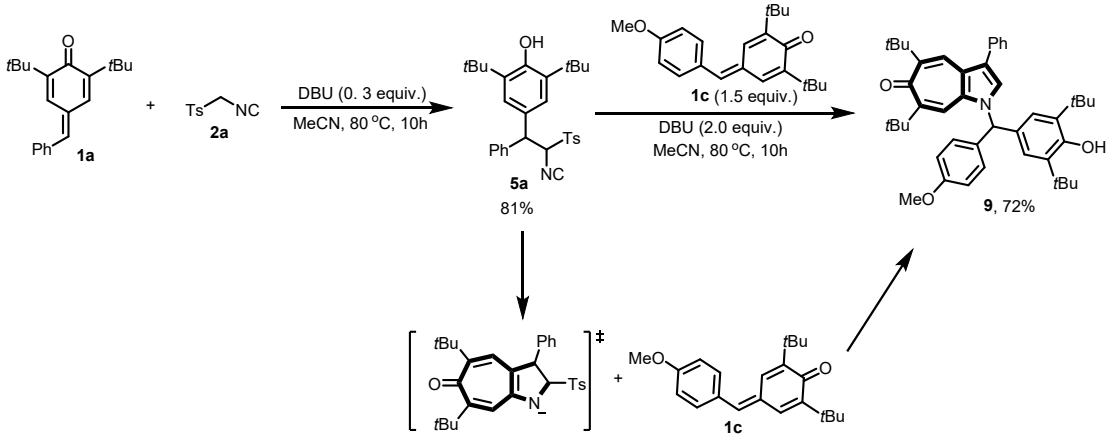
According to a procedure reported by D. W. Ma,[3] an oven-dried glass tube (10 mL) was equipped with a magnetic stir bar, **3a** (0.2 mmol, 67 mg), 4-methoxy iodobenzene (1.1 eq., 0.22 mmol, 52 mg), CuI (10 mol%, 4 mg), L-proline (20 mol%, 5 mg) and K_2CO_3 (2.0 eq., 0.4 mmol, 56 mg) and purged by evacuating the flask and backfilling with argon three times. 1.0 ml DMSO was added with syringe and the flask was sealed. The resulting solution was stirred at 80 °C for 24h and monitored by TLC. After the reaction was finished, the mixture was extracted with ethyl acetate and water, and the organic phase was dried with anhydrous sodium sulfate and concentrated, the residue was purified by chromatography on silica gel (EA/PE = 1/10) to afford the **6** (83 mg, 95% yield), brown oil.



Scheme S3. Vilsmeier-Haack reaction of **3a** and cyclization of 7 with TosMIC

An oven-dried glass tube (10 mL) was equipped with a magnetic stir bar, DMF (12.5 eq., 2.5 mmol, 200 ul), $POCl_3$ (5 eq., 1 mmol, 91 uL) was added with syringe. The resulting solution was stirred at 0 °C for 1.5h. The solution of **3a** (0.2 mmol, 67 mg) and 1 mL dry DCM was added into the reaction solution with a syringe. The resulting solution was stirred at room temperature 10h and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove DCM, and the residue was purified by chromatography on silica gel (ethyl acetate/hexane = 5% ~ 10%) to afford the **7** (69 mg, 96% yield), yellow solid.

According to a procedure reported by A-Builla,[4] an oven-dried glass tube (10 mL) was equipped with a magnetic stir bar, **6** (0.19 mmol, 69 mg), TosMIC (1.1 eq., 0.21 mmol, 42 mg), DBU (1.1 eq., 0.21 mmol, 32 uL), 1.0 ml THF was added with syringe. The resulting solution was stirred at room temperature for 2h and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove THF, and the residue was purified by chromatography on silica gel (ethyl acetate/hexane = 5% ~ 10%) to afford the **8** (73 mg, 72% yield), yellow solid.



Scheme S4. The synthesis of diarylmethane pyrrolotropone **9**

In an oven-dried glass tubes (10 mL) was equipped with a magnetic stir bar, *p*-QM **1a** (0.2 mmol, 59 mg, 1.0 eq.), *p*-toluenesulfonyl isonitrile **2a** (0.4 mmol, 78 mg, 2.0 eq.), DBU (9 uL, 0.06 mmol, 0.3 eq) were dissolved in MeCN (1 mL) and the reaction mixture was stirred at 80 °C for 10 h and monitored by TLC. Then the reaction mixture was concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 10/1~5/1 as eluent to afford the desired product **5a**, colorless oil, 79 mg, 81% yield.

An oven-dried glass tube (10 mL) was equipped with a magnetic stir bar, **5a** (0.16 mmol, 79 mg), *p*-QM **1c** (1.5 eq., 0.24 mmol, 78 mg), DBU (2.0 eq., 0.32 mmol, 49 uL), 1.0 ml MeCN was added with syringe. The resulting solution was stirred at 80 °C for 10h and monitored by TLC. After the reaction

was finished, the mixture was concentrated under vacuum to remove MeCN, and the residue was purified by chromatography on silica gel (ethyl acetate/hexane = 5% ~ 10%) to afford the **9** (76 mg, 72% yield), yellow solid.

6. Anticancer evaluation of compounds

The human prostate cancer cell line DU1145, breast cancer cell line MDA-MB-231, oral cancer cell line SCC15, head and neck cancer cell line Cal33, colon cancer cell line SW620 were purchased from Cobier Biotechnology (Cobier, Nanjing, China). DU145, MDA-MB-231, SCC15, Cal33, SW620 cells were cultured in high-glucose DMEM (Hyclone, SH30022.01, USA) medium supplemented with 10% fetal bovine serum (FBS, Gibco, 10100147, Australia). All cells were cultured in an incubator at 37℃ under a humidified atmosphere of 5% CO_2.

The anticancer effect of compounds in DU145, MDA-MB-231, SCC15, Cal33 and SW620 was measured by 3-(4, 5-dimethyl-2-thiazolyl)-2, 5-diphenyl-2-H-tetrazolium bromide (MTT) assay. Briefly, cells were seeded into 96-well plates ($2X10^3$ cell per well) containing 100 μL complete medium. After incubating for 24 hours, cells were supplemented with another 100 μL complete medium containing 20 μM compounds and incubated for another 72 hours. All cells were treated with MTT (Beyotime, ST316, Shanghai, China) solution (5 mg/mL, 20 μL per well) for another 4 hours. Next, the medium was removed, 150 μL DMSO (Dimethylsulfoxide) was added to each well. The absorbance (OD) was measured at 570 nm by a microplate reader (Bio-Tek, Winooski, VT, USA) after shaking the plate on shaker for 10 minutes. All experiments were repeated three times, each experiment was conducted in triplicate. The proliferation inhibition rate was compared with control. Inhibition rate=$100\%*(1-OD_{compound}/OD_{control})$, the value below 0 was adjusted to 0.

Table S2. The proliferation inhibition rate of derivatives in different human cancer cell lines. The data is mean of three experiments.

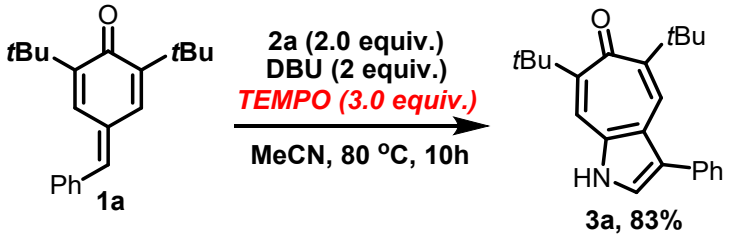
	Inhibition rate (%)				
compound ID	DU145	MDA-MB-231	SCC15	Cal33	SW620
3a	0.0	7.3	1.5	56.8	35.8
3b	1.4	27.0	1.2	14.9	3.8
3c	20.3	10.2	20.5	45.6	20.8
3d	2.2	16.3	0.0	35.8	13.0
3e	8.5	16.2	11.0	39.0	12.8
3f	6.2	17.2	9.2	13.2	0.0
3g	0.0	15.0	0.0	26.7	9.9
3h	26.5	14.4	25.0	18.5	3.9
3i	3.4	16.3	7.8	6.9	0.0
3j	52.7	17.6	53.8	48.2	18.9
3k	46.0	10.5	48.1	42.2	34.6
3l	0.0	18.1	0.0	16.5	3.2
3m	0.0	10.6	0.6	18.1	23.6
3n	0.0	22.1	0.0	2.0	0.0
3o	0.0	13.4	1.8	0.7	0.7
3r	1.9	0.0	0.0	40.9	0.0
3s	0.0	15.0	5.1	7.7	0.0

3t	55.8	5.5	56.8	29.6	4.9
3u	26.5	31.2	0.0	0.0	0.0
3v	60.9	31.1	18.2	41.2	31.1
3w	13.1	32.6	0.0	3.0	0.0
3x	3.3	20.7	0.0	0.0	0.0
3y	13.0	31.9	0.0	4.8	0.0
3z	79.4	65.6	79.7	49.3	64.6
3aa	36.3	25.9	5.1	52.5	0.0
3ab	30.7	18.6	32.7	21.8	0.0
3ac	27.0	29.2	11.0	7.6	0.0
3ad	18.5	21.6	10.4	13.5	0.0
3ae	24.9	20.1	21.1	12.2	0.0
3af	25.0	0.6	3.5	13.7	0.0
3ag	33.1	5.5	19.8	15.2	0.0
3ah	27.6	2.6	0.0	32.2	0.0
6	19.5	29.0	0.0	0.0	0.0
8	37.3	31.7	0.0	0.0	0.0
9	26.0	42.0	9.3	5.3	0.0

7. Mechanistic studies

A. Trapping experiment with TEMPO radical

The most common used for intermediate identification is adding an additional reagent to trap the species. The persistent radical 2,2,6,6-tetramethylpiperdine 1-oxyl (TEMPO) is usually served as a trapping reagent of carbon-centered radicals, also for intramolecular radical cyclization. Based on above reasons, we applied this radical trapping agent in our reaction to examine its behavior. Under the standard reaction, when 3.0 equivalent of TEMPO (with respect to **1a**) was added to the reactions, the reaction could be proceeded smoothly (Scheme S5). This phenomenon shows that the reaction is not a radical-mediated reaction.

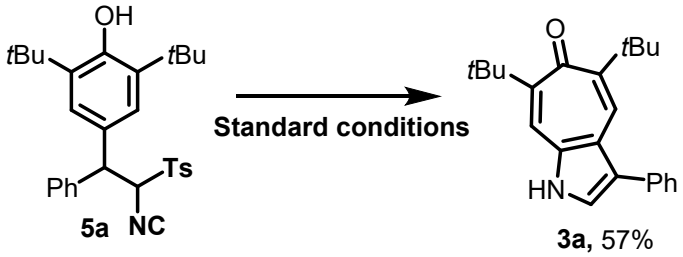


Scheme S5. Radical trapping experiment

Procedure: In an oven-dried glass tubes *p*-QM **1a** (59 mg, 0.2 mmol, 1.0 eq.), *p*-toluenesulfonyl isonitrile **2a** (78 mg, 0.4 mmol, 2.0 eq.), DBU (60 uL, 0.4 mmol, 2.0 eq.), and TEMPO (94 mg, 0.6 mmol, 3.0 eq.) were dissolved in MeCN (1 mL) and the reaction mixture was stirred for 10 h at 80 °C and monitored by TLC. Then the reaction mixture was concentrated under reduced pressure followed by column chromatography over silica gel using petroleum/EtOAc = 10/1 as eluent to afford the desired product **3a** (55 mg, 83%).

B. Synthesis 3a from 5a

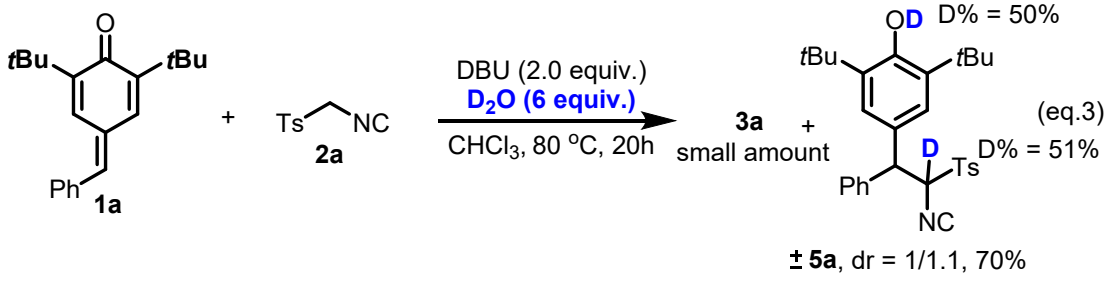
Procedure: An oven-dried glass tube (10 mL) was equipped with a magnetic stir bar, **5a** (33 mg, 0.07 mmol, 1.0 eq.) and DBU (21 uL., 0.14 mmol, 2.0 eq.). 1.0 ml MeCN was added. The resulting solution was stirred at 80 °C for 10h and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove MeCN, and the residue was purified by chromatography on silica gel (ethyl acetate/hexane = 5% ~ 10%) to afford the **3a** ***by*** ^{1}***H-NMR*** (13 mg, 57% yield).



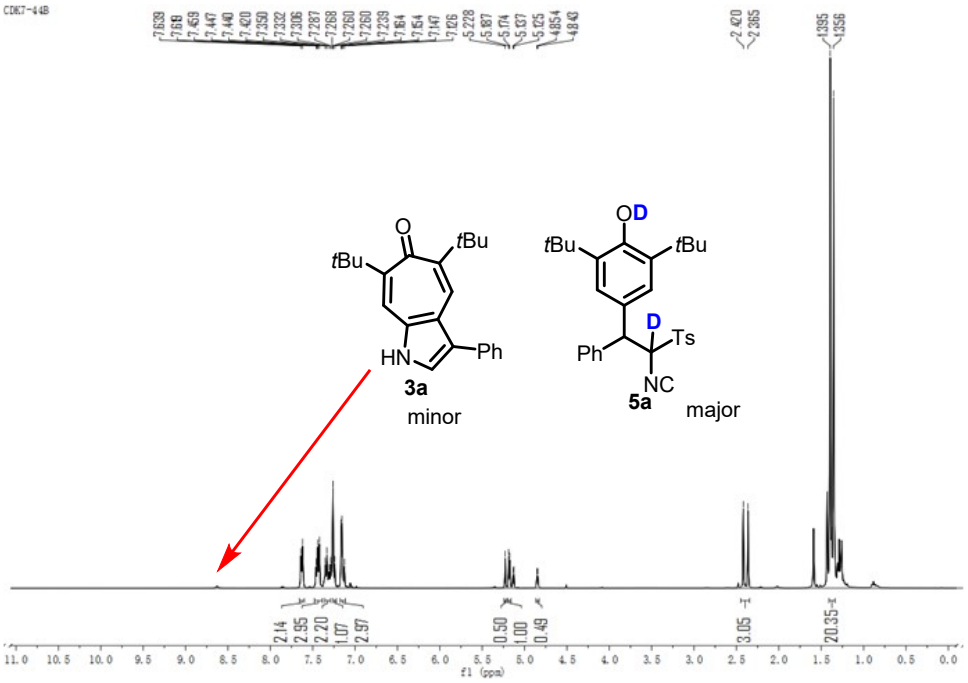
Scheme S6. Transformation of **5a** to **3a**

C. D_2O experiment

Procedure: An oven-dried glass tube (10 mL) was equipped with a magnetic stir bar. **1a** (60 mg, 0.2 mmol, 1.0 eq.), DBU (60 uL., 0.4 mmol, 2.0 eq.), D_2O (22 uL, 1.2 mmol, 6.0 eq.), and 1.0 ml MeCN were added. The resulting solution was stirred at 80 °C for 10h and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove MeCN, and the residue was purified by chromatography on silica gel (ethyl acetate/hexane = 5% ~ 10%) to afford the **3a** + **5a** (68 mg, 70% yield).



Scheme S7. Anion trapping experiment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HN
Ph
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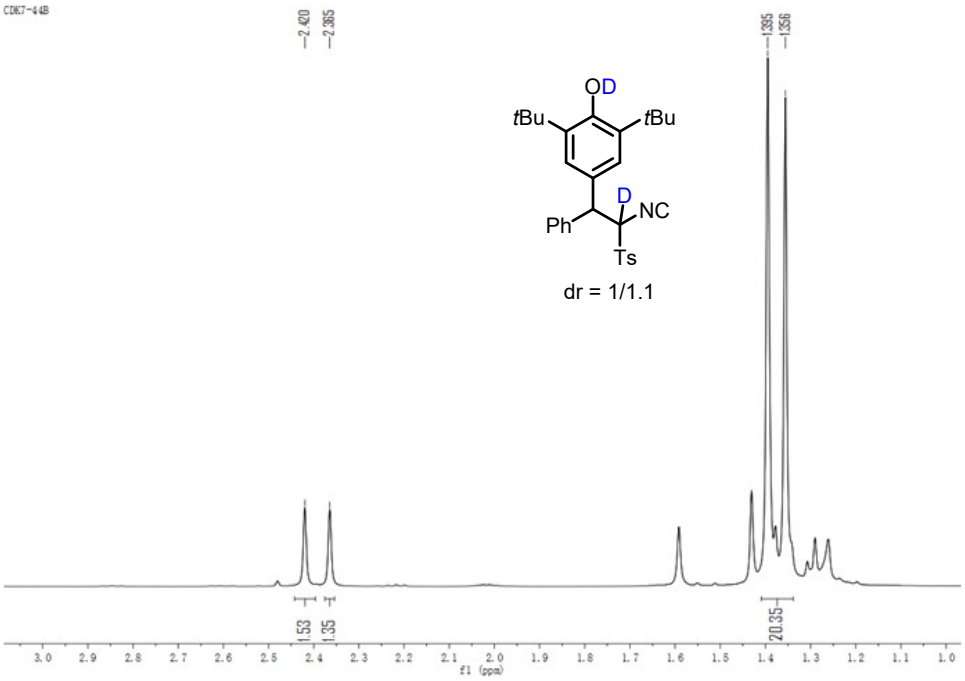
minor
OD
tBu
tBu
D
Ts
Ph
NC
5a
major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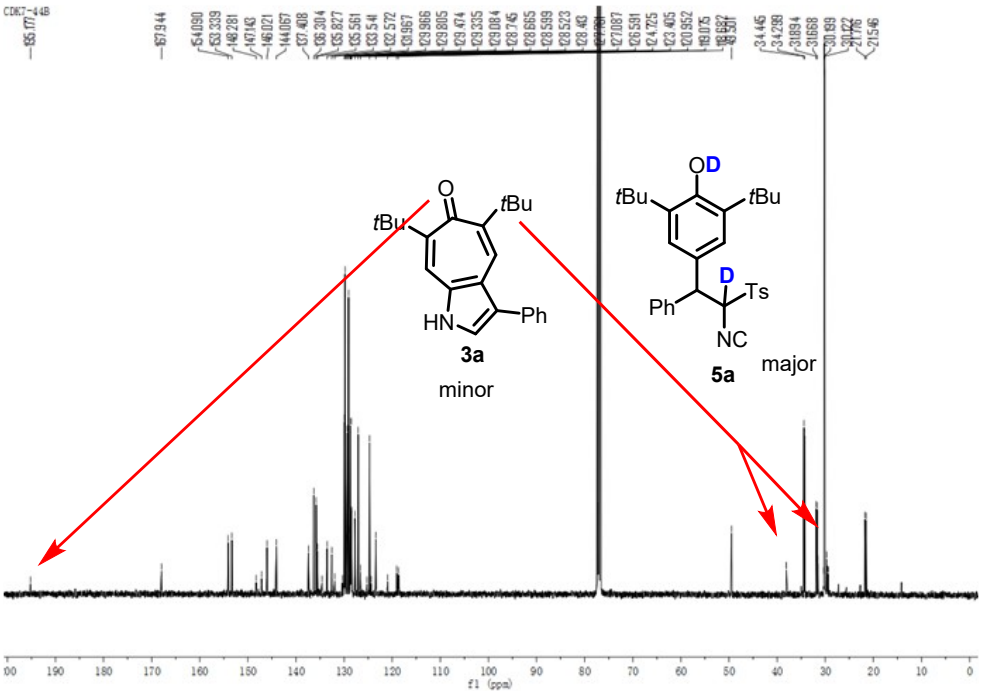
tBu
D
NC
Ph
Ts
dr = 1/1.1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tBu
tBu
HN
Ph
3a
minor
OD
tBu
tBu
D
Ts
Ph
NC
5a
major
f1 (ppm)

8. Substrate scope

Table S3. *p*-QMs scope

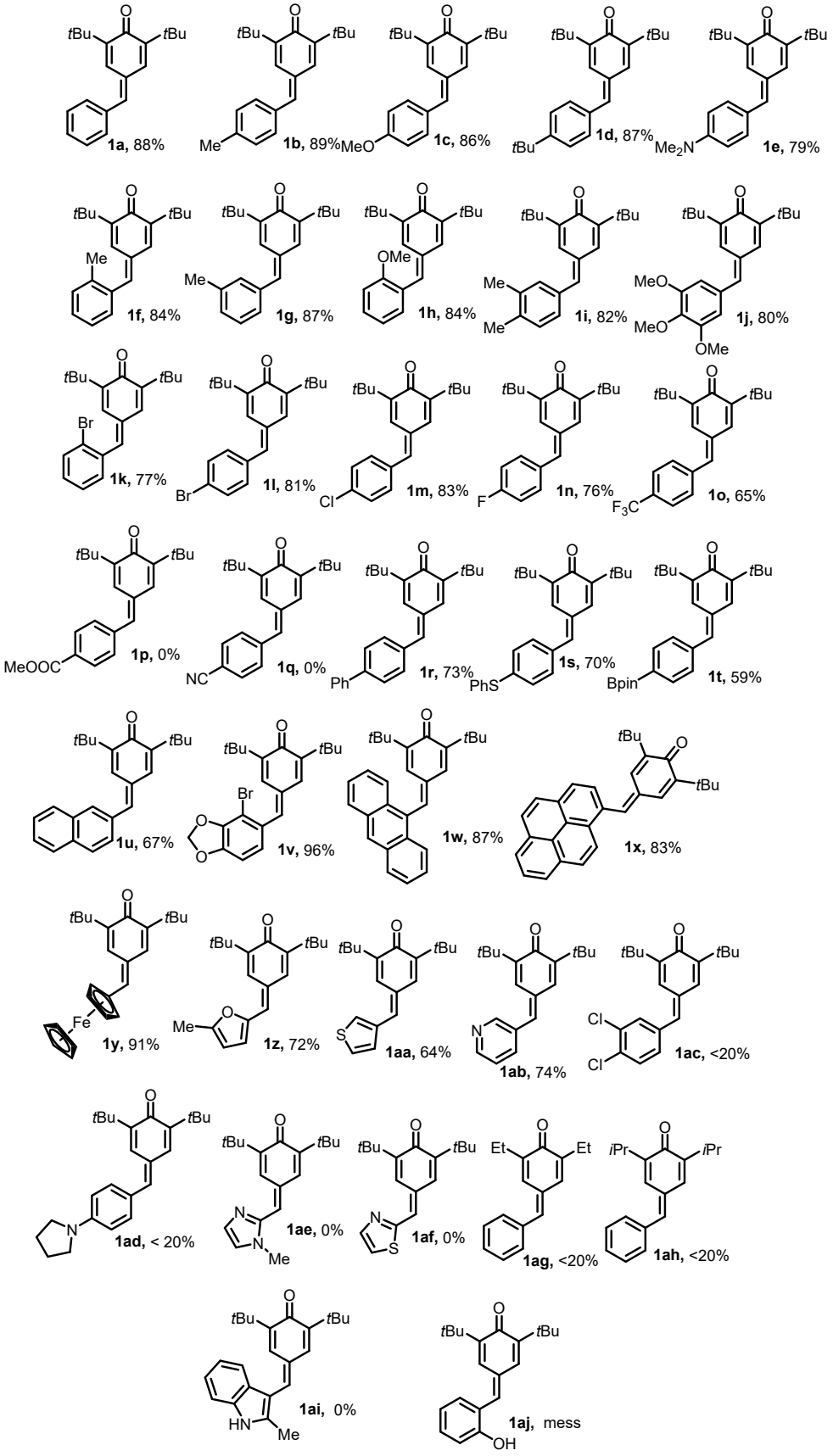
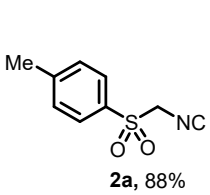
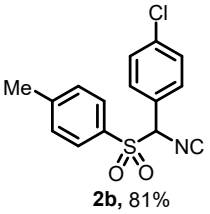


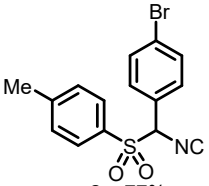
Table S4. TosMIC scope



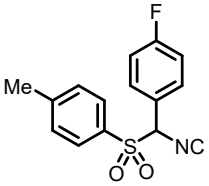
2a, 88%



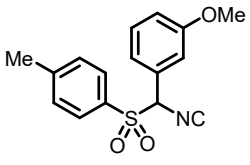
2b, 81%



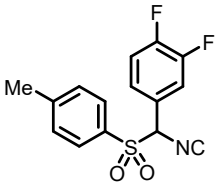
2c, 77%



2d, 86%



2e, 92%



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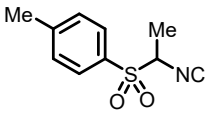
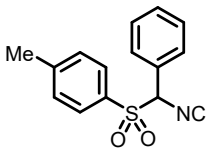
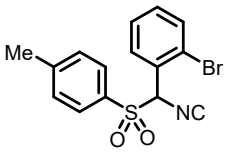


2g, 84%



2h, <30%



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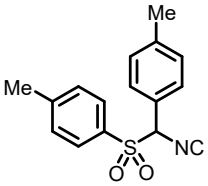

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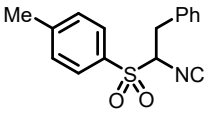
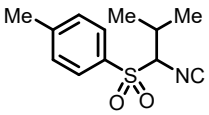
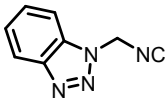


2k, 0%

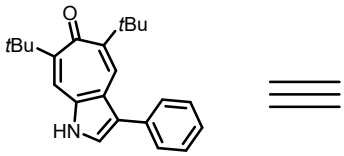


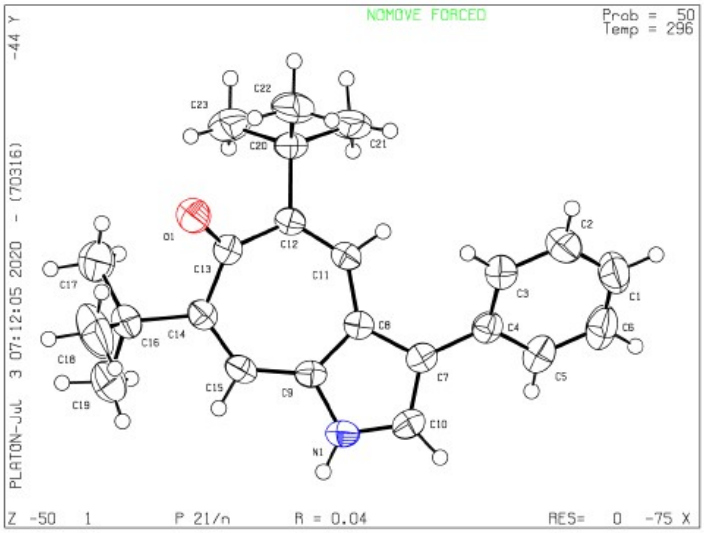
2l, 0%



2m, <20%

9. Crystal Structure determinationof 3a (CCDC: 2096456)





Datablock: 1

Bond precision: C-C = 0.0022 A Wavelength=0.71073

Cell: a=9.4574(11) b=10.1927(12) c=21.398(3)
alpha=90 beta=94.088(2) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	2057.4(4)	2057.5(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C23 H27 N O	?
Sum formula	C23 H27 N O	C23 H27 N O
Mr	333.46	333.45
Dx,g cm-3	1.077	1.076
Z	4	4
Mu (mm-1)	0.065	0.065
F000	720.0	720.0
F000'	720.27	
h,k,lmax	11,12,25	11,12,25
Nref	3836	3826
Tmin,Tmax	0.983,0.985	
Tmin'	0.983	

Correction method= Not given

Data completeness= 0.997 Theta(max)= 25.498

R(reflections)= 0.0417(3021) wR2(reflections)= 0.1211(3826)

S = 0.983 Npar= 233

Alert level C

PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C16 Check
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	3.008 Check
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).	5 Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	6 Report

Alert level G

PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	1 Report
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	4 Note
PLAT941_ALERT_3_G	Average HKL Measurement Multiplicity	2.8 Low
PLAT961_ALERT_5_G	Dataset Contains no Negative Intensities	Please Check
PLAT965_ALERT_2_G	The SHELXL WEIGHT Optimisation has not Converged	Please Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	6 Info

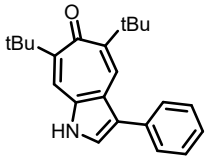
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

10. Characterization data of compounds

Note: Due to the poor solubility of some compounds in deuterated chloroform, the product is dissolved in dimethyl sulfoxide chloride after concentrating under reduced pressure, so there may be residual chloroform peaks in the spectrum.

5,7-di-tert-butyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3a)



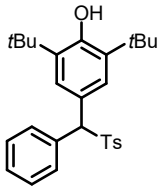
Yellow solid, m. p. 219-223 °C, 59 mg, 88% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.62 (s, 1H), 7.45 (d, J = 4.3 Hz, 4H), 7.35 – 7.30 (m, 2H), 7.06 (d, J = 2.5 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 148.2, 147.1, 134.6, 132.0, 128.8, 128.6 126.6, 125.2, 123.5, 121.0, 119.2, 118.8, 38.2, 38.1, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{23}H_{28}NO^+$ $(M+H)^+$ 334.2165, found *m/z* 334.2160.

2,6-di-tert-butyl-4-(phenyl(tosyl)methyl)phenol (4a)



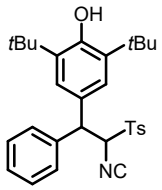
Colorless oil, Rf = 0.3 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.09 (s, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.15 (s, 1H), 5.10 (s, 1H), 2.29 (s, 3H), 1.28 (s, 18H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 144.1, 135.8, 135.6, 133.6, 130.0, 129.1, 129.1, 128.6, 128.4, 127.1, 123.4, 34.3, 30.1, 21.5 ppm;

This is a known compund and can not be detected in the HRMS ESI positive ion mode.

2,6-di-tert-butyl-4-(2-isocyano-1-phenyl-2-tosylethyl)phenol (±5a)



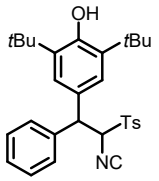
Colorless oil, dr = 1/1, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 1.25H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.4 Hz, 1.38H), 7.26 (dd, *J* = 12.6, 4.8 Hz, 2.4H), 7.19 (dd, *J* = 7.2, 2.1 Hz, 1.65H), 7.16–7.02 (m, 4.4H), 5.10 (tdd, *J* = 13.8, 7.8, 5.6 Hz, 2H), 4.76 (dd, *J* = 4.6, 1.9 Hz, 1H), 2.32 (d, *J* = 9.9 Hz, 3H), 1.30 (d, *J* = 7.2 Hz, 18H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 153.6, 153.3, 146.0, 145.9, 139.3, 137.4, 136.3, 135.7, 132.6, 132.0, 130.2, 129.8, 129.6, 129.5, 129.3, 129.1, 129.0, 128.5, 127.9, 127.8, 127.6, 127.1, 126.8, 126.3, 124.74, 77.9, 49.8, 49.5, 34.5, 34.4, 30.3, 30.2, 30.1, 21.8 ppm;

HRMS (ESI) m/z calcd for $C_{30}H_{36}NO_3S^+$ $(M+H)^+$ 490.2410, found *m/z* 490.2416.

2,6-di-tert-butyl-4-(2-isocyano-1-phenyl-2-tosylethyl)phenol (5a-up)



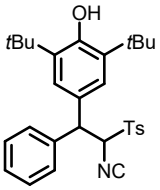
Colorless oil, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.39–7.31 (m, 4H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.17 (s, 2H), 5.19 (d, *J* = 4.9 Hz, 1H), 5.17 (s, 1H), 4.84 (d, *J* = 4.9 Hz, 1H), 2.39 (s, 3H), 1.38 (s, 18H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ167.9, 153.6, 145.9, 139.3, 135.7, 132.0, 130.2, 129.5, 129.0, 127.9, 127.6, 126.8, 126.3, 77.9, 49.8, 34.4, 30.2, 21.8 ppm;

HRMS (ESI) m/z calcd for $C_{30}H_{36}NO_3S^+$ $(M+H)^+$ 490.2410, found *m/z* 490.2410.

2,6-di-tert-butyl-4-(2-isocyano-1-phenyl-2-tosylethyl)phenol (5a-down)



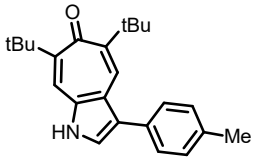
Colorless oil, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.48–7.41 (m, 2H), 7.29 (ddd, *J* = 5.5, 4.2, 2.5 Hz, 4H), 7.24 (s, 1H), 7.16 (s, 2H), 5.19 (s, 1H), 5.14 (d, *J* = 4.8 Hz, 1H), 4.85 (d, *J* = 4.8 Hz, 1H), 2.42 (s, 3H), 1.40 (s, 18H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ167.9, 153.3, 146.0, 137.4, 136.3, 132.6, 129.8, 129.5, 129.3, 128.5, 127.8, 124.7, 77.22, 49.5, 34.4, 30.2, 21.8 ppm;

HRMS (ESI) m/z calcd for $C_{30}H_{36}NO_3S^+$ $(M+H)^+$ 490.2410, found *m/z* 490.2420.

5,7-di-tert-butyl-3-(p-tolyl)cyclohepta[b]pyrrol-6(1H)-one (3b)



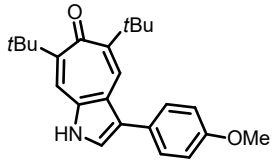
Yellow-brown solid, m. p. 215-220 °C, 62 mg, 89% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.63 (s, 1H), 7.37 – 7.30 (m, 3H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 2.41 (s, 3H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 148.1, 147.0, 136.3, 132.0, 131.6, 129.5, 128.5, 125.2, 123.7, 121.1, 119.2, 118.6, 38.1, 38.1, 31.9, 31.7, 21.2 ppm;

HRMS (ESI) m/z calcd for $C_{24}H_{30}NO^+$ $(M+H)^+$ 348.2322, found *m/z* 348.2321.

5,7-di-tert-butyl-3-(4-methoxyphenyl)cyclohepta[b]pyrrol-6(1H)-one (3c)



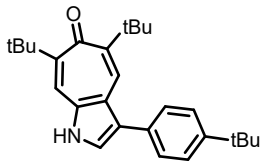
Yellowish solid, m. p. 202-205 °C, 62 mg, 86% yield, Rf = 0.4 (ethyl acetate/hexane = 20%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.59 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.31 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 3H), 3.86 (s, 3H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 158.5, 148.1, 146.9, 131.9, 129.7, 127.0, 124.9, 123.6, 121.1, 119.2, 118.4, 114.2, 55.4, 38.1, 38.1, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{24}H_{30}NO_2^+$ $(M+H)^+$ 364.2271, found *m/z* 364.2282.

5,7-di-tert-butyl-3-(4-(tert-butyl)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3d)



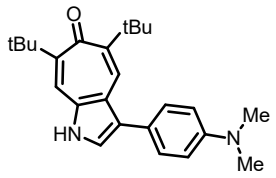
Yellow-brown solid, m. p. 207-212 °C, 68 mg, 87% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.67 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.32 (s, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 1.43 (s, 9H), 1.41 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 149.5, 148.1, 147.0, 132.0, 131.6, 128.1, 125.7, 125.1, 123.7, 121.0, 119.2, 118.7, 38.1, 38.1, 34.6, 32.0, 31.7, 31.4 ppm;

HRMS (ESI) m/z calcd for $C_{27}H_{36}NO^+$ $(M+H)^+$ 390.2791, found *m/z* 390.2782.

5,7-di-tert-butyl-3-(4-(dimethylamino)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3e)



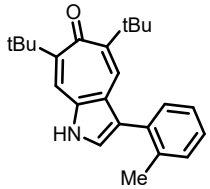
Brown solid, m. p. 147-150 °C, 59 mg, 79% yield, Rf = 0.2 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.65 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.00 (s, 6H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 149.5, 147.9, 146.7, 131.8, 129.4, 125.5, 123.9, 122.7, 121.1, 119.2, 118.0, 112.9, 40.7, 38.1, 38.1, 31.9, 31.7 ppm;

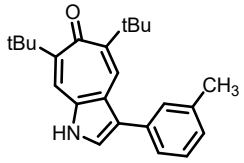
HRMS (ESI) m/z calcd for $C_{25}H_{33}N_2O^+$ $(M+ H)^+$ 377.2587, found *m/z* 377.2584.

5,7-di-tert-butyl-3-(o-tolyl)cyclohepta[b]pyrrol-6(1H)-one (3f)



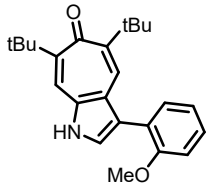
Reddish brown solid, m. p. 201-205 °C, 58 mg, 84% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.34 – 7.27 (m, 3H), 7.24 (d, *J* = 3.7 Hz, 2H), 7.15 (s, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 2.22 (s, 3H), 1.44 (s, 9H), 1.32 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 148.2, 147.0, 137.2, 133.6, 131.2 (d, *J* = 8.7 Hz), 130.3, 127.4, 125.6, 124.5, 123.9, 122.2, 119.3, 119.0, 38.1, 38.1, 31.7 (d, *J* = 6.2 Hz), 20.5 ppm;
HRMS (ESI) m/z calcd for $C_{24}H_{30}NO^+$ $(M+H)^+$ 348.2322, found *m/z* 348.2321.

5,7-di-tert-butyl-3-(m-tolyl)cyclohepta[b]pyrrol-6(1H)-one (3g)



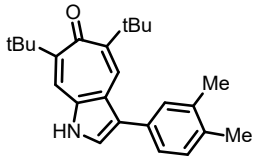
Yellow-brown solid, m. p. 158-163 °C, 60 mg, 87% yield, Rf = 0.4 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, D6-DMSO) δ 11.78 (s, 1H), 7.56 (s, 1H), 7.50 (s, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.27 (s, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 9H), 1.32 (s, 9H) ppm;
^{13}C NMR (100 MHz, D6-DMSO) δ 194.5, 146.6, 145.7, 138.3, 134.9, 132.5, 129.2, 129.1, 127.3, 125.5, 123.8, 123.5, 120.7, 120.3, 120.2, 32.0, 31.8, 21.6 ppm;
HRMS (ESI) m/z calcd for $C_{24}H_{30}NO^+$ $(M+H)^+$ 348.2322, found *m/z* 348.2332.

5,7-di-tert-butyl-3-(2-methoxyphenyl)cyclohepta[b]pyrrol-6(1H)-one (3h)



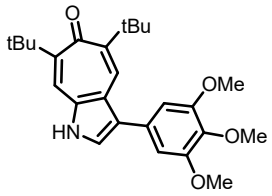
Yellowish solid, m. p. 150-155 °C, 61 mg, 84% yield, Rf = 0.4 (ethyl acetate/hexane = 20%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.39 – 7.29 (m, 4H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 12.5, 7.8 Hz, 2H), 3.81 (s, 3H), 1.42 (s, 9H), 1.36 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 156.9, 148.0, 146.4, 131.6, 131.4, 128.4, 124.8, 123.2, 122.1, 121.0, 120.7, 120.3, 119.1, 110.9, 55.4, 38.1, 38.0, 31.8, 31.7 ppm;
HRMS (ESI) m/z calcd for $C_{24}H_{30}NO_2^+$ $(M+H)^+$ 364.2271, found *m/z* 364.2278.

5,7-di-tert-butyl-3-(3,4-dimethylphenyl)cyclohepta[b]pyrrol-6(1H)-one (3i)



Yellow-brown solid, m. p. 178-180 °C, 59 mg, 82% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.65 (s, 1H), 7.30 (s, 1H), 7.25 – 7.17 (m, 3H), 7.05 (d, *J* = 2.4 Hz, 1H), 2.32 (s, 6H), 1.43 (s, 9H), 1.39 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 148.2, 147.0, 136.9, 135.0, 132.0, 131.9, 130.0, 129.9, 125.9, 125.3, 123.7, 121.0, 119.0, 118.4, 38.1, 38.1, 31.9, 31.7, 19.9, 19.5 ppm;
HRMS (ESI) m/z calcd for $C_{25}H_{32}NO^+$ $(M+H)^+$ 362.2478, found *m/z* 362.2470.

5,7-di-tert-butyl-3-(3,4,5-trimethoxyphenyl)cyclohepta[b]pyrrol-6(1H)-one (3j)



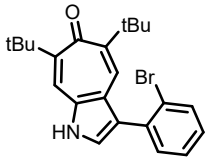
Yellow-brown solid, m. p. 205-208 °C, 68 mg, 80% yield, Rf = 0.3 (ethyl acetate/hexane = 30%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.67 (s, 1H), 7.34 (s, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.67 (s, 2H), 3.92 (s, 3H), 3.90 (s, 6H), 1.41 (d, *J* = 5.7 Hz, 18H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 153.4, 148.4, 147.0, 136.8, 132.1, 130.4, 125.1, 123.5, 120.8, 119.2, 118.6, 105.6, 61.0, 56.1, 38.1, 38.1, 32.0, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{26}H_{34}NO_4^+$ $(M+H)^+$ 424.2482, found *m/z* 424.2477.

3-(2-bromophenyl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3k)



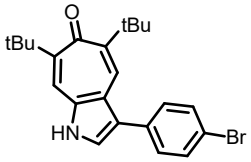
Yellow-brown solid, m. p. 210-215 °C, 63 mg, 77% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, DMSO) δ 11.75 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.45 (s, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.04 (s, 1H), 1.31 (s, 9H), 1.19 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.2, 146.7, 145.5, 135.6, 133.4, 133.2, 131.8, 129.5, 128.2, 124.2, 124.2, 122.6, 122.0, 121.2, 120.2, 38.1, 38.0, 31.8, 31.8 ppm;

HRMS (ESI) m/z calcd for $C_{23}H_{27}BrNO^+$ $(M+H)^+$ 412.1271, found *m/z* 412.1284.

3-(4-bromophenyl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3l)



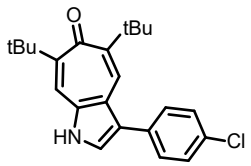
Yellow-brown solid, m. p. 202-206 °C, 67 mg, 81% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.52 (s, 1H), 7.33 – 7.28 (m, 3H), 7.05 (d, *J* = 2.5 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 148.6, 147.4, 133.5, 132.1, 131.9, 130.1, 124.1, 122.9, 120.8, 120.6, 118.9, 118.6, 38.1, 38.0, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{23}H_{27}BrNO^+$ $(M+H)^+$ 412.1271, found *m/z* 412.1282.

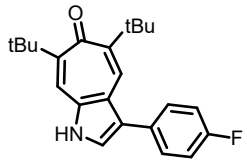
5,7-di-tert-butyl-3-(4-chlorophenyl)cyclohepta[b]pyrrol-6(1H)-one (3m)



Yellow solid, m. p. 156-161 °C, 61 mg, 83% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

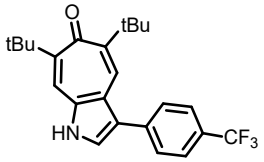
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.52 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 148.5, 147.4, 133.0, 132.5, 132.0, 129.8, 128.9, 124.1, 123.0, 120.8, 118.9, 118.6, 38.1, 38.0, 31.9, 31.6 ppm;
HRMS (ESI) m/z calcd for $C_{23}H_{27}ClNO^+$ $(M+H)^+$ 368.1776, found *m/z* 368.1779.

5,7-di-tert-butyl-3-(4-fluorophenyl)cyclohepta[b]pyrrol-6(1H)-one (3n)



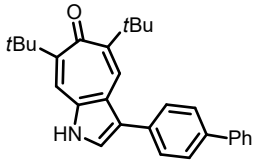
Yellowish solid, m. p. 214-220 °C, 53 mg, 76% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.52 (s, 1H), 7.39 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.31 (s, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 2.2 Hz, 1H), 1.43 (s, 9H), 1.38 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 163.1, 160.7, 148.4, 147.3, 131.9, 130.5, 130.1 (d, *J* = 7.9 Hz), 124.3, 123.1, 121.0, 119.0, 118.5, 115.7, 115.5, 38.1, 38.1, 31.9, 31.7 ppm;
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.00 – -116.07 (m, 1F) ppm;
HRMS (ESI) m/z calcd for $C_{23}H_{27}FNO^+$ $(M+H)^+$ 352.2071, found *m/z* 352.2064.

5,7-di-tert-butyl-3-(4-(trifluoromethyl)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3o)



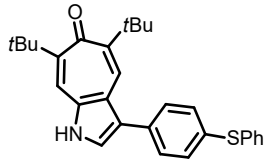
Yellow-brown solid, m. p. 198-200 °C, 52 mg, 65% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.51 (m, 3H), 7.30 (s, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 1.43 (s, 9H), 1.39 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 148.9, 147.7, 138.3, 132.2, 128.6, 125.7 (q, *J* = 3.7 Hz), 125.3 (q, *J* = 272.0 Hz), 123.9, 122.7, 120.8, 119.0, 118.8, 38.2, 38.1, 31.9, 31.7 ppm;
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.29 (s, 3F) ppm;
HRMS (ESI) m/z calcd for $C_{24}H_{27}F_3NO^+$ $(M+H)^+$ 402.2039, found *m/z* 402.2032.

3-([1,1'-biphenyl]-4-yl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3r)



Yellow solid, m. p. 163-166 °C, 60 mg, 73% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.68 (dd, *J* = 10.7, 7.1 Hz, 5H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.48 (dd, *J* = 12.8, 5.2 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.32 (s, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 1.44 (s, 9H), 1.41 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 148.4, 147.2, 140.8, 139.4, 133.6, 132.1, 128.9, 128.8, 127.5, 127.3, 127.0, 124.9, 123.4, 121.0, 119.0, 118.7, 38.2, 38.1, 31.9, 31.7 ppm;
HRMS (ESI) m/z calcd for $C_{29}H_{32}NO^+$ $(M+H)^+$ 410.2478, found *m/z* 410.2473.

5,7-di-tert-butyl-3-(4-(phenylthio)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3s)



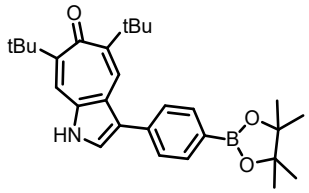
Yellow solid, m. p. 182-185 °C, 62 mg, 70% yield, Rf = 0.3 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.57 (s, 1H), 7.41 (t, *J* = 7.2 Hz, 5H), 7.34 (dd, *J* = 14.3, 6.7 Hz, 3H), 7.28 (d, *J* = 10.3 Hz, 2H), 7.06 (d, *J* = 2.5 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 148.5, 147.3, 135.7, 133.9, 133.5, 132.0, 131.3, 131.2, 129.3, 129.2, 127.2, 124.5, 123.1, 120.9, 119.0, 118.7, 38.2, 38.1, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{29}H_{32}NOS^+$ $(M+H)^+$ 442.2199, found *m/z* 442.2200.

5,7-di-tert-butyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3t)



Yellow solid, m. p. 224-226 °C, 54 mg, 59% yield, Rf = 0.3 (ethyl acetate/hexane = 15%);

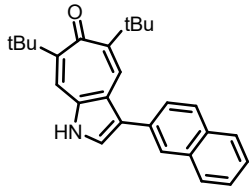
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.62 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.29 (s, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 1.42 (s, 9H), 1.37 (s, 21H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 148.5, 147.3, 137.4, 135.2, 132.1, 127.8, 125.2, 123.4, 118.9, 118.8, 83.8, 38.1, 38.1, 31.9, 31.7, 24.9 ppm;

HRMS (ESI) m/z calcd for $C_{29}H_{39}BNO_3^+$ $(M+H)^+$ 460.3018, found *m/z* 460.3024.

Because the NMR instrument does not have a boron spectrum probe, it cannot do boron spectrum.

5,7-di-tert-butyl-3-(naphthalen-2-yl)cyclohepta[b]pyrrol-6(1H)-one (3u)



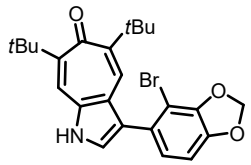
Yellowish solid, m. p. 227-230 °C, 51 mg, 67% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, DMSO) δ 11.93 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 3H), 7.70 (d, *J* = 5.2 Hz, 2H), 7.60 – 7.50 (m, 4H), 1.42 (s, 9H), 1.37 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.5, 146.8, 145.9, 133.9, 132.7, 132.6, 132.0, 128.7, 128.1, 128.0, 127.4, 126.9, 126.3, 126.1, 123.6, 123.4, 121.3, 120.3, 120.3, 38.1, 32.1, 31.8 ppm;

HRMS (ESI) m/z calcd for $C_{27}H_{30}NO^+$ $(M+H)^+$ 384.2322, found *m/z* 384.2323.

3-(4-bromobenzo[d][1,3]dioxol-5-yl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3v)



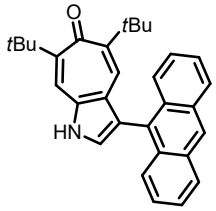
Yellow solid, m. p. 212-216 °C 88mg, 96% yield, Rf = 0.4 (ethyl acetate/hexane = 20 %);

^{1}H NMR (400 MHz, DMSO) δ 11.73 (s, 1H), 7.54 – 7.47 (m, 1H), 7.38 – 7.31 (m, 1H), 7.22 (dd, *J* = 4.1, 2.7 Hz, 1H), 7.17 – 7.07 (m, 1H), 6.97 – 6.87 (m, 1H), 6.18 – 6.09 (m, 2H), 1.37 (s, 9H), 1.27 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.1, 148.1, 147.6, 146.6, 145.4, 131.6, 128.6, 124.3, 122.8, 121.9, 121.3, 120.2, 114.8, 113.0, 112.4, 102.6, 38.1, 37.9, 31.9, 31.8 ppm;

HRMS (ESI) m/z calcd for $C_{24}H_{27}BrNO_3^+$ $(M+H)^+$ 456.1169, found *m/z* 456.1167.

3-(anthracen-9-yl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3w)



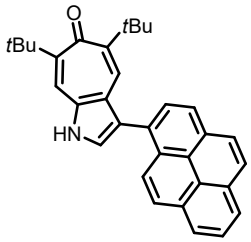
Yellow solid, m. p. 193-196 °C, 75 mg, 87% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.52 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.33 (ddd, *J* = 8.6, 6.5, 1.1 Hz, 2H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.84 (s, 1H), 1.48 (s, 9H), 1.08 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 148.4, 147.4, 131.7, 131.5, 128.4, 127.1, 127.0, 125.4, 125.2, 124.3, 124.1, 121.9, 120.0, 119.1, 38.2, 37.8, 31.7, 31.5 ppm;

HRMS (ESI) m/z calcd for $C_{31}H_{32}NO^+$ $(M+H)^+$ 434.2478, found *m/z* 434.2481.

5,7-di-tert-butyl-3-(pyren-1-yl)cyclohepta[b]pyrrol-6(1H)-one (3x)



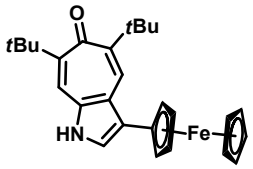
Yellow solid, m. p. 147-151 °C, 76 mg, 83% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, DMSO) δ 11.99 (s, 1H), 8.29 – 8.17 (m, 4H), 8.12 (d, *J* = 2.4 Hz, 1H), 8.03 – 7.96 (m, 4H), 7.60 (s, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.08 (s, 1H), 1.35 (s, 9H), 1.03 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.3, 146.9, 145.9, 132.3, 131.5, 131.0, 130.3, 130.2, 129.4, 129.1, 127.9, 127.6, 127.5, 126.8, 126.0, 125.6, 125.4, 125.4, 124.8, 124.5, 124.1, 122.8, 122.2, 122.1, 120.4, 38.2, 37.9, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{33}H_{32}NO^+$ $(M+H)^+$ 458.2478, found *m/z* 458.2475.

5,7-di-tert-butyl-3-(ferrocene)cyclohepta[b]pyrrol-6(1H)-one (3y)



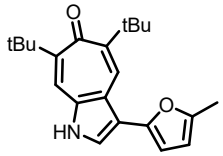
Black solid, m. p. 175-177 °C, 80 mg, 91% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, DMSO) δ 11.51 (s, 1H), 7.85 (s, 1H), 7.39 (s, 1H), 7.22 (s, 1H), 4.46 (s, 2H), 4.24 (s, 2H), 4.02 (s, 5H), 1.37 (s, 9H), 1.31 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.5, 146.4, 145.2, 132.6, 124.0, 120.8, 120.5, 120.4, 119.3, 80.8, 69.3, 68.2, 67.1, 38.2, 38.0, 32.2, 31.8 ppm;

HRMS (ESI) m/z calcd for $C_{27}H_{31}FeNO$ (M) 441.1755, found *m/z* 441.1742.

5,7-di-tert-butyl-3-(5-methylfuran-2-yl)cyclohepta[b]pyrrol-6(1H)-one (3z)



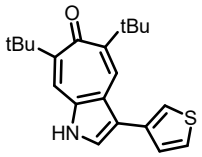
Brown yellow solid, m. p. 130-134 °C, 49 mg, 72% yield, Rf = 0.3 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.83 (s, 1H), 7.26 (s, 1H), 7.21 (d, *J* = 2.6 Hz, 1H), 6.30 (d, *J* = 3.0 Hz, 1H), 6.08 (d, *J* = 2.8 Hz, 1H), 2.37 (s, 3H), 1.44 (s, 9H), 1.41 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 150.6, 148.5, 147.7, 147.3, 131.8, 123.6, 119.8, 118.8, 117.8, 115.5, 107.1, 105.9, 38.2, 38.1, 31.9, 31.6, 13.6 ppm;

HRMS (ESI) m/z calcd for $C_{22}H_{28}NO_2^+$ $(M+H)^+$ 338.2115, found *m/z* 338.2112.

5,7-di-tert-butyl-3-(thiophen-3-yl)cyclohepta[b]pyrrol-6(1H)-one (3aa)



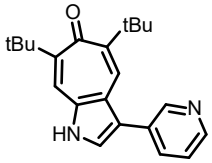
Brown yellow solid, m. p. 104-110 °C, 43 mg, 64% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.78 (s, 1H), 7.29 (d, *J* = 3.6 Hz, 2H), 7.13 (dd, *J* = 5.5, 2.9 Hz, 2H), 7.11 – 7.07 (m, 1H), 1.42 (d, *J* = 2.8 Hz, 18H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 148.6, 147.4, 136.4, 132.1, 127.7, 124.4, 124.0, 123.3, 120.9, 119.1, 118.9, 118.0, 38.2, 38.1, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{21}H_{26}NOS^+$ $(M+H)^+$ 340.1730, found *m/z* 340.1728.

5,7-di-tert-butyl-3-(pyridin-3-yl)cyclohepta[b]pyrrol-6(1H)-one (3ab)



Brown yellow solid, m. p. 121-124 °C, 49 mg, 74% yield, Rf = 0.4 (ethyl acetate/hexane = 30%);

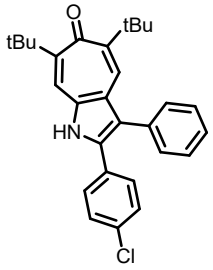
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.72 (s, 1H), 8.57 (d, *J* = 4.7 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.48 (s, 1H), 7.39 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.32 (s, 1H), 7.11 (d, *J* = 2.6 Hz, 1H), 1.42 (s, 9H),

1.38 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 149.3, 148.8, 147.7, 147.6, 135.8, 132.3, 130.7, 123.6, 122.4, 121.4, 120.9, 119.0, 118.9, 38.1, 38.1, 31.9, 31.7 ppm;

HRMS (ESI) m/z calcd for $C_{22}H_{27}N_2O^+$ $(M+H)^+$ 335.2118, found *m/z* 335.2116.

5,7-di-tert-butyl-2-(4-chlorophenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ac)



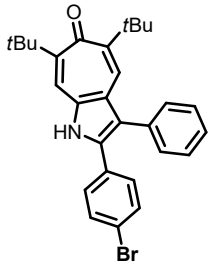
Brown yellow solid, m. p. 150-154 °C, 72 mg, 81% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, DMSO) δ 12.10 (s, 1H), 7.56 (s, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.33 – 7.30 (m, 2H), 7.25 – 7.22 (m, 2H), 7.21 (s, 1H), 1.38 (s, 9H), 1.24 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.3, 147.7, 146.4, 134.5, 132.3, 132.3, 130.9, 130.8, 130.2, 129.3, 129.2, 129.1, 127.6, 123.2, 123.2, 121.5, 119.9, 38.2, 38.1, 31.9, 31.8 ppm;

HRMS (ESI) m/z calcd for $C_{29}H_{31}ClNO^+$ $(M+H)^+$ 444.2089, found *m/z* 444.2087.

2-(4-bromophenyl)-5,7-di-tert-butyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ad)



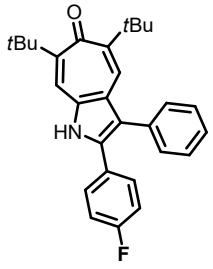
Brown yellow solid, m. p. 169-173 °C, 75 mg, 77% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, DMSO) δ 7.55 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.20 (s, 1H), 1.37 (s, 9H), 1.23 (s, 9H) ppm;

^{13}C NMR (100 MHz, DMSO) δ 194.3, 147.7, 146.4, 136.5, 134.4, 132.3, 132.0, 131.3, 130.8, 130.8, 130.3, 130.2, 129.5, 129.3, 127.6, 123.2, 123.2, 121.5, 120.8, 119.9, 38.2, 38.1, 31.9, 31.9 ppm;

HRMS (ESI) m/z calcd for $C_{29}H_{31}BrNO^+$ $(M+H)^+$ 488.1584, found *m/z* 488.1581.

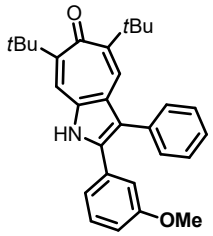
5,7-di-tert-butyl-2-(4-fluorophenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ae)



Brown yellow solid, m. p. 143-146 °C, 73 mg, 86% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

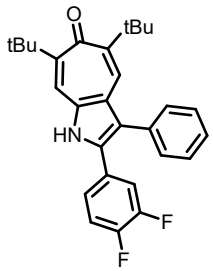
^{1}H NMR (400 MHz, DMSO) δ 12.06 (s, 1H), 7.56 (s, 1H), 7.47 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 7.25 – 7.15 (m, 5H), 1.39 (s, 9H), 1.25 (s, 9H) ppm;
^{13}C NMR (100 MHz, DMSO) δ 194.2, 147.4, 146.3, 134.6, 132.1, 130.8, 130.6, 129.8, 129.7, 129.2, 128.6 (d, J = 3.3 Hz), 127.5, 123.3, 123.1, 121.0, 119.9, 116.1, 115.9, 38.2, 38.1, 31.9, 31.8 ppm;
^{19}F NMR (376 MHz, DMSO) δ -114.33 – -114.41 (m, 1F) ppm;
HRMS (ESI) m/z calcd for $C_{29}H_{31}FNO^+$ $(M+H)^+$ 428.2384, found *m/z* 428.2384.

5,7-di-tert-butyl-2-(3-methoxyphenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3af)



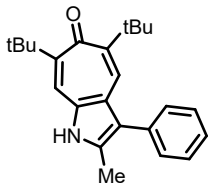
Brown yellow solid, m. p. 135-140 °C, 81 mg, 92% yield, Rf = 0.4 (ethyl acetate/hexane = 20%);
^{1}H NMR (400 MHz, DMSO) δ 11.98 (s, 1H), 7.52 (s, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.22 – 7.15 (m, 3H), 7.14 (s, 1H), 6.88 – 6.81 (m, 2H), 6.75 (dd, J = 7.9, 2.2 Hz, 1H), 3.56 (s, 3H), 1.33 (s, 9H), 1.18 (s, 9H) ppm;
^{13}C NMR (100 MHz, DMSO) δ 194.2, 159.6, 147.4, 146.3, 134.8, 133.2, 132.0, 131.2, 130.9, 130.1, 129.2, 127.5, 123.3, 121.3, 120.0, 119.8, 113.4, 112.9, 55.3, 38.2, 38.1, 31.9, 31.8 ppm;
HRMS (ESI) m/z calcd for $C_{30}H_{34}NO_2^+$ $(M+H)^+$ 440.2584, found *m/z* 440.2585.

5,7-di-tert-butyl-2-(3,4-difluorophenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ag)



Note: because the compound has poor solubility in deuterated chloroform, and NMR shimming is not good
colorless oil, 33 mg, 38% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.43-7.31 (m, 6H), 7.25 (s, 1H), 7.10-6.98 (m, 3H), 1.42 (s, 9H), 1.33 (s, 9H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 149.2, 147.9, 133.5, 131.7, 130.6, 130.3, 129. 8, 128.8, 123.8, 123.3, 118.6, 117.6, 116.2, 38.2, 38.1, 31.8, 31.7 ppm;
^{19}F NMR (376 MHz, $CDCl_3$) -136.6--136.7 (m), -138.6--138.7 (m),
HRMS (ESI) m/z calcd for $C_{29}H_{30}F_2NO^+$ $(M+H)^+$ 446.2290, found *m/z* 446.2288.

5,7-di-tert-butyl-2-methyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ah)



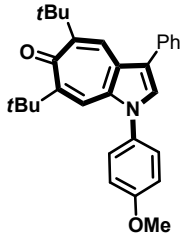
Brown yellow solid, m. p. 120-125 °C, 58 mg, 84% yield, Rf = 0.4 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.36 – 7.30 (m, 4H), 2.37 (s, 3H), 1.42 (s, 9H), 1.37 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 147.1, 147.0, 134.4, 130.3, 130.1, 128.5, 126.4, 123.9, 122.6, 121.4, 119.1, 38.2, 38.1, 31.8, 31.7, 12.1 ppm;

HRMS (ESI) m/z calcd for $C_{24}H_{30}NO^+$ $(M+H)^+$ 348.2322, found *m/z* 348.2327.

5,7-di-tert-butyl-1-(4-methoxyphenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (6)



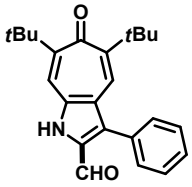
Brown solid, m. p. 143-147 °C, 83 mg, 95% yield, Rf = 0.3 (ethyl acetate/hexane = 5%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.52 – 7.45 (m, 3H), 7.41 – 7.36 (m, 1H), 7.35 – 7.26 (m, 4H), 7.12 (d, *J* = 10.1 Hz, 1H), 7.13 – 7.04 (m, 2H), 3.90 (s, 3H), 1.41 (s, 9H), 1.34 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 159.2 (d, *J* = 4.5 Hz), 147.7 (d, *J* = 11.1 Hz), 147.1 (d, *J* = 13.7 Hz), 136.4, 134.3, 132.5 (d, *J* = 7.9 Hz), 131.6 (d, *J* = 5.6 Hz), 131.3, 129.5, 128.7 (d, *J* = 11.1 Hz), 128.6, 127.2, 126.7, 124.5 (d, *J* = 3.9 Hz), 123.5 (t, *J* = 14.6 Hz), 121.9 (d, *J* = 5.5 Hz), 118.0, 114.7 (d, *J* = 1.8 Hz), 55.6, 38.2 (d, *J* = 9.2 Hz), 31.8 (d, *J* = 15.7 Hz) ppm;

HRMS (ESI) m/z calcd for $C_{30}H_{34}NO_2^+$ $(M+H)^+$ 440.2584, found *m/z* 440.2579.

5,7-di-tert-butyl-6-oxo-3-phenyl-1,6-dihydrocyclohepta[b]pyrrole-2-carbaldehyde (7)



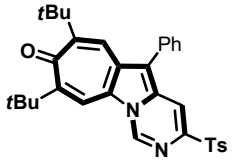
Yellow solid, m. p. 179-182 °C, 69 mg, 96% yield, Rf = 0.5 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 9.60 (s, 1H), 7.58 – 7.51 (m, 3H), 7.48 (t, *J* = 7.1 Hz, 3H), 7.29 (s, 1H), 1.43 (s, 9H), 1.34 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 181.3, 154.7, 148.6, 136.6, 135.7, 131.3, 130.8, 129.3, 128.8, 128.4, 122.4, 122.4, 118.8, 38.6, 38.0, 31.8, 31.6 ppm;

HRMS (ESI) m/z calcd for $C_{24}H_{28}NO_2^+$ $(M+H)^+$ 362.2115, found *m/z* 362.2119.

7,9-di-tert-butyl-5-phenyl-3-tosyl-8H-cyclohepta[4,5]pyrrolo[1,2-c]pyrimidin-8-one (8)



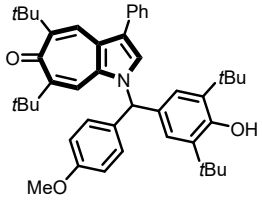
Yellow solid, m. p. 228-231 °C, 73 mg, 72% yield, Rf = 0.3 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.30 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.55 (m, 3H), 7.48 (dd, *J* = 14.5, 9.4 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 1.44 (s, 9H), 1.36 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 152.9, 151.6, 144.8, 143.4, 136.8, 136.0, 131.1, 129.9, 129.8, 129.3, 128.8, 128.1, 127.8, 127.5, 123.9, 121.8, 120.1, 114.0, 113.6, 38.6, 38.5, 31.8, 31.8, 21.7 ppm;

HRMS (ESI) m/z calcd for $C_{33}H_{35}N_2O_3S^+$ $(M+H)^+$ 539.2363, found *m/z* 539.2362.

5,7-di-tert-butyl-1-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (9)



Yellow solid, m. p. 223-226 °C, 76 mg, 72% yield, Rf = 0.7 (ethyl acetate/hexane = 10%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.40 (q, *J* = 7.4 Hz, 4H), 7.32 (s, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.65 (s, 1H), 6.61 (s, 1H), 5.25 (s, 1H), 3.81 (s, 3H), 1.38 (s, 9H), 1.36 (s, 18H), 1.27 (s, 9H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 159.2, 153.6, 147.1, 147.0, 136.3, 134.9, 132.2, 131.6, 129.6, 129.5, 128.6, 126.3, 125.2, 123.8, 122.8, 122.4, 122.3, 118.2, 114.1, 64.7, 55.3, 38.3, 38.1, 34.4, 31.8, 31.6, 30.2 ppm;

HRMS (ESI) m/z calcd for $C_{45}H_{56}NO_3^+$ $(M+H)^+$ 658.4255, found *m/z* 658.4254.

11. Reference

1. (a) W. Chu, L. Zhang, C. Zeng, J. Du, G. Zhang, F. Wang, X. Ma, C. Fan, *Angew. Chem. Int. Ed.* **2013**, *52*, 9229. (b) D. Richter, N. Hampel, T. Singer, R. A. Ofial, H. Mayr, *Eur. J. Org. Chem*. **2009**, 3203. (c) T. Uno, M. Minari, M. Kubo, T. Itoh, *J. Polym. Sci., Part A: Polym. Chem.***2004**, *42*, 4548.

2. W. E. Savige, A. Fontana, *Methods Enzymol.* **1977**, *47*, 442–453.

3. H. Zhang, Q. Cai, D. W. Ma, *J. Org. Chem.* **2005**, *70*, 5164-5173.

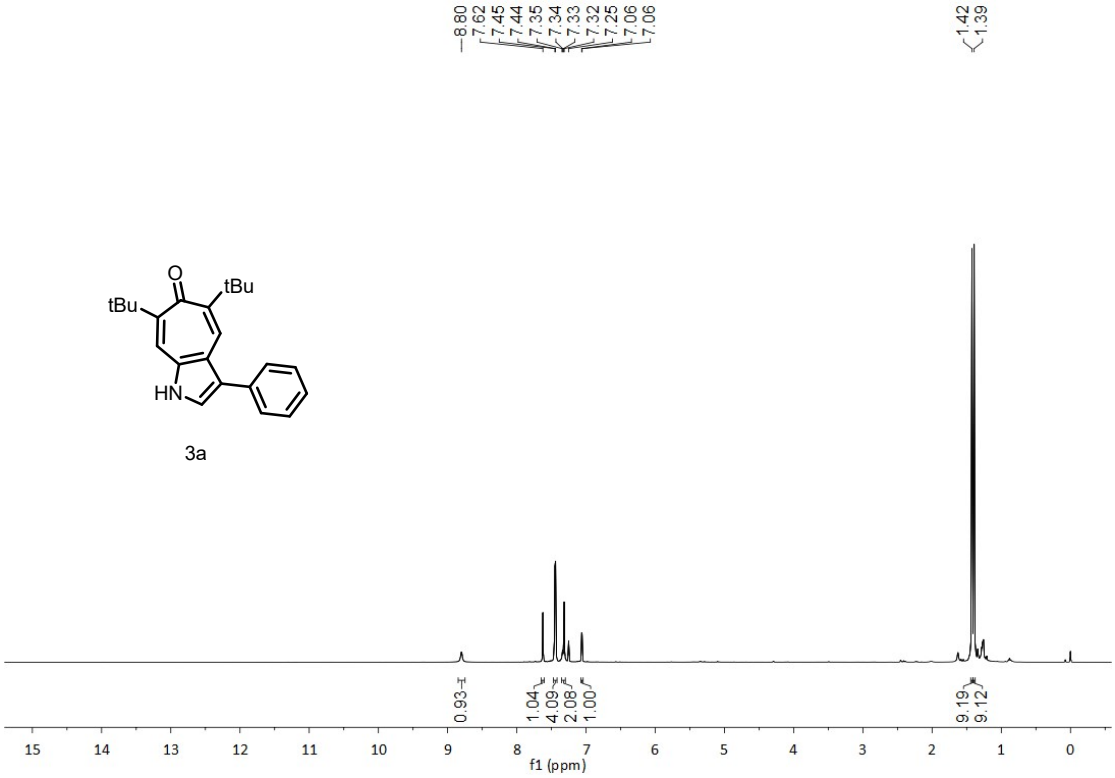
4. J. M. Minguez, J. J. Vanquero, J. L. G-Navio, J. A-Builla, *Tetrahedron Lett.* **1996**, *37*, 4263–6266.

5. X. Guan, L. Zhang, P. You, S. Liu, Z. Liu, Tetrahedron Lett. **2019**, *60*, 244-247.

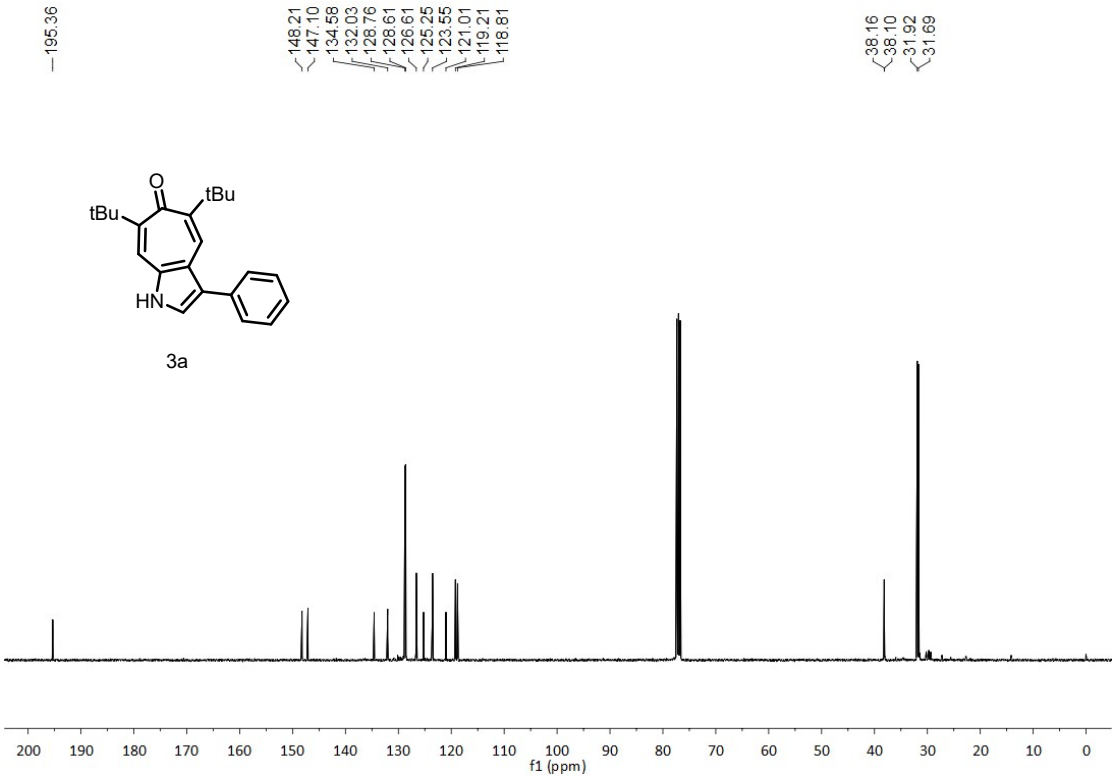
12. Copies ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HRMS

5,7-di-tert-butyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3a)

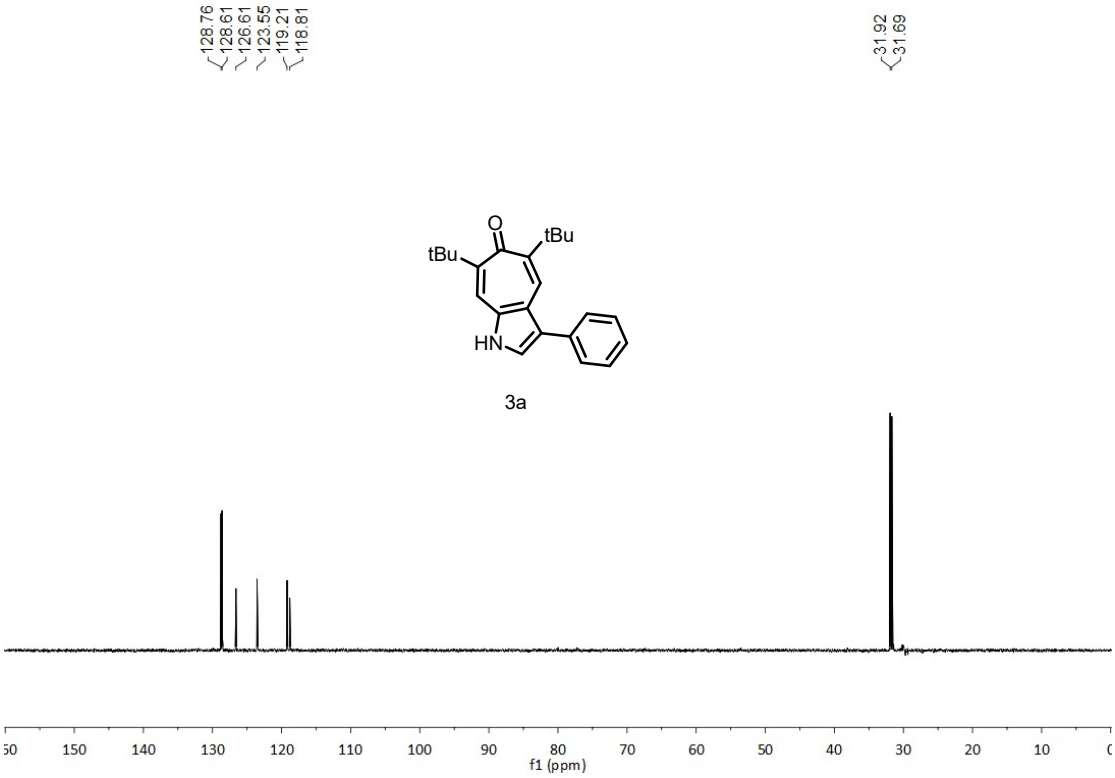
^{1}H NMR (400 MHz, $CDCl_3$):



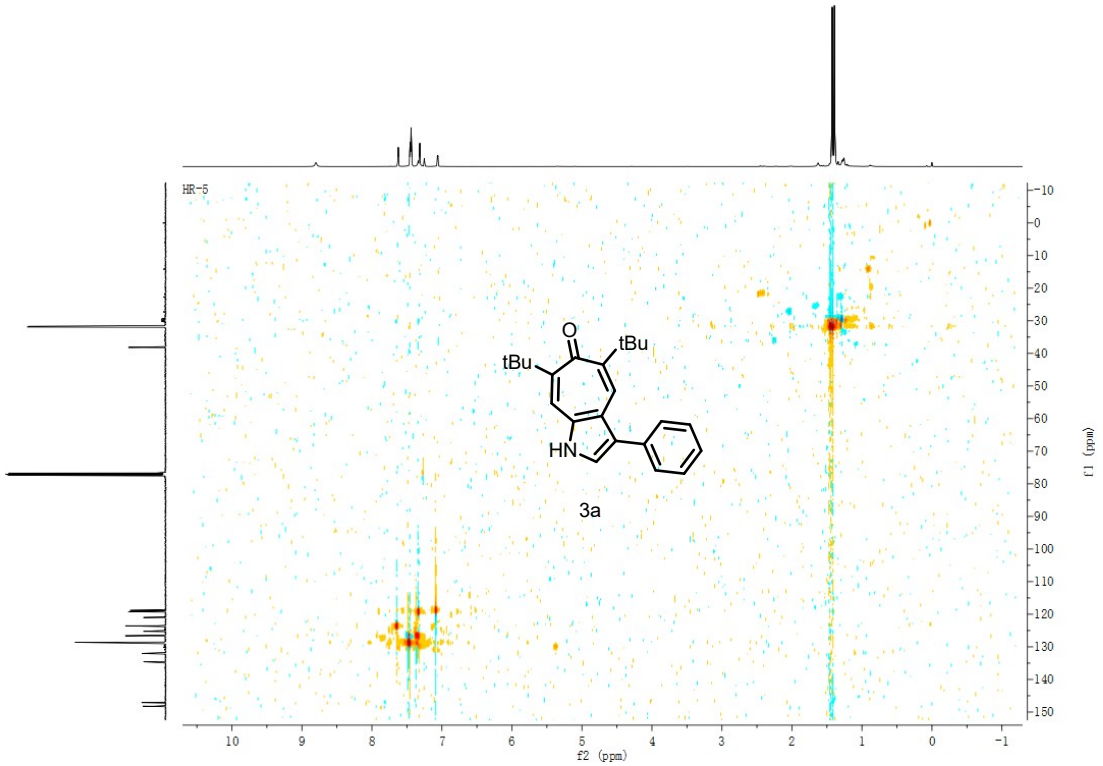
^{13}C NMR (100 MHz, $CDCl_3$):



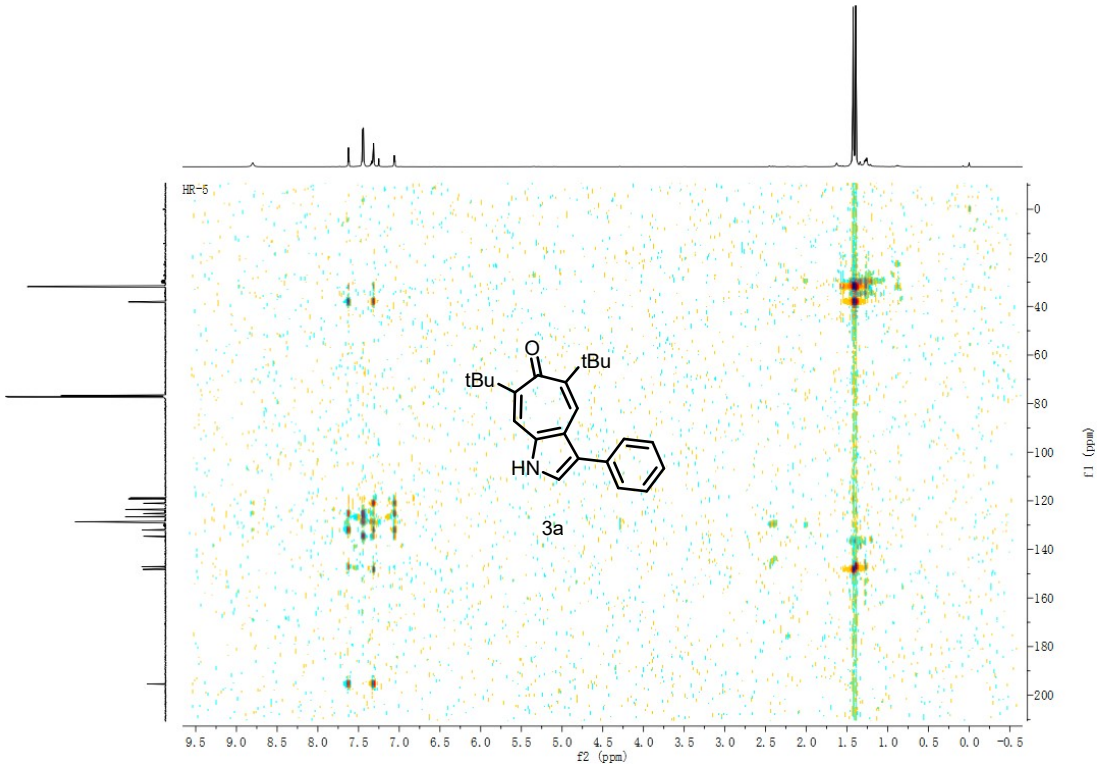
DEPT135



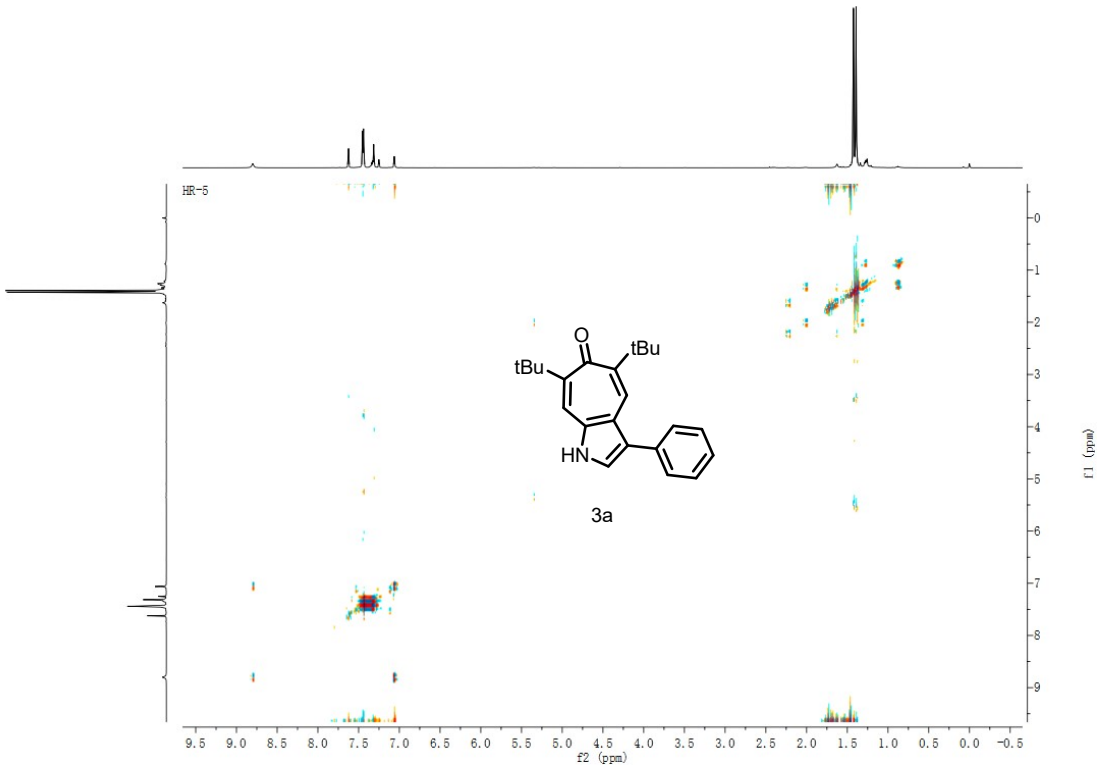
HMQC spectra of 3a



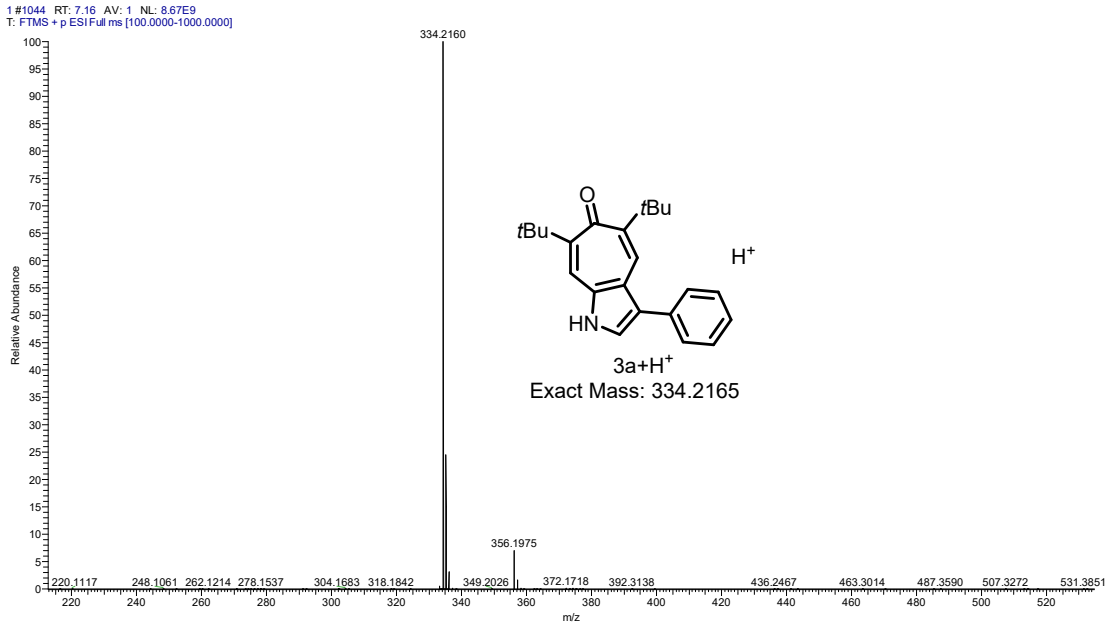
HMBC spectra of 3a



H-H Cosy spectra of 3a

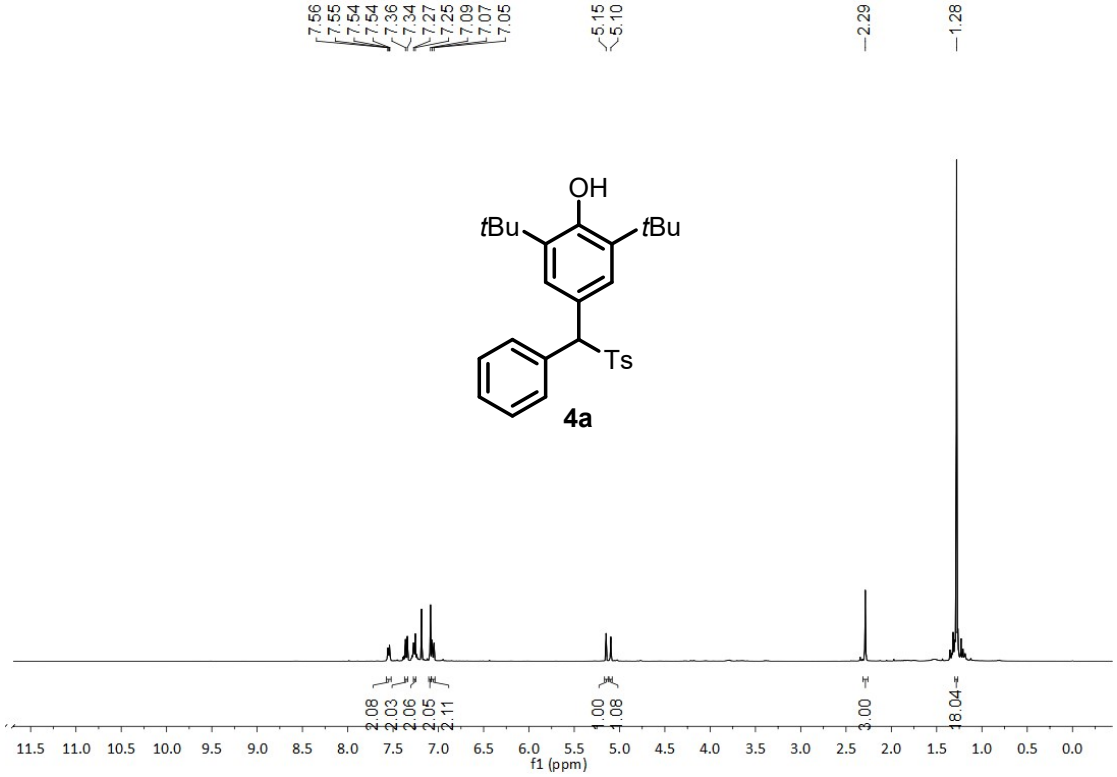


HRMS of 3a

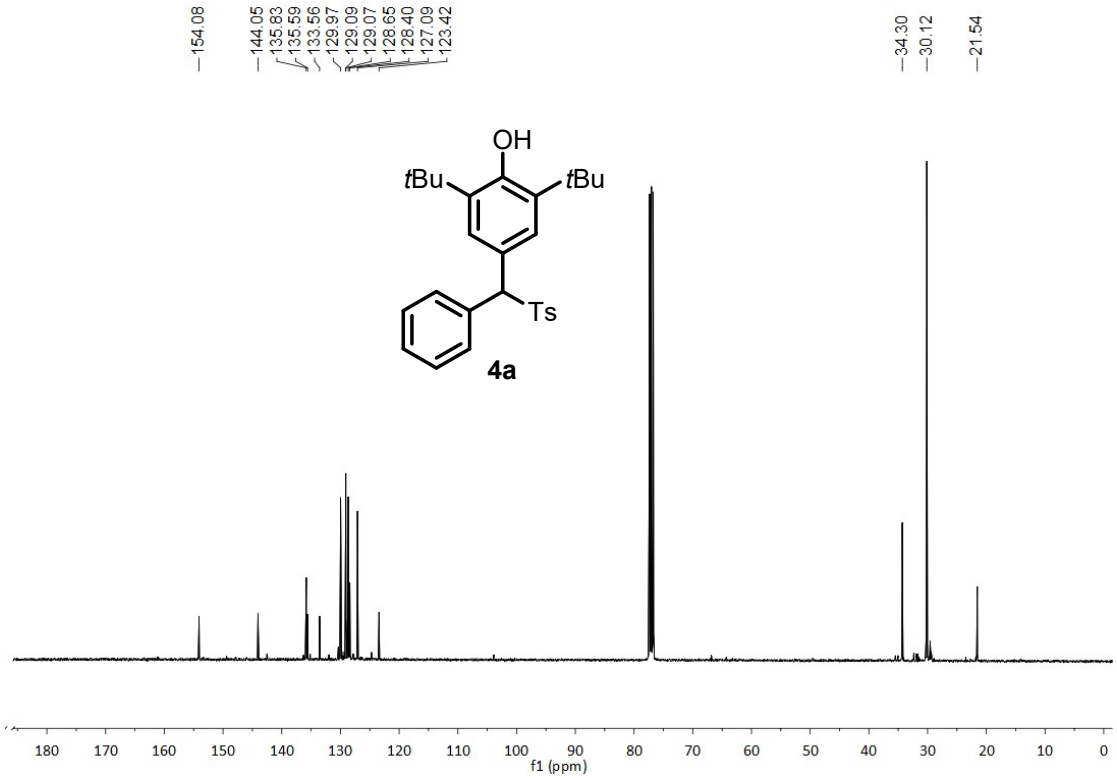


2,6-di-tert-butyl-4-(phenyl(tosyl)methyl)phenol (4a)

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

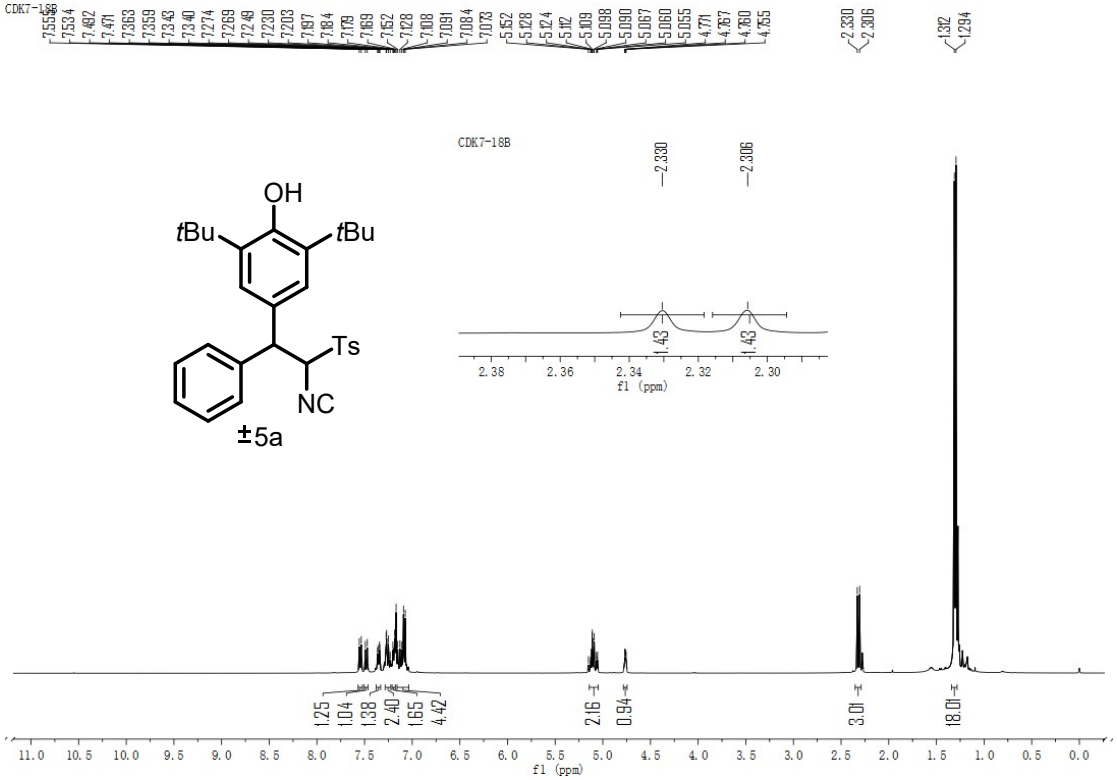


^{13}C NMR (100 MHz, $CDCl_3$):

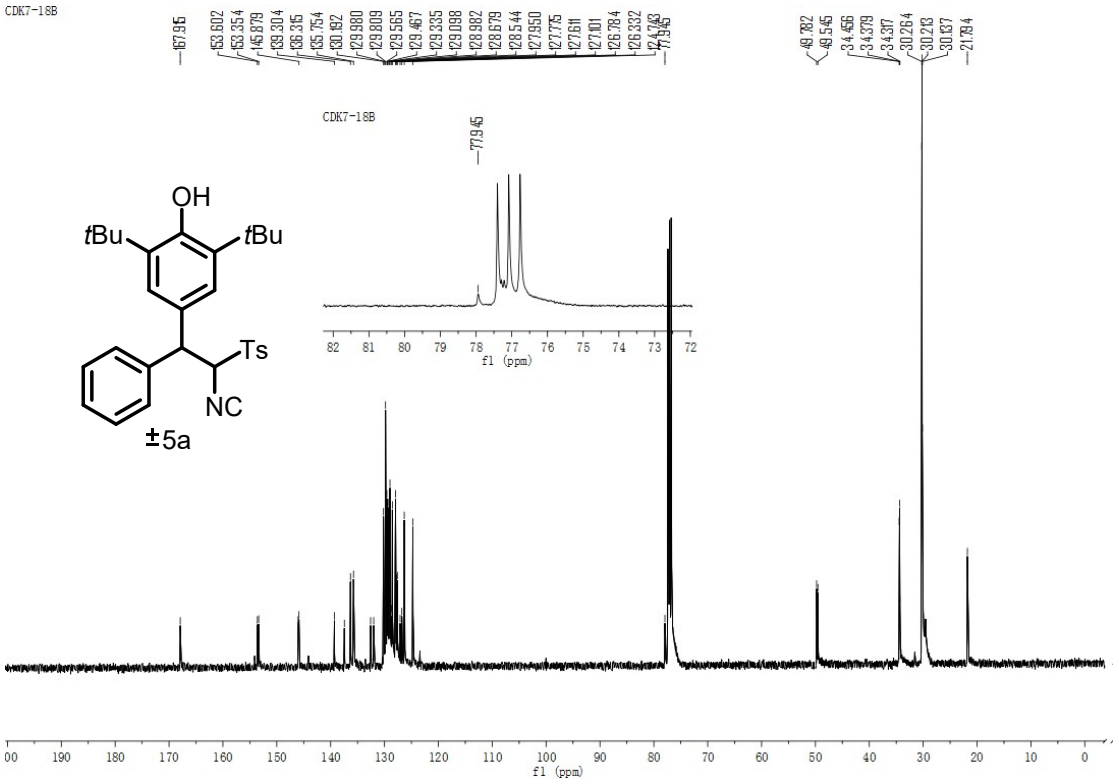


(±) 2,6-di-tert-butyl-4-(2-isocyano-1-phenyl-2-tosylethyl)phenol (±5a)

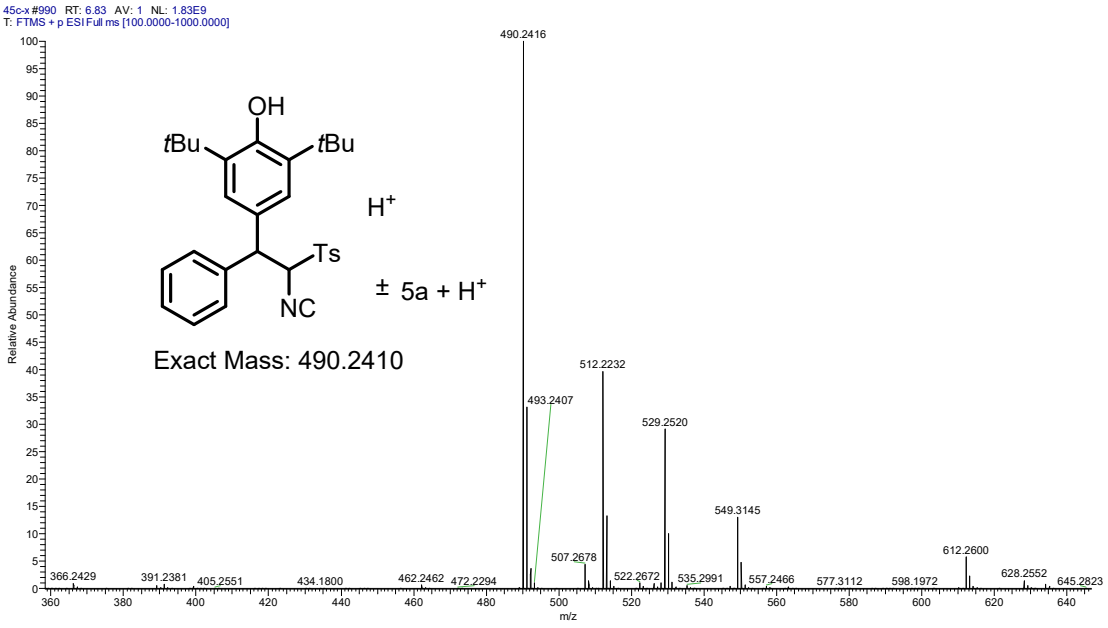
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

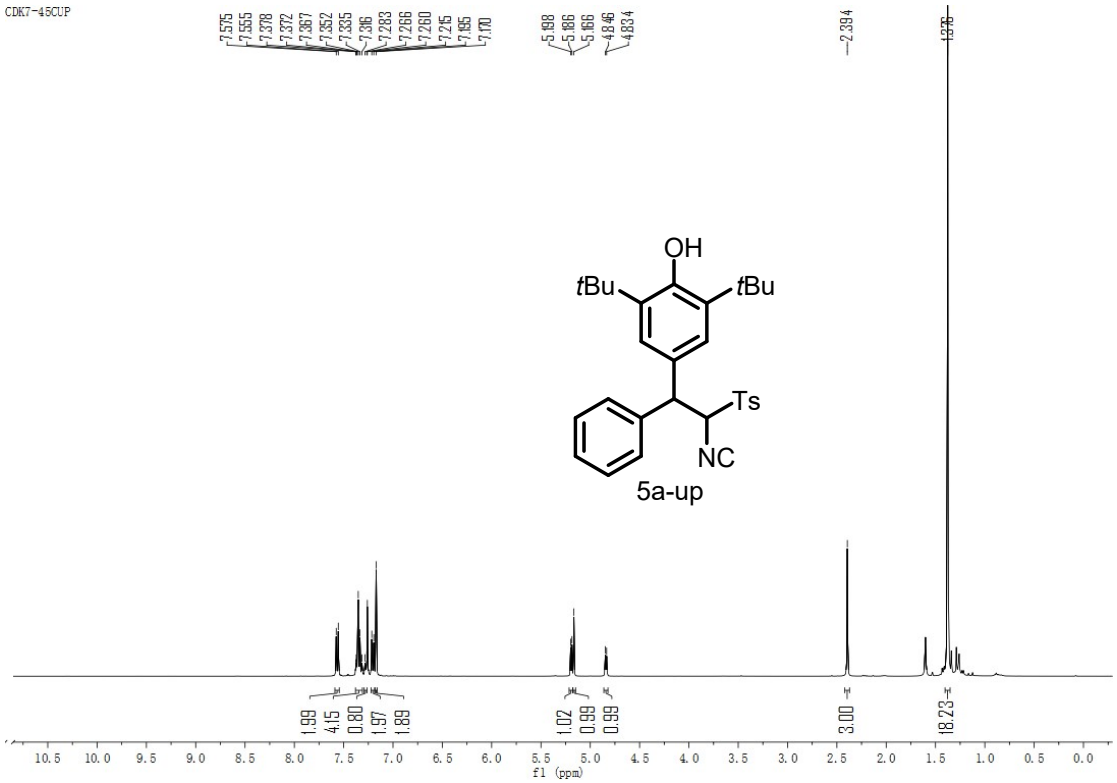


HRMS of ±5a

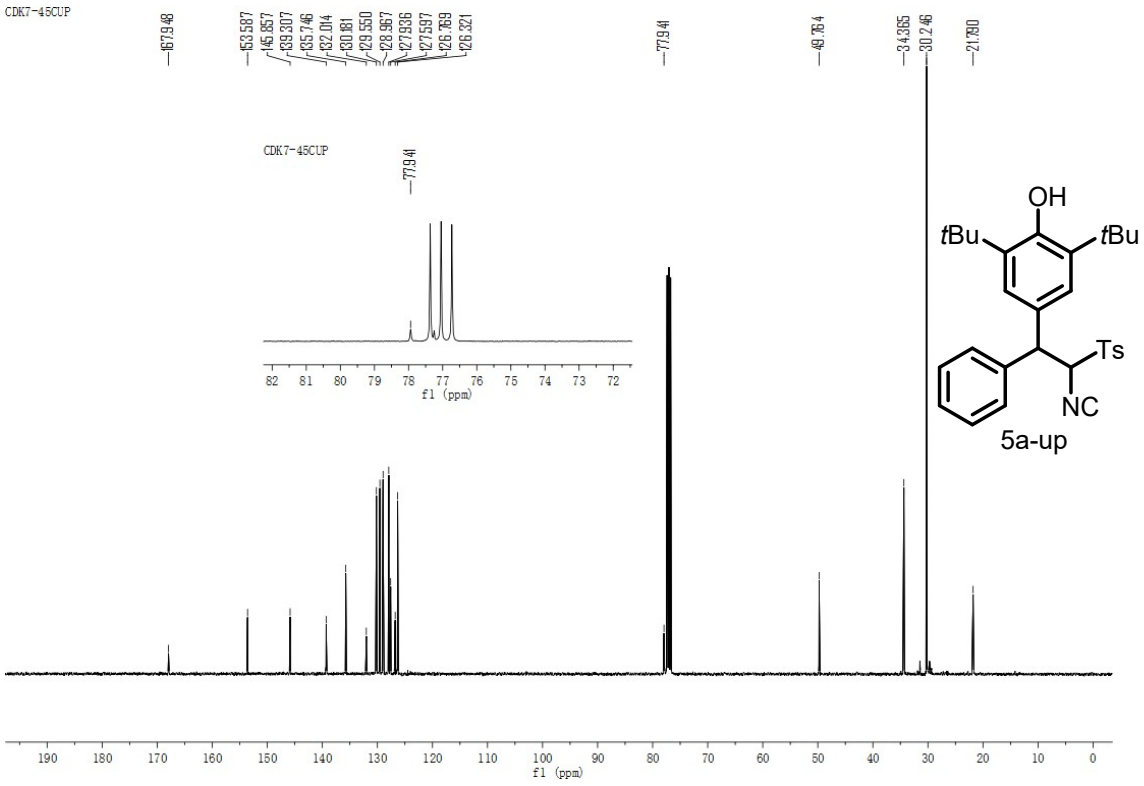


2,6-di-tert-butyl-4-(2-isocyano-1-phenyl-2-tosylethyl)phenol (5a-up)

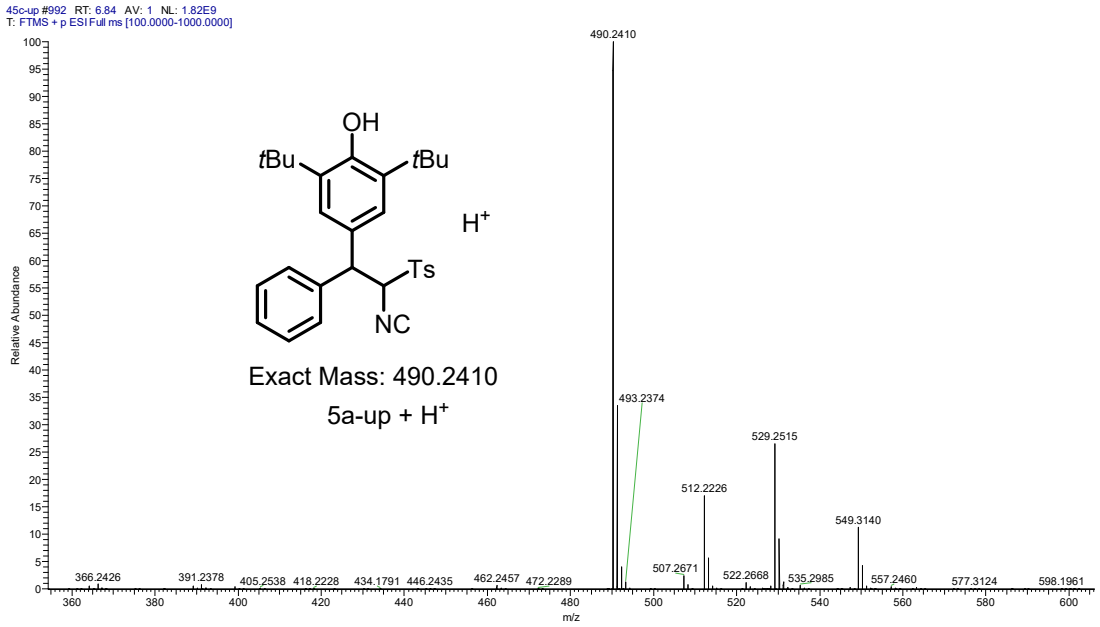
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

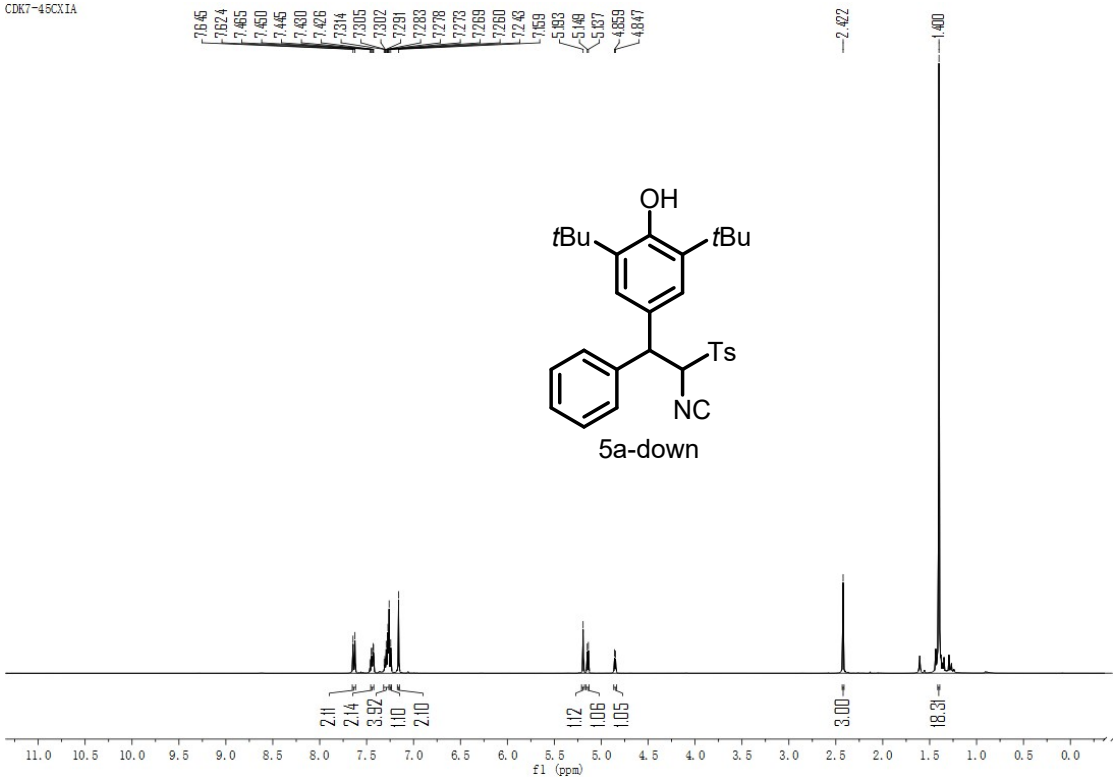


HRMS of 5a-up

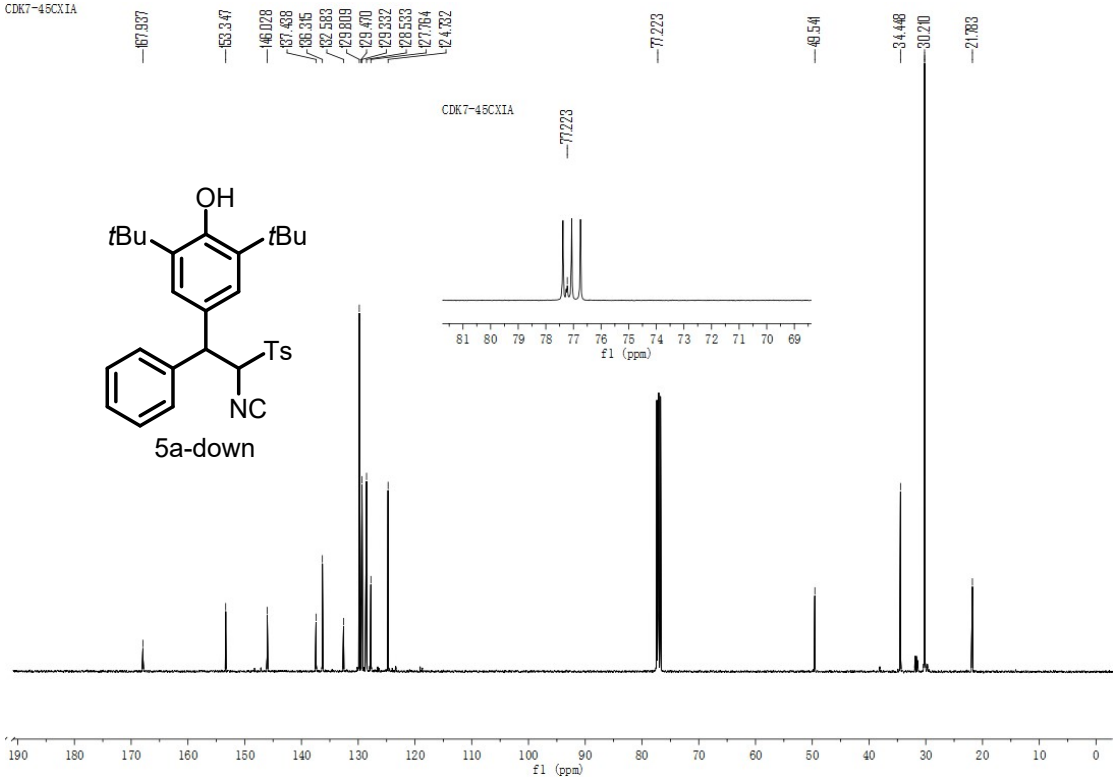


2,6-di-tert-butyl-4-(2-isocyano-1-phenyl-2-tosylethyl)phenol (5a-down)

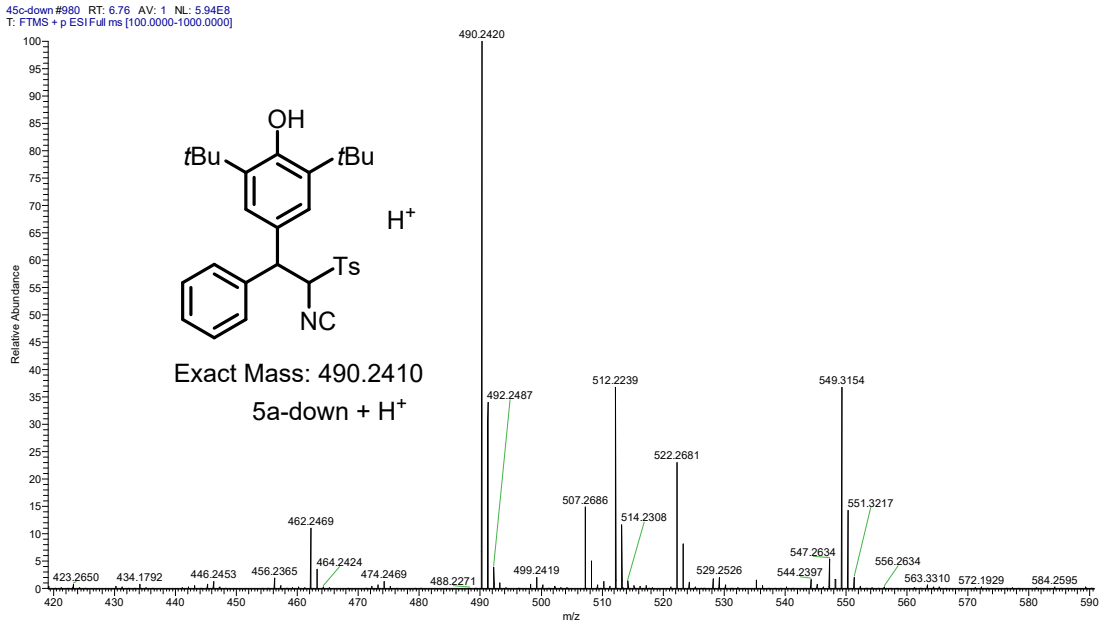
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

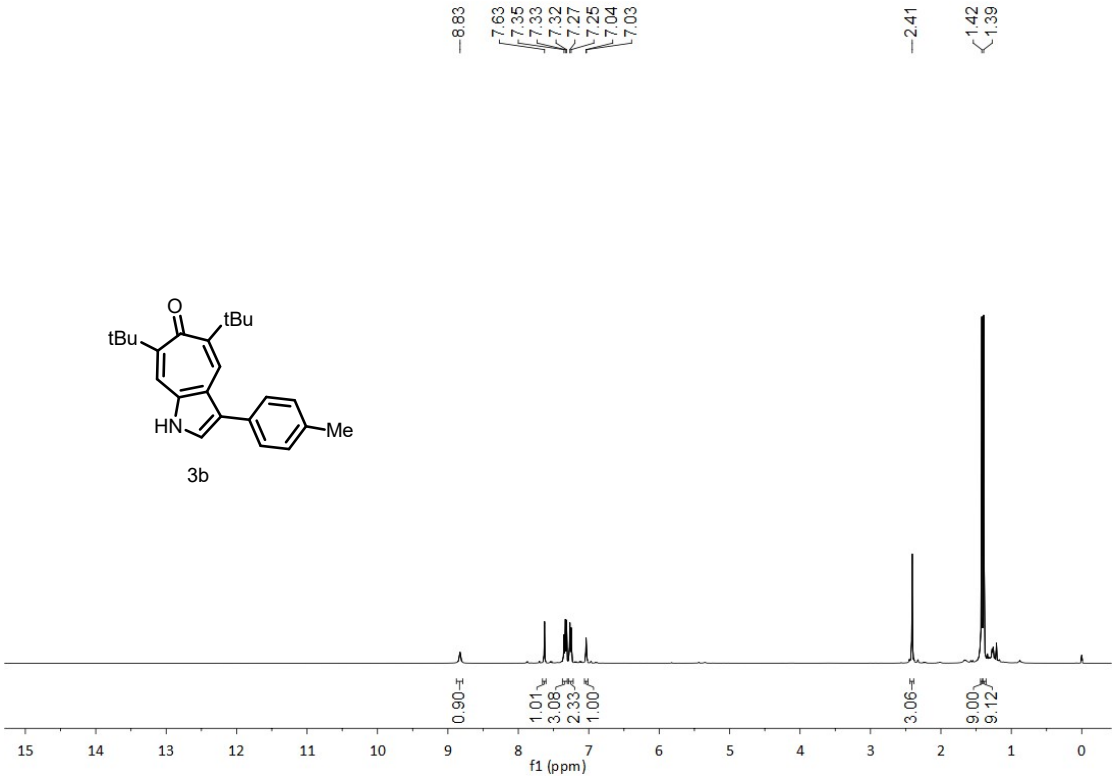


HRMS of 5a-down

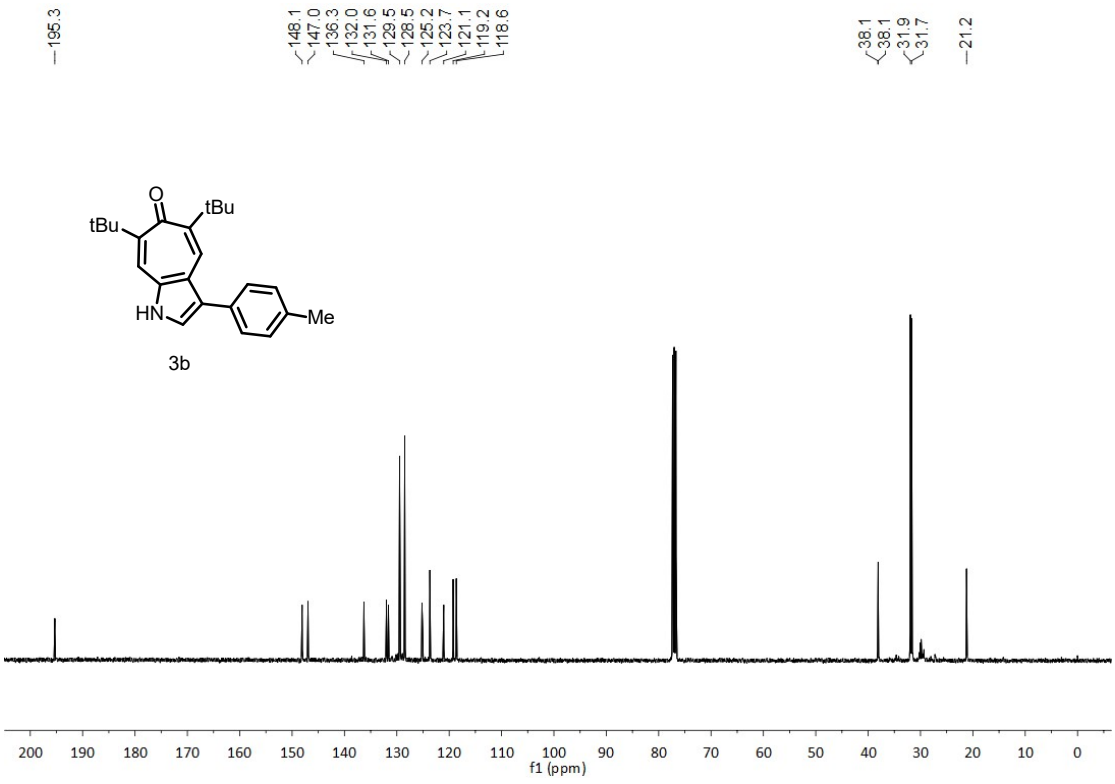


5,7-di-tert-butyl-3-(p-tolyl)cyclohepta[b]pyrrol-6(1H)-one (3b)

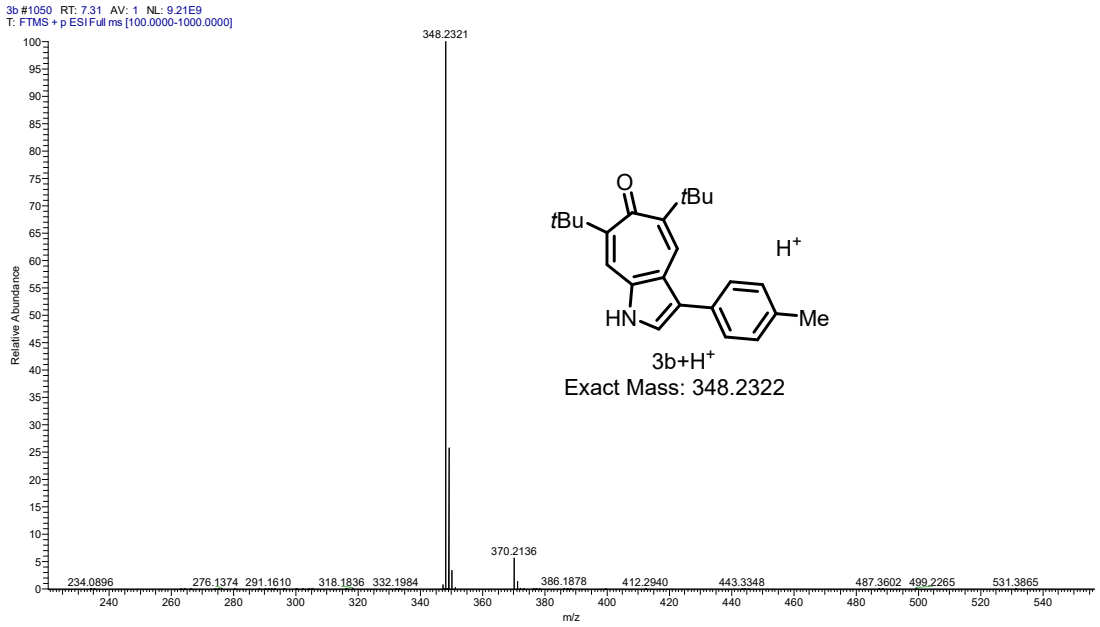
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

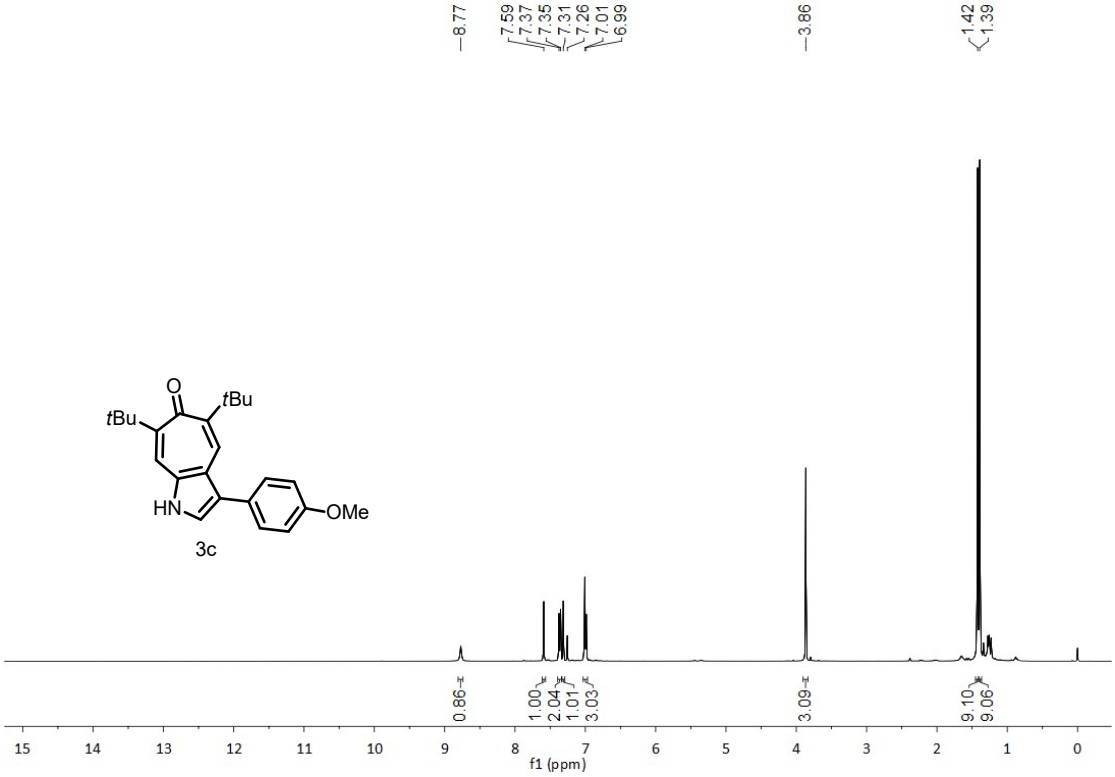


HRMS of 3b

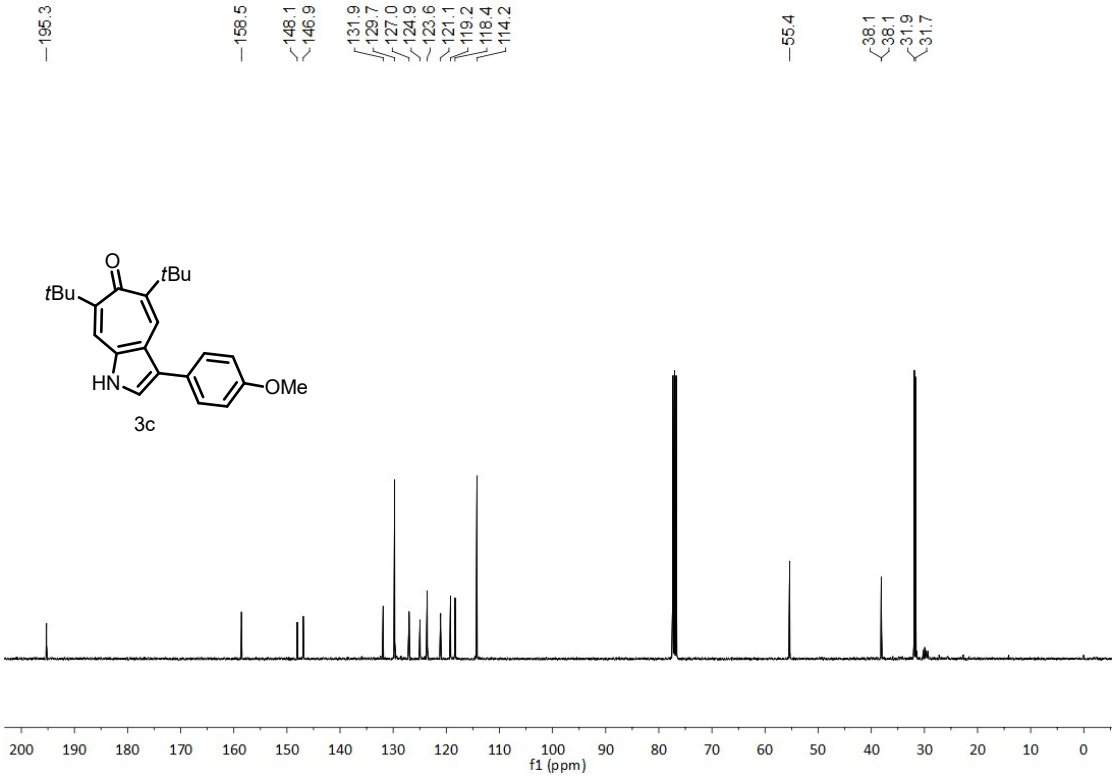


5,7-di-tert-butyl-3-(4-methoxyphenyl)cyclohepta[b]pyrrol-6(1H)-one (3c)

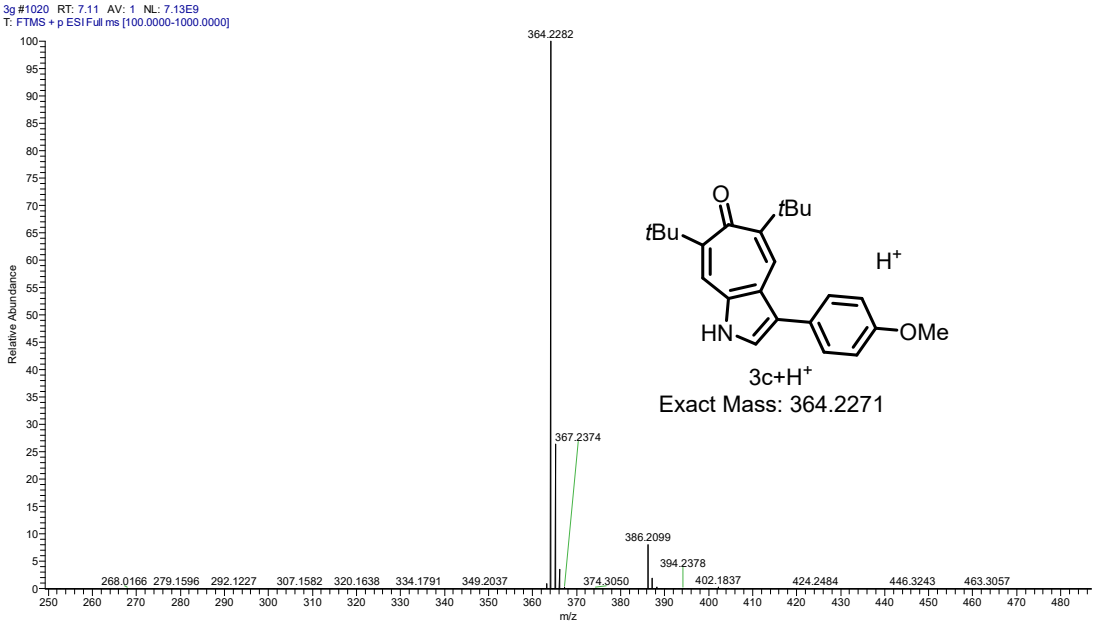
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

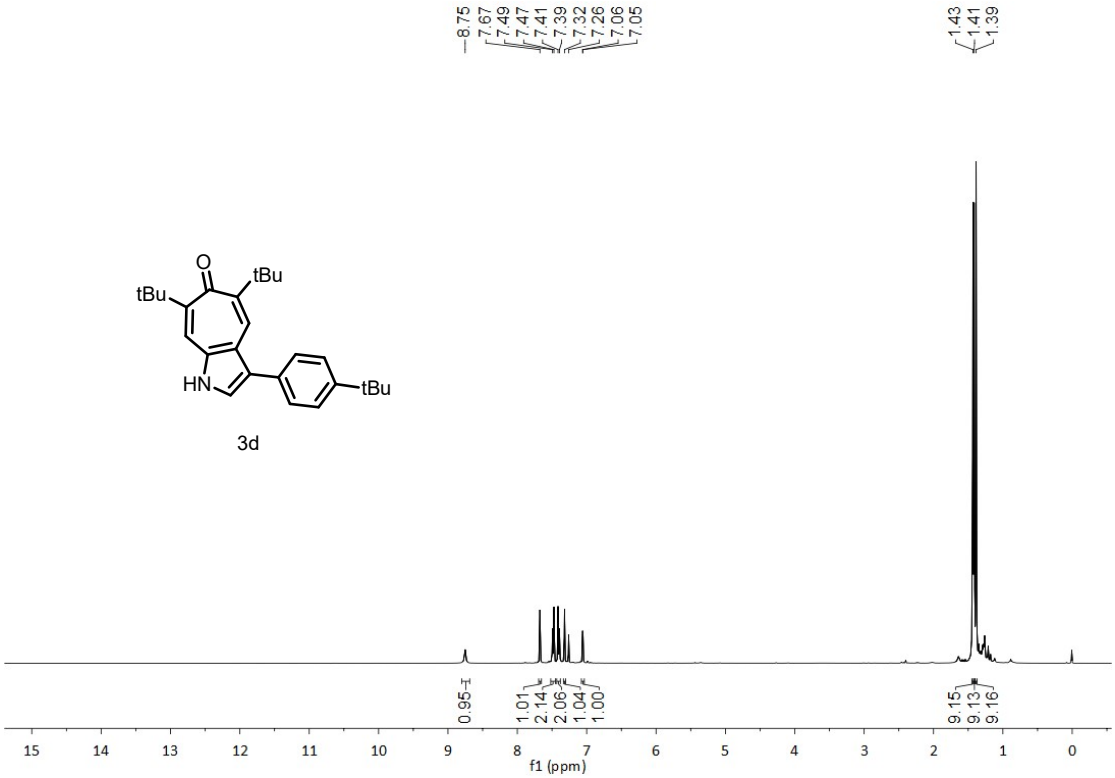


HRMS of 3c

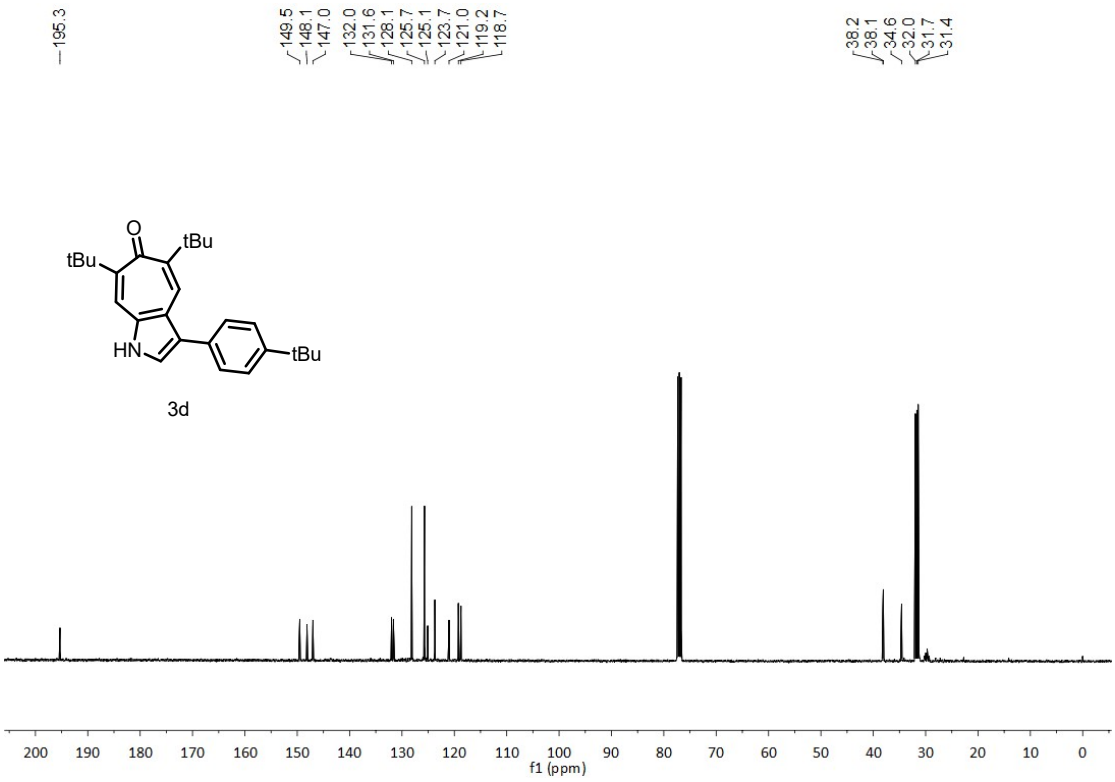


5,7-di-tert-butyl-3-(4-(tert-butyl)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3d)

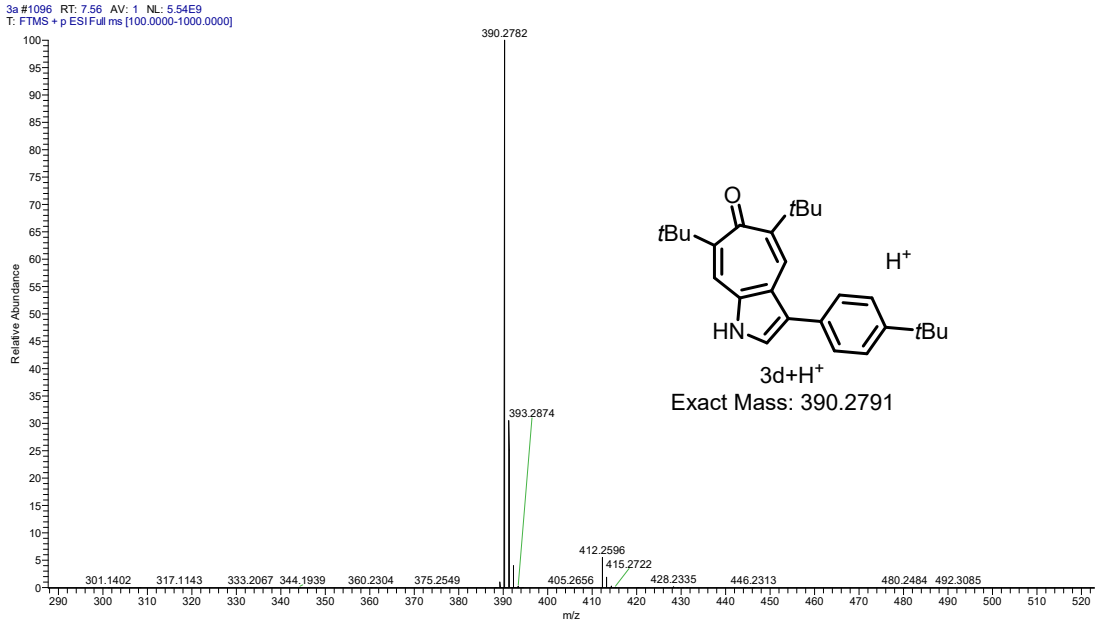
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

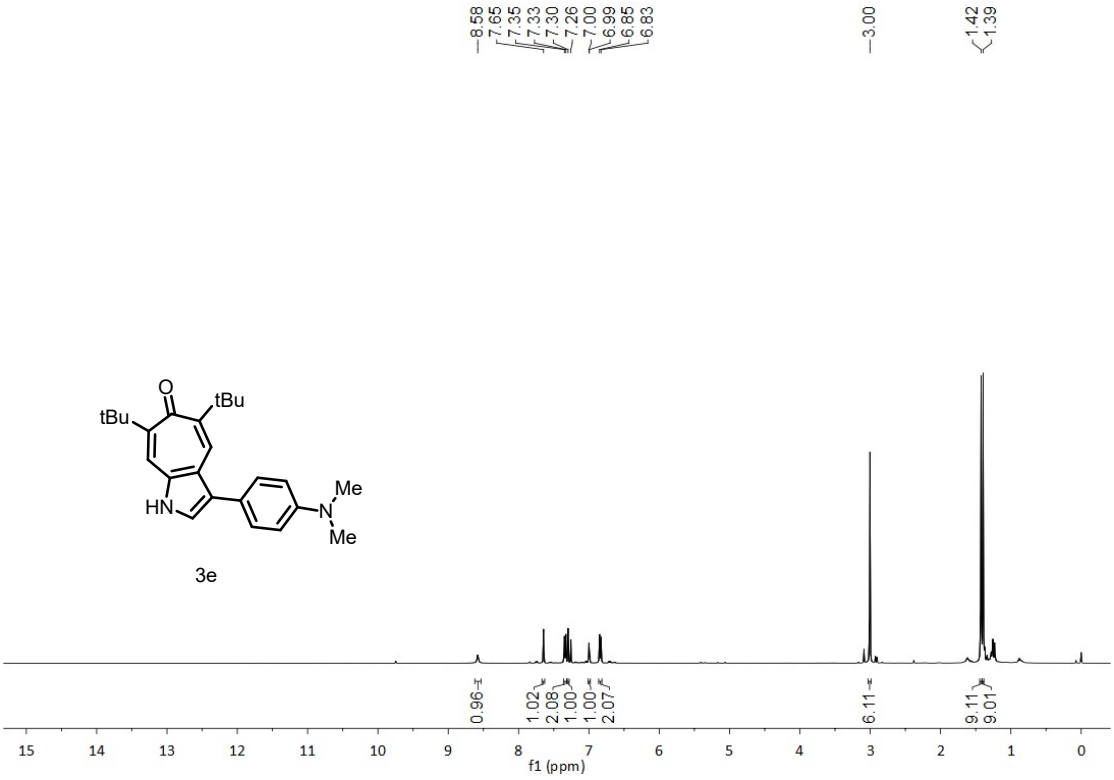


HRMS of 3d

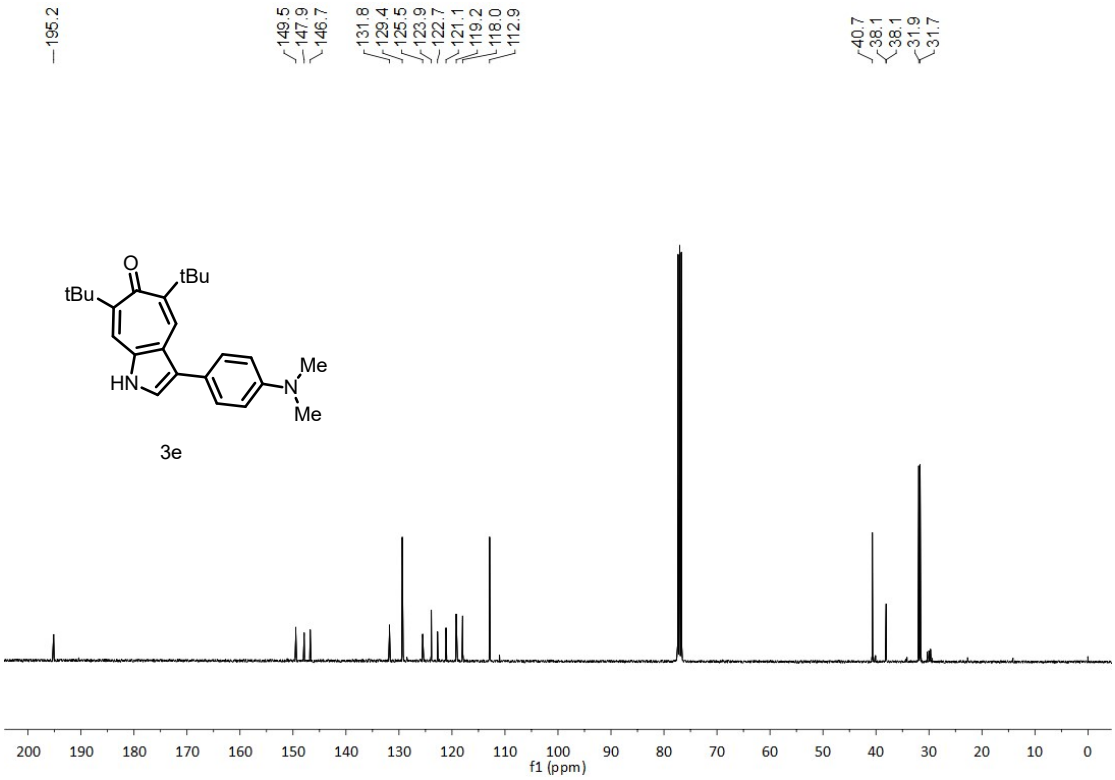


5,7-di-tert-butyl-3-(4-(dimethylamino)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3e)

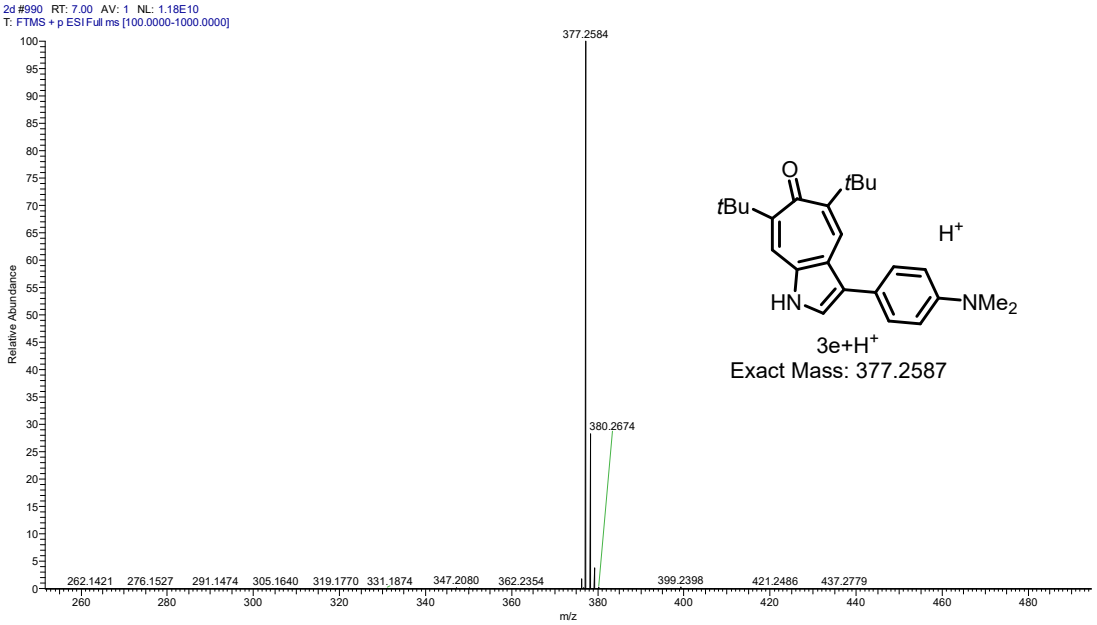
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

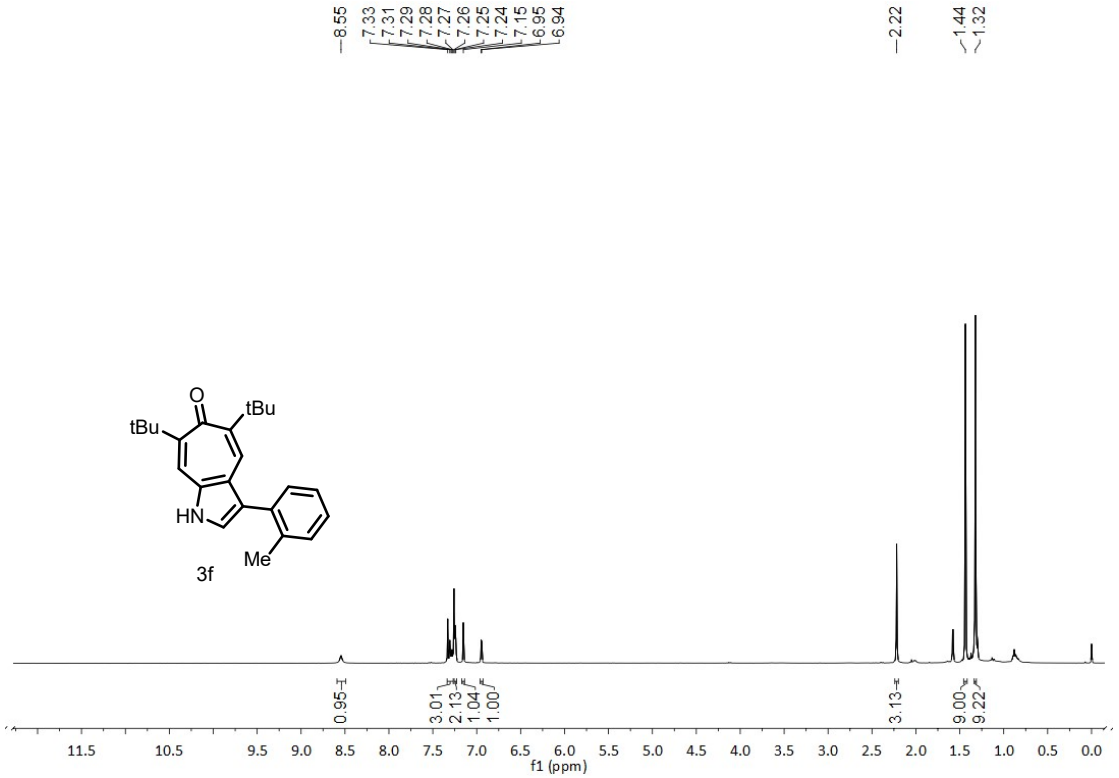


HRMS of 3e

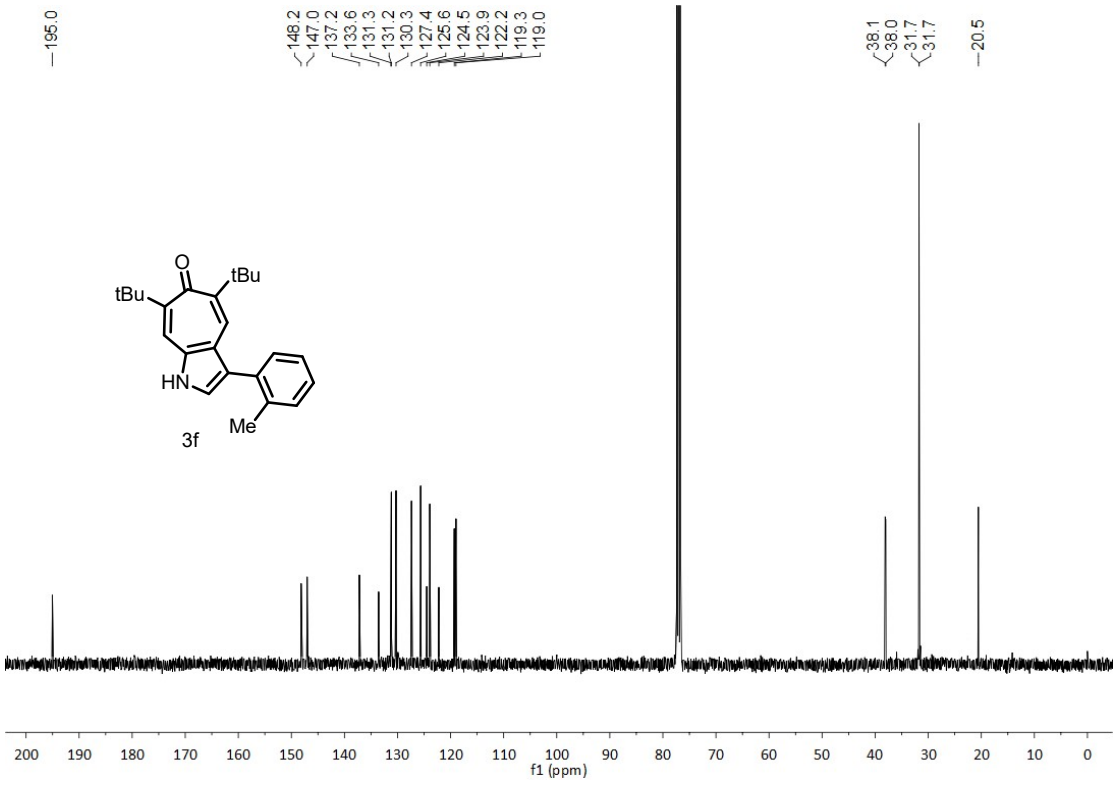


5,7-di-tert-butyl-3-(o-tolyl)cyclohepta[b]pyrrol-6(1H)-one (3f)

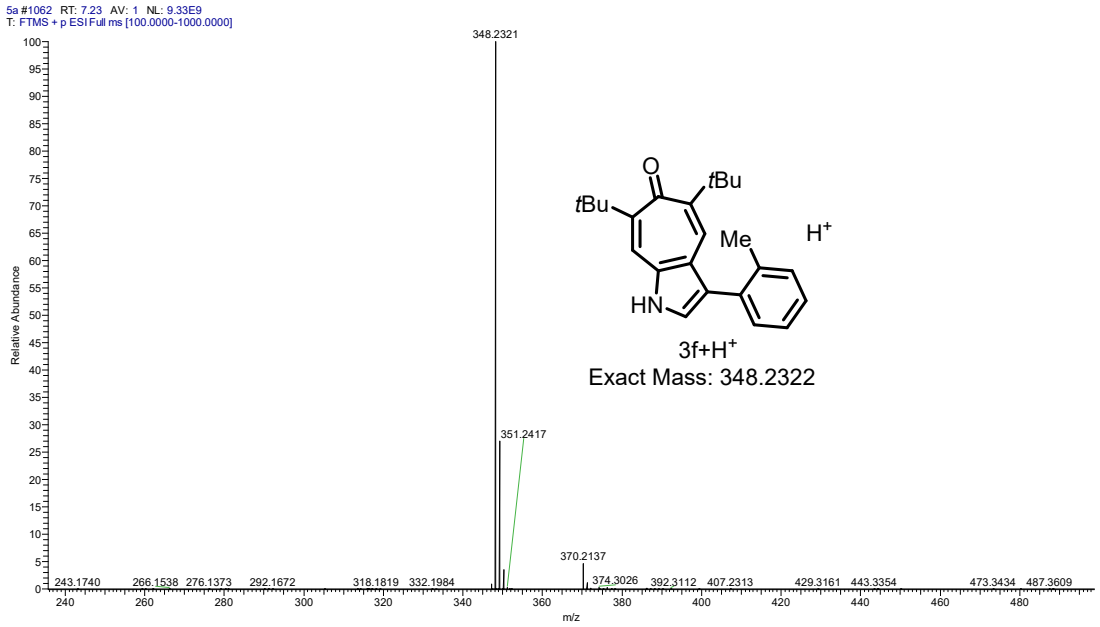
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

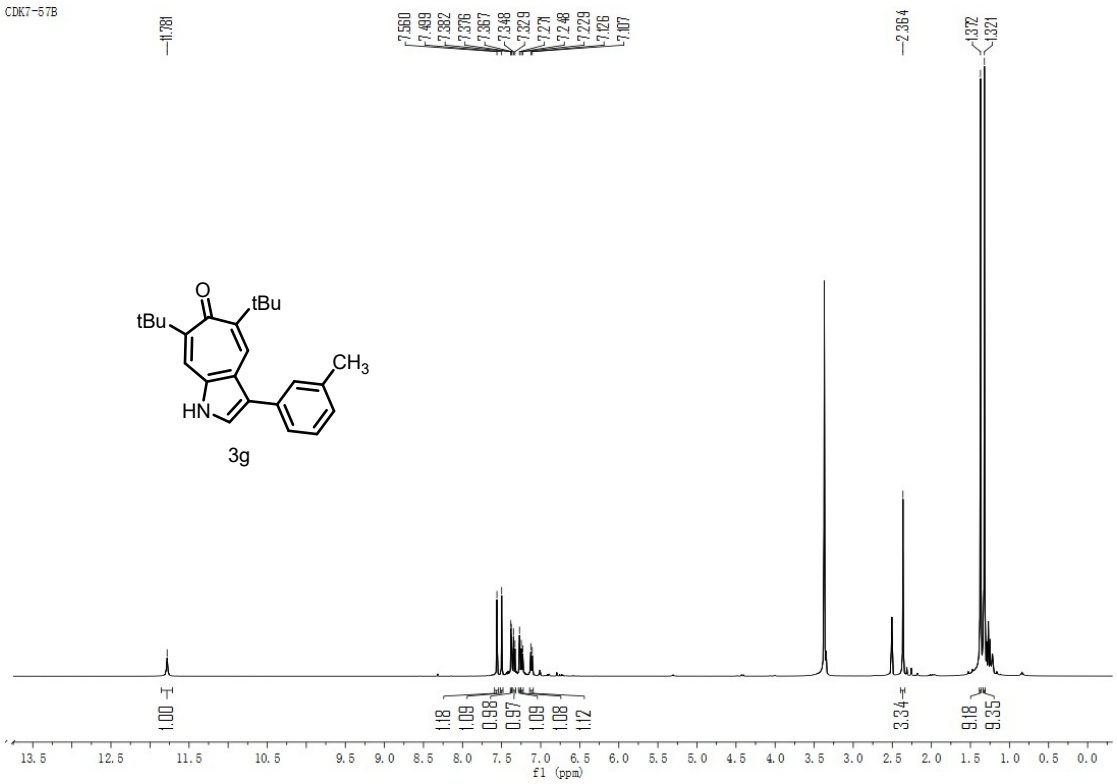


HRMS of 3f

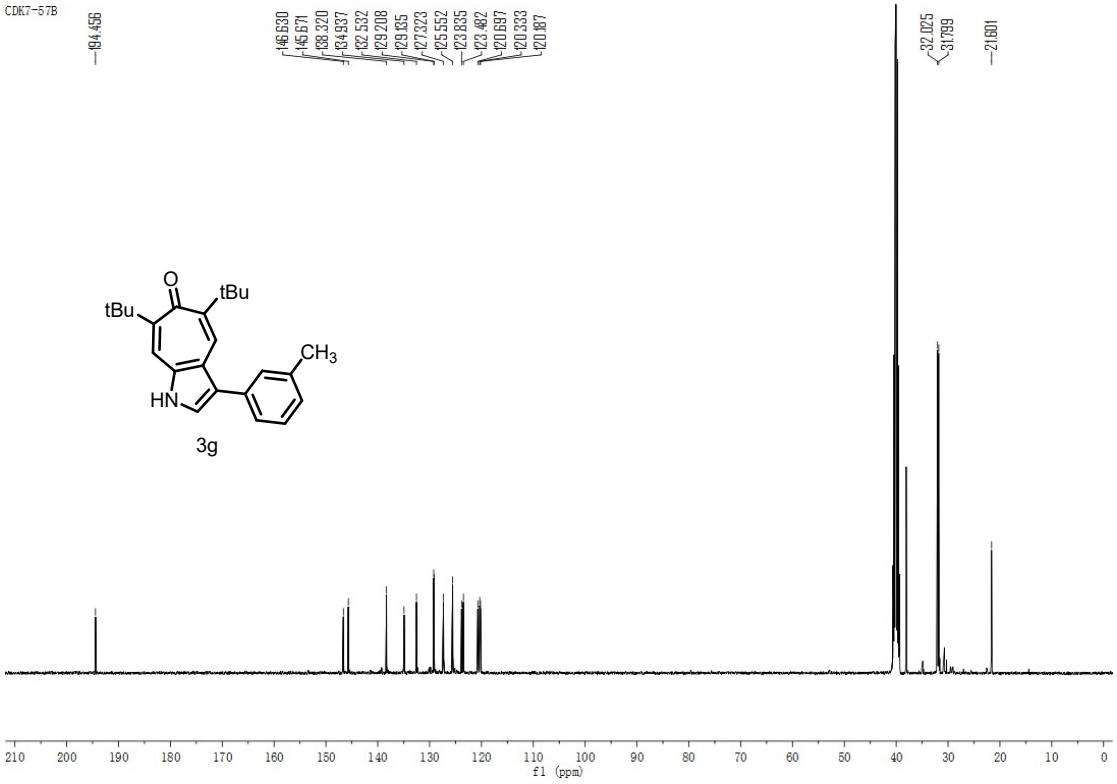


5,7-di-tert-butyl-3-(m-tolyl)cyclohepta[b]pyrrol-6(1H)-one (3g)

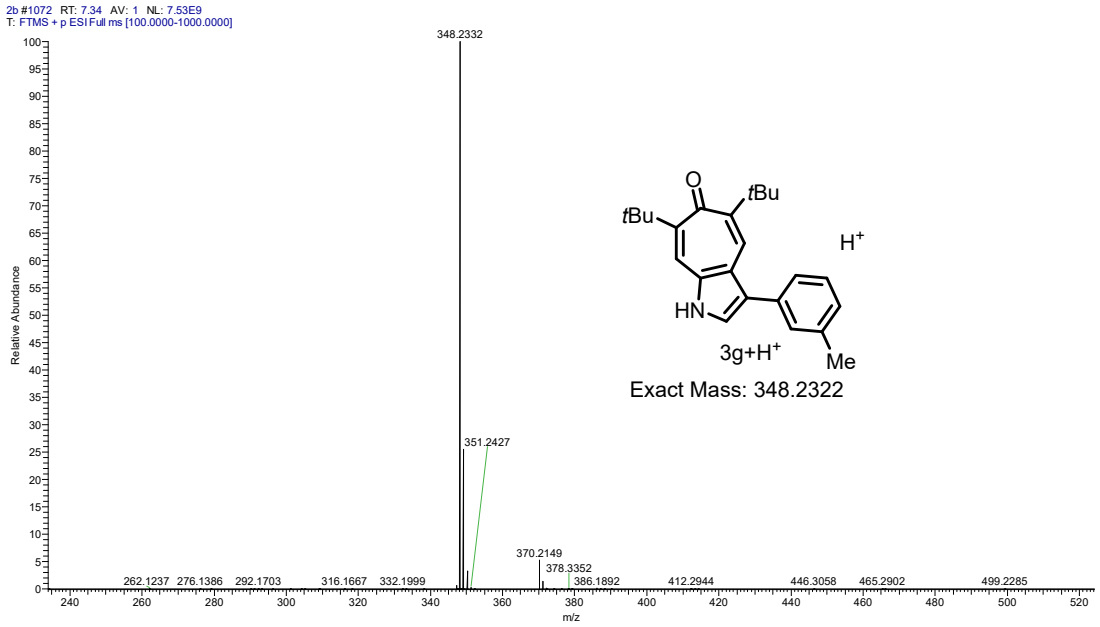
^{1}H NMR (400 MHz, D6-DMSO):



^{13}C NMR (100 MHz, D6-DMSO):

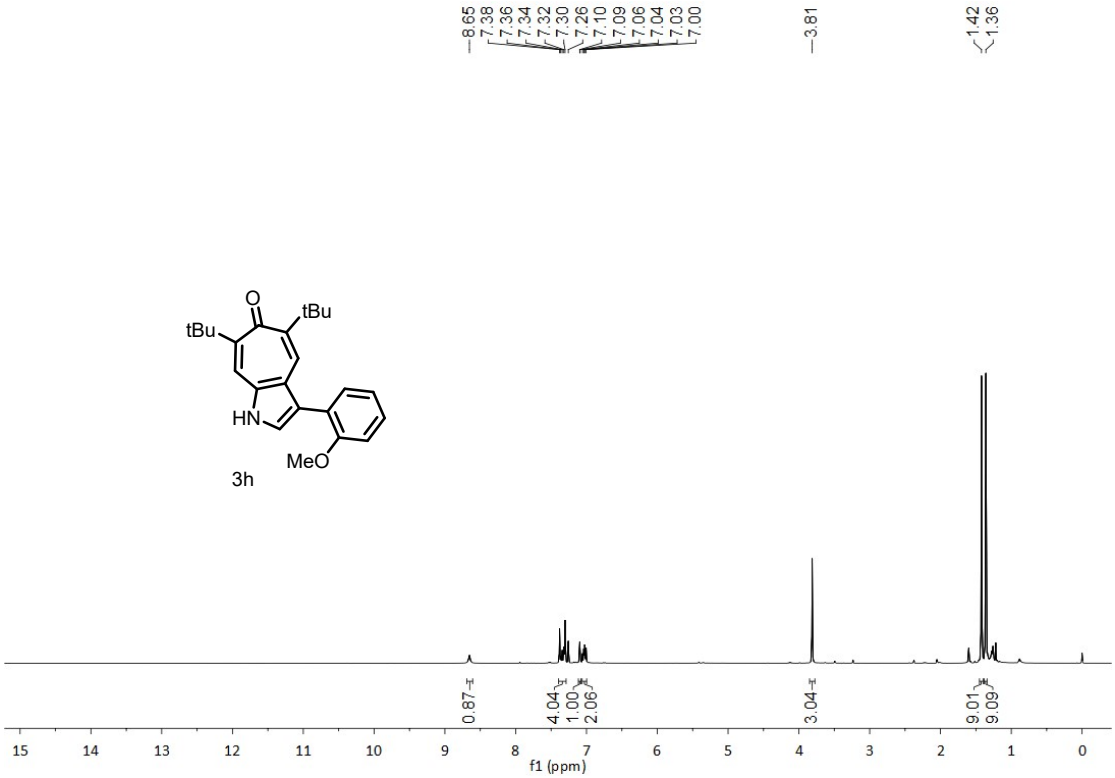


HRMS of 3g

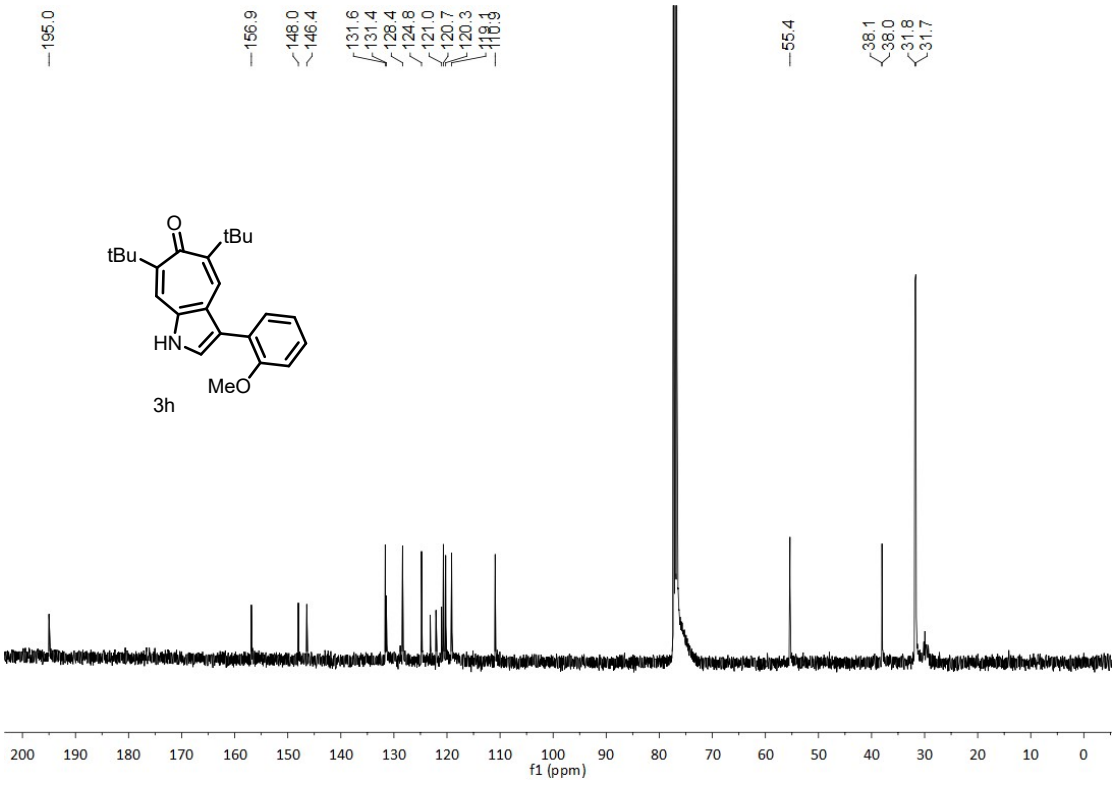


5,7-di-tert-butyl-3-(2-methoxyphenyl)cyclohepta[b]pyrrol-6(1H)-one (3h)

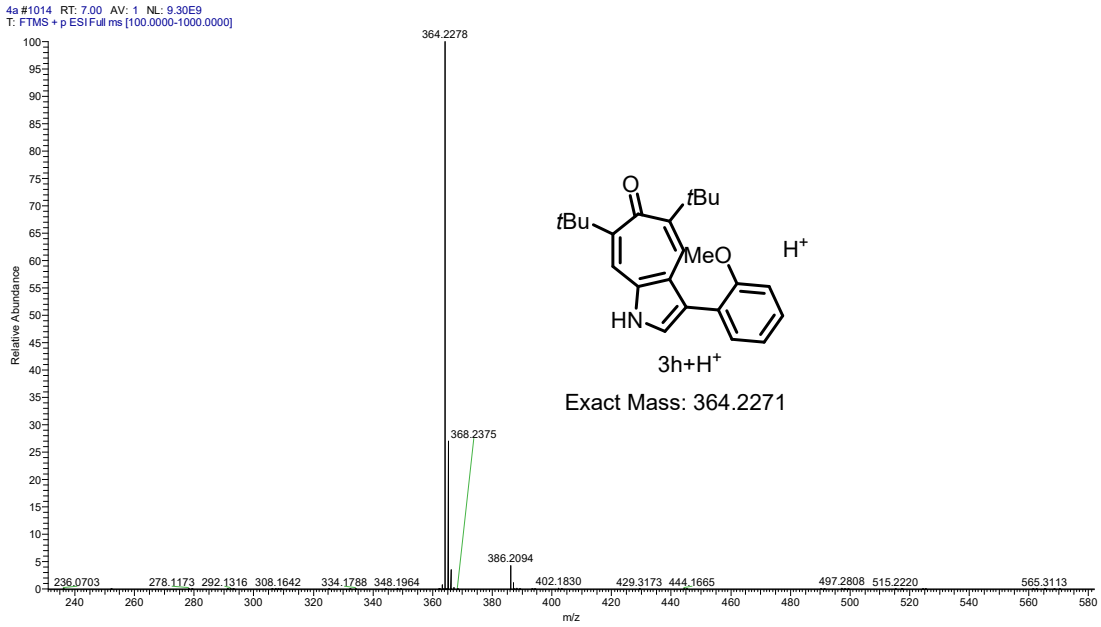
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

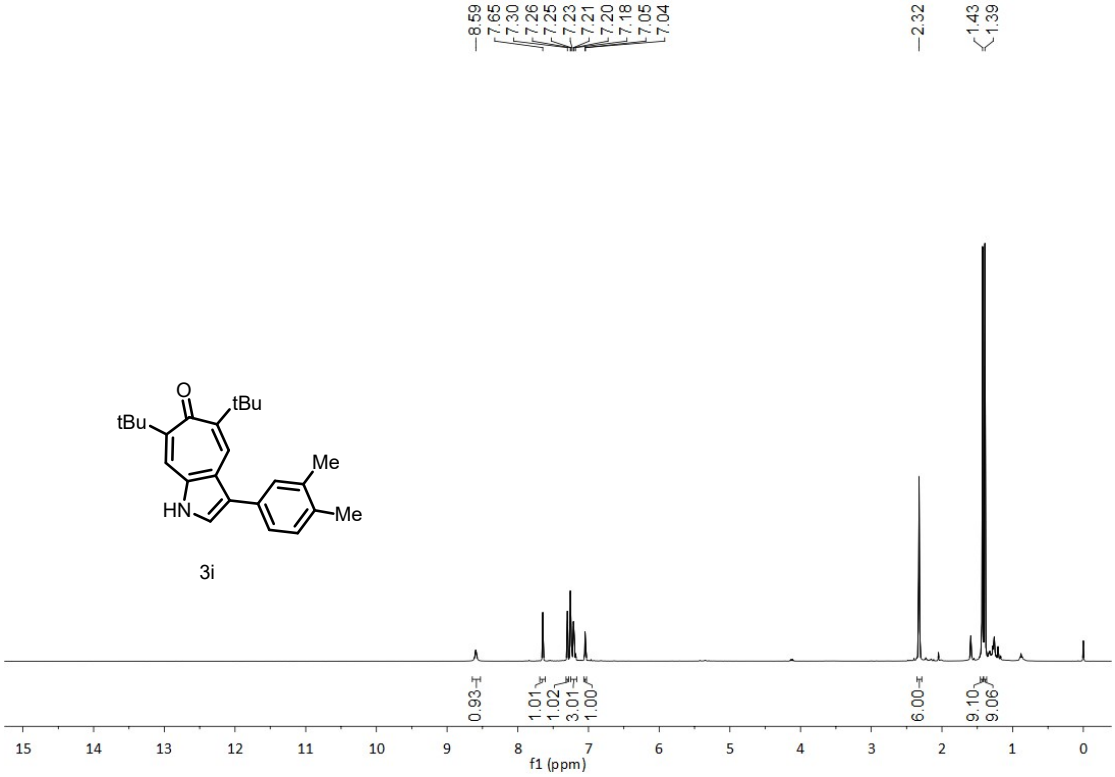


HRMS of 3h

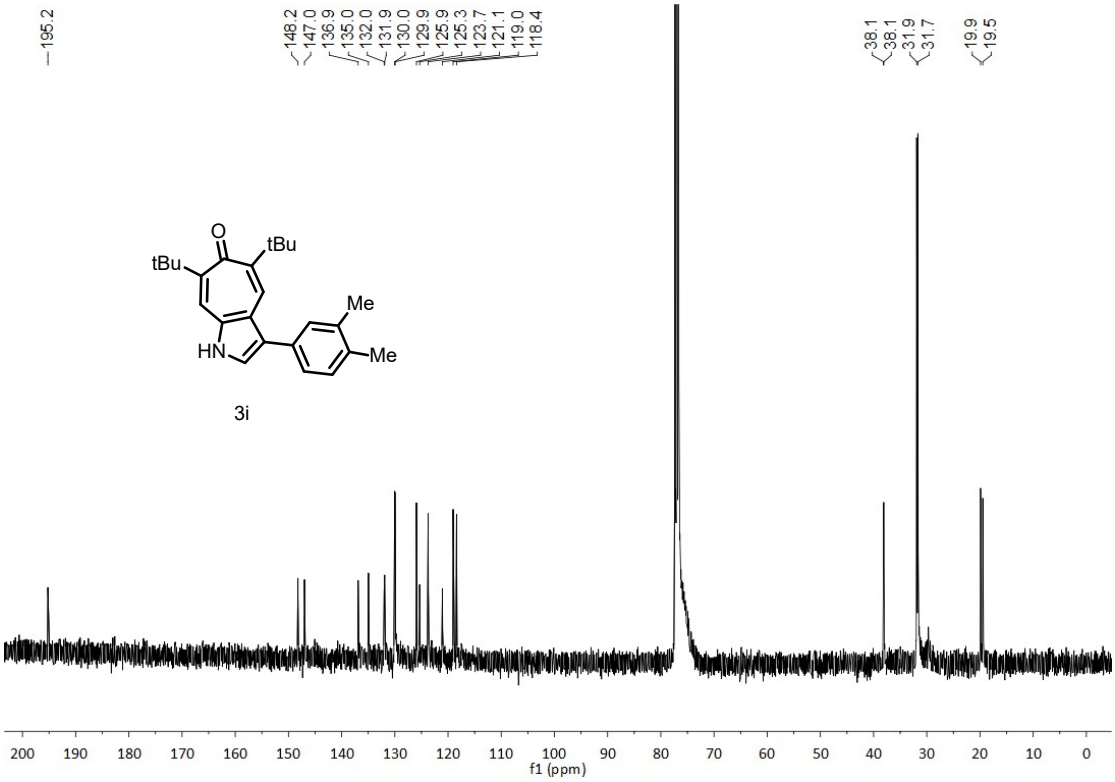


5,7-di-tert-butyl-3-(3,4-dimethylphenyl)cyclohepta[b]pyrrol-6(1H)-one (3i)

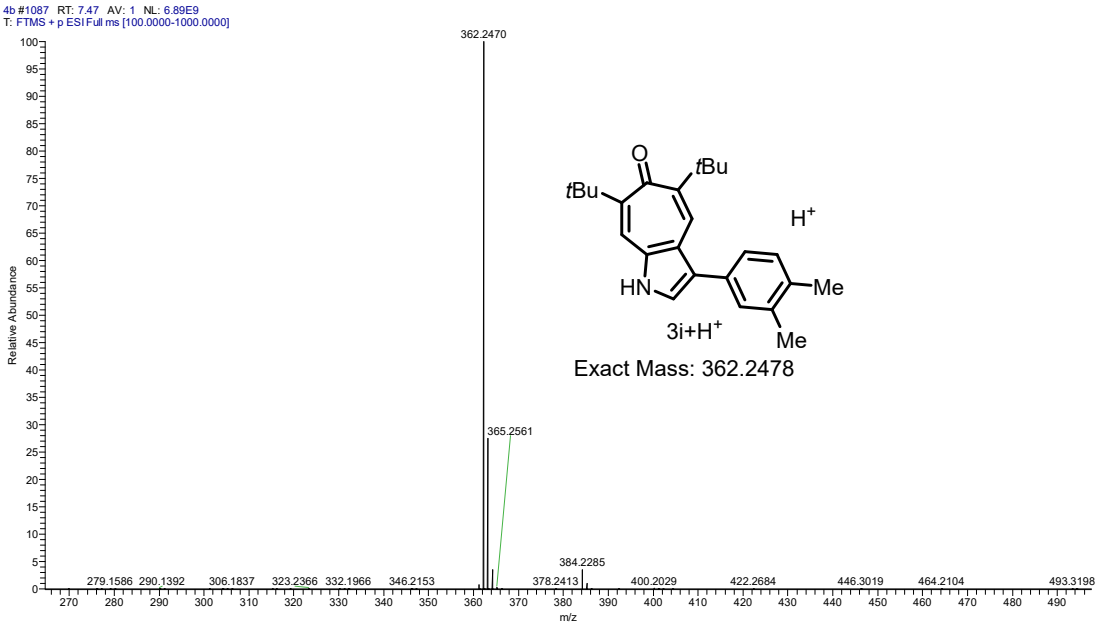
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

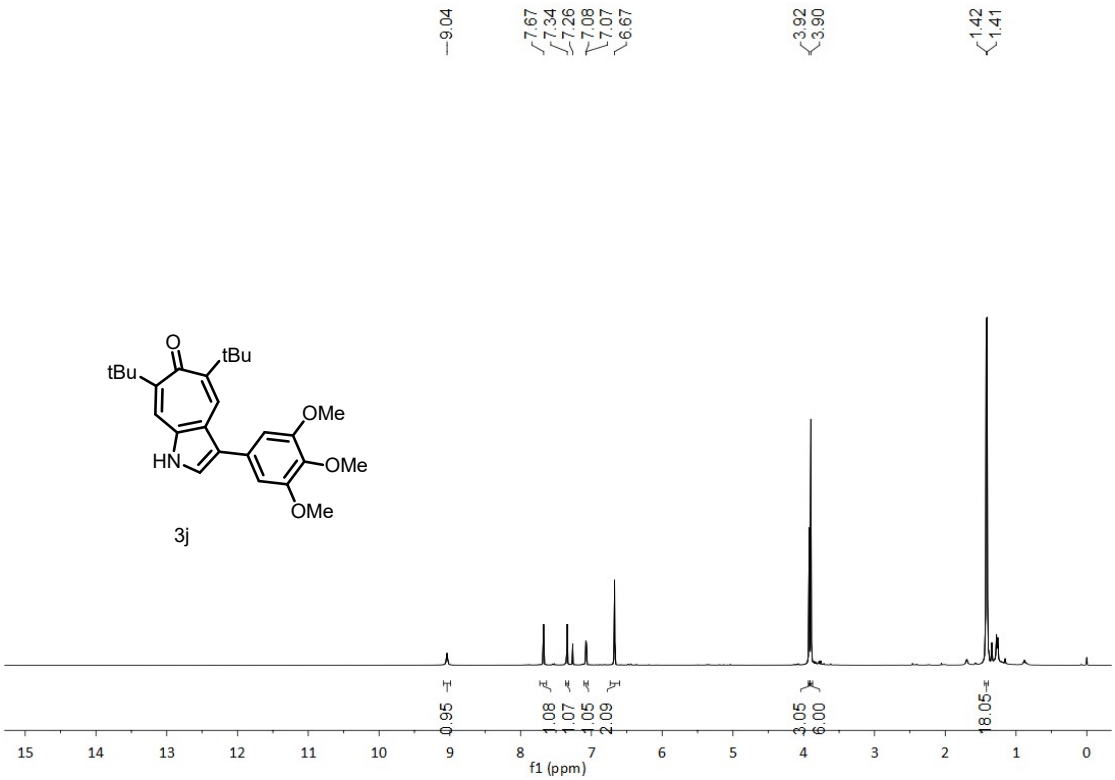


HRMS of 3i

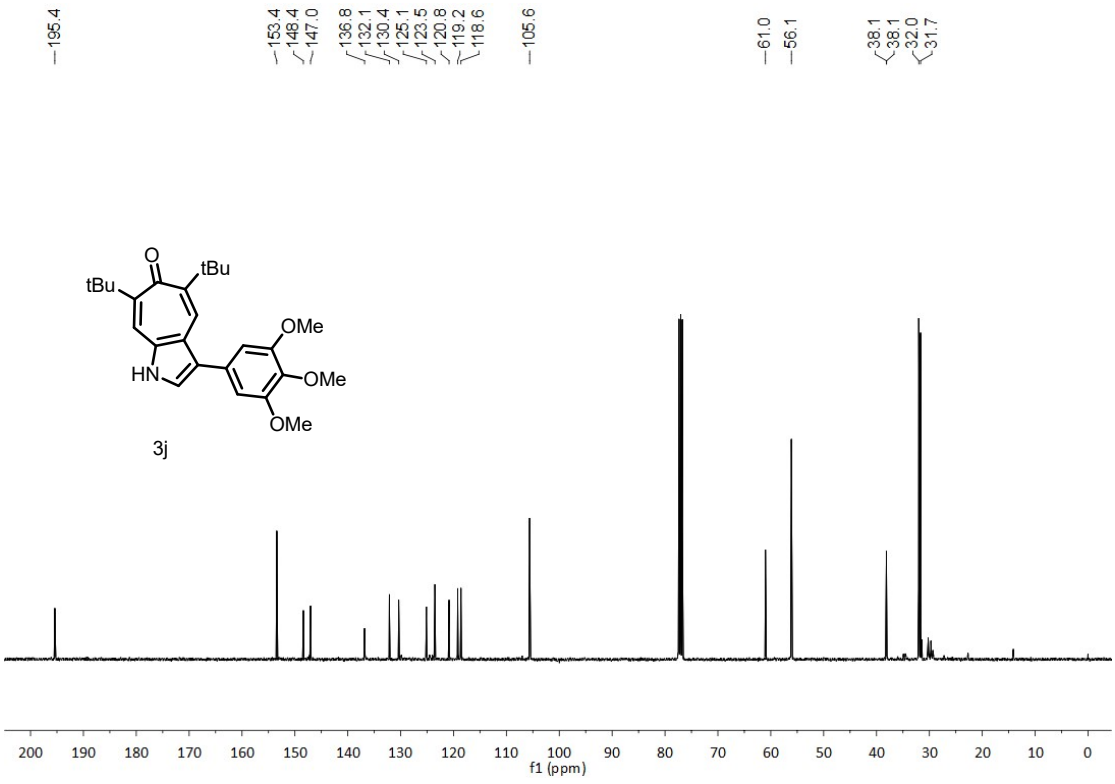


5,7-di-tert-butyl-3-(3,4,5-trimethoxyphenyl)cyclohepta[b]pyrrol-6(1H)-one (3j)

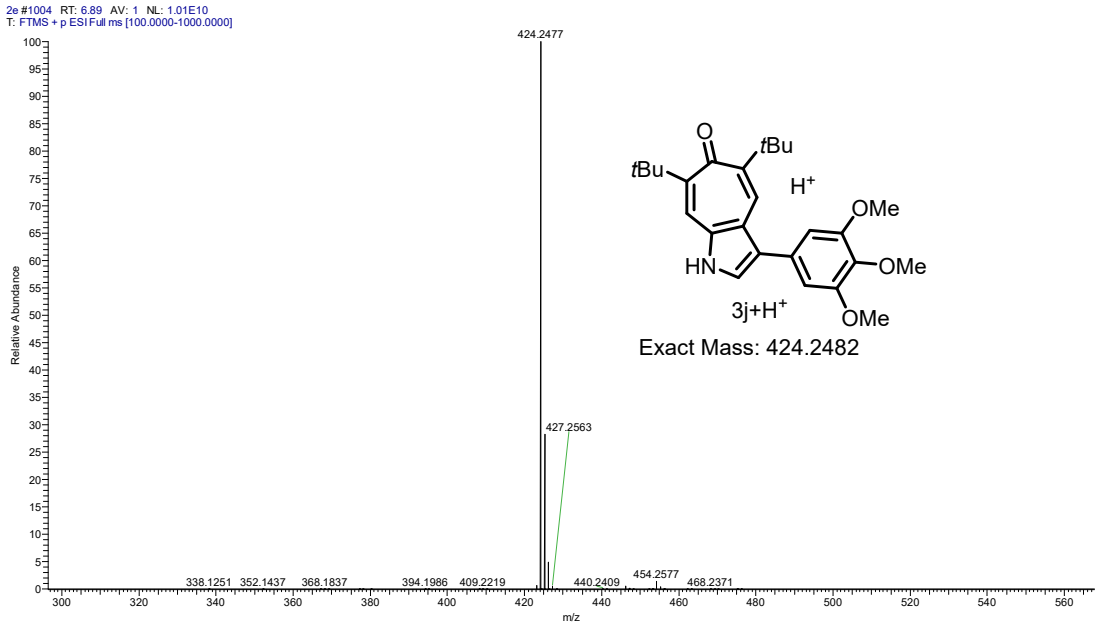
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

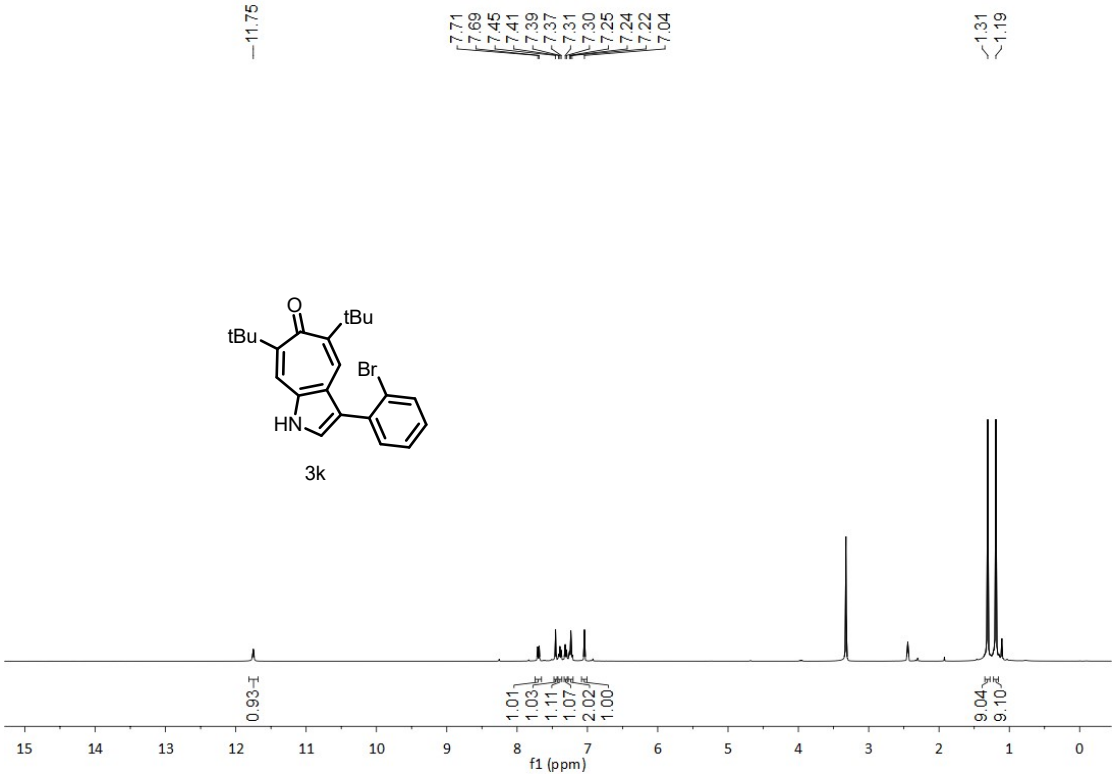


HRMS of 3j

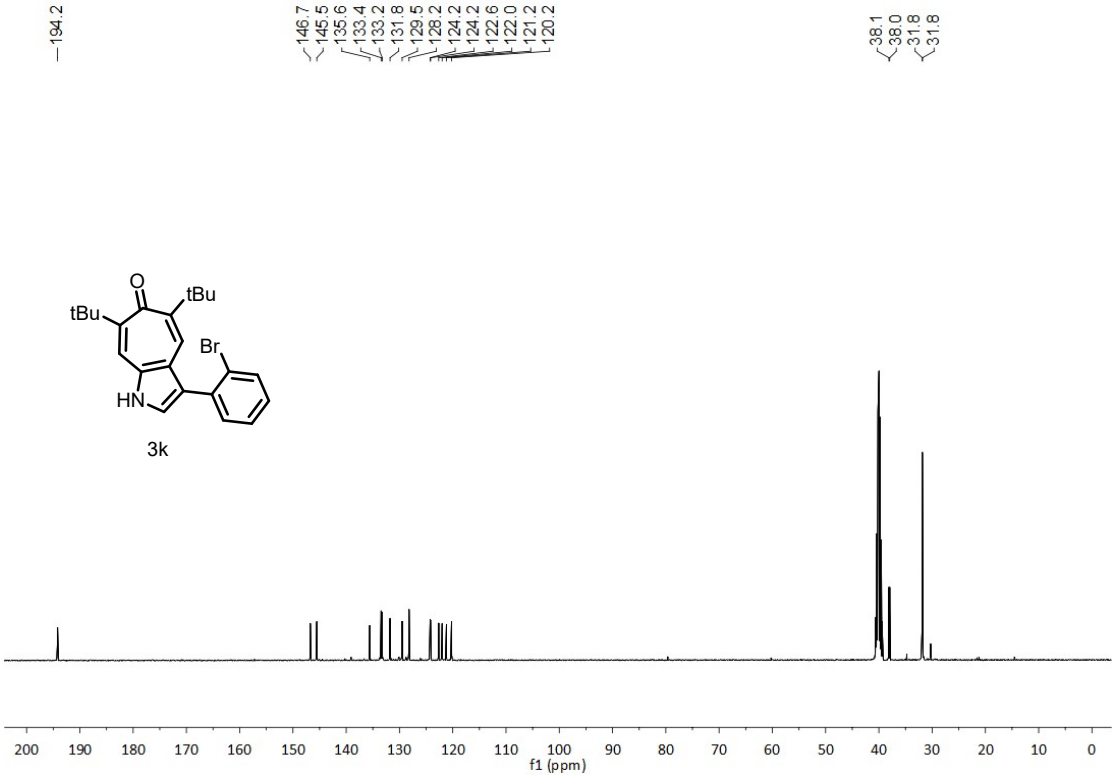


3-(2-bromophenyl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3k)

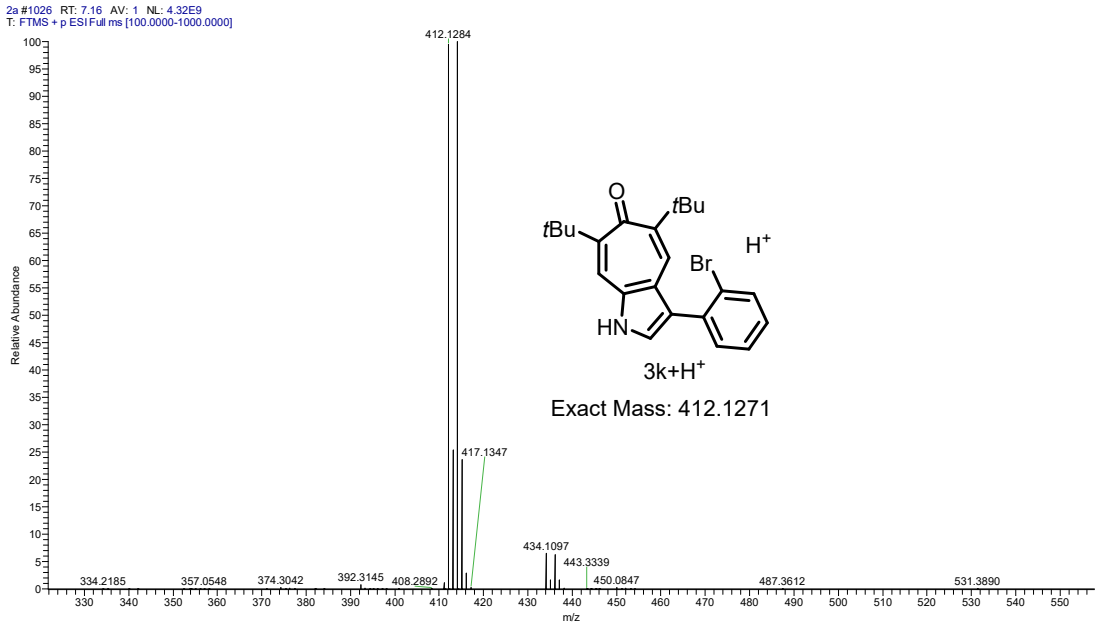
^{1}H NMR (400 MHz, D^{6}-DMSO):



^{13}C NMR (100 MHz, D^6-DMSO):

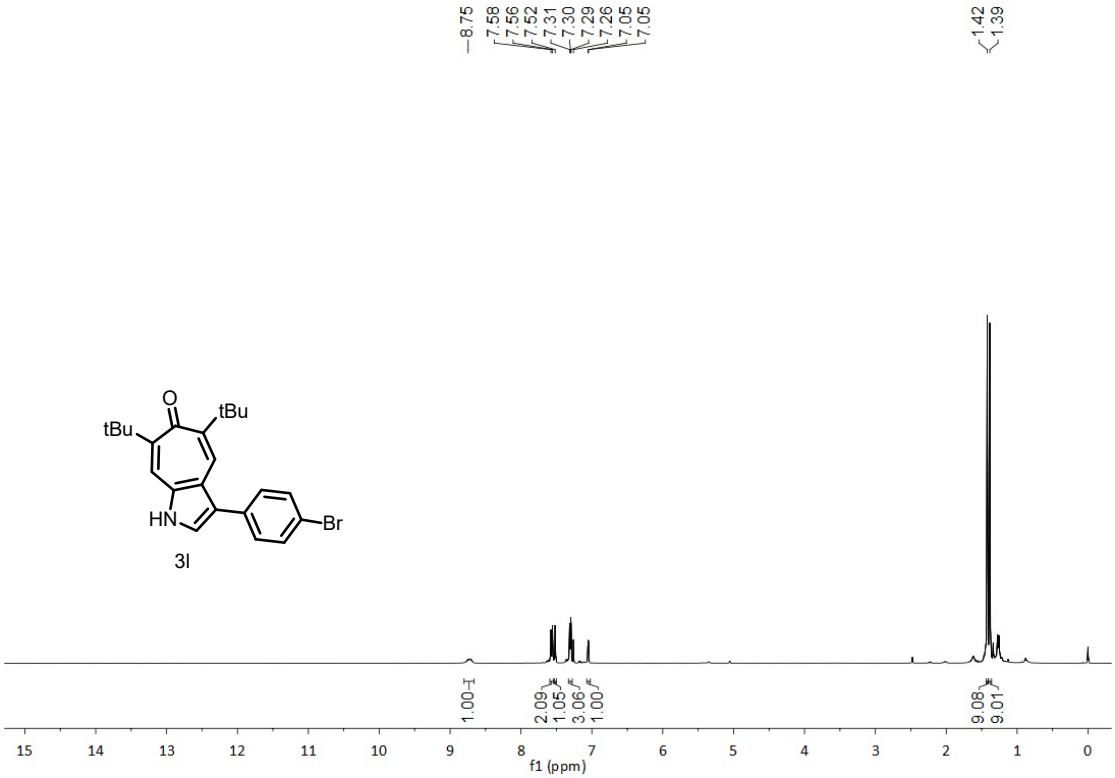


HRMS of 3k

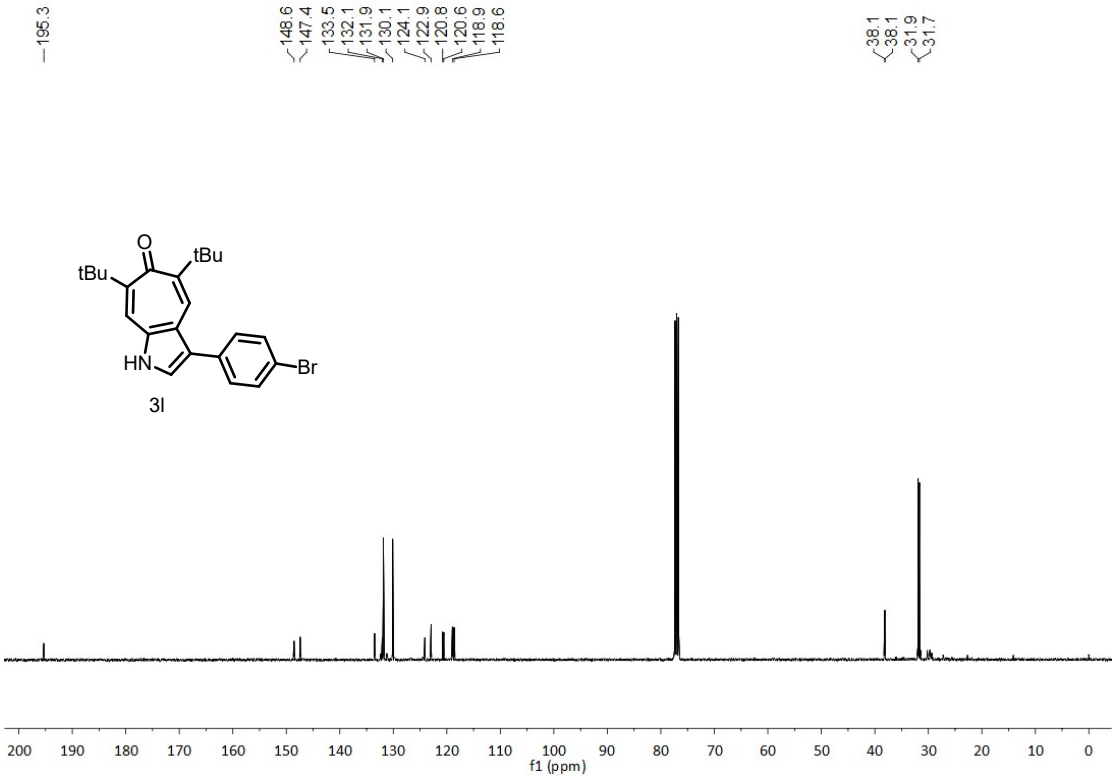


3-(4-bromophenyl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3l)

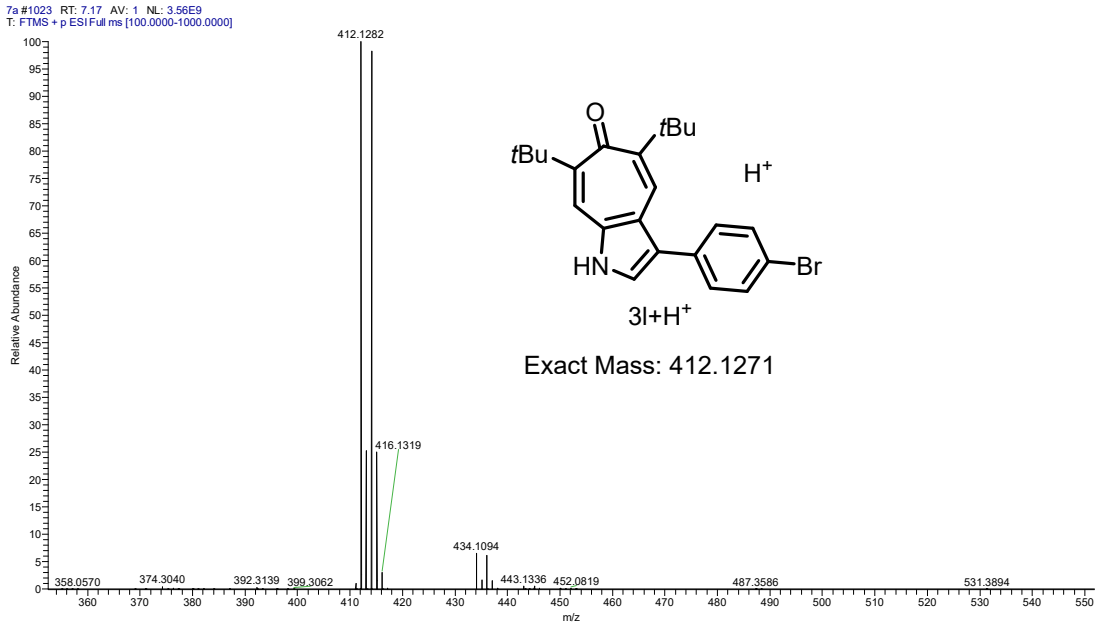
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

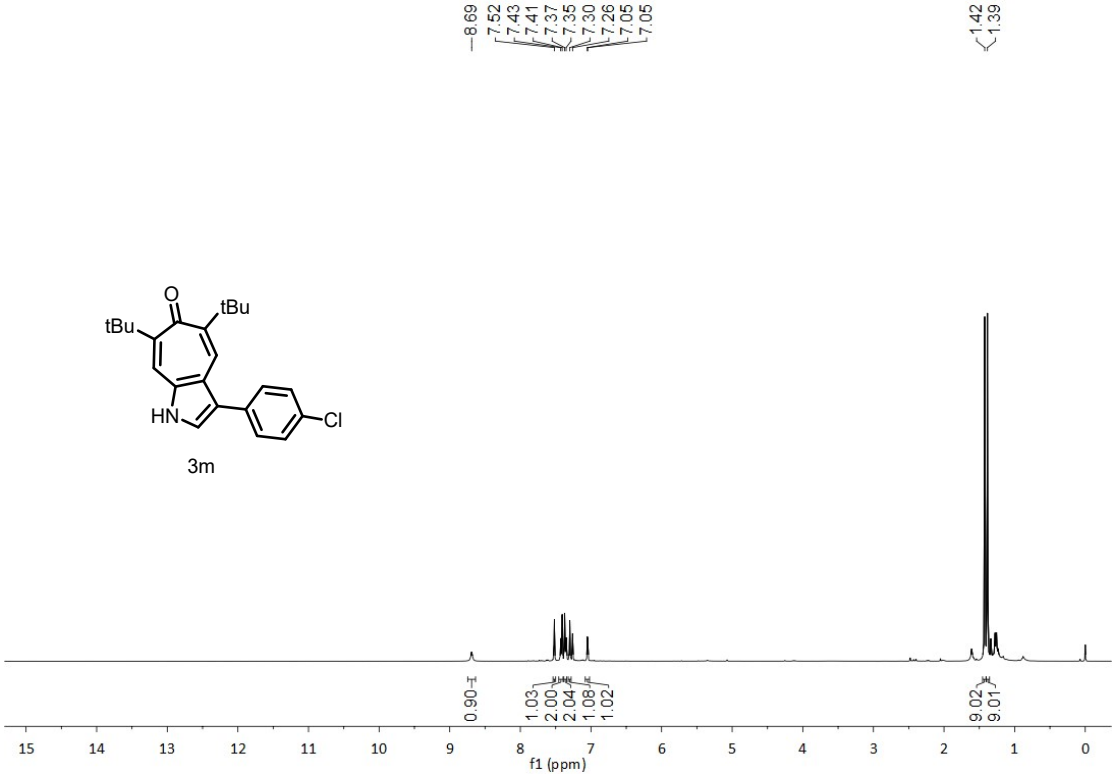


HRMS of 3l

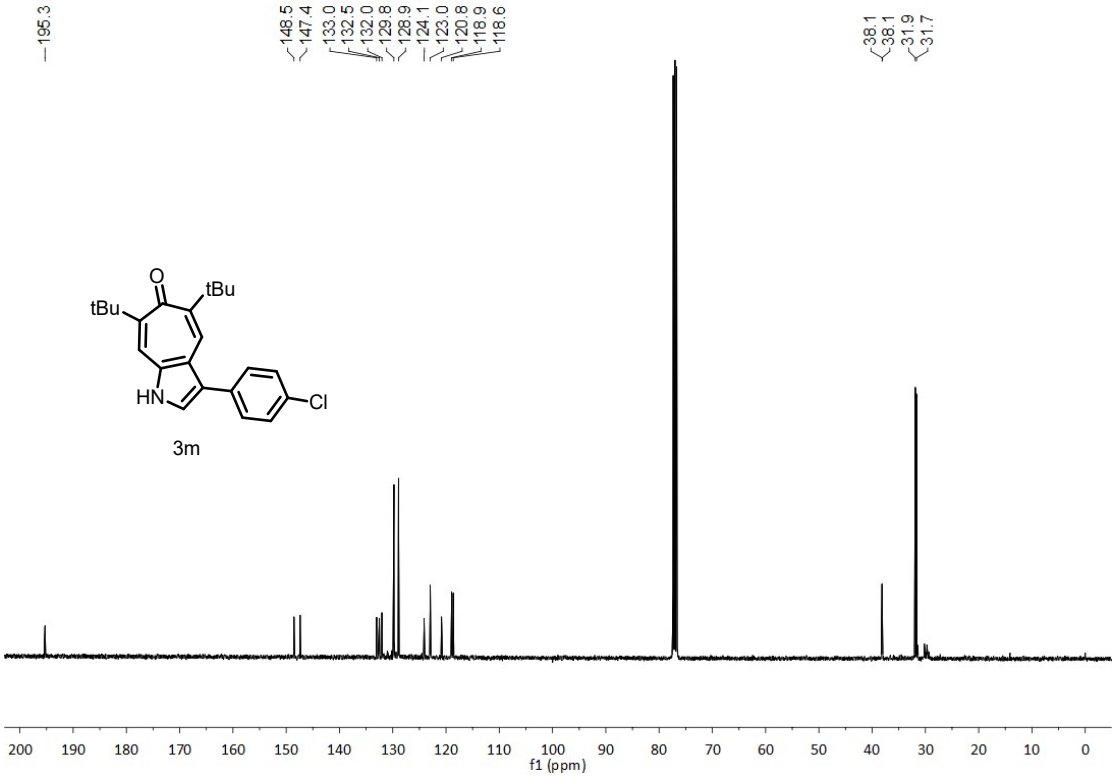


5,7-di-tert-butyl-3-(4-chlorophenyl)cyclohepta[b]pyrrol-6(1H)-one (3m)

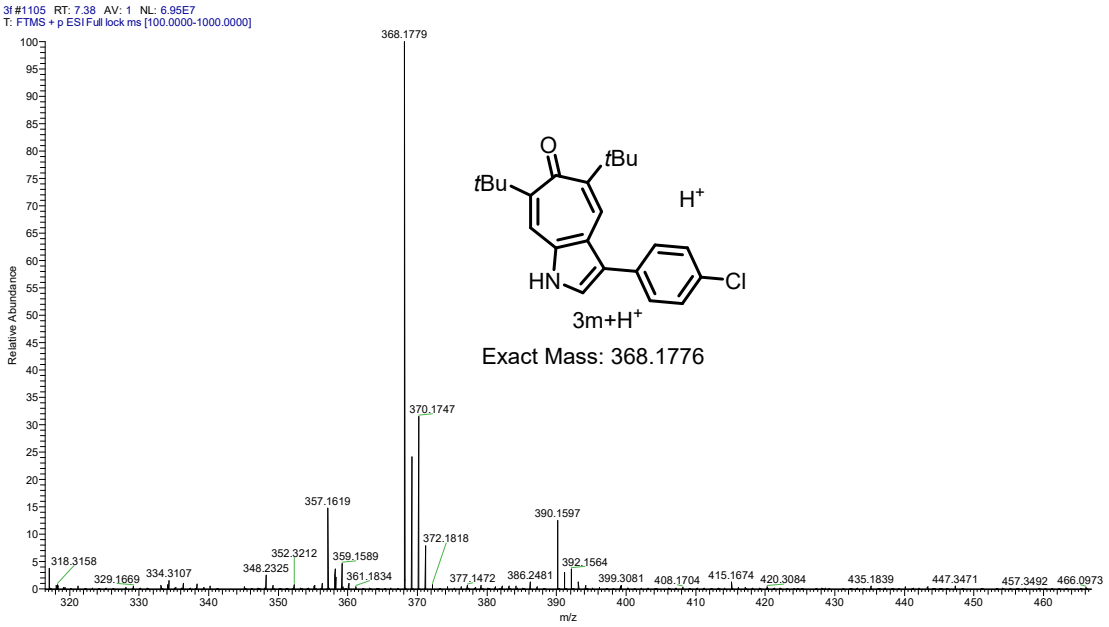
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

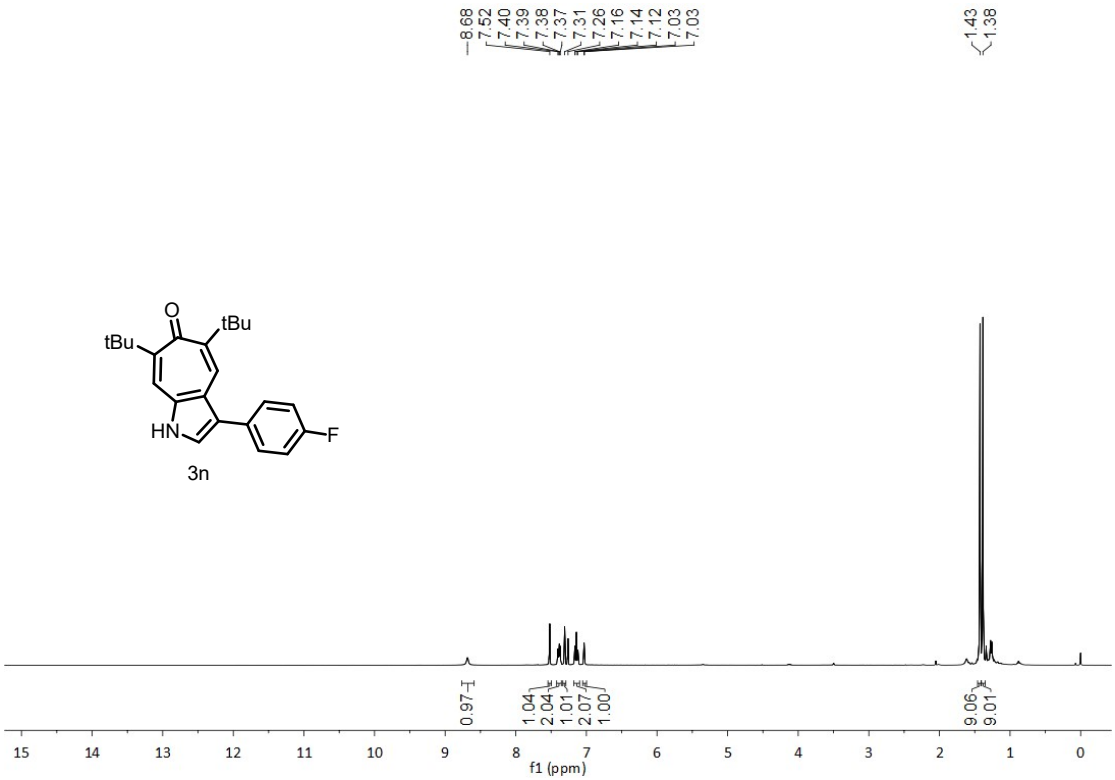


HRMS of 3m

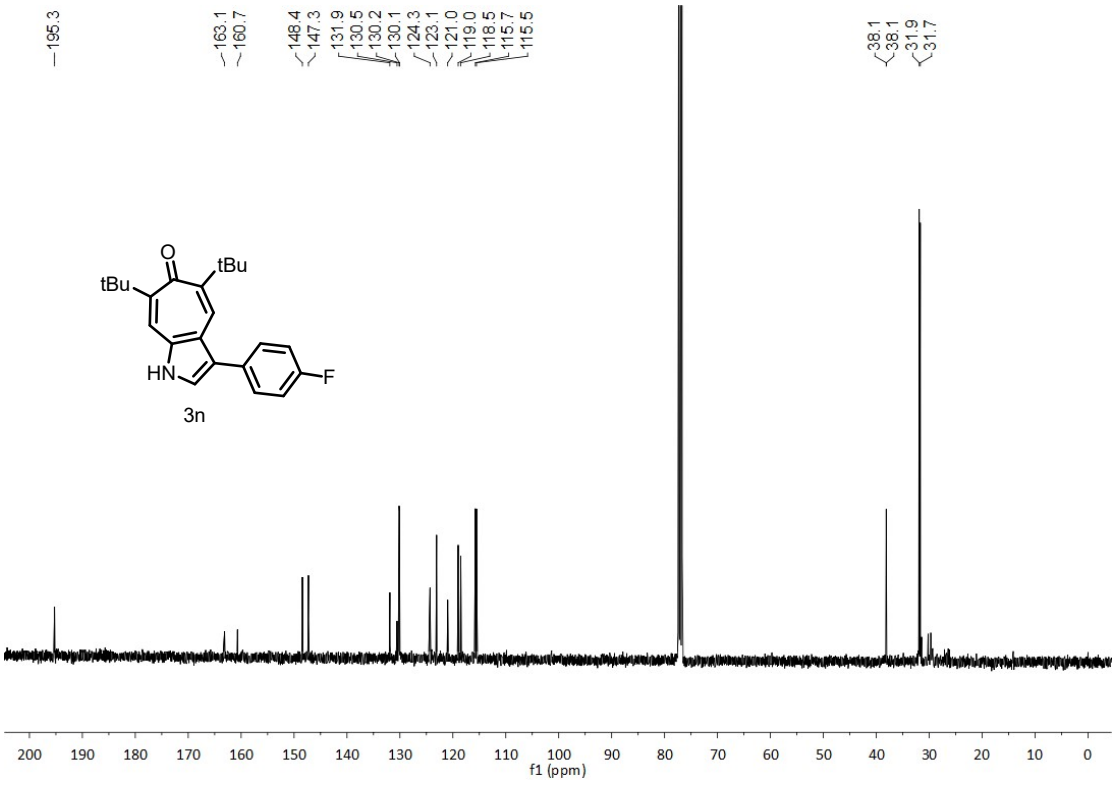


5,7-di-tert-butyl-3-(4-fluorophenyl)cyclohepta[b]pyrrol-6(1H)-one (3n)

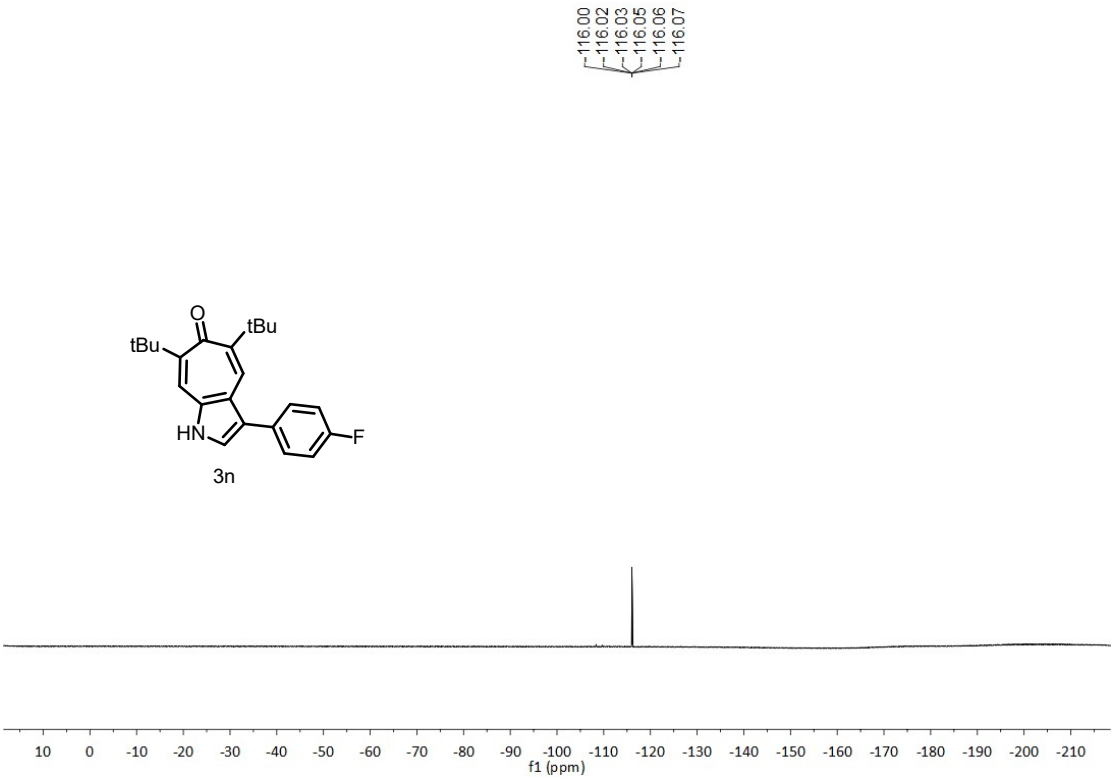
^{1}H NMR (400 MHz, $CDCl_3$):



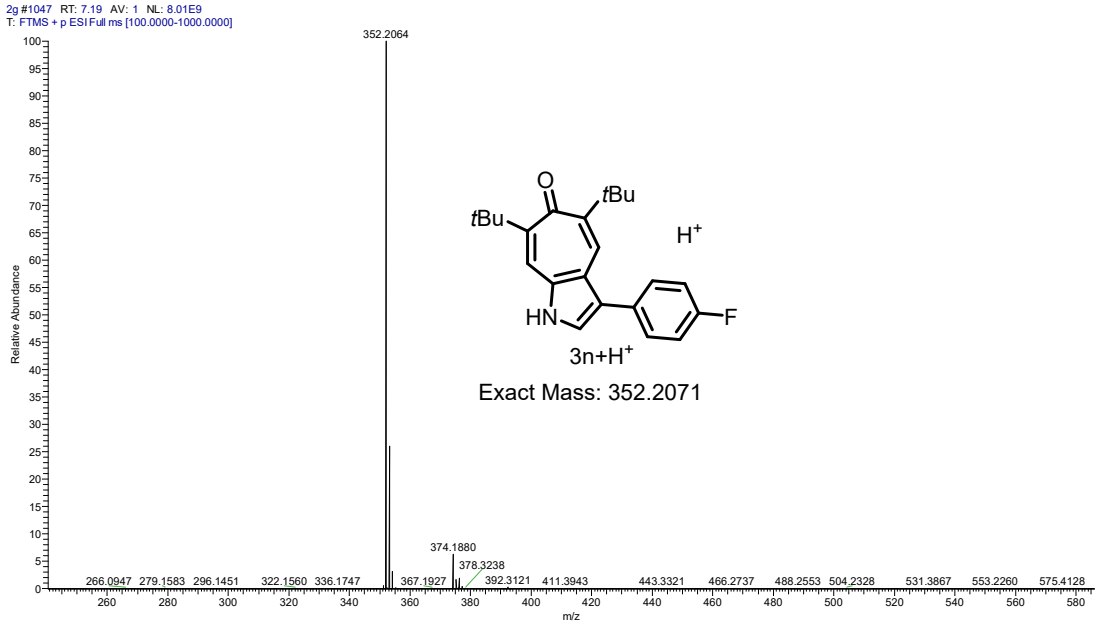
^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):

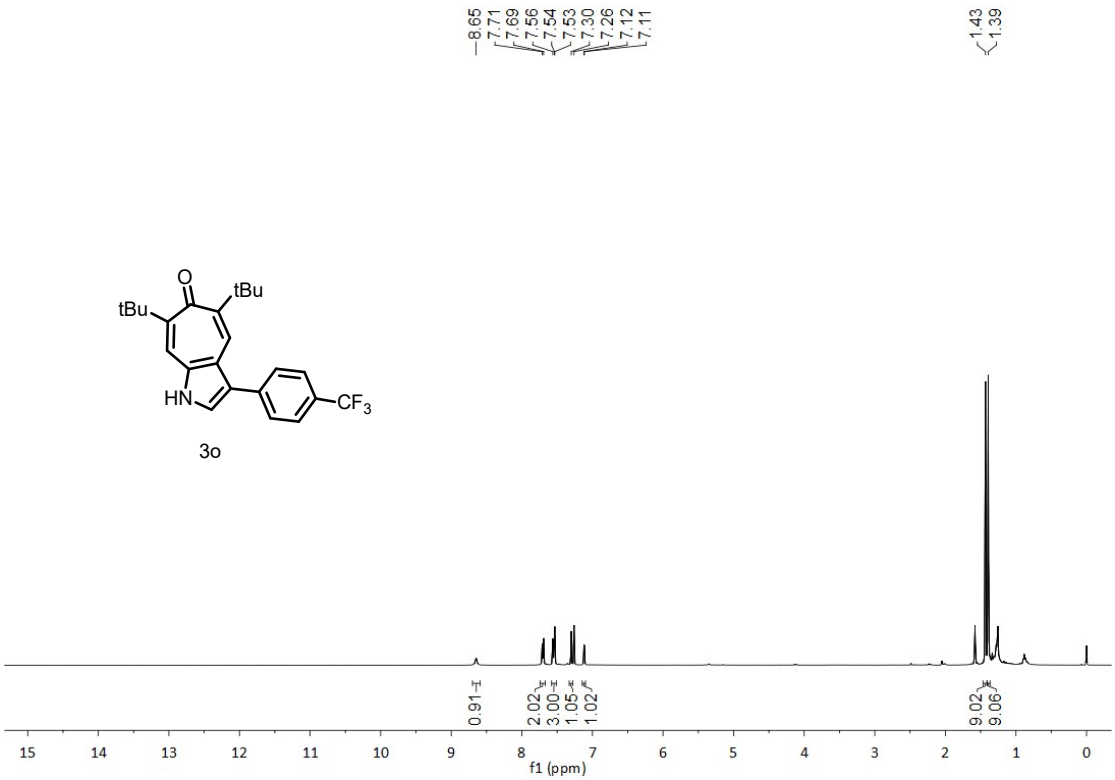


HRMS of 3n

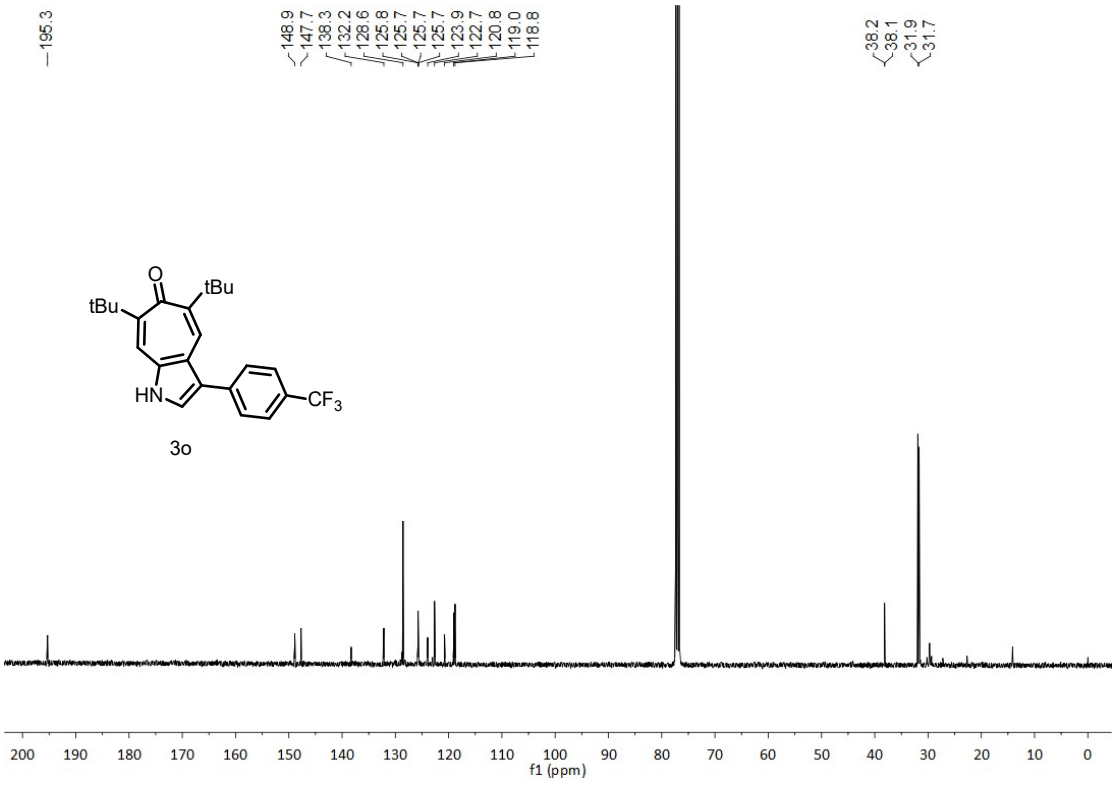


5,7-di-tert-butyl-3-(4-(trifluoromethyl)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3o)

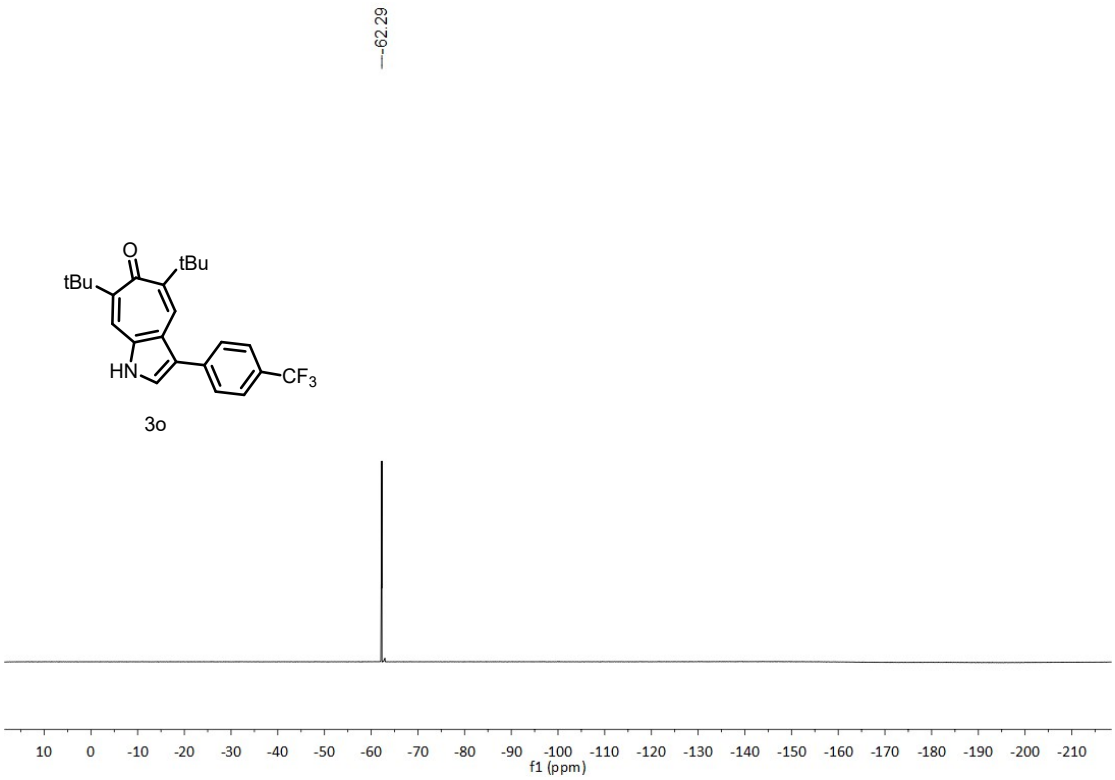
^{1}H NMR (400 MHz, $CDCl_3$):



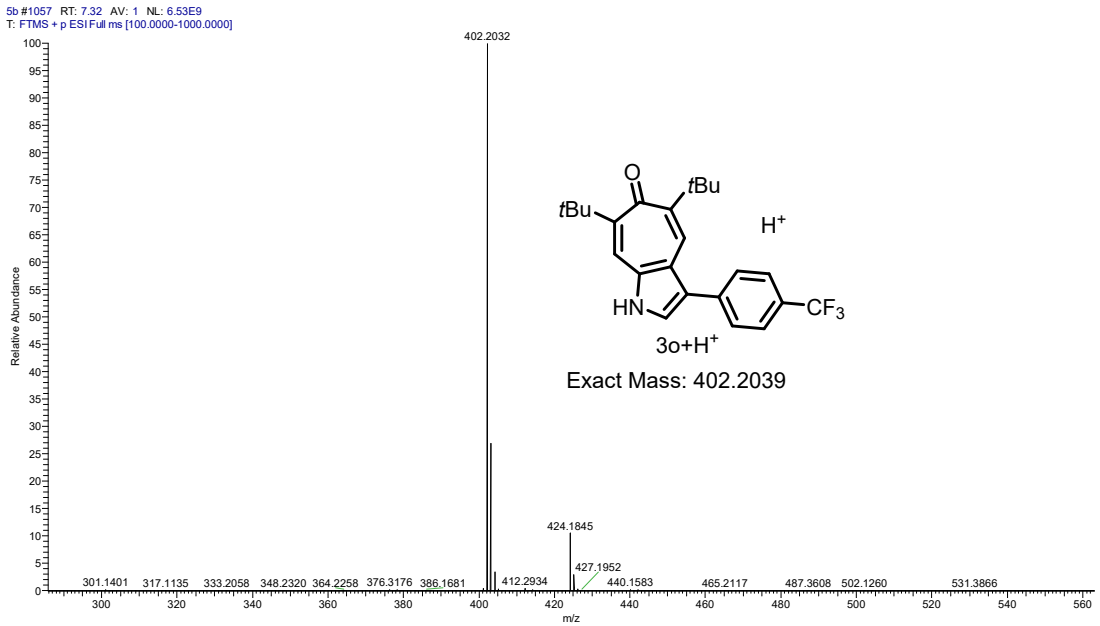
^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):

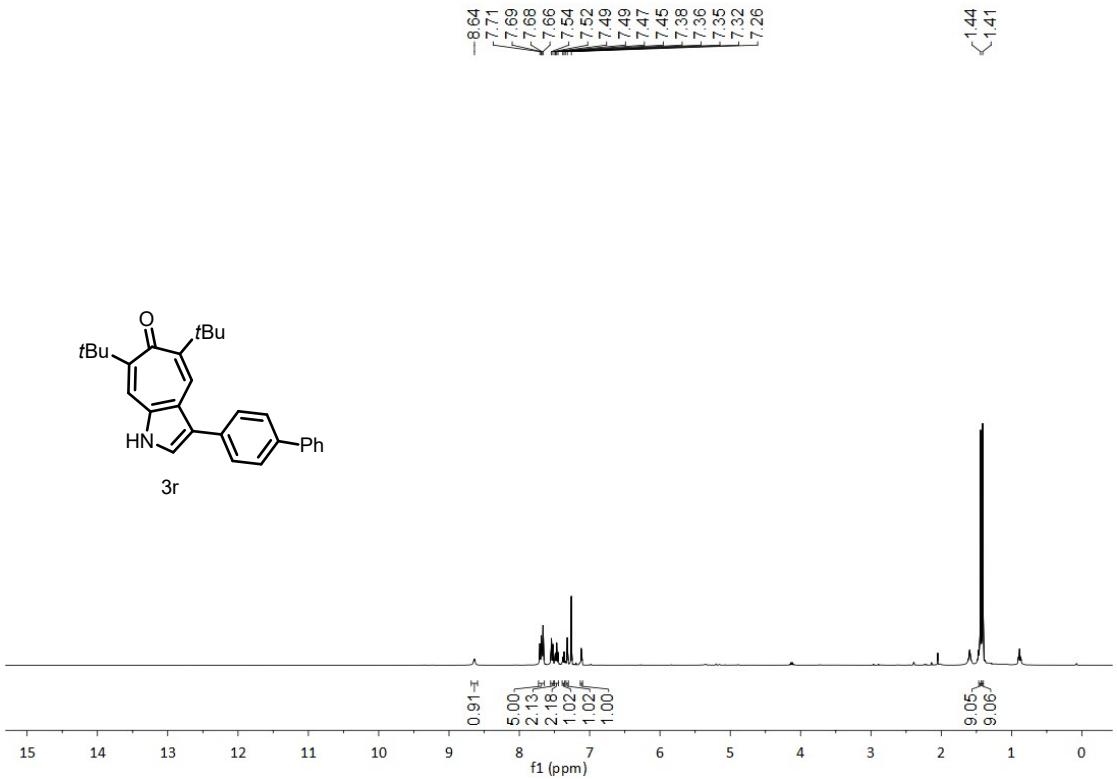


HRMS of 3o

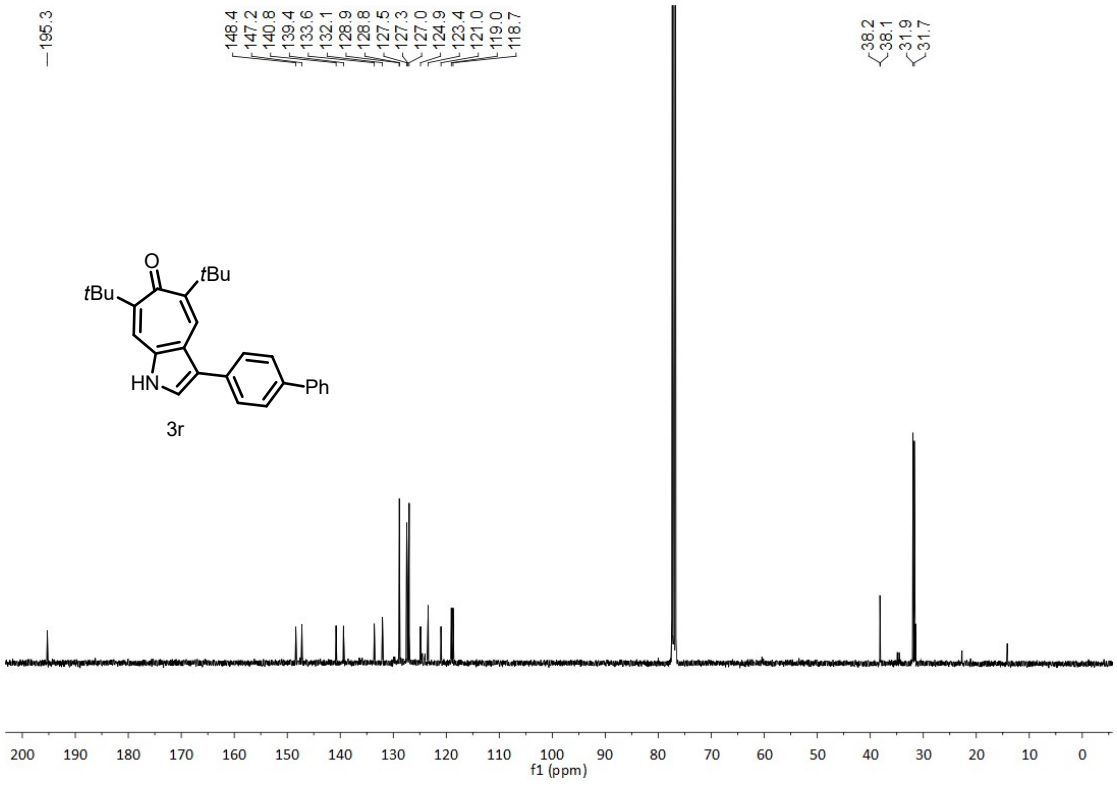


3-([1,1'-biphenyl]-4-yl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3r)

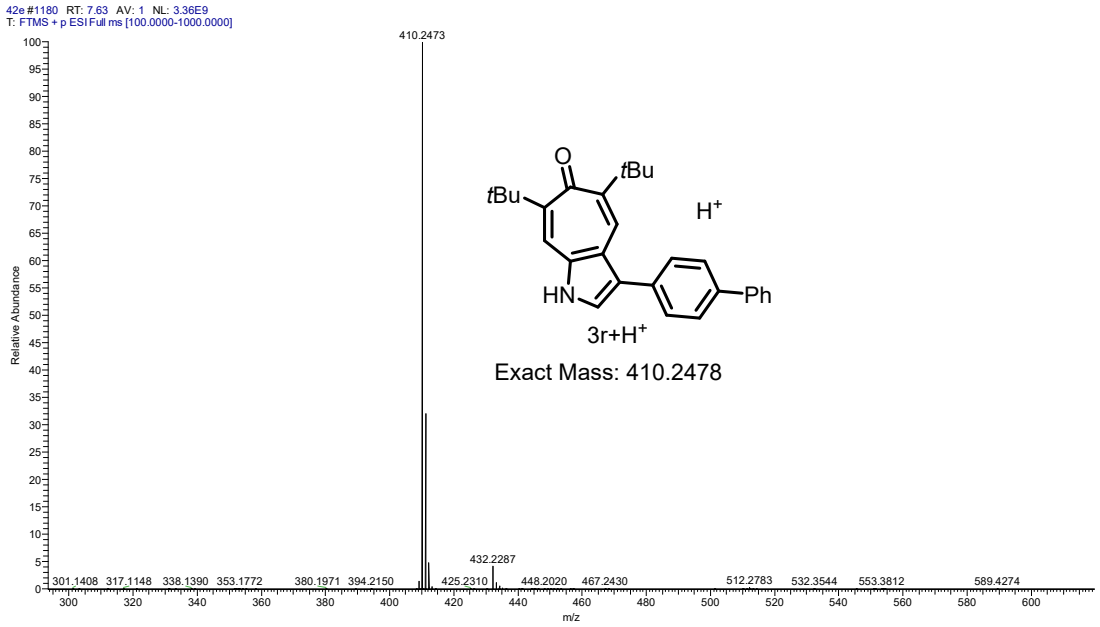
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

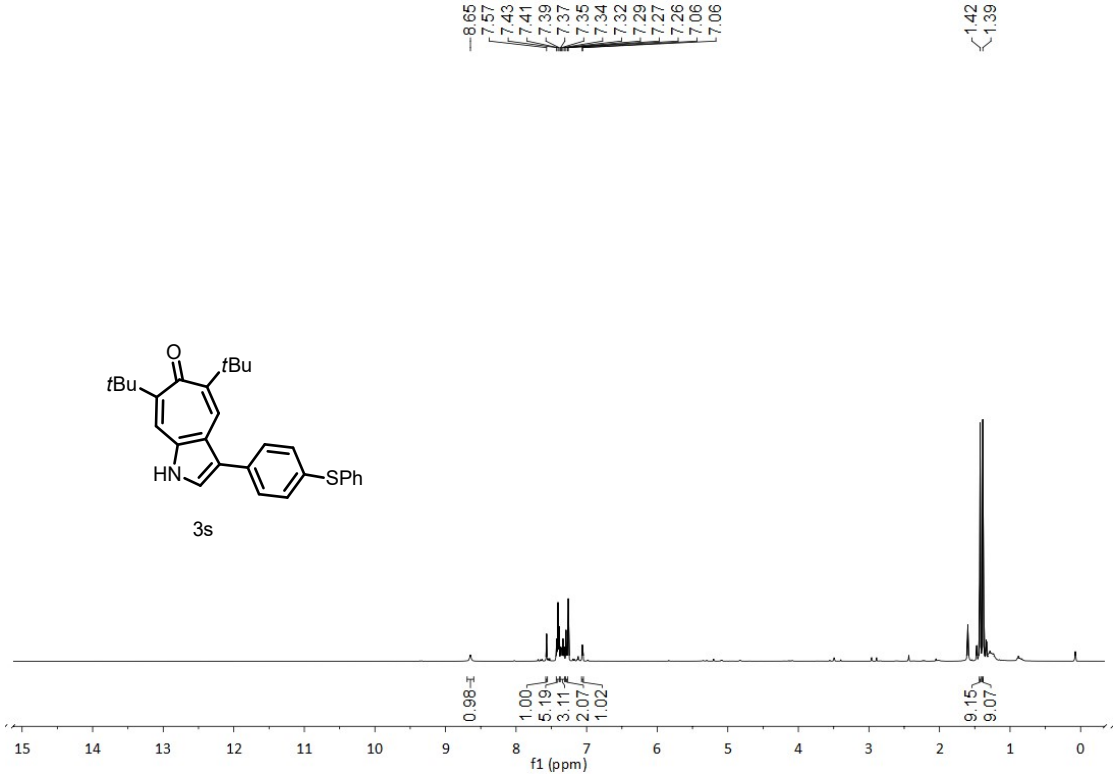


HRMS of 3r

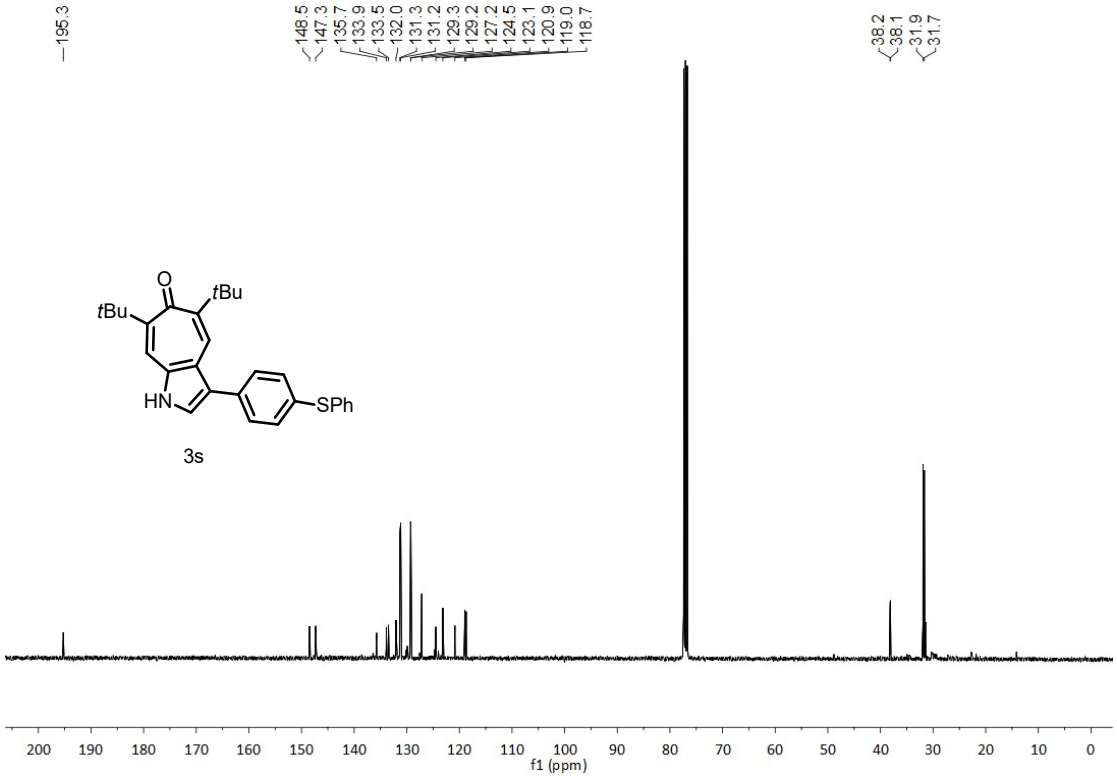


5,7-di-tert-butyl-3-(4-(phenylthio)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3s)

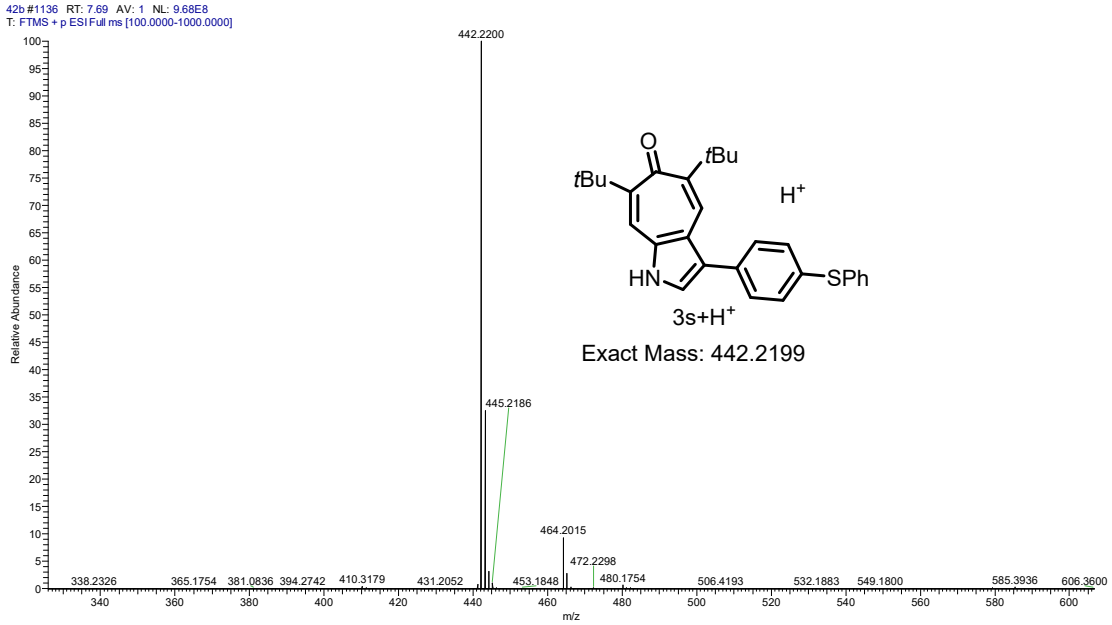
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

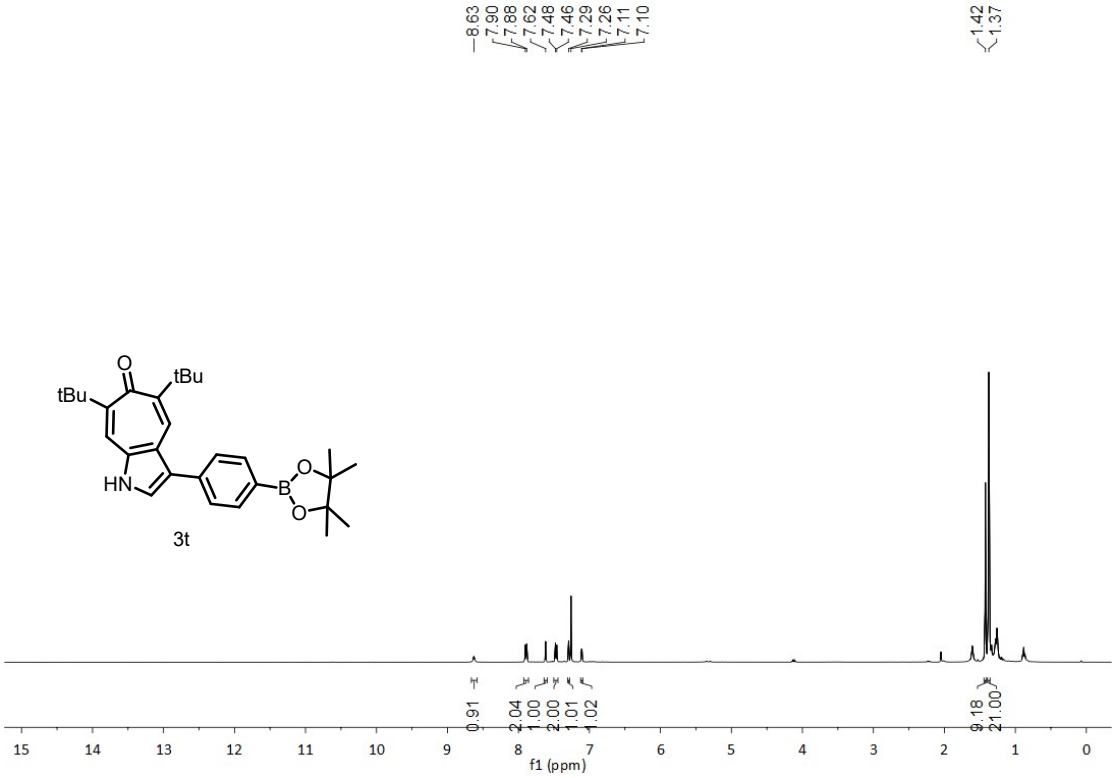


HRMS of 3s

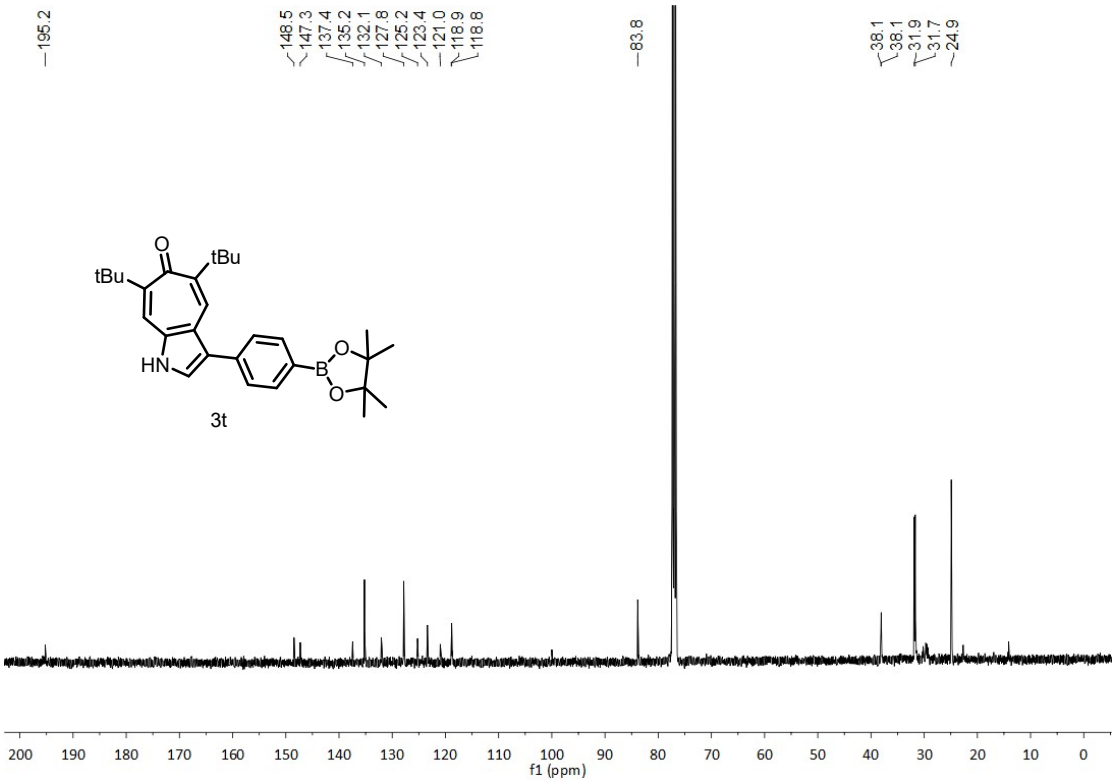


5,7-di-tert-butyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclohepta[b]pyrrol-6(1H)-one (3t)

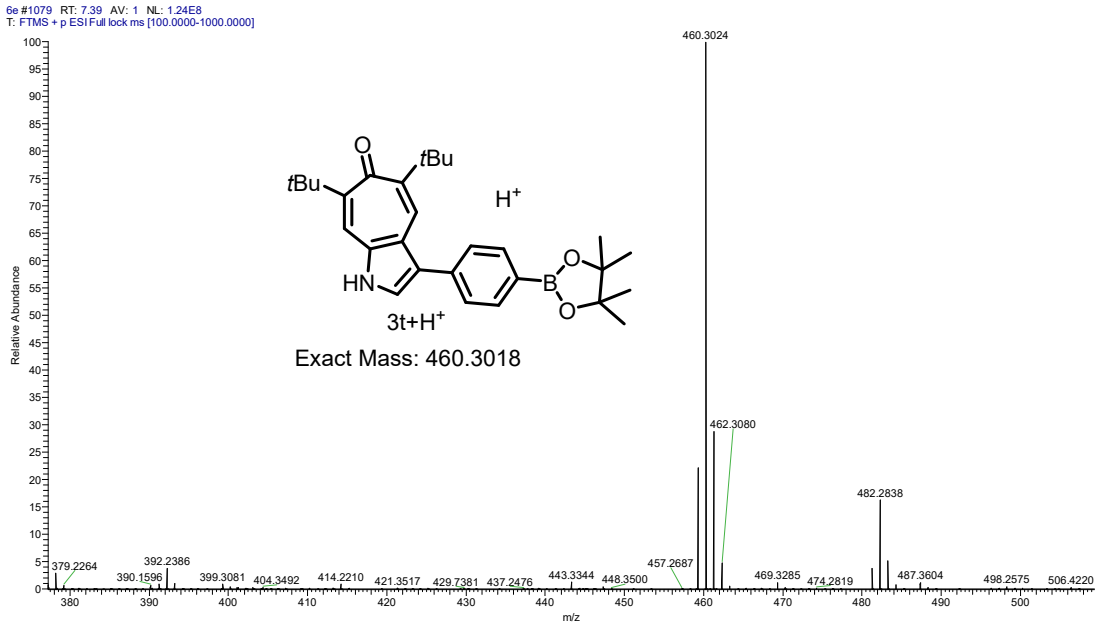
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

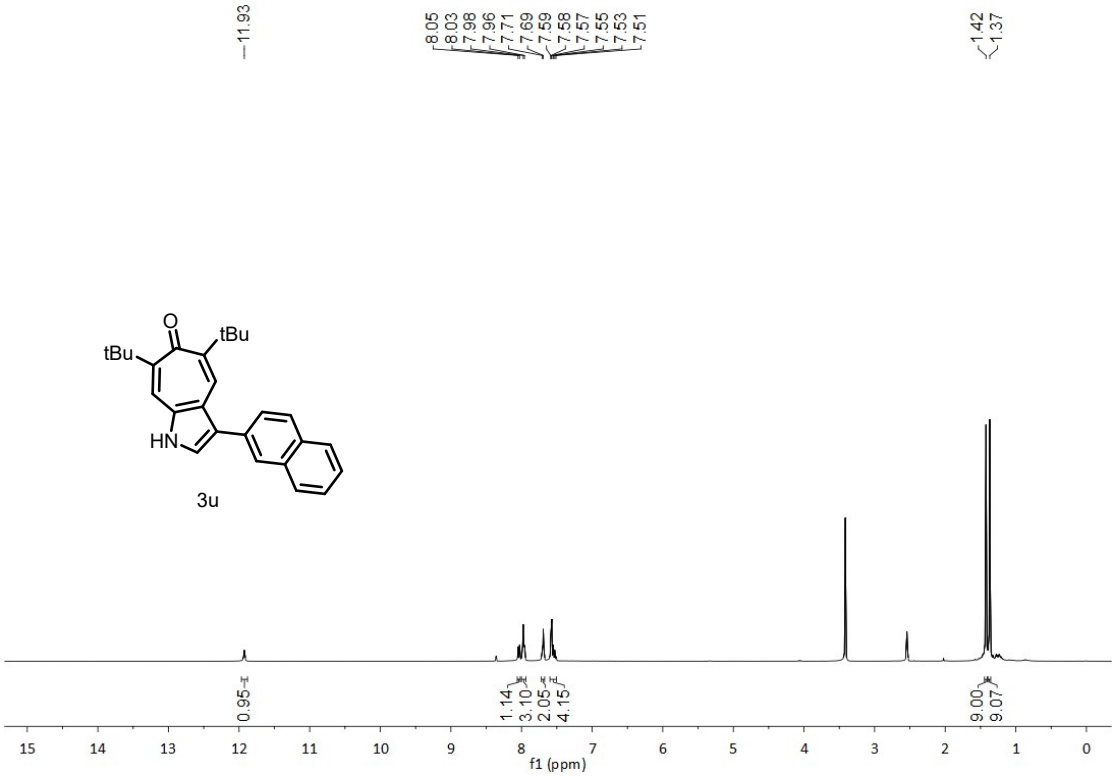


HRMS of 3t

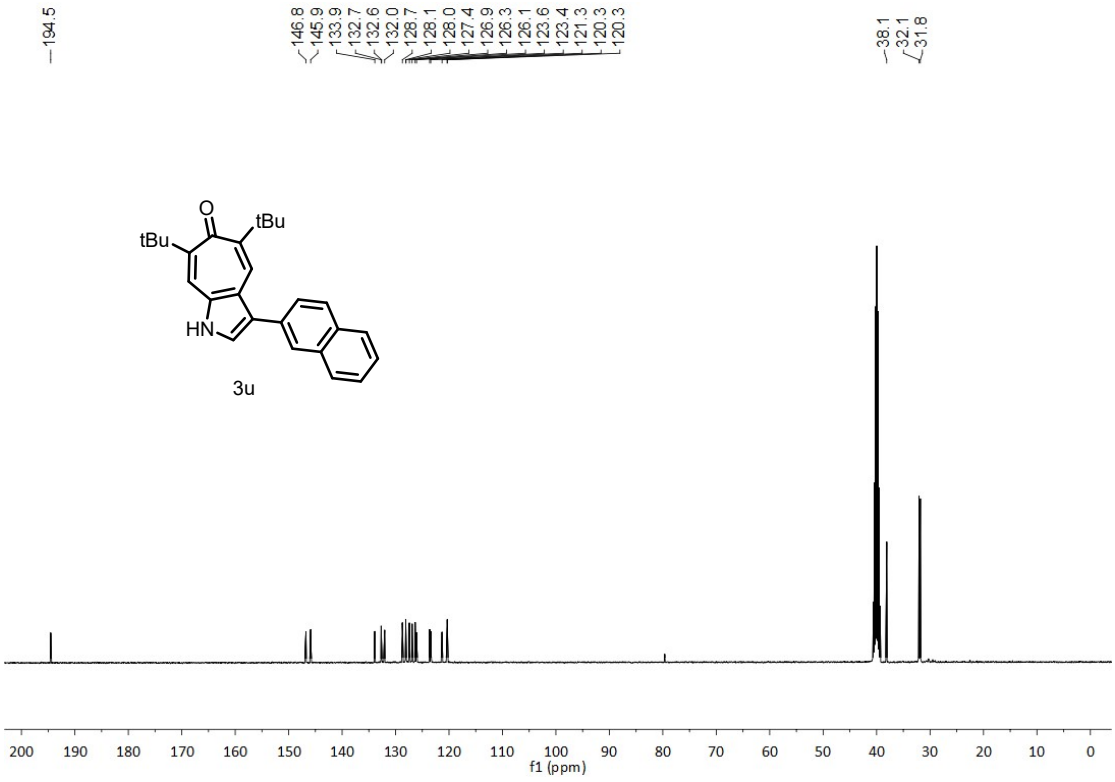


5,7-di-tert-butyl-3-(naphthalen-2-yl)cyclohepta[b]pyrrol-6(1H)-one (3u)

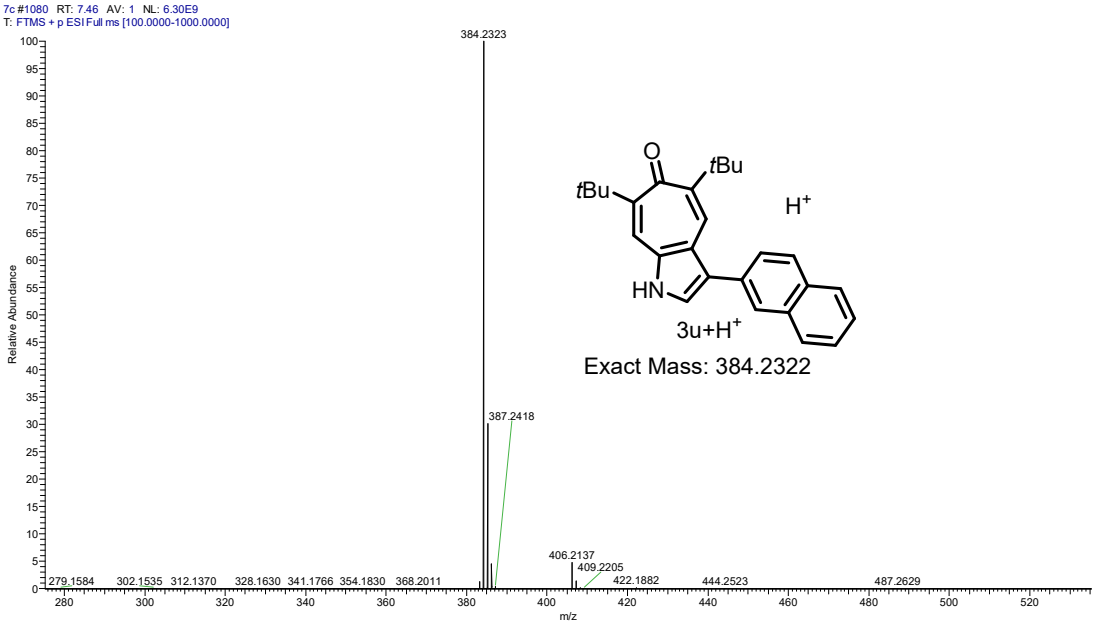
^{1}H NMR (400 MHz, D^{6}-DMSO):



^{13}C NMR (100 MHz, D^6-DMSO):

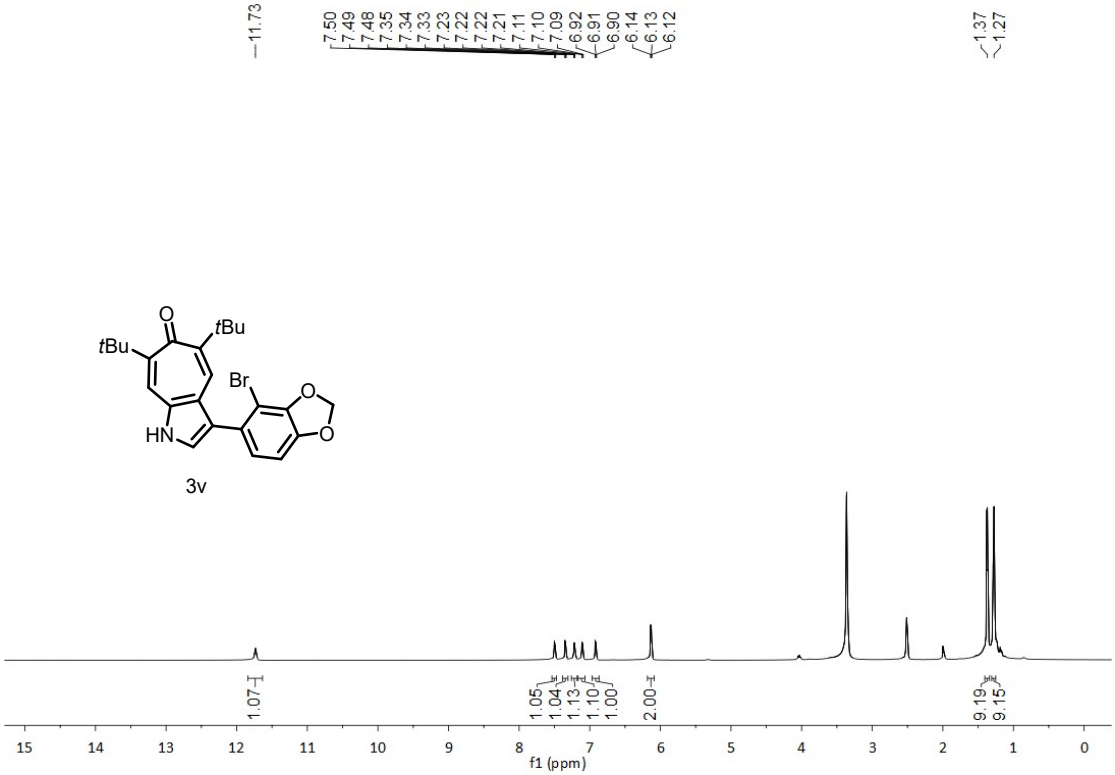


HRMS of 3u

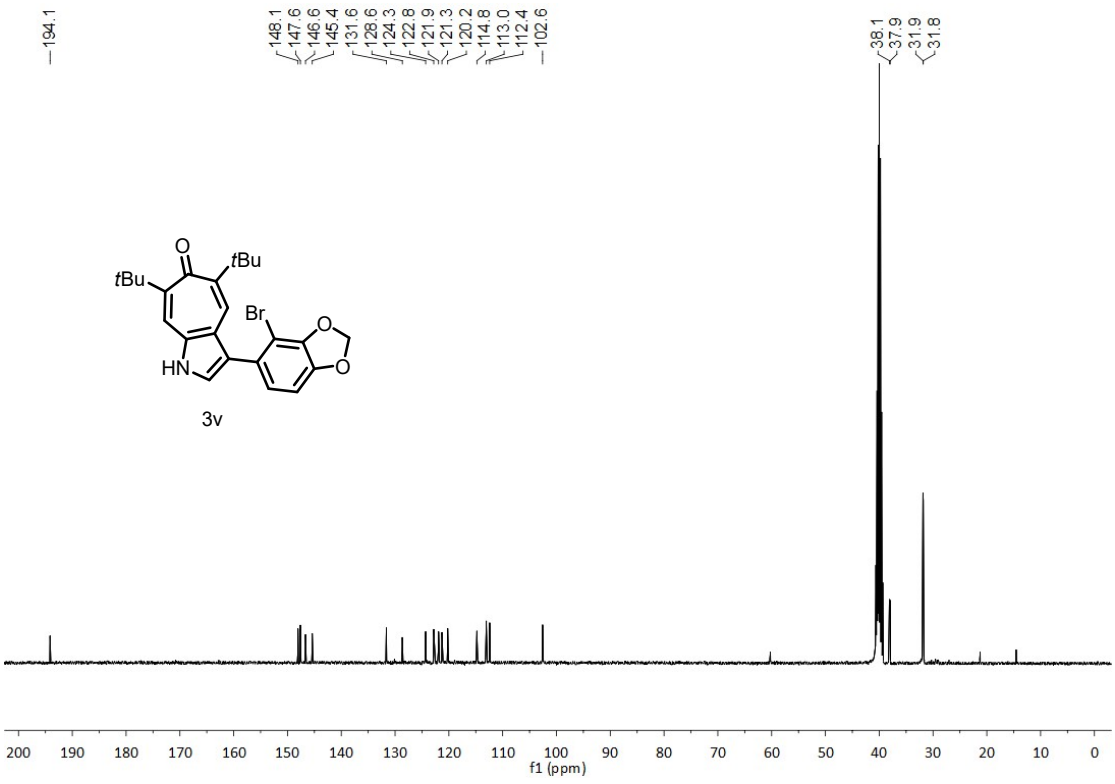


3-(4-bromobenzo[d][1,3]dioxol-5-yl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3v)

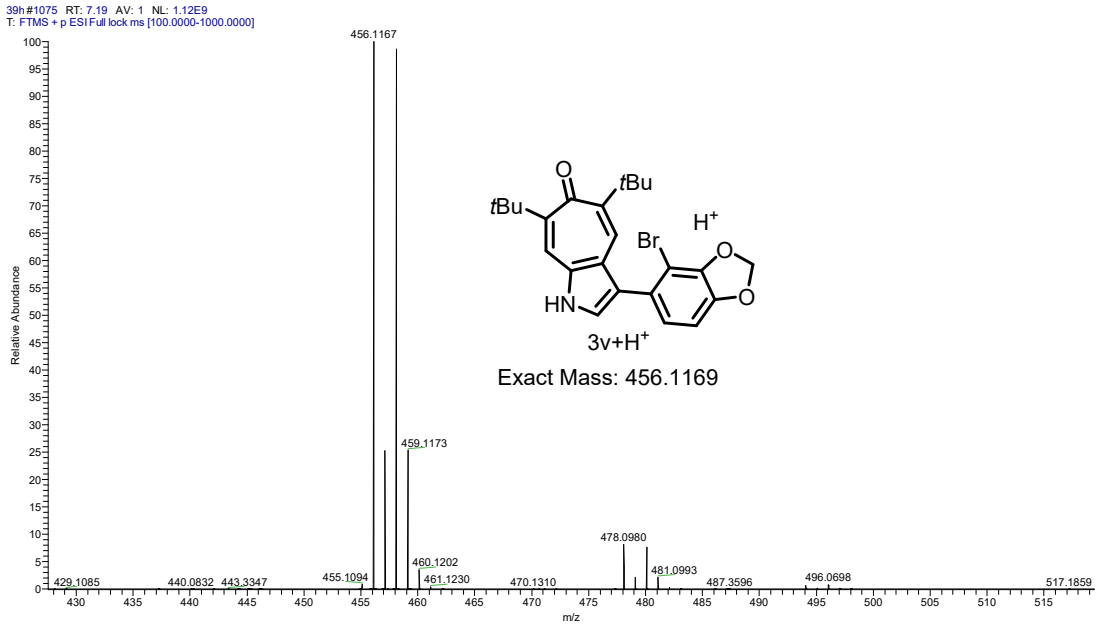
^{1}H NMR (400 MHz, D^{6}-DMSO)：



^{13}C NMR (100 MHz, D^{6}-DMSO):

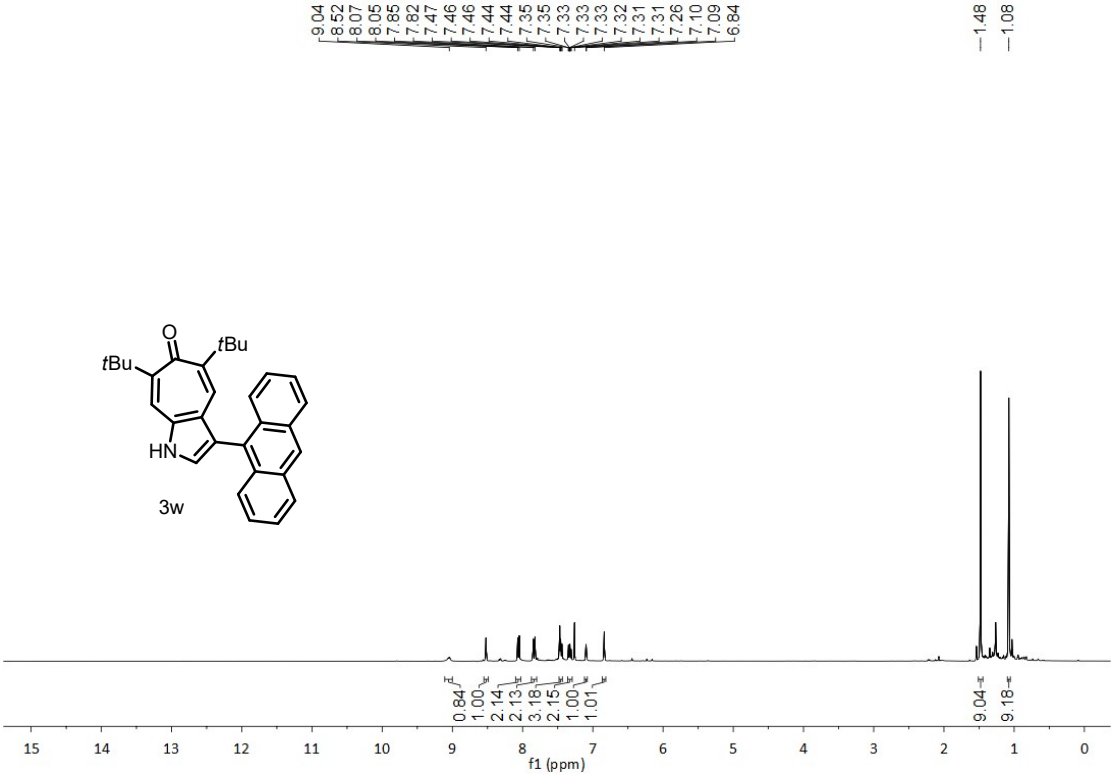


HRMS of 3v

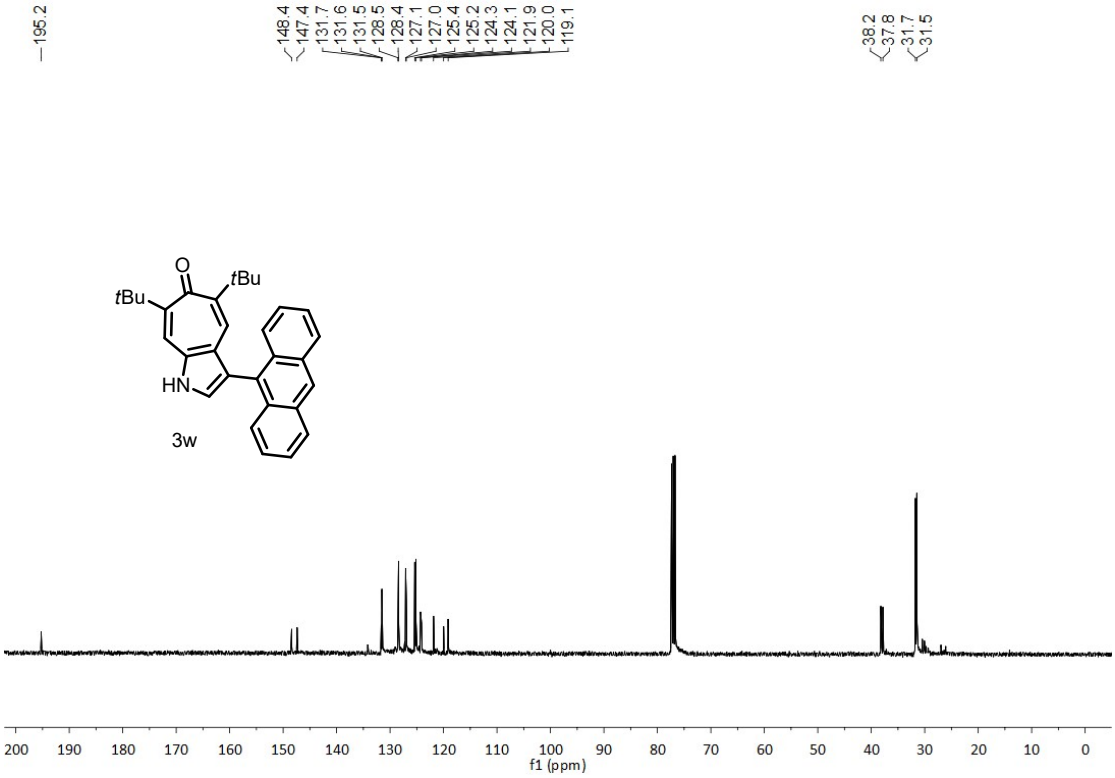


3-(anthracen-9-yl)-5,7-di-tert-butylcyclohepta[b]pyrrol-6(1H)-one (3w)

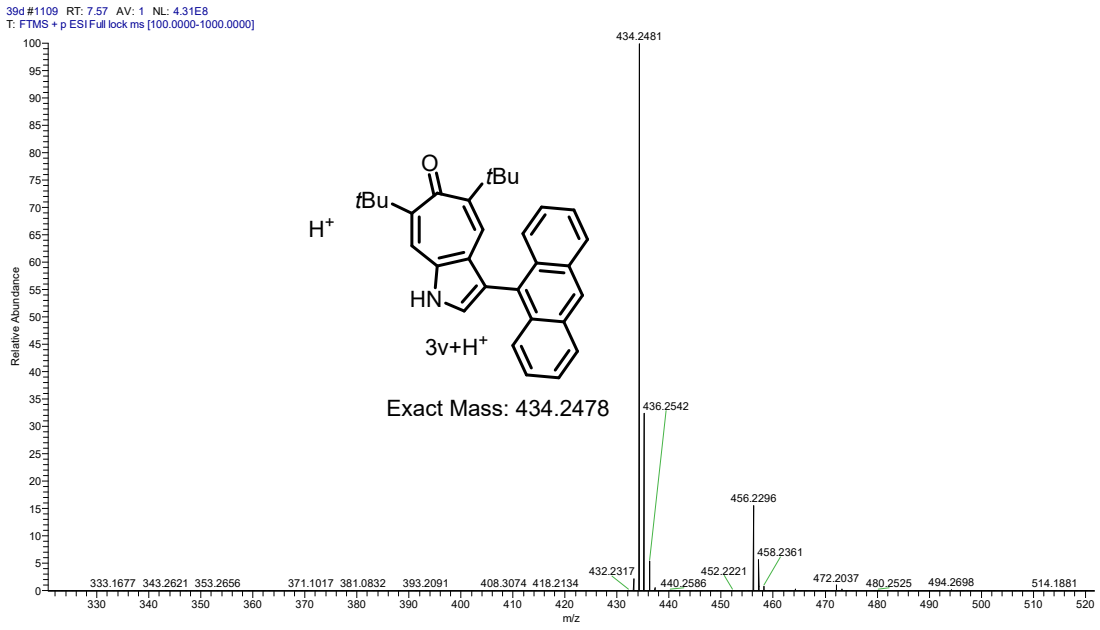
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

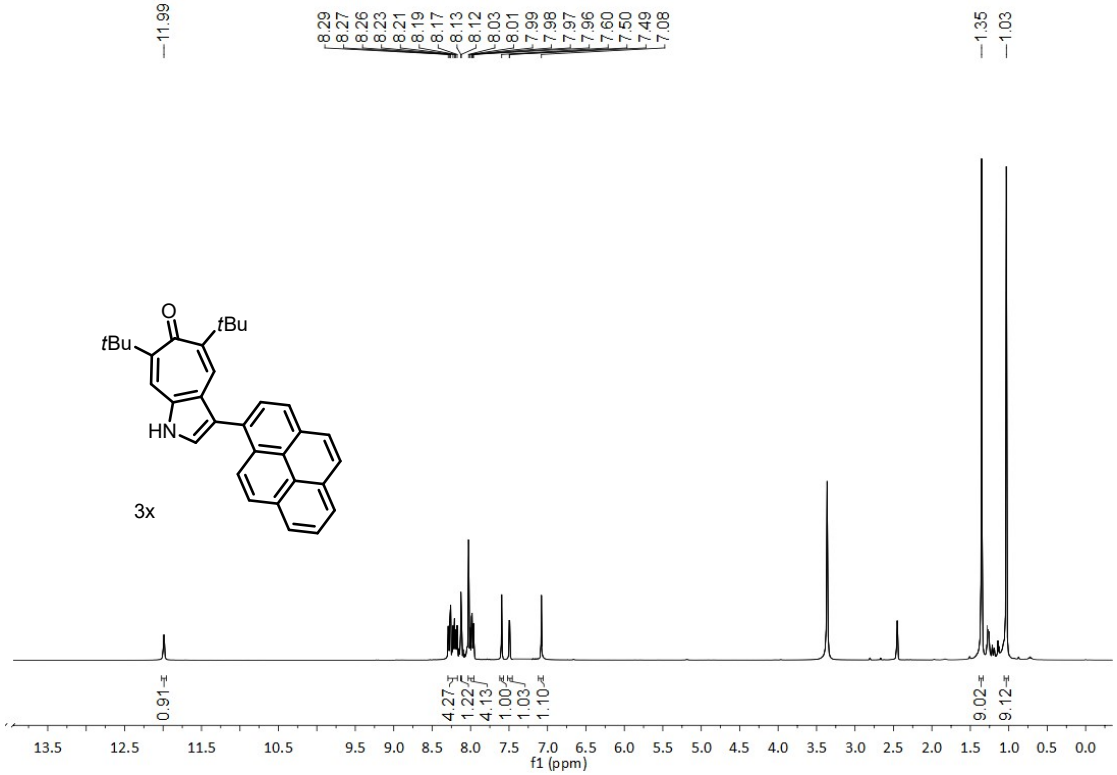


HRMS of 3w

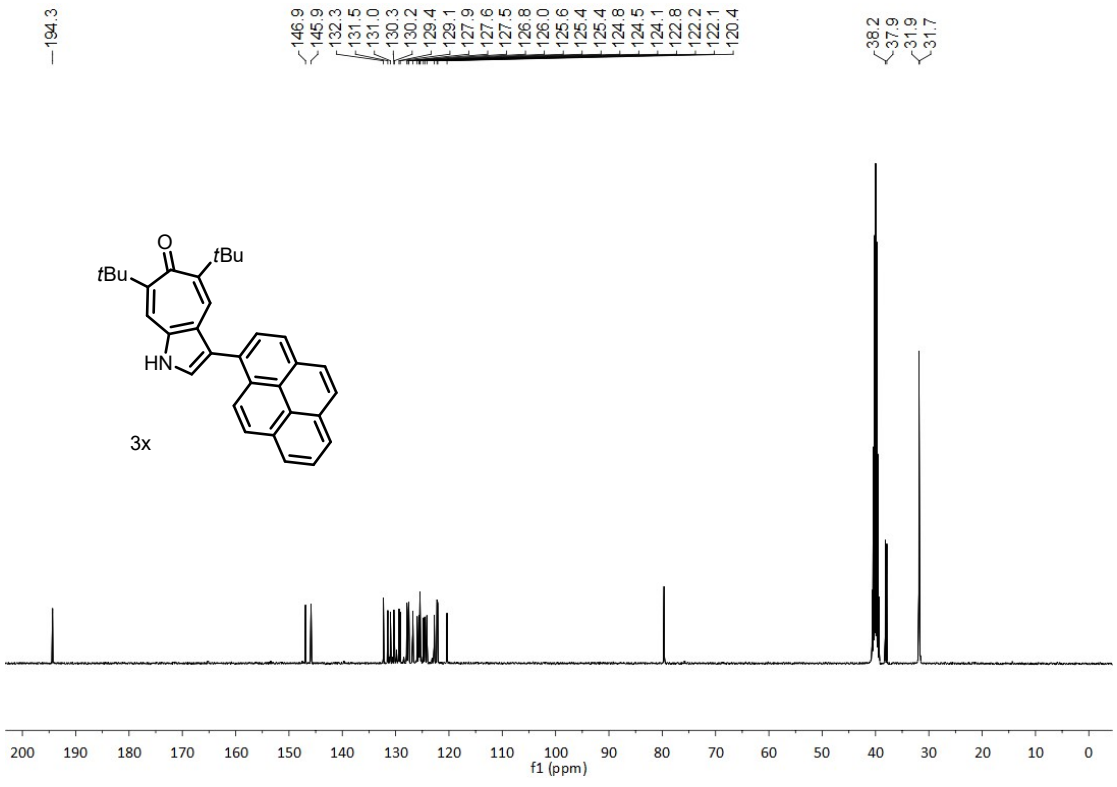


5,7-di-tert-butyl-3-(pyren-1-yl)cyclohepta[b]pyrrol-6(1H)-one (3x)

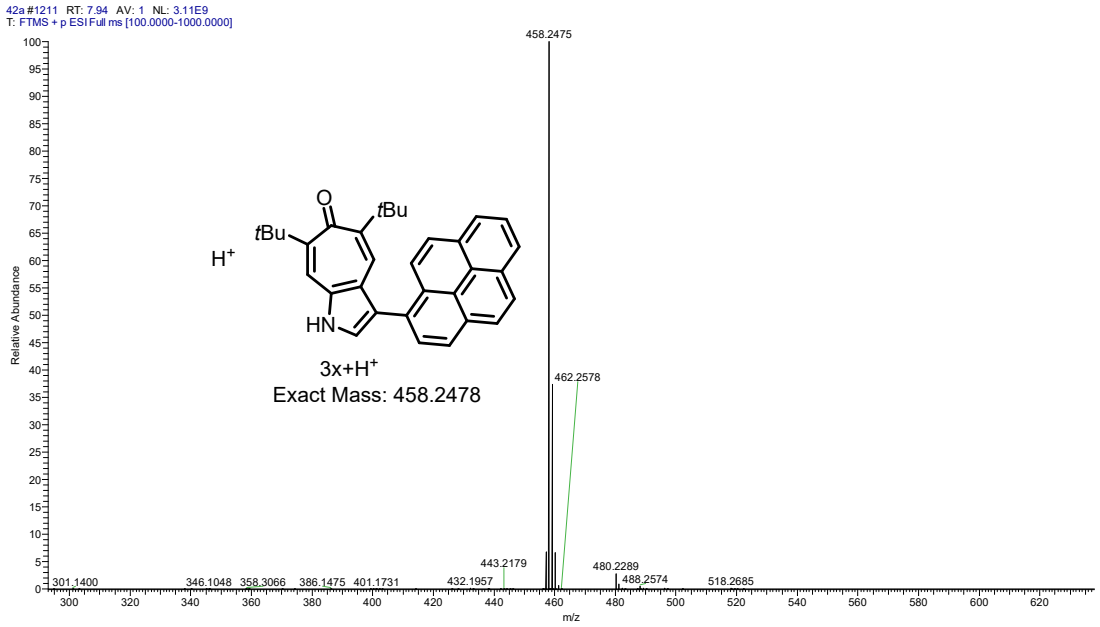
^{1}H NMR (400 MHz, D^{6}-DMSO)：



^{13}C NMR (100 MHz, D^{6}-DMSO):

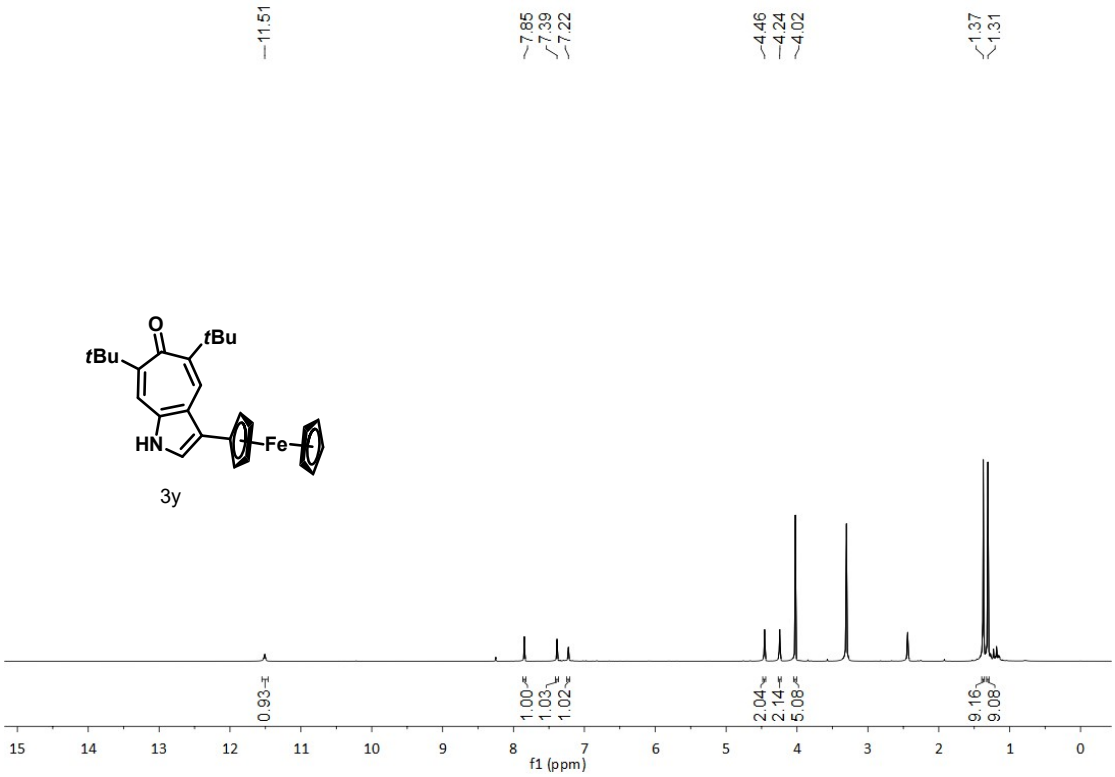


HRMS of 3x

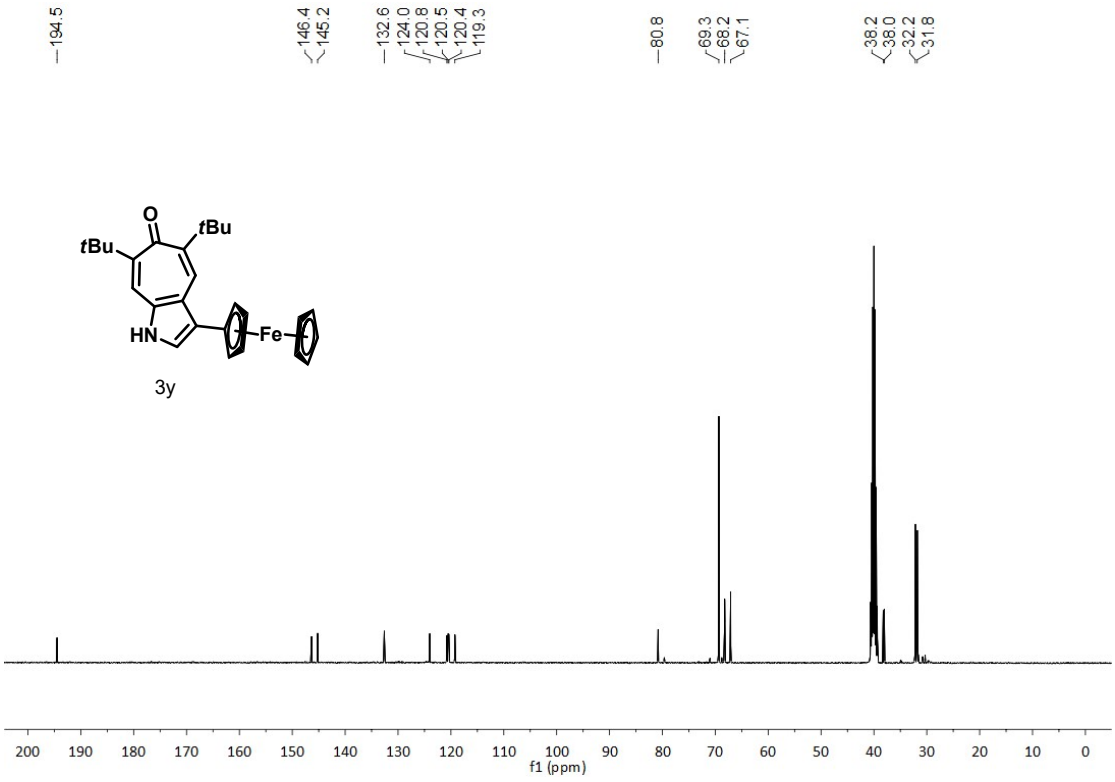


5,7-di-tert-butyl-3-(ferrocene)cyclohepta[b]pyrrol-6(1H)-one (3y)

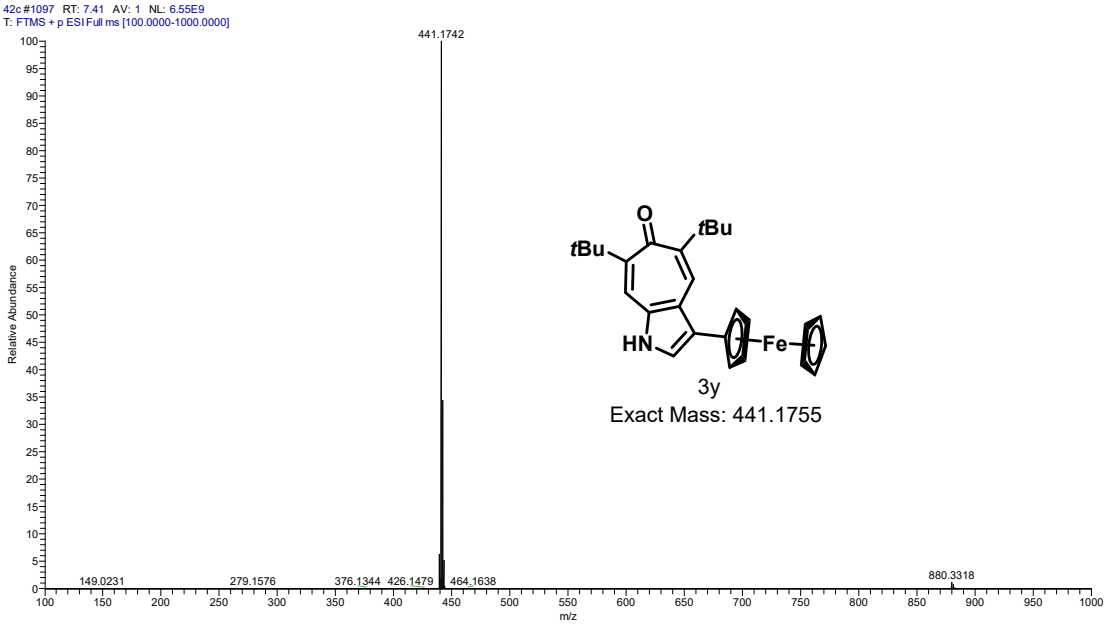
^{1}H NMR (400 MHz, D^{6}-DMSO)：



^{13}C NMR (100 MHz, D^6-DMSO):

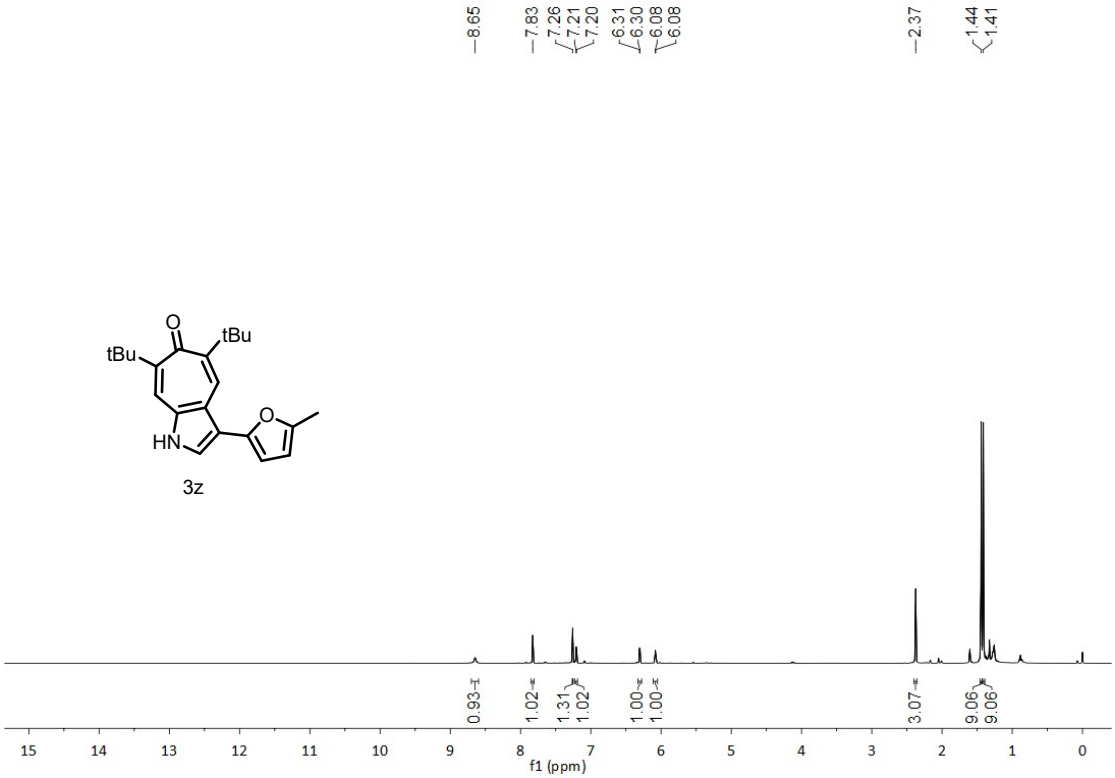


HRMS of 3y

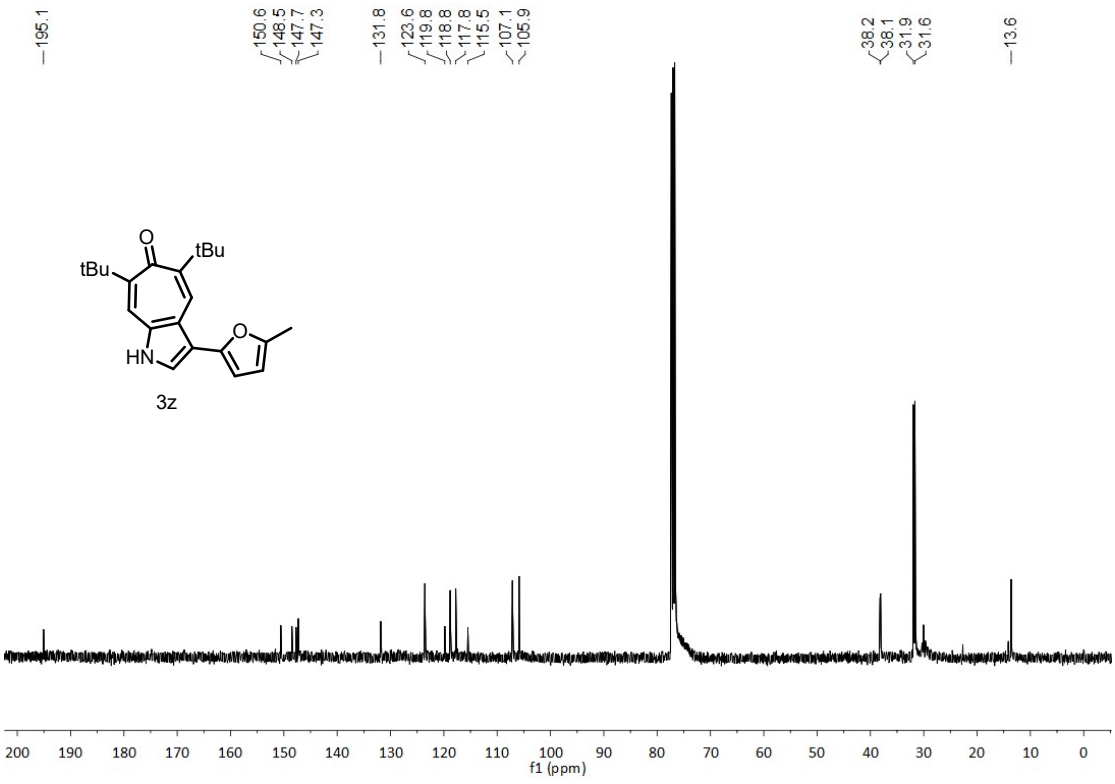


5,7-di-tert-butyl-3-(5-methylfuran-2-yl)cyclohepta[b]pyrrol-6(1H)-one (3z)

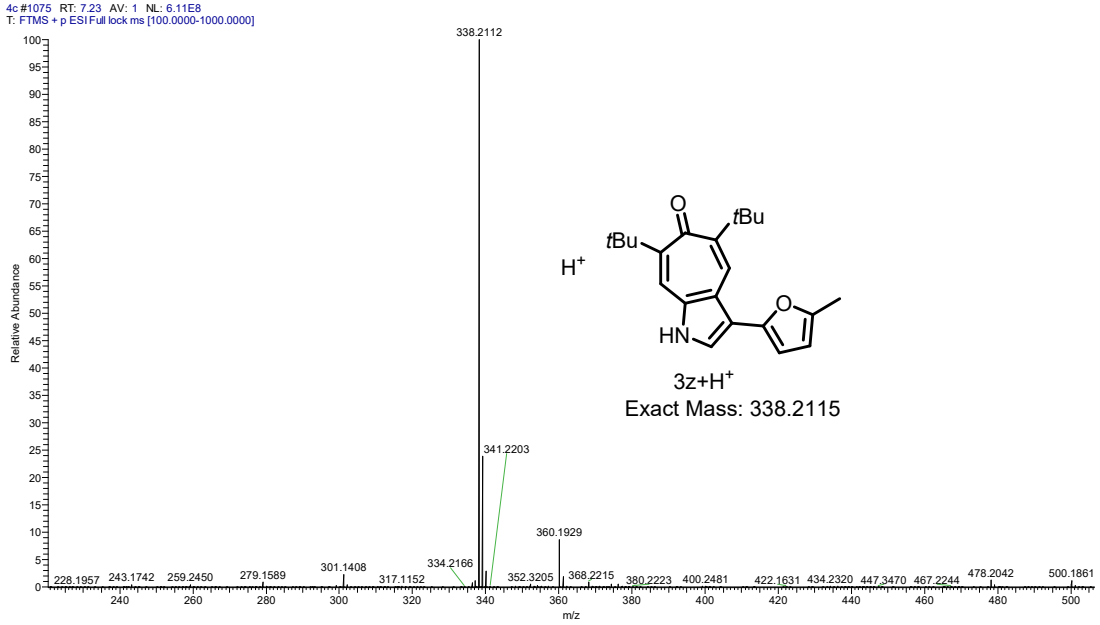
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

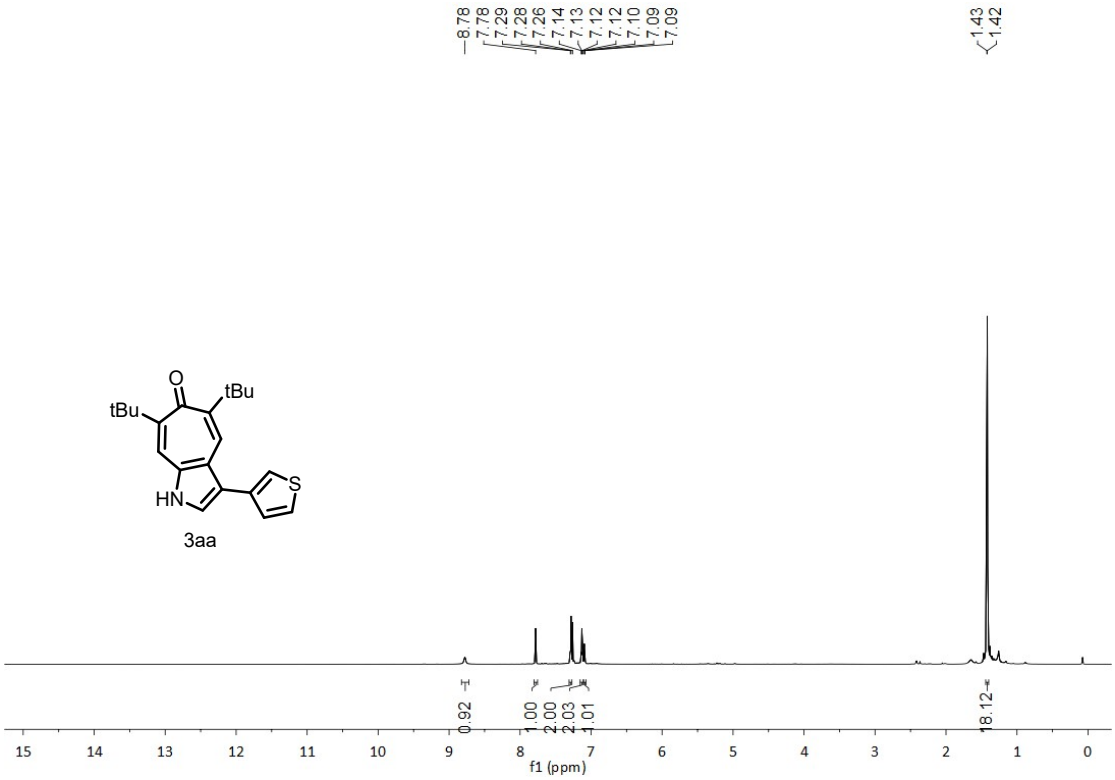


HRMS of 3z

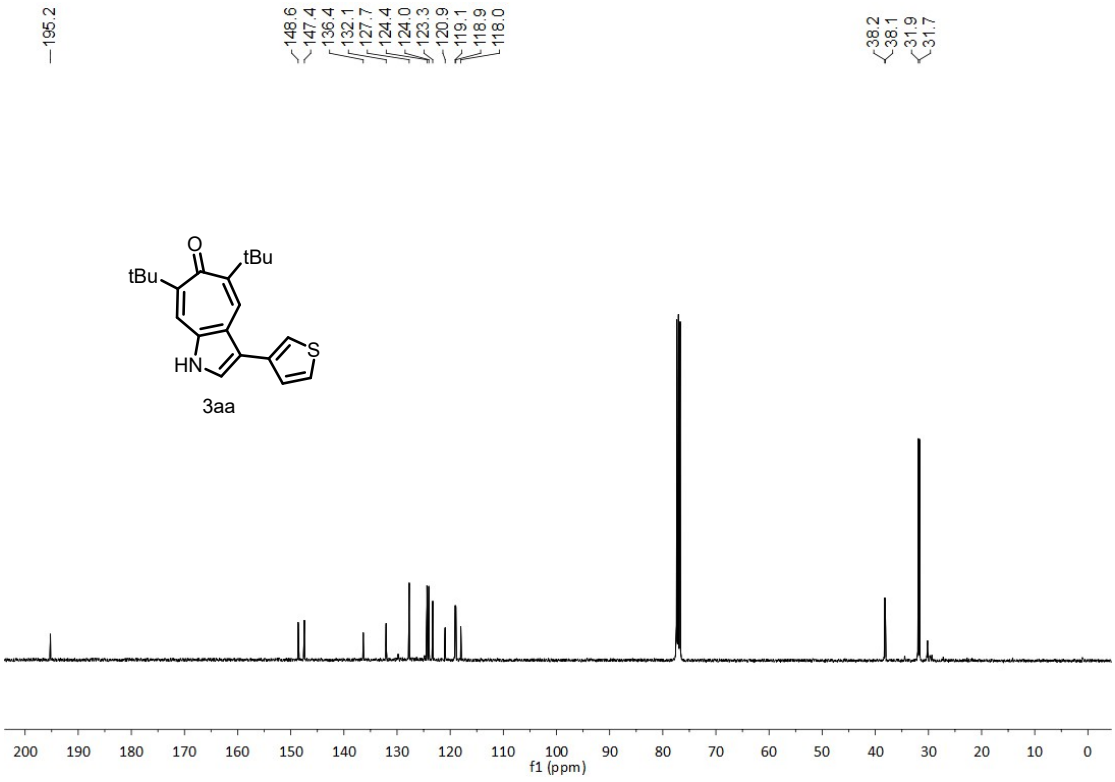


5,7-di-tert-butyl-3-(thiophen-3-yl)cyclohepta[b]pyrrol-6(1H)-one (3aa)

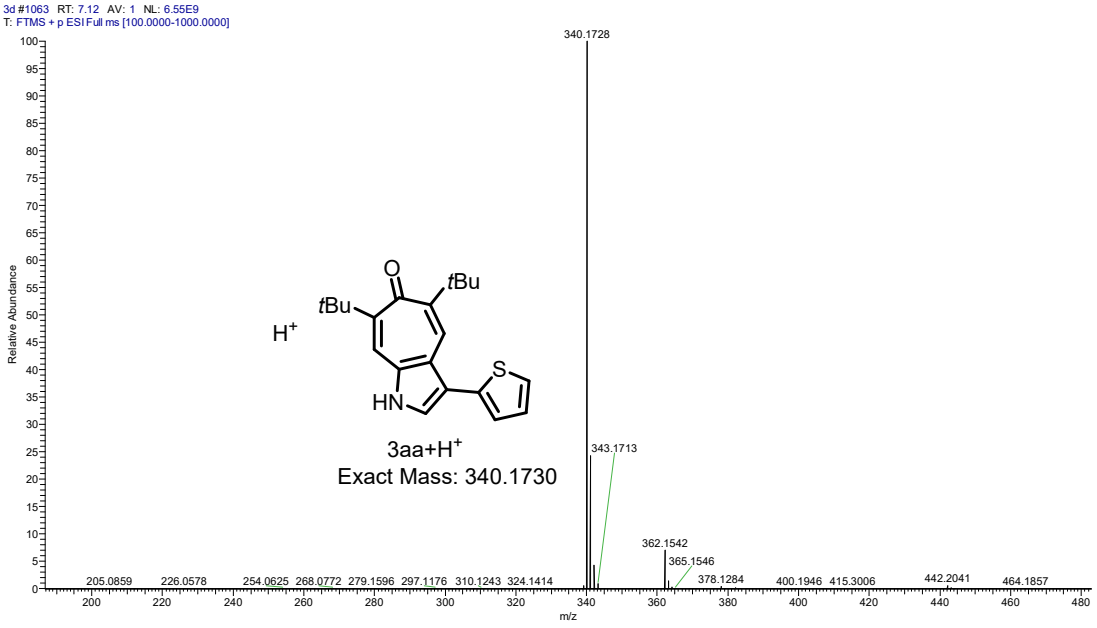
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

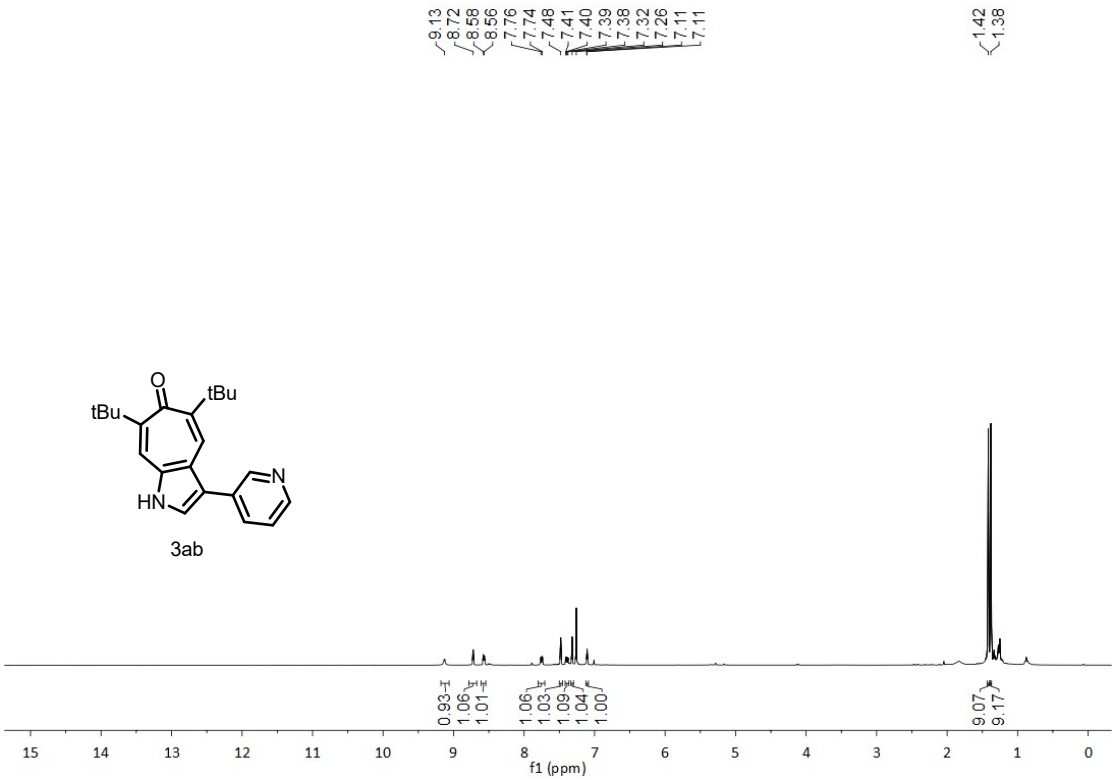


HRMS of 3aa

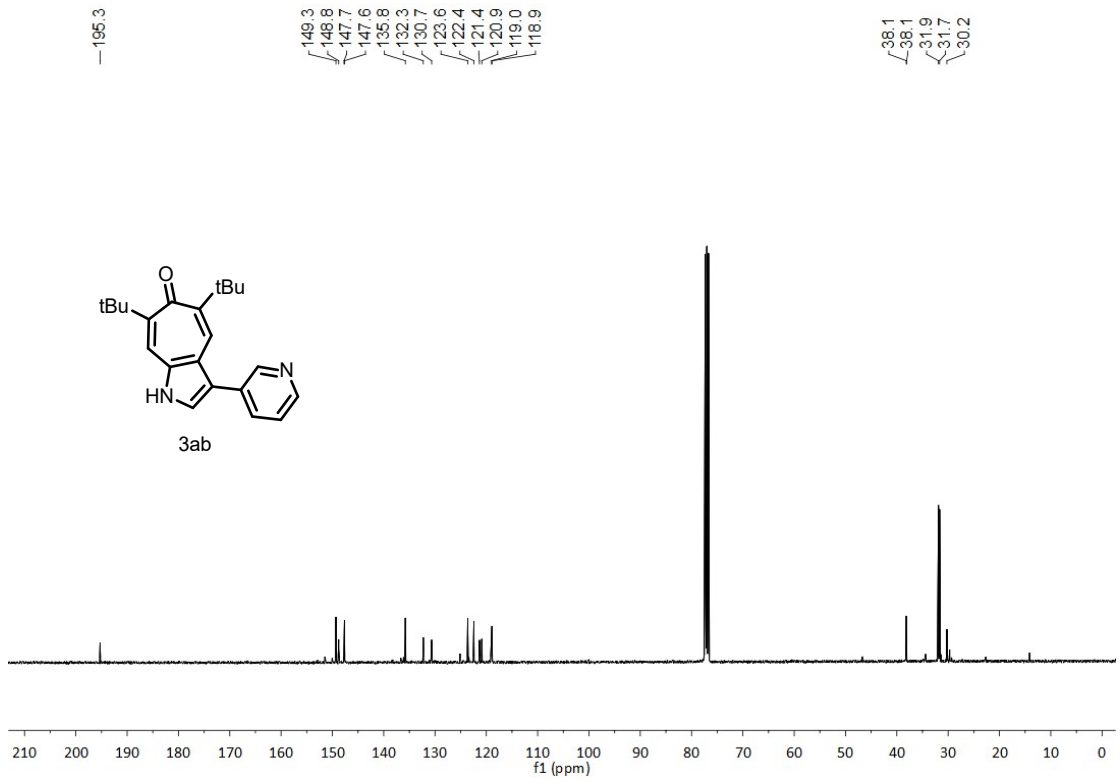


5,7-di-tert-butyl-3-(pyridin-3-yl)cyclohepta[b]pyrrol-6(1H)-one (3ab)

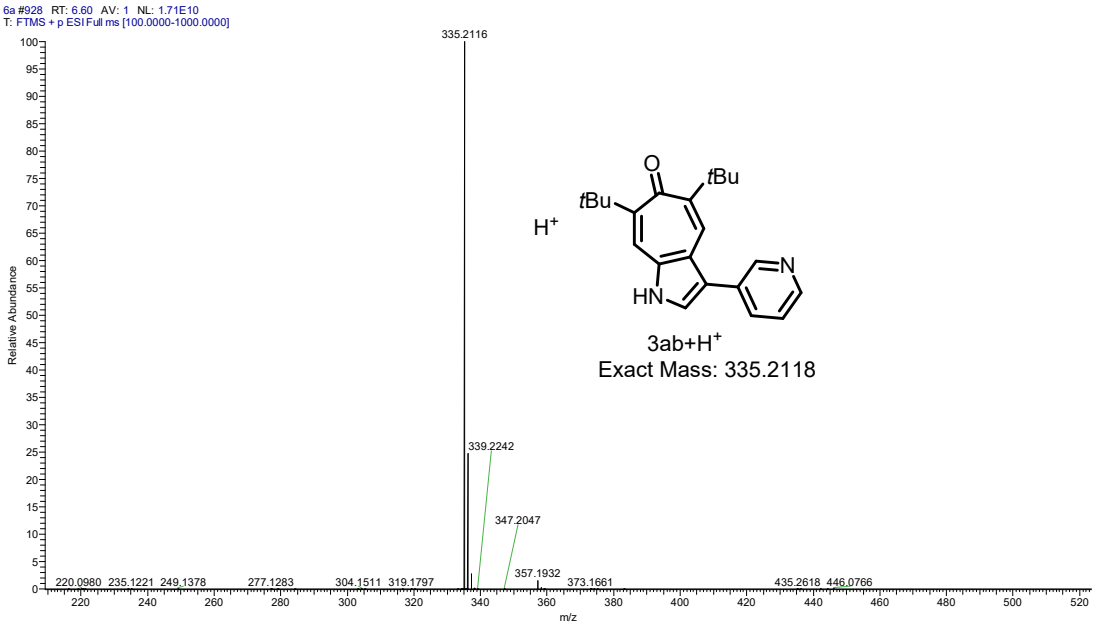
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

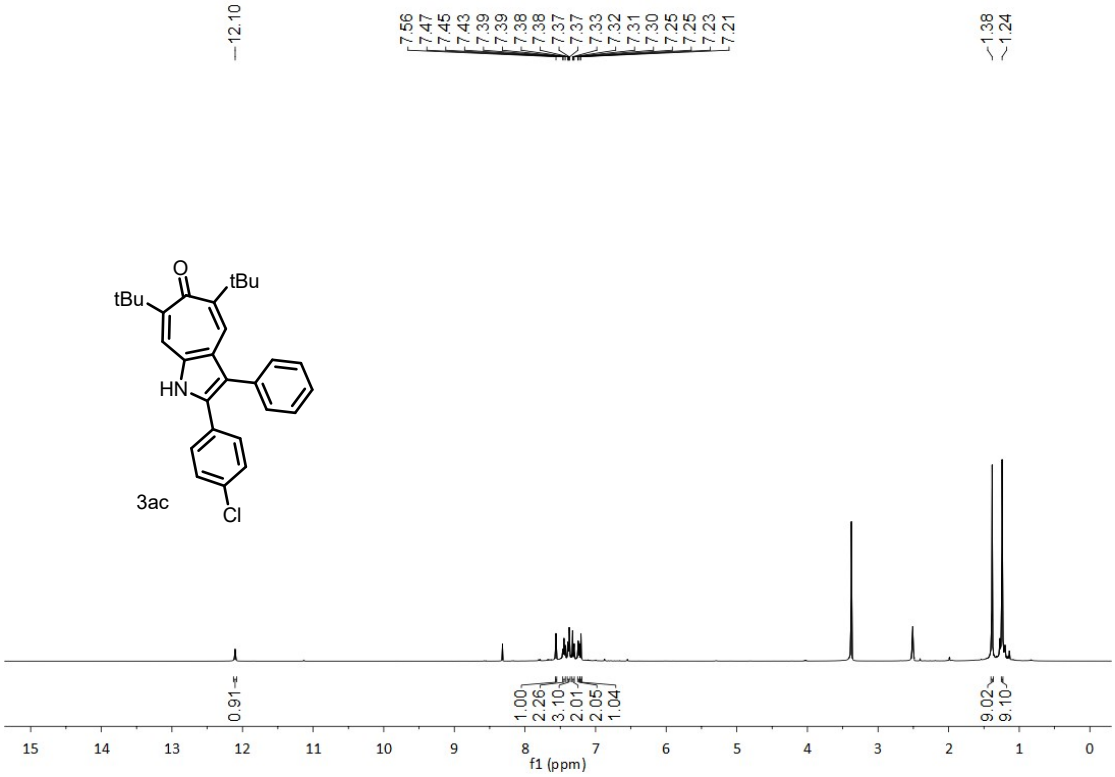


HRMS of 3ab

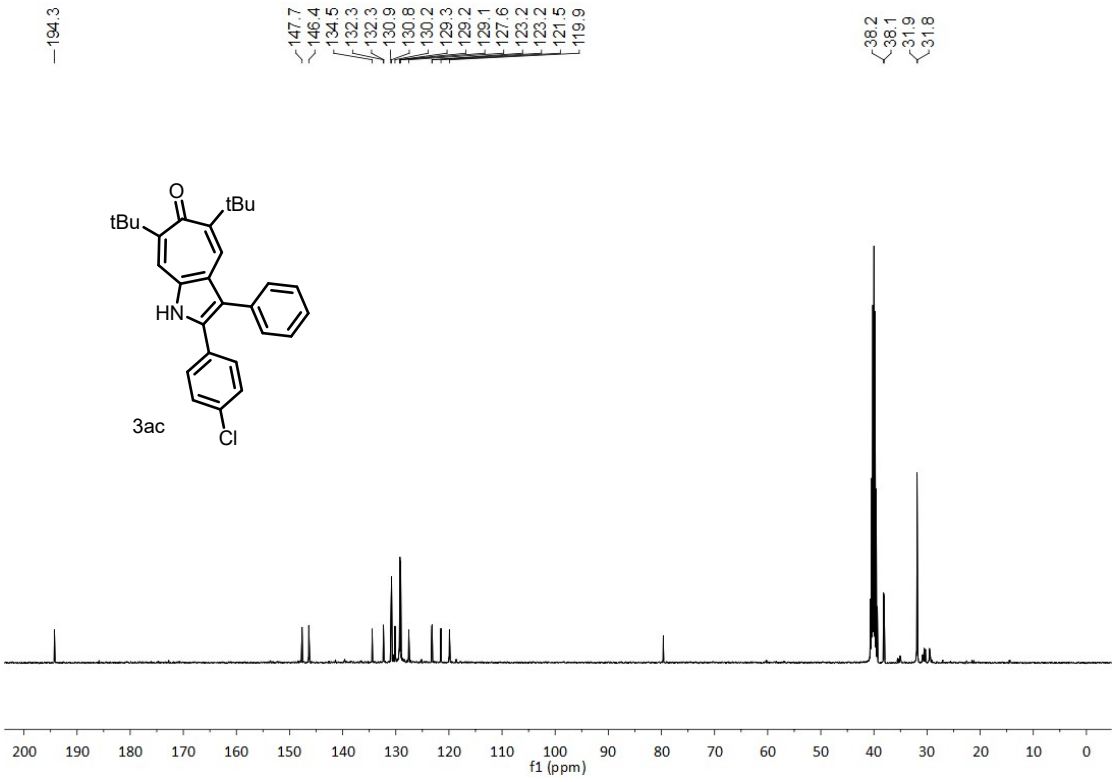


5,7-di-tert-butyl-2-(4-chlorophenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ac)

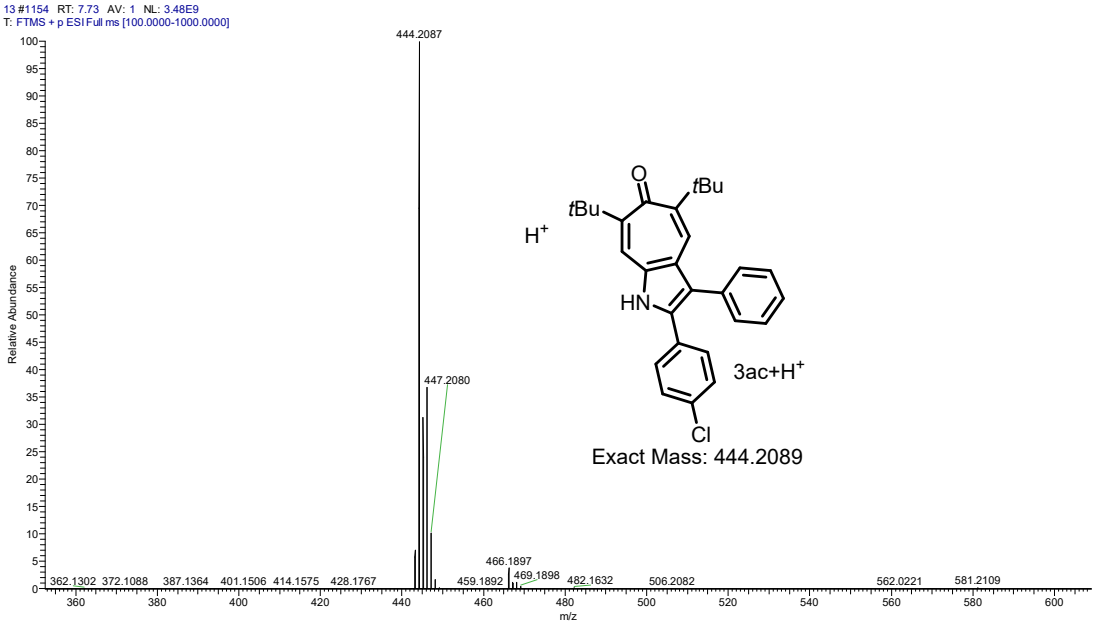
^{1}H NMR (400 MHz, D^{6}-DMSO):



^{13}C NMR (100 MHz, D^6-DMSO):

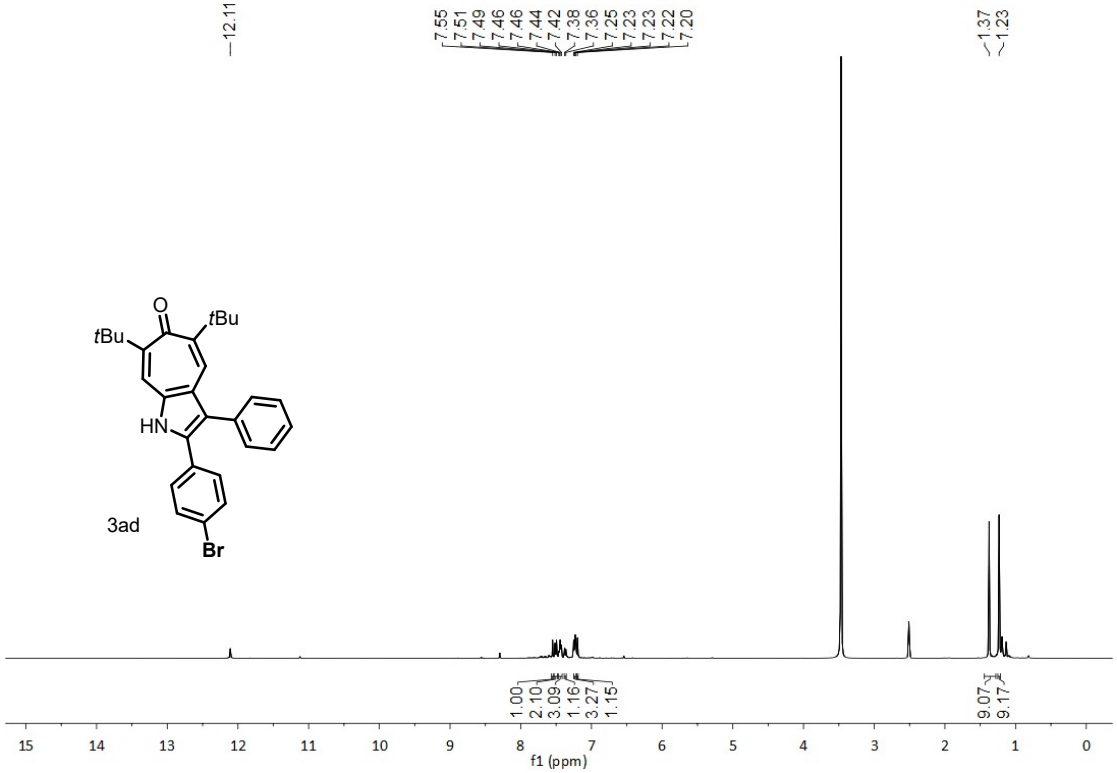


HRMS of 3ac

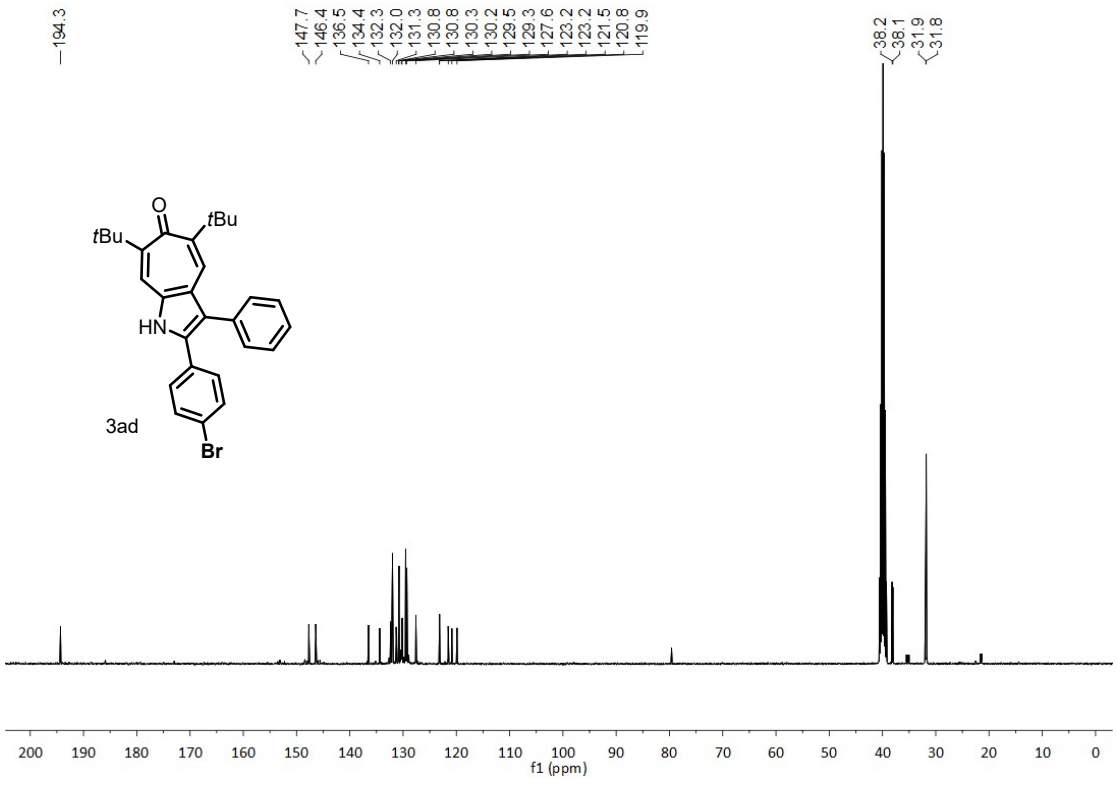


2-(4-bromophenyl)-5,7-di-tert-butyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ad)

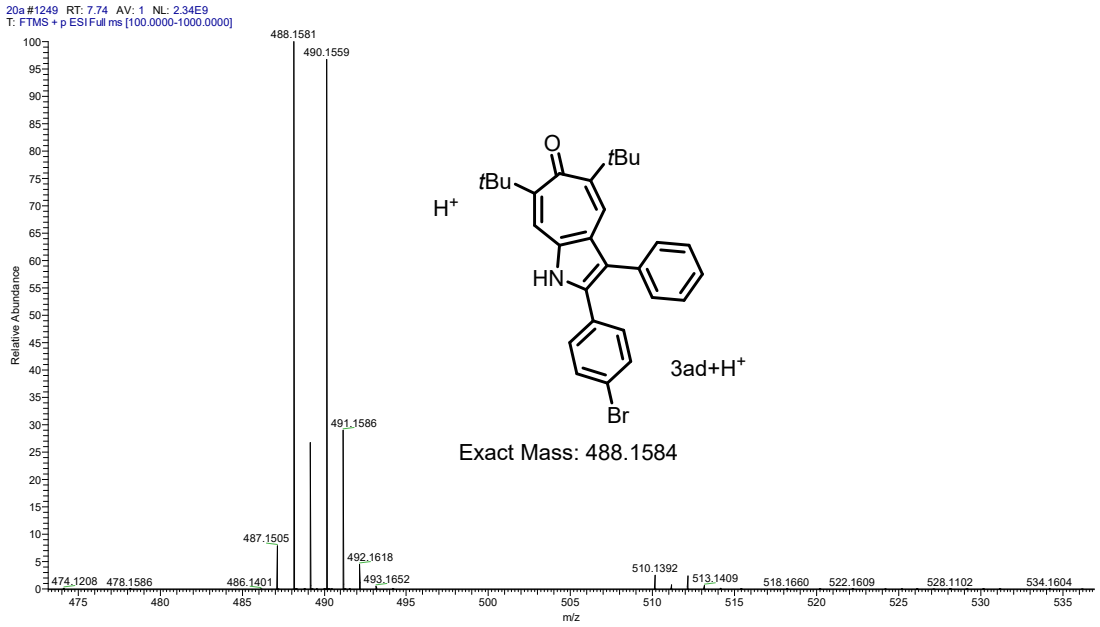
^{1}H NMR (400 MHz, D^{6}-DMSO)：



^{13}C NMR (100 MHz, D^{6}-DMSO):

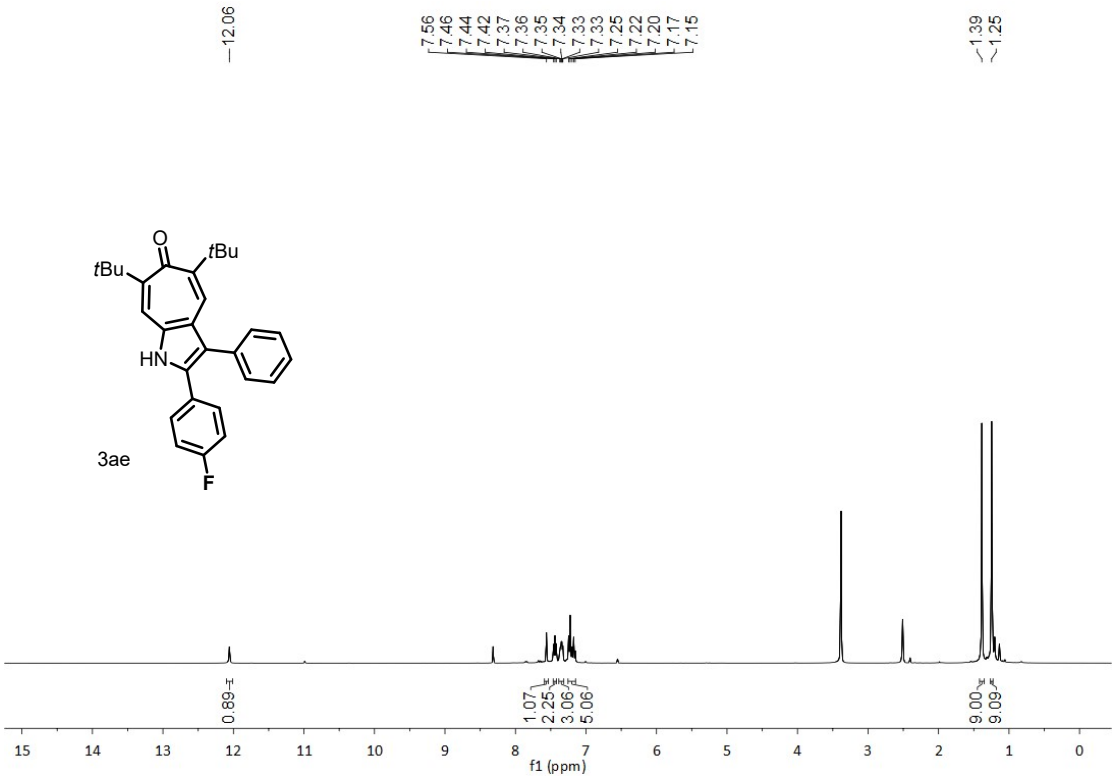


HRMS of 3ad

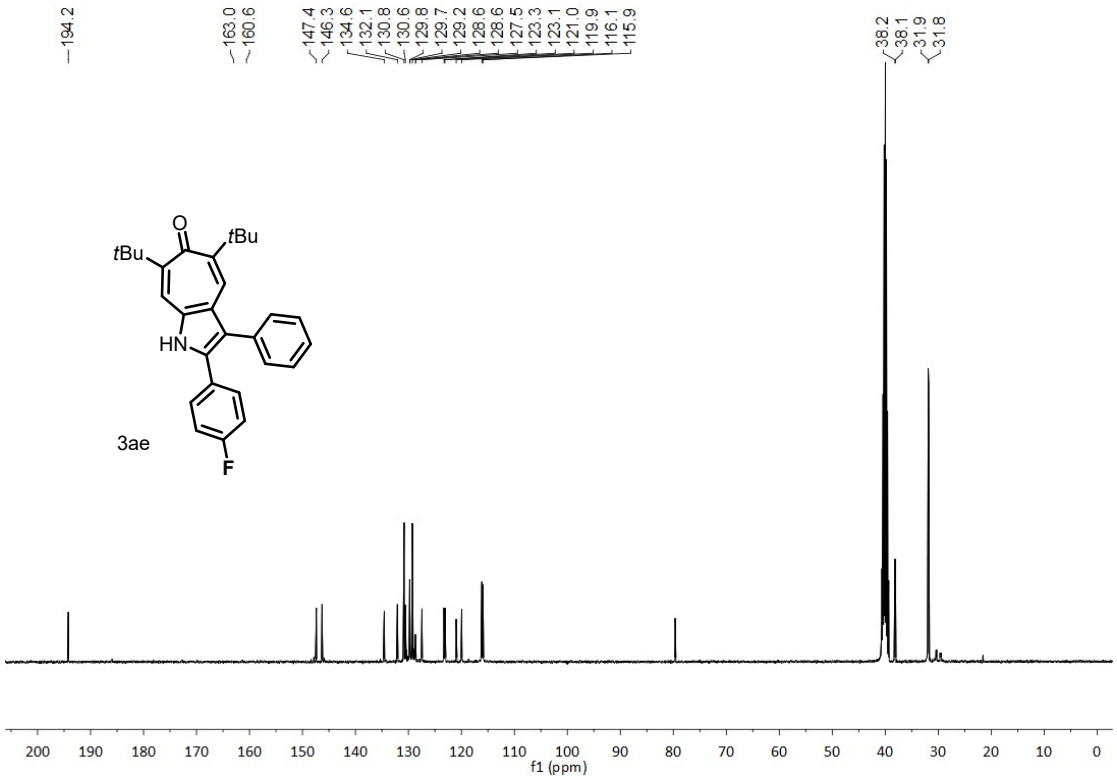


5,7-di-tert-butyl-2-(4-fluorophenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ae)

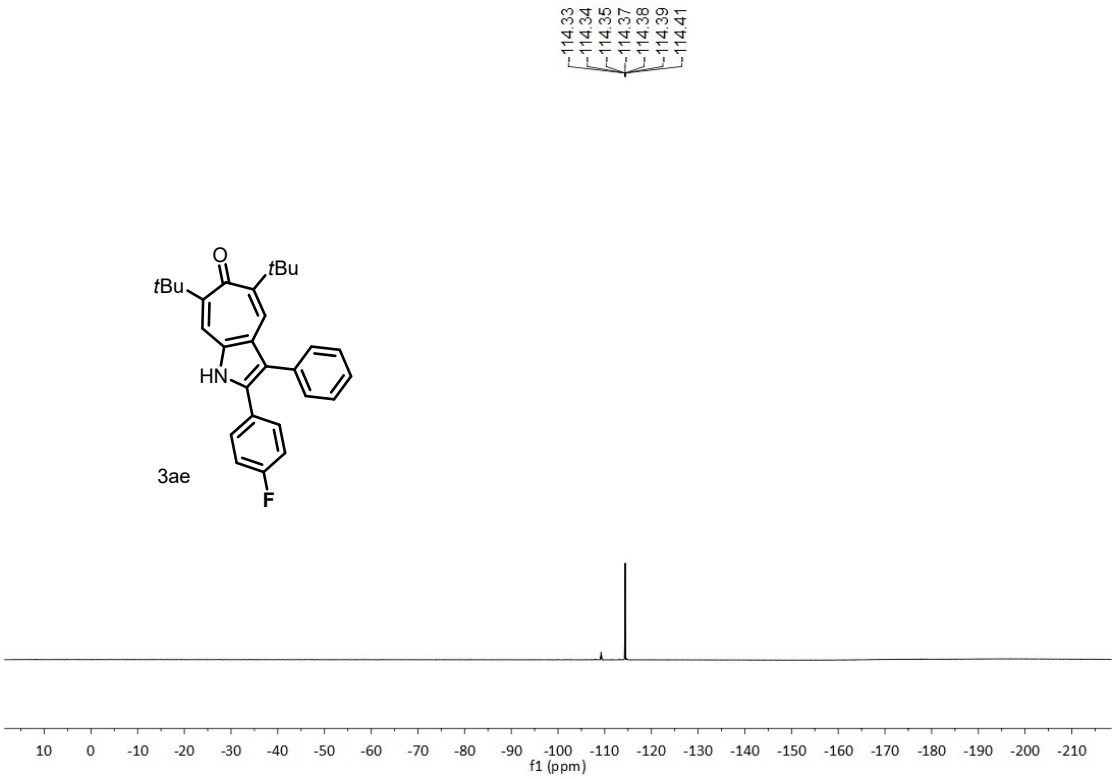
^{1}H NMR (400 MHz, D^{6}-DMSO):



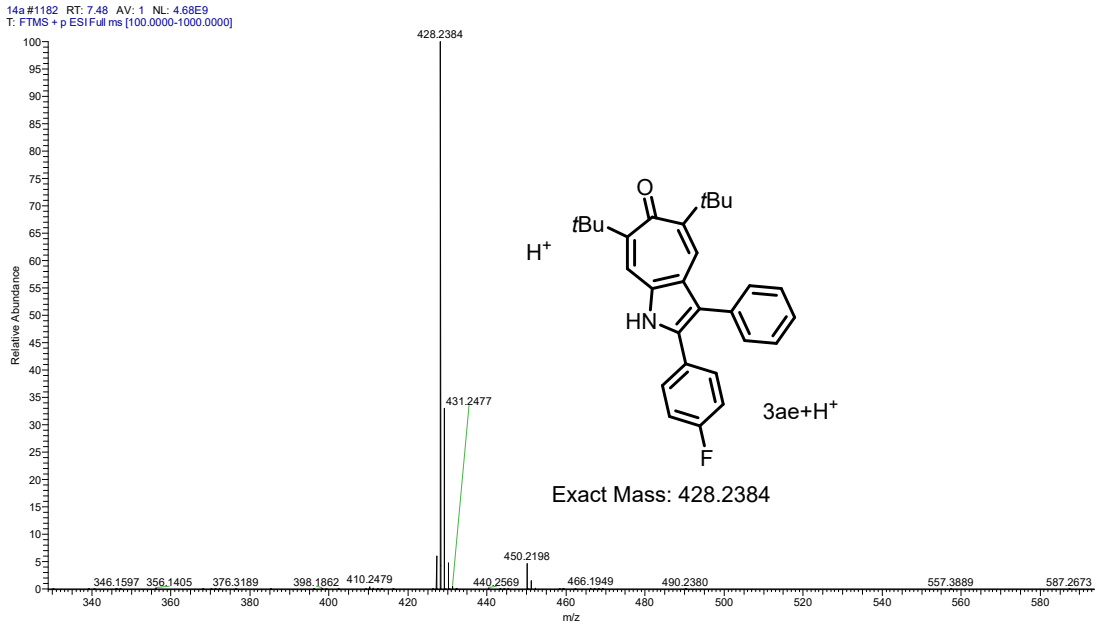
^{13}C NMR (100 MHz, D^{6}-DMSO):



^{19}F NMR (376 MHz, D^{6}-DMSO):

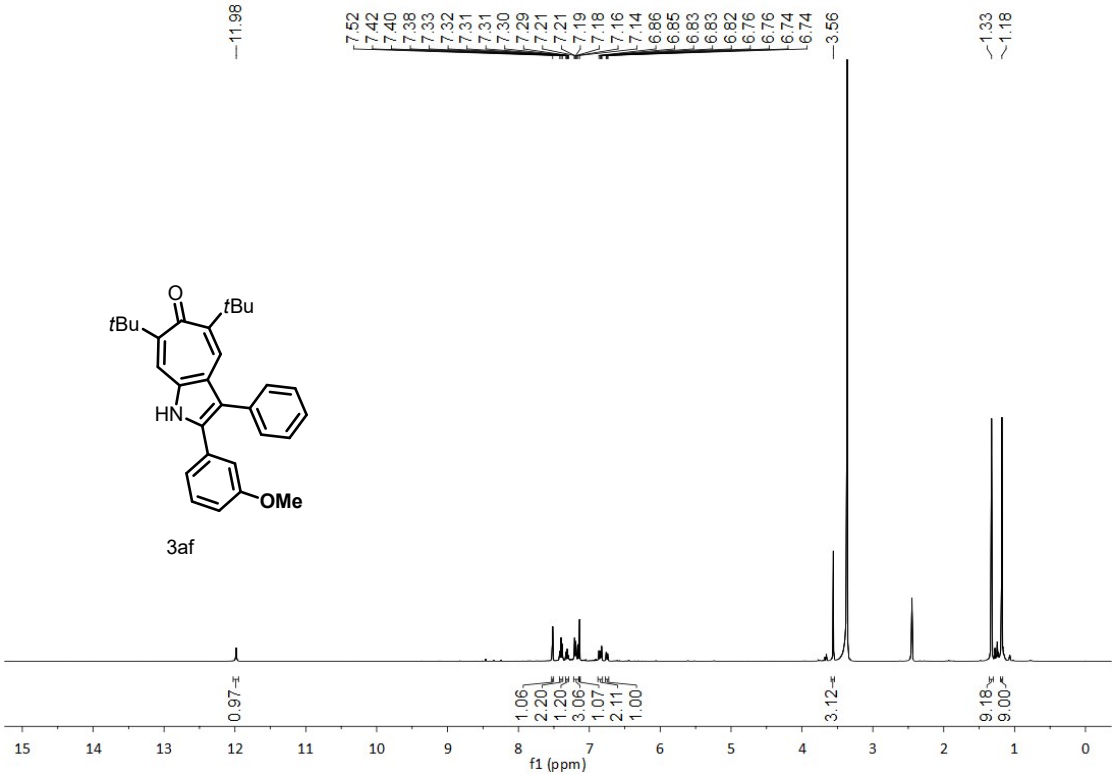


HRMS of 3ae

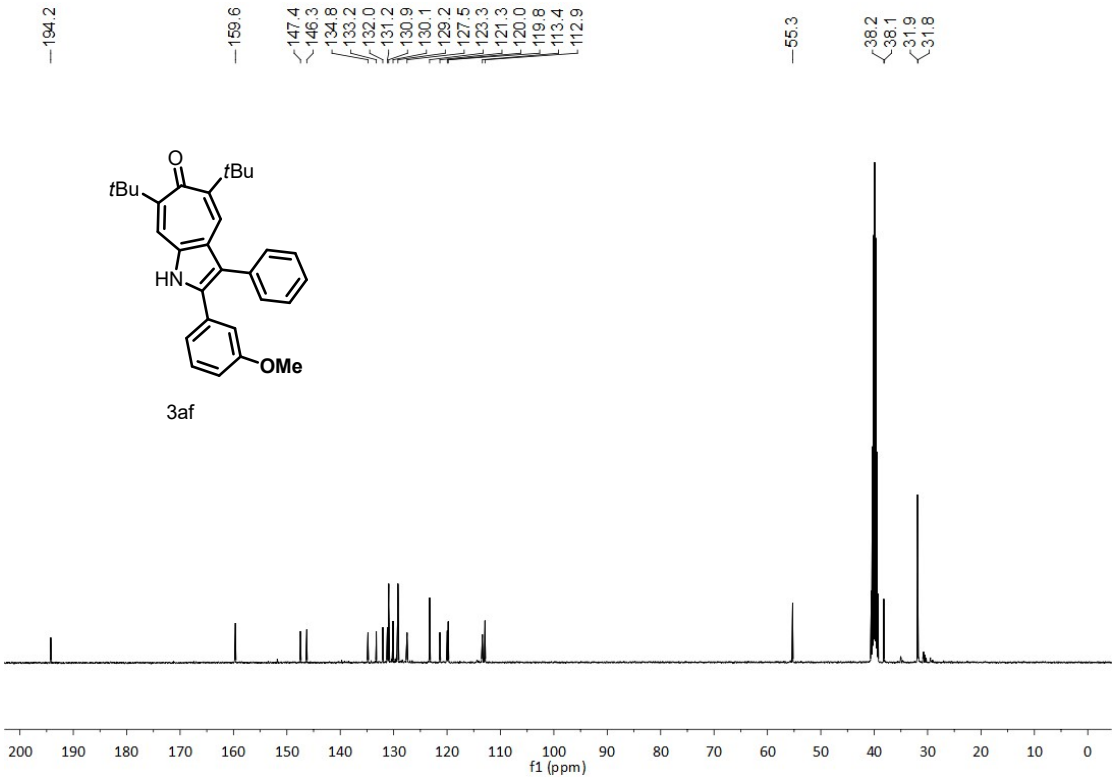


5,7-di-tert-butyl-2-(3-methoxyphenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3af)

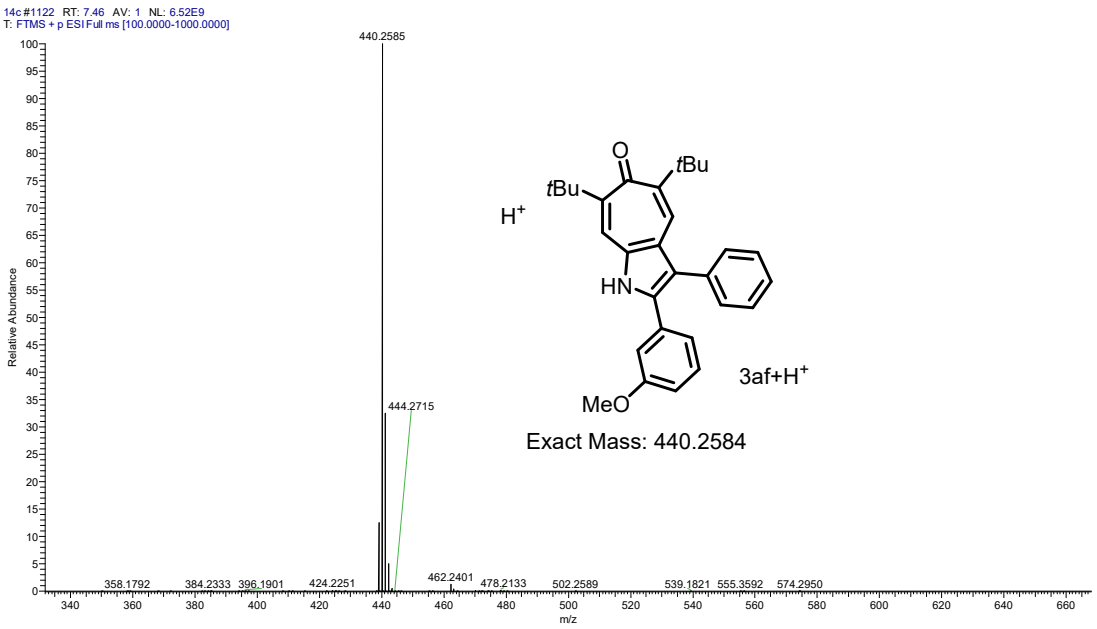
^{1}H NMR (400 MHz, D^{6}-DMSO):



^{13}C NMR (100 MHz, D^6-DMSO):

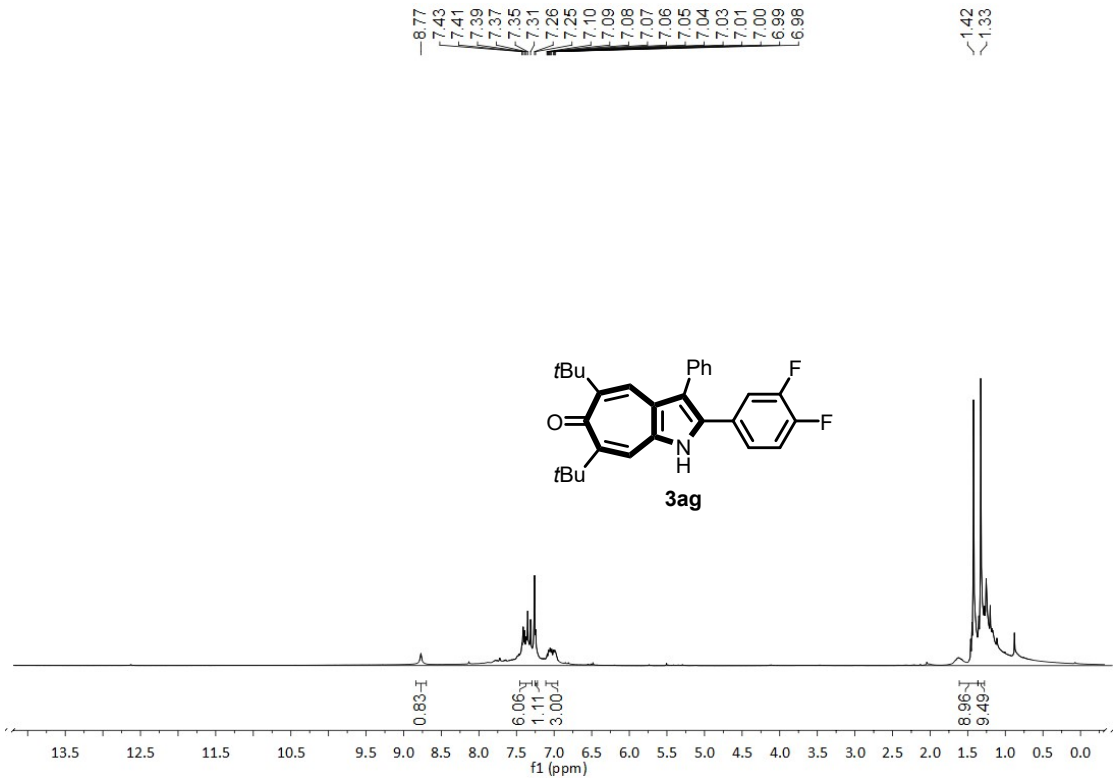


HRMS of 3af

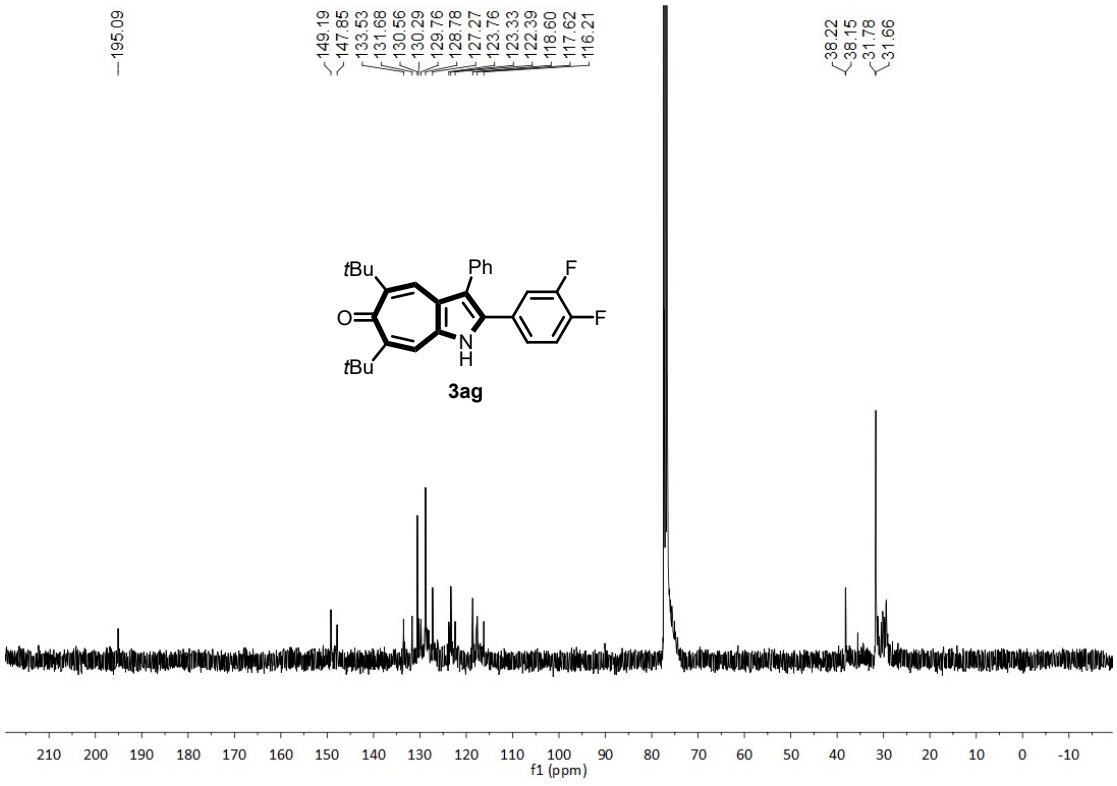


5,7-di-tert-butyl-2-(3,4-difluorophenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ag)

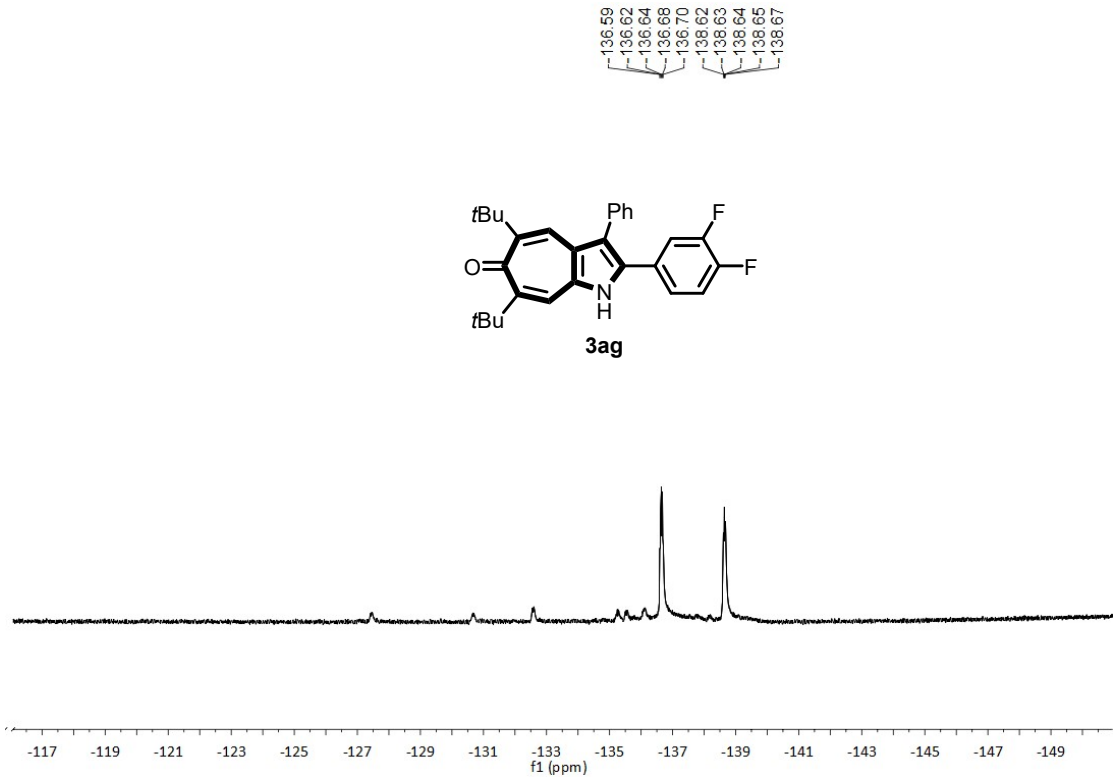
^{1}H NMR (400 MHz, $CDCl_3$):



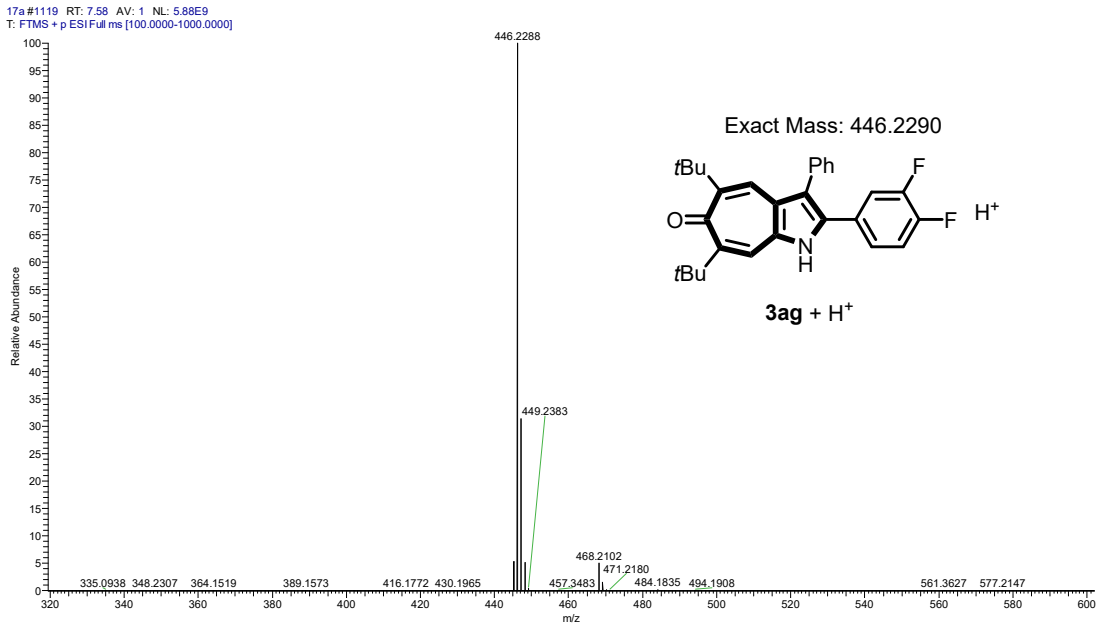
^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):

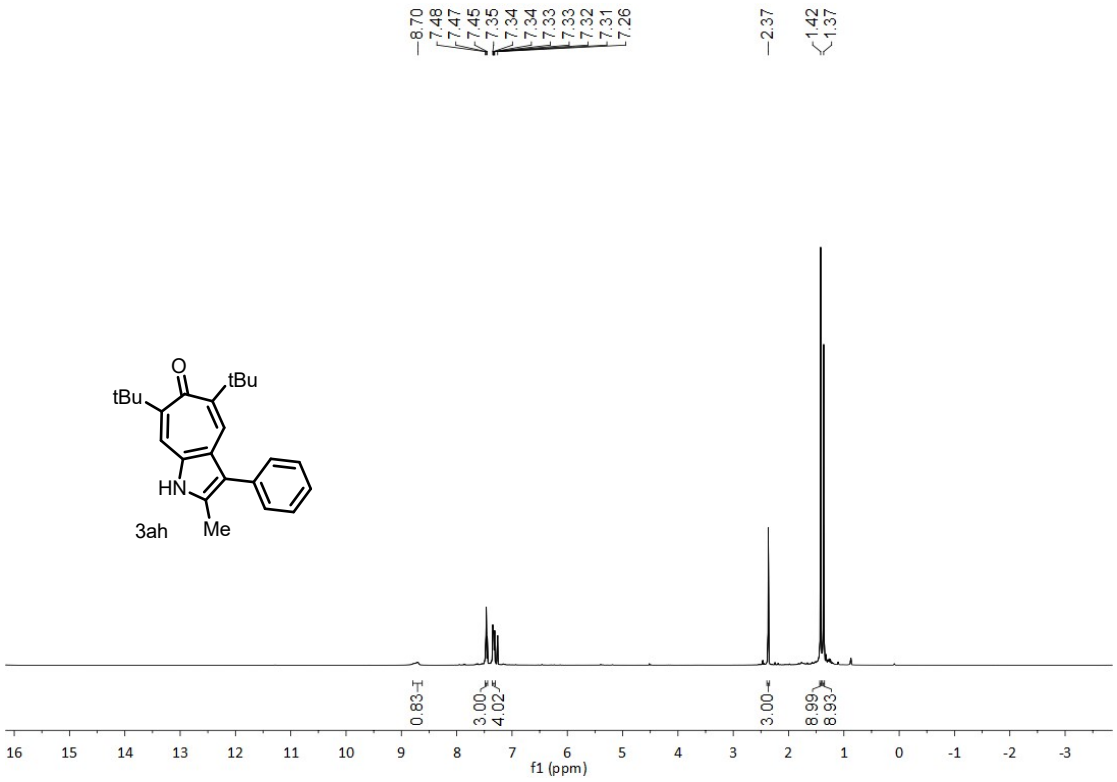


HRMS of 3ag

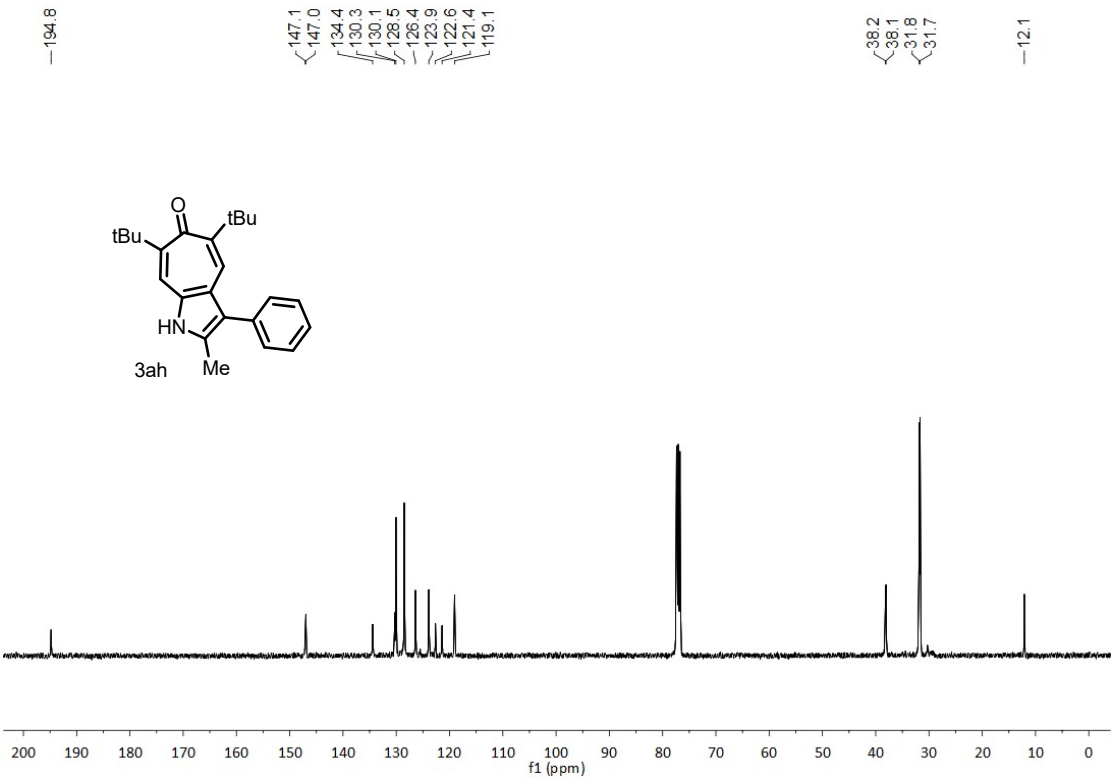


5,7-di-tert-butyl-2-methyl-3-phenylcyclohepta[b]pyrrol-6(1H)-one (3ah)

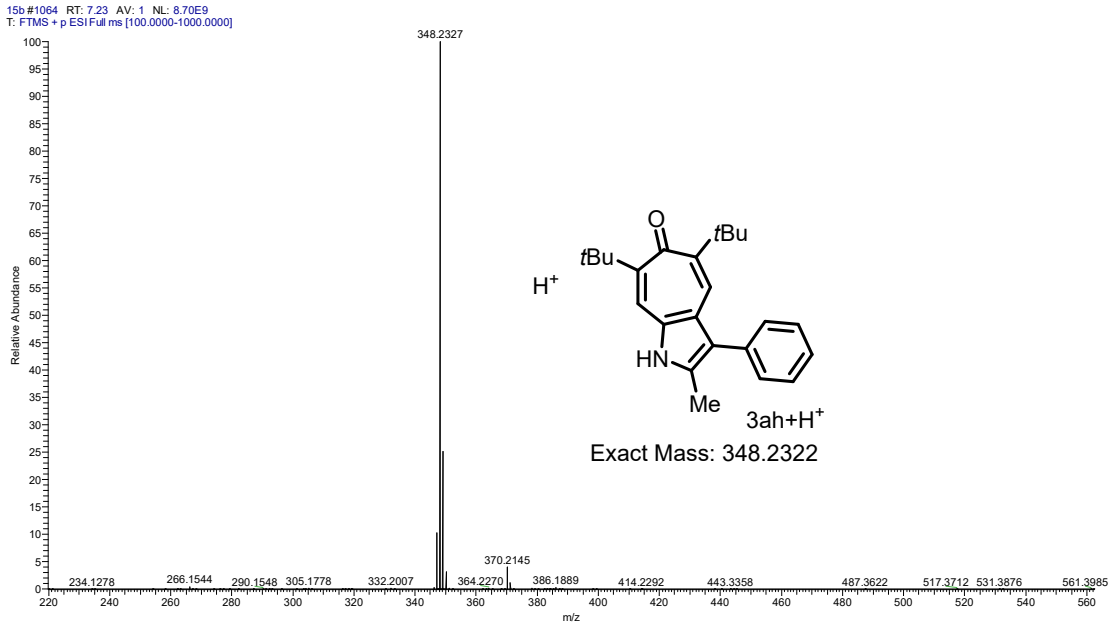
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

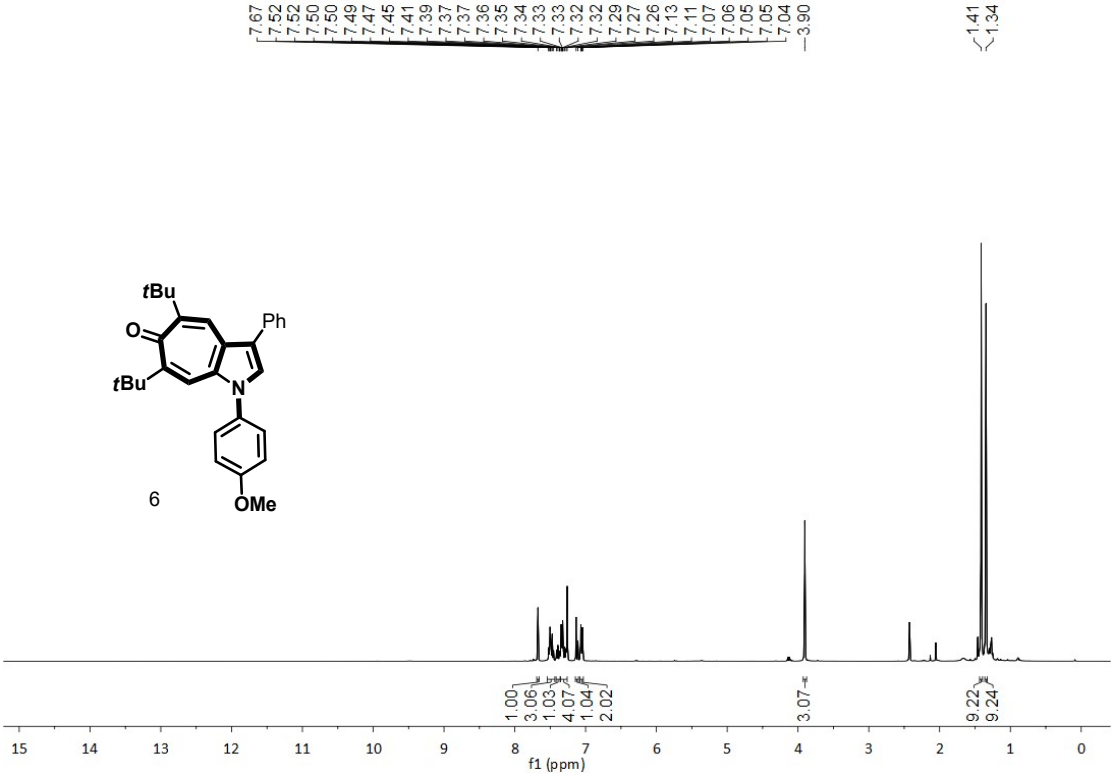


HRMS of 3ah

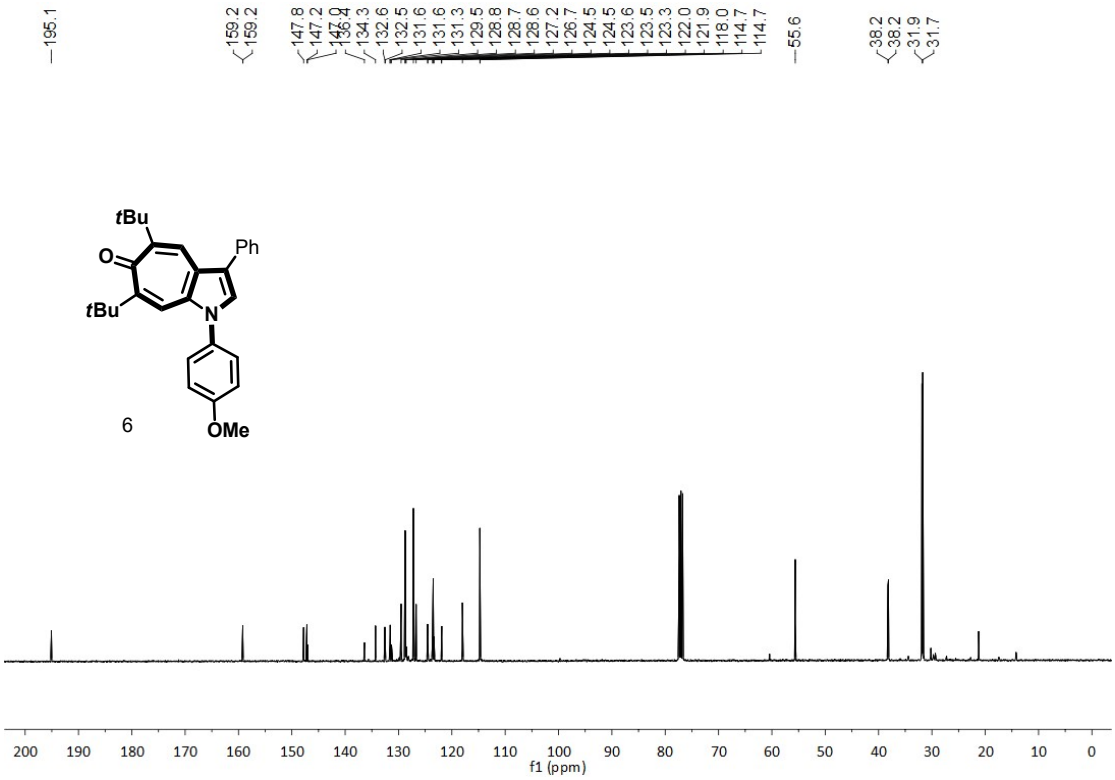


5,7-di-tert-butyl-1-(4-methoxyphenyl)-3-phenylcyclohepta[b]pyrrol-6(1H)-one (6)

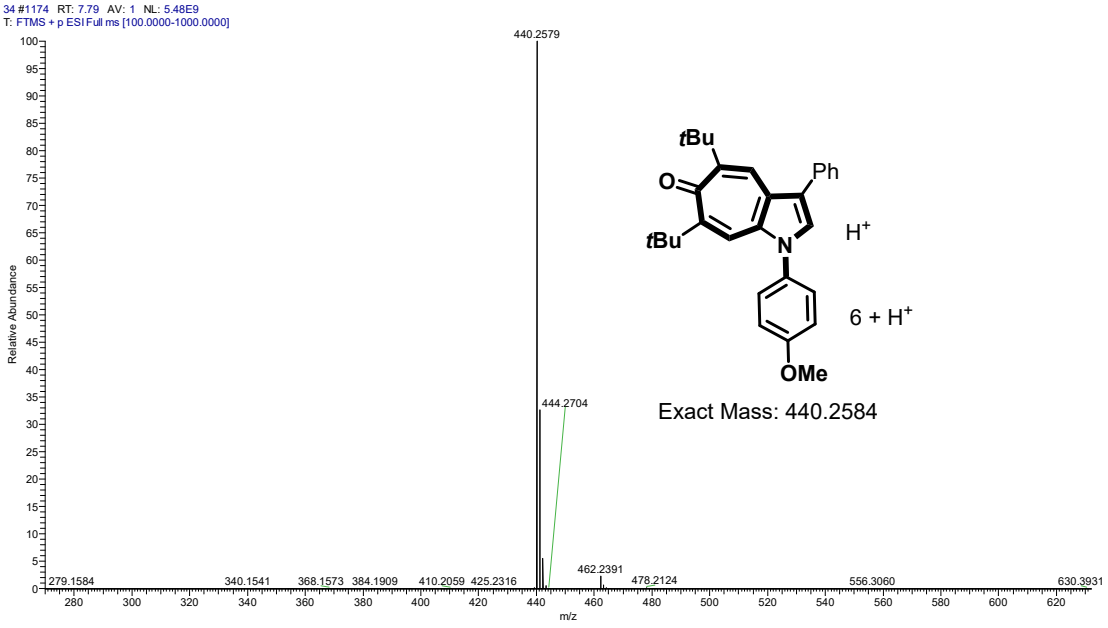
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

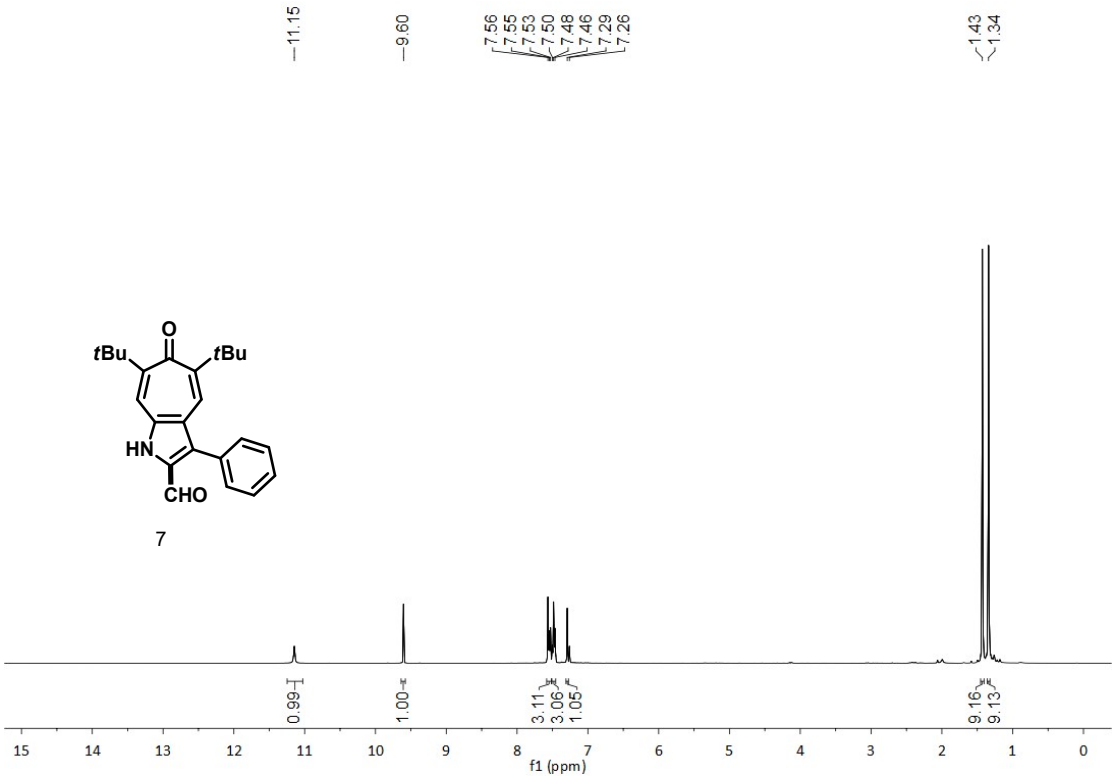


HRMS of 6



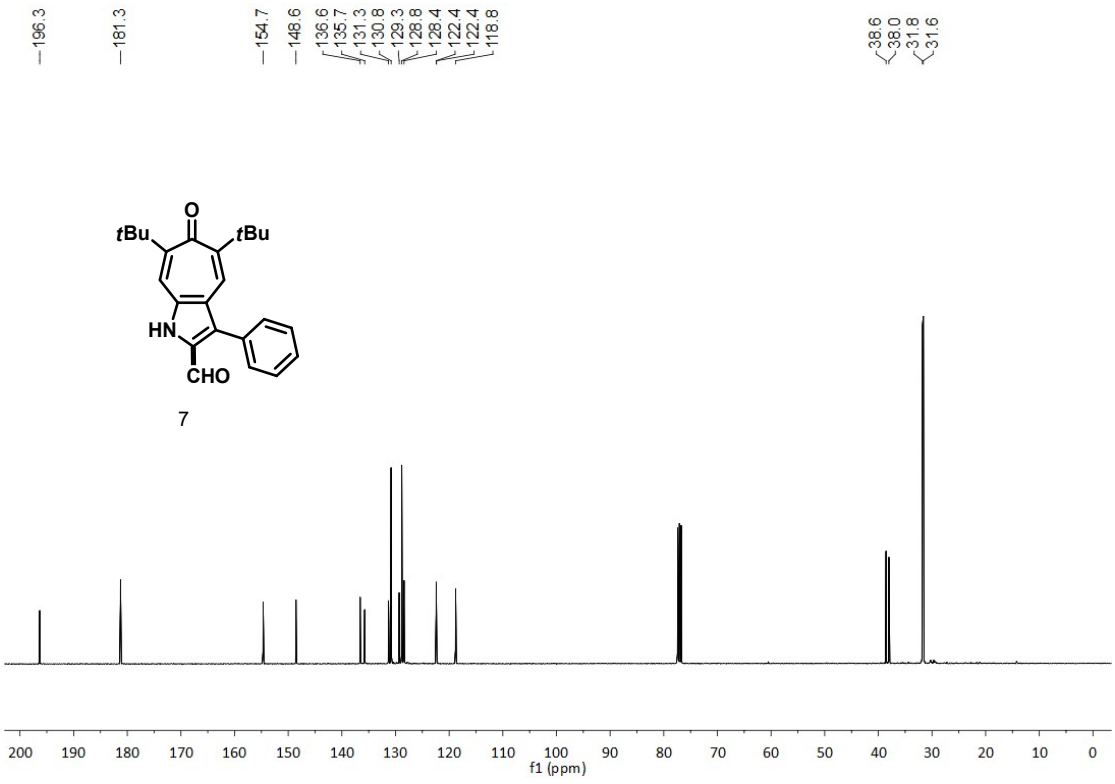
5,7-di-tert-butyl-6-oxo-3-phenyl-1,6-dihydrocyclohepta[b]pyrrole-2-carbaldehyde (7)

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



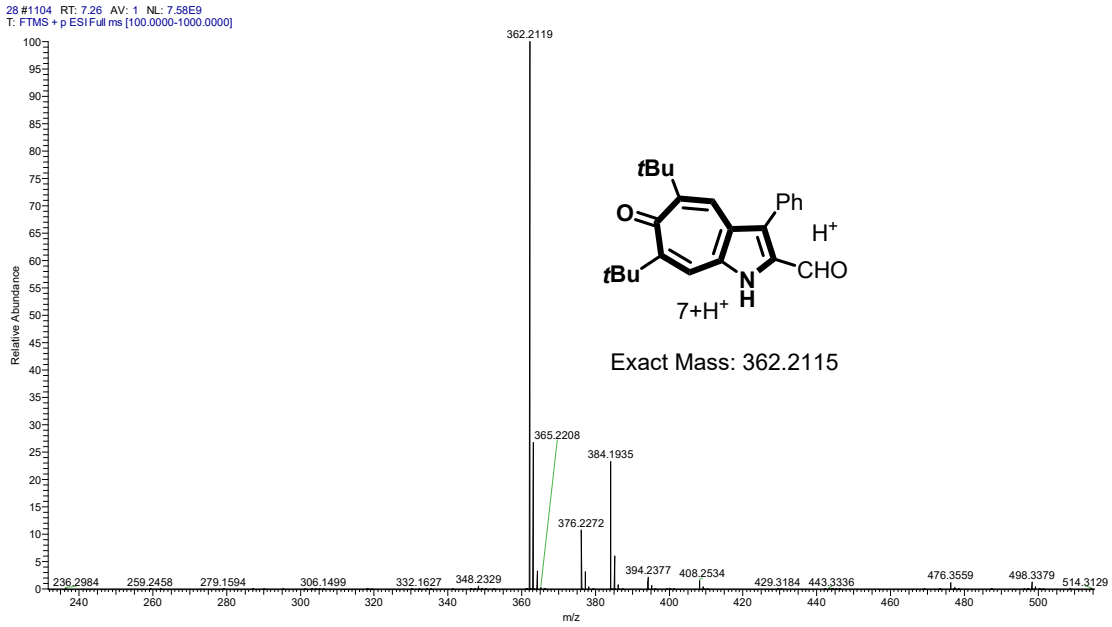
7

^{13}C NMR (100 MHz, $CDCl_3$):



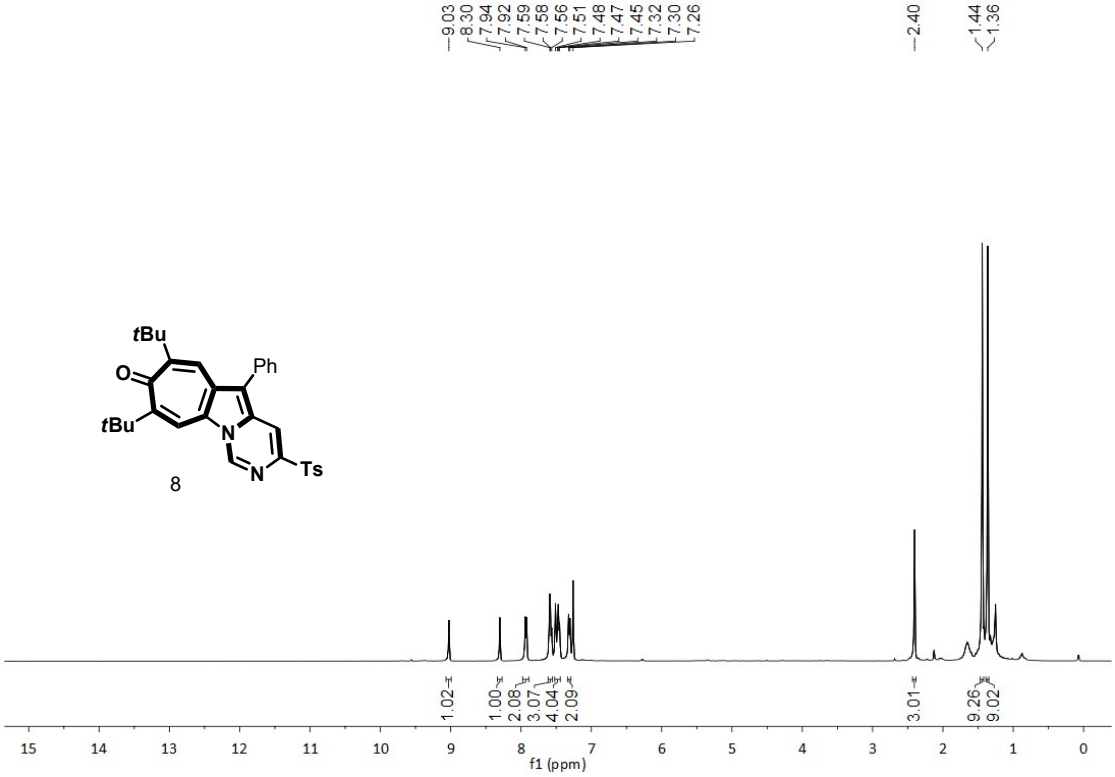
7

HRMS of 7

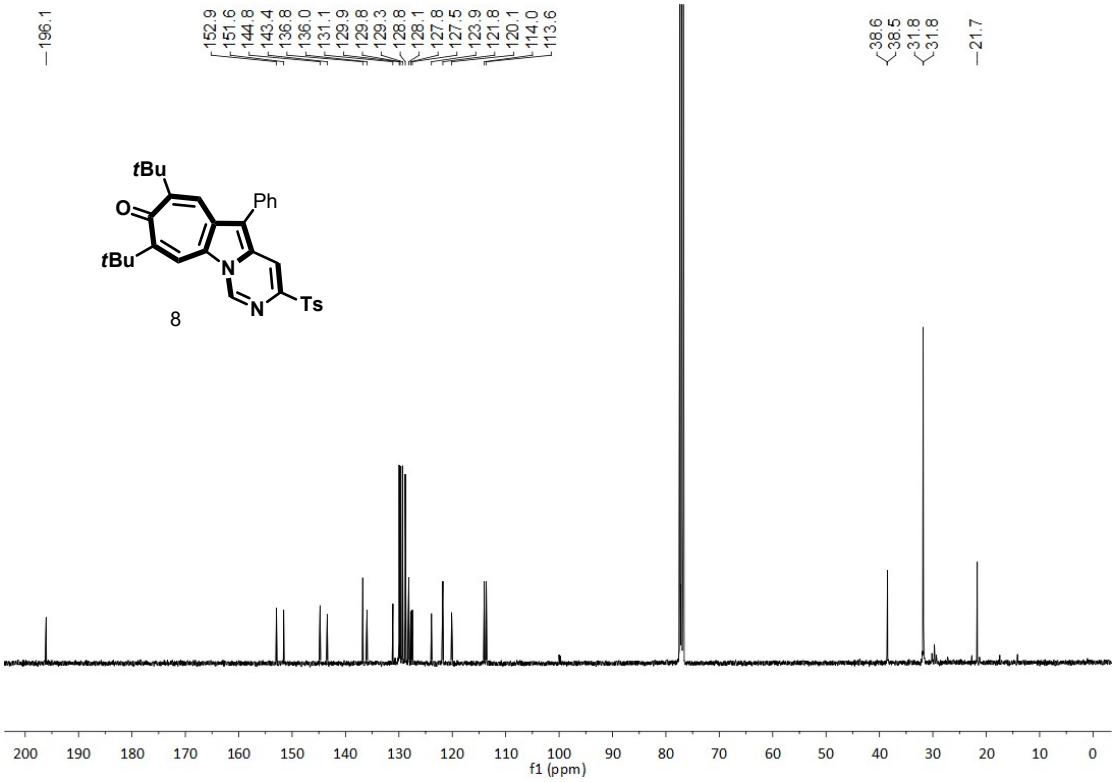


7,9-di-tert-butyl-5-phenyl-3-tosyl-8H-cyclohepta[4,5]pyrrolo[1,2-c]pyrimidin-8-one (8)

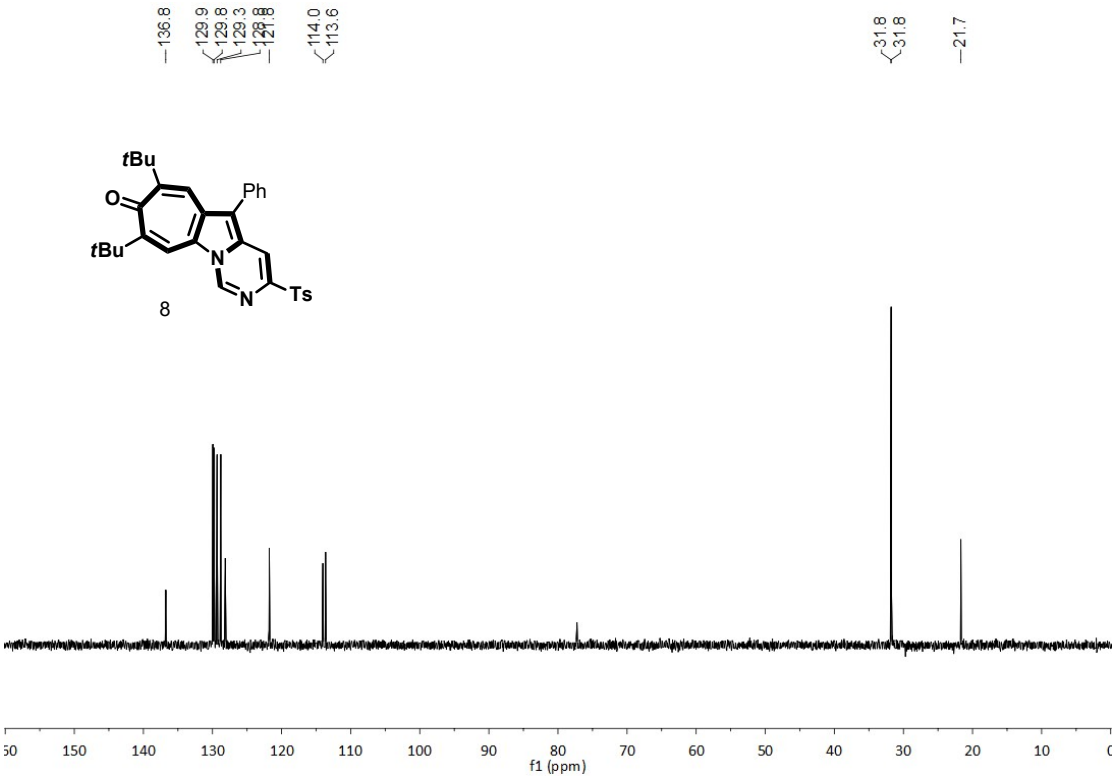
^{1}H NMR (400 MHz, $CDCl_3$):



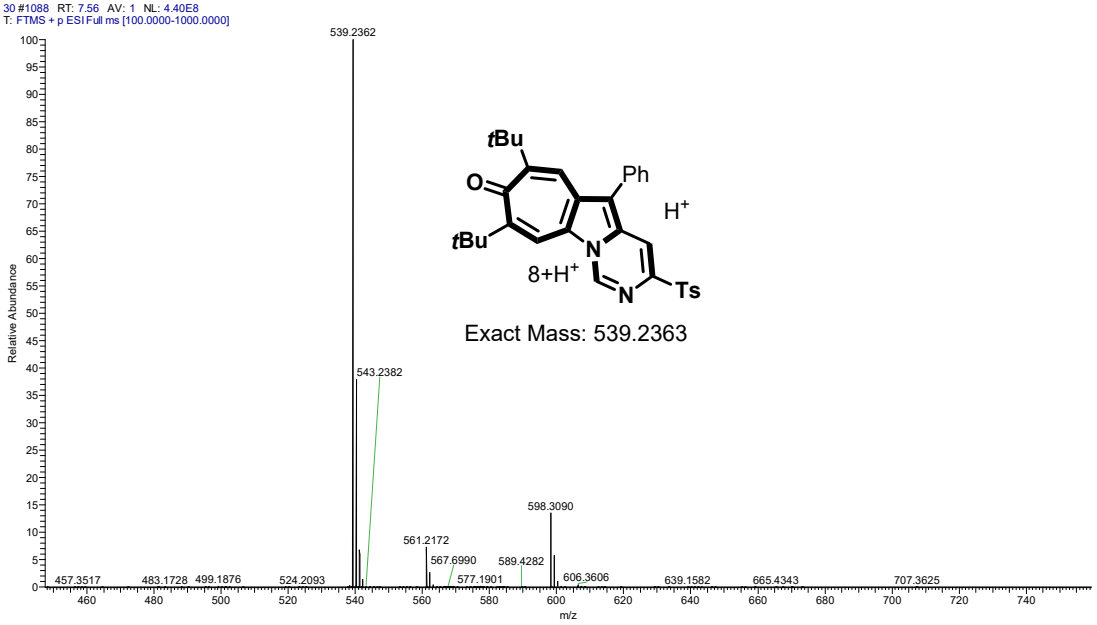
^{13}C NMR (100 MHz, $CDCl_3$):



DEPT 135

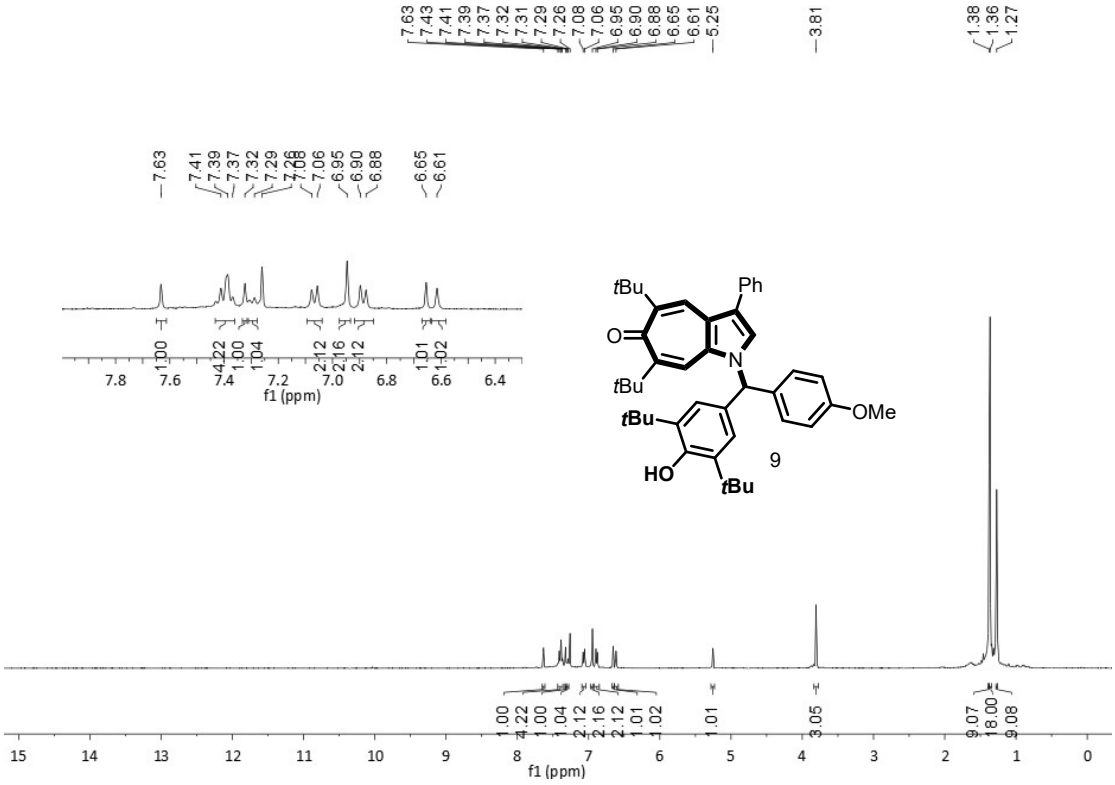


HRMS of 8

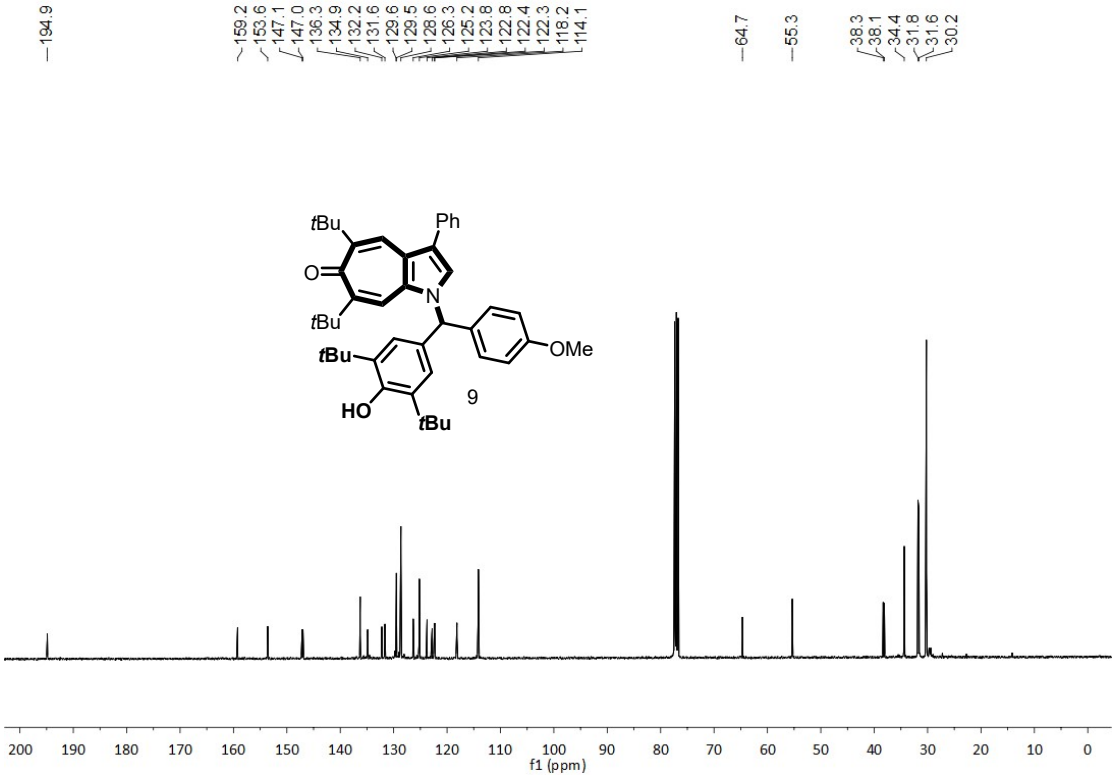


5,7-di-tert-butyl-2-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-3-(4-methoxyphenyl)cyclo-hepta[b]pyrrol-6(1H)-one (9)

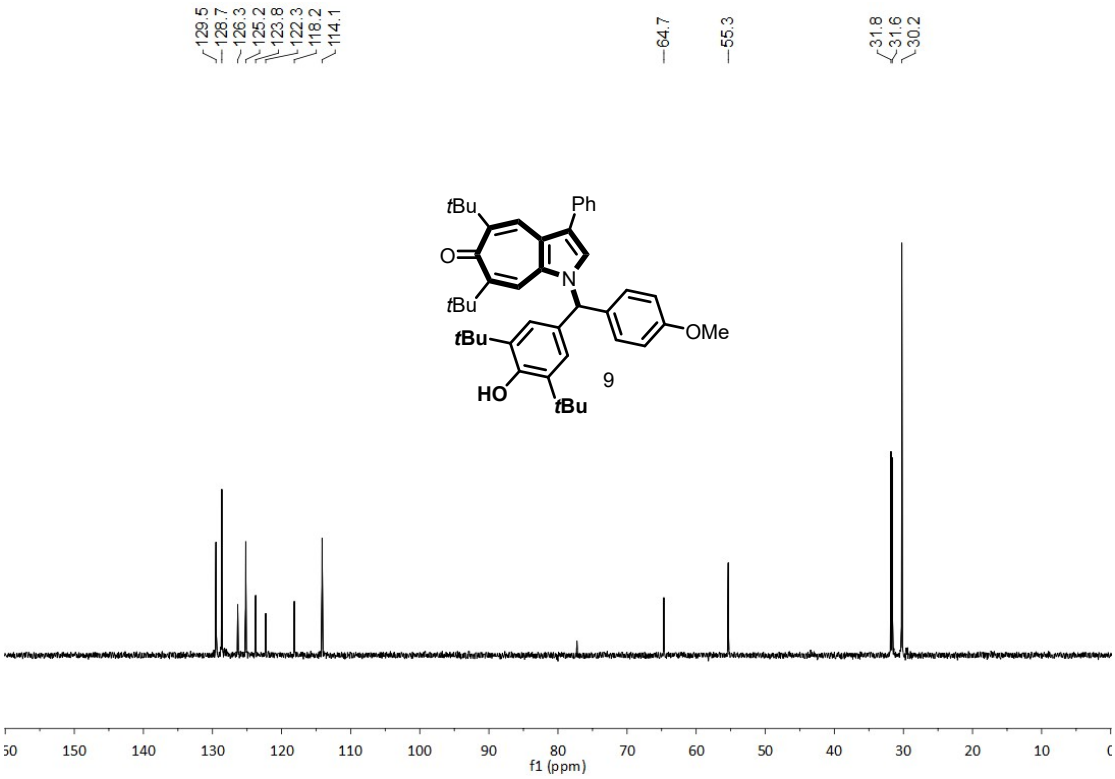
^{1}H NMR (400 MHz, $CDCl_3$):



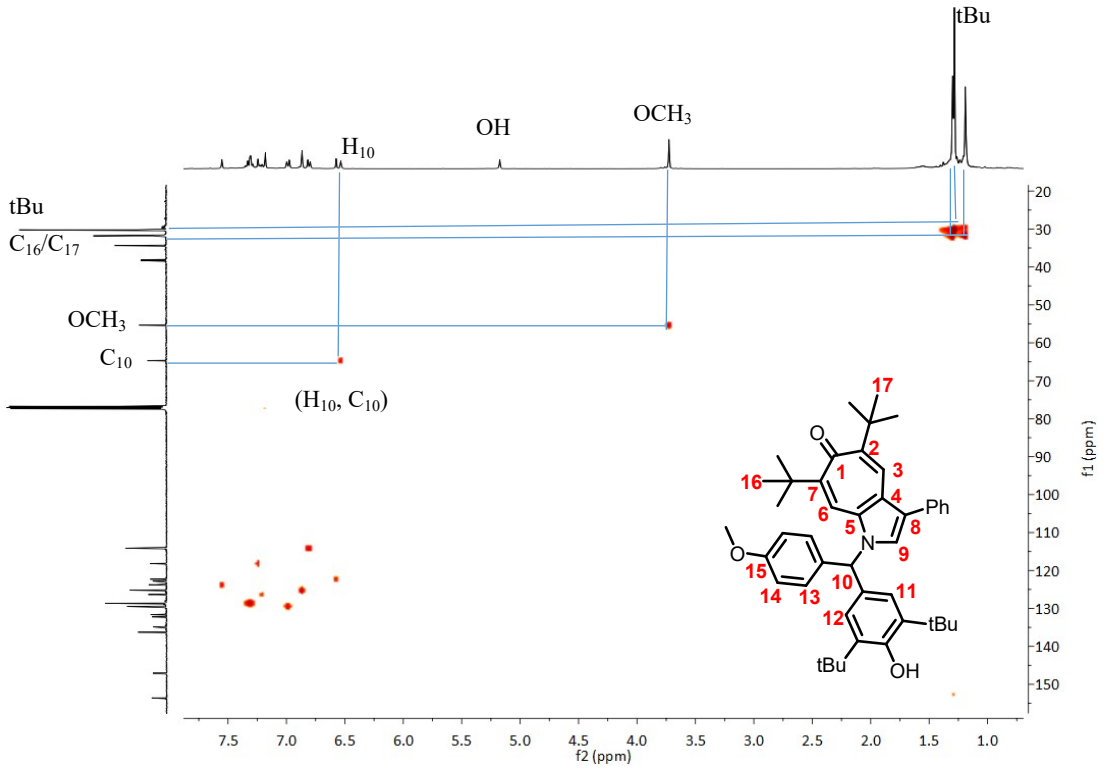
^{13}C NMR (100 MHz, $CDCl_3$):



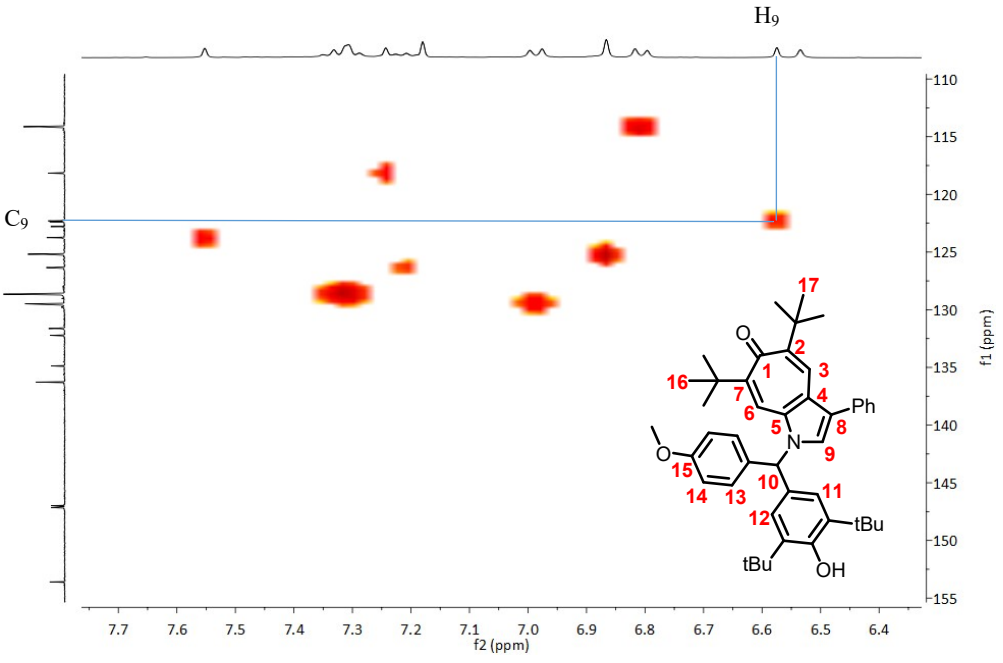
DEPT 135



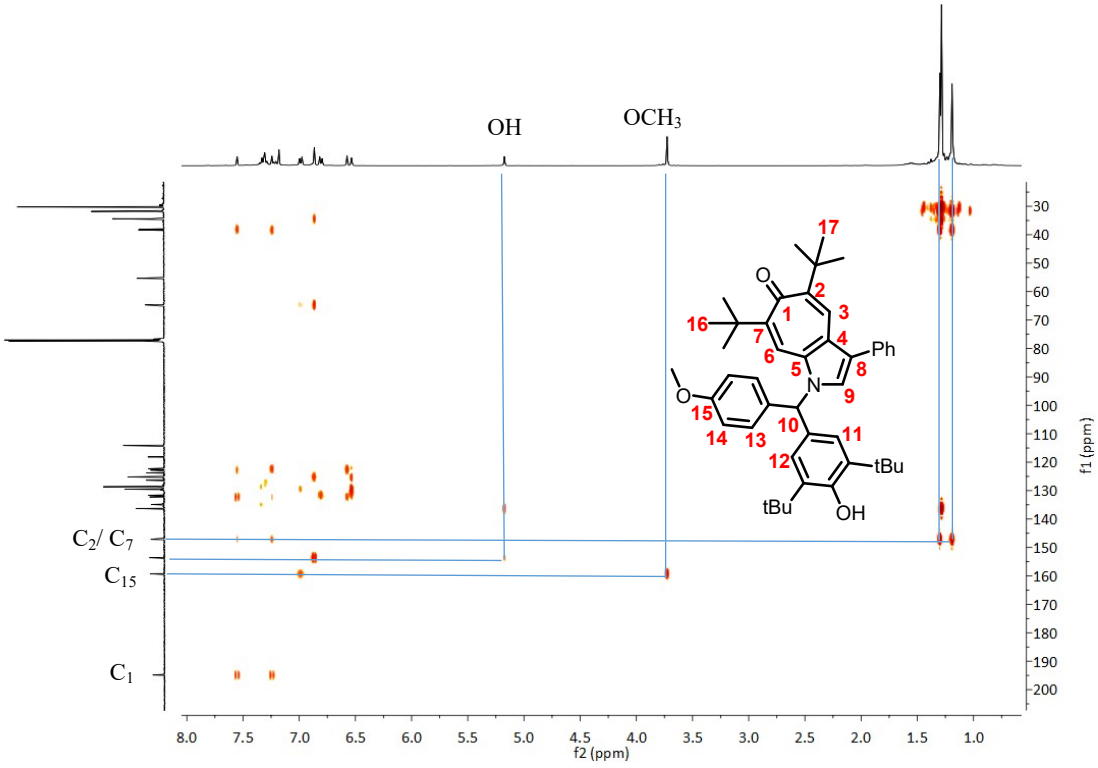
HSQC


tBu
OCH3
OH
H10
tBu
C16/C17
OCH3
C10
(H10, C10)
f2 (ppm)
f1 (ppm)

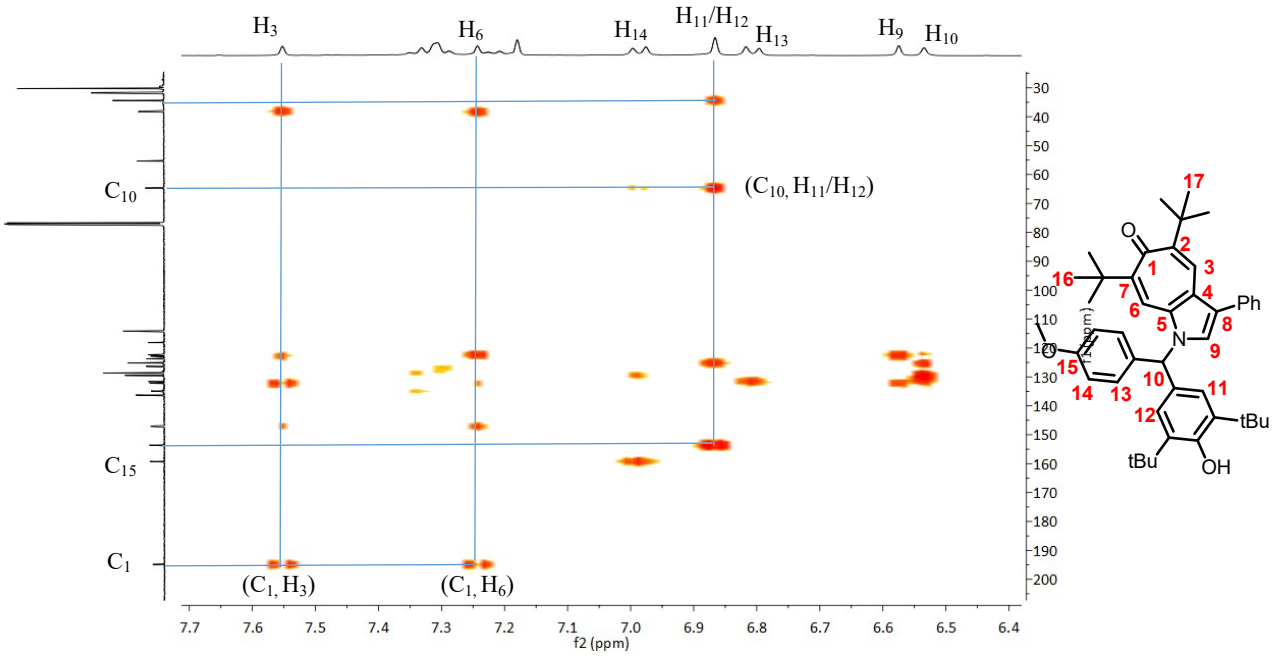
HSQC


H9
C9
f2 (ppm)
f1 (ppm)

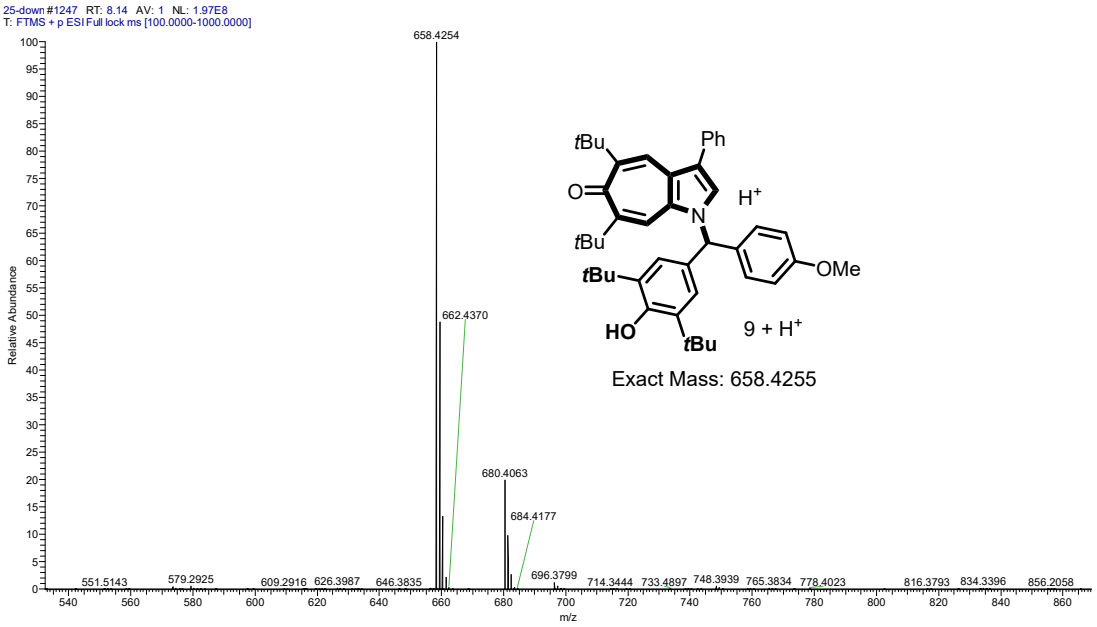
HMBC


OH
OCH3
C2/ C7
C15
C1
f2 (ppm)
f1 (ppm)
Ph
tBu
tBu
OH

HMBC


H3
H6
H14
H11/H12
H13
H9
H10
C10
C15
C1
(C10, H11/H12)
(C1, H3)
(C1, H6)
f2 (ppm)
f1 (ppm)
Ph
tBu
tBu
OH

HRMS of 9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684.4177
551.5143
579.2925
609.2916
626.3987
646.3835
696.3799
714.3444
733.4897
748.3939
765.3834
778.4023
816.3793
834.3396
856.2058
Relative Abundance
m/z
tBu
Ph
O
H+
N
tBu
tBu
OMe
HO
tBu
9 + H+
Exact Mass: 658.4255