Supporting Information

Brønsted acid-catalyzed cascade cyclization: an efficient strategy for divergent synthesis of cyclohepta[*b*]indole derivatives

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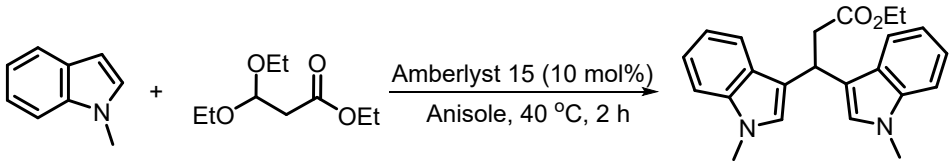
1. General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The reactions were monitored by TLC with Haiyang GF-254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or $KMnO_4$ as visualizing agents as needed. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra and ^{13}C NMR spectra were respectively recorded on Brüker AV-400 spectrometers. Chemical shifts (δ) were expressed in ppm relative to Me_4Si in $CDCl_3$, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra (HRMS) were recorded on Brüker Compass Data Analysis 4.0. IR spectra were recorded on a Bruker FT-IR (EQUINOX 55) using KBr pellets or neat liquid technology.

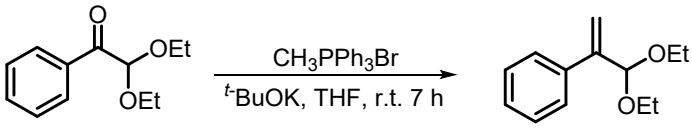
2. Preparation of materials.

2.1 Preparation of bis(indolyl)methane (BIM)



To the solution of *N*-methylindole (1.31 g, 10 mmol) in anisole (15.0 mL) was added ethyl 3,3-diethoxypropionate (0.95 g, 5 mmol) and Amberlyst 15 (0.11g, 0.5 mmol). The reaction mixture was stirred at 40 °C for 2 h. After the completion of the reaction, resulting mixture was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by column chromatography (PE/EA = 5/1) to afford the desired BIM (94%).

2.2 Preparation of atropaldehyde acetal

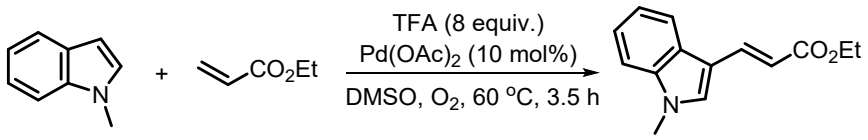


According to literature report,[1] atropaldehyde acetal was synthesized by the methods below:

A suspension of 8.57 g (24 mmol) of methyltriphenylphosphonium bromide and 2.69 g (24 mmol) of potassium *t*-butoxide in 35 mL of dried THF was stirred at room temperature for 30 min. Subsequently, 4.16 g (20 mmol) of 2,2-diethoxyacetophenone was added, and the reaction mixture

was stirred at room temperature for 7 h. The reaction mixture was then filtered through a pad of Celite and the filtrate was concentrated on a rotary evaporator and then purified by silica gel column chromatography (PE/EA = 20/1) to give the pure product.

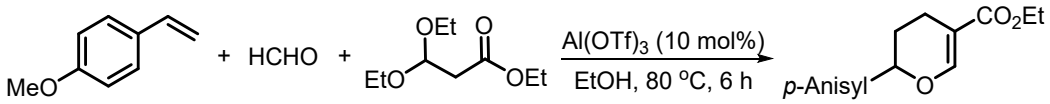
2.3 Preparation of 3-vinylindole



According to literature report,[2] atropaldehyde acetal was synthesized by the methods below:

A sealed tube containing N-methylindoles (1 mmol) and $Pd(OAc)_2$ (10 mol %), was evacuated and filled with dioxygen gas using an oxygen containing balloon. Then, DMSO (5.0 mL) and trifluoroacetic acid (TFA) (8.0 mmol) were sequentially added to the system via syringe under an oxygen atmosphere. After that, ethyl acrylate (1.50 mmol) was added and the reaction mixture was stirred at 60 °C until completion of the reaction (TLC). Then the reaction was cooled to room temperature and partitioned between water and ethyl acetate. The layers were separated and the organic layer was washed with aqueous saturated brine solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography (PE/EA = 20/1) to afford the desired C-3 alkenylated indole product (83%).

2.4 Preparation of 2-aryl 3,4-dihydropyran

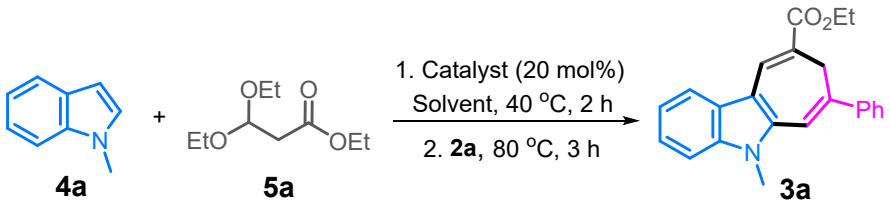


According to similar literature reports,[3] 2-aryl 3,4-dihydropyran was synthesized by the methods below:

The synthesis was performed in a 25 ml of round bottomed flask equipped with magnetic stirring. 4-Methoxystyrene (1.34 g, 10 mmol), ethyl 3,3-diethoxypropionate (1.9 g, 10 mmol) and an aqueous solution of formaldehyde (30 wt %, 4.0 g, 40 mmol) were mixed in EtOH (15 mL), and then stirred at 80 °C for 6 hours. After the completion of the reaction, resulting mixture was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by column chromatography (PE/EA = 10/1) to afford the desired 2-aryl 3,4-dihydropyran (86%).

3. Optimization of the reaction conditions

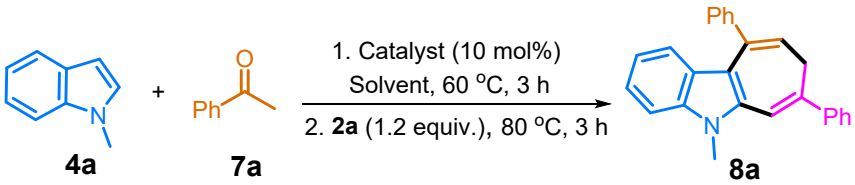
Table S1 Optimization of the reaction of **4a**, **5a** and **2a** for the synthesis of **3a**.[a]



Entry	Catalyst	Solvent	Ratio (**4a**/**5a**/**2a**)	Yield (%)[b]
1	$ZnCl_2$	Toluene	1 : 1 : 1	Trace
2	$FeCl_3$	Toluene	1 : 1 : 1	Messy
3	$BiCl_3$	Toluene	1 : 1 : 1	Messy
4	$Sc(OTf)_3$	Toluene	1 : 1 : 1	28
5	$Bi(OTf)_3$	Toluene	1 : 1 : 1	45
6	PTSA	Toluene	1 : 1 : 1	63
7	MsOH	Toluene	1 : 1 : 1	51
8	Amberlyst 15	Toluene	1 : 1 : 1	35
9	PTSA	DCE	1 : 1 : 1	43
10	PTSA	1,4-Dioxane	1 : 1 : 1	48
11	PTSA	Anisole	1 : 1 : 1	67, (65)[c]
12	PTSA	PhCl	1 : 1 : 1	56
13[c]	PTSA	Anisole	1.2 : 1 : 1	72
14[c]	PTSA	Anisole	1.5 : 1 : 1.2	80
15[c]	PTSA	Anisole	2 : 1 : 1.5	84

[a] Unless otherwise noted, all reactions were performed in one pot stepwise manner. Reaction conditions: a mixture of **4a** (0.2 mmol), **5a** (0.2 mmol) and catalyst (20 mol%) was firstly stirred in solvent (1 mL) at 40 °C for 2 h, and then **2a** (0.2 mmol) was added, and the mixture was stirred at 80 °C for another 3 h. [b] Isolated yield based on **5a**. [c] PTSA, 0.02 mmol.

Table S2 Optimization of the reaction of **4a**, **7a** and **2a** for the synthesis of **8a**.[a]

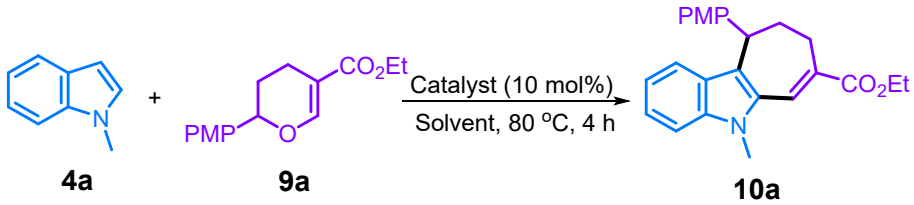


Entry	Catalyst	Solvent	Yield (%)[b]
1	$Al(OTf)_3$	Anisole	28
2	$AlCl_3$	Anisole	ND
3	PTSA	Anisole	59
4	MsOH	Anisole	42
5	TfOH	Anisole	Trace

6	PTSA	CH_3CN	27
7	PTSA	DCE	ND
8	PTSA	1,4-Dioxane	12
9	PTSA	EtOH	Trace
10	PTSA	DEC	31

[a] Unless otherwise noted, all reactions were performed in one pot stepwise manner. Reaction conditions: a mixture of **4a** (0.2 mmol), **7a** (0.2 mmol) and catalyst (10 mol%) was firstly stirred in solvent (1 mL) at 60 °C for 3 h, and then **2a** (0.24 mmol) was added, and the mixture was stirred at 80 °C for another 3 h. [b] Isolated yield based on **4a**. DEC = Diethyl carbonate. ND = No desired product.

Table S3 Optimization of the reaction of **4a** and **9a** for the synthesis of **10a**.[a]

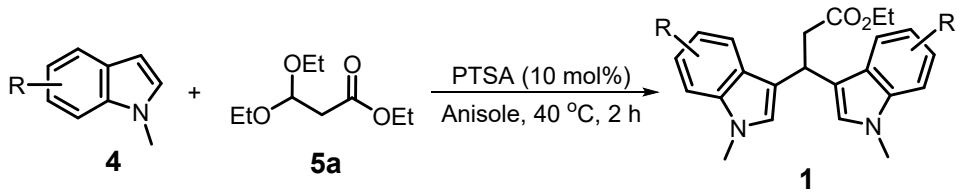


Entry	Catalyst	Solvent	Yield (%)[b]
1	$Al(OTf)_3$	EtOH	23
2	$AlCl_3$	EtOH	17
3	TFA	EtOH	Trace
4	PTSA	EtOH	46, (85)[c]
5	TfOH	EtOH	55, (88)[c]
6[c]	TfOH	^iPrOH	63
7[c]	TfOH	CH_3CN	34
8[c]	TfOH	1,4-Dioxane	56
9[c]	TfOH	DCE	23
10[c]	TfOH	CH_3NO_2	19
11[c]	TfOH	Toluene	74

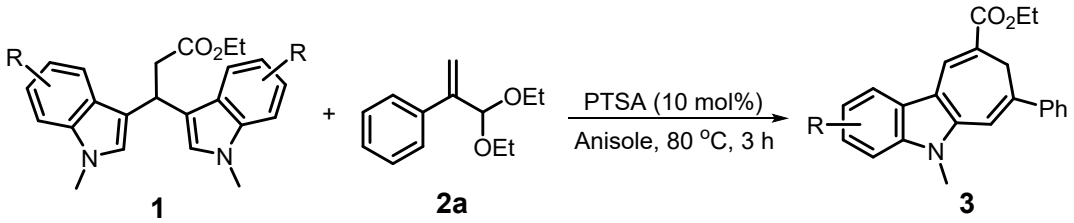
[a] Unless otherwise noted, all reactions were performed with **4a** (0.36 mmol), **9a** (0.3 mmol), catalyst (10 mol%), solvent (1 mL) in sealed tube at 80 °C for 4 h. [b] Isolated yield. [c] Performing the reaction at 100 °C.

4. General procedure

4.1 General procedure for the synthesis of compounds 3 in two separate steps

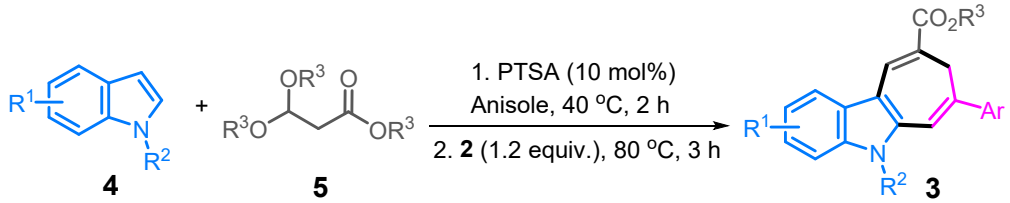


The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **4** (0.3 mmol), **5a** (0.2 mmol) and PTSA (0.02 mmol, 10 mol%) in anisole (1 mL) was stirred at 40 °C for 2 h. Subsequently, the resulting mixture was extracted with 5 mL ethyl acetate, washed with 2 mL water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography using PE/EA as eluent to afford the desired product BIM **1**.



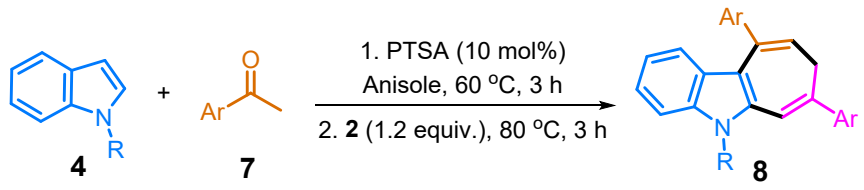
The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The resulting BIM **1** was mixed with **2a** (1.2 equiv.) and PTSA (10 mol%) in anisole (0.5 mL) and was stirred at 80 °C for 3 h. Subsequently, the resulting mixture was extracted with 4 mL ethyl acetate, washed with 2 mL water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography using PE/EA as eluent to afford the desired product **3**.

4.2 General procedure for the synthesis of compounds 3 in one-pot manner



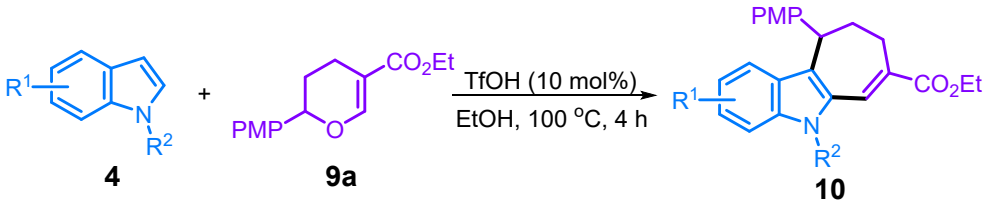
The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **4** (0.3 mmol), **5** (0.2 mmol) and PTSA (0.02 mmol, 10 mol%) in anisole (1 mL) was stirred at 40 °C for 2 h. Subsequently, **2** (0.24 mmol) was added to the mixture and stirred at 80 °C for another 3 h. After the completion of the reaction, the mixture cooled to room temperature, and the resulting mixture was extracted with 5 mL ethyl acetate, washed with 2 mL water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography using PE/EA as eluent to afford the desired product.

4.3 General procedure for the synthesis of compounds 8 in one-pot manner



The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **4** (0.2 mmol), **7** (0.2 mmol) and PTSA (0.02 mmol, 10 mol%) in anisole (1 mL) was stirred at 60 °C for 3 h. Subsequently, **2** (0.24 mmol) was added to the mixture and stirred at 80 °C for another 3 h. After the completion of the reaction, the mixture cooled to room temperature, and the resulting mixture was extracted with 5 mL ethyl acetate, washed with 2 mL water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography using PE/EA as eluent to afford the desired product.

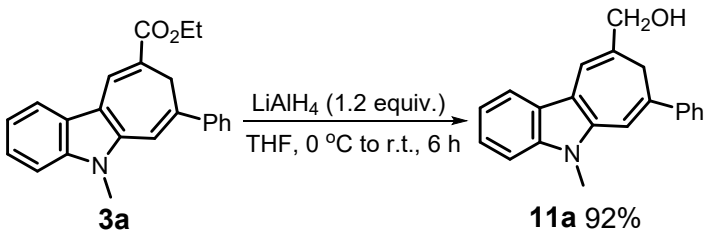
4.4 General procedure for the synthesis of compounds 10



The reactions were conducted in a 15 mL 15mL glass pressure tube equipped with oil bath and magnetic stirring. The mixture of **4** (0.36 mmol), **9a** (0.30 mmol) and TfOH (0.03 mmol, 10 mol%) in EtOH (1 mL) was stirred at 100 °C for 4 h. After the completion of the reaction, the mixture cooled to room temperature, and the resulting mixture was extracted with 5 mL ethyl acetate, washed with 2 mL water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography using PE/EA as eluent to afford the desired product.

5. Derivatization of products

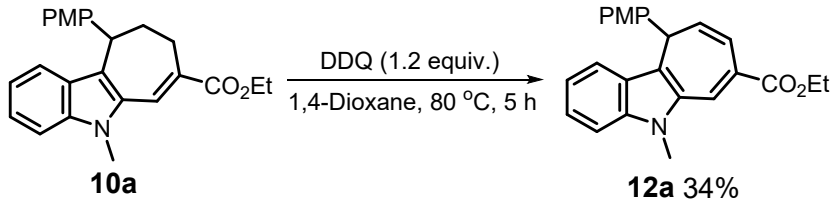
5.1 The reduction of 3a



To the suspension of $LiAlH_4$ (0.24 mmol) in THF (1.5 mL) was added dropwise a solution of **3a**

(0.2 mmol) in THF (1 mL) at 0 °C with continual stirring. Subsequently, the mixture was allowed to raise to room temperature, and stirred for 6 h. The reaction mixture was quenched with an aqueous NH_4Cl solution, worked up with EA and purified by silica gel column chromatography (PE/EA = 5/1 as eluent) to afford the desired alcohol product **11a** with 92% yield.

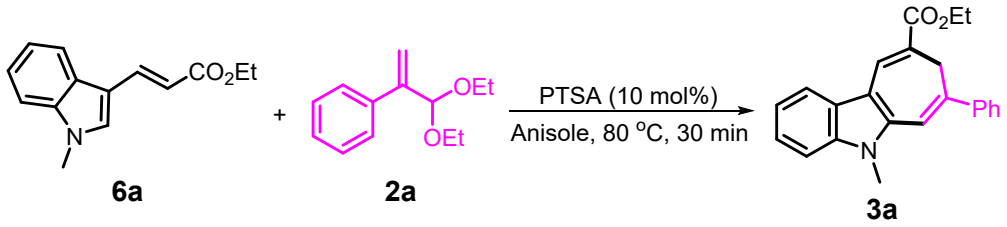
5.2 The oxidation of 10a



The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **10a** (0.2 mmol) and DDQ (0.24 mmol) in 1,4-dioxane (1 mL) was stirred at 80 °C for 5 h. After the completion of the reaction, the mixture cooled to room temperature, and the resulting mixture was filtered. Afterwards, the filtrate was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography (PE/EA = 12/1 as eluent) as eluent to afford the desired product **12a** with 34% yield.

6. Mechanism study

6.1 The synthesis of compounds 3 from 2a and 6a



The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **6a** (0.2 mmol), **2a** (0.2 mmol) and PTSA (0.02 mmol, 10 mol%) in anisole (1 mL) was stirred at 80 °C for 30 min. After that, the mixture cooled to room temperature, and the resulting mixture was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by silica gel column chromatography using PE/EA as eluent to afford the product **3a** with 92% yield.

6.2 The products detected by HRMS in the reaction of 4a and 5a

The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle

magnetic stirring. The mixture of **4a** (0.3 mmol), **5a** (0.2 mmol) and PTSA (0.02 mmol, 10 mol%) in anisole (1 mL) was stirred at 40 °C for 2 h. Subsequently, the resulting mixture was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Then the mixture was detected by HRMS.

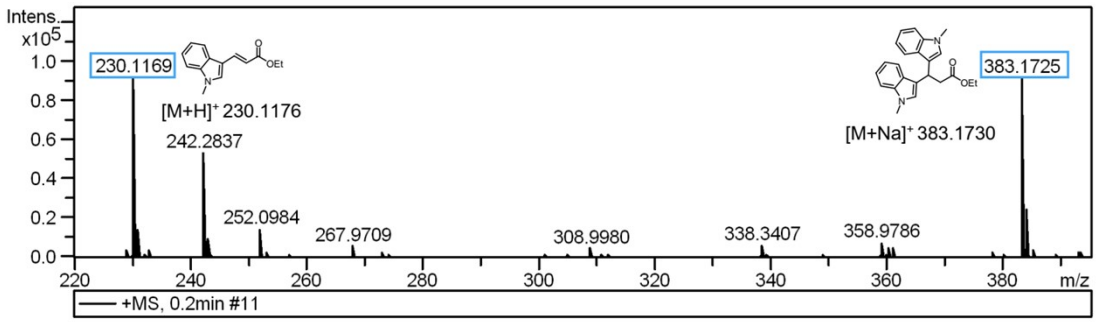


Fig. S1 The products detected by HRMS in the reaction of **4a** and **5a**.

6.3 The products detected by HRMS in the reaction of 4a and 7a

The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **4a** (0.2 mmol), **7a** (0.2 mmol) and PTSA (0.02 mmol, 10 mol%) in anisole (1 mL) was stirred at 60 °C for 3 h. Subsequently, the resulting mixture was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Then the mixture was detected by HRMS.

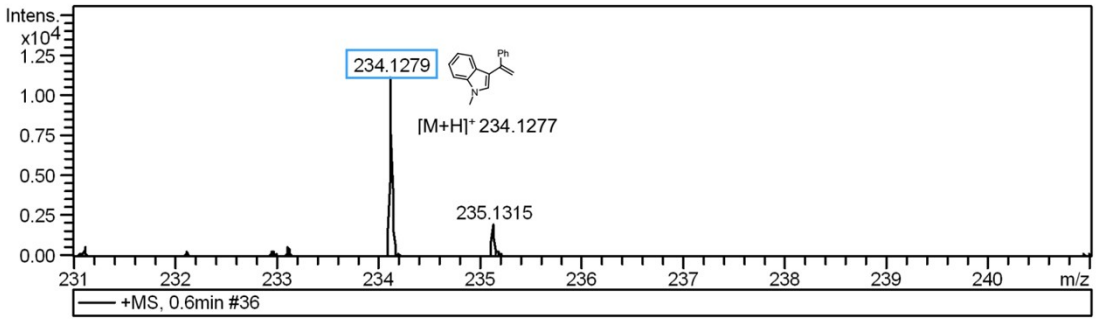


Fig. S2 The products detected by HRMS in the reaction of **4a** and **7a**.

6.4 The key intermediates detected by HRMS for the synthesis of compounds 10a

The reactions were conducted in a 15 mL of sealed tube equipped with oil bath and magnetic stirring. The mixture of **4** (0.36 mmol), **9a** (0.30 mmol) and TfOH (0.03 mmol, 10 mol%) in EtOH (1 mL) was stirred at 100 °C for 4 h. After the completion of the reaction, the mixture cooled to room temperature, and the resulting mixture was extracted with ethyl acetate, washed with water, and then concentrated by removing the solvent under vacuum. Then the mixture was detected by HRMS.

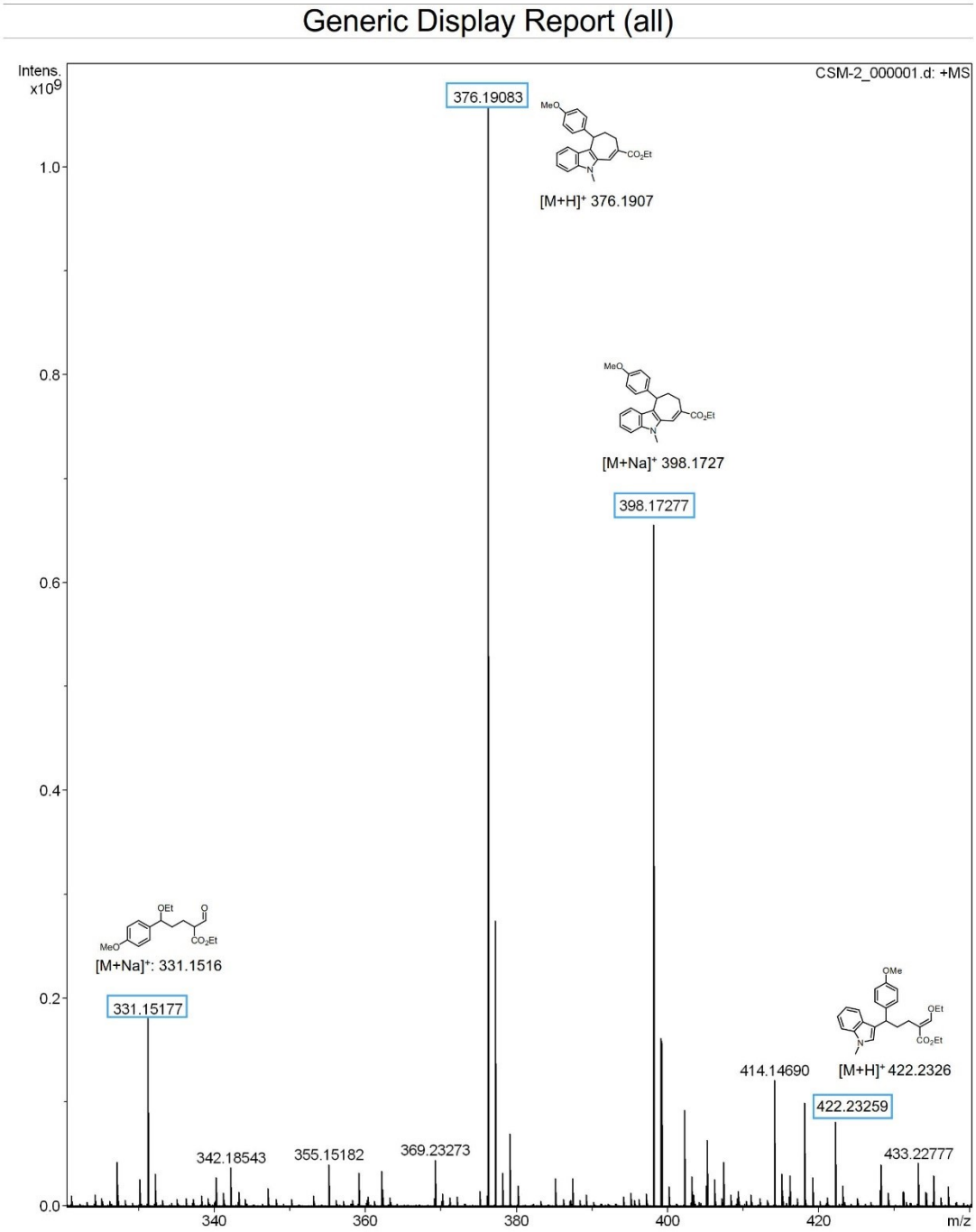


Fig. S3 The key intermediates detected by HRMS for the synthesis of compounds **10a**.

6.5 Proposed mechanism for the formation of 10a

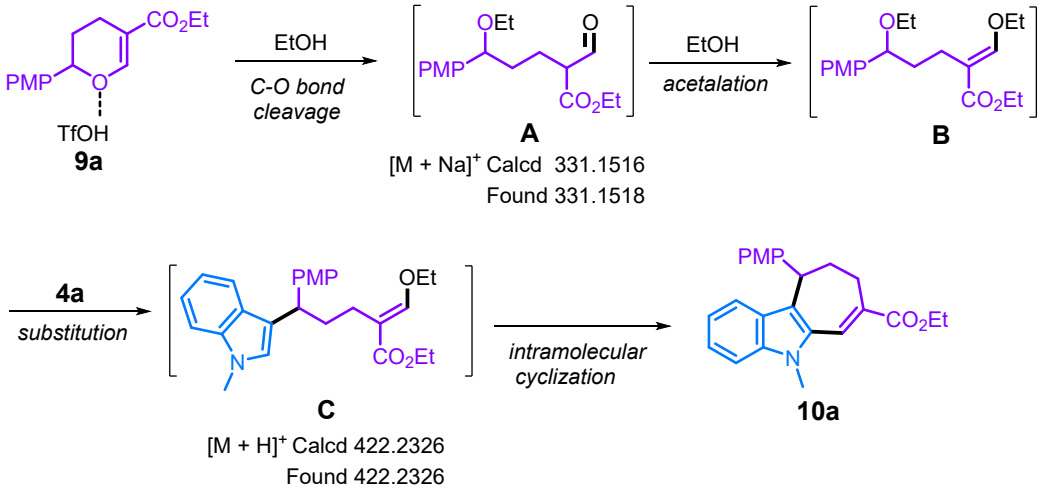


Fig. S4 A possible mechanism for the formation of 10a.

7. X-ray crystallographic analysis

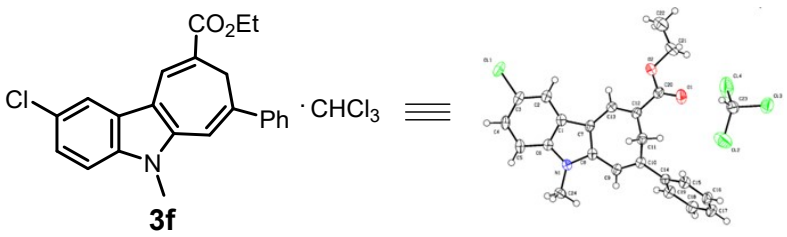


Fig. S5 The X-ray diffraction structure of **3f**.

Table S4 Crystal data and structure refinement for 3f.

Identification code	exp_4129
Empirical formula	$C_{24}H_{21}Cl_4NO_2$
Formula weight	497.22
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.8280(9)
b/Å	9.9575(4)
c/Å	16.1714(9)
α/°	90
β/°	116.785(7)
γ/°	90
Volume/Å^3	2275.3(2)
Z	4
ρ_{calc}g/cm^3	1.452
μ/mm^{-1}	4.907
F(000)	1024.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	6.256 to 133.186
Index ranges	$-18 \leq h \leq 15$, $-7 \leq k \leq 11$, $-18 \leq l \leq 19$
Reflections collected	7879
Independent reflections	4011 [R_{int} = 0.0857, R_{sigma} = 0.0975]
Data/restraints/parameters	4011/0/282
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0866, wR_2 = 0.2314
Final R indexes [all data]	R_1 = 0.1107, wR_2 = 0.2709
Largest diff. peak/hole / e $Å^{-3}$	0.58/-0.69

Single crystal of **3f** [$\mathbf{C_{24}H_{21}Cl_4NO_2}$] was obtained from chloroform by slow evaporation method at room temperature. CCDC 2193701 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center.

8. Evaluation of green metrics

$$E-factor = \frac{Mass\ (waste)}{Mass\ (product)}$$

$$Solvent\ assessment = 10 - score\ of\ greenness$$

$$Catalyst\ cost = \frac{Cost\ of\ catalyst\ needed}{Mass\ (product)}$$

Notes: **(a)** As our synthesized products are new, we chose some similar cyclohepta[*b*]indole compounds as the references.[4] **(b)** While calculating the E-factors,[5] it should be mentioned that we didn't consider the amounts of solvents used in post-processing and other materials consumption, such as drying agent and silica gel used for flash column chromatography as it is not reported in the cited synthesis references. Also, the recovery of organic solvents was out of consideration the consideration. Thus E-factor was roughly calculated to make a relative comparison. **(c)** The score of greenness of solvent was calculated according to the score in GSK's solvent sustainability guide.[6] The lower solvent assessment value indicate that the solvent is greener and recommended to be used. **(d)** The prices of catalysts refer to Sigma-Aldrich Co. LLC. **(e)** The preparation of self-made catalyst is complex so that the cost is considered extremely expensive.

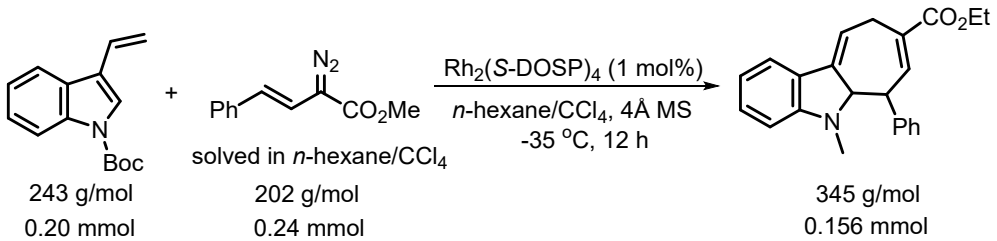
Table S5 Calculation of green metrics for the synthesis of cyclohepta[*b*]indoles.[*a*]

	Sun-2018	Huang-2020	Deng-2020	Nishida-2018	This work[*b*]
E-factor	98.92	31.07	36.84	29.69	19.49

Solvent assessment	9.5	2.5	5.5	5.5	1
Catalyst cost (CNY/per gram of product)	717.5	226.6	Self-made	68.9	0.2
Reaction time (h)	12	16	22	5	5
Steps to obtain substrates	2	3	2	3	1

[a] Unless otherwise noted, only model products in references were calculated and assessed. [b] The synthesis of **3a** in a one-pot stepwise manner was assessed.

(1) G. Xu, L. Chen and J. Sun, *Org. Lett.*, 2018, **20**, 3408-3412.

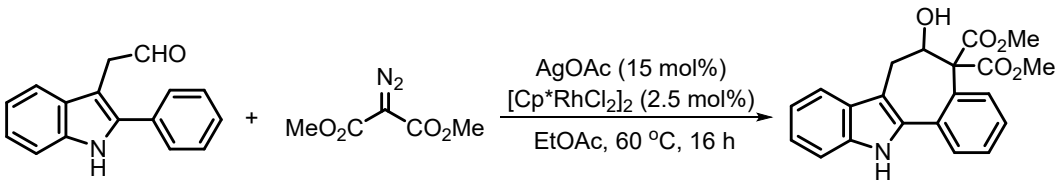


Reagent	**Amount**
tert-butyl 3-vinyl-1*H*-indole-1-carboxylate	243 g/mol x 0.20 mmol x 10^{-3} = 48.6 mg
methyl 2-diazo-4-phenylbut-3-enoate	202 g/mol x 0.24 mmol x 10^{-3} = 48.48 mg
Rh_2(*S*-DOSP)$_4$	1896 g/mol x 0.002 mmol x 10^{-3} = 3.79 mg
n-hexane	0.659 g/mL x 4.8 mL = 3163.2 mg
CCl_4	1.595 g/mL x 1.2 mL = 1914 mg
4Å MS	200 mg
Total	**5378.07 mg**
product	345 g/mol x 0.156 mmol x 10^{-3} = 53.82 mg

E-factor = (5378.07-53.82) mg / 53.82 mg = 98.92

Catalyst cost = (3.79 x 10^{-3} g x 10188.5 CNY/g) / (53.82 x 10^{-3} g) = 717.5 CNY/g

(2) Y. Yuan, X. Guo, X. Zhang, B. Li and Q. Huang, *Org. Chem. Front.*, 2020, **7**, 3146-3159.



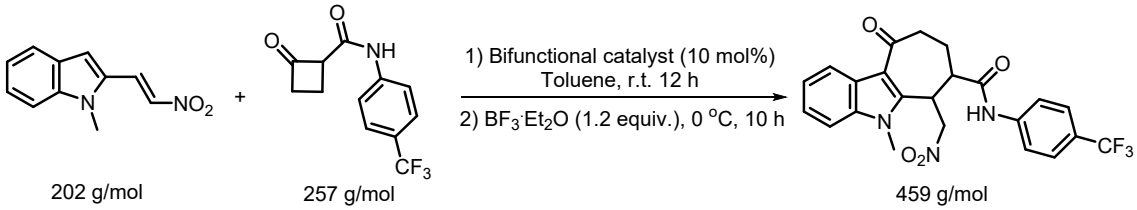
235 g/mol 158 g/mol 365 g/mol
0.20 mmol 0.24 mmol 0.162 mmol

Reagent	Amount
2-(2-phenyl-1*H*-indol-3-yl)acetaldehyde	235 g/mol x 0.20 mmol x 10^{-3} = 47 mg
dimethyl 2-diazomalonate	158 g/mol x 0.24 mmol x 10^{-3} = 37.92 mg
$[Cp^*RhCl_2]_2$	618 g/mol x 0.005 mmol x 10^{-3} = 3.09 mg
AgOAc	166.9 g/mol x 0.03 mmol x 10^{-3} = 5 mg
EtOAc	0.902 g/mL x 2 mL = 1804 mg
Total	**1897.01 mg**
product	365 g/mol x 0.162 mmol x 10^{-3} = 59.15 mg

E-factor = (1897.01-59.15) mg / 59.15 mg = 31.07

Catalyst cost = (3.09 x 10^{-3} g x 4338 CNY/g) / (59.15 x 10^{-3} g) = 226.6 CNY/g

(3) W. L. Yang, W. Li, Z. T. Yang and W. P. Deng, *Org. Lett.*, 2020, **22**, 4026-4032.



202 g/mol 257 g/mol 459 g/mol
0.20 mmol 0.22 mmol 0.108 mmol

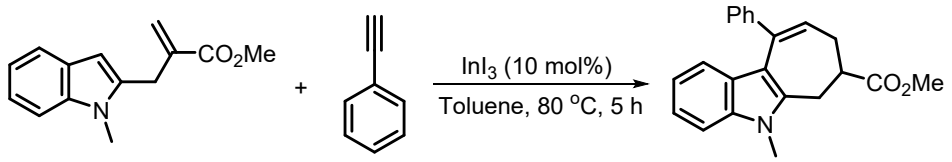
Reagent	Amount
1-methyl-2-(2-nitrovinyl)-1*H*-indole	202 g/mol x 0.20 mmol x 10^{-3} = 40.4 mg
2-amide-substituted cyclobutanone	257 g/mol x 0.22 mmol x 10^{-3} = 56.54 mg
Bifunctional catalyst	12.9 mg
Toluene	0.866 g/mL x 2 mL = 1732 mg

$BF_3 \cdot Et_2O$	141.9 g/mol x 0.24 mmol x 10^{-3} = 34 mg
Total	**1875.84 mg**
product	459 g/mol x 0.108 mmol x 10^{-3} = 49.57 mg

E-factor = (1875.84-49.57) mg / 49.57 mg = 36.84

The bifunctional catalyst used in the reaction is not commercially available.

(4) T. Takeda, S. Harada, A. Okabe and A. Nishida, *J. Org. Chem.*, 2018, **83**, 11541-11551



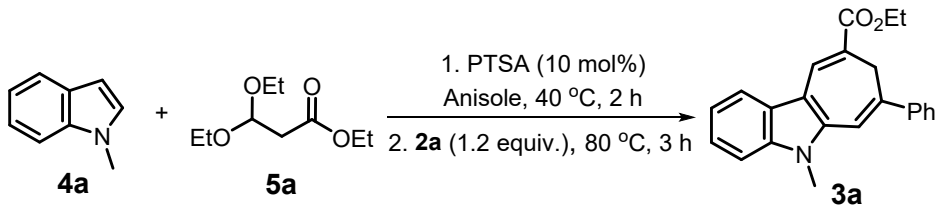
229 g/mol 0.20 mmol | 102 g/mol 0.80 mmol | 331g/mol 0.184 mmol

Reagent	Amount
methyl 2-((1-methyl-1*H*-indol-2-yl)methyl)acrylate	229 g/mol x 0.20 mmol x 10^{-3} = 45.8 mg
phenylacetylene	102 g/mol x 0.80 mmol x 10^{-3} = 81.6 mg
InI_3	495 g/mol x 0.02 mmol x 10^{-3} = 9.9 mg
Toluene	0.866 g/mL x 2 mL = 1732 mg
Total	**1869.3 mg**
product	331 g/mol x 0.184 mmol x 10^{-3} = 60.9 mg

E-factor = (1869.3-60.9) mg / 60.9 mg = 29.69

Catalyst cost = (9.9 x 10^{-3} g x 424 CNY/g) / (60.9 x 10^{-3} g) = 68.9 CNY/g

(5) This work (one-pot stepwise manner)



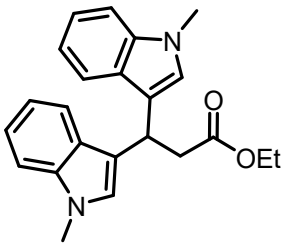
4a 131 g/mol 0.30 mmol | **5a** 190 g/mol 0.20 mmol | **3a** 343 g/mol 0.16 mmol

Reagent	Amount
4a	131 g/mol x 0.30 mmol x 10^{-3} = 39.3 mg
5a	190 g/mol x 0.20 mmol x 10^{-3} = 38 mg
PTSA	172 g/mol x 0.02 mmol x 10^{-3} = 3.44 mg
Anisole	0.995 g/mL x 1 mL = 995 mg
2a	206 g/mol x 0.24 mmol x 10^{-3} = 49.4 mg
Total	**1125.14 mg**
product	343 g/mol x 0.16 mmol x 10^{-3} = 54.9 mg

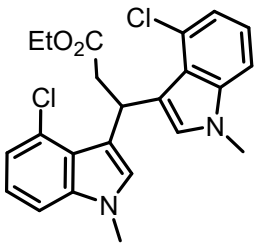
E-factor = (1125.14-54.9) mg / 54.9 mg = 19.49

Catalyst cost = (3.44 x 10^{-3} g x 3.2 CNY/g) / (54.9 x 10^{-3} g) = 0.2 CNY/g

9. Characterization data of products

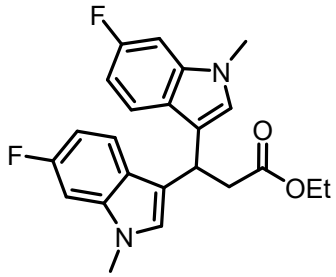


Ethyl 3,3-bis(1-methyl-1*H*-indol-3-yl)propanoate (**1a**): yellow oil (49 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.60 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.19 (q, J = 7.9, 6.5 Hz, 2H), 7.03 (t, J = 7.5 Hz, 2H), 6.85 (s, 2H), 5.10 (t, J = 7.7 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 3.67 (s, 6H), 3.15 (d, J = 7.7 Hz, 2H), 1.09 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 172.6, 137.3, 127.1, 126.5, 121.5, 119.7, 118.7, 117.4, 109.2, 60.3, 41.6, 32.7, 30.7, 14.1 ppm. IR (KBr) ν = 3052, 2933, 1730, 1614, 1472, 1371, 1328, 1152, 740, 428 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{24}N_2NaO_2$, $[M + Na]^+$ 383.1730, found 383.1725.

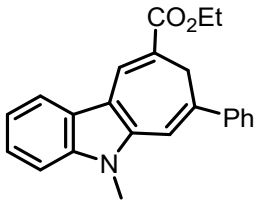


Ethyl 3,3-bis(4-chloro-1-methyl-1*H*-indol-3-yl)propanoate (**1b**): yellow oil (56 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.07 (td, J = 7.9, 4.8 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.85 (s, 2H), 6.71 (dd, J = 11.3, 7.6 Hz, 2H), 5.35 (t, J = 7.9 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.66 (s, 6H), 3.20 (d, J = 7.8 Hz, 2H), 1.06 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 172.5, 158.2, 155.7, 140.1, 140.0, 126.9, 126.9, 121.9, 121.8, 116.7, 116.7, 115.7, 115.5, 105.3, 105.3, 104.4, 104.2, 60.1, 42.0, 33.0, 32.0, 14.1 ppm. IR (KBr) ν

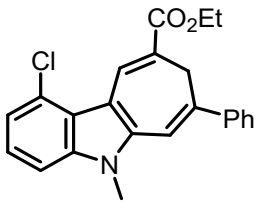
= 3067, 2936, 1731, 1628, 1498, 1372, 1235, 777, 737 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{22}Cl_2N_2NaO_2$, [M + Na]$^+$ 451.0951, found 451.0950.



Ethyl 3,3-bis(6-fluoro-1-methyl-1*H*-indol-3-yl)propanoate (**1c**): yellow oil (53 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.44 (dd, J = 8.7, 5.3 Hz, 2H), 6.92 (dd, J = 9.9, 2.3 Hz, 2H), 6.83 (s, 2H), 6.78 (td, J = 9.2, 2.3 Hz, 2H), 5.01 (t, J = 7.7 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 3.65 (s, 6H), 3.10 (d, J = 7.7 Hz, 2H), 1.10 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 172.29, 161.1 (d, $^1J_{C\text{-}F}$ = 236.0 Hz), 137.4 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 126.6 (d, $^4J_{C\text{-}F}$ = 4.0 Hz), 123.5, 120.3 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 117.5, 107.6 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 95.7 (d, $^2J_{C\text{-}F}$ = 26.0 Hz), 60.4, 41.5, 32.8, 30.6, 14.1 ppm; ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C) δ = -121.1 ppm (m, 1F). IR (KBr) ν = 3069, 2935, 1730, 1623, 1478, 1373, 1334, 1106, 801, 733 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{22}F_2N_2NaO_2$, [M + Na]$^+$ 419.1542, found 419.1545.

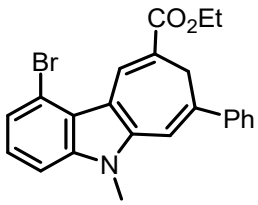


Ethyl 5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3a**): yellow solid (55 mg, 80% yield), mp: 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 8.23 (s, 1H), 7.90–7.82 (m, 3H), 7.45–7.36 (m, 4H), 7.32 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.05 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.34 (s, 2H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 166.5, 141.2, 140.4, 137.6, 136.2, 130.3, 128.6, 127.9, 127.1, 126.7, 123.8, 120.6, 119.1, 115.7, 115.4, 113.5, 109.3, 60.6, 30.1, 30.0, 14.5 ppm. IR (KBr) ν = 3056, 2979, 1690, 1604, 1495, 1370, 1260, 1194, 1088, 743, 428 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}NNaO_2$, [M + Na]$^+$ 366.1465, found 366.1462.

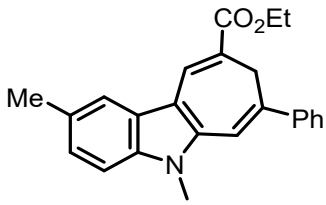


Ethyl 1-chloro-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3b**): yellow solid (55 mg, 73% yield), mp: 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 8.27 (s, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.4 Hz, 1H), 7.17 (q, J = 3.5, 3.0 Hz, 1H), 7.06 (d, J = 8.2 Hz, 1H), 6.95–6.92 (m, 1H), 6.82 (dd, J = 10.5, 7.9 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.75 (s, 3H), 3.24 (s, 2H), 1.27 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 166.4, 141.1, 140.2, 137.1, 131.9, 131.8, 128.7, 128.1, 127.1, 124.2, 124.1, 116.2, 113.0, 106.2, 106.0, 105.31, 105.27, 60.6, 30.5, 29.8, 14.4 ppm. IR (KBr) ν = 3060, 2979, 1690, 1611,

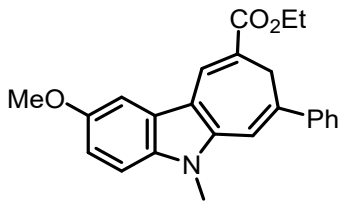
1495, 1314, 1242, 1092, 731, 426 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}ClNO_2$, $[M + H]^+$ 378.1255, found 378.1251 (^{35}Cl) and 380.1227 (^{37}Cl).



Ethyl 1-bromo-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3c**): yellow solid (59 mg, 71% yield), mp: 133–135 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.89 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.45–7.39 (m, 3H), 7.34 (dd, J = 7.8, 5.7 Hz, 2H), 7.18 (t, J = 7.9 Hz, 1H), 7.02 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.27 (s, 2H), 1.34 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.4, 141.8, 140.0, 138.8, 138.7, 131.4, 128.7, 128.2, 127.2, 125.0, 124.8, 124.2, 115.8, 115.6, 115.1, 112.8, 108.4, 60.6, 30.3, 29.6, 14.4 ppm. IR (KBr) ν = 3057, 2930, 1690, 1599, 1453, 1311, 1244, 1192, 1091, 733, 426 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}BrNO_2$, $[M + H]^+$ 422.0750, found 422.0750 (^{79}Br) and 424.0733 (^{81}Br).

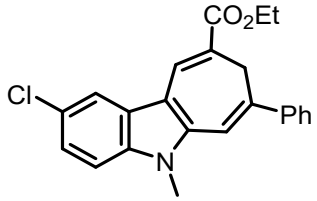


Ethyl 2,5-dimethyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3d**): yellow solid (48 mg, 68% yield), mp: 92–94 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.20 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.65 (s, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 6.5 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.04 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 3.33 (s, 2H), 2.52 (s, 3H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.6, 141.2, 140.5, 136.0, 135.9, 130.4, 130.1, 128.6, 127.8, 127.1, 126.8, 125.3, 118.8, 115.3, 115.0, 113.6, 108.9, 60.6, 30.1, 30.0, 21.5, 14.5 ppm. IR (KBr) ν = 3029, 2930, 1689, 1607, 1494, 1369, 1263, 1194, 1087, 745, 432 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{24}NO_2$, $[M + H]^+$ 358.1802, found 358.1803.

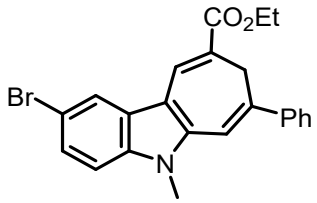


Ethyl 2-methoxy-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3e**): yellow solid (47 mg, 64% yield), mp: 83–85 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.18 (s, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 9.4 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 3H), 3.34 (s, 2H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.6, 155.0, 141.5, 140.5, 136.1, 132.7, 130.4, 129.7, 128.6, 127.9, 127.1, 115.3, 115.0, 114.0, 113.6, 110.1, 100.8, 60.6, 56.0, 30.2, 30.0, 14.5 ppm. IR (KBr) ν = 3059, 2929, 1689, 1619, 1489, 1269, 1234, 1089, 697, 426 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{24}NO_3$, [M +

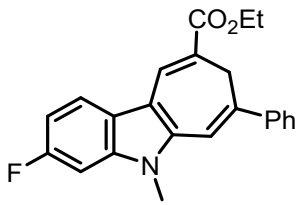
H]$^+$ 374.1751, found 374.1748.



Ethyl 2-chloro-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3f**): yellow solid (58 mg, 77% yield), mp: 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.12 (s, 1H), 7.85 (d, J = 7.4 Hz, 2H), 7.79 (s, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.31–7.27 (m, 2H), 7.00 (s, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.33 (s, 2H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.3, 142.0, 140.3, 137.2, 135.9, 129.7, 128.7, 128.1, 127.6, 127.1, 126.3, 123.9, 118.6, 116.4, 114.7, 113.3, 110.3, 60.7, 30.2, 30.0, 14.5 ppm. IR (KBr) ν = 3059, 2980, 1690, 1620, 1472, 1286, 1247, 1194, 1090, 734, 444 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}ClNO_2$, [M + H]$^+$ 378.1255, found 378.1255 (^{35}Cl) and 380.1228 (^{37}Cl).

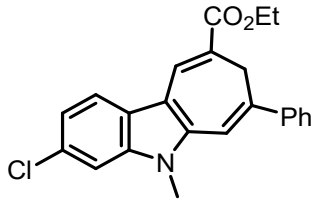


Ethyl 2-bromo-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3g**): yellow solid (61 mg, 73% yield), mp: 198–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.11 (s, 1H), 7.95 (d, J = 1.9 Hz, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.45–7.39 (m, 3H), 7.33 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 7.00 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.33 (s, 2H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.3, 141.9, 140.2, 137.2, 136.2, 129.7, 128.7, 128.2, 128.1, 127.1, 126.5, 121.7, 116.5, 114.6, 113.8, 113.2, 110.7, 60.7, 30.2, 30.0, 14.4 ppm. IR (KBr) ν = 3058, 2979, 1690, 1619, 1470, 1286, 1248, 1194, 1089, 731, 429 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}BrNO_2$, [M + H]$^+$ 422.0750, found 422.0754 (^{79}Br) and 424.0733 (^{81}Br).

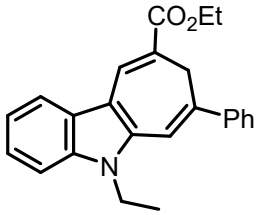


Ethyl 3-fluoro-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3h**): yellow solid (54 mg, 75% yield), mp: 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.15 (s, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.75 (dd, J = 8.6, 5.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.07–6.96 (m, 3H), 4.29 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.32 (s, 2H), 1.35 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.4, 162.2 (d, $^1J_{C\text{-}F}$ = 239.0 Hz), 141.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 140.3, 138.0 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 135.7, 129.8, 128.6, 128.0, 127.1, 123.1, 120.1 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 116.0, 115.4, 113.3, 109.2 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 96.1 (d, $^2J_{C\text{-}F}$ = 26.0 Hz), 60.7, 30.3, 30.0, 14.4 ppm; ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C) δ = -117.6 (m, 1F) ppm. IR (KBr)

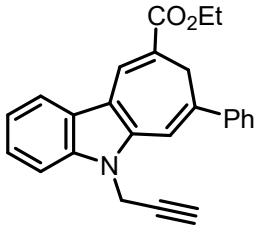
ν = 3059, 2930, 1690, 1608, 1494, 1370, 1254, 1195, 1089, 751, 428 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}FNO_2$, $[M + H]^+$ 362.1551, found 362.1552.



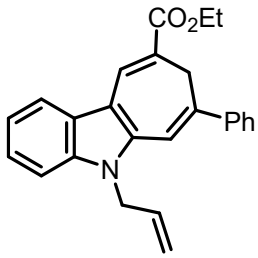
Ethyl 3-chloro-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3i**): yellow solid (52 mg, 70% yield), mp: 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.14 (s, 1H), 7.85 (d, J = 7.5 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.37–7.31 (m, 2H), 7.20 (dd, J = 8.4, 1.8 Hz, 1H), 7.02 (s, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.33 (s, 2H), 1.35 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.4, 141.7, 140.2, 138.1, 136.6, 129.8, 129.7, 128.7, 128.1, 127.1, 125.2, 121.2, 120.0, 116.4, 115.3, 113.2, 109.4, 60.7, 30.2, 30.0, 14.4 ppm. IR (KBr) ν = 3060, 2980, 1691, 1602, 1496, 1256, 1195, 1090, 696, 439 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}ClNO_2$, $[M + H]^+$ 378.1255, found 378.1252 (^{35}Cl) and 380.1228 (^{37}Cl).



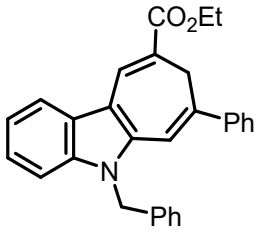
Ethyl 5-ethyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3j**): yellow solid (55 mg, 78% yield), mp: 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.23 (s, 1H), 7.86 (d, J = 7.7 Hz, 3H), 7.45–7.36 (m, 4H), 7.33 (d, J = 6.9 Hz, 1H), 7.24 (d, J = 7.0 Hz, 1H), 7.05 (s, 1H), 4.32 (dq, J = 18.4, 7.2 Hz, 4H), 3.35 (s, 2H), 1.46 (t, J = 7.2 Hz, 3H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.6, 140.5, 140.2, 136.5, 136.3, 130.4, 128.6, 127.9, 127.1, 126.9, 123.7, 120.5, 119.2, 115.7, 115.5, 113.3, 109.3, 60.6, 38.4, 30.1, 14.7, 14.5 ppm. IR (KBr) ν = 3055, 2978, 1690, 1619, 1495, 1369, 1249, 1193, 1083, 742, 429 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{24}NO_2$, $[M + H]^+$ 358.1802, found 358.1799.



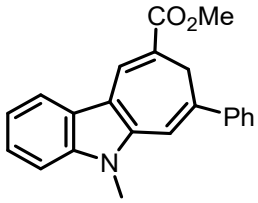
Ethyl 7-phenyl-5-(prop-2-yn-1-yl)-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3k**): yellow solid (64 mg, 88% yield), mp: 114–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.21 (s, 1H), 7.87 (t, J = 8.2 Hz, 3H), 7.48–7.39 (m, 4H), 7.34 (d, J = 7.3 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 4.99 (d, J = 2.5 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.35 (s, 2H), 2.34 (s, 1H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.4, 140.4, 140.2, 136.6, 136.5, 130.1, 128.7, 128.0, 127.2, 127.0, 124.2, 121.1, 119.3, 116.5, 116.2, 113.0, 109.4, 73.1, 60.7, 33.1, 30.1, 14.5 ppm. IR (KBr) ν = 3290, 3057, 2980, 2210, 1690, 1618, 1465, 1246, 1191, 1092, 743, 431 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{22}NO_2$, $[M + H]^+$ 368.1645, found 368.1647.



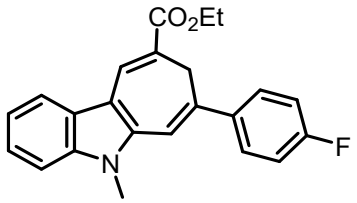
Ethyl 5-allyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3l**): yellow solid (60 mg, 82% yield), mp: 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.24 (s, 1H), 7.85 (dd, *J* = 11.2, 7.8 Hz, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37–7.31 (m, 3H), 7.28–7.25 (m, 1H), 7.02 (s, 1H), 6.02 (ddt, *J* = 17.0, 9.8, 4.6 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.96 (d, *J* = 17.0 Hz, 1H), 4.91–4.87 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 2H), 1.36 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.5, 140.9, 140.4, 137.0, 136.3, 132.2, 130.3, 128.6, 127.9, 127.1, 126.8, 123.9, 120.7, 119.2, 117.0, 116.0, 115.7, 113.4, 109.6, 60.6, 45.9, 30.1, 14.5 ppm. IR (KBr) ν = 3057, 2981, 1691, 1618, 1465, 1244, 1190, 1091, 742, 431 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{24}NO_2$, $[M + H]^+$ 370.1802, found 370.1802.



Ethyl 5-benzyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3m**): yellow solid (70 mg, 84% yield), mp: 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.26 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32–7.24 (m, 7H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.00 (s, 1H), 5.50 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.35 (s, 2H), 1.36 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.5, 141.1, 140.3, 137.3, 136.7, 136.6, 130.3, 129.0, 128.6, 127.9, 127.7, 127.1, 126.9, 126.2, 124.1, 120.9, 119.2, 116.1, 115.9, 113.5, 109.8, 60.7, 47.2, 30.1, 14.5 ppm. IR (KBr) ν = 3058, 2980, 1690, 1618, 1496, 1463, 1243, 1188, 1091, 739, 452 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{29}H_{26}NO_2$, $[M + H]^+$ 420.1958, found 420.1962.

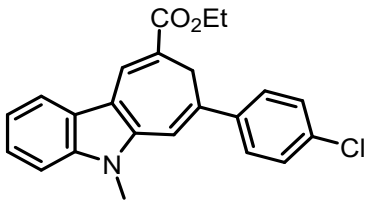


Methyl 5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3n**): yellow solid (50 mg, 77% yield), mp: 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.22 (s, 1H), 7.85 (t, *J* = 7.1 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39–7.36 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.05 (s, 1H), 3.85 (d, *J* = 3.9 Hz, 6H), 3.35 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 167.0, 141.2, 140.5, 137.6, 136.2, 130.5, 128.7, 128.0, 127.1, 126.6, 123.8, 120.7, 119.0, 115.3, 113.6, 109.3, 51.9, 30.1, 30.0 ppm. IR (KBr) ν = 3056, 2947, 1693, 1603, 1495, 1261, 1197, 1089, 741, 442 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{22}H_{20}NO_2$, $[M + H]^+$ 330.1489, found 330.1485.

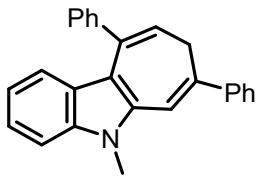


Ethyl 7-(4-fluorophenyl)-5-methyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3o**): yellow solid (53

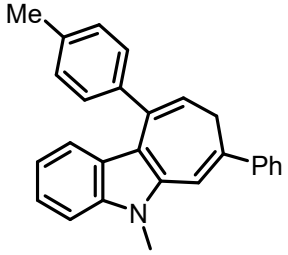
mg, 74% yield), mp: 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.22 (s, 1H), 7.89–7.80 (m, 3H), 7.41–7.36 (m, 2H), 7.26 (d, J = 4.3 Hz, 1H), 7.10 (t, J = 8.6 Hz, 2H), 6.98 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.30 (s, 2H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.5, 163.8 (d, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 141.1, 137.6, 136.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 134.9, 130.3, 128.9 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 126.6, 123.9, 120.7, 119.1, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 115.5, (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 113.2, 109.3, 60.7, 30.2, 30.1, 14.5 ppm; ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C) δ = -113.9 (m, 1F) ppm. IR (KBr) ν = 3055, 2980, 1689, 1601, 1510, 1260, 1194, 1088, 831, 742, 427 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}FNO_2$, $[M + H]^+$ 362.1551, found 362.1547.



Ethyl 7-(4-chlorophenyl)-5-methyl-5,8-dihydrocyclohepta[*b*]indole-9-carboxylate (**3p**): yellow solid (58 mg, 78% yield), mp: 126–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.22 (s, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.38 (dd, J = 6.2, 3.8 Hz, 4H), 7.28 (s, 1H), 7.03 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.29 (s, 2H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 166.5, 140.9, 138.8, 137.6, 134.6, 133.7, 130.3, 128.8, 128.4, 126.6, 124.0, 120.7, 119.2, 115.7, 115.6, 113.6, 109.3, 60.7, 30.1, 30.0, 14.5 ppm. IR (KBr) ν = 3057, 2928, 1690, 1603, 1492, 1260, 1194, 1091, 823, 741, 443 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}ClNO_2$, $[M + H]^+$ 378.1255, found 378.1259 (^{35}Cl) and 380.1229 (^{37}Cl).

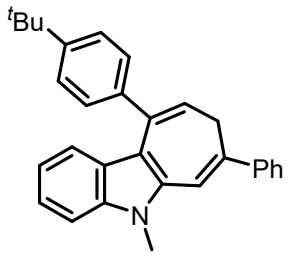


5-Methyl-7,10-diphenyl-5,8-dihydrocyclohepta[*b*]indole (**8a**): yellow solid (40 mg, 59% yield), mp: 193–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.64 (d, J = 7.4 Hz, 2H), 7.37 (dt, J = 20.5, 8.0 Hz, 6H), 7.29 (q, J = 3.5 Hz, 4H), 7.24–7.21 (m, 1H), 6.97 (s, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.62 (t, J = 7.4 Hz, 1H), 3.86 (s, 3H), 3.00 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.7, 141.1, 140.0, 137.83, 137.77, 137.1, 129.0, 128.6, 128.0, 127.6, 127.2, 127.1, 126.0, 122.6, 122.2, 119.1, 116.4, 116.0, 113.5, 108.8, 31.6, 30.1 ppm. IR (KBr) ν = 3054, 2931, 1599, 1492, 1468, 909, 742, 698, 446 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{26}H_{22}N$, $[M + H]^+$ 348.1747, found 348.1746.

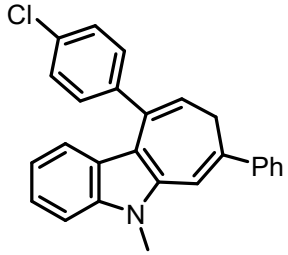


5-Methyl-7-phenyl-10-(*p*-tolyl)-5,8-dihydrocyclohepta[*b*]indole (**8b**): yellow solid (48 mg, 67% yield), mp: 188–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.56 (d, J = 6.9 Hz, 2H), 7.32 (t, J = 7.6 Hz,

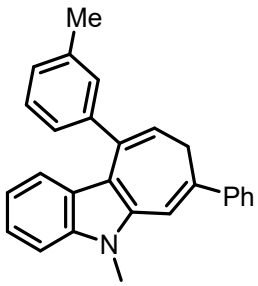
2H), 7.24 (d, J = 7.1 Hz, 1H), 7.19–7.13 (m, 4H), 7.02 (d, J = 7.7 Hz, 2H), 6.89 (s, 1H), 6.86–6.77 (m, 2H), 5.52 (t, J = 7.4 Hz, 1H), 3.79 (s, 3H), 2.91 (d, J = 7.2 Hz, 2H), 2.29 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.1, 140.0, 138.8, 137.9, 137.6, 137.1, 136.7, 128.8, 128.7, 128.5, 127.5, 127.2, 126.1, 122.5, 122.3, 119.0, 116.2, 115.8, 113.4, 108.7, 31.6, 30.1, 21.2 ppm. IR (KBr) ν = 3025, 2926, 1599, 1467, 908, 819, 740, 696, 447 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{27}H_{24}N$, $[M + H]^+$ 362.1903, found 362.1902.



10-(4-(*tert*-Butyl)phenyl)-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole (**8c**): yellow solid (57 mg, 71% yield), mp: 167–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.55 (d, J = 6.9 Hz, 2H), 7.33–7.29 (m, 2H), 7.24–7.16 (m, 7H), 6.88 (s, 1H), 6.85–6.78 (m, 2H), 5.54 (t, J = 7.4 Hz, 1H), 3.78 (s, 3H), 2.90 (d, J = 8.0 Hz, 2H), 1.25 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 150.0, 141.2, 140.0, 138.7, 137.9, 137.4, 137.1, 128.5, 128.5, 127.5, 127.2, 126.1, 124.9, 122.5, 122.3, 119.0, 116.2, 116.1, 113.4, 108.7, 34.5, 31.6, 31.4, 30.1 ppm. IR (KBr) ν = 3027, 2961, 1614, 1467, 909, 831, 739, 696, 426 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{30}H_{30}N$, $[M + H]^+$ 404.2373, found 404.2372.

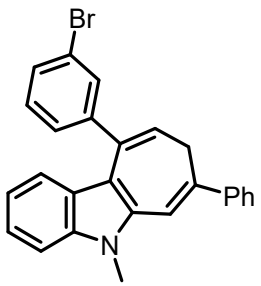


10-(4-Chlorophenyl)-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole (**8d**): yellow solid (39 mg, 52% yield), mp: 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.64 (d, J = 7.1 Hz, 2H), 7.44–7.30 (m, 5H), 7.25 (d, J = 3.5 Hz, 4H), 6.97 (s, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.60 (t, J = 7.4 Hz, 1H), 3.86 (s, 3H), 2.99 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 140.9, 140.13, 140.08, 137.9, 137.1, 136.6, 132.9, 130.2, 128.6, 128.2, 127.7, 127.2, 125.8, 122.7, 122.0, 119.2, 116.6, 115.5, 113.5, 108.9, 31.5, 30.1 ppm. IR (KBr) ν = 3055, 2931, 1597, 1490, 1468, 1091, 908, 828, 740, 427 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{26}H_{21}ClN$, $[M + H]^+$ 382.1357, found 382.1357 (^{35}Cl) and 384.1331 (^{37}Cl).

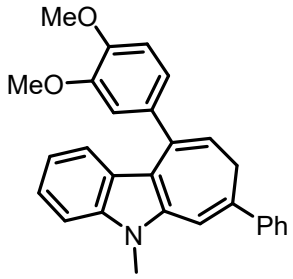


5-Methyl-7-phenyl-10-(*m*-tolyl)-5,8-dihydrocyclohepta[*b*]indole (**8e**): yellow solid (41 mg, 58% yield), mp: 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.64 (d, J = 7.0 Hz, 2H), 7.42–7.34 (m, 3H), 7.31 (d, J = 7.3 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1H), 7.20–7.14 (m, 2H), 7.10 (d, J = 7.5 Hz, 2H), 6.97 (s, 1H), 6.92–6.82 (m, 2H), 5.62 (t, J = 7.4 Hz, 1H),

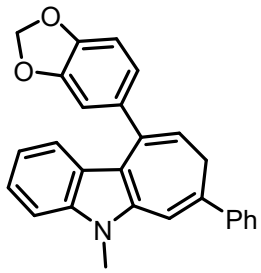
3.86 (s, 3H), 2.99 (d, J = 7.2 Hz, 2H), 2.30 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.6, 141.1, 139.9, 137.83, 137.81, 137.5, 137.1, 129.6, 128.5, 127.85, 127.81, 127.5, 127.2, 126.2, 126.1, 122.5, 122.2, 119.0, 116.3, 116.1, 113.5, 108.7, 31.6, 30.1, 21.4 ppm. IR (KBr) ν = 3053, 2931, 1601, 1492, 1468, 909, 741, 697, 447 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{27}H_{24}N$, $[M + H]^+$ 362.1903, found 362.1902.



10-(3-Bromophenyl)-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole (**8f**): yellow solid (45 mg, 53% yield), mp: 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.64 (d, J = 7.7 Hz, 2H), 7.54 (s, 1H), 7.43–7.35 (m, 4H), 7.32 (d, J = 7.3 Hz, 1H), 7.26–7.20 (m, 2H), 7.13 (t, J = 7.8 Hz, 1H), 7.00–6.90 (m, 2H), 6.84 (d, J = 7.9 Hz, 1H), 5.62 (t, J = 7.4 Hz, 1H), 3.86 (s, 3H), 2.99 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 143.8, 140.9, 140.1, 137.8, 137.1, 136.5, 131.7, 130.0, 129.5, 128.6, 127.73, 127.68, 127.2, 125.7, 122.7, 122.2, 122.0, 119.3, 117.2, 115.3, 113.5, 108.9, 31.5, 30.1 ppm. IR (KBr) ν = 3056, 2932, 1592, 1494, 1469, 908, 734, 694, 427 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{26}H_{21}BrN$, $[M + H]^+$ 426.0852, found 426.0853 (^{79}Br) and 428.0831 (^{81}Br).

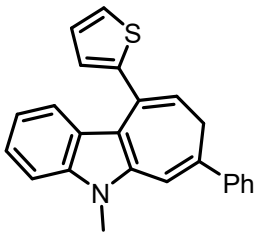


10-(3,4-Dimethoxyphenyl)-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole (**8g**): yellow solid (58 mg, 72% yield), mp: 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.65 (d, J = 7.1 Hz, 2H), 7.39 (q, J = 7.0, 6.5 Hz, 3H), 7.31 (dd, J = 14.7, 7.3 Hz, 2H), 7.22 (dd, J = 8.4, 2.9 Hz, 1H), 6.97 (s, 1H), 6.93 (dd, J = 8.3, 1.9 Hz, 1H), 6.91–6.88 (m, 2H), 6.86 (d, J = 2.0 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 5.60 (t, J = 7.4 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.72 (s, 3H), 2.98 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 148.34, 148.31, 141.0, 140.0, 137.9, 137.4, 137.1, 134.8, 128.6, 127.5, 127.2, 126.0, 122.6, 122.3, 121.3, 119.0, 116.1, 115.2, 113.4, 112.5, 110.7, 108.7, 55.9, 55.8, 31.5, 30.1 ppm. IR (KBr) ν = 3055, 2932, 1600, 1511, 1466, 1263, 1246, 1138, 1027, 909, 733, 697, 562 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{28}H_{26}NO_2$, $[M + H]^+$ 408.1958, found 408.1956.

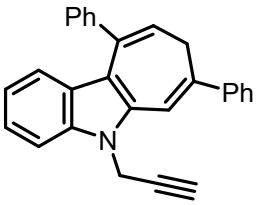


10-(Benzo[*d*][1,3]dioxol-5-yl)-5-methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indole (**8h**): yellow solid (60 mg, 77% yield), mp: 202–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.66–7.60 (m, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.33 (dd, J = 15.1, 7.8 Hz, 2H), 7.29–7.20

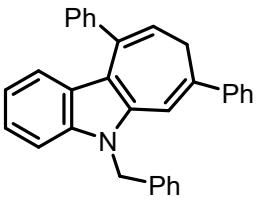
(m, 2H), 6.98–6.91 (m, 3H), 6.86–6.78 (m, 2H), 6.74 (d, J = 8.0 Hz, 1H), 5.94 (s, 2H), 5.55 (t, J = 7.4 Hz, 1H), 3.84 (s, 3H), 2.95 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 147.3, 146.8, 141.0, 140.0, 138.0, 137.3, 137.1, 136.2, 128.6, 127.6, 127.2, 126.0, 122.6, 122.5, 122.2, 119.2, 116.1, 115.5, 113.4, 109.6, 108.8, 107.9, 100.9, 31.5, 30.1 ppm. IR (KBr) ν = 3055, 2931, 1598, 1485, 1436, 1239, 1039, 909, 811, 743, 697 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{27}H_{22}NO_2$, [M + H]$^+$ 392.1645, found 392.1646.



5-Methyl-10-(thiophen-2-yl)-7-(*p*-tolyl)-5,8-dihydrocyclohepta[*b*]indole (**8i**): yellow solid (57 mg, 79% yield), mp: 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.56 (d, J = 7.4 Hz, 2H), 7.35–7.27 (m, 3H), 7.24–7.16 (m, 2H), 7.14–7.07 (m, 2H), 6.94–6.85 (m, 4H), 5.68 (t, J = 7.4 Hz, 1H), 3.77 (s, 3H), 2.88 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 144.7, 140.8, 139.9, 138.5, 137.1, 130.4, 128.6, 127.7, 127.2, 127.0, 126.0, 125.8, 124.2, 122.7, 122.2, 119.1, 116.8, 115.8, 113.6, 108.9, 31.4, 30.1 ppm. IR (KBr) ν = 3056, 2923, 1597, 1493, 1468, 1261, 908, 830, 741, 695, 424 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{22}NS$, [M + H]$^+$ 368.1467, found 368.1466.

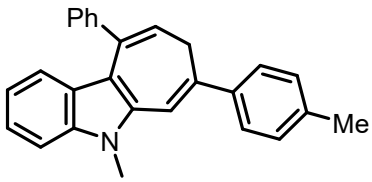


7,10-Diphenyl-5-(prop-2-yn-1-yl)-5,8-dihydrocyclohepta[*b*]indole (**8j**): yellow solid (54 mg, 74% yield), mp: 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.58 (d, J = 7.4 Hz, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 3.3 Hz, 1H), 7.23 (q, J = 4.4, 3.6 Hz, 4H), 7.19 (d, J = 3.3 Hz, 2H), 6.99 (s, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.58 (t, J = 7.4 Hz, 1H), 4.94 (d, J = 2.5 Hz, 2H), 2.94 (d, J = 7.3 Hz, 2H), 2.27 ppm (d, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.4, 140.8, 139.3, 138.2, 137.7, 136.3, 129.0, 128.6, 128.0, 127.7, 127.3, 127.2, 126.4, 123.0, 122.4, 119.6, 116.93, 116.90, 112.9, 109.0, 78.1, 72.7, 33.2, 31.7 ppm. IR (KBr) ν = 3055, 2923, 1600, 1463, 1260, 1022, 800, 747, 698, 440 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{28}H_{22}N$, [M + H]$^+$ 372.1747, found 372.1748.

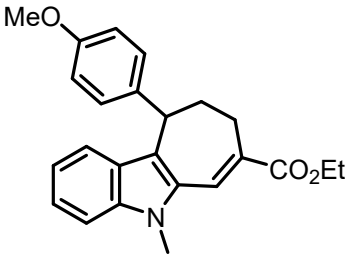


5-Benzyl-7,10-diphenyl-5,8-dihydrocyclohepta[*b*]indole (**8k**): yellow solid (68 mg, 81% yield), mp: 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, J = 7.4 Hz, 2H), 7.40–7.33 (m, 4H), 7.30 (td, J = 8.8, 7.8, 3.3 Hz, 7H), 7.25 (dd, J = 7.1, 2.6 Hz, 2H), 7.18 (d, J = 7.4 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 6.92–6.83 (m, 3H), 5.66 (t, J = 7.4 Hz, 1H), 5.51 (s, 2H), 3.01 ppm

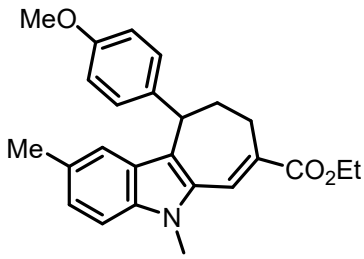
(d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 141.6, 140.9, 140.0, 138.2, 137.8, 137.5, 136.9, 129.0, 128.9, 128.5, 128.1, 127.54, 127.47, 127.20, 127.17, 126.3, 126.2, 122.8, 122.3, 119.4, 116.8, 116.5, 113.3, 109.4, 47.2, 31.7 ppm. IR (KBr) ν = 3057, 2925, 1599, 1494, 1337, 908, 741, 699, 441 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{32}H_{26}N$, $[M + H]^+$ 424.2060, found 424.2061.



5-Methyl-10-phenyl-7-(*p*-tolyl)-5,8-dihydrocyclohepta[*b*]indole (**8l**): yellow solid (56 mg, 78% yield), mp: 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.54 (d, J = 7.9 Hz, 2H), 7.37–7.31 (m, 3H), 7.30–7.26 (m, 3H), 7.24–7.17 (m, 3H), 6.94 (s, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 5.60 (t, J = 7.4 Hz, 1H), 3.85 (s, 3H), 2.98 (d, J = 7.3 Hz, 2H), 2.38 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 141.7, 140.2, 138.2, 137.8, 137.7, 137.5, 137.1, 129.3, 129.0, 128.0, 127.1, 127.0, 126.0, 122.4, 122.1, 119.0, 116.4, 115.8, 112.8, 108.8, 31.6, 30.1, 21.2 ppm. IR (KBr) ν = 3052, 2924, 1600, 1510, 1467, 1336, 815, 740, 700, 442 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{27}H_{24}N$, $[M + H]^+$ 362.1903, found 362.1904.

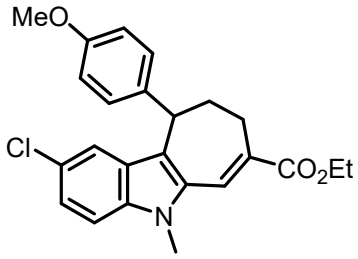


Ethyl 10-(4-methoxyphenyl)-5-methyl-5,8,9,10-tetrahydrocyclohepta[*b*]indole-7-carboxylate (**10a**): yellow oil (99 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.93 (d, J = 2.3 Hz, 1H), 7.26 (dd, J = 11.8, 8.2 Hz, 2H), 7.22 – 7.18 (m, 1H), 6.96 (dd, J = 13.1, 8.3 Hz, 3H), 6.75 (d, J = 8.6 Hz, 2H), 4.74 (d, J = 4.3 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 2.88 (dd, J = 18.1, 6.4 Hz, 1H), 2.41 – 2.24 (m, 2H), 2.15 – 2.07 (m, 1H), 1.33 ppm (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 168.3, 157.8, 138.5, 138.1, 132.2, 131.9, 129.2, 127.4, 126.2, 123.6, 121.9, 120.1, 119.6, 113.6, 109.4, 61.0, 55.2, 41.3, 31.1, 29.7, 24.6, 14.4 ppm. IR (KBr) ν = 3055, 2932, 1698, 1625, 1510, 1248, 1032, 910, 831, 739 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{26}NO_3$, $[M + H]^+$ 376.1907, found 376.1909.

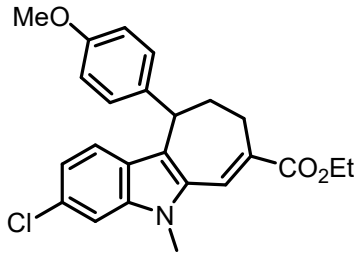


Ethyl 10-(4-methoxyphenyl)-2,5-dimethyl-5,8,9,10-tetrahydrocyclohepta[*b*]indole-7-carboxylate (**10b**): yellow oil (108 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.91 (d, J = 2.5 Hz, 1H), 7.16 (d, J = 8.3 Hz, 1H), 7.03 (d, J = 9.2 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 6.76 (d, J = 8.3 Hz, 2H),

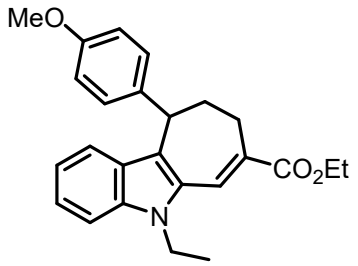
4.72 (d, J = 4.2 Hz, 1H), 4.24 (q, J = 7.3 Hz, 2H), 3.82 (s, 3H), 3.72 (s, 3H), 2.88 (dd, J = 17.8, 5.3 Hz, 1H), 2.30 (s, 5H), 2.09 (t, J = 12.5 Hz, 1H), 1.32 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 168.4, 157.8, 138.4, 136.6, 132.2, 131.3, 129.2, 128.9, 127.5, 126.3, 125.5, 121.4, 119.3, 113.6, 109.2, 60.9, 55.2, 41.0, 30.9, 29.7, 24.7, 21.4, 14.4 ppm. IR (KBr) ν = 3056, 2931, 1698, 1625, 1509, 1247, 1032, 910, 831, 736 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{28}NO_3$, $[M + H]^+$ 390.2064, found 390.2065.



Ethyl 2-chloro-10-(4-methoxyphenyl)-5-methyl-5,8,9,10-tetrahydrocyclohepta[*b*]indole-7-carboxylate (**10c**): yellow oil (104 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.88 (d, J = 2.4 Hz, 1H), 7.21–7.15 (m, 2H), 7.12 (dd, J = 8.8, 1.9 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 4.65 (d, J = 4.2 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 2.88 (dd, J = 18.2, 6.4 Hz, 1H), 2.38–2.23 (m, 2H), 2.13–2.04 (m, 1H), 1.33 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 168.1, 158.0, 137.9, 136.4, 133.3, 132.9, 129.1, 128.2, 125.7, 125.2, 123.8, 121.2, 119.2, 113.7, 110.5, 61.1, 55.2, 41.0, 30.9, 29.9, 24.6, 14.4 ppm. IR (KBr) ν = 3056, 2978, 2931, 1699, 1625, 1509, 1247, 1033, 910, 832, 737 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{25}ClNO_3$, $[M + H]^+$ 410.1517, found 410.1520 (^{35}Cl) and 412.1489 (^{37}Cl).

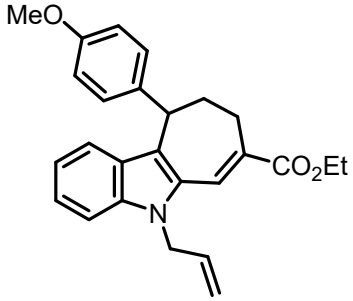


Ethyl 3-chloro-10-(4-methoxyphenyl)-5-methyl-5,8,9,10-tetrahydrocyclohepta[*b*]indole-7-carboxylate (**10d**): yellow oil (111 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.87 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 1.7 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 8.3 Hz, 2H), 6.87 (dd, J = 8.4, 1.8 Hz, 1H), 6.75 (d, J = 8.3 Hz, 2H), 4.66 (d, J = 4.4 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 2.87 (dd, J = 18.1, 6.5 Hz, 1H), 2.37 (dd, J = 18.0, 11.8 Hz, 1H), 2.25 (dt, J = 11.6, 5.0 Hz, 1H), 2.14–2.04 (m, 1H), 1.33 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 168.1, 157.9, 138.4, 138.2, 132.9, 132.7, 129.5, 129.1, 126.0, 125.7, 121.9, 121.0, 120.3, 113.7, 109.3, 61.1, 55.2, 41.3, 31.1, 29.9, 24.6, 14.4 ppm. IR (KBr) ν = 3057, 2931, 1699, 1625, 1509, 1248, 1032, 909, 833, 735 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{25}ClNO_3$, $[M + H]^+$ 410.1517, found 410.1519 (^{35}Cl) and 412.1488 (^{37}Cl).

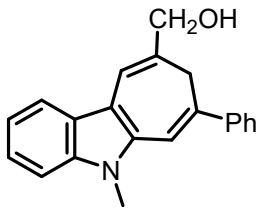


Ethyl 5-ethyl-10-(4-methoxyphenyl)-5,8,9,10-

tetrahydrocyclohepta[*b*]indole-7-carboxylate (**10e**): yellow oil (103 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.91 (d, J = 2.2 Hz, 1H), 7.27 (dd, J = 15.8, 8.2 Hz, 2H), 7.18 (t, J = 7.7 Hz, 1H), 6.96 (dd, J = 13.2, 8.0 Hz, 3H), 6.76 (d, J = 8.3 Hz, 2H), 4.74 (d, J = 4.3 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 2.88 (dd, J = 18.1, 6.4 Hz, 1H), 2.37 (dd, J = 18.5, 11.6 Hz, 1H), 2.27 (dt, J = 11.5, 5.0 Hz, 1H), 2.17–2.09 (m, 1H), 1.42 (t, J = 7.2 Hz, 3H), 1.33 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 168.3, 157.8, 138.5, 137.1, 132.0, 131.1, 129.2, 127.6, 126.1, 123.5, 122.0, 120.2, 119.5, 113.6, 109.3, 61.0, 55.2, 41.3, 37.7, 31.1, 24.6, 15.7, 14.4 ppm. IR (KBr) ν = 3055, 2978, 2931, 1699, 1624, 1509, 1246, 1033, 910, 832, 740 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{28}NO_3$, $[M + H]^+$ 390.2064, found 390.2065.

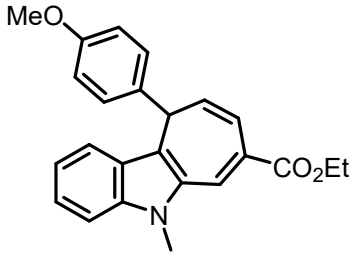


Ethyl 5-allyl-10-(4-methoxyphenyl)-5,8,9,10-tetrahydrocyclohepta[*b*]indole-7-carboxylate (**10f**): yellow oil (97 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.85 (d, J = 2.3 Hz, 1H), 7.27–7.23 (m, 2H), 7.21–7.15 (m, 1H), 6.97 (t, J = 8.4 Hz, 3H), 6.76 (d, J = 8.6 Hz, 2H), 6.02 (ddt, J = 16.8, 9.9, 4.7 Hz, 1H), 5.20 (dd, J = 10.1, 1.7 Hz, 1H), 5.01 (d, J = 17.3 Hz, 1H), 4.90 (d, J = 4.8 Hz, 2H), 4.79–4.71 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.73 (s, 3H), 2.92–2.82 (m, 1H), 2.41–2.24 (m, 2H), 2.17–2.09 (m, 1H), 1.32 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 168.2, 157.8, 138.4, 137.6, 133.4, 132.0, 131.7, 129.2, 127.5, 126.3, 123.7, 122.2, 120.1, 119.8, 116.7, 113.7, 109.4, 60.9, 55.2, 45.3, 41.3, 31.1, 24.6, 14.4 ppm. IR (KBr) ν = 3055, 2931, 1699, 1625, 1509, 1247, 1033, 914, 831, 740 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{26}H_{28}NO_3$, $[M + H]^+$ 402.2064, found 402.2064.



(5-Methyl-7-phenyl-5,8-dihydrocyclohepta[*b*]indol-9-yl)methanol (**11a**): yellow solid (55 mg, 92% yield), mp: 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.74 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.34–7.28 (m, 3H), 7.17 (ddd, J = 8.0, 5.1, 2.9 Hz, 1H), 7.00 (s, 1H), 6.93 (s, 1H), 4.32 (s, 2H), 3.76 (s, 3H), 3.02 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 140.9, 138.6, 137.3, 133.1, 128.8, 128.7, 127.7, 127.1, 126.3, 123.2, 119.7, 119.0, 118.0, 115.8, 113.9, 109.0, 67.1, 32.1, 29.9 ppm. IR (KBr) ν = 3552, 3053, 2978, 1601, 1499, 1374, 1054, 747 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{21}H_{20}NO$, $[M + H]^+$ 302.1539, found

302.1542.



Ethyl 10-(4-methoxyphenyl)-5-methyl-5,10-dihydrocyclohepta[*b*]indole-7-carboxylate (**12a**): yellow solid (25 mg, 34% yield), mp: 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.51 (t, J = 8.2 Hz, 3H), 7.35 (d, J = 8.3 Hz, 1H), 7.23 (dd, J = 8.3, 1.2 Hz, 1H), 6.96 (d, J = 8.3 Hz, 2H), 6.91 (d, J = 7.5 Hz, 1H), 6.74 (d, J = 6.8 Hz, 1H), 6.66 (d, J = 8.1 Hz, 1H), 6.23 (s, 1H), 4.41–4.17 (m, 3H), 3.95 (s, 3H), 3.89 (s, 3H), 1.34 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 165.0, 160.3, 146.1, 137.9, 136.8, 134.1, 130.3, 128.5, 125.5, 123.2, 121.1, 120.6, 119.7, 115.9, 115.4, 114.0, 110.1, 61.8, 55.4, 29.9, 25.6, 14.3 ppm. IR (KBr) ν = 3054, 2936, 1698, 1599, 1498, 1245, 1033, 907, 698 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{24}NO_3$, $[M + H]^+$ 374.1751, found 374.1750.

10. References

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(6) C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879-3890.

11. Copies of NMR spectra

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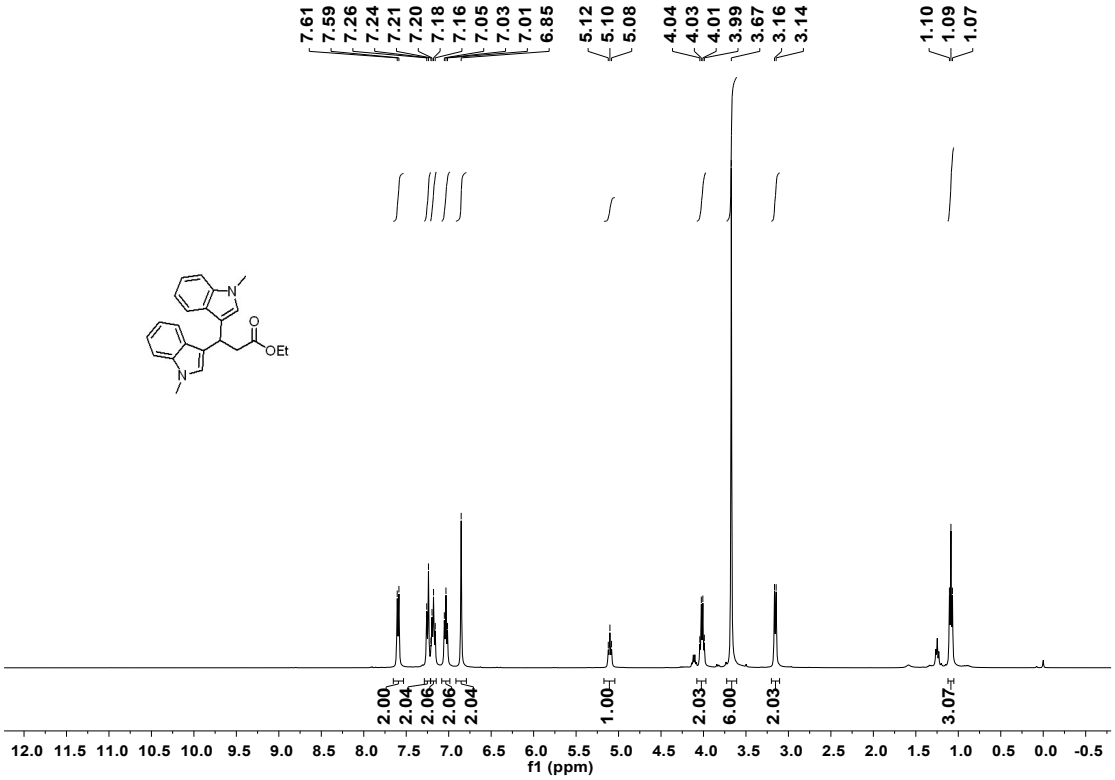

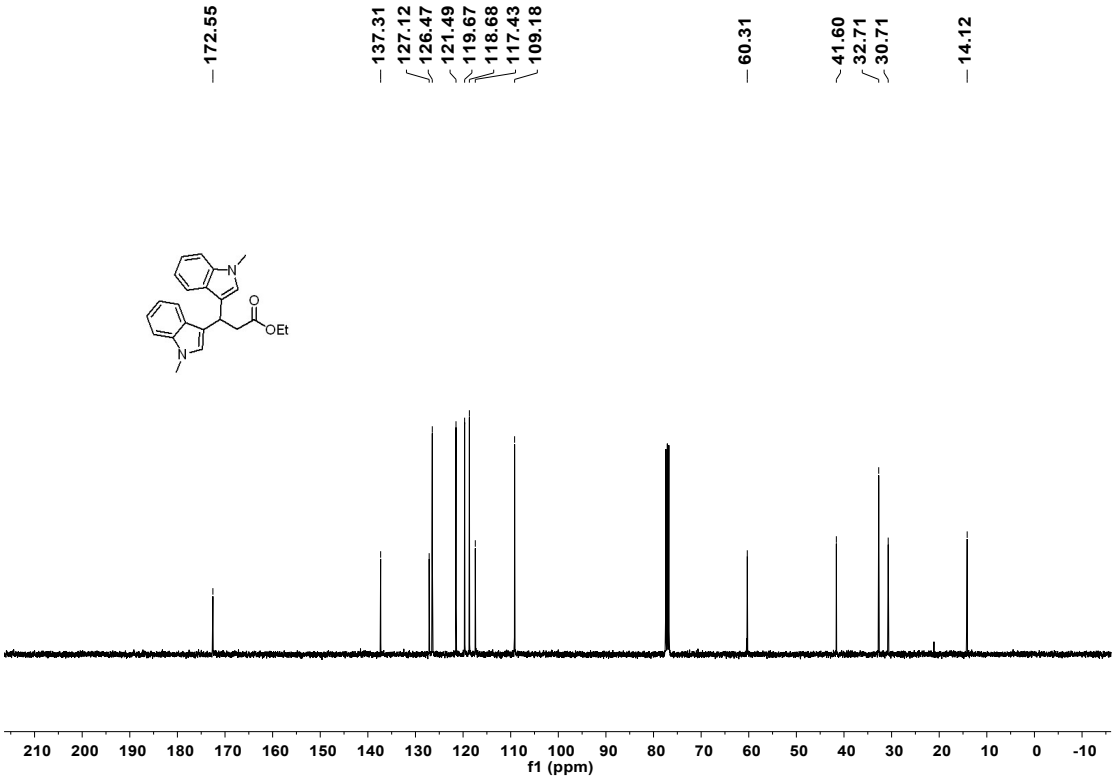

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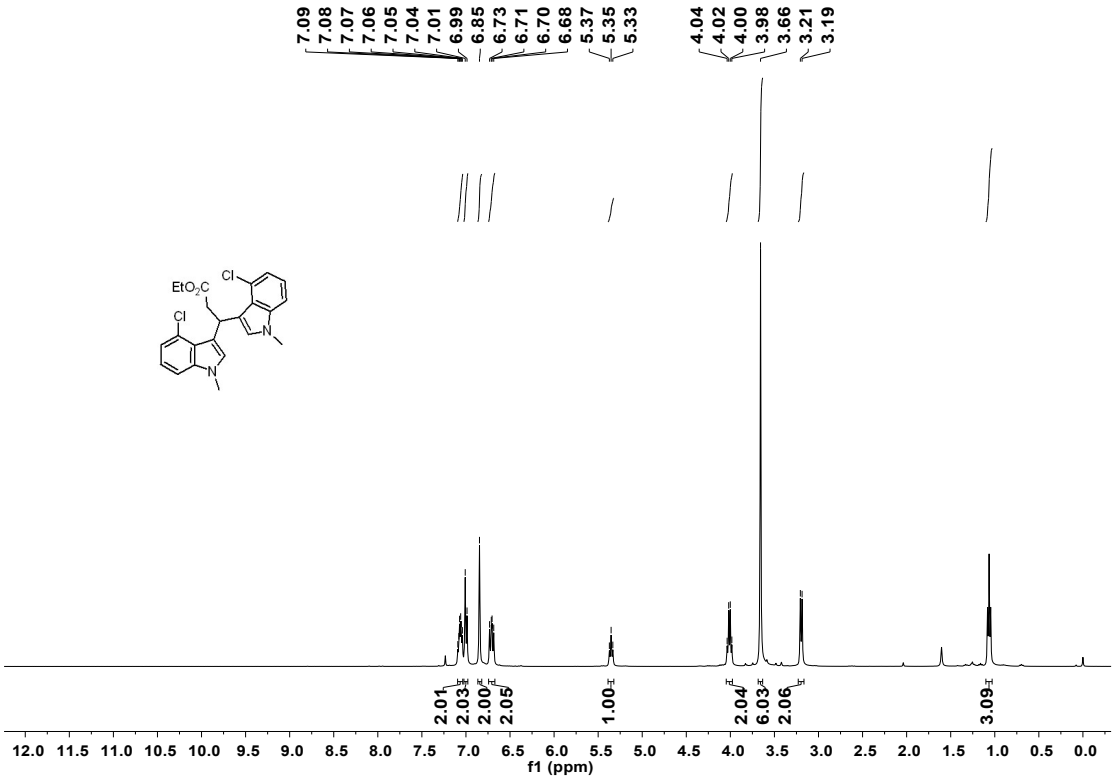
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Cl
Cl
N
N
2.01 2.03 2.00 2.05 1.00 2.04 6.03 2.06 3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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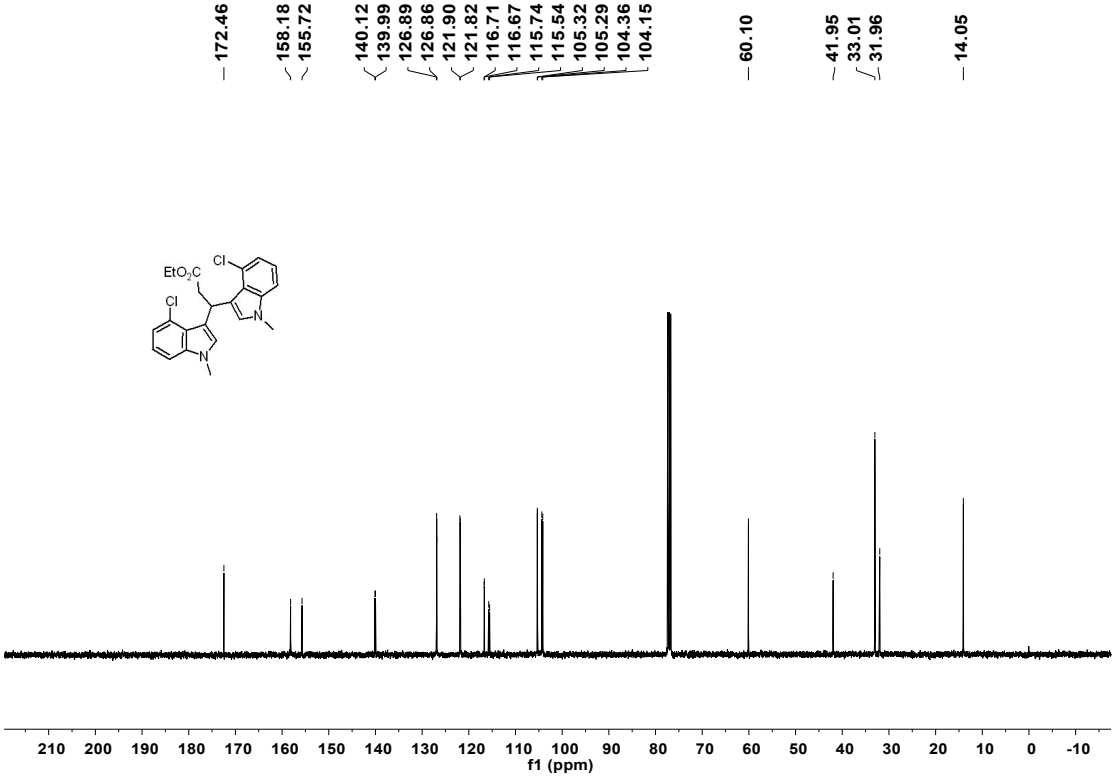
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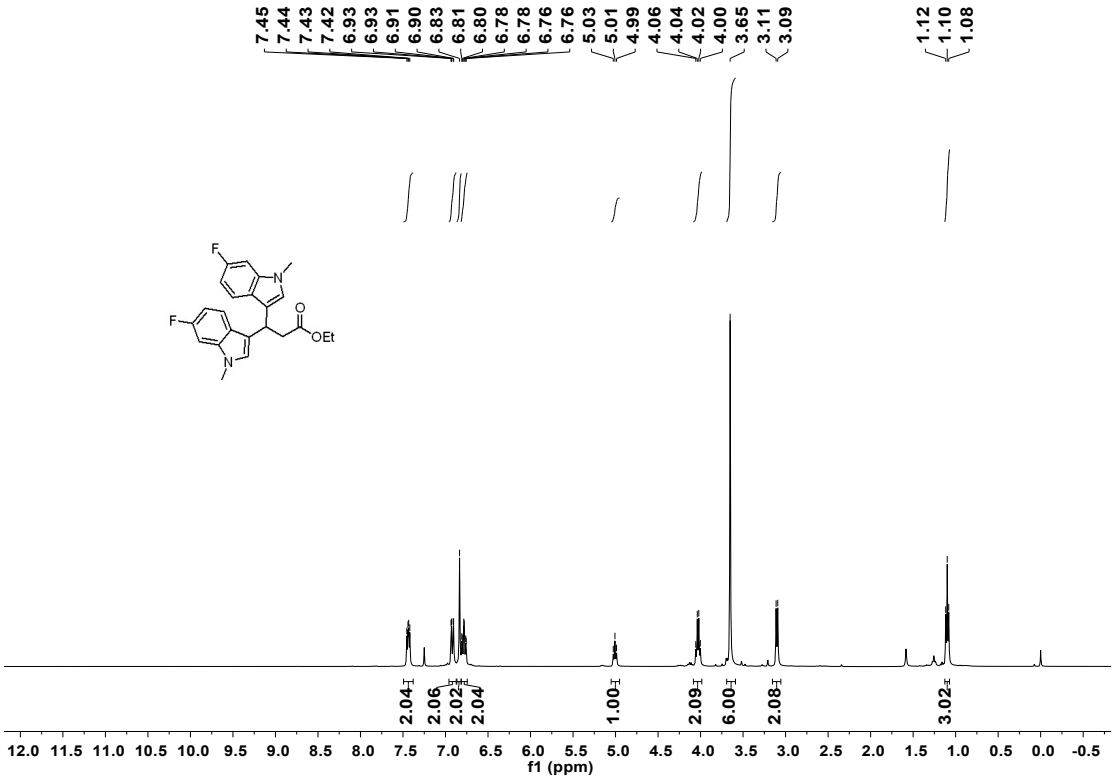
Cl
Cl
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1c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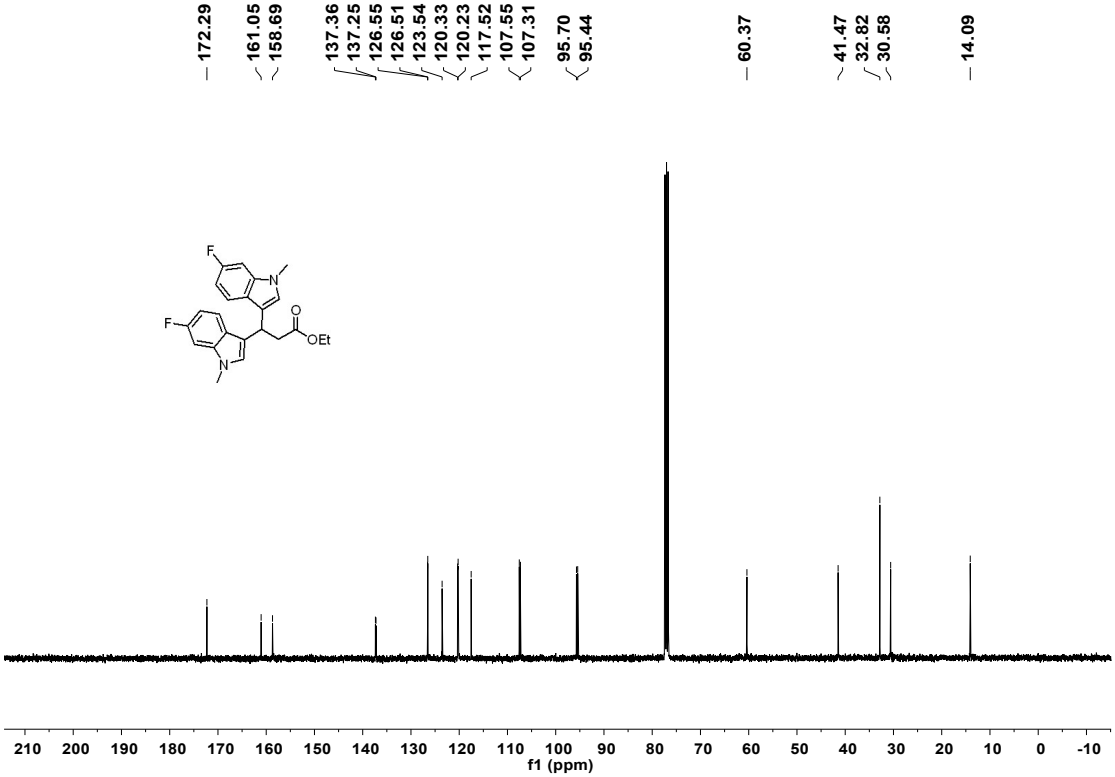
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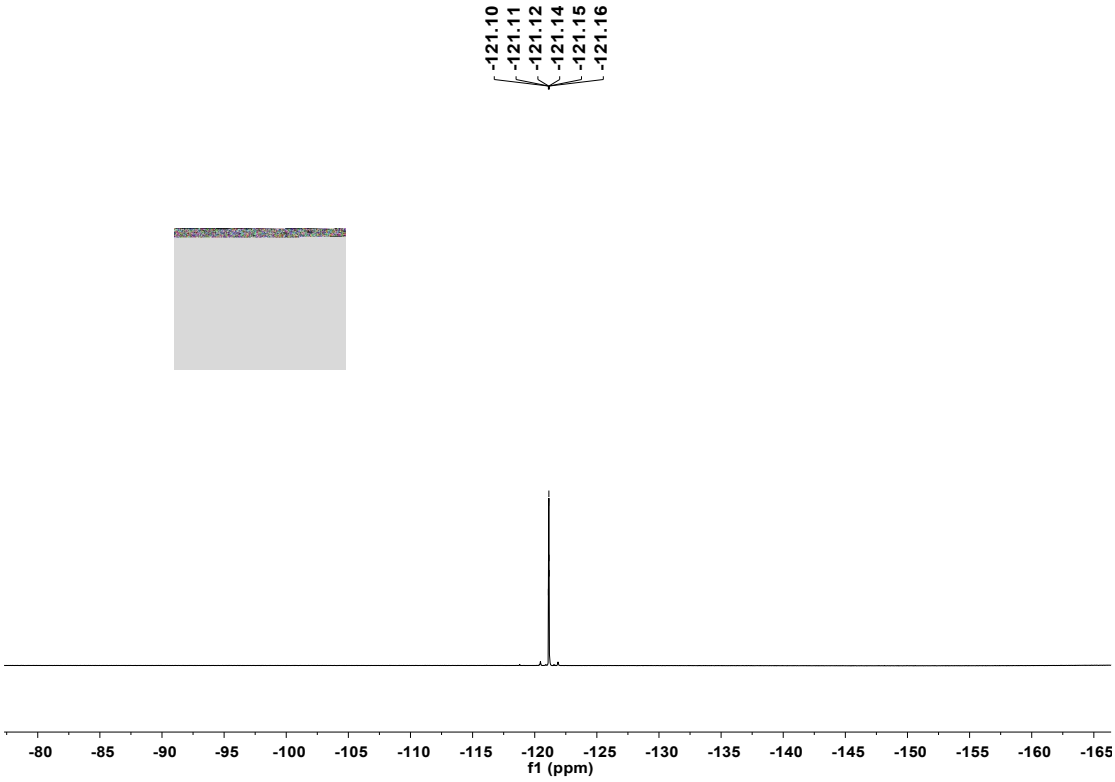
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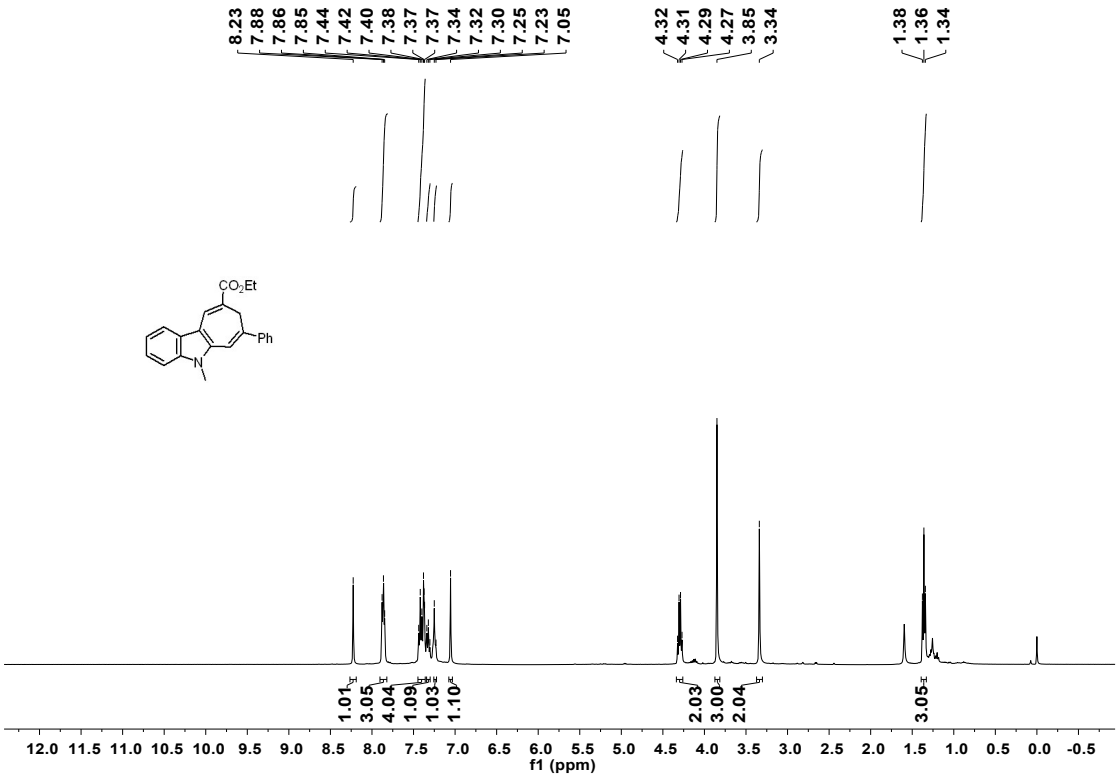
3a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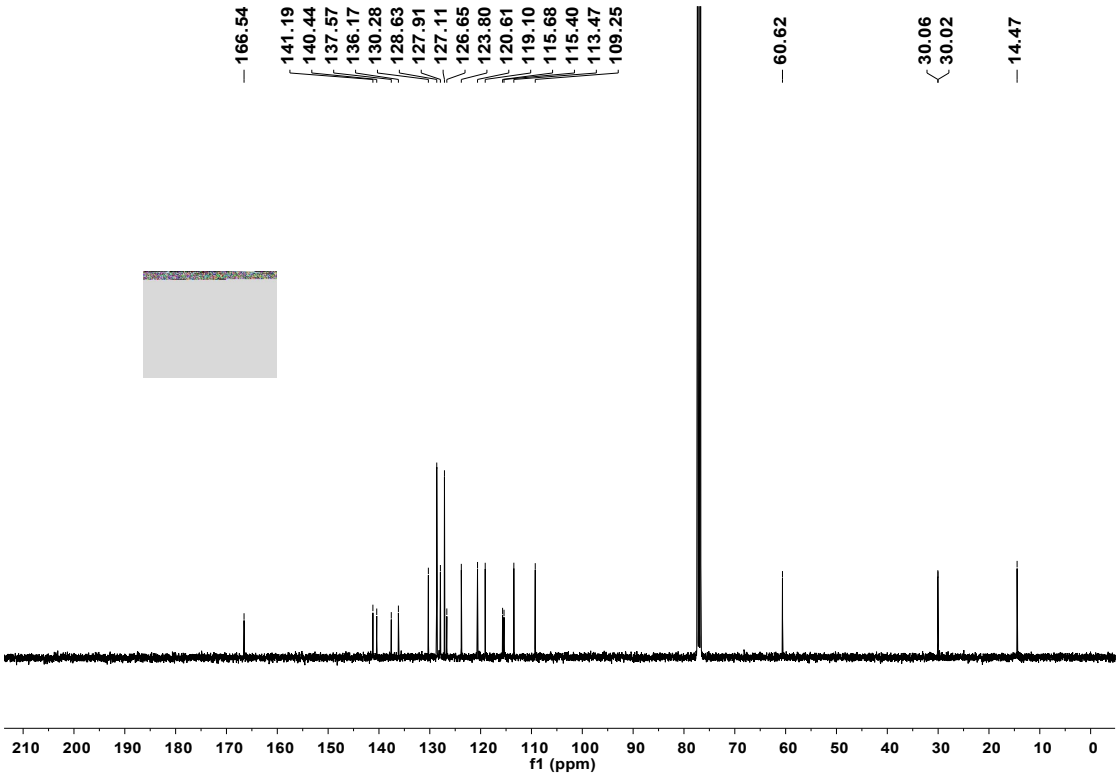
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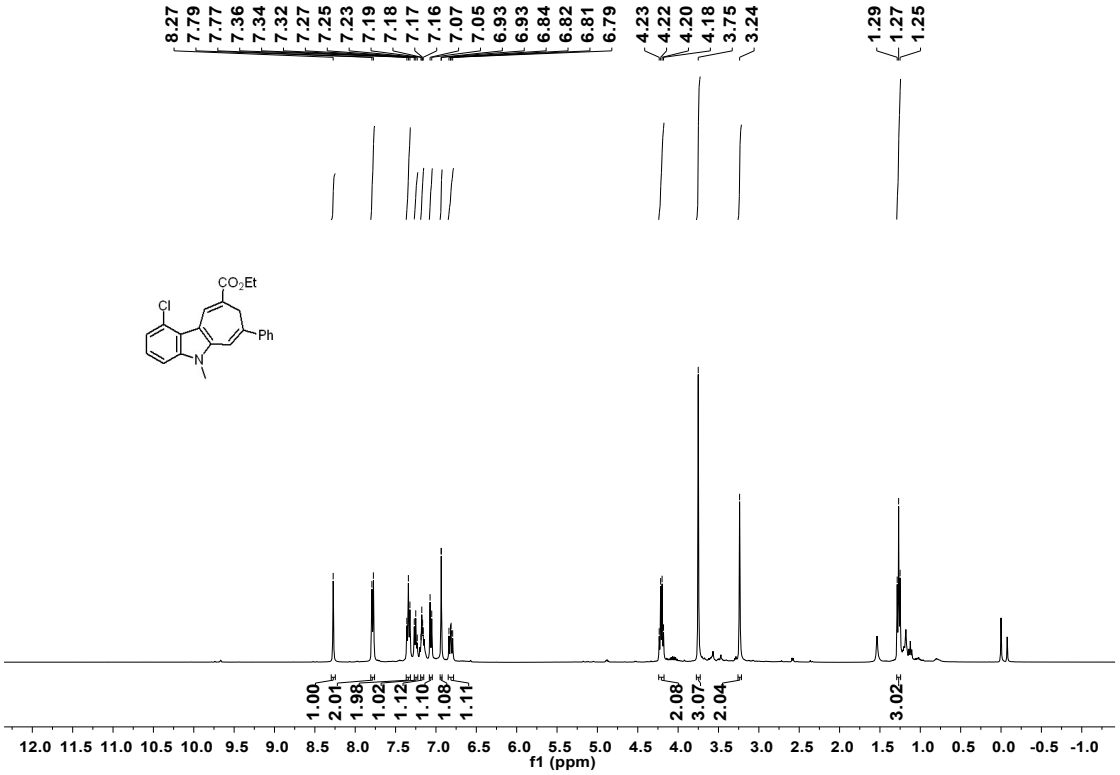
3b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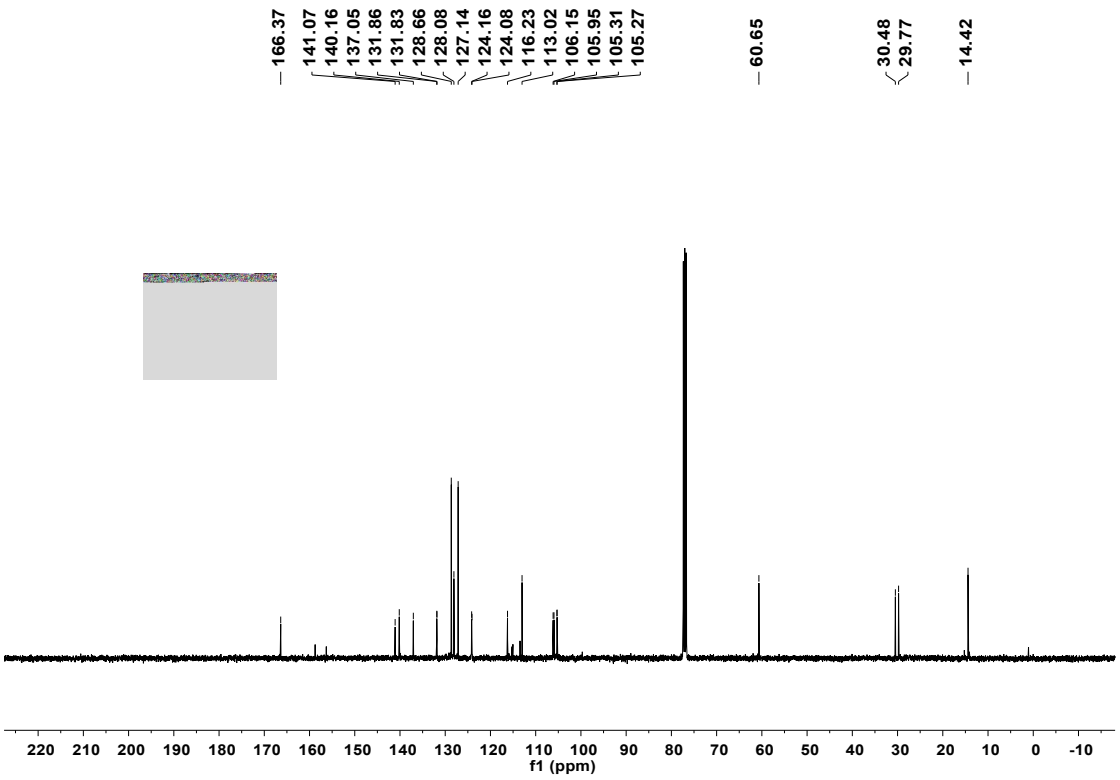
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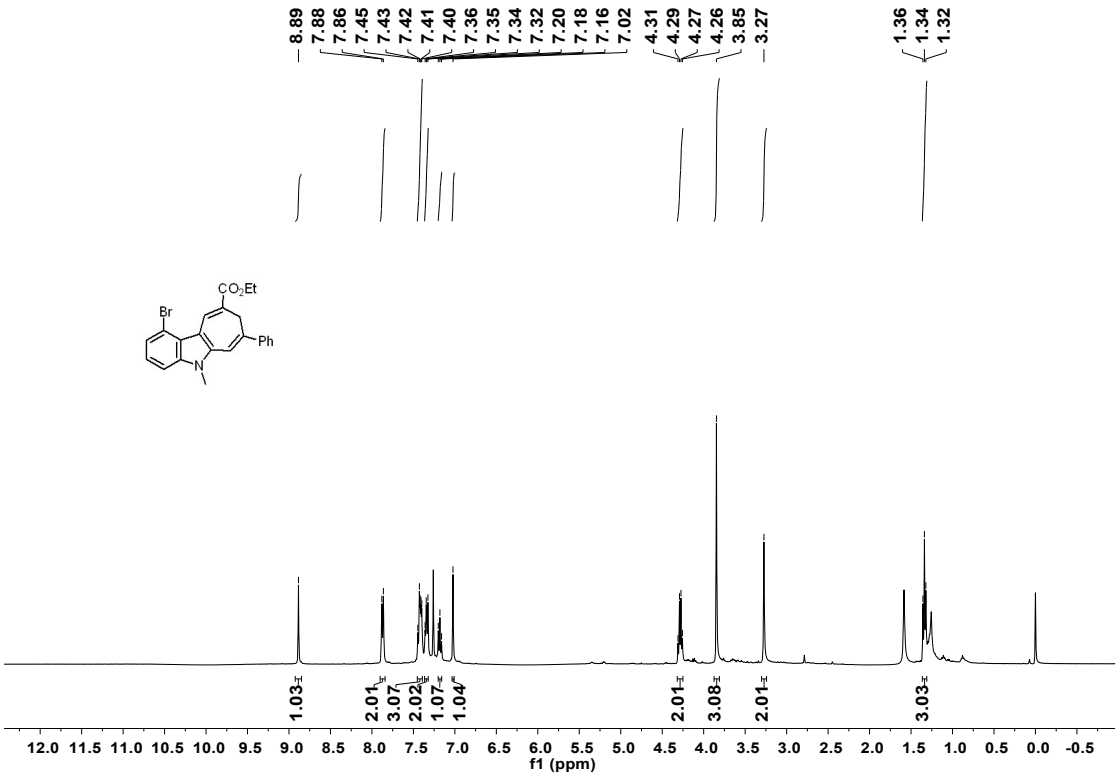
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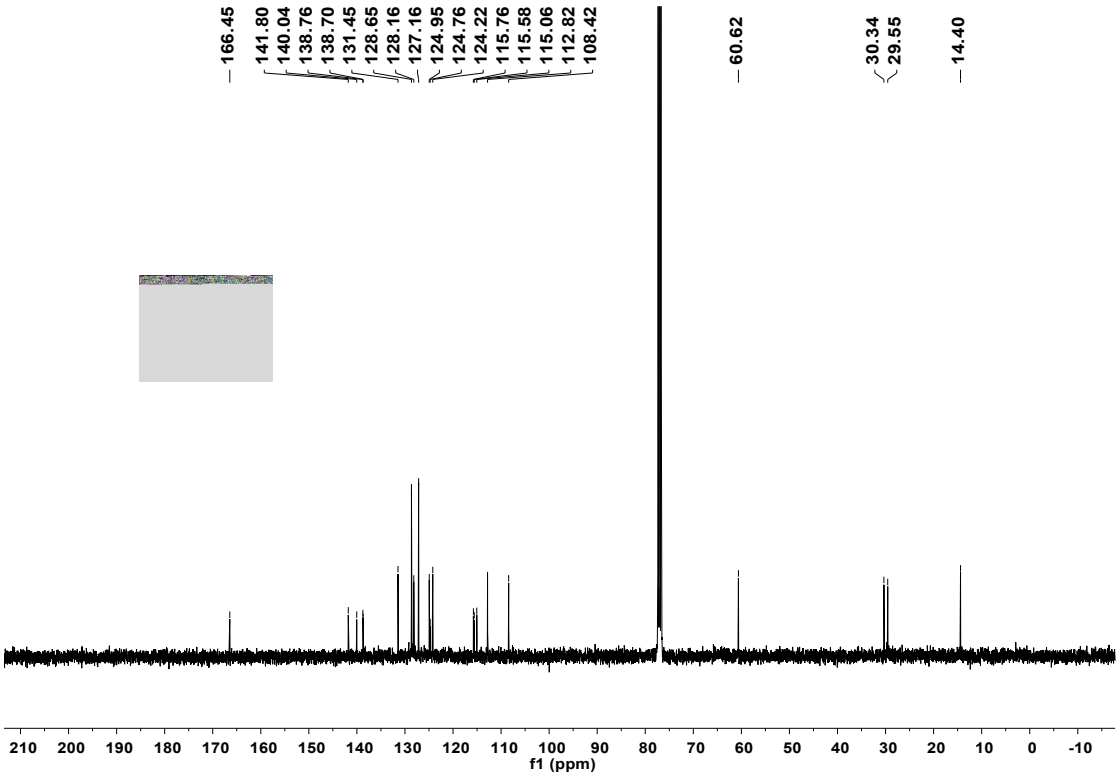
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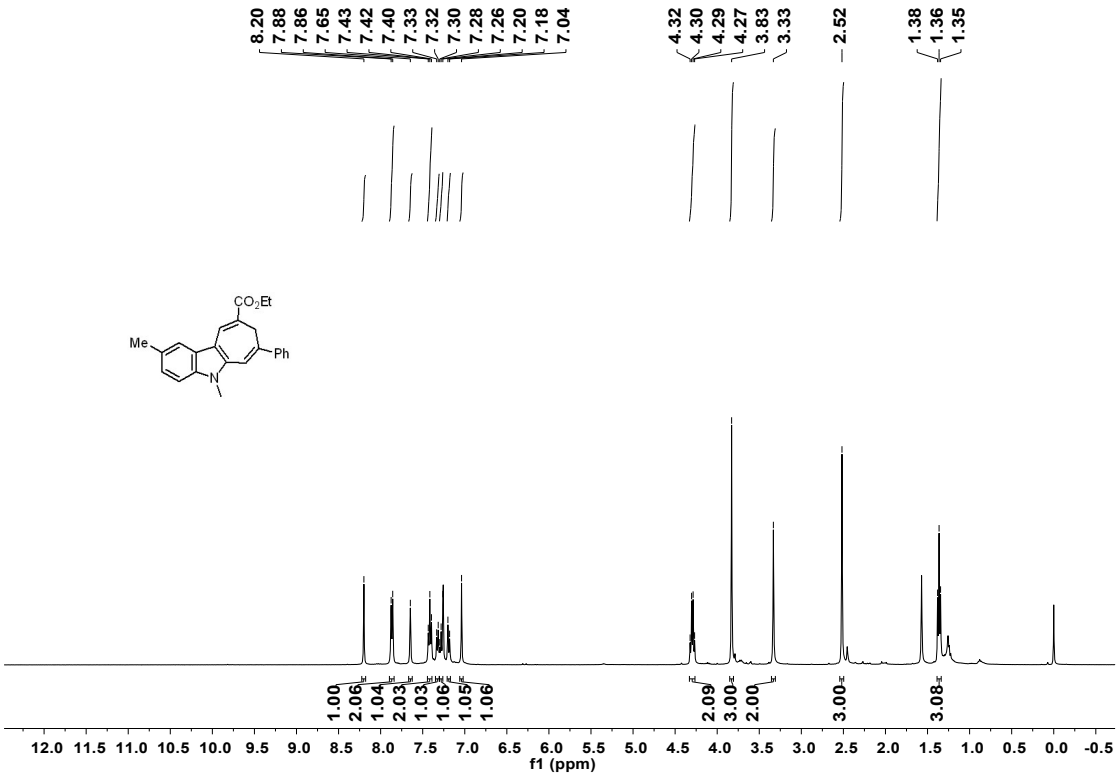
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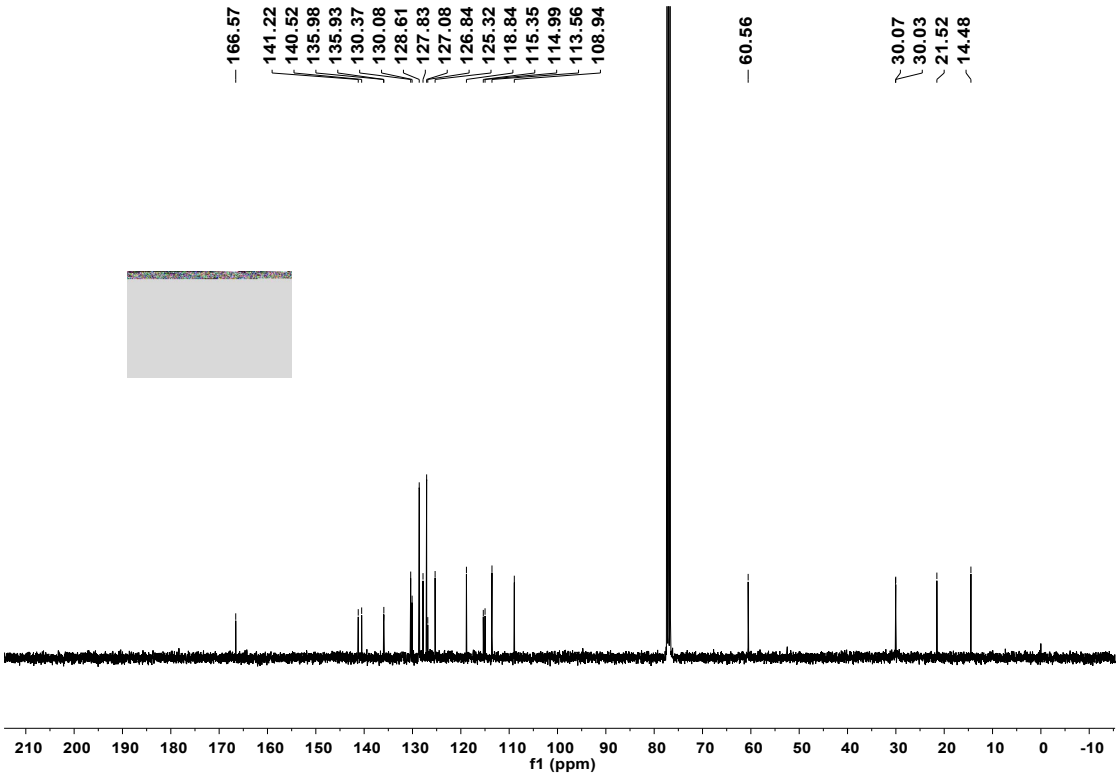
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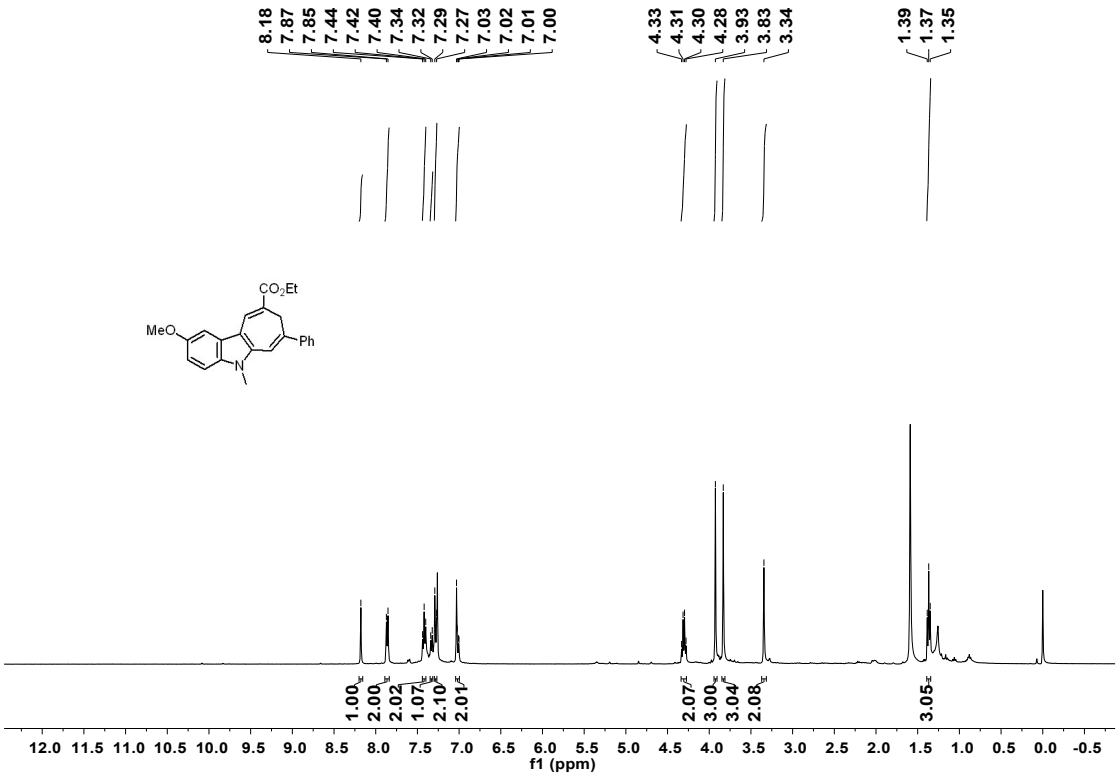
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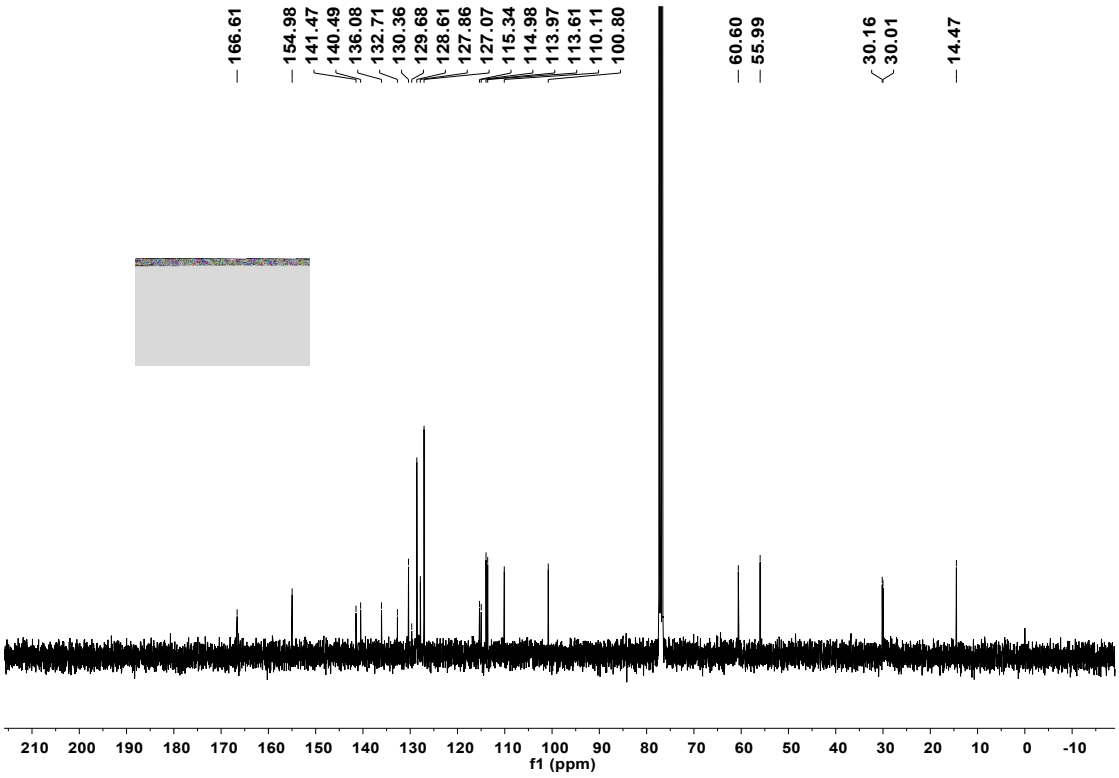
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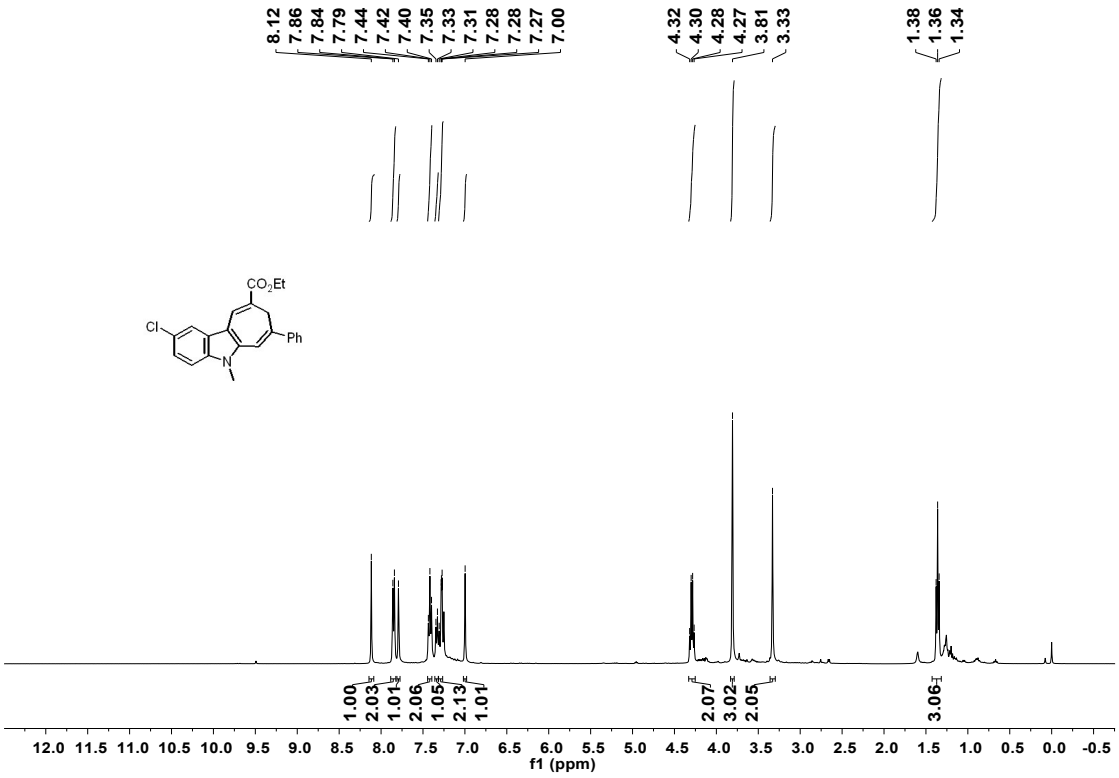
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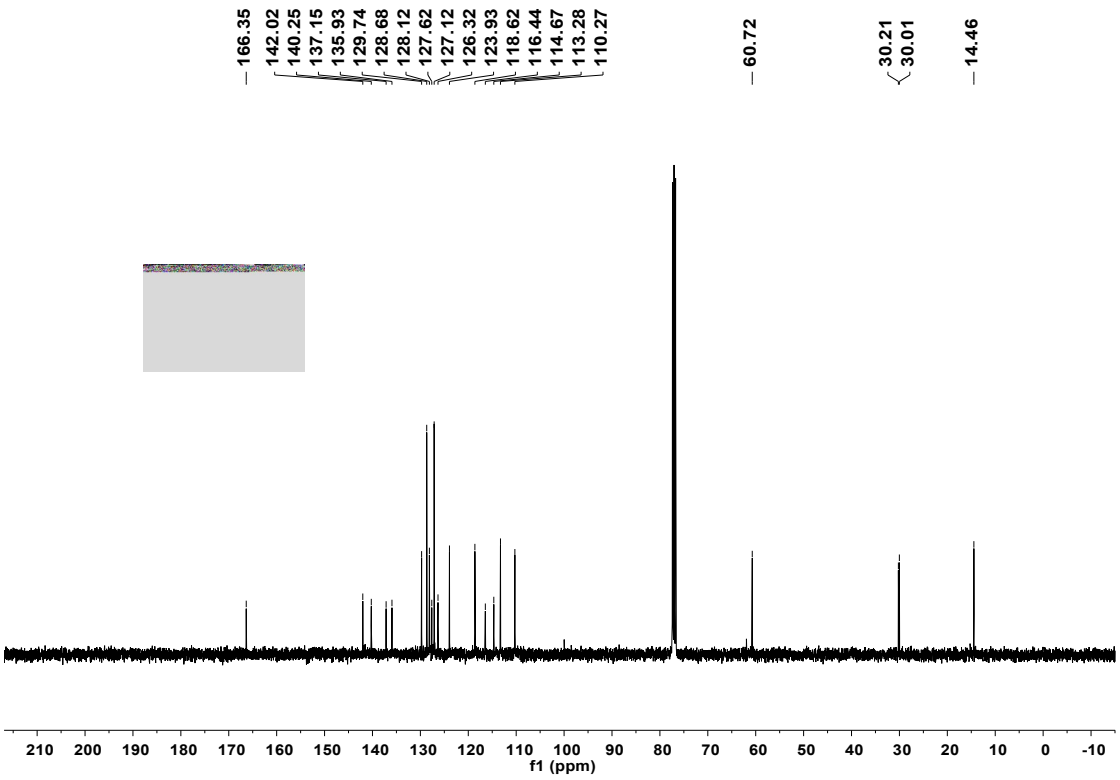
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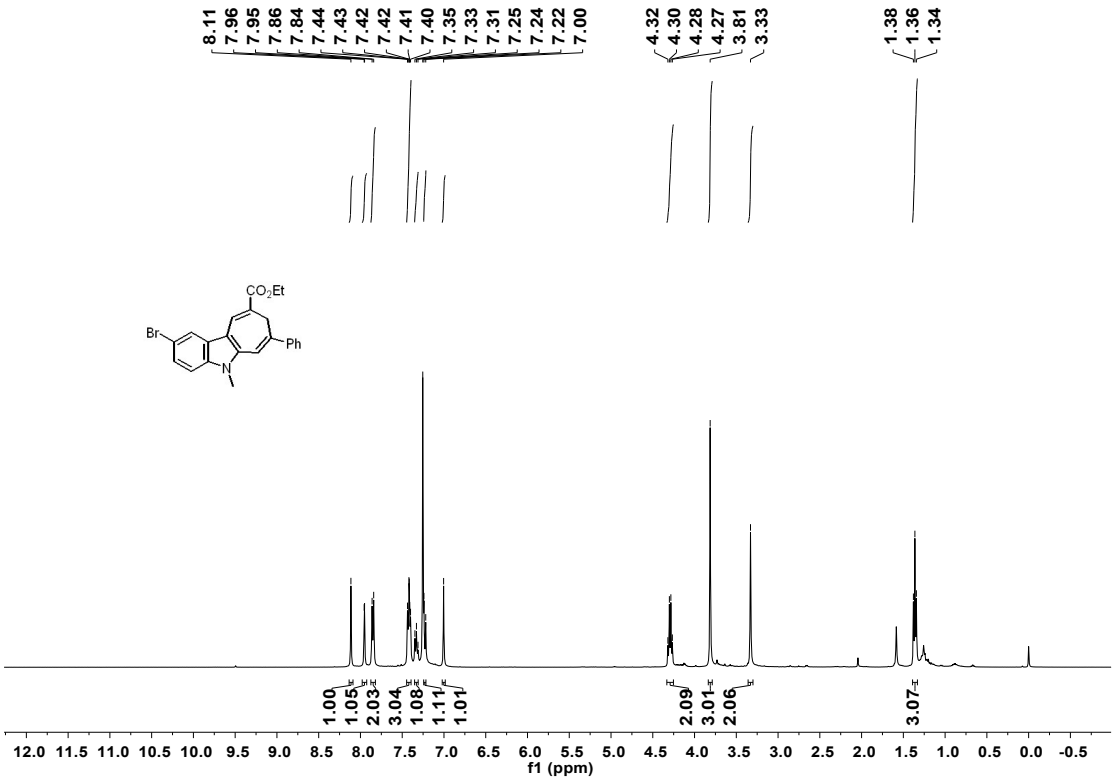
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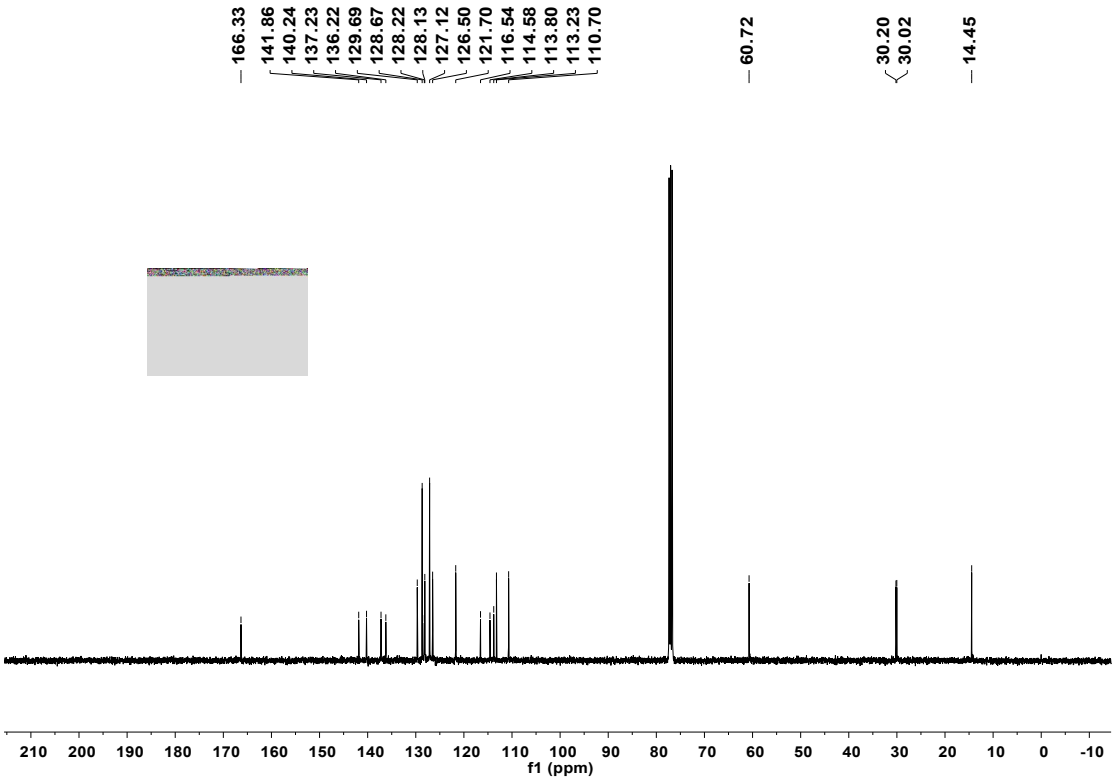
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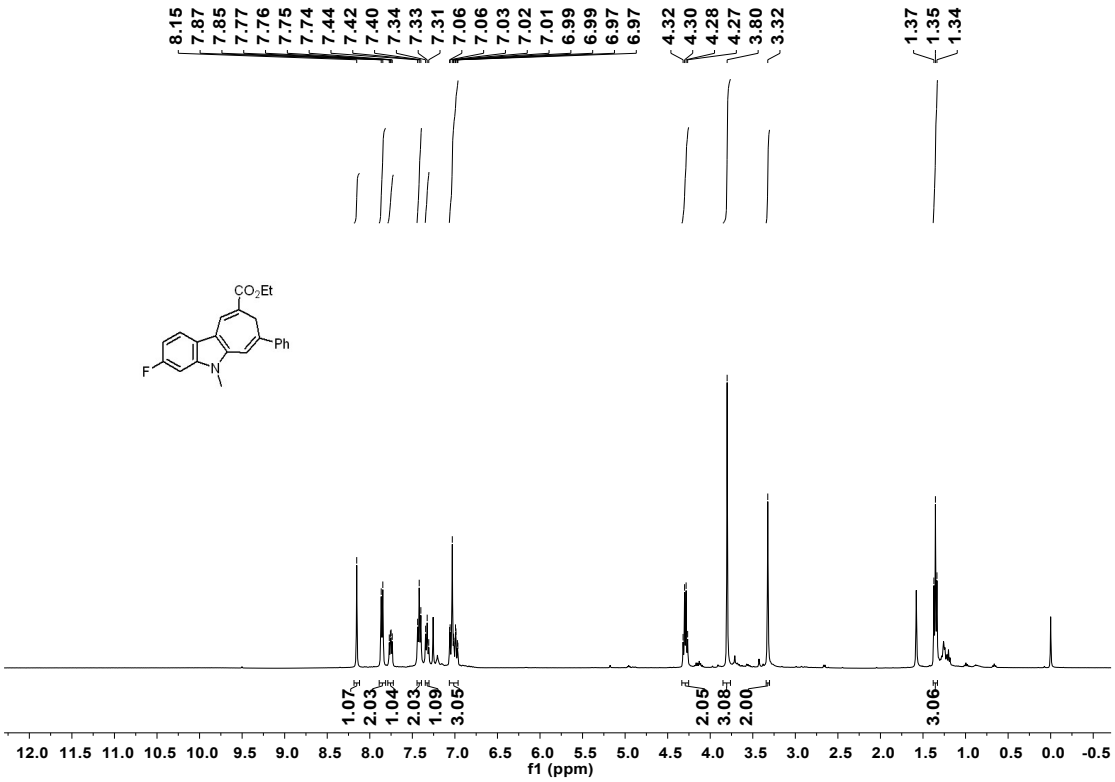
f1 (ppm)

3h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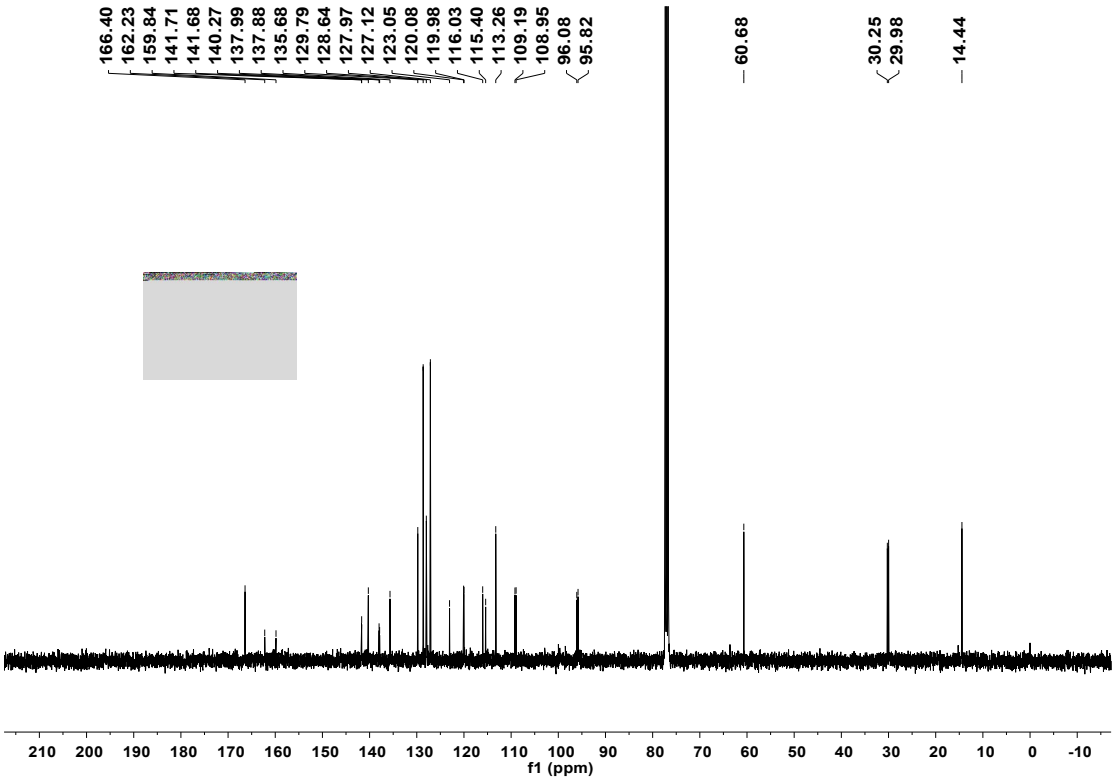
7.85
7.77
7.76
7.75
7.74
7.44
7.42
7.40
7.34
7.33
7.31
7.06
7.06
7.03
7.02
7.01
6.99
6.99
6.97
6.97
4.32
4.30
4.28
4.27
3.80
3.32
1.37
1.35
1.34
CO2Et
Ph
F
N
1.07
2.03
1.04
2.03
1.09
3.05
2.05
3.08
2.00
3.06
f1 (ppm)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162.23
159.84
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141.68
140.27
137.99
137.88
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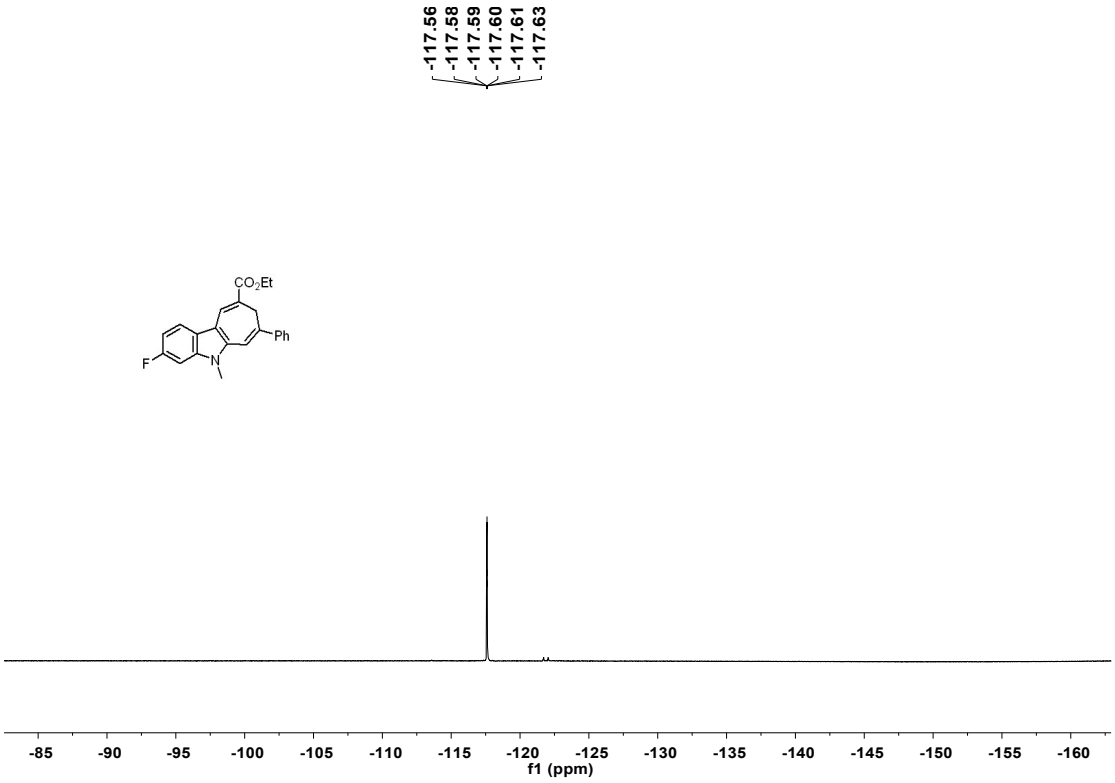
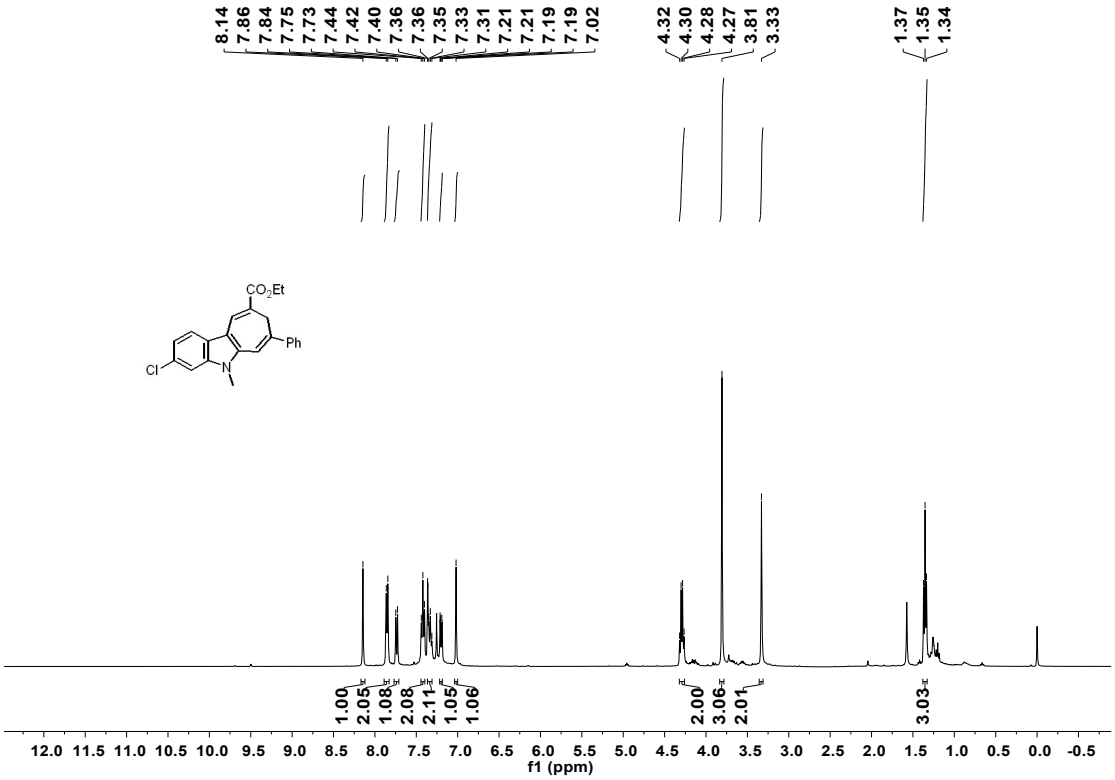
129.79
128.64
127.97
127.12
123.05
120.08
119.98
116.03
115.40
113.26
109.19
108.95
96.08
95.82
60.68
30.25
29.98
14.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-117.56
-117.58
-117.59
-117.60
-117.61
-117.63
CO2Et
Ph
F
N
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160
f1 (ppm)

3i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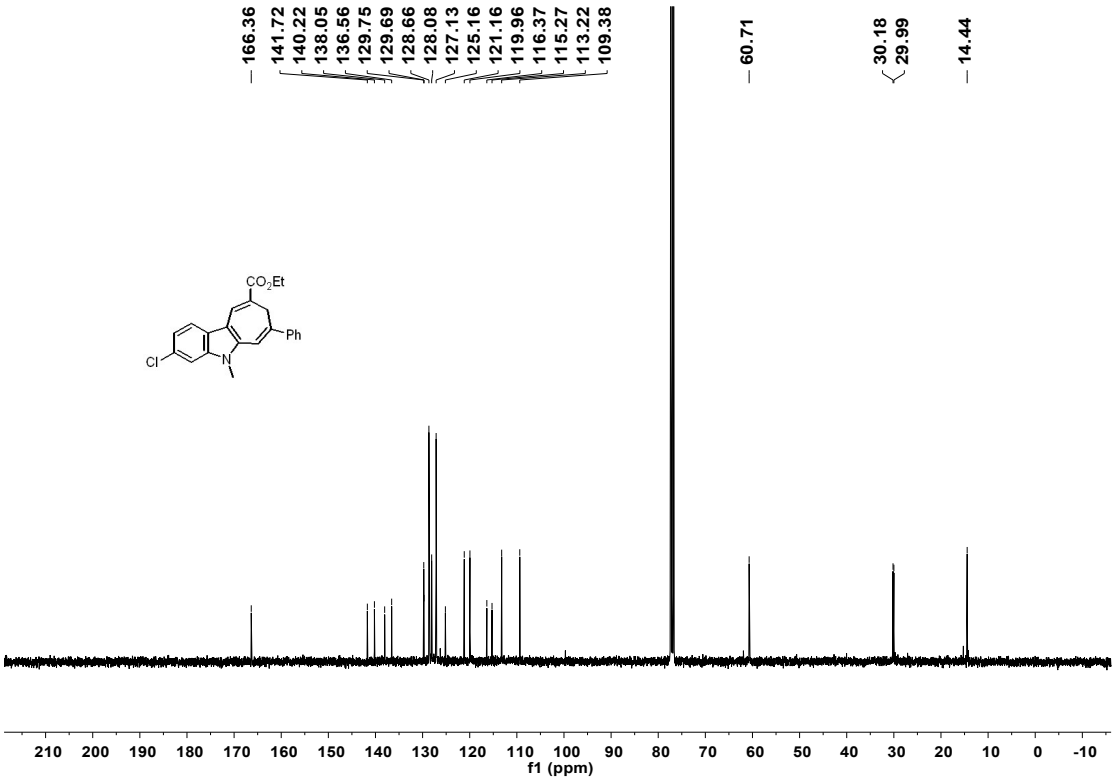
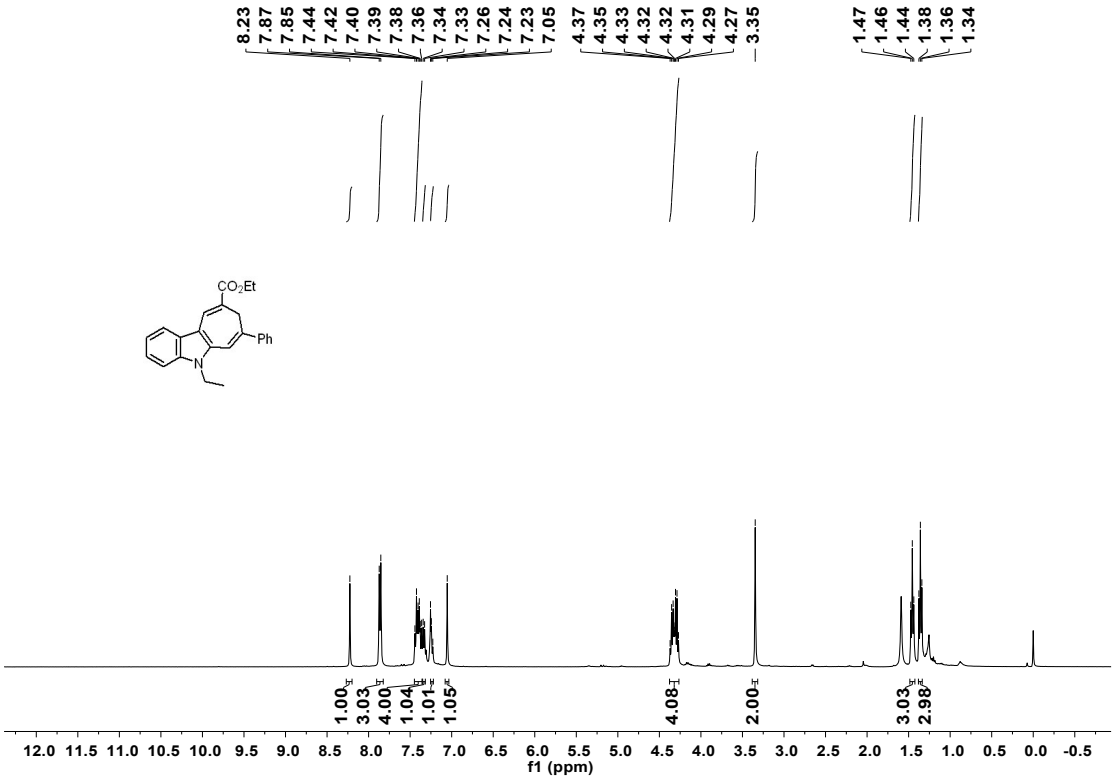
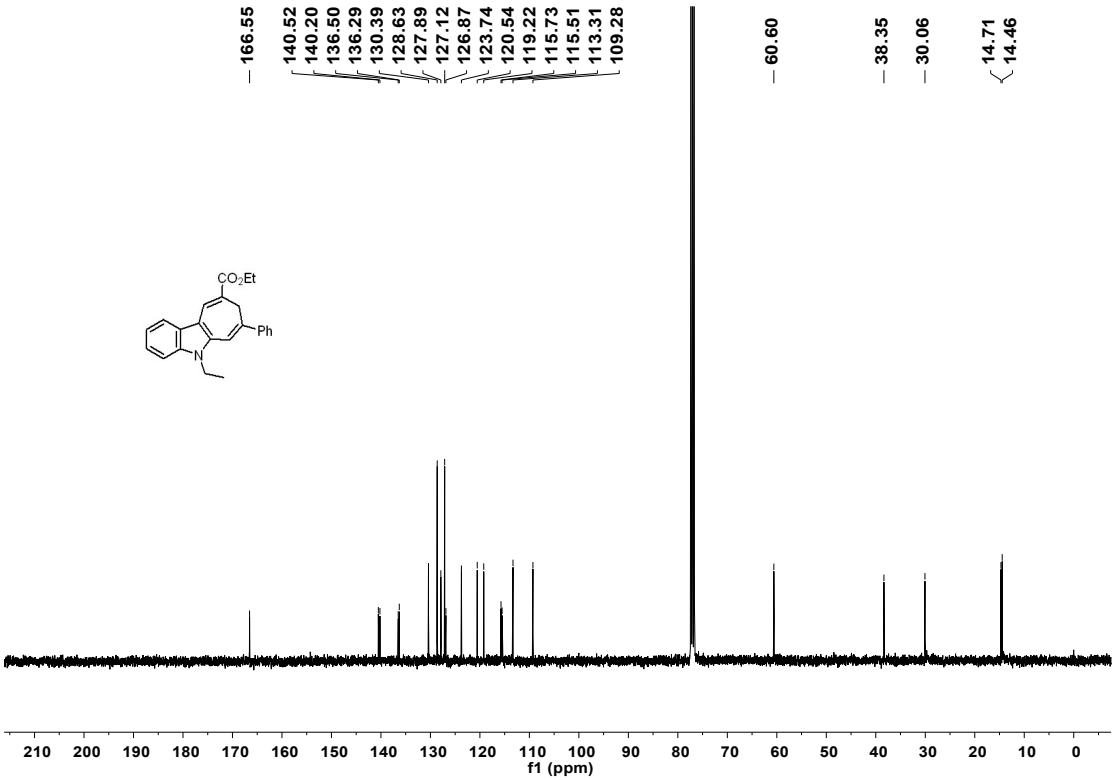
7.44
7.42
7.40
7.36
7.36
7.35
7.33
7.31
7.21
7.21
7.19
7.19
7.02
4.32
4.30
4.28
4.27
3.81
3.33
1.37
1.35
1.34
CO2Et
Ph
Cl
N
1.00
2.05
1.08
2.08
2.11
1.05
1.06
2.00
3.06
2.01
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

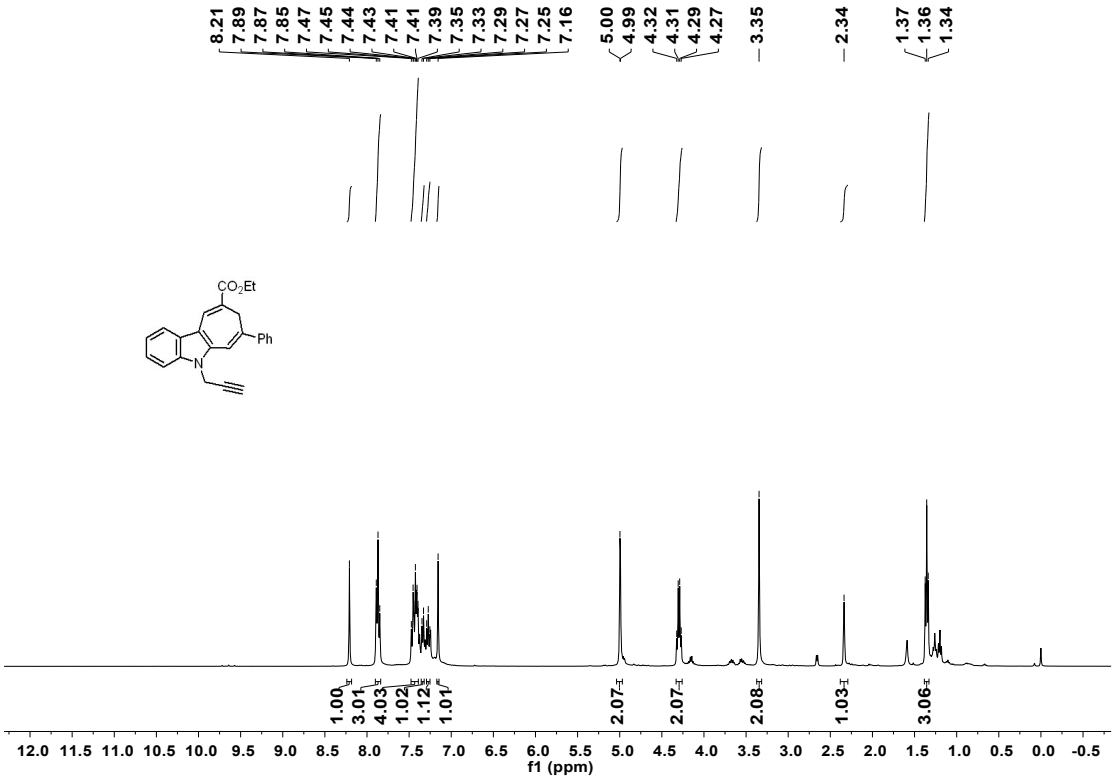

166.36
141.72
140.22
138.05
136.56
129.75
129.69
128.66
128.08
127.13
125.16
121.16
119.96
116.37
115.27
113.22
109.38
60.71
30.18
29.99
14.44
CO2Et
Ph
Cl
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

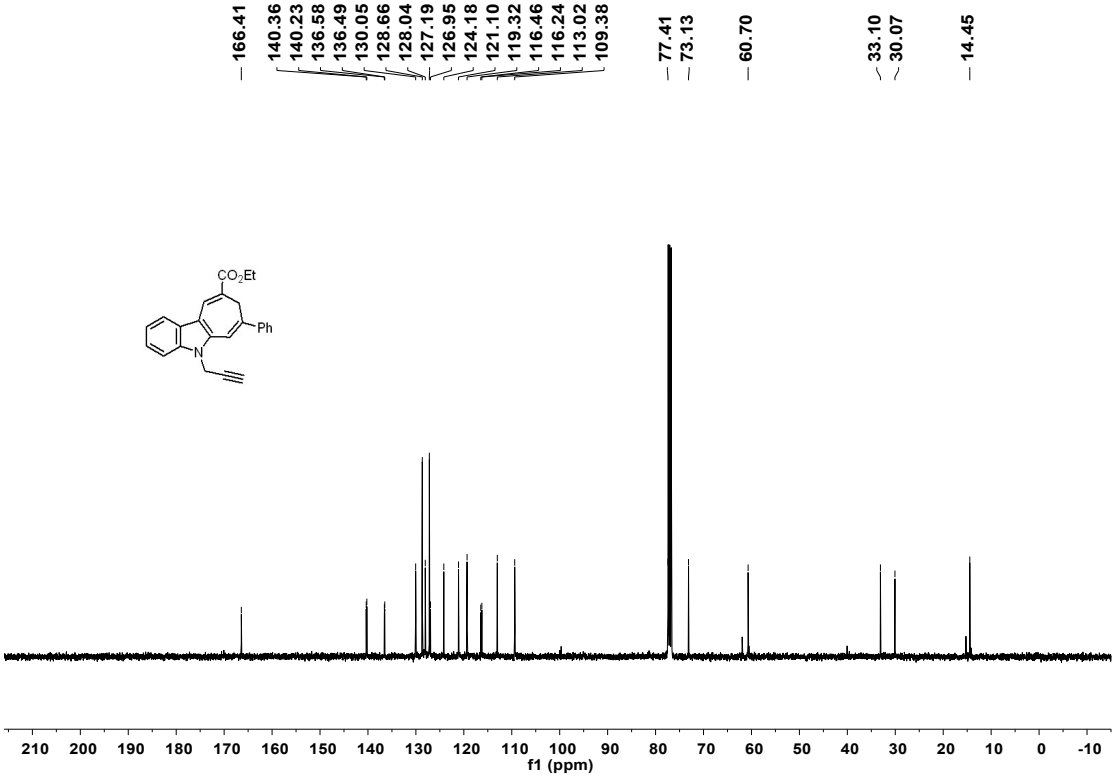
3j


8.23
7.87
7.85
7.44
7.42
7.40
7.39
7.38
7.36
7.34
7.33
7.26
7.24
7.23
7.05
4.37
4.35
4.33
4.32
4.32
4.31
4.29
4.27
3.35
1.47
1.46
1.44
1.38
1.36
1.34
CO2Et
Ph
N
1.00
3.03
4.00
1.04
1.01
1.05
4.08
2.00
3.03
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

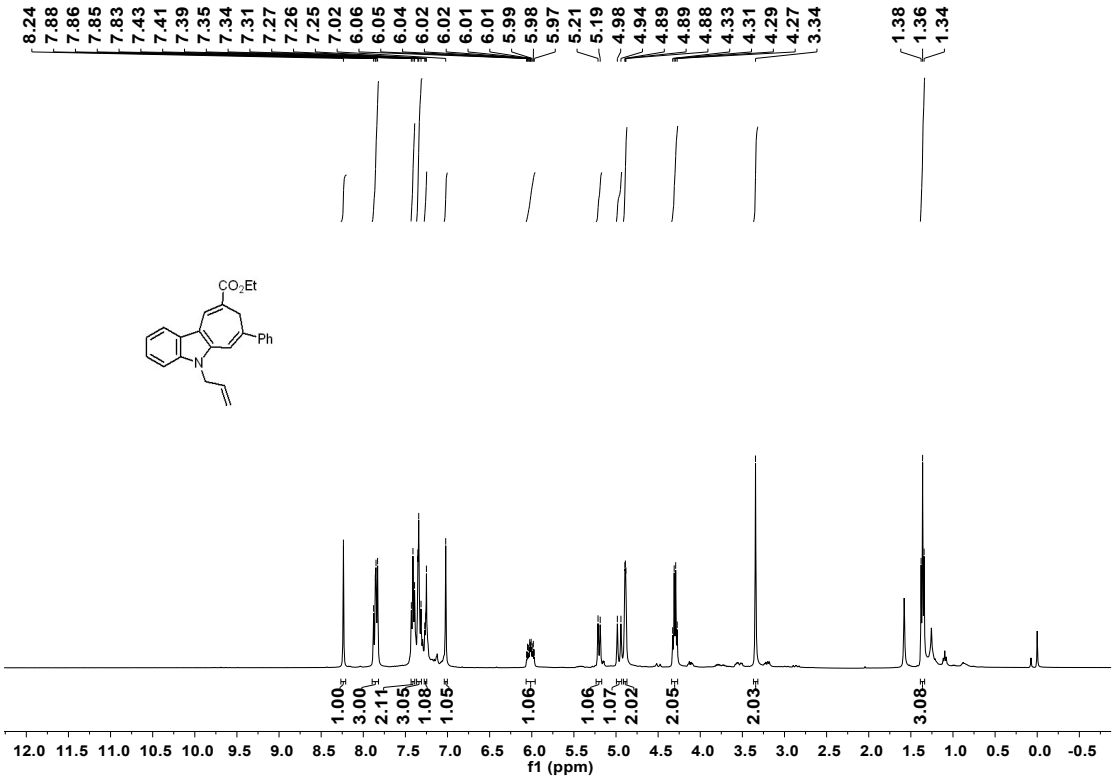

166.55
140.52
140.20
136.50
136.29
130.39
128.63
127.89
127.12
126.87
123.74
120.54
119.22
115.73
115.51
113.31
109.28
60.60
38.35
30.06
14.71
14.46
CO2Et
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

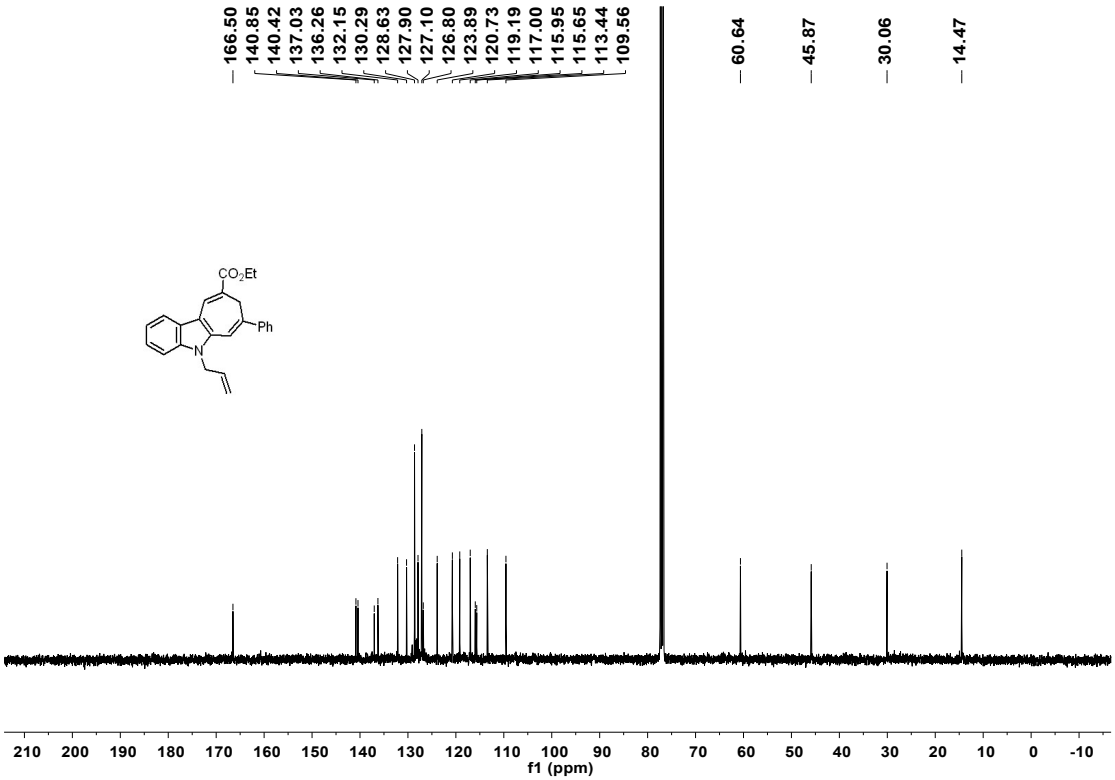
3k


8.21
7.89
7.87
7.85
7.47
7.45
7.44
7.43
7.41
7.41
7.39
7.35
7.33
7.29
7.27
7.25
7.16
5.00
4.99
4.32
4.31
4.29
4.27
3.35
2.34
1.37
1.36
1.34
CO2Et
Ph
N
1.00
3.01
4.03
1.02
1.12
1.01
2.07
2.07
2.08
1.03
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

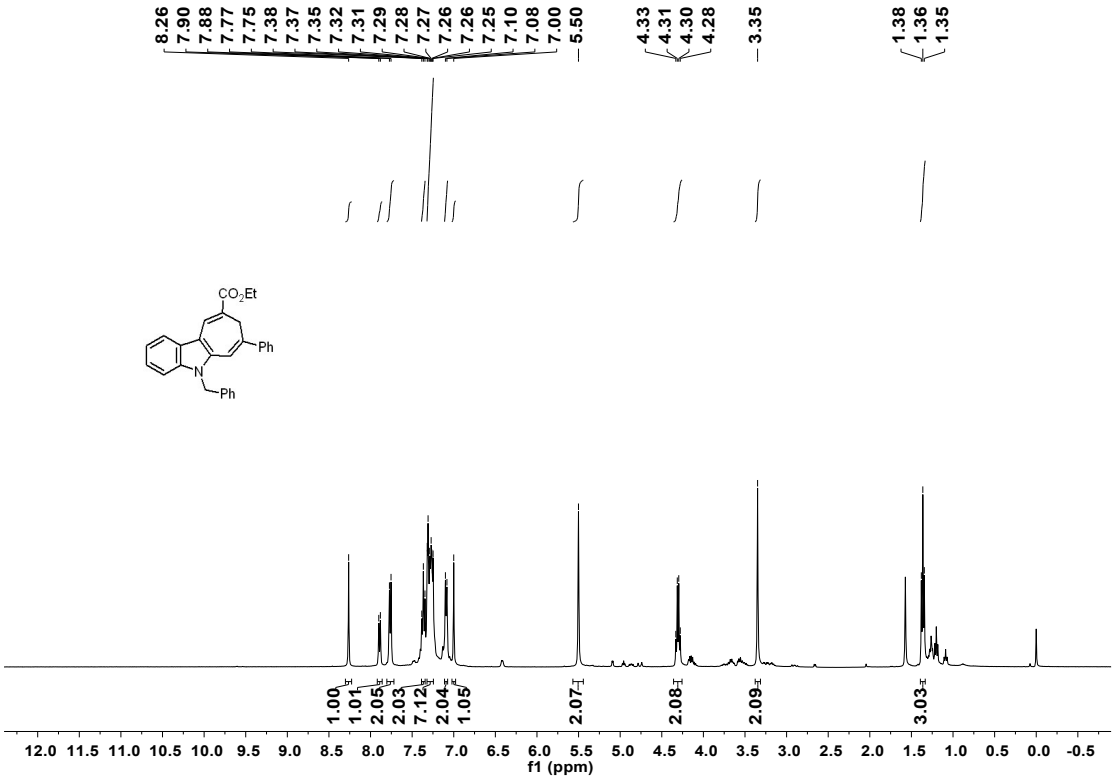

166.41
140.36
140.23
136.58
136.49
130.05
128.66
128.04
127.19
126.95
124.18
121.10
119.32
116.46
116.24
113.02
109.38
77.41
73.13
60.70
33.10
30.07
14.45
CO2Et
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3l


8.24 7.88 7.86 7.85 7.83 7.43 7.41 7.39 7.35 7.34 7.31 7.27 7.26 7.25 7.02 6.06 6.05 6.04 6.02 6.02 6.01 6.01 5.99 5.98 5.97 5.21 5.19 4.98 4.94 4.89 4.89 4.88 4.33 4.31 4.29 4.27 3.34 1.38 1.36 1.34
CO2Et
Ph
N
1.00 3.00 2.11 3.05 1.08 1.05 1.06 1.06 1.07 2.02 2.05 2.03 3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.50 140.85 140.42 137.03 136.26 132.15 130.29 128.63 127.90 127.10 126.80 123.89 120.73 119.19 117.00 115.95 115.65 113.44 109.56
60.64 45.87 30.06 14.47
CO2Et
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3m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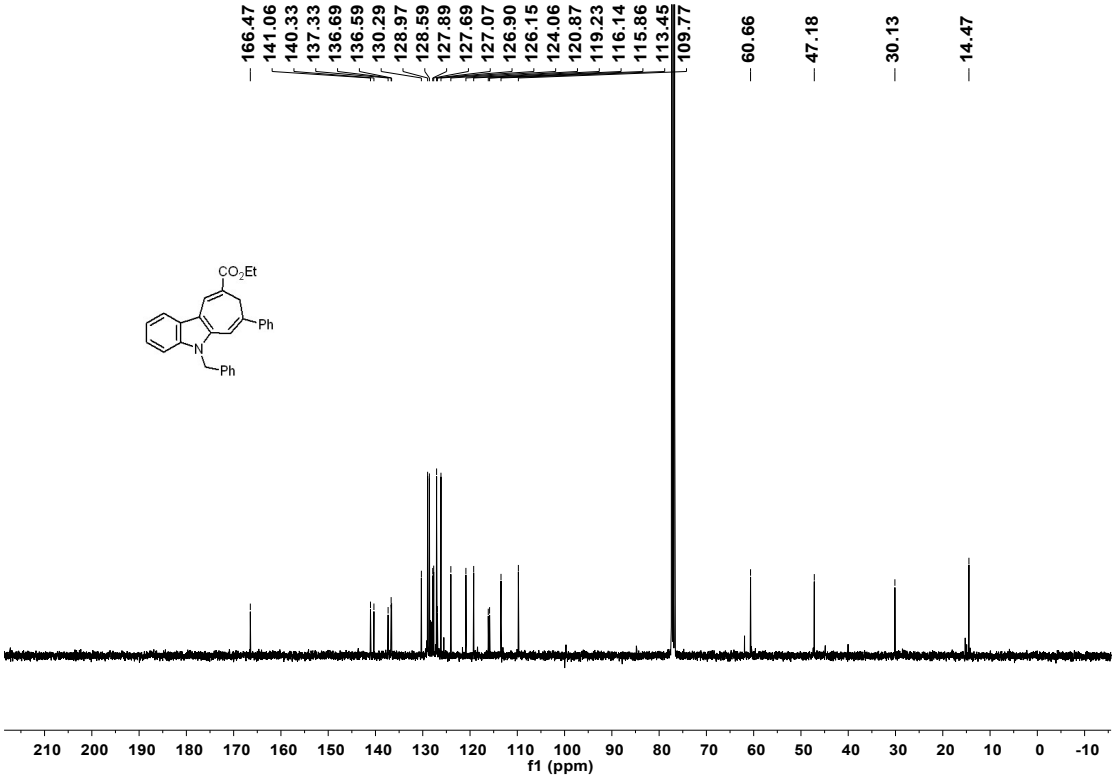
7.88
7.77
7.75
7.38
7.37
7.35
7.32
7.31
7.29
7.28
7.27
7.26
7.26
7.25
7.10
7.08
7.00
5.50
4.33
4.31
4.30
4.28
3.35
1.38
1.36
1.35
CO2Et
Ph
N
Ph
1.00
1.01
2.05
2.03
7.12
2.04
1.05
2.07
2.08
2.09
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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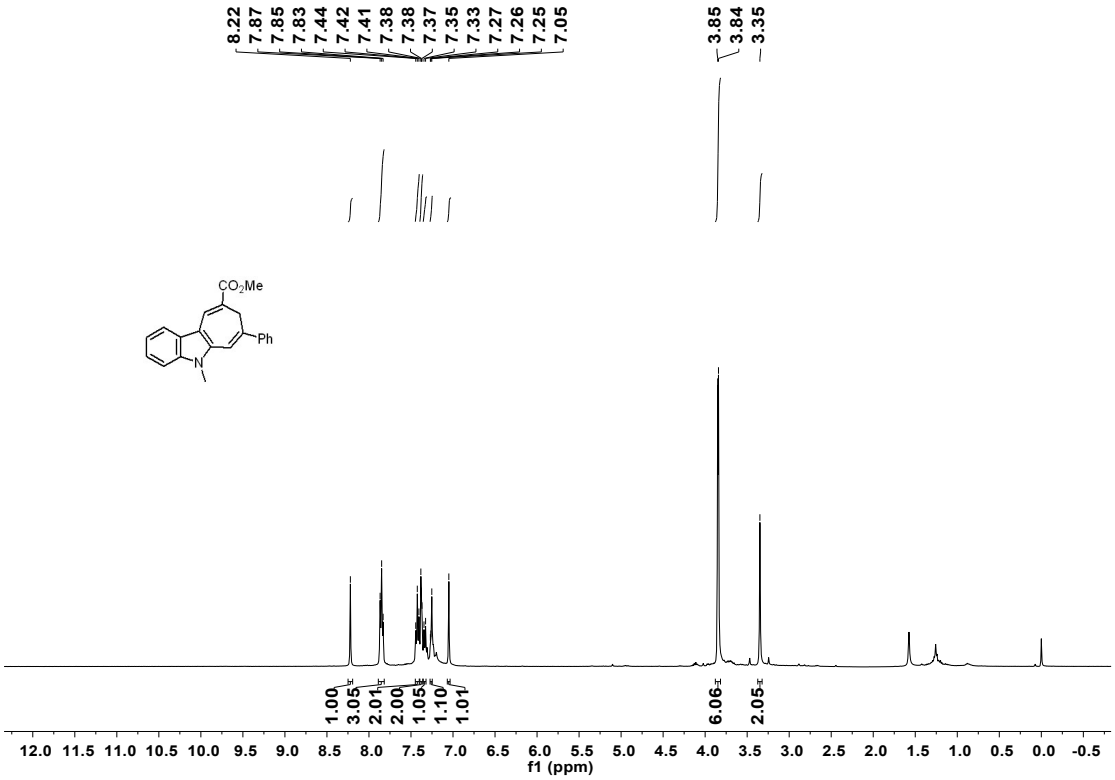
137.33
136.69
136.59
130.29
128.97
128.59
127.89
127.69
127.07
126.90
126.15
124.06
120.87
119.23
116.14
115.86
113.45
109.77
60.66
47.18
30.13
14.47
CO2Et
Ph
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3n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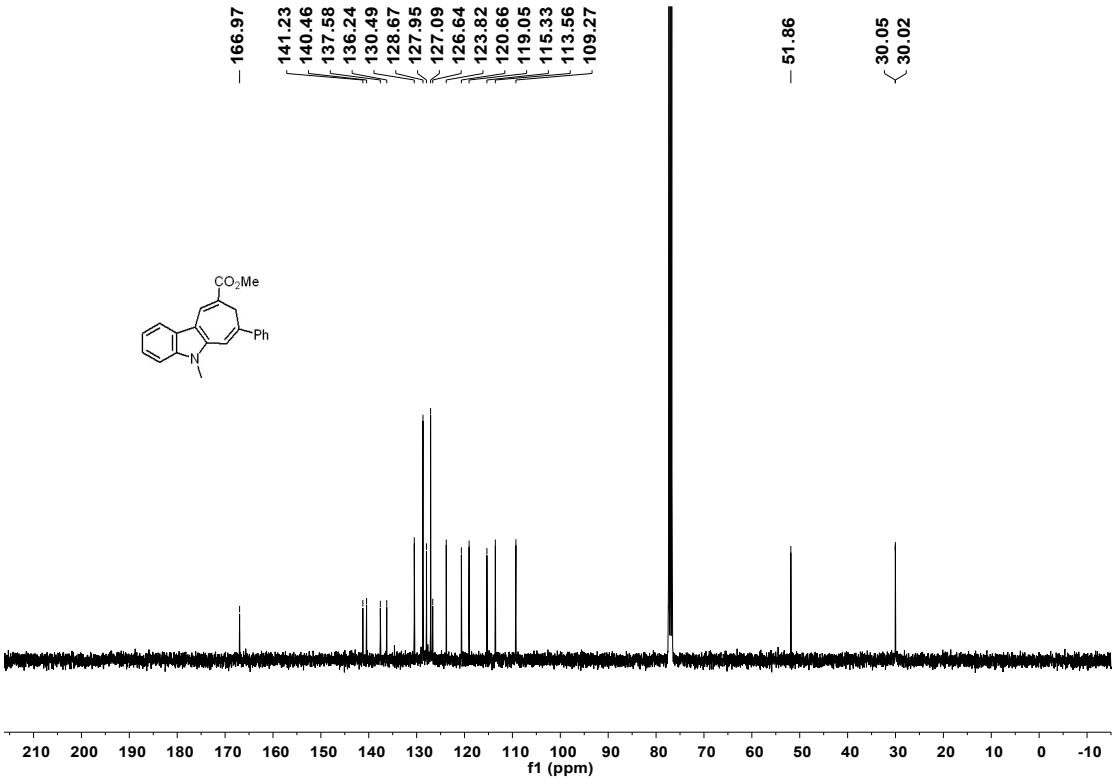
7.87
7.85
7.83
7.44
7.42
7.41
7.38
7.37
7.35
7.33
7.27
7.26
7.25
7.05
3.85
3.84
3.35
CO2Me
Ph
N
1.00
3.05
2.01
2.00
1.05
1.10
1.01
6.06
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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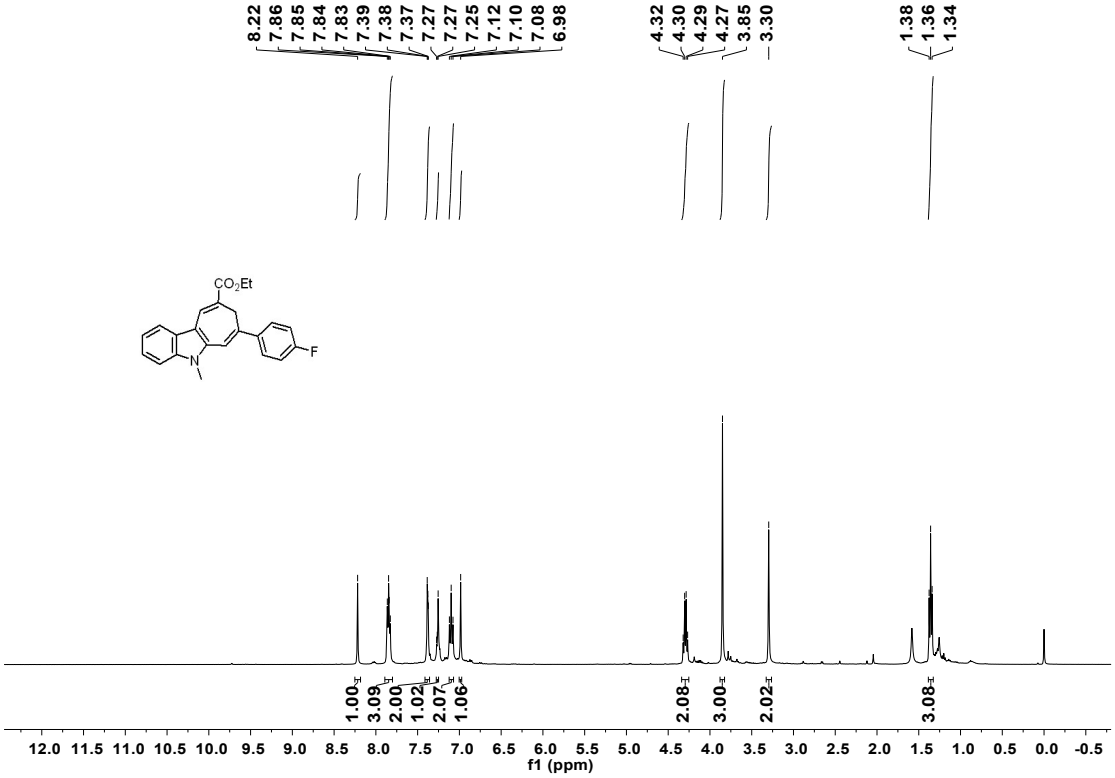
130.49
128.67
127.95
127.09
126.64
123.82
120.66
119.05
115.33
113.56
109.27
51.86
30.05
30.02
CO2Me
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3o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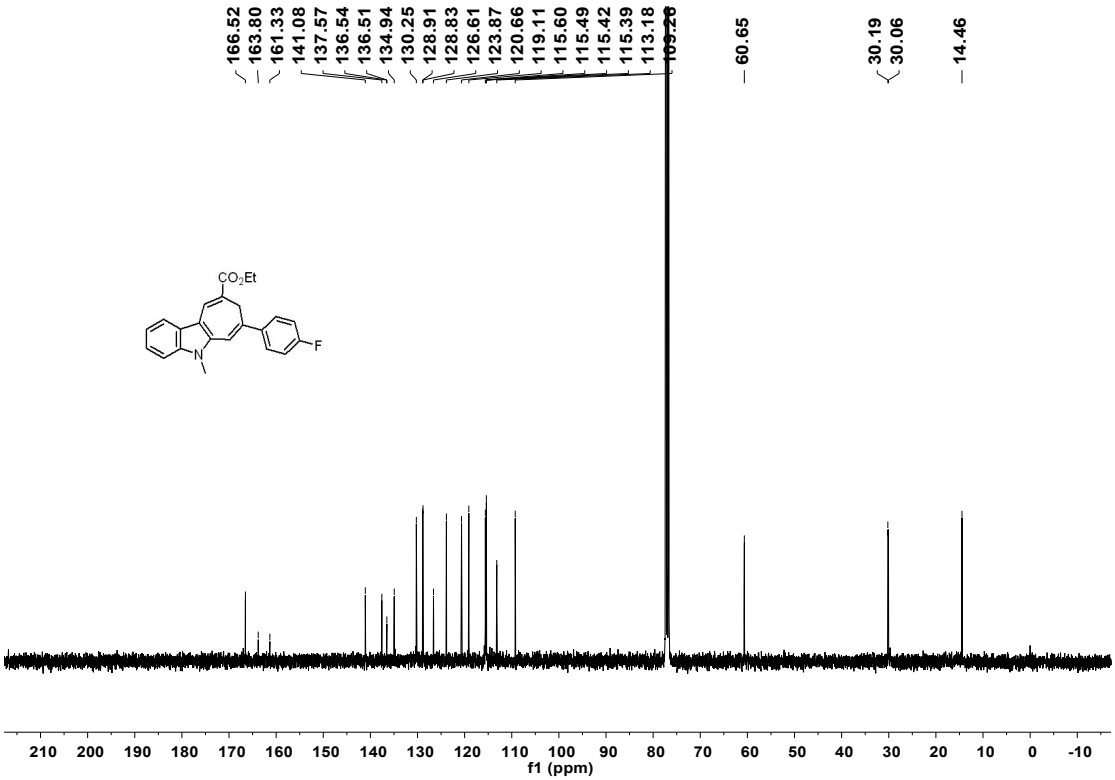
7.86
7.85
7.84
7.83
7.39
7.38
7.37
7.27
7.27
7.25
7.12
7.10
7.08
6.98
4.32
4.30
4.29
4.27
3.85
3.30
1.38
1.36
1.34
CO2Et
N
F
1.00
3.09
2.00
1.02
2.07
1.06
2.08
3.00
2.02
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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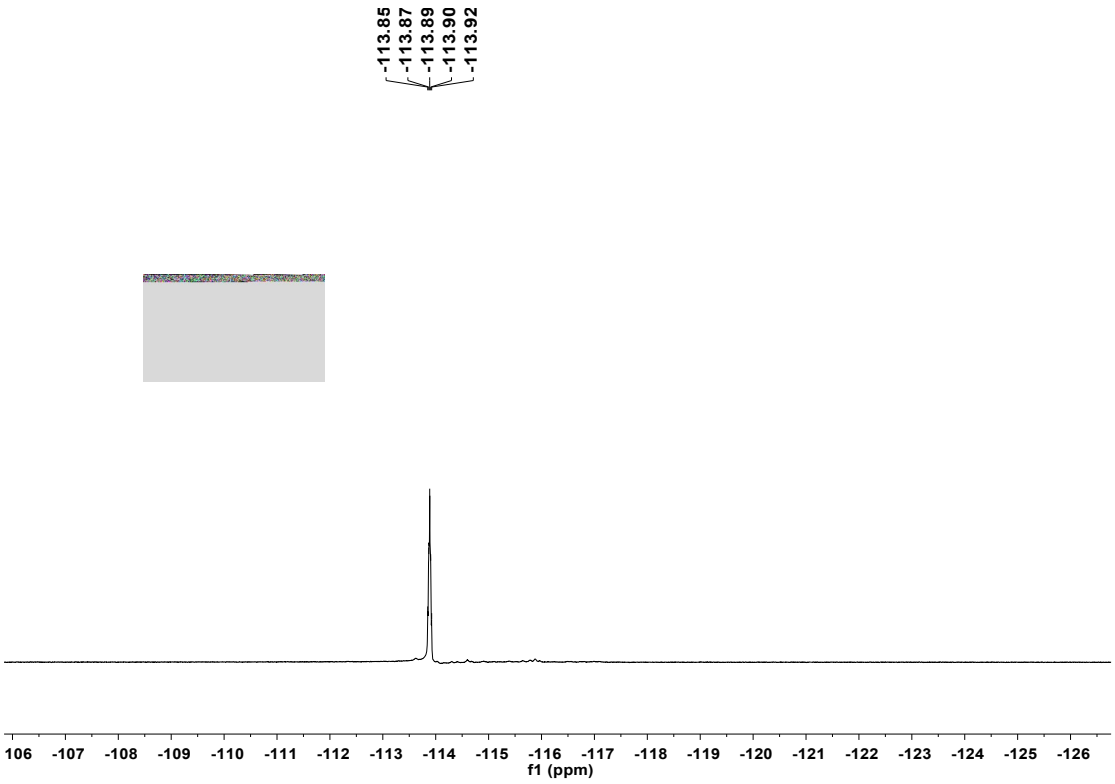
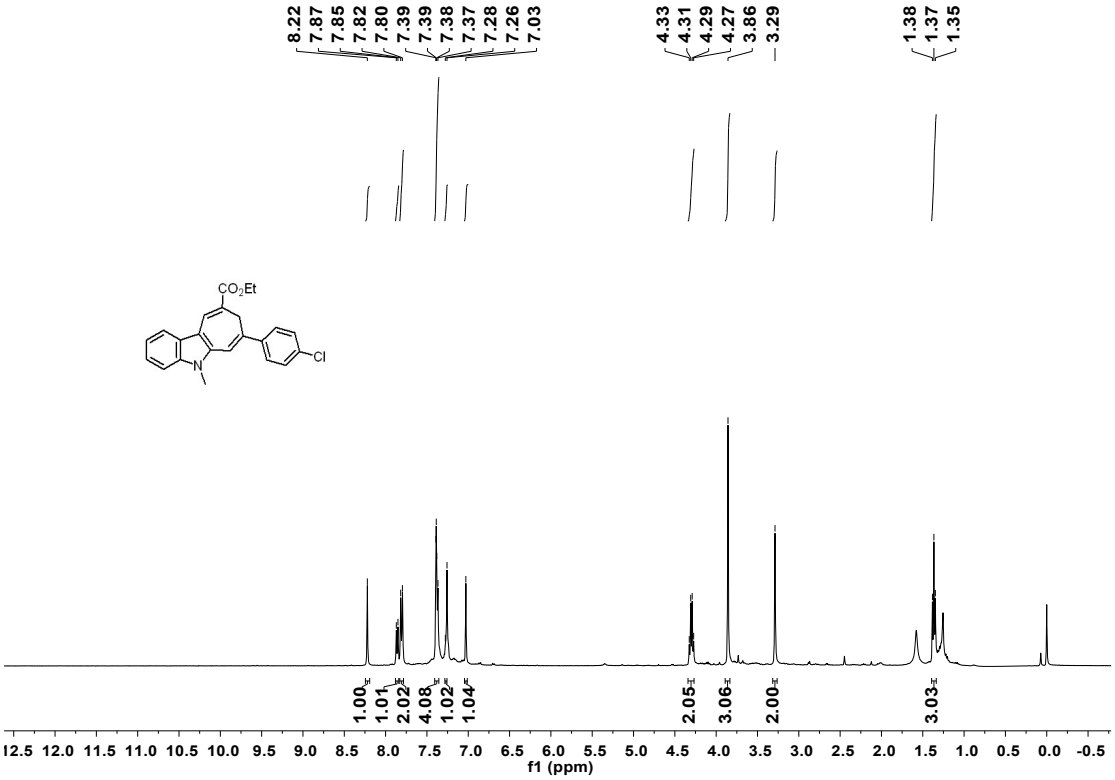
130.25
128.91
128.83
126.61
123.87
120.66
119.11
115.60
115.49
115.42
115.39
113.18
60.65
30.19
30.06
14.46
CO2Et
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-113.85
-113.87
-113.89
-113.90
-113.92
106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126
f1 (ppm)

3p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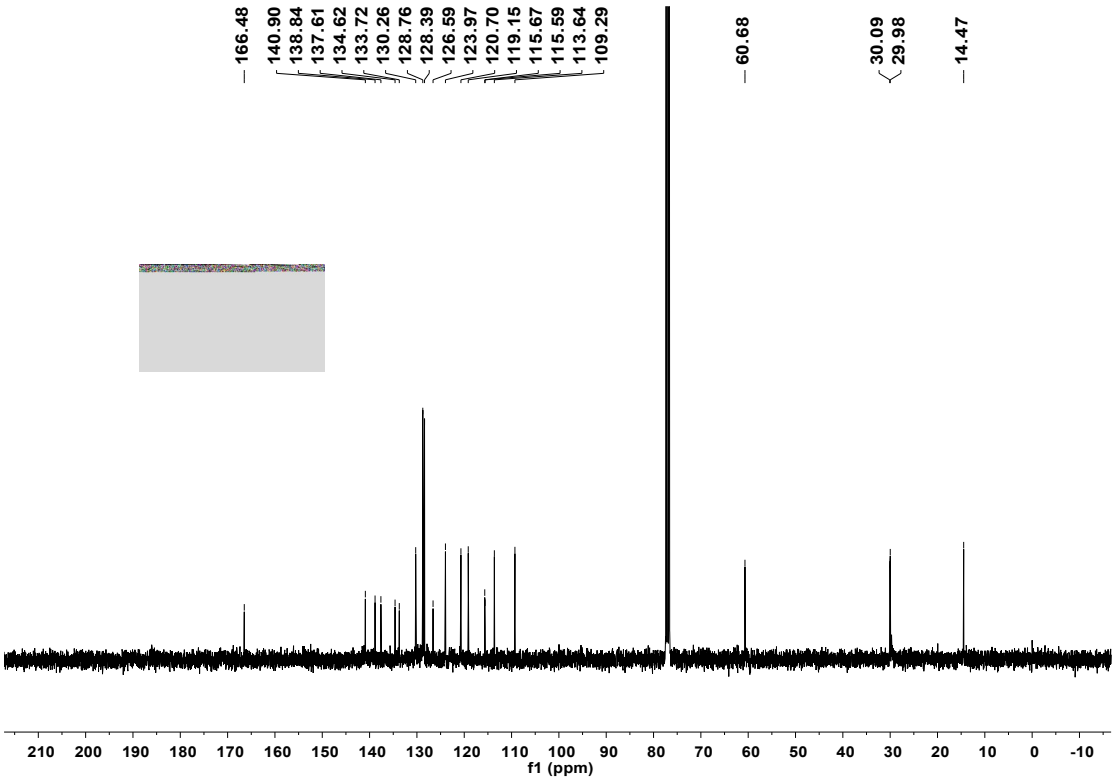
7.80
7.39
7.39
7.38
7.37
7.28
7.26
7.03
4.33
4.31
4.29
4.27
3.86
3.29
1.38
1.37
1.35
CO2Et
Cl
N
1.00
1.01
2.02
4.08
1.02
1.04
2.05
3.06
2.00
3.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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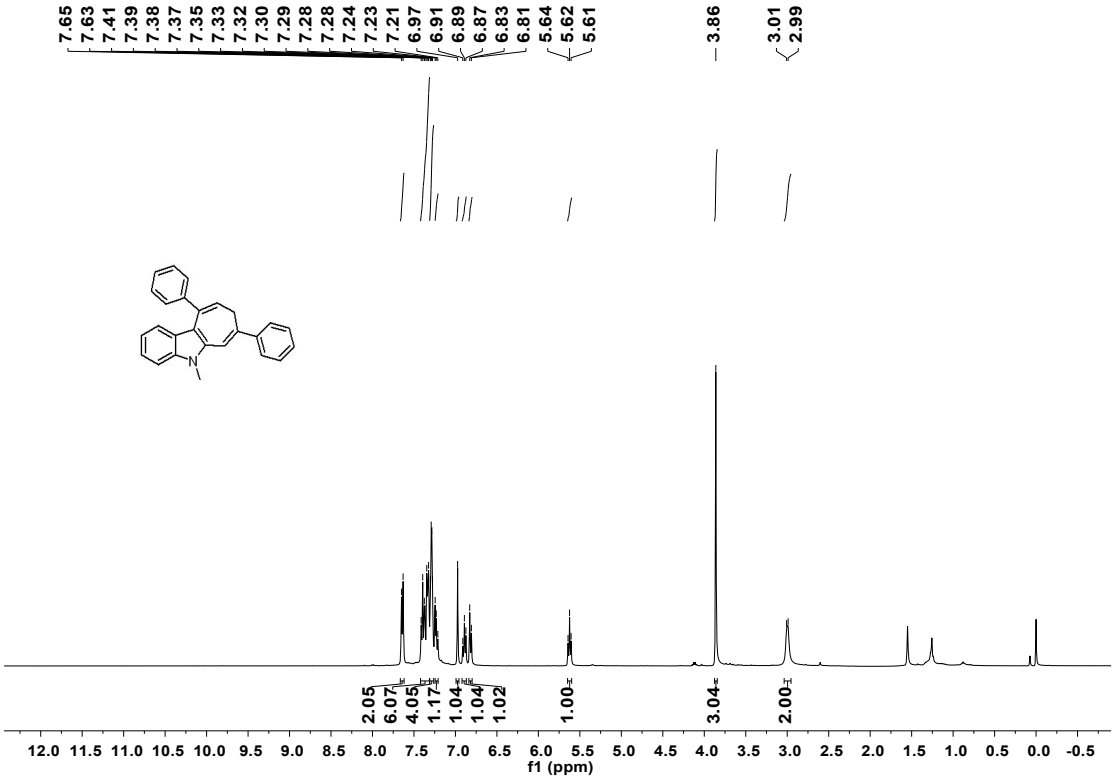
126.59
123.97
120.70
119.15
115.67
115.59
113.64
109.29
60.68
30.09
29.98
14.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8a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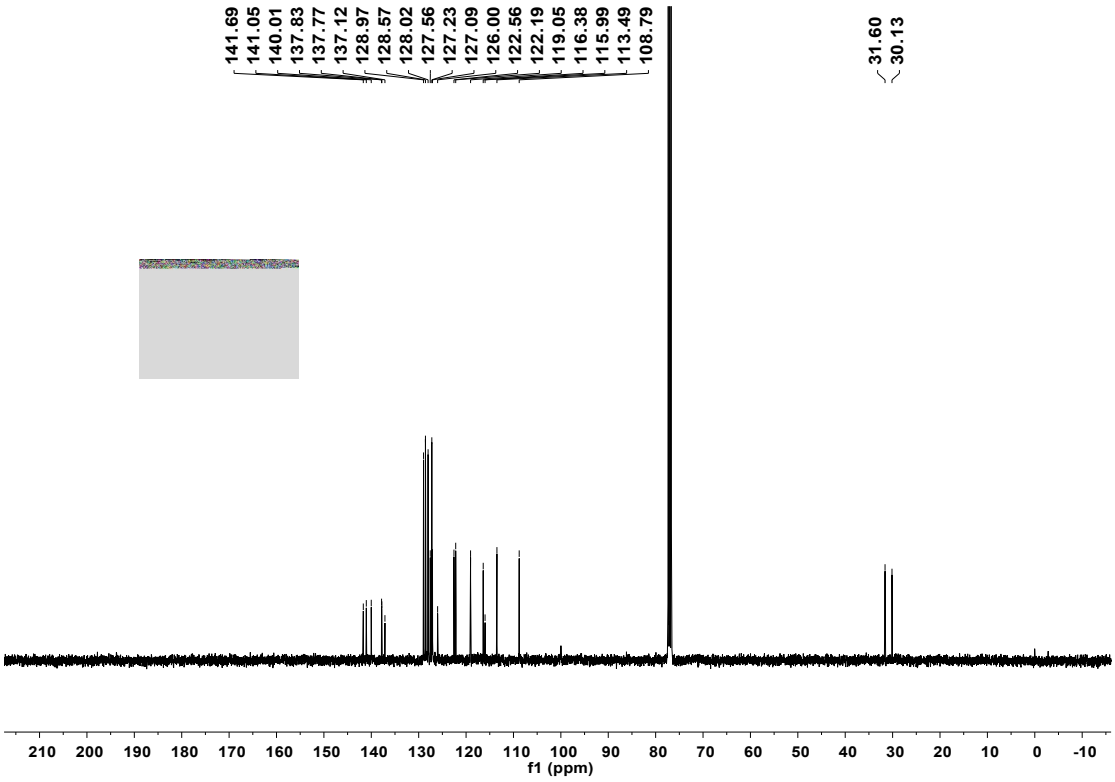
7.33
7.32
7.30
7.29
7.28
7.28
7.24
7.23
7.21
6.97
6.91
6.89
6.87
6.83
6.81
5.64
5.62
5.61
3.86
3.01
2.99
N
2.05
6.07
4.05
1.17
1.04
1.04
1.02
1.00
3.04
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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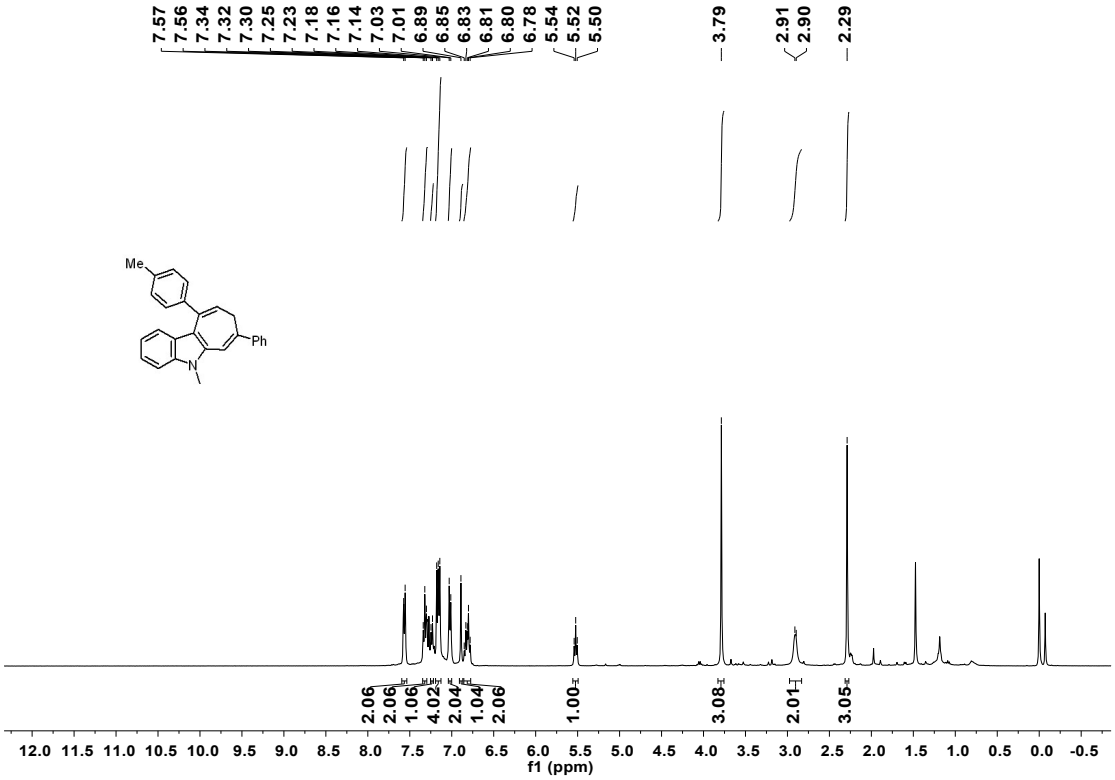
140.01
137.83
137.77
137.12
128.97
128.57
128.02
127.56
127.23
127.09
126.00
122.56
122.19
119.05
116.38
115.99
113.49
108.79
31.60
30.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8b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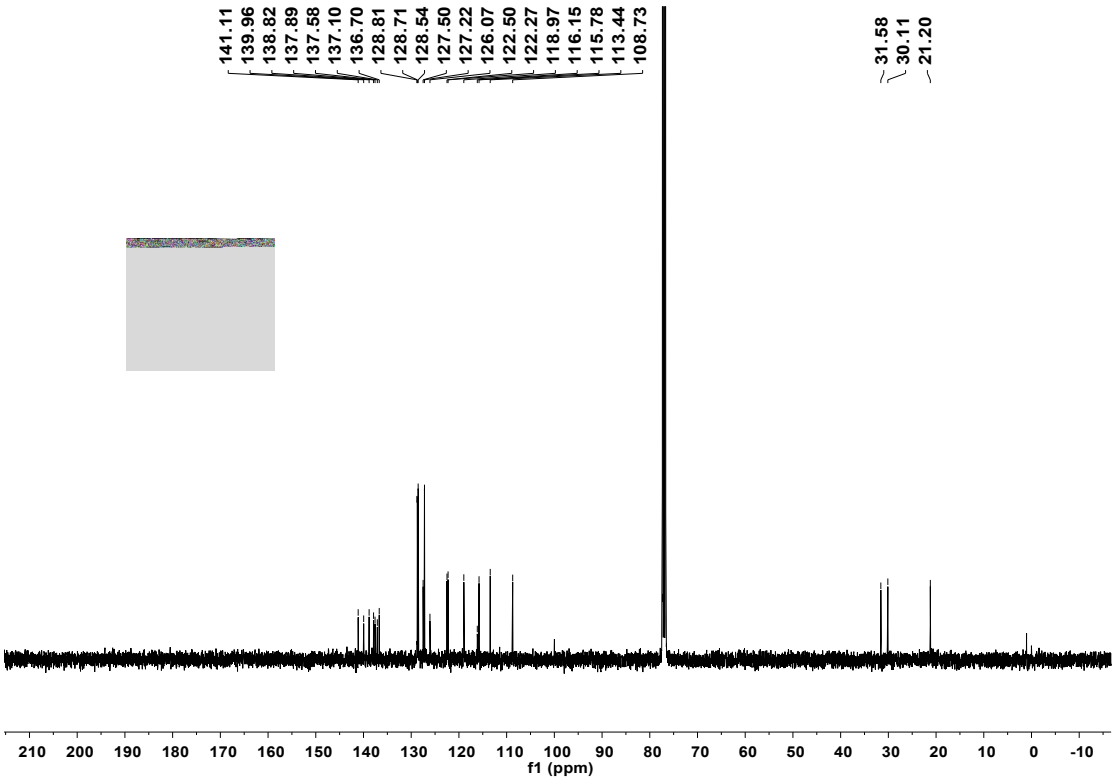
7.56
7.34
7.32
7.30
7.25
7.23
7.18
7.16
7.14
7.03
7.01
6.89
6.85
6.83
6.81
6.80
6.78
5.54
5.52
5.50
3.79
2.91
2.90
2.29
Me
Ph
N
2.06
2.06
1.06
4.02
2.04
1.04
2.06
1.00
3.08
2.01
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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137.10
136.70
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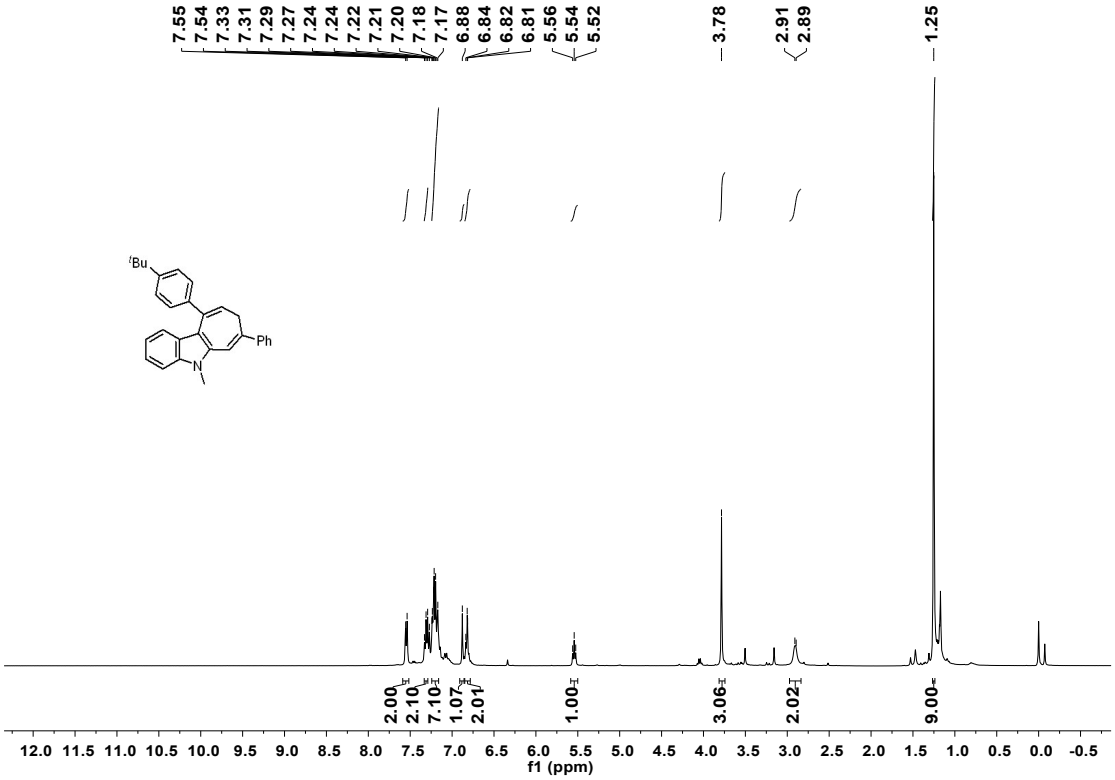
128.71
128.54
127.50
127.22
126.07
122.50
122.27
118.97
116.15
115.78
113.44
108.73
31.58
30.11
21.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8c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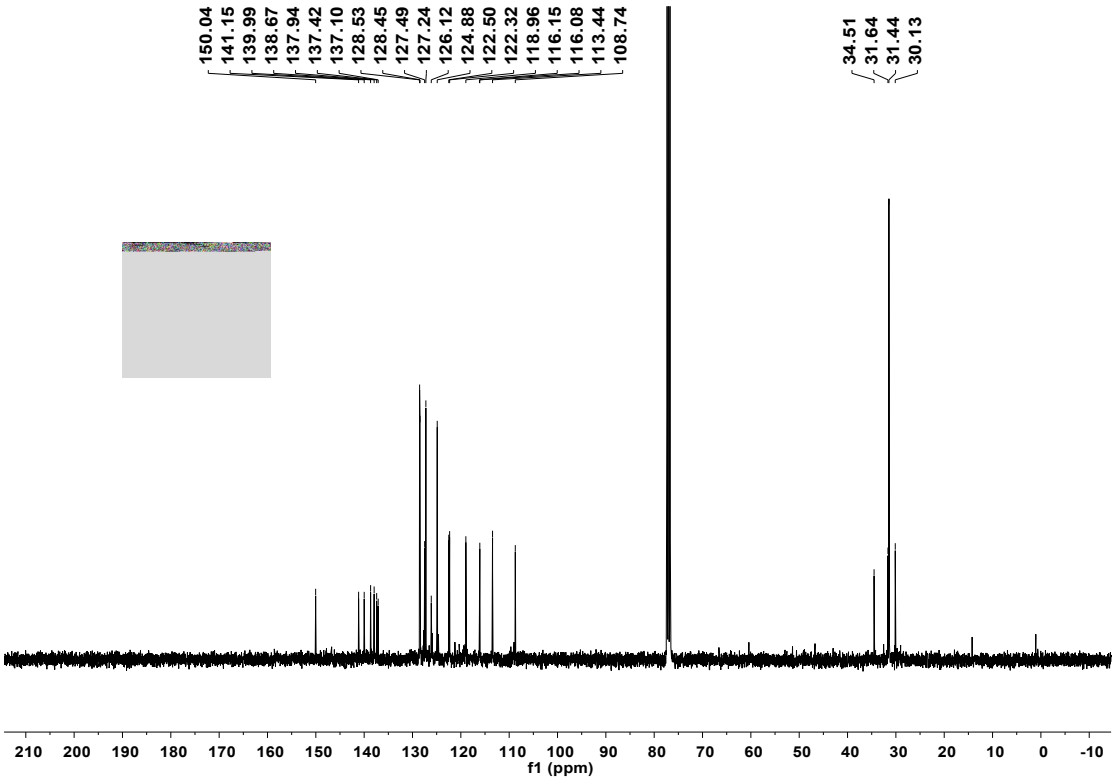
7.27
7.24
7.24
7.22
7.21
7.20
7.18
7.17
6.88
6.84
6.82
6.81
5.56
5.54
5.52
3.78
2.91
2.89
1.25
tBu
Ph
N
2.00
2.10
7.10
1.07
2.01
1.00
3.06
2.02
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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127.49
127.24
126.12
124.88
122.50
122.32
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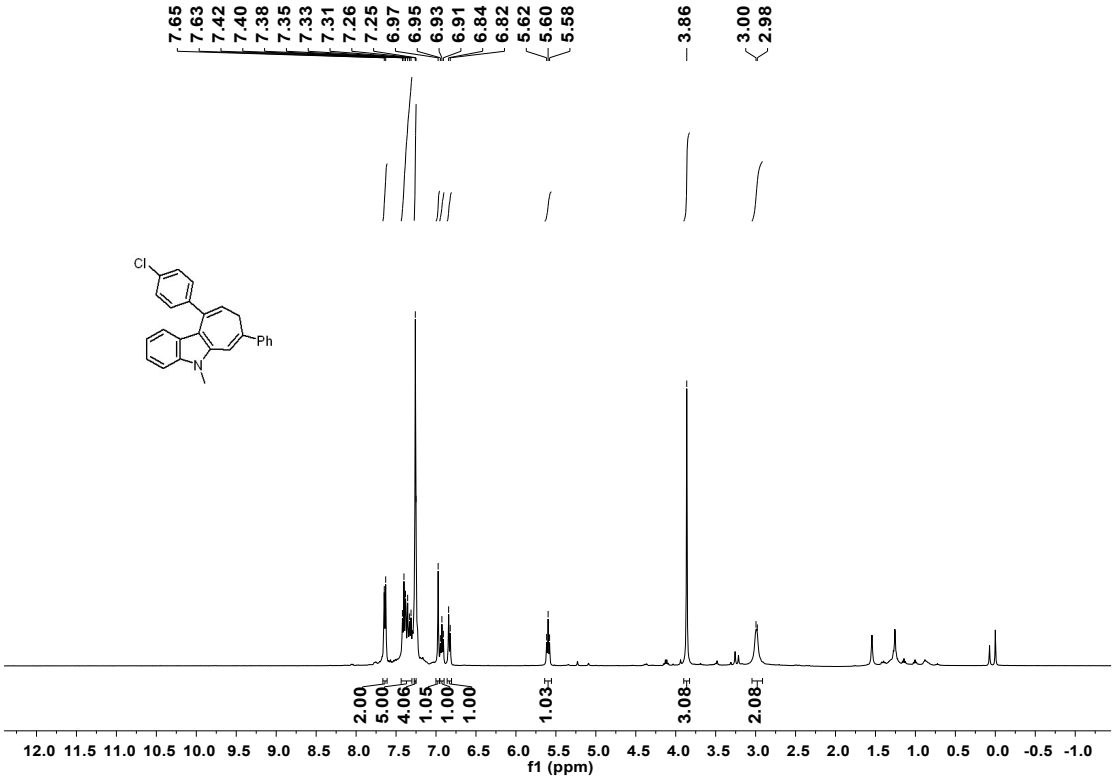
116.15
116.08
113.44
108.74
34.51
31.64
31.44
30.13
f1 (ppm)

8d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7.33
7.31
7.26
7.25
6.97
6.95
6.93
6.91
6.84
6.82
5.62
5.60
5.58
3.86
3.00
2.98
Cl
Ph
N
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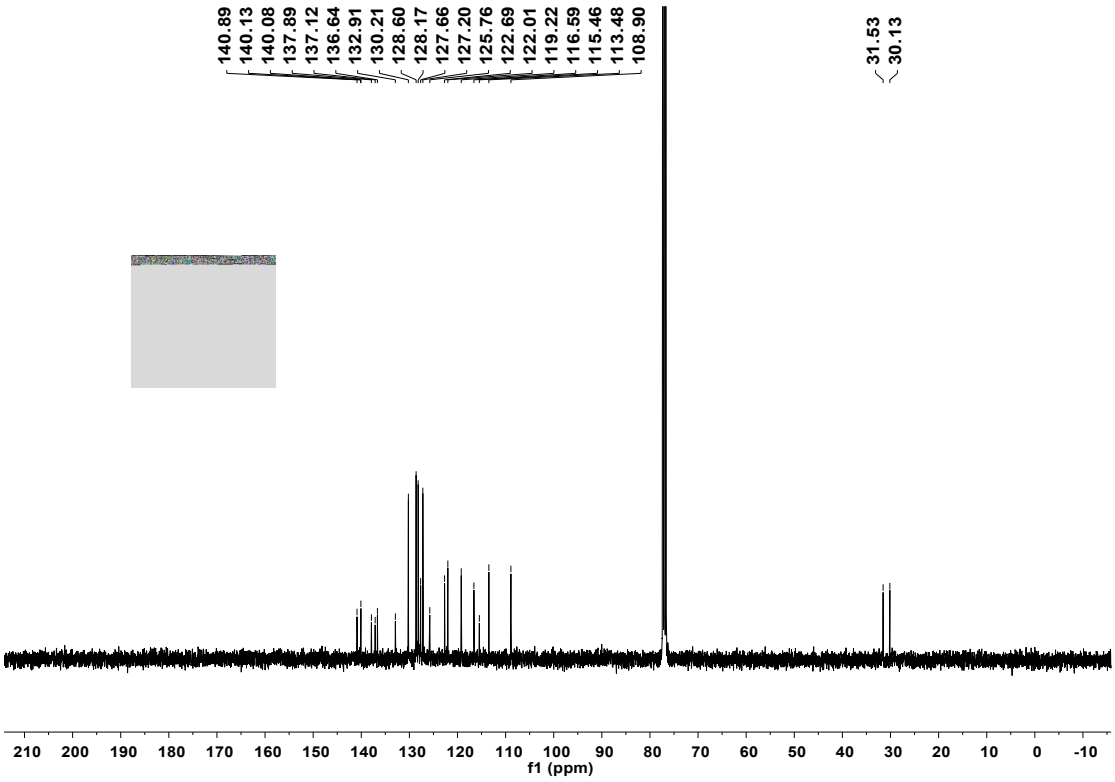
5.00
4.06
1.05
1.00
1.00
1.03
3.08
2.08
f1 (ppm)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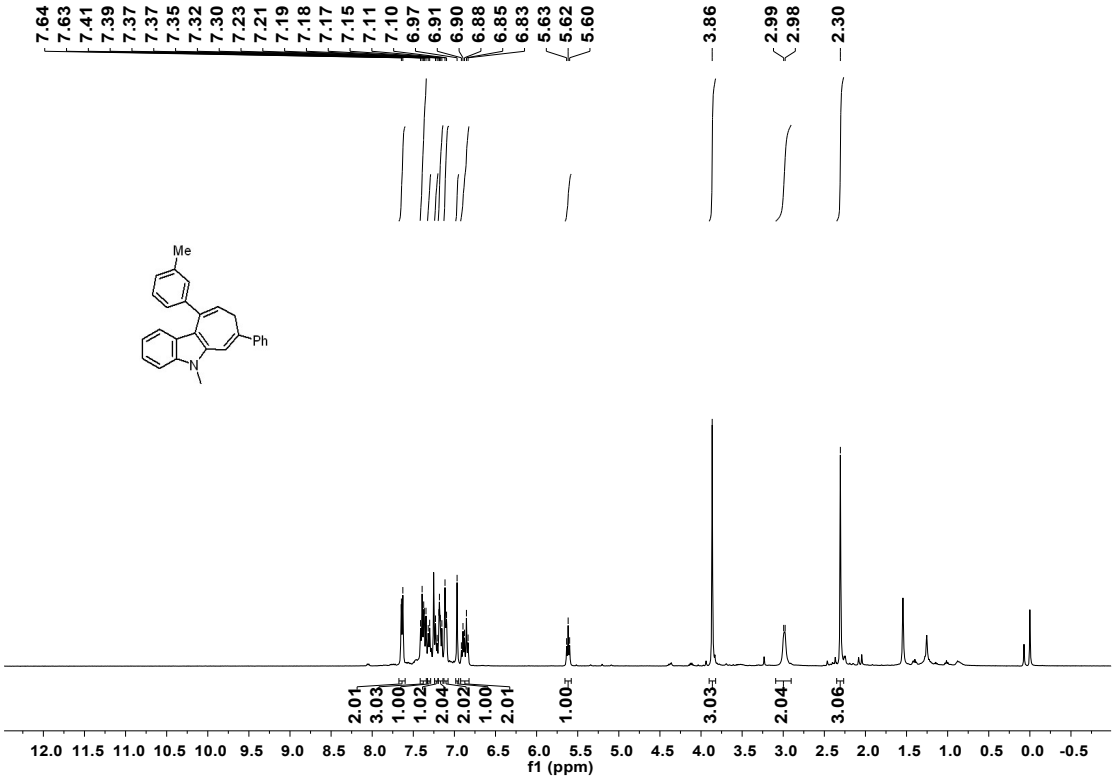
140.13
140.08
137.89
137.12
136.64
132.91
130.21
128.60
128.17
127.66
127.20
125.76
122.69
122.01
119.22
116.59
115.46
113.48
108.90
31.53
30.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8e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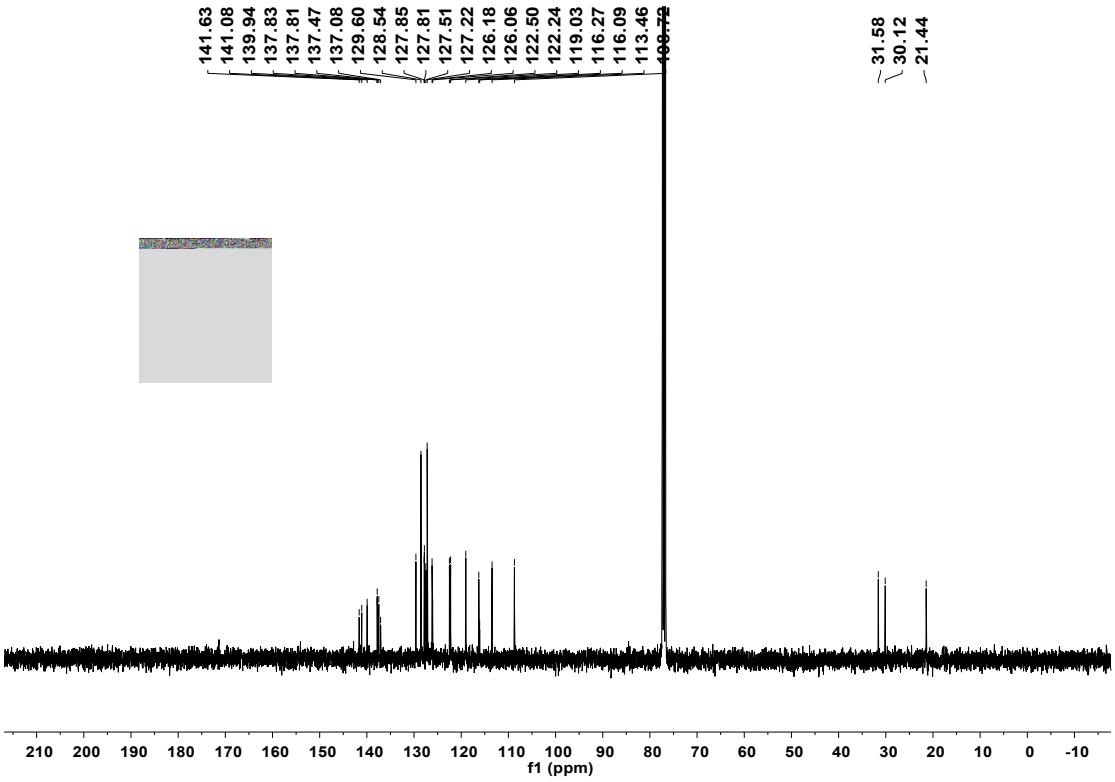
7.35
7.32
7.30
7.23
7.21
7.19
7.18
7.17
7.15
7.11
7.10
6.97
6.91
6.90
6.88
6.85
6.83
5.63
5.62
5.60
3.86
2.99
2.98
2.30
Me
Ph
N
2.01
3.03
1.00
1.02
2.04
2.02
1.00
2.01
1.00
3.03
2.04
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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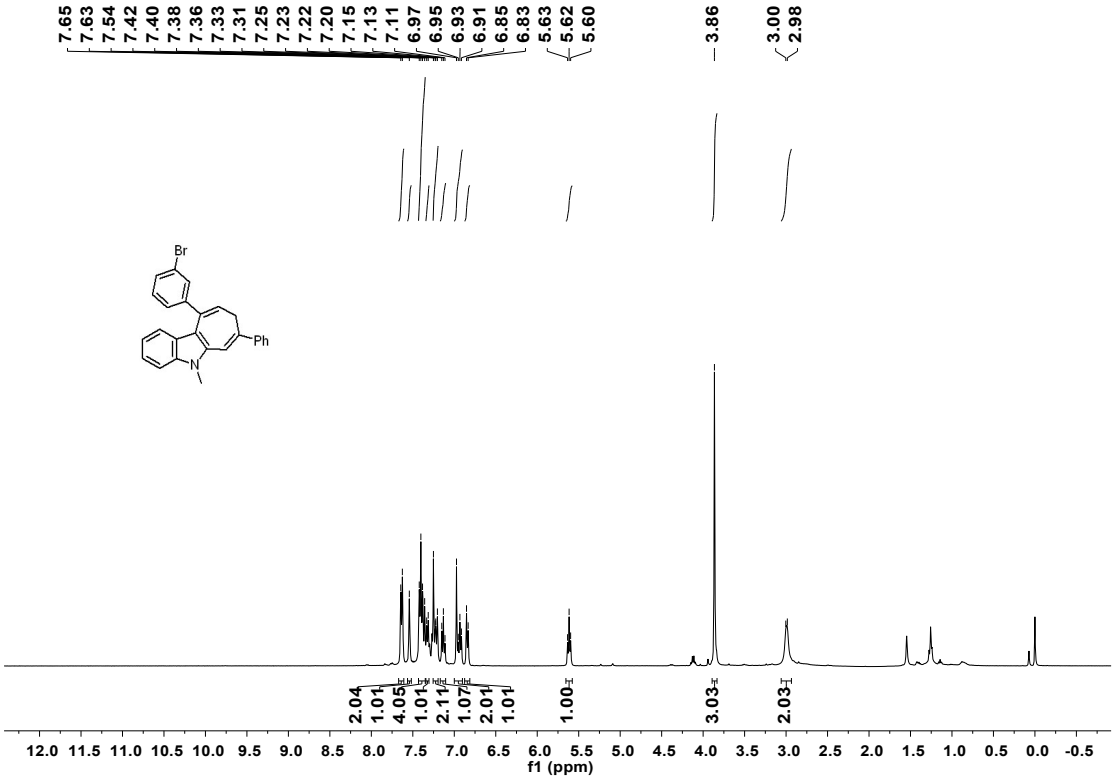
137.81
137.47
137.08
129.60
128.54
127.85
127.81
127.51
127.22
126.18
126.06
122.50
122.24
119.03
116.27
116.09
113.46
31.58
30.12
21.44
f1 (ppm)

8f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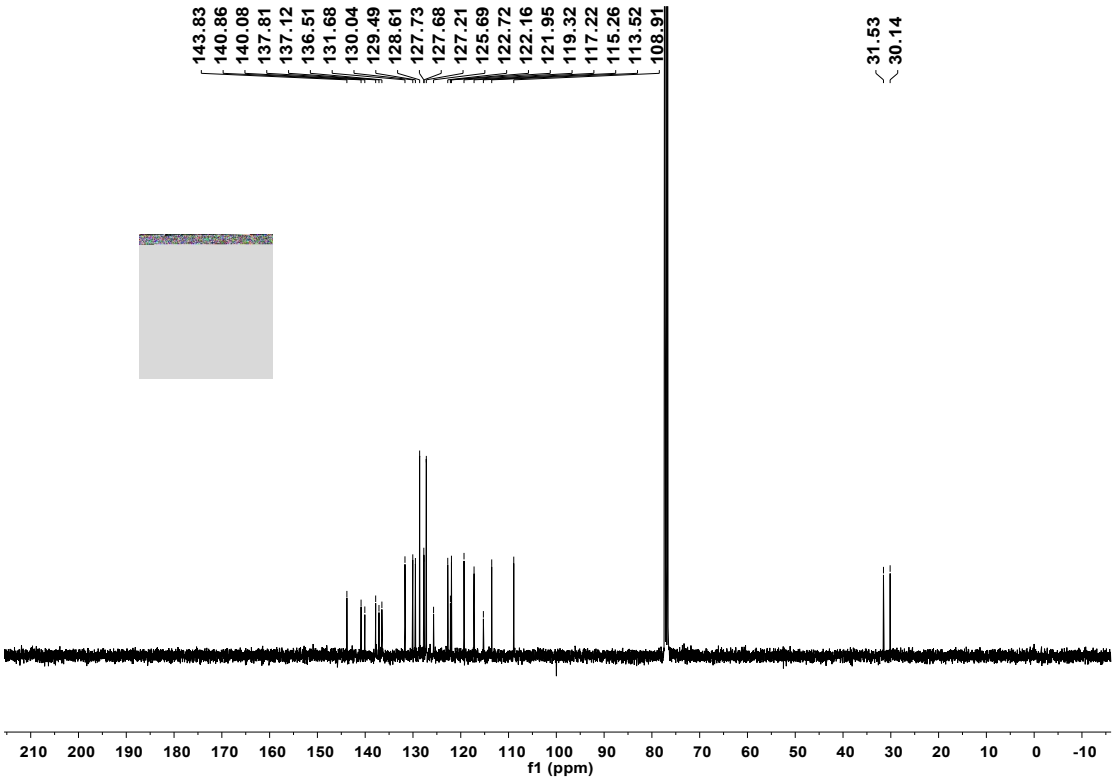
7.42
7.40
7.38
7.36
7.33
7.31
7.25
7.23
7.22
7.20
7.15
7.13
7.11
6.97
6.95
6.93
6.91
6.85
6.83
5.63
5.62
5.60
3.86
3.00
2.98
Br
Ph
N
2.04
1.01
4.05
1.01
2.11
1.07
2.01
1.01
1.00
3.03
2.03
f1 (ppm)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137.81
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136.51
131.68
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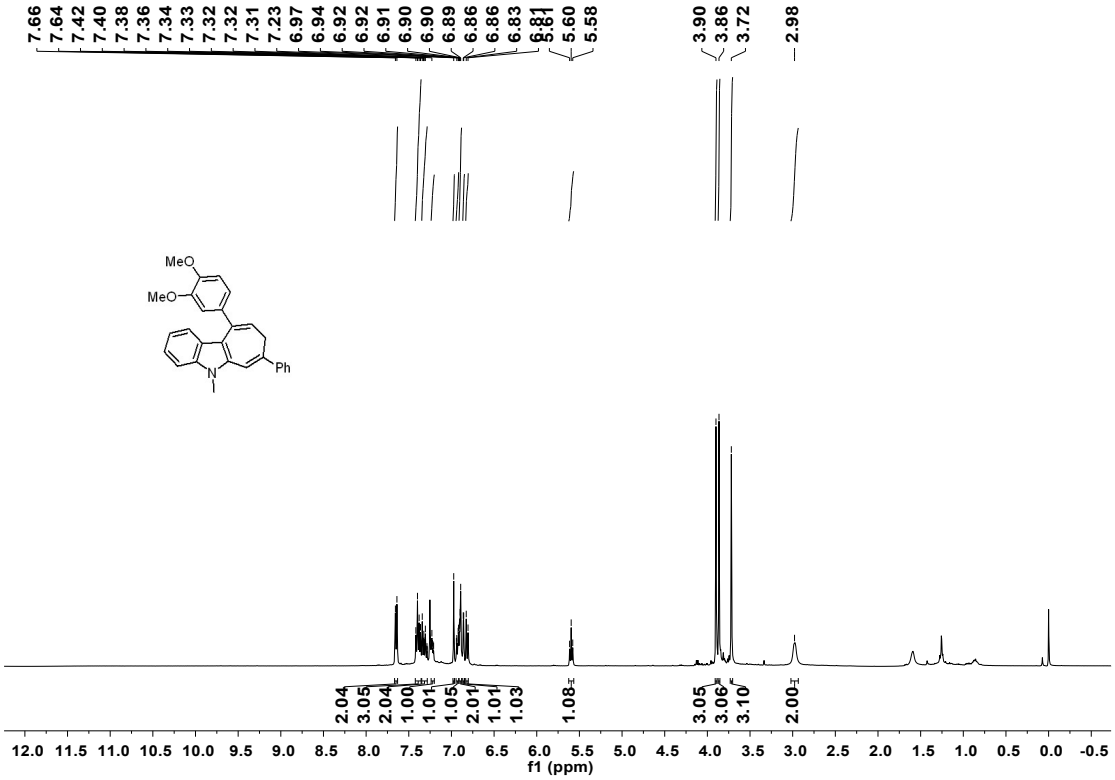
129.49
128.61
127.73
127.68
127.21
125.69
122.72
122.16
121.95
119.32
117.22
115.26
113.52
108.91
31.53
30.14
f1 (ppm)

8g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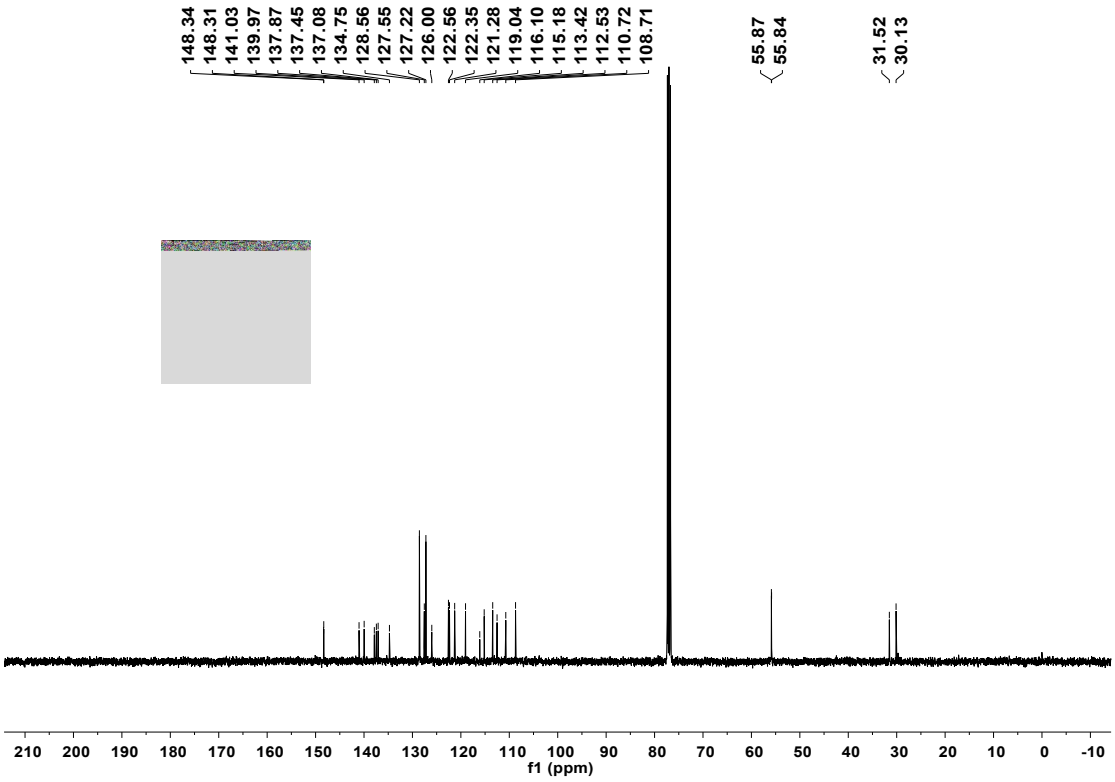
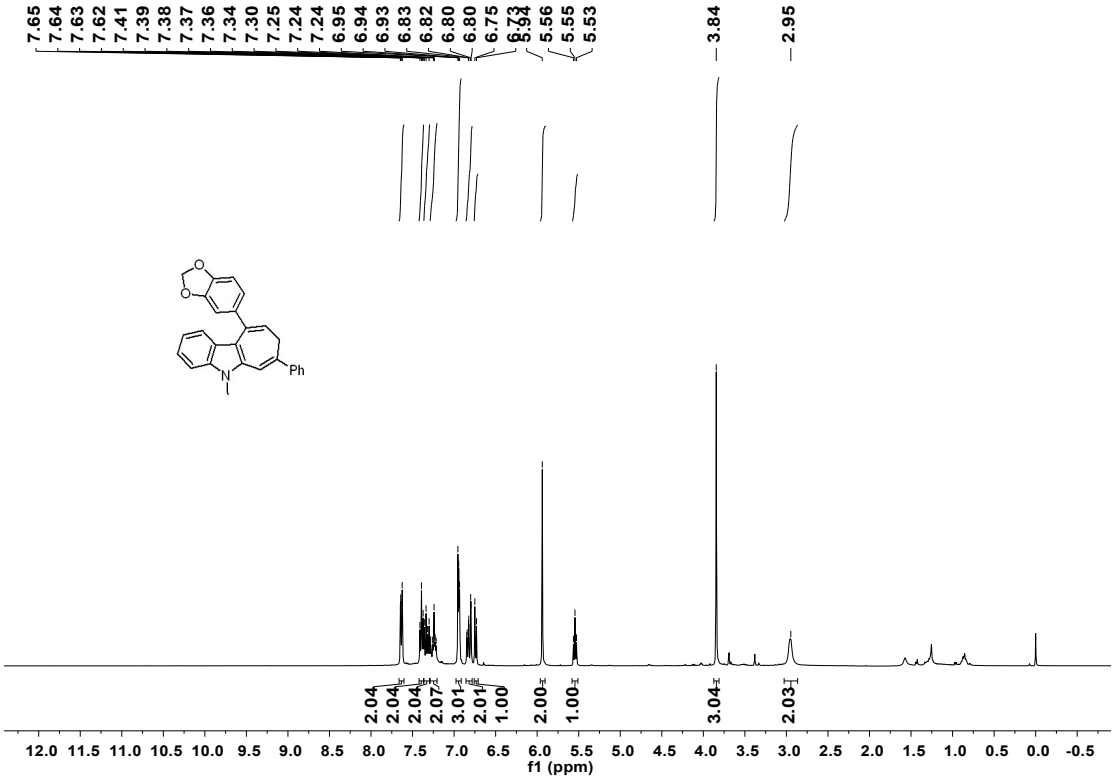
7.64
7.42
7.40
7.38
7.36
7.34
7.33
7.32
7.32
7.31
7.23
6.97
6.94
6.92
6.92
6.91
6.90
6.90
6.89
6.86
6.86
6.83
5.60
5.58
3.90
3.86
3.72
2.98
MeO
MeO
N
Ph
2.04
3.05
2.04
1.00
1.01
1.05
2.01
1.01
1.03
1.08
3.05
3.06
3.10
2.00
f1 (ppm)


148.34
148.31
141.03
139.97
137.87
137.45
137.08
134.75
128.56
127.55
127.22
126.00
122.56
122.35
121.28
119.04
116.10
115.18
113.42
112.53
110.72
108.71
55.87
55.84
31.52
30.13
f1 (ppm)

8h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7.62
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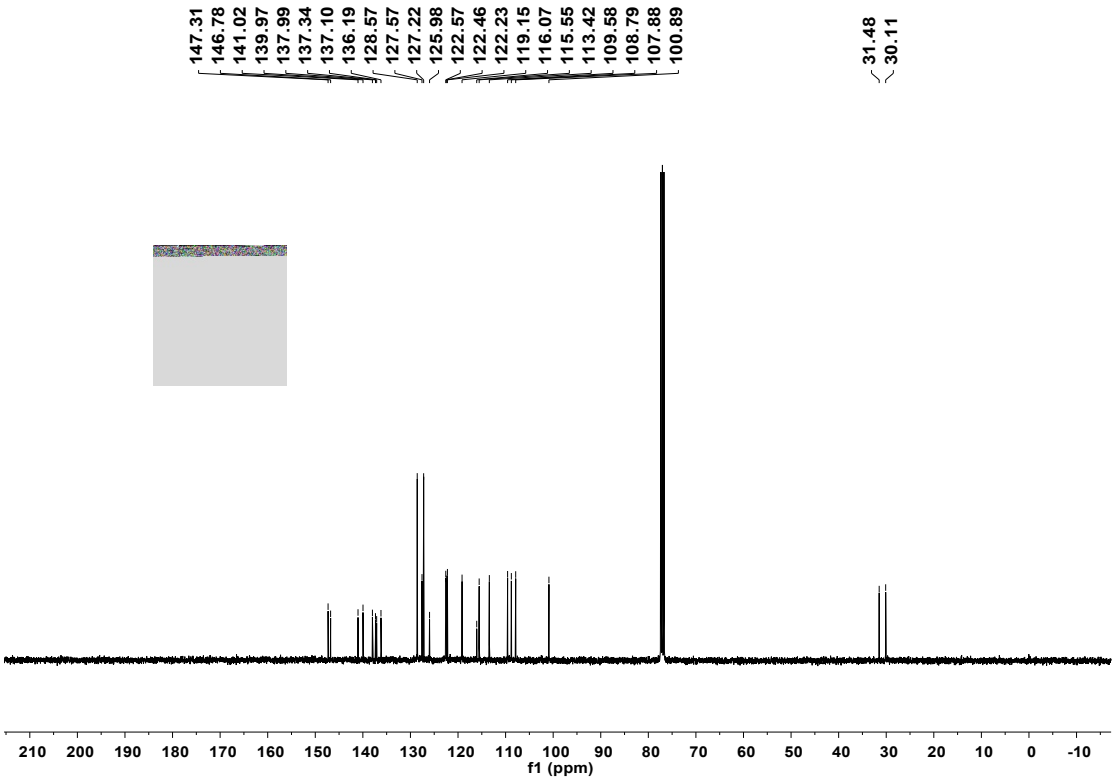
7.39
7.38
7.37
7.36
7.34
7.30
7.25
7.24
7.24
6.95
6.94
6.93
6.83
6.82
6.80
6.80
6.75
6.73
5.94
5.56
5.55
5.53
3.84
2.95
O
O
N
Ph
2.04
2.04
2.07
3.01
2.01
1.00
2.00
1.00
3.04
2.03
f1 (ppm)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139.97
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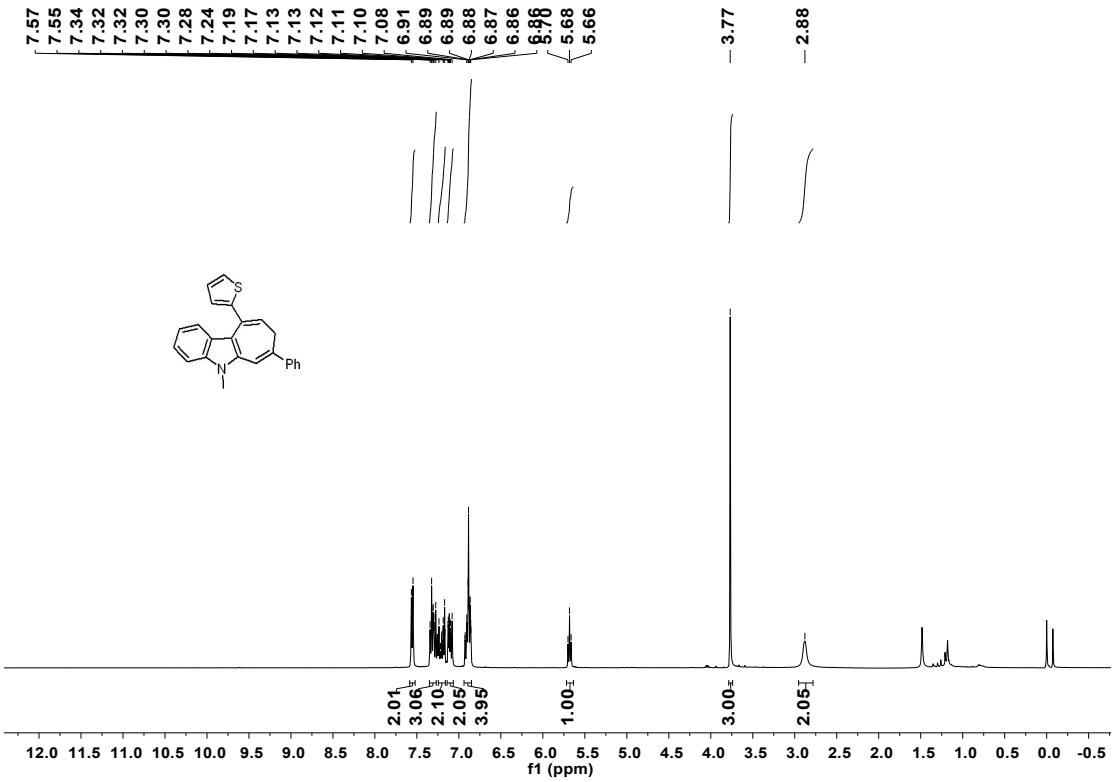
137.34
137.10
136.19
128.57
127.57
127.22
125.98
122.57
122.46
122.23
119.15
116.07
115.55
113.42
109.58
108.79
107.88
100.89
31.48
30.11
f1 (ppm)

8i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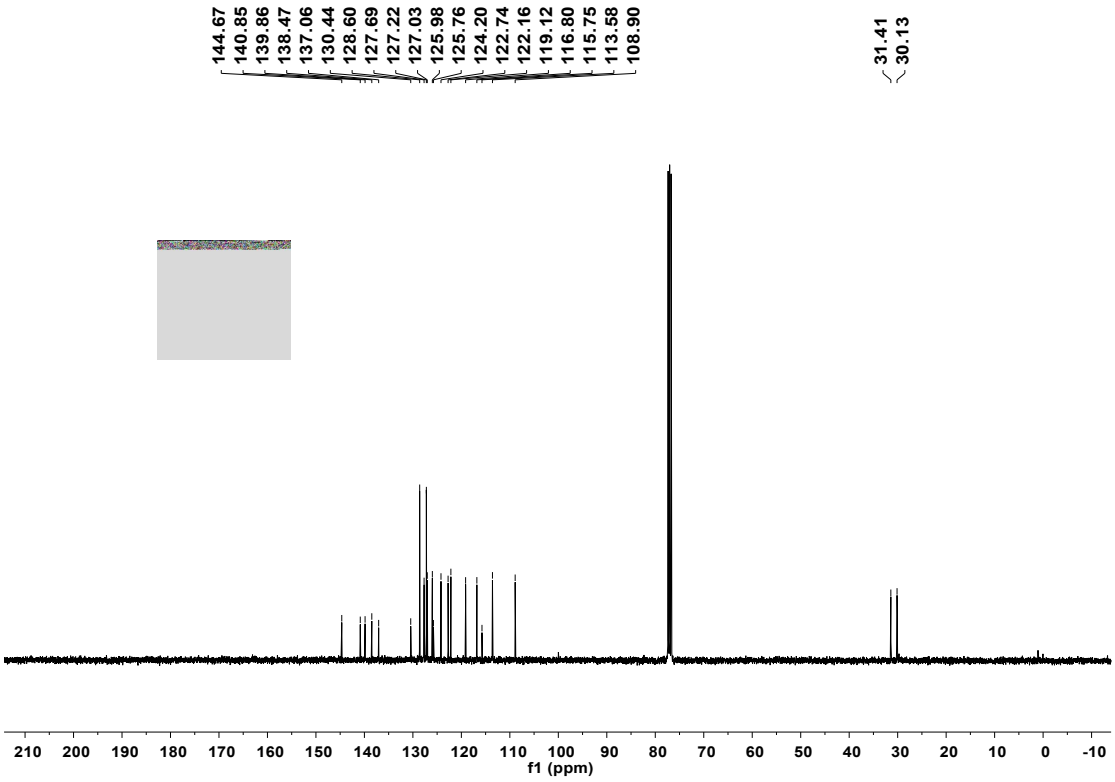
7.34
7.32
7.32
7.30
7.30
7.28
7.24
7.19
7.17
7.13
7.13
7.12
7.11
7.10
7.08
6.91
6.89
6.89
6.88
6.87
6.86
5.68
5.66
3.77
2.88
S
N
Ph
2.01
3.06
2.10
2.05
3.95
1.00
3.00
2.05
f1 (ppm)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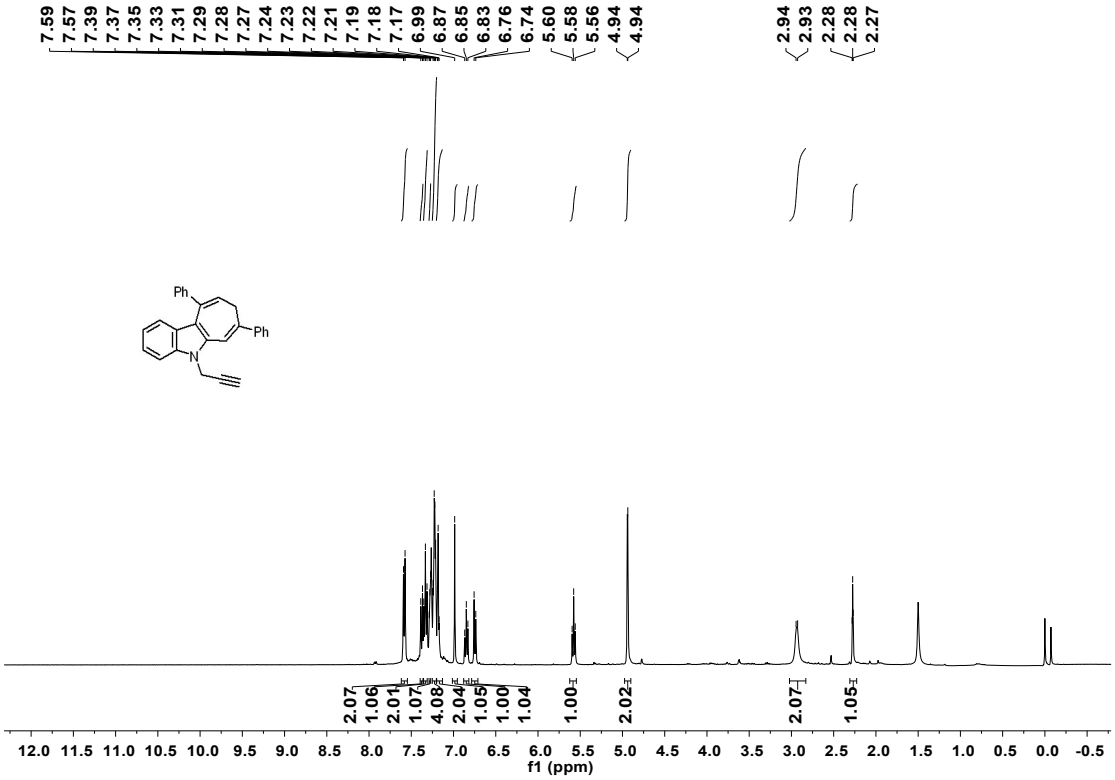
127.69
127.22
127.03
125.98
125.76
124.20
122.74
122.16
119.12
116.80
115.75
113.58
108.90
31.41
30.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8j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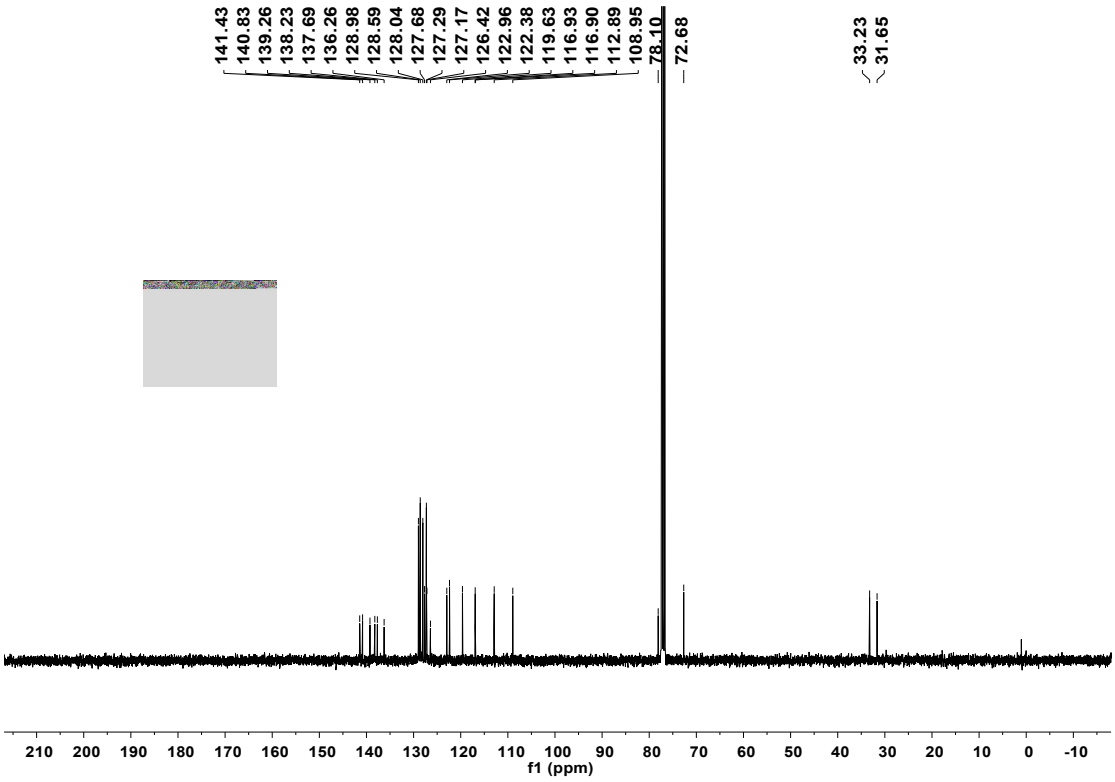
7.29
7.28
7.27
7.24
7.23
7.22
7.21
7.19
7.18
7.17
6.99
6.87
6.85
6.83
6.76
6.74
5.60
5.58
5.56
4.94
4.94
2.94
2.93
2.28
2.28
2.27
Ph
Ph
N
2.07
1.06
2.01
1.07
4.08
2.04
1.05
1.00
1.04
1.00
2.02
2.07
1.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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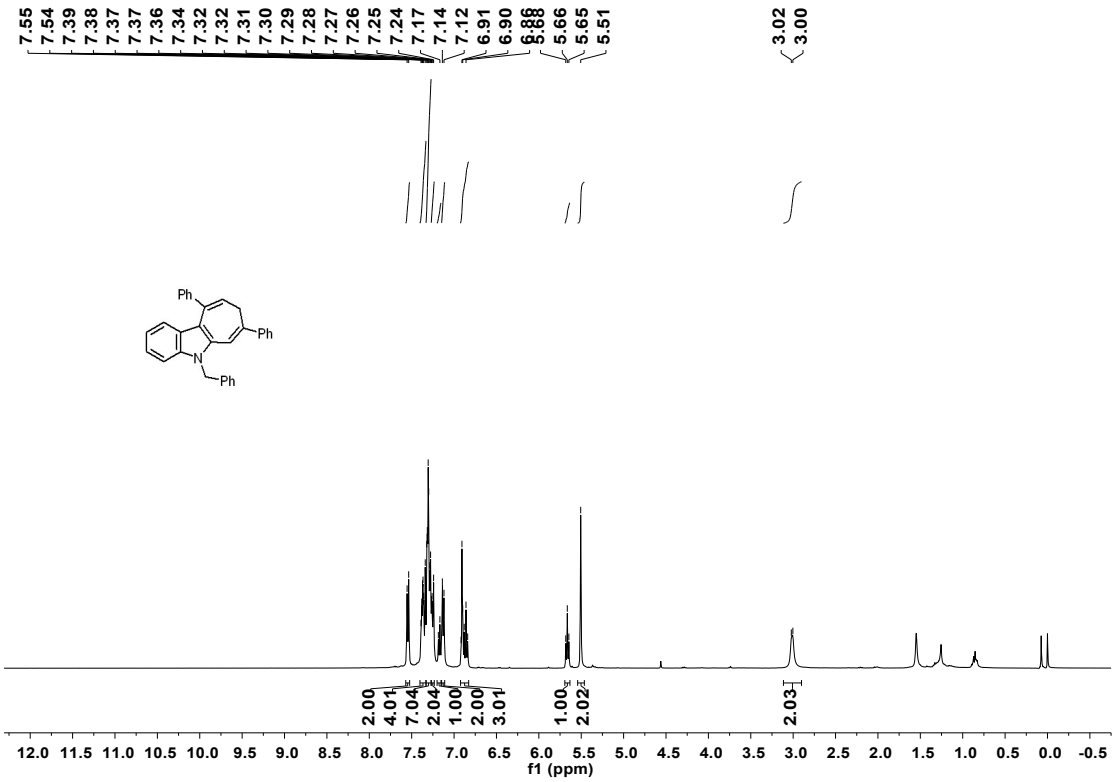
136.26
128.98
128.59
128.04
127.68
127.29
127.17
126.42
122.96
122.38
119.63
116.93
116.90
112.89
108.95
78.10
72.68
33.23
31.65
f1 (ppm)

8k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7.37
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7.34
7.32
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.17
7.14
7.12
6.91
6.90
5.66
5.65
5.51
3.02
3.00
Ph
Ph
N
Ph
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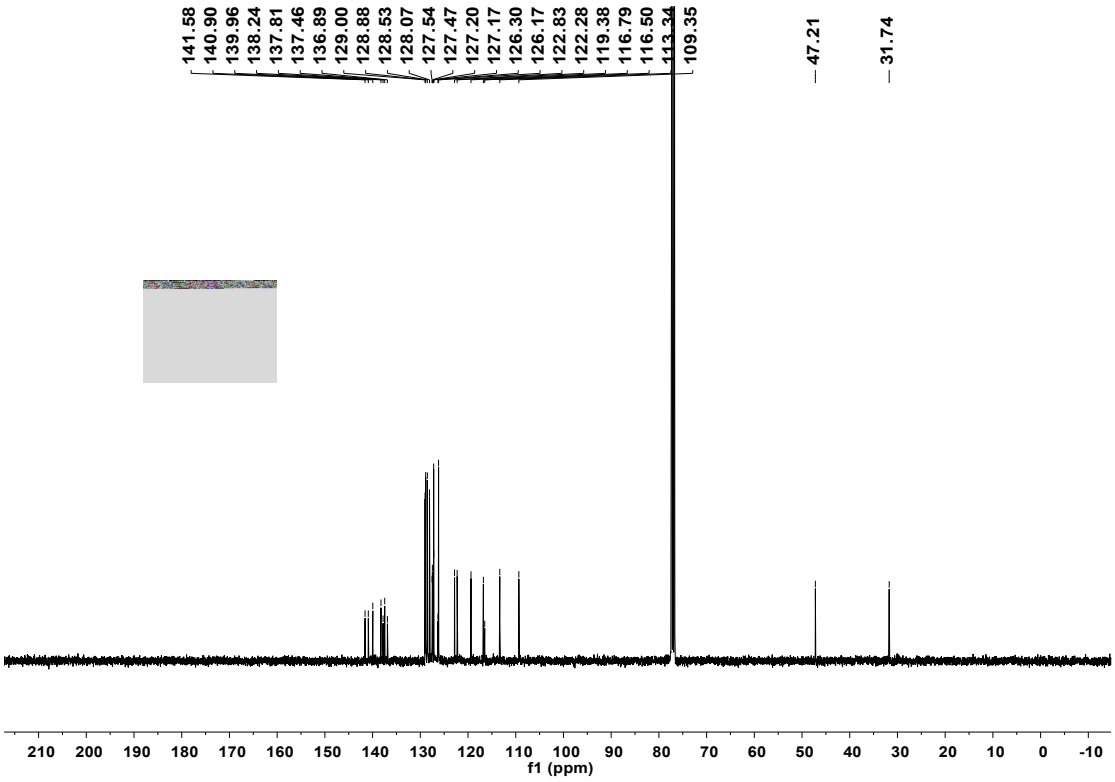
4.01
7.04
2.04
1.00
2.00
3.01
1.00
2.02
2.03
f1 (ppm)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140.90
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138.24
137.81
137.46
136.89
129.00
128.88
128.53
128.07
127.54
127.47
127.20
127.17
126.30
126.17
122.83
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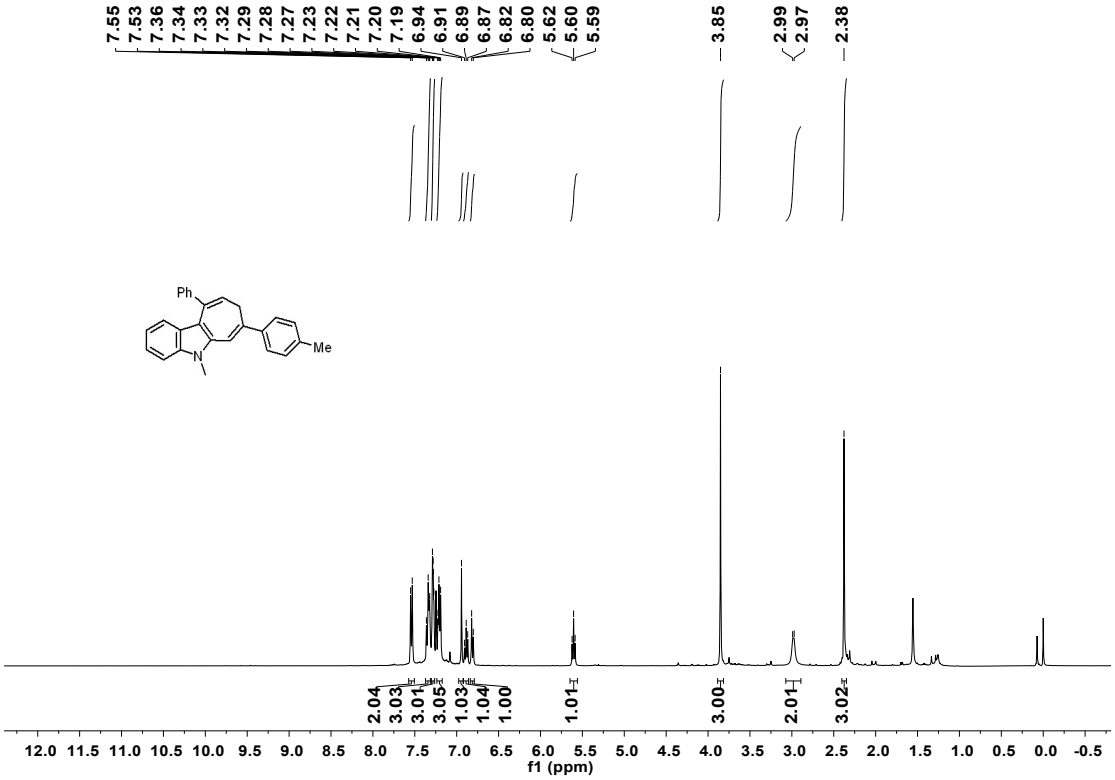
119.38
116.79
116.50
113.34
109.35
47.21
31.74
f1 (ppm)

8l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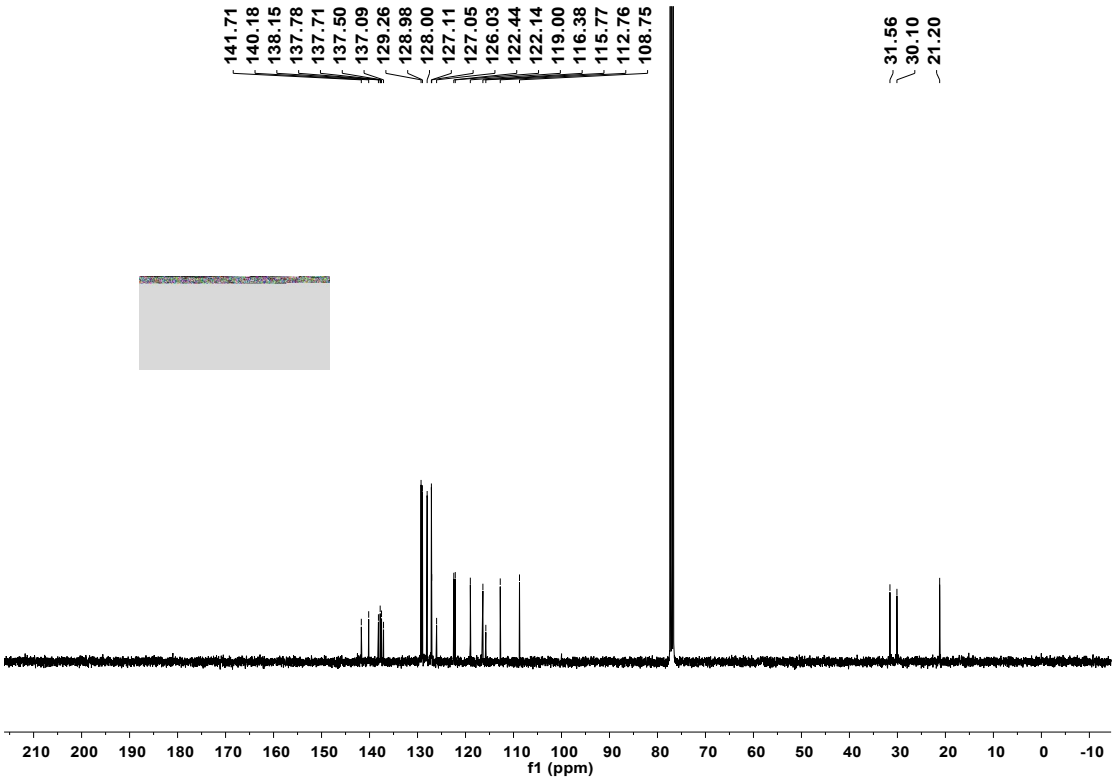
7.32
7.29
7.28
7.27
7.23
7.22
7.21
7.20
7.19
6.94
6.91
6.89
6.87
6.82
6.80
5.62
5.60
5.59
3.85
2.99
2.97
2.38
Ph
Me
N
2.04
3.03
3.01
3.05
1.03
1.04
1.00
1.01
3.00
2.01
3.02
f1 (ppm)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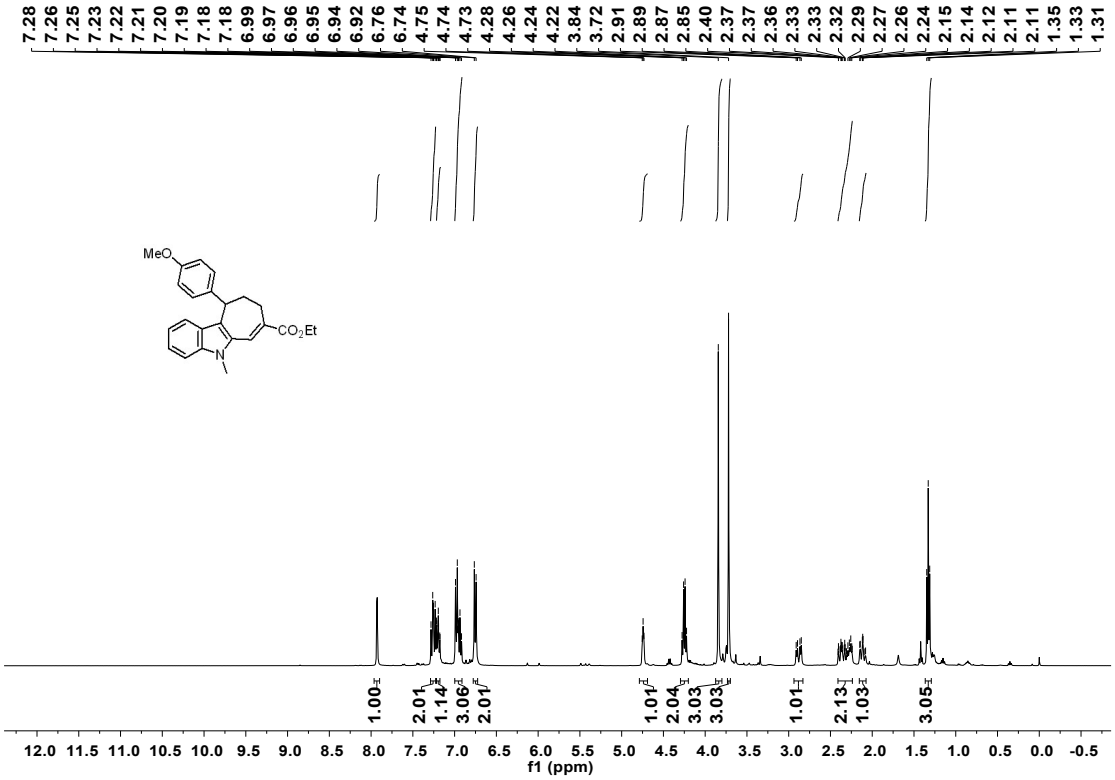
137.78
137.71
137.50
137.09
129.26
128.98
128.00
127.11
127.05
126.03
122.44
122.14
119.00
116.38
115.77
112.76
108.75
31.56
30.10
21.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

10a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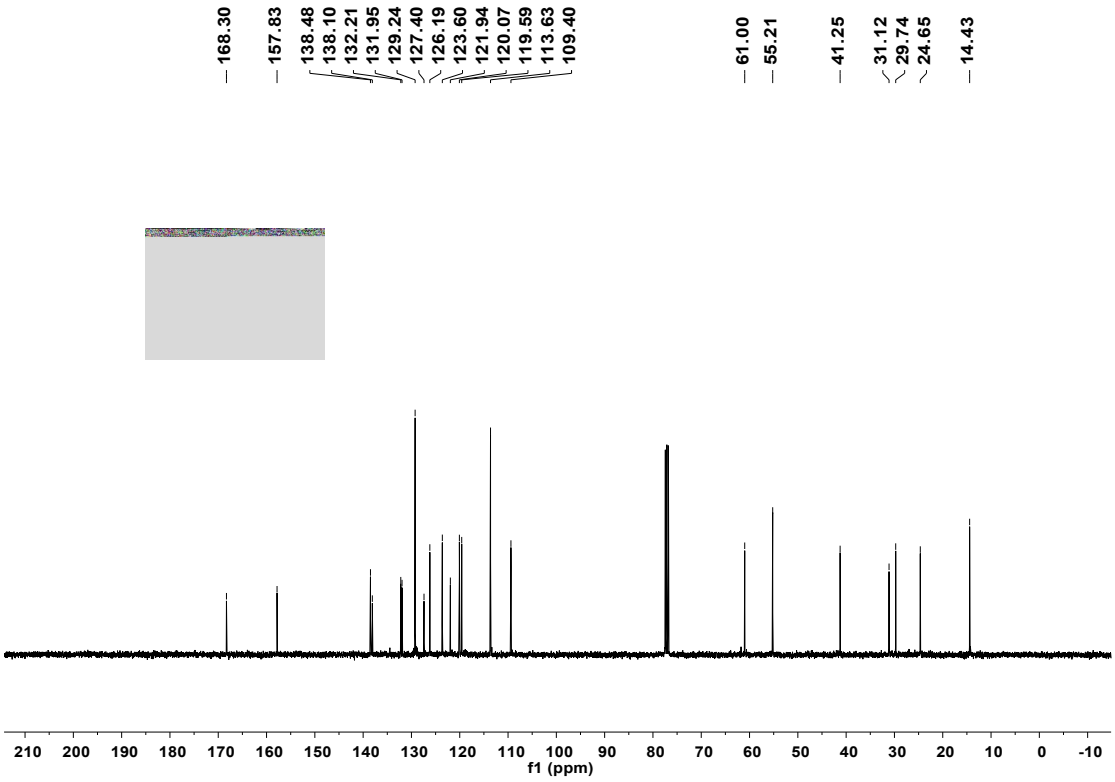
7.26
7.25
7.23
7.22
7.21
7.20
7.19
7.18
7.18
6.99
6.97
6.96
6.95
6.94
6.92
6.76
6.74
4.75
4.74
4.73
4.28
4.26
4.24
4.22
3.84
3.72
2.91
2.89
2.87
2.85
2.40
2.37
2.37
2.36
2.33
2.33
2.32
2.29
2.27
2.26
2.24
2.15
2.14
2.12
2.11
2.11
1.35
1.33
1.31
MeO
CO2Et
N
1.00
2.01
1.14
3.06
2.01
1.01
2.04
3.03
3.03
1.01
2.13
1.03
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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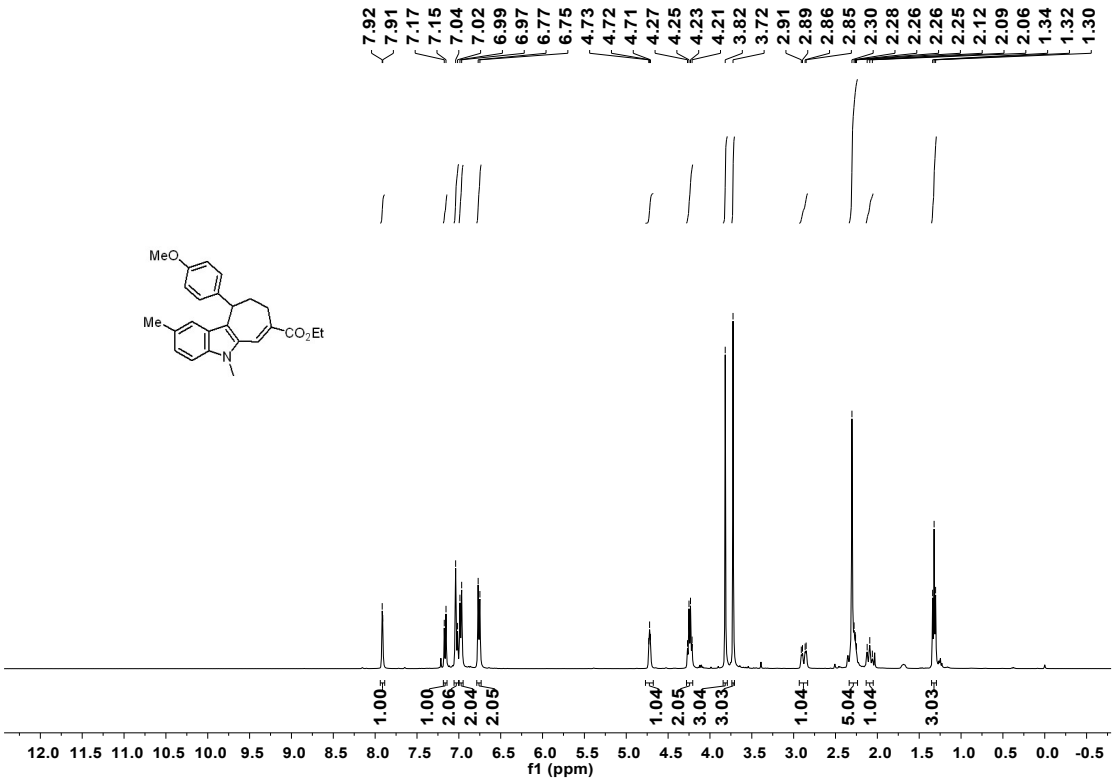
157.83
138.48
138.10
132.21
131.95
129.24
127.40
126.19
123.60
121.94
120.07
119.59
113.63
109.40
61.00
55.21
41.25
31.12
29.74
24.65
14.43
f1 (ppm)

10b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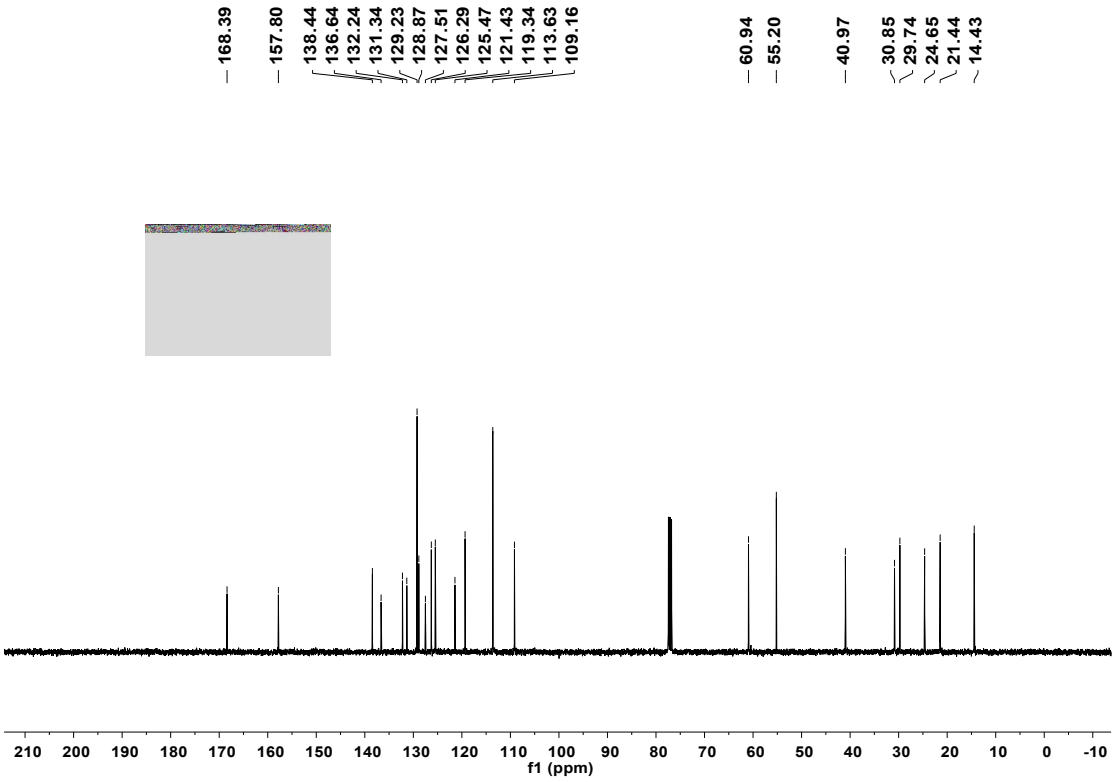
7.91
7.17
7.15
7.04
7.02
6.99
6.97
6.77
6.75
4.73
4.72
4.71
4.27
4.25
4.23
4.21
3.82
3.72
2.91
2.89
2.86
2.85
2.30
2.28
2.26
2.26
2.25
2.12
2.09
2.06
1.34
1.32
1.30
MeO
Me
CO2Et
N
1.00
1.00
2.06
2.04
2.05
1.04
2.05
3.04
3.03
1.04
5.04
1.04
3.03
f1 (ppm)


168.39
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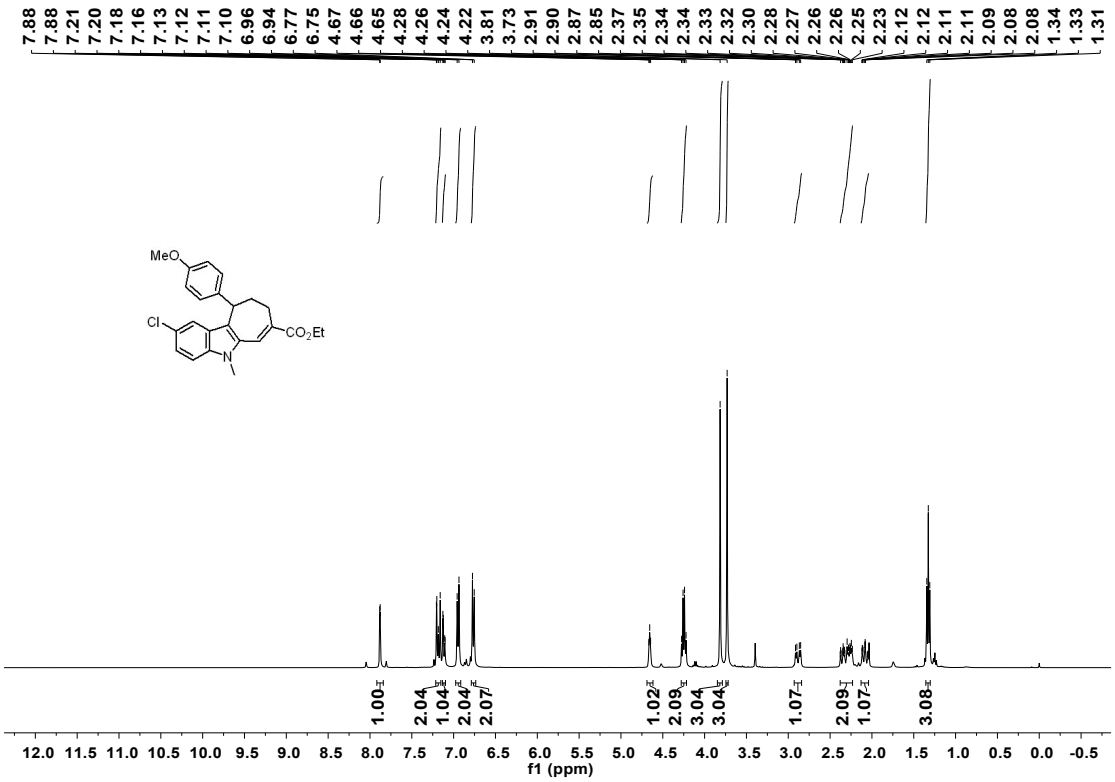
138.44
136.64
132.24
131.34
129.23
128.87
127.51
126.29
125.47
121.43
119.34
113.63
109.16
60.94
55.20
40.97
30.85
29.74
24.65
21.44
14.43
f1 (ppm)

10c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7.88
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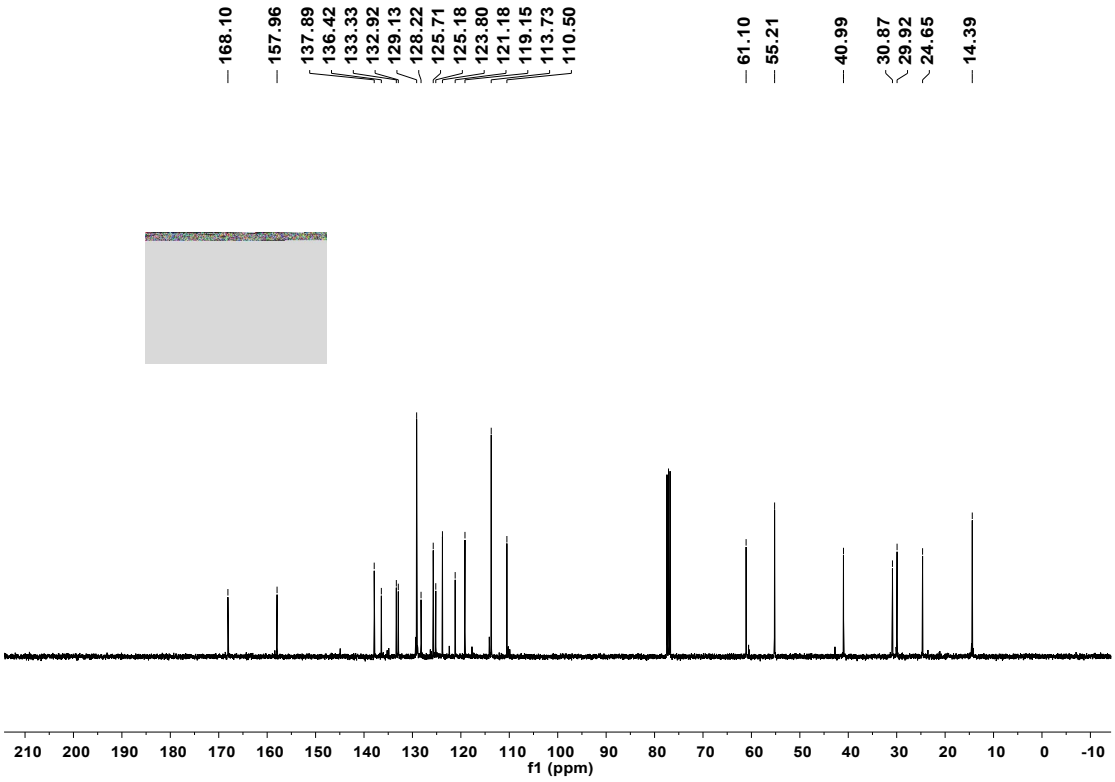
7.20
7.18
7.16
7.13
7.12
7.11
7.10
6.96
6.94
6.77
6.75
4.67
4.66
4.65
4.28
4.26
4.24
4.22
3.81
3.73
2.91
2.90
2.87
2.85
2.37
2.35
2.34
2.34
2.33
2.32
2.30
2.28
2.27
2.26
2.26
2.25
2.23
2.12
2.12
2.11
2.11
2.09
2.08
1.34
1.33
1.31
MeO
Cl
CO2Et
N
1.00
2.04
1.04
2.04
2.07
1.02
2.09
3.04
3.04
1.07
2.09
1.07
3.08
f1 (ppm)


168.10
157.96
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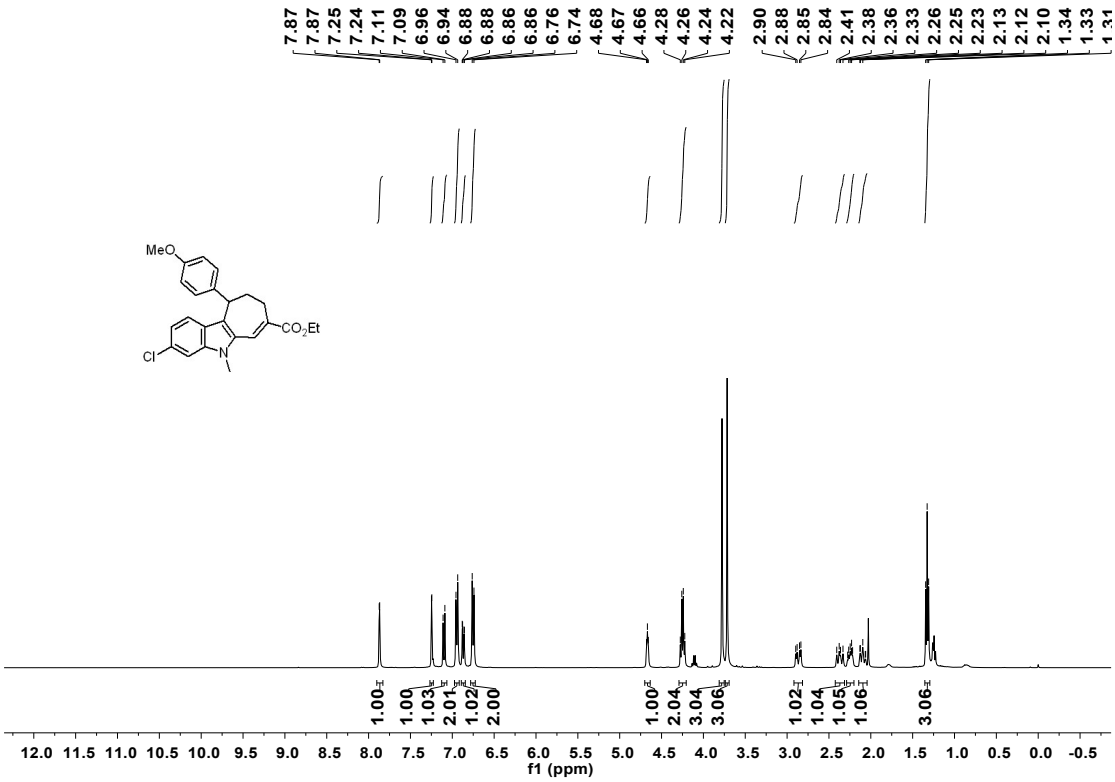
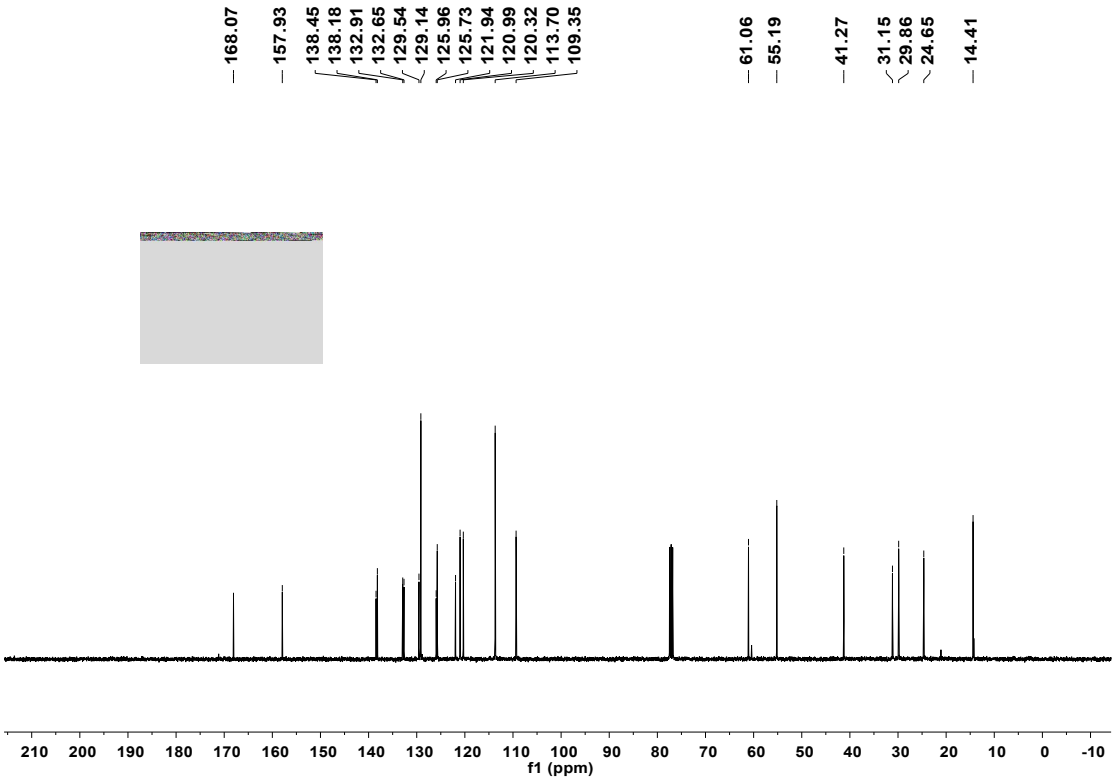
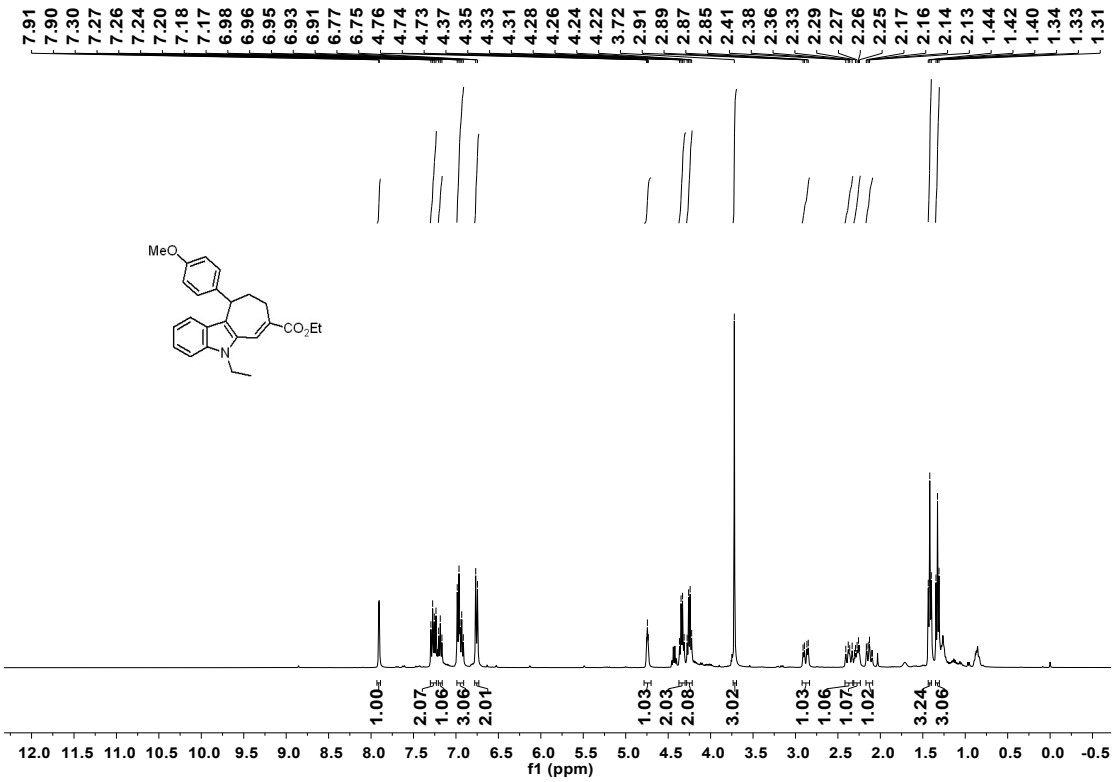
136.42
133.33
132.92
129.13
128.22
125.71
125.18
123.80
121.18
119.15
113.73
110.50
61.10
55.21
40.99
30.87
29.92
24.65
14.39
f1 (ppm)

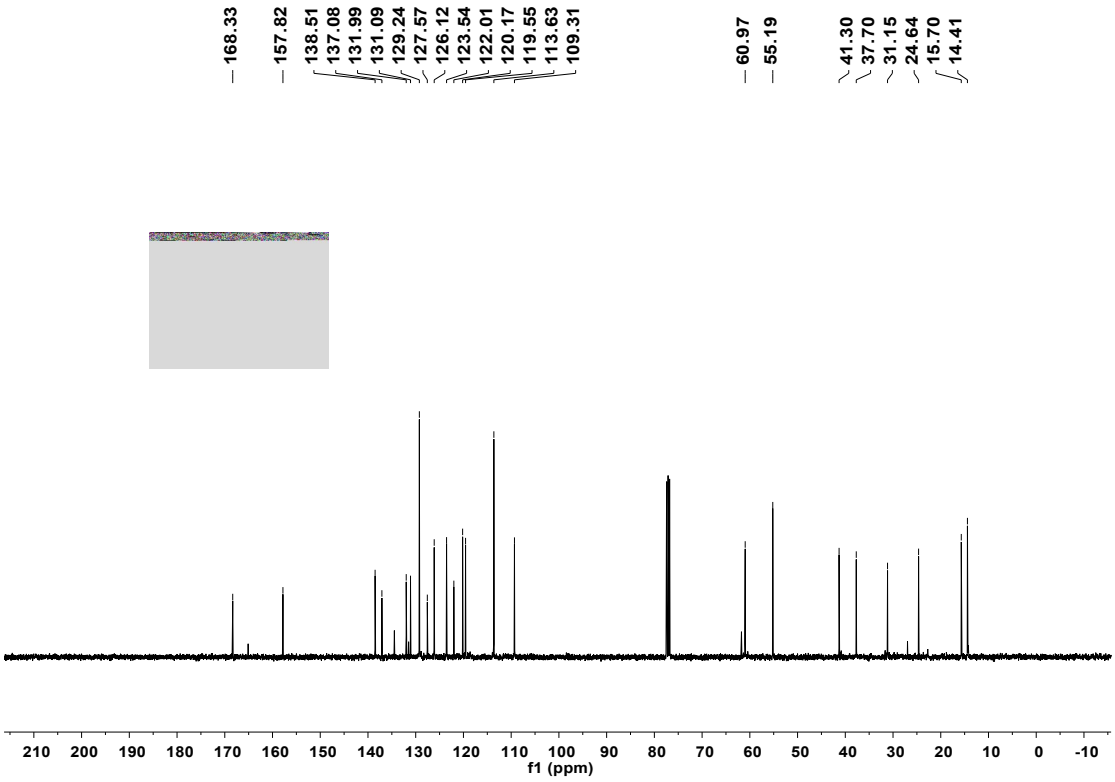
10d


7.87
7.87
7.25
7.24
7.11
7.09
6.96
6.94
6.88
6.88
6.86
6.86
6.76
6.74
4.68
4.67
4.66
4.28
4.26
4.24
4.22
2.90
2.88
2.85
2.84
2.41
2.38
2.36
2.33
2.26
2.25
2.23
2.13
2.12
2.10
1.34
1.33
MeO
CO2Et
Cl
N
1.00
1.00
1.03
2.01
1.02
2.00
1.00
2.04
3.04
3.06
1.02
1.04
1.05
1.06
3.06
f1 (ppm)


168.07
157.93
138.45
138.18
132.91
132.65
129.54
129.14
125.96
125.73
121.94
120.99
120.32
113.70
109.35
61.06
55.19
41.27
31.15
29.86
24.65
14.41
f1 (ppm)

10e


MeO
CO2Et
N
f1 (ppm)


168.33
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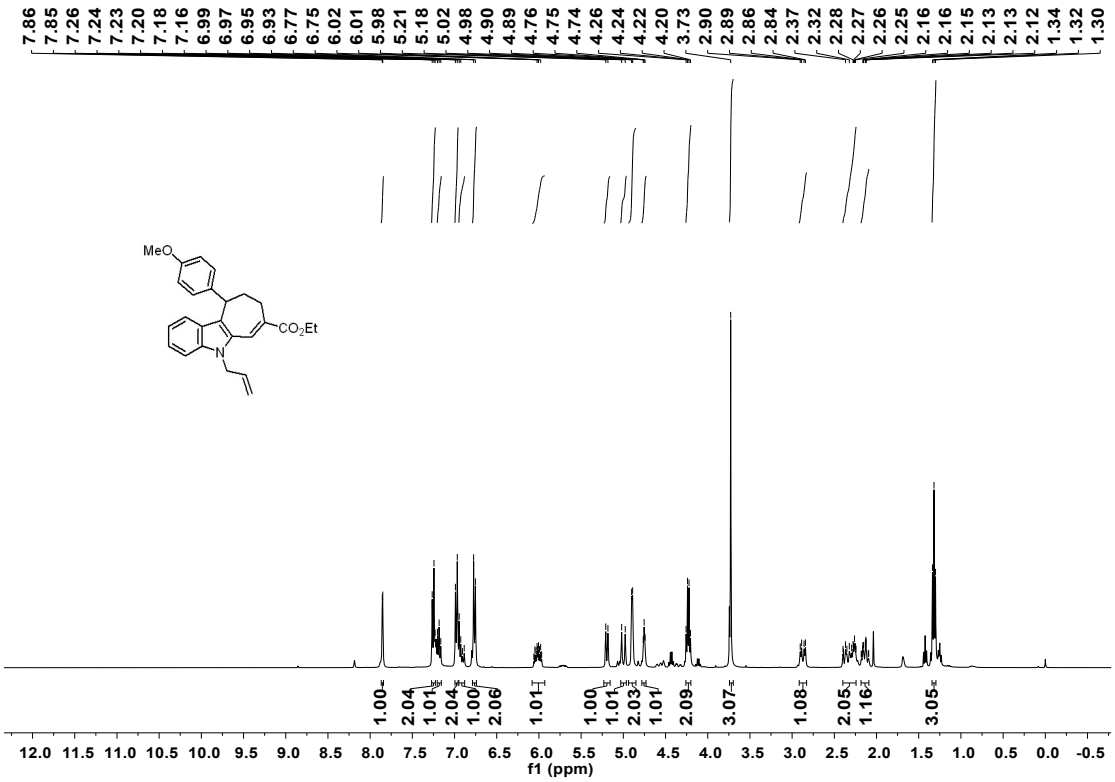
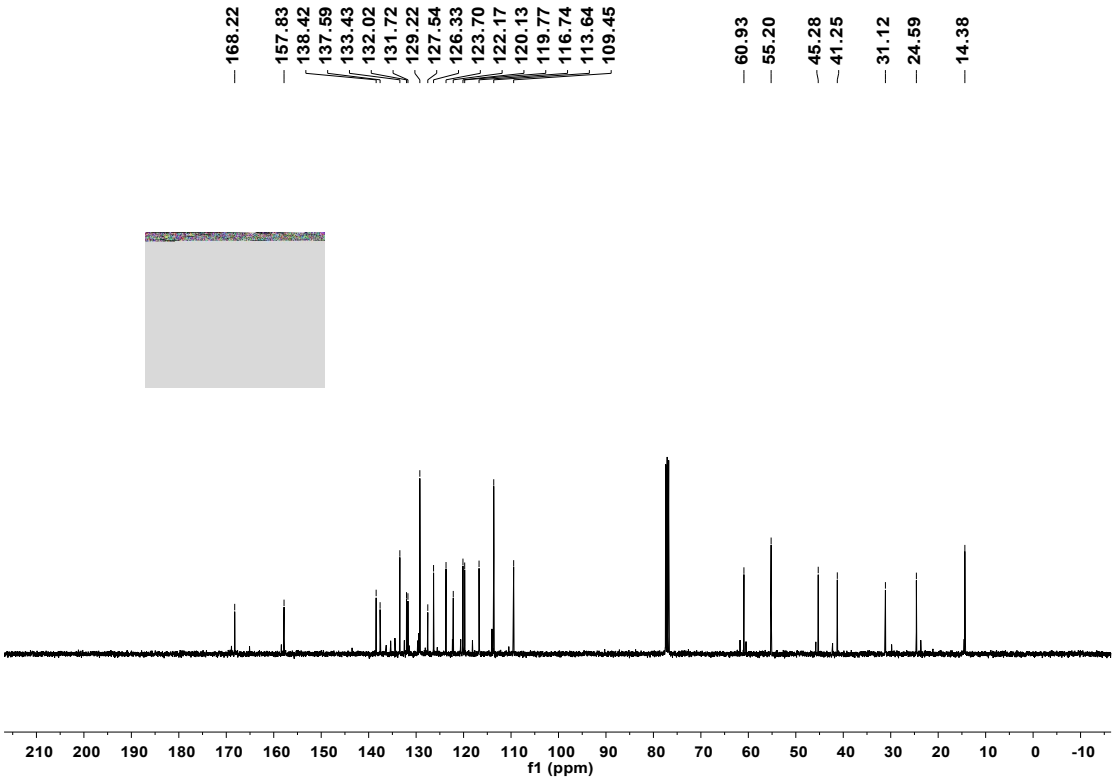
138.51
137.08
131.99
131.09
129.24
127.57
126.12
123.54
122.01
120.17
119.55
113.63
109.31
60.97
55.19
41.30
37.70
31.15
24.64
15.70
14.41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

10f


7.86
7.85
7.26
7.24
7.23
7.20
7.18
7.16
6.99
6.97
6.95
6.93
6.77
6.75
6.02
6.01
5.98
5.21
5.18
5.02
4.98
4.90
4.89
4.76
4.75
4.74
4.26
4.24
4.22
4.20
3.73
2.90
2.89
2.86
2.84
2.37
2.32
2.28
2.27
2.26
2.25
2.16
2.16
2.15
2.13
2.13
2.12
1.34
1.32
1.30
MeO
CO2Et
N
1.00
2.04
1.01
2.04
1.00
2.06
1.01
1.00
1.01
2.03
1.01
2.09
3.07
1.08
2.05
1.16
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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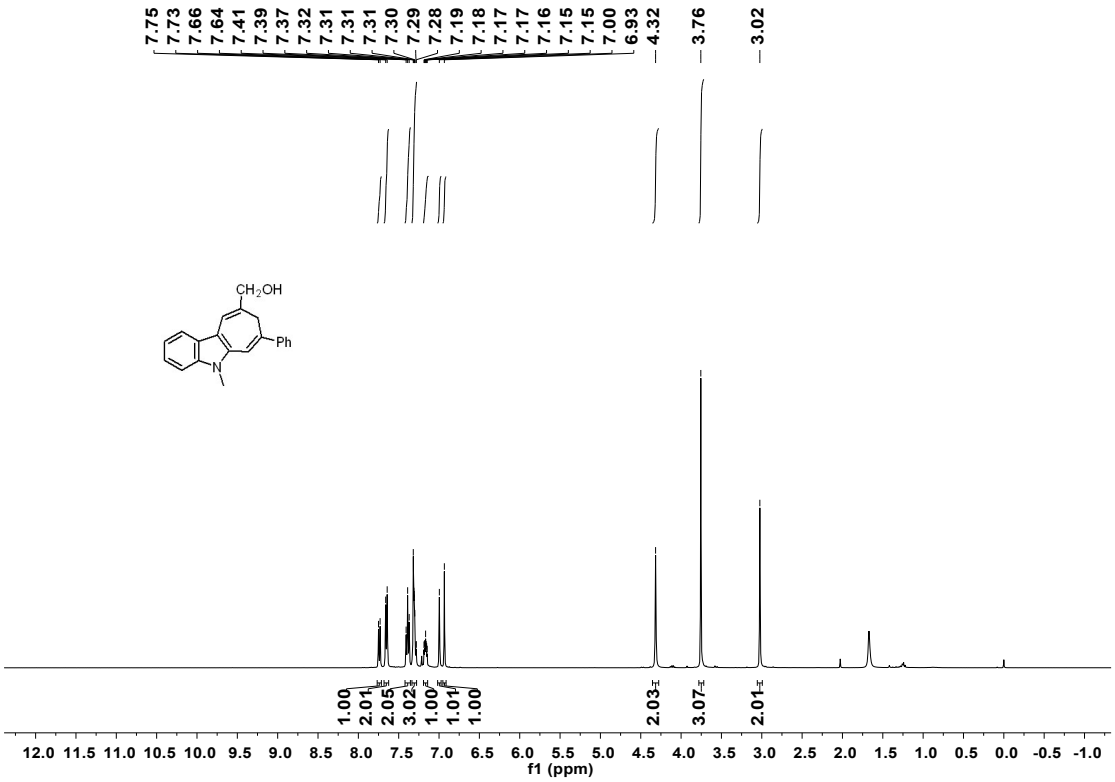
157.83
138.42
137.59
133.43
132.02
131.72
129.22
127.54
126.33
123.70
122.17
120.13
119.77
116.74
113.64
109.45
60.93
55.20
45.28
41.25
31.12
24.59
14.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

11a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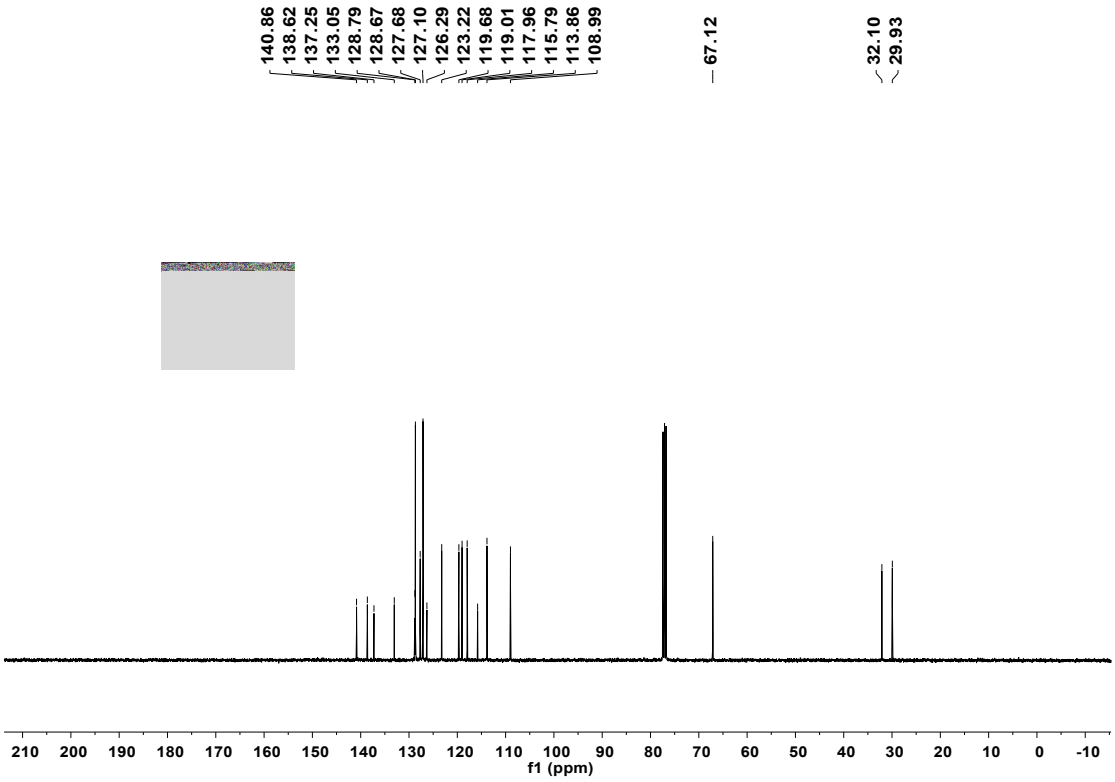
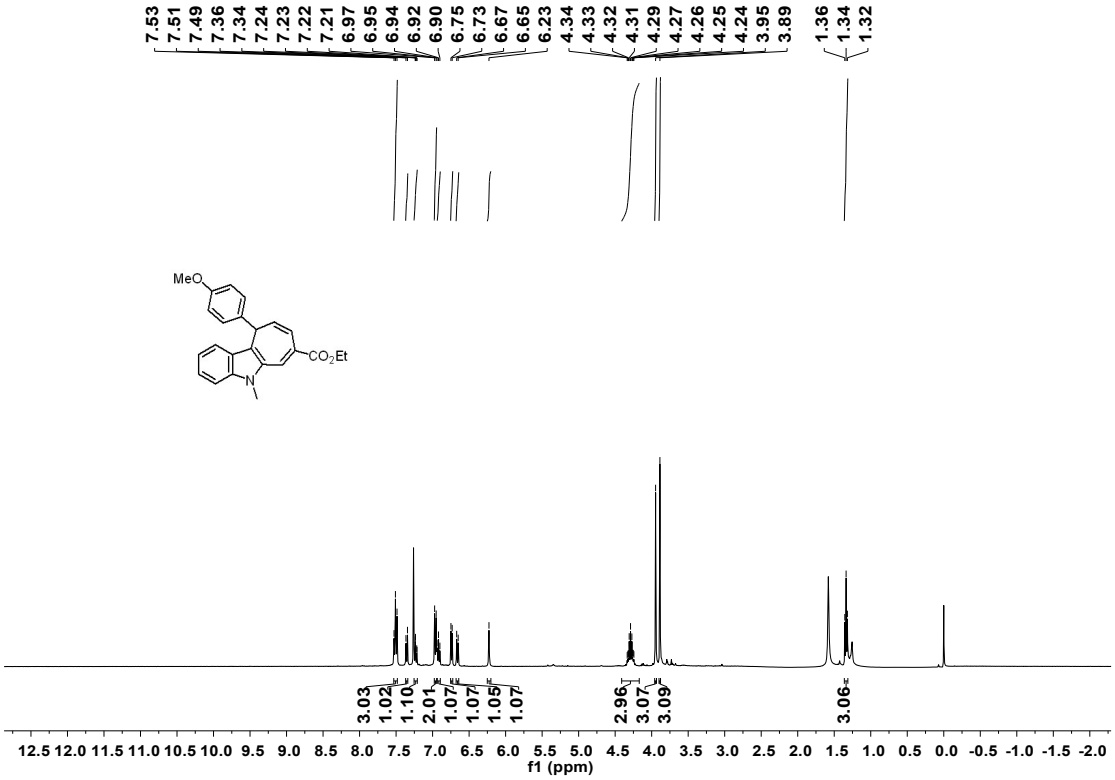
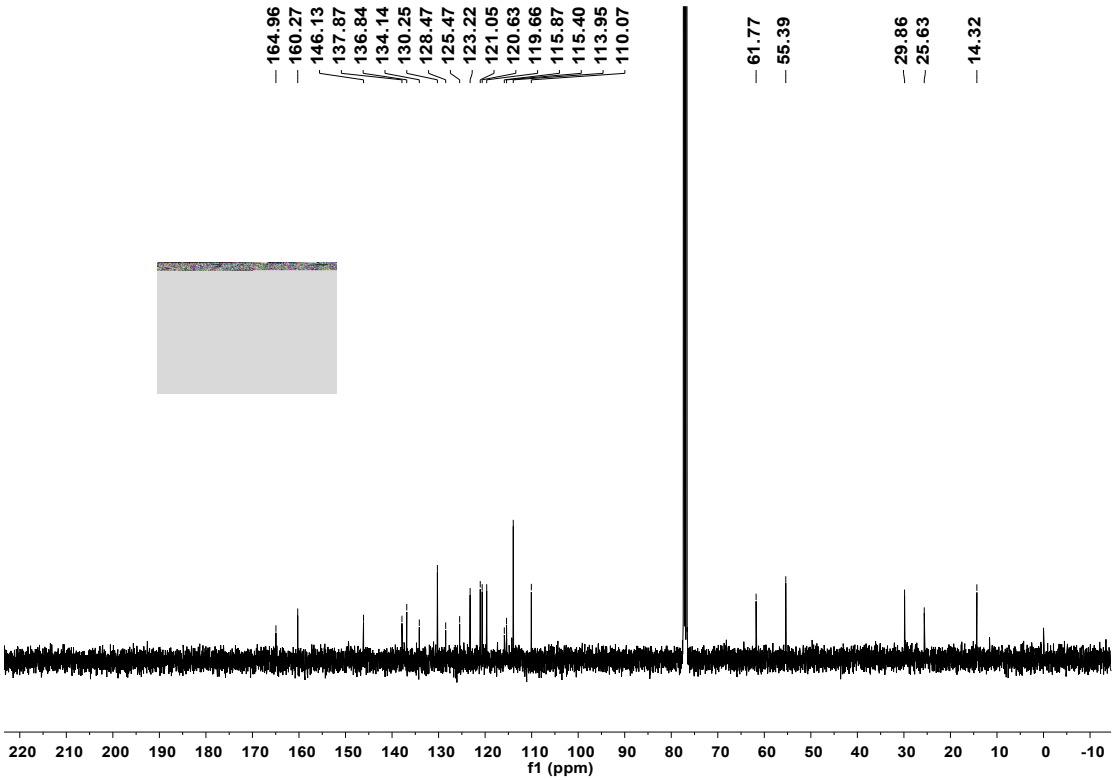
7.73
7.66
7.64
7.41
7.39
7.37
7.32
7.31
7.31
7.31
7.30
7.29
7.28
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.00
6.93
4.32
3.76
3.02
CH2OH
Ph
N
1.00
2.01
2.05
3.02
1.00
1.01
1.00
2.03
3.07
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


140.86
138.62
137.25
133.05
128.79
128.67
127.68
127.10
126.29
123.22
119.68
119.01
117.96
115.79
113.86
108.99
67.12
32.10
29.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

12a


7.53
7.51
7.49
7.36
7.34
7.24
7.23
7.22
7.21
6.97
6.95
6.94
6.92
6.90
6.75
6.73
6.67
6.65
6.23
4.34
4.33
4.32
4.31
4.29
4.27
4.26
4.25
4.24
3.95
3.89
1.36
1.34
1.32
MeO
CO2Et
N
3.03
1.02
1.10
2.01
1.07
1.07
1.05
1.07
2.96
3.07
3.09
3.06
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


164.96
160.27
146.13
137.87
136.84
134.14
130.25
128.47
125.47
123.22
121.05
120.63
119.66
115.87
115.40
113.95
110.07
61.77
55.39
29.86
25.63
14.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)