Supplementary Information

One-Step Synthesis of Azepino[3,4-b]indoles by Cooperative Aza-[4+3] Cycloaddition from Readily Available Feedstocks

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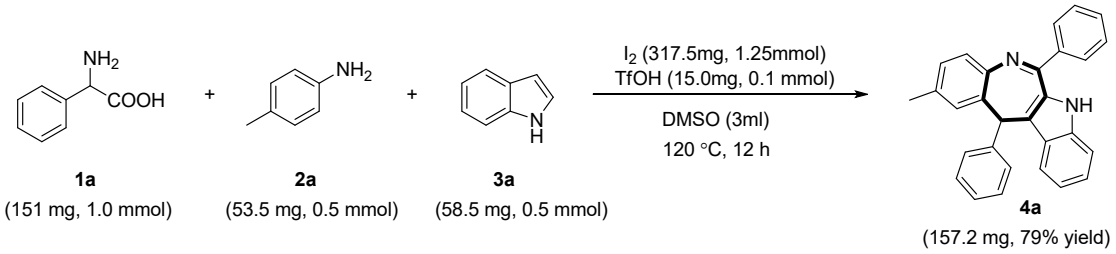
1. General

All other substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H spectra were recorded in $CDCl_3$/DMSO-d_6 on 600/400 MHz NMR spectrometers and resonances (δ) are given in parts per million relatives to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$/DMSO-d_6 on 150/100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of **4b**, **4r** and **8d** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

2. General procedure for the synthesis of 4, 5 and 6(4a as an example)

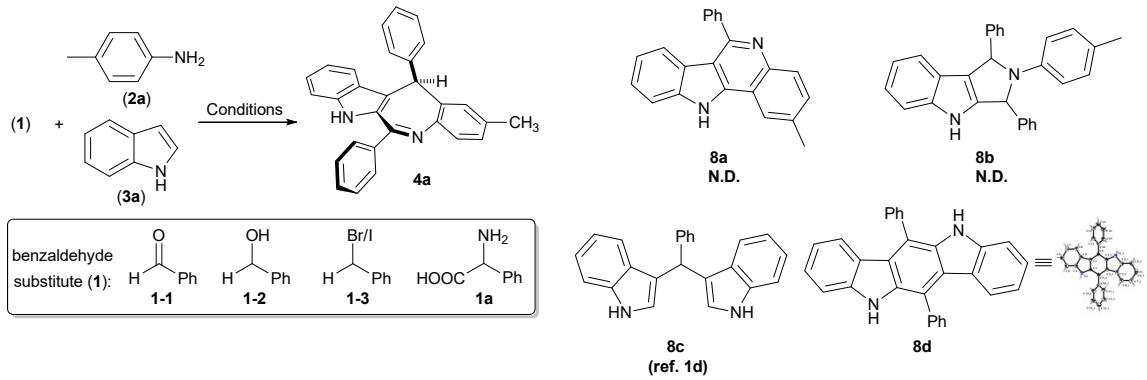


1a (151 mg, 1.0 mmol) + **2a** (53.5 mg, 0.5 mmol) + **3a** (58.5 mg, 0.5 mmol) → **4a** (157.2 mg, 79% yield)

A sealed tube was charged with phenylglycine (**1a**) (151 mg, 1.0 mmol), p-toluidine (**2a**) (53.5 mg, 0.5 mmol), indole (**3a**) (58.5 mg, 0.5 mmol), I_2 (317.5mg, 1.25mmol), TfOH (15.0mg, 0.1 mmol) and DMSO (3.0 mL, *c* 0.17 M) at 120 °C (heating block) for 12 h till almost completed conversion of the substrates by TLC analysis, the mixture was quenched with saturation $Na_2S_2O_3$ solution (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 12:1) to afford the product **4a** (157.2 mg, 79% yield).

3. Optimization of the reaction conditions

Our study commenced with the reaction of benzaldehyde (**1-1**), p-toluidine (**2a**), and indole (**3a**) in present of Lewis or Bronsted acid (Supplementary Table 1). Unfortunately, after several varied conditions were tried, we did not obtain any aza-seven-membered ring adducts (Supplementary Table 1, entry 1). Attempts to use *in situ* generated benzaldehyde species from either phenylmethanol (**1-2**) or benzyl halide (**1-3**) in I_2-DMSO system in present of TfOH turns out to be a failure (Supplementary Table 1, entries 2-3). Phenylglycine (**1a**) was then tested as a substrate under similar conditions since it was reported by our previous work[1] that amino acid could be converted to corresponding aldehyde by I_2 mediated Strecker degradation[2]. Delightfully, desired azepino[3,4-b]indole product **4a** could be formed in 40% yield (Supplementary Table 1, entry 4). Encouraged by this result, we turn to optimize the reaction conditions by increased the dose of iodine. A much higher yield (75%) was detected when 2.5 equiv of I_2 was used (Supplementary Table 1, entries 5–11). Changing the amount of TfOH did not increase the yield (Supplementary Table 1, entries 12–15), and only a trace of **4a** could be observed when TfOH was not present (Supplementary Table 1, entry 16). Next, we tried a variety of different Brønsted and Lewis acids, but none improved yield was obtained (Supplementary Table 1, entries 17–24). We also found that the yield of **4a** is better when the reaction is performed at 120 °C and the amount of by-products is significantly reduced (Supplementary Table 1, entries 25–30). Upon optimizing the type and amount of acid, the temperature, and the iodine loading, we derived the following conditions: I_2 (2.5 equiv), TfOH (0.2 equiv), at 120 °C for 12 h under air. More importantly, in the whole process of carefully screening, we did not isolate any competitive aza-[3+2] or aza-[4+2] products under our conditions (Supplementary Table 1, **8a** and **8b** were not detected), although some other unwanted by-products were found (Supplementary Table 1, **8c** see reference 1d, **8d** was unambiguously comformed by X-ray crystallographic analysis).



entry	**1**	catalyst (equiv)	I_2 (equiv)	temp(°C)	yield[a] (%)
1	**1-1**	TfOH(0.2)	-	100	N.D.
2	**1-2**	TfOH(0.2)	I_2(1.0)	100	N.D.
3	**1-3**	TfOH(0.2)	I_2(1.0)	100	N.D.
4	**1a**	TfOH(0.2)	I_2(1.0)	100	40
5[b]	**1a**	TfOH(0.2)	I_2(0.1)	100	8
6[b]	**1a**	TfOH(0.2)	I_2(0.2)	100	11
7	**1a**	TfOH(0.2)	I_2(0.5)	100	16
8	**1a**	TfOH(0.2)	I_2(1.5)	100	56
9	**1a**	TfOH(0.2)	I_2(2.0)	100	68
10	**1a**	TfOH(0.2)	I_2(2.5)	100	75
11	**1a**	TfOH(0.2)	I_2(3.0)	100	71
12	**1a**	TfOH(0.02)	I_2(2.5)	100	16
13	**1a**	TfOH(0.1)	I_2(2.5)	100	42
14	**1a**	TfOH(0.3)	I_2(2.5)	100	71
15	**1a**	TfOH(0.4)	I_2(2.5)	100	69
16[b]	**1a**	-	I_2(2.5)	100	trace
17	**1a**	TsOH(0.2)	I_2(2.5)	100	66
18	**1a**	TFA(0.2)	I_2(2.5)	100	8
19[c]	**1a**	HI(2.0)	I_2(2.5)	100	trace
20	**1a**	$CuCl_2$(0.2)	I_2(2.5)	100	14
21	**1a**	$FeCl_3$(0.2)	I_2(2.5)	100	20
22	**1a**	$InBr_3$(0.2)	I_2(2.5)	100	49
23	**1a**	$GaBr_3$(0.2)	I_2(2.5)	100	58
24	**1a**	$Ga(OTf)_3$(0.2)	I_2(2.5)	100	68
25	**1a**	TfOH(0.2)	I_2(2.5)	r.t.	n.d.
26	**1a**	TfOH(0.2)	I_2(2.5)	40	n.d.

27	**1a**	TfOH(0.2)	I_2(2.5)	60	trace
28	**1a**	TfOH(0.2)	I_2(2.5)	80	52
29	**1a**	TfOH(0.2)	I_2(2.5)	120	79
30	**1a**	TfOH(0.2)	I_2(2.5)	140	73

Supplementary Table 1. Optimization of Reaction Conditions[a,b]

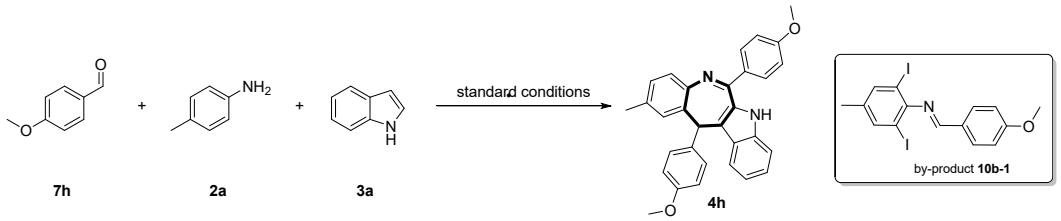
[a]Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), **3a** (0.5 mmol), I_2, catalyst, and DMSO (3.0 mL, *c* 0.17 M) were added to a pressure vessel and stirred for 12 h. N. D. refers to not detected. Yields refer to isolated product. [b]The reaction time was extended to 48 h. [c]Using HI, 50 wt % solution in H_2O.

4. Mechanistic studies

4.1 Studies of Different Additives

Based on the experimental observation that benzaldehyde is not converted into **4a** under our reaction conditions while its amino acid precursor is, we speculated that the by-products in I_2-mediated Strecker degradation, i.e., ammonia and HI, would somehow participate in and promote the whole transformation. Indeed, when *p*-methoxybenzaldehyde **7h** instead of an amino acid was reacted with **2a** and **3a** under standard conditions, **4h** was obtained in less than 5% yield (Supplementary Table 2, entry 1). However, when ammonium iodide was added to the reaction mixture, azepino[3,4-b]indole **4h** was generated in 62% yield (Supplementary Table 2, entry 2). Tetramethylammonium iodide (TMAI) and tetrabutylammonium iodide (TBAI) were also found to promote the reaction, but with a lower yield (Supplementary Table 2, entries 3-4). We also tried other iodine anion compounds (Supplementary Table 2, entries 5–6), inorganic ammonium salts (Supplementary Table 2, entries 7–9), ammonia spirit (Supplementary Table 2, entry 10) and alkyl amines (Supplementary Table 2, entries 11–13), but other additives with different ion-pair combinations showed much lower reactivities.

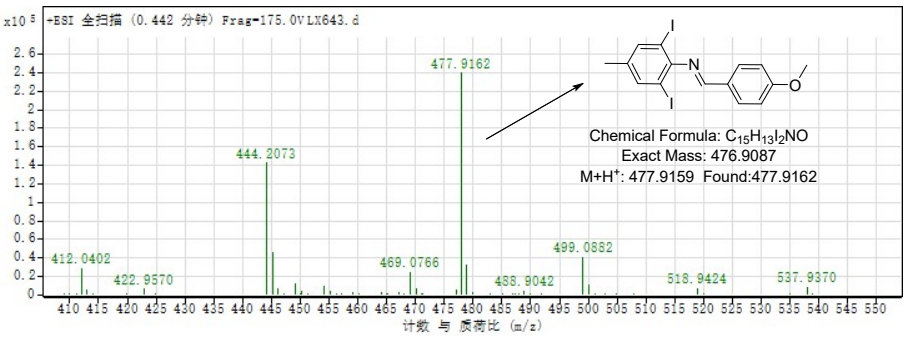
Because of the high catalytic reactivity and metal-free nature of ion-pairs, numerous new organic ion-pair species have been reported for various transformations, especially asymmetric catalysis.[3] We speculated that when benzaldehyde **7h** was used to replace amino acid, the process of iodine-promoted amino acid catabolism would be absent, so that a large amount of iodine anions couldn't be produced in the solvent. Therefore, the above ammonium source could't have a good effect. The above process implied that the *in-situ* generated endogenous by-product ammonium iodide acted as ion-pair promoters.



entry	additive (equiv)	yield[a] (%)
1	-	5
2	NH_4I(1.0)	62
3	$(CH_3)_4NI$(1.0)	56
4	$(n\text{-}Bu)_4NI$(1.0)	52
5	NaI(1.0)	18
6	KI(1.0)	19
7	$(Et)_3N$(1.0)	trace
8	DIPEA(1.0)	trace
9	$(n\text{-}Pr)_3N$(1.0)	trace
10	$NH_3\cdot H_2O$(1.0)	15
11	NH_4Cl(1.0)	13
12	NH_4Br(1.0)	11
13	NH_4OAc(1.0)	18

Supplementary Table 2. Optimization of additives [a,b]

[a]Reaction conditions: **7h** (1.0 mmol), **2a** (0.5 mmol), **3a** (0.5 mmol), I_2 (1.25 mmol), TfOH (0.1 mmol), additives and DMSO (3.0 mL, *c* 0.17 M) were added to a pressure vessel and stirred at 120 °C for 12 h. Yields refer to isolated product.

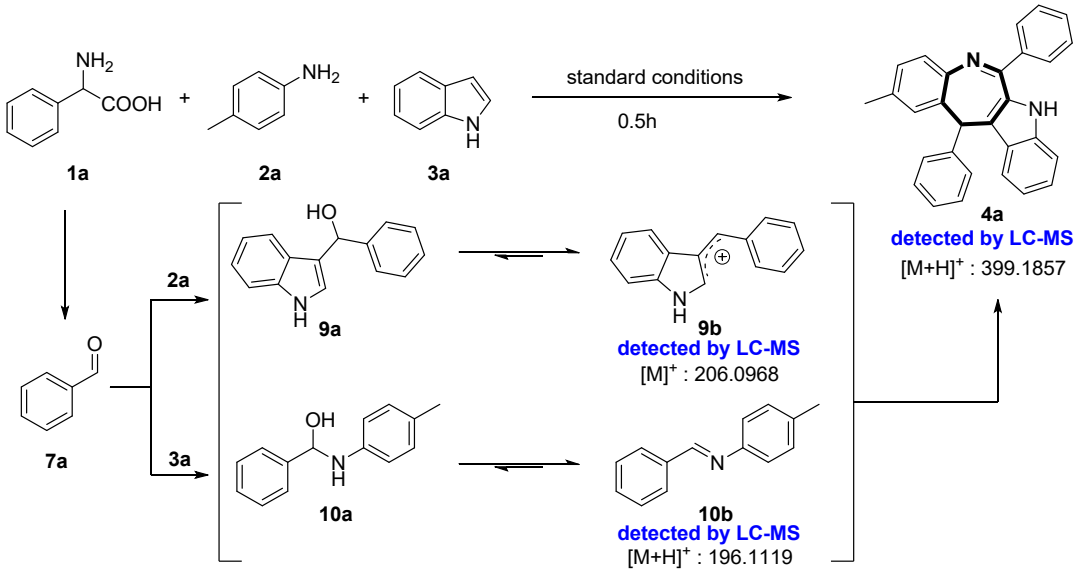


Supplementary Figure 1. Detection for the generation of 10b-1

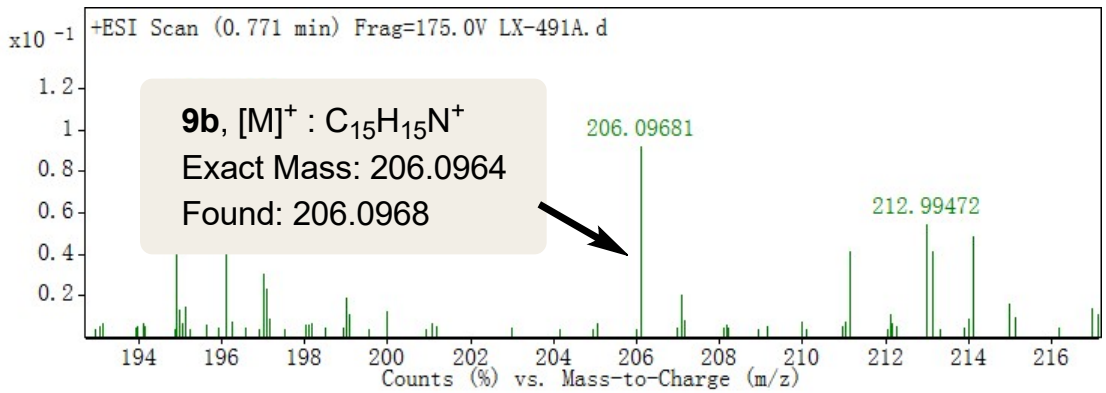
After monitoring the reaction in Supplementary Table 2, we found that most of attempts gave relative messy results. We found that in Supplementary Table 2 entry 1, the main product is the iodinized imine **10b-1** in around 40% yield. This by-product was also detected in other entries in Table 2. We believe that due to the lack of ammonium iodide, the indole cation cannot be stably produced in the reaction, resulting in the continuous formation of imines that are continuously oxidized by iodine. It is notable that the 3,3'-(phenylmethylene)bis(1H-indole) product was also not detected in those experiments.

4.2 Studies of intermediates 8b and 9b

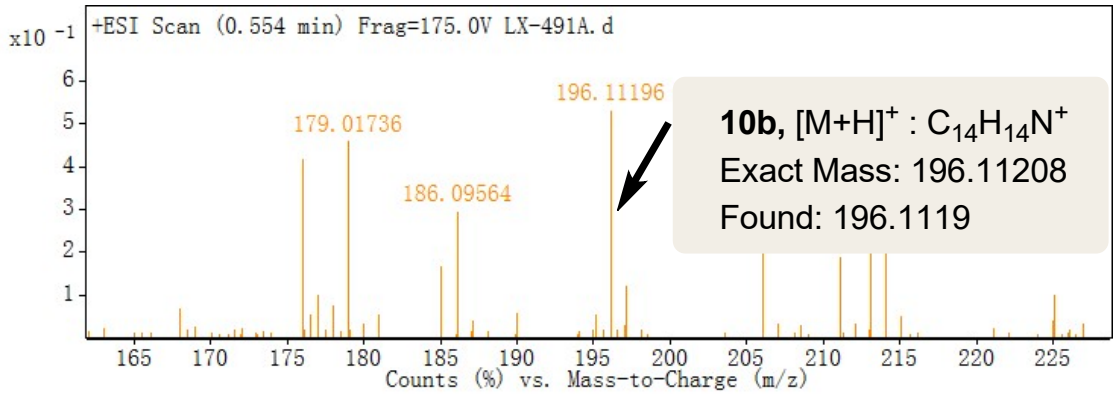
1a (1.0 mmol), **2a** (0.5 mmol), **3a** (0.5 mmol), I_2 (1.25 mmol), TfOH (0.1 mmol) and DMSO (3.0 mL, *c* 0.17 M) reacted at 120 °C for 0.5 h, obtained the intermediates **8b** and **9b**(detected by LC-MS), then could converted to **4a** after 12h under standard conditions. Obviously, **8b** and **9b** are possible intermediates for this protocol.



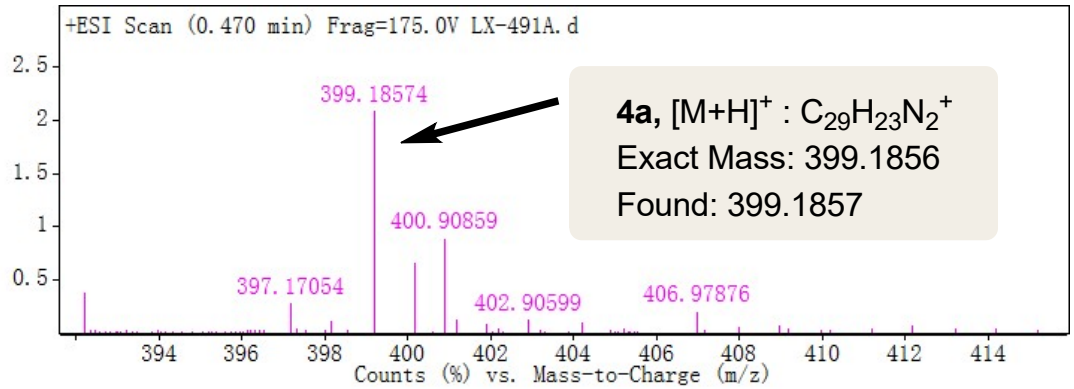
The LC-MS Spectra is listed below:



Supplementary Figure 2. Detection for the generation of 9b



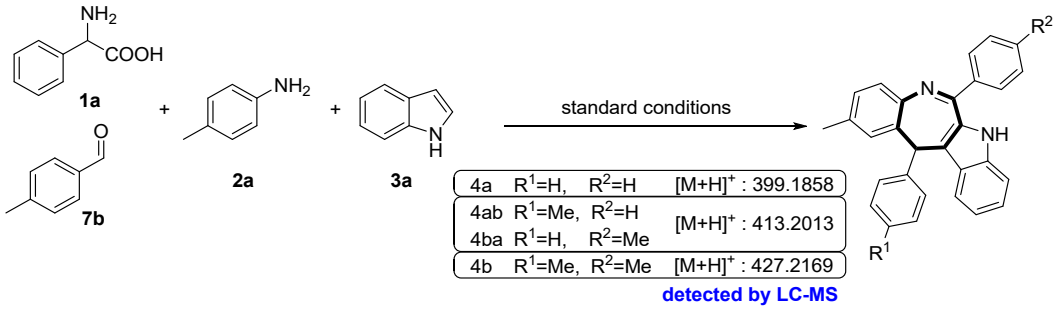
Supplementary Figure 3. Detection for the generation of 10b



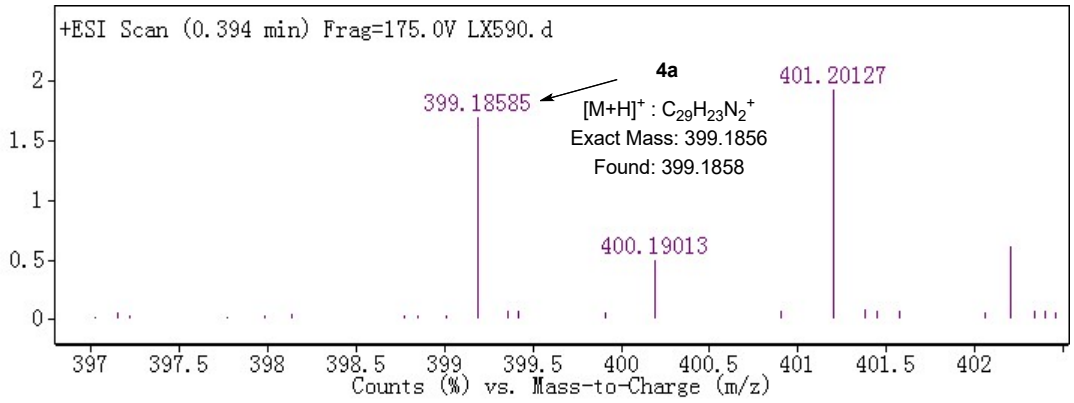
Supplementary Figure 4. Detection for the generation of 4a

4.2 Studies of cross-coupling reaction

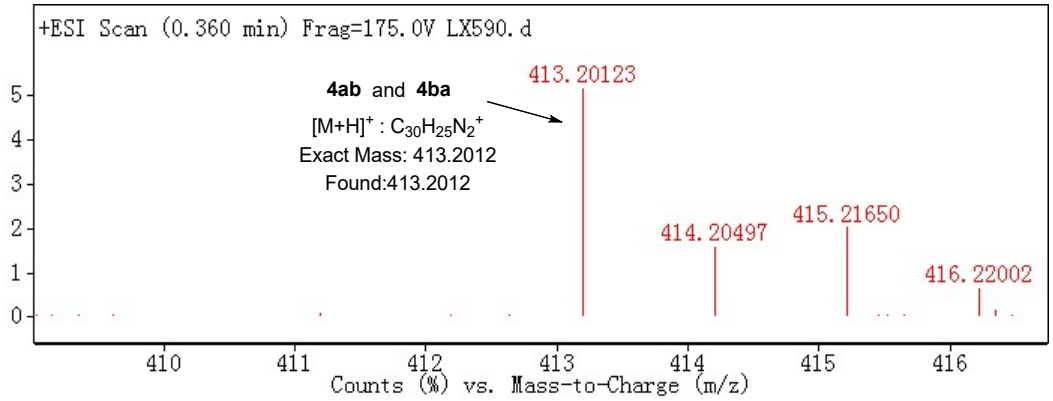
We investigated the cross-coupling reaction using **1a** (0.5 mmol), **7b** (0.5 mmol), **2a** (0.5 mmol) and **3a** (0.5 mmol) under the standard conditions. All the products were successfully identified by LC-MS analysis of the crude reaction extract, including the crossed products **4ab** and **4ba**.



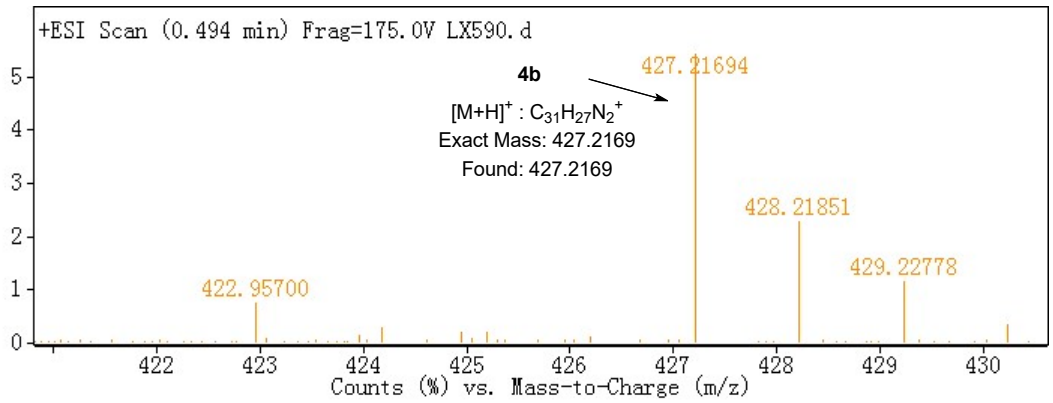
The LC-MS Spectra is listed below:



Supplementary Figure 5. Detection for the generation of 4a

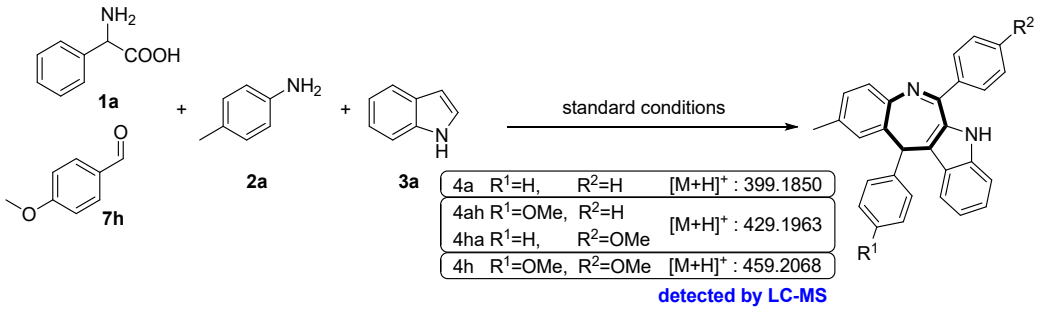


Supplementary Figure 6. Detection for the generation of 4ab and 4ba

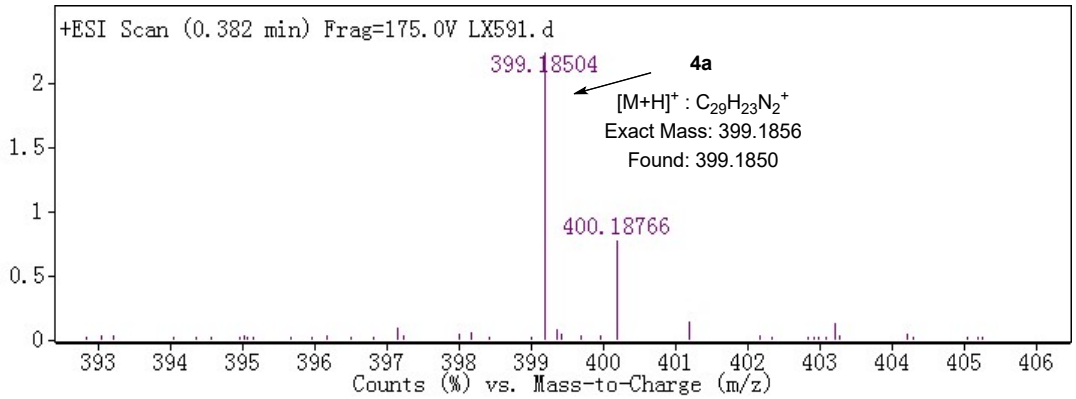


Supplementary Figure 7. Detection for the generation of 4b

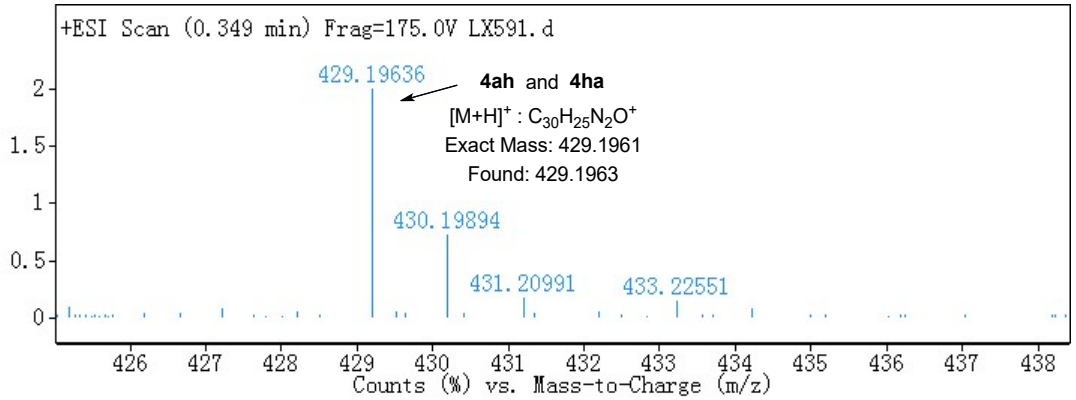
Then we investigated the cross-coupling reaction using **1a** (0.5 mmol), **7h** (0.5 mmol), **2a** (0.5 mmol) and **3a** (0.5 mmol) under the standard conditions. All the products were successfully identified by LC-MS analysis of the crude reaction extract, including the crossed products **4ah** and **4ha**.



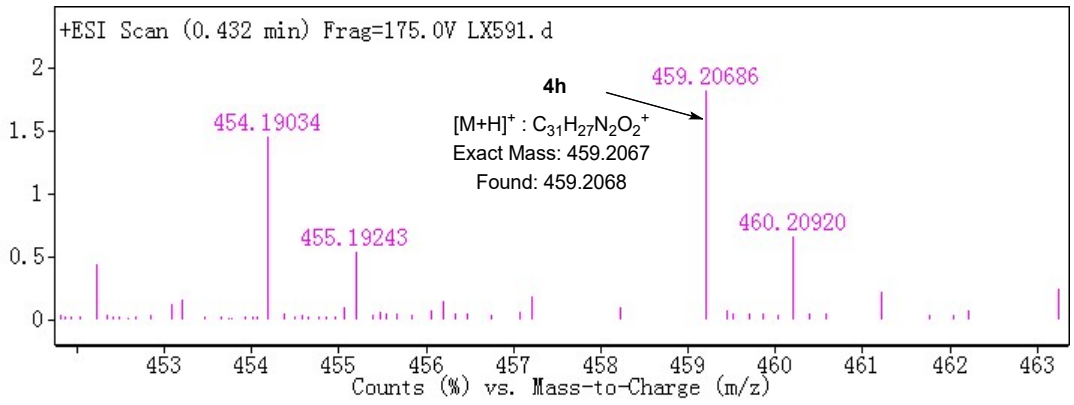
The LC-MS Spectra is listed below:



Supplementary Figure 8. Detection for the generation of 4a

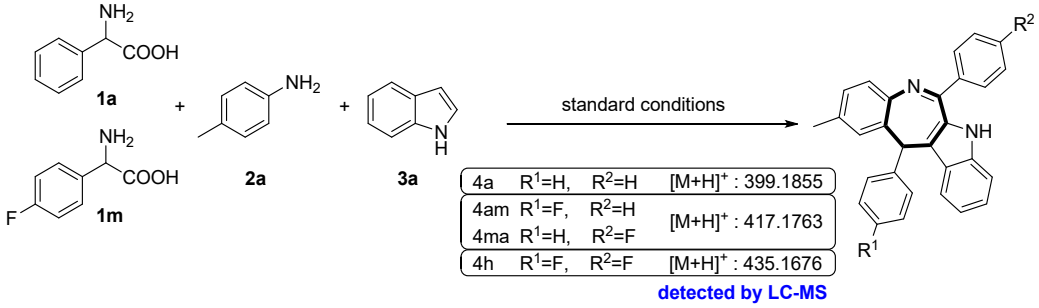


Supplementary Figure 9. Detection for the generation of 4ah and 4ha

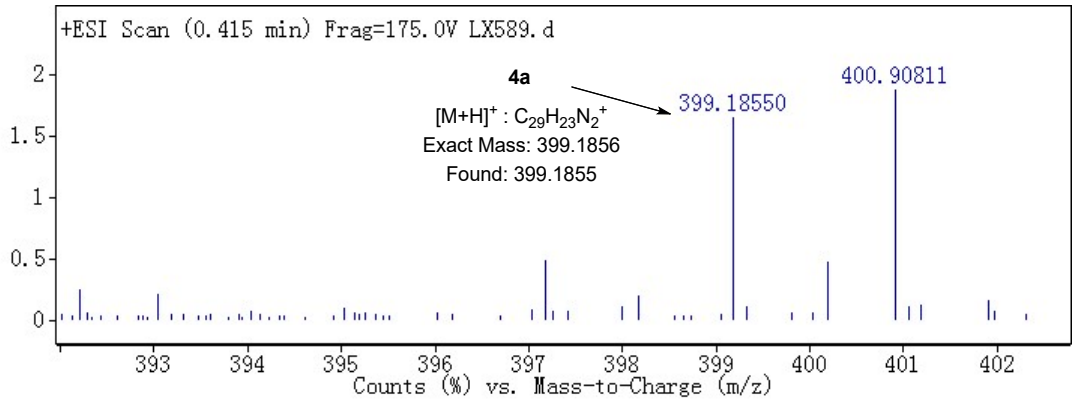


Supplementary Figure 10. Detection for the generation of 4h

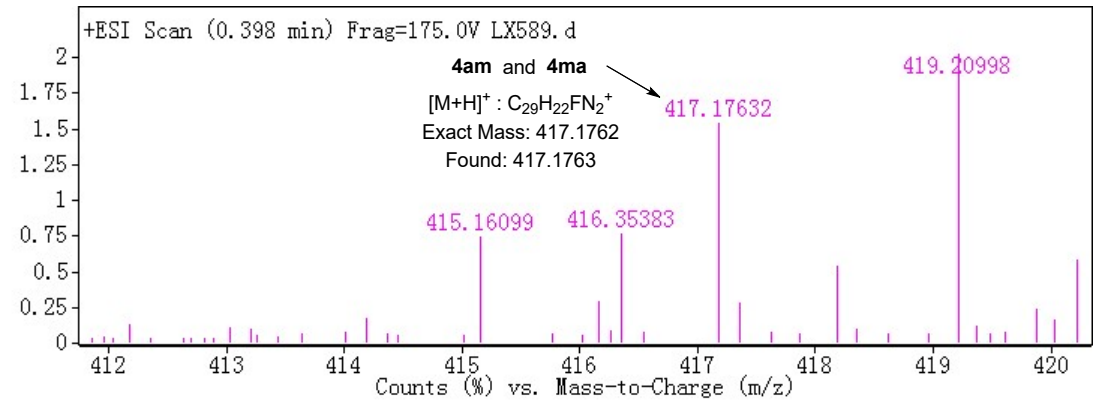
Next we investigated the cross-coupling reaction using **1a** (0.5 mmol), **1m** (0.5 mmol), **2a** (0.5 mmol) and **3a** (0.5 mmol) under the standard conditions. All the products were successfully identified by LC-MS analysis of the crude reaction extract, including the crossed products **4am** and **4ma**.



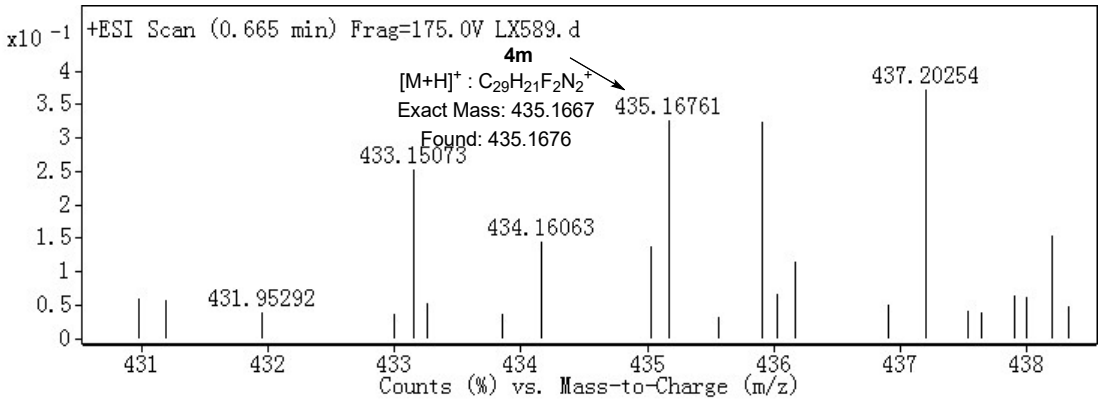
The LC-MS Spectra is listed below:



Supplementary Figure 11. Detection for the generation of 4a



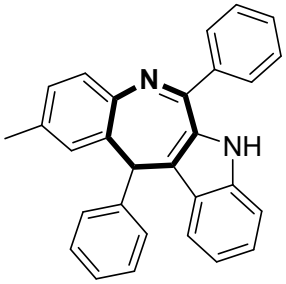
Supplementary Figure 12. Detection for the generation of 4am and 4ma



Supplementary Figure 13. Detection for the generation of 4m

Obviously, the above three sets of cross-coupling reactions clearly confirms our proposed mechanism by LC-MS analysis. In the presence of iodine-mediated amino acid catabolism, endogenous ammonium iodide can be obtained in the system, and aldehyde can participate in the consecutive reaction. On the one hand, it shows that amino acid is first catabolized into aldehyde and then participate in the subsequent process. On the other hand, it proves that endogenous ammonium iodide is indispensable to the reaction system.

5. Characterization data for compounds 4, 5 and 6.



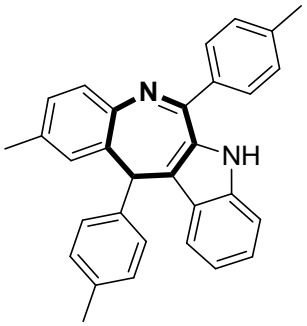
10-methyl-6,12-di-p-tolyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4a)

Yield 79%; 157.2 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 113-115 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.76–7.70 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.8 Hz, 3H), 7.33 (d, *J* = 3.6 Hz, 2H), 7.28 (s, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.06–6.93 (m, 5H), 5.73 (s, 1H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 143.6, 141.8, 139.2, 137.6, 136.8, 134.7, 130.4, 130.2, 129.5, 129.1, 128.5, 127.9, 127.8, 126.9, 126.8, 126.5, 126.3, 126.0, 125.0, 120.5, 119.2, 111.6, 45.2, 21.0.

HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2^+$ $(M+H)^+$ 399.1856, found: 399.1858.



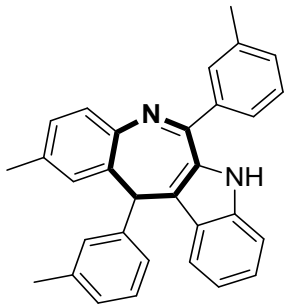
10-methyl-6,12-di-p-tolyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4b)

Yield 77%; 164.0 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 245-247 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.26–7.12 (m, 7H), 6.82 (s, 4H), 5.65 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.12 (s, 3H);

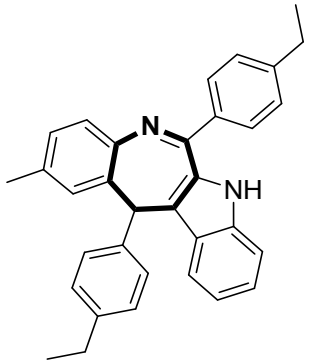
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 143.6, 140.3, 138.7, 137.2, 136.6, 136.4, 135.4, 135.2, 130.2, 129.3, 129.1, 128.5, 127.7, 126.8, 126.7, 126.2, 124.7, 120.3, 119.0, 111.6, 44.9, 21.4, 20.9, 20.8;

HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2^+$ $(M+H)^+$ 427.2168, found 427.2169



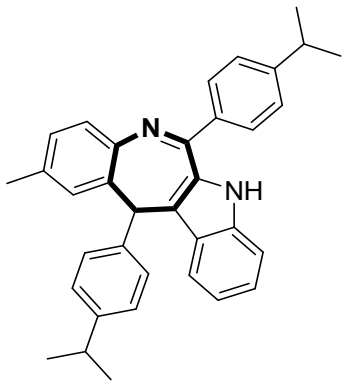
10-methyl-6,12-di-m-tolyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4c)
Yield 76%, 161.9 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 103-104℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35–7.26 (m, 5H), 7.25 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.82–6.75 (m, 3H), 5.68 (s, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 143.6, 141.6, 139.2, 138.4, 137.4, 137.2, 136.7, 135.1, 131.0, 130.3, 129.6, 129.4, 128.3, 127.8, 127.7, 127.5, 126.9, 126.8, 126.4, 126.3, 126.0, 124.9, 124.2, 120.4, 119.2, 111.6, 45.2, 21.45, 21.38, 21.0;
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2^+$ $(M+H)^+$ 427.2168, found 427.2168



6,12-bis(4-ethylphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4d)
Yield 78%; 177.1 mg; yellow oil; column chromatography, silica gel (PE/EA, 12:1); mp 141-143℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 15.6, 9.6 Hz, 6H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 4H), 5.67 (s, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.43 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H).;
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 146.7, 143.6, 141.8, 139.0, 137.3, 136.7, 135.1, 130.3, 129.5, 129.3, 128.0, 127.7, 127.3, 126.9, 126.8, 126.3, 126.1, 124.8, 120.3, 119.1, 111.6, 45.0, 28.8, 28.2, 20.9, 15.4;
HRMS (ESI) m/z calcd for $C_{33}H_{31}N_2^+$ $(M+H)^+$ 455.2481, found 455.2482.



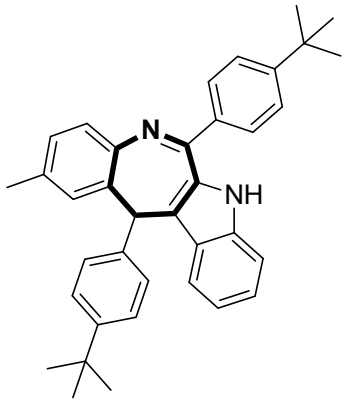
6,12-bis(4-isopropylphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4e)

Yield 72%; 173.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 212-214 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 5H), 7.22 (t, *J* = 4.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 4H), 5.68 (s, 1H), 2.94 (m, *J* = 13.6, 6.8 Hz, 1H), 2.69 (m, *J* = 13.6, 6.8 Hz, 1H), 2.40 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 6H), 1.07 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 151.2, 146.4, 143.7, 139.2, 137.3, 137.0, 136.7, 135.0, 130.4, 129.6, 129.3, 127.8, 127.0, 126.8, 126.6, 126.3, 125.9, 124.8, 120.3, 119.2, 111.6, 45.1, 34.1, 33.5, 24.0, 23.9, 23.8, 21.0.

HRMS (ESI) m/z calcd for $C_{35}H_{35}N_2^+$ $(M+H)^+$ 483.2794, found 483.2793.

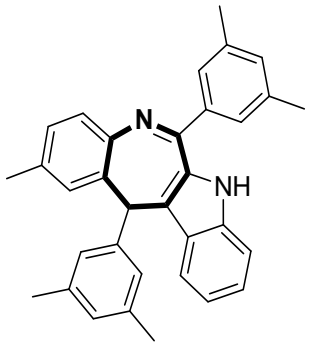


6,12-bis(4-(tert-butyl)phenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4f)

Yield 65%; 165.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 158-160 ℃;

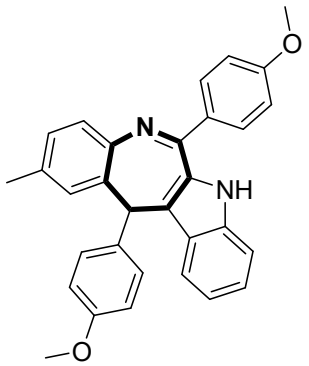
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 3.6 Hz, 2H), 7.24 (dd, *J* = 9.6, 6.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.70 (s, 1H), 2.41 (s, 3H), 1.34 (s, 9H), 1.14 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.6, 148.7, 143.4, 138.7, 137.5, 136.8, 136.4, 134.9, 130.4, 129.6, 129.0, 127.8, 127.0, 126.5, 126.3, 125.9, 125.5, 125.0, 124.8, 120.4, 119.2, 111.6, 45.0, 34.8, 34.1, 31.2, 21.0;
HRMS (ESI) m/z calcd for $C_{37}H_{39}N_2^+$ $(M+H)^+$ 511.3107, found 511.3111.



6,12-bis(3,5-dimethylphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4g)
Yield 73%; 165.7 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 122-124 ℃;

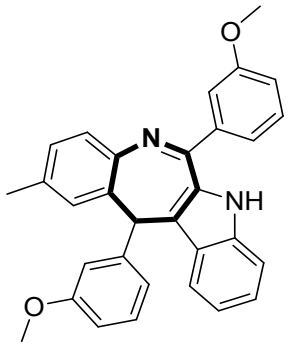
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.35 (s, 2H), 7.31 (d, J = 4.0 Hz, 2H), 7.26–7.20 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.07 (s, 1H), 6.59 (d, J = 17.6 Hz, 3H), 5.63 (s, 1H), 2.41 (s, 3H), 2.34 (s, 6H), 2.05 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 143.5, 141.5, 139.2, 138.1, 137.2, 137.1, 136.7, 135.6, 131.9, 130.2, 129.2, 127.8, 127.6, 127.0, 126.9, 126.2, 125.8, 124.9, 124.7, 120.3, 119.2, 111.6, 45.0, 21.3, 21.2, 21.0;
HRMS (ESI) m/z calcd for $C_{33}H_{31}N_2^+$ $(M+H)^+$ 455.2481, found 455.2482.



6,12-bis(4-methoxyphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4h)
Yield 81%; 185.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 158-160 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 3.6 Hz, 2H), 7.25 (s, 2H),

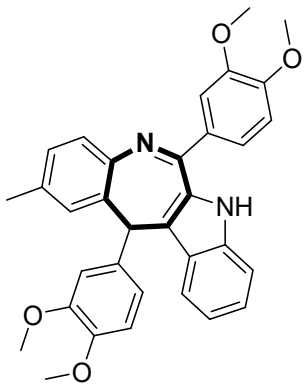
7.16 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 8.8 Hz, 2H), 5.65 (s, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 2.41 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 157.7, 155.6, 143.4, 137.2, 136.7, 135.2, 133.9, 131.6, 130.8, 130.2, 129.2, 127.84, 127.77, 126.8, 126.6, 126.2, 124.9, 120.4, 119.1, 113.9, 113.2, 111.6, 55.4, 55.1, 44.5, 21.0;
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2O_2^+$ $(M+H)^+$ 459.2067, found 459.2067.



6,12-bis(3-methoxyphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4i)
Yield 78%; 178.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 228-230 ℃;

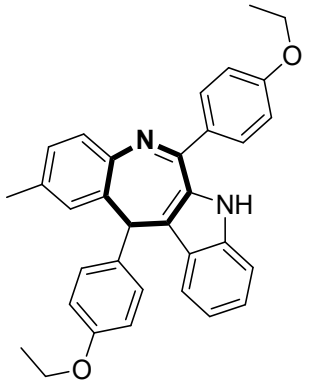
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.35–7.16 (m, 8H), 7.01–6.91 (m, 2H), 6.59–6.48 (m, 3H), 5.68 (s, 1H), 3.82 (s, 3H), 3.55 (s, 3H), 2.41 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.1, 155.8, 143.5, 143.4, 140.6, 137.6, 136.8, 134.8, 130.3, 129.53, 129.46, 128.7, 127.8, 126.8, 126.2, 125.8, 125.0, 121.7, 120.5, 119.5, 119.1, 116.2, 114.0, 113.5, 111.6, 110.9, 55.4, 55.0, 45.2, 21.0;
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2O_2^+$ $(M+H)^+$ 459.2067, found 459.2068.



6,12-bis(3,4-dimethoxyphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4j)
Yield 70%; 181.3 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1);

mp 261-263 ℃;

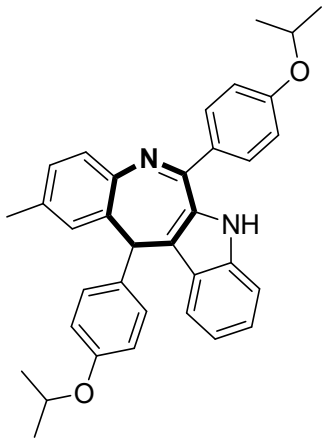
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.37 (dd, *J* = 15.6, 7.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.23–7.15 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 7.2 Hz, 3H), 5.67 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.67 (s, 3H), 3.54 (s, 3H), 2.41 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.8, 148.9, 148.3, 147.3, 143.3, 137.2, 136.7, 135.4, 134.5, 131.9, 130.1, 129.2, 127.7, 126.7, 126.1, 125.8, 124.8, 122.7, 120.3, 119.2, 119.0, 111.7, 111.4, 110.7, 110.6, 110.2, 55.82, 55.79, 55.76, 55.7, 45.0, 20.9;
HRMS (ESI) m/z calcd for $C_{33}H_{31}N_2O_4^+$ $(M+H)^+$ 519.2278, found 519.2280.



6,12-bis(4-ethoxyphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4k)
Yield 74%; 179.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 154-156 ℃;

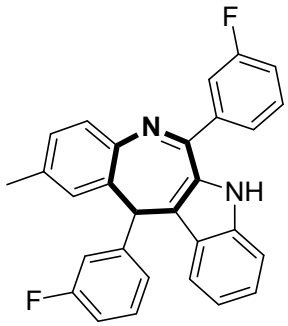
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29–7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 17.6, 8.8 Hz, 4H), 6.54 (d, *J* = 8.8 Hz, 2H), 5.63 (s, 1H), 4.02 (d, *J* = 7.2 Hz, 2H), 3.80 (dd, *J* = 7.2, 3.2 Hz, 2H), 2.39 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.0, 155.6, 143.6, 137.0, 136.6, 135.2, 133.8, 131.6, 130.7, 130.2, 129.2, 127.8, 127.7, 126.8, 126.4, 126.2, 124.8, 120.3, 119.0, 114.4, 113.8, 111.6, 63.6, 63.2, 44.5, 21.0, 14.8;
HRMS (ESI) m/z calcd for $C_{33}H_{31}N_2O_2^+$ $(M+H)^+$ 487.2380, found 487.2376.



6,12-bis(4-isopropoxyphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4l)

Yield 65%; 167.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 141-143 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 2H), 7.24 (s, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.64 (s, 1H), 4.60 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.32 (m, *J* = 12.0, 6.0 Hz, 1H), 2.40 (s, 3H), 1.35 (dd, *J* = 6.0, 3.6 Hz, 6H), 1.17 (dd, *J* = 6.0, 1.6 Hz, 6H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.0, 155.7, 143.6, 137.1, 136.6, 135.2, 133.8, 131.5, 130.7, 130.2, 129.3, 127.9, 127.8, 126.9, 126.4, 126.2, 124.8, 120.4, 119.1, 115.6, 115.3, 111.6, 70.0, 69.7, 44.5, 22.04, 21.96, 21.0;
HRMS (ESI) m/z calcd for $C_{35}H_{35}N_2O_2^+$ $(M+H)^+$ 515.2693, found 515.2694.



6,12-bis(3-fluorophenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4m)

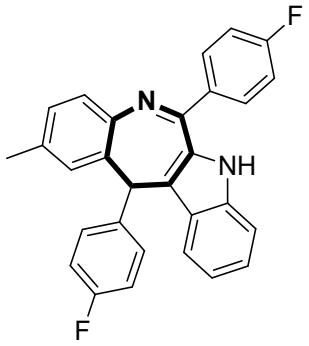
Yield 77%; 167.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 123-125 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.55–7.47 (m, 3H), 7.39 (dd, *J* = 14.4, 6.0 Hz, 3H), 7.29–7.21 (m, 3H), 7.15 (dd, *J* = 12.0, 4.8 Hz, 1H), 7.00 (d, *J* = 6.4 Hz, 1H), 6.77–6.55 (m, 3H), 5.69 (s, 1H), 2.43 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9(d, *J* = 246.0 Hz, $^1J_{CF}$), 162.5(d, *J* = 244.0 Hz, $^1J_{CF}$), 154.5, 144.5, 144.4(d, *J* = 7.0 Hz, $^3J_{CF}$), 141.3(d, *J* = 7.0 Hz, $^3J_{CF}$), 138.1, 136.8,

134.1, 130.3, 130.1(d, J = 8.0 Hz, $^3J_{CF}$), 129.6, 129.2(d, J = 8.0 Hz, $^3J_{CF}$), 128.2, 126.3, 126.0, 125.4, 124.8(d, J = 3.0 Hz, $^4J_{CF}$), 122.5(d, J = 2.0 Hz, $^4J_{CF}$), 120.8, 119.0, 117.2(d, J = 22.0 Hz, $^2J_{CF}$), 115.9(d, J = 23.0 Hz, $^2J_{CF}$), 114.0(d, J = 22.0 Hz, $^2J_{CF}$), 113.1(d, J = 21.0 Hz, $^2J_{CF}$), 111.8, 44.8, 21.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.20, -113.59.

HRMS (ESI) m/z calcd for $C_{29}H_{21}F_2N_2^+$ $(M+H)^+$ 435.1667, found 435.1668.



6,12-bis(4-fluorophenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4n)

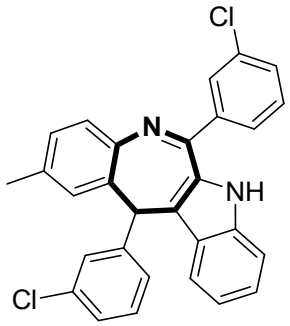
Yield 80%; 173.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 228-230 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.72 (dd, J = 8.8, 5.6 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.37–7.32 (m, 2H), 7.27 (dd, J = 10.4, 4.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 8.8 Hz, 2H), 6.87 (dd, J = 8.0, 5.6 Hz, 2H), 6.71 (t, J = 8.8 Hz, 2H), 5.66 (s, 1H), 2.42 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2(d, J = 249.0 Hz, $^1J_{CF}$), 161.2(d, J = 243.0 Hz, $^1J_{CF}$), 155.0, 143.2, 137.9, 137.4, 137.3, 136.9, 135.0, 134.6, 131.2(d, J = 9.0 Hz, $^3J_{CF}$), 130.2, 129.3, 128.4, 128.2(d, J = 8.0 Hz, $^3J_{CF}$), 126.9, 126.4, 126.1, 125.4, 120.8, 119.1, 115.7(d, J = 22.0 Hz, $^2J_{CF}$), 114.6(d, J = 22.0 Hz, $^2J_{CF}$), 111.8, 44.5, 21.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.07, -117.32.

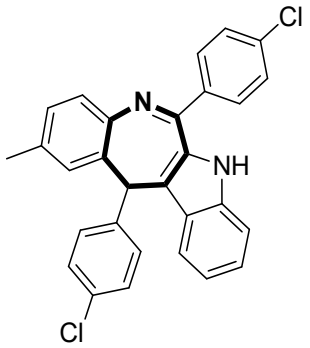
HRMS (ESI) m/z calcd for $C_{29}H_{21}F_2N_2^+$ $(M+H)^+$ 435.1667, found 435.1667.



6,12-bis(3-chlorophenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4o)

Yield 69%; 161.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 149-151℃;

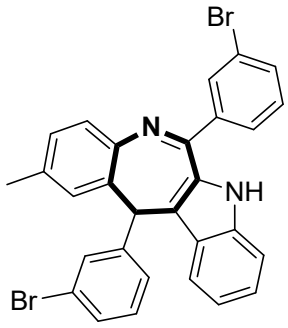
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.41 (dd, *J* = 22.4, 9.6 Hz, 4H), 7.29 (d, *J* = 11.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 4.8 Hz, 2H), 6.85 (d, *J* = 42.4 Hz, 2H), 5.67 (s, 1H), 2.44 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.8, 143.2, 140.8, 138.1, 136.9, 134.8, 134.2, 133.8, 130.4, 130.2, 129.8, 129.6, 129.1, 129.0, 128.2, 127.3, 127.1, 126.43, 126.36, 126.0, 125.9, 125.4, 125.2, 120.8, 119.1, 111.8, 44.8, 21.0;
HRMS (ESI) m/z calcd for $C_{29}H_{21}Cl_2N_2^+$ $(M+H)^+$ 467.1076, found 467.1080.



6,12-bis(4-chlorophenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4p)

Yield 62%; 144.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 296-298℃;

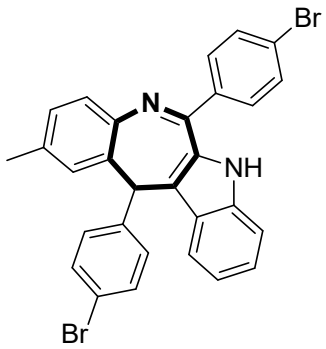
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 10.0 Hz, 2H), 7.37–7.28 (m, 2H), 7.21–7.10 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.89 (s, 1H), 2.38 (s, 3H);
^{13}C NMR (100 MHz, DMSO-d_6) δ 154.9, 143.1, 141.3, 137.9, 137.4, 136.9, 135.2, 135.1, 130.8, 130.5, 130.2, 128.7, 128.6, 128.5, 127.8, 127.7, 126.3, 125.5, 124.8, 124.6, 119.9, 119.2, 112.5, 43.2, 20.6;
HRMS (ESI) m/z calcd for $C_{29}H_{21}Cl_2N_2^+$ $(M+H)^+$ 467.1076, found 467.1078.



6,12-bis(3-bromophenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4q)

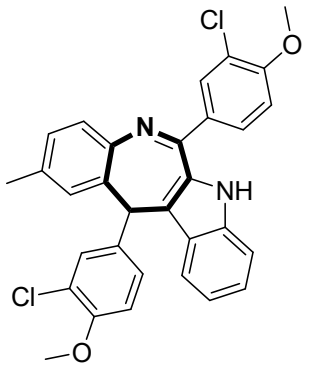
Yield 57%; 158.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 137-139 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.96 (t, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.65–7.57 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 2H), 7.30–7.25 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.67 (s, 1H), 2.43 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 144.0, 143.1, 141.0, 138.1, 136.9, 134.3, 133.3, 131.9, 130.2, 130.1, 129.9, 129.5, 129.39, 129.36, 128.2, 127.7, 126.3, 125.9, 125.8, 125.7, 125.4, 123.0, 122.2, 120.8, 119.1, 111.8, 44.7, 21.0;
HRMS (ESI) m/z calcd for $C_{29}H_{21}Br_2N_2^+$ $(M+H)^+$ 557.0045, found 557.0048.



6,12-bis(4-bromophenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4r)
Yield 51%; 141.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 320-322 ℃;

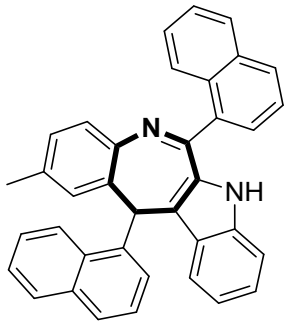
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 4H), 7.47–7.43 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.20 (dd, *J* = 7.6, 4.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.89 (s, 1H), 2.38 (s, 3H);
^{13}C NMR (100 MHz, DMSO-d_6) δ 155.3, 142.8, 141.7, 138.0, 137.6, 137.1, 135.3, 131.6, 131.2, 130.7, 130.2, 129.0, 128.6, 127.9, 126.2, 125.5, 125.1, 124.8, 124.2, 120.0, 119.3, 119.1, 112.6, 43.2, 20.7;
HRMS (ESI) m/z calcd for $C_{29}H_{21}Br_2N_2^+$ $(M+H)^+$ 557.0045, found 557.0048.



6,12-bis(3-chloro-4-methoxyphenyl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4s)

Yield 70%; 184.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 173-175 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.94–7.85 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31 (s, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.92 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 5.60 (s, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 2.41 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 154.3, 153.0, 143.1, 137.5, 136.8, 134.80, 134.76, 132.3, 130.6, 130.0, 129.1, 128.8, 128.6, 128.0, 126.2, 126.1, 125.9, 125.1, 122.7, 121.6, 120.6, 118.9, 111.8, 111.5, 111.2, 56.1, 55.9, 44.0, 20.9;
HRMS (ESI) m/z calcd for $C_{31}H_{25}Cl_2N_2O_2^+$ $(M+H)^+$ 527.1287, found 527.1289.

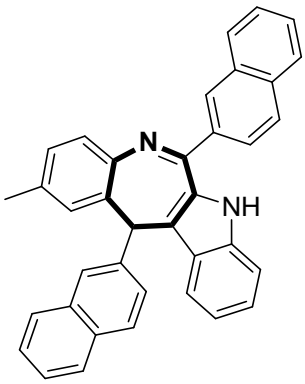


10-methyl-6,12-di(naphthalen-1-yl)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4t)

Yield 62%; 154.4 mg; yellow solid; column chromatography; silica gel (PE/EA, 12:1); mp 287-289 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.89–7.81 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.67–7.59 (m, 2H), 7.53 (s, 1H), 7.50–7.46 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.36–7.31 (m, 2H), 7.27–7.18 (m, 3H), 7.13 (d, *J* = 6.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.48 (s, 3H), 2.44 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 144.6, 138.6, 136.8, 136.3, 134.6, 134.2, 134.1, 133.5, 131.3, 131.0, 130.1, 129.9, 129.7, 129.0, 128.8, 127.94, 127.89, 127.4, 127.3, 126.2, 125.89, 125.86, 125.7, 125.5, 125.22, 125.16, 125.1, 124.8, 124.7, 124.3, 120.6, 119.4, 111.9, 43.7, 21.1;

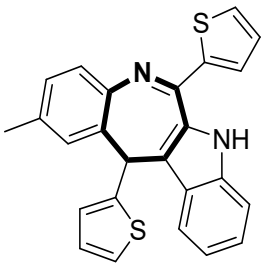
HRMS (ESI) m/z calcd for $C_{37}H_{27}N_2^+$ $(M+H)^+$ 499.2168, found 499.2170.



10-methyl-6,12-di(naphthalen-2-yl)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4u)

Yield 68%; 169.3 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 181-183 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 11.2 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 3H), 7.60–7.45 (m, 6H), 7.34 (d, *J* = 2.4 Hz, 2H), 7.29–7.18 (m, 7H), 5.88 (s, 1H), 2.44 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.6, 138.8, 137.7, 136.8, 136.3, 134.7, 134.2, 132.9, 132.8, 132.0, 130.4, 129.6, 129.4, 128.7, 128.3, 128.0, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 126.4, 126.2, 126.0, 125.8, 125.6, 125.2, 125.0, 120.6, 119.2, 111.7, 45.5, 21.0;
HRMS (ESI) m/z calcd for $C_{37}H_{27}N_2^+$ $(M+H)^+$ 499.2168, found 499.2166.

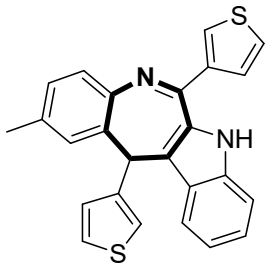


10-methyl-6,12-di(thiophen-2-yl)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4v)

Yield 72%; 147.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 10:1); mp 168-170 ℃;

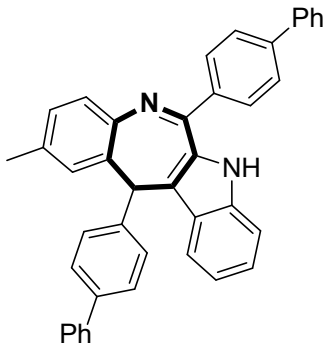
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 16.0, 4.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 5.6 Hz, 2H), 7.24 (d, *J* = 11.2 Hz, 2H), 7.16–7.08 (m, 2H), 6.89 (d, *J* = 4.8 Hz, 1H), 6.68–6.62 (m, 1H), 6.48 (s, 1H), 5.81 (s, 1H), 2.39 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 146.2, 145.2, 142.9, 137.6, 136.5, 134.8, 129.7, 129.40, 129.36, 128.2, 127.8, 126.4, 126.2, 125.3, 125.1, 124.8, 124.3, 123.7, 120.6, 119.0, 111.7, 41.7, 21.0;
HRMS (ESI) m/z calcd for $C_{25}H_{19}N_2S_2^+$ $(M+H)^+$ 411.0984, found 411.0986.



10-methyl-6,12-di(thiophen-3-yl)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4w)
Yield 73%; 149.7 mg; yellow solid; column chromatography, silica gel (PE/EA, 10:1); mp 152-154 ℃;

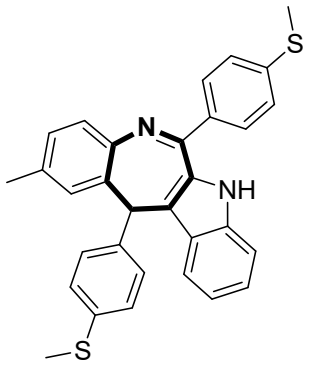
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.59 (d, *J* = 4.8 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34–7.20 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.01–6.96 (m, 1H), 6.66 (d, *J* = 4.8 Hz, 1H), 6.54 (s, 1H), 5.61 (s, 1H), 2.39 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 143.3, 142.3, 142.2, 137.5, 136.5, 134.8, 129.63, 129.57, 128.1, 127.9, 127.6, 127.2, 126.9, 126.1, 125.5, 125.4, 125.1, 124.9, 120.5, 119.0, 111.6, 42.0, 21.0;
HRMS (ESI) m/z calcd for $C_{25}H_{19}N_2S_2^+$ $(M+H)^+$ 411.0984, found 411.0990.



6,12-di([1,1'-biphenyl]-4-yl)-10-methyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4x)
Yield 63%; 173.3 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 208-210 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45–7.33 (m, 5H), 7.33–7.14 (m, 10H), 7.03 (d, *J* = 6.8 Hz, 2H), 5.74 (s, 1H);

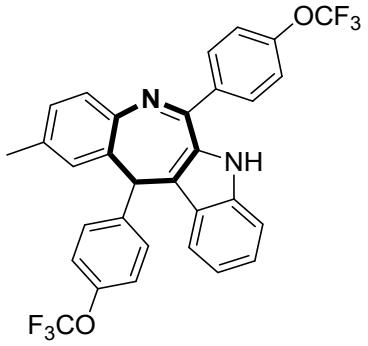
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 143.6, 143.0, 140.9, 140.3, 138.9, 137.9, 137.6, 136.8, 134.8, 130.3, 129.6, 129.5, 128.8, 128.5, 128.0, 127.7, 127.3, 127.2, 127.1, 126.9, 126.8, 126.6, 126.2, 125.0, 120.5, 119.1, 111.7, 44.9, 21.0;
HRMS (ESI) m/z calcd for $C_{41}H_{31}N_2^+$ $(M+H)^+$ 551.2481, found 551.2484.



10-methyl-6,12-bis(4-(methylthio)phenyl)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4y)

Yield 69%; 169.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 10:1); mp 142-144 ℃;

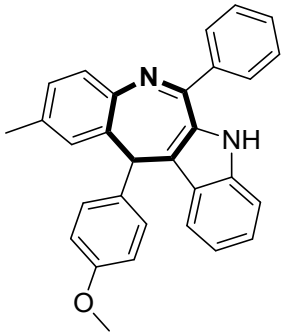
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33–7.28 (m, 2H), 7.27–7.23 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, *J* = 30.8, 8.4 Hz, 4H), 5.65 (s, 1H), 2.49 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 143.5, 141.8, 138.9, 137.5, 136.7, 135.6, 135.5, 134.7, 130.3, 129.5, 129.4, 128.0, 127.4, 126.6, 126.5, 126.2, 126.1, 125.8, 125.0, 120.5, 119.1, 111.7, 44.7, 21.0, 16.0, 15.3;
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2S_2^+$ $(M+H)^+$ 491.1610, found 491.1610.



10-methyl-6,12-bis(4-(trifluoromethoxy)phenyl)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4z)

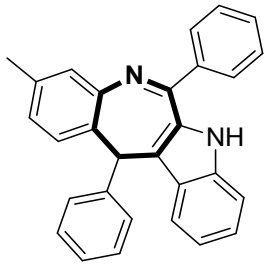
Yield 61%; 172.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 119-120 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.35 (s, 2H), 7.24 (dd, *J* = 18.4, 8.8 Hz, 5H), 6.91 (dd, *J* = 21.6, 8.8 Hz, 4H), 5.69 (s, 1H), 2.43 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 150.7, 147.5, 143.3, 140.4, 138.2, 137.5, 136.9, 134.1, 130.6, 130.3, 129.6, 128.3, 128.1, 126.5, 126.3, 126.0, 125.5, 120.93, 120.89, 120.4(q, *J* = 256.0 Hz, $^1J_{CF}$), 120.34, 120.32(q, *J* = 255.0 Hz, $^1J_{CF}$), 111.8, 44.6, 21.0;
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.64, -57.97.
HRMS (ESI) m/z calcd for $C_{31}H_{21}F_6N_2O_2^+$ $(M+H)^+$ 567.1501, found 567.1508.



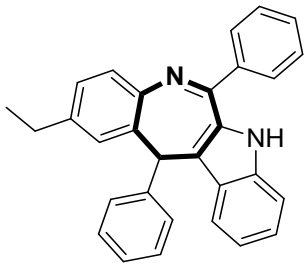
12-(4-methoxyphenyl)-10-methyl-6-phenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (4ah)
Yield 29%; 62.2 mg; yellow solid; column chromatography, silica gel (PE/EA, 10:1); mp 203-205 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.75–7.69 (m, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 6.4 Hz, 3H), 7.31 (s, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.8 Hz, 2H), 5.67 (s, 1H), 3.60 (s, 3H), 2.41 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.1, 143.4, 139.1, 137.6, 136.8, 135.1, 133.9, 130.2, 129.5, 129.2, 128.6, 127.9, 127.8, 126.8, 126.7, 126.2, 125.0, 120.5, 119.1, 113.2, 111.7, 55.1, 44.5, 21.0.
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1963.



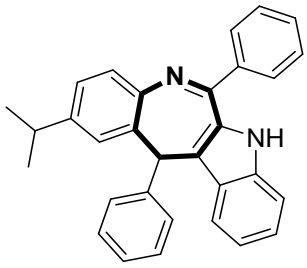
9-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5a)
Yield 61%; 121.4 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 146-148 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 6.0 Hz, 4H), 7.37–7.28 (m, 3H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06–6.92 (m, 5H), 5.74 (s, 1H), 2.40 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 145.7, 141.8, 139.2, 136.8, 132.4, 130.3, 129.8, 129.7, 129.2, 128.5, 128.3, 127.8, 126.9, 126.7, 126.2, 126.0, 125.0, 120.5, 119.2, 111.6, 44.8, 20.9.
HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2^+$ $(M+H)^+$ 399.1855, found 399.1858.



10-ethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5b)
Yield 75%; 154.5 mg; white solid; column chromatography, silica gel (PE/EA, 12:1); mp 131-133 ℃;

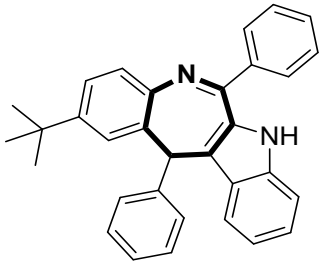
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 6.0 Hz, 2H), 7.56 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 3H), 7.35–7.22 (m, 4H), 7.10–6.94 (m, 4H), 5.75 (s, 1H), 2.73 (d, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 143.9, 143.6, 141.8, 139.1, 136.8, 134.7, 130.2, 129.5, 129.2, 128.5, 127.8, 126.84, 126.78, 126.6, 126.2, 126.0, 125.0, 120.5, 119.2, 111.7, 45.3, 28.4, 15.6.
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2014.



10-isopropyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5c)
Yield 72%; 153.4 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 105-107 ℃;

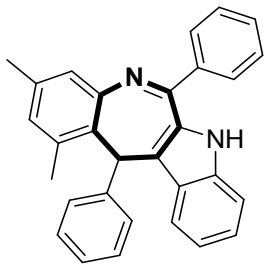
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.30 (m, *J* = 33.0, 14.4, 7.8 Hz, 4H), 7.00 (m, *J* = 37.8, 22.8, 7.2 Hz, 4H), 5.75 (s, 1H), 1.42–1.25 (m, 6H), 1.20 (d, *J* = 7.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.0, 148.5, 143.7, 141.8, 139.2, 136.8, 134.6, 130.2, 129.6, 129.2, 128.5, 127.8, 127.1, 126.8, 126.5, 126.3, 126.0, 125.1, 125.0, 120.4, 119.2, 115.2, 111.7, 45.4, 33.7, 24.1.
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2^+$ $(M+H)^+$ 427.2168, found 427.2170.



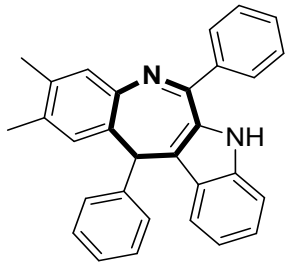
10-(tert-butyl)-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5d)
Yield 62%; 136.4 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 125-127 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 6.6 Hz, 2H), 7.59 (s, 1H), 7.52–7.24 (m, 9H), 7.07–6.91 (m, 4H), 5.77 (s, 1H), 1.38 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.2, 151.0, 143.6, 143.2, 141.8, 139.0, 136.9, 134.2, 130.9, 130.3, 129.2, 128.5, 127.8, 126.8, 126.6, 126.3, 126.0, 125.1, 124.3, 120.5, 119.3, 114.9, 111.7, 45.6, 34.6, 31.4.
HRMS (ESI) m/z calcd for $C_{32}H_{29}N_2^+$ $(M+H)^+$ 441.2325, found 441.2328.



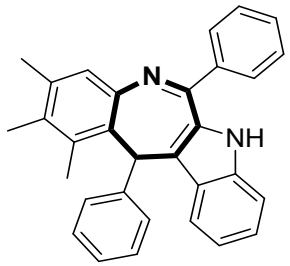
9,11-dimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5e)
Yield 58 %; 119.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 119-121 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 6.6 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 3H), 7.36–7.18 (m, 4H), 6.98 (m, *J* = 48.6, 36.6, 16.2 Hz, 6H), 6.18 (s, 1H), 2.64 (s, 3H), 2.35 (s, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.0, 146.2, 141.4, 138.9, 136.7, 135.8, 135.0, 132.1, 130.2, 130.1, 129.1, 128.5, 127.7, 127.5, 127.1, 126.7, 126.4, 125.9, 124.9, 120.5, 119.1, 111.7, 38.0, 20.8, 20.6;
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2013.



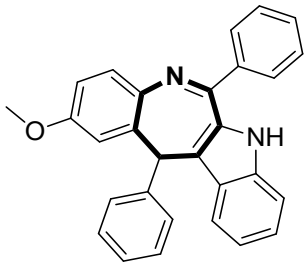
9,10-dimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5f)
Yield 67%; 138.0 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 282-284 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.74–7.69 (m, 2H), 7.40 (d, *J* = 4.8 Hz, 4H), 7.31–7.21 (m, 4H), 7.04–6.94 (m, 5H), 5.70 (s, 1H), 2.31 (d, *J* = 7.2 Hz, 6H).
^{13}C NMR 100 MHz, $CDCl_3$) δ 156.0, 143.7, 142.0, 139.3, 136.7, 136.3, 135.3, 132.4, 130.9, 130.5, 130.1, 129.1, 128.5, 127.8, 126.84, 126.75, 126.5, 126.2, 125.9, 124.9, 120.4, 119.1, 111.6, 44.7, 19.27, 19.25.
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2014.



9,10,11-trimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5g)
Yield 52%; 111.8 mg; white solid; column chromatography, silica gel (PE/EA, 12:1); mp 267-269 ℃;

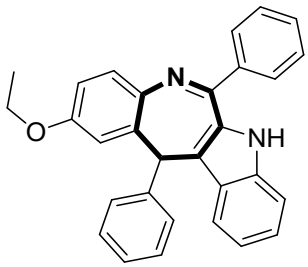
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 6.4 Hz, 3H), 7.33 (d, *J* = 4.8 Hz, 2H), 7.29 (s, 1H), 7.08–6.88 (m, 6H), 6.32 (s, 1H), 2.61 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.9, 141.7, 139.0, 136.7, 134.8, 134.5, 133.3, 132.7, 130.1, 129.1, 128.5, 127.9, 127.7, 127.3, 126.8, 126.6, 125.9, 124.8, 120.4, 119.1, 111.7, 38.7, 20.9, 16.7, 16.4.
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2^+$ $(M+H)^+$ 427.2168, found 427.2171.



10-methoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5h)
Yield 73%; 151.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 269-271 ℃;

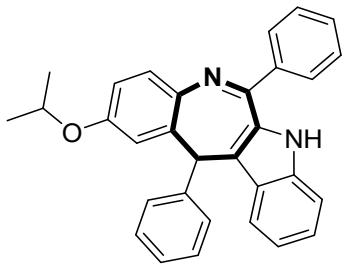
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 5.6 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 6.0 Hz, 3H), 7.27 (dd, *J* = 19.2, 9.2 Hz, 3H), 6.97 (m, *J* = 16.8, 12.8, 4.8 Hz, 7H), 5.70 (s, 1H), 3.86 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 154.9, 141.6, 139.7, 139.2, 136.7, 135.9, 131.3, 130.0, 129.0, 128.5, 127.8, 126.9, 126.8, 126.2, 126.1, 125.5, 124.9, 120.5, 119.0, 114.5, 112.7, 111.6, 55.5, 45.4.
HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2O^+$ $(M+H)^+$ 415.1804, found 415.1805.



10-ethoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5i)
Yield 71%; 151.9 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 207-209 ℃;

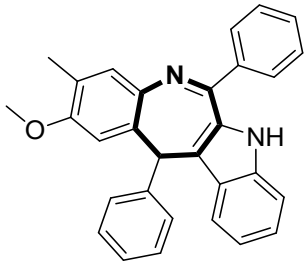
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.74–7.70 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 6.4 Hz, 3H), 7.32 (s, 2H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.05–6.92 (m, 7H), 5.70 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 154.8, 141.6, 139.3, 136.7, 135.9, 131.3, 130.1, 129.1, 128.5, 127.8, 126.9, 126.8, 126.3, 126.1, 125.0, 120.5, 119.0, 115.2, 113.1, 111.6, 63.7, 45.4, 14.9.
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1963.



10-isopropoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5j)
Yield 66%; 145.9 mg; yellow solid; column chromatography; silica gel (PE/EA, 8:1);

mp 132-134 ℃;

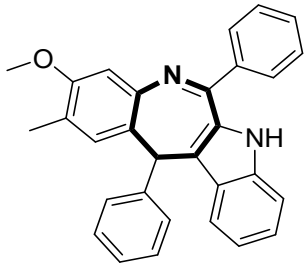
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 5.2 Hz, 2H), 7.59 (s, 1H), 7.41 (d, *J* = 5.6 Hz, 3H), 7.34 (d, *J* = 3.6 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.07–6.91 (m, 7H), 5.69 (s, 1H), 4.63 (m, *J* = 12.0, 6.0 Hz, 1H), 1.37 (dd, *J* = 8.4, 6.4 Hz, 6H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.7, 136.1, 131.2, 130.1, 129.35, 129.29, 129.1, 128.7, 128.5, 128.2, 127.8, 127.0, 126.8, 126.3, 126.1, 125.0, 120.5, 119.1, 116.7, 114.0, 111.6, 70.1, 45.4, 22.2, 22.1.
HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2O^+$ $(M+H)^+$ 443.2117, found 443.2121.



10-methoxy-9-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5k)
Yield 75%; 160.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 285-287 ℃;

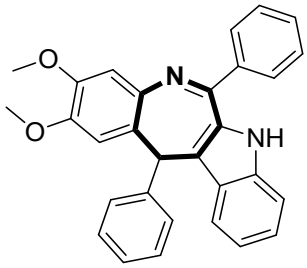
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.43 (dd, *J* = 9.6, 6.4 Hz, 4H), 7.32 (s, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.05–7.00 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 4H), 5.70 (s, 1H), 3.92 (s, 3H), 2.24 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.0, 141.2, 138.7, 137.7, 136.4, 132.4, 130.4, 128.6, 128.1, 127.1, 126.5, 125.8, 125.7, 124.73, 124.65, 123.6, 123.3, 123.0, 118.6, 117.4, 111.4, 109.5, 54.5, 43.8, 14.7;
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1964.



9-methoxy-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5l)
Yield 76%; 162.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 300-302 ℃;

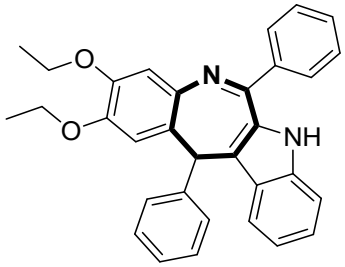
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.73–7.69 (m, 2H), 7.42–7.37 (m, 3H), 7.29–7.20 (m, 4H), 7.09 (s, 1H), 7.04–6.99 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 3H), 5.68 (s, 1H), 3.87 (s, 3H), 2.28 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 156.2, 144.7, 142.2, 139.3, 136.7, 131.7, 130.1, 129.1, 128.5, 127.7, 127.0, 126.9, 126.8, 126.7, 126.3, 126.1, 125.9, 125.0, 120.4, 119.2, 111.6, 110.8, 55.5, 44.3, 15.9;
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1963.



9,10-dimethoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5m)
Yield 73%; 162.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1);

mp 280-282 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 4.4 Hz, 2H), 7.41 (d, *J* = 4.8 Hz, 3H), 7.35 (d, *J* = 3.6 Hz, 2H), 7.27 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.19 (s, 1H), 7.06–6.94 (m, 6H), 5.70 (s, 1H), 3.96 (d, *J* = 6.0 Hz, 6H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 148.8, 147.6, 142.0, 139.6, 139.3, 136.8, 130.1, 129.0, 128.6, 127.9, 126.9, 126.83, 126.78, 126.2, 126.1, 125.1, 120.5, 119.1, 112.8, 112.1, 111.7, 56.1, 56.0, 44.9;
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O_2^+$ $(M+H)^+$ 445.1910, found 445.1910.

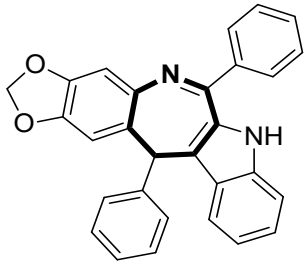


9,10-diethoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5n)
Yield 73%; 172.3 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1);

mp 263-265 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 3.6 Hz, 2H), 7.33 (d, *J* = 4.4 Hz, 3H), 7.27–7.16 (m, 4H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.97–6.91 (m, 4H), 5.65 (s, 1H), 4.12 (dd, *J* = 9.6, 4.8 Hz, 4H), 1.45–1.40 (m, 6H);

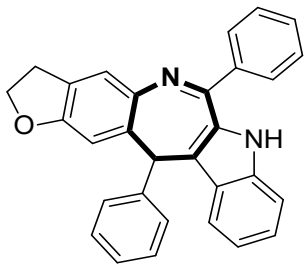
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 148.3, 147.2, 142.1, 139.4, 139.2, 136.7, 129.9, 128.9, 128.4, 127.7, 127.0, 126.8, 126.7, 126.0, 125.9, 124.8, 120.3, 118.9, 114.5, 114.0, 111.7, 64.6, 64.4, 44.7, 14.8, 14.7;
HRMS (ESI) m/z calcd for $C_{32}H_{29}N_2O_2^+$ $(M+H)^+$ 473.2223, found 473.2222.



6,12-diphenyl-7,12-dihydro-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':6,7]azepino[3,4-b]indole (5o)
Yield 72%; 154.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1);

mp 191-193 ℃;

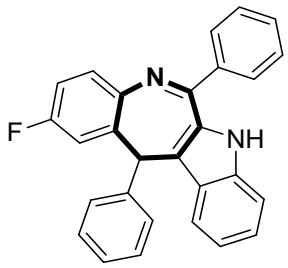
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 6.4 Hz, 2H), 7.40 (d, *J* = 6.4 Hz, 3H), 7.35–7.29 (m, 2H), 7.24 (d, *J* = 4.4 Hz, 1H), 7.01 (ddd, *J* = 24.4, 18.4, 10.8 Hz, 7H), 6.04 (s, 1H), 5.95 (s, 1H), 5.64 (s, 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 147.6, 146.7, 141.6, 140.7, 139.1, 136.8, 130.2, 129.1, 128.5, 128.4, 127.8, 126.84, 126.75, 126.09, 126.06, 125.1, 120.5, 119.1, 111.7, 109.5, 109.0, 101.6, 44.9;
HRMS (ESI) m/z calcd for $C_{29}H_{21}N_2O_2^+$ $(M+H)^+$ 429.1597, found 429.1599.



6,12-diphenyl-2,3,7,12-tetrahydrobenzofuro[6',5':6,7]azepino[3,4-b]indole (5p)
Yield 73%; 155.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 184-186 ℃;

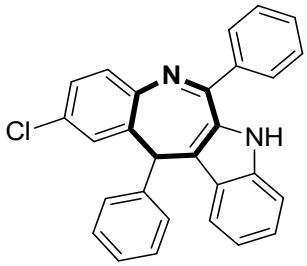
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.80 (dd, *J* = 64.4, 25.2 Hz, 3H), 7.54–7.11 (m, 7H), 7.07–6.79 (m, 6H), 5.68 (s, 1H), 4.71–4.48 (m, 2H), 3.26 (dd, *J* = 37.6, 7.6 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 154.1, 140.8, 137.6, 137.3, 136.9, 134.4, 129.0, 128.2, 127.2, 126.5, 125.6, 125.5, 125.1, 124.8, 124.5, 124.3, 123.9, 123.5, 118.8, 117.5, 111.5, 108.3, 70.8, 28.0;
HRMS (ESI) m/z calcd for $C_{30}H_{23}N_2O^+$ $(M+H)^+$ 427.1804, found 427.1806.



10-fluoro-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5q)
Yield 66%; 132.7 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 291-293 ℃;

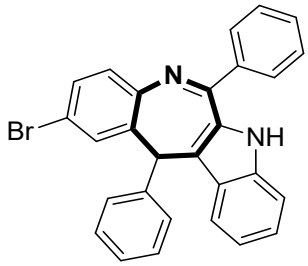
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 6.4 Hz, 2H), 7.58 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.49–7.41 (m, 3H), 7.36 (d, *J* = 3.6 Hz, 2H), 7.28 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.06 (m, *J* = 21.6, 11.2, 4.8 Hz, 4H), 6.94 (d, *J* = 7.6 Hz, 2H), 5.71 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2(d, *J* = 246.0 Hz, $^1J_{CF}$), 156.3, 142.3, 140.9, 138.9, 136.8, 136.5(d, *J* = 7.0 Hz, $^3J_{CF}$), 131.2(d, *J* = 9.0 Hz, $^3J_{CF}$), 130.4, 129.1, 128.6, 127.9, 126.8, 126.6, 126.3, 126.1, 125.7, 125.3, 120.7, 119.1, 116.0(d, *J* = 22.0 Hz, $^2J_{CF}$), 114.0(d, *J* = 22.0 Hz, $^2J_{CF}$), 111.7, 45.0;
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.29.
HRMS (ESI) m/z calcd for $C_{28}H_{20}FN_2^+$ $(M+H)^+$ 403.1605, found 403.1604.



10-chloro-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5r)
Yield 59%; 123.6 mg; white solid; column chromatography, silica gel (PE/EA, 12:1);

mp 166-168 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.94 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 5.4 Hz, 2H), 7.49 (dd, *J* = 46.2, 19.2 Hz, 6H), 7.35 (s, 3H), 7.05 (t, *J* = 20.4 Hz, 3H), 6.94 (s, 2H), 5.71 (s, 1H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.0, 144.5, 140.8, 138.8, 136.8, 136.3, 132.8, 130.7, 130.5, 129.7, 129.3, 129.2, 128.6, 127.9, 127.1, 126.8, 126.3, 126.1, 125.8, 125.3, 120.8, 119.1, 111.8, 44.9;
HRMS (ESI) m/z calcd for $C_{28}H_{20}ClN_2^+$ $(M+H)^+$ 419.1309, found 419.1312.



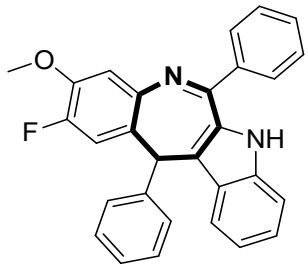
10-bromo-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5s)

Yield 49%; 113.4 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1); mp 124-126 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 6.6 Hz, 2H), 7.63 (s, 1H), 7.45 (dd, *J* = 19.8, 9.6 Hz, 5H), 7.37 (s, 2H), 7.28 (s, 1H), 7.03 (dd, *J* = 22.2, 6.6 Hz, 3H), 6.94 (d, *J* = 6.6 Hz, 2H), 5.72 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 144.9, 140.8, 138.8, 136.8, 136.7, 132.2, 130.9, 130.6, 130.1, 129.2, 128.6, 127.9, 126.8, 126.6, 126.3, 126.2, 126.0, 125.4, 120.9, 120.8, 119.2, 111.8, 44.8.

HRMS (ESI) m/z calcd for $C_{28}H_{20}BrN_2^+$ $(M+H)^+$ 463.0804, found 463.0807.



10-fluoro-9-methoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5t)

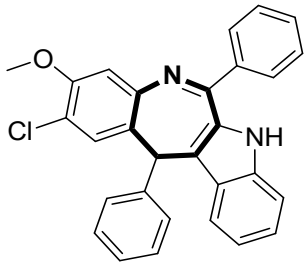
Yield 72%; 155.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 259-261 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.70–7.65 (m, 2H), 7.37 (d, *J* = 6.4 Hz, 3H), 7.21 (m, *J* = 29.6, 16.8, 10.4 Hz, 5H), 7.03–6.91 (m, 5H), 5.61 (s, 1H), 3.88 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 151.5(d, *J* = 246.0 Hz, $^1J_{CF}$), 146.0(d, *J* = 21.0 Hz, $^2J_{CF}$), 142.4, 141.4, 138.9, 136.7, 130.3, 129.0, 128.5, 127.8, 127.6(d, *J* = 5.0 Hz, $^3J_{CF}$), 126.7, 126.5, 126.2, 126.1, 125.9, 125.2, 120.6, 119.1, 116.7(d, *J* = 20.0 Hz, $^2J_{CF}$), 114.2, 111.7, 56.2, 44.1;

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.28.

HRMS (ESI) m/z calcd for $C_{29}H_{22}FN_2O^+$ $(M+H)^+$ 433.1710, found 433.1713.



10-chloro-9-methoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5u)

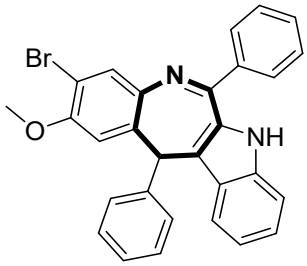
Yield 62 %; 139.2 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 248-250 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.43 (dd, *J* = 15.6, 8.8 Hz, 4H), 7.34 (d, *J* = 5.2 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.18 (s, 1H), 7.08–6.97 (m, 3H), 6.94 (d, *J* = 7.6 Hz, 2H), 5.67 (s, 1H), 3.94 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.6, 145.5, 141.3, 138.8, 136.8, 130.7, 130.5, 129.1, 128.6, 128.3, 127.9, 126.8, 126.6, 126.2, 126.0, 125.4, 121.1, 120.8, 119.2, 112.6, 111.7, 56.3, 44.0;

HRMS (ESI) m/z calcd for $C_{29}H_{22}ClN_2O^+$ $(M+H)^+$ 449.1415, found 449.1418.



9-bromo-10-methoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5v)

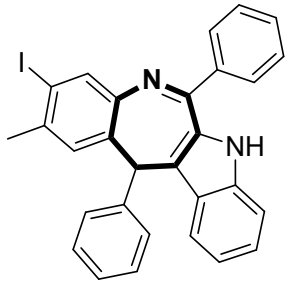
Yield 57%; 140.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 291-293 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 2.4 Hz, 4H), 7.43 (dd, *J* = 17.6, 10.0 Hz, 5H), 7.09–6.92 (m, 6H), 5.74 (s, 1H), 3.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.9, 140.4, 138.9, 138.0, 136.9, 134.8, 132.3, 129.3, 129.1, 128.4, 127.4, 126.8, 125.8, 125.2, 124.7, 123.7, 119.1, 117.7, 111.7, 111.5, 108.0, 55.6, 43.9.

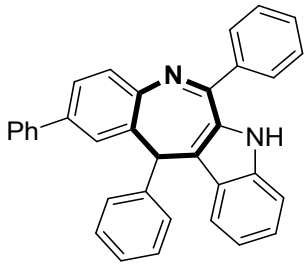
HRMS (ESI) m/z calcd for $C_{29}H_{22}BrN_2O^+$ $(M+H)^+$ 493.0910, found 493.0911.



9-iodo-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5w)
Yield 33%; 86.5 mg; white solid; column chromatography, silica gel (PE/EA, 12:1);

mp 318-320 ℃;

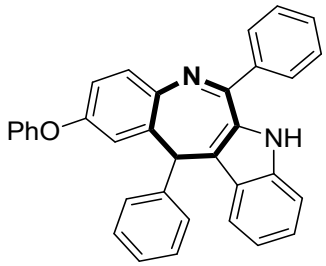
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 11.2 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 6.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 3H), 7.39–7.33 (m, 3H), 7.29 (d, *J* = 3.2 Hz, 1H), 7.04 (m, *J* = 14.0, 6.8 Hz, 3H), 6.94 (d, *J* = 7.2 Hz, 2H), 5.70 (s, 1H), 2.49 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 145.0, 141.1, 140.4, 139.5, 139.2, 138.9, 136.8, 135.0, 130.5, 130.4, 129.2, 128.6, 127.9, 126.8, 126.7, 126.2, 126.1, 125.3, 120.7, 119.2, 111.7, 98.2, 44.8, 27.3.
HRMS (ESI) m/z calcd for $C_{29}H_{22}IN_2^+$ $(M+H)^+$ 525.0822, found 525.0824.



6,10,12-triphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5x)
Yield 65%; 149.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 274-276 ℃;

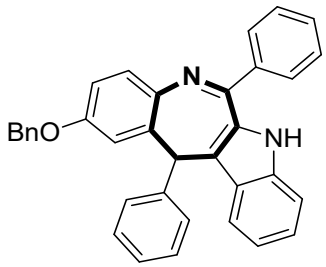
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.70 (s, 1H), 7.69–7.65 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.46–7.39 (m, 5H), 7.35–7.21 (m, 5H), 7.05–7.02 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 5.84 (s, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 145.1, 141.5, 140.3, 140.2, 139.0, 136.8, 135.4, 130.3, 130.0, 129.2, 128.8, 128.5, 128.3, 127.8, 127.3, 127.0, 126.9, 126.8, 126.4, 126.13, 126.11, 125.7, 125.1, 120.5, 119.2, 111.7, 45.4.
HRMS (ESI) m/z calcd for $C_{34}H_{25}N_2^+$ $(M+H)^+$ 461.2012, found 461.2010.



10-phenoxy-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5y)
Yield 60%; 142.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 10:1);

mp 150-152 ℃;

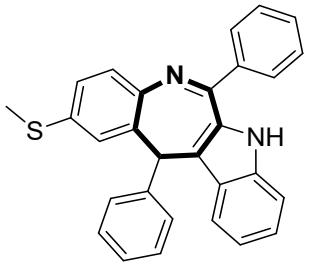
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76–7.72 (m, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 6.0 Hz, 3H), 7.36 (t, *J* = 8.0 Hz, 4H), 7.29–7.26 (m, 1H), 7.13 (s, 2H), 7.09–7.00 (m, 6H), 6.95 (d, *J* = 7.6 Hz, 2H), 5.68 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.9, 155.8, 141.3, 136.8, 136.3, 131.2, 130.3, 129.8, 129.2, 128.6, 127.9, 126.8, 126.2, 125.2, 123.5, 120.6, 119.24, 119.22, 119.17, 117.2, 111.7, 45.2.
HRMS (ESI) m/z calcd for $C_{34}H_{25}N_2O^+$ $(M+H)^+$ 477.1961, found 477.1962.



10-(benzyloxy)-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5z)
Yield 61%; 149.5 mg; yellow solid; column chromatography; silica gel (PE/EA, 10:1);

mp 149-151 ℃;

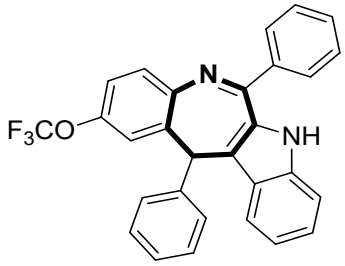
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.74–7.70 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.42 (m, *J* = 12.0, 7.6 Hz, 9H), 7.34 (d, *J* = 4.0 Hz, 3H), 7.29–7.25 (m, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.02 (m, *J* = 6.0, 5.2 Hz, 4H), 6.95 (d, *J* = 7.6 Hz, 2H), 5.71 (s, 1H), 5.12 (s, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 155.0, 141.5, 136.7, 136.0, 131.2, 130.1, 129.1, 128.6, 128.5, 128.0, 127.9, 127.6, 126.9, 126.8, 126.2, 126.1, 125.0, 120.5, 119.1, 115.6, 113.4, 111.7, 70.3, 45.4;
HRMS (ESI) m/z calcd for $C_{35}H_{27}N_2O^+$ $(M+H)^+$ 491.2117, found 491.2118.



10-(methylthio)-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5aa)
Yield 68%; 146.2 mg; yellow solid; column chromatography, silica gel (PE/EA, 10:1);

mp 190-192 ℃;

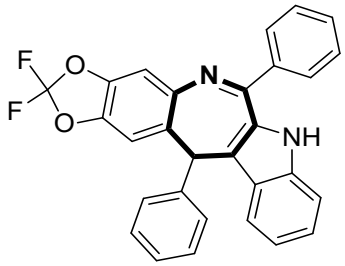
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.8, 4.8 Hz, 3H), 7.33 (dd, *J* = 8.4, 4.4 Hz, 3H), 7.27–7.23 (m, 2H), 7.06–6.93 (m, 5H), 5.72 (s, 1H), 2.53 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 143.3, 141.3, 139.0, 137.8, 136.8, 135.3, 130.3, 130.1, 129.1, 128.5, 127.8, 127.3, 126.8, 126.2, 126.1, 125.1, 125.0, 120.6, 119.1, 111.7, 45.2, 15.9;
HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2S^+$ $(M+H)^+$ 431.1576, found 431.1579.



6,12-diphenyl-10-(trifluoromethoxy)-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (5ab)
Yield 59%; 138.1 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1);

mp 153-155 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 6.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.48–7.41 (m, 3H), 7.38 (d, *J* = 3.6 Hz, 2H), 7.34 (s, 1H), 7.30 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.23 (s, 1H), 7.09–6.99 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 2H), 5.74 (s, 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 148.3, 144.5, 140.7, 138.8, 136.8, 136.3, 130.8, 130.6, 129.2, 128.6, 128.0, 126.8, 126.6, 126.4, 126.1, 125.4, 120.8, 120.5(q, *J* = 239.0 Hz, $^1J_{CF}$), 119.2, 111.8, 45.0;
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.65.
HRMS (ESI) m/z calcd for $C_{29}H_{20}F_3N_2O^+$ $(M+H)^+$ 469.1522, found 469.1523.



2,2-difluoro-6,12-diphenyl-7,12-dihydro-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':6,7]azepino[3,4-b]indole (5ac)

Yield 52%; 120.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1);

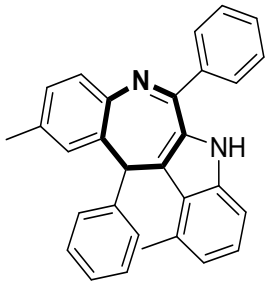
mp 319-321 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.45–7.37 (m, 3H), 7.35–7.30 (m, 1H), 7.25 (t, *J* = 6.8 Hz, 3H), 7.14 (s, 1H), 7.01 (dq, *J* = 13.6, 6.8 Hz, 3H), 6.89 (d, *J* = 7.6 Hz, 2H), 5.68 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 143.1, 142.7, 142.3, 140.7, 138.5, 136.9, 130.6, 130.5, 129.2, 128.6, 128.1(dd, *J* = 252.0 Hz, $^1J_{CF}$), 127.9, 126.7, 126.4, 126.2, 125.8, 125.4, 120.8, 119.0, 111.8, 110.0, 109.7, 44.9;

^{19}F NMR (376 MHz, $CDCl_3$) δ -49.43, -49.69, -49.97, -50.22.

HRMS (ESI) m/z calcd for $C_{29}H_{19}F_2N_2O_2^+$ $(M+H)^+$ 465.1409, found 465.1412.



1,10-dimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6a)

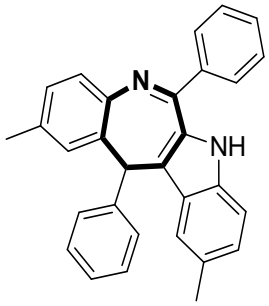
Yield 41%; 76.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 185-187 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.65 (d, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 6.8 Hz, 3H), 7.25 (s, 1H), 7.17 (dd, *J* = 14.4, 6.8 Hz, 3H), 7.06–6.92 (m, 6H), 6.13 (s, 1H), 2.93 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 143.6, 142.2, 139.3, 137.2, 136.9, 135.5, 131.8, 130.3, 130.1, 129.1, 129.0, 128.4, 127.9, 127.64, 127.56, 126.9, 126.8, 125.9, 124.7, 122.3, 109.7, 46.5, 21.0.

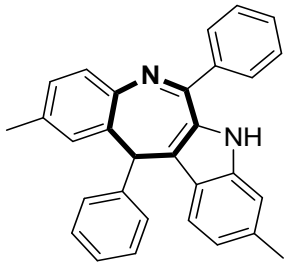
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2013.



2,10-dimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6b)
Yield 75%; 88.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 211-213 ℃;

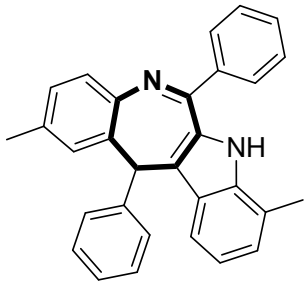
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.69 (s, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 6.4 Hz, 3H), 7.22–7.05 (m, 4H), 7.03–6.92 (m, 5H), 5.67 (s, 1H), 2.49 (s, 3H), 2.40 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 143.6, 141.8, 139.3, 137.4, 135.1, 134.8, 130.3, 130.1, 129.8, 129.4, 129.1, 128.4, 127.8, 126.9, 126.83, 126.77, 126.4, 125.9, 118.4, 111.3, 45.1, 21.6, 21.0.
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2017.



3,10-dimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6c)
Yield 73%; 91.2 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 170-172 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 6.8 Hz, 3H), 7.26 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 6.4 Hz, 2H), 7.03–6.92 (m, 5H), 5.68 (s, 1H), 2.46 (s, 3H), 2.41 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 143.6, 141.8, 139.3, 137.4, 137.2, 135.3, 134.7, 130.3, 130.1, 129.4, 129.1, 128.5, 127.81, 127.76, 126.8, 126.5, 126.3, 126.0, 124.2, 122.5, 118.8, 111.4, 45.3, 22.0, 21.0.
HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2014.



4,10-dimethyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6d)

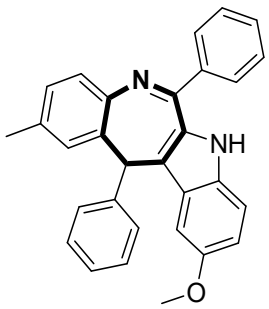
Yield 52%; 91.0 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 264-266 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.79 (dd, *J* = 30.6, 7.2 Hz, 3H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 3H), 7.27 (s, 1H), 7.22–7.12 (m, 3H), 7.07–6.93 (m, 5H), 5.71 (s, 1H), 2.41 (d, *J* = 8.4 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 143.5, 141.7, 139.2, 137.5, 136.5, 134.8, 130.3, 130.2, 129.3, 129.2, 128.6, 127.8, 127.2, 126.8, 126.5, 126.0, 125.8, 125.4, 120.9, 120.8, 116.8, 115.3, 45.3, 21.0, 16.6.

HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2^+$ $(M+H)^+$ 413.2012, found 413.2019.



2-methoxy-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6e)

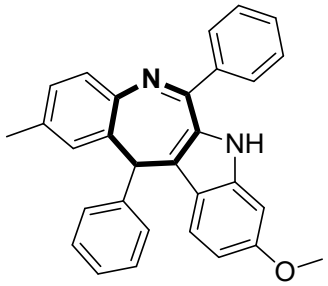
Yield 76%; 70.5 mg; white solid; column chromatography, silica gel (PE/EA, 8:1);

mp 291-293 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.72 (s, 2H), 7.51 (s, 1H), 7.42 (s, 3H), 7.31 (s, 2H), 7.25–7.18 (m, 2H), 7.09–6.94 (m, 6H), 5.66 (s, 1H), 3.93 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.0, 154.7, 143.6, 141.8, 139.3, 137.4, 134.8, 132.1, 130.3, 130.1, 129.5, 129.1, 128.5, 127.9, 127.8, 127.6, 126.8, 126.5, 126.0, 125.9, 116.1, 112.6, 99.6, 55.8, 45.3, 21.0.

HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1965.



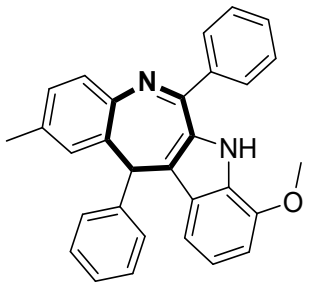
3-methoxy-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6f)

Yield 75%; 83.9 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 136-138 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.73 (s, 2H), 7.46 (t, *J* = 19.6 Hz, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.09–6.90 (m, 7H), 6.81 (s, 1H), 5.68 (s, 1H), 3.86 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 155.8, 143.8, 141.8, 139.4, 137.8, 137.4, 134.6, 130.4, 130.1, 129.6, 129.2, 128.5, 127.9, 127.8, 126.8, 126.7, 126.02, 126.00, 120.8, 120.1, 111.4, 94.0, 55.6, 45.4, 21.0.

HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1963.



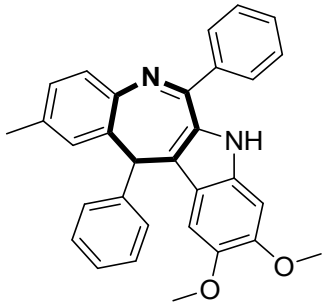
4-methoxy-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6g)

Yield 34%; 82.6 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 234-236 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.73 (d, *J* = 6.4 Hz, 2H), 7.53 (t, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 6.4 Hz, 3H), 7.27 (s, 1H), 7.17 (dd, *J* = 14.8, 7.2 Hz, 2H), 7.05–7.01 (m, 2H), 6.96 (t, *J* = 9.2 Hz, 3H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.69 (s, 1H), 3.89 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 146.4, 143.6, 141.8, 139.2, 137.4, 134.7, 130.4, 130.1, 129.4, 129.1, 128.5, 127.84, 127.77, 127.4, 126.9, 126.7, 126.5, 126.0, 120.9, 111.6, 104.2, 55.3, 45.5, 21.0.

HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O^+$ $(M+H)^+$ 429.1961, found 429.1966.



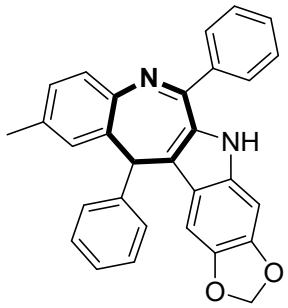
2,3-dimethoxy-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6h)

Yield 41%; 91.3 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1); mp 126-128 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 3H), 7.29 (d, *J* = 6.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.07–6.99 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.82 (s, 1H), 5.64 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 149.8, 146.1, 141.9, 139.6, 137.3, 134.6, 131.9, 130.4, 130.1, 129.6, 129.3, 128.6, 128.5, 128.1, 127.9, 126.8, 126.0, 119.2, 99.7, 94.0, 56.4, 56.1, 45.5, 29.7, 21.0.

HRMS (ESI) m/z calcd for $C_{31}H_{27}N_2O_2^+$ $(M+H)^+$ 459.2067, found 459.2067.



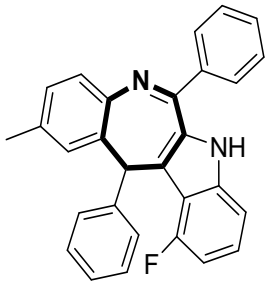
10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b][1,3]dioxolo[4,5-f]indole (6i)

Yield 39%; 86.9 mg; yellow solid; column chromatography, silica gel (PE/EA, 5:1); mp 157-159 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.71 (d, *J* = 5.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 3H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 6.8 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.76 (s, 1H), 6.00 (d, *J* = 8.4 Hz, 2H), 5.56 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 147.6, 143.9, 143.8, 141.8, 139.5, 137.3, 134.5, 132.6, 130.4, 130.1, 129.6, 129.2, 128.5, 127.8, 126.8, 126.6, 126.3, 126.0, 120.4, 101.1, 97.1, 92.0, 45.6, 21.0.

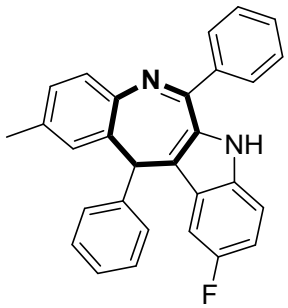
HRMS (ESI) m/z calcd for $C_{30}H_{23}N_2O_2^+$ $(M+H)^+$ 443.1754, found 443.1756.



1-fluoro-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6j)
Yield 43%; 72.2 mg; white solid; column chromatography, silica gel (PE/EA, 12:1);

mp 135-137 ℃;

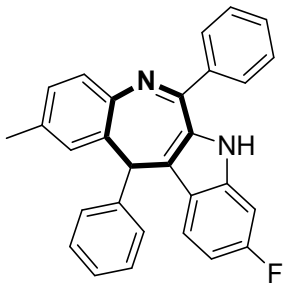
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.42 (q, *J* = 6.0 Hz, 3H), 7.31 (s, 1H), 7.20 (d, *J* = 6.4 Hz, 2H), 7.08–7.03 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 3H), 6.87 (dd, *J* = 11.2, 8.0 Hz, 1H), 6.04 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8(d, *J* = 247.0 Hz, $^{1}J_{CF}$), 155.5, 143.5, 141.9, 139.1, 138.8(d, *J* = 11.0 Hz, $^{2}J_{CF}$), 137.8, 135.0, 130.6, 130.3, 129.4, 129.0, 128.6, 128.0, 127.8, 127.0, 126.8, 126.0, 125.2(d, *J* = 8.0 Hz, $^{3}J_{CF}$), 124.4, 115.4(d, *J* = 19.0 Hz, $^{2}J_{CF}$), 107.7, 105.5(d, *J* = 19.0 Hz, $^{2}J_{CF}$), 46.3, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -122.37.
HRMS (ESI) m/z calcd for $C_{29}H_{22}FN_2^+$ $(M+H)^+$ 417.1761, found 417.1762.



2-fluoro-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6k)
Yield 68%; 77.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 147-149 ℃;

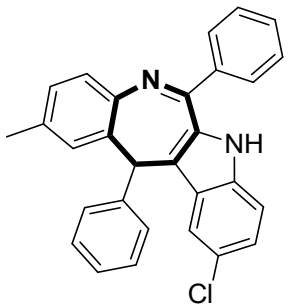
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.71 (d, *J* = 6.4 Hz, 2H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 (q, *J* = 6.0 Hz, 3H), 7.25–7.19 (m, 3H), 7.09–6.98 (m, 4H), 6.93 (d, *J* = 7.6 Hz, 2H), 5.60 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2(d, *J* = 236.0 Hz, $^{1}J_{CF}$), 155.8, 143.4, 141.5, 139.0, 137.8, 134.6, 133.2, 130.4, 130.3, 129.6, 129.1, 128.6, 128.4, 128.0, 127.9, 126.8, 126.5(d, *J* = 10.0 Hz, $^{3}J_{CF}$), 126.2, 113.8(d, *J* = 26.0 Hz, $^{2}J_{CF}$), 112.5 (d, *J* = 9.0 Hz, $^{3}J_{CF}$), 103.7(d, *J* = 23.0 Hz, $^{3}J_{CF}$), 45.3, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -122.68.
HRMS (ESI) m/z calcd for $C_{29}H_{22}FN_2^+$ $(M+H)^+$ 417.1761, found 417.1765.



3-fluoro-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6l)
Yield 63%; 72.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 252-254 ℃;

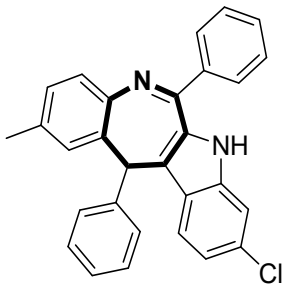
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.86 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.71 (d, *J* = 6.4 Hz, 2H), 7.46 (dd, *J* = 30.0, 7.2 Hz, 4H), 7.27 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.02 (m, *J* = 21.6, 7.6 Hz, 5H), 6.93 (d, *J* = 7.6 Hz, 2H), 5.66 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6(d, *J* = 240.0 Hz, $^{1}J_{CF}$), 155.6, 143.6, 141.5, 139.1, 137.7, 136.7(d, *J* = 13.0 Hz, $^{3}J_{CF}$), 134.5, 130.34, 130.26, 129.6, 129.1, 128.6, 128.0, 127.9, 127.3, 126.8, 126.3, 126.1, 123.0, 120.3(d, *J* = 10.0 Hz, $^{3}J_{CF}$), 109.8(d, *J* = 25.0 Hz, $^{2}J_{CF}$), 97.8(d, *J* = 26.0 Hz, $^{2}J_{CF}$), 45.2, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.00.
HRMS (ESI) m/z calcd for $C_{29}H_{22}FN_2^+$ $(M+H)^+$ 417.1761, found 417.1765.



2-chloro-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6m)
Yield 56%; 92.4 mg; yellow solid; column chromatography; silica gel (PE/EA, 12:1);

mp 152-154 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.91 (s, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.8 Hz, 3H), 7.29–7.25 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.07–6.98 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 2H), 5.63 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 143.4, 141.4, 139.0, 137.9, 134.9, 134.5, 130.4, 130.3, 129.6, 129.1, 128.6, 128.0, 127.9, 127.2, 126.8, 126.3, 126.2, 125.6, 125.3, 118.5, 112.8, 45.2, 21.0.
HRMS (ESI) m/z calcd for $C_{29}H_{22}ClN_2^+$ $(M+H)^+$ 433.1466, found 433.1467.



3-chloro-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6n)

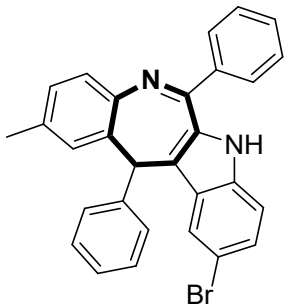
Yield 48%; 90.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 153-155 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 6.4 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 6.4 Hz, 3H), 7.30 (s, 1H), 7.23 (dd, *J* = 16.0, 2.8 Hz, 3H), 7.01 (dd, *J* = 14.4, 6.0 Hz, 3H), 6.90 (d, *J* = 7.2 Hz, 2H), 5.65 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 143.4, 141.4, 138.8, 137.8, 136.9, 134.5, 130.9, 130.4, 129.5, 129.1, 128.6, 128.1, 127.9, 127.3, 126.8, 126.3, 126.2, 124.8, 121.5, 120.1, 111.5, 45.1, 21.0.

HRMS (ESI) m/z calcd for $C_{29}H_{22}ClN_2^+$ $(M+H)^+$ 433.1466, found 433.1468.



2-bromo-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6o)

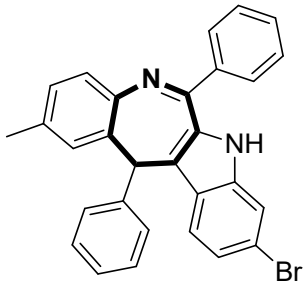
Yield 51%; 72.0 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 188-190 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.06 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.28 (s, 1H), 7.18 (t, *J* = 10.0 Hz, 2H), 7.07–6.99 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 2H), 5.62 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 143.4, 141.3, 138.9, 137.9, 135.1, 134.5, 130.4, 130.3, 129.6, 129.0, 128.6, 128.1, 127.89, 127.86, 127.8, 126.8, 126.2, 125.4, 121.7, 113.7, 113.2, 45.1, 21.0.

HRMS (ESI) m/z calcd for $C_{29}H_{22}BrN_2^+$ $(M+H)^+$ 477.0960, found 477.0968.



3-bromo-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6p)

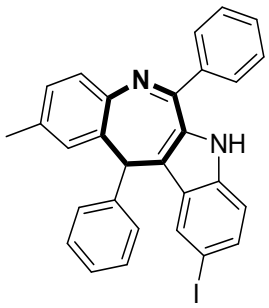
Yield 43%; 61.9 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 109-111 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 6.0 Hz, 2H), 7.44–7.42 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 10.2 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.05–7.02 (m, 2H), 6.99 (d, *J* = 6.0 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 2H), 5.66 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.6, 143.4, 141.4, 138.9, 137.8, 137.2, 134.5, 130.4, 129.7, 129.6, 129.1, 128.6, 128.1, 127.9, 127.2, 126.8, 126.2, 125.1, 124.0, 120.4, 118.5, 115.3, 114.6, 45.1, 21.0.

HRMS (ESI) m/z calcd for $C_{29}H_{22}BrN_2^+$ $(M+H)^+$ 477.0960, found 477.0965.



2-iodo-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6q)

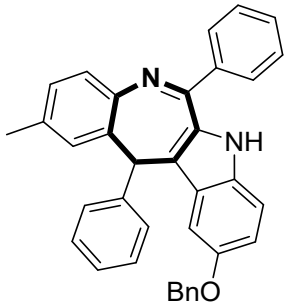
Yield 73%; 91.2 mg; yellow solid; column chromatography, silica gel (PE/EA, 12:1);

mp 255-257 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.12 (s, 1H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 3H), 7.29 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.07–6.98 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 2H), 5.62 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 143.4, 141.3, 139.0, 137.9, 135.6, 134.5, 133.2, 130.4, 130.3, 129.6, 129.1, 128.7, 128.6, 128.0, 127.9, 127.4, 126.8, 126.2, 125.1, 113.6, 83.7, 45.1, 21.0.

HRMS (ESI) m/z calcd for $C_{29}H_{22}IN_2^+$ $(M+H)^+$ 525.0822, found 525.0826.



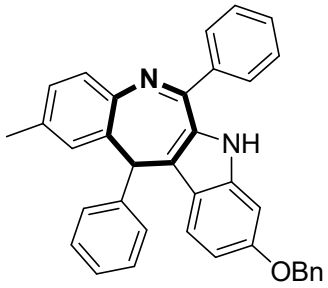
2-(benzyloxy)-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6r)

Yield 53%; 76.8 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 88-90 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.73–7.69 (m, 2H), 7.50 (d, *J* = 7.2 Hz, 3H), 7.44–7.32 (m, 7H), 7.20 (dd, *J* = 16.4, 8.0 Hz, 3H), 7.09–6.97 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 2H), 5.64 (s, 1H), 5.17 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.8, 143.6, 141.8, 139.2, 137.5, 137.2, 134.7, 132.3, 130.4, 130.2, 129.5, 129.2, 128.6, 128.5, 127.92, 127.88, 127.8, 127.7, 127.6, 126.8, 126.5, 126.0, 116.7, 112.6, 101.4, 70.8, 45.3, 21.0.

HRMS (ESI) m/z calcd for $C_{36}H_{29}N_2O^+$ $(M+H)^+$ 505.2274, found 505.2276.



3-(benzyloxy)-10-methyl-6,12-diphenyl-5,12-dihydrobenzo[6,7]azepino[3,4-b]indole (6s)

Yield 49%; 88.5 mg; yellow solid; column chromatography, silica gel (PE/EA, 8:1); mp 128-130 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.41 (m, *J* = 15.6, 7.6 Hz, 7H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.06–6.97 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.82 (s, 1H), 5.65 (s, 1H), 5.11 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.7, 143.8, 141.8, 139.4, 137.7, 137.4, 137.0, 134.5, 130.4, 130.1, 129.6, 129.2, 128.6, 128.5, 128.0, 127.9, 127.8, 127.4, 126.8, 126.6, 126.1, 126.0, 121.0, 120.1, 112.0, 95.5, 70.4, 45.4, 26.9, 21.0.

HRMS (ESI) m/z calcd for $C_{36}H_{29}N_2O^+$ $(M+H)^+$ 505.2274, found 505.2275.

6. Crystallographic data and molecular structure of 4b, 4r and 8d

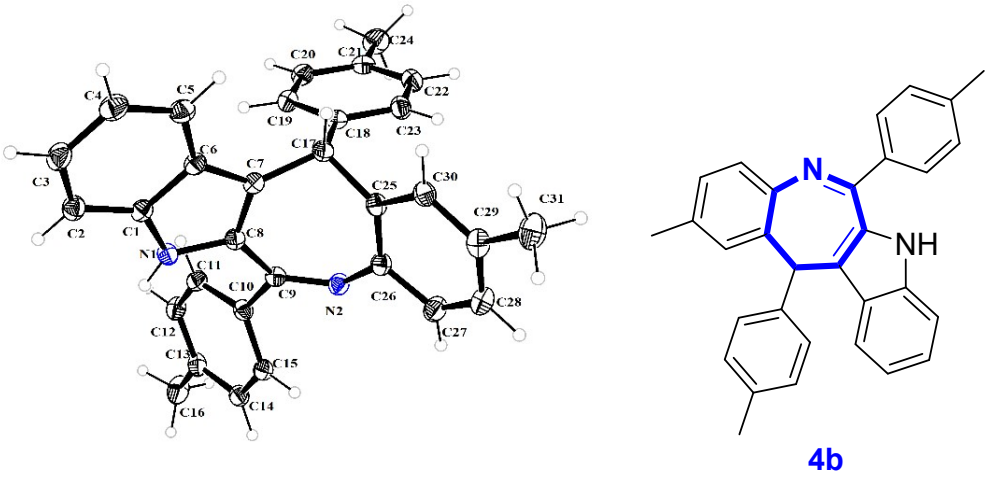


Figure S1. X-ray crystal structure of **4b**, thermal ellipsoids shown at 50% probability level. Sample preparation: 35 mg of **4b** was dissolved in 6 ml CH_2Cl_2 and 1 ml CH_3OH at room temperature for slow evaporation about a week. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. Crystal Data for Compound **4b**: CCDC 2131536 contains the supplementary crystallographic data for this paper. These data could be obtained free of charge from The Cambridge Crystallographic.

Bond precision: C-C = 0.0028 A Wavelength=1.34139

Cell: a=28.4438(13) b=28.4438(13) c=15.374(1)
alpha=90 beta=90 gamma=120
Temperature: 200 K

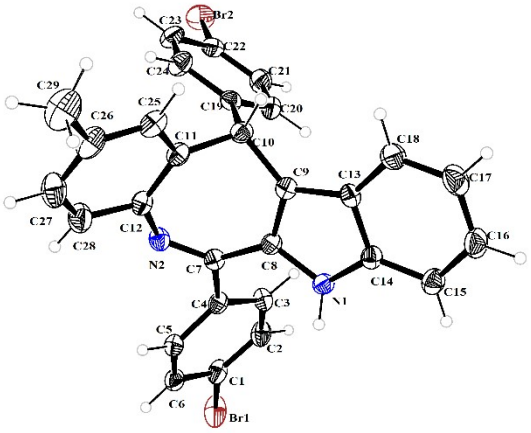
	Calculated	Reported
Volume	10771.9(12)	10771.9(12)
Space group	R -3	R -3
Hall group	-R 3	-R 3
Moiety formula	C31 H26 N2 [+ solvent]	C31 H26 N2
Sum formula	C31 H26 N2 [+ solvent]	C31 H26 N2
Mr	426.54	426.54
Dx,g cm-3	1.184	1.184
Z	18	18
Mu (mm-1)	0.335	0.335
F000	4068.0	4068.0
F000'	4075.85	
h,k,lmax	35,35,19	35,35,19
Nref	4932	4926
Tmin,Tmax	0.961,0.967	0.697,0.751
Tmin'	0.961	

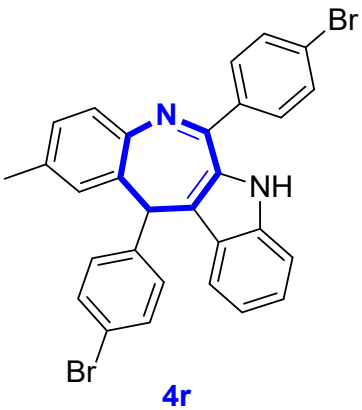
Correction method= # Reported T Limits: Tmin=0.697 Tmax=0.751
AbsCorr = NONE

Data completeness= 0.999 Theta(max)= 57.061

R(reflections)= 0.0551(4024) wR2(reflections)= 0.1712(4926)

S = 1.082 Npar= 301





4r

Figure S2. X-ray crystal structure of **4r**, thermal ellipsoids shown at 50% probability level. Sample preparation: 20 mg of **4r** was dissolved in 4 ml CH_2Cl_2 and 1 ml CH_3OH at room temperature for slow evaporation about a week. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. Crystal Data for Compound **4r**: CCDC 2143004 contains the

supplementary crystallographic data for this paper. These data could be obtained free of charge from The Cambridge Crystallographic.

Bond precision: C-C = 0.0058 A Wavelength=0.71073

Cell: a=28.250(5) b=28.250(5) c=15.849(3)
alpha=90 beta=90 gamma=120
Temperature: 296 K

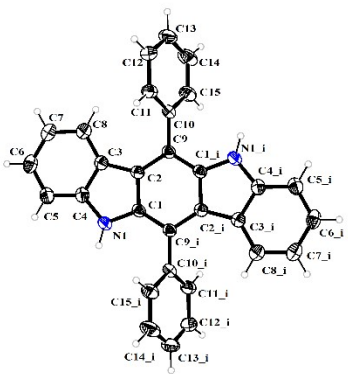
	Calculated	Reported
Volume	10954(4)	10953(5)
Space group	R -3	R -3
Hall group	-R 3	-R 3
Moiety formula	C29 H20 Br2 N2 [+ solvent]	C29 H20 Br2 N2
Sum formula	C29 H20 Br2 N2 [+ solvent]	C29 H20 Br2 N2
Mr	556.27	556.29
Dx,g cm-3	1.518	1.518
Z	18	18
Mu (mm-1)	3.350	3.350
F000	5004.0	5004.0
F000'	4995.43	
h,k,lmax	35,35,19	35,35,19
Nref	5026	5018
Tmin,Tmax	0.623,0.715	0.481,0.745
Tmin'	0.507	

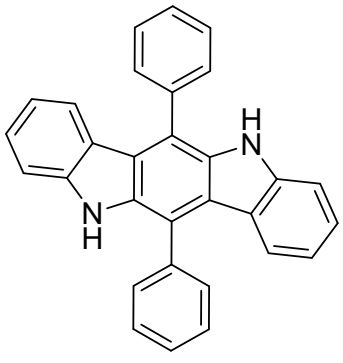
Correction method= # Reported T Limits: Tmin=0.481 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 26.434

R(reflections)= 0.0440(3046) wR2(reflections)= 0.1004(5018)

S = 1.011 Npar= 299





8d

Figure S2. X-ray crystal structure of **8d**, thermal ellipsoids shown at 30% probability level. Sample preparation: 20 mg of **8d** was dissolved in 4 ml CH_2Cl_2 and 1 ml CH3OH at room temperature for slow evaporation about a week. The crystals were

mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. Crystal Data for Compound **8d**: CCDC 2173150 contains the supplementary crystallographic data for this paper. These data could be obtained free of charge from The Cambridge Crystallographic.

```
Bond precision:  C-C = 0.0041 A          Wavelength=0.71073

Cell:          a=12.108(2)       b=12.563(2)      c=12.924(2)
               alpha=95.671(3)   beta=91.801(3)   gamma=90.084(3)
Temperature:   296 K

                Calculated                Reported
Volume          1955.3(5)                 1955.2(6)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C30 H20 N2 [+ solvent]    3(C15 H10 N)
Sum formula     C30 H20 N2 [+ solvent]    C45 H30 N3
Mr              408.48                    612.72
Dx,g cm-3       1.041                     1.041
Z               3                         2
Mu (mm-1)       0.061                     0.061
F000            642.0                     642.0
F000'           642.23
h,k,lmax        14,14,15                  14,14,15
Nref            6915                      6856
Tmin,Tmax       0.985,0.988               0.632,0.746
Tmin'           0.982

Correction method= # Reported T Limits: Tmin=0.632 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.991          Theta(max)= 25.025

R(reflections)= 0.0705( 4724)     wR2(reflections)= 0.2472( 6856)

S = 1.035                 Npar= 433
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Click on the hyperlinks for more details of the test.
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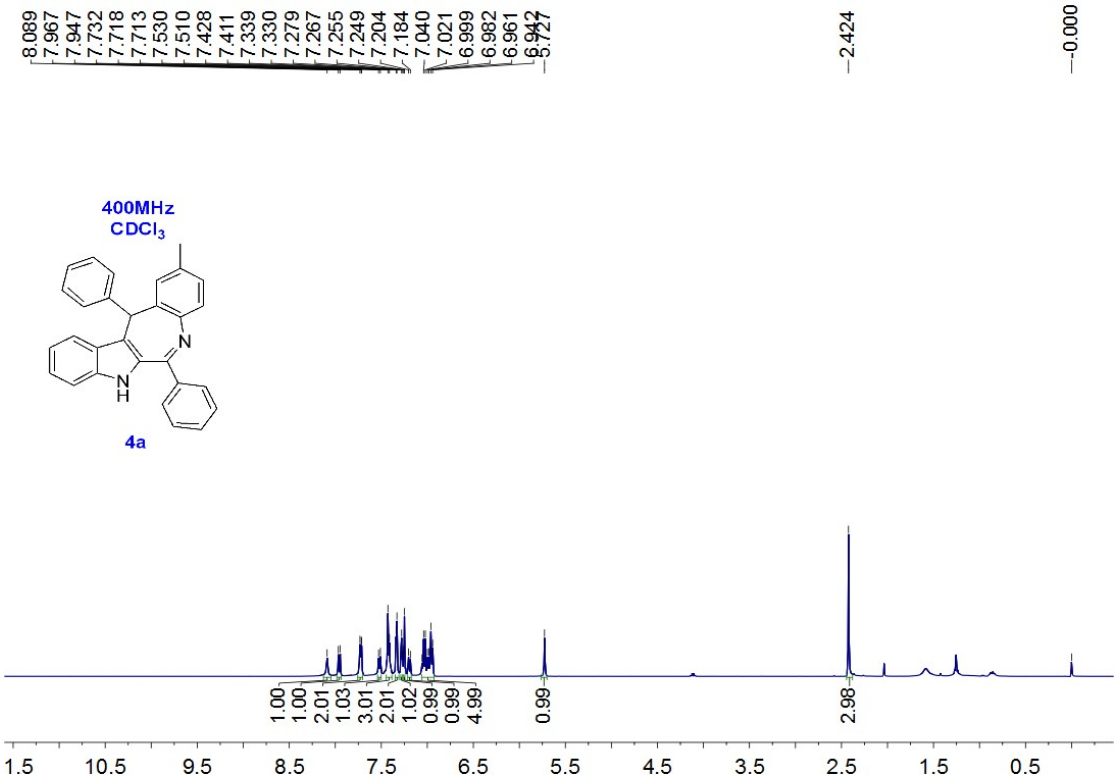
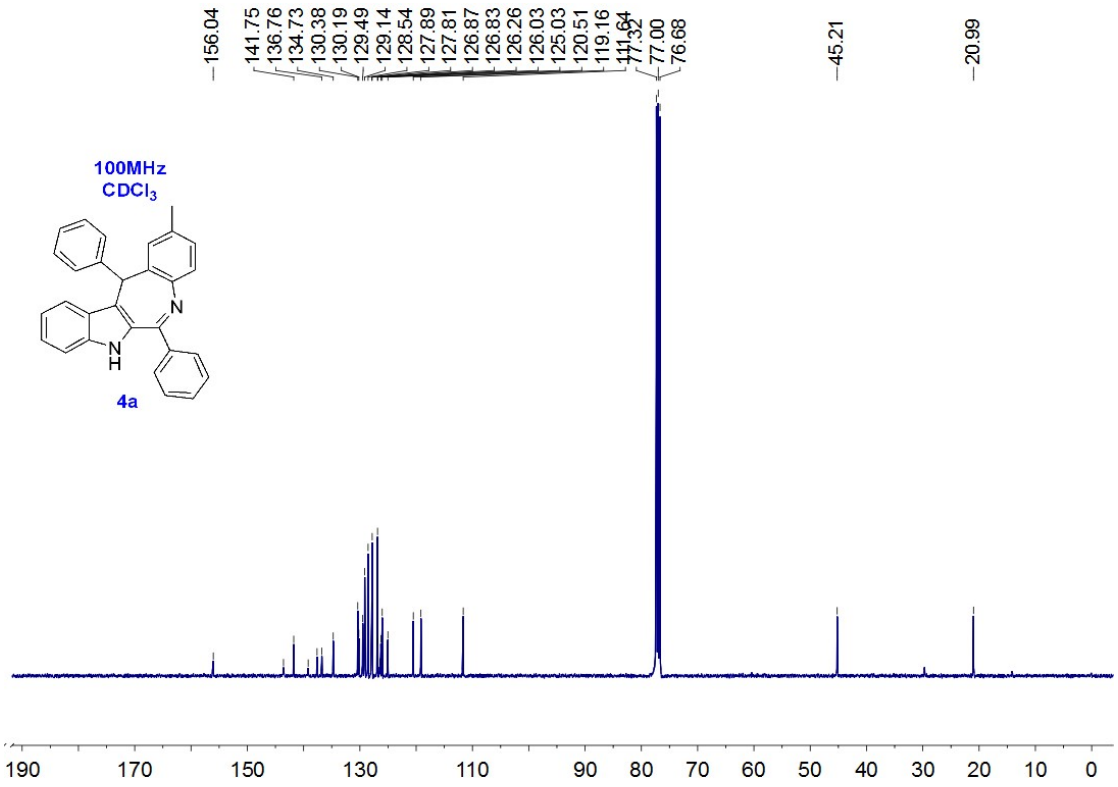
7. ^{1}H and ^{13}C NMR spectra of compounds 4, 5 and 6

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126.26
126.03
125.03
120.51
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111.64
77.32
77.00
76.68
45.21
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130
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30
20
10
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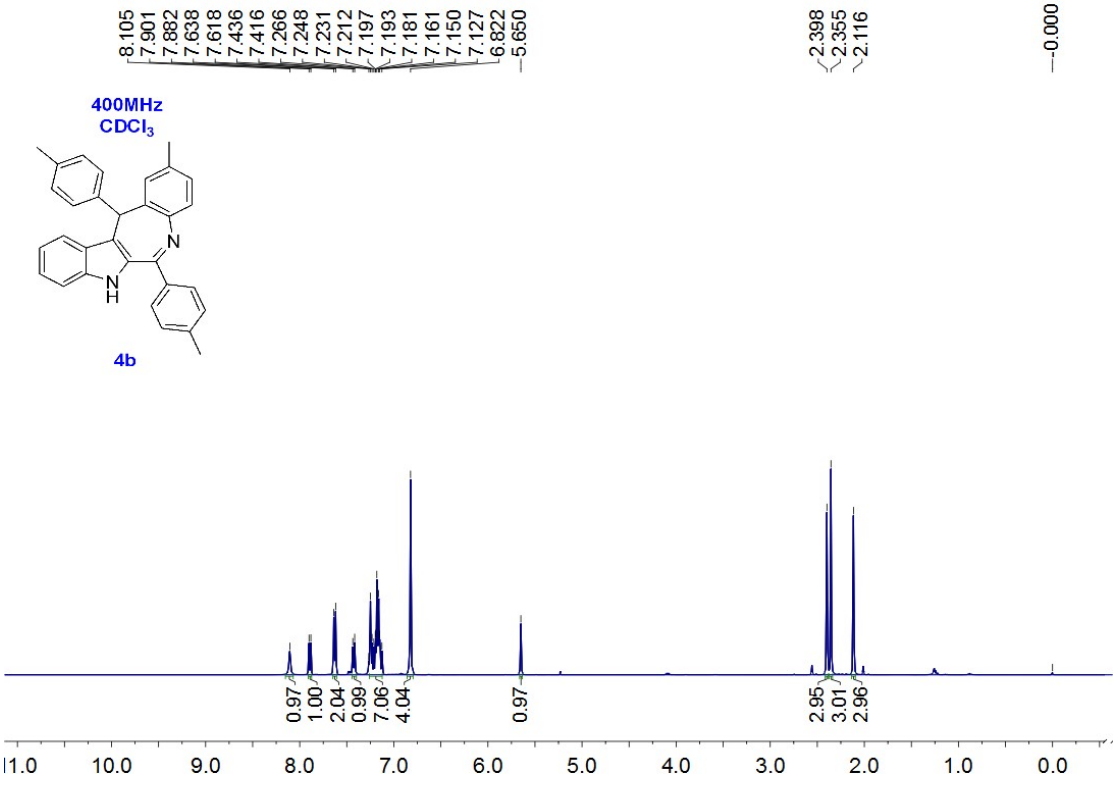
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7.161
7.150
7.127
6.822
5.650
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2.355
2.116
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4.04
0.97
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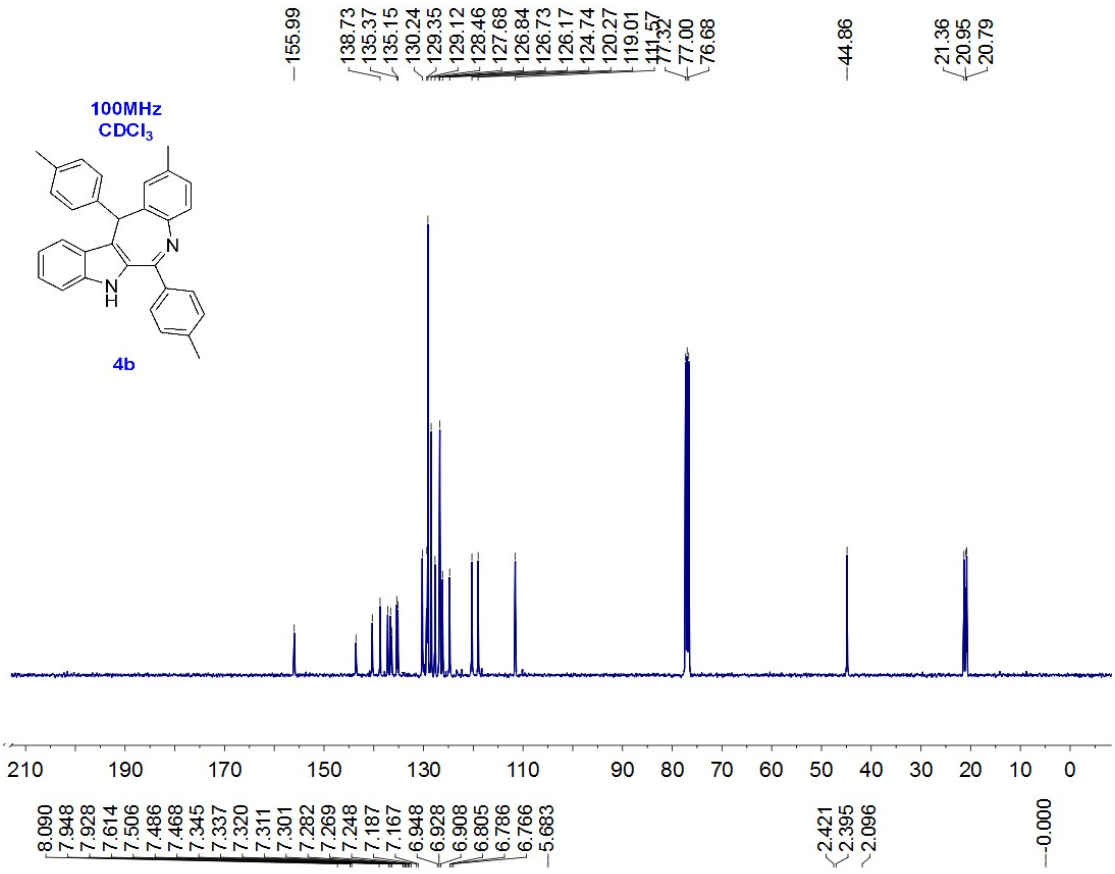
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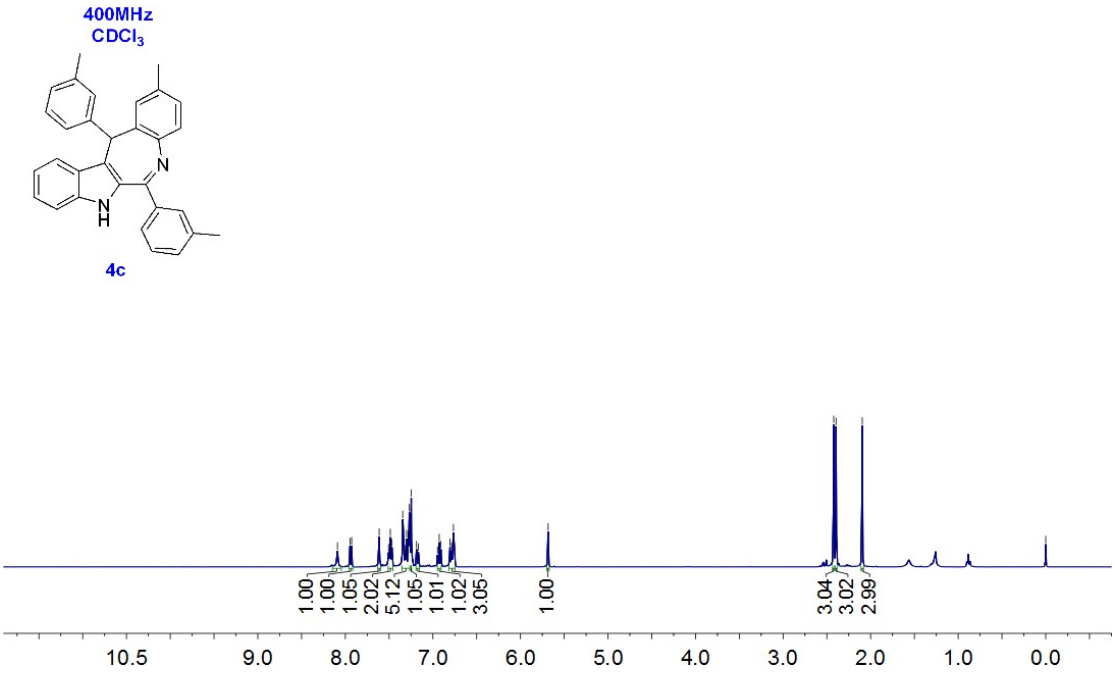
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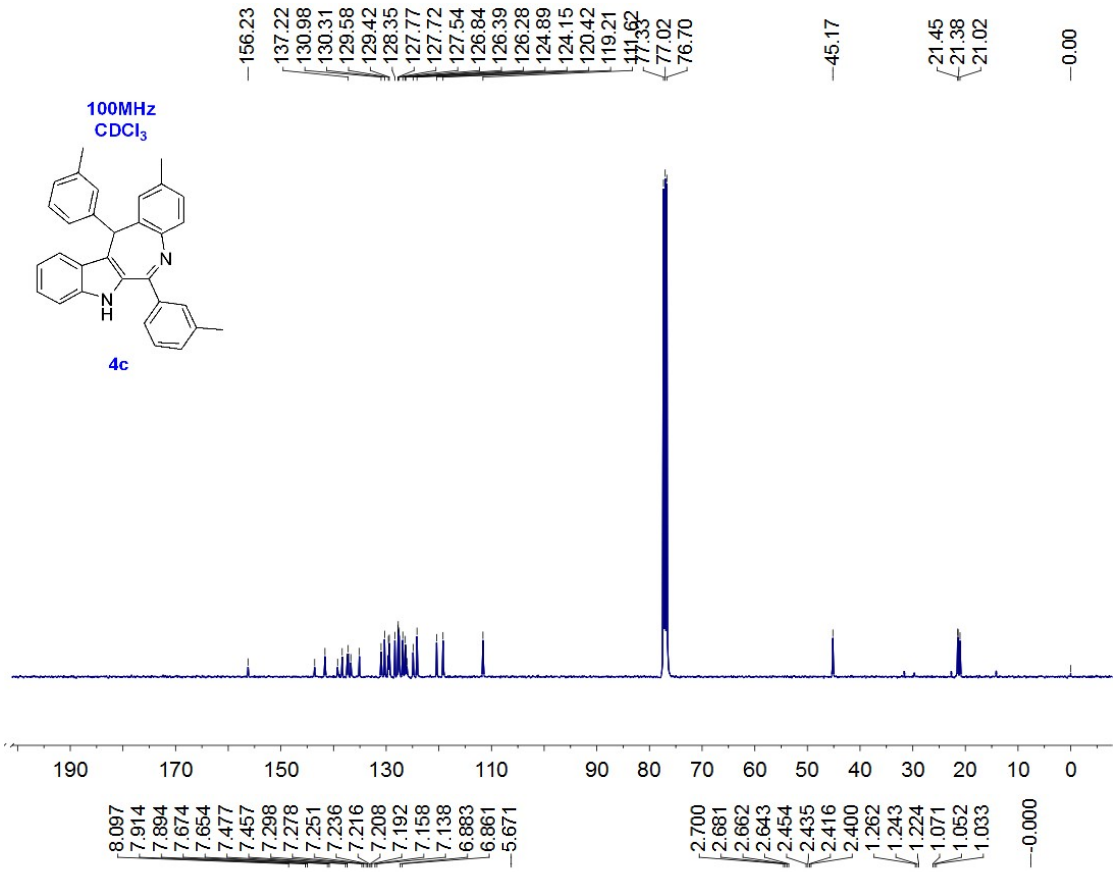
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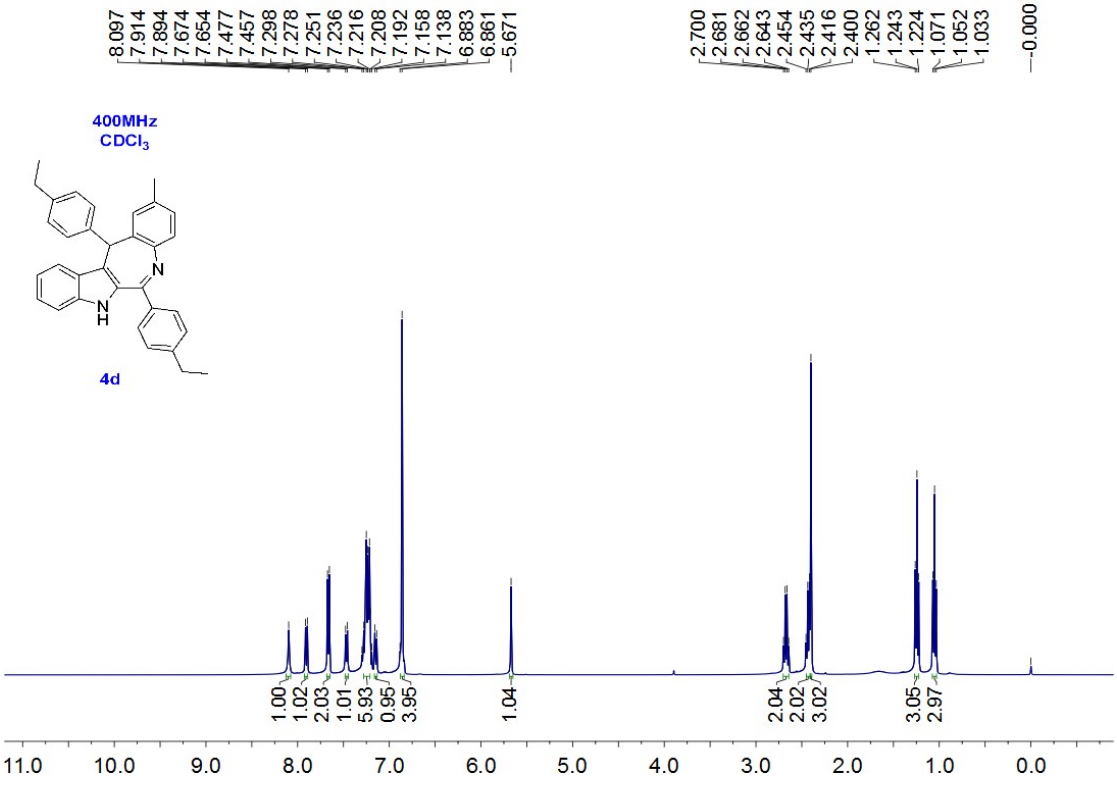
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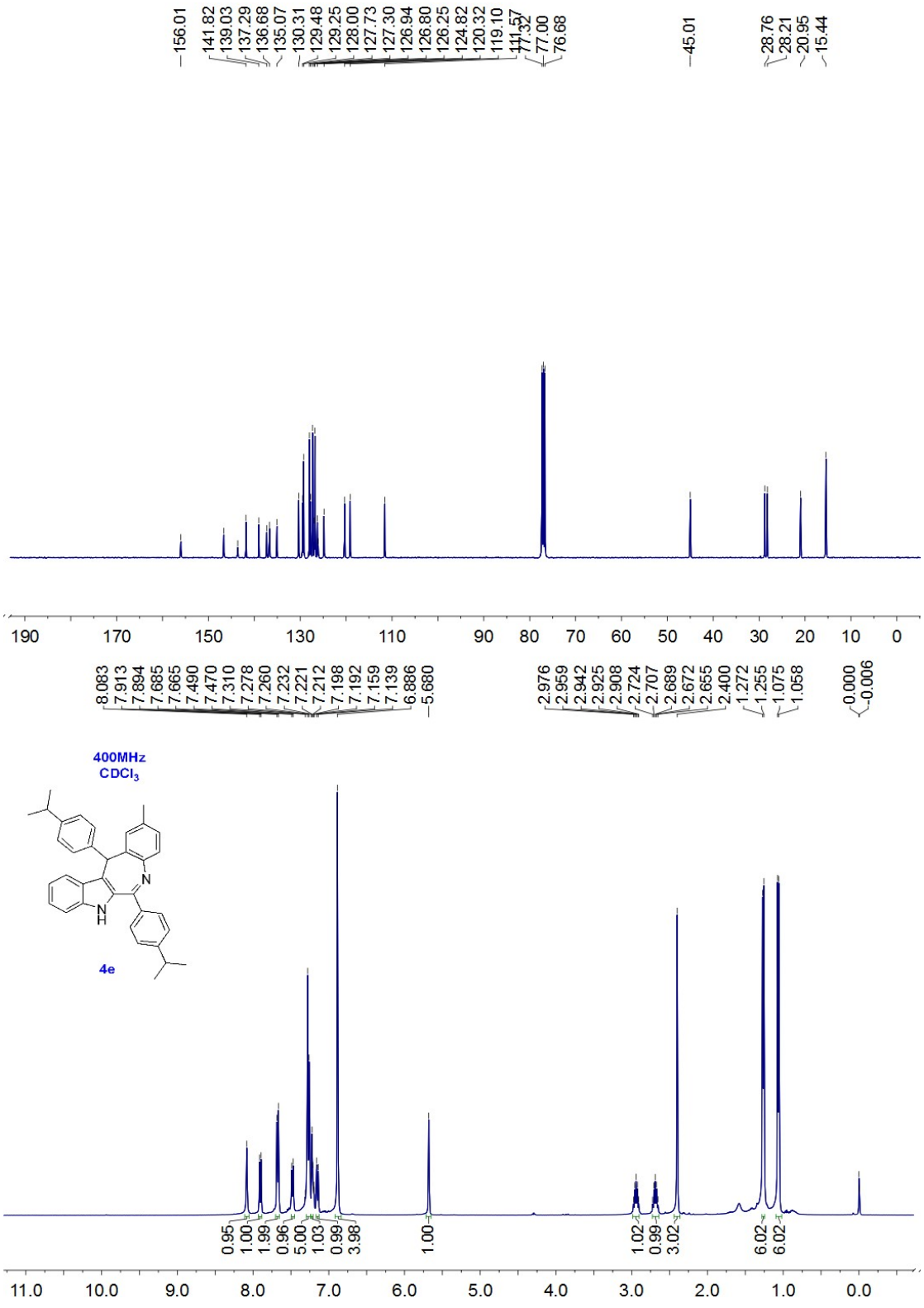
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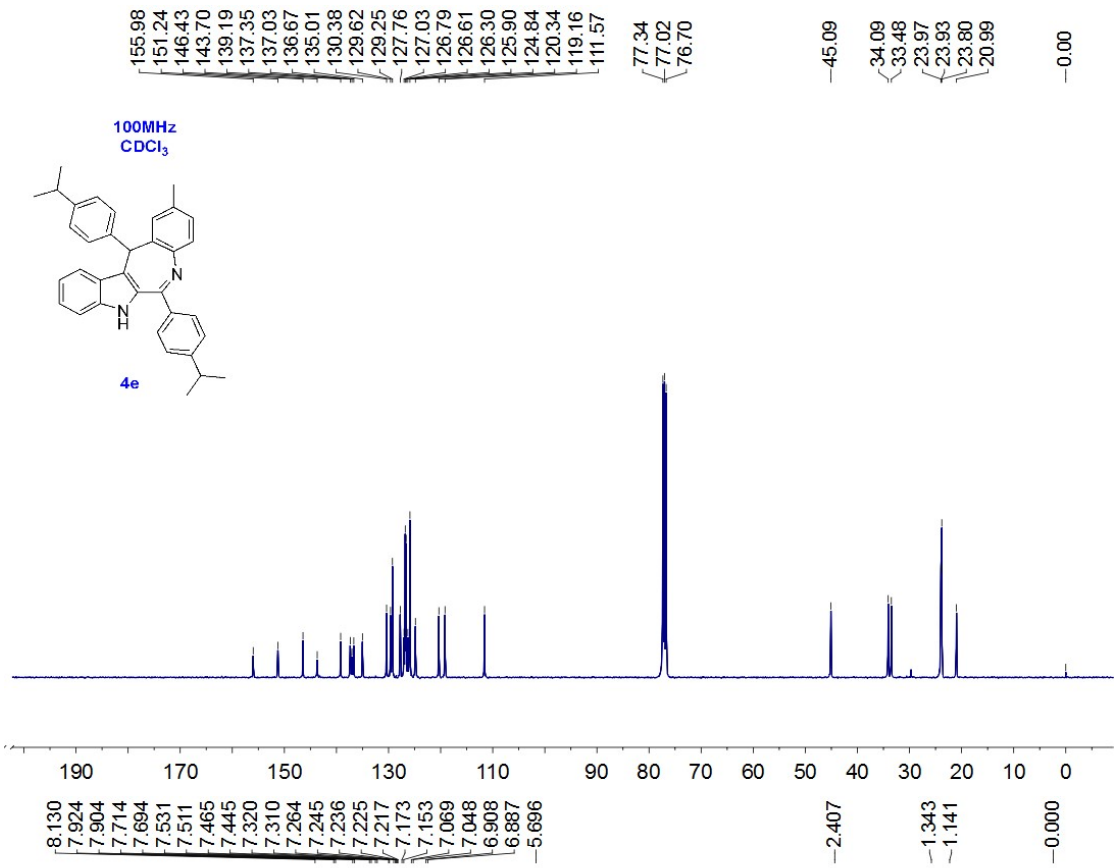
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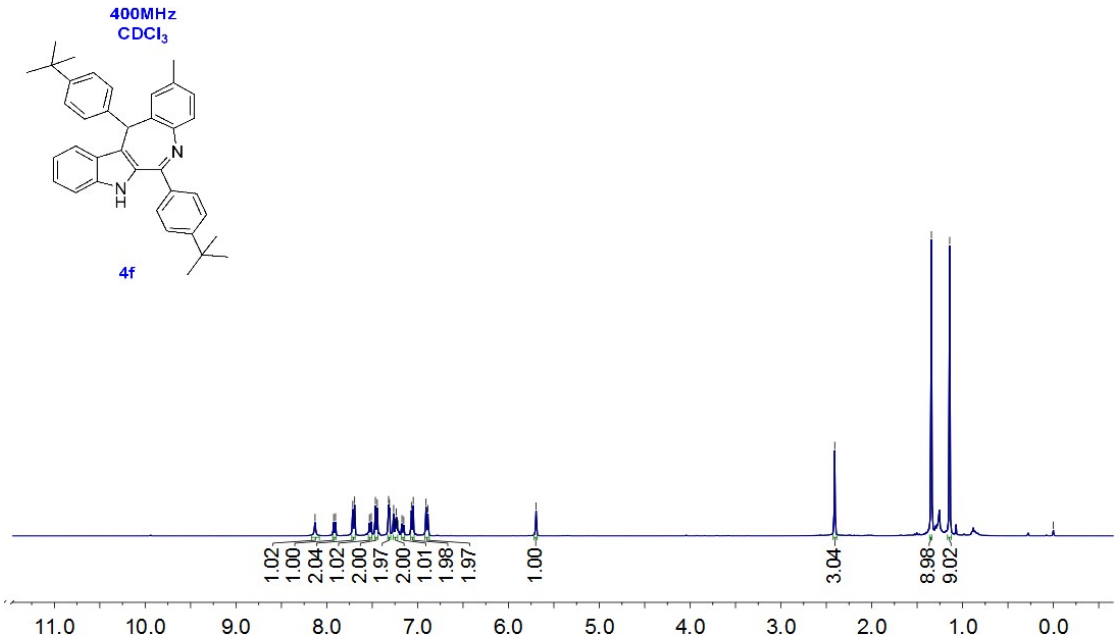
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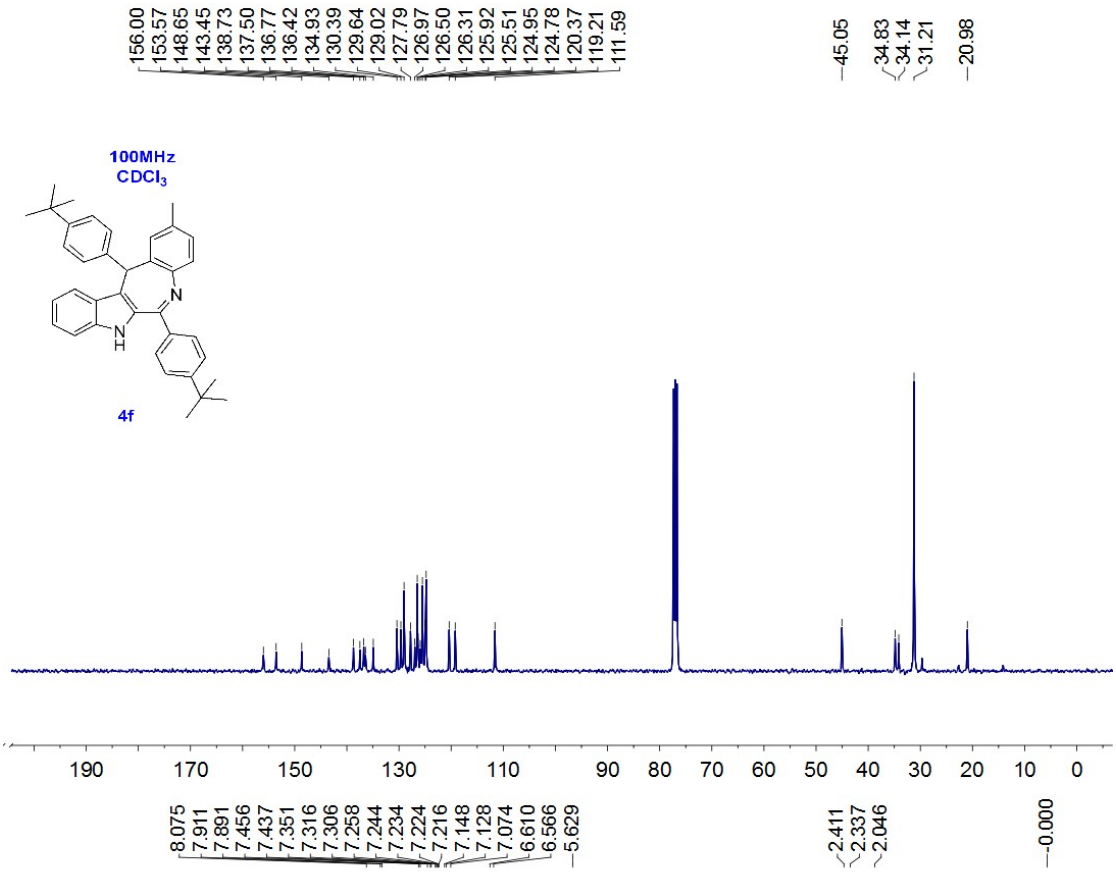
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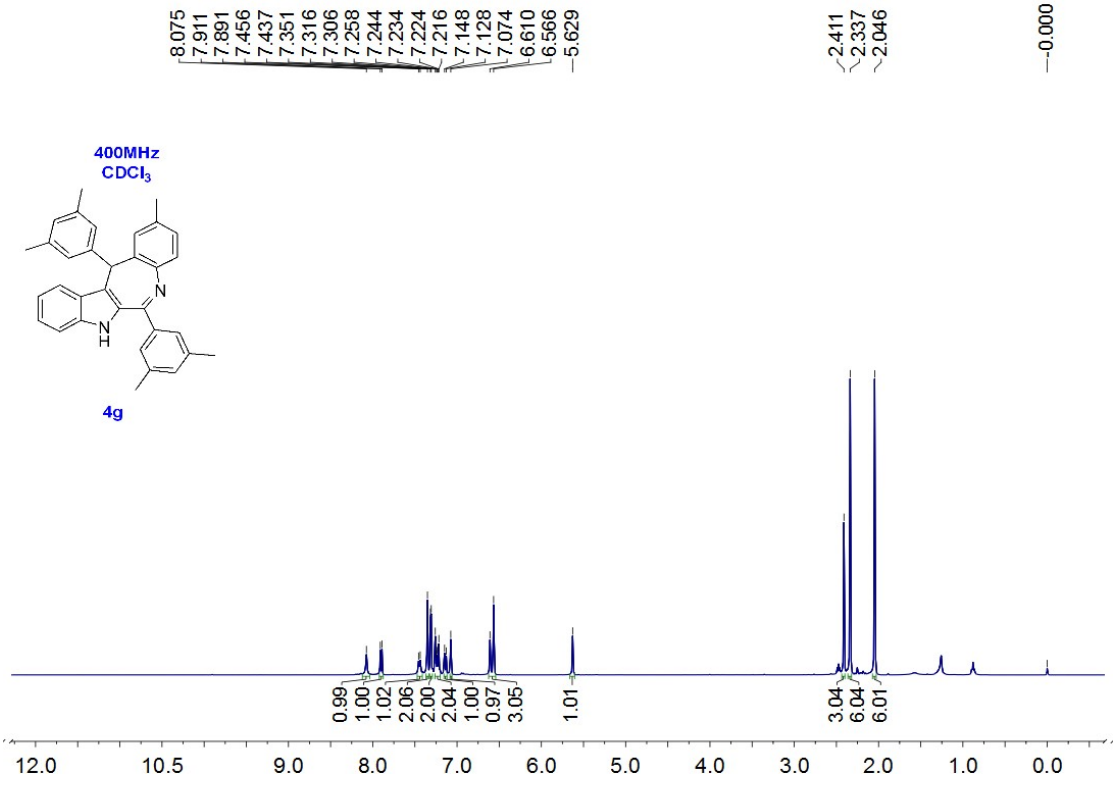
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2.04
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1.01
3.04
6.04
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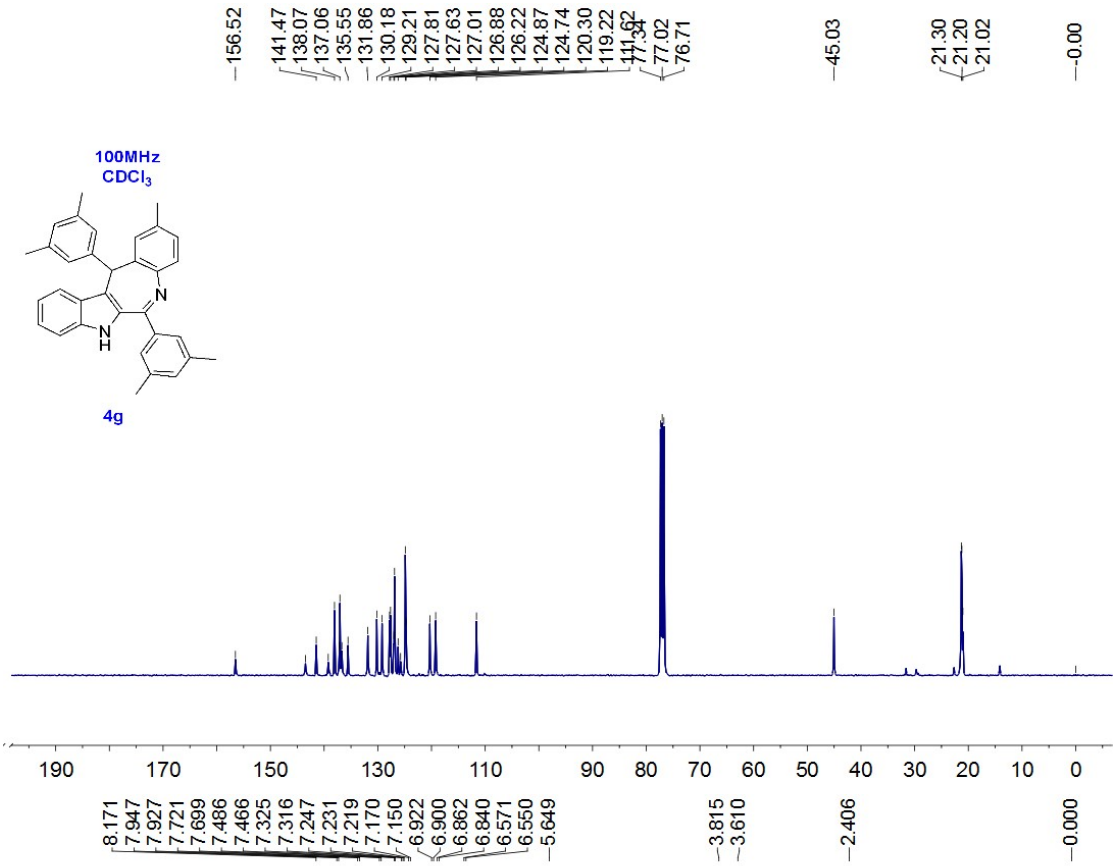
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76.71
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21.30
21.20
21.02
0.00
100MHz
CDCl3
4g
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150
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110
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80
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60
50
40
30
20
10
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7.927
7.721
7.699
7.486
7.466
7.325
7.316
7.247
7.231
7.219
7.170
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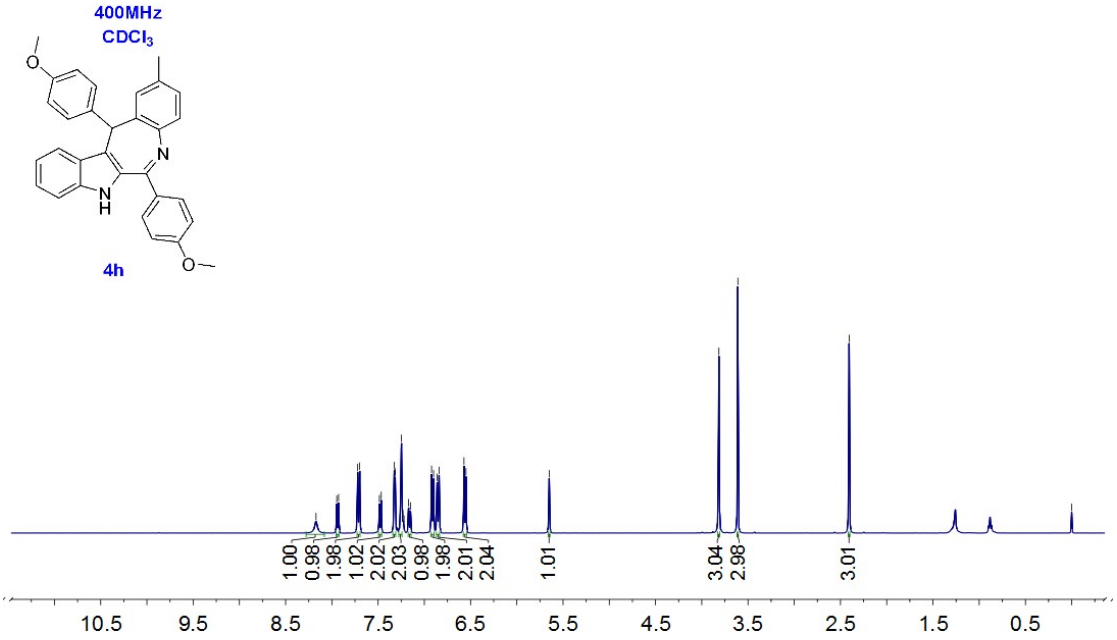
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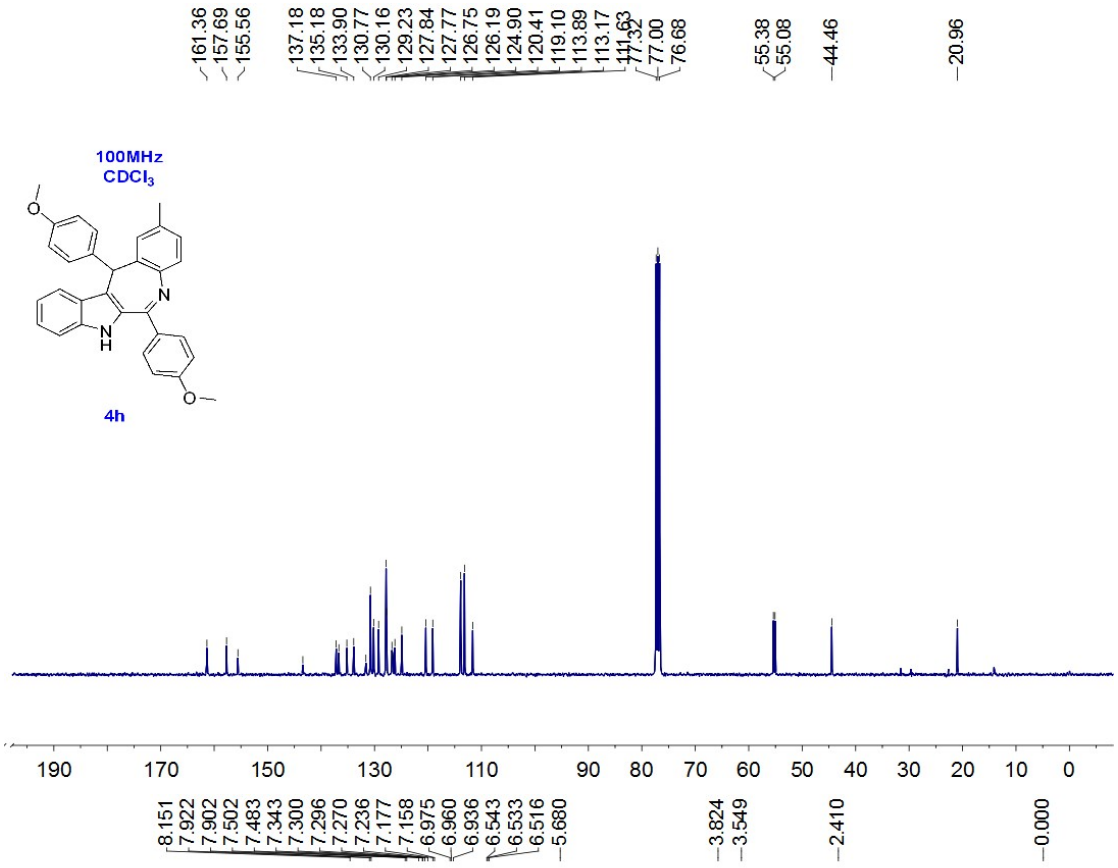
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77.00
76.68
55.38
55.08
44.46
20.96
100MHz
CDCl3
4h
190
170
150
130
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90
80
70
60
50
40
30
20
10
0
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7.502
7.483
7.343
7.300
7.296
7.270
7.236
7.177
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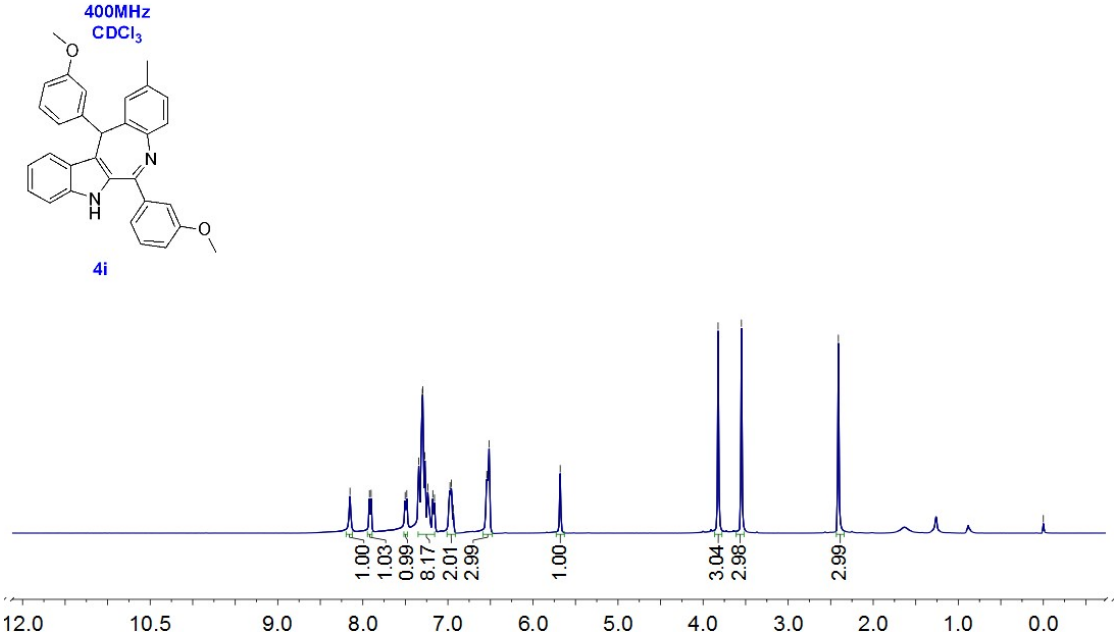
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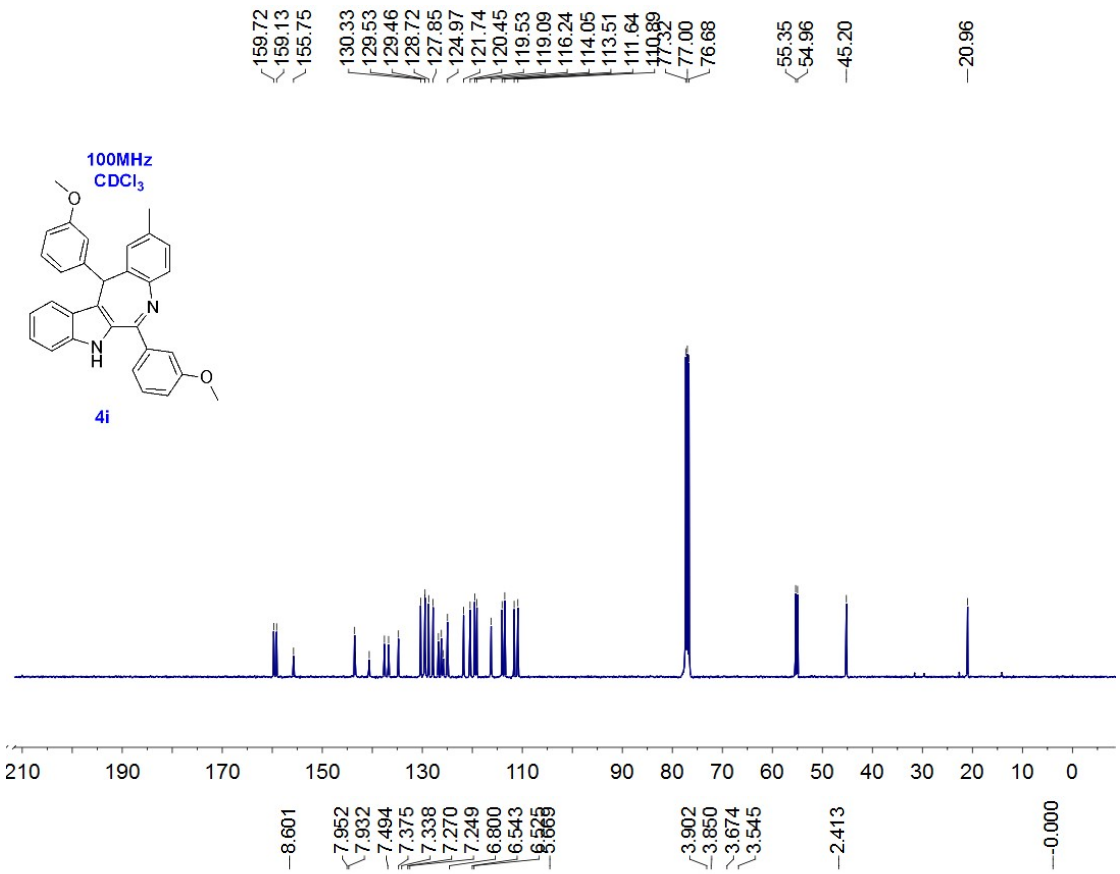
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113.51
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54.96
45.20
20.96
100MHz
CDCl3
4i
210
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150
130
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80
70
60
50
40
30
20
10
0
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7.932
7.494
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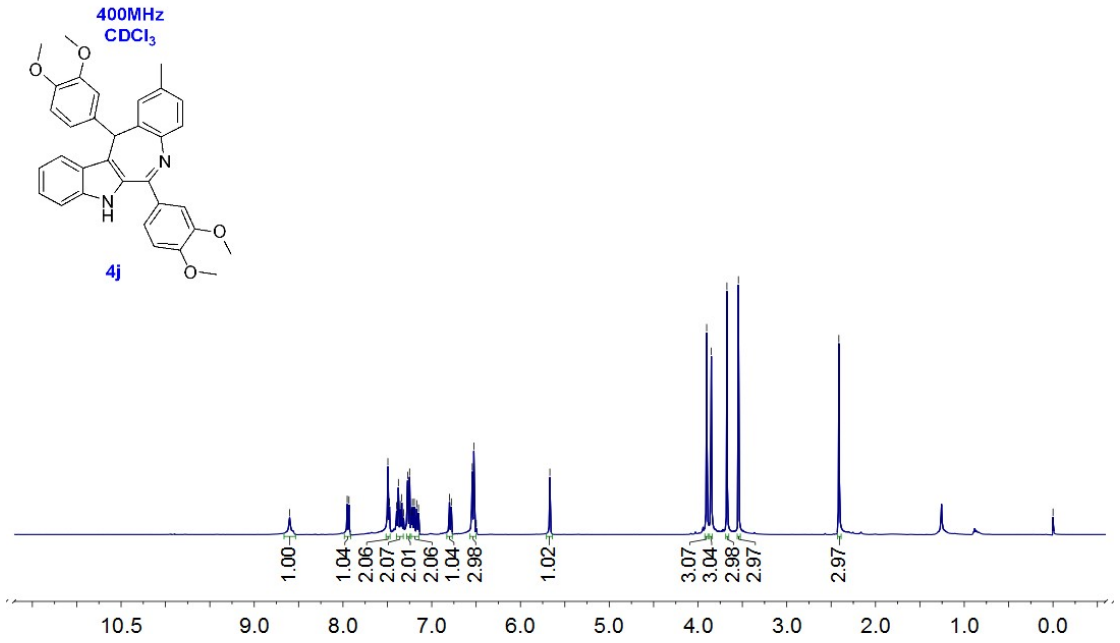
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2.97
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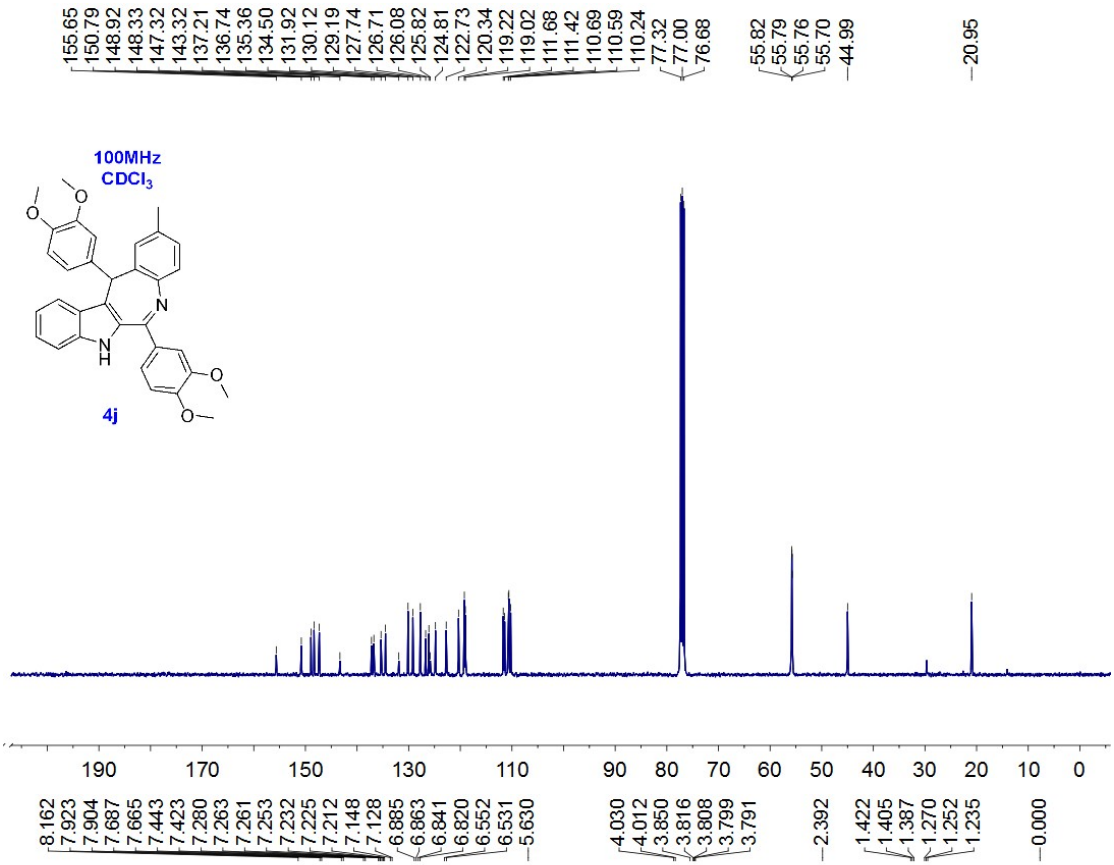
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131.92
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129.19
127.74
126.71
126.08
125.82
124.81
122.73
120.34
119.22
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111.42
110.69
110.59
110.24
77.32
77.00
76.68
55.82
55.79
55.76
55.70
44.99
20.95
100MHz
CDCl3
4j
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
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7.923
7.904
7.687
7.665
7.443
7.423
7.280
7.263
7.261
7.253
7.232
7.225
7.212
7.148
7.128
6.885
6.863
6.841
6.820
6.552
6.531
5.630
4.030
4.012
3.850
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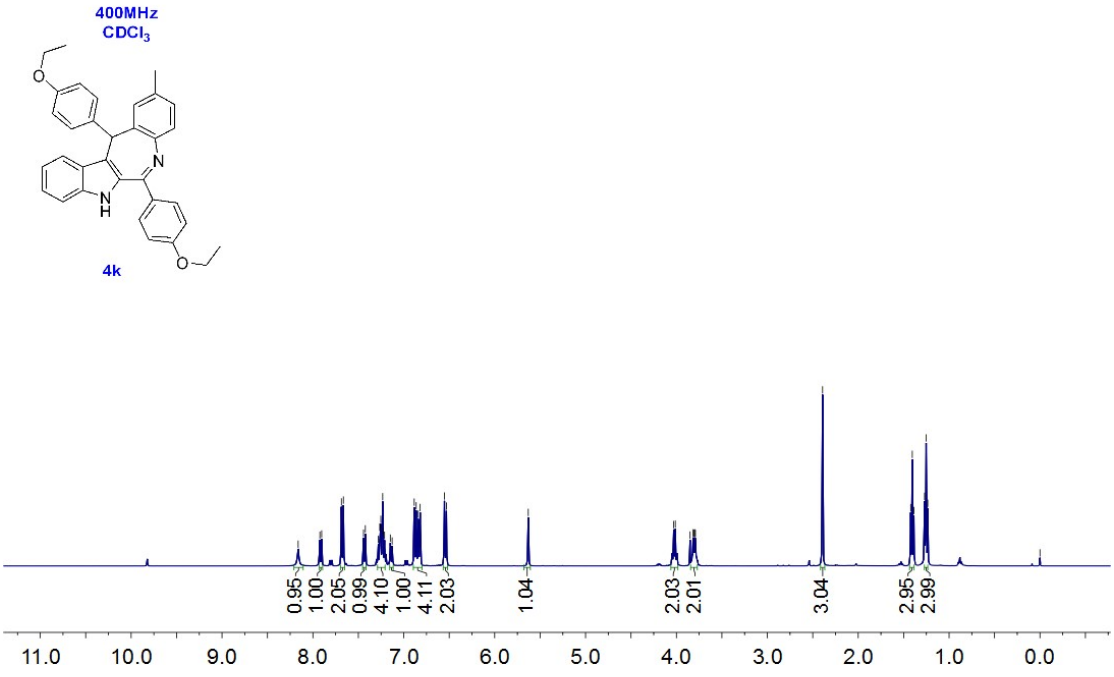
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1.00
4.11
2.03
1.04
2.03
2.01
3.04
2.95
2.99
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8.0
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4.0
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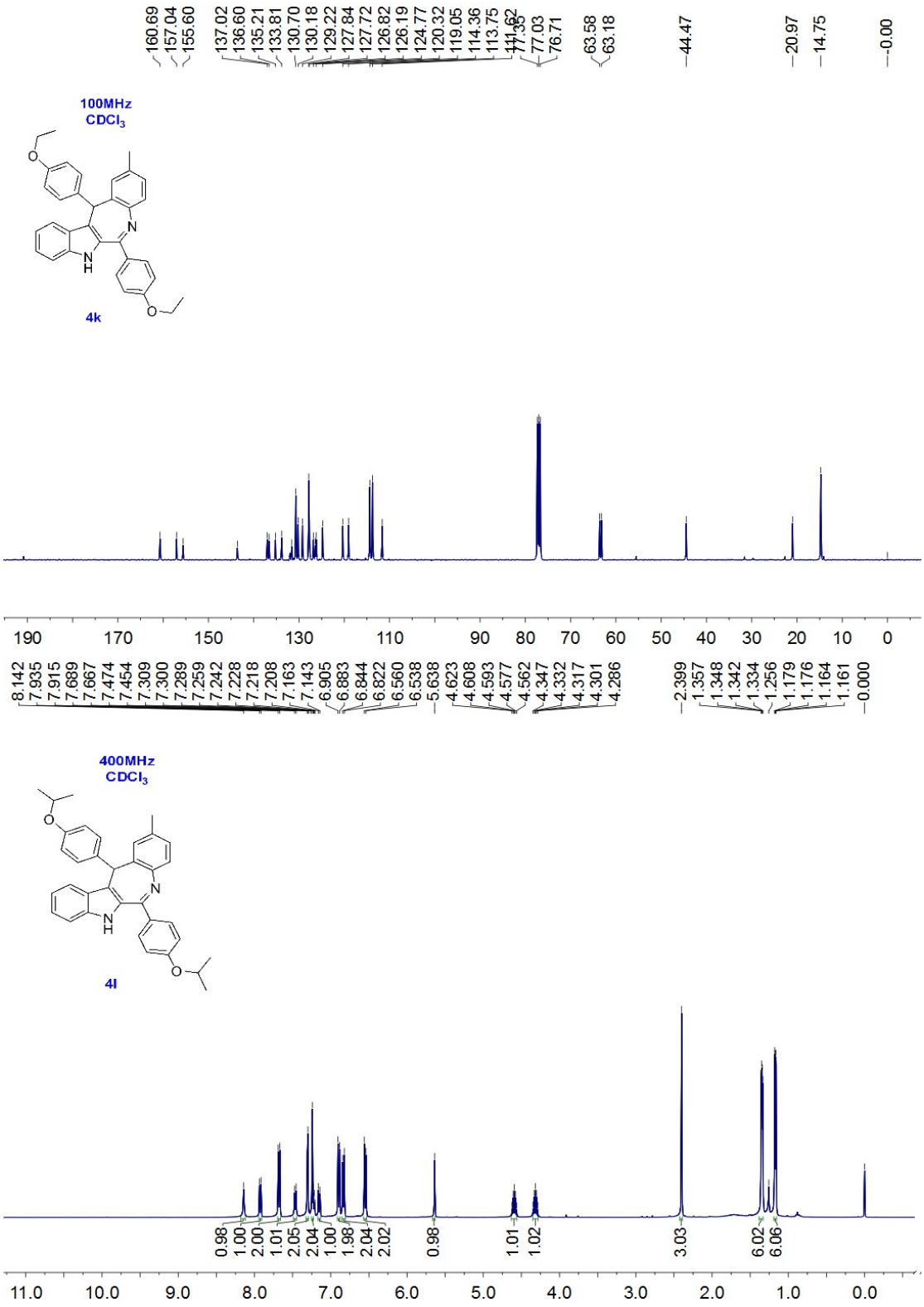
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126.19
124.77
120.32
119.05
114.36
113.75
77.03
76.71
63.58
63.18
44.47
20.97
14.75
0.00
100MHz
CDCl3
4k
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
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7.935
7.915
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7.667
7.474
7.454
7.309
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7.259
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7.228
7.218
7.208
7.163
7.143
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6.883
6.844
6.822
6.560
6.538
5.638
4.623
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4.577
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4.332
4.317
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4.286
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1.357
1.348
1.342
1.334
1.256
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CDCl3
4l
0.98
1.00
2.00
1.01
2.05
2.04
1.00
1.98
2.04
2.02
0.98
1.01
1.02
3.03
6.02
6.06
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4.0
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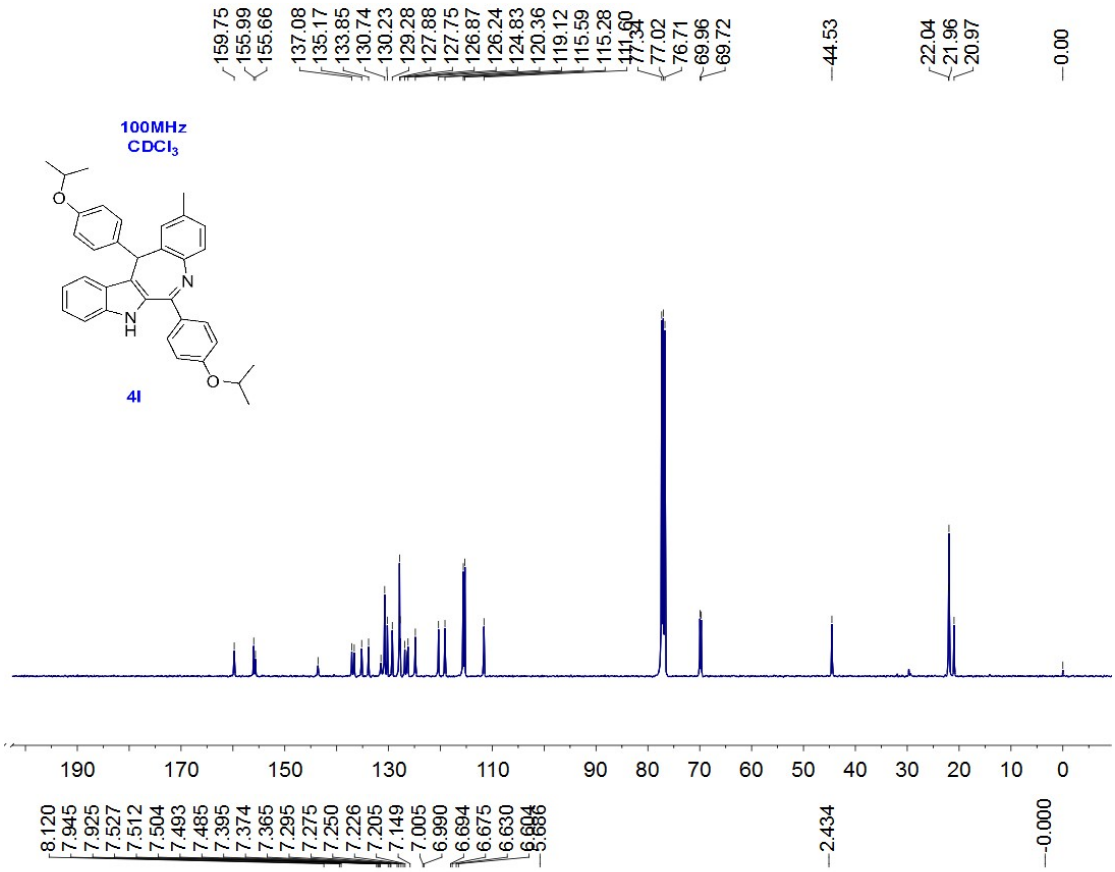
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126.24
124.83
120.36
119.12
115.59
115.28
111.60
77.34
77.02
76.71
69.96
69.72
44.53
22.04
21.96
20.97
0.00
100MHz
CDCl3
4l
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.120
7.945
7.925
7.527
7.512
7.504
7.493
7.485
7.395
7.374
7.365
7.295
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7.205
7.149
7.005
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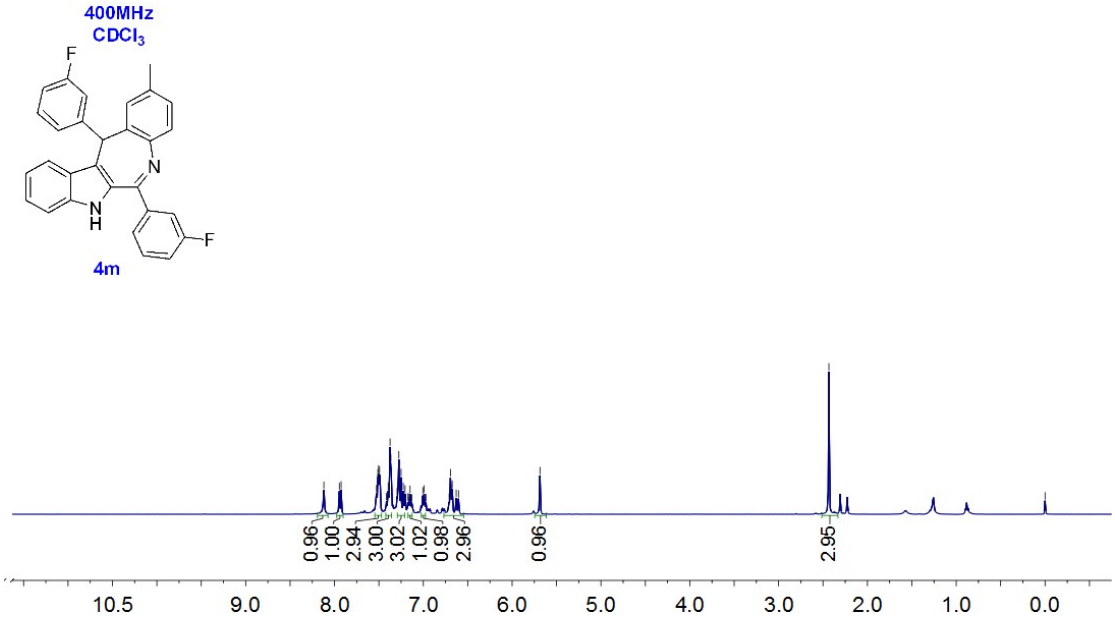
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CDCl3
4m
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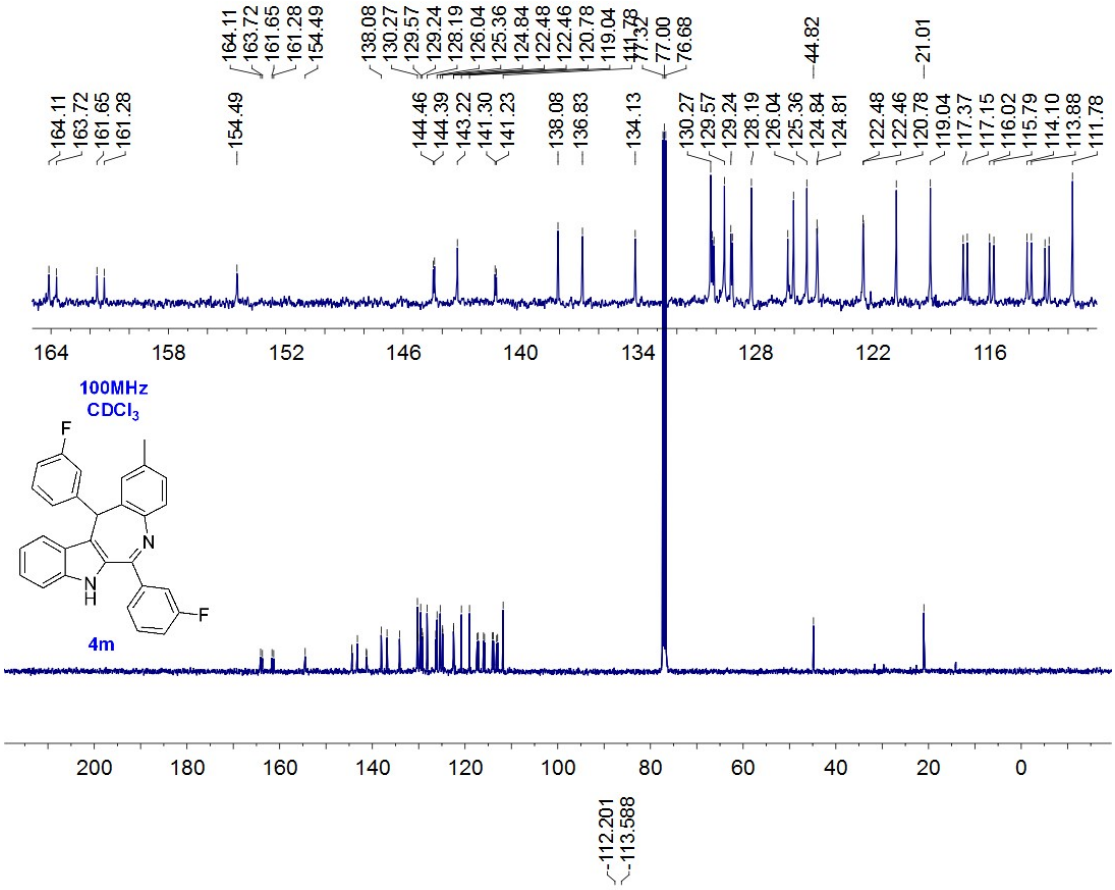
1.00
2.94
3.00
3.02
1.02
0.98
2.96
0.96
2.95
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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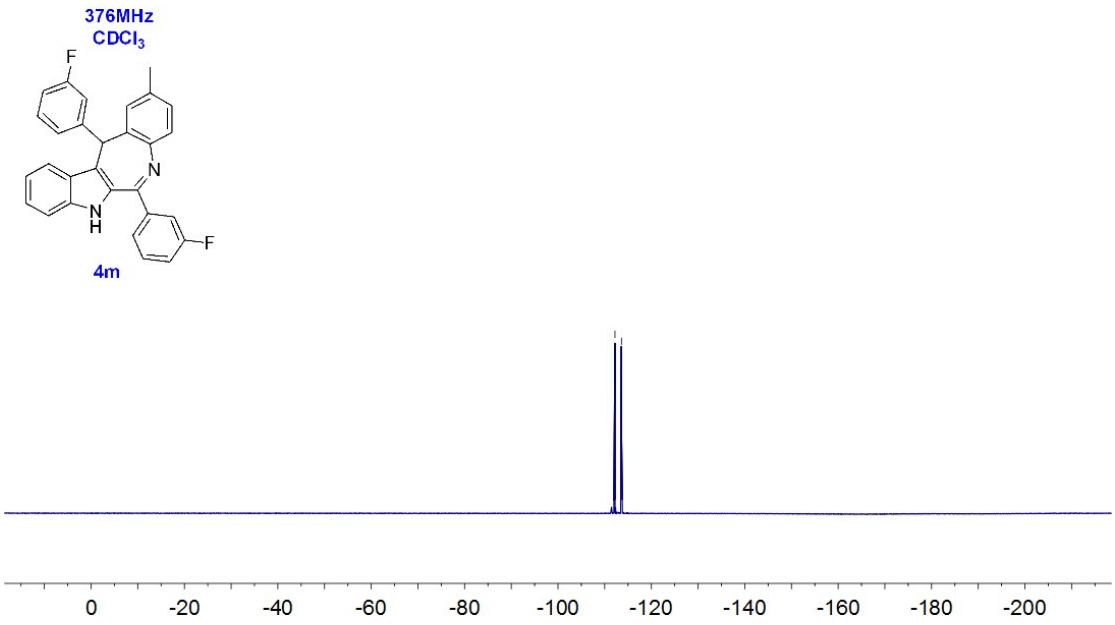
4m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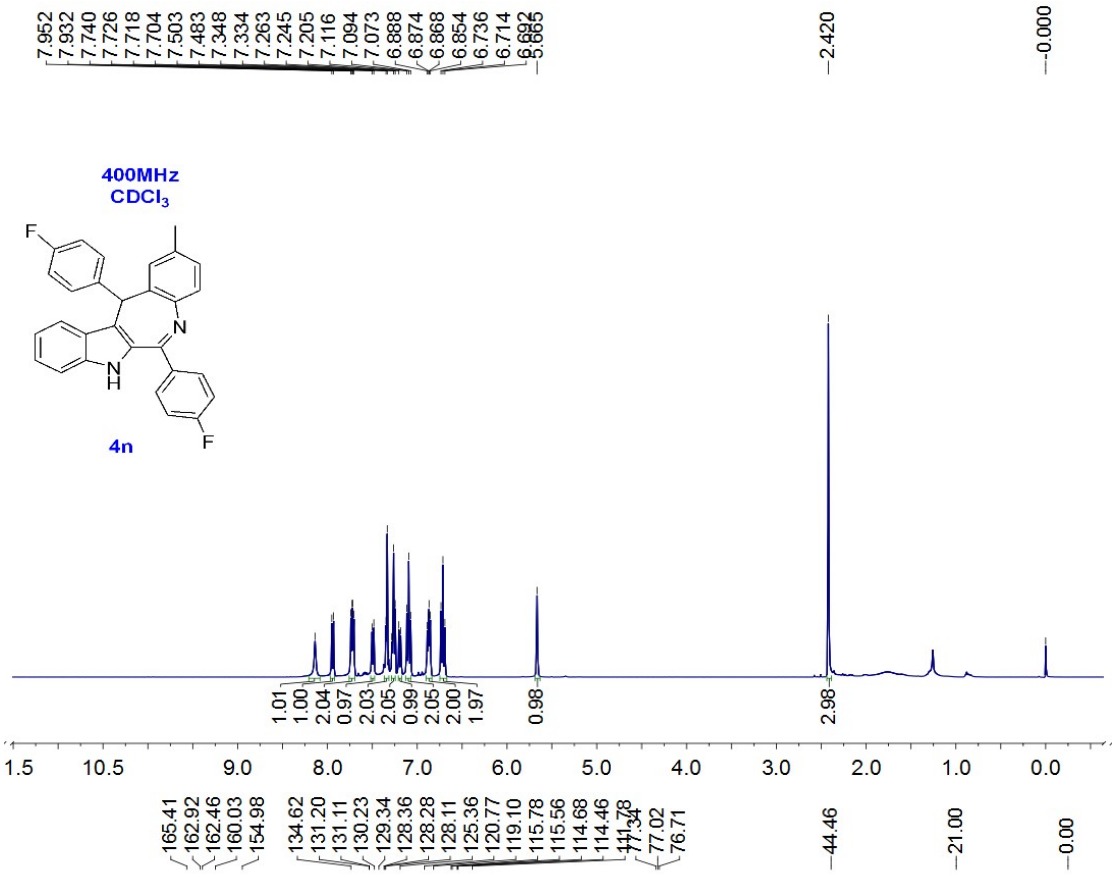
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7.483
7.348
7.334
7.263
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7.205
7.116
7.094
7.073
6.888
6.874
6.868
6.854
6.736
6.714
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400MHz
CDCl3
4n
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1.00
2.04
0.97
2.03
2.05
0.99
2.05
2.00
1.97
0.98
2.98
1.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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162.92
162.46
160.03
154.98
134.62
131.20
131.11
130.23
129.34
128.36
128.28
128.11
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114.46
77.02
76.71
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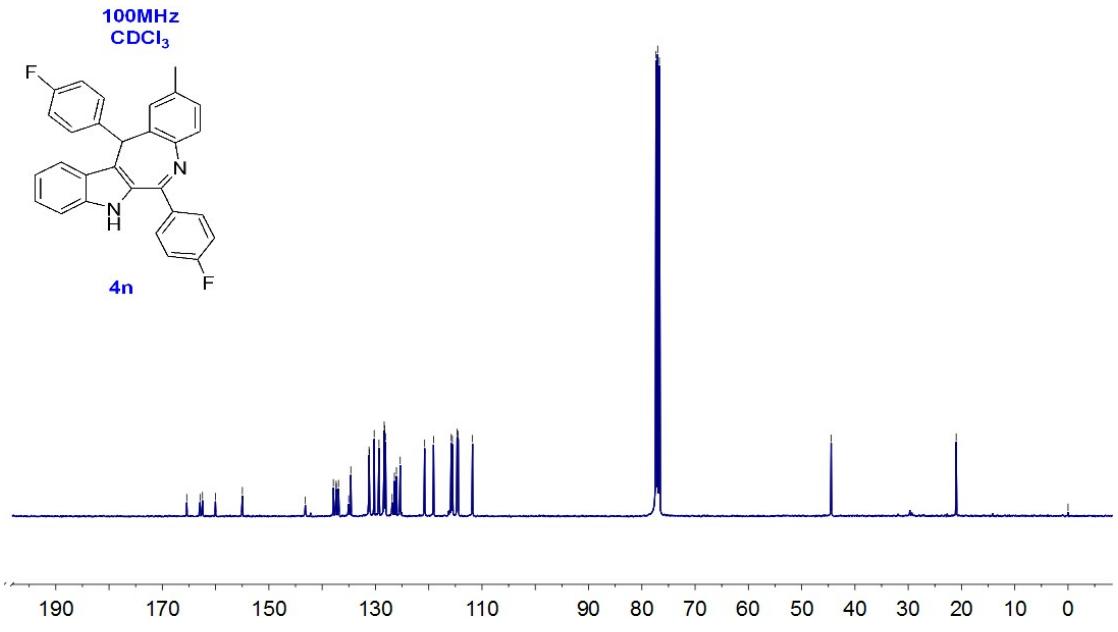
21.00
0.00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150
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110
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80
70
60
50
40
30
20
10
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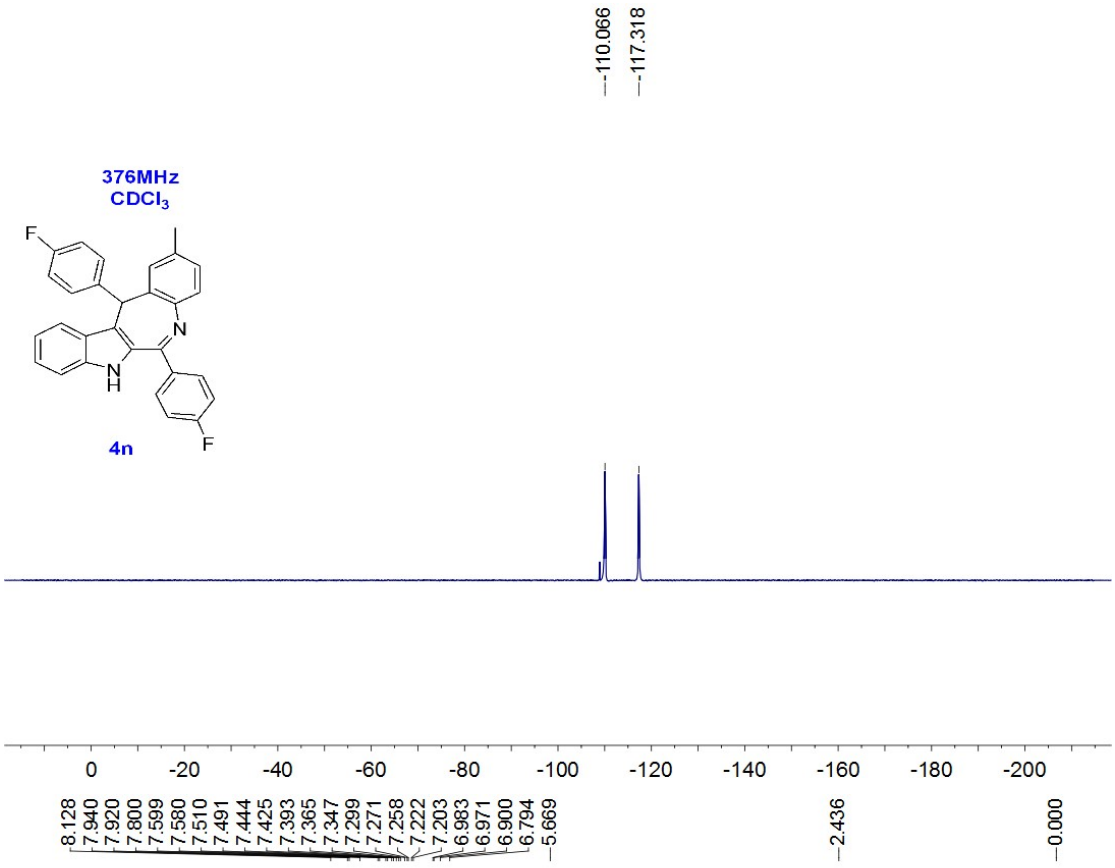
376MHz
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-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
8.128
7.940
7.920
7.800
7.599
7.580
7.510
7.491
7.444
7.425
7.393
7.365
7.347
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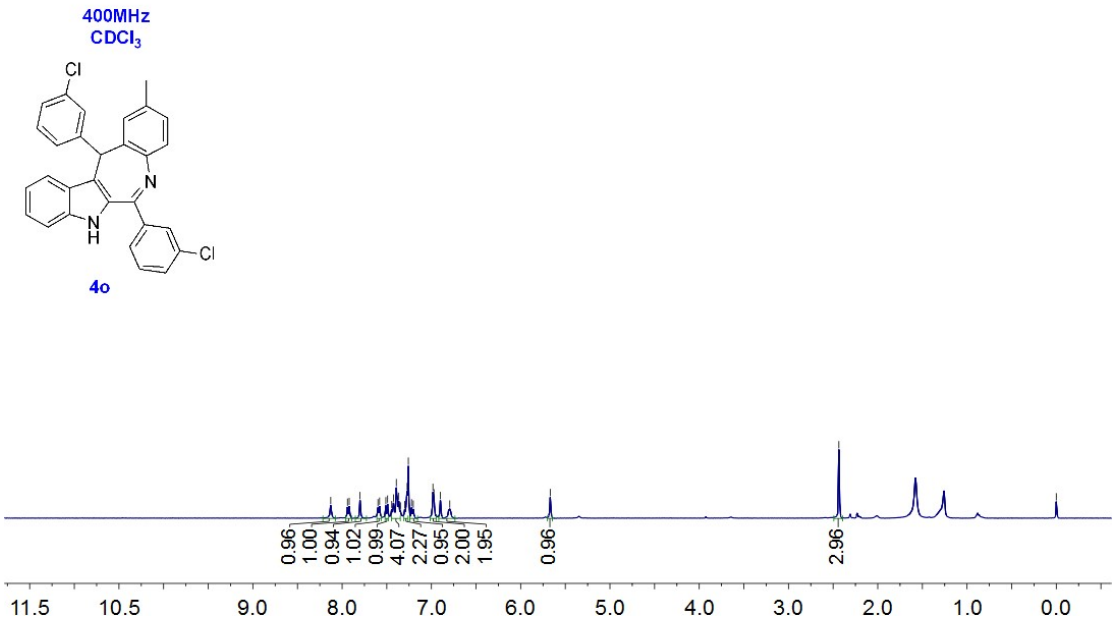
400MHz
CDCl3
4o
0.96
1.00
0.94
1.02
0.99
4.07
2.27
0.95
2.00
1.95
0.96
2.96
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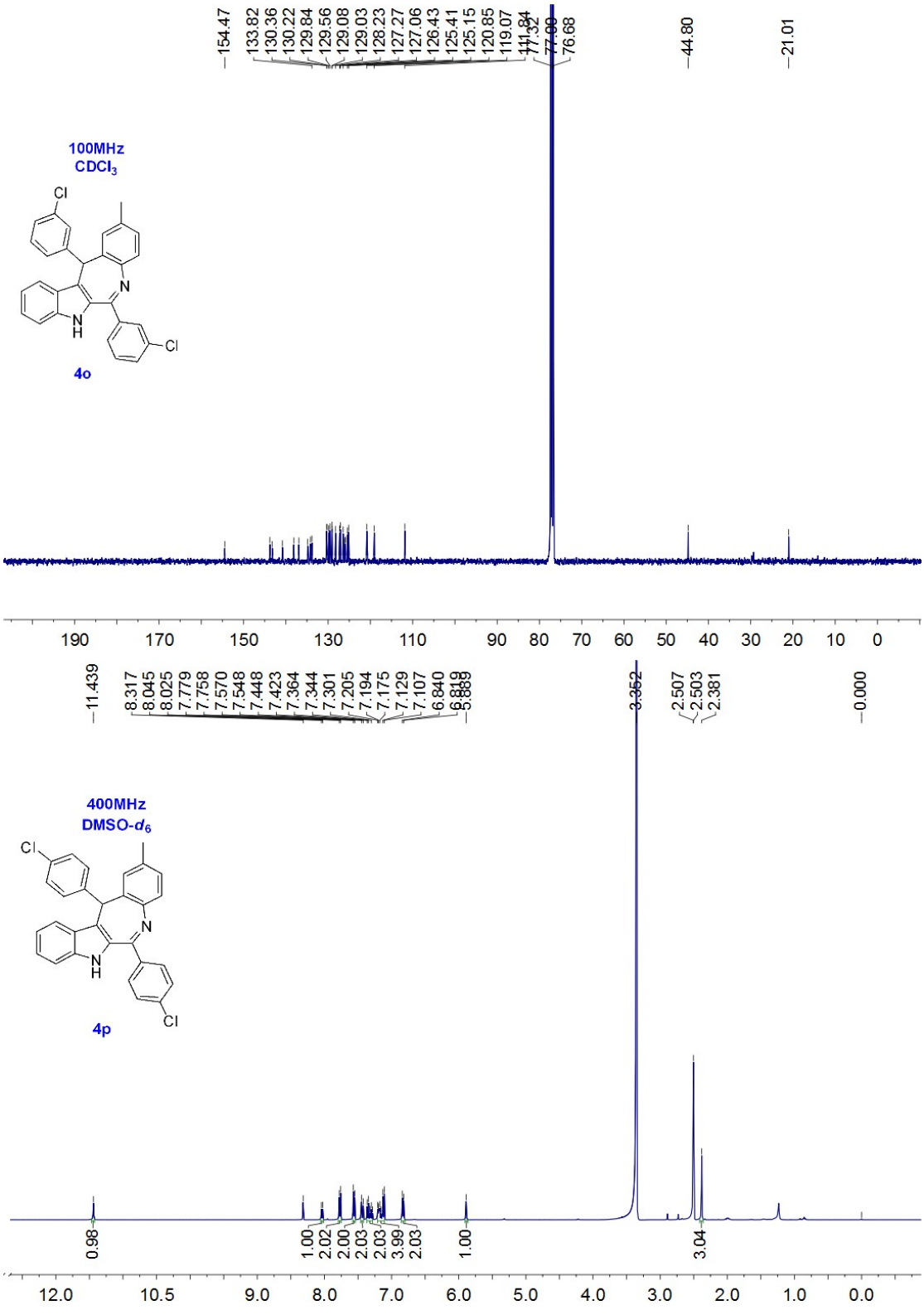
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


100MHz
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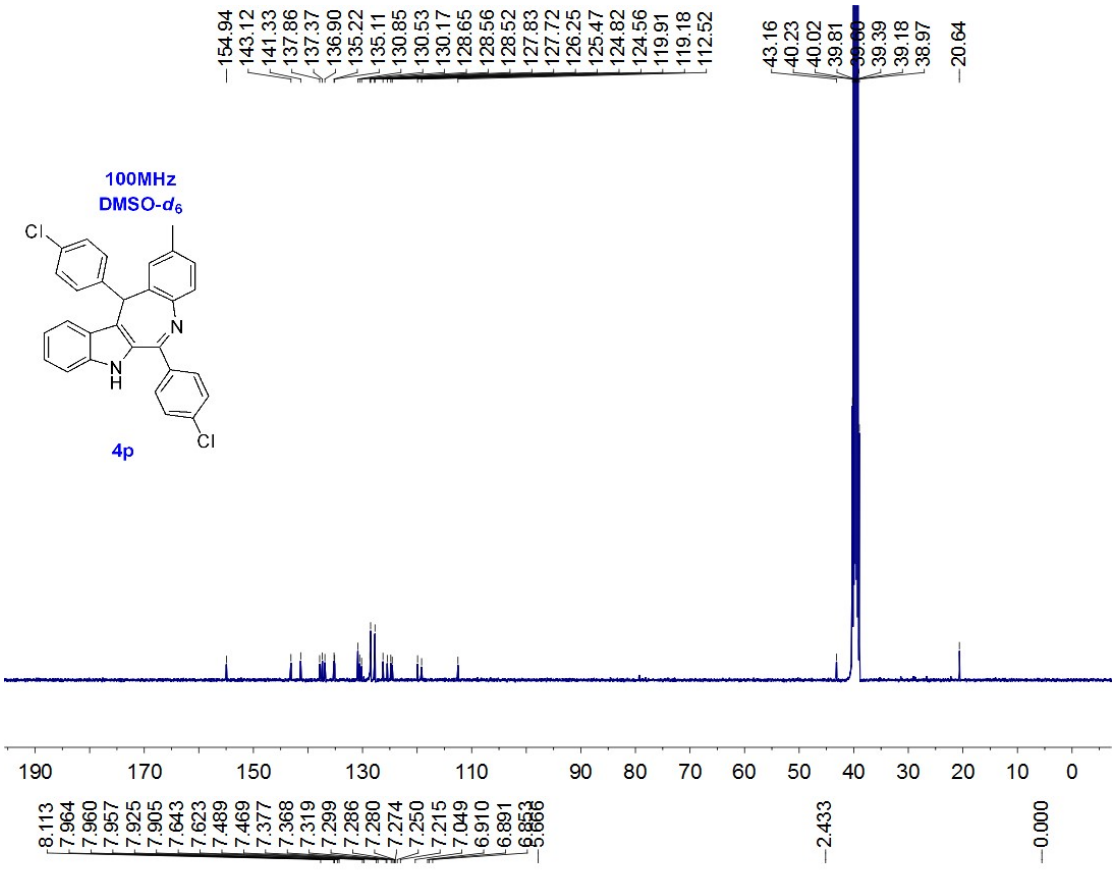
4o
400MHz
DMSO-d6
4p


100MHz
DMSO-d_6
Cl
N
H
Cl
4p
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141.33
137.86
137.37
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135.22
135.11
130.85
130.53
130.17
128.65
128.56
128.52
127.83
127.72
126.25
125.47
124.82
124.56
119.91
119.18
112.52
43.16
40.23
40.02
39.81
39.39
39.18
38.97
20.64
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.113
7.964
7.960
7.957
7.925
7.905
7.643
7.623
7.489
7.469
7.377
7.368
7.319
7.299
7.286
7.280
7.274
7.250
7.215
7.049
6.910
6.891
2.433
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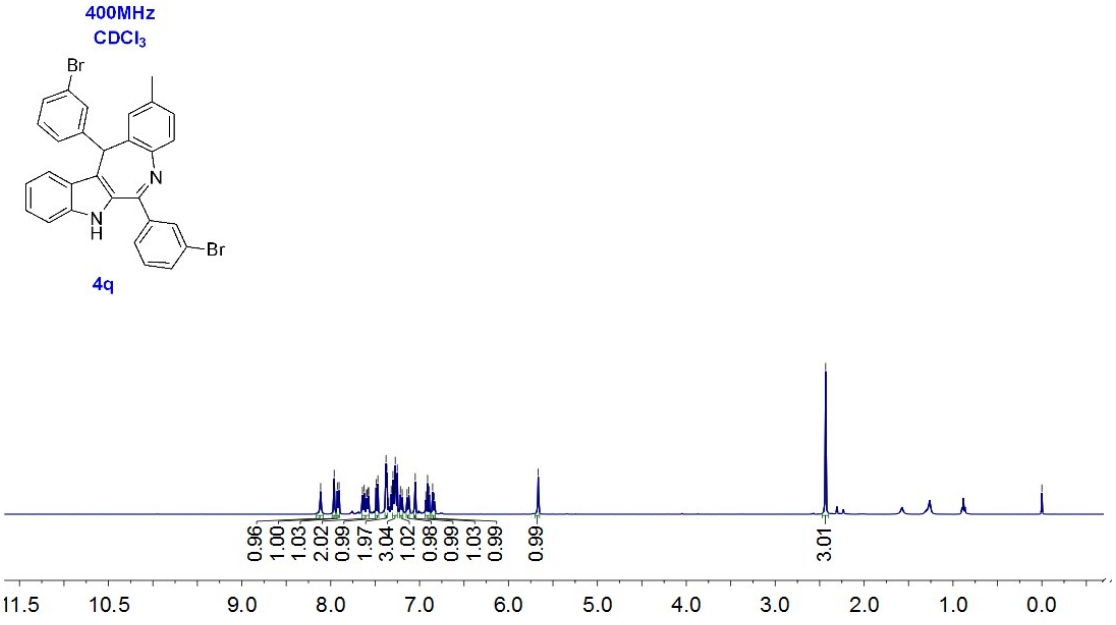
400MHz
$CDCl_3$
Br
N
H
Br
4q
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1.00
1.03
2.02
0.99
1.97
3.04
1.02
0.98
0.99
1.03
0.99
0.99
3.01
11.5
10.5
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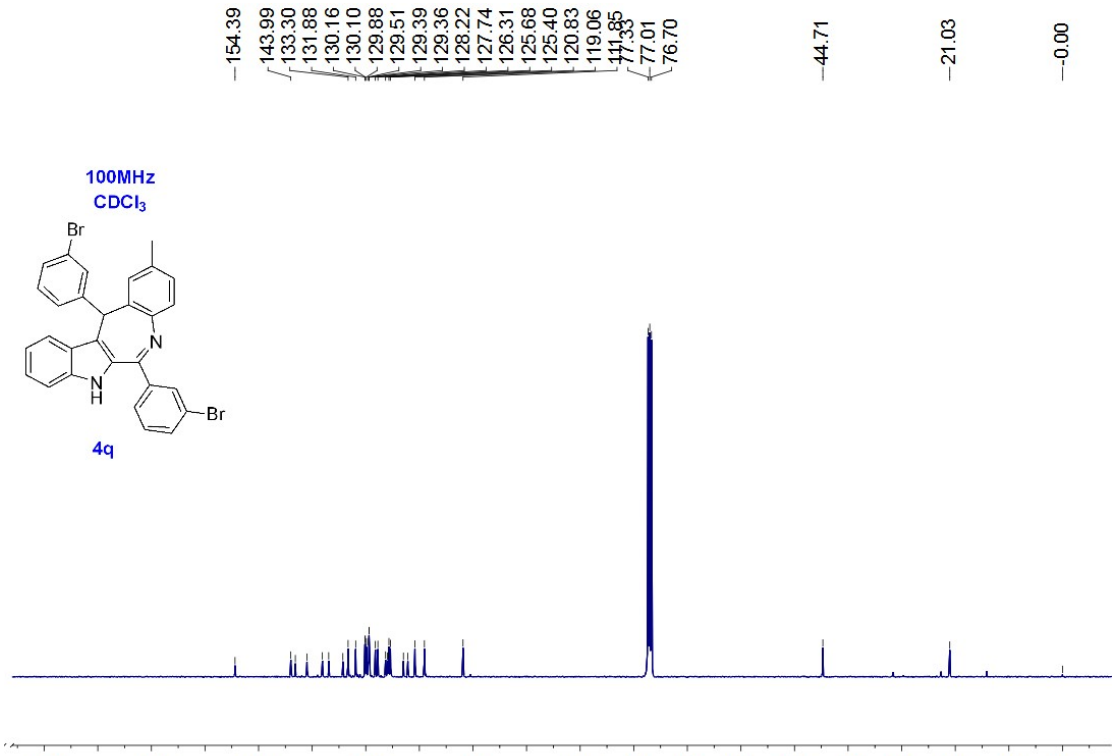
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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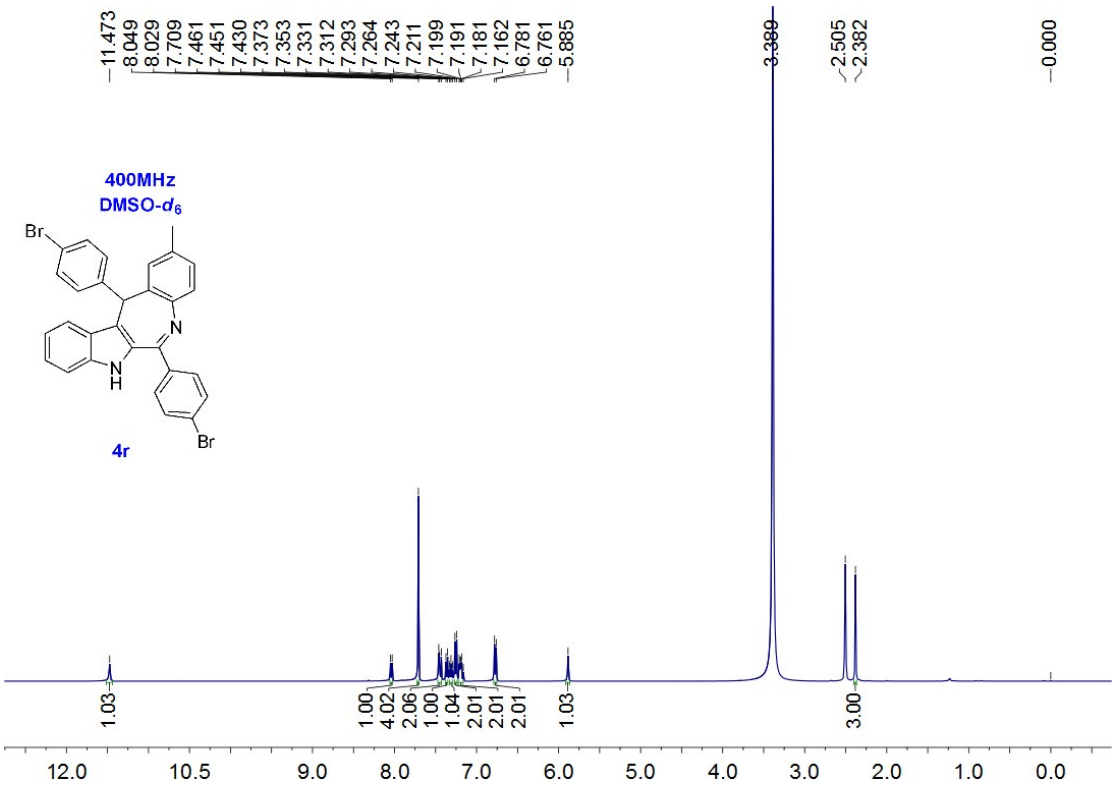
129.36
128.22
127.74
126.31
125.68
125.40
120.83
119.06
111.85
111.33
77.01
76.70
44.71
21.03
0.00
100MHz
CDCl3
Br
N
H
Br
4q
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.430
7.373
7.353
7.331
7.312
7.293
7.264
7.243
7.211
7.199
7.191
7.181
7.162
6.781
6.761
5.885
3.389
2.505
2.382
0.000
400MHz
DMSO-d6
Br
N
H
Br
4r
1.03
1.00
4.02
2.06
1.00
1.04
2.01
2.01
1.03
3.00
12.0
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8.0
7.0
6.0
5.0
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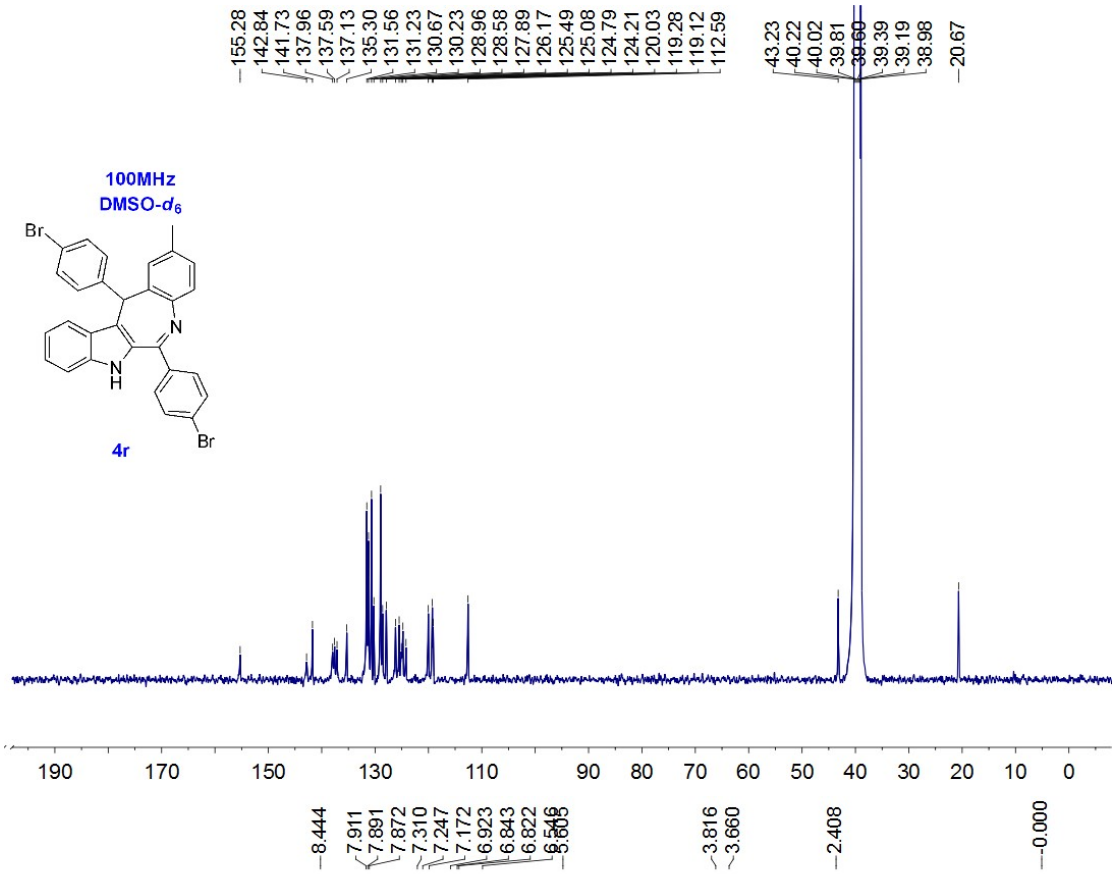
0.0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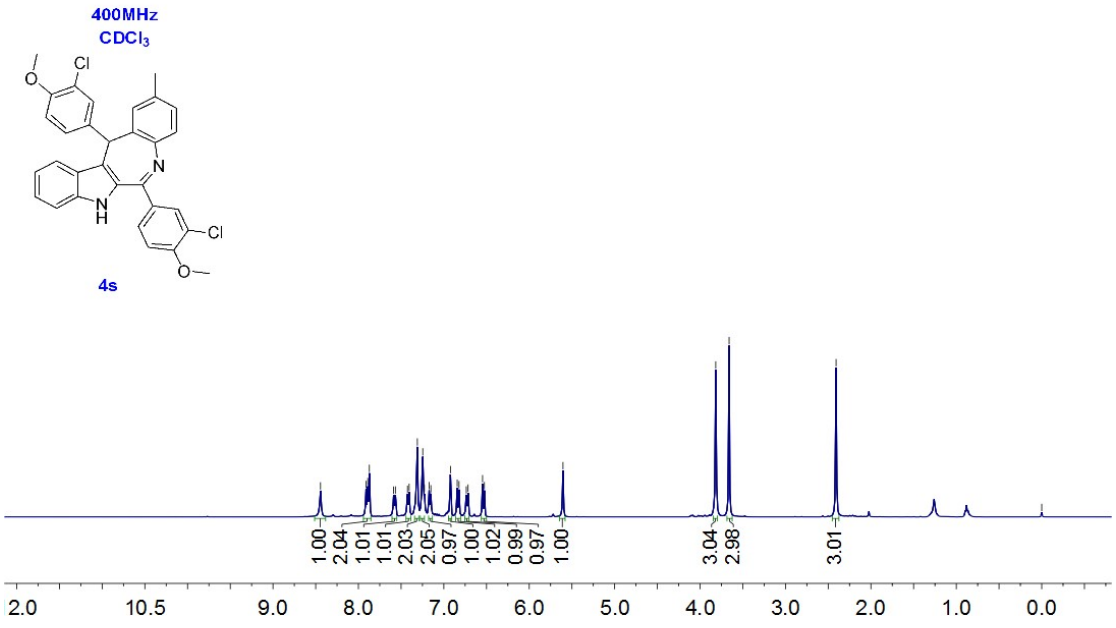
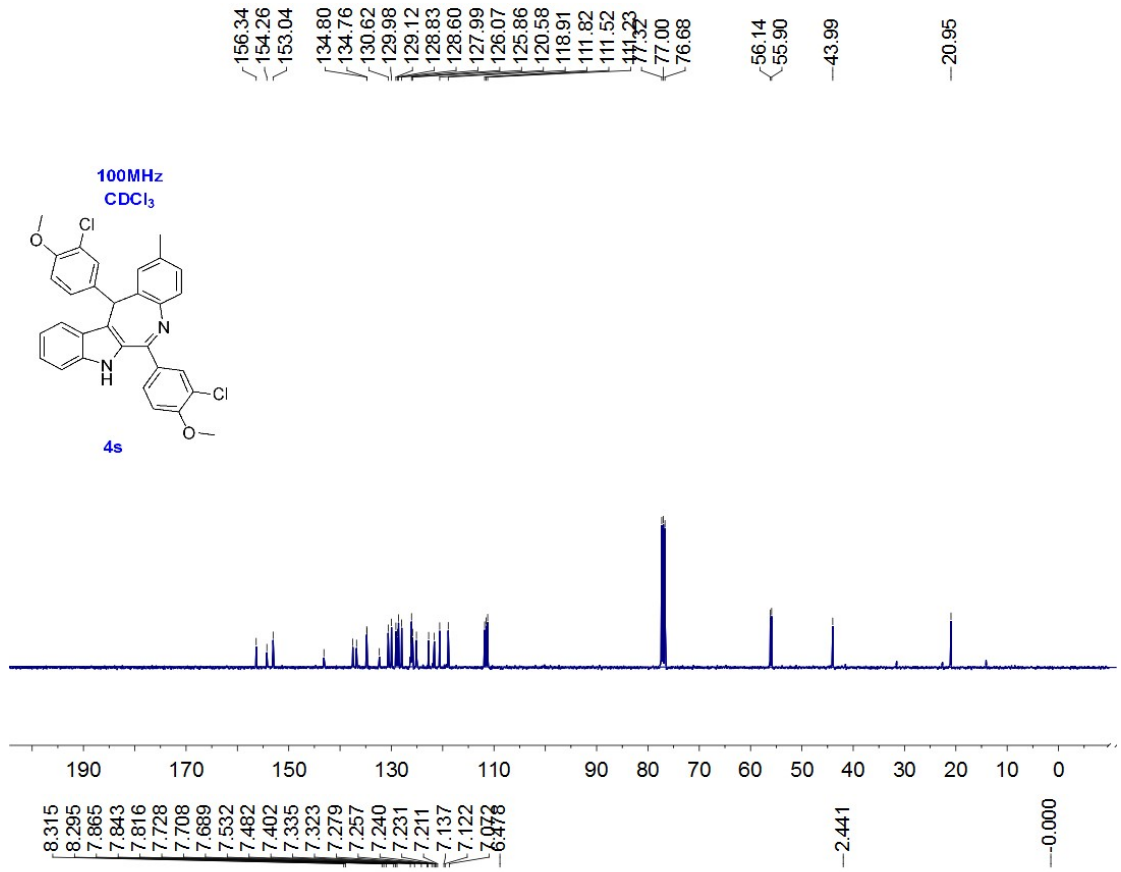
127.89
126.17
125.49
125.08
124.79
124.21
120.03
119.28
119.12
112.59
43.23
40.22
40.02
39.81
39.60
39.39
39.19
38.98
20.67
100MHz
DMSO-d_6
Br
N
H
Br
4r
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.444
7.911
7.891
7.872
7.310
7.247
7.172
6.923
6.843
6.822
3.816
3.660
2.408
0.000


400MHz
$CDCl_3$
O
Cl
N
H
Cl
O
4s
1.00
2.04
1.01
1.01
2.03
2.05
0.97
1.00
1.02
0.99
0.97
1.00
3.04
2.98
3.01
2.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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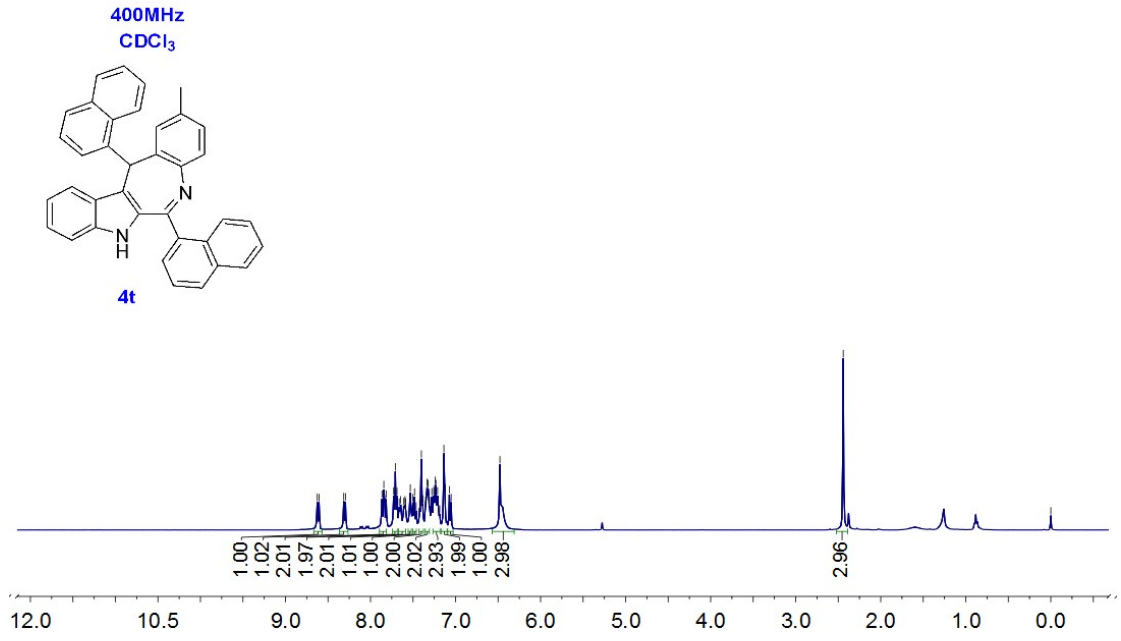
154.26
153.04
134.80
134.76
130.62
129.98
129.12
128.83
128.60
127.99
126.07
125.86
120.58
118.91
111.82
111.52
77.32
77.00
76.68
56.14
55.90
43.99
20.95
100MHz
CDCl3
Cl
O
N
H
Cl
O
4s
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.315
8.295
7.865
7.843
7.816
7.728
7.708
7.689
7.532
7.482
7.402
7.335
7.323
7.279
7.257
7.240
7.231
7.211
7.137
7.122
2.441
0.000


400MHz
CDCl3
N
H
4t
1.00
1.02
2.01
1.97
2.01
1.01
1.00
2.00
2.02
2.93
1.99
1.00
2.98
2.96
12.0
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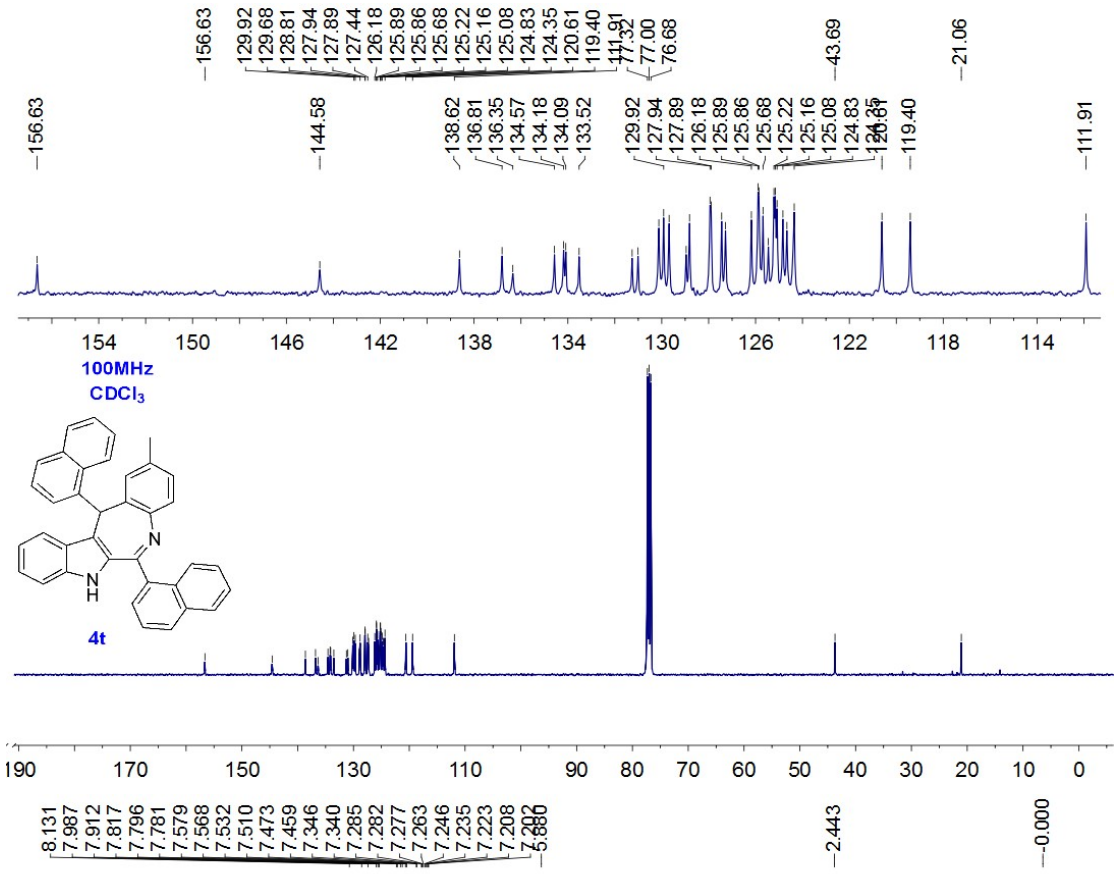
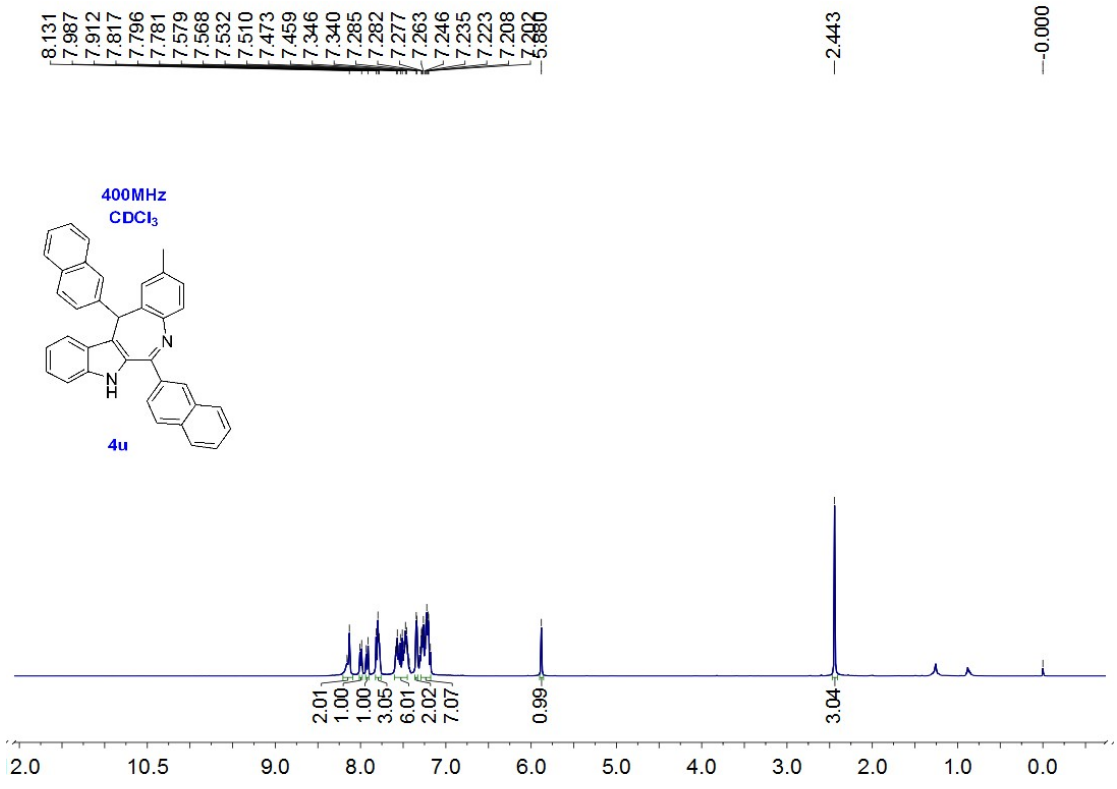
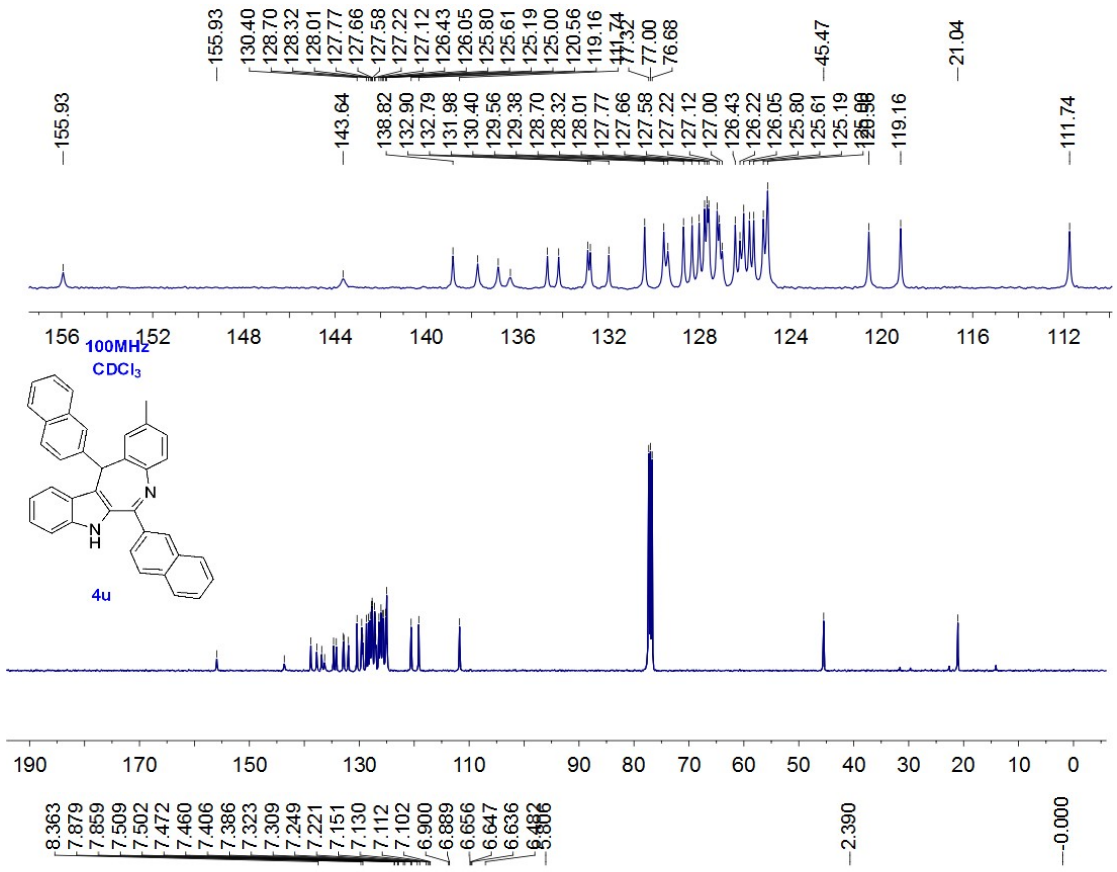
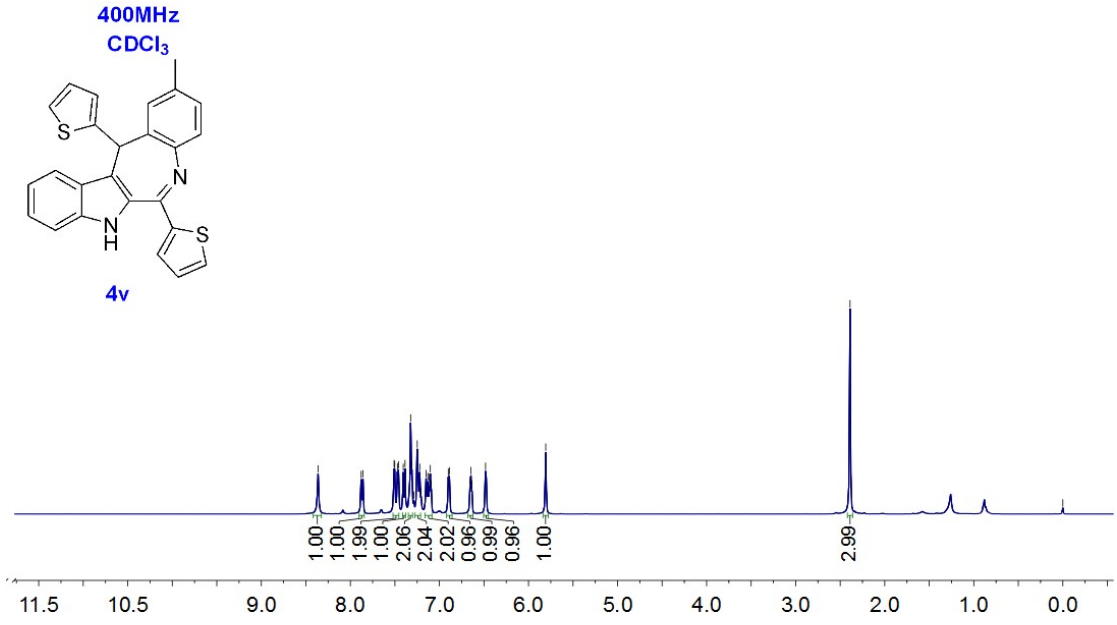
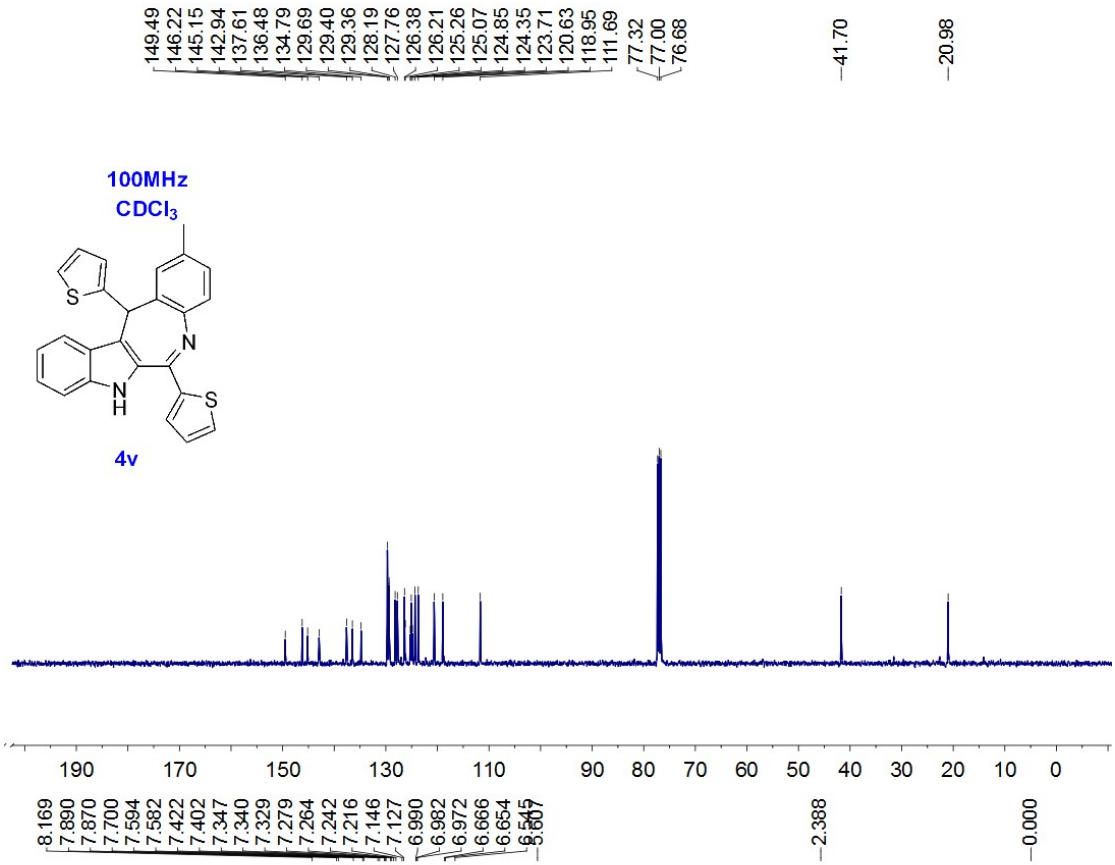
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

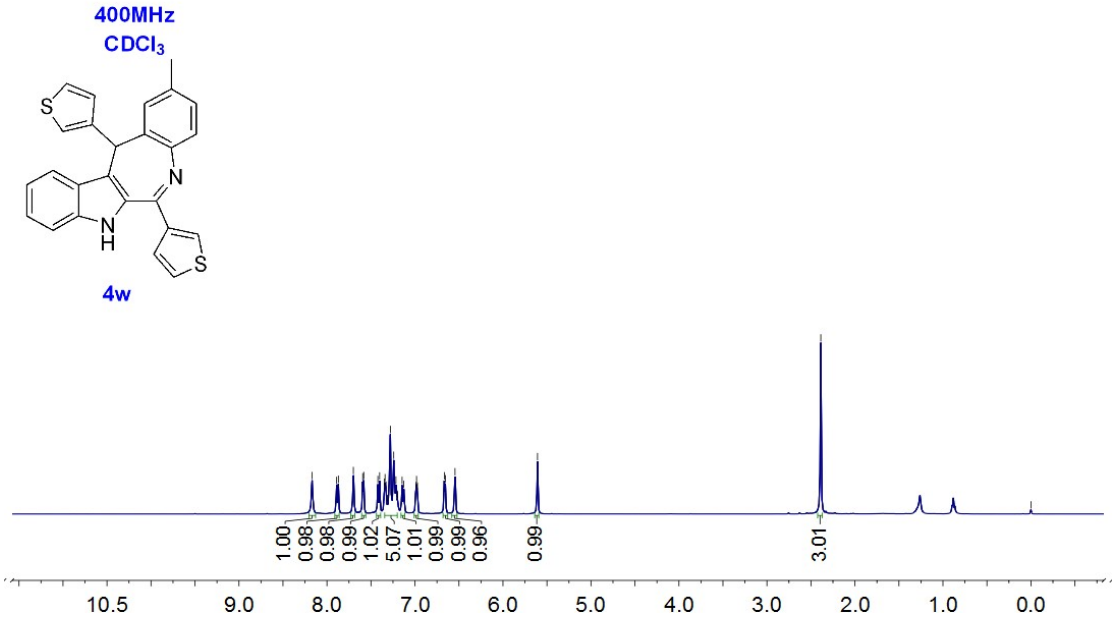

156.63
129.92
129.68
128.81
127.94
127.89
127.44
126.18
125.89
125.86
125.68
125.22
125.16
125.08
124.83
124.35
120.61
119.40
111.91
77.32
77.00
76.68
43.69
21.06
144.58
138.62
136.81
136.35
134.57
134.18
134.09
133.52
119.40
111.91
100MHz
CDCl3
4t


8.131
7.987
7.912
7.817
7.796
7.781
7.579
7.568
7.532
7.510
7.473
7.459
7.346
7.340
7.285
7.282
7.277
7.263
7.246
7.235
7.223
7.208
5.880
2.443
0.000
400MHz
CDCl3
4u
2.01
1.00
1.00
3.05
6.01
2.02
7.07
0.99
3.04

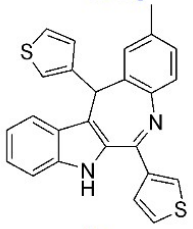

155.93
130.40
128.70
128.32
128.01
127.77
127.66
127.58
127.22
127.12
126.43
126.05
125.80
125.61
125.19
125.00
120.56
119.16
111.74
77.32
77.00
76.68
45.47
21.04
155.93
143.64
138.82
132.90
132.79
131.98
130.40
129.56
129.38
128.70
128.32
128.01
127.77
127.66
127.58
127.22
127.12
127.00
126.43
126.22
126.05
125.80
125.61
125.19
119.16
111.74
156
152
148
144
140
136
132
128
124
120
116
112
100MHz
CDCl3
4u
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.363
7.879
7.859
7.509
7.502
7.472
7.460
7.406
7.386
7.323
7.309
7.249
7.221
7.151
7.130
7.112
7.102
6.900
6.889
6.656
6.647
6.636
2.390
0.000


400MHz
CDCl3
4v
1.00
1.00
1.99
1.00
2.06
2.04
2.02
0.96
0.99
0.96
1.00
2.99
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

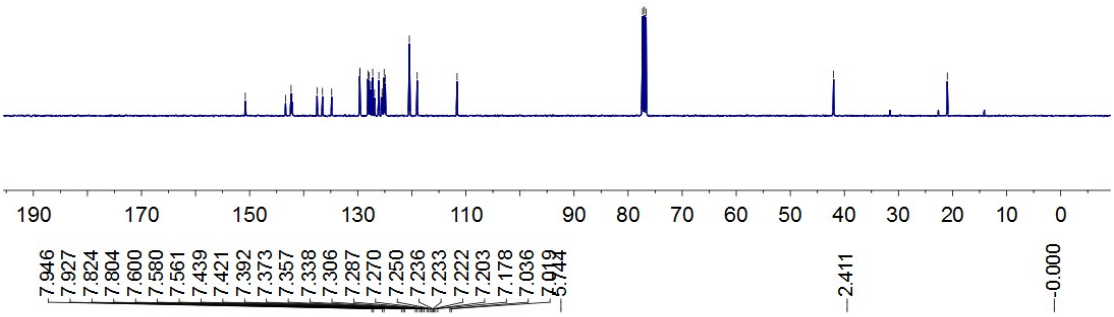

149.49
146.22
145.15
142.94
137.61
136.48
134.79
129.69
129.40
129.36
128.19
127.76
126.38
126.21
125.26
125.07
124.85
124.35
123.71
120.63
118.95
111.69
77.32
77.00
76.68
41.70
20.98
100MHz
CDCl3
S
N
N
H
S
4v
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.169
7.890
7.870
7.700
7.594
7.582
7.422
7.402
7.347
7.340
7.329
7.279
7.264
7.242
7.216
7.146
7.127
6.990
6.982
6.972
6.666
6.654
2.388
0.000


400MHz
CDCl3
S
N
N
H
S
4w
1.00
0.98
0.98
0.99
1.02
5.07
1.01
0.99
0.99
0.96
0.99
3.01
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

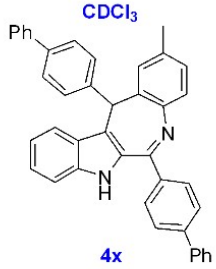
100MHz
$CDCl_3$



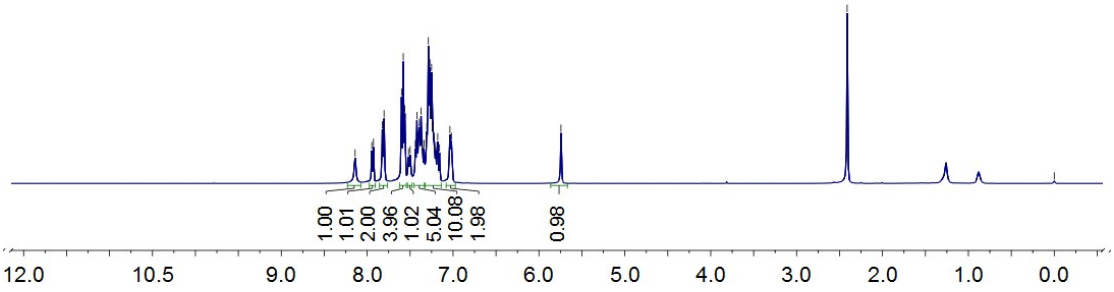
4w

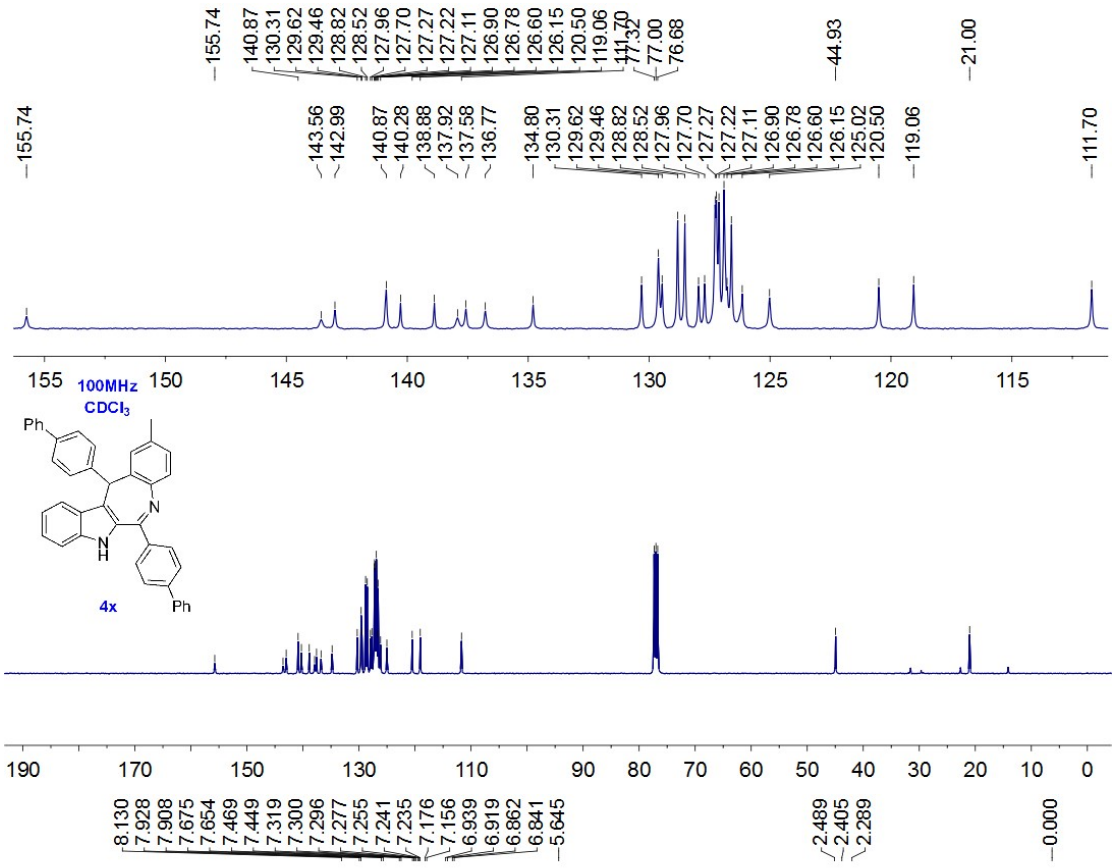


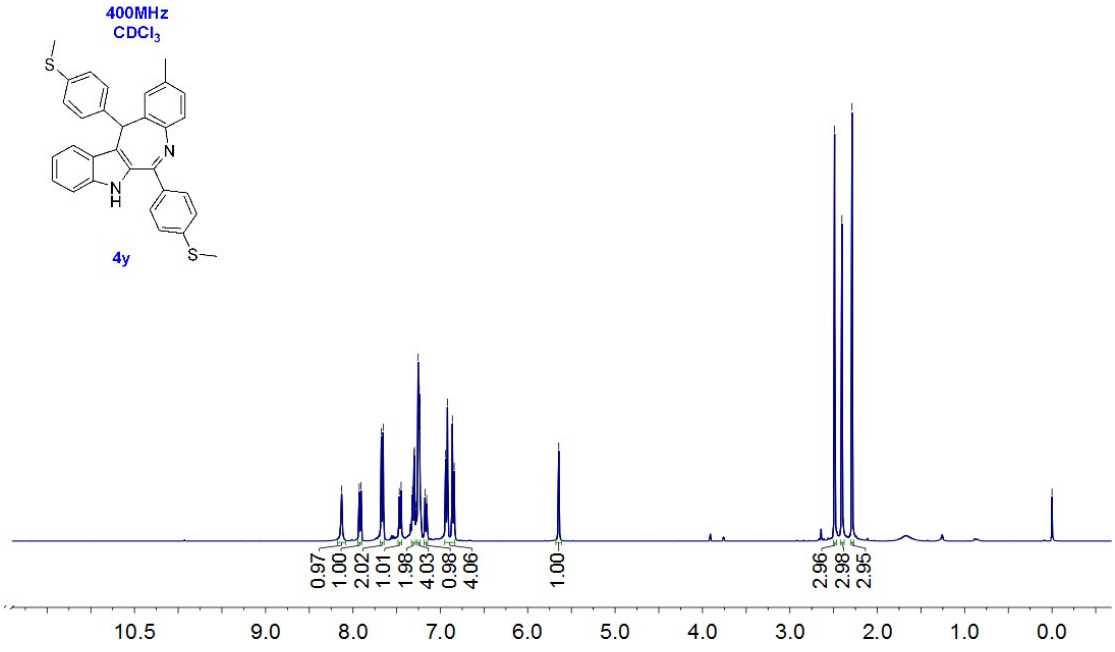
400MHz
$CDCl_3$

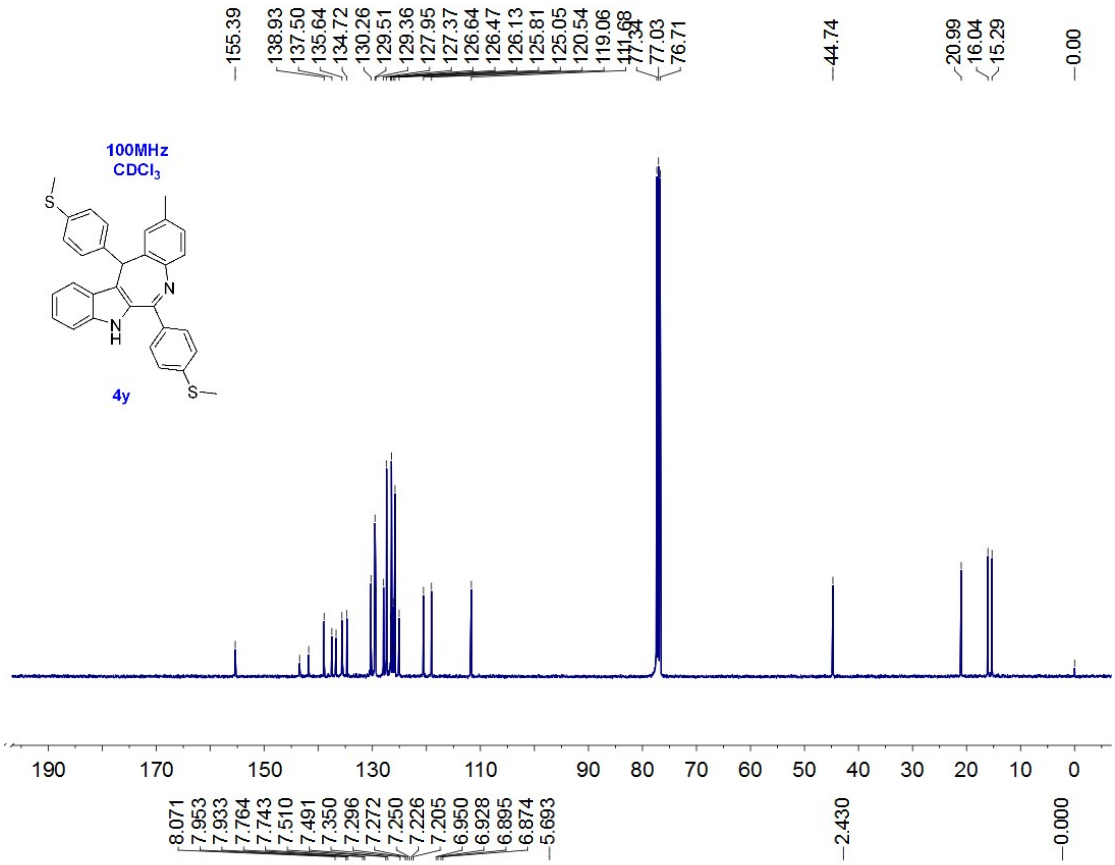


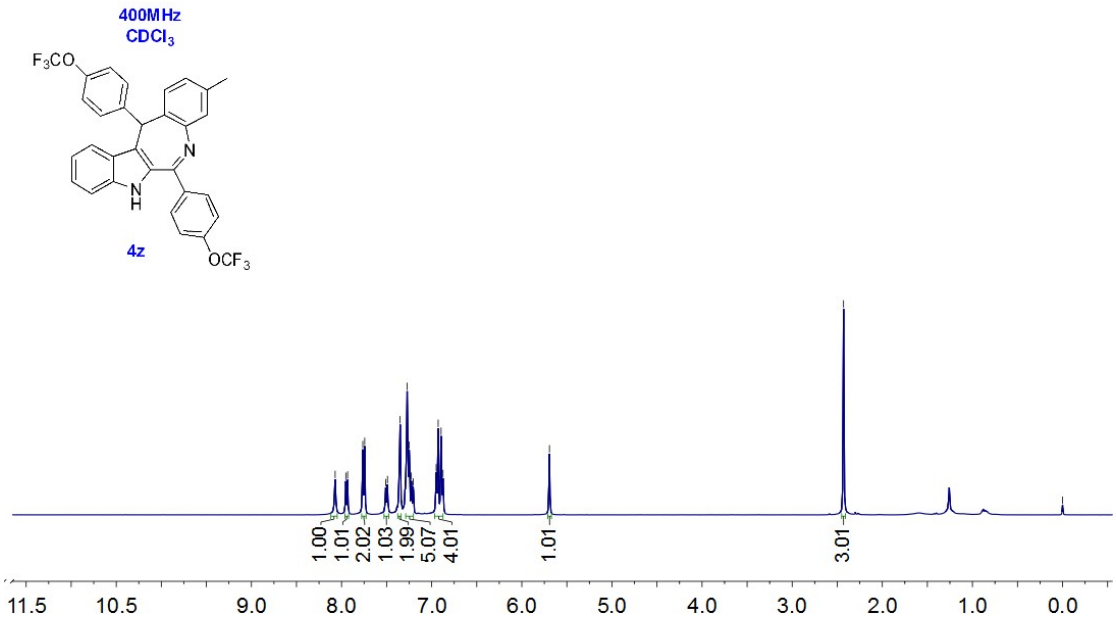
4x

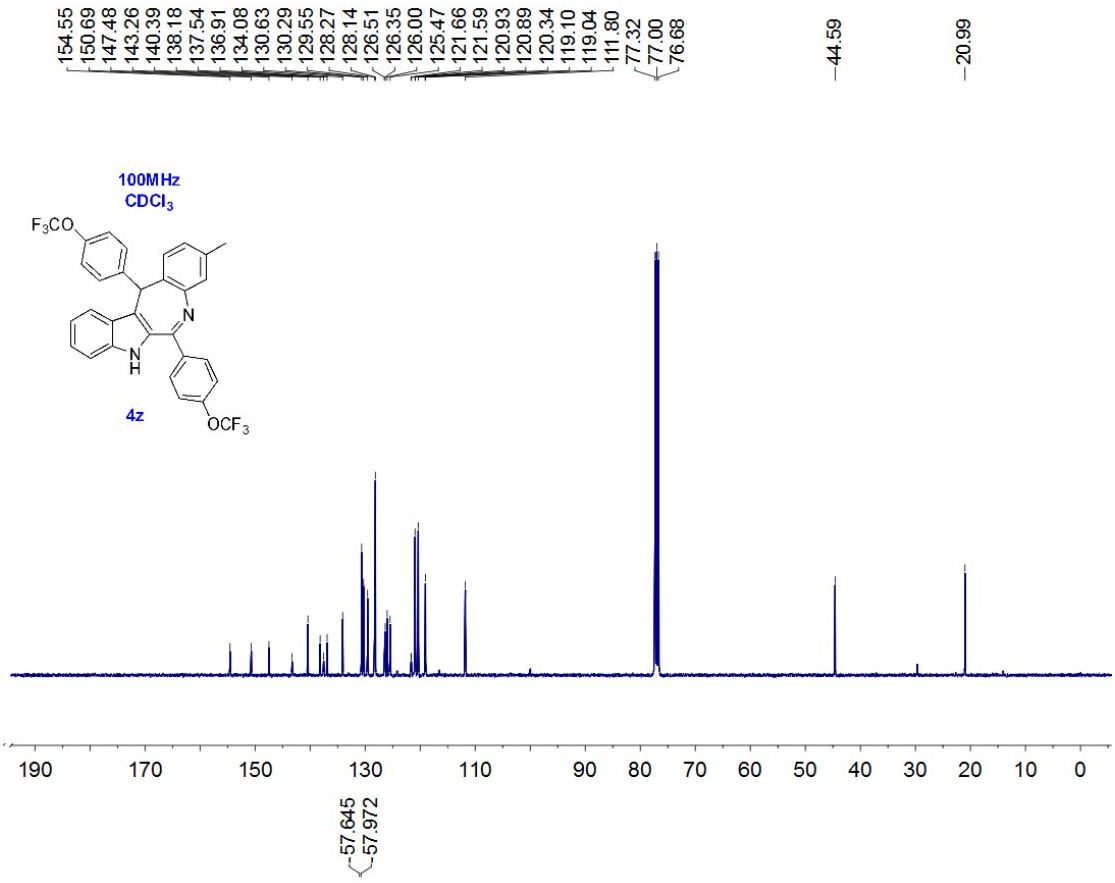


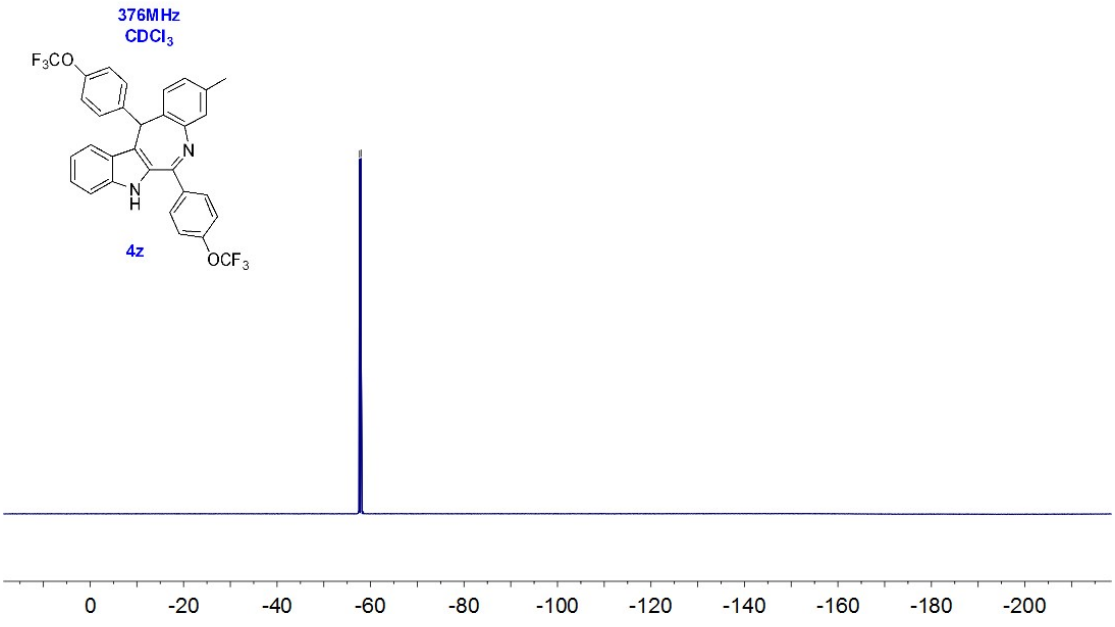

155.74
140.87
130.31
129.62
129.46
128.82
128.52
127.96
127.70
127.27
127.22
127.11
126.90
126.78
126.60
126.15
120.50
119.06
111.70
77.32
77.00
76.68
44.93
21.00
155.74
143.56
142.99
140.87
140.28
138.88
137.92
137.58
136.77
134.80
130.31
129.62
129.46
128.82
128.52
127.96
127.70
127.27
127.22
127.11
126.90
126.78
126.60
126.15
125.02
120.50
119.06
111.70
155
150
145
140
135
130
125
120
115
100MHz
CDCl3
Ph
N
H
Ph
4x
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.130
7.928
7.908
7.675
7.654
7.469
7.449
7.319
7.300
7.296
7.277
7.255
7.241
7.235
7.176
7.156
6.939
6.919
6.862
6.841
5.645
2.489
2.405
2.289
0.000

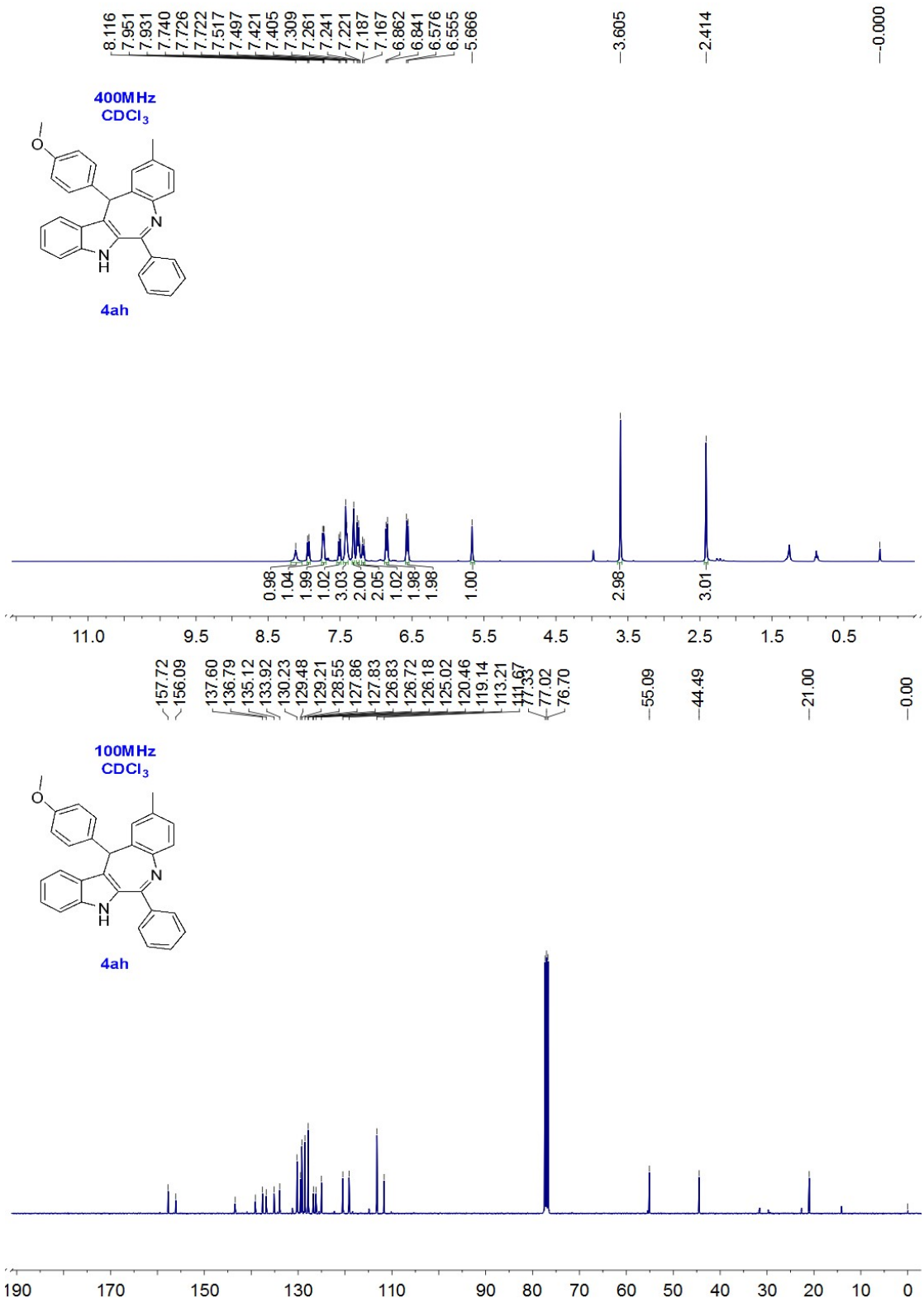

400MHz
CDCl3
S
N
H
S
4y
0.97
1.00
2.02
1.01
1.98
4.03
0.98
4.06
1.00
2.96
2.98
2.95
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

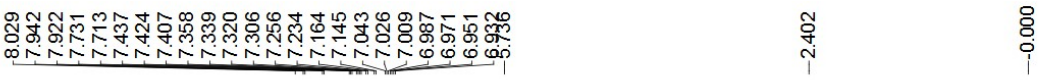

155.39
138.93
137.50
135.64
134.72
130.26
129.51
129.36
127.95
127.37
126.64
126.47
126.13
125.81
125.05
120.54
119.06
111.68
77.34
77.03
76.71
44.74
20.99
16.04
15.29
0.00
100MHz
CDCl3
4y
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.071
7.953
7.933
7.764
7.743
7.510
7.491
7.350
7.296
7.272
7.250
7.226
7.205
6.950
6.928
6.895
6.874
5.693
2.430
0.000
400MHz
CDCl3
F3CO
OCF3
4z
1.00
1.01
2.02
1.03
1.99
5.07
4.01
1.01
3.01
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

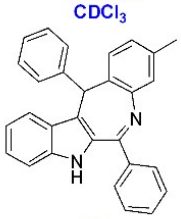

154.55
150.69
147.48
143.26
140.39
138.18
137.54
136.91
134.08
130.63
130.29
129.55
128.27
128.14
126.51
126.35
126.00
125.47
121.66
121.59
120.93
120.89
120.34
119.10
119.04
111.80
77.32
77.00
76.68
44.59
20.99
100MHz
CDCl3
F3CO
N
H
4z
OCF3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


-57.645
-57.972
376MHz
CDCl3
F3CO
N
H
4z
OCF3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

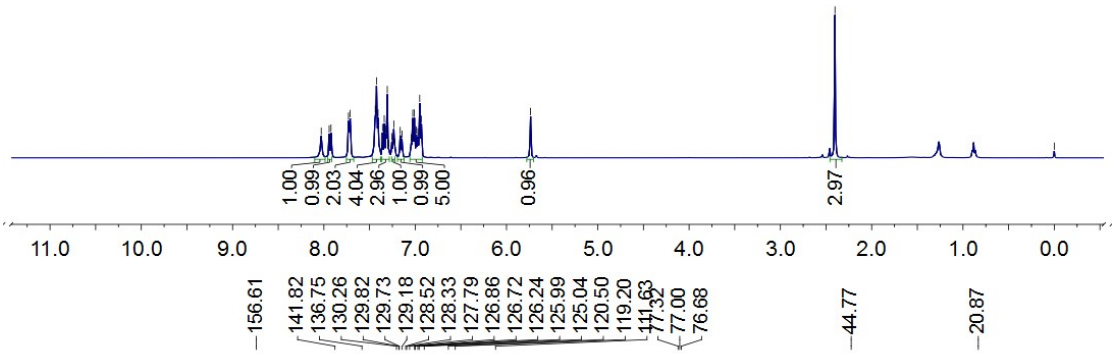

8.116
7.951
7.931
7.740
7.726
7.722
7.517
7.497
7.421
7.405
7.309
7.261
7.241
7.221
7.187
7.167
6.862
6.841
6.576
6.555
5.666
3.605
2.414
0.000
400MHz
CDCl3
4ah
0.98
1.04
1.99
1.02
3.03
2.00
2.05
1.02
1.98
1.98
1.00
2.98
3.01
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
157.72
156.09
137.60
136.79
135.12
133.92
130.23
129.48
129.21
128.55
127.86
127.83
126.83
126.72
126.18
125.02
120.46
119.14
113.21
111.67
77.33
77.02
76.70
55.09
44.49
21.00
0.00
100MHz
CDCl3
4ah
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



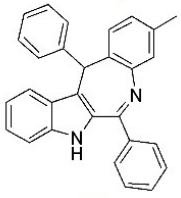
400MHz
$CDCl_3$



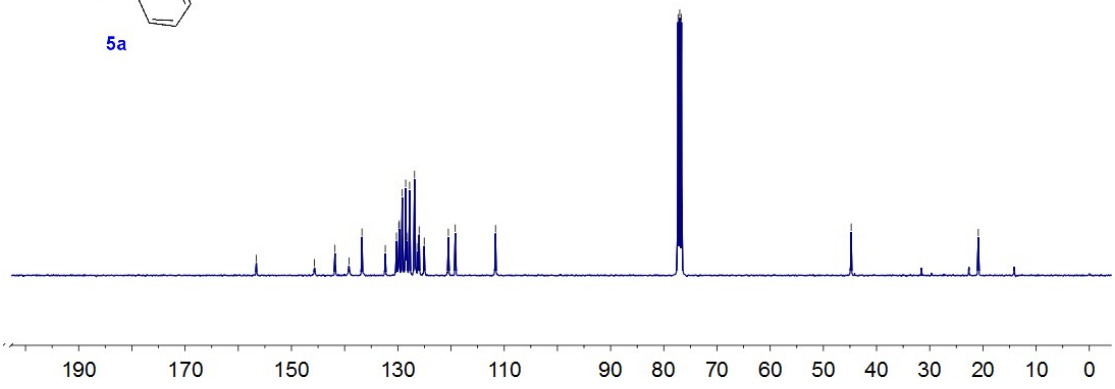
5a

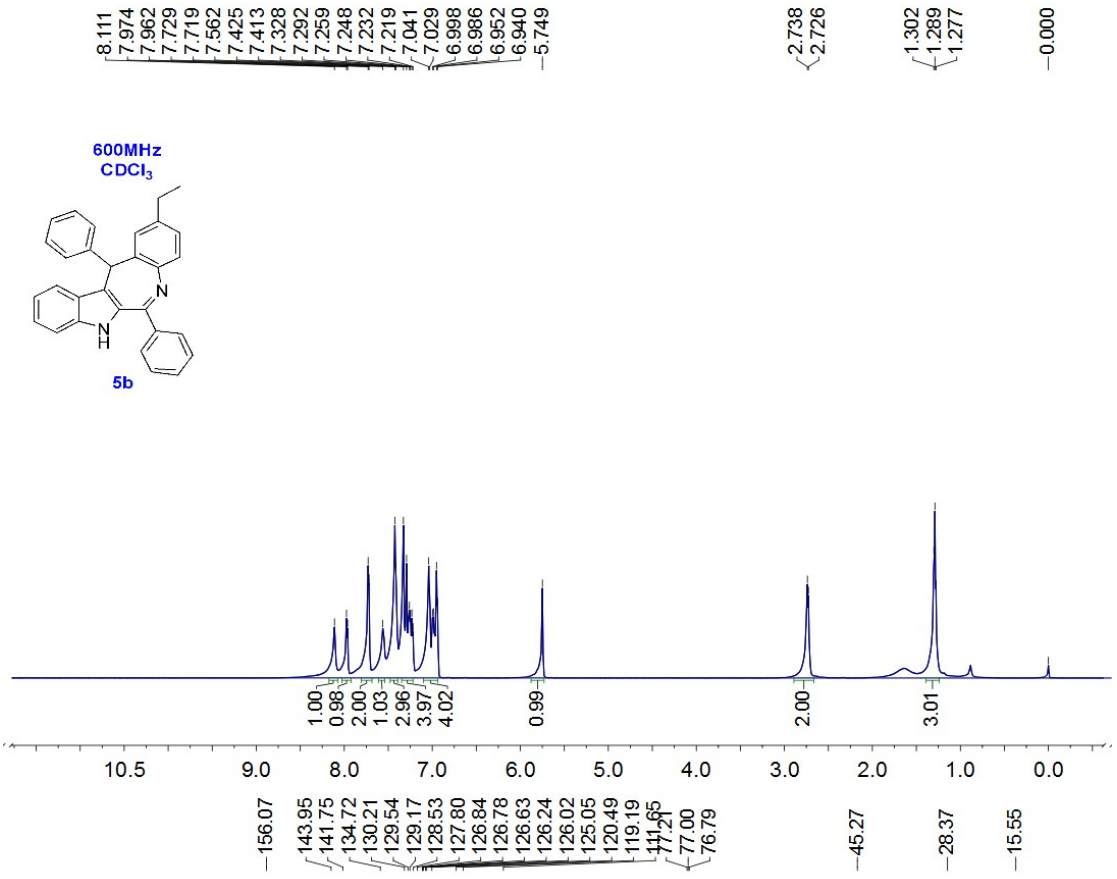


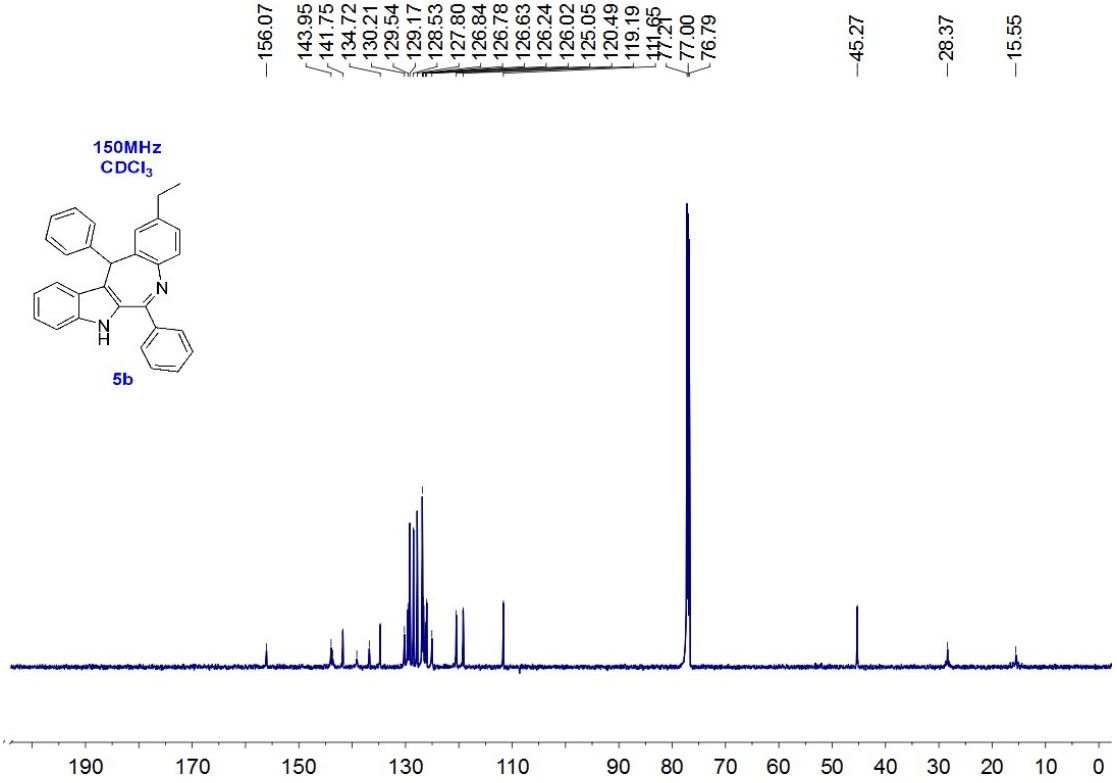
100MHz
$CDCl_3$

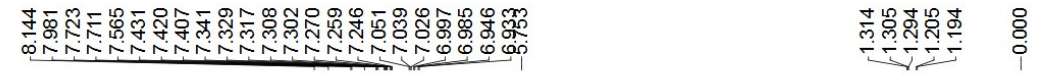


5a

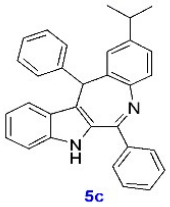



8.111
7.974
7.962
7.729
7.719
7.562
7.425
7.413
7.328
7.292
7.259
7.248
7.232
7.219
7.041
7.029
6.998
6.986
6.952
6.940
5.749
2.738
2.726
1.302
1.289
1.277
0.000
600MHz
CDCl3
5b
1.00
0.98
2.00
1.03
2.96
3.97
4.02
0.99
2.00
3.01
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

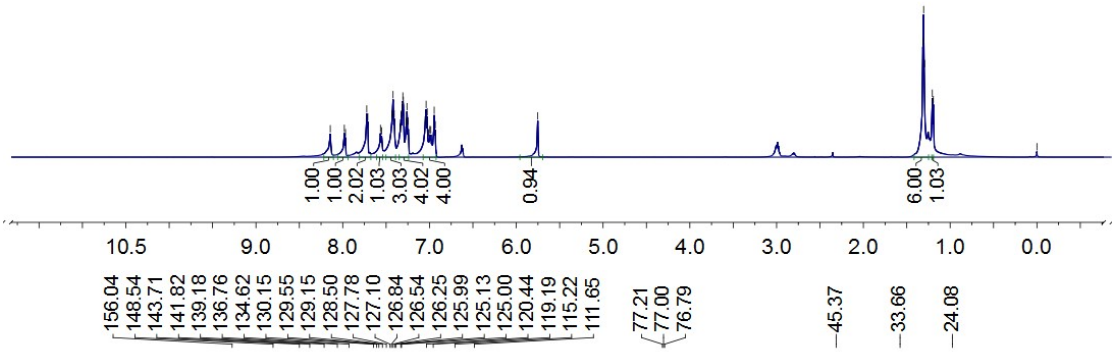

156.07
143.95
141.75
134.72
130.21
129.54
129.17
128.53
127.80
126.84
126.78
126.63
126.24
126.02
125.05
120.49
119.19
111.65
77.21
77.00
76.79
45.27
28.37
15.55
150MHz
CDCl3
5b
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



600MHz
$CDCl_3$



5c



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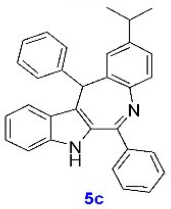

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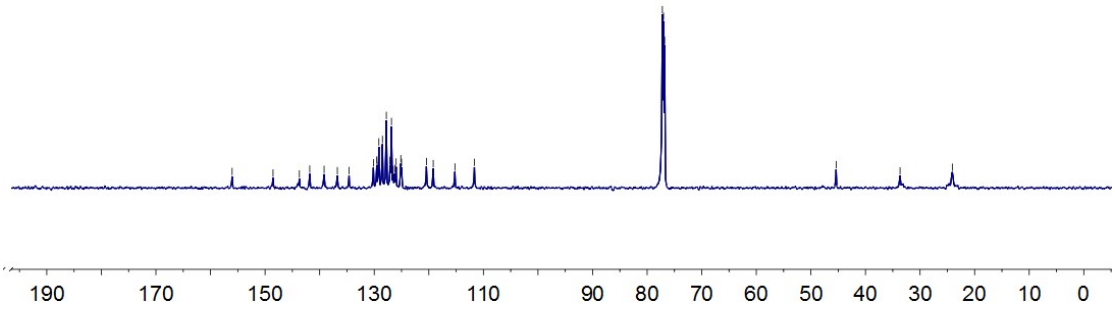

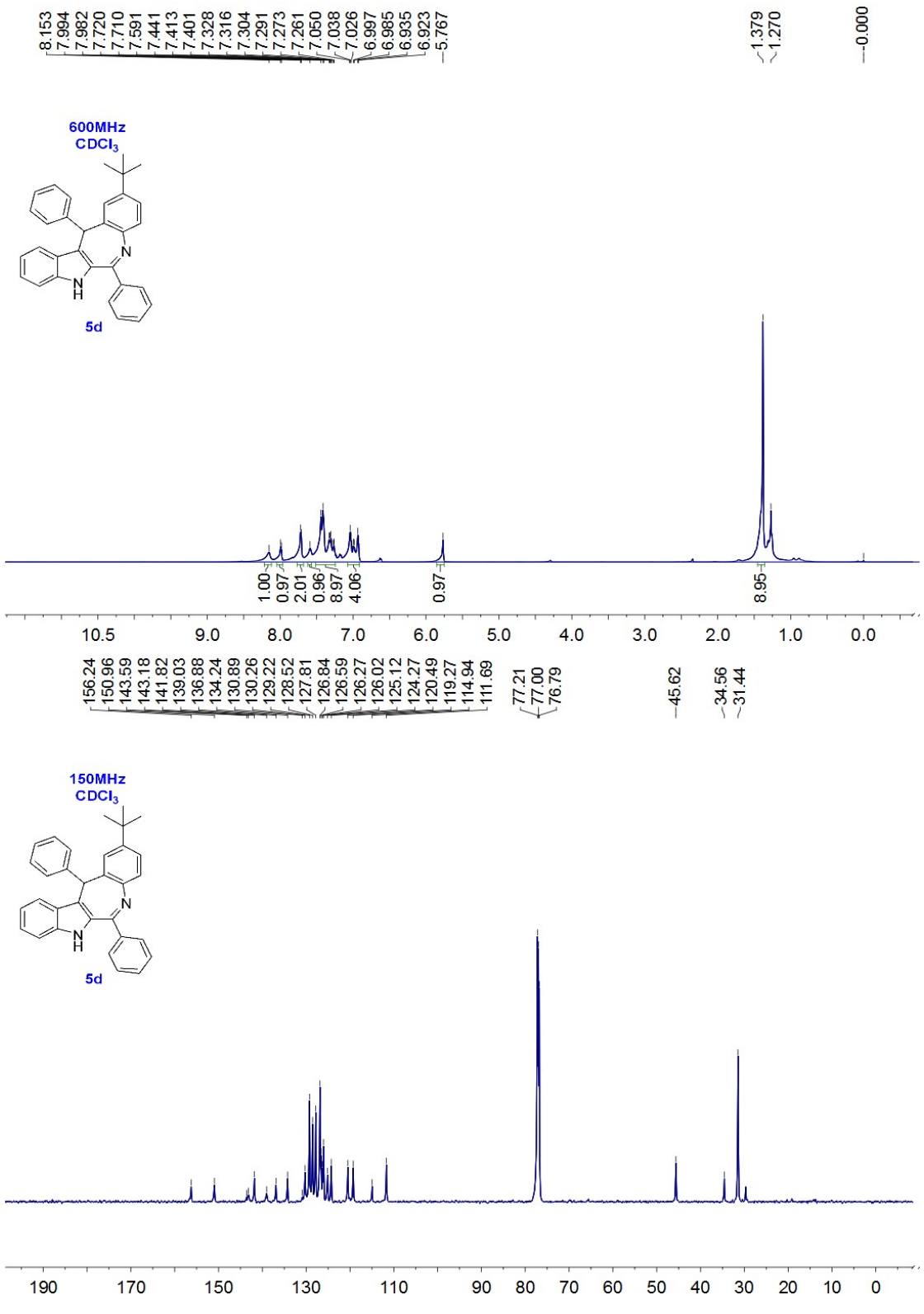
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7.982
7.720
7.710
7.591
7.441
7.413
7.401
7.328
7.316
7.304
7.291
7.273
7.261
7.050
7.038
7.026
6.997
6.985
6.935
6.923
5.767
1.379
1.270
0.000
600MHz
CDCl3
5d
1.00
0.97
2.01
0.96
8.97
4.06
0.97
8.95
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
156.24
150.96
143.59
143.18
141.82
139.03
136.88
134.24
130.89
130.26
129.22
128.52
127.81
126.84
126.59
126.27
126.02
125.12
124.27
120.49
119.27
114.94
111.69
77.21
77.00
76.79
45.62
34.56
31.44
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5d
190
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130
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70
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20
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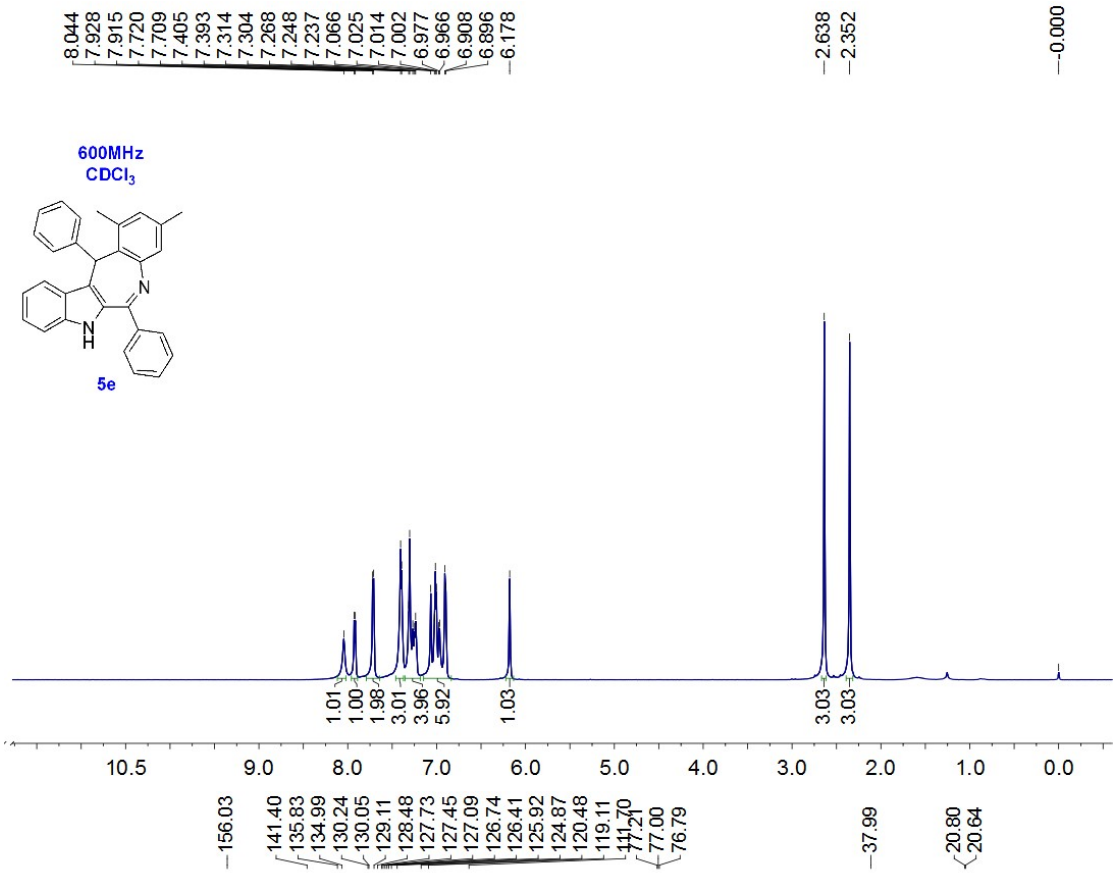
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7.915
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7.393
7.314
7.304
7.268
7.248
7.237
7.066
7.025
7.014
7.002
6.977
6.966
6.908
6.896
6.178
2.638
2.352
0.000
600MHz
CDCl3
5e
1.01
1.00
1.98
3.01
3.96
5.92
1.03
3.03
3.03
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
156.03
141.40
135.83
134.99
130.24
130.05
129.11
128.48
127.73
127.45
127.09
126.74
126.41
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77.00
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37.99
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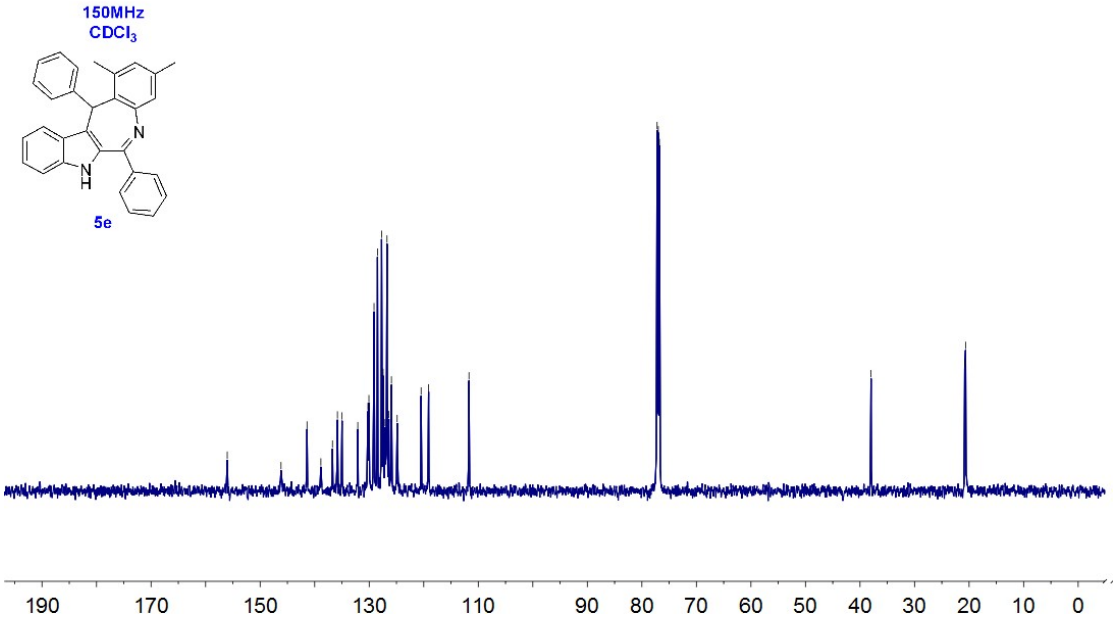
20.64


150MHz
CDCl3
5e
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90
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70
60
50
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30
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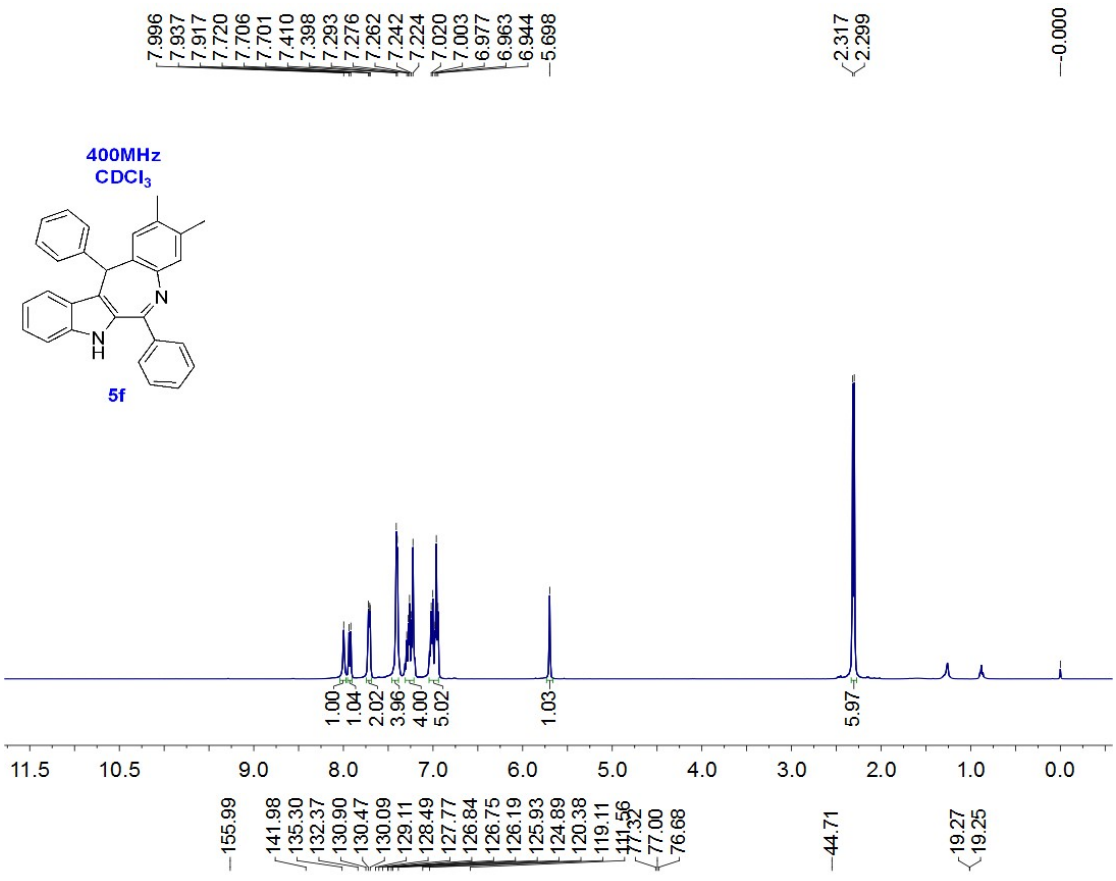
0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7.937
7.917
7.720
7.706
7.701
7.410
7.398
7.293
7.276
7.262
7.242
7.224
7.020
7.003
6.977
6.963
6.944
5.698
2.317
2.299
0.000
400MHz
CDCl3
5f
1.00
1.04
2.02
3.96
4.00
5.02
1.03
5.97
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8.0
7.0
6.0
5.0
4.0
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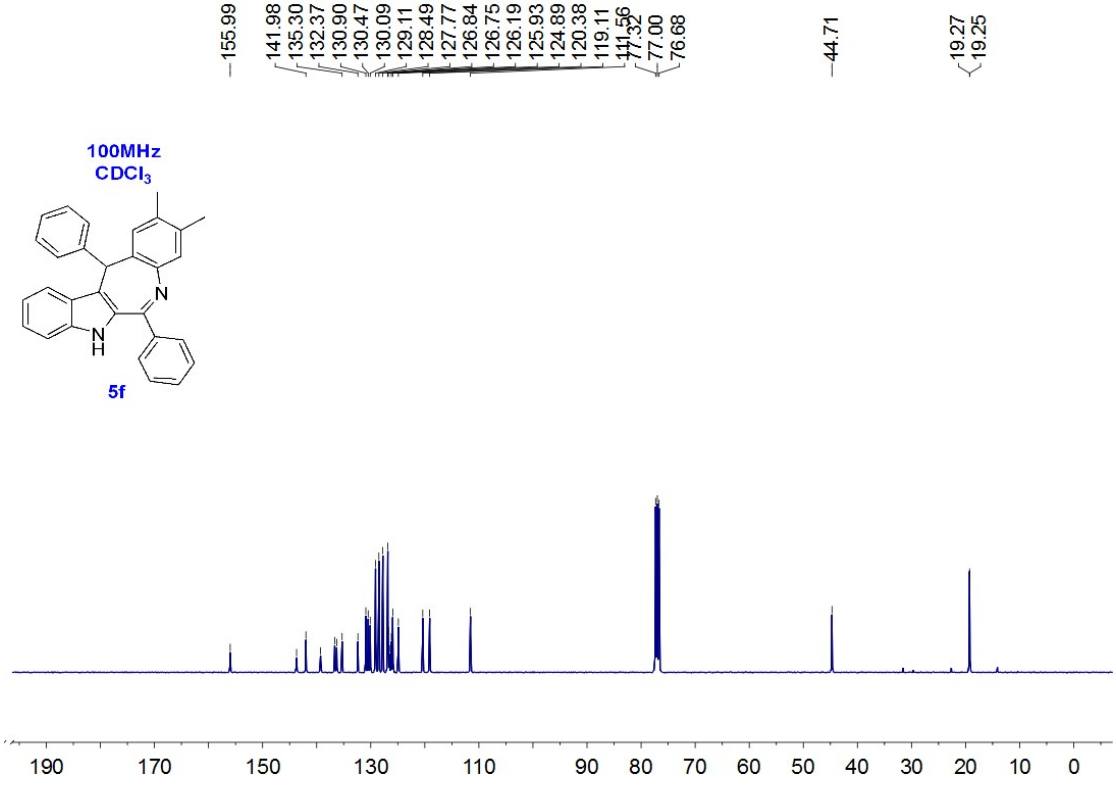
2.0
1.0
0.0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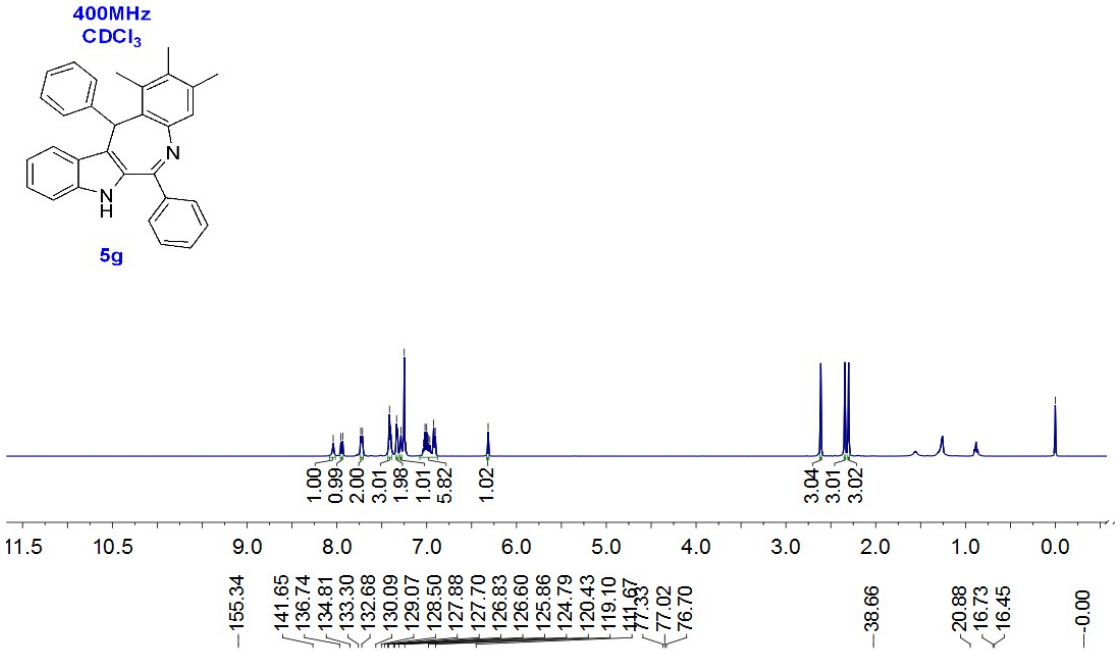
141.98
135.30
132.37
130.90
130.47
130.09
129.11
128.49
127.77
126.84
126.75
126.19
125.93
124.89
120.38
119.11
111.56
77.32
77.00
76.68
44.71
19.27
19.25
100MHz
CDCl3
5f
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.041
7.955
7.935
7.735
7.715
7.414
7.398
7.387
7.335
7.322
7.287
7.250
7.231
7.036
7.019
7.000
6.982
6.965
6.922
6.904
6.316
0.000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CDCl3
N
H
5g
1.00
0.99
2.00
3.01
1.98
1.01
5.82
1.02
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3.01
3.02
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
155.34
141.65
136.74
134.81
133.30
132.68
130.09
129.07
128.50
127.88
127.70
126.83
126.60
125.86
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111.67
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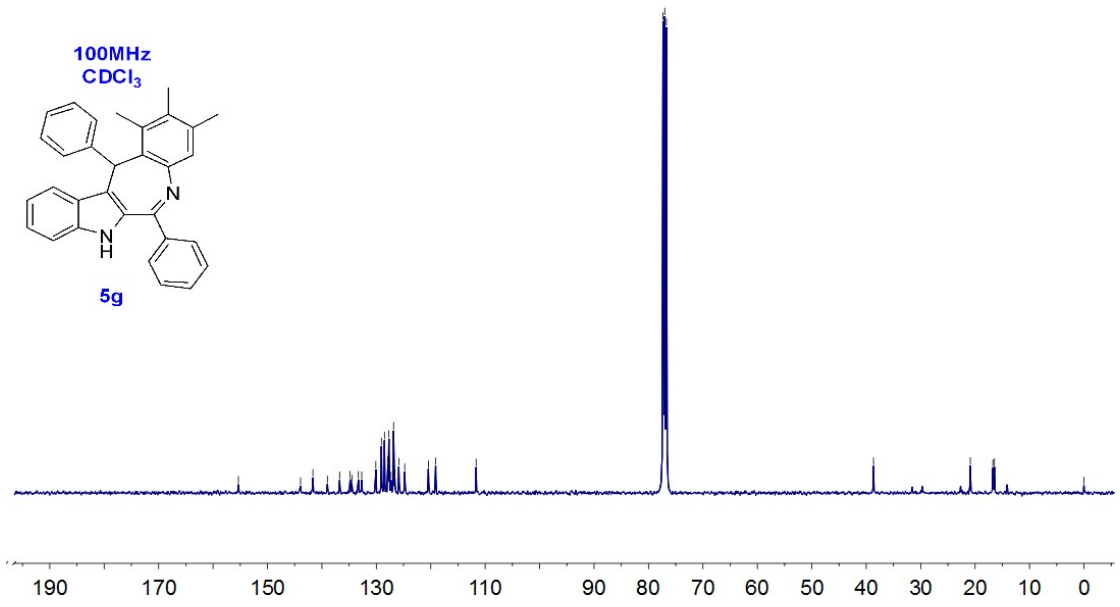
77.02
76.70
38.66
20.88
16.73
16.45
0.00


100MHz
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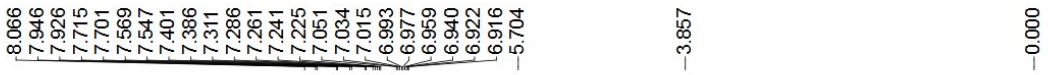
N
H
5g
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.715
7.701
7.569
7.547
7.401
7.386
7.311
7.286
7.261
7.241
7.225
7.051
7.034
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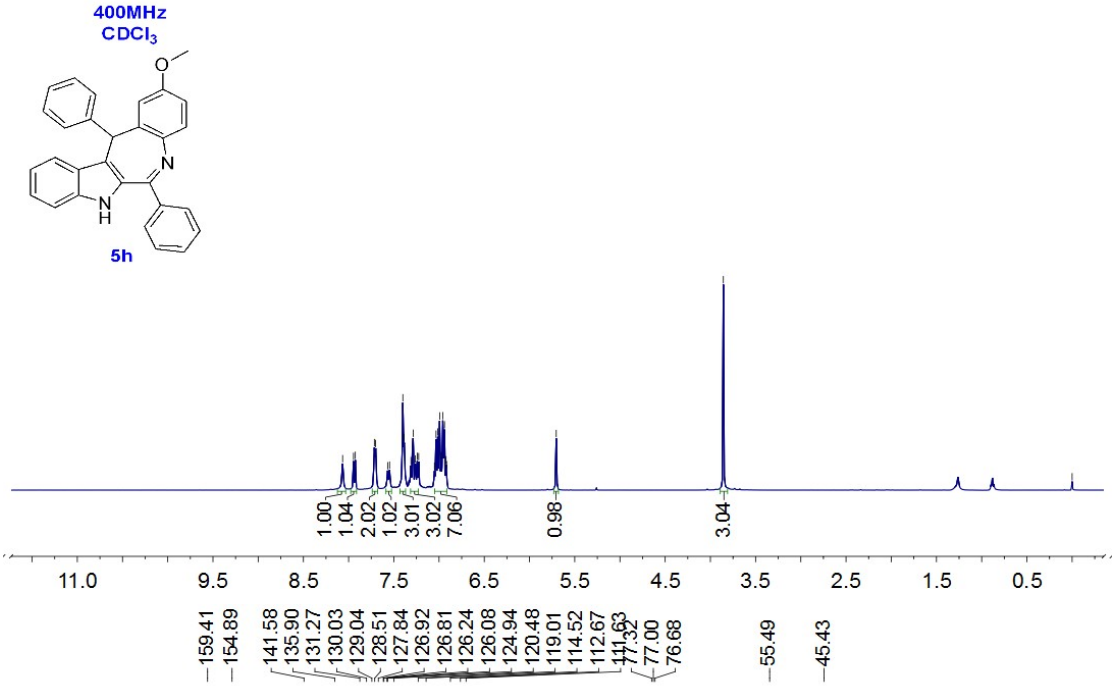
6.977
6.959
6.940
6.922
6.916
5.704
3.857
0.000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O
N
H
5h
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1.04
2.02
1.02
3.01
3.02
7.06
0.98
3.04
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

159.41
154.89
141.58
135.90
131.27
130.03
129.04
128.51
127.84
126.92
126.81
126.24
126.08
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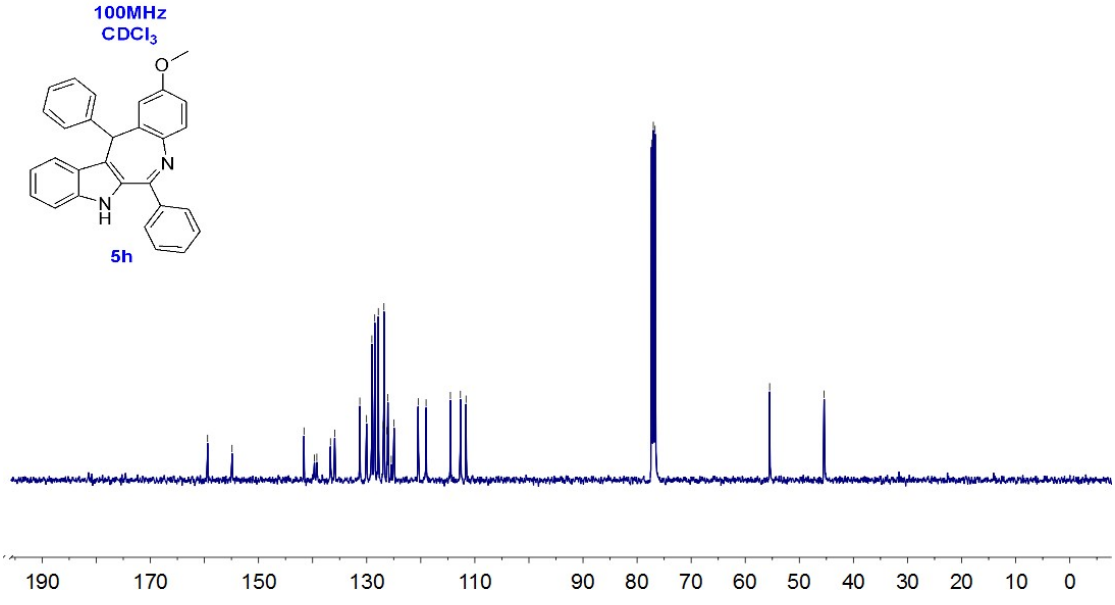
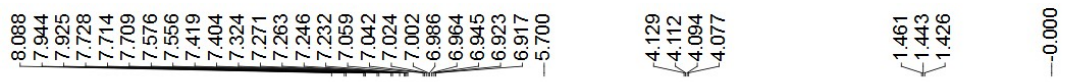
111.63
77.32
77.00
76.68
55.49
45.43


100MHz
CDCl3
O
N
H
5h
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.556
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7.404
7.324
7.271
7.263
7.246
7.232
7.059
7.042
7.024
7.002
6.986
6.964
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6.917
5.700
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4.112
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4.077
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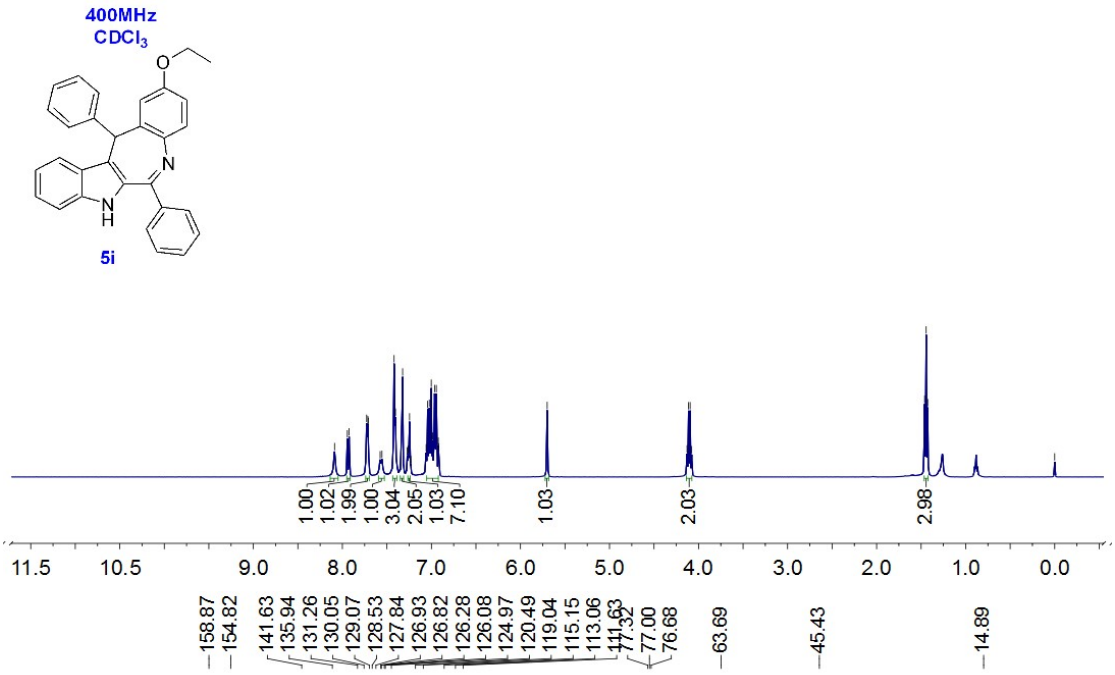
1.443
1.426
0.000


400MHz
CDCl3
O
N
H
5i
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1.02
1.99
1.00
3.04
2.05
1.03
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2.03
2.98
11.5
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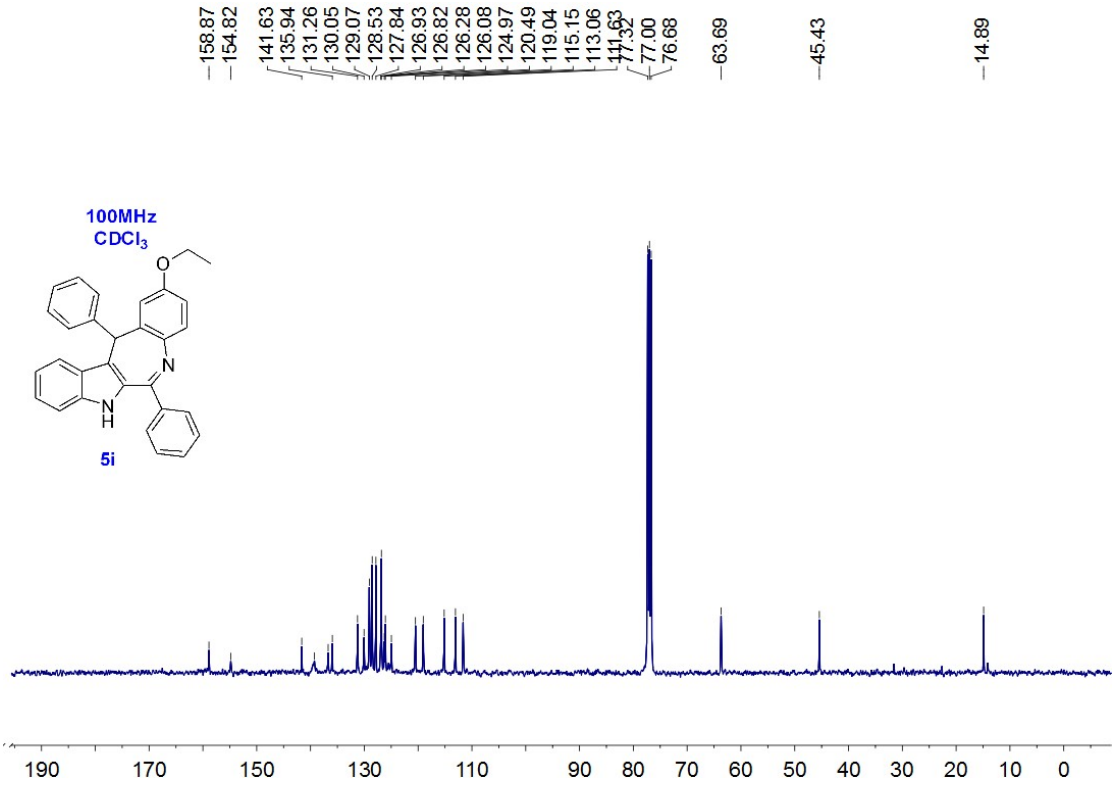
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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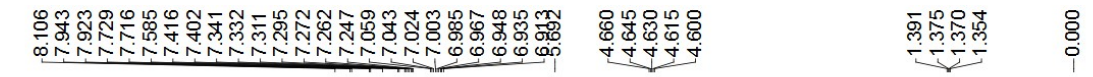
135.94
131.26
130.05
129.07
128.53
127.84
126.93
126.82
126.28
126.08
124.97
120.49
119.04
115.15
113.06
111.63
77.32
77.00
76.68
63.69
45.43
14.89
100MHz
CDCl3
O
N
H
5i
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.402
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7.332
7.311
7.295
7.272
7.262
7.247
7.059
7.043
7.024
7.003
6.985
6.967
6.948
6.935
6.913
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4.615
4.600
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1.370
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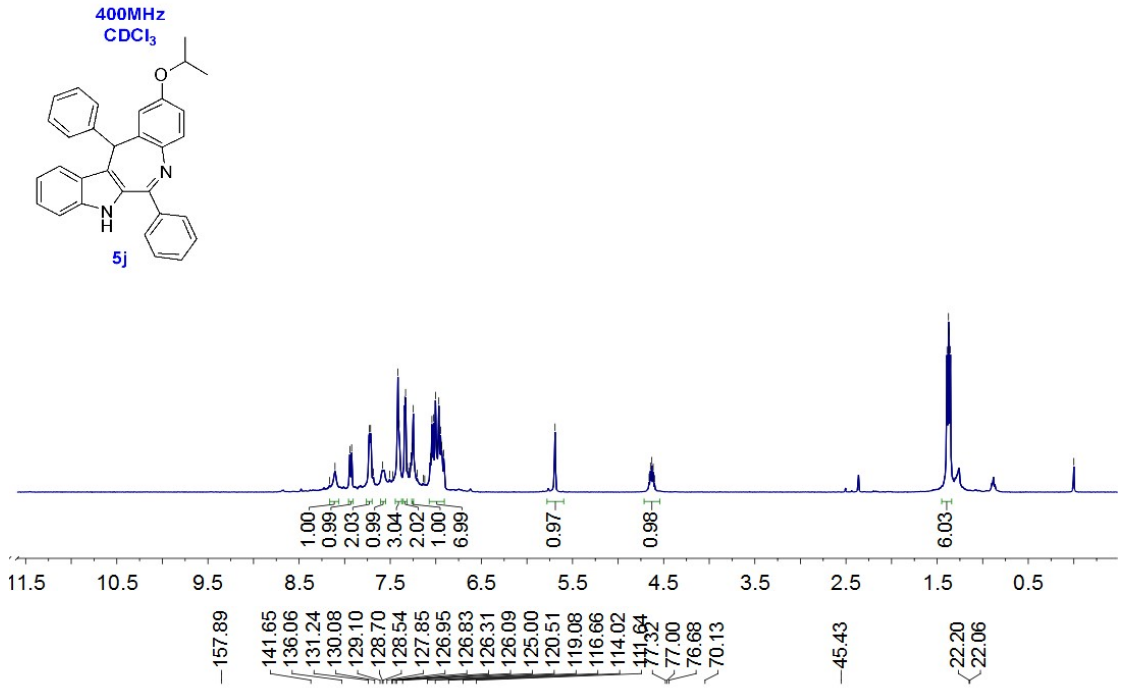
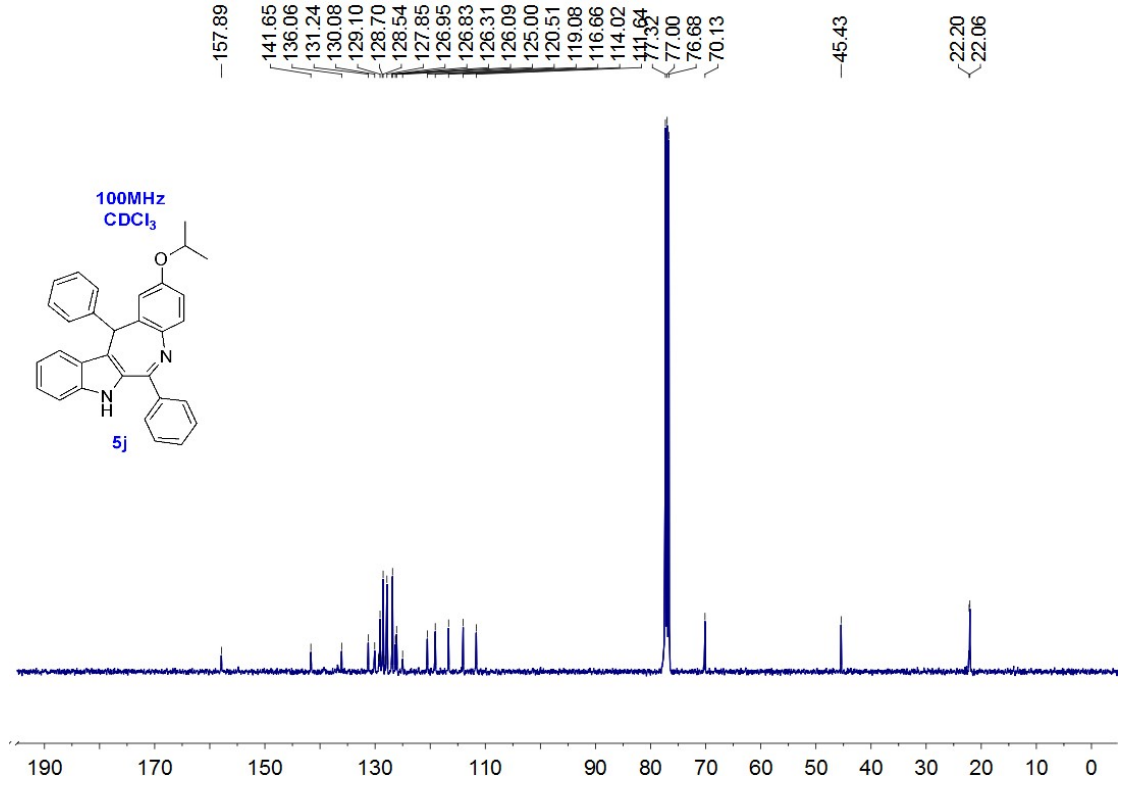
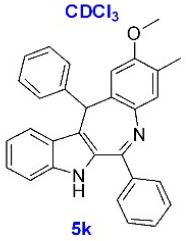
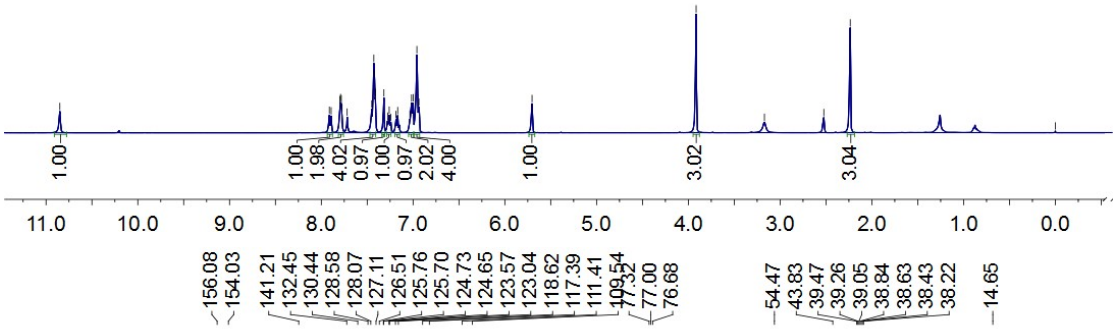

400MHz
CDCl3
O
N
H
5j
1.00
0.99
2.03
0.99
3.04
2.02
1.00
6.99
0.97
0.98
6.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5


157.89
141.65
136.06
131.24
130.08
129.10
128.70
128.54
127.85
126.95
126.83
126.31
126.09
125.00
120.51
119.08
116.66
114.02
111.64
77.32
77.00
76.68
70.13
45.43
22.20
22.06
100MHz
CDCl3
O
N
H
5j
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

400MHz
$CDCl_3$



5k



100MHz
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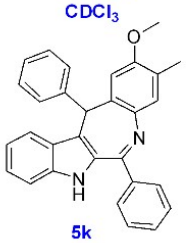
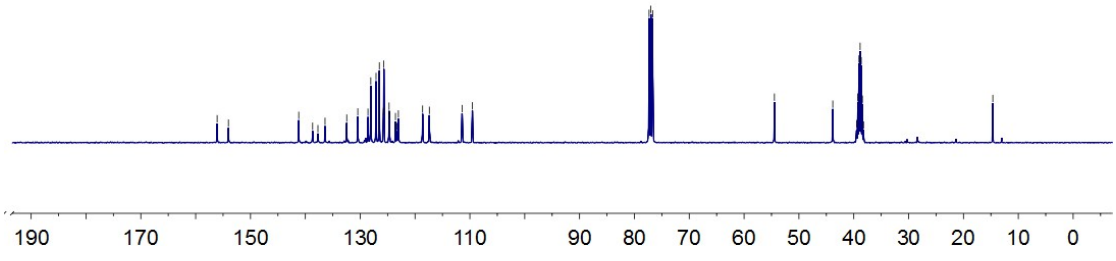


5k



400MHz
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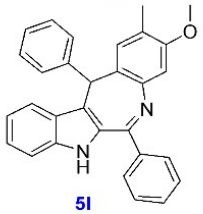
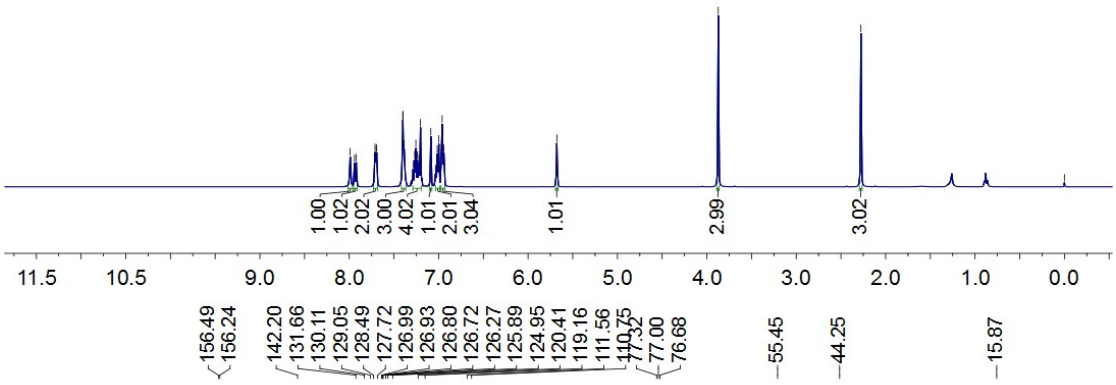


5l



100MHz
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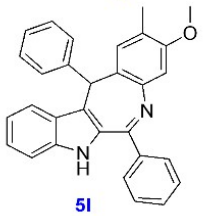
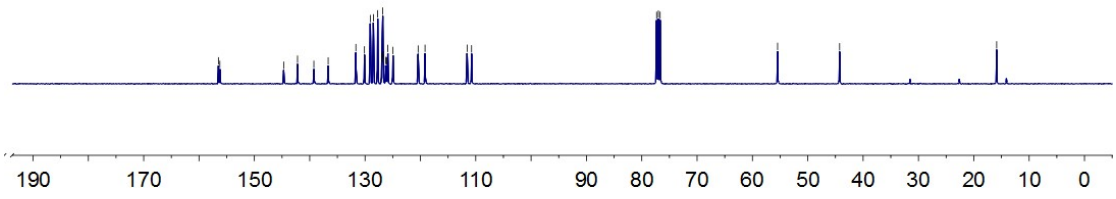
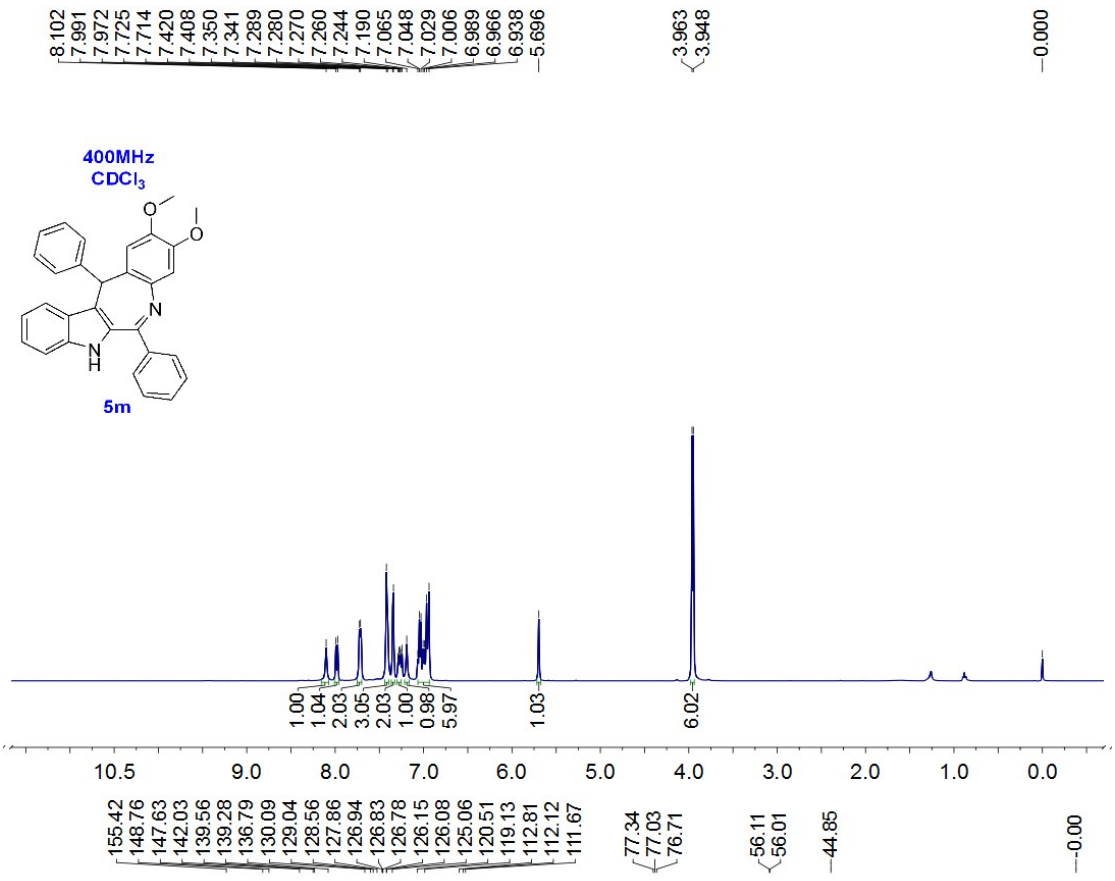


5l

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7.714
7.420
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7.350
7.341
7.289
7.280
7.270
7.260
7.244
7.190
7.065
7.048
7.029
7.006
6.989
6.966
6.938
5.696
3.963
3.948
0.000
400MHz
CDCl3
5m
1.00
1.04
2.03
3.05
2.03
1.00
0.98
5.97
1.03
6.02
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9.0
8.0
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6.0
5.0
4.0
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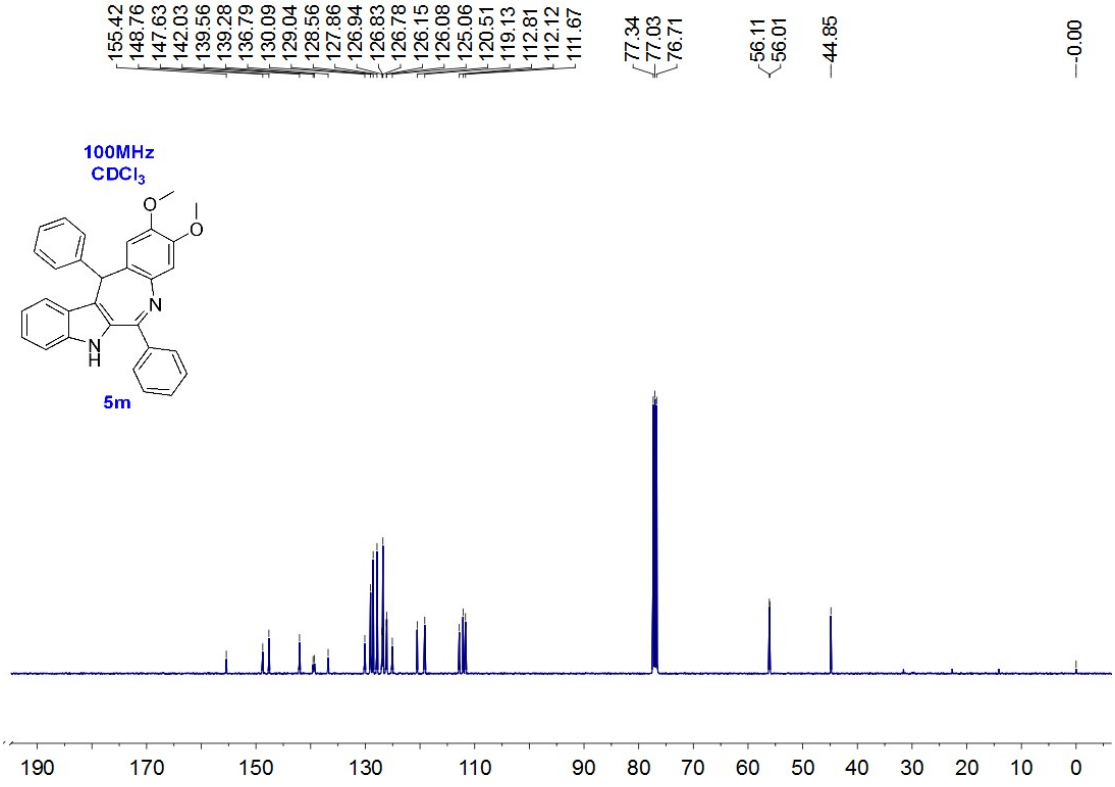
2.0
1.0
0.0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139.28
136.79
130.09
129.04
128.56
127.86
126.94
126.83
126.78
126.15
126.08
125.06
120.51
119.13
112.81
112.12
111.67
77.34
77.03
76.71
56.11
56.01
44.85
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5m
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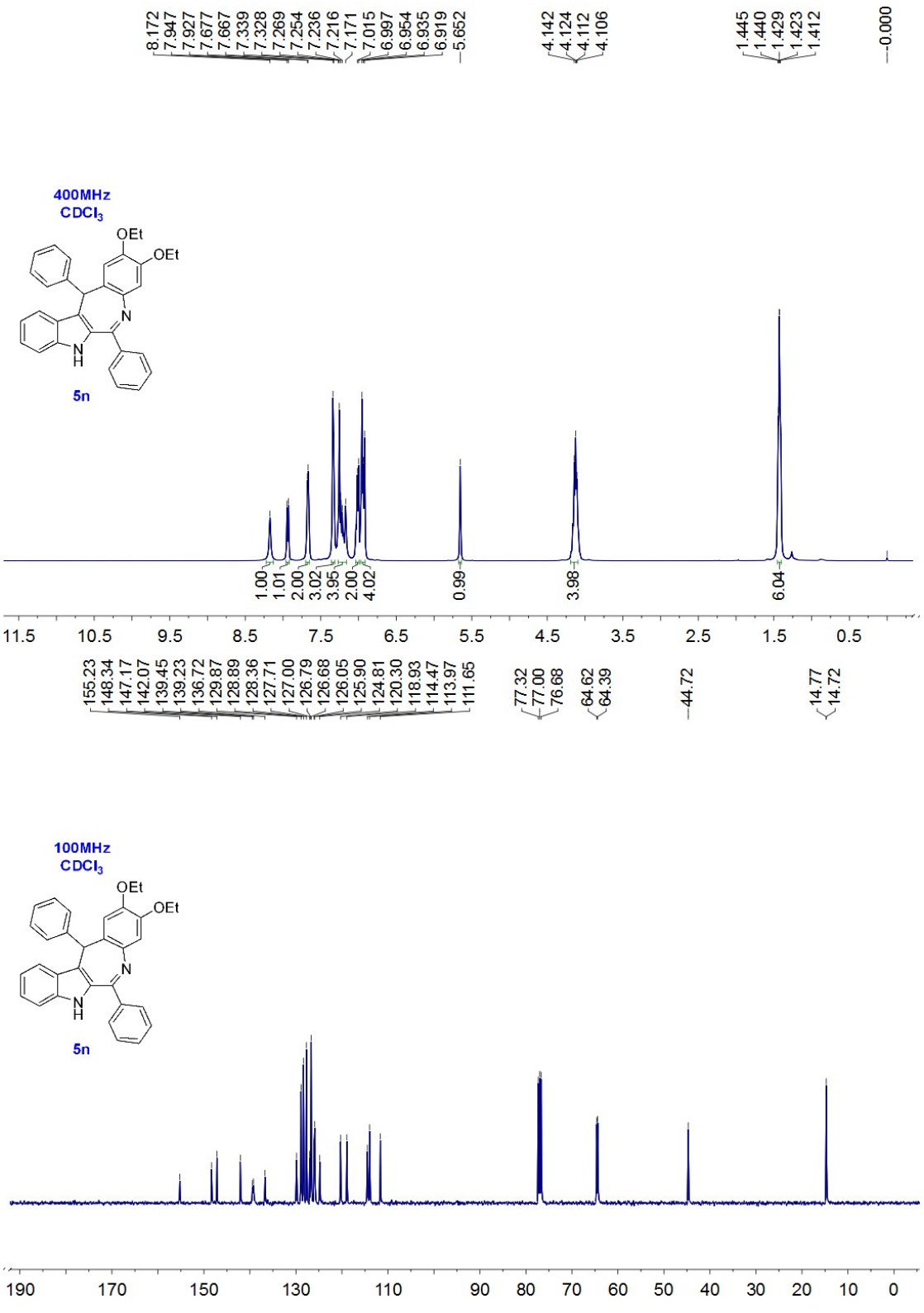
30
20
10
0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7.269
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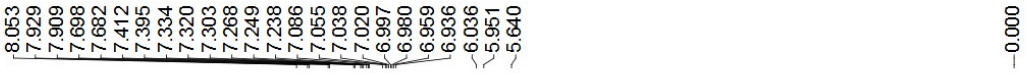
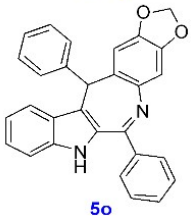
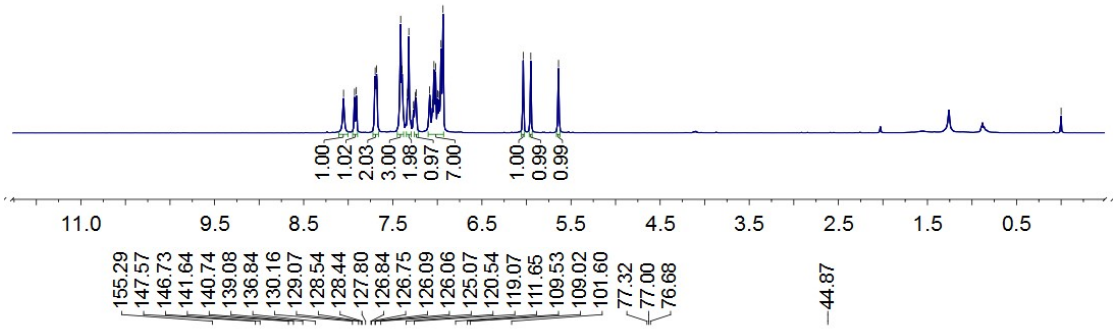
7.236
7.216
7.171
7.015
6.997
6.954
6.935
6.919
5.652
4.142
4.124
4.112
4.106
1.445
1.440
1.429
1.423
1.412
0.000
400MHz
CDCl3
OEt
OEt
N
H
5n
1.00
1.01
2.00
3.02
3.95
2.00
4.02
0.99
3.98
6.04
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
155.23
148.34
147.17
142.07
139.45
139.23
136.72
129.87
128.89
128.36
127.71
127.00
126.79
126.68
126.05
125.90
124.81
120.30
118.93
114.47
113.97
111.65
77.32
77.00
76.68
64.62
64.39
44.72
14.77
14.72
100MHz
CDCl3
OEt
OEt
N
H
5n
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



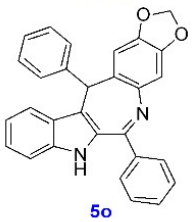
400MHz
$CDCl_3$



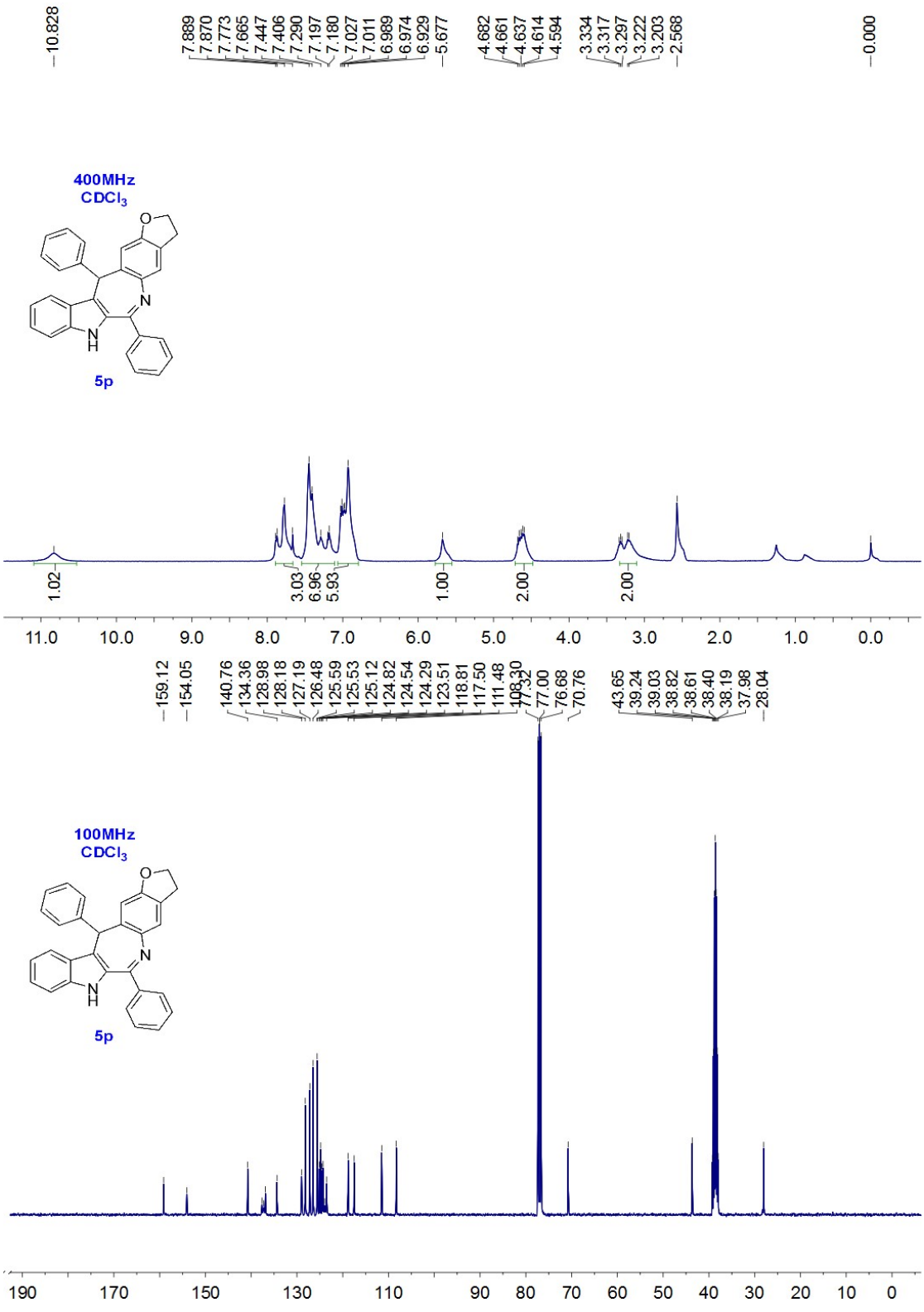
5o

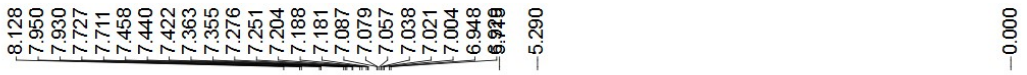


100MHz
$CDCl_3$

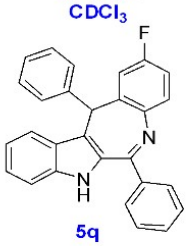


5o

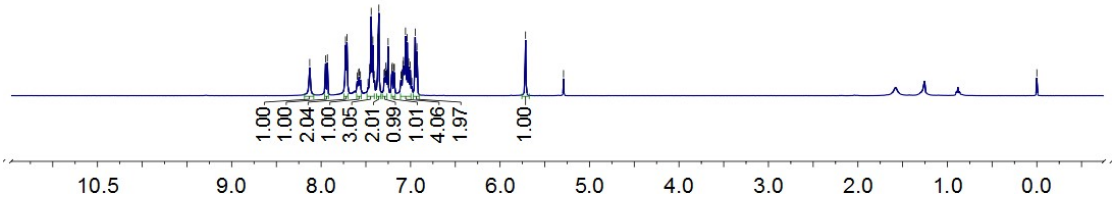

10.828
7.889
7.870
7.773
7.665
7.447
7.406
7.290
7.197
7.180
7.027
7.011
6.989
6.974
6.929
5.677
4.682
4.661
4.637
4.614
4.594
3.334
3.317
3.297
3.222
3.203
2.568
0.000
400MHz
CDCl3
O
N
H
5p
1.02
3.03
6.96
5.93
1.00
2.00
2.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
159.12
154.05
140.76
134.36
128.98
128.18
127.19
126.48
125.59
125.53
125.12
124.82
124.54
124.29
123.51
118.81
117.50
111.48
108.30
77.32
77.00
76.68
70.76
43.65
39.24
39.03
38.82
38.61
38.40
38.19
37.98
28.04
100MHz
CDCl3
O
N
H
5p
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

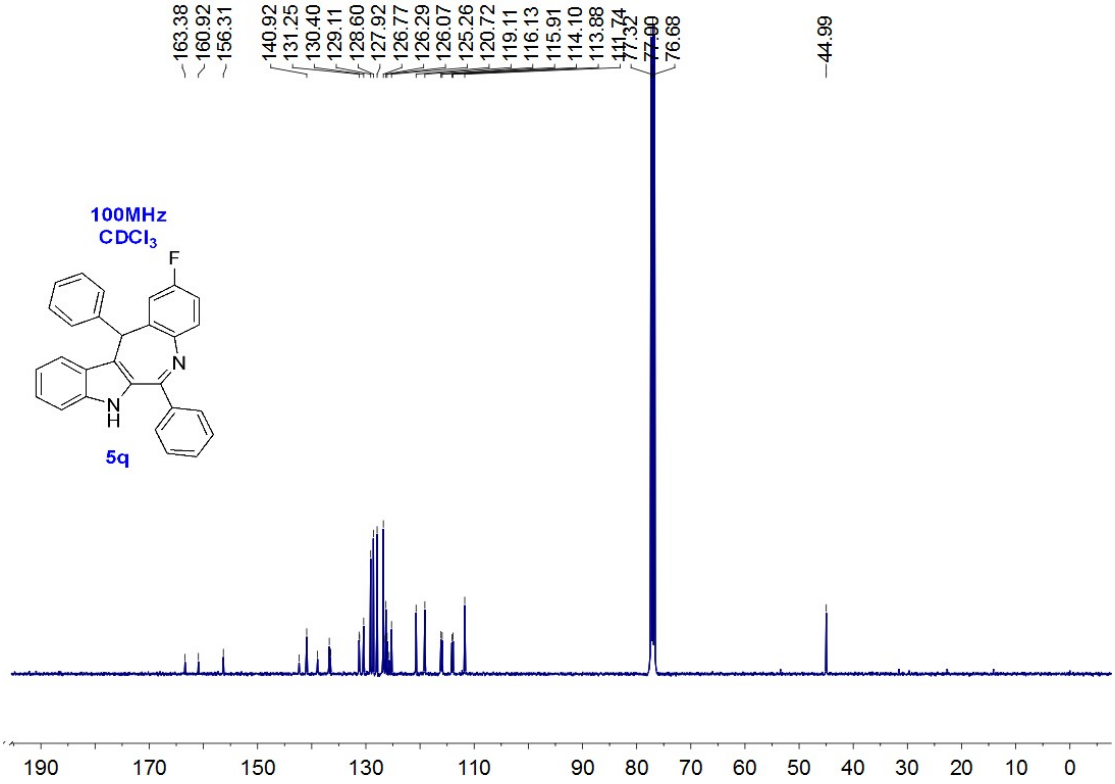


400MHz
$CDCl_3$



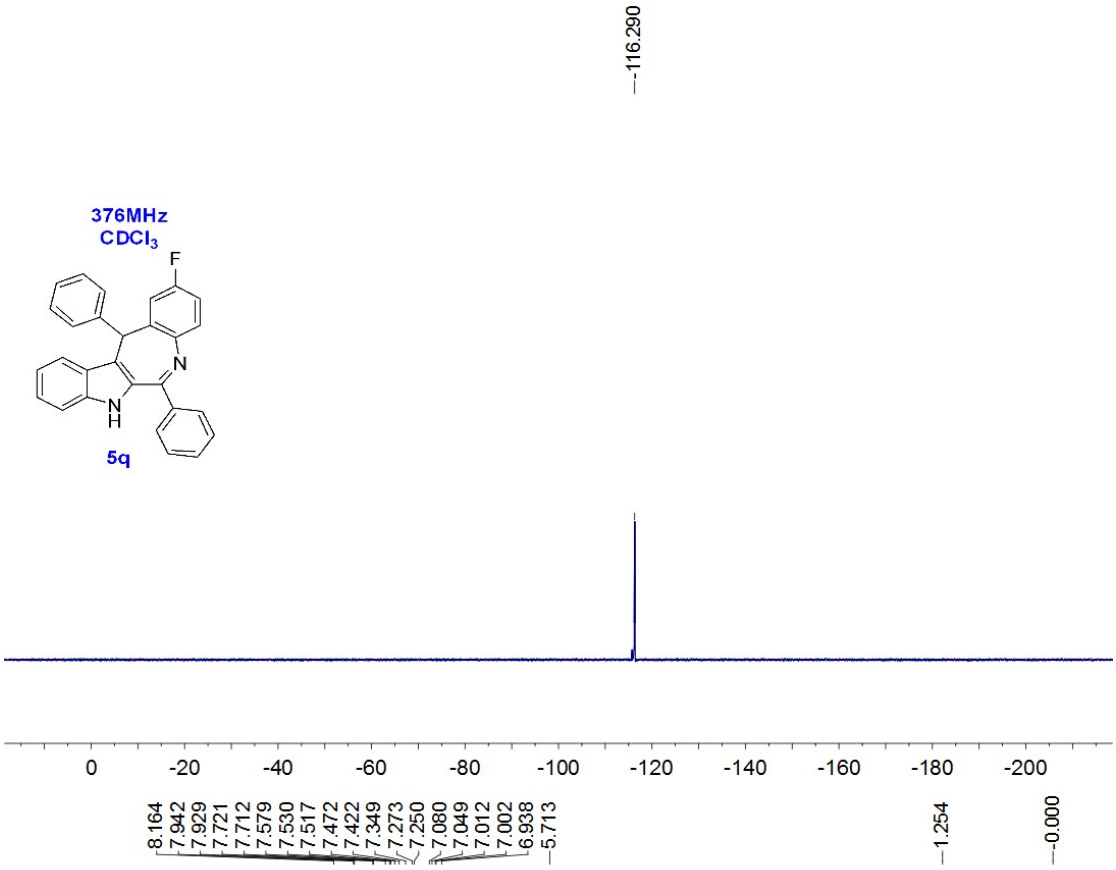
5q

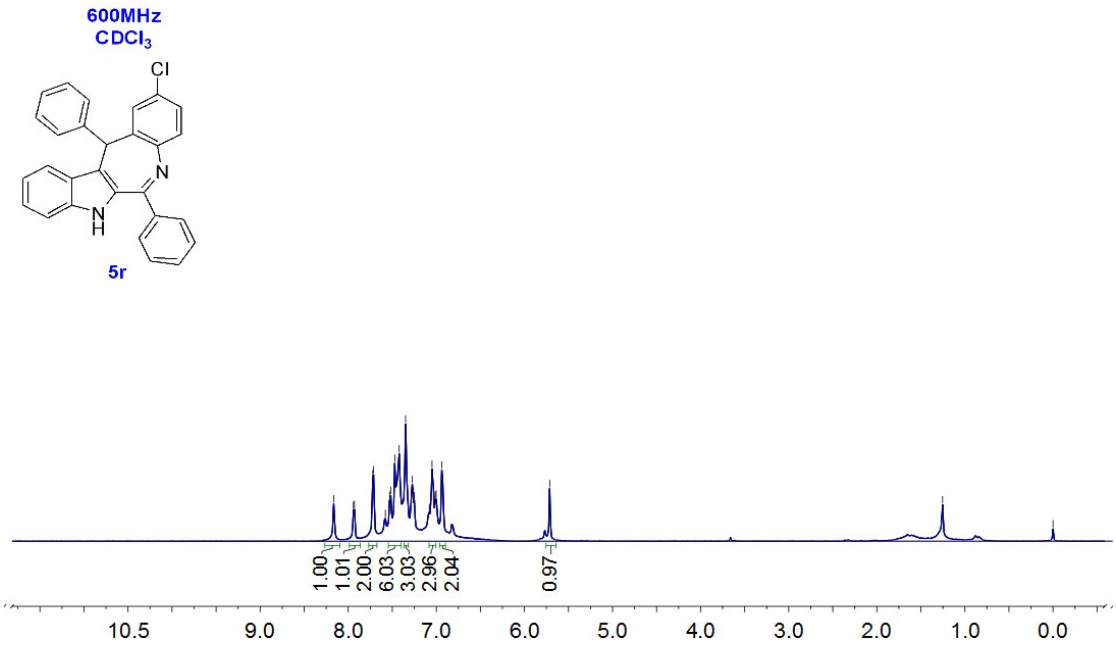


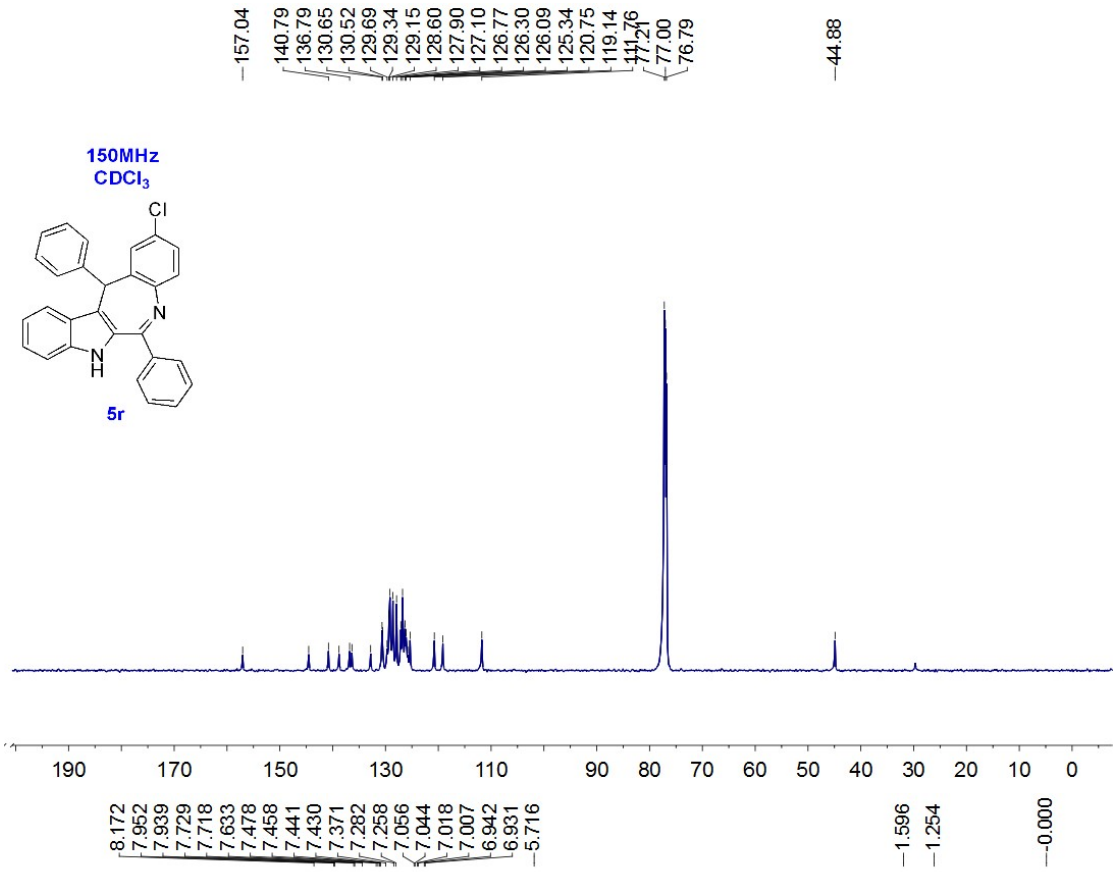


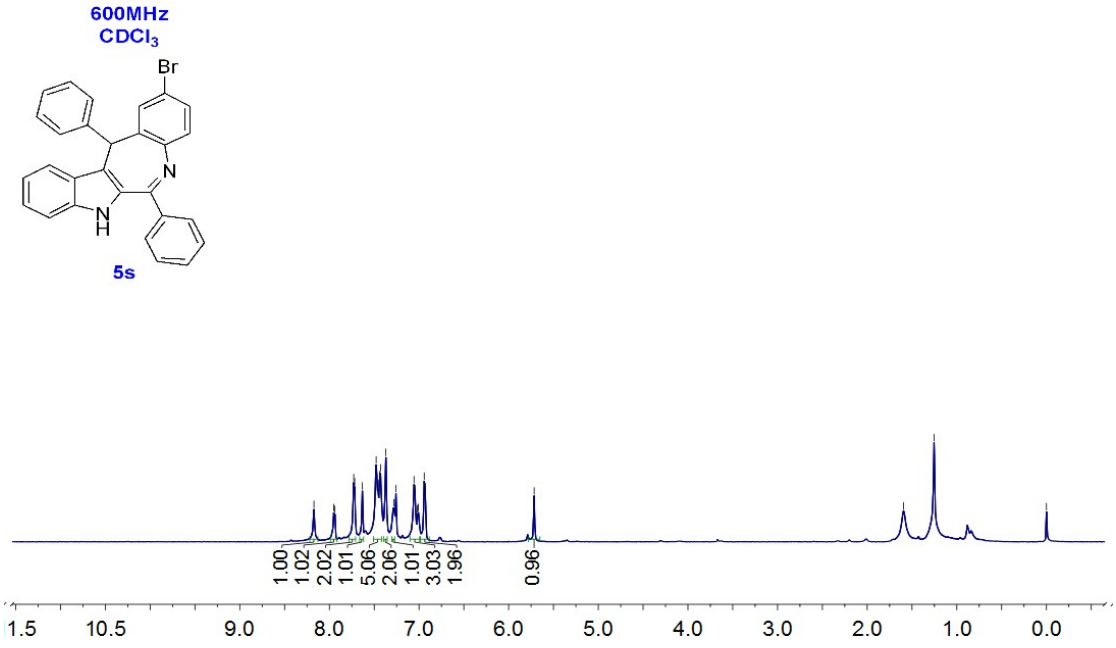
100MHz
$CDCl_3$

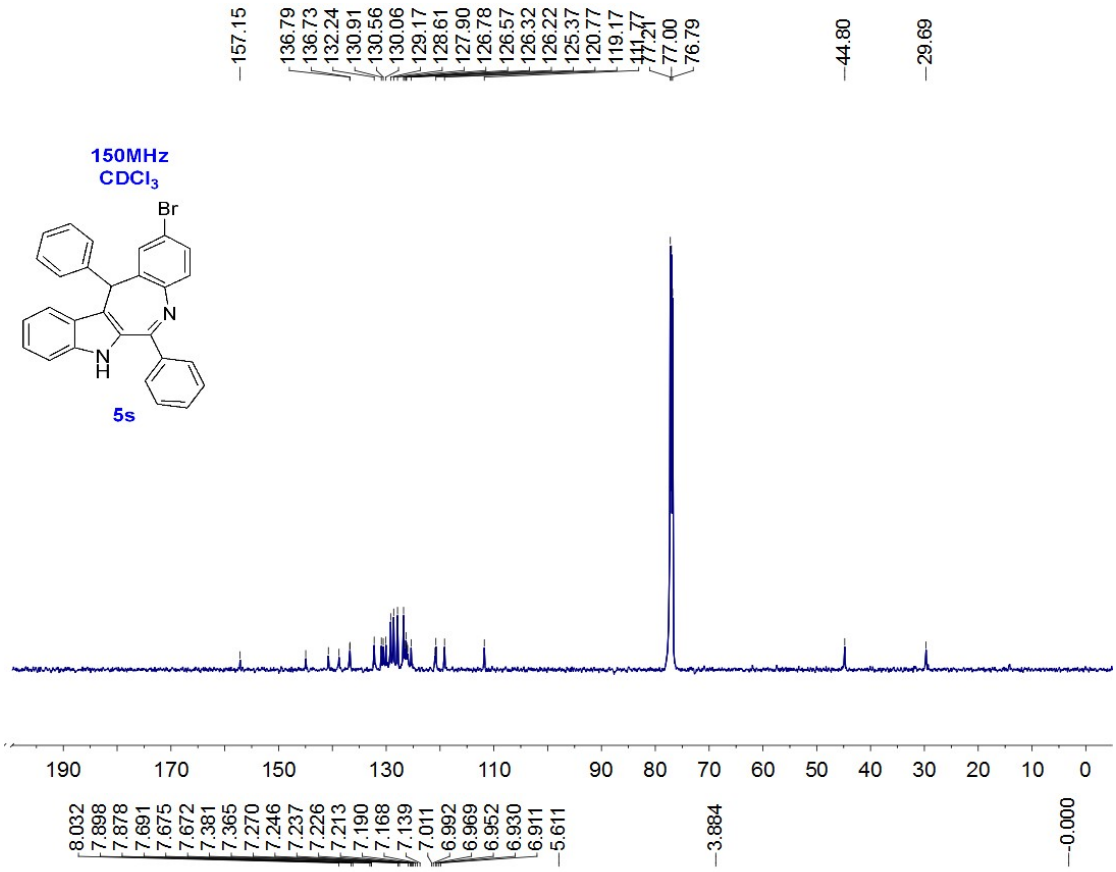
5q

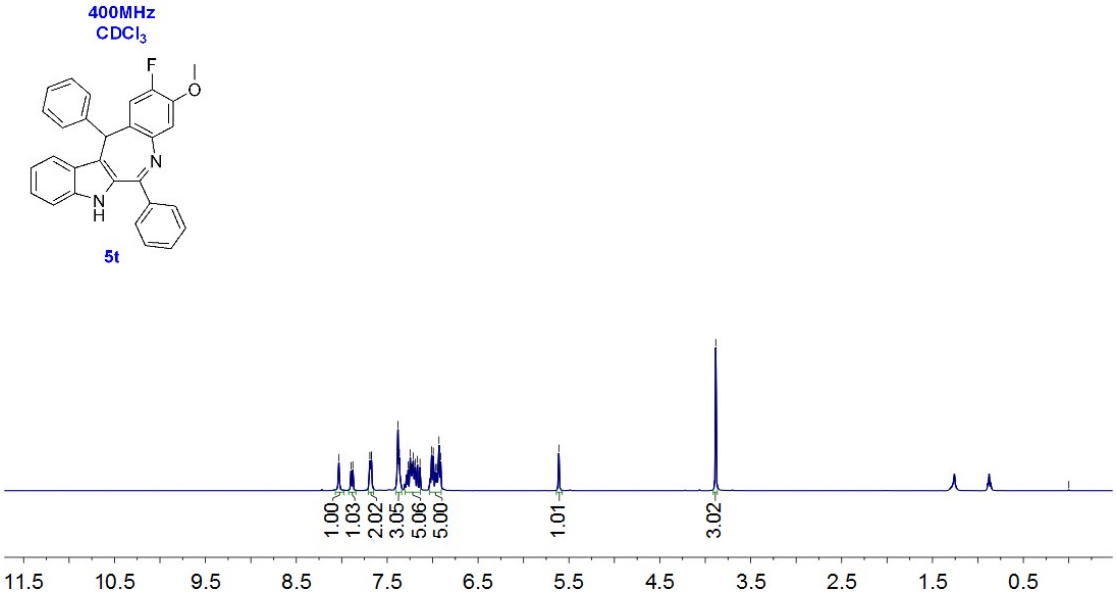

376MHz
CDCl3
F
N
N
H
5q
-116.290
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
8.164
7.942
7.929
7.721
7.712
7.579
7.530
7.517
7.472
7.422
7.349
7.273
7.250
7.080
7.049
7.012
7.002
6.938
5.713
1.254
0.000

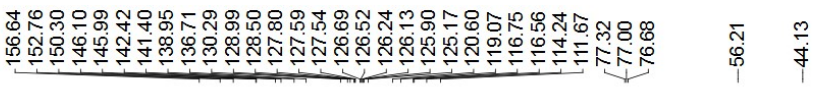

600MHz
CDCl3
Cl
N
N
H
5r
1.00
1.01
2.00
6.03
3.03
2.96
2.04
0.97
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


157.04
140.79
136.79
130.65
130.52
129.69
129.34
129.15
128.60
127.90
127.10
126.77
126.30
126.09
125.34
120.75
119.14
111.76
77.21
77.00
76.79
44.88
150MHz
CDCl3
Cl
N
N
H
5r
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.172
7.952
7.939
7.729
7.718
7.633
7.478
7.458
7.441
7.430
7.371
7.282
7.258
7.056
7.044
7.018
7.007
6.942
6.931
5.716
1.596
1.254
0.000

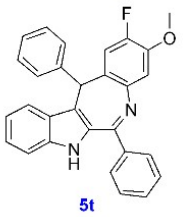

600MHz
CDCl3
Br
N
N
H
5s
1.00
1.02
2.02
1.01
5.06
2.06
1.01
3.03
1.96
0.96
1.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


157.15
136.79
136.73
132.24
130.91
130.56
130.06
129.17
128.61
127.90
126.78
126.57
126.32
126.22
125.37
120.77
119.17
111.77
77.21
77.00
76.79
44.80
29.69
150MHz
CDCl3
Br
N
N
H
5s
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
8.032
7.898
7.878
7.691
7.675
7.672
7.381
7.365
7.270
7.246
7.237
7.226
7.213
7.190
7.168
7.139
7.011
6.992
6.969
6.952
6.930
6.911
5.611
3.884
0.000

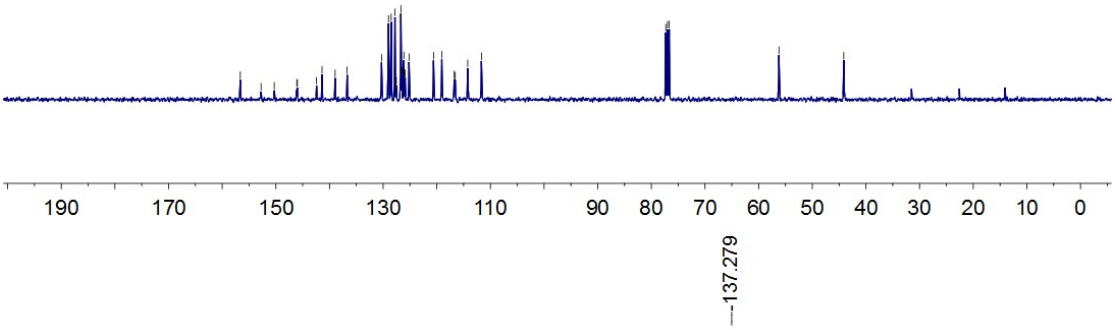

400MHz
CDCl3
F
O
N
N
H
5t
1.00
1.03
2.02
3.05
5.06
5.00
1.01
3.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5



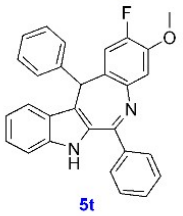
100MHz
$CDCl_3$



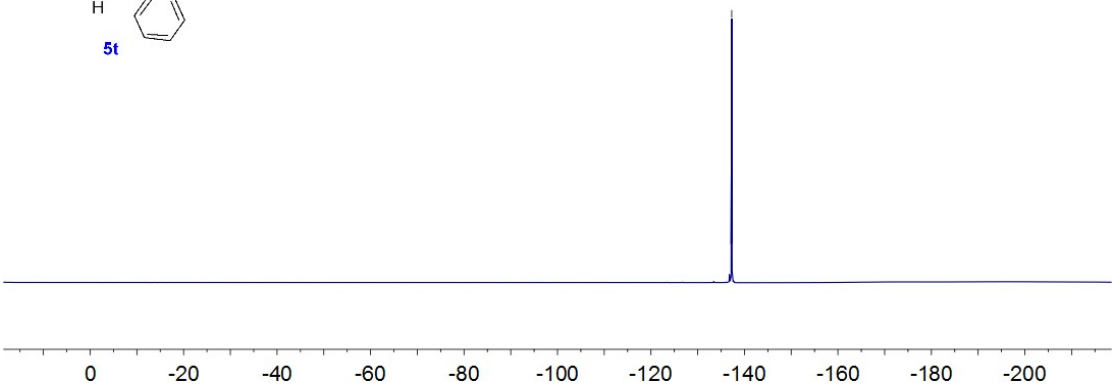
5t

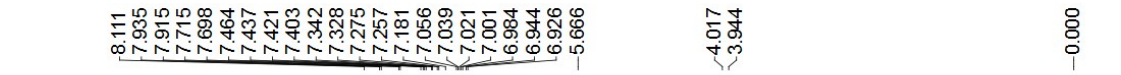


376MHz
$CDCl_3$

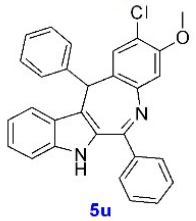


5t

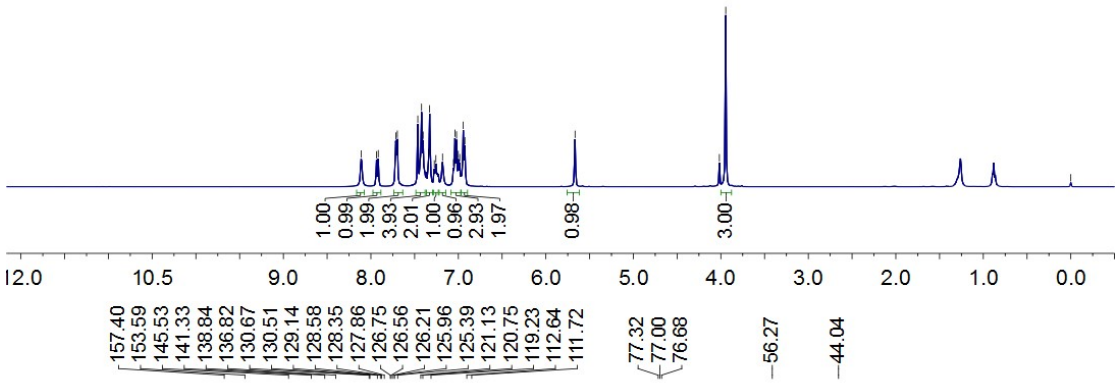




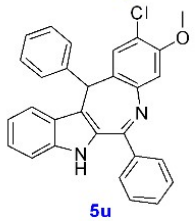
400MHz
$CDCl_3$



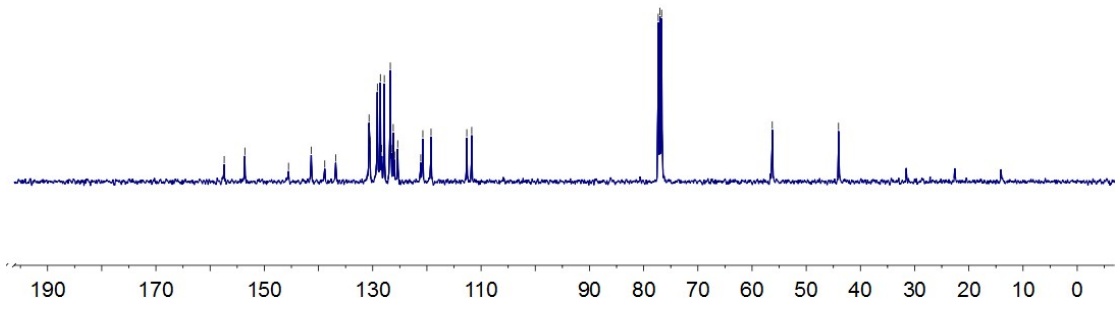
5u

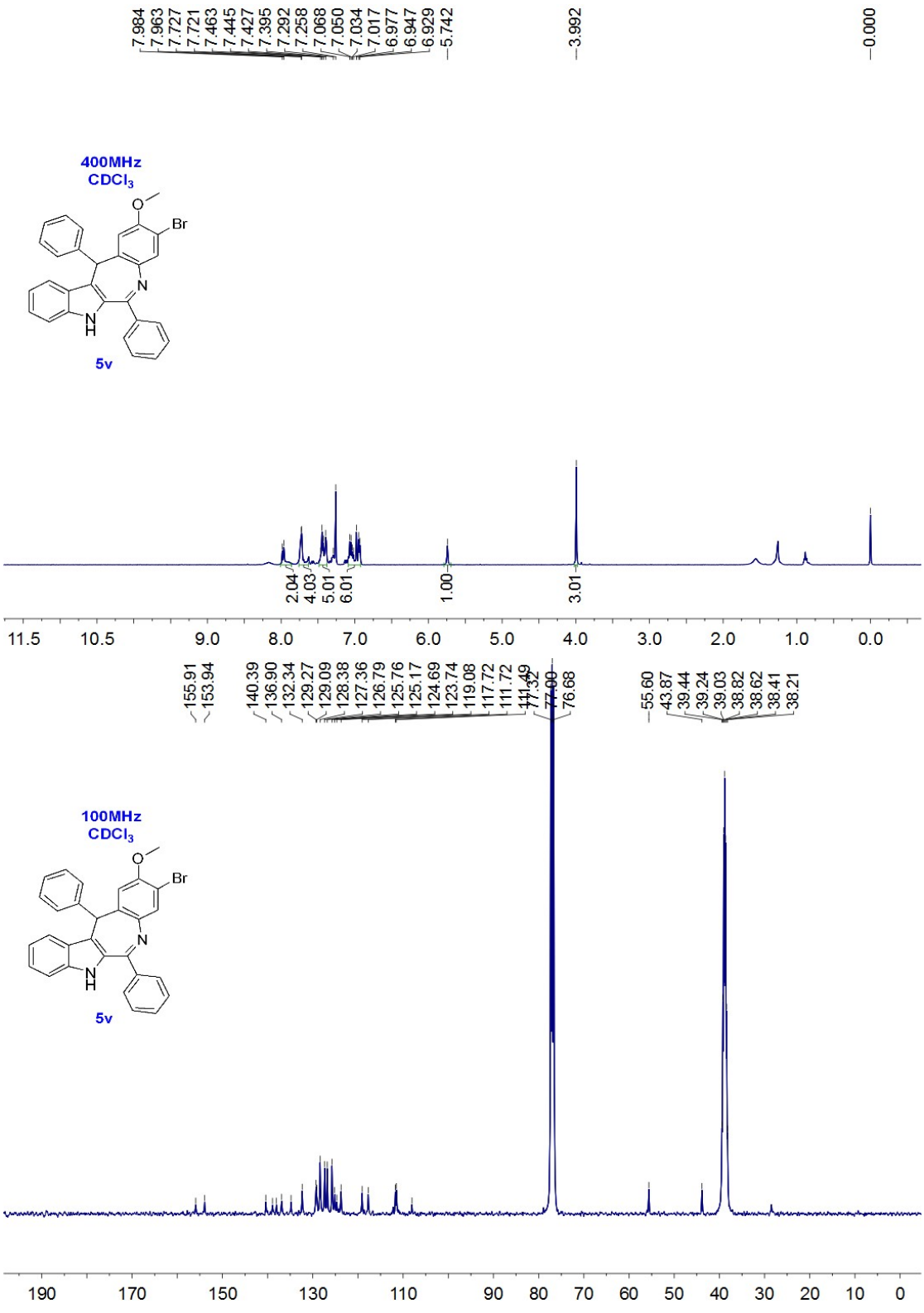


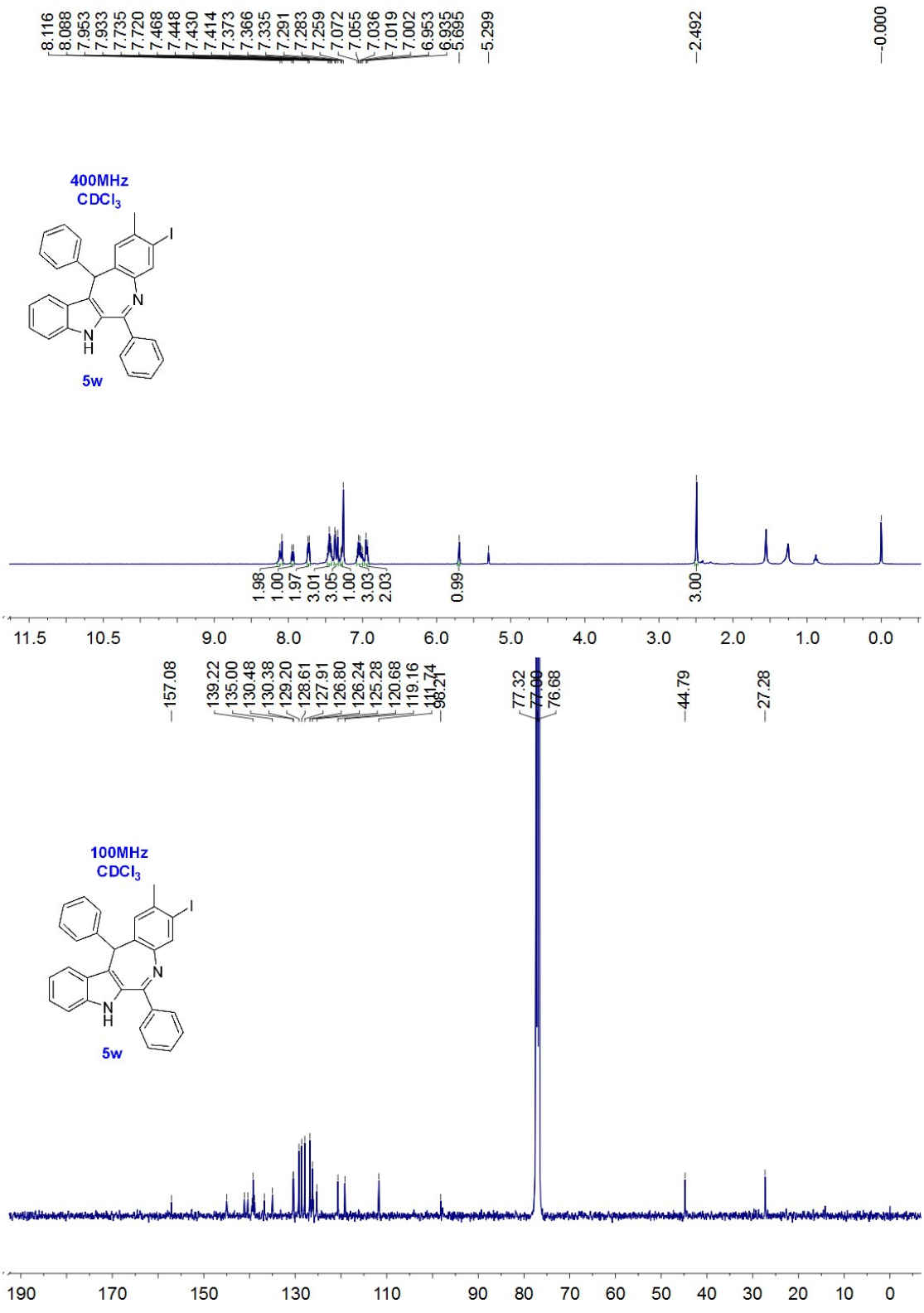
100MHz
$CDCl_3$

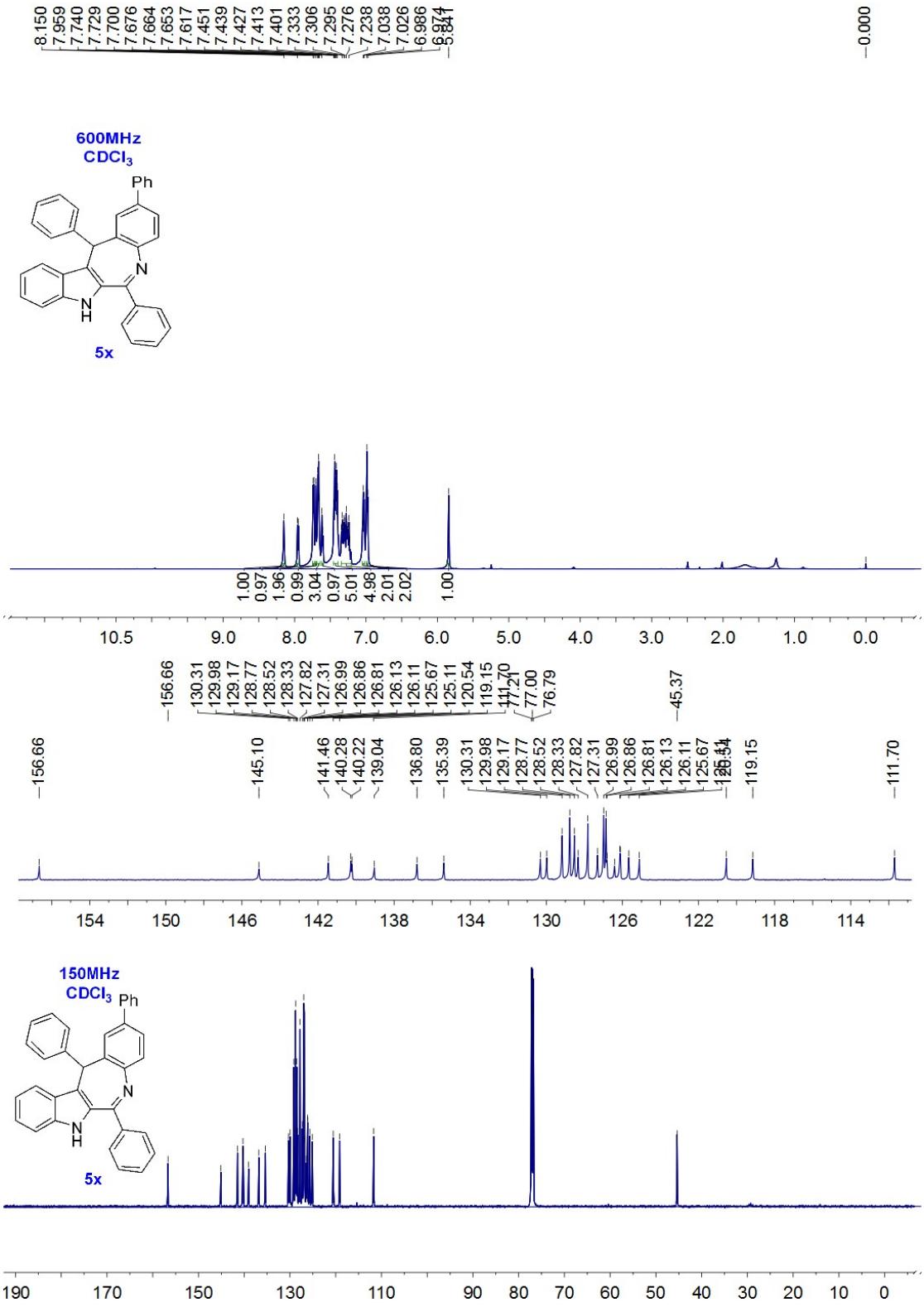


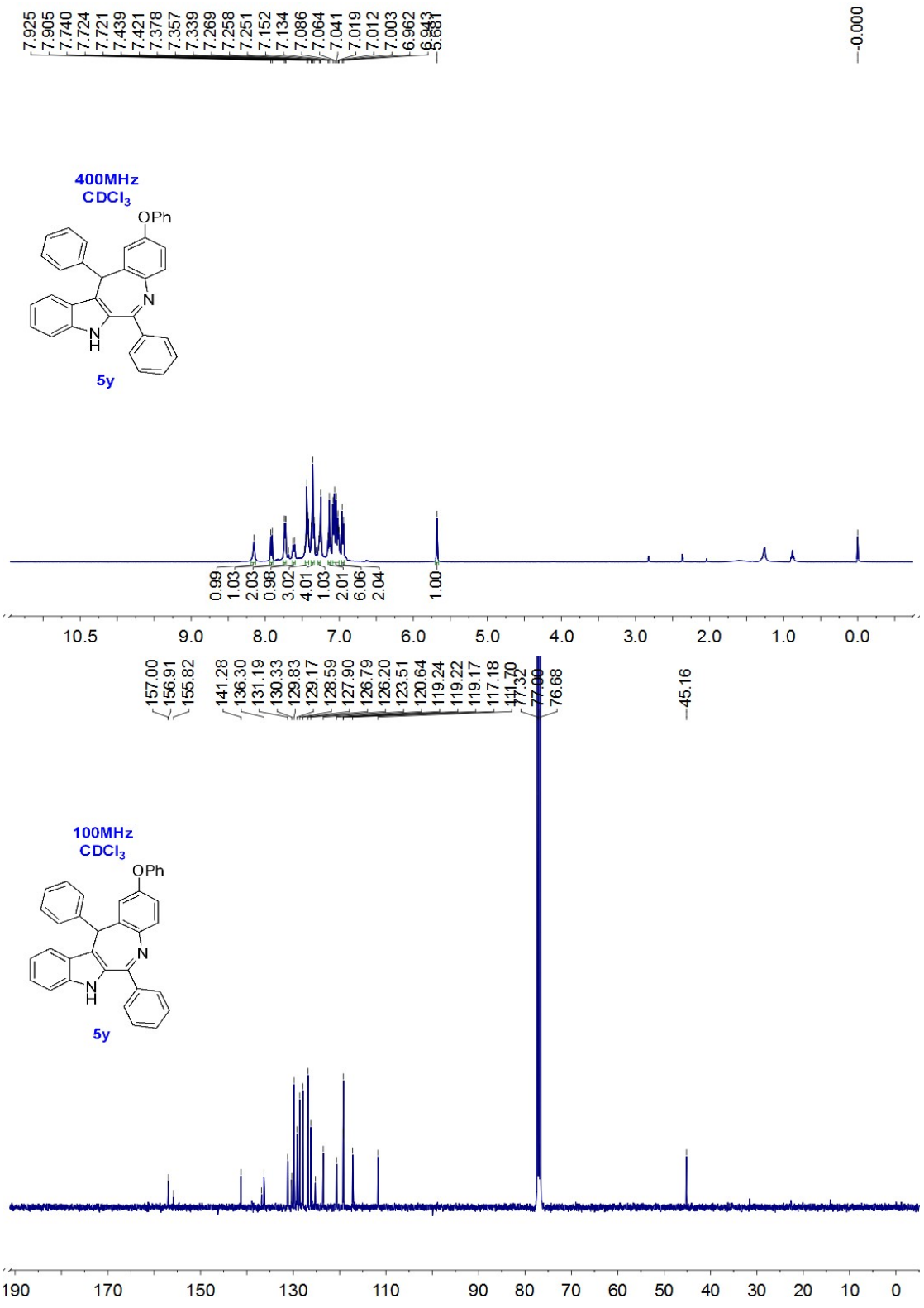
5u

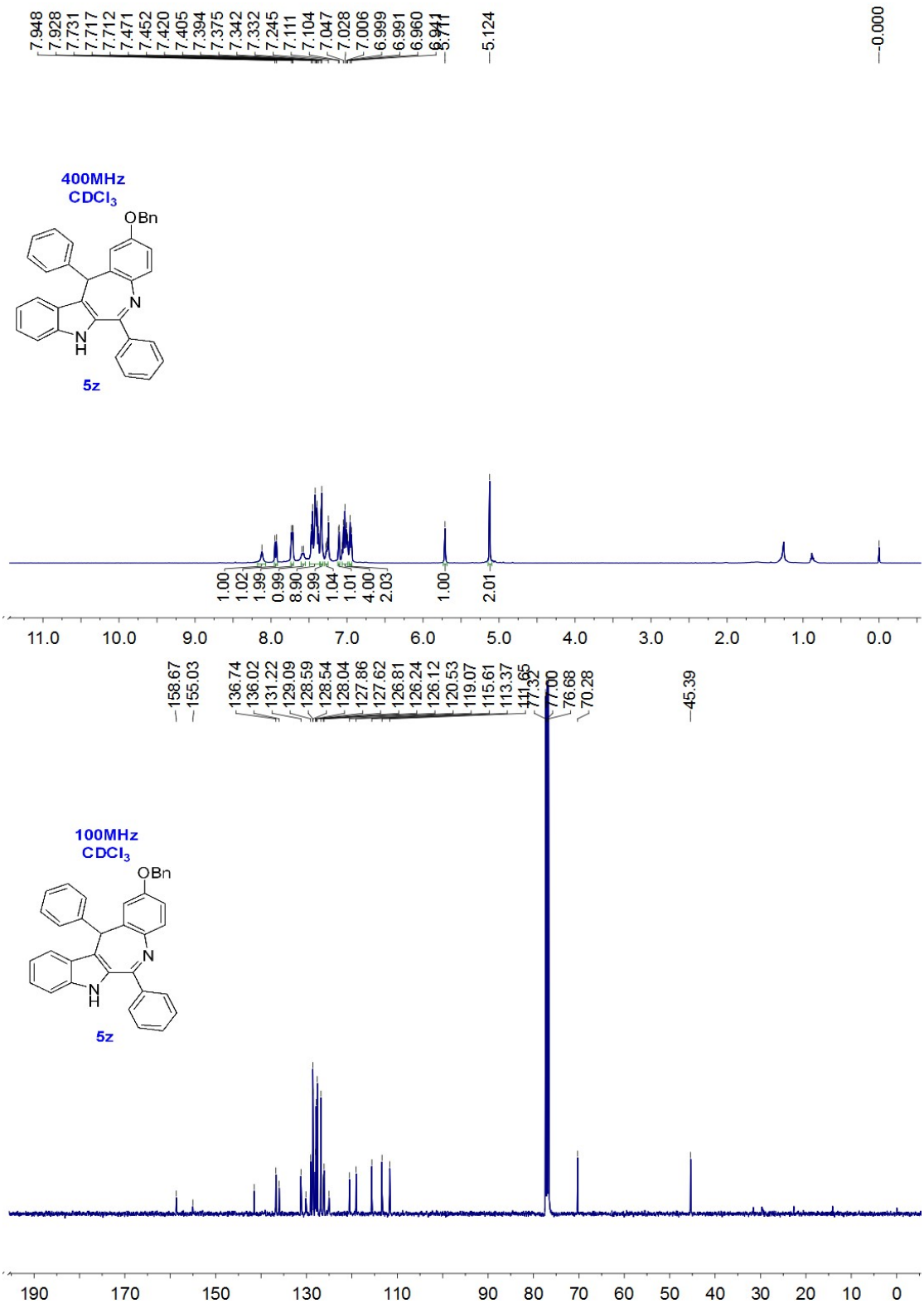


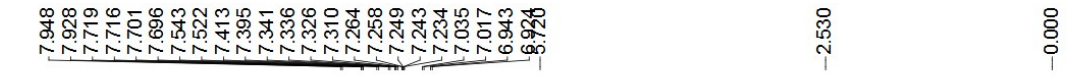

7.984
7.963
7.727
7.721
7.463
7.445
7.427
7.395
7.292
7.258
7.068
7.050
7.034
7.017
6.977
6.947
6.929
5.742
3.992
0.000
400MHz
CDCl3
O
Br
N
N
H
5v
2.04
4.03
5.01
6.01
1.00
3.01
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
155.91
153.94
140.39
136.90
132.34
129.27
129.09
128.38
127.36
126.79
125.76
125.17
124.69
123.74
119.08
117.72
111.72
111.49
77.32
77.00
76.68
55.60
43.87
39.44
39.24
39.03
38.82
38.62
38.41
38.21
100MHz
CDCl3
O
Br
N
N
H
5v
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.116
8.088
7.953
7.933
7.735
7.720
7.468
7.448
7.430
7.414
7.373
7.366
7.335
7.291
7.283
7.259
7.072
7.055
7.036
7.019
7.002
6.953
6.935
5.695
5.299
2.492
0.000
400MHz
CDCl3
I
N
N
H
5w
1.98
1.00
1.97
3.01
3.05
1.00
3.03
2.03
0.99
3.00
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
157.08
139.22
135.00
130.48
130.38
129.20
128.61
127.91
126.80
126.24
125.28
120.68
119.16
111.74
98.21
77.32
77.00
76.68
44.79
27.28
100MHz
CDCl3
I
N
N
H
5w
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


600MHz
CDCl3
Ph
N
N
H
5x
8.150
7.959
7.740
7.729
7.700
7.676
7.664
7.653
7.617
7.451
7.439
7.427
7.413
7.401
7.333
7.306
7.295
7.276
7.238
7.038
7.026
6.986
0.000
1.00
0.97
1.96
0.99
3.04
0.97
5.01
4.98
2.01
2.02
1.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
156.66
130.31
129.98
129.17
128.77
128.52
128.33
127.82
127.31
126.99
126.86
126.81
126.13
126.11
125.67
125.11
120.54
119.15
111.70
77.21
77.00
76.79
45.37
156.66
145.10
141.46
140.28
140.22
139.04
136.80
135.39
130.31
129.98
129.17
128.77
128.52
128.33
127.82
127.31
126.99
126.86
126.81
126.13
126.11
125.67
119.15
111.70
154
150
146
142
138
134
130
126
122
118
114
150MHz
CDCl3
Ph
N
N
H
5x
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


7.925
7.905
7.740
7.724
7.721
7.439
7.421
7.378
7.357
7.339
7.269
7.258
7.251
7.152
7.134
7.086
7.064
7.041
7.019
7.012
7.003
6.962
6.943
5.881
0.000
400MHz
CDCl3
OPh
N
H
5y
0.99
1.03
2.03
0.98
3.02
4.01
1.03
2.01
6.06
2.04
1.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
157.00
156.91
155.82
141.28
136.30
131.19
130.33
129.83
129.17
128.59
127.90
126.79
126.20
123.51
120.64
119.24
119.22
119.17
117.18
111.70
77.32
77.00
76.68
45.16
100MHz
CDCl3
OPh
N
H
5y
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


7.948
7.928
7.731
7.717
7.712
7.471
7.452
7.420
7.405
7.394
7.375
7.342
7.332
7.245
7.111
7.104
7.047
7.028
7.006
6.999
6.991
6.960
5.711
5.124
-0.000
400MHz
CDCl3
OBn
N
H
5z
1.00
1.02
1.99
0.99
8.90
2.99
1.04
1.01
4.00
2.03
1.00
2.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
158.67
155.03
136.74
136.02
131.22
129.09
128.59
128.54
128.04
127.86
127.62
126.81
126.24
126.12
120.53
119.07
115.61
113.37
111.65
77.32
77.00
76.68
70.28
45.39
100MHz
CDCl3
OBn
N
H
5z
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



400MHz
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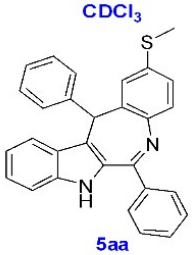
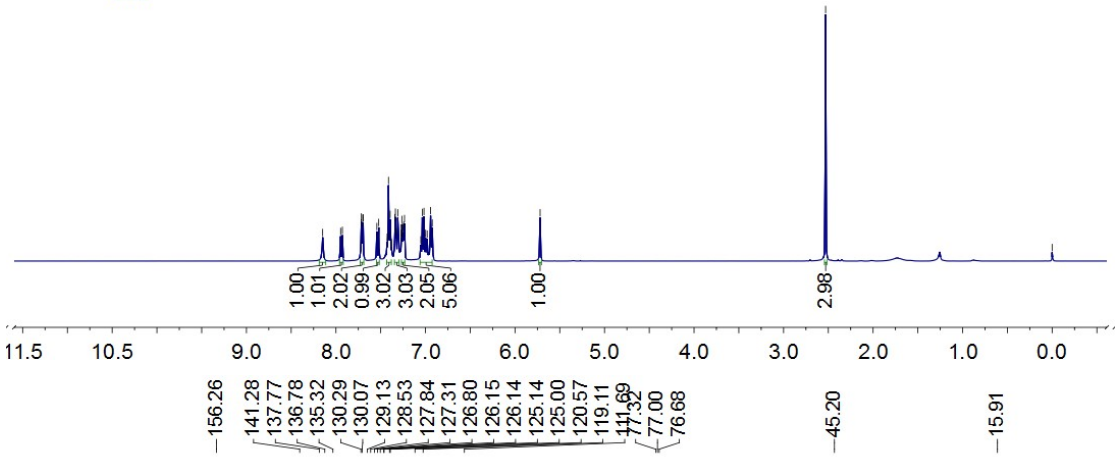
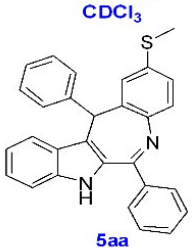


5aa



100MHz
$CDCl_3$



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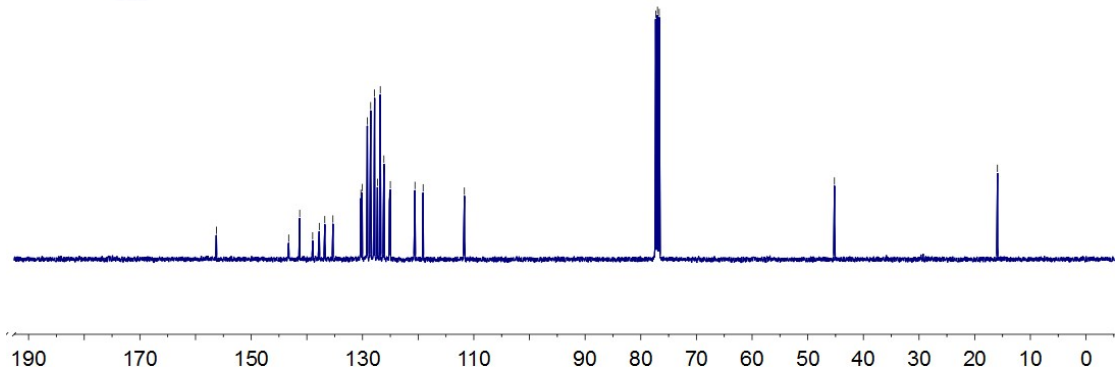
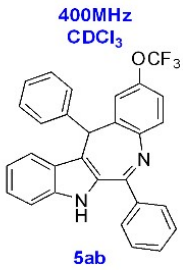
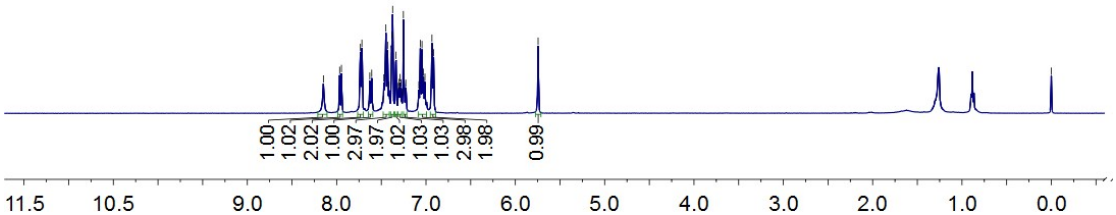
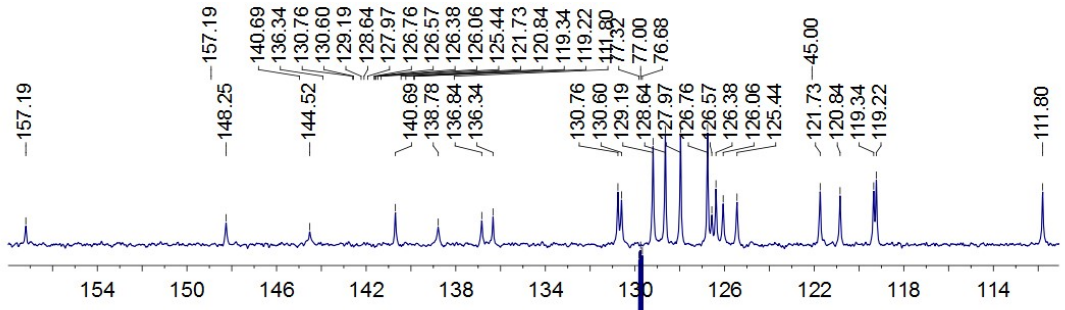
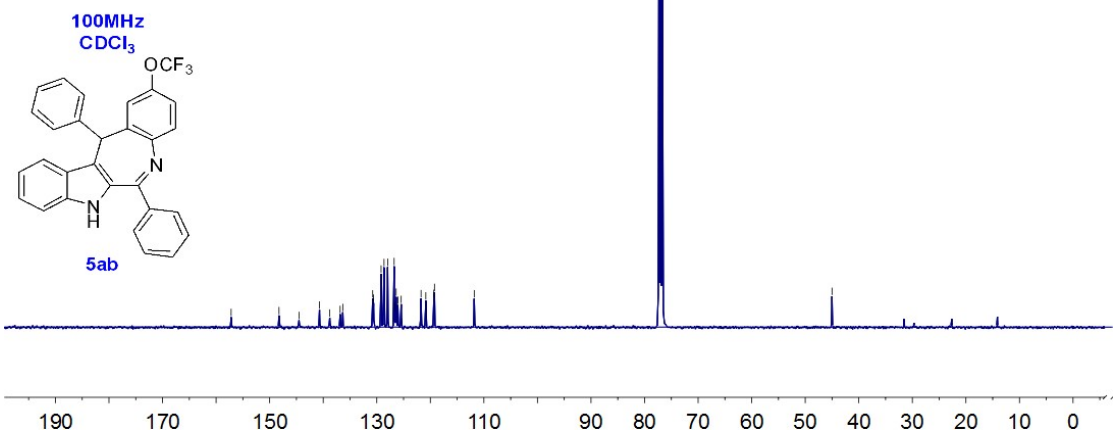


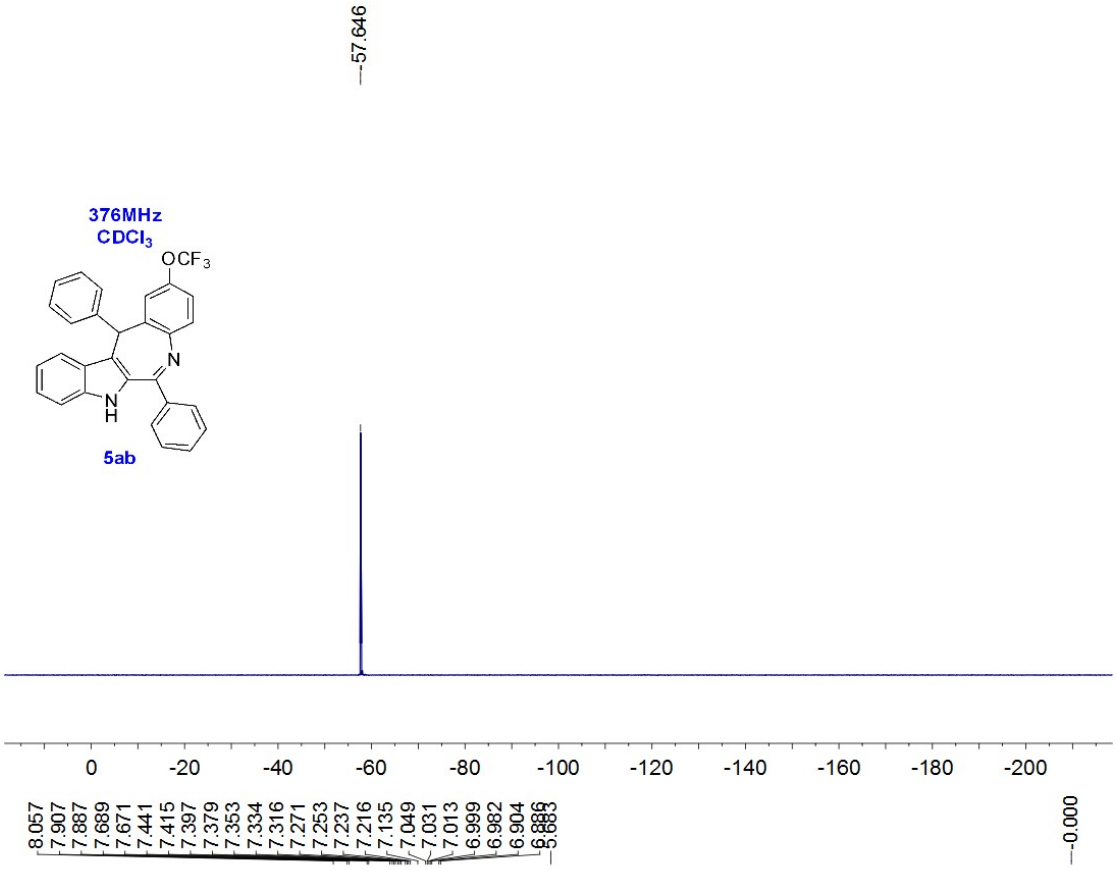

8.148
7.966
7.946
7.734
7.717
7.629
7.607
7.471
7.449
7.430
7.382
7.373
7.335
7.301
7.290
7.280
7.253
7.063
7.044
7.029
7.012
6.933
6.915
6.745
0.000


400MHz
CDCl3
OCF3
N
H
5ab


1.00
1.02
2.02
1.00
2.97
1.97
1.02
1.03
1.03
2.98
1.98
0.99
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


157.19
148.25
144.52
140.69
138.78
136.84
136.34
130.76
130.60
129.19
128.64
127.97
126.76
126.57
126.38
126.06
125.44
121.73
120.84
119.34
119.22
111.80
45.00
154
150
146
142
138
134
130
126
122
118
114


100MHz
CDCl3
OCF3
N
H
5ab
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


-57.646
376MHz
CDCl3
OCF3
N
N
H
5ab
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
8.057
7.907
7.887
7.689
7.671
7.441
7.415
7.397
7.379
7.353
7.334
7.316
7.271
7.253
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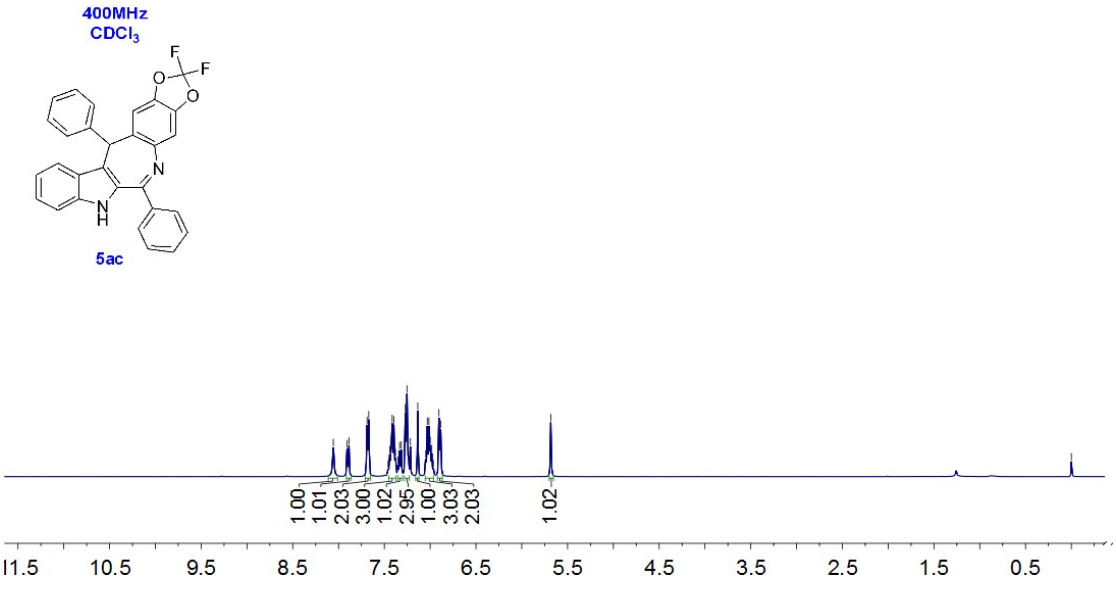
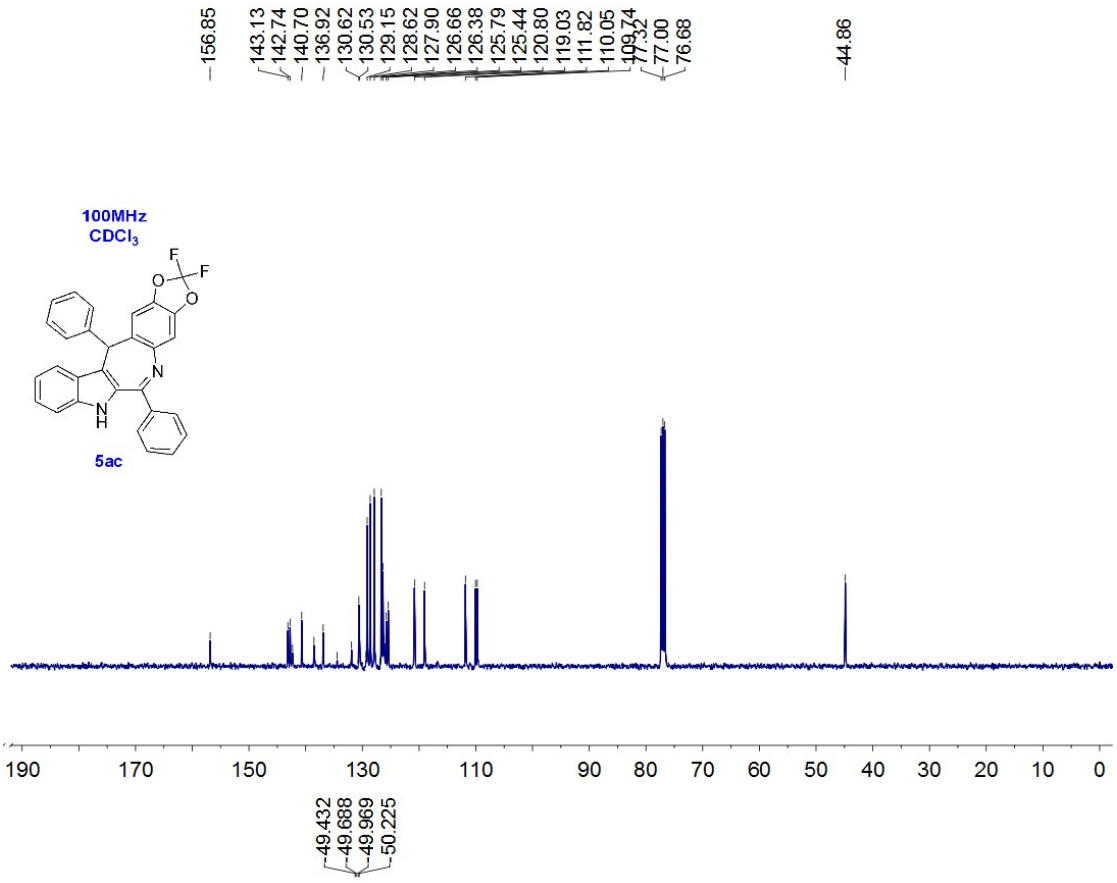
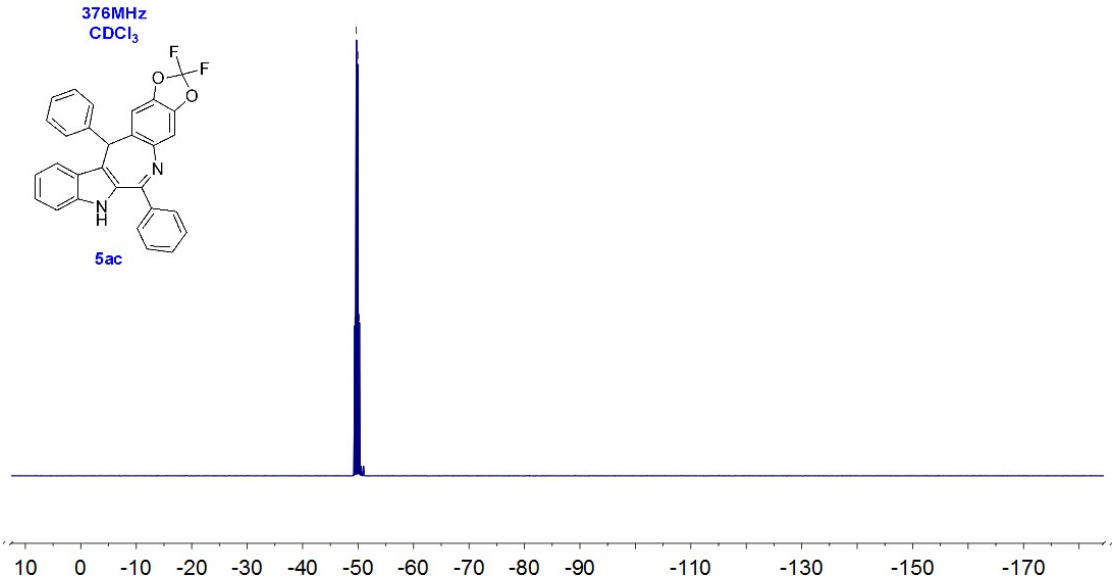
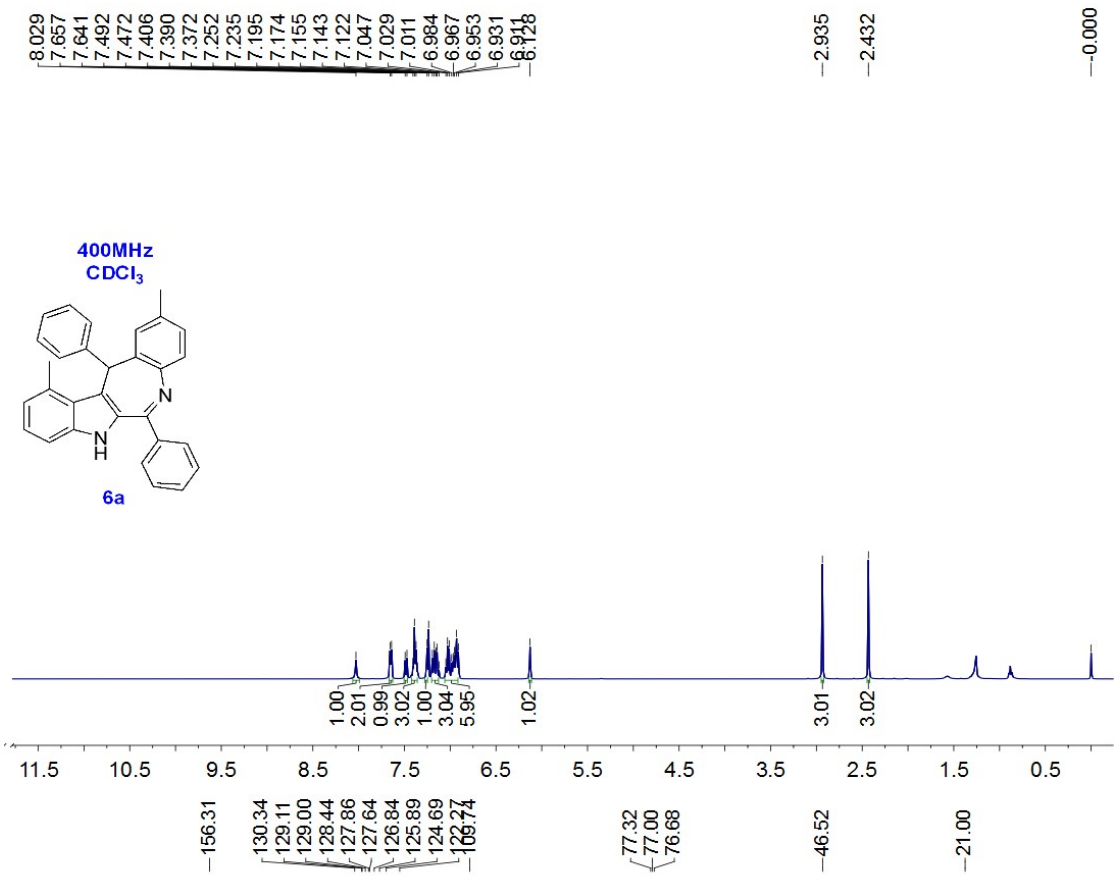
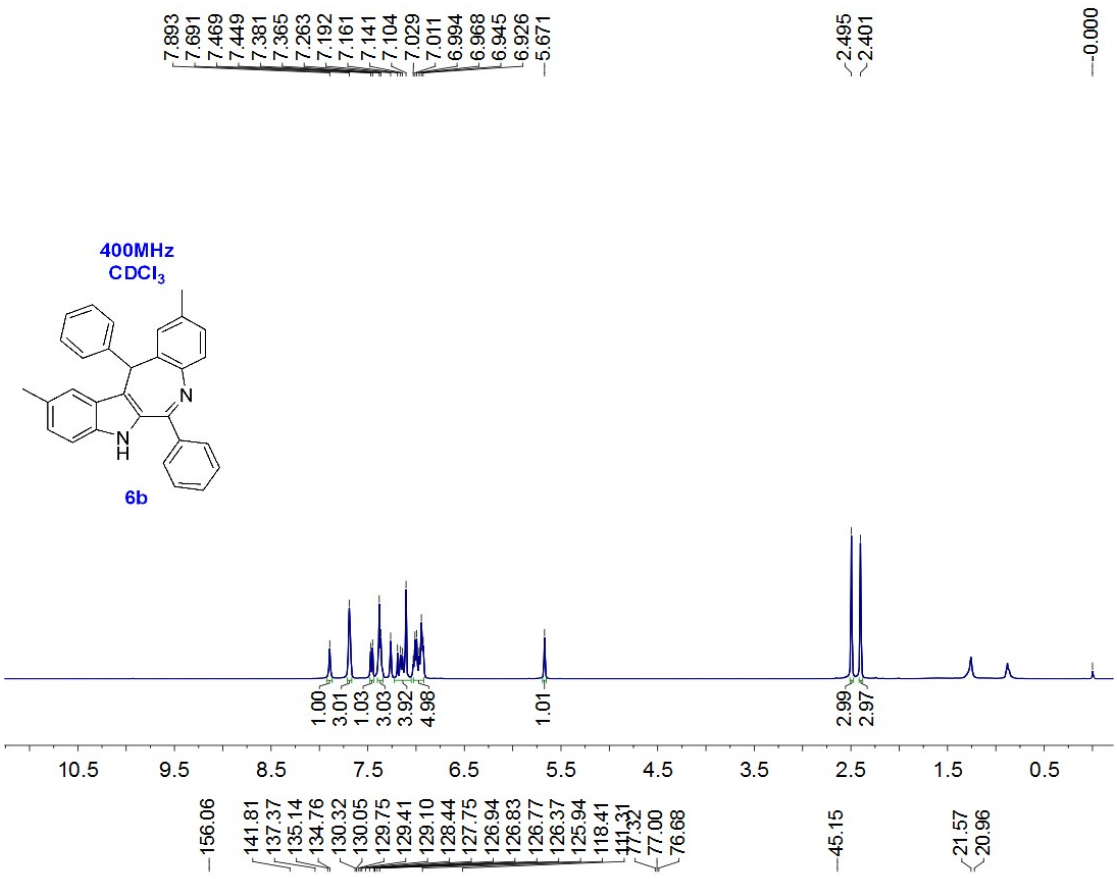
7.216
7.135
7.049
7.031
7.013
6.999
6.982
6.904
-0.000


400MHz
CDCl3
F
F
O
O
N
N
H
5ac
1.00
1.01
2.03
3.00
1.02
2.95
1.00
3.03
2.03
1.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5


156.85
143.13
142.74
140.70
136.92
130.62
130.53
129.15
128.62
127.90
126.66
126.38
125.79
125.44
120.80
119.03
111.82
110.05
109.74
77.32
77.00
76.68
44.86
100MHz
CDCl3
5ac
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
49.432
49.688
49.969
50.225


376MHz
CDCl3
5ac
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170


8.029
7.657
7.641
7.492
7.472
7.406
7.390
7.372
7.252
7.235
7.195
7.174
7.155
7.143
7.122
7.047
7.029
7.011
6.984
6.967
6.953
6.931
6.911
6.128
2.935
2.432
0.000
400MHz
CDCl3
N
H
6a
1.00
2.01
0.99
3.02
1.00
3.04
5.95
1.02
3.01
3.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
156.31
130.34
129.11
129.00
128.44
127.86
127.64
126.84
125.89
124.69
122.27
109.74
77.32
77.00
76.68
46.52
21.00
100MHz
CDCl3
N
H
6a
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.469
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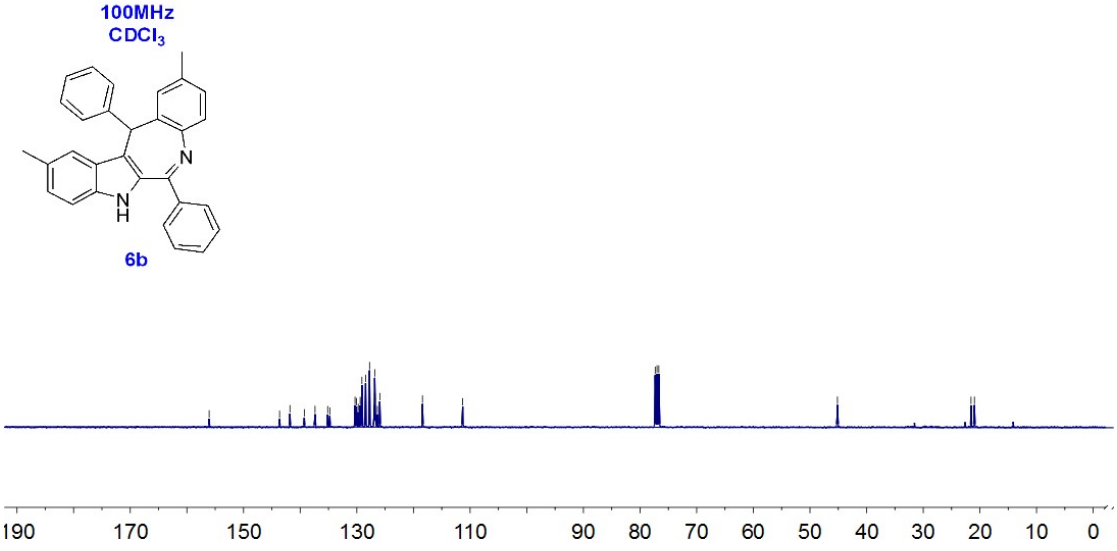
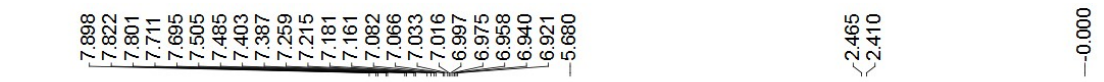
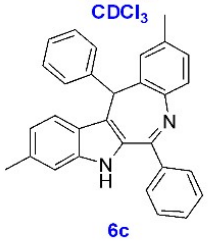
7.365
7.263
7.192
7.161
7.141
7.104
7.029
7.011
6.994
6.968
6.945
6.926
5.671
2.495
2.401
0.000
400MHz
CDCl3
N
H
6b
1.00
3.01
1.03
3.03
3.92
4.98
1.01
2.99
2.97
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
156.06
141.81
137.37
135.14
134.76
130.32
130.05
129.75
129.41
129.10
128.44
127.75
126.94
126.83
126.77
126.37
125.94
118.41
111.31
77.32
77.00
76.68
45.15
21.57
20.96

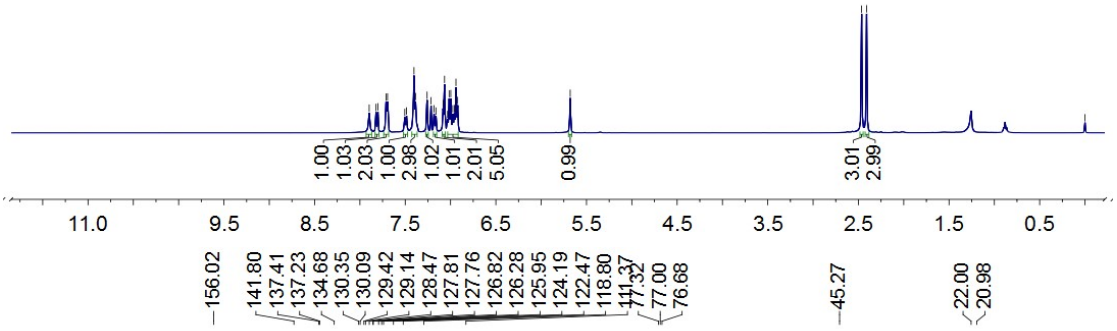

100MHz
CDCl3
N
H
6b
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



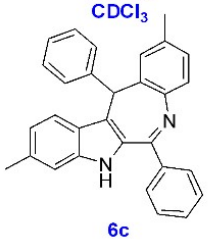
400MHz
$CDCl_3$



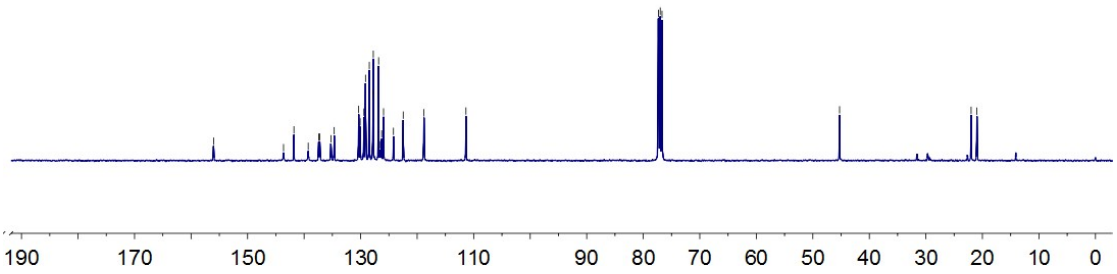
6c



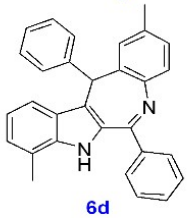
100MHz
$CDCl_3$



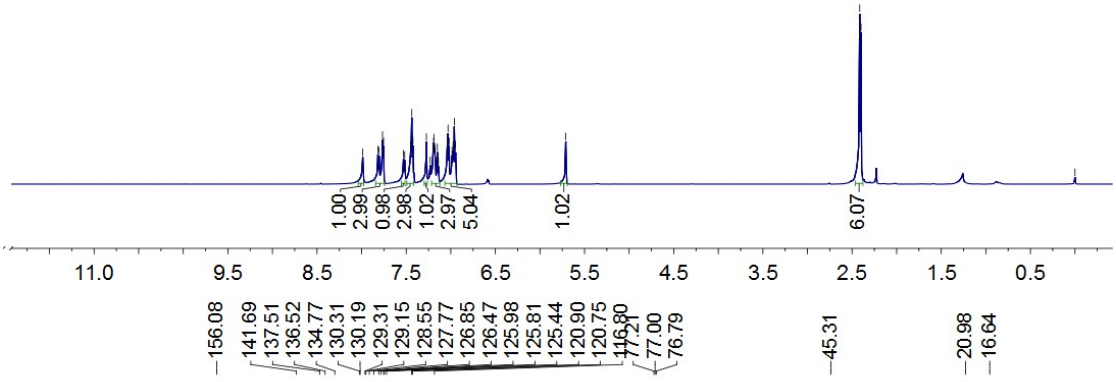
6c



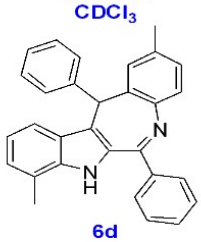
600MHz
$CDCl_3$



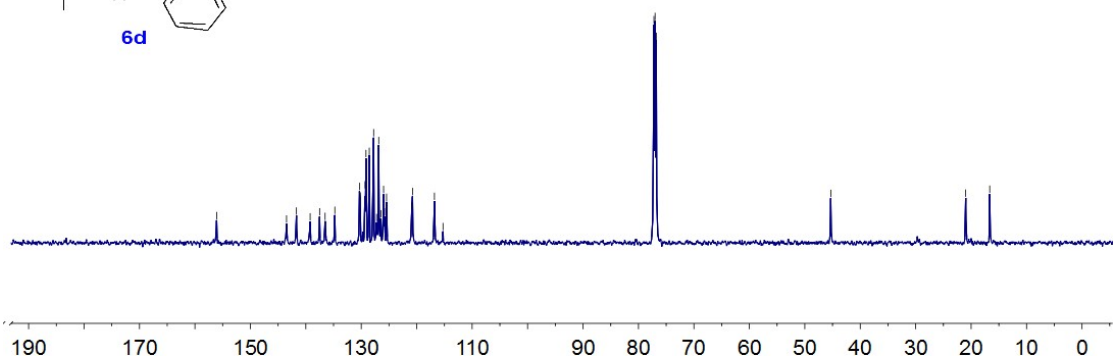
6d

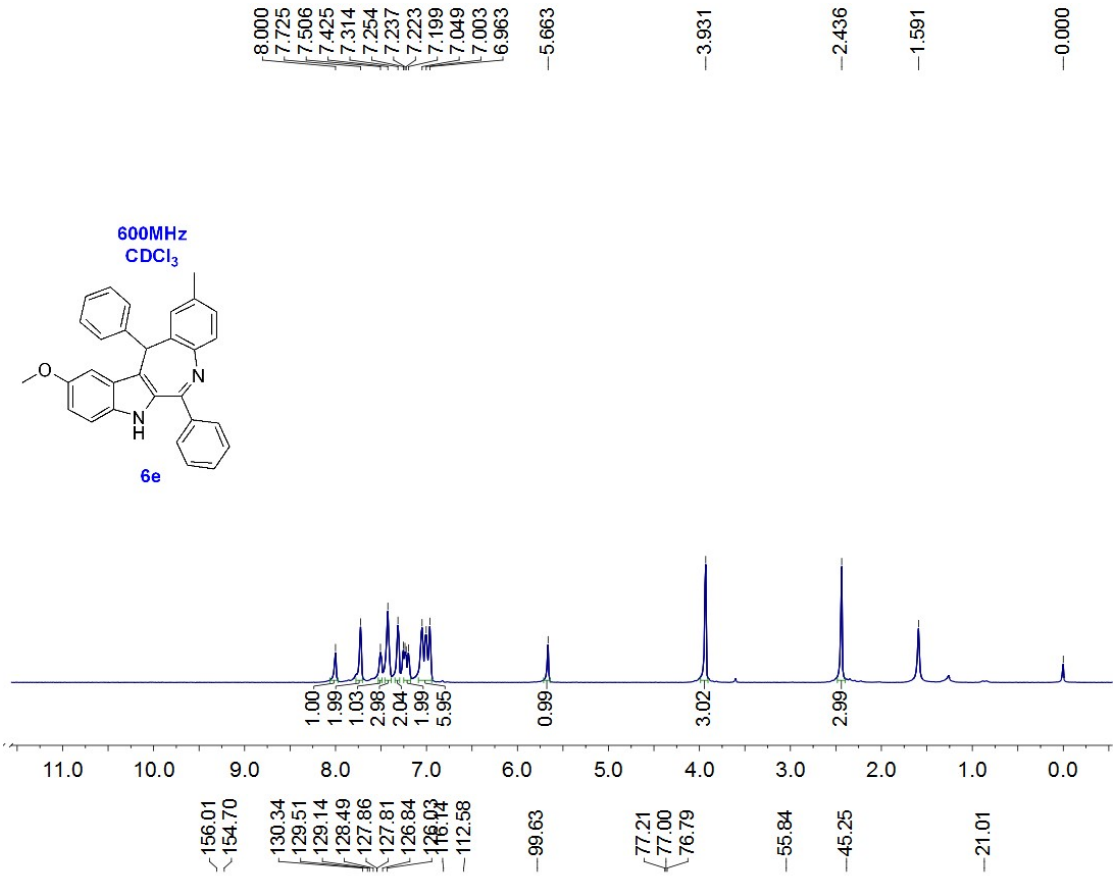


150MHz
$CDCl_3$



6d

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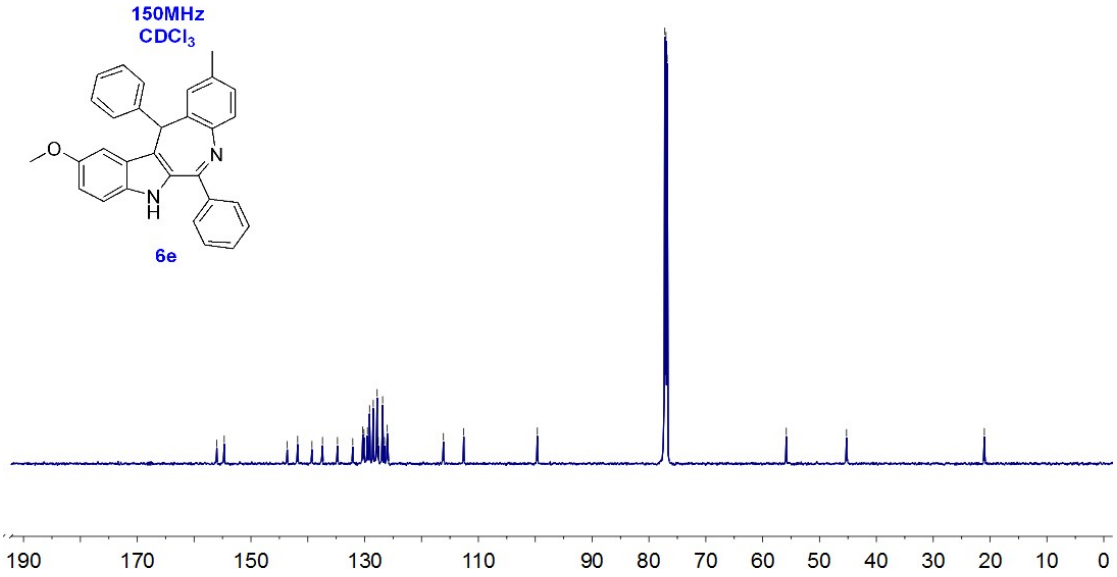
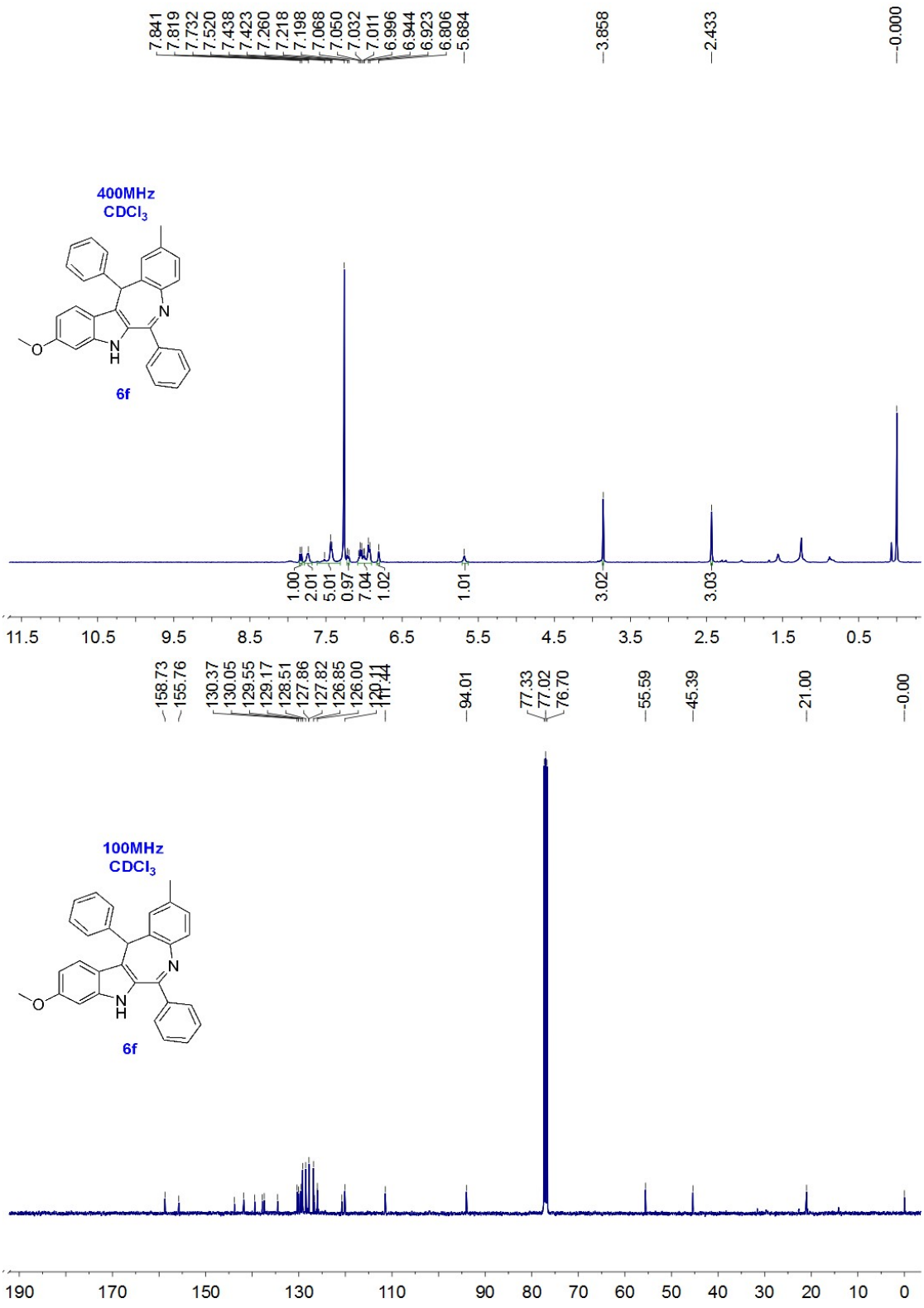
7.725
7.506
7.425
7.314
7.254
7.237
7.223
7.199
7.049
7.003
6.963
5.663
3.931
2.436
1.591
0.000
600MHz
CDCl3
O
N
H
6e
1.00
1.99
1.03
2.98
2.04
1.99
5.95
0.99
3.02
2.99
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
156.01
154.70
130.34
129.51
129.14
128.49
127.86
127.81
126.84
112.58
99.63
77.21
77.00
76.79
55.84
45.25
21.01


150MHz
CDCl3
O
N
H
6e
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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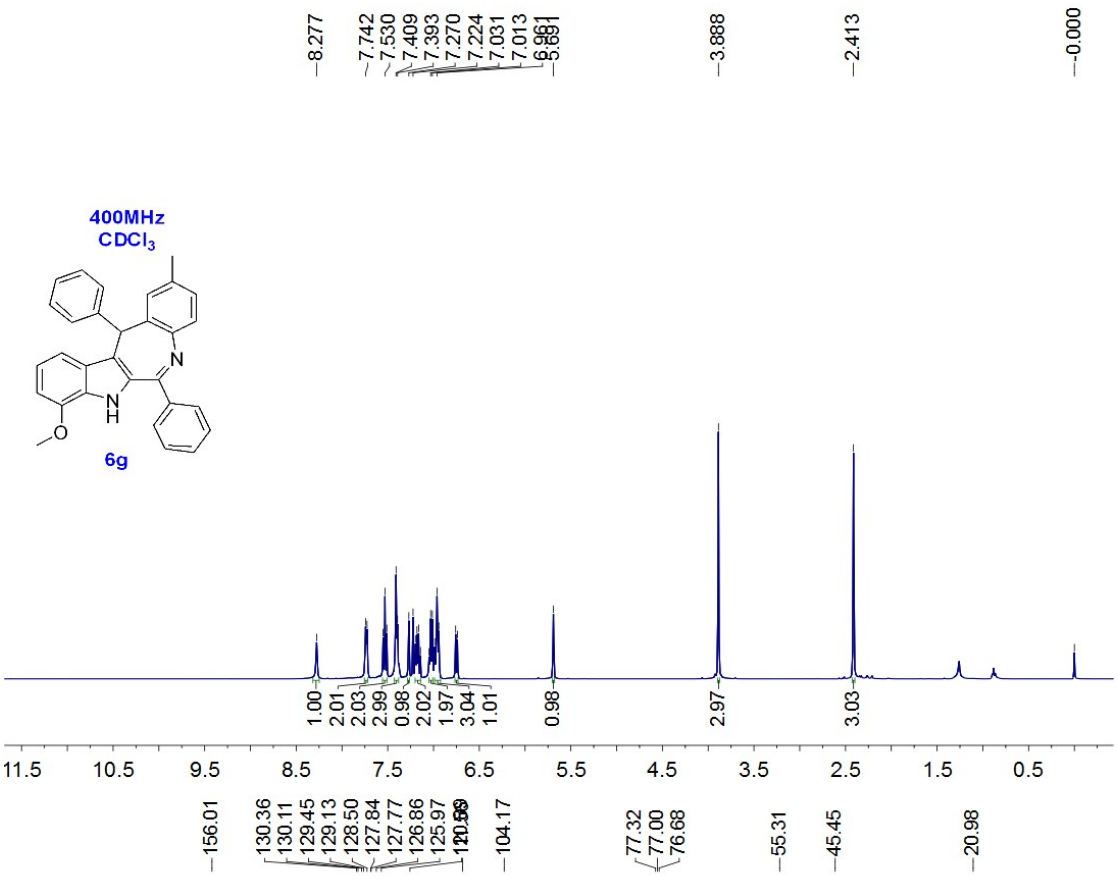
7.732
7.520
7.438
7.423
7.260
7.218
7.198
7.068
7.050
7.032
7.011
6.996
6.944
6.923
6.806
5.684
3.858
2.433
0.000
400MHz
CDCl3
6f
1.00
2.01
5.01
0.97
7.04
1.02
1.01
3.02
3.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
158.73
155.76
130.37
130.05
129.55
129.17
128.51
127.86
127.82
126.85
126.00
120.11
111.44
94.01
77.33
77.02
76.70
55.59
45.39
21.00
0.00
100MHz
CDCl3
6f
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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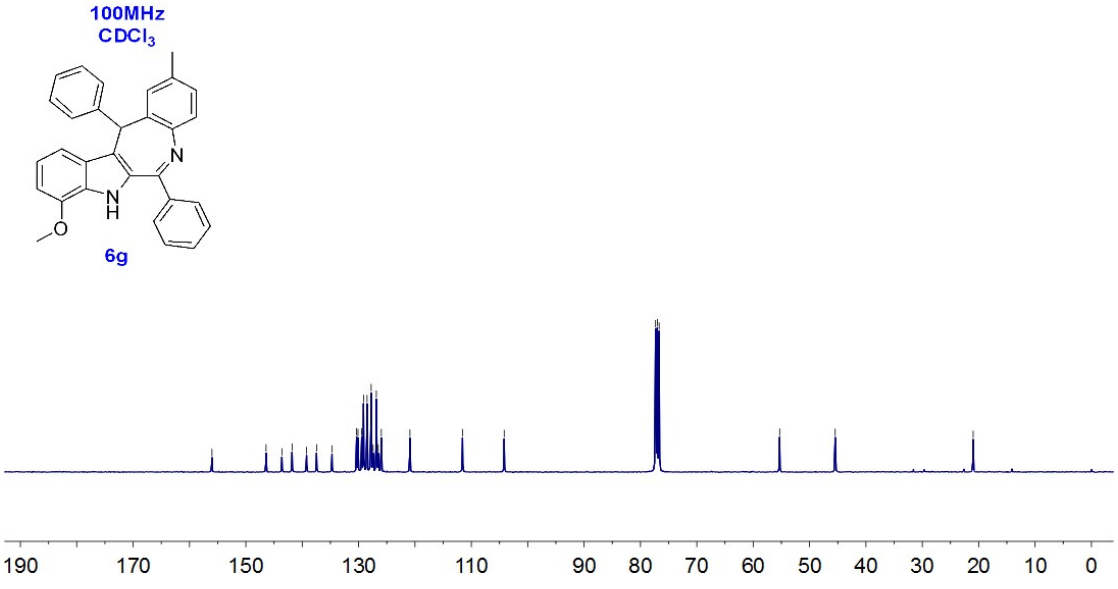
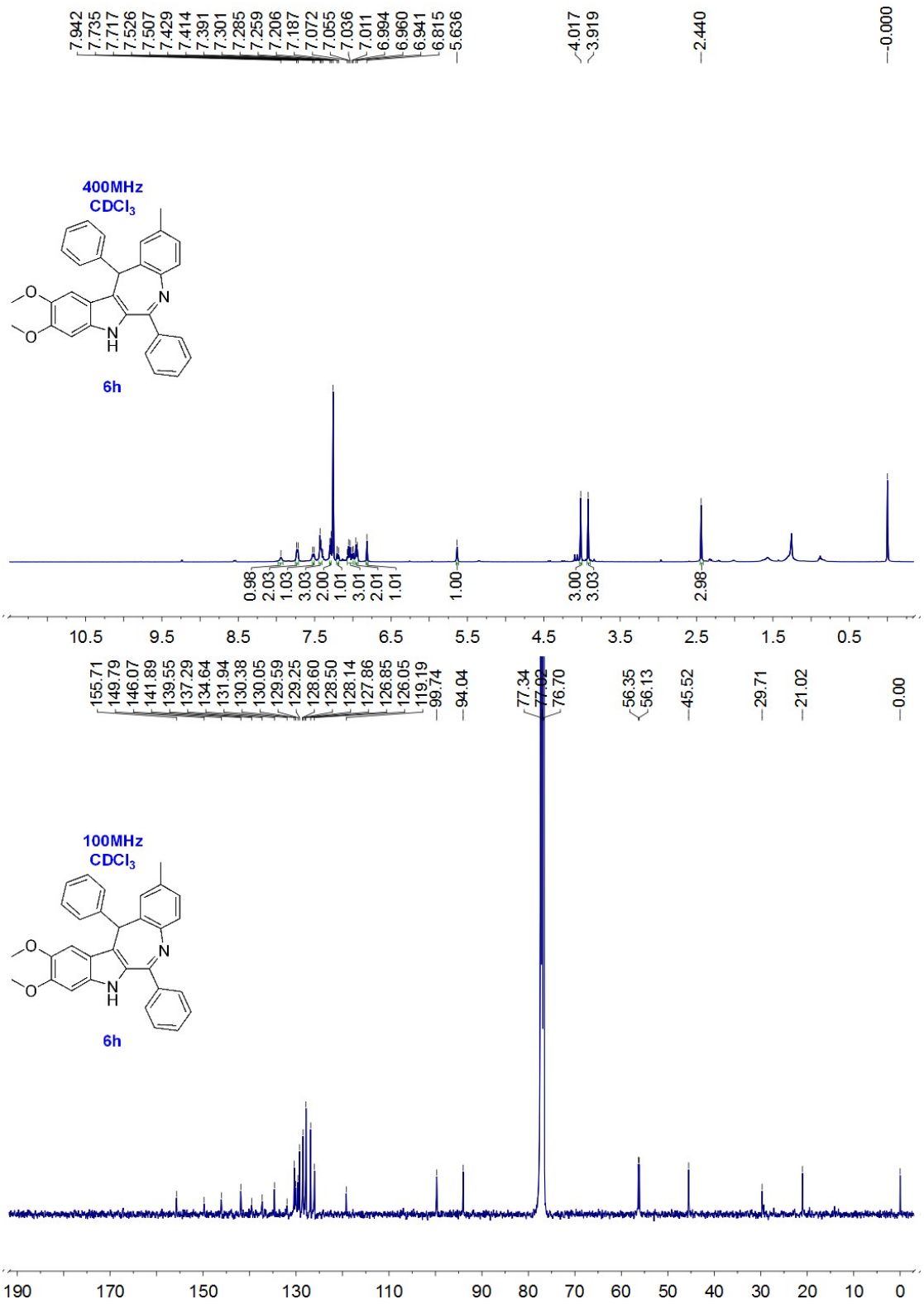
7.409
7.393
7.270
7.224
7.031
7.013
3.888
2.413
0.000
400MHz
CDCl3
6g
1.00
2.01
2.03
2.99
0.98
2.02
1.97
3.04
1.01
0.98
2.97
3.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
156.01
130.36
130.11
129.45
129.13
128.50
127.84
127.77
126.86
125.97
104.17
77.32
77.00
76.68
55.31
45.45
20.98


100MHz
CDCl3
6g
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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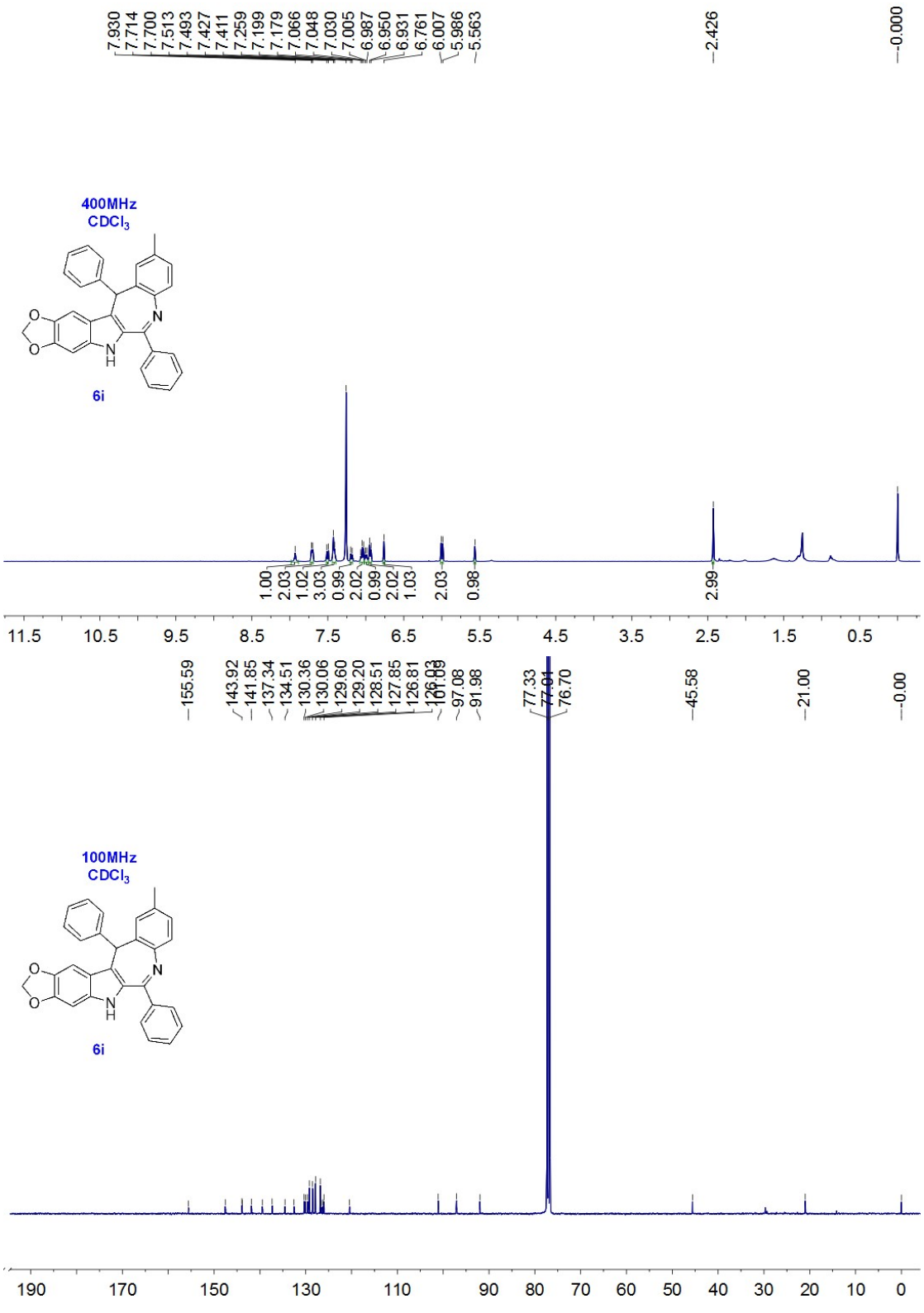
7.717
7.526
7.507
7.429
7.414
7.391
7.301
7.285
7.259
7.206
7.187
7.072
7.055
7.036
7.011
6.994
6.960
6.941
6.815
5.636
4.017
3.919
2.440
0.000
400MHz
CDCl3
6h
0.98
2.03
1.03
3.03
2.00
1.01
3.01
2.01
1.01
1.00
3.00
3.03
2.98
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
155.71
149.79
146.07
141.89
139.55
137.29
134.64
131.94
130.38
130.05
129.59
129.25
128.60
128.50
128.14
127.86
126.85
126.05
119.19
99.74
94.04
77.34
77.02
76.70
56.35
56.13
45.52
29.71
21.02
0.00
100MHz
CDCl3
6h
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.513
7.493
7.427
7.411
7.259
7.199
7.179
7.066
7.048
7.030
7.005
6.987
6.950
6.931
6.761
6.007
5.986
5.563
2.426
0.000
400MHz
CDCl3
6i
1.00
2.03
1.02
3.03
0.99
2.02
0.99
2.02
1.03
2.03
0.98
2.99
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
155.59
143.92
141.85
137.34
134.51
130.36
130.06
129.60
129.20
128.51
127.85
126.81
97.08
91.98
77.33
77.04
76.70
45.58
21.00
0.00
100MHz
CDCl3
6i
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.106
7.703
7.685
7.510
7.490
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7.409
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7.251
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7.194
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7.068
7.056
7.050
7.031
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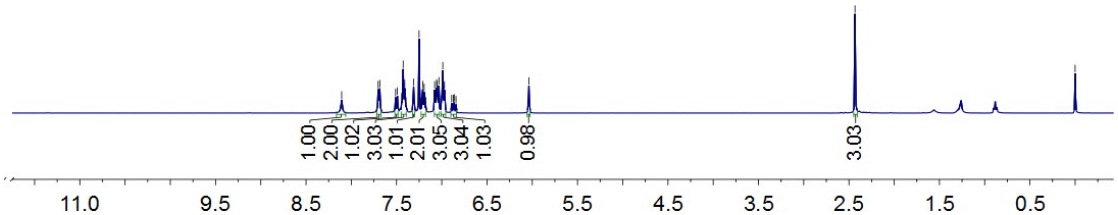
N
H
6j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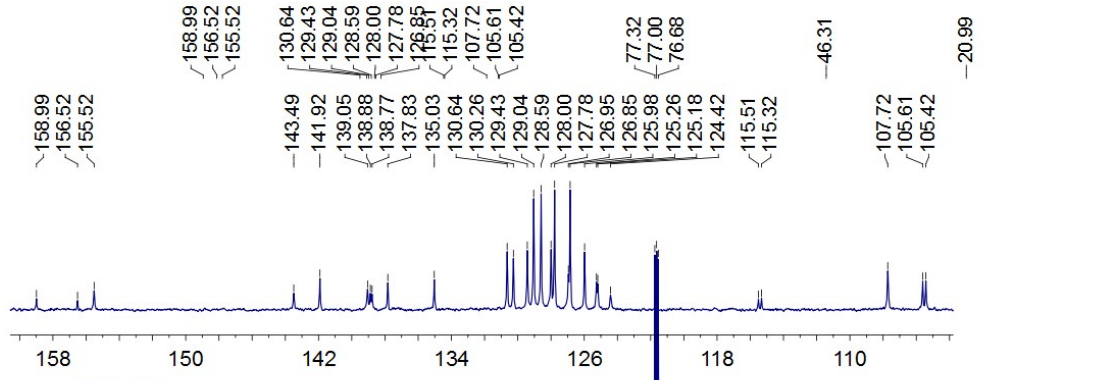
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77.00
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46.31
20.99
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130.64
130.26
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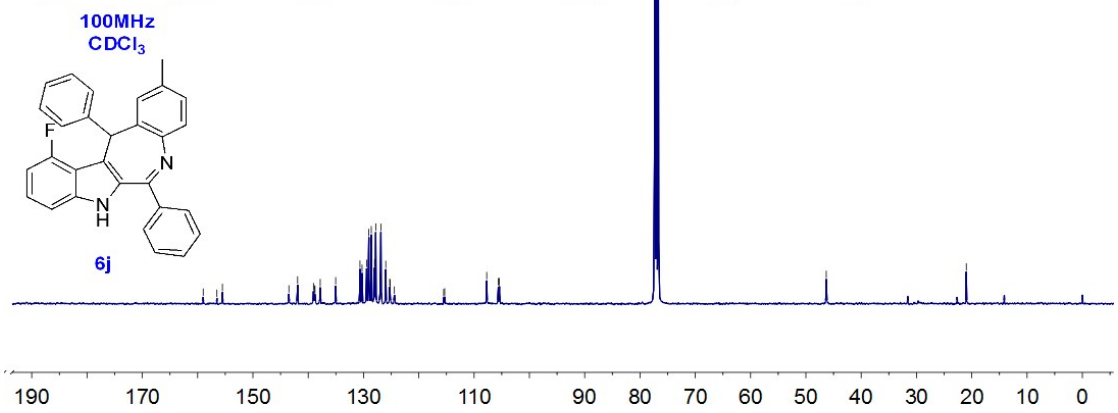
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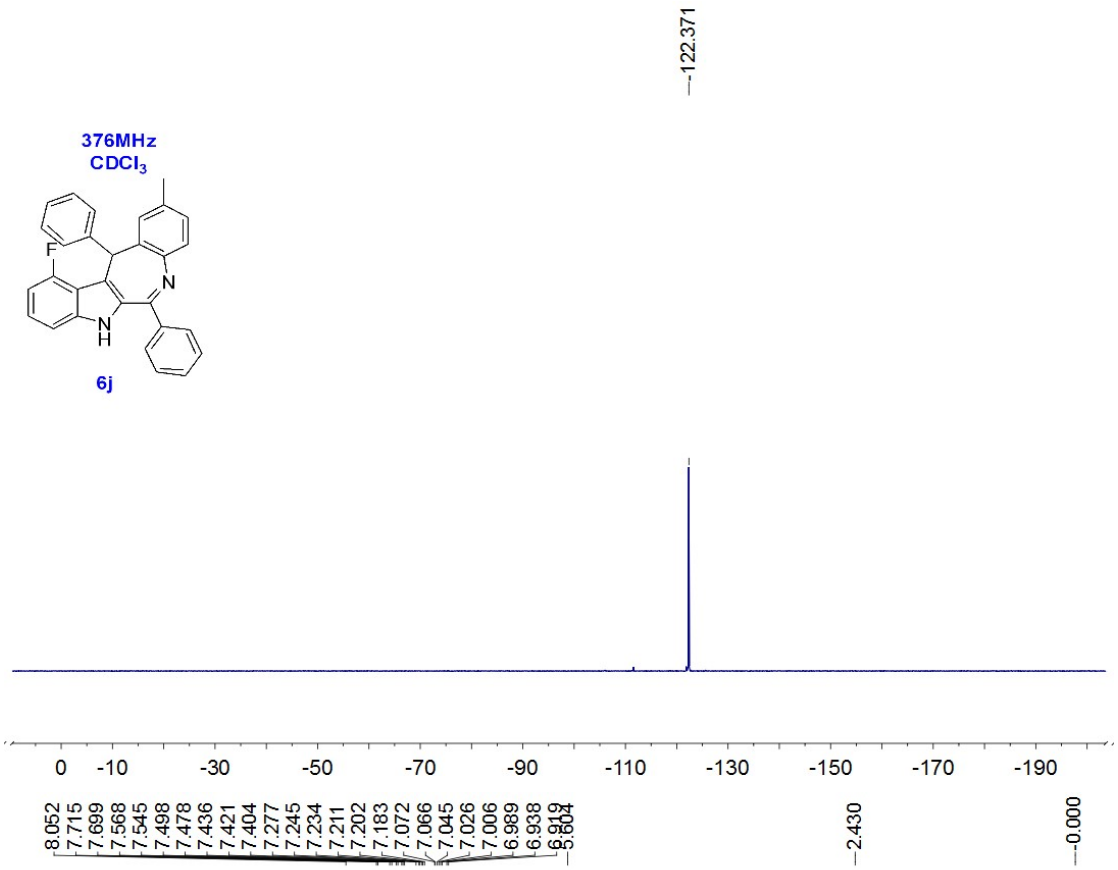
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-150
-170
-190
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7.715
7.699
7.568
7.545
7.498
7.478
7.436
7.421
7.404
7.277
7.245
7.234
7.211
7.202
7.183
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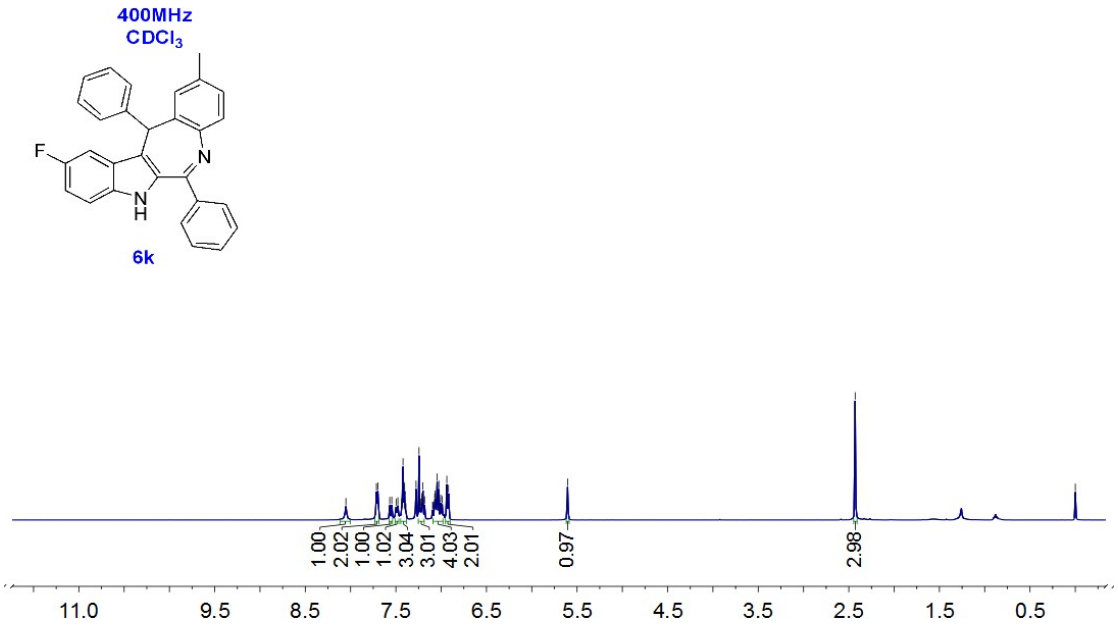
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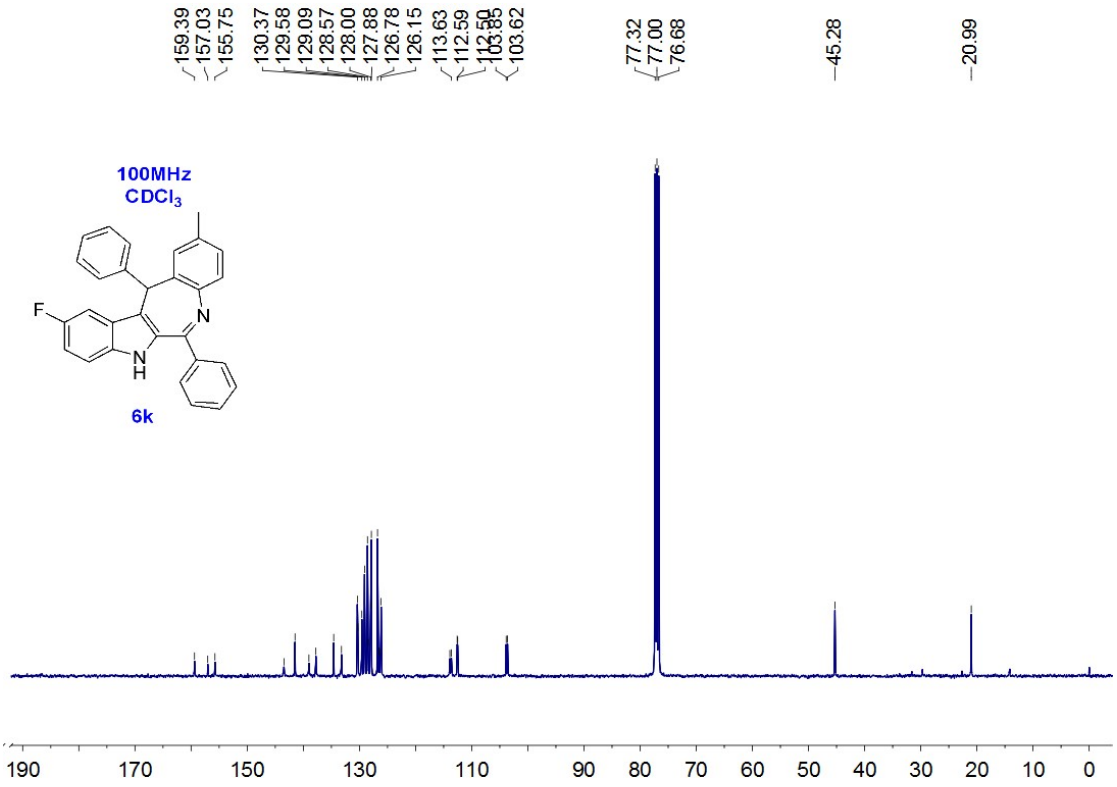
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103.62
77.32
77.00
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45.28
20.99
100MHz
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150
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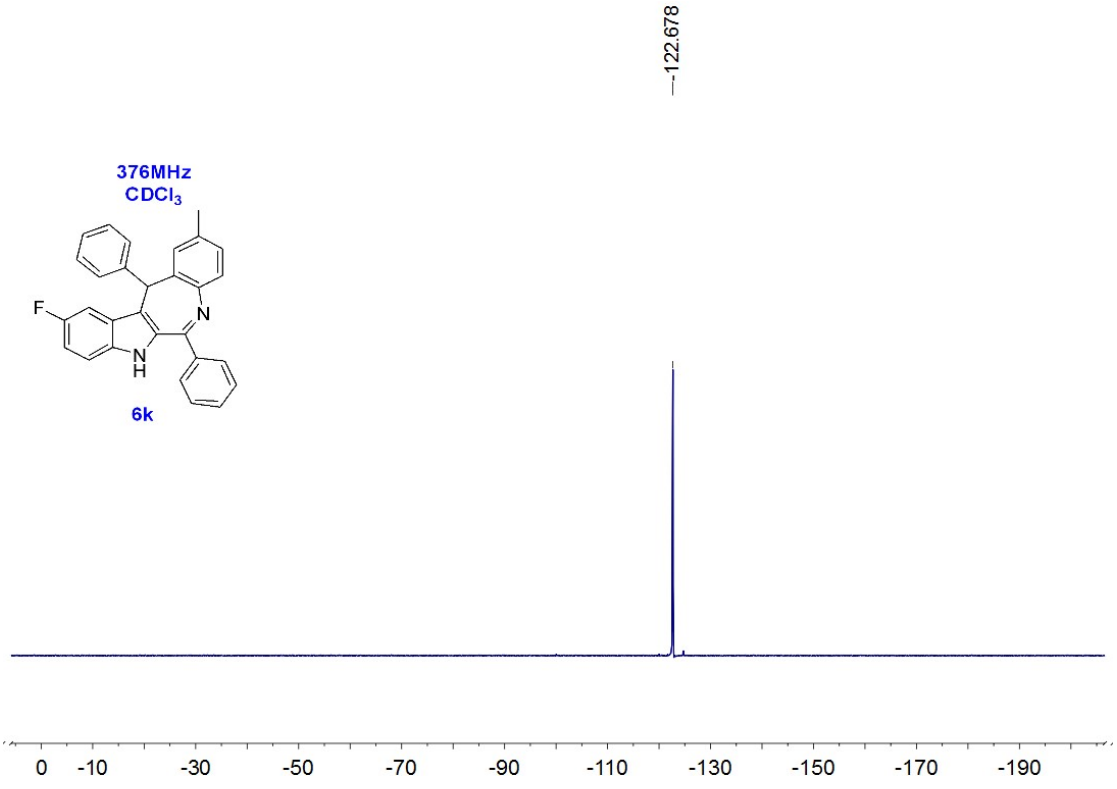
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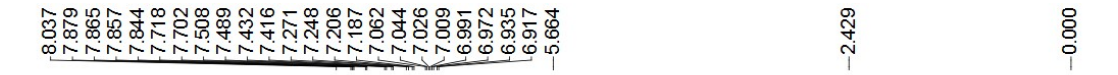
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7.271
7.248
7.206
7.187
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7.026
7.009
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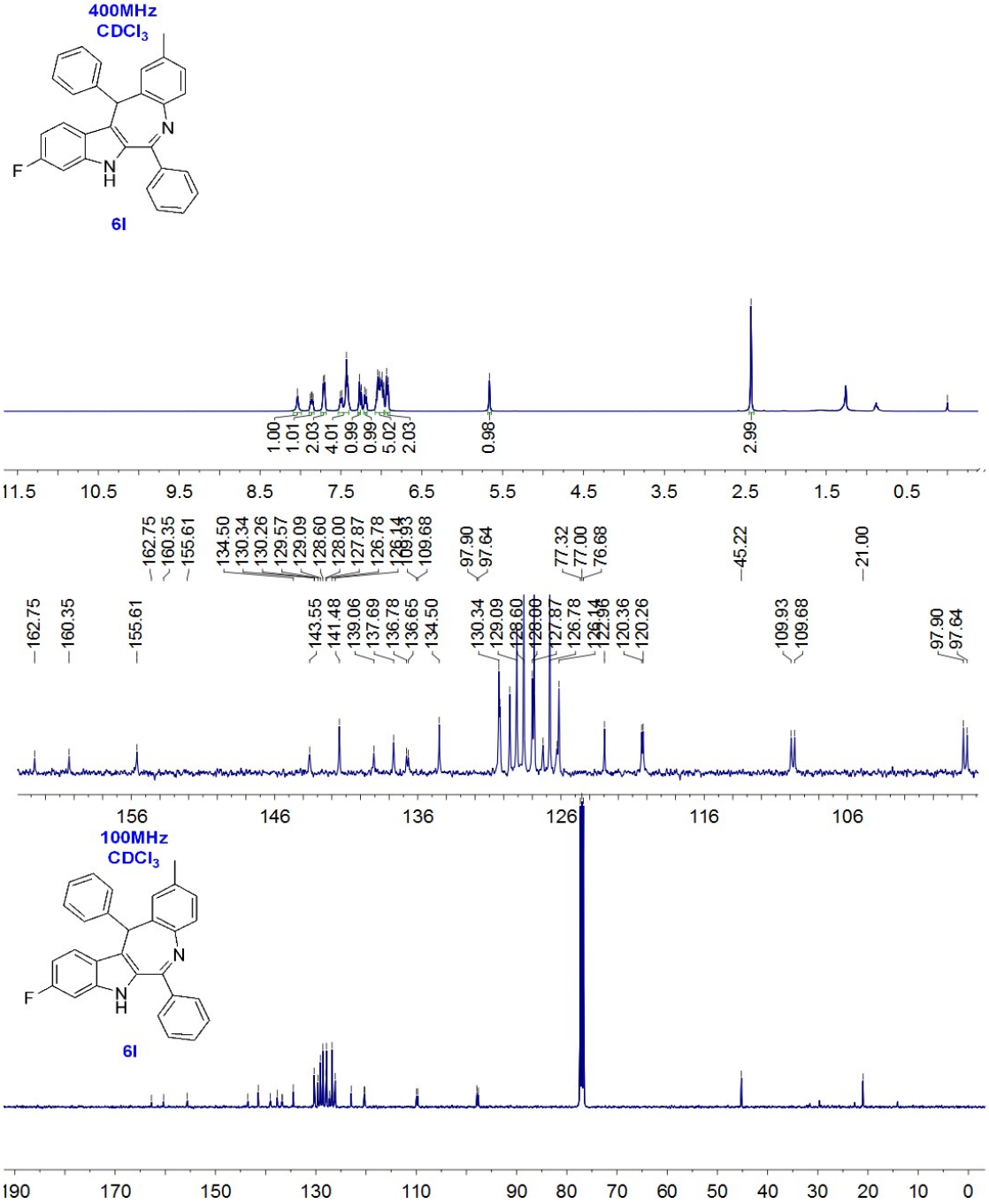
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H
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2.99
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
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1.5
0.5
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97.64
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76.68
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21.00
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136.78
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129.09
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126.78
120.36
120.26
109.93
109.68
97.90
97.64
156
146
136
126
116
106
100MHz
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H
6l
190
170
150
130
110
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70
60
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30
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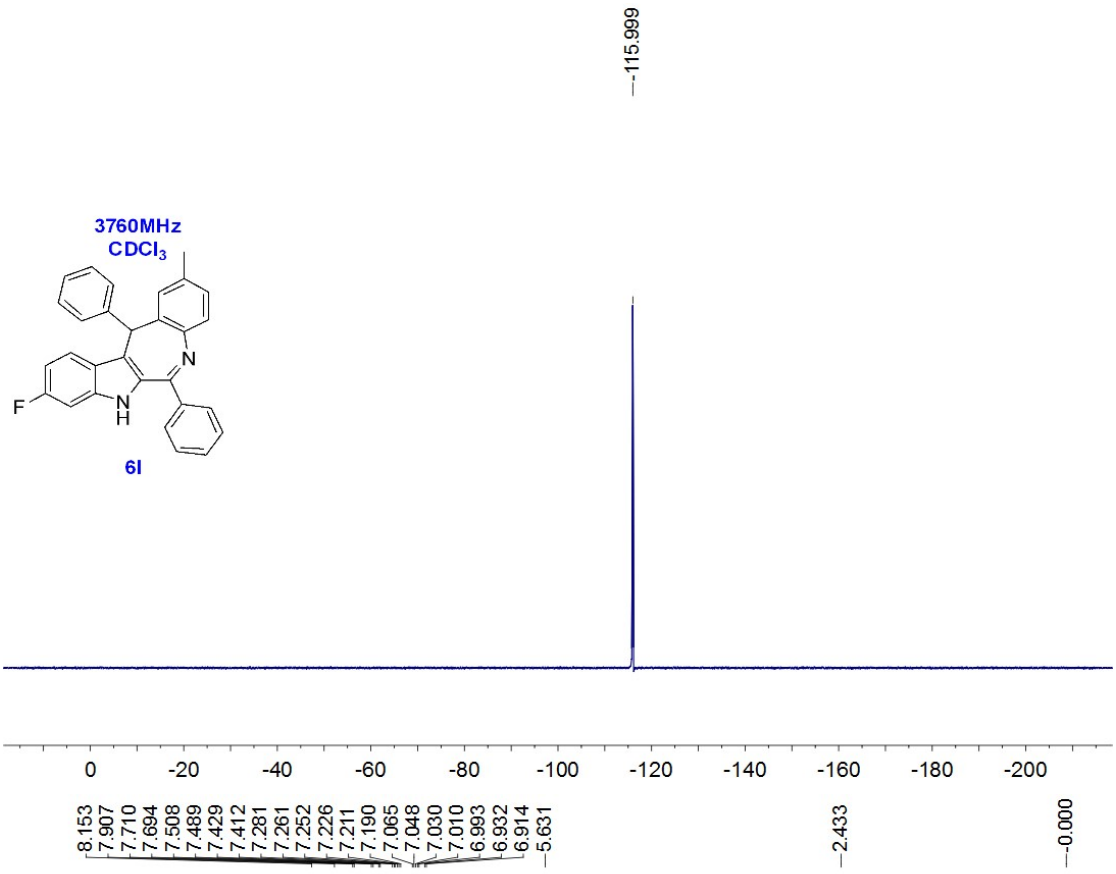
10
0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-180
-200
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7.907
7.710
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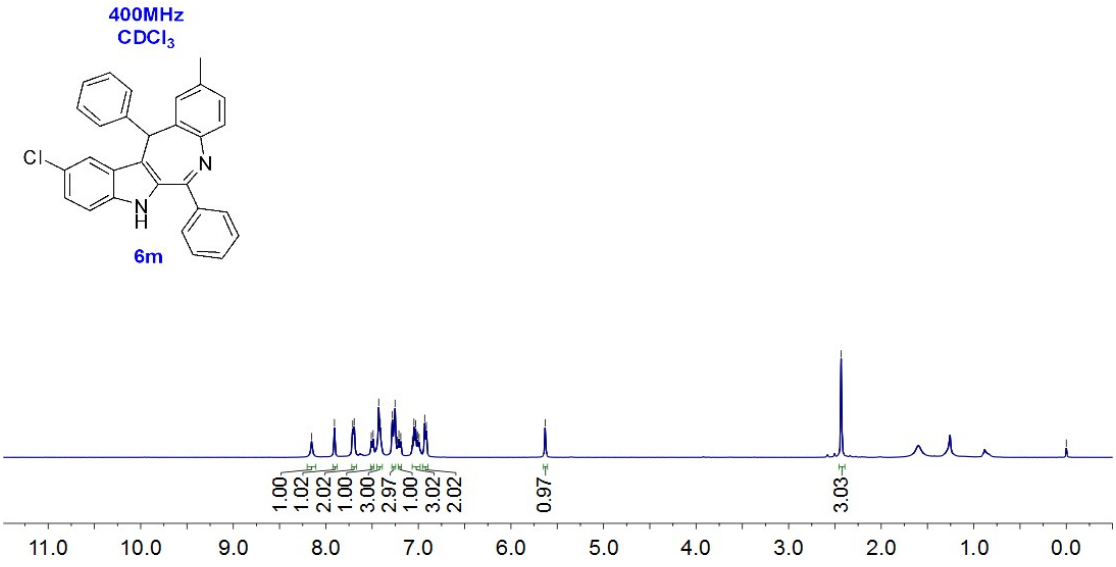
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N
H
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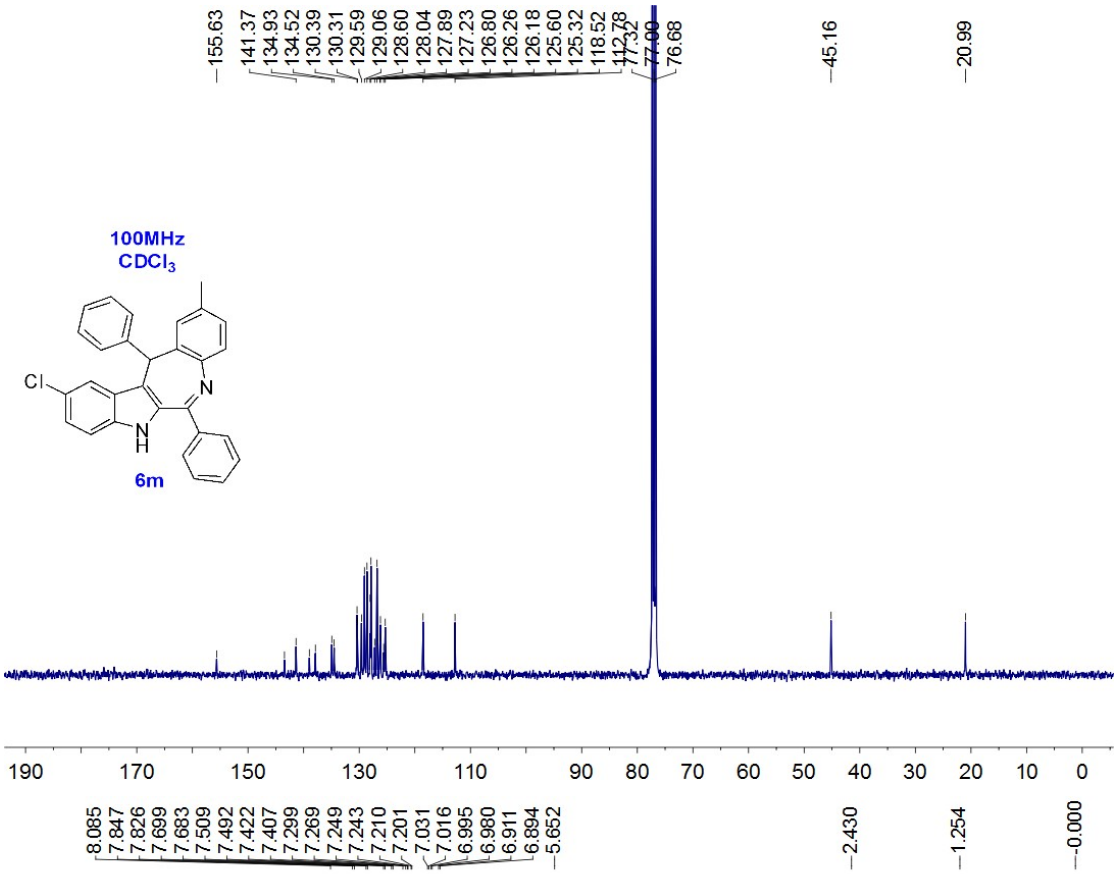
1.02
2.02
1.00
3.00
2.97
1.00
3.02
2.02
0.97
3.03
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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126.26
126.18
125.60
125.32
118.52
112.78
77.32
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76.68
45.16
20.99
100MHz
CDCl3
Cl
N
H
6m
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
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7.847
7.826
7.699
7.683
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7.422
7.407
7.299
7.269
7.249
7.243
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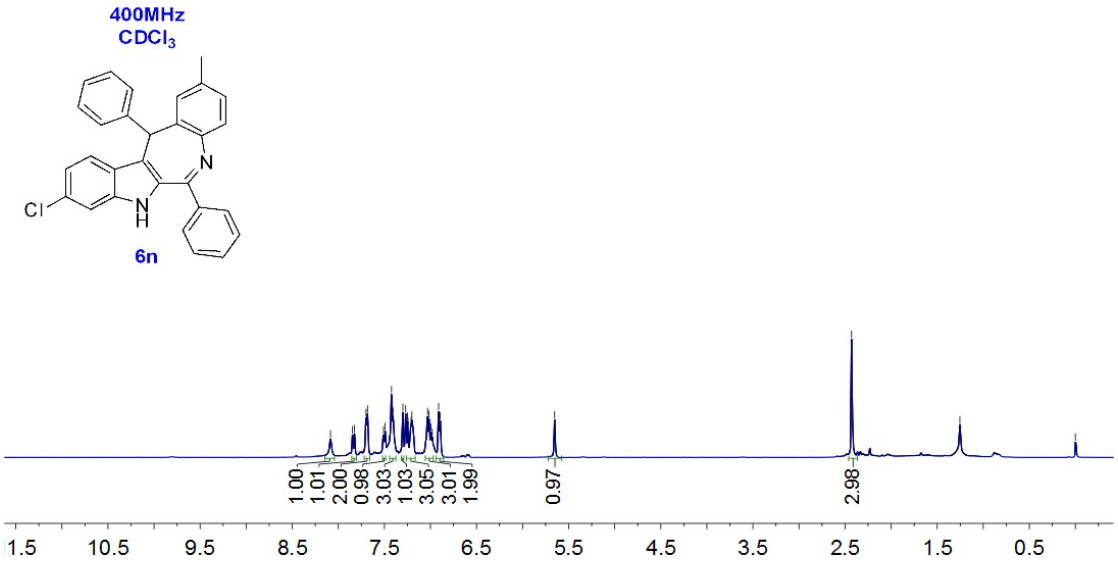
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Cl
N
H
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2.00
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1.03
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3.01
1.99
0.97
2.98
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8.5
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2.5
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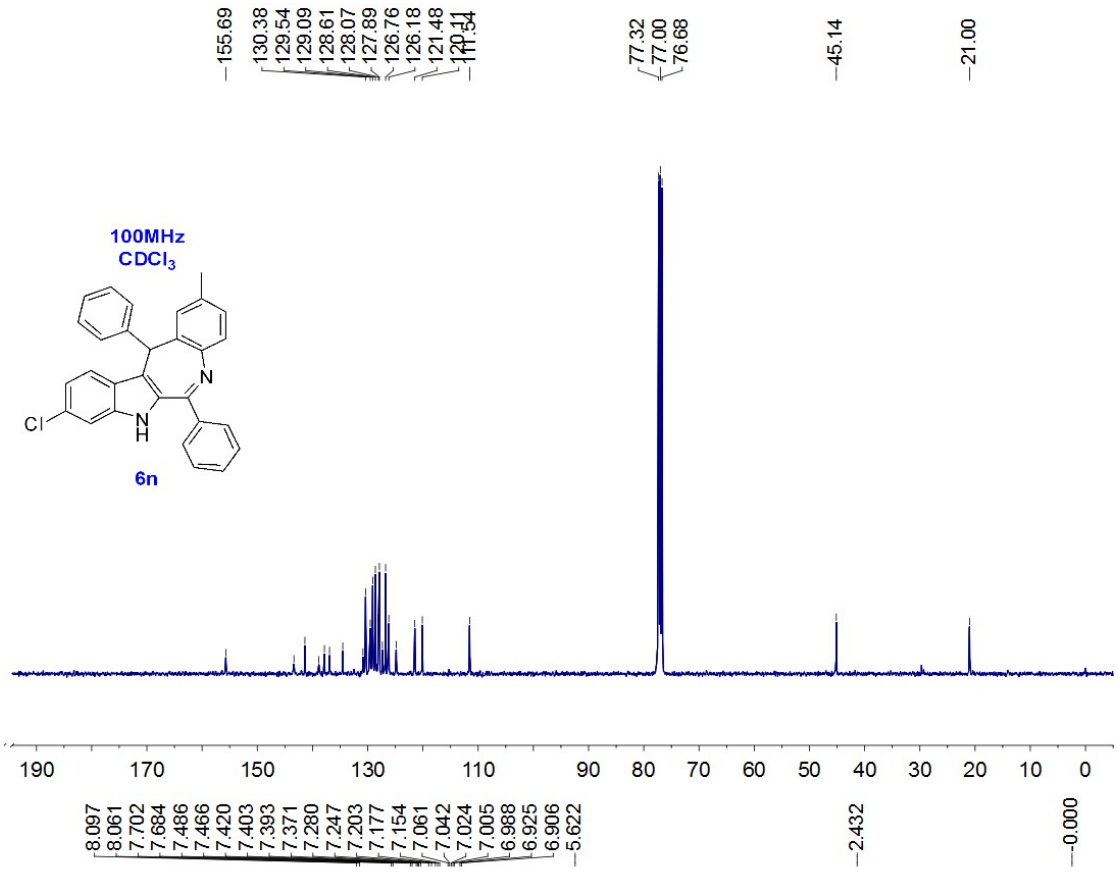
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77.32
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76.68
45.14
21.00
100MHz
CDCl3
Cl
N
H
6n
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
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8.061
7.702
7.684
7.486
7.466
7.420
7.403
7.393
7.371
7.280
7.247
7.203
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7.042
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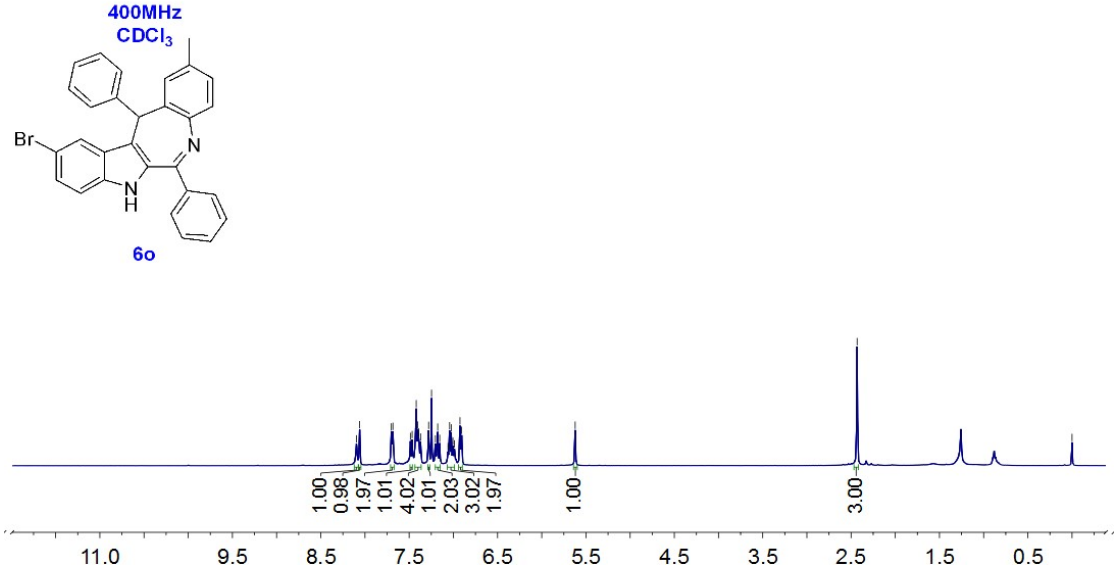
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Br
N
H
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1.97
1.01
4.02
1.01
2.03
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1.00
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4.5
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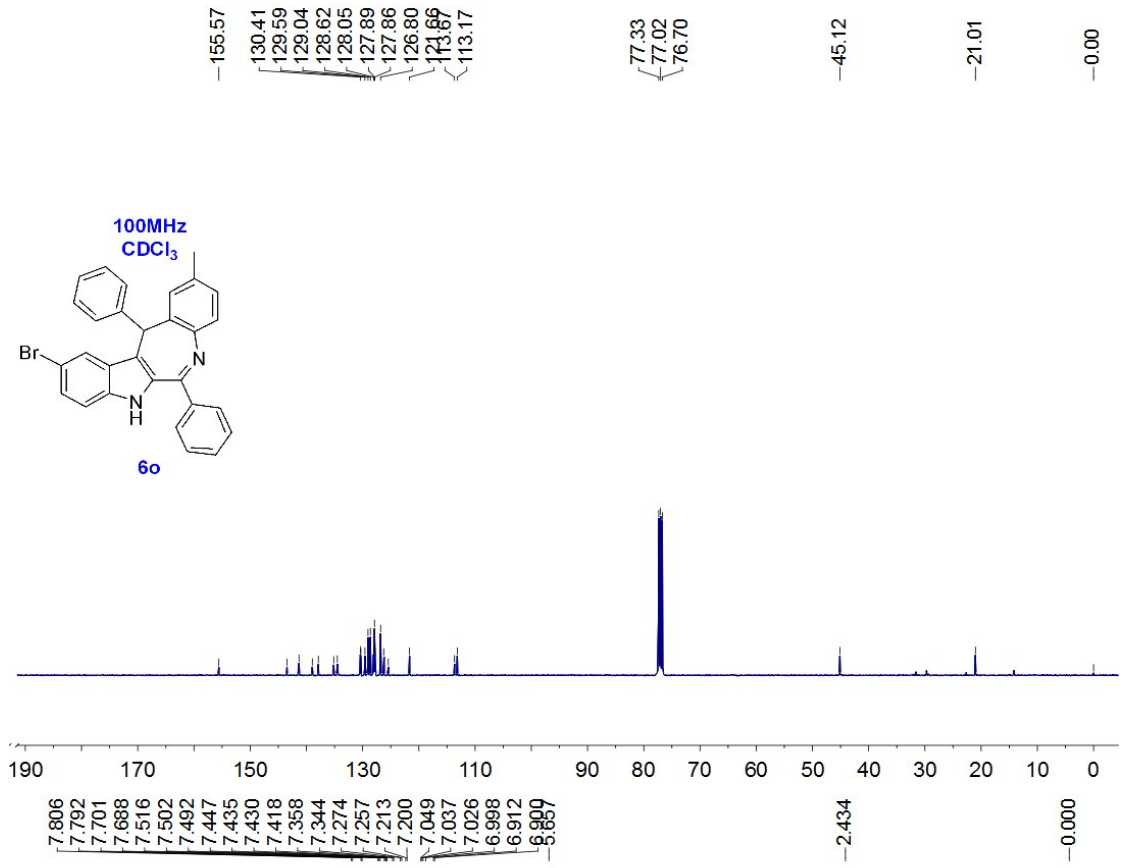
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127.86
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113.17
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45.12
21.01
0.00
100MHz
CDCl3
Br
N
H
6o
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
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7.792
7.701
7.688
7.516
7.502
7.492
7.447
7.435
7.430
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7.358
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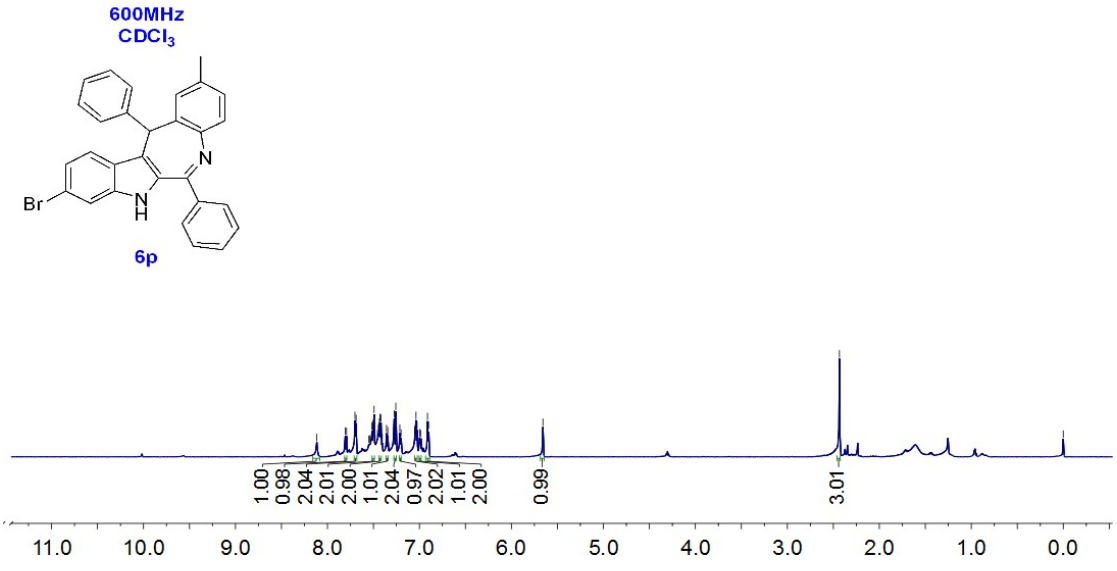
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2.01
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1.01
2.04
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2.02
1.01
2.00
0.99
3.01
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8.0
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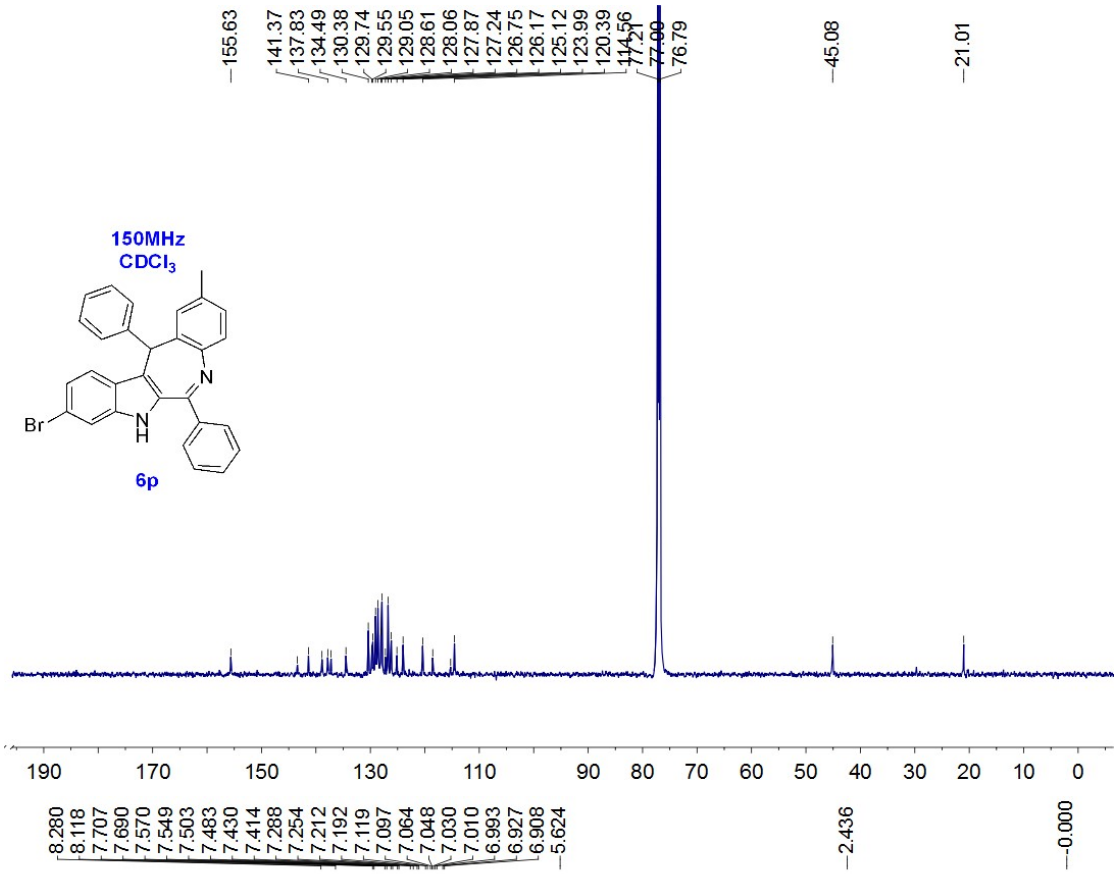
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126.17
125.12
123.99
120.39
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77.21
77.00
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45.08
21.01
150MHz
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Br
N
H
6p
190
170
150
130
110
90
80
70
60
50
40
30
20
10
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7.212
7.192
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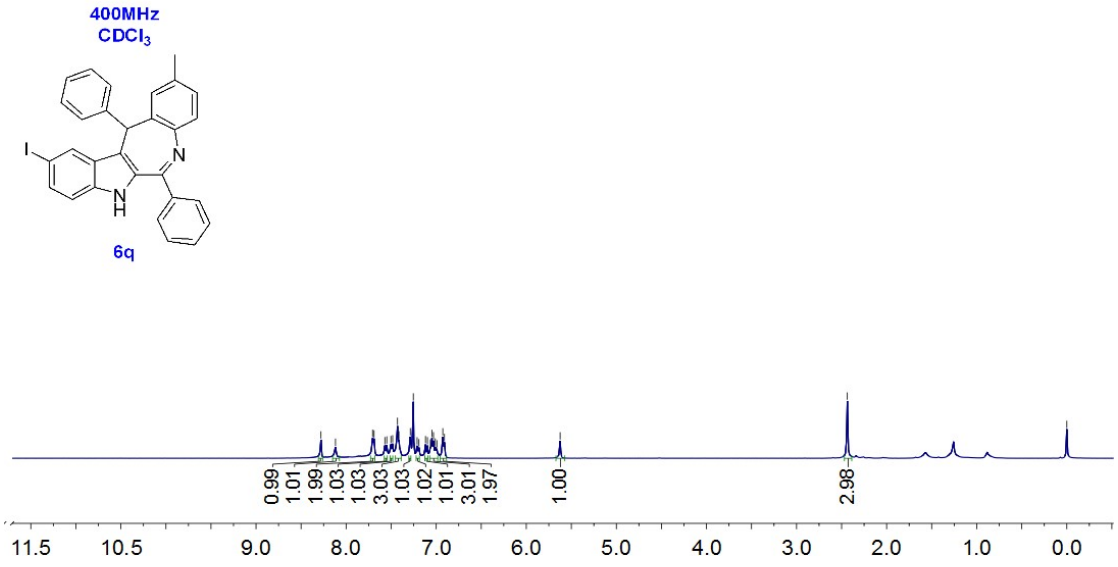
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N
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1.03
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3.03
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1.01
3.01
1.97
1.00
2.98
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8.0
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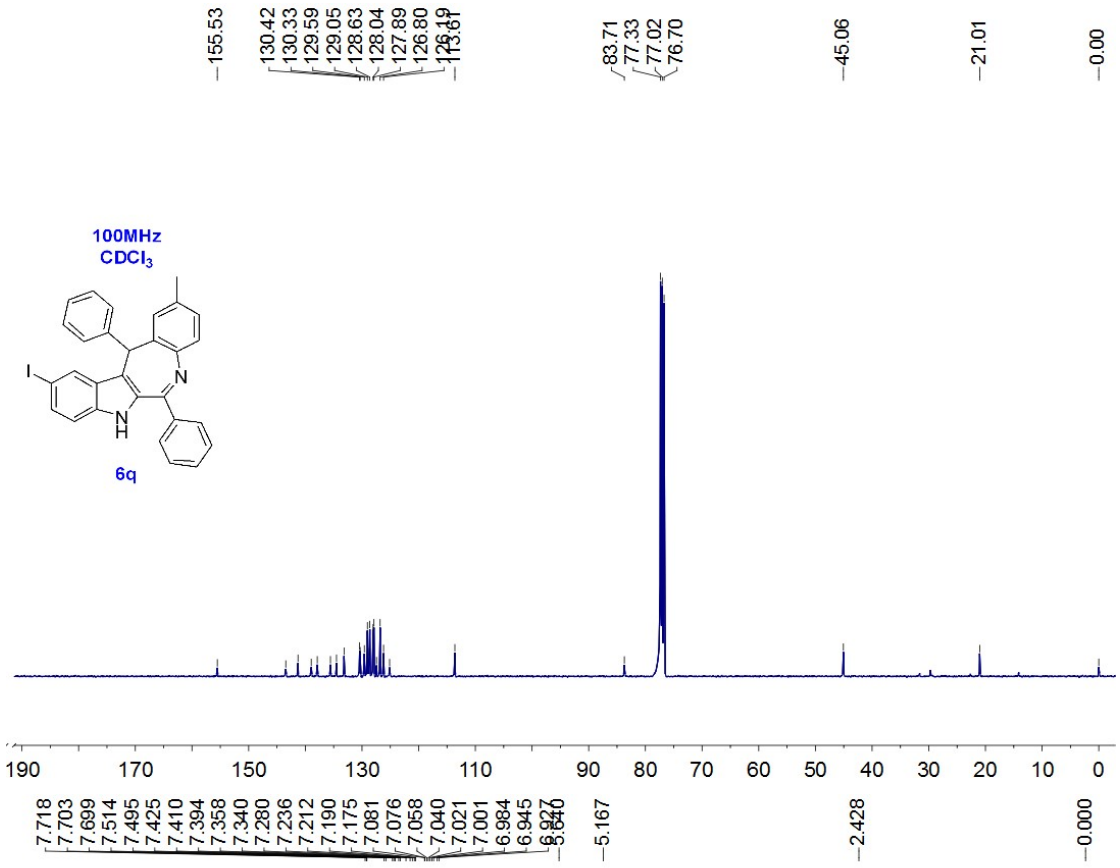
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0.00
100MHz
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I
N
H
6q
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170
150
130
110
90
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70
60
50
40
30
20
10
0
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7.703
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7.495
7.425
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7.358
7.340
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7.212
7.190
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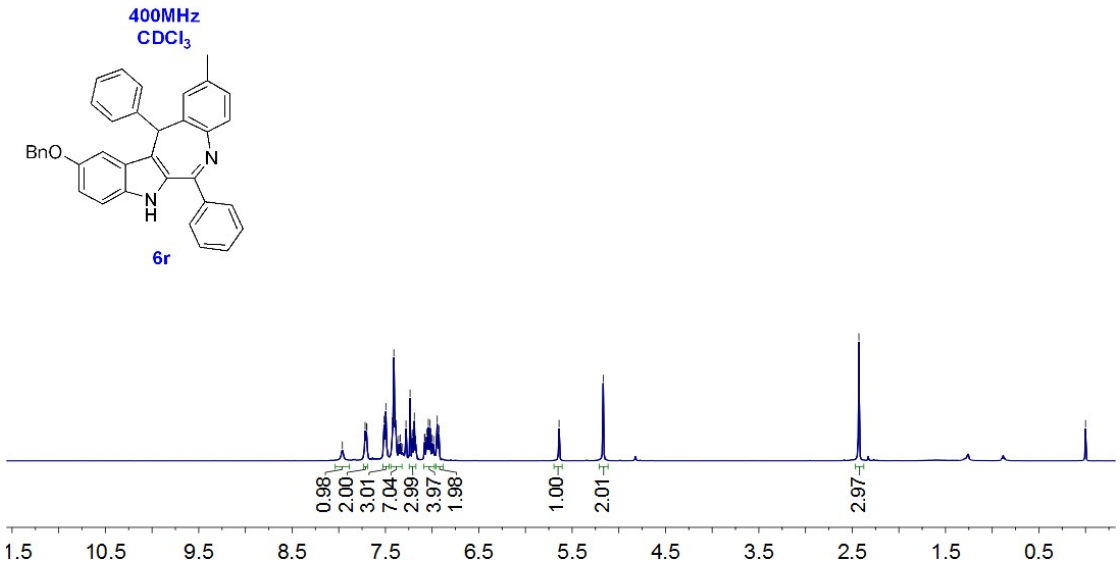
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2.97
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8.5
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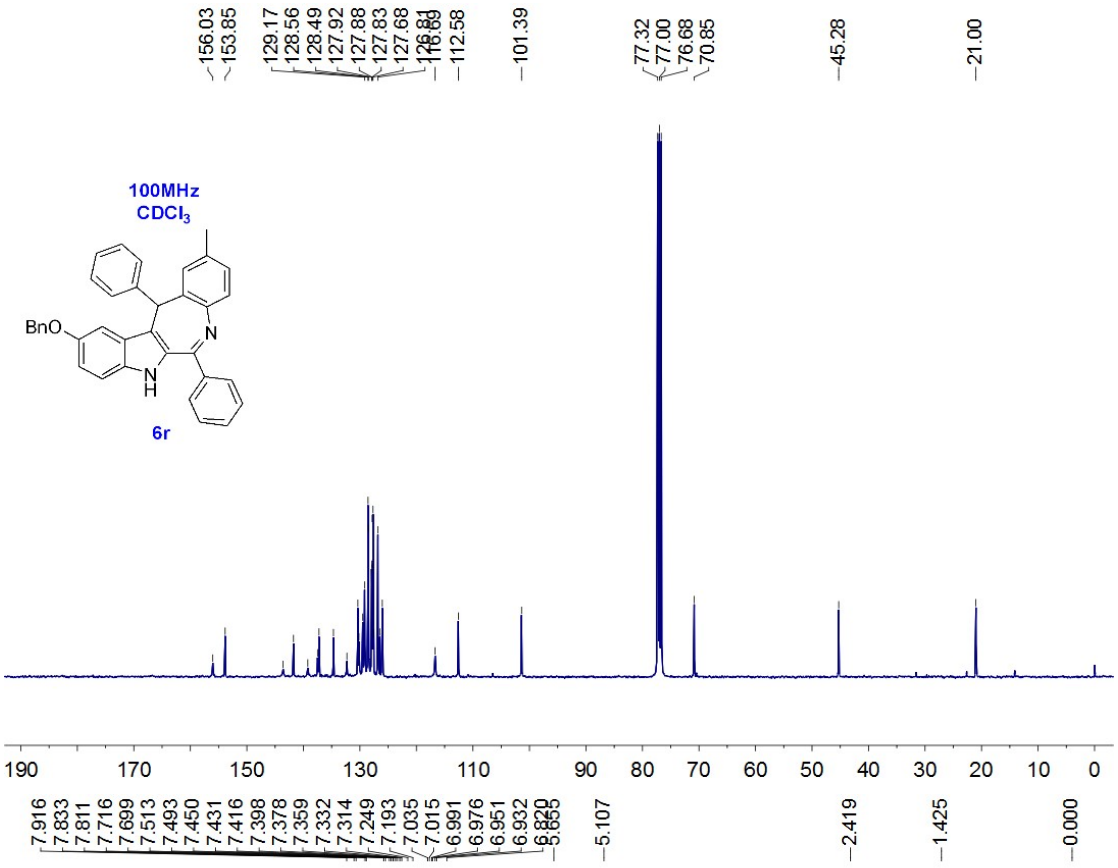
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127.83
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112.58
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77.00
76.68
70.85
45.28
21.00
100MHz
CDCl3
BnO
N
H
6r
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
7.916
7.833
7.811
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7.513
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7.378
7.359
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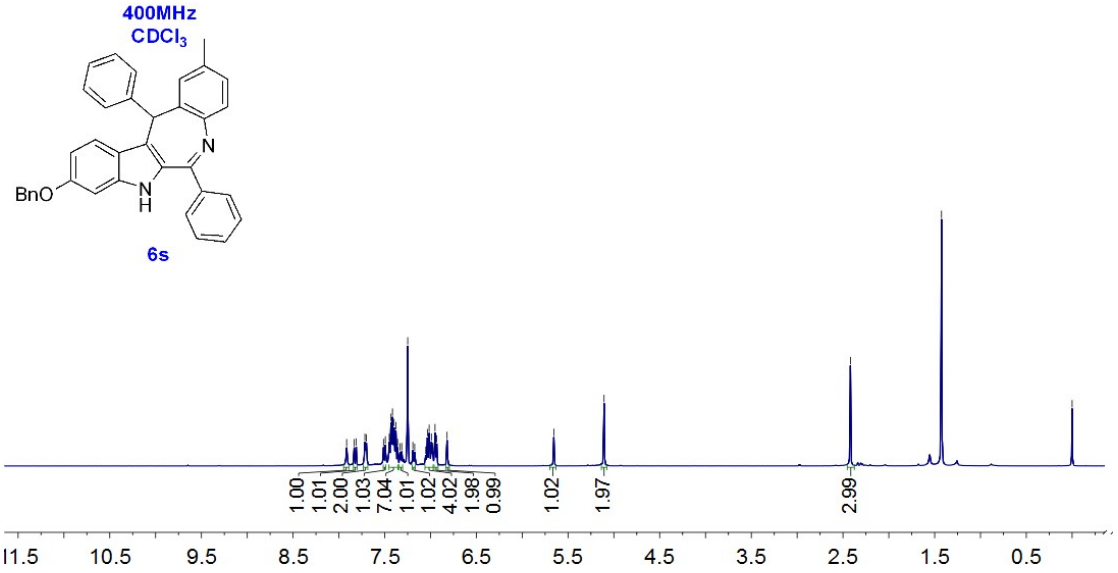
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7.04
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1.02
4.02
1.98
0.99
1.02
1.97
2.99
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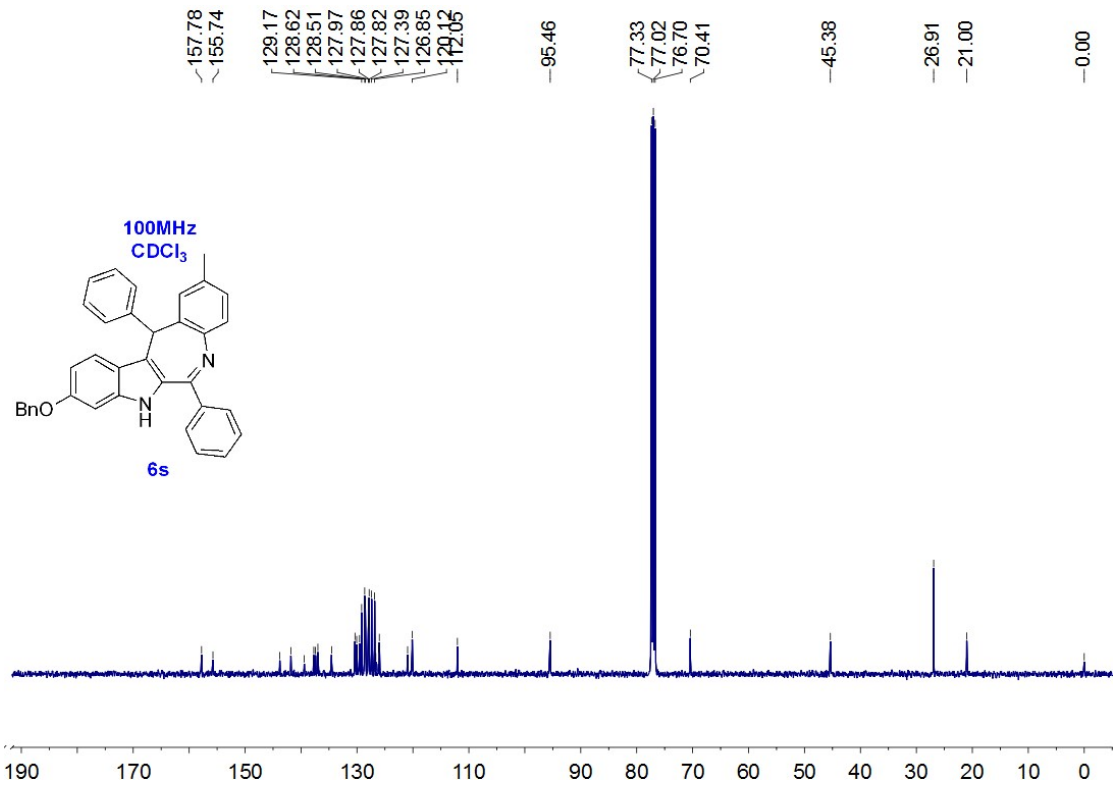
0.5



7. References

(1) (a) J. C. Xiang, M. Wang, Y. Cheng and A. X. Wu, Molecular Iodine-Mediated Chemoselective Synthesis of Multisubstituted Pyridines Through Catabolism and Reconstruction Behavior of Natural Amino Acids. *Org. Lett.*, 2015, **18**, 24-27; (b) J. C. Xiang, Y. Cheng, Z. X. Wang, J. T. Ma, M. Wang, B. C. Tang, Y. D. Wu and A. X. Wu, Oxidative Trimerization of Amino Acids: Selective Synthesis of 2,3,5-Trisubstituted Pyridines. *Org. Lett.*, 2017, **19**, 2997-3000; (c) J. C. Xiang, Z. X. Wang, Y. Cheng, S. Q. Xia, M. Wang, B. C. Tang, Y. D. Wu and A. X. Wu, Divergent Synthesis of Functionalized Quinolines from Aniline and Two Distinct Amino Acids. *J. Org. Chem.*, 2017, **82**, 9210-9216. (d) J. C. Xiang, J. G. Wang, M. Wang, X. G. Meng and A. X. Wu, One-pot Total Synthesis of Streptindole, Arsindoline B and Their Congeners

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