Supporting Information

Copper-Catalyzed N-arylation of Iminodibenzyls and Iminostilbenes Using Unactivated Aryl Halides

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Contents

1. General considerations

1.1 Materials

Unless other specified, all manipulations were carried out using standard schlenk, high vacuum, and glovebox techniques. Glassware was dried in a 140 ^{o}C oven over 4 hours before used. The 2-(3-butenyl)bromobenzene was synthesized according to literature procedures.[1] Iminodibenzyl and iminostilbene derivatives were purchased from Accela ChemBio Co., Ltd, China and used as received. Flash colum chromatography was performed on silica gel (particle size 300-400 mesh ASTM), purchased from Yantai, China. Hg (99.999% metals basis) and PMe_3 (97%) were purchased from Aladdin Industrial Corporation. The all solvents, bases and aryl halides were obtained from commerical sources and dried and degassed according to known procedure to ensure in absence of water and oxygen.

1.2 Analytical Methods

NMR spectra data were obtained on AVANCE (III) HD 400 MHz instruments. ^{1}H NMR spectra were referenced to residual protio solvent peaks or TMS signal (0 ppm) and ^{13}C NMR spectra were referenced to the solvent resonance. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectrometer (HRMS) were carried out by Jiyun Biotech using the Thermo Scientific LTQ Orbitrap XL. GC was performed on a Shimadzu GC-2010 plus spectrometer. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer.

2. Typical procedures for N-arylation of dibenzazepines

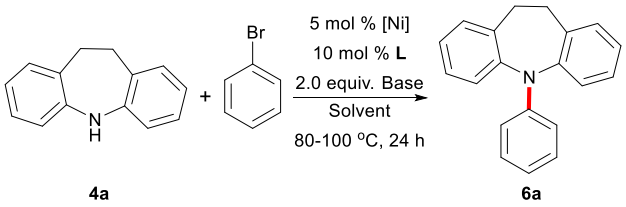
2.1 Cu-catalytic system

In an argon filled glovebox, a 5 mL dried schlenk tube equipped with a magnetic stir bar was charged with the CuO (4.0 mg, 50.0 μmol, 5.0 mol %), iminodibenzyl (0.2 g, 1.0 mmol, 1.0 equiv.), bromobenzene (210 μL, 2.0 mmol, 2.0 equiv.), KO*t*Bu (0. 2 g, 2.0 mmol, 2.0 equiv.), DMSO (2.0 mL), then stirred at 80 ^{o}C oil bath for 18 h. After that, the reaction mixture was cooled to room temperature, and dissolved in ethyl acetate and filtrated though celite. The filtrate was collected and the volatiles were removed under reduced pressure and the crude product was analyzed by GC analysis, with mesitylene (139 μL, 1.0 mmol, 1.0 equiv) as interal standard to obtain the GC yields (95%). After that, the total crude products were purified by silica gel column chromatography using petroleum ether to afford the product as pale yellow solid (258 mg, 90%).

2.2 Ni-catalytic system

In an argon filled glovebox, a 5 mL dried schlenk tube equipped with a magnetic stir bar was charged with the NiO (3.7 mg, 50.0 μmol, 5.0 mol %), PPh_3 (26.2 mg, 0.1 mmol, 10.0 mol %), iminodibenzyl (0.2 g, 1.0 mmol, 1.0 equiv.), bromobenzene (210 μL, 2.0 mmol, 2.0 equiv.), KO*t*Bu (0. 2 g, 2.0 mmol, 2.0 equiv.), THF (2.0 mL), then stirred at 100 ^{o}C oil bath for 24 h. After that, the reaction mixture was cooled to room temperature, and dissolved in ethyl acetate and filtrated though celite. The filtrate was collected and the volatiles were removed under reduced pressure and the crude product was analyzed by GC analysis, with mesitylene (139 μL, 1.0 mmol, 1.0 equiv) as interal standard to obtain the GC yields (86%). After that, the total crude products were purified by silica gel column chromatography using petroleum ether to afford the product as pale yellow solid (229 mg, 80%).

3. Optimization of catalysts and reaction conditions (Ni) [a]

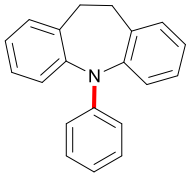


4a 6a

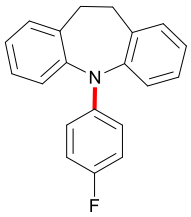
Entry	[Ni]	L	T (°C)	Solvent	Base	Yield (%)[b]
1	$NiCl_2$	BINAP	100	THF	KO*t*Bu	41
2	$NiCl_2$	Ph_3P	100	THF	KO*t*Bu	71
3	$NiCl_2$	DPPF	100	THF	KO*t*Bu	58
4	$NiCl_2$	PhDavePhos	100	THF	KO*t*Bu	54
5	$NiCl_2$	1, 10-Phenanthroline	100	THF	KO*t*Bu	54
6	$NiCl_2$	Ph_3P	100	DMF	KO*t*Bu	22
7	$NiCl_2$	Ph_3P	100	CH_3CN	KO*t*Bu	0
8	$NiCl_2$	Ph_3P	100	1, 4-dioxane	KO*t*Bu	47
9	$NiCl_2$	Ph_3P	100	PhMe	KO*t*Bu	7
10	$Ni(OAc)_2$	Ph_3P	100	THF	KO*t*Bu	63
11	Ni(COD)	Ph_3P	100	THF	KO*t*Bu	79
12	Ni_2CO_3	Ph_3P	100	THF	KO*t*Bu	70
13	$Ni(NO_3)_2$	Ph_3P	100	THF	KO*t*Bu	52
14	NiO	Ph_3P	100	THF	KO*t*Bu	86(80)
15	NiO	Ph_3P	100	THF	KOH	10
16	NiO	Ph_3P	100	THF	KOMe	0
17	NiO	Ph_3P	100	THF	K_2CO_3	0
18	NiO	Ph_3P	100	THF	KOAc	0
19	NiO	Ph_3P	80	THF	KO*t*Bu	64

[a]Reaction conditions: **4a** (1.0 mmol), bromobenzene (2.0 mmol), NiO (50 μmol, 5 mol %), Ligand (0.1 mmol, 10 mol %), KO*t*Bu (2.0 mmol) and Solvent (2.0 mL) under Ar at 80-100 °C for 24 h; [b]Yields determined by GC; The value in parenthese is the isolated yield.

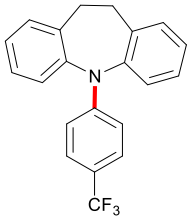
4. NMR spectra data of dibenzazepines



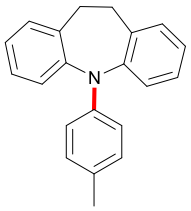
5-phenyl-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow solid (217 mg, 80%, from **3a**-Cl; 244 mg, 90%, from **3a**-Br; 239 mg, 88%, from **3a**-I; 217 mg, 80%, from **6a**-Br; 220 mg, 81%, from **6a**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.32-7.16 (m, 7H), 7.14-7.05 (m, 2H), 6.75-6.68 (m, 1H), 6.58 (d, J = 8.0 Hz, 2H), 2.99 (s, 4H). These spectroscopic data correspond to reported data.[2]



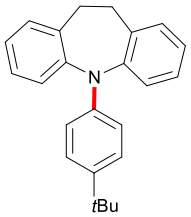
5-(4-fluorophenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave colorless oil (191 mg, 66%, from **3b**-Cl; 237 mg, 82%, from **3b**-Br; 225 mg, 78%, from **3b**-I; 211 mg, 73%, from **6b**-Br; 179 mg, 62%, from **6b**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.28-7.20 (m, 6H), 7.01(q, J = 12.0 Hz, J = 8.0 Hz, 1H), 6.78 (t, J = 8.0 Hz, 1H), 6.51-6.47 (m, 1H), 6.41-6.23 (m, 1H), 2.98 (s, 4H). These spectroscopic data correspond to reported data.[2]



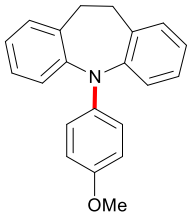
5-[4-(trifluoromethyl)phenyl]-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave colorless oil (176 mg, 52%, from **3c**-Cl; 231 mg, 68%, from **3c**-Br; 224 mg, 66%, from **3c**-I; 248 mg, 73%, from **6c**-Br; 210 mg, 62%, from **6c**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.32-7.27 (m, 2H), 7.25-7.22 (m, 3H), 7.15 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.78 (s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 2.97 (s, 4H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 149.4, 142.9 (d, J = 6.1 Hz), 138.2 (d, J = 9.5 Hz), 131.3, 129.7 (d, J = 9.1 Hz), 129.5, 127.6, 126.4 (d, J = 3.7 Hz), 121.3 (q, J =366.6 Hz , J = 30.3 Hz), 115.6, 114.1, 112.1, 108.9 (d, J = 5.1 Hz), 30.8; HRMS (ESI) m/z calcd for $C_{21}H_{17}F_3N^+$ $(M+H)^+$ 340.13076, found 340.13086.



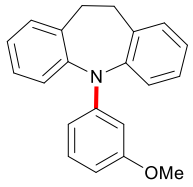
5-(p-tolyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow oil (231 mg, 81%, from **3d**-Cl; 257 mg, 90%, from **3d**-Br; 237 mg, 83%, from **3d**-I; 240 mg, 84%, from **6d**-Br; 225 mg, 79%, from **6d**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 4.0 Hz, 2H), 7.27-7.19 (m, 6H), 7.00 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.54 (m, 1H), 6.40 (d, J = 8.0 Hz, 1H), 3.00 (s, 4H), 2.20 (s, 3H). These spectroscopic data correspond to reported data.[2]



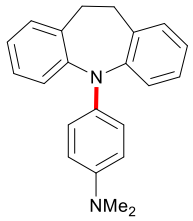
5-[4-(tert-butyl)phenyl]-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave colorless oil (272 mg, 83%, from **3e**-Cl; 288 mg, 88%, from **3e**-Br; 255 mg, 78%, from **3e**-I; 269 mg, 82%, from **6e**-Br; 265 mg, 81%, from **6e**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.22 (m, 4H), 7.12 (d, J = 8.0 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.66 (s, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 3.00 (s, 4H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 148.9, 143.8, 138.5, 130.9, 130.2, 128.5, 125.7，127.0, 114.8, 112.4, 110.1, 34.8, 31.7, 31.4；HRMS (ESI) m/z calcd for $C_{24}H_{26}N^+$ $(M+H)^+$ 328.20598, found 328.20593.



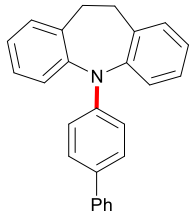
5-(4-methoxyphenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (262 mg, 87%, from **3f**-Cl; 274 mg, 91%, from **3f**-Br; 259 mg, 86%, from **3f**-I; 274 mg, 91%, from **6f**-Br; 248 mg, 87%, from **6f**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.28-7.21 (m, 6H), 7.03 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 4.0 Hz, 1H), 6.59 (d, J = 4.0 Hz, 1H), 6.31 (d, J = 8.0 Hz, 1H), 6.21-6.17 (m, 1H), 3.73 (s, 3H), 3.02 (s, 4H).



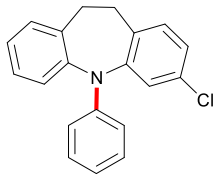
5-(3-methoxyphenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (238 mg, 79%, from **3g**-Cl; 250 mg, 83%, from **3g**-Br; 253 mg, 84%, from **3g**-I; 250 mg, 83%, from **6g**-Br; 262 mg, 87%, from **6g**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.21 (m, 5H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.18-6.14 (m, 2H), 3.67 (s, 3H), 2.99 (s, 4H).



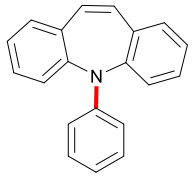
4-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-N,N-dimethylaniline. Purification by silica gel column chromatography using petroleum ether gave pale yellow solid (185 mg, 59%, from **3h**-Cl; 217 mg, 69%, from **3h**-Br; 220 mg, 70%, from **3h**-I; 179 mg, 57%, from **6h**-Br; 154 mg, 49%, from **6h**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.22 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.66 (s, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 3.00 (s, 4H), 1.18 (s, 9H)；^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 150.2, 143.9, 138.6, 130.9, 130.4, 129.5, 127.0，126.9, 102.9, 102.6, 97.8, 40.7, 31.1；HRMS (ESI) m/z calcd for $C_{22}H_{23}N_2^+$(M+H)$^+$ 315.18558, found 315.18552.



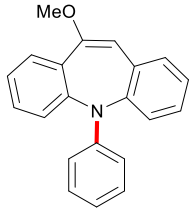
5-([1,1'-biphenyl]-4-yl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow oil (250 mg, 72%, from **3i**-Cl; 278 mg, 80%, from **3i**-Br; 260 mg, 75%, from **3i**-I; 257 mg, 74%, from **6i**-Br; 267 mg, 77%, from **6i**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0, 1H), 7.40-7.34 (m, 3H), 7.31-7.26 (m, 3H), 7.23-7.19 (m, 3H), 7.17-7.14 (m, 2H), 7.12-7.05 (m, 1H), 6.91-6.83 (m, 1H), 6.76-6.71 (m, 1H), 6.62-6.56 (m, 1H), 6.54-6.46 (m, 1H), 2.94 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 148.6, 143.5 (d, *J* = 7.1 Hz), 142.0 (d, *J* = 17.2 Hz), 141.2, 138.5, 131.1, 130.2 (d, *J* = 4.0 Hz), 129.3, 128.71 (d, *J* = 9.1 Hz), 127.65 (s), 127.3 (d, *J* = 6.1 Hz), 126.4, 126.2, 116.8, 113.1, 111.8, 111.5, 31.0; HRMS (ESI) m/z calcd for $C_{26}H_{22}N^+$ (M+H)$^+$ 348.17468, found 348.17484.



3-chloro-5-phenyl-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (260 mg, 85%, from **3j**-Cl; 263 mg, 86%, from **3j**-Br; 253 mg, 83%, from **3j**-I; 275 mg, 90%, from **6j**-Br; 275 mg, 90%, from **6j**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 2H), 7.27-7.25 (m, 3H), 7.18 (d, *J* = 4.0 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 12.0 Hz, 2H), 2.96 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 144.4, 143.3, 138.6, 136.8, 132.3, 131.9, 130.9, 130.3, 129.1, 127.6, 127.4 (d, *J* = 8.1 Hz), 118.2, 112.9, 30.7, 30.6; HRMS (ESI) m/z calcd for $C_{20}H_{17}NCl^+$ $(M+H)^+$ 306.10440, found 306.10443.



5-phenyl-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (194 mg, 72%, from **3k**-Cl; 191 mg, 71%, from **3k**-Br; 199 mg, 74%, from **3k**-I; 229 mg, 85%, from **6k**-Br; 183 mg, 68%, from **6k**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36-7.34 (m, 2H), 7.04-6.95 (m, 2H), 6.83 (s, 2H), 6.73-6.65 (m, 1H), 6.30-6.24 (m, 2H). These spectroscopic data correspond to reported data.[2]



10-methoxy-5-phenyl-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow solid (177 mg, 59%, from **3l**-Cl; 207 mg, 69%, from **3l**-Br; 189 mg, 63%, from **3l**-I; 189 mg, 63%, from **6l**-Br; 171 mg, 57%, from **6l**-I). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.44-7.37 (m, 3H), 7.31-7.28 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 2H), 6.60 (t, *J* = 8.0 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 2H), 5.95 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 148.4, 143.4, 141.7, 136.2, 134.6, 130.8, 130.2, 130.0 (d, *J* = 5.1 Hz), 128.7, 128.5, 127.6, 127.0 (d, *J* = 17.2 Hz), 117.9, 111.8, 102.5, 55.5; HRMS (ESI) m/z calcd for $C_{21}H_{18}NO^+$ $(M+H)^+$ 300.13829, found 300.13821.

5. Reference

[1] I. D. Watson, S. Ritter and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 2056.

[2] W. Huang, S. L. Buchwald, *Chem. Eur. J.,* 2016, **22**, 14186.

6. NMR and HRMS (ESI) spectra

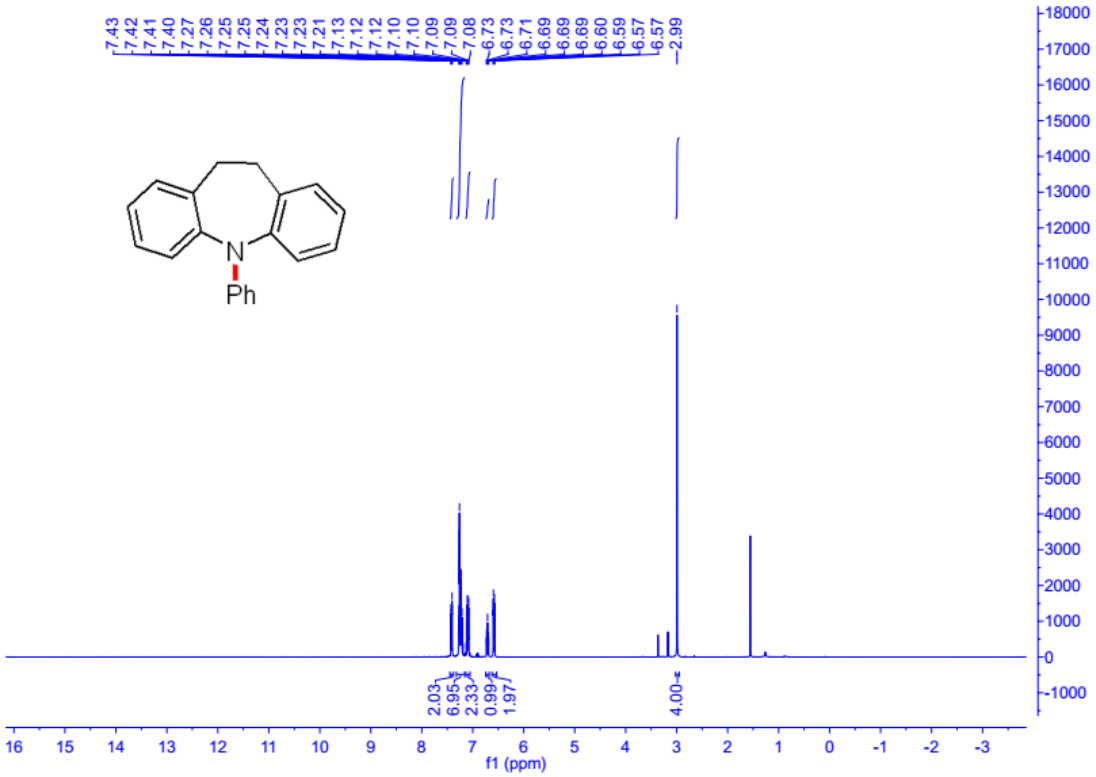


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3a**

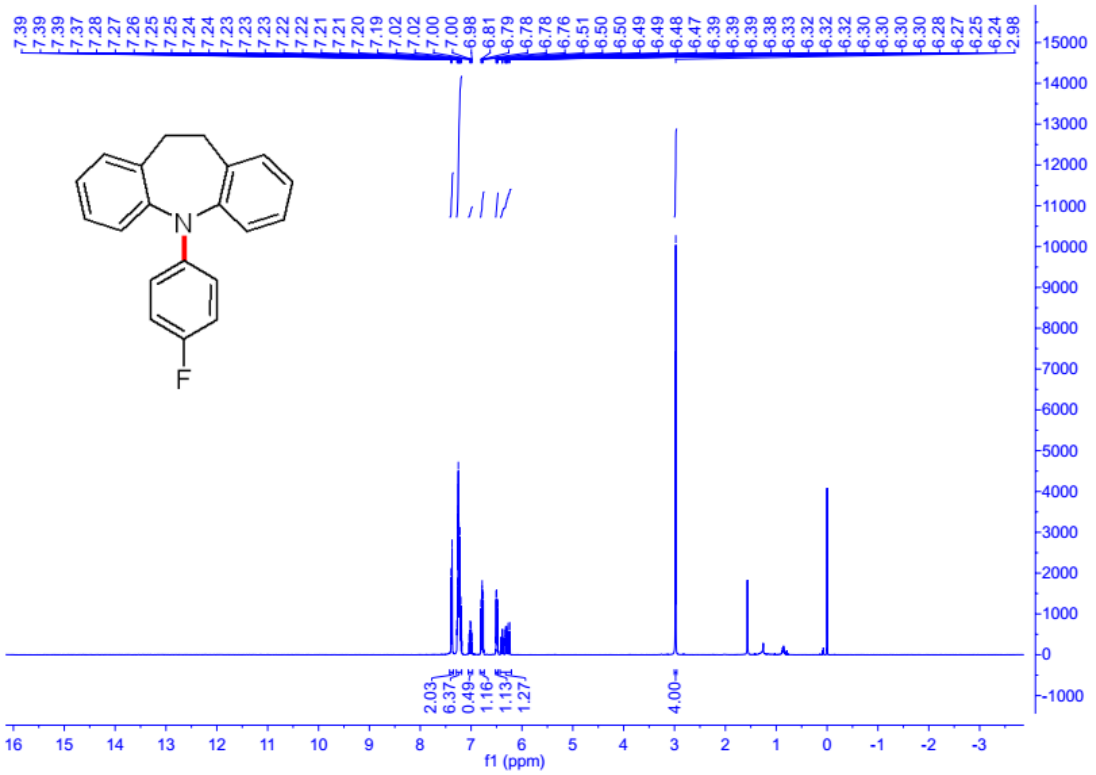


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3b**

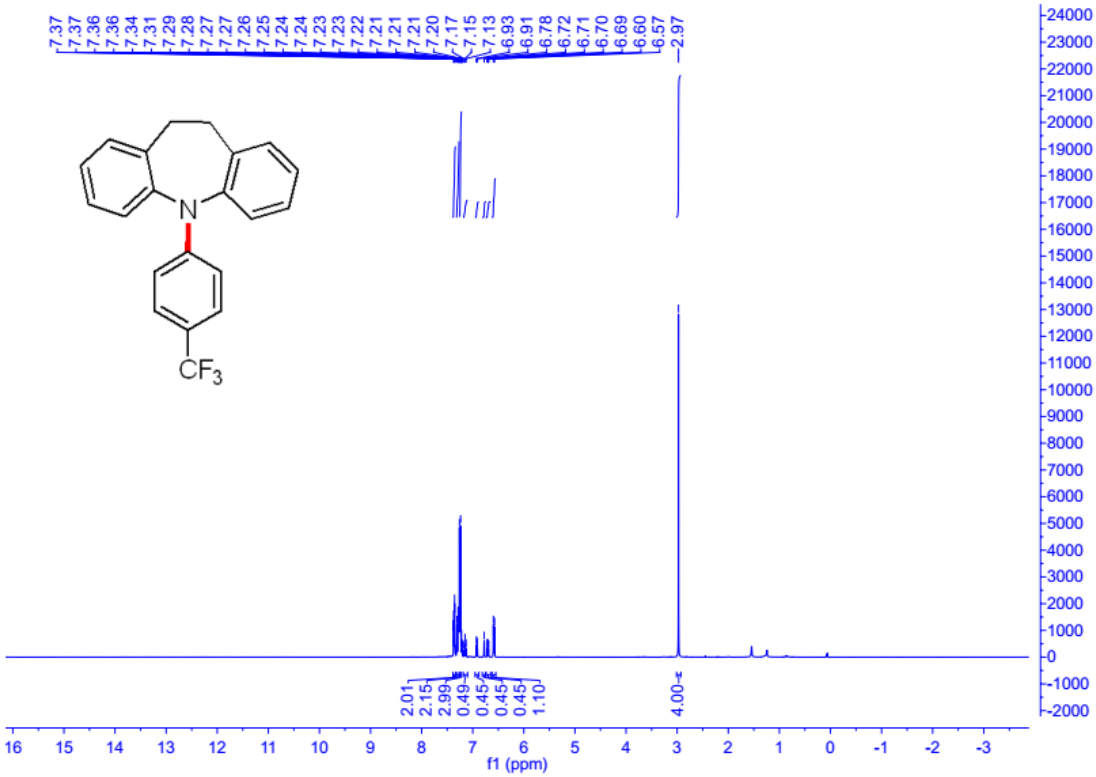


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3c**

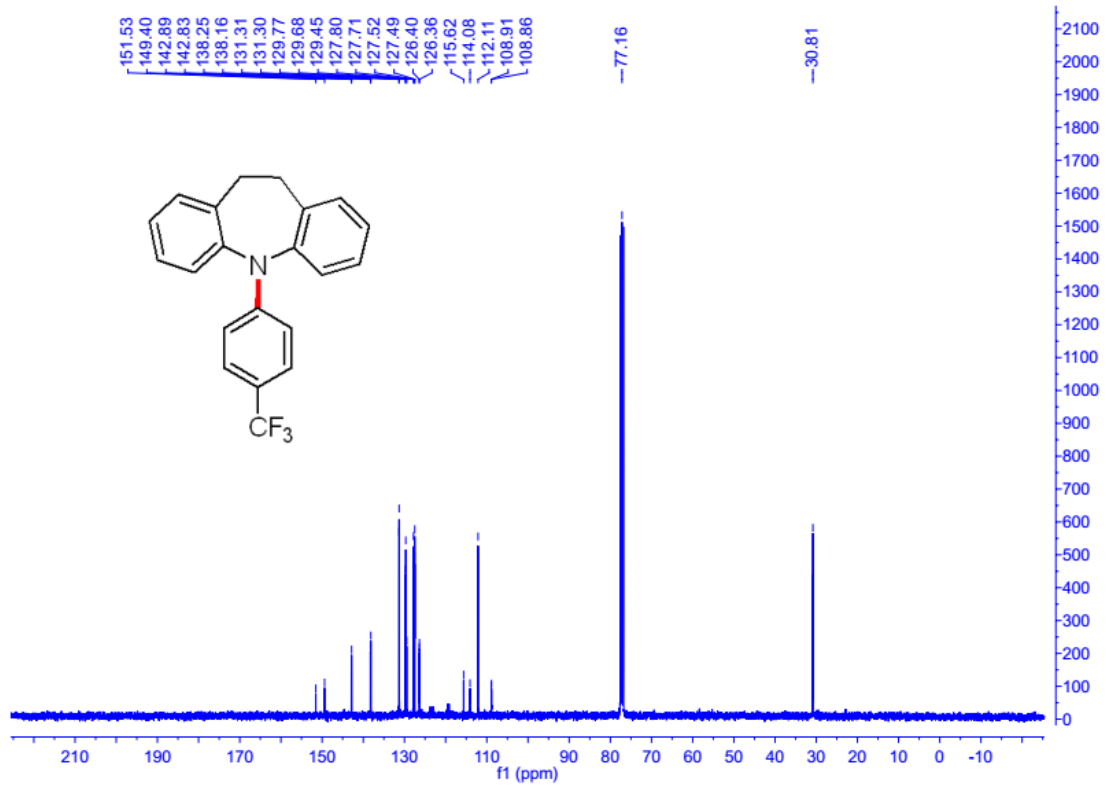


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$, 20 ^{o}C) of **3c**

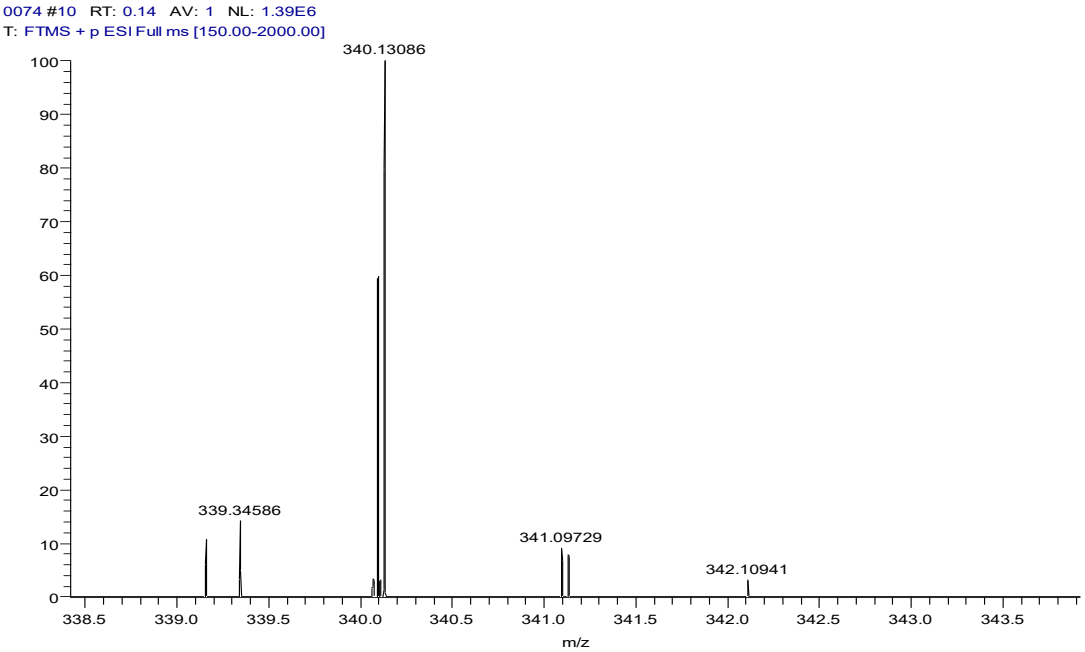


Figure S5. HRMS (ESI) of **3c**

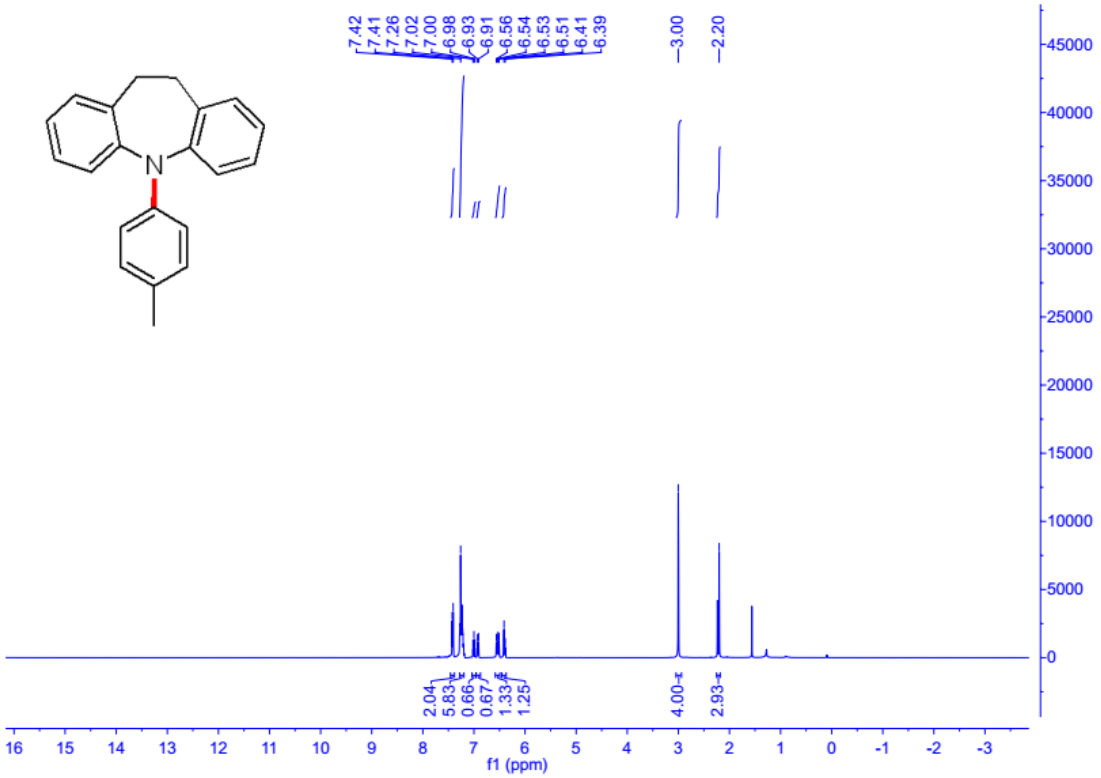


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3d**

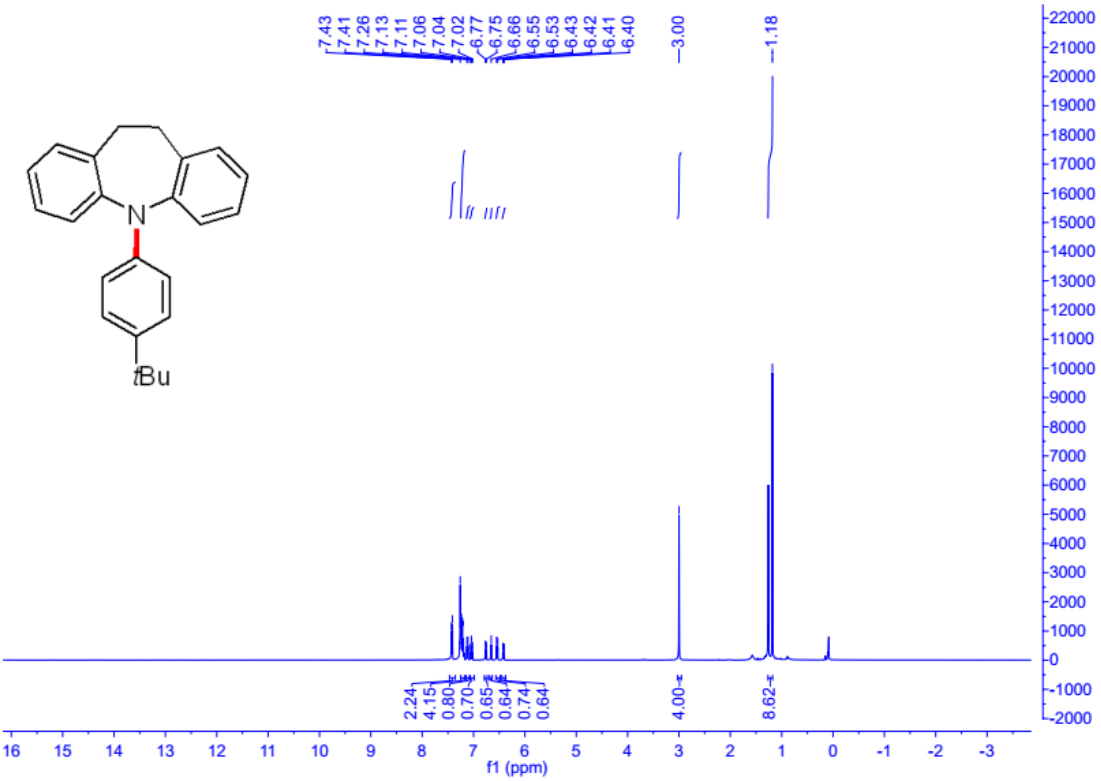


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3e**

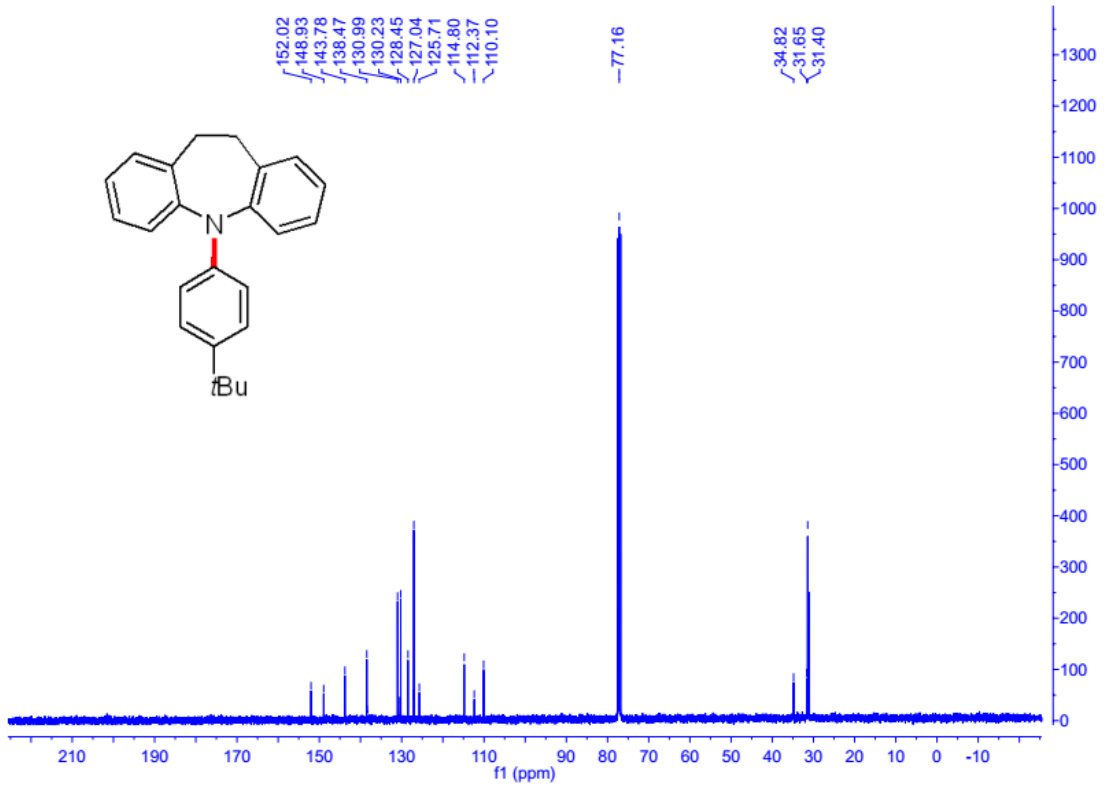


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$, 20 ^{o}C) of **3e**

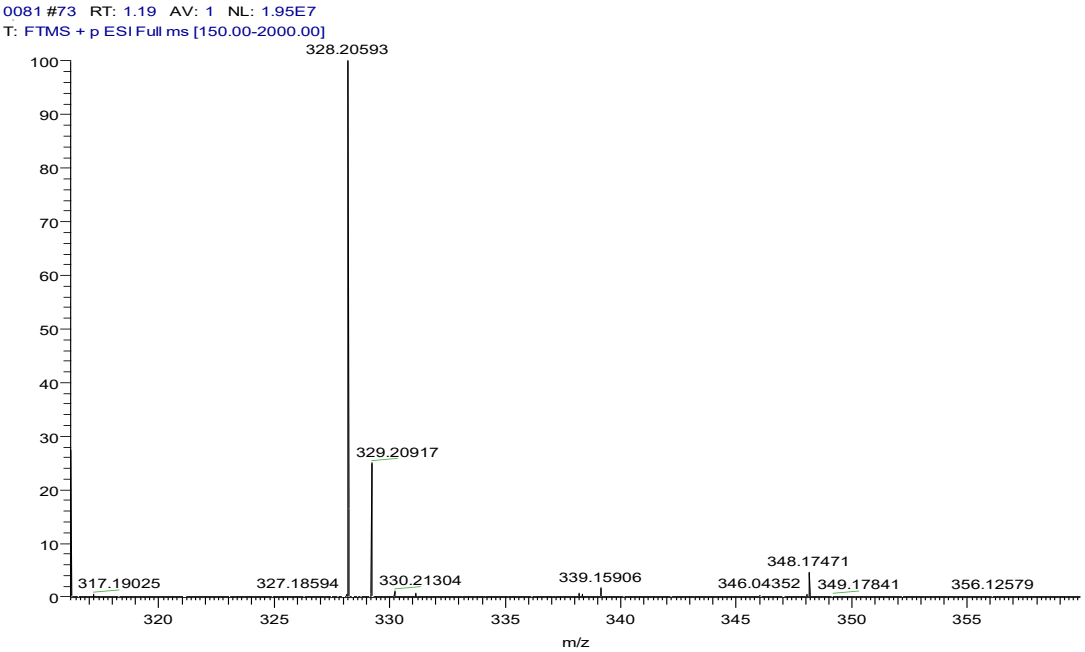


Figure S9. HRMS (ESI) of **3e**

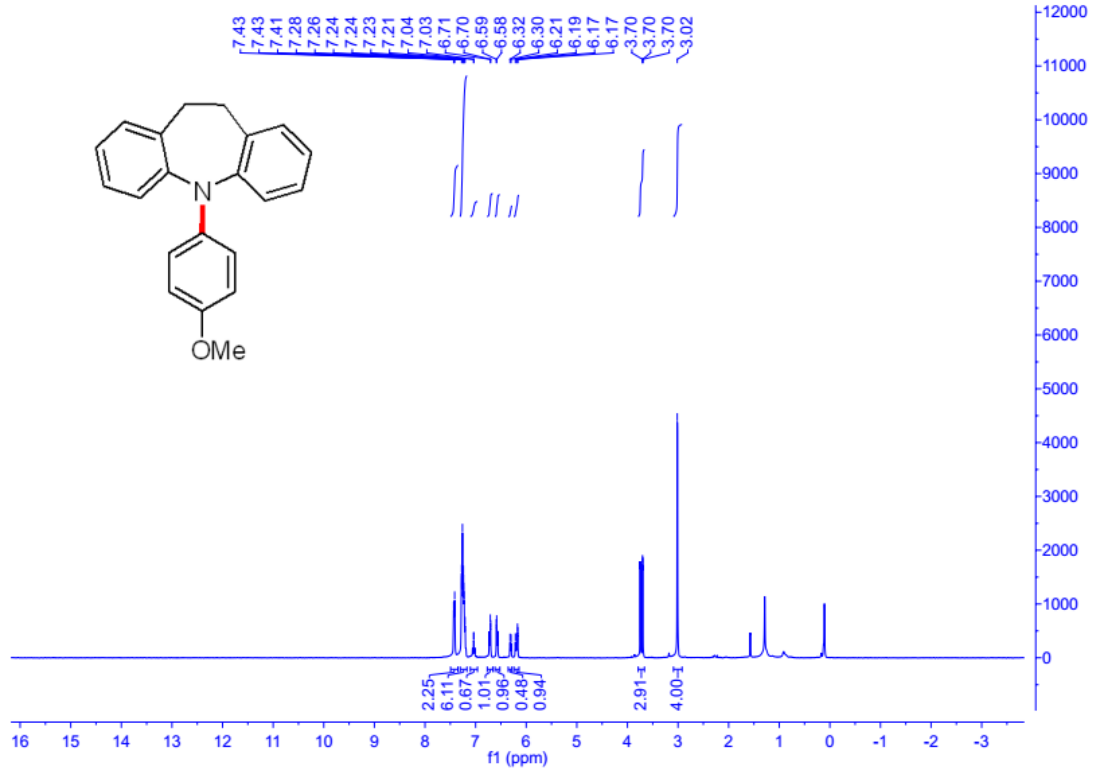


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3f**

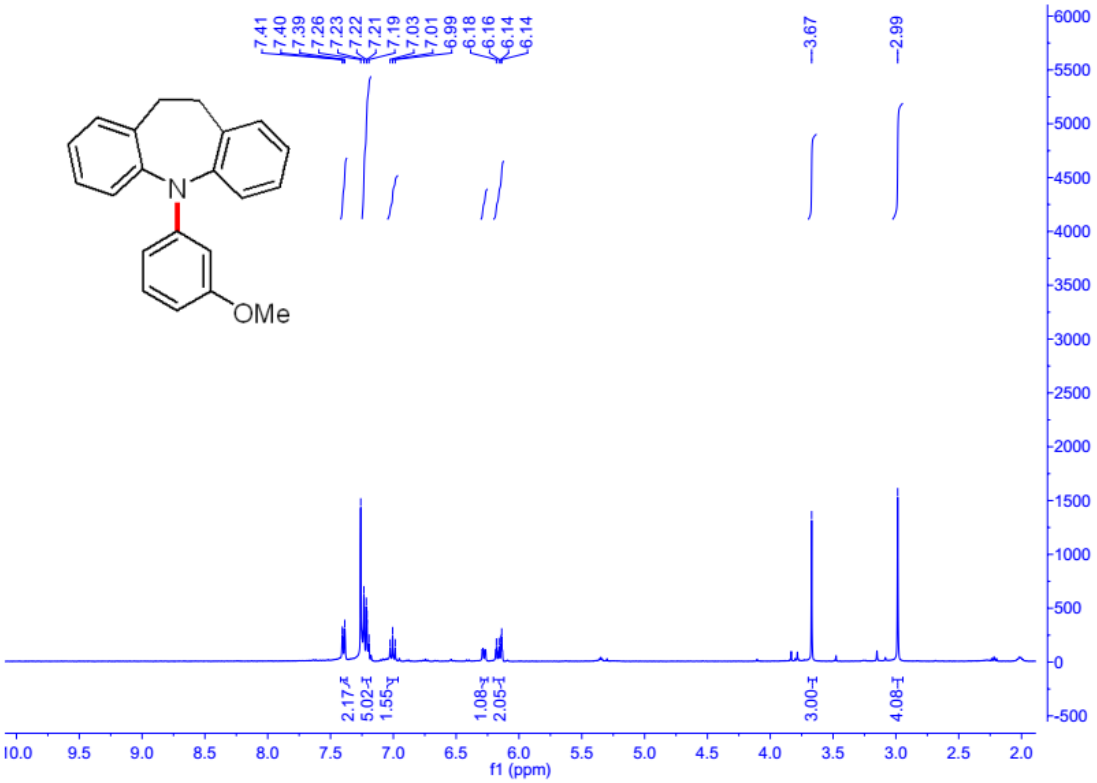


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3g**

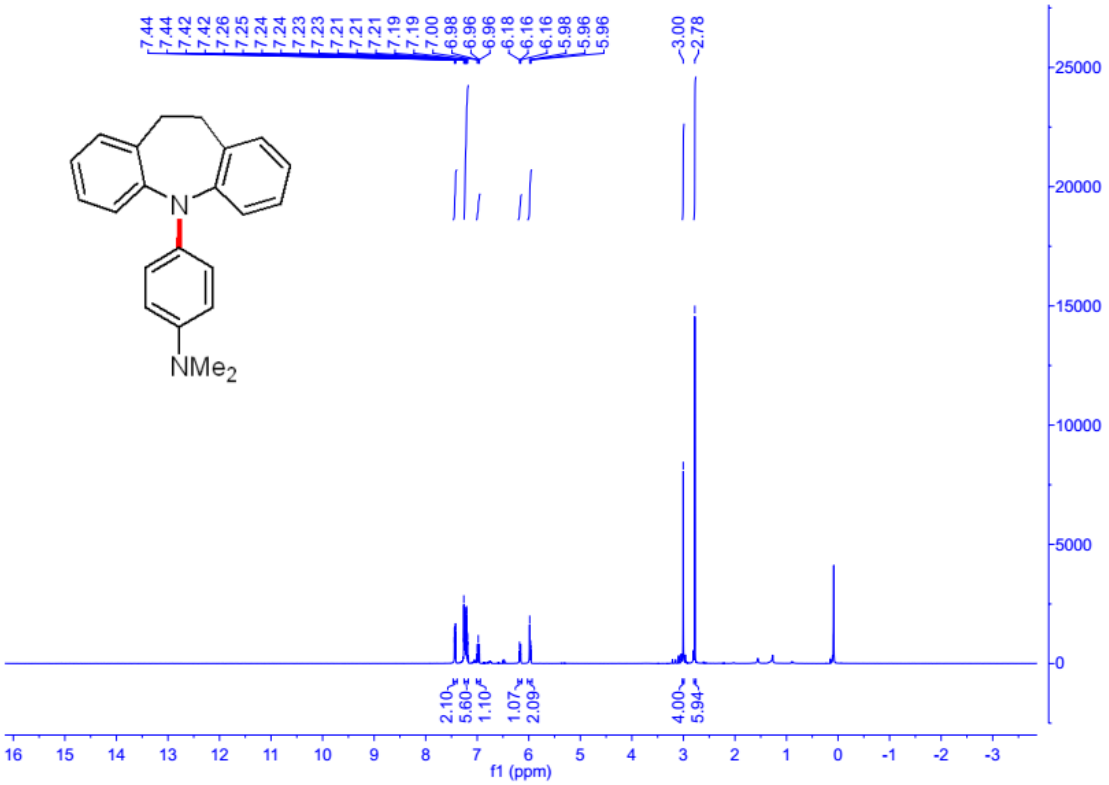


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3h**

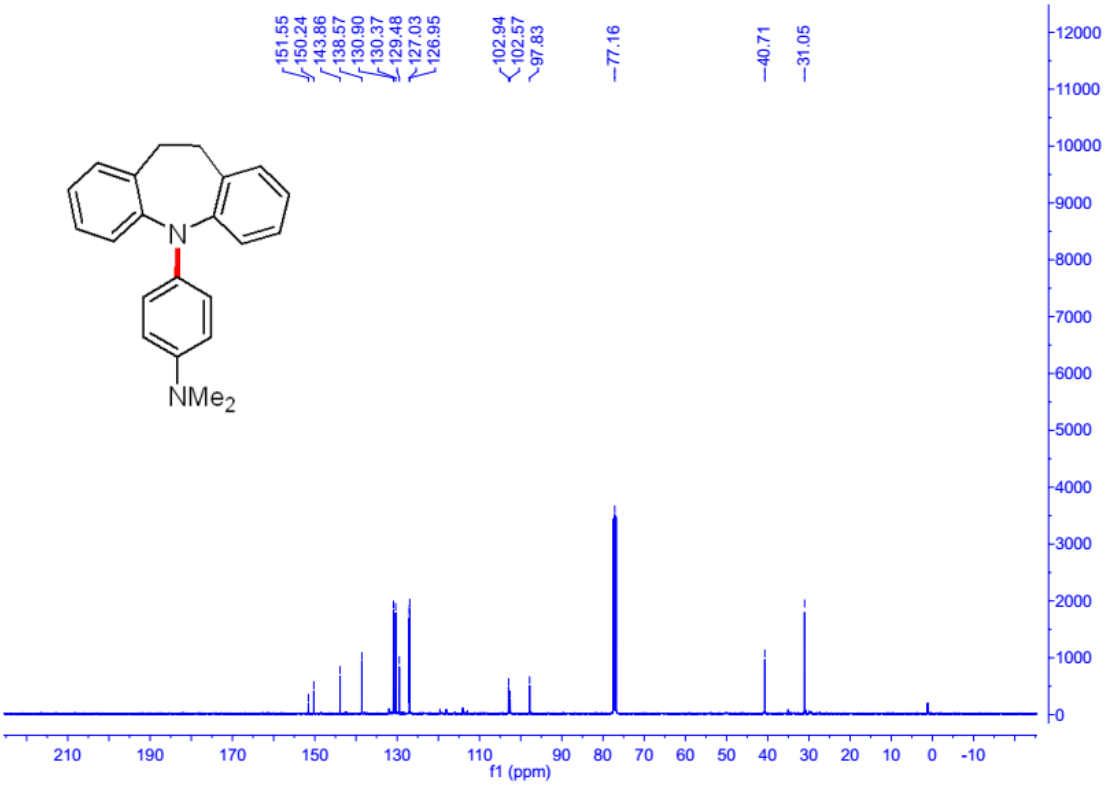


Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$, 20 ^{o}C) of **3h**

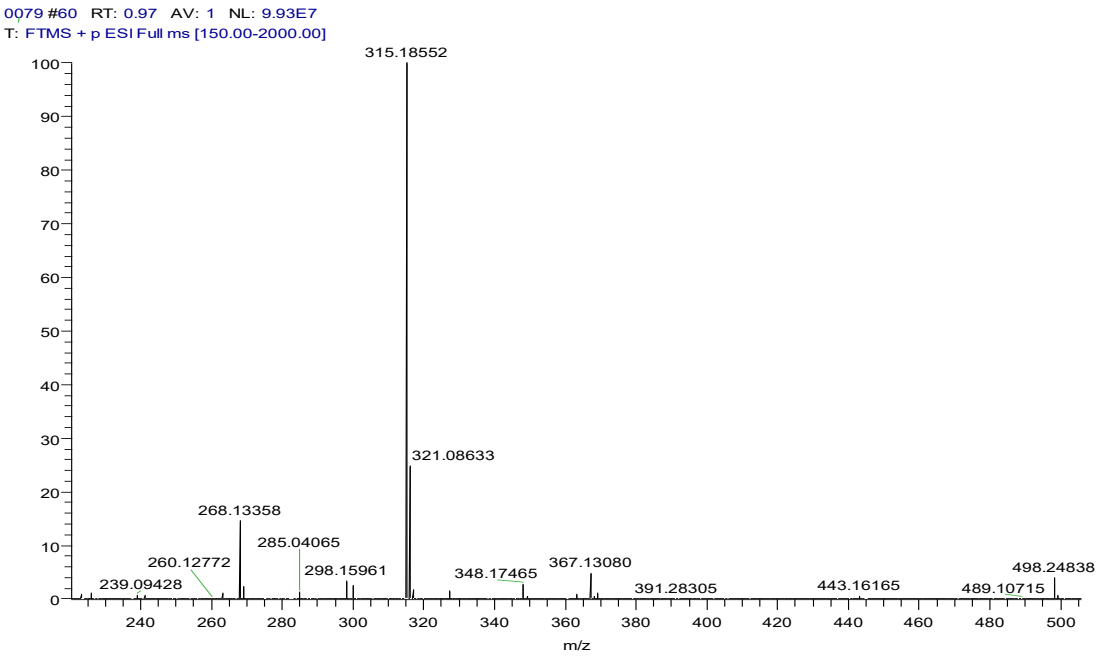


Figure S14. HRMS (ESI) of **3h**

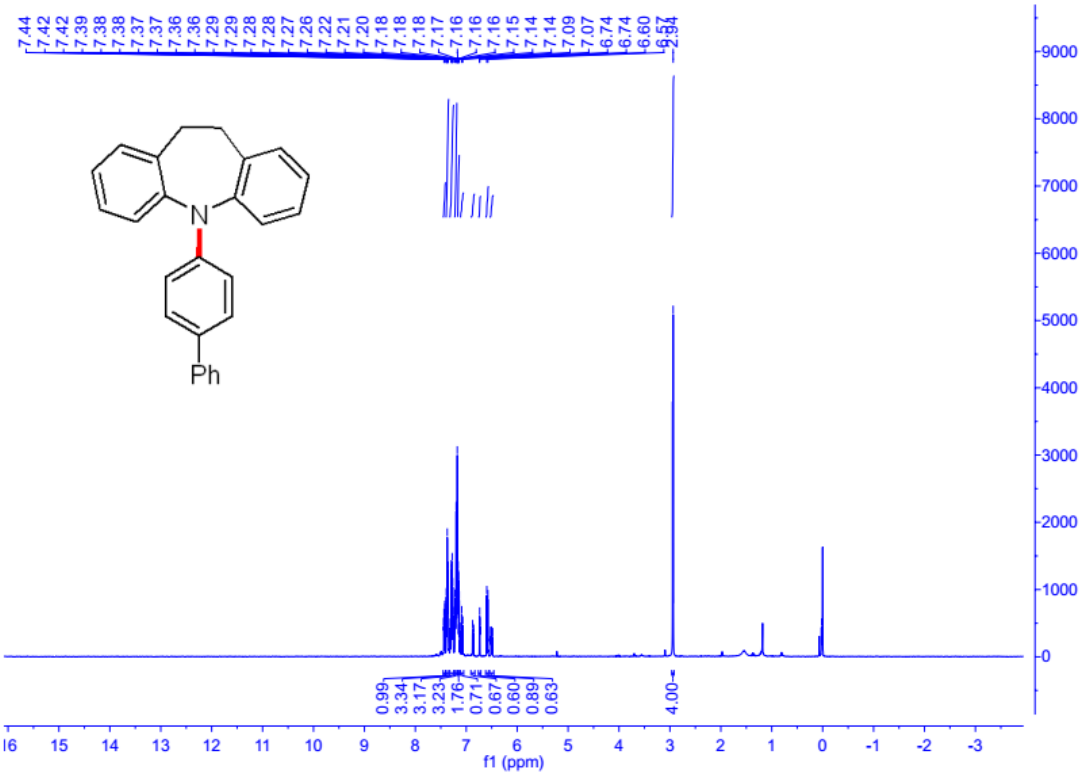


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3i**

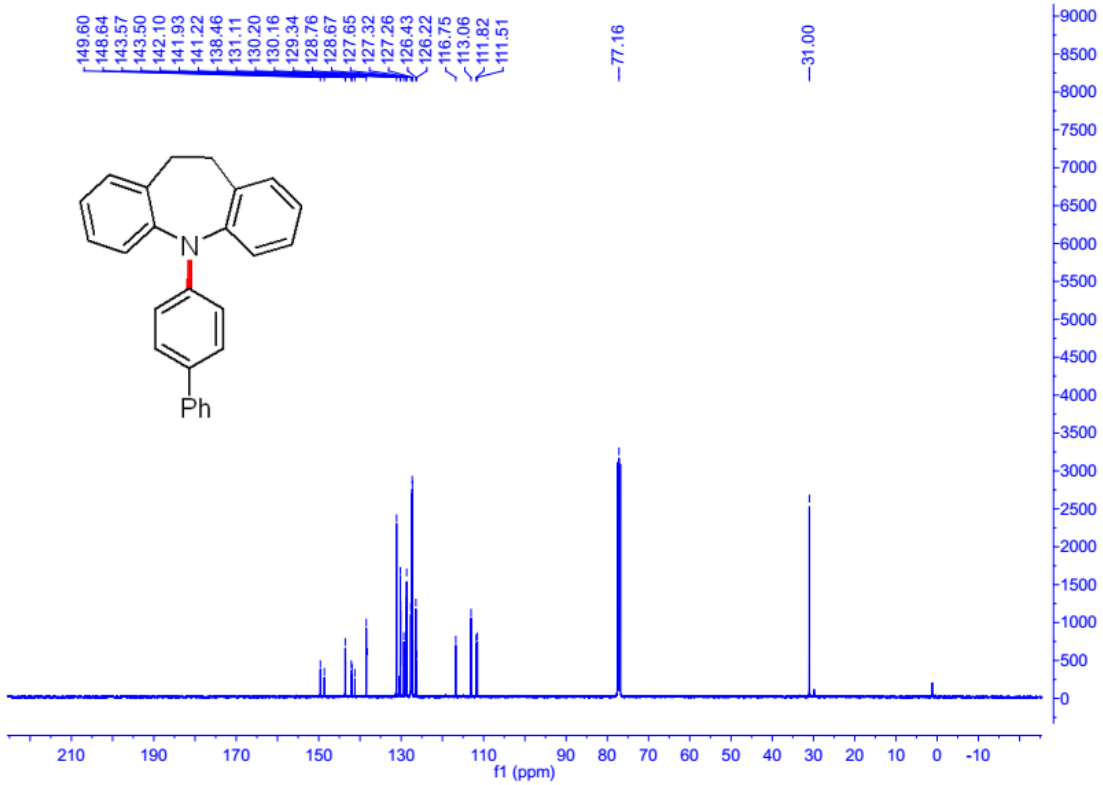


Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$, 20 ^{o}C) of **3i**

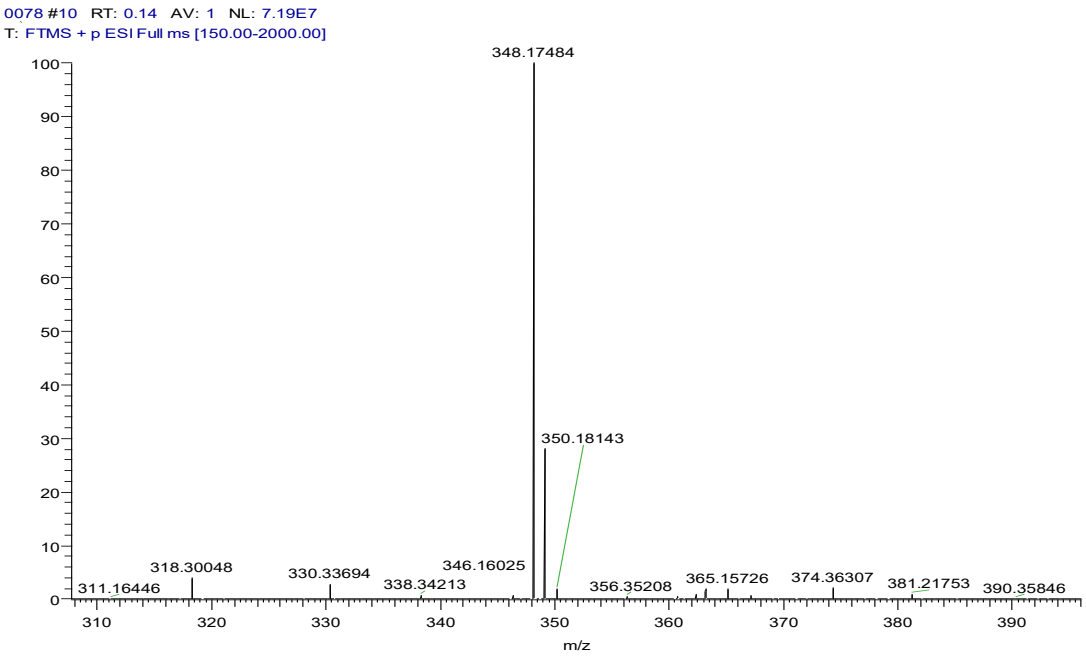


Figure S17. HRMS (ESI) of **3i**

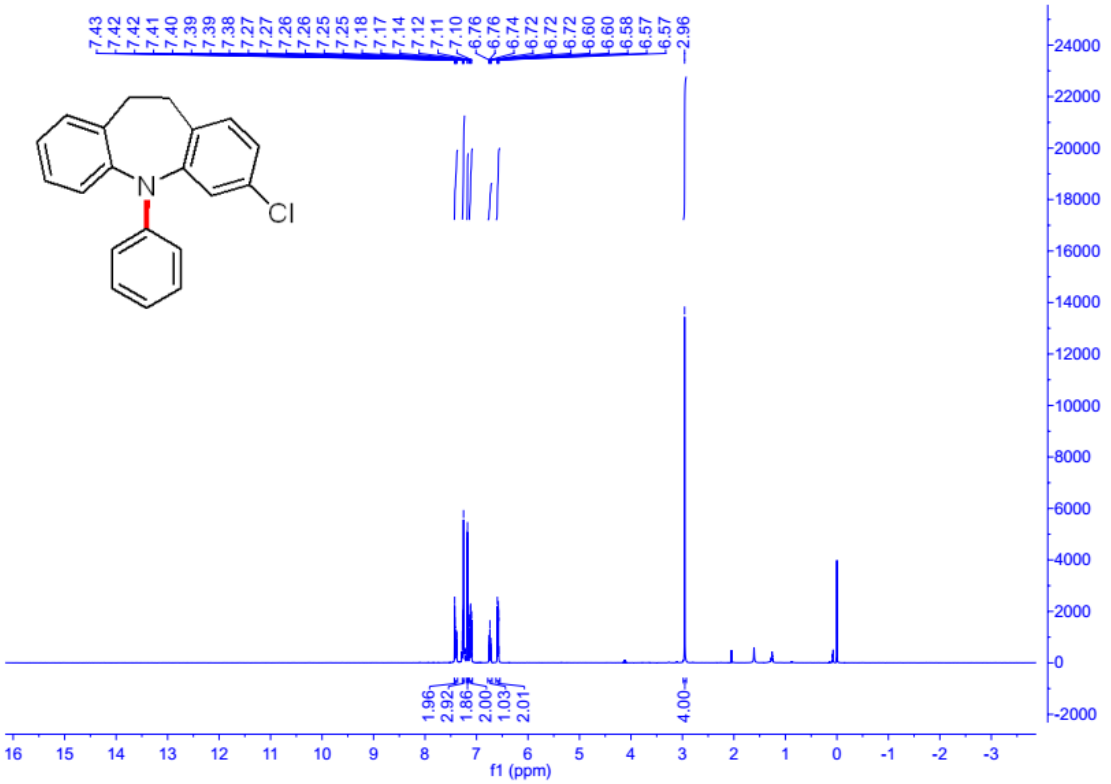


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3j**

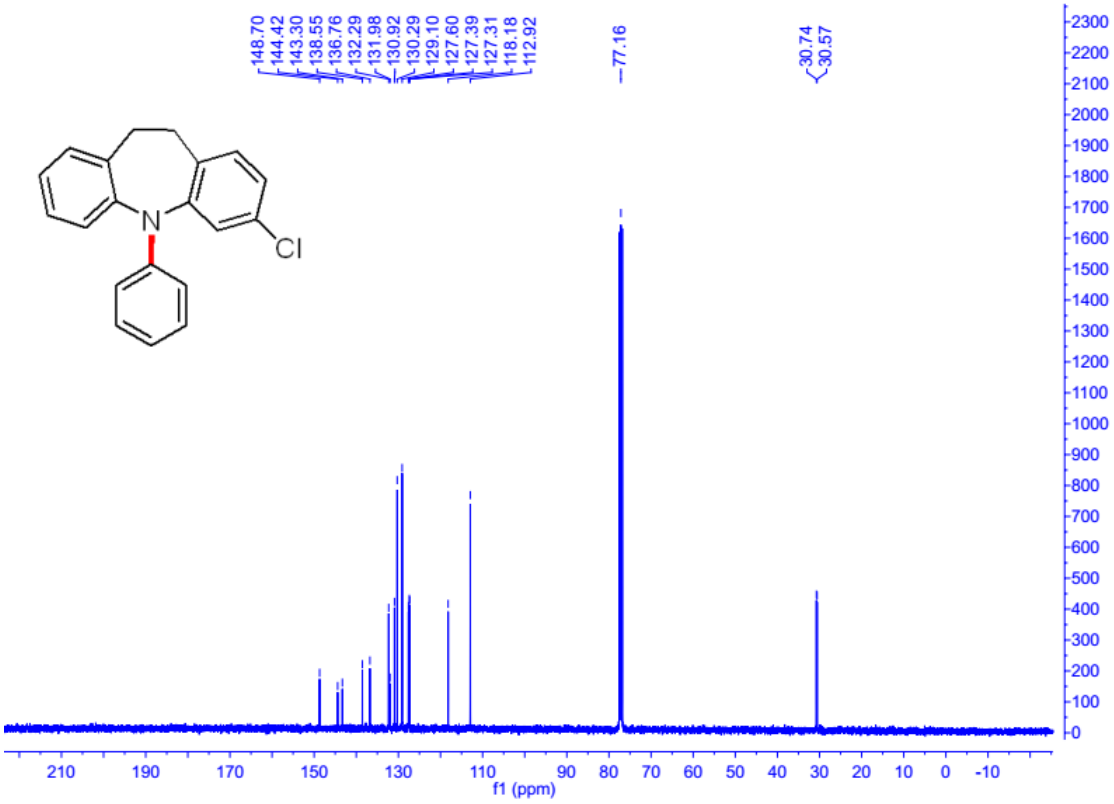


Figure S19. ^{13}C NMR (101 MHz, $CDCl_3$, 20 ^{o}C) of **3j**

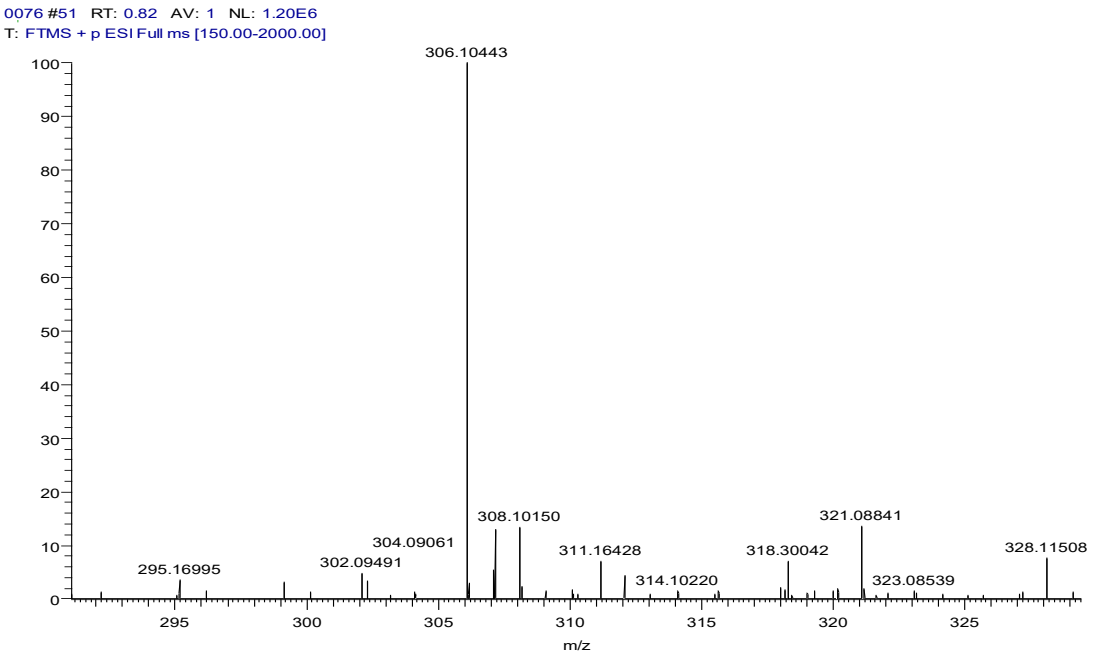


Figure S20. HRMS (ESI) of **3j**

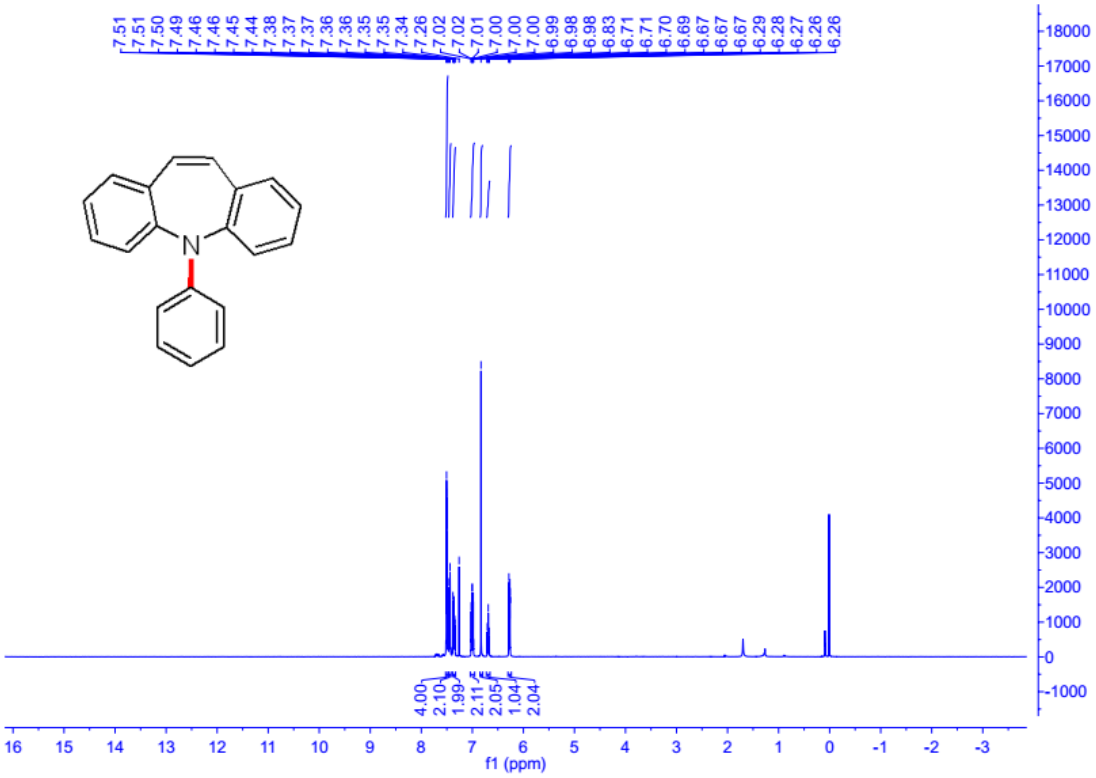


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3k**

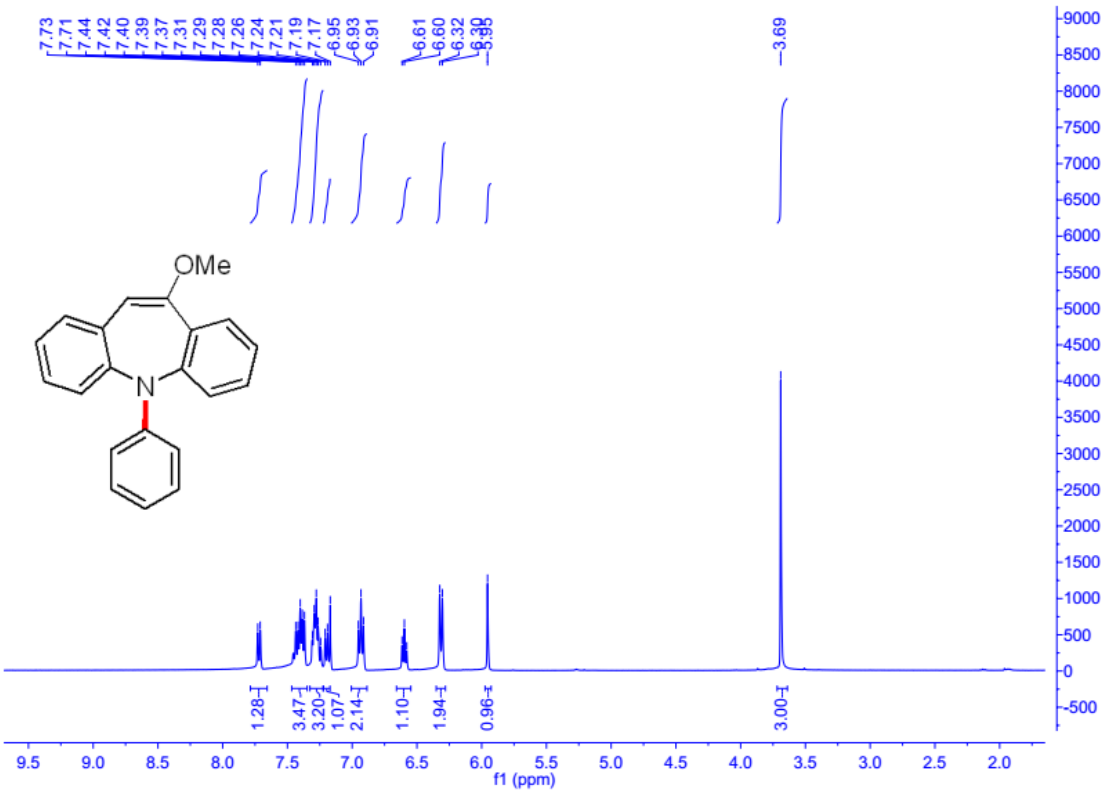


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3l**

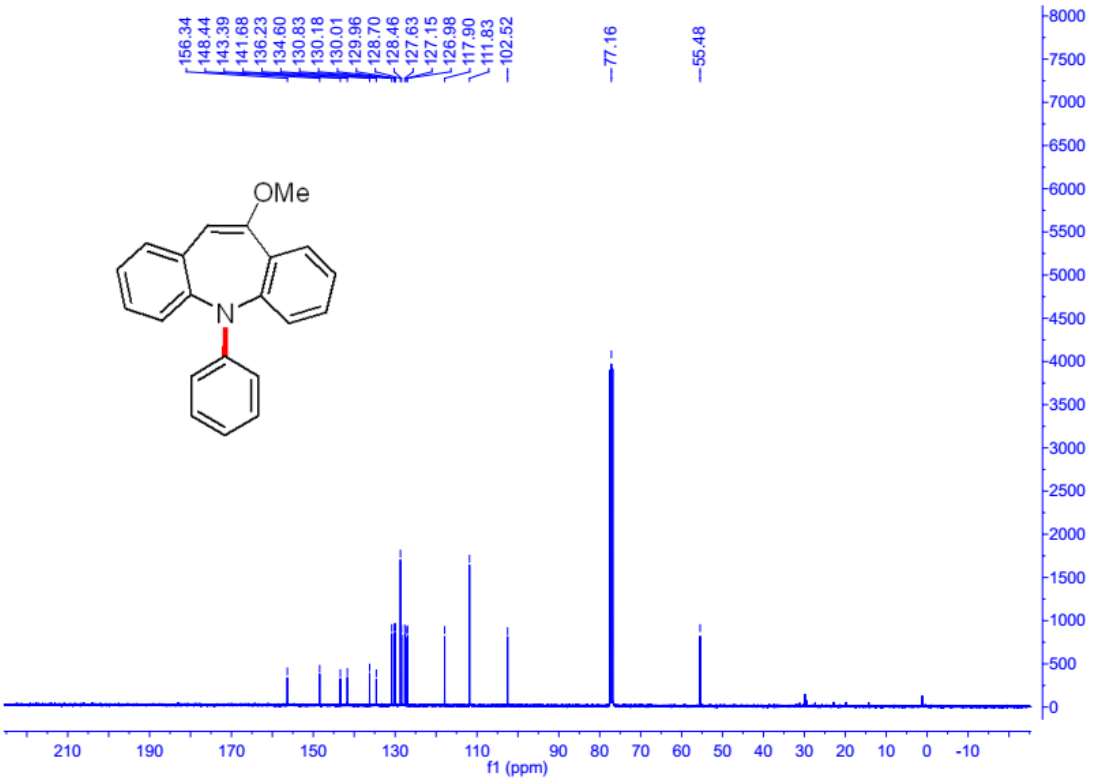


Figure S23. ^{13}C NMR (101 MHz, $CDCl_3$, 20 ^{o}C) of **3l**

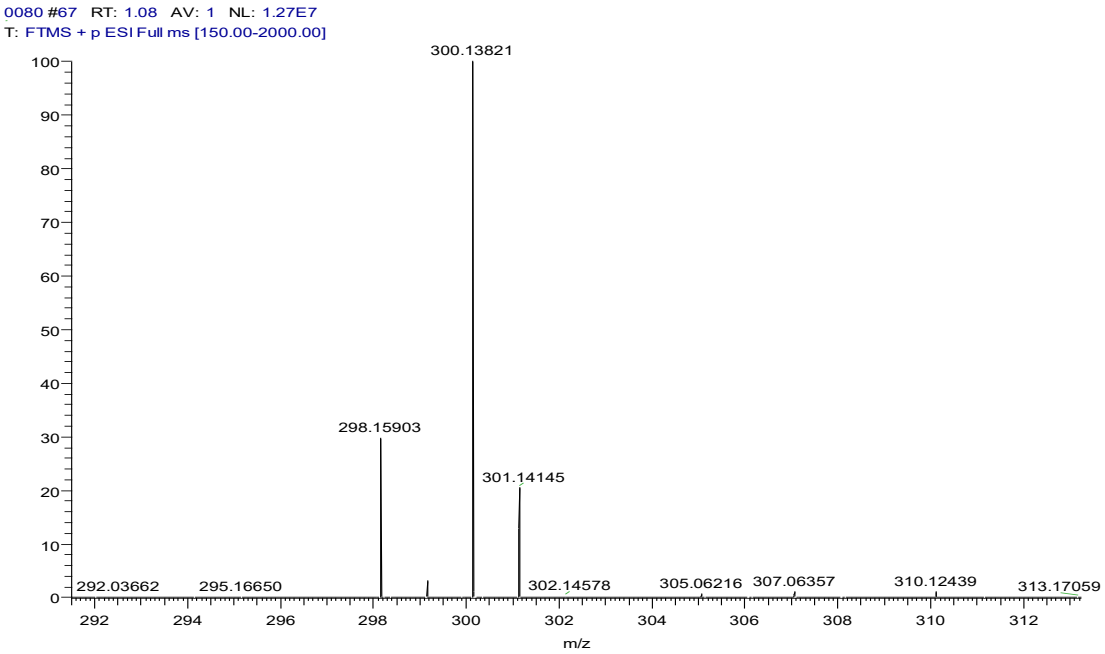


Figure S24. HRMS (ESI) of **3l**