Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Light blue and Green Thermally Activated Delayed Fluorescence from 10*H*-Phenoxaborin-Derivatives and Their Application to Organic Light-Emitting Diodes

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Supplementary Information

Contents:

1. Photoluminescence characteristic of compounds 9-11

Table S1. UV-vis and photoluminescence characteristics of compounds **9**, **10**, and **11** in toluene at 77 and 300 K.[a]

compound	$\lambda_{UV\text{-}max\text{-}300K}$ / nm	$\lambda_{Flu\text{-}300\ K}$ / nm	$\lambda_{Flu\text{-}77\ K}$ / nm	$\lambda_{Phos\text{-}77\ K}$ / nm
9	294,	401	382 (360.62)	440 (401.55)
10	290	472	434 (392.14)	432, 440 (393.78)
11	282	522	460, 470 (430.48)	460, 472 (434.72)

[a] Concentration of each compound is 1.0×10^{-5} M. The parentheses represent onset wavelengths of the PL spectra. The fluorescence and phosphorescence spectra were measured at ex. 290 nm.

2. Schematic structure and energy diagram of OLED devices

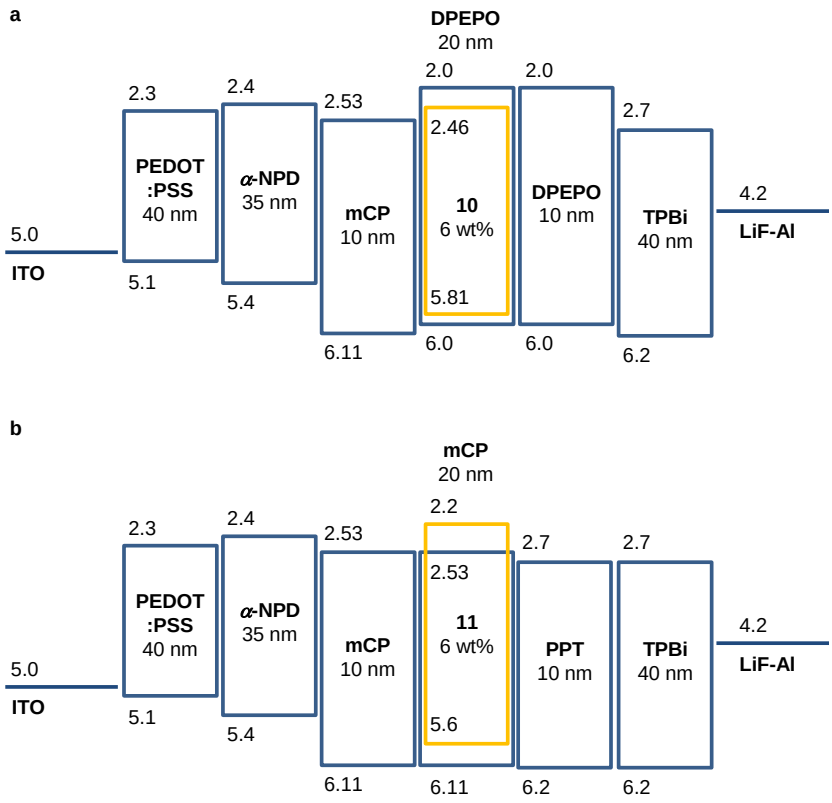
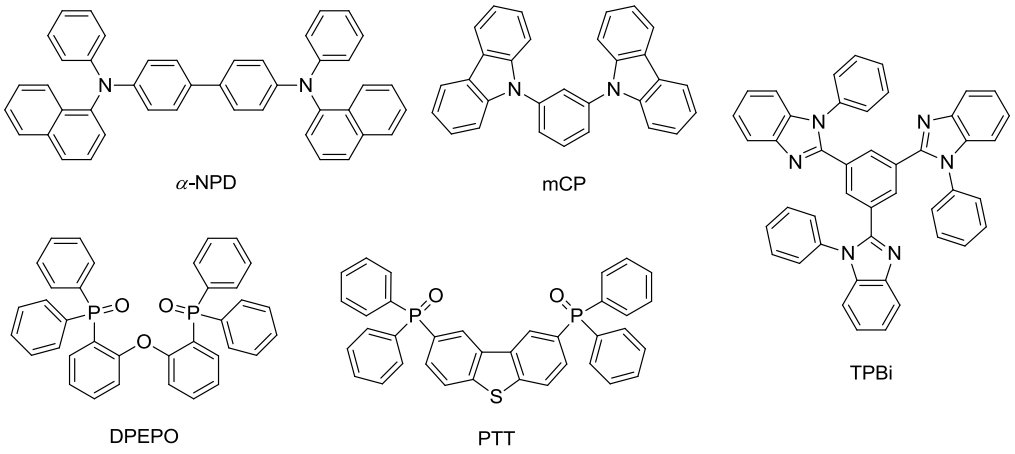


Figure S1. The schematic structure and energy diagram of OLED devices using a) compounds **10** and b) **11** showing in Figs. 5-7.



Scheme S1. Molecular structures used in the OLED devices showing Figs. 5-7.

3. Theoretical calculation

Theoretical calculations to determine the HOMO and LUMO of compounds **9-11** were carried out using the Gaussian 09 package[S1] at the M06/6-31G* level. After the optimization, the TD-DFT calculations were also conducted at the M06/6-31G* level. The output views of compounds **9-11** were obtained by the GaussView version 5.0.[S2]

Table S2. Calculated ΔE_{ST}, emission spectra, and oscillator strength (*f*), of compounds **9-11** by DFT and TD-DFT at the M06/6-31G* level.[a]

compound	ΔE_{ST} / meV	λ (S_1) [a]/ nm	*f*
9	295	367	0.1597
10	2.7	424	0.0012
11	3.6	470	0.0024

[a] Calculated through the TD-DFT results based on S_0 geometry.

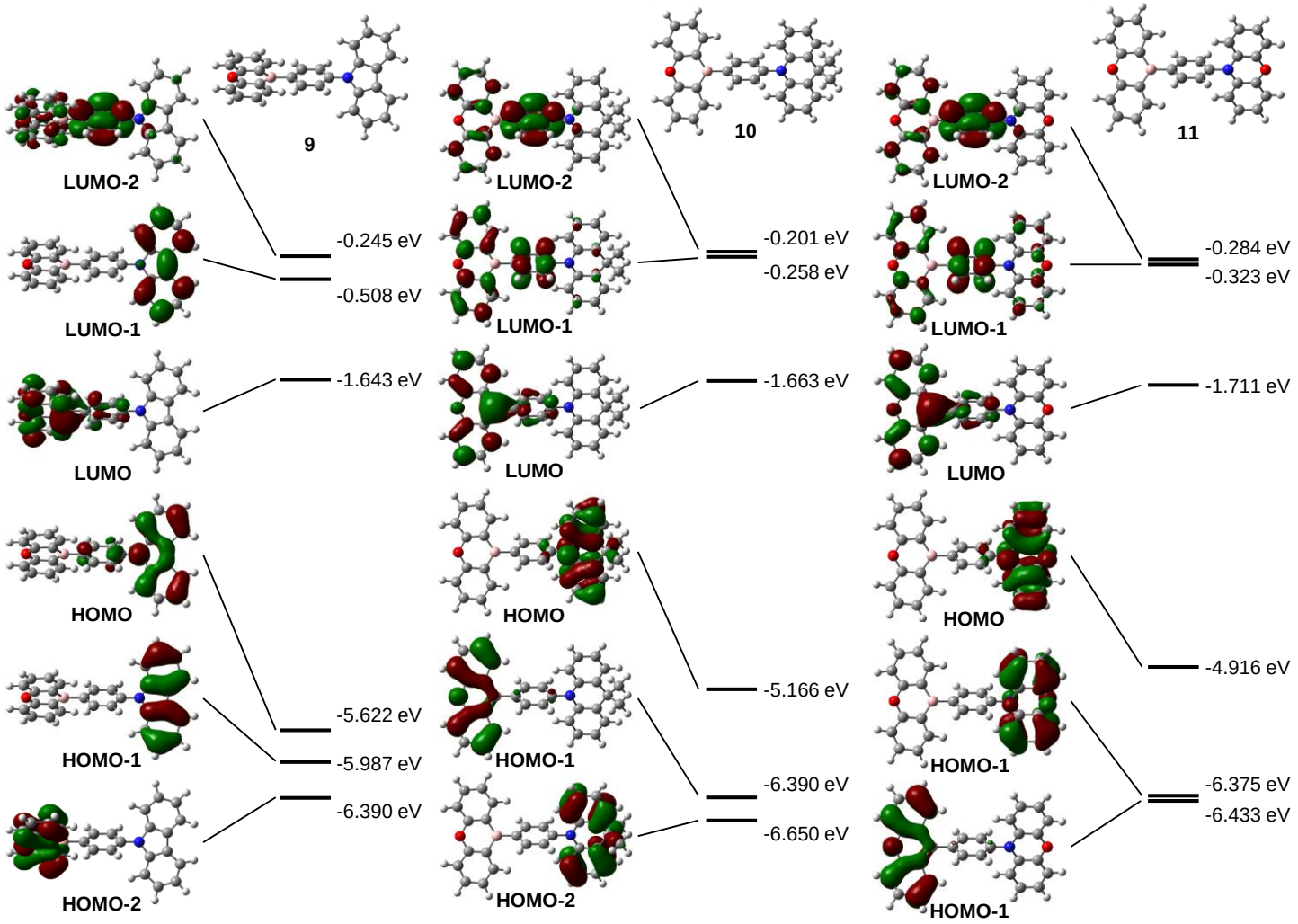


Figure S2. HOMO and LUMO levels for compounds **9-11** at the M06/6-31G* level theory.

Table S3 The energy and coordinates of **9** in ground state optimized at M06/6-31G*

Energy = −1309.1638571 Hartrees

	Coordinates (Angstroms)		
	X	Y	Z
B	3.303156439	-0.8311992	-4.724724141
C	1.888945404	-0.941166592	-4.064820428
C	1.73833097	-1.193134639	-2.692446961
H	2.62615388	-1.315453532	-2.070434272
C	-0.54408341	-0.892212272	-4.241985061
C	-0.662177662	-1.139138933	-2.874212633
H	-1.445304118	-0.760659795	-4.839382835
N	-1.939585175	-1.238172323	-2.278019488
C	0.714774154	-0.792031173	-4.81892795
H	0.787934592	-0.595108857	-5.88942252
C	0.487209907	-1.287747701	-2.09798809
H	0.387948321	-1.496932093	-1.033667965
C	-2.391422031	-0.495359718	-1.188131836
C	-4.391095036	-0.255652672	0.161067572
H	-5.414188351	-0.541944045	0.403693344
C	-3.744666908	0.734722528	0.885510074
H	-4.260304599	1.227782645	1.707374952
C	-2.434381086	1.112102912	0.564885325
H	-1.948357859	1.898616898	1.13975646
C	-1.74010256	0.507269078	-0.474306006
H	-0.726064403	0.811730446	-0.726987505

C	-5.230142672	-2.665892437	-2.036770405
H	-6.100248854	-2.526398614	-1.395672023
C	-5.24735127	-3.607468251	-3.054936723
H	-6.138766398	-4.209616456	-3.220013853
C	-4.124100284	-3.796162298	-3.870267518
H	-4.154777621	-4.5473587	-4.657707824
C	-2.967795924	-3.047847363	-3.694900874
H	-2.093459188	-3.205905995	-4.32368476
C	-2.963338582	-2.095385038	-2.679114496
C	4.375134812	-1.924280563	-4.583303689
C	6.636440538	-2.687911779	-5.156485082
H	7.575474094	-2.483461109	-5.666030024
C	6.421414284	-3.85941516	-4.456632664
H	7.212146822	-4.606229881	-4.406723619
C	5.19482078	-4.095742126	-3.823163291
H	5.030435837	-5.027427218	-3.285558141
C	4.198340997	-3.142568343	-3.894698883
H	3.236471662	-3.329192914	-3.416926515
C	5.510770903	1.456687914	-6.877991442
H	6.521026576	1.403942389	-7.27776906
C	4.691701018	2.547673593	-7.095522772
H	5.060269919	3.384700668	-7.686304557
C	3.400461539	2.58801836	-6.554465803
H	2.767724718	3.457629514	-6.720296008

C	2.944107798	1.521810844	-5.805086992
H	1.945860441	1.555890111	-5.368475449
C	3.736303306	0.378981775	-5.568407356
C	5.61438588	-1.737660767	-5.216941244
C	5.029355651	0.389438901	-6.116115481
C	-4.080415072	-1.901876463	-1.838398111
C	-3.716547121	-0.878223932	-0.888849795
O	5.914343373	-0.627979973	-5.942880915

Table S4 The energy and coordinates of **10** in ground state optimized at M06/6-31G*

Energy = –1426.9926636 Hartrees

	Coordinates (Angstroms)		
	X	Y	Z
B	-2.837599616	0.00016267	-0.000720838
C	-1.27222081	0.000156864	-0.000973795
C	-0.54136524	-0.417144514	1.122933053
H	-1.074922792	-0.740808526	2.017689737
C	0.847770169	0.409618163	-1.134507665
C	1.54518942	0.00023403	-0.001355636
H	1.409781581	0.721768959	-2.01418749
N	2.972491665	0.000347891	-0.001554688
C	-0.541686284	0.417437419	-1.125074648
H	-1.075495143	0.741071092	-2.019692048

C	0.848067523	-0.409260104	1.13198248
H	1.410341758	-0.72136468	2.011523087
C	3.655103588	-1.143848594	-0.436640409
C	5.680779222	-2.346875056	-0.889678825
H	6.76992304	-2.388509373	-0.90386508
C	4.969113905	-3.460382599	-1.312389713
H	5.493669121	-4.352292301	-1.648762385
C	3.580980005	-3.411451367	-1.295449555
H	2.99257176	-4.268536147	-1.619052991
C	2.930284461	-2.267900184	-0.862771695
H	1.843555534	-2.241645741	-0.853103897
C	5.680770485	2.344924224	0.893485258
H	6.769908991	2.386435656	0.907975063
C	4.969149174	3.457529403	1.318624609
H	5.493716965	4.348537694	1.657356927
C	3.581015986	3.408959302	1.300814187
H	2.992627192	4.265403642	1.626139041
C	2.930302806	2.266588736	0.865067326
H	1.843575234	2.240602101	0.854797999
C	3.655088605	1.143399034	0.436558337
C	-3.670336378	1.231074775	-0.395713473
C	-5.903661026	2.205954572	-0.69411103
H	-6.981604124	2.06620324	-0.652677007
C	-5.333426852	3.41015017	-1.058602816

H	-5.975082699	4.250904358	-1.317132411
C	-3.941001992	3.558460697	-1.087416557
H	-3.50039478	4.514546091	-1.36266847
C	-3.1364186	2.485986033	-0.757167854
H	-2.052573988	2.601846092	-0.763218844
C	-5.903437496	-2.20548995	0.69410291
H	-6.981393351	-2.065691835	0.653167371
C	-5.333086238	-3.409698809	1.058366322
H	-5.974658109	-4.250419497	1.317213139
C	-3.940654324	-3.558065936	1.086547756
H	-3.499959584	-4.514161119	1.361625646
C	-3.136177976	-2.485631368	0.75590876
H	-2.052335142	-2.601533908	0.761475189
C	-3.670209762	-1.230711247	0.394655594
C	-5.071003155	1.134384918	-0.363100994
C	-5.070886783	-1.13396472	0.362679786
C	5.059160945	1.177209674	0.448096201
C	5.059171118	-1.177960027	-0.447452237
O	-5.726502054	0.000222386	-6.74094E-05
C	5.916030125	0.000702738	-0.002509745
C	6.807883111	-0.442604884	1.169600975
H	6.194144805	-0.761178318	2.02193422
H	7.455088055	-1.281859156	0.884604808
H	7.458493877	0.374584324	1.506883807

C	6.797757695	0.4466312	-1.181366198
H	6.176735973	0.763979897	-2.028871917
H	7.444712195	1.287625326	-0.900785038
H	7.447740339	-0.368926473	-1.523956406

Table S5 The energy and coordinates of **11** in ground state optimized at M06/6-31G*

Energy = −1384.3301943 Hartrees

	Coordinates (Angstroms)		
	X	Y	Z
B	3.135571808	-0.838014808	-4.670089516
C	1.723693236	-0.951066065	-4.002315091
C	1.554600298	-0.781058886	-2.619007191
H	2.425141042	-0.5731056	-1.995409057
C	-0.680396567	-1.318351449	-4.178063981
C	-0.81579433	-1.154112968	-2.801775851
H	-1.569545198	-1.520325037	-4.774451065
N	-2.099951014	-1.256650304	-2.194710906
C	0.576438764	-1.226342272	-4.763345044
H	0.669175347	-1.357295418	-5.842328422
C	0.30567217	-0.889388493	-2.019695001
H	0.181135997	-0.768434606	-0.944097071
O	-4.637023269	-1.459929794	-1.000845974
C	-2.928945815	-0.129716091	-2.099061321

C	-5.036191364	0.824906825	-1.377057277
H	-6.001264018	0.665736718	-0.900414651
C	-4.648098951	2.075031314	-1.856539861
H	-5.319289736	2.925163668	-1.757034608
C	-3.4054033	2.218331541	-2.453779579
H	-3.084140434	3.186423136	-2.832941759
C	-2.550632615	1.123799108	-2.574414391
H	-1.575304155	1.240650092	-3.042212901
C	-4.300938687	-3.749552626	-0.593407405
H	-5.29387204	-3.74719222	-0.148466945
C	-3.526158354	-4.906484242	-0.660939085
H	-3.913348629	-5.841319732	-0.261825683
C	-2.268387533	-4.849530075	-1.24083234
H	-1.649367151	-5.742277322	-1.304023201
C	-1.781468468	-3.647614243	-1.752211702
H	-0.79443835	-3.607322431	-2.208178033
C	-2.547382636	-2.485800463	-1.689358045
C	3.709250186	-1.926160886	-5.592042721
C	5.589171897	-2.676783117	-6.981116811
H	6.579533494	-2.468203701	-7.37967881
C	4.911820312	-3.844726337	-7.272976535
H	5.37470086	-4.584734619	-7.923755847
C	3.643113882	-4.086363593	-6.730889095
H	3.122307643	-5.01485476	-6.955904726

C	3.065455086	-3.141707755	-5.906071953
H	2.084893694	-3.332863936	-5.469962355
C	6.208785063	1.443487762	-4.973684865
H	7.16213639	1.390669611	-5.494746361
C	5.857378958	2.5289419	-4.194973046
H	6.551180677	3.361577405	-4.091331269
C	4.615192835	2.569371349	-3.549064506
H	4.341531207	3.434138844	-2.948021309
C	3.742362836	1.50856116	-3.687775235
H	2.76849794	1.543150367	-3.199285985
C	4.061906099	0.370279372	-4.457739065
C	4.986553853	-1.735043808	-6.143789929
C	5.310356088	0.38152493	-5.100932802
C	-3.817949421	-2.557832062	-1.100090484
C	-4.188865958	-0.260366471	-1.497158009
O	5.739314691	-0.629384465	-5.901970035

4. References

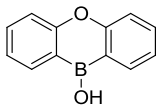
(S1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 (Revision D.01)*, Gaussian, Inc., Wallingford CT, 2009.

(S2) R. Dennington, T. Keith and J. Millam, *GaussView (Version 5)*, Semichem, Inc., Shawnee Mission, KS, 2009.

5. ^{1}H, ^{13}C, and ^{11}B NMR spectra of synthesized compounds

5.1. 10*H*-phenoxaborin-10-ol (7)

[^{1}H NMR spectrum]



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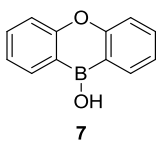
[^{13}C NMR spectrum]



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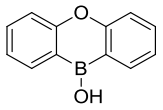
[^{11}B NMR spectrum]



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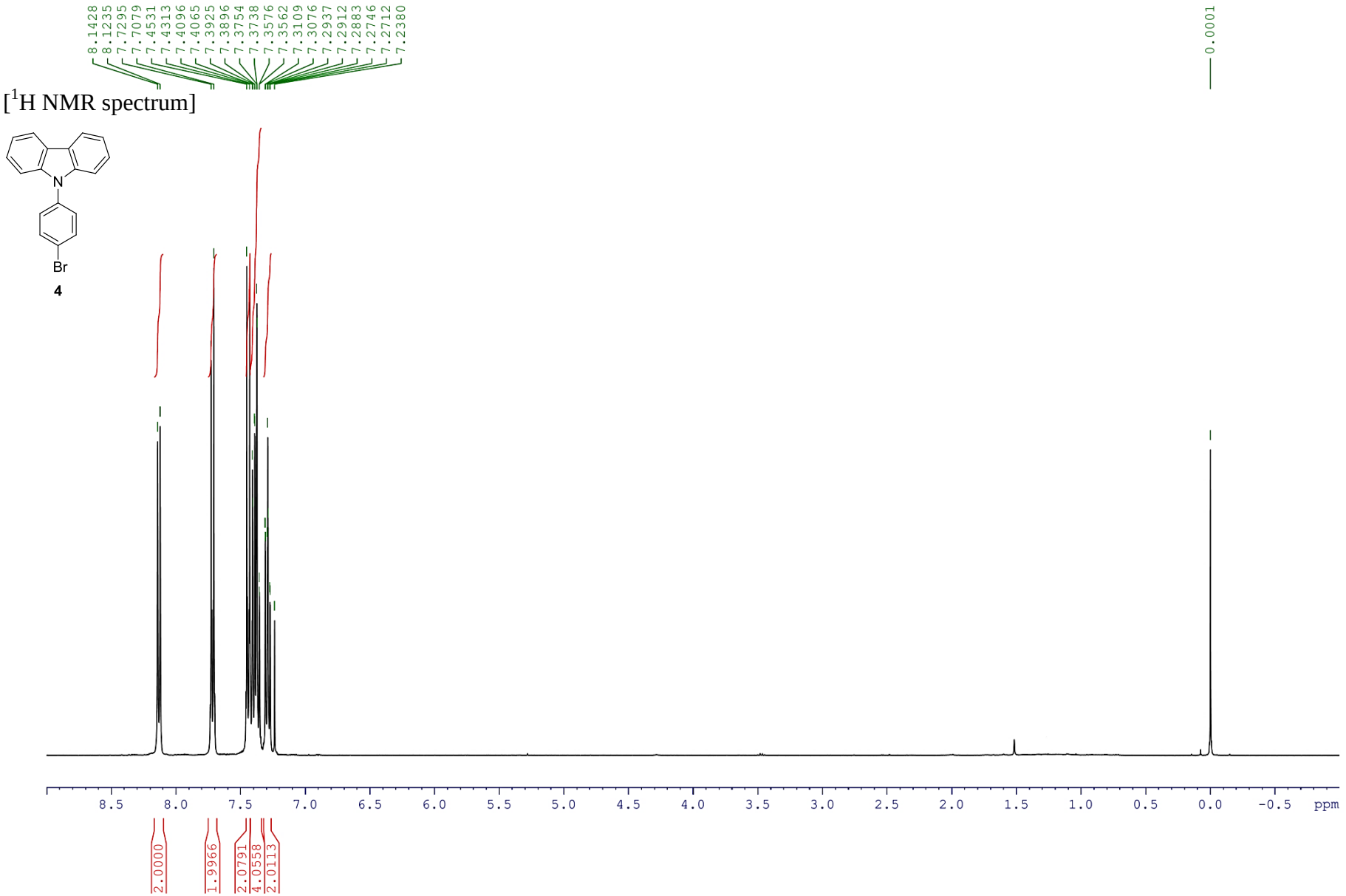
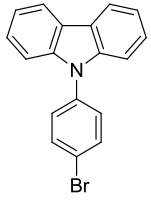
5.2. 9-(4-bromophenyl)-9*H*-carbazole (4)



[^{1}H NMR spectrum]

[^{13}C NMR spectrum]



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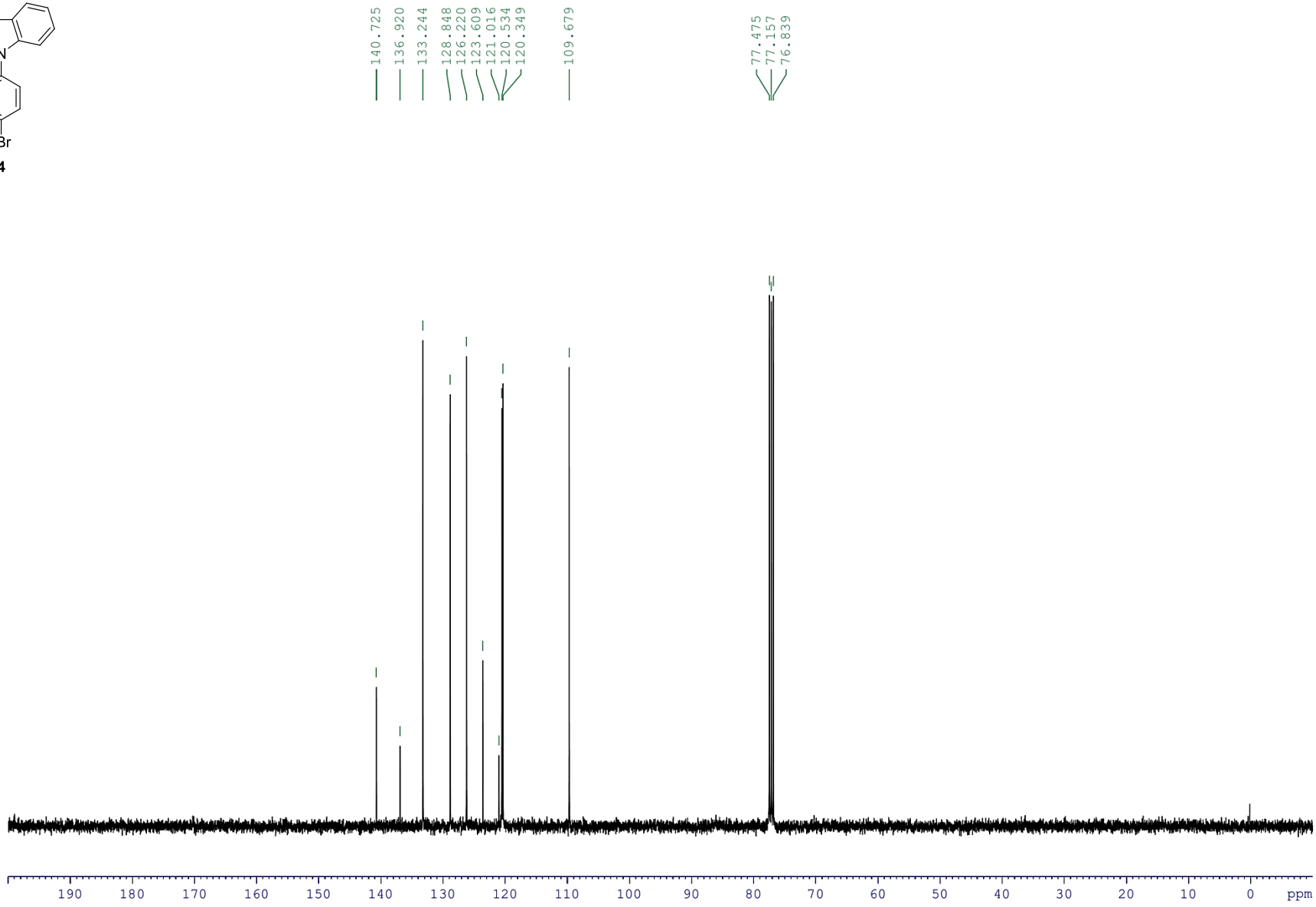
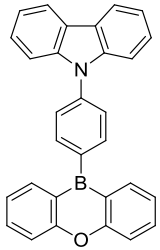


5.3. 9-(4-(10*H*-phenoxaboryl)phenyl)-9*H*-carbazole (9)

[^{1}H NMR spectrum]



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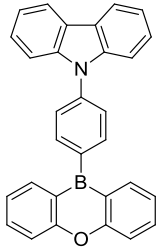
[^{13}C NMR spectrum]



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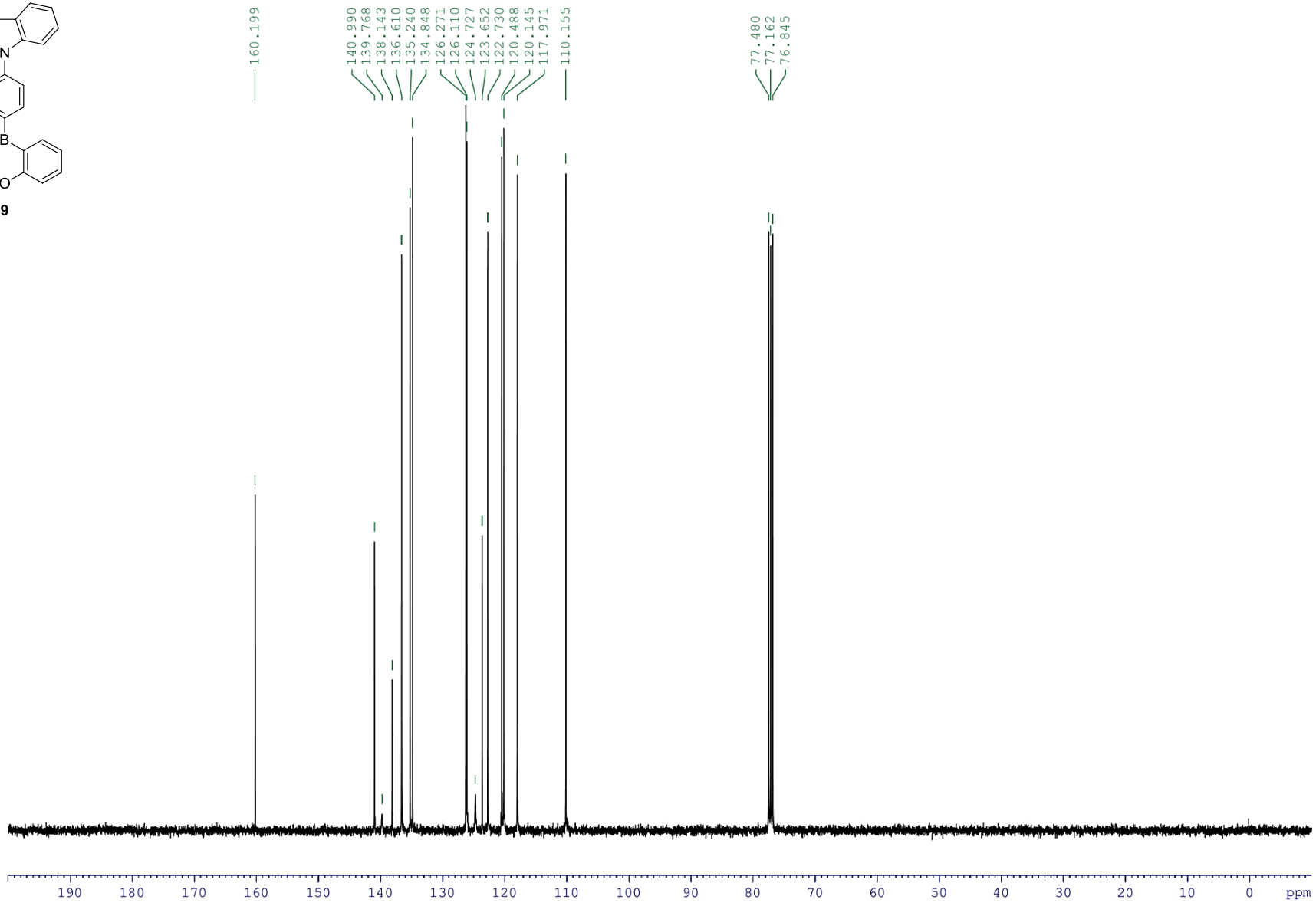
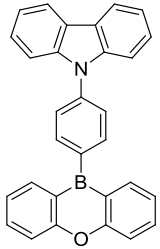


[^{11}B NMR spectrum]



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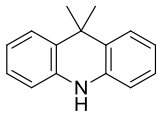
5.4. 9,9-dimethyl-9,10-dihydroacridine (2)

[^{1}H NMR spectrum]



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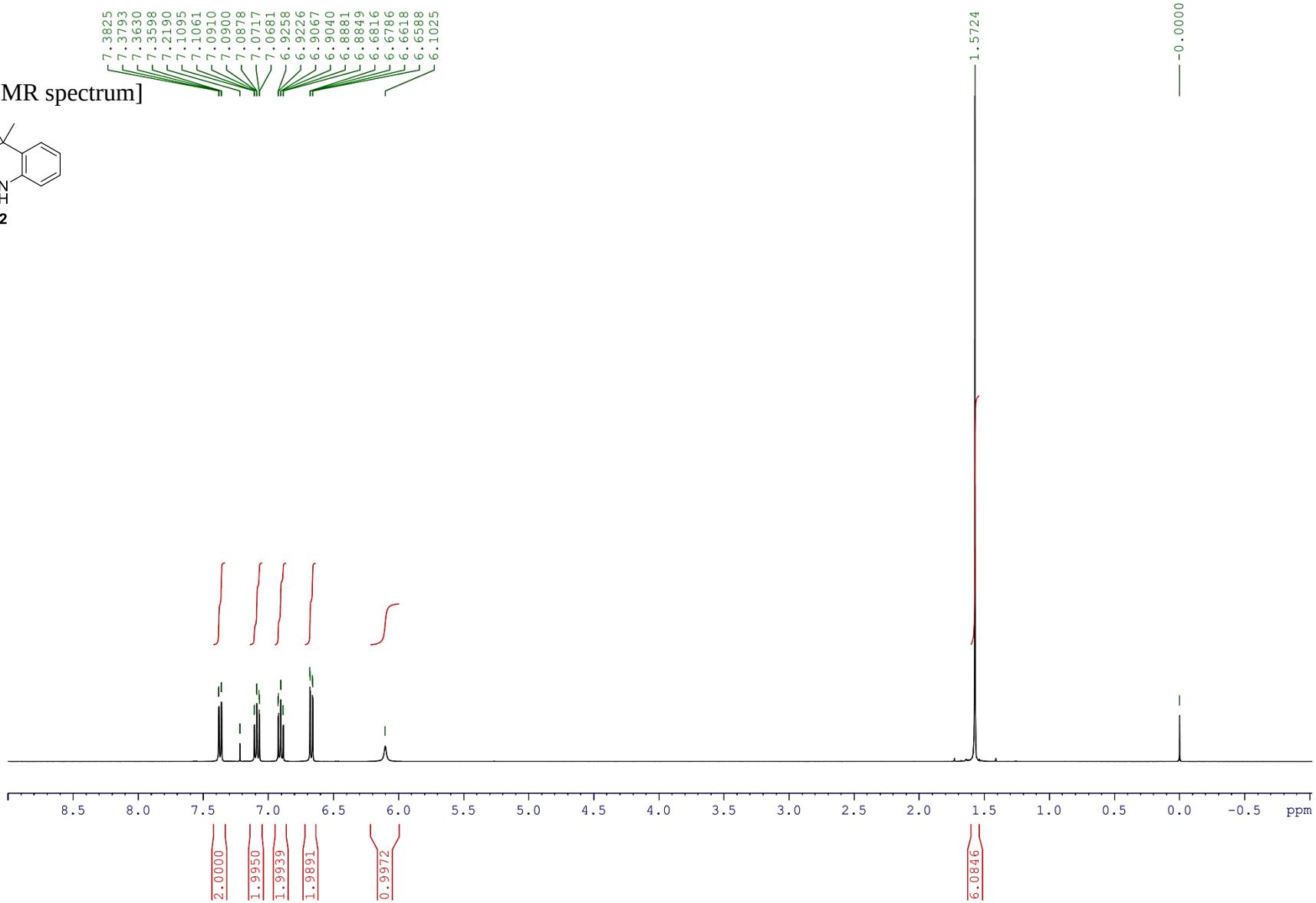
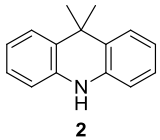
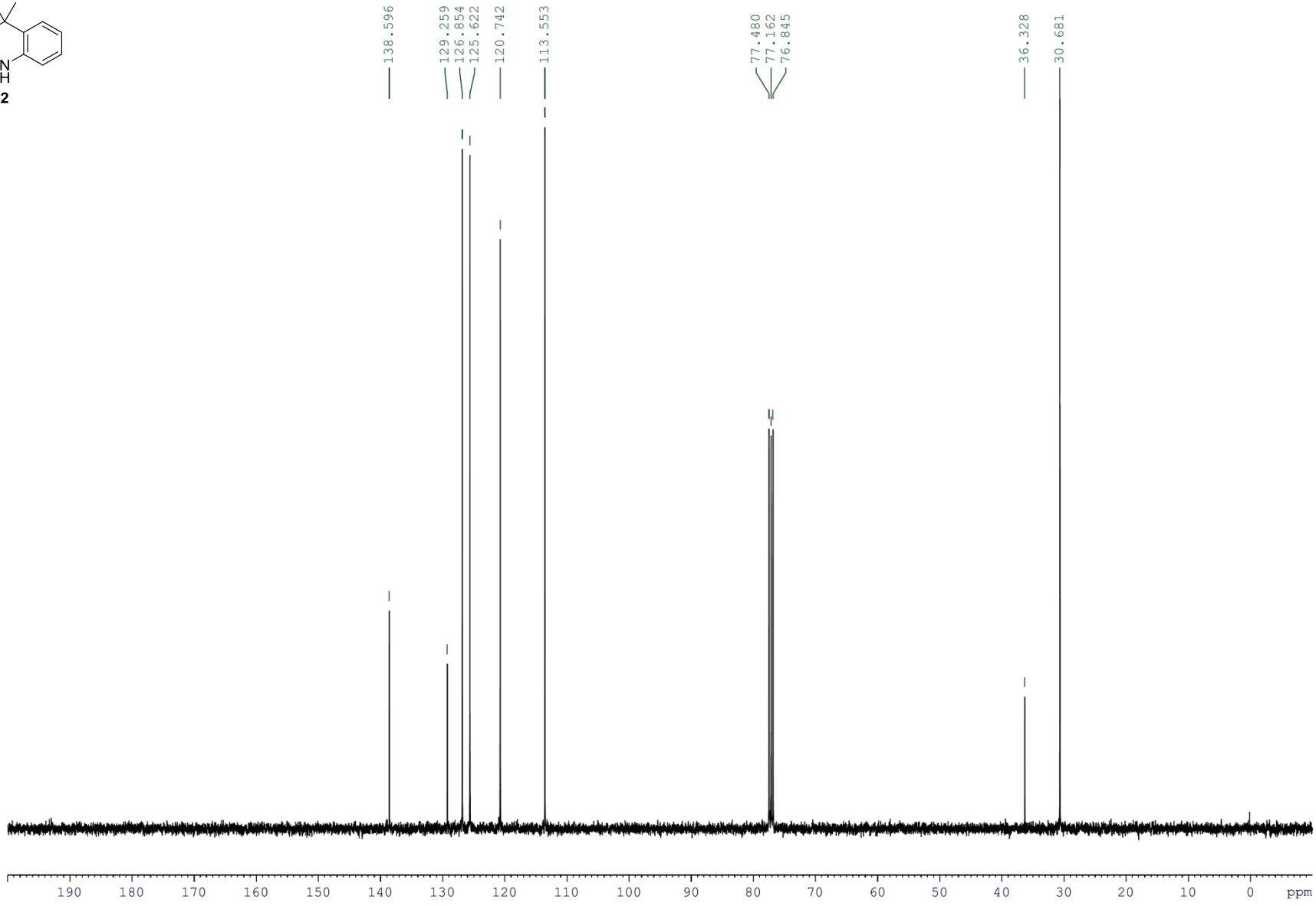


[^{13}C NMR spectrum]

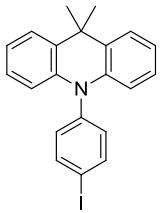


2



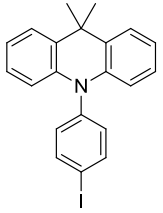
5.5. 9.9-dimethyl-10-(4-iodophenyl)-9,10-dihydroacridine (5)

[^{1}H NMR spectrum]

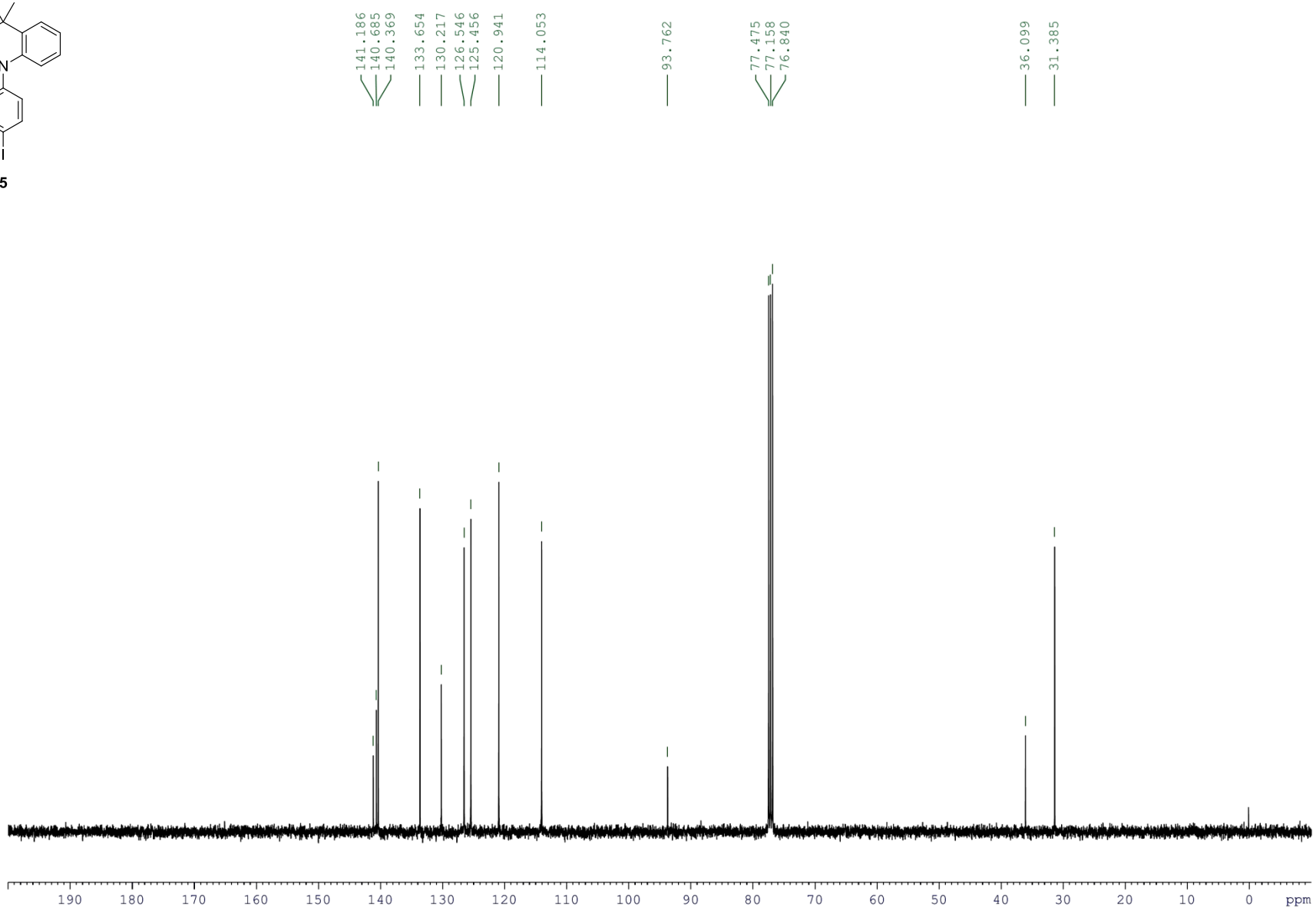


5

[^{13}C NMR spectrum]

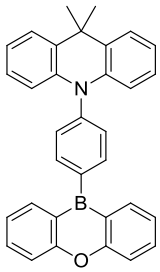


5



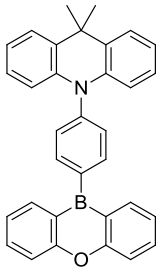
5.6. 9,9-dimethyl-10-(4-(10*H*-phenoxaboryl)phenyl)-9,10-dihydroacridine (10)

[^{1}H NMR spectrum]



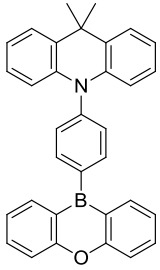
10

[^{13}C NMR spectrum]



10

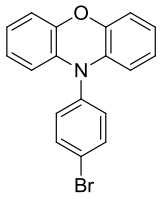
[^{11}B NMR spectrum]



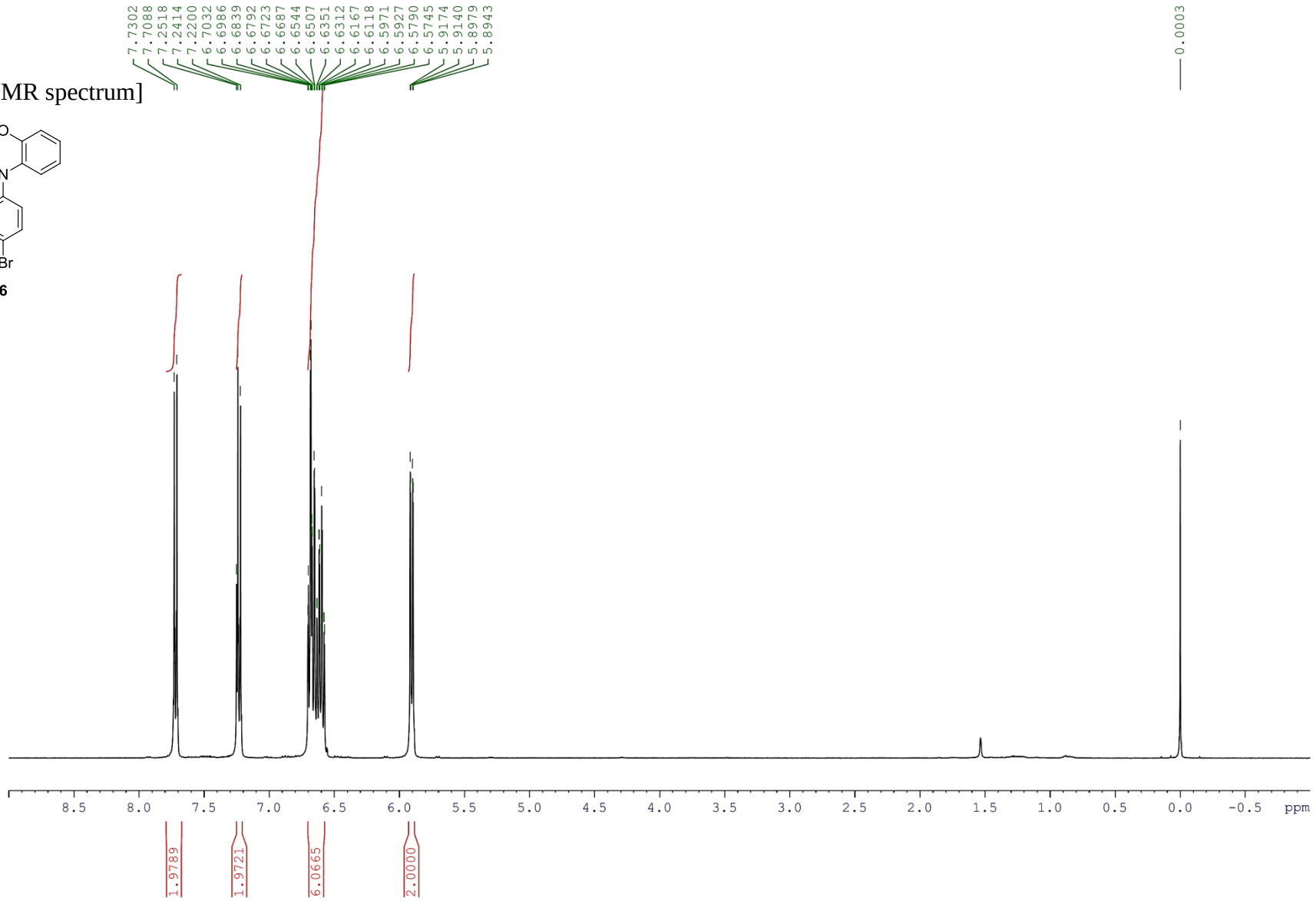
10

5.7. 10-(4-bromophenyl)-10*H*-phenoxazine (6)

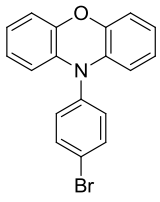
[^{1}H NMR spectrum]



6



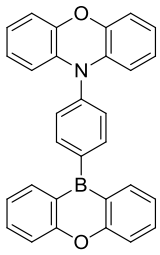
[^{13}C NMR spectrum]



6

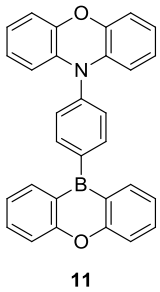
5.8. 10-(4-(10*H*-phenoxaboryl)phenyl)-10*H*-phenoxazine (11)

[^{1}H NMR spectrum]



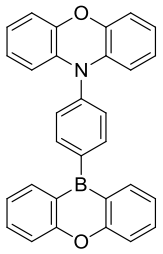
11

[^{13}C NMR spectrum]



11

[^{11}B NMR spectrum]



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