Supporting Information for the Paper

Synthesis of BN-Embedded Tetraphenes and Their Photophysical Properties

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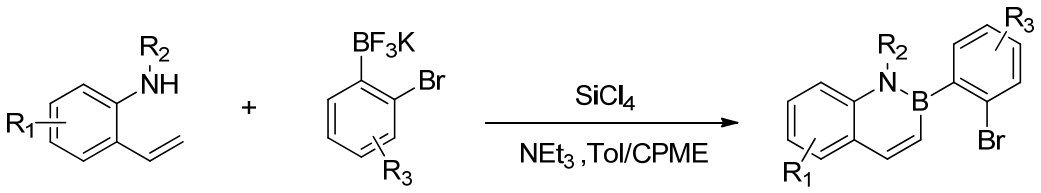
Contents

General Information. All operations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon by using a modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na or P_2O_5. The ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts are referenced against external $BF_3 \cdot Et_2O$ (^{11}B), and $CFCl_3$ (^{19}F). High-resolution mass spectra (HRMS) were obtained on a Varian 7.0T FTMS spectrometer. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrometer. Fluorescence spectra were obtained with a VARIAN CARY Eclipse spectrometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer in dichloromethane solutions. All measurements were carried out at room temperature with a conventional three-electrode (the working electrode: glassy carbon electrode, the reference electrode: saturated calomel electrode (SCE), and a Pt wire as the counter electrode). Ferrocene/ferrocenium redox couple (Fc/Fc^{+}) was used as an internal reference for all measurements. The commercially available catalysts and reagents were purchased from J&K Scientific.

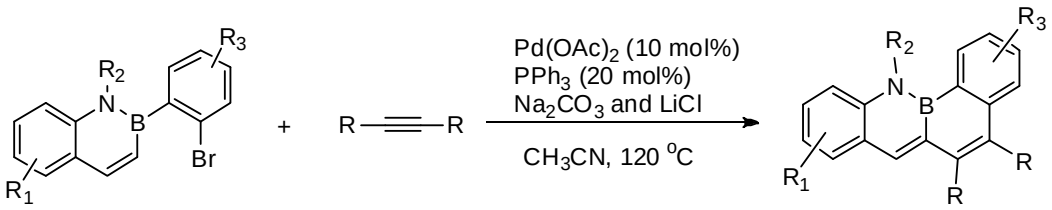
Synthesis of BN Naphthalenes 2a-2i



R_1= H, CH_3, F R_3= H, CH_3, F
R_2= H, Bn, *n*-butyl

These BN-naphthalene derivatives are new compounds and have been prepared by a modified procedure[S1]. To an oven-dried Schlenk flask with a stir bar was added a potassium organotrifluoroborate. After the flask was evacuated under vacuum and purged with argon, cyclopentyl methyl ether (CPME) in toluene were added (0.5 M, CPME/toluene = 1:1) followed by the addition of 2-vinylaniline derivatives (1.2 or 1.5 equivalents), $SiCl_4$ (1 equivalent), and NEt_3 (1.5 equivalents if required). The mixture was stirred at 80 °C for 18 h. It was filtered and the remaining residues were washed with *n*-hexane. The combined solution was evaporated to dryness under vacuum to give the crude product, which was purified by flash column chromatography.

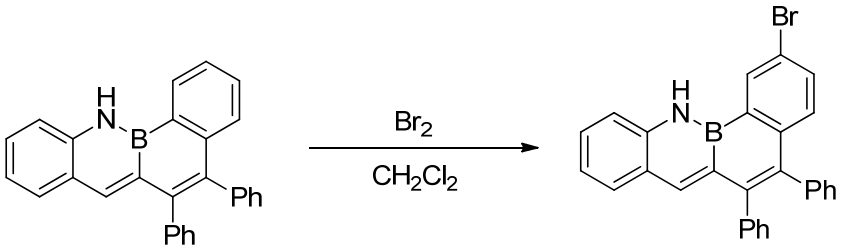
Typical Procedures for the Synthesis of Compound 3-15.



To a sealed tube was added an alkyne (0.5 mmol for compounds **3-6** and **8-15**, 1.0 mmol for **7**),

$Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), Na_2CO_3 (2 equiv), LiCl (1 equiv) and acetonitrile (2 mL) under argon followed by the addition of a borazaronaphthalene **2** (0.75 mmol for compounds **3**-**6** and **8**-**15**, 0.5 mmol for **7**). After the mixture was stirred at 120 °C for 8-24 h, it was cooled down to room temperature. It was filtered and washed with CH_2Cl_2. The combined filtrate was evaporated to dryness to give a crude product, which was purified by silica gel chromatography. The yields for compounds **3**-**6** and **8**-**15** were obtained based on the alkynes, whereas the yield for **7** was obtained based on the BN-naphthalene.

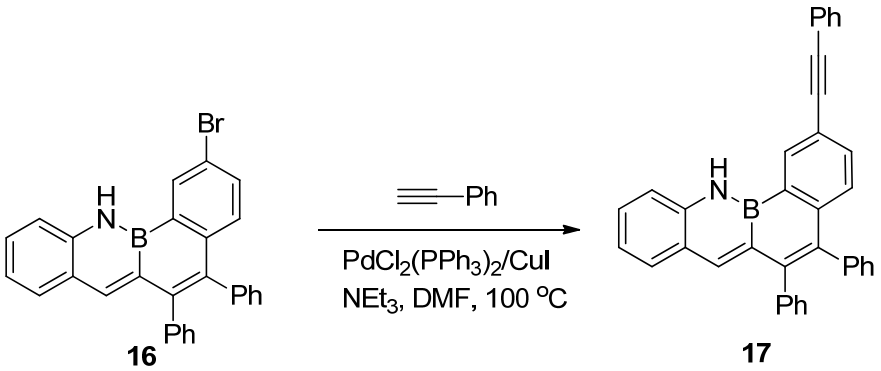
Procedure for the Bromination of 3



3 **16**

To a cooled solution (0 °C) of **3** (190 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was slowly added a solution of bromine (1M in CH_2Cl_2, 0.65 mL, 1.0-1.3 equivalents) diluted with CH_2Cl_2 (5 mL). After the addition, the mixture was stirred at 0 °C for 45 min, and then at room temperature for 2 h. The resulting mixture was evaporated to dryness to give the crude product, which was purified by flash column chromatography to give **16** as yellow solid (60%).

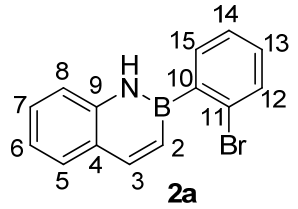
Sonogashira-Coupling of 16 with Phenylacetylene



16 **17**

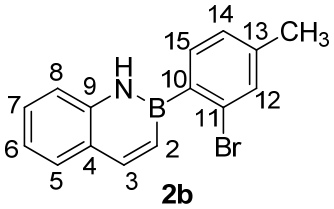
To a dried Schlenk flask charged with **16** (230 mg, 0.5 mmol), phenylacetylene (153 mg, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (18 mg, 5 mol %), and CuI (5.0 mg, 5 mol %) was added triethylamine (153 mg, 1.5 mmol) and DMF (5 mL). The mixture was heated and stirred at 80°C for 17 h. The resulting mixture was successively washed with water (50 mL) and extracted twice with EtOAc (30 mL). The combined organic layers were dried over Na_2SO_4. Analytically pure **17** was obtained as yellow powder (82%) by silica gel chromatography.

Characterization Data for the New Compounds Reported in the Paper



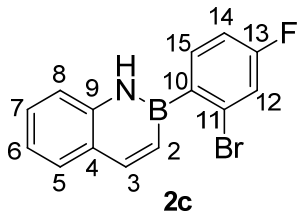
2a

2-(2-bromophenyl)-1, 2-dihydrobenzo[e][1, 2] azaborinine (2a). 2a was obtained as white solid (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (1H, br s, N*H*), 8.12 (1H, d, *J* = 12.0 Hz, 2-C*H*), 7.65 (1H, d, *J* = 8.0 Hz, Ar-H), 7.59 (2H, d, *J* = 8.0 Hz, Ar-H), 7.41 (1H, t, *J* = 6.0 Hz, Ar-H), 7.33 (1H, t, *J* = 6.0 Hz, Ar-H), 7.27 (1H, d, *J* = 8.0 Hz, Ar-H), 7.14-7.23 (3H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.1 (br, s). ^{13}C NMR (101MHz, $CDCl_3$): δ 145.3 (s, CH, C-3), 139.6 (s, quaternary-C, C-9), 135.8 (s, Ar-C), 132.7 (s, Ar-C), 130.4 (s, CH), 129.6 (s, CH, C-13), 128.5 (s, Ar-C), 127.5 (s, quaternary-C, C-4), 126.9 (s, Ar-C), 125.5 (s, quaternary-C, C-11), 121.5 (s, Ar-C), 118.6 (s, Ar-C), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{14}H_{11}BBrN$: 283.01; Found: 283.07.



2b

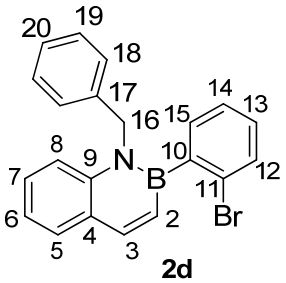
2-(2-bromo-4-methylphenyl)-1, 2-dihydrobenzo[e][1, 2] azaborinine (2b). **2b** was obtained as white solid (72%). ^{1}H NMR (400 MHz,$CDCl_3$): *δ* 8.41 (1H, br s, N*H*), 8.12 (1H, d, *J* = 12.0 Hz, 2-C*H*), 7.66 (1H, d, *J* = 8.0 Hz, Ar-H), 7.54 (1H, d, *J* = 8.0 Hz, Ar-H), 7.45 (1H, s, 12-C*H*), 7.42 (1H, d, *J* = 8.0 Hz, Ar-H), 7.30 (1H, d, *J* = 8.0 Hz, Ar-H), 7.15-7.22 (3H, m, Ar-H), 2.36 (3H, s, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.2 (br, s). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 145.1 (s, C-7), 140.7 (s, quaternary-C, C-13), 139.7 (s, quaternary-C, C-9), 135.8 (s, Ar-C), 133.3 (s, Ar-C), 129.5 (s, Ar-C), 128.4 (s, Ar-C), 127.8 (s, Ar-C), 127.5 (s, quaternary-C, C-4), 125.4 (s, quaternary-C, C-11), 121.4 (s, Ar-C), 118.5 (s, Ar-C), 21.0 (s, CH_3), C-2 and C-10 could not be not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{14}H_{11}BBrN$: 297.03; Found: 297.07.



2c

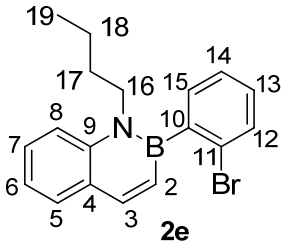
2-(2-bromo-4-fluorophenyl)-1, 2-dihydrobenzo[e][1, 2] azaborinine (2c). 2c was obtained as whit e solid (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (1H, br s, N*H*), 8.13 (1H, d, *J* = 12 Hz, 2-C*H*), 7.66 (1H, d, *J* = 8.0 Hz, Ar-H), 7.58 (1H, t, *J* = 8.0 Hz, Ar-H), 7.44 (1H, t, *J* = 8.0 Hz, Ar-H), 7.36 (1H, d, *J* = 8.0 Hz, Ar-H), 7.21 (1H, t, *J* = 8.0 Hz, Ar-H), 7.06-7.13 (2H, m, Ar-H). ^{11}B NMR (128 MHz, CDCl

$_3$): δ 34.2 (s, br). ^{19}F NMR (376 MHz, $CHCl_3$): δ -110.8 . ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8 (d, J_{C-F} = 253.5 Hz, quaternary-C, C-13), 144.3 (s, CH, C-3), 138.4 (s, quaternary-C, C-9), 135.7 (d, J_{C-F} = 8.1 Hz, C-15), 128.4 (s, Ar-C), 127.5 (s, Ar-C), 126.2 (d, J_{C-F} = 10.1 Hz, quaternary-C, C-11), 124.3 (s, quaternary-C, C-4) 120.5 (s, Ar-C), 119.0 (d, J_{C-F} = 23.2 Hz, Ar-C), 117.4 (s, Ar-C), 113.2 (d, J_{C-F} = 19.2 Hz, Ar-C), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{14}H_{10}BBrFN$: 301.01; Found: 301.02.



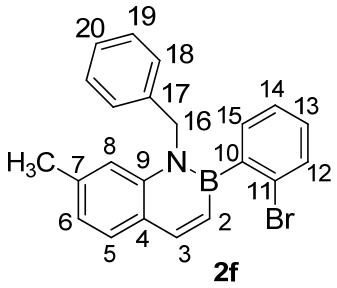
2d

1-benzyl-2-(2-bromophenyl)-1, 2-dihydrobenzo[e][1, 2] azaborinine (2d). 2d was obtained as white solid (53%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 8.12 (1H, d, *J* = 12 Hz, 2-C*H*), 7.71 (1H, d, *J* = 8.0 Hz, Ar-H), 7.55 (1H, d, *J* = 8.0 Hz, Ar-H), 7.06-7.35 (11H, m, Ar-H), 6.96 (1H, d, *J* = 12 Hz, Ar-H), 5.29 (2H, q, *J* = 18.67 Hz, 16-CH_2). ^{11}B NMR (128 MHz, $CDCl_3$): δ 36.7 (s, br). ^{13}C NMR(101 MHz, $CDCl_3$): δ 145.4 (s, CH, C-3), 140.8 (s, quaternary-C, C-17), 138.6 (s, quaternary-C, C-9), 132.9 (s, Ar-C), 131.8 (s, Ar-C), 130.4 (s, Ar-C), 129.4 (s, Ar-C), 128.7 (s, 2*Ar-C, overlap), 128.6 (s, Ar-C), 127.5 (s, quaternary-C, C-4), 126.9 (s, Ar-C), 126.5 (s, Ar-C), 126.4 (s, quaternary-C, C-11), 125.9 (s, 2* Ar-C, overlap), 121.3 (s, Ar-C), 117.2 (s, Ar-C), 52.6 (s, C-16), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{21}H_{17}BBrN$: 373.06; Found: 373.08.



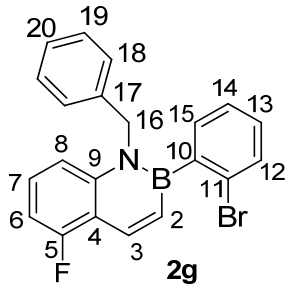
2e

2-(2-bromophenyl)-1-butyl-1, 2-dihydrobenzo[e][1, 2] azaborinine (2e). 2e was obtained as white solid (53%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 8.04 (1H, d, *J* =12 Hz, 2-C*H*), 7.71 (1H, d, *J* = 4.0 Hz, Ar-H), 7.51-7.59 (3H, m, Ar-H), 7.19-7.33 (4H, m, Ar-H), 6.83-6.85 (1H, m, Ar-H), 3.88-4.09 (2H, m, 16-CH_2), 1.81-1.86 (2H, m, 17-CH_2), 1.20-1.26 (2H, m, 18-CH_2), 0.75-0.79 (3H, m, 19-CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 36.2 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9 (s, CH, C-3), 140.9 (s, quaternary-C-9), 133.1 (s, Ar-C), 131.8 (s, Ar-C), 130.7 (s, Ar-C), 129.1 (s, Ar-C), 128.6 (s, Ar-C), 127.4 (s, quaternary-C, C-4), 126.4 (s, Ar-C), 126.2 (s, quaternary-C-11), 120.9 (s, Ar-C), 115.6 (s, Ar-C), 48.2 (s, C-16), 31.9 (s, C-17), 20.3 (s, C-18), 13.7 (s, C-19), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{18}H_{19}BBrN$: 339.08; Found: 339.08.



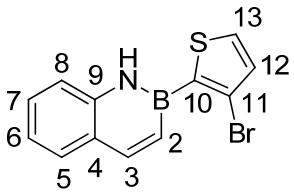
2f

1-benzyl-2-(2-bromophenyl)-7-methyl-1, 2-dihydrobenzo[e][1, 2] azaborinine (2f). 2f was obtain -ed as white solid (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (1H, d, *J* = 8 Hz, Ar-H), 7.61 (1H, d, *J* = 8 Hz, Ar-H), 7.6056 (1H, d, *J* = 8 Hz, Ar-H), 7.13-7.24 (7H, m, Ar-H), 7.03-7.09 (2H, m, Ar-H), 6.90 (1H, d, *J* = 12 Hz, Ar-H), 5.29 (2H, q, *J* = 20 Hz, 16-CH_2), 2.34 (3H, s, CH_3). ^{11}B NMR (128 MHz, CD Cl_3): δ 36.7 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2 (s, CH, C-3), 141.0 (s, quaternary-C-17), 13 8.8 (s, quaternary- C-7 + C-9, overlap), 132.9 (s, Ar-C), 131.8 (s, Ar-C), 130.2 (s, Ar-C), 129.3 (s, Ar-C), 128.6 (s, 2*Ar-C, overlap), 126.8 (s, Ar-C), 126.5 (s, Ar-C), 126.4 (s, quaternary-C-4), 126.0 (s, 2* Ar-C, overlap), 125.3 (s, quaternary-C-11), 122.7 (s, Ar-C), 117.2 (s, Ar-C), 52.4 (s, C-16), 22.2 (s, CH_3), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{22}H_{19}BBrN$: 387.08; Found: 387.06.



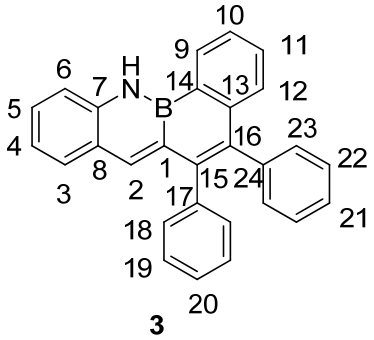
2g

1-benzyl-2-(2-bromophenyl)-5-fluoro-1, 2-dihydrobenzo[e][1, 2] azaborinine (2g). 2g was obtain ed as white solid (47%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (1H, d, *J* = 12 Hz, 2-C*H*), 7.55 (1H, d, *J* = 8 Hz, Ar-H), 7.13-7.24 (8H, m, Ar-H), 7.01-7.06 (3H, m, Ar-H), 6.89 (1H, t, *J* = 8 Hz, Ar-H), 5.28 (2 H, q, *J* = 16 Hz,16-CH_2). ^{11}B NMR (128 MHz, $CDCl_3$): δ 36.8 (s, br). ^{19}F NMR (376 MHz, $CHCl_3$): δ -120.2. ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.1 (d, quaternary-C-5, J_{C-F} = 250.48 Hz), 142.1 (d, quaternar y-C-9, J_{C-F} = 6.1 Hz), 138.3 (s, quaternary-C-17), 136.7 (d, J_{C-F} = 7.1 Hz, C-3), 132.8 (s, Ar-C), 131.9 (s, Ar-C), 129.5 (s, Ar-C), 128.7 (s, 2*Ar-C, overlap), 128.4 (d, J_{C-F} = 10.1 Hz, Ar-C), 127.0 (s, Ar-C), 126.6 (s, Ar-C), 126.3 (s, quaternary-C-11), 125.9 (s, 2*Ar-C, overlap), 117.0 (d, quaternary-C-4, J_{C-F} =16.2), 113.1 (d, J_{C-F} = 3.0 Hz, C-8), 106.8 (d, J_{C-F} = 21.2 Hz, C-6), 53.0 (s, C-16), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for $[M]^+$ $C_{22}H_{19}BBrN$: 391.05; Found: 391.06.



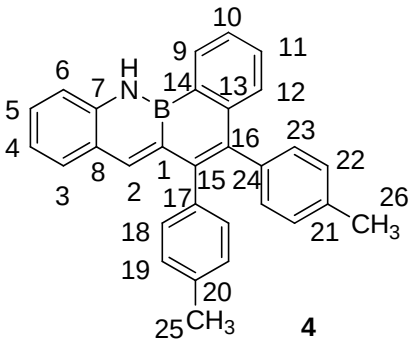
2h

2-(3-bromothiophen-2-yl)-1, 2-dihydrobenzo[e][1, 2] azaborinine (**2h**). **2h** was obtained as white solid (45%).^{1}H NMR (400 MHz,$CDCl_3$): δ 9.01 (1H, br s, N*H*), 8.09 (1H, d, *J* = 12.0 Hz, 2-C*H*), 7.63 (1H, d, *J* = 4.0 Hz, Ar-H), 7.54 (1H, d, *J* = 4.0 Hz, Ar-H), 7.42-7.46 (1H, m, Ar-H), 7.33-7.35 (1H, m, v), 7.16-7.23 (3H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 36.68 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.8 (s, CH, C-3), 140.5 (s, quaternary-C-9), 132.9 (s, Ar-C), 131.2 (s, Ar-C), 129.5 (s, Ar-C), 128.7 (s, Ar-C), 125.5 (s, quaternary-C-4), 121.4 (s, Ar-C), 118.7 (s, Ar-C), 115.3 (s, quaternary-C-11), C-2, C-10 were not observed. EI-MS (*m/z)*: calcd for [M]$^{+}$ 288.97; Found: 289.05.



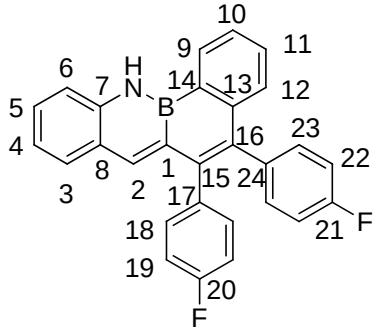
3

5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (3). 3 was obtained as y -ellow-green solid (73%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.90 (1H, br s, N*H*), 8.42 (1H, q, *J* = 2.7 Hz, 5-*CH*), 8.00 (1H, s, 2-C*H*), 7.69 (1H, d, *J* = 8 Hz, 3-C*H*), 7.49-7.57 (4H, m), 7.33-7.36 (1H, m, 4-C*H*), 7.12-7.22 (11H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 29.13. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 143. 1 (s, quaternary-C), 142.4 (s, C-2), 141.3 (s, quaternary-C), 140.3 (s, quaternary-C), 140.2 (s, quaterna ry-C), 139.2 (s, quaternary-C), 138.5 (s, quaternary-C), 131.2 (s, 2*Ar-C, overlap), 131.0 (s, 2*Ar-C, overlap), 130.6 (s, C-3), 130.1 (s, Ar-C), 129.5 (s, C-5), 129.0 (s, C-4), 128.9 (s, Ar-C), 127.6 (s, 2*Ar-C, overlap), 127.4 (s, 2*Ar-C, overlap), 126.1 (s, Ar-C), 126.0 (s, Ar-C), 125.5 (s, quaternary-C), 125. 2 (s, Ar-C), 121.1 (s, Ar-C), 118.5 (s, C-6), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^{+}$ $C_{28}H_{20}BN$: 381.1689; Found: 381.1688.



4

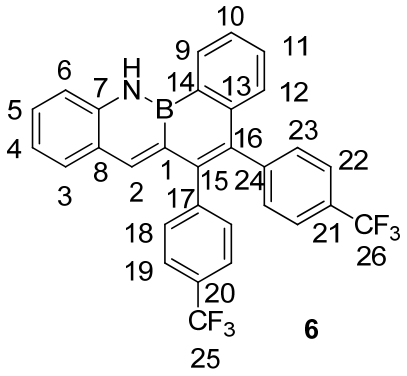
5, 6-di-p-tolyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (4). 4 was obtained as yellow-green solid (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (1H, br s, N*H*), 8.38-8.41 (1H, q, *J* = 4 Hz, 5-C*H)*, 8.01 (1H, s, 2-C*H*), 7.71 (1H, d, *J* = 8.0 Hz, 3-C*H*), 7.48-7.60 (4H, m, Ar-H), 7.33-7.35 (1 H, m, 4-C*H*), 7.22-7.25 (1H, m, Ar-H), 7.03 (8H, s, 18-C*H* + 19-C*H* + 22-C*H* + 23-C*H*), 2.32-2.30 (6 H, d, 25-CH_3 + 26-CH_3). ^{11}B NMR (128 MHz ,$CDCl_3$): δ 30.7 (br, s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 1 43.5 (s, quaternary-C), 142.21 (s, C-2), 140.2 (s, quaternary-C), 139.2 (s, quaternary-C), 138.4 (s, quate rnary-C), 138.4 (s, quaternary-C), 137.2 (s, quaternary-C), 135.3 (s, quaternary-C), 135.2 (s, quaternary -C), 131.0 (s, 2*Ar-C, overlap), 130.8 (s, 2*Ar-C, overlap), 130.6 (s, C-3), 130.0 (s, C-11), 129.3 (s, C-5), 129.0 (s, C-4), 128.7 (s, Ar-C), 128.3 (s, 2*Ar-C, overlap), 128.1 (s, 2*Ar-C, overlap), 125.6 (s, qua ternary-C), 125.0 (s, Ar-C), 121.0 (s, Ar-C), 118.3 (s, C-6), 21.3 (s, CH_3), 21.3 (s, CH_3), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{30}H_{24}BN$: 409.2002, Found: 409.2001.



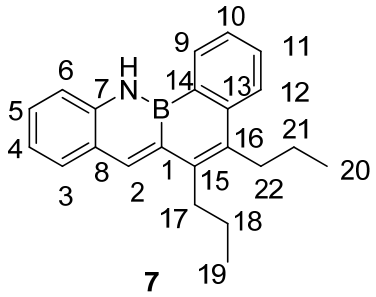
5

5, 6-bis(4-fluorophenyl)-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (5). 5 was obtained as yellow-green solid (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (1H, br s, N*H*), 8.41-8.43 (1 H, q, *J* = 2.7 Hz, 5-C*H*), 7.97 (1H, s, 2-C*H*), 7.72 (1H, d, *J* = 8.0 Hz, 3-C*H*), 7.52-7.63 (4H, m, Ar-H), 7.25-7.32 (2H, m, Ar-H), 7.05-7.10 (4H, m, Ar-H), 6.90-6.96 (4H, m, Ar-H). ^{11}B NMR (128 MHz, CD Cl_3): δ 29.6 (br, s). ^{19}F NMR (376 MHz, $CHCl_3$): -115.4, -115.3. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (d, $J_{C\text{-}F}$ = 245.4 Hz, CF, quaternary-C), 160.1 (d, $J_{C\text{-}F}$ =245.4 Hz, CF, quaternary-C), 142.9 (s, quaterna ry-C), 142.4 (s, C-2), 139.7 (s, quaternary-C), 139.3 (s, quaternary-C),137.8 (s, quaternary-C), 137.0 (d, $J_{C\text{-}F}$ = 3.0 Hz, quaternary-C), 136.0 (d, $J_{C\text{-}F}$ = 4.0 Hz, quaternary-C), 132.5 (d, $J_{C\text{-}F}$ = 26.3 Hz, 2*Ar-C, overlap), 132.4 (d, $J_{C\text{-}F}$ = 27.3 Hz, 2*Ar-C, overlap), 130.6 (s, C-3), 130.1 (s, Ar-C), 129.5 (s, C-5), 129.1 (s, C-4), 128.8 (s, Ar-C), 125.43 (s, quaternary-C), 125.41 (s, Ar-C), 121.2 (s, Ar-C), 118.4 (s, C-6), 114.7 (d, $J_{C\text{-}F}$ = 21.2 Hz, 2*Ar-C, overlap), 114.5 (d, $J_{C\text{-}F}$ = 20.2 Hz, 2*Ar-C, overlap), C-1, C-14 we

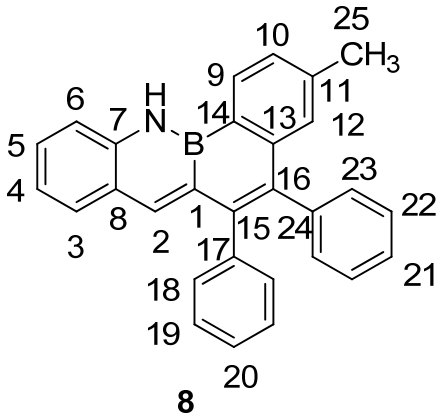
re not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{28}H_{18}BF_2N$: 417.1500; Found: 417.1501.



5, 6-bis(4-(trifluoromethyl)phenyl)-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (6). 6 was obtained as yellow-green solid (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (1H, br s, N*H*), 8. 46 (1H, d, *J* = 8 Hz, Ar-H), 7.91 (1H, s, 2-C*H*), 7.74 (1H, d, *J* = 8 Hz, 3-C*H*), 7.49-7.66 (8H, m, Ar-H), 7.21-7.31 (6H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0 (br, s). ^{19}F NMR (376 MHz, $CHCl_3$): -6 2.4, -62.5. ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8 (s, quaternary-C), 143.7 (s, quaternary-C), 142.6 (s, C -2), 142.0 (s, quaternary-C), 139.4 (s, quaternary-C), 139.3 (s, quaternary-C) ,137.4 (s, quaternary-C), 1 31.4 (s, 2*Ar-C, overlap), 131.1 (s, 2*Ar-C, overlap), 130.7 (s, C-3), 130.3 (s, Ar-C), 129.7 (s, C-5), 12 9.5 (s, Ar-C), 128.7 (s, Ar-C), 125.8 (s, Ar-C), 125.4 (s, quaternary-C), 124.8 (s, 2*Ar-C, overlap), 124. 6 (s, 2*Ar-C, overlap), 124.4 ($J_{C\text{-}F}$ = 272.7 Hz, *CF*$_3$), 124.3 ($J_{C\text{-}F}$ = 273.7 Hz, *CF*$_3$), 121.4 (s, Ar-C), 11 8.5 (s, C-6), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{30}H_{18}BF_6N$: 517.1436; Found: 517.1435.

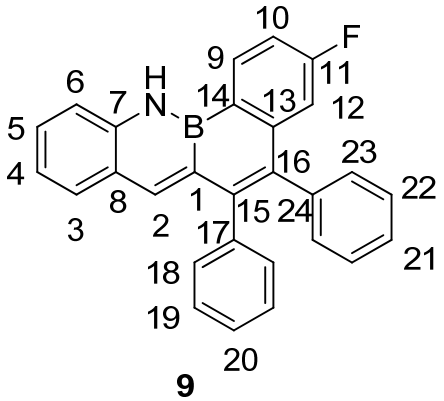


5, 6-dipropyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (7). 7 was obtained as y -ellow-green solid (20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (1H, br s, N*H*), 8.50 (1H, s, 2-C*H*), 8.30 (1H, d, *J* = 8.0 Hz, 3-C*H*), 7.93 (2H, t, *J* = 8.0 Hz, Ar-H).7.66 (1H, t, *J* = 8.0 Hz, Ar-H), 7.52-7.57 (2 H, m, Ar-H),7.45 (1H, t, *J* = 8Hz, Ar-H), 7.30 (1H, t, *J* = 8 Hz, Ar-H), 2.95-3.04 (4H, m, 17-C*H*$_2$ + 22-C*H*$_2$), 1.68-1.78 (4H, m, 18-C*H*$_2$ + 21-C*H*$_2$), 1.13-1.18 (6H, m, 19-C*H*$_3$ + 20-C*H*$_3$). ^{11}B NMR (128 MH z, $CDCl_3$): δ 22.4 (br, s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6 (s, quaternary-C), 138.7 (s, quaternary-C), 138.1 (s, C-2), 136.7 (s, quaternary-C), 135.1 (s, quaternary-C), 130.4 (s, C-3), 130.2 (s, C-11), 12 9.5 (s, C-5), 128.2 (s, C-4), 125.6 (s, quaternary-C), 125.6 (s, Ar-C),124.4 (s, Ar-C),120.9 (s, Ar-C), 11 8.2 (s, C-6), 32.5 (s, *C*H$_2$), 31.2 (s, *C*H$_2$), 24.2 (s, *C*H$_2$), 23.6 (s, *C*H$_2$), 15.0 (s, *C*H$_3$), 14.9 (s, *C*H$_3$), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{22}H_{24}BN$: 314.2080; Found: 314.2078.



8

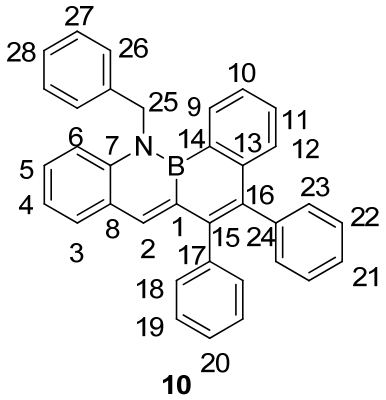
3-methyl-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (8). 8 was ob -tained as yellow-green solid (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (1H, br s, N*H*), 8.23 (1H, d, *J* = 4Hz, Ar-H), 7.89 (1H, s, 2-C*H,* Ar-H), 7.62 (1H, d, *J* = 4Hz, Ar-H), 7.44-7.52 (2H, m, Ar-H), 7.27 (1H, d, *J* = 4Hz, Ar-H), 7.04-7.16 (12H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.2 (br, s). ^{13}C NM R (101 MHz, $CDCl_3$): δ 143.3 (s, quaternary-C-7), 142.1 (s, CH), 141.3 (s, quaternary-C), 140.4 (s, qua ternary-C), 140.4 (s, quaternary-C), 140.1 (s, quaternary-C), 139.3 (s, quaternary-C), 138.5 (s, quaterna ry-C), 131.2 (s, 2*CH, overlap), 131.0 (s, 2*CH, overlap), 130.6 (s, C-3), 129.5 (s, C-4), 129.4 (s, C-5), 128.7 (s, Ar-C), 127.5 (s, 2*Ar-C, overlap), 127.3 (s, 2*Ar-C, overlap), 126.4 (s, Ar-C), 126.0 (s, Ar-C), 125.9 (s, Ar-C), 125.5 (s, quaternary-C), 120.9 (s, Ar-C), 118.3 (s, C-6), 22.2 (s, C-25), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M+Na]^+C_{29}H_{22}BN$:418.1743; Found: 418.1740.



9

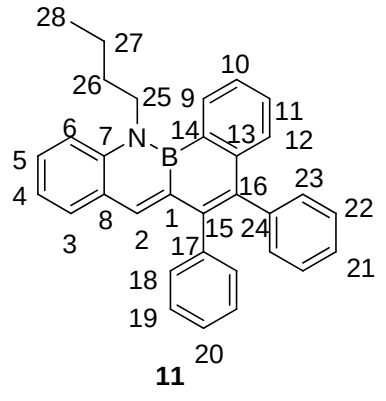
3-fluoro-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (9). 9 was obt -ained as yellow-green solid (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (1H, br s, N*H*), 8.40 (1H, t, *J* = 8 Hz, 5-C*H*), 8.05 (s, 2-C*H*), 7.74 (1H, d, *J* = 8 Hz, 3-C*H*), 7.57-7.64 (2H, m, Ar-H), 7.15-7.29 (12H, m, Ar-H), 7.03-7.06 (1H, d, *J* = 12 Hz, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.4 (s, br). ^{19}F NMR (376 MHz, $CDCl_3$): -109.2. ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3 (d, quaternary-C, J_{C-F} = 248.5 Hz, C -11), 145.7 (d, quaternary-C-13, J_{C-F} = 8.1 Hz), 143.0 (s, C-2), 141.6 (s, quaternary-C), 140.7 (s, quater nary-C), 139.9 (s, quaternary-C), 139.3 (s, quaternary-C), 137.7 (d, quaternary-C-16*,* J_{C-F} = 2.0 Hz), 13 1.5 (d, J_{C-F} = 8.1 Hz, C-9), 131.0 (s, 2*Ar-C, overlap), 130.8 (s, 2*Ar-C, overlap), 130.7 (s, Ar-C), 129. 1 (s, Ar-C), 127.8(s, 2*Ar-C, overlap), 127.4 (s, 2*Ar-C, overlap), 126.4 (s, Ar-C), 126.1 (s, Ar-C), 12 5.4 (s, quaternary-C), 121.1 (s, Ar-C), 118.4 (s, CH, C-6), 115.0 (d, J_{C-F} = 21.2 Hz, Ar-C), 112.8 (d, J_{C-F}

= 22.2 Hz, Ar-C), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{28}H_{19}BFN$: 395.1595; F ound: 395.1593.



10

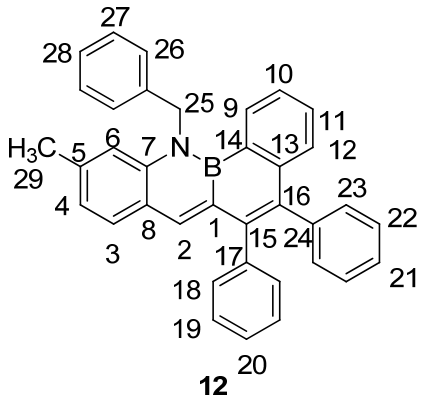
12-benzyl-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (10). 10 was obtained as yellow-green solid (55%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (1H, d, *J* = 8Hz, Ar-H), 8.0 2 (1H, s, 2-*CH*), 7.71 (1H, d, *J* = 8 Hz, 3-*CH*), 7.57 (1H, d, *J* = 8 Hz, Ar-H), 7.06-7.48 (20H, m, Ar-H), 6.49 (1H, d, *J* = 16Hz, 25-CH_2), 5.61(1H, d, *J* = 20Hz, 25-CH_2). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.4 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.3 (s, quaternary-C), 142.9 (s, C-2), 141.7 (s, quaternary-C), 141.6 (s, quaternary-C), 140.44 (s, quaternary-C), 140.40 (s, quaternary-C), 138.6 (s, quaternary-C), 138.5 (s, quaternary-C), 133.6 (s, Ar-C), 131.5 (s, Ar-C), 131.2 (s, Ar-C), 130.9 (s, Ar-C), 129.6 (s, Ar-C), 129.29 (s, Ar-C), 129.25 (s, Ar-C), 129.23 (s, Ar-C, overlap), 127.6 (s, Ar-C), 127.4 (s, Ar-C), 1 27.3 (s, Ar-C), 126.3 (s, quaternary-C), 126.2 (s, Ar-C, overlap), 126.0 (s, Ar-C), 126.0 (s, Ar-C), 125.2 (s, Ar-C), 121.0 (s, Ar-C), 116.7 (s, Ar-C), 55.5 (s, CH_2, C-25), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{35}H_{26}BN$:471.2158; Found: 471.2155.



11

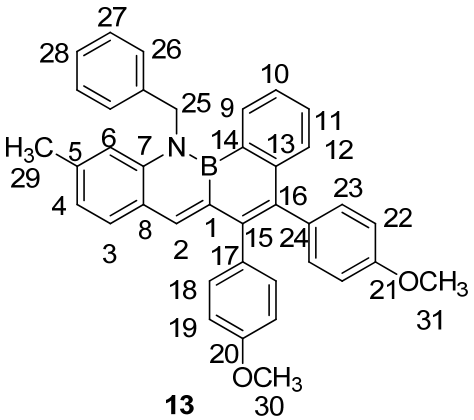
12-butyl-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (11). 11 was o -btained as yellow-green solid (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (1H, d, *J* = 8 Hz, Ar-H), 7.9 5 (1H, s, 2-C*H*), 7.88 (1H, d, *J* = 8 Hz, Ar-H), 7.64-7.71 (2H, m, Ar-H), 7.47-7.55 (2H, m, Ar-H), 7.39-7.41 (1H, m, Ar-H), 7.13-7.24 (11H, m, Ar-H), 5.15 (1H, s, 25-CH_2), 4.46 (1H, s, 25-CH_2), 2.24-2.39 (2H, m, 26-CH_2), 1.76-1.77 (2H, m, 27-CH_2), 1.12 (3H, t, *J* = 6 Hz, 28-CH_3). ^{11}B NMR (128 MHz, CD Cl_3): δ 30.1 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5 (s, quaternary-C), 142.6 (s, C-2), 141.7 (s, qu aternary-C), 141.4 (s, quaternary-C), 140.6 (s, quaternary-C), 140.6(s, quaternary-C) , 138.2(s, quaterna

ry-C) , 133.438 (s, Ar-C), 131.5 (s, Ar-C), 131.0 (s, Ar-C), 129.5 (s, C-5), 129.3 (s, C-4), 129.2 (s, Ar-C), 127.6 (s, Ar-C, overlap), 127.3 (s, Ar-C), 126.2 (s, quaternary-C), 126.0 (s, Ar-C), 125.9 (s, Ar-C), 125.1 (s, Ar-C), 120.6 (s, Ar-C), 115.4 (s, C-6), 49.2 (s, C-25), 32.1 (s, C-26), 20.3 (s, C-27), 14.1 (s, C-28), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{32}H_{28}BN$: 437.2315; Found: 437.2312.



12

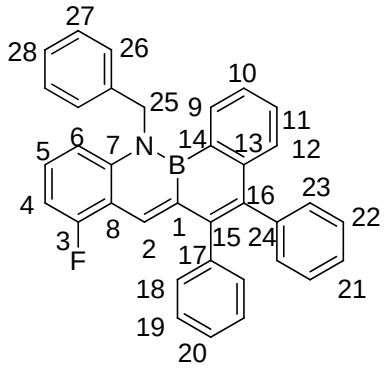
12-benzyl-10-methyl-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2]azaborinine (12). 12 was obtained as yellow-green solid (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (1H, d, *J* = 8Hz, Ar-H), 8.00 (1H, s, 2-C*H*), 7.60 (1H, d, *J* = 4 Hz, Ar-H), 7.36-7.44 (8H, m, Ar-H), 7.06-7.25 (12H, m, Ar-H), 6.45 (1H, d, *J* = 16 Hz, 25-CH_2), 5.59 (1H, d, *J* = 16 Hz, 25-CH_2), 2.40 (3H, s, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.4 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.3 (s, quaternary-C), 142.9 (s, C-2), 142.0 (s, quaternary-C) , 141.7 (s, quaternary-C), 140.6 (s, quaternary-C), 140.6 (s, quaternary-C), 139.8 (s, quaternary-C), 138.7 (s, quaternary-C), 137.9 (s, quaternary-C), 133.6 (s, Ar-C), 131.6 (s, Ar-C), 131.3 (s, Ar-C), 131.1 (s, Ar-C), 130.9 (s, Ar-C), 129.4 (s, Ar-C), 129.2 (s, Ar-C, overlap), 127.6 (s, Ar-C, overlap), 127.4 (s, Ar-C), 127.3 (s, Ar-C), 126.3 (s, Ar-C, overlap), 126.0 (s, Ar-C), 125.9 (s, Ar-C), 125.1 (s, Ar-C), 124.2 (s, quaternary-C), 122.7 (s, Ar-C), 116.7 (s, C-6), 54.4 (s, C-25), 22.6 (s, C-29), C-1, C-14 were not observed. HR-MS (*m/z*) calcd for $[M]^+$ $C_{36}H_{28}BN$: 485.2315; Found: 485.2312.



13

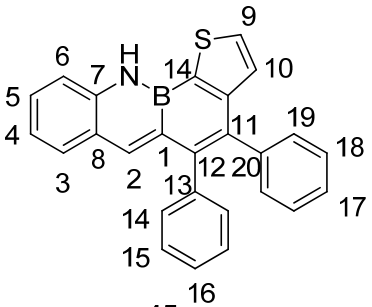
12-benzyl-5, 6-bis(4-methoxyphenyl)-10-methyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2]azaborinine (13). 13 was obtained as yellow-green solid (61%). ^{1}H NMR (400 MHz,$CDCl_3$): δ 8.20 (1H, d, *J* = 8 Hz, 3-C*H*), 8.01 (1H, s, 2-C*H*), 7.61 (1H, d, *J* = 8 Hz, 4-C*H*), 7.35-7.43 (8H, m, Ar-H), 7.21

-7.25 (2H, m, Ar-H), 6.76-7.13 (8H, m, Ar-H), 6.45 (1H, d, J = 20Hz, 25-CH_2), 5.58 (1H, d, J = 16 Hz, 25-CH_2), 3.78-3.81 (6H, d, 30-OCH_3 + 31-OCH_3), 2.40 (3H, s, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.0 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.6 (s, quaternary-C, C-20 or C-21), 157.5 (s, quaternary -C, C-21 or C-20), 144.8 (s, quaternary-C), 142.7 (s, CH, C-2), 141.6 (s, quaternary-C), 140.4 (s, quater nary-C), 139.7 (s, quaternary-C), 138.7 (s, quaternary-C), 137.7 (s, quaternary-C), 134.2 (s, quaternary-C), 133.5 (s, CH), 133.0 (s, quaternary-C), 132.5 (s, Ar-C), 132.2 (s, Ar-C), 131.8 (s, Ar-C), 131.0 (s, A r-C), 129.4 (s, Ar-C), 129.2 (s, Ar-C, overlap), 129.1 (s, Ar-C), 127.2 (s, Ar-C), 126.2 (s, Ar-C, overla p), 124.9 (s, Ar-C), 124.2 (s, quaternary-C), 122.6 (s, Ar-C), 116.6 (s, Ar-C), 113.1 (s, Ar-C), 55.1 (s, ov erlap, C-30 + C-31), 54.3 (s, C-25), 22.5 (s, C-29). HR-MS (*m/z*) calcd for $[M]^+$ $C_{38}H_{32}BNO_2$: 545.252 6; Found: 545.2528.



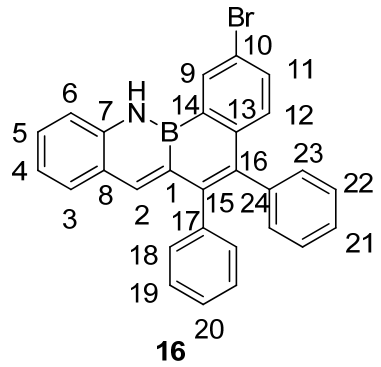
14

12-benzyl-8-fluoro-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (1 4). 14 was obtained as yellow-green solid (31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (1H, s, 2-CH), 8. 20 (1H, d, J = 8 Hz, Ar-H), 6.91-7.44 (21H, m, Ar-H), 6.47 (1H, d, J = 20 Hz, 25-CH_2), 5.56 (1H, d, J = 20 Hz, 25-CH_2). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.4 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2 (d, $J_{C\text{-}F}$ = 252.5 Hz, quaternary-C, C-3), 144.5 (s, quaternary-C), 142.7 (d, $J_{C\text{-}F}$ = 5.1 Hz, quaternary-C, C-7), 141.4 (s, quaternary-C), 140.5 (s, quaternary-C), 140.1 (s, quaternary-C), 139.1 (s, quaternary-C), 138.3 (s, quaternary-C), 134.1 (d, $J_{C\text{-}F}$ = 7.1 Hz, C-2), 133.6 (s, Ar-C), 131.4 (s, Ar-C), 131.1 (s, Ar-C), 130.8 (s, Ar-C), 129.8 (s, Ar-C), 129.4 (s, Ar-C), 129.3 (Ar-C, overlap), 128.8 (d, $J_{C\text{-}F}$ = 10.1 Hz, C-5), 127.6 (s, Ar-C), 127.5 (s, Ar-C), 126.2 (Ar-C, overlap), 126.1 (s, Ar-C), 125.4 (s, Ar-C), 116.3 (d, $J_{C\text{-}F}$ = 16.2 Hz, quaternary-C, C-8), 112.6 (d, $J_{C\text{-}F}$ = 3.0 Hz, C-6), 106.2 (d, $J_{C\text{-}F}$ = 21.2 Hz, C-4), 54.9 (s, C-2 5). HR-MS (*m/z*) calcd for $[M]^+$ $C_{35}H_{25}BFN$: 489.2064; Found: 489.2062.



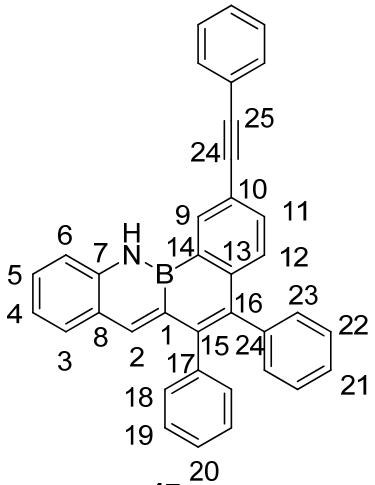
15

4, 5-diphenyl-11 H-benzo[e]thieno[3', 2': 5, 6]borinino[1, 2-b][1, 2] azaborinine (15). **15** was obt -ained as yellow-green solid (23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (1H, s br, N*H*), 8.24 (1H, s, 2-C*H*), 7.74 (1H, d, *J* = 8 Hz, Ar-H), 7.69 (1H, d, *J* = 4 Hz, Ar-H), 7.58-7.62 (2H, m, Ar-H), 7.11-7.27 (12H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 27.7 (s, br). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1 (s, quaternary-C), 144.7 (s, C-2), 141.6 (s, quaternary-C), 139.7 (s, quaternary-C), 139.1 (s, quaternary-C), 138.2 (s, quaternary-C), 135.1 (s, quaternary-C), 131.4 (s, 2*Ar-C, overlap), 130.9 (s, Ar-C), 130.6 (s, 2*Ar-C, overlap), 130.0 (s, Ar-C), 129.3 (s, Ar-C), 129.2 (s, Ar-C), 127.5 (s, 2* Ar-C, overlap), 127.4 (s, 2*Ar-C, overlap), 126.2 (s, Ar-C), 126.1 (s, Ar-C), 125.1 (s, quaternary-C), 121.0 (s, Ar-C), 118.3 (s, C-6). HR-MS (*m/z*) calcd for $[M]^+$ $C_{26}H_{18}BNS$: 387.1253; Found:387.1250.



16

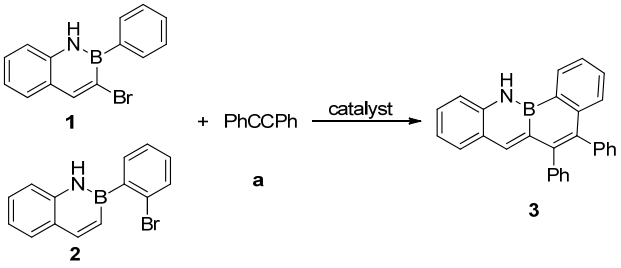
2-bromo-5, 6-diphenyl-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (16). 16 was obtained as yellow-green solid (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (1H, s, N*H*), 8.84 (1H, s, 9-C*H*), 8.02 (1H, s, 2-C*H*), 7.72 (1H, d, *J* = 8 Hz, Ar-H), 7.57-7.60 (3H, m, Ar-H), 7.10-7.27 (12H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.0. ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9 (s, C-2), 141.6 (s, quaternary-C), 140.8 (s, quaternary-C), 140.8 (s, quaternary-C), 139.9 (s, quaternary-C), 139.1 (s, quaternary-C), 137.6 (s, quaternary-C), 132.7(s, Ar-C), 132.1(s, Ar-C), 131.1 (s, 2*Ar-C, overlap), 130.83 (s, 2*Ar-C, overlap), 130.78 (s, Ar-C), 130.7 (s, Ar-C), 129.2 (s, Ar-C), 127.7 (s, 2*Ar-C, overlap), 127.4 (s, 2*Ar-C, overlap), 126.3 (s, Ar-C), 126.1 (s, Ar-C), 125.6 (s, quaternary-C), 121.4 (s, Ar-C), 119.9 (s, quaternary-C), 118.5 (s, C-6).



17

5, 6-diphenyl-2-(phenylethynyl)-12 H-benzo[e]benzo[5, 6]borinino[1, 2-b][1, 2] azaborinine (17). 17 was obtained as yellow-green solid (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (1H, s, N*H*), 8.61 (1H, s, 9-C*H*), 8.04 (1H, s, 2-C*H*), 7.73 (1H, d, *J* = 8 Hz, 3-C*H*), 7.59-7.66 (5H, m, Ar-H), 7.32-7.39 (5H, m, Ar-H), 7.13-7.29 (10H, m, Ar-H). ^{11}B NMR (128 MHz, $CDCl_3$):δ 31.1. ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.8 (s, C-2), 142.6 (s, quaternary-C), 141.3 (s, quaternary-C), 140.9 (s, quaternary-C), 140.0 (s, quaternary-C), 139.3 (s, quaternary-C), 138.1 (s, quaternary-C), 132.9 (s, Ar-C), 132.6 (s, Ar-C), 131.7 (s, 2*Ar-C, overlap), 131.1 (s, 2*Ar-C, overlap), 130.9 (s, 2*Ar-C, overlap), 130.7 (s, Ar-C), 129.1 (s, Ar-C), 128.8 (s, Ar-C), 128.4 (s, 2*Ar-C, overlap), 128.3 (s, Ar-C), 127.7 (s, 2*Ar-C, overlap), 127.4 (s, 2*Ar-C, overlap), 126.2 (s, Ar-C), 126.1 (s, Ar-C), 125.655 (s, quaternary-C), 123.5 (s, quaternary-C), 121.2 (s, CH), 119.7 (s, quaternary-C), 118.5 (s, C-6), 90.3 (s, quaternary-C, C≡C), 90.1 (s, quaternary-C，C≡C). HR-MS (*m/z*) calcd for $[M]^+$ $C_{36}H_{24}BN$: 481.2002; Found: 481.1998.

Table S1. Optimization of Cyclization Conditions



entry	cat	ligand	base	additive	time/h	yield[c]
1[a]	5%$Pd(OAc)_2$	10%$P(Cy)_3$	100%Na_2CO_3	----	24h	43%
2[a]	5%$[Cp^*RhCl_2]_2$	----	100%Na_2CO_3	----	24h	0%
3[a]	5%$[RuCl_2(p\text{-cymene})]_2$	----	100%Na_2CO_3	----	24h	0%
4[a]	10%$Pd(OAc)_2$	20%$P(Cy)_3$	100%Na_2CO_3	----	24h	50%
5[b]	10%$Pd(OAc)_2$	20%$P(Cy)_3$	100%Na_2CO_3	----	24h	58%
6[b]	10%$Pd(OAc)_2$	20%$P(Cy)_3$	200%Na_2CO_3	----	24h	68%
7[b]	10%$Pd(OAc)_2$	20%$P(Ph)_3$	200%Na_2CO_3	----	24h	58%
8[b]	10%$Pd(OAc)_2$		200%Na_2CO_3		24h	32%
9[b]	10%$Pd(OAc)_2$	20%$P(Ph)_3$	200%Na_2CO_3	100%LiCl	24h	74%
10[b]	10%$Pd(OAc)_2$	20%$P(Ph)_3$	200%Na_2CO_3	100%LiCl	8h	73%
11[d]	10%$Pd(OAc)_2$	20%$P(Ph)_3$	200%Na_2CO_3	100%LiCl	8h	10%

[a] **a**/**2** = 1/1, [b] **a**/**2** = 1/1.5. [c] Isolated yields . [d] Compound **1** as starting material.

X-ray Crystallographic Studies of Compound 3 and 17:

Data collections for compounds **3** and **17** were performed at 113 K on a Rigaku Saturn CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures of **3** and **17** were solved by use of SHELXTL program[S2]. Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squaresmethod. CCDC numbers: 1406577 for compound **3** and 1406578 for compound **17**.

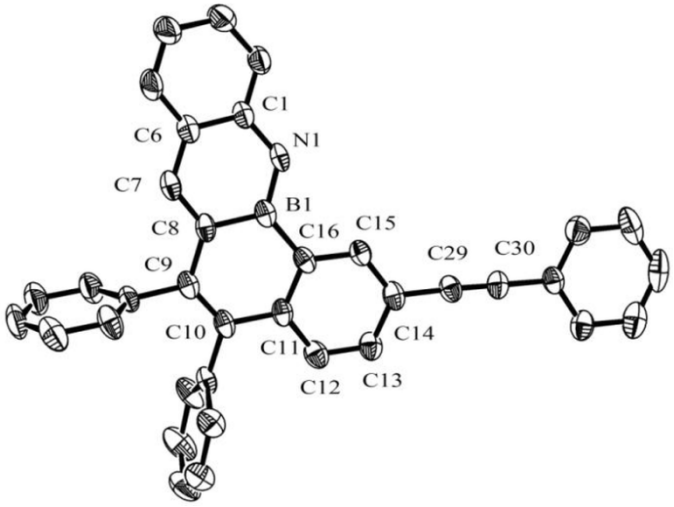


Figure S1. Molecular structure of **17. Hydrogen atoms have been omitted for clarity.** Selected bond lengths (Å) and bond angles (deg) for **17**: B1−N11.417(5), B1−C8 1.526(5), B1−C16 1.542(5), C29−C30 1.200(4); N1−B1−C8116.6(3), N1−B1−C16 124.8(3), C8−B1−C16 118.6(3).

Table S2. Crystallographic data and structure refinement details for **3** and **17.**

	3	**17**

Empirical formula	$C_{28}H_{20}BN$	$C_{36}H_{24}BN$
Formula weight	381.25	481.37
Temperature	113(2) K	113(2) K
Wavelength	0.71073Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions	a = 11.899(2) Å b =13.110(3) Å c =18.036(4) Å α = 73.51(3) deg. β = 89.05(3) deg. γ = 64.38(3) deg.	a = 9.942(2) Å b = 16.900(4) Å c = 18.738(4) Å α = 105.481(6) deg. β = 92.118(4) deg. γ = 92.215(5) deg.
Volume	2414.0(8) $Å^3$	3028.2(12) $Å^3$
Z, Calculated density	4, 1.046 Mg/m^3	4, 1.056 Mg/m^3
Absorption coefficient	0.060 mm^{-1}	0.060 mm^{-1}
F(000)	796	1008
Crystal size	0.22 x 0.20 x 0.18 mm	0.220 x 0.180 x 0.160 mm
Theta range for data collection	1.19 to 27.98 deg	3.011 to 25.004 deg.
Limiting indices	-15<=h<=13, -17<=k<=17, -23<=l<=23	-11<=h<=11, -20<=k<=20, -22<=l<=22
Reflections collected / unique	25245 / 11371 [R(int)= 0.0448]	33253/10571[R(int)=0.0712]
Completeness to theta = 27.98	97.7 %	(Completeness to theta = 25.004) 99.1 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9893 and 0.9870	1.000 and 0.887
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11371 / 0 / 542	10571 / 2 / 692
Goodness-of-fit on F^2	0.952	1.060
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0693, $wR2$ = 0.192	$R1$ = 0.0769, $wR2$ = 0.1838
R indices (all data)	$R1$ = 0.1141, $wR2$ = 0.2158	$R1$ = 0.1450, $wR2$ = 0.2095
Extinction coefficient	0.013(2)	0.0007(9)

UV-Vis and FL Studies of Compound 3 -15

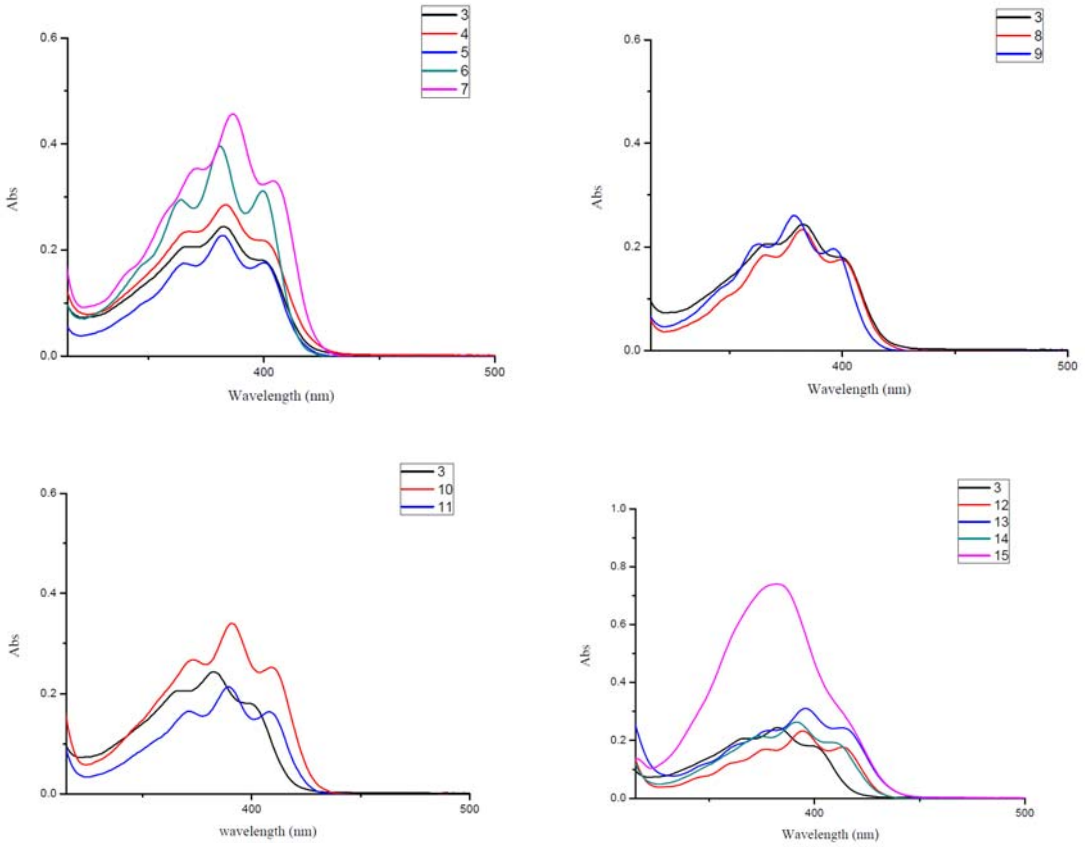


Figure S2. UV−vis spectra of **3-15**. All experiments were performed in CH_2Cl_2 solution at 10^{-5} M.

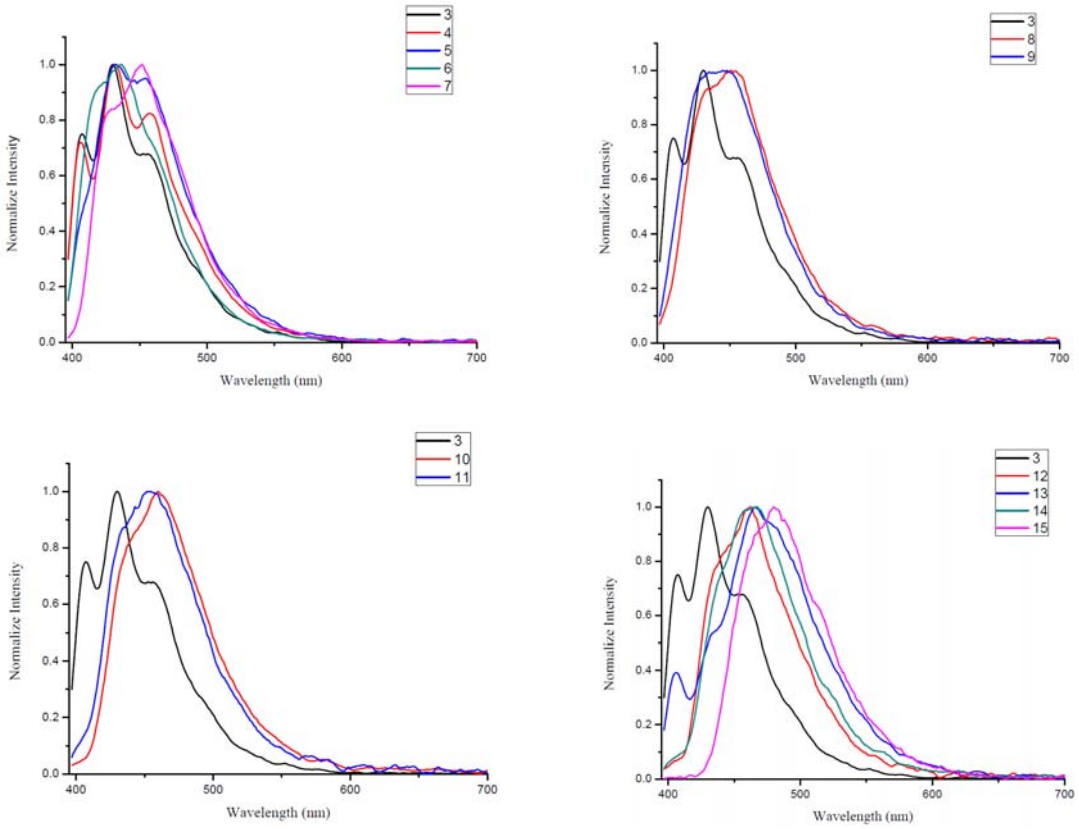


Figure S3. Normalized fluorescence emission spectra of **3-15**. All experiments were performed in CH_2Cl_2 solution at 10^{-6} M and λ_{ex} = 383 nm.

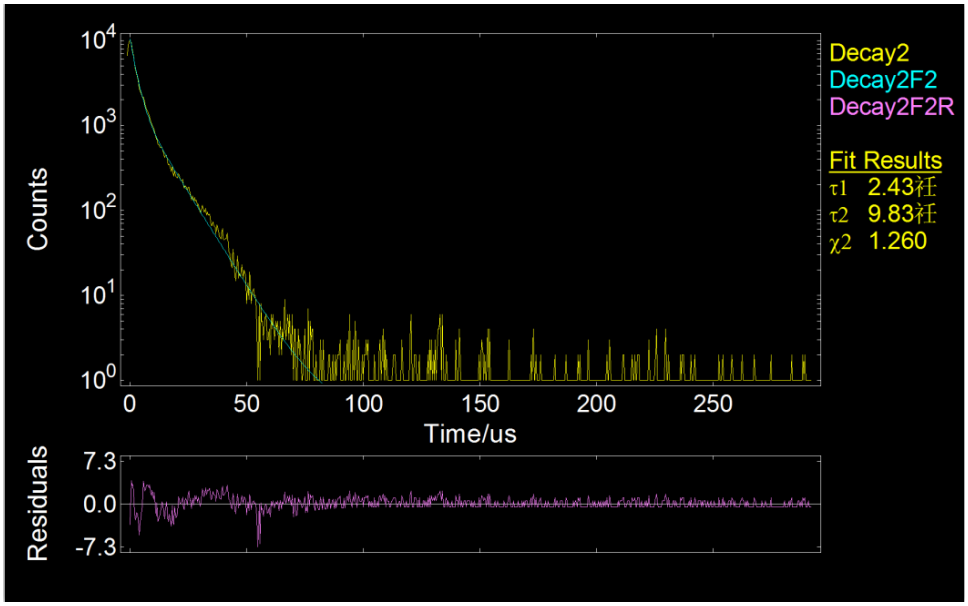


Figure S4. The fluorescence decay of **3** was measured in dichloromethane excited at 383 nm and emission was monitored at 430 nm.

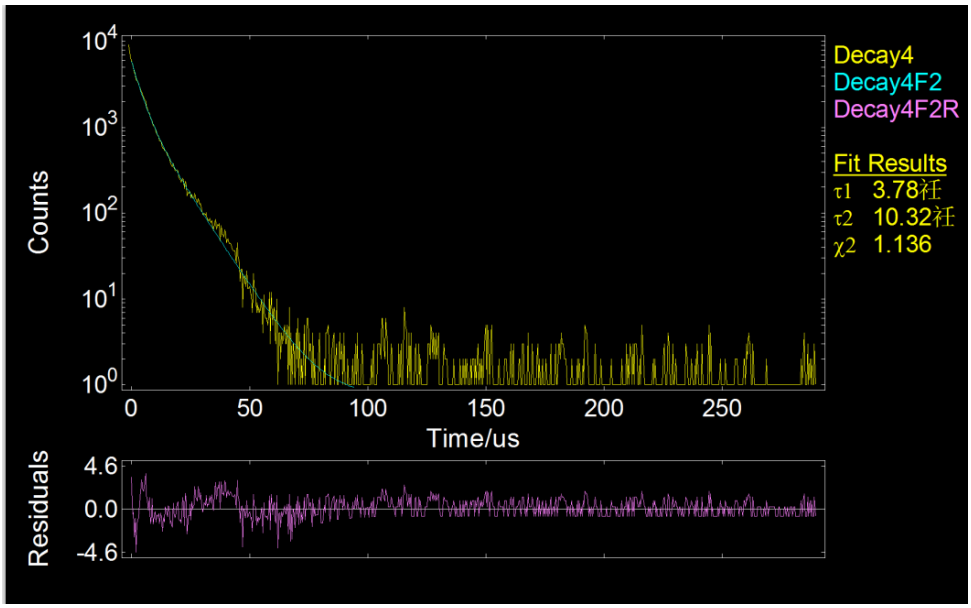


Figure S5. The fluorescence decay of **4** was measured in dichloromethane excited at 384 nm and emission was monitored at 458 nm.

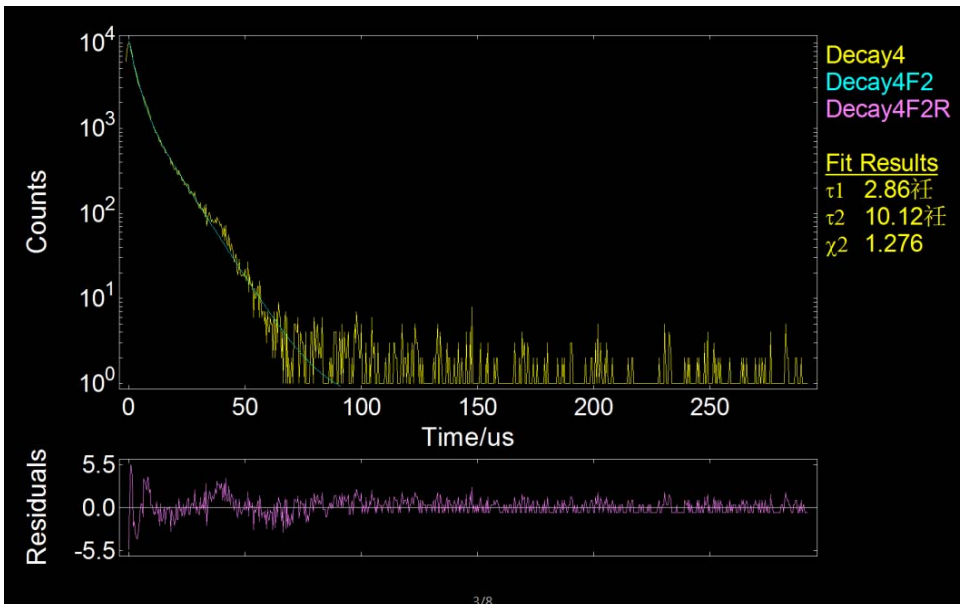


Figure S6. The fluorescence decay of **10** was measured in dichloromethane excited at 391 nm and emission was monitored at 460 nm.

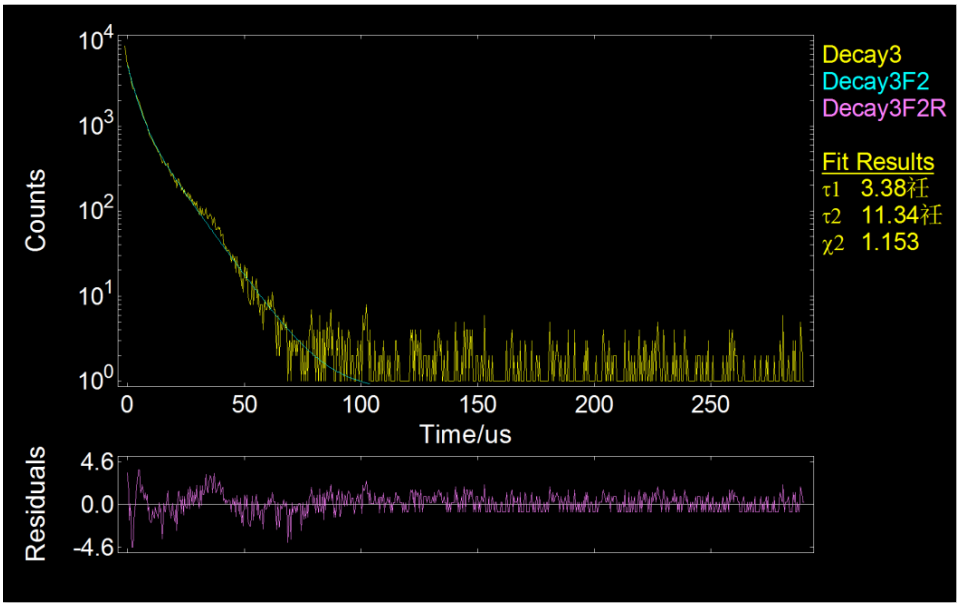


Figure S7. The fluorescence decay of **12** was measured in dichloromethane excited at 394 nm and emission was monitored at 463 nm.

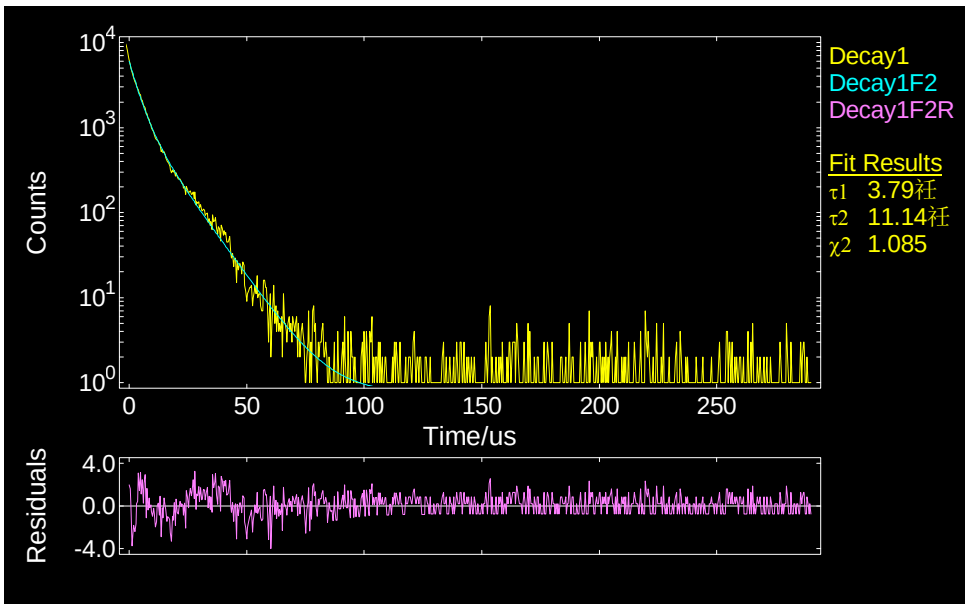


Figure S8. The fluorescence decay of **13** was measured in dichloromethane excited at 396 nm and emission was monitored at 466 nm.

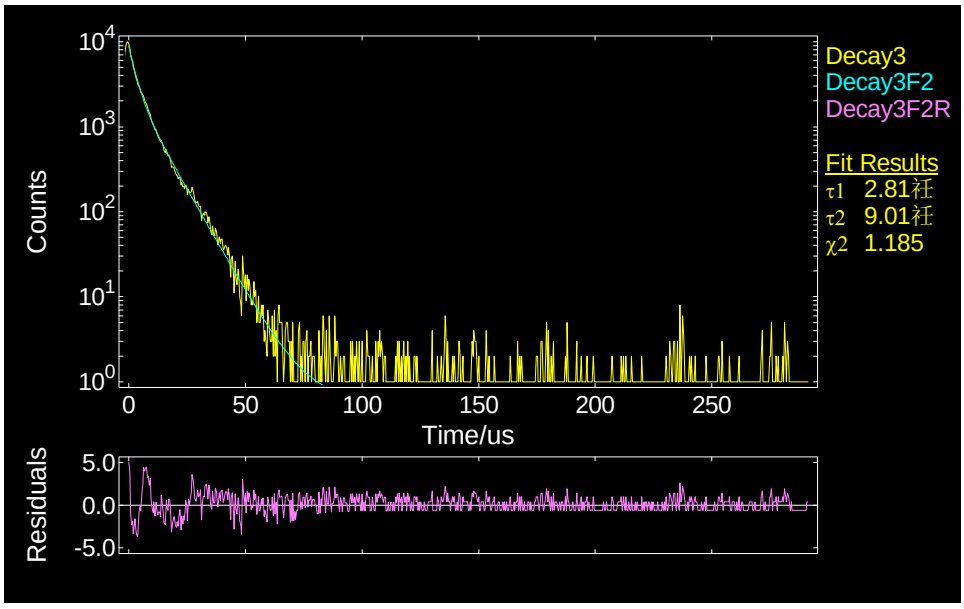


Figure S9. The fluorescence decay of **14** was measured in dichloromethane excited at 392 nm and emission was monitored at 468 nm.

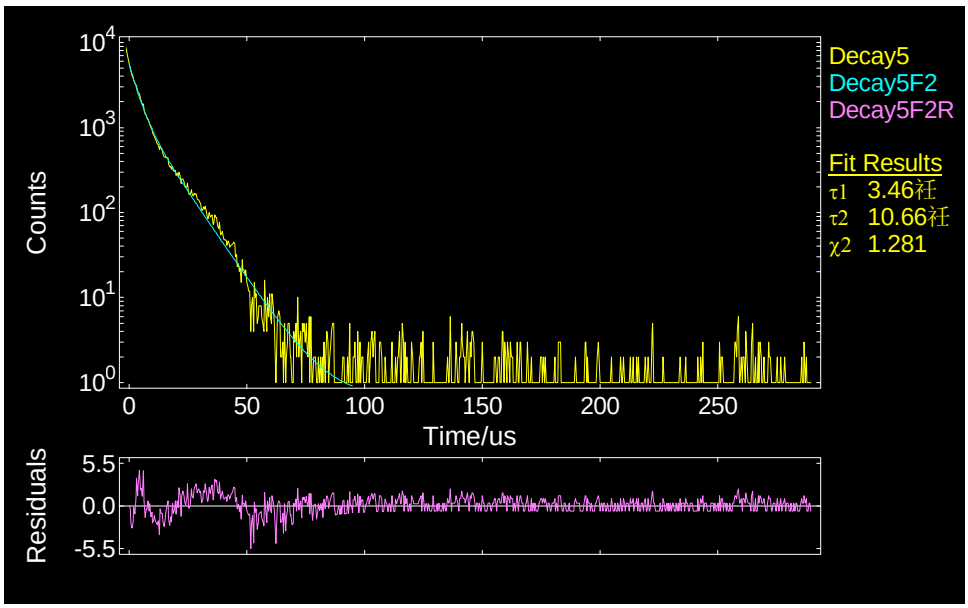


Figure S10. The fluorescence decay of **15** was measured in dichloromethane excited at 390 nm and emission was monitored at 460 nm.

Cyclic Votammetry. All measurements were carried out at room temperature with a conventional three-electrode (glassy carbon electrode as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode) with ferrocene/ferrocenium redox couple (Fc/Fc^{+}) as an internal reference

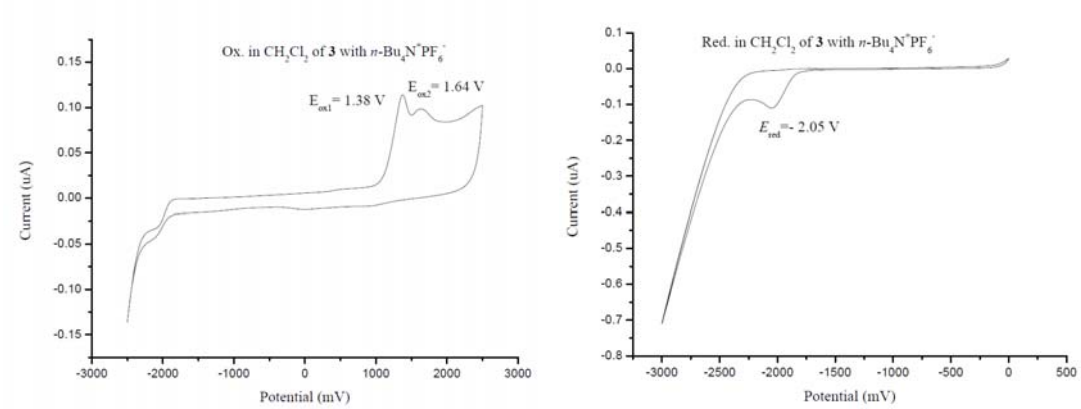


Figure S11. Cyclic voltammograms of 2 mM **3** measured in CH_2Cl_2 solution, containing 0.1 M $TBAPF_6$ as the supporting electrolyte at room temperature. Ferrocene/ferrocenium redox couple (Fc/Fc^{+}) was used as an internal reference and the scan rate at 100 mVs^{-1}.

DFT Calculations. All calculations carried out on **3** and **3′** were performed using the Gaussian 03 suite of programs, revision C. 02.[S3] The structures of **3** and **3′** were optimized at the RB3LYP/6-311+G (d, p) level of theory, using the geometry obtained from X-ray single crystal analysis and verified by harmonic vibrational analysis. TD-DFT calculations were carried out at the RTD-B3LYP/6-311G (d, p)

level of theory.

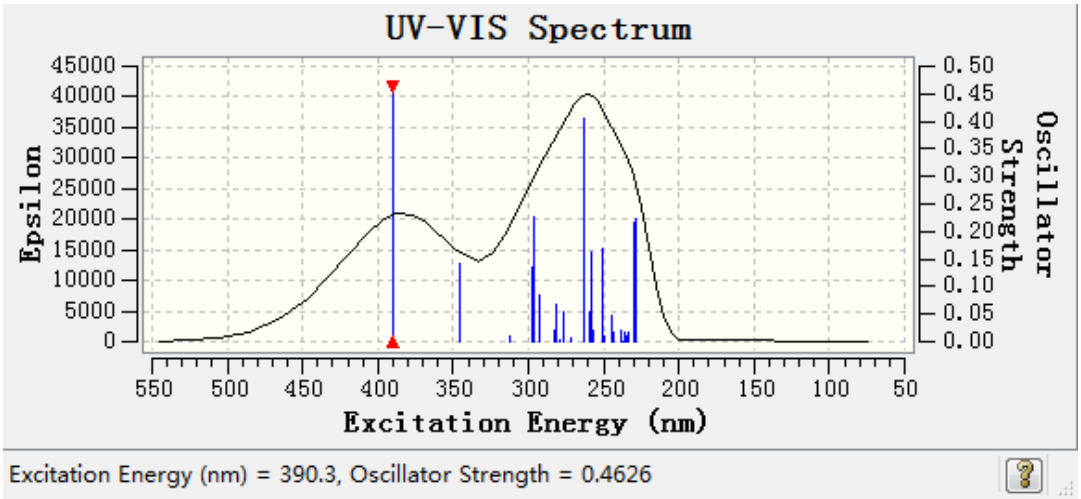


Figure S12.Calculated UV-vis absorption for **3**

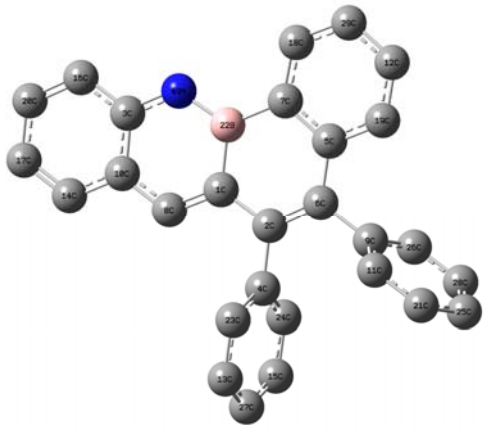


Figure S13. Optimized geometry of **3**. Selected bond parameters: B22-N49 1.42842, B22-C1 1.53054, B22-C7 1.54056, N49-B22-C7 124.722252, N49-B22-C1 116.46935, C1-B22-C7 118.80810.

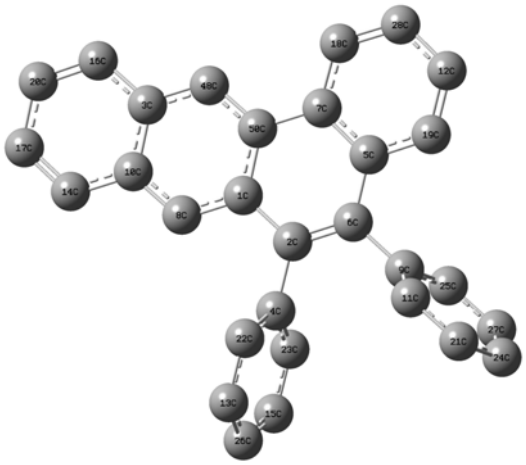


Figure S14. Optimized geometry of **3′**.

Table S3. Cartesian coordinates for reorganization energy

3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.077853	-0.124837	0.018526
2	6	0	-0.355909	-0.394940	-0.015332
3	6	0	3.876868	0.526651	0.115708
4	6	0	-0.798257	-1.834307	-0.050977
5	6	0	-0.871784	2.056403	-0.035896
6	6	0	-1.261515	0.618325	-0.005459
7	6	0	0.491085	2.448935	0.054850
8	6	0	2.027313	-1.108739	0.005895
9	6	0	-2.729787	0.325643	0.026843
10	6	0	3.429606	-0.812075	0.030302
11	6	0	-3.464824	0.182582	-1.142680
12	6	0	-1.522410	4.383098	-0.269712
13	6	0	-0.900053	-3.946389	-1.234159
14	6	0	4.397499	-1.835265	-0.031377
15	6	0	-1.615669	-3.820063	1.055714
16	6	0	5.246587	0.789260	0.165673
17	6	0	5.739424	-1.559900	0.004347
18	6	0	0.791096	3.814477	0.005760
19	6	0	-1.862569	3.043395	-0.198118
20	6	0	6.160671	-0.221764	0.106363
21	6	0	-4.832561	-0.047946	-1.098817
22	5	0	1.550531	1.328478	0.098619
23	6	0	-0.604549	-2.593714	-1.205152
24	6	0	-1.312941	-2.463471	1.071250
25	6	0	-5.466686	-0.166916	0.139759
26	6	0	-3.381476	0.231319	1.251064
27	6	0	-1.401324	-4.563728	-0.087493
28	6	0	-4.746758	-0.033176	1.297207
29	6	0	-0.191095	4.780696	-0.157224
30	1	0	1.747733	-2.017111	-0.019312

31	1	0	-3.026366	0.243748	-1.983734
32	1	0	-2.201759	5.035640	-0.396000
33	1	0	-0.764300	-4.449025	-2.028080
34	1	0	4.113058	-2.737602	-0.100046
35	1	0	-1.969635	-4.235273	1.833874
36	1	0	5.548324	1.687727	0.242270
37	1	0	6.375471	-2.262948	-0.039705
38	1	0	1.695622	4.089348	0.086328
39	1	0	-2.775517	2.786720	-0.259502
40	1	0	7.088586	-0.020079	0.134991
41	1	0	-5.331192	-0.124933	-1.902463
42	1	0	-0.263225	-2.174058	-1.987241
43	1	0	-1.462729	-1.959218	1.862271
44	1	0	-6.399707	-0.342032	0.178251
45	1	0	-2.894380	0.347275	2.057776
46	1	0	-1.595066	-5.494194	-0.092166
47	1	0	-5.182762	-0.121695	2.137339
48	1	0	0.041341	5.701378	-0.192175
49	7	0	2.948504	1.558444	0.156399
50	1	0	3.357313	2.453509	-0.021746

Table S4. Cartesian coordinates for reorganization energy

3’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.084914	-0.121180	0.019076
2	6	0	-0.348145	-0.394946	-0.015094
3	6	0	3.882235	0.537453	0.116884
4	6	0	-0.786802	-1.835435	-0.051034
5	6	0	-0.870287	2.055071	-0.035395
6	6	0	-1.256343	0.615997	-0.005243
7	6	0	0.491555	2.451076	0.055668
8	6	0	2.036891	-1.102648	0.006479
9	6	0	-2.723868	0.319554	0.026737
10	6	0	3.438416	-0.802400	0.031196
11	6	0	-3.458315	0.174785	-1.142946

12	6	0	-1.526821	4.380129	-0.268991
13	6	0	-0.882970	-3.947596	-1.234547
14	6	0	4.408935	-1.823102	-0.030451
15	6	0	-1.599340	-3.823440	1.055209
16	6	0	5.251268	0.803559	0.167147
17	6	0	5.750144	-1.544309	0.005569
18	6	0	0.788080	3.817389	0.006836
19	6	0	-1.863564	3.039550	-0.197658
20	6	0	6.167946	-0.205114	0.107861
21	6	0	-4.825467	-0.059248	-1.099375
22	6	0	-0.590934	-2.594173	-1.205285
23	6	0	-1.300087	-2.466080	1.071003
24	6	0	-5.459519	-0.180023	0.139063
25	6	0	-3.375545	0.223382	1.250821
26	6	0	-1.382876	-4.566385	-0.088067
27	6	0	-4.740154	-0.044612	1.296667
28	6	0	-0.196549	4.781116	-0.156192
29	1	0	1.759640	-2.011729	-0.018914
30	1	0	-3.019857	0.237198	-1.983907
31	1	0	-2.207813	5.030949	-0.395311
32	1	0	-0.745781	-4.449765	-2.028516
33	1	0	4.126817	-2.726153	-0.099306
34	1	0	-1.952389	-4.239669	1.833241
35	1	0	5.550690	1.702783	0.243934
36	1	0	6.387996	-2.245721	-0.038467
37	1	0	1.691885	4.094562	0.087615
38	1	0	-2.775841	2.780548	-0.259253
39	1	0	7.095337	-0.001060	0.136694
40	1	0	-5.323746	-0.137391	-1.903127
41	1	0	-0.250537	-2.173530	-1.987247
42	1	0	-1.451314	-1.962329	1.862070
43	1	0	-6.392095	-0.357532	0.177352
44	1	0	-2.888899	0.340464	2.057643
45	1	0	-1.574236	-5.497342	-0.092913
46	1	0	-5.176089	-0.134370	2.136704
47	1	0	0.033537	5.702395	-0.190963
48	6	0	2.951226	1.566861	0.157551
49	1	0	3.405418	2.516335	-0.035085

50	6	0	1.553856	1.333328	0.099472

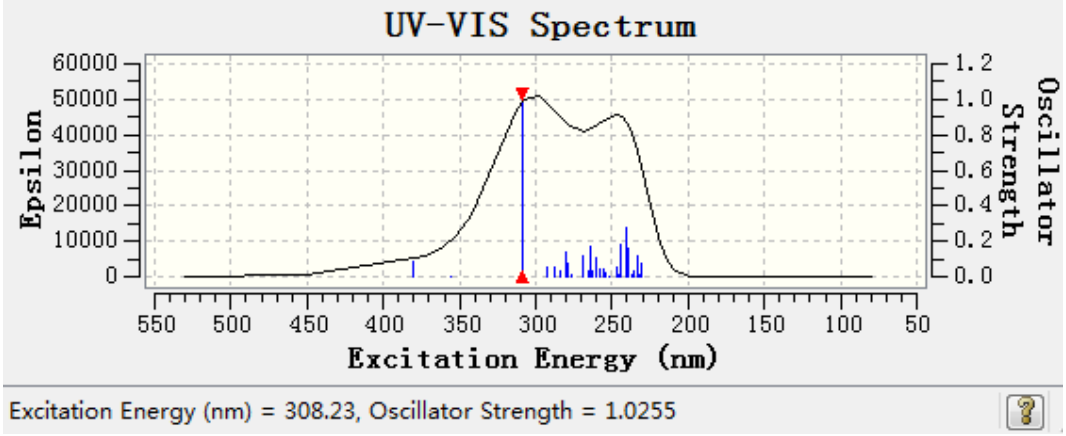
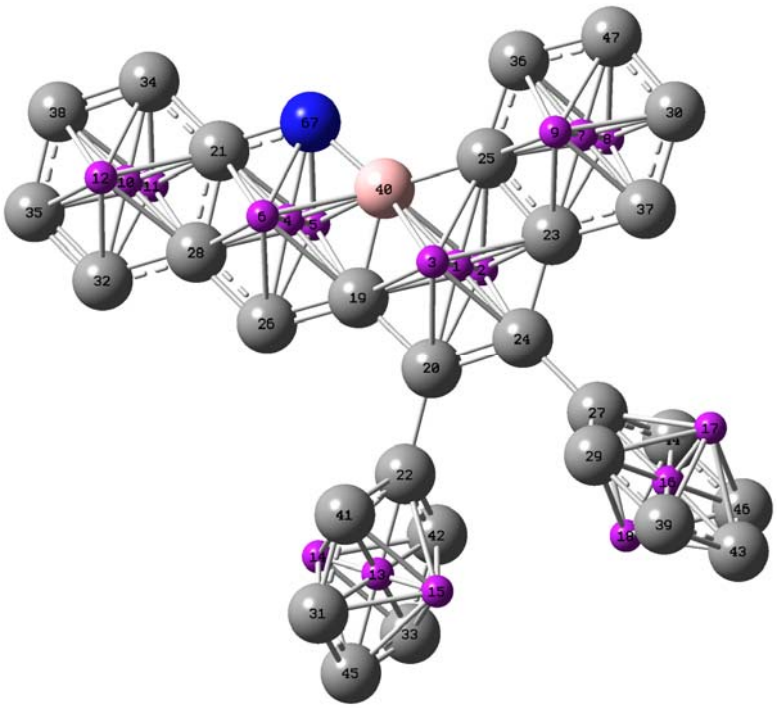
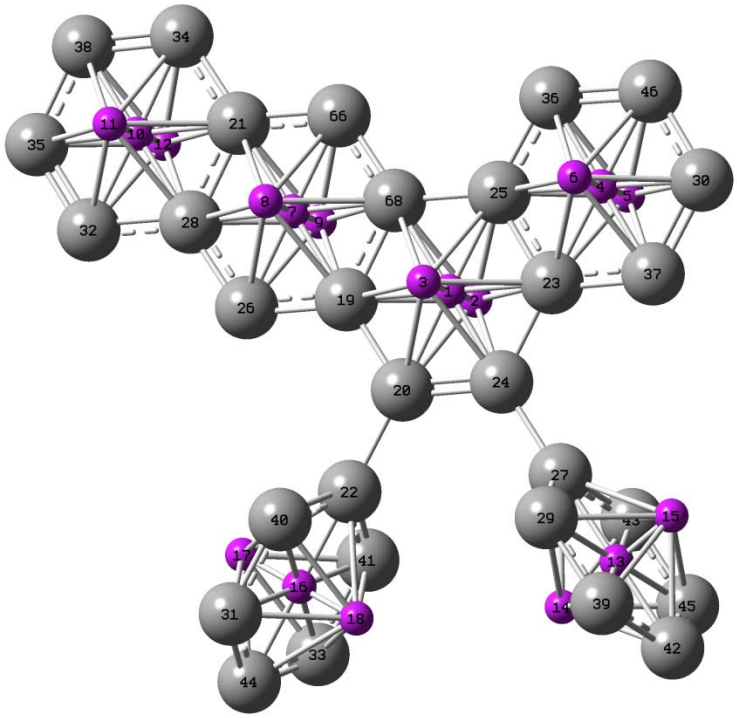


Figure S15.Calculated UV-vis absorption for **3′**



3 Bq Isotropic = 2.6456, NICS(1) = -2.6456. **6** Bq Isotropic = 7.2765, NICS(1) = -7.2765, **9** Bq Isotropic = 10.0142, NICS(1) = -10.0142, **12** Bq Isotropic = 10.4429, NICS(1) = -10.4429, **15** Bq Isotropic = 10.0811, NICS(1) = -10.0811**, 17** Bq Isotropic = 9.1955, NICS(1) = -9.1955.



2 Bq Isotropic = 5.3250, NICS(1) = -5.3250, **5** Bq Isotropic = 9.8588,NICS(1) = -9.8588, **9** Bq Isotropic = 11.9530, NICS(1) = -11.9530, **12** Bq Isotropic = 10.1199, NICS(1) = -10.1199, **15** Bq Isotropic = 9.2058, NICS(1) = -9.2058, **18** Bq Isotropic = 10.0280, NICS(1) = -10.0280.

Figure S16. NICS(1)zz values (in ppm) of **3** (up) and **3'** (down) calculated at the GIAO-B3LYP16-311+G(d.p) level.

Reference

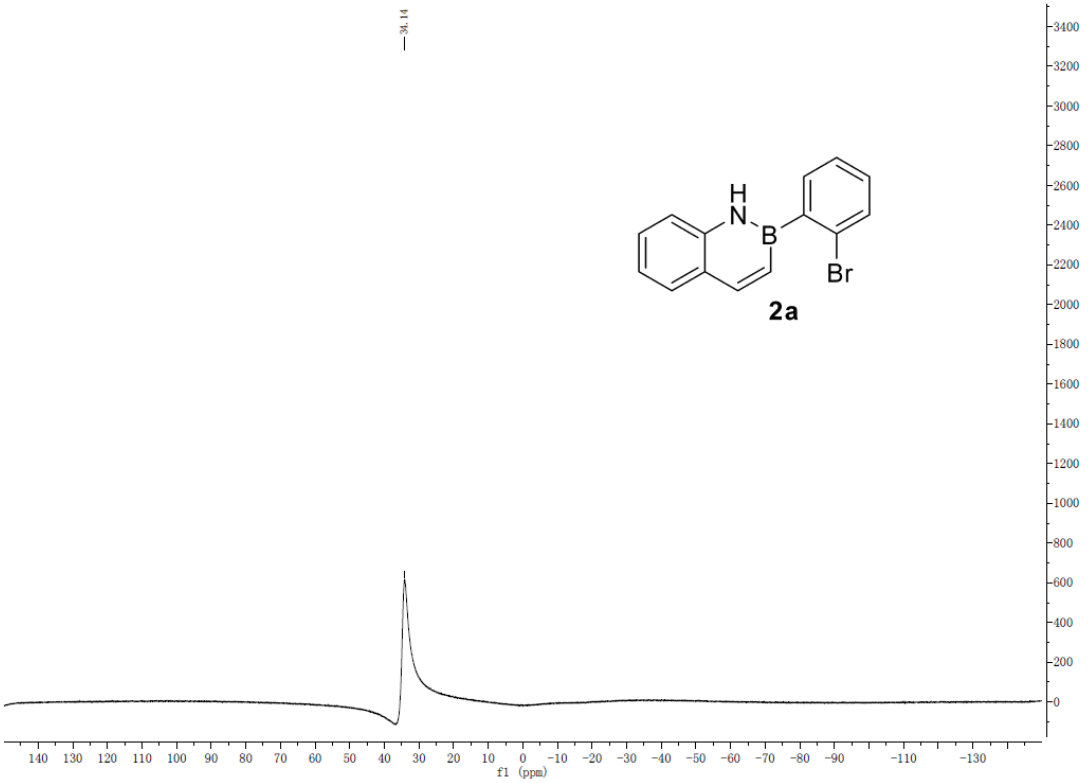
S1 S. R. Wisniewski, C. L. Guenther, O. A. Argintaru, G. A. Molander. *J. Org. Chem*. **2014**, *79*, 365.

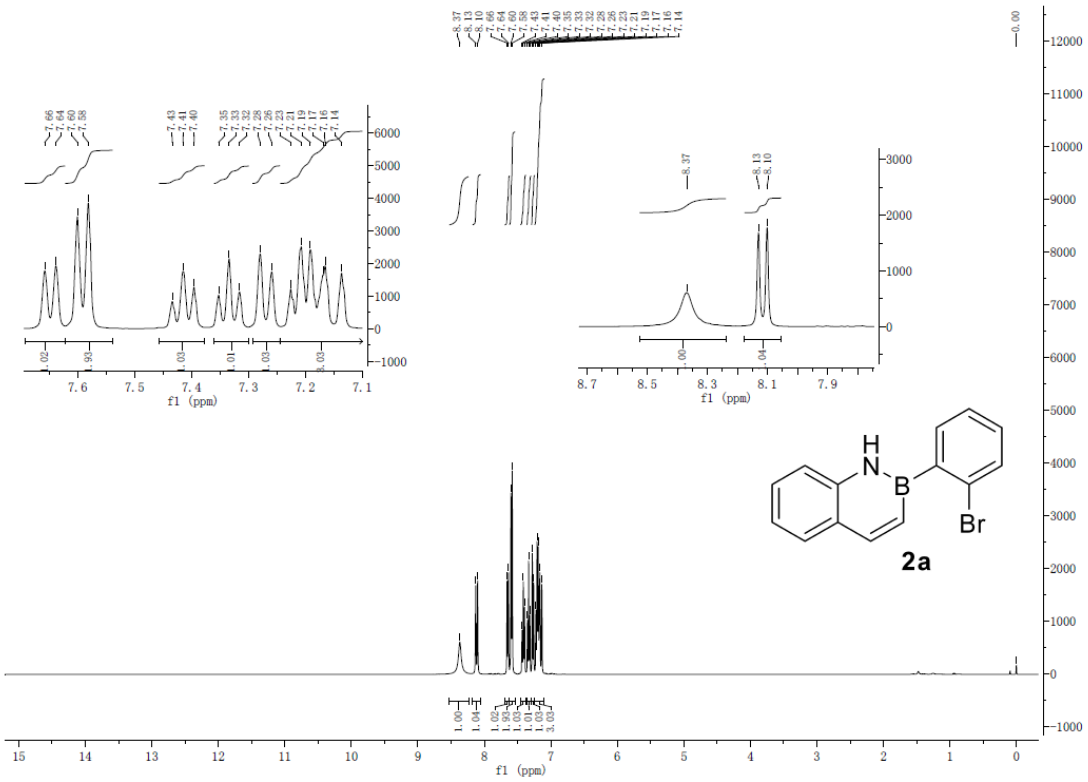
S2 G. M. Sheldrick. SHELXS-90/96, Program for Structure Solution, *Acta. Crystallogr. Sect. A* **1990**, *46*, 467.

S3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y.

Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian* 03, *Revision* C.02, Gaussian, Inc., Wallingford CT, **2004**.

Scanned NMR Spectra of All New Compounds

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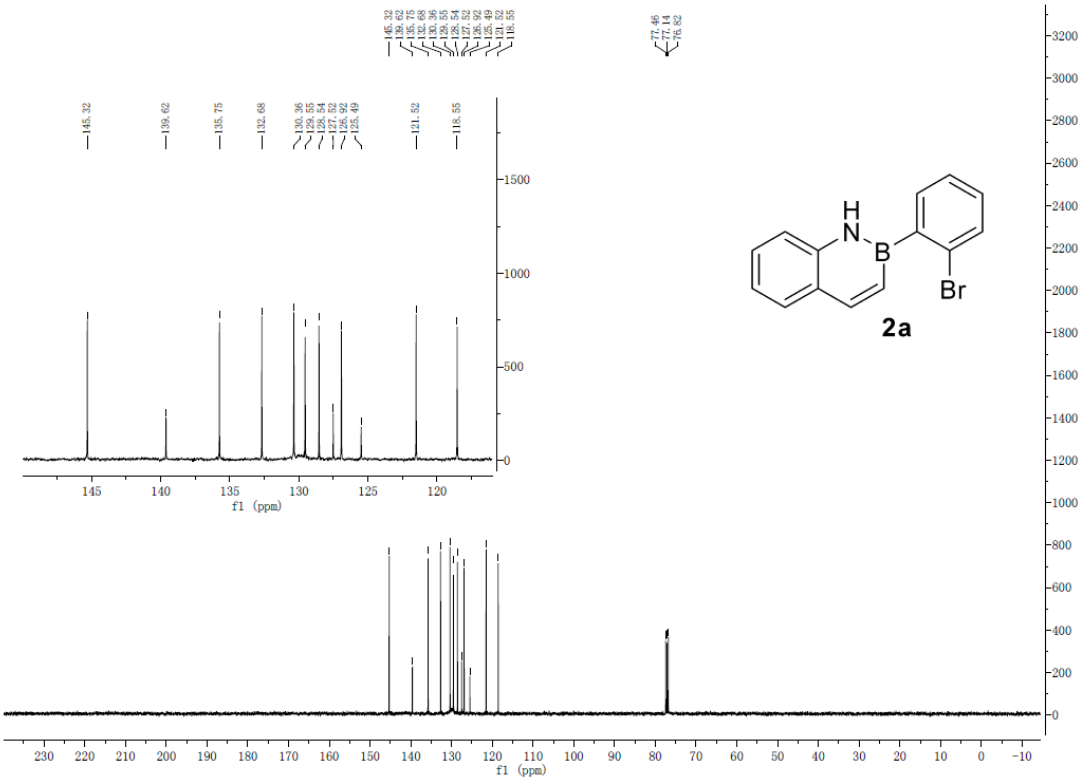
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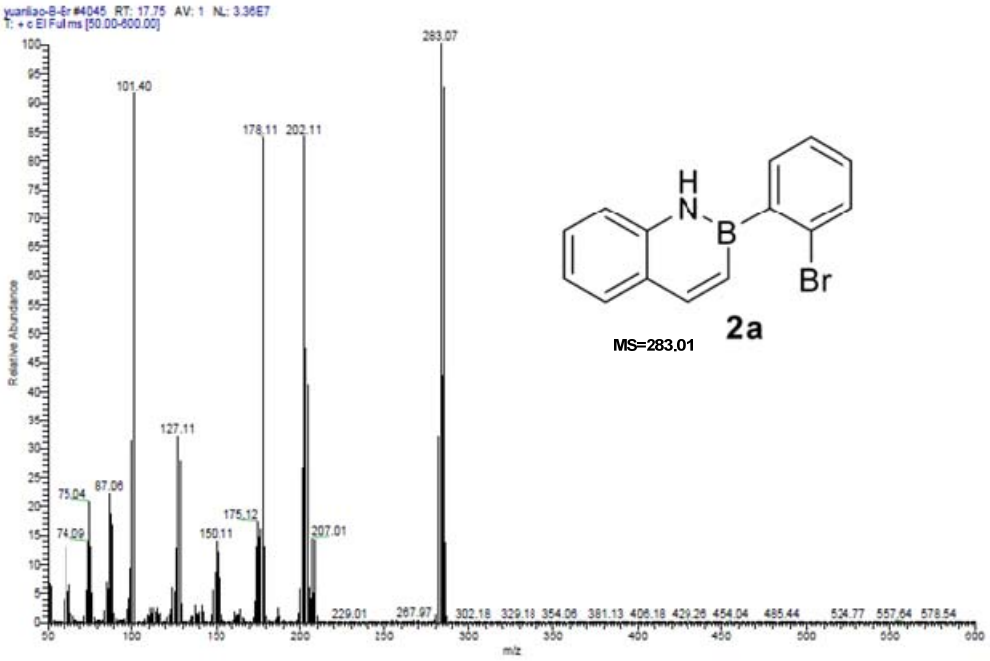
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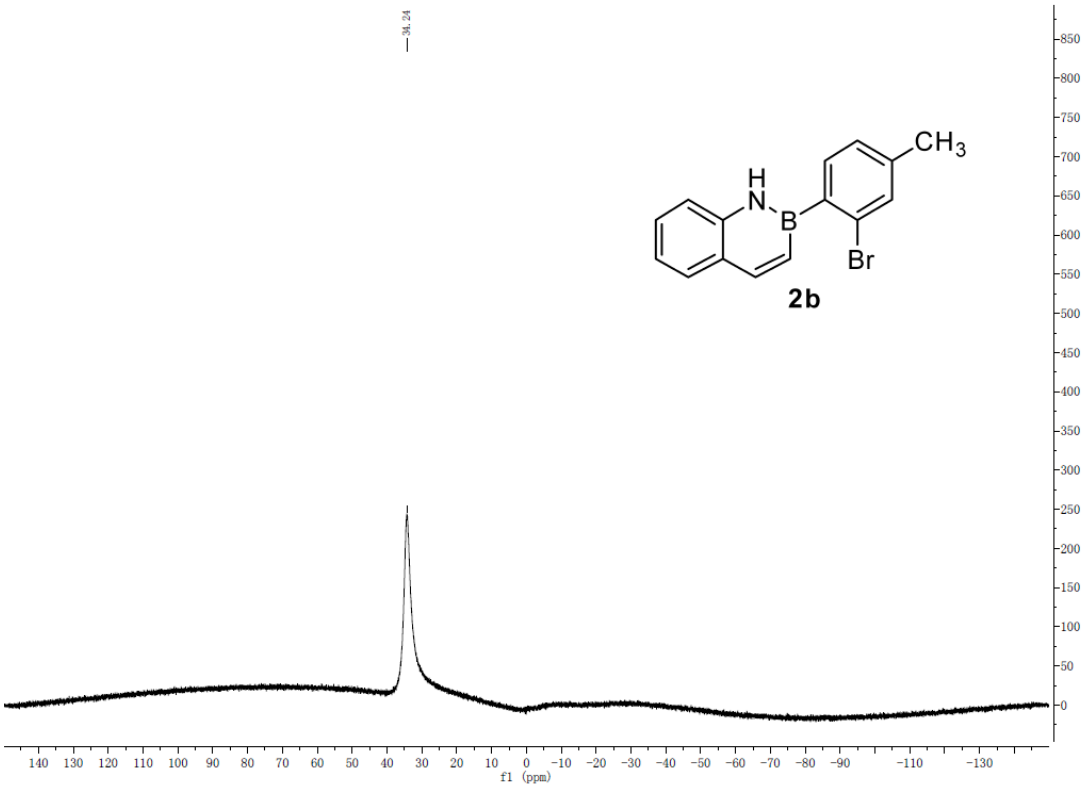
178.11
202.11
127.11
75.04
87.06
74.09
175.12
150.11
207.01
229.01
267.97
302.18
329.18
354.06
381.13
406.18
429.26
454.04
485.44
524.77
557.64
578.54
Relative Abundance
m/z
H
N
B
Br
2a
MS=283.01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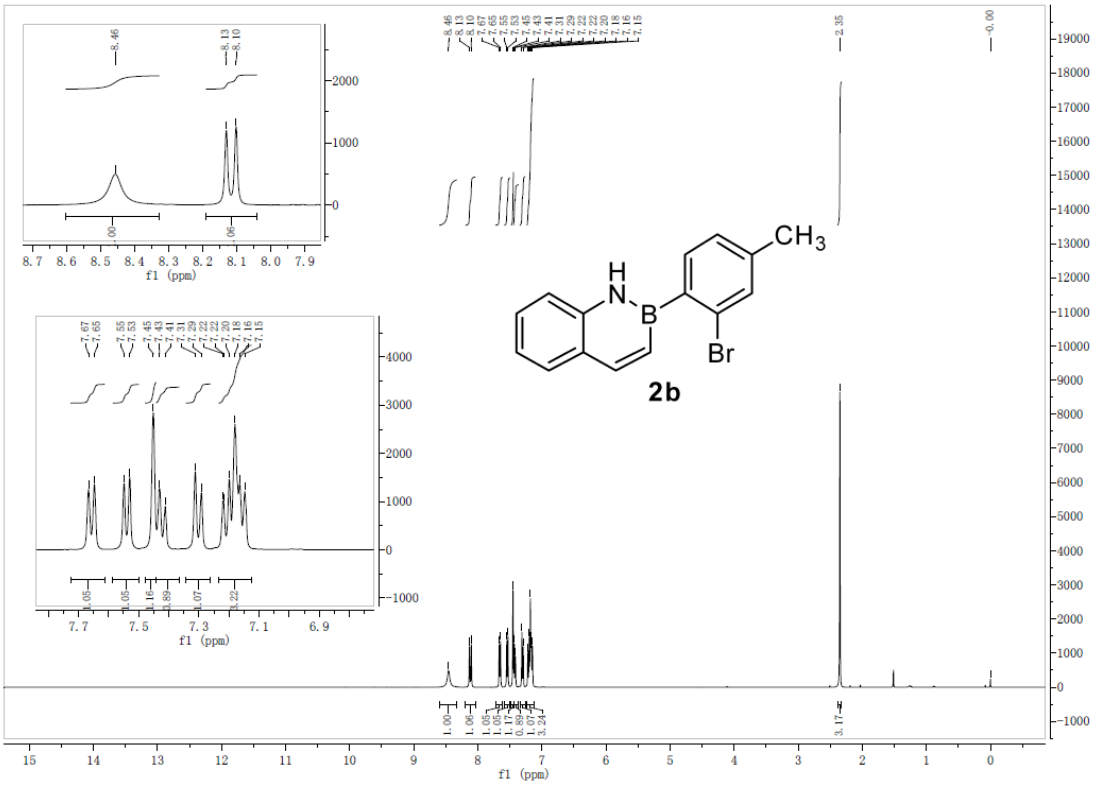
CH3
H
N
B
Br
2b
f1 (ppm)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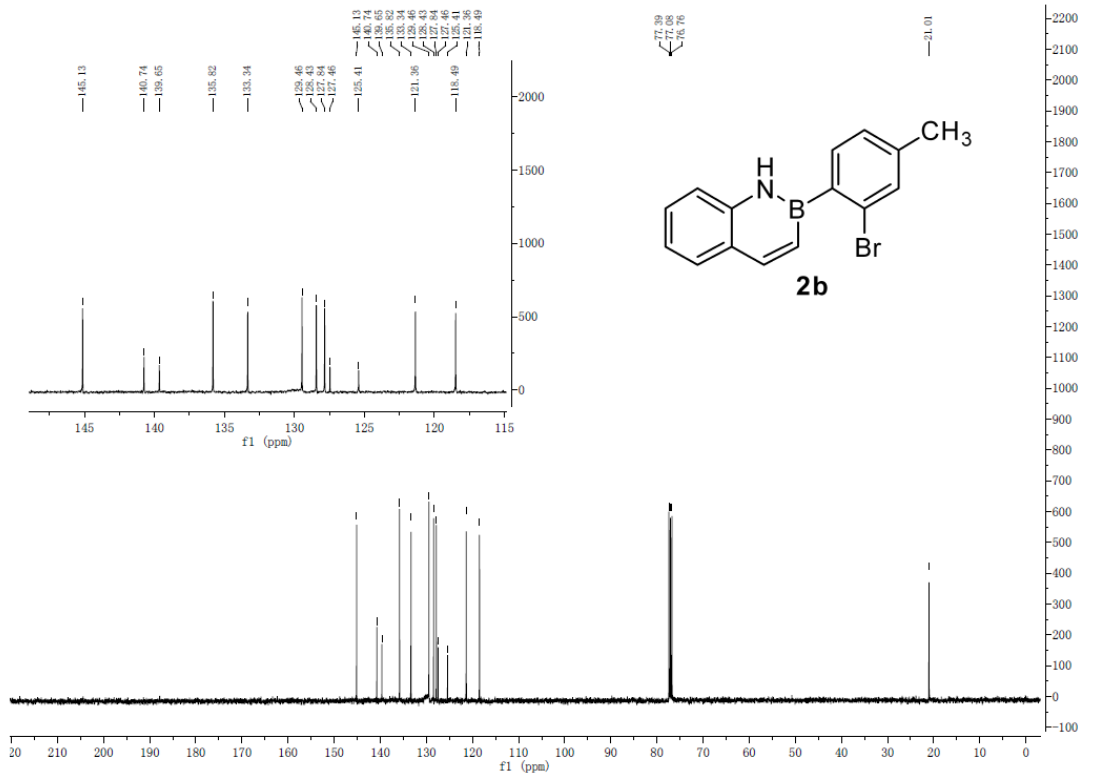
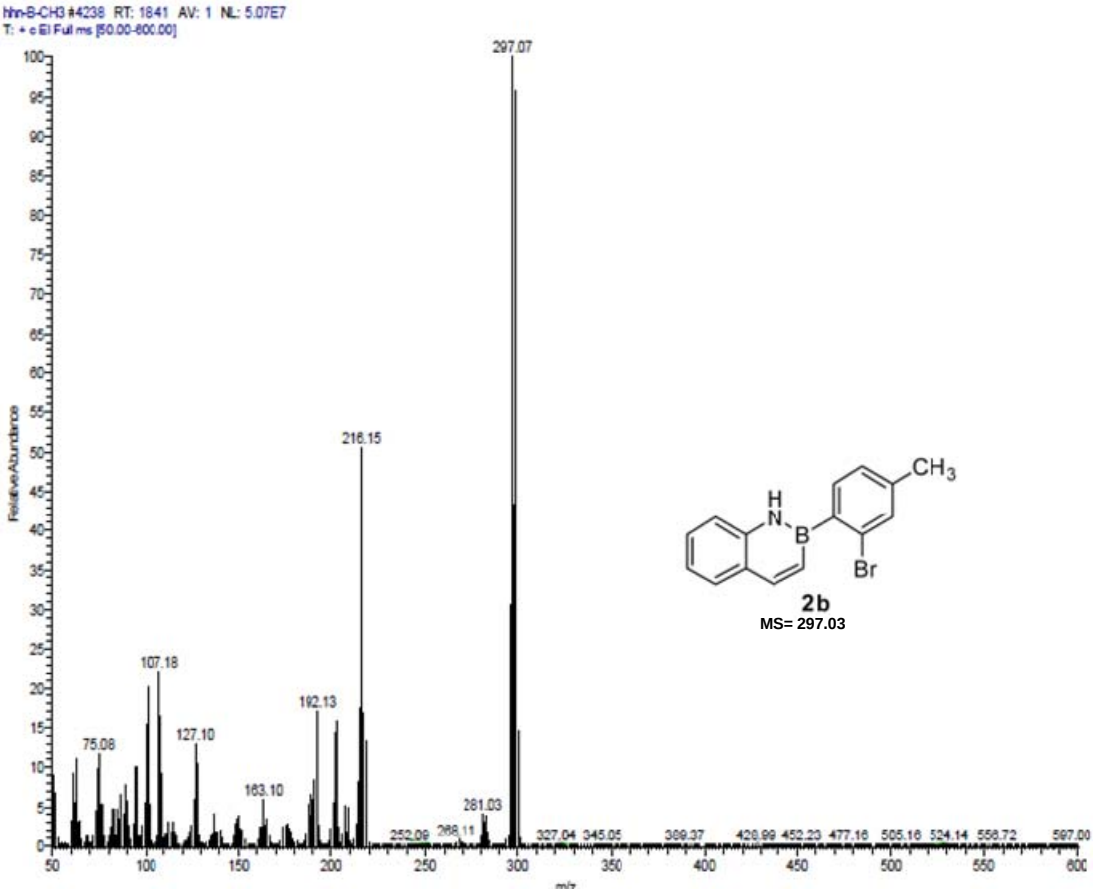
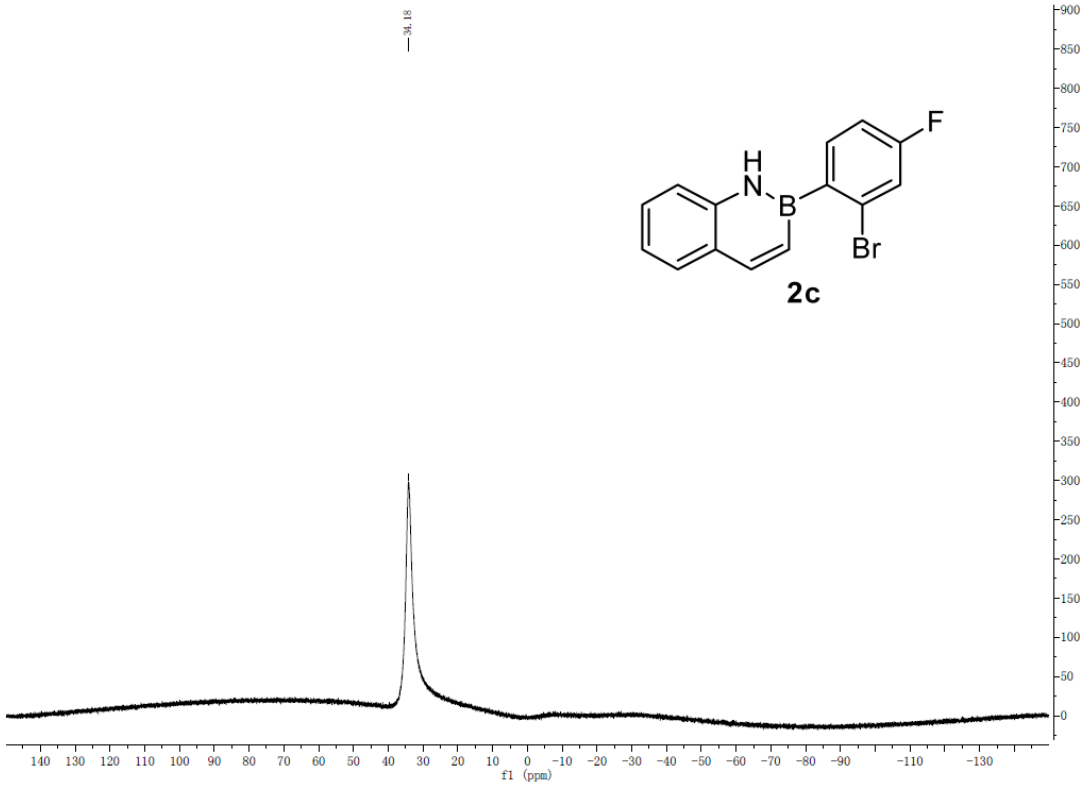
8.13
8.10
7.67
7.65
7.55
7.53
7.45
7.43
7.41
7.31
7.29
7.22
7.20
7.18
7.16
7.15
2.35
-0.00
f1 (ppm)
CH3
H
N
B
Br
2b


145.13
140.74
139.65
135.82
133.34
129.46
128.43
127.84
127.46
125.41
121.36
118.49
77.39
77.08
76.76
21.01
f1 (ppm)
CH3
H
N
B
Br
2b

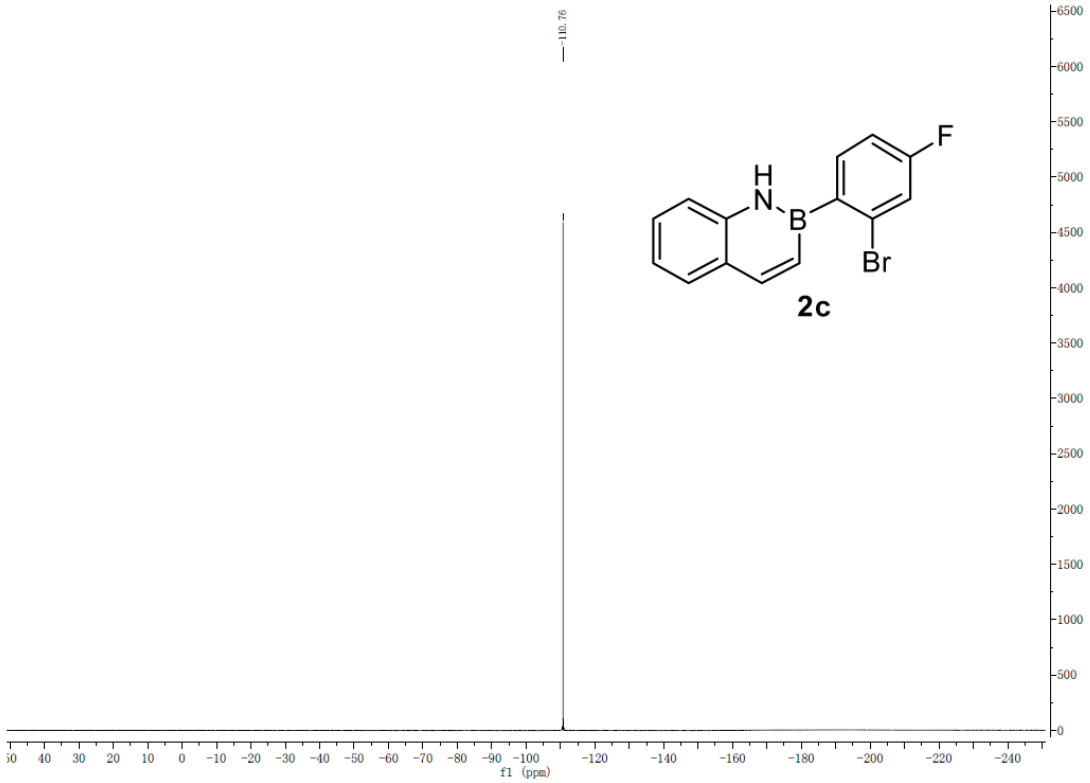


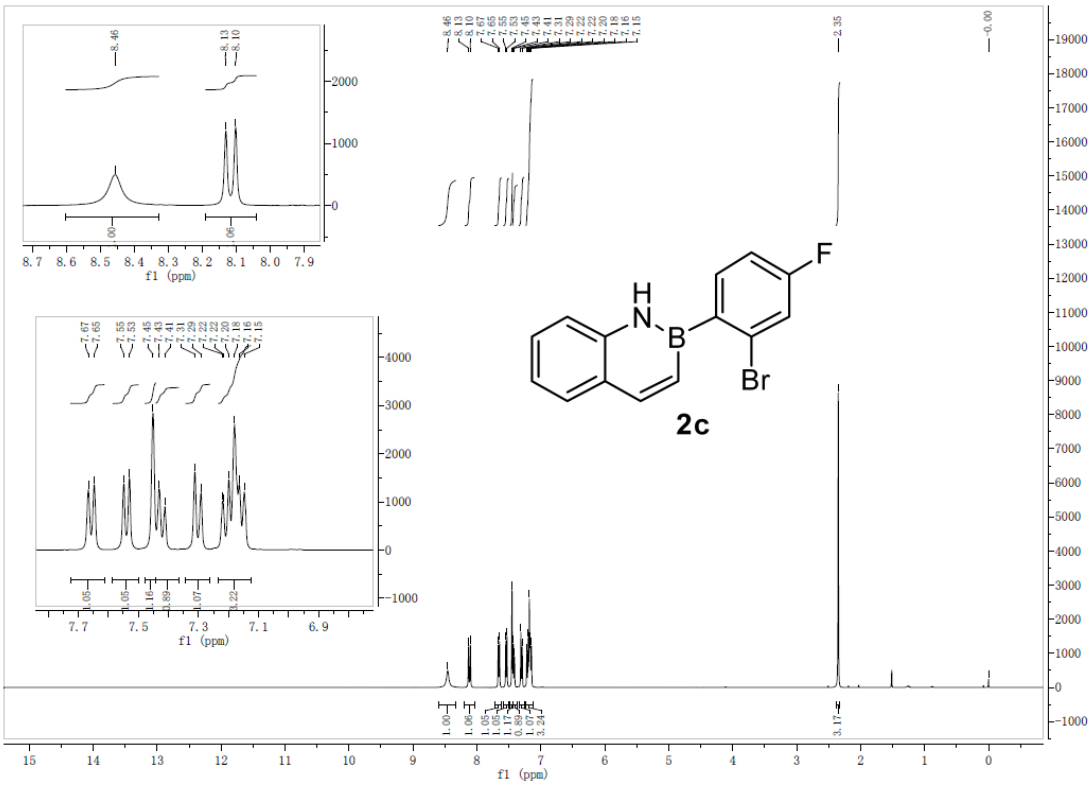
2b

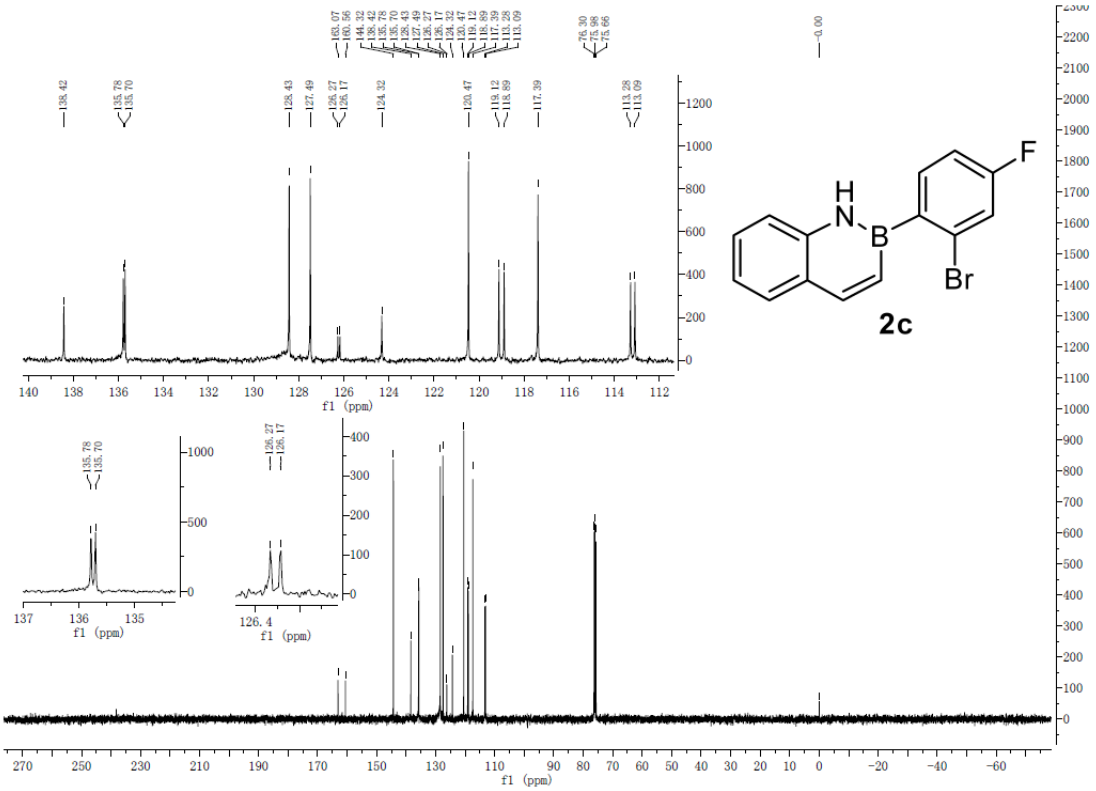
MS= 297.03

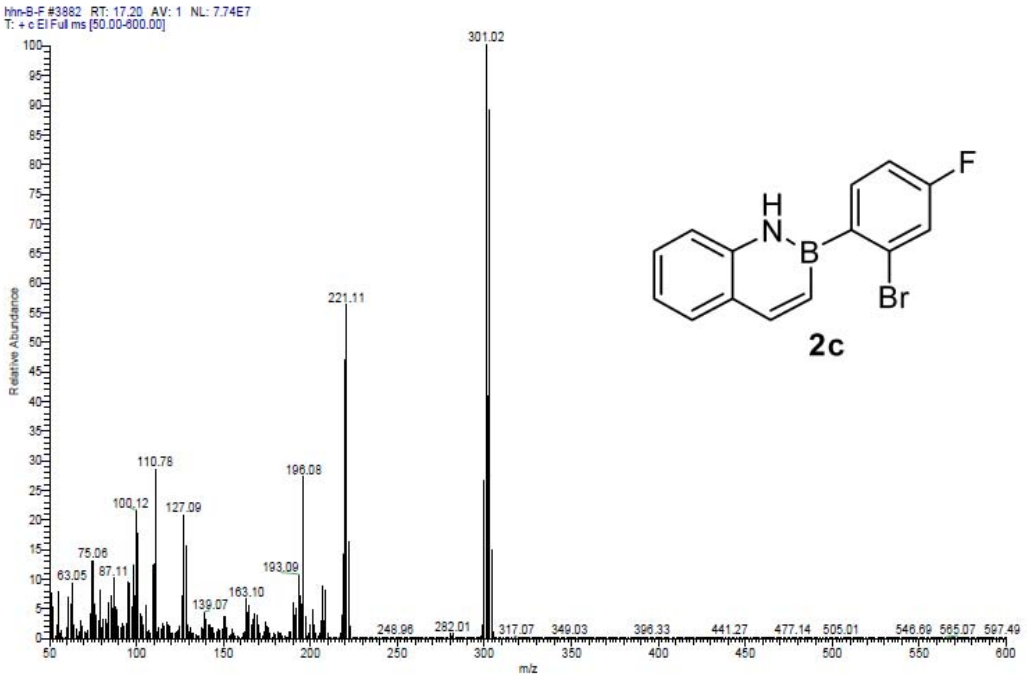


2c


-110.76
F
H
N
B
Br
2c
f1 (ppm)


8.46
8.13
8.10
2.35
-0.00
F
H
N
B
Br
2c
f1 (ppm)


F
H
N
B
Br
2c
f1 (ppm)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T: + c EI Full ms [50.00-600.00]
Relative Abundance
m/z
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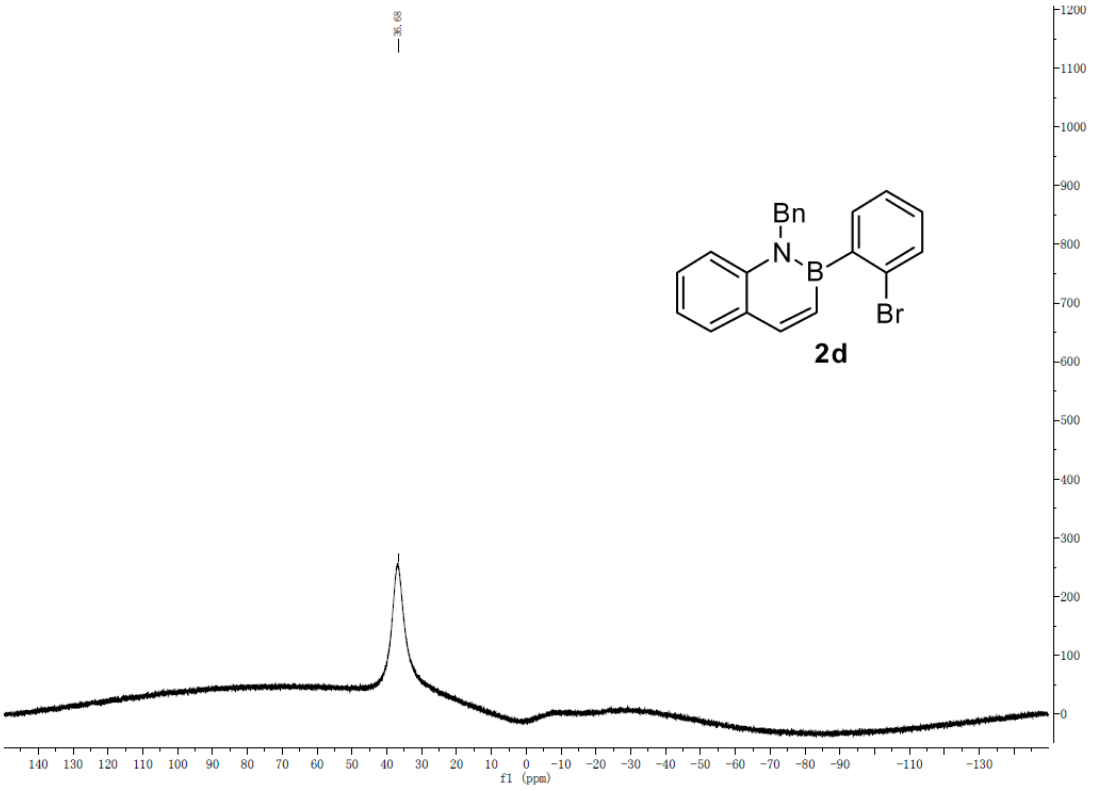
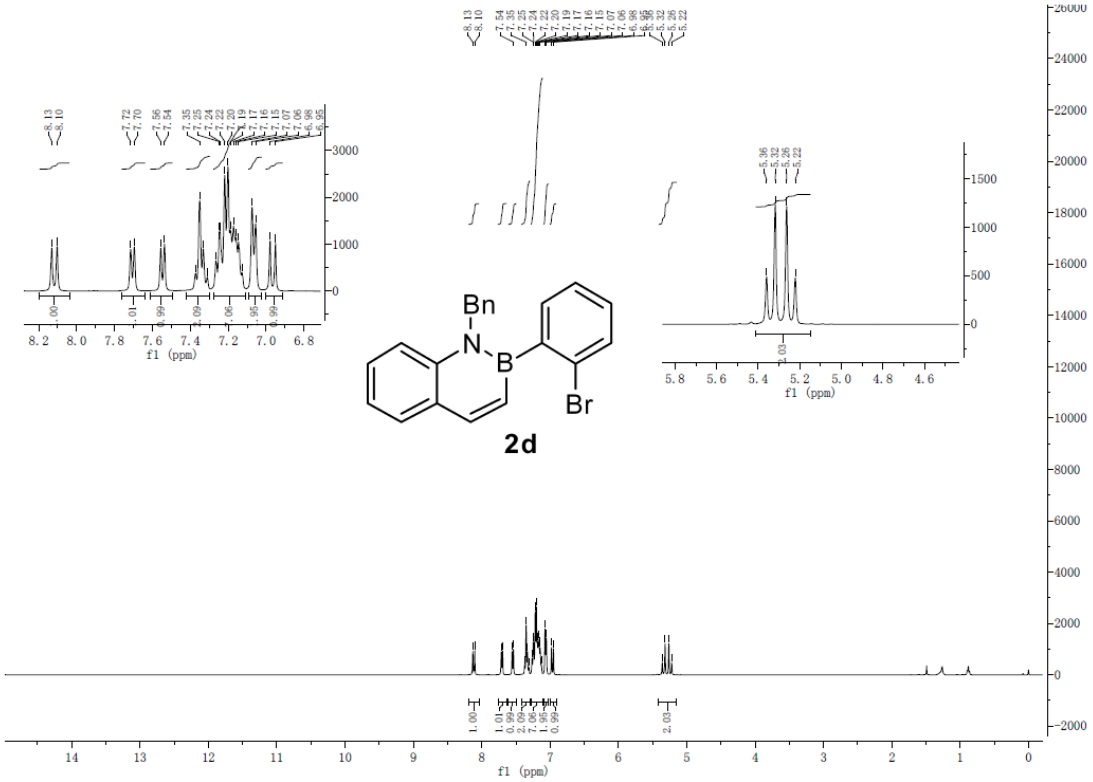
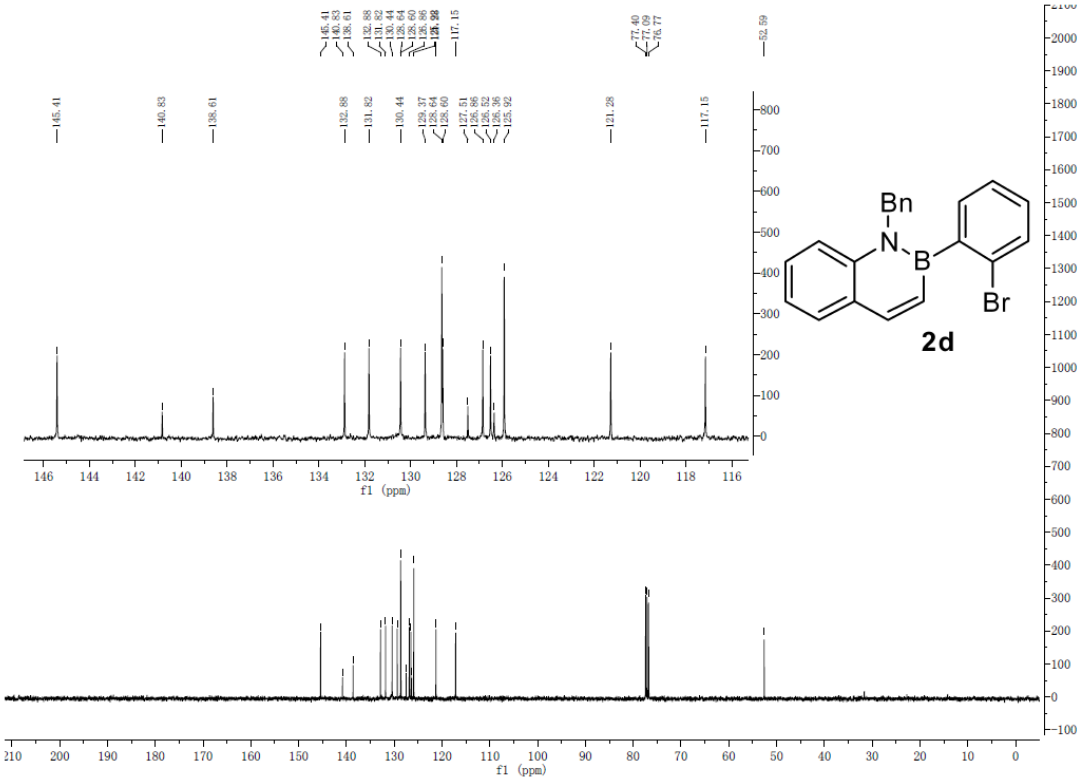
221.11
110.78
196.08
100.12
127.09
75.06
63.05
87.11
193.09
163.10
139.07
F
H
N
B
Br
2c


36.68
Bn
N
B
Br
2d
f1 (ppm)


Bn
N
B
Br
2d
f1 (ppm)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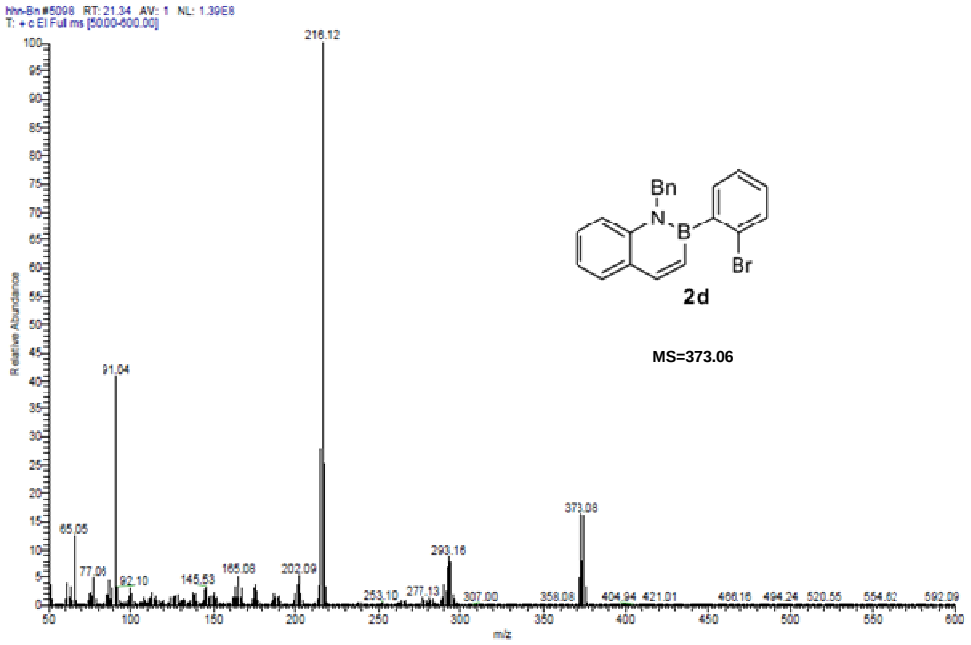
138.61
132.88
131.82
130.44
129.37
128.64
128.60
127.51
126.86
126.52
126.36
125.92
121.28
117.15
77.40
77.09
76.77
52.59
Bn
N
B
Br
2d
f1 (ppm)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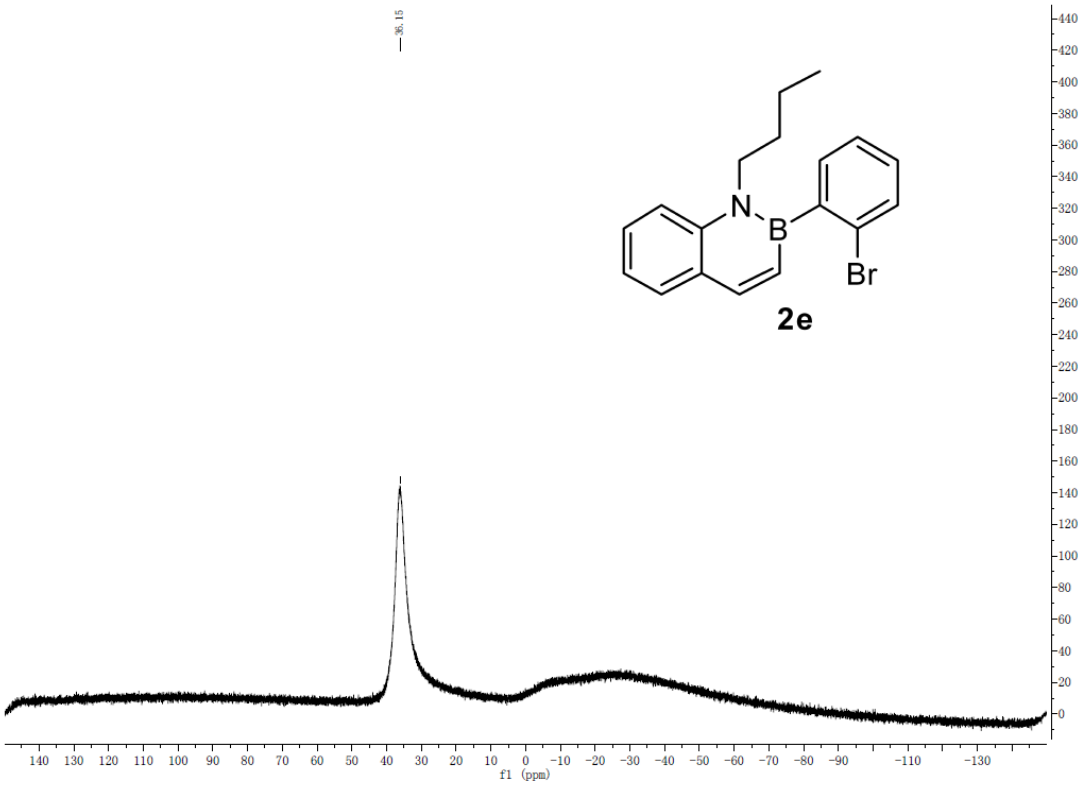
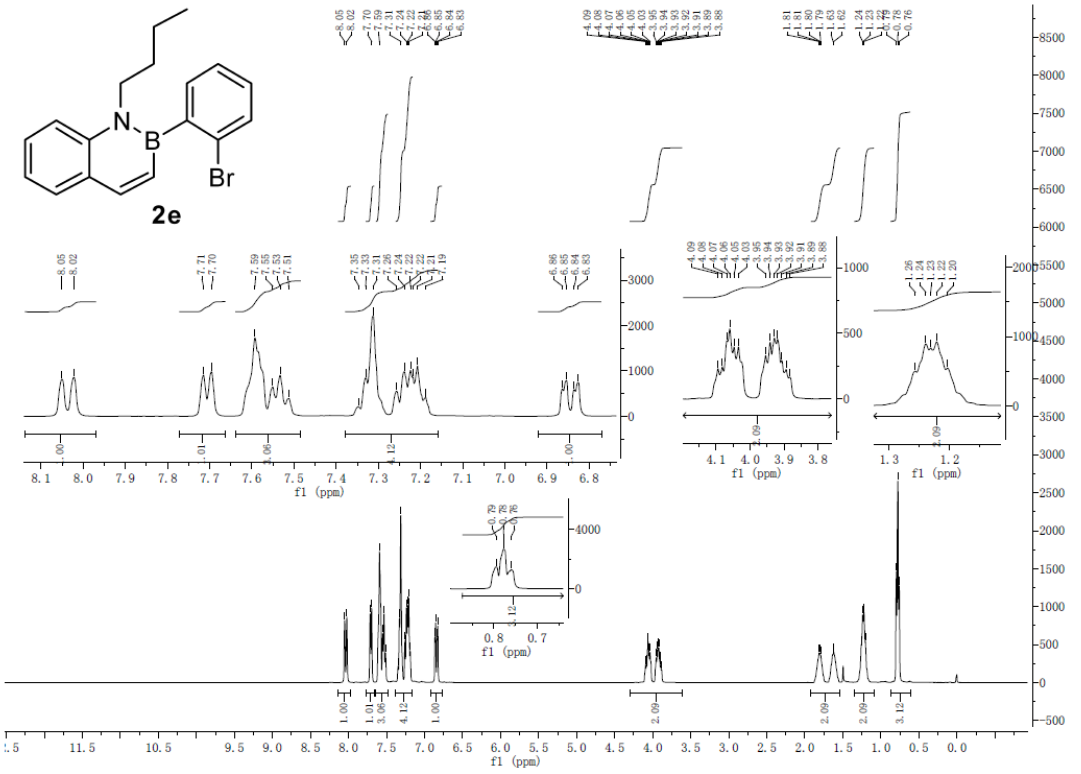
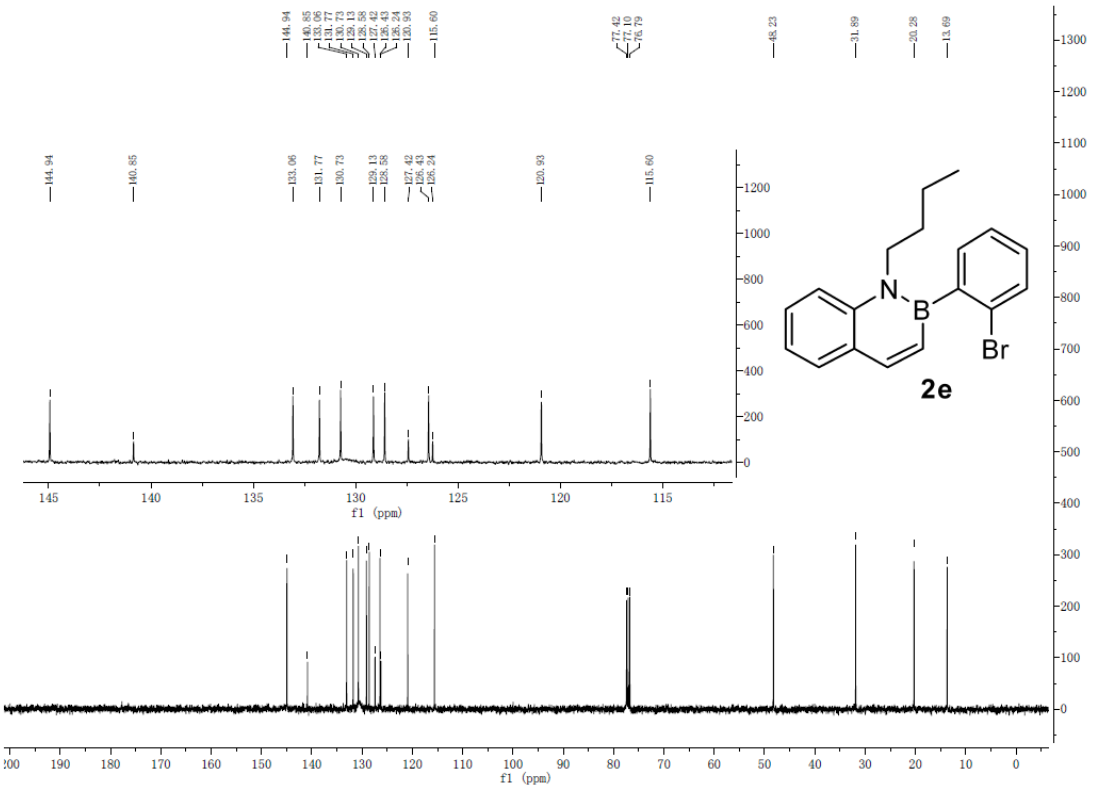
91.04
65.05
77.06
92.10
145.53
165.09
202.09
253.10
277.13
293.16
307.00
358.08
373.08
404.94
421.01
466.16
494.24
520.55
554.62
592.09
Relative Abundance
m/z
Bn
N
B
Br
2d
MS=373.06


36.15
N
B
Br
2e
f1 (ppm)


N
B
Br
2e
f1 (ppm)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126.24
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77.16
76.79
48.23
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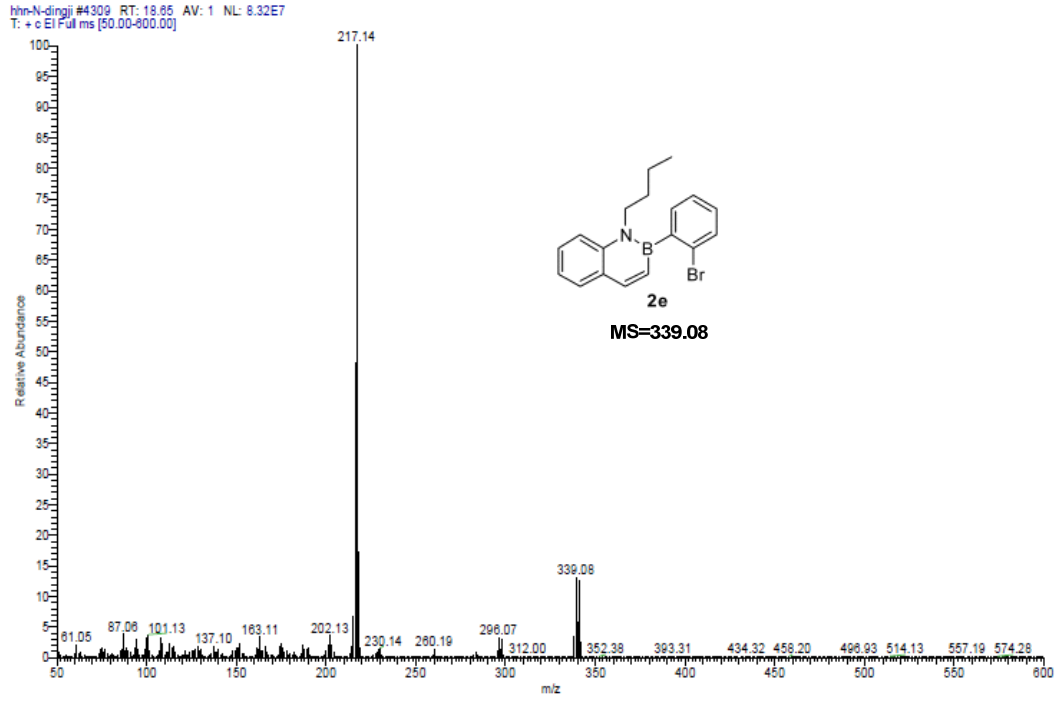
20.28
13.69
f1 (ppm)
N
B
Br
2e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T: + c EI Full ms [50.00-600.00]
Relative Abundance
m/z
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339.08
61.05
87.06
101.13
137.10
163.11
202.13
230.14
260.19
296.07
312.00
352.38
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458.20
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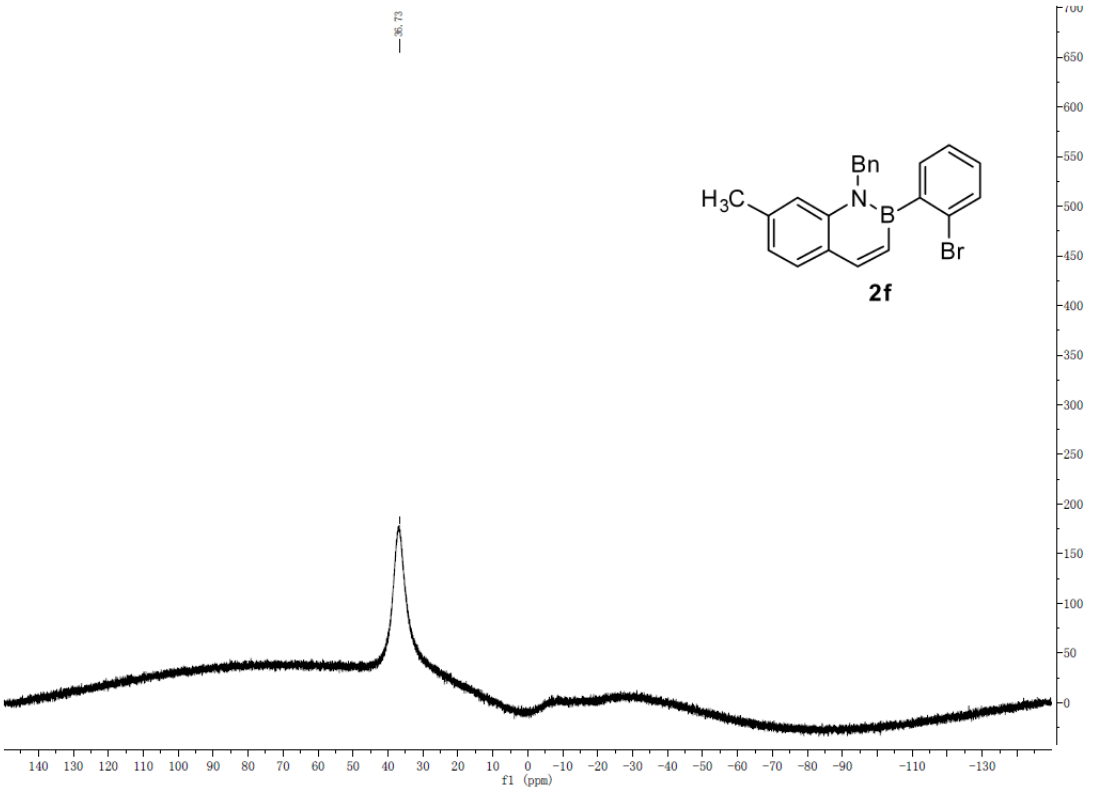
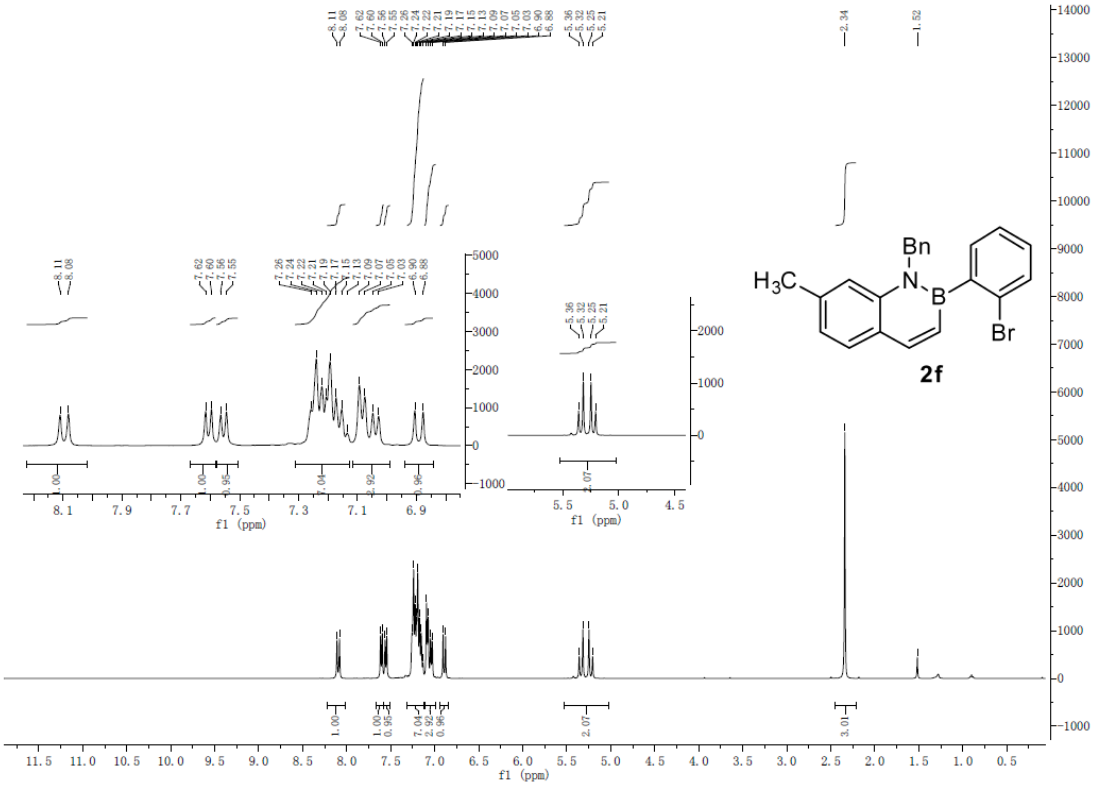
557.19
574.28
N
B
Br
2e
MS=339.08


36.73
Bn
N
B
H3C
Br
2f
f1 (ppm)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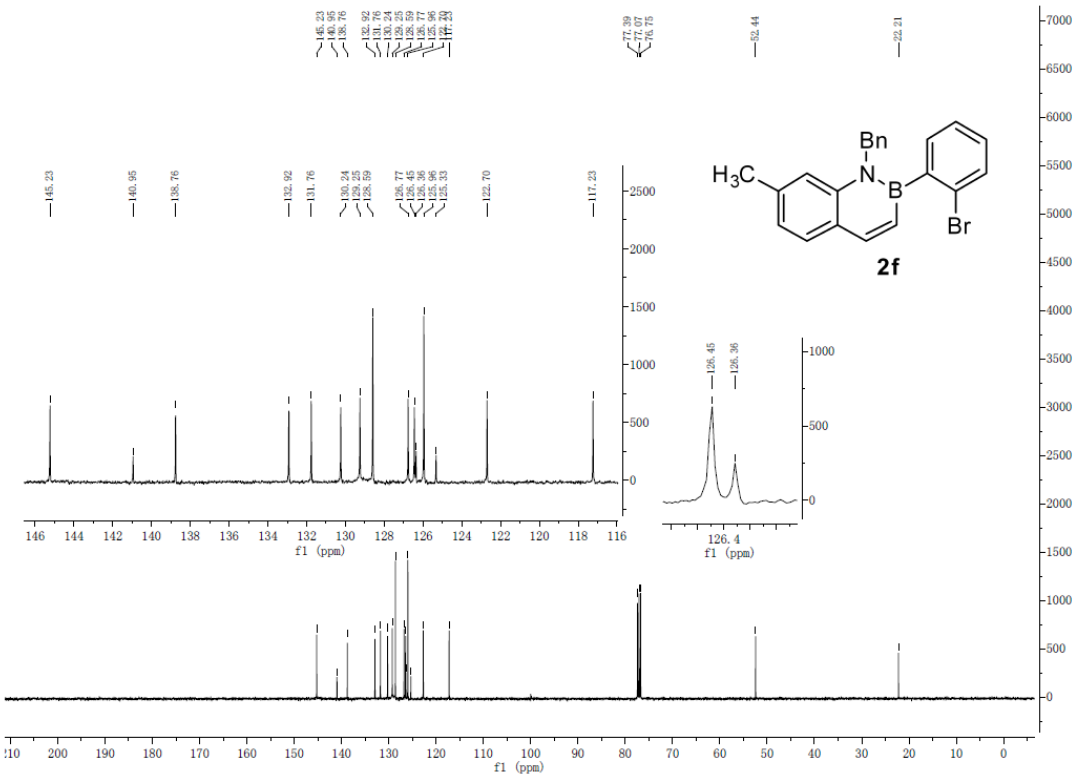
7.62
7.60
7.56
7.55
7.26
7.24
7.22
7.21
7.19
7.17
7.15
7.13
7.09
7.07
7.05
7.03
6.90
6.88
5.36
5.32
5.25
5.21
2.34
1.52
Bn
N
B
H3C
Br
2f
f1 (ppm)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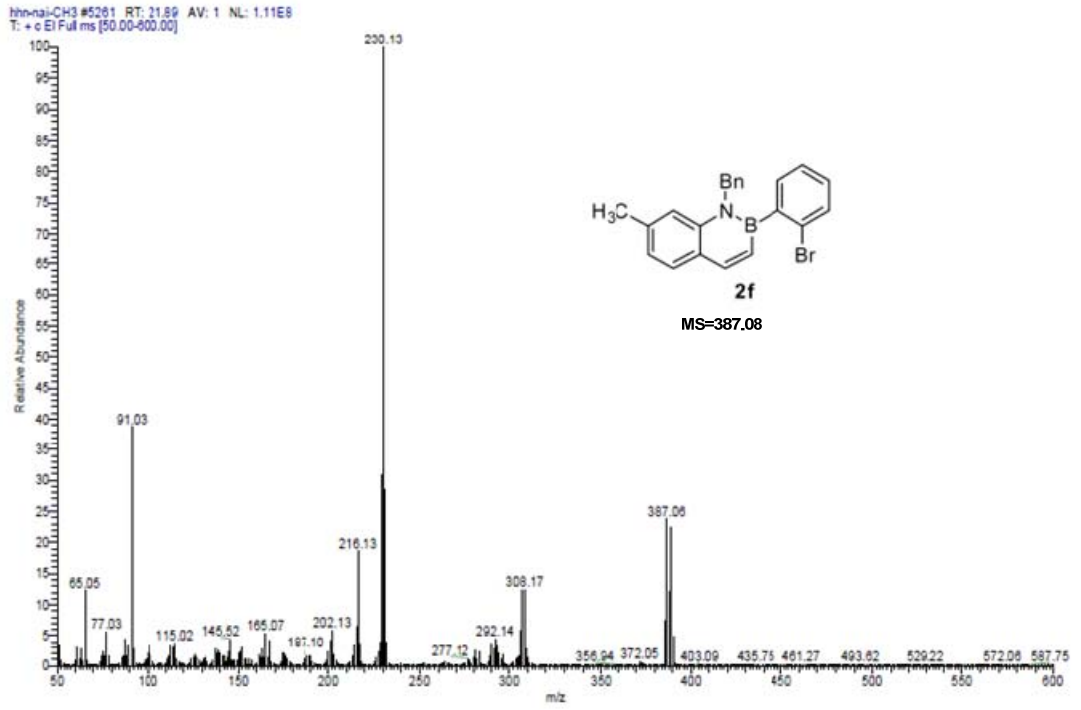
138.76
132.92
131.76
130.24
129.25
128.59
126.77
126.45
126.36
125.96
125.33
122.70
117.23
77.39
77.07
76.75
52.44
22.21
Bn
N
B
H3C
Br
2f
f1 (ppm)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T: + c EI Full ms [50.00-600.00]
Relative Abundance
m/z
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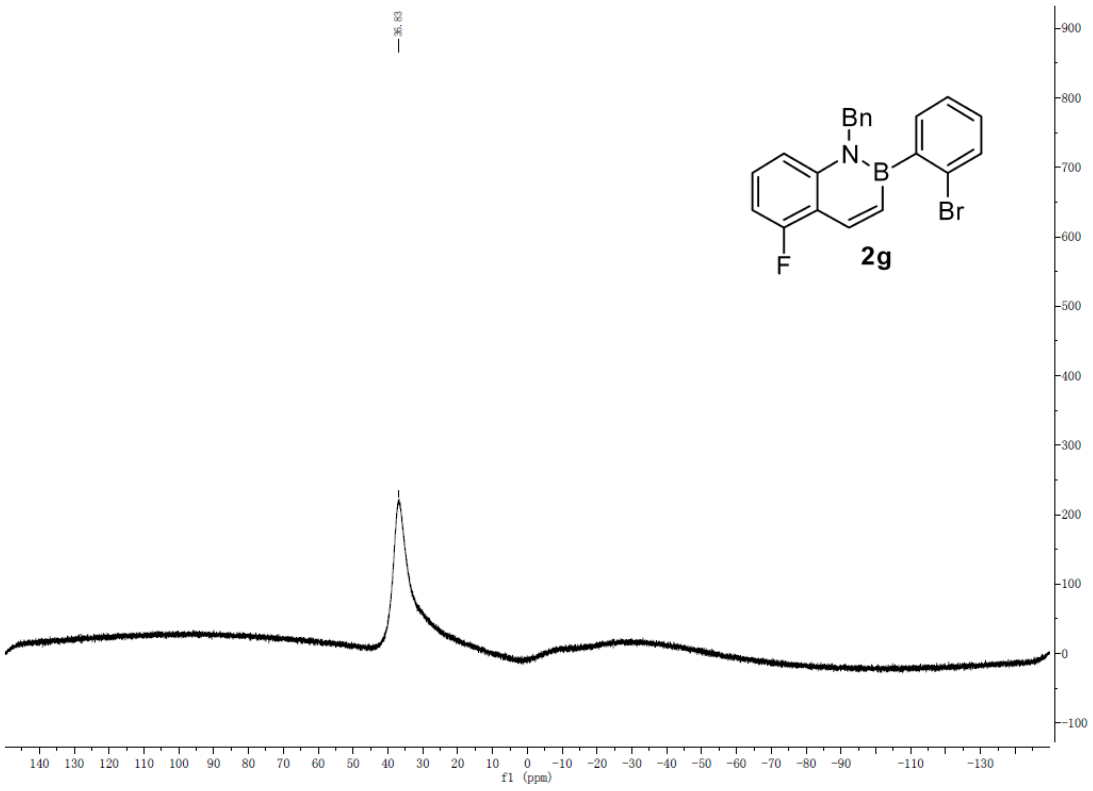
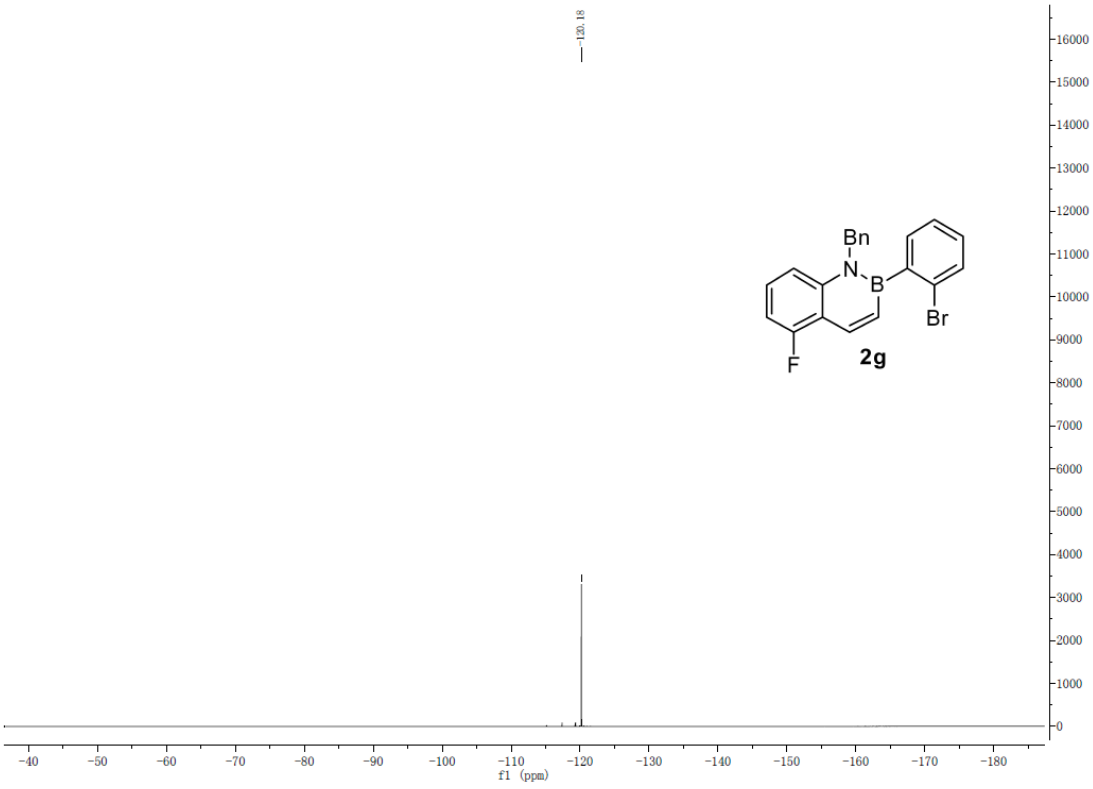
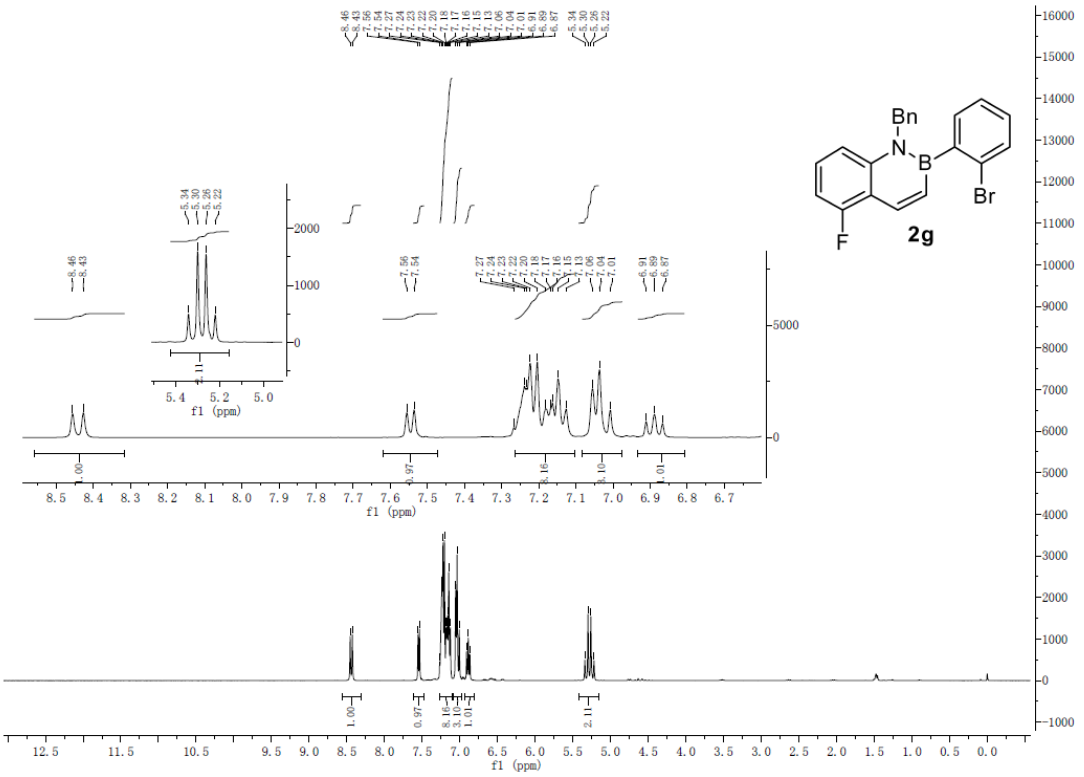
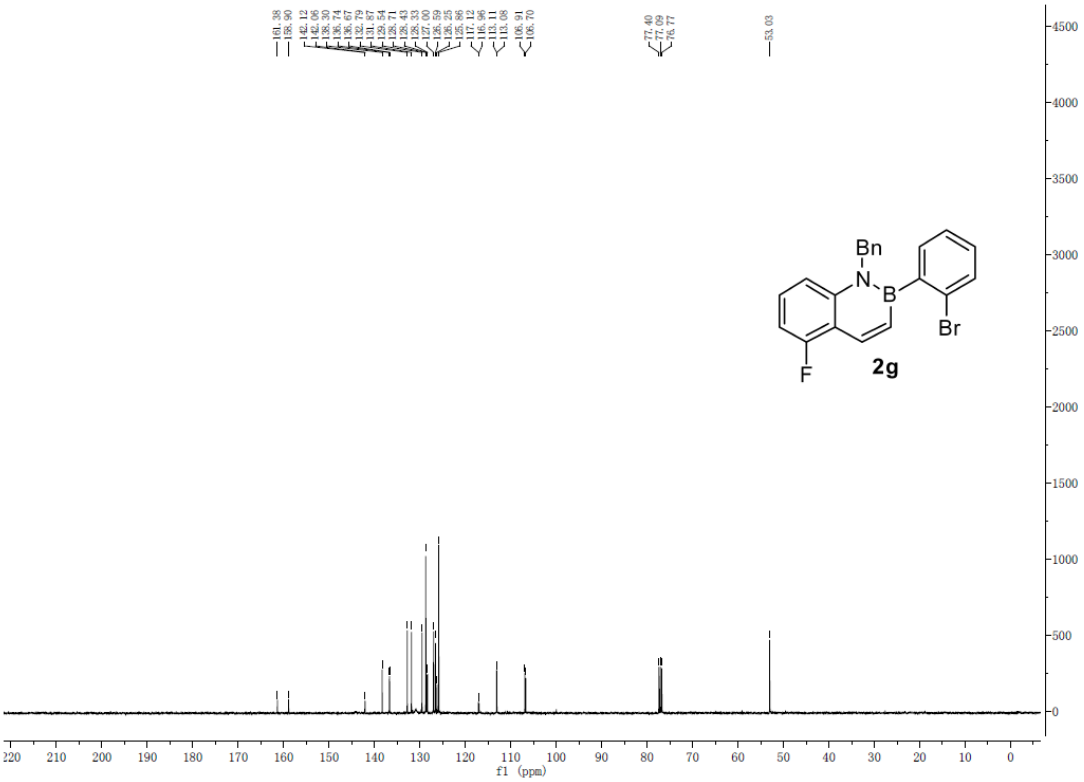
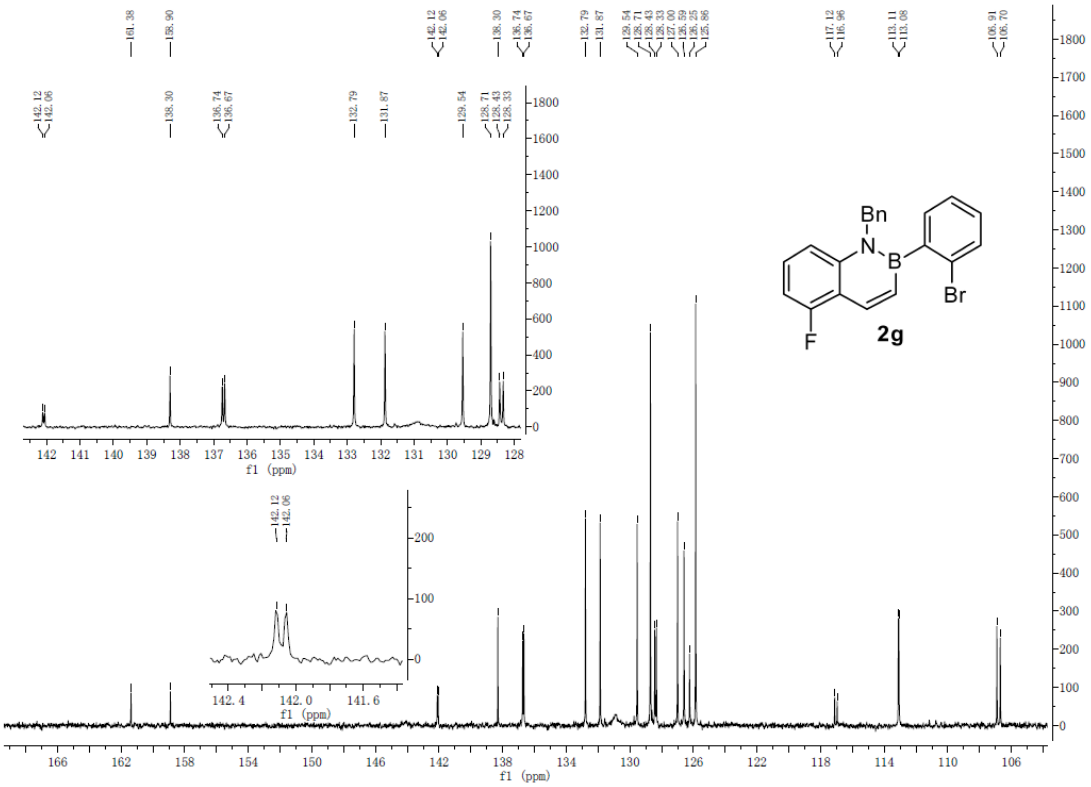
91.03
65.05
77.03
115.02
145.52
165.07
197.10
202.13
216.13
277.12
292.14
308.17
356.94
372.05
387.06
403.09
435.75
461.27
493.62
529.22
572.06
587.75
Bn
N
B
H3C
Br
2f
MS=387.08

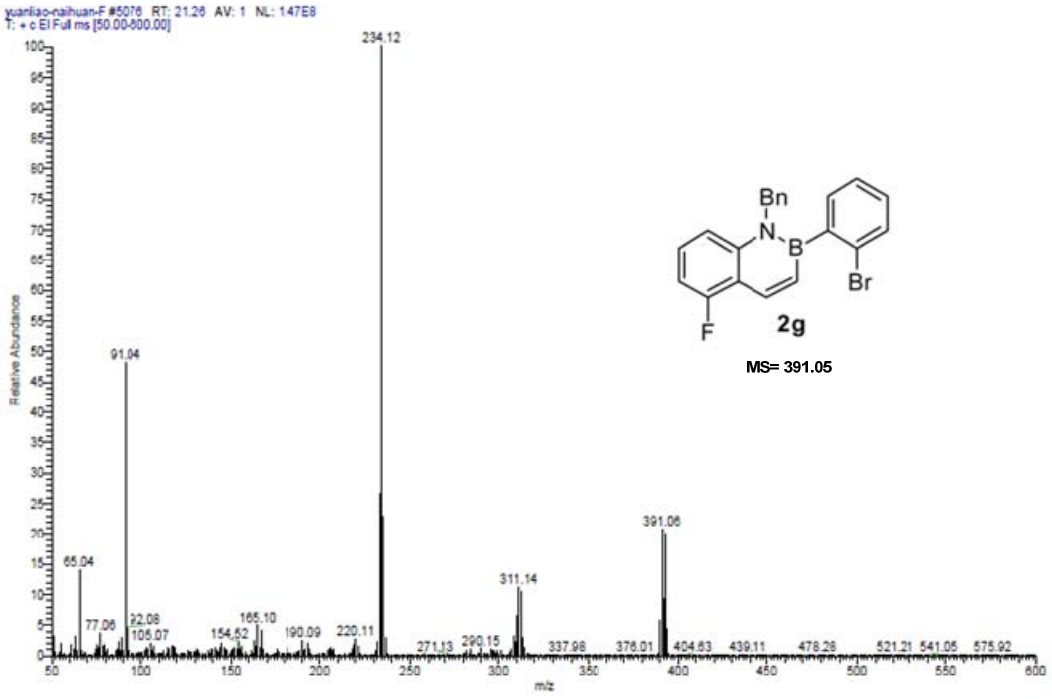

36.83
Bn
N
B
Br
F
2g
900
800
700
600
500
400
300
200
100
0
-100
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)


-120.18
Bn
N
B
Br
F
2g
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

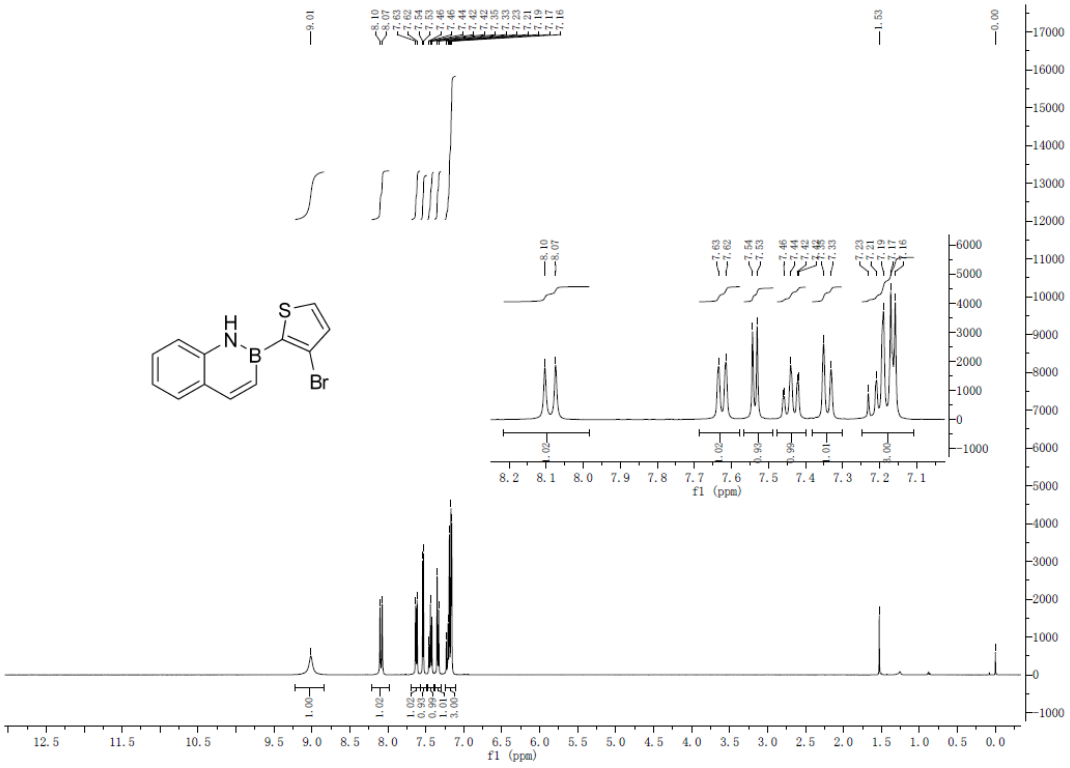

Bn
N
B
Br
F
2g
f1 (ppm)

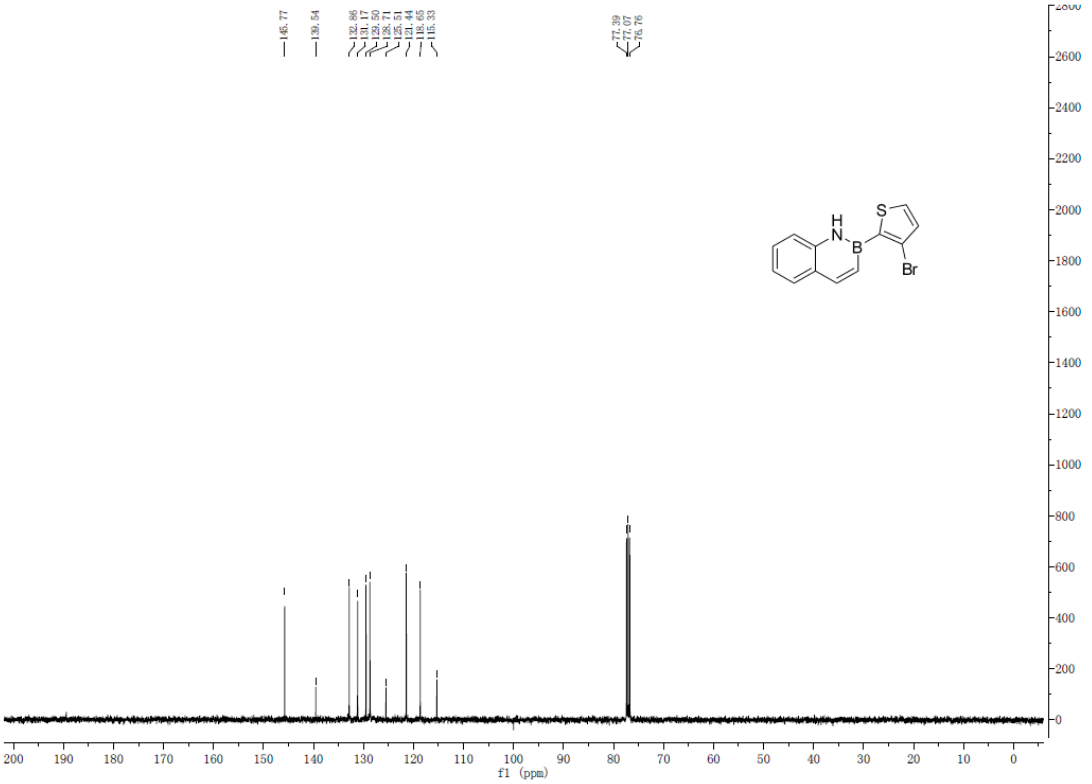

Bn
N
B
Br
F
2g
f1 (ppm)

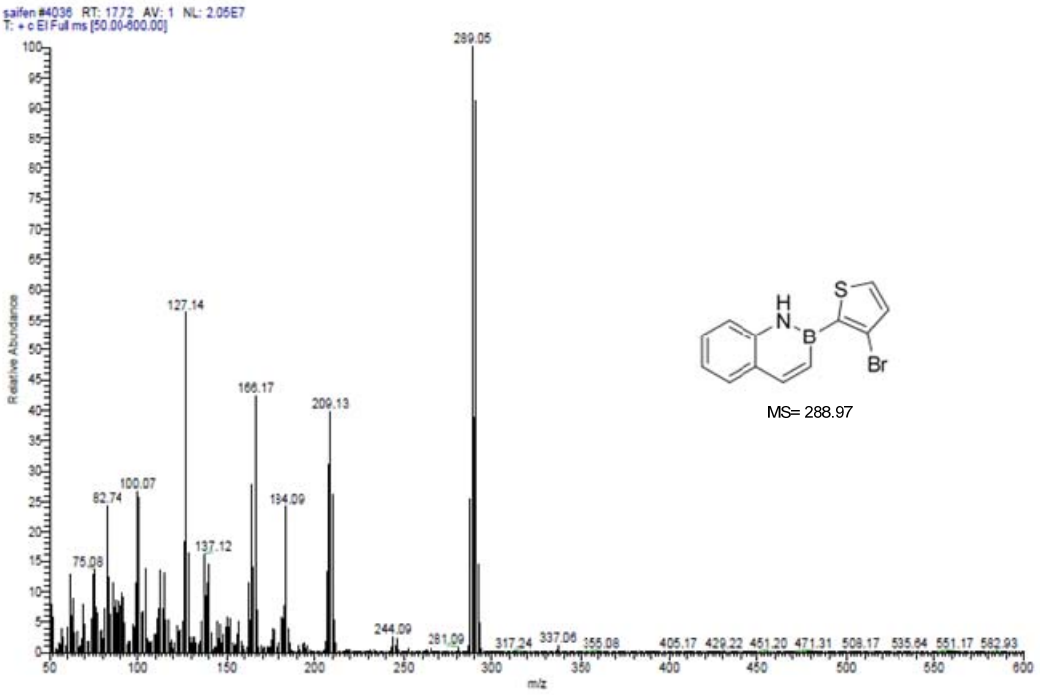

Bn
N
B
Br
F
2g
f1 (ppm)


yuanliao-naihuan-F #5076 RT: 21.26 AV: 1 NL: 147E8
T: + c EI Full ms [50.00-600.00]
Relative Abundance
m/z
234.12
91.04
391.06
311.14
65.04
Bn
N
B
Br
F
2g

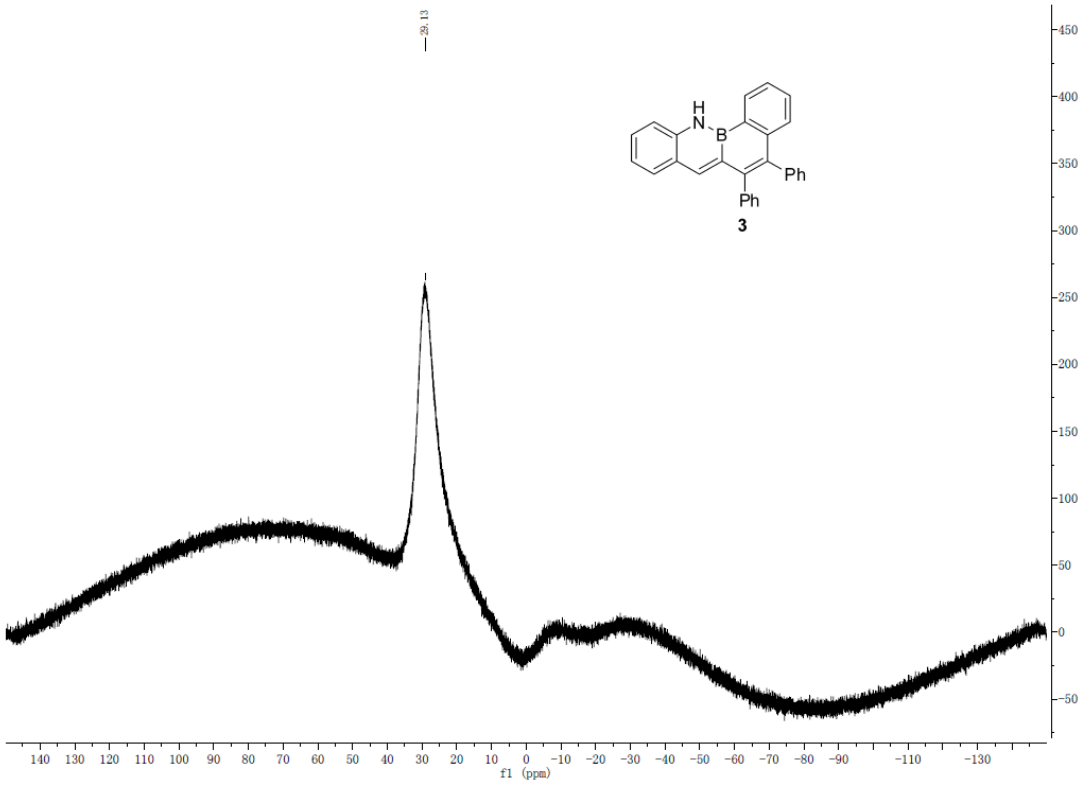
MS= 391.05


9.01
8.10
8.07
7.63
7.62
7.54
7.53
7.46
7.44
7.42
7.35
7.33
7.23
7.21
7.19
7.17
7.16
1.53
0.00
H
N
B
S
Br
f1 (ppm)

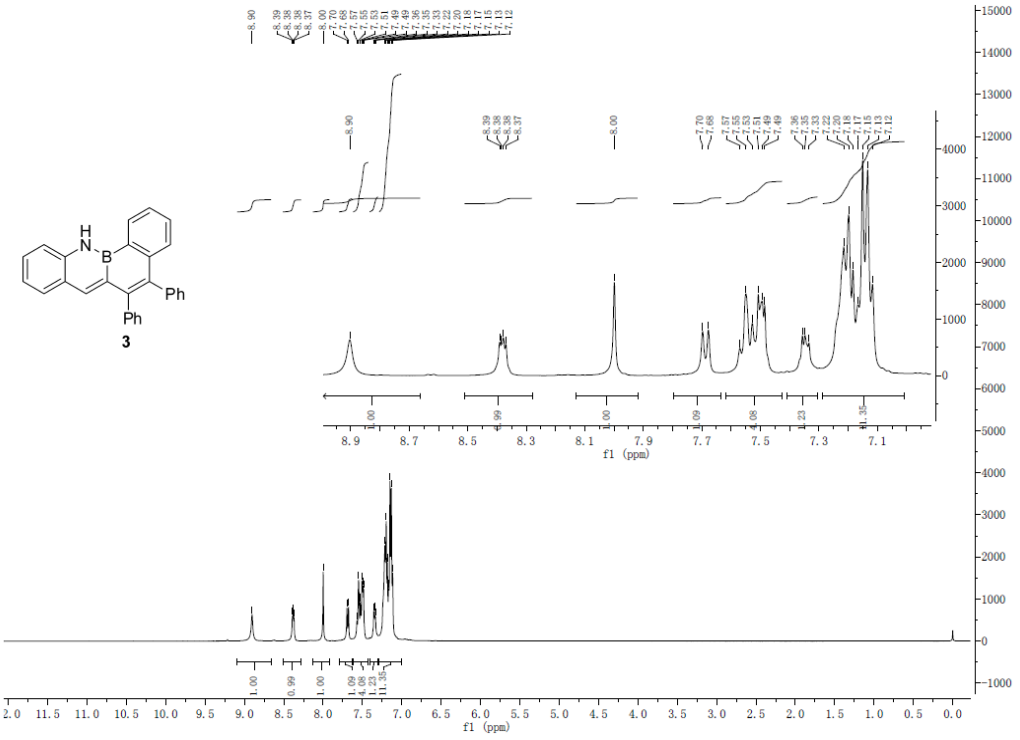

145.77
139.54
132.86
131.17
128.50
126.71
125.51
121.44
118.65
115.33
77.39
77.07
76.76
H
N
B
S
Br
f1 (ppm)

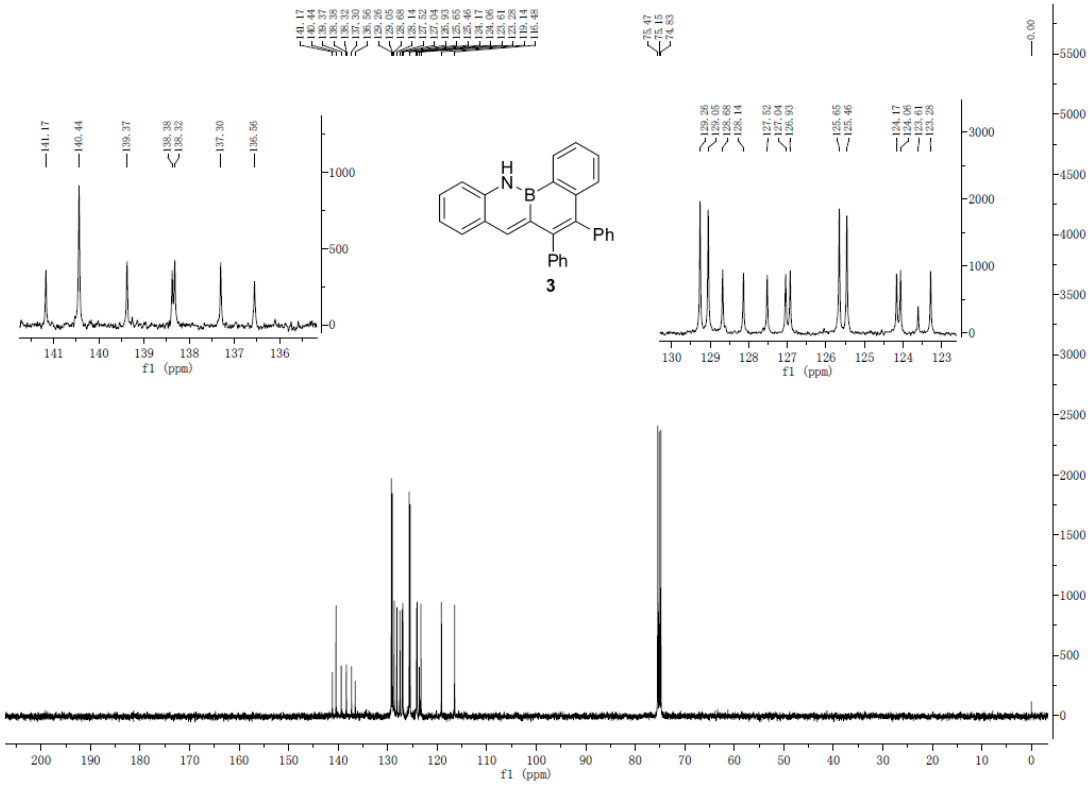

saifen #4036 RT: 17.72 AV: 1 NL: 2.05E7
T: + c EI Full ms [50.00-600.00]
Relative Abundance
m/z
289.05
127.14
166.17
209.13
100.07
82.74
194.09
137.12
75.08
244.09
281.09
317.24
337.06
355.08
405.17
429.22
451.20
471.31
508.17
535.64
551.17
582.93
H
N
B
S
Br

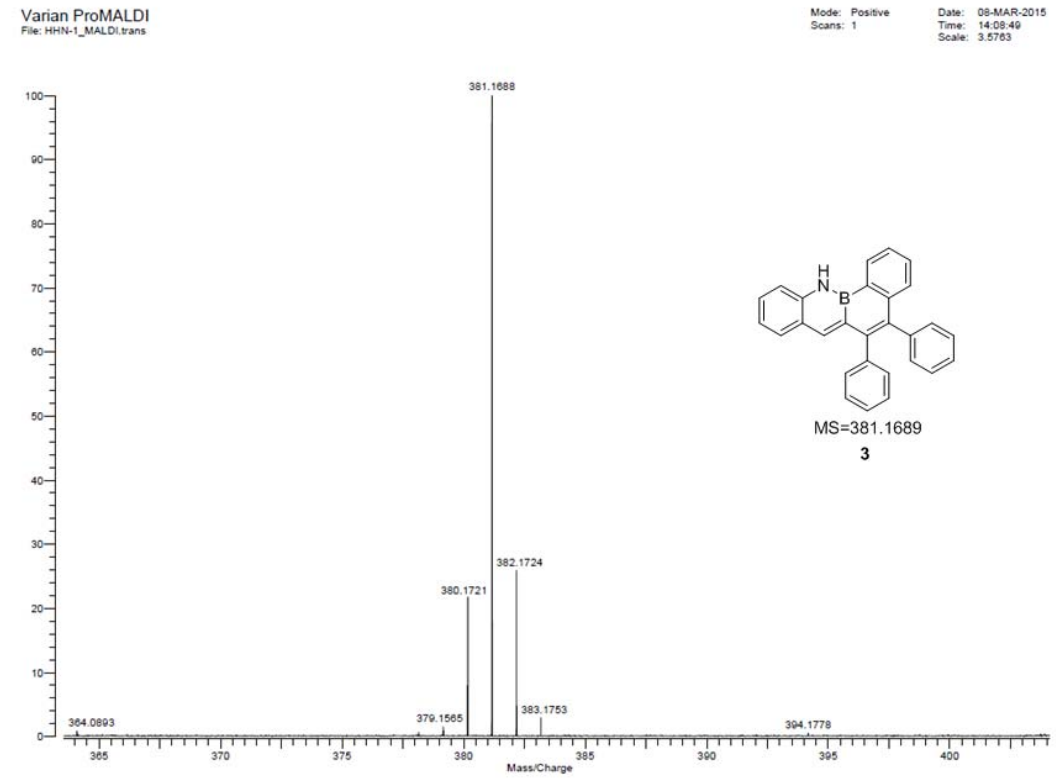
MS= 288.97

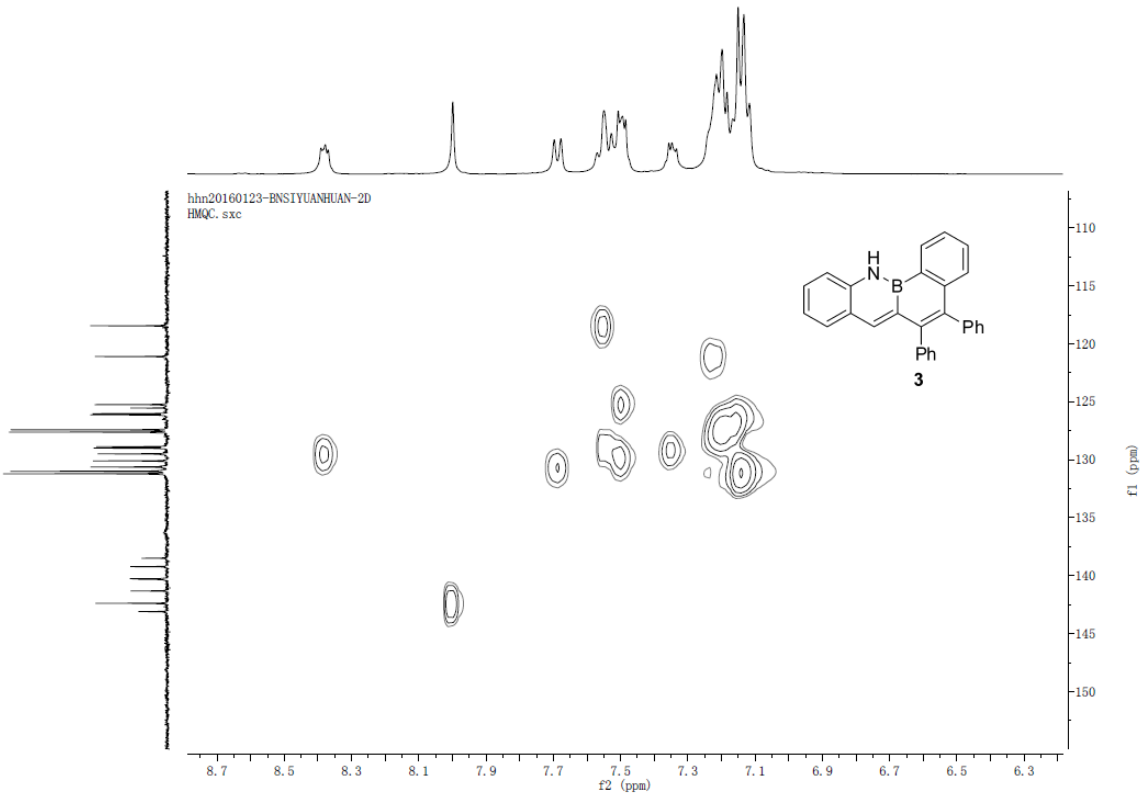

29.13
H
N
B
Ph
Ph
f1 (ppm)

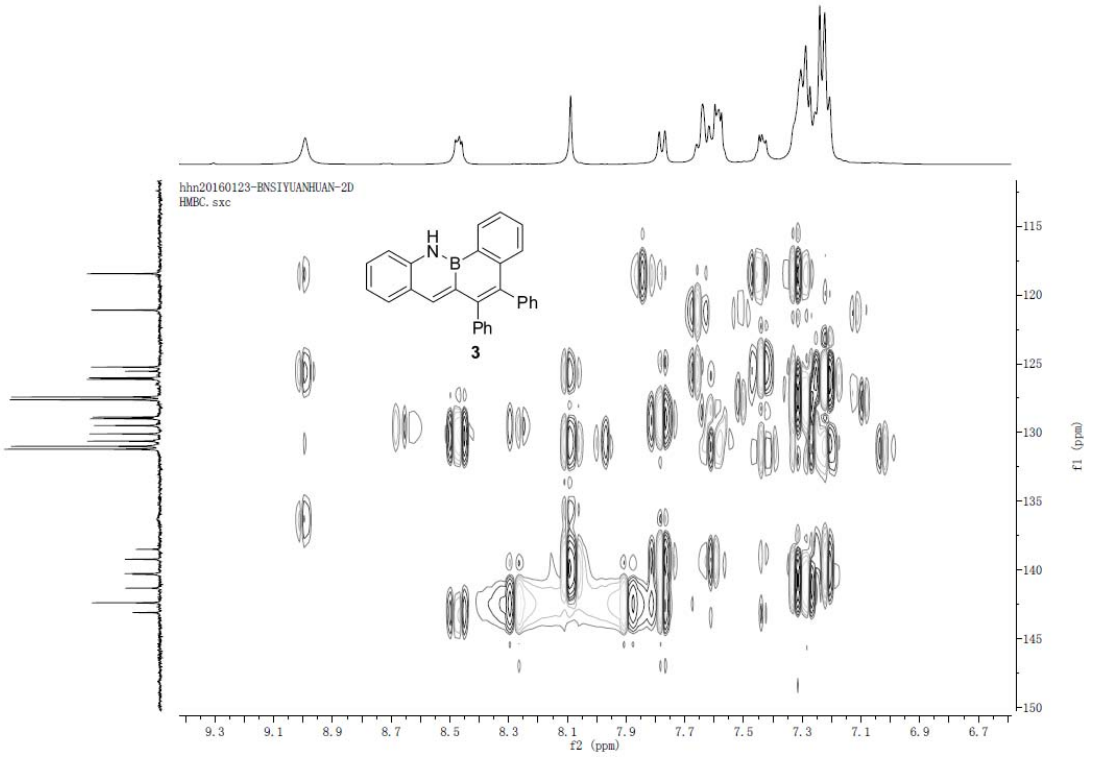
3

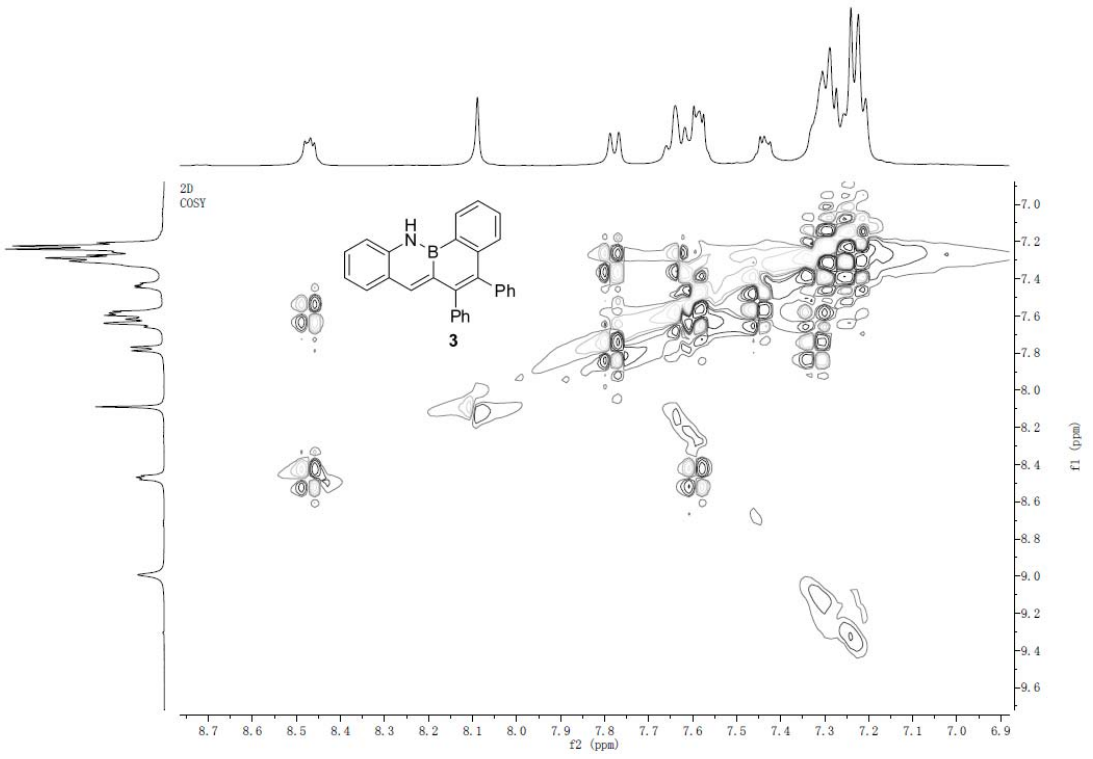

H
N
B
Ph
Ph
3
f1 (ppm)

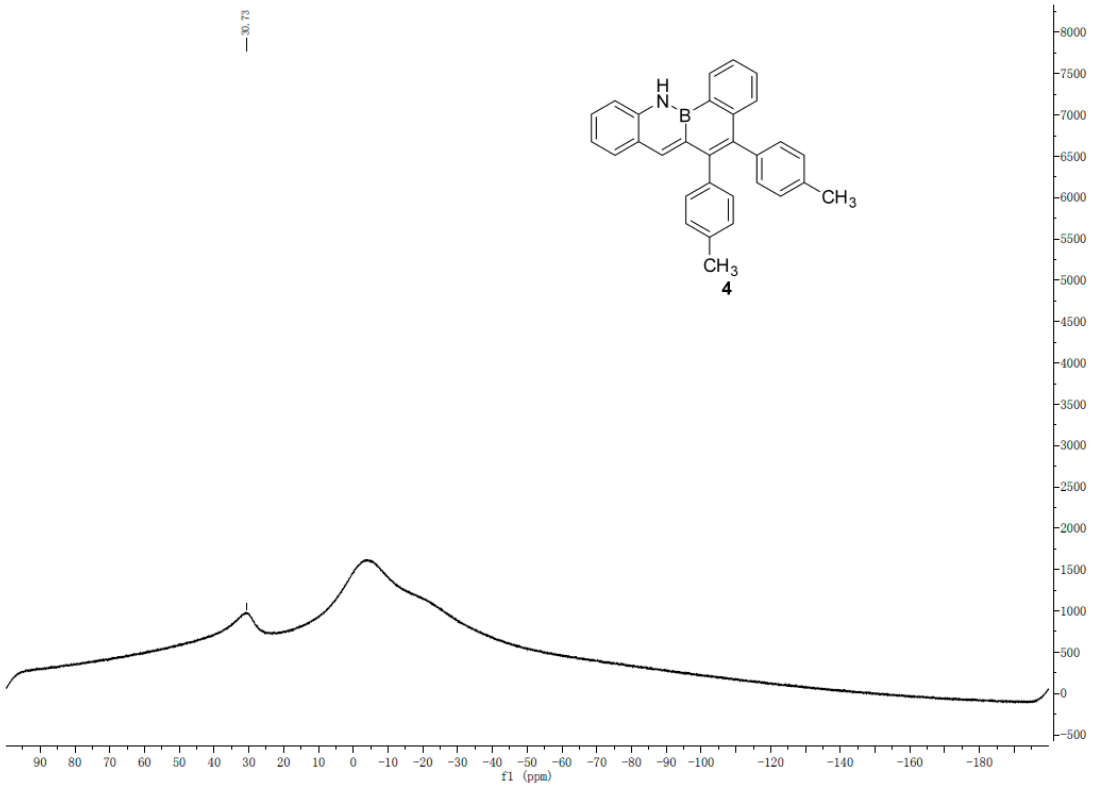

H
N
B
Ph
Ph
3
f1 (ppm)

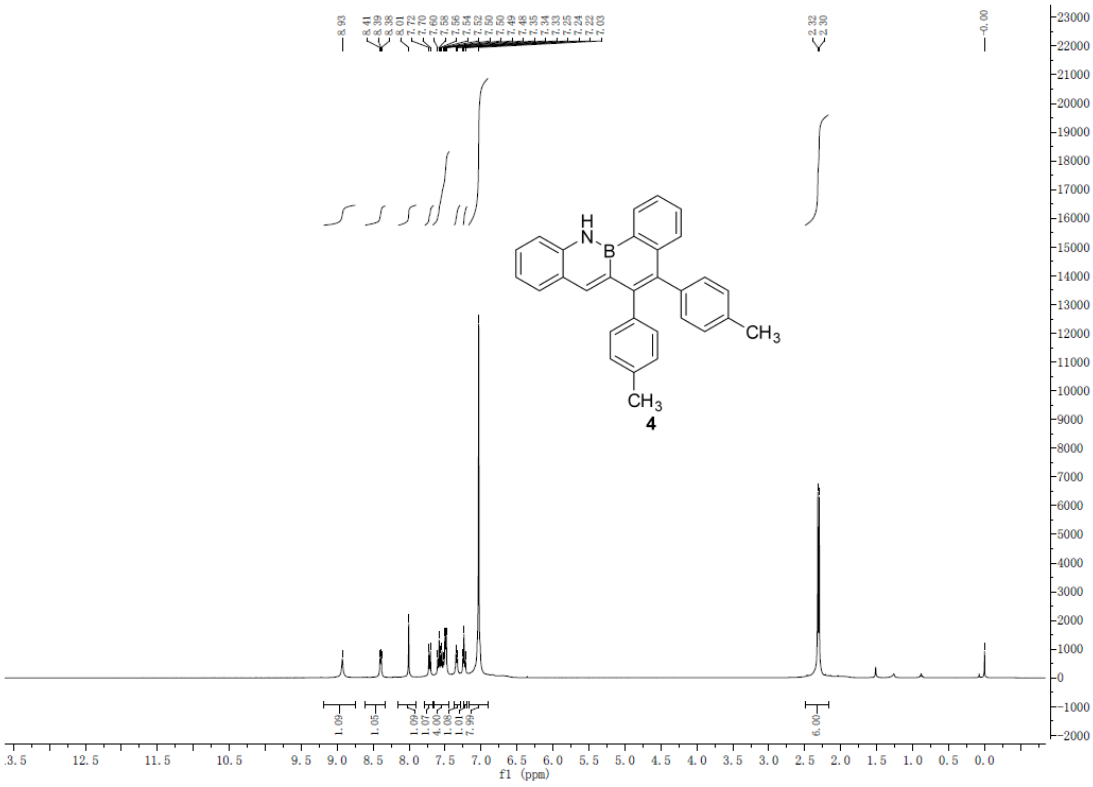

Varian ProMALDI
File: HHN-1_MALDI.trans
Mode: Positive
Scans: 1
Date: 08-MAR-2015
Time: 14:08:49
Scale: 3.5763
381.1688
382.1724
380.1721
364.0893
379.1565
383.1753
394.1778
Mass/Charge
MS=381.1689
3

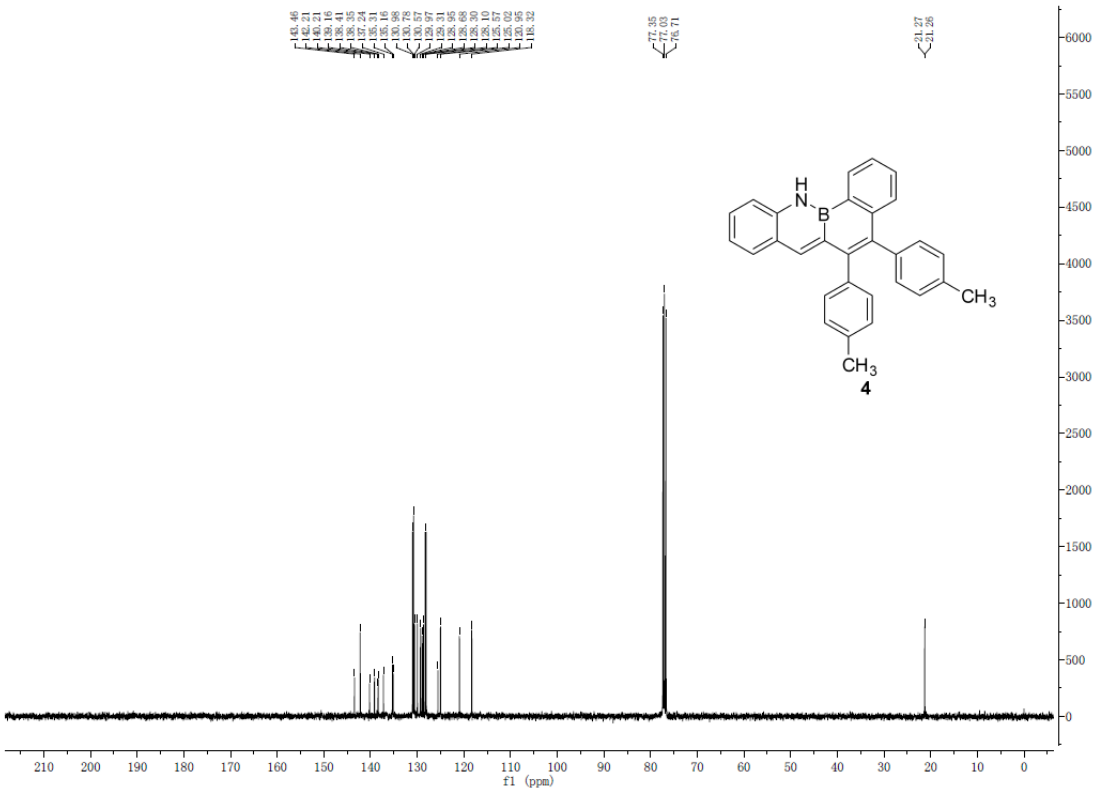

hhn20160123-BNSIYUANHUAN-2D
HMQC.sxc
Ph
Ph
3
f2 (ppm)
f1 (ppm)

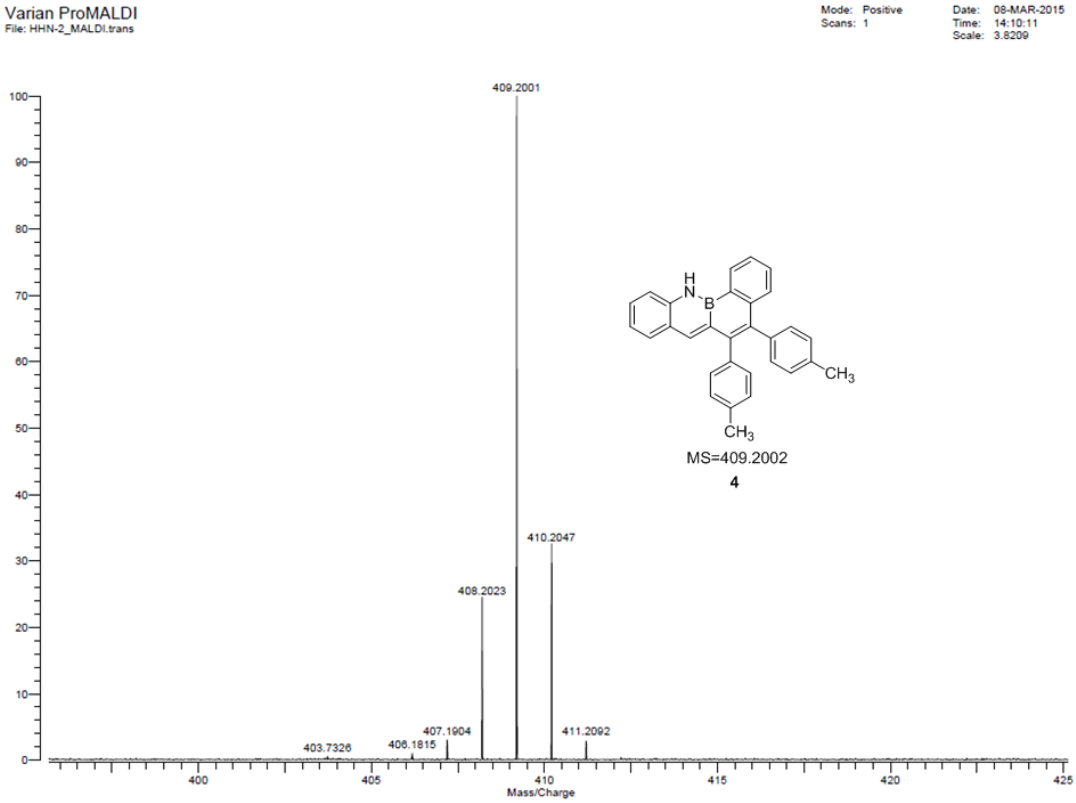

hhn20160123-BNSIYUANHUAN-2D
HMBC. sxc
H
N
B
Ph
Ph
3
f2 (ppm)
f1 (ppm)

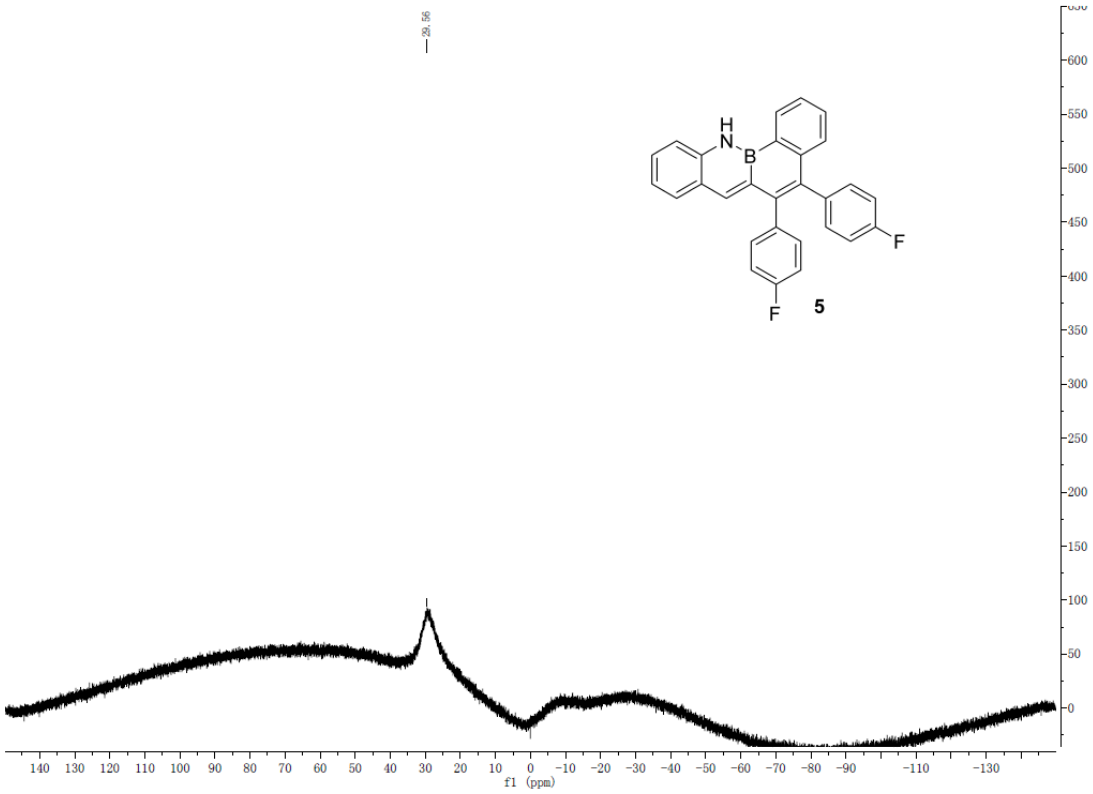

2D
COSY
H
N
B
Ph
Ph
3
f2 (ppm)
f1 (ppm)

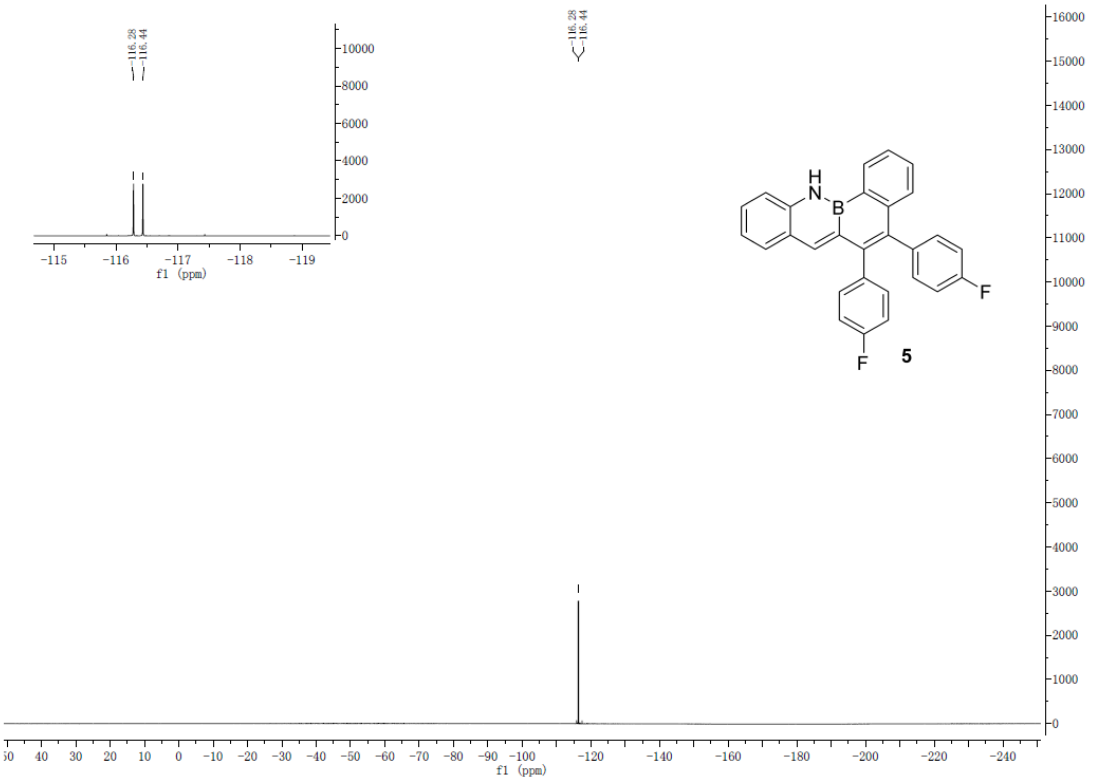

30.73
H
N
B
CH3
CH3
4
f1 (ppm)

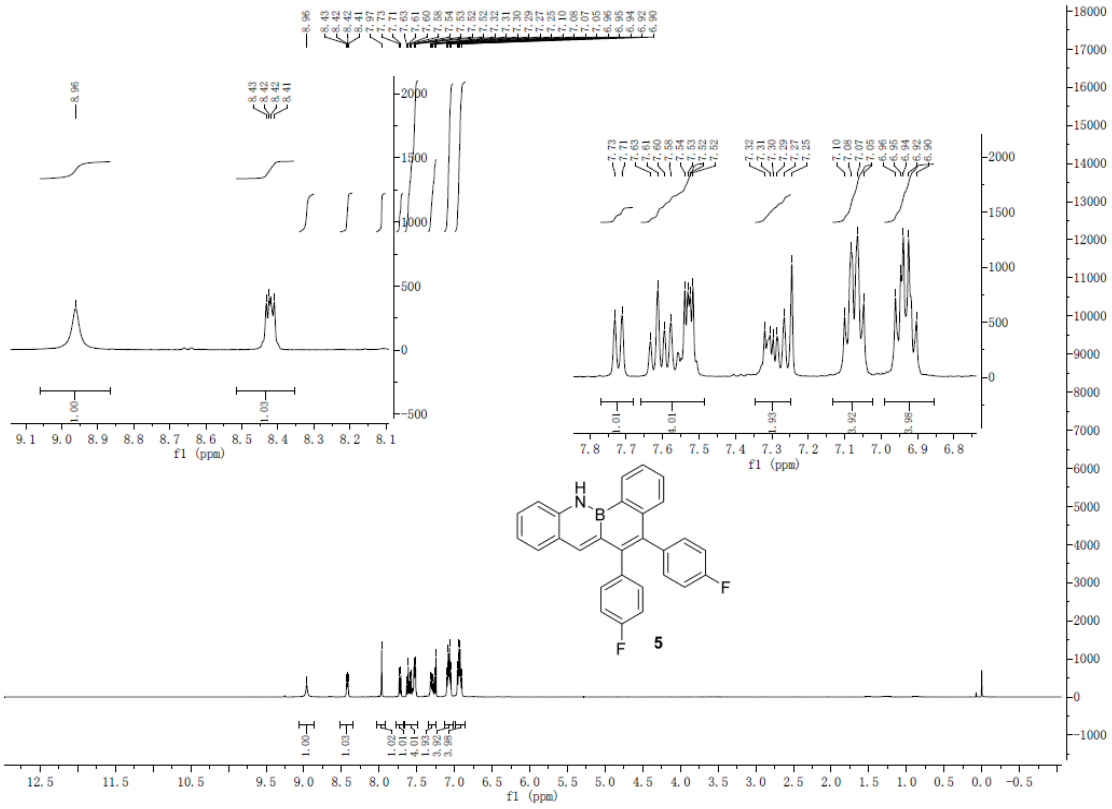

8.93
8.41
8.39
8.38
8.01
7.72
7.70
7.68
7.66
7.58
7.56
7.54
7.52
7.50
7.49
7.48
7.35
7.34
7.33
7.25
7.24
7.22
7.03
2.32
2.30
0.00
H
N
B
CH3
CH3
4
1.09
1.05
1.09
1.07
4.00
1.08
1.01
7.99
6.00
f1 (ppm)

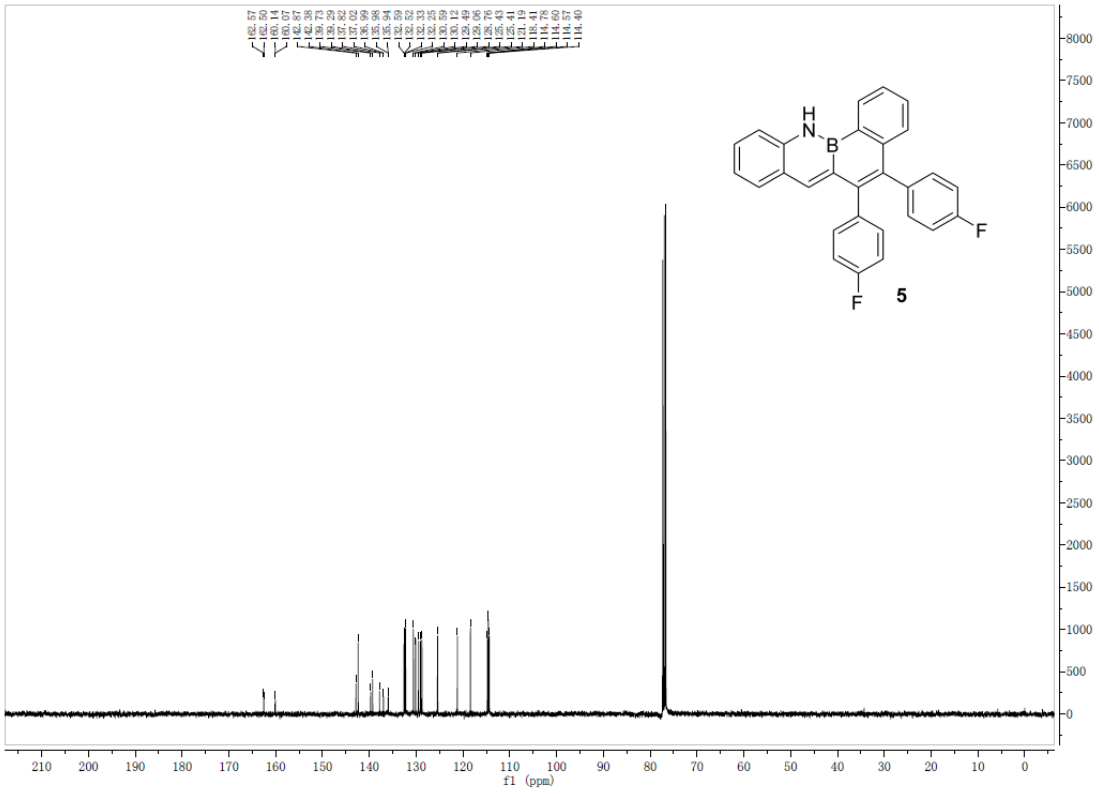

f1 (ppm)
CH3
CH3
4

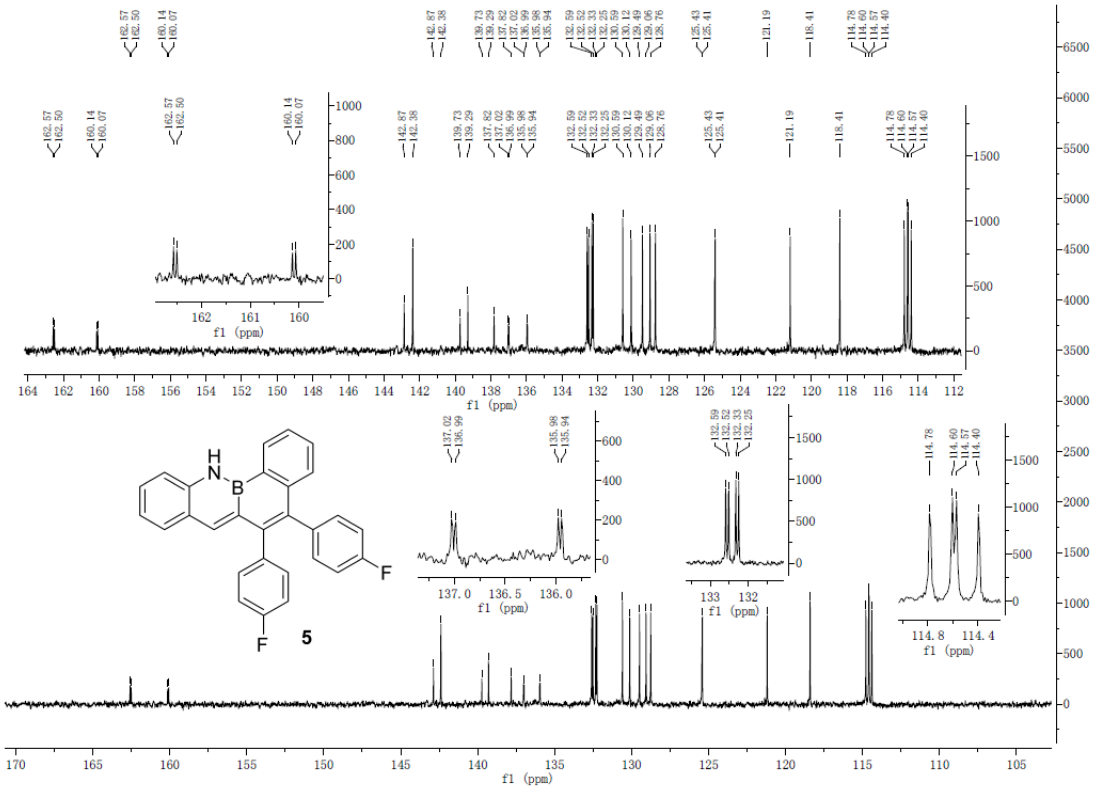

Varian ProMALDI
File: HHN-2_MALDI.trans
Mode: Positive
Scans: 1
Date: 08-MAR-2015
Time: 14:10:11
Scale: 3.8209
409.2001
410.2047
408.2023
407.1904
406.1815
403.7326
411.2092
Mass/Charge
CH3
CH3
MS=409.2002
4

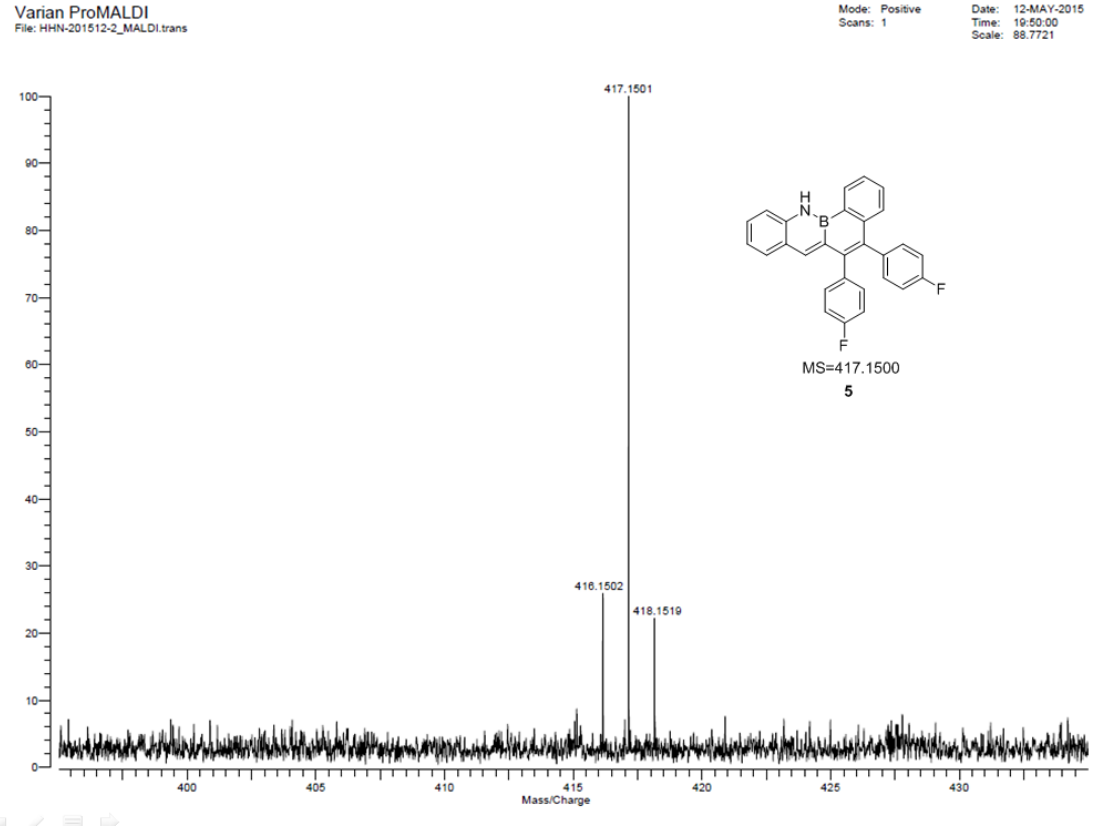

29.56
H
N
B
F
F
5
600
550
500
450
400
350
300
250
200
150
100
50
0
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)

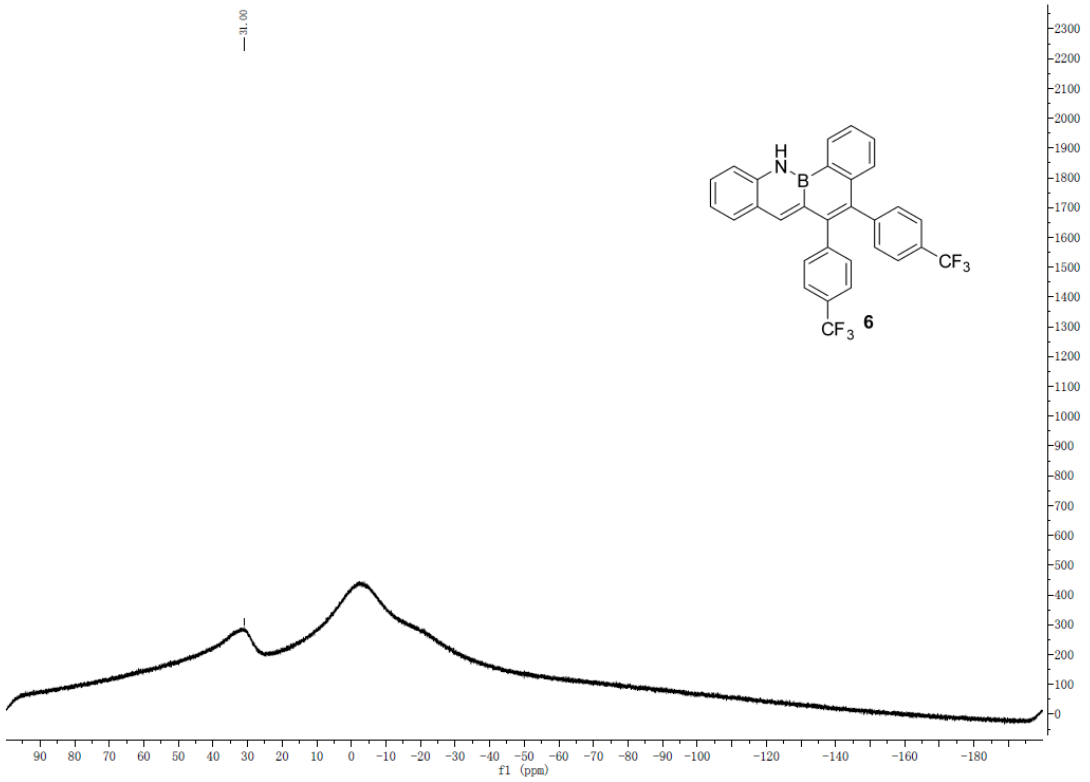

-116.28
-116.44
10000
8000
6000
4000
2000
0
-115 -116 -117 -118 -119
f1 (ppm)
-116.28
-116.44
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
H
N
B
F
F
5
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

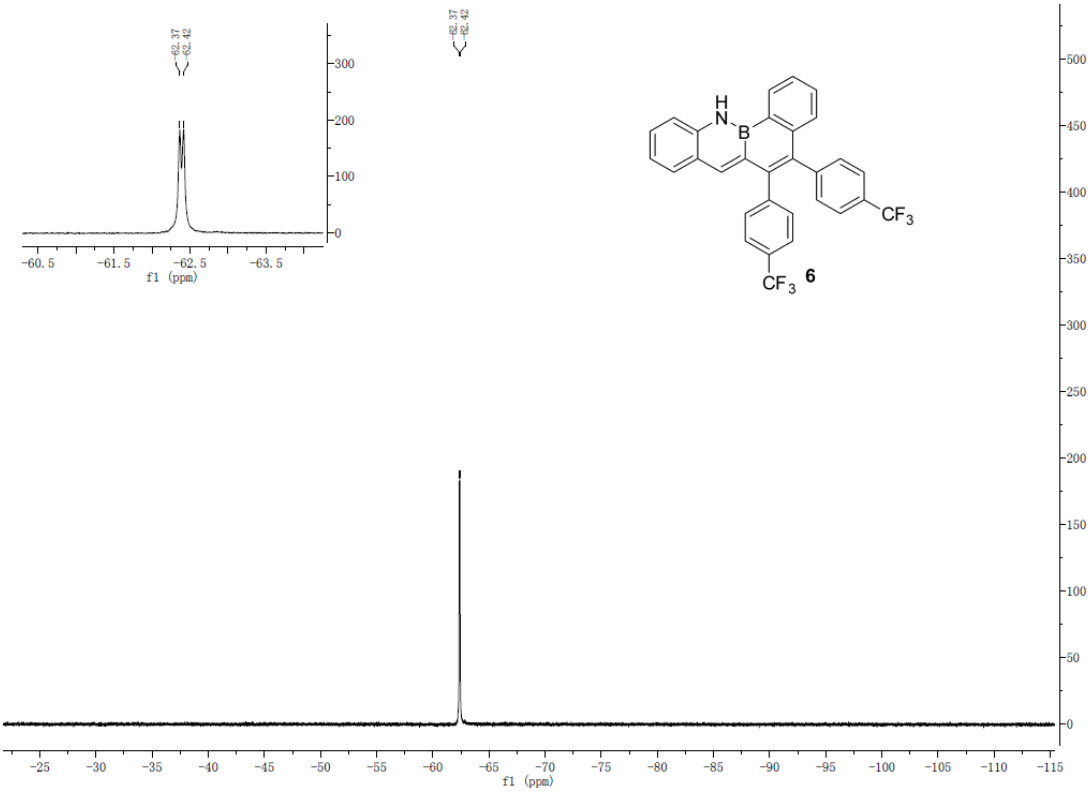

5
f1 (ppm)

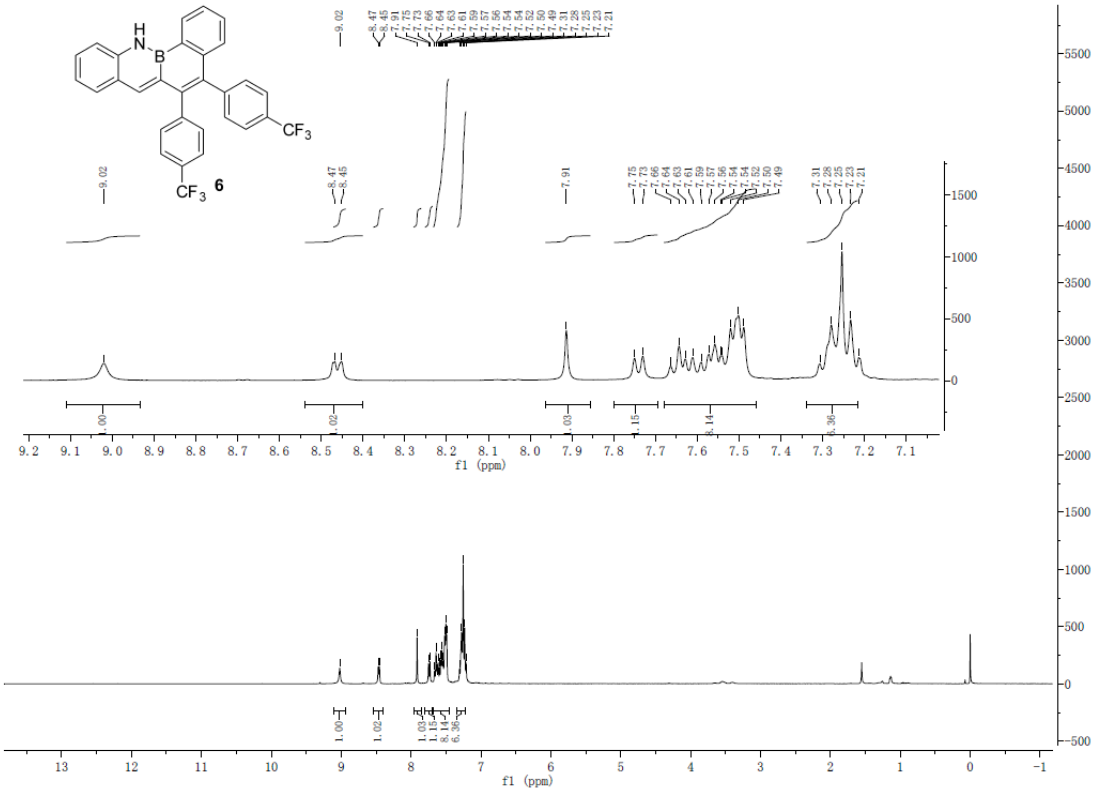

5
f1 (ppm)

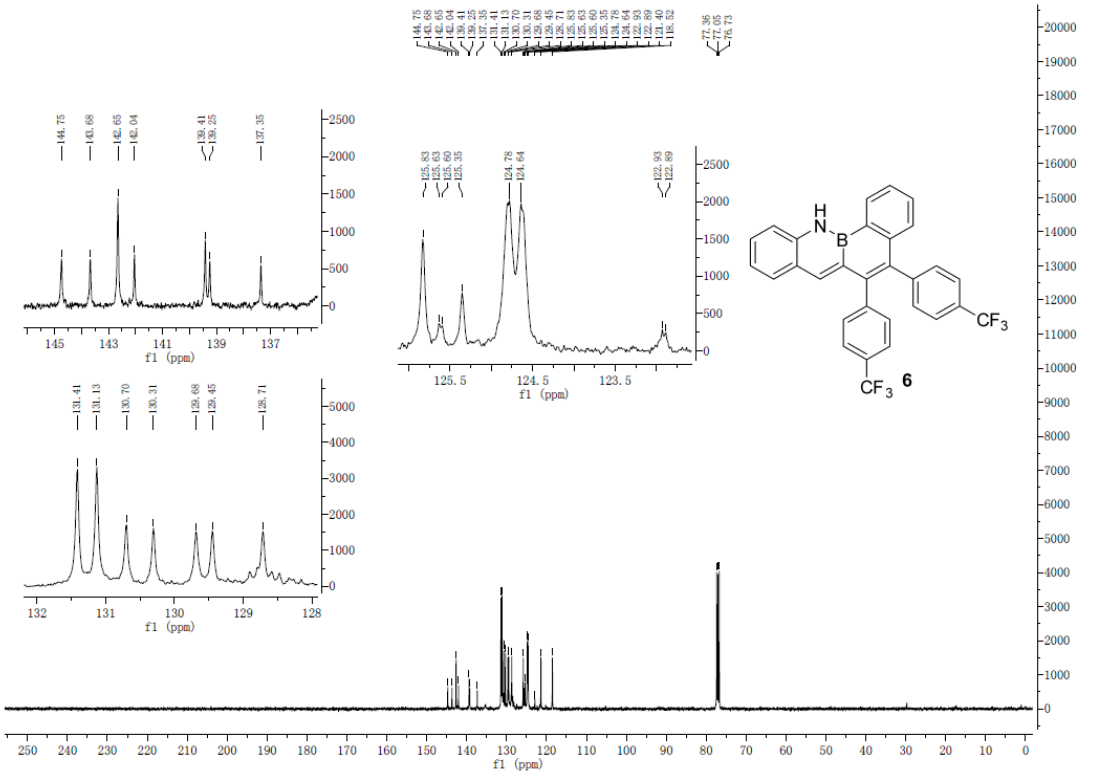

f1 (ppm)
5

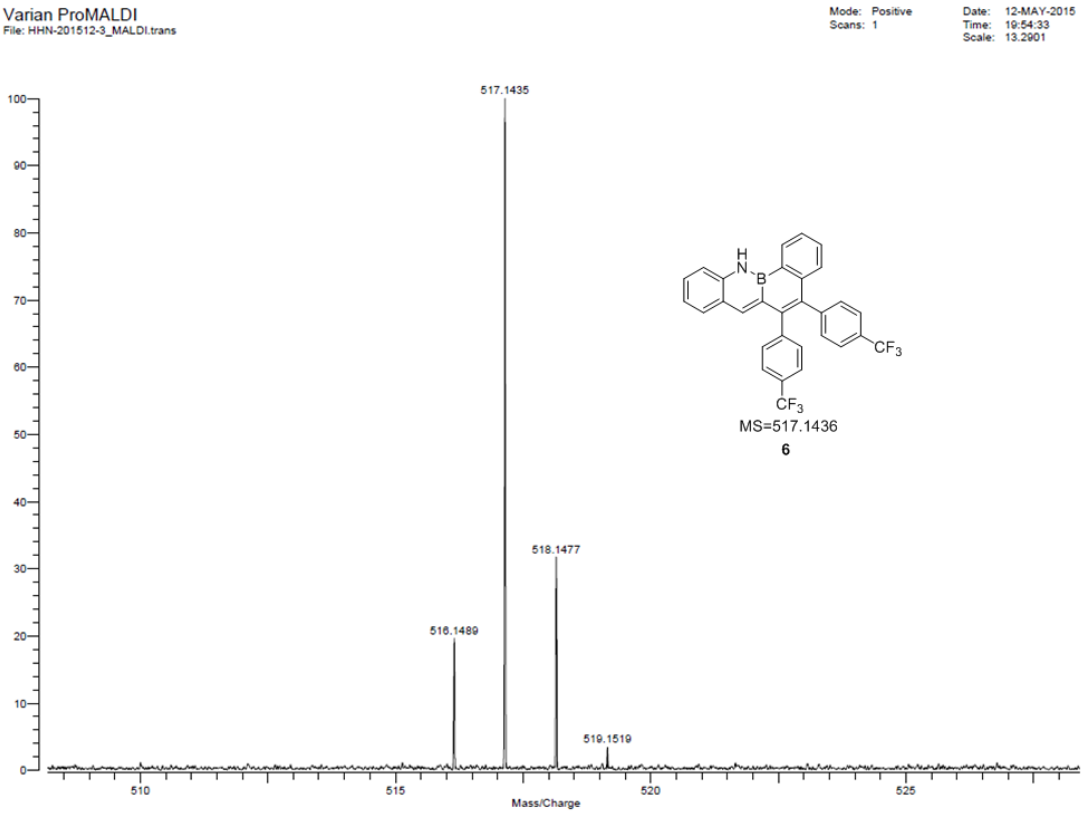

Varian ProMALDI
File: HHN-201512-2_MALDI.trans
Mode: Positive
Scans: 1
Date: 12-MAY-2015
Time: 19:50:00
Scale: 88.7721
417.1501
416.1502
418.1519
Mass/Charge
MS=417.1500
5

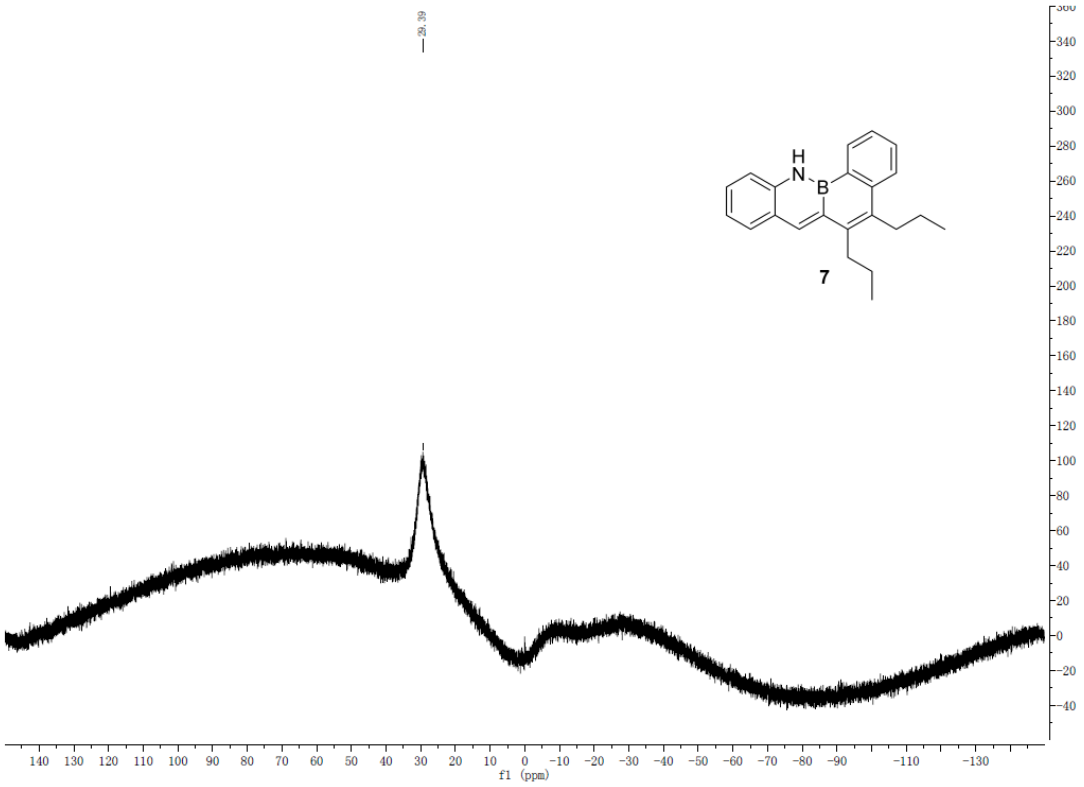

31.00
H
N
B
CF3
CF3
6
f1 (ppm)

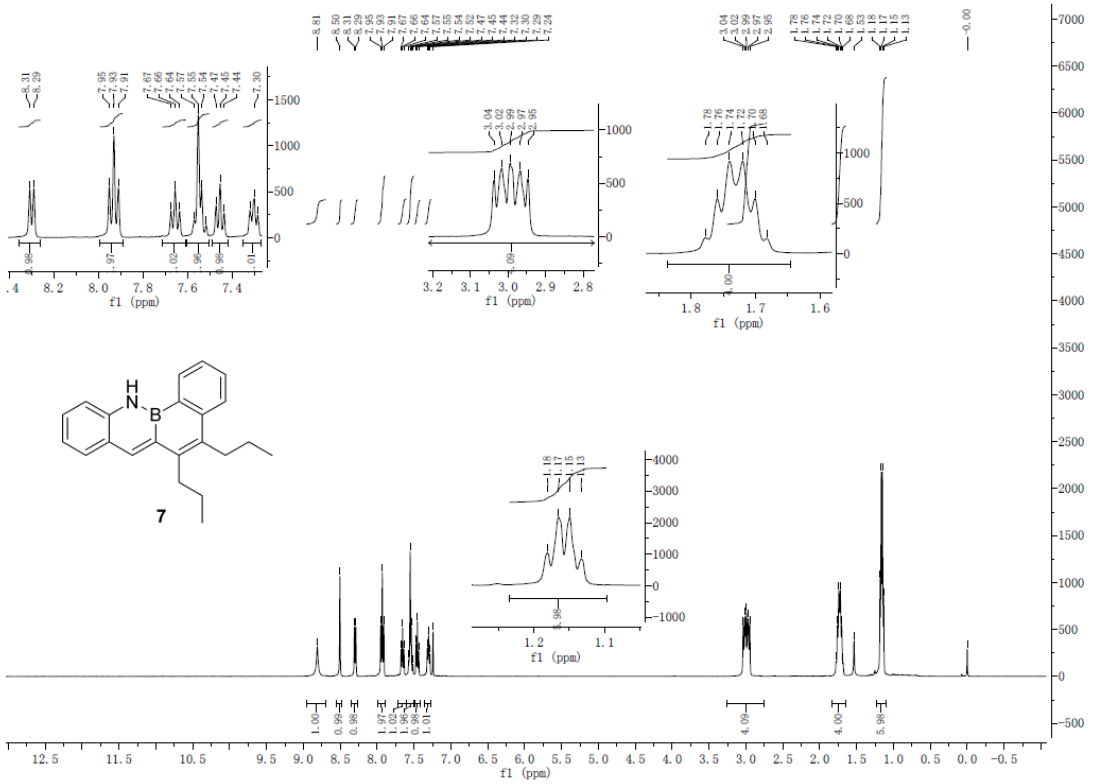

-62.37
-62.42
H
N
B
CF3
CF3
6
f1 (ppm)

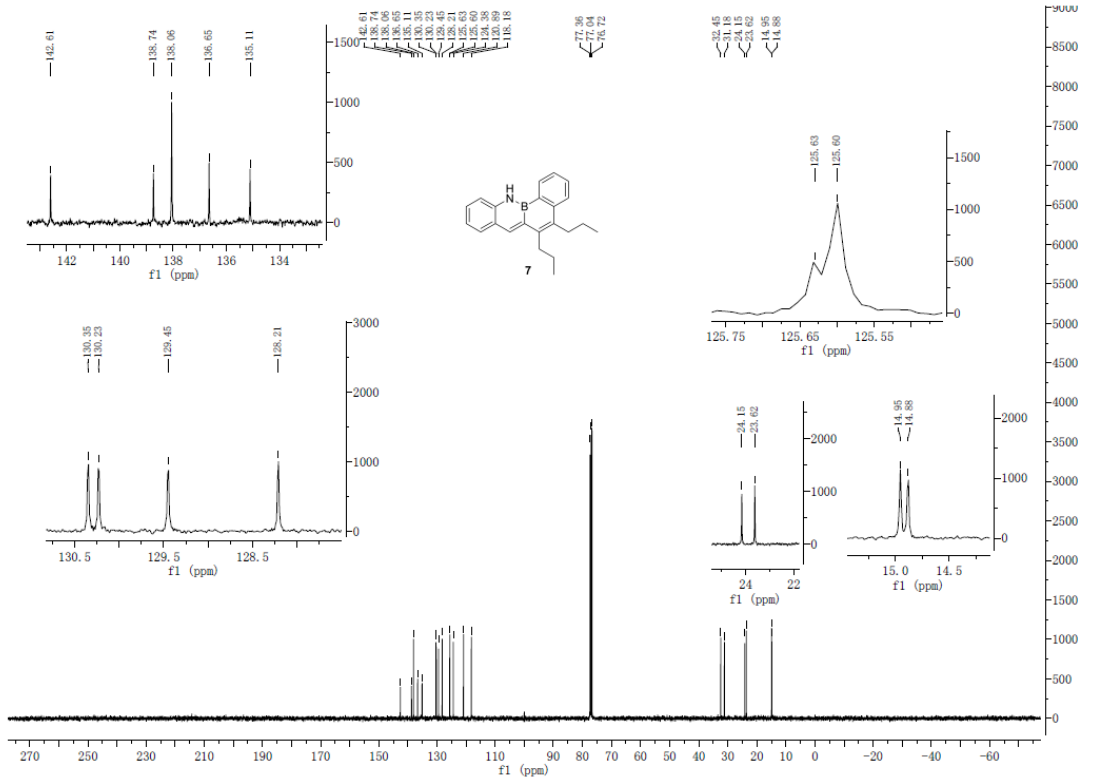

6
f1 (ppm)

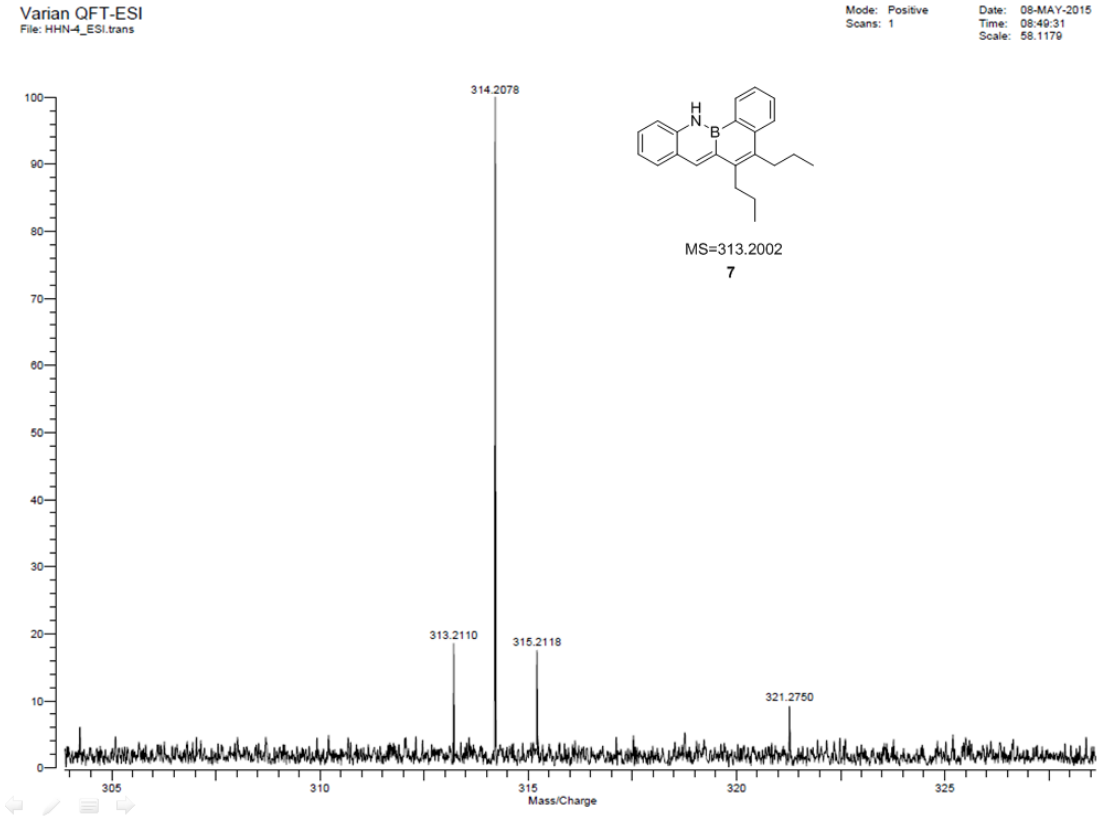

6
f1 (ppm)

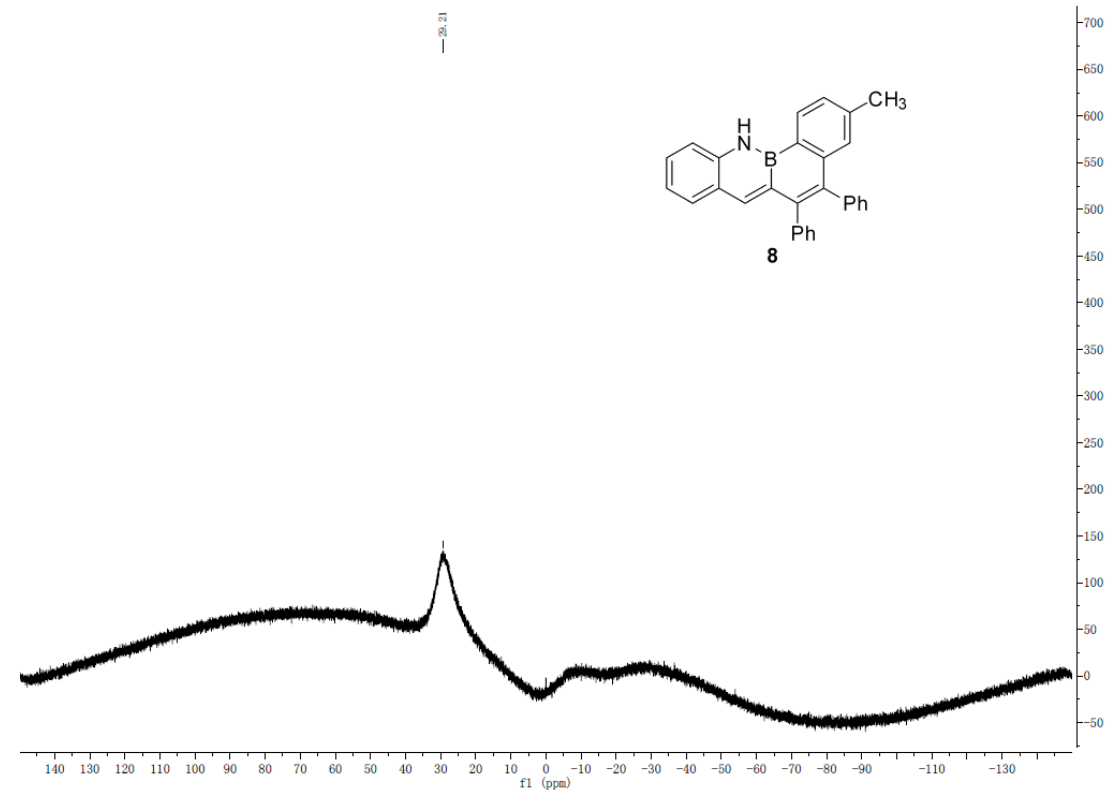

Varian ProMALDI
File: HHN-201512-3_MALDI.trans
Mode: Positive
Scans: 1
Date: 12-MAY-2015
Time: 19:54:33
Scale: 13.2901
517.1435
518.1477
516.1489
519.1519
Mass/Charge
MS=517.1436
6

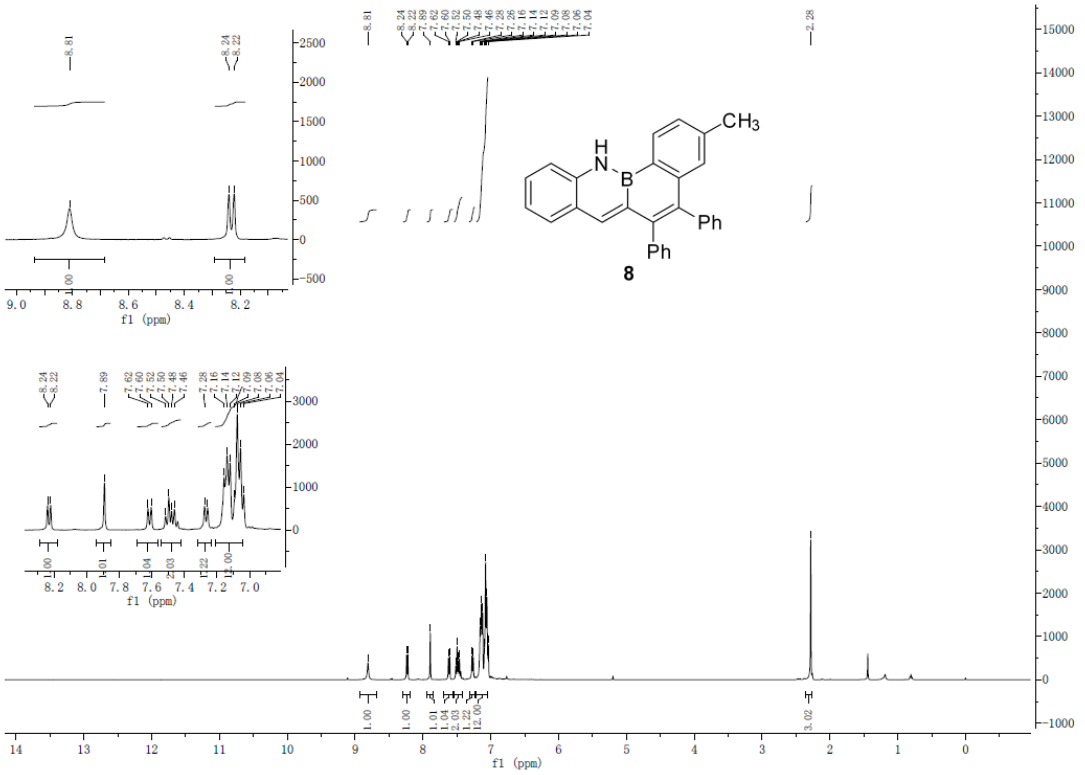

29.39
7
f1 (ppm)

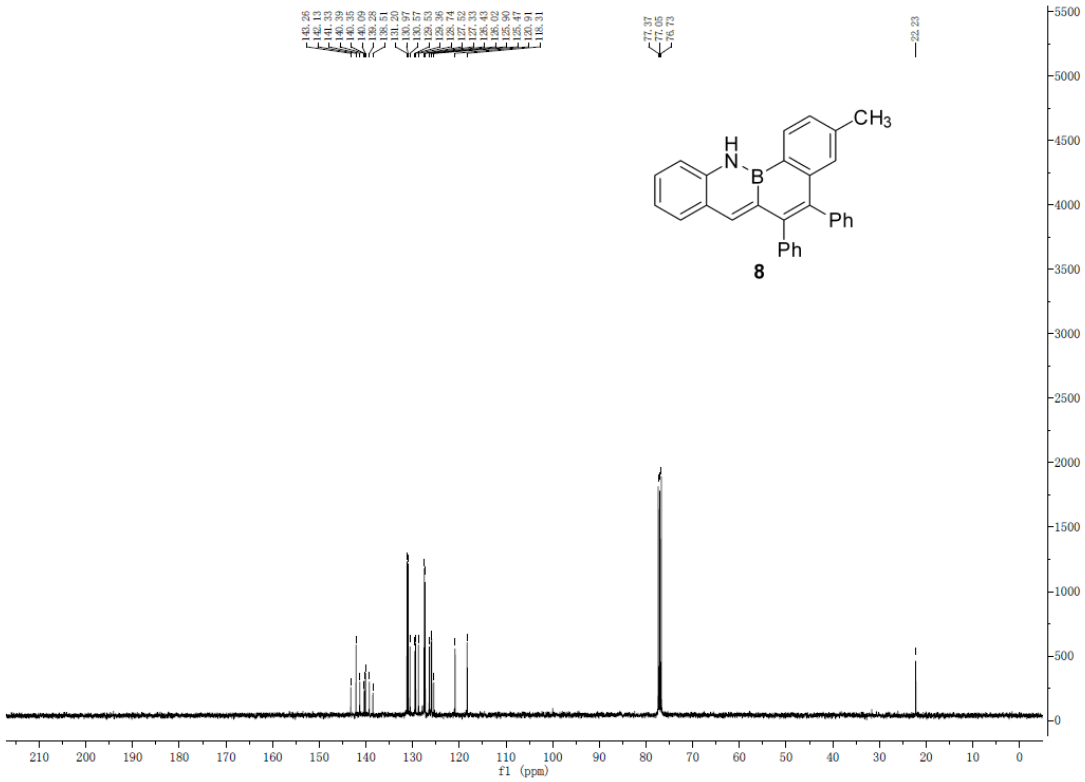

7
f1 (ppm)

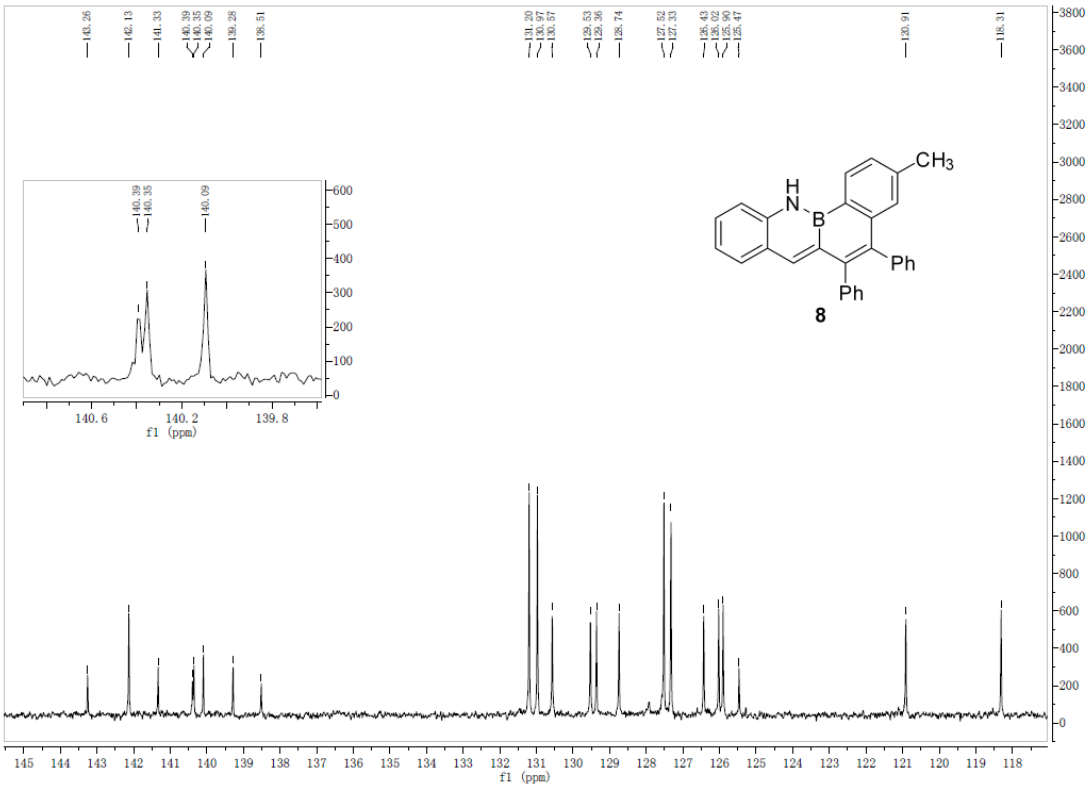

7
f1 (ppm)

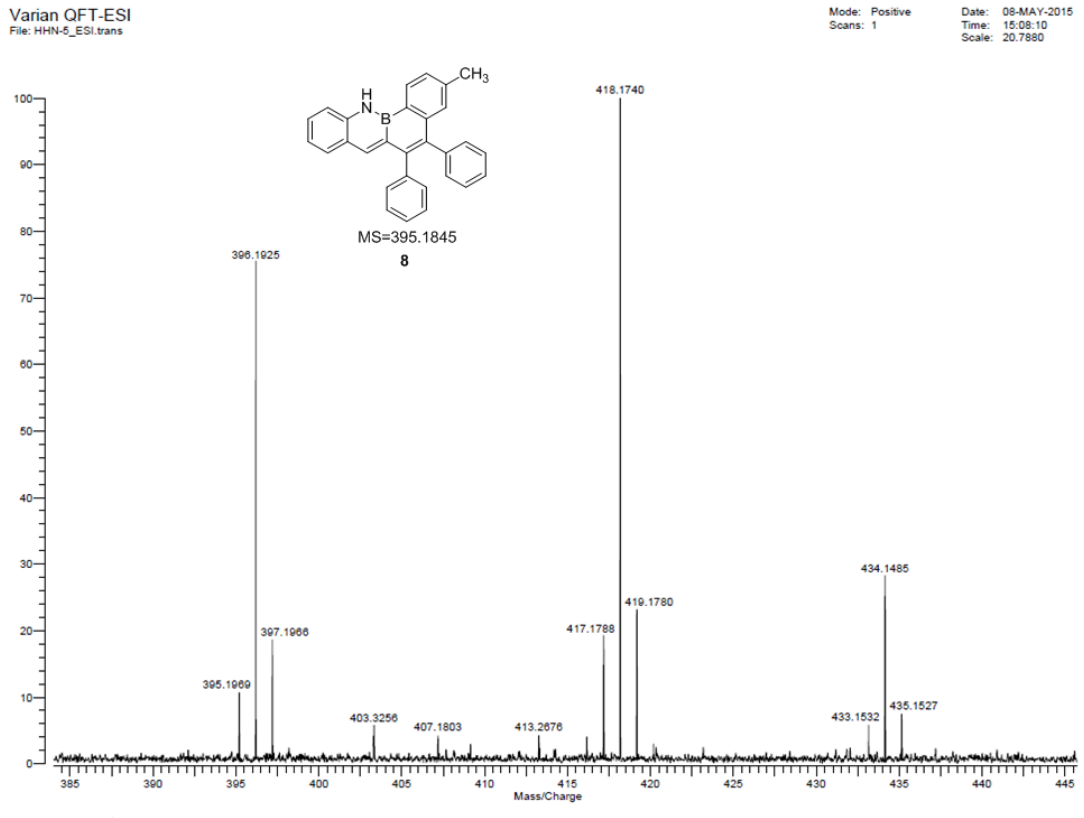

Varian QFT-ESI
File: HHN-4_ESI.trans
Mode: Positive
Scans: 1
Date: 08-MAY-2015
Time: 08:49:31
Scale: 58.1179
314.2078
313.2110
315.2118
321.2750
Mass/Charge
MS=313.2002
7

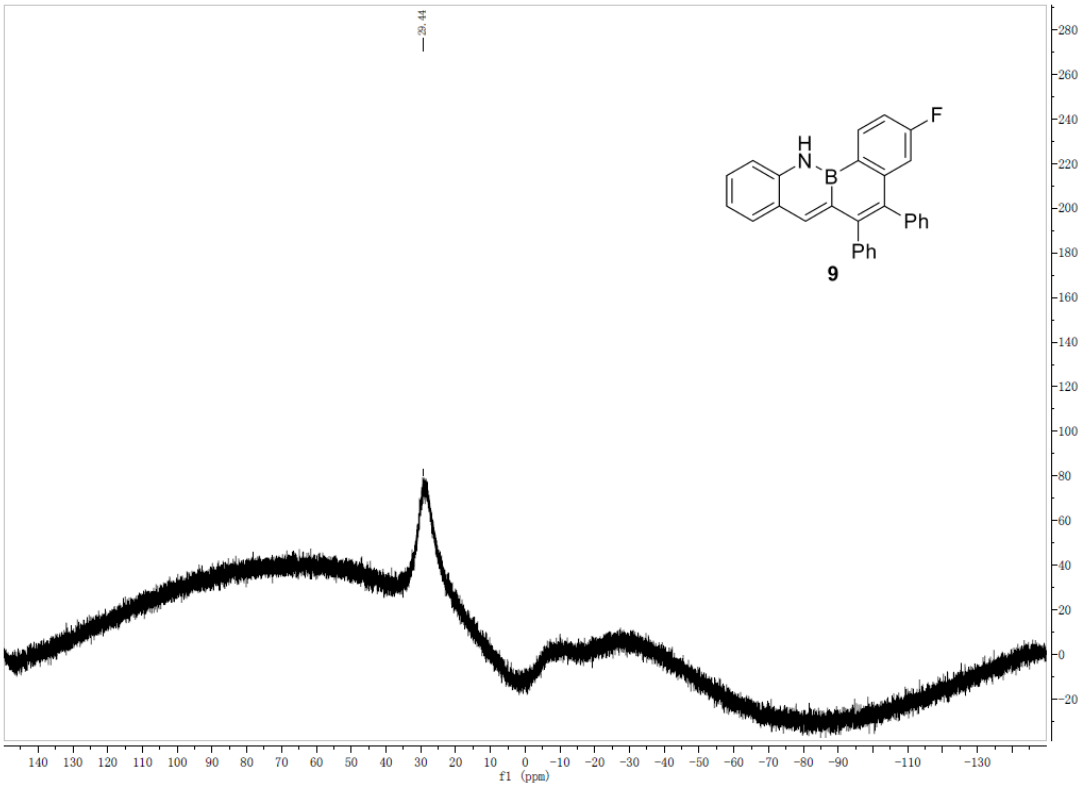

29.21
f1 (ppm)
8

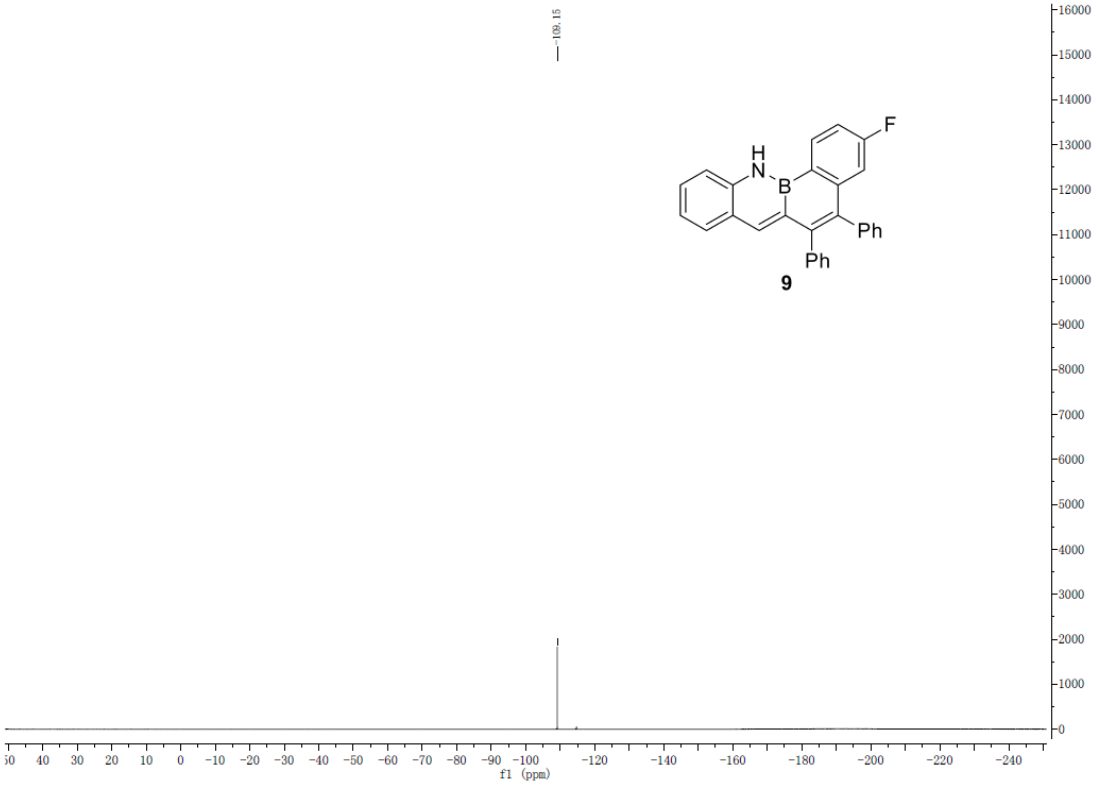

8.81
8.24
8.22
7.89
7.62
7.60
7.52
7.50
7.48
7.46
7.28
7.16
7.14
7.12
7.09
7.08
7.06
7.04
2.28
CH3
H
N
B
Ph
Ph
8
f1 (ppm)

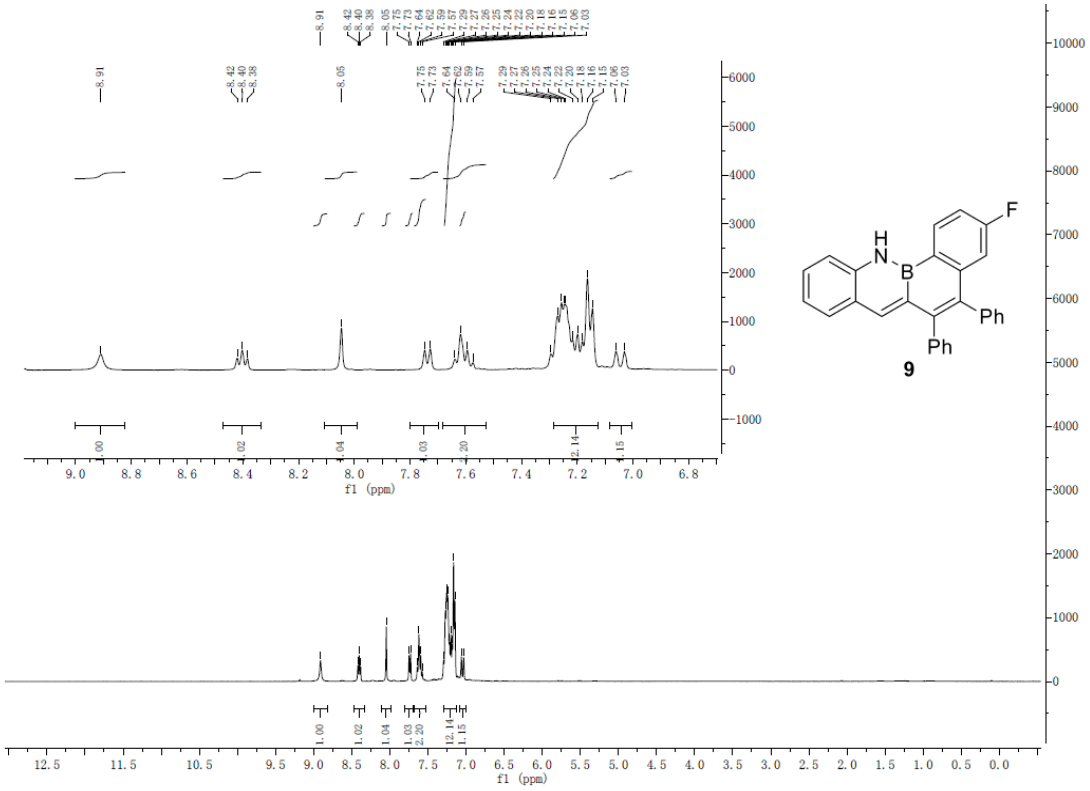

143.26
142.15
141.33
140.39
140.35
140.09
139.26
138.51
131.20
130.97
130.77
130.53
130.36
128.74
127.52
127.33
126.43
125.02
125.90
125.47
120.91
118.31
77.37
77.05
76.73
22.23
CH3
H
N
B
Ph
Ph
8
f1 (ppm)


143.26
142.13
141.33
140.39
140.35
140.09
138.28
138.51
131.20
130.97
130.57
129.53
129.36
128.74
127.52
127.33
126.43
126.02
125.56
125.47
120.91
118.31
CH3
H
N
B
Ph
Ph
8
f1 (ppm)

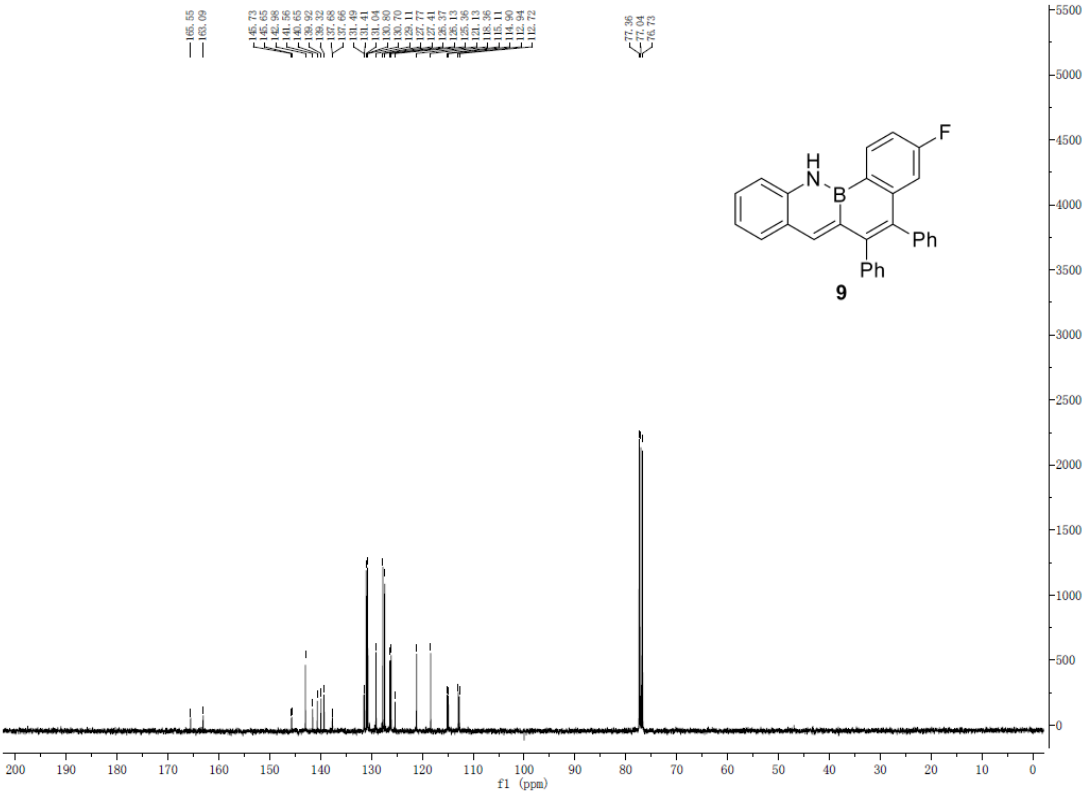

Varian QFT-ESI
File: HHN-5_ESI.trans
Mode: Positive
Scans: 1
Date: 08-MAY-2015
Time: 15:08:10
Scale: 20.7880
CH3
H
N
B
MS=395.1845
8
418.1740
396.1925
434.1485
419.1780
417.1788
397.1966
395.1969
435.1527
433.1532
403.3256
407.1803
413.2676
Mass/Charge


29.44
F
H
N
B
Ph
Ph
9
f1 (ppm)

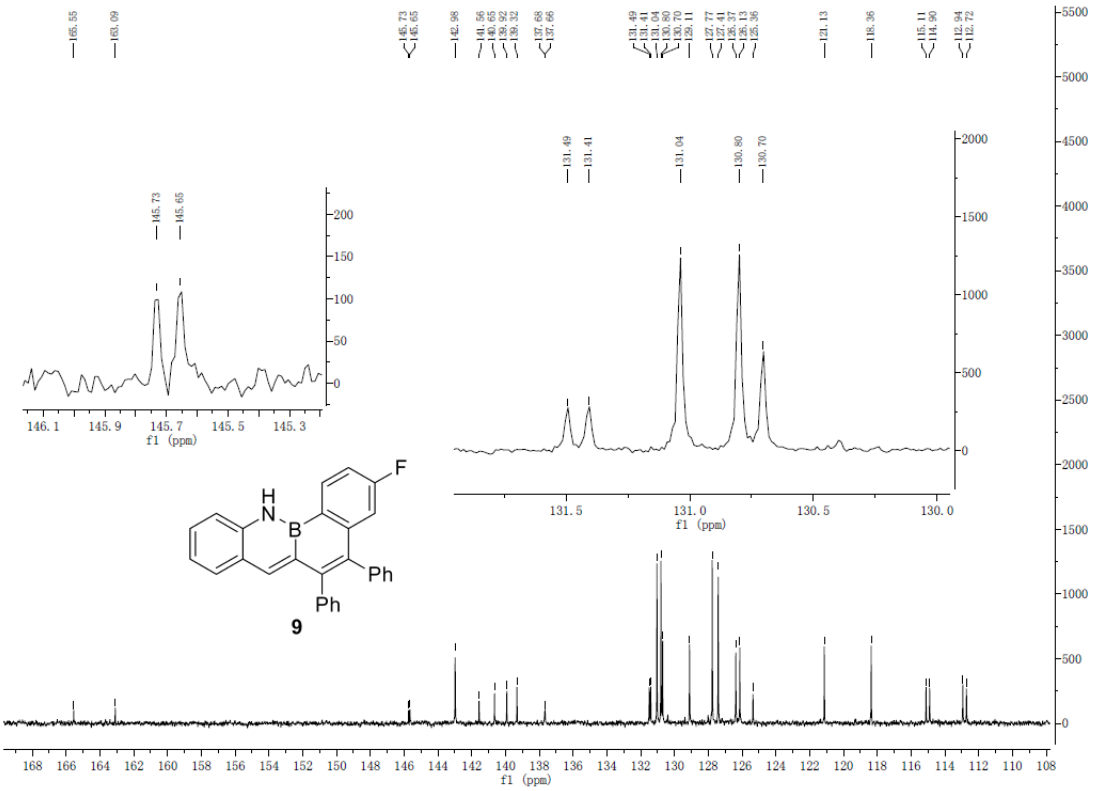

-109.15
F
H
N
B
Ph
Ph
9
f1 (ppm)

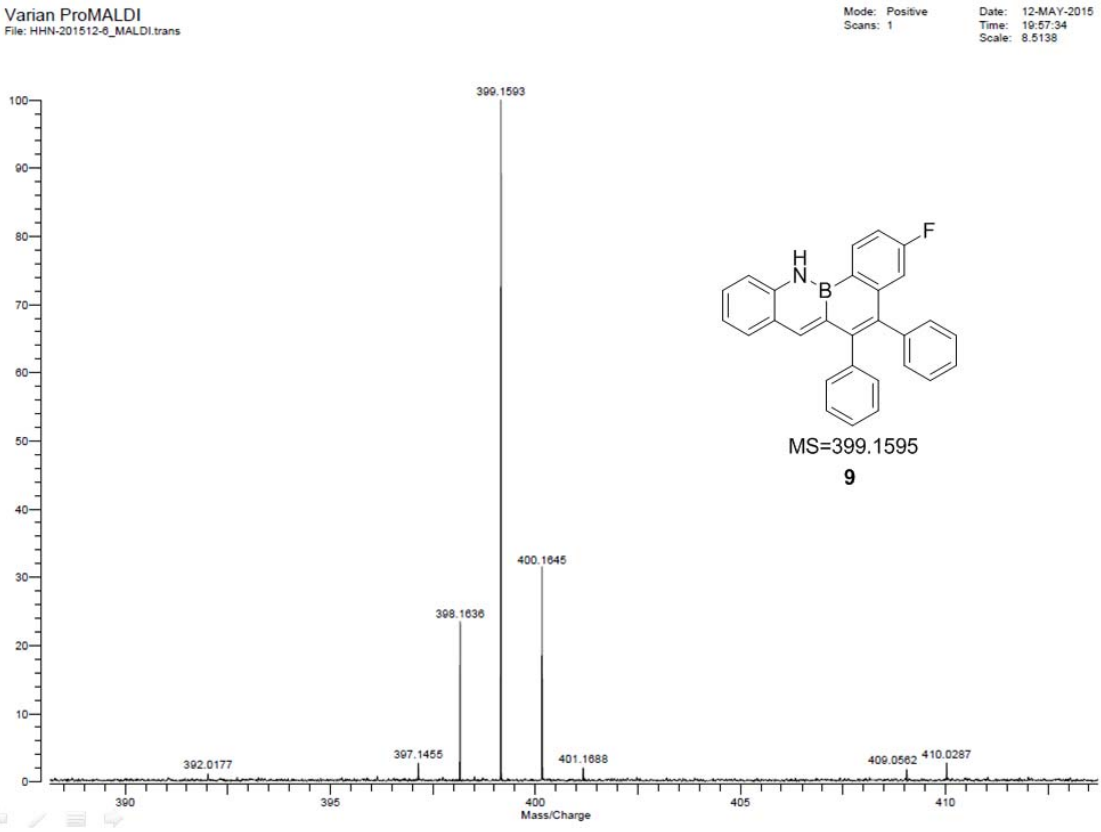


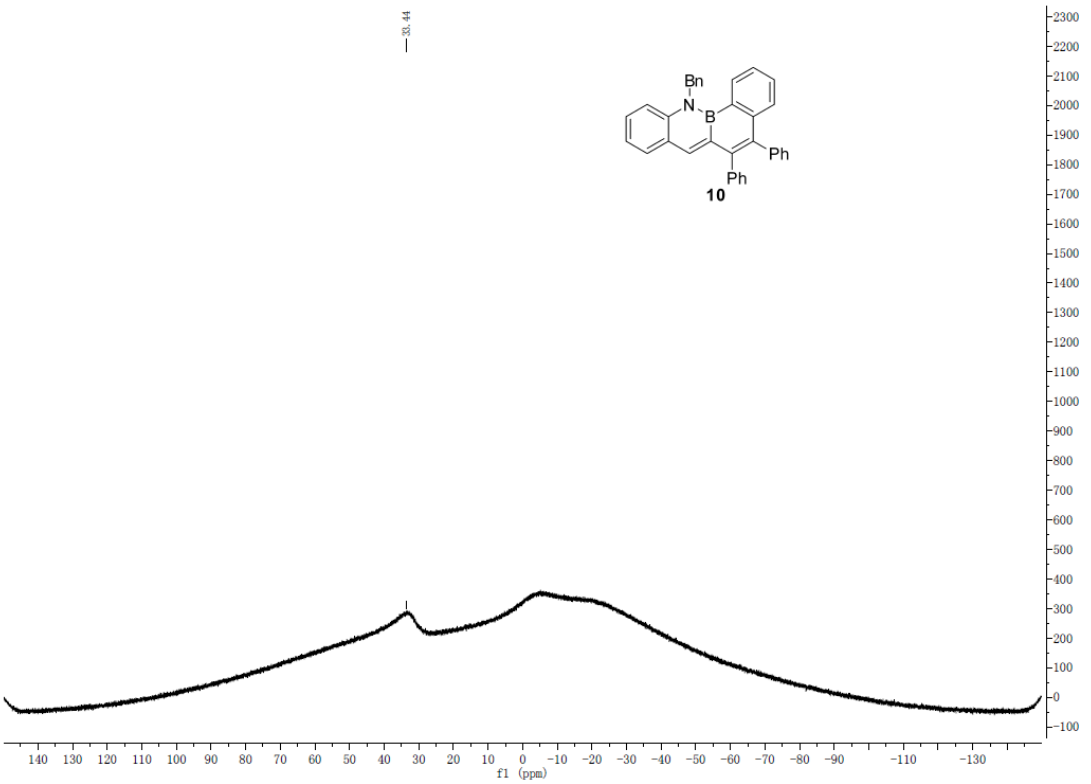
9

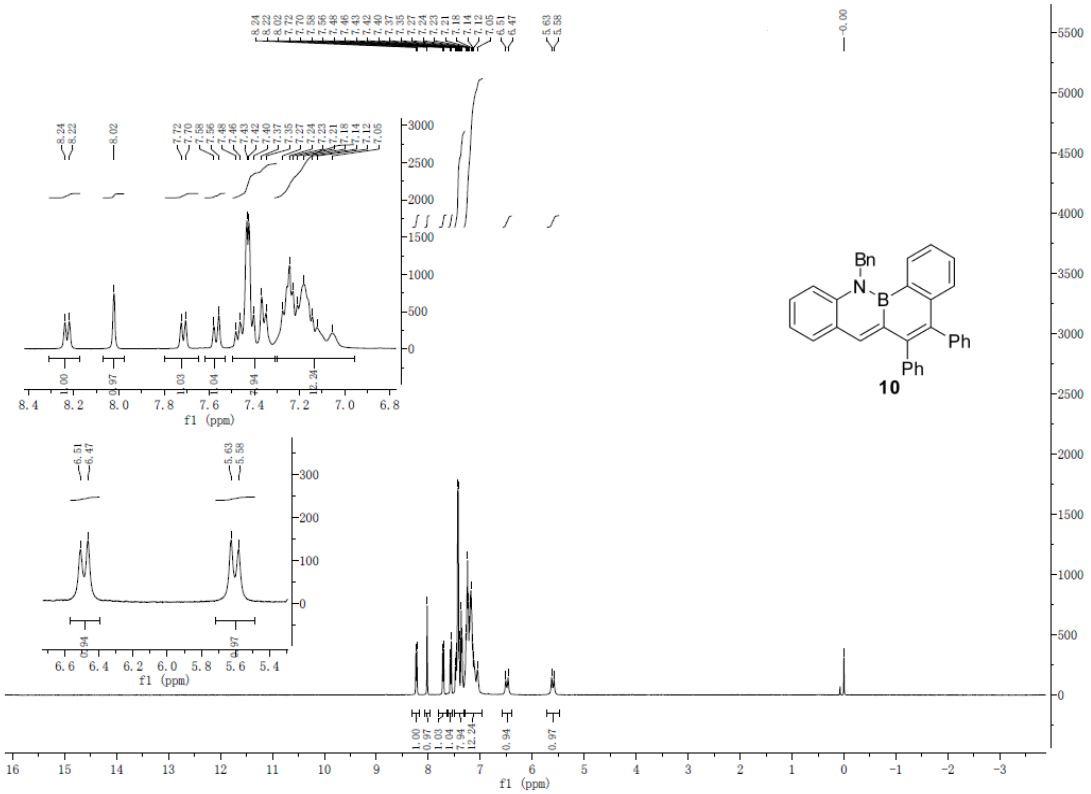


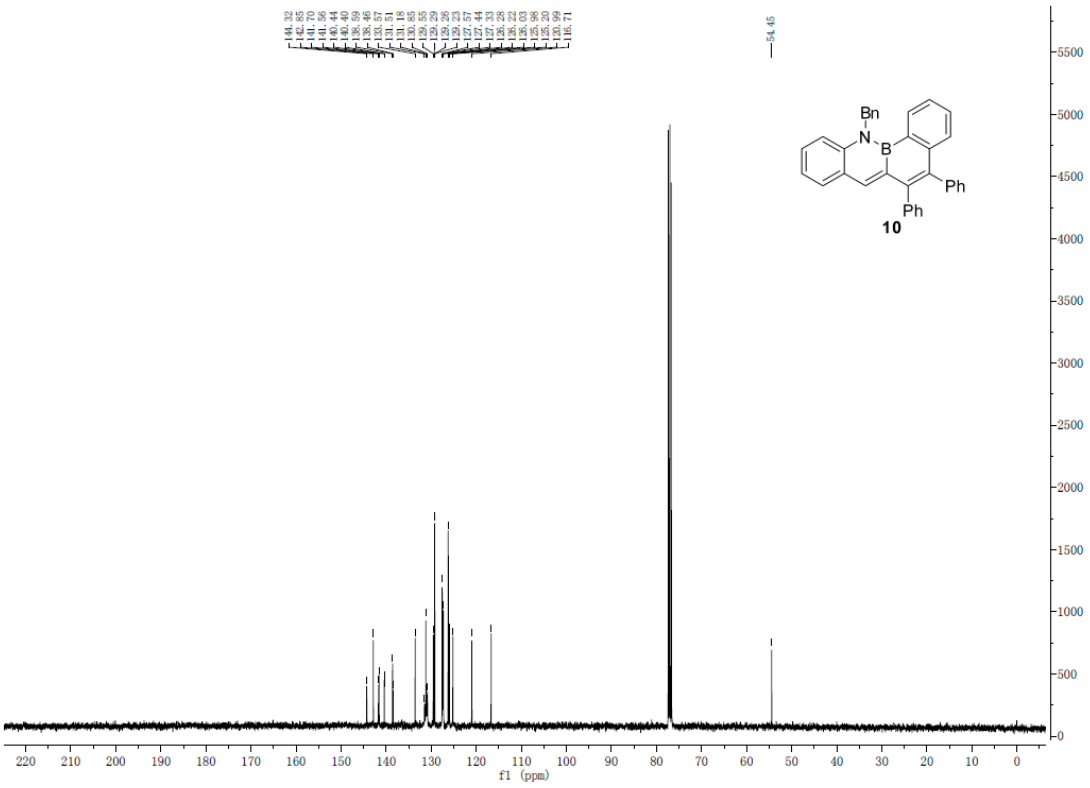
9

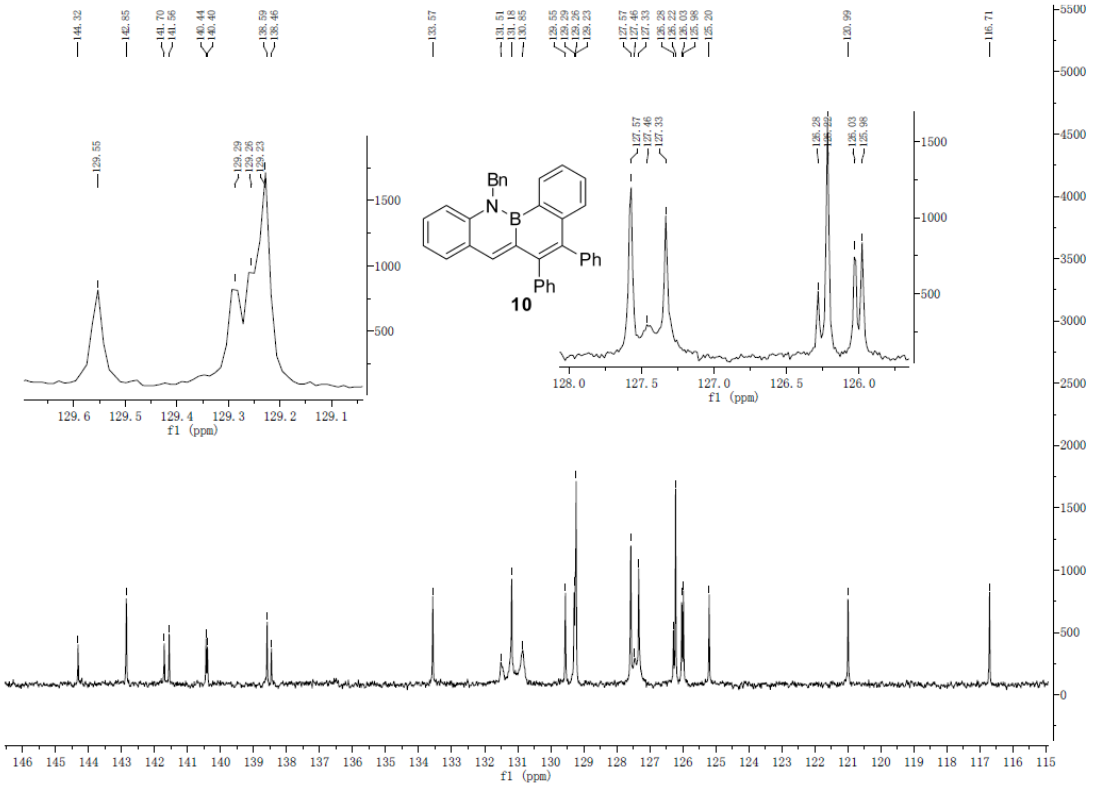

165.55
163.09
145.73
145.65
142.98
141.56
140.65
139.92
139.32
137.68
137.46
131.49
131.41
131.04
130.80
130.70
129.11
127.77
127.41
126.37
126.13
125.36
121.13
118.36
115.11
114.90
112.94
112.72
F
H
N
B
Ph
Ph
9
f1 (ppm)

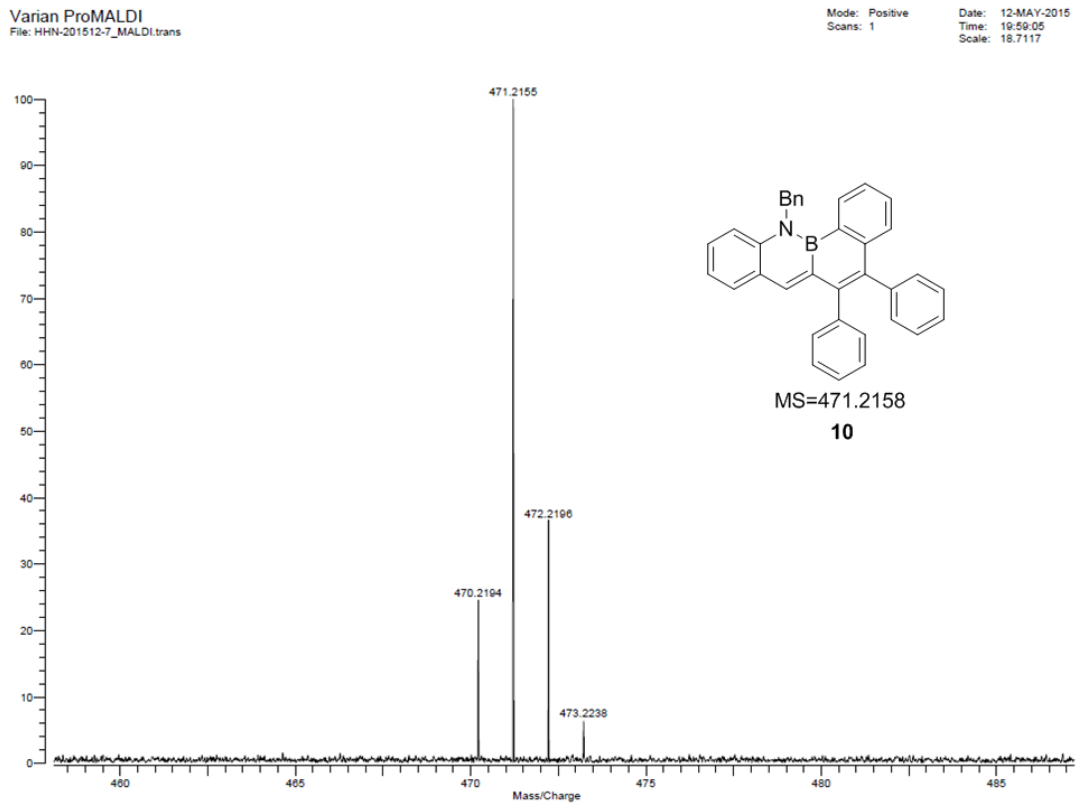

Varian ProMALDI
File: HHN-201512-6_MALDI.trans
Mode: Positive
Scans: 1
Date: 12-MAY-2015
Time: 19:57:34
Scale: 8.5138
399.1593
400.1645
398.1636
392.0177
397.1455
401.1688
409.0562
410.0287
Mass/Charge
MS=399.1595
9

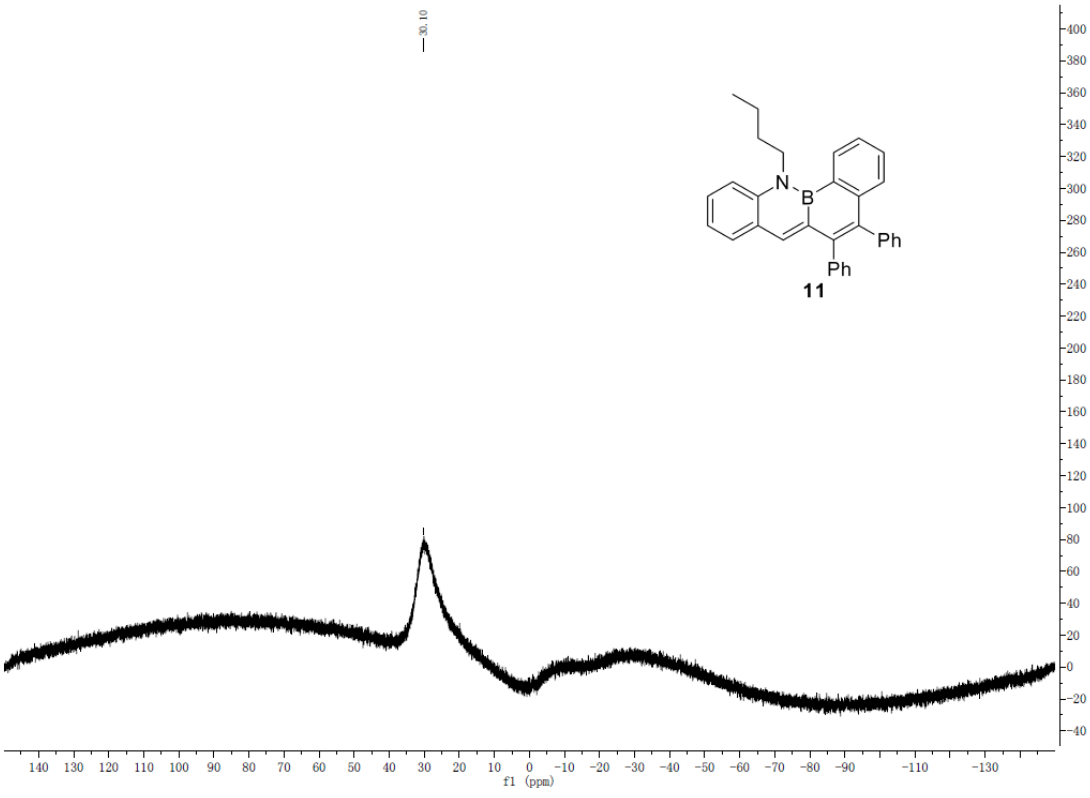

33.44
Bn
N
B
Ph
Ph
10
f1 (ppm)

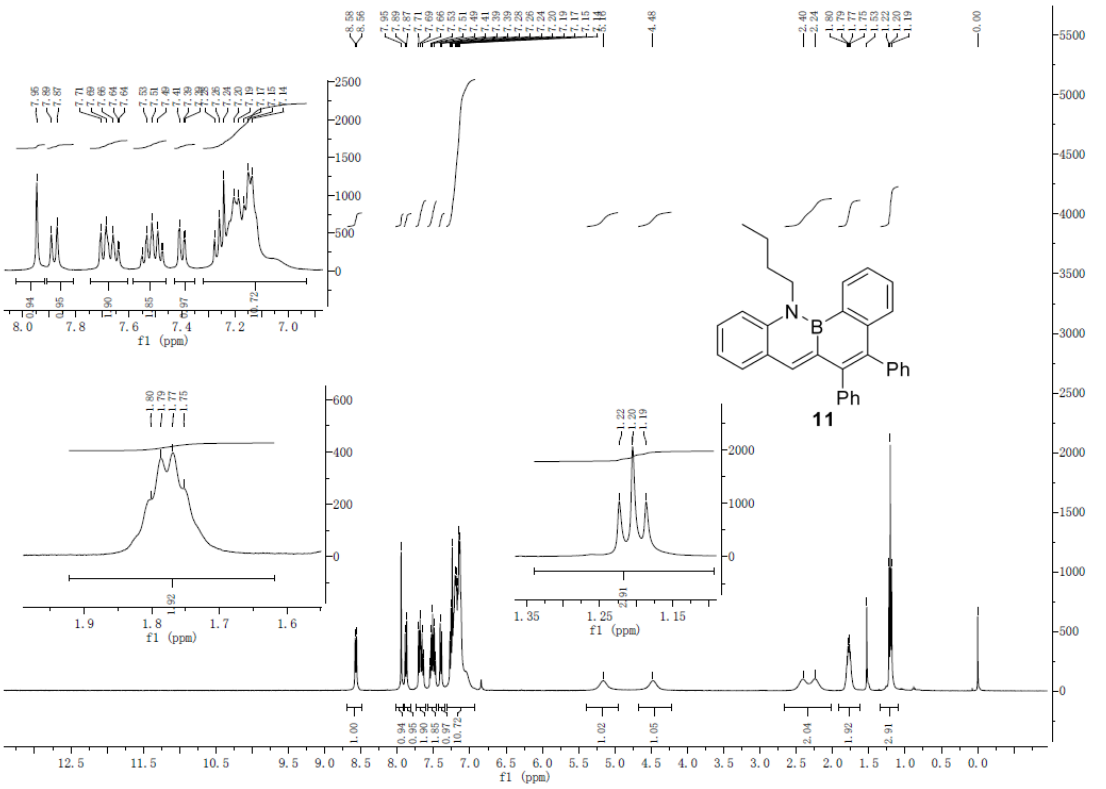

8.24
8.22
8.02
7.72
7.70
7.58
7.56
7.48
7.46
7.43
7.42
7.40
7.37
7.35
7.27
7.24
7.23
7.21
7.18
7.14
7.12
7.05
6.51
6.47
5.63
5.58
0.00
Bn
N
B
Ph
Ph
10
f1 (ppm)

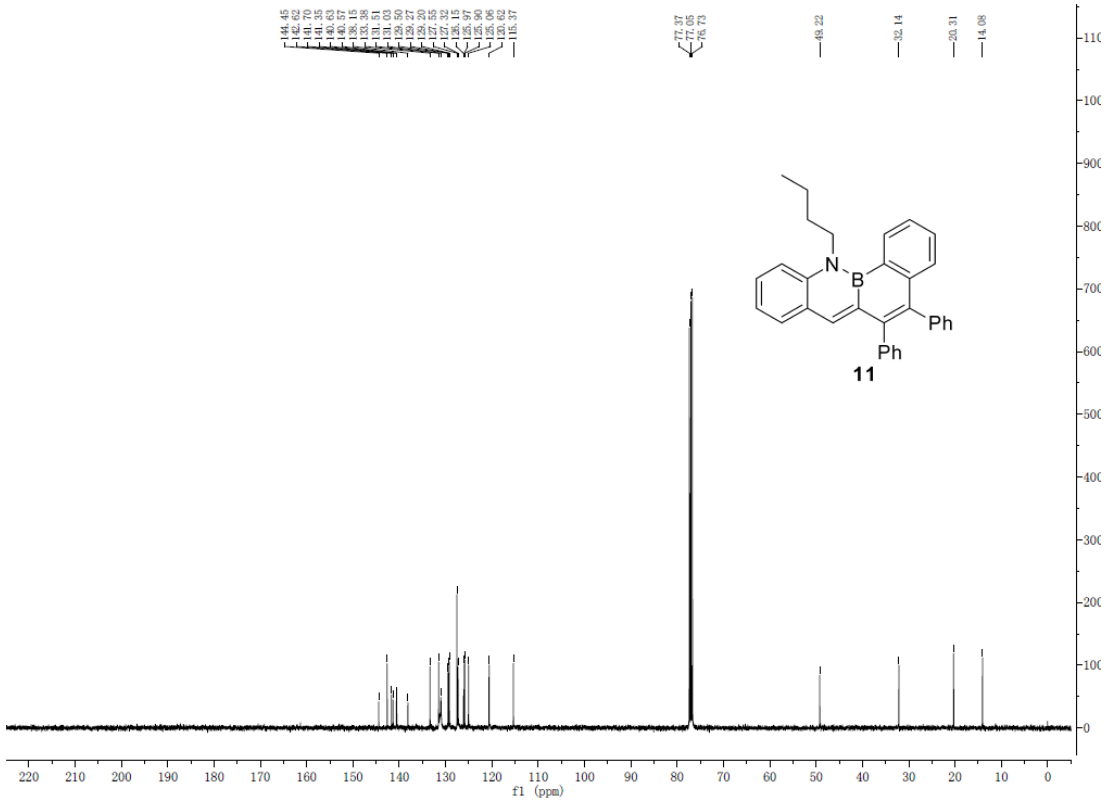

Bn
N
B
Ph
Ph
10
f1 (ppm)

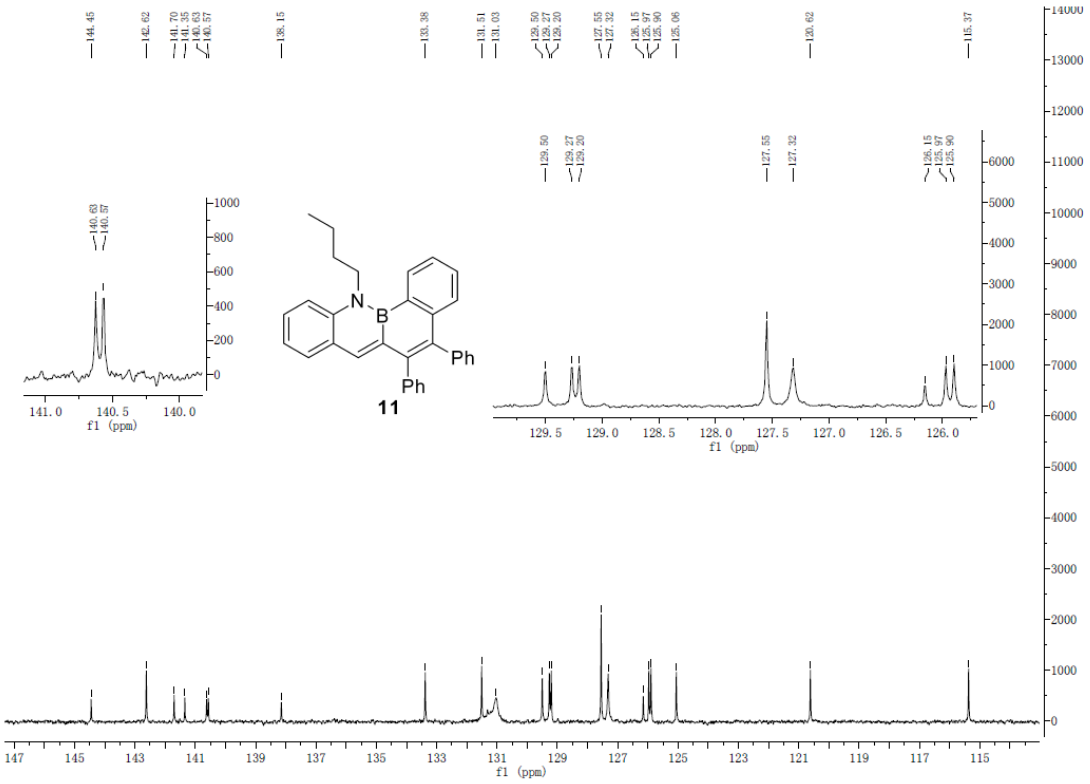

Bn
N
B
Ph
Ph
10
f1 (ppm)
f1 (ppm)
f1 (ppm)

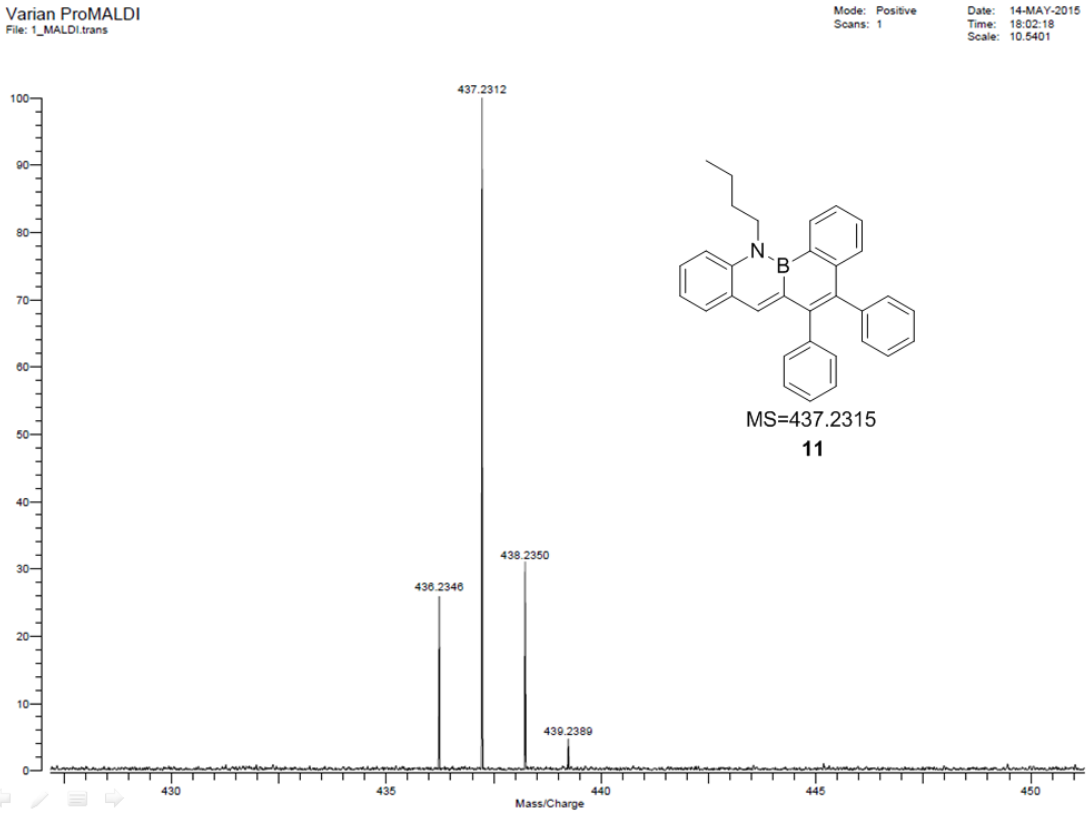

Varian ProMALDI
File: HHN-201512-7_MALDI.trans
Mode: Positive
Scans: 1
Date: 12-MAY-2015
Time: 19:59:05
Scale: 18.7117
471.2155
472.2196
470.2194
473.2238
Mass/Charge
Bn
N
B
MS=471.2158
10

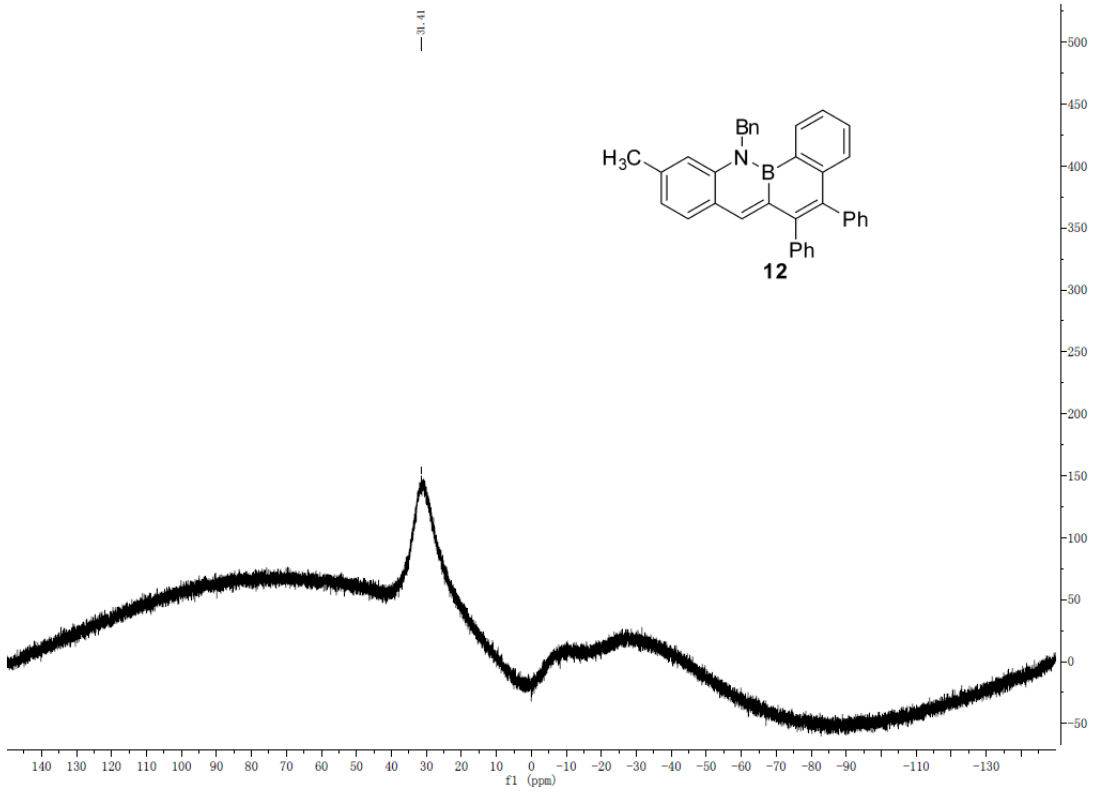

30.10
N
B
Ph
Ph
11
f1 (ppm)

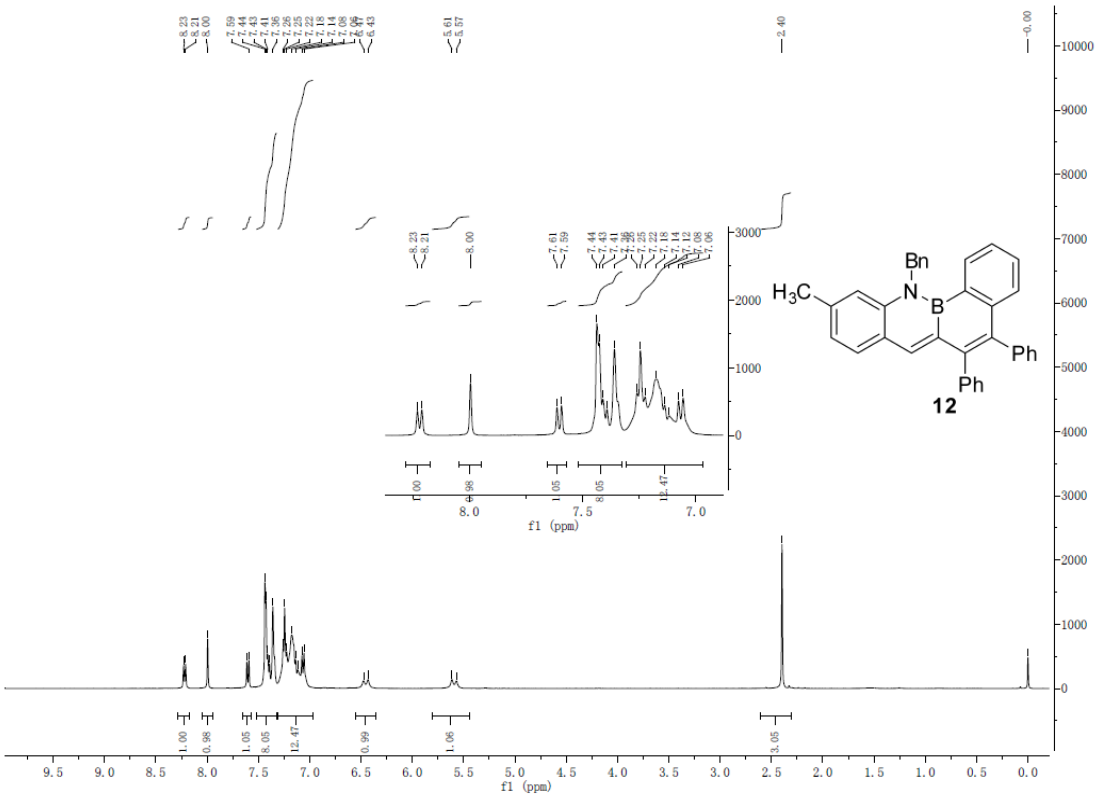

11
f1 (ppm)

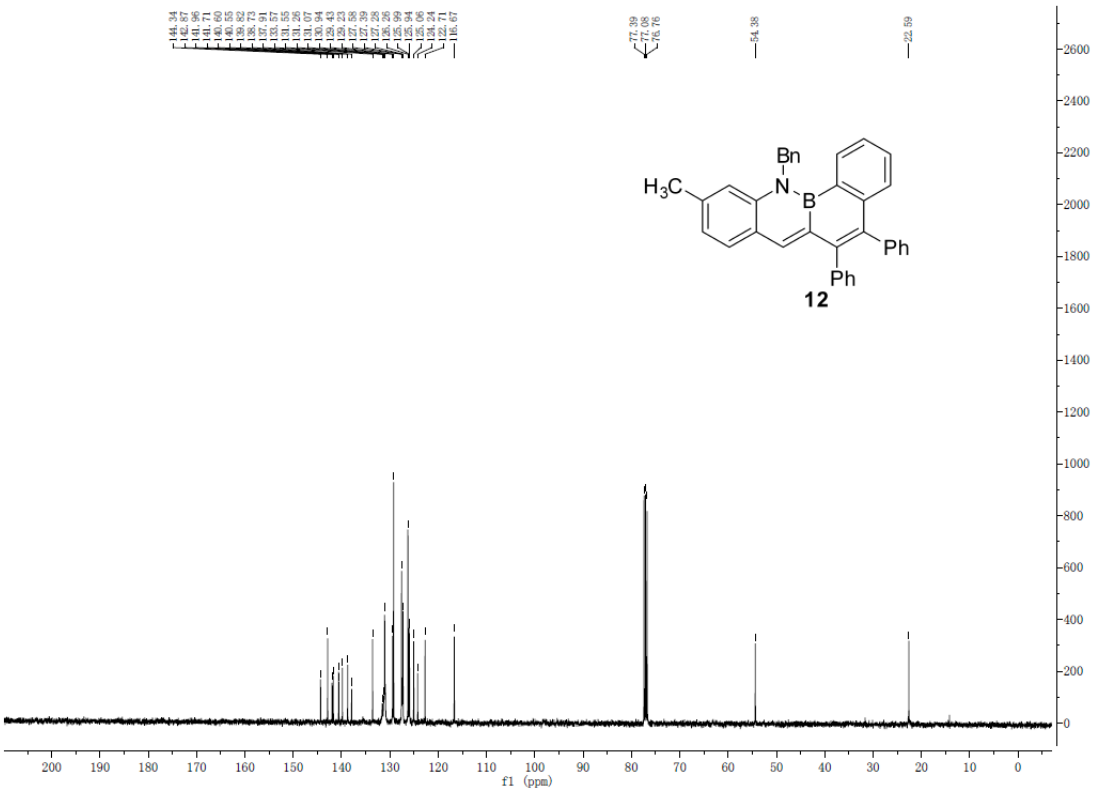

11
f1 (ppm)

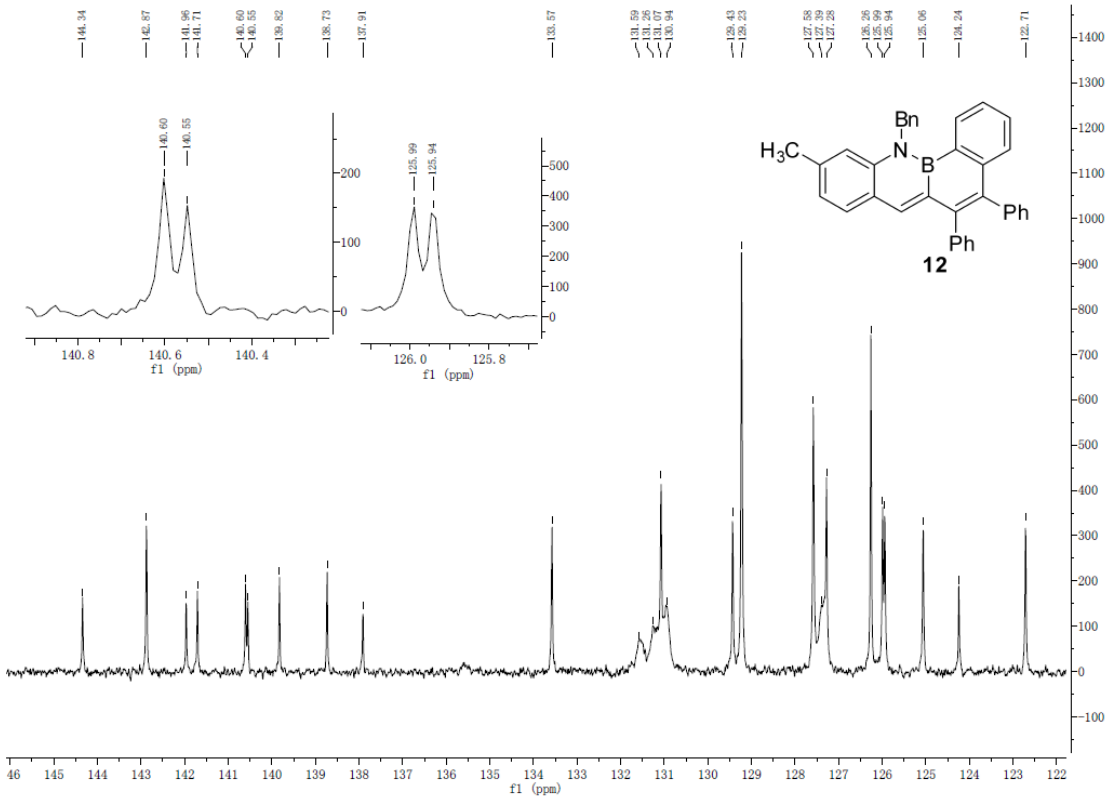

144.45
142.62
141.70
141.35
140.63
140.57
138.15
133.38
131.51
131.03
129.50
129.27
129.20
127.55
127.32
126.15
125.97
125.90
125.06
120.62
115.37
140.63
140.57
141.0
140.5
140.0
f1 (ppm)
N
B
Ph
Ph
11
129.50
129.27
129.20
127.55
127.32
126.15
125.97
125.90
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
f1 (ppm)
147
145
143
141
139
137
135
133
131
129
127
125
123
121
119
117
115
f1 (ppm)

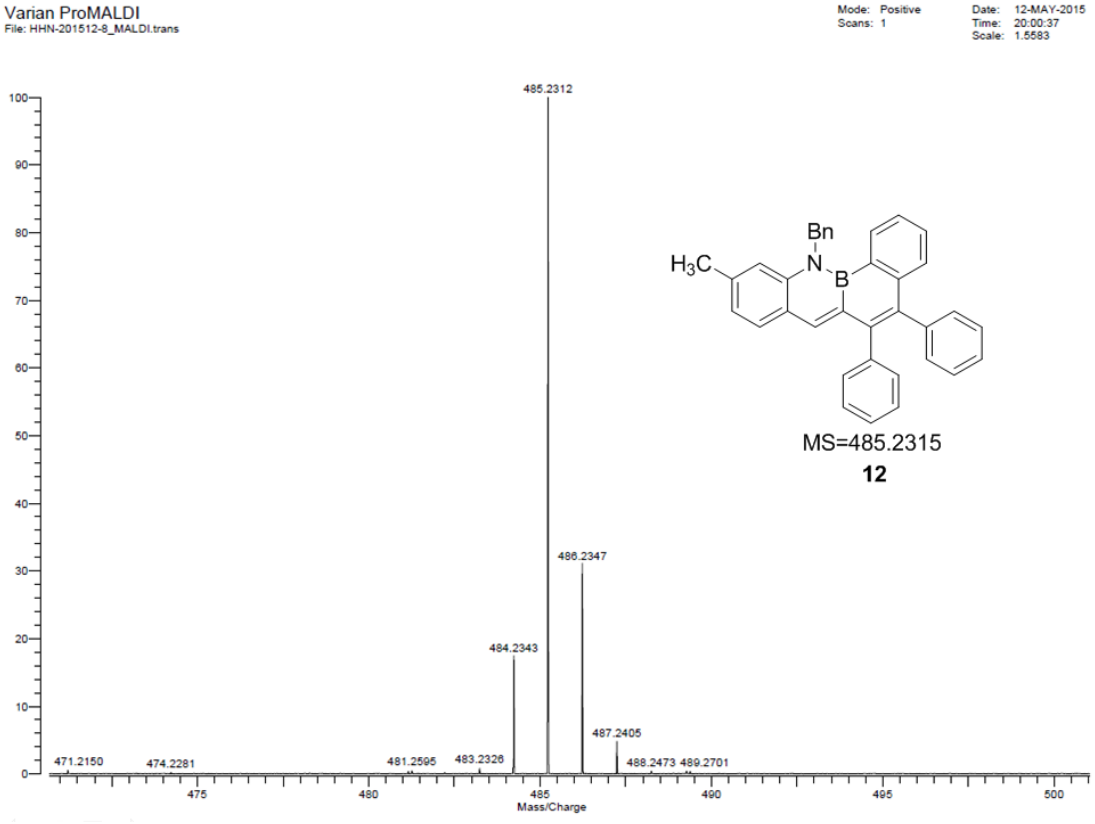

Varian ProMALDI
File: 1_MALDI.trans
Mode: Positive
Scans: 1
Date: 14-MAY-2015
Time: 18:02:18
Scale: 10.5401
437.2312
438.2350
436.2346
439.2389
N
B
MS=437.2315
11
Mass/Charge

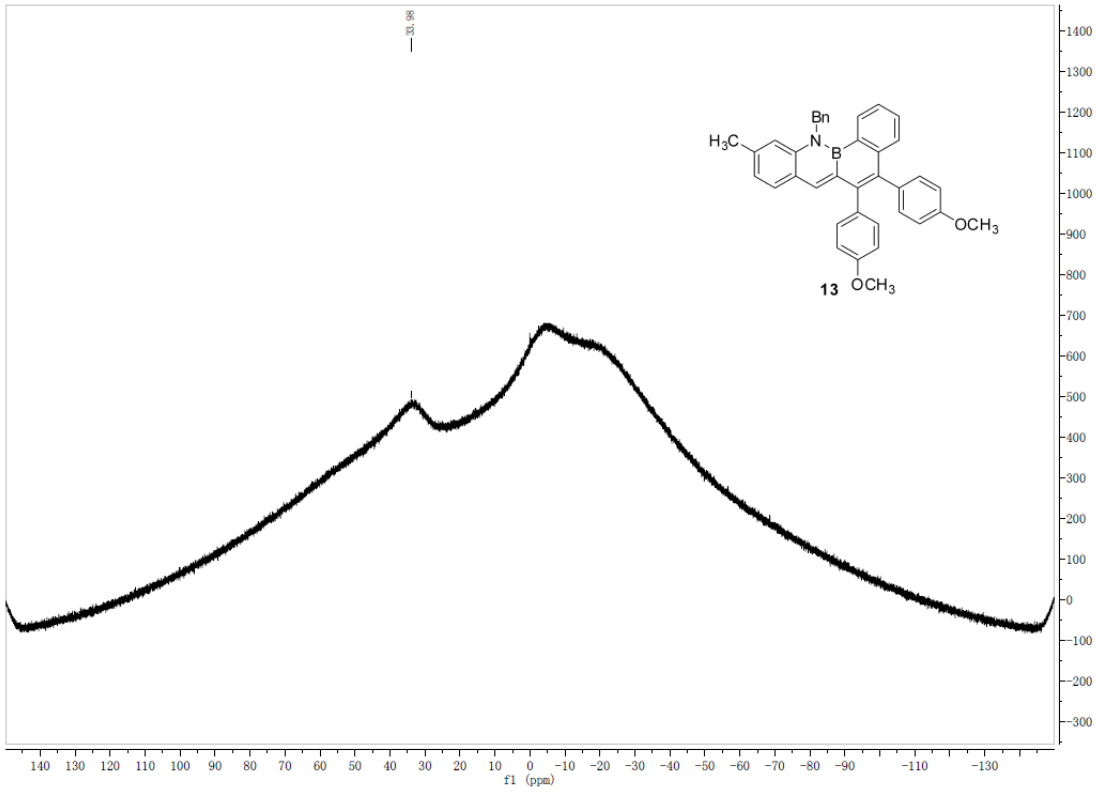

31.41
Bn
N
B
H3C
Ph
Ph
12
f1 (ppm)

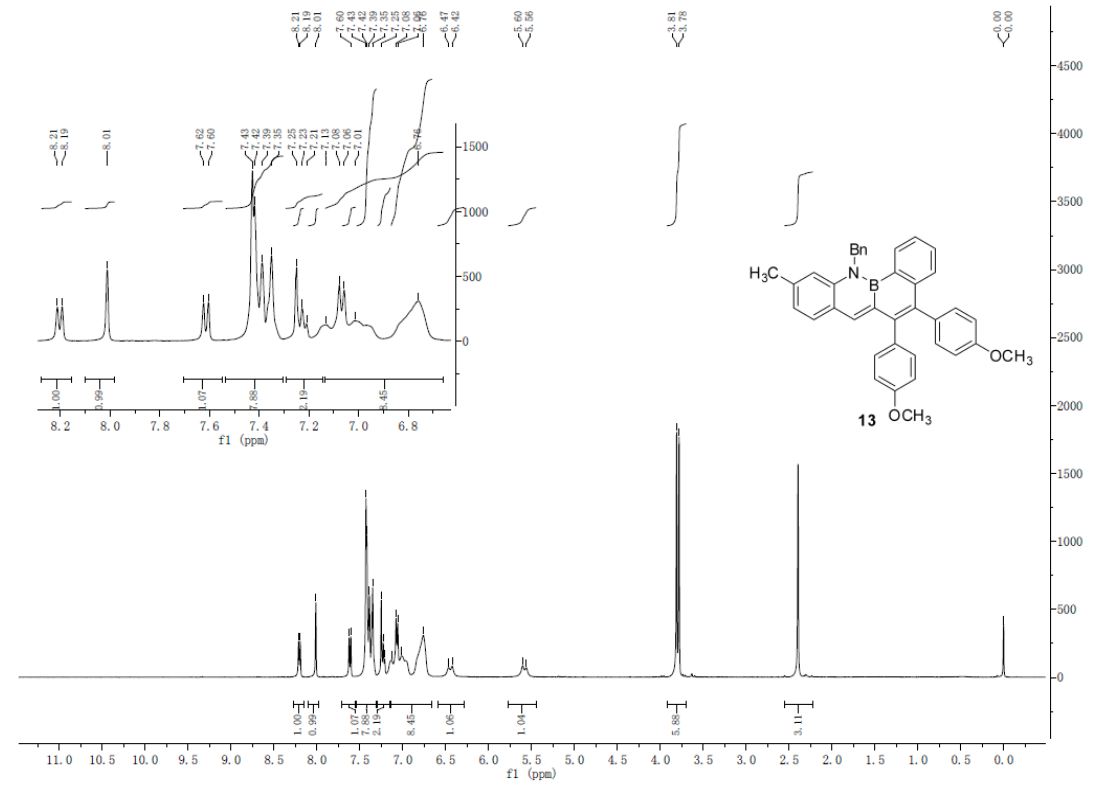

8.23
8.21
8.00
7.89
7.44
7.43
7.41
7.36
7.28
7.25
7.22
7.18
7.14
7.08
6.47
6.43
5.61
5.57
2.40
0.00
Bn
N
B
H3C
Ph
Ph
12
f1 (ppm)

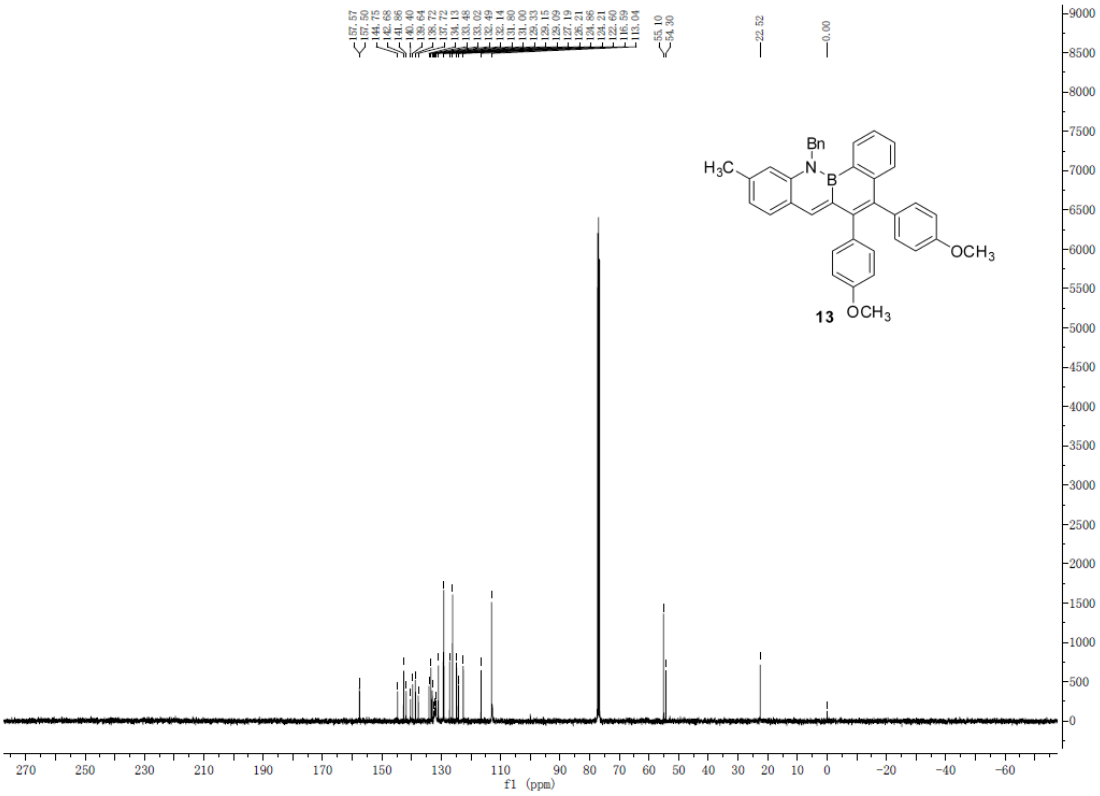

144.34
142.87
141.96
141.71
140.60
140.55
139.82
138.73
137.91
133.57
131.59
131.26
131.07
130.94
129.43
129.23
127.58
127.39
127.28
126.26
125.99
125.94
125.06
124.24
122.71
116.67
77.39
77.08
76.76
54.38
22.59
Bn
N
B
H3C
Ph
Ph
12
f1 (ppm)

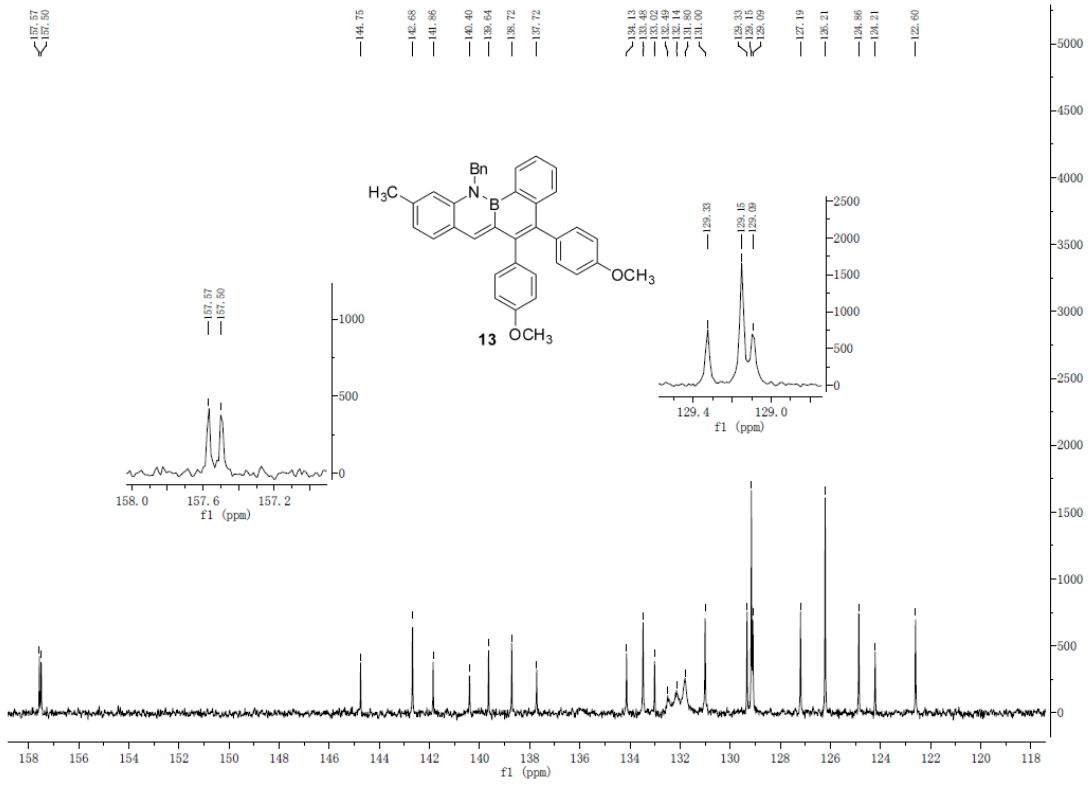

144.34
142.87
141.96
141.71
140.60
140.55
139.82
138.73
137.91
133.57
131.59
131.26
131.07
130.94
129.43
129.23
127.58
127.39
127.28
126.26
125.99
125.94
125.06
124.24
122.71
140.60
140.55
125.99
125.94
Bn
N
B
H3C
Ph
Ph
12
f1 (ppm)

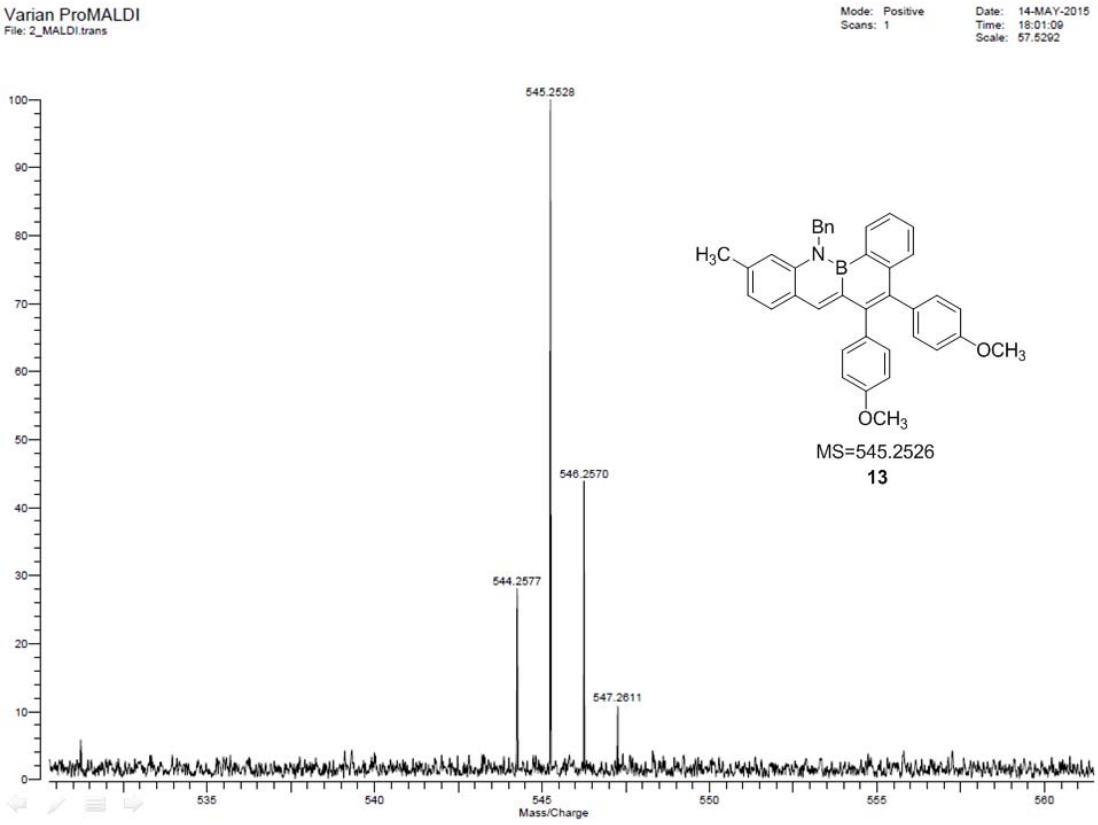

Varian ProMALDI
File: HHN-201512-8_MALDI.trans
Mode: Positive
Scans: 1
Date: 12-MAY-2015
Time: 20:00:37
Scale: 1.5583
485.2312
486.2347
484.2343
487.2405
471.2150
474.2281
481.2595
483.2326
488.2473
489.2701
Mass/Charge
Bn
N
B
H3C
MS=485.2315
12

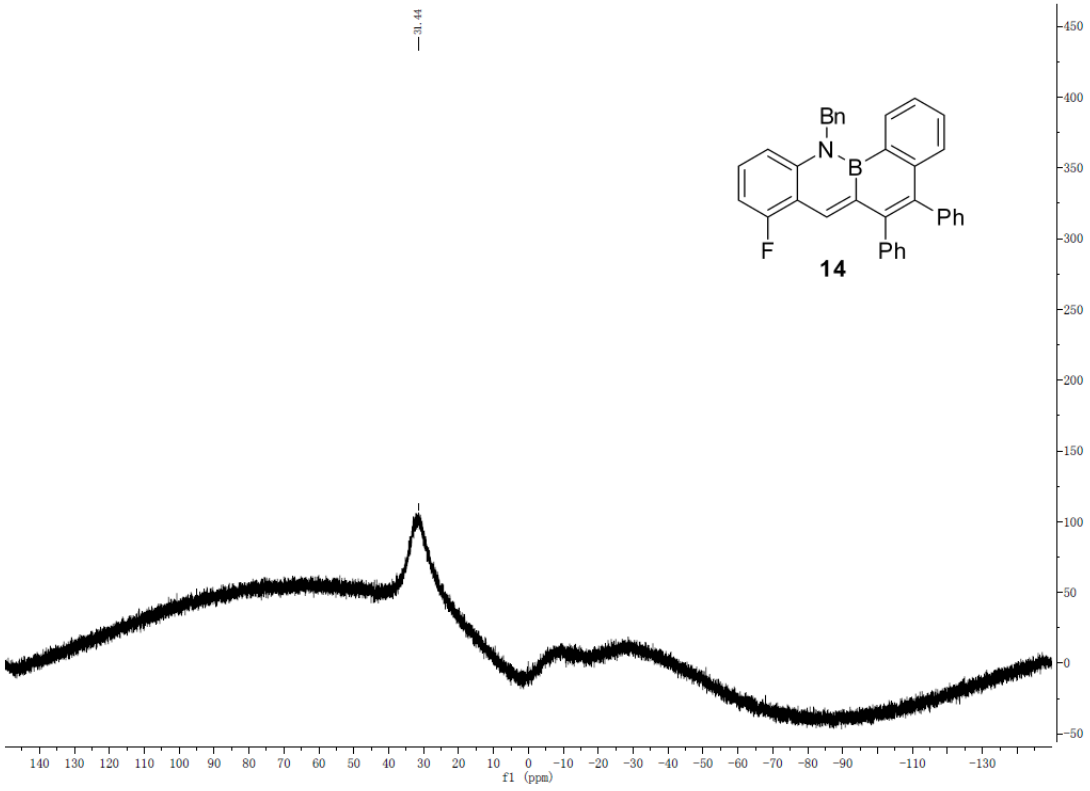

33.98
Bn
N
B
H3C
OCH3
OCH3
13
f1 (ppm)

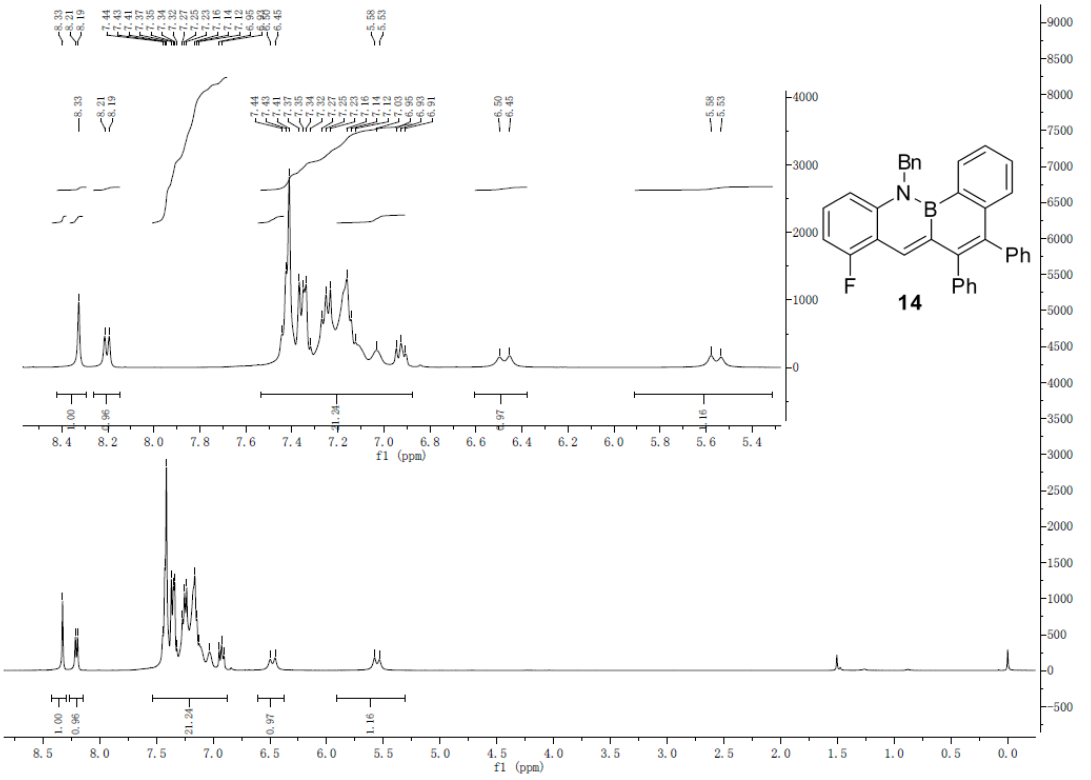

Bn
N
B
H3C
OCH3
OCH3
13
f1 (ppm)

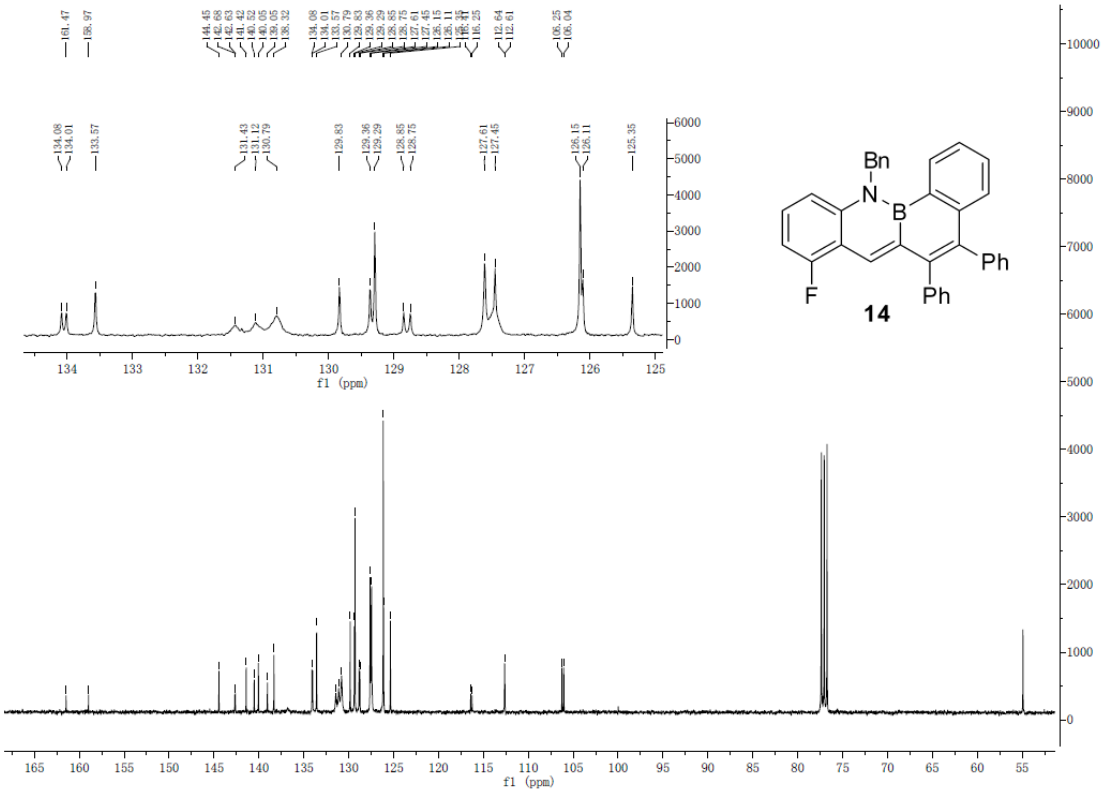

Bn
N
B
H3C
OCH3
OCH3
13
f1 (ppm)

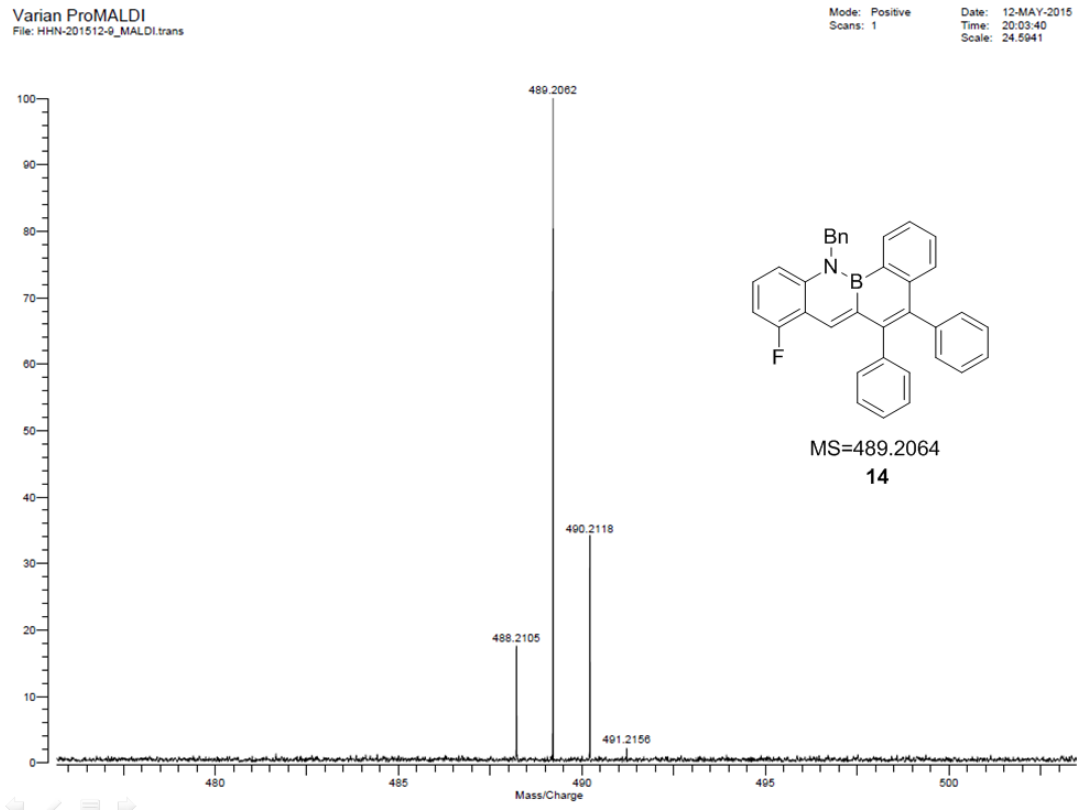

157.57
157.50
144.75
142.68
141.86
140.40
139.64
138.72
137.72
134.13
133.48
133.02
132.49
132.14
131.80
131.00
129.33
129.15
129.09
127.19
126.21
126.86
126.21
122.60
Bn
H3C
N
B
OCH3
OCH3
13
f1 (ppm)
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118

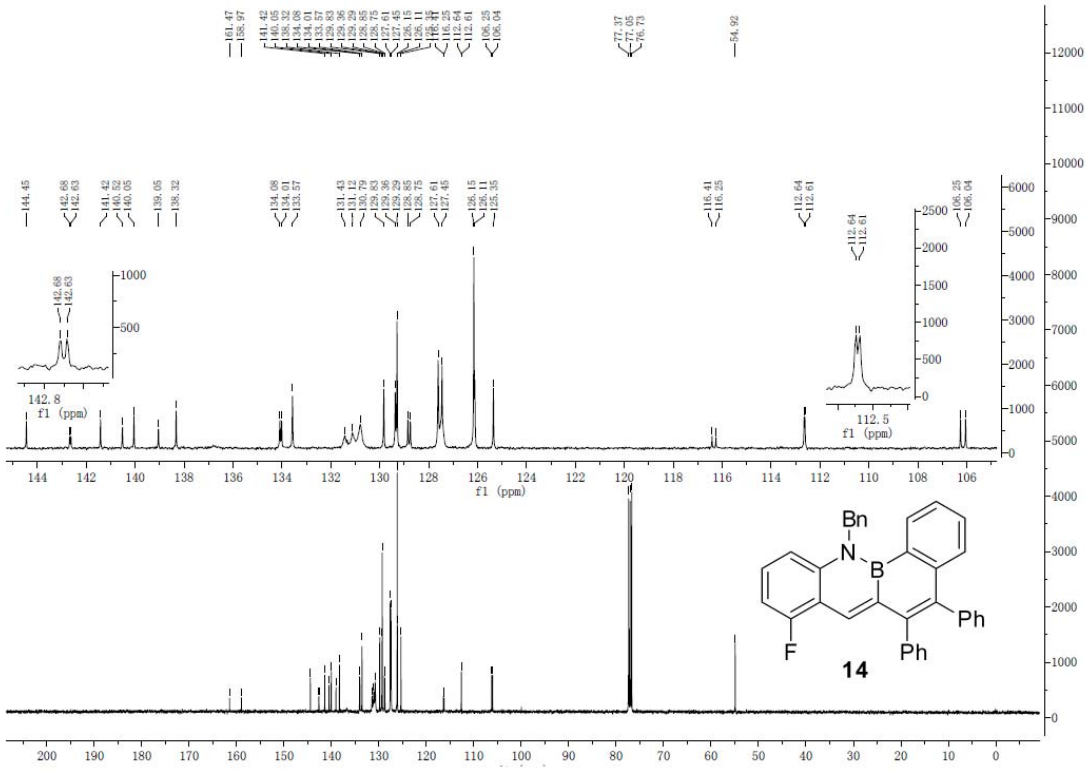

Varian ProMALDI
File: 2_MALDI.trans
Mode: Positive
Scans: 1
Date: 14-MAY-2015
Time: 18:01:09
Scale: 57.5292
545.2528
546.2570
544.2577
547.2611
Bn
H3C
N
B
OCH3
OCH3
MS=545.2526
13
Mass/Charge

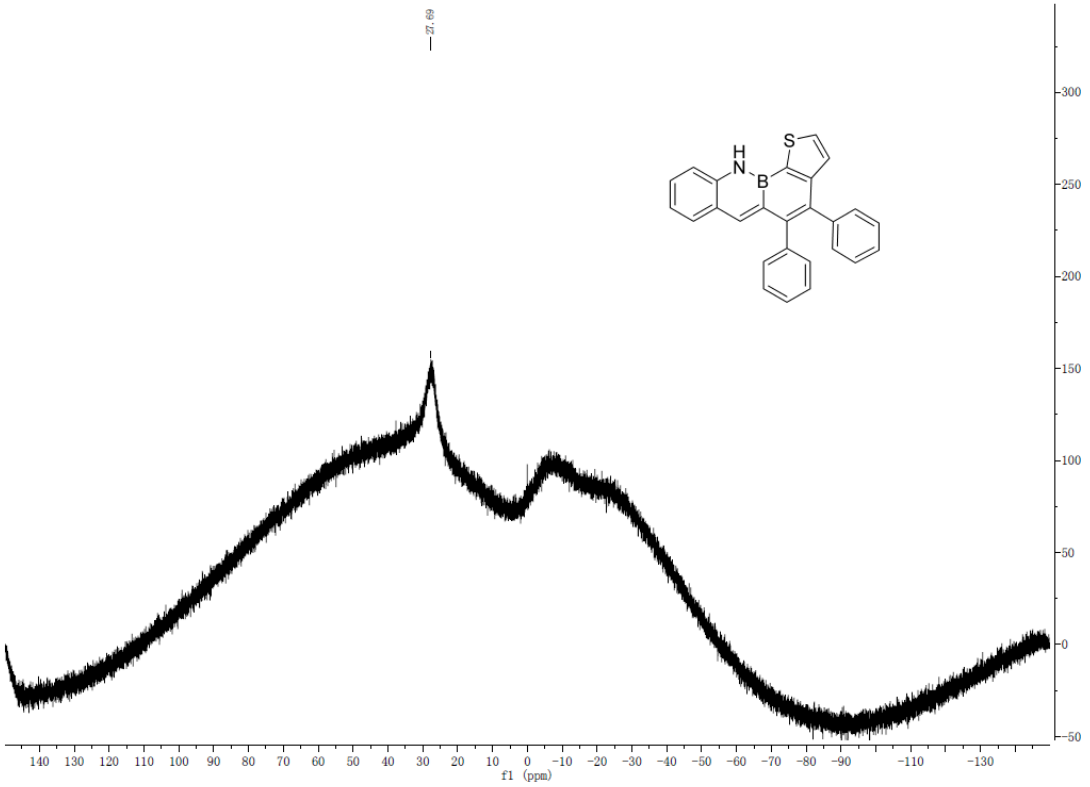

31.44
Bn
N
B
Ph
F
Ph
14
f1 (ppm)

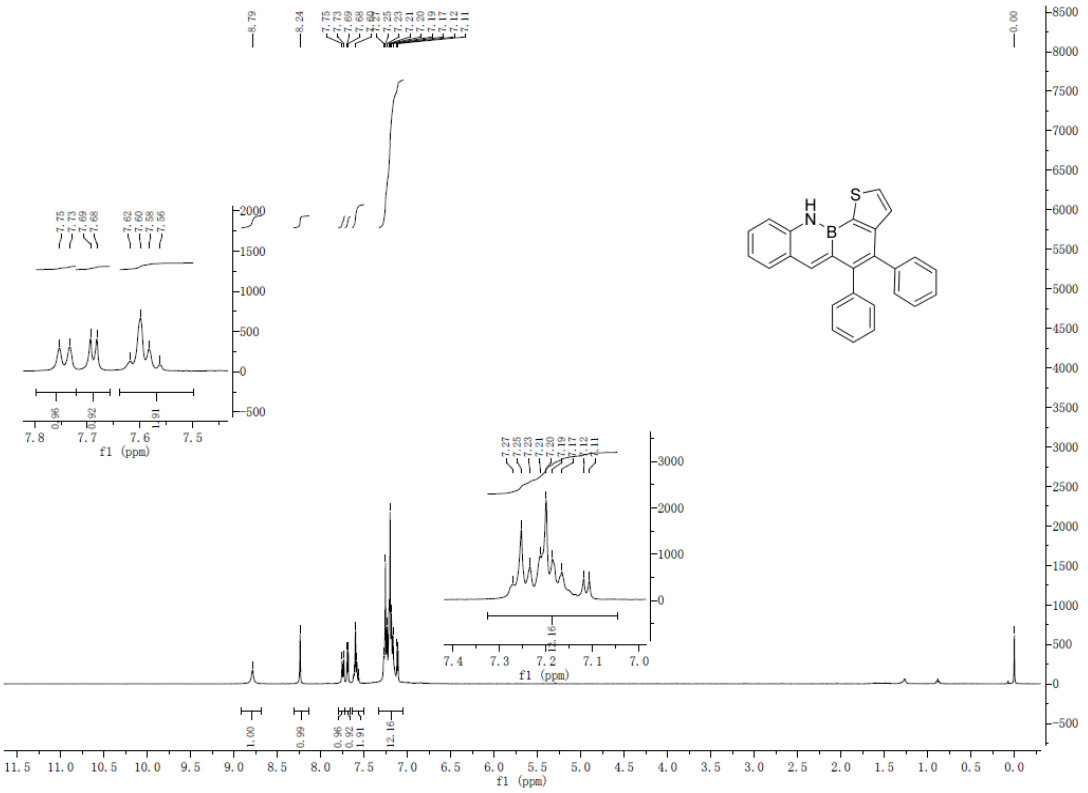

8.33
8.21
8.19
7.44
7.43
7.41
7.37
7.35
7.34
7.32
7.27
7.25
7.23
7.16
7.14
7.12
6.95
6.93
6.91
6.50
6.45
5.58
5.53
1.00
0.96
21.24
0.97
1.16
Bn
N
B
Ph
F
Ph
14
f1 (ppm)

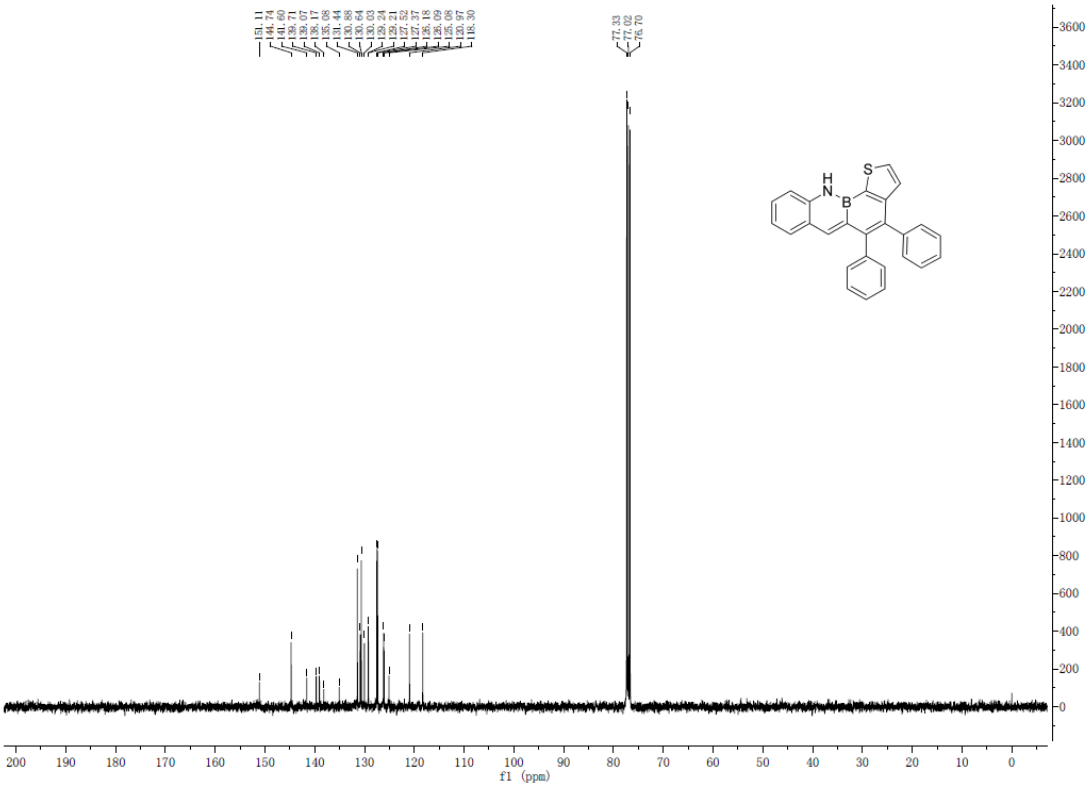

Bn
N
B
Ph
F
Ph
14
f1 (ppm)
f1 (ppm)

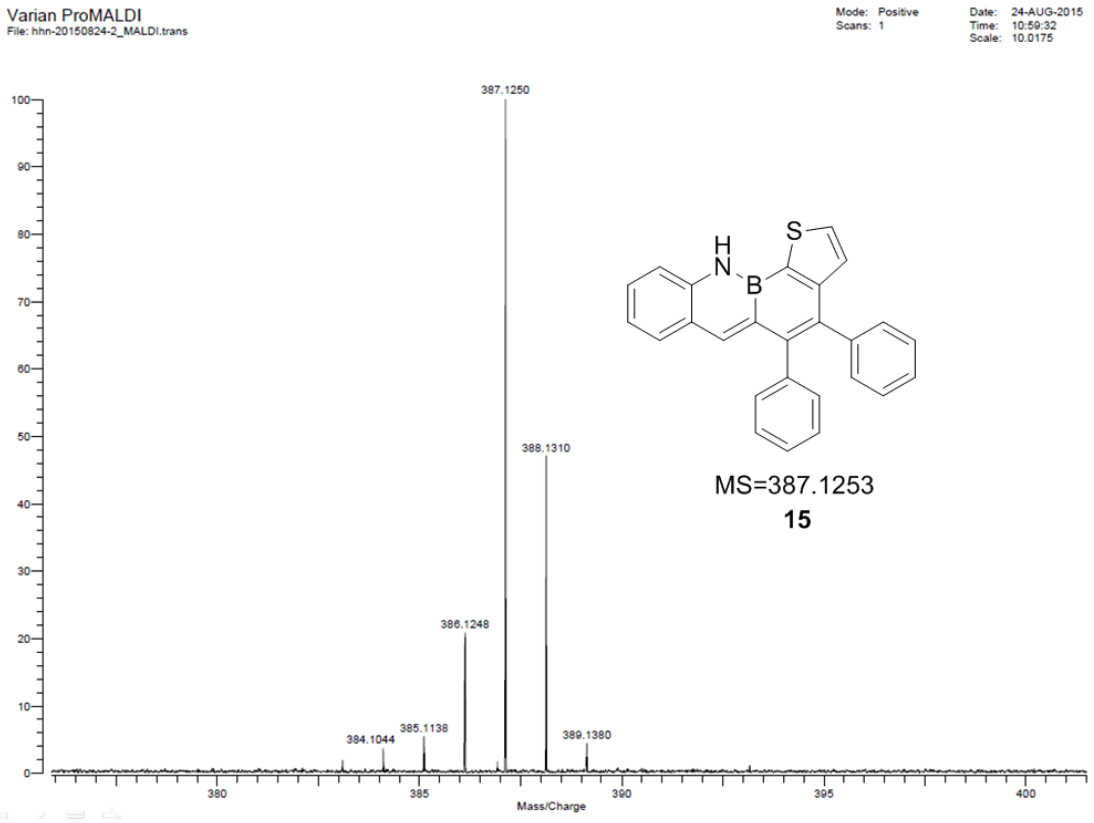

Varian ProMALDI
File: HHN-201512-9_MALDI.trans
Mode: Positive
Scans: 1
Date: 12-MAY-2015
Time: 20:03:40
Scale: 24.5941
489.2062
490.2118
488.2105
491.2156
Bn
N
B
F
MS=489.2064
14
Mass/Charge

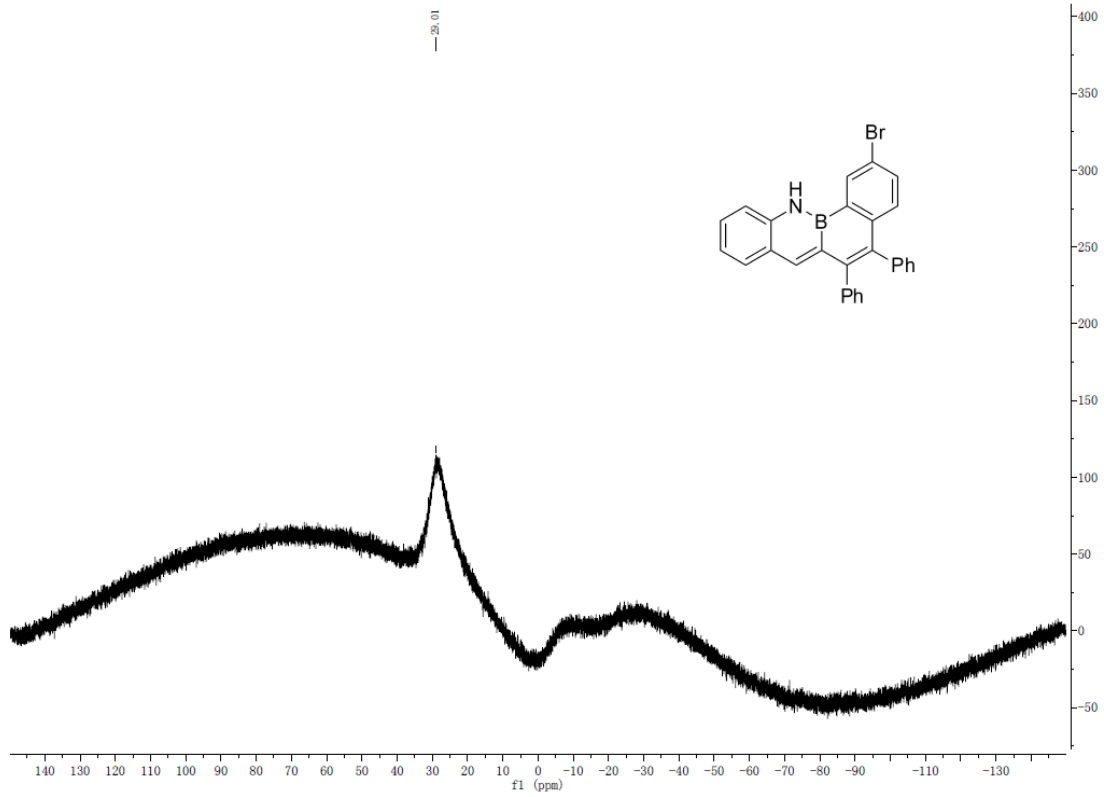

Bn
N
B
F
Ph
Ph
14
f1 (ppm)

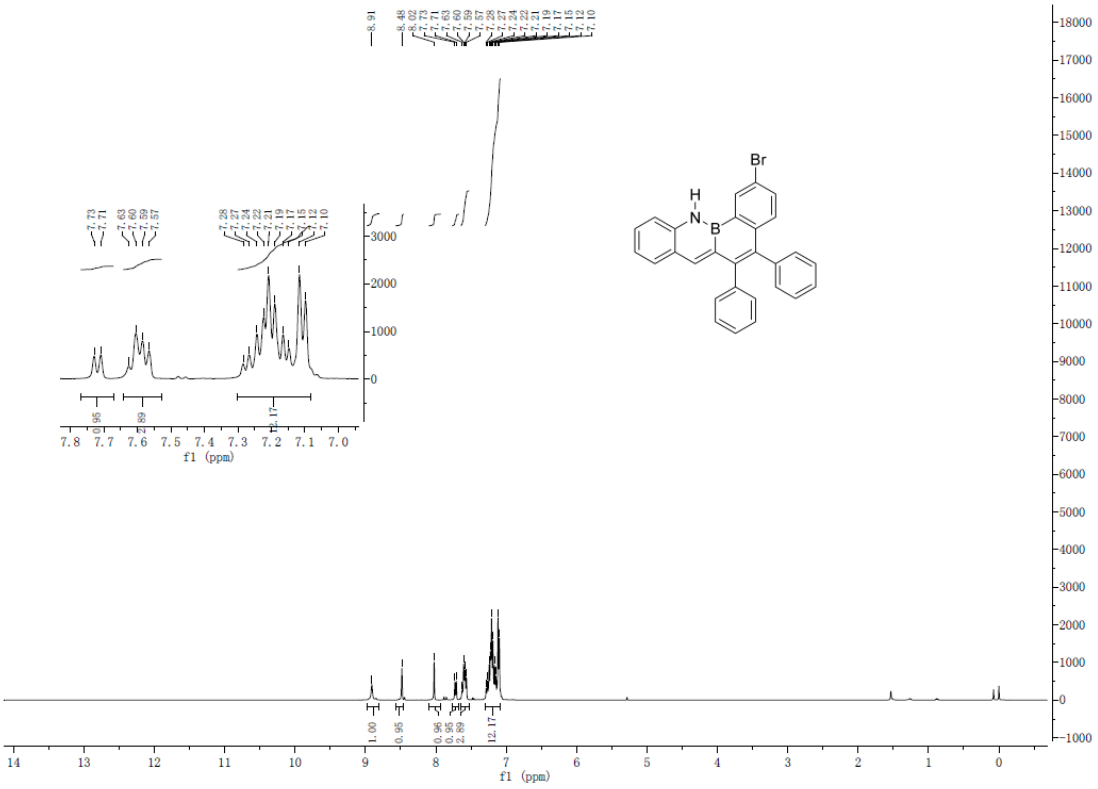

H
N
B
S
f1 (ppm)

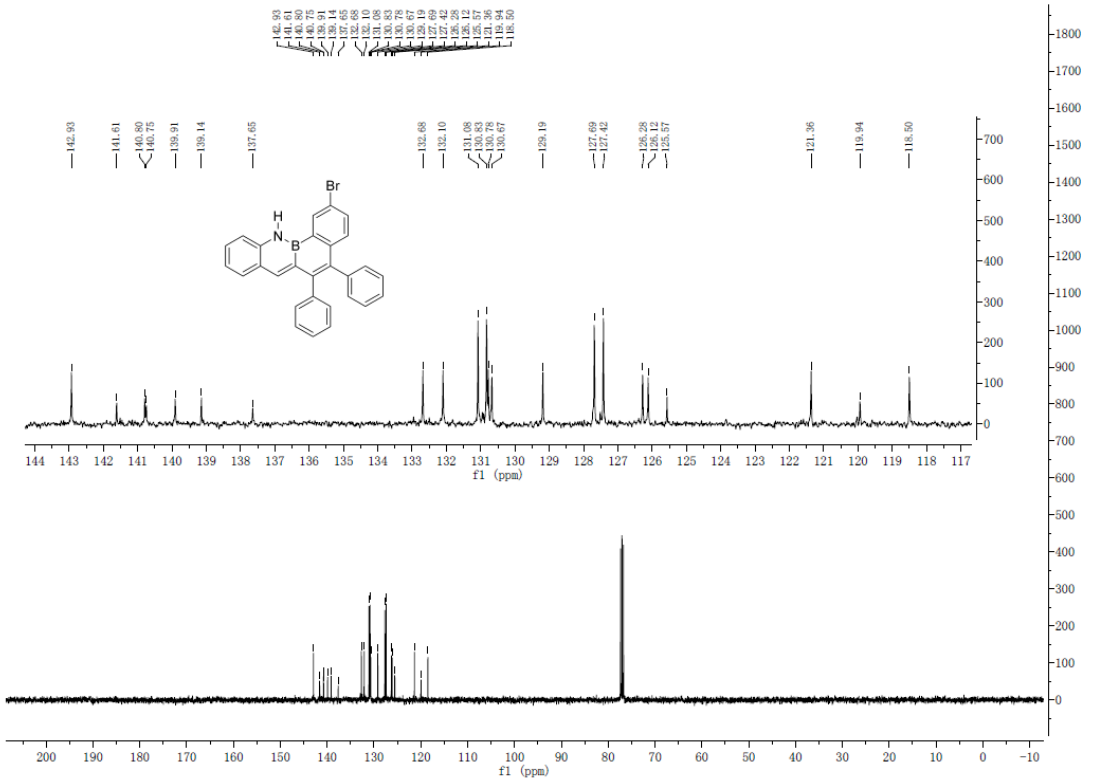


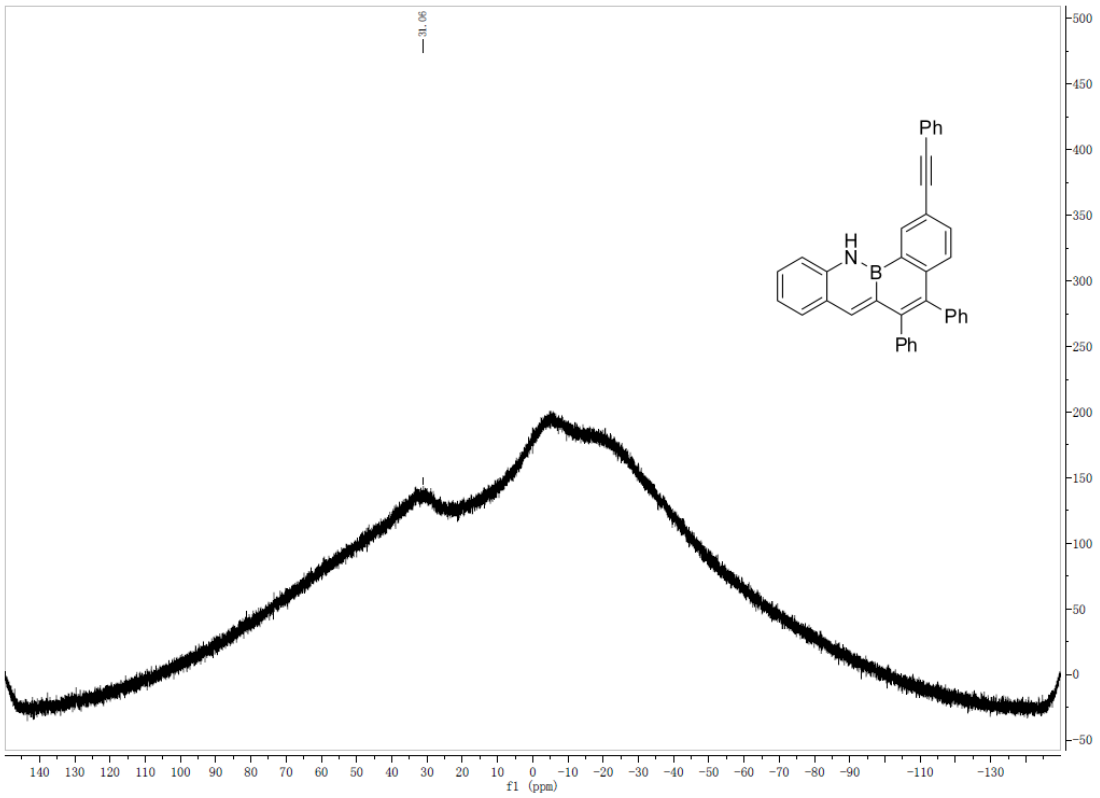


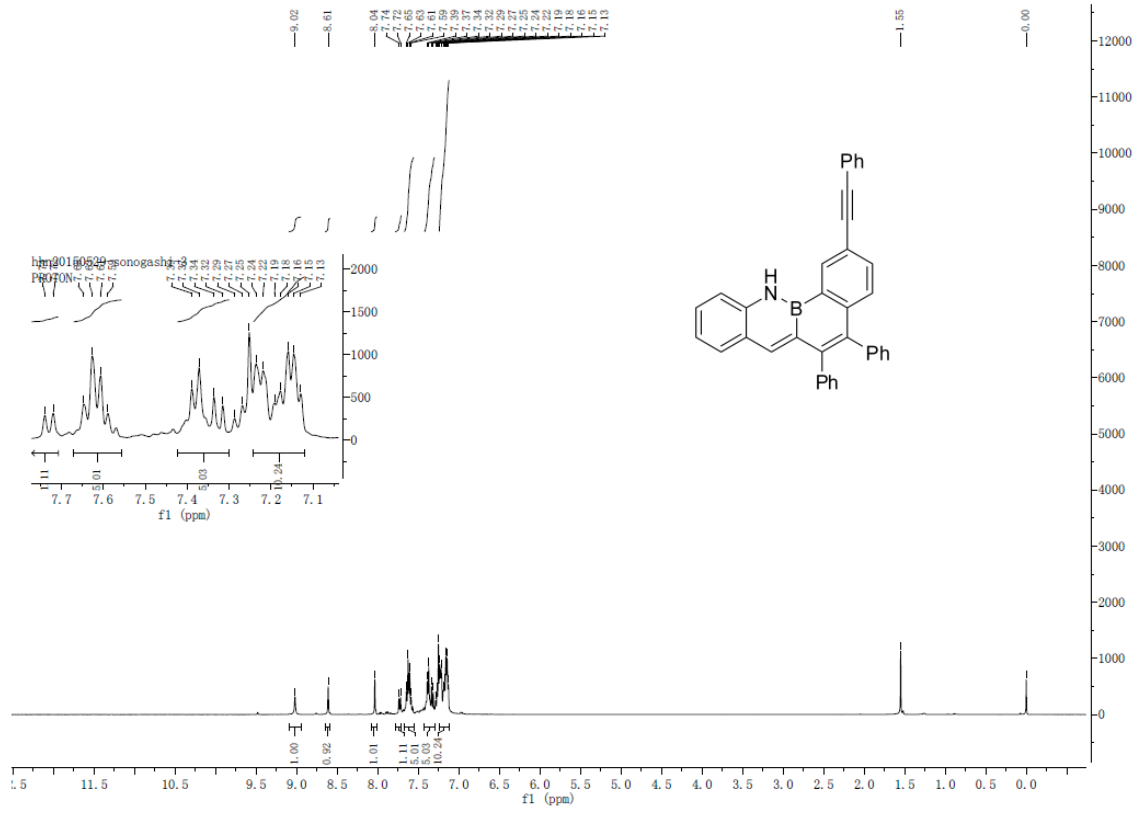

Varian ProMALDI
File: hhn-20150824-2_MALDI.trans
Mode: Positive
Scans: 1
Date: 24-AUG-2015
Time: 10:59:32
Scale: 10.0175
387.1250
388.1310
386.1248
384.1044
385.1138
389.1380
Mass/Charge
MS=387.1253
15


29.01
Br
Ph
Ph
f1 (ppm)


Br
H
N
B
f1 (ppm)


Br
H
N
B
f1 (ppm)


31.06
Ph
H
N
B
Ph
Ph
f1 (ppm)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8.04
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7.72
7.65
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7.61
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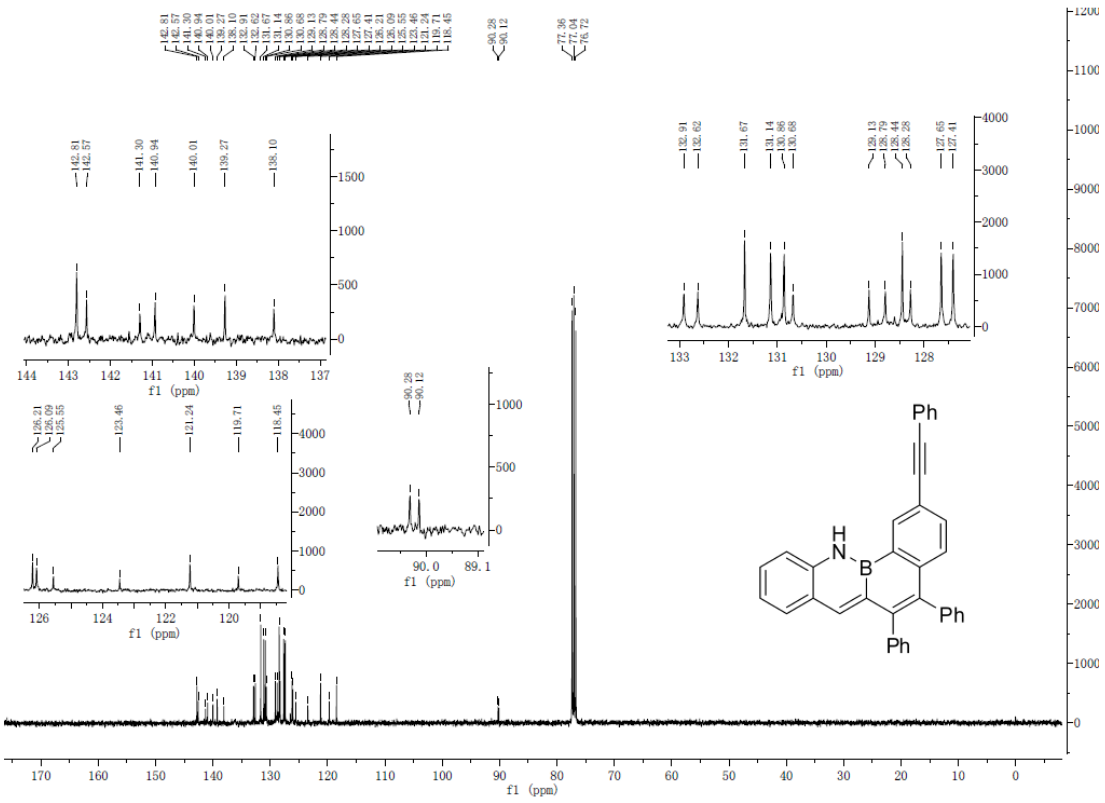
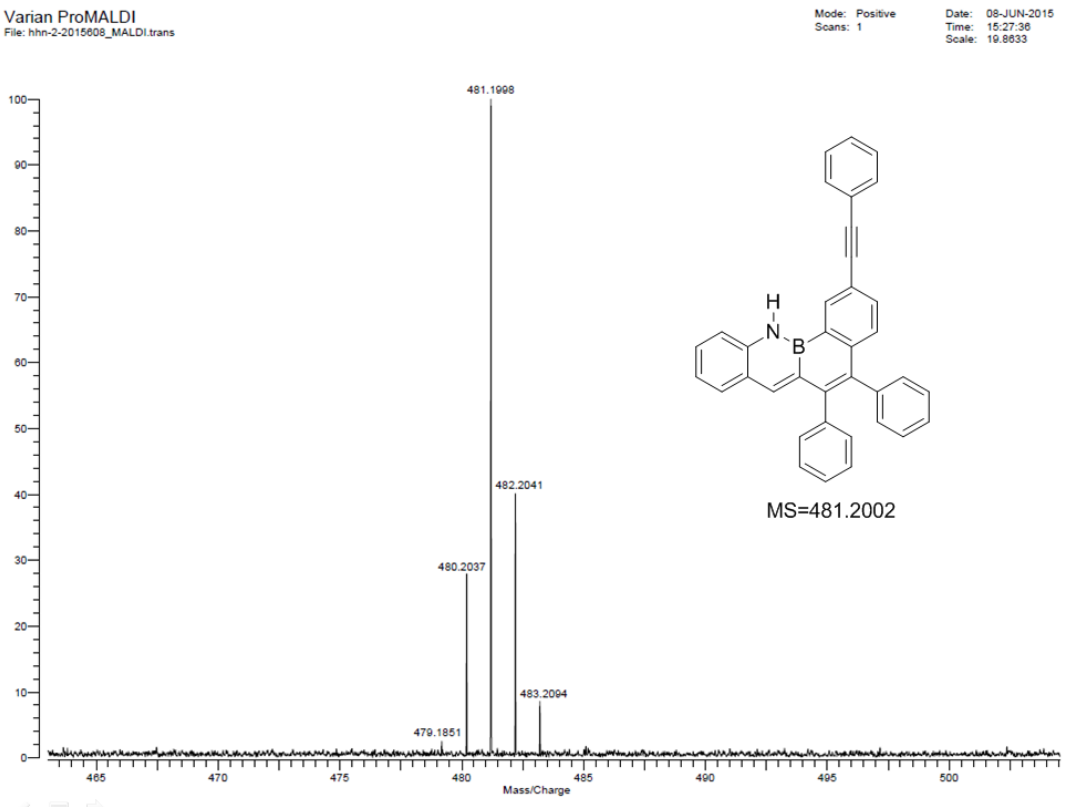
7.34
7.32
7.29
7.27
7.25
7.24
7.22
7.19
7.18
7.16
7.15
7.13
1.55
0.00
Ph
H
N
B
Ph
Ph
1.00
0.92
1.01
1.11
5.01
5.03
10.24
f1 (ppm)


Ph
Ph
Ph
H
N
B
f1 (ppm)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Mass/Charge
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