Supporting Information

For

Rapid Construction of Fold-Line-Shaped BN-Embedded Polycyclic Aromatic Compounds through Diels−Alder Reaction

Peng-Fei Zhang, Fang-Dong Zhuang, Ze-Hao Sun, Yang Lu, Jie-Yu Wang,* and Jian Pei*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

*E-mail: jieyuwang@pku.edu.cn
*E-mail: jianpei@pku.edu.cn

Table of Contents

1. Computational Studies.....S2
2. Cyclic Voltammograms.....S6
3. Single Crystal Structures.....S7
4. NMR Spectra.....S8
5. References.....S23

1. Computational Studies

The optimization of molecular geometries and calculation of HOMO and LUMO were carried out at the B3LYP/6-311G(d,p) level using the Gaussian 16 software package[1]. The excitation energies and the oscillator strengths based on the TDDFT wB97XD/6-31G(d,p) were also calculated using the same program package. Nucleus independent chemical shifts (NICS) were calculated with the same software using the gauge invariant atomic orbital (GIAO) approach at the GIAO-B3LYP/6-311+G(2d,p) level.

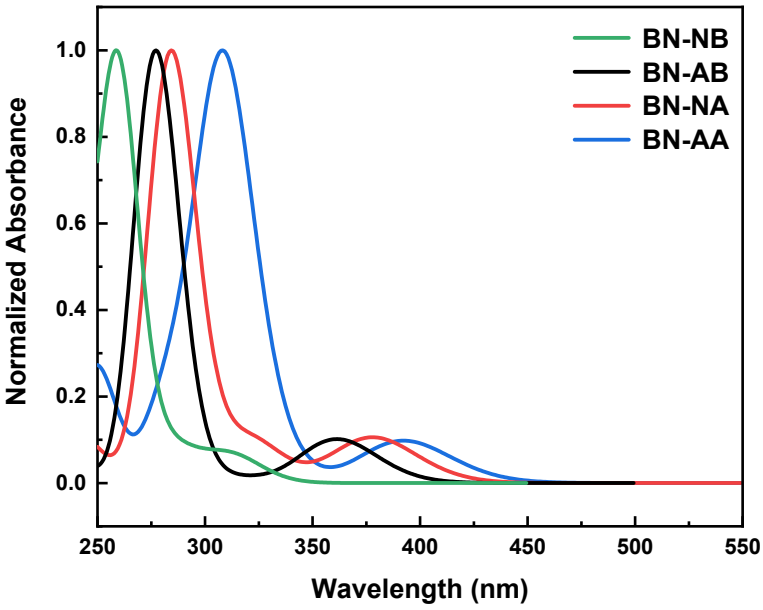


Figure S1 UV-vis absorption spectra of **BN-NB**, **BN-AB**, **BN-NA**, and **BN-AA** calculated at the wB97XD/6-31G(d,p) level, each compound having 0, 1 (−25.67 cm^{-1}), 1 (−22.09 cm^{-1}), 0 imaginary frequency, respectively (Table S1). The peak half-width at half maximum (HWHW) was set to be 0.333 eV.

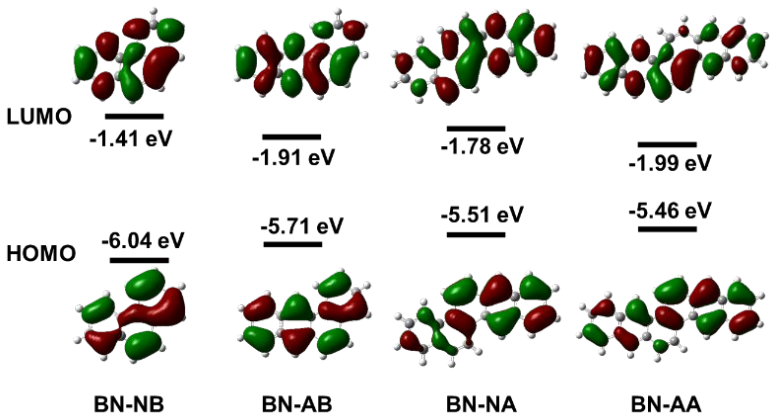


Figure S2. HOMOs, LUMOs, and energy levels of compounds **BN-NB**, **BN-AB**, **BN-NA**, and **BN-AA** calculated at the B3LYP/6-311G(d,p) level. Their single point energies were calculated to be −543.0864149 a.u., −696.7602789 a.u., −850.4450937 a.u., and −1004.118970 a.u., respectively (Table S1).

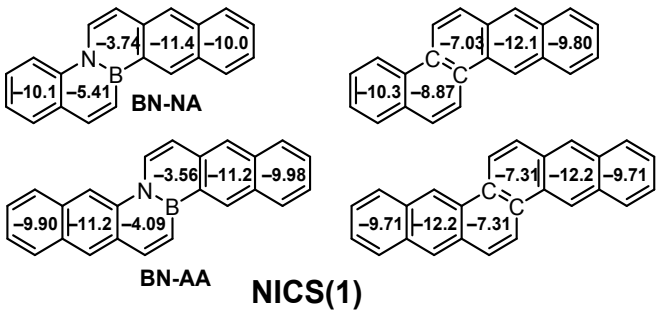


Figure S3 Calculated NICS(1) values (in ppm, calculated at the GIAO-B3LYP/6-311+G(2d,p) level)

Table S1 The number of imaginary frequencies and computed single point energies of optimized structures of **BN-NB**, **BN-AB**, **BN-NA** and **BN-AA**.

	Imaginary frequencies	Single point energies (Hartree)
BN-NB	0	-543.0864149
BN-AB	1	-696.7602789
BN-NA	1	-850.4450937
BN-AA	0	-1001.118970

Table S2 Cartesian coordinates (Å) of the optimized geometries of **BN-NB**, **BN-AB**, **BN-NA** and **BN-AA**. The coordinates of ghost atoms (Bq) for NICS calculations are also given.

BN-NB

No.	Atom	X	Y	Z
1	C	−3.53135	−0.35958	−0.01495
2	C	−2.82909	−1.54764	−0.13965
3	C	−1.42773	−1.55285	−0.15983
4	H	−0.91342	−2.49312	−0.31668
5	C	−0.70875	−0.36006	−0.02628
6	C	−1.42505	0.87542	0.05988
7	C	−2.82192	0.84278	0.07375
8	H	−3.35859	1.78378	0.15363
9	C	−0.7187	2.13517	0.10388
10	H	−1.33857	3.02814	0.16853
11	C	0.64679	2.22612	0.02177
12	H	1.09318	3.21786	0.03252
13	C	1.40592	−1.45959	0.26224
14	H	0.86646	−2.34054	0.58877
15	C	2.807	−1.51858	0.1544
16	H	3.25582	−2.49273	0.31995
17	C	3.60952	−0.40451	−0.1183
18	C	2.9764	0.85425	−0.19612
19	B	1.47752	0.97109	−0.07802
20	N	0.68587	−0.32953	0.01146
21	H	4.68224	−0.52819	−0.21914
22	H	3.60001	1.73783	−0.31569
23	H	−3.35856	−2.49046	−0.23054
24	H	−4.61548	−0.35692	0.00379
25	Bq	−2.12398	−0.35032	−0.03451
26	Bq	−2.11706	−0.43976	0.96146
27	Bq	−2.13091	−0.26088	−1.03048
28	Bq	−0.00705	0.9197	0.01545
29	Bq	0.03185	0.89255	1.01432
30	Bq	−0.04596	0.94685	−0.98342
31	Bq	2.16037	−0.31448	0.00594
32	Bq	2.22003	−0.17746	0.99471
33	Bq	2.10071	−0.45149	−0.98283

BN−AB

No.	Atom	X	Y	Z
1	C	−2.9829	−1.70522	0.00014

2	H	−2.67577	−2.74732	0.00023
3	C	−4.35759	−1.38251	0.0001
4	H	−5.09615	−2.17652	0.00016
5	C	−4.75013	−0.05536	−0.00002
6	H	−5.80379	0.20366	−0.00006
7	C	−3.78787	0.96745	−0.0001
8	H	−4.10273	2.00691	−0.00018
9	C	−2.41339	0.66674	−0.00006
10	C	−2.01027	−0.70719	0.00006
11	C	−0.61268	−1.00981	0.00011
12	H	−0.35963	−2.06173	0.00028
13	C	0.37735	−0.02427	−0.00001
14	C	−0.02007	1.35277	−0.00006
15	C	−1.40827	1.65105	−0.00011
16	H	−1.70091	2.69809	−0.00018
17	C	0.92795	2.40228	−0.00002
18	H	0.53239	3.41671	−0.00005
19	C	2.29161	2.16711	0.00009
20	H	2.9622	3.02262	0.00015
21	C	2.17667	−1.63259	−0.00022
22	H	1.43154	−2.41318	−0.00045
23	C	3.49735	−1.98264	−0.00017
24	H	3.72772	−3.04237	−0.00032
25	C	4.55041	−1.02363	0.00005
26	C	4.24107	0.30788	0.00017
27	B	2.78544	0.75434	0.00009
28	N	1.74499	−0.32602	−0.00004
29	H	5.57623	−1.38295	0.0001
30	H	5.05129	1.03414	0.0003
31	Bq	−3.38369	−0.36935	0.00002
32	Bq	−3.3837	−0.36926	1.00002
33	Bq	−3.38368	−0.36943	−0.99998
34	Bq	−1.01455	0.32155	−0.00001
35	Bq	−1.01456	0.32162	0.99999
36	Bq	−1.01455	0.32148	−1.00001
37	Bq	1.35121	1.05437	0.00001
38	Bq	1.35116	1.05435	1.00001
39	Bq	1.35126	1.05438	−0.99999
40	Bq	3.16599	−0.65044	−0.00002
41	Bq	3.16592	−0.65056	0.99998
42	Bq	3.16606	−0.65033	−1.00002

BN−NA

No.	Atom	X	Y	Z
1	N	1.64745	−0.55861	0
2	C	−4.26391	1.66823	0.00002
3	H	−4.00161	2.72126	0.00003
4	C	3.48373	1.05234	−0.00001
5	C	−3.21696	0.70512	0.00001
6	C	−2.52255	−1.6424	−0.00001
7	H	−2.77864	−2.69791	−0.00002
8	C	−0.11835	−2.22215	−0.00002
9	H	−0.36435	−3.2779	−0.00003
10	C	2.54693	2.14612	−0.00002
11	H	2.97403	3.1468	−0.00004
12	C	1.20806	1.94692	−0.00001
13	H	0.56032	2.8182	−0.00001
14	C	1.18629	−1.88171	−0.00001
15	H	1.93092	−2.65971	−0.00002
16	C	−4.93459	−1.0548	−0.00001
17	H	−5.1941	−2.1084	−0.00002
18	C	4.00864	−1.31763	0.00003
19	H	3.7273	−2.3596	0.00006
20	C	−5.57878	1.28002	0.00001
21	H	−6.36759	2.02373	0.00002
22	C	−1.85465	1.07198	0.00001
23	H	−1.61655	2.13105	0.00002
24	C	3.03629	−0.2981	0
25	C	−3.55874	−0.6892	0
26	C	−1.18895	−1.25658	−0.00001
27	C	4.86712	1.31889	−0.00002
28	H	5.1845	2.35638	−0.00003
29	C	−5.91636	−0.09803	0
30	H	−6.96032	−0.3912	0
31	C	−0.83138	0.13436	0
32	C	5.36116	−1.02046	0.00003
33	H	6.07844	−1.83338	0.00005
34	C	5.80407	0.30582	0
35	H	6.86348	0.53261	0
36	B	0.66593	0.52314	0.00001
37	Bq	4.43215	0.01351	0.00001
38	Bq	4.43214	0.01353	1.00001
39	Bq	4.43216	0.01349	−0.99999
40	Bq	2.11308	0.81355	−0.00001
41	Bq	2.11308	0.81355	−1.00001
42	Bq	2.11309	0.81356	0.99999
43	Bq	0.22109	−0.87172	−0.00001
44	Bq	0.22109	−0.87173	0.99999
45	Bq	0.22109	−0.87171	−1.00001

46	Bq	−2.20078	−0.29126	0
47	Bq	−2.20078	−0.29125	−1
48	Bq	−2.20078	−0.29127	1
49	Bq	−4.57967	0.29367	0
50	Bq	−4.57967	0.29366	1
51	Bq	−4.57967	0.29368	−1

BN−AA

No.	Atom	X	Y	Z
1	C	−5.31344	1.65104	0.09809
2	H	−5.03419	2.699	0.13321
3	C	−6.63514	1.28557	0.10627
4	H	−7.40733	2.04549	0.14832
5	C	−7.00519	−0.0832	0.05978
6	H	−8.05479	−0.35399	0.06674
7	C	−6.04142	−1.05635	0.00746
8	H	−6.31782	−2.10503	−0.02661
9	C	−4.66121	−0.71174	−0.00228
10	C	−4.28606	0.66819	0.04169
11	C	−2.9195	1.01674	0.02942
12	H	−2.69324	2.07169	0.08011
13	C	−1.91311	0.06341	−0.02935
14	C	−2.2894	−1.32702	−0.05316
15	C	−3.63507	−1.66928	−0.04436
16	H	−3.89874	−2.72219	−0.06496
17	C	−1.28799	−2.36744	−0.07058
18	H	−1.65944	−3.38976	−0.09137
19	C	0.03455	−2.09377	−0.05053
20	H	0.73071	−2.92679	−0.05546
21	C	−0.14275	1.73434	−0.10915
22	H	−0.92773	2.46935	−0.17167
23	C	1.14217	2.14352	−0.10704
24	H	1.33373	3.2093	−0.15553
25	C	2.25996	1.23455	−0.0541
26	C	1.97346	−0.17293	−0.02777
27	C	3.04233	−1.05751	0.01462
28	H	2.8578	−2.12695	0.03629
29	C	4.38413	−0.62219	0.03341
30	C	4.65489	0.78739	0.00635
31	C	3.57231	1.68673	−0.03781
32	H	3.77535	2.75348	−0.05918
33	C	6.01025	1.22223	0.02489
34	H	6.21647	2.28733	0.00449
35	C	7.03867	0.31671	0.06774
36	H	8.0663	0.66255	0.08146
37	C	6.7712	−1.07634	0.09453
38	H	7.59631	−1.77871	0.12838
39	C	5.47781	−1.53072	0.07776
40	H	5.2688	−2.59541	0.09819
41	B	0.4991	−0.63755	−0.04146
42	N	−0.53377	0.39098	−0.05721
43	Bq	−5.65994	0.28537	0.05186
44	Bq	−5.67622	0.32332	−0.94728
45	Bq	−5.64367	0.24742	1.05101
46	Bq	−3.29004	−0.34067	−0.00867
47	Bq	−3.27681	−0.37233	0.99074
48	Bq	−3.30326	−0.30901	−1.00808
49	Bq	−0.92954	−1.00994	−0.05363
50	Bq	−0.92928	−1.01257	−1.05363
51	Bq	−0.9298	−1.00731	0.94636
52	Bq	0.8721	0.77712	−0.06823
53	Bq	0.85412	0.80077	0.93132
54	Bq	0.89008	0.75346	−1.06779
55	Bq	3.31906	0.32148	−0.01104
56	Bq	3.34003	0.29867	−1.01056
57	Bq	3.29809	0.34429	0.98848
58	Bq	5.72379	−0.14221	0.05062
59	Bq	5.70264	−0.11892	1.05012
60	Bq	5.74493	−0.16549	−0.94889

2. Cyclic Voltammograms

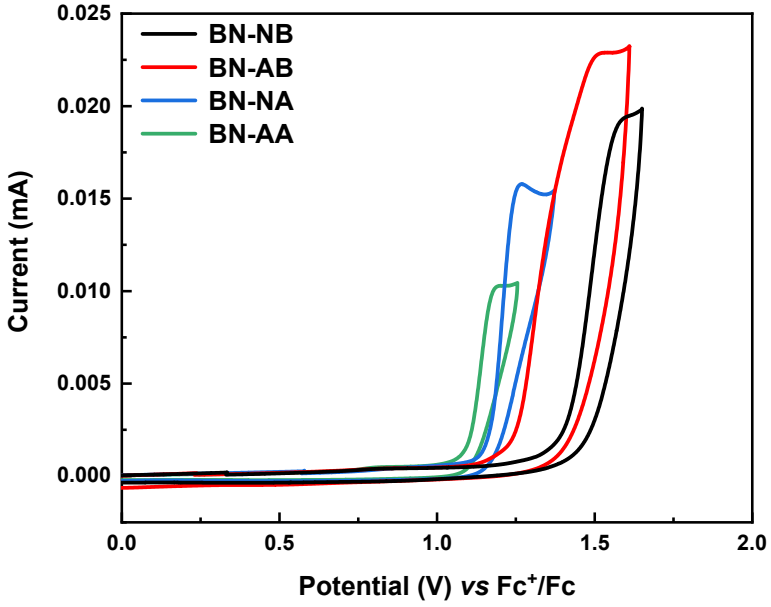


Figure S4 Cyclic voltammogram of **BN-NB** (black line), **BN-AB** (red line), **BN-NA** (blue line), and **BN-AA** (green line). The onset potential of the Fc^+/Fc couple as internal reference was measured to be $E_{ref} = 0.42$ V in a parallel experiment. The HOMO levels were then calculated using the equation[2] IP = $-(E_{ref} - E_{ox\ onset} - 4.80)$ eV: IP(**BN-NB**) = 5.80 eV; IP(**BN-AB**) = 5.64 eV; IP(**BN-NA**) = 5.53 eV; IP(**BN-AA**) = 5.47 eV.

3. Single Crystal Structures

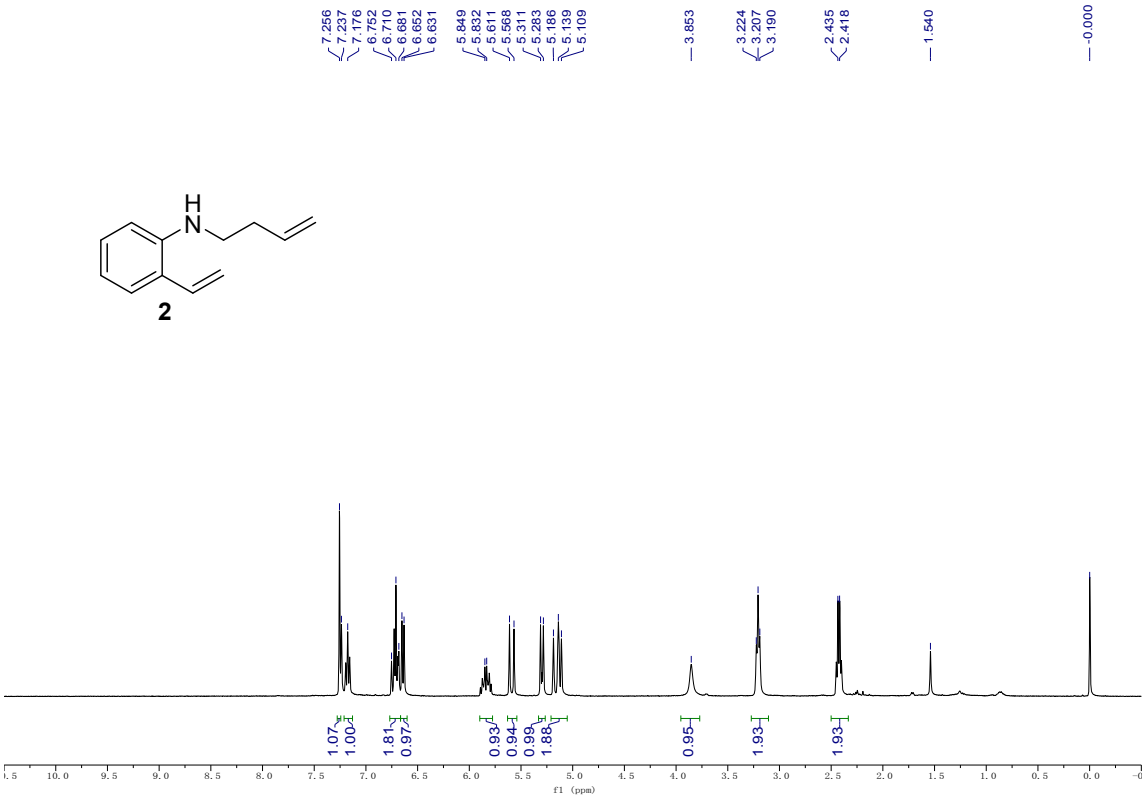
Crystallographic data of the compounds were collected on a Rigaku MM-07 Saturn 724 CCD diffractometer (Rigaku International Corp., Tokyo, Japan) using graphite-monochromated Mo Kα radiation.

Table S3 Crystal data and structure refinement for **BN-NA** and **BN-AA** crystals.

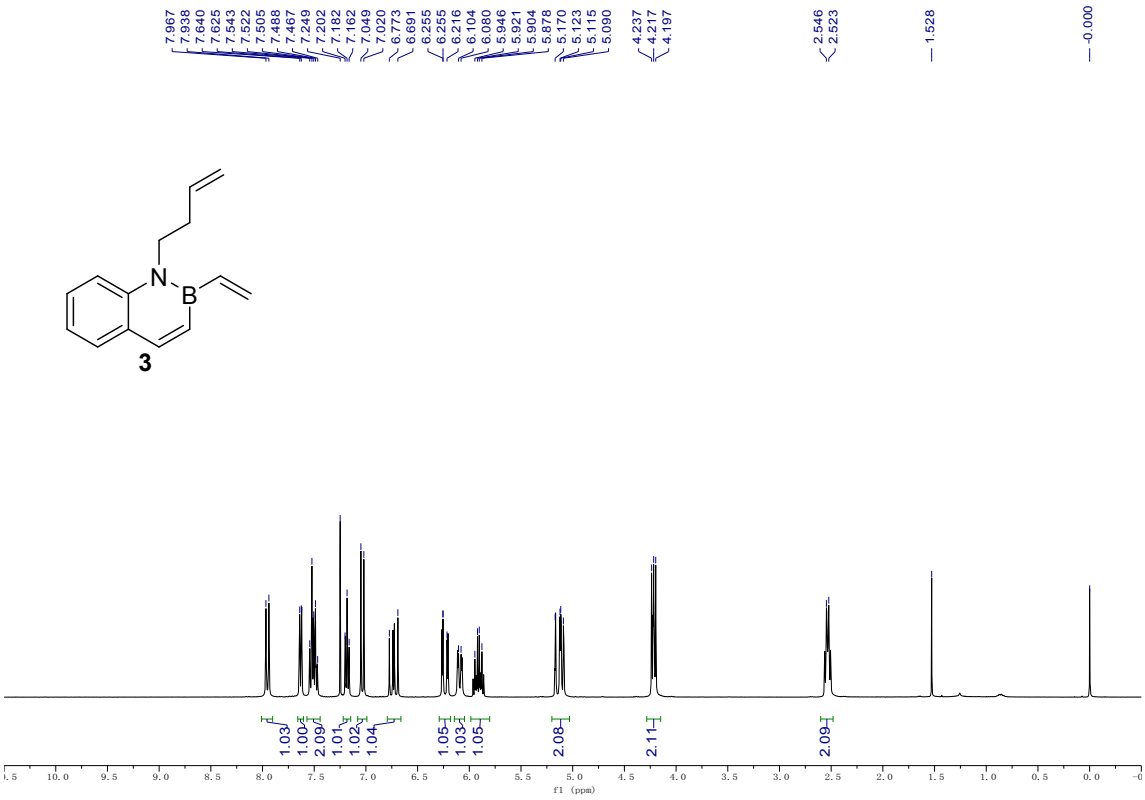
Cultivation method	**BN-NA**	**BN-AA**
Empirical formula	$C_{20}H_{14}BN$	$C_{24}H_{16}BN$
Formula weight	279.13	329.19
Temperature / K	153.15	179.99(10)
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a / Å	8.2149(16)	6.6742(2)
b / Å	6.3407(13)	7.4741(3)
c / Å	13.524(3)	16.3336(6)
α / °	90	90
β / °	95.51(3)	90.847(3)
γ / °	90	90
Volume/Å^3	701.2(2)	814.69(5)
Z	2	2
ρ_{calc} / (g cm^{-3})	1.322	1.342
μ / mm^{-1}	0.076	0.077
F(000)	292.0	344.0
Crystal size / mm^3	0.24 × 0.21 × 0.12	0.1 × 0.05 × 0.03
Radiation	Mo Kα (λ = 0.71073)	Mo K/α (λ = 0.71073)
2θ range for data collection / °	5.576 to 54.986	4.988 to 54.95
Index ranges	$-10 \le h \le 10$, $-8 \le k \le 8$, $-17 \le l \le 17$	$-8 \le h \le 8$, $-9 \le k \le 9$, $-21 \le l \le 20$
Reflections collected	8417	11744
Independent reflections	3171 [R_{int} = 0.0399, R_{sigma} = 0.0394]	3580 [R_{int} = 0.0196, R_{sigma} = 0.0209]
Data/restraints/parameters	3171/1/199	3580/1/236
Goodness-of-fit on F^2	1.075	1.042
Final R indices [$I \ge 2\sigma(I)$]	R_1 = 0.0616, wR_2 = 0.1529	R_1 = 0.0532, wR_2 = 0.1359
Final R indices [all data]	R_1 = 0.0663, wR_2 = 0.1577	R_1 = 0.0579, wR_2 = 0.1390
Largest diff. peak/hole / (e Å^{-3})	0.30/−0.20	0.47/−0.21

4. NMR Spectra

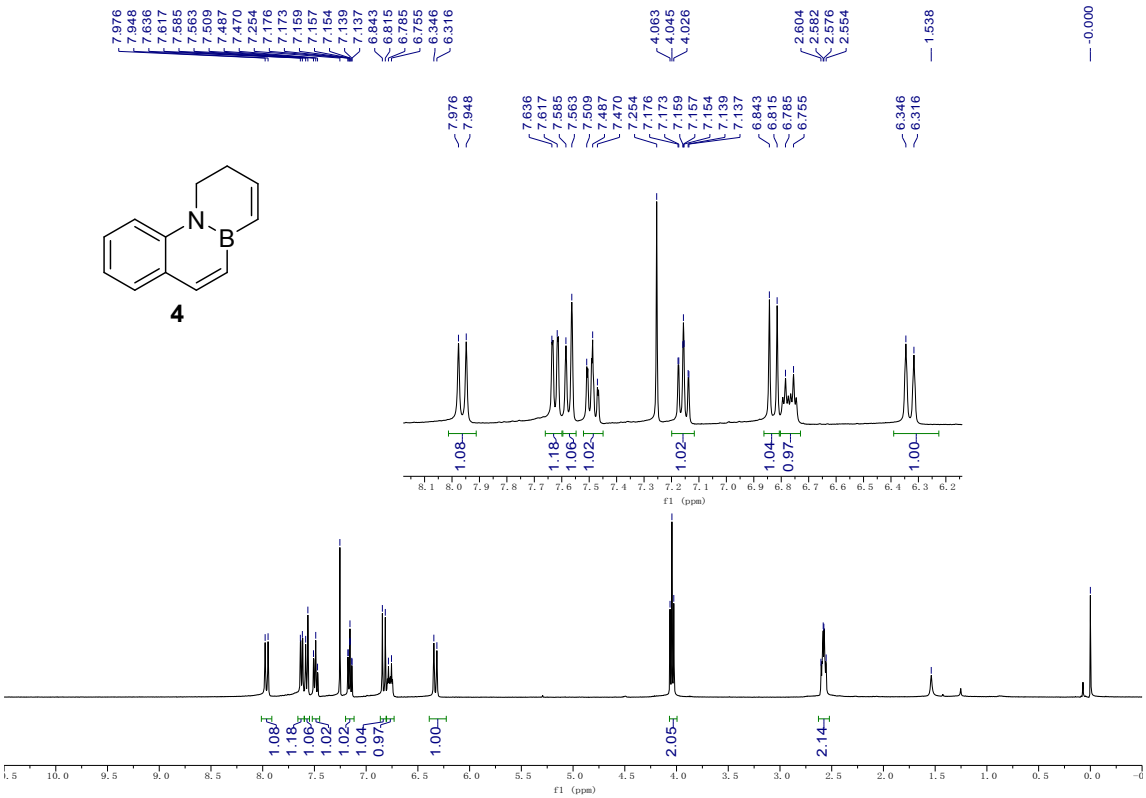
^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$, 298 K)



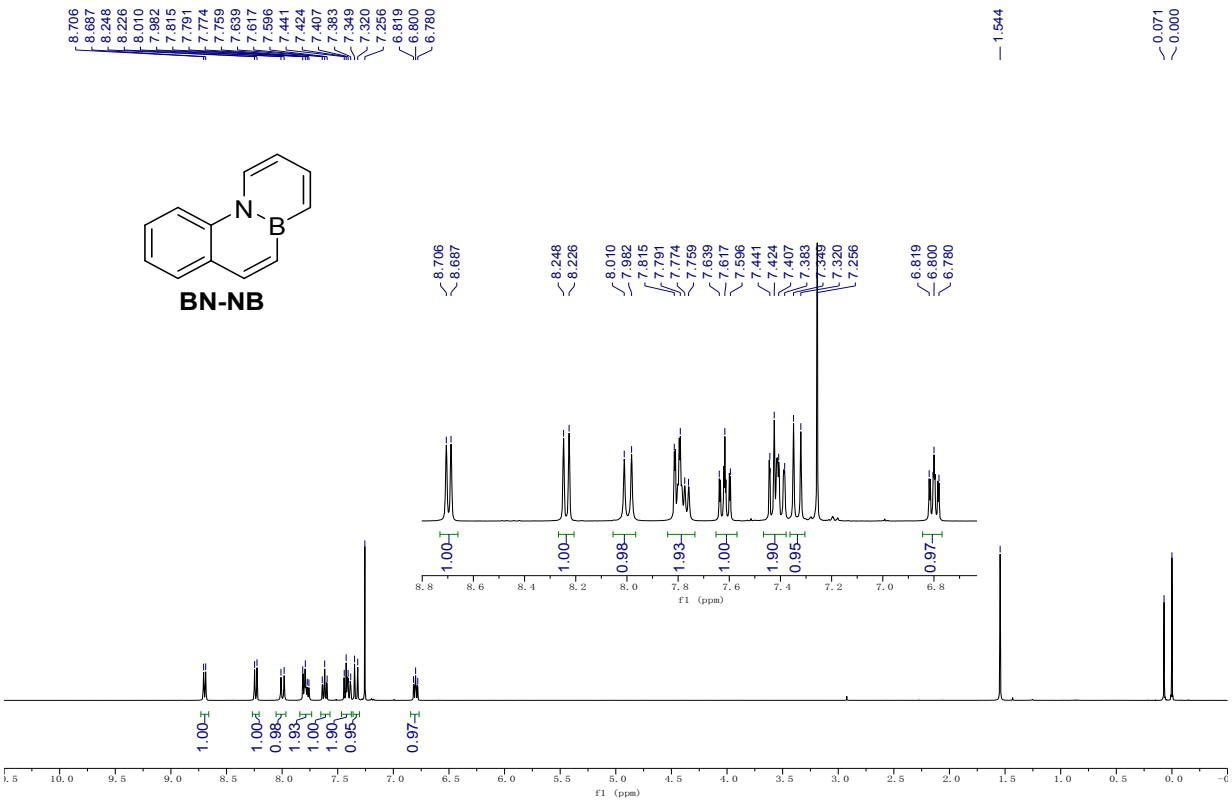
^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$, 298 K)



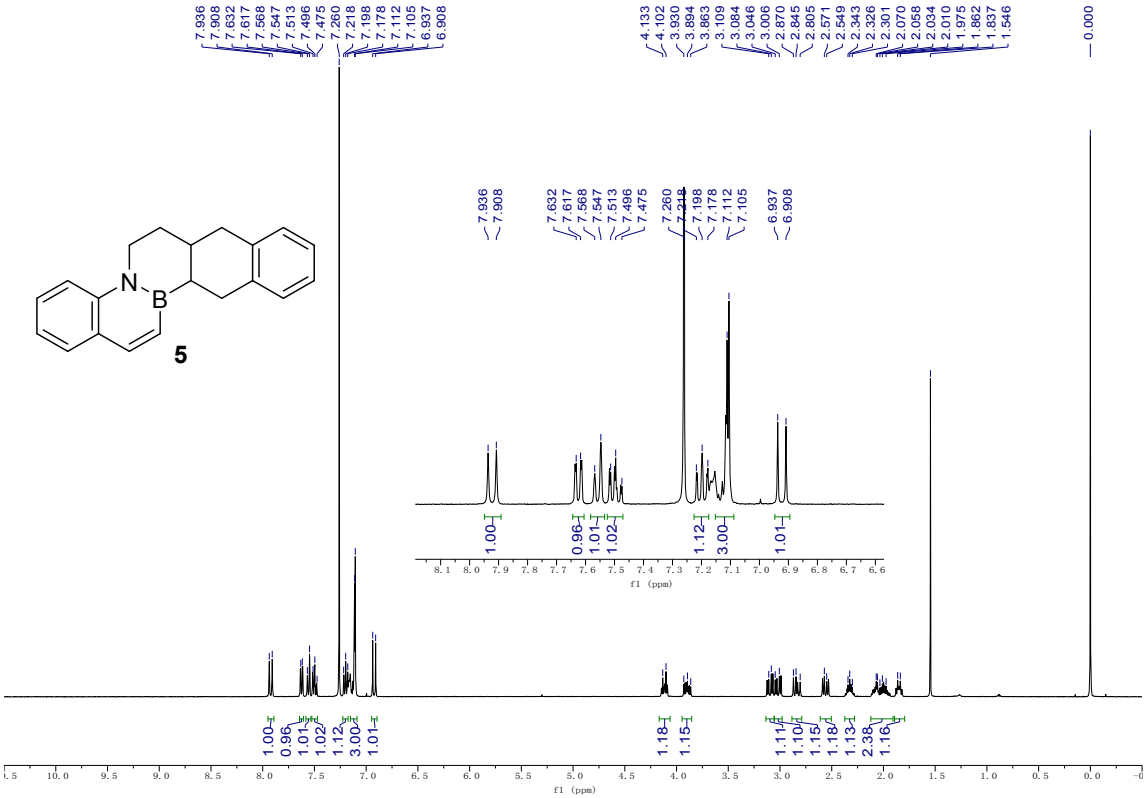
^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$, 298 K)



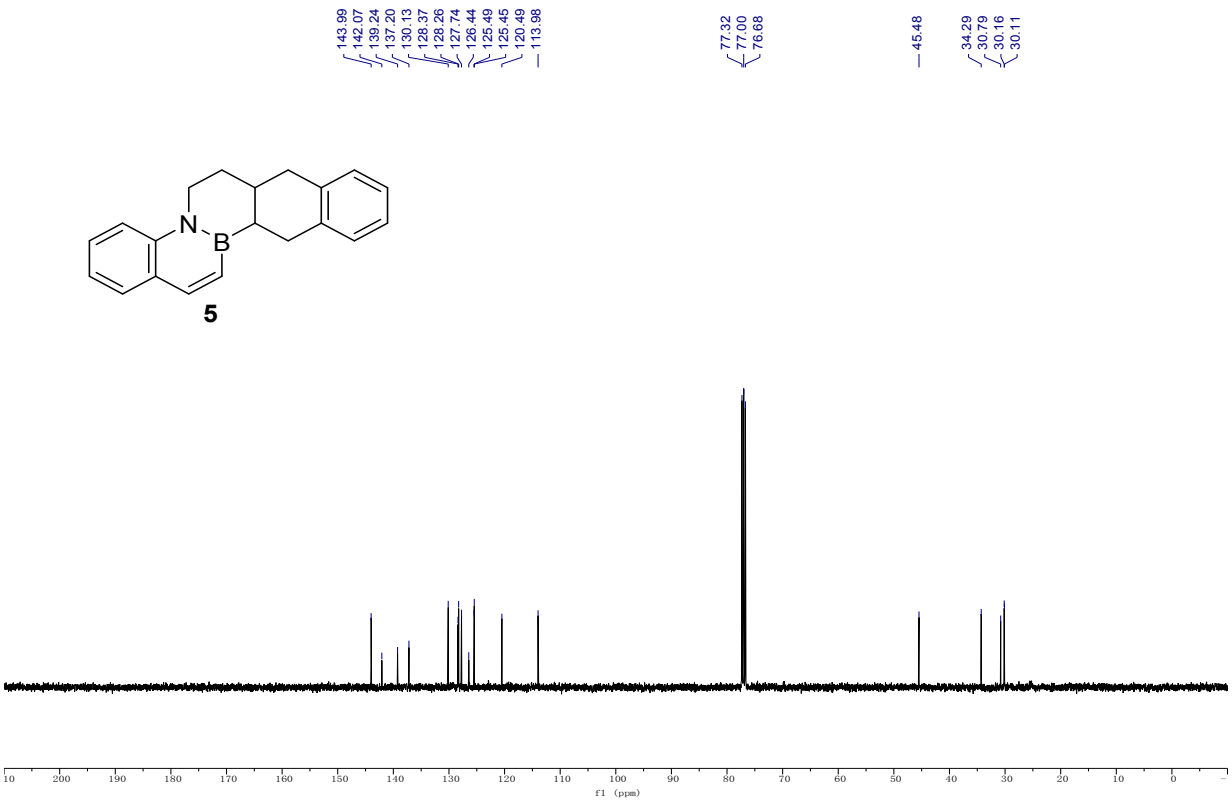
^{1}H NMR spectrum of **BN-NB** (400 MHz, $CDCl_3$, 298 K)



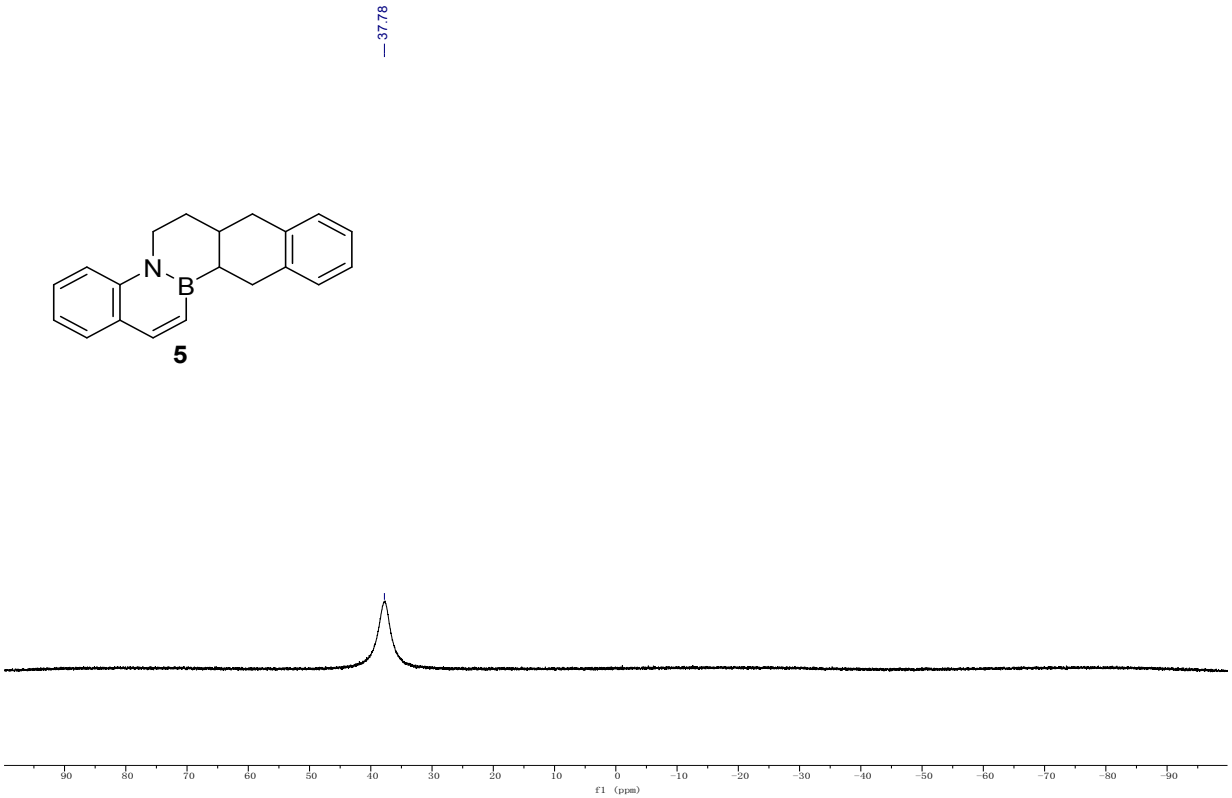
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$, 298 K)



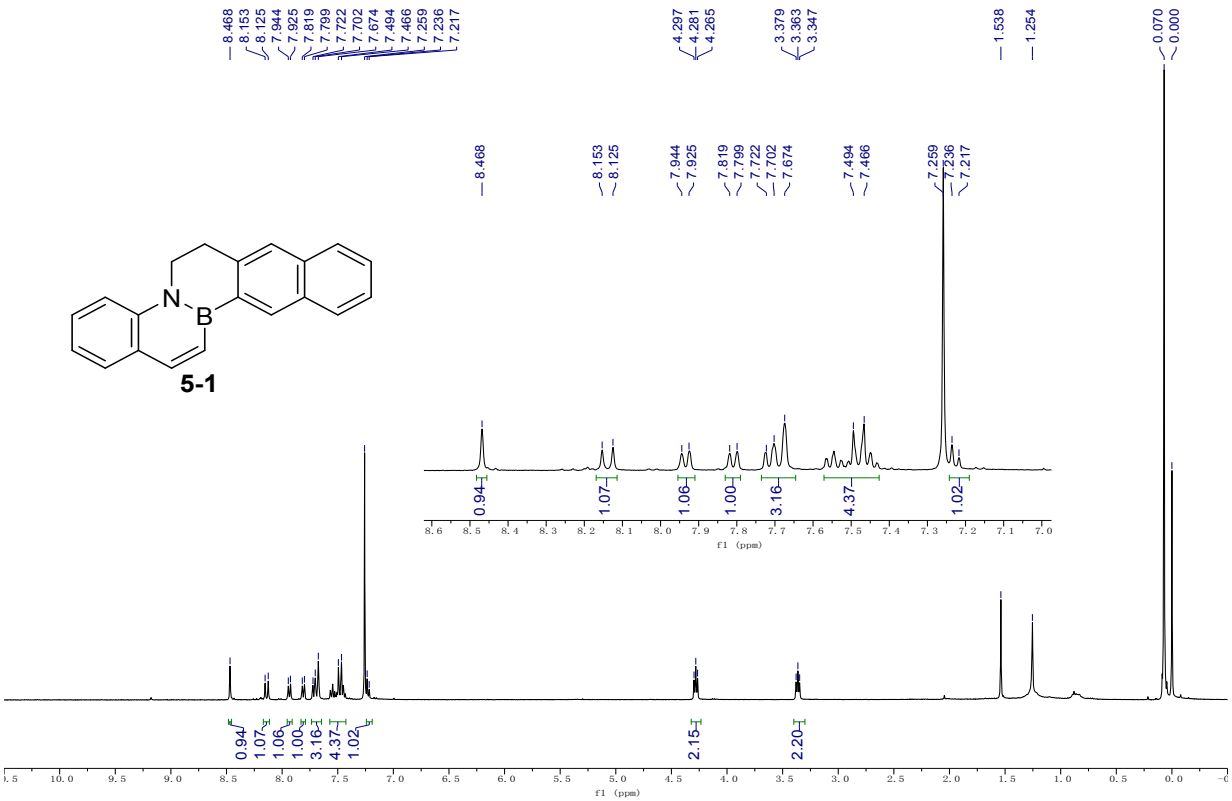
^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$, 298 K)



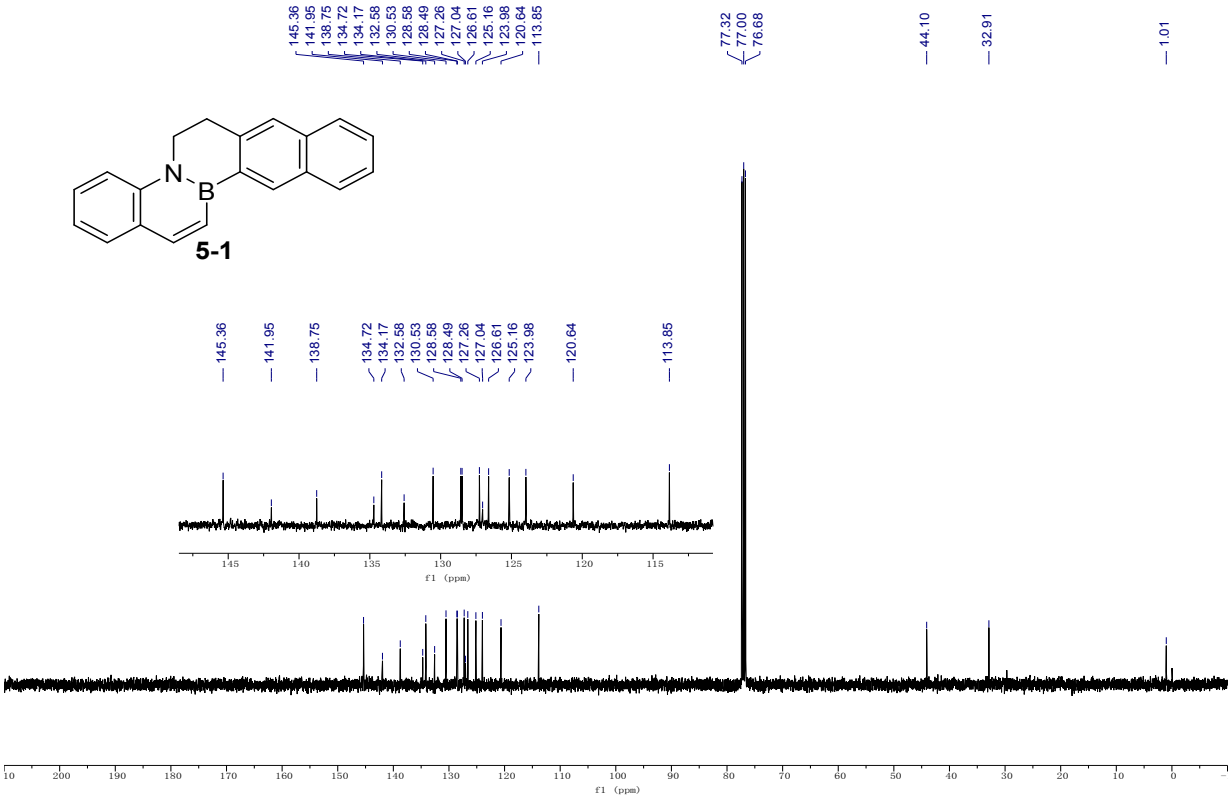
^{11}B NMR spectrum of **5** (160 MHz, $CDCl_3$, 298 K)



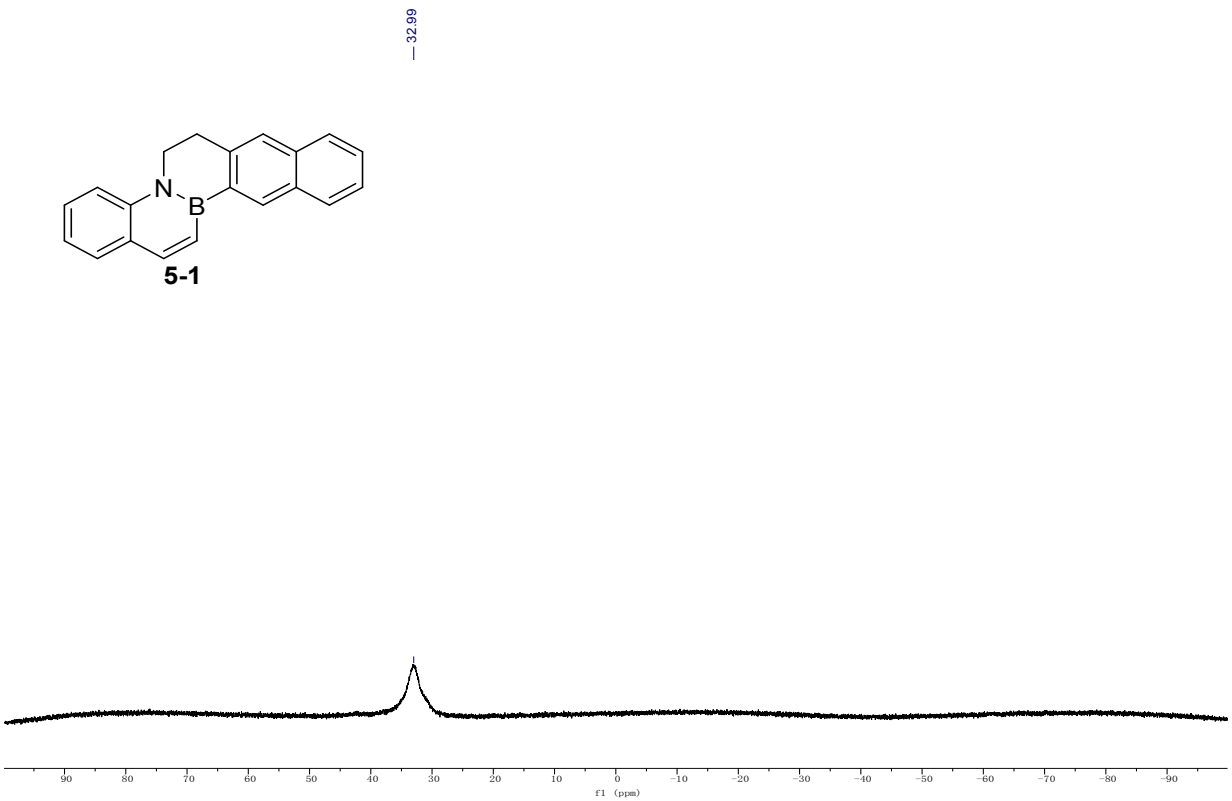
^{1}H NMR spectrum of **5-1** (400 MHz, $CDCl_3$, 298 K)



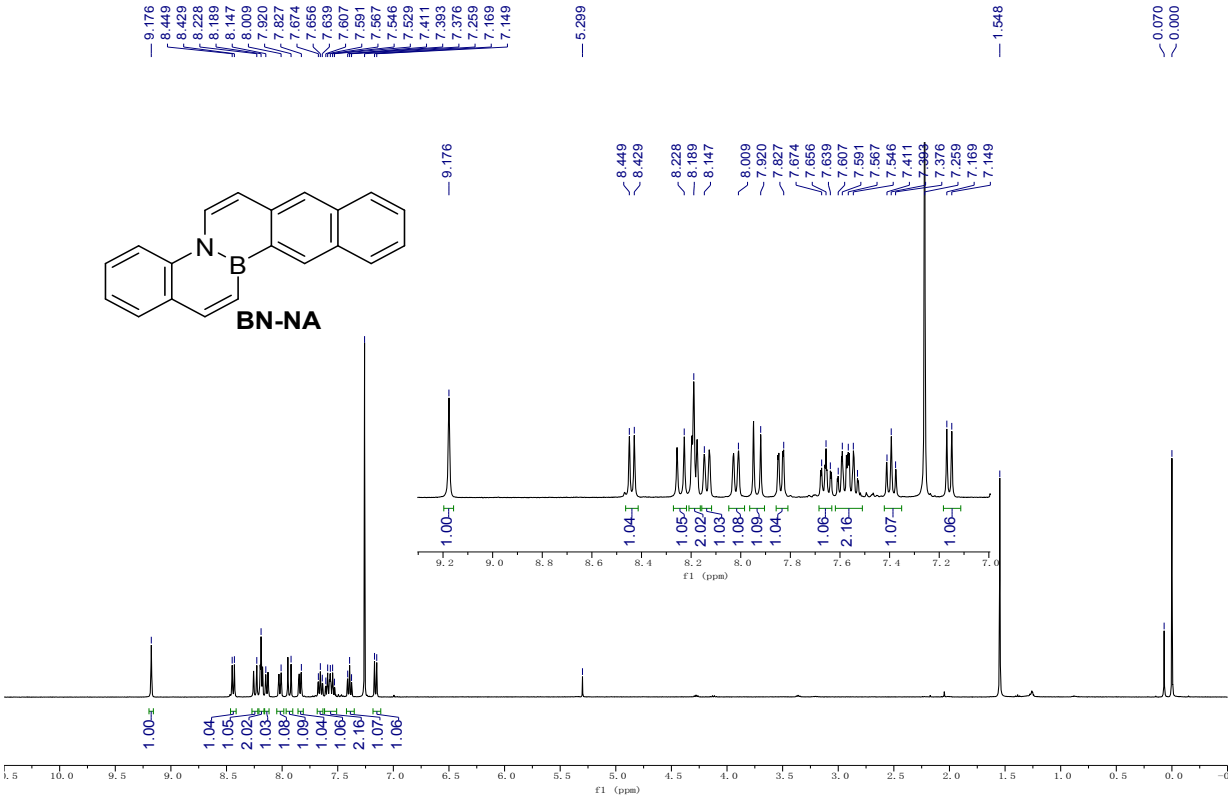
^{13}C NMR spectrum of **5-1** (100 MHz, $CDCl_3$, 298 K)



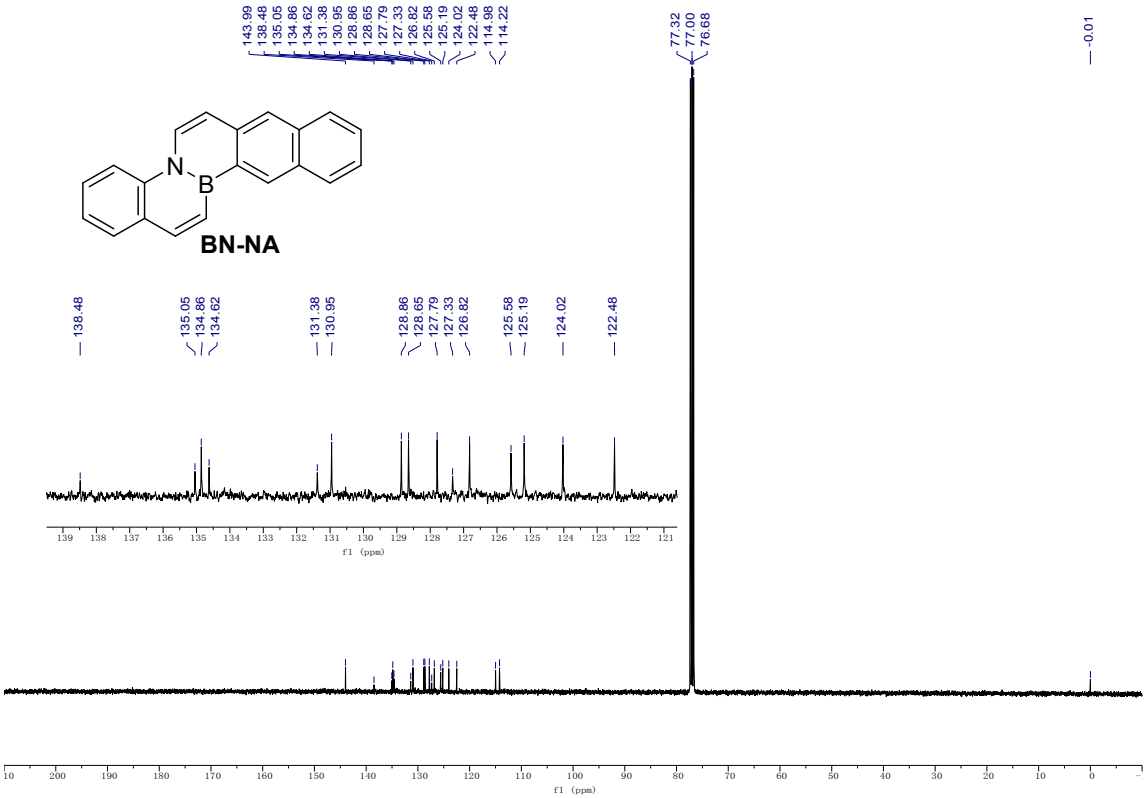
^{11}B NMR spectrum of **5-1** (160 MHz, $CDCl_3$, 298 K)



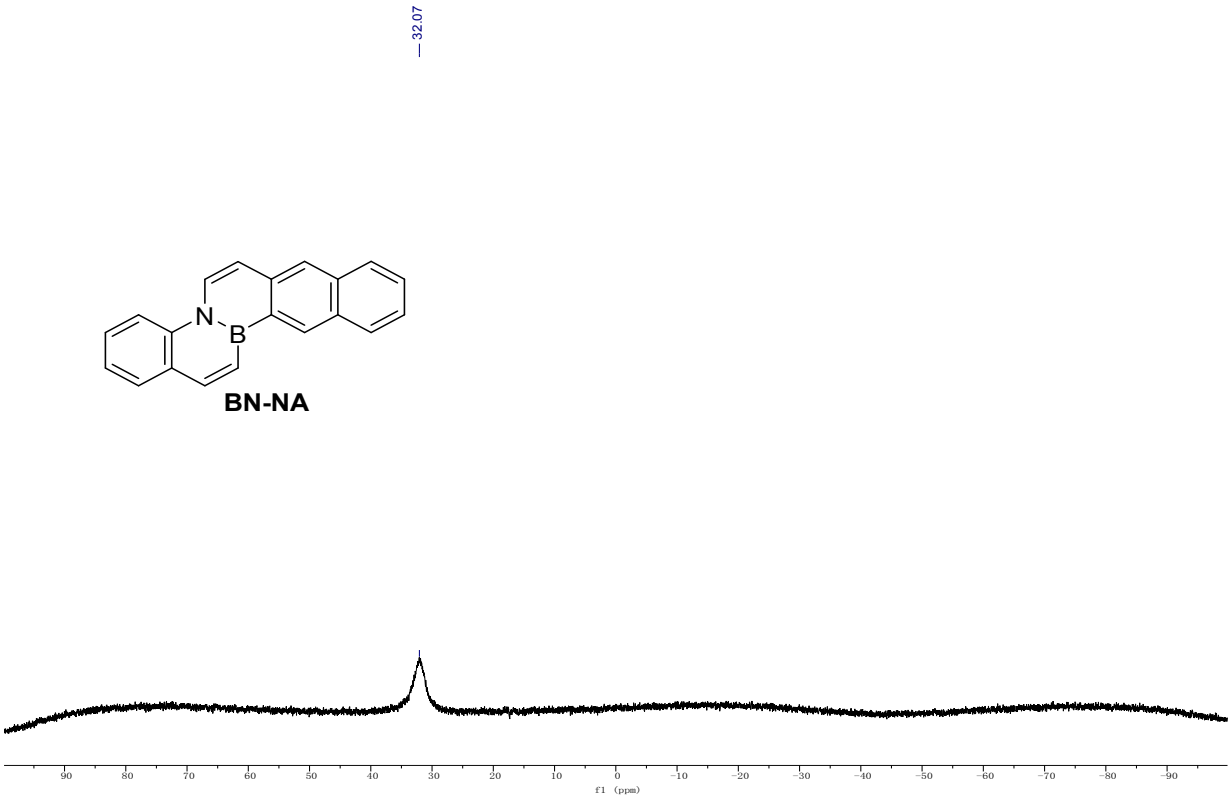
^{1}H NMR spectrum of **BN-NA** (400 MHz, $CDCl_3$, 298 K)



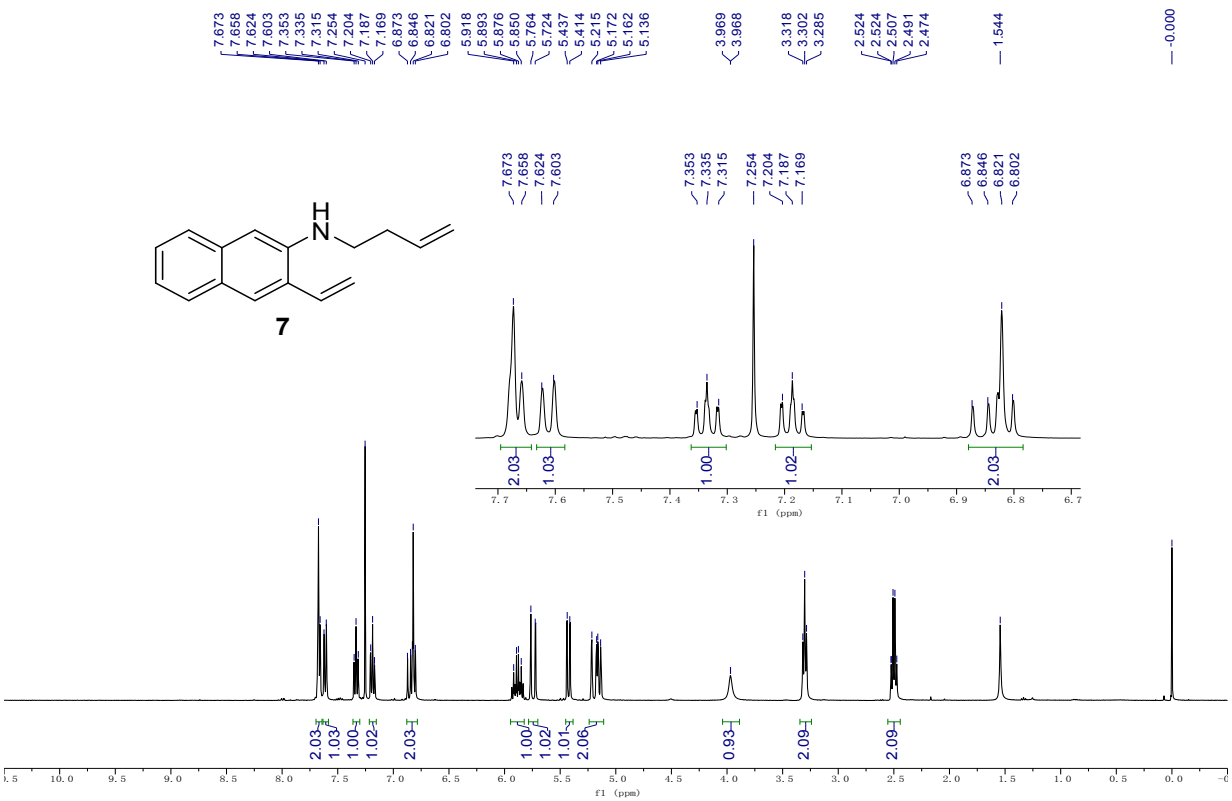
^{13}C NMR spectrum of **BN-NA** (100 MHz, $CDCl_3$, 298 K)



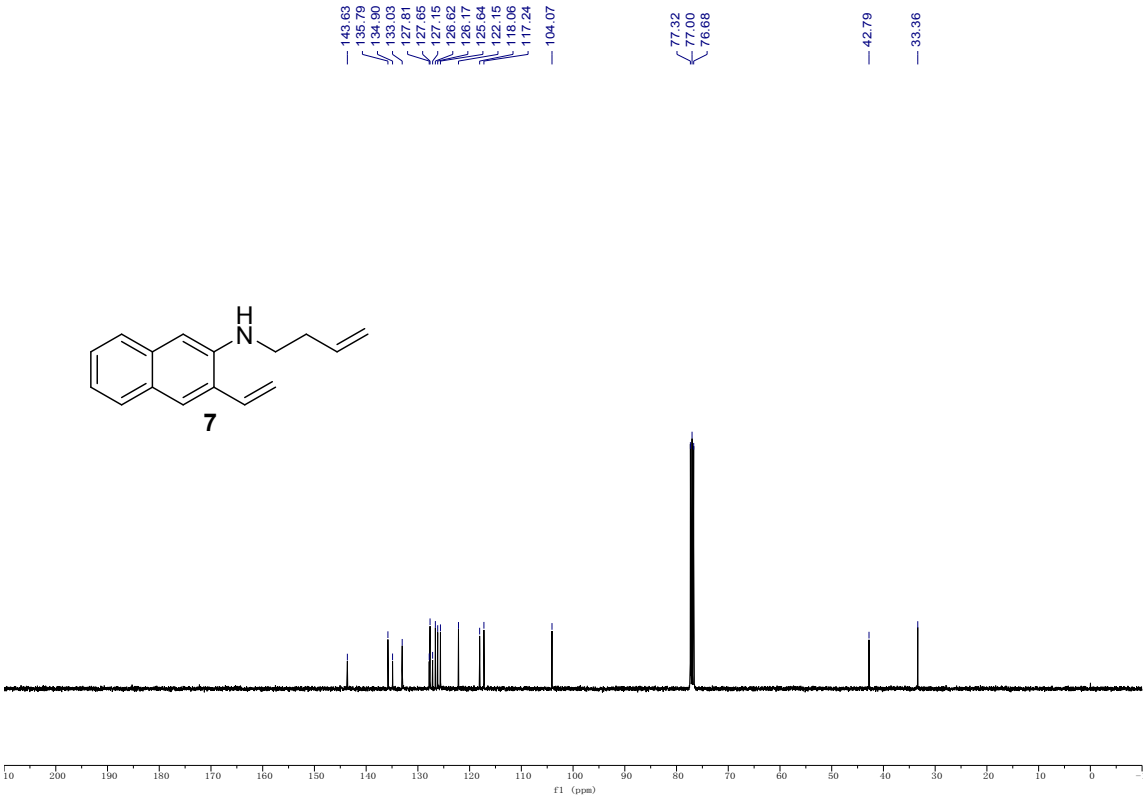
^{11}B NMR spectrum of **BN-NA** (160 MHz, $CDCl_3$, 298 K)



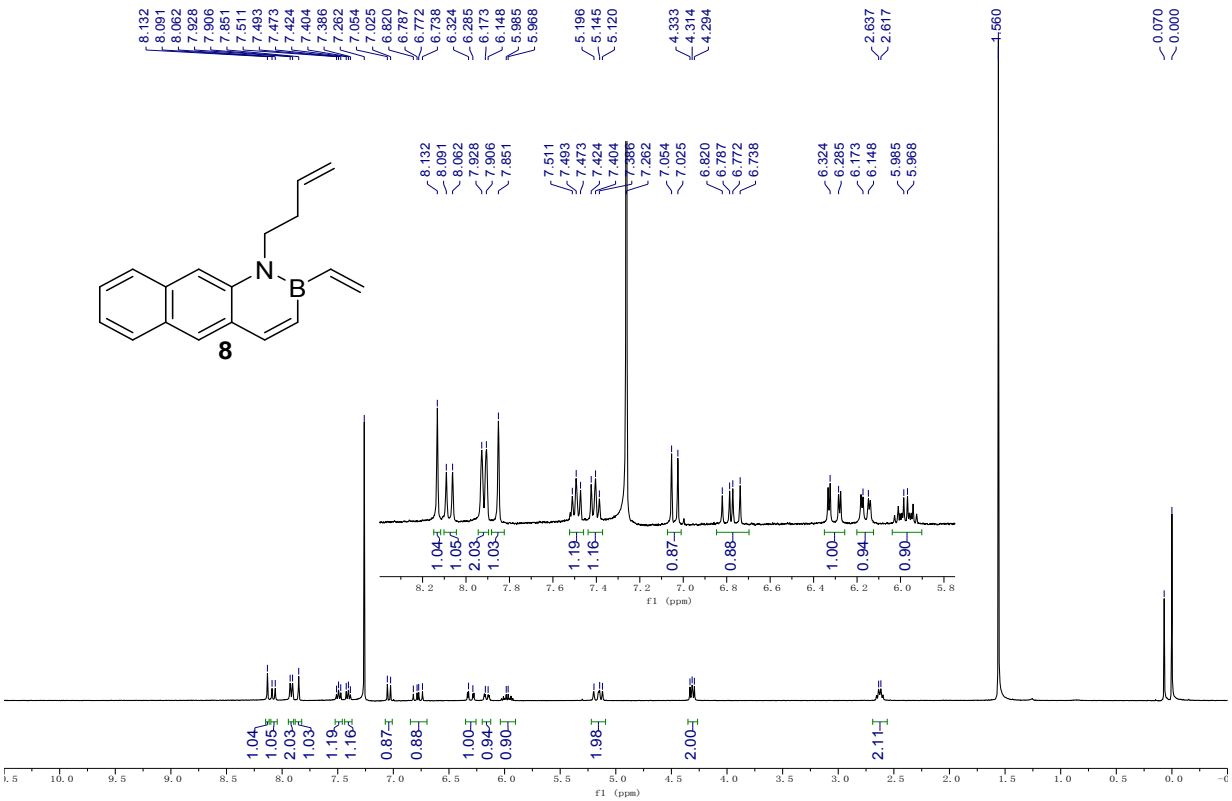
^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$, 298 K)



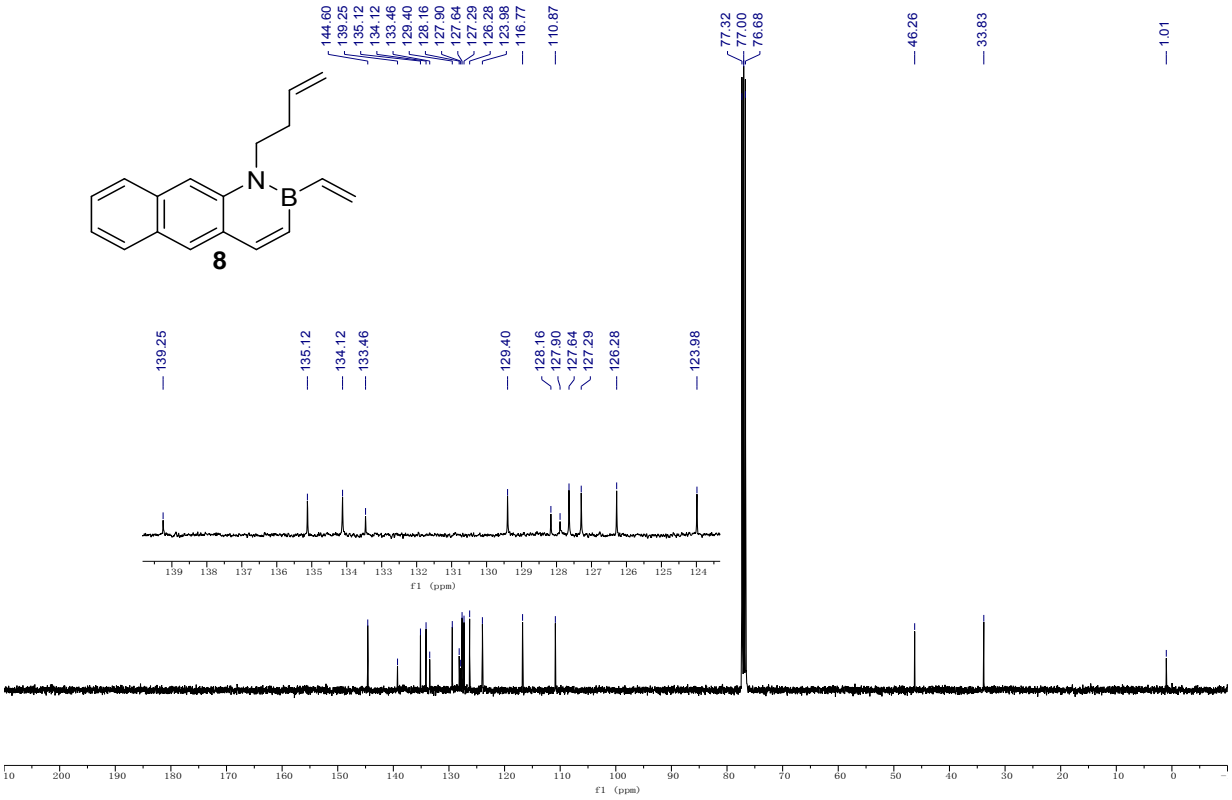
^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$, 298 K)



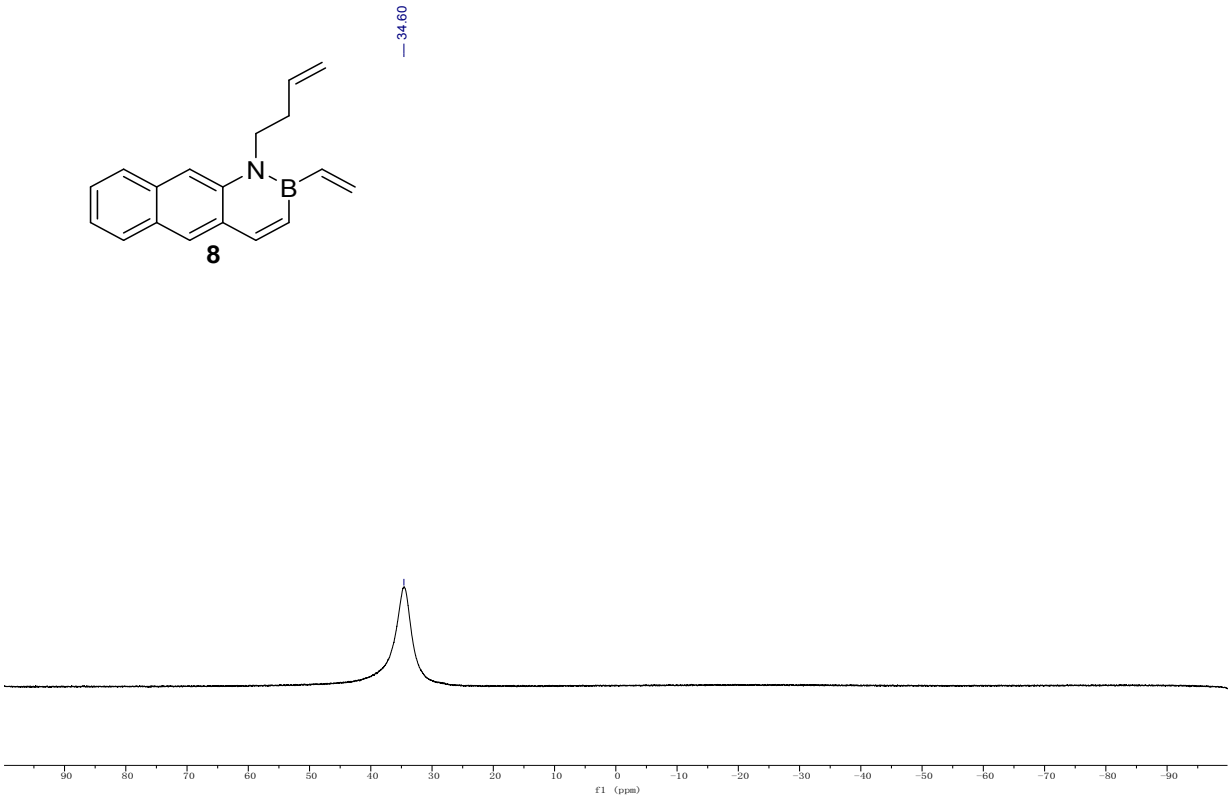
^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$, 298 K)



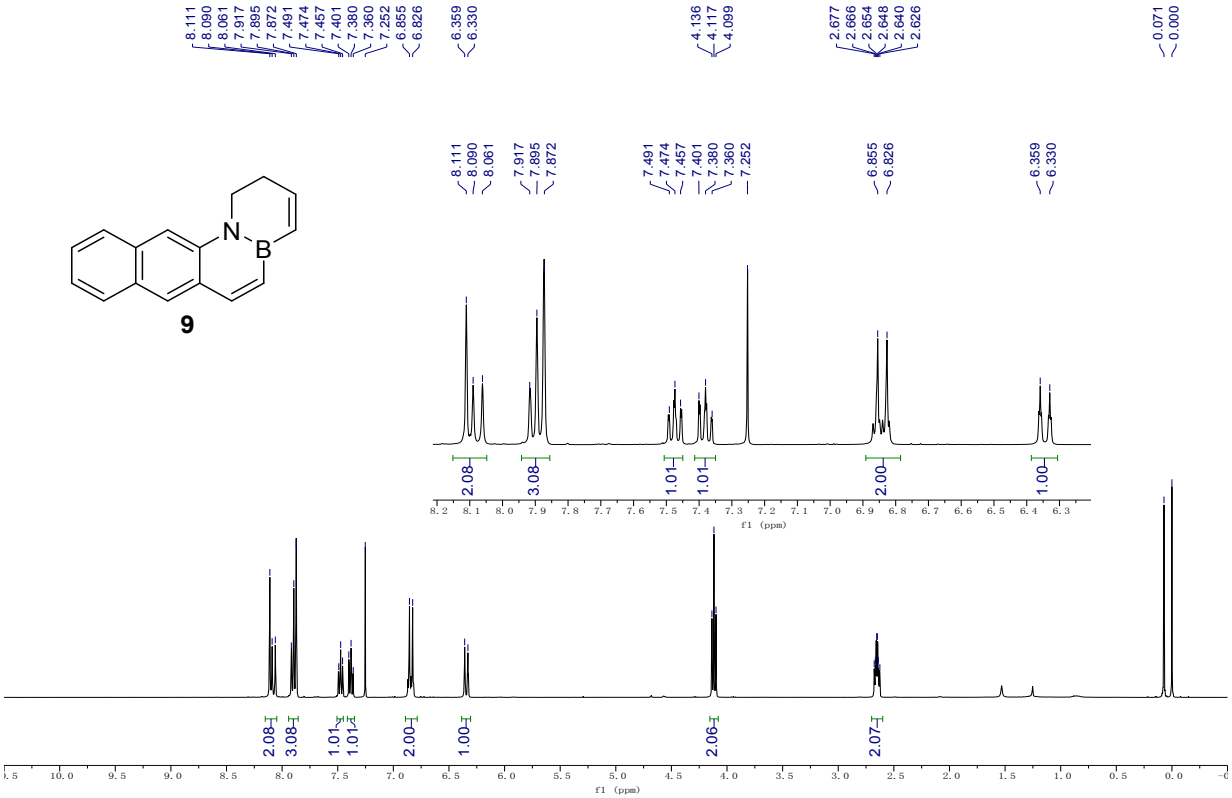
^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$, 298 K)



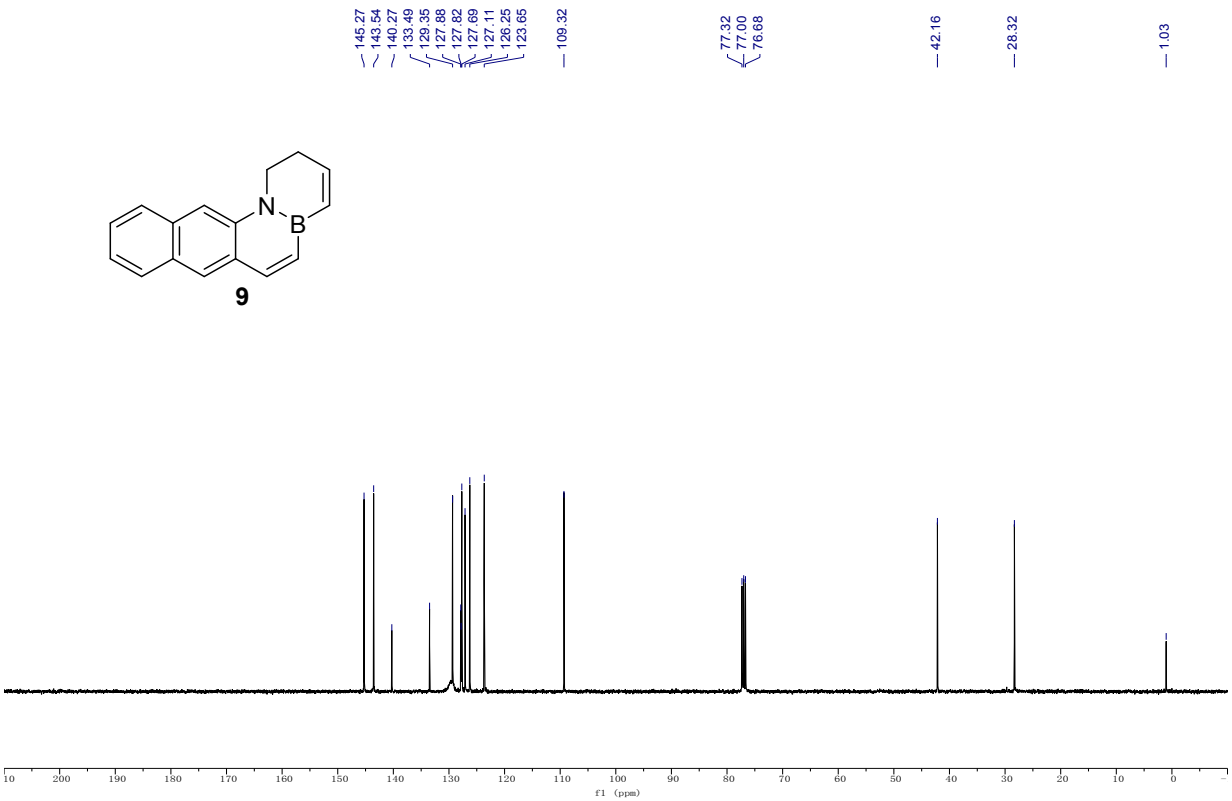
^{11}B NMR spectrum of **8** (160 MHz, $CDCl_3$, 298 K)



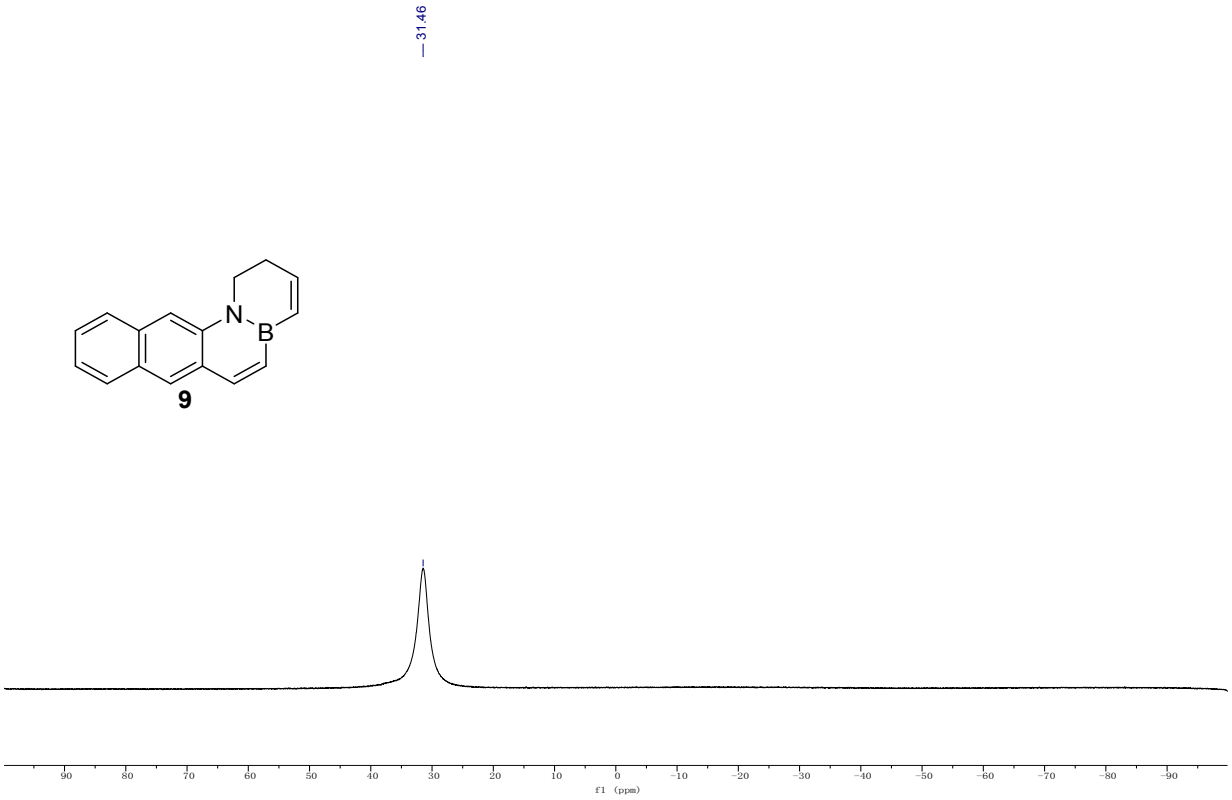
^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$, 298 K)



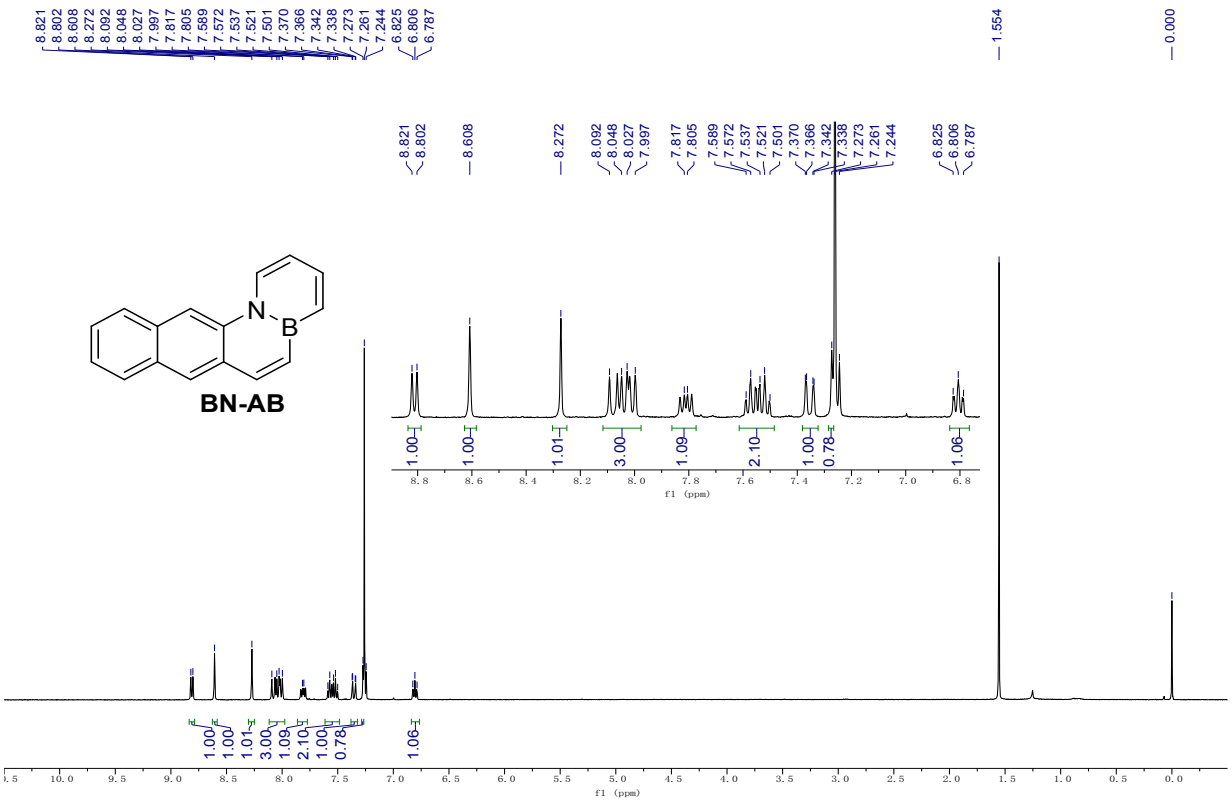
^{13}C NMR spectrum of **9** (100 MHz, $CDCl_3$, 298 K)



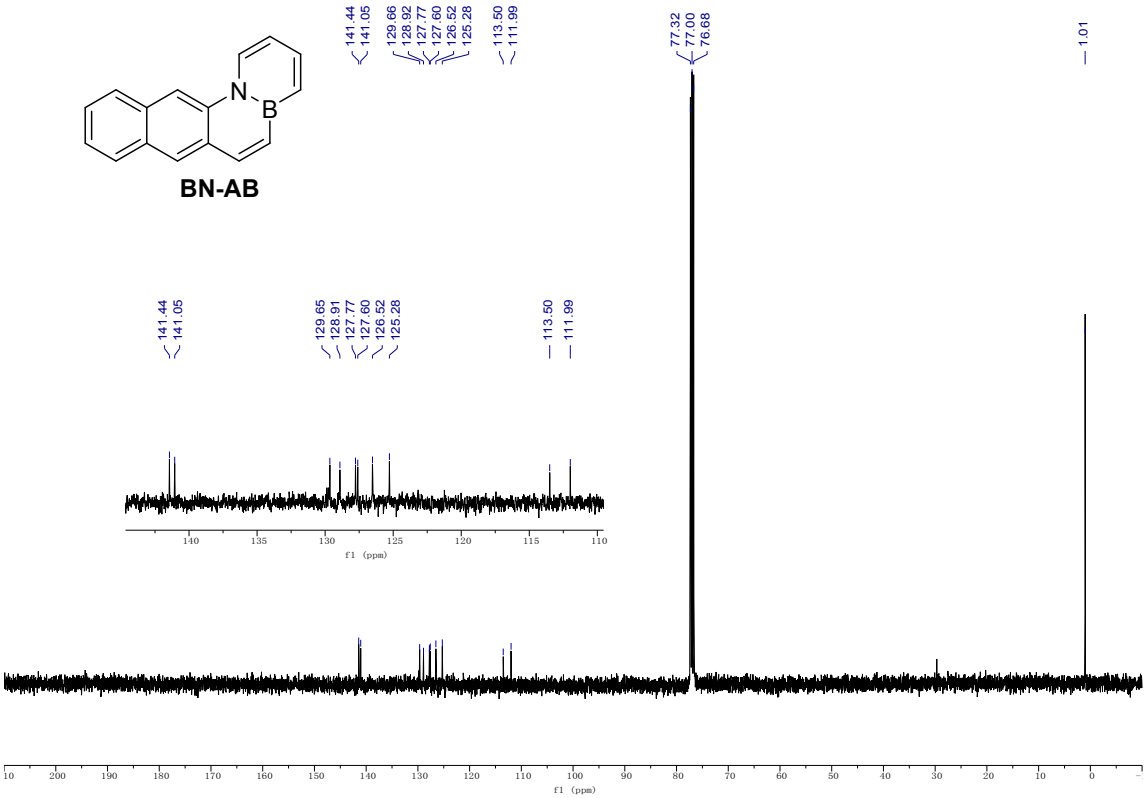
^{11}B NMR spectrum of **9** (160 MHz, $CDCl_3$, 298 K)



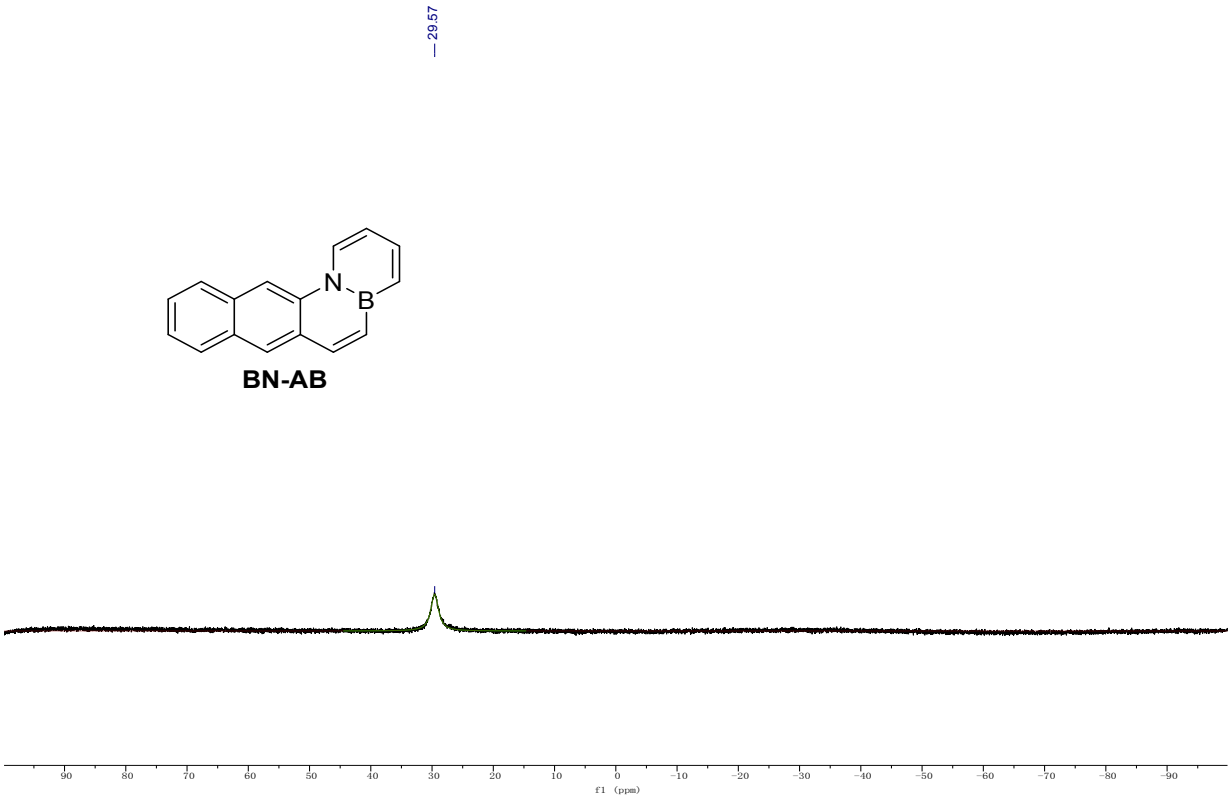
^{1}H NMR spectrum of **BN-AB** (400 MHz, $CDCl_3$, 298 K)



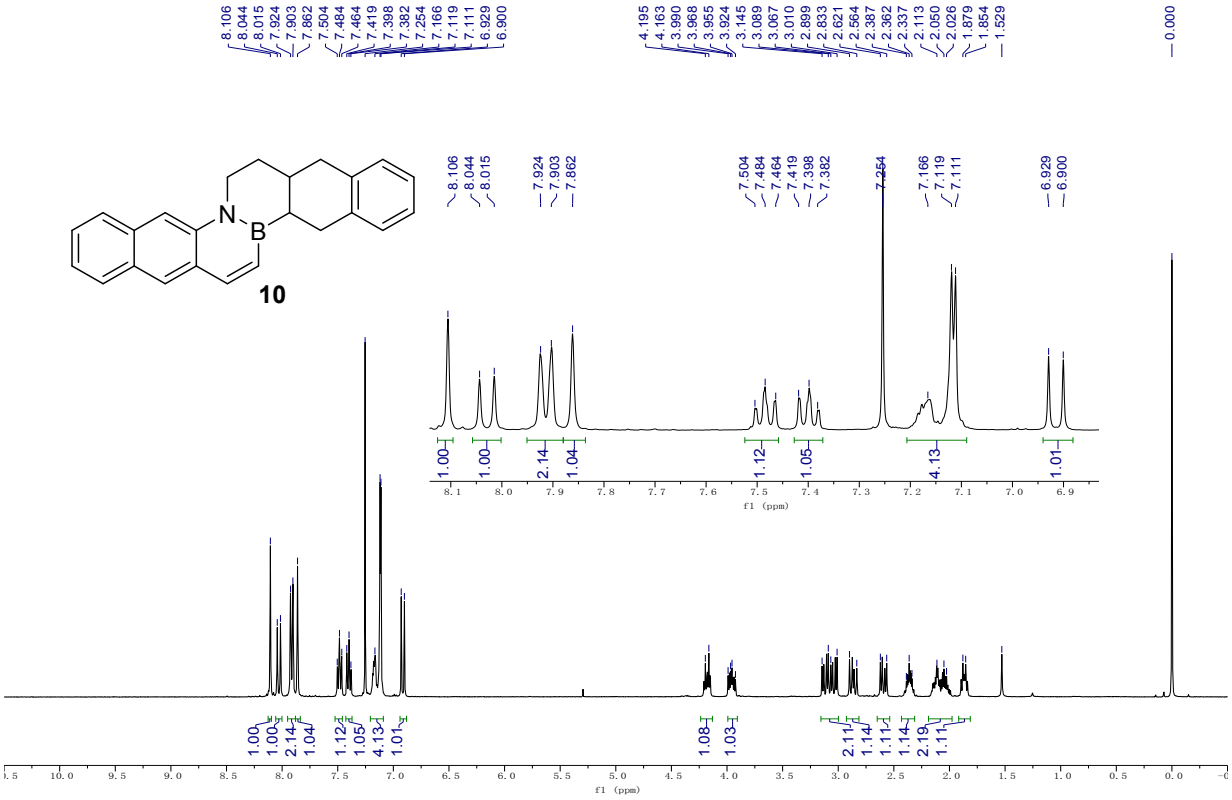
^{13}C NMR spectrum of **BN-AB** (100 MHz, $CDCl_3$, 298 K)



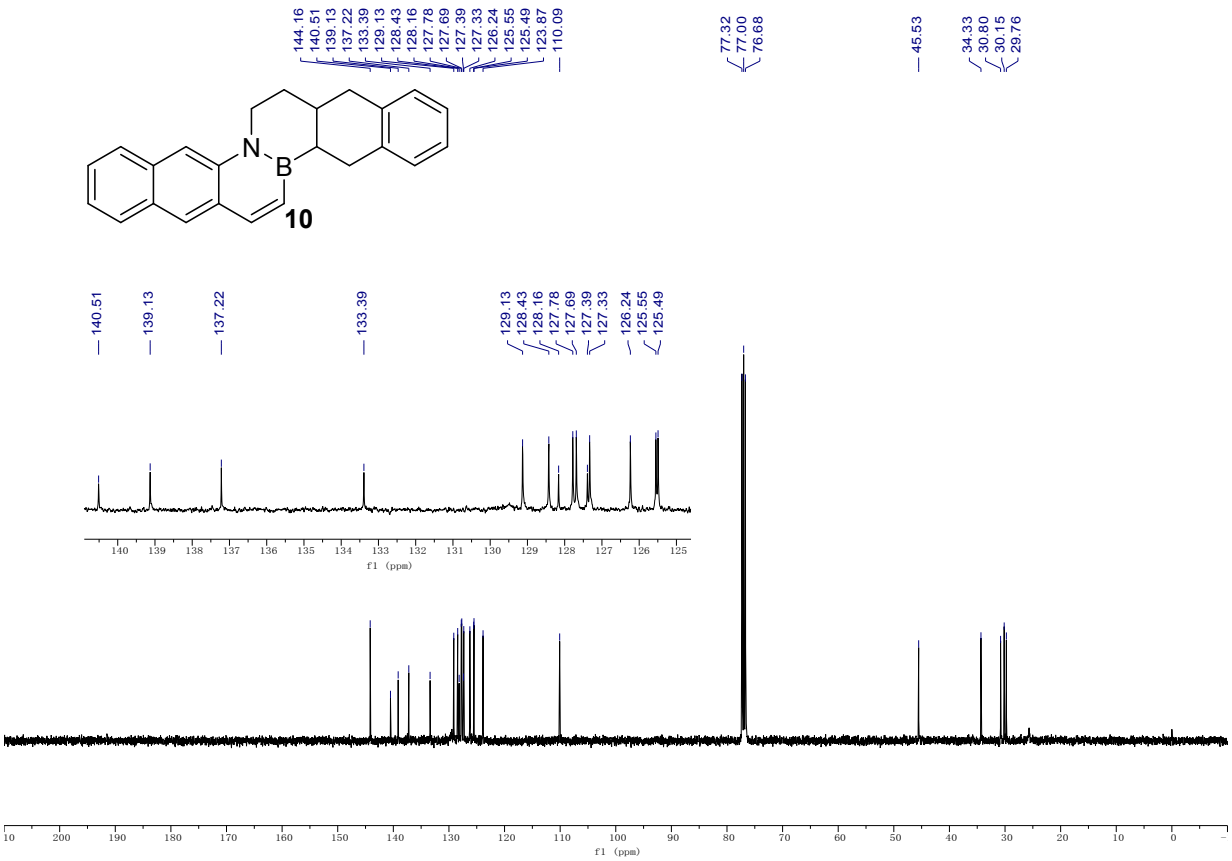
^{11}B NMR spectrum of **BN-AB** (160 MHz, $CDCl_3$, 298 K)



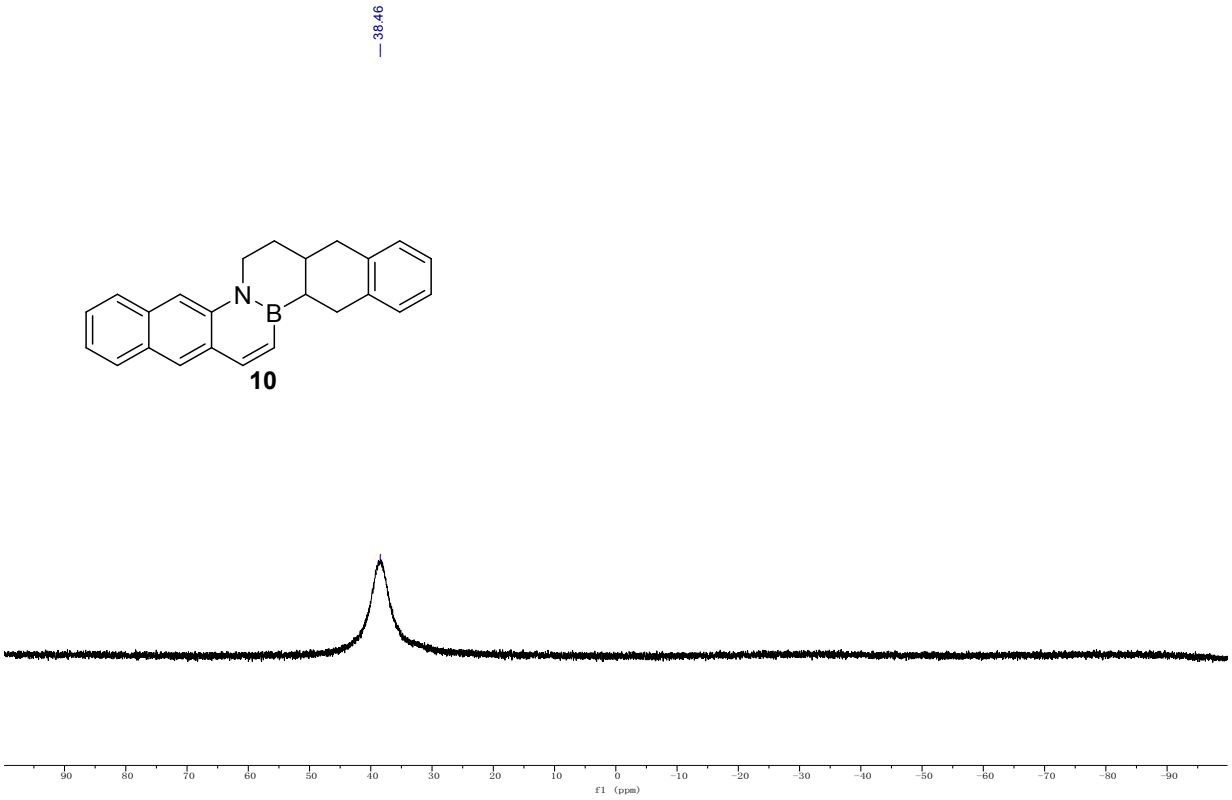
^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$, 298 K)



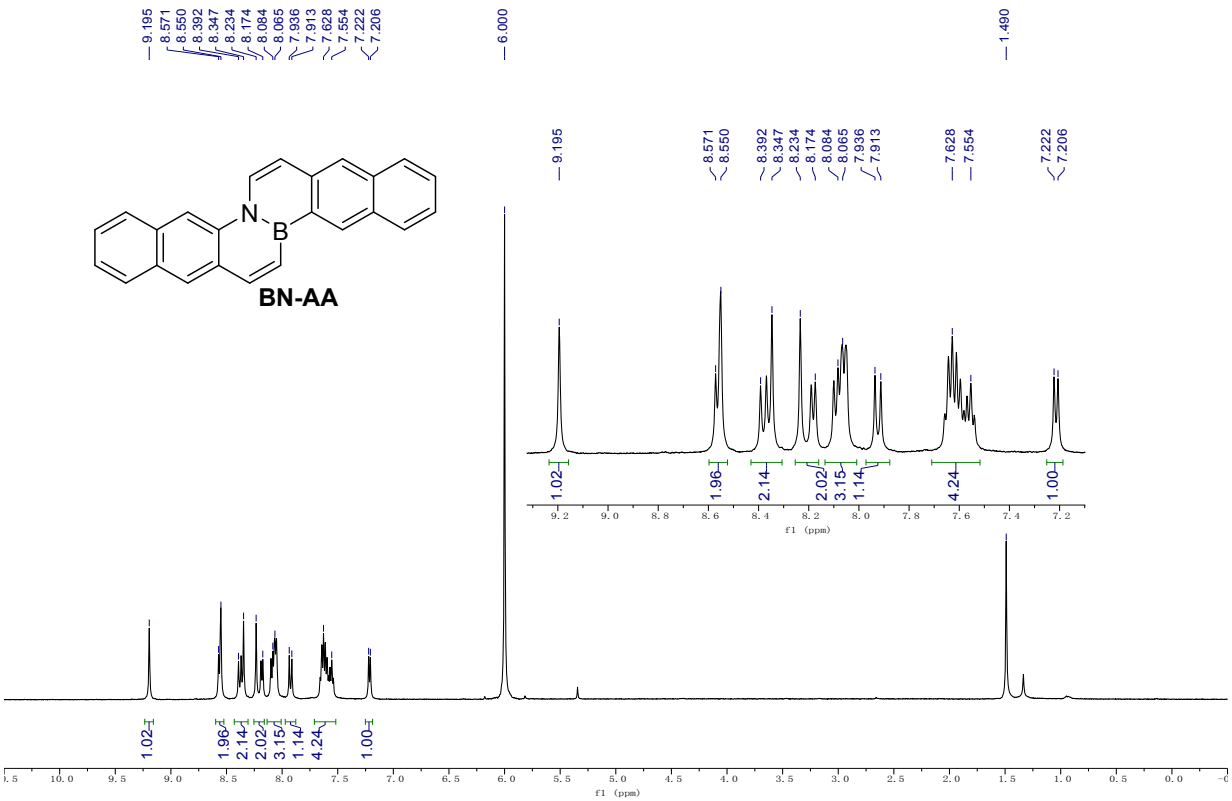
^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$, 298 K)



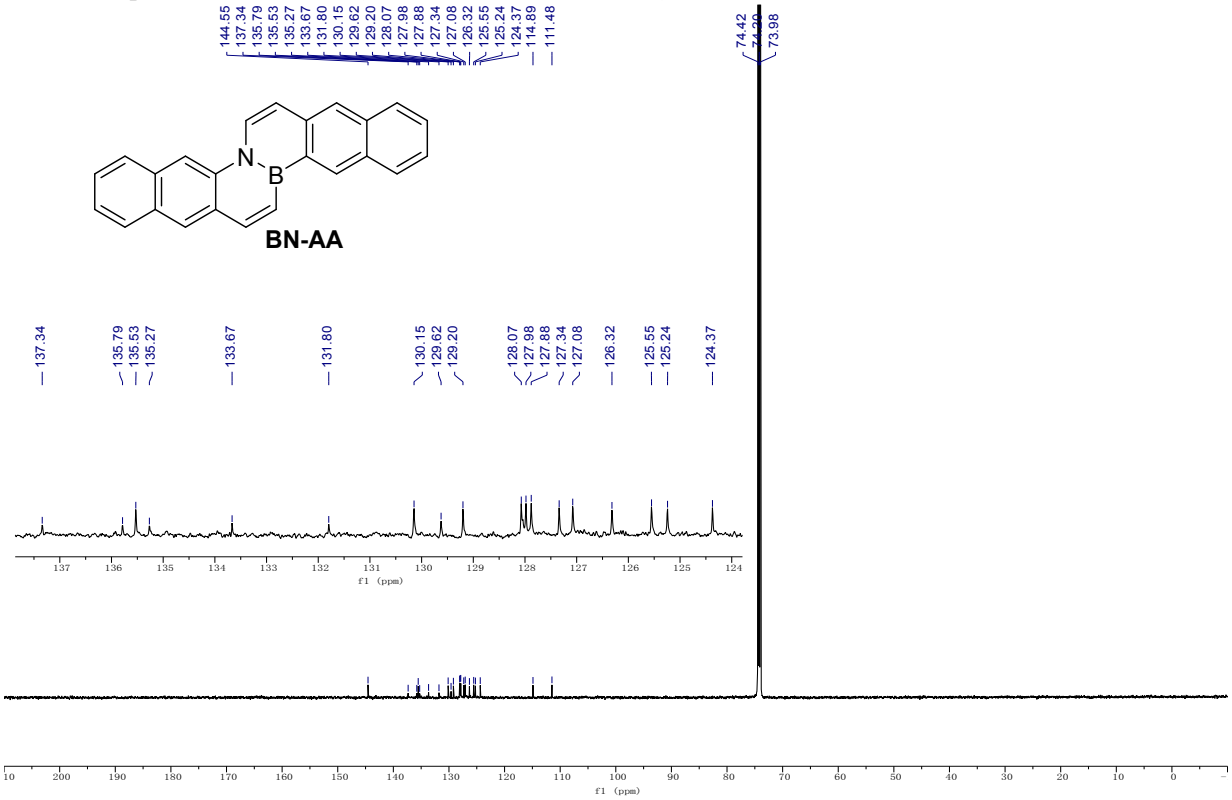
^{11}B NMR spectrum of **10** (160 MHz, $CDCl_3$, 298 K)



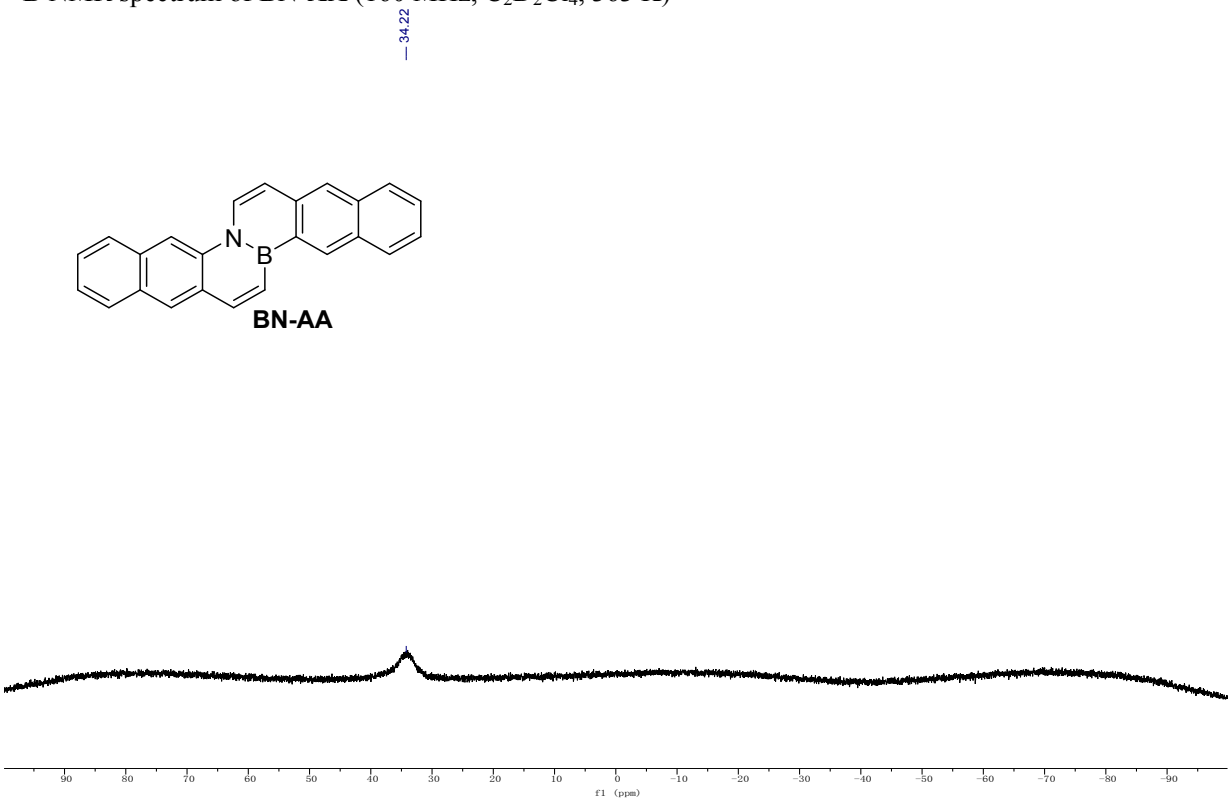
^{1}H NMR spectrum of **BN-AA** (500 MHz, $C_2D_2Cl_4$, 363 K)



^{13}C NMR spectrum of **BN-AA** (125 MHz, $C_2D_2Cl_4$, 363 K)



^{11}B NMR spectrum of **BN-AA** (160 MHz, $C_2D_2Cl_4$, 363 K)



5. References

[1] Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; R. Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox. D. J. Gaussian, Inc., Wallingford CT, **2016**.

[2] Datta, S.; Forrest, S. R.; Djurovich, P.; Polikarpov, E.; Thompson, M. E. *Org. Electron.* **2005**, *6*, 11.