

Supporting Information

Synthesis of Nitrile-Containing *Ortho*-Amide Benzoxazines for Achieving Thermosets with Low Curing Temperature and Superior Performance

Yin Lu, Jiaqi Wang, Yi Yang, Yichen Jing, and Kan Zhang *

Institute of Polymer Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China.

*: To whom correspondence should be addressed:

Kan Zhang: zhangkan@ujs.edu.cn

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S1 Synthesis of nitrile modified *ortho*-amide benzoxazine monomers.

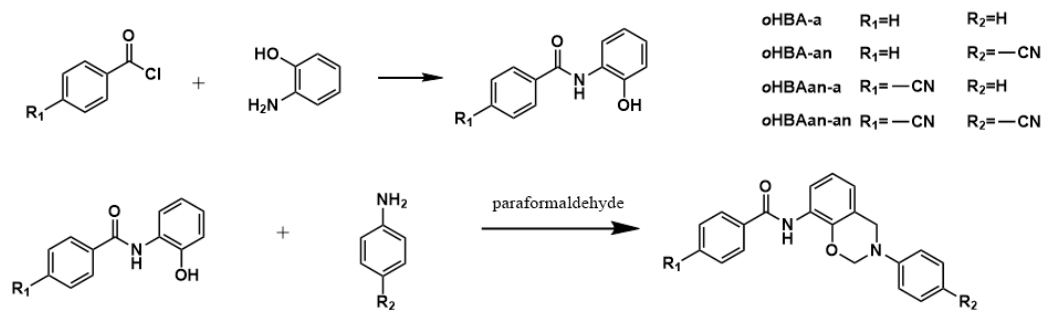


Fig. S1 Synthesis of nitrile modified *ortho*-amide benzoxazine monomers.

S2 FT-IR spectra.

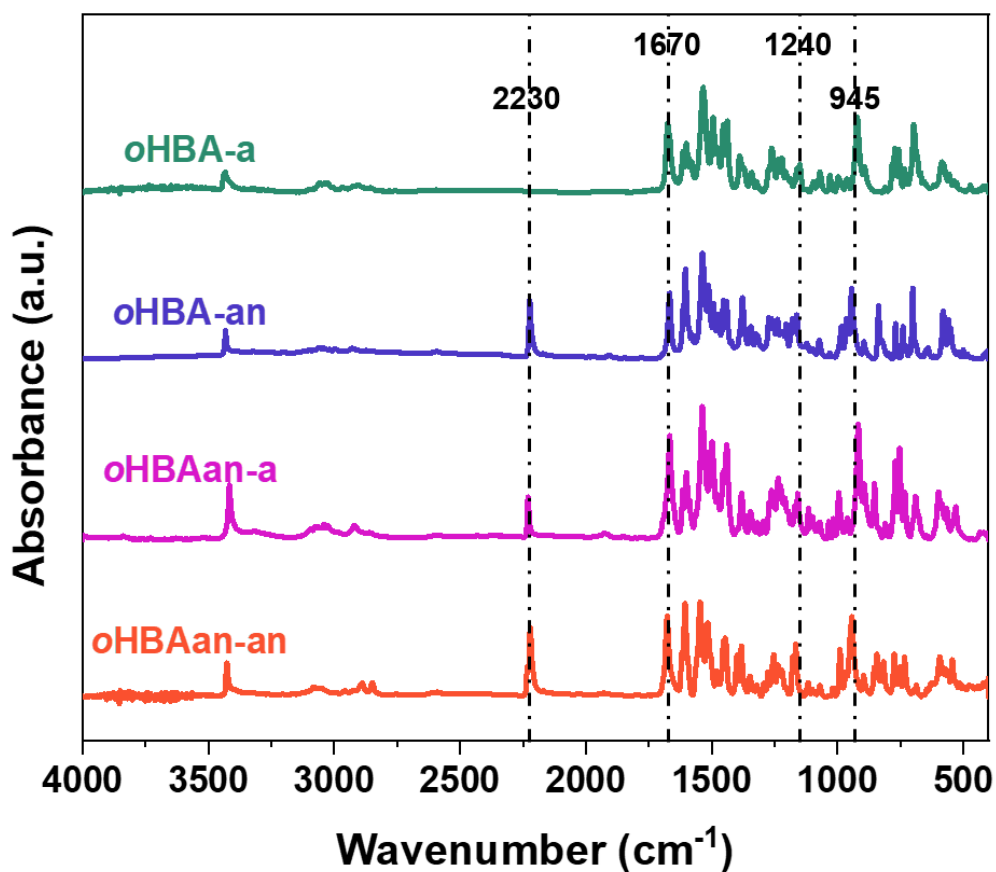


Fig. S2 FT-IR spectra of the *ortho*-amide benzoxazine monomers.

S3 2D ^1H - ^{13}C HMQC.

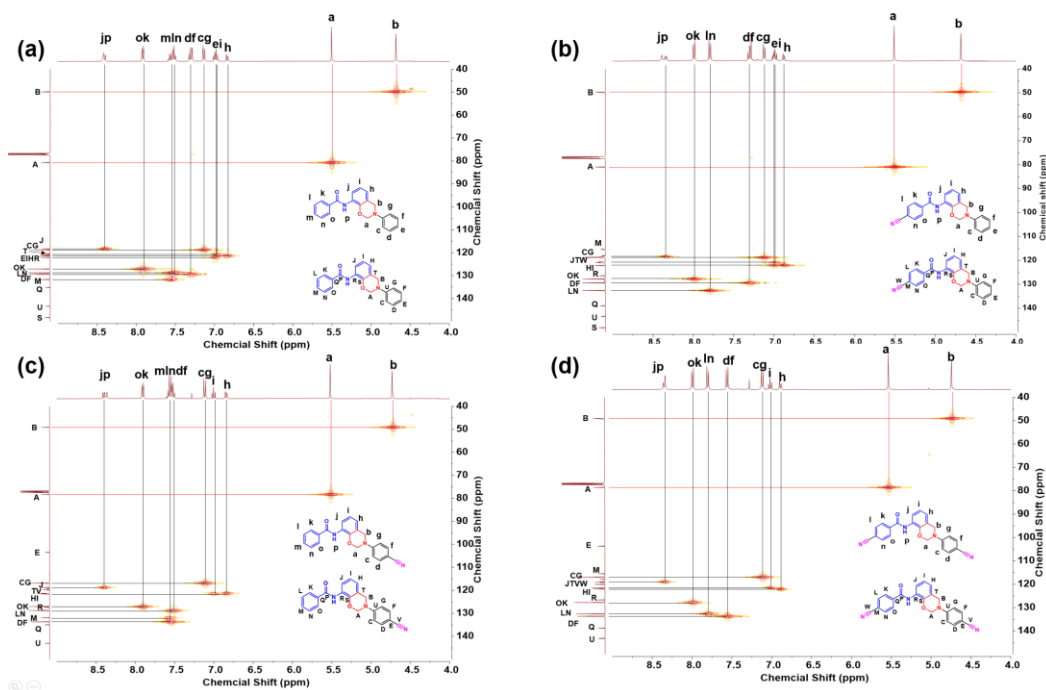


Fig. S3 2D ^1H - ^{13}C HMQC of the *o*HBA-a (a), *o*HBA-an(b), *o*HBAAn-a (c), and *o*HBAAn-an (d) in CDCl_3 .

S4 DSC thermograms.

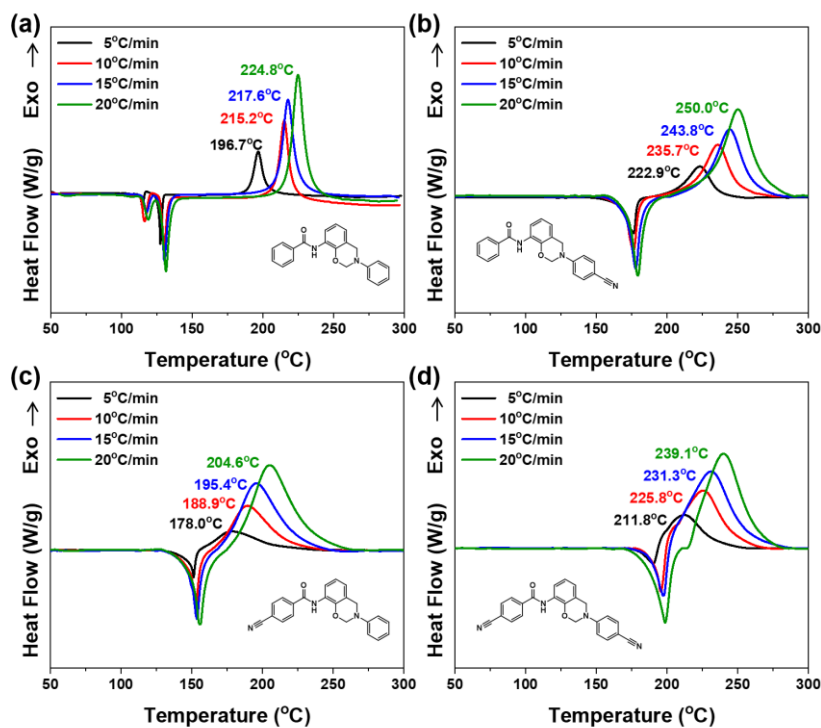


Fig. S4 DSC thermograms of *o*HBA-a (a), *o*HBA-an(b), *o*HBAAn-a (c), and *o*HBAAn-an (d) at different heating rates.

S5 Calculation of activation energy for the monomers.

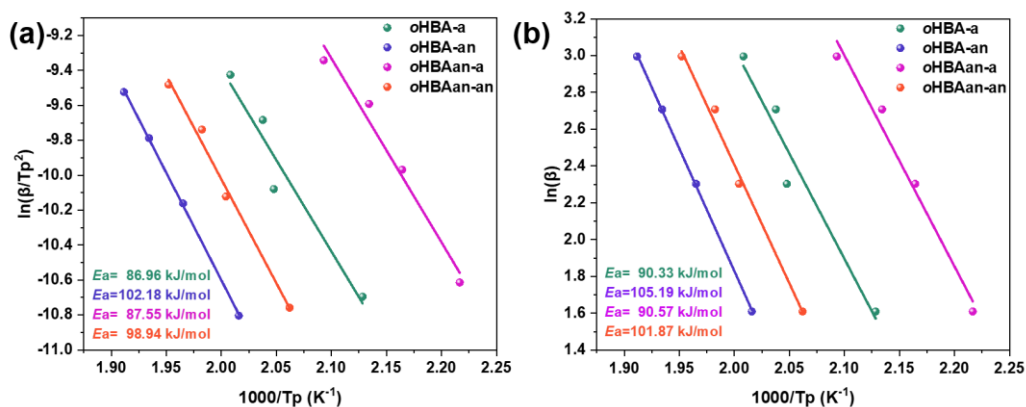


Fig. S5 Representations of the calculation of activation energy for the monomers using Kissinger method (a) and Ozawa method (b).

S6 Conversion versus temperature profile for the monomers.

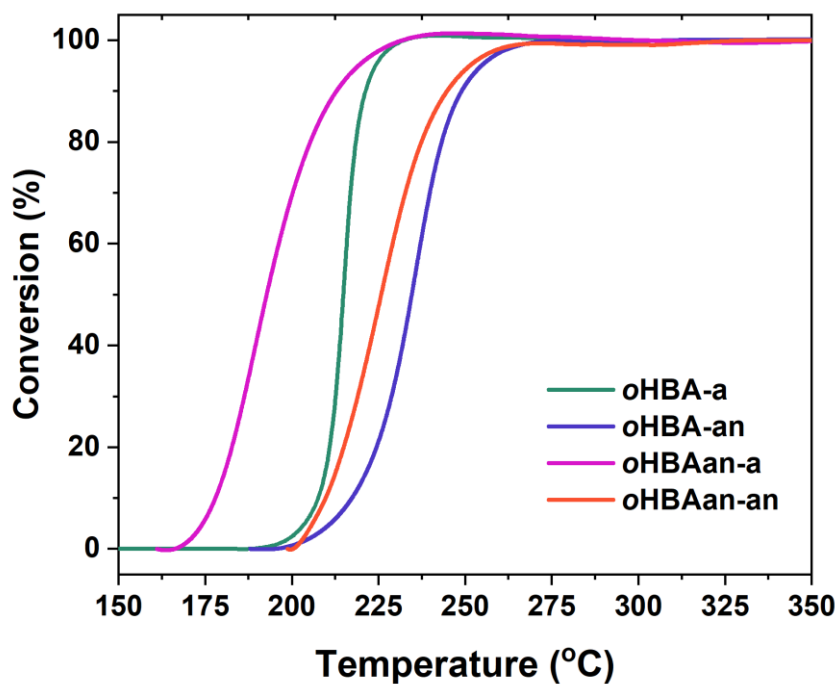


Fig. S6 The plots of conversion vs temperature at heating rate of 10 °C/min obtained by DSC.

S7 In situ FT-IR spectra.

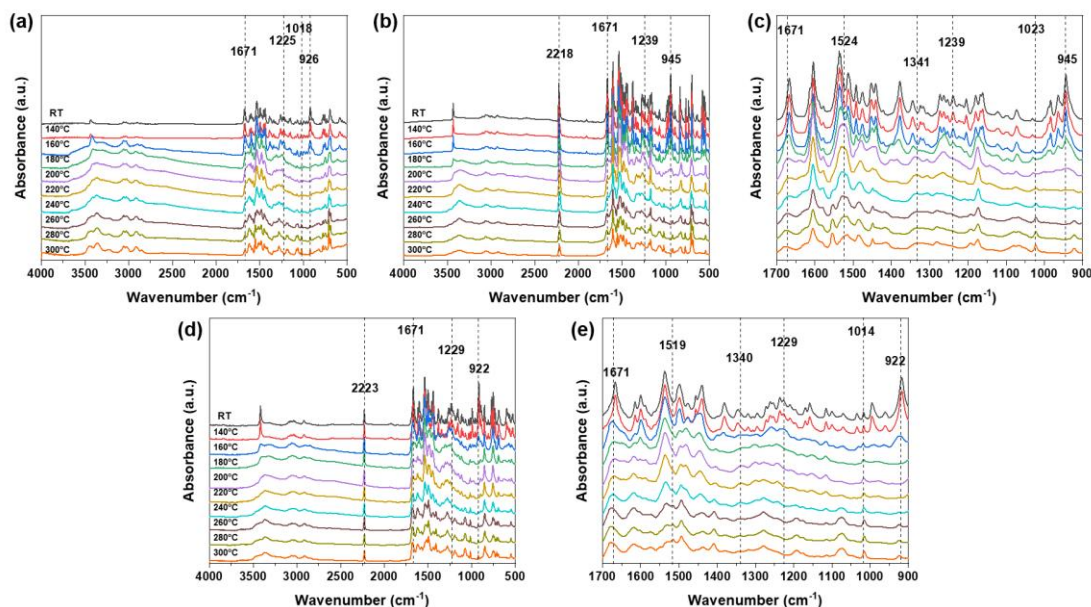


Fig. S7 In situ FT-IR spectra of *o*HBA-a (a), *o*HBA-an(b), partially enlarged *o*HBA-an (c), *o*HBAAn-a (d), partially enlarged *o*HBAAn-a(e).

S8 The data corresponding to the thermal stability and flame retardancy.

Table S1 The thermal stability and flame retardancy of the thermosets.

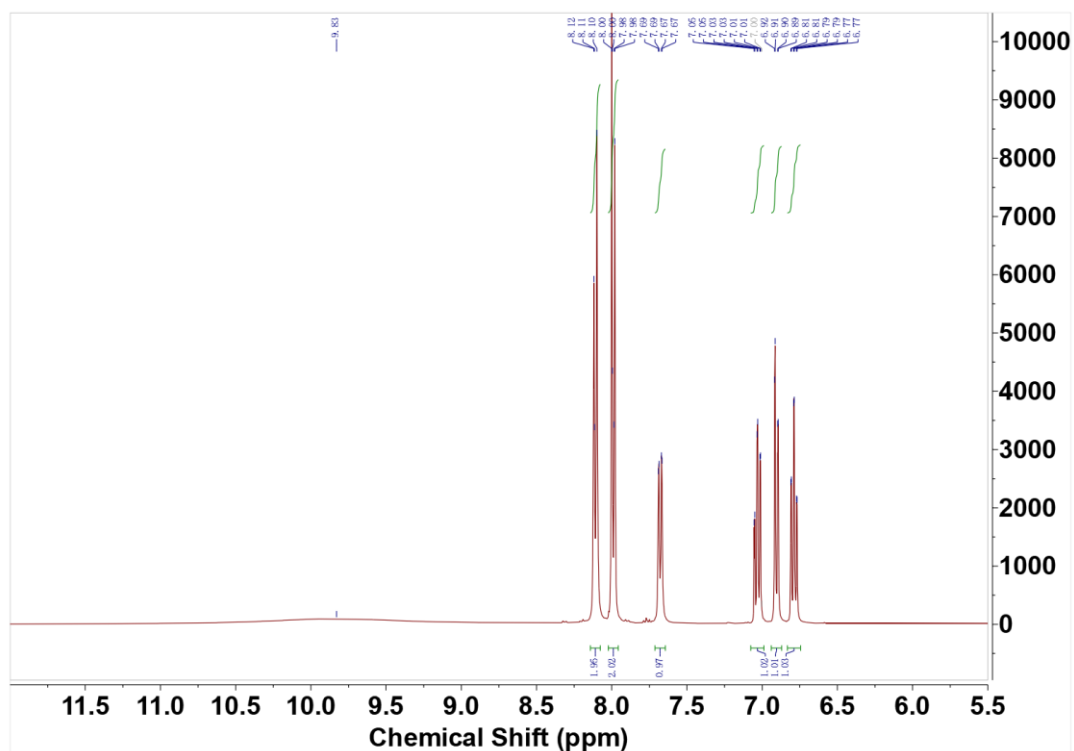
Samples	T _{d5} (°C)	T _{d10} (°C)	Y _c (%)	HRC (J·g ⁻¹ ·K ⁻¹)	THR (kJ·g ⁻¹)	T _g (°C) (DMA)
poly(<i>o</i> HBA-a)	354.0	396.7	42.3	210.2	24.6	280
poly(<i>o</i> HBA-an)	362.0	396.4	54.9	40.2	10.0	304
poly(<i>o</i> HBAAn-a)	392.5	456.3	63.8	56.0	7.5	326
poly(<i>o</i> HBAAn-an)	392.5	429.0	68.0	23.9	3.9	331

S9 The data corresponding to the mechanical property.

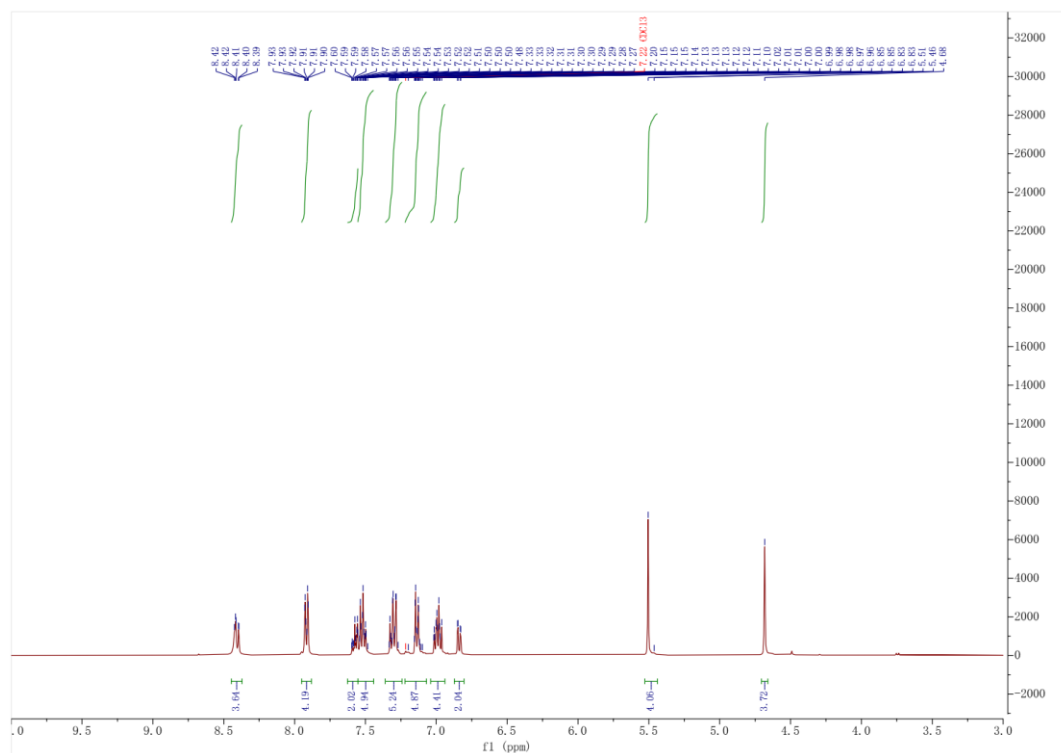
Table S2 The mechanical property of the thermosets.

Samples	Tensile property			Flexural property	
	Modulus (GPa)	Strength (MPa)	Elongation at break (%)	Modulus (GPa)	Strength (MPa)
poly(<i>o</i> HBA-a)	4.6±0.3	62.0±7.2	1.21±0.18	6.0±0.4	63.2±4.6
poly(<i>o</i> HBA-an)	5.0±0.4	70.1±7.6	1.02±0.19	6.3±0.5	52.2±5.8
poly(<i>o</i> HBAAn-a)	4.9±0.6	71.2±9.3	1.03±0.21	6.1±0.7	53.4±6.7
poly(<i>o</i> HBAAn-an)	5.2±0.3	75.4±5.0	0.95±0.12	7.1±0.4	50.6±4.1

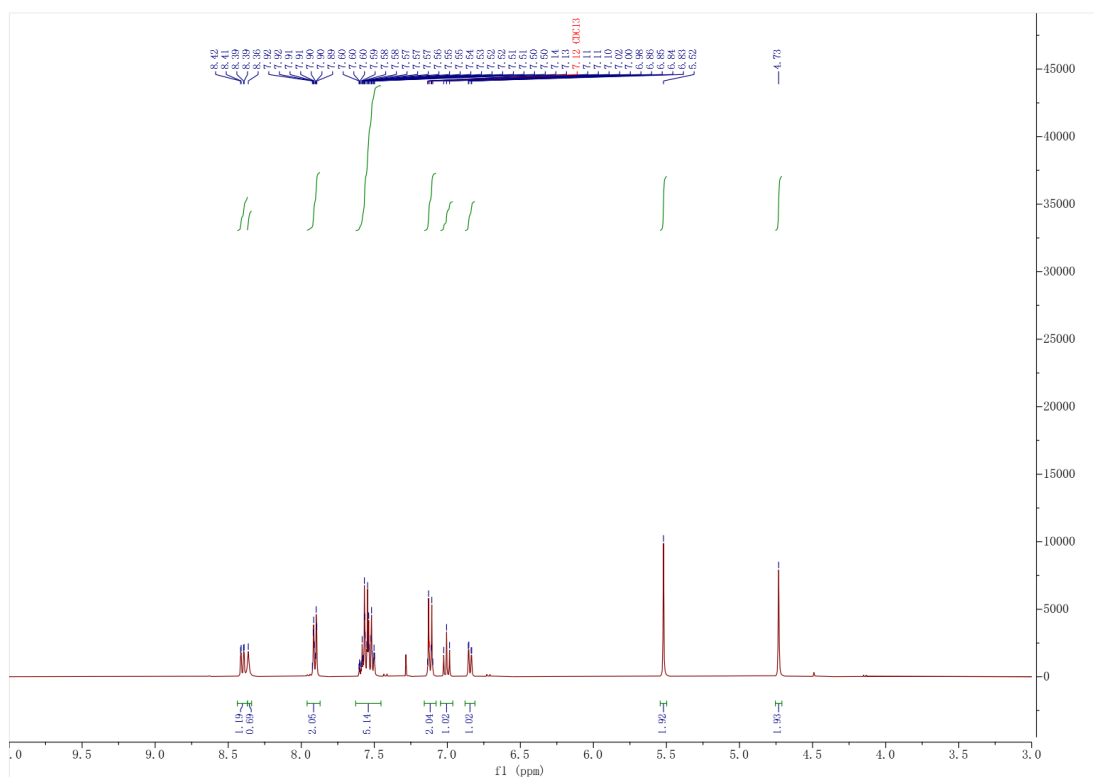
S10 ^1H NMR Spectrum



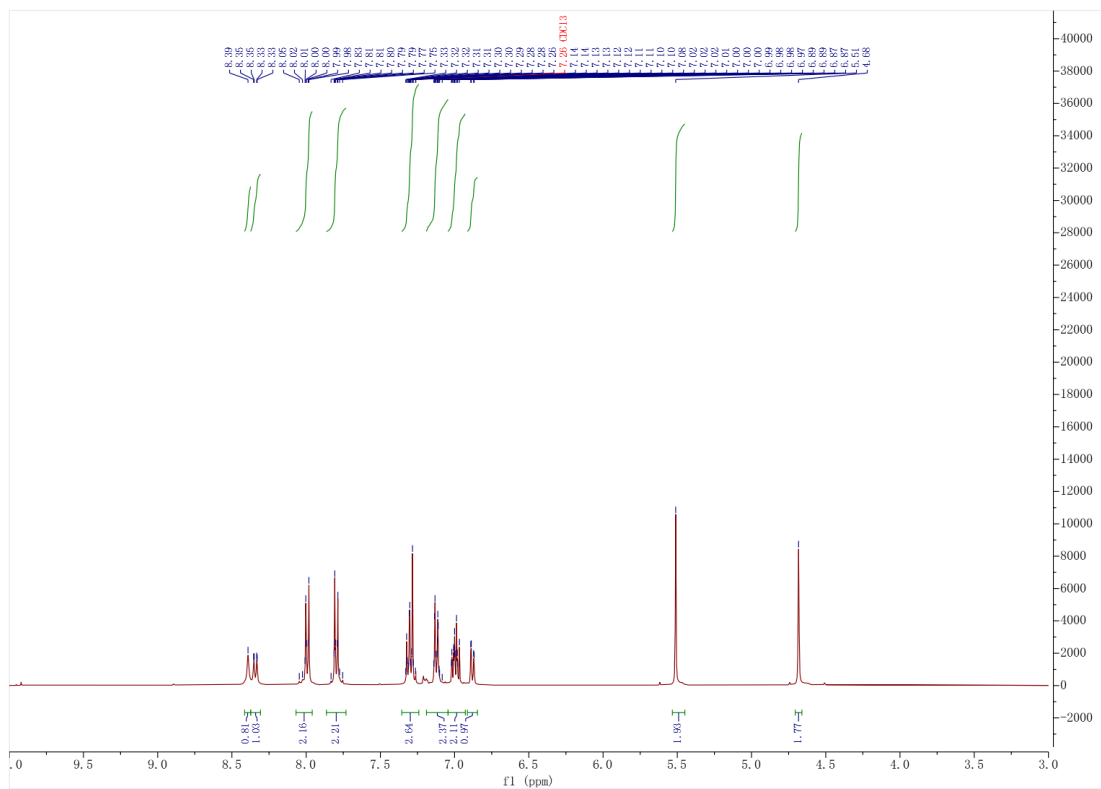
^1H NMR Spectrum of *o*-HBAAn



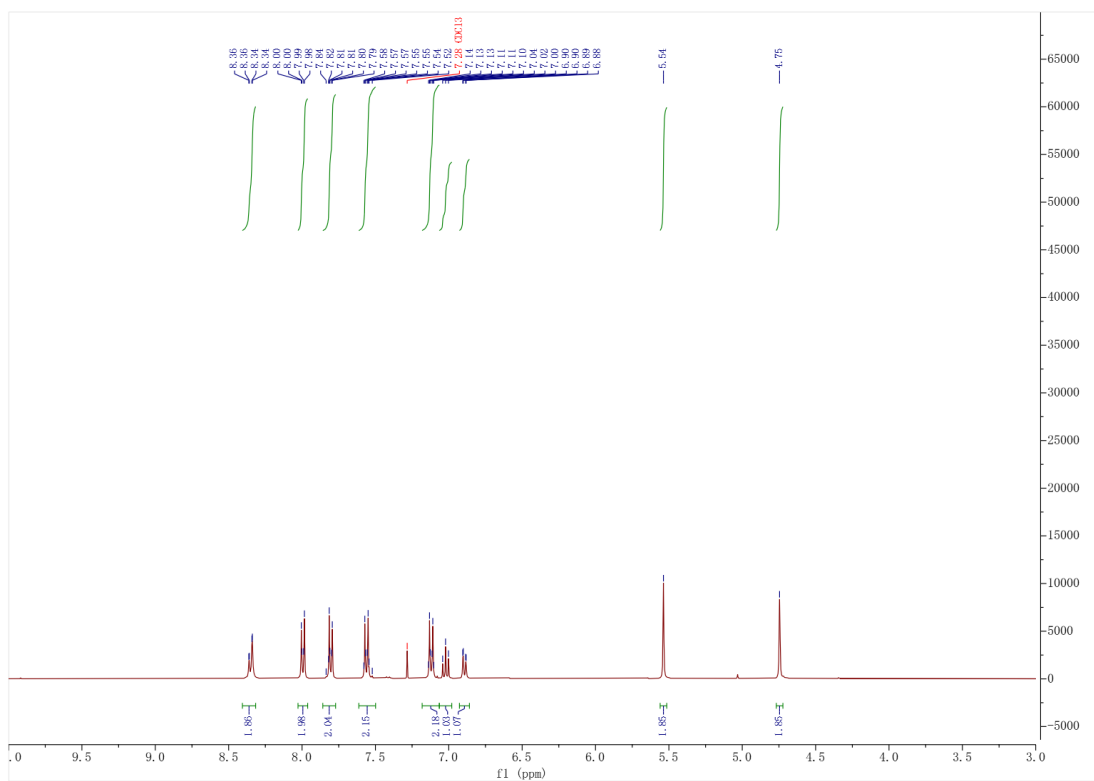
^1H NMR Spectrum of *o*HBA-a



¹H NMR Spectrum of oHBA-an

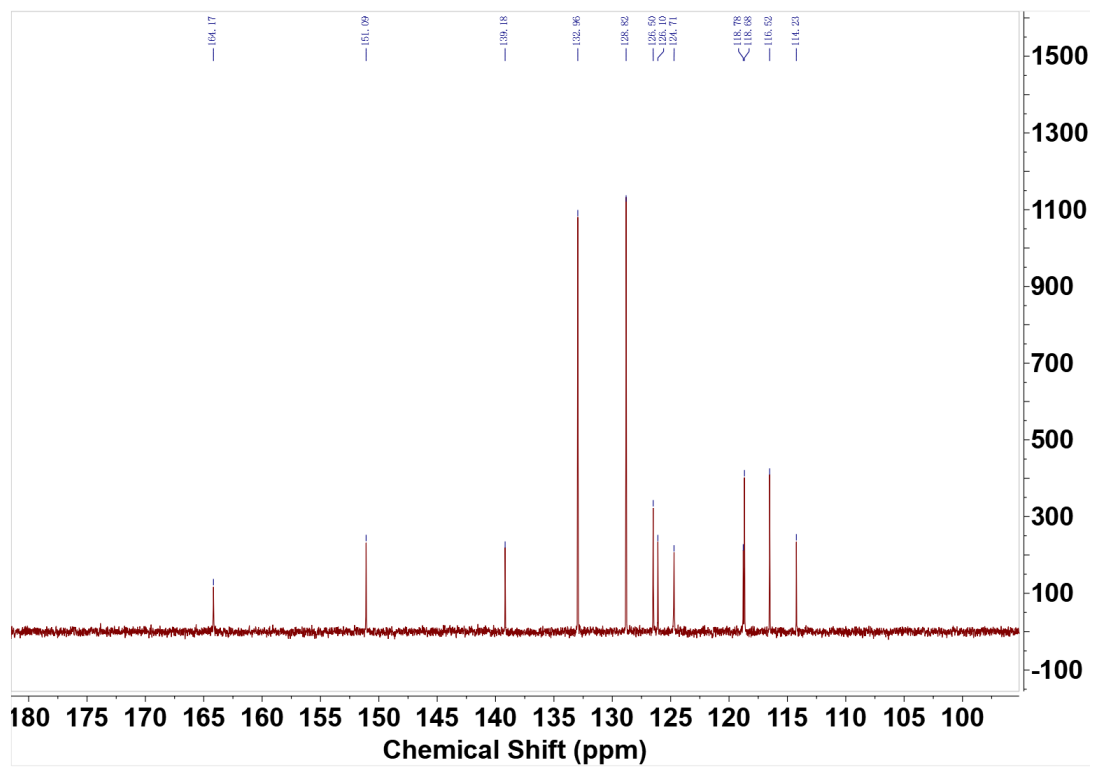


¹H NMR Spectrum of oHBAAn-a

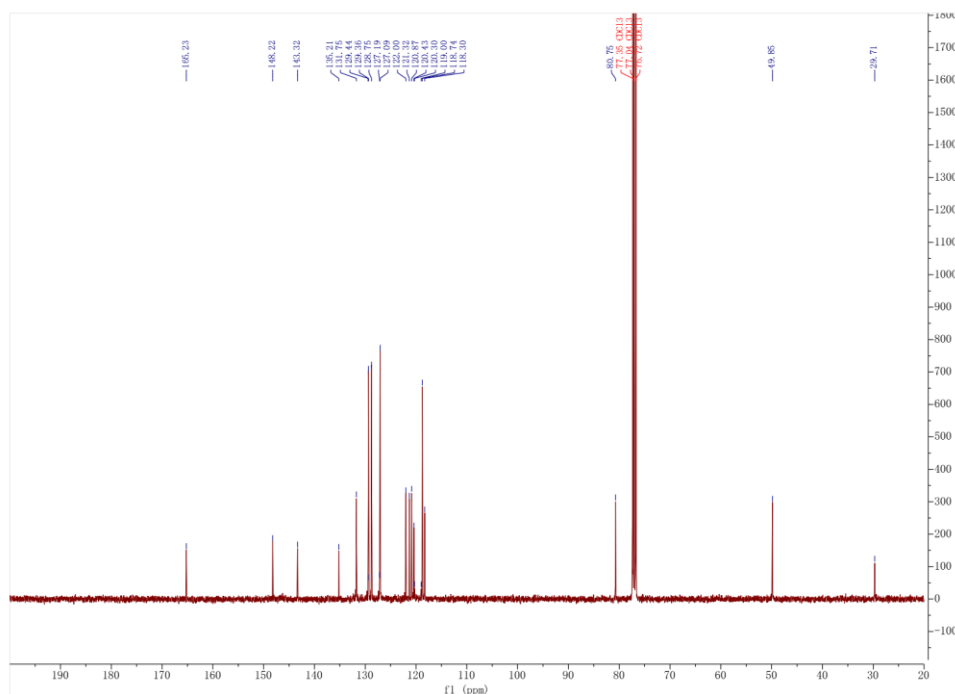


¹H NMR Spectrum of oHBAAn-an

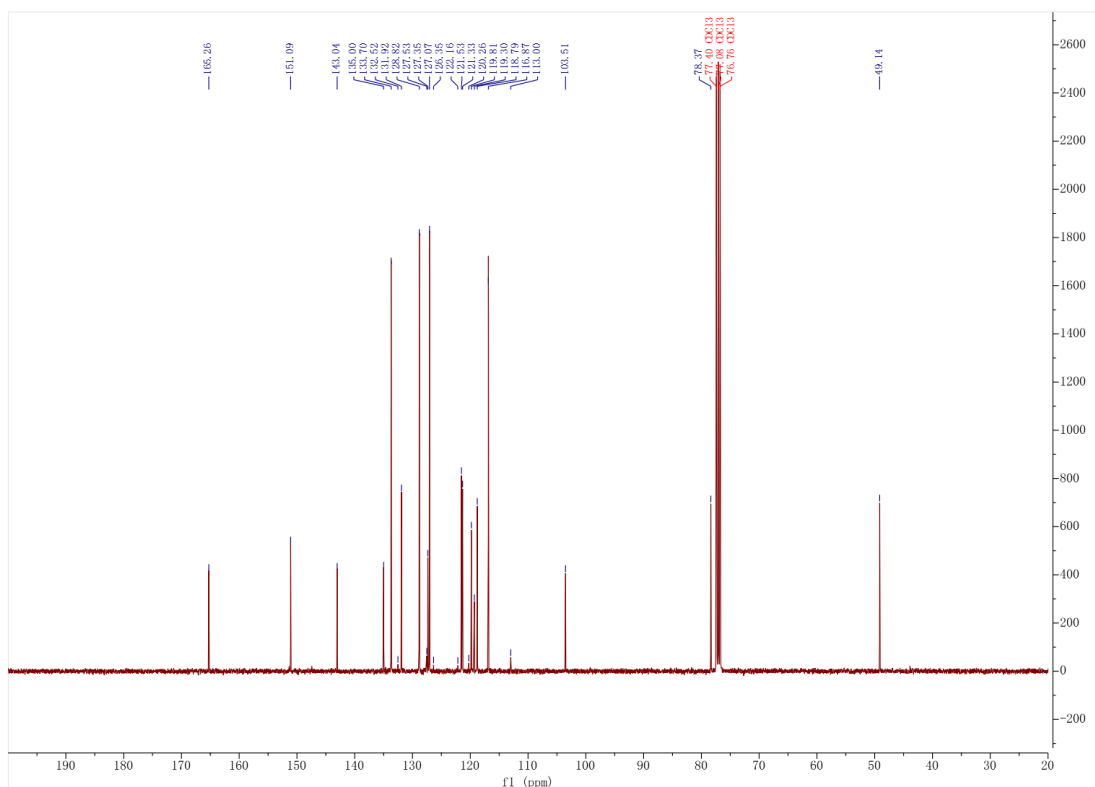
S11 ¹³C NMR Spectrum



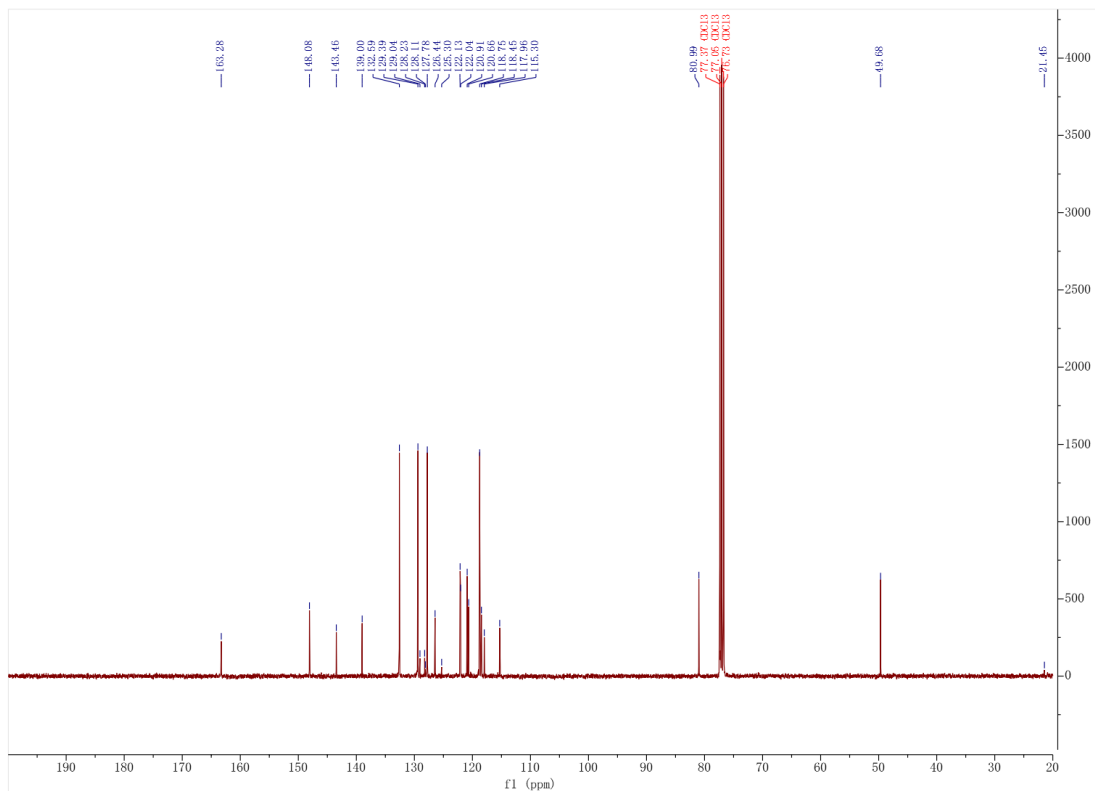
¹³C NMR Spectrum of *o*-HBAan



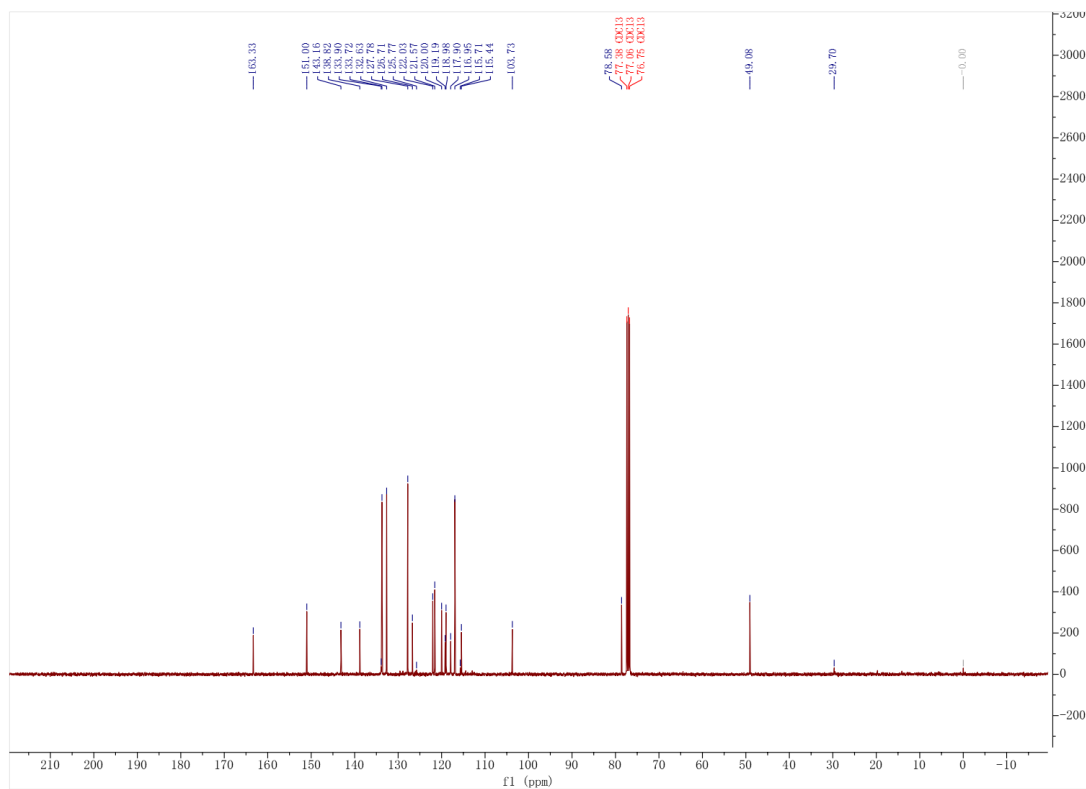
¹³C NMR Spectrum of *o*HBA-a



¹³C NMR Spectrum of *o*HBA-an

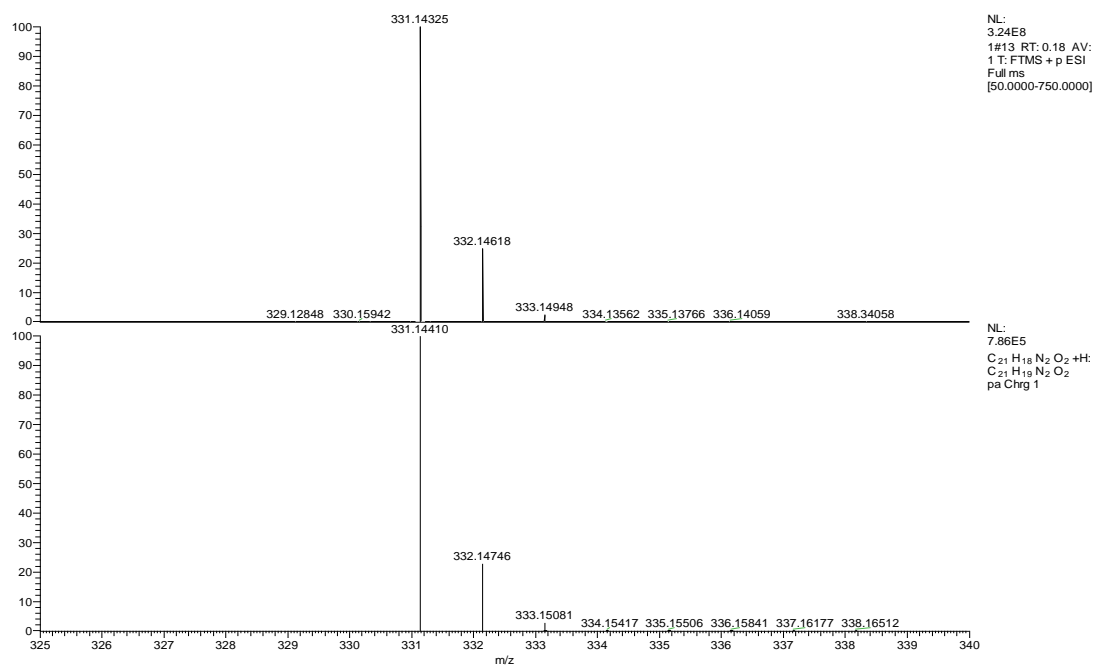


¹³C NMR Spectrum of *o*HBAan-a

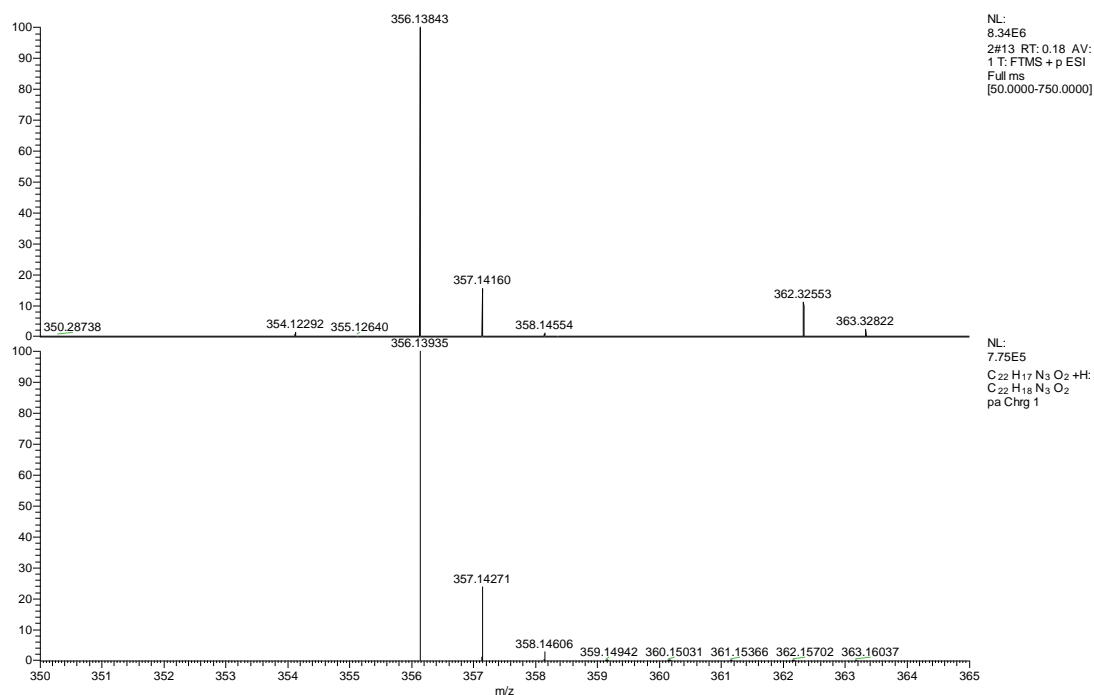


^{13}C NMR Spectrum of *o*HBAAn-an

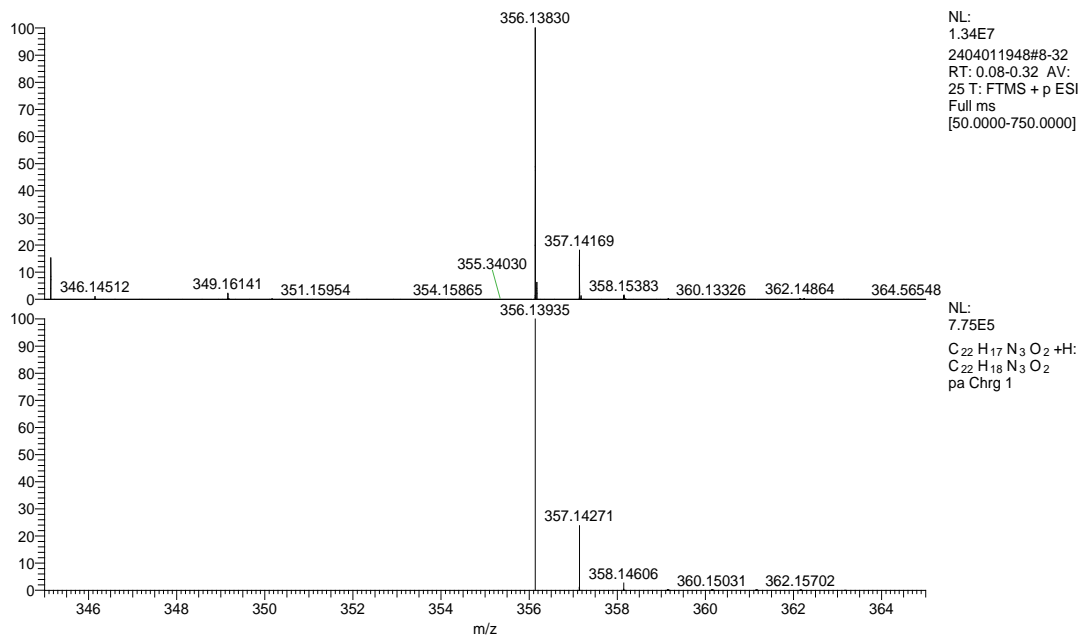
S12. HR-MS Spectrum.



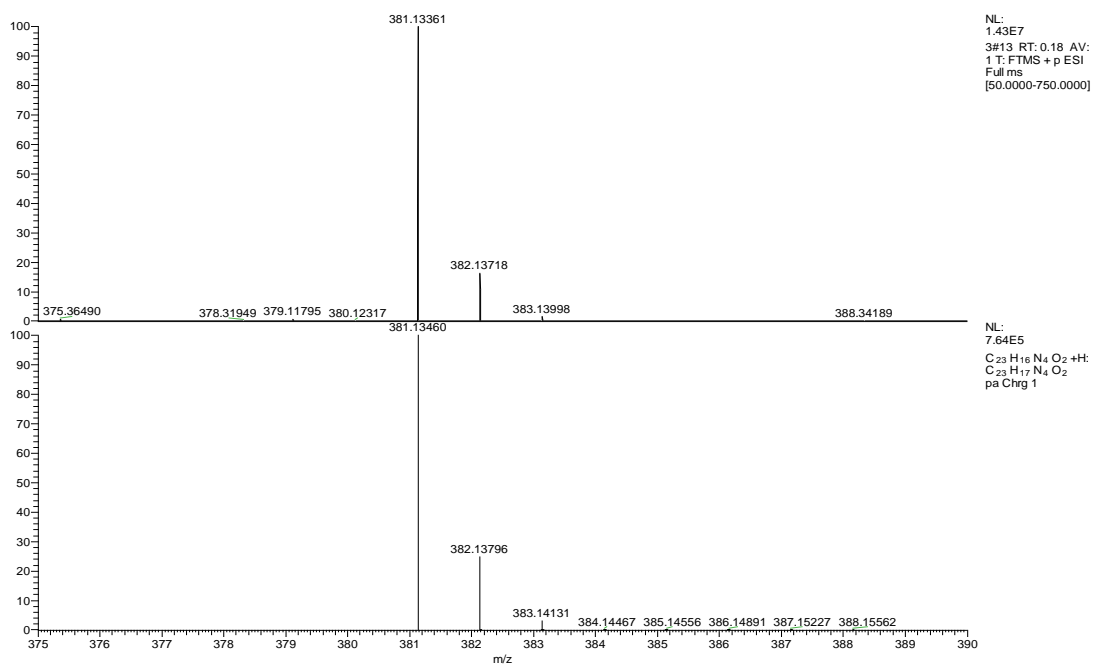
HR-MS Spectrum of *o*HBA-a



HR-MS Spectrum of *o*HBA-an



HR-MS Spectrum of *o*HBAan-a



HR-MS Spectrum of *o*HBAan-an

S13. Detailed DFT optimized structure

1.oHBA-a

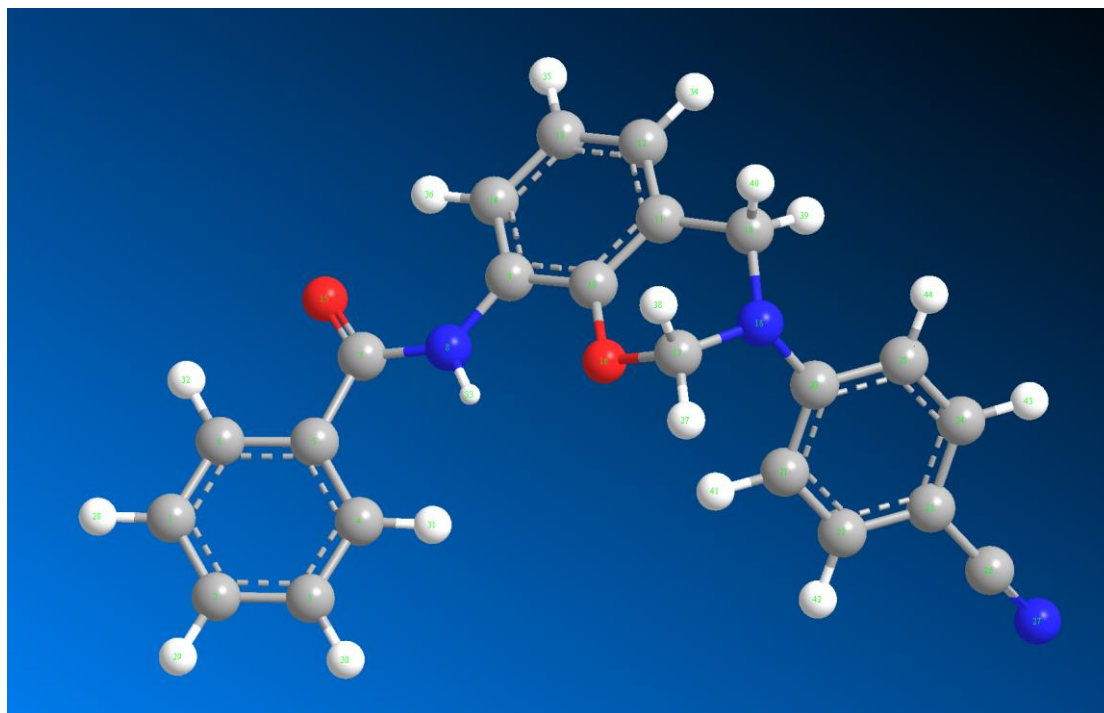


Tag	Symbol	X	Y	Z
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3	C	-4.2755	-3.1223	0.4882
4	C	-3.5484	-1.9811	0.1494
5	C	-4.212	-0.8028	-0.2236
6	C	-5.6128	-0.7938	-0.2703
7	C	-3.5069	0.4673	-0.6135
8	N	-2.2272	0.5964	-0.1199
9	C	-1.3178	1.6476	-0.3183
10	C	-0.0814	1.5309	0.3539
11	C	0.9116	2.505	0.231
12	C	0.6562	3.625	-0.5701
13	C	-0.5599	3.7523	-1.2332
14	C	-1.5488	2.7719	-1.1177
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18	N	2.3925	0.9566	1.4573
19	C	2.2405	2.3315	0.9513
20	C	3.2021	0.0422	0.7539
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22	C	3.6086	-2.1496	-0.217

23	C	4.9227	-1.782	-0.5455
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25	C	4.5233	0.4037	0.4224
26	C	5.7955	-2.708	-1.2007
27	N	6.5063	-3.4612	-1.7321
28	H	-7.4237	-1.9101	0.0447
29	H	-6.236	-3.9867	0.7257
30	H	-3.7513	-4.0328	0.7653
31	H	-2.4626	-2.0325	0.1404
32	H	-6.1111	0.1175	-0.5837
33	H	-1.9077	-0.0984	0.541
34	H	1.4219	4.3903	-0.6759
35	H	-0.7486	4.6215	-1.8564
36	H	-2.4969	2.8648	-1.6275
37	H	1.2972	-0.4811	2.503
38	H	0.8871	1.2288	2.8353
39	H	3.0636	2.5539	0.2694
40	H	2.3223	3.0347	1.7925
41	H	1.7302	-1.5378	0.6009
42	H	3.2483	-3.1393	-0.479
43	H	6.3841	-0.1944	-0.4629
44	H	4.8991	1.3823	0.7042

Total Energy: -1071.037738 au

2.oHBA-an

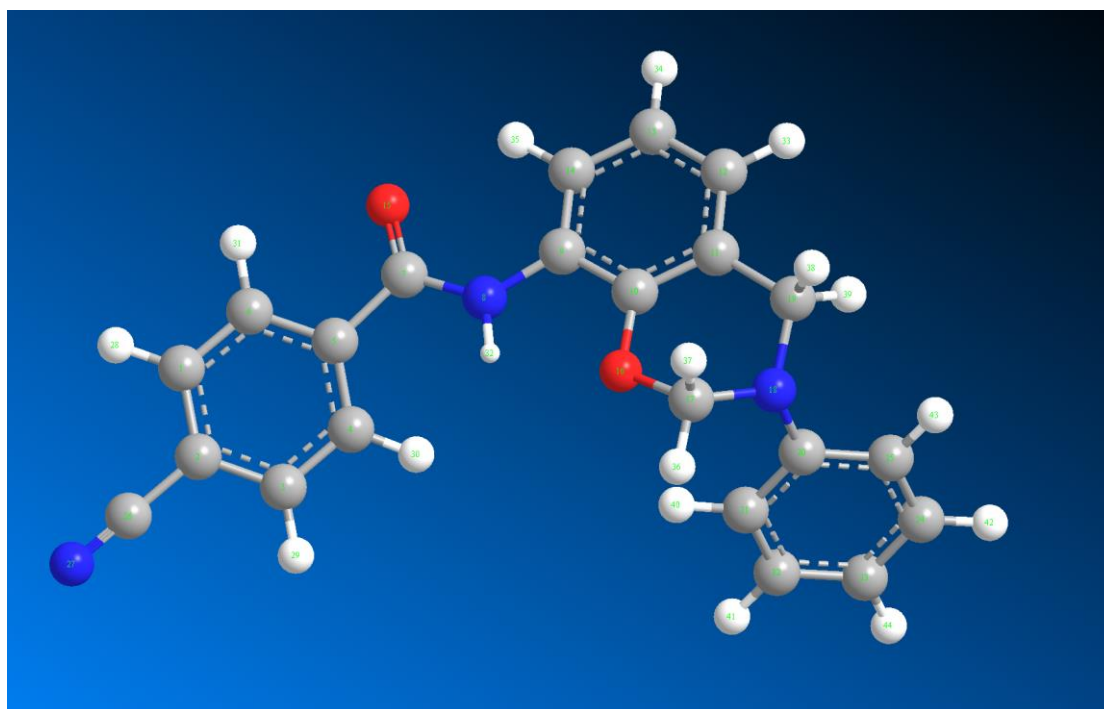


Tag	Symbol	X	Y	Z
1	C	-6.1618	-1.157	0.0975
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4	C	-3.4167	-1.6533	0.0269
5	C	-3.8911	-0.3484	-0.1732
6	C	-5.2727	-0.114	-0.1491
7	C	-3.0008	0.8336	-0.4484
8	N	-1.7035	0.696	-0.0124
9	C	-0.6351	1.5993	-0.1422
10	C	0.5892	1.1887	0.4305
11	C	1.7312	1.9895	0.3591
12	C	1.6399	3.2293	-0.2856
13	C	0.437	3.646	-0.8469
14	C	-0.7027	2.84	-0.7835
15	O	-3.4286	1.8383	-1.0089
16	O	0.5855	-0.0477	1.0455
17	C	1.7409	-0.275	1.8914
18	N	2.9803	0.0596	1.2739
19	C	3.0335	1.5002	0.9728
20	C	3.5545	-0.8495	0.3408

21	C	2.8242	-1.8971	-0.2414
22	C	3.452	-2.8017	-1.1001
23	C	4.8033	-2.6666	-1.4143
24	C	5.5306	-1.6159	-0.8491
25	C	4.9187	-0.7238	0.0271
26	H	-7.2305	-0.9616	0.1225
27	H	-6.3753	-3.2671	0.4972
28	H	-3.9305	-3.7073	0.4095
29	H	-2.3542	-1.8732	-0.0402
30	H	-5.6256	0.8961	-0.3291
31	H	-1.4771	-0.1186	0.5418
32	H	2.5232	3.861	-0.3505
33	H	0.3769	4.6077	-1.3481
34	H	-1.6421	3.1549	-1.2149
35	H	1.7047	-1.3317	2.1542
36	H	1.6156	0.3418	2.7904
37	H	3.864	1.6875	0.2887
38	H	3.2529	2.0499	1.9
39	H	1.7599	-1.9853	-0.0532
40	H	2.8678	-3.6052	-1.5413
41	H	5.2844	-3.3672	-2.0906
42	H	6.5873	-1.5001	-1.0758
43	H	5.503	0.0631	0.4961

Total Energy: -1163.282571 au

3.oHBAan-a

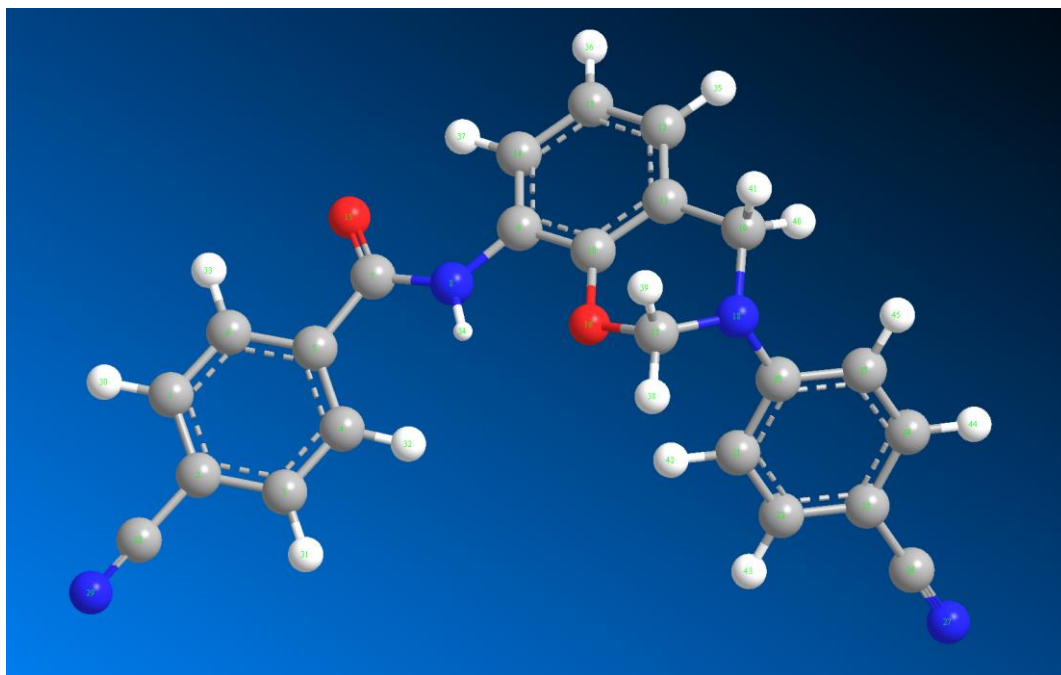


Tag	Symbol	X	Y	Z
1	C	-5.7781	0.0578	-0.066
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5	C	-3.3983	0.4821	-0.2631
6	C	-4.7226	0.9414	-0.2503
7	C	-2.3199	1.5141	-0.4795
8	N	-1.0746	1.1525	-0.0323
9	C	0.1302	1.8744	-0.1185
10	C	1.2581	1.2508	0.4586
11	C	2.5174	1.8545	0.4251
12	C	2.641	3.1102	-0.182
13	C	1.5336	3.7355	-0.7464
14	C	0.2764	3.1261	-0.7232
15	O	-2.5776	2.5899	-1.0101
16	O	1.0398	0.0164	1.0345
17	C	2.1315	-0.4258	1.8853
18	N	3.4164	-0.2807	1.2915
19	C	3.7114	1.1393	1.0374
20	C	3.8531	-1.2453	0.3389
21	C	2.9738	-2.1423	-0.2868
22	C	3.4635	-3.1124	-1.1639
23	C	4.8248	-3.1902	-1.4531

24	C	5.7019	-2.2892	-0.844
25	C	5.2255	-1.3349	0.0507
26	C	-6.6043	-2.2352	0.2818
27	N	-7.4824	-2.9824	0.4363
28	H	-6.8018	0.4172	-0.0468
29	H	-4.0036	-2.8487	0.1626
30	H	-2.1363	-1.2803	-0.1778
31	H	-4.9009	2.0018	-0.3922
32	H	-0.9899	0.2948	0.4967
33	H	3.6167	3.5897	-0.2159
34	H	1.6412	4.7077	-1.2184
35	H	-0.59	3.6032	-1.1586
36	H	1.9164	-1.4694	2.1119
37	H	2.093	0.1762	2.8017
38	H	4.0034	1.6187	1.9832
39	H	4.5715	1.2069	0.3679
40	H	1.9056	-2.0628	-0.1169
41	H	2.7658	-3.7974	-1.6388
42	H	6.7676	-2.341	-1.0506
43	H	5.9203	-0.6685	0.5541
44	H	5.1988	-3.9404	-2.1438

Total Energy: -1163.279761 au

4.oHBAan-an



Tag	Symbol	X	Y	Z
1	C	-6.1178	-0.5783	-0.2092
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4	C	-3.3811	-1.1231	-0.0344
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6	C	-5.1905	0.4189	-0.4822
7	C	-2.8862	1.3081	-0.7007
8	N	-1.6272	1.199	-0.1626
9	C	-0.5433	2.0854	-0.2914
10	C	0.6311	1.724	0.4036
11	C	1.7813	2.5142	0.35
12	C	1.7474	3.6948	-0.4023
13	C	0.5931	4.0622	-1.0865
14	C	-0.5538	3.2656	-1.0408
15	O	-3.2635	2.2562	-1.3808
16	O	0.5734	0.5444	1.1233
17	C	1.6455	0.4139	2.0813
18	N	2.9341	0.6741	1.5226
19	C	3.0364	2.0787	1.0912
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21	C	2.9418	-1.5042	0.3608
22	C	3.6419	-2.5033	-0.3055
23	C	5.0078	-2.3515	-0.5893

24	C	5.6602	-1.1739	-0.1828
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26	C	5.7256	-3.3777	-1.2826
27	N	6.3104	-4.2119	-1.8454
28	C	-6.6267	-2.8983	0.4387
29	N	-7.3963	-3.7387	0.6721
30	H	-7.1817	-0.3758	-0.2765
31	H	-3.9628	-3.1299	0.4932
32	H	-2.3221	-1.3636	-0.0038
33	H	-5.5103	1.4117	-0.7793
34	H	-1.4503	0.437	0.478
35	H	2.6369	4.3183	-0.455
36	H	0.5779	4.9772	-1.6711
37	H	-1.455	3.5444	-1.5678
38	H	1.5786	-0.6021	2.4678
39	H	1.4642	1.1337	2.889
40	H	3.9077	2.1914	0.4433
41	H	3.2075	2.7135	1.9722
42	H	1.8755	-1.621	0.5148
43	H	3.1242	-3.4003	-0.6303
44	H	6.7187	-1.0496	-0.3875
45	H	5.496	0.695	0.8442

Total Energy: -1255.523967 au