Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Elucidating the Role of Acetylene in *Ortho*-Phthalimide Functional Benzoxazines: Design, Synthesis, and Structure−Property Investigations

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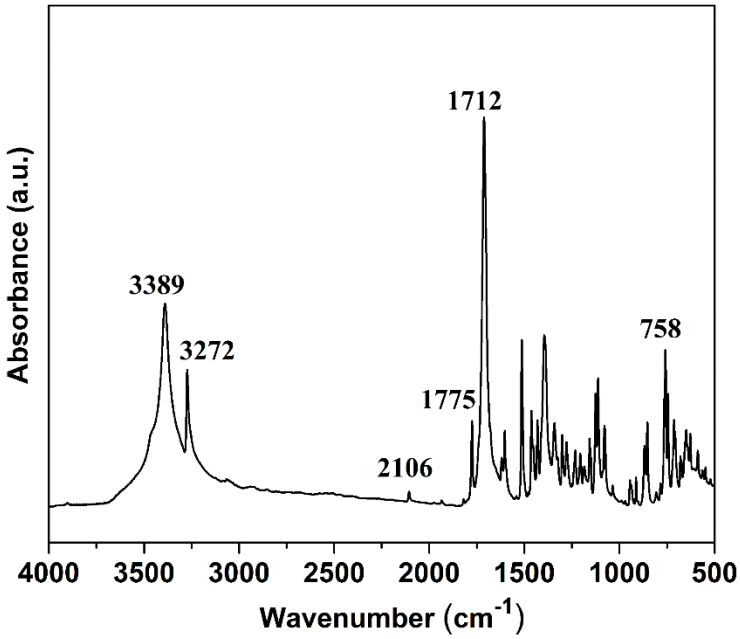


Figure S1. FTIR spectrum of ***o*PPac**.

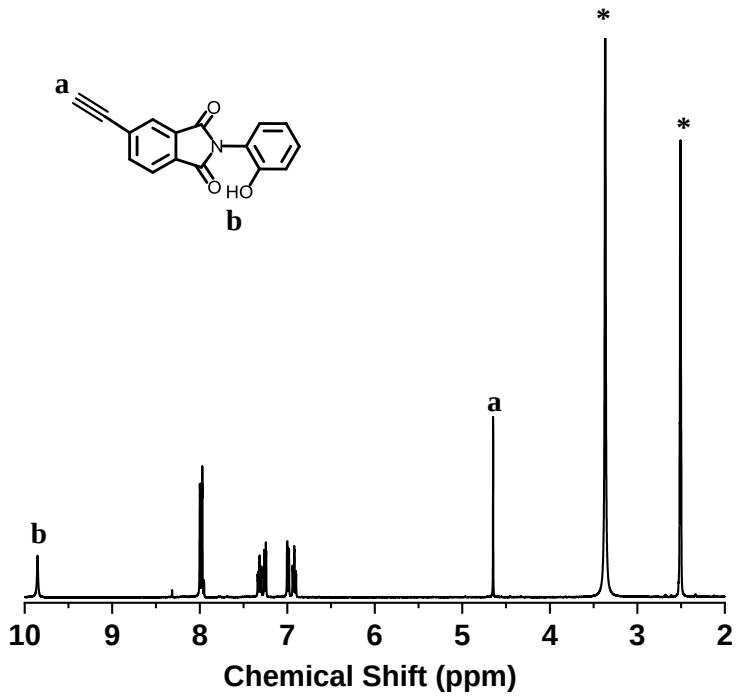


Figure S2. ^{1}H NMR spectrum of ***o*PPac** (DMSO-d_6, 20^{o}C).

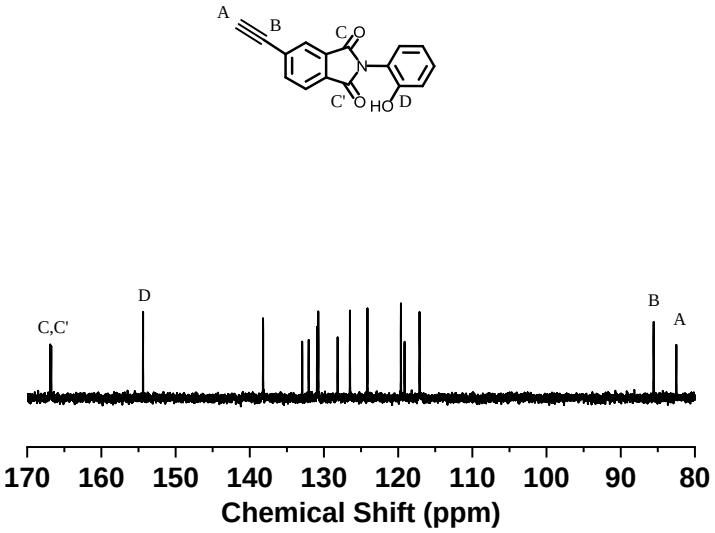


Figure S3. ^{13}C NMR spectrum of ***o*PPac** (DMSO-d_6, 20^{o}C).

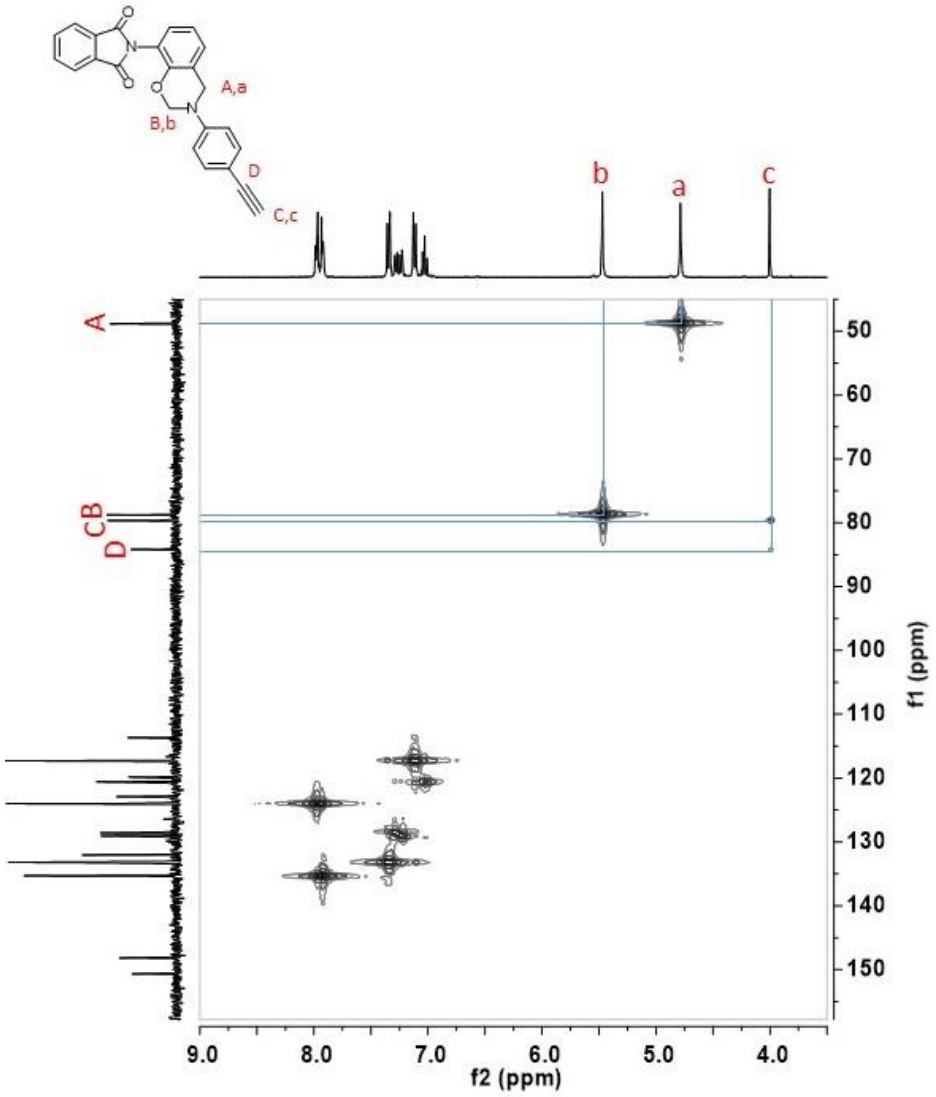


Figure S4. 2D ^{1}H-^{13}C HMQC NMR spectrum of ***o*PP-ac**.

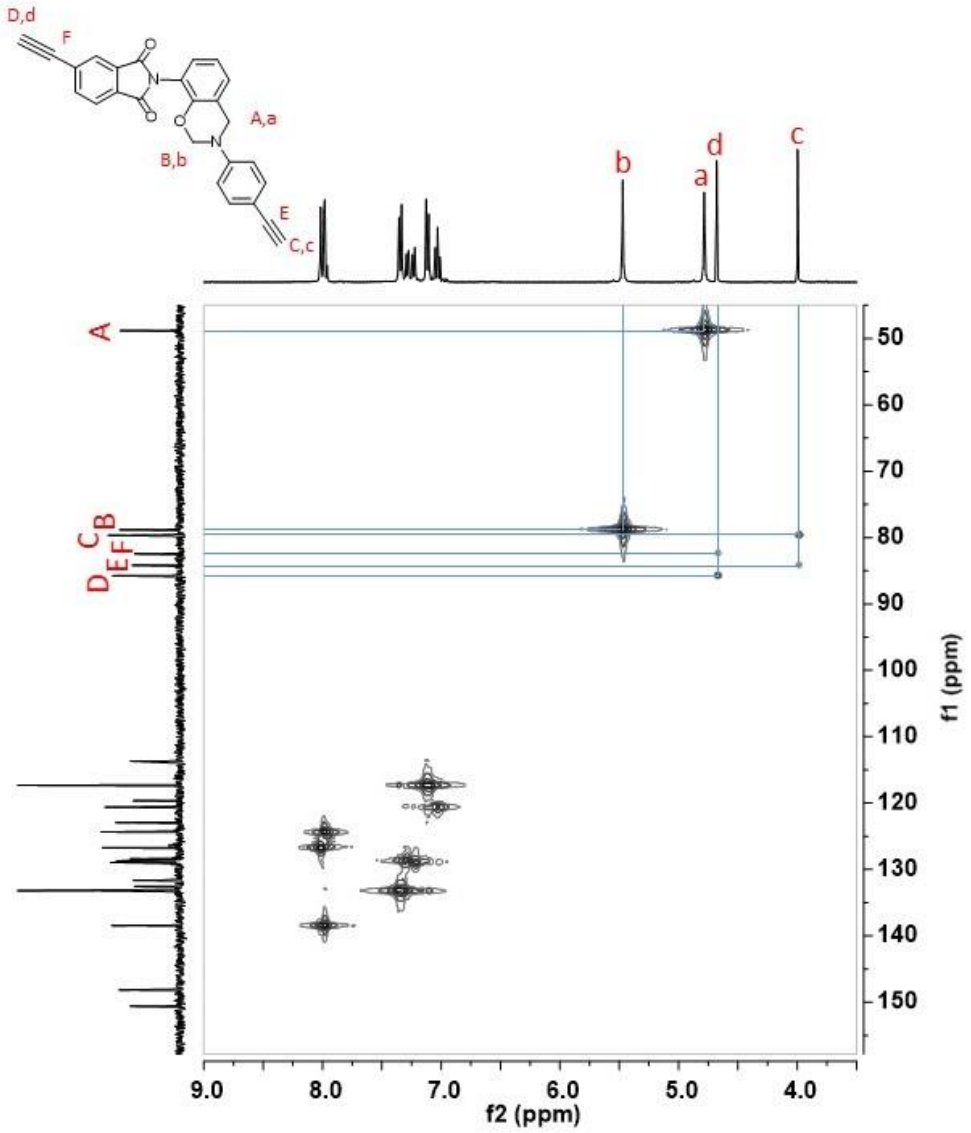


Figure S5. 2D ^{1}H-^{13}C HMQC NMR spectrum of ***o*PPac-ac**.

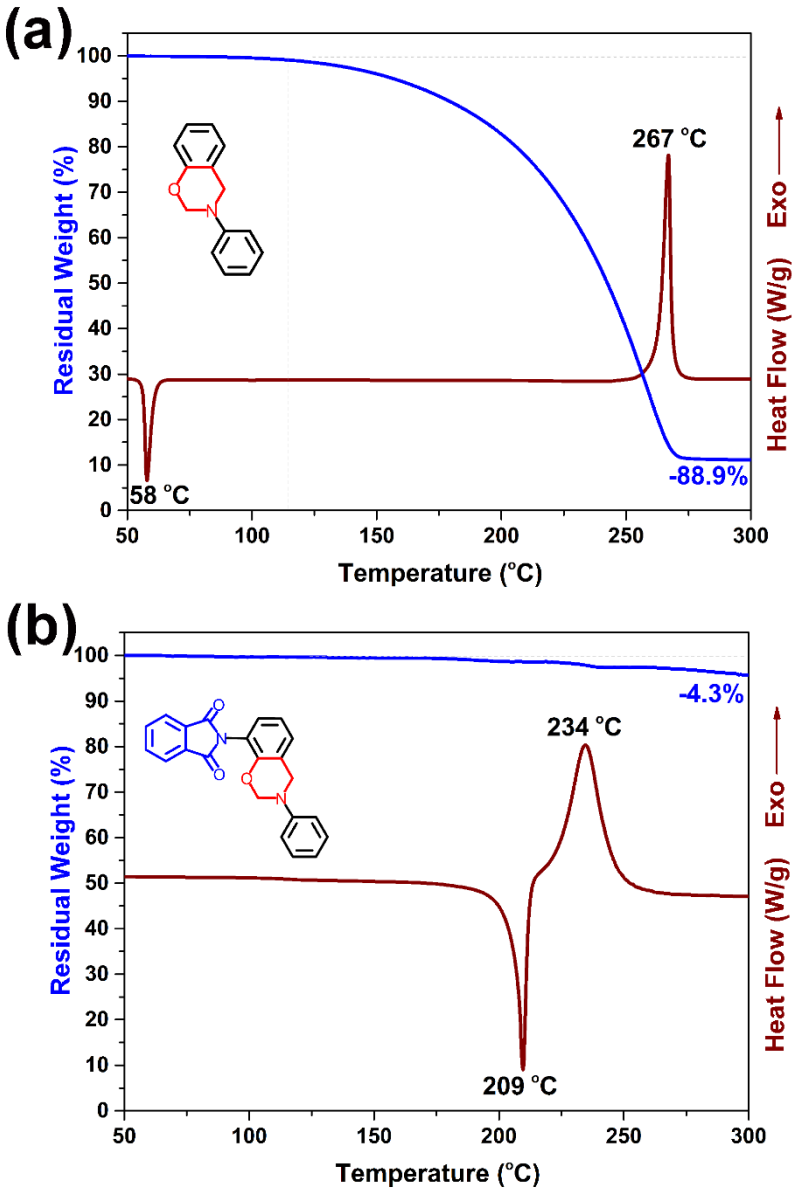


Figure S6. TGA vs DSC plots of benzoxazine monomers (heating rate: 10 °C/min, under a N_2 atmosphere): (a) PH-a and (b) *o*PP-a.

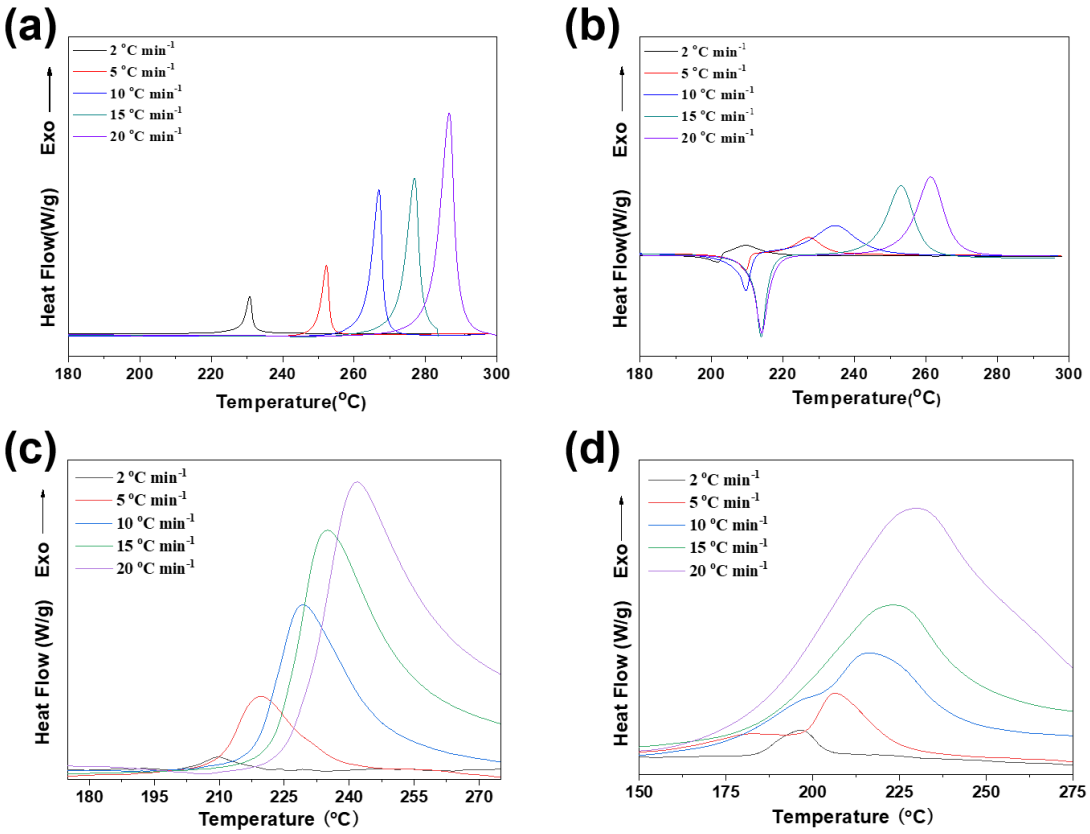


Figure S7. DSC thermograms of PH-a (a), *o*PP-a (b), *o*PP-ac (c) and *o*PPac-ac (d) at different heating rates.

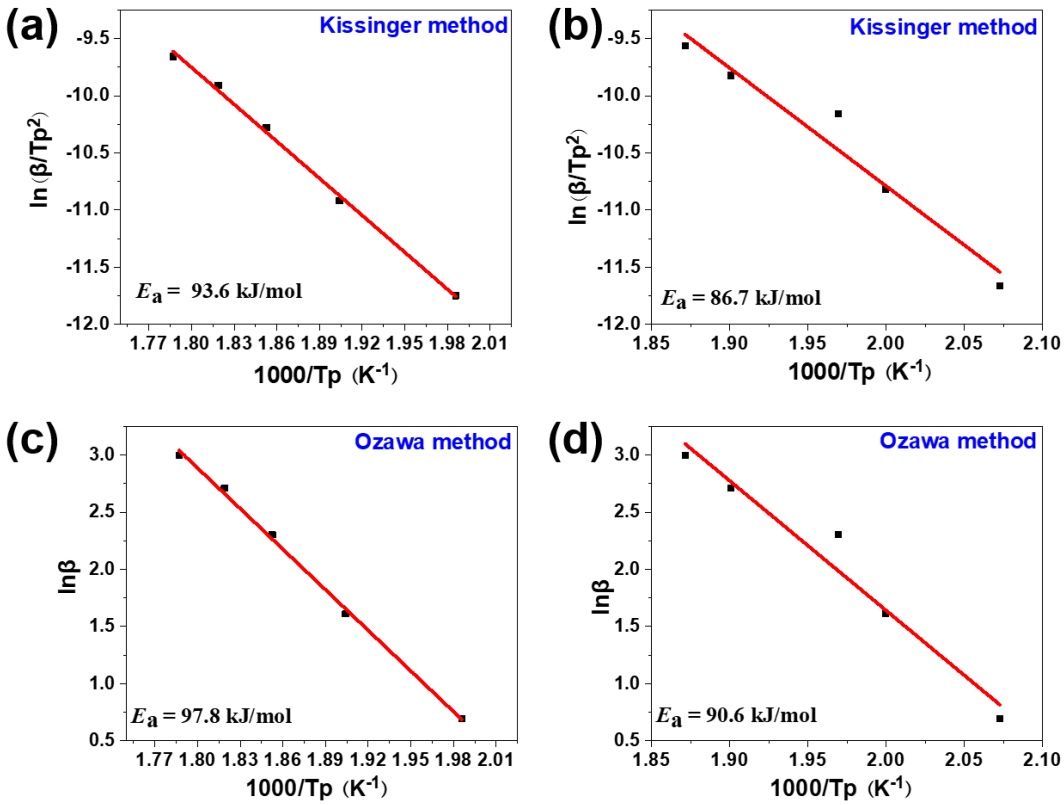
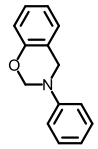
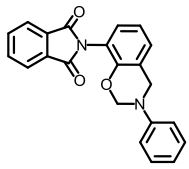
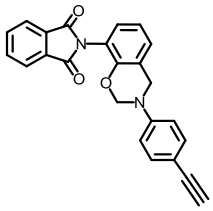
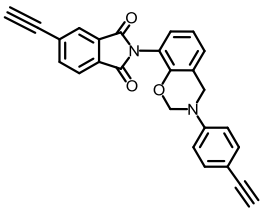
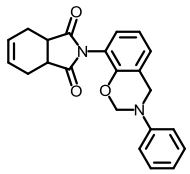
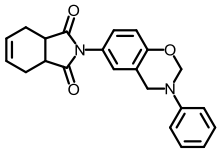
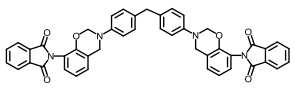
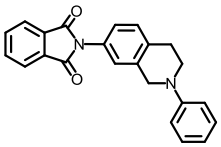
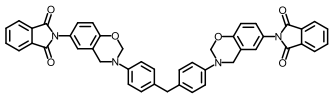
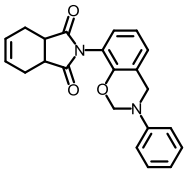
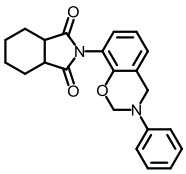
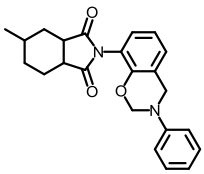
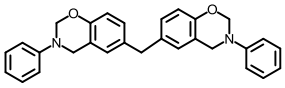
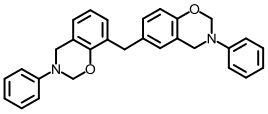
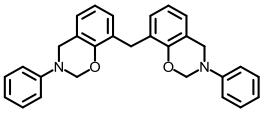
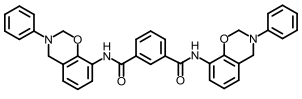
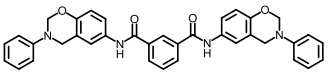


Figure S8. Representations of the Kissinger method for the calculation of activation energy for PH-a (a) and *o*PP-a (b), and representations of the Ozawa method for PH-a (c) and *o*PP-a (d).

Table S1. The thermal properties of benzoxazines obtained in this work comparing with other imide-containing benzoxazine and difunctional benzoxazines.

Sample	Monomer Structure	T_g(DSC) (°C)	T_g(DMA) (°C)	T_{d5} (°C)	T_{d10} (°C)	Yc (%)	LOI* (%)	Reference
poly(PH-a)		/	133	292	351	38	32.7	this work
poly(*o*PP-a)		/	194	307	336	56	39.9	
poly(*o*PP-ac)		/	231	341	396	55	39.5	
poly(*o*PPac-ac)		/	297	404	474	65	43.5	
poly(*o*HTI-a)		/	241	305	346	47	36.3	S1
poly(*p*HTI-a)		/	215	334	377	28	28.7	
poly(*o*PP-ddm)		201	/	303	354	58	40.7	S2
poly(*p*PP-a)		162	/	289	318	39	33.1	

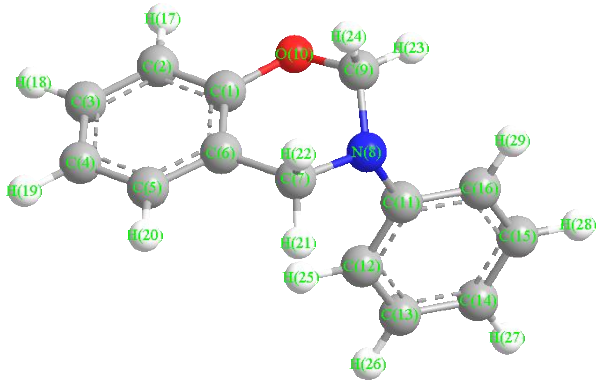
poly(*p*PP-ddm)		204	/	343	384	53	38.7	
poly(*o*HTI-a)		233	/	342	382	48	36.7	
poly(*o*HHI-a)		180	/	340	375	28	28.7	S3
poly(*o*MHI-a)		173	/	327	367	26	27.9	
poly(4,4′-BF-a)		/	161	263	341	53	38.7	
poly(2,4′-BF-a)		/	180	294	349	51	37.9	S4
poly(2,2′-BF-a)		/	218	353	403	61	41.9	
poly(*o*-hydroxyamide)		/	212	250	280	53	38.7	S5
poly(*p*-hydroxyamide)		/	/	280	320	50	37.5	

/: not reported

*: LOI value was calculated by Krevelen equation.

Atomic Coordinates of the Atoms in Calculated Equilibrium Structures.

PH-a

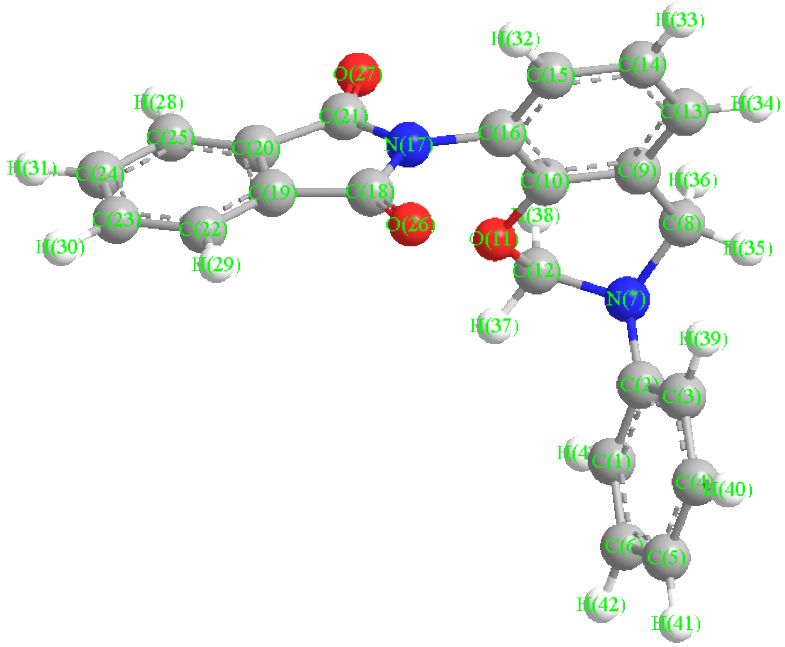


C(1)	-1.7298	0.6036	-0.5147
C(2)	-2.7692	0.2971	-1.4015
C(3)	-3.7186	-0.6606	-1.0505
C(4)	-3.6369	-1.3189	0.1828
C(5)	-2.5902	-1.0136	1.0538
C(6)	-1.6223	-0.0581	0.7215
C(7)	-0.4685	0.2891	1.6453
N(8)	0.6144	0.9787	0.9342
C(9)	0.0673	2.0283	0.1213
O(10)	-0.8192	1.5476	-0.9173
C(11)	1.6784	0.2086	0.3749
C(12)	1.5869	-1.1742	0.1513
C(13)	2.6798	-1.8825	-0.3585
C(14)	3.8708	-1.2271	-0.6734
C(15)	3.9639	0.1528	-0.4607
C(16)	2.8861	0.8608	0.0677
H(17)	-2.8144	0.8195	-2.3526
H(18)	-4.5255	-0.8929	-1.7409
H(19)	-4.3762	-2.0660	0.4579
H(20)	-2.5129	-1.5313	2.0091
H(21)	-0.0666	-0.6018	2.1351
H(22)	-0.8116	0.9571	2.4492
H(23)	0.8463	2.5720	-0.4096
H(24)	-0.5047	2.7129	0.7605
H(25)	0.6597	-1.7019	0.3496
H(26)	2.5861	-2.9530	-0.5243
H(27)	4.7151	-1.7805	-1.0751
H(28)	4.8882	0.6788	-0.6873

H(29)	**2.9836**	**1.9239**	**0.2716**

Total Energy = -671.303245 **au**

*o*PP-a



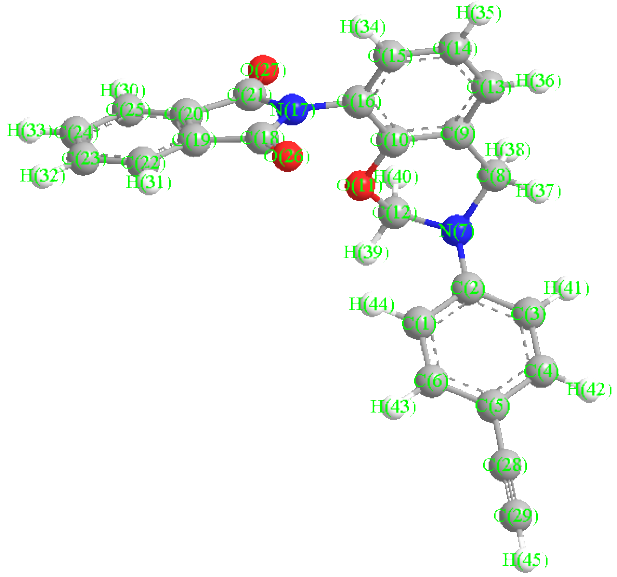
C(1)	**3.8371**	**-2.0787**	**-0.9873**
C(2)	**3.4855**	**-0.8208**	**-0.4675**
C(3)	**3.7272**	**-0.5615**	**0.8900**
C(4)	**4.3130**	**-1.5376**	**1.7024**
C(5)	**4.6477**	**-2.7892**	**1.1838**
C(6)	**4.4006**	**-3.0551**	**-0.1674**
N(7)	**2.9253**	**0.1466**	**-1.3585**
C(8)	**2.9850**	**1.5668**	**-0.9946**
C(9)	**1.7434**	**2.0201**	**-0.2462**
C(10)	**0.5846**	**1.2271**	**-0.3172**
O(11)	**0.5458**	**0.0480**	**-1.0003**

C(12)	**1.6450**	**-0.1575**	**-1.9275**
C(13)	**1.7098**	**3.1978**	**0.5066**
C(14)	**0.5563**	**3.5908**	**1.1870**
C(15)	**-0.5921**	**2.8004**	**1.1080**
C(16)	**-0.5824**	**1.6260**	**0.3583**
N(17)	**-1.7480**	**0.8115**	**0.2661**
C(18)	**-2.2367**	**0.0020**	**1.3175**
C(19)	**-3.3974**	**-0.7417**	**0.7452**
C(20)	**-3.5438**	**-0.3718**	**-0.5931**
C(21)	**-2.4865**	**0.6277**	**-0.9258**
C(22)	**-4.2507**	**-1.6601**	**1.3430**
C(23)	**-5.2690**	**-2.2066**	**0.5490**
C(24)	**-5.4172**	**-1.8339**	**-0.7951**
C(25)	**-4.5511**	**-0.9038**	**-1.3876**
O(26)	**-1.7850**	**-0.0456**	**2.4433**
O(27)	**-2.2846**	**1.1975**	**-1.9783**
H(28)	**-4.6577**	**-0.6079**	**-2.4270**
H(29)	**-4.1277**	**-1.9410**	**2.3849**
H(30)	**-5.9556**	**-2.9301**	**0.9804**
H(31)	**-6.2165**	**-2.2741**	**-1.3853**
H(32)	**-1.5030**	**3.0867**	**1.6250**
H(33)	**0.5497**	**4.5045**	**1.7738**
H(34)	**2.6080**	**3.8103**	**0.5671**
H(35)	**3.8902**	**1.7491**	**-0.4096**
H(36)	**3.0932**	**2.1424**	**-1.9257**
H(37)	**1.5703**	**-1.2052**	**-2.2118**
H(38)	**1.4675**	**0.4888**	**-2.7951**

H(39)	**3.4386**	**0.3889**	**1.3274**
H(40)	**4.4889**	**-1.3172**	**2.7524**
H(41)	**5.0966**	**-3.5467**	**1.8204**
H(42)	**4.6672**	**-4.0201**	**-0.5915**
H(43)	**3.6889**	**-2.2765**	**-2.0459**

Total Energy = -1183.212877 au

***o*PP-ac**



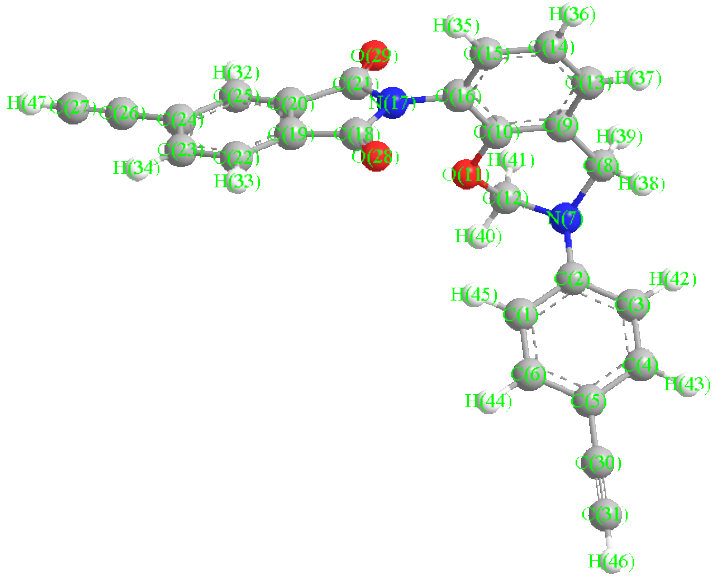
C(1)	**-2.7367**	**1.1392**	**-0.5804**
C(2)	**-3.1584**	**-0.1751**	**-0.8492**
C(3)	**-4.5031**	**-0.5084**	**-0.5965**
C(4)	**-5.3910**	**0.4329**	**-0.0912**
C(5)	**-4.9749**	**1.7547**	**0.1664**
C(6)	**-3.6334**	**2.0875**	**-0.0925**
N(7)	**-2.2978**	**-1.1538**	**-1.4078**
C(8)	**-2.1595**	**-2.4532**	**-0.7308**

C(9)	**-0.8942**	**-2.4982**	**0.1136**
C(10)	**0.1103**	**-1.5358**	**-0.0848**
O(11)	**-0.0086**	**-0.5308**	**-1.0026**
C(12)	**-1.0527**	**-0.7543**	**-1.9819**
C(13)	**-0.7044**	**-3.4736**	**1.0980**
C(14)	**0.4515**	**-3.5024**	**1.8784**
C(15)	**1.4474**	**-2.5460**	**1.6699**
C(16)	**1.2818**	**-1.5684**	**0.6917**
N(17)	**2.2932**	**-0.5917**	**0.4588**
C(18)	**2.5501**	**0.5072**	**1.3110**
C(19)	**3.6131**	**1.3032**	**0.6297**
C(20)	**3.9279**	**0.6787**	**-0.5789**
C(21)	**3.0831**	**-0.5441**	**-0.7134**
C(22)	**4.2488**	**2.4708**	**1.0318**
C(23)	**5.2225**	**3.0033**	**0.1748**
C(24)	**5.5399**	**2.3754**	**-1.0386**
C(25)	**4.8930**	**1.1957**	**-1.4336**
O(26)	**2.0028**	**0.7224**	**2.3730**
O(27)	**3.0618**	**-1.3578**	**-1.6138**
C(28)	**-5.8903**	**2.7266**	**0.6763**
C(29)	**-6.6684**	**3.5502**	**1.1088**
H(30)	**5.1320**	**0.7013**	**-2.3706**
H(31)	**3.9964**	**2.9482**	**1.9741**
H(32)	**5.7410**	**3.9166**	**0.4540**
H(33)	**6.2996**	**2.8115**	**-1.6817**
H(34)	**2.3583**	**-2.5503**	**2.2607**
H(35)	**0.5774**	**-4.2624**	**2.6437**

H(36)	**-1.4838**	**-4.2160**	**1.2607**
H(37)	**-3.0347**	**-2.6250**	**-0.1010**
H(38)	**-2.1445**	**-3.2504**	**-1.4882**
H(39)	**-1.1477**	**0.1848**	**-2.5249**
H(40)	**-0.7019**	**-1.5442**	**-2.6570**
H(41)	**-4.8615**	**-1.5075**	**-0.8287**
H(42)	**-6.4254**	**0.1561**	**0.0903**
H(43)	**-3.2864**	**3.0957**	**0.1142**
H(44)	**-1.6982**	**1.4195**	**-0.7191**
H(45)	**-7.3515**	**4.2755**	**1.4910**

Total Energy = -1259.362995 au

***o*PPac-ac**



C(1)	**-2.9620**	**1.4000**	**-0.5013**
C(2)	**-3.5197**	**0.1927**	**-0.9582**

C(3)	**-4.9098**	**0.0092**	**-0.8274**
C(4)	**-5.7110**	**0.9911**	**-0.2583**
C(5)	**-5.1569**	**2.2078**	**0.1882**
C(6)	**-3.7697**	**2.3921**	**0.0507**
N(7)	**-2.7463**	**-0.8162**	**-1.5864**
C(8)	**-2.8183**	**-2.1941**	**-1.0743**
C(9)	**-1.6341**	**-2.5040**	**-0.1699**
C(10)	**-0.5076**	**-1.6641**	**-0.1852**
O(11)	**-0.4342**	**-0.5504**	**-0.9727**
C(12)	**-1.4231**	**-0.5171**	**-2.0318**
C(13)	**-1.6383**	**-3.6058**	**0.6916**
C(14)	**-0.5556**	**-3.8778**	**1.5284**
C(15)	**0.5625**	**-3.0417**	**1.5020**
C(16)	**0.5901**	**-1.9419**	**0.6479**
N(17)	**1.7280**	**-1.0845**	**0.6000**
C(18)	**2.0556**	**-0.1404**	**1.6013**
C(19)	**3.2529**	**0.5866**	**1.0893**
C(20)	**3.5754**	**0.0790**	**-0.1709**
C(21)	**2.5987**	**-0.9992**	**-0.5101**
C(22)	**3.9990**	**1.6047**	**1.6700**
C(23)	**5.0859**	**2.1066**	**0.9485**
C(24)	**5.4208**	**1.5978**	**-0.3277**
C(25)	**4.6497**	**0.5605**	**-0.8998**
C(26)	**6.5400**	**2.1336**	**-1.0379**
C(27)	**7.4882**	**2.5875**	**-1.6401**
O(28)	**1.4649**	**0.0137**	**2.6504**
O(29)	**2.5441**	**-1.6865**	**-1.5083**

C(30)	**-5.9818**	**3.2228**	**0.7643**
C(31)	**-6.6833**	**4.0830**	**1.2530**
H(32)	**4.8951**	**0.1594**	**-1.8779**
H(33)	**3.7441**	**1.9960**	**2.6503**
H(34)	**5.6937**	**2.9032**	**1.3663**
H(35)	**1.4197**	**-3.2351**	**2.1396**
H(36)	**-0.5807**	**-4.7332**	**2.1967**
H(37)	**-2.5124**	**-4.2543**	**0.7126**
H(38)	**-3.7521**	**-2.3244**	**-0.5238**
H(39)	**-2.8444**	**-2.8902**	**-1.9251**
H(40)	**-1.3619**	**0.4844**	**-2.4549**
H(41)	**-1.1223**	**-1.2598**	**-2.7805**
H(42)	**-5.3694**	**-0.9001**	**-1.2047**
H(43)	**-6.7818**	**0.8313**	**-0.1729**
H(44)	**-3.3186**	**3.3152**	**0.4028**
H(45)	**-1.8898**	**1.5582**	**-0.5441**
H(46)	**-7.2989**	**4.8403**	**1.6844**
H(47)	**8.3236**	**2.9862**	**-2.1723**

Total Energy = -1335.510271 au

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