A Possible B–C Bonding Formation in Hydroboration of Benzonitrile by External Electric Field

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Contents

directions. (**Table S6**, **page 12**)

9. Key bond lengths (in Å) of transition states (TS_{AM} and TS_M) without and with external electric field (F_x = 0, and ±50 (×10^{-4}) a.u.) along F_x directions. (**Table S7**, **page 13**)

10. Relative energies (in kJ/mol) of transition states and products in two pathways as external electric field (in ×10^{-4} a.u.) are perpendicular (F_X) to nitrogen−carbon triple bond. (**Table S8, page 14**)

11. Variations of barrier heights for path AM and path M along with electric field by method of CCSD(T)/6-311++G(2d,2p)//B3LYP/6-31G(d) (the orange line is for path M, and the light blue line is for path AM). (**Figure S1, page 15**)

12. Variations of barrier heights for path AM and path M along with electric field by method of B3LYP-D3/6-311++G(d,p)//BP86-D3/6-31+G(d) (the orange line is for path M, and the light blue line is for path AM). (**Figure S2, page 16**)

13. Variations of barrier heights for path AM and path M along with electric field by method of B3LYP/6-311++G(d,p)//BP86/6-31+G(d) (the orange line is for path M, and the light blue line is for path AM). (**Figure S3, page 17**)

14. a) IRC profiles with the variations of key bonds in the hydroboration of path AM; b) IRC profiles with the variations of key bonds in the hydroboration of path M; c) Changes of Mayer bond orders as the reaction proceeding in path AM; d) Changes of Mayer bond orders as the reaction proceeding in path M; e) Electron localization function (ELF) isosurface for path AM (the five points are selected from transition state and twentieth and fortieth points before and after transition states along IRC); f) Electron localization function isosurface for path M, the points are selected as same as path AM. (**Figure S4, page 18**)

15. Geometries of stationary points along potential energy surfaces with key bond lengths and angles as external electric field is equal to 50 (×10^{-4}) a.u., the black are those optimized as electric field along Z axis, and the blue is for X axis (The values in square brackets are given in −50 (×10^{-4}) a.u.; the bond lengths are given in Å, and angles in deg). (**Figure S5, page 19**)

16. Barrier heights of two pathways (a for TS_{AM}, b for TS_M) as the external electric field (F_Z) is equal to −50, 0, and 50 (×10^{-4}) a.u. in gas phase (the black line), THF (the blue line), DMSO (the red line), and C_6H_6 (the orange line) solvents. **(Figure**

Reference (13)

(13) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

Reaction coordinates:

F = 0

TS_{AM}

C,0,0.0146008244,-0.0304946072,1.2065745958

N,0,-0.0138415021,-0.0578221944,0.0027788774

B,0,1.6354006119,-0.0342013647,0.3743781106

H,0,1.6287905828,-0.0057217842,1.6429933383

C,0,-0.6461225041,-0.007807471,2.4953724999

C,0,-2.0532307243,-0.0213147916,2.4968165218

C,0,0.0615376298,0.0258913915,3.7030054134

C,0,-2.7376470661,-0.0009912202,3.7074829456

H,0,-2.588867584,-0.0475932168,1.5532530726

C,0,-0.6349954087,0.0460159507,4.9093332418

H,0,1.1470811728,0.0360169056,3.6903535813

C,0,-2.0311700185,0.0326028056,4.9136399164

H,0,-3.8235749428,-0.0114022246,3.7107526856

H,0,-0.0862376419,0.0722304456,5.8459403767

H,0,-2.5702843112,0.0483981379,5.8565928626

H,0,2.1079840545,-1.0902320586,0.0740966407

H,0,2.0885589577,1.0157605064,0.0266444693

TS_{M}

B,0,1.599989338,-0.0594997869,1.0277253208

H,0,1.5058927091,-0.0481353116,-0.248038172

N,0,-0.0101827888,0.0318714444,0.101881728

C,0,0.0183571533,0.0243380173,1.3384784393

C,0,-0.9242292163,0.0690954003,2.441575995

C,0,-2.3077194761,0.1485272068,2.200760556

C,0,-0.4422936463,0.0324015329,3.7578550725

C,0,-3.1937615056,0.1905921485,3.2720752321

H,0,-2.6716264505,0.1762831309,1.1780548803

C,0,-1.335656842,0.0745942541,4.8262608863

H,0,0.628186878,-0.0290349205,3.9273162992

C,0,-2.7087730165,0.1536085107,4.5838361507

H,0,-4.2625067669,0.252046374,3.0881554773

H,0,-0.9624341449,0.0461521327,5.8457890509

H,0,-3.4044825532,0.186558835,5.4178818717

H,0,2.1331686383,0.9895702974,1.2571544865

H,0,2.0170845604,-1.161931866,1.2471524956

F_Z = +50 (×10^{-4}) a.u.

TS_{AM}

C,0,0.0104852277,-0.0207230628,1.2023054566

N,0,-0.0108522868,-0.0452824482,0.0010176136

B,0,1.6478251504,-0.0228849541,0.3828787222

H,0,1.6415976276,0.0033997084,1.6517582418

C,0,-0.6525614869,-0.0015947325,2.4909398519

C,0,-2.0590383118,-0.0128279508,2.4969262681

C,0,0.0576783723,0.0263122119,3.6966793722

C,0,-2.740042582,0.0037732247,3.7104364078

H,0,-2.5978017433,-0.0342530744,1.5551224405

C,0,-0.6347149245,0.0426567964,4.9053937374

H,0,1.1429937666,0.0349995,3.6764373963

C,0,-2.0307076202,0.0313735742,4.9146972305

H,0,-3.8260569408,-0.0047017068,3.7143993403

H,0,-0.0805283834,0.0645031806,5.8398794749

H,0,-2.5679167447,0.044406172,5.8596595246

H,0,2.1076648986,-1.0806929286,0.0760632199

H,0,2.0891989811,1.0291894901,0.0326357014

TS_M

B,0,1.5972857188,-0.064983282,1.0210691738

H,0,1.5272509877,-0.0585134964,-0.2522534391

N,0,-0.0094229805,0.0225344809,0.0928938555

C,0,0.0132913326,0.0184138038,1.32676261

C,0,-0.9307154364,0.0653153788,2.4306410923

C,0,-2.3143411272,0.1447531432,2.1956753338

C,0,-0.4437493252,0.0306082017,3.7445940189

C,0,-3.1960585548,0.1888749383,3.2718830173

H,0,-2.6835460624,0.1709740654,1.1750659856

C,0,-1.3318292046,0.0747208887,4.8171733016

H,0,0.6281498846,-0.0309509326,3.9053517706

C,0,-2.706117067,0.1538536754,4.5812513729

H,0,-4.2651149533,0.2503143761,3.0900613808

H,0,-0.952031055,0.0475773812,5.8353153197

H,0,-3.3993400254,0.1883922416,5.4182158973

H,0,2.1257334395,0.9855758377,1.2564760573

H,0,2.0113934286,-1.1666337018,1.2518552516

F_Z = -50 (×10^{-4}) a.u.

TS_{AM}

C,0,0.0202327389,-0.0204151983,1.211369158

N,0,-0.0164589707,-0.0424065557,0.0041471737

B,0,1.6227873961,-0.0235208705,0.3635101893

H,0,1.6150248547,-0.0016674797,1.6333537543

C,0,-0.6385387542,-0.001604235,2.4996994679

C,0,-2.0467732416,-0.0135737298,2.4958072552

C,0,0.0653191228,0.0270977837,3.7108378106

C,0,-2.7353440608,0.0034056688,3.7032493386

H,0,-2.5786064469,-0.0362990584,1.5496868395

C,0,-0.6362036812,0.0439833371,4.9144969521

H,0,1.1511367828,0.035865443,3.7066588303

C,0,-2.0328282954,0.0321868519,4.9126155404

H,0,-3.8212495364,-0.0060231499,3.7047764286

H,0,-0.0936622301,0.0661693502,5.8542697797

H,0,-2.5747612259,0.0452492913,5.8535222808

H,0,2.1066455784,-1.0766284507,0.0630006359

H,0,2.0905029694,1.0258340019,0.026228565

TS_M

B,0,1.5988706442,-0.0661295506,1.0185973425

H,0,1.479384717,-0.0543440672,-0.259751565

N,0,-0.0162910833,0.0259851424,0.0966702368

C,0,0.0199248338,0.0191855549,1.336495548

C,0,-0.9187662723,0.0653158272,2.4401991392

C,0,-2.3029700068,0.1438372033,2.1958532099

C,0,-0.439909489,0.0313767225,3.7587286929

C,0,-3.1912851139,0.1876129821,3.2637420478

H,0,-2.6633547995,0.169437403,1.1713492291

C,0,-1.3366637065,0.0754310557,4.8245595306

H,0,0.629411627,-0.0292686439,3.9354180517

C,0,-2.7091831348,0.1534087386,4.5776125742

H,0,-4.2600515787,0.2483416059,3.0792218955

H,0,-0.9683412526,0.0493659301,5.8453459606

H,0,-3.4061163715,0.1877376834,5.4100301697

H,0,2.1370785736,0.9821562375,1.2380475442

H,0,2.0191014133,-1.1686228248,1.2299123922

F_X = +50 (×10^{-4}) a.u.

TS_{AM}

C,0,0.0432825507,-0.0196304023,1.2172912004

N,0,-0.0031677162,-0.0429960589,0.0051671855

B,0,1.6065839057,-0.0234340866,0.3407441107

H,0,1.5541992748,0.0006239967,1.6316869218

C,0,-0.6378154167,-0.0013859696,2.497823581

C,0,-2.0450647423,-0.0121516027,2.4940709095

C,0,0.0655822459,0.0256250718,3.7090341965

C,0,-2.7326335309,0.0041977633,3.7039980876

H,0,-2.5811341589,-0.0330838294,1.5507337213

C,0,-0.6328711051,0.0417614122,4.9131380509

H,0,1.1520704557,0.0337471562,3.6989015481

C,0,-2.0296757061,0.0310574273,4.9125070931

H,0,-3.8181196885,-0.0039425469,3.7055195393

H,0,-0.0879255646,0.0628344028,5.8525190024

H,0,-2.5728415913,0.0437845144,5.8528897735

H,0,2.1169387302,-1.0756732865,0.0805058755

H,0,2.0998150576,1.0263190383,0.0406992029

TS_M

B,0,1.5971131586,-0.0658782011,1.0242572336

H,0,1.4846653301,-0.0555387188,-0.2529986468

N,0,-0.0053559333,0.0260076338,0.093194377

C,0,0.016479775,0.0191561104,1.332522377

C,0,-0.9268141548,0.0658822765,2.432574015

C,0,-2.3117197692,0.1444704702,2.1940066717

C,0,-0.4418521369,0.0315952377,3.7489925138

C,0,-3.1951464646,0.1882370167,3.2678147967

H,0,-2.6817780524,0.1696556272,1.1735856649

C,0,-1.3321792868,0.0756355938,4.8184104843

H,0,0.6294973617,-0.030125584,3.9153010792

C,0,-2.7066012178,0.153911293,4.5783849237

H,0,-4.2640626253,0.2481991543,3.0877572317

H,0,-0.9587775622,0.0485277677,5.8381158702

H,0,-3.4012802612,0.187658679,5.4127867485

H,0,2.1430795917,0.9787747511,1.2526299541

H,0,2.0255712474,-1.1653421074,1.2446967054

F_X = -50 (×10^{-4}) a.u.

TS_{AM}

C,0,-0.0318245718,-0.0207374833,1.1894218942

N,0,-0.0225264567,-0.042419636,-0.0041652553

B,0,1.6941153487,-0.0220961469,0.4202244431

H,0,1.7309760192,0.0007373685,1.6644840814

C,0,-0.6663785499,-0.0018356626,2.4881901543

C,0,-2.0737473221,-0.0134517163,2.5015417875

C,0,0.0515994476,0.0266032764,3.6895321531

C,0,-2.7494867183,0.0034953397,3.7164243699

H,0,-2.6141417228,-0.0357726434,1.5603459734

C,0,-0.6376999441,0.043396537,4.9012305102

H,0,1.1362584715,0.0352375235,3.6686009893

C,0,-2.0334590697,0.0318980867,4.9170490912

H,0,-3.8362484883,-0.0056237583,3.7265098615

H,0,-0.0804359616,0.0654252032,5.8326017512

H,0,-2.5640644485,0.0450341651,5.8652775296

H,0,2.1049138375,-1.0803825658,0.054152815

H,0,2.0893731293,1.0281451126,0.0158078507

TS_M

B,0,1.5999686678,-0.0653837938,1.0147607868

H,0,1.5222247405,-0.0576506892,-0.2592535018

N,0,-0.0211139147,0.0219527371,0.0979596551

C,0,0.0176748867,0.0182991678,1.3320486099

C,0,-0.92255934,0.0653701131,2.4392685695

C,0,-2.3054666107,0.1446226398,2.1981149904

C,0,-0.4419272119,0.0307997704,3.7552510888

C,0,-3.1929919449,0.1882401412,3.2679722071

H,0,-2.664780863,0.1715552841,1.1735356491

C,0,-1.3370848795,0.0745020221,4.8235165235

H,0,0.628158908,-0.0295758762,3.9267356477

C,0,-2.7096176463,0.1530151675,4.5804947887

H,0,-4.2622788772,0.2503614454,3.0814813914

H,0,-0.962480702,0.0482075757,5.8424481724

H,0,-3.4053738831,0.1877236648,5.4151758276

H,0,2.1216745071,0.989213569,1.2384190884

H,0,2.0068131633,-1.1704259387,1.2341025054

Table S1. Relative energies (in kJ/mol) of transition states, and products in two pathways with and without external electric field (F_Z in $\times 10^{-4}$ a.u.) by method of CCSD(T)/6-311++G(2d,2p)//B3LYP/6-31G(d).

structure / F_Z	TS_{AM}	P_{AM}	TS_M	P_M
50	23.52	−153.80	76.33	−44.66
30	23.41	−149.61	80.09	−38.29
0	23.23	−143.86	85.91	−28.62
−30	23.02	−122.04	91.90	−18.84
−50	22.86	−135.84	96.00	−12.26

Table S2. Relative energies (in kJ/mol) of transition states, and products in two pathways with and without external electric field (F_Z in $\times10^{-4}$ a.u.) by method of B3LYP-D3/6-311++G(d,p)//BP86-D3/6-31+G(d).

structure / F_Z	TS_{AM}	P_{AM}	TS_M	P_M
50	7.68	−180.94	58.93	−54.35
30	6.58	−176.09	62.65	−47.89
0	5.21	−169.44	68.46	−38.05
−30	3.93	−163.69	74.40	−28.15
−50	1.90	−160.37	78.43	−21.46

Table S3. Relative energies (in kJ/mol) of transition states, and products in two pathways with and without external electric field (F_Z in $\times 10^{-4}$ a.u.) by method of B3LYP/6-311++G(d,p)//BP86/6-31+G(d).

structure / F_Z	TS_{AM}	P_{AM}	TS_M	P_M
50	16.61	−173.64	67.10	−45.32
0	14.36	−162.14	76.59	−29.10
−50	11.00	−153.09	86.57	−12.51

Table S4. Relative energies (in kJ/mol) of products in two pathways with and without external electric field (the direction is oriented to F_Z in $\times 10^{-4}$ a.u.).

Structure / F_Z	P_{AM}	P_M
100	–162.00	–56.80
80	–157.03	–50.54
50	–150.17	–41.14
30	–146.00	–34.86
0	–140.35	–25.39
–30	–118.77	–15.86
–50	–132.62	–9.48
–80	–129.06	0.14
–100	–127.16	6.60

Table S5. Harmonic vibration frequencies (in cm^{-1}) of transition states and products in two pathways with and without external electric field (in $\times10^{-4}$ a.u.).

Structure / EEF		TS_{AM}	P_{AM}	TS_M	P_M
F_Z	**100**	1 (–317.4i)	0	1 (–821.4i)	0
	80	1 (–320.7i)	0	1 (–836.4i)	0
	50	1 (–327.4i)	0	1 (–859.2i)	0
	30	1 (–331.3i)	0	1 (–874.5i)	0
	0	1 (–337.9i)	0	1 (–896.5i)	0
	–30	1 (–346.0i)	0	1 (–918.9i)	0
	–50	1 (–351.9i)	0	1 (–932.8i)	0
	–80	1 (–359.7i)	0	1 (–952.7i)	0
	–100	1 (–366.3i)	0	1 (–965.1i)	0
F_X	**50**	1 (–441.7i)	0	1 (–928.8i)	0
	–50	1 (–200.9i)	0	1 (–858.9i)	0

Table S6. Key bond lengths (in Å) of transition states (TS_{AM} and TS_M) without and with external electric field (F_Z = 0, ±30, ±50, ±80, and ±100 (×10^{-4}) a.u.) along F_Z directions.

Structure	EEF / Bond	0	30	–30	50	–50	80	–80	100	–100
TS_{AM}	N–C	1.204	1.203	1.206	1.202	1.208	1.200	1.210	1.200	1.212
	N–B	1.691	1.698	1.683	1.702	1.678	1.709	1.671	1.713	1.666
	C–H	1.672	1.684	1.659	1.692	1.650	1.705	1.637	1.713	1.628
	B–H	1.269	1.269	1.269	1.269	1.270	1.270	1.271	1.270	1.272
	C–C	1.448	1.449	1.448	1.449	1.447	1.450	1.446	1.450	1.445
TS_M	N–C	1.237	1.235	1.239	1.234	1.240	1.233	1.243	1.232	1.244
	C–B	1.614	1.615	1.613	1.615	1.613	1.616	1.612	1.617	1.612
	B–H	1.279	1.277	1.282	1.275	1.284	1.273	1.287	1.272	1.289
	N–H	1.558	1.569	1.547	1.577	1.540	1.589	1.529	1.597	1.523
	C–C	1.452	1.453	1.450	1.453	1.450	1.454	1.448	1.454	1.447

Table S7. Key bond lengths (in Å) of transition states (TS_{AM} and TS_M) without and with external electric field (F_x = 0, and ±50 (×10^{-4}) a.u.) along F_x directions.

Structure	**EEF / Bond**	**0**	**50**	**–50**
TS_{AM}	**N–C**	1.204	1.213	1.194
	N–B	1.691	1.644	1.768
	C–H	1.672	1.567	1.826
	B–H	1.269	1.292	1.245
	C–C	1.448	1.451	1.446
TS_M	**N–C**	1.237	1.240	1.235
	C–B	1.614	1.613	1.616
	B–H	1.279	1.282	1.276
	N–H	1.558	1.532	1.586
	C–C	1.452	1.450	1.453

Table S8. Relative energies (in kJ/mol) of transition states and products in two pathways as external electric field (in ×10^{-4} a.u.) are perpendicular (F_X) to nitrogen−carbon triple bond.

Structure / F_X	TS_{AM}	P_{AM}	TS_M	P_M	u
50	5.99	−141.26	67.93	−25.36	4.57
−50	33.87	−138.14	94.39	−27.96	4.55

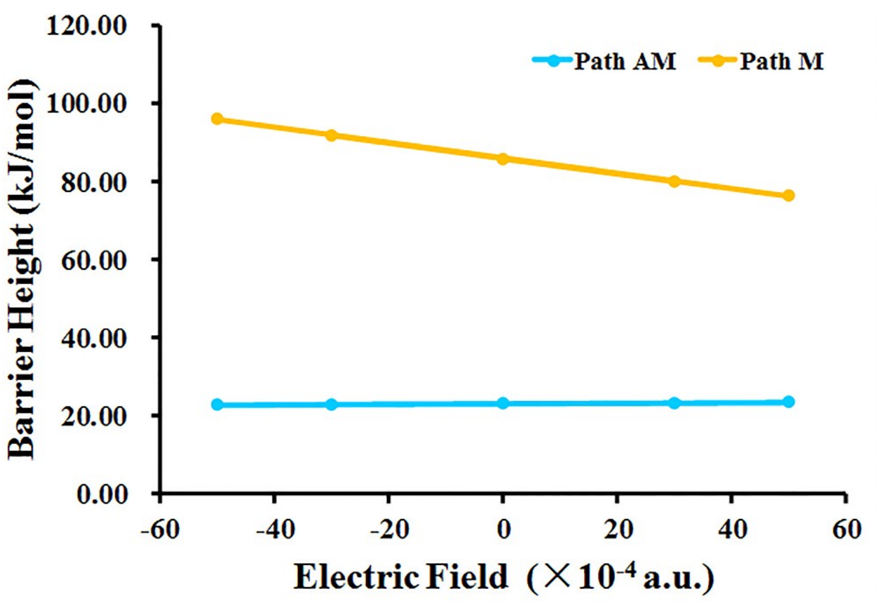

Figure S1. Variations of barrier heights for path AM and path M along with electric field by method of CCSD(T)/6-311++G(2d,2p)//B3LYP/6-31G(d) (the orange line is for path M, and the light blue line is for path AM).

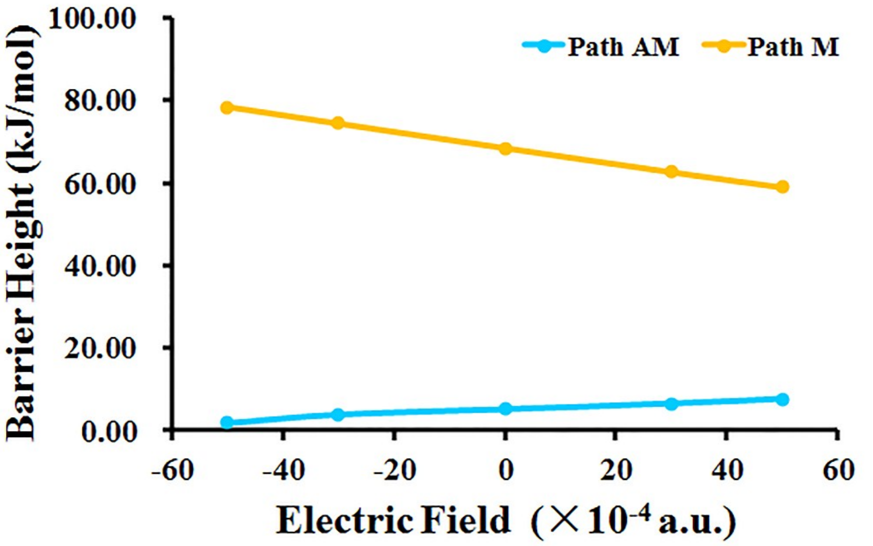

Figure S2. Variations of barrier heights for path AM and path M along with electric field by method of B3LYP-D3/6-311++G(d,p)//BP86-D3/6-31+G(d) (the orange line is for path M, and the light blue line is for path AM).

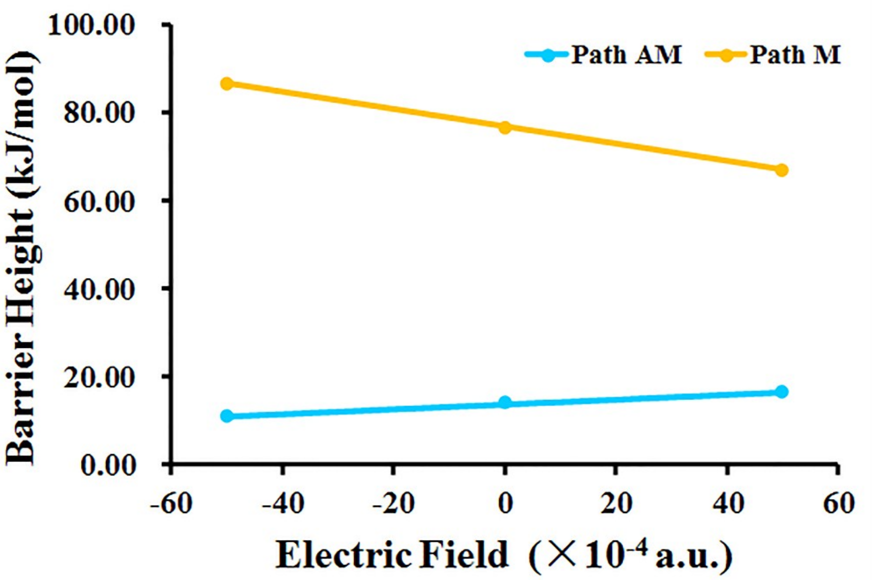

Figure S3. Variations of barrier heights for path AM and path M along with electric field by method of B3LYP/6-311++G(d,p)//BP86/6-31+G(d) (the orange line is for path M, and the light blue line is for path AM).

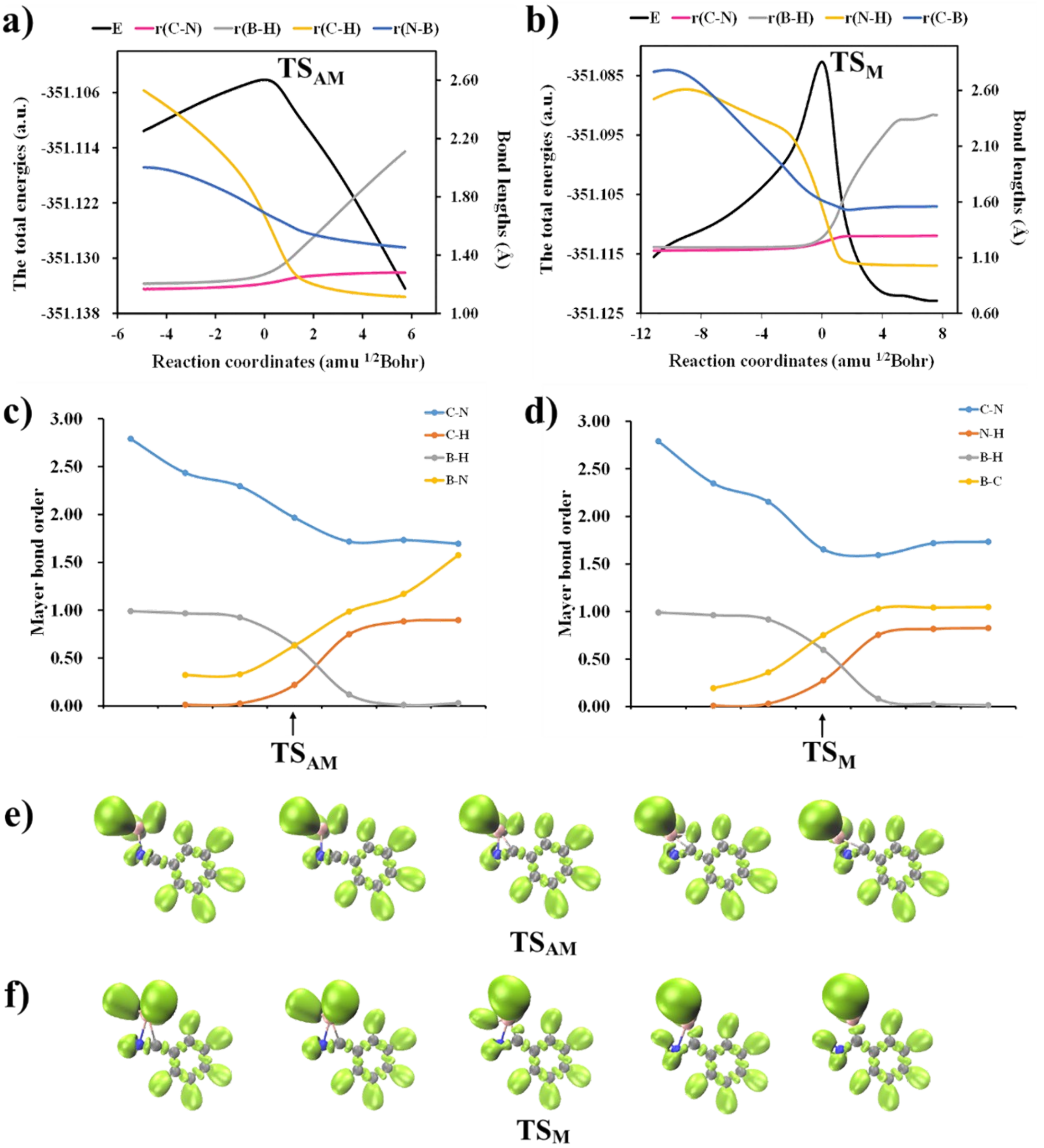

Figure S4. a) IRC profiles with the variations of key bonds in the hydroboration of path AM; b) IRC profiles with the variations of key bonds in the hydroboration of path M; c) Changes of Mayer bond orders as the reaction proceeding in path AM; d) Changes of Mayer bond orders as the reaction proceeding in path M; e) Electron localization function (ELF) isosurface for path AM (the five points are selected from transition state and twentieth and fortieth points before and after transition states along IRC); f) Electron localization function isosurface for path M, the points are selected as same as path AM.

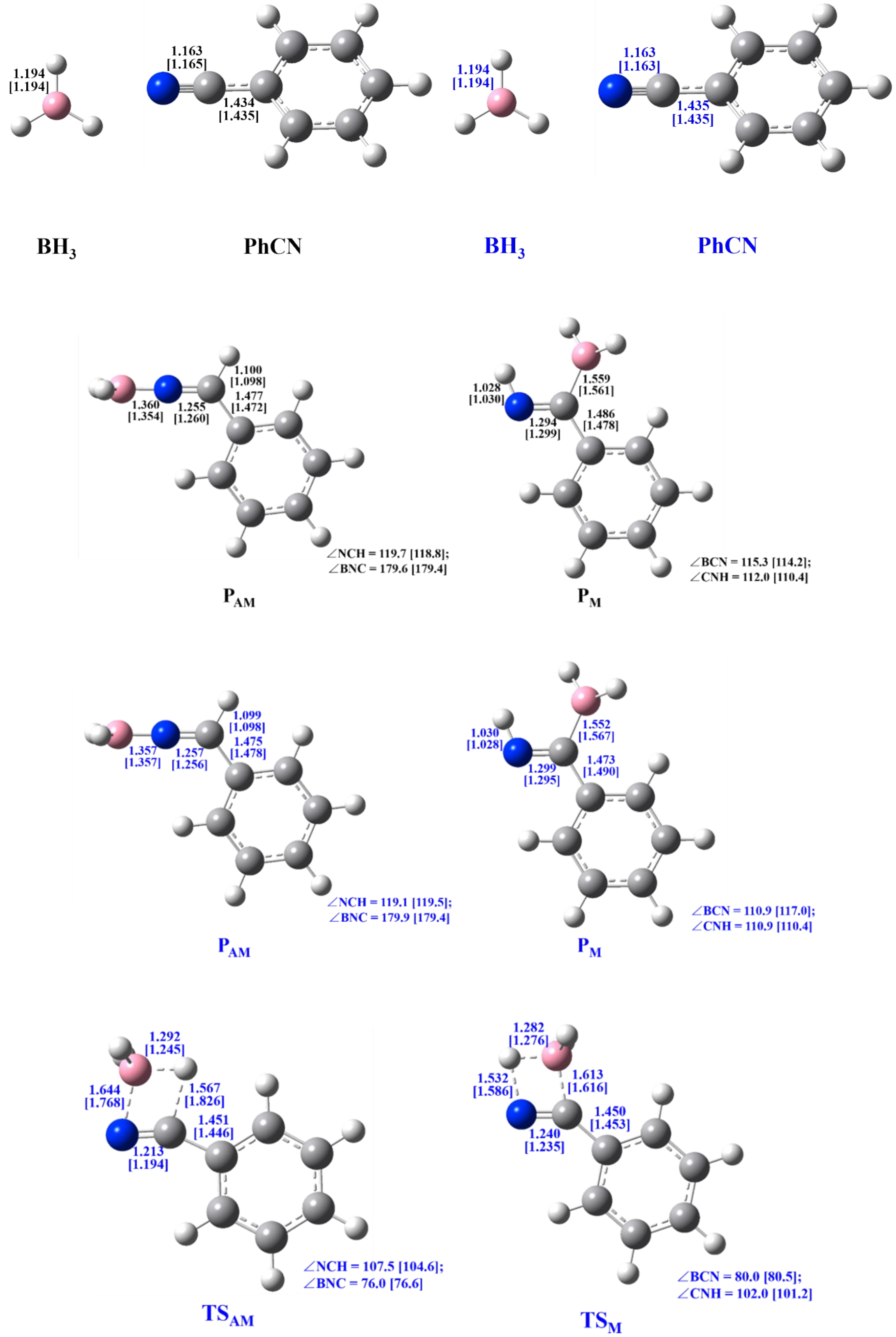

Figure S5. Geometries of stationary points along potential energy surfaces with key bond lengths and angles as external electric field is equal to 50 ($\times10^{-4}$) a.u., the black are those optimized as electric field along Z axis, and the blue is for X axis (The values in square brackets are given in −50 (×10^{-4}) a.u.; the bond lengths are given in Å, and angles in deg).

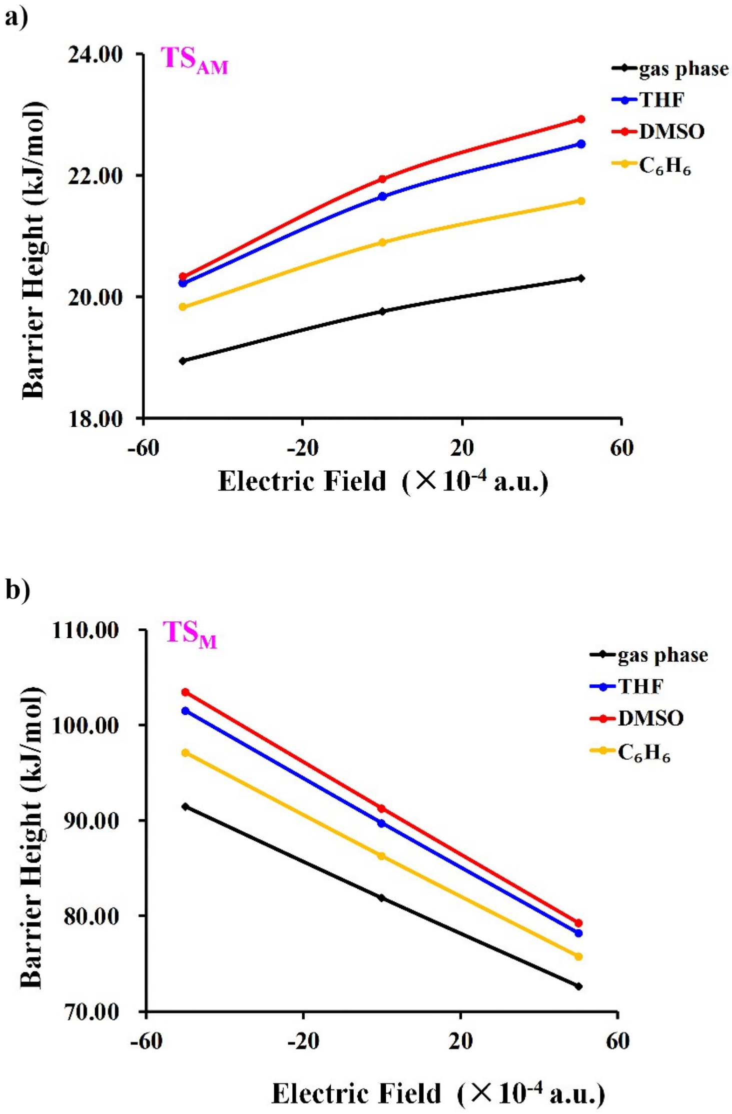

Figure S6. Barrier heights of two pathways (a for TS_{AM}, b for TS_{M}) as the external electric field (F_Z) is equal to −50, 0, and 50 (×10^{-4}) a.u. in gas phase (the black line), THF (the blue line), DMSO (the red line), and C_6H_6 (the orange line) solvents.

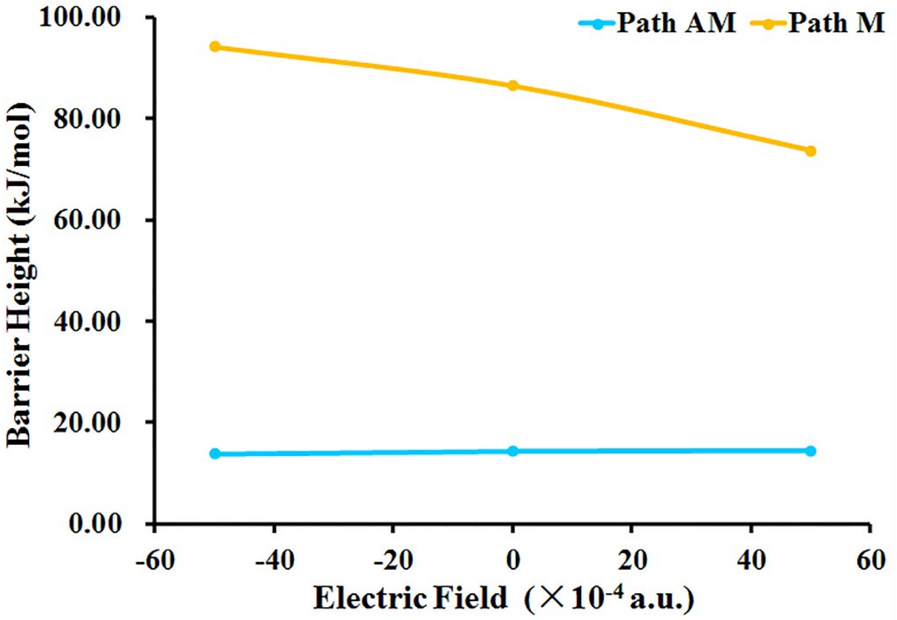

Figure S7. Variations of barrier heights for path AM and path M with EEF in hydroboration of ^{t}BuCN (the pink line is for path M, and the orange line is for path AM).