Supporting Information for

CATALYTIC AROMATIC BORYLATION *VIA IN SITU*-GENERATED BORENIUM SPECIES

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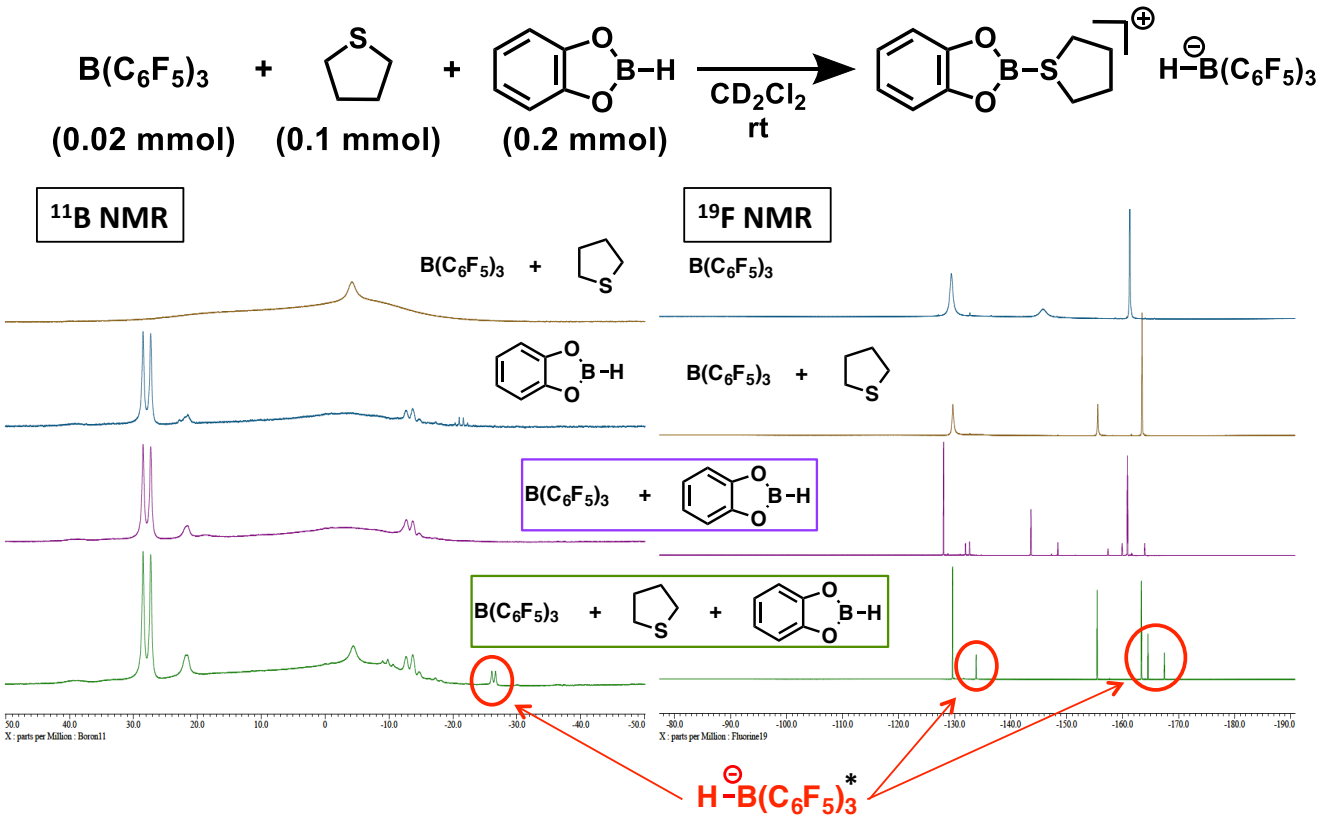
1. General

NMR spectra were obtained on a JEOL-AL300 or 400, or an ECA500 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H, ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard. ^{11}B and ^{19}F NMR spectra were unreferenced. The following abbreviations are used: s = singlet, d = doublet, t = triplet, m = multiplet, and sept = septet. ESI mass spectra were measured on a Bruker micrOTOF-II spectrometer. Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques or in a globe box under argon atmosphere. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was purchased from Tokyo Chemical Industry Co., Ltd. and purified by the sublimation after treatment with triethylsilane. Catecholborane was purchased from AstaTech Inc. and used as received. Tetrahydrothiophene, 1,2-dichloroethane, and arene substartes were used after distillation. Normal-phase column chromatography was performed with silica gel 60 (230-400 mesh) from Merck, silica gel 60N (spherical, neutral, 40-50 μm) from Kanto Chemical Co. Ltd., or CHROMATOREX-DIOL MB 100-40/75 from Fuji Silysia Chemical and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254).

2. ^{11}B and ^{19}F NMR Spectra of Reaction Conditions



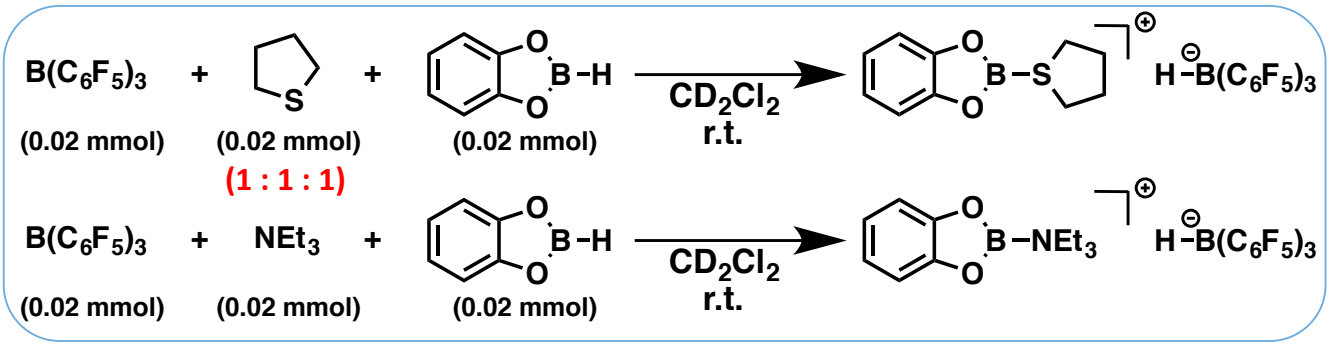
* Stephan, D. W. *et al*. *JACS* **2007**, *129*, 1880.

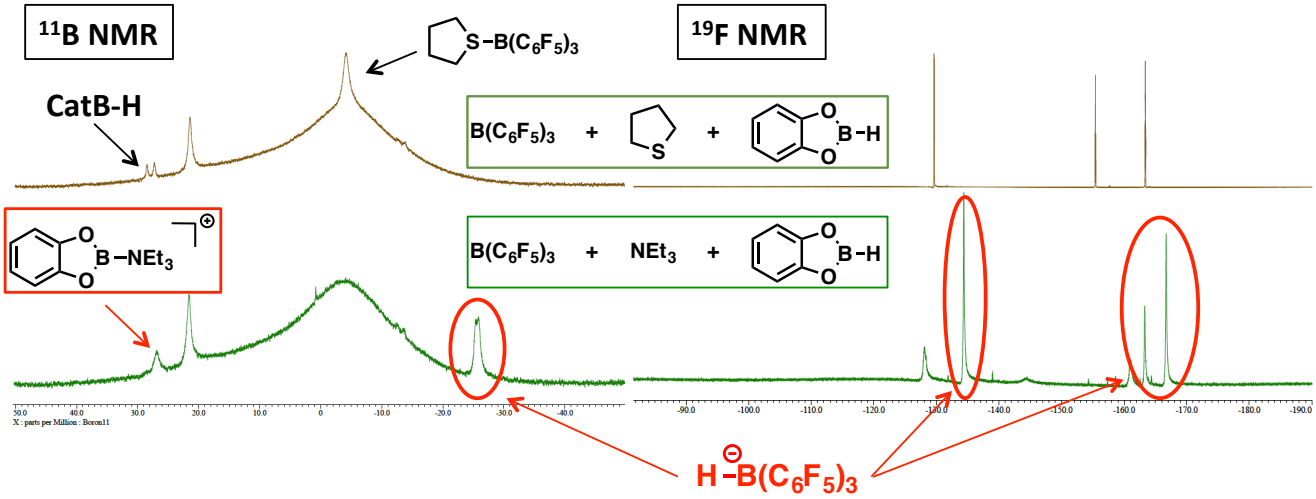
The peak corresponding to the borenium species ([CatB-THT]$^+$) would be overlapped with the peak of catecholborane in ^{11}B NMR spectrum (since the peak of [CatB-NEt$_3$]$^+$) is found to be overlapped with the peak of catecholborane, see the next section.) Judged from the ^{19}F NMR spectrum, 23% of B(C$_6$F$_5$)$_3$ was converted to [H–B(C$_6$F$_5$)$_3$]$^-$ under these conditions.

Combined with the results of the Lewis base effects (**4d** vs NEt$_3$ (or NMe$_3$)) shown in the next section and DFT calculations about the borylation step (Figure 1 in the manuscript), the generation of borenium species using **2**, **4d**, and B(C$_6$F$_5$)$_3$ should be thermodynamically unfavorable in the equilibrium. But, once generated, the **4d**-based borenium species is sufficiently reactive in the borylation reaction with a reasonable activation barrier ($\Delta E^{\ddagger}$ = 8.0 kcal/mol), which gives the stable intermediate (*i.e.*, **IM2**$_{THT}$). Furthermore, in **IM2**$_{THT}$, **4d** is already released, making the catalytic cycle feasible.

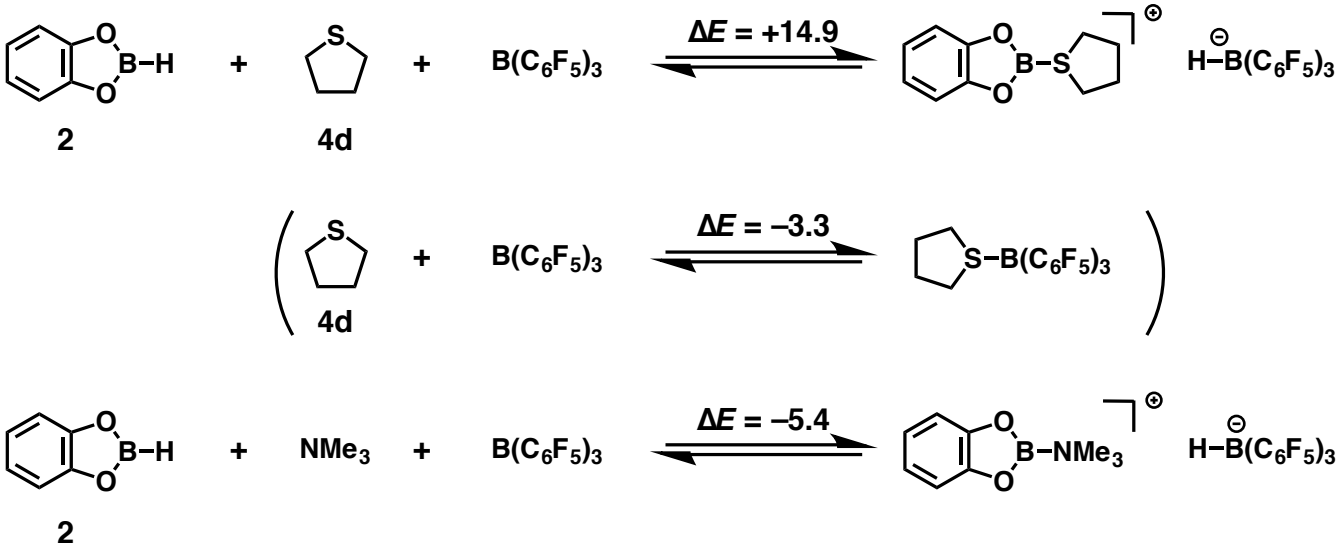
3. Effects of Lewis Base on the Generation of Borenium Species: NMR Studies and DFT Calculations

• NMR Studies





• Results of DFT Calculations (at B3LYP/6-31++G**, energies shown in kcal/mol)



4. Computational Details

4-1. Methods

All calculations were carried with the Gaussian 09 program package.[S1] The molecular structures and harmonic vibrational frequencies were obtained using the hybrid density functionals based on Becke's three-parameter exchange function and the Lee-Yang-Parr nonlocal correlation functional (B3LYP).[S2] We used 6–31++G** basis set for all other atoms. We used an additional Integral keyword to specify an ultrafine grid. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the B3LYP/6-31++G** of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.[S3]

[S1] Gaussian 09, Revision C.01 or D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[S2] (a) Beche, A. D. *Phys. Rev.* **1988**, *A38*, 3098-3100. (b) Beche, A. D. *J. Chem. Phys.* **1993**, *98*. 1372-1377. (c) Beche, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (d) Lee, C; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785-788.

[S3] (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363-368. (b) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* **1977**, *66*, 2153-2156. (c) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154-2161. (d) Schlegel, H. B.; Gonzalez, C. *J. Phys. Chem.* **1990**, *94*, 5523-5527.

4-2. Cartesian Coordinates and Energies (Figure 1)

IM1$_{THT}$
Energy (B3LYP) = –1327.93211089 (A. U.)
Gibbs Free Energy = –1327.606732 (A. U.)

C	-4.80226300	-2.19909700	0.29223000
C	-3.93957700	-1.56911500	1.20150900
C	-3.22543300	-0.49389500	0.70529200
C	-3.34896400	-0.05798300	-0.61173000
C	-4.19421200	-0.66651100	-1.52123400
C	-4.92631500	-1.75956600	-1.03426100
H	-5.39042300	-3.04684700	0.62719000
H	-3.84025400	-1.89837200	2.22944300
H	-4.28565000	-0.31783100	-2.54348900
H	-5.60757800	-2.27530300	-1.70259300
O	-2.50013200	1.04511800	-0.80467000
O	-2.30239400	0.32670300	1.37104300
B	-1.91160100	1.20634600	0.41211400
C	2.33137500	-1.26203100	-1.27429400
C	0.98497800	-1.62603200	-1.23965700
C	0.36049600	-1.98335100	-0.03980700
C	1.12568200	-1.98265100	1.13151600
C	2.47254600	-1.61839900	1.11582800
C	3.11352000	-1.23786800	-0.09116200
H	2.77927000	-1.02634000	-2.23162400
H	0.42806800	-1.65832000	-2.17258200
H	-0.67574000	-2.30572600	-0.02642100
H	0.67938600	-2.29252900	2.07271100
H	3.03028800	-1.66134200	2.04280700
N	4.44653400	-0.84228300	-0.11144800
C	5.14108600	-0.77374300	-1.39526700
H	6.16400700	-0.43609800	-1.22605100
H	5.17628200	-1.74572200	-1.90996700
H	4.66451900	-0.04860600	-2.06221900
C	5.27731100	-1.10572400	1.06151000
H	6.27672400	-0.70771200	0.88313400
H	4.87770300	-0.60038300	1.94597800
H	5.36549300	-2.17941000	1.28598500
S	-0.74456000	2.62930300	0.79611200
C	-0.18699100	3.20544100	-0.89402400
C	0.89779500	1.79938700	1.21680600
C	1.14687200	2.49461200	-1.14667400
H	-0.08623700	4.28811500	-0.79653900
H	-0.97869300	2.97199600	-1.60722700
C	1.87876000	2.38982000	0.19843900
H	0.76709600	0.72111900	1.10986200
H	1.11007100	2.05385600	2.25550700

H	0.97133200	1.49474700	-1.55570500
H	1.72656200	3.06323700	-1.88043600
H	2.75104000	1.73202400	0.13407600
H	2.22218200	3.37652000	0.52883900

TS1$_{THT}$

Energy (B3LYP) = –1327.91937944 (A. U.)

Gibbs Free Energy = –1327.588363 (A. U.)

C	-5.36937000	-1.31680900	0.73551800
C	-4.29880500	-0.75858600	1.45151300
C	-3.24748300	-0.26556300	0.69791100
C	-3.24375600	-0.31981000	-0.69787800
C	-4.29127400	-0.87015400	-1.41628600
C	-5.36565900	-1.37127300	-0.66464900
H	-6.21901100	-1.71307200	1.28159100
H	-4.29421500	-0.70859800	2.53460000
H	-4.28116700	-0.90429600	-2.49994800
H	-6.21256200	-1.80882900	-1.18273400
O	-2.07083600	0.25519300	-1.18175800
O	-2.07664600	0.34510800	1.14190600
B	-1.33024600	0.51988800	-0.02663600
C	2.12960200	-1.34095400	-1.18608700
C	0.75046300	-1.29640000	-1.17389300
C	0.01243900	-1.19265100	0.03824300
C	0.75834600	-1.21607700	1.25016100
C	2.13781500	-1.26147000	1.25712700
C	2.87523000	-1.34289500	0.03465200
H	2.64215800	-1.42494900	-2.13580600
H	0.21116100	-1.36058100	-2.11508000
H	-0.98782900	-1.62071400	0.05651700
H	0.22475200	-1.21731800	2.19683100
H	2.65609400	-1.28449600	2.20718900
N	4.23386700	-1.42681900	0.03251600
C	4.96391400	-1.62172700	-1.22240300
H	6.03235800	-1.63050100	-1.01289200
H	4.69916100	-2.57201900	-1.70203000
H	4.76667400	-0.80571000	-1.92554100
C	4.97311400	-1.53422900	1.29243800
H	6.04022300	-1.55143300	1.07669600
H	4.77578900	-0.67407300	1.94075500
H	4.71669300	-2.45170500	1.83626400
S	-0.48007100	2.26694500	-0.08598500
C	0.81113100	2.32621500	-1.42390200
C	0.73054400	2.42611500	1.30732300
C	2.16630300	2.41734700	-0.70351500
H	0.57584200	3.22074000	-2.00330100

H	0.69899600	1.44577200	-2.05711100
C	1.94310100	3.10081000	0.65454000
H	0.95511200	1.42602300	1.68018600
H	0.25239300	3.01992100	2.08726300
H	2.56584200	1.41072100	-0.55377900
H	2.87639700	2.97306800	-1.32316500
H	2.81569500	3.00427500	1.30769600
H	1.75066900	4.17120300	0.52107800

IM2$_{THT}$

Energy (B3LYP) = –1327.94224033 (A. U.)

Gibbs Free Energy = –1327.617401 (A. U.)

C	-4.96294800	-0.60210600	0.68903100
C	-3.80309500	-0.90180700	1.42109100
C	-2.66723200	-1.17369600	0.67918000
C	-2.66621800	-1.15578500	-0.71421000
C	-3.80108800	-0.86496700	-1.45052800
C	-4.96196200	-0.58414100	-0.71266700
H	-5.88215400	-0.38509800	1.22312100
H	-3.79633400	-0.92641200	2.50509800
H	-3.79281100	-0.86206100	-2.53481200
H	-5.88046900	-0.35365200	-1.24229300
O	-1.38910600	-1.47628400	-1.16988600
O	-1.39076400	-1.50624500	1.12826300
B	-0.64918800	-1.65780700	-0.02247700
C	2.73759400	-1.12030800	-1.25060700
C	1.58053300	-1.82254600	-1.26254500
C	0.86091400	-2.20799800	-0.02867500
C	1.57604500	-1.86151900	1.21926800
C	2.73280600	-1.15888800	1.23364800
C	3.35083200	-0.72208600	-0.00082000
H	3.20480700	-0.85168000	-2.18845400
H	1.13684300	-2.10354600	-2.21328000
H	0.67483000	-3.30030900	-0.04623800
H	1.12913100	-2.17249000	2.15910400
H	3.19624200	-0.91929600	2.18117700
N	4.45987700	0.01459900	0.01283900
C	5.09172300	0.46632800	-1.24197300
H	5.96018300	1.07363100	-0.99818000
H	5.42369200	-0.38778700	-1.83879800
H	4.39552000	1.07498900	-1.82500400
C	5.08697500	0.42671000	1.28360600
H	5.95849100	1.03819300	1.06218800

H	4.38969500	1.01983900	1.88123200
H	5.41357600	-0.44584500	1.85616700
S	0.36962700	1.59870500	0.01986600
C	-0.53789800	2.49208700	-1.33308900
C	-0.56207500	2.45175900	1.38167500
C	-1.28173400	3.64744300	-0.65051900
H	-1.23006500	1.79278700	-1.80932100
H	0.18410000	2.83568200	-2.07697600
C	-1.76381100	3.12895200	0.71070100
H	0.10025900	3.18381800	1.85144700
H	-0.85454900	1.71015700	2.12818200
H	-0.60014300	4.49400200	-0.50665600
H	-2.11237100	3.99360800	-1.27485400
H	-2.15362900	3.93543700	1.34105100
H	-2.56927500	2.39924300	0.56834800

IM1$_{THF}$

Energy (B3LYP) = –1004.96846840 (A. U.)

Gibbs Free Energy = –1004.637790 (A. U.)

C	-5.41821300	-1.14735800	0.68679700
C	-4.41434500	-0.47651900	1.40342500
C	-3.37204400	0.02830900	0.65027600
C	-3.31240700	-0.11375200	-0.73451500
C	-4.29127500	-0.76974000	-1.45558300
C	-5.35830400	-1.29011000	-0.70591400
H	-6.26107000	-1.56368100	1.22809300
H	-4.45261600	-0.35944700	2.48039200
H	-4.23702300	-0.87349700	-2.53322900
H	-6.15572500	-1.81472200	-1.22131300
O	-2.14068200	0.50385200	-1.20903700
O	-2.24031400	0.74058500	1.08753500
B	-1.56121800	0.96853300	-0.06923000
C	2.26355600	-1.42852800	-1.04818100
C	0.91792000	-1.76353800	-0.89463900
C	0.31391800	-1.78405300	0.36780800
C	1.10070100	-1.47576200	1.48385700
C	2.44799300	-1.13904200	1.34956200
C	3.06950800	-1.10122300	0.07379100
H	2.69567600	-1.46393200	-2.04051800
H	0.34504900	-2.04403700	-1.77478900
H	-0.71754000	-2.10122600	0.48635000
H	0.67174900	-1.52965800	2.48122500
H	3.02528200	-0.94689200	2.24533900
N	4.40442300	-0.75194900	-0.07178500
C	5.06984400	-1.01138600	-1.34662300
H	6.10051400	-0.66131700	-1.28523100

H	5.08089700	-2.08007300	-1.60740100
H	4.58671400	-0.46291000	-2.16147100
C	5.25620800	-0.69718500	1.11402700
H	6.25714600	-0.38386700	0.81631700
H	4.88296000	0.04013100	1.83175300
H	5.33376100	-1.66881800	1.62417900
C	0.44379900	1.99673300	-1.35667500
C	0.35671700	2.22226700	1.14807700
C	1.75520400	2.51885100	-0.79379100
H	-0.14213600	2.73111800	-1.90989400
H	0.50419600	1.04522100	-1.88172900
C	1.37163100	3.17544900	0.54791800
H	0.78943400	1.33034200	1.60255900
H	-0.41378700	2.66710200	1.77566800
H	2.45225500	1.69169100	-0.63511500
H	2.21154400	3.23260800	-1.48382800
H	2.23342100	3.28544900	1.21042300
H	0.92907800	4.16428300	0.39383600
O	-0.36239300	1.72139200	-0.09483100

TS1$_{THF}$

Energy (B3LYP) = –1004.95888443 (A. U.)

Gibbs Free Energy = –1004.622941 (A. U.)

C	-5.27357500	-1.07722200	0.68642900
C	-4.14852100	-0.67619400	1.42553400
C	-3.03918800	-0.29080000	0.69435700
C	-3.02915500	-0.30079600	-0.70172200
C	-4.12848500	-0.69622100	-1.44269700
C	-5.26378000	-1.08692600	-0.71380300
H	-6.16856200	-1.38728400	1.21551700
H	-4.14702300	-0.66536200	2.50982000
H	-4.11187600	-0.70045200	-2.52689600
H	-6.15138000	-1.40431200	-1.25094000
O	-1.78962400	0.14054300	-1.16062200
O	-1.80615900	0.15792400	1.16448800
B	-1.03272800	0.28155400	0.00608700
C	2.26883300	-1.21930300	-1.20229300
C	0.90715700	-1.44592100	-1.18514100
C	0.16963000	-1.48722300	0.02895300
C	0.91274900	-1.40751900	1.23765100
C	2.27462900	-1.18108100	1.24105700
C	3.00540200	-1.08588900	0.01592000
H	2.78340300	-1.19419600	-2.15433900
H	0.38400700	-1.58861800	-2.12649600
H	-0.79221300	-1.99585100	0.03891700
H	0.39410300	-1.51846200	2.18572500

H	2.79349100	-1.12564100	2.18949600
N	4.35294300	-0.88971600	0.00955600
C	5.09922400	-0.90528000	-1.25010300
H	6.14670200	-0.69030400	-1.04430400
H	5.03941000	-1.88196500	-1.74611300
H	4.72847300	-0.13854400	-1.93867900
C	5.10555400	-0.86854100	1.26532600
H	6.15255200	-0.66307900	1.04775500
H	4.74045700	-0.07988800	1.93188300
H	5.04553900	-1.82930900	1.79143800
C	0.25244300	2.16031600	-1.25588700
C	0.28410500	2.18889100	1.22893200
C	1.10698400	3.30576700	-0.74120500
H	-0.71199800	2.46941900	-1.66018900
H	0.74922800	1.46406000	-1.92922500
C	0.54431400	3.57714400	0.66648300
H	1.16406900	1.70973600	1.65877700
H	-0.57350100	2.09805800	1.89272200
H	2.15917400	3.00922700	-0.68974200
H	1.02872600	4.17588700	-1.39727300
H	1.24411200	4.13074000	1.29699400
H	-0.38729800	4.14837300	0.60868700
O	-0.04252700	1.38388200	-0.00231500

IM2$_{THF}$

Energy (B3LYP) = –1004.96274578 (A. U.)

Gibbs Free Energy = –1004.627988 (A. U.)

C	-5.27582900	-0.90401300	0.70910700
C	-4.08955500	-0.71505600	1.44002800
C	-2.92042000	-0.59086700	0.70991100
C	-2.91159600	-0.65387900	-0.68596200
C	-4.07134800	-0.84191500	-1.41754800
C	-5.26708200	-0.96590400	-0.68811900
H	-6.21471100	-1.00641000	1.24341500
H	-4.08657300	-0.67127100	2.52385400
H	-4.05392700	-0.89521900	-2.50082700
H	-6.19914900	-1.11579200	-1.22312200
O	-1.61505100	-0.51384400	-1.15600300
O	-1.62977300	-0.40928400	1.18148500
B	-0.81100000	-0.32386700	0.01010600
C	2.59758300	-1.02297600	-1.20953800
C	1.27703000	-1.35680600	-1.17632500
C	0.50704200	-1.41997000	0.06150500
C	1.29625800	-1.25402900	1.27730900
C	2.61769400	-0.92143300	1.26126200
C	3.32794700	-0.78917000	0.01225700

H	3.10869600	-0.97076500	-2.16184600
H	0.75547700	-1.56144400	-2.10737500
H	-0.13123500	-2.31354100	0.10520500
H	0.79109000	-1.38167400	2.23103600
H	3.14466500	-0.79281200	2.19762900
N	4.63283400	-0.47865700	-0.01104800
C	5.36848800	-0.38995000	-1.28344500
H	6.39005000	-0.07711600	-1.07834400
H	5.39857300	-1.36041100	-1.78897200
H	4.91102600	0.34906800	-1.94718400
C	5.39055600	-0.29160200	1.23741800
H	6.41003200	-0.00310500	0.99058000
H	4.94863500	0.50174900	1.84687600
H	5.42460900	-1.21797400	1.81955000
C	-0.45793100	2.04402300	-1.25348700
C	-0.03766600	2.01957100	1.15542000
C	-0.09442500	3.44010300	-0.77315100
H	-1.51557900	1.93335300	-1.49316500
H	0.14907400	1.66005900	-2.07298200
C	-0.48715800	3.40539000	0.71295200
H	1.01884300	1.98204800	1.43038100
H	-0.65318100	1.55835700	1.92549400
H	0.97889800	3.62567900	-0.88729900
H	-0.63369500	4.20484900	-1.33750600
H	-0.00349600	4.18964400	1.30035200
H	-1.57035200	3.51175100	0.82899600
O	-0.17519400	1.18210500	-0.06992000

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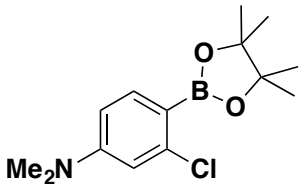
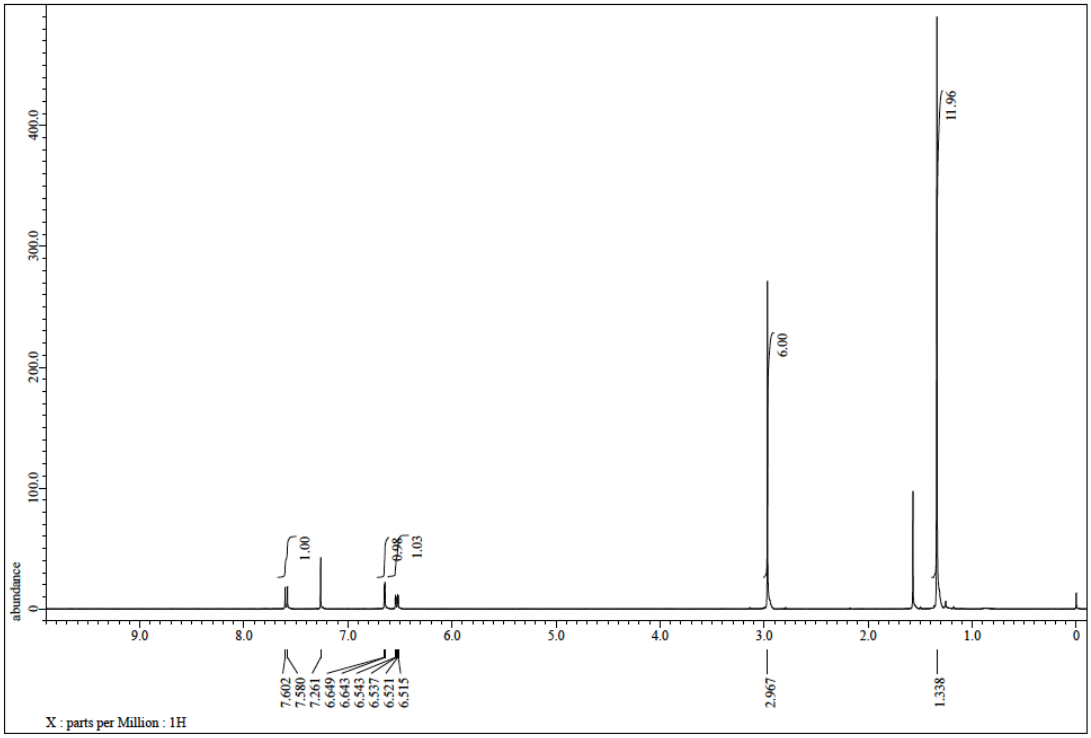
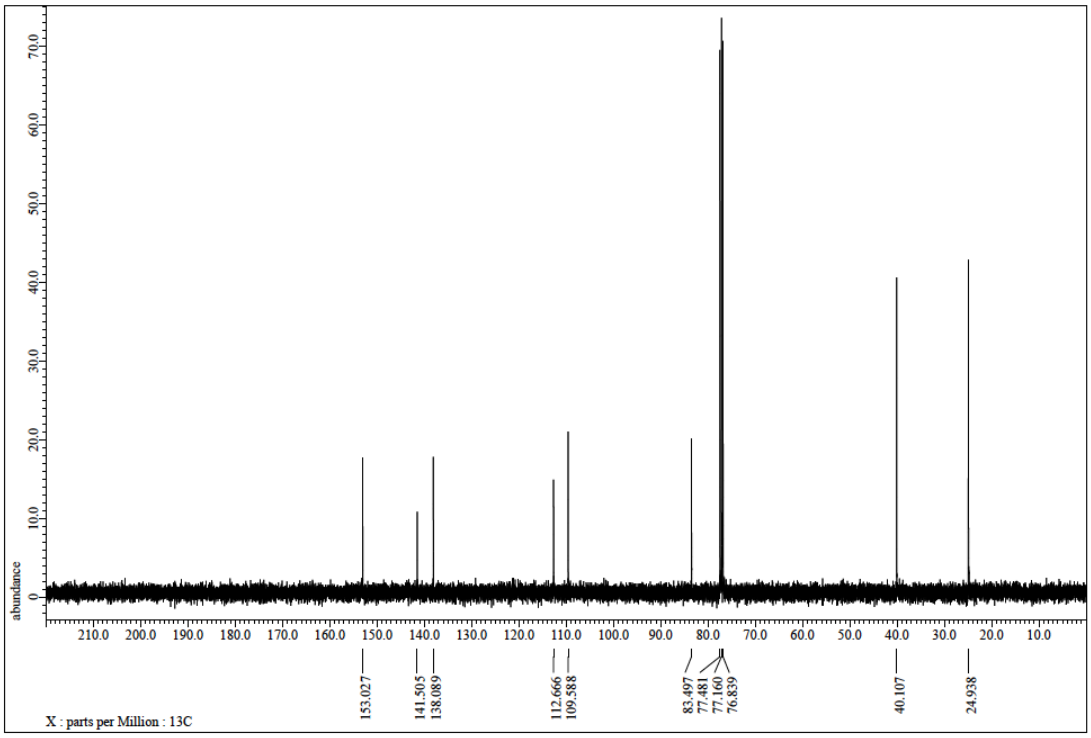
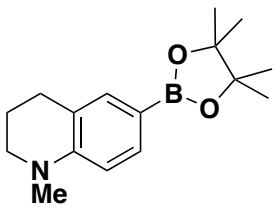
5. ^{1}H and ^{13}C NMR Spectra of New Compounds



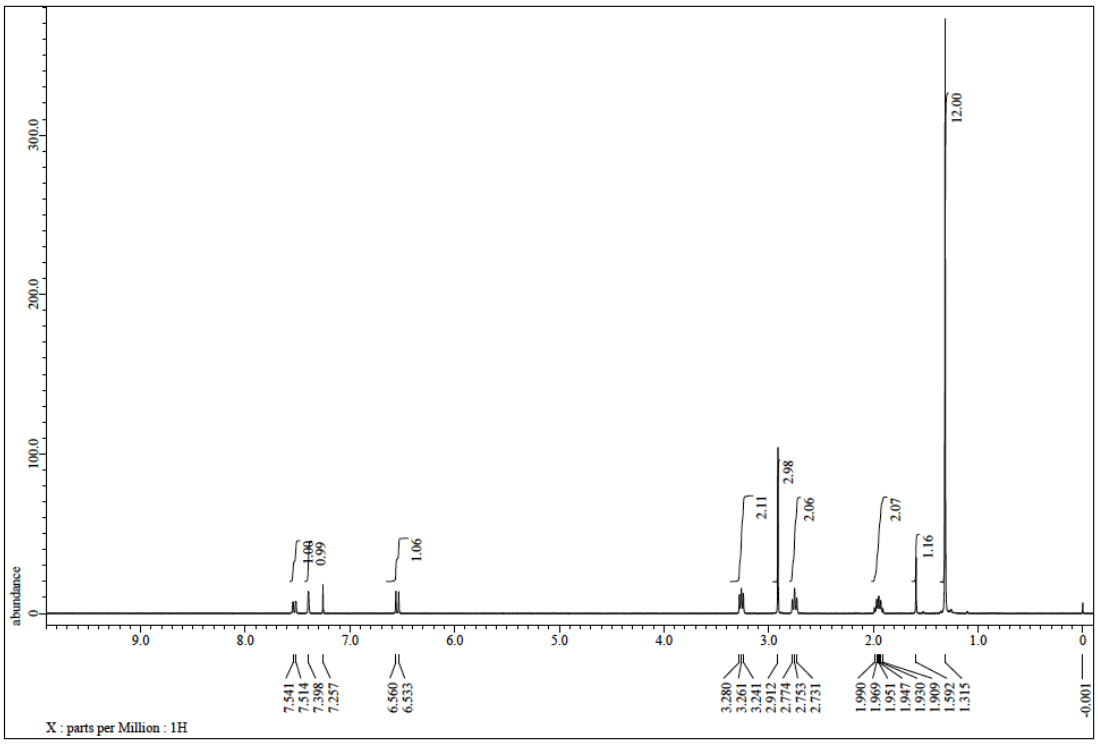
3b

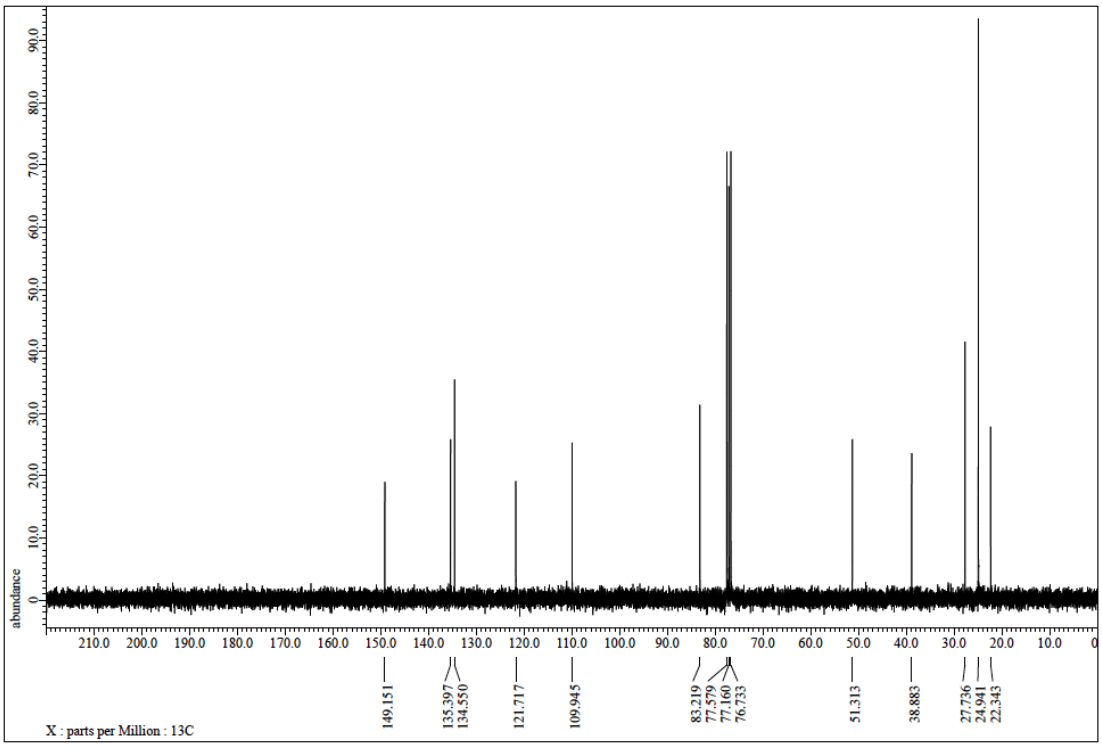


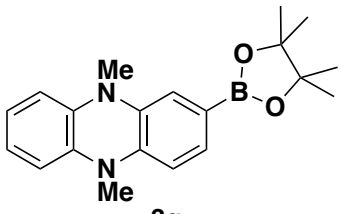



O
B
O
N
Me

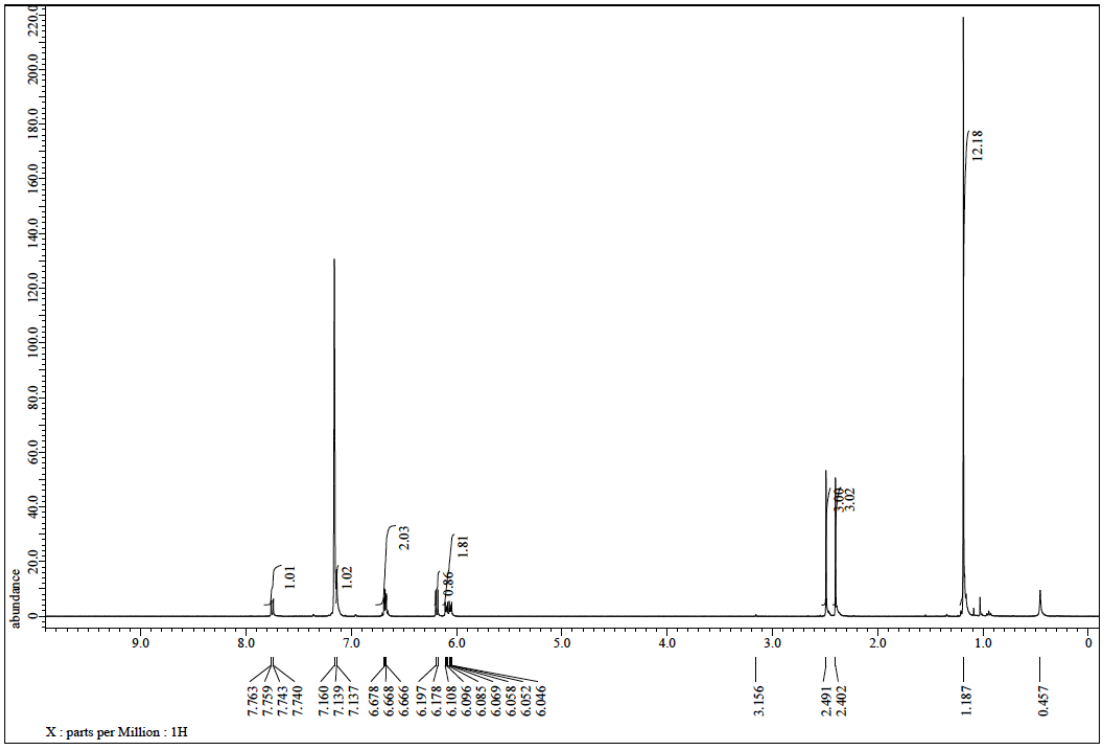
3f

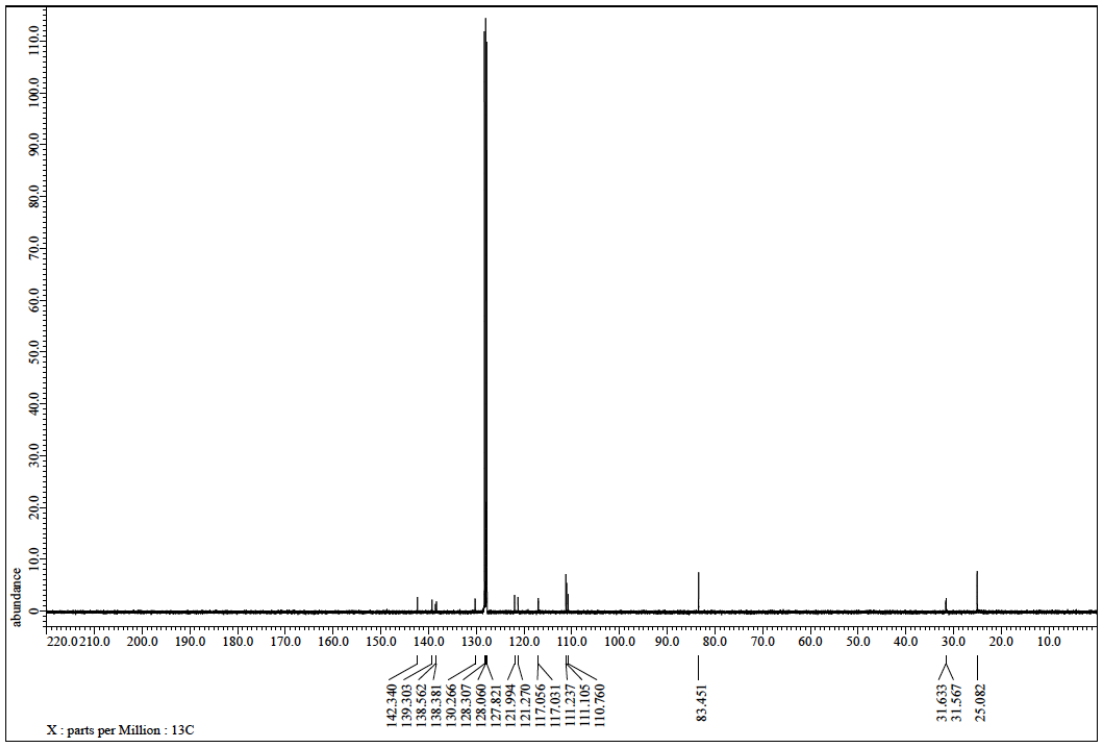

abundance
12.00
2.98
2.11
2.06
2.07
1.16
1.06
1.00
0.99
7.541
7.514
7.398
7.257
6.560
6.533
3.280
3.261
3.241
2.912
2.774
2.753
2.731
1.990
1.969
1.951
1.947
1.930
1.909
1.592
1.315
-0.001
X : parts per Million : 1H


abundance
149.151
135.397
134.550
121.717
109.945
83.219
77.579
77.160
76.733
51.313
38.883
27.736
24.941
22.343
X : parts per Million : 13C


Me
N
B
O
O
N
Me

3g


abundance
X : parts per Million : 1H
12.18
2.03
1.81
1.02
1.01
0.86
3.06
3.02
7.763
7.759
7.743
7.740
7.160
7.139
7.137
6.678
6.668
6.666
6.197
6.178
6.108
6.096
6.085
6.069
6.058
6.052
6.046
3.156
2.491
2.402
1.187
0.457


abundance
X : parts per Million : 13C
142.340
139.303
138.562
138.381
130.266
128.307
128.060
127.821
121.994
121.270
117.056
117.031
111.237
111.105
110.760
83.451
31.633
31.567
25.082