Supporting Information

Pd/Cu/TsOH-Cocatalysed Direct Synthesis of 1,3-Dienyl-2-boronic Acid: A New Reagent for Homoallenylboration

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1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III (500 MHz) and BRUKER AVANCE NEO (500 MHz) spectrometers. ^{11}B NMR spectra were recorded on BRUKER AVANCE NEO (500 MHz). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C), CD_3CN (internal standard: 1.94 ppm, ^{1}H; 118.2, 1.3 ppm, ^{13}C), C_6D_6 (internal standard: 7.16 ppm, ^{1}H; 128.1 ppm, ^{13}C) and DMSO-d_6 (internal standard: 2.49 ppm, ^{1}H; 39.5 ppm,^{13}C). ^{11}B NMR chemical shifts were quoted relative to BF_3 Et_2O as external standard. High-resolution mass spectra (HRMS) were obtained on a Thermo Scientific Q Exactive Combined Quadrupole Orbitrap Mass Spectrometer and Waters Xevo G2QTOF Mass Spectrometer. Column chromatography and filtration via silica plug were carried out employing silica gel (Qingdao Haiyang Chem, neutral, 300-400 Mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck). Density functional theory (DFT) calculations were performed using the Gaussian16 program package.[1] All calculations were carried out at the B3LYP-D3(BJ)/def2-SVP level of theory. For all transition states, intrinsic reaction coordinate (IRC) calculations were performed to confirm the connection between the reactant and product.

2. Materials

Unless otherwise noted, commercially available chemicals were used as received. 2,3-Allenols **1** were synthesized according to reported procedures by Szabó[2], Ma[3], Lipshutz[4] and Krause[5]. The structures of new products were determined by ^{1}H, ^{13}C, ^{11}B NMR, and high-resolution mass (HRMS).

3. DFT calculation of Gibbs Free Energy changes in the reaction between 1,3-dienyl-2-boron reagents and benzaldehyde

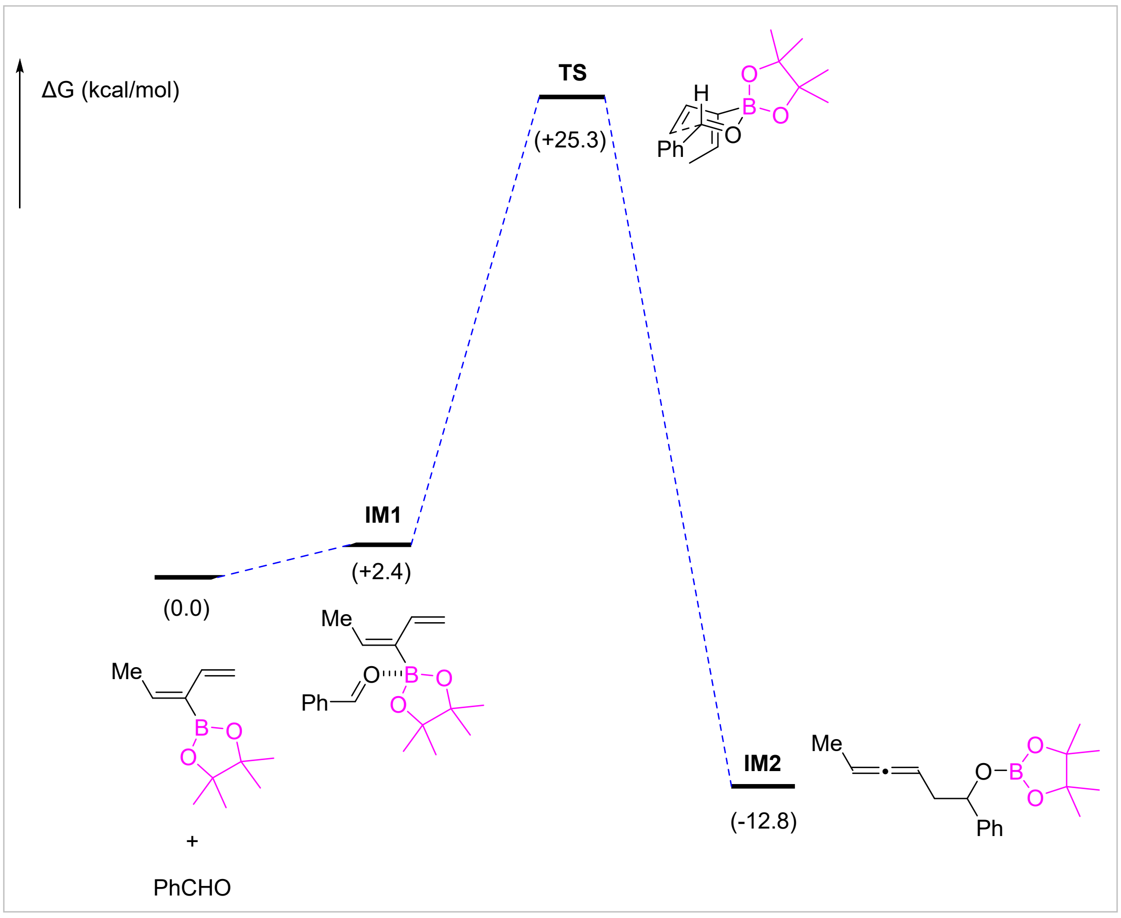

Figure S1. Gibbs Free Energy changes in the reaction between 1,3-dienyl-2-boronic acid pinacol ester and benzaldehyde

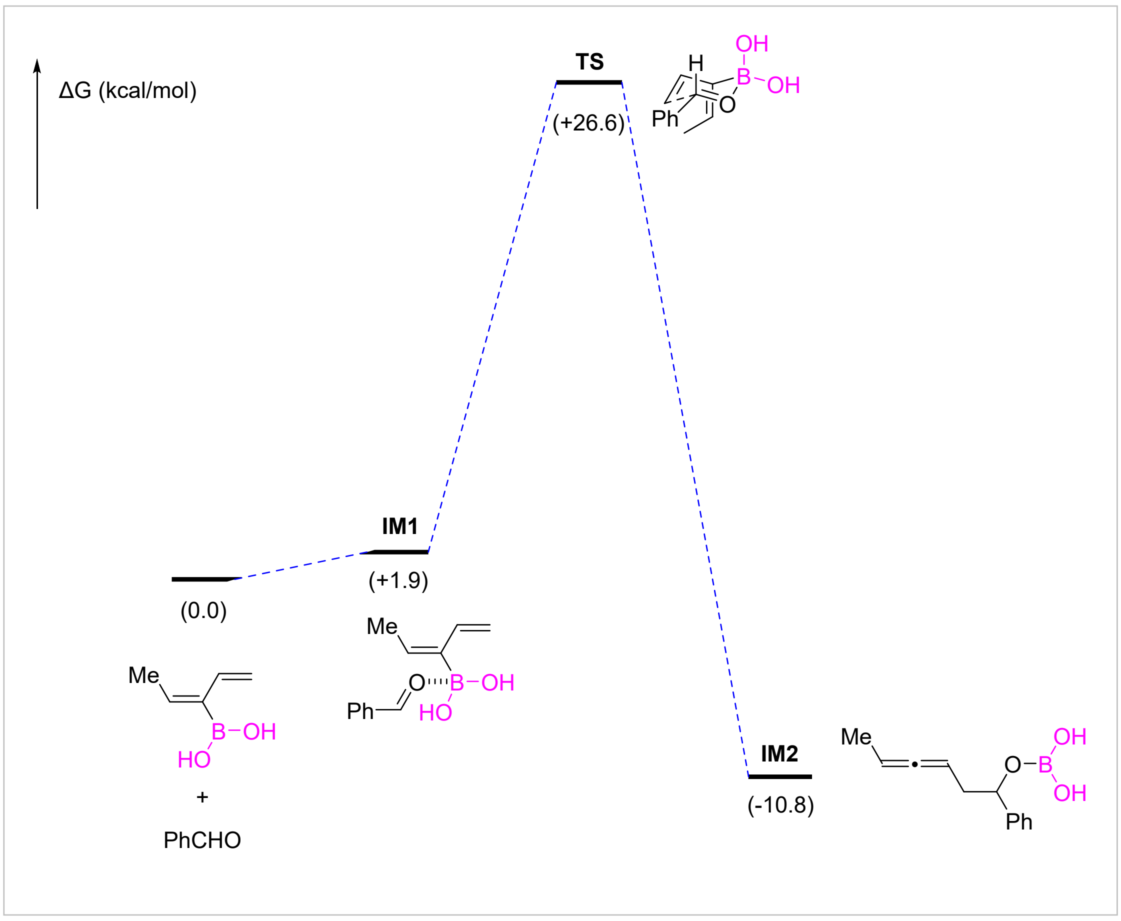

Figure S2. Gibbs Free Energy changes in the reaction between 1,3-dienyl-2-boronic acid and benzaldehyde

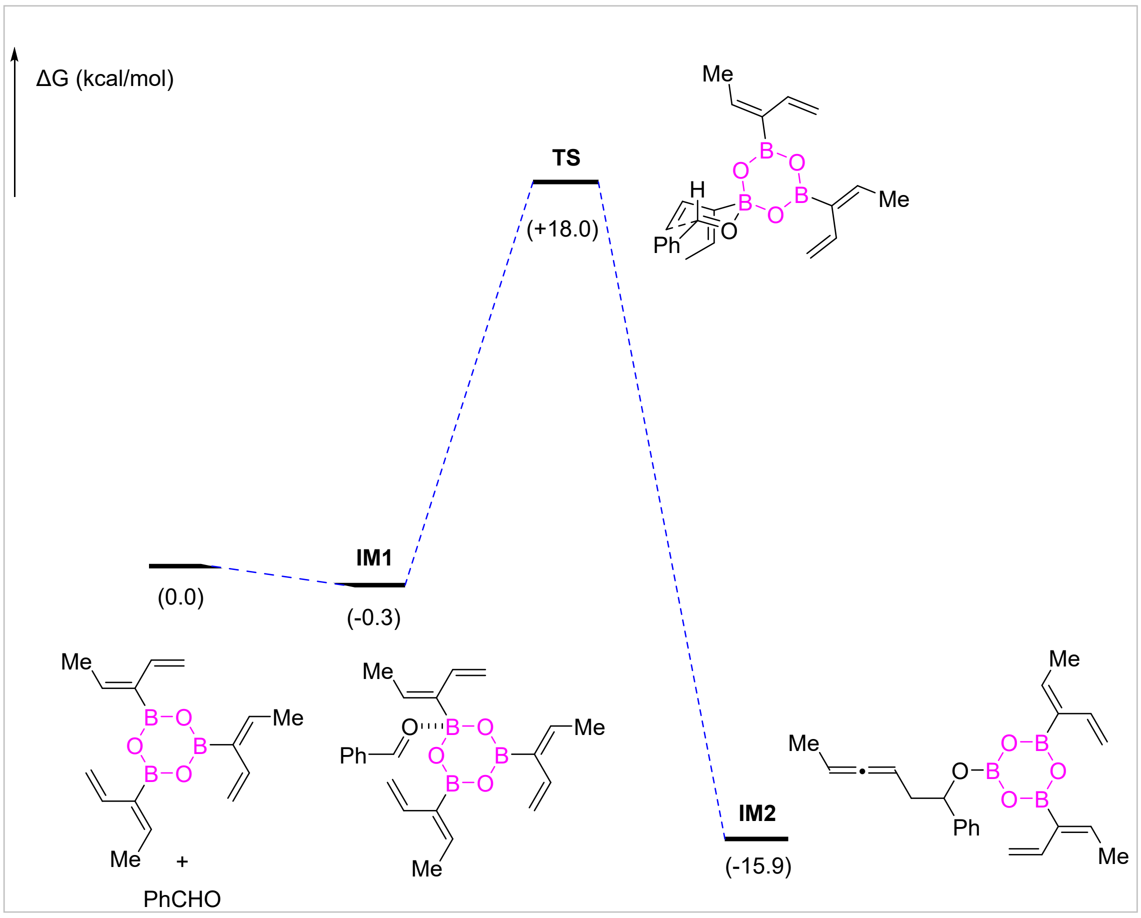

Figure S3. Gibbs Free Energy changes in the reaction between 1,3-dienyl-2-boroxine and benzaldehyde

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Structure: PhCHO

Charge = 0, Multiplicity = 1

Final SCF Energy = -345.349126465 Hartree

Gibbs Free Energy = -345.269551 Hartree

Thermal Correction = 0.079576 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

C	1.634857	-1.213467	-0.000000
C	1.335393	0.149878	-0.000000
C	-0.000000	0.577247	0.000000
C	-1.038545	-0.368658	0.000000
C	-0.739058	-1.728559	-0.000000
C	0.597264	-2.150922	-0.000000
H	2.674875	-1.547503	-0.000000
H	2.138356	0.892864	-0.000000
H	-2.069129	-0.007562	0.000000
H	-1.544221	-2.467045	-0.000000
H	0.829928	-3.218683	-0.000000
C	-0.315375	2.025938	0.000000

O	-1.432861	2.488081	0.000000
H	0.585864	2.694539	0.000000

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Structure: RBpin

Charge = 0, Multiplicity = 1

Final SCF Energy = -605.614313361 Hartree

Gibbs Free Energy = -605.371862 Hartree

Thermal Correction = 0.242451 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	0.416964	1.075217	0.353034
O	0.413545	-1.094590	-0.354402
B	-0.346032	-0.012642	0.014088
C	-1.901764	-0.012932	0.063299
C	-2.533321	-1.206595	-0.071848
H	-1.890480	-2.075329	-0.257230
C	-2.567668	1.280472	0.308879
H	-2.001424	1.974383	0.942054
C	-3.730422	1.709968	-0.206260
H	-4.116207	2.705335	0.030947
H	-4.318356	1.107239	-0.902927
C	-3.997413	-1.497954	0.032852
H	-4.166100	-2.467329	0.529586
H	-4.540067	-0.712277	0.578767
H	-4.458250	-1.578652	-0.969134
C	1.791346	-0.797325	-0.030964
C	1.790417	0.780483	0.006769
C	2.048680	1.413393	-1.362725
H	1.816687	2.486785	-1.305648
H	3.097737	1.299087	-1.672840
H	1.404228	0.967731	-2.134259
C	2.707674	1.397926	1.054082
H	3.755729	1.115415	0.869599
H	2.635667	2.494668	1.007930
H	2.431051	1.084266	2.068575
C	2.075800	-1.429047	1.334148
H	1.846720	-2.503354	1.281326
H	3.129629	-1.311435	1.626263

H	1.443834	-0.985528	2.117273
C	2.692100	-1.412665	-1.093727
H	3.742756	-1.129165	-0.926272
H	2.622084	-2.509563	-1.047400
H	2.398267	-1.098430	-2.103137

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Structure: IM1_RBpin

Charge = 0, Multiplicity = 1

Final SCF Energy = -950.978152329 Hartree

Gibbs Free Energy = -950.637593 Hartree

Thermal Correction = 0.340560 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	-1.652199	-0.404063	1.007975
O	-2.542109	0.758119	-0.745068
B	-1.556644	0.705384	0.203926
C	-0.471847	1.805131	0.401758
C	-0.524002	2.898103	-0.397861
H	-1.320949	2.908521	-1.150760
C	0.527071	1.585601	1.464420
H	0.141161	1.105396	2.372502
C	1.844077	1.836571	1.399013
H	2.507090	1.606055	2.237157
H	2.313749	2.238279	0.497874
C	0.353936	4.109761	-0.371404
H	-0.241090	5.023366	-0.536105
H	0.907807	4.205725	0.573565
H	1.097649	4.074278	-1.188794
C	2.832267	-0.907572	-0.256500
C	3.465784	-1.270290	0.940099
C	4.857077	-1.228591	1.036828
C	5.616972	-0.820888	-0.064566
C	4.987762	-0.458337	-1.262938
C	3.598936	-0.502760	-1.360383
H	2.858071	-1.575358	1.796514
H	5.351855	-1.509664	1.969347
H	6.706660	-0.784676	0.010208
H	5.587843	-0.141052	-2.119117

H	3.077769	-0.225042	-2.278899
C	1.354384	-0.944776	-0.349259
O	0.728619	-0.669123	-1.351549
H	0.826582	-1.252080	0.583913
C	-3.501746	-0.281499	-0.456754
C	-2.673013	-1.272240	0.457426
C	-1.959319	-2.367022	-0.337678
H	-1.281756	-2.910922	0.337579
H	-2.674172	-3.089846	-0.757289
H	-1.355477	-1.937017	-1.147400
C	-3.459372	-1.887107	1.608903
H	-4.297235	-2.492582	1.229999
H	-2.799775	-2.545379	2.193692
H	-3.856672	-1.120241	2.285844
C	-4.668466	0.384200	0.278060
H	-5.063233	1.196738	-0.349160
H	-5.482962	-0.326642	0.480792
H	-4.340169	0.822580	1.231633
C	-3.983334	-0.879839	-1.772479
H	-4.659609	-1.729813	-1.592337
H	-4.535233	-0.117613	-2.342329
H	-3.142167	-1.220059	-2.389047

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Structure: TS_RBpin

Charge = 0, Multiplicity = 1

Final SCF Energy = -950.948327397 Hartree

Gibbs Free Energy = -950.601130 Hartree

Thermal Correction = 0.347197 Hartree

Imaginary Frequencies = -490.21 cm^-1

Cartesian Coordinates (Angstrom):

O	1.441122	-0.493124	-1.070026
O	1.721339	-0.049259	1.193079
B	0.875794	0.163436	0.077687
C	0.680108	1.851535	-0.288818
C	1.209360	2.762693	0.526381
H	1.731522	2.396098	1.415802
C	-0.108794	1.809036	-1.458174
H	0.383139	1.554428	-2.405814

C	-1.489865	1.612381	-1.333249
H	-2.097576	1.497305	-2.235726
H	-1.990179	2.095225	-0.489053
C	1.174074	4.248864	0.308710
H	2.193441	4.654820	0.183470
H	0.585227	4.519905	-0.580327
H	0.741142	4.762312	1.184861
C	-2.835769	-0.399170	-0.114533
C	-3.812693	-0.813191	-1.031823
C	-5.134683	-0.990170	-0.621623
C	-5.490186	-0.754444	0.710114
C	-4.517544	-0.345300	1.629058
C	-3.195434	-0.167045	1.221390
H	-3.531416	-1.002090	-2.071728
H	-5.889197	-1.317122	-1.340915
H	-6.524590	-0.894002	1.032998
H	-4.792130	-0.168328	2.671723
H	-2.423095	0.140901	1.928006
C	-1.433281	-0.201137	-0.565440
O	-0.516369	-0.204198	0.375950
H	-1.160418	-0.727971	-1.492497
C	2.914897	-0.690137	0.730821
C	2.422972	-1.412649	-0.580756
C	1.729526	-2.749723	-0.285224
H	1.217954	-3.089203	-1.198640
H	2.445069	-3.528617	0.018766
H	0.975704	-2.636962	0.506951
C	3.494967	-1.606097	-1.647064
H	4.324502	-2.223228	-1.267209
H	3.061796	-2.117734	-2.520275
H	3.897622	-0.643114	-1.986814
C	3.970264	0.384787	0.442167
H	4.112427	0.992946	1.348088
H	4.940417	-0.055979	0.167503
H	3.642543	1.051818	-0.367154
C	3.416550	-1.628780	1.823719
H	4.275888	-2.221315	1.471635
H	3.740352	-1.040523	2.695725
H	2.625337	-2.312803	2.156237

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Structure: IM2_RBpin

Charge = 0, Multiplicity = 1

Final SCF Energy = -951.008075915 Hartree

Gibbs Free Energy = -950.661860 Hartree

Thermal Correction = 0.346216 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	1.114811	-0.970859	-0.895136
O	1.556431	-0.854386	1.354799
B	0.639666	-0.652736	0.356739
C	0.814047	2.798397	-0.363788
C	1.569780	3.555225	0.396096
H	2.189563	3.060123	1.156627
C	0.037605	2.053826	-1.115374
H	0.439552	1.646767	-2.052749
C	-1.366245	1.644036	-0.744853
H	-2.063793	1.893580	-1.562120
H	-1.698474	2.186574	0.152882
C	1.658932	5.057892	0.318046
H	2.692874	5.379949	0.105680
H	1.003084	5.459717	-0.467543
H	1.371523	5.517341	1.279194
C	-2.904615	-0.254291	-0.119221
C	-3.840373	-0.452263	-1.143620
C	-5.170918	-0.752083	-0.844232
C	-5.580242	-0.861731	0.488050
C	-4.650483	-0.670857	1.513818
C	-3.320006	-0.367205	1.213263
H	-3.522015	-0.377199	-2.187681
H	-5.888902	-0.907903	-1.653254
H	-6.619841	-1.100584	0.725122
H	-4.962567	-0.760911	2.557405
H	-2.587082	-0.226563	2.008781
C	-1.482541	0.129770	-0.465749
O	-0.613514	-0.205930	0.605045
H	-1.175037	-0.418815	-1.372222
C	2.827652	-1.104955	0.714346

C	2.389805	-1.627226	-0.711188
C	2.127677	-3.134593	-0.740129
H	1.622873	-3.388457	-1.683681
H	3.061553	-3.712235	-0.678349
H	1.472448	-3.439087	0.089019
C	3.317287	-1.228666	-1.851239
H	4.327648	-1.636290	-1.692857
H	2.931545	-1.630891	-2.799903
H	3.388235	-0.138102	-1.949750
C	3.569930	0.232294	0.651673
H	3.646573	0.639410	1.670529
H	4.585548	0.117412	0.245584
H	3.023382	0.959484	0.034841
C	3.611982	-2.108345	1.548876
H	4.548135	-2.389826	1.042229
H	3.869647	-1.659024	2.519358
H	3.027719	-3.016736	1.742848

****

Structure: RB(OH)2

Charge = 0, Multiplicity = 1

Final SCF Energy = -371.081123620 Hartree

Gibbs Free Energy = -370.979098 Hartree

Thermal Correction = 0.102026 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

C	-1.341291	-0.843719	-0.000050
H	-1.080674	-1.907496	-0.000058
C	-0.305077	0.038699	-0.000006
C	-0.545931	1.490574	-0.000000
H	-1.598522	1.793357	-0.000064
C	0.361819	2.481837	0.000121
H	1.434607	2.289463	0.000197
H	0.032377	3.524627	0.000118
B	1.135492	-0.596598	-0.000020
O	1.229672	-1.966599	0.000165
H	2.126352	-2.319149	0.000121
O	2.249349	0.203411	-0.000184
H	3.091687	-0.266326	-0.000157

C	-2.813483	-0.573327	-0.000035
H	-3.287383	-1.041322	-0.881404
H	-3.287339	-1.041131	0.881461
H	-3.076950	0.492088	-0.000144

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Structure: IM1_RB(OH)2

Charge = 0, Multiplicity = 1

Final SCF Energy = -716.446668001 Hartree

Gibbs Free Energy = -716.245558 Hartree

Thermal Correction = 0.201110 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	-2.303491	-1.970739	1.091133
O	-3.336599	-1.610778	-0.980121
B	-2.654571	-1.103790	0.091171
C	-2.322190	0.424288	0.295196
C	-2.943285	1.356761	-0.463399
H	-3.654022	0.996910	-1.221075
C	-1.356060	0.752162	1.362677
H	-1.487095	0.191906	2.296507
C	-0.308253	1.583678	1.261436
H	0.379495	1.736009	2.097709
H	-0.078727	2.110382	0.331118
C	-2.833185	2.848709	-0.388025
H	-3.830088	3.315637	-0.456405
H	-2.343813	3.182296	0.537532
H	-2.246642	3.245062	-1.236934
C	1.933561	-0.605010	-0.169388
C	2.696420	-0.648612	1.005817
C	3.964604	-0.067091	1.040011
C	4.471174	0.559552	-0.103125
C	3.712252	0.604780	-1.280398
C	2.446838	0.024143	-1.314706
H	2.284193	-1.135105	1.894345
H	4.559210	-0.098942	1.955865
H	5.463535	1.016595	-0.077943
H	4.114676	1.096221	-2.169414
H	1.829222	0.044436	-2.214998

C	0.582873	-1.211544	-0.193364
O	-0.146124	-1.214621	-1.163491
H	0.253638	-1.679396	0.764078
H	-3.406762	-0.986836	-1.711238
H	-2.542740	-2.878006	0.858428

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Structure: TS_RB(OH)2

Charge = 0, Multiplicity = 1

Final SCF Energy = -716.413899453 Hartree

Gibbs Free Energy = -716.206221 Hartree

Thermal Correction = 0.207678 Hartree

Imaginary Frequencies = -479.43 cm^-1

Cartesian Coordinates (Angstrom):

O	2.036100	-2.084680	-0.773926
O	2.351572	-1.509653	1.575266
B	1.775982	-1.187708	0.323172
C	2.298518	0.375970	-0.228340
C	3.101047	1.123829	0.528720
H	3.395931	0.718681	1.502499
C	1.601109	0.505659	-1.448327
H	1.979547	-0.035864	-2.324261
C	0.256583	0.896794	-1.418322
H	-0.313237	0.924850	-2.351904
H	-0.031393	1.640113	-0.669358
C	3.651153	2.470293	0.152211
H	4.752082	2.442185	0.068884
H	3.244938	2.825236	-0.806737
H	3.418115	3.218708	0.929637
C	-1.834439	-0.237980	-0.115639
C	-2.862357	-0.331562	-1.065301
C	-4.154583	0.089773	-0.749171
C	-4.429071	0.608010	0.520327
C	-3.407159	0.699086	1.471824
C	-2.114341	0.279536	1.157898
H	-2.646431	-0.741867	-2.055896
H	-4.951046	0.009881	-1.492731
H	-5.440697	0.936933	0.769730
H	-3.621835	1.096591	2.466712

H	-1.308248	0.333876	1.891307
C	-0.457656	-0.674092	-0.467657
O	0.345702	-0.925309	0.541529
H	-0.388392	-1.372612	-1.315603
H	3.279639	-1.737844	1.453681
H	1.991295	-2.995097	-0.454104

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Structure: IM2_RB(OH)2

Charge = 0, Multiplicity = 1

Final SCF Energy = -716.472239628 Hartree

Gibbs Free Energy = -716.265833 Hartree

Thermal Correction = 0.206407 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	-1.291925	2.342393	-1.153102
O	-2.073440	2.137493	1.141395
B	-1.222490	1.812292	0.114095
C	-2.719775	-0.914317	-0.430223
C	-3.703062	-0.926928	0.437270
H	-3.890122	0.004571	0.990167
C	-1.705619	-0.887542	-1.264076
H	-1.880704	-0.589534	-2.306640
C	-0.274284	-1.114453	-0.843674
H	0.274368	-1.677118	-1.615918
H	-0.237326	-1.698048	0.088283
C	-4.577238	-2.110774	0.759622
H	-5.638836	-1.882603	0.562186
H	-4.297209	-2.992512	0.165494
H	-4.500127	-2.373149	1.828611
C	1.897413	-0.026928	-0.158875
C	2.873694	-0.319596	-1.120997
C	4.185747	-0.607311	-0.739562
C	4.538031	-0.601283	0.613450
C	3.570318	-0.304675	1.577068
C	2.256676	-0.020309	1.194460
H	2.604877	-0.315628	-2.181570
H	4.937423	-0.829908	-1.501027
H	5.565053	-0.821979	0.914456

H	3.840247	-0.292472	2.636170
H	1.497574	0.221093	1.939519
C	0.468209	0.222100	-0.589775
O	-0.226230	0.935351	0.414212
H	0.474186	0.804231	-1.526454
H	-2.711429	2.827234	0.933121
H	-2.053416	2.904582	-1.325043

****

Structure: boroxine

Charge = 0, Multiplicity = 1

Final SCF Energy = -884.144655765 Hartree

Gibbs Free Energy = -883.860309 Hartree

Thermal Correction = 0.284347 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	-0.583980	-1.162846	-0.052803
O	-0.645764	1.205362	-0.021952
B	-1.320096	0.004844	-0.066447
C	-2.874773	-0.055285	-0.139287
C	-3.550533	1.117811	-0.244258
H	-2.942696	2.029923	-0.224051
C	-3.504544	-1.391150	-0.140106
H	-2.946519	-2.166533	-0.678609
C	-4.631215	-1.754355	0.491168
H	-4.998681	-2.782874	0.439585
H	-5.205864	-1.054825	1.103966
C	-5.020360	1.328976	-0.419643
H	-5.210667	2.152555	-1.127262
H	-5.534219	0.422342	-0.769798
H	-5.491125	1.627530	0.535219
B	0.735188	1.263054	0.000766
O	1.425625	0.072698	0.003723
C	1.455849	2.649679	0.053431
C	0.665718	3.714994	0.359170
H	-0.400309	3.509177	0.505774
C	2.902194	2.801255	-0.172378
H	3.327755	3.778235	0.080715
C	3.745927	1.884161	-0.674533

H	3.415319	0.886076	-0.964171
H	4.803636	2.123370	-0.812632
C	1.047100	5.152090	0.520194
H	0.747349	5.519717	1.517442
H	2.118959	5.348530	0.389469
H	0.497221	5.773451	-0.209258
B	0.793075	-1.157649	-0.002184
C	1.644710	-2.466771	0.038484
C	2.994776	-2.288403	0.074432
C	1.048165	-3.812839	0.028667
H	3.353311	-1.253738	0.087251
C	4.078676	-3.317412	0.116853
H	1.753296	-4.642737	-0.088003
C	-0.249429	-4.137738	0.157402
H	4.686934	-3.188168	1.029894
H	3.716986	-4.353284	0.095143
H	4.772797	-3.175733	-0.730421
H	-1.030189	-3.388609	0.288835
H	-0.554766	-5.187452	0.140924

****

Structure: IM1_boroxine

Charge = 0, Multiplicity = 1

Final SCF Energy = -1229.51170275 Hartree

Gibbs Free Energy = -1229.130348 Hartree

Thermal Correction = 0.381355 Hartree

Imaginary Frequencies = none

Cartesian Coordinates (Angstrom):

O	0.521015	0.546847	1.415912
O	1.599269	-1.415871	0.622923
B	0.527247	-0.827115	1.251706
C	-0.663667	-1.671343	1.799557
C	-0.588294	-3.022137	1.732764
H	0.325866	-3.435900	1.290791
C	-1.826747	-0.928236	2.327087
H	-1.593646	-0.109048	3.018848
C	-3.107265	-1.111492	1.973570
H	-3.906490	-0.490110	2.386788
H	-3.397442	-1.865568	1.236737

C	-1.586034	-4.029195	2.210201
H	-1.083009	-4.833723	2.773064
H	-2.367143	-3.581977	2.840389
H	-2.084313	-4.519903	1.354185
C	-3.099918	0.284801	-1.213235
C	-4.111223	1.139273	-0.751238
C	-5.424373	0.970140	-1.191668
C	-5.726471	-0.055466	-2.093542
C	-4.718200	-0.911220	-2.557885
C	-3.407012	-0.742171	-2.120197
H	-3.858921	1.930624	-0.039937
H	-6.214321	1.633669	-0.832571
H	-6.754830	-0.190649	-2.437819
H	-4.963099	-1.709822	-3.262132
H	-2.598638	-1.393216	-2.459290
C	-1.717083	0.459863	-0.722408
O	-0.777251	-0.229767	-1.068200
H	-1.578255	1.283032	0.015260
B	2.565957	-0.654853	-0.000793
O	2.436315	0.715451	0.044236
C	3.748083	-1.356429	-0.748688
C	3.585317	-2.685859	-0.989430
H	2.663819	-3.142140	-0.611659
C	4.944237	-0.630887	-1.204255
H	5.622506	-1.187959	-1.859655
C	5.303572	0.625018	-0.888861
H	4.697914	1.257593	-0.238992
H	6.231852	1.048593	-1.281499
C	4.497209	-3.631074	-1.705415
H	3.969428	-4.106969	-2.550839
H	5.412588	-3.164747	-2.091985
H	4.794673	-4.454750	-1.031862
B	1.393906	1.335605	0.703968
C	1.230769	2.889184	0.598438
C	2.139002	3.522133	-0.194978
C	0.153576	3.633411	1.269984
H	2.895685	2.889564	-0.671213
C	2.254034	4.976000	-0.525099
H	0.131401	4.711609	1.078439

C	-0.802322	3.147727	2.082318
H	2.182786	5.124101	-1.617373
H	1.497855	5.609969	-0.044564
H	3.250802	5.352667	-0.234414
H	-0.863524	2.090676	2.339721
H	-1.546996	3.820666	2.516101

****

Structure: TS_boroxine

Charge = 0, Multiplicity = 1

Final SCF Energy = -1229.48966547 Hartree

Gibbs Free Energy = -1229.101122 Hartree

Thermal Correction = 0.388544 Hartree

Imaginary Frequencies = -480.02 cm^-1

Cartesian Coordinates (Angstrom):

O	0.399556	1.080077	0.196903
O	0.752273	-1.293954	-0.085898
B	-0.121504	-0.260090	0.332583
C	-0.574310	-0.518720	1.991068
C	-0.147954	-1.599886	2.644566
H	0.472717	-2.312409	2.091263
C	-1.402588	0.594827	2.246904
H	-0.930772	1.567717	2.435398
C	-2.733824	0.558920	1.813128
H	-3.361586	1.446682	1.933365
H	-3.254765	-0.400445	1.875658
C	-0.422446	-1.908334	4.088540
H	0.514343	-1.925806	4.672676
H	-1.098726	-1.170847	4.545957
H	-0.872606	-2.910592	4.194503
C	-3.719181	0.147820	-0.674444
C	-4.664627	1.162373	-0.884481
C	-5.927805	0.853196	-1.390179
C	-6.254406	-0.473118	-1.689544
C	-5.312157	-1.487284	-1.485034
C	-4.049149	-1.181383	-0.978475
H	-4.404398	2.199651	-0.655552
H	-6.657836	1.648689	-1.556195
H	-7.242588	-0.716262	-2.087034

H	-5.563766	-2.522708	-1.726382
H	-3.300129	-1.959533	-0.823251
C	-2.381981	0.488495	-0.124099
O	-1.431199	-0.396834	-0.321928
H	-2.085958	1.541254	-0.240818
B	2.065859	-1.063149	-0.362921
O	2.533836	0.237485	-0.362027
C	3.013027	-2.273647	-0.701796
C	2.389729	-3.458581	-0.943061
H	1.297505	-3.459783	-0.854307
C	4.476276	-2.146468	-0.783117
H	5.012470	-3.015352	-1.180992
C	5.225293	-1.096291	-0.404708
H	4.783230	-0.188653	0.007246
H	6.313962	-1.131663	-0.501329
C	2.986885	-4.780346	-1.313508
H	2.560469	-5.142082	-2.266108
H	4.080150	-4.766250	-1.412924
H	2.726489	-5.542562	-0.557075
B	1.694992	1.317442	-0.132877
C	2.287344	2.769406	-0.263582
C	3.559884	2.851807	-0.739546
C	1.531121	3.978787	0.095871
H	4.050332	1.903625	-0.984584
C	4.399791	4.064238	-0.992050
H	2.071351	4.926554	-0.005242
C	0.262177	4.058208	0.534180
H	4.701075	4.103826	-2.054070
H	3.908501	5.014118	-0.744039
H	5.339310	4.003837	-0.414281
H	-0.356896	3.170000	0.658484
H	-0.180941	5.029670	0.769527

****

Structure: IM2_boroxine

Charge = 0, Multiplicity = 1

Final SCF Energy = -1229.54315307 Hartree

Gibbs Free Energy = -1229.155153 Hartree

Thermal Correction = 0.388000 Hartree

Imaginary Frequencies = none

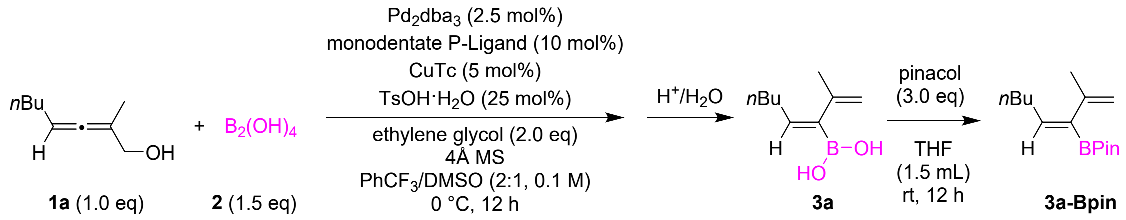
Cartesian Coordinates (Angstrom):

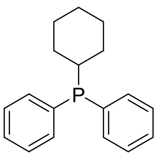
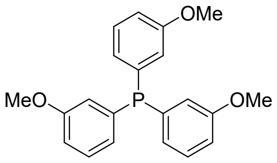
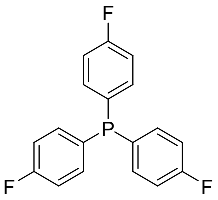
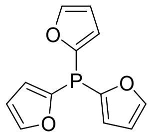
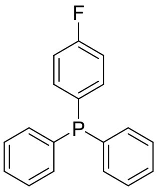
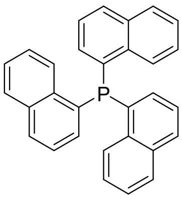
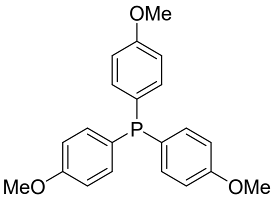
O	0.136508	1.118422	-0.433564
O	0.693202	-1.166533	-0.817671
B	-0.252949	-0.202725	-0.561484
C	-0.168720	-0.786841	2.463182
C	0.693266	-1.760359	2.634501
H	1.310207	-2.055110	1.773859
C	-1.049285	0.171054	2.278021
H	-0.745237	1.211227	2.456786
C	-2.431010	-0.055092	1.713149
H	-3.169719	0.580776	2.226770
H	-2.734576	-1.103239	1.853139
C	0.906856	-2.524404	3.915360
H	1.949364	-2.420906	4.261421
H	0.239303	-2.169986	4.713651
H	0.725757	-3.601737	3.761382
C	-3.884194	-0.002380	-0.352441
C	-4.869788	0.986882	-0.236914
C	-6.171974	0.748612	-0.681449
C	-6.501102	-0.484106	-1.252541
C	-5.520630	-1.472555	-1.375458
C	-4.219133	-1.235112	-0.926253
H	-4.613168	1.956561	0.199815
H	-6.929938	1.530302	-0.588983
H	-7.518006	-0.671322	-1.605762
H	-5.770257	-2.436150	-1.826702
H	-3.447479	-1.999517	-1.027303
C	-2.499348	0.254359	0.195972
O	-1.551720	-0.568014	-0.467645
H	-2.244305	1.314892	0.036572
B	2.038179	-0.862097	-0.779050
O	2.395109	0.455909	-0.595283
C	3.093578	-2.005840	-0.932489
C	2.589457	-3.232276	-1.243672
H	1.500562	-3.303807	-1.339667
C	4.540317	-1.786445	-0.771631
H	5.185782	-2.614985	-1.082598
C	5.150997	-0.698734	-0.272002

H	4.595507	0.173434	0.073473
H	6.240985	-0.667531	-0.192860
C	3.318915	-4.517981	-1.468774
H	3.084989	-4.919799	-2.470524
H	4.409619	-4.438184	-1.376290
H	2.971563	-5.280993	-0.749454
B	1.466466	1.467001	-0.427440
C	1.957488	2.940213	-0.246360
C	3.270561	3.160399	-0.533671
C	1.074683	4.031299	0.194459
H	3.856067	2.290110	-0.849128
C	4.044098	4.439253	-0.487362
H	1.537088	5.021968	0.256649
C	-0.221337	3.949333	0.541125
H	4.485017	4.653498	-1.476961
H	3.453979	5.312240	-0.180648
H	4.896640	4.341017	0.208098
H	-0.772397	3.009989	0.506162
H	-0.762785	4.842402	0.863751

4. Optimization of Phosphine Ligands

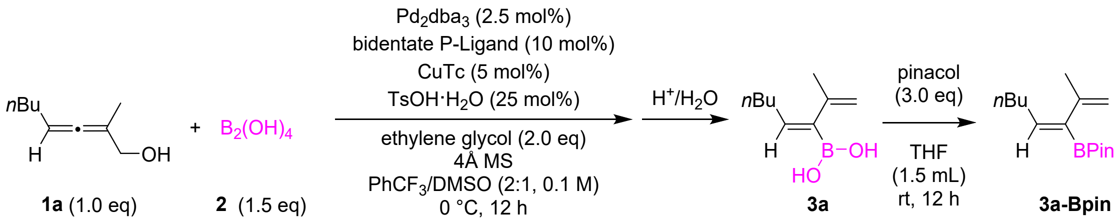
Table S1. Detailed optimization of monodentate P-ligand[a]

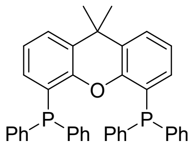
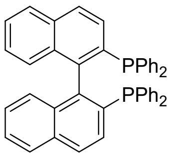
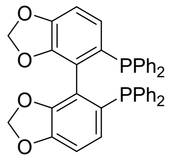
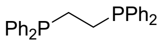
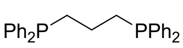


entry	mono P-Ligand	Yield[b]	entry	mono P-Ligand	Yield[b]
1		trace	5		trace
2		trace	6		trace
3		trace	7		trace
4		trace			

[a] General reaction condition: a mixture of **1a** (0.3 mmol, 1.0 equiv), $B_2(OH)_4$ (**2**, 0.45 mmol, 1.5 equiv), Pd_2dba_3 (2.5 mol%), CuTc (5 mol%), monodentate P-Ligand (10 mol%), TsOH·H_2O (25 mol%), ethylene glycol (2.0 equiv), and 4 Å MS in a mixed solution of $PhCF_3$ (2 mL) / DMSO (1 mL) was reacted at 0 °C for 12 h under Ar. Then, the reaction mixture was quenched by aqueous HCl (0.5 M, 1.5 mL), followed by addition of pinacol (3.0 equiv) and THF (1.5 mL). The resulting solution was further stirred at rt for 12 h. [b] The yields of **3a-Bpin** were determined by crude ^1H NMR spectrum with naphthalene as an internal standard.

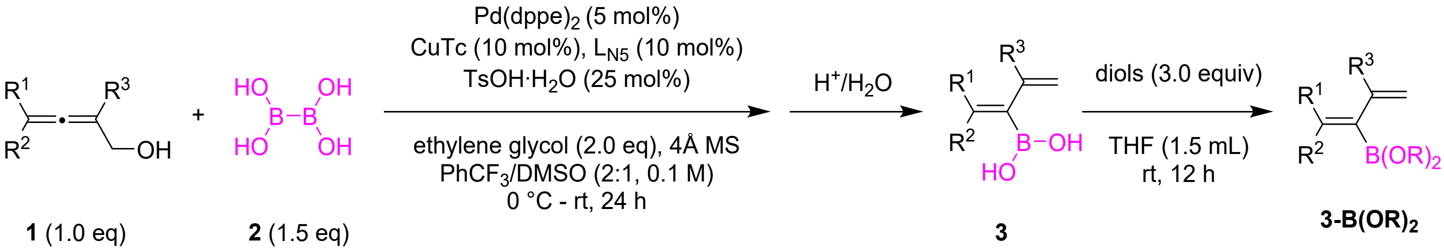
Table S2. Detailed optimization of bidentate P-ligand[a]



entry	bidentate P-Ligand	Yield[b]
1		trace
2		trace
3		trace
4		27%[c]
5		trace

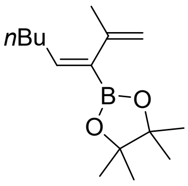
[a] General reaction condition: a mixture of **1a** (0.3 mmol, 1.0 equiv), $B_2(OH)_4$ (**2**, 0.45 mmol, 1.5 equiv), Pd_2dba_3 (2.5 mol%), CuTc (5 mol%), bidentate P-Ligand (10 mol%), TsOH·H_2O (25 mol%), ethylene glycol (2.0 equiv) and 4 Å MS in a mixed solution of $PhCF_3$ (2 mL) / DMSO (1 mL) was reacted at 0 °C for 12 h under Ar. Then, the reaction mixture was quenched by aqueous HCl (0.5 M, 1.5 mL), followed by addition of pinacol (3.0 equiv) and THF (1.5 mL). The resulting solution was further stirred at rt for 12 h. [b] The yields of **3a-Bpin** were determined by crude ^1H NMR spectrum with naphthalene as an internal standard. [c] *E*/*Z* = 1:9. The *E*/*Z* of **3a-Bpin** were determined by crude ^1H NMR spectrum.

5. Procedure A for synthesis of 1,3-dienyl-2-boronic acids 3



A Schlenk flask equipped with a Teflon coated stirrer bar was charged with 4 Å molecular sieves, $B_2(OH)_4$ (**2**, 1.5 equiv), CuTc (0.1 equiv), $Pd(dppe)_2$ (0.05 equiv), L_{N5} (4,7-dimethoxy-1,10-phenanthroline, 0.1 equiv), $TsOH{\cdot}H_2O$ (0.25 equiv) and $PhCF_3$ (2 mL) under Ar atmosphere. The reaction mixture was stirred at rt for 5 min and cooled to 0 °C for 5 min. Then, 2,3-allenol **1** (0.3 mmol), ethylene glycol (2.0 equiv), and DMSO (1 mL) were sequentially added to the reaction mixture via syringe. The reaction mixture was gradually warmed and stirred at rt. After a complete conversion of 2,3-allenol **1** (monitored by TLC), the reaction mixture was quenched with aqueous HCl (0.5 M). After that, diols (3.0 equiv) and THF (1.5 mL) were added to the reaction mixture. The resulting reaction mixture was allowed to stir at rt for 12 hours. Then, the reaction mixture was extracted with EtOAc (3×20 mL), washed with brine (3 × 20 mL), dried (with $MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography using a mixture of petroleum ether/EtOAc as eluent to yield the desired products **3-B(OR)$_2$**.

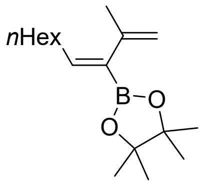
(*Z*)-4,4,5,5-Tetramethyl-2-(2-methylocta-1,3-dien-3-yl)-1,3,2-dioxaborolane (3a-Bpin)



3a-Bpin

This compound was prepared according to procedure A. Product **3a-Bpin** was isolated in 69% yield (51mg, 0.21 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (t, *J* = 7.2 Hz, 1H), 4.94 (d, *J* = 1.0 Hz, 1H), 4.56 (d, *J* = 1.5 Hz, 1H), 2.18 (dt, *J* = 7.3, 7.1 Hz, 2H), 1.82 (s, 3H), 1.38-1.30 (m, 4H), 1.26 (s, 12H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 144.8, 111.8, 83.2, 31.6, 29.4, 24.7, 23.9, 22.5, 14.0. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30. HRMS (ESI): m/z calcd. for $[C_{15}H_{27}BO_2Na]^+$ 273.2002, found 273.2010.

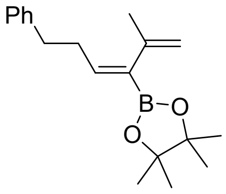
(*Z*)-4,4,5,5-Tetramethyl-2-(2-methyldeca-1,3-dien-3-yl)-1,3,2-dioxaborolane (3b-Bpin)



3b-Bpin

This compound was prepared according to procedure A. Product **3b-Bpin** was isolated in 77% yield (64 mg, 0.23 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.30 (t, *J* = 7.2 Hz, 1H), 4.94 (d, *J* = 0.8 Hz, 1H), 4.55 (d, *J* = 1.5 Hz, 1H), 2.17 (dt, *J* = 7.5, 7.3 Hz, 2H), 1.82 (s, 3H), 1.43-1.28 (m, 8H), 1.26 (s, 12H), 0.87 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.4, 144.8, 111.7, 83.2, 31.7, 29.7, 29.4, 29.2, 24.7, 23.9, 22.6, 14.1. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{17}H_{31}BO_2Na$]$^+$ 301.2315, found 301.2312.

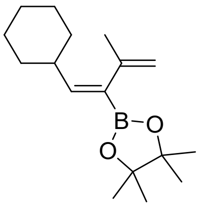
(*Z*)-4,4,5,5-Tetramethyl-2-(2-methyl-6-phenylhexa-1,3-dien-3-yl)-1,3,2-dioxaborolane (3c-Bpin)



3c-Bpin

This compound was prepared according to procedure A. Product **3c-Bpin** was isolated in 83% yield (74 mg, 0.25 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36-7.33 (m, 3H), 7.25-7.23 (m, 2H), 6.45 (t, *J* = 7.2 Hz, 1H), 5.00 (s, 1H), 4.60 (s, 1H), 2.79-2.75 (m, 2H), 2.61-2.56 (m, 2H), 1.85 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.9, 144.6, 142.0, 128.3, 128.2, 125.8, 111.9, 83.3, 35.8, 31.8, 24.7, 23.8. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{19}H_{27}BO_2Na$]$^+$ 321.2002, found 321.2006.

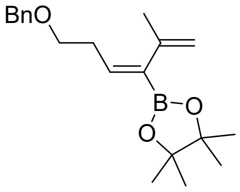
(*Z*)-2-(1-Cyclohexyl-3-methylbuta-1,3-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d-Bpin)



3d-Bpin

This compound was prepared according to procedure A. Product **3d-Bpin** was isolated in 72% yield (61 mg, 0.22 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.08 (d, *J* = 9.8 Hz, 1H), 4.91 (s, 1H), 4.55 (s, 1H), 2.48-2.40 (m, 1H), 1.83 (s, 3H), 1.29-1.07 (m, 10H), 1.26 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 151.4, 145.2, 111.3, 83.2, 38.4, 33.0, 26.0, 25.7, 24.7, 24.3. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{17}H_{29}BO_2Na$]$^+$ 299.2158, found 299.2160.

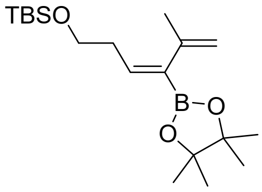
(*Z*)-2-(6-(Benzyloxy)-2-methylhexa-1,3-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e-Bpin)



3e-Bpin

This compound was prepared according to procedure A. Product **3e-Bpin** was isolated in 70% yield (69 mg, 0.21 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 to 50:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34-7.27 (m, 5H), 6.32 (t, *J* = 7.1 Hz, 1H), 4.96 (s, 1H), 4.58 (s, 1H), 4.51 (s, 2H), 3.51 (t, *J* = 7.1 Hz, 2H), 2.55 (dt, *J* = 7.1, 7.1 Hz, 2H), 1.83 (s, 3H), 1.26 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.5, 141.5, 138.5, 128.3, 127.6, 127.5, 112.1, 83.3, 72.8, 69.7, 30.3, 24.7, 23.8. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{20}H_{29}BO_3Na$]$^+$ 351.2107, found 351.2115.

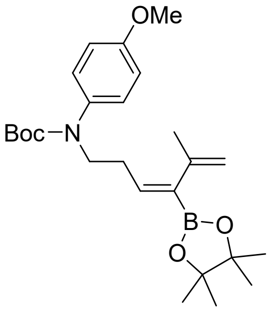
(*Z*)-Tert-butyldimethyl((5-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-3,5-dien-1-yl)oxy)silane (3f-Bpin)



3f-Bpin

This compound was prepared according to procedure A. Product **3f-Bpin** was isolated in 66% yield (71 mg, 0.20 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.29 (t, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 1.0 Hz, 1H), 4.58 (d, *J* = 1.4 Hz, 1H), 3.65 (t, *J* = 7.2 Hz, 2H), 2.44 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.83 (s, 3H), 1.26 (s, 12H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.5, 141.9, 112.0, 83.3, 62.9, 33.5, 26.0, 24.7, 23.8, 18.4, -5.3. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{19}H_{37}BO_3NaSi$]$^+$ 375.2503, found 375.2512.

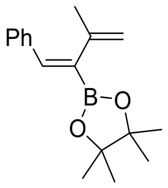
Tert-butyl (*Z*)-(4-methoxyphenyl)(5-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-3,5-dien-1-yl)carbamate (3g-Bpin)



3g-Bpin

This compound was prepared according to procedure A. Product **3g-Bpin** was isolated in 67% yield (89 mg, 0.20 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.08 (br s, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.26 (t, *J* = 7.2 Hz, 1H), 4.92 (s, 1H), 4.53 (s, 1H), 3.79 (s, 3H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.45 (dt, *J* = 7.3, 7.3 Hz, 2H), 1.80 (s, 3H), 1.44 (br s, 9H), 1.25 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 157.6, 154.9, 144.3, 142.2, 135.5, 128.4, 113.9, 112.1, 83.2, 79.9, 55.3, 49.9, 29.0, 28.3, 24.6, 23.7. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{25}H_{38}BNO_5Na$]$^+$ 466.2741, found 466.2751.

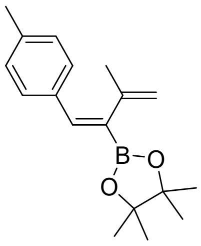
(*Z*)-4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylbuta-1,3-dien-2-yl)-1,3,2-dioxaborolane (3h-Bpin)



3h-Bpin

This compound was prepared according to procedure A. Product **3h-Bpin** was isolated in 63% yield (51 mg, 0.19 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.32-7.28 (m, 2H), 7.23-7.20 (m, 1H), 7.10 (s, 1H), 5.00 (s, 1H), 4.78 (s, 1H), 1.91 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.0, 141.2, 137.3, 129.5, 128.0, 127.7, 112.9, 83.6, 24.7, 22.9. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for $[C_{17}H_{23}BO_2Na]^+$ 293.1689, found 293.1687.

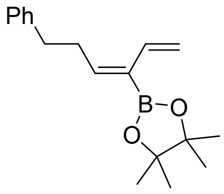
(*Z*)-4,4,5,5-Tetramethyl-2-(3-methyl-1-(p-tolyl)buta-1,3-dien-2-yl)-1,3,2-dioxaborolane (3i-Bpin)



3i-Bpin

This compound was prepared according to procedure A. Product **3i-Bpin** was isolated in 61% yield (52 mg, 0.18 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.10-7.07 (m, 3H), 5.01 (s, 1H), 4.78 (s, 1H), 2.32 (s, 3H), 1.91 (s, 3H), 1.30 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.2, 141.1, 137.7, 134.5, 129.5, 128.7, 112.7, 83.5, 24.7, 22.9, 21.3. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for $[C_{18}H_{25}BO_2Na]^+$ 307.1845, found 307.1850.

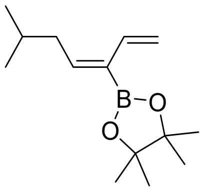
(*Z*)-4,4,5,5-Tetramethyl-2-(6-phenylhexa-1,3-dien-3-yl)-1,3,2-dioxaborolane (3j-Bpin)



3j-Bpin

This compound was prepared according to procedure A. Product **3j-Bpin** was isolated in 75% yield (64 mg, 0.22 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30-7.27 (m, 2H), 7.21-7.17 (m, 3H), 6.68 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.39 (t, *J* = 7.1 Hz, 1H), 5.68 (dd, *J* = 17.5, 2.2 Hz, 1H), 5.18 (dt, *J* = 11.1, 1.7 Hz, 1H), 2.75-2.69 (m, 2H), 2.63-2.55 (m, 2H), 1.29 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.5, 141.8, 133.6, 128.3, 128.2, 125.9, 118.0, 83.2, 35.3, 30.8, 24.8. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 31. HRMS (ESI): m/z calcd. for [$C_{18}H_{25}BO_2Na$]$^+$ 307.1845, found 307.1851. This compound was reported in previous literature[6].

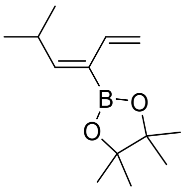
(*Z*)-4,4,5,5-Tetramethyl-2-(6-methylhepta-1,3-dien-3-yl)-1,3,2-dioxaborolane (3k-Bpin)



3k-Bpin

This compound was prepared according to procedure A. Product **3k-Bpin** was isolated in 63% yield (45 mg, 0.19 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.69 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.34 (t, *J* = 7.5 Hz, 1H), 5.67 (dd, *J* = 17.5, 2.3 Hz, 1H), 5.16 (dt, *J* = 11.1, 1.6 Hz, 1H), 2.15 (t, *J* = 7.2 Hz, 2H), 1.78-1.68 (m, 1H), 1.29 (s, 12H), 0.91 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.1, 134.0, 117.4, 83.1, 37.8, 28.5, 24.8, 22.6. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for [$C_{14}H_{25}BO_2Na$]$^+$ 259.1845, found 259.1849. This compound was reported in previous literature[6].

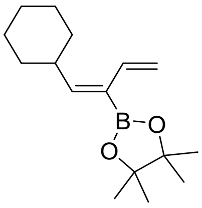
(Z)-4,4,5,5-Tetramethyl-2-(5-methylhexa-1,3-dien-3-yl)-1,3,2-dioxaborolane (3l-Bpin)



3l-Bpin

This compound was prepared according to procedure A. Product **3l-Bpin** was isolated in 45% yield (30 mg, 0.14 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (dd, J = 17.4, 11.0 Hz, 1H), 6.12 (d, J = 9.4 Hz, 1H), 5.66 (ddd, J = 17.5, 2.2, 0.4 Hz, 1H), 5.15 (ddd, J = 11.0, 2.2, 1.6 Hz, 1H), 2.93-2.83 (m, 1H), 1.29 (s, 12H), 1.00 (d, J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 133.8, 117.5, 83.1, 27.5, 24.8, 22.5. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31. HRMS (ESI): m/z calcd. for $[C_{13}H_{24}BO_2]^+$ 223.1864, found 223.1860.

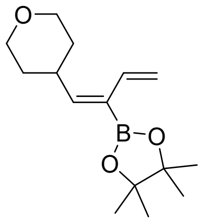
(Z)-2-(1-Cyclohexylbuta-1,3-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m-Bpin)



3m-Bpin

This compound was prepared according to procedure A. Product **3m-Bpin** was isolated in 65% yield (51 mg, 0.19 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (dd, J = 17.5, 11.0 Hz, 1H), 6.13 (d, J = 9.3 Hz, 1H), 5.66 (dd, J = 17.5, 2.3 Hz, 1H), 5.15 (dt, J = 11.0, 1.7 Hz, 1H), 2.58-2.50 (m, 1H), 1.74-1.64 (m, 6H), 1.28 (s, 12H), 1.21-1.08 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 134.0, 117.4, 83.1, 37.5, 32.5, 26.0, 25.8, 24.8. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31. HRMS (ESI): m/z calcd. for $[C_{16}H_{27}BO_2Na]^+$ 285.2002, found 285.1995. This compound was reported in previous literature[6].

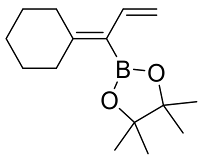
(*Z*)-4,4,5,5-Tetramethyl-2-(1-(tetrahydro-2*H*-pyran-4-yl)buta-1,3-dien-2-yl)-1,3,2-dioxaborolane (3n-Bpin)



3n-Bpin

This compound was prepared according to procedure A. Product **3n-Bpin** was isolated in 68% yield (54 mg, 0.20 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.69 (dd, *J* = 17.4, 11.1 Hz, 1H), 6.10 (d, *J* = 9.1 Hz, 1H), 5.69 (dd, *J* = 17.5, 1.6 Hz, 1H), 5.19 (d, *J* = 11.0 Hz, 1H), 3.96 (d, *J* = 11.3 Hz, 2H), 3.44 (td, *J* = 11.1, 3.8 Hz, 2H), 2.85-2.77 (m, 1H), 1.55-1.51 (m, 4H), 1.29 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.4, 133.5, 118.3, 83.3, 67.5, 34.6, 32.1, 24.7. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30. HRMS (ESI): m/z calcd. for $[C_{15}H_{26}BO_3]^+$ 265.1969, found 265.1965.

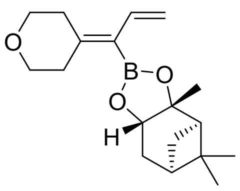
2-(1-Cyclohexylideneallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o-Bpin)



3o-Bpin

This compound was prepared according to procedure A. Product **3o-Bpin** was isolated in 70% yield (52.1 mg, 0.21 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.77 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.17 (dd, *J* = 17.6, 1.5 Hz, 1H), 5.01 (dd, *J* = 10.9, 1.5 Hz, 1H), 2.34-2.28 (m, 4H), 1.62-1.56 (m, 6H), 1.33 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 153.5, 135.6, 114.6, 83.4, 36.3, 30.4, 28.6, 27.9, 26.8, 24.9. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 31. HRMS (ESI): m/z calcd. for $[C_{15}H_{26}BO_2]^+$ 249.2026, found 249.2022. This compound was reported in previous literature[6].

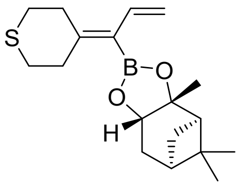
(3aR,4R,6R,7aS)-3a,5,5-Trimethyl-2-(1-(tetrahydro-4*H*-pyran-4-ylidene)allyl)hexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (3p-B(pinanediol))



3p-B(pinanediol)

This compound was prepared according to procedure A. Product **3p-B(pinanediol)** was isolated in 71% yield (64 mg, 0.21 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (80:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.31 (d, *J* = 17.5 Hz, 1H), 5.11 (d, *J* = 10.9 Hz, 1H), 4.38 (dd, *J* = 9.1, 1.7 Hz, 1H), 3.77-3.67 (m, 4H), 2.58-2.47 (m, 4H), 2.42-2.37 (m, 1H), 2.28-2.23 (m, 1H), 2.11 (t, *J* = 5.3 Hz, 1H), 1.96-1.89 (m, 2H), 1.44 (s, 3H), 1.30 (s, 3H), 1.23 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 134.9, 116.2, 85.9, 77.7, 69.2, 68.6, 51.2, 39.5, 38.2, 36.2, 35.5, 31.4, 28.8, 27.0, 26.7, 24.1. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30. HRMS (ESI): m/z calcd. for $[C_{18}H_{27}BO_3Na]^+$ 325.1951, found 325.1956.

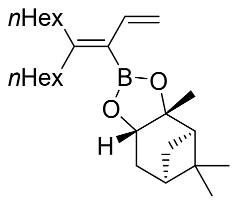
(3aR,4R,6R,7aS)-3a,5,5-Trimethyl-2-(1-(tetrahydro-4*H*-thiopyran-4-ylidene)allyl)hexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (3q-B(pinanediol))



3q-B(pinanediol)

This compound was prepared according to procedure A. Product **3q-B(pinanediol)** was isolated in 79% yield (76 mg, 0.24 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (80:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.27 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.12 (dd, *J* = 10.9, 1.4 Hz, 1H), 4.40 (dd, *J* = 9.0, 2.1 Hz, 1H), 2.76-2.66 (m, 8H), 2.43-2.37 (m, 1H), 2.29-2.24 (m, 1H), 2.12 (t, *J* = 5.3 Hz, 1H), 1.97-1.89 (m, 2H), 1.45 (s, 3H), 1.31 (s, 3H), 1.24 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 134.8, 116.5, 86.0, 77.8, 51.2, 39.5, 38.2, 38.1, 35.6, 32.5, 31.1, 30.4, 28.8, 27.0, 26.8, 24.1. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30. HRMS (ESI): m/z calcd. for $[C_{18}H_{27}BO_2NaS]^+$ 341.1723, found 341.1728.

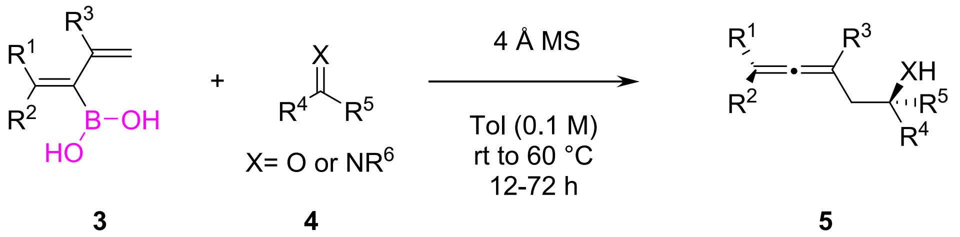
(3aR,4R,6R,7aS)-2-(4-Hexyldeca-1,3-dien-3-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (3r-B(pinanediol))



3r-B(pinanediol)

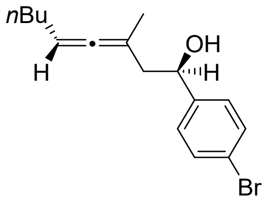
This compound was prepared according to procedure A. Product **3r-B(pinanediol)** was isolated in 70% yield (84 mg, 0.21 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.71 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.21 (dd, *J* = 17.6, 1.6 Hz, 1H), 5.03 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.38 (dd, *J* = 9.2, 2.0 Hz, 1H), 2.42-2.36 (m, 1H), 2.27-2.15 (m, 5H), 2.12 (t, *J* = 5.2 Hz, 1H), 1.96-1.90 (m, 2H), 1.45 (s, 3H), 1.42-1.37 (m, 4H), 1.32-1.27 (m, 16H), 0.89-0.86 (m, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 155.2, 136.4, 114.5, 85.7, 77.6, 51.1, 39.5, 38.2, 37.9, 35.6, 32.2, 31.8, 31.7, 29.7, 29.6, 29.5, 29.0, 28.9, 27.1, 26.8, 24.1, 22.6, 22.5, 14.1. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 31. HRMS (ESI): m/z calcd. for $[C_{26}H_{45}BO_2Na]^+$ 423.3410, found 423.3417.

6. Procedure B for synthesis of homoallenyl alcohols or amines 5



A Schlenk flask equipped with a Teflon coated stirrer bar was charged with 4Å molecular sieve, carbonyls or imines (**4**, 2.0 equiv) under Ar atmosphere. Then, a solution of 1,3-dienyl-2-boronic acid **3** (0.15 mmol, *ca.* 0.1 M in toluene) was added to the Schlenk flask via syringe at rt. The reaction mixture was allowed to stir at rt (or elevated temperature) until reaction completion (monitored by TLC). After a complete conversion of 1,3-dienyl-2-boronic acid **3**, the reaction mixture was diluted with petroleum ether/EtOAc (1:1 v/v). The precipitate was filtered off through a short silica pad using EtOAc as an eluent. Then, the solvent was removed in vacuo and the residue was purified by a rapid silica gel chromatography using a mixture of petroleum ether/EtOAc as eluent to yield the desired products **5**.

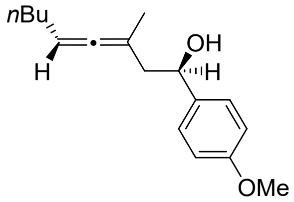
1-(4-Bromophenyl)-3-methylnona-3,4-dien-1-ol (5aa)



5aa

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5aa** was isolated in 87% yield (40 mg, 0.13 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.30 (d, *J* = 4.4 Hz, 1H), 4.87-4.80 (m, 1H), 4.60 (dd, *J* = 11.5, 6.6 Hz, 1H), 2.31 (ddd, *J* = 13.6, 6.2, 2.2 Hz, 1H), 2.16 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.69-1.55 (m, 5H), 1.25-1.04 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 202.5, 145.0, 130.7, 128.4, 119.7, 95.1, 89.2, 70.6, 44.3, 30.8, 28.2, 21.6, 19.0, 13.8. HRMS (ESI): m/z calcd. for $[C_{16}H_{21}ONaBr]^+$ 331.0673, found 331.0674. This compound was reported in previous literature[7].

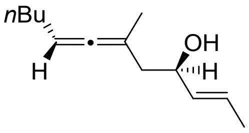
1-(4-Methoxyphenyl)-3-methylnona-3,4-dien-1-ol (5ab)



5ab

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5ab** was isolated in 90% yield (35.2 mg, 0.14 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.12-5.06 (m, 1H), 4.78 (dd, *J* = 8.9, 4.3 Hz, 1H), 3.80 (s, 3H), 2.41-2.28 (m, 2H), 1.96-1.92 (m, 2H), 1.71 (d, *J* = 2.8 Hz, 3H), 1.37-1.31 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.0, 159.0, 136.2, 127.1, 113.7, 96.1, 91.2, 71.8, 55.3, 44.5, 31.4, 28.9, 22.2, 19.5, 13.9. HRMS (ESI): m/z calcd. for [$C_{17}H_{24}O_2Na$]$^+$ 283.1674, found 283.1676.

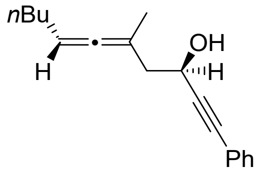
(*E*)-6-Methyldodeca-2,6,7-trien-4-ol (5ac)



5ac

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5ac** was isolated in 88% yield (26 mg, 0.13 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.74-5.67 (m, 1H), 5.54-5.49 (m, 1H), 5.09-5.04 (m, 1H), 4.20 (dt, *J* = 6.8, 6.3 Hz, 1H), 2.19-2.13 (m, 2H), 1.98 (dt, *J* = 6.9, 6.8 Hz, 2H), 1.71-1.68 (m, 6H), 1.40-1.33 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.0, 133.4, 126.6, 95.7, 90.9, 70.6, 42.6, 31.4, 28.9, 22.2, 19.6, 17.7, 13.9. HRMS (ESI): m/z calcd. for [$C_{13}H_{22}ONa$]$^+$ 217.1568, found 217.1569.

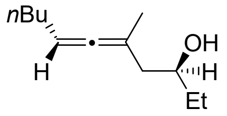
5-Methyl-1-phenylundeca-5,6-dien-1-yn-3-ol (5ad)



5ad

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5ad** was isolated in 80% yield (31 mg, 0.12 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44-7.42 (m, 2H), 7.31-7.29 (m, 3H), 5.15-5.11 (m, 1H), 4.74 (t, *J* = 6.6 Hz, 1H), 2.48-2.47 (m, 2H), 2.02-1.95 (m, 2H), 1.77 (d, *J* = 2.9 Hz, 3H), 1.41-1.25 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.0, 131.7, 128.3, 128.2, 122.8, 94.9, 91.6, 89.9, 84.7, 61.5, 42.6, 31.4, 29.0, 22.2, 19.7, 13.9. HRMS (ESI): m/z calcd. for [C$_{18}$H$_{23}$O]$^+$ 255.1749, found 255.1752.

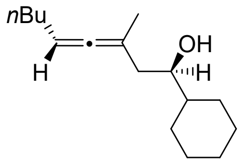
5-Methylundeca-5,6-dien-3-ol (5ae)



5ae

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5ae** was isolated in 73% yield (20 mg, 0.11 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.10-5.04 (m, 1H), 3.70-3.65 (m, 1H), 2.11 (dt, *J* = 14.8, 3.2 Hz, 1H), 2.05-1.97 (m, 3H), 1.70 (d, *J* = 2.8 Hz, 3H), 1.55-1.49 (m, 2H), 1.41-1.31 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 201.6, 96.3, 91.0, 71.0, 41.9, 31.4, 29.6, 29.0, 22.2, 19.7, 13.9, 10.0. HRMS (ESI): m/z calcd. for [C$_{12}$H$_{23}$O]$^+$ 183.1749, found 183.1740.

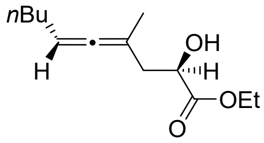
1-Cyclohexyl-3-methylnona-3,4-dien-1-ol (5af)



5af

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5af** was isolated in 73% yield (26 mg, 0.11 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.08-5.04 (m, 1H), 3.53-3.49 (m, 1H), 2.16-2.12 (m, 1H), 2.05-1.95 (m, 3H), 1.84 (d, *J* = 12.7 Hz, 1H), 1.78-1.73 (m, 2H), 1.70 (d, *J* = 2.8 Hz, 3H), 1.43-1.33 (m, 4H), 1.28-1.00 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 201.6, 96.5, 90.9, 73.6, 43.1, 39.3, 31.4, 29.2, 29.0, 28.0, 26.6, 26.4, 26.3, 22.2, 19.6, 13.9. HRMS (ESI): m/z calcd. for [C$_{16}$H$_{28}$ONa]$^+$ 259.2038, found 259.2043.

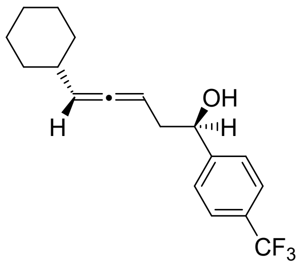
Ethyl 2-hydroxy-4-methyldeca-4,5-dienoate (5ag)



5ag

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5ag** was isolated in 41% yield (14 mg, 0.06 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.09-5.05 (m, 1H), 4.31 (dd, *J* = 7.5, 4.1 Hz, 1H), 4.28-4.19 (m, 2H), 2.48 (ddd, *J* = 15.0, 3.3, 3.3 Hz, 1H), 2.32 (ddd, *J* = 14.8, 7.5, 2.0 Hz, 1H), 1.96 (dt, *J* = 6.9, 6.8 Hz, 2H), 1.73 (d, *J* = 2.8 Hz, 3H), 1.39-1.29 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.0, 174.4, 94.7, 91.2, 69.6, 61.5, 39.1, 31.3, 28.9, 22.1, 19.7, 14.2, 13.9. HRMS (ESI): m/z calcd. for [C$_{13}$H$_{23}$O$_3$]$^+$ 227.1647, found 227.1646.

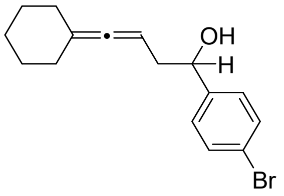
5-Cyclohexyl-1-(4-(trifluoromethyl)phenyl)penta-3,4-dien-1-ol (5mh)



5mh

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5mh** was isolated in 98% yield (45.6 mg, 0.14 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 5.16-5.13 (m, 1H), 5.12-5.07 (m, 1H), 4.83 (t, *J* = 6.5 Hz, 1H), 2.48-2.39 (m, 2H), 1.95-1.88 (m, 1H), 1.70-1.61 (m, 5H), 1.29-0.96 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.2, 147.6, 129.6 (q, *J* = 31.9 Hz), 126.2, 125.2 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.2 Hz), 97.8, 87.1, 73.0, 39.5, 37.0, 33.0, 32.9, 26.0, 25.9. HRMS (ESI): m/z calcd. for $[C_{18}H_{22}OF_3]^+$ 311.1617, found 311.1611.

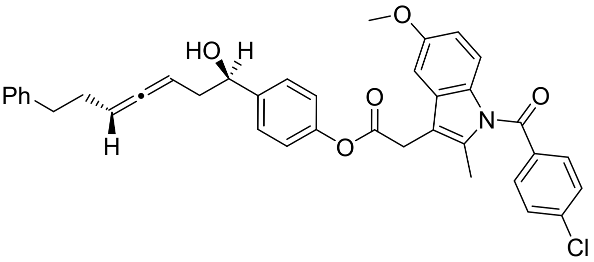
1-(4-Bromophenyl)-4-cyclohexylidenebut-3-en-1-ol (5oa)



5oa

This compound was prepared according to procedure B with the addition of hexafluoroisopropanol (HFIP, 2.0 equiv.). The final reaction mixture was stirred at 60°C for 48 hours. Product **5oa** was isolated in 60% yield (28 mg, 0.09 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 10:1 v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 4.96-4.92 (m, 1H), 4.72 (dd, *J* = 7.7, 4.9 Hz, 1H), 2.43-2.31 (m, 2H), 2.09-2.04 (m, 4H), 1.57-1.47 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 142.8, 131.3, 127.7, 121.1, 103.3, 84.2, 72.9, 39.6, 31.6, 31.5, 27.3, 26.0. HRMS (ESI): m/z calcd. for $[C_{16}H_{18}OBr]^-$ 305.0535, found 305.0544.

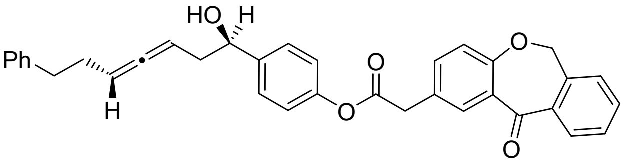
4-(1-Hydroxy-7-phenylhepta-3,4-dien-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (5ji)



5ji

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5ji** was isolated in 95% yield (88 mg, 0.14 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (30:1 to 3:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.36-7.33 (m, 2H), 7.26-7.23 (m, 3H), 7.14-7.11 (m, 3H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.78 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.27-5.21 (m, 1H), 5.16-5.11 (m, 1H), 4.74 (t, *J* = 6.6 Hz, 1H), 3.97 (s, 2H), 3.91 (s, 3H), 2.79-2.73 (m, 2H), 2.53 (s, 3H), 2.43-2.30 (m, 4H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 205.4, 169.3, 168.3, 156.1, 149.9, 141.6, 141.5, 139.3, 136.2, 133.8, 131.2, 130.8, 130.5, 129.1, 128.5, 128.2, 126.9, 125.8, 121.2, 114.9, 111.9, 111.7, 101.1, 90.7, 87.1, 72.9, 55.6, 39.0, 35.2, 30.4, 30.3, 13.3. HRMS (ESI): m/z calcd. for $[C_{38}H_{34}NO_5ClNa]^+$ 642.2017, found 642.2010.

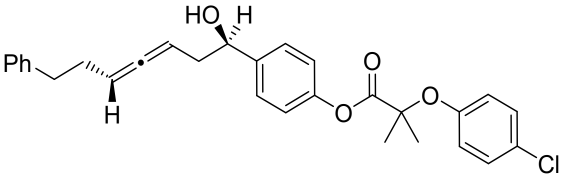
4-(1-Hydroxy-7-phenylhepta-3,4-dien-1-yl)phenyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (5jj)



5jj

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5jj** was isolated in 97% yield (77 mg, 0.14 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (20:1 to 3:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.58-7.47 (m, 3H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28-7.25 (m, 2H), 7.18-7.15 (m, 3H), 7.08-7.05 (m, 3H), 5.21 (s, 2H), 5.18-5.14 (m, 1H), 5.09-5.03 (m, 1H), 4.68 (t, *J* = 6.5 Hz, 1H), 3.88 (s, 2H), 2.72-2.63 (m, 2H), 2.36-2.22 (m, 4H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 205.4, 190.8, 169.8, 160.6, 149.9, 141.6, 141.4, 140.4, 136.3, 135.5, 132.8, 132.6, 129.5, 129.3, 128.5, 128.2, 127.8, 127.2, 126.9, 125.8, 125.2, 121.3, 121.2, 90.7, 87.1, 73.6, 73.0, 40.2, 39.0, 35.2, 30.3. HRMS (ESI): m/z calcd. for $[C_{35}H_{30}O_5Na]^+$ 553.1985, found 553.1978.

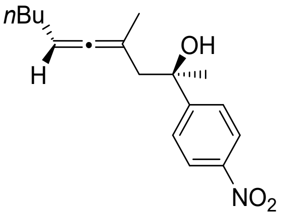
4-(1-Hydroxy-7-phenylhepta-3,4-dien-1-yl)phenyl 2-(4-chlorophenoxy)-2-methylpropanoate (5jk)



5jk

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 12 hours. Product **5jk** was isolated in 95% yield (68 mg, 0.14 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (20:1 to 5:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, *J* = 8.5 Hz, 2H), 7.30-7.24 (m, 4H), 7.20-7.17 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.20-5.15 (m, 1H), 5.10-5.05 (m, 1H), 4.69 (t, *J* = 6.5 Hz, 1H), 2.74-2.65 (m, 2H), 2.37-2.24 (m, 4H), 1.74 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 205.4, 172.6, 153.9, 149.7, 141.7, 141.6, 129.2, 128.5, 128.2, 127.5, 127.0, 125.8, 121.0, 120.5, 90.8, 87.0, 79.5, 73.0, 39.0, 35.2, 30.3, 25.3, 25.2. HRMS (ESI): m/z calcd. for [$C_{29}H_{29}O_4ClNa$]$^+$ 499.1646, found 499.1640.

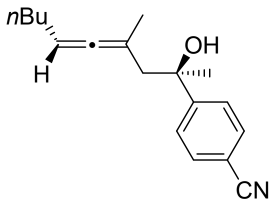
4-Methyl-2-(4-nitrophenyl)deca-4,5-dien-2-ol (5al)



5al

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 72 hours. Product **5al** was isolated in 89% yield (39 mg, 0.13 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 5.03-4.98 (m, 1H), 2.93 (s, 1H), 2.64 (dd, *J* = 15.6, 2.5 Hz, 1H), 2.54 (dd, *J* = 15.6, 2.8 Hz, 1H), 1.64-1.56 (m, 5H), 1.53 (s, 3H), 1.28-1.02 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.3, 155.7, 146.5, 126.0, 123.3, 94.9, 92.3, 74.4, 46.9, 31.3, 30.9, 28.6, 22.1, 21.2, 13.8. HRMS (ESI): m/z calcd. for [$C_{17}H_{23}NO_3Na$]$^+$ 312.1576, found 312.1576.

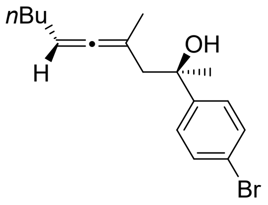
4-(2-Hydroxy-4-methyldeca-4,5-dien-2-yl)benzonitrile (5am)



5am

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 72 hours. Product **5am** was isolated in 93% yield (38 mg, 0.14 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 5.02-4.96 (m, 1H), 2.61 (dd, *J* = 15.6, 2.5 Hz, 1H), 2.51 (dd, *J* = 15.6, 2.9 Hz, 1H), 1.65-1.55 (m, 5H), 1.50 (s, 3H), 1.24-1.02 (m, 4H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.3, 153.6, 131.9, 125.9, 118.9, 110.2, 94.9, 92.2, 74.3, 46.9, 31.2, 30.9, 28.6, 22.1, 21.2, 13.8. HRMS (ESI): m/z calcd. for [$C_{18}H_{23}NONa$]$^+$ 292.1677, found 292.1667.

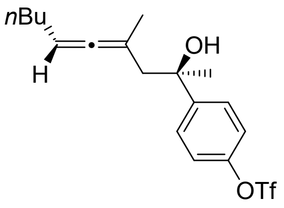
2-(4-Bromophenyl)-4-methyldeca-4,5-dien-2-ol (5an)



5an

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 72 hours. Product **5an** was isolated in 83% yield (40 mg, 0.12 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43, (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 5.03-4.97 (m, 1H), 2.56 (dd, *J* = 15.4, 2.4 Hz, 1H), 2.47 (dd, *J* = 15.4, 2.7 Hz, 1H), 1.67 (dt, *J* = 7.4, 7.1 Hz, 2H), 1.54 (d, *J* = 2.9 Hz, 3H), 1.48 (s, 3H), 1.24-1.05 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.4, 147.2, 131.0, 126.8, 120.2, 95.2, 91.9, 74.1, 47.1, 31.2, 31.0, 28.7, 22.2, 21.2, 13.8. HRMS (ESI): m/z calcd. for [$C_{17}H_{23}ONaBr$]$^+$ 345.0830, found 345.0829.

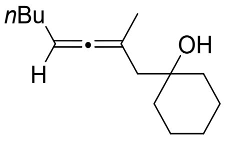
4-(2-Hydroxy-4-methyldeca-4,5-dien-2-yl)phenyl trifluoromethanesulfonate (5ao)



5ao

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 72 hours. Product **5ao** was isolated in 70% yield (41 mg, 0.10 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 5.10 (s, 1H), 4.60-4.53 (m, 1H), 2.34 (d, *J* = 13.4 Hz, 1H), 2.27 (d, *J* = 13.7 Hz, 1H), 1.71 (dt, *J* = 6.8, 6.7 Hz, 2H), 1.52 (d, *J* = 2.8 Hz, 3H), 1.48 (s, 3H), 1.24-1.16 (m, 4H), 0.81 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 203.5, 149.7, 147.5, 127.6, 120.2, 118.3 (q, *J* = 321.4 Hz), 94.9, 88.1, 73.6, 48.4, 30.8, 29.6, 28.1, 21.4, 20.8, 13.7. HRMS (ESI): m/z calcd. for $[C_{18}H_{23}F_3O_4SNa]^+$ 415.1161, found 415.1148.

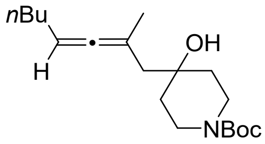
1-(2-Methylocta-2,3-dien-1-yl)cyclohexan-1-ol (5ap)



5ap

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 72 hours. Product **5ap** was isolated in 81% yield (27 mg, 0.12 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.06-5.00 (m, 1H), 2.14-2.07 (m, 2H), 1.98 (dt, *J* = 7.2, 6.8 Hz, 2H), 1.75 (d, *J* = 3.0 Hz, 3H), 1.66-1.23 (m, 14H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.7, 95.1, 90.3, 71.9, 46.2, 37.7, 37.5, 31.4, 29.1, 25.9, 22.3, 22.2, 21.9, 13.9. HRMS (ESI): m/z calcd. for $[C_{15}H_{26}ONa]^+$ 245.1881, found 245.1884.

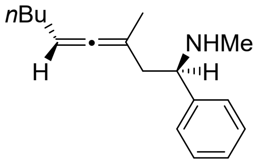
Tert-butyl 4-hydroxy-4-(2-methylocta-2,3-dien-1-yl)piperidine-1-carboxylate (5aq)



5aq

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 72 hours. Product **5aq** was isolated in 90% yield (44 mg, 0.13 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (40:1 to 5:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.10-5.05 (m, 1H), 3.80 (d, *J* = 10.2 Hz, 2H), 3.17 (t, *J* = 11.8 Hz, 2H), 2.16-2.05 (m, 2H), 1.99 (dt, *J* = 7.1, 6.9 Hz, 2H), 1.74 (d, *J* = 2.9 Hz, 3H), 1.63 (d, *J* = 12.7 Hz, 2H), 1.54-1.48 (m, 2H), 1.46 (s, 9H), 1.41-1.30 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.4, 154.8, 94.5, 91.1, 79.3, 70.0, 46.6, 39.8, 36.9, 36.8, 31.3, 29.0, 28.5, 22.2, 22.0, 13.9. HRMS (ESI): m/z calcd. for $[C_{19}H_{33}NO_3Na]^+$ 346.2358, found 346.2363.

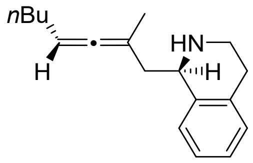
N,3-Dimethyl-1-phenylnona-3,4-dien-1-amine (5ar)



5ar

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 24 hours. Product **5ar** was isolated in 60% yield (22 mg, 0.09 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (10:1 to 1:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39-7.27 (m, 5H), 5.02-4.96 (m, 1H), 3.73 (t, *J* = 7.1 Hz, 1H), 2.55-2.51 (m, 1H), 2.43-2.38 (m, 1H), 2.30 (s, 3H), 1.82 (dt, *J* = 6.9, 6.8 Hz, 2H), 1.65 (d, *J* = 2.7 Hz, 3H), 1.33-1.23 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 202.0, 128.4, 127.5, 127.3, 95.9, 90.8, 63.3, 42.6, 34.1, 31.4, 28.9, 22.2, 19.4, 13.9. HRMS (ESI): m/z calcd. for $[C_{17}H_{26}N]^+$ 244.2065, found 244.2065.

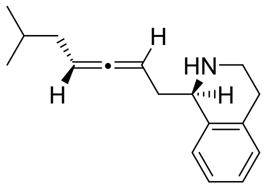
1-(2-Methylocta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (5as)



5as

This compound was prepared according to procedure B. The final reaction mixture was stirred at rt for 24 hours. Product **5as** was isolated in 87% yield (33 mg, 0.13 mmol) as an orange oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (10:1 to 1:1 v/v). NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.16-7.06 (m, 4H), 5.09-5.03 (m, 1H), 4.04 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.16-3.11 (m, 1H), 2.89-2.84 (m, 1H), 2.78-2.68 (m, 2H), 2.45 (ddd, *J* = 14.7, 3.3, 3.3 Hz, 1H), 2.30 (ddd, *J* = 14.6, 9.6, 1.9 Hz, 1H), 1.92-1.90 (m, 2H), 1.73 (d, *J* = 2.9 Hz, 3H), 1.36-1.31 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CD_3CN) δ 203.0, 140.3, 136.5, 130.0, 127.2, 126.8, 126.5, 97.5, 91.2, 54.7, 41.6, 41.1, 32.1, 30.5, 29.6, 22.8, 19.6, 14.2. HRMS (ESI): m/z calcd. for $[C_{18}H_{25}NNa]^+$ 278.1885, found 278.1876.

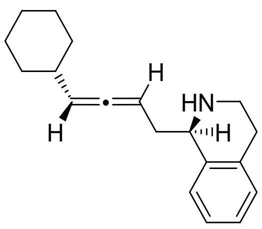
1-(6-Methylhepta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (5ks)



5ks

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 48 hours. Product **5ks** was isolated in 71% yield (26 mg, 0.11 mmol) as an orange oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (10:1 to 1:1 v/v). NMR data: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.14-7.02 (m, 4H), 5.17-5.12 (m, 1H), 5.07-5.02 (m, 1H), 3.90-3.88 (m, 1H), 3.08-3.03 (m, 1H), 2.82-2.78 (m, 1H), 2.72-2.60 (m, 2H), 2.46-2.41 (m, 1H), 2.36-2.30 (m, 1H), 1.87-1.76 (m, 2H), 1.63-1.55 (m, 1H), 1.25-1.22 (m, 1H), 0.86(7) (d, *J* = 6.6 Hz, 3H), 0.86(4) (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 204.8, 139.0, 135.4, 128.9, 126.1, 125.6, 125.4, 88.7, 87.7, 55.1, 40.2, 37.7, 35.7, 29.4, 27.8, 22.0, 21.9. HRMS (ESI): m/z calcd. for $[C_{17}H_{24}N]^+$ 242.1903, found 242.1896.

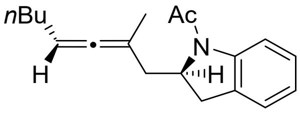
1-(4-Cyclohexylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (5ms)



5ms

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 48 hours. Product **5ms** was isolated in 60% yield (24 mg, 0.09 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (10:1 to 1:1 v/v). NMR data: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.14-7.02 (m, 4H), 5.22-5.17 (m, 1H), 5.10-5.07 (m, 1H), 3.91-3.89 (m, 1H), 3.08-3.03 (m, 1H), 2.82-2.78 (m, 1H), 2.72-2.60 (m, 2H), 2.47-2.41 (m, 1H), 2.38-2.31 (m, 1H), 1.95-1.88 (m, 1H), 1.68-1.62 (m, 4H), 1.58-1.54 (m, 1H), 1.29-0.94 (m, 5H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 203.1, 139.0, 135.4, 128.9, 126.1, 125.6, 125.4, 96.4, 89.2, 55.2, 40.2, 36.4, 35.8, 32.6, 32.5, 29.4, 25.7, 25.4. HRMS (ESI): m/z calcd. for $[C_{19}H_{26}N]^+$ 268.2059, found 268.2053.

1-(2-(2-Methylocta-2,3-dien-1-yl)indolin-1-yl)ethan-1-one (5at-Ac)

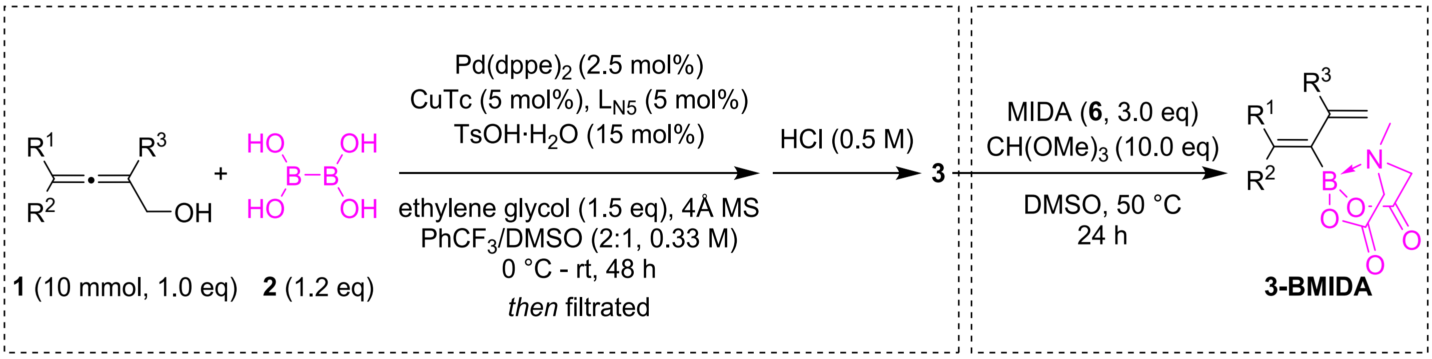


5at-Ac

This compound was prepared according to procedure B. The final reaction mixture was stirred at 35°C for 48 hours. After a complete conversion of 1,3-dienyl-2-boronic acid **3a** (monitored by TLC), DCM (4 mL) was added and the mixture was stirred at 0 °C. After that, Et_3N (5.0 equiv) and acetyl chloride (3.0 equiv) were sequentially added to the Schlenk flask via syringe at 0 °C. After a complete conversion of **5at** (monitored by TLC), the reaction mixture was diluted with petroleum ether/EtOAc (1:1 v/v). The precipitate was filtered off through a short silica pad using EtOAc as an eluent. Then, the solvent was removed in vacuo and the residue was purified by a rapid silica gel chromatography.

Product **5at-Ac** was isolated in 51% yield (22 mg, 0.08 mmol) as an orange oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (20:1 to 5:1 v/v). NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.02 (d, J = 7.0 Hz, 1H), 7.22-7.15 (m, 2H), 7.01 (t, J = 7.6 Hz, 1H), 5.16-5.02 (m, 1H), 4.59-4.40 (m, 1H), 3.31-3.27 (m, 1H), 2.86 (d, J = 15.8 Hz, 1H), 2.34 (d, J = 14.0 Hz, 1H), 2.21 (s, 3H), 2.09-1.97 (m, 3H), 1.69 (d, J = 2.6 Hz, 3H), 1.43-1.32 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CD_3CN) δ 203.1, 169.2, 143.4, 132.1, 127.9, 126.1, 124.5, 118.1, 96.1, 91.7, 59.9, 40.1, 34.6, 32.2, 29.6, 23.6, 22.9, 19.6, 14.2. HRMS (ESI): m/z calcd. for $[C_{19}H_{26}NO]^+$ 284.2009, found 284.2002.

7. Procedure C for synthesis of boronic MIDA esters 3-BMIDA

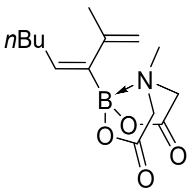


Step i *Step ii*

Step i: A Schlenk flask equipped with a Teflon coated stirrer bar was charged with 4 Å molecular sieves, $B_2(OH)_4$ (**2**, 1.2 equiv), CuTc (0.05 equiv), $Pd(dppe)_2$ (0.025 equiv), L_{N5} (4,7-dimethoxy-1,10-phenanthroline, 0.05 equiv), $TsOH\cdot H_2O$ (0.15 equiv) and $PhCF_3$ (20 mL) under Ar atmosphere. The reaction mixture was stirred at rt for 5 min and cooled to 0 °C for 5 min. Then, 2,3-allenols **1** (10 mmol), ethylene glycol (1.5 equiv), and DMSO (10 mL) were sequentially added to the reaction mixture via syringe. The reaction mixture was gradually warmed and stirred at rt. After a complete conversion of 2,3-allenols **1** (monitored by TLC), the reaction mixture was filtered off through a short anhydrous $MgSO_4$ pad using $PhCF_3$ as an eluent. Then, the solvent was washed with aqueous HCl (0.5 M) to yield the $PhCF_3$ solution of **3**.

Step ii: A Schlenk flask equipped with a Teflon coated stirrer bar was charged with MIDA (**6**, N-methyliminodiacetic acid, 3.0 equiv) and DMSO (10 mL) under Ar atmosphere. The mixture was stirred at rt. Then, the filtrated $PhCF_3$ solution of **3** and $CH(OMe)_3$ (10.0 equiv) was added via syringe at rt. The reaction was allowed to stir at 50°C for 24 hours. After a complete conversion of boronic acid **3**, the reaction mixture was diluted with EtOAc (30 mL). The organic phase was washed with brine (3×50 mL), dried (with $MgSO_4$), filtered, and concentrated in vacuo. Then, the residue was purified by flash column chromatography using a mixture of petroleum ether/EtOAc as eluent to yield the desired products **3-BMIDA**.

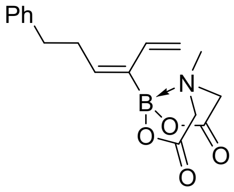
(*Z*)-4-Methyl-8-(2-methylocta-1,3-dien-3-yl)dihydro-4λ⁴,8λ⁴-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (3a-BMIDA)



3a-BMIDA

This compound was prepared according to procedure C. The final reaction mixture was stirred at 50 °C for 24 hours. Product **3a-BMIDA** was isolated in 58% yield over two steps (1.6 g, 5.8 mmol) as a white solid by silica gel chromatography using petroleum ether/EtOAc eluent mixture (5:1 to pure EtOAc v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.97 (t, *J* = 7.2 Hz, 1H), 4.96 (s, 1H), 4.46 (s, 1H), 3.76 (d, *J* = 16.2 Hz, 2H), 3.70 (d, *J* = 16.2 Hz, 2H), 2.87 (s, 3H), 2.12 (dt, *J* = 7.2, 7.0 Hz, 2H), 1.87 (s, 3H), 1.36-1.25 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.2, 148.0, 141.4, 111.9, 62.0, 46.6, 31.8, 29.1, 24.5, 22.5, 14.0. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 11. HRMS (ESI): m/z calcd. for [$C_{14}H_{22}BNO_4Na$]$^+$ 302.1534, found 302.1527.

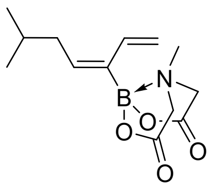
(*Z*)-4-Methyl-8-(6-phenylhexa-1,3-dien-3-yl)dihydro-4λ⁴,8λ⁴-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (3j-BMIDA)



3j-BMIDA

This compound was prepared according to procedure C. The final reaction mixture was stirred at 50 °C for 24 hours. Product **3j-BMIDA** was isolated in 53% yield over two steps (1.6 g, 5.3 mmol) as a white solid by silica gel chromatography using petroleum ether/EtOAc eluent mixture (5:1 to pure EtOAc v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27-7.24 (m, 2H), 7.18-7.14 (m, 3H), 6.48 (dd, *J* = 18.0, 11.6 Hz, 1H), 6.00 (t, *J* = 7.2 Hz, 1H), 5.22 (dd, *J* = 18.0, 1.8 Hz, 1H), 5.14 (d, *J* = 11.6 Hz, 1H), 3.69 (d, *J* = 16.3 Hz, 2H), 3.51 (d, *J* = 16.3 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.61 (dt, *J* = 7.3, 7.3 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.2, 142.6, 141.8, 135.4, 128.5, 128.4, 125.9, 117.7, 61.8, 46.6, 35.2, 30.1. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, CDCl$_3$) δ 11. HRMS (ESI): m/z calcd. for [$C_{17}H_{20}BNO_4Na$]$^+$ 336.1377, found 336.1366.

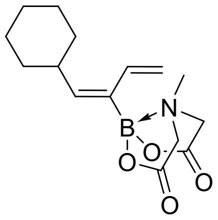
(*Z*)-4-Methyl-8-(6-methylhepta-1,3-dien-3-yl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (3k-BMIDA)



3k-BMIDA

This compound was prepared according to procedure C. The final reaction mixture was stirred at 50 °C for 24 hours. Product **3k-BMIDA** was isolated in 55% yield over two steps (1.4 g, 5.5 mmol) as a white solid by silica gel chromatography using petroleum ether/EtOAc eluent mixture (5:1 to pure EtOAc v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 18.0, 11.6 Hz, 1H), 6.07 (t, *J* = 7.2 Hz, 1H), 5.24 (dd, *J* = 18.0, 1.7 Hz, 1H), 5.17 (d, *J* = 11.6 Hz, 1H), 3.93 (d, *J* = 16.6 Hz, 2H), 3.69 (d, *J* = 16.5 Hz, 2H), 2.80 (s, 3H), 2.12 (t, *J* = 7.1 Hz, 2H), 1.73-1.65 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 143.0, 135.9, 117.3, 62.1, 47.0, 37.9, 28.7, 22.5. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 11. HRMS (ESI): m/z calcd. for $[C_{13}H_{20}BNO_4Na]^+$ 288.1377, found 288.1372.

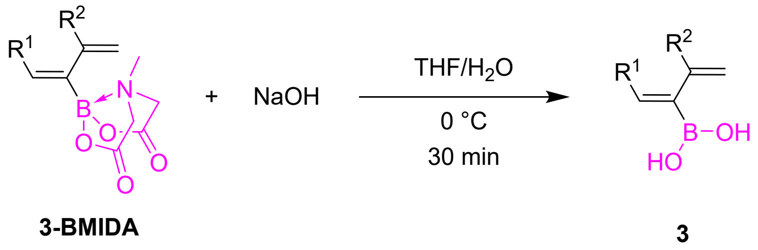
(*Z*)-8-(1-Cyclohexylbuta-1,3-dien-2-yl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (3m-BMIDA)



3m-BMIDA

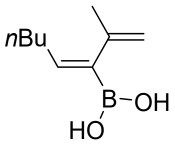
This compound was prepared according to procedure C. The final reaction mixture was stirred at 50°C for 24 hours. Product **3m-BMIDA** was isolated in 60% yield over two steps (1.7 g, 6.0 mmol) as a white solid by silica gel chromatography using petroleum ether/EtOAc eluent mixture (5:1 to pure EtOAc v/v). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 18.0, 11.6 Hz, 1H), 5.88 (d, *J* = 9.4 Hz, 1H), 5.27 (d, *J* = 17.6 Hz, 1H), 5.16 (d, *J* = 11.6 Hz, 1H), 3.82 (d, *J* = 16.4 Hz, 2H), 3.67 (d, *J* = 16.4 Hz, 2H), 2.79 (s, 3H), 2.55-2.48 (m, 1H), 1.73-1.60 (m, 5H), 1.32-1.06 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 149.6, 135.8, 117.2, 62.1, 46.9, 37.5, 32.8, 25.9, 25.7. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, $CDCl_3$) δ 11. HRMS (ESI): m/z calcd. for $[C_{15}H_{22}BNO_4Na]^+$ 314.1534, found 314.1528.

8. Procedure D for preparation of 3 in toluene solution



A Schlenk flask equipped with a Teflon-coated stirrer bar was charged with purified **3-BMIDA** (2.0 mmol). THF (5 mL) was added under argon atmosphere, and the resulting solution was stirred at 0°C. Aqueous NaOH (2.5 equiv., 1 M) was added to the flask via syringe at 0°C. The reaction mixture was allowed to stir at 0 °C for 30 min. After a complete conversion of **3-BMIDA**, a buffer solution (KH_2PO_4/K_2HPO_4, pH = 6.5) was introduced to neutralize the reaction mixture. The organic phase was extracted with degassed toluene (4×5 mL) and transferred to another Schlenk flask equipped with a Teflon-coated stirrer bar under Ar atmosphere. Then, the solvent was removed at 0 °C in vacuo. Subsequently, degassed toluene (5 mL) was added under Ar atmosphere. The organic phase was washed with brine (3×10 mL). The concentration of **3** in toluene solution was determined by ^{1}H NMR using naphthalene as an internal standard.

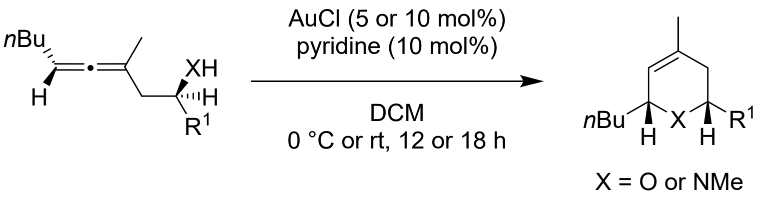
(*Z*)-(2-Methylocta-1,3-dien-3-yl)boronic acid (3a)



3a

For NMR analysis: this compound was prepared according to procedure D with THF-d_8. After a complete conversion of **3a-BMIDA**, a buffer solution (KH_2PO_4/K_2HPO_4, pH = 6.5) was introduced to neutralize the reaction mixture. The organic phase was extracted with C_6D_6. Product **3a** was obtained in 94% NMR yield, which was determined by ^{1}H NMR using naphthalene as an internal standard. NMR data: ^{1}H NMR (500 MHz, THF-d_8/C_6D_6) δ 6.54 (t, *J* = 7.2 Hz, 1H), 6.25 (s, 2H), 4.97 (s, 1H), 4.67 (d, *J* = 1.7 Hz, 1H), 2.19 (dt, *J* = 7.3, 7.2 Hz, 2H), 1.88 (s, 3H), 1.35-1.22 (m, 4H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, THF-d_8/C_6D_6) δ 147.3, 143.7, 111.6, 32.2, 30.1, 24.5, 22.9, 14.2. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. ^{11}B NMR (160 MHz, THF-d_8/C_6D_6) δ 30. HRMS (ESI): m/z calcd. for $[C_9H_{16}BO_2]^-$ 167.1238, found 167.1235.

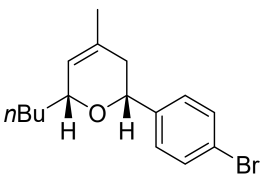
9. Procedure E for Au catalysed cyclization of homoallenyl alcohols or amines 5



5 **6**

A Schlenk flask equipped with a Teflon coated stirrer bar was charged with AuCl (5-10 mol%) and DCM (2 mL) under Ar atmosphere. The reaction mixture was cooled to 0 °C or stirred at rt. Then, homoallenyl alcohols or amines **5** (1.0 equiv, 0.15 mmol) and pyridine (10 mol%) were sequentially added to the reaction mixture via syringe. The reaction mixture was stirred at 0 °C or rt. After a complete conversion of **5** (monitored by TLC), the reaction mixture was filtered off through a short silica pad using EtOAc as an eluent. Then, the solvent was removed in vacuo and the residue was purified by a rapid silica gel chromatography using a mixture of petroleum ether/EtOAc as eluent to yield the desired products **6.**

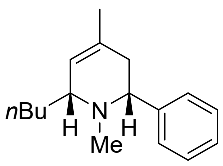
2-(4-Bromophenyl)-6-butyl-4-methyl-3,6-dihydro-2*H*-pyran (6aa)



6aa

This compound was prepared according to procedure E. The final reaction mixture was stirred at 0°C for 12 hours. Product **6aa** was isolated in 79% yield (36.5 mg, 0.12 mmol) as a colorless oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (100:1 v/v). NMR data: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 9.1 Hz, 2H), 5.43-5.38 (m, 1H), 4.52 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.25-4.18 (m, 1H), 2.20-2.10 (m, 1H), 2.09-2.01 (m, 1H), 1.73 (s, 3H), 1.62-1.55 (m, 2H), 1.49-1.29 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 142.1, 131.9, 131.3, 127.4, 124.1, 120.8, 75.3, 74.9, 37.9, 35.5, 27.2, 22.8(7), 22.8(2), 14.1. HRMS (ESI): m/z calcd. for [$C_{16}H_{22}OBr$]$^+$ 309.0848, found 309.0832.

6-Butyl-1,4-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine (6ar)



6ar

This compound was prepared according to procedure E. The final reaction mixture was stirred at rt for 18 hours. Product **6ar** was isolated in 85% yield (31.0 mg, 0.13 mmol) as a yellow oil by silica gel chromatography using petroleum ether/EtOAc eluent mixture (50:1 to 20:1 v/v). NMR data: ^{1}H NMR (500 MHz, C_6D_6) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.22-7.17 (m, 2H), 7.13-7.09 (m, 1H), 5.32-5.26 (m, 1H), 3.25 (dd, *J* = 10.7, 3.7 Hz, 1H), 2.89-2.80 (m, 1H), 2.35-2.24 (m, 1H), 2.04 (s, 3H), 1.86-1.79 (m, 1H), 1.75-1.60 (m, 2H), 1.57 (s, 3H), 1.55-1.50 (m, 1H), 1.42-1.29 (m, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 145.9, 132.0, 128.8, 127.2, 124.4, 66.9, 63.7, 41.1, 40.6, 34.3, 26.9, 23.7, 22.8, 14.5. HRMS (ESI): m/z calcd. for $[C_{17}H_{26}N]^+$ 244.2059, found 244.2052.

10. Stability of boronic acid 3a in a mixture solvent of $PhCF_3$/THF-d_8/C_6D_6

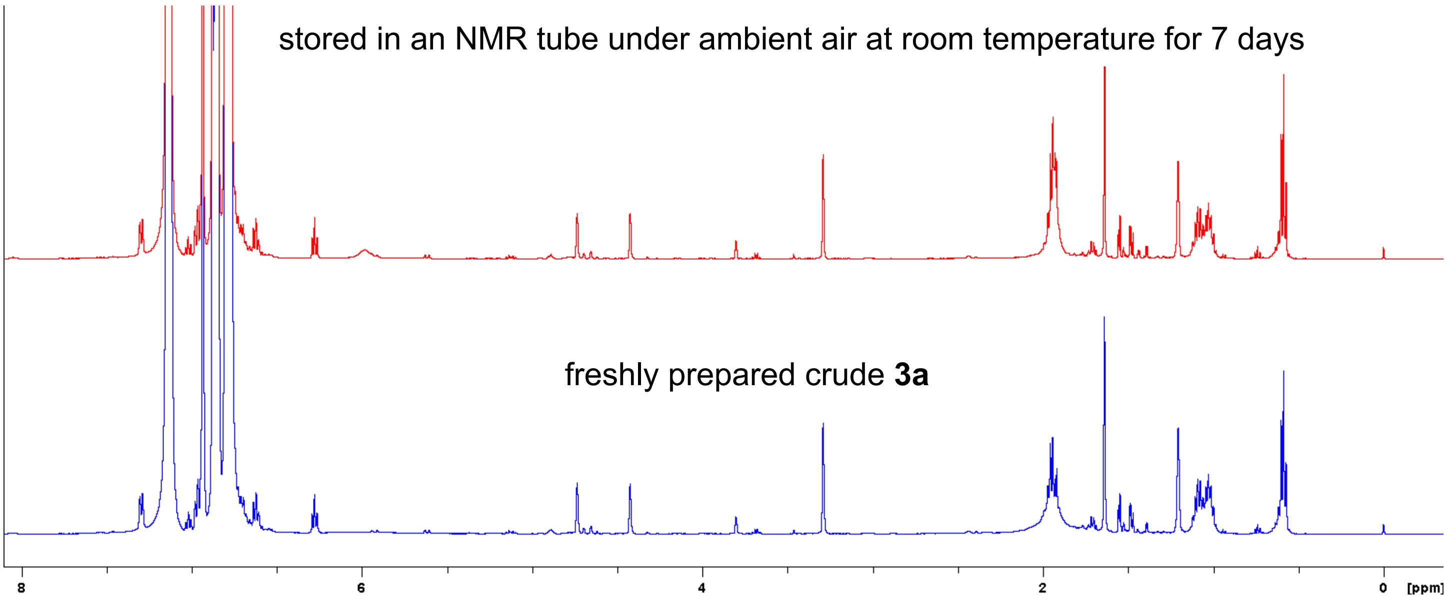
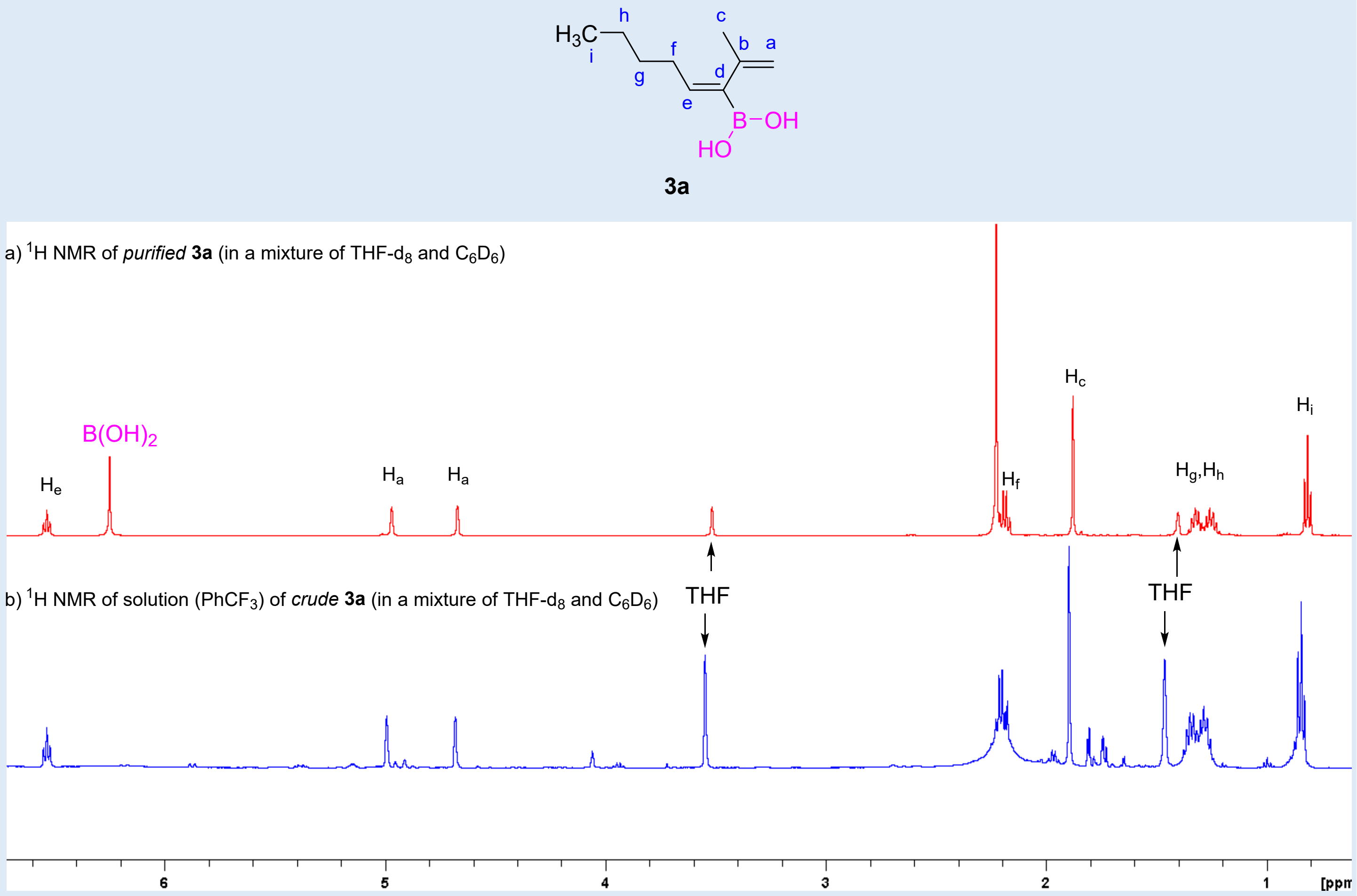


Figure S4. A study on the stability of boronic acid **3a**

11. Comparison of ^1H NMR spectra of crude 3a and purified 3a



3a

a) ^1H NMR of *purified* **3a** (in a mixture of THF-d_8 and C_6D_6)

b) ^1H NMR of solution ($PhCF_3$) of *crude* **3a** (in a mixture of THF-d_8 and C_6D_6)

Figure S5. Comparison of ^1H NMR spectra of crude **3a** and purified **3a**

12. Determination of the stereochemistry of 3a-Bpin, 6aa and 6ar using a NOESY spectrum

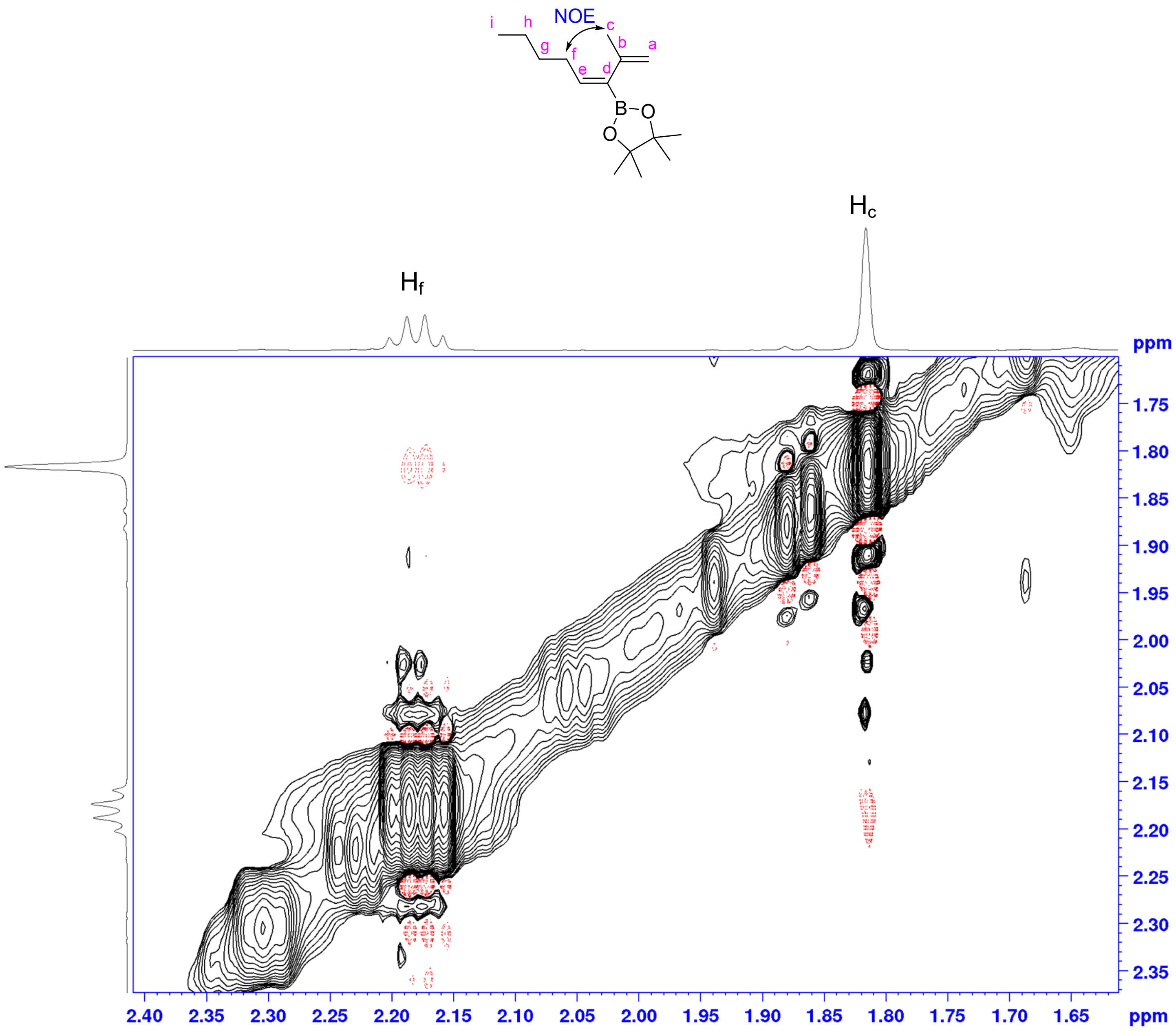
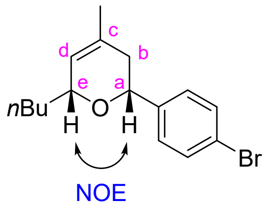


Figure S6. Observed NOESY effect between the C$_c$-H and C$_f$-H

The NOESY experiment (**Figure S6**) indicated a through space NOE effect between C$_c$-H and C$_f$-H. This indicates that C$_c$-H and C$_f$-H are close in space. Therefore, the relative configuration of **3a-Bpin** is ***Z***.



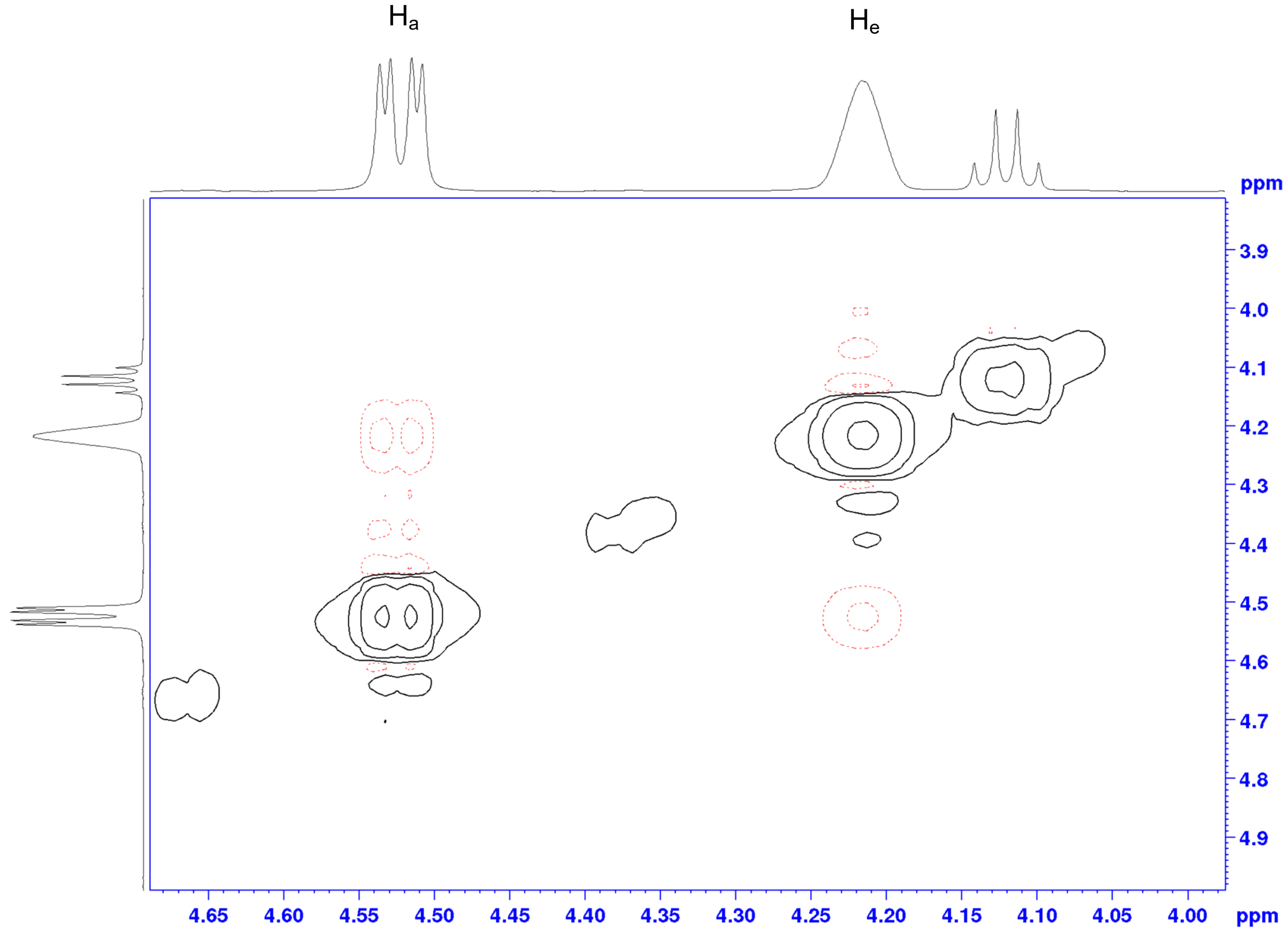
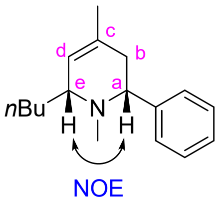


Figure S7. Observed NOESY effect between the C$_a$-H and C$_e$-H

The NOESY experiment (**Figure S7**) indicated a through space NOE effect between C$_a$-H and C$_e$-H. This indicates that C$_a$-H and C$_e$-H are close in space. Therefore, the relative configuration of **6aa** is ***cis***.



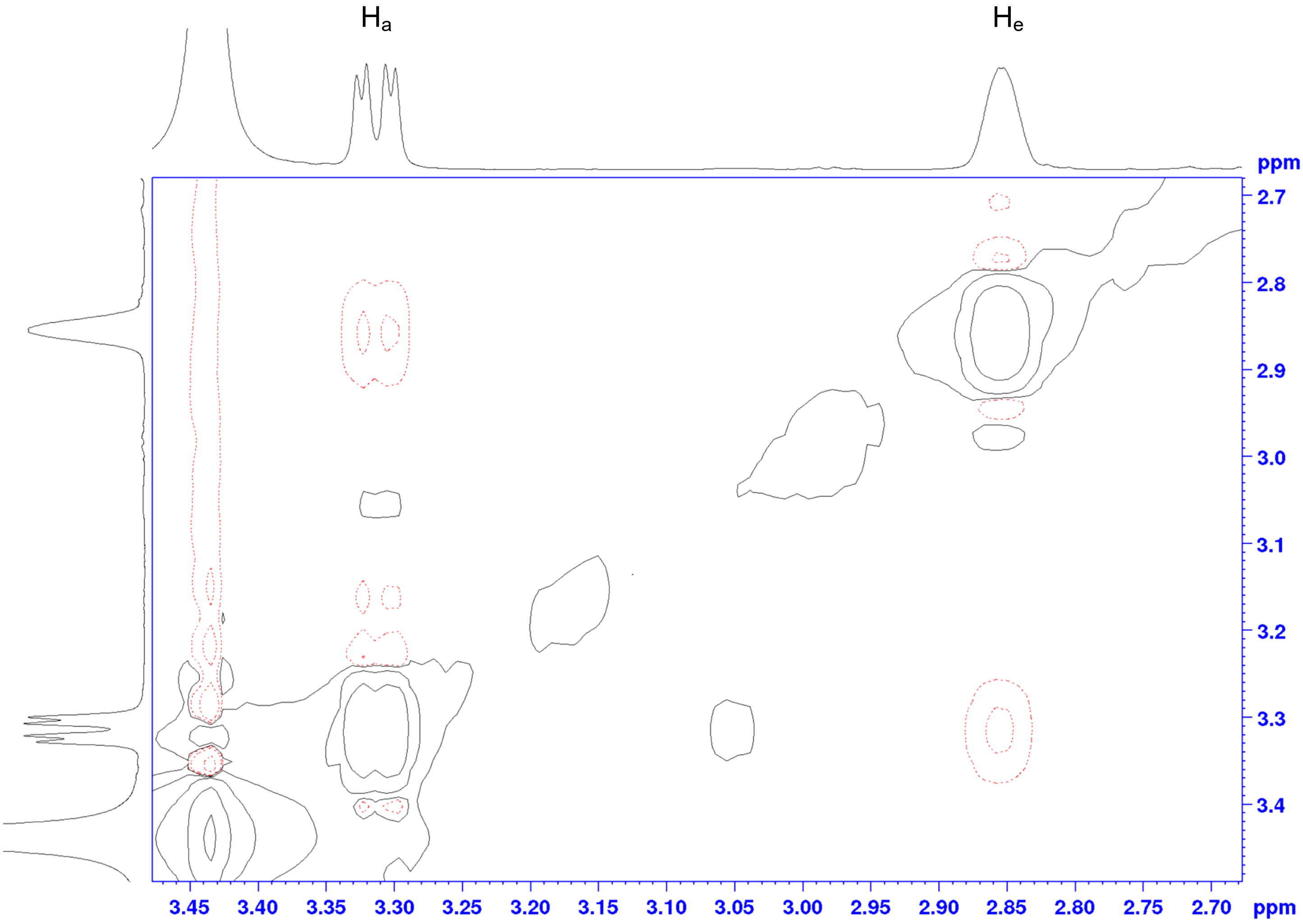


Figure S8. Observed NOESY effect between the C_a-H and C_e-H

The NOESY experiment (**Figure S8**) indicated a through space NOE effect between C_a-H and C_e-H. This indicates that C_a-H and C_e-H are close in space. Therefore, the relative configuration of **6ar** is ***cis***.

13. Notes and references

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