Supporting Information

Ruthenium(II)-catalysed 1,2-selective hydroboration of aldazines

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General Experimental:

All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBraun glove box. Catalyst **1** and HBpin were purchased from Sigma-Aldrich and stored inside the glove box. Chemicals were purchased from commercial vendors such as Sigma-Aldrich, Alfa-aesar, and Acros, and used without further purification. ^{1}H and ^{13}C spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz). ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet. Aldazine derivatives were synthesized from the reported procedures.[1]

General procedure for the synthesis of aldazine derivatives

Aldehyde (2 mmol), hydrazine hydrate (1 mmol), ethanol (5 mL) were taken in a 50 mL round bottom flask with a stir bar and refluxed for 3-4 h. After completion, the reaction mixture was cooled to room temperature; the solid precipitate was filtered and then crystallized using ethanol. ^{1}H and ^{13}C NMR spectra were recorded in order to check the purity of aldazines prior to their use in catalysis.

General optimization procedure for the 1,2-selective hydroboration of benzalazine

To a screw cap scintillation vial benzalazine (0.25 mmol), pinacolborane (0.25-0.55 mmol), catalyst **1** (0.00025-0.0025 mmol) in $CDCl_3$ (0.3 mL) were charged with a stir bar under nitrogen atmosphere. The reaction mixture was allowed to stir at the indicated temperature for 12 h or 24 h. After completion, the reaction mixture was taken to inside the glove box, internal standard tetraethylsilane (0.25 mmol) was added and stirred for 10 minutes. From the resulting mixture, 200 µl was taken and submitted for NMR analysis. The product **2a** is highly

air and moisture-sensitive. All experimental procedures were carried out under nitrogen atmosphere, and the reaction mixture NMR samples were prepared under the nitrogen atmosphere Glove-box.

General procedure for the 1,2-hydroboration of aldazine derivatives

To a screw cap scintillation vial aldazine derivatives (0.25 mmol), pinacolborane (0.275 mmol), catalyst **1** (0.0005 mmol) in $CDCl_3$ (0.3 mL) or DCE (1 mL) were charged with a stir bar under nitrogen atmosphere. The reaction mixture was allowed to stir at 60 °C for 12 h. After 12 h, the reaction mixture was taken inside the glove box, internal standard tetraethylsilane (0.25 mmol) was added and stirred for 10 minutes. From the resulting mixture 200 µl was taken and submitted for NMR analysis. The products are highly air and moisture-sensitive. All experimental procedures were carried out under nitrogen atmosphere, and reaction mixture NMR samples were prepared under the nitrogen atmosphere Glove-box.

General procedure for the conversion of N-borylated benzyl hydrazones to Benzyl hydrazones

After completion of catalysis, reaction mixtures of compounds **2m**, **2n**, and **2q** were taken inside the glove box, filtered through celite pad using chloroform as a solvent. The volatiles are removed under vacuum, and the resulted residue recrystallised in dry dichloromethane and hexane. Then, the solvents were decanted after recrystallization, washed with cold hexane, and dried under vacuum to obtain the corresponding benzyl hydrazone products **3a-c**.

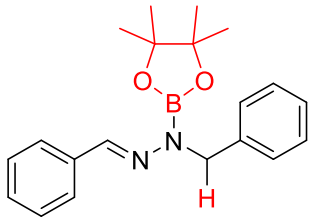
Procedure for synthesis of N-benzyl N-benzylidenebenzohydrazide

After completion of catalysis, the reaction mixture was taken inside glove box and passed through a pad of celite bed to remove the catalyst. The volatiles were removed under vacuum, dry acetonitrile (2 mL) added as solvent and the flast was taken out of the glove box. Sodium

hydride (2 equiv, 0.5 mmol) pre-washed with hexane was added under nitrogen atmosphere at ice cold condition and the reaction mixture allowed to stir for 10 minutes. Benzoyl chloride (1 equiv, 0.25 mmol) was added drop wise, and rection mixture stirred for 12 hours at room temperature under nitrogen atmosphere. Upon completion, the reaction mixture was filetered through a pad of celite, which provide the pure amide product **4**.

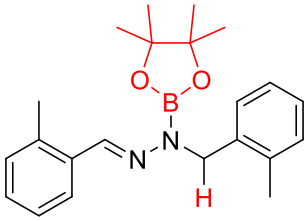
Spectral data of the 1,2-selective hydroboration of aldazine products

(*E*)-1-Benzyl-2-benzylidene-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2a):



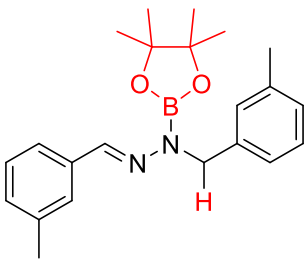
Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.46 (m, 3H, ArC*H*, N=C*H*), 7.03-7.22 (m, 8H, ArC*H*), 4.66 (s, 2H, CH_2), 1.23 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 139.41, 137.70, 135.91, 128.68, 128.29, 128.22, 126.84, 126.70, 126.35, 83.58, 77.48, 77.16, 76.84, 48.79, 24.70.

(*E*)-1-(2-Methylbenzyl)-2-(2-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2b):



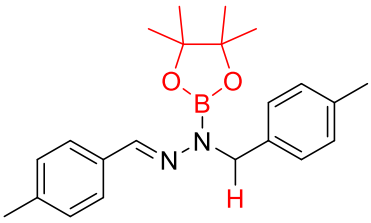
Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J_1 = 7.1, J_2 = 2.2 Hz, 1H, ArC*H*), 7.47 (s, 1H, N=C*H*), 6.98-7.10 (m, 6H, ArC*H*), 6.87-6.93 (m, 1H, ArC*H*), 4.63 (s, 2H, CH_2), 2.29 (s, 3H, Ar-CH_3), 1.90 (s, 3H, Ar-CH_3), 1.25 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 138.53, 135.68, 134.69, 134.10, 130.39, 130.20, 128.17, 126.69, 126.32, 126.02, 125.75, 83.63, 77.47, 77.16, 76.84, 46.84, 24.77, 19.20, 18.93.

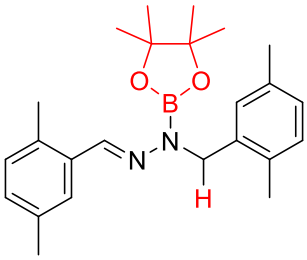
(*E*)-1-(3-Methylbenzyl)-2-(3-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2c):

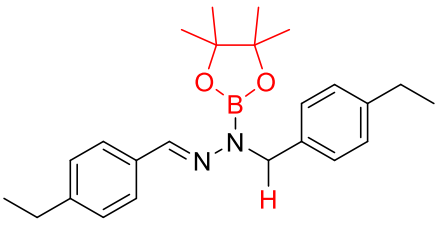


Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H, N=C*H*), 7.28 (s, 1H, ArC*H*), 7.20 (d, *J* = 7.7 Hz, 1H, ArC*H*), 7.04 (dt, J_1 = 17.8 Hz, J_2 = 7.5 Hz, 2H, ArC*H*), 6.85-6.97 (m, 4H,

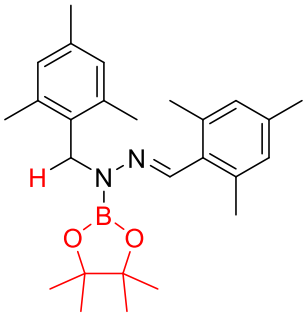
ArC*H*), 4.63 (s, 2H, CH_2), 2.18 (d, *J* = 6.8 Hz, 6H, 2×CH_3), 1.23 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 139.57, 138.23, 137.72, 137.62, 135.81, 129.13, 128.55, 128.09, 127.59, 127.12, 126.89, 124.15, 123.38, 83.56, 77.48, 77.16, 76.84, 48.57, 24.68, 21.46, 21.27.

(*E*)-1-(4-Methylbenzyl)-2-(4-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2d):  Yield: 91%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H, N=C*H*), 7.35 (d, *J* = 8.0 Hz, 2H, ArC*H*), 6.95-7.10 (m, 6H, ArC*H*), 4.64 (s, 2H, CH_2), 2.21 (d, *J* = 2.4 Hz, 6H, 2×CH_3), 1.26 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 139.59, 138.22, 136.34, 134.77, 133.30, 129.41, 129.00, 126.76, 126.36, 83.61, 77.48, 77.16, 76.84, 48.48, 24.81, 21.43, 21.16.

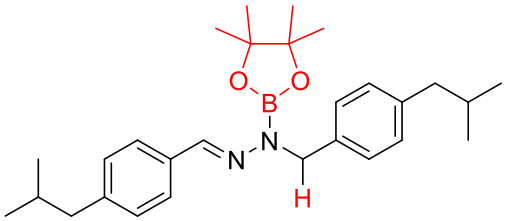
(*E*)-1-(2,5-Dimethylbenzyl)-2-(2,5-dimethylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2e):  Yield: 89%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H, N=C*H*), 7.42 (d, *J* = 2.4 Hz, 1H, ArC*H*), 6.92 (d, *J* = 7.4 Hz, 1H, ArC*H*), 6.80 (dd, J_1 = 11.8, J_2 = 6.2 Hz, 4H, ArC*H*), 4.58 (s, 2H, CH_2), 2.22 (s, 3H, Ar-CH_3), 2.17 (s, 3H, Ar-CH_3), 2.12 (s, 3H, Ar-CH_3), 1.83 (s, 3H, Ar-CH_3), 1.24 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 138.59, 135.64, 135.30, 134.25, 133.66, 132.65, 131.42, 130.26, 130.07, 129.00, 127.29, 126.31, 126.18, 83.56, 77.47, 77.16, 76.84, 46.57, 24.68, 21.11, 20.92, 18.67, 18.36.

(*E*)-1-(4-Ethylbenzyl)-2-(4-ethylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2f):  Yield: 94%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H, N=C*H*), 7.36 (d, *J* = 7.9 Hz, 2H, ArC*H*), 7.06 (d, *J* = 8.0 Hz, 2H, ArC*H*), 6.95-7.04 (m, 4H, ArC*H*), 4.64 (s, 2H, N-CH_2), 2.49 (qd, J_1 = 7.6, J_1 = 4.3 Hz, 4H, 2×CH_2), 1.23 (s, 12H, 4×CH_3), 1.09 (q, *J* = 8.0 Hz, 6H, 2×CH_3). $^{13}C\{^1H\}$ NMR (100.6

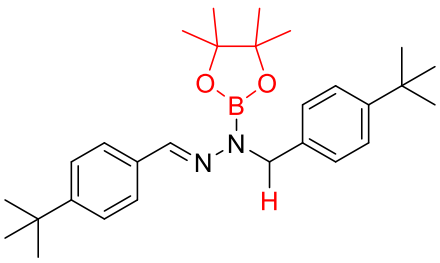
MHz, $CDCl_3$): δ 144.55, 142.67, 139.54, 135.02, 133.59, 128.16, 127.76, 126.80, 126.40, 83.52, 77.48, 77.16, 76.84, 48.48, 28.79, 28.56, 24.74, 15.65, 15.61.

(*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(2,4,6-trimethylbenzyl)-2-(2,4,6-trimethylbenzylidene)hydrazine (2g): 

Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 2.3 Hz, 1H, N=C*H*), 6.62 (dd, J_1 = 21.3, J_2 = 7.6 Hz, 4H, ArC*H*), 4.64 (s, 2H, CH_2), 2.24 (d, J = 10.0 Hz, 6H, 2×Ar-CH_3), 2.09 (d, J = 9.7 Hz, 6H, 2×Ar-CH_3), 1.94 (d, J = 7.9 Hz, 6H, 2×Ar-CH_3), 1.20 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 143.23, 136.91, 136.89, 136.83, 135.98, 131.24, 130.84, 129.51, 128.82, 128.80, 83.13, 77.48, 77.16, 76.84, 46.00, 24.72, 20.98, 20.76, 20.61, 20.42, 20.40.

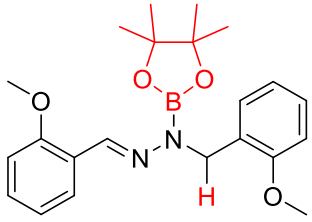
(*E*)-1-(4-Isobutylbenzyl)-2-(4-isobutylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan-2-yl)hydrazine (2h): 

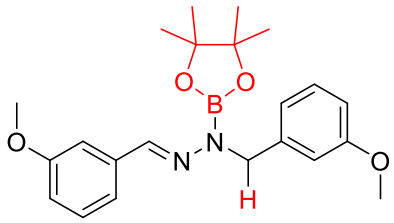
Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H, N=C*H*), 7.35 (d, J = 8.0 Hz, 2H, ArC*H*), 7.06 (d, J = 7.8 Hz, 2H, ArC*H*), 6.95 (dd, J_1 = 12.8, J_2 = 7.8 Hz, 4H, ArC*H*), 4.63 (s, 2H, N-CH_2), 2.32 (dd, J_1 = 7.3, J_2 = 3.0 Hz, 4H, 2×Ar-CH_2), 1.78 – 1.65 (m, 2H, 2×C*H*), 1.23 (s, 12H, 4×CH_3), 0.77 (dd, J_1 = 11.0, J_2 = 6.7 Hz, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 141.96, 140.12, 139.48, 135.09, 133.65, 129.41, 129.02, 126.53, 126.20, 83.48, 77.48, 77.16, 76.84, 48.56, 45.31, 45.16, 30.29, 30.27, 24.72, 22.45, 22.34.

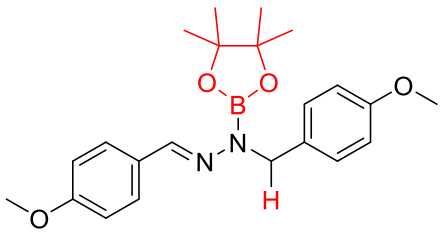
(*E*)-1-(4-(Tert-butyl)benzyl)-2-(4-(tert-butyl)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2i): 

Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H, N=C*H*), 7.39 (d, J = 8.2 Hz, 2H, ArC*H*), 7.19 (t, J = 7.3 Hz, 4H, ArC*H*), 7.08 (d, J =

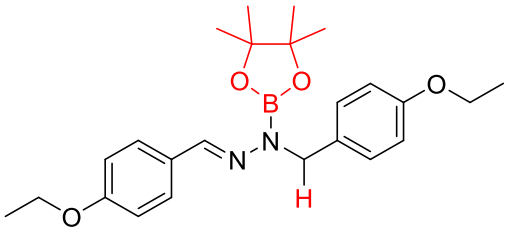
8.0 Hz, 2H, ArC*H*), 4.64 (s, 2H, CH_2), 1.23 (s, 12H, 4×CH_3), 1.18 (d, *J* = 5.4 Hz, 18H, 4×Ar-CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 151.31, 149.52, 139.33, 134.75, 133.41, 126.52, 126.15, 125.56, 125.15, 83.49, 77.48, 77.16, 76.84, 48.33, 34.65, 34.46, 31.45, 31.32, 24.76.

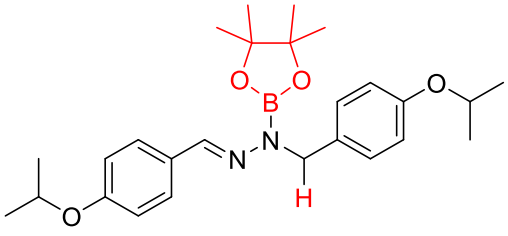
(*E*)-1-(2-Methoxybenzyl)-2-(2-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2j): 
Yield: 89%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, J_1 = 7.7, J_2 = 1.8 Hz, 1H, ArC*H*), 7.74 (s, 1H, N=C*H*), 7.05 (td, J_1 = 12.4, J_2 = 10.6, J_3 = 4.8 Hz, 3H, ArC*H*), 6.70-6.83 (m, 3H, ArC*H*), 6.63 (d, *J* = 8.3 Hz, 1H, ArC*H*), 4.67 (s, 2H, CH_2), 3.76 (s, 3H, O-CH_3), 3.52 (s, 3H, O-CH_3), 1.23 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 157.18, 156.73, 134.81, 129.16, 127.63, 127.20, 126.41, 125.20, 125.00, 83.42, 77.48, 77.16, 76.84, 55.66, 55.26, 42.53, 24.72.

(*E*)-1-(3-Methoxybenzyl)-2-(3-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2k): 
Yield: 92%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 3.3 Hz, 1H, N=C*H*), 7.00-7.13 (m, 3H, ArC*H*), 6.96 (d, *J* = 7.6 Hz, 1H, ArC*H*), 6.58-6.77 (m, 4H, ArC*H*), 4.62 (s, 2H, CH_2), 3.63 (d, *J* = 9.2 Hz, 6H, 2×O-CH_3), 1.22 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 160.07, 159.63, 139.43, 139.32, 137.35, 129.68, 129.17, 119.74, 118.65, 114.45, 112.30, 111.83, 111.15, 83.60, 77.47, 77.16, 76.84, 55.14, 55.03, 48.82, 24.67.

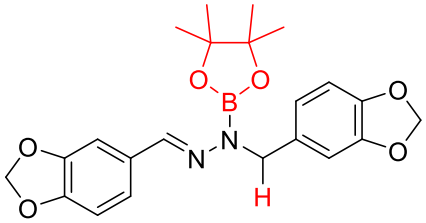
(*E*)-1-(4-Methoxybenzyl)-2-(4-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2l): 
Yield: 96%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H, N=C*H*), 7.35 (dd, J_1 = 8.8, J_2 = 2.6 Hz, 2H, ArC*H*), 7.09 (d, *J* = 8.1 Hz, 2H,

ArC*H*), 6.74 (dd, J_1 = 11.3 Hz, J_2 = 8.1 Hz, 4H, ArC*H*), 4.58 (s, 2H, CH_2), 1.24 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 159.63, 158.24, 138.48, 129.60, 128.59, 127.43, 127.34, 113.74, 113.49, 83.13, 77.48, 77.16, 76.84, 54.92, 54.86, 47.79, 24.34.

(*E*)-1-(4-Ethoxybenzyl)-2-(4-ethoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2m):  Yield: 90%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H, N=C*H*), 7.36 (d, *J* = 8.3 Hz, 2H, ArC*H*), 7.07 (d, *J* = 8.2 Hz, 2H, ArC*H*), 6.73 (dd, J_1 = 12.8, J_2 = 8.3 Hz, 4H, ArC*H*), 4.59 (s, 2H, CH_2), 3.91 (dp, J_1 = 7.5, J_2 = 3.7, J_3 =3.2 Hz, 4H, O-CH_2), 1.29 (t, *J* = 7.0 Hz, 6H, 2×CH_2-CH_3), 1.25 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 159.18, 157.78, 138.97, 129.69, 128.68, 127.76, 127.48, 114.52, 114.16, 83.34, 77.48, 77.16, 76.84, 63.34, 63.30, 48.06, 43.59, 24.59, 14.78, 14.70.

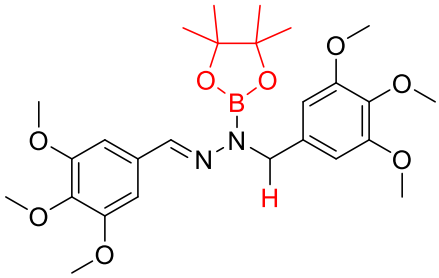
(*E*)-1-(4-Isopropoxybenzyl)-2-(4-isopropoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2n):  Yield: 81%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H, N=C*H*), 7.33 (d, *J* = 8.4 Hz, 2H, ArC*H*), 7.06 (d, *J* = 8.1 Hz, 2H, ArC*H*), 6.72 (t, *J* = 8.7 Hz, 4H, ArC*H*), 4.56 (s, 2H, CH_2), 4.42 (dt, J_1 = 13.0, J_2 = 6.3 Hz, 2H, O-C*H*), 1.20 (dd, J_1 = 19.5, J_2 =13.2 Hz, 24H, 4×CH-CH_3, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 157.92, 156.51, 138.42, 129.33, 128.27, 127.35, 127.30, 115.59, 115.29, 83.05, 77.48, 77.16, 76.84, 69.45, 69.41, 47.71, 43.61, 24.29, 24.17, 21.67, 21.58.

(*E*)-1-(Benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzo[d][1,3]dioxol-5-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2o):



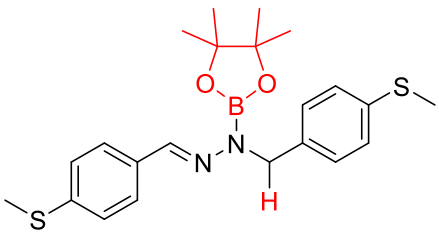
Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H, N=C*H*), 7.05-7.13 (m, 1H, ArC*H*), 6.74 (d, J = 7.6 Hz, 1H, ArC*H*), 6.59-6.67 (m, 4H, ArC*H*), 5.82 (dd, J_1 = 8.0, J_2 = 2.4 Hz, 4H, 2×O-CH_2), 4.51 (s, 2H, CH_2), 1.23 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 147.76, 147.68, 146.15, 138.48, 131.67, 130.46, 121.23, 119.28, 107.93, 107.54, 106.63, 104.86, 100.97, 100.76, 83.12, 77.48, 77.16, 76.84, 48.44, 43.60, 24.22.

(*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3,4,5-trimethoxybenzyl)-2-(3,4,5-trimethoxybenzylidene)hydrazine (2p):

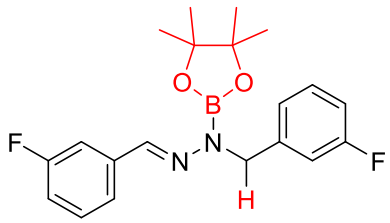


Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H, N=C*H*), 6.69 (s, 2H, ArC*H*), 6.42 (s, 2H, ArC*H*), 4.57 (s, 2H, CH_2), 1.25 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 153.24, 152.99, 139.03, 138.29, 136.38, 133.43, 131.25, 103.32, 102.88, 83.23, 77.48, 77.16, 76.84, 60.21, 60.14, 55.70, 55.59, 49.03, 43.53, 24.22.

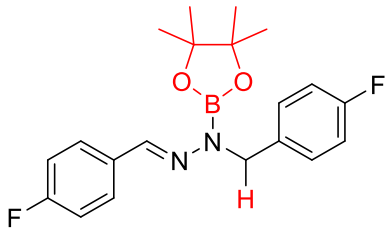
(*E*)-1-(4-(Methylthio)benzyl)-2-(4-(methylthio)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2q):



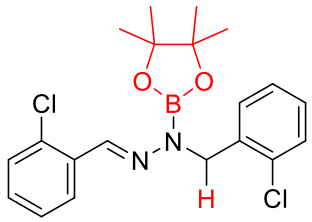
Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H, N=C*H*), 7.35 (d, J = 8.1 Hz, 2H, ArC*H*), 7.03-7.13 (m, 6H, ArC*H*), 4.61 (s, 2H, CH_2), 2.36 (s, 6H, 2×S-CH_3), 1.25 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 138.67, 138.30, 136.54, 134.39, 132.50, 126.76, 126.56, 125.71, 83.32, 77.48, 77.16, 76.84, 48.06, 24.35, 15.45, 15.13.

(*E*)-1-(3-Fluorobenzyl)-2-(3-fluorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2r): 

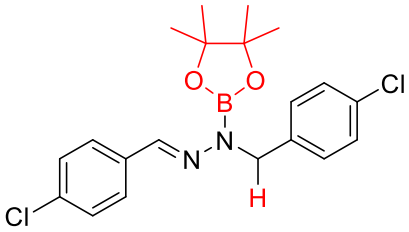
Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H, N=C*H*), 7.23 (dd, J_1 = 10.5, J_2 = 2.6 Hz, 1H, ArC*H*), 7.12 (td, J_1 = 12.7, J_2 = 6.8 Hz, 3H, ArC*H*), 6.92 (d, J = 7.7 Hz, 1H, ArC*H*), 6.74-6.88 (m, 3H, ArC*H*), 4.63 (s, 2H, CH_2), 1.24 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 164.63, 164.28, 162.19, 161.84, 140.52, 140.45, 138.36, 138.33, 138.29, 138.21, 130.35, 130.27, 129.80, 129.72, 122.80, 122.78, 122.03, 122.00, 115.38, 115.17, 114.08, 113.87, 113.47, 113.25, 112.95, 112.73, 83.90, 77.48, 77.16, 76.84, 48.79, 24.70.

(*E*)-1-(4-Fluorobenzyl)-2-(4-fluorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2s): 

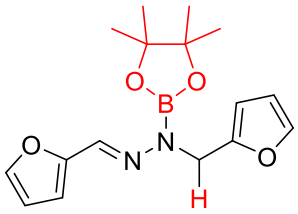
Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.49 (m, 3H, N=C*H,* ArC*H*), 7.10-7.20 (m, 2H, ArC*H*), 6.91 (q, J = 9.0 Hz, 4H, ArC*H*), 4.61 (s, 2H, CH_2), 1.24 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 163.83, 162.75, 161.37, 160.33, 137.84, 133.42, 133.38, 132.05, 132.02, 130.38, 130.29, 127.93, 127.85, 115.32, 115.17, 115.11, 114.96, 83.38, 77.47, 77.16, 76.84, 48.16, 43.59, 24.34.

(*E*)-1-(2-Chlorobenzyl)-2-(2-chlorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2t): 

Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (t, J = 6.1 Hz, 1H, ArC*H*), 7.65 (s, 1H, N=C*H*), 7.28-7.34 (m, 1H, ArC*H*), 7.02-7.20 (m, 6H, ArC*H*), 4.77 (s, 2H, CH_2), 1.25 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 135.74, 133.66, 132.91, 132.88, 132.39, 129.25, 129.16, 129.10, 127.97, 127.13, 126.83, 126.49, 83.51, 77.48, 77.16, 76.84, 46.19, 43.61, 24.27.

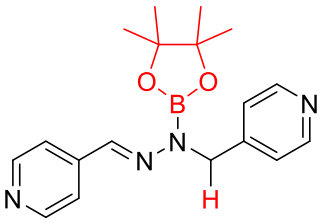
(*E*)-1-(4-Chlorobenzyl)-2-(4-chlorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2u): 

Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H, N=C*H*), 7.39 (d, *J* = 8.5 Hz, 2H, ArC*H*), 7.11-7.32 (m, 6H, ArC*H*), 4.32 (s, 2H, CH_2), 1.19 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 136.67, 135.88, 134.35, 133.62, 129.56, 128.81, 128.74, 127.06, 83.17, 77.48, 77.16, 76.84, 52.65, 43.60, 24.53.

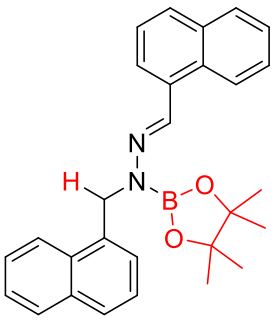
(*E*)-1-(Furan-2-ylmethyl)-2-(furan-2-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2v): 

Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H, N=C*H*), 7.16-7.33 (m, 2H, ArC*H*), 6.36-6.48 (m, 1H, ArC*H*), 6.23-6.30 (m, 1H, ArC*H*), 6.18 (q, *J* = 2.7 Hz, 1H, ArC*H*), 6.05 (d, *J* = 3.3 Hz, 1H, ArC*H*), 4.58 (s, 2H, CH_2), 1.22 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 151.38, 151.17, 150.97, 149.54, 145.81, 142.74, 130.04, 116.68, 112.30, 111.23, 110.38, 109.61, 106.93, 83.76, 77.47, 77.16, 76.84, 42.44, 24.60.

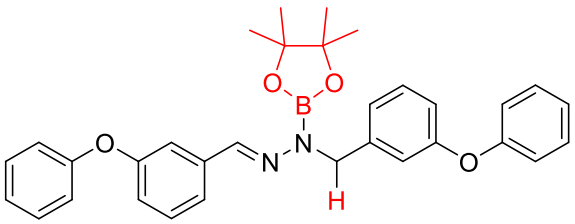
(*E*)-4-((2-(Pyridin-4-ylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazineylidene)methyl)pyridine (2w): Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (dd, J_1 = 16.0, J_2 = 5.4 Hz, 4H, ArC*H*), 7.33 (d, *J* = 4.3 Hz, 3H, ArC*H,* N=C*H*), 7.08 (d, *J* = 5.0 Hz, 2H, ArC*H*), 4.69 (s, 2H, CH_2), 1.27 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 150.70, 150.27, 149.93, 146.49, 142.72, 137.08, 122.20, 121.52, 120.82, 84.26, 77.48, 77.16, 76.84, 48.55, 24.69.



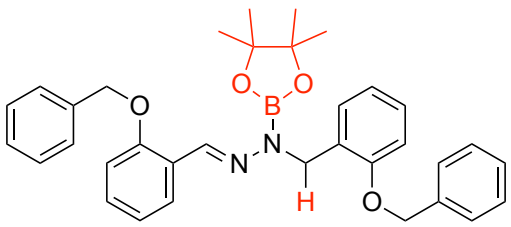
(*E*)-1-(Naphthalen-1-ylmethyl)-2-(naphthalen-1-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2y): Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 1H, ArC*H*), 8.05 (s, 1H, N=C*H*), 7.85 (dd, J_1 = 8.1, J_2 = 2.7 Hz, 1H, ArC*H*), 7.70 (ddt, J_1 = 31.0, J_2 = 15.9, J_3 = 8.4 Hz, 5H, ArC*H*), 7.49 (dt, J_1 = 21.2, J_2 = 6.7 Hz, 2H, ArC*H*), 7.30 (td, J_1 = 12.7, J_2 = 7.5 Hz, 4H, ArC*H*), 7.14-7.22 (m, 1H, ArC*H*), 5.24 (s, 2H, CH_2), 1.28 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 138.61, 133.85, 133.56, 131.49, 130.63, 128.62, 128.36, 127.31, 126.12, 126.02, 125.63, 125.60, 125.44, 125.32, 123.62, 123.42, 122.63, 83.61, 77.43, 77.16, 76.84, 46.40, 43.59, 24.59.



(*E*)-1-(3-phenoxybenzyl)-2-(3-phenoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2z): Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.3 Hz, 1H, N=C*H*), 7.35 (dtd, J_1 = 16.0 Hz, J_2 =12.6 Hz, J_3 =11.8 Hz, J_4 =5.6 Hz, 8H, ArC*H*), 6.99-7.18 (m, 8H, ArC*H*), 6.95 (d, J = 8.0 Hz, 2H, ArC*H*), 4.80 (s, 2H, CH_2), 1.38 (s, 12H, 4×CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 157.82, 157.55, 157.21, 157.10, 139.94, 138.79, 138.03, 130.07, 129.77, 129.73, 129.57, 123.28, 123.01, 122.04, 121.37, 119.06, 118.97, 118.56, 117.51, 117.48, 116.95, 83.71, 77.48, 77.15, 76.84, 48.91, 24.68.

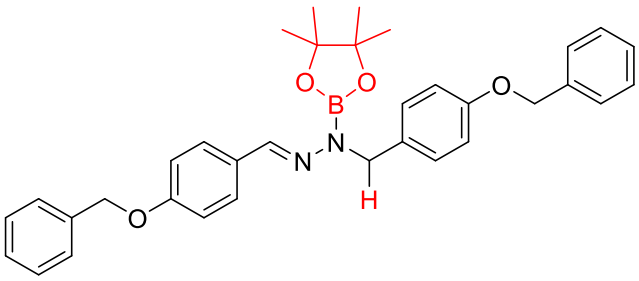


(*E*)-1-(2-(Benzyloxy)benzyl)-2-(2-(benzyloxy)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2ab): Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 11.1 Hz, 2H, ArC*H,* N=C*H*), 7.17-7.31 (m, 5H, ArC*H*), 7.09-7.16 (m, 3H, ArC*H*), 7.05 (tt, J_1 = 7.8, J_2 = 2.2 Hz, 2H, ArC*H*), 6.95-7.01 (m, 3H, ArC*H*), 6.68-6.86 (m, 4H, ArC*H*), 4.84 (s, 2H, O-CH_2), 4.75 (s, 2H,



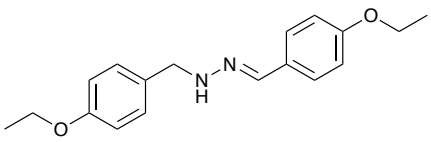
O-CH_2), 4.72 (s, 2H, CH_2), 1.22 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 156.29, 155.88, 137.36, 137.15, 135.16, 132.43, 129.23, 128.72, 128.57, 128.49, 127.82, 127.56, 127.53, 127.18, 127.11, 126.80, 126.60, 125.53, 125.51, 121.24, 120.98, 112.79, 111.59, 83.50, 77.48, 77.16, 76.84, 70.37, 69.87, 43.53, 24.76.

(*E*)-1-(4-(Benzyloxy)benzyl)-2-(4-(benzyloxy)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (2ac): Yield: 78%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H, N=C*H*), 7.30 (ddt, J_1 = 23.8, J_2 = 16.7, J_3 = 8.8 Hz, 12H, ArC*H*), 7.09 (d, J = 8.2 Hz, 2H, ArC*H*), 6.82 (t, J = 9.2 Hz, 4H, ArC*H*), 4.93 (d, J = 8.5 Hz, 4H, O-CH_2), 4.58 (s, 2H, CH_2), 1.24 (s, 12H, 4×CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 158.71, 157.40, 138.28, 136.91, 136.66, 129.87, 128.80, 128.21, 127.64, 127.59, 127.34, 127.25, 114.59, 114.38, 83.07, 77.48, 77.16, 76.84, 69.56, 47.74, 43.61, 24.27.



Spectral data of the benzyl hydrazone products:

(*E*)-1-(4-Ethoxybenzyl)-2-(4-ethoxybenzylidene)hydrazine (3a): White solid. M.pt: 137-139 °C. Yield: 64 mg, 95%. IR (DCM): 3331, 3052, 2982, 2929, 1512, 1248, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, J = 4.7 Hz, 1H, N=C*H*), 7.41 (t, J = 7.6 Hz, 2H, ArC*H*), 7.21 (t, J = 7.4 Hz, 2H, ArC*H*), 6.81 (d, J = 7.6 Hz, 4H, ArC*H*), 5.35 (s, 1H, N*H*), 4.27 (s, 2H, CH_2), 3.97 (q, J = 6.8 Hz, 4H, O-CH_2), 1.35 (t, J = 7.4 Hz, 6H, 2×CH_3). ^1H NMR (400 MHz) in CD_3OD provided similar spectrum with disappearance of NH signal at δ 5.35 ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 159.23, 158.50, 137.91, 130.28, 130.26, 129.75, 128.72, 127.40, 114.85, 114.69, 114.66, 63.60, 63.58, 53.30, 14.99, 14.97. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2$ $(M+H)^+$: 299.1754, found: 299.1768.



(*E*)-1-(4-Isopropoxybenzyl)-2-(4-isopropoxybenzylidene)hydrazine (3b): White solid. M.pt: 142-144 °C. Yield: 78 mg, 96%. IR (DCM): 3240, 2977, 2928, 1509, 1246, 1114, 951, 829 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H, N=C*H*), 7.40 (d, *J* = 8.3 Hz, 2H, ArC*H*), 7.19 (d, *J* = 8.0 Hz, 2H, ArC*H*), 6.83 – 6.71 (m, 4H, ArC*H*), 5.33 (s, 1H, N*H*), 4.47 (tt, J_1 = 11.8, J_2 = 6.0 Hz, 2×C*H*), 4.25 (s, 2H, CH_2), 1.26 (d, *J* = 6.1 Hz, 12H, 2×CH_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 158.19, 157.44, 137.93, 130.28, 130.24, 129.77, 128.63, 127.42, 126.76, 116.06, 115.99, 115.92, 70.02, 53.31, 22.20, 22.18. HRMS (ESI) m/z calcd for $C_{20}H_{26}N_2O_2$ $(M+H)^+$: 327.2067, found: 327.2056.

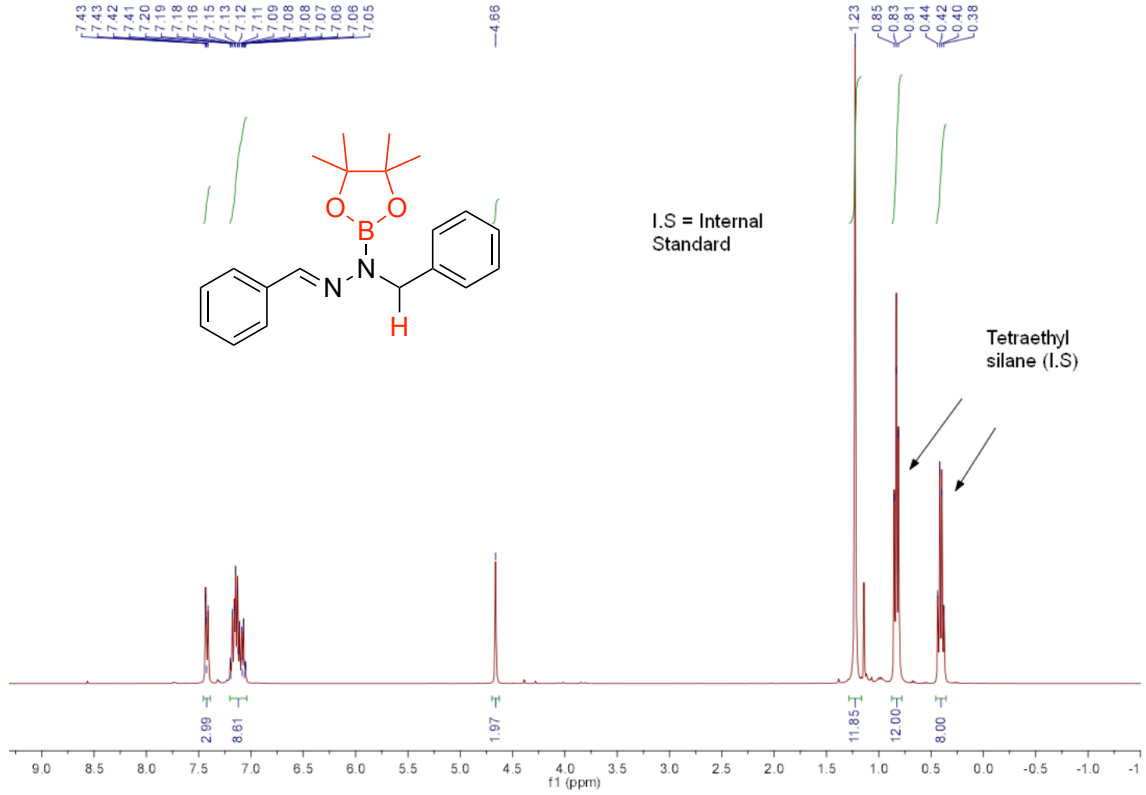
(*E*)-1-(4-(Methylthio)benzyl)-2-(4-(methylthio)benzylidene)hydrazine (3c): White solid. M.pt: 139-141 °C. Yield: 61 mg, 94%. IR (DCM): 3303, 3054, 2980, 2926, 1450, 1340, 1143, 732 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H, N=C*H*), 7.42 – 7.35 (m, 2H, ArC*H*), 7.27 – 7.10 (m, 6H, ArC*H*), 5.52 (s, 1H, N*H*), 4.30 (s, 2H, CH_2), 2.41 (d, *J* = 1.8 Hz, 6H, 2×CH_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 137.75, 137.12, 135.11, 128.95, 126.97, 126.58, 126.43, 53.20, 16.04, 15.87. HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2S_2$ $(M+H)^+$: 303.0984, found: 303.1006.

(*E*)-*N*-Benzyl-*N*'-benzylidenebenzohydrazide (4a): Pale yellow viscous oil. Yield: 75 mg, 95%. IR (DCM): 3060, 2923, 2843, 1658, 1606, 1446, 1412, 1335, 1224, 981, 731, 512 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.3 Hz, 2H, ArC*H*), 7.59 (s, 1H, N=C*H*), 7.45 – 7.33 (m, 3H, ArC*H*), 7.31 – 7.11 (m, 10H, ArC*H*), 5.35 (s, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 171.56, 140.26, 135.20, 135.09, 134.62, 130.53, 130.05, 129.71, 129.12, 128.89, 128.69, 128.65, 127.56, 127.53,

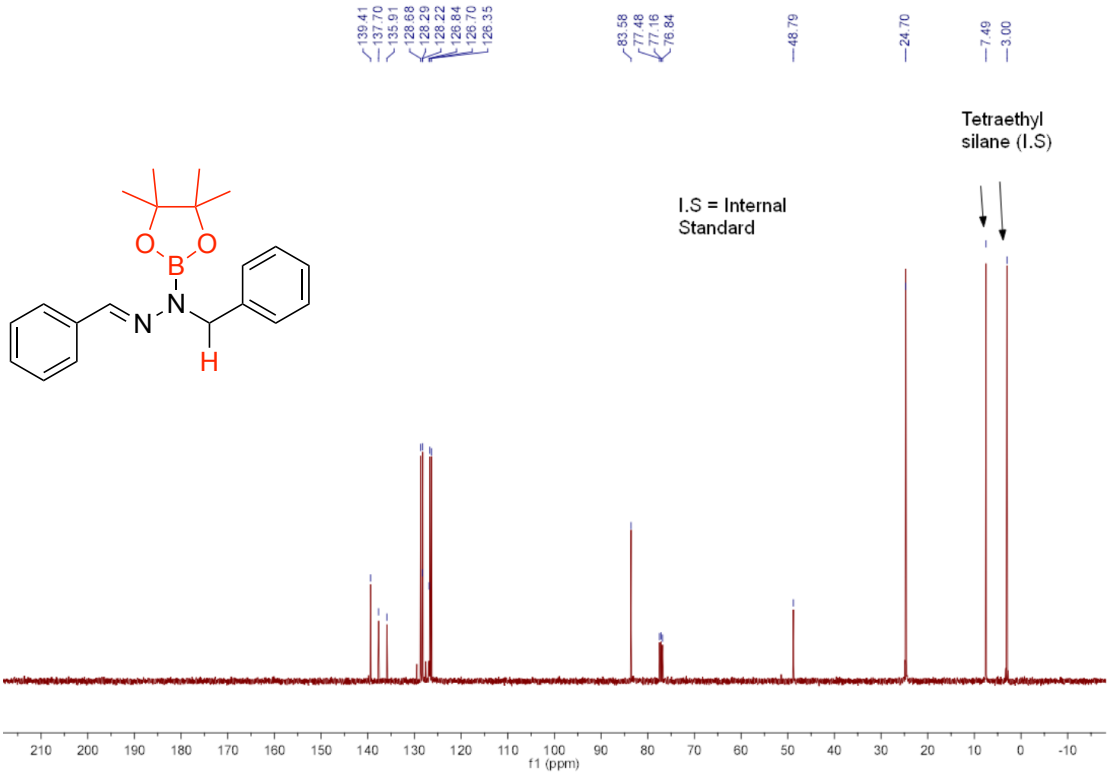
127.25, 126.51, 45.57. HRMS (ESI) m/z calcd for $C_{21}H_{18}N_2O$ $(M+H)^+$: 315.1492, found: 315.1489.

NMR spectra of the products from 1,2-selective hydroboration of aldazine:

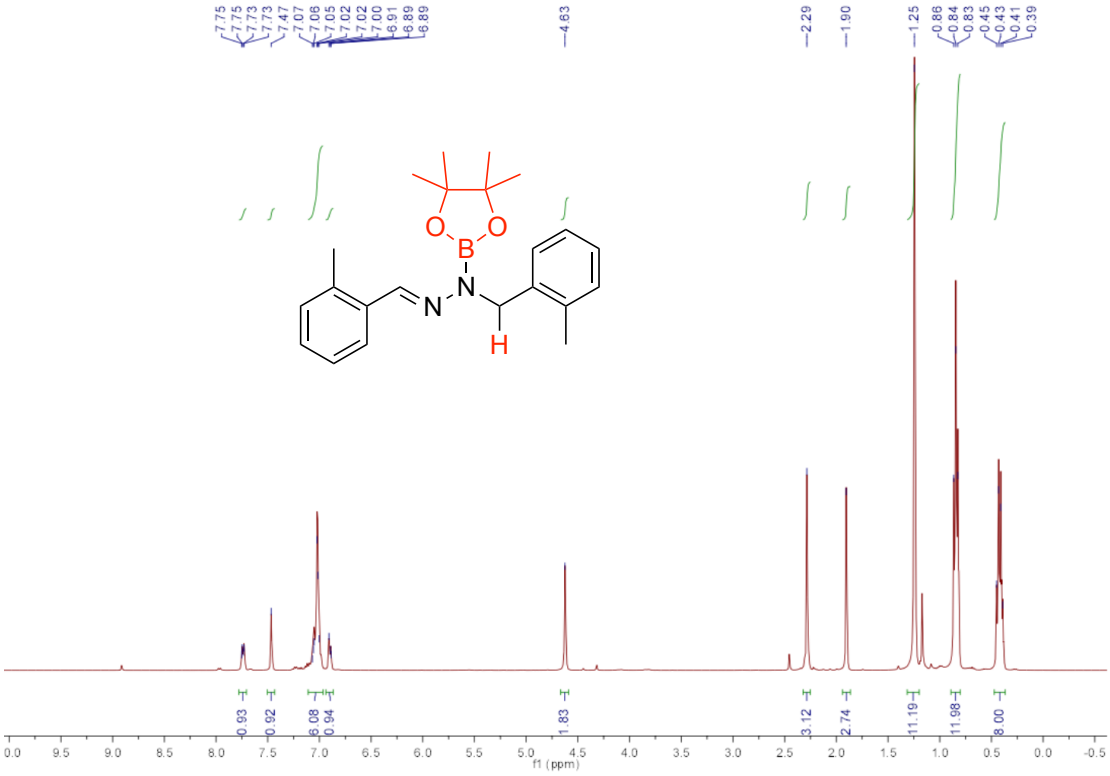
^{1}H NMR spectrum of (*E*)-1-benzyl-2-benzylidene-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2a**, 400 MHz, $CDCl_3$):



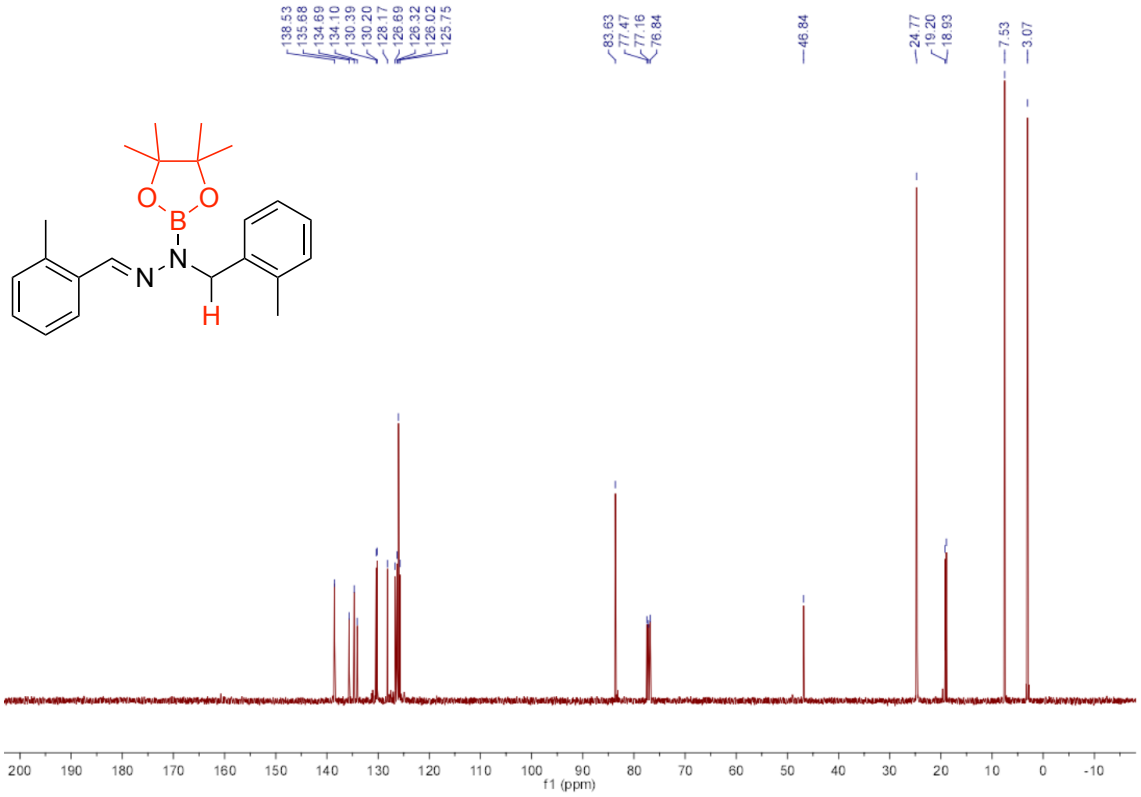
^{13}C NMR spectrum of (*E*)-1-benzyl-2-benzylidene-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2a**, 100.6 MHz, $CDCl_3$):



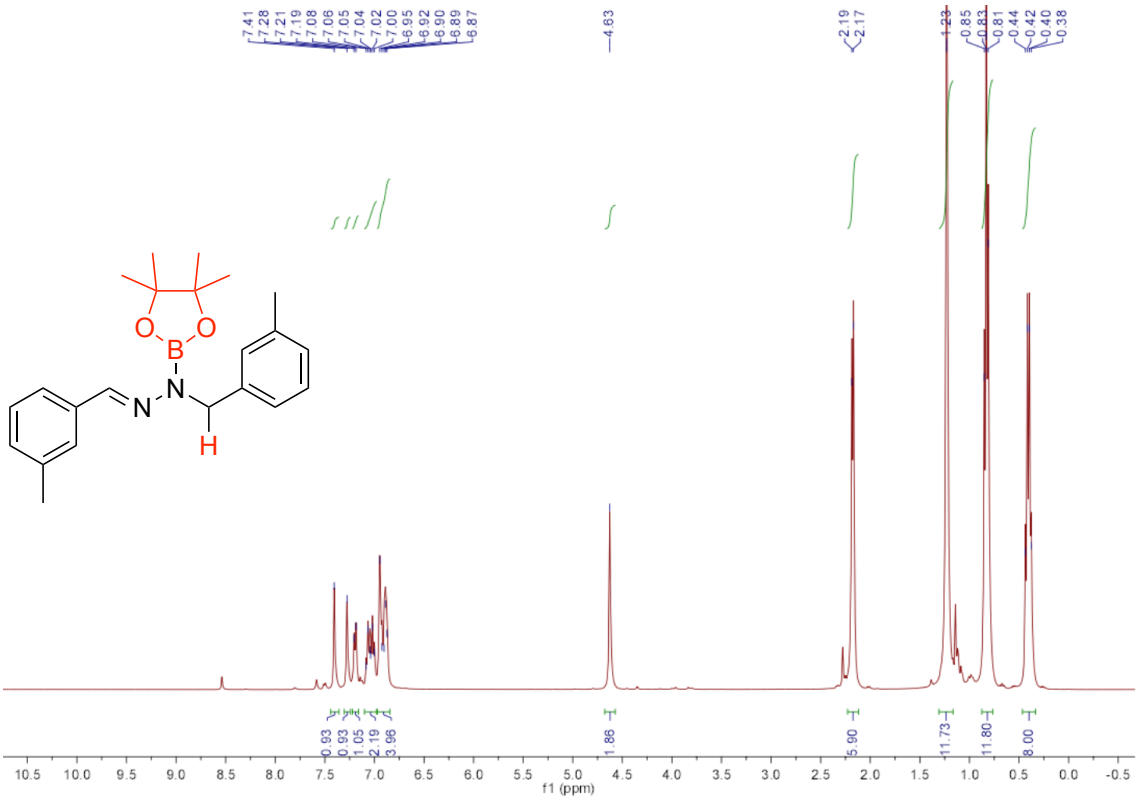
^{1}H NMR spectrum of (*E*)-1-(2-methylbenzyl)-2-(2-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2b**, 400 MHz, $CDCl_3$):



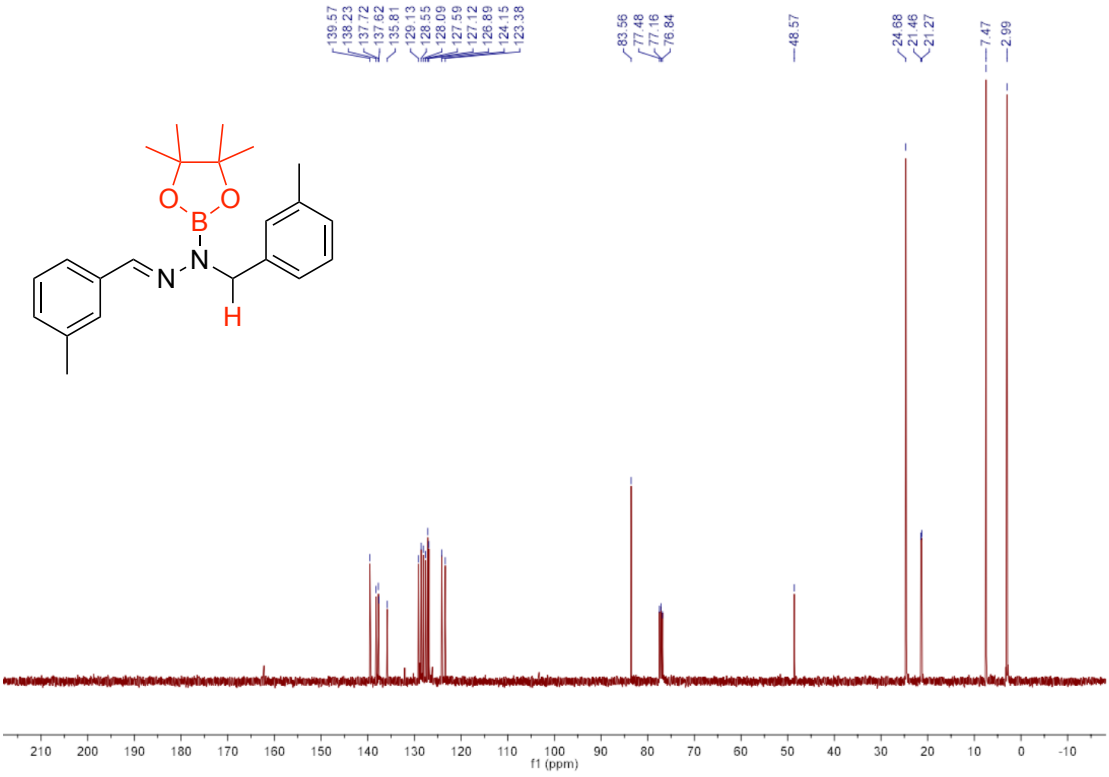
^{13}C NMR spectrum of (*E*)-1-(2-methylbenzyl)-2-(2-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2b**, 100.6 MHz, $CDCl_3$):



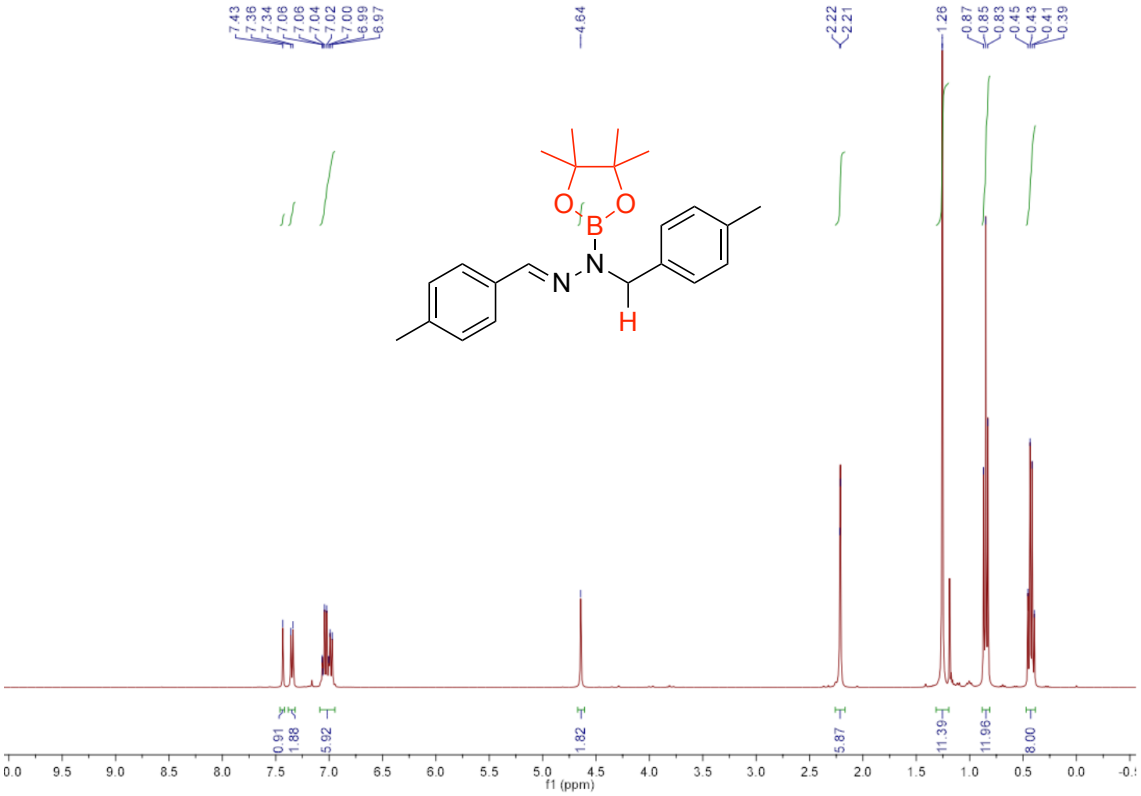
^{1}H NMR spectrum of (*E*)-1-(3-methylbenzyl)-2-(3-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2c**, 400 MHz, $CDCl_3$):



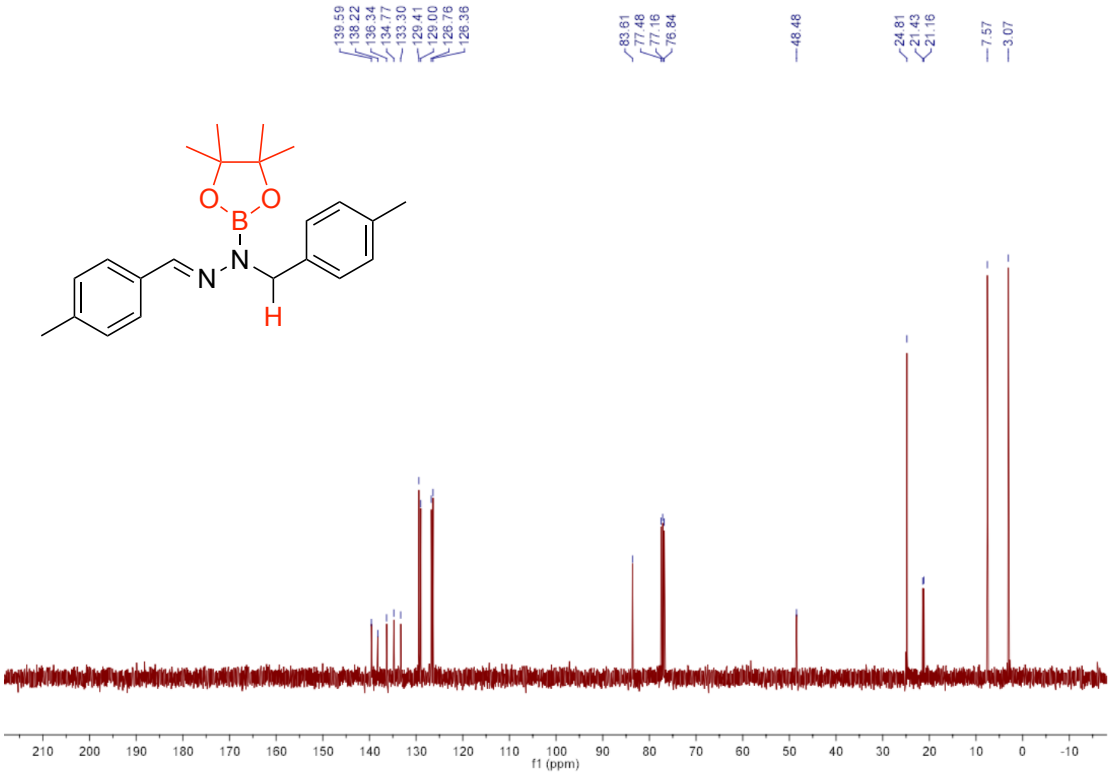
^{13}C NMR spectrum of (*E*)-1-(3-methylbenzyl)-2-(3-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2c**, 100.6 MHz, $CDCl_3$):



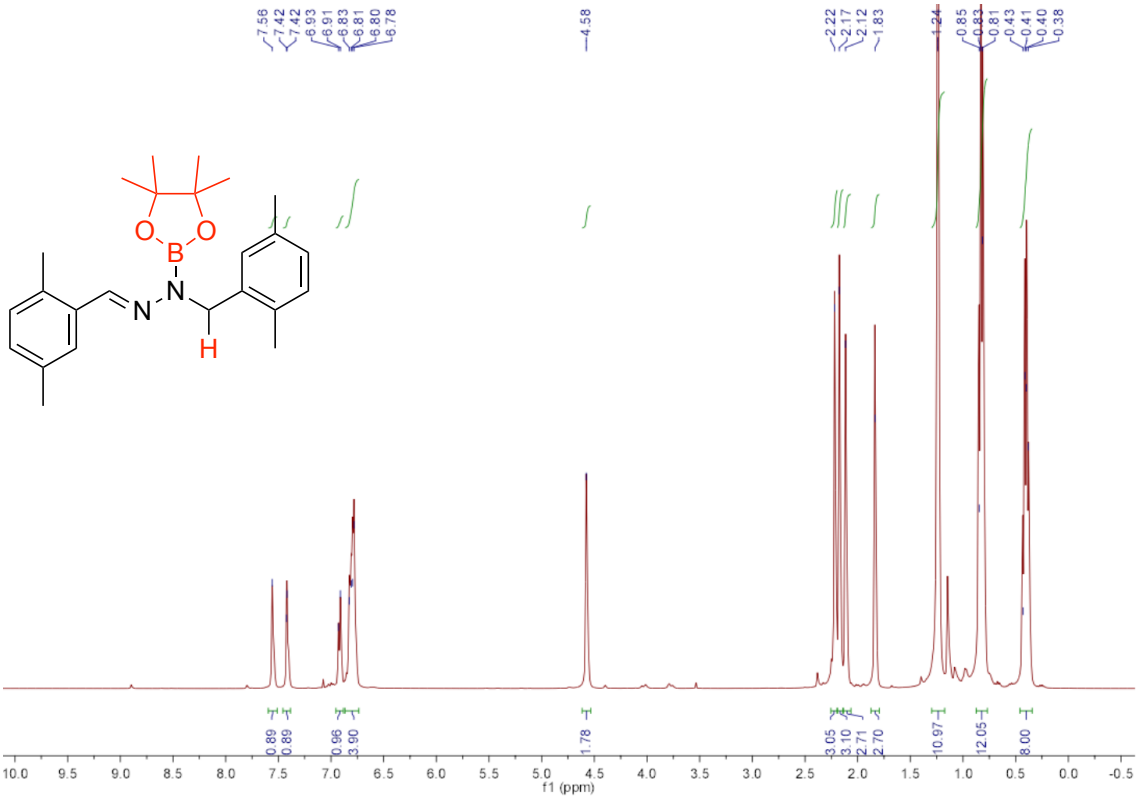
^{1}H NMR spectrum of (*E*)-1-(4-methylbenzyl)-2-(4-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2d**, 400 MHz, $CDCl_3$):



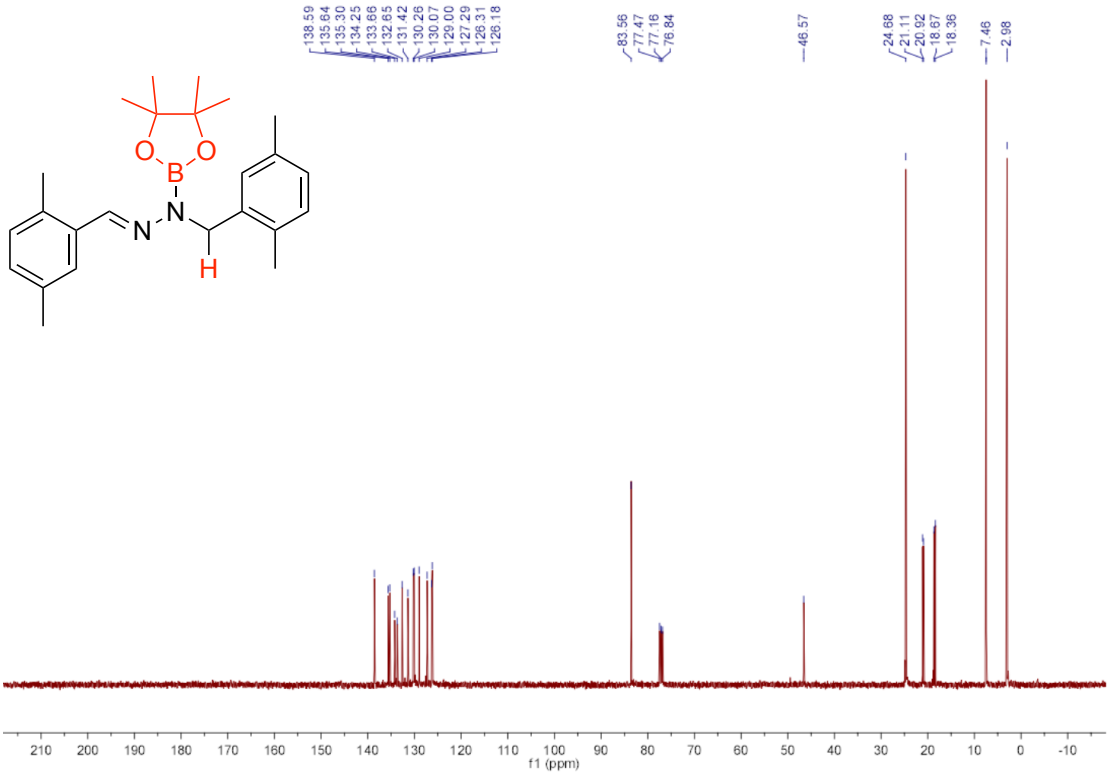
^{13}C NMR spectrum of (*E*)-1-(4-methylbenzyl)-2-(4-methylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2d**, 100.6 MHz, $CDCl_3$):



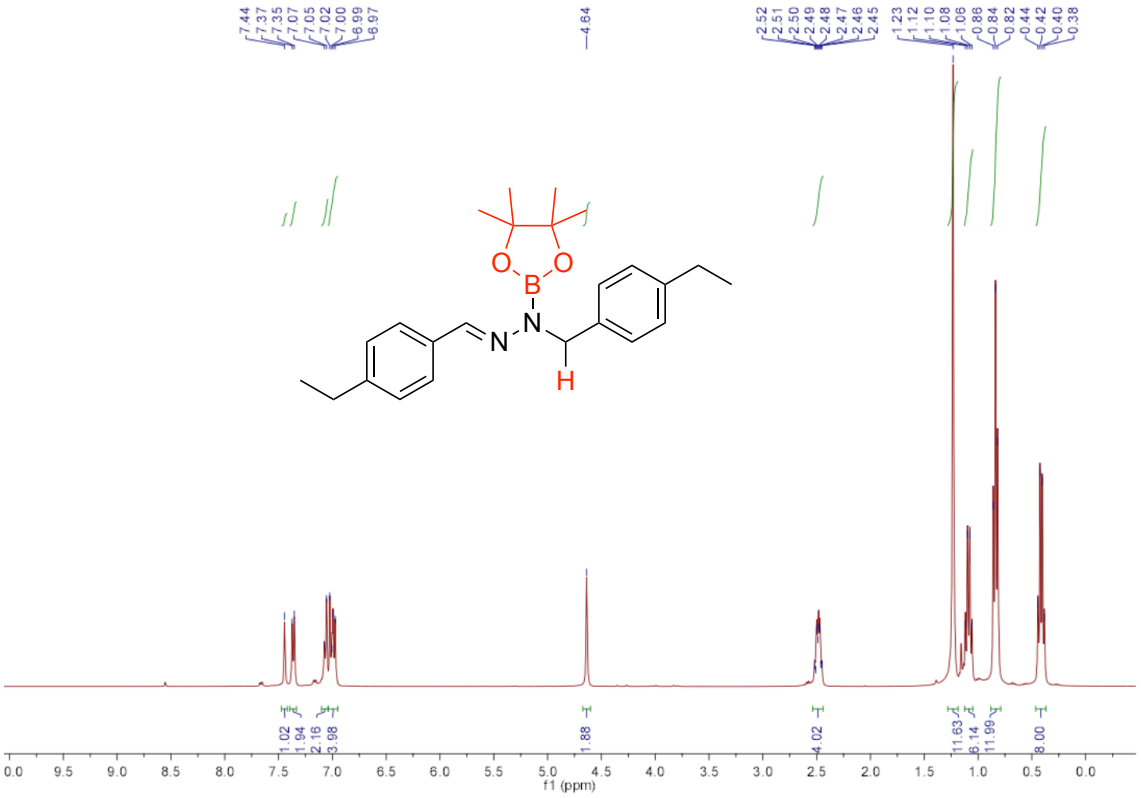
^{1}H NMR spectrum of (*E*)-1-(2,5-dimethylbenzyl)-2-(2,5-dimethylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2e**, 400 MHz, $CDCl_3$):



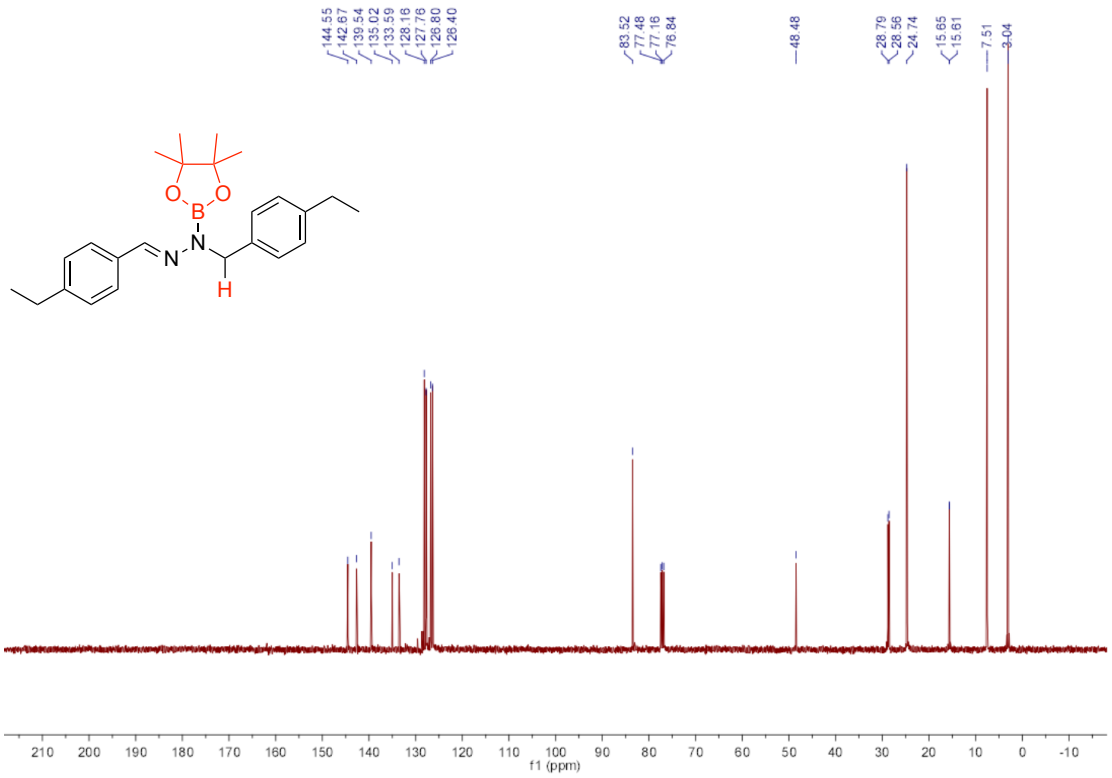
^{13}C NMR spectrum of (*E*)-1-(2,5-dimethylbenzyl)-2-(2,5-dimethylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2e**, 100.6 MHz, $CDCl_3$):



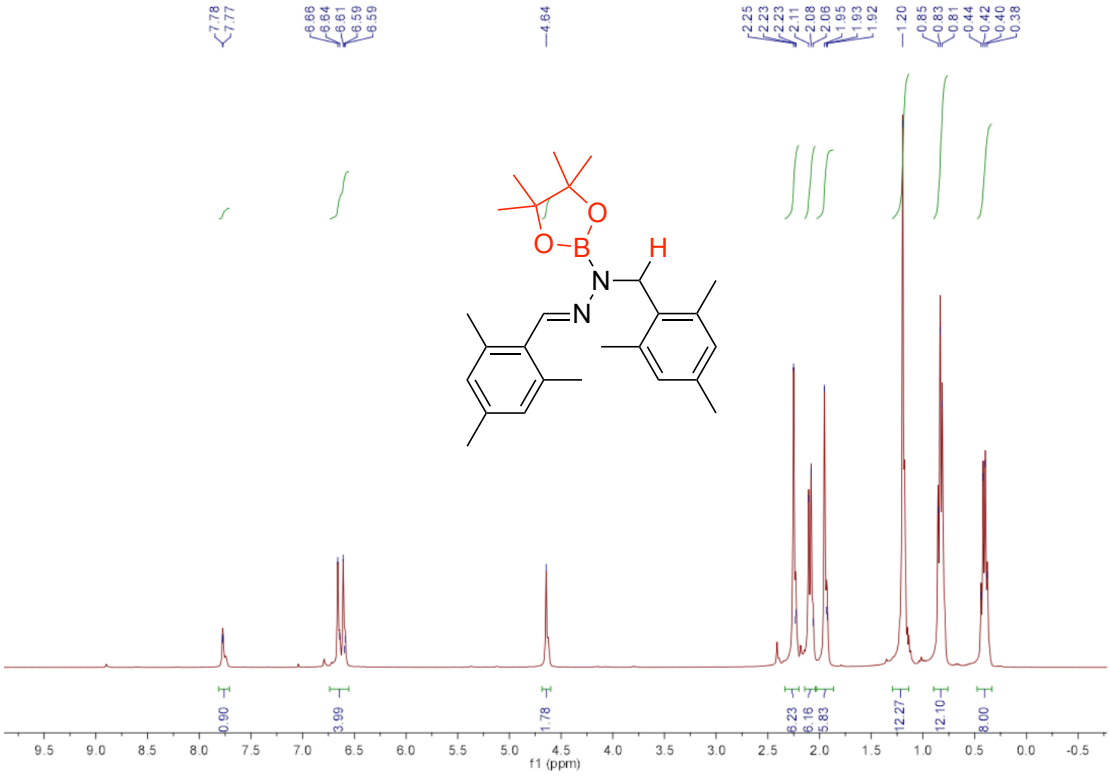
^{1}H NMR spectrum of (*E*)-1-(4-ethylbenzyl)-2-(4-ethylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2f**, 400 MHz, $CDCl_3$):



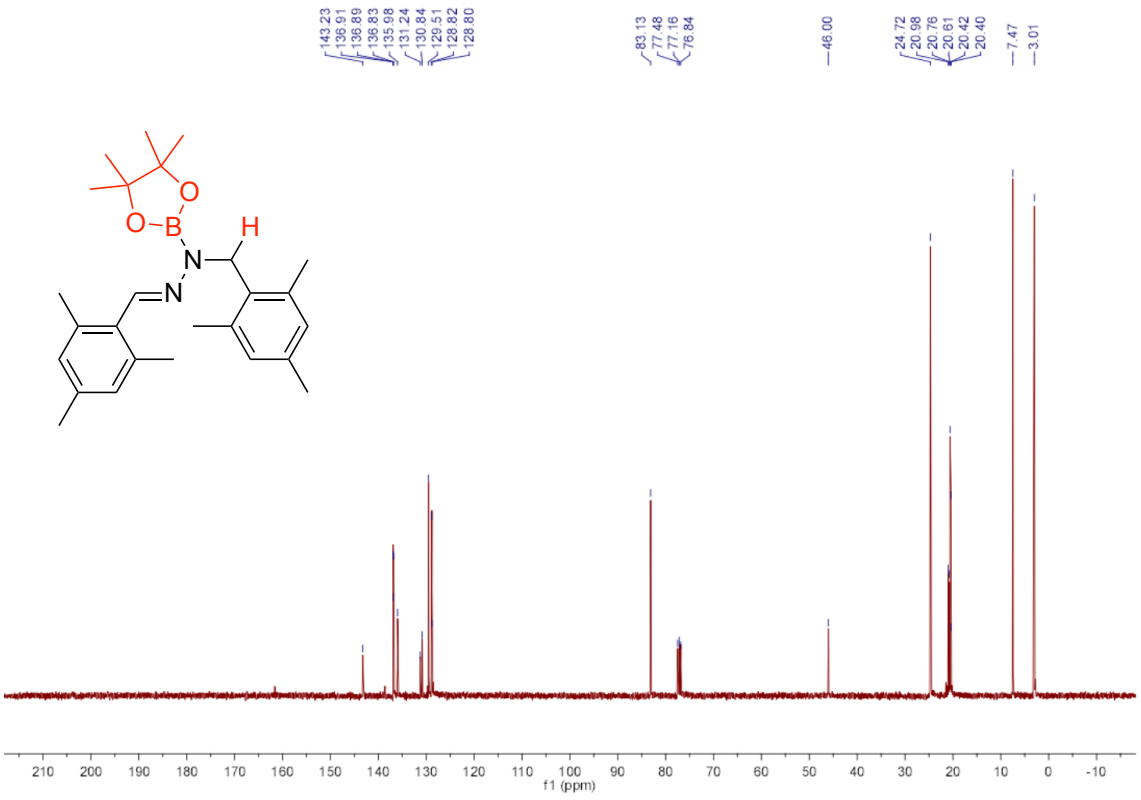
^{13}C NMR spectrum of (*E*)-1-(4-ethylbenzyl)-2-(4-ethylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2f**, 100.6 MHz, $CDCl_3$):



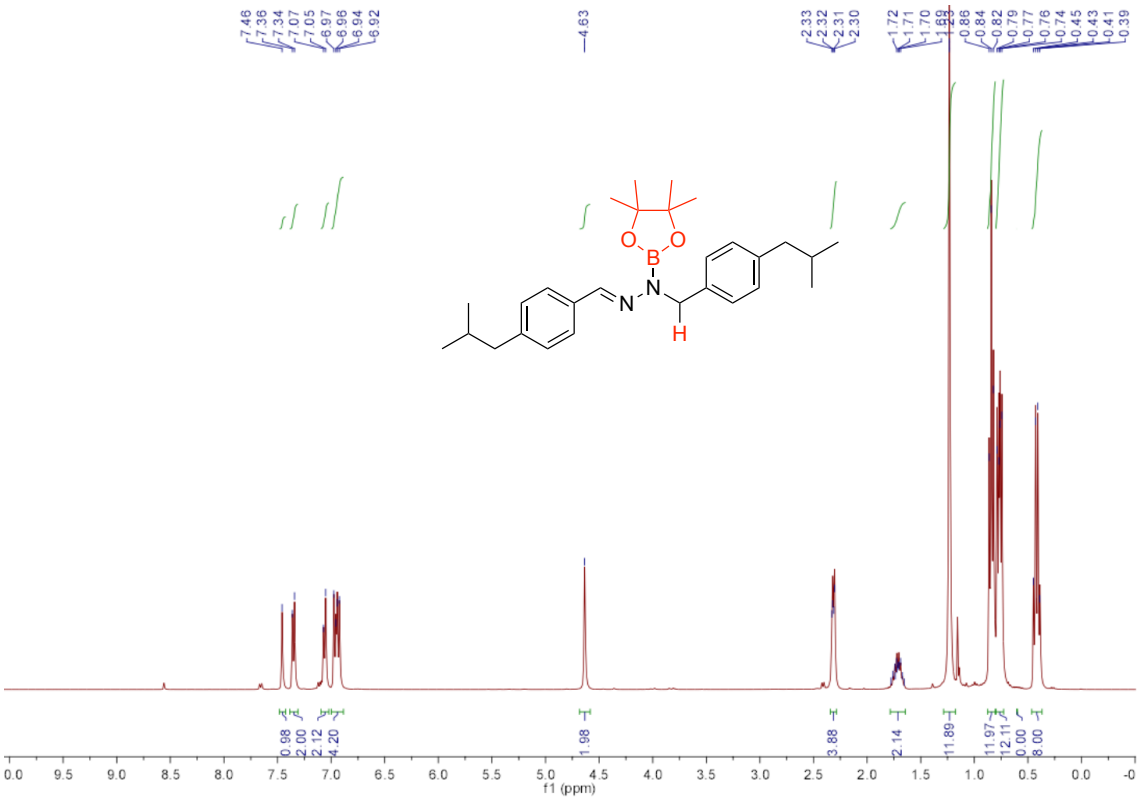
^{1}H NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(2,4,6-trimethylbenzyl)-2-(2,4,6-trimethylbenzylidene)hydrazine (**2g**, 400 MHz, $CDCl_3$):



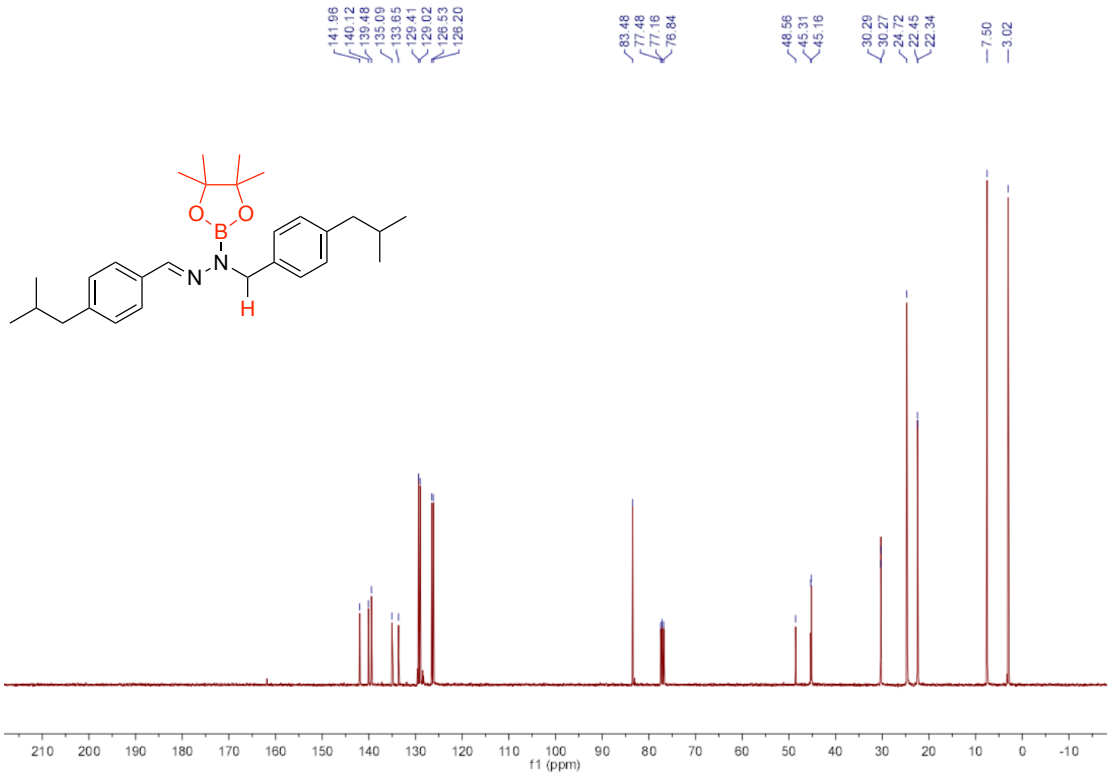
^{13}C NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(2,4,6-trimethylbenzyl)-2-(2,4,6-trimethylbenzylidene)hydrazine (**2g**, 100.6 MHz, $CDCl_3$):



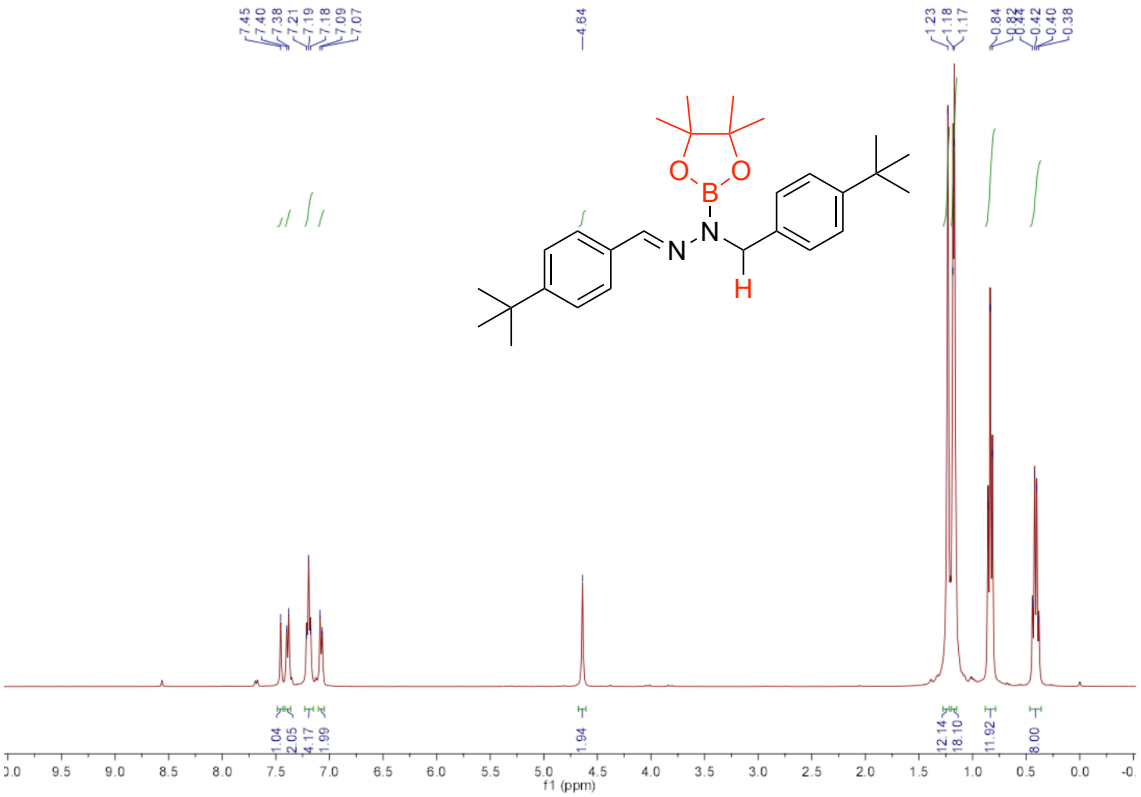
^{1}H NMR spectrum of (*E*)-1-(4-isobutylbenzyl)-2-(4-isobutylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan-2-yl)hydrazine (**2h**, 400 MHz, $CDCl_3$):



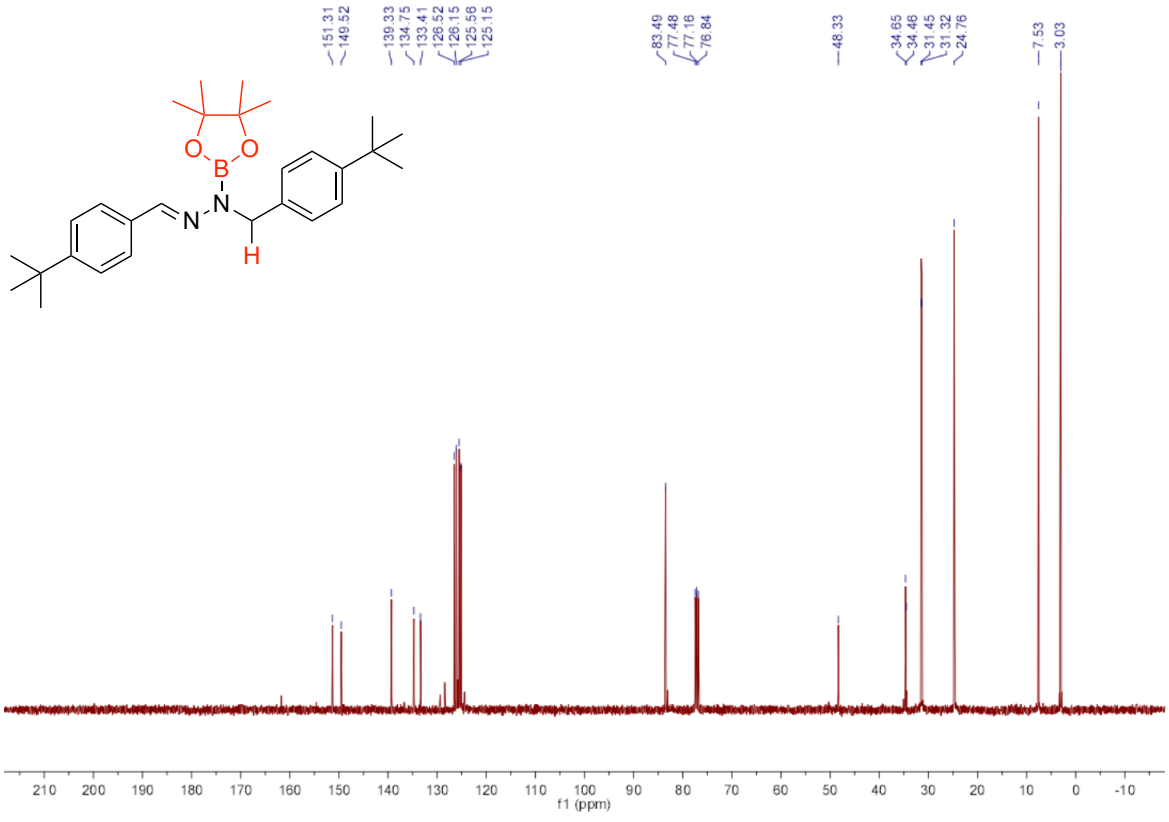
^{13}C NMR spectrum of (*E*)-1-(4-isobutylbenzyl)-2-(4-isobutylbenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan-2-yl)hydrazine (**2h**, 100.6 MHz, $CDCl_3$):



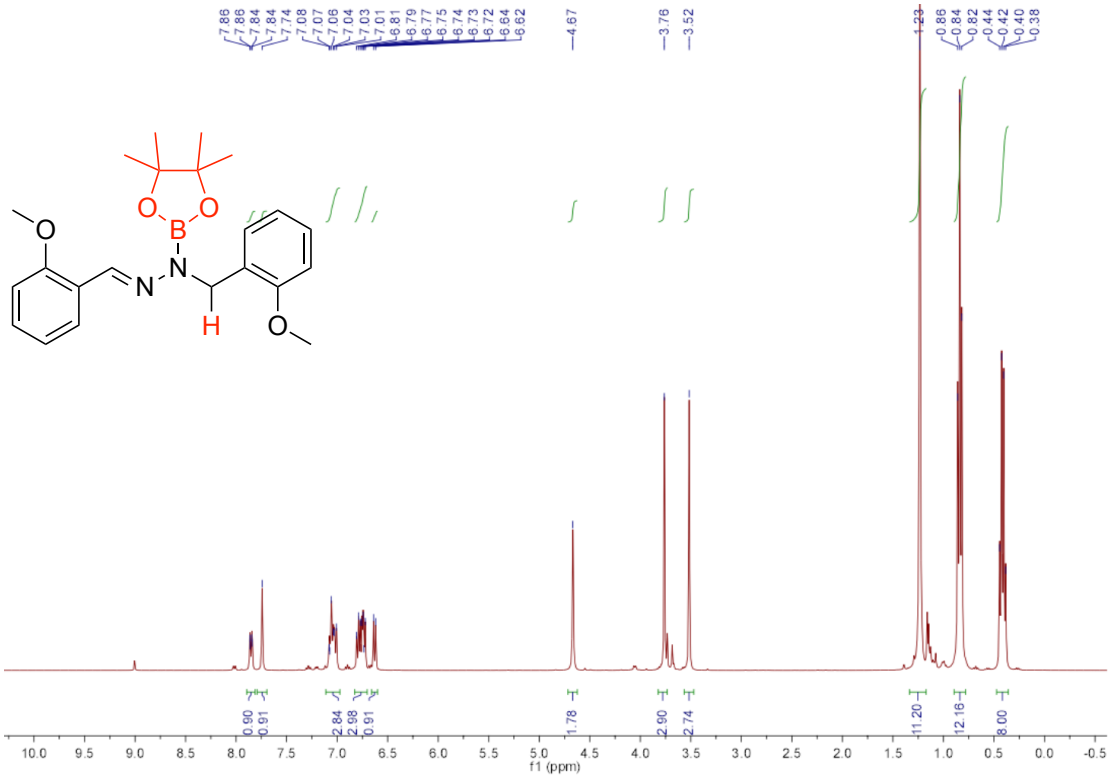
^{1}H NMR spectrum of (*E*)-1-(4-(tert-butyl)benzyl)-2-(4-(tert-butyl)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2i**, 400 MHz, $CDCl_3$):



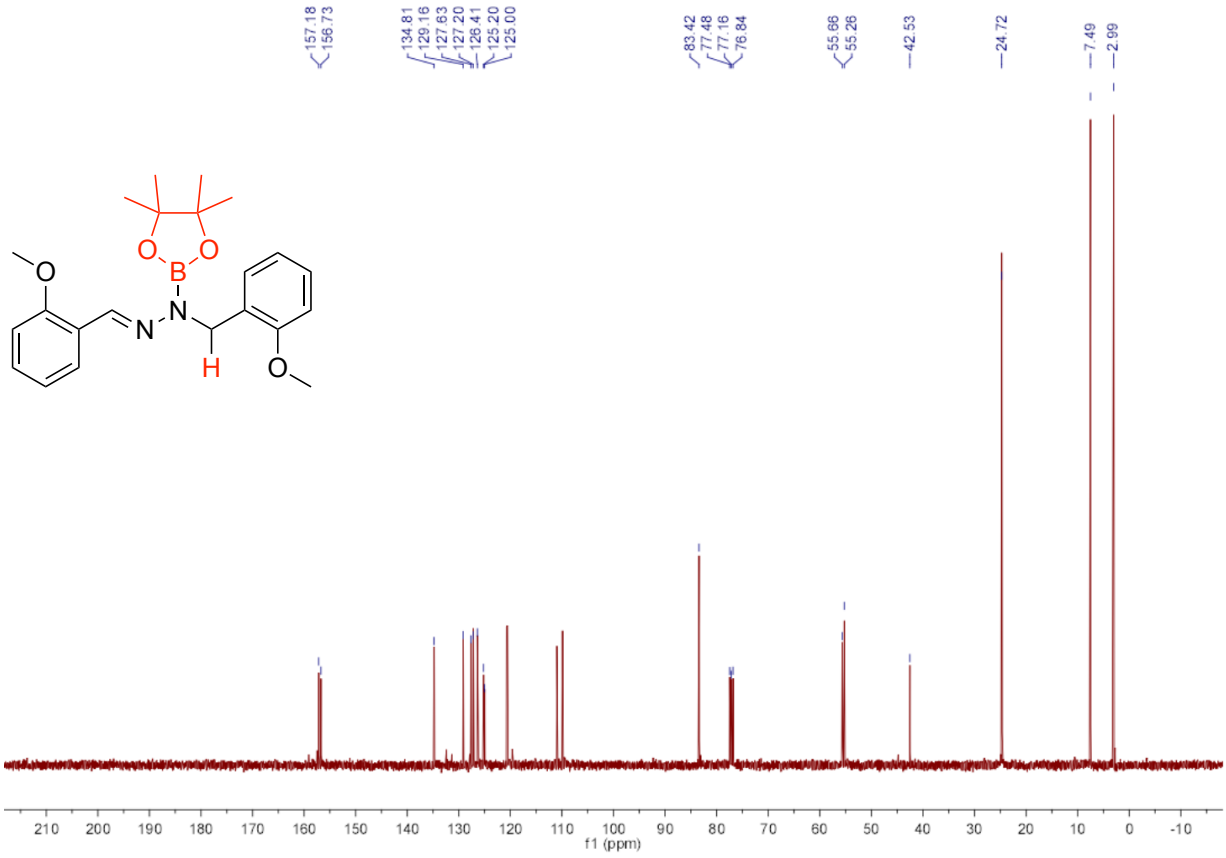
^{13}C NMR spectrum of (*E*)-1-(4-(tert-butyl)benzyl)-2-(4-(tert-butyl)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2i**, 100.6 MHz, $CDCl_3$):



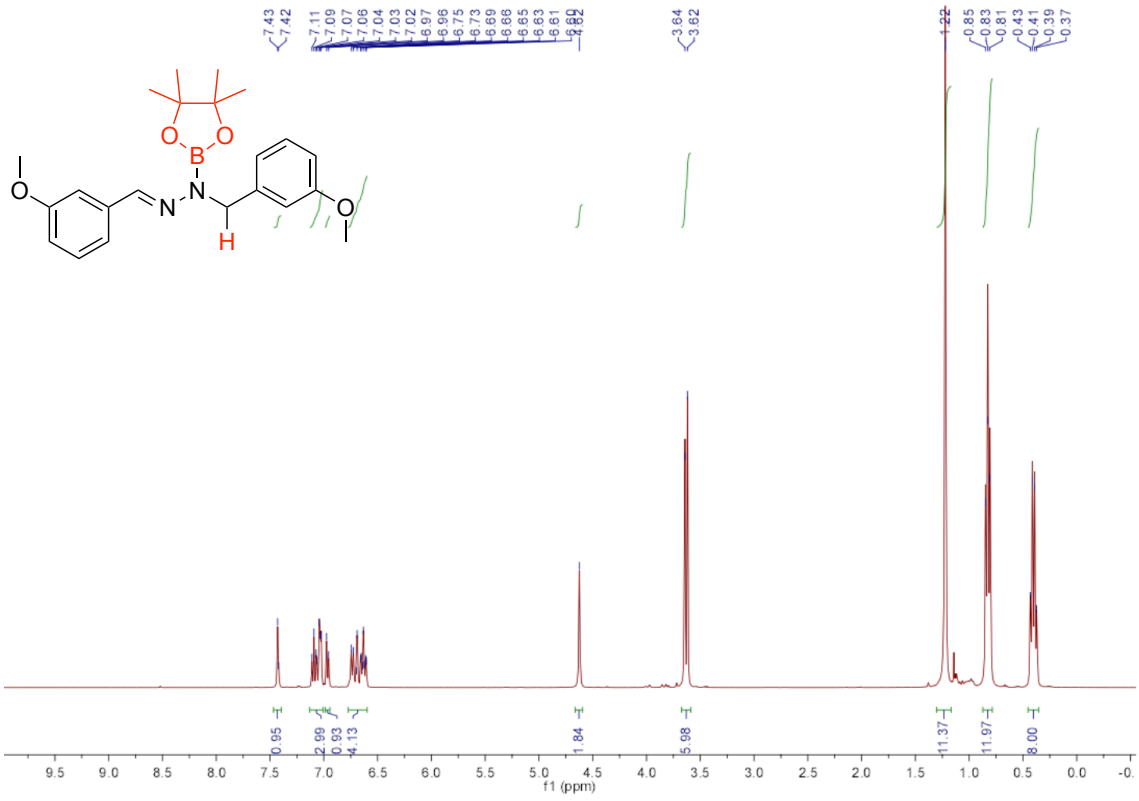
^{1}H NMR spectrum of (*E*)-1-(2-methoxybenzyl)-2-(2-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2j**, 400 MHz, $CDCl_3$):



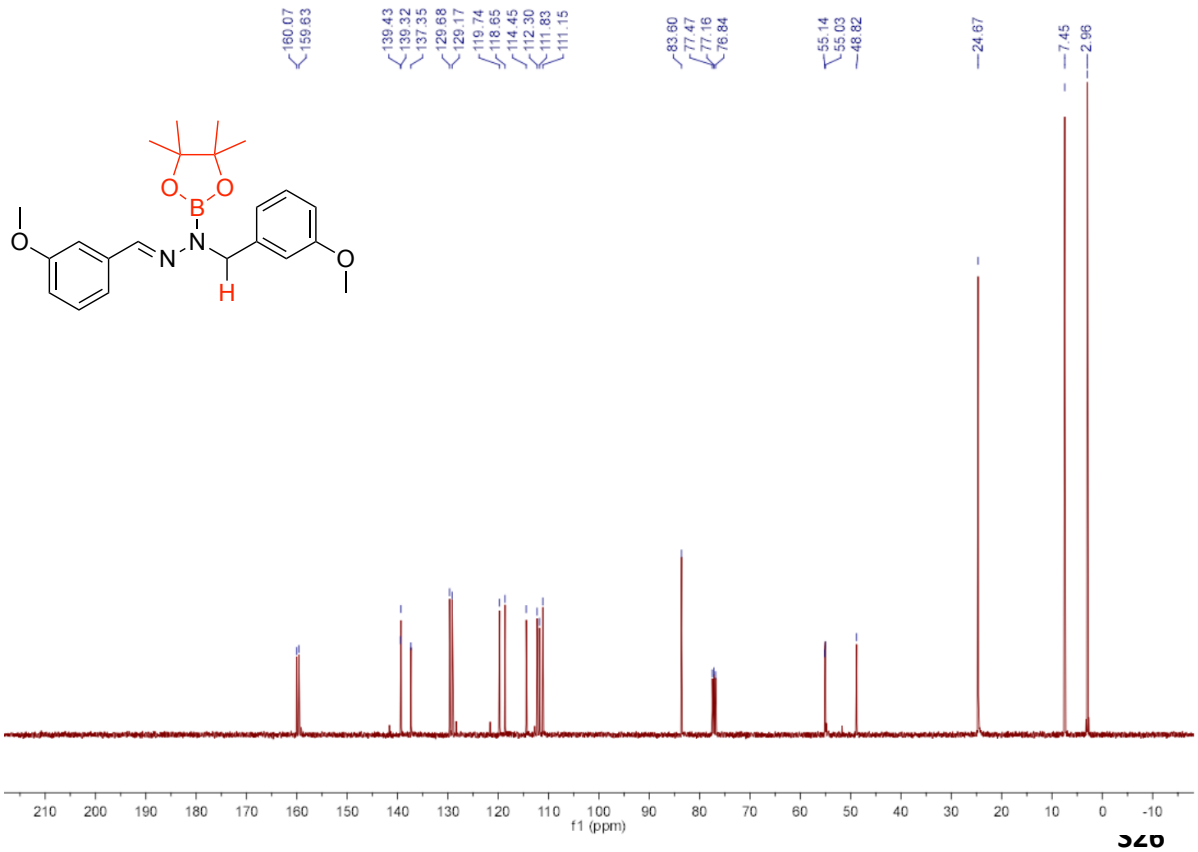
^{13}C NMR spectrum of (*E*)-1-(2-methoxybenzyl)-2-(2-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2j**, 100.6 MHz, $CDCl_3$):



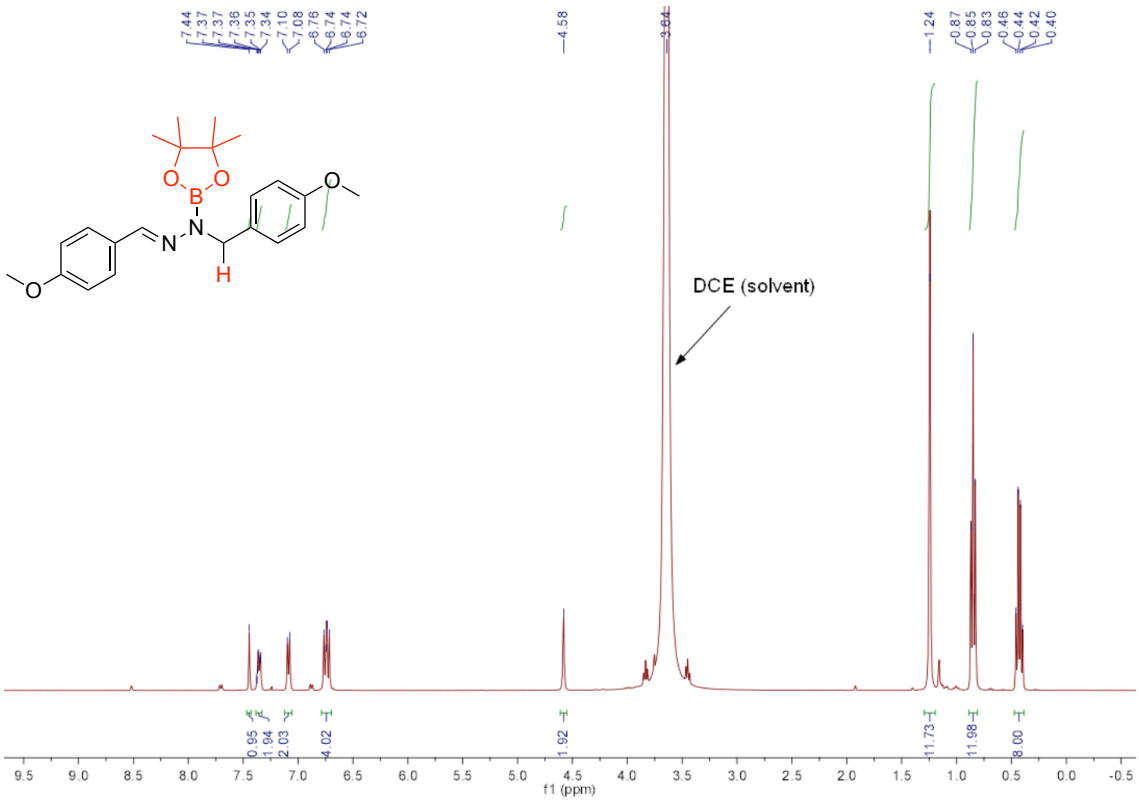
^{1}H NMR spectrum of (*E*)-1-(3-methoxybenzyl)-2-(3-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2k**, 400 MHz, $CDCl_3$):



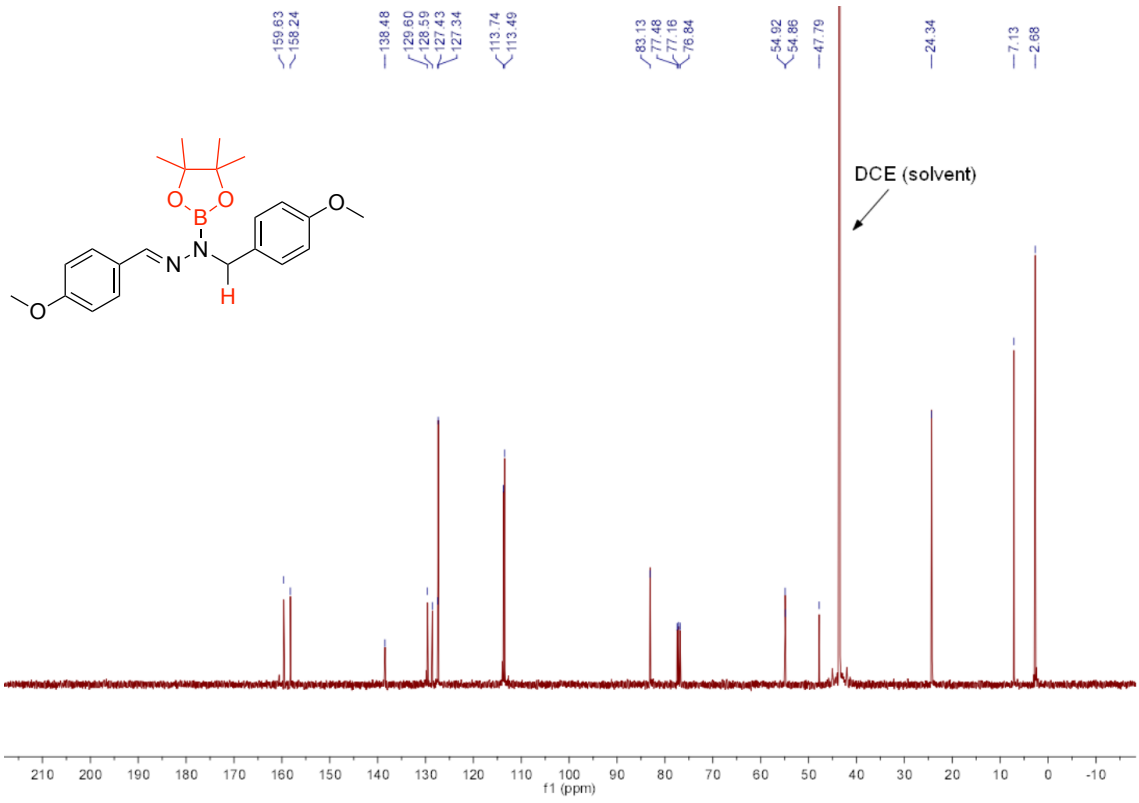
^{13}C NMR spectrum of (*E*)-1-(3-methoxybenzyl)-2-(3-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2k**, 100.6 MHz, $CDCl_3$):



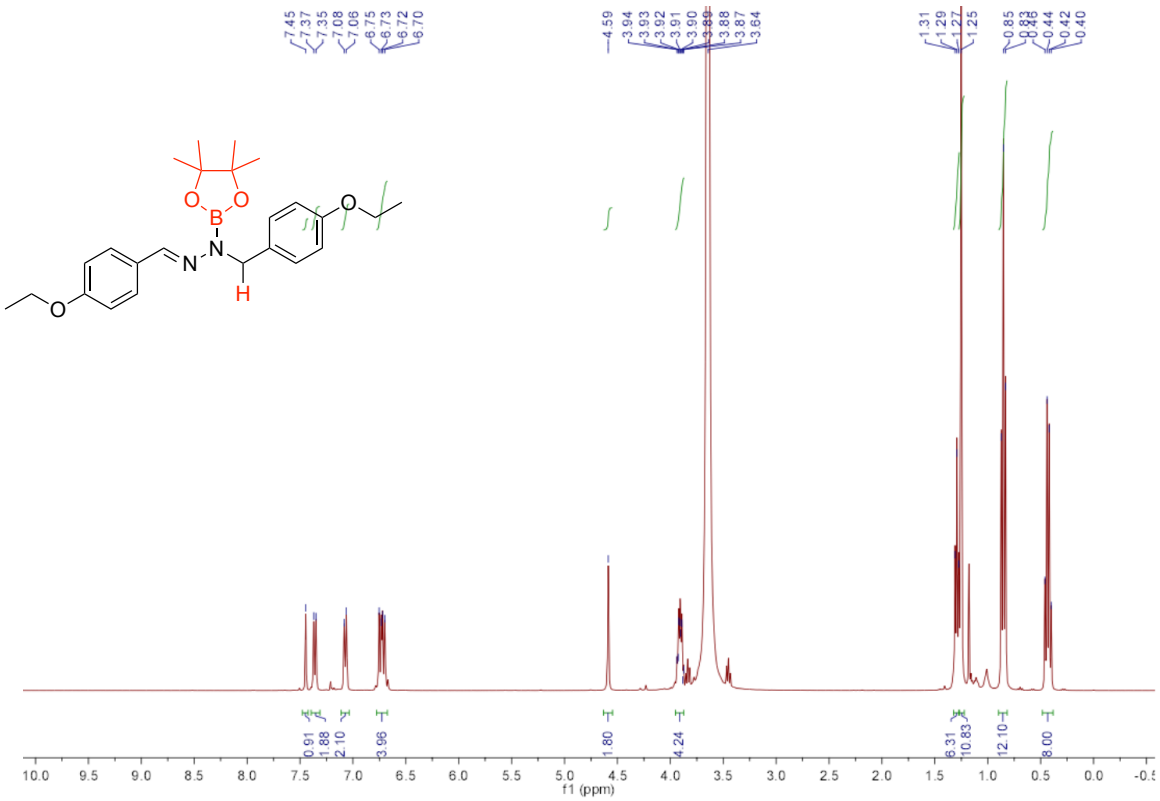
^{1}H NMR spectrum of (*E*)-1-(4-methoxybenzyl)-2-(4-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2l**, 400 MHz, $CDCl_3$):



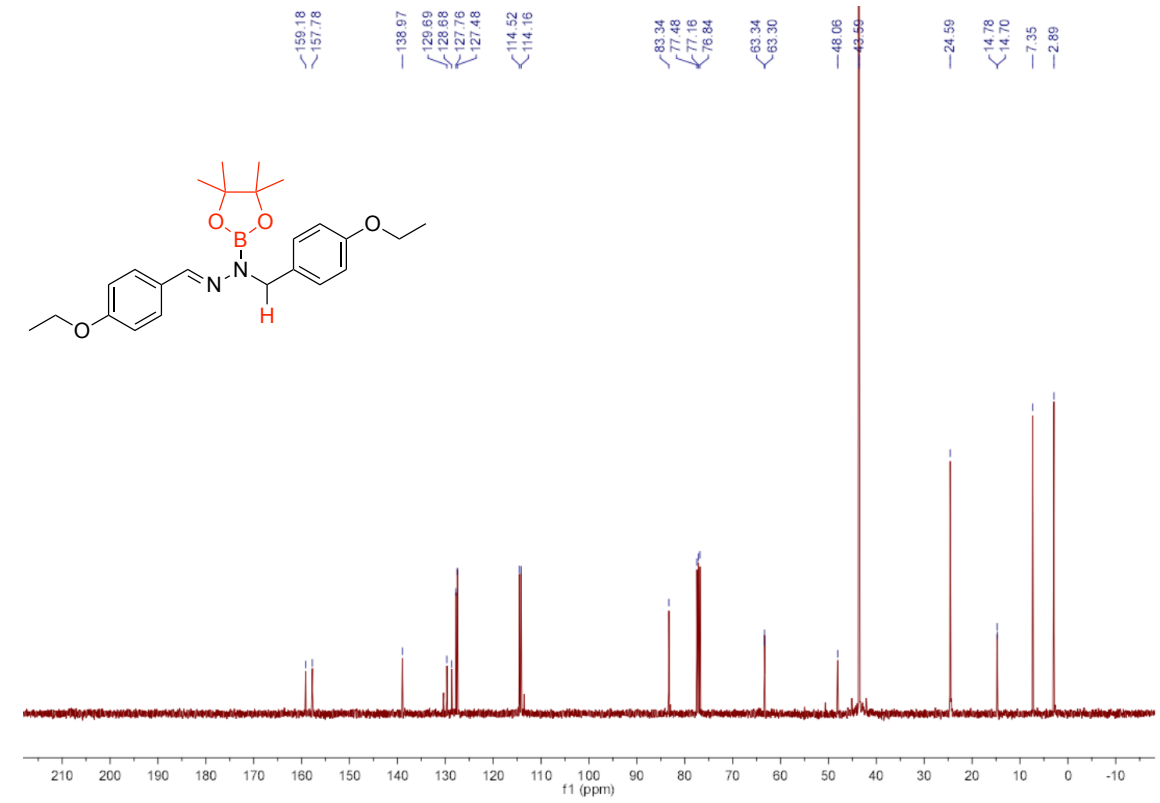
^{13}C NMR spectrum of (*E*)-1-(4-methoxybenzyl)-2-(4-methoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2l**, 100.6 MHz, $CDCl_3$):



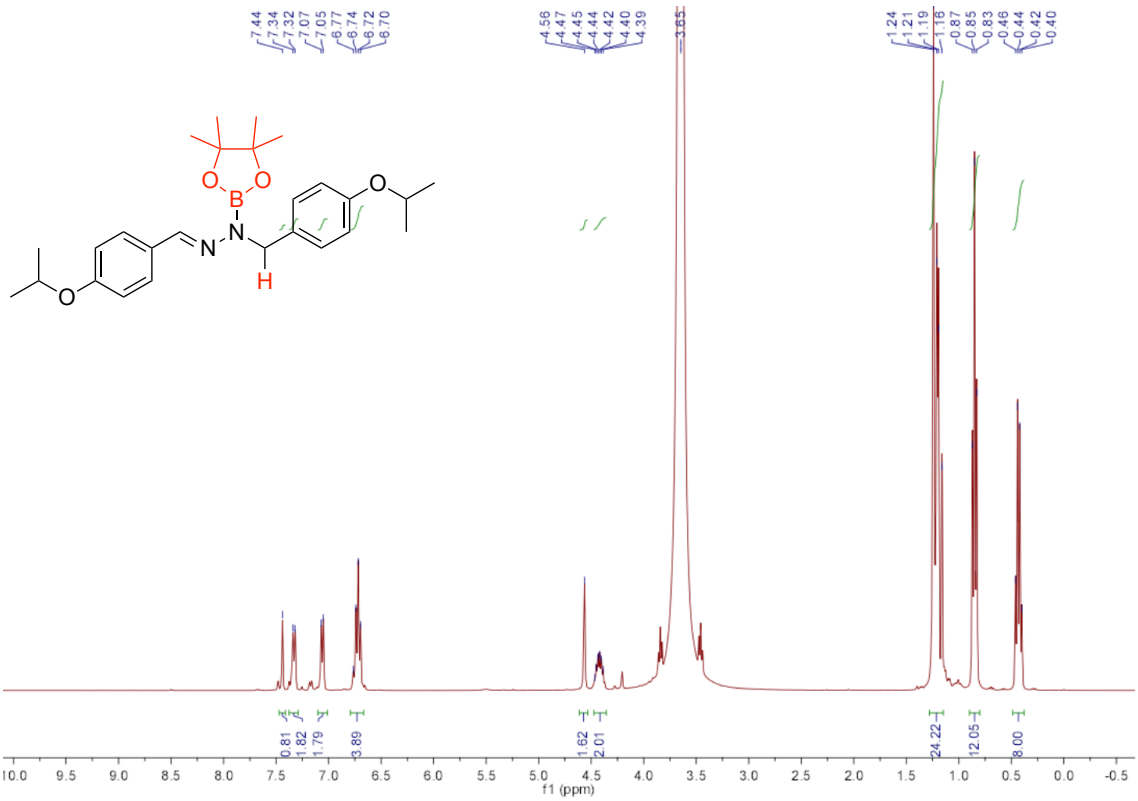
^{1}H NMR spectrum of (*E*)-1-(4-ethoxybenzyl)-2-(4-ethoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2m**, 400 MHz, $CDCl_3$):



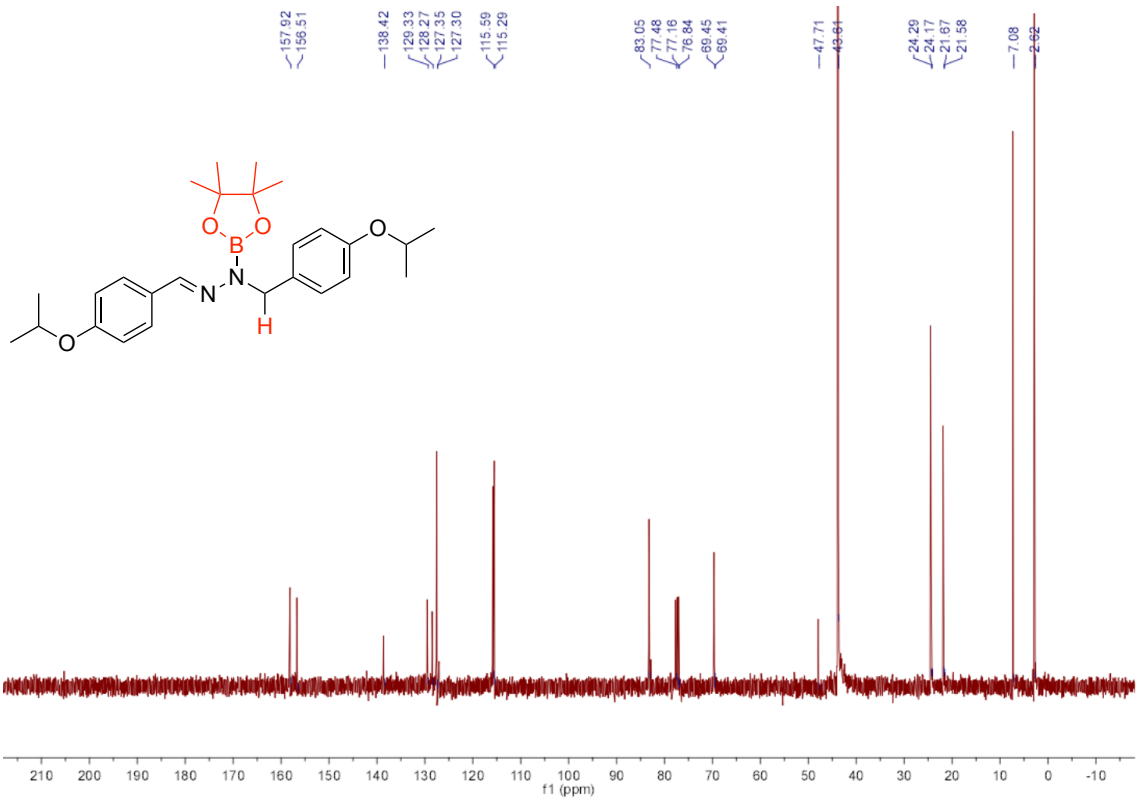
^{13}C NMR spectrum of (*E*)-1-(4-ethoxybenzyl)-2-(4-ethoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2m**, 100.6 MHz, $CDCl_3$):



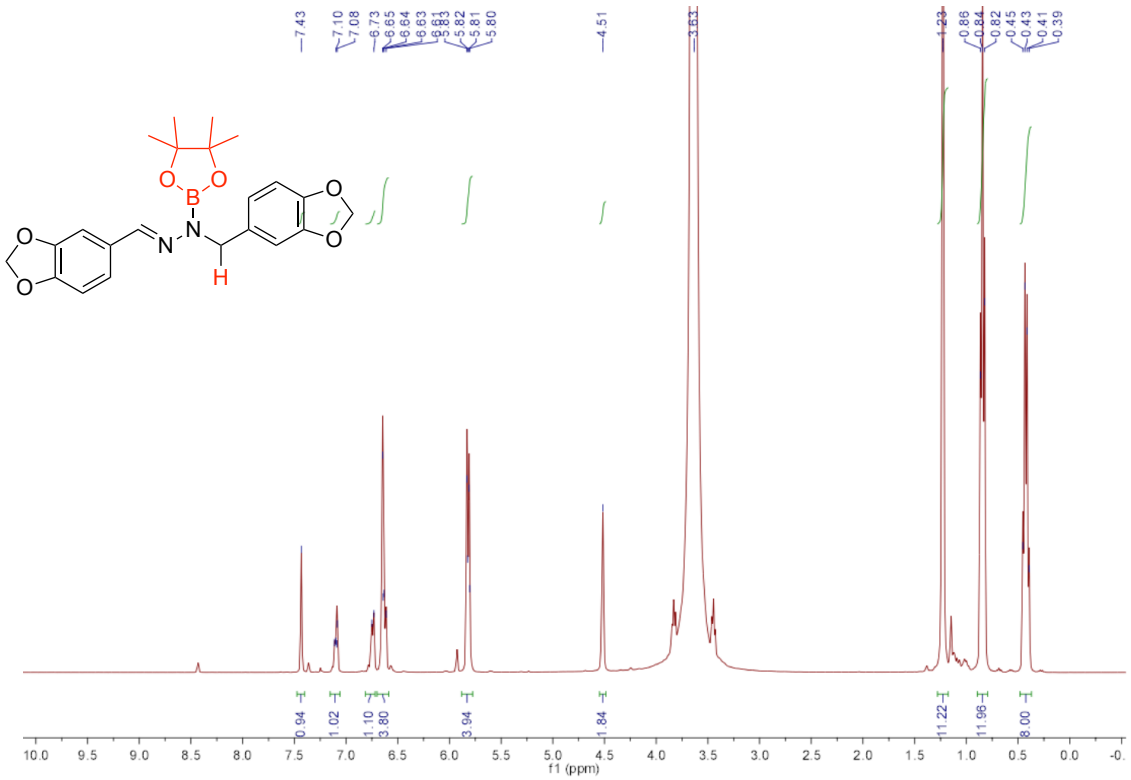
^{1}H NMR spectrum of (*E*)-1-(4-isopropoxybenzyl)-2-(4-isopropoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2n**, 400 MHz, $CDCl_3$):



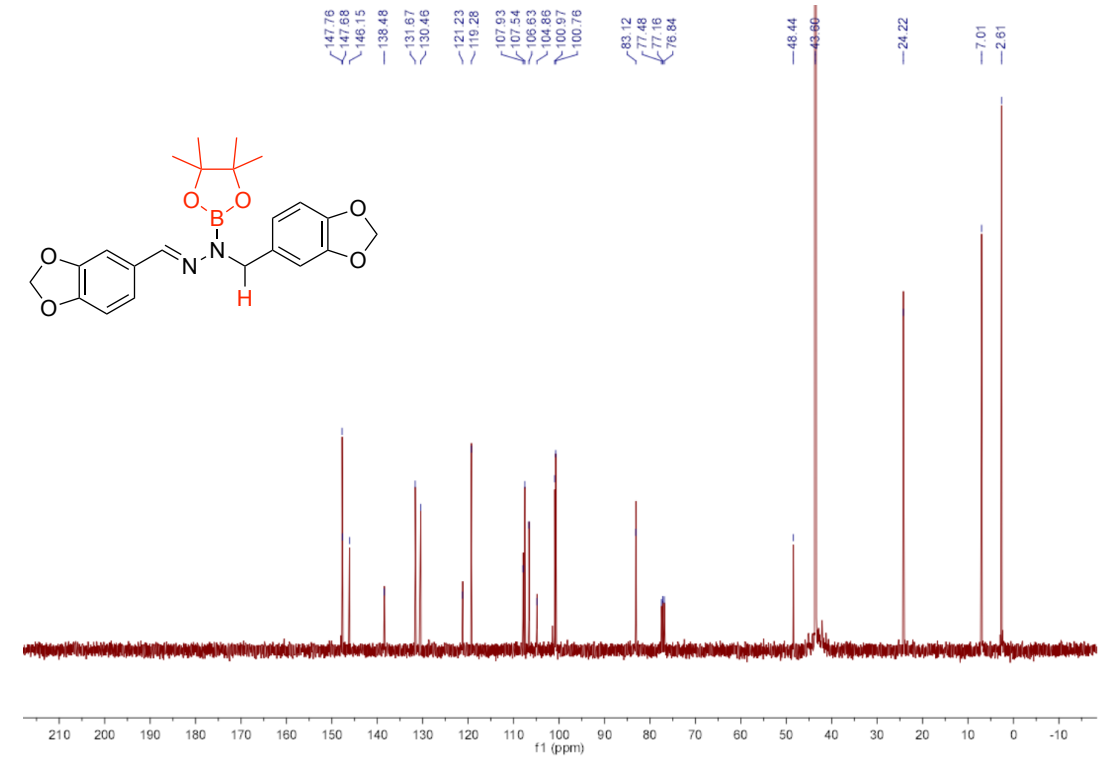
^{13}C NMR spectrum of (*E*)-1-(4-isopropoxybenzyl)-2-(4-isopropoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2n**, 100.6 MHz, $CDCl_3$):



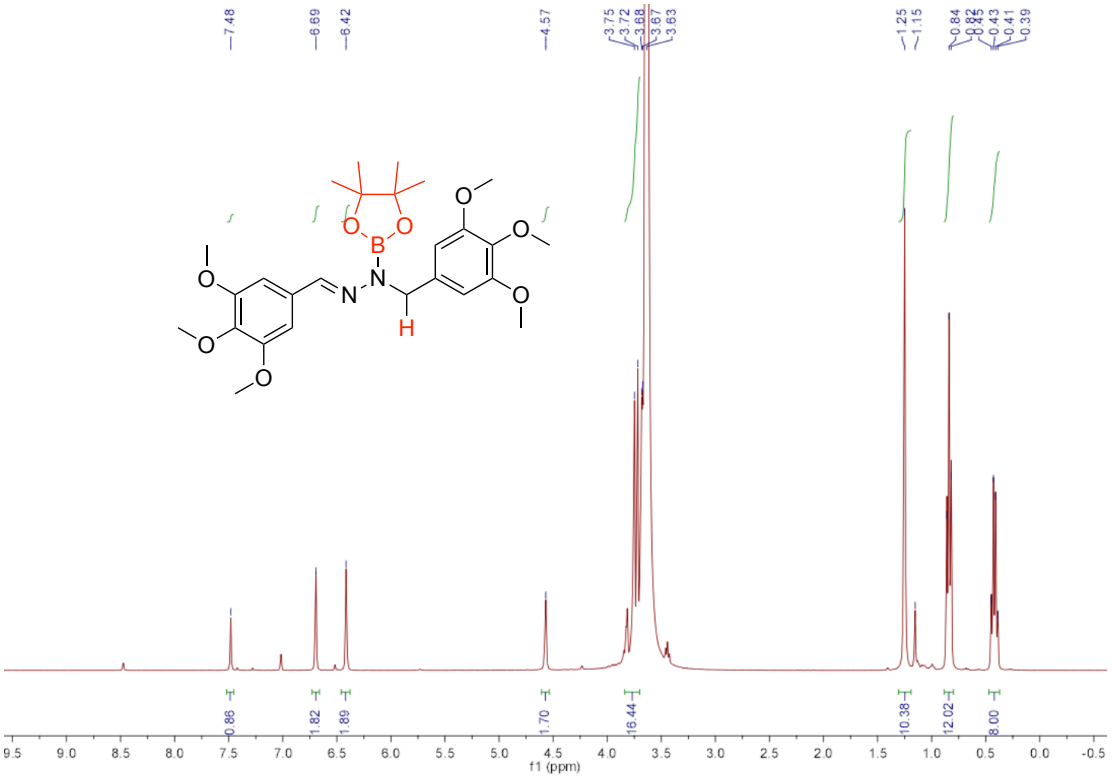
^{1}H NMR spectrum of (*E*)-1-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzo[d][1,3]dioxol-5-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2o**, 400 MHz, $CDCl_3$):



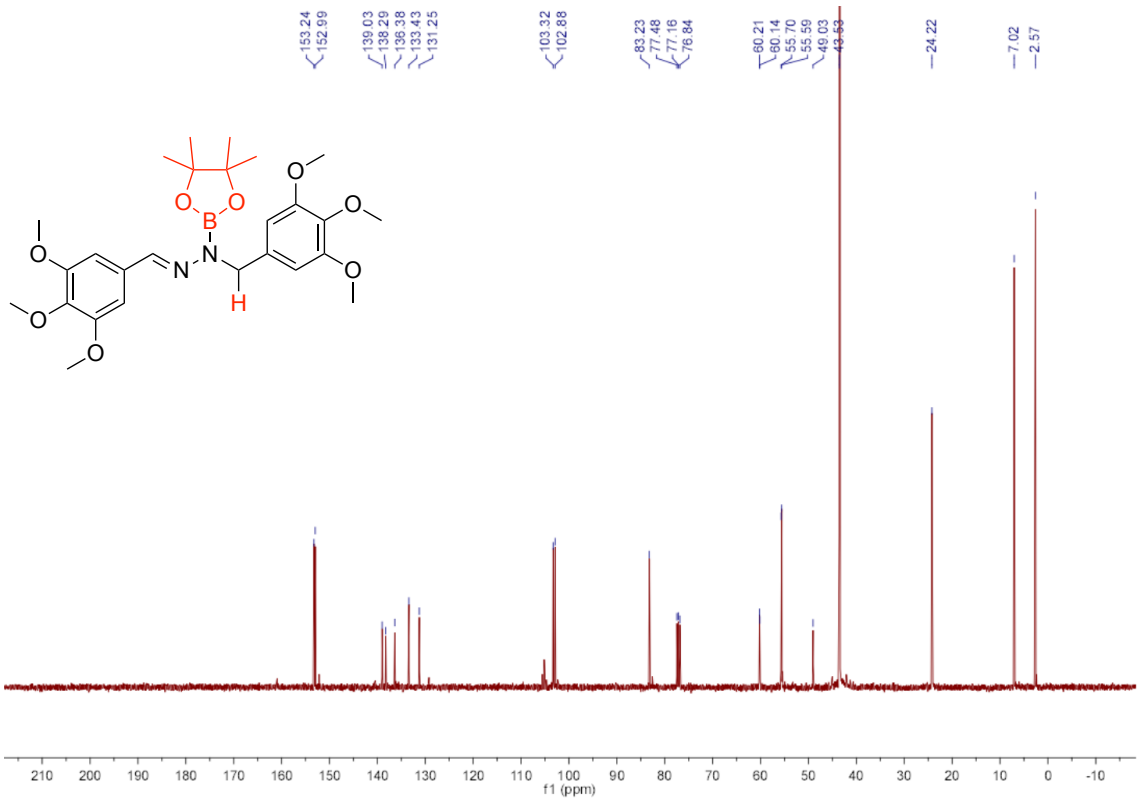
^{13}C NMR spectrum of (*E*)-1-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzo[d][1,3]dioxol-5-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2o**, 100.6 MHz, $CDCl_3$):



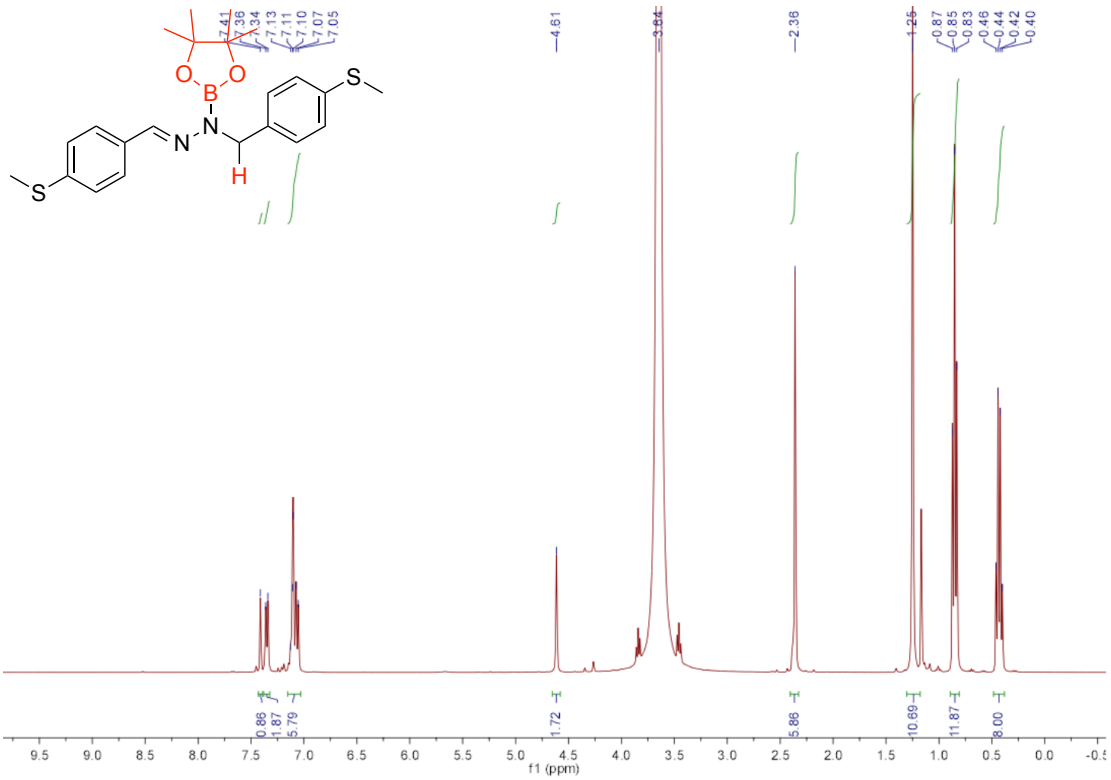
^{1}H NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3,4,5-trimethoxybenzyl)-2-(3,4,5-trimethoxybenzylidene)hydrazine (**2p**, 400 MHz, $CDCl_3$):



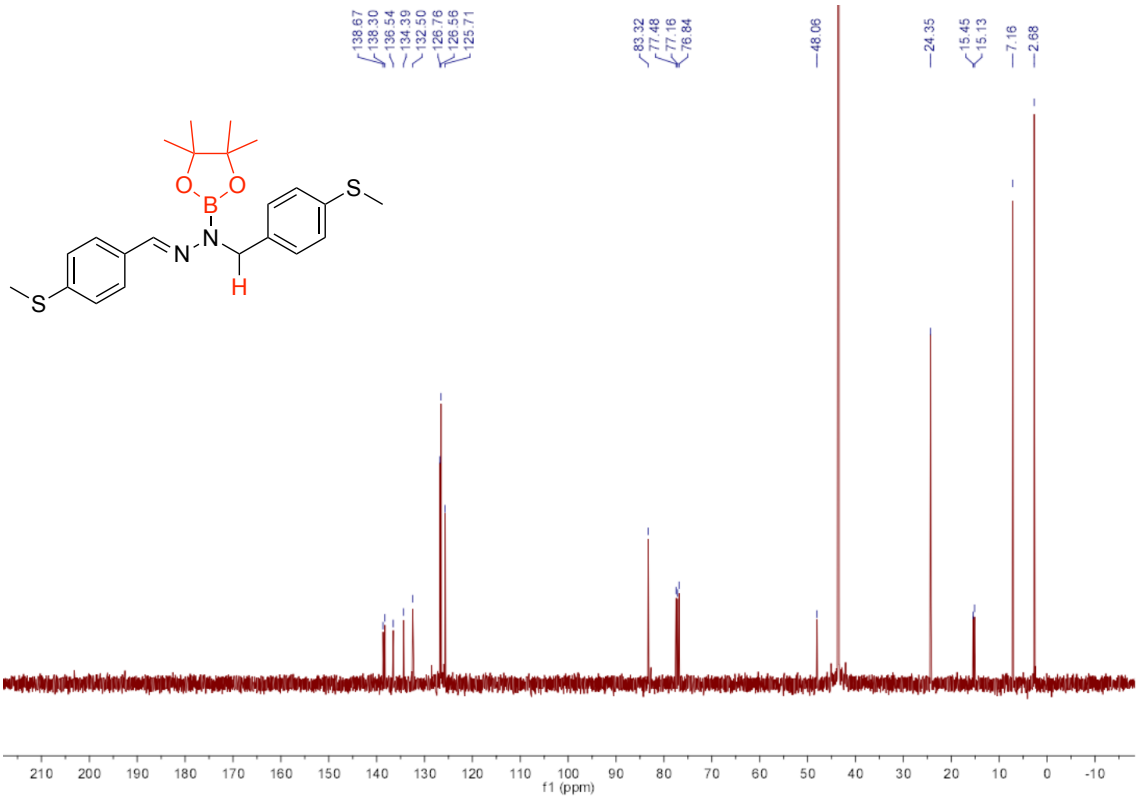
^{13}C NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3,4,5-trimethoxybenzyl)-2-(3,4,5-trimethoxybenzylidene)hydrazine (**2p**, 100.6 MHz, $CDCl_3$):



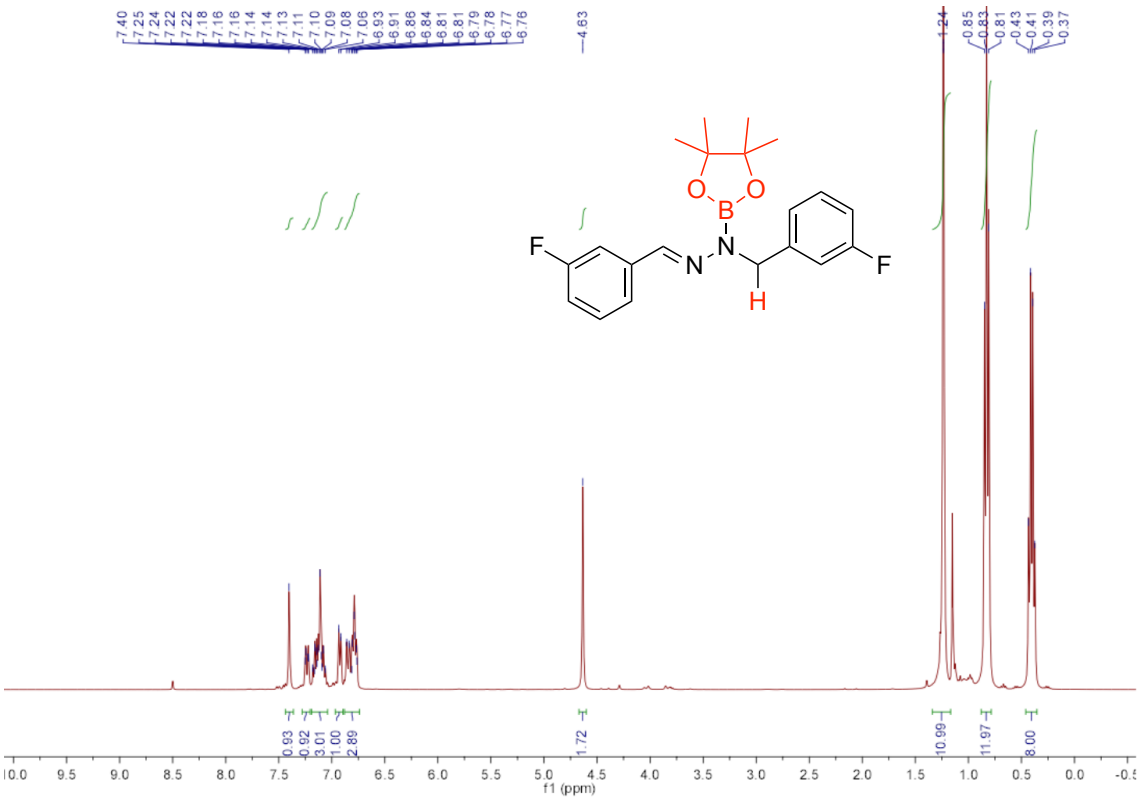
^{1}H NMR spectrum of (*E*)-1-(4-(methylthio)benzyl)-2-(4-(methylthio)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2q**, 400 MHz, $CDCl_3$):



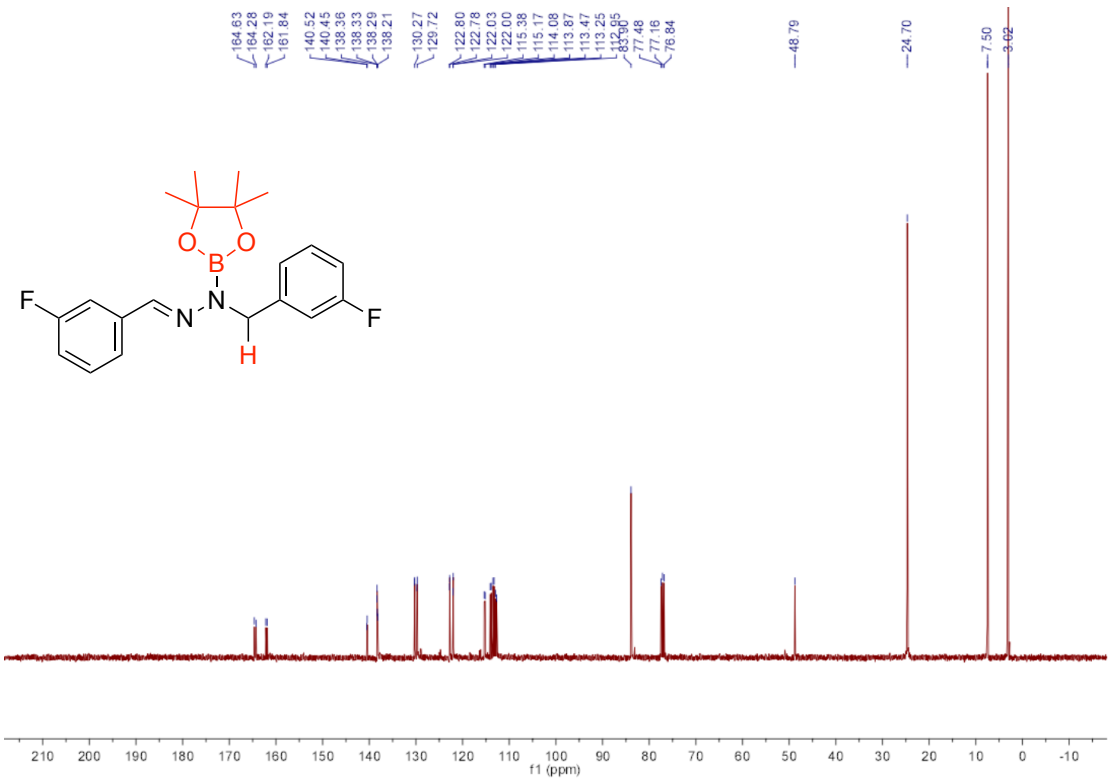
^{13}C NMR spectrum of (*E*)-1-(4-(methylthio)benzyl)-2-(4-(methylthio)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2q**, 100.6 MHz, $CDCl_3$):



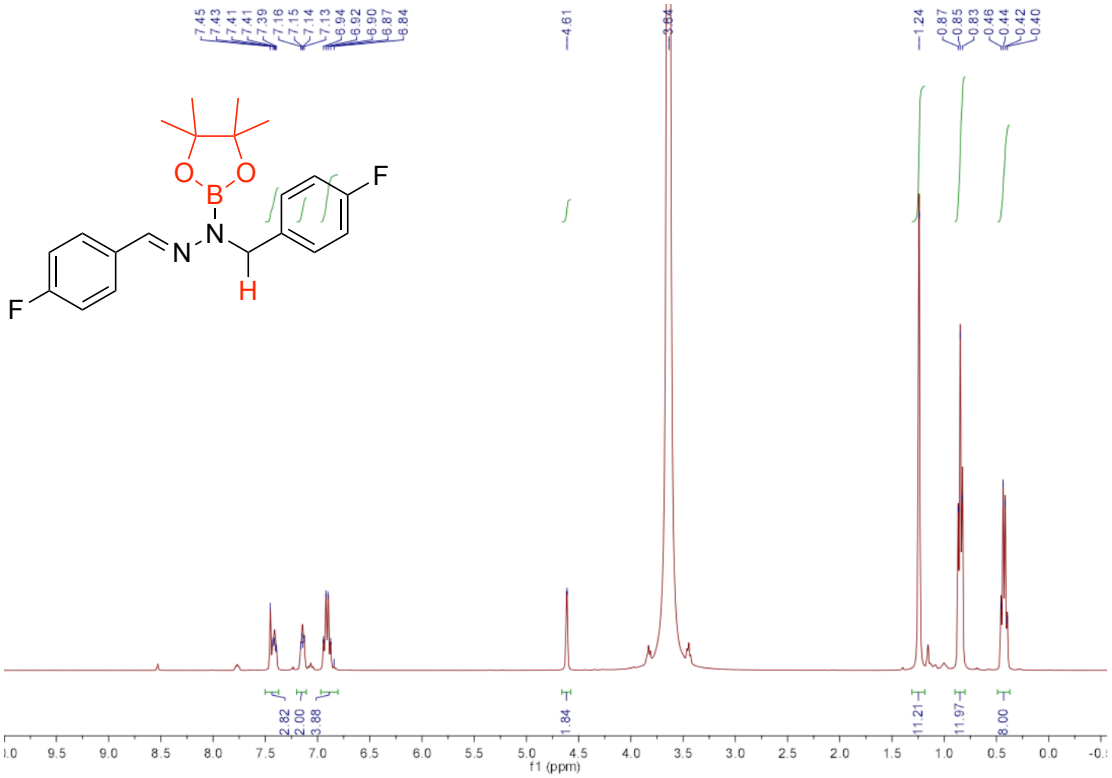
^{1}H NMR spectrum of (*E*)-1-(3-fluorobenzyl)-2-(3-fluorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2r**, 400 MHz, $CDCl_3$):



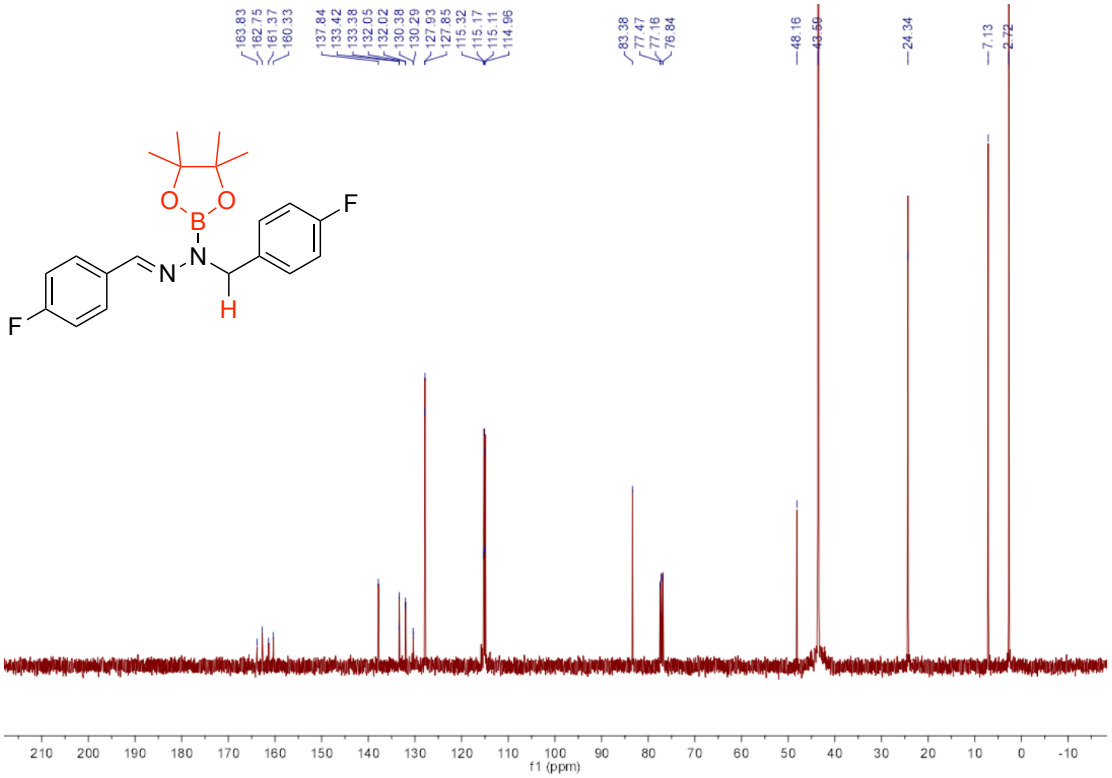
^{13}C NMR spectrum of (*E*)-1-(3-fluorobenzyl)-2-(3-fluorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2r**, 100.6 MHz, $CDCl_3$):



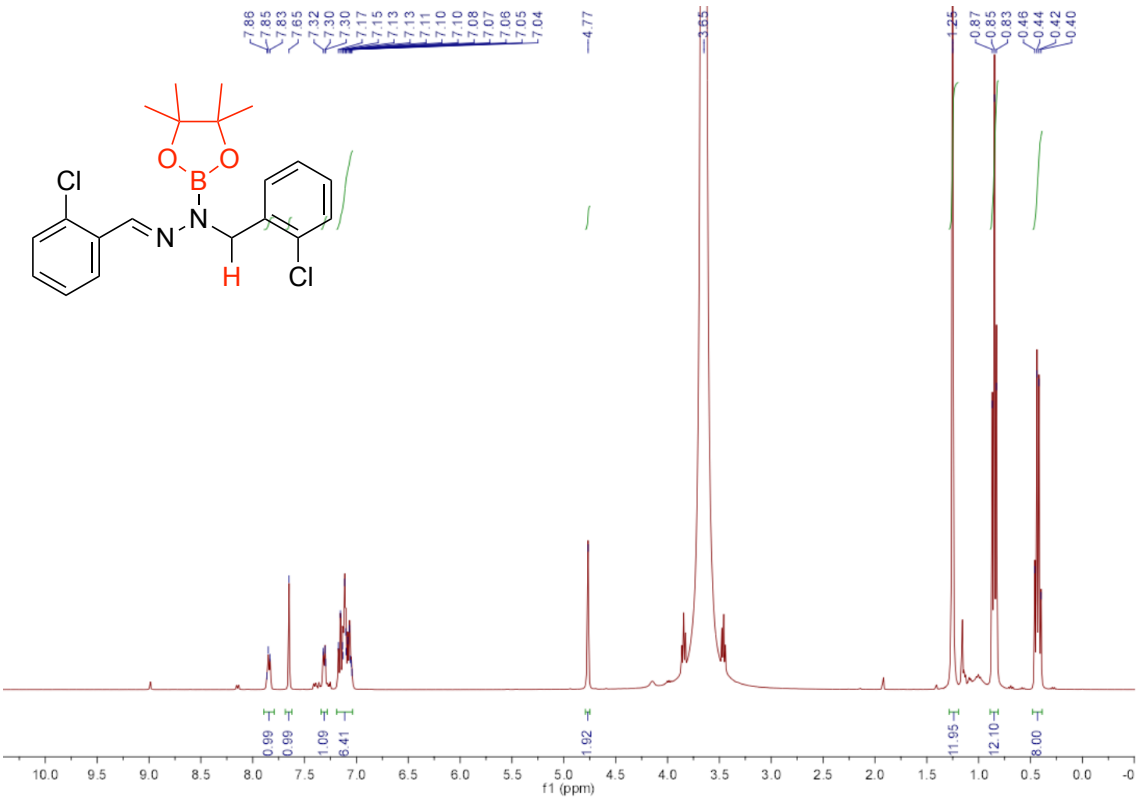
^{1}H NMR spectrum of (*E*)-1-(4-fluorobenzyl)-2-(4-fluorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2s**, 400 MHz, $CDCl_3$):



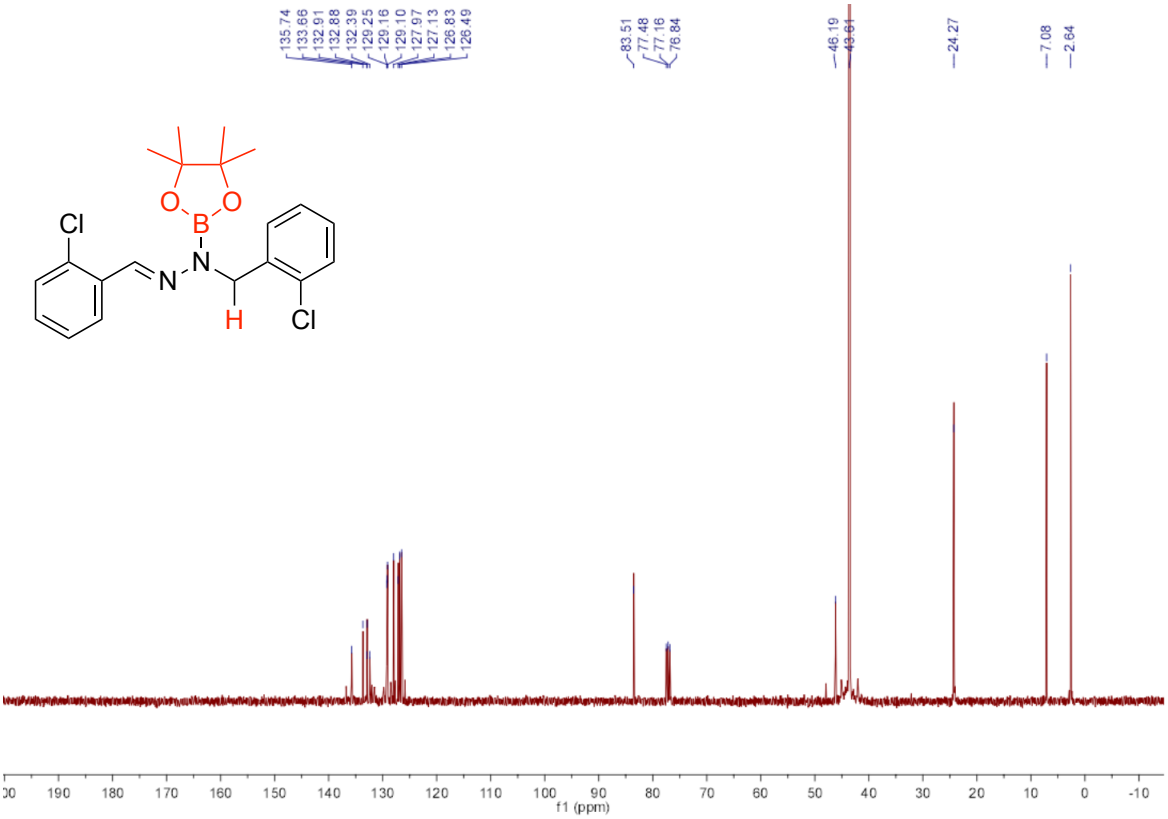
^{13}C NMR spectrum of (*E*)-1-(4-fluorobenzyl)-2-(4-fluorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2s**, 100.6 MHz, $CDCl_3$):



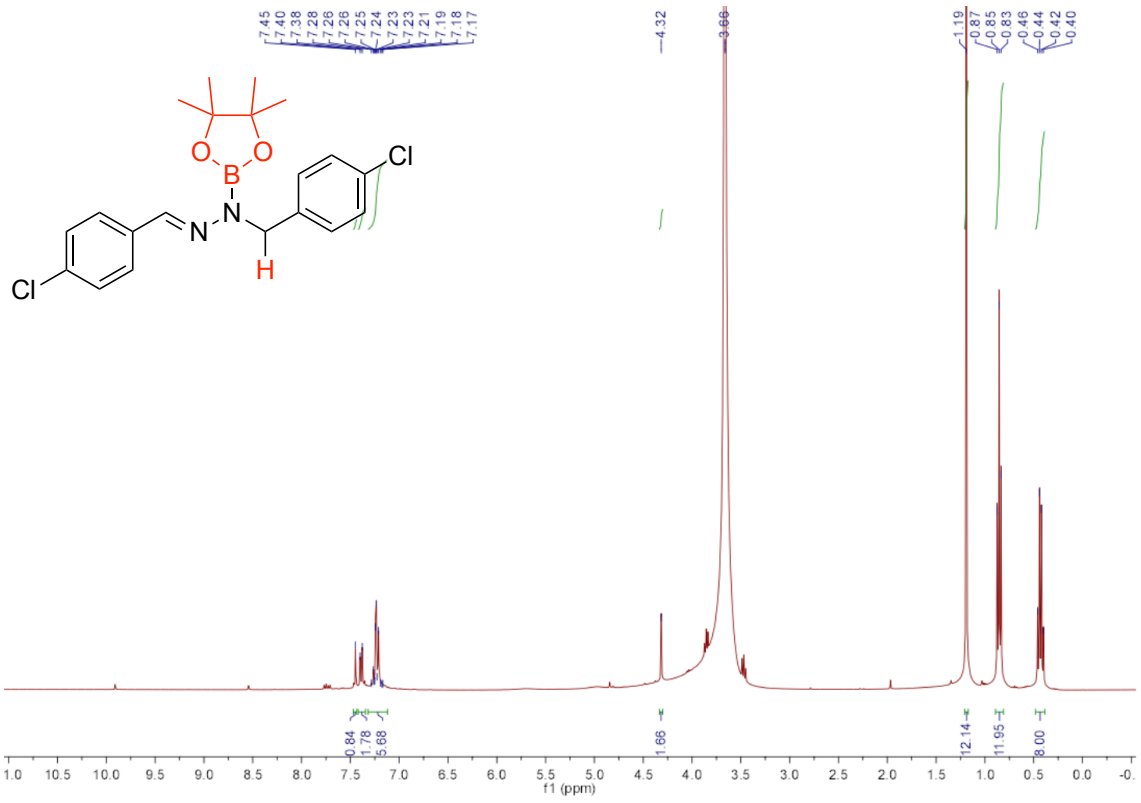
^{1}H NMR spectrum of (*E*)-1-(2-chlorobenzyl)-2-(2-chlorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2t**, 400 MHz, $CDCl_3$)



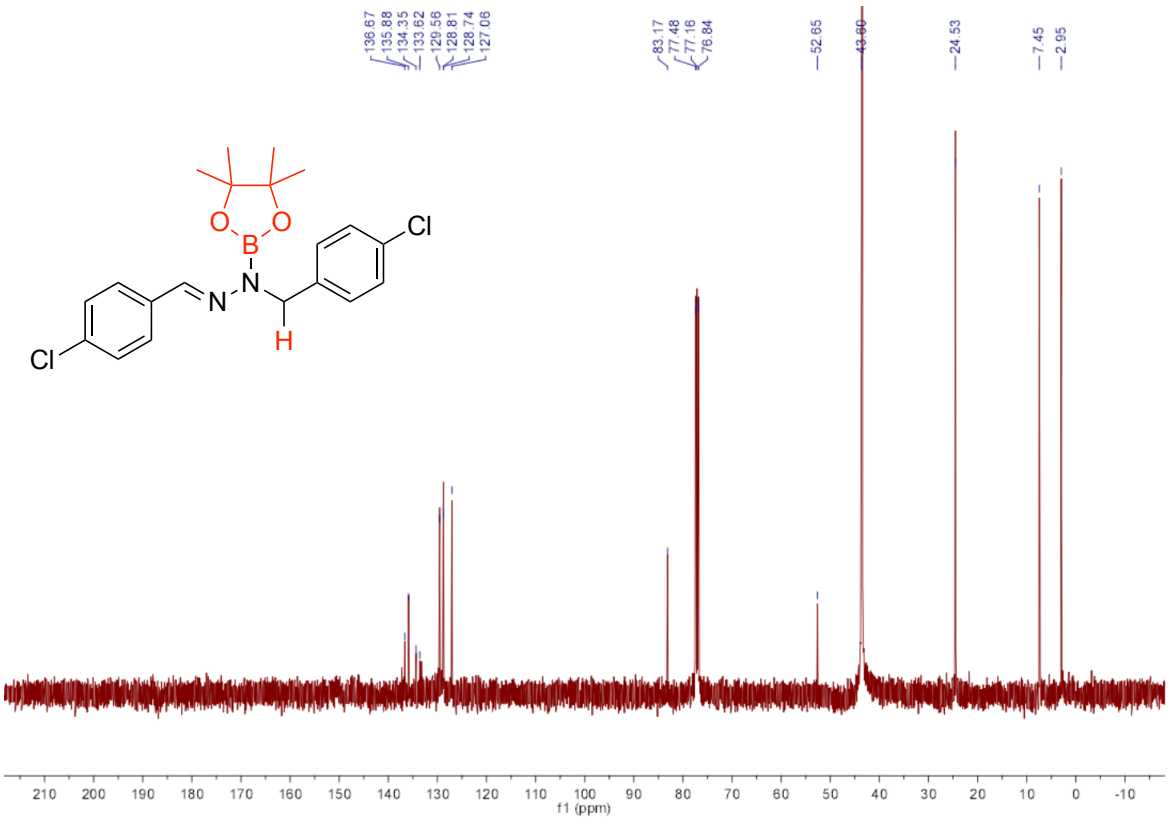
^{13}C NMR spectrum of (*E*)-1-(2-chlorobenzyl)-2-(2-chlorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2t**, 100.6 MHz, $CDCl_3$):



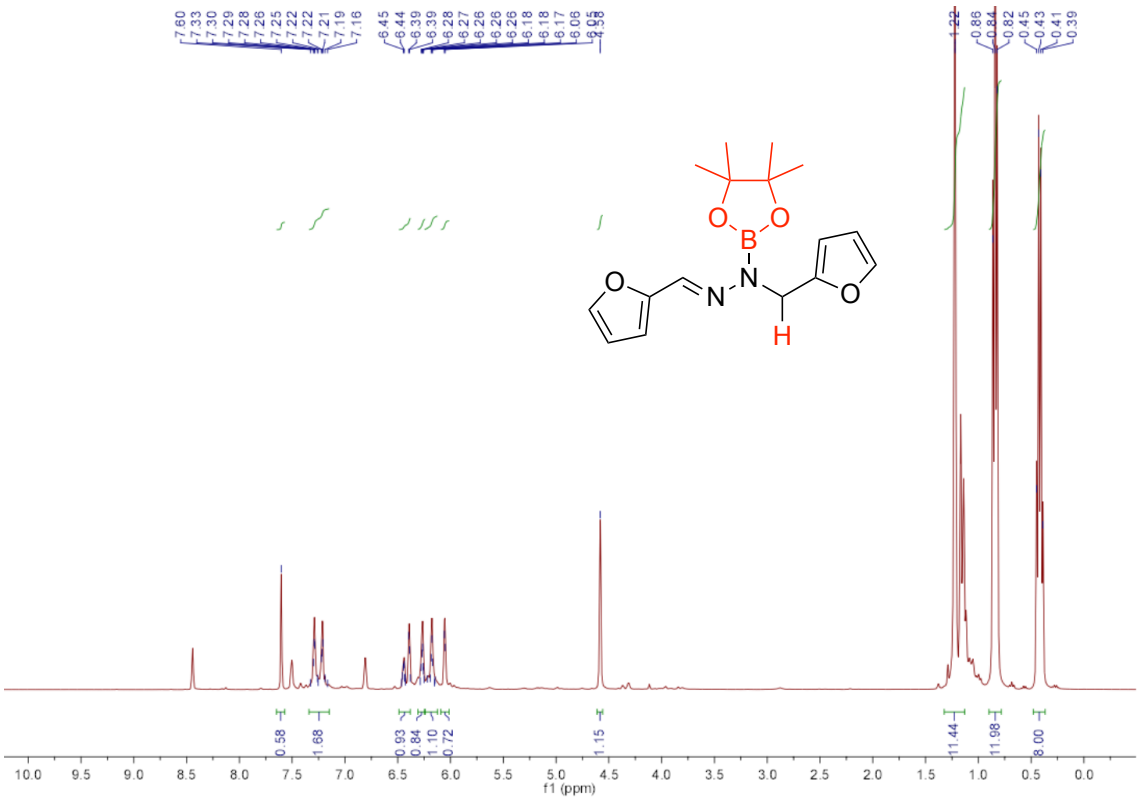
^{1}H NMR spectrum of (*E*)-1-(4-chlorobenzyl)-2-(4-chlorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2u**, 400 MHz, $CDCl_3$):



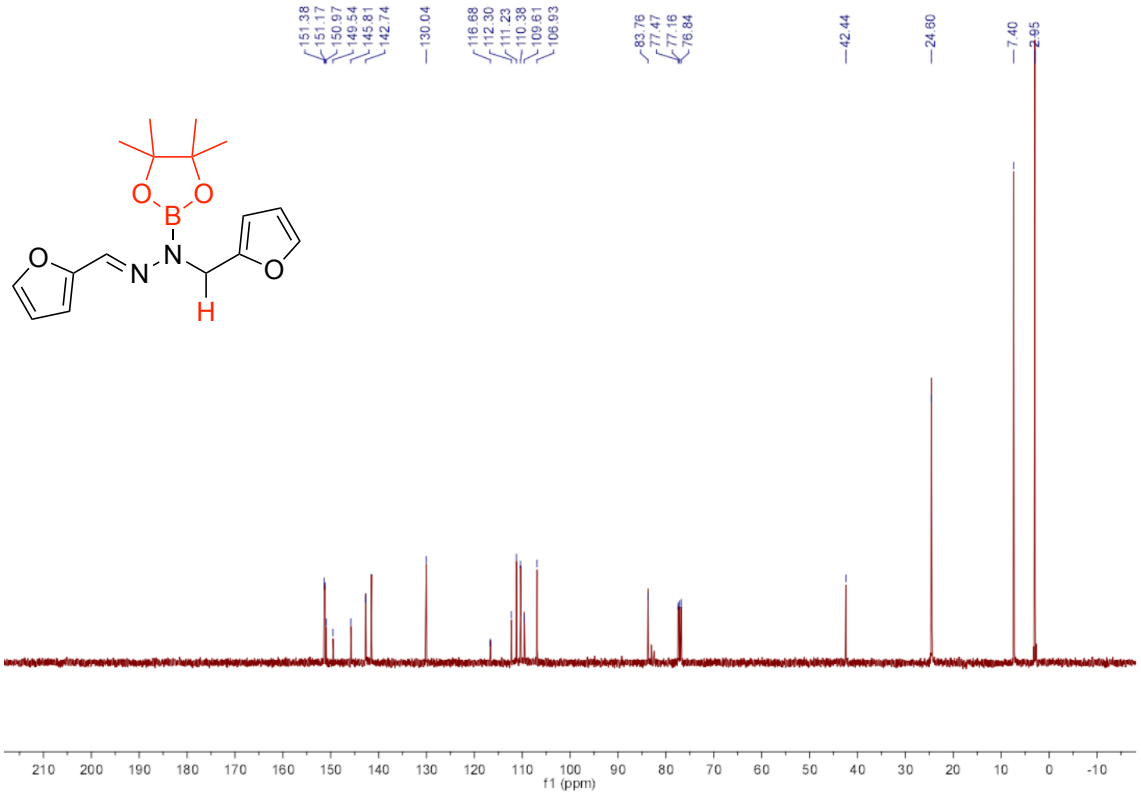
^{13}C NMR spectrum of (*E*)-1-(4-chlorobenzyl)-2-(4-chlorobenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2u**, 100.6 MHz, $CDCl_3$):



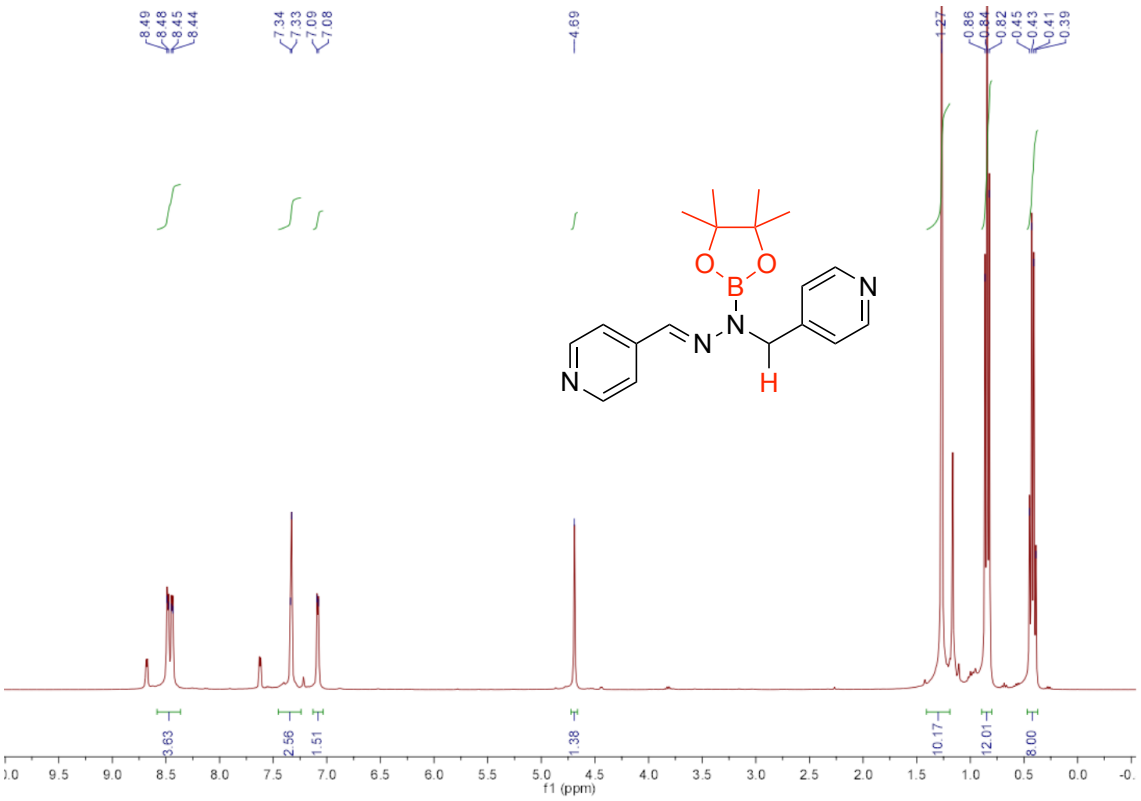
^{1}H NMR spectrum of (*E*)-1-(furan-2-ylmethyl)-2-(furan-2-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2v**, 400 MHz, $CDCl_3$):



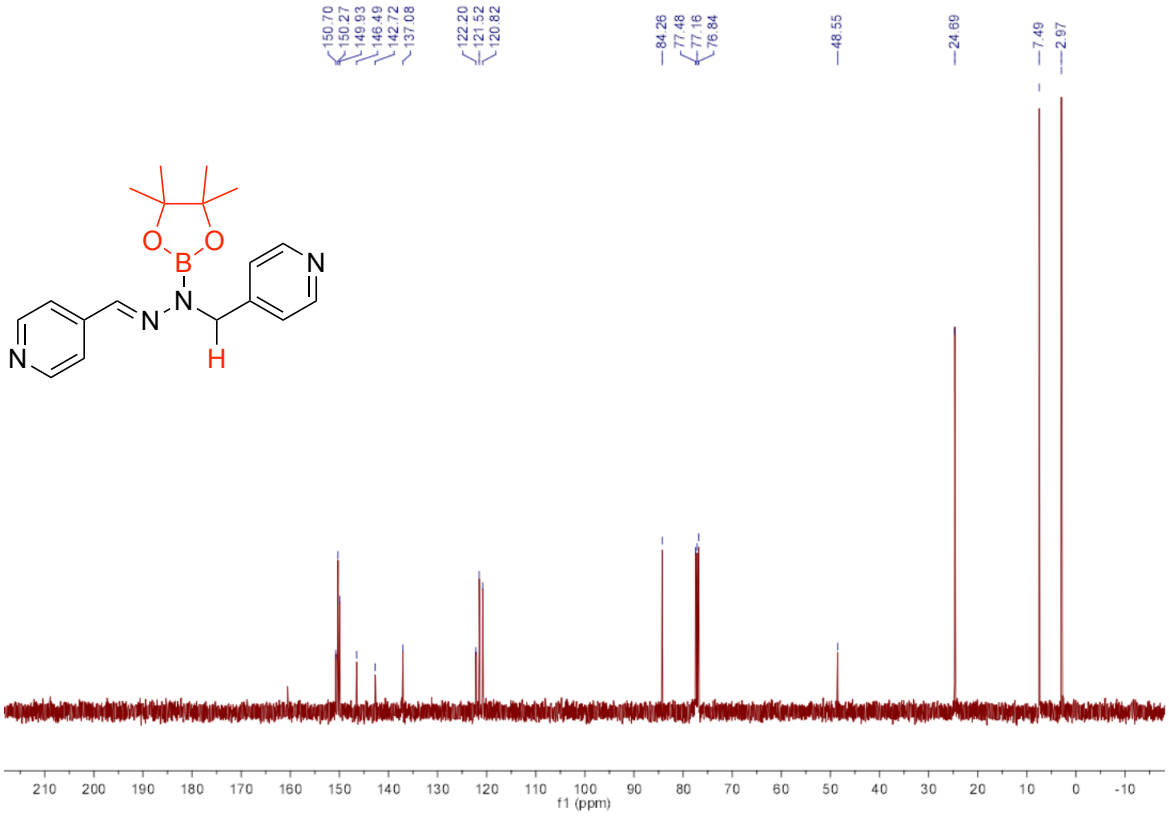
^{13}C NMR spectrum of (*E*)-1-(furan-2-ylmethyl)-2-(furan-2-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2v**, 100.6 MHz, $CDCl_3$):



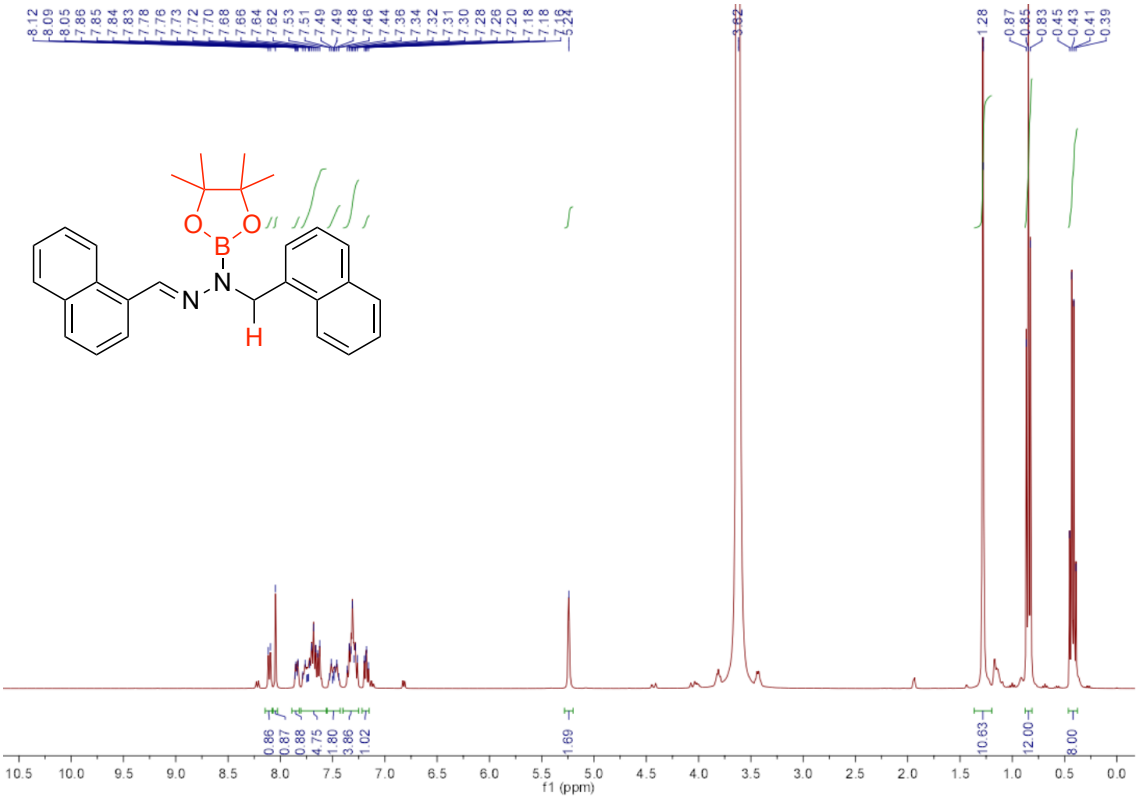
^{1}H NMR spectrum of (*E*)-4-((2-(pyridin-4-ylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazineylidene)methyl)pyridine (**2w**, 400 MHz, $CDCl_3$):



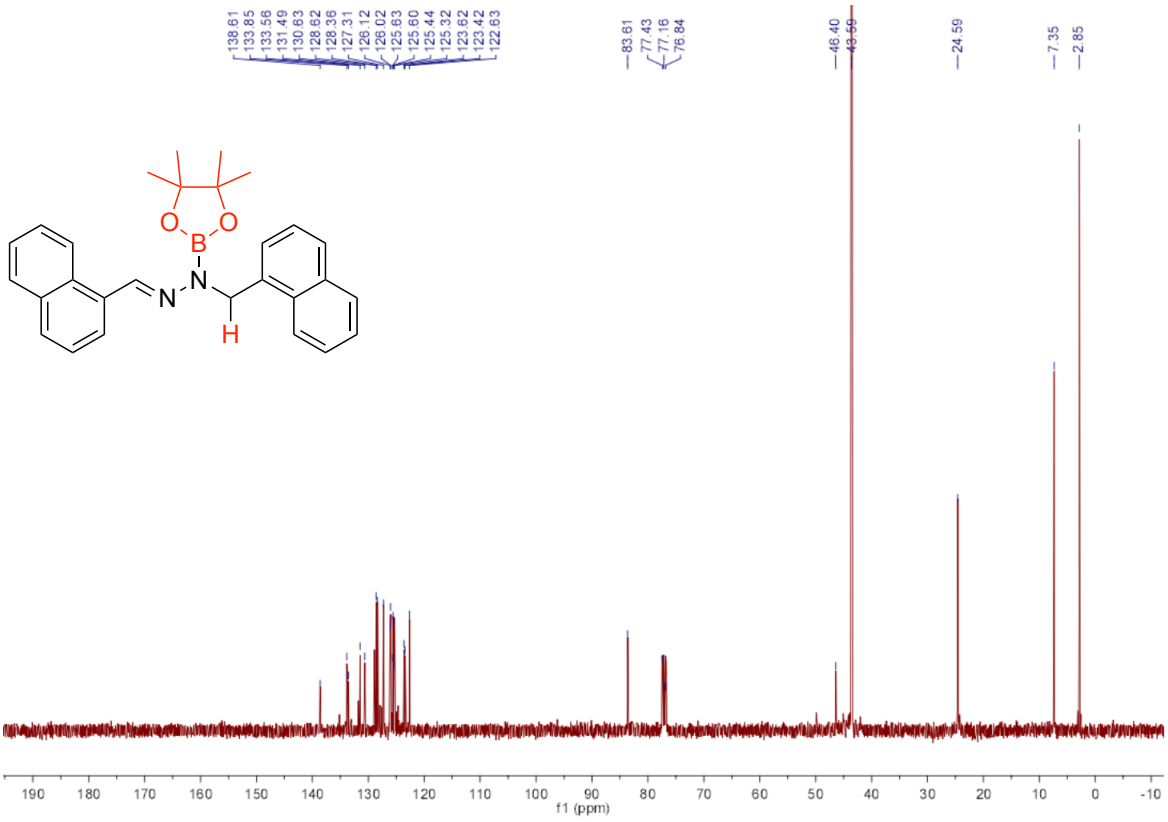
^{13}C NMR spectrum of (*E*)-4-((2-(pyridin-4-ylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazineylidene)methyl)pyridine (**2w**, 100.6 MHz, $CDCl_3$):



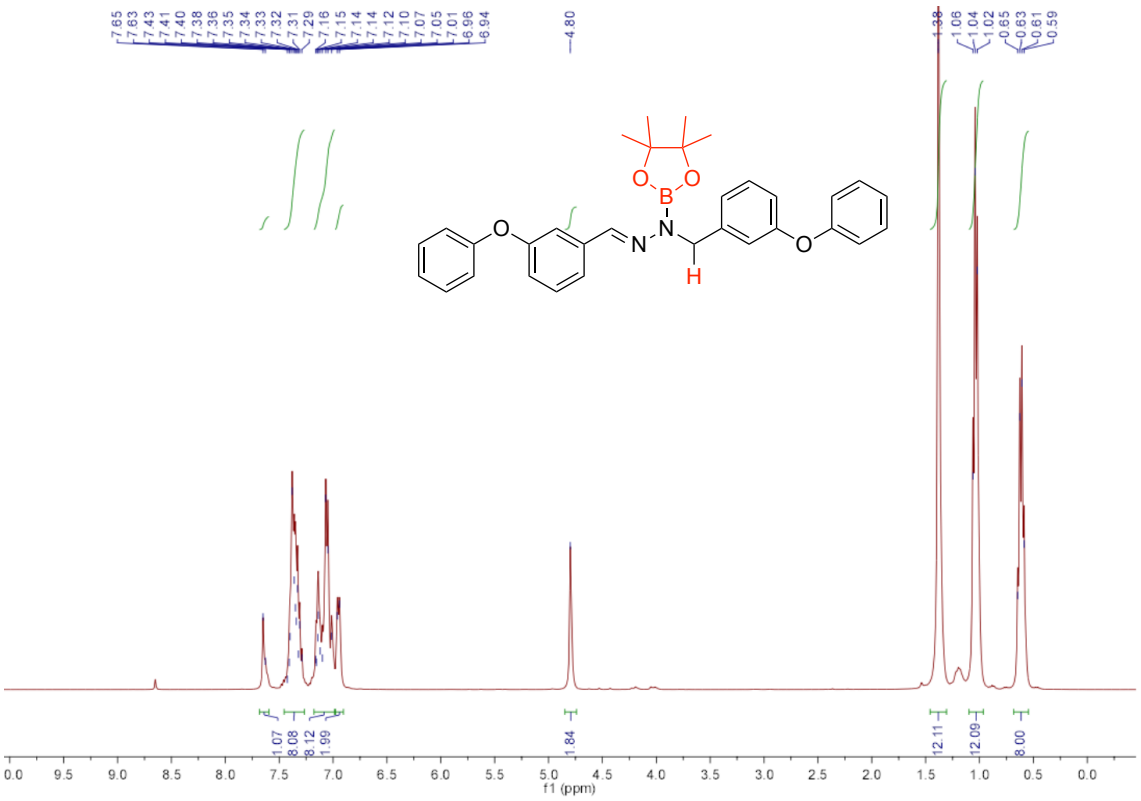
^{1}H NMR spectrum of (*E*)-1-(naphthalen-1-ylmethyl)-2-(naphthalen-1-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2y**, 400 MHz, $CDCl_3$):



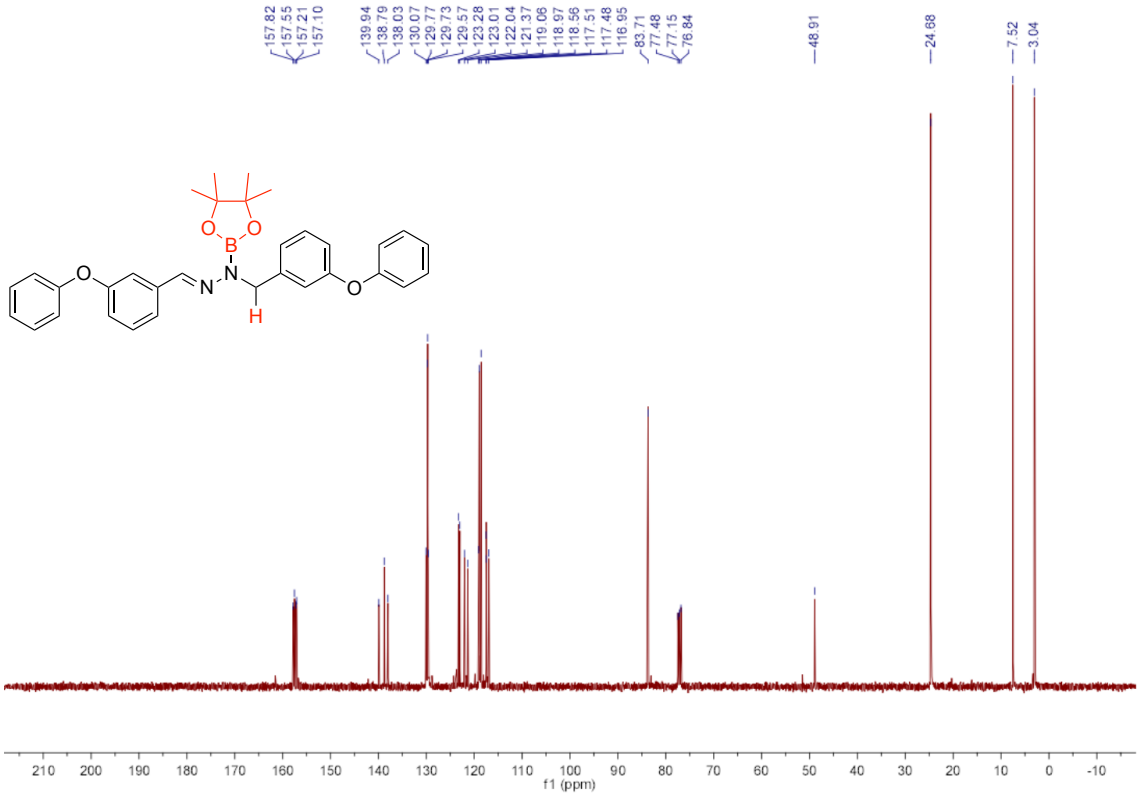
^{13}C NMR spectrum of (*E*)-1-(naphthalen-1-ylmethyl)-2-(naphthalen-1-ylmethylene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2y**, 100.6 MHz, $CDCl_3$):



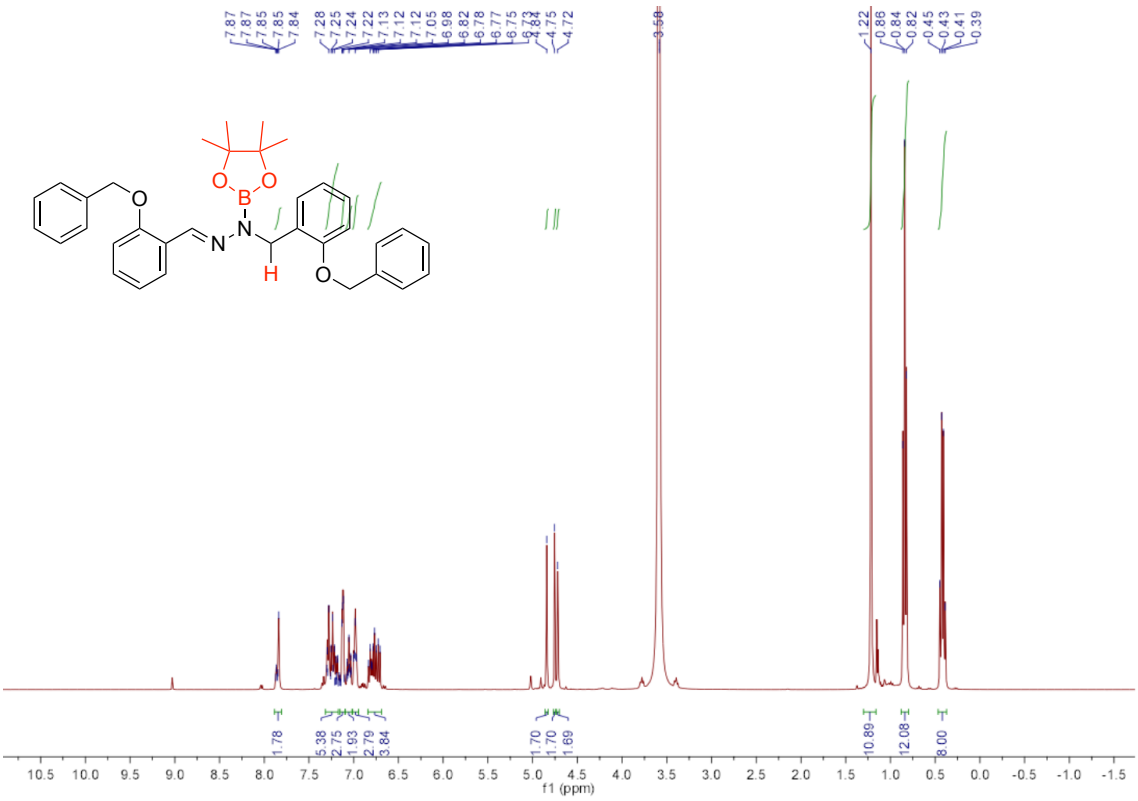
^{1}H NMR spectrum of (*E*)-1-(3-phenoxybenzyl)-2-(3-phenoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2z**, 400 MHz, $CDCl_3$):



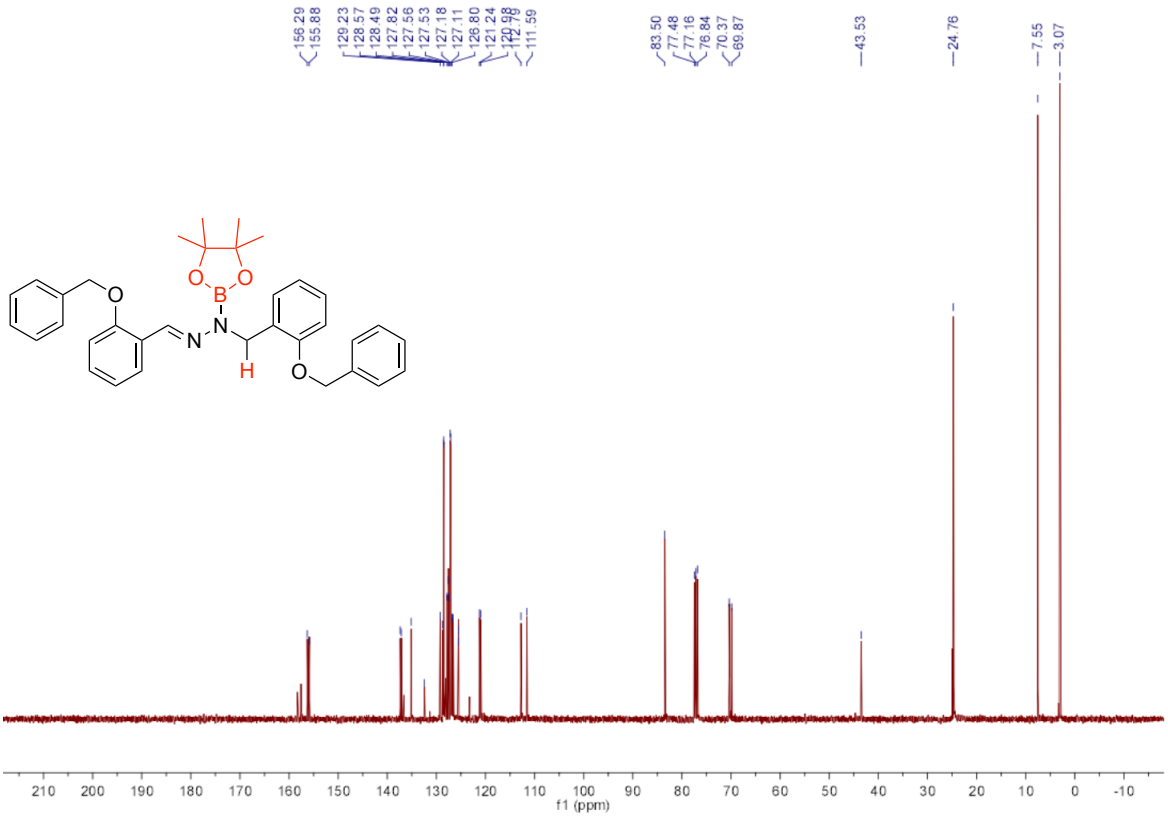
^{13}C NMR spectrum of (*E*)-1-(3-phenoxybenzyl)-2-(3-phenoxybenzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2z**, 100.6 MHz, $CDCl_3$):



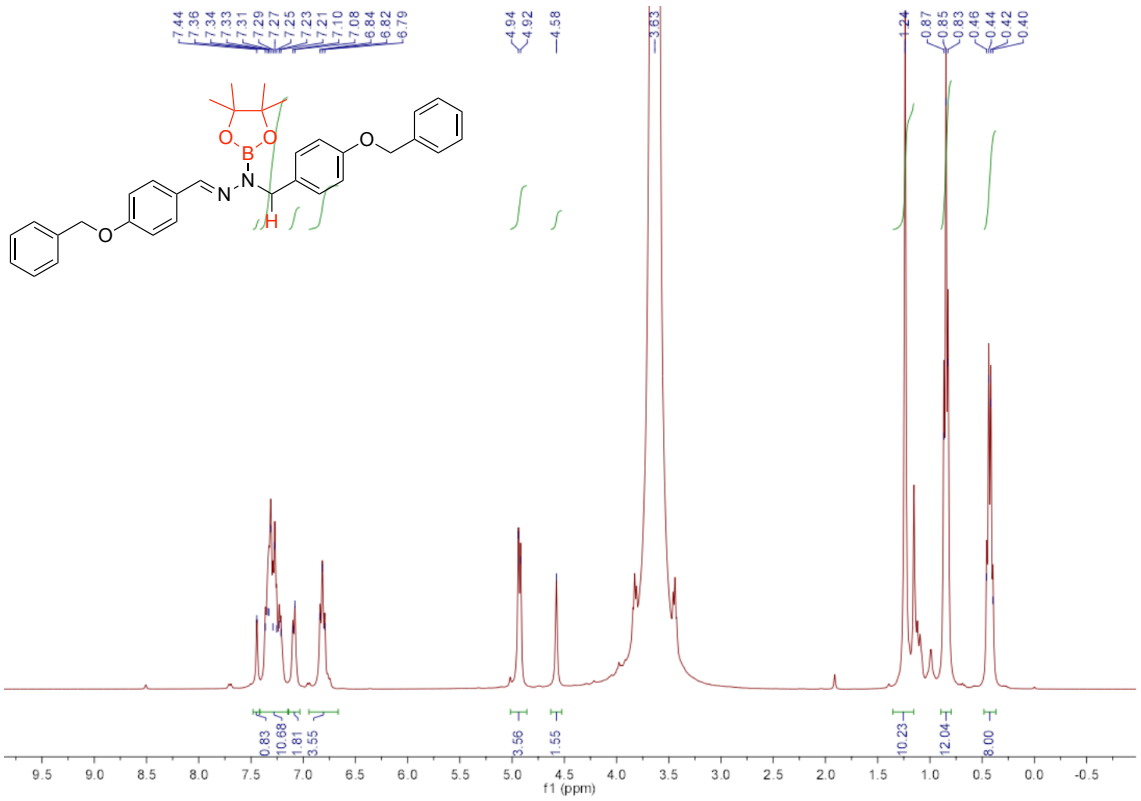
^{1}H NMR spectrum of (*E*)-1-(2-(benzyloxy)benzyl)-2-(2-(benzyloxy)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2ab**, 400 MHz, $CDCl_3$):



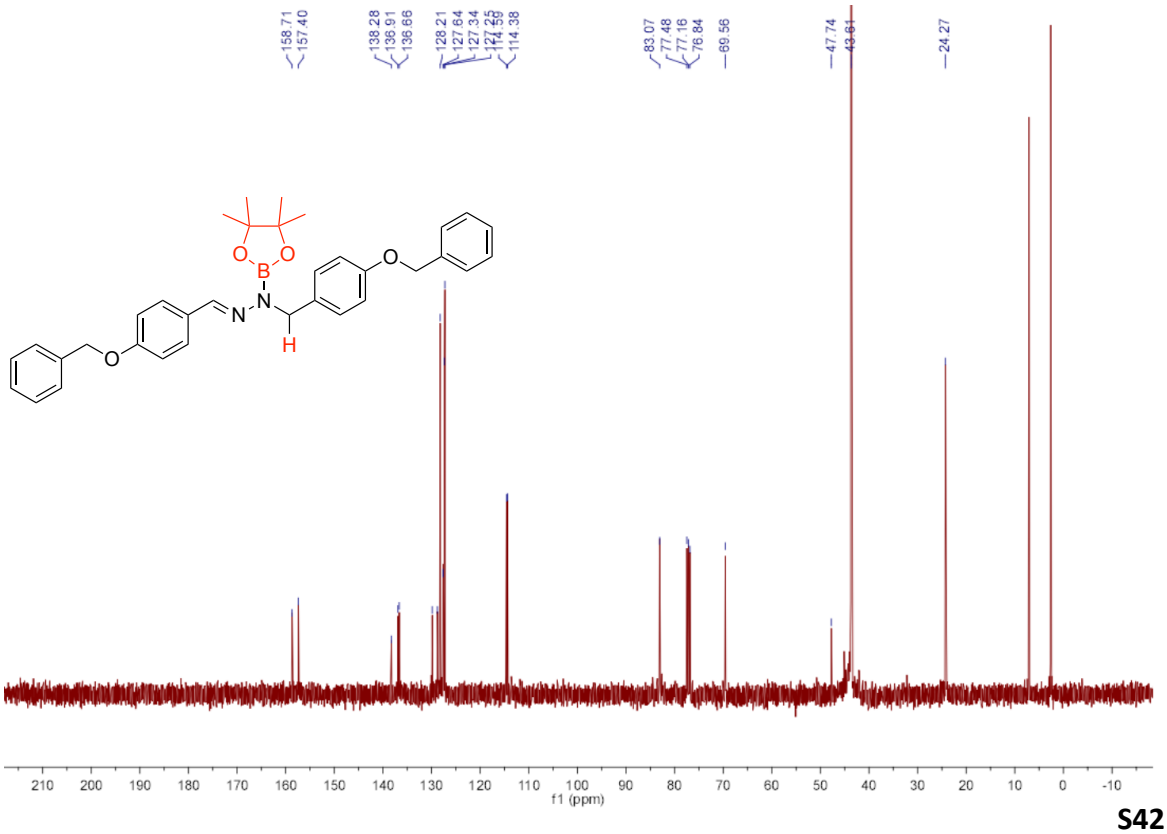
^{13}C NMR spectrum of (*E*)-1-(2-(benzyloxy)benzyl)-2-(2-(benzyloxy)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2ab**, 100.6 MHz, $CDCl_3$):



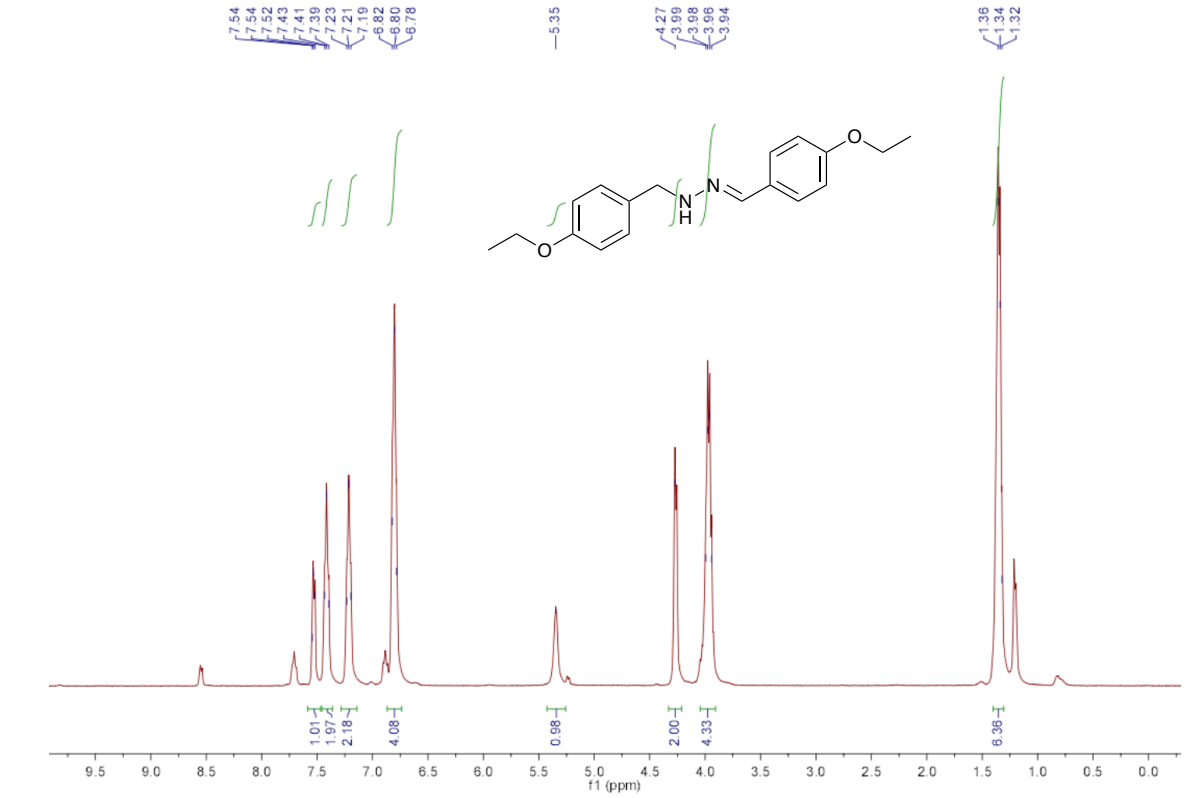
^{1}H NMR spectrum of (*E*)-1-(4-(benzyloxy)benzyl)-2-(4-(benzyloxy)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2ac**, 400 MHz, $CDCl_3$):



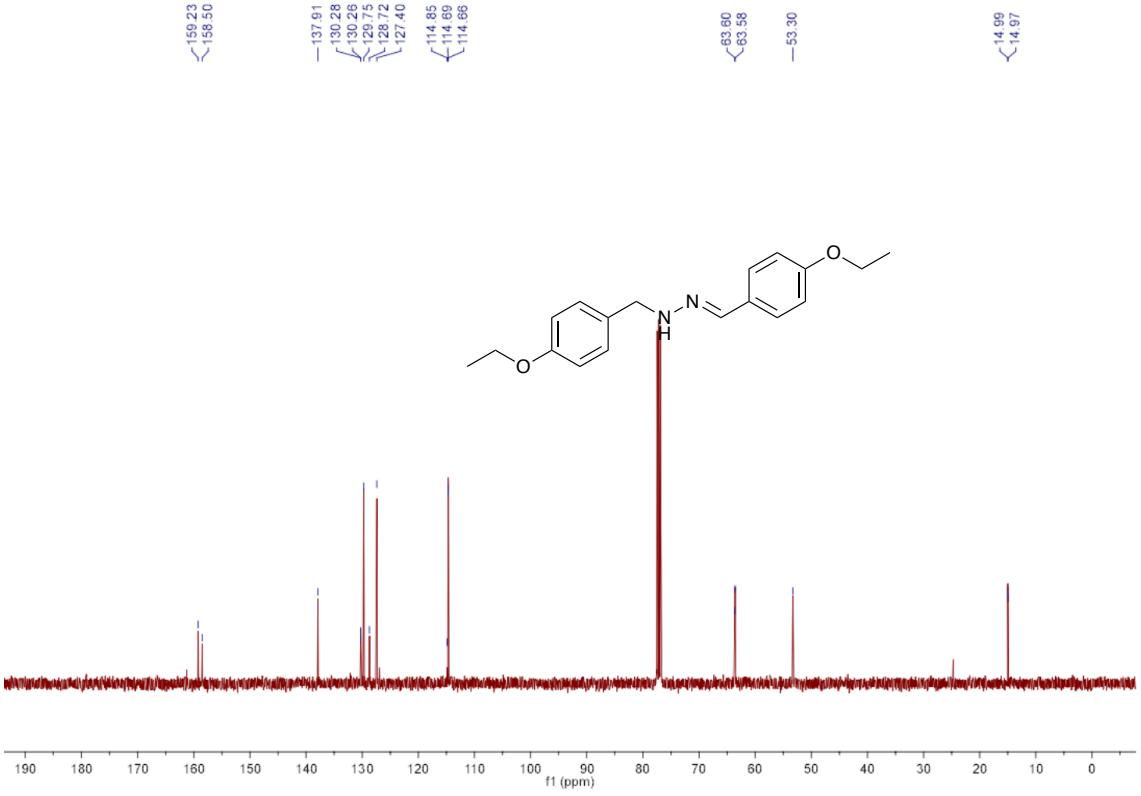
^{13}C NMR spectrum of (*E*)-1-(4-(benzyloxy)benzyl)-2-(4-(benzyloxy)benzylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**2ac**, 100.6 MHz, $CDCl_3$):



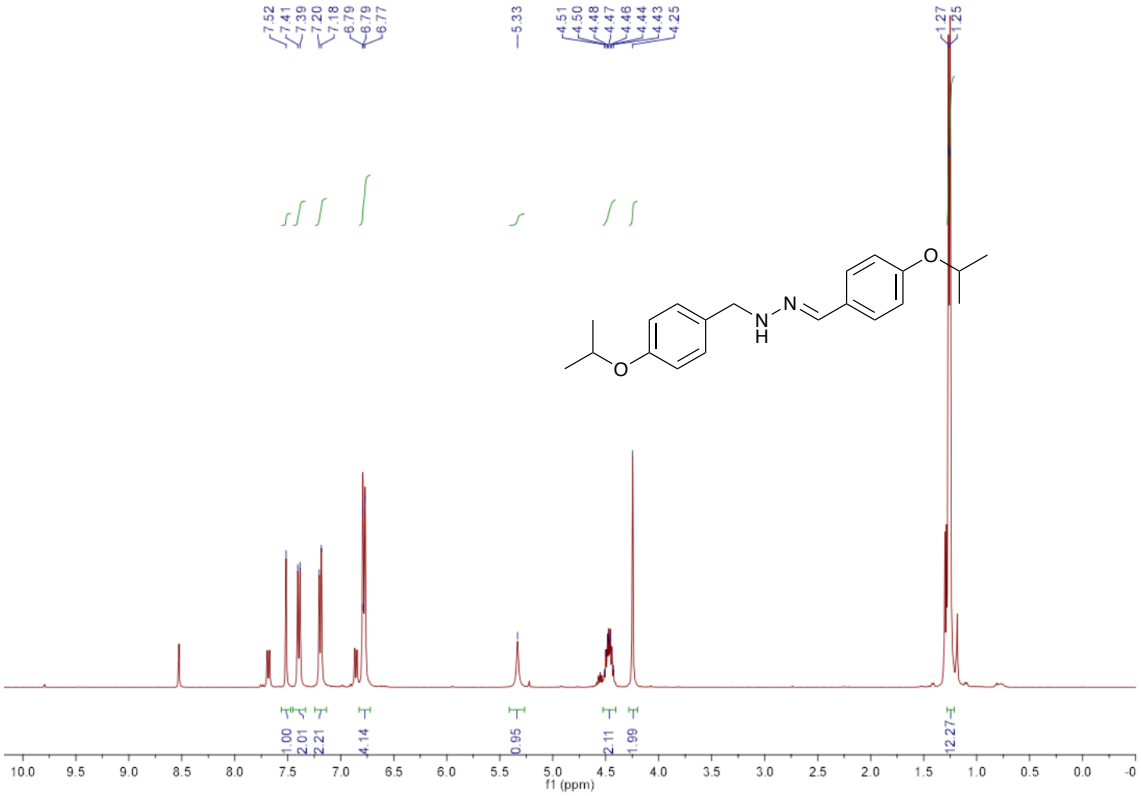
^{1}H NMR spectrum of (*E*)-1-(4-Ethoxybenzyl)-2-(4-ethoxybenzylidene)hydrazine (**3a**, 400 MHz, $CDCl_3$):



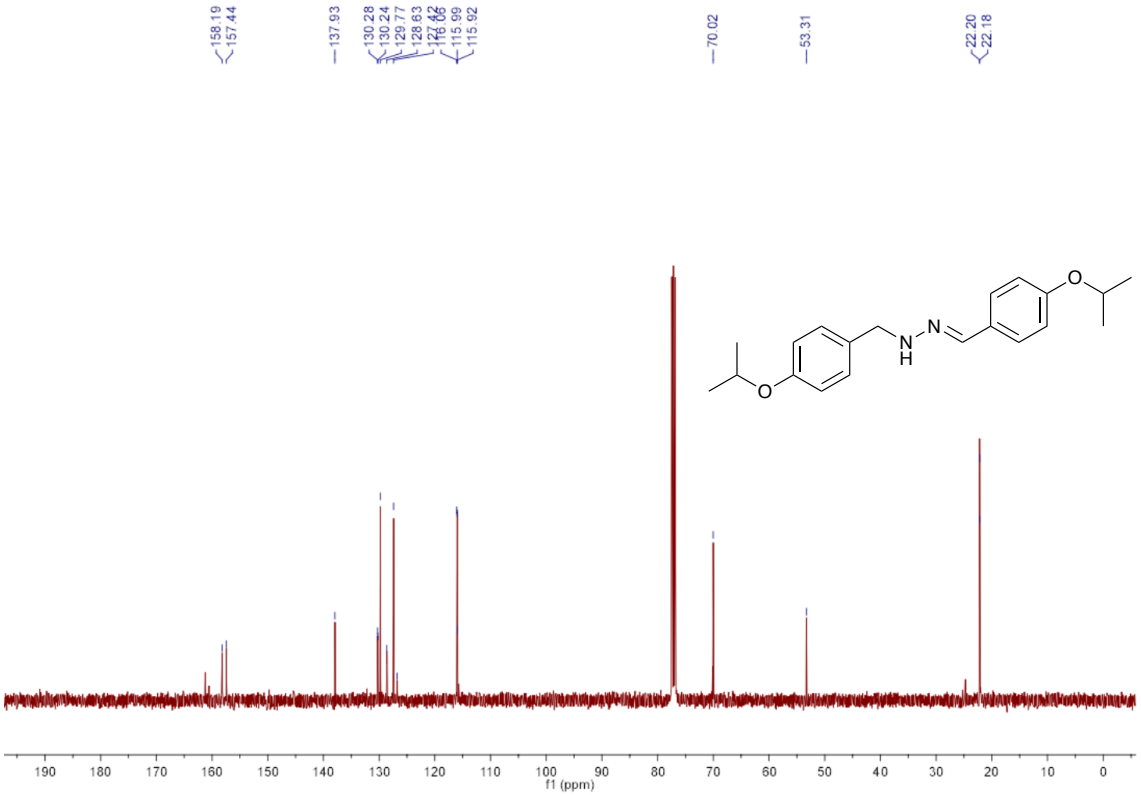
^{13}C NMR spectrum of (*E*)-1-(4-Ethoxybenzyl)-2-(4-ethoxybenzylidene)hydrazine (**3a**, 100.6 MHz, $CDCl_3$):



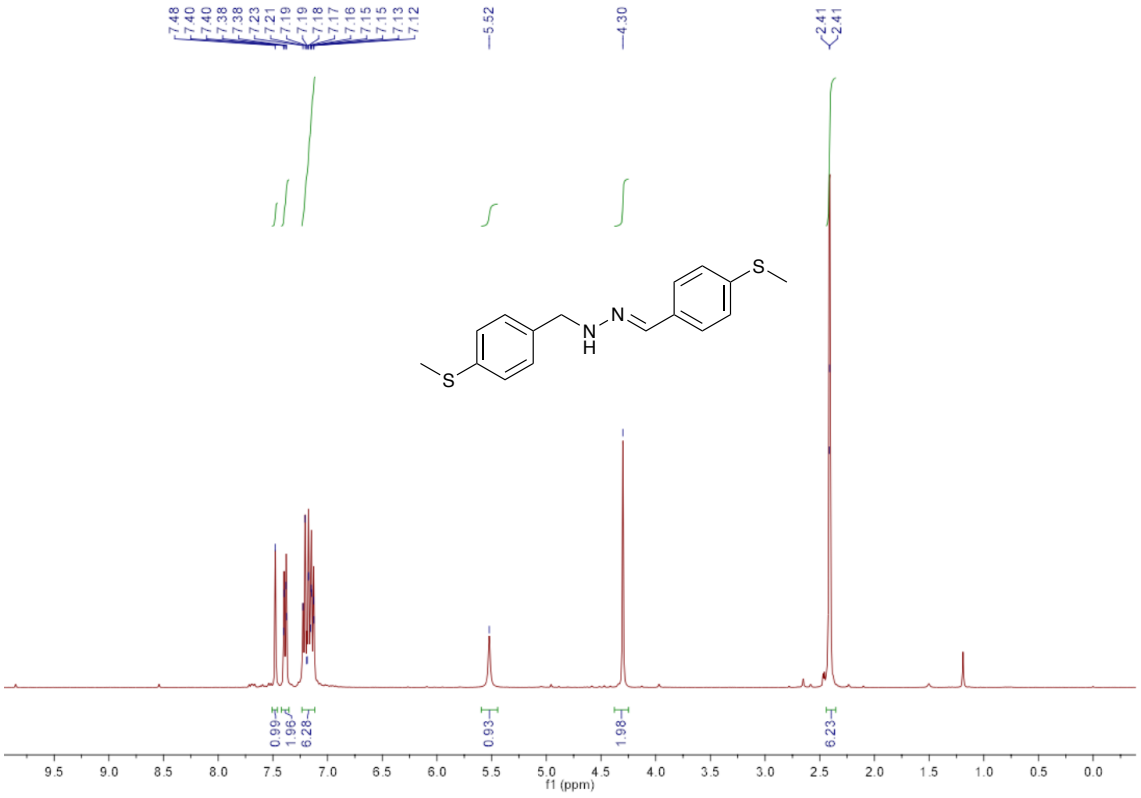
^{1}H NMR spectrum of (*E*)-1-(4-isopropoxybenzyl)-2-(4-isopropoxybenzylidene)hydrazine (**3b**, 400 MHz, $CDCl_3$):



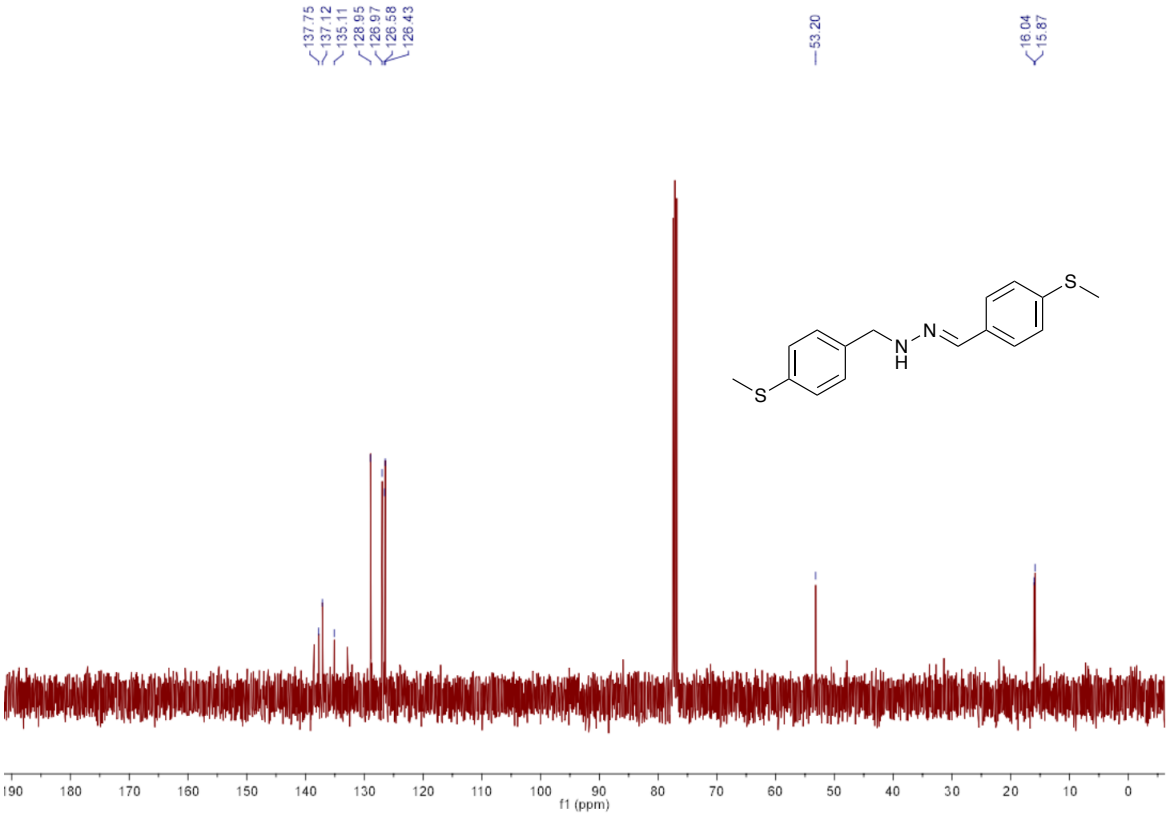
^{13}C NMR spectrum of (*E*)-1-(4-isopropoxybenzyl)-2-(4-isopropoxybenzylidene)hydrazine (**3b**, 100.6 MHz, $CDCl_3$):



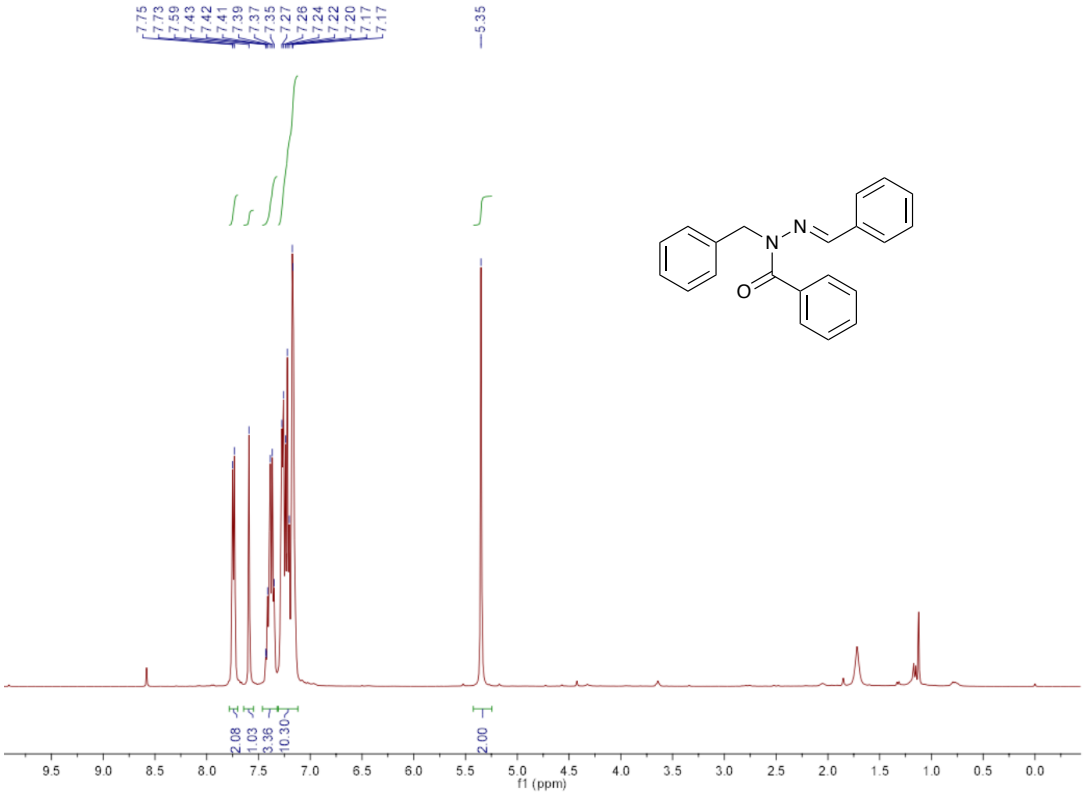
^{1}H NMR spectrum of (*E*)-1-(4-(methylthio)benzyl)-2-(4-(methylthio)benzylidene)hydrazine (**3c**, 400 MHz, $CDCl_3$):



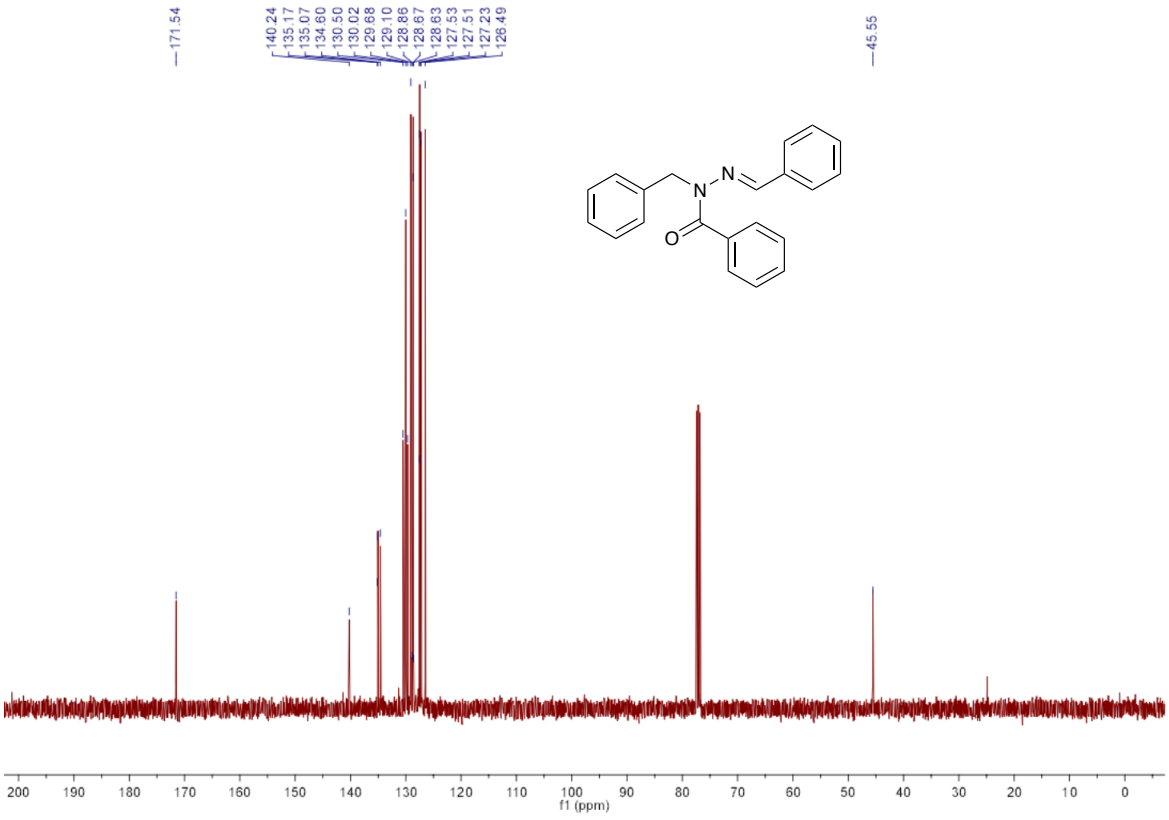
^{13}C NMR spectrum of (*E*)-1-(4-(methylthio)benzyl)-2-(4-(methylthio)benzylidene)hydrazine (**3c**, 100.6 MHz, $CDCl_3$):



^{1}H NMR spectrum of (*E*)-*N*-benzyl-*N*'-benzylidenebenzohydrazide (**4a**, 400 MHz, $CDCl_3$):

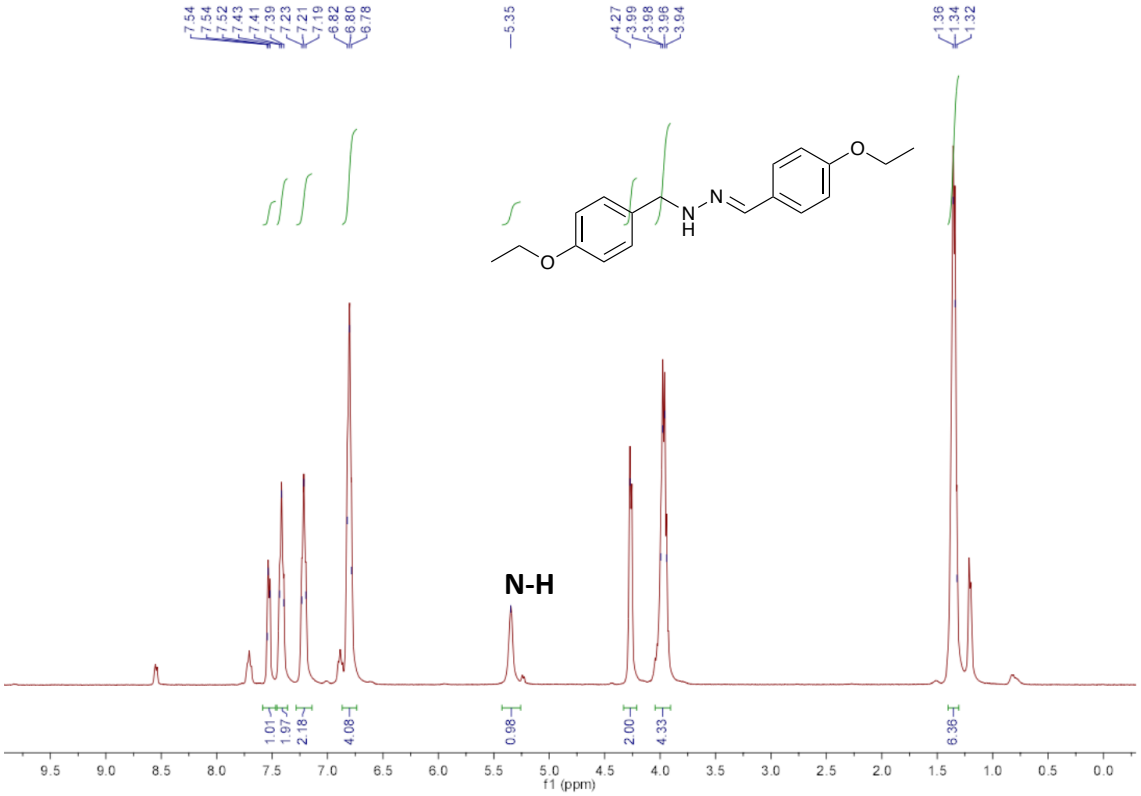


^{13}C NMR spectrum of (*E*)-*N*-benzyl-*N*'-benzylidenebenzohydrazide (**4a**, 100.6 MHz, $CDCl_3$):

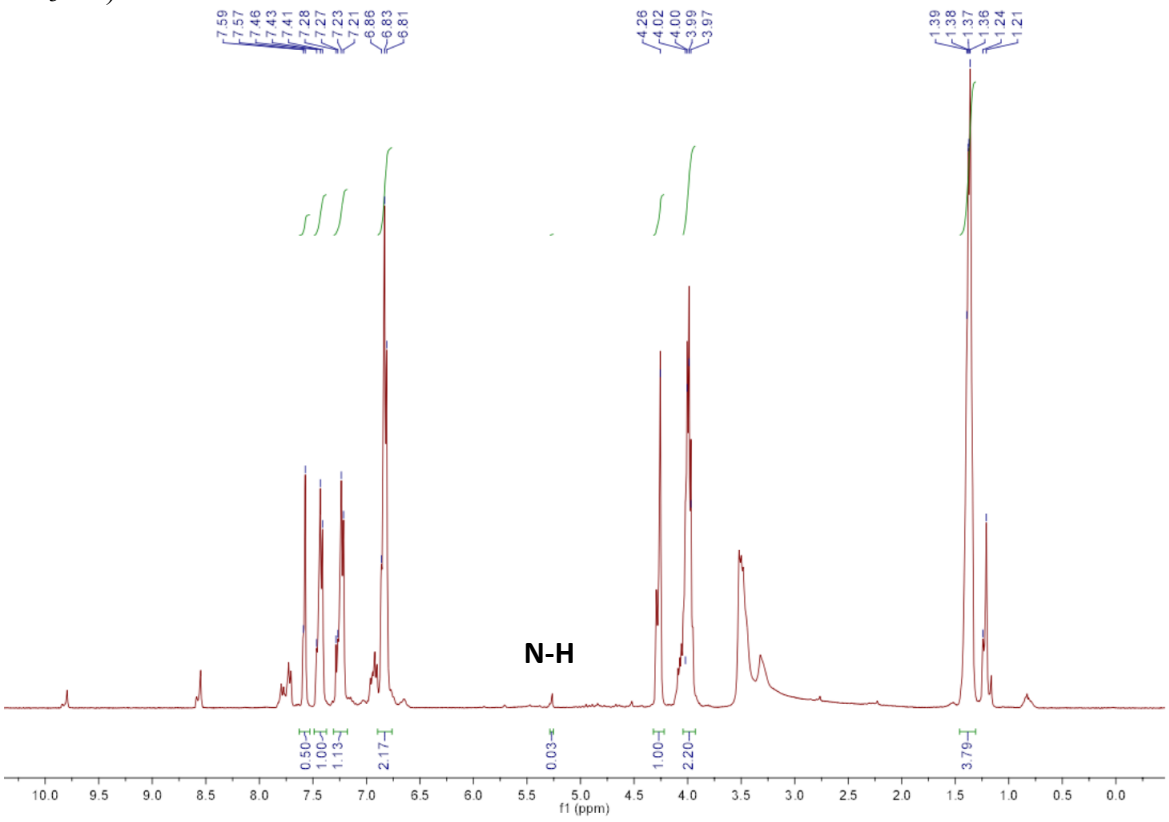


Deuterium labelling experiment:

^{1}H NMR spectrum of (*E*)-1-(4-Ethoxybenzyl)-2-(4-ethoxybenzylidene)hydrazine (**3a**, 400 MHz, $CDCl_3$):

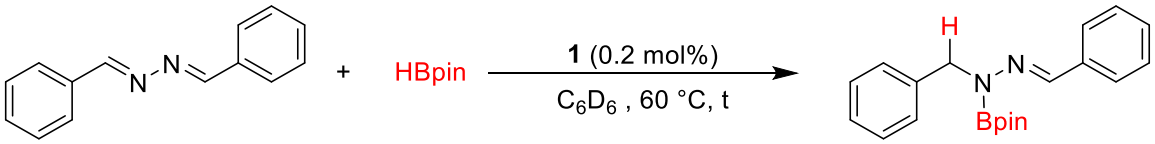


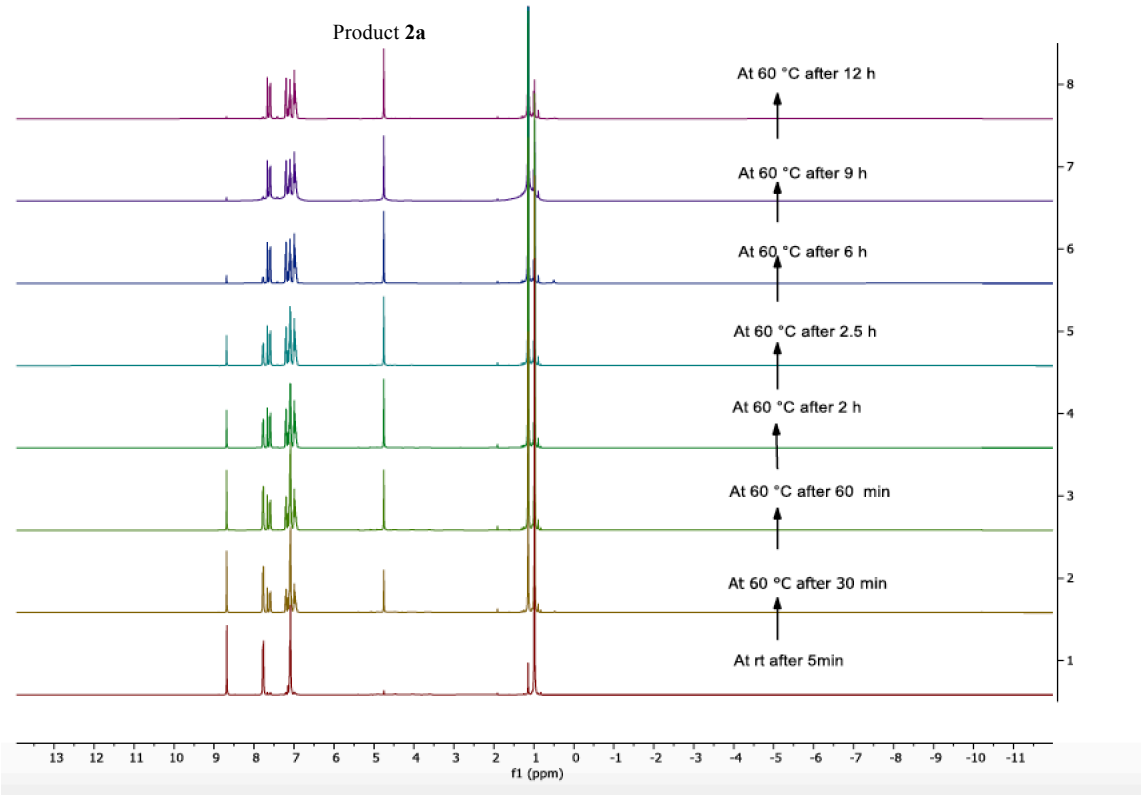
^{1}H NMR spectrum of (*E*)-1-(4-Ethoxybenzyl)-2-(4-ethoxybenzylidene)hydrazine-D (**3a'**, 400 MHz, CD_3OD)**:**



Mechanistic studies:

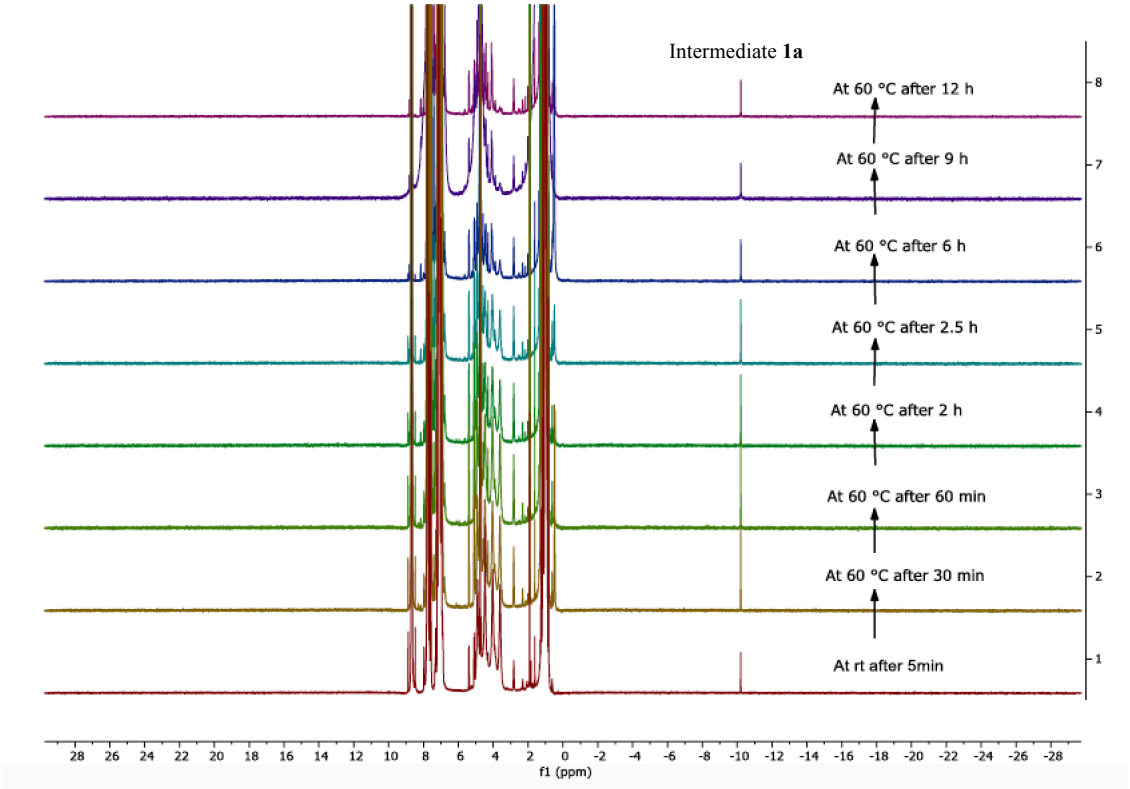
Benzalazine (20.83 mg, 0.1 mmol), HBpin (15.96 µL, 0.11 mmol) and benzene-d_6 (0.5 mL) were charged in a Teflon tapped NMR tube inside the Glove box. The NMR tube was heated at 60 °C. ^{1}H NMR of the reaction mixture were measured at different time intervals.





Stacked ^{1}H NMR spectra of the catalytic reaction of benzalazine, HBpin and catalyst **1**:

Stacked ^{1}H NMR spectra of the catalytic reaction of benzalazine, HBpin and **1**: (intermediate **1a** in situ observed throughout the reaction)



In situ monitoring of the reaction progress:

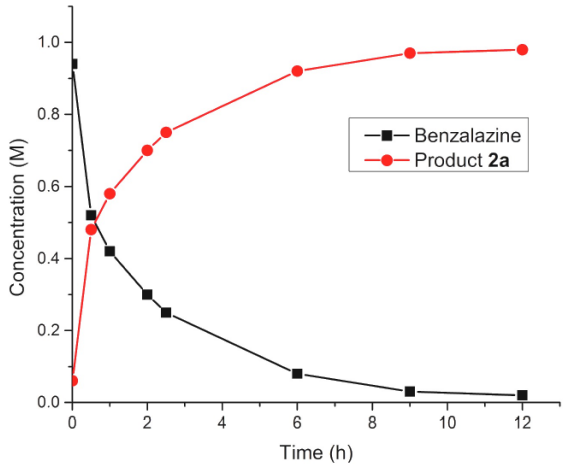


Figure S1. Catalytic hydroboration of benzalazine with HBpin and precatalyst **1**.

X-ray analysis of hydrazone products 2ga and 2ma: Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smart lab X-ray diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART[2] software packages and corrected for absorption with SADABS.[3] The structure was solved by direct methods and refined on F2withSHELXL-97[4] using Olex-2[5] software.

Crystal data of hydrazone product 2ga: $C_{20}H_{26}N_2$, colorless white block, M= 294.43 gm/mol, monoclinic with space group P121/C1, a = 8.2530(2) Å, b = 8.2551(2) Å, c = 14.7902(2) Å, α = 94. 559°(2), β = 102.195°(2), γ = 117.627°(3), V = 854.10 (4) Å3, Z = 2, F(000) = 320, μ-(CuKα) = 0.278 mm^{-1}, $2\theta_{max}$= 150.568, ρcalcd = 1.145 g/cm^3, T = 100.01(10) K, 11061 Reflections collected, 2655 unique, R1= 0.0602, WR2= 0.1630 (all data). Residual electron density max/min = 0.559/-0.554e.$Å^{-3}$. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 2077412.**

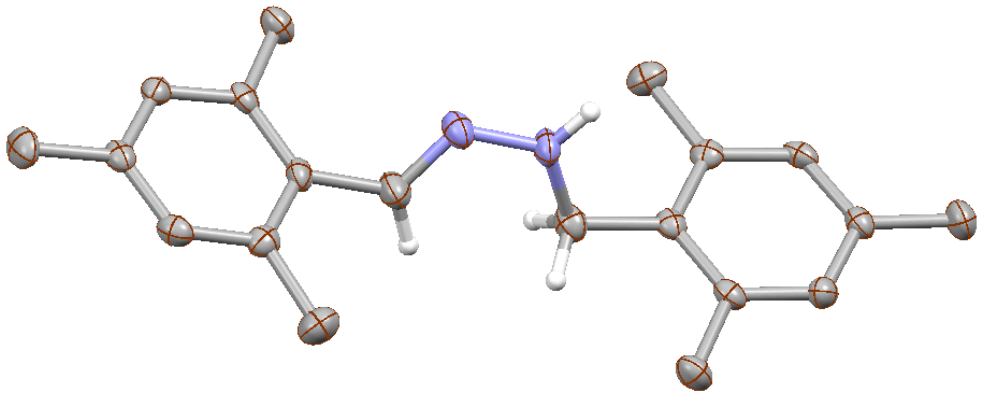


Figure S2: Ortep structure of (*Z*)-1-(2,4,6-trimethylbenzyl)-2-(2,4,6-trimethylbenzylidene)hydrazine (2ga). Ellipsoids are drawn with 50% probability.

Crystal data of hydrazone product 2ma: $C_{18}H_{22}N_2O_2$, colorless white block, M= 298.37 gm/mol, monoclinic with space group P121/C1, a = 6.2951(2) Å, b = 7.8493(3) Å, c = 16.3441(5) Å, α = 80.613°(3), β = 85.440°(3), γ = 89.520°, V = 794.25 (5) Å3, Z = 2, F(000) = 320, μ-(CuKα) = 0.278 mm^{-1}, 2θmax= 151.662, ρcalcd = 1.248 g/cm^3, T = 100 (10) K, 12051 Reflections collected, 3191 unique, R1= 0.0464, WR2= 0.1353 (all data). Residual electron density max/min = 0.405/-0.394e.$Å^{-3}$. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 2077411.**

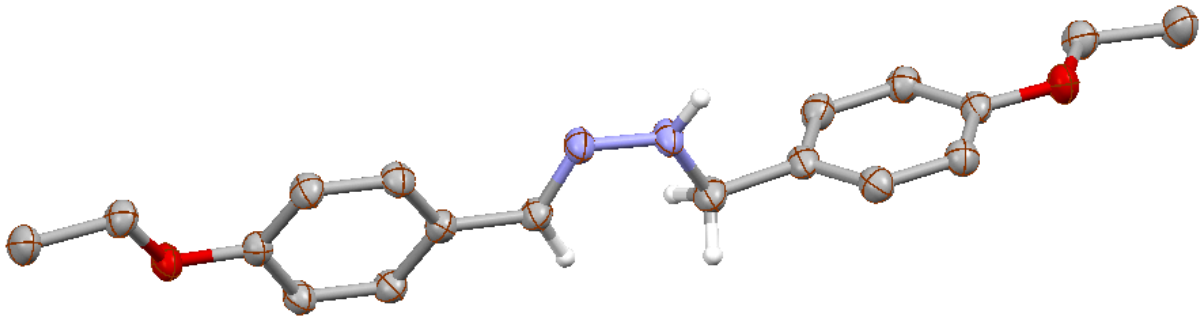


Figure S3: Ortep structure of (*Z*)-1-(4-ethoxybenzyl)-2-(4-ethoxybenzylidene)hydrazine (2ma). Ellipsoids are drawn with 50% probability.

X-Ray analysis of hydrazone product 2qa:

Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smart lab X-ray diffractometer equipped with graphite-monochromated Cu-K_α radiation (λ= 1.54184 Å, multilayer optics). Intensities were integrated with SAINT+[2] and corrected for absorption with SADABS.[3] The structures were solved by direct methods and refined on F2 with SHELXL-97[4] using Olex-2[5] software.

Crystal data of hydrazone product 2qa: $C_{16}H_{18}N_2S_2$, colorless white block, M= 301.43 gm/mol, monoclinic with space group P121/C1, a = 5.3374(1) Å, b = 17.4593(2) Å, c = 16.6786(2) Å, α = 90°, β = 93.097°(1), γ = 90°, V = 1551.96 (4) Å3, Z = 4, F(000) = 640, μ-(CuKα) = 0.278 mm^{-1}, 2θmax= 122.998, ρcalcd = 1.294 g/cm^3, T = 246 K, 10487 Reflections collected, 2388 unique, R1= 0.0360, WR2= 0.1037 (all data). Residual electron density max/min = 0.328/-0.289e.$Å^{-3}$. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 2077413.**

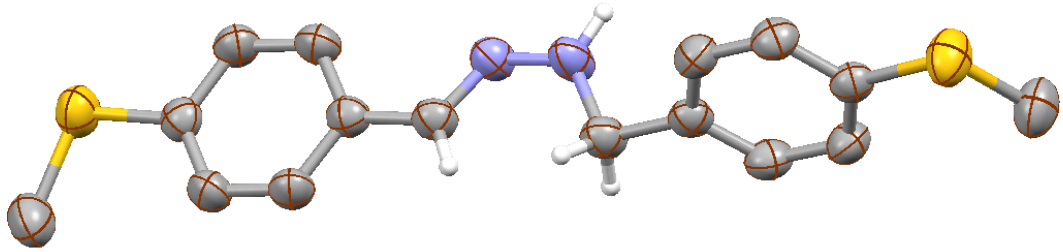


Figure S4: Ortep structure of (*Z*)-1-(4-(methylthio)benzyl)-2-(4-(methylthio)benzylidene)hydrazine (2qa). Ellipsoids are drawn with 50% probability.

References:

1) M. Carmeli and S. Rozen, *Tetrahedron Lett.* 2006, **47**, 763-766.

2) SMART and SAINT Software Reference Manuals Version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.

3) Bruker AXS, SADABS, Program for Empirical Absorption Correction of Area Detector Data V2004/1, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.

4) G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**,112-122.

5) O. V. Dolomanov, L. J. Bourhis, R. J. Gilea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339-341.