Supporting Information for:

Mechanistic Studies of Copper(I)-Catalyzed 1,3-Halogen Migration

Ryan Van Hoveln,[†] Brandi M. Hudson,[‡] Henry B. Wedler,[‡] Desiree M. Bates,[†] Gabriel Le Gros,[†] Dean J. Tantillo[‡]* and Jennifer M. Schomaker [†]*

[†]*Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue Madison, Wisconsin, 53706-1396*

[‡] *Department of Chemistry, University of California-Davis, One Shields Avenue, Davis, California 95616*

I. General Information

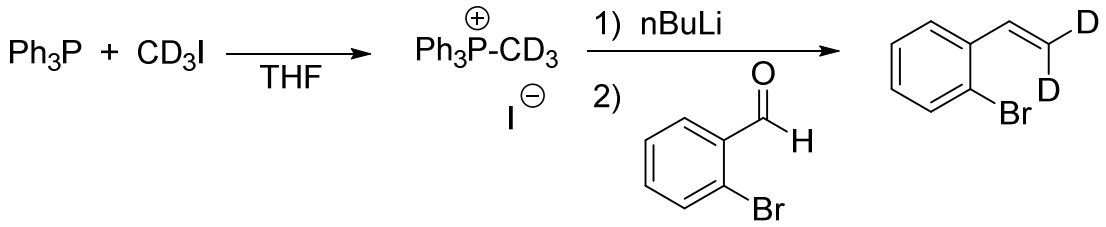
All glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Tetrahydrofuran and diethyl ether were freshly distilled from purple Na/benzophenone ketyl. Dichloromethane, acetonitrile and toluene were dried over CaH_2 and freshly distilled prior to use. All other solvents were purified in accordance with "Purification of Laboratory Chemicals".[1] Air- and moisture-sensitive reactions were performed either in a Braun LabStar glovebox under an atmosphere of nitrogen or using standard Schlenk techniques under an atmosphere of nitrogen. Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{254} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[2] Unless otherwise stated, the mobile phases for column chromatography were mixtures of hexanes/ethyl acetate. Columns were typically run using a gradient method, beginning with 100% hexanes and gradually increasing the polarity using ethyl acetate. Various stains were used to visualize reaction products, including *p*-anisaldehyde, $KMnO_4$, ceric ammonium nitrate and phosphomolybdic acid in ethanol stain.

^1H NMR and ^{13}C NMR spectra were obtained using Bruker-300, Varian Inova-500, Varian Unity-500 or Varian Inova-600 NMR spectrometers. For ^1H NMR, chemical

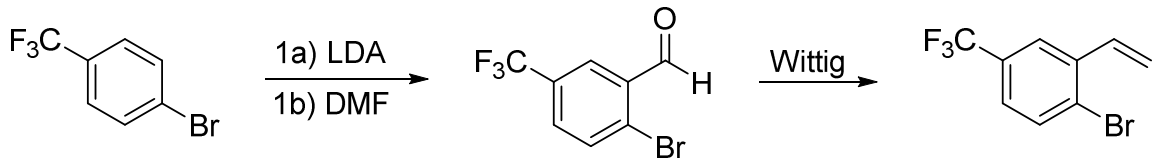
shifts are reported relative to residual protiated solvent peaks (δ 7.26, 2.49, 7.15 and 4.80 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6 and CD_3OD respectively). ^{13}C NMR spectra were measured at either 125 MHz or 150 MHz on the same instruments noted above for recording ^1H NMR spectra. Chemical shifts were again reported in accordance to residual protiated solvent peaks (δ 77.0, 39.5, 128.0 and 49.0 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6, and CD_3OD, respectively). IR spectral data were obtained using a Bruker Vector 22 spectrometer using either a thin film or an ATR adapter. Melting points were obtained with a Mel-Temp II (Laboratory Devices, Inc.) melting point apparatus. High-pressure liquid chromatography (HPLC) analyses were performed at 224 and 254 nm using Shimadzu HPLC, Model LC-20AB. An AD-H column (4.6 μm diameter x 258 mm) at a temperature of 40 ºC was employed, using a flow rate of 1 mL/min and a gradient starting at 10% isopropanol in hexanes for 10 min and increasing to 30% isopropanol in hexanes. The eluant was then held at 30% isopropanol in hexanes until the run was completed. Accurate mass measurements were acquired at the University of Wisconsin, Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods). The NMR and Mass Spectrometry facilities are funded by the NSF (CHE-9974839, CHE-9304546, CHE-9208463, CHE-9629688) and the University of Wisconsin, as well as the NIH (RR08389-01).

II. Preparation of Substrates for 1,3-halogen Migration

Substrates 2-bromostyrene (Table 1, entries 1-4), 2-bromo-5-methoxystyrene (entries 9-11), and 2-bromo-5-fluorostyrene (entries 5-6) were prepared according to previously reported procedures.[3]



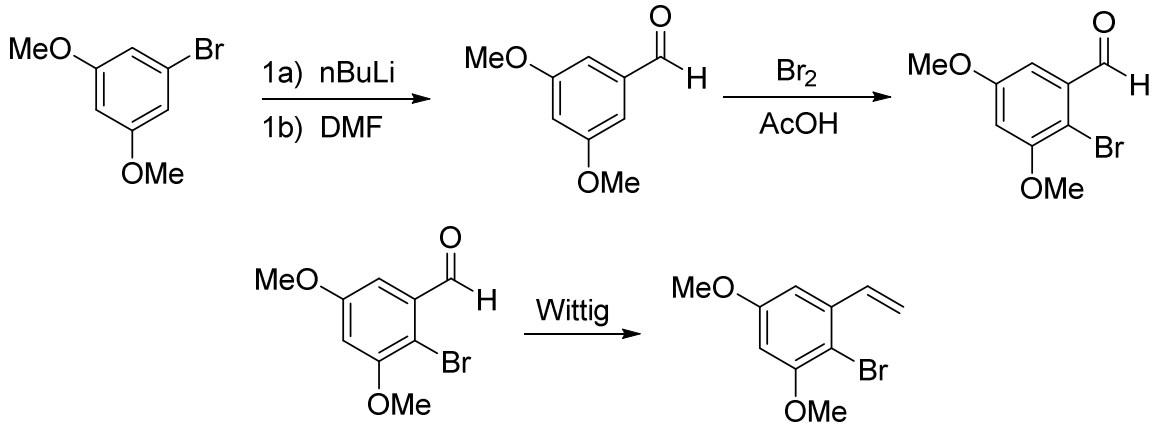
2-Bromo-β,β-dideuterostyrene (eq 4 in manuscript). A flame-dried 250 mL flask was charged with iodomethane-d_3 (0.93 mL, 14.9 mmol, 1.16 equiv), triphenylphosphine (3.96 g, 15.1 mmol, 1.18 equiv) and 70 mL of dry THF and equipped with a reflux condenser under an atmosphere of nitrogen. The reaction was refluxed for 6 h and then cooled in an ice bath. To the slurry was added nBuLi (6.0 mL of a 2.5 M solution in hexanes, 15 mmol, 1.17 equiv) in a dropwise fashion. The reaction was allowed to stir for 30 min and then 2-bromobenzaldehyde (1.5 mL, 12.8 mmol, 1.0 equiv) was added slowly. The reaction was allowed to stir at ambient temperature for 1 h and then quenched by adding silica gel. The mixture was concentrated *in vacuo* to a slurry. The slurry was poured onto the top of a pad of silica and then washed with ~500 mL of hexanes. The hexanes were removed *in vacuo* and the crude product was purified by column chromatography using hexanes as the eluant. The styrene was isolated as a clear, colorless oil in 18% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.0, 1.4 Hz, 2H), 7.28 (td, J = 7.8, 0.8 Hz, 1H), 7.11 (td, J = 7.8, 1.7 Hz, 1H), 7.05 (broad s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 135.6, 132.9, 129.1, 127.5, 126.8, 123.6, 116.1 (m). HRMS (EI) *m/z* calculated for $C_8H_5D_2Br$ $[M]^+$ 183.9852, found 183.9855.



2-Bromo-5-trifluoromethylstyrene (Table 1, entries 7-8).[4] A 250 mL three-neck round bottom flask was flame-dried, equipped with an addition funnel was placed under an atmosphere of nitrogen andcharged with 50 mL of THF. A portion of 10 mL of THF was placed in the addition funnel and the flask was placed in an acetone/CO_2 bath. Diisopropylamine (8.5 mL, 60.6 mmol, 1.21 equiv) was added to the flask and then nBuLi (26.0 mL of a 2.38 M solution in hexanes, 61.9 mmol, 1.24 equiv) was added dropwise. The reaction was allowed to stir at -78 ^{o}C for 20 min. then a solution of 4-trifluoromethylbromobenzene (7.0 mL, 50.0 mmol, 1.0 equiv) in THF was added dropwise over 10 min. Once the addition was complete, the reaction was allowed to stir for 30 min at -78 ^{o}C. A portion of dry DMF (11.0 mL, 142 mmol, 2.84 equiv) was added in one aliquot. After 5 min, the acetone/dry ice bath was removed and the reaction was allowed to warm to ambient temperature. After 1 h, 100 mL of 1 M HCl was added and the reaction was allowed to stir for 5 min. The mixture was extracted with CH_2Cl_2 three times and the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The product was purified by column chromatography using hexanes/EtOAc as the eluant. A gradient was employed using 0-10% EtOAc in 2% increments. The aldehyde was isolated as a yellow oil in 74% yield.

A flame-dried 500 mL round bottom flask was charged with triphenylmethylphosphonium iodide (9.64 g, 23.8 mmol, 1.20 equiv) and 200 mL of THF under an atmosphere of nitrogen and placed in an ice bath. To the slurry was added nBuLi (9.5 mL of a 2.38 M solution in hexanes, 22.6 mmol, 1.14 equiv) dropwise. The

reaction was allowed to stir for 30 min and then 2-bromo-5-trifluoromethylbenzaldehyde (3.0 mL, 19.9 mmol, 1.0 equiv) was added slowly. The reaction was allowed to stir at ambient temperature for 1 h and then quenched by adding silica gel. The mixture was concentrated *in vacuo* to a slurry. The slurry was poured onto the top of a pad of silica and washed with ~500 mL of hexanes. The hexanes were removed *in vacuo* and the crude product was purified by column chromatography using hexanes as the eluant. The styrene was isolated as a clear, colorless oil in 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.5 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.06 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.78 (d, *J* = 17.4 Hz, 1H), 5.48 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 134.8, 133.5, 130.1 (q, *J* = 32.8 Hz), 127.1 (q, *J* = 1.7 Hz), 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.4 Hz), 123.6 (q, *J* = 3.9 Hz). HRMS (EI) *m/z* calculated for $C_9H_6BrF_3$ $[M]^+$ 249.9600, found 249.9606.



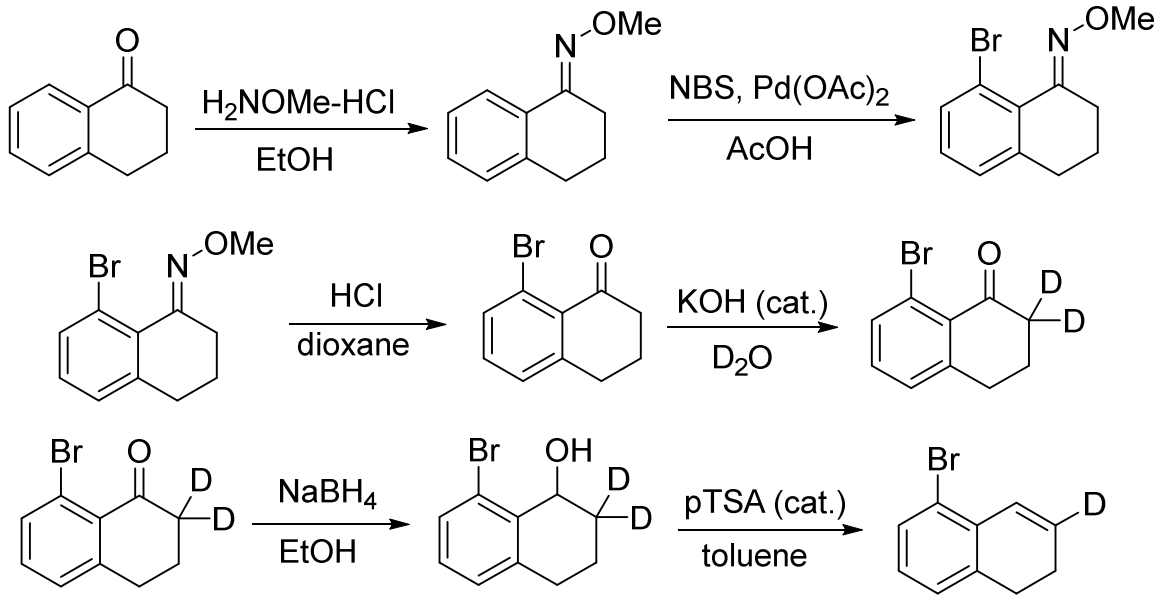
2-Bromo-3,5-dimethoxystyrene (Table 1, entries 12-14). A flame-dried 250 mL flask was charged with 3,5-dimethoxybromobenzene (5.00 g, 23.0 mmol, 1.0 equiv) and 150 mL of dry THF under an atmosphere of nitrogen. The flask was transferred to an acetone/dry ice bath and allowed to stir for 10 min. An aliquot of nBuLi (13.5 mL of a

2.08 M solution in hexanes, 28.1 mmol, 1.22 equiv) was added slowly. The reaction was allowed to stir for 20 min and then DMF (5.5 mL, 71.0 mmol, 3.09 equiv) was added in one aliquot. The reaction was allowed to stir for 20 min and then allowed to warm to ambient temperature. A portion of 100 mL 1 M HCl was added and the mixture was allowed to stir for 5 min. The aqueous mixture was extracted three times with CH_2Cl_2 and the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude material was purified by column chromatography using hexanes/EtOAc as the eluant. A gradient was employed using 0-30% EtOAc in 6% increments. The 3,5-dimethoxybenzaldehyde was isolated as a pale yellow solid in 78% yield.

A 100 mL round bottom flask was charged with 20 mL acetic acid, 3,5-dimethoxybenzaldehyde (3.00 g, 18.1 mmol, 1.0 equiv), and bromine (0.83 mL, 16.2 mmol, 0.90 equiv). The reaction was allowed to stir for 10 min and then poured into water/CH_2Cl_2. The organic layer was washed three times with water, once with saturated $NaHSO_3$ and once with 1 M KOH. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The solid crude product was placed in a Büchner funnel and washed with a small amount of cold methanol to remove the remaining starting material. The yellow solid was isolated in 71% yield and used without further purification.

The aldehyde was used in the subsequent Wittig olefination to prepare 2-bromo-3,5-dimethoxystyrene in a fashion similar to that described for the synthesis of 2-bromo-β,β-dideuterostyrene. The 2-bromo-3,5-dimethoxystyrene was purified by column chromatography using hexanes/CH_2Cl_2 as the eluant. A gradient was employed using 0-30% CH_2Cl_2 in 6% increments. The 2-bromo-3,5-dimethoxystyrene was isolated as a thick, clear oil in 29% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, J = 17.3, 10.9 Hz,

1H), 6.70 (d, *J* = 2.7 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 5.68 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.37 (dd, *J* = 10.8, 1.1 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 156.7, 139.1, 136.3, 116.9, 104.5, 102.8, 99.2, 56.4, 55.5. HRMS (EI) *m/z* calculated for $C_{10}H_{11}BrO_2$ $[M]^+$ 241.9937, found 241.9934.



5-Bromo(3-D)-1,2-dihydronaphthalene 6.1.[5] A 250 mL round bottom flask was charged with tetralone (6.5 mL, 48.9 mmol, 1.0 equiv) and methoxyamine hydrochloride (6.55 g, 78.4 mmol, 1.60 equiv) in 100 mL ethanol. The reaction was refluxed for 1.5 h, allowed to cool to ambient temperature and poured into water/CH_2Cl_2. The water layer was extracted 2x with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude product was used without further purification.

A 500 mL round bottom flask was charged with tetralone O-methyloxime (used directly from previous reaction), palladium acetate (0.559 g, 2.49 mmol, 5 mol%) and NBS (8.97 g, 50.4 mmol, ~1 equiv) in 350 mL of acetic acid. The reaction was refluxed under an atmosphere of nitrogen for 1.5 h. The reaction was allowed to cool to ambient

temperature and then poured into water and CH_2Cl_2. The organic layer was washed with water and then a portion of 1 M KOH. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The crude product was used without further purification.

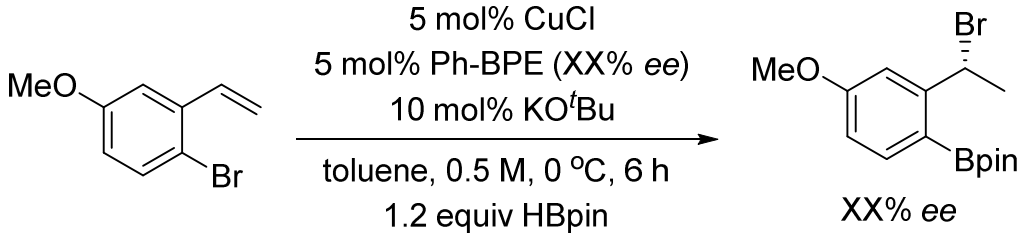
A 500 mL round bottom flask was charged with the crude bromotetralone O-methyloxime, 200 mL of 6 M HCl and 120 mL of dioxane. The reaction was refluxed for 2.5 h, allowed to cool to ambient temperature and poured into CH_2Cl_2/water. The layers were separated, the aqueous layer extracted twice with CH_2Cl_2, the combined organic layers dried with Na_2SO_4 and then concentrated *in vacuo*. The crude material was used without further purification.

A 250 mL round bottom flask was charged with 100 mL D_2O, bromotetralone (used directly from previous reaction), KOH (0.298 g, 5.31 mmol, 10 mol%), and 18-crown-6 (0.622 g, 2.35 mmol, 5 mol%). The reaction was refluxed for 1 h, allowed to cool to ambient temperature and poured into CH_2Cl_2. The aqueous layer was extracted twice with CH_2Cl_2 and the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude material was used without further purification.

A 250 mL round bottom flask was charged with deuterated bromotetralone (used directly from previous reaction) and $NaBH_4$ (3.681 g, 97.3 mmol, ~2 equiv) in 100 mL of EtOH. The reaction was allowed to stir at 0 ^oC for 30 min. Saturated NH_4Cl was added until the effervescence ceased. The reaction was then poured into water and CH_2Cl_2 and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude material was used without further purification. A 100 mL round bottom flask was charged with the deuterated bromotetralol (used directly from the previous reaction) and *para*-toluenesulfonic acid

(0.977 g, 5.14 mmol, ~10 mol%) in 50 mL of toluene. The flask was equipped with a Dean-Stark trap and a reflux condenser and the reaction refluxed for 30 min. The reaction was cooled to ambient temperature and poured into saturated $NaHCO_3$, the aqueous layer extracted with EtOAc, the combined organic layersdried with Na_2SO_4 and concentrated *in vacuo*. The product was purified by column chromatography using hexanes as the eluant. The deuterated bromodihydronaphthalene was isolated as a clear, colorless oil in 47% yield over the six steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.95 (t, J = 7.7 Hz, 1H), 6.83 (broad s, 1H), 2.78 (t, J = 8.2 Hz, 2H), 2.29 (t, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 133.0, 130.7, 130.6 (1,1,1-triplet, J = 24.6 Hz), 127.8, 126.7, 126.2, 121.9, 28.2, 22.7. HRMS (EI) *m/z* calculated for $C_{10}H_8DBr$ $[M]^+$ 208.9945, found 208.9946.

III. Non-linear effects study.



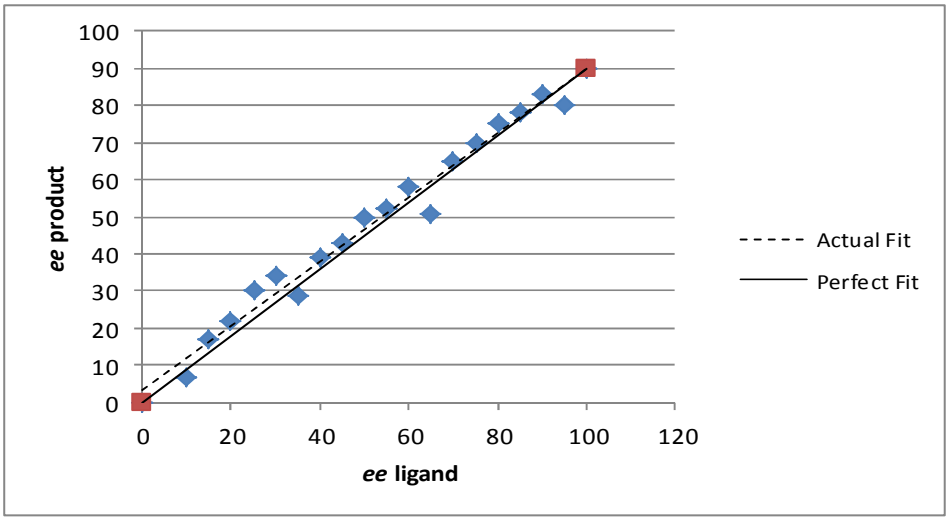
In a glovebox, a scintillation vial was charged with a solution of (*S,S*)-Ph-BPE (56 mg) in 4.0 mL of toluene (0.027 M). Another scintillation vial was charged with a solution of (*R,R*)-Ph-BPE (18 mg) in 1.3 mL of toluene (0.027 M). A mixture of CuCl (15 mg) and KO^{t}Bu (34 mg) was thoroughly ground together to form a homogenous, fine powder. A 1.5 mL vial was charged with 1.6 mg of the CuCl/KO^{t}Bu mixture (5 mol% CuCl, 10 mol% KO^{t}Bu) and the ligand solutions (5 mol% total ligand loading) so that the total volume was 250 μL; for exact amounts, see Table 1). The vial was equipped with a screw cap that had a septum and the reaction was removed from the glovebox. The reaction was allowed to stir for 10 min and then HBpin (22 μL, 0.15 mmol, 1.2 equiv) was added in one aliquot. The reaction was transferred to an ice bath and 2-bromo-5-methoxystyrene (19 μL, 0.125 mmol, 1.0 equiv) was added. The reaction was allowed to stir at 0 °C for 6 h and then passed through a plug of silica gel using diethyl ether as the eluant. The volatiles were removed *in vacuo* and the crude material was used for chiral HPLC analysis without further purification (in general, rigorous purification of enantioenriched benzyl bromides resulted in the degradation of *ee*). Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH

in hexanes; Detector: UV @ 254 nm and 225 nm. t_R = 4.15 min, t_S = 5.03 min, t_{SM} = 4.56 min.

Table 1: Tabulation of non-linear effects

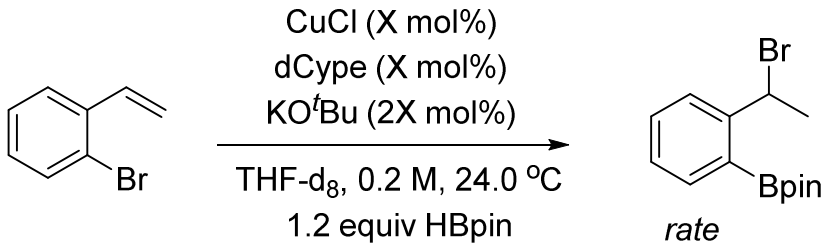
entry	*S* soln. (µL)	*R* soln. (µL)	ligand *ee*	product *ee*
1	250	0	100	90
2	244	6.0	95	80
3	238	12	90	83
4	231	19	85	78
5	225	26	80	75
6	219	31	75	70
7	213	37	70	65
8	206	44	65	51
9	200	50	60	58
10	194	56	55	52
11	188	62	50	50
12	181	69	45	43
13	175	75	40	39
14	169	81	35	29
15	163	87	30	34
16	156	94	25	30
17	150	100	20	22
18	144	106	15	17
19	138	112	10	7

Figure 1: Graph of non-linear effects with trend lines

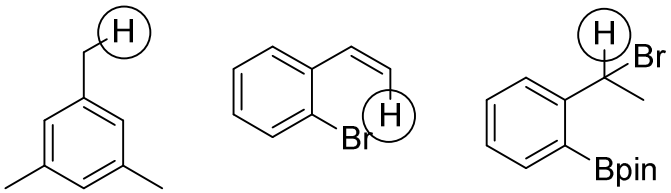


Perfect Linear Fit Equation: y = 0.9x
Actual Linear Fit Equation: y = 0.868x + 3.305; R^2 = 0.9801

IV. Kinetic studies of 1,3-halogen migration.



In a glovebox, CuCl, KOtBu, dCype and dry, degassed THF-d_8 (see Table 2 for exact amounts at different catalyst loadings) were added to a dry NMR tube. A rubber septum was placed on the tube and the tube was removed from the glovebox. Mesitylene (10 μL) was added to the NMR tube as an internal standard and the tube was sonicated for 10 min. Pinacol borane (HBpin, see Table 2) was added in one aliquot and the NMR tube was inverted once. The 2-bromostyrene (see Table 2) was immediately added and the tube was inverted once, a stopwatch was started, and the tube was placed in the spectrometer. The sample was locked and shimmed and then a pulse program was used that acquired a one-scan spectrum every 30 sec. The time from the injection of the 2-bromostyrene to the first scan was typically 1-4 min. The sample was spun at frequency of 20 Hz and the probe temperature was held steady at 24.0 °C. Typically, a sample from a previous run was used to set receiver gain, lock and shim so that minimal shim time on the new sample was required. For all runs, the circled protons were integrated.



The reaction showed first-order rate dependence on catalyst concentration displaying saturation between 5 mol% and 10 mol% catalyst loading (Fig. 2, 3; Table 3). This rate

dependence is likely due to catalyst solubility, as not all of the pre-catalyst went into solution (visually).

Table 2: Amounts of reagents for different catalyst loadings

cat. loading	CuCl (mg)	KOtBu (mg)	dCype (mg)	THF-d_8 (mL)	substrate (µL)	HBpin (µL)
1%	2.0 mL of a stock solution of CuCl (1.3 mg), KO^{t}Bu (2.9 mg) and dCype (5.5 mg) in 6.5 THF-d_8 was used.				50	70
2.5%	1.2	2.8	5.5	2.50	63	87
5%	1.2	2.8	5.5	1.25	31	44
10%	2.5	5.6	11	1.25	31	44
20%	5	11	21	1.25	31	44

Figure 2: Time courses with different catalyst loadings

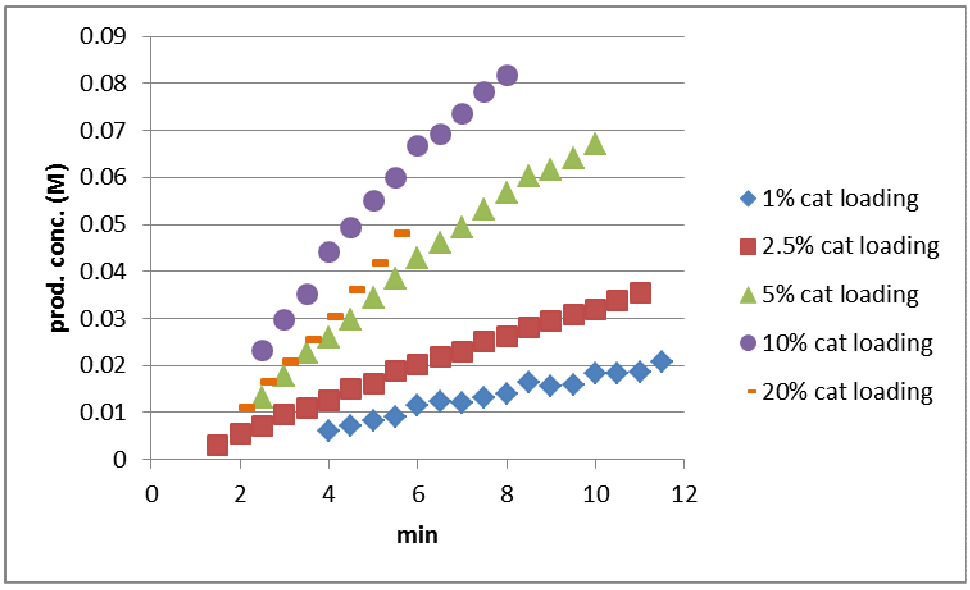
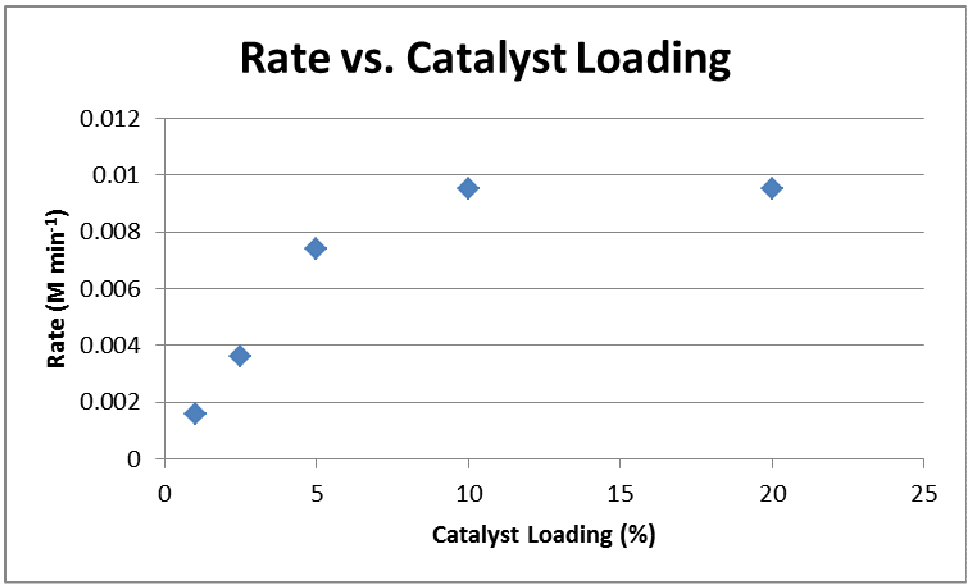


Table 3: Summary of kinetics studies with different catalyst loadings

catalystloading	initial rates	average	standard deviation
1%	0.001518	0.001604	8.38547E-05
1%	0.00161		
1%	0.001685		
2.50%	0.003248	0.003633	0.000405858
2.50%	0.003342		

2.50%	0.003838		
2.50%	0.004102		
5%	0.006305	0.007388	0.000483438
5%	0.006985		
5%	0.007241		
5%	0.009021		
10%	0.008738	0.009506	0.00107051
10%	0.00905		
10%	0.010729		
20%	0.008699	0.009539	0.000737983
20%	0.00921		
20%	0.009863		
20%	0.010385		

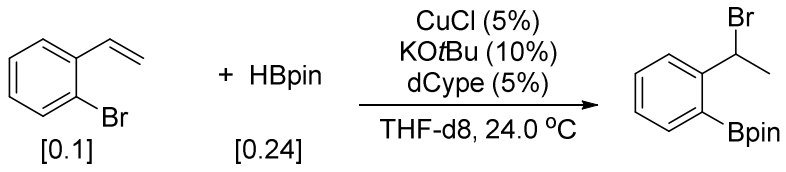
Figure 3: Rate vs. catalyst loading

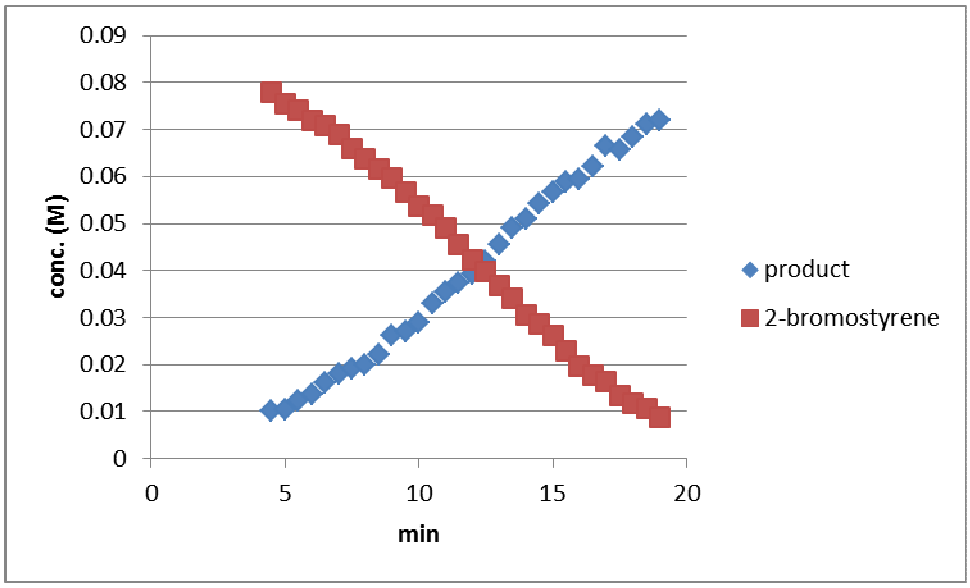


Over the course of the entire reaction, the rate of the reaction did not change as both the concentration of the 2-bromostyrene and HBpin changed (Figure 4). From this observation, it was determined that the reaction rate is not dependent on either 2-bromostyrene or HBpin. However, most time courses showed dramic changes in rate over time as catalyst death occurred,[6] eventually halting the reaction altogether.

Deuterating the substrate at the terminal position of the styrene resulted in a small normal KIE of 1.19 ±0.1 (Figure 5, Table 4).

Figure 4: Time course over entire reaction

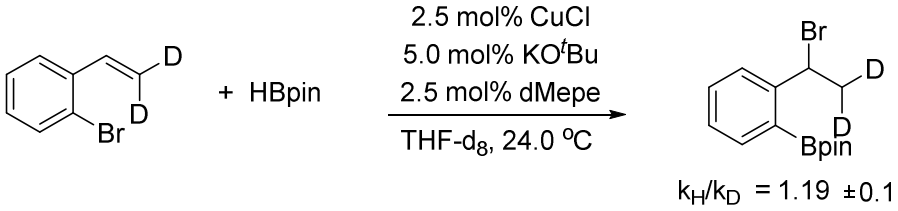




To determine if there was a change in rate if the terminal position of the styrene was deuterated, the reaction was run using 2-bromo-β,β-dideuterostyrene. The same procedure was used as described above except 13 µL of 2-bromo-β,β-dideuterostyrene (0.099 mmol, 1.0 equiv), 17 µL HBpin (0.117 mmol, 1.18 equiv), and 0.5 mL of a stock solution of 1.5 mg CuCl, 3.4 mg KO^{t}Bu, and 6.3 mg dCype in 3.0 mL of THF-d_8 was used (2.5 mol% catalyst loading). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.46 (td, *J* = 7.7, 1.5 Hz, 1H), 7.26 (td, *J* = 7.3, 1.1 Hz, 1H), 6.24 (d, *J* = 6.8 Hz, 1H), 1.99 (broad-d, *J* = 7.0 Hz, 1H), 1.37 (s, 6H), 1.36

(s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 135.9, 131.5, 127.2, 126.4, 83.9, 48.5, 26.5 (1:2:3:2:1-pentet, J = 19.9 Hz), 25.0, 24.7. HRMS (ESI) *m/z* calculated for $C_{14}H_{22}D_2BBrNO_2$ $[M+NH_4]^+$ 330.1206, found 330.1215.

Figure 5: Time courses of unlabeled *vs*. deuterated substrate



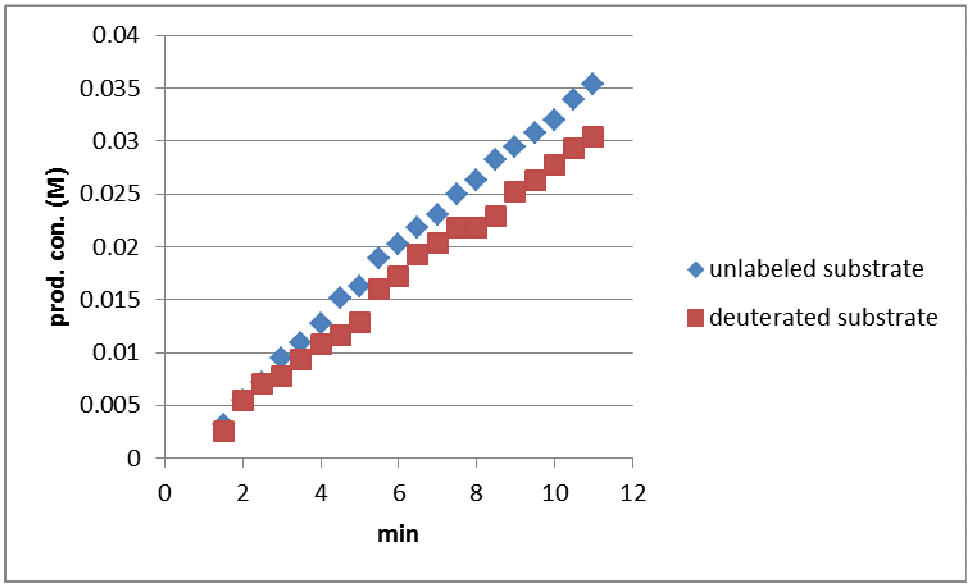
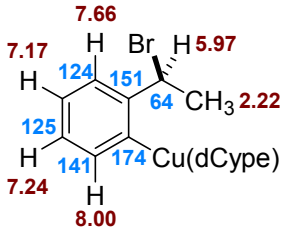


Table 4: Summary of KIE studies

substrate	initial rate	average	standard deviation	k_H/k_D	error
deuterated	0.003202	0.00304	0.000175	1.194901	0.105191
deuterated	0.003063				
deuterated	0.002855				
unlabeled	0.003248	0.003633	0.000406		
unlabeled	0.003342				
unlabeled	0.003838				
unlabeled	0.004102				

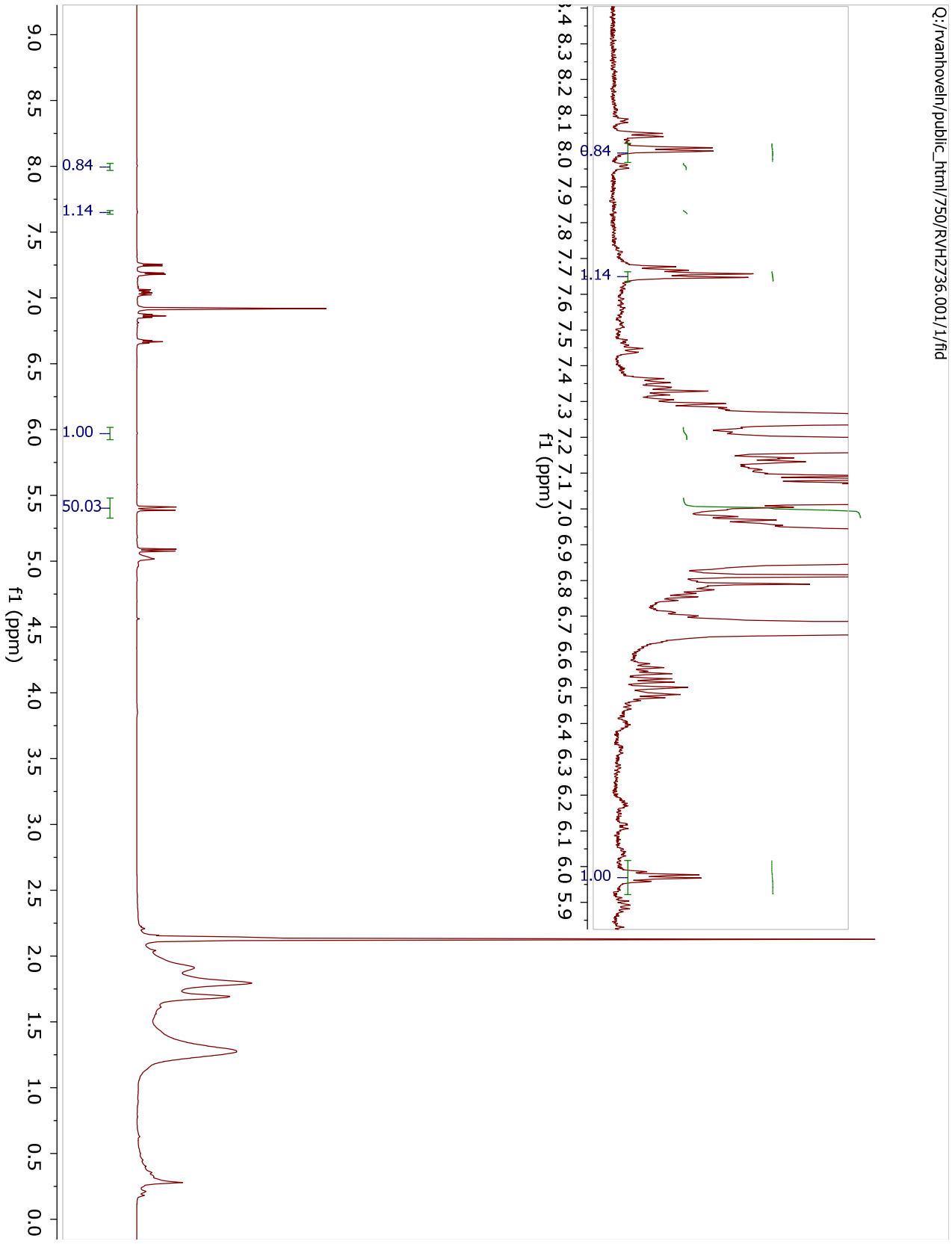
V. Stoichiometric Characterization of Aryl Copper

In a glovebox, a dry NMR tube was charged with $Cu(OAc)_2$ (4.5 mg, 24.8 μmol, 1.0 equiv), dCype (11 mg, 26.0 μmol, 1.05 equiv) and 0.5 mL of *p*-xylene-d_{10}. The NMR tube was equipped with a septum and removed from the glovebox where the septum was wrapped with parafilm. The NMR tube was shaken, then PHMS (3.0 μL, 50.2 μmol, 2.03 equiv) and then shaken again. Just before placing in the spectrometer, 2-bromostyrene (3.1 μL, 24.7 μmol, 1.0 equiv) was injected and then the NMR tube was warmed in 40-45 °C water for 1.5-2 minutes. The NMR tube was then placed in an NMR spectrometer where the probe had been pre-cooled to 10 °C. At this temperature, the aryl copper species was stable for 1.5-2 hours before significant degradation occurred.

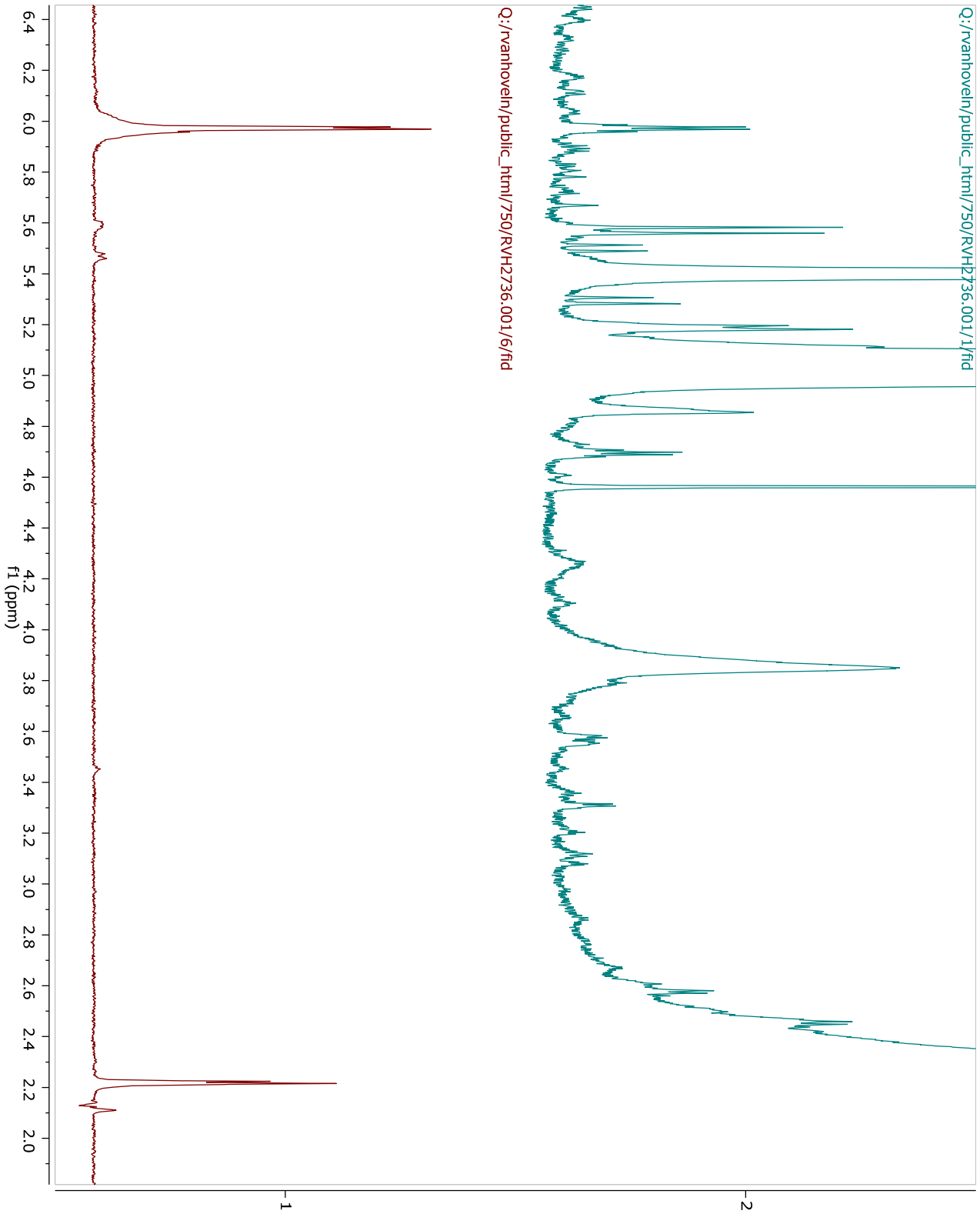


All spectra were acquired on a 750 MHz NMR.

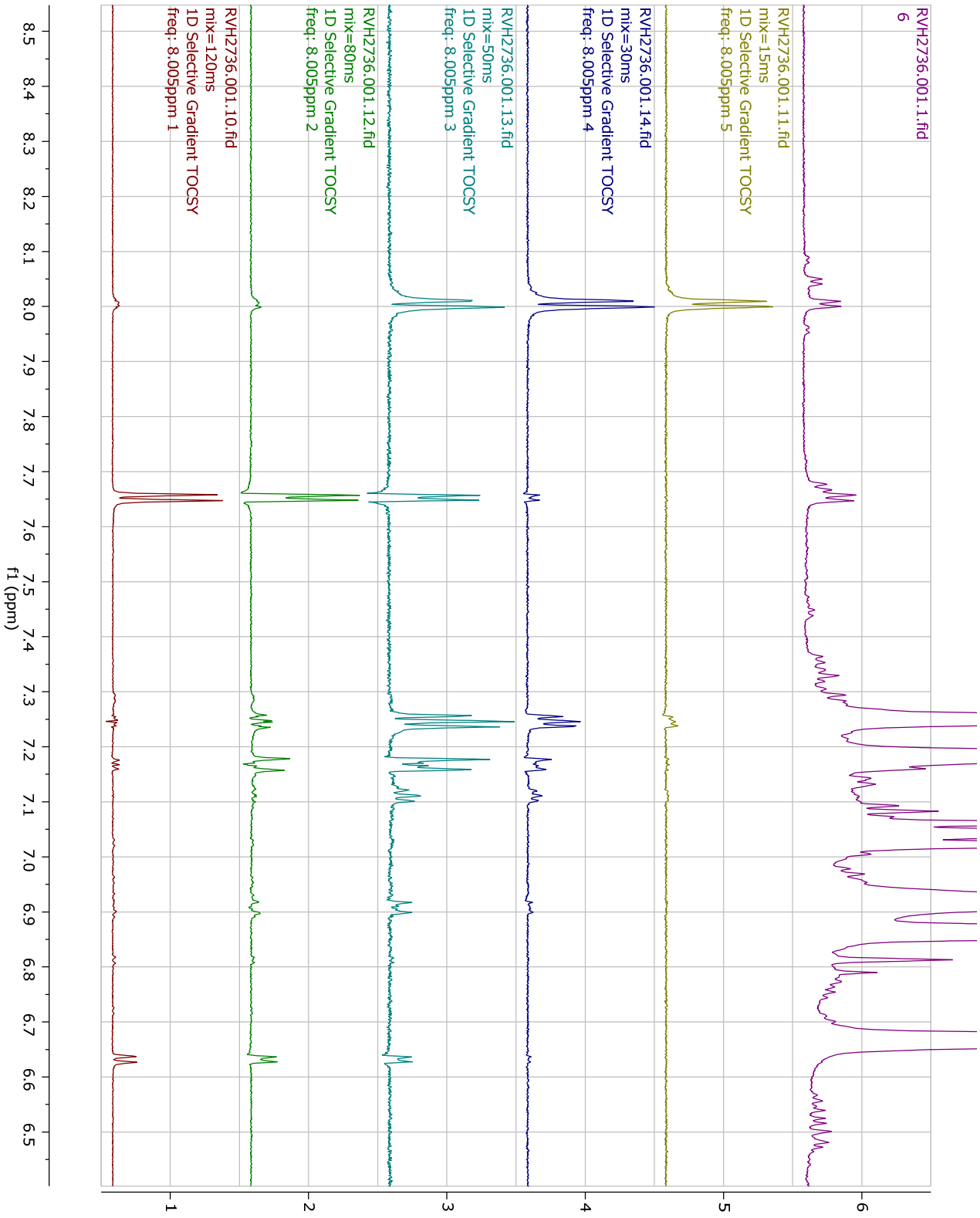
^{1}H-NMR of aryl copper



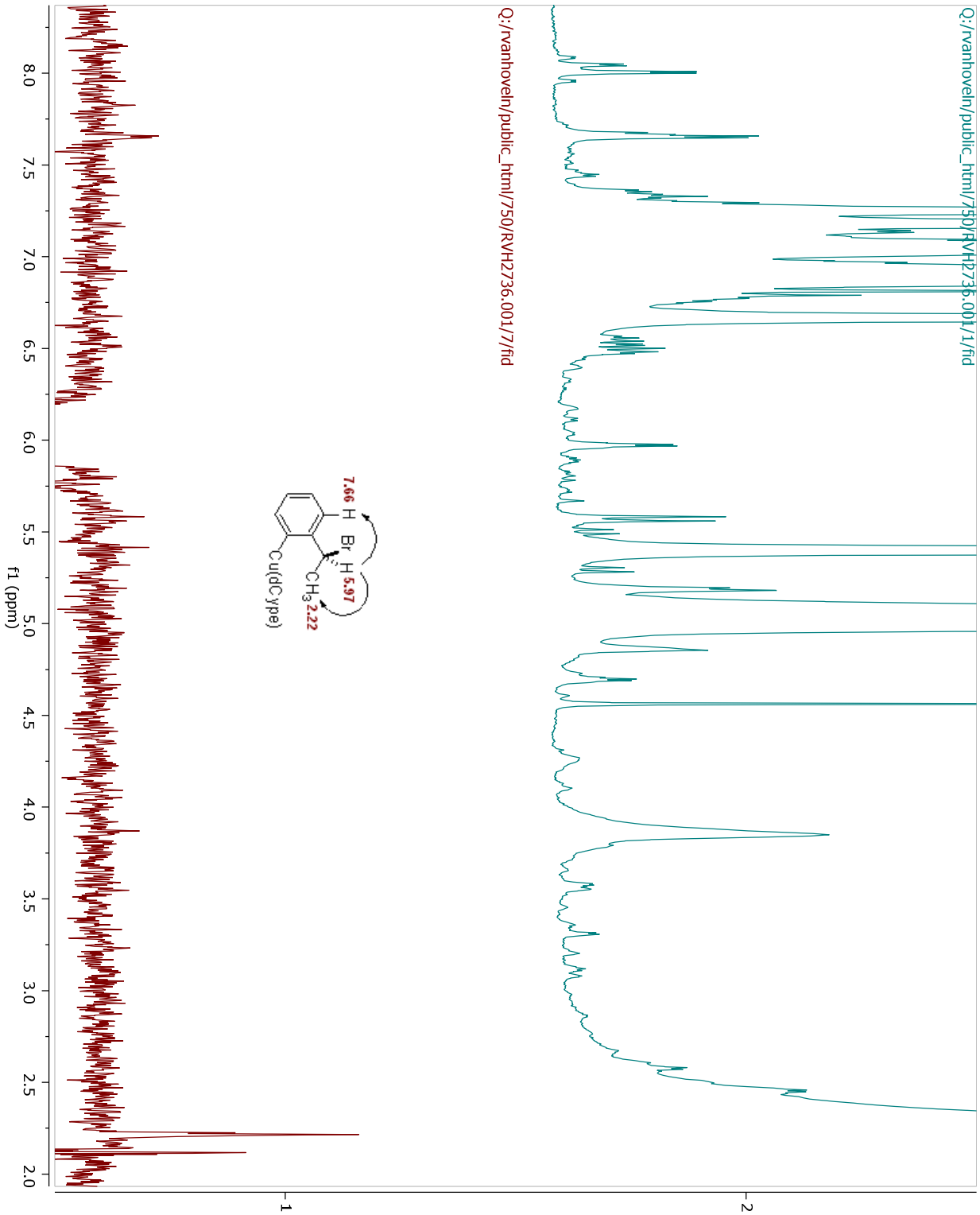
1D-TOCSY selecting proton at 5.97 ppm (stacked with ^{1}H-NMR)



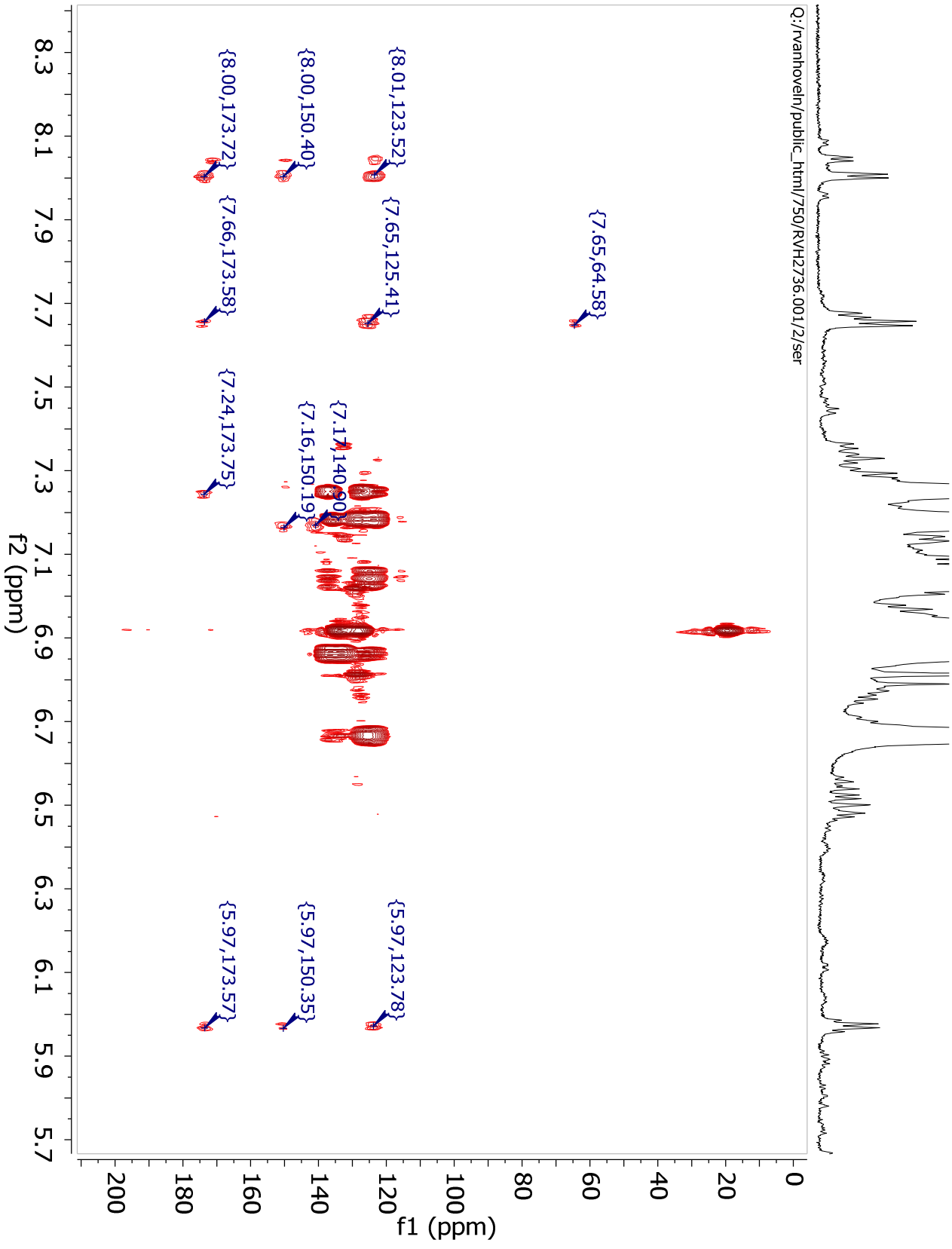
1D-TOCSY selecting proton at 8.00 ppm (stacked with ^{1}H, various mix times)



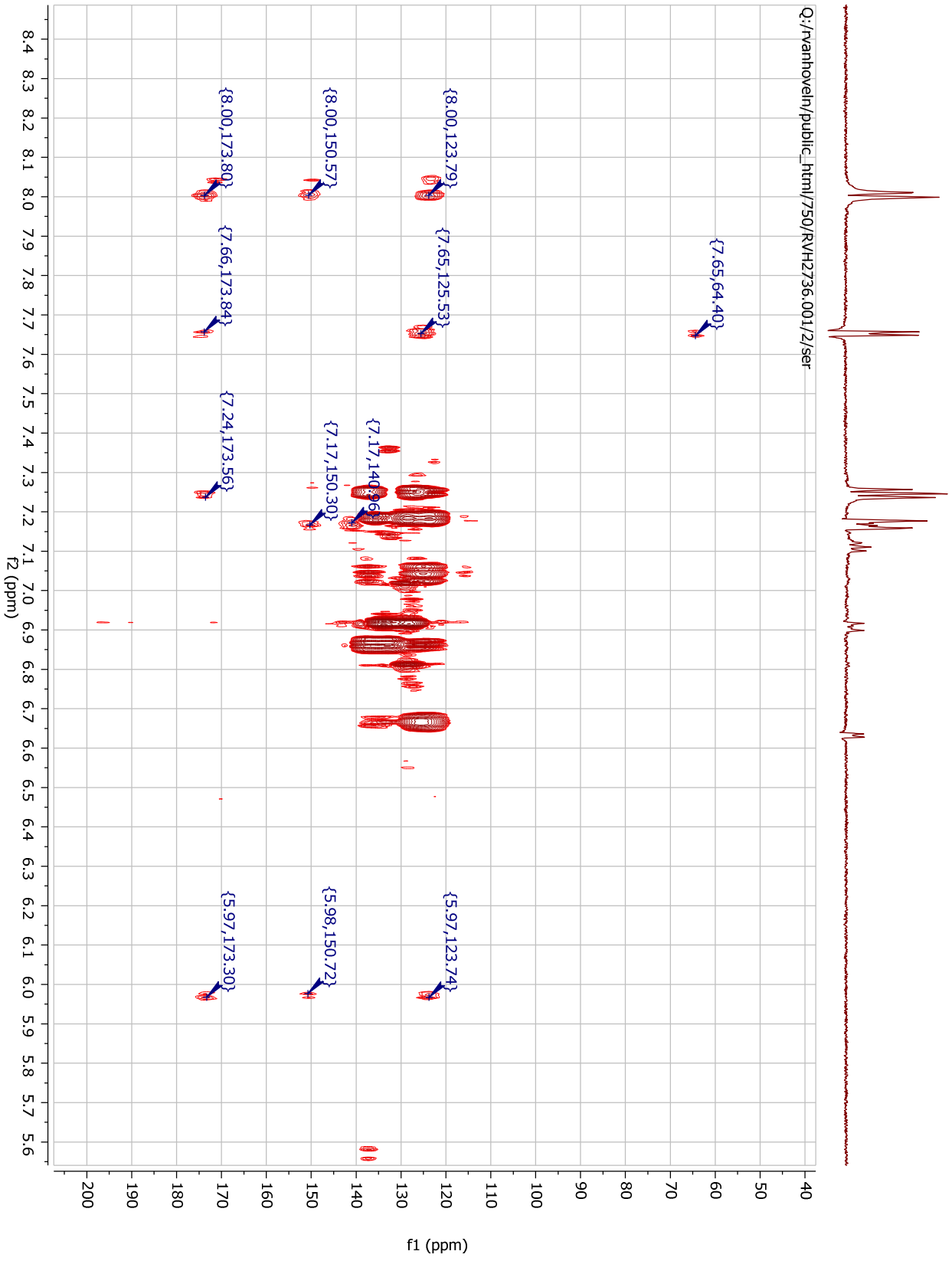
1D-NOESY selecting proton at 5.97 ppm (stacked with ^{1}H)



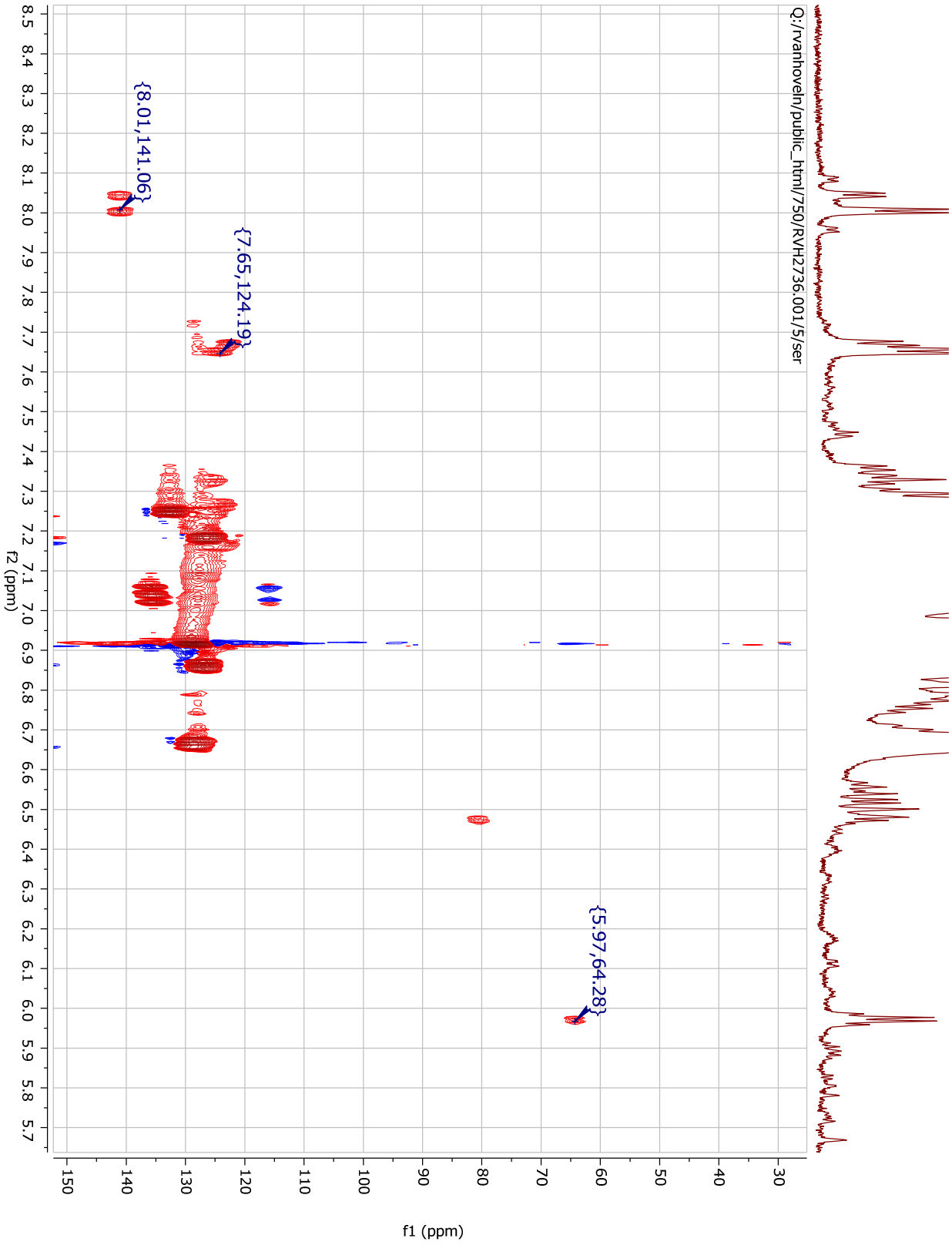
HMBC with ^{1}H trace



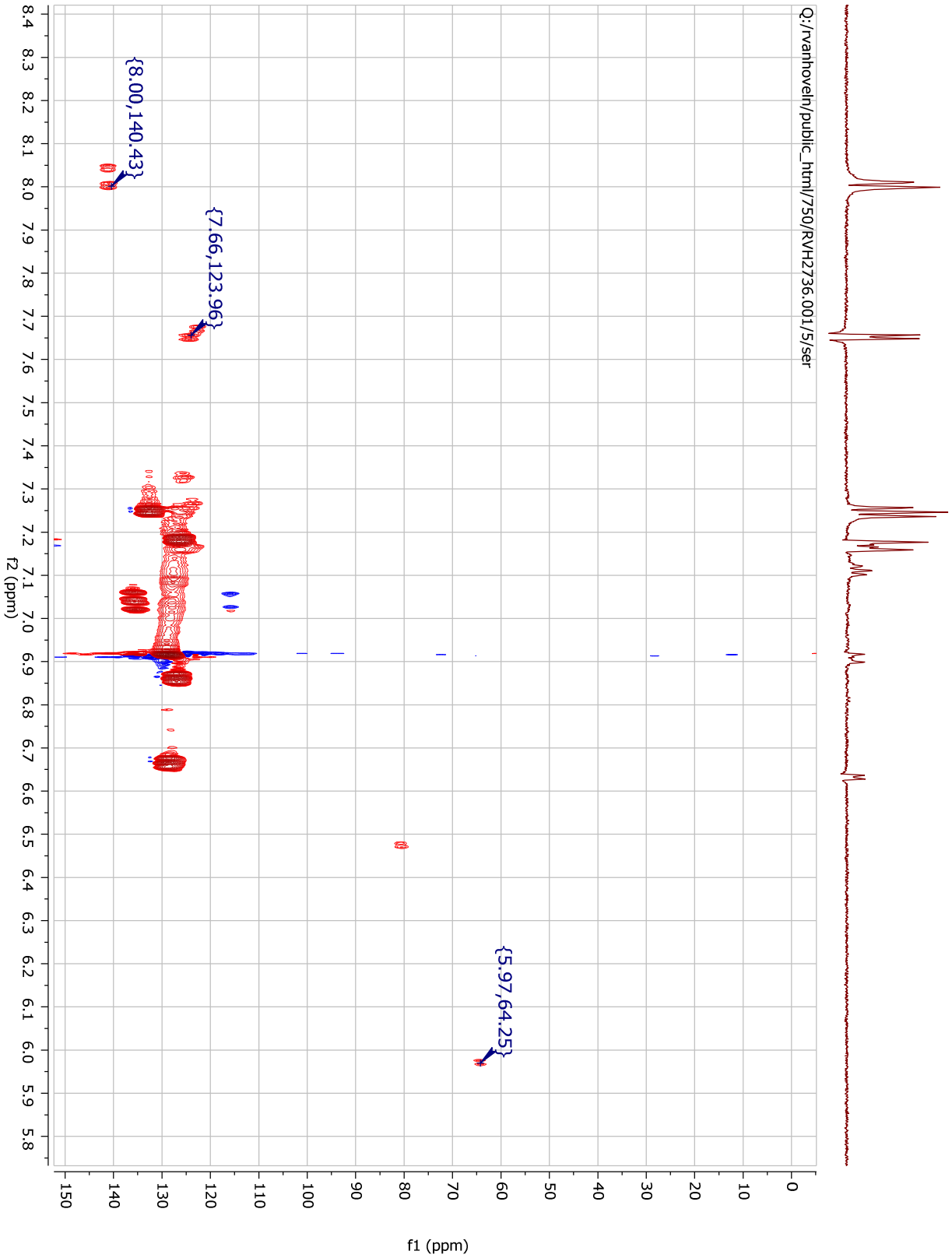
HMBC with 1D-TOCSY trace



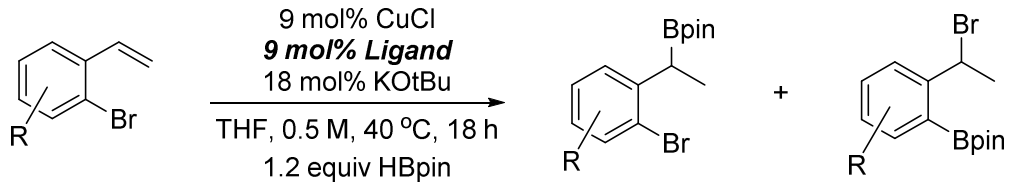
HSQC with ^{1}H trace



HSQC with 1D-TOCSY trace



VI. Factors impacting selectivity.



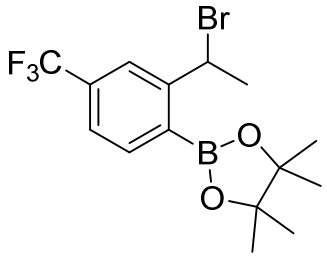
In a glovebox, CuCl (2.5 mg, 0.025 mmol, 10 mol%), KO^{t}Bu (5.6 mg, 0.050 mmol, 20 mol%), the ligand (see Table 5 for exact amount, 0.025 mmol, 10 mol%) and 0.5 mL of dry, degassed THF were added to a dry round bottom flask. A rubber septum was placed on the flask and the flask was removed from the glovebox. Pinacol borane (HBpin, 0.05 mL, 0.35 mmol, 1.4 equiv) was added in one aliquot and then a 2-bromostyrene (see Table 2, 0.25 mmol, 1.0 equiv) was added. The reaction was transferred to a sand bath set to 40 °C and stirred for at least 30 min (typically, overnight). The reaction was quenched by filtering through a pad of celite eluted with diethyl ether. The solvent was removed *in vacuo* and the NMR yield was determined by using 1,1,1,2-tetrachloroethane as an internal standard (see Table 5).

Table 5: Effects of ligand sterics and substrate electronics

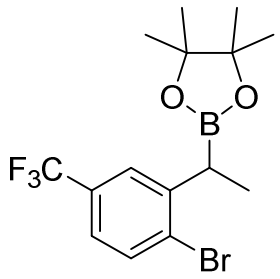
entry	Ligand	Substrate	Ligand Amt. (mg or μL)	Substrate amt. (μL)	Hydroboration (%)	Migration (%)
1	dCype	H	11 mg	40	0	94
2	dMepe	H	4.0 μL	40	91	0
3	dEtpe	H	6 μL	40	98	0
4	Ph-BPE	H	13 mg	40	0	37
5	dCype	5-F	11 mg	40	28	49
6	Ph-BPE	5-F	13 mg	40	0	21
7	dCype	5-CF_3	11 mg	40	31	28
8	Ph-BPE	5-CF_3	13 mg	40	6	14
9	dCype	5-OMe	11 mg	40	0	87
10	dMepe	5-OMe	4.0 μL	40	52	0
11	dEtpe	5-OMe	6 μL	40	100	0

12	dCype	3,5-OMe	11 mg	50	0	98
13	dMepe	3,5-OMe	4.0 μL	50	40	16
14	dEtpe	3,5-OMe	6 μL	50	32	17

Spectra of benzyl bromides and boronic esters for entries 1-6,[3] 9-11[7] match previously reported data.

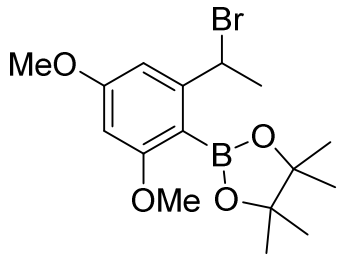


2-[2-(1-bromoethyl)-4-trifluoromethylphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entries 7-8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.86 (m, 2H), 7.49 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.22 (q, *J* = 6.9 Hz, 1H), 2.03 (d, *J* = 6.9 Hz, 3H), 1.39 (s, 6H), 1.37 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 136.4, 133.2 (q, *J* = 32.3 Hz), 123.9 (q, *J* = 272.6 Hz), 123.7 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 3.8 Hz), 84.4, 46.9, 26.8, 25.0, 24. HRMS (EI) *m/z* calculated for $C_{15}H_{19}BBrF_3O_2$ $[M]^+$ 378.0611, found 378.0608.

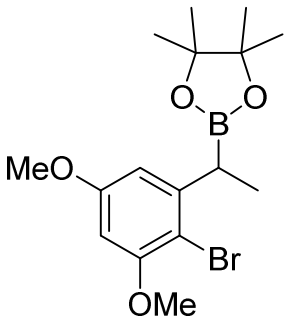


2-[1-(2-bromo-5-trifluoromethylphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entries 7-8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.26 (dd, *J* = 8.3, 2.2 Hz, 1H), 2.82 (q, *J* = 7.5 Hz, 1H), 1.37 (d, *J* = 7.5 Hz, 3H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 133.0,

129.8 (q, J = 32.4 Hz), 128.7 (q, J = 1.6 Hz), 125.5 (q, J = 3.8 Hz), 124.1 (q, J = 272.2 Hz), 123.4 (q, J = 3.8 Hz), 83.7, 24.7, 24.6, 15.5. HRMS (EI) *m/z* calculated for $C_{15}H_{19}BBrF_3O_2$ $[M]^+$ 377.0645, found 377.0646.



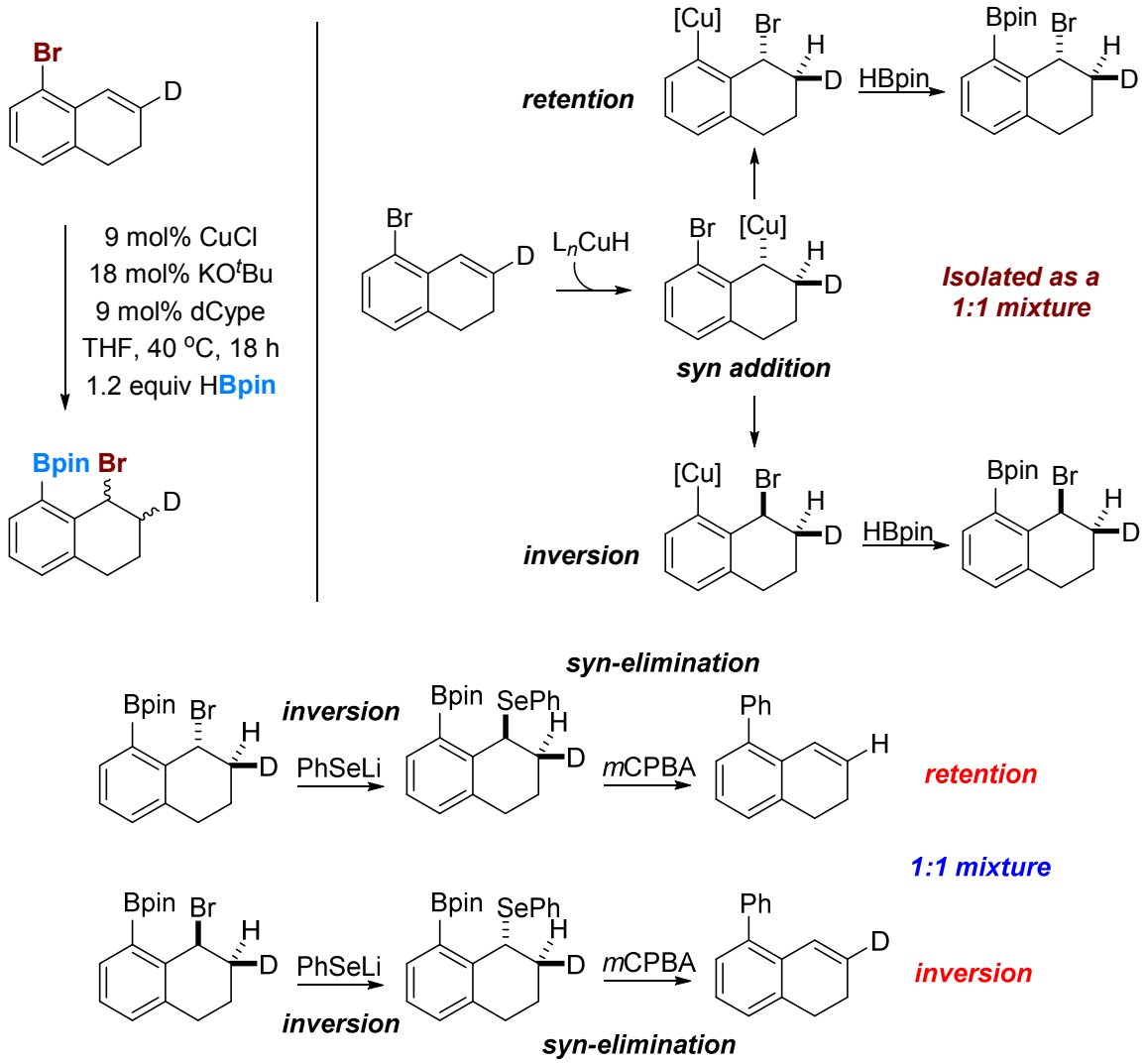
2-[2-(1-bromoethyl)-4,6-dimethoxyphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entries 12-14). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (d, J = 2.0 Hz, 1H), 6.31 (d, J = 2.0 Hz, 1H), 5.45 (q, J = 6.8 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 2.00 (d, J = 6.8 Hz, 3H), 1.40 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 162.3, 149.5, 103.2, 97.5, 83.8, 55.7, 55.3, 48.8, 27.1, 24.9, 24.7. HRMS (ESI) *m/z* calculated for $C_{16}H_{25}BBrO_4$ $[M+H]^+$ 371.1027, found 371.1032.



2-[1-(2-bromo-3,5-dimethoxyphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entries 12-14). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (d, J = 2.7 Hz, 1H), 6.35 (d, J = 2.7 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.83 (q, J = 7.5 Hz, 1H), 1.35 (d, J = 7.7 Hz, 3H), 1.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 156.4, 146.6, 105.6, 105.1,

96.8, 83.5, 56.2, 55.4, 24.8, 24.7, 15.7. HRMS (EI) *m/z* calculated for $C_{16}H_{25}BBrO_4$ $[M+H]^+$ 370.1061, found 370.1057.

VII. Transfer of stereochemistry with deuterated dihydronaphthalene.



To better understand the nature of the 1,3-halogen migration, an experiment was designed to explore how stereochemical information in the reaction is transferred from the benzyl copper to the aryl copper species, and eventually to the final product. A deuterated dihydronaphthalene substrate was designed to determine if the stereochemistry set during the initial hydrocupration step was retained, inverted or ablated during the 1,3-halogen migration event. Since the hydrocupration of a π-bond occurs in a syn fashion to give a benzyl copper, the stereochemistry of the bromine relative to the deuterium in the

final product should indicate whether migration occurs with retention or inversion of stereochemistry. In the case of retention, the product should display an *anti* relationship between the two protons on adjacent carbons. If inversion is taking place, then the product should display a *syn* relationship between these same two protons. The benzyl bromide could not be isolated, as it degraded during attempted purification by column chromatography. Even so, NMRs of the two diastereomers of the product would be nearly identical, and therefore not diagnostic. An alternative strategy involved displacement of the benzyl bromide with lithium phenylselenoate, which proceeds with excellent inversion of stereochemistry.[7] Selenoxide eliminations are known to proceed through a *syn* elimination.[8] Thus, if migration occurs through inversion of stereochemistry, then deuterium should be incorporated into the final product. If migration occurs through retention of stereochemistry, then the final product should contain exclusively protons. Interestingly, the olefin that was isolated was nearly 50:50 proto:deutero, as supported by both the mass spec and NMR data, indicating the presence of a stereo-ablative step in the migration process.

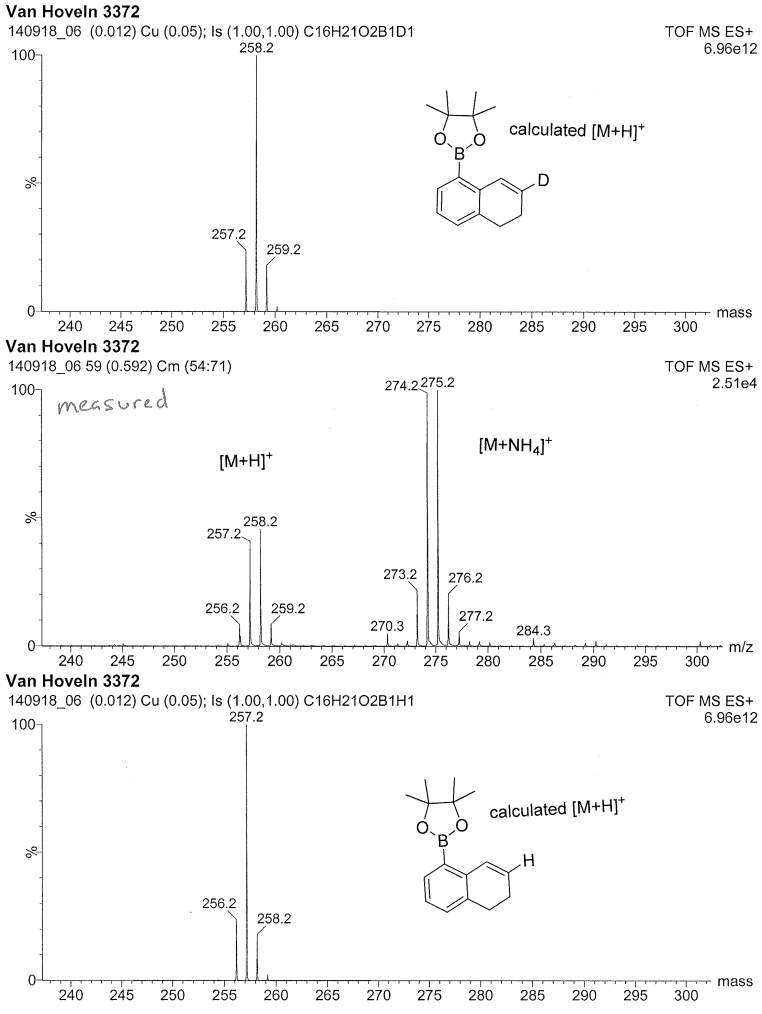
8-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)]-1-(phenylselenyl)(2-D)-1,2,3,4-tetrahydronaphthalene. In a glovebox, a dry 25 mL round bottom flask was charged with CuCl (50 mg, 0.51 mmol, 10 mol%), KO^{t}Bu (112 mg, 1.0 mmol, 20 mol%), and dCype (211 mg, 0.50 mmol, 10 mol%) in 10 mL of THF and allowed to stir for 10 min. HBpin (0.87 mL, 6.00 mmol, 1.21 equiv) was added in one aliquot and the reaction was stirred for a few minutes, followed by addition ofthe deuterated bromodihydronaphthalene (0.72 mL, 4.94 mmol, 1.0 equiv). The reaction was allowed to stir for 3 h at 40 ^{o}C. Meanwhile, lithium phenylselenoate was prepared by treating

selenium metal (0.394 g, 4.99 mmol, 1.01 equiv) in 5 mL of THF with phenyllithium (2.8 mL of a 1.8 M solution in dibutylether, 5.04 mmol, 1.01 equiv) and allowing it to stir for 30 min. The LiSePh solution was then transferred to the round bottom flask containing the 1,3-halogen migration reaction mixture, and allowed to stir at ambient temperature for 3 h. The reaction mixture was filtered through a pad of celite, washed with Et_2O (2x10 mL) and the solvent removed *in vacuo*. The crude material was purified by column chromatography using hexanes/CH_2Cl_2 as the eluant. A gradient was employed using 0-50% CH_2Cl_2 in 10% increments. The purified product was isolated as a pale yellow, viscous oil in 47% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.53 (m, 3H), 7.30–7.08 (m, 3H), 7.13–7.09 (m, 2H), 5.78 (s, 1H), 2.90–2.73 (m, 2H), 2.41–2.22 (m, 1H), 2.06–1.92 (m, 1H), 1.79–1.66 (m, 1H), 1.33 (s, 6H), 1.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 136.9, 133.4, 132.8, 132.1, 131.9, 128.8, 126.6, 126.0, 83.7, 42.9, 29.6, 27.8 (1,1,1-triplet, J = 19.6 Hz), 25.1, 24.6, 18.5. HRMS (EI) *m/z* calculated for $C_{22}H_{30}DBSeO_2$ $[M+NH_4]^+$ 433.1675, found 433.1670.

8-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)]-2-deutero-3,4-dihydronaphthalene.[9]

It was necessary to run the reaction at cold temperatures, using *m*CPBA as the oxidant to prevent competing oxidation of the boronic ester and olefin. The phenylselenide from above (0.206 g, 0.50 mmol, 1.0 equiv) was dissolved in ~1.5 mL of CH_2Cl_2 in a vial. The vial was placed in an acetone/CO_2 bath and then *m*CPBA (0.125 g, 0.72 mmol, 1.45 equiv) in ~1 mL of CH_2Cl_2 was added to the vial slowly. The reaction was allowed to stir for 15 min at -78 ^{o}C and then poured into 30 mL of 50:50 CH_2Cl_2:Et_3N. The organic was washed with water and the aqueous layer was extracted once with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude

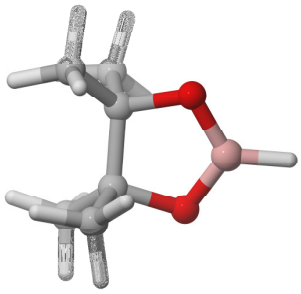
product was purified by column chromatography using hexanes/CH_2Cl_2 as the eluant. A gradient was employed using 0-50% CH_2Cl_2 in 10% increments. The product was isolated in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.17 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.10 (dt, *J* = 9.8, 4.4 Hz, 0.5H), 2.78 (t, *J* = 8.2 Hz, 2H), 2.36 – 2.21 (m, 2H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6, 135.4, 134.2, 130.4, 129.3, 129.0 (1,1,1-triplet, *J* = 24.3 Hz), 128.2, 128.0, 125.9, 83.5, 28.3, 24.9, 22.8, 22.7. HRMS (ESI) *m/z* calculated for $C_{16}H_{24}BNO_2$ $[M+NH_4]^+$ 273.2009, found 273.2012.



VIII. Computational details and optimized geometries.

All structures throughout these studies (except where noted) were optimized with Gaussian 09[10] using the M06[11] functional (unless otherwise noted) with a 6-311G* basis set for H, B, C, O, P, and Br[12] and a LANL2TZ+ basis set designed for copper (unless otherwise indicated).[13] An SMD continuum solvent model was used with THF as the solvent.[14] All minima were checked for absence of imaginary vibrational modes and all transition states were checked for one imaginary vibrational mode and confirmed with IRC[15] calculations.

A. Impact of steric bulk on hydroboration of benzyl copper.



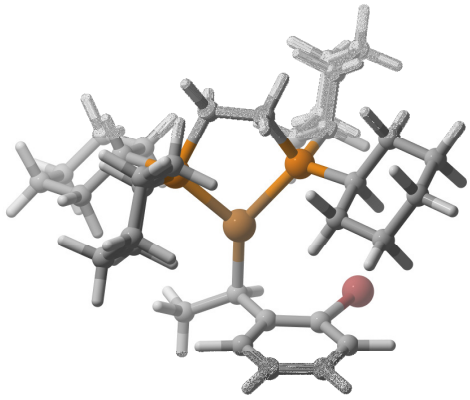
pinacol borane (HBpin) (entry 1)

RM06 energy: -411.6949742

Sum of electronic and thermal Free Energies: -411.53869

6	-0.777774	-0.188563	0.054067
8	-1.065963	1.191305	0.407590
5	-0.000002	1.928162	0.000002
8	1.065962	1.191309	-0.407584
6	0.777774	-0.188562	-0.054067
6	1.472695	-0.446512	1.269144
1	1.379804	-1.492214	1.581852
1	2.539302	-0.221746	1.159936
1	1.079216	0.190231	2.069403
6	1.341781	-1.095676	-1.120875
1	2.435189	-1.024740	-1.126912
1	1.078151	-2.141385	-0.921025
1	0.984050	-0.833537	-2.120512

1	-0.000002	3.114082	0.000009
6	-1.472695	-0.446506	-1.269146
1	-1.079218	0.190242	-2.069402
1	-1.379803	-1.492207	-1.581859
1	-2.539302	-0.221743	-1.159936
6	-1.341778	-1.095684	1.120869
1	-2.435187	-1.024749	1.126908
1	-1.078148	-2.141391	0.921014
1	-0.984047	-0.833551	2.120508



benzyl copper (dCype) (entry 2)

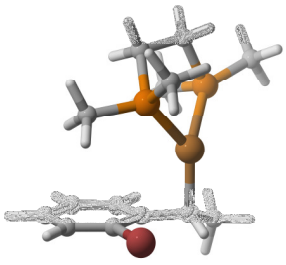
RM06 energy: -4781.6101141

Sum of electronic and thermal Free Energies: -4780.849906

6	0.005603	0.788502	2.453552
6	-1.463952	1.080488	2.154490
15	-2.126424	0.070605	0.739439
6	-2.811384	-1.484297	1.514505
1	-3.844916	-1.256138	1.830206
6	-2.041506	-1.967758	2.741485
6	-2.665458	-3.237553	3.307585
6	-2.736595	-4.341855	2.264151
6	-3.466496	-3.869233	1.015892
6	-2.837532	-2.598523	0.465636
1	-3.357433	-2.277093	-0.446021
1	-1.796825	-2.805521	0.160982
1	-4.523863	-3.674401	1.259384
1	-3.464760	-4.653614	0.247664

1	-3.220561	-5.234377	2.682183
1	-1.713146	-4.643367	1.988553
1	-3.681747	-3.007743	3.665959
1	-2.097518	-3.572666	4.185594
1	-0.996961	-2.176444	2.455276
1	-2.008863	-1.192901	3.517407
6	-3.639584	1.049942	0.276196
1	-4.156020	1.323068	1.214608
6	-3.212766	2.325855	-0.451476
6	-4.410359	3.154938	-0.892460
6	-5.352279	2.339147	-1.762438
6	-5.792654	1.076009	-1.040483
6	-4.598017	0.242372	-0.596990
1	-4.950548	-0.651393	-0.066338
1	-4.054299	-0.115241	-1.487580
1	-6.389730	1.351790	-0.156204
1	-6.449293	0.472049	-1.680489
1	-6.223378	2.939260	-2.056077
1	-4.835246	2.062989	-2.695951
1	-4.953605	3.510935	-0.002243
1	-4.068384	4.051549	-1.425622
1	-2.552773	2.933375	0.181340
1	-2.615370	2.044289	-1.336183
29	-0.336394	0.064735	-0.758431
15	1.051288	0.869539	0.917830
6	2.572206	-0.100555	1.350891
6	3.305677	0.313334	2.622724
6	4.546601	-0.542523	2.850028
6	4.210927	-2.025769	2.863983
6	3.493011	-2.432924	1.586119
6	2.241779	-1.594274	1.368020
1	1.531356	-1.805973	2.183889
1	1.740028	-1.881487	0.431889
1	4.171766	-2.298833	0.727912
1	3.231759	-3.499322	1.609165
1	3.563084	-2.244093	3.728845
1	5.121775	-2.623267	3.001533
1	5.271217	-0.344367	2.043846
1	5.038930	-0.247953	3.786323
1	3.591988	1.372002	2.577232
1	2.627330	0.208272	3.485251
1	3.236306	0.079297	0.486382
6	1.610724	2.642195	0.760178
6	1.629553	3.469886	2.042580
6	2.161150	4.874028	1.782201
6	1.348696	5.582027	0.709025

6	1.301379	4.761847	-0.571193
6	0.781205	3.355557	-0.310698
1	0.769911	2.765816	-1.237168
1	-0.268639	3.413384	0.025585
1	0.680477	5.260315	-1.327337
1	2.315291	4.694698	-0.998078
1	0.321656	5.736509	1.078173
1	1.759403	6.580941	0.512271
1	2.158551	5.455021	2.714298
1	3.213259	4.809052	1.460852
1	0.603735	3.547884	2.437694
1	2.222766	2.978438	2.823413
1	2.646158	2.556862	0.382955
6	-0.197901	-0.477476	-2.709392
6	-1.546594	-0.781825	-3.330399
1	-1.480338	-1.318880	-4.295672
1	-2.199147	-1.386830	-2.685009
1	-2.097828	0.148072	-3.524731
6	0.690868	-1.604338	-2.475614
6	0.190618	-2.916085	-2.267577
6	1.001632	-3.994629	-1.961779
6	2.380411	-3.843663	-1.860621
6	2.922150	-2.582460	-2.081456
6	2.099776	-1.510332	-2.378325
35	2.968710	0.179066	-2.654365
1	3.998902	-2.432938	-2.024604
1	3.027258	-4.685759	-1.626086
1	0.548133	-4.973319	-1.808865
1	-0.883587	-3.073500	-2.348244
1	0.314916	0.331860	-3.240605
1	-2.085256	0.944611	3.050233
1	-1.580155	2.133305	1.862455
1	0.116016	-0.232144	2.840218
1	0.380497	1.456792	3.237769

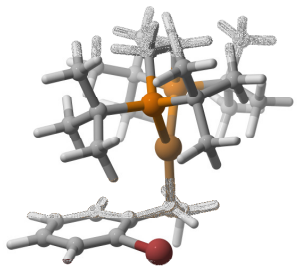


benzyl copper (dMepe) (entry 3)

RM06 energy: -4000.5973263

Sum of electronic and thermal Free Energies: -4000.30738

6	-2.345235	1.670202	1.334663
6	-3.460983	1.030160	0.521344
15	-2.919571	-0.571402	-0.236522
6	-2.823427	-1.651164	1.245010
1	-3.706453	-1.534632	1.886804
1	-2.758303	-2.698123	0.928950
1	-1.924936	-1.426656	1.830486
6	-4.491654	-1.142130	-0.985158
1	-5.303123	-1.149603	-0.246562
1	-4.776275	-0.486740	-1.814639
1	-4.369578	-2.154394	-1.383886
29	-0.655152	-0.172280	-0.834138
15	-0.777527	1.804830	0.358551
6	0.408333	2.303742	1.656993
1	1.359817	2.598702	1.202555
1	0.020864	3.147583	2.242077
1	0.601796	1.461628	2.330955
6	-1.028826	3.370864	-0.554172
1	-0.119673	3.621669	-1.111565
1	-1.843159	3.261139	-1.278090
1	-1.264905	4.197964	0.127181
6	0.762528	-1.535971	-1.294469
6	0.169721	-2.887092	-1.639289
1	0.895110	-3.719724	-1.578020
1	-0.681506	-3.170674	-1.003844
1	-0.217796	-2.880095	-2.665646
6	1.430349	-1.408264	-0.007875
6	1.081200	-2.223869	1.098967
6	1.640015	-2.069808	2.355294
6	2.607033	-1.098272	2.592293
6	2.996586	-0.285683	1.533670
6	2.423686	-0.442446	0.284825
35	3.010023	0.764124	-1.085067
1	3.755771	0.480110	1.682251
1	3.059408	-0.977527	3.573588
1	1.322537	-2.729307	3.162125
1	0.331354	-2.999331	0.950628
1	1.380395	-1.144729	-2.108695
1	-4.354869	0.860775	1.138547
1	-3.764275	1.688626	-0.305628
1	-2.115698	1.059193	2.219460
1	-2.637391	2.662879	1.705317



benzyl copper (dtBupe) (entry 4)

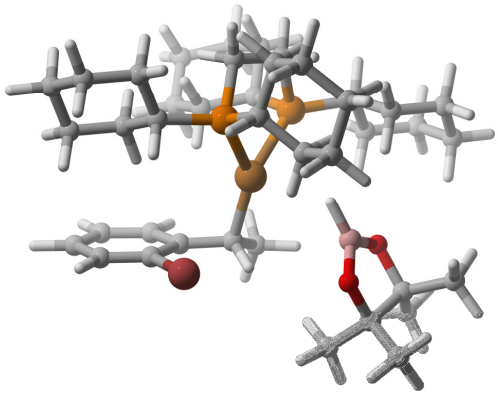
RM06 energy: -4472.0714495

Sum of electronic and thermal Free Energies: -4471.456222

6	-1.430885	2.148981	1.238630
6	-2.667975	1.555534	0.558961
15	-2.507872	-0.223075	0.021793
6	-3.221742	-1.233080	1.460105
6	-4.713112	-1.055638	1.704382
1	-5.324934	-1.470598	0.897203
1	-4.996018	-1.588885	2.623849
1	-4.995902	-0.005105	1.844992
6	-2.904784	-2.708776	1.231459
1	-1.827305	-2.871583	1.101633
1	-3.220125	-3.288830	2.110364
1	-3.415867	-3.131727	0.361881
6	-2.465540	-0.801426	2.712941
1	-1.381969	-0.927571	2.597446
1	-2.671312	0.236595	2.997772
1	-2.774640	-1.434642	3.556077
6	-3.673486	-0.293811	-1.475630
6	-4.992392	0.453618	-1.317373
1	-4.853350	1.520303	-1.108597
1	-5.557122	0.386887	-2.258857
1	-5.628573	0.037031	-0.531751
6	-2.895671	0.332829	-2.631678
1	-1.921093	-0.150333	-2.785686
1	-3.472326	0.225462	-3.561035
1	-2.724203	1.404875	-2.486911
6	-3.953674	-1.747405	-1.838409
1	-3.031643	-2.335500	-1.924739
1	-4.613224	-2.242593	-1.118595

1	-4.458570	-1.785429	-2.813875
29	-0.188864	-0.351535	-0.535314
15	0.199386	1.762739	0.419323
6	1.398360	1.804398	1.892022
6	2.837632	1.888755	1.395980
1	3.518273	1.699017	2.238363
1	3.061358	1.139577	0.626729
1	3.087845	2.877733	0.997919
6	1.147615	2.917856	2.902724
1	1.863911	2.814695	3.730846
1	1.287864	3.916705	2.482125
1	0.145763	2.873881	3.344167
6	1.222702	0.460499	2.596102
1	1.952491	0.376152	3.413905
1	0.228391	0.350893	3.042452
1	1.389831	-0.384378	1.917081
6	0.524730	3.224729	-0.744595
6	1.707930	2.874613	-1.642077
1	1.556101	1.917044	-2.155589
1	1.825120	3.652646	-2.410137
1	2.654382	2.809159	-1.098478
6	-0.703259	3.347319	-1.640291
1	-0.922561	2.405701	-2.157468
1	-1.598736	3.665996	-1.094637
1	-0.512162	4.103808	-2.414078
6	0.766497	4.563190	-0.062308
1	1.709504	4.590756	0.493042
1	0.822682	5.352814	-0.825815
1	-0.044375	4.837965	0.623326
6	0.798945	-1.929508	-1.381627
6	-0.144162	-3.057718	-1.756926
1	0.377236	-4.005474	-1.988572
1	-0.884611	-3.294910	-0.981078
1	-0.722554	-2.790725	-2.651047
6	1.721293	-2.195801	-0.286602
6	1.361465	-3.038406	0.796461
6	2.173418	-3.242174	1.896804
6	3.416832	-2.624413	1.989334
6	3.831287	-1.819204	0.935583
6	3.011649	-1.631495	-0.164522
35	3.718998	-0.548986	-1.583238
1	4.809249	-1.341836	0.963096
1	4.061400	-2.776617	2.851571
1	1.830898	-3.897469	2.696757
1	0.394895	-3.539073	0.756985
1	1.334437	-1.567424	-2.265640

1	-3.543755	1.687852	1.208775
1	-2.887854	2.119072	-0.353493
1	-1.351314	1.747476	2.254654
1	-1.558187	3.233891	1.357069



benzyl copper (dCype) – Hbpin complex

RM06 energy: -5193.3191934

Sum of electronic and thermal Free Energies: -5192.375813

6	-1.710495	1.692197	2.079932
6	-0.356743	2.396917	2.053770
15	0.576976	2.179445	0.460192
6	-0.143363	3.429280	-0.716108
1	0.594014	3.431548	-1.536903
6	-0.288603	4.857969	-0.206852
6	-0.734441	5.784703	-1.332942
6	-2.023328	5.297357	-1.981681
6	-1.896613	3.856954	-2.458587
6	-1.458835	2.942783	-1.323438
1	-1.357138	1.904169	-1.670692
1	-2.244932	2.936932	-0.552060
1	-1.154630	3.802415	-3.272626
1	-2.847480	3.504754	-2.881939
1	-2.306244	5.955656	-2.813770
1	-2.841006	5.359888	-1.245456
1	0.061717	5.830753	-2.093535
1	-0.859072	6.808122	-0.953875
1	-1.037771	4.884424	0.600695
1	0.651831	5.224298	0.227819
6	2.234033	2.907814	0.908470
1	2.058581	3.869025	1.423228

6	2.977034	1.970856	1.864824
6	4.373478	2.480215	2.195336
6	5.188001	2.707601	0.932684
6	4.468079	3.666058	-0.001254
6	3.072263	3.163446	-0.344279
1	2.574568	3.885705	-1.004095
1	3.157152	2.224158	-0.916312
1	4.390337	4.654374	0.480819
1	5.044776	3.816689	-0.923623
1	6.188951	3.085343	1.179429
1	5.330877	1.743653	0.417770
1	4.297003	3.426622	2.755306
1	4.879820	1.766911	2.859748
1	2.407552	1.830452	2.793629
1	3.061650	0.979160	1.394388
29	-0.130473	0.021996	-0.282038
15	-1.598203	-0.078949	1.522393
6	-3.364179	-0.569751	1.222197
6	-4.328006	-0.350268	2.386128
6	-5.728683	-0.848926	2.047298
6	-6.255463	-0.207977	0.773035
6	-5.297168	-0.438319	-0.384690
6	-3.899094	0.068875	-0.058301
1	-3.937760	1.163977	0.061923
1	-3.216473	-0.136098	-0.894562
1	-5.244109	-1.517610	-0.604783
1	-5.666548	0.043758	-1.299810
1	-7.253322	-0.597853	0.531588
1	-6.377215	0.875681	0.934488
1	-5.700148	-1.942593	1.917758
1	-6.408135	-0.655119	2.888036
1	-3.966081	-0.854403	3.292347
1	-4.378343	0.724994	2.622102
1	-3.282528	-1.656242	1.036938
6	-1.138176	-1.083806	3.036963
6	-1.279123	-0.370296	4.378899
6	-0.922577	-1.292809	5.538056
6	0.479194	-1.861194	5.383625
6	0.629044	-2.575754	4.050125
6	0.266539	-1.665377	2.886586
1	0.348020	-2.208456	1.935486
1	0.994979	-0.839356	2.827563
1	1.652416	-2.954234	3.924581
1	-0.030138	-3.458817	4.035383
1	1.211751	-1.039206	5.439888
1	0.713079	-2.540220	6.214090

1	-1.018047	-0.751136	6.488696
1	-1.648999	-2.120671	5.579212
1	-0.604740	0.501252	4.401028
1	-2.294029	0.024154	4.513327
1	-1.851638	-1.927166	3.015713
5	2.771564	-1.389875	0.031716
1	1.902656	-0.882636	0.656616
8	3.772033	-0.669085	-0.546460
6	4.775468	-1.625494	-0.978579
6	3.946091	-2.939020	-1.111245
8	2.884812	-2.733009	-0.139735
6	4.695004	-4.201007	-0.757002
1	4.041763	-5.070437	-0.890918
1	5.563874	-4.333206	-1.413296
1	5.041218	-4.198472	0.280251
6	3.277285	-3.093753	-2.464709
1	2.536812	-3.899558	-2.406052
1	2.749669	-2.184403	-2.774722
1	4.001947	-3.354847	-3.244158
6	5.403894	-1.131855	-2.259205
1	4.661903	-0.924935	-3.035250
1	5.954735	-0.203300	-2.066909
1	6.117992	-1.866047	-2.652247
6	5.816644	-1.683308	0.124684
1	6.654916	-2.338096	-0.138274
1	6.216961	-0.677036	0.293123
1	5.390557	-2.035318	1.071219
1	-0.468004	3.461637	2.300300
1	0.290345	1.970651	2.833073
1	-2.406693	2.185286	1.389373
1	-2.158899	1.773554	3.077037
6	0.153728	-0.709876	-2.163552
6	1.086266	0.182933	-2.959178
1	1.204843	-0.122450	-4.016795
1	0.771166	1.237463	-2.979699
1	2.088251	0.182192	-2.510802
6	-1.176822	-0.911518	-2.715348
6	-1.759394	0.003223	-3.626444
6	-3.045932	-0.134605	-4.119073
6	-3.834155	-1.220031	-3.755477
6	-3.297212	-2.161267	-2.884768
6	-2.016427	-2.001594	-2.387743
35	-1.396534	-3.347731	-1.169530
1	-3.883689	-3.028958	-2.588343
1	-4.843203	-1.342520	-4.142126
1	-3.433085	0.612840	-4.810758

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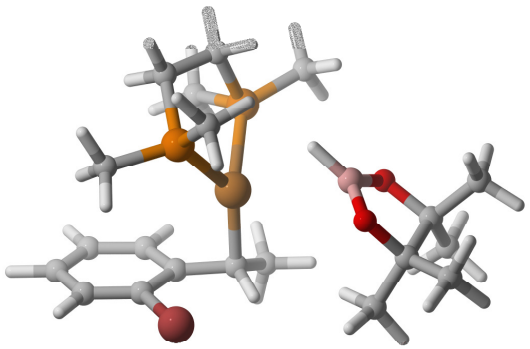
1	0.624081	-1.676218	-1.938763



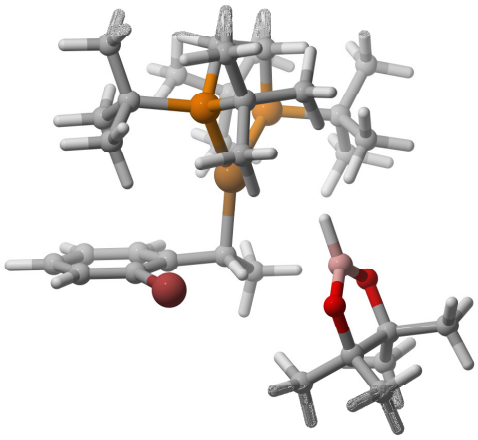
benzyl copper (dMepe) – Hbpin complex

RM06 energy: -4412.3061779

Sum of electronic and thermal Free Energies: -4411.833638

29	0.323582	-0.528732	-0.114799
15	0.119787	-2.849204	-0.527758
6	0.588065	-3.584911	1.106498
6	1.766097	-2.846128	1.728323
15	1.436607	-1.026038	1.853339
6	3.097607	-0.391877	2.279628
1	3.036377	0.667820	2.549281
1	3.528405	-0.945669	3.123714
1	3.765471	-0.483872	1.416058
6	0.568006	-0.901896	3.459616
1	-0.375016	-1.457684	3.427705
1	1.182880	-1.294758	4.279266
1	0.328494	0.146972	3.668458
1	2.665218	-2.962490	1.105225
1	2.015761	-3.249677	2.719882
1	0.804081	-4.656538	0.988958
1	-0.298653	-3.508967	1.753187
6	1.393433	-3.563682	-1.636491
1	1.138599	-3.341726	-2.678874
1	2.373100	-3.117521	-1.433460
1	1.467074	-4.652678	-1.520161
6	-1.346167	-3.853400	-0.966878

1	-1.112307	-4.925845	-0.975288
1	-2.154202	-3.675703	-0.249685
1	-1.709817	-3.561910	-1.957996
5	-2.543715	-0.371322	0.745492
8	-3.269015	-0.721942	-0.352444
6	-4.372032	0.220503	-0.433513
6	-3.819858	1.445964	0.355751
8	-2.904515	0.818252	1.294797
6	-4.855922	2.224382	1.129590
1	-4.377495	3.062837	1.648327
1	-5.613924	2.640510	0.454508
1	-5.361077	1.610578	1.880519
6	-2.992316	2.383144	-0.502743
1	-2.443119	3.074121	0.146911
1	-2.256408	1.840714	-1.105872
1	-3.620878	2.978628	-1.174234
6	-4.692610	0.487744	-1.883832
1	-3.821890	0.831521	-2.448413
1	-5.058675	-0.430354	-2.357135
1	-5.482004	1.244265	-1.971728
6	-5.556415	-0.442398	0.244554
1	-6.462059	0.169507	0.171886
1	-5.758873	-1.400795	-0.246192
1	-5.361853	-0.645093	1.303901
1	-1.710571	-1.073685	1.224965
6	0.390387	0.922156	-1.527268
6	-0.221207	0.458321	-2.832296
1	0.069925	1.072831	-3.704922
1	0.026957	-0.581306	-3.088905
1	-1.317199	0.490181	-2.773646
6	1.840098	0.994299	-1.454998
6	2.669751	0.161069	-2.250662
6	4.048986	0.151093	-2.147059
6	4.704039	0.991731	-1.252716
6	3.935050	1.837298	-0.460697
6	2.556049	1.830365	-0.563875
35	1.603430	3.006287	0.613933
1	4.415515	2.508723	0.248486
1	5.788310	0.999739	-1.173484
1	4.624857	-0.517558	-2.785935
1	2.192552	-0.508604	-2.964179
1	-0.076833	1.838790	-1.155192



benzyl copper (dtBupe) – Hbpin complex

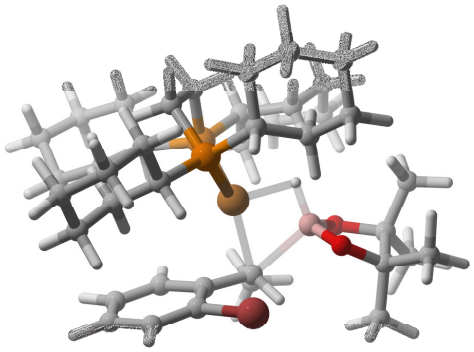
RM06 energy: -4883.7770041

Sum of electronic and thermal Free Energies: -4882.983967

29	-0.595242	0.152397	-0.233959
15	-2.005350	2.074893	-0.249412
6	-3.046620	1.799466	1.271939
6	-3.332695	0.337981	1.624555
15	-1.884815	-0.828919	1.479477
6	-2.746857	-2.467287	1.058860
6	-1.781053	-3.626842	1.270704
1	-2.196736	-4.533045	0.807116
1	-0.803548	-3.443188	0.809926
1	-1.622223	-3.853080	2.330366
6	-4.037973	-2.744936	1.821514
1	-4.799906	-1.973102	1.666862
1	-4.467798	-3.690840	1.460881
1	-3.883142	-2.853795	2.898544
6	-3.069668	-2.389115	-0.432624
1	-3.853984	-1.655537	-0.649338
1	-2.186952	-2.134718	-1.033782
1	-3.438036	-3.364278	-0.781480
6	-1.135994	-0.905075	3.217878
6	0.177846	-1.682836	3.163868
1	0.036807	-2.751498	2.980690
1	0.853139	-1.303985	2.387231
1	0.693284	-1.584454	4.130188
6	-0.798041	0.533238	3.600672
1	-1.688107	1.154379	3.754136

1	-0.240985	0.532691	4.547867
1	-0.158334	1.014508	2.851032
6	-2.039211	-1.498358	4.288473
1	-2.204418	-2.572013	4.151866
1	-1.566392	-1.371502	5.273479
1	-3.017519	-1.005195	4.338369
1	-4.091235	-0.057887	0.941324
1	-3.780521	0.283893	2.626497
1	-3.993566	2.351841	1.197850
1	-2.492538	2.268085	2.092151
6	-3.255362	2.284491	-1.662552
6	-2.507735	2.265034	-2.993605
1	-3.235595	2.279147	-3.817274
1	-1.842708	3.122070	-3.133442
1	-1.909263	1.352003	-3.100456
6	-4.150366	1.049844	-1.638950
1	-4.819626	1.072236	-2.510323
1	-3.564440	0.125182	-1.706019
1	-4.785496	1.001132	-0.747455
6	-4.133043	3.524588	-1.582644
1	-4.897710	3.476213	-2.371768
1	-4.664860	3.607171	-0.626684
1	-3.569558	4.449277	-1.742646
6	-1.182174	3.742204	0.136147
6	-2.085586	4.781843	0.789197
1	-2.910660	5.104375	0.147462
1	-2.512550	4.432448	1.736163
1	-1.491149	5.677469	1.022094
6	-0.036649	3.423087	1.093073
1	-0.385237	3.020538	2.051408
1	0.671832	2.708644	0.657546
1	0.519651	4.344984	1.315750
6	-0.571920	4.319112	-1.135571
1	-1.325530	4.692995	-1.836083
1	0.072197	5.170646	-0.873847
1	0.055762	3.585807	-1.657951
5	2.930956	0.885393	1.120614
1	1.856572	0.744961	1.603811
8	3.256147	1.960854	0.352664
6	4.694883	1.922127	0.160114
6	5.034948	0.422271	0.436907
8	3.952726	0.012142	1.315983
6	6.347855	0.193061	1.148629
1	6.495440	-0.879800	1.315608
1	7.189057	0.554996	0.544184
1	6.381133	0.692930	2.121224

6	4.955054	-0.451884	-0.801330
1	5.016289	-1.503614	-0.501512
1	4.011240	-0.316899	-1.343403
1	5.783586	-0.248780	-1.489619
6	5.014236	2.398308	-1.236891
1	4.477252	1.830907	-2.003007
1	4.732452	3.452456	-1.341534
1	6.090470	2.319896	-1.437089
6	5.287238	2.873405	1.183707
1	6.374356	2.962004	1.080055
1	4.852548	3.868953	1.038741
1	5.062433	2.559029	2.209535
6	0.965588	-0.271732	-1.483339
6	1.311475	0.901588	-2.381400
1	2.002254	0.635736	-3.205367
1	0.437546	1.370278	-2.855926
1	1.803067	1.689562	-1.796225
6	0.443189	-1.463137	-2.135663
6	-0.365747	-1.377843	-3.296933
6	-0.950930	-2.480033	-3.892407
6	-0.756947	-3.756337	-3.373557
6	0.062225	-3.897145	-2.260235
6	0.649268	-2.785772	-1.679711
35	1.820333	-3.108525	-0.194183
1	0.259222	-4.884644	-1.846618
1	-1.213918	-4.629275	-3.833086
1	-1.566197	-2.340841	-4.780280
1	-0.535969	-0.393140	-3.730117
1	1.810502	-0.525913	-0.832592



Hydroboration for benzyl copper (dCype) – TS (entry 5)

RM06 energy: -5193.2978242

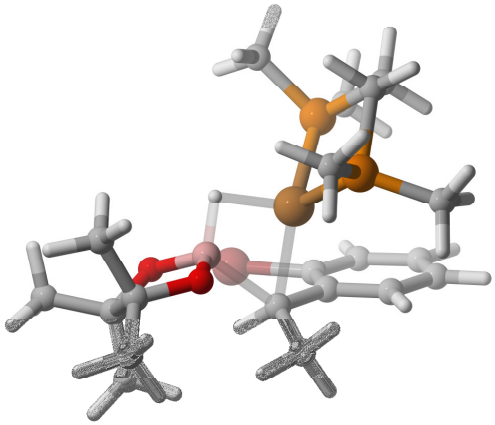
Sum of electronic and thermal Free Energies: -5192.352459

Imaginary frequency: -100.2408

6	-1.860942	0.873112	2.194737
6	-0.732831	1.898639	2.259853
15	0.035485	2.271108	0.610304
6	-1.006075	3.614178	-0.141394
1	-0.482512	3.828855	-1.089683
6	-1.120071	4.919157	0.641910
6	-1.877224	5.964773	-0.170606
6	-3.246282	5.462882	-0.606942
6	-3.141736	4.137028	-1.347695
6	-2.399180	3.106482	-0.510508
1	-2.335244	2.146951	-1.040833
1	-2.973776	2.920188	0.410693
1	-2.602643	4.283982	-2.298636
1	-4.140021	3.762924	-1.612360
1	-3.748690	6.215149	-1.229003
1	-3.880674	5.324218	0.283623
1	-1.282222	6.219318	-1.062668
1	-1.975904	6.892799	0.408136
1	-1.655714	4.732839	1.586621
1	-0.131933	5.310567	0.916396
6	1.599502	3.146930	1.102669
1	1.331358	3.898278	1.866491
6	2.613298	2.174346	1.709110
6	3.888393	2.897644	2.122848
6	4.512775	3.627148	0.943383
6	3.514431	4.575708	0.299476
6	2.232322	3.854766	-0.095584
1	1.535378	4.569525	-0.552548
1	2.458933	3.100345	-0.868193
1	3.268751	5.384613	1.007068
1	3.956255	5.060480	-0.581274
1	5.413388	4.171553	1.257045
1	4.839848	2.888362	0.194406
1	3.659498	3.622378	2.921096
1	4.601216	2.180253	2.552735
1	2.188814	1.643903	2.573072
1	2.858789	1.408307	0.958264
29	0.161733	0.115675	-0.277744
15	-1.385783	-0.691920	1.310089
6	-3.033717	-1.454462	0.888971

6	-3.920759	-1.849543	2.067351
6	-5.198458	-2.531404	1.589340
6	-5.965720	-1.663096	0.604324
6	-5.081228	-1.267000	-0.566795
6	-3.813949	-0.573984	-0.085286
1	-4.103121	0.363701	0.415863
1	-3.185132	-0.293395	-0.939153
1	-4.809480	-2.168976	-1.139227
1	-5.623015	-0.611912	-1.262671
1	-6.864746	-2.185403	0.251730
1	-6.316581	-0.753446	1.118505
1	-4.935189	-3.484253	1.102408
1	-5.828488	-2.789460	2.451160
1	-3.387341	-2.515944	2.756719
1	-4.188152	-0.947885	2.642378
1	-2.745254	-2.374586	0.347712
6	-0.724598	-1.857047	2.626645
6	-1.093649	-1.504772	4.066616
6	-0.617648	-2.579991	5.035566
6	0.881381	-2.806723	4.920505
6	1.269734	-3.132629	3.487396
6	0.784876	-2.066411	2.514891
1	1.065842	-2.334734	1.489520
1	1.298841	-1.113834	2.730248
1	2.358057	-3.251661	3.398144
1	0.829456	-4.102444	3.203576
1	1.409969	-1.894224	5.240886
1	1.203974	-3.605815	5.601104
1	-0.889368	-2.303832	6.063319
1	-1.148552	-3.521267	4.817269
1	-0.617413	-0.547622	4.335724
1	-2.173642	-1.354317	4.181423
1	-1.203642	-2.818750	2.369115
5	2.154788	-0.791018	-0.616944
1	1.667696	-0.416651	0.470102
8	3.363414	-0.107445	-0.929093
6	4.426426	-1.034229	-0.718899
6	3.750617	-2.396499	-1.053516
8	2.408443	-2.185389	-0.620036
6	4.321811	-3.583251	-0.305748
1	3.807889	-4.500973	-0.616127
1	5.390534	-3.714195	-0.519499
1	4.194114	-3.482503	0.776482
6	3.753690	-2.703513	-2.545518
1	3.060554	-3.530469	-2.738614
1	3.427974	-1.849907	-3.149603

1	4.746325	-3.008468	-2.899554
6	5.592336	-0.665741	-1.609880
1	5.292453	-0.572741	-2.658118
1	6.010474	0.298486	-1.296978
1	6.394515	-1.411811	-1.544221
6	4.854147	-0.936915	0.740778
1	5.721807	-1.568305	0.965459
1	5.129911	0.101916	0.962442
1	4.040713	-1.214919	1.422530
1	-1.081327	2.822873	2.741312
1	0.080896	1.513985	2.890773
1	-2.708857	1.284104	1.636087
1	-2.236966	0.661366	3.201824
6	0.942312	-0.342807	-2.270770
6	1.642656	0.805196	-2.986223
1	1.382080	0.845740	-4.056121
1	1.402007	1.788417	-2.560352
1	2.726469	0.701373	-2.908017
6	-0.512337	-0.405926	-2.622461
6	-1.211221	0.745574	-3.047970
6	-2.518755	0.713082	-3.502173
6	-3.209908	-0.488619	-3.574855
6	-2.570223	-1.645861	-3.154327
6	-1.268748	-1.595579	-2.679631
35	-0.513591	-3.255681	-2.111573
1	-3.087844	-2.602066	-3.193518
1	-4.231531	-0.531730	-3.945072
1	-2.996688	1.641753	-3.811767
1	-0.697073	1.704144	-3.030014
1	1.372346	-1.294849	-2.601678



hydroboration of benzyl copper (dMepe) – TS (entry 6)

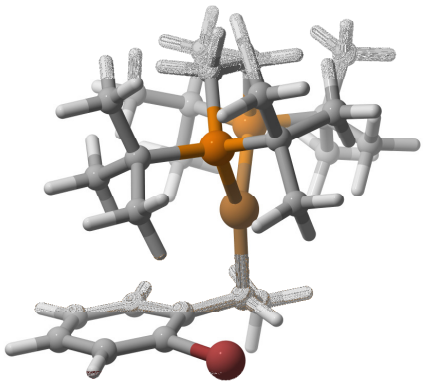
RM06 energy: -4412.2883274

Sum of electronic and thermal Free Energies: -4411.815599

Imaginary frequency: -105.5431

29	0.496483	-0.585916	0.117355
15	1.288127	-2.690624	-0.471593
6	2.508625	-3.012378	0.881564
6	3.337050	-1.771225	1.190311
15	2.260754	-0.328029	1.616501
6	3.504493	0.985870	1.885616
1	3.011888	1.903827	2.223150
1	4.238586	0.682740	2.643125
1	4.028740	1.206531	0.950084
6	1.751416	-0.713336	3.331475
1	1.053633	-1.557393	3.338890
1	2.608646	-0.949566	3.974781
1	1.221569	0.149892	3.749989
1	3.926740	-1.470344	0.310549
1	4.050573	-1.961845	2.004466
1	3.149498	-3.863720	0.612010
1	1.932938	-3.319663	1.766282
6	2.292175	-3.029716	-1.964920
1	1.677088	-2.938722	-2.866416
1	3.116559	-2.312819	-2.041722
1	2.711453	-4.043213	-1.930205
6	0.215608	-4.166631	-0.397675
1	0.797866	-5.096905	-0.390156
1	-0.407125	-4.125648	0.502617
1	-0.452539	-4.174930	-1.265890
5	-1.667378	-0.275018	0.224212
8	-2.479640	-1.253029	-0.415563
6	-3.816998	-1.056886	0.038091
6	-3.844820	0.464906	0.373296
8	-2.511390	0.707303	0.808408
6	-4.798169	0.845724	1.487748
1	-4.768794	1.930536	1.647004
1	-5.832630	0.575494	1.238910
1	-4.533036	0.366826	2.434531
6	-4.141000	1.340911	-0.838707
1	-3.902548	2.381056	-0.584406
1	-3.541326	1.070869	-1.714072
1	-5.198729	1.302692	-1.127469

6	-4.783505	-1.484787	-1.045063
1	-4.583556	-0.984176	-1.996898
1	-4.700022	-2.565204	-1.214791
1	-5.821739	-1.274484	-0.757399
6	-4.025631	-1.929986	1.269444
1	-5.056788	-1.894098	1.640971
1	-3.800163	-2.970595	1.007039
1	-3.356358	-1.642922	2.088633
1	-0.911745	-0.753420	1.135692
6	-0.649082	0.626520	-1.320517
6	-1.075940	-0.086387	-2.593476
1	-0.844623	0.503152	-3.494899
1	-0.601254	-1.069484	-2.717319
1	-2.151165	-0.277044	-2.592650
6	0.729935	1.200118	-1.426609
6	1.688483	0.656414	-2.309481
6	2.969517	1.166448	-2.433812
6	3.356362	2.282200	-1.702537
6	2.435180	2.870131	-0.845887
6	1.164205	2.336918	-0.714132
35	-0.004641	3.189287	0.531973
1	2.710924	3.748233	-0.266071
1	4.354547	2.702190	-1.801904
1	3.667255	0.694905	-3.124108
1	1.410092	-0.207333	-2.908367
1	-1.315520	1.472821	-1.122111



Hydroboration of benzyl copper (dtBupe) – TS (entry 7)

RM06 energy: -4883.7540547

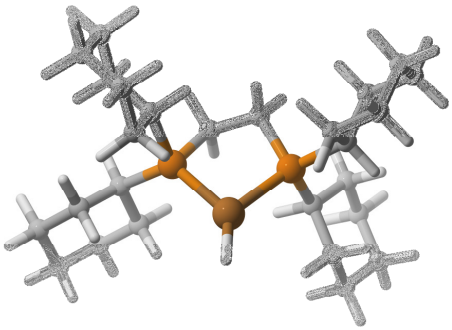
Sum of electronic and thermal Free Energies: -4882.956181

Imaginary frequency: -118.9103

29	-0.333110	0.129105	-0.169449
15	-2.460375	1.240908	-0.239896
6	-3.189326	0.560887	1.337337
6	-2.848145	-0.879603	1.718836
15	-1.069391	-1.392319	1.507543
6	-1.246079	-3.263291	1.225259
6	0.125431	-3.920107	1.339937
1	0.068572	-4.951336	0.962854
1	0.885958	-3.398085	0.746931
1	0.480406	-3.974434	2.374619
6	-2.234716	-3.987569	2.133240
1	-3.245833	-3.569407	2.076670
1	-2.308706	-5.034996	1.805835
1	-1.933452	-4.002716	3.182926
6	-1.727408	-3.421311	-0.214846
1	-2.754330	-3.066066	-0.358252
1	-1.081245	-2.895716	-0.923422
1	-1.718868	-4.486625	-0.485335
6	-0.266344	-1.072758	3.201849
6	1.250264	-1.187479	3.060458
1	1.580530	-2.198643	2.804006
1	1.657685	-0.506491	2.303521
1	1.718572	-0.928666	4.021619
6	-0.589353	0.365795	3.599427
1	-1.656415	0.520599	3.797687
1	-0.053321	0.605375	4.528428
1	-0.262025	1.087811	2.843516
6	-0.747221	-1.987411	4.319997
1	-0.404624	-3.019339	4.197596
1	-0.338704	-1.629113	5.276129
1	-1.839298	-1.995255	4.422137
1	-3.429653	-1.570074	1.099253
1	-3.176385	-1.063608	2.751260
1	-4.280841	0.680914	1.326469
1	-2.828834	1.234739	2.121834
6	-3.742147	0.816770	-1.580893
6	-3.202167	1.204653	-2.955194
1	-3.898580	0.847709	-3.727226
1	-3.093228	2.283054	-3.094862
1	-2.231032	0.741782	-3.158582
6	-3.892364	-0.702227	-1.567506
1	-4.511699	-1.011493	-2.420995

1	-2.927240	-1.213573	-1.665952
1	-4.390609	-1.067600	-0.662855
6	-5.116365	1.441555	-1.392536
1	-5.812396	1.003931	-2.122830
1	-5.539713	1.255233	-0.398561
1	-5.112309	2.521963	-1.568212
6	-2.524077	3.109710	0.130853
6	-3.790323	3.580653	0.839430
1	-4.703167	3.417989	0.261309
1	-3.924327	3.111730	1.820480
1	-3.712858	4.663146	1.016818
6	-1.329532	3.424518	1.028934
1	-1.351584	2.879396	1.980599
1	-0.376200	3.216244	0.533508
1	-1.349414	4.495652	1.277610
6	-2.344814	3.900199	-1.159751
1	-3.237154	3.879967	-1.794685
1	-2.151939	4.953427	-0.912082
1	-1.489462	3.545735	-1.749862
5	1.542770	1.339325	0.085582
1	0.607636	1.178177	0.895079
8	1.659316	2.674107	-0.396047
6	2.805981	3.249709	0.227181
6	3.722356	2.009987	0.444881
8	2.776949	0.968515	0.676864
6	4.639711	2.105264	1.645927
1	5.251793	1.198005	1.717076
1	5.322889	2.960288	1.562037
1	4.078506	2.199741	2.580409
6	4.554912	1.673640	-0.785530
1	4.979143	0.670347	-0.663025
1	3.962453	1.672154	-1.707049
1	5.385820	2.377093	-0.920268
6	3.380503	4.314722	-0.681630
1	3.587868	3.928739	-1.684288
1	2.665501	5.139784	-0.785261
1	4.309779	4.731274	-0.272001
6	2.358629	3.890781	1.535248
1	3.176595	4.411916	2.046440
1	1.578401	4.630615	1.320044
1	1.934236	3.153499	2.227984
6	1.297125	0.262654	-1.691341
6	0.959831	1.262208	-2.793279
1	1.330523	0.932926	-3.777772
1	-0.115990	1.446171	-2.905202
1	1.412704	2.231863	-2.574561

6	0.945394	-1.139359	-2.083948
6	-0.104896	-1.397374	-2.990195
6	-0.396825	-2.657817	-3.479979
6	0.359478	-3.755106	-3.089870
6	1.400616	-3.554981	-2.197091
6	1.678378	-2.283281	-1.713561
35	3.169283	-2.145458	-0.524830
1	2.015312	-4.393538	-1.876484
1	0.148154	-4.751404	-3.470838
1	-1.220330	-2.779198	-4.181898
1	-0.702955	-0.559689	-3.336263
1	2.384450	0.254439	-1.559967



Copper-Hydride (dCype) (entry 8)

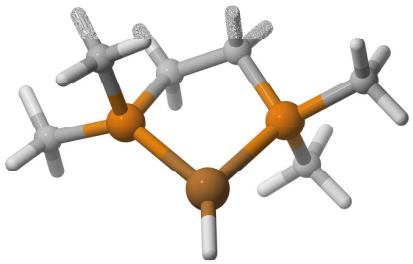
RM06 energy: -1898.6704047

Sum of electronic and thermal Free Energies: -1898.030668

6	-0.549247	0.274726	1.684626
15	-1.595267	0.073050	0.163103
6	-2.184727	-1.678993	0.372747
1	-1.254798	-2.202978	0.661950
6	-3.213131	-1.913122	1.474342
6	-3.534884	-3.396212	1.616871
6	-3.998915	-3.987561	0.293863
6	-2.962671	-3.766165	-0.797849
6	-2.629619	-2.289343	-0.956510
1	-3.513959	-1.755355	-1.336196
1	-1.842129	-2.144981	-1.710353
1	-2.043663	-4.318510	-0.542181
1	-3.314162	-4.177380	-1.753184
1	-4.946454	-3.509275	-0.003418
1	-4.215678	-5.058020	0.406945

1	-2.635187	-3.932697	1.958966
1	-4.297222	-3.542186	2.393850
1	-2.857347	-1.509847	2.432550
1	-4.141530	-1.372633	1.234704
6	-3.010454	1.230786	0.479182
1	-3.403317	1.045707	1.493995
29	-0.105853	0.148796	-1.626981
1	-0.211540	0.262910	-3.216296
15	1.622038	0.020853	-0.065553
6	0.804506	-0.415184	1.541278
1	1.443194	-0.182874	2.402216
1	0.680981	-1.506950	1.538971
6	2.268945	1.737428	0.210027
1	1.353174	2.302416	0.469253
6	3.288579	1.932694	1.326581
6	3.674254	3.400705	1.466899
6	4.204627	3.957775	0.154329
6	3.195763	3.764370	-0.967327
6	2.793504	2.303155	-1.110325
1	3.668566	1.715043	-1.433770
1	2.034283	2.184200	-1.895617
1	2.296719	4.364726	-0.754368
1	3.597861	4.138333	-1.918027
1	5.140882	3.438159	-0.106306
1	4.460568	5.020002	0.262564
1	4.418681	3.519143	2.265557
1	2.789692	3.980060	1.777158
1	4.194067	1.350145	1.094256
1	2.905827	1.550432	2.282665
6	3.064887	-1.142519	-0.197989
1	3.820119	-0.586671	-0.780977
6	3.694780	-1.603146	1.116254
6	4.847623	-2.568512	0.869160
6	4.399653	-3.767988	0.048563
6	3.770234	-3.324091	-1.262686
6	2.625278	-2.348551	-1.033785
1	1.798845	-2.865776	-0.513163
1	2.213366	-2.005586	-1.992263
1	4.536508	-2.833817	-1.884499
1	3.416621	-4.191006	-1.835990
1	3.662169	-4.347184	0.627778
1	5.244398	-4.443428	-0.139761
1	5.654917	-2.041967	0.335069
1	5.273046	-2.894420	1.827733
1	4.041157	-0.747448	1.708567
1	2.932564	-2.113258	1.725853

1	-1.080320	-0.100411	2.570211
1	-0.401713	1.349679	1.848325
6	-5.246862	2.043510	-0.364658
6	-4.720534	3.467593	-0.437214
6	-3.613880	3.684386	0.581983
6	-2.492675	2.670345	0.402215
1	-2.018488	2.822258	-0.582664
1	-1.710481	2.846093	1.152043
1	-4.030177	3.589338	1.597882
1	-3.210430	4.702708	0.506184
1	-4.324026	3.656481	-1.447658
1	-5.534064	4.188693	-0.282906
6	-4.129098	1.024700	-0.542176
1	-4.541062	0.010262	-0.470862
1	-3.704604	1.116376	-1.556241
1	-5.729597	1.883656	0.613261
1	-6.023695	1.879488	-1.123021



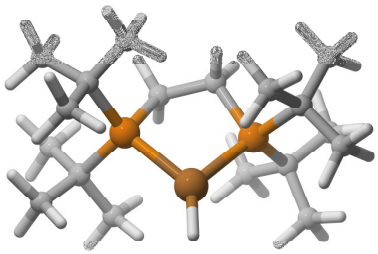
Copper-hydride (dMepe) (entry 9)

RM06 energy: -1117.6625474

Sum of electronic and thermal Free Energies: -1117.491407

6	-0.665206	-1.704445	0.370213
6	0.665305	-1.704618	-0.369319
15	1.602976	-0.136381	-0.068587
6	2.173506	-0.386729	1.653772
1	2.610322	-1.383458	1.796475
1	2.928226	0.367331	1.900115
1	1.340600	-0.256174	2.352550
6	3.137168	-0.450309	-1.014752
1	3.591888	-1.406784	-0.727811
1	2.921676	-0.468999	-2.087756

1	3.857847	0.352372	-0.830347
29	-0.000159	1.576557	-0.000142
15	-1.602939	-0.136434	0.068541
6	-3.137317	-0.450002	1.014499
1	-3.857914	0.352673	0.829751
1	-3.592036	-1.406524	0.727720
1	-2.922022	-0.468418	2.087547
6	-2.173049	-0.387594	-1.653839
1	-2.927490	0.366527	-1.900839
1	-1.339902	-0.257680	-2.352449
1	-2.610086	-1.384290	-1.796100
1	0.000297	3.166011	0.000168
1	1.283876	-2.565160	-0.076931
1	0.503472	-1.784406	-1.453466
1	-0.503400	-1.783583	1.454414
1	-1.283732	-2.565183	0.078310



Copper hydride (dtBupe) (entry 10)

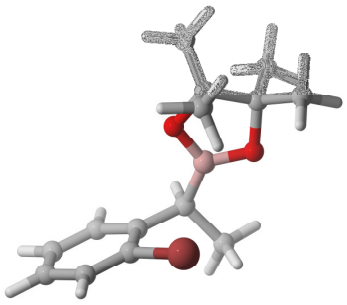
RM06 energy: -1589.1361155

Sum of electronic and thermal Free Energies: -1588.636059

6	0.304676	-0.703869	-1.628812
6	-0.304676	0.703869	-1.628812
15	0.000000	1.668386	-0.059676
6	1.515591	2.741334	-0.423903
6	1.289053	3.873995	-1.414165
1	0.626182	4.649883	-1.018446
1	2.251108	4.358277	-1.637222
1	0.876184	3.523552	-2.368623
6	2.030987	3.302053	0.899819
1	2.203081	2.506974	1.636675
1	2.988561	3.815247	0.731888

1	1.348856	4.028782	1.350574
6	2.593049	1.814221	-0.978421
1	2.808502	0.984899	-0.294834
1	2.336641	1.401980	-1.960929
1	3.525822	2.381771	-1.100505
6	-1.557725	2.726305	0.106748
6	-2.022772	3.435621	-1.158286
1	-2.144166	2.751404	-2.005766
1	-3.006638	3.892009	-0.975427
1	-1.351862	4.240744	-1.469108
6	-2.655014	1.758160	0.550936
1	-2.347748	1.148862	1.413255
1	-3.547271	2.327367	0.846779
1	-2.962524	1.082884	-0.254373
6	-1.350512	3.742371	1.223910
1	-1.003257	3.266751	2.150216
1	-0.637157	4.526333	0.950260
1	-2.305823	4.238309	1.445681
29	0.000000	0.000000	1.588633
15	0.000000	-1.668386	-0.059676
6	1.557725	-2.726305	0.106748
6	1.350512	-3.742371	1.223910
1	2.305823	-4.238309	1.445681
1	1.003257	-3.266751	2.150216
1	0.637157	-4.526333	0.950260
6	2.022772	-3.435621	-1.158286
1	3.006638	-3.892009	-0.975427
1	1.351862	-4.240744	-1.469108
1	2.144166	-2.751404	-2.005766
6	2.655014	-1.758160	0.550936
1	3.547271	-2.327367	0.846779
1	2.962524	-1.082884	-0.254373
1	2.347748	-1.148862	1.413255
6	-1.515591	-2.741334	-0.423903
6	-2.030987	-3.302053	0.899819
1	-2.203081	-2.506974	1.636675
1	-2.988561	-3.815247	0.731888
1	-1.348856	-4.028782	1.350574
6	-2.593049	-1.814221	-0.978421
1	-2.808502	-0.984899	-0.294834
1	-2.336641	-1.401980	-1.960929
1	-3.525822	-2.381771	-1.100505
6	-1.289053	-3.873995	-1.414165
1	-0.626182	-4.649883	-1.018446
1	-2.251108	-4.358277	-1.637222
1	-0.876184	-3.523552	-2.368623

1	0.000000	0.000000	3.190624
1	0.046094	1.265175	-2.505842
1	-1.392431	0.629816	-1.736561
1	1.392431	-0.629816	-1.736561
1	-0.046094	-1.265175	-2.505842



Hydroboration product (entry 11)

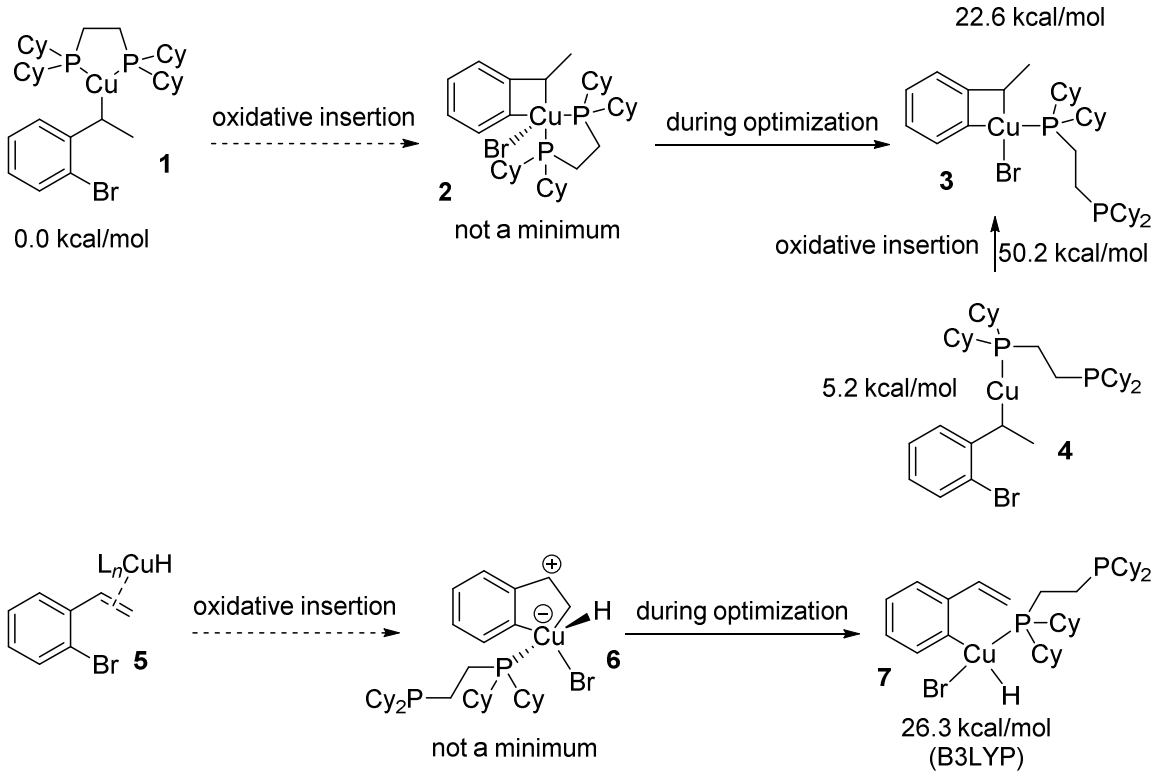
RM06 energy: -3294.6307469

Sum of electronic and thermal Free Energies: -3294.36006

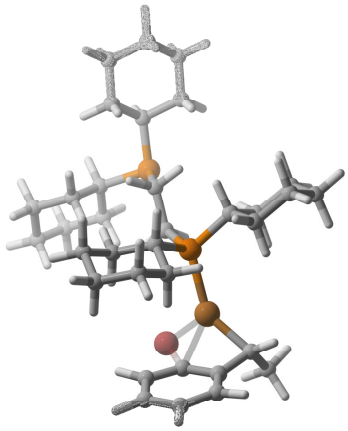
6	-0.525407	-1.128257	1.191725
6	-0.710529	-0.624410	2.623127
1	-0.832501	0.462609	2.668496
1	-1.592751	-1.078374	3.091485
1	0.160859	-0.876349	3.237088
6	-1.768266	-0.965701	0.355742
6	-2.236185	0.258447	-0.126941
6	-3.407024	0.373263	-0.862766
6	-4.153825	-0.760105	-1.144620
6	-3.719434	-1.994683	-0.685793
6	-2.548976	-2.084563	0.050734
1	-2.215999	-3.057242	0.411164
1	-4.293736	-2.892878	-0.900765
1	-5.070754	-0.672098	-1.722307
1	-3.732436	1.347629	-1.218600
35	-1.266080	1.875804	0.197047
5	0.802241	-0.634428	0.506918
8	1.078863	-0.841037	-0.814770
6	2.360404	-0.223984	-1.088122
6	3.006197	-0.151709	0.329935
8	1.848595	-0.093291	1.198671
6	3.868487	1.062856	0.579224

1	3.306084	1.995849	0.485721
1	4.279437	1.022151	1.594284
1	4.712191	1.094790	-0.121108
6	3.768035	-1.410193	0.703655
1	4.023269	-1.371500	1.768265
1	3.172511	-2.314970	0.536768
1	4.700782	-1.503286	0.136574
6	3.108646	-1.077696	-2.084922
1	2.584577	-1.066606	-3.047235
1	4.119862	-0.687062	-2.251950
1	3.188754	-2.118930	-1.761166
6	2.080312	1.139681	-1.691237
1	1.429601	1.015172	-2.563792
1	1.565763	1.801783	-0.987966
1	3.001103	1.633361	-2.021914
1	-0.359306	-2.218095	1.266058

B. Cu(I)/Cu(III) pathways.



Three oxidative insertion pathways were ultimately considered: 1) oxidative insertion from the benzyl copper **1**, 2) oxidative insertion from the π-acid complex **5**, 3) oxidative insertion of the copper-hydride. The pentacoordinate complex **2** that results from oxidative insertion from the benzyl copper always dissociated a phosphine ligand during the optimization. The tetracoordinate oxidative insertion product **3** was energetically feasible, but the transition state energy leading to this intermediate was far too high. The oxidative insertion intermediate from the π-acid complex **5** always broke a carbon-copper bond to form the intermediate that results from direct oxidative insertion of copper-hydride into the aryl-bromine bond (**7**). The direct oxidative insertion intermediate was also too high in energy (relative to the benzyl copper); thus, it is reasonable to expect that the transition state energy would also be too high in energy.



Oxidative insertion from benzyl copper to cupracyclobutane – TS – dCype (entry 13)

RM06 energy: -4781.5217209

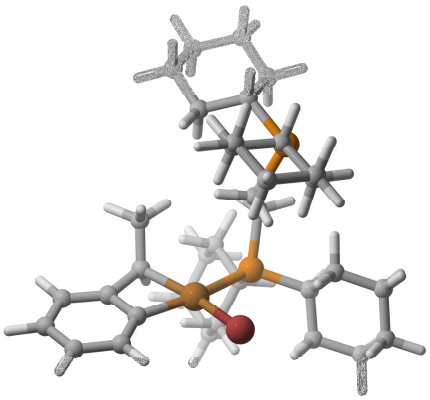
Sum of electronic and thermal Free Energies: -4780.769833

Imaginary frequency: -278.1170

6	-2.247489	0.249004	0.049050
6	-0.870954	-0.121036	-0.484392
15	0.573033	0.839606	0.136540
6	0.023744	2.598010	-0.065992
1	-0.915271	2.716052	0.500756
6	-0.248828	2.868874	-1.547466
6	-0.673697	4.309378	-1.791877
6	0.352035	5.289094	-1.247206
6	0.601534	5.035316	0.230132
6	1.036136	3.598576	0.488066
1	1.173630	3.449026	1.566122
1	2.016909	3.420359	0.016598
1	-0.322978	5.240474	0.794062
1	1.360241	5.726361	0.620208
1	0.023923	6.323824	-1.410902
1	1.297232	5.169983	-1.801108
1	-1.645641	4.486897	-1.302259
1	-0.835402	4.470833	-2.865526
1	0.671147	2.655835	-2.119227
1	-1.018575	2.188980	-1.937105
6	0.704573	0.529877	1.966228
1	-0.008164	1.194764	2.484072
6	0.375675	-0.922461	2.314070
6	0.597985	-1.210069	3.793892
6	2.016807	-0.876588	4.224953

6	2.353209	0.567798	3.894679
6	2.133998	0.852529	2.417118
1	2.399473	1.891028	2.185480
1	2.821393	0.226785	1.824680
1	1.721667	1.239679	4.498439
1	3.394008	0.794160	4.163194
1	2.148513	-1.070632	5.297459
1	2.722368	-1.540202	3.698893
1	-0.111330	-0.611057	4.387707
1	0.365498	-2.262244	4.004924
1	-0.659904	-1.162337	2.044328
1	1.018330	-1.590880	1.715280
29	2.567914	0.247862	-0.839406
6	4.333075	1.114295	-1.398641
6	4.544880	0.834633	-2.870721
1	5.592169	0.996995	-3.183802
1	4.294479	-0.199719	-3.137806
1	3.921008	1.482029	-3.499877
6	4.940100	0.146418	-0.460738
6	5.944951	0.335859	0.493594
6	6.186418	-0.643855	1.452205
6	5.406558	-1.790165	1.516114
6	4.328543	-1.968138	0.636541
6	4.181157	-1.011709	-0.334381
1	3.668373	-2.825133	0.731369
1	5.622198	-2.564400	2.249696
1	6.986444	-0.503019	2.176400
1	6.483648	1.284250	0.510668
1	4.557680	2.153753	-1.128618
35	2.366382	-2.027872	-1.763079
1	-0.636457	-1.178090	-0.307290
1	-0.832331	-0.010932	-1.577818
15	-3.592800	-0.326686	-1.102980
6	-5.125209	0.425155	-0.339880
6	-5.387299	0.152488	1.137611
6	-6.701122	0.777090	1.593975
6	-6.737195	2.269647	1.305235
6	-6.483765	2.545928	-0.168956
6	-5.170825	1.926323	-0.629482
1	-4.339098	2.428943	-0.107574
1	-5.015720	2.109490	-1.702123
1	-7.309009	2.123234	-0.764084
1	-6.481822	3.626400	-0.365455
1	-5.962947	2.773730	1.906545
1	-7.698202	2.698974	1.617783
1	-7.535888	0.285382	1.068756

1	-6.856358	0.587504	2.664681
1	-5.401260	-0.927274	1.335155
1	-4.565104	0.572382	1.739158
1	-5.939884	-0.044620	-0.921116
6	-3.810347	-2.153063	-0.716417
6	-3.218598	-2.666849	0.593192
6	-3.521447	-4.146119	0.797148
6	-3.010686	-4.976813	-0.369889
6	-3.580519	-4.474358	-1.687436
6	-3.296616	-2.992304	-1.889031
1	-3.745646	-2.639947	-2.827564
1	-2.209162	-2.838368	-1.997623
1	-3.178188	-5.054900	-2.528205
1	-4.671204	-4.633910	-1.694526
1	-1.910692	-4.912959	-0.403467
1	-3.254277	-6.037562	-0.224480
1	-3.079391	-4.494057	1.740571
1	-4.610466	-4.283953	0.895931
1	-2.125301	-2.536123	0.571615
1	-3.581874	-2.085879	1.449866
1	-4.906506	-2.285598	-0.673516
1	-2.367951	1.339367	0.082414
1	-2.385364	-0.106556	1.077625



Cupracyclobutane – dCype (entry 14)

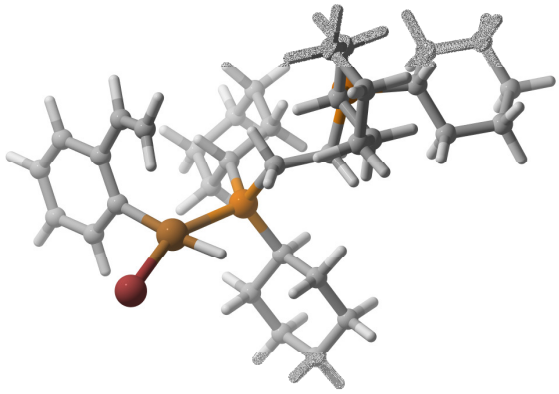
RM06 energy: -4781.5722064

Sum of electronic and thermal Free Energies: -4780.81397

6	1.516403	0.153170	-0.462048
6	0.579098	1.087878	-1.224903
15	-1.153303	0.446557	-1.180505

6	-2.293735	1.850628	-1.645879
1	-2.329398	1.846349	-2.748910
6	-1.809055	3.232100	-1.206110
6	-2.794908	4.317706	-1.620801
6	-4.195927	4.038797	-1.099288
6	-4.678267	2.671983	-1.555874
6	-3.709748	1.581914	-1.122244
1	-4.071403	0.599399	-1.449305
1	-3.690694	1.536971	-0.023738
1	-4.770389	2.664054	-2.653793
1	-5.679368	2.460606	-1.158706
1	-4.889897	4.823709	-1.426881
1	-4.188466	4.070790	0.002717
1	-2.823506	4.374782	-2.720736
1	-2.437134	5.294816	-1.270409
1	-1.680969	3.258202	-0.112765
1	-0.825432	3.448366	-1.641020
6	-1.192875	-0.579561	-2.743738
1	-1.055368	0.178848	-3.537741
6	-0.041735	-1.579093	-2.857915
6	-0.106702	-2.355476	-4.166414
6	-1.442628	-3.061268	-4.323155
6	-2.579594	-2.056506	-4.253582
6	-2.545974	-1.255869	-2.958267
1	-3.348307	-0.508821	-2.982716
1	-2.753698	-1.918819	-2.105253
1	-2.502923	-1.365166	-5.108823
1	-3.551109	-2.558805	-4.349428
1	-1.478652	-3.619367	-5.268016
1	-1.559845	-3.802429	-3.515868
1	0.041330	-1.664361	-5.012375
1	0.722319	-3.074364	-4.205561
1	0.924308	-1.062603	-2.793737
1	-0.086371	-2.284998	-2.018045
29	-1.636428	-0.476855	0.934838
6	-1.720854	1.280200	2.036322
6	-0.362959	1.892509	2.178051
1	-0.416216	2.719309	2.906678
1	0.363621	1.173682	2.576713
1	0.028398	2.304546	1.243372
6	-2.249864	0.580680	3.234547
6	-2.608419	0.906433	4.533240
6	-2.989453	-0.155434	5.349948
6	-2.983543	-1.468699	4.876895
6	-2.596595	-1.772306	3.571818
6	-2.239676	-0.704228	2.762276

1	-2.578265	-2.800671	3.216121
1	-3.285117	-2.273889	5.545809
1	-3.292061	0.036114	6.377902
1	-2.598940	1.929304	4.907999
1	-2.447246	1.873568	1.473308
35	-1.398581	-2.824257	0.426999
1	0.607049	2.090747	-0.785861
1	0.874174	1.205598	-2.278330
15	3.270908	0.208431	-1.072758
6	4.023343	-1.219746	-0.129641
6	3.826246	-1.251752	1.383327
6	4.522610	-2.453053	2.012100
6	4.057357	-3.755582	1.380926
6	4.272167	-3.734921	-0.124372
6	3.576725	-2.539959	-0.762374
1	2.487788	-2.660413	-0.636276
1	3.760490	-2.521063	-1.846061
1	5.352192	-3.683175	-0.338242
1	3.910347	-4.666808	-0.578703
1	2.984199	-3.896642	1.590913
1	4.576599	-4.610855	1.833360
1	5.611796	-2.352017	1.876680
1	4.345275	-2.463775	3.095939
1	4.200566	-0.326597	1.840431
1	2.749904	-1.306719	1.616062
1	5.104930	-1.108043	-0.329406
6	4.015592	1.715012	-0.230043
6	3.275274	2.279112	0.980452
6	4.016080	3.467574	1.580696
6	4.229956	4.562180	0.547161
6	4.953029	4.021656	-0.677248
6	4.229971	2.819314	-1.268000
1	4.787182	2.424636	-2.128234
1	3.249219	3.137490	-1.662962
1	5.067366	4.806563	-1.436916
1	5.973153	3.718863	-0.390219
1	3.250645	4.965308	0.241096
1	4.786133	5.402403	0.983503
1	3.462321	3.856958	2.445786
1	4.992399	3.130137	1.964568
1	2.273408	2.613857	0.666279
1	3.113356	1.510226	1.745870
1	5.012262	1.371453	0.101580
1	1.210871	-0.893409	-0.581591
1	1.451804	0.356776	0.612453



Copper-hydride oxidative insertion into Ar-Br bond (entry 15)

RB3LYP energy: -4782.7628464

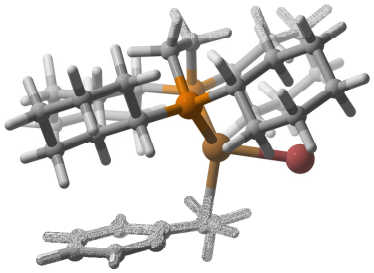
Sum of electronic and thermal Free Energies: -4782.008426

6	0.665830	0.330206	-0.080771
15	-0.895274	-0.579334	0.370733
6	-1.184869	-1.794600	-1.038852
1	-1.516674	-1.130219	-1.843891
6	0.092661	-2.519861	-1.511379
6	-0.200918	-3.399491	-2.739907
6	-1.339483	-4.391879	-2.487494
6	-2.597941	-3.668592	-1.999084
6	-2.310051	-2.807285	-0.759613
1	-2.014892	-3.467695	0.063435
1	-3.221702	-2.291485	-0.453285
1	-2.991830	-3.030093	-2.799171
1	-3.386736	-4.389948	-1.760573
1	-1.024091	-5.124034	-1.732247
1	-1.554959	-4.959523	-3.399155
1	-0.463484	-2.751675	-3.585698
1	0.714276	-3.928457	-3.026964
1	0.871908	-1.803900	-1.777665
1	0.489776	-3.146432	-0.703519
6	-0.754986	-1.529253	1.970728
1	-0.267454	-2.475940	1.707385
6	0.093572	-0.811493	3.038444
6	0.172359	-1.634961	4.334760
6	-1.213720	-1.976331	4.889942

6	-2.079089	-2.660798	3.827782
6	-2.161512	-1.828188	2.540230
1	-2.658331	-0.875691	2.759168
1	-2.783749	-2.343818	1.808946
1	-3.090875	-2.830884	4.210729
1	-1.664603	-3.650226	3.595049
1	-1.709579	-1.054787	5.220554
1	-1.120182	-2.614727	5.775014
1	0.725859	-2.562212	4.137448
1	0.754583	-1.078855	5.077097
1	-0.352290	0.166516	3.256794
1	1.103163	-0.624385	2.672846
29	-2.574453	0.947373	0.478875
15	3.306033	0.192959	-1.094596
6	2.039465	-0.314536	0.197645
1	2.374790	-0.046579	1.198686
1	1.996246	-1.403675	0.163114
6	3.547963	2.027500	-0.729964
1	2.536993	2.438793	-0.862814
6	4.040747	2.425500	0.672424
6	4.134963	3.952505	0.827685
6	5.022750	4.577262	-0.254997
6	4.549099	4.183218	-1.659090
6	4.438880	2.659385	-1.819810
1	5.444037	2.220681	-1.770750
1	4.044852	2.416651	-2.812296
1	3.567539	4.636401	-1.850371
1	5.229264	4.587249	-2.417441
1	6.058127	4.239512	-0.113254
1	5.036656	5.667941	-0.152098
1	4.518772	4.200149	1.823937
1	3.128245	4.386564	0.767329
1	5.032188	1.991957	0.848284
1	3.380215	2.018312	1.444564
6	4.905182	-0.635701	-0.505603
1	5.678581	0.119270	-0.700507
6	4.994278	-1.035650	0.979703
6	6.352446	-1.672593	1.317017
6	6.652952	-2.878224	0.419398
6	6.560709	-2.501827	-1.063635
6	5.212303	-1.851580	-1.407024
1	4.412632	-2.597154	-1.298214
1	5.203453	-1.546800	-2.458386
1	7.369639	-1.801129	-1.309752
1	6.716865	-3.385891	-1.692090
1	5.932506	-3.678524	0.635860

1	7.644478	-3.284735	0.647516
1	7.145015	-0.922082	1.197282
1	6.366858	-1.970868	2.371706
1	4.825379	-0.170929	1.625867
1	4.202494	-1.757805	1.212772
1	0.602346	1.297537	0.416546
1	0.528915	0.533276	-1.147901
6	-2.425346	1.489163	-2.881682
6	-1.605443	2.322121	-2.230497
1	-1.769496	2.611218	-1.196273
1	-0.758617	2.780863	-2.731632
1	-2.227351	1.312098	-3.938882
6	-3.619394	0.803572	-2.351171
6	-3.825161	0.538138	-0.975984
6	-5.035683	-0.071400	-0.613576
6	-6.008592	-0.429310	-1.549641
6	-5.782866	-0.187339	-2.904087
6	-4.595560	0.421885	-3.293535
1	-4.419482	0.622684	-4.347926
1	-6.523906	-0.466955	-3.647026
1	-6.931428	-0.901915	-1.223684
1	-5.236845	-0.277882	0.435354
35	-3.610456	2.817585	1.604561
1	-1.497643	1.029208	1.540954

C. Pathways involving one-electron changes at copper.



Benzyl copper bromide/aryl radical (triplet) (entry 16)

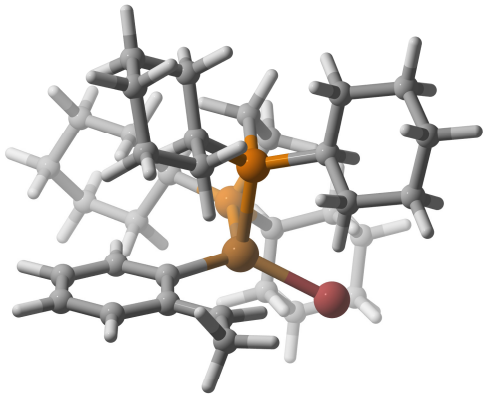
UM06 energy: -4781.5688977

Sum of electronic and thermal Free Energies: -4780.812989

6	-0.716844	0.490610	-2.321180
6	0.788850	0.221130	-2.362715
15	1.492663	-0.758055	-0.943948
6	1.327650	-2.525911	-1.527087
1	1.775207	-2.556659	-2.537259
6	-0.138250	-2.941749	-1.624557
6	-0.301827	-4.393889	-2.051698
6	0.460947	-5.333620	-1.133476
6	1.926879	-4.939750	-1.068989
6	2.095469	-3.492853	-0.626181
1	3.162846	-3.240584	-0.601842
1	1.726137	-3.388559	0.408386
1	2.382644	-5.069811	-2.063945
1	2.478617	-5.601828	-0.388779
1	0.353408	-6.373571	-1.468433
1	0.026037	-5.286562	-0.121235
1	0.069758	-4.513426	-3.082254
1	-1.368812	-4.653627	-2.075636
1	-0.619801	-2.795001	-0.642811
1	-0.673646	-2.295448	-2.329483
6	3.342975	-0.490027	-1.087075
1	3.719059	-1.275052	-1.767082
6	3.746671	0.864935	-1.668899
6	5.262393	1.022952	-1.706429
6	5.888475	0.823042	-0.337008

6	5.497482	-0.529774	0.236317
6	3.983965	-0.674428	0.291914
1	3.710460	-1.646621	0.721896
1	3.567880	0.088900	0.967479
1	5.924015	-1.330766	-0.390453
1	5.923058	-0.662569	1.239867
1	6.980690	0.921167	-0.395169
1	5.538443	1.616810	0.342631
1	5.682843	0.283549	-2.407978
1	5.519993	2.011202	-2.109843
1	3.351685	0.985487	-2.684957
1	3.308917	1.670844	-1.056735
29	0.361187	0.346299	0.809462
15	-1.349185	1.054484	-0.662826
6	-3.128422	0.492436	-0.696234
6	-3.967799	1.048666	-1.845891
6	-5.408724	0.555318	-1.773899
6	-5.480674	-0.962356	-1.736902
6	-4.657562	-1.508948	-0.581726
6	-3.213562	-1.033260	-0.660447
1	-2.761338	-1.452912	-1.572941
1	-2.631284	-1.427270	0.182833
1	-5.099130	-1.172226	0.369892
1	-4.688319	-2.607049	-0.564299
1	-5.093509	-1.368718	-2.685624
1	-6.523750	-1.296383	-1.660356
1	-5.882047	0.962490	-0.865909
1	-5.980370	0.950895	-2.623935
1	-3.960169	2.145748	-1.844169
1	-3.528419	0.734150	-2.806341
1	-3.546220	0.867906	0.254169
6	-1.472838	2.897979	-0.845157
6	-0.139392	3.524128	-1.252100
6	-0.247396	5.041540	-1.330100
6	-0.736118	5.628435	-0.015470
6	-2.072964	5.020858	0.381536
6	-1.984397	3.502921	0.461653
1	-2.965908	3.081922	0.721619
1	-1.294689	3.218809	1.273081
1	-2.413644	5.427100	1.343250
1	-2.835710	5.302741	-0.362913
1	0.005345	5.416934	0.771294
1	-0.815657	6.721413	-0.086388
1	0.725253	5.470209	-1.605921
1	-0.948784	5.318917	-2.134424
1	0.632368	3.251703	-0.515907

1	0.187124	3.128620	-2.223445
1	-2.199764	3.109591	-1.646768
6	0.220872	-0.786589	2.903016
6	1.527912	-1.479435	3.042186
1	1.572561	-2.048408	3.985740
1	1.723125	-2.196041	2.235339
1	2.349414	-0.757503	3.055015
6	-1.001946	-1.463769	2.676918
6	-1.100245	-2.835509	2.302866
6	-2.328311	-3.462174	2.209289
6	-3.517265	-2.775990	2.472320
6	-3.470170	-1.416643	2.808882
6	-2.238755	-0.837730	2.875906
1	-4.384957	-0.858770	3.004429
1	-4.475210	-3.288295	2.408454
1	-2.368740	-4.515352	1.937808
1	-0.188427	-3.400494	2.110722
1	0.135913	0.207592	3.341089
35	1.699433	2.126592	1.832539
1	1.067126	-0.250891	-3.316457
1	1.311441	1.183050	-2.331840
1	-1.278758	-0.410025	-2.589307
1	-0.973536	1.239570	-3.083299



Aryl copper bromide/benzyl radical (triplet) (entry 17)

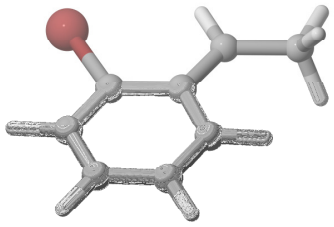
UM06 energy: -4781.5787403

Sum of electronic and thermal Free Energies: -4780.825517

6	0.190172	0.060376	-2.294520
15	1.289894	-0.274444	-0.845528
6	2.023016	-1.935685	-1.215889
6	2.921662	-2.022437	-2.447564
6	3.294695	-3.473010	-2.731265
6	3.960983	-4.119898	-1.526271
6	3.087834	-4.004716	-0.285659
6	2.712800	-2.557354	-0.000543
1	3.621279	-1.985573	0.248261
1	2.049650	-2.503858	0.870737
1	2.163266	-4.587776	-0.429131
1	3.595148	-4.440633	0.585022
1	4.195357	-5.171588	-1.737377
1	4.924932	-3.620174	-1.336455
1	2.383901	-4.035948	-2.991140
1	3.951664	-3.525025	-3.609676
1	3.841383	-1.445246	-2.267834
1	2.438320	-1.578715	-3.328007
1	1.114427	-2.534396	-1.414720
6	2.561000	1.073136	-0.957421
1	2.013945	1.929674	-0.521243
6	3.026478	1.492657	-2.353393
6	3.908686	2.733436	-2.259745
6	5.098515	2.514185	-1.336415
6	4.649213	2.043006	0.038531
6	3.773107	0.803075	-0.065898
1	4.362250	-0.019810	-0.500053
1	3.459583	0.472501	0.931464
1	4.078884	2.844183	0.536745
1	5.517180	1.836321	0.679267
1	5.692504	3.433861	-1.254310
1	5.764273	1.754609	-1.777736
1	3.304135	3.573159	-1.880989
1	4.248850	3.025214	-3.262221
1	3.595822	0.674863	-2.818496
1	2.175668	1.696675	-3.014719
29	-0.288719	-0.256244	0.925664
6	0.473923	1.306681	1.879179
6	1.608026	1.148243	2.726973
6	2.168803	2.324768	3.297041
6	1.618897	3.570158	3.067340
6	0.485869	3.699609	2.265405
6	-0.071901	2.560599	1.677544
1	-0.951062	2.674968	1.043611

1	0.041115	4.678269	2.090702
1	2.068544	4.451647	3.521296
1	3.040165	2.238102	3.945438
6	2.166779	-0.121768	2.977649
1	1.617530	-0.988221	2.609286
6	3.424975	-0.350789	3.729048
1	3.746532	-1.394530	3.655805
1	4.250992	0.277474	3.361622
1	3.324711	-0.121900	4.801955
15	-2.134430	0.198745	-0.672893
6	-1.234764	-0.475102	-2.152321
1	-1.803566	-0.275731	-3.072266
1	-1.204154	-1.565550	-2.035988
6	-2.862865	1.804998	-1.305763
6	-1.818153	2.773869	-1.858015
6	-2.418035	4.123725	-2.231522
6	-3.179911	4.740157	-1.071442
6	-4.277583	3.798048	-0.611221
6	-3.708982	2.446760	-0.202628
1	-3.094449	2.574242	0.703595
1	-4.530229	1.776244	0.080118
1	-5.001323	3.658365	-1.430289
1	-4.839163	4.230002	0.227244
1	-2.484970	4.930387	-0.236177
1	-3.597252	5.714351	-1.357215
1	-1.622149	4.794858	-2.580176
1	-3.105976	3.991403	-3.082269
1	-1.014537	2.926699	-1.119042
1	-1.345137	2.341521	-2.747515
1	-3.533710	1.520901	-2.136500
6	-3.692782	-0.834553	-0.534908
6	-3.589686	-2.237320	-1.131948
6	-4.899099	-3.000080	-0.964409
6	-5.332213	-3.063464	0.491755
6	-5.442258	-1.667067	1.082341
6	-4.129913	-0.911961	0.931899
1	-3.342865	-1.427490	1.502488
1	-4.216097	0.091838	1.369184
1	-6.247907	-1.115165	0.569662
1	-5.726562	-1.716604	2.141808
1	-4.589892	-3.640142	1.066949
1	-6.285480	-3.600812	0.585849
1	-5.685846	-2.500601	-1.553490
1	-4.795719	-4.010407	-1.382409
1	-2.778799	-2.788679	-0.631013
1	-3.332373	-2.187308	-2.197999

1	-4.466070	-0.286964	-1.102242
35	-0.736159	-2.535226	1.585094
1	0.650792	-0.345545	-3.205198
1	0.185243	1.147819	-2.416122

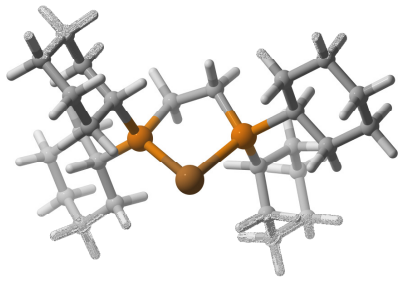


Benzyl radical (doublet) (entry 18)

UM06 energy: -2883.4665678

Sum of electronic and thermal Free Energies: -2883.371259

6	1.916405	2.754636	0.000192
6	0.774073	1.809571	-0.000259
6	0.915901	0.411494	-0.000117
6	-0.181750	-0.495589	-0.000021
6	-0.008352	-1.864221	0.000080
6	1.274348	-2.405908	0.000066
6	2.378891	-1.556252	-0.000028
6	2.205416	-0.190301	-0.000101
1	3.079204	0.457409	-0.000182
1	3.383972	-1.971768	-0.000058
1	1.402972	-3.485170	0.000120
1	-0.875688	-2.519916	0.000182
35	-1.974662	0.156429	0.000010
1	-0.230509	2.225134	-0.000480
1	2.564384	2.623663	0.879422
1	2.566072	2.622843	-0.877646
1	1.573182	3.792228	-0.000577



Copper(0) – dCype (entry 19)

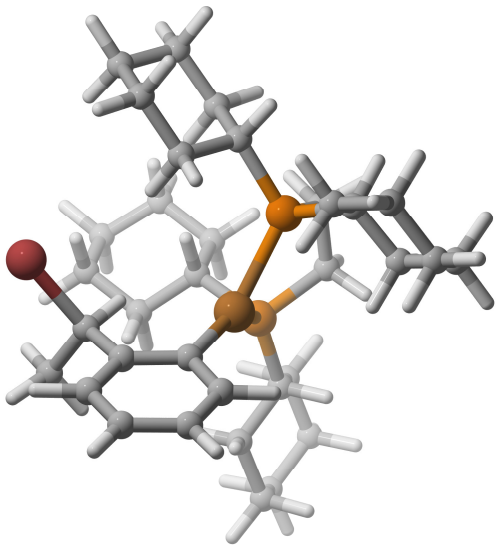
UM06 energy: -1898.0253665

Sum of electronic and thermal Free Energies: -1897.391555

6	0.591449	-0.447884	1.678737
15	1.603128	-0.169880	0.139635
6	1.953958	1.653975	0.276218
1	0.966297	2.064698	0.551293
6	2.940482	2.071703	1.362165
6	3.039698	3.590182	1.449839
6	3.404738	4.199349	0.104343
6	2.413439	3.786385	-0.974067
6	2.306150	2.271660	-1.077329
1	3.260282	1.861032	-1.444070
1	1.546751	1.981802	-1.821288
1	1.421044	4.201972	-0.733020
1	2.699289	4.212722	-1.944606
1	4.413865	3.861506	-0.183603
1	3.456555	5.293499	0.180777
1	2.071075	3.997260	1.782795
1	3.774215	3.876588	2.214382
1	2.644875	1.656069	2.335601
1	3.938070	1.662521	1.137819
6	3.177226	-1.077549	0.525796
1	3.554390	-0.741729	1.507715
6	2.886550	-2.578507	0.598520
6	4.155392	-3.387839	0.830918
6	5.202431	-3.098628	-0.232542
6	5.503509	-1.610131	-0.301970
6	4.236788	-0.799360	-0.540287
1	4.480630	0.270037	-0.574531

1	3.819443	-1.051318	-1.529969
1	5.967070	-1.287546	0.644464
1	6.236186	-1.400037	-1.092227
1	4.827776	-3.437980	-1.211502
1	6.119364	-3.669586	-0.035314
1	4.565780	-3.138196	1.822671
1	3.915244	-4.458970	0.856651
1	2.417901	-2.894653	-0.349470
1	2.160029	-2.796831	1.391600
29	0.118191	-0.389338	-1.695623
15	-1.583735	-0.107827	-0.058913
6	-0.780699	0.216534	1.591387
1	-1.414964	-0.101181	2.429624
1	-0.682050	1.306815	1.680720
6	-2.292112	-1.816380	0.136562
1	-1.396076	-2.417214	0.385962
6	-3.331674	-2.030308	1.231050
6	-3.737839	-3.496878	1.320088
6	-4.260513	-4.004203	-0.015605
6	-3.239048	-3.784332	-1.121008
6	-2.813793	-2.325328	-1.207527
1	-3.674871	-1.710578	-1.519990
1	-2.039948	-2.186812	-1.978871
1	-2.350377	-4.404604	-0.922018
1	-3.638057	-4.118805	-2.087781
1	-5.188610	-3.465770	-0.267478
1	-4.529342	-5.066598	0.054558
1	-4.493209	-3.631446	2.106022
1	-2.864414	-4.097313	1.621727
1	-4.226097	-1.430581	0.999944
1	-2.961317	-1.679722	2.203864
6	-2.988514	1.104443	-0.154065
1	-3.725896	0.619431	-0.817772
6	-3.676749	1.479896	1.157549
6	-4.794129	2.489772	0.924280
6	-4.280742	3.736375	0.220247
6	-3.585987	3.377497	-1.084516
6	-2.475651	2.361420	-0.863659
1	-1.679580	2.819806	-0.250546
1	-2.004410	2.085029	-1.818044
1	-4.323855	2.953947	-1.784786
1	-3.182777	4.277313	-1.567791
1	-3.567483	4.256863	0.880014
1	-5.102428	4.441313	0.037280
1	-5.580645	2.023164	0.309564
1	-5.265803	2.753184	1.880476

1	-4.074508	0.591753	1.662369
1	-2.936697	1.919602	1.844914
1	1.133559	-0.102952	2.570844
1	0.469114	-1.532280	1.792536



Aryl copper/benzyl bromide (entry 20)

RM06 energy: -4781.6125195

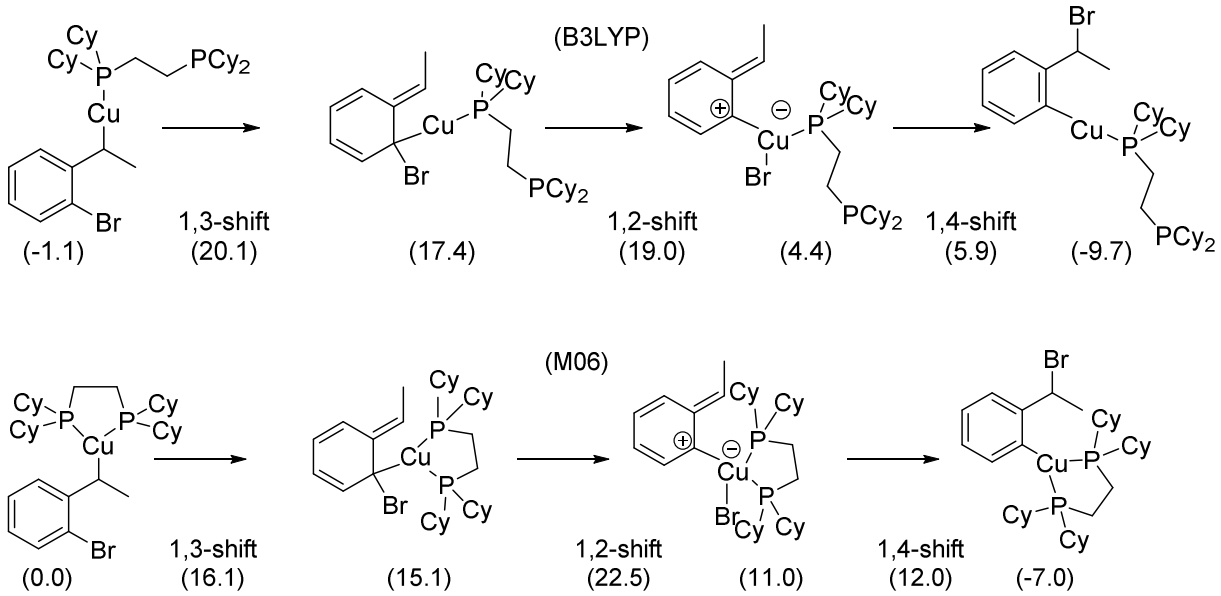
Sum of electronic and thermal Free Energies: -4780.851193

6	1.637405	2.235275	-1.461448
15	1.926353	0.861289	-0.248804
6	2.145196	-0.634884	-1.334447
6	2.929779	-0.505354	-2.636705
6	2.773240	-1.773751	-3.469517
6	3.195555	-3.012097	-2.691757
6	2.455603	-3.119523	-1.365696
6	2.624687	-1.850009	-0.543291
1	3.688107	-1.724083	-0.286073
1	2.083927	-1.928111	0.408747
1	1.380301	-3.283885	-1.555619
1	2.805033	-3.991958	-0.797334
1	3.035925	-3.915536	-3.294611
1	4.278399	-2.960236	-2.492987
1	1.718124	-1.876335	-3.772816
1	3.352667	-1.689925	-4.398495

1	3.994676	-0.344696	-2.415161
1	2.601207	0.365181	-3.219336
1	1.093444	-0.842552	-1.611074
6	3.528039	1.361469	0.545330
1	3.320534	2.413031	0.819186
6	4.782392	1.343082	-0.323113
6	5.981547	1.893342	0.441058
6	6.206451	1.130597	1.738176
6	4.956571	1.142391	2.605034
6	3.754618	0.593717	1.848962
1	3.926200	-0.470903	1.624343
1	2.850780	0.633562	2.472444
1	4.742594	2.176458	2.920085
1	5.119396	0.565961	3.525205
1	7.059598	1.550857	2.286716
1	6.473283	0.087576	1.501914
1	5.807761	2.957103	0.669891
1	6.879330	1.855506	-0.190149
1	4.998717	0.306795	-0.624955
1	4.625579	1.912723	-1.249187
29	-0.161353	0.574977	0.762570
6	-1.006469	-0.134750	2.396214
6	-1.153813	-1.518430	2.619347
6	-1.775604	-2.023124	3.764084
6	-2.281151	-1.166366	4.728422
6	-2.152807	0.206766	4.545810
6	-1.528703	0.696655	3.405256
1	-1.450898	1.782201	3.296632
1	-2.546596	0.894643	5.294399
1	-2.771570	-1.564728	5.615083
1	-1.881411	-3.100937	3.899284
6	-0.532084	-2.463434	1.634480
35	-1.877018	-3.730144	0.845234
1	-0.209672	-1.893925	0.754348
6	0.611911	-3.275763	2.188120
1	1.373807	-2.588292	2.584061
1	0.292493	-3.921232	3.014071
1	1.080603	-3.904680	1.422415
15	-1.069318	1.459416	-1.209284
6	0.350249	2.044470	-2.264124
1	0.076067	2.968407	-2.791417
1	0.519288	1.291565	-3.041215
6	-2.063726	3.005268	-0.948862
6	-1.238691	4.022943	-0.163116
6	-2.038824	5.276633	0.163405
6	-3.324660	4.937307	0.899081

6	-4.159556	3.955101	0.093928
6	-3.371648	2.691604	-0.224047
1	-3.143347	2.159624	0.714894
1	-3.989267	2.008560	-0.822266
1	-4.478984	4.433596	-0.846031
1	-5.078046	3.692783	0.634913
1	-3.076941	4.487601	1.874305
1	-3.898357	5.848523	1.113501
1	-1.423004	5.966965	0.754799
1	-2.283556	5.804033	-0.772907
1	-0.895835	3.552435	0.775094
1	-0.334287	4.296879	-0.722501
1	-2.295295	3.422712	-1.945195
6	-2.170247	0.409844	-2.302158
6	-1.461695	-0.240828	-3.487836
6	-2.402413	-1.144756	-4.275453
6	-3.046723	-2.199742	-3.390249
6	-3.765185	-1.552554	-2.218036
6	-2.818468	-0.666373	-1.425633
1	-2.020479	-1.292964	-0.992756
1	-3.333998	-0.217520	-0.566194
1	-4.607831	-0.948588	-2.592306
1	-4.198149	-2.315682	-1.558004
1	-2.267259	-2.878894	-3.005542
1	-3.736816	-2.821817	-3.975371
1	-3.190825	-0.526603	-4.734133
1	-1.856913	-1.614043	-5.105042
1	-0.609316	-0.840645	-3.124179
1	-1.045743	0.521397	-4.158663
1	-2.957689	1.074361	-2.697639
1	2.492311	2.361037	-2.138388
1	1.586628	3.148452	-0.852495

D. Dearomative pathway.

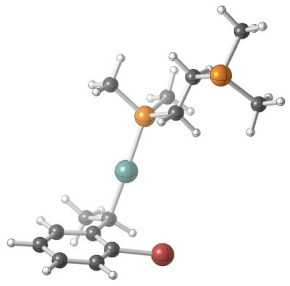


Computational strategy:

The computational mechanistic investigation began with the dMepe ligan system. Once all intermediates and transition state structures (TSSs) were confirmed by checking for the absence or presence of an imaginary frequency, respectively, intrinsic reaction coordinate (IRC)[15] calculations were performed to confirm that the intermediates of the pathway were connected to their corresponding TSSs. Then, the dCpye ligand system was optimized using various basis sets. Monodentate versus bidentate systems were also compared. Structural drawings were produced using *CYLview*.[21]

Calculated coordinates and energies (dMepe):
B3LYP/6-311G(d):LANL2DZ(Cu)

INT-4.1



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Imaginary Frequencies: none found
Zero-point correction = 0.344090 (Hartree/Particle)

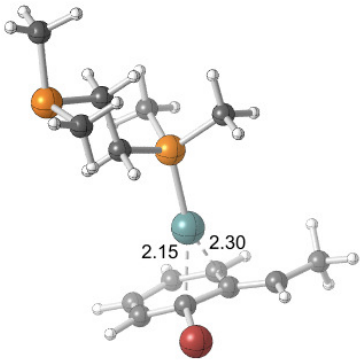
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.895192 hartrees -2510601.74193 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.734716	-1.113819	1.253273
2	6	3.080662	-0.232133	0.352444
3	6	2.893711	1.074058	0.865475
4	6	3.278820	1.468559	2.140736
5	6	3.898473	0.556536	2.994343
6	6	4.125669	-0.739981	2.532853
7	1	3.102927	2.487168	2.467784
8	1	4.201499	0.861942	3.990269
9	1	4.617699	-1.466915	3.173011
10	6	2.640059	-0.673633	-0.983428
11	1	2.646723	0.172029	-1.676265
12	6	3.418951	-1.846431	-1.592520
13	1	3.113043	-2.004141	-2.631550
14	1	4.509444	-1.681606	-1.601328
15	1	3.252998	-2.799045	-1.078653
16	1	3.929221	-2.129679	0.927131
17	29	0.674282	-1.136152	-0.836838
18	15	-1.530862	-1.730748	-0.700003
19	6	-2.292409	-2.208291	-2.305539
20	1	-3.321826	-2.554774	-2.189979
21	1	-2.276690	-1.359089	-2.992662
22	1	-1.702751	-3.011585	-2.753549
23	6	-1.887894	-3.181917	0.373626
24	1	-1.576484	-2.967260	1.398330
25	1	-2.947162	-3.449116	0.371779
26	1	-1.311979	-4.039871	0.019153
27	6	-2.608340	-0.370982	-0.037280
28	1	-2.230088	-0.164384	0.969958
29	1	-2.366424	0.512398	-0.636003

30	6	-4.120137	-0.612827	-0.016426
31	1	-4.358173	-1.536570	0.520087
32	1	-4.510533	-0.717893	-1.033782
33	15	-5.056803	0.752314	0.861918
34	6	-6.792883	0.235576	0.454540
35	1	-7.491151	1.008155	0.787508
36	1	-6.944566	0.068913	-0.616779
37	1	-7.043738	-0.684256	0.989638
38	6	-4.851054	2.149607	-0.344323
39	1	-5.065405	1.853316	-1.376554
40	1	-5.529214	2.962300	-0.069801
41	1	-3.834638	2.547234	-0.295671
42	35	2.049417	2.437086	-0.231868

TS-4.2



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HF = -4001.1475672 hartrees (-2510760.10989367 kcal/mol)
Imaginary Frequencies: 1 (-101.9708 1/cm)
Zero-point correction = 0.341926 (Hartree/Particle)

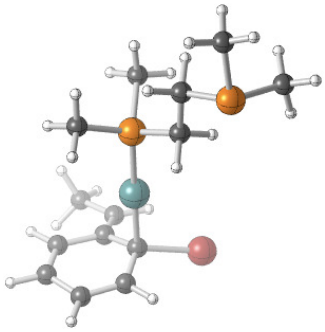
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.861820 hartrees (-2510580.8006682 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.503014	-1.534399	0.738875
2	6	3.148242	-0.442080	-0.177823
3	6	2.557439	0.702137	0.539528

4	6	2.596647	0.817646	1.947096
5	6	3.031597	-0.223351	2.743242
6	6	3.470377	-1.412612	2.102459
7	1	2.258128	1.743999	2.399500
8	1	3.001926	-0.145015	3.824039
9	1	3.802974	-2.251326	2.709428
10	6	3.302479	-0.546572	-1.545579
11	1	3.099851	0.325382	-2.156219
12	6	3.873341	-1.759282	-2.234252
13	1	3.839793	-1.633643	-3.320330
14	1	4.925944	-1.957511	-1.977316
15	1	3.330183	-2.688691	-2.011688
16	1	3.898559	-2.443959	0.299350
17	29	0.850514	-0.463075	-0.041207
18	15	-1.243583	-1.263081	-0.301099
19	6	-1.696057	-1.814033	-1.994997
20	1	-2.694970	-2.254566	-2.030480
21	1	-1.654449	-0.966913	-2.683252
22	1	-0.972210	-2.558181	-2.334010
23	6	-1.573100	-2.745345	0.734386
24	1	-1.456515	-2.491426	1.790218
25	1	-2.575772	-3.146392	0.571465
26	1	-0.842545	-3.519876	0.491377
27	6	-2.542614	-0.028142	0.176962
28	1	-2.287262	0.291698	1.192351
29	1	-2.369615	0.841008	-0.465398
30	6	-4.002034	-0.485125	0.104635
31	1	-4.161914	-1.352910	0.751739
32	1	-4.273097	-0.783594	-0.913231
33	15	-5.196940	0.829797	0.701143
34	6	-6.796761	-0.052998	0.373627
35	1	-7.631751	0.633483	0.537560
36	1	-6.863094	-0.443368	-0.646965
37	1	-6.913895	-0.884051	1.074116
38	6	-5.180384	2.000372	-0.741049
39	1	-5.313874	1.489301	-1.700134
40	1	-5.986501	2.729519	-0.622140
41	1	-4.241404	2.558526	-0.768164
42	35	2.339180	2.399418	-0.440575

INT-4.3



Charge = 0 Multiplicity = 1

Link 0: opt freq=noraman b3lyp/gen scrf=(smd,solvent=thf) nosymm pseudo=read
HF = -4001.1515178 hartrees (-2510549.59209 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.342264 (Hartree/Particle)

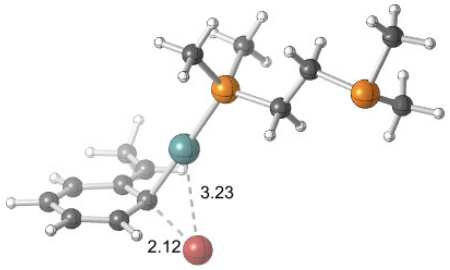
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.867494 hartrees (-2510584.36116 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.733719	-1.648421	0.556733
2	6	3.448435	-0.526505	-0.352034
3	6	2.560187	0.482990	0.280379
4	6	2.543724	0.602446	1.718778
5	6	2.991419	-0.409861	2.523781
6	6	3.547370	-1.577171	1.903075
7	1	2.101407	1.492510	2.154471
8	1	2.879667	-0.354177	3.601216
9	1	3.848637	-2.415777	2.526011
10	6	3.939633	-0.492574	-1.620933
11	1	3.713578	0.370380	-2.237629
12	6	4.747444	-1.591617	-2.263397
13	1	5.155802	-1.256802	-3.221095
14	1	5.601430	-1.916136	-1.655391
15	1	4.160993	-2.498584	-2.476442
16	1	4.221417	-2.522315	0.137084
17	29	0.692502	-0.320190	0.050868
18	15	-1.394651	-1.188580	-0.203179
19	6	-1.787208	-1.751344	-1.907937
20	1	-2.776165	-2.210397	-1.973851
21	1	-1.738972	-0.905342	-2.597182

22	1	-1.040135	-2.483399	-2.222512
23	6	-1.722353	-2.675924	0.825608
24	1	-1.658842	-2.413918	1.884130
25	1	-2.704556	-3.108531	0.623407
26	1	-0.958412	-3.428296	0.618218
27	6	-2.730312	0.020016	0.238686
28	1	-2.501582	0.354269	1.256031
29	1	-2.564391	0.887250	-0.408167
30	6	-4.177988	-0.468216	0.143485
31	1	-4.330304	-1.337798	0.790024
32	1	-4.425485	-0.774396	-0.878128
33	15	-5.409106	0.822858	0.718124
34	6	-6.984765	-0.091455	0.361903
35	1	-7.836421	0.577529	0.511371
36	1	-7.024401	-0.481489	-0.660183
37	1	-7.097441	-0.925824	1.059153
38	6	-5.390777	1.994780	-0.722931
39	1	-5.503664	1.482494	-1.684004
40	1	-6.209386	2.711431	-0.614171
41	1	-4.460087	2.567169	-0.736963
42	35	2.483556	2.267153	-0.636423

TS-4.4



Charge = 0 Multiplicity = 1

Link 0: opt=(ts,calcfc,noeigen) freq=noraman b3lyp/gen scrf=(smd,solvent=thf) pseudo=read nosymm
HF = -4001.1487499 hartrees (-2510760.85205 kcal/mol)
Imaginary Frequencies: 1 (-55.2919 1/cm)
Zero-point correction = 0.342849 (Hartree/Particle)

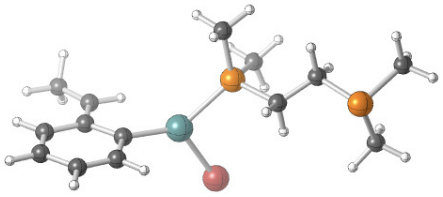
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.862605 hartrees (-2510581.29326 kcal/mol)

Coordinates (from last standard orientation):

Center	Atomic	Coordinates (Angstroms)

Number	Number	X	Y	Z
1	6	-4.635887	0.838368	0.642636
2	6	-3.577803	0.269657	-0.196711
3	6	-2.546362	-0.563195	0.523041
4	6	-2.773296	-0.828702	1.938606
5	6	-3.737244	-0.199697	2.658272
6	6	-4.696421	0.639627	1.980108
7	1	-2.093574	-1.516660	2.432078
8	1	-3.801466	-0.332799	3.733963
9	1	-5.508528	1.079137	2.553056
10	6	-3.515225	0.500672	-1.535601
11	6	-4.447332	1.309531	-2.386017
12	1	-5.239520	1.809511	-1.827146
13	1	-3.901495	2.086218	-2.938667
14	1	-4.931425	0.685897	-3.149629
15	1	-5.426234	1.403241	0.160318
16	29	-0.698994	0.222487	0.384695
17	15	1.367823	1.148033	0.247004
18	6	1.642282	2.184802	-1.246622
19	1	2.630526	2.649507	-1.252317
20	1	1.529336	1.575427	-2.146047
21	1	0.885161	2.971704	-1.276060
22	6	1.762793	2.290144	1.632226
23	1	1.770679	1.737856	2.574707
24	1	2.727451	2.784957	1.498930
25	1	0.984678	3.054049	1.695331
26	6	2.742957	-0.097437	0.237087
27	1	2.577123	-0.729834	1.115207
28	1	2.551694	-0.734463	-0.632148
29	6	4.176475	0.440524	0.224795
30	1	4.359499	1.051884	1.113545
31	1	4.355520	1.074115	-0.650053
32	15	5.457164	-0.927706	0.266480
33	6	6.998576	0.101003	0.159900
34	1	7.861754	-0.552520	0.008433
35	1	6.968164	0.830380	-0.655951
36	1	7.152836	0.636323	1.100563
37	6	5.365410	-1.541688	-1.483402
38	1	5.399159	-0.730795	-2.218305
39	1	6.203526	-2.217713	-1.673190
40	1	4.447648	-2.114963	-1.635567
41	35	-2.319955	-2.466554	-0.394188
42	1	-2.710579	0.013399	-2.082969

INT-4.5



Charge = 0 Multiplicity = 1

Link 0: opt freq=noraman b3lyp/gen scrf=(smd,solvent=thf) pseudo=read nosymm
HF = -4001.1731892 hartrees (-2510776.18795 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.344078 (Hartree/Particle)

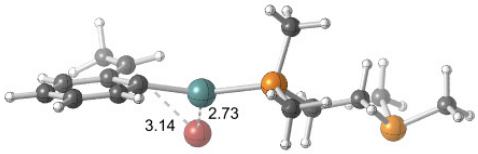
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.888588 hartrees (-2510597.59786 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.215635	-1.027610	-0.487594
2	6	-3.998209	-0.560293	0.135318
3	6	-2.753780	-0.423196	-0.617872
4	6	-2.849016	-0.781404	-1.986124
5	6	-4.024542	-1.221550	-2.565465
6	6	-5.222683	-1.350210	-1.812198
7	1	-1.967514	-0.704231	-2.616885
8	1	-4.042536	-1.476535	-3.621859
9	1	-6.127997	-1.701339	-2.295203
10	6	-3.965345	-0.221077	1.472226
11	6	-5.047981	-0.236486	2.473933
12	1	5.153371	0.771068	2.897620
13	1	-6.016488	-0.570003	2.106761
14	1	-4.746738	-0.868224	3.319875
15	1	-6.124556	-1.123540	0.095216
16	35	-0.323239	2.685081	0.053444
17	29	-1.040393	0.238092	0.100241
18	15	0.926123	-0.696547	1.007036
19	6	1.496407	0.077054	2.578210
20	1	2.418415	-0.371673	2.954863
21	1	1.651621	1.145503	2.417857
22	1	0.719439	-0.036099	3.338637
23	6	0.968525	-2.495418	1.418462
24	1	0.799399	-3.084311	0.513572

25	1	1.913604	-2.805378	1.871792
26	1	0.159877	-2.721282	2.118301
27	6	2.348256	-0.467134	-0.167948
28	1	2.060637	-0.988481	-1.087620
29	1	2.340708	0.599229	-0.410796
30	6	3.736268	-0.919397	0.292582
31	1	3.733294	-1.989560	0.522932
32	1	4.041208	-0.391115	1.201909
33	15	5.045409	-0.671275	-1.025051
34	6	6.549312	-1.173298	-0.058154
35	1	7.447421	-0.974973	-0.649330
36	1	6.635341	-0.639409	0.893699
37	1	6.520385	-2.247369	0.144221
38	6	5.243320	1.174261	-0.974576
39	1	5.354059	1.556676	0.045463
40	1	6.128526	1.458885	-1.550134
41	1	4.383606	1.662883	-1.439050
42	1	-2.996444	0.112595	1.840185

TS-4.6



Charge = 0 Multiplicity = 1

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HF = -4001.1685731 hartrees (-2510773.29130598 kcal/mol)
Imaginary Frequencies: 1 (-61.6907 1/cm)
Zero-point correction = 0.342951 (Hartree/Particle)

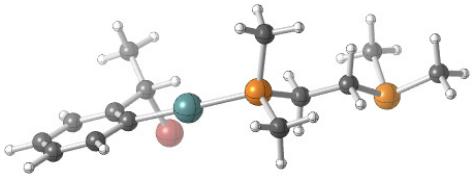
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.884245 hartrees (-2510594.87257995 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.171258	0.244775	0.189421
2	6	-3.761738	0.264419	0.442459
3	6	-2.909090	-0.852152	0.094907
4	6	-3.580420	-1.976140	-0.423806

5	6	-4.952909	-1.989853	-0.655848
6	6	-5.757280	-0.873526	-0.350961
7	1	-3.012561	-2.864554	-0.688169
8	1	-5.417371	-2.871096	-1.090980
9	1	-6.825827	-0.905448	-0.534386
10	6	-3.172955	1.355553	1.088322
11	6	-3.820113	2.607324	1.531193
12	1	-3.126148	3.443508	1.421126
13	1	-4.755414	2.842298	1.025368
14	1	-4.022169	2.526685	2.610165
15	1	-5.786932	1.096424	0.455980
16	35	-0.773219	1.958296	-0.848367
17	29	-0.927463	-0.633550	-0.013755
18	15	1.231372	-1.414290	0.238624
19	6	1.628291	-1.940991	1.959643
20	1	2.616769	-2.398918	2.043181
21	1	1.578768	-1.079506	2.630189
22	1	0.879864	-2.664285	2.291497
23	6	1.620653	-2.928010	-0.737948
24	1	1.513224	-2.714936	-1.804103
25	1	2.631094	-3.299696	-0.550955
26	1	0.907796	-3.714605	-0.479770
27	6	2.581290	-0.220891	-0.211749
28	1	2.443880	-0.015852	-1.278505
29	1	2.329197	0.711959	0.299844
30	6	4.023754	-0.638646	0.085549
31	1	4.259992	-1.590580	-0.400704
32	1	4.177005	-0.776327	1.161105
33	15	5.279205	0.596365	-0.554570
34	6	6.826158	-0.163061	0.138461
35	1	7.671994	0.507987	-0.034253
36	1	6.755427	-0.362437	1.212720
37	1	7.043842	-1.102143	-0.377305
38	6	5.043729	1.986179	0.654681
39	1	5.036313	1.640651	1.693750
40	1	5.854588	2.710121	0.535911
41	1	4.107565	2.511804	0.452397
42	1	-2.149122	1.220548	1.410883

INT-4.7



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Link 0: opt freq=noraman b3lyp/gen scrf=(smd,solvent=thf) pseudo=read nosymm
HF = -4001.1927182 hartrees (-2510788.4426 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.345433 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.905147 hartrees (-2510607.98879 kcal/mol)

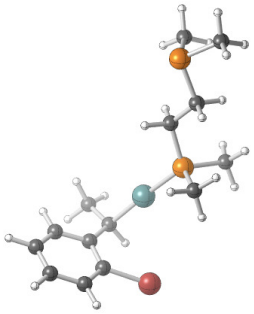
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.485007	0.587590	-0.141465
2	6	-3.122445	0.322517	0.070819
3	6	-2.586537	-0.978636	-0.093422
4	6	-3.508658	-1.981173	-0.466263
5	6	-4.863857	-1.724754	-0.678613
6	6	-5.356053	-0.428685	-0.517988
7	1	-3.159784	-3.003543	-0.601435
8	1	-5.534261	-2.529161	-0.971431
9	1	-6.407428	-0.212801	-0.684155
10	6	-2.213747	1.428060	0.525677
11	6	-2.694131	2.288311	1.679852
12	1	-1.946078	3.032512	1.959330
13	1	-3.627082	2.808320	1.456014
14	1	-2.870576	1.642232	2.547555
15	1	-4.870367	1.596888	-0.026629
16	35	-1.781316	2.701077	-1.050802
17	29	-0.676049	-1.418401	0.156550
18	15	1.522779	-1.926362	0.472747
19	6	1.949554	-2.366658	2.208147
20	1	2.993881	-2.667364	2.317722
21	1	1.752799	-1.515935	2.864793
22	1	1.313384	-3.193429	2.532492
23	6	2.137468	-3.372404	-0.482559
24	1	2.053226	-3.170604	-1.552862
25	1	3.175752	-3.616260	-0.246604
26	1	1.515525	-4.241379	-0.255671
27	6	2.674518	-0.539902	0.028942
28	1	2.476453	-0.319880	-1.025547
29	1	2.318281	0.330288	0.589194
30	6	4.170352	-0.765256	0.266150
31	1	4.511164	-1.661552	-0.261323
32	1	4.379515	-0.914740	1.330660

33	15	5.220709	0.643737	-0.383300
34	6	6.885103	0.076226	0.211309
35	1	7.625490	0.857733	0.020341
36	1	6.895554	-0.157740	1.280707
37	1	7.196294	-0.812665	-0.343967
38	6	4.867168	1.958674	0.879597
39	1	4.945259	1.587412	1.906734
40	1	5.578635	2.779307	0.752386
41	1	3.867014	2.372213	0.729711
42	1	-1.225643	1.020289	0.726581

Calculated coordinates and energies (dMepe, monodentate):
B3LYP/6-311G(d):LANL2TZ+(Cu)

INT-4.1



Charge = 0 Multiplicity = 1

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HF = -4000.5879638 hartrees (-2510408.95316414 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.343012 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.301292 hartrees (-2510229.06374292 kcal/mol)

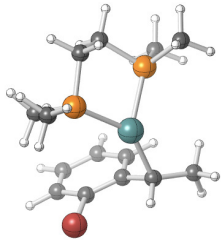
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.050432	2.423753	-0.111951
2	6	2.882329	1.083735	0.296553
3	6	3.342452	0.131739	-0.636477
4	6	3.899941	0.463220	-1.858632
5	6	4.031251	1.797404	-2.222677
6	6	3.599450	2.773464	-1.334545
7	1	4.233097	-0.324536	-2.530888

8	1	4.467349	2.061721	-3.182971
9	1	3.697507	3.826583	-1.593329
10	6	2.257257	0.730871	1.577186
11	6	2.176726	1.842231	2.606768
12	1	1.804513	1.453989	3.562441
13	1	3.152042	2.319002	2.813646
14	1	1.491189	2.651061	2.319748
15	1	2.730198	3.215208	0.562535
16	35	3.175603	-1.738801	-0.244307
17	1	2.750068	-0.154582	2.002740
18	29	0.493058	0.007937	1.072309
19	15	-1.410028	-0.869996	0.290911
20	6	-2.798047	0.311308	0.036800
21	1	-2.996398	0.753782	1.023212
22	1	-2.396635	1.125443	-0.583113
23	6	-4.066937	-0.255917	-0.571782
24	1	-4.491048	-1.051984	0.058126
25	1	-3.864177	-0.694921	-1.558127
26	15	-5.361465	1.054939	-0.833565
27	6	-6.749790	-0.046426	-1.344838
28	1	-6.912711	-0.867963	-0.634632
29	1	-7.676730	0.532732	-1.420887
30	1	-6.548036	-0.475119	-2.332693
31	6	-5.859608	1.332504	0.921574
32	1	-6.800442	1.893383	0.951440
33	1	-6.001043	0.388267	1.464413
34	1	-5.110145	1.931984	1.448844
35	6	-2.138769	-2.222085	1.277681
36	1	-2.487662	-1.840323	2.242899
37	1	-2.975314	-2.702823	0.759296
38	1	-1.371740	-2.978601	1.472882
39	6	-1.170229	-1.656605	-1.339000
40	1	-0.880751	-0.902168	-2.078059
41	1	-0.355103	-2.384376	-1.266990
42	1	-2.069148	-2.177224	-1.686910

Calculated coordinates and energies (dMepe, bidentate):
B3LYP/6-311G(d):LANL2TZ+(Cu)

INT-4.1



Charge = 0 Multiplicity = 1

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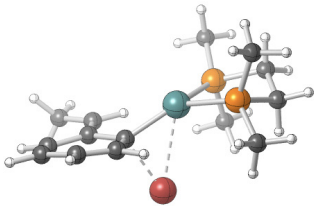
Imaginary Frequencies: none found
Zero-point correction = 0.343221 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.308255 hartrees (-2510233.43309505 kcal/mol)
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.899988	2.414336	0.636725
2	6	-1.379043	1.397569	-0.230889
3	6	-2.326482	0.532635	0.369875
4	6	-2.737174	0.643778	1.686318
5	6	-2.224785	1.646641	2.501065
6	6	-1.301105	2.531970	1.955036
7	1	-3.469320	-0.059070	2.079482
8	1	-2.550670	1.734671	3.534520
9	1	-0.890725	3.335620	2.565406
10	6	-0.866514	1.249275	-1.584136
11	6	-0.328236	2.490726	-2.264338
12	1	-0.057407	2.267620	-3.303755
13	1	-1.052161	3.326181	-2.297450
14	1	0.583960	2.889053	-1.797624
15	1	-0.174021	3.124173	0.242844
16	35	-3.097075	-0.897402	-0.649756
17	1	-1.564896	0.702781	-2.224407
18	29	0.586526	0.015701	-0.905147
19	15	0.911425	-1.968792	0.218778
20	6	2.687964	-1.959749	0.736752
21	1	2.850015	-2.709638	1.524186
22	1	3.279856	-2.276875	-0.133755
23	6	3.115235	-0.573230	1.200194
24	1	4.192856	-0.536898	1.413489
25	1	2.599629	-0.305611	2.133593
26	15	2.680696	0.730859	-0.042447
27	6	3.082063	2.255661	0.887428
28	1	4.099288	2.220730	1.298446
29	1	3.000281	3.126292	0.227892
30	1	2.372172	2.388433	1.710905
31	6	4.093705	0.620173	-1.203420

32	1	4.027238	1.421236	-1.947221
33	1	5.053735	0.703025	-0.678432
34	1	4.064326	-0.333150	-1.741873
35	6	0.648796	-3.732629	-0.183539
36	1	1.229698	-4.010893	-1.068697
37	1	0.941966	-4.380216	0.652225
38	1	-0.409089	-3.907674	-0.406480
39	6	0.061915	-1.823062	1.835869
40	1	0.152930	-0.802197	2.224281
41	1	-1.005315	-2.033942	1.708568
42	1	0.474119	-2.525503	2.571995

TS-4.4



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HF = -4000.5616798 hartrees (-2510392.4596913 kcal/mol)
Imaginary Frequencies: 1 (-37.5302 1/cm)
Zero-point correction = 0.341291 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4000.274584 hartrees (-2510212.30420584 kcal/mol)

Coordinates (from last standard orientation):
25 - 3 Br C distance = 2.167
25 - 16 Br Cu distance = 2.842
Valence > maximum for atom=25 type=Br valence=2 max=1

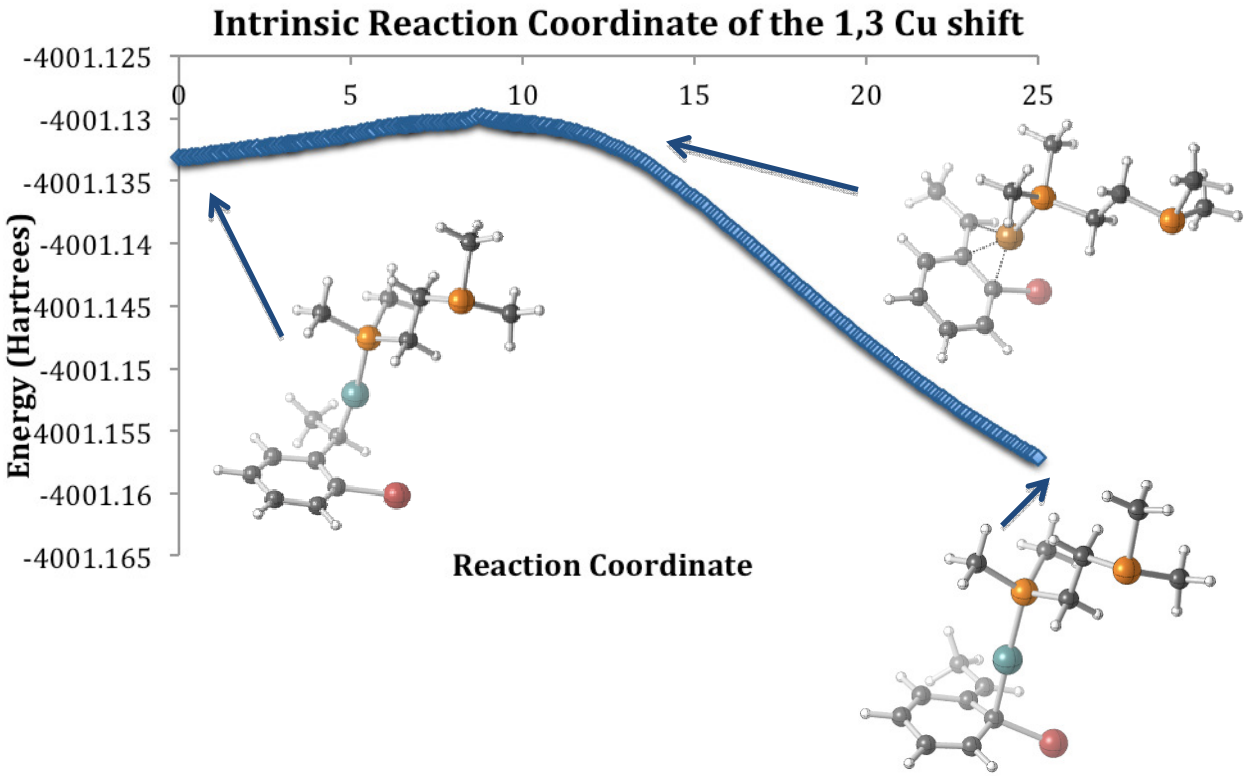
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.988043	-0.024314	-0.834670
2	6	2.673898	0.497384	-0.493834
3	6	1.582886	-0.487961	-0.254976
4	6	1.904229	-1.878054	-0.519001
5	6	3.096014	-2.273580	-1.022609
6	6	4.176027	-1.328536	-1.123822
7	1	1.123583	-2.615479	-0.323642
8	1	3.263164	-3.311685	-1.305172

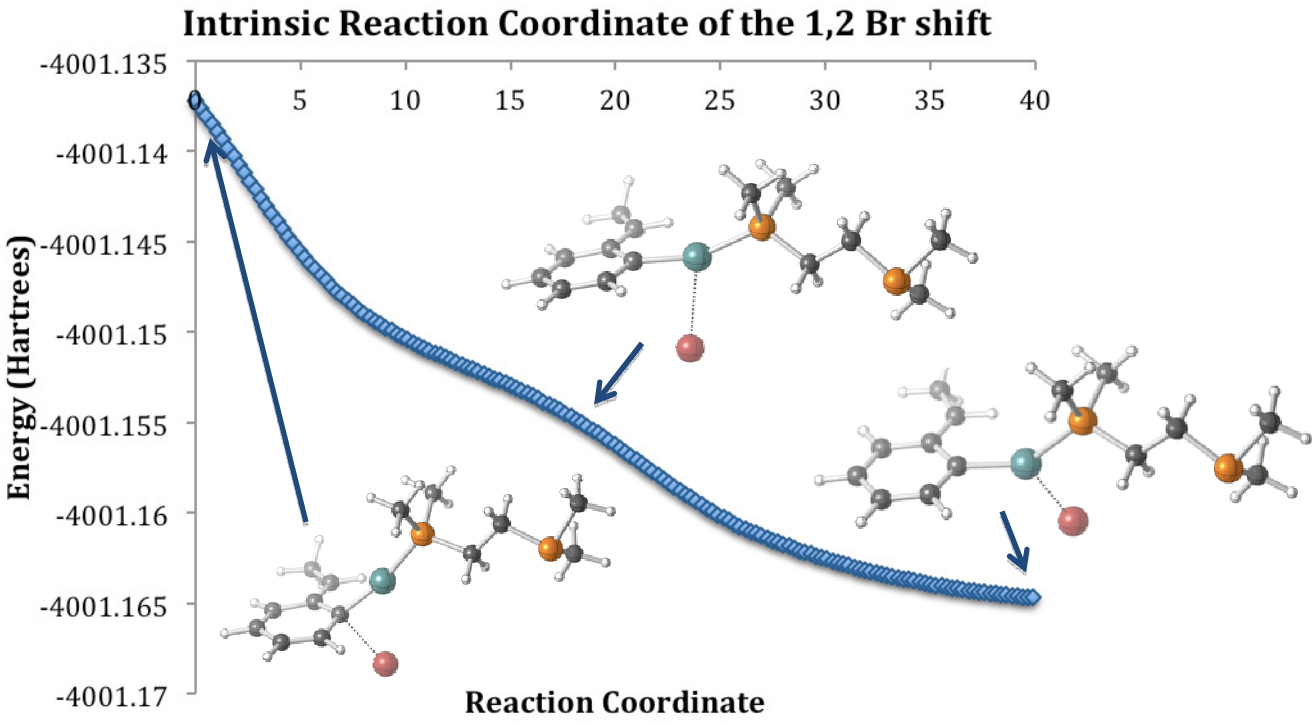
9	1	5.166448	-1.688227	-1.399978
10	6	2.455981	1.830227	-0.412537
11	6	3.489233	2.892732	-0.582654
12	1	3.048303	3.891770	-0.511184
13	1	4.280545	2.838569	0.179951
14	1	3.996315	2.833785	-1.555573
15	1	4.836233	0.659143	-0.850714
16	29	-0.343270	-0.058438	-0.537951
17	15	-2.219153	-1.442207	-0.403818
18	6	-3.395191	-0.327076	0.493992
19	1	-4.401323	-0.769537	0.495743
20	1	-3.061072	-0.295670	1.541764
21	6	-3.406867	1.073276	-0.106581
22	1	-4.073072	1.743574	0.454594
23	1	-3.781543	1.045411	-1.139939
24	15	-1.699303	1.787824	-0.162581
25	35	1.112689	-0.511313	1.860655
26	1	1.443104	2.151132	-0.157976
27	6	-1.959887	3.325282	-1.118123
28	1	-2.782837	3.918498	-0.700623
29	1	-1.046494	3.929532	-1.099131
30	1	-2.186118	3.089774	-2.162800
31	6	-1.515760	2.440821	1.537329
32	1	-0.563610	2.974655	1.629023
33	1	-2.332769	3.127964	1.791352
34	1	-1.497250	1.618639	2.259301
35	6	-2.300308	-2.954940	0.618899
36	1	-1.771331	-3.772150	0.117120
37	1	-1.808767	-2.778531	1.581685
38	1	-3.336691	-3.266841	0.799555
39	6	-3.207085	-1.924953	-1.868828
40	1	-2.685675	-2.711526	-2.424129
41	1	-4.197643	-2.297040	-1.578210
42	1	-3.331243	-1.071233	-2.542903

Intrinsic Reaction Coordinates:

Intrinsic reaction coordinate (IRC) calculations were performed for the dMepe ligand system using Gaussian03[S10A] at the SMD(THF)-B3LYP/6-311G(d):LANL2DZ (Cu) level of theory. To confirm minima and TSSs are connected for the dCype ligand system,

SMD(THF)-B3LYP/6-311G(d):LANL2TZ (Cu) level of theory was used in the Gaussian09 suite[S10B]. The manual displacement option was used under the "Vibrations" tab in GaussView 5.0 to optimize the 2 structures resulting from the vibration. This led to reactants and products, which provided support that the TSS found was in fact the correct one.

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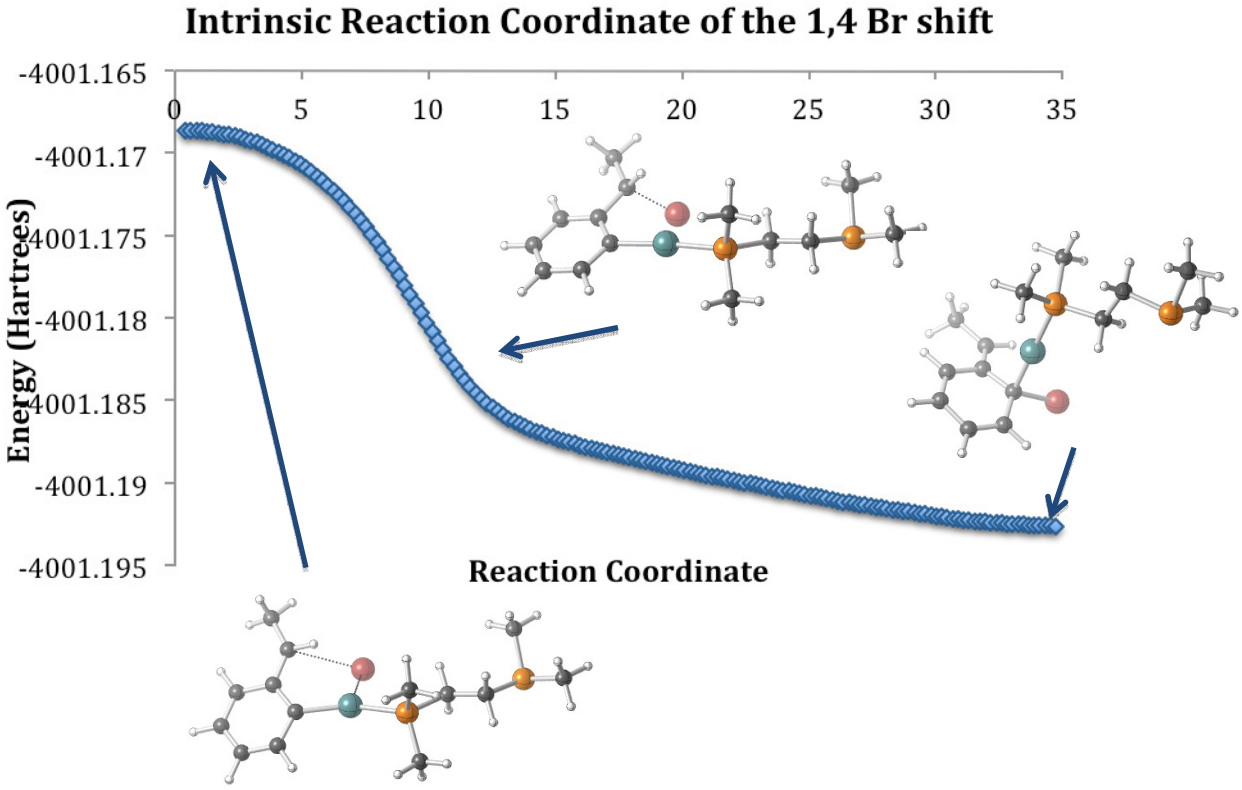
-4001.14
-4001.145
-4001.15
-4001.155
-4001.16
-4001.165
-4001.17
Energy (Hartrees)
0
5
10
15
20
25
30
35
40
Reaction Coordinate


Intrinsic Reaction Coordinate of the 1,4 Br shift
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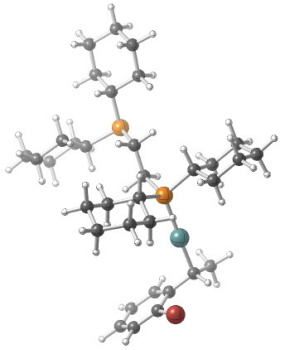
-4001.17
-4001.175
-4001.18
-4001.185
-4001.19
-4001.195
Energy (Hartrees)
0
5
10
15
20
25
30
35
Reaction Coordinate

Calculated coordinates and energies (dCype, monodentate):
B3LYP/6-311G(d):LANL2TZ(Cu)

INT-4.1:



Charge = 0 Multiplicity = 1

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Imaginary Frequencies: none found
Zero-point correction = 0.836912 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.049880 hartrees (-3000784.1201988 kcal/mol)

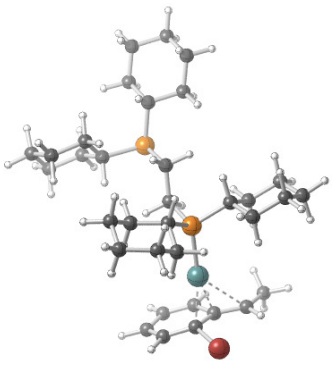
Coordinates (from last standard orientation):
atom 25 is isolated, type=P

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.995305	-2.284279	-2.412048
2	6	4.386447	-1.170365	-1.623439
3	6	5.174318	-1.513667	-0.499164
4	6	5.516043	-2.817491	-0.161072
5	6	5.086486	-3.878451	-0.957325
6	6	4.325123	-3.595238	-2.091367
7	1	6.123349	-3.006740	0.716944
8	1	5.353355	-4.897309	-0.697198
9	1	3.988851	-4.401916	-2.736719
10	6	3.981614	0.206512	-1.969631
11	1	4.726656	0.915025	-1.597563
12	6	3.722715	0.470107	-3.459396
13	1	3.568164	1.539891	-3.631962
14	1	4.561919	0.159536	-4.103852
15	1	2.830003	-0.031874	-3.846221

16	1	3.402775	-2.100725	-3.301732
17	29	2.347687	0.627525	-0.891925
18	15	0.414937	1.113823	0.201922
19	6	-0.997830	0.119806	-0.506970
20	1	-0.933409	0.262653	-1.589476
21	1	-0.731426	-0.926393	-0.340706
22	6	-2.418586	0.422674	-0.014934
23	1	-2.628652	1.487392	-0.129266
24	1	-2.529208	0.193374	1.049213
25	15	-3.736445	-0.458094	-1.030248
26	35	5.852380	-0.122273	0.674119
27	6	-3.485114	-2.247379	-0.468373
28	6	-3.878266	-2.588585	0.979679
29	6	-4.100024	-3.255324	-1.461744
30	1	-2.395462	-2.362644	-0.550332
31	6	-3.505416	-4.036996	1.337152
32	1	-4.958506	-2.459961	1.109899
33	1	-3.396757	-1.900035	1.681464
34	6	-3.734358	-4.702120	-1.096759
35	1	-5.191173	-3.153375	-1.471823
36	1	-3.761030	-3.029493	-2.478261
37	6	-4.116342	-5.039377	0.350002
38	1	-3.831598	-4.262920	2.358874
39	1	-2.412448	-4.141788	1.330254
40	1	-4.223637	-5.395263	-1.790382
41	1	-2.653493	-4.844961	-1.227840
42	1	-3.798286	-6.058049	0.598607
43	1	-5.210054	-5.023914	0.449440
44	6	-5.302223	0.143243	-0.159898
45	6	-5.478386	1.663534	-0.364863
46	6	-6.547625	-0.605243	-0.677494
47	1	-5.201554	-0.047269	0.916241
48	6	-6.778602	2.187401	0.264702
49	1	-5.483489	1.884221	-1.440554
50	1	-4.631700	2.210788	0.059005
51	6	-7.846510	-0.080280	-0.046660
52	1	-6.605951	-0.495040	-1.768436
53	1	-6.459275	-1.676647	-0.481187
54	6	-8.008359	1.429968	-0.247250
55	1	-6.878552	3.259287	0.059556
56	1	-6.718490	2.086032	1.356456
57	1	-8.703153	-0.614981	-0.472333
58	1	-7.844304	-0.306210	1.028060
59	1	-8.912644	1.787197	0.258032
60	1	-8.145856	1.641027	-1.316104
61	6	-0.153047	2.891042	-0.015324

62	6	0.809418	3.918144	0.613291
63	6	-0.354743	3.188968	-1.517449
64	1	-1.120028	2.978984	0.494671
65	6	0.356341	5.363321	0.351881
66	1	1.817057	3.773451	0.203598
67	1	0.882316	3.760922	1.691688
68	6	-0.802495	4.636795	-1.766587
69	1	0.590342	3.008684	-2.046274
70	1	-1.088761	2.505049	-1.952330
71	6	0.164430	5.646489	-1.140947
72	1	1.088576	6.055406	0.782051
73	1	-0.589382	5.545691	0.879419
74	1	-0.891394	4.808523	-2.844832
75	1	-1.805809	4.784354	-1.345726
76	1	-0.201893	6.668074	-1.290213
77	1	1.134562	5.585865	-1.651718
78	6	0.426840	0.767134	2.050829
79	6	0.151438	-0.718827	2.363645
80	6	1.780054	1.175743	2.674862
81	1	-0.370861	1.372775	2.499826
82	6	0.194842	-0.998514	3.874488
83	1	0.903218	-1.339421	1.858836
84	1	-0.820622	-1.025652	1.972558
85	6	1.817016	0.911656	4.186600
86	1	2.576217	0.599562	2.189011
87	1	2.003736	2.226321	2.480615
88	6	1.517882	-0.555822	4.508126
89	1	0.025971	-2.066552	4.050752
90	1	-0.635357	-0.469352	4.360889
91	1	2.798164	1.196370	4.582075
92	1	1.081792	1.555276	4.687719
93	1	1.490681	-0.713050	5.592018
94	1	2.332609	-1.182294	4.122449

TS-4.2:



Charge = 0 Multiplicity = 1

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Imaginary Frequencies: 1 (-60.4798 1/cm)
Zero-point correction = 0.834437 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.018038 hartrees (-3000764.13902538 kcal/mol)

Coordinates (from last standard orientation):
atom 25 is isolated, type=P

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.242903	-0.817744	-3.184589
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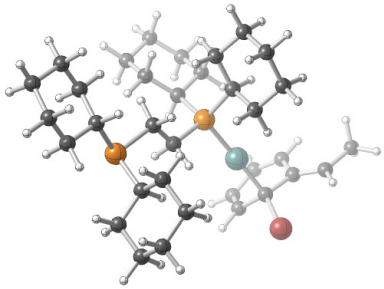
3	6	4.385158	-1.094906	-1.050728
4	6	4.190438	-2.489760	-1.157479
5	6	3.504487	-3.044280	-2.220318
6	6	3.019912	-2.169045	-3.227213
7	1	4.585099	-3.127429	-0.373168
8	1	3.313965	-4.110653	-2.262015
9	1	2.465356	-2.579642	-4.067482
10	6	4.345824	1.185107	-2.176195
11	1	5.011898	1.582661	-1.419563
12	6	3.959793	2.099338	-3.309760
13	1	4.233704	3.132656	-3.077960
14	1	4.456449	1.850985	-4.261251
15	1	2.882908	2.103457	-3.526649
16	1	2.900626	-0.200575	-4.008301
17	29	2.553162	-0.137872	-0.471104
18	15	0.683570	0.485461	0.601411
19	6	-0.810563	0.040913	-0.424636
20	1	-0.607943	0.438136	-1.422961
21	1	-0.776550	-1.045082	-0.536723
22	6	-2.183420	0.521154	0.064031
23	1	-2.186102	1.610536	0.121310
24	1	-2.406017	0.151737	1.069205
25	15	-3.559936	0.057041	-1.133113
26	35	5.758655	-0.538238	0.246624
27	6	-3.763328	-1.780107	-0.718868
28	6	-4.395456	-2.129595	0.640064
29	6	-4.445749	-2.560812	-1.861017

30	1	-2.720420	-2.125104	-0.693875
31	6	-4.370964	-3.645562	0.898918
32	1	-5.435891	-1.786583	0.663980
33	1	-3.877974	-1.609536	1.452771
34	6	-4.424383	-4.074451	-1.598015
35	1	-5.485205	-2.231063	-1.971561
36	1	-3.949182	-2.339124	-2.811516
37	6	-5.041680	-4.425678	-0.238582
38	1	-4.864019	-3.866328	1.852667
39	1	-3.330262	-3.979712	1.003477
40	1	-4.952614	-4.599364	-2.402021
41	1	-3.385637	-4.429496	-1.626610
42	1	-4.966682	-5.503245	-0.054509
43	1	-6.114073	-4.189071	-0.255829
44	6	-5.038524	0.925236	-0.338924
45	6	-4.863726	2.458629	-0.389075
46	6	-6.349070	0.525935	-1.048056
47	1	-5.101862	0.621349	0.713520
48	6	-6.083440	3.198888	0.182269
49	1	-4.708627	2.770928	-1.430306
50	1	-3.970945	2.766506	0.162353
51	6	-7.568485	1.264657	-0.475985
52	1	-6.260601	0.752414	-2.118963
53	1	-6.512572	-0.551741	-0.974901
54	6	-7.382549	2.784889	-0.516694
55	1	-5.930272	4.280256	0.092628
56	1	-6.165088	2.986162	1.256536
57	1	-8.467056	0.975719	-1.032738
58	1	-7.731834	0.945373	0.561949
59	1	-8.240091	3.287086	-0.055083
60	1	-7.353077	3.117698	-1.562675
61	6	0.496716	2.330475	0.882201
62	6	1.570754	2.912945	1.820965
63	6	0.499930	3.074328	-0.469573
64	1	-0.482543	2.467758	1.357459
65	6	1.415754	4.432407	1.991083
66	1	2.566406	2.692280	1.415854
67	1	1.517672	2.439250	2.804125
68	6	0.344596	4.591618	-0.288870
69	1	1.445196	2.867738	-0.986923
70	1	-0.297898	2.702164	-1.118098
71	6	1.414460	5.164879	0.645850
72	1	2.221541	4.808574	2.630954
73	1	0.476696	4.642211	2.520407
74	1	0.390965	5.080112	-1.268316
75	1	-0.651283	4.809489	0.119167

76	1	1.252535	6.237678	0.797234
77	1	2.400681	5.061759	0.174826
78	6	0.456669	-0.341557	2.275535
79	6	-0.193573	-1.734548	2.151612
80	6	1.806805	-0.466883	3.015713
81	1	-0.210183	0.305689	2.859137
82	6	-0.355397	-2.407845	3.523301
83	1	0.429899	-2.369321	1.508822
84	1	-1.170755	-1.665925	1.670220
85	6	1.646033	-1.133678	4.389710
86	1	2.489610	-1.064741	2.399207
87	1	2.281024	0.509512	3.134684
88	6	0.974595	-2.506136	4.276920
89	1	-0.793204	-3.403180	3.390188
90	1	-1.071928	-1.831842	4.123614
91	1	2.628172	-1.226826	4.865703
92	1	1.045792	-0.484933	5.041272
93	1	0.816647	-2.936833	5.271701
94	1	1.643975	-3.193153	3.742899

INT-4.3:



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Imaginary Frequencies: none found
Zero-point correction = 0.834797 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.017771 hartrees (-3000763.97148021 kcal/mol)

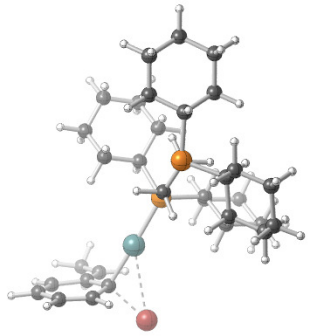
Coordinates (from last standard orientation):
atom 25 is isolated, type=P

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.849957	0.444771	-0.760891
2	6	5.276135	-0.692381	-0.023938
3	6	4.167355	-1.339596	-0.776957
4	6	4.152875	-1.237494	-2.220309
5	6	4.854281	-0.262444	-2.873491
6	6	5.674197	0.624406	-2.097839
7	1	3.512496	-1.915859	-2.774847
8	1	4.753785	-0.128232	-3.945181
9	1	6.186782	1.443429	-2.596096
10	6	5.726574	-1.039996	1.211973
11	1	5.281502	-1.901021	1.698568
12	6	6.784200	-0.296345	1.987899
13	1	7.091545	-0.872427	2.865181
14	1	7.693447	-0.103562	1.404922
15	1	6.445976	0.682032	2.362009
16	1	6.534138	1.095646	-0.226318
17	29	2.556916	-0.171473	-0.395705
18	15	0.695015	1.033407	0.051339
19	6	-0.790618	0.074137	-0.543195
20	1	-0.709809	0.123208	-1.635699
21	1	-0.564667	-0.963463	-0.287760
22	6	-2.212836	0.432261	-0.088426
23	1	-2.391982	1.501664	-0.194332
24	1	-2.352731	0.189081	0.967652
25	15	-3.520851	-0.423281	-1.140237
26	35	3.672802	-3.188927	-0.153257
27	6	0.767085	2.633771	-0.923808
28	6	-0.536589	3.416063	-1.172907
29	6	1.875257	3.548562	-0.361905
30	1	1.112331	2.270672	-1.901408
31	6	-0.278808	4.630865	-2.081132
32	1	-0.963659	3.759534	-0.225722
33	1	-1.282435	2.769546	-1.642183
34	6	2.113807	4.764875	-1.268656
35	1	1.591305	3.897101	0.637833
36	1	2.807049	2.984454	-0.245448
37	6	0.818759	5.544579	-1.524459
38	1	-1.210898	5.191114	-2.213818
39	1	0.015136	4.277840	-3.078324
40	1	2.869407	5.416568	-0.816559
41	1	2.528948	4.424659	-2.225967
42	1	1.006350	6.373670	-2.215493
43	1	0.474052	5.996867	-0.585025

44	6	0.559131	1.393995	1.882457
45	6	-0.512275	2.392677	2.360504
46	6	0.472203	0.068463	2.669197
47	1	1.540677	1.835047	2.100645
48	6	-0.408645	2.624496	3.877163
49	1	-1.511274	2.015417	2.122227
50	1	-0.402088	3.346693	1.840373
51	6	0.564734	0.308177	4.183181
52	1	-0.476611	-0.432532	2.441318
53	1	1.269474	-0.611962	2.351936
54	6	-0.487812	1.312725	4.666371
55	1	-1.201975	3.309384	4.196454
56	1	0.541979	3.126477	4.100645
57	1	0.454642	-0.644740	4.712206
58	1	1.566543	0.684695	4.426712
59	1	-0.361563	1.507142	5.736940
60	1	-1.488462	0.876314	4.546893
61	6	-3.310950	-2.215675	-0.570390
62	6	-3.729726	-2.545206	0.873550
63	6	-3.928149	-3.216986	-1.568911
64	1	-2.222622	-2.350456	-0.636500
65	6	-3.385886	-3.998432	1.240583
66	1	-4.809294	-2.397005	0.988479
67	1	-3.245394	-1.863550	1.580187
68	6	-3.589735	-4.667881	-1.194345
69	1	-5.017272	-3.098857	-1.594060
70	1	-3.571858	-2.999931	-2.581433
71	6	-3.997673	-4.994654	0.247840
72	1	-3.730603	-4.215588	2.258103
73	1	-2.294732	-4.120492	1.250390
74	1	-4.079516	-5.355773	-1.892820
75	1	-2.509410	-4.827792	-1.309227
76	1	-3.698361	-6.017093	0.504224
77	1	-5.092359	-4.962600	0.331448
78	6	-5.098662	0.205822	-0.312919
79	6	-5.251001	1.724965	-0.542803
80	6	-6.341047	-0.534350	-0.849491
81	1	-5.025279	0.026999	0.767515
82	6	-6.557888	2.273179	0.050909
83	1	-5.230856	1.929351	-1.621516
84	1	-4.406463	2.268255	-0.109645
85	6	-7.647151	0.014724	-0.255243
86	1	-6.373307	-0.438036	-1.942889
87	1	-6.270366	-1.603845	-0.636906
88	6	-7.785271	1.524052	-0.478911
89	1	-6.639855	3.343400	-0.170241

90	1	-6.523229	2.185406	1.144954
91	1	-8.500538	-0.515042	-0.693433
92	1	-7.671995	-0.197139	0.822033
93	1	-8.696157	1.899115	0.000981
94	1	-7.896013	1.722708	-1.553252

TS-4.4:



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Imaginary Frequencies: 1 (-46.6945 1/cm)
Zero-point correction = 0.834532 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.022158 hartrees (-3000766.72436658 kcal/mol)

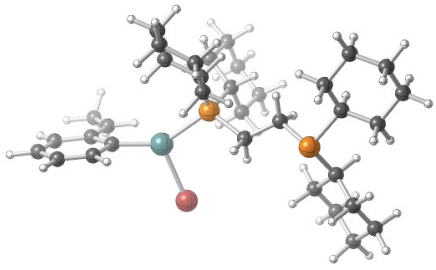
Coordinates (from last standard orientation):
atom 39 is isolated, type=P

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.358658	0.168539	-0.082163
2	6	-0.905753	-0.031407	-0.534490
3	15	0.498706	0.519735	0.561139
4	6	0.416432	2.380139	0.779729
5	1	1.364179	2.594266	1.291089
6	6	-0.716883	2.948911	1.654209
7	6	-0.562524	4.468536	1.827431
8	6	-0.498232	5.191035	0.476339
9	6	0.608616	4.613899	-0.414799
10	6	0.470234	3.093565	-0.586283
11	1	1.304145	2.707046	-1.181998
12	1	-0.444566	2.877086	-1.151202

13	1	1.587370	4.838096	0.028590
14	1	0.595825	5.097013	-1.397943
15	1	-0.340300	6.264394	0.627708
16	1	-1.465216	5.089253	-0.034191
17	1	0.353760	4.676056	2.395577
18	1	-1.393303	4.856122	2.427509
19	1	-1.687597	2.740648	1.193614
20	1	-0.726193	2.468237	2.636310
21	6	0.190054	-0.219056	2.247220
22	1	-0.783889	0.145412	2.594029
23	6	0.138359	-1.758618	2.177616
24	6	-0.072998	-2.380419	3.566293
25	6	0.992828	-1.916234	4.565459
26	6	1.060343	-0.386357	4.634318
27	6	1.271338	0.238717	3.247453
28	1	1.280515	1.329032	3.334667
29	1	2.257968	-0.052565	2.865391
30	1	0.128830	0.001287	5.067388
31	1	1.867759	-0.070567	5.303896
32	1	0.789130	-2.332185	5.558212
33	1	1.971154	-2.308429	4.258524
34	1	-1.067939	-2.104243	3.939506
35	1	-0.065895	-3.472587	3.481814
36	1	-0.658392	-2.086532	1.503737
37	1	1.078879	-2.132596	1.754035
38	29	2.474248	-0.087089	-0.363794
39	15	-3.594153	-0.443985	-1.371618
40	6	-5.057142	0.717846	-1.099924
41	6	-5.577349	0.866151	0.340527
42	6	-6.790705	1.808001	0.415002
43	6	-6.488355	3.177689	-0.204507
44	6	-5.972050	3.035565	-1.641200
45	6	-4.758312	2.097213	-1.722262
46	1	-3.912562	2.564746	-1.201335
47	1	-4.449103	1.976138	-2.765906
48	1	-6.774857	2.640112	-2.277123
49	1	-5.709017	4.017704	-2.050021
50	1	-5.731958	3.691856	0.403763
51	1	-7.382998	3.809819	-0.183502
52	1	-7.636385	1.349567	-0.114515
53	1	-7.105913	1.923175	1.458444
54	1	-5.848715	-0.110795	0.751714
55	1	-4.780711	1.263366	0.981361
56	1	-5.854208	0.264673	-1.703572
57	6	-4.185210	-2.068635	-0.615066
58	6	-3.060273	-3.122608	-0.670707

59	6	-3.514141	-4.483706	-0.121478
60	6	-4.768068	-4.995487	-0.839634
61	6	-5.894179	-3.957149	-0.789603
62	6	-5.442710	-2.593500	-1.335027
63	1	-6.265106	-1.878321	-1.242700
64	1	-5.231548	-2.685711	-2.408829
65	1	-6.763248	-4.309828	-1.356282
66	1	-6.230295	-3.836932	0.248752
67	1	-4.522018	-5.213914	-1.887381
68	1	-5.101863	-5.940351	-0.396342
69	1	-2.698169	-5.209102	-0.215547
70	1	-3.723702	-4.390808	0.952435
71	1	-2.732313	-3.245687	-1.711078
72	1	-2.185864	-2.778168	-0.109677
73	1	-4.434045	-1.891723	0.439549
74	6	5.692551	0.915034	0.161140
75	6	6.708167	1.971516	0.477838
76	1	6.947317	2.624389	-0.363216
77	1	6.358135	2.613099	1.296100
78	1	7.653710	1.532428	0.826074
79	6	5.243567	0.517083	-1.059557
80	6	5.729990	1.127231	-2.299780
81	6	5.290569	0.750067	-3.523034
82	6	4.341735	-0.326936	-3.679628
83	6	3.897332	-0.991805	-2.583228
84	6	4.201977	-0.562265	-1.221841
85	35	4.767435	-2.331418	-0.176041
86	1	3.235876	-1.844527	-2.700407
87	1	3.999808	-0.604323	-4.672182
88	1	5.693565	1.229387	-4.411167
89	1	6.510230	1.877487	-2.231103
90	1	5.312376	0.375511	1.026055
91	1	-0.703288	-1.087943	-0.730234
92	1	-0.735709	0.468712	-1.492673
93	1	-2.560731	1.231268	0.055222
94	1	-2.547914	-0.315883	0.879528

INT-4.5:



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HF = -4782.7961182 hartrees (-3001252.39213168 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.835676 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.043591 hartrees (-3000780.17378841 kcal/mol)

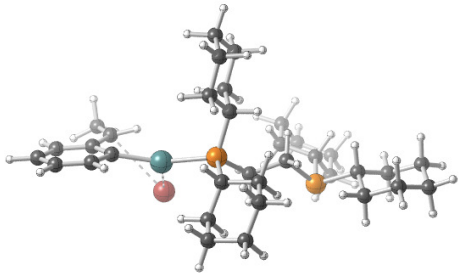
Coordinates (from last standard orientation):
atom 25 is isolated, type=P

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	6.977295	-0.071114	-0.952079
2	6	5.672346	-0.283713	-0.365823
3	6	4.443727	-0.026944	-1.116333
4	6	4.650814	0.446063	-2.439699
5	6	5.905504	0.656693	-2.975465
6	6	7.086636	0.394154	-2.227694
7	1	3.787674	0.654569	-3.066218
8	1	6.002760	1.028498	-3.992180
9	1	8.058814	0.560821	-2.678841
10	6	5.541478	-0.737270	0.929245
11	6	6.585056	-1.104443	1.907009
12	1	6.431523	-2.147253	2.214960
13	1	7.609493	-0.987092	1.559237
14	1	6.446094	-0.515220	2.822610
15	1	7.872217	-0.282717	-0.378291
16	35	1.951305	-2.814535	-1.078034
17	29	2.632031	-0.426737	-0.534860
18	15	0.720234	0.550126	0.383010
19	6	-0.828456	-0.176272	-0.362272
20	1	-0.775159	0.060102	-1.428429
21	1	-0.687410	-1.256484	-0.313849
22	6	-2.182468	0.247178	0.225413
23	1	-2.195315	1.324775	0.403586
24	1	-2.356300	-0.223451	1.197221
25	15	-3.648419	-0.074814	-0.916682
26	1	4.517930	-0.847856	1.282225
27	6	0.444452	0.318140	2.231291
28	6	0.429849	-1.184262	2.580217

29	6	1.467387	1.067427	3.106259
30	1	-0.547924	0.733754	2.446832
31	6	0.190888	-1.426027	4.077672
32	1	1.387606	-1.631529	2.290499
33	1	-0.333740	-1.705860	1.997188
34	6	1.236393	0.810867	4.604438
35	1	2.482660	0.752048	2.834448
36	1	1.414039	2.142801	2.920372
37	6	1.217340	-0.683807	4.939601
38	1	0.224720	-2.501587	4.283965
39	1	-0.819854	-1.090983	4.346379
40	1	2.011272	1.323623	5.185309
41	1	0.279870	1.260320	4.902157
42	1	1.001403	-0.831521	6.003553
43	1	2.214098	-1.109487	4.763098
44	6	0.563468	2.412028	0.101917
45	6	1.931251	3.115972	0.241331
46	6	-0.039894	2.748002	-1.278383
47	1	-0.110807	2.797861	0.877740
48	6	1.818626	4.634194	0.039449
49	1	2.614751	2.702166	-0.508820
50	1	2.386352	2.906297	1.211840
51	6	-0.149575	4.264909	-1.499749
52	1	0.590976	2.311965	-2.064189
53	1	-1.029247	2.301255	-1.394382
54	6	1.194750	4.976026	-1.317953
55	1	2.811282	5.090058	0.128016
56	1	1.206811	5.066225	0.842714
57	1	-0.551343	4.458208	-2.500518
58	1	-0.877774	4.678572	-0.789328
59	1	1.068671	6.059747	-1.419426
60	1	1.879834	4.666436	-2.118065
61	6	-4.908240	1.055489	-0.059363
62	6	-4.621753	2.528585	-0.421089
63	6	-6.370714	0.713633	-0.399960
64	1	-4.771626	0.927209	1.023958
65	6	-5.602612	3.495362	0.259112
66	1	-4.697243	2.647182	-1.509671
67	1	-3.597443	2.806550	-0.154282
68	6	-7.359410	1.679455	0.273551
69	1	-6.509893	0.755894	-1.488067
70	1	-6.607293	-0.308635	-0.094074
71	6	-7.057692	3.142996	-0.066819
72	1	-5.381130	4.523161	-0.050096
73	1	-5.453294	3.460166	1.346465
74	1	-8.382560	1.422660	-0.023745

75	1	-7.310632	1.542510	1.362041
76	1	-7.741910	3.807919	0.472262
77	1	-7.239323	3.311193	-1.136659
78	6	-4.243613	-1.806398	-0.418034
79	6	-5.137155	-2.385870	-1.536368
80	6	-3.094744	-2.788791	-0.120454
81	1	-4.842214	-1.699338	0.497069
82	6	-5.669604	-3.784471	-1.190401
83	1	-4.545299	-2.444908	-2.458819
84	1	-5.972591	-1.715499	-1.755469
85	6	-3.617568	-4.191875	0.227347
86	1	-2.435774	-2.858853	-0.994898
87	1	-2.479448	-2.424214	0.705664
88	6	-4.528071	-4.755526	-0.868642
89	1	-6.271763	-4.166337	-2.022684
90	1	-6.344489	-3.714864	-0.326663
91	1	-2.769810	-4.864291	0.400377
92	1	-4.174521	-4.144520	1.172791
93	1	-4.927900	-5.730190	-0.566862
94	1	-3.935730	-4.929771	-1.776481

TS-4.6:



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Imaginary Frequencies: 1 (-55.9633 1/cm)
Zero-point correction = 0.836589 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.036992 hartrees (-3000776.03284992 kcal/mol)

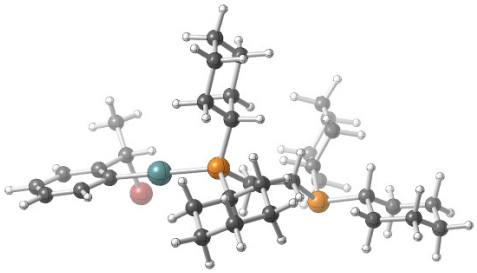
Coordinates (from last standard orientation):
atom 25 is isolated, type=P

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-6.794128	1.258307	-0.262502
2	6	-5.380306	1.171288	-0.052703
3	6	-4.677955	-0.093665	-0.108408
4	6	-5.500609	-1.223292	-0.293830
5	6	-6.874942	-1.129055	-0.486874
6	6	-7.530651	0.118740	-0.474213
7	1	-5.051050	-2.212426	-0.322393
8	1	-7.457933	-2.029649	-0.662106
9	1	-8.604204	0.171779	-0.620035
10	6	-4.638410	2.314179	0.261524
11	6	-5.117765	3.709149	0.358829
12	1	-4.324684	4.400178	0.066166
13	1	-6.016702	3.922076	-0.217829
14	1	-5.331254	3.925081	1.416993
15	1	-7.296274	2.218392	-0.219118
16	35	-2.345154	2.036242	-1.820055
17	29	-2.721906	-0.163683	-0.265996
18	15	-0.668655	-1.074301	0.208087
19	6	0.778265	-0.137044	-0.523435
20	1	0.815193	-0.445125	-1.573283
21	1	0.452714	0.903700	-0.552294
22	6	2.167854	-0.260851	0.117921
23	1	2.468567	-1.307553	0.173274
24	1	2.170187	0.115303	1.144248
25	15	3.529246	0.598800	-0.867951
26	1	-3.625007	2.144090	0.599212
27	6	-0.564981	-2.828618	-0.444711
28	6	-0.987323	-2.881112	-1.927656
29	6	0.764703	-3.572063	-0.230469
30	1	-1.343034	-3.349970	0.127314
31	6	-1.057439	-4.327523	-2.440766
32	1	-0.271218	-2.316768	-2.537482
33	1	-1.958146	-2.390680	-2.056171
34	6	0.681246	-5.021993	-0.733841
35	1	1.561377	-3.056999	-0.778160
36	1	1.049236	-3.561699	0.826550
37	6	0.256258	-5.083003	-2.205969
38	1	-1.310635	-4.327481	-3.506709
39	1	-1.874692	-4.851726	-1.927886
40	1	1.649260	-5.517138	-0.596818
41	1	-0.041131	-5.577720	-0.121526
42	1	0.156953	-6.124969	-2.529872

43	1	1.045019	-4.638927	-2.827501
44	6	-0.314838	-1.193281	2.043957
45	6	-0.438074	0.202881	2.688248
46	6	-1.248855	-2.193301	2.753361
47	1	0.716907	-1.544126	2.161380
48	6	-0.171975	0.160776	4.199834
49	1	-1.451385	0.584871	2.510818
50	1	0.246112	0.910271	2.209757
51	6	-0.989640	-2.232232	4.267803
52	1	-2.292391	-1.907526	2.569544
53	1	-1.123888	-3.197938	2.339919
54	6	-1.092285	-0.841968	4.905140
55	1	-0.302182	1.162149	4.624941
56	1	0.875290	-0.117737	4.377239
57	1	-1.696810	-2.921683	4.742159
58	1	0.012357	-2.641892	4.451450
59	1	-0.849896	-0.895595	5.972391
60	1	-2.129824	-0.488620	4.839413
61	6	5.006625	-0.334182	-0.124403
62	6	5.143528	-1.708774	-0.812443
63	6	6.343647	0.424556	-0.211771
64	1	4.780406	-0.496179	0.939084
65	6	6.300431	-2.537297	-0.233507
66	1	5.317015	-1.550818	-1.884716
67	1	4.212224	-2.278516	-0.734376
68	6	7.506811	-0.398976	0.365608
69	1	6.560271	0.664847	-1.260702
70	1	6.282763	1.376374	0.322231
71	6	7.627387	-1.772969	-0.301575
72	1	6.379508	-3.487846	-0.773224
73	1	6.079096	-2.791761	0.811533
74	1	8.442653	0.160675	0.254612
75	1	7.352259	-0.532036	1.444688
76	1	8.428181	-2.355081	0.168065
77	1	7.914455	-1.641240	-1.353229
78	6	3.655588	2.306393	-0.052319
79	6	4.467569	3.256859	-0.959385
80	6	2.286171	2.942028	0.253653
81	1	4.188607	2.179951	0.900021
82	6	4.627063	4.652813	-0.339519
83	1	3.949070	3.346707	-1.922535
84	1	5.451826	2.838700	-1.184312
85	6	2.431740	4.340733	0.874761
86	1	1.703307	3.019269	-0.672644
87	1	1.709122	2.310376	0.933881
88	6	3.268726	5.277694	-0.003039

89	1	5.184403	5.300514	-1.025800
90	1	5.231374	4.577753	0.574520
91	1	1.437868	4.769042	1.047281
92	1	2.905083	4.248814	1.861627
93	1	3.404959	6.244322	0.495083
94	1	2.724943	5.481852	-0.934717

INT-4.7:



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Imaginary Frequencies: none found
Zero-point correction = 0.838076 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.061142 hartrees (-3000791.18721642 kcal/mol)

Coordinates (from last standard orientation):
atom 25 is isolated, type=P

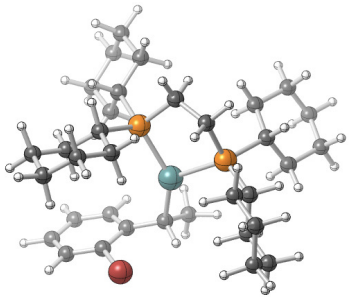
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	6.272928	-1.466255	-0.718885
2	6	4.941768	-1.123245	-0.433086
3	6	4.475447	0.208395	-0.564866
4	6	5.436175	1.156403	-0.982625
5	6	6.760433	0.822363	-1.267422
6	6	7.182350	-0.501557	-1.137846
7	1	5.141889	2.198526	-1.094078
8	1	7.460860	1.587826	-1.592616
9	1	8.208653	-0.778491	-1.360729
10	6	3.996580	-2.176539	0.068566
11	6	4.490411	-3.073842	1.188218
12	1	3.719666	-3.781199	1.499766
13	1	5.382565	-3.638852	0.912897

14	1	4.744559	-2.447303	2.051092
15	1	6.604873	-2.496679	-0.626983
16	35	3.392585	-3.408280	-1.484812
17	29	2.639084	0.771439	-0.226924
18	15	0.502157	1.456652	0.160614
19	6	-0.716457	0.196354	-0.477079
20	1	-0.494318	0.118460	-1.546785
21	1	-0.403520	-0.758638	-0.047020
22	6	-2.215663	0.438663	-0.265090
23	1	-2.496209	1.388876	-0.721046
24	1	-2.462306	0.508006	0.798929
25	15	-3.279982	-0.866450	-1.107474
26	1	3.047937	-1.713663	0.329290
27	6	0.036834	3.048735	-0.729416
28	6	-1.055277	3.916407	-0.072677
29	6	1.284886	3.899205	-1.047229
30	1	-0.355817	2.678316	-1.686020
31	6	-1.410537	5.120818	-0.959288
32	1	-0.700372	4.284326	0.896154
33	1	-1.953387	3.327745	0.129064
34	6	0.931803	5.111687	-1.920068
35	1	1.742873	4.242989	-0.111799
36	1	2.036477	3.282178	-1.549798
37	6	-0.175388	5.966483	-1.291117
38	1	-2.167545	5.733989	-0.457763
39	1	-1.868154	4.762652	-1.890615
40	1	1.829121	5.716325	-2.091944
41	1	0.601316	4.759060	-2.905983
42	1	-0.447626	6.788433	-1.962278
43	1	0.202967	6.430473	-0.370571
44	6	0.133366	1.671708	1.981804
45	6	0.207007	0.318057	2.717801
46	6	1.112389	2.678226	2.622171
47	1	-0.885938	2.063245	2.076544
48	6	-0.040674	0.478329	4.225565
49	1	1.198526	-0.125336	2.557892
50	1	-0.519122	-0.386531	2.303056
51	6	0.857849	2.840109	4.127786
52	1	2.139567	2.325671	2.464638
53	1	1.041450	3.652264	2.130359
54	6	0.916049	1.494604	4.859226
55	1	0.057792	-0.495777	4.717352
56	1	-1.076497	0.804094	4.388314
57	1	1.591579	3.535518	4.549922
58	1	-0.128081	3.298195	4.282270
59	1	0.679300	1.627257	5.920520

60	1	1.941069	1.103727	4.815443
61	6	-3.020952	-2.331579	0.062514
62	6	-3.673572	-2.241422	1.453434
63	6	-3.347747	-3.679295	-0.613612
64	1	-1.932089	-2.319570	0.208767
65	6	-3.269925	-3.430512	2.341160
66	1	-4.764331	-2.235139	1.350458
67	1	-3.402596	-1.303062	1.948401
68	6	-2.953115	-4.867118	0.277629
69	1	-4.419490	-3.737414	-0.836371
70	1	-2.829825	-3.746434	-1.575984
71	6	-3.589074	-4.772435	1.670221
72	1	-3.779025	-3.360356	3.309373
73	1	-2.193518	-3.377337	2.551972
74	1	-3.238889	-5.807057	-0.207757
75	1	-1.860039	-4.891749	0.380056
76	1	-3.247316	-5.601466	2.300078
77	1	-4.678223	-4.881801	1.580112
78	6	-5.009850	-0.209434	-0.722266
79	6	-5.243020	1.144529	-1.426286
80	6	-6.089413	-1.221424	-1.157586
81	1	-5.092117	-0.051414	0.360442
82	6	-6.668203	1.676333	-1.206816
83	1	-5.063945	1.027117	-2.503329
84	1	-4.527390	1.891962	-1.072991
85	6	-7.513262	-0.687274	-0.936697
86	1	-5.954135	-1.454168	-2.222091
87	1	-5.968945	-2.164402	-0.618706
88	6	-7.730517	0.658903	-1.634878
89	1	-6.796806	2.616423	-1.755131
90	1	-6.804682	1.916742	-0.144033
91	1	-8.240912	-1.424350	-1.294761
92	1	-7.694578	-0.571869	0.140256
93	1	-8.733938	1.042606	-1.419268
94	1	-7.679656	0.515804	-2.722393

Calculated coordinates and energies (dCype, bidentate):
B3LYP/6-311G(d):LANL2TZ(Cu)

INT-4.1



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Imaginary Frequencies: none found
Zero-point correction = 0.836291 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.044428 hartrees (-3000780.69901428 kcal/mol)

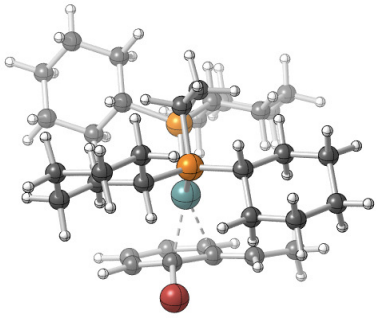
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.659918	-0.129729	-3.169762
2	6	1.877224	0.859280	-2.509991
3	6	2.646643	1.932071	-1.992104
4	6	4.031431	2.007706	-2.071381
5	6	4.751744	0.993766	-2.703667
6	6	4.044697	-0.074302	-3.258112
7	1	4.550206	2.861213	-1.649087
8	1	5.833236	1.050907	-2.768604
9	1	4.576627	-0.870275	-3.772330
10	6	0.418942	0.749874	-2.405336
11	1	-0.027712	1.745813	-2.350580
12	6	-0.265203	-0.063702	-3.511161
13	1	-1.350950	0.062786	-3.456004
14	1	0.039646	0.239913	-4.527868
15	1	-0.080643	-1.141753	-3.445355
16	1	2.145503	-0.974269	-3.614922
17	29	-0.129371	-0.041856	-0.577831
18	15	0.702778	-1.282876	1.269029
19	6	-0.817517	-1.670662	2.298416

20	1	-1.197183	-2.626268	1.939026
21	1	-0.538543	-1.825769	3.346075
22	6	-1.934347	-0.608371	2.218311
23	1	-1.625015	0.272317	2.780336
24	1	-2.836672	-0.987925	2.710128
25	15	-2.333514	-0.003110	0.486872
26	35	1.763874	3.426964	-1.115808
27	6	-3.747970	-1.131167	-0.052462
28	6	-4.347568	-0.683332	-1.400313
29	6	-3.315921	-2.607976	-0.123052
30	1	-4.522889	-1.034250	0.720638
31	6	-5.491699	-1.602390	-1.855335
32	1	-3.559785	-0.684119	-2.163938
33	1	-4.715922	0.343746	-1.335503
34	6	-4.460265	-3.523685	-0.584581
35	1	-2.471121	-2.704788	-0.817202
36	1	-2.961585	-2.948929	0.852763
37	6	-5.053070	-3.068806	-1.921852
38	1	-5.859816	-1.269363	-2.832133
39	1	-6.334315	-1.505619	-1.157848
40	1	-4.096558	-4.554734	-0.658047
41	1	-5.248832	-3.527360	0.179624
42	1	-5.898682	-3.707302	-2.200625
43	1	-4.299916	-3.186706	-2.712008
44	6	-3.250555	1.640015	0.749346
45	6	-2.930154	2.369442	2.067343
46	6	-2.984656	2.574037	-0.450540
47	1	-4.318628	1.387907	0.763300
48	6	-3.697513	3.697349	2.180751
49	1	-1.853228	2.571108	2.127639
50	1	-3.181892	1.741812	2.926362
51	6	-3.760640	3.893712	-0.337370
52	1	-1.910476	2.786883	-0.498121
53	1	-3.232451	2.072697	-1.390468
54	6	-3.449734	4.614605	0.978412
55	1	-3.415304	4.202943	3.111126
56	1	-4.771961	3.484385	2.258144
57	1	-3.518968	4.536325	-1.191214
58	1	-4.838414	3.690820	-0.396684
59	1	-4.050589	5.526583	1.066671
60	1	-2.399173	4.933848	0.975538
61	6	1.879144	-0.469336	2.492747
62	6	3.245865	-0.189473	1.837504
63	6	1.304270	0.823136	3.100469
64	1	2.022056	-1.198267	3.302918
65	6	4.229312	0.460160	2.822887

66	1	3.100773	0.474683	0.977326
67	1	3.683131	-1.111322	1.443534
68	6	2.287993	1.474264	4.086035
69	1	1.077786	1.532188	2.294271
70	1	0.361598	0.619070	3.615601
71	6	3.653302	1.738373	3.441878
72	1	5.171333	0.677847	2.307725
73	1	4.470103	-0.255209	3.620675
74	1	1.859858	2.407787	4.468280
75	1	2.417756	0.814442	4.954154
76	1	4.348620	2.149695	4.182188
77	1	3.544486	2.501290	2.660354
78	6	1.566057	-2.953442	0.993990
79	6	0.716725	-4.206838	1.271892
80	6	2.155493	-3.006777	-0.430281
81	1	2.399187	-2.961916	1.707565
82	6	1.522477	-5.493561	1.028337
83	1	-0.167392	-4.212398	0.622284
84	1	0.350167	-4.202920	2.302225
85	6	2.951718	-4.295500	-0.677728
86	1	1.335431	-2.939379	-1.156229
87	1	2.789592	-2.134695	-0.611818
88	6	2.113034	-5.544375	-0.384933
89	1	0.881707	-6.364620	1.206036
90	1	2.335736	-5.552836	1.763832
91	1	3.312791	-4.311316	-1.712051
92	1	3.845138	-4.299052	-0.039045
93	1	2.717804	-6.449336	-0.510757
94	1	1.296470	-5.612646	-1.116159

TS-4.2



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HF = -4782.7805125 hartrees (-3001242.59939888 kcal/mol)
Imaginary Frequencies: 1 (-77.7351 1/cm)

Zero-point correction = 0.835044 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.021930 hartrees (-3000766.5812943 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.578668	-2.185124	2.627282
2	6	-0.179197	-2.059102	2.213998
3	6	0.430533	-0.785372	2.636552
4	6	-0.255986	0.120251	3.481895
5	6	-1.573794	-0.072138	3.841448
6	6	-2.219828	-1.260162	3.404046
7	1	0.282810	0.988396	3.848383
8	1	-2.099602	0.665530	4.437737
9	1	-3.246842	-1.450014	3.707019
10	6	0.467206	-3.049470	1.498684
11	1	1.536026	-2.954648	1.347211
12	6	-0.173003	-4.352083	1.095206
13	1	0.498216	-4.926204	0.449322
14	1	-0.415503	-5.006063	1.948784
15	1	-1.110886	-4.226417	0.538016
16	1	-2.091350	-3.108495	2.377831
17	29	-0.021132	-0.344070	0.557684
18	15	1.609698	0.399380	-0.984642
19	15	-1.782922	0.334188	-0.881661
20	35	2.400294	-0.754647	2.876522
21	6	-2.426029	2.088357	-0.630064
22	6	-3.534629	2.539163	-1.599497
23	6	-2.812627	2.385076	0.831901
24	1	-1.533372	2.690570	-0.848205
25	6	-3.881062	4.023706	-1.398480
26	1	-4.436642	1.939807	-1.433871
27	1	-3.234841	2.370417	-2.638665
28	6	-3.163197	3.868128	1.026033
29	1	-3.671059	1.770750	1.125522
30	1	-1.992570	2.102433	1.498179
31	6	-4.258760	4.327707	0.056331
32	1	-4.699760	4.304888	-2.070455
33	1	-3.018385	4.638990	-1.686520
34	1	-3.475000	4.041267	2.062000
35	1	-2.261703	4.475287	0.868707

36	1	-4.451547	5.398999	0.181343
37	1	-5.197822	3.813873	0.301348
38	6	-3.245841	-0.723897	-1.406953
39	6	-2.784306	-2.127602	-1.850409
40	6	-4.298254	-0.841358	-0.285964
41	1	-3.708009	-0.226776	-2.269220
42	6	-3.971268	-3.010223	-2.267095
43	1	-2.246052	-2.607710	-1.024518
44	1	-2.080316	-2.062044	-2.684098
45	6	-5.484407	-1.722002	-0.707885
46	1	-3.827992	-1.270404	0.606373
47	1	-4.663363	0.147047	0.002464
48	6	-5.025847	-3.112213	-1.160176
49	1	-3.606693	-4.006786	-2.539994
50	1	-4.432353	-2.590586	-3.171080
51	1	-6.192299	-1.805147	0.124340
52	1	-6.026364	-1.232424	-1.528073
53	1	-5.881903	-3.703469	-1.503877
54	1	-4.599969	-3.649375	-0.302714
55	6	2.738882	-0.761815	-1.941237
56	6	3.887946	-1.292470	-1.062923
57	6	1.950473	-1.931940	-2.563688
58	1	3.168761	-0.171823	-2.760311
59	6	4.801963	-2.252573	-1.839300
60	1	3.468021	-1.814100	-0.195326
61	1	4.484928	-0.466617	-0.665709
62	6	2.868870	-2.892401	-3.335664
63	1	1.432455	-2.483759	-1.769721
64	1	1.176630	-1.554466	-3.238254
65	6	4.015718	-3.411414	-2.462067
66	1	5.579444	-2.637008	-1.169759
67	1	5.322752	-1.698584	-2.631868
68	1	2.277241	-3.728489	-3.724751
69	1	3.283968	-2.373797	-4.210094
70	1	4.682720	-4.050882	-3.050954
71	1	3.605646	-4.042136	-1.662691
72	6	2.739435	1.799588	-0.444901
73	6	3.559837	2.464426	-1.565057
74	6	1.964890	2.857615	0.366428
75	1	3.434722	1.311398	0.248185
76	6	4.497517	3.547069	-1.006559
77	1	2.882644	2.921526	-2.296942
78	1	4.149812	1.720444	-2.107219
79	6	2.905692	3.937325	0.922791
80	1	1.212633	3.337690	-0.271787
81	1	1.419915	2.375973	1.183646

82	6	3.736607	4.594713	-0.185866
83	1	5.037166	4.027608	-1.830528
84	1	5.258157	3.072041	-0.373305
85	1	2.322366	4.693126	1.460386
86	1	3.578535	3.481964	1.660782
87	1	4.435525	5.320878	0.243637
88	1	3.070420	5.161381	-0.850270
89	6	0.547956	1.175727	-2.321860
90	6	-0.838262	0.524191	-2.486113
91	1	0.428944	2.231012	-2.062683
92	1	1.078333	1.154095	-3.278713
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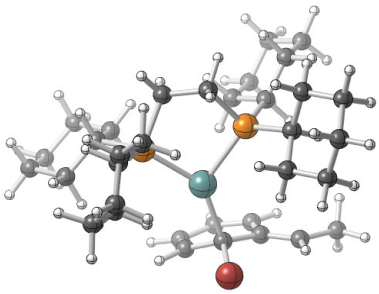
94	1	-1.429812	1.097775	-3.206865

INT-4.3



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Link 0: opt=(calcfc,ts,noeigen) freq=noraman b3lyp/gen scrf=(solvent=thf,smd) pseudo=read
HF = -4782.7805125 hartrees (-3001242.59939888 kcal/mol)
Imaginary Frequencies: 1 (-77.7351 1/cm)
Zero-point correction = 0.835044 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.021930 hartrees (-3000766.5812943 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.578668	-2.185124	2.627282
2	6	-0.179197	-2.059102	2.213998
3	6	0.430533	-0.785372	2.636552
4	6	-0.255986	0.120251	3.481895
5	6	-1.573794	-0.072138	3.841448
6	6	-2.219828	-1.260162	3.404046

7	1	0.282810	0.988396	3.848383
8	1	-2.099602	0.665530	4.437737
9	1	-3.246842	-1.450014	3.707019
10	6	0.467206	-3.049470	1.498684
11	1	1.536026	-2.954648	1.347211
12	6	-0.173003	-4.352083	1.095206
13	1	0.498216	-4.926204	0.449322
14	1	-0.415503	-5.006063	1.948784
15	1	-1.110886	-4.226417	0.538016
16	1	-2.091350	-3.108495	2.377831
17	29	-0.021132	-0.344070	0.557684
18	15	1.609698	0.399380	-0.984642
19	15	-1.782922	0.334188	-0.881661
20	35	2.400294	-0.754647	2.876522
21	6	-2.426029	2.088357	-0.630064
22	6	-3.534629	2.539163	-1.599497
23	6	-2.812627	2.385076	0.831901
24	1	-1.533372	2.690570	-0.848205
25	6	-3.881062	4.023706	-1.398480
26	1	-4.436642	1.939807	-1.433871
27	1	-3.234841	2.370417	-2.638665
28	6	-3.163197	3.868128	1.026033
29	1	-3.671059	1.770750	1.125522
30	1	-1.992570	2.102433	1.498179
31	6	-4.258760	4.327707	0.056331
32	1	-4.699760	4.304888	-2.070455
33	1	-3.018385	4.638990	-1.686520
34	1	-3.475000	4.041267	2.062000
35	1	-2.261703	4.475287	0.868707
36	1	-4.451547	5.398999	0.181343
37	1	-5.197822	3.813873	0.301348
38	6	-3.245841	-0.723897	-1.406953
39	6	-2.784306	-2.127602	-1.850409
40	6	-4.298254	-0.841358	-0.285964
41	1	-3.708009	-0.226776	-2.269220
42	6	-3.971268	-3.010223	-2.267095
43	1	-2.246052	-2.607710	-1.024518
44	1	-2.080316	-2.062044	-2.684098
45	6	-5.484407	-1.722002	-0.707885
46	1	-3.827992	-1.270404	0.606373
47	1	-4.663363	0.147047	0.002464
48	6	-5.025847	-3.112213	-1.160176
49	1	-3.606693	-4.006786	-2.539994
50	1	-4.432353	-2.590586	-3.171080
51	1	-6.192299	-1.805147	0.124340
52	1	-6.026364	-1.232424	-1.528073

53	1	-5.881903	-3.703469	-1.503877
54	1	-4.599969	-3.649375	-0.302714
55	6	2.738882	-0.761815	-1.941237
56	6	3.887946	-1.292470	-1.062923
57	6	1.950473	-1.931940	-2.563688
58	1	3.168761	-0.171823	-2.760311
59	6	4.801963	-2.252573	-1.839300
60	1	3.468021	-1.814100	-0.195326
61	1	4.484928	-0.466617	-0.665709
62	6	2.868870	-2.892401	-3.335664
63	1	1.432455	-2.483759	-1.769721
64	1	1.176630	-1.554466	-3.238254
65	6	4.015718	-3.411414	-2.462067
66	1	5.579444	-2.637008	-1.169759
67	1	5.322752	-1.698584	-2.631868
68	1	2.277241	-3.728489	-3.724751
69	1	3.283968	-2.373797	-4.210094
70	1	4.682720	-4.050882	-3.050954
71	1	3.605646	-4.042136	-1.662691
72	6	2.739435	1.799588	-0.444901
73	6	3.559837	2.464426	-1.565057
74	6	1.964890	2.857615	0.366428
75	1	3.434722	1.311398	0.248185
76	6	4.497517	3.547069	-1.006559
77	1	2.882644	2.921526	-2.296942
78	1	4.149812	1.720444	-2.107219
79	6	2.905692	3.937325	0.922791
80	1	1.212633	3.337690	-0.271787
81	1	1.419915	2.375973	1.183646
82	6	3.736607	4.594713	-0.185866
83	1	5.037166	4.027608	-1.830528
84	1	5.258157	3.072041	-0.373305
85	1	2.322366	4.693126	1.460386
86	1	3.578535	3.481964	1.660782
87	1	4.435525	5.320878	0.243637
88	1	3.070420	5.161381	-0.850270
89	6	0.547956	1.175727	-2.321860
90	6	-0.838262	0.524191	-2.486113
91	1	0.428944	2.231012	-2.062683
92	1	1.078333	1.154095	-3.278713
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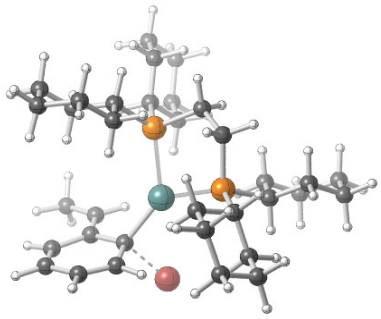
94	1	-1.429812	1.097775	-3.206865

TS-4.4



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Imaginary Frequencies: 1 (-48.3289 1/cm)
Zero-point correction = 0.834769 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.020819 hartrees (-3000765.88413069 kcal/mol)

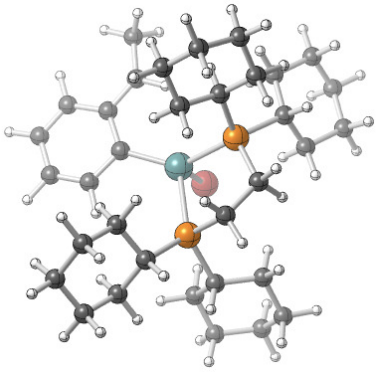
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.436096	1.803506	-2.053610
2	6	-0.999258	1.287522	-2.277167
3	15	-1.837504	0.565452	-0.763986
4	6	-2.716059	2.001685	0.071747
5	1	-3.325480	1.503468	0.835819
6	6	-3.653462	2.834913	-0.819778
7	6	-4.389612	3.909397	-0.002154
8	6	-3.413490	4.812790	0.761118
9	6	-2.456382	3.990383	1.632497
10	6	-1.723526	2.913898	0.817557
11	1	-1.086958	2.315053	1.475586
12	1	-1.059847	3.403475	0.095223
13	1	-3.022941	3.506614	2.438463
14	1	-1.726031	4.646513	2.119052
15	1	-3.965056	5.530712	1.378178
16	1	-2.832319	5.405370	0.041726
17	1	-5.064045	3.418171	0.711160

18	1	-5.023426	4.508728	-0.665526
19	1	-3.072068	3.326235	-1.608978
20	1	-4.383024	2.193263	-1.322140
21	6	-3.231737	-0.423693	-1.554948
22	1	-3.671854	0.212074	-2.334628
23	6	-2.690559	-1.703041	-2.225741
24	6	-3.812621	-2.518134	-2.886133
25	6	-4.921082	-2.868536	-1.887301
26	6	-5.456723	-1.611734	-1.192858
27	6	-4.335617	-0.786140	-0.541773
28	1	-4.765503	0.115718	-0.098187
29	1	-3.896351	-1.358728	0.284758
30	1	-5.983335	-0.987638	-1.927031
31	1	-6.197052	-1.884021	-0.432450
32	1	-5.735735	-3.398915	-2.392816
33	1	-4.523011	-3.558960	-1.132180
34	1	-4.238847	-1.941296	-3.717580
35	1	-3.393018	-3.430134	-3.325266
36	1	-1.932210	-1.460023	-2.975382
37	1	-2.191964	-2.321859	-1.470023
38	29	-0.025198	-0.445108	0.415004
39	15	1.533095	0.690060	-1.015000
40	6	2.847500	1.869511	-0.368736
41	6	3.556880	2.719132	-1.439472
42	6	4.659260	3.596272	-0.823513
43	6	4.121242	4.475240	0.311290
44	6	3.404919	3.635112	1.375209
45	6	2.299173	2.760860	0.763162
46	1	1.506503	3.411741	0.375191
47	1	1.840685	2.140743	1.539729
48	1	4.135043	2.989705	1.880533
49	1	2.977044	4.283040	2.148098
50	1	3.419339	5.211925	-0.102123
51	1	4.936872	5.047634	0.766751
52	1	5.458581	2.951172	-0.435849
53	1	5.114475	4.217465	-1.603150
54	1	3.990509	2.081853	-2.215479
55	1	2.825308	3.365670	-1.938903
56	1	3.587650	1.198665	0.083564
57	6	2.457490	-0.353690	-2.277961
58	6	1.514904	-1.361250	-2.966975
59	6	2.260494	-2.245307	-3.978439
60	6	3.448660	-2.968639	-3.336064
61	6	4.390646	-1.974694	-2.648695
62	6	3.649741	-1.089978	-1.634781
63	1	4.355125	-0.377181	-1.198942

64	1	3.286040	-1.712455	-0.808299
65	1	5.203845	-2.507000	-2.142818
66	1	4.862775	-1.336447	-3.407509
67	1	3.078069	-3.688871	-2.594913
68	1	3.992269	-3.549532	-4.089606
69	1	1.563145	-2.969423	-4.414336
70	1	2.619415	-1.622578	-4.808709
71	1	1.049504	-1.998459	-2.204983
72	1	0.702566	-0.836877	-3.477609
73	1	2.840561	0.332440	-3.043609
74	6	2.343862	-1.106090	2.857515
75	6	3.704373	-1.168343	3.480213
76	1	4.183901	-2.145324	3.405227
77	1	4.378564	-0.436946	3.016709
78	1	3.666284	-0.904634	4.546572
79	6	1.570509	-2.130897	2.406920
80	6	2.036882	-3.517145	2.424827
81	6	1.315480	-4.528594	1.884439
82	6	0.002333	-4.295036	1.337659
83	6	-0.550411	-3.054425	1.419197
84	6	0.199344	-1.881611	1.839794
85	35	-1.073515	-0.995995	3.406568
86	1	-1.577942	-2.904168	1.104509
87	1	-0.549817	-5.119263	0.895028
88	1	1.703001	-5.543672	1.908784
89	1	2.979011	-3.744012	2.912686
90	1	1.904024	-0.111586	2.822363
91	1	-1.611959	2.083639	-2.709585
92	1	-0.985671	0.484316	-3.016737
93	1	0.402924	2.762477	-1.530591
94	1	0.906851	1.997944	-3.022277

INT-4.5



Charge = 0 Multiplicity = 1

Link 0: opt freq=noraman b3lyp/gen scrf=(smd,solvent=thf) pseudo=read

HF = -4782.7899656 hartrees (-3001248.53131366 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.835762 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-4782.035211 hartrees (-3000774.91525461 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
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4	6	-1.713920	-1.795165	2.477657
5	6	-2.090361	-2.600991	3.534313
6	6	-1.127472	-3.214094	4.381787
7	1	-2.498617	-1.325203	1.892399
8	1	-3.145468	-2.768527	3.736524
9	1	-1.452689	-3.820446	5.220415
10	6	1.944314	-2.059717	2.696208
11	6	3.135760	-2.546454	3.420519
12	1	3.768835	-1.687383	3.678803
13	1	2.928589	-3.114110	4.325786
14	1	3.747958	-3.159207	2.745988
15	1	0.940846	-3.456982	4.785242
16	35	0.254157	1.884449	2.426782
17	29	0.068791	-0.150121	0.786347
18	15	-1.806693	0.382953	-0.962757
19	6	-0.819247	0.313275	-2.561752
20	1	-0.836972	-0.732395	-2.873640
21	1	-1.345040	0.869535	-3.345222
22	6	0.638403	0.797774	-2.476637
23	1	0.655678	1.882523	-2.364729
24	1	1.156619	0.578900	-3.415708
25	15	1.605292	0.128695	-1.022388
26	1	2.146807	-1.477128	1.800588
27	6	-3.213302	-0.775751	-1.498832
28	6	-2.758789	-2.249027	-1.452941
29	6	-4.517153	-0.606265	-0.696652
30	1	-3.429750	-0.514159	-2.544709
31	6	-3.854285	-3.205428	-1.948633
32	1	-2.493587	-2.510508	-0.422199
33	1	-1.853859	-2.397542	-2.048001

34	6	-5.615983	-1.564650	-1.185056
35	1	-4.321965	-0.793853	0.366739
36	1	-4.884949	0.419740	-0.770476
37	6	-5.158265	-3.026660	-1.163907
38	1	-3.501504	-4.240146	-1.871015
39	1	-4.042491	-3.021397	-3.014736
40	1	-6.513129	-1.436525	-0.568863
41	1	-5.902869	-1.289703	-2.208783
42	1	-5.941252	-3.676579	-1.570606
43	1	-5.001192	-3.343025	-0.124148
44	6	-2.643322	2.080411	-1.020981
45	6	-3.196445	2.444822	0.373548
46	6	-1.714157	3.204776	-1.517814
47	1	-3.478689	1.997849	-1.730601
48	6	-3.911853	3.804092	0.372897
49	1	-2.361014	2.467873	1.081864
50	1	-3.880661	1.672450	0.734285
51	6	-2.424787	4.568007	-1.521766
52	1	-0.832907	3.260385	-0.868513
53	1	-1.354052	2.989751	-2.527459
54	6	-2.999622	4.921241	-0.145760
55	1	-4.257064	4.037281	1.386611
56	1	-4.811809	3.747848	-0.255063
57	1	-1.724977	5.344140	-1.852537
58	1	-3.236985	4.548835	-2.261255
59	1	-3.545612	5.870460	-0.194473
60	1	-2.175196	5.071202	0.562916
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63	6	4.124491	0.809331	0.071216
64	1	3.532612	1.309896	-1.941829
65	6	3.865233	3.691957	-0.521453
66	1	2.110492	2.755719	0.344158
67	1	1.962105	3.136097	-1.363212
68	6	5.333796	1.753211	0.156518
69	1	3.655446	0.737030	1.060099
70	1	4.470845	-0.195677	-0.187266
71	6	4.911096	3.189780	0.479418
72	1	3.526698	4.696604	-0.243951
73	1	4.328722	3.784644	-1.513388
74	1	6.035686	1.382267	0.912205
75	1	5.872835	1.738255	-0.800251
76	1	5.784505	3.851675	0.483211
77	1	4.489406	3.224624	1.492126
78	6	2.394944	-1.474135	-1.635223
79	6	1.349914	-2.590412	-1.826040

80	6	3.297394	-1.365492	-2.878413
81	1	3.026419	-1.773889	-0.788438
82	6	2.013132	-3.936395	-2.155268
83	1	0.674239	-2.322454	-2.646186
84	1	0.732186	-2.683489	-0.928064
85	6	3.957562	-2.713485	-3.215297
86	1	2.701709	-1.035917	-3.738459
87	1	4.076256	-0.611946	-2.732828
88	6	2.924455	-3.832970	-3.384138
89	1	1.241879	-4.698194	-2.315754
90	1	2.602544	-4.270403	-1.291025
91	1	4.559632	-2.610743	-4.125259
92	1	4.655500	-2.982502	-2.411442
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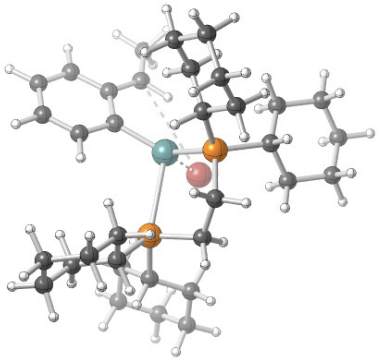
94	1	2.312180	-3.629242	-4.272869

TS-4.6



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Imaginary Frequencies: 1 (-35.4837 1/cm)
Zero-point correction = 0.835979 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
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Coordinates (from last standard orientation):

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4	6	0.697829	1.907900	2.647348
5	6	0.891187	2.653137	3.795180
6	6	0.185257	2.366499	4.993702
7	1	1.266358	2.176912	1.761994
8	1	1.597726	3.479558	3.789801
9	1	0.352554	2.970782	5.878832
10	6	-1.772888	-0.544702	3.835210
11	6	-2.610089	-1.058115	4.937066
12	1	-2.354673	-2.110581	5.116429
13	1	-2.539621	-0.510636	5.874968
14	1	-3.658176	-1.075252	4.609765
15	1	-1.243599	1.101410	5.918996
16	35	-0.262192	-2.782134	1.209292
17	29	-0.377635	-0.218500	0.901806
18	15	2.070611	0.133108	-0.852328
19	6	1.076666	-0.230307	-2.404188
20	1	1.676275	-0.025169	-3.298731
21	1	0.879531	-1.302567	-2.403165
22	6	-0.259332	0.529135	-2.505226
23	1	-0.738030	0.290943	-3.460372
24	1	-0.084237	1.605643	-2.515000
25	15	-1.483080	0.224869	-1.117325
26	1	-1.838146	-1.102911	2.904138
27	6	3.192843	1.549553	-1.439667
28	6	2.404839	2.789599	-1.900818
29	6	4.206155	1.936280	-0.343266
30	1	3.751006	1.161723	-2.303722
31	6	3.329193	3.941620	-2.326543
32	1	1.749550	3.131675	-1.088668
33	1	1.753982	2.533914	-2.740514
34	6	5.128831	3.084399	-0.778974
35	1	3.660750	2.238222	0.560421
36	1	4.813790	1.072219	-0.061075
37	6	4.330865	4.312556	-1.228336
38	1	2.725260	4.813319	-2.603624
39	1	3.878114	3.646184	-3.230501
40	1	5.801942	3.347182	0.045093
41	1	5.768757	2.744390	-1.604115
42	1	5.006720	5.100506	-1.579401
43	1	3.789807	4.727839	-0.367498
44	6	3.361347	-1.267270	-0.788054
45	6	3.711473	-1.569121	0.685098
46	6	2.973217	-2.569904	-1.511038
47	1	4.258098	-0.871428	-1.283366
48	6	4.820884	-2.623365	0.809373

49	1	2.807010	-1.926954	1.188836
50	1	4.011498	-0.653233	1.204058
51	6	4.078928	-3.632410	-1.387290
52	1	2.043327	-2.961551	-1.083213
53	1	2.783944	-2.378703	-2.571281
54	6	4.451802	-3.915512	0.072563
55	1	5.015723	-2.832215	1.867617
56	1	5.756776	-2.222141	0.396133
57	1	3.755498	-4.555561	-1.882125
58	1	4.971315	-3.288143	-1.927961
59	1	5.279149	-4.633125	0.119787
60	1	3.600587	-4.388425	0.578401
61	6	-2.685068	-1.007870	-1.878329
62	6	-1.956313	-2.260724	-2.405667
63	6	-3.793848	-1.413059	-0.886655
64	1	-3.148320	-0.500863	-2.734465
65	6	-2.939388	-3.266164	-3.025727
66	1	-1.416300	-2.736374	-1.579934
67	1	-1.212032	-1.981718	-3.157098
68	6	-4.773635	-2.422137	-1.505765
69	1	-3.328758	-1.855124	0.001907
70	1	-4.347168	-0.533393	-0.547139
71	6	-4.049891	-3.660481	-2.045519
72	1	-2.391405	-4.155806	-3.356222
73	1	-3.389626	-2.827653	-3.926805
74	1	-5.521068	-2.713009	-0.758815
75	1	-5.324758	-1.938151	-2.323473
76	1	-4.763046	-4.336693	-2.530604
77	1	-3.611692	-4.218011	-1.207835
78	6	-2.370852	1.891231	-1.104684
79	6	-3.149335	2.244458	-2.385384
80	6	-3.242342	2.129326	0.142401
81	1	-1.520186	2.582982	-1.026453
82	6	-3.676194	3.688391	-2.341739
83	1	-3.999546	1.561519	-2.496685
84	1	-2.522163	2.109103	-3.272027
85	6	-3.756946	3.576461	0.188473
86	1	-4.099981	1.447270	0.139335
87	1	-2.667302	1.904864	1.044995
88	6	-4.520596	3.949371	-1.088566
89	1	-4.262641	3.894548	-3.244441
90	1	-2.826171	4.383161	-2.359607
91	1	-4.396527	3.714874	1.067433
92	1	-2.904809	4.257257	0.315013
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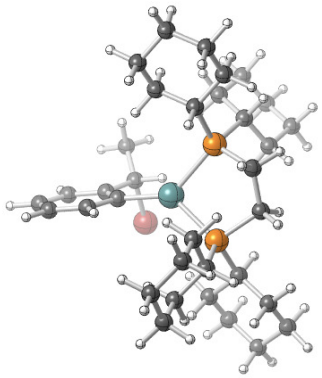
94	1	-5.442742	3.355356	-1.143768

INT-4.7



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Imaginary Frequencies: none found
Zero-point correction = 0.837889 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
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Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
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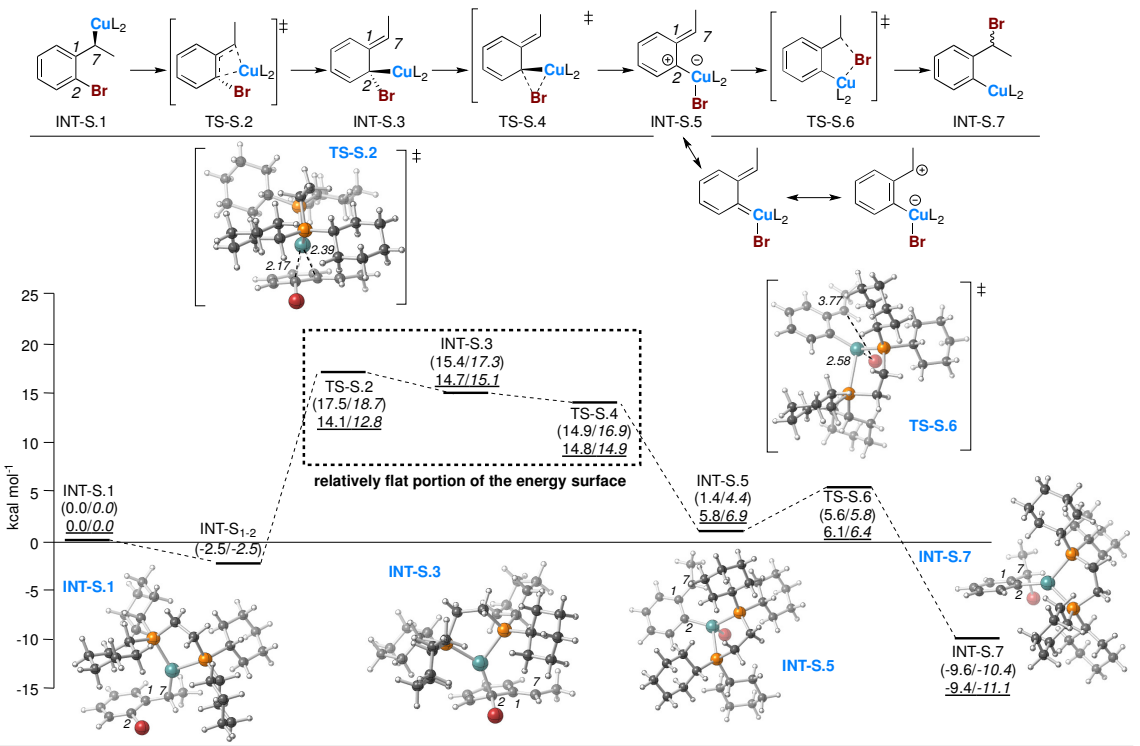
4	6	-0.301729	0.365623	3.490122
5	6	-0.335311	1.012879	4.725175
6	6	-0.074373	2.383050	4.797434
7	1	-0.517409	-0.701994	3.478549
8	1	-0.570675	0.455445	5.629173
9	1	-0.105813	2.904392	5.749868
10	6	0.668712	3.169956	1.163006
11	6	1.937974	3.996587	1.256636
12	1	2.177508	4.474709	0.304861
13	1	1.875577	4.771906	2.022384
14	1	2.767875	3.332471	1.523277
15	1	0.423284	4.139779	3.682020
16	35	-0.844766	4.455861	0.556897
17	29	0.015540	-0.037881	0.584788
18	15	-1.630578	-1.218536	-0.692518
19	6	-0.667056	-2.012489	-2.097760

20	1	-1.171475	-2.920265	-2.443017
21	1	-0.719593	-1.298814	-2.923218
22	6	0.807118	-2.331541	-1.782741
23	1	1.341314	-2.551411	-2.712056
24	1	0.863506	-3.238034	-1.175277
25	15	1.717708	-1.010086	-0.804318
26	1	0.701011	2.489787	0.315632
27	6	-2.875675	-0.208328	-1.681947
28	6	-3.886703	-1.030698	-2.500789
29	6	-3.583776	0.883805	-0.855875
30	1	-2.216138	0.313275	-2.389815
31	6	-4.755647	-0.127049	-3.390583
32	1	-4.538130	-1.591048	-1.820727
33	1	-3.371101	-1.770553	-3.121408
34	6	-4.449655	1.781919	-1.753598
35	1	-4.218917	0.426967	-0.089770
36	1	-2.843977	1.485450	-0.320228
37	6	-5.455898	0.967249	-2.575948
38	1	-5.493967	-0.735171	-3.925534
39	1	-4.123130	0.339097	-4.157520
40	1	-4.971753	2.523041	-1.138505
41	1	-3.799491	2.347764	-2.433965
42	1	-6.025966	1.627088	-3.239482
43	1	-6.185790	0.502984	-1.899522
44	6	-2.559922	-2.667794	0.067423
45	6	-1.570740	-3.663133	0.708391
46	6	-3.607012	-2.208306	1.100006
47	1	-3.079830	-3.183403	-0.749897
48	6	-2.293452	-4.846269	1.370925
49	1	-0.969239	-3.139363	1.462461
50	1	-0.871430	-4.043321	-0.041737
51	6	-4.324149	-3.396550	1.759098
52	1	-3.116258	-1.605923	1.874272
53	1	-4.347344	-1.559063	0.627216
54	6	-3.334867	-4.379364	2.393306
55	1	-1.557564	-5.503299	1.847940
56	1	-2.788738	-5.446692	0.596325
57	1	-5.029340	-3.025588	2.511125
58	1	-4.924192	-3.922220	1.004283
59	1	-3.867890	-5.239952	2.812479
60	1	-2.825326	-3.889617	3.233576
61	6	2.978397	-2.082533	0.098023
62	6	4.022037	-2.781275	-0.792744
63	6	3.655121	-1.369450	1.284666
64	1	2.331734	-2.860691	0.527451
65	6	4.890245	-3.752689	0.023902

66	1	4.670975	-2.029149	-1.256514
67	1	3.534472	-3.321328	-1.610686
68	6	4.519533	-2.344395	2.098415
69	1	4.288572	-0.553611	0.921066
70	1	2.897310	-0.911053	1.926398
71	6	5.554359	-3.057559	1.218599
72	1	5.650223	-4.203164	-0.624548
73	1	4.263527	-4.577986	0.386617
74	1	5.018524	-1.805459	2.911463
75	1	3.870405	-3.091254	2.574545
76	1	6.120342	-3.784637	1.811646
77	1	6.284220	-2.323781	0.850659
78	6	2.650950	-0.059478	-2.136242
79	6	1.666975	0.552569	-3.154455
80	6	3.553320	1.034026	-1.532604
81	1	3.283322	-0.782494	-2.666483
82	6	2.387837	1.378894	-4.230400
83	1	0.949172	1.194833	-2.627660
84	1	1.084912	-0.233897	-3.641996
85	6	4.268202	1.856590	-2.615782
86	1	2.943000	1.703350	-0.913853
87	1	4.295879	0.591052	-0.864918
88	6	3.279405	2.462923	-3.616800
89	1	1.648039	1.826977	-4.903020
90	1	3.002704	0.710127	-4.847034
91	1	4.863809	2.644607	-2.141798
92	1	4.977633	1.212397	-3.151767
93	1	3.817016	3.003442	-4.403683
94	1	2.651141	3.203512	-3.104576

Mono- vs. bidentate comparison (dCype):



(Free energies/*electronic energies*) of the monodentate system followed by free energies/*electronic energies* of the bidentate system relative to INT-S.1 shown in kcal mol^{-1} computed using SMD(THF)-B3LYP/6-311G(d):LANL2TZ (Cu). Energy of INT-S$_{1-2}$ represents a bidentate system becoming a monodentate system. Structures of the bidentate (dCype) system shown. Select bond distances shown in Ångstroms.

Comparison of basis sets for monodentate dMepe and dCype ligand systems:

Table S2. Free and electronic energies of stationary points for varied ligand conformations at multiple basis sets.

Stationary Point	LANL2DZ[S13] (ΔG/*ΔE*) (Methyl)	LANL2DZ (ΔG/*ΔE*)	LANL2TZ (ΔG/*ΔE*)	Def2-SVP[S16] single point (*ΔE*)
INT-S.1	0/*0*	0/*0*	0/*0*	*0*
TS-S.2	20.9/*21.0*	19.4/*20.5*	20.0/*21.2*	*19.8*
INT-S.3	17.4/*18.5*	20.0/*22.0*	17.9/*19.8*	*22.8*
TS-S.4	20.4/*20.2*	18.2/*20.0*	17.4/*19.4*	*23.6*
INT-S.5	4.1/*4.9*	5.5/*8.2*	3.9/*6.8*	*10.7*
TS-S.6	6.9/*7.8*	8.6/*9.0*	8.1/*8.2*	*11.8*
INT-S.7	-6.2/*-7.4*	-6.4/*-7.1*	-7.1/*-7.9*	*-5.4*

*Free energies (ΔG) and *electronic energies* (*ΔE*) in kcal/mol using the B3LYP functional. Single point energies were computed from B3LYP/def2-SVP//B3LYP/6-311G(d):LANL2TZ+(Cu).

Table S3. Free and electronic energies of stationary points from conformations shown in the figure above at multiple basis sets.

Stationary Point	LANL2DZ (ΔG/*ΔE*)	LANL2TZ+ (ΔG/*ΔE*)
INT-S.1	0/0	0/*0*
TS-S.2	18.9/20.9	22.5/*21.2*
INT-S.3	15.5/18.7	18.6/*18.5*
TS-S.4	17.5/20.7	20.1/*20.1*
INT-S.5	-1.9/2.5	4.3/*5.6*
TS-S.6	6.3/8.3	8.9/*7.0*
INT-S.7	-13.7/-12.0	-7.4/*-8.6*

*Free energies (ΔG) and *electronic energies* (*ΔE*) in kcal/mol using the B3LYP functional.

Comparison of functionals for monodentate dCype ligand system:

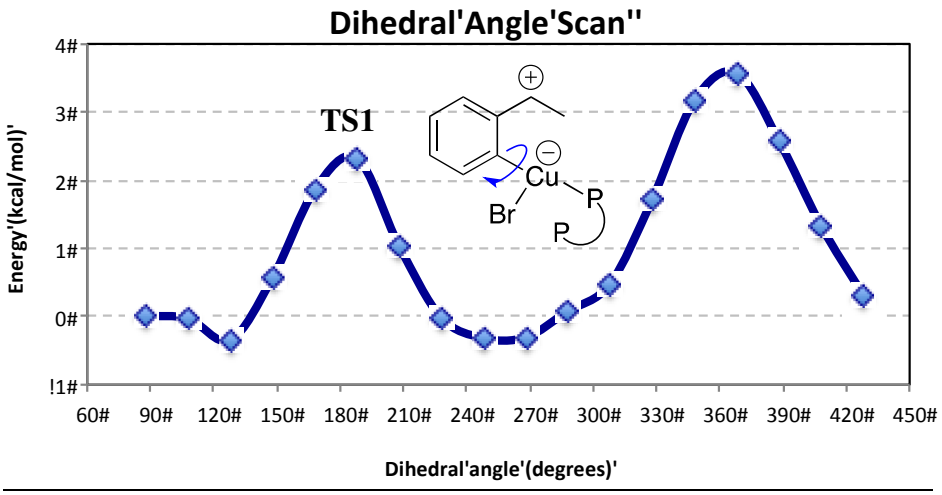
Table S4. Electronic energies of stationary points for varied ligand conformations/conformations shown in the figure above at multiple functionals.

Stationary point	B3LYP	B3LYP-D3[S18]	M06-2X[S19]	ωB97xD[S20]
INT-S.1	*0.0/0.0*	*0.0/0.0*	*0.0/0.0*	*0.0/0.0*
TS-S.2	*21.2/21.5*	*20.0/22.8*	*14.1/16.4*	*19.3/21.4*
INT-S.3	*19.8/19.0*	*19.3/21.6*	*17.7/19.1*	*19.9/21.5*
TS-S.4	*19.4/20.7*	*19.8/23.9*	*22.1/25.3*	*22.4/26.1*
INT-S.5	*6.8/6.1*	*6.7/8.8*	*12.8/14.0*	*10.6/12.0*
TS-S.6	*8.2/7.5*	*7.5/9.7*	*13.2/14.3*	*12.4/13.8*
INT-S.7	*-7.9/-8.0*	*-7.7/-4.4*	*-5.4/-3.2*	*-7.1/-4.7*

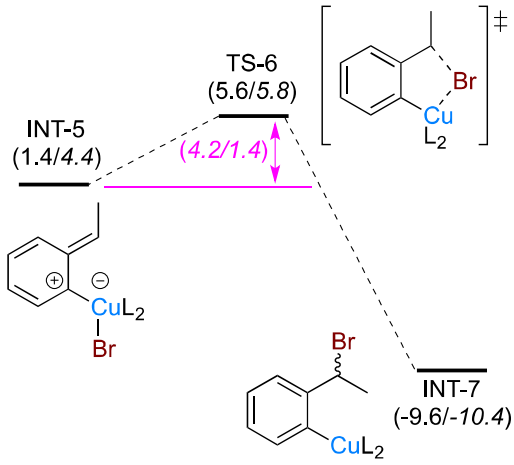
*Single point *electronic energies* (*ΔE*) in kcal/mol using the 6-311G(d):LANL2TZ(Cu) split basis set.

Stereoablative step:

A transition state optimization of the first maxima (TS1) from the dihedral angle scan (below) allows us to compare the barrier for rotation about the C-Cu bond (scrambling) to the barrier for the 1,4-shift (stereochemical-determining step) (Energies shown below in Table S.5). The rotational barrier is comparable to the barrier for the 1,4-shift; therefore, the stereochemical scrambling is a result of the reversibility of INT-4.5 ←→ INT4.7 reaction.



Dihedral angle scan (done in 10° increments) that rotates about the C-Cu bond (highlighted) using SMD(THF)-B3LYP/6-311G(d):LANL2TZ(Cu) for the monodentate dCype ligand system.



(Free energies/*electronic energies*) computed using SMD(THF)-B3LYP/6-311G(d):LANL2TZ (Cu) of the monodentate dCype ligand in kcal mol^{-1} relative to INT-1.

Table S.5 Comparing C-Cu rotational barrier to the 1,4-Br shift to investigate stereochemical scrambling.

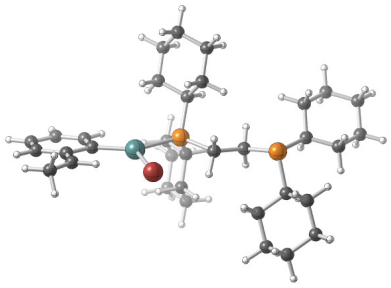
TS1 energy relative to:	**ΔG**	**ΔHF**	**ΔZPE**
INT-S.1	6.1	6.7	6.3
INT-S.5	4.6	2.4	2.6
TS-S.6 energy relative to:	**ΔG**	**ΔHF**	**ΔZPE**
INT-S.1	5.6	5.8	5.8
INT-S.5	4.2	1.4	2.0

* G= Free Energy; HF= Electronic Energy, ZPE= Electronic Energy+zero-point correction. All energies shown in kcal/mol.

Calculated coordinates and energies (dCype, monodentate) of stationary points from dihedral angle scan:

B3LYP/6-311G(d):LANL2TZ(Cu)

TS1 from dihedral angle scan of INT-4.5



Charge = 0 Multiplicity = 1

Link 0: opt=(calcfc,ts,noeigen) freq=noraman b3lyp/gen scrf=(solvent=thf,smd) pseudo=read
HF=-4782.7923667 hartrees (-3001266.50106652 kcal/mol)
Imaginary Frequencies: 1 (-27.59 1/cm)
Zero-point correction= 0.835996 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies=
-4782.036196 hartrees (-3000775.53335 kcal/mol)

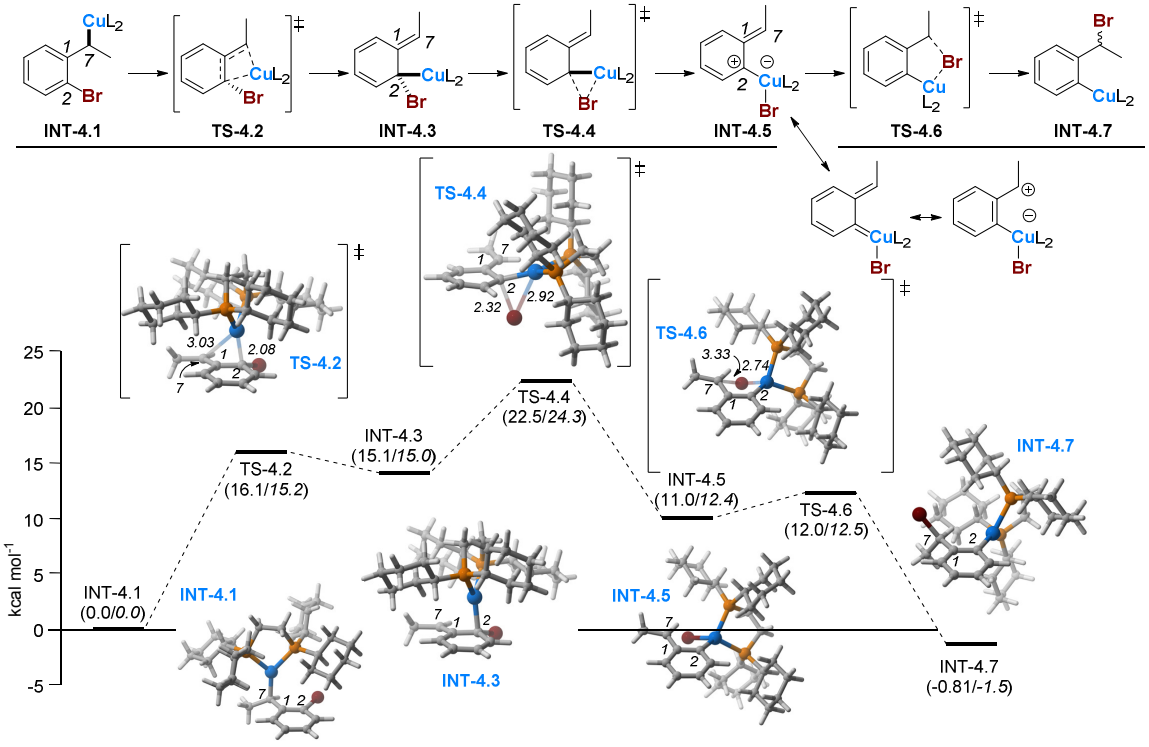
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	7.013980	-0.382598	-0.928314
2	6	5.604727	-0.652368	-1.078179
3	6	4.625055	-0.191704	-0.099386
4	6	5.182049	0.524523	0.987414
5	6	6.540964	0.753663	1.128838
6	6	7.471473	0.301895	0.161382
7	1	4.522536	0.914383	1.757159
8	1	6.907850	1.296581	1.996147
9	1	8.529167	0.504782	0.289176
10	6	5.130851	-1.363526	-2.167814
11	6	5.867131	-1.907165	-3.322451
12	1	5.461076	-1.451882	-4.237043
13	1	6.946020	-1.771333	-3.305443
14	1	5.633267	-2.974613	-3.423296
15	1	7.717278	-0.723182	-1.679381
16	35	1.915250	-2.930884	-0.594449

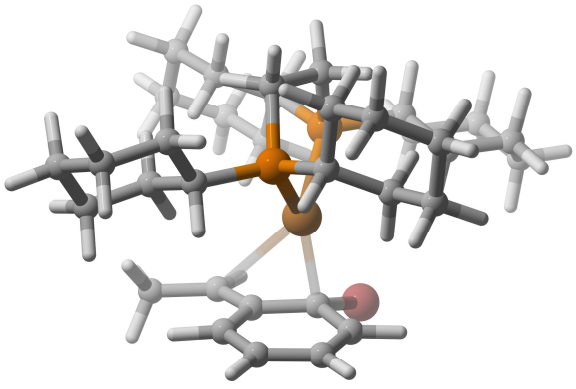
17	29	2.684149	-0.515410	-0.151217
18	15	0.709901	0.662904	0.325193
19	6	-0.826477	-0.250178	-0.218041
20	1	-0.748839	-0.305343	-1.306521
21	1	-0.686986	-1.278283	0.112654
22	6	-2.195619	0.303668	0.206179
23	1	-2.209371	1.392604	0.115808
24	1	-2.400582	0.082037	1.257863
25	15	-3.629440	-0.271450	-0.873541
26	1	4.062422	-1.570991	-2.163945
27	6	0.390912	0.944136	2.158474
28	6	0.441169	-0.404145	2.907078
29	6	1.338459	1.964773	2.816327
30	1	-0.630156	1.338760	2.232784
31	6	0.153275	-0.240551	4.406161
32	1	1.434025	-0.852673	2.777212
33	1	-0.272177	-1.110264	2.472590
34	6	1.058340	2.114930	4.320912
35	1	2.378840	1.648018	2.670332
36	1	1.237807	2.943857	2.339760
37	6	1.103171	0.771045	5.055307
38	1	0.232955	-1.213811	4.902885
39	1	-0.884097	0.093068	4.543009
40	1	1.780430	2.813387	4.758390
41	1	0.068162	2.569768	4.458119
42	1	0.854038	0.906870	6.113449
43	1	2.126797	0.374530	5.025608
44	6	0.555660	2.372378	-0.465262
45	6	1.928572	3.077982	-0.508706
46	6	-0.035174	2.312376	-1.887681
47	1	-0.122511	2.959957	0.167237
48	6	1.835968	4.477539	-1.134648
49	1	2.619229	2.462320	-1.097744
50	1	2.363934	3.144264	0.490792
51	6	-0.131117	3.708238	-2.521418
52	1	0.596684	1.672810	-2.518463
53	1	-1.026214	1.856124	-1.879181
54	6	1.221853	4.426729	-2.537905
55	1	2.833229	4.929902	-1.170174
56	1	1.224898	5.125035	-0.491776
57	1	-0.530968	3.622359	-3.537781
58	1	-0.854473	4.309274	-1.954709
59	1	1.111994	5.438178	-2.944468
60	1	1.905512	3.892976	-3.211225
61	6	-4.928031	0.975386	-0.272052
62	6	-4.682495	2.350470	-0.929254

63	6	-6.380237	0.532376	-0.531548
64	1	-4.792021	1.078441	0.814037
65	6	-5.691762	3.409898	-0.460390
66	1	-4.754940	2.241721	-2.019144
67	1	-3.667646	2.704812	-0.724208
68	6	-7.393443	1.587921	-0.059166
69	1	-6.521594	0.357116	-1.606271
70	1	-6.592363	-0.414229	-0.028391
71	6	-7.136792	2.957015	-0.696742
72	1	-5.499198	4.356549	-0.977943
73	1	-5.541470	3.605201	0.609738
74	1	-8.410308	1.247606	-0.285348
75	1	-7.334830	1.679890	1.033503
76	1	-7.839610	3.699456	-0.302149
77	1	-7.324269	2.895623	-1.777054
78	6	-4.202681	-1.888619	-0.067157
79	6	-5.069132	-2.676875	-1.074337
80	6	-3.046689	-2.778019	0.426935
81	1	-4.816603	-1.625940	0.804680
82	6	-5.586985	-4.000148	-0.491709
83	1	-4.460181	-2.887847	-1.962865
84	1	-5.911323	-2.072351	-1.421923
85	6	-3.559275	-4.103843	1.013386
86	1	-2.364384	-2.995157	-0.404545
87	1	-2.457375	-2.256157	1.185012
88	6	-4.436721	-4.873284	0.020328
89	1	-6.165714	-4.536949	-1.252159
90	1	-6.281123	-3.788559	0.332935
91	1	-2.707172	-4.719268	1.322291
92	1	-4.138787	-3.896958	1.923292
93	1	-4.825608	-5.786361	0.484679
94	1	-3.822136	-5.193633	-0.831139

Figure 4 showing free energies and electronic energies:



(Free energies shown/*electronic energies*) are in kcal mol^{-1} relative to INT-4.1 computed at SMD(THF)-M06/6-311G(d):LANL2TZ+ (Cu).
Select bond lengths shown in Angstroms.



κ-2 dearomative transition state (entry 23)

RM06 energy: -4781.5858654

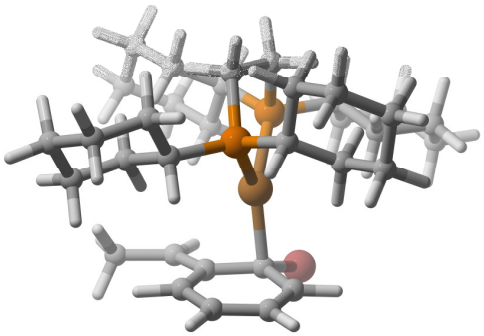
Sum of electronic and thermal Free Energies: -4780.824178

Imaginary frequency: -27.3185

6	-1.404219	0.044602	-2.261837
6	0.002918	0.566270	-2.555456
15	1.311390	0.022707	-1.341173
6	2.019314	-1.531472	-2.088768
1	2.612183	-1.230925	-2.971585
6	0.910129	-2.479393	-2.545917
6	1.468100	-3.784060	-3.098877
6	2.372353	-4.476588	-2.092807
6	3.484076	-3.544016	-1.644310
6	2.919817	-2.248661	-1.079811
1	3.733849	-1.599685	-0.740709
1	2.321711	-2.471096	-0.181046
1	4.139832	-3.316697	-2.500794
1	4.117690	-4.031350	-0.891709
1	2.786133	-5.400839	-2.517390
1	1.776386	-4.775678	-1.214790
1	2.040612	-3.570831	-4.016295
1	0.641573	-4.442627	-3.397290
1	0.255466	-2.702014	-1.684771
1	0.280813	-2.002894	-3.307758
6	2.576983	1.361375	-1.632482
1	2.547747	1.590886	-2.713386
6	2.152651	2.605188	-0.848234
6	3.127210	3.758606	-1.037624
6	4.540552	3.347515	-0.659193
6	4.972572	2.126449	-1.454483
6	4.005099	0.964581	-1.266383
1	4.334688	0.113621	-1.875689
1	4.033965	0.634497	-0.214990
1	5.020692	2.388597	-2.523850
1	5.985400	1.814340	-1.167279
1	5.241229	4.178028	-0.816081
1	4.573222	3.110558	0.416805
1	3.111182	4.082810	-2.090830
1	2.802316	4.622579	-0.443018
1	1.140753	2.919264	-1.135962
1	2.099078	2.342915	0.221823
29	0.087770	0.046017	0.614949
15	-1.914332	0.339679	-0.502328
6	-3.232708	-0.912021	-0.156043

6	-4.481453	-0.896515	-1.030913
6	-5.482247	-1.948143	-0.562679
6	-4.862202	-3.336246	-0.505485
6	-3.612440	-3.344284	0.362086
6	-2.610052	-2.307136	-0.120544
1	-2.268272	-2.585802	-1.131061
1	-1.716878	-2.299466	0.519054
1	-3.885265	-3.121976	1.406885
1	-3.151467	-4.341027	0.367143
1	-4.594247	-3.655821	-1.525811
1	-5.593714	-4.066635	-0.135567
1	-5.843024	-1.671996	0.441097
1	-6.363289	-1.946008	-1.218044
1	-4.956279	0.092406	-1.013412
1	-4.202161	-1.095994	-2.078622
1	-3.530676	-0.660084	0.878039
6	-2.761556	1.995594	-0.440313
6	-3.440979	2.463671	-1.725742
6	-4.160066	3.790015	-1.510761
6	-3.207299	4.859322	-0.998468
6	-2.498770	4.400732	0.267088
6	-1.792303	3.069929	0.056091
1	-1.300436	2.740063	0.981355
1	-0.991775	3.199447	-0.691691
1	-1.780952	5.159720	0.604875
1	-3.236504	4.289217	1.078116
1	-2.456138	5.074871	-1.775815
1	-3.744965	5.799805	-0.819975
1	-4.635690	4.114162	-2.445854
1	-4.973658	3.646423	-0.781753
1	-2.677439	2.599259	-2.508922
1	-4.141192	1.710181	-2.106802
1	-3.533672	1.854504	0.338462
6	0.805220	-2.398866	2.256906
6	0.176822	-3.755342	2.300356
1	-0.076714	-4.096433	3.319291
1	-0.759404	-3.832340	1.722729
1	0.856185	-4.509051	1.884036
6	0.170933	-1.243033	2.636334
6	-1.208107	-1.237863	3.111461
6	-1.833677	-0.122892	3.580731
6	-1.197075	1.144229	3.593260
6	0.092548	1.221670	3.123475
6	0.764732	0.099751	2.583953
35	2.709826	0.234919	2.576616
1	0.626224	2.172252	3.146884

1	-1.713942	2.032465	3.948240
1	-2.850172	-0.213093	3.965254
1	-1.717569	-2.199231	3.177021
1	1.861425	-2.342509	2.003363
1	0.314300	0.295553	-3.574560
1	0.002534	1.664661	-2.522680
1	-1.444334	-1.042177	-2.403775
1	-2.123734	0.470918	-2.971123



κ-2 dearomatized intermediate (entry 26)

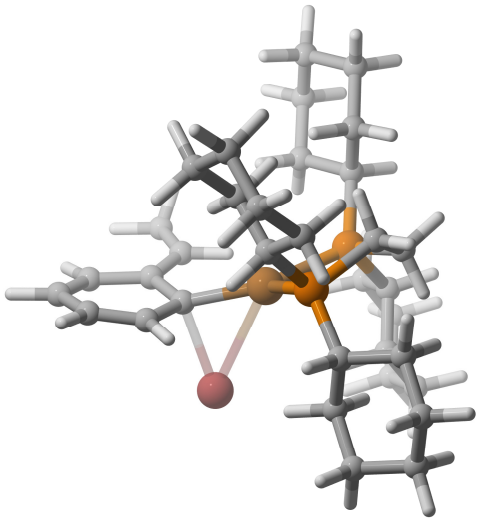
RM06 energy: -4781.586216

Sum of electronic and thermal Free Energies: -4780.825867

6	-0.925679	0.077780	-2.660864
6	0.479971	0.669243	-2.654197
15	1.536173	0.156555	-1.205250
6	2.515428	-1.282110	-1.868196
1	3.220509	-0.876543	-2.616526
6	1.599886	-2.294770	-2.557734
6	2.376494	-3.499504	-3.072561
6	3.161141	-4.175019	-1.960375
6	4.076790	-3.177958	-1.270709
6	3.292272	-1.981458	-0.751165
1	3.963785	-1.287529	-0.235075
1	2.569270	-2.322984	0.006907
1	4.844167	-2.831178	-1.982214
1	4.616095	-3.656221	-0.442570
1	3.735565	-5.023501	-2.354459
1	2.457984	-4.591175	-1.219945
1	3.073318	-3.169309	-3.860109
1	1.686657	-4.209416	-3.547848
1	0.842414	-2.637994	-1.830937

1	1.055110	-1.828917	-3.388307
6	2.696113	1.617477	-1.182891
1	2.834266	1.916134	-2.238206
6	2.010172	2.758569	-0.427860
6	2.867072	4.015283	-0.396901
6	4.235625	3.725676	0.199172
6	4.925438	2.602993	-0.558728
6	4.073784	1.340038	-0.588123
1	4.591289	0.561047	-1.162461
1	3.957353	0.956097	0.437752
1	5.123555	2.930732	-1.592234
1	5.903654	2.379754	-0.113007
1	4.857556	4.630435	0.198307
1	4.115505	3.431577	1.254894
1	2.989520	4.401046	-1.421989
1	2.355138	4.803108	0.171268
1	1.028180	2.984086	-0.866888
1	1.813491	2.424339	0.604118
29	-0.083530	0.070885	0.483584
15	-1.814938	0.257631	-1.039789
6	-3.037748	-1.137191	-1.183687
6	-2.318860	-2.451830	-0.879089
6	-3.248384	-3.651676	-0.979414
6	-4.454598	-3.482406	-0.069120
6	-5.182280	-2.184464	-0.379747
6	-4.253858	-0.981366	-0.273660
1	-3.912443	-0.878550	0.769390
1	-4.808043	-0.065635	-0.517673
1	-5.595650	-2.235643	-1.400209
1	-6.038926	-2.050595	0.293872
1	-4.115805	-3.467754	0.980096
1	-5.135875	-4.338010	-0.163404
1	-3.589517	-3.767549	-2.020926
1	-2.698159	-4.568913	-0.729292
1	-1.452998	-2.591112	-1.540765
1	-1.916598	-2.390679	0.144361
1	-3.382774	-1.143344	-2.233938
6	-2.830394	1.807947	-1.213718
6	-2.085288	2.934547	-1.927407
6	-2.952633	4.182093	-2.040515
6	-3.442700	4.652794	-0.680228
6	-4.166038	3.534017	0.052304
6	-3.289001	2.295313	0.162940
1	-3.813352	1.504405	0.713614
1	-2.394111	2.532753	0.762756
1	-4.476038	3.863856	1.052572

1	-5.090612	3.277703	-0.490271
1	-2.580344	4.979307	-0.077013
1	-4.093997	5.529744	-0.789503
1	-2.393768	4.979836	-2.547482
1	-3.820454	3.957165	-2.681403
1	-1.172777	3.179075	-1.357800
1	-1.758718	2.622328	-2.927319
1	-3.714672	1.541790	-1.820141
6	0.552974	-2.516304	2.147305
6	0.004379	-3.903920	2.046113
1	-0.313834	-4.331487	3.012926
1	-0.875116	-3.983983	1.385183
1	0.757208	-4.590939	1.640194
6	-0.192203	-1.416593	2.480069
6	-1.612954	-1.515259	2.792494
6	-2.363384	-0.461066	3.214983
6	-1.823072	0.845562	3.334048
6	-0.500811	1.023662	3.016190
6	0.308744	-0.032995	2.522277
35	2.219565	0.219723	2.843550
1	-0.038827	2.004795	3.128277
1	-2.441198	1.684898	3.642900
1	-3.407866	-0.632102	3.478331
1	-2.061328	-2.508550	2.783184
1	1.625163	-2.388305	2.014624
1	1.010287	0.437083	-3.588827
1	0.421922	1.763635	-2.606356
1	-0.883661	-0.999892	-2.859317
1	-1.530847	0.509738	-3.469783



κ-2 1,2-bromide shift (entry 29)

RM06 energy: -4781.5714587

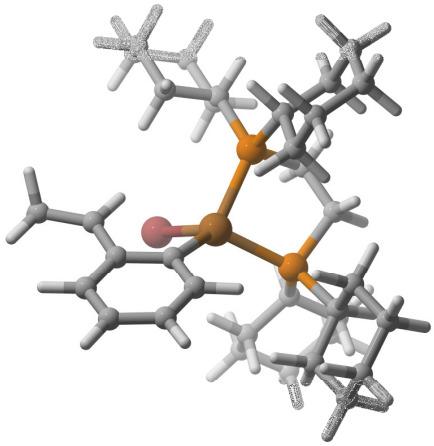
Sum of electronic and thermal Free Energies: -4780.814047

Imaginary frequency: -109.1455

6	-1.625992	-0.048725	-2.258448
6	-0.369941	0.737045	-2.624848
15	1.099244	0.319580	-1.559633
6	2.001693	-0.992863	-2.537869
1	2.522421	-0.475216	-3.363995
6	1.040097	-2.017826	-3.138706
6	1.782175	-3.088864	-3.927328
6	2.832686	-3.787890	-3.079819
6	3.786455	-2.778316	-2.463377
6	3.028555	-1.724464	-1.668240
1	3.732935	-1.024879	-1.202202
1	2.494741	-2.214144	-0.836204
1	4.366829	-2.285831	-3.260428
1	4.516062	-3.281600	-1.815059
1	3.381999	-4.525767	-3.679078
1	2.333752	-4.350136	-2.274140
1	2.269543	-2.618730	-4.797163
1	1.065040	-3.815650	-4.331713
1	0.470330	-2.494909	-2.322080
1	0.306636	-1.532459	-3.792889
6	2.111929	1.867022	-1.776020

1	2.079117	2.124353	-2.850687
6	1.477602	3.000307	-0.966768
6	2.277955	4.290962	-1.068312
6	3.718528	4.076481	-0.634286
6	4.362837	2.970773	-1.453339
6	3.569683	1.673700	-1.362422
1	4.047550	0.908140	-1.986152
1	3.602666	1.302018	-0.323614
1	4.420357	3.286116	-2.507844
1	5.396342	2.796096	-1.126617
1	4.292337	5.008264	-0.724079
1	3.737769	3.798681	0.432268
1	2.261278	4.654756	-2.108679
1	1.801957	5.071050	-0.459805
1	0.442474	3.179865	-1.286884
1	1.419536	2.690206	0.089565
29	0.162389	-0.151114	0.505675
15	-1.992325	0.040826	-0.438895
6	-3.084867	-1.425581	-0.132490
6	-4.335968	-1.542003	-0.998736
6	-5.165815	-2.756142	-0.597104
6	-4.344492	-4.035892	-0.640474
6	-3.094910	-3.917250	0.220245
6	-2.260777	-2.712031	-0.187188
1	-1.887657	-2.867572	-1.213346
1	-1.371676	-2.618137	0.452801
1	-3.385810	-3.812187	1.277912
1	-2.492927	-4.833050	0.155204
1	-4.047030	-4.239833	-1.682258
1	-4.952744	-4.892360	-0.320695
1	-5.549081	-2.605634	0.424977
1	-6.046576	-2.841037	-1.247458
1	-4.947171	-0.632510	-0.923190
1	-4.041323	-1.636534	-2.056560
1	-3.405313	-1.282333	0.915440
6	-3.113162	1.512997	-0.179634
6	-3.777023	2.079552	-1.431586
6	-4.688716	3.251411	-1.089000
6	-3.932886	4.342810	-0.346492
6	-3.264669	3.787834	0.901988
6	-2.358610	2.611586	0.570521
1	-1.896513	2.204537	1.480154
1	-1.518320	2.959589	-0.053954
1	-2.692303	4.570888	1.416501
1	-4.040078	3.455523	1.611124
1	-3.162275	4.764501	-1.012322

1	-4.606118	5.171282	-0.089463
1	-5.143777	3.651437	-2.005113
1	-5.519821	2.891710	-0.461327
1	-2.998387	2.428815	-2.129356
1	-4.342996	1.303939	-1.963769
1	-3.904708	1.132344	0.490352
6	2.927287	-1.349677	1.904419
6	4.299012	-1.875798	2.087534
1	4.448718	-2.426106	3.020649
1	4.571529	-2.545808	1.258565
1	5.034666	-1.059074	2.059832
6	1.859836	-1.442994	2.733128
6	1.908891	-2.184243	3.981150
6	0.780940	-2.465831	4.664857
6	-0.489729	-1.962087	4.220433
6	-0.553891	-1.098046	3.180212
6	0.585978	-0.790409	2.342007
35	0.838840	1.455730	2.853577
1	-1.506554	-0.629048	2.926380
1	-1.392555	-2.246068	4.759549
1	0.825772	-3.052808	5.580815
1	2.869033	-2.527907	4.362388
1	2.756587	-0.781951	0.988178
1	-0.114136	0.608168	-3.685900
1	-0.552994	1.811388	-2.490087
1	-1.487258	-1.113922	-2.481655
1	-2.478464	0.281902	-2.862793



κ-2 aryl copper with bromine on copper (entry 32)

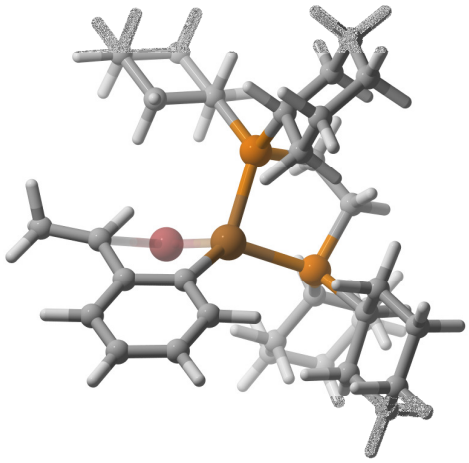
RM06 energy: -4781.590401

Sum of electronic and thermal Free Energies: -4780.832421

6	-0.648658	0.494479	-2.470057
6	-0.607159	0.427409	-2.504032
6	0.854725	0.832411	-2.361724
15	1.665768	-0.023053	-0.919833
6	2.146894	-1.645769	-1.698296
1	1.198456	-1.961775	-2.170331
6	2.492291	-2.715479	-0.661818
6	2.651694	-4.073671	-1.329257
6	3.701240	-4.031021	-2.430698
6	3.389612	-2.944722	-3.450166
6	3.216642	-1.583214	-2.785317
1	2.972657	-0.828372	-3.545300
1	4.175882	-1.276644	-2.338433
1	2.460967	-3.203165	-3.984310
1	4.179550	-2.893635	-4.211808
1	3.783866	-5.007530	-2.926648
1	4.687012	-3.829736	-1.979972
1	1.681095	-4.377992	-1.754637
1	2.910935	-4.834731	-0.581158
1	3.431958	-2.456043	-0.151416
1	1.707632	-2.754345	0.103307
6	3.245504	0.949723	-0.731867
1	3.745133	0.980270	-1.715584
6	2.940902	2.385122	-0.299760
6	4.208610	3.188496	-0.047441
6	5.097653	2.511690	0.982014
6	5.433424	1.097026	0.542163
6	4.177460	0.277746	0.277900
1	4.464516	-0.720846	-0.071522
1	3.630931	0.126080	1.224302
1	6.038479	1.138947	-0.378235
1	6.052467	0.591457	1.294928
1	6.013882	3.093873	1.146659
1	4.571526	2.477510	1.950328
1	4.764821	3.295038	-0.993045
1	3.946050	4.205609	0.272783
1	2.330734	2.897384	-1.053833
1	2.335886	2.362206	0.622292
29	-0.067673	-0.085629	0.704411
15	-1.551408	0.708759	-0.935082
6	-3.259444	0.051084	-1.305897
6	-3.277901	-1.220670	-2.150420

6	-4.703305	-1.712012	-2.375310
6	-5.442485	-1.920360	-1.062238
6	-5.431083	-0.649552	-0.226565
6	-4.004127	-0.178080	0.011474
1	-3.464153	-0.955098	0.575635
1	-3.994451	0.731170	0.630877
1	-6.000399	0.137637	-0.747504
1	-5.937676	-0.814623	0.734389
1	-4.951579	-2.728851	-0.496430
1	-6.472483	-2.251927	-1.249695
1	-5.250442	-0.972937	-2.983851
1	-4.687865	-2.641679	-2.959855
1	-2.798647	-1.043655	-3.121780
1	-2.690892	-1.999827	-1.639202
1	-3.783952	0.842953	-1.869603
6	-1.900711	2.541954	-0.876176
6	-2.147064	3.213960	-2.223773
6	-2.549510	4.672655	-2.041591
6	-1.504356	5.437746	-1.243630
6	-1.236652	4.766986	0.095651
6	-0.843750	3.306967	-0.082017
1	-0.682824	2.826017	0.893112
1	0.121664	3.254952	-0.610511
1	-0.453289	5.304762	0.646351
1	-2.144940	4.821783	0.717294
1	-0.567117	5.477971	-1.822791
1	-1.819715	6.479197	-1.096336
1	-2.708371	5.145352	-3.020206
1	-3.516118	4.717952	-1.514529
1	-1.225349	3.172831	-2.826159
1	-2.915749	2.678765	-2.798240
1	-2.840606	2.588914	-0.295888
6	-1.830349	-1.041688	3.135481
6	-2.841420	-1.816902	3.858619
1	-3.151175	-2.664808	3.234907
1	-2.532280	-2.185896	4.838818
1	-3.745950	-1.200271	3.978169
6	-0.640582	-0.502638	3.603376
6	-0.300965	-0.571384	4.989057
6	0.772227	0.128252	5.460374
6	1.528760	0.905649	4.561177
6	1.223927	0.951207	3.214167
6	0.163856	0.217534	2.647490
35	-0.966756	-2.717579	0.634960
1	1.861548	1.557223	2.566956
1	2.381477	1.468257	4.941063

1	1.034732	0.104327	6.514882
1	-0.917732	-1.144532	5.678162
1	-2.082650	-0.762302	2.114846
1	1.406019	0.618374	-3.287285
1	0.932615	1.914000	-2.198371
1	-0.673847	-0.651590	-2.696067
1	-1.075984	0.926155	-3.362991



κ-2 1,4-bromide shift (entry 35)

RM06 energy: -4781.5901184

Sum of electronic and thermal Free Energies: -4780.830862

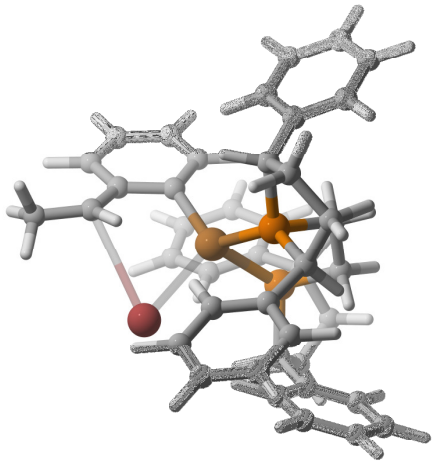
Imaginary frequency: -10.8903

6	-0.570848	0.207979	-2.499086
6	0.890231	0.620777	-2.372591
15	1.687982	-0.120898	-0.861383
6	2.188020	-1.794765	-1.510329
1	1.239416	-2.156978	-1.947498
6	2.550887	-2.778213	-0.397236
6	2.726947	-4.181261	-0.960630
6	3.768250	-4.209134	-2.070342
6	3.434277	-3.209481	-3.167694
6	3.252319	-1.804272	-2.604332
1	3.001091	-1.108153	-3.416079
1	4.211795	-1.461730	-2.185462
1	2.503881	-3.518643	-3.670503
1	4.217215	-3.208464	-3.938226

1	3.861082	-5.220107	-2.489546
1	4.754444	-3.959764	-1.645314
1	1.757879	-4.530044	-1.353188
1	3.002522	-4.878661	-0.158009
1	3.488006	-2.468572	0.088263
1	1.767448	-2.770135	0.369659
6	3.259566	0.877849	-0.732497
1	3.771875	0.837859	-1.709659
6	2.938038	2.338611	-0.411819
6	4.192063	3.170479	-0.181688
6	5.064938	2.572093	0.908184
6	5.424490	1.136652	0.566576
6	4.181742	0.287861	0.335511
1	4.484804	-0.728113	0.058163
1	3.620988	0.191904	1.281259
1	6.044930	1.126934	-0.344478
1	6.036056	0.687714	1.360246
1	5.970827	3.175074	1.053808
1	4.518167	2.593570	1.865357
1	4.768820	3.224849	-1.119400
1	3.910875	4.202519	0.067126
1	2.348400	2.792467	-1.217925
1	2.304370	2.377327	0.490224
29	-0.085070	-0.098528	0.734603
15	-1.528786	0.640758	-0.972062
6	-3.255126	0.009462	-1.310953
6	-3.318665	-1.272106	-2.137195
6	-4.760824	-1.721158	-2.342135
6	-5.491653	-1.890629	-1.019099
6	-5.433834	-0.610305	-0.199443
6	-3.991299	-0.177965	0.017432
1	-3.466809	-0.960743	0.588389
1	-3.947002	0.741154	0.621344
1	-5.985265	0.186543	-0.724827
1	-5.935627	-0.748320	0.768198
1	-5.018512	-2.705794	-0.447942
1	-6.533096	-2.193895	-1.190780
1	-5.290963	-0.972739	-2.954139
1	-4.780820	-2.657963	-2.914916
1	-2.842154	-1.123308	-3.114843
1	-2.751973	-2.061268	-1.619744
1	-3.766110	0.805817	-1.881007
6	-1.832156	2.482373	-1.079366
6	-1.973184	3.036027	-2.493444
6	-2.321605	4.519318	-2.476570
6	-1.296089	5.314744	-1.683173

6	-1.157789	4.769232	-0.269689
6	-0.809751	3.287002	-0.280103
1	-0.741039	2.894550	0.744250
1	0.190010	3.154796	-0.722078
1	-0.397685	5.331942	0.288652
1	-2.108393	4.913477	0.269194
1	-0.319564	5.251285	-2.191028
1	-1.565728	6.378880	-1.662078
1	-2.394453	4.900331	-3.504075
1	-3.317274	4.654634	-2.024318
1	-1.021615	2.903600	-3.032787
1	-2.729910	2.475739	-3.060122
1	-2.806416	2.600268	-0.570073
6	-1.923758	-0.842231	3.231011
6	-2.986235	-1.488042	4.002813
1	-3.179477	-2.479159	3.569618
1	-2.796073	-1.592747	5.072755
1	-3.924479	-0.931277	3.856891
6	-0.764059	-0.234046	3.669427
6	-0.482383	-0.106854	5.068208
6	0.577407	0.641105	5.482232
6	1.376638	1.287050	4.513573
6	1.125053	1.155238	3.163654
6	0.083374	0.351685	2.654181
35	-0.983453	-2.688836	0.624816
1	1.792530	1.667463	2.468017
1	2.220556	1.890544	4.847786
1	0.802651	0.756991	6.539369
1	-1.129695	-0.584298	5.800853
1	-2.079479	-0.799307	2.154092
1	1.450340	0.340290	-3.274724
1	0.965379	1.711986	-2.290192
1	-0.642892	-0.883448	-2.594074
1	-1.023832	0.631349	-3.405185

E. Transition state structures in enantiodetermining step



Transfer of bromine from copper to benzyl copper with (*S,S*)-Ph-BPE ligand setting the *R* stereocenter – TS (entry 39)

RB3LYP energy: -5079.019292

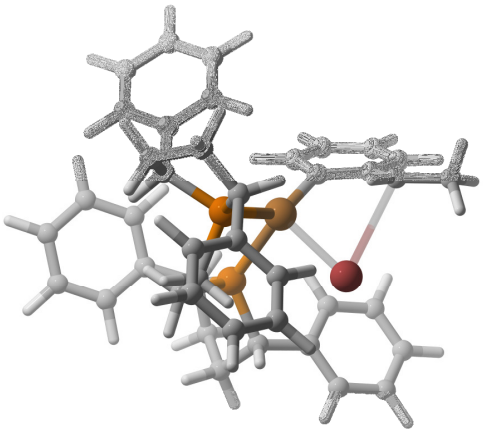
Sum of electronic and thermal Free Energies: -5078.357036

Imaginary frequency: -37.7769

6	0.664227	-0.515679	-2.387095
6	0.763429	0.991737	-2.159884
15	1.292634	1.313028	-0.406304
6	3.150959	1.124274	-0.610684
6	3.598167	2.509579	-1.102387
6	2.862204	3.551085	-0.272125
6	1.370157	3.198938	-0.220519
1	0.977517	3.381643	0.787985
6	0.457131	3.879701	-1.196657
6	-0.909266	3.935198	-0.913359
6	-1.807939	4.472674	-1.821411
6	-1.356504	4.980518	-3.033051
6	0.000462	4.948542	-3.319710
6	0.897834	4.402038	-2.411373
1	1.956750	4.382873	-2.662404
1	0.367939	5.351171	-4.261634
1	-2.058541	5.405275	-3.747159
1	-2.868471	4.498356	-1.576851

1	-1.271885	3.526650	0.030478
1	3.024062	4.570282	-0.644712
1	3.264233	3.528612	0.749603
1	4.686297	2.628284	-1.024107
1	3.345929	2.617658	-2.166014
1	3.307840	0.379806	-1.405231
6	3.909618	0.659837	0.612239
6	5.282236	0.425221	0.485860
6	6.038641	-0.012355	1.560422
6	5.434034	-0.235368	2.792625
6	4.072748	-0.018301	2.929685
6	3.318539	0.429259	1.850432
1	2.243224	0.546244	1.979041
1	3.576710	-0.210777	3.878950
1	6.023164	-0.586287	3.637188
1	7.105021	-0.190386	1.435049
1	5.761997	0.575205	-0.481986
1	1.453978	1.447570	-2.881785
1	-0.212894	1.475669	-2.307780
15	-0.488203	-1.281964	-1.137738
29	-0.446053	0.195619	0.686115
6	-2.167056	1.054742	1.163856
6	-2.609639	1.090947	2.533479
6	-3.991483	1.223742	2.877105
6	-4.921183	1.401030	1.895470
6	-4.499762	1.446017	0.550460
6	-3.171183	1.299074	0.208722
1	-2.908343	1.307194	-0.851759
1	-5.248508	1.569965	-0.232265
1	-5.974272	1.517474	2.140118
1	-4.301212	1.226968	3.920376
6	-1.629597	1.062814	3.514523
6	-1.803759	1.033326	4.971769
1	-1.069323	0.345900	5.406409
1	-1.565675	2.023795	5.388282
1	-2.802134	0.745663	5.307156
1	-0.607678	1.170148	3.156738
35	0.067856	-1.388412	2.662786
6	-1.951433	-1.723821	-2.214878
6	-1.531998	-3.049327	-2.868998
6	-0.891394	-3.922924	-1.795946
6	0.064816	-3.081723	-0.933808
1	-0.119548	-3.276458	0.131794
6	1.539466	-3.220628	-1.167146
6	2.076051	-3.600867	-2.396432
6	3.449593	-3.603540	-2.601481

6	4.311133	-3.219891	-1.582625
6	3.788554	-2.852299	-0.348388
6	2.417121	-2.857194	-0.142566
1	2.009739	-2.555744	0.824723
1	4.452154	-2.556725	0.462604
1	5.386829	-3.215660	-1.746371
1	3.848849	-3.904823	-3.568224
1	1.415166	-3.885406	-3.214362
1	-0.381381	-4.789345	-2.233902
1	-1.679591	-4.331612	-1.151408
1	-2.388950	-3.546844	-3.344027
1	-0.805851	-2.837696	-3.666865
1	-2.042070	-0.935486	-2.976722
6	-3.256373	-1.807323	-1.465264
6	-4.441375	-1.528700	-2.147132
6	-5.669500	-1.581371	-1.504673
6	-5.734914	-1.916076	-0.158359
6	-4.565913	-2.202172	0.531307
6	-3.338838	-2.148739	-0.115526
1	-2.435451	-2.343092	0.462112
1	-4.600697	-2.455094	1.589169
1	-6.695311	-1.950057	0.352113
1	-6.579595	-1.355314	-2.057243
1	-4.394437	-1.258138	-3.202595
1	0.338141	-0.734739	-3.412631
1	1.652337	-0.979194	-2.274912



Transfer of bromine from copper to benzyl copper with (*S,S*)-Ph-BPE ligand setting the *S* stereocenter – TS (entry 40)

RM06 energy: -5079.0159294

Sum of electronic and thermal Free Energies: -5078.352705

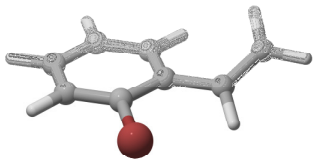
Imaginary frequency: -4.2147

6	1.668074	1.036731	-1.497599
6	1.052978	-0.184163	-2.176624
15	-0.571422	-0.674074	-1.405593
6	-1.804552	0.036025	-2.616238
6	-1.789094	-0.968533	-3.777493
6	-1.858866	-2.362148	-3.169230
6	-0.865075	-2.463975	-1.999438
1	-1.356261	-2.948066	-1.144410
6	0.418699	-3.192223	-2.253452
6	1.104923	-3.758840	-1.177919
6	2.328455	-4.385999	-1.360308
6	2.895373	-4.456590	-2.626036
6	2.223589	-3.897093	-3.704539
6	0.998205	-3.272931	-3.519632
1	0.492011	-2.831973	-4.376904
1	2.656993	-3.947368	-4.701422
1	3.853078	-4.951247	-2.772568
1	2.836567	-4.829489	-0.506207
1	0.669553	-3.702070	-0.178660
1	-1.684288	-3.146353	-3.915535
1	-2.873044	-2.526880	-2.784842
1	-2.621828	-0.784429	-4.469398
1	-0.863204	-0.848876	-4.357360
1	-1.418086	1.013261	-2.937397
6	-3.192034	0.228055	-2.056782
6	-4.044873	1.131365	-2.690045
6	-5.336531	1.339219	-2.233698
6	-5.806879	0.636739	-1.131740
6	-4.975451	-0.275324	-0.500277
6	-3.680961	-0.476666	-0.960544
1	-3.034893	-1.169399	-0.421607
1	-5.325275	-0.828797	0.369607
1	-6.818117	0.803422	-0.766428
1	-5.977569	2.061903	-2.734692
1	-3.675852	1.697401	-3.545793
1	0.949211	-0.006186	-3.255336
1	1.727420	-1.044371	-2.072952
15	1.710227	0.810040	0.340862
29	-0.436494	0.107609	0.834525
6	-1.570327	-0.776716	2.162733

6	-2.602653	-0.070266	2.881376
6	-3.733197	-0.748712	3.438739
6	-3.811121	-2.107667	3.374197
6	-2.765821	-2.827254	2.755189
6	-1.686787	-2.182770	2.189394
1	-0.916059	-2.786112	1.705003
1	-2.829983	-3.914560	2.714459
1	-4.653701	-2.638616	3.810228
1	-4.512332	-0.187970	3.951055
6	-2.414878	1.286022	3.086061
6	-3.314467	2.241417	3.741134
1	-2.881387	2.552779	4.703579
1	-3.361058	3.153567	3.133858
1	-4.328883	1.876977	3.914245
1	-1.448353	1.676943	2.773797
35	-1.545398	2.473786	0.254453
6	3.177974	-0.345421	0.537895
6	4.369188	0.585350	0.819140
6	3.870141	1.738916	1.678864
6	2.607451	2.330608	1.042130
1	1.932892	2.709508	1.820908
6	2.816740	3.435362	0.039975
6	4.038988	3.677779	-0.585933
6	4.172812	4.694561	-1.523663
6	3.085860	5.487821	-1.856931
6	1.864877	5.262876	-1.233879
6	1.734120	4.251915	-0.295525
1	0.765745	4.068887	0.171763
1	1.002733	5.879641	-1.479744
1	3.190286	6.281170	-2.594023
1	5.138554	4.864918	-1.995807
1	4.912719	3.078260	-0.338869
1	4.638448	2.507277	1.830964
1	3.621626	1.355691	2.677734
1	5.189710	0.039211	1.302904
1	4.757528	0.962076	-0.136064
1	3.329238	-0.848201	-0.427868
6	3.008972	-1.410842	1.589774
6	3.642253	-2.640289	1.400984
6	3.559480	-3.646845	2.351000
6	2.841378	-3.440390	3.521800
6	2.211469	-2.221981	3.727877
6	2.294917	-1.217661	2.771952
1	1.763882	-0.282314	2.941627
1	1.639284	-2.048750	4.637103
1	2.770455	-4.227897	4.268990

1	4.058258	-4.598819	2.176265
1	4.205712	-2.808922	0.482729
1	2.673107	1.227952	-1.898035
1	1.070243	1.937419	-1.687150

F. Starting materials, product, and other intermediates

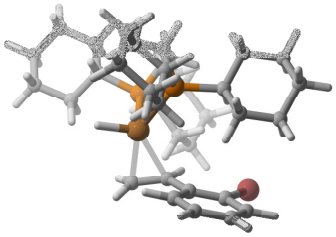


2-bromostyrene (entry 41)

RM06 energy: -2882.881315

Sum of electronic and thermal Free Energies: -2882.792882

6	-2.653897	-1.080356	-0.023764
6	-1.720826	-2.104393	0.071642
6	-0.367800	-1.803615	0.070051
6	0.040759	-0.481561	-0.024571
6	-0.872611	0.574420	-0.117262
6	-2.230825	0.233028	-0.121168
1	-2.965768	1.028374	-0.229276
6	-0.457157	1.977099	-0.222253
6	-1.148943	3.009548	0.249803
1	-2.083780	2.884559	0.794216
1	-0.793083	4.028685	0.123363
1	0.492271	2.168392	-0.722567
35	1.920127	-0.143108	0.013889
1	0.371356	-2.596704	0.146315
1	-2.040699	-3.141125	0.141325
1	-3.716946	-1.308421	-0.034370



π-acid complex between (dCype)CuH and 2-bromostyrene (entry 42)

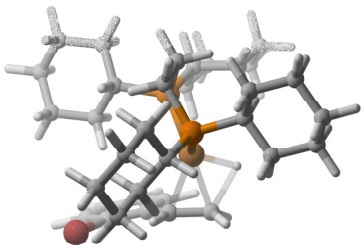
RM06 energy: -4781.5718157

Sum of electronic and thermal Free Energies: -4780.817536

6	0.861220	1.655967	1.716481
15	-0.659036	1.368299	0.705079
6	-1.656694	0.206626	1.775349
1	-1.170716	-0.772008	1.604130
6	-1.640885	0.487270	3.275379
6	-2.436628	-0.566118	4.039422
6	-3.862900	-0.683241	3.524974
6	-3.879256	-0.957336	2.029410
6	-3.096876	0.106225	1.272928
1	-3.598834	1.077042	1.415076
1	-3.114800	-0.099099	0.196597
1	-3.436207	-1.947195	1.829175
1	-4.910069	-0.999957	1.651608
1	-4.399242	0.258726	3.725369
1	-4.403566	-1.468802	4.069244
1	-1.932579	-1.540464	3.930524
1	-2.430420	-0.333613	5.112708
1	-0.614322	0.513437	3.660612
1	-2.072268	1.483380	3.468578
6	-1.580596	2.988749	0.774114
1	-2.196438	2.974661	1.690072
6	-0.657128	4.204522	0.847179
6	-1.455171	5.502402	0.862506
6	-2.384170	5.610255	-0.335902
6	-3.304122	4.402237	-0.414677
6	-2.502637	3.109385	-0.441975
1	-1.880376	3.082797	-1.351081
1	-3.175478	2.245288	-0.509967
1	-3.947952	4.462495	-1.302231
1	-3.978175	4.397239	0.457859
1	-1.782378	5.665070	-1.257205
1	-2.966597	6.540083	-0.288687
1	-2.051896	5.545335	1.788463
1	-0.769462	6.359375	0.897709
1	0.019907	4.198988	-0.022909
1	-0.021694	4.157580	1.740185
29	0.276272	0.682753	-1.313336
1	0.748424	2.004203	-2.139017
15	2.295186	-0.050391	0.040601
6	1.743848	0.414841	1.751456
1	2.594862	0.575117	2.424966
1	1.187984	-0.444674	2.151861
6	3.681725	1.147222	-0.293734
1	3.174983	2.127692	-0.243125

6	4.856951	1.168178	0.677308
6	5.852453	2.260940	0.304416
6	6.347248	2.088454	-1.123423
6	5.185366	2.049188	-2.104479
6	4.173669	0.973335	-1.730814
1	4.643694	-0.018393	-1.841594
1	3.319527	0.996446	-2.421601
1	4.678195	3.027213	-2.109374
1	5.549955	1.885530	-3.127418
1	6.915566	1.146734	-1.196473
1	7.046852	2.892217	-1.388448
1	6.695851	2.259180	1.007973
1	5.365571	3.244237	0.405731
1	5.375887	0.196900	0.649776
1	4.512260	1.312756	1.710126
6	3.130317	-1.711171	0.285809
1	3.979741	-1.700569	-0.419326
6	3.668467	-2.003140	1.686108
6	4.335407	-3.371218	1.752594
6	3.374314	-4.470891	1.330025
6	2.820028	-4.200517	-0.059462
6	2.176877	-2.824034	-0.152251
1	1.275825	-2.794540	0.486904
1	1.832062	-2.641892	-1.179407
1	3.640151	-4.259671	-0.793343
1	2.094307	-4.973926	-0.345341
1	2.541912	-4.520312	2.051068
1	3.868927	-5.450542	1.362481
1	5.216775	-3.381471	1.091073
1	4.710097	-3.555132	2.768524
1	4.368538	-1.224797	2.010754
1	2.835395	-1.988231	2.405945
1	0.608519	1.987698	2.731820
1	1.402758	2.485996	1.245438
6	-0.641808	-1.202163	-2.078995
6	0.143243	-0.585182	-3.014215
1	-0.278108	-0.024936	-3.844820
1	1.194136	-0.848212	-3.108332
1	-0.177963	-1.925092	-1.412931
6	-2.105395	-1.142406	-2.061913
6	-2.893753	-2.112288	-1.429974
6	-4.280983	-2.064346	-1.438557
6	-4.928048	-1.024800	-2.086469
6	-4.176344	-0.041983	-2.721430
6	-2.796218	-0.104367	-2.706003
1	-2.220986	0.687101	-3.183169

1	-4.671460	0.784272	-3.226561
1	-6.014457	-0.984378	-2.092495
1	-4.853196	-2.838195	-0.932672
35	-2.094637	-3.579163	-0.496297



Hydrometallation (entry 43)

RM06 energy: -4781.557306

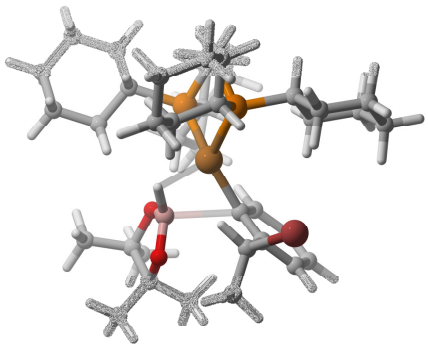
Sum of electronic and thermal Free Energies: -4780.801848

Imaginary frequency: -869.8164

6	0.880692	1.709272	1.871005
15	-0.628295	1.432485	0.829952
6	-1.710101	0.527966	2.047378
1	-1.004902	-0.203581	2.484117
6	-2.273759	1.369532	3.189229
6	-3.026089	0.495829	4.186588
6	-4.123025	-0.307086	3.503311
6	-3.558381	-1.146510	2.366773
6	-2.805920	-0.284972	1.363445
1	-3.517331	0.386748	0.857636
1	-2.364963	-0.907863	0.575899
1	-2.871124	-1.903373	2.779532
1	-4.359552	-1.701334	1.859243
1	-4.879113	0.386689	3.100370
1	-4.643658	-0.942511	4.231830
1	-2.316296	-0.195051	4.669664
1	-3.445758	1.118049	4.988223
1	-1.476185	1.923240	3.703541
1	-2.965406	2.124803	2.785061
6	-1.331294	3.143822	0.649505
6	-2.701167	3.090349	-0.026541

6	-3.281414	4.481817	-0.235960
6	-2.332224	5.362177	-1.032032
6	-0.969577	5.427922	-0.361474
6	-0.384860	4.036840	-0.153891
1	-0.197215	3.565869	-1.132698
1	0.592435	4.116973	0.339856
1	-1.068579	5.930612	0.614329
1	-0.275898	6.038227	-0.954816
1	-2.217073	4.945916	-2.045851
1	-2.751054	6.369689	-1.155290
1	-3.472136	4.946363	0.745445
1	-4.255493	4.408373	-0.737390
1	-2.592250	2.587355	-1.002224
1	-3.401819	2.478648	0.555509
1	-1.444180	3.571023	1.660779
6	1.773266	0.474371	1.907506
15	2.267043	-0.052029	0.201283
6	3.575145	1.175792	-0.282105
1	3.015912	2.129913	-0.299433
6	4.771004	1.336044	0.650300
6	5.708887	2.429211	0.151300
6	6.170393	2.156849	-1.272083
6	4.983833	1.986145	-2.208836
6	4.037064	0.902005	-1.713043
1	4.553236	-0.071461	-1.754188
1	3.165248	0.823184	-2.376810
1	4.433126	2.938026	-2.278002
1	5.325204	1.751881	-3.225875
1	6.776599	1.236239	-1.284555
1	6.826761	2.963626	-1.624401
1	6.571246	2.520873	0.825007
1	5.184605	3.397835	0.185343
1	5.327602	0.386040	0.702158
1	4.443017	1.563941	1.673503
6	3.146793	-1.681129	0.451468
1	3.983412	-1.661222	-0.268144
6	3.717311	-1.934795	1.845773
6	4.405883	-3.291635	1.923672
6	3.455762	-4.414023	1.536476
6	2.875357	-4.179220	0.150863
6	2.206561	-2.816780	0.045355
1	1.311309	-2.791381	0.691862
1	1.841551	-2.650781	-0.977787
1	3.684657	-4.239404	-0.594967
1	2.157537	-4.969293	-0.108411
1	2.635382	-4.463257	2.271043

1	3.967231	-5.384625	1.579860
1	5.275602	-3.299690	1.246897
1	4.801294	-3.452106	2.935711
1	4.413305	-1.139003	2.138231
1	2.899324	-1.916145	2.582557
1	2.641607	0.650846	2.553544
1	1.230197	-0.375104	2.345259
1	0.588200	2.001047	2.888904
1	1.432609	2.559325	1.452358
29	0.235959	0.358277	-1.005008
1	0.577494	1.269525	-2.325082
6	-0.650730	-1.213233	-2.209656
6	0.060222	-0.283324	-3.003144
1	-0.468399	0.302582	-3.750863
1	1.067314	-0.557569	-3.310697
1	-0.113900	-2.084330	-1.846756
6	-2.091001	-1.219246	-2.093666
6	-2.821429	-2.279375	-1.522982
6	-4.203433	-2.277267	-1.421410
6	-4.934329	-1.193450	-1.886512
6	-4.251600	-0.118897	-2.448847
6	-2.874283	-0.135012	-2.547121
1	-2.366239	0.729952	-2.970424
1	-4.801830	0.748683	-2.809356
1	-6.018563	-1.191184	-1.807175
1	-4.710382	-3.126225	-0.968040
35	-1.908832	-3.792068	-0.778891



Hydroboration of aryl copper (entry 44)

RM06 energy: -5193.3131562

Sum of electronic and thermal Free Energies: -5192.369021

Imaginary frequency: -120.0498

6	-0.735927	-2.874707	1.301367
15	-1.693312	-1.454401	0.597537
6	-2.726276	-2.305561	-0.703193
6	-3.738072	-3.341733	-0.222415
6	-4.384025	-4.064247	-1.398986
6	-5.036690	-3.080907	-2.358644
6	-4.037244	-2.037560	-2.833440
6	-3.387118	-1.315752	-1.661793
1	-4.154088	-0.738631	-1.121826
1	-2.656688	-0.578597	-2.013618
1	-3.254690	-2.529907	-3.433724
1	-4.524339	-1.311276	-3.498923
1	-5.477980	-3.611428	-3.212776
1	-5.870115	-2.574864	-1.844191
1	-3.614452	-4.641728	-1.936320
1	-5.119393	-4.793683	-1.033621
1	-4.524904	-2.836242	0.358345
1	-3.269624	-4.069697	0.453009
1	-1.947636	-2.837355	-1.284105
6	-2.743999	-0.913655	2.037908
1	-1.986633	-0.383446	2.647920
6	-3.370776	-1.968967	2.948464
6	-3.994475	-1.302241	4.170736
6	-5.020152	-0.249295	3.773878
6	-4.417146	0.784687	2.834581
6	-3.788104	0.122417	1.617132
1	-4.579444	-0.382055	1.037899
1	-3.347867	0.870268	0.944702
1	-3.646577	1.363201	3.371071
1	-5.180812	1.508716	2.518516
1	-5.436799	0.234483	4.667340
1	-5.865394	-0.743901	3.267534
1	-3.197893	-0.827649	4.766249
1	-4.454285	-2.060348	4.818941
1	-4.150827	-2.524961	2.408465
1	-2.624162	-2.707720	3.267918
29	0.081574	-0.000443	-0.098773
6	0.360896	1.889489	0.580484
6	1.515641	2.667663	0.373150
6	1.869543	3.690964	1.257663
6	1.101046	3.962286	2.377670
6	-0.053723	3.219485	2.604057

6	-0.408475	2.219886	1.708563
1	-1.339209	1.677158	1.889083
1	-0.675599	3.427215	3.474914
1	1.395650	4.753265	3.065311
1	2.772407	4.277136	1.079497
6	2.343868	2.452283	-0.858189
35	4.216961	1.890905	-0.371194
1	1.973102	1.578746	-1.401386
6	2.467256	3.646673	-1.771620
1	1.467568	3.908098	-2.136492
1	2.888604	4.515908	-1.254790
1	3.098639	3.426529	-2.638679
15	1.576962	-1.772552	0.125635
6	0.461281	-3.226794	0.424779
1	1.031950	-4.052426	0.870112
1	0.118067	-3.578264	-0.558175
6	2.635413	-1.797221	1.672619
6	2.091564	-0.762208	2.662194
6	2.887960	-0.740681	3.957835
6	4.359939	-0.479139	3.682818
6	4.915699	-1.509708	2.713511
6	4.118986	-1.545889	1.414904
1	4.232217	-0.584126	0.894443
1	4.537653	-2.312611	0.750953
1	4.885843	-2.505366	3.185606
1	5.971905	-1.304415	2.493316
1	4.470270	0.527099	3.246222
1	4.936048	-0.478202	4.617668
1	2.478315	0.023160	4.632364
1	2.778037	-1.707619	4.476049
1	2.138610	0.233077	2.192429
1	1.027637	-0.943428	2.870941
1	2.522527	-2.803338	2.113394
6	2.641783	-2.349422	-1.281485
6	3.101582	-3.803635	-1.213169
6	3.995192	-4.147657	-2.397728
6	3.278232	-3.883080	-3.713469
6	2.798146	-2.442078	-3.795918
6	1.927017	-2.068117	-2.604458
1	0.983018	-2.639242	-2.642877
1	1.644951	-1.007496	-2.659577
1	3.671636	-1.770803	-3.821190
1	2.249703	-2.270086	-4.731451
1	2.412325	-4.560370	-3.793468
1	3.932597	-4.117663	-4.563226
1	4.912630	-3.538761	-2.351995

1	4.315346	-5.196311	-2.337474
1	2.222618	-4.465991	-1.232618
1	3.618249	-4.007858	-0.265499
1	3.529382	-1.696043	-1.245100
1	-1.370948	-3.758231	1.443578
1	-0.400886	-2.570108	2.302767
1	-0.476821	0.499330	-1.830084
5	-0.943000	1.569343	-1.420503
8	-2.246751	1.659230	-0.948921
6	-2.857647	2.806658	-1.558645
6	-1.629602	3.685704	-1.953141
8	-0.597952	2.699193	-2.149190
6	-1.790051	4.459508	-3.243983
1	-0.883527	5.046304	-3.436213
1	-1.948209	3.803466	-4.104481
1	-2.630863	5.161777	-3.181796
6	-1.199973	4.642160	-0.852558
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1	-1.919113	5.461726	-0.736669
1	-1.087795	4.141465	0.112880
6	-3.805649	3.441150	-0.563926
1	-4.217033	4.382387	-0.950134
1	-4.649969	2.766432	-0.374367
1	-3.318600	3.643097	0.395958
6	-3.641401	2.307067	-2.762470
1	-2.990027	1.816519	-3.495730
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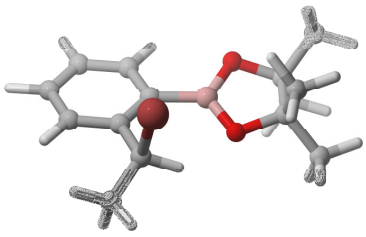

Benzyl bromide product (entry 45)

RM06 energy: -3294.6411658

Sum of electronic and thermal Free Energies: -3294.368892

6	1.824469	-0.699921	0.853291
6	1.800762	0.734079	0.416232
6	0.590109	1.360324	0.057351
6	0.636075	2.691353	-0.370698
6	1.825886	3.399667	-0.438908
6	3.009986	2.772269	-0.083066
6	2.992976	1.450317	0.335895
1	3.933999	0.972524	0.598806
1	3.954270	3.310450	-0.133511
1	1.828990	4.435382	-0.770989
1	-0.292633	3.182883	-0.654385
5	-0.817370	0.687916	0.081260
8	-1.163380	-0.436244	0.780201
6	-2.491443	-0.821610	0.341491
6	-3.064834	0.527516	-0.182150
8	-1.868670	1.224526	-0.608742
6	-3.698850	1.372489	0.907301
1	-4.652925	0.953069	1.245006
1	-3.041705	1.477892	1.777946
1	-3.893541	2.375849	0.512971
6	-4.004039	0.404212	-1.357965
1	-4.356338	1.397541	-1.657668
1	-3.521117	-0.054660	-2.225373
1	-3.259542	-2.262278	-1.096870
6	-3.237831	-1.422407	1.508099
1	-4.275514	-1.646160	1.232130
1	-2.763365	-2.363750	1.806820
1	-3.247643	-0.760184	2.378126
6	-2.302145	-1.860771	-0.747035
1	-4.883996	-0.195042	-1.093957
1	-1.758688	-1.457577	-1.609025
1	-1.715859	-2.693835	-0.344803
6	2.916147	-1.102304	1.810755
1	2.784873	-2.140944	2.128258
1	3.919244	-1.012108	1.382822
1	2.871362	-0.468638	2.706002
35	1.973710	-1.846692	-0.785882
1	0.849918	-0.993314	1.242026

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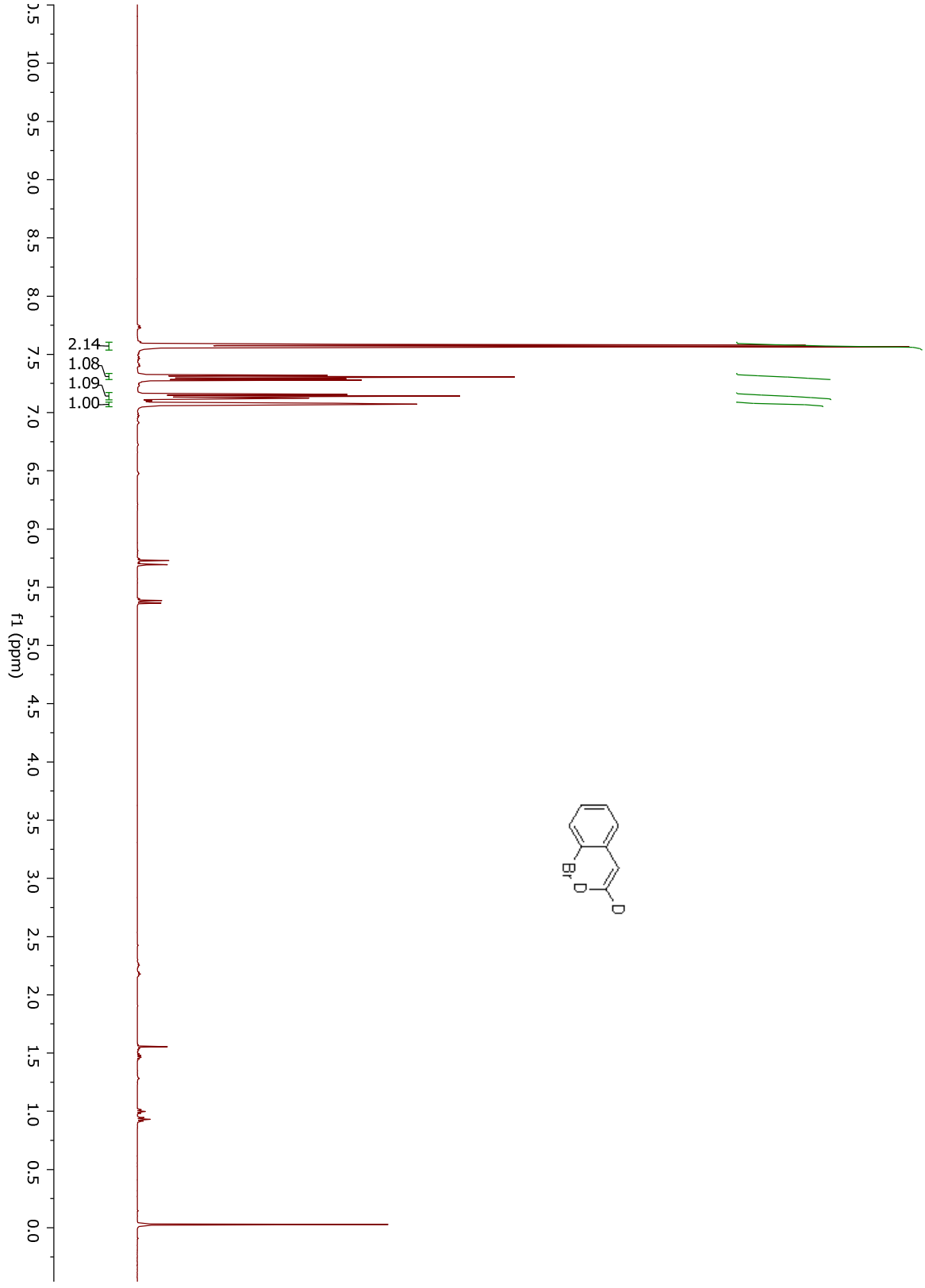
X. NMR Spectra

2-bromo-β,β-dideuterostyrene



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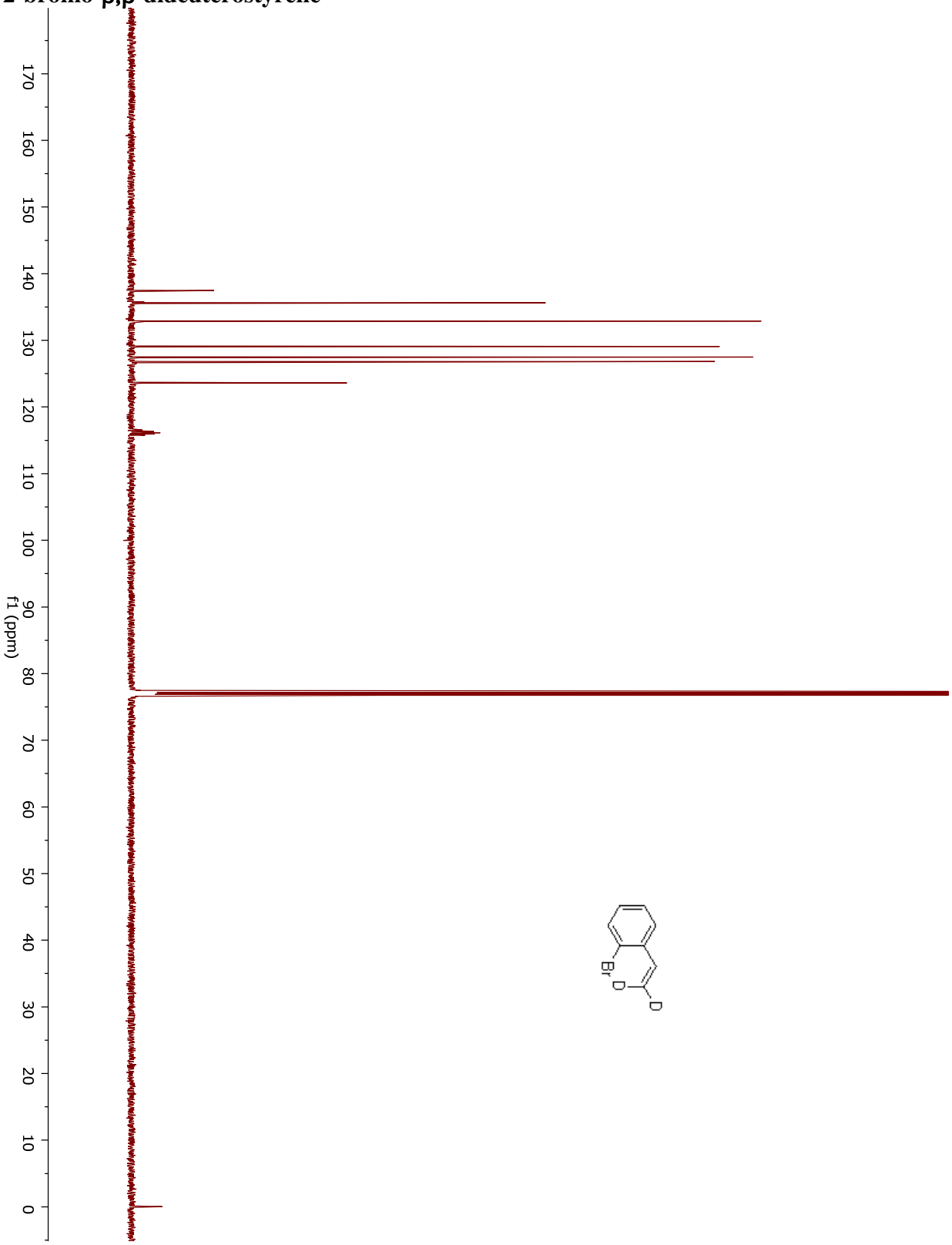

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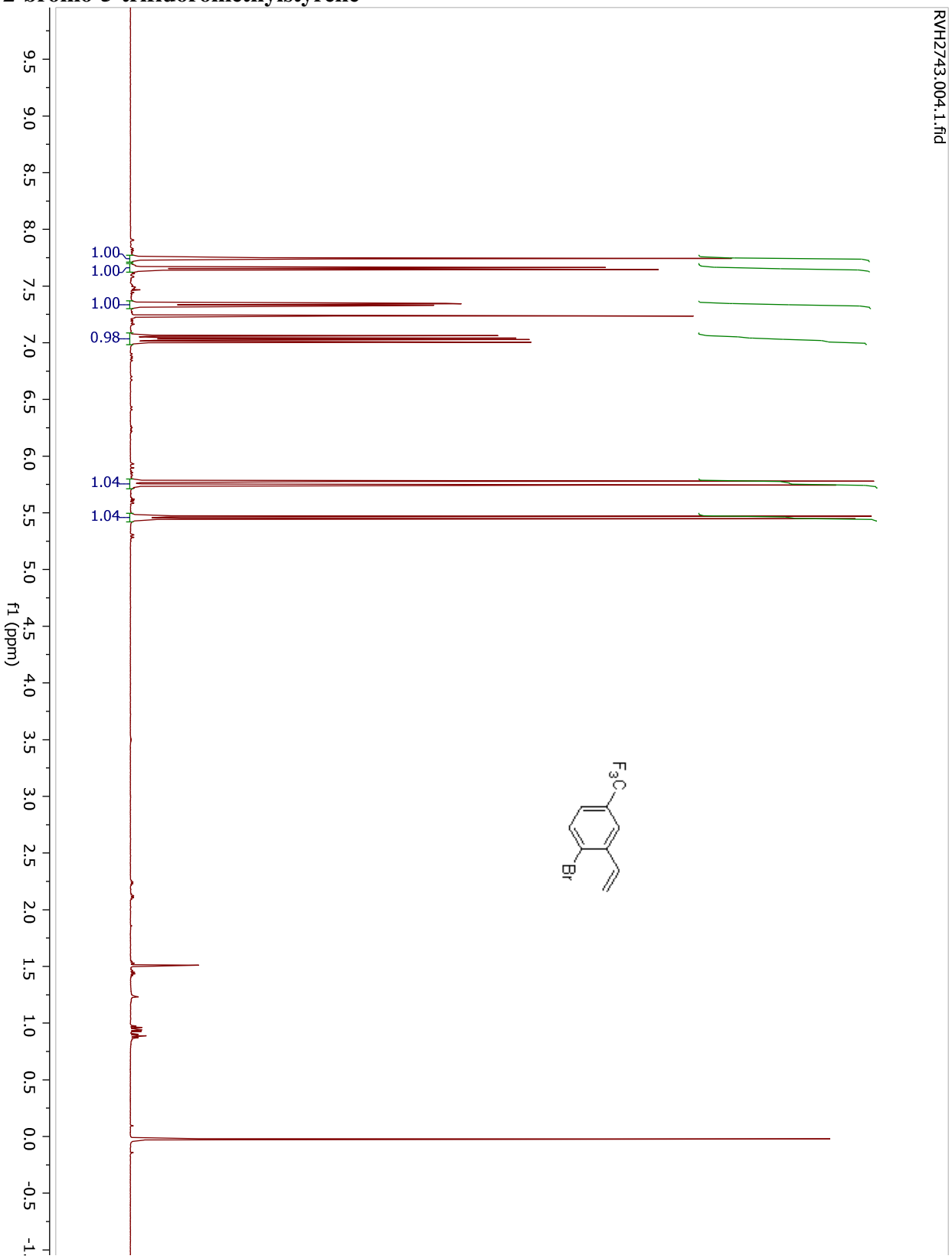

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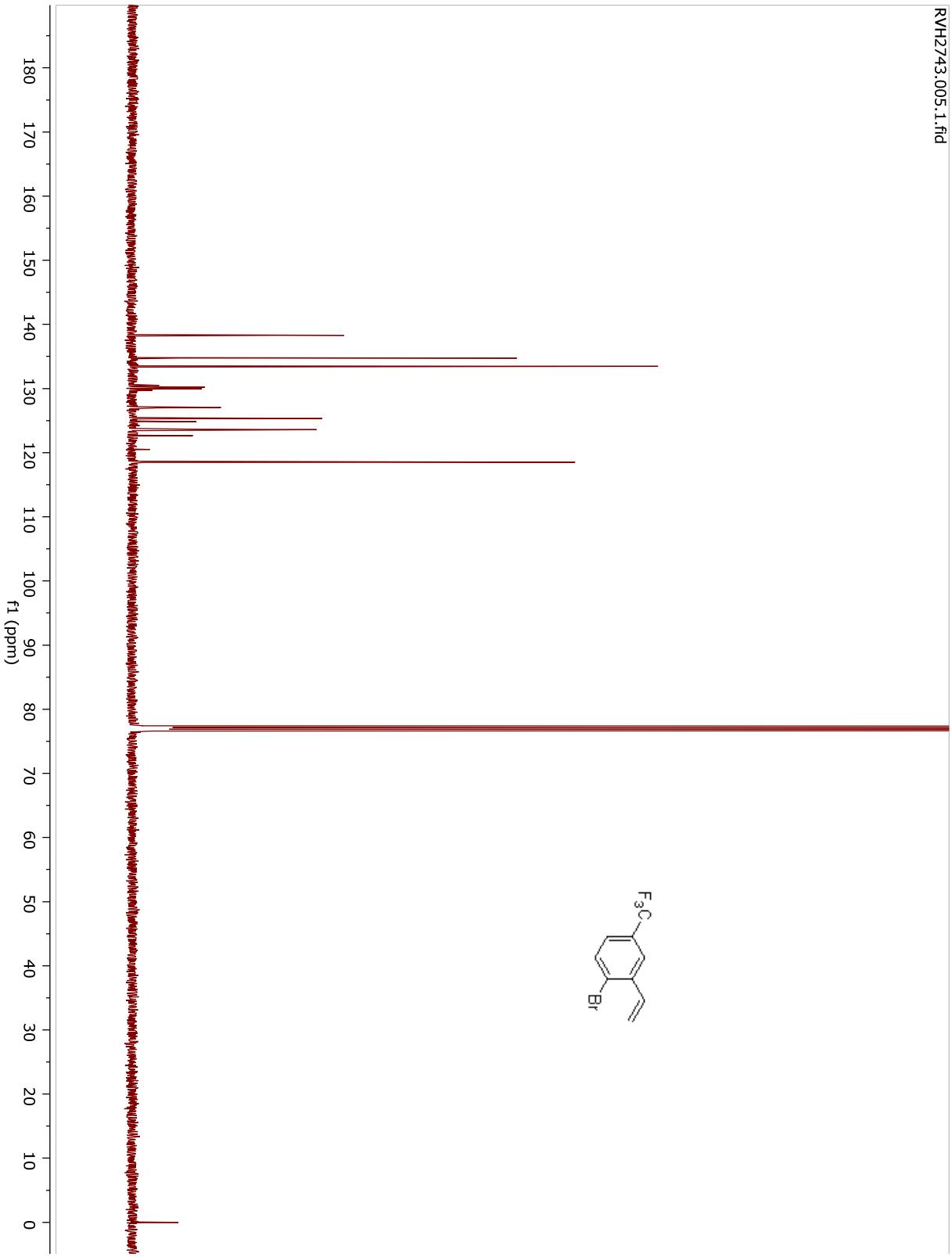

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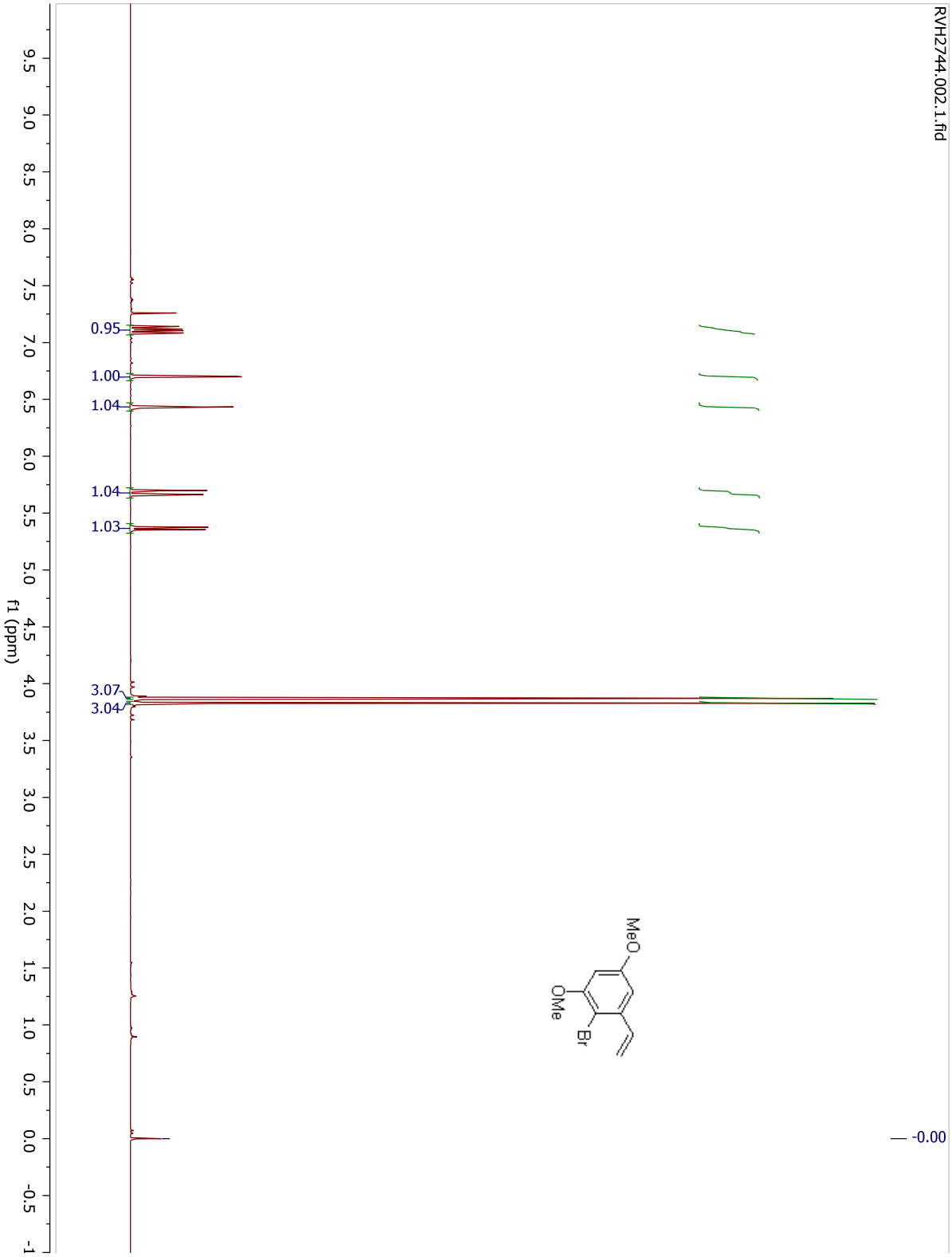

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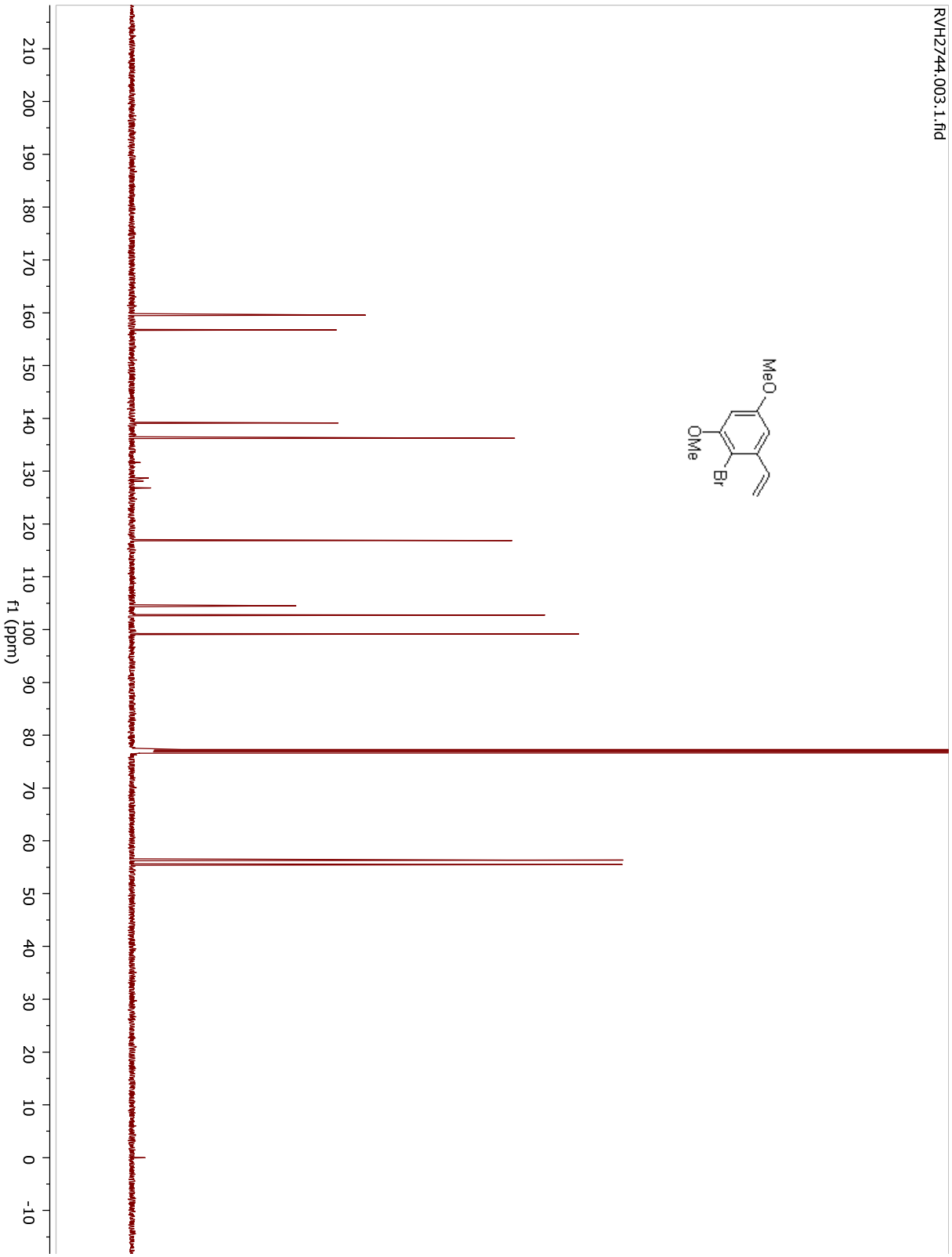

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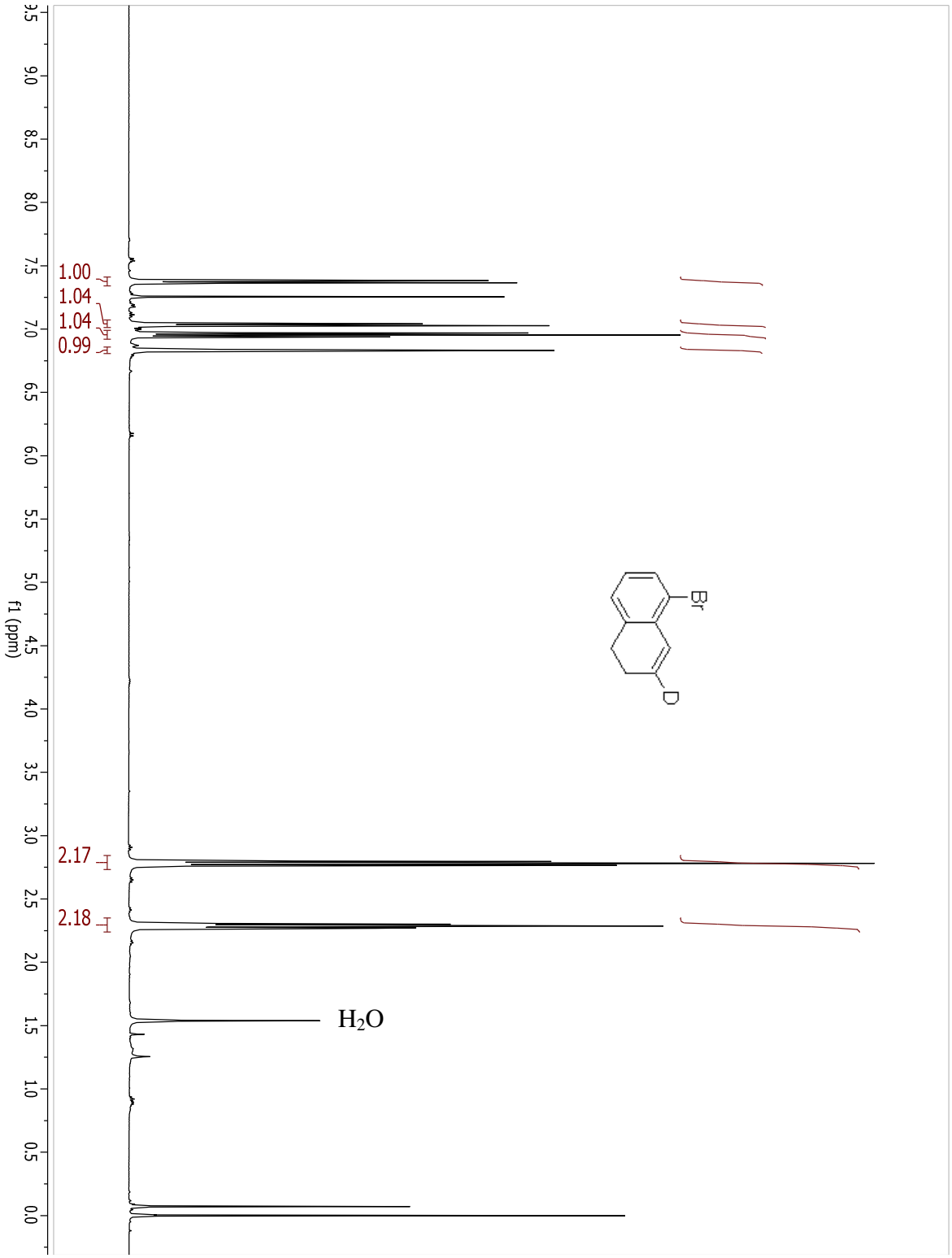

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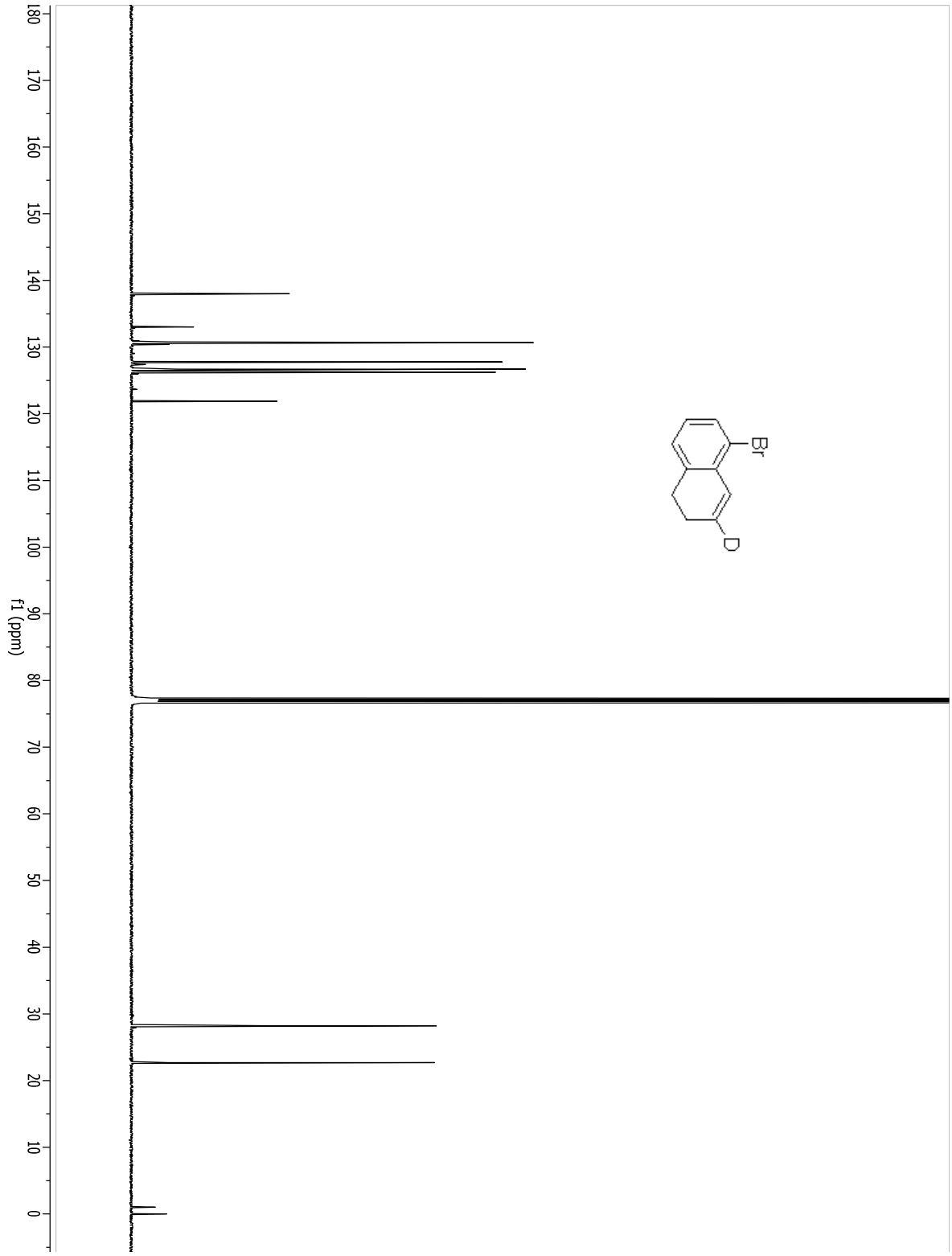

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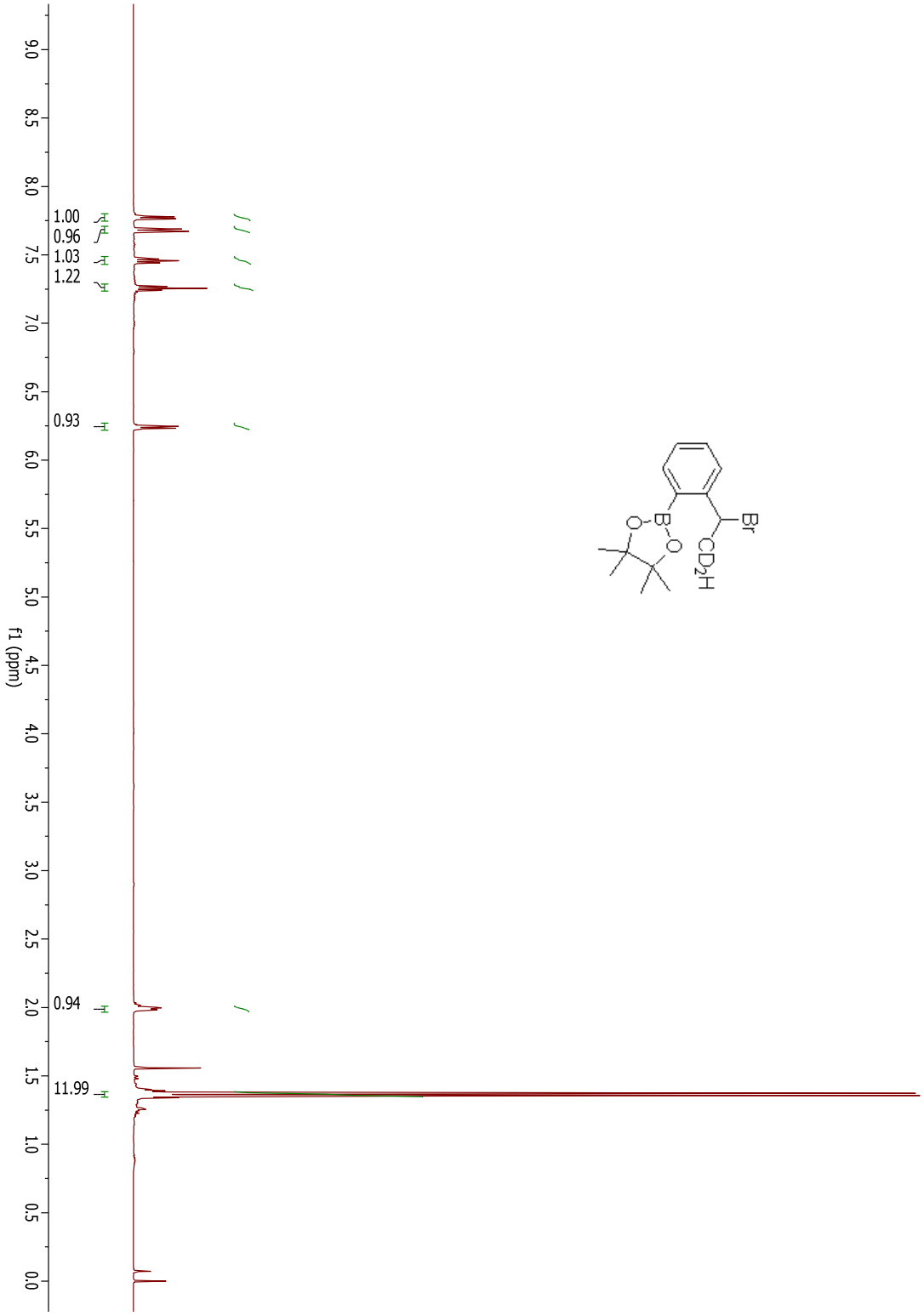
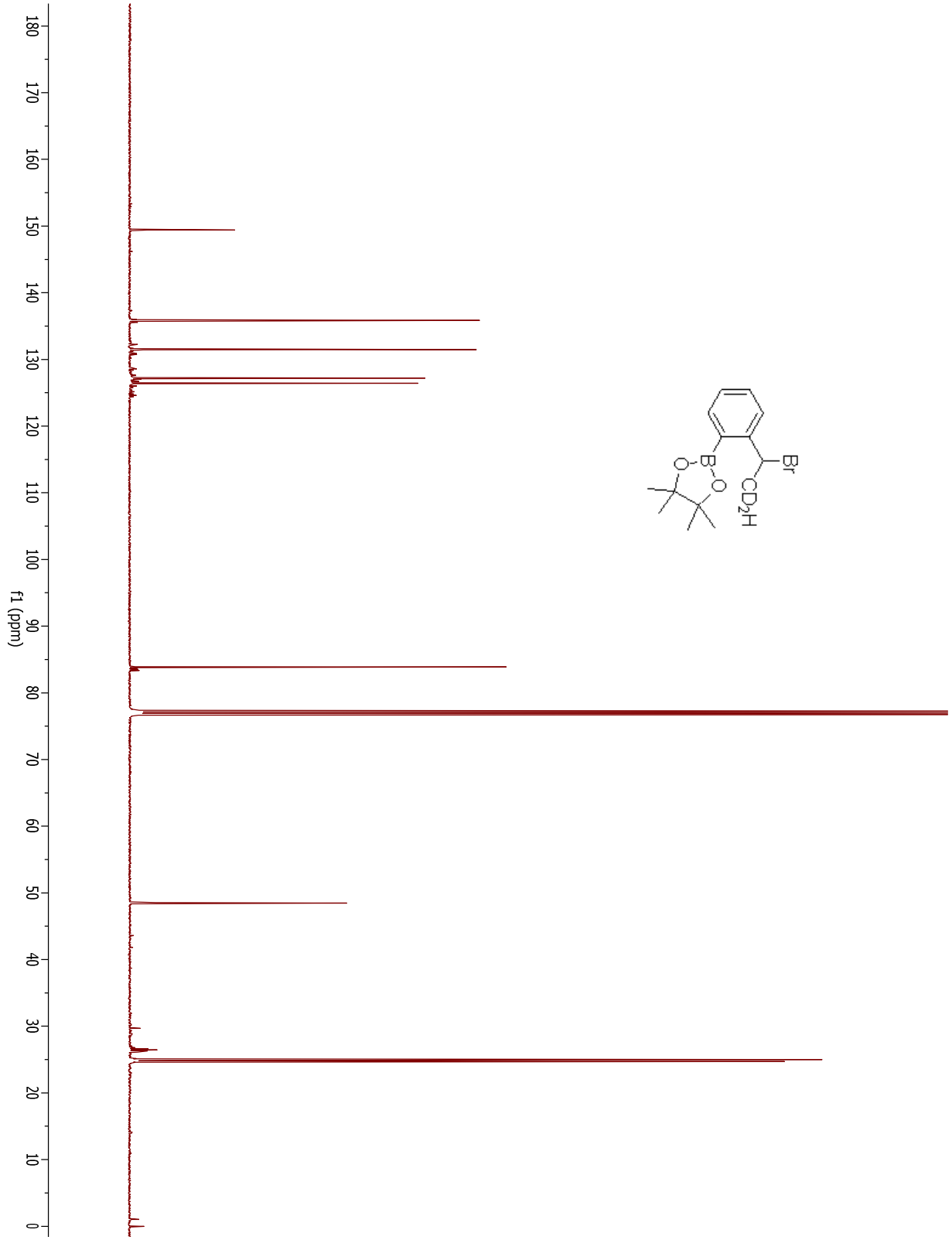
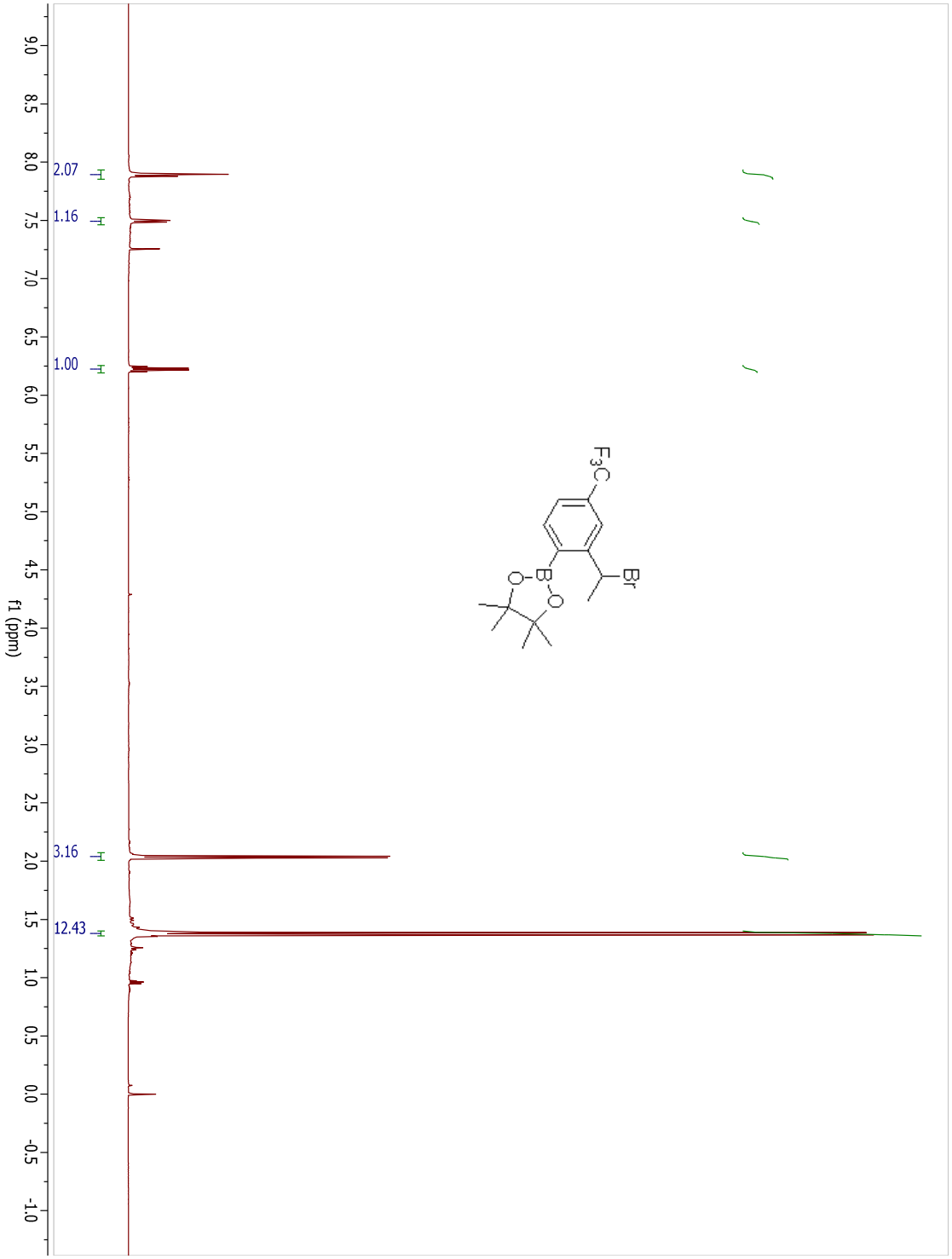


2-[2-(1-bromo-2-dideutero-ethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



2-[2-(1-bromoethyl)-4-trifluoromethylphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



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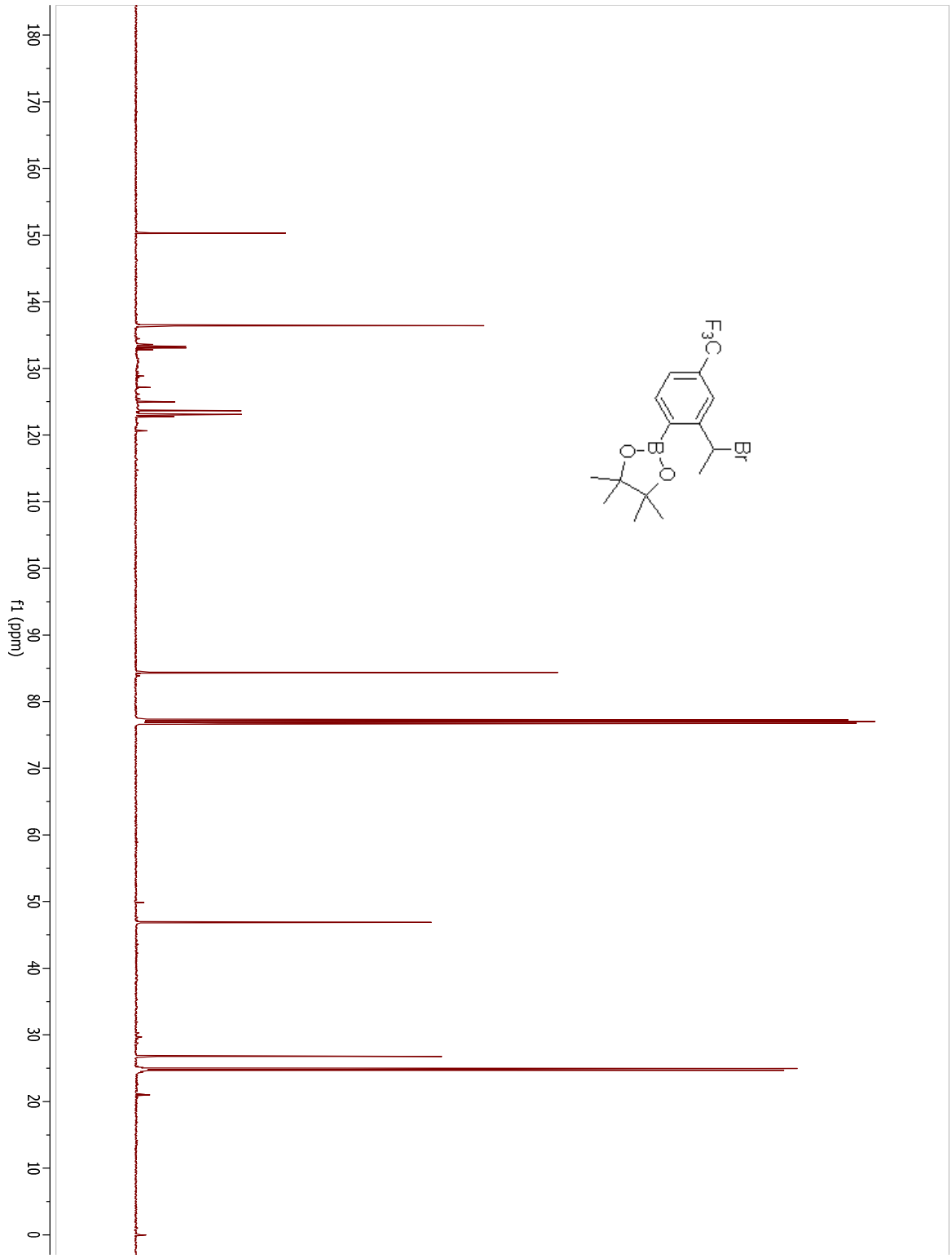

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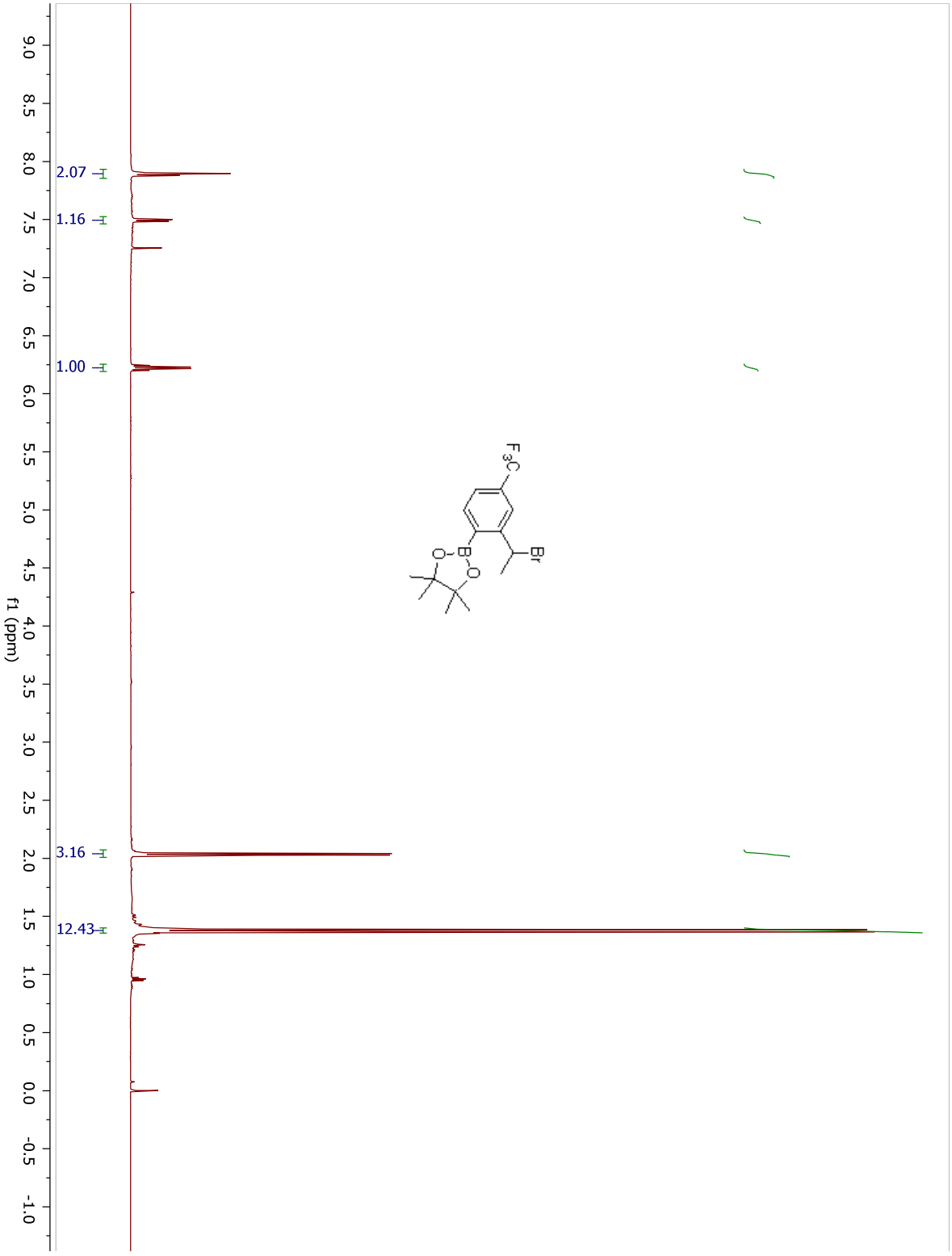

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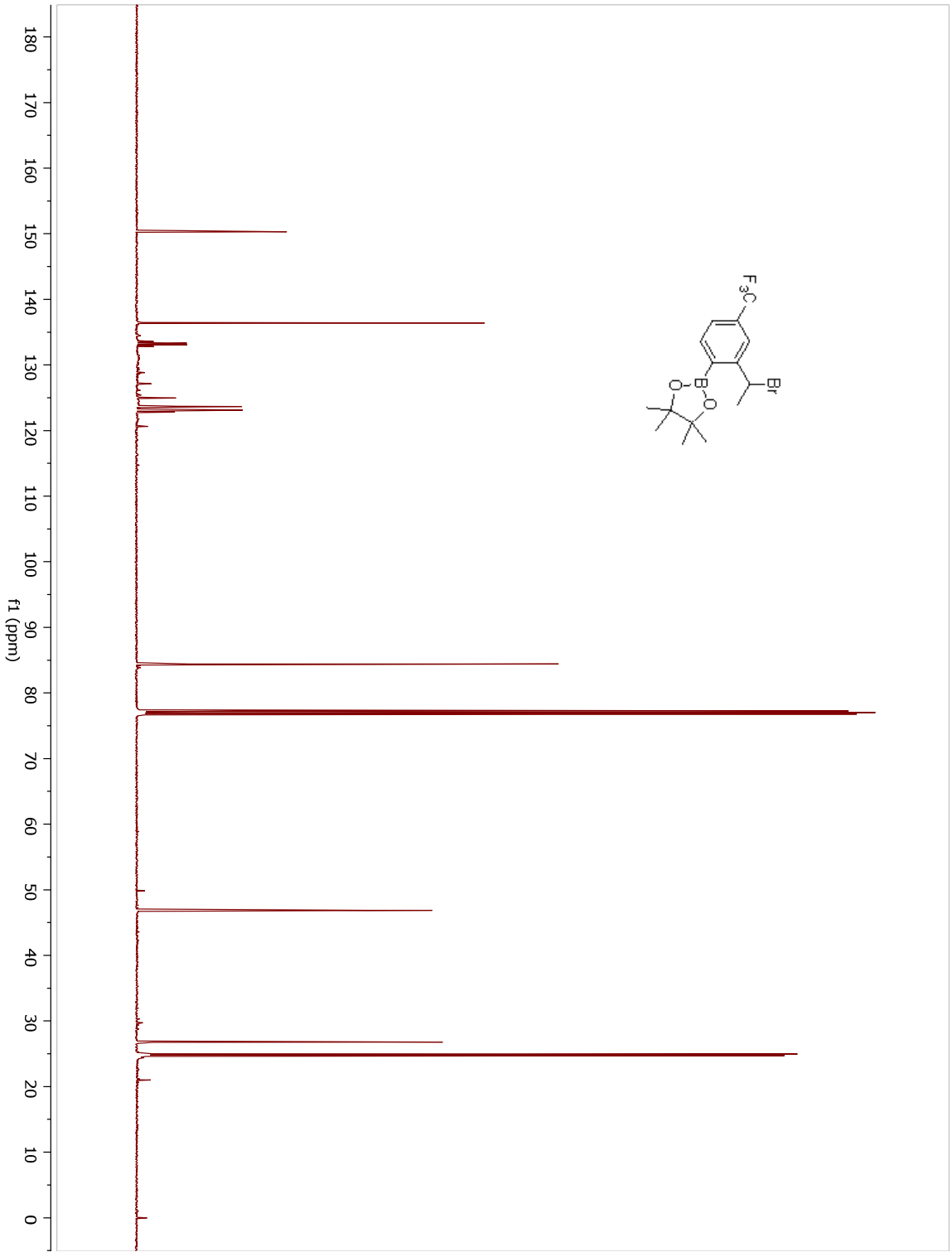
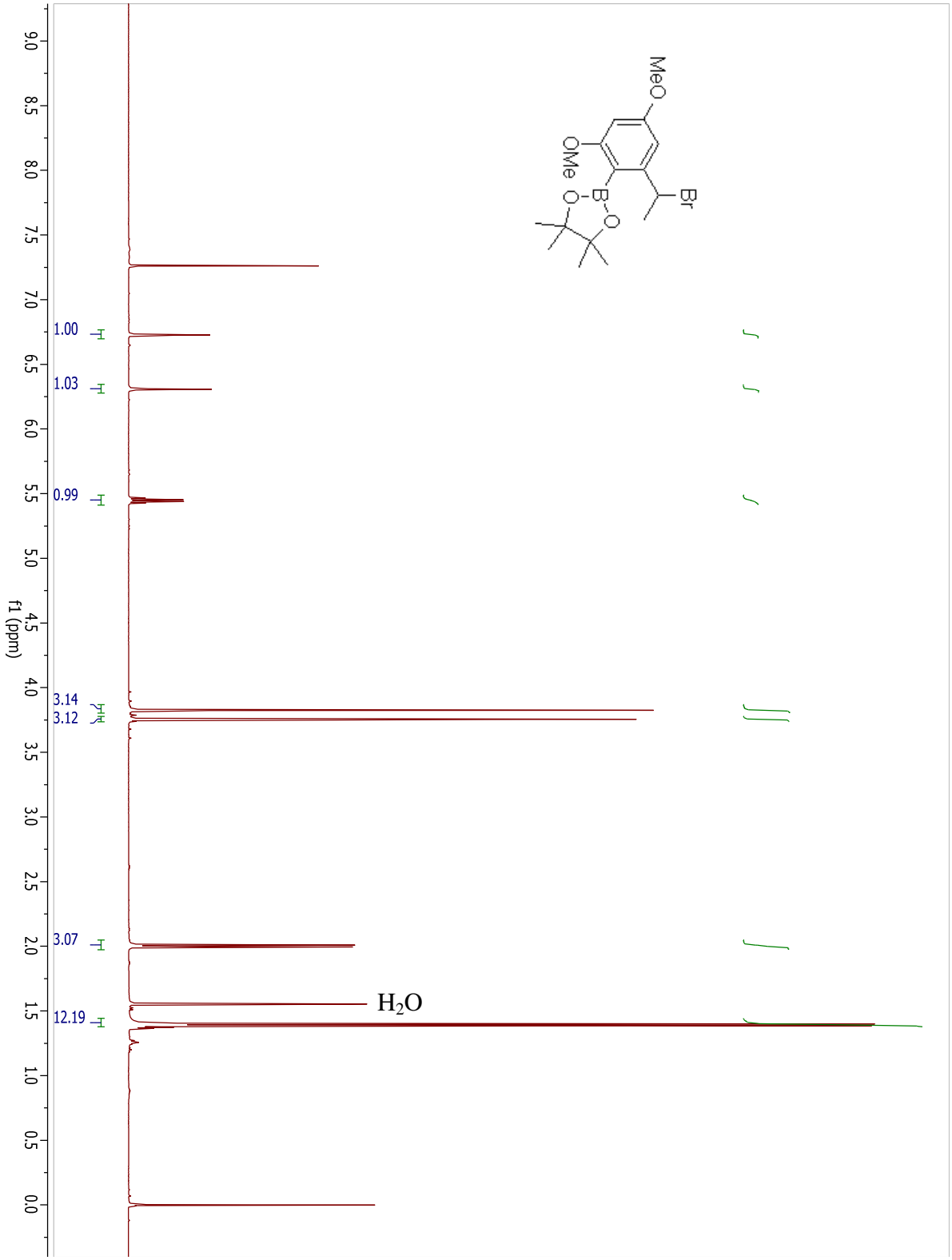


2-[2-(1-bromoethyl)-4,6-dimethoxyphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



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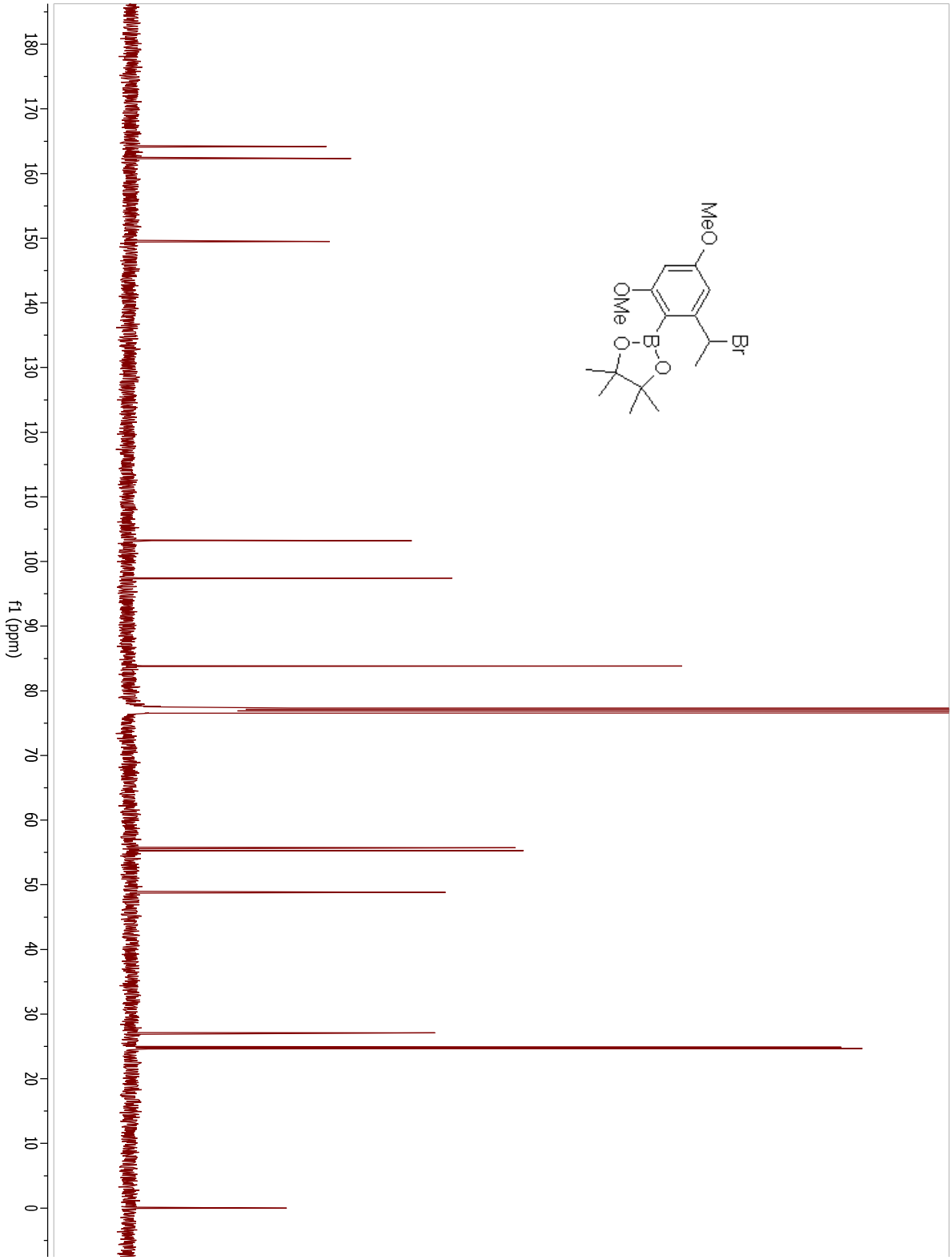

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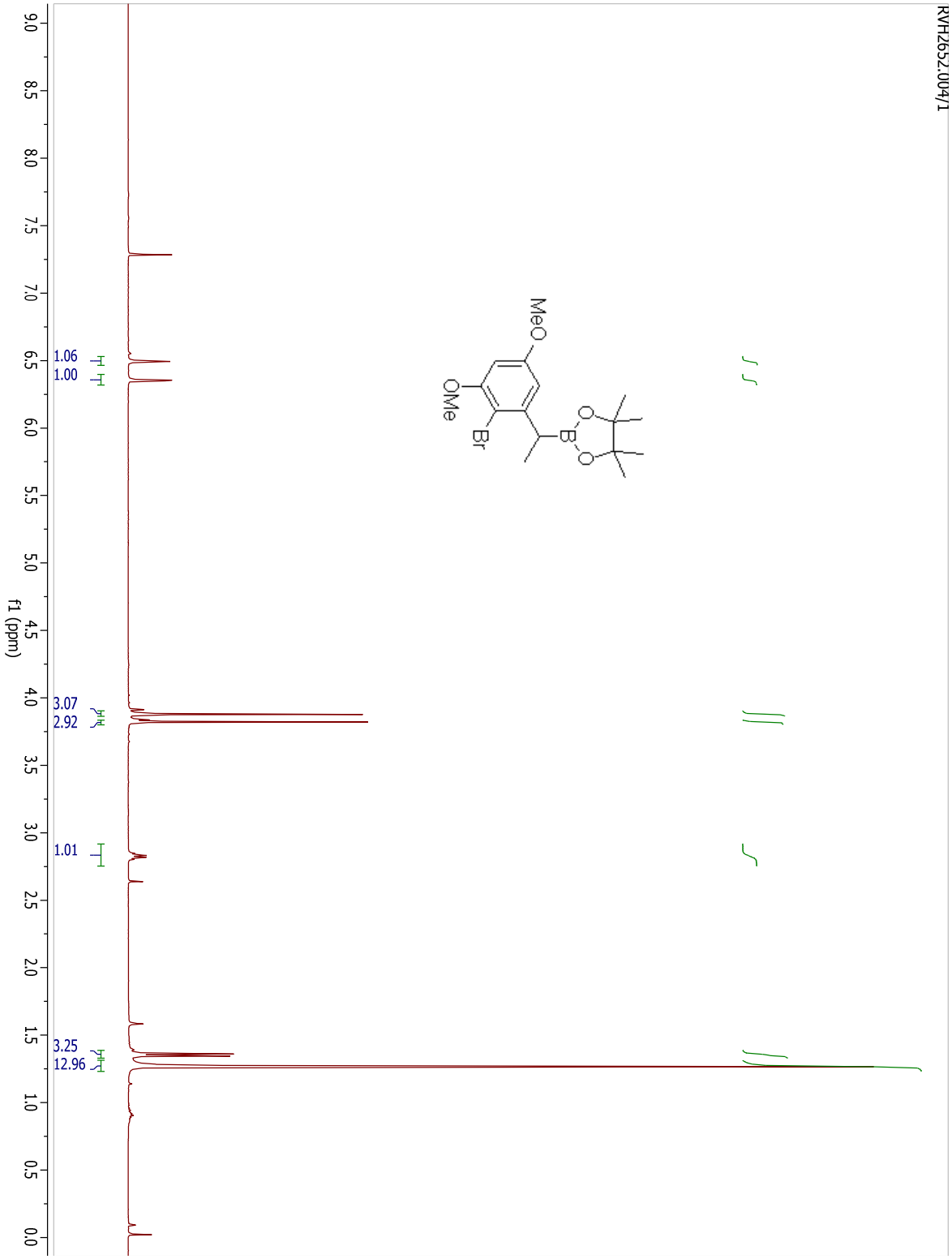

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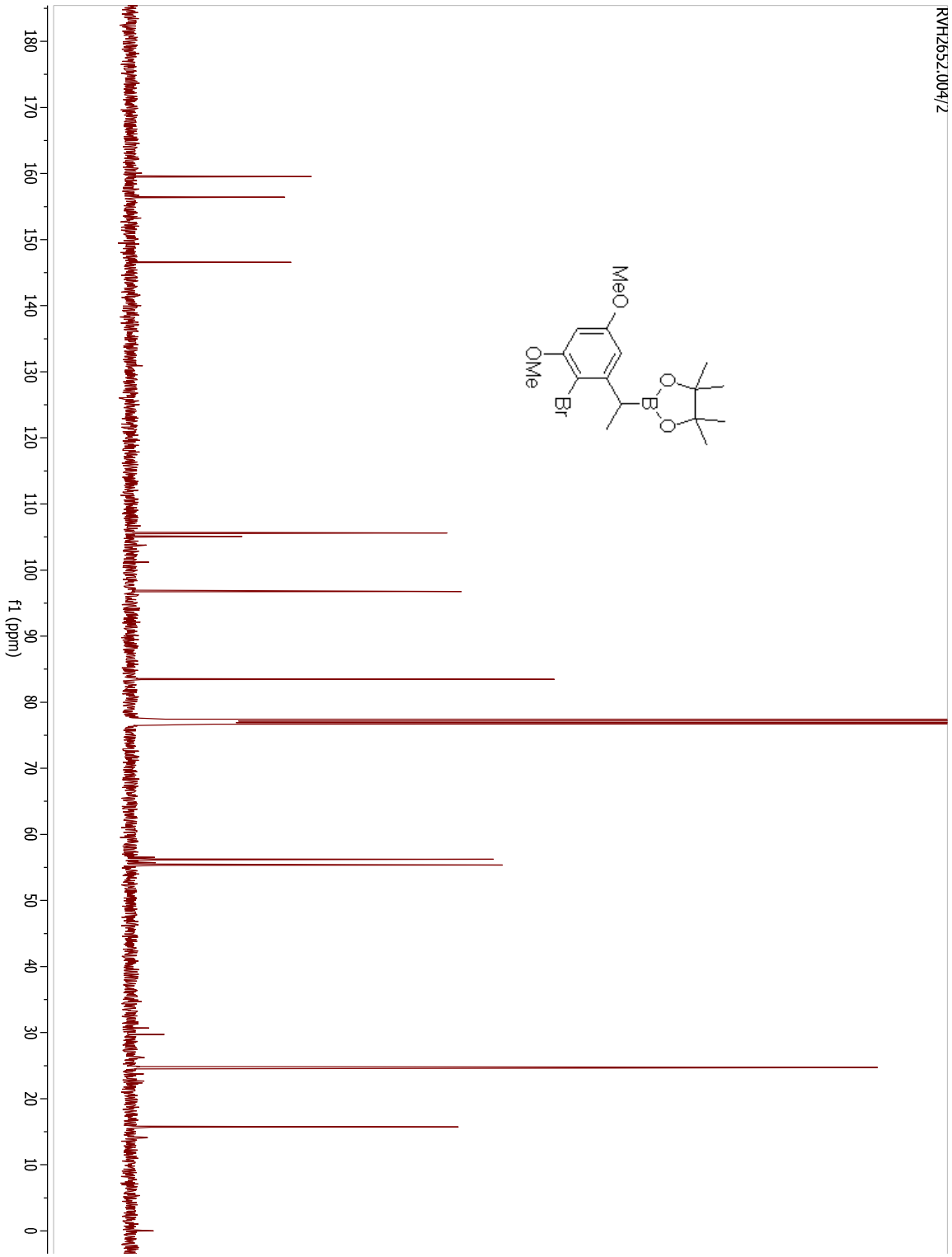
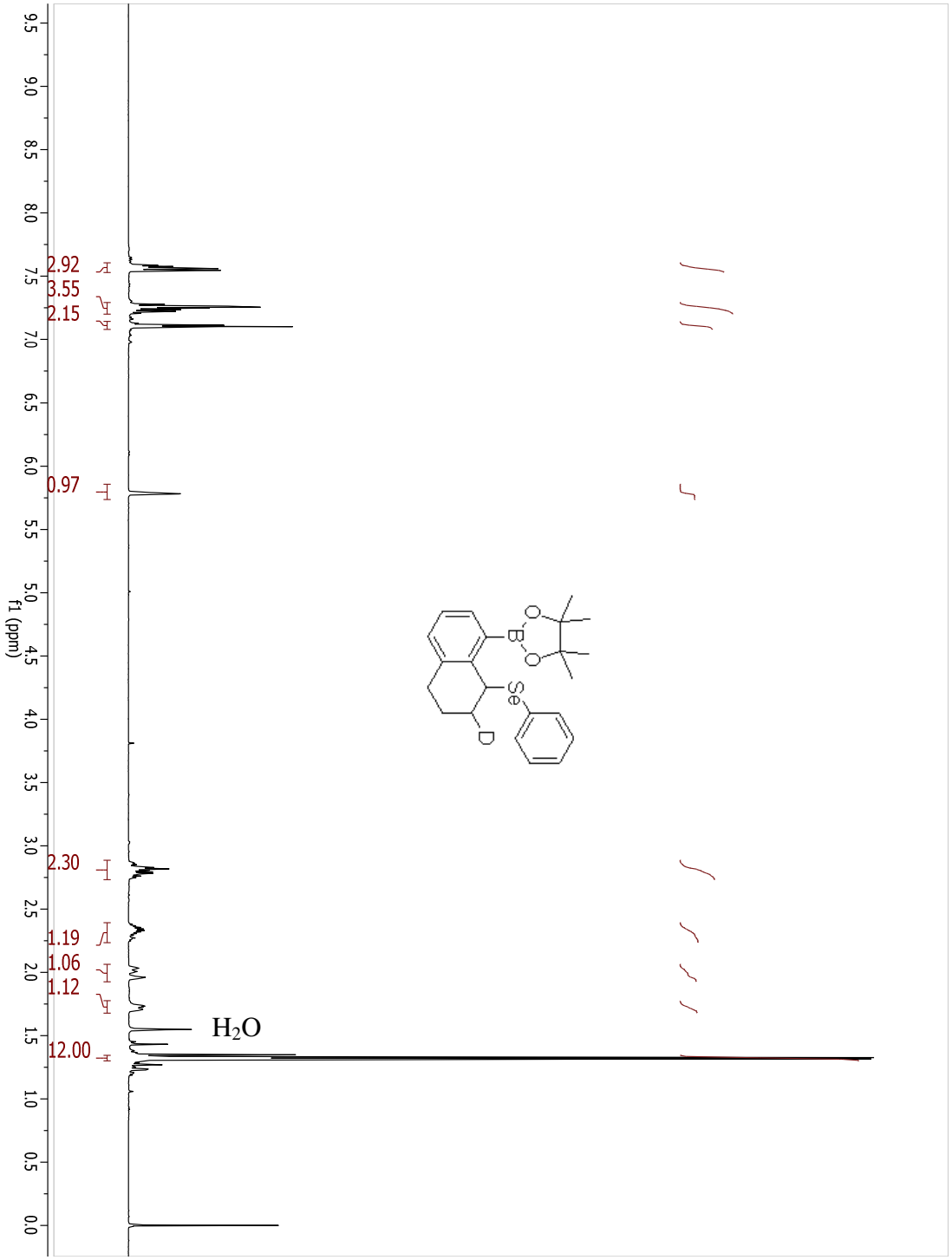
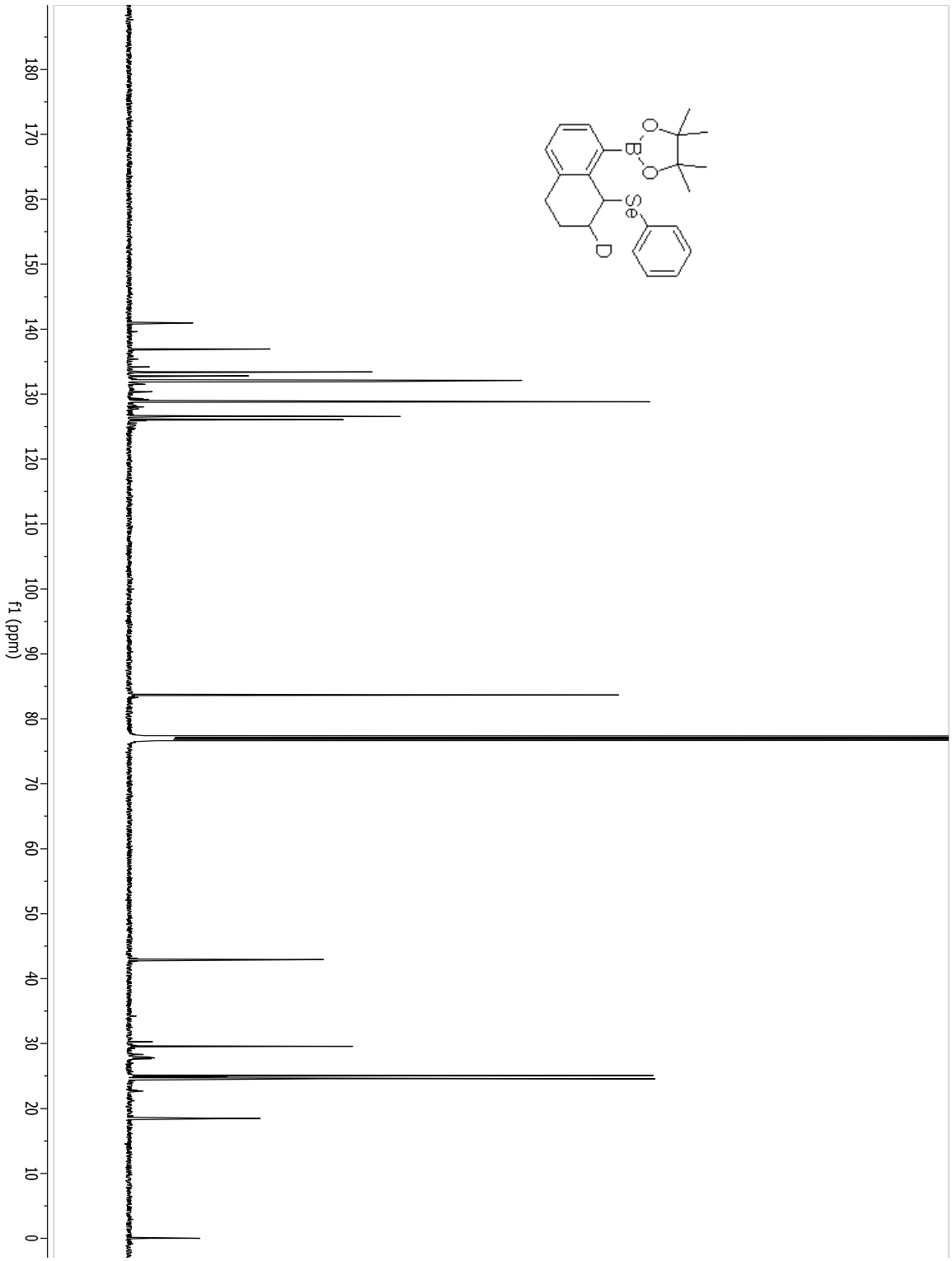


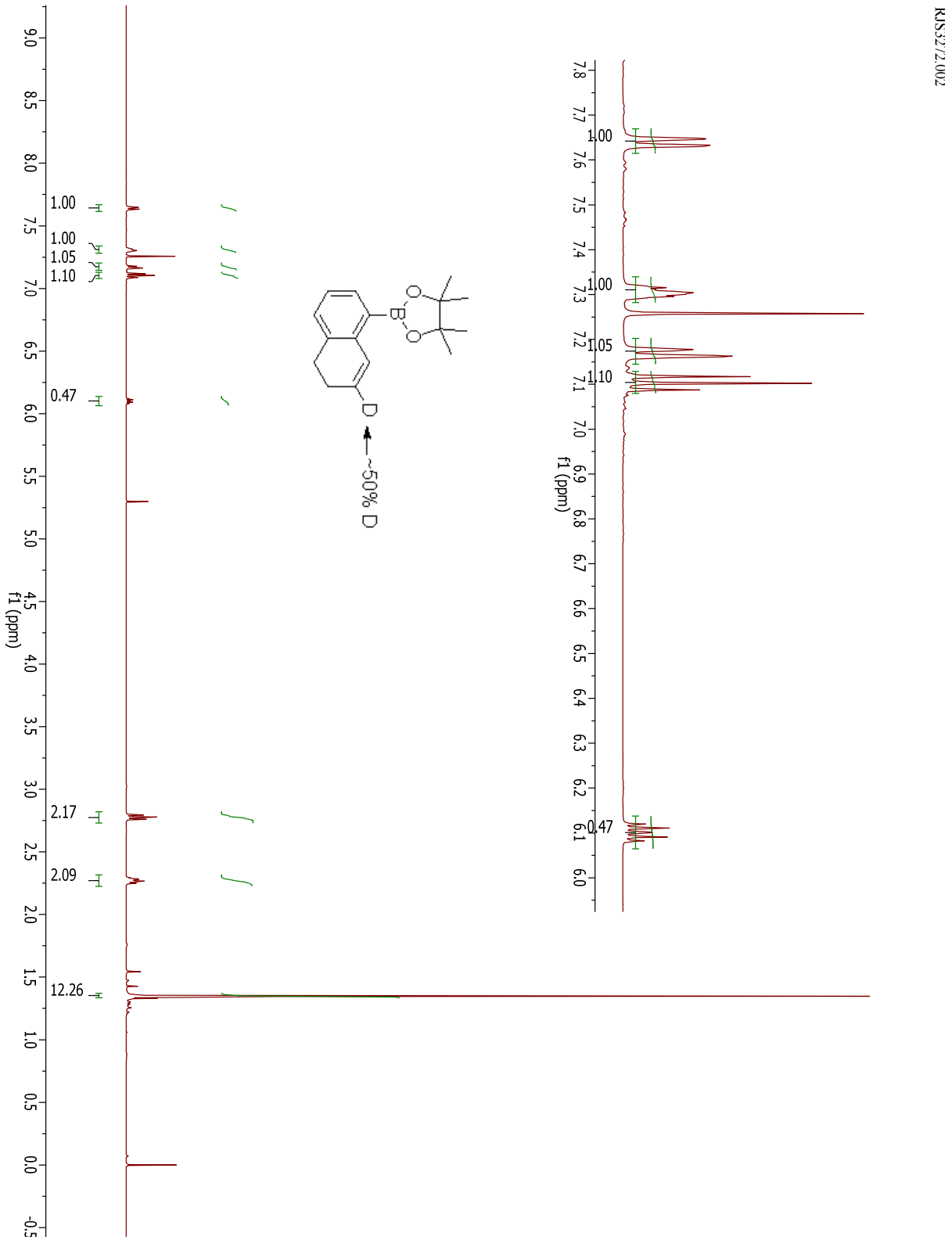
8-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)]-1-(phenylselenyl)(2-D)-1,2,3,4-tetrahydronaphthalene



8-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)]-1-(phenylselenyl)(2-D)-1,2,3,4-tetrahydronaphthalene



8-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)]-2-deutero-3,4-dihydronaphthalene



8-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)]-2-deutero-3,4-dihydronaphthalene