A short synthesis of delavatine A unveils new insights into site-selective cross-coupling of 3,5-dibromo-2-pyrone

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Supporting Information

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1 General Considerations

Unless otherwise noted, all reactions were performed in flame or oven-dried glassware fitted with rubber septa under a positive pressure of nitrogen using standard Schlenk techniques. Air- and moisture-sensitive liquids were transferred using syringe or stainless steel cannula through rubber septa. Solids were added under inert gas or were dissolved in appropriate solvents. Low temperature-reactions were carried out in a Dewar vessel filled with a cooling agent: acetone/dry ice (−78 °C), H_2O/ice (0 °C). Reaction temperatures above 23 °C were conducted in an oil bath or in a heated metal block (reactions conducted in vials). The reactions were magnetically stirred and monitored by NMR spectroscopy or analytical thin-layer chromatography (TLC), using glass plates precoated with silica gel (Silicycle Siliaplates, glass backed, extra hard layer, 60 Å, 250 μm thickness, F254 indicator). TLC plates were visualized by exposure to ultraviolet light (254 nm), were stained by submersion in aqueous potassium permanganate solution ($KMnO_4$) or ceric ammonium molybdate solution (CAM), and were developed by heating with a heat gun. Flash-column chromatography on silica gel was performed as described by Still et al.,[1] employing silica gel (Silicycle silica gel, 40–63 μm particle size). Organic solutions were concentrated under reduced pressure on a Heidolph temperature-controlled rotary evaporator equipped with a dry ice/isopropanol condenser. All yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) pure material.

1.1 Materials

Unless noted below, commercial reagents were purchased from MilliporeSigma, Acros Organics, Chem-Impex, Oakwood Chemical, Combi-blocks, TCI, and/or Alfa Aesar, and used without additional purification. Solvents were purchased from Fisher Scientific, Acros Organics, Alfa Aesar, and MilliporeSigma Aldrich. Tetrahydrofuran (THF), diethyl ether (Et_2O), acetonitrile (CH_3CN), benzene, toluene (PhMe), methanol (MeOH), and triethylamine (Et_3N) were sparged with argon and dried by passing through alumina columns using argon in a Glass Contour solvent purification system. Dichloromethane (CH_2Cl_2, DCM) was freshly distilled over calcium hydride under a N_2 atmosphere prior to each use.

1.2 NMR spectroscopy

NMR spectral data were obtained using deuterated solvents, obtained from Cambridge Isotope Laboratories, Inc. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker AVB-400, AVQ-400, AV-500, DRX-500, AV-600 or AV-700 spectrometers operating at 400 MHz, 400 MHz, 500 MHz, 500 MHz, 600 MHz, 700 MHz for proton nuclei (100 MHz, 100 MHz, 125 MHz, 125 MHz, 150 MHz, 175 MHz for carbon nuclei), respectively. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Carbon chemical shifts are expressed in parts per million (δ scale, assigned carbon atom) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$: δ 77.16). ^{1}H NMR spectroscopic data are reported as follows: Chemical shift in ppm (multiplicity, coupling constants *J* (Hz), integration) (e.g. "5.21 (t, ^3J = 7.3 Hz, 1H)"). The multiplicities are abbreviated as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), se (sextet), h (heptet), m (multiplet) and app (apparent multiplicity). In case of combined multiplicities, the multiplicity with the larger coupling constant is stated first. Except for multiplets, the chemical shift of all signals, as well for centrosymmetric multiplets, is reported as the center of the resonance range. In addition to 1D NMR experiments, 2D NMR techniques such as homonuclear correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond coherence (HMBC) and nuclear Overhauser enhancement spectroscopy (NOESY) were used to assist structure elucidation. All raw FID files were processed and the spectra analyzed using the program *MestReNOVA 11.0* from *Mestrelab Research S. L*.

Note: The AVB-400, AVQ-400, AV-500, DRX-500 and AV-600 instruments were partially supported by NIH grants SRR023679A, RR02424A-01, S10RR03353-01 and 1S10RR016634-01, and NSF grants CHE-9633007, CHE-8208992, CHE-0130862, and CHE-8703048. The AV-700 instrument was supported by the Berkeley College of Chemistry NMR facility.

1.3 Mass spectrometry

Mass spectral data were obtained from the Catalysis Facility at the University of California, Berkeley, on a PerkinElmer AxION 2 UHPLC-TOF system (ESI). Data acquisition and processing were performed using the XcaliburTM software.

1.4 IR spectroscopy

IR spectroscopic data were recorded on a Bruker ALPHA FT-IR spectrophotometer using a diamond attenuated total reflectance (ATR) accessory. If required, substances were dissolved in dichloromethane prior to direct application on the ATR unit. Data are represented as follows: frequency of absorption (cm^{-1}), and intensity of absorption (s = strong, m = medium, w = weak, br = broad).

1.5 Optical rotation

Optical rotation values were recorded on a Perkin-Elmer 241 polarimeter using the Na D-line (path length 1 dm, cell volume 1 mL). The specific rotation is calculated as follows:

$$[\alpha]_{\lambda}^{\varphi} = \frac{[\alpha] \times 100}{c \times d}$$

The wavelength (λ) is reported in nm and the measuring temperature (φ) in °C. The term α represents the recorded optical rotation, *c* the concentration of the analyte in 10 mg/mL and *d* the length of the cuvette in dm. Thus, the specific rotation is given in $10^{-1}\cdot deg\cdot cm^2\cdot g^{-1}$. Usage of the sodium D line (λ = 589 nm) is indicated by D instead of the wavelength in nm. The respective concentration as well as the solvent is reported at the relevant section of the experimental section.

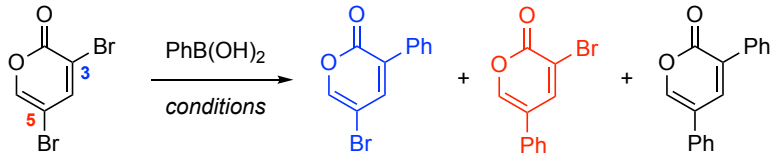
1.6 X-ray analysis

Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of all compounds were performed on a Rigaku XtaLAB P200 rotating anode equipped with a Pilatus 200K hybrid pixel array detector. Data were collected using Cu Kα radiation (λ = 1.54184 Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with CrysAlis^{Pro}.[2] Data processing was done using CrysAlis^{Pro} and included either a multi-scan absorption or face-indexed absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis^{Pro}. All structures were solved with SHELXT.[3] Structures were refined with SHELXL.[4] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were either included at the geometrically calculated positions and refined using a riding model or located as Q peaks in the Fourier difference map.

Note: The instruments are supported by an NIH Shared Instrumentation Grant S10-RR027172.

2 Site-selective cross coupling results

2.1 Site-selective Suzuki coupling with 3,5-dibromo-2-pyrone



8 **9** **10** **11**

General procedure for Suzuki couplings

An oven-dried vial was charged with a magnetic stir bar, 3,5-dibromo-2-pyrone[5] (1.0 equiv), phenylboronic acid (1.2 equiv), tetrakis(triphenylphosphine)palladium(0) (10 mol%), copper(I) iodide (1.0 equiv), and potassium carbonate (2.0 equiv). The vial was flushed with nitrogen and sealed with a septum cap. After addition of the appropriate solvent to achieve a concentration of 0.1 M, the vial was placed in a preheated (reported temperature) heating block. Stirring was continued at this temperature for the indicated time period. The mixture was then cooled to 23 °C, concentrated in vacuo, and the residue was filtered through a short pad of silica gel (8:1, hexanes:ethyl acetate) in order to remove polar impurities. The filtrate was concentrated in vacuo, and the residue was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Table S1 summarizes the results of the site-selective Suzuki coupling with 3,5-dibromo-2-pyrone.

Table S1. Site-selective Suzuki couplings with 3,5-dibromo-2-pyrone

	ε[6]	Solvent	yield[a] (%) **9:10:11** temp, time			
			rt (w/o CuI)	Δ (w/o CuI)	rt (w/ CuI)	Δ (w/ CuI)
increasing polarity ↑	47	DMSO	nr 23 °C, 14 h	--[b] 50 °C, 14 h	nd:12(21):nd 23 °C, 12 h	8(10):13(17):nd 50 °C, 14 h
	38.25	DMF	nr 23 °C, 15 h	3:nd:nd 50 °C, 15 h	nd:18(34):nd 23 °C, 20 h	15(19):37(46):nd 50 °C, 15 h
	21.01	acetone	nr 23 °C, 17 h	53:nd:nd 60 °C, 17 h	6(10):32(48):nd 23 °C, 16 h	16:29:nd 60 °C, 17 h
	10.42	DCE	nr 23 °C, 16 h	70:nd:nd 70 °C, 15 h	57(63):13(15):nd 23 °C, 16 h	58:4:11 70 °C, 15 h
	7.52	THF	nr 23 °C, 15 h	47:nd:19 70 °C, 14 h	27(54):8(16):nd 23 °C, 15 h	49:17:nd 70 °C, 14 h
	2.38	toluene	nr 23 °C, 17 h	52:nd:nd 100 °C, 4 h	55(70):2(3):nd 23 °C, 17 h	56:1:6 100 °C, 4 h

[a]Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The yields in bracket indicate the yield based on recovered starting material. [b]Decomposition of **8**. nr = no reaction, nd = not detectable. Dielectric constants t T = 20 °C.[6]

Data for C3-coupled product **9**:

Appearance: pale yellow solid
TLC (5:1, hexanes:ethyl acetate): R_f = 0.50 (UV/$KMnO_4$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.59 (d, *J* = 2.6 Hz, 1H), 7.47 (d, *J* = 2.6 Hz, 1H), and 7.46 – 7.37 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 148.4, 142.1, 133.5, 129.5, 129.4, 128.7, 128.4, and 101.4.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3079 (m), 3058 (m), 3030 (w), 1720 (s), 1610 (m), 1544 (w), 1447 (w), 1191 (m), 1050 (w), 850 (m), 785 (m), 735 (w), 694 (m), 623 (m), and 550 (w).
HRMS (APCI): calcd for ([M+H], $C_{11}H_8BrO_2)^+$: 250.9702, found: 250.9703.
mp: 62–65 °C.
The characterization data for **9** are in full agreement with values previously reported.[7]

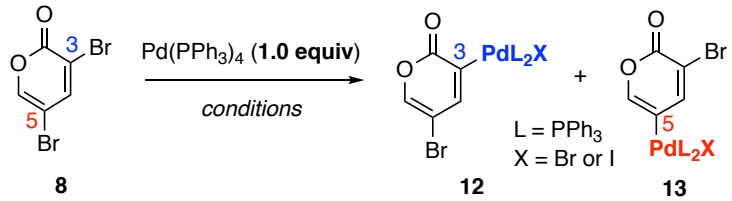
Data for C5-coupled product **10**:

Appearance: off-white solid
TLC (5:1, hexanes:ethyl acetate): R_f = 0.42 (UV/$KMnO_4$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.3 Hz, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), and 7.50 – 7.35 (m, 5H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 147.2, 145.3, 132.5, 129.5, 128.9, 126.3, 121.7, and 112.8.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3094 (w), 3059 (w), 2922 (w), 2853 (w), 1738 (s), 1716 (m), 1199 (w), 973 (w), 859 (w), 760 (w), and 696 (w).
HRMS (APCI): calcd for ([M+H], $C_{11}H_8BrO_2)^+$: 250.9702, found: 250.9706.
mp: 83–95 °C.
The characterization data for **10** are in full agreement with values previously reported.[7]

Data for *bis*-coupled product **11**:

Appearance: pale yellow oil.
TLC (5:1, hexanes:ethyl acetate): R_f = 0.33 (UV/$KMnO_4$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.6 Hz, 1H), 7.74 – 7.68 (m, 3H), and 7.50 – 7.37 (m, 8H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 147.2, 140.6, 134.7, 133.9, 129.4, 129.0, 128.6, 128.5, 128.4, 128.1, 126.2, and 121.5.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3057 (m), 3030 (m), 2923 (w), 2853 (w), 1707 (s), 1635 (w), 1602 (w), 1549 (w), 1497 (w), 1450 (w), 1342 (w), 1309 (w), 1194 (m), 1104, 1010, 972, 863 (m), 788 (m), 760 (m), 745 (m), 694 (s), and 593 (w).
HRMS (ESI): calcd for ([M+H], $C_{17}H_{13}O_2)^+$: 249.0910, found: 249.0907.

2.2 Oxidative addition experiment with equimolar tetrakis(triphenylphosphine)palladium(0)



8 **12** **13**

General procedure for the oxidative addition experiment

An oven-dried vial was charged with a magnetic stir bar, 3,5-dibromo-2-pyrone[5] (1.0 equiv), tetrakis(triphenylphosphine)palladium(0) (1.0 equiv), and copper(I) iodide (1.0 equiv). The vial was flushed with nitrogen and sealed with a septum cap. After addition of the appropriate solvent (to achieve a concentration of 0.1 M), the vial was placed in a preheated (reported temperature) heating block. Stirring was continued at this temperature for the indicated time period. The mixture was then cooled to 23 °C, concentrated in vacuo and the residue was filtered through a short pad of silica gel (3:1, hexanes:ethyl acetate) in order to remove non-polar impurities. The filtrate was concentrated in vacuo, and the residue was analyzed by ^{1}H NMR spectroscopy. Table S2 summarizes the ratio of C3-Pd complex **12** to C5-Pd complex **13** formed under various reaction conditions.

Table S2. Oxidative addition experiments with stoichiometric amount of Pd(0).

Entry	Conditions	Ratio (12:13)
1	toluene, RT, 12 h	1:0
2	toluene, 100 °C, 4 h	1:0
3	toluene, CuI, RT, 12 h	1:0
4	toluene, CuI, 100 °C, 4 h	1:0
5	DMF, RT, 12 h	1:0
6	DMF, 50 °C, 12 h	1:0
7	DMF, CuI, RT, 12 h	1:0
8	DMF, CuI, 50 °C, 12 h	1:tr
9	DMF, CuI, RT, 10 min	1:0
10	DMF, CuI, –40 to –10 °C, 1 h	1:0
11	DMSO, CuI, 50 °C, 1.5 h	1:tr
12	acetone, CuI, 60 °C, 12 h	1:0

Conditions = 3,5-dibromo-2-pyrone **8** (1.0 equiv), $Pd(PPh_3)_4$ (1.0 equiv), CuI (w/ or w/o, 1.0 equiv), and solvent (0.1 M). Δ = higher temperature. tr = trace amount observed.

Data for C3-Pd complex **12-trans**:

Appearance: yellow solid
TLC (3:1, hexanes:ethyl acetate): R_f = 0.27 (UV/$KMnO_4$)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.65 (m, 12H), 7.45 – 7.30 (m, 18H), 6.57 – 6.52 (m, 1H), and 6.42 – 6.37 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2 (t, *J* = 3.2 Hz), 154.1 (t, *J* = 5.4 Hz), 147.5 (t, *J* = 5.3 Hz), 143.5, 135.0 (t, *J* = 6.3 Hz), 134.9 (t, *J* = 6.5 Hz), 130.8 (t, *J* = 23.9 Hz), 130.5, 128.3 (t, *J* = 5.4 Hz), 128.3 (t, *J* = 5.3 Hz), and 101.4.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3074 (w), 3054 (m), 3021 (w), 3005 (w), 2988 (w), 2244 (w), 2227 (w), 1684 (s), 1598 (w), 1480 (w), 1433 (s), 1094 (s), 906 (s), 725 (s), 690 (s), and 508 (s).
HRMS (ESI): calcd for ([M–Br], $C_{41}H_{32}BrO_2P_2Pd)^+$: 803.0090, found: 803.0088.
mp: Decomposed at 180 °C.
The characterization data for **12** are in full agreement with values previously reported.[7]

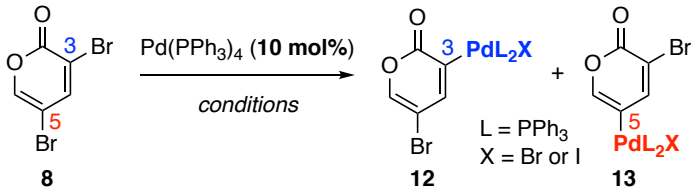
Recrystallization (ethyl acetate/dichloromethane) of the product gave crystals suitable for X-ray diffraction (see Section 5).

Data for C5-Pd complex **13-trans**:

Appearance: orange solid
TLC (3:1, hexanes:ethyl acetate): R_f = 0.35 (UV/$KMnO_4$)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 12H), 7.47 – 7.35 (m, 18H), 6.51 (s, 1H), and 6.27 (s, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 150.8, 144.3, 135.3 (t, *J* = 6.0 Hz), 134.7 (t, *J* = 6.3 Hz), 131.0, 130.1 (t, *J* = 23.8 Hz), 128.6 (t, *J* = 5.1 Hz), and 110.7.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3076 (w), 2955 (m), 2924 (s), 2854 (m), 2243 (w), 1729 (s), 1716 (s), 1435 (s), 1099 (m), 910 (m), 731 (s), 693 (s), 522 (m), and 513 (m).
HRMS (ESI): calcd for ([M–Br], $C_{41}H_{32}BrO_2P_2Pd)^+$: 803.0090, found: 803.0091.
mp: Decomposed at 90 °C.
The characterization data for **13** were in full agreement with values previously reported.[7]

Recrystallization (ethyl acetate/dichloromethane) of the product gave crystals suitable for X-ray diffraction (see Section 5).

2.3 Oxidative addition experiment with catalytic tetrakis(triphenylphosphine)palladium(0)



General procedure for the oxidative addition experiment

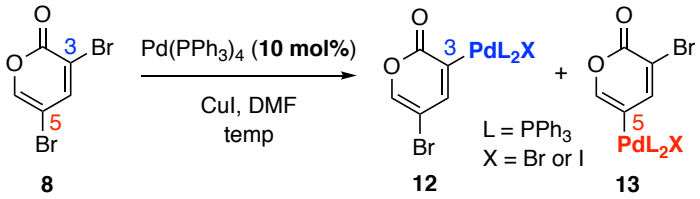
An oven-dried vial was charged with a magnetic stir bar, 3,5-dibromo-2-pyrone[5] (1.0 equiv), and copper(I) iodide (1.0 equiv). The vial was flushed with nitrogen and sealed with a septum cap. After addition of the appropriate solvent (to bring the concentration to 0.1 M), the vial was placed in a preheated (reported temperature) heating block. Tetrakis(triphenylphosphine)palladium(0) (10 mol%) was added in one portion to the reaction mixture at this temperature and stirring was continued for the indicated time period. The mixture was then cooled to 23 °C, and diluted with saturated aqueous ammonium chloride solution, and diethyl ether. The layers were separated, the aqueous layer was extracted with diethyl ether and the combined organic extracts were washed with saturated aqueous sodium chloride solution. The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was filtered through a short pad of silica gel (3:1, hexanes:ethyl acetate) in order to remove non-polar impurities. The filtrate was then concentrated in vacuo, and the residue was analyzed by ^{1}H NMR spectroscopy. Table S3 summarizes the observed ratio of C3-Pd complex **12** to C5-Pd complex **13** formed under various reaction conditions.

Table S3. Oxidative addition experiments with catalytic amount of Pd(0).

Solvent	yield[a] (%) **12:13** temp, time			
	rt (w/o CuI)	Δ (w/o CuI)	rt (w/ CuI)	Δ (w/ CuI)
DMF	31:nd 23 °C, 15 min	39:nd 50 °C, 15 min	11:20 23 °C, 15 min	14:23 50 °C, 15 min
toluene	32:nd 23 °C, 15 min	50:nd 100 °C, 15 min	29:nd 23 °C, 15 min	50:nd 100 °C, 15 min

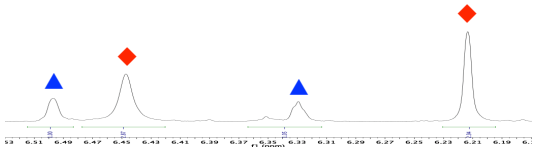
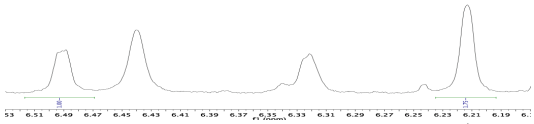
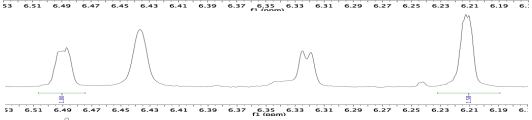
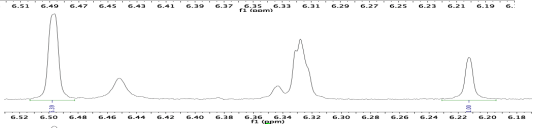
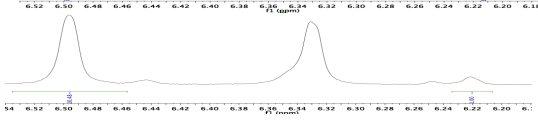
[a]Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The NMR yields with respect to the amount of $Pd(PPh_3)_4$ used (10 mol%). nd = not detectable.

2.4 Experiments to demonstrate effect of temperature on the ratio of C3 to C5-Pd complex.



Following the results of the oxidative addition experiments using a catalytic amount of tetrakis(triphenylphosphine)palladium(0), we conducted further studies to understand the relative stabilities of C3-Pd complex **12** and C5-Pd complex **13**. We chose to conduct these experiments at varying temperatures, in *N*,*N*-dimethylformamide (0.1 M) and in the presence of copper(I) iodide (1.0 equiv), since formation of C5-Pd complex **13** was observed only under these conditions (Table S3). The experimental observations of the ratio of **12** to **13** formed at different temperatures is presented in Table S4.

Table S4. Oxidative addition experiments conducted at different temperatures.

temp	NMR spectra showing 12 and 13	Ratio (12:13)
0 °C		0.34:1
RT		0.57:1
50 °C		0.63:1
70 °C		5:1
100 °C		10.5:1

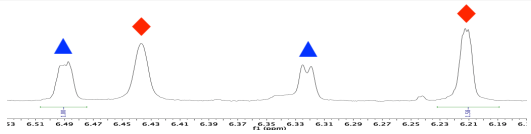
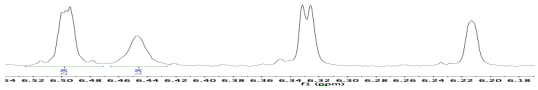
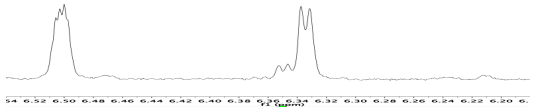
▲ = C3-Pd complex **12**. ◆ = C5-Pd complex **13**.

From these experiments, it was deduced that formation of C3-Pd complex **12** is observed at higher temperature, while formation of C5-Pd complex **13** is favored at lower temperature. Consequently we hypothesized that C3-Pd complex **12** is *thermodynamically* favored, while C5-Pd complex **13** is *kinetically* favored.

Further experiments were then carried out in order to investigate the interconversion between C3-Pd complex **12** and C5-Pd complex **13**. An oxidative addition experiment with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (10 mol%) in *N*,*N*-dimethylformamide (0.1 M) and in the presence of copper(I) iodide (1.0 equiv) was conducted at 50 °C. After 15 min, an aliquot of the reaction

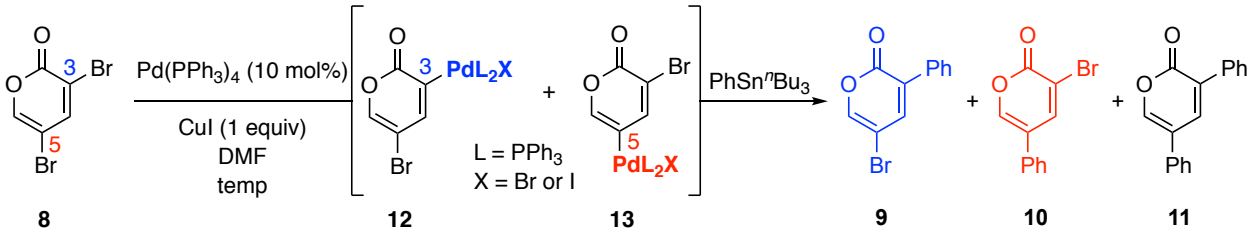
mixture was analyzed by ^{1}H NMR spectroscopy, while the remaining mixture was heated to 100 °C and held at this temperature. Table S5 summarizes the observed ratios of C3 to C5-Pd complexes (**12**:**13**) formed at varying time intervals. These experiments highlight that C5-Pd complex **13** converts to C3-Pd complex **12** as the reaction mixture is heated over a period of time. This corroborates the hypothesis that C3-Pd complex **12** is *thermodynamically* favored, and that C5-Pd complex **13** interconverts to the C3-Pd complex **12** at higher temperature.

Table S5. Oxidative addition experiments demonstrating the interconversion between 12 and 13.

temp, time	NMR spectra showing 12 and 13	Ratio (12:13)
50 °C, 15 min		0.67:1
100 °C, 15 min		2:1
100 °C, 4 h		1:tr

▲ = C3-Pd complex **12**. ◆ = C5-Pd complex **13**. tr = trace.

2.5 Experiment to demonstrate the difference in the rate of transmetallation between 12 and 13.



Since the oxidative addition experiments demonstrate that C3-Pd complex **12** is *thermodynamically* favored and that C5-Pd complex **13** interconverts to C3-Pd complex **12** at higher temperature, we also sought to investigate how the ratio of Pd complexes (**12**:**13**) would translate to the ratio of the subsequently formed cross-coupled products. Toward this end, we decided to conduct the oxidative addition experiment, analyze the ratio of the intermediate Pd complexes **12**:**13** after a certain time period, and then add a cross-coupling partner. Tributylphenylstannane was chosen as the cross-coupling partner in these experiments.

An oven-dried vial was charged with a magnetic stir bar, 3,5-dibromo-2-pyrone[5] (1.0 equiv), and copper(I) iodide (1.0 equiv). The vial was flushed with nitrogen and sealed with a septum cap. *N*,*N*-dimethylformamide (0.1 M) was added, and the vial was placed in a preheated (reported temperature) heating block. Tetrakis(triphenylphosphine)palladium(0) (10 mol%) was added in one portion to the reaction mixture. Stirring was continued at this temperature for the indicated time period. An aliquot of the reaction mixture was analyzed by ^{1}H NMR spectroscopy to determine the ratio of **12**:**13**. Tributylphenylstannane (1.2 equiv) was then added in one portion, and the reaction mixture was heated at 50 °C. After 3 h, the mixture was cooled to 23 °C, and diluted with saturated aqueous ammonium chloride solution and diethyl ether. The layers were separated, the aqueous layer was extracted with diethyl ether and the combined organic extracts were washed with saturated aqueous sodium chloride solution. The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The residue was analyzed by ^{1}H NMR spectroscopy and if necessary was purified by flash chromatography. The results of these experiments are summarized in Table S6.

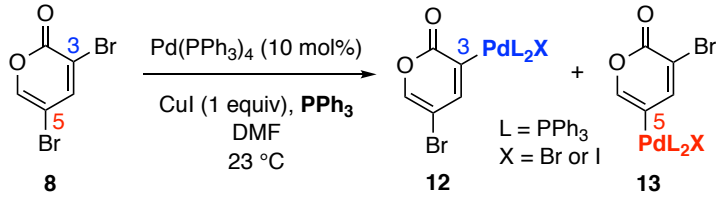
Table S6. Experiments to demonstrate the difference in rate of transmetallation between 12 and 13.

temp, time	Ratio (12:13)	Comments
50 °C, 15 min	0.67:1	Only C5 coupled product **10** (51%, 59% brsm)[a] observed
100 °C, 15 min	10.5:1	Only C5 coupled product **10** (80%) isolated

[a]Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

These experimental results highlight that C3-Pd complex **12** can also interconvert to C5-Pd complex **13**. Moreover, C5-Pd complex **13** transmetallates at a faster rate than C3-Pd complex **12**, thus leading to exclusive formation of C5 coupled product **10** in these experiments.

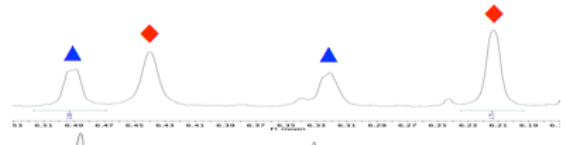
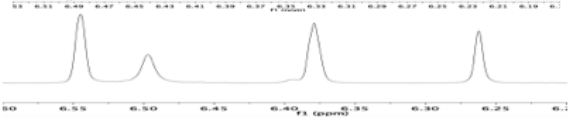
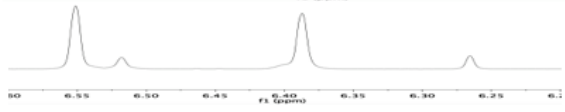
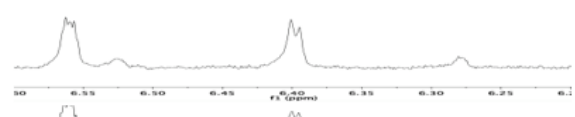
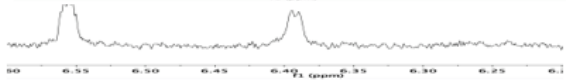
2.6 Experiment to demonstrate the effect of triphenylphosphine on the ratio of C3 to C5-Pd complex.



We next aimed to gain experimental evidence to support the mono-phosphine ligated Pd complex pathway (see computational studies) and regarding the preferred formation of C5-Pd complex **13** and C3-Pd complex **12** under kinetic and thermodynamic conditions, respectively. For this purpose, we decided to analyze the ratio of C3 and C5-Pd complexes **12**:**13** formed in the oxidative addition experiment depending on the amount of triphenylphosphine.

An oven-dried vial was charged with a magnetic stir bar, 3,5-dibromo-2-pyrone[5] (1.0 equiv), copper(I) iodide (1.0 equiv), and triphenylphosphine (equivalents stated in Table 7). The vial was flushed with nitrogen and sealed with a septum cap. *N*,*N*-dimethylformamide (0.1 M) was added, and tetrakis(triphenylphosphine)palladium(0) (10 mol%) was added in one portion to the resulting reaction mixture at 23 °C. After 15 min, the mixture was diluted with saturated aqueous ammonium chloride solution, and diethyl ether. The layers were separated, the aqueous layer was extracted with diethyl ether and the combined organic extracts were washed with saturated aqueous sodium chloride solution. The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was filtered through a short pad of silica gel (3:1, hexanes:ethyl acetate) in order to remove non-polar impurities. The filtrate was then concentrated in vacuo, and the residue was analyzed by ^{1}H NMR spectroscopy. Table S7 summarizes the observed ratio of C3-Pd complex **12** to C5-Pd complex **13** formed with varying equivalents of triphenylphosphine.

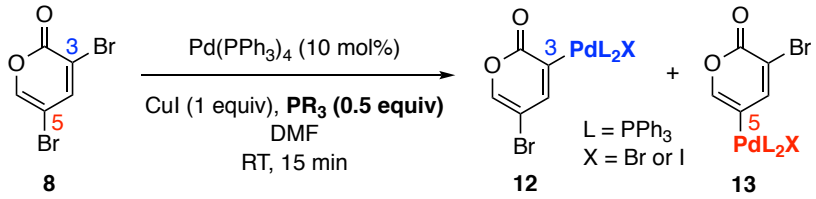
Table S7. Oxidative addition experiments demonstrating the effect of triphenylphosphine.

PPh_3 (equiv)	NMR spectra showing 12 and 13	Ratio (12:13)
0		1:1.75
0.5		1:0.60
1		1:0.19
2		1:0.15
5		only trace **12**

▲ = C3-Pd complex **12**. ◆ = C5-Pd complex **13**. tr = trace.

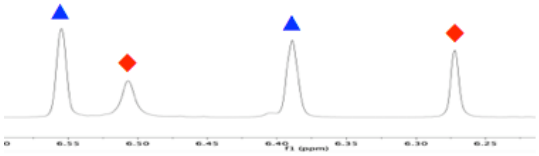
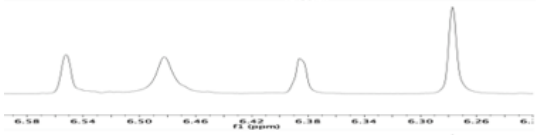
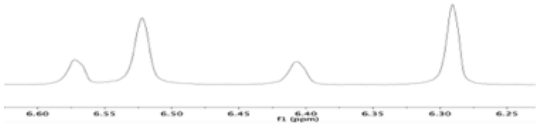
From the result of these experiments, it can be deduced that C5-Pd complex **13** is kinetically favored at lower triphenylphosphine concentration, while C3-Pd complex **12** is kinetically favored at higher triphenylphosphine concentration. These results support the hypothesis of the computational studies, where at lower triphenylphosphine concentration the oxidative addition proceeds mostly through the mono-phosphine ligated Pd complex pathway that kinetically favors C5-Pd complex **13**, while at higher triphenylphosphine concentration the oxidative addition proceeds via the bis-phosphine ligated Pd complex pathway that kinetically favors C3-Pd complex **12**.

2.7 Experiment to demonstrate the effect of other phosphine ligands on the ratio of C3 to C5-Pd complex.



Following the experimental result using varying concentrations of triphenylphosphine in the oxidative addition experiment, we were intrigued to also investigate the effect of other phosphine ligands on this transformation. We especially focused on using phosphine ligands that are sterically bulkier yet exhibit a similar electronic nature when compared to that of triphenylphosphine. Toward this end, we decided to use tri-1-naphthylphosphine and tri(*o*-tolyl)phosphine ligands. The reactions were conducted with 0.5 equivalents of the phosphine ligands. Table S8 summarizes the observed ratio of C3-Pd complex **12** to C5-Pd complex **13** formed in the presence of the different phosphine ligands.

Table S8. Oxidative addition experiments demonstrating the effect of bulky phosphine ligands.

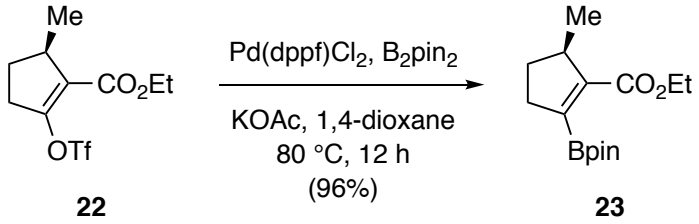
R group	NMR spectra showing 12 and 13	Ratio (12:13)
triphenylphosphine		1:0.60
tri-1-naphthylphosphine		1:1.8
tri(o-tolyl)phosphine		1:2.5

▲ = C3-Pd complex **12**. ◆ = C5-Pd complex **13**. tr = trace.

From the above results, it can be concluded that increasing the bulk of the phosphine ligand, leads to preferred formation of C5-Pd complex **13**. The hypothesis of the computational studies is thus further supported, as the mono-phosphine ligated Pd complex pathway is favored when bulky phosphine ligands are employed.

3 Synthesis of delavatine A

3.1 Synthesis of boronate ester 23

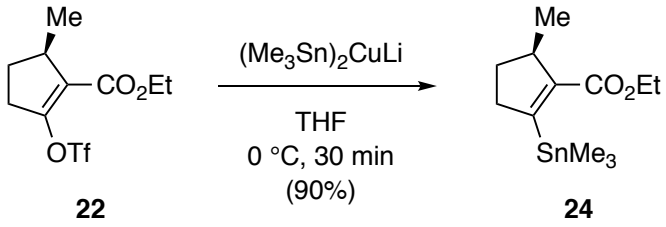


22 **23**

A round-bottomed flask was charged with [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1.69 g, 2.30 mmol, 3 mol%), bis(pinacolato)diboron (20.5 g, 80.7 mmol, 1.05 equiv), and potassium acetate (15.0 g, 153 mmol, 2.0 equiv). A solution of known vinyl triflate[8] **22** (23.1 g, 76.5 mmol, 1.0 equiv) in 1,4-dioxane (380 mL) was then added at 23 °C, and the resulting red mixture was heated to 80 °C and held at this temperature. After 12 h, the dark brown mixture was concentrated in vacuo, and the residue was suspended in ethyl acetate. The mixture was filtered through a pad of celite, the filtrate was concentrated and the residue was purified by flash-column chromatography on silica gel (30:1 → 5:1, hexanes:ethyl acetate) to give a mixture of boronate ester **23** and the corresponding boronic acid (20.0 g) in a ratio of 5:1 (as determined by ^{1}H NMR analysis). The mixture was dissolved in tetrahydrofuran (200 mL) and was treated with pinacol (2.0 g, 17 mmol, 1.4 equiv with resepct to the amount of boronic acid) and magnesium sulfate (0.50 g), and the resulting mixture was heated to 70 °C and held at this temperature. After 12 h, the reaction mixture was filtered through a pad of celite, and was concentrated in vacuo. The yellow residue was subjected to Kugelrohr distillation (110—115 °C, 0.25 torr) to distill off excess pinacol to provide the residual boronate ester **23** (20.6 g, 73.5 mmol, 96%) as a yellow oil.

TLC (5:1, hexanes:ethyl acetate): R_f = 0.52 and 0.22 (UV/$KMnO_4$) [Note: hydrolyzes during TLC analysis]
^{1}H NMR (700 MHz, $CDCl_3$) δ 4.25 – 4.15 (m, 2H), 3.05 – 2.98 (m, 1H), 2.64 – 2.57 (m, 1H), 2.49 – 2.42 (m, 1H), 2.18 – 2.11 (m, 1H), 1.57 – 1.51 (m, 1H), 1.323 (s, 6H), 1.319 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H), and 1.10 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 166.0, 147.7, 84.0, 60.2, 41.0, 35.4, 33.3, 24.91, 24.90, 19.6, and 14.5.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2977 (m), 2955 (m), 2932 (m), 2870 (w), 1708 (s), 1633 (w), 1355 (m), 1307 (s), 1142 (s), and 853 (m).
HRMS (ESI): calcd for ([M+H], $C_{15}H_{26}BO_4$)$^+$: 281.1919, found: 281.1916.
$[\alpha]^{20}_D$ = +4.4° (c = 1.15, $CHCl_3$)

3.2 Synthesis of stannane ester 24

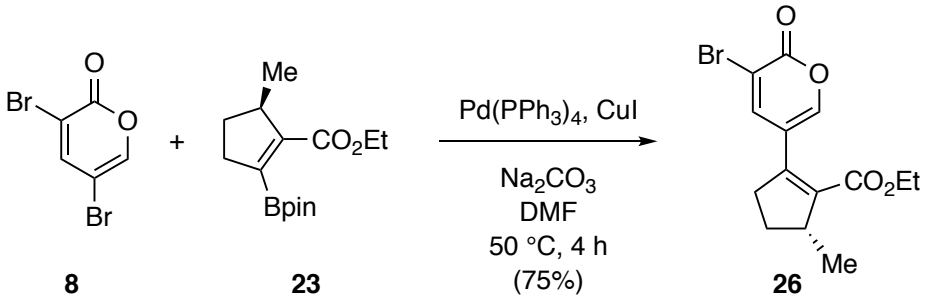


22 **24**

Stannane ester **24** was synthesized similarly to the reported procedure by Zhang et al.[9] A solution of vinyl triflate[8] **22** (2.38 g, 7.90 mmol, 1.0 equiv) in tetrahydrofuran (20 mL) was added to a stirred solution of $(Me_3Sn)_2CuLi$[10] (8.70 mmol, 1.1 equiv) in tetrahydrofuran (90 mL) at 0 °C. After 30 min, the black reaction mixture was diluted with saturated aqueous ammonium chloride solution (100 mL), and the resulting mixture was filtered through a pad of celite. The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 100 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (200 mL). The organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (20:1, pentanes:diethyl ether) to give stannane ester **24** (2.30 g, 7.10 mmol, 90%) as a pale yellow oil.

TLC (30:1, hexanes:ethyl acetate): R_f = 0.32 (UV/$KMnO_4$)
^{1}H NMR (700 MHz, $CDCl_3$) δ 4.22 – 4.17 (m, 2H), 3.07 – 3.00 (m, 1H), 2.65 – 2.57 (m, 1H), 2.55 – 2.47 (m, 1H), 2.16 – 2.08 (m, 1H), 1.58 – 1.52 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), and 0.17 (s, 9H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 166.5, 165.4, 148.9, 60.2, 40.8, 39.0, 33.6, 20.4, 14.5, and –8.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2976 (m), 2954 (m), 2870 (w), 1696 (s), 1367 (w), 1289 (m), 1245 (s), 770 (m), and 524 (w).
HRMS (APCI): calcd for ([M+Na], $C_{12}H_{22}NaO_2Sn)^+$: 341.0534, found: 341.0533.
$[\alpha]^{20}_D$ = –20.0° (c = 1.18, $CHCl_3$)

3.3 Synthesis of *mono*-coupled pyrone 26 via Suzuki-Miyaura coupling

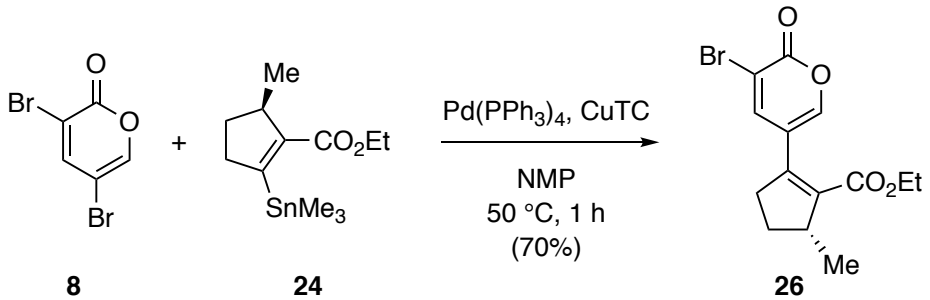


8 **23** **26**

A round-bottomed flask was charged with tetrakis(triphenylphosphine)palladium(0) (2.20 g, 1.90 mmol, 10 mol%), copper(I) iodide (3.56 g, 18.7 mmol, 1.0 equiv), and anhydrous sodium carbonate (3.95 g, 37.3 mmol, 2.0 equiv). A solution of 3,5-dibromo-2-pyrone[5] **8** (4.73 g, 18.7 mmol, 1.0 equiv) and boronate ester **23** (5.85 g, 20.9 mmol, 1.1 equiv) in *N*,*N*-dimethylformamide (180 mL) was then added at 23 °C, and the resulting brown mixture was heated to 50 °C and held at this temperature. After 4 h, the dark brown reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (100 mL), saturated aqueous ammonium chloride solution (50 mL), and diethyl ether (300 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 200 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (300 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (8:1, hexanes:ethyl acetate) to give *mono*-coupled pyrone **26** (4.60 g, 14.0 mmol, 75%) as a yellow oil.

TLC (5:1, hexanes:ethyl acetate): R_f = 0.31 (UV/$KMnO_4$)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 4.25 – 4.14 (m, 2H), 3.23 – 3.16 (m, 1H), 2.79 – 2.72 (m, 1H), 2.63 – 2.56 (m, 1H), 2.24 – 2.16 (m, 1H), 1.59 – 1.53 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), and 1.16 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 165.4, 157.6, 149.5, 146.0, 142.0, 137.8, 117.2, 110.8, 60.8, 42.3, 36.9, 30.6, 19.8, and 14.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2957 (m), 2929 (m), 2871 (w), 1744 (s), 1705 (s), 1246 (m), and 753 (w).
HRMS (ESI): calcd for ([M+Na], $C_{14}H_{15}BrNaO_4$)$^+$: 349.0046, found: 349.0046.
$[\alpha]^{20}_D$ = –2.7° (c = 1.05, $CHCl_3$)

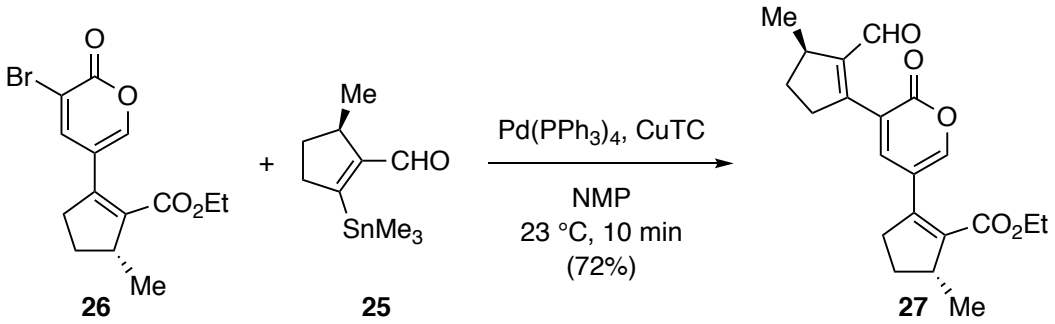
3.4 Synthesis of *mono*-coupled pyrone 26 via Stille coupling



8 **24** **26**

A round-bottomed flask was charged with 3,5-dibromo-2-pyrone[5] **8** (200 mg, 0.79 mmol, 1.0 equiv), stannane ester **24** (278 mg, 0.87 mmol, 1.1 equiv) and *N*-methylpyrrolidine (8 mL). Tetrakis(triphenylphosphine)palladium(0) (92.0 mg, 0.08 mmol, 10 mol%) and copper(I) thiophene-2-carboxylate (151 mg, 0.79 mmol, 1.0 equiv) were then sequentially added at 23 °C, and the resulting mixture was heated to 50 °C. After 1 h, the mixture was cooled to 23 °C, diluted with saturated aqueous sodium bicarbonate solution (10 mL) and diethyl ether (10 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (20 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (10:1, hexanes:ethyl acetate) to give *mono*-coupled pyrone **26** (182 mg, 0.56 mmol, 70%) as a yellow oil. The characterization data of **26** were in agreement with the values reported above.

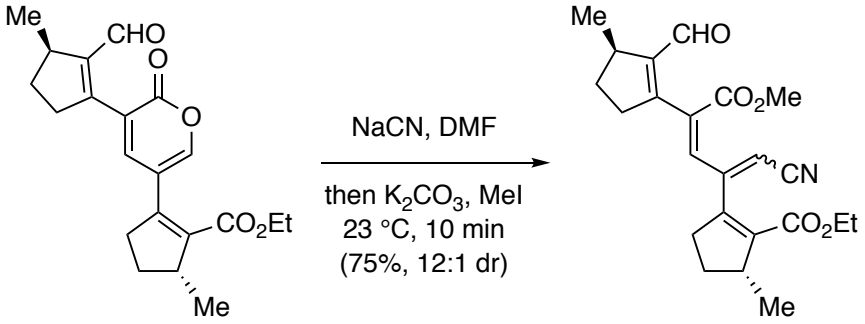
3.5 Synthesis of *bis*-coupled pyrone 27



Tetrakis(triphenylphosphine)palladium(0) (3.17 g, 2.70 mmol, 14 mol%), and copper(I) thiophene-2-carboxylate (5.75 g, 30.2 mmol, 1.5 equiv) were added sequentially to a solution of *mono*-coupled pyrone **26** (9.10 g, 27.8 mmol, 1.4 equiv) and stannane aldehyde[9] **25** (5.48 g, 20.0 mmol, 1.0 equiv) in *N*-methyl-2-pyrrolidone (200 mL) at 23 °C. After 10 min, the dark pink reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (100 mL), saturated aqueous ammonium chloride solution (50 mL), and diethyl ether (300 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 200 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (300 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (12:1 → 3:1, hexanes:ethyl acetate) to give recovered *mono*-coupled product **26** (2.66 g, 8.10 mmol), and *bis*-coupled pyrone **27** (5.10 g, 14.3 mmol, 72%) each as a yellow oil, in order of elution.

TLC (5:1, hexanes:ethyl acetate): R_f = 0.21 (UV/$KMnO_4$)
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.37 (d, *J* = 2.6 Hz, 1H), 4.24 – 4.13 (m, 2H), 3.22 – 3.15 (m, 2H), 3.06 – 2.99 (m, 1H), 2.90 – 2.84 (m, 1H), 2.81 – 2.74 (m, 1H), 2.64 – 2.58 (m, 1H), 2.25 – 2.15 (m, 2H), 1.62 – 1.54 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 5.3 Hz, 3H), and 1.16 (d, *J* = 5.2 Hz, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 189.4, 165.6, 159.4, 156.0, 150.6, 147.6, 144.2, 143.4, 137.5, 121.6, 116.5, 60.8, 42.1, 38.8, 36.8, 36.0, 31.1, 30.7, 19.9, 19.4, and 14.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2955 (m), 2937 (m), 2870 (w), 1728 (s), 1707 (s), 1665 (m), 1248 (w), and 1174 (w).
HRMS (ESI): calcd for ([M+H], $C_{21}H_{25}O_5$)$^+$: 357.1697, found: 357.1695.
$[\alpha]^{20}_D$ = +1.2° (c = 0.75, $CHCl_3$)

3.6 Synthesis of vinyl nitrile 28

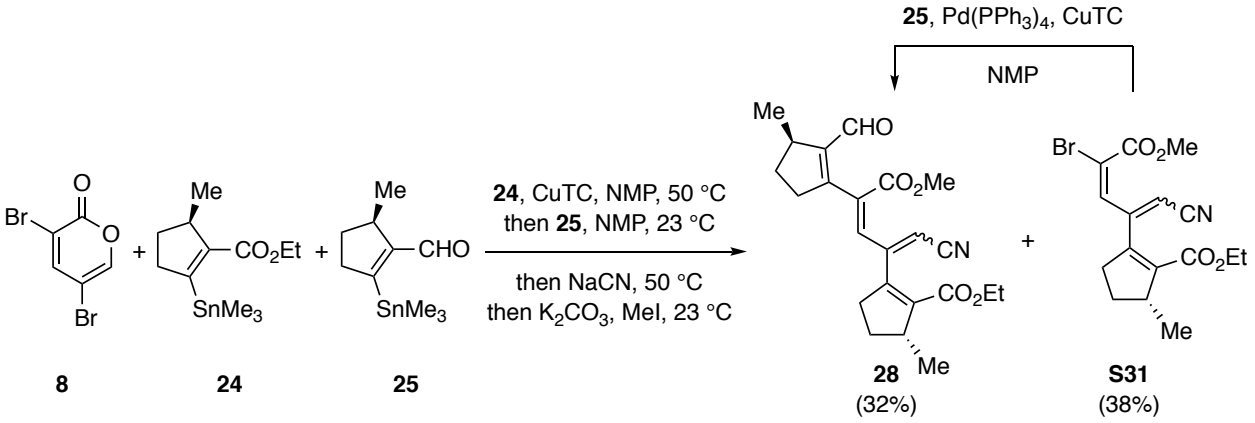


27 **28**

Sodium cyanide (356 mg, 7.25 mmol, 1.3 equiv) was added to a solution of *bis*-coupled pyrone **27** (2.00 g, 5.60 mmol, 1.0 equiv) in *N*,*N*-dimethylformamide (110 mL) at 23 °C. After 10 min, anhydrous potassium carbonate (3.90 g, 28.2 mmol, 5.0 equiv) and methyl iodide (1.80 mL, 28.9 mmol, 5.0 equiv) were sequentially added to the red reaction mixture. After 5 min, the reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (50 mL) and diethyl ether (200 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 200 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (200 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (5:1, hexanes:ethyl acetate) to give vinyl nitrile **28** (1.67 g, 4.20 mmol, 75%, 12:1 dr) as a yellow oil.

TLC (5:1, hexanes:ethyl acetate): R_f = 0.21 (UV/$KMnO_4$)
In cases where the proton or carbon atoms show a double set of signals, the signal of the second diastereomer is marked with an asterisk.
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.83* (s, 1H), 9.49 (s, 1H), 7.79 (d, *J* = 1.5 Hz, 1H), 6.84* (d, *J* = 1.3 Hz, 1H), 5.41 (d, *J* = 1.4 Hz, 1H), 5.40* (d, *J* = 1.3 Hz, 1H), 4.31 – 4.19* (m, 2H), 4.19 – 4.08 (m, 2H), 3.80 (s, 3H), 3.68* (s, 3H), 3.23 – 3.14* (m, 2H), 3.13 – 3.02 (m, 2H), 2.91 – 2.84 (m, 1H), 2.82 – 2.74* (m, 1H), 2.73 – 2.66* (m, 1H), 2.66 – 2.58 (m, 1H), 2.42 – 2.36 (m, 1H), 2.29 – 2.23 (m, 1H), 2.21 – 2.09* (m, 2H), 2.09 – 2.01 (m, 2H), 2.01 – 1.97* (m, 2H), 1.58 – 1.49 (m, 2H), 1.50 – 1.46* (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.23* (t, *J* = 7.1 Hz, 3H), 1.12* (d, *J* = 7.0 Hz, 3H), 1.10* (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 188.84*, 188.80, 169.0*, 166.0*, 164.87, 164.85, 164.7*, 156.0, 155.1*, 154.0*, 153.5, 150.2*, 147.8, 146.6*, 145.2, 141.1, 140.1*, 139.04, 139.02, 134.2*, 133.1*, 131.6, 115.9*, 115.6, 102.8*, 102.3, 61.4*, 61.2, 53.0, 42.5*, 42.3, 42.2*, 39.2*, 38.5, 37.3*, 36.8, 36.6*, 36.3*, 31.2, 30.6, 19.7*, 19.5*, 19.1, 18.9, 14.1*, and 14.02.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2957 (s), 2870 (w), 2844 (w), 2215 (m), 1711 (s), 1669 (s), 1448 (w), 1369 (w), 1234 (s), 1033 (m), and 768 (w).
HRMS (ESI): calcd for ([M+H], $C_{23}H_{28}NO_5$)$^+$: 398.1962, found: 398.1969.
$[\alpha]^{20}_D$ = +192.2° (c = 1.35, $CHCl_3$)

3.7 One-pot sequential Stille-Stille-cyanide opening reaction

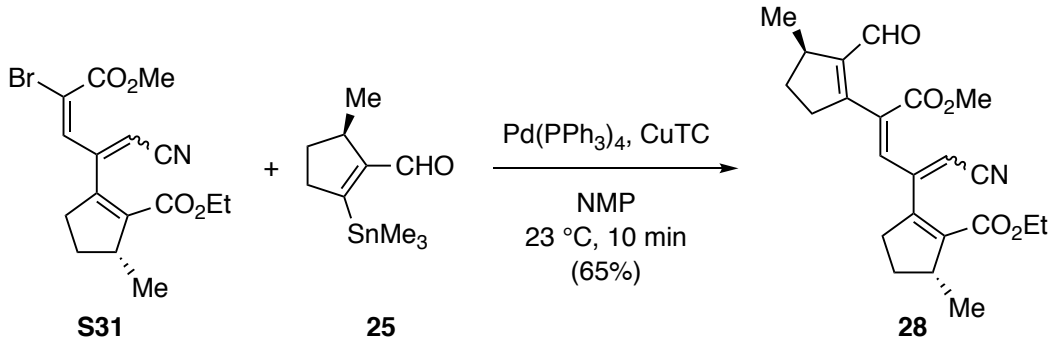


A round-bottomed flask was charged with 3,5-dibromo-2-pyrone **8** (151 mg, 0.60 mmol, 1.2 equiv), stannane ester **24** (210 mg, 0.66 mmol, 1.32 equiv) and *N*-methylpyrrolidine (3 mL). Tetrakis(triphenylphosphine)palladium(0) (58.0 mg, 0.05 mmol, 10 mol%) and copper(I) thiophene-2-carboxylate (114 mg, 0.60 mmol, 1.2 equiv) were then sequentially added at 23 °C, and the resulting mixture was heated to 50 °C. After 20 min, the mixture was cooled to 23 °C, whereupon a solution of stannane aldehyde[9] **25** (137 mg, 0.50 mmol, 1.0 equiv) in *N*-methylpyrrolidine (2 mL) was rapidly added via syringe. After 10 min, sodium cyanide (245 mg, 5.00 mmol, 10.0 equiv) was added to the intermediate mixture of *mono*- and *bis*-coupled pyrones. The resulting red mixture was warmed to 50 °C. After 10 min, TLC analysis indicated complete consumption of the pyrones and the mixture was cooled to 23 °C. Anhydrous potassium carbonate (1.38 g, 10.0 mmol, 20.0 equiv) and methyl iodide (0.62 mL, 10.0 mmol, 20.0 equiv) were then sequentially added. After 15 min, the mixture was diluted with saturated aqueous sodium bicarbonate solution (30 mL) and diethyl ether (30 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 30 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (40 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (12:1 to 3:1, hexanes:ethyl acetate) to give bromide **S31** (83.0 mg, 0.23 mmol, 38%) and vinyl nitrile **28** (64.0 mg, 0.16 mmol, 32%, 12:1 dr) each as a yellow oil, in order of elution. The characterization data of **28** were in agreement with the values reported above. Additionally, it was found that bromide **S31** can be converted to the desired vinyl nitrile **28** when coupled with stannane aldehyde **25** (see below for experimental procedure)

Data for bromide **S31**:

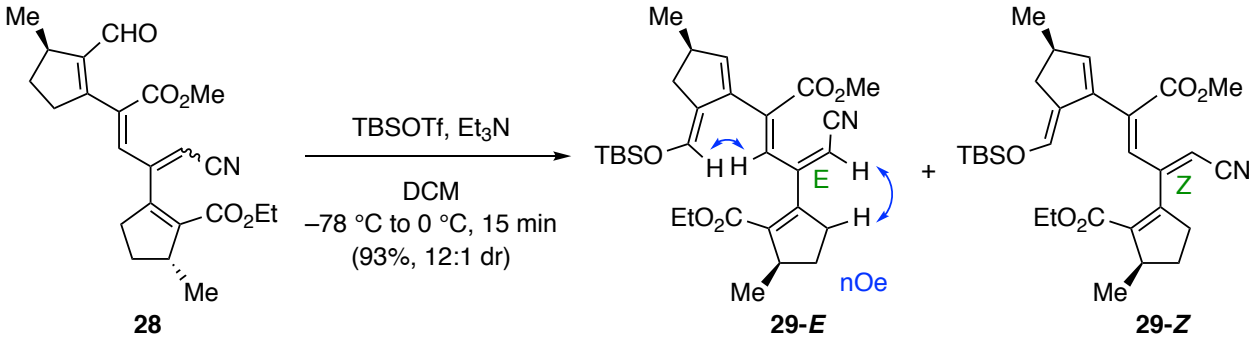
TLC (5:1, hexanes:ethyl acetate): R_f = 0.26 (UV/$KMnO_4$)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (s, 1H), 5.33 (s, 1H), 4.24 – 4.16 (m, 2H), 3.75 (s, 3H), 3.14 – 3.06 (m, 1H), 2.75 – 2.67 (m, 1H), 2.63 – 2.55 (m, 1H), 2.22 – 2.13 (m, 1H), 1.58 – 1.50 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), and 1.10 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 162.6, 153.2, 143.8, 141.4, 137.3, 117.4, 115.9, 99.0, 61.3, 53.4, 42.8, 36.2, 30.7, 19.3, and 14.2.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2957 (s), 2930 (s), 2870 (m), 2215 (m), 1710 (s), 1448 (m), 1300 (m), 1222 (s), 1178 (m), 1036 (m), and 816 (w).
HRMS (ESI): calcd for ([M+H], $C_{16}H_{19}BrNO_4$)$^+$: 368.0492, found: 368.0496.
$[\alpha]^{20}_D$ = +71.7° (c = 1.15, $CHCl_3$)

3.8 Synthesis of vinyl nitrile 28 from bromide S31



Tetrakis(triphenylphosphine)palladium(0) (15.7 mg, 0.013 mmol, 10 mol%), and copper(I) thiophene-2-carboxylate (25.9 mg, 0.136 mmol, 1.0 equiv) were added sequentially to a solution of bromide **S31** (50.0 mg, 0.136 mmol, 1.0 equiv) and stannane aldehyde[9] **25** (44.8 mg, 0.163 mmol, 1.2 equiv) in *N*-methyl-2-pyrrolidone (1.8 mL) at 23 °C. After 10 min, the dark reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (10 mL) and diethyl ether (20 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (20 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (4:1, hexanes:ethyl acetate) to give vinyl nitrile **28** (35.5 mg, 0.089 mmol, 65%, 12:1 dr) as a yellow oil. The characterization data of **28** were in agreement with the values reported above.

3.9 Synthesis of silyl enol ether 29



Tert-Butyldimethylsilyl trifluoromethanesulfonate (0.23 mL, 1.00 mmol, 5.0 equiv) was added dropwise to a solution of enal **28** (78.0 mg, 0.20 mmol, 1.0 equiv) and triethylamine (0.28 mL, 2.00 mmol, 10.0 equiv) in dichloromethane (4 mL) at –78 °C, and the resulting yellow reaction mixture was warmed to 23 °C. After 15 min, the bright yellow reaction mixture was diluted with aqueous sodium bicarbonate solution (5 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 × 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (5 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (15:1, hexanes:ethyl acetate) to give (*E*)-silyl enol ether **29-*E*** (86.0 mg, 0.17 mmol, 86%) and (*Z*)-silyl enol ether **29-*Z*** (7.00 mg, 0.01 mmol, 7%) each as a yellow oil, in order of elution.

Data for (*E*)-silyl enol ether **29-*E***:

TLC (8:1, hexanes:ethyl acetate): R_f = 0.32 (UV/$KMnO_4$)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 1H), 5.96 – 5.93 (m, 1H), 5.56 – 5.52 (m, 1H), 5.34 – 5.31 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.10 – 2.99 (m, 2H), 2.68 – 2.60 (m, 1H), 2.55 – 2.41 (m, 2H), 2.10 – 1.97 (m, 2H), 1.44 – 1.36 (m, 1H), 1.28 (d, *J* = 7.7 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), and 0.08 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 164.8, 155.3, 147.3, 139.1, 136.1, 136.0, 135.1, 133.73, 133.72, 133.4, 116.1, 101.3, 60.7, 52.6, 42.1, 40.8, 37.9, 33.9, 31.0, 25.7, 20.4, 19.7, 18.3, 14.2, –5.2, and –5.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2955 (s), 2930 (s), 2858 (w), 2214 (w), 1715 (s), 1435 (w), 1251 (s), 1167 (s), 839 (s), and 783 (m).
HRMS (ESI): calcd for ([M+Na], $C_{29}H_{41}NNaO_5Si)^+$: 534.2646, found: 534.2647.
$[\alpha]^{20}_D$ = –10.1° (c = 1.45, $CHCl_3$)

Data for (*Z*)-silyl enol ether **29-*Z***:

TLC (8:1, hexanes:ethyl acetate): R_f = 0.22 (UV/$KMnO_4$)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.23 (s, 1H), 5.97 (s, 1H), 5.59 (s, 1H), 5.54 – 5.51 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.14 – 3.06 (m, 2H), 2.73 – 2.61 (m, 2H), 2.57 – 2.50 (m, 1H), 2.13 – 2.06 (m, 1H), 2.06 – 2.00 (m, 1H), 1.55 – 1.48 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), and 0.08 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 164.1, 156.0, 148.5, 139.2, 137.3, 135.2, 134.3, 133.43, 133.40, 128.5, 116.3, 102.5, 60.4, 52.7, 41.1, 40.8, 37.3, 33.8, 31.2, 25.7, 20.4, 19.7, 18.3, 14.2, –5.2, and –5.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2956 (s), 2929 (s), 2857 (m), 2215 (w), 1714 (s), 1251 (s), 1165 (m), 839 (m), and 783 (w).
HRMS (ESI): calcd for ([M+Na], $C_{29}H_{41}NNaO_5Si)^+$: 534.2646, found: 534.2643.
$[\alpha]^{20}_D$ = –116.6° (c = 0.5, $CHCl_3$)

3.10 Synthesis of indane aldehyde 30

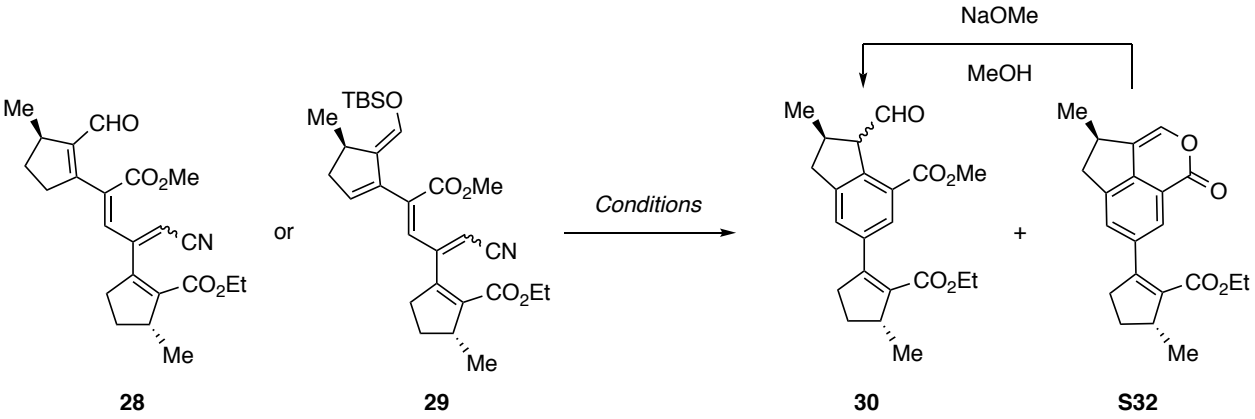


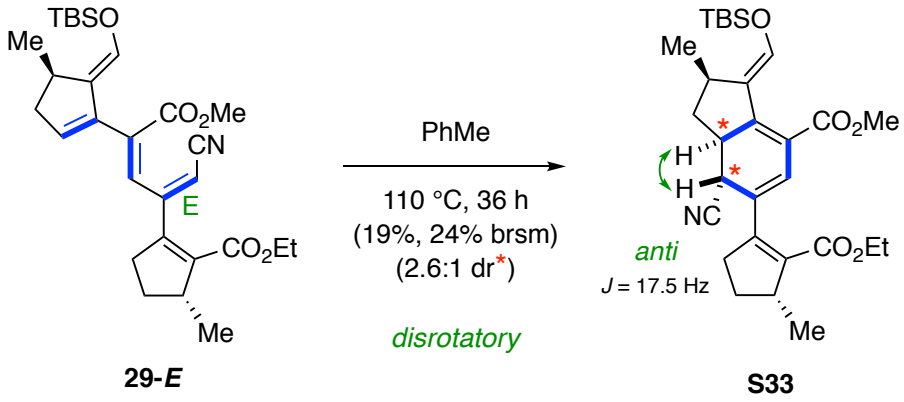
Table S9. Initial discovery and optimization of the cascade sequence.

Entry	Reactant	Conditions	Comments
1	**28**	KHMDS, THF, –78 °C	decomposed at –78 °C
2	**28**	NaHMDS, THF, –78 °C	decomposed at –78 °C
3	**28**	NaH, THF, –78 °C to 70 °C	decomposed at 70 °C
4	**28**	KHMDS, benzyl bromide, THF, –78 °C	decomposed at –78 °C
5	**28**	KHMDS, CBr_4, THF, –78 °C to 0 °C	decomposed at 0 °C
6	**28**	**TBSOTf, Et_3N, DCM, –78 °C**	**silyl enol ether 29 (93%) isolated**
7	**28**	DMSO, rt to 100 °C	decomposed at 100 °C
8	**28**	toluene, 100 °C	decomposed at 100 °C
9	**28**	bis(trimethylsilyl)acetamide, 110 °C	benzocoumarin **S32** (~10%) isolated
10	**29**	**1) PhMe, 110 °C, 2) DBU, PhMe**	**30 (15% over 2 steps, 1:0.7 dr) isolated**
11	**29**	Et_3N, PhMe, 120 °C	No reaction. Slow decomposition of **29**
12	**29**	DBU, PhMe, 120 °C	indane aldehyde **30** (23% over 2 steps) isolated
13	**28**	$(Me_3O)^+(BF_4)^-$, proton sponge, DCE, rt to 70 °C	No reaction. Slow decomposition of **28**
14	**28**	1) TMSOTf, Et_3N, DCM, 2) DBU, PhMe, 115 °C	messy reaction
15	**28**	**1) TIPSOTf, Et_3N, DCM, 2) DBU, PhMe, 115 °C, then TBAF**	**indane aldehyde 30 (26% over 2 steps) isolated**
16	**28**	TBSOTf, Et_3N, PhMe, then DBU, 115 °C, then TBAF	indane aldehyde **30** (30%) isolated
17	**28**	TBSOTf, Et_3N, PhMe, then DABCO, 115 °C	messy reaction
18	**28**	TBSOTf, Et_3N, toluene, BHT, then DBU, 115 °C	benzocoumarin **S32** (~20%) isolated
19	**28**	**TBSOTf (4 equiv), Et_3N (8 equiv), PhMe, then DBU (10 equiv), 115 °C**	**both 30 (15%) and S32 (9%) isolated**
20	**28**	TBSOTf (5 equiv), Et_3N (10 equiv), PhMe, then DBU (10 equiv), 115 °C	only indane aldehyde **30** (32%) isolated
21	**28**	TBSOTf (5 equiv), Et_3N (10 equiv), PhMe, then DBU (20 equiv), 115 °C	only indane aldehyde **30** (28%) isolated
22	**28**	**TBSOTf (5 equiv), Et_3N (10 equiv), PhMe, then DBU (50 equiv), 115 °C**	**only benzocoumarin S32 (15%) isolated**
23	**29**	DMSO, 100 °C	decomposition of **29**
24	**29**	$(CuOTf)_2$.PhMe, CH_3CN, rt	decomposed after 1 h
25	**29**	TBAF, PhMe, rt to 100 °C	decomposed at 100 °C
26	**29**	BF_3.OEt_2, DCM, –78 °C to 0 °C	only desilylated product observed
27	**29**	Me_2AlCl, DCM, –78 °C to rt	decomposed at rt

The reaction conditions of the initial attempts to access indane aldehyde **30** and subsequent optimization of this cascade reaction are summarized in table S9. Entries 1–6 disclose attempts to deprotonate the γ-hydrogen of the enal moiety in vinyl nitrile **28**. Only the soft enolization condition (entry 6) led to the desired silyl enol ether **29**. We then began exploring conditions for the 6π-electrocyclization and found that the desired transformation occurred when silyl enol ether **29** was heated at elevated temperature. The intermediate cyclized product **S33** (shown below), was converted to indane aldehyde **30** upon treatment with diazabicyclo(5.4.0)undec-7-ene (DBU) (entry 10). Next, the synthesis of other enol ethers (entry 13–15) was explored. It was found that in addition to the TBS silyl enol ether, the TIPS silyl enol ether also proved to be a suitable precursor for the synthesis of indane aldehyde **30** (entry 15) via the 6π-

electrocyclization. Entries 19–22 highlight the optimization of the one-pot cascade reaction by modifying the equivalents of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf), triethylamine, and DBU. We observed that a relatively smaller excess of TBSOTf and triethylamine gave a mixture of both the indane aldehyde **30** and benzocoumarin **S32** (entry 19), while the use of a very large excess of DBU only provided benzocoumarin **S32** in poor yield (entry 21). Hence, a 10-fold excess of both DBU and triethylamine was determined to be best for the exclusive formation of indane aldehyde **30** (entry 20, see below for experimental procedure). Moreover, it was found that benzocoumarin **S32** can be converted to indane aldehyde **30** upon treatment with sodium methoxide in methanol (see below for experimental procedure). With the TBS silyl enol ether in hand, several Mukaiyama–Michael-type reaction conditions (entry 24–27) were also investigated to intiate the desired cascade sequence. Unfortunately, all these conditions did not give rise to any of the desired product.

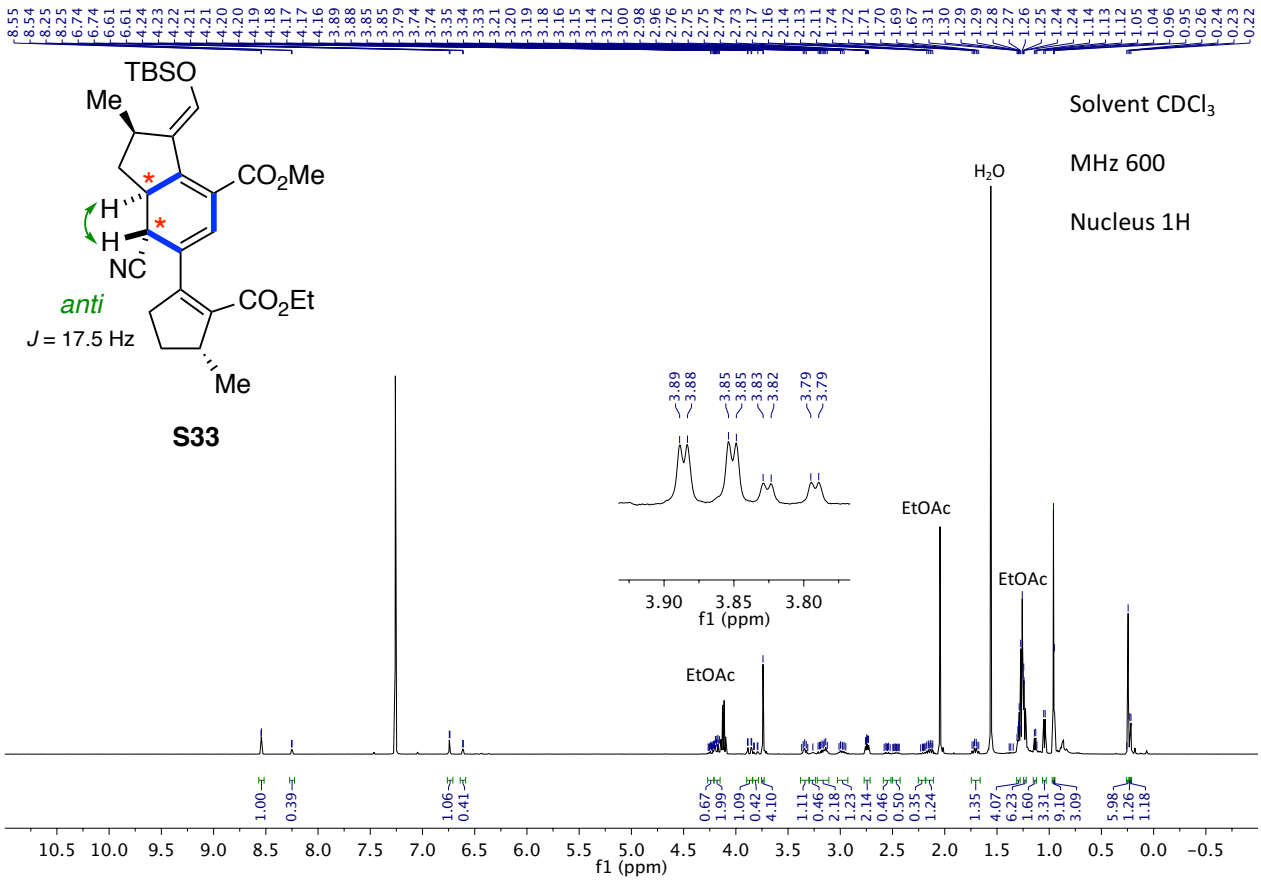
Procedure to obtain the cyclized product **S33:**



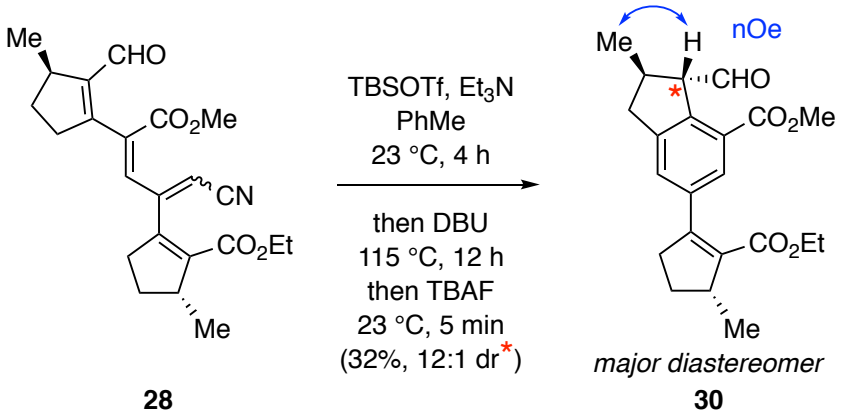
29-*E* **S33**

A solution of silyl enol ether **29-*E*** (31.0 mg, 0.06 mmol, 1.0 equiv) in toluene (3 mL) was heated to 110 °C. After 36 h, the reaction mixture was concentrated in vacuo and the resulting crude residue was purified by flash chromatography (12:1, hexanes:ethyl acetate) to give the cyclized product **S33** (6.0 mg, 0.01 mmol, 19%, 24% brsm, 2.6:1 dr) and unreacted silyl enol ether **29-*E*** (6.0 mg, 0.01 mmol), in order of elution, each as a bright yellow oil. Cyclized product **S33** proved to be unstable and could not be fully characterized except for ^{1}H NMR analysis. The 6π electrocyclization gave rise to two diastereomers in a 2.6:1 ratio, where the highlighted hydrogen atoms adopt an *anti*-relationship, as determined by analysis of the coupling constant (^3J = 17.5 Hz), see ^{1}H NMR spectrum below. This indicates the thermal disrotatory ring closure of the major *E* isomer **29-*E***. The absolute stereochemistry of the highlighted hydrogen atoms in the major diastereomer could not be determined.

TLC (8:1, hexanes:ethyl acetate): R_f = 0.48 (UV/$KMnO_4$)
In cases where the proton or carbon atoms show a double set of signals, the signal of the second diastereomer is marked with an asterisk.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.5 Hz, 1H), 8.25* (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 2.9 Hz, 1H), 6.61* (d, *J* = 2.8 Hz, 1H), 4.27 – 4.20* (m, 2H), 4.27 – 4.15 (m, 2H), 3.87 (dd, *J* = 17.5, 2.8 Hz, 1H), 3.81* (dd, *J* = 17.1, 2.9 Hz, 1H), 3.74 (s, 3H), 3.38 – 3.30 (m, 1H), 3.29 – 3.23* (m, 1H), 3.22 – 3.17 (m, 1H), 3.17 – 3.11 (m, 1H), 3.02 – 2.93 (m, 1H), 2.77 – 2.71 (m, 2H), 2.59 – 2.51* (m, 1H), 2.51 – 2.42* (m, 1H), 2.25 – 2.19* (m, 1H), 2.18 – 2.10 (m, 1H), 1.75 – 1.66 (m, 1H), 1.31 – 1.22 (m, 7H), 1.14* (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.95* (s, 9H), 0.24 (s, 6H), 0.23* (s, 3H), and 0.22* (s, 3H).
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2955 (s), 2928 (s), 2858 (m), 2246 (w), 1709 (s), 1447 (w), 1254 (m), 1220 (s), 1176 (m), 1157 (m), 1052 (w), and 827 (m).
HRMS (ESI): calcd for ([M+Na], $C_{29}H_{41}NNaO_5Si)^+$: 534.2646, found: 534.2646.


TBSO
Me
CO2Me
H
H
NC
anti
J = 17.5 Hz
CO2Et
Me
S33
Solvent CDCl3
MHz 600
Nucleus 1H
H2O
EtOAc
EtOAc
EtOAc
f1 (ppm)
f1 (ppm)

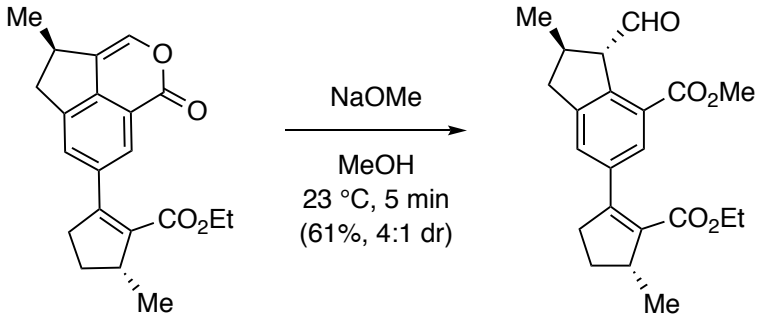
Procedure that provides only indane aldehyde **30** from vinyl nitrile **28**:



28 **30**

Tert-Butyldimethylsilyl trifluoromethanesulfonate (1.10 mL, 5.00 mmol, 5.0 equiv) was added to a solution of vinyl nitrile **28** (395 mg, 1.00 mmol, 1.0 equiv) and triethylamine (1.40 mL, 10.0 mmol, 10.0 equiv) in toluene (50 mL) at 23 °C. After 4 h, the bright yellow reaction mixture was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (1.50 mL, 10.0 mmol, 10.0 equiv), and the resulting mixture was heated to 115 °C and held at this temperature. After 12 h, the dark brown reaction mixture was cooled to 23 °C and tetrabutylammonium fluoride solution (1.0 M in THF, 5.00 mL, 5.00 mmol, 5.0 equiv) was added. After 5 min, the brown reaction mixture was diluted with aqueous sodium bicarbonate solution (50 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 × 50 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (100 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy (8:1, hexanes:ethyl acetate) to give indane aldehyde **30** (118 mg, 0.32 mmol, 32%, 12:1 dr) as a blue oil.

Procedure that provides indane aldehyde **30** from benzocoumarin **S32**:



S32 **30**

A solution of benzocoumarin **S32** (70.0 mg, 0.21 mmol, 1.0 equiv) in methanol (5 mL) was treated with a sodium methoxide solution (0.5 M in methanol, 0.60 mL, 0.30 mmol, 1.5 equiv) at 23 °C. After 5 min, the reaction mixture was diluted with aqueous sodium bicarbonate solution (5 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (5 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was

purified by flash chromatograpy (5:1, hexanes:ethyl acetate) to give indane aldehyde **30** (50.0 mg, 0.14 mmol, 61%, 4:1 dr) as a blue oil.

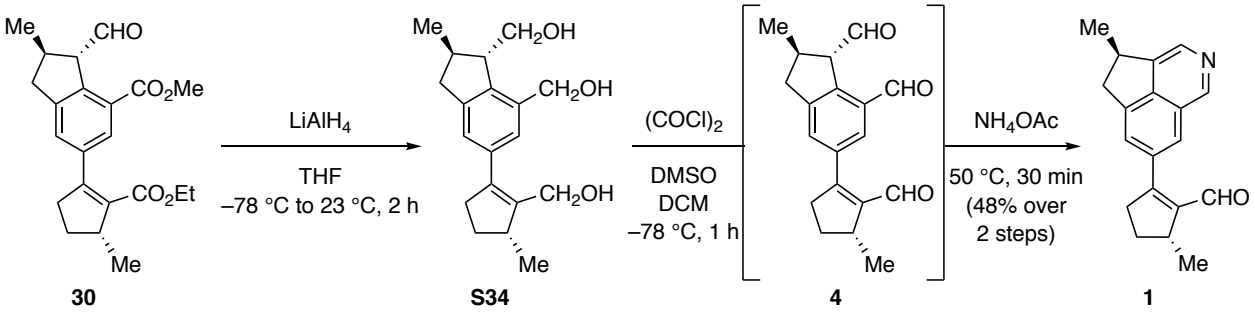
Data for indane aldehyde **30**:

TLC (5:1, hexanes:ethyl acetate): R_f = 0.36 (UV/$KMnO_4$)
In cases where the proton or carbon atoms show a double set of signals, the signal of the second diastereomer is marked with an asterisk.
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.80* (d, *J* = 3.2 Hz, 1H), 9.68 (d, *J* = 2.3 Hz, 1H), 7.85 (s, 1H), 7.75* (d, *J* = 4.3 Hz, 1H), 7.39 (s, 1H), 4.16 – 4.03 (m, 3H), 3.86 (s, 3H), 3.84* (s, 3H), 3.29 – 3.21 (m, 1H), 3.18 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.07* (dd, *J* = 15.6, 7.8 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.81 – 2.68 (m, 2H), 2.57 (dd, *J* = 16.0, 4.8 Hz, 1H), 2.48 – 2.40* (m, 4H), 2.28 – 2.19 (m, 1H), 2.20 – 2.11* (m, 1H), 1.92 – 1.84* (m, 2H), 1.67 – 1.55 (m, 1H), 1.31* (d, *J* = 6.7 Hz, 3H), 1.28* (d, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.15* (t, *J* = 7.2 Hz, 3H), and 1.10 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 166.9, 166.4, 150.1, 145.5, 140.1, 137.5, 135.7, 129.0, 128.3, 126.8, 65.5, 60.2, 52.1, 42.4, 39.6, 38.1, 35.2, 31.1, 20.6, 19.8, and 14.0.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2956 (s), 2870 (w), 1717 (s), 1436 (w), 1280 (m), 1236 (w), 1200 (w), and 1034 (w).
HRMS (ESI): calcd for ([M+Na], $C_{22}H_{26}NaO_5$)$^+$: 393.1672, found: 393.1673.
$[\alpha]^{20}_D$ = +0.5° (c = 0.98, $CHCl_3$)

Data for benzocoumarin **S32**:

TLC (5:1, hexanes:ethyl acetate): R_f = 0.18 (UV/$KMnO_4$)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.52 (s, 1H), 7.16 (d, *J* = 1.6 Hz, 1H), 4.16 – 4.04 (m, 2H), 3.57 – 3.50 (m, 2H), 3.28 – 3.22 (m, 1H), 2.95 – 2.89 (m, 1H), 2.87 – 2.81 (m, 1H), 2.77 – 2.70 (m, 1H), 2.28 – 2.22 (m, 1H), 1.63 – 1.58 (m, 1H), 1.36 (d, *J* = 6.5 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), and 1.13 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 166.2, 162.1, 150.9, 143.6, 141.1, 139.6, 139.0, 136.0, 129.8, 128.7, 124.5, 118.5, 60.2, 42.4, 40.9, 38.4, 34.2, 31.1, 21.6, 19.9, and 14.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2955 (s), 2935 (s), (2869 (m), 1731 (s), 1249 (w), 1074 (w), 1040 (w), and 789 (w).
HRMS (ESI): calcd for ([M+H], $C_{21}H_{23}O_4$)$^+$: 339.1591, found: 339.1592.
$[\alpha]^{20}_D$ = +10.9° (c = 0.95, $CHCl_3$)

3.11 Synthesis of delavatine A 1



A solution of indane aldehyde **30** (45.0 mg, 0.12 mmol, 1.0 equiv) in tetrahydrofuran (6 mL) was treated with lithium aluminium hydride (23.0 mg, 0.60 mmol, 5.0 equiv) at –78 °C, and the resulting turquoise reaction mixture was slowly warmed to 23 °C. After 2 h, the yellow mixture was cooled to 0 °C, and was carefully diluted with aqueous sodium bicarbonate solution (5 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (5 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo to provide triol **S34**, which was used in the next step without further purification.

An analytically pure sample could be obtained by purification by flash chromatography (10% methanol in dichloromethane), to give triol **S34** (75% yield) as a yellow oil.

Data for triol **S34**:

TLC (100% ethyl acetate): R_f = 0.43 (UV/$KMnO_4$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H), 7.04 (s, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.25 (d, *J* = 11.9 Hz, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 3.77 (dd, *J* = 10.7, 5.1 Hz, 1H), 3.50 (dd, *J* = 10.6, 8.0 Hz, 1H), 3.14 (dd, *J* = 16.0, 7.4 Hz, 1H), 3.04 – 2.94 (m, 2H), 2.70 – 2.62 (m, 2H), 2.43 – 2.36 (m, 1H), 2.34 – 2.25 (m, 1H), 2.21 – 2.10 (m, 1H), 1.52 – 1.41 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), and 0.99 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.4, 141.2, 140.0, 137.5, 137.2, 127.1, 124.3, 64.9, 63.3, 57.8, 54.3, 41.8, 39.3, 37.0, 36.0, 31.6, 21.1, and 19.5.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3324 (s), 2949 (s), 2926 (s), 2865 (m), 1455 (w), 1027 (m), 988 (m), 908 (w), and 730 (m).
HRMS (ESI): calcd for ([M+Na], $C_{19}H_{26}NaO_3$)$^+$: 325.1774, found: 325.1778.
$[\alpha]^{20}_D$ = –16.8° (c = 0.25, $CHCl_3$)

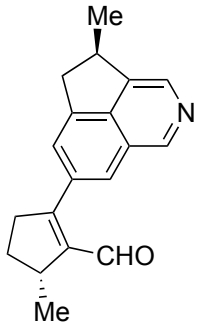
Dimethyl sulfoxide (0.17 mL, 2.40 mmol, 20.0 equiv) was added to a solution of oxalyl chloride (0.10 mL, 1.20 mmol, 10.0 equiv) in dichloromethane (3 mL) at –78 °C. After 15 min, a solution of crude triol **S34** (0.12 mmol) in dichloromethane (3 mL) was added dropwise. After 1 h, triethylamine (0.70 mL, 5.00 mmol, 40.0 equiv) was added to the orange reaction mixture, and the resulting mixture was warmed to 0 °C. After 15 min, the intermediate trialdehyde **4** was treated with ammonium acetate (185 mg, 2.40 mmol, 20.0 equiv), and the resulting mixture was heated to 50 °C. After 30 min, the orange mixture was diluted with aqueous sodium bicarbonate solution (5 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 × 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (5 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatograpy

(3:1 → 1:1, hexanes:ethyl acetate) to provide delavatine A (**1**) (16.0 mg, 0.06 mmol, 48% over 2 steps) as a yellow oil.

TLC (1:1, hexanes:ethyl acetate): R_f = 0.40 (UV/$KMnO_4$)
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.81 (s, 1H), 9.12 (s, 1H), 8.47 (s, 1H), 7.71 (s, 1H), 7.43 (s, 1H), 3.94 – 3.85 (m, 1H), 3.74 – 3.65 (m, 1H), 3.36 – 3.27 (m, 1H), 3.16 – 3.07 (m, 1H), 3.03 – 2.91 (m, 2H), 2.34 – 2.24 (m, 1H), 1.72 – 1.63 (m, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), and 1.25 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.5, 162.4, 146.8, 144.56, 144.54, 144.1, 142.0, 137.1, 136.6, 126.1, 123.9, 122.6, 39.8, 39.4, 38.3, 37.6, 31.0, 21.7, and 19.7.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2956 (s), 2928 (s), 2867 (m), 2838 (m), 1660 (s), 1450 (w), 1371 (w), and 892 (w).
HRMS (ESI): calcd for ([M+H], $C_{19}H_{20}NO)^+$: 278.1539, found: 278.1540.
$[\alpha]^{20}_D$ = +34.5° (c = 0.55, $CHCl_3$)

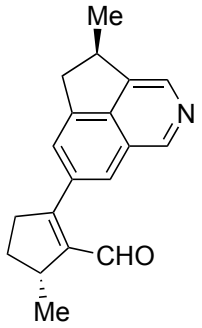
4 ^{1}H and ^{13}C NMR comparison of natural and synthetic delavatine A

4.1 ^{1}H NMR comparison of natural and synthetic delavatine A



Natural[11] (600 MHz, $CDCl_3$)	Synthetic (600 MHz, $CDCl_3$)	$\Delta\delta$ (ppm)
9.82 (s, 1H)	9.81 (s, 1H)	0.01
9.11 (s, 1H)	9.12 (s, 1H)	0.01
8.47 (s, 1H)	8.47 (s, 1H)	0
7.71 (s, 1H)	7.71 (s, 1H)	0
7.43 (s, 1H)	7.43 (s, 1H)	0
3.90 (m, 1H)	3.94 – 3.85 (m, 1H)	-
3.69 (dd, 17.6, 7.9, 1H)	3.74 – 3.65 (m, 1H)	-
3.31 (m, 1H)	3.36 – 3.27 (m, 1H)	-
3.11 (ddd, 13.8, 9.6, 5.6, 1H)	3.16 – 3.07 (m, 1H)	-
2.98 (dd, 17.4, 3.6, 1H)	3.03 – 2.91 (m, 2H)	-
2.96 (ddd, 13.8, 9.6, 5.6, 1H)	-	-
2.29 (m, 1H)	2.34 – 2.24 (m, 1H)	-
1.68 (m, 1H)	1.72 – 1.63 (m, 1H)	-
1.51 (d, 7.2, 3H)	1.50 (d, 7.2, 3H)	0.01
1.25 (d, 6.9, 3H)	1.25 (d, 6.8, 3H)	0

4.2 ^{13}C NMR comparison of natural and synthetic delavatine A



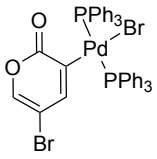
Natural[11] (150 MHz, $CDCl_3$)	Synthetic (150 MHz, $CDCl_3$)	$\Delta\delta$ (ppm)
190.33	190.48	0.15
162.27	162.37	0.10
146.83	146.82	0.01
144.35	144.56	0.21
144.33	144.54	0.21
143.74	144.11	0.37
141.74	141.97	0.23
137.25	137.10	0.15
136.27	136.55	0.28
125.93	126.09	0.16
123.53	123.88	0.35
122.41	122.63	0.22
39.63	39.79	0.16
39.21	39.38	0.17
38.10	38.28	0.18
37.39	37.59	0.20
30.84	31.01	0.17
21.50	21.68	0.18
19.54	19.72	0.18

5 X-Ray Crystallographic Data

X-ray crystallographic data for C3-Pd and C5-Pd complexes **12-trans** and **13-trans** (along with their .cif files) are provided along with this supporting information. The ORTEP renderings shown below were visualized using Mercury.[12]

	12-trans	**13-trans**
Chemical formula	$C_{41}H_{32}Br_2O_2P_2Pd$, $2(CH_2Cl_2)$	$C_{41}H_{32}Br_2O_2P_2Pd$
Formula weight	1054.68	972.93
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	1.54184
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 21/n
a (Å)	9.4219(2)	18.1079(10)
b (Å)	11.7273(2)	11.4361(10)
c (Å)	20.2438(3)	19.9348(10)
α (°)	85.1460(10)	90
β (°)	82.3560(10)	95.68
γ (°)	70.742(2)	90
V ($Å^3$)	2090.89(7)	4107.89(5)
Z	2	4
Densitiy (Mg m^{-3})	1.675	1.573
Absorption coefficient (mm^{-1})	2.724	6.996
F(000)	1048	1952
Crystal size (mm^3)	0.10 x 0.09 x 0.07	0.09 x 0.09 x 0.04
Theta range for data collection (°)	3.049 to 26.371	3.146 to 74.504
Index ranges	-11<=h<=11, -14<=k<=14, -25<=1<=24	-22<=h<=22, -14<=k<=14, -24<=1<=24
Reflections collected	44551	120390
Independent reflections	8554 [R(int) = 0.0681]	8404 [R(int) = 0.0609]
Completeness to theta = 26.371°	99.8%	100.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0 and 0.89695	1.0 and 0.75414
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8554/0/487	8404/0/433
Goodness-of-fit on F^2	1.02	1.07
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1032	R1 = 0.0676, wR2 = 0.2063
R indices (all data)	R1 = 0.0581, wR2 = 0.1085	R1 = 0.0694, wR2 = 0.2080
Extinction coefficient	n/a	n/a
Largest diff. Peak and hole (e.$Å^{-3}$)	1.925 and -1.227	2.007 and -4.327

a) C3-Pd complex **12-trans**



12-trans

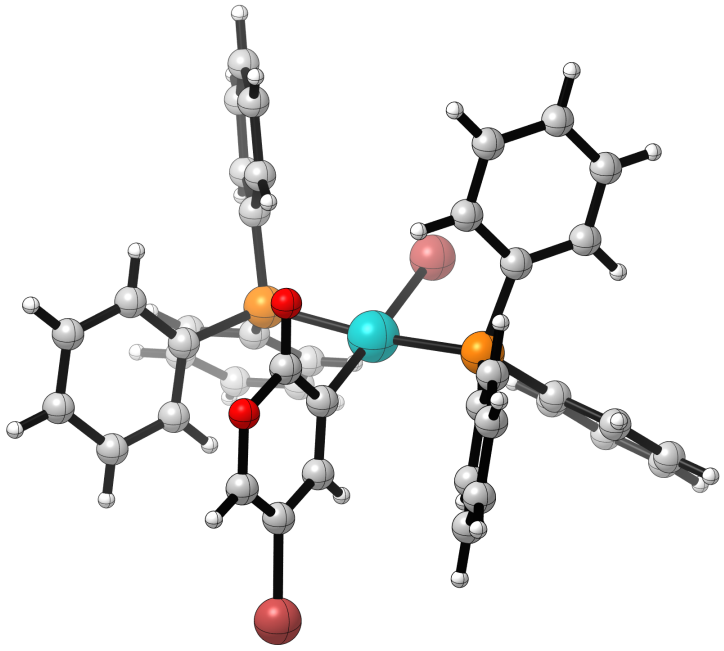


Figure S1. ORETP rendering of C3-Pd complex **12-trans**.

This crystal structure has been deposited at the Cambride Crystallographic Data Center under **CCDC 1882829**.

b) C5-Pd complex **13-trans**

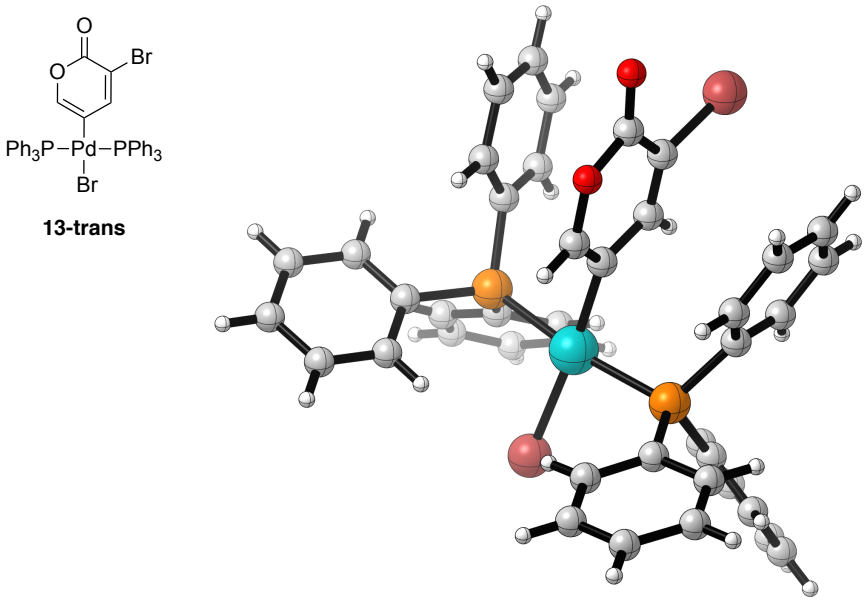


Figure S2. ORETP rendering of C5-Pd complex **13-trans**.

This crystal structure has been deposited at the Cambride Crystallographic Data Center under **CCDC 1882830**.

6 Computational results

6.1 Computational details

All calculations were carried out with the Gaussian 09 package.[13] Geometry optimizations were performed with B3LYP.[14] Mixed basis set of SDD was used for palladium and tin, and 6-31G(d) for other atoms. Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or saddle points and to obtain zero-point energy (ZPE) and thermal energy corrections at 298.15 K. Single-point energy calculations on B3LYP-optimized geometries were performed with the M06 functional,[15] a mixed basis set of SDD for palladium and tin, and 6-311+G(d,p) for other atoms, and the SMD solvation model[16] with DMF as the solvent. The computed gas-phase activation energy ($\Delta E^{\ddagger}$) was studied using the distortion-interaction analysis The distortion energy (ΔE_{dist}) is the sum of the energies required to distort the LCuH catalyst and the substrate into their transition state geometries. ΔE_{int} was calculated using the equation $\Delta E_{int} = \Delta E^{\ddagger} - \Delta E_{dist}$. The LUMO coefficients of **8** were calculated using HF/STO-3G. BDE was computed using B3LYP/6-31G(d). Computed structures are illustrated with CYLView.[17]

6.2 Alternative oxidative addition pathways.

Other oxidative addition pathways where CuI plays different roles have been considered. The mechanism involving DMF bound *mono*-phosphine ligated palladium complex **17** leads to a decreased regioselectivity when compared to the pathway involving *bis*-phosphine ligated palladium complex **14**. On the other hand, pathway where either CuI, or $Cu(DMF)^{+}$ act as lewis acid, the regioselectivity still favors the coupling to occur at the 3-position and the selectivity isn't different from the *bis*-phosphine ligated palladium pathway. Finally, anionic pathway involving *mono*-phosphine ligated palladium involving iodide was considered. This pathway also favors the coupling to occur at the 3-position with a similar selectivity to the *bis*-phosphine ligated pathway.

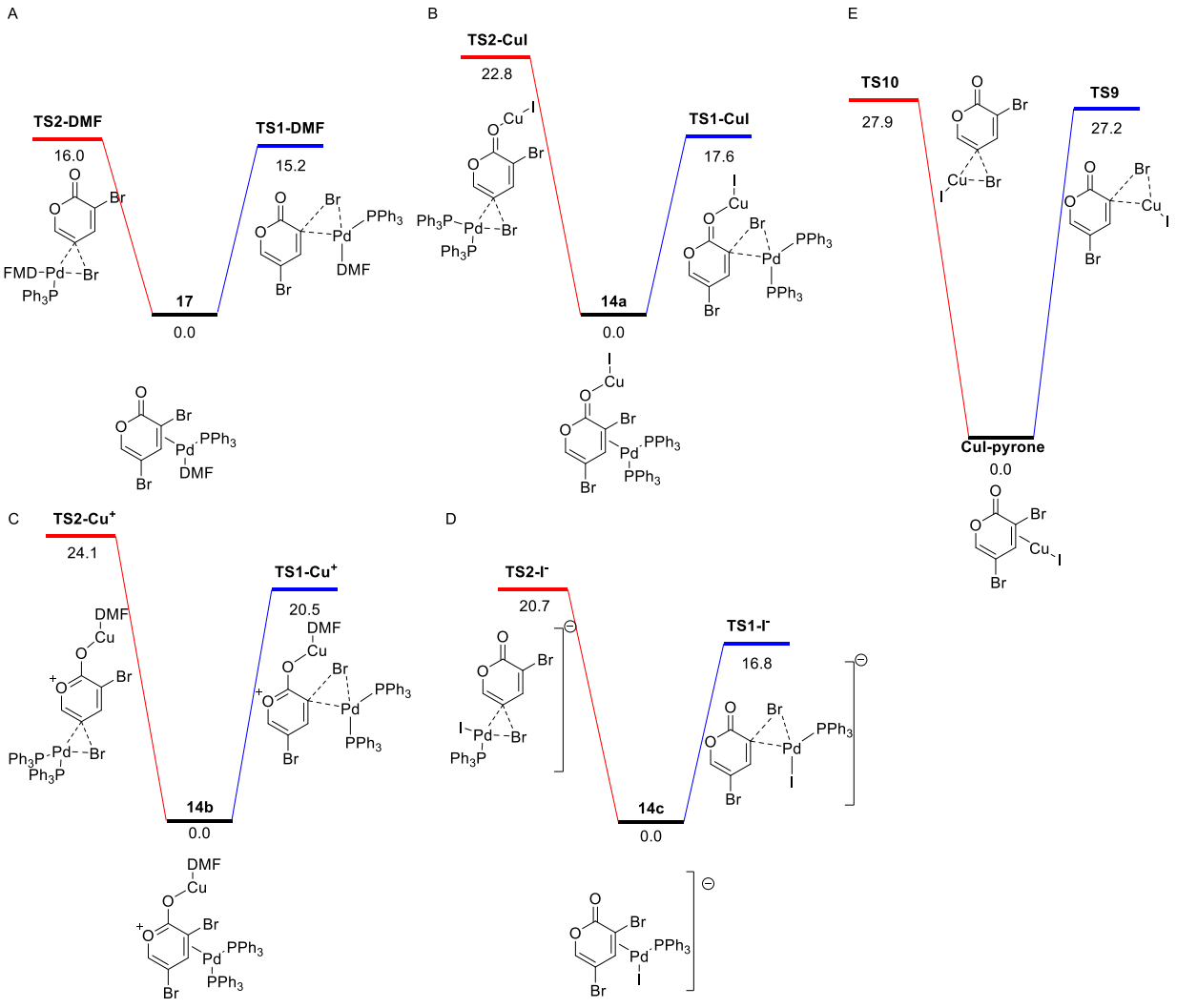


Figure S3. A) Oxidative addition with *mono*-phosphine ligated palladium bound to DMF. **B)** Oxidative addition with CuI acting as a Lewis acid. **C)** Oxidative addition with $Cu(DMF)^+$ acting as a Lewis acid. **D)** Anionic oxidative additon with *mono*-phosphine ligated Pd bound to iodide. **E)** Oxidative addition of pyrone onto CuI leading to Cu(III) intermediate.

6.3 Oxidative addition step calculated in toluene.

The oxidative addition step was calculated in toluene. The calculations show that, in accordance with the experiment, C3-oxidative adduct is strongly favored kinetically. Furthermore, products of the oxidative addition in toluene are also favored thermodynamically.

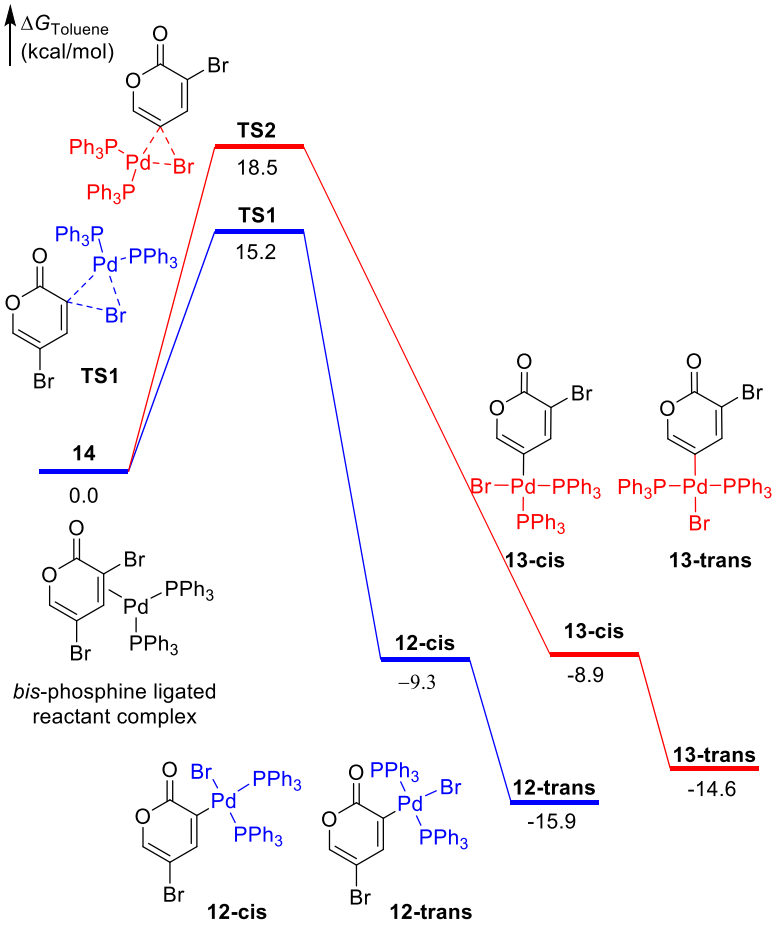


Figure S4. Oxidative addition reaction mechanism in toluene.

6.4 Farther details of the mechanism following the oxidative addition.

Following oxidative addition, cis-products can undergo the transmetallation, however cis-transmetallation pathways (**TS5-cis**, **TS6-cis**) are 5-6 kcal/mol higher in energy than their respective trans-pathways (**TS5**, **TS6**). Following transmetallation, our calculations indicate the four-coordinate Pd^{II} intermediates **20** and **21** are ~3 kcal/mol more stable than the respective three-coordinate mono-phosphine intermediates **20a** and **21a**, but the barriers for reductive elimination from the bis-phosphine and the mono-phosphine ligated Pd complexes are comparable. In fact, the reductive elimination for the C3-adduct proceeds preferably through a bis-phosphine ligated Pd complex (i.e., **TS7-bis**), with mono-phosphine ligated Pd complex (**TS7-mono**)[18] being 0.6 kcal/mol less favorable. On the other hand, the reductive elimination for the C5-adduct proceeds through a mono-phosphine ligated Pd complex (**TS8-mono**), with it being 3.5 kcal/mol more favorable than the bis-phosphine ligated Pd complex pathway (**TS8-bis**).

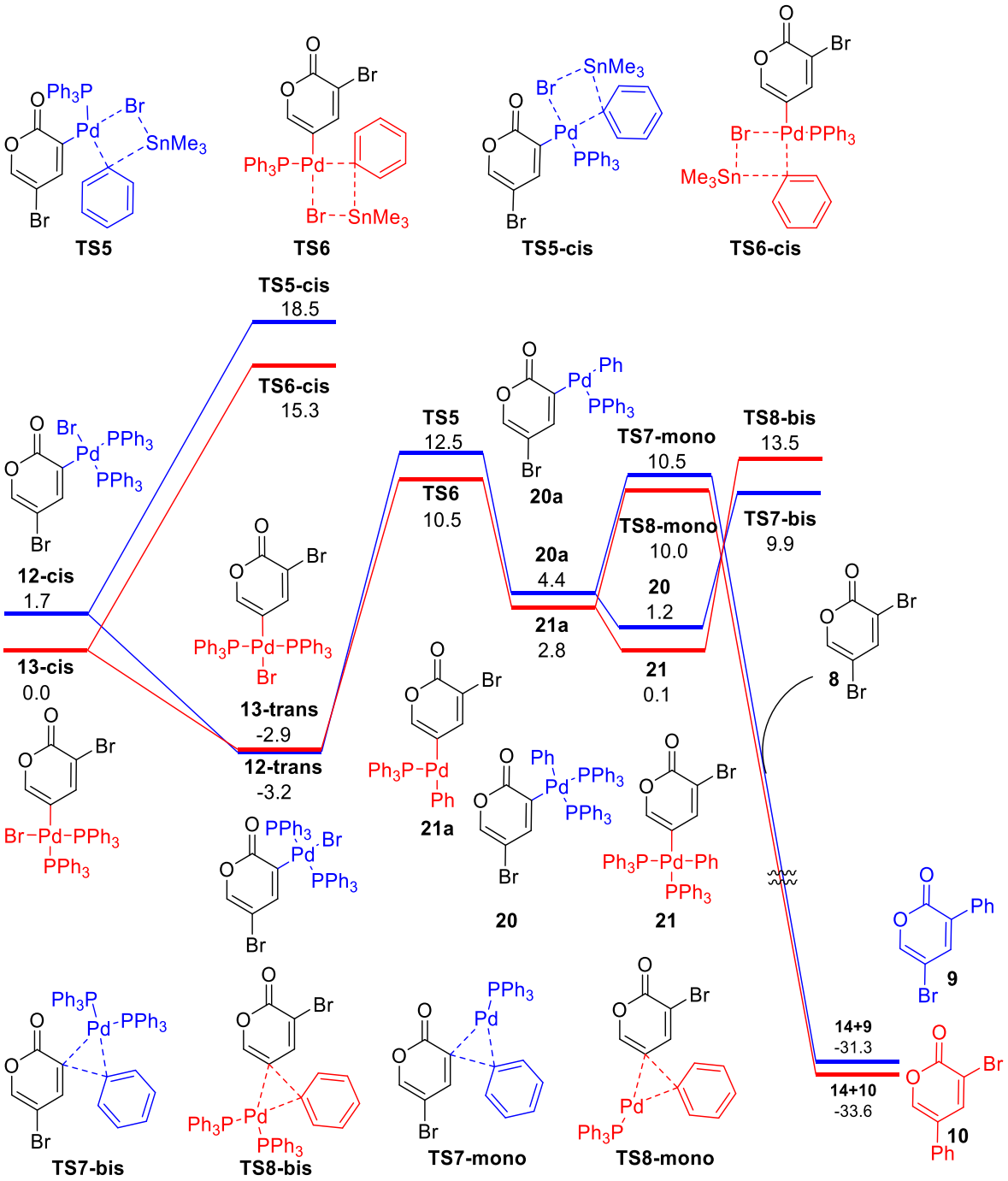
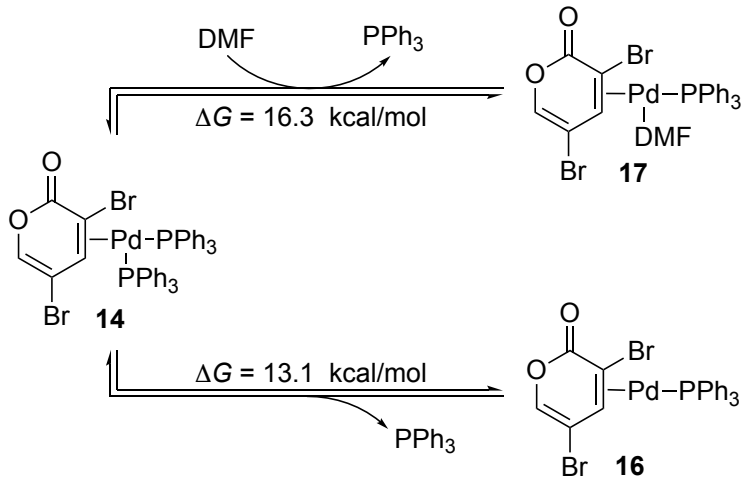


Figure S5. Reaction energy profile following the oxidative addition in the presence of CuI. All energies are relative to **13-cis**. Ligand exchanges with copper species are omitted for clarity.

6.5 Phosphine ligand exchange in the absence of CuI

To study the effect of the CuI, phosphine dissociation in the absence of CuI additives was considered. The calculations show that the phosphine dissociation is highly endergonic and it is unlikely that the mono-phosphine ligated Pd complex would exist in the solution in the absence of the copper additive.

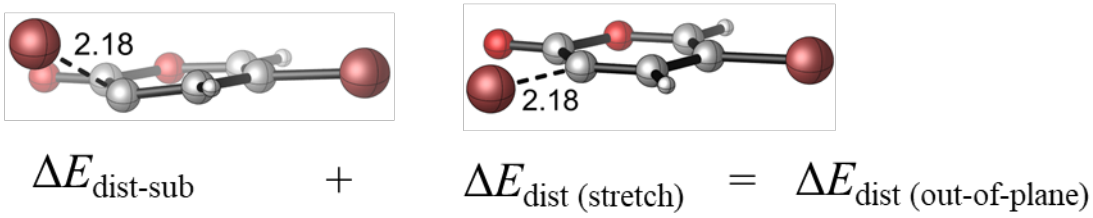
Scheme S1. Phosphine ligand exchange in the absence of copper additives is highly endergonic.



6.6 BDEs of C-Br bond and farther decomposition of substrate distortion energy.

The bond dissociation energy for C-Br bond in 3,5-dibromo-2-pyrone (**8**) was calculated to analyse the distortion of the substrate (Figure S6B). BDE is a good descriptor of stretching distortion of the substrate. The analysis showed that the BDE of these two bonds don't differ significantly and the stretching of the bond shouldn't significantly affect the differences between the coupling at these two positions. To farther analyse the distortion of the substrate, we farther decomposed the substrate distortion into the stretching distortion and out of plane distortion by calculating the energy required to stretch the C-Br bond into the transition state distance (Figure S6A). This analysis shows that the out of plane bending of C-Br bond always requires higher energy for the C3-Br bond. This is likely due to the presence of carbonyl group next to the C3 carbon.

A



Structure	$\Delta E_{\text{dist-sub}}$	$\Delta E_{\text{dist (stretch)}}$	$\Delta E_{\text{dist (out-of-plane)}}$
TS1	24.2	13.5	10.7
TS2	26.6	18.3	8.3
TS3	23.5	15.6	7.9
TS4	21.2	14.5	6.7

B

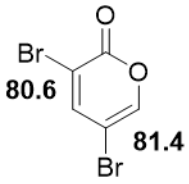
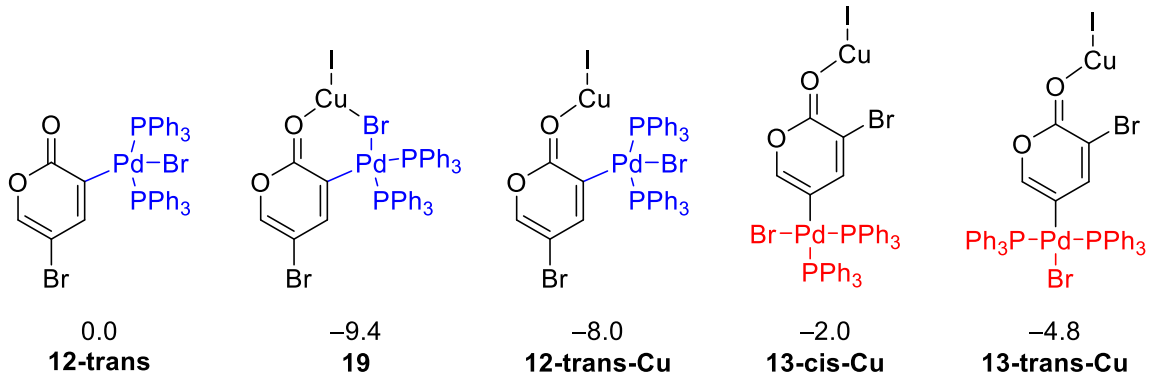


Figure S6. A. The decomposition of substrate distortion energy ($\Delta E_{\text{dist-sub}}$) into the energy required to stretch the C-Br bond to the transition state geometry ($\Delta E_{\text{dist (stretch)}}$), and the energy required for out of plane bending of the C-Br bond ($\Delta E_{\text{dist (out-of-plane)}}$).

6.7 Binding of CuI to other oxidative adducts.

The binding of CuI to different possible oxidative addition products was calculated. These calculations show that the binding is highly favorable for the **12-cis** product, leading to the formation of six-member metallacycle **19** with a favorable interaction with the partially negatively charged bromide. The other CuI complexes are much less stable due to the lack of effcive chelating interactions with he bromide to form a six-membered metallacycle.

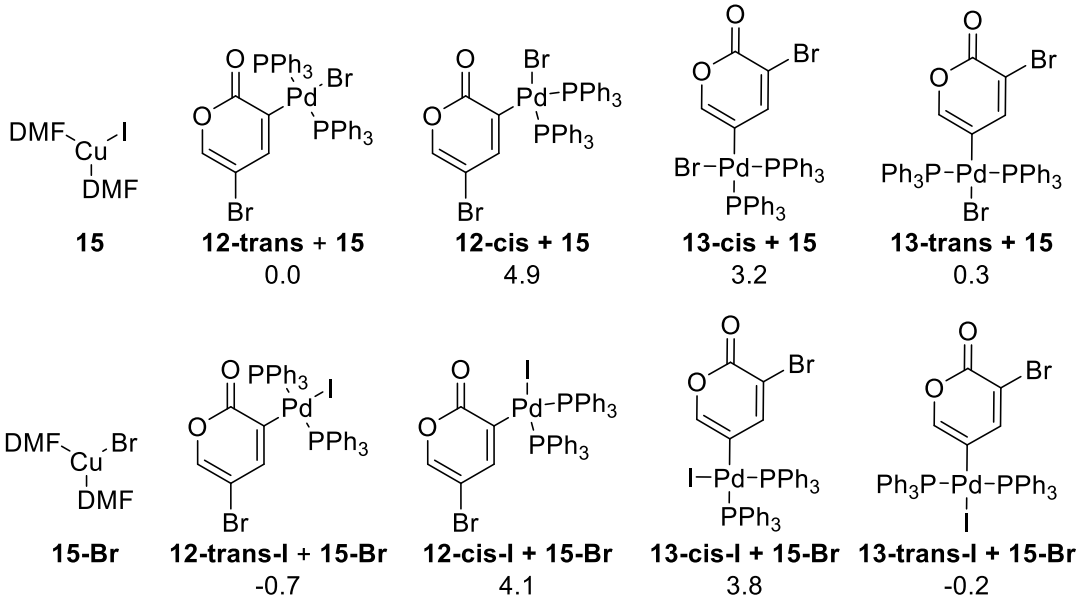
Scheme S2. Binding of CuI to all *bis*-phosphine ligated palladium (II) oxidative addition products. All energies are Gibbs free energies in kcal/mol with respect to **12-trans** and **15**.



6.8 Halide exchange intermediates.

Halide exchange intermediates have been calculated, where I^- in **15** and Br^- in **12**-**13** species are exchanged. These results suggest that these species should exist in an equilibrium. The existence of these species shouldn't affect the reaction mechanism because, from previous computational studies, it is understood that bromide reacts faster than iodide in stille coupling transmetallation.

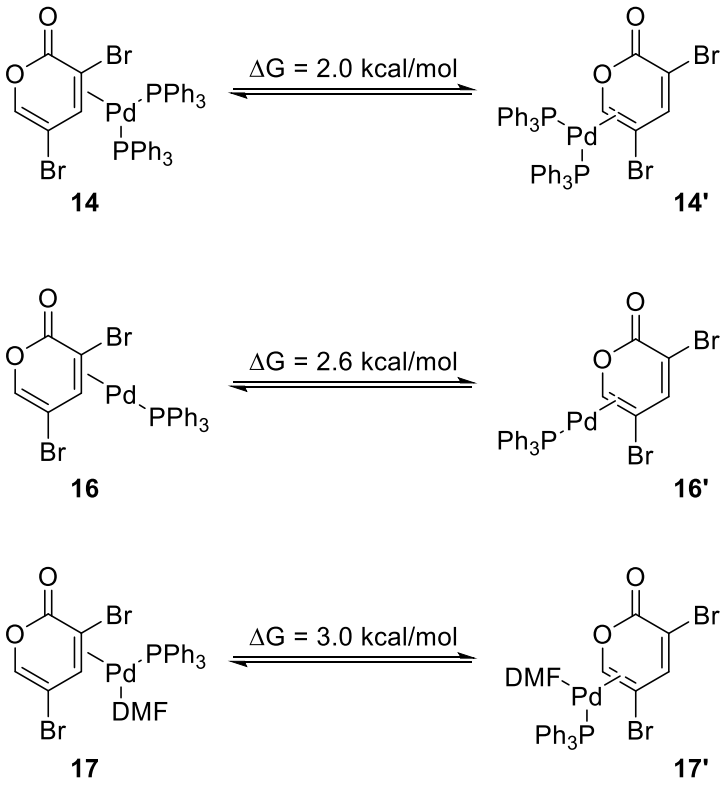
Scheme S3. Energies of halide exchange intermediates after the oxidative addition. All energies are Gibbs free energies relative to **15** and **12-trans**.



6.9 Isomers of 14, 16, and 17.

Isomers of **14**, **16**, and **17**, were calculated where Pd is associated with the C5=C6 bond of the pyrone rather than the C3=C4 bond. These isomers are slightly higher in energy than **14**, **16**, and **17**.

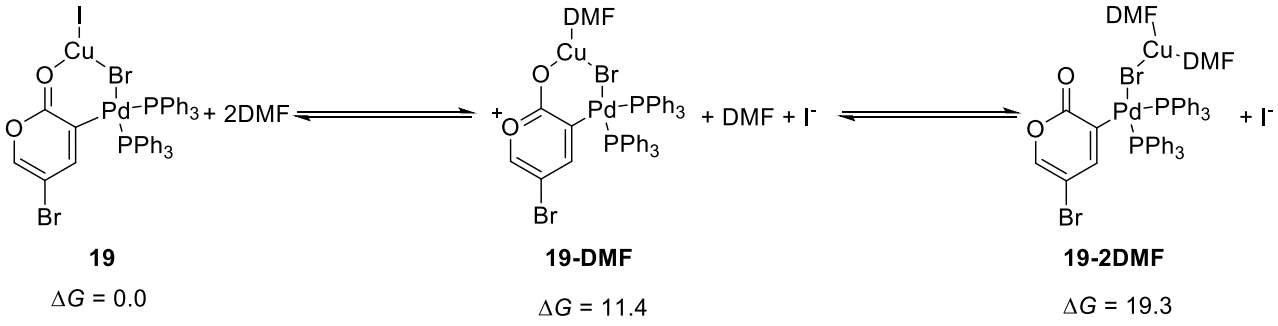
Scheme S4. Isomers of **14**, **16**, and **17**.



6.10 Halide-DMF Exchange and addition of DMF

Halide DMF exchange with **19** was calculated. Additionally, binding of a secondary DMF was calculated. These complexes are higher in energy. All energies are with respect to **19** and two separate DMF molecules.

Scheme S5. Halide/DMF exchange



6.11 Cartesian Coordinates (Å) and Energies of the Optimized Structures.

```
14
B3LYP electronic energy:     -7685.53434014 a.u.
B3LYP enthalpy:   -7684.875687 a.u.
B3LYP free energy:      -7685.009571 a.u.
M06 SCF energy in solution:       -7689.94752135 a.u.
M06 enthalpy in solution:    -7689.288868 a.u.
M06 free energy in solution:      -7689.422752 a.u.
Three lowest frequencies (cm-1):      10.0329      13.41      17.26

Cartesian coordinates
ATOM       X           Y           Z
Pd      -0.022170   -0.575499   -0.259638
P       -1.778958    1.057781   -0.229631
P        2.132895    0.399400    0.284813
C        2.907759    4.940391   -0.484097
C        1.910542    4.522733    0.401292
C       -5.292942   -0.864032   -1.245072
C        4.663668   -1.502713   -2.341109
C       -2.010540    1.828950    3.803216
C       -1.591861    1.421662    2.534840
C        1.694501    3.164001    0.622842
C       -0.120964    3.682417   -2.923396
C       -4.160417   -0.414233   -0.566651
C        1.755744   -0.765136    2.815356
C        3.549342   -0.924087   -1.731310
C        3.477779    2.625602   -0.912109
C       -3.272352    2.400652    3.972402
C        1.939871   -0.920184    4.190665
C        5.871617   -1.592514   -1.650044
C        3.686004    3.988597   -1.141718
C       -0.456583    2.545047   -2.188027
C       -2.423425    1.591357    1.417074
C        2.393559    0.272805    2.117425
C       -1.334122    2.631734   -1.095107
C       -4.115254    2.560625    2.869619
C       -1.508194    5.025113   -1.472784
C       -3.695980    2.158283    1.600742
C        2.760943   -0.035293    4.891626
C        4.852758   -0.512960    0.262159
C        3.396289    1.005092    4.210247
C       -1.855006    3.885757   -0.744102
C       -3.321039    0.559990   -1.135050
C        3.633256   -0.414102   -0.427320
C       -5.604211   -0.356306   -2.508780
C        2.481543    2.195451   -0.023867
C        3.214373    1.159363    2.834617
C       -0.644710    4.926072   -2.565374
C        5.962084   -1.101142   -0.345415
C       -4.775034    0.606107   -3.084667
C       -3.643462    1.063571   -2.404495
H       -3.016192    1.817263   -2.868123
```

H	-5.007520	1.009990	-4.066609
H	-6.484180	-0.709838	-3.039333
H	-5.929266	-1.615717	-0.785323
H	-3.929547	-0.824853	0.411267
H	-0.031383	1.580956	-2.456103
H	0.559587	3.597555	-3.766106
H	-0.377207	5.814259	-3.131655
H	-1.916746	5.990922	-1.186332
H	-2.528715	3.978953	0.101541
H	-0.619203	0.954022	2.410369
H	-1.353600	1.686713	4.657056
H	-3.602978	2.711642	4.959869
H	-5.103020	2.995852	2.997119
H	-4.365512	2.275183	0.753836
H	2.605182	-0.893420	-2.266146
H	4.574974	-1.905423	-3.345947
H	6.735905	-2.055247	-2.119107
H	6.897311	-1.178155	0.203158
H	4.938213	-0.137806	1.276897
H	1.104311	-1.448470	2.277759
H	1.437148	-1.730052	4.712717
H	2.902370	-0.152775	5.962763
H	4.034850	1.700268	4.749134
H	3.707412	1.977761	2.319379
H	4.101047	1.898675	-1.422122
H	4.465522	4.301839	-1.831578
H	3.073977	6.000013	-0.659389
H	1.293339	5.255125	0.914335
H	0.911365	2.856963	1.310480
C	0.143486	-2.598597	-1.098145
C	1.216830	-3.458378	-0.587183
C	-1.114073	-2.452721	-0.441116
Br	0.167310	-2.383115	-3.023700
O	1.021245	-3.929710	0.720693
O	2.228581	-3.793875	-1.151434
C	-0.157366	-3.769325	1.382736
H	-0.155152	-4.260284	2.347425
C	-1.197113	-3.089941	0.865625
H	-2.026192	-2.309335	-1.010803
Br	-2.809817	-3.008797	1.883639

15
B3LYP electronic energy: -705.90188015 a.u.
B3LYP enthalpy: -705.672691 a.u.
B3LYP free energy: -705.745198 a.u.
M06 SCF energy in solution: -705.74106749 a.u.
M06 enthalpy in solution: -705.511878 a.u.
M06 free energy in solution: -705.584385 a.u.
Three lowest frequencies (cm-1): 15.3098 17.12 27.65

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.000720	-0.364620	0.000590
I	0.001291	2.177861	-0.000162
O	-1.787469	-1.404739	-0.000750
C	-2.831993	-0.729972	-0.000500
H	-2.796978	0.368119	-0.000655
N	-4.069591	-1.255806	-0.000013
C	-4.275244	-2.698331	-0.000024
H	-4.838433	-3.000076	0.891182
H	-4.839383	-2.999889	-0.890693
H	-3.301933	-3.188133	-0.000584
C	-5.250359	-0.405059	0.000004
H	-5.861451	-0.596669	0.890354
H	-4.948702	0.644963	0.000064
H	-5.861453	-0.596579	-0.890371
O	1.786249	-1.406242	0.001003
C	2.830784	-0.731499	0.000704
H	2.795751	0.366587	0.001207
N	4.068422	-1.257288	-0.000390
C	4.274140	-2.699795	-0.000937
C	5.249120	-0.406454	-0.000078
H	4.838925	-3.000867	-0.891352
H	4.836712	-3.002007	0.890515
H	3.300843	-3.189622	-0.002423
H	5.859988	-0.597256	-0.890760
H	4.947348	0.643534	0.000822
H	5.860505	-0.598622	0.889962

16
B3LYP electronic energy: -6649.22833100 a.u.
B3LYP enthalpy: -6648.863276 a.u.
B3LYP free energy: -6648.959038 a.u.
M06 SCF energy in solution: -6653.98215865 a.u.
M06 enthalpy in solution: -6653.617104 a.u.
M06 free energy in solution: -6653.712866 a.u.
Three lowest frequencies (cm-1): 5.2804 16.40 20.33

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.649710	-0.707914	0.129882
P	1.607974	-0.093288	0.040067
C	1.980114	1.484583	3.816581
C	3.142288	-3.839029	-0.670499
C	2.325189	-2.709158	-0.627136
C	1.573280	2.685651	-2.986309
C	1.568218	0.750440	2.704094
C	4.387176	-3.826514	-0.037385
C	1.244269	1.908358	-1.876458
C	2.748192	-1.546520	0.039471
C	2.102407	0.881586	-1.447443
C	4.811913	-2.679790	0.636395

C	3.606748	1.414519	-3.278083
C	3.999085	-1.544765	0.674978
C	3.285735	0.640273	-2.160009
C	2.185898	0.937556	1.457015
C	3.005487	2.425002	3.693344
C	2.754123	2.438721	-3.691582
C	3.618295	2.626364	2.454997
C	3.212795	1.887055	1.341772
H	3.691609	2.055219	0.381637
H	4.411773	3.361878	2.352326
H	3.320816	3.003642	4.557407
H	1.493107	1.328977	4.775386
H	0.755932	0.033299	2.797724
H	0.315912	2.096481	-1.343088
H	0.901178	3.477341	-3.306222
H	3.004668	3.038580	-4.562383
H	4.524460	1.214044	-3.824661
H	3.956052	-0.154291	-1.847546
H	1.348855	-2.728409	-1.106280
H	2.800811	-4.731184	-1.188204
H	5.020116	-4.709445	-0.062356
H	5.776605	-2.667272	1.136695
H	4.336909	-0.660931	1.207261
C	-2.761767	-1.052325	0.070185
C	-3.281246	-1.142943	1.446354
C	-2.528288	0.196607	-0.550401
Br	-3.030995	-2.632216	-1.001201
O	-3.471247	0.094454	2.085764
O	-3.549173	-2.139097	2.067407
C	-3.318388	1.291482	1.462651
H	-3.592245	2.124933	2.096283
C	-2.854128	1.388788	0.202743
H	-2.448262	0.267165	-1.629880
Br	-2.641356	3.097212	-0.606990

17
B3LYP electronic energy: -6897.75976219 a.u.
B3LYP enthalpy: -6897.282043 a.u.
B3LYP free energy: -6897.395154 a.u.
M06 SCF energy in solution: -6902.42725536 a.u.
M06 enthalpy in solution: -6901.949536 a.u.
M06 free energy in solution: $ -6902.062647 a.u.
Three lowest frequencies (cm-1): 4.9685 12.99 18.79

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.724340	-0.002246	-0.141073
P	-1.578844	0.548623	-0.087200
C	-3.418349	-2.354817	-2.348671
C	-2.117642	0.077678	3.959483
C	-1.570084	0.291281	2.694022

C	-1.347914	4.331653	-1.680587
C	-2.593699	-1.673581	-1.454323
C	-3.475914	-0.218685	4.093456
C	-1.144213	2.982900	-1.388263
C	-2.376629	0.223181	1.546230
C	-1.898673	2.345256	-0.389276
C	-4.283977	-0.299434	2.957550
C	-3.040940	4.448115	0.037938
C	-3.739290	-0.079450	1.690564
C	-2.846491	3.094083	0.323140
C	-2.708240	-0.282759	-1.293491
C	-4.360936	-1.655860	-3.107139
C	-2.296115	5.068738	-0.965889
C	-4.479173	-0.273746	-2.958220
C	-3.661510	0.410237	-2.054597
H	-3.767175	1.484749	-1.946371
H	-5.209303	0.277974	-3.544743
H	-4.996567	-2.185478	-3.811849
H	-3.317112	-3.431291	-2.458514
H	-1.860425	-2.226739	-0.875020
H	-0.387421	2.421292	-1.929389
H	-0.759744	4.808440	-2.460463
H	-2.450404	6.121350	-1.188548
H	-3.777700	5.015418	0.600839
H	-3.434866	2.622963	1.104226
H	-0.508958	0.503606	2.587935
H	-1.481154	0.132391	4.838704
H	-3.901427	-0.393575	5.078083
H	-5.340077	-0.537049	3.055377
H	-4.375349	-0.149851	0.813113
C	2.454372	-1.161904	-0.442741
C	3.300074	-1.156362	0.754561
C	1.299089	-2.011602	-0.553692
Br	3.362598	-0.588980	-2.062363
O	2.902343	-2.008314	1.781005
O	4.281248	-0.468284	0.956481
C	1.887532	-2.915600	1.638204
H	1.801606	-3.569392	2.495458
C	1.103862	-2.943959	0.549202
H	0.951757	-2.316674	-1.535703
Br	-0.266029	-4.266649	0.431995
O	1.452312	2.128400	0.400108
C	2.650482	2.353223	0.647765
N	3.151496	3.581814	0.879582
H	3.394159	1.547989	0.695507
C	2.302973	4.764742	0.848968
H	2.262744	5.232551	1.840644
H	2.703629	5.494711	0.135319
H	1.298915	4.469147	0.544927
C	4.561885	3.765590	1.188511
H	5.034625	4.422983	0.448391
H	4.683194	4.216549	2.181362
H	5.069552	2.798284	1.176884

18
B3LYP electronic energy: -1493.68891906 a.u.
B3LYP enthalpy: -1493.278669 a.u.
B3LYP free energy: -1493.375762 a.u.
M06 SCF energy in solution: -1493.25270437 a.u.
M06 enthalpy in solution: -1492.842454 a.u.
M06 free energy in solution: -1492.939547 a.u.
Three lowest frequencies (cm-1): 6.3860 16.90 20.33

Cartesian coordinates

ATOM	X	Y	Z
Cu	-0.941983	-0.479764	-0.035873
I	-2.485721	-2.499848	-0.035916
O	-2.204818	1.317132	-0.058728
C	-3.439088	1.182482	-0.029141
H	-3.897781	0.184365	-0.054314
N	-4.316168	2.201609	0.038510
C	-3.866536	3.585347	0.094014
H	-4.226754	4.139647	-0.781361
H	-4.251955	4.071322	0.998326
H	-2.777109	3.596325	0.110961
C	-5.750859	1.957539	0.058540
H	-6.235379	2.437204	-0.800804
H	-5.942114	0.882789	0.014557
H	-6.196542	2.357647	0.977483
P	1.205261	0.126990	-0.008578
C	1.694268	1.087950	1.488373
C	2.394716	-1.277811	-0.050862
C	1.680563	1.208235	-1.425925
C	2.555612	2.194045	1.445302
C	1.166211	0.682682	2.726129
C	1.968678	-2.486419	-0.624039
C	3.697091	-1.185907	0.466434
C	0.750763	2.176945	-1.843286
C	2.902614	1.097602	-2.105202
H	2.962271	2.529296	0.495942
C	2.889219	2.875005	2.618636
H	0.484808	-0.163726	2.771616
C	1.506716	1.360308	3.896443
H	0.950057	-2.580392	-0.991345
C	2.838101	-3.576144	-0.696857
H	4.033095	-0.265217	0.934808
C	4.561257	-2.279385	0.396237
H	-0.208396	2.255642	-1.337596
C	1.049904	3.027634	-2.907421
H	3.624800	0.344608	-1.805597
C	3.193867	1.946449	-3.175657
H	3.556369	3.731767	2.571548
C	2.368977	2.458532	3.844902
H	1.092728	1.034602	4.846877

H	2.494630	-4.507476	-1.138375
C	4.134195	-3.474228	-0.188542
H	5.565958	-2.199200	0.802948
C	2.271075	2.913713	-3.576535
H	0.323735	3.772669	-3.221824
H	4.142167	1.847553	-3.697288
H	2.629065	2.990285	4.756268
H	4.807215	-4.326145	-0.237704
H	2.498595	3.570905	-4.411623

DMF

B3LYP electronic energy: -248.50755221 a.u.
B3LYP enthalpy: -248.397451 a.u.
B3LYP free energy: -248.433544 a.u.
M06 SCF energy in solution: -248.42889544 a.u.
M06 enthalpy in solution: -248.318794 a.u.
M06 free energy in solution: -248.354887 a.u.
Three lowest frequencies (cm-1): 122.4940 179.93 232.09

Cartesian coordinates

ATOM	X	Y	Z
O	1.952194	-0.101709	-0.000138
C	0.863050	-0.651054	0.000065
H	0.751355	-1.753498	0.000268
N	-0.348781	-0.019111	0.000364
C	-1.596681	-0.755045	-0.000128
H	-2.196718	-0.516999	0.888702
H	-2.195560	-0.517887	-0.890004
H	-1.389687	-1.829260	0.000502
C	-0.412245	1.432153	-0.000012
H	-0.939726	1.797859	-0.890873
H	-0.940407	1.798385	0.890220
H	0.609912	1.812520	0.000191

TS1

B3LYP electronic energy: -7685.51414440 a.u.
B3LYP enthalpy: -7684.857007 a.u.
B3LYP free energy: -7684.991600 a.u.
M06 SCF energy in solution: -7689.92044623 a.u.
M06 enthalpy in solution: -7689.263309 a.u.
M06 free energy in solution: -7689.397902 a.u.
Three lowest frequencies (cm-1): -158.5282 8.72 12.29
Imaginary frequency: -158.5282 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.027711	-0.260837	-0.540517
P	2.334498	-0.206458	0.063103
P	-1.328623	1.638689	0.191185

C	0.669535	4.436961	3.353895
C	1.268396	4.198993	2.113963
C	3.417902	-4.020002	-1.055674
C	-4.154205	-0.224859	2.521267
C	3.561324	2.429013	-2.849953
C	2.801522	1.697848	-1.934305
C	0.656723	3.352536	1.191529
C	2.245668	0.568171	4.092299
C	2.859873	-2.742979	-1.008944
C	-1.723330	2.469530	-2.467050
C	-2.963779	0.166477	1.908315
C	-1.165351	2.983632	2.729751
C	4.928070	2.179111	-2.981109
C	-2.022677	3.380799	-3.482497
C	-5.358658	0.383293	2.158458
C	-0.546109	3.825805	3.658004
C	1.952254	0.131793	2.801007
C	3.401057	0.715532	-1.130723
C	-1.733624	2.876072	-1.124099
C	2.793112	0.459144	1.724327
C	5.532310	1.191884	-2.198281
C	4.210076	1.698995	3.260157
C	4.774630	0.462280	-1.281175
C	-2.330555	4.705475	-3.170925
C	-4.169277	1.787483	0.582280
C	-2.342441	5.119910	-1.836403
C	3.923841	1.251808	1.967841
C	3.117516	-1.888816	0.078270
C	-2.954637	1.188340	0.942919
C	4.232465	-4.470190	-0.013071
C	-0.571938	2.735364	1.483748
C	-2.044576	4.212841	-0.819257
C	3.376015	1.355382	4.324813
C	-5.362731	1.382909	1.184854
C	4.488930	-3.632557	1.072284
C	3.938395	-2.348389	1.118749
H	4.149932	-1.708694	1.969335
H	5.119941	-3.974592	1.888627
H	4.660338	-5.468593	-0.045985
H	3.208590	-4.666343	-1.903930
H	2.214632	-2.408756	-1.816897
H	1.060170	-0.463595	2.621291
H	1.585351	0.304006	4.913885
H	3.601097	1.703682	5.329327
H	5.088665	2.315499	3.432472
H	4.583165	1.525698	1.150334
H	1.731360	1.870720	-1.855636
H	3.080972	3.183080	-3.467620
H	5.519255	2.742336	-3.698297
H	6.593777	0.984539	-2.306135
H	5.250230	-0.313678	-0.688024
H	-2.032823	-0.328142	2.175608
H	-4.141226	-1.011464	3.271192

H	-6.289367	0.072959	2.626024
H	-6.297714	1.850701	0.888221
H	-4.188033	2.562897	-0.176097
H	-1.500025	1.438344	-2.716126
H	-2.015092	3.049278	-4.517301
H	-2.559918	5.413797	-3.962919
H	-2.581253	6.150444	-1.586278
H	-2.048510	4.547121	0.213809
H	-2.117666	2.528258	2.979513
H	-1.023797	4.007190	4.617562
H	1.148519	5.093552	4.075331
H	2.217464	4.666765	1.866743
H	1.137042	3.178480	0.232345
C	-1.528537	-1.565166	-1.181011
C	-1.255460	-2.703921	-0.438563
C	-2.920298	-1.173818	-1.465228
Br	-0.281092	-1.381678	-2.957083
C	-3.604481	-2.949943	0.039689
H	-4.489038	-3.384619	0.484411
H	-0.251039	-3.106357	-0.379334
O	-3.300948	-0.300229	-2.207525
O	-3.889115	-1.906204	-0.780396
C	-2.331522	-3.362137	0.229970
Br	-1.978921	-4.840484	1.378130

TS2

B3LYP electronic energy: -7685.50777919 a.u.
B3LYP enthalpy: -7684.850451 a.u.
B3LYP free energy: -7684.987184 a.u.
M06 SCF energy in solution: -7689.91285283 a.u.
M06 enthalpy in solution: -7689.255525 a.u.
M06 free energy in solution: -7689.392258 a.u.
Three lowest frequencies (cm-1): -169.2719 7.35 10.81
Imaginary frequency: -169.2719 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.222531	-0.436176	-0.338047
P	0.946410	1.654820	-0.007668
P	-2.612867	-0.544386	0.169333
C	-3.919615	0.386535	4.544044
C	-2.681986	0.810826	4.059912
C	3.451041	1.707504	-3.265851
C	-3.369524	-4.578190	0.538820
C	-2.050776	4.482477	-0.209809
C	-1.316879	3.320615	0.027349
C	-2.305855	0.515645	2.747299
C	2.232783	0.979084	3.848499
C	2.342246	1.612999	-2.425760
C	-3.242631	0.739392	-2.222189
C	-2.935909	-3.271059	0.753150

C	-4.403808	-0.634336	2.402906
C	-1.458523	5.563856	-0.865535
C	-3.978378	1.546834	-3.090209
C	-4.175141	-4.878424	-0.563708
C	-4.778255	-0.340000	3.714096
C	1.765345	0.823285	2.542036
C	0.023873	3.221053	-0.377474
C	-3.662582	0.546874	-0.894367
C	1.546965	1.940898	1.720183
C	-0.128103	5.476117	-1.277613
C	2.250703	3.377081	3.551165
C	0.609606	4.314886	-1.035132
C	-5.131106	2.192933	-2.638225
C	-4.118968	-2.547438	-1.224387
C	-5.546766	2.021917	-1.316654
C	1.790818	3.221681	2.242423
C	2.466472	1.848987	-1.043802
C	-3.307950	-2.236539	-0.124783
C	4.706916	2.021513	-2.737436
C	-3.165039	-0.199389	1.899421
C	-4.821225	1.200797	-0.450072
C	2.475587	2.256994	4.355371
C	-4.546410	-3.860745	-1.441408
C	4.843160	2.243402	-1.367110
C	3.730716	2.161738	-0.524240
H	3.854018	2.336949	0.539435
H	5.817148	2.479020	-0.946807
H	5.573637	2.083117	-3.389852
H	3.336534	1.522875	-4.330645
H	1.375751	1.338589	-2.841146
H	1.558094	-0.171513	2.157372
H	2.401526	0.102490	4.467959
H	2.834396	2.380458	5.373707
H	2.432775	4.374653	3.942457
H	1.616289	4.099600	1.627579
H	-1.793842	2.482655	0.524968
H	-3.089412	4.534010	0.104955
H	-2.031721	6.466803	-1.058510
H	0.341120	6.312049	-1.790062
H	1.643024	4.262547	-1.361738
H	-2.313412	-3.049868	1.617137
H	-3.077267	-5.362525	1.232089
H	-4.509149	-5.898110	-0.734609
H	-5.174979	-4.083161	-2.299749
H	-4.423245	-1.767526	-1.914848
H	-2.331066	0.259433	-2.569763
H	-3.642438	1.681089	-4.114940
H	-5.698259	2.831279	-3.310447
H	-6.440128	2.525754	-0.956532
H	-5.157641	1.078250	0.574236
H	-5.071212	-1.214608	1.772223
H	-5.738681	-0.682845	4.090012
H	-4.211935	0.610517	5.566503

H	-2.001059	1.362126	4.702622
H	-1.331587	0.827170	2.382046
C	1.316120	-1.826246	-0.561957
C	2.722011	-1.548271	-0.662584
C	3.581623	-2.155253	0.196475
H	3.078308	-0.837057	-1.397802
C	3.141485	-3.112580	1.213342
Br	5.441797	-1.782674	0.159380
Br	0.201416	-1.892943	-2.513083
C	0.918710	-2.836289	0.275316
H	-0.060886	-3.293383	0.291311
O	3.811084	-3.653623	2.059374
O	1.780370	-3.421833	1.151453

12-cis

B3LYP electronic energy: -7685.56349438 a.u.
B3LYP enthalpy: -7684.903780 a.u.
B3LYP free energy: -7685.035459 a.u.
M06 SCF energy in solution: -7689.96945105 a.u.
M06 enthalpy in solution: -7689.309737 a.u.
M06 free energy in solution: -7689.441416 a.u.
Three lowest frequencies (cm-1): 12.7642 14.21 19.60

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.216180	-0.648418	-0.220843
Br	0.211164	-3.142047	-0.467633
P	0.520716	1.647355	0.131568
P	-2.248638	-0.799987	0.013745
C	-1.501212	3.577339	3.223492
H	-2.120366	4.459619	3.360031
C	-2.240868	-1.615636	-2.684728
H	-1.173947	-1.750548	-2.544267
C	-4.421474	-1.022719	-1.819849
H	-5.053702	-0.660790	-1.015053
C	-0.740040	2.141338	-2.324070
H	-0.773292	1.060423	-2.409794
C	-1.966960	-2.368324	2.312261
H	-1.070731	-1.776423	2.472204
C	-0.056519	4.131716	-1.128992
H	0.435968	4.604803	-0.284595
C	-0.170630	2.731062	-1.186734
C	-3.858424	-2.976611	0.937862
H	-4.454506	-2.854430	0.039955
C	-0.550334	4.923216	-2.165165
H	-0.461070	6.004637	-2.106425
C	2.865410	2.581408	1.482615
H	2.322654	2.448933	2.412138
C	-3.813925	0.629225	1.929693
H	-3.616613	-0.195637	2.605587
C	2.248915	2.303232	0.255026

C	-4.207996	-3.962705	1.862631
H	-5.074443	-4.591188	1.674520
C	-3.300844	0.606051	0.624033
C	-3.447464	-4.145144	3.018154
H	-3.720288	-4.914579	3.735463
C	-1.018199	3.268636	1.949740
H	-1.279937	3.907662	1.114767
C	4.899595	3.235927	0.343293
H	5.924287	3.595789	0.377864
C	2.977706	2.499074	-0.931493
H	2.522132	2.284323	-1.892947
C	-2.816828	-1.902120	-3.924750
H	-2.183798	-2.241457	-4.739923
C	-0.227072	2.130174	1.748860
C	-1.140672	4.326712	-3.283151
H	-1.515981	4.945003	-4.094238
C	-3.037956	-1.175166	-1.616165
C	4.182774	3.045105	1.524060
H	4.643934	3.259633	2.484412
C	-2.736938	-2.165902	1.156257
C	-0.423902	1.613009	4.120425
H	-0.192758	0.961470	4.958864
C	-4.993188	-1.316565	-3.057859
H	-6.064377	-1.196748	-3.197519
C	-4.191256	-1.756524	-4.113835
H	-4.637097	-1.981501	-5.079198
C	-2.325622	-3.344255	3.241786
H	-1.716361	-3.492288	4.129351
C	-1.224589	2.936799	-3.365711
H	-1.654635	2.464061	-4.244167
C	0.049013	1.295506	2.847194
H	0.635104	0.391267	2.701394
C	-4.595539	1.700001	2.369445
H	-4.989623	1.692633	3.382279
C	-3.582822	1.690740	-0.225021
H	-3.207525	1.699390	-1.242678
C	-1.198115	2.759484	4.312011
H	-1.571898	3.006389	5.302003
C	4.292164	2.961380	-0.884392
H	4.841041	3.105439	-1.811009
C	-4.365855	2.757734	0.215379
H	-4.579832	3.579756	-0.462774
C	-4.878184	2.765291	1.514589
H	-5.495202	3.592701	1.855205
C	2.203592	-0.824351	-0.628922
C	2.560410	-0.529813	-2.008605
C	3.158636	-1.272487	0.232072
C	4.510137	-1.452073	-0.214152
H	2.913269	-1.529228	1.257734
C	4.825596	-1.202681	-1.502521
H	5.804227	-1.322744	-1.949602
O	1.832260	-0.087011	-2.879856
O	3.896962	-0.763471	-2.379138

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Br       5.853494   -2.060761    0.991430



 12-trans
B3LYP electronic energy:    -7685.57738338 a.u.
B3LYP enthalpy:    -7684.917667 a.u.
B3LYP free energy:    -7685.051089 a.u.
M06 SCF energy in solution:    -7689.97551929 a.u.
M06 enthalpy in solution:    -7689.315803 a.u.
M06 free energy in solution:    -7689.449225 a.u.
Three lowest frequencies (cm-1):      13.3095      14.62      16.54

Cartesian coordinates
ATOM       X           Y           Z
Pd       0.025351   -0.537679    0.146874
Br       0.101569   -2.933930    1.012533
P        2.411438   -0.527243    0.034001
P       -2.356402   -0.673126    0.034078
C        4.285563   -3.835115   -1.617530
H        5.061824   -4.542916   -1.339175
C       -2.478364   -0.897503    2.818272
H       -1.539292   -0.351709    2.793467
C       -4.290845   -1.999523    1.657157
H       -4.779623   -2.300608    0.736411
C        2.648643   -1.153477    2.783236
H        1.591694   -1.390508    2.733763
C       -3.152054    1.461443   -1.611078
H       -2.598773    0.941716   -2.388323
C        4.700813   -0.470757    1.695662
H        5.236380   -0.134379    0.813091
C        3.321768   -0.739547    1.624465
C       -3.968400    1.594301    0.661178
H       -4.061250    1.179603    1.659563
C        5.390029   -0.622564    2.898401
H        6.455810   -0.413758    2.937661
C        3.792893    1.002860   -1.950930
H        3.770939    0.115844   -2.573716
C       -4.282027   -1.646402   -1.807001
H       -4.923481   -0.847487   -1.448450
C        3.236696    0.974860   -0.665001
C       -4.573579    2.820106    0.367616
H       -5.126847    3.343314    1.142937
C       -2.983025   -1.797392   -1.288842
C       -4.472772    3.365623   -0.911310
H       -4.944435    4.317946   -1.138003
C        3.939307   -2.809831   -0.734633
H        4.445323   -2.732990    0.221855
C        4.419302    3.324429   -1.658812
H        4.876883    4.231994   -2.043443
C        3.277397    2.143413    0.116082
H        2.854983    2.142174    1.116696
C       -3.037765   -1.263189    4.042412
```

H	-2.540127	-0.983874	4.967101
C	2.933473	-1.897393	-1.076517
C	4.711008	-1.034451	4.047951
H	5.248110	-1.147901	4.985982
C	-3.105544	-1.252808	1.614082
C	4.380307	2.171981	-2.442429
H	4.807279	2.175568	-3.441631
C	-3.252364	0.902457	-0.324372
C	2.630582	-3.047055	-3.191118
H	2.116576	-3.136347	-4.144454
C	-4.842042	-2.375410	2.883563
H	-5.756506	-2.962171	2.903715
C	-4.220738	-2.004491	4.077080
H	-4.650947	-2.299982	5.030264
C	-3.760826	2.681285	-1.901005
H	-3.676296	3.097817	-2.901103
C	3.342563	-1.297963	3.986964
H	2.808141	-1.621551	4.876040
C	2.269762	-2.028153	-2.309336
H	1.478124	-1.332196	-2.576927
C	-4.754210	-2.509538	-2.796003
H	-5.760231	-2.380362	-3.186312
C	-2.165776	-2.822714	-1.788425
H	-1.168505	-2.961154	-1.386067
C	3.636359	-3.953682	-2.846746
H	3.907907	-4.752736	-3.531583
C	3.865654	3.307151	-0.375475
H	3.889495	4.199930	0.243477
C	-2.643380	-3.681536	-2.780357
H	-1.998495	-4.470707	-3.157071
C	-3.934742	-3.528819	-3.285786
H	-4.301538	-4.197766	-4.059891
C	-0.012976	1.390742	-0.470081
C	0.138065	1.620301	-1.903232
C	-0.168762	2.465218	0.357413
C	-0.168297	3.800850	-0.164922
H	-0.296493	2.332497	1.428095
C	-0.016822	3.996794	-1.491627
H	0.002535	4.956536	-1.992460
O	0.259321	0.777689	-2.774813
O	0.131486	2.957531	-2.339542
Br	-0.368898	5.295535	0.999528

13-cis
B3LYP electronic energy: -7685.55721957 a.u.
B3LYP enthalpy: -7684.897598 a.u.
B3LYP free energy: -7685.030810 a.u.
M06 SCF energy in solution: -7689.97054655 a.u.
M06 enthalpy in solution: -7689.310925 a.u.
M06 free energy in solution: -7689.444137 a.u.
Three lowest frequencies (cm-1): 6.9228 10.81 17.06

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.154780	-0.594442	-0.421156
Br	-0.168945	-3.022836	-1.023416
P	-0.421991	1.693226	0.035933
P	2.276830	-0.853661	0.065908
C	2.331086	4.560907	-1.202188
H	2.865559	5.407229	-0.779678
C	1.579042	-2.680278	2.104763
H	0.624108	-2.739405	1.594294
C	3.839885	-1.834880	2.244258
H	4.637797	-1.198625	1.875329
C	0.043727	1.106956	2.748382
H	0.215852	0.092925	2.399570
C	2.672535	-1.515403	-2.625772
H	1.795024	-0.898925	-2.794783
C	-0.530856	3.412384	2.299656
H	-0.823605	4.196322	1.607728
C	-0.265358	2.115648	1.824303
C	4.220727	-2.586084	-1.110724
H	4.572691	-2.792062	-0.105274
C	-0.447249	3.696739	3.662255
H	-0.651474	4.703927	4.015078
C	-2.183807	3.381124	-1.458117
H	-1.333275	3.636905	-2.080248
C	4.267708	1.056293	-0.667340
H	4.303610	0.547894	-1.624749
C	-2.034101	2.502223	-0.376905
C	4.859552	-3.189031	-2.195724
H	5.702642	-3.852095	-2.021045
C	3.401944	0.600538	0.338217
C	4.415411	-2.947340	-3.496627
H	4.912665	-3.419809	-4.339457
C	1.485833	3.805535	-0.386583
H	1.380009	4.070067	0.659383
C	-4.540530	3.633986	-0.959710
H	-5.511120	4.063844	-1.190083
C	-3.157369	2.201996	0.413536
H	-3.066998	1.522148	1.255064
C	1.802444	-3.452525	3.246941
H	1.004252	-4.083479	3.628434
C	0.795303	2.705481	-0.911066
C	-0.120528	2.687366	4.572218
H	-0.066639	2.909309	5.634505
C	2.595782	-1.860975	1.587956
C	-3.431463	3.942577	-1.745322
H	-3.530243	4.621635	-2.587856
C	3.123327	-1.738701	-1.315912
C	1.818032	3.130490	-3.078298
H	1.944658	2.860617	-4.123194
C	4.060085	-2.611049	3.382663
H	5.028685	-2.579523	3.874579

C	3.040899	-3.420922	3.888434
H	3.212784	-4.023590	4.776310
C	3.320210	-2.108070	-3.709726
H	2.954735	-1.930990	-4.717550
C	0.116864	1.391085	4.114609
H	0.352080	0.595811	4.816446
C	0.983204	2.366817	-2.262568
H	0.469160	1.502567	-2.676518
C	5.104071	2.152495	-0.444432
H	5.772575	2.483289	-1.234788
C	3.388428	1.281436	1.568364
H	2.736953	0.948291	2.369039
C	2.491836	4.233198	-2.548810
H	3.145629	4.827846	-3.180944
C	-4.399184	2.762511	0.123748
H	-5.258359	2.509883	0.738361
C	4.228901	2.371889	1.791095
H	4.211182	2.873489	2.755186
C	5.092799	2.810377	0.785354
H	5.753256	3.655450	0.960814
C	-2.157991	-0.712321	-0.817488
C	-2.712567	-0.328195	-1.989262
C	-3.055502	-1.284768	0.146634
C	-4.391117	-1.372216	-0.105493
H	-2.670126	-1.657844	1.090350
C	-4.980319	-0.924112	-1.361362
O	-4.041812	-0.433889	-2.268922
Br	-5.595034	-2.100359	1.174458
O	-6.144955	-0.934663	-1.686817
H	-2.183539	0.098898	-2.833045

13-trans
B3LYP electronic energy: -7685.57169214 a.u.
B3LYP enthalpy: -7684.911845 a.u.
B3LYP free energy: -7685.044964 a.u.
M06 SCF energy in solution: -7689.97554185 a.u.
M06 enthalpy in solution: -7689.315695 a.u.
M06 free energy in solution: -7689.448814 a.u.
Three lowest frequencies (cm-1): 12.6748 14.90 17.18

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.000095	-0.696367	-0.045079
Br	0.000290	-3.170753	0.544670
Br	-0.000605	5.069234	1.181562
P	2.396224	-0.668083	-0.035521
P	-2.396026	-0.668614	-0.035500
O	-0.000431	2.918337	-2.343473
O	-0.001155	5.122746	-1.955351
C	3.120278	-1.526298	1.426320
C	2.428221	-1.482415	2.646006

H	1.450943	-1.011436	2.692392
C	2.975142	-2.062313	3.790558
H	2.427441	-2.023690	4.728157
C	4.210389	-2.709901	3.724634
H	4.631226	-3.172343	4.613384
C	4.897661	-2.771400	2.511298
H	5.854724	-3.282527	2.451208
C	4.358903	-2.179745	1.367473
H	4.901199	-2.238082	0.429301
C	3.192979	0.998290	0.014520
C	3.658468	1.540205	1.221554
H	3.631501	0.949270	2.131061
C	4.168269	2.840296	1.266279
H	4.524505	3.242950	2.210544
C	4.220611	3.615820	0.108961
H	4.609605	4.629363	0.146190
C	3.764247	3.084123	-1.100068
H	3.798069	3.681112	-2.007041
C	3.252727	1.788195	-1.147500
H	2.902163	1.391500	-2.094584
C	3.146105	-1.475085	-1.515158
C	4.424254	-1.123400	-1.983077
H	4.988300	-0.338007	-1.490610
C	4.974272	-1.770512	-3.090447
H	5.962292	-1.486249	-3.442437
C	4.257587	-2.775228	-3.743779
H	4.686041	-3.275802	-4.607978
C	2.990407	-3.134137	-3.281896
H	2.429030	-3.919021	-3.781434
C	2.434597	-2.489631	-2.175419
H	1.460593	-2.789348	-1.802358
C	-3.120054	-1.527006	1.426261
C	-4.358650	-2.180498	1.367322
H	-4.900912	-2.238783	0.429125
C	-4.897423	-2.772277	2.511075
H	-5.854462	-3.283439	2.450903
C	-4.210188	-2.710868	3.724433
H	-4.631037	-3.173390	4.613135
C	-2.974968	-2.063238	3.790450
H	-2.427286	-2.024695	4.728066
C	-2.428027	-1.483220	2.645971
H	-1.450787	-1.012183	2.692437
C	-3.145662	-1.475646	-1.515218
C	-2.433791	-2.489786	-2.175703
H	-1.459655	-2.789198	-1.802738
C	-2.989386	-3.134287	-3.282294
H	-2.427726	-3.918861	-3.782000
C	-4.256717	-2.775769	-3.744059
H	-4.685014	-3.276336	-4.608339
C	-4.973756	-1.771432	-3.090522
H	-5.961889	-1.487467	-3.442438
C	-4.423948	-1.124330	-1.983047
H	-4.988240	-0.339192	-1.490449

C	-3.193014	0.997657	0.014544
C	-3.253091	1.787509	-1.147479
H	-2.902654	1.390837	-2.094624
C	-3.764783	3.083377	-1.099989
H	-3.798862	3.680328	-2.006978
C	-4.220988	3.615052	0.109101
H	-4.610114	4.628541	0.146371
C	-4.168309	2.839574	1.266443
H	-4.524406	3.242225	2.210760
C	-3.658332	1.539562	1.221662
H	-3.631143	0.948648	2.131178
C	-0.000119	1.258332	-0.609279
C	-0.000274	1.622561	-1.913364
H	-0.000263	0.944254	-2.759979
C	-0.000761	4.011887	-1.477407
C	-0.000488	3.636682	-0.067787
C	-0.000190	2.338566	0.341243
H	0.000013	2.123283	1.405472

TS3

B3LYP electronic energy: -6649.21309552 a.u.
B3LYP enthalpy: -6648.849287 a.u.
B3LYP free energy: -6648.944527 a.u.
M06 SCF energy in solution: -6653.95961716 a.u.
M06 enthalpy in solution: -6653.595809 a.u.
M06 free energy in solution: -6653.691049 a.u.
Three lowest frequencies (cm-1): -118.3835 4.87 15.54
Imaginary frequency: -118.3835 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.372075	-0.558964	0.021220
P	1.850673	0.265182	-0.032717
C	1.104516	4.079647	-1.364077
C	2.882888	-0.112256	3.924197
C	2.309588	-0.286944	2.664624
C	3.349970	-2.610782	-2.552158
C	1.032311	2.843048	-0.723794
C	3.773734	0.939985	4.149134
C	2.508855	-1.733572	-1.866427
C	2.631493	0.581984	1.608837
C	3.024584	-0.874460	-0.882584
C	4.090813	1.814967	3.108708
C	5.233617	-1.807003	-1.268208
C	3.524718	1.638034	1.844058
C	4.395314	-0.924121	-0.584909
C	2.026143	1.870756	-0.928991
C	2.164115	4.357482	-2.231426
C	4.713605	-2.648676	-2.254001
C	3.150299	3.394761	-2.450737
C	3.084854	2.158519	-1.802760

H	3.856223	1.416830	-1.985550
H	3.973592	3.602165	-3.129196
H	2.216265	5.317073	-2.738612
H	0.328496	4.821053	-1.193923
H	0.196128	2.625190	-0.063033
H	1.443399	-1.725226	-2.085048
H	2.935753	-3.272073	-3.308098
H	5.367529	-3.338361	-2.780902
H	6.292537	-1.840156	-1.025757
H	4.807364	-0.281844	0.187884
H	1.602892	-1.096143	2.498229
H	2.625035	-0.792072	4.731753
H	4.213359	1.081194	5.132848
H	4.778205	2.639335	3.279373
H	3.774563	2.328109	1.043718
C	-2.324738	-1.067958	-0.123530
C	-3.067178	-0.064701	0.465283
C	-2.709877	-1.648217	-1.420892
Br	-1.437802	-2.588232	1.206618
C	-4.519536	-0.021537	-1.451266
H	-5.347023	0.313404	-2.063284
H	-2.832985	0.284966	1.464362
O	-2.186720	-2.553497	-2.019204
O	-3.820750	-1.027212	-2.023644
C	-4.181604	0.482437	-0.241798
Br	-5.190973	1.906188	0.513067

TS4

B3LYP electronic energy: -6649.21056152 a.u.
B3LYP enthalpy: -6648.846660 a.u.
B3LYP free energy: -6648.942831 a.u.
M06 SCF energy in solution: -6653.95894914 a.u.
M06 enthalpy in solution: -6653.595048 a.u.
M06 free energy in solution: -6653.691219 a.u.
Three lowest frequencies (cm-1): -122.5451 4.07 12.88
Imaginary frequency: -122.5451 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.249267	-0.603831	0.194762
P	-1.945448	0.241943	-0.007485
C	-3.971743	-0.836390	-4.055841
C	-3.091201	-1.722099	-3.430473
C	-1.013646	4.234079	-0.303449
C	-2.486056	-1.371637	-2.223312
C	-2.668477	-0.535927	2.576600
C	-0.986831	2.841165	-0.370524
C	-3.648314	0.750242	-2.255668
C	-3.522547	-0.984276	3.583619
C	-2.102737	4.884778	0.281106
C	-4.246092	0.399988	-3.468343

C	-3.136989	-0.371787	1.262426
C	-4.853613	-1.289145	3.287793
C	-3.142312	2.742453	0.721171
C	-5.325818	-1.139287	1.983121
C	-2.054016	2.079774	0.133815
C	-2.765222	-0.134783	-1.618480
C	-4.474428	-0.681034	0.974582
C	-3.163927	4.137146	0.794722
H	-0.128762	2.337074	-0.809747
H	-0.179810	4.809199	-0.696614
H	-2.120180	5.969486	0.342931
H	-4.010363	4.638044	1.257048
H	-3.970007	2.170603	1.129776
H	-1.628811	-0.314922	2.806592
H	-3.146317	-1.105417	4.595834
H	-5.517173	-1.648008	4.069894
H	-6.358613	-1.380407	1.745871
H	-4.852320	-0.570441	-0.037117
H	-3.865228	1.716489	-1.810554
H	-4.924622	1.096255	-3.954084
H	-4.436321	-1.105605	-5.000600
H	-2.865837	-2.682156	-3.886807
H	-1.786521	-2.055808	-1.749594
C	2.212563	-1.072847	0.424789
C	3.148504	-0.437245	-0.465889
C	4.160426	0.305405	0.053003
H	3.023792	-0.540001	-1.538024
C	4.362485	0.465019	1.495398
Br	5.394689	1.208912	-1.063391
Br	1.330996	-2.930807	-0.351894
C	2.431094	-0.981533	1.775572
H	1.881140	-1.518205	2.537376
O	5.209843	1.109888	2.056987
O	3.444631	-0.246780	2.286963

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B3LYP electronic energy: -7894.43776861 a.u.
B3LYP enthalpy: -7893.772045 a.u.
B3LYP free energy: -7893.916592 a.u.
M06 SCF energy in solution: -7898.86005189 a.u.
M06 enthalpy in solution: -7898.194328 a.u.
M06 free energy in solution: -7898.338875 a.u.
Three lowest frequencies (cm-1): 6.8189 15.78 18.55

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.247282	0.076201	-0.538665
Br	-0.425620	-1.169688	-2.663017
P	0.928773	0.551994	1.643287
P	-1.765858	1.536462	-0.748472
C	-1.791569	1.097907	4.731028

H	-1.964670	1.803279	5.539285
C	-0.318246	2.606632	-2.922808
H	0.192487	1.649211	-2.933615
C	-1.987512	4.094334	-2.007026
H	-2.768195	4.313367	-1.286183
C	1.768527	3.082745	0.767402
H	1.344005	2.780731	-0.186189
C	-3.617502	-0.546622	-0.976039
H	-2.999024	-1.062322	-0.248128
C	2.282712	2.599803	3.080913
H	2.281366	1.920800	3.928155
C	1.706088	2.205417	1.860037
C	-4.059842	1.337320	-2.429128
H	-3.794132	2.312084	-2.824447
C	2.878254	3.854569	3.207877
H	3.316175	4.148040	4.157871
C	1.794337	-1.816115	2.944922
H	0.746114	-2.079438	3.024999
C	-3.667055	2.166754	1.272578
H	-4.234260	1.319245	0.903553
C	2.185999	-0.601861	2.360080
C	-5.199469	0.691145	-2.910098
H	-5.807045	1.173264	-3.671453
C	-2.449349	2.515268	0.669694
C	-5.553351	-0.569130	-2.423343
H	-6.437531	-1.071962	-2.805957
C	-0.729441	1.311036	3.850779
H	-0.099278	2.183330	3.980843
C	4.110454	-2.403451	3.337060
H	4.853443	-3.099712	3.716030
C	3.556983	-0.307941	2.260642
H	3.886795	0.620037	1.805800
C	0.016167	3.570953	-3.876171
H	0.793618	3.355949	-4.604205
C	-0.497165	0.414025	2.798643
C	2.922829	4.725491	2.115674
H	3.393928	5.699428	2.215718
C	-1.323001	2.855634	-1.972228
C	2.752393	-2.708128	3.429474
H	2.428907	-3.644376	3.874667
C	-3.259665	0.722730	-1.453900
C	-2.412746	-0.897442	3.519498
H	-3.056885	-1.759746	3.373039
C	-1.651169	5.055957	-2.960995
H	-2.177741	6.006551	-2.972539
C	-0.646646	4.798686	-3.896323
H	-0.385858	5.549004	-4.637806
C	-4.760513	-1.187657	-1.455320
H	-5.002192	-2.178799	-1.083157
C	2.373133	4.335962	0.893937
H	2.415748	5.001905	0.036598
C	-1.359553	-0.683336	2.630113
H	-1.219695	-1.384407	1.810617

C	-4.169888	2.913938	2.340005
H	-5.117694	2.630310	2.789271
C	-1.743650	3.622723	1.171286
H	-0.802630	3.920158	0.721181
C	-2.627978	-0.008658	4.574250
H	-3.449425	-0.172767	5.266487
C	4.510100	-1.200516	2.751120
H	5.565236	-0.952807	2.672632
C	-2.252450	4.372207	2.231580
H	-1.697284	5.233428	2.594155
C	-3.469549	4.020860	2.819172
H	-3.869079	4.606855	3.642565
C	2.064587	-0.820204	-0.811334
C	2.194575	-2.259093	-0.650482
C	3.146323	-0.107627	-1.242842
C	4.396604	-0.758045	-1.506630
H	3.089414	0.967337	-1.388075
C	4.501393	-2.090460	-1.315061
H	5.390179	-2.689482	-1.465581
O	1.322132	-3.052240	-0.317710
O	3.444109	-2.819363	-0.901739
Br	5.902009	0.245166	-2.094692
Cu	-0.786599	-2.844364	-0.890228
I	-2.420954	-4.153732	0.502906

PhSnMe3

B3LYP electronic energy: -354.75448533 a.u.
B3LYP enthalpy: -354.540438 a.u.
B3LYP free energy: -354.598069 a.u.
M06 SCF energy in solution: -354.55521423 a.u.
M06 enthalpy in solution: -354.341167 a.u.
M06 free energy in solution: -354.398798 a.u.
Three lowest frequencies (cm-1): 19.0185 65.74 75.29

Cartesian coordinates

ATOM	X	Y	Z
C	-1.805695	-1.204258	0.002471
C	-1.078187	-0.001612	-0.001346
C	-1.804574	1.201535	-0.001264
C	-3.202046	1.206129	0.007043
C	-3.904282	-0.000381	0.013817
C	-3.202980	-1.207639	0.010836
H	-1.283481	-2.159607	-0.005684
H	-1.280781	2.155852	-0.012224
H	-3.741789	2.150244	0.006010
H	-4.991387	0.000019	0.019280
H	-3.743548	-2.151278	0.012792
Sn	1.097732	-0.000375	-0.000105
C	1.790323	1.854736	-0.911409
H	1.454939	2.725399	-0.338906
H	2.884240	1.875454	-0.947887

H	1.411233	1.949638	-1.933580
C	1.854141	-0.134553	2.042119
H	1.525982	-1.064153	2.517415
H	2.948782	-0.113687	2.046199
H	1.491539	0.703938	2.644720
C	1.797602	-1.714031	-1.151267
H	1.449809	-1.649813	-2.186826
H	2.891685	-1.749998	-1.157577
H	1.430351	-2.652804	-0.724482

TS5

B3LYP electronic energy: -7004.00765026 a.u.
B3LYP enthalpy: -7003.426381 a.u.
B3LYP free energy: -7003.549864 a.u.
M06 SCF energy in solution: -7008.57065364 a.u.
M06 enthalpy in solution: -7007.989384 a.u.
M06 free energy in solution: -7008.112867 a.u.
Three lowest frequencies (cm-1): -37.3210 19.06 21.58
Imaginary frequency: -37.3210 cm-1

Cartesian coordinates

ATOM	X	Y	Z
P	0.454012	1.924246	0.177050
C	4.116966	3.571635	-0.863992
H	4.909422	4.135419	-0.379088
C	0.563535	1.986181	3.008427
H	0.582329	0.903675	2.951517
C	0.516791	4.149593	1.929833
H	0.474746	4.755711	1.029425
C	0.538374	2.746455	1.831034
C	0.539548	4.773081	3.176016
H	0.526446	5.858085	3.235890
C	-0.813974	3.665401	-1.736092
H	0.141263	3.742696	-2.242597
C	-0.940046	2.882747	-0.581046
C	2.986726	3.203756	-0.130416
H	2.914762	3.485072	0.914276
C	-3.156470	4.272902	-1.615739
H	-4.011934	4.809328	-2.017420
C	-2.193697	2.809386	0.051391
H	-2.311558	2.218465	0.954998
C	1.956118	2.472311	-0.737171
C	0.569307	4.005021	4.343785
H	0.581529	4.491960	5.315259
C	-1.916302	4.355489	-2.247711
H	-1.799351	4.958112	-3.144444
C	3.212119	2.478853	-2.817038
H	3.295815	2.190350	-3.861528
C	0.577401	2.613547	4.257410
H	0.595990	2.009290	5.160267
C	2.087136	2.093641	-2.086184

H	1.310032	1.498581	-2.557612
C	4.229534	3.218529	-2.208826
H	5.107765	3.510326	-2.778500
C	-3.292232	3.497861	-0.461069
H	-4.252388	3.428394	0.042970
C	-1.577920	-0.454100	-0.551117
C	-1.580053	-0.017560	-1.942317
C	-2.775880	-0.704159	0.060220
C	-4.013401	-0.516629	-0.637553
H	-2.811917	-1.054040	1.086493
C	-3.994455	-0.114538	-1.926496
O	-2.830838	0.114145	-2.567368
Br	-5.675514	-0.828852	0.236883
Pd	0.214245	-0.556817	0.378502
Br	2.562006	-0.626685	1.453716
C	-0.252870	-2.512462	0.906430
C	-1.027838	-3.416616	0.155622
C	0.064479	-2.877259	2.230586
C	-1.458659	-4.632364	0.695356
H	-1.313177	-3.173601	-0.861809
C	-0.386418	-4.082022	2.779795
H	0.679702	-2.224668	2.840543
C	-1.143308	-4.969108	2.012961
H	-2.049159	-5.311211	0.084023
H	-0.131848	-4.328676	3.808167
H	-1.482553	-5.911155	2.436111
Sn	2.138710	-2.347891	-0.968028
C	0.896577	-2.804131	-2.703188
H	0.216564	-3.633364	-2.499461
H	0.334784	-1.925456	-3.023544
H	1.586966	-3.096416	-3.504097
C	2.734850	-4.147721	0.086945
H	1.860882	-4.713691	0.414727
H	3.332548	-4.767090	-0.592445
H	3.340407	-3.884623	0.956624
C	3.874391	-1.288696	-1.740562
H	4.684589	-1.327925	-1.008849
H	4.194973	-1.773692	-2.670595
H	3.641803	-0.243276	-1.949861
O	-0.613947	0.242769	-2.639924
H	-4.861273	0.052174	-2.553273

TS6
B3LYP electronic energy: -7003.99848006 a.u.
B3LYP enthalpy: -7003.417372 a.u.
B3LYP free energy: -7003.542880 a.u.
M06 SCF energy in solution: -7008.57168797 a.u.
M06 enthalpy in solution: -7007.990580 a.u.
M06 free energy in solution: -7008.116088 a.u.
Three lowest frequencies (cm-1): -31.7895 12.15 21.71
Imaginary frequency: -31.7895 cm-1

Cartesian coordinates

ATOM	X	Y	Z
P	-0.786243	1.801776	0.147703
C	0.039556	4.798964	-2.610429
H	0.226076	5.869412	-2.602479
C	0.343383	2.968324	2.463856
H	1.114507	2.212423	2.367157
C	-1.685144	4.019432	1.669073
H	-2.510387	4.068356	0.964971
C	-0.697314	3.028236	1.525545
C	-1.621943	4.935232	2.718397
H	-2.391519	5.696225	2.815486
C	-3.364084	1.541209	-1.084665
H	-2.913264	1.892500	-2.006500
C	-2.601657	1.450742	0.087676
C	-0.216538	4.136709	-1.407354
H	-0.225855	4.699620	-0.480455
C	-5.324361	0.745124	0.093789
H	-6.372789	0.461200	0.093981
C	-3.226807	1.011871	1.269107
H	-2.658797	0.943021	2.191898
C	-0.452324	2.755408	-1.394582
C	-0.578622	4.868330	3.646151
H	-0.534186	5.578813	4.467151
C	-4.717329	1.190125	-1.079067
H	-5.292615	1.265084	-1.997740
C	-0.172080	2.716322	-3.812193
H	-0.153963	2.157227	-4.743758
C	0.400525	3.883702	3.517904
H	1.212013	3.821954	4.237706
C	-0.410829	2.050557	-2.609870
H	-0.566446	0.974298	-2.617564
C	0.055993	4.094638	-3.814234
H	0.251743	4.613256	-4.748618
C	-4.575195	0.661838	1.271021
H	-5.039497	0.316677	2.190474
C	-0.856063	-1.344806	0.807140
C	-1.247255	-1.811564	2.019038
C	-1.685411	-1.731639	-0.302389
C	-2.780502	-2.522984	-0.129286
H	-1.445419	-1.390449	-1.304592
C	-3.207957	-2.982697	1.186197
O	-2.360913	-2.569931	2.216777
Br	-3.856783	-3.058359	-1.600584
Pd	0.745648	-0.121509	0.576357
Br	2.773973	1.432376	0.133967
C	1.896042	-1.629424	1.424902
C	1.684277	-3.014729	1.292958
C	2.835378	-1.203880	2.385752
C	2.384839	-3.936056	2.077086
H	0.960089	-3.388355	0.577809
C	3.518129	-2.123619	3.188516

H	3.048881	-0.146960	2.505769
C	3.301773	-3.493787	3.032827
H	2.202917	-5.000217	1.945371
H	4.229086	-1.763406	3.928651
H	3.841388	-4.208748	3.648505
Sn	2.732770	-1.067208	-1.423478
H	-0.727782	-1.649233	2.955587
O	-4.175274	-3.649679	1.468385
C	1.500509	-2.750023	-2.094645
H	1.929141	-3.682303	-1.717082
H	0.464646	-2.681187	-1.761482
H	1.521532	-2.760060	-3.189983
C	4.669961	-1.740285	-0.724104
H	4.559200	-2.425242	0.118405
H	5.177424	-2.257673	-1.546854
H	5.272765	-0.883518	-0.415408
C	2.941787	0.240492	-3.152269
H	3.850347	0.838206	-3.043137
H	3.015633	-0.372888	-4.058150
H	2.093921	0.920863	-3.249946

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B3LYP electronic energy: -5345.73439178 a.u.
B3LYP enthalpy: -5344.982328 a.u.
B3LYP free energy: -5345.122131 a.u.
M06 SCF energy in solution: -5347.41143544 a.u.
M06 enthalpy in solution: -5346.659372 a.u.
M06 free energy in solution: -5346.799175 a.u.
Three lowest frequencies (cm-1): 11.0377 14.37 15.23

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.177583	-0.531950	0.154257
P	-0.440559	1.873770	-0.188579
P	2.251093	-0.745801	0.002350
C	1.955262	3.650790	-3.109786
H	2.671851	4.463968	-3.186160
C	2.051736	-1.253623	2.762159
H	0.995148	-1.039237	2.627369
C	4.284386	-1.477389	1.856794
H	4.972564	-1.427715	1.017529
C	0.549551	2.506460	2.354678
H	0.553304	1.431190	2.502013
C	2.456136	-1.900835	-2.533786
H	1.976134	-0.984911	-2.870247
C	0.038507	4.433493	0.984725
H	-0.343915	4.863294	0.063330
C	0.121900	3.037160	1.128981
C	3.331567	-3.286009	-0.759764
H	3.536753	-3.462858	0.290063
C	0.423646	5.276571	2.026263

H	0.359834	6.354104	1.899516
C	-2.705570	2.836981	-1.683090
H	-2.086395	2.799319	-2.572782
C	4.222221	0.689408	-1.555228
H	4.184903	-0.117297	-2.277996
C	-2.175057	2.485989	-0.435250
C	3.628847	-4.282349	-1.692738
H	4.070298	-5.216046	-1.354815
C	3.425624	0.645747	-0.402788
C	3.356970	-4.086052	-3.046350
H	3.591696	-4.862202	-3.769792
C	1.335431	3.395676	-1.883565
H	1.589015	4.007384	-1.025810
C	-4.851895	3.320091	-0.668721
H	-5.886158	3.640577	-0.759833
C	-3.004744	2.560356	0.697755
H	-2.612403	2.299071	1.676236
C	2.543121	-1.549411	4.037124
H	1.860549	-1.567528	4.882389
C	0.416761	2.345768	-1.755479
C	0.873348	4.737464	3.235364
H	1.164868	5.396090	4.049244
C	2.915947	-1.222975	1.658218
C	-4.036205	3.250842	-1.797035
H	-4.429600	3.522686	-2.773107
C	2.752686	-2.078485	-1.170555
C	0.756624	1.811364	-4.109494
H	0.525938	1.189874	-4.970923
C	4.769903	-1.782695	3.127242
H	5.829078	-1.982942	3.266126
C	3.898731	-1.820403	4.220394
H	4.279710	-2.053960	5.211151
C	2.768133	-2.890627	-3.465161
H	2.540070	-2.732366	-4.516066
C	0.924616	3.353589	3.401507
H	1.245542	2.926890	4.347793
C	0.150513	1.543910	-2.881807
H	-0.534426	0.703937	-2.793340
C	5.091217	1.760631	-1.781096
H	5.703412	1.769848	-2.679282
C	3.528690	1.701424	0.519762
H	2.936535	1.688831	1.428617
C	1.662089	2.868966	-4.226672
H	2.141419	3.074702	-5.179964
C	-4.330174	2.974550	0.580784
H	-4.955442	3.025515	1.468067
C	4.398231	2.767624	0.295512
H	4.463053	3.568198	1.027770
C	5.183574	2.802543	-0.859267
H	5.865361	3.630800	-1.033811
C	-2.162840	-0.744812	0.613813
C	-2.453790	-0.498561	2.021048
C	-3.188646	-1.099537	-0.213619

C	-4.530306	-1.205345	0.281782
H	-3.008575	-1.323610	-1.260736
C	-4.781949	-0.973848	1.587156
H	-5.749822	-1.035390	2.068347
O	-1.660056	-0.172439	2.890894
O	-3.789545	-0.635372	2.439675
Br	-5.960958	-1.681912	-0.884928
C	-0.291813	-2.600795	0.179259
C	-0.411909	-3.278090	-1.046243
C	-0.328305	-3.373322	1.351136
C	-0.535011	-4.669985	-1.102389
H	-0.402745	-2.720099	-1.980107
C	-0.445735	-4.767383	1.300321
H	-0.281760	-2.892327	2.324184
C	-0.547352	-5.423417	0.072960
H	-0.621105	-5.163794	-2.068361
H	-0.468468	-5.337303	2.227238
H	-0.643050	-6.505790	0.032602

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B3LYP electronic energy: -5345.72707931 a.u.
B3LYP enthalpy: -5344.974917 a.u.
B3LYP free energy: -5345.115095 a.u.
M06 SCF energy in solution: -5347.41286315 a.u.
M06 enthalpy in solution: -5346.660701 a.u.
M06 free energy in solution: -5346.800879 a.u.
Three lowest frequencies (cm-1): 9.6174 11.81 18.96

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.078912	-0.571934	0.309114
P	-0.441201	1.838366	-0.007500
P	2.355568	-0.700852	-0.052396
C	1.706347	4.130368	-2.754670
H	2.276975	5.055020	-2.767598
C	2.563335	-1.560557	2.625113
H	1.482622	-1.478723	2.627269
C	4.670646	-1.385827	1.455269
H	5.237651	-1.146670	0.560267
C	0.701476	2.320760	2.506960
H	0.903308	1.252935	2.493982
C	2.272714	-1.666550	-2.675988
H	1.690325	-0.769752	-2.870242
C	-0.236262	4.284059	1.455689
H	-0.773498	4.751056	0.635455
C	0.061428	2.910809	1.407260
C	3.486618	-3.092300	-1.151794
H	3.853908	-3.321165	-0.157767
C	0.132308	5.050382	2.561193
H	-0.101571	6.111354	2.583360
C	-2.758301	2.580506	-1.519956

H	-2.136739	2.529680	-2.407162
C	4.032287	0.961735	-1.721652
H	3.917684	0.223362	-2.506633
C	-2.203361	2.364686	-0.250820
C	3.722070	-3.994041	-2.192564
H	4.275794	-4.907455	-1.993007
C	3.408494	0.778535	-0.480113
C	3.246555	-3.730220	-3.476789
H	3.432326	-4.433124	-4.284282
C	1.131070	3.695138	-1.558442
H	1.268629	4.284764	-0.659033
C	-4.941619	2.951585	-0.539903
H	-6.000419	3.166632	-0.651872
C	-3.041733	2.456091	0.874172
H	-2.638036	2.298107	1.868744
C	3.239793	-1.954180	3.783252
H	2.677452	-2.171636	4.687317
C	0.396379	2.503104	-1.515050
C	0.785253	4.453650	3.643572
H	1.063397	5.050956	4.507672
C	3.268293	-1.278218	1.448027
C	-4.117292	2.873489	-1.661226
H	-4.528015	3.037455	-2.653833
C	2.768291	-1.912382	-1.383293
C	0.832771	2.190687	-3.892418
H	0.711252	1.600060	-4.796731
C	5.343901	-1.787211	2.607765
H	6.427396	-1.870394	2.597505
C	4.628963	-2.072578	3.775134
H	5.155852	-2.381574	4.673958
C	2.519680	-2.561655	-3.716588
H	2.135087	-2.351474	-4.711147
C	1.062811	3.086618	3.618611
H	1.553491	2.612325	4.464280
C	0.270569	1.747044	-2.694912
H	-0.277178	0.807507	-2.675503
C	4.827990	2.085847	-1.959819
H	5.306958	2.204018	-2.928271
C	3.604400	1.751440	0.515564
H	3.147954	1.628639	1.492045
C	1.551904	3.387409	-3.925123
H	1.994537	3.733452	-4.855203
C	-4.397900	2.745421	0.730218
H	-5.031116	2.798736	1.611216
C	4.400057	2.870850	0.278029
H	4.541665	3.605010	1.066838
C	5.016462	3.042623	-0.963570
H	5.641550	3.912015	-1.149371
C	-2.076196	-0.800734	0.748324
C	-2.556960	-0.656343	2.005488
C	-3.063686	-1.100658	-0.254132
C	-4.386983	-1.183518	0.055888
H	-2.755396	-1.269798	-1.281444

C	-4.887498	-0.985276	1.410227
O	-3.879053	-0.746340	2.341022
Br	-5.693147	-1.563095	-1.275359
O	-6.034298	-1.009579	1.796675
H	-1.964003	-0.456459	2.891533
C	-0.148422	-2.639638	0.444723
C	-0.165354	-3.397265	-0.738099
C	-0.267915	-3.340241	1.656793
C	-0.266012	-4.793280	-0.712115
H	-0.092924	-2.904014	-1.704284
C	-0.356930	-4.735212	1.691034
H	-0.319634	-2.798926	2.599039
C	-0.354185	-5.470461	0.504110
H	-0.274985	-5.347739	-1.648283
H	-0.445672	-5.244682	2.648462
H	-0.432727	-6.554524	0.527594

TS7-bis

B3LYP electronic energy: -5345.71687036 a.u.
B3LYP enthalpy: -5344.966641 a.u.
B3LYP free energy: -5345.105606 a.u.
M06 SCF energy in solution: -5347.39664892 a.u.
M06 enthalpy in solution: -5346.646420 a.u.
M06 free energy in solution: -5346.785385 a.u.
Three lowest frequencies (cm-1): -322.8741 7.19 13.67
Imaginary frequency: -322.8741 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.007804	-0.457267	0.110795
P	2.461710	-0.402223	-0.104291
P	-0.852602	1.819092	-0.038527
C	0.582945	5.020406	3.038484
C	1.292603	3.833583	2.858076
C	3.456495	-3.352526	-2.795979
C	-4.639069	1.769799	1.574006
C	3.689064	3.204734	-1.710867
C	2.969926	2.197700	-1.065667
C	0.848367	2.885244	1.933314
C	2.869526	-0.420523	4.003228
C	2.964256	-2.194714	-2.197054
C	-0.425031	1.670787	-2.790885
C	-3.256065	1.744304	1.401239
C	-1.024879	4.304341	1.376732
C	4.903692	2.910373	-2.331274
C	-0.216666	2.145263	-4.086903
C	-5.481511	1.984444	0.479514
C	-0.579610	5.252087	2.297984
C	2.355167	-0.481148	2.704893
C	3.449566	0.880649	-1.022425
C	-0.542299	2.559871	-1.709174

C	3.201395	-0.319732	1.594909
C	5.393118	1.603207	-2.299976
C	5.079934	-0.027513	3.111339
C	4.674002	0.596923	-1.652388
C	-0.103353	3.517277	-4.318922
C	-3.543599	2.151517	-0.963556
C	-0.204478	4.409745	-3.249879
C	4.569482	-0.087641	1.814578
C	3.157478	-1.956971	-0.824726
C	-2.690709	1.942887	0.128823
C	4.133327	-4.304857	-2.029054
C	-0.306535	3.112057	1.171024
C	-0.426774	3.936269	-1.954997
C	4.230920	-0.195076	4.208903
C	-4.930256	2.172337	-0.787298
C	4.312685	-4.088269	-0.663550
C	3.830712	-2.921257	-0.063904
H	3.984925	-2.763934	0.998369
H	4.832658	-4.825778	-0.057698
H	4.514485	-5.210119	-2.494255
H	3.307761	-3.513648	-3.860670
H	2.438404	-1.461580	-2.804332
H	1.289864	-0.642904	2.558746
H	2.198942	-0.544567	4.849186
H	4.630106	-0.144834	5.218677
H	6.140541	0.154784	3.264567
H	5.238378	0.055851	0.971419
H	2.023921	2.442299	-0.598798
H	3.289999	4.215011	-1.736309
H	5.462727	3.691553	-2.839698
H	6.337224	1.362020	-2.781858
H	5.066720	-0.414471	-1.645961
H	-2.614063	1.569146	2.260383
H	-5.057536	1.617335	2.565283
H	-6.559654	2.000104	0.614240
H	-5.576806	2.337093	-1.645161
H	-3.131330	2.304521	-1.955763
H	-0.484367	0.600403	-2.605923
H	-0.131738	1.442615	-4.911700
H	0.068378	3.888636	-5.325684
H	-0.112479	5.479065	-3.422209
H	-0.499940	4.644026	-1.135900
H	-1.944856	4.484281	0.828480
H	-1.146195	6.168046	2.444240
H	0.924463	5.757317	3.760626
H	2.186696	3.633732	3.442204
H	1.394553	1.955393	1.819028
C	-1.773545	-1.453815	0.536150
C	-2.113859	-1.347438	1.963523
C	-2.812517	-1.656877	-0.351123
O	-3.431597	-1.606894	2.334740
O	-1.349898	-1.052019	2.867500
C	-4.417028	-1.840406	1.433426

H	-5.382920	-1.999761	1.892706
C	-4.144718	-1.849935	0.109288
H	-2.621582	-1.725152	-1.416907
Br	-5.557831	-2.151090	-1.135517
C	-0.217359	-2.577667	0.231177
C	-0.214934	-3.264775	-1.003212
C	0.191848	-3.292159	1.375658
C	0.184877	-4.594433	-1.089863
H	-0.546883	-2.755145	-1.904930
C	0.580694	-4.631649	1.285864
H	0.175869	-2.805005	2.344003
C	0.581565	-5.291607	0.057341
H	0.185082	-5.092215	-2.056835
H	0.883286	-5.158685	2.188211
H	0.882668	-6.333599	-0.009683

TS8-mono
B3LYP electronic energy: -4309.41313161 a.u.
B3LYP enthalpy: -4308.956213 a.u.
B3LYP free energy: -4309.058769 a.u.
M06 SCF energy in solution: -4311.42951064 a.u.
M06 enthalpy in solution: -4310.972592 a.u.
M06 free energy in solution: -4311.075148 a.u.
Three lowest frequencies (cm-1): -269.8826 5.53 14.06
Imaginary frequency: -269.8826 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.237366	0.063677	-0.401081
P	2.077459	-0.372116	-0.006350
C	3.804197	-3.599681	-2.881742
C	2.824117	-2.701464	-3.309920
C	1.705124	-2.340659	3.580878
C	2.317689	-1.747705	-2.426729
C	2.751002	2.326777	0.246593
C	1.485048	-1.825712	2.303536
C	3.776583	-2.579298	-0.685732
C	3.566499	3.452987	0.135920
C	2.872078	-2.012421	4.275237
C	4.276840	-3.538092	-1.569371
C	3.200864	1.076445	-0.210116
C	4.833053	3.348764	-0.444012
C	3.602654	-0.661616	2.402535
C	5.282890	2.112393	-0.910326
C	2.434968	-0.987484	1.696523
C	2.793476	-1.670896	-1.106943
C	4.473341	0.980101	-0.793417
C	3.817067	-1.171119	3.685505
H	0.566692	-2.068503	1.773558
H	0.961420	-2.988466	4.036928
H	3.040449	-2.405359	5.274245

H	4.723643	-0.907542	4.223768
H	4.342930	-0.005546	1.954765
H	1.758718	2.420243	0.678432
H	3.204837	4.413588	0.492202
H	5.464062	4.228546	-0.537798
H	6.265121	2.025719	-1.367380
H	4.833028	0.023934	-1.160804
H	4.147162	-2.543232	0.334204
H	5.034745	-4.238935	-1.229587
H	4.192619	-4.349216	-3.565885
H	2.445454	-2.749609	-4.327238
H	1.542994	-1.059894	-2.758002
C	-2.240811	0.301358	-0.715793
C	-2.672806	0.280701	-2.008141
H	-2.102931	0.620913	-2.864905
C	-4.862936	-0.624859	-1.483707
C	-3.193028	-0.141249	0.271686
H	-2.925151	-0.125495	1.323052
O	-5.921456	-0.996479	-1.925579
C	-4.423998	-0.588354	-0.091828
O	-3.900606	-0.147148	-2.386211
Br	-5.676099	-1.202194	1.196250
C	-1.079206	1.920545	-0.120864
C	-0.890047	2.896888	-1.114525
C	-1.315363	2.334495	1.200547
C	-0.888650	4.252091	-0.781056
H	-0.736565	2.602561	-2.148571
C	-1.312316	3.694720	1.526199
H	-1.485450	1.602202	1.984380
C	-1.098221	4.658877	0.539939
H	-0.729160	4.992507	-1.561260
H	-1.482134	3.995615	2.557221
H	-1.106220	5.715169	0.793984

9
B3LYP electronic energy: -3145.21040515 a.u.
B3LYP enthalpy: -3145.046520 a.u.
B3LYP free energy: -3145.097871 a.u.
M06 SCF energy in solution: -3147.60242692 a.u.
M06 enthalpy in solution: -3147.438542 a.u.
M06 free energy in solution: -3147.489893 a.u.
Three lowest frequencies (cm-1): 53.8223 75.44 82.96

Cartesian coordinates

ATOM	X	Y	Z
C	1.964835	1.519499	-0.166760
C	1.814622	0.186045	-0.004623
C	0.497707	-0.359429	0.064159
C	-0.612415	0.437182	-0.038513
C	-0.434954	1.889707	-0.180668
H	2.909155	2.045825	-0.234490

```
H         0.385804   -1.427812    0.215272
O         0.900375    2.336340   -0.255793
O        -1.289202    2.740903   -0.242241
Br        3.335898   -0.942580    0.134965
C        -1.981168   -0.130878   -0.014876
C        -3.056946    0.550067    0.583480
C        -2.221423   -1.397906   -0.578270
C        -4.321944   -0.033414    0.634190
H        -2.899041    1.535354    1.003046
C        -3.487875   -1.975896   -0.528202
H        -1.416181   -1.922118   -1.085681
C        -4.544032   -1.296492    0.082532
H        -5.138653    0.505444    1.106723
H        -3.651702   -2.951497   -0.977744
H        -5.533638   -1.743739    0.118645



 10
B3LYP electronic energy:    -3145.21023230 a.u.
B3LYP enthalpy:    -3145.046424 a.u.
B3LYP free energy:    -3145.098034 a.u.
M06 SCF energy in solution:    -3147.60569741 a.u.
M06 enthalpy in solution:    -3147.441889 a.u.
M06 free energy in solution:    -3147.493499 a.u.
Three lowest frequencies (cm-1):      45.2945      66.92      77.92

Cartesian coordinates
ATOM       X           Y           Z
C        -0.488962    1.834614   -0.253524
C        -0.822659    0.528727   -0.074146
C         0.274586   -0.395774    0.050154
C         1.562052    0.033688    0.000719
C         1.904827    1.442350   -0.175838
H        -1.200967    2.639448   -0.396922
H         0.064617   -1.448996    0.205606
O         0.780342    2.279521   -0.297817
O         2.995768    1.948352   -0.225760
Br        3.015977   -1.165473    0.177779
C        -2.234453    0.080402   -0.021293
C        -3.210688    0.848892    0.634759
C        -2.626388   -1.123193   -0.630654
C        -4.541312    0.433528    0.666584
H        -2.919228    1.762870    1.145132
C        -3.955764   -1.541860   -0.590183
H        -1.891557   -1.723954   -1.160022
C        -4.918824   -0.764060    0.055851
H        -5.280867    1.039803    1.182422
H        -4.240200   -2.473545   -1.071463
H        -5.954359   -1.090946    0.087020
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TS1-DMF
B3LYP electronic energy: -6897.73430665 a.u.
B3LYP enthalpy: -6897.258120 a.u.
B3LYP free energy: -6897.371602 a.u.
M06 SCF energy in solution: -6902.40110421 a.u.
M06 enthalpy in solution: -6901.924918 a.u.
M06 free energy in solution: -6902.038400 a.u.
Three lowest frequencies (cm-1): -94.2333 7.62 11.25
Imaginary frequency: -94.2333 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.437235	0.029432	-0.589013
P	-1.716022	-0.689158	0.082795
C	-1.974915	-4.179868	-2.073478
C	-1.112755	-0.735548	4.143232
C	-1.082252	-0.420312	2.784594
C	-3.954591	2.414478	-1.422043
C	-1.511179	-3.057189	-1.386247
C	-1.868117	-1.819691	4.597656
C	-2.988705	1.427432	-1.224506
C	-1.822808	-1.181131	1.861902
C	-3.035527	0.596519	-0.092485
C	-2.597488	-2.585328	3.686954
C	-5.025536	1.779462	0.648805
C	-2.577905	-2.268030	2.326150
C	-4.062207	0.785816	0.844031
C	-2.413080	-2.135216	-0.832009
C	-3.346799	-4.388840	-2.227463
C	-4.975501	2.594015	-0.484221
C	-4.252890	-3.471182	-1.691342
C	-3.790400	-2.351416	-0.997429
H	-4.504403	-1.640706	-0.591721
H	-5.321837	-3.624063	-1.815554
H	-3.708752	-5.258065	-2.770180
H	-1.263899	-4.883292	-2.498401
H	-0.442854	-2.881551	-1.288597
H	-2.186107	1.301662	-1.947530
H	-3.907090	3.045786	-2.305588
H	-5.727142	3.364334	-0.636186
H	-5.816113	1.914002	1.382740
H	-4.108559	0.160163	1.730327
H	-0.483159	0.415407	2.431774
H	-0.534990	-0.140656	4.845943
H	-1.882272	-2.070324	5.655142
H	-3.182102	-3.434105	4.032453
H	-3.146210	-2.873837	1.627129
C	2.403476	0.325015	-1.058122
C	2.889043	1.711936	-0.982756
C	3.036909	-0.691956	-0.358753
Br	1.588496	-0.162903	-2.960897
O	3.913228	1.924629	-0.060509
O	2.492139	2.671181	-1.605660

C	4.493071	0.931379	0.662894
H	5.277864	1.293652	1.312810
C	4.091504	-0.353655	0.541335
H	2.762676	-1.728157	-0.514678
Br	4.938731	-1.709708	1.573628
O	0.289694	2.176267	0.960745
C	0.186572	3.302633	0.460341
N	-0.694823	4.250252	0.857829
H	0.835202	3.620551	-0.368635
C	-1.646406	3.994848	1.928048
H	-1.551851	4.760395	2.708271
H	-2.672689	4.007739	1.541163
H	-1.436171	3.013353	2.351659
C	-0.760357	5.541471	0.195371
H	-1.744974	5.691596	-0.265953
H	-0.586466	6.354604	0.911742
H	0.002804	5.594176	-0.585222

TS2-DMF

B3LYP electronic energy: -6897.73090242 a.u.
B3LYP enthalpy: -6897.254562 a.u.
B3LYP free energy: -6897.369193 a.u.
M06 SCF energy in solution: -6902.39885395 a.u.
M06 enthalpy in solution: -6901.922514 a.u.
M06 free energy in solution: -6902.037145 a.u.
Three lowest frequencies (cm-1): -114.9961 9.36 11.66
Imaginary frequency: -114.9961 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.172292	-0.926359	-0.282600
P	-2.228423	0.167972	0.104065
C	-2.736455	4.154390	-2.250584
C	-2.135398	3.039011	-2.839947
C	-1.514742	1.553109	3.899831
C	-1.984455	1.859706	-2.110127
C	-3.672867	-2.184750	-0.337722
C	-1.399395	1.224210	2.549064
C	-3.046626	2.897819	-0.203424
C	-4.792614	-2.955796	-0.654020
C	-2.686341	1.257221	4.601994
C	-3.188341	4.081586	-0.932104
C	-3.745068	-0.782823	-0.352025
C	-5.994452	-2.335501	-1.000642
C	-3.645368	0.311646	2.590156
C	-6.073720	-0.941259	-1.027462
C	-2.471385	0.603702	1.881293
C	-2.445440	1.772916	-0.786049
C	-4.957150	-0.168272	-0.704217
C	-3.749161	0.635807	3.945512
H	-0.484144	1.454761	2.009077

H	-0.682234	2.034927	4.405821
H	-2.768489	1.507006	5.656625
H	-4.662610	0.400319	4.485536
H	-4.478497	-0.171501	2.089743
H	-2.732674	-2.669839	-0.087603
H	-4.721427	-4.040064	-0.639604
H	-6.864218	-2.935289	-1.255351
H	-7.005007	-0.453119	-1.302680
H	-5.028381	0.914978	-0.733434
H	-3.397060	2.853624	0.823226
H	-3.651989	4.947152	-0.466162
H	-2.847249	5.076348	-2.815149
H	-1.777997	3.089381	-3.865256
H	-1.502671	0.997680	-2.565980
C	1.686496	-1.658643	-0.655333
C	1.944208	-1.088467	-1.877386
H	1.361300	-1.233585	-2.776489
C	4.032340	-0.113729	-1.122218
Br	0.510759	-3.479286	-0.592643
C	2.682374	-1.544122	0.376729
H	2.521605	-2.028525	1.333229
O	4.954860	0.616400	-1.406376
C	3.797344	-0.803717	0.145019
O	3.063158	-0.349280	-2.098517
Br	5.128869	-0.583136	1.475222
O	1.250944	2.003617	0.667334
C	1.637900	2.516721	-0.381627
N	2.828785	3.137018	-0.563581
H	1.014493	2.514199	-1.293482
C	3.256977	3.597119	-1.874677
H	3.550854	4.653416	-1.832921
H	4.107037	3.001606	-2.227572
H	2.433516	3.493174	-2.586913
C	3.791199	3.234029	0.525845
H	4.680795	2.636082	0.300233
H	4.088278	4.280226	0.669980
H	3.319218	2.858264	1.433787

14a
B3LYP electronic energy: -7894.40997756 a.u.
B3LYP enthalpy: -7893.744835 a.u.
B3LYP free energy: -7893.890514 a.u.
M06 SCF energy in solution: -7898.83206097 a.u.
M06 enthalpy in solution: -7898.166918 a.u.
M06 free energy in solution: -7898.312597 a.u.
Three lowest frequencies (cm-1): 8.5408 13.02 14.92

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.693120	0.334786	-0.169467
P	2.857249	-0.020606	0.800208

P	-0.475465	-1.748848	-0.685724
C	2.000480	-5.342708	-2.338341
C	2.461943	-4.590864	-1.256067
C	3.703446	3.540503	2.678885
C	-2.317313	-0.706844	-4.213432
C	1.716810	-2.489612	3.909180
C	1.743165	-1.755374	2.720787
C	1.715905	-3.510170	-0.786161
C	4.911034	-1.177666	-2.563612
C	3.095127	2.363426	2.245169
C	-2.023984	-1.679910	1.649179
C	-1.380362	-0.935710	-3.207355
C	0.035430	-3.932734	-2.466902
C	2.807488	-2.452354	4.777526
C	-2.748616	-2.215659	2.714935
C	-3.665965	-1.000980	-3.995016
C	0.785997	-5.011190	-2.940690
C	4.016352	-0.584321	-1.672887
C	2.861579	-0.980381	2.382326
C	-1.390348	-2.523005	0.721009
C	4.077702	-0.869695	-0.298467
C	3.921783	-1.670515	4.459458
C	5.931580	-2.379249	-0.734330
C	3.947784	-0.934654	3.275068
C	-2.831215	-3.599991	2.878882
C	-3.129180	-1.774657	-1.762711
C	-2.195609	-4.446055	1.967409
C	5.044213	-1.777136	0.160938
C	3.744602	1.515479	1.330125
C	-1.774084	-1.482095	-1.973018
C	4.968622	3.893181	2.200673
C	0.493846	-3.165138	-1.383995
C	-1.483500	-3.913627	0.890952
C	5.869773	-2.079108	-2.096325
C	-4.068826	-1.529148	-2.768687
C	5.619695	3.059063	1.292088
C	5.013675	1.876213	0.858544
H	5.535016	1.236682	0.153791
H	6.605089	3.324085	0.917836
H	5.441641	4.812310	2.535260
H	3.188967	4.182210	3.389086
H	2.112142	2.096629	2.627270
H	3.260993	0.102486	-2.045200
H	4.851202	-0.943520	-3.622995
H	6.561258	-2.548964	-2.790477
H	6.673014	-3.082368	-0.363807
H	5.103601	-2.023752	1.215937
H	0.879683	-1.770825	2.065308
H	0.837346	-3.078709	4.153343
H	2.787458	-3.019208	5.704416
H	4.768612	-1.625930	5.139150
H	4.808969	-0.311894	3.051551
H	-0.334219	-0.694757	-3.383980

H	-1.996625	-0.287707	-5.163406
H	-4.398768	-0.810775	-4.774319
H	-5.116251	-1.748848	-2.583293
H	-3.462102	-2.187604	-0.816789
H	-1.962884	-0.601604	1.537983
H	-3.253590	-1.548012	3.406526
H	-3.393190	-4.017020	3.710144
H	-2.258559	-5.524394	2.087918
H	-1.001880	-4.582701	0.185382
H	-0.909532	-3.691751	-2.941783
H	0.416081	-5.592831	-3.780958
H	2.583785	-6.180879	-2.710159
H	3.408683	-4.834681	-0.782451
H	2.089697	-2.935239	0.053724
C	1.138856	2.811539	-1.734154
C	0.312062	2.721214	-2.790346
C	0.692581	2.471352	-0.392787
Br	2.914450	3.432919	-2.011320
O	-0.996184	2.339279	-2.660651
C	-1.561507	2.075609	-1.444787
C	-0.680302	2.059854	-0.298048
H	1.175284	2.965735	0.443201
Br	-1.551825	2.263386	1.413860
H	0.563924	2.950268	-3.816191
O	-2.782771	1.884379	-1.475871
Cu	-4.145527	1.355805	-0.206706
I	-6.013196	0.629729	1.194412

TS1-CuI

B3LYP electronic energy: -7894.38380876 a.u.
B3LYP enthalpy: -7893.720407 a.u.
B3LYP free energy: -7893.864767 a.u.
M06 SCF energy in solution: -7898.80355857 a.u.
M06 enthalpy in solution: -7898.140157 a.u.
M06 free energy in solution: -7898.284517 a.u.
Three lowest frequencies (cm-1): -77.9504 9.73 15.50
Imaginary frequency: -77.9504 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.422276	-0.167314	-0.403768
P	1.966929	1.729080	-0.264133
P	-0.443860	-0.752163	1.774238
C	2.663586	-3.303340	4.133997
C	2.955717	-2.826263	2.856113
C	-0.746427	4.479025	-1.700574
C	-3.089291	-3.917568	2.041876
C	3.805035	1.756121	3.423633
C	3.322294	1.383378	2.169976
C	2.015612	-2.055338	2.166665
C	4.490722	0.734685	-3.362284

C	-0.158010	3.349871	-1.125966
C	-1.558891	1.774239	2.200917
C	-1.933236	-3.144202	1.936644
C	0.484915	-2.253327	4.024995
C	3.564869	3.042669	3.913109
C	-1.833654	2.951335	2.897518
C	-4.329542	-3.305903	2.231417
C	1.425245	-3.016853	4.716383
C	3.376360	0.931779	-2.548080
C	2.605223	2.295016	1.374998
C	-0.737968	0.781419	2.765525
C	3.512461	1.489806	-1.264544
C	2.841401	3.949787	3.139297
C	5.911555	1.635933	-1.632583
C	2.367419	3.582218	1.877269
C	-1.268916	3.168702	4.156091
C	-3.247409	-1.137937	2.216524
C	-0.429089	2.202744	4.711152
C	4.793948	1.844199	-0.818709
C	1.237570	3.246051	-1.022493
C	-1.994362	-1.742889	2.028256
C	0.055518	5.515107	-2.180125
C	0.774350	-1.750928	2.743611
C	-0.166409	1.015186	4.024550
C	5.764657	1.081304	-2.903753
C	-4.403225	-1.914960	2.318093
C	1.447318	5.420597	-2.085146
C	2.036248	4.293500	-1.512565
H	3.118688	4.224855	-1.452634
H	2.075642	6.223125	-2.462727
H	-0.399884	6.391600	-2.633387
H	-1.828689	4.531896	-1.778905
H	-0.792239	2.543400	-0.771764
H	2.389534	0.660749	-2.914628
H	4.364500	0.306511	-4.353209
H	6.634839	0.920450	-3.534343
H	6.897592	1.913334	-1.268957
H	4.926455	2.282836	0.164672
H	3.510507	0.377029	1.807449
H	4.362692	1.038427	4.019546
H	3.936787	3.332909	4.892116
H	2.645135	4.951249	3.512923
H	1.812094	4.302354	1.286161
H	-0.976429	-3.639277	1.797185
H	-3.018511	-5.000043	1.974323
H	-5.230761	-3.907711	2.310233
H	-5.361631	-1.424991	2.465533
H	-3.332508	-0.060207	2.294206
H	-1.995426	1.631663	1.215585
H	-2.484161	3.696682	2.448521
H	-1.476141	4.088595	4.696410
H	0.026885	2.369656	5.683516
H	0.493690	0.280442	4.471229

H	-0.482562	-2.056584	4.477416
H	1.188224	-3.395280	5.707195
H	3.391755	-3.904444	4.672080
H	3.909336	-3.058792	2.389638
H	2.234372	-1.692371	1.165629
C	-0.218340	-1.710640	-1.725065
C	0.996732	-2.358273	-1.988466
C	-1.400355	-2.515465	-1.421479
Br	-0.623001	-0.101790	-2.921885
C	0.021889	-4.442448	-1.276026
H	-0.021742	-5.492740	-1.030511
H	1.834244	-1.819667	-2.411675
O	-2.573090	-2.132021	-1.359174
O	-1.198422	-3.831786	-1.168869
C	1.105249	-3.739809	-1.686091
Br	2.776659	-4.626566	-1.868692
Cu	-3.356729	-0.355881	-1.290247
I	-4.506574	1.796592	-1.065912

TS2-CuI

B3LYP electronic energy: -7894.37822060 a.u.
B3LYP enthalpy: -7893.714686 a.u.
B3LYP free energy: -7893.864890 a.u.
M06 SCF energy in solution: -7898.78954042 a.u.
M06 enthalpy in solution: -7898.126006 a.u.
M06 free energy in solution: -7898.276210 a.u.
Three lowest frequencies (cm-1): -157.5284 2.88 7.86
Imaginary frequency: -157.5284 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	1.495391	-0.252189	0.590765
P	0.724797	1.922661	-0.123608
P	3.525779	-1.136150	-0.441681
C	3.194245	-2.287113	-4.941827
C	2.289800	-1.396774	-4.362158
C	-0.186797	3.558597	3.536350
C	3.640885	-5.059161	0.816756
C	3.906748	3.598770	-2.128305
C	2.929862	2.723969	-1.656082
C	2.401260	-1.068571	-3.008939
C	-2.079271	0.667222	-2.873332
C	0.445428	2.914809	2.472912
C	5.101832	0.781907	0.824629
C	3.313381	-3.870961	0.166101
C	4.320776	-2.525681	-2.812344
C	3.980730	4.902016	-1.630411
C	6.194185	1.632111	0.999444
C	4.731540	-5.103295	1.690126
C	4.207586	-2.853542	-4.163595
C	-1.141411	0.715198	-1.839218

C	2.002581	3.138847	-0.685747
C	5.004438	-0.034551	-0.315006
C	-0.462622	1.907058	-1.539501
C	3.068740	5.323652	-0.662795
C	-1.658495	2.998727	-3.352142
C	2.083682	4.450349	-0.193648
C	7.194403	1.694721	0.027189
C	5.170465	-2.762709	1.242751
C	7.098872	0.899642	-1.116421
C	-0.724510	3.048020	-2.316501
C	-0.168622	2.843869	1.208220
C	4.077220	-2.707099	0.367839
C	-1.452684	4.125694	3.359587
C	3.423480	-1.619252	-2.220494
C	6.014129	0.036695	-1.286242
C	-2.342014	1.811567	-3.628417
C	5.492265	-3.953770	1.900020
C	-2.075726	4.049211	2.113854
C	-1.438232	3.416477	1.042409
H	-1.938111	3.367326	0.080897
H	-3.062701	4.479994	1.969595
H	-1.951370	4.616760	4.190613
H	0.303508	3.606222	4.504965
H	1.416668	2.450870	2.626847
H	-0.924546	-0.181355	-1.264936
H	-2.602343	-0.260608	-3.087632
H	-3.074108	1.777217	-4.430172
H	-1.854117	3.889530	-3.942982
H	-0.196949	3.975340	-2.112449
H	2.889889	1.710811	-2.044551
H	4.617302	3.257277	-2.875788
H	4.746036	5.582718	-1.993419
H	3.117096	6.336330	-0.271083
H	1.378069	4.795816	0.554487
H	2.467551	-3.852607	-0.517447
H	3.044752	-5.950886	0.641931
H	4.984625	-6.028109	2.201049
H	6.344531	-3.979268	2.573885
H	5.777848	-1.879366	1.411656
H	4.311544	0.756499	1.570803
H	6.255708	2.254499	1.888035
H	8.040247	2.364450	0.156793
H	7.870915	0.947669	-1.879959
H	5.954043	-0.572130	-2.182470
H	5.099923	-2.986887	-2.212416
H	4.907096	-3.556762	-4.607644
H	3.105099	-2.548116	-5.992839
H	1.489807	-0.963788	-4.956340
H	1.680247	-0.393426	-2.556463
C	-0.151925	-0.967366	1.654023
C	-1.324479	-0.225698	2.013698
C	-2.548863	-0.636245	1.571690
H	-1.226030	0.675237	2.607756

C	-2.694825	-1.830653	0.769009
Br	-4.117979	0.344778	1.969296
Br	1.454968	-1.023001	3.146249
C	-0.339193	-2.188439	1.045174
H	0.402466	-2.961634	0.913286
O	-3.720517	-2.276568	0.237490
O	-1.570523	-2.572988	0.595170
Cu	-5.406570	-1.498405	-0.319218
I	-7.482835	-0.676001	-1.295090

14b

B3LYP electronic energy: -8131.29219865 a.u.
B3LYP enthalpy: -8130.516676 a.u.
B3LYP free energy: -8130.673119 a.u.
M06 SCF energy in solution: -8135.67082402 a.u.
M06 enthalpy in solution: -8134.895301 a.u.
M06 free energy in solution: -8135.051744 a.u.
Three lowest frequencies (cm-1): 8.7722 11.40 15.95

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.580897	-0.308041	-0.189118
P	-2.823919	-0.284092	0.684746
P	0.204227	1.968189	-0.518148
C	-2.115618	4.505761	-3.661280
C	-2.643850	3.307927	-3.180280
C	-2.393916	-3.363337	3.382789
C	3.551417	1.962380	-2.944753
C	-3.666189	3.461985	2.181285
C	-3.312480	2.400791	1.350336
C	-1.931842	2.555880	-2.242435
C	-4.890669	-0.627383	-2.864480
C	-2.188107	-2.228413	2.597931
C	0.376407	2.225826	2.251291
C	2.239510	1.906504	-2.474473
C	-0.154159	4.192484	-2.276604
C	-3.995823	3.227576	3.518698
C	0.430812	2.893102	3.476043
C	4.605688	2.195525	-2.058259
C	-0.866981	4.943840	-3.210633
C	-3.890909	-0.642185	-1.889590
C	-3.292781	1.083495	1.840096
C	0.216489	2.940373	1.052446
C	-4.167657	-0.228641	-0.577044
C	-3.975661	1.924867	4.015527
C	-6.463186	0.220501	-1.236368
C	-3.629413	0.857202	3.182787
C	0.310858	4.283029	3.519810
C	3.020791	2.322423	-0.225601
C	0.138544	5.001429	2.334722
C	-5.465642	0.207456	-0.260804

C	-3.161998	-1.807061	1.675002
C	1.955950	2.097051	-1.110950
C	-3.570309	-4.104723	3.244812
C	-0.686641	2.993557	-1.767586
C	0.093944	4.336941	1.108258
C	-6.177970	-0.196480	-2.539116
C	4.336679	2.368945	-0.697450
C	-4.538635	-3.699372	2.325870
C	-4.340296	-2.555764	1.547894
H	-5.105241	-2.253929	0.840213
H	-5.455015	-4.271792	2.212043
H	-3.728653	-4.993538	3.848838
H	-1.634348	-3.671054	4.096269
H	-1.265193	-1.662480	2.705401
H	-2.889713	-0.973184	-2.149729
H	-4.662229	-0.951435	-3.876039
H	-6.955939	-0.182665	-3.297281
H	-7.462777	0.559242	-0.978846
H	-5.696351	0.540726	0.746406
H	-3.063164	2.602684	0.312965
H	-3.680504	4.472905	1.784047
H	-4.269620	4.055505	4.166601
H	-4.237612	1.731125	5.052098
H	-3.633398	-0.150353	3.583620
H	1.431620	1.730697	-3.179280
H	3.748363	1.825680	-4.004270
H	5.626482	2.254030	-2.426135
H	5.147986	2.565414	-0.001766
H	2.826693	2.483050	0.830089
H	0.449238	1.141456	2.223262
H	0.553547	2.325759	4.394521
H	0.344237	4.803751	4.472713
H	0.037521	6.082931	2.363038
H	-0.049551	4.911492	0.199792
H	0.827204	4.532000	-1.959257
H	-0.443652	5.868725	-3.592428
H	-2.666422	5.091599	-4.391699
H	-3.605682	2.949005	-3.535563
H	-2.343365	1.616502	-1.889231
C	-0.655451	-2.966514	-1.567623
C	0.024617	-2.755778	-2.707478
C	-0.203559	-2.409998	-0.300948
Br	-2.218424	-4.041107	-1.609758
O	1.217072	-2.067001	-2.722266
C	1.824125	-1.655995	-1.583578
C	1.068109	-1.725208	-0.359596
H	-0.505175	-2.921861	0.606944
Br	2.125521	-1.643110	1.270022
H	-0.243680	-3.107573	-3.693037
O	2.994369	-1.252491	-1.744259
Cu	4.354845	-0.849633	-0.489188
O	5.941510	-0.622408	0.537330
C	7.049044	-1.196794	0.400792

N	8.090369	-0.993517	1.203757
H	7.223448	-1.914594	-0.408498
C	9.360421	-1.684789	0.989604
H	9.285725	-2.344517	0.122516
H	10.158895	-0.956195	0.814160
H	9.614567	-2.282926	1.870870
C	8.016343	-0.068762	2.335402
H	7.015079	0.356013	2.384697
H	8.235753	-0.606632	3.263504
H	8.752464	0.731691	2.206574

TS1-Cu

B3LYP electronic energy: -8131.26298870 a.u.
B3LYP enthalpy: -8130.489172 a.u.
B3LYP free energy: -8130.647444 a.u.
M06 SCF energy in solution: -8135.63652697 a.u.
M06 enthalpy in solution: -8134.862710 a.u.
M06 free energy in solution: -8135.020982 a.u.
Three lowest frequencies (cm-1): -159.1044 8.62 11.74
Imaginary frequency: -159.1044 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.410636	-0.157653	0.196765
P	2.298925	-1.517520	-0.556269
P	0.022193	1.873694	-1.053214
C	3.360342	3.213463	-4.018012
C	2.822903	1.924858	-4.066258
C	2.248224	-4.301106	2.476548
C	0.616236	4.689082	1.875199
C	0.601755	-3.233410	-3.894309
C	0.896374	-2.380197	-2.828888
C	1.839775	1.542766	-3.155553
C	5.346136	1.226516	-0.622516
C	1.889040	-3.446031	1.435618
C	-2.236466	0.695940	-2.252489
C	0.754722	3.616760	0.994801
C	1.912645	3.738061	-2.148031
C	1.330290	-4.411079	-4.068544
C	-3.310513	0.625203	-3.145559
C	-0.542972	5.470466	1.849015
C	2.903395	4.116150	-3.058139
C	4.181798	0.520955	-0.321656
C	1.930754	-2.688310	-1.931167
C	-1.419680	1.835483	-2.208014
C	3.834142	-0.628942	-1.049818
C	2.351938	-4.735458	-3.172206
C	5.828299	-0.334690	-2.402473
C	2.650184	-3.882408	-2.109038
C	-3.579281	1.693889	-4.001573
C	-1.412200	4.108501	0.042717

C	-2.763833	2.828962	-3.973241
C	4.668417	-1.049836	-2.095334
C	2.855551	-2.640322	0.806077
C	-0.251468	3.322299	0.055431
C	3.575429	-4.356741	2.912717
C	1.370329	2.444934	-2.186481
C	-1.686854	2.896992	-3.089546
C	6.170748	0.800789	-1.666744
C	-1.555720	5.173010	0.937416
C	4.539141	-3.558672	2.296830
C	4.184693	-2.705928	1.246937
H	4.946808	-2.095256	0.774292
H	5.573075	-3.598350	2.628267
H	3.854255	-5.018768	3.727537
H	1.492017	-4.921842	2.949413
H	0.853226	-3.407253	1.107021
H	3.534712	0.863648	0.482478
H	5.605036	2.112039	-0.048820
H	7.074503	1.353692	-1.906864
H	6.465495	-0.669606	-3.216343
H	4.416632	-1.932770	-2.673952
H	0.311525	-1.475766	-2.685228
H	-0.199697	-2.979939	-4.582934
H	1.100104	-5.077643	-4.894953
H	2.916110	-5.655284	-3.298480
H	3.438884	-4.150316	-1.412053
H	1.656065	3.009228	1.029743
H	1.411983	4.914018	2.580229
H	-0.654604	6.304542	2.536028
H	-2.462802	5.770428	0.916089
H	-2.210171	3.893727	-0.659417
H	-2.013419	-0.146232	-1.602619
H	-3.929532	-0.267355	-3.173558
H	-4.411608	1.640155	-4.697731
H	-2.960559	3.657940	-4.647222
H	-1.045601	3.773714	-3.094084
H	1.564499	4.457753	-1.415163
H	3.311752	5.122227	-3.016460
H	4.129607	3.510710	-4.725061
H	3.174388	1.213324	-4.807890
H	1.435266	0.535916	-3.203669
C	-0.867251	0.102406	1.801896
C	0.081906	-0.161198	2.796700
C	-1.841755	1.153857	2.031355
Br	-1.786018	-1.727617	1.014751
C	-0.560660	1.868027	3.918153
H	-0.525770	2.665465	4.644936
H	0.663902	-1.075882	2.791432
O	-2.894387	1.367072	1.398310
O	-1.594887	2.012036	3.040709
C	0.263217	0.795063	3.834894
Br	1.647915	0.572688	5.108768
Cu	-3.990519	0.126911	0.473981

O	-5.413770	-0.868378	-0.293100
C	-5.659752	-2.088940	-0.128970
H	-4.956910	-2.743563	0.399324
N	-6.761753	-2.684859	-0.574201
C	-6.988773	-4.113646	-0.364944
C	-7.801115	-1.939741	-1.286676
H	-7.907339	-4.265869	0.211176
H	-7.087385	-4.622841	-1.329361
H	-6.150002	-4.548942	0.182469
H	-7.926480	-2.352537	-2.293164
H	-8.749366	-2.026860	-0.746448
H	-7.509903	-0.892598	-1.351250

TS2-Cu

B3LYP electronic energy: -8131.25666102 a.u.
B3LYP enthalpy: -8130.482659 a.u.
B3LYP free energy: -8130.641810 a.u.
M06 SCF energy in solution: -8135.63068802 a.u.
M06 enthalpy in solution: -8134.856686 a.u.
M06 free energy in solution: -8135.015837 a.u.
Three lowest frequencies (cm-1): -148.6053 8.95 10.39
Imaginary frequency: -148.6053 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-1.140457	0.097373	-0.613051
P	-1.623896	-1.867976	0.702494
P	-2.305076	2.186283	-0.079295
C	-6.093816	2.804602	-2.703355
C	-5.618028	1.522405	-2.424589
C	1.925009	-2.030838	2.767051
C	0.090781	4.866900	-2.088076
C	-5.005406	-0.956341	2.854717
C	-4.061582	-1.109152	1.841050
C	-4.473111	1.356782	-1.642950
C	-2.923668	-4.359257	-2.320247
C	0.761355	-1.608116	2.124672
C	-2.018611	2.039209	2.692216
C	-0.730899	3.791111	-1.753478
C	-4.277966	3.757908	-1.417266
C	-4.700332	-1.348317	4.160908
C	-2.365931	2.247603	4.026535
C	0.414601	5.828924	-1.126204
C	-5.420537	3.921382	-2.201315
C	-2.373037	-3.292081	-1.605839
C	-2.801524	-1.667715	2.113686
C	-2.859984	2.474742	1.655470
C	-2.363831	-3.300378	-0.202534
C	-3.449570	-1.897017	4.443597
C	-3.492079	-5.453902	-0.242473
C	-2.504117	-2.059106	3.427043

C	-3.570782	2.879041	4.343910
C	-0.925275	4.636353	0.503897
C	-4.420225	3.304474	3.321519
C	-2.943812	-4.388983	0.472448
C	-0.101700	-2.535530	1.512543
C	-1.252265	3.664784	-0.452003
C	2.257573	-3.388772	2.790745
C	-3.796431	2.471189	-1.122575
C	-4.067343	3.108469	1.984493
C	-3.479000	-5.443411	-1.640013
C	-0.094357	5.709612	0.166707
C	1.418858	-4.314776	2.170839
C	0.245303	-3.893855	1.538268
H	-0.397685	-4.629766	1.067087
H	1.672858	-5.371073	2.179303
H	3.165292	-3.720430	3.286939
H	2.570612	-1.301755	3.250170
H	0.514950	-0.549198	2.097406
H	-1.973673	-2.435840	-2.142464
H	-2.927587	-4.335408	-3.406552
H	-3.911429	-6.271684	-2.194251
H	-3.937443	-6.288483	0.291968
H	-2.978603	-4.399200	1.558147
H	-4.307069	-0.793155	0.830340
H	-5.976013	-0.525108	2.626507
H	-5.434292	-1.225805	4.952434
H	-3.206056	-2.207267	5.456239
H	-1.538927	-2.495703	3.662230
H	-0.980276	3.051202	-2.510152
H	0.474431	4.956227	-3.100963
H	1.054125	6.667671	-1.386870
H	0.145511	6.456909	0.918403
H	-1.320648	4.563778	1.511772
H	-1.089307	1.529542	2.449725
H	-1.703872	1.905497	4.817161
H	-3.848052	3.033597	5.382934
H	-5.360586	3.792971	3.561885
H	-4.737186	3.447052	1.200808
H	-3.755932	4.632869	-1.040857
H	-5.782777	4.921357	-2.423376
H	-6.981158	2.935030	-3.316437
H	-6.130306	0.651029	-2.823036
H	-4.088733	0.358943	-1.448630
C	0.539798	-0.476913	-1.706207
C	1.375432	0.566594	-1.345608
H	1.185372	1.624233	-1.446946
C	3.191852	-0.912724	-0.861108
Br	-0.779942	0.012804	-3.316266
C	1.114782	-1.788356	-1.769634
H	0.519559	-2.614994	-2.140777
O	4.365957	-1.026967	-0.426863
Cu	5.543327	0.283219	0.144110
O	6.789072	1.535843	0.748617

C	8.040849	1.559108	0.612197
N	8.810751	2.522624	1.099766
H	8.570554	0.767694	0.072084
C	8.250792	3.651114	1.847318
H	8.500996	4.586788	1.337220
H	7.169385	3.541512	1.906875
H	8.677625	3.669304	2.855212
C	10.261892	2.501236	0.912954
H	10.553285	1.615956	0.343979
H	10.580279	3.396131	0.368783
H	10.762163	2.480720	1.886443
O	2.651816	0.315129	-0.897370
C	2.397218	-2.003296	-1.346319
Br	3.184354	-3.719858	-1.391990

14c
B3LYP electronic energy: -6660.78261664 a.u.
B3LYP enthalpy: -6660.415479 a.u.
B3LYP free energy: -6660.516099 a.u.
M06 SCF energy in solution: -6665.58003127 a.u.
M06 enthalpy in solution: -6665.212894 a.u.
M06 free energy in solution: -6665.313514 a.u.
Three lowest frequencies (cm-1): 8.6816 12.73 20.44

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.635038	-0.032068	-0.170582
P	-1.712730	-0.038669	0.204606
C	-4.110082	-0.275182	-3.794078
C	-2.984567	-1.072912	-3.571850
C	-2.447875	3.771927	1.587781
C	-2.283791	-0.984905	-2.369010
C	-1.545743	-2.019602	2.170087
C	-1.920072	2.658284	0.932331
C	-3.839797	0.695390	-1.591964
C	-1.986009	-3.090156	2.948842
C	-3.546042	3.631927	2.437703
C	-4.533756	0.610064	-2.802314
C	-2.359119	-1.491567	1.156055
C	-3.238911	-3.660396	2.713901
C	-3.585925	1.254977	1.975074
C	-4.048810	-3.154949	1.695312
C	-2.483835	1.386197	1.113406
C	-2.708741	-0.101775	-1.360428
C	-3.612119	-2.077017	0.921363
C	-4.112695	2.369920	2.630463
H	-1.049868	2.784232	0.298849
H	-1.976301	4.740102	1.445636
H	-3.951398	4.497567	2.956948
H	-4.963836	2.248686	3.297141
H	-4.032420	0.279633	2.141010

H	-0.553772	-1.605435	2.326188
H	-1.338879	-3.492255	3.724160
H	-3.576695	-4.503366	3.312371
H	-5.020576	-3.601772	1.497370
H	-4.247579	-1.695002	0.127478
H	-4.180371	1.388777	-0.829407
H	-5.405626	1.239412	-2.966959
H	-4.649579	-0.339435	-4.736415
H	-2.641161	-1.761411	-4.340073
H	-1.400576	-1.598372	-2.208037
C	1.676599	1.821927	-0.277055
C	1.651772	2.663602	0.924963
C	2.609460	0.733543	-0.416313
Br	1.203885	2.815124	-1.898857
O	2.411986	2.201968	2.000083
O	1.044379	3.701719	1.089958
C	3.326380	1.188350	1.871832
H	3.901410	1.041181	2.776060
C	3.460998	0.486595	0.735319
H	2.980504	0.453441	-1.396121
Br	4.821977	-0.846080	0.632514
I	1.052187	-2.759100	-0.770479

TS1-I
B3LYP electronic energy: -6660.75341455 a.u.
B3LYP enthalpy: -6660.387750 a.u.
B3LYP free energy: -6660.488274 a.u.
M06 SCF energy in solution: -6665.55189452 a.u.
M06 enthalpy in solution: -6665.186230 a.u.
M06 free energy in solution: -6665.286754 a.u.
Three lowest frequencies (cm-1): -104.5962 11.13 14.04
Imaginary frequency: -104.5962 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.352715	-0.335901	0.522577
P	1.837781	0.342951	-0.080830
C	2.047516	3.765827	2.199547
C	4.029082	-2.877170	1.232214
C	3.034161	-2.057323	0.698209
C	1.453578	0.565926	-4.167278
C	1.767655	2.488526	1.713682
C	5.209529	-2.321839	1.732367
C	1.202982	0.510533	-2.795085
C	3.215085	-0.663929	0.646845
C	2.259570	0.368265	-1.883281
C	5.392558	-0.938588	1.694647
C	3.817455	0.297768	-3.748803
C	4.402215	-0.113857	1.154263
C	3.568433	0.248432	-2.375697
C	2.271559	2.065326	0.470841

C	2.820893	4.651850	1.444746
C	2.760497	0.462625	-4.646899
C	3.313327	4.248981	0.202907
C	3.044209	2.964872	-0.279470
H	3.433455	2.666035	-1.247732
H	3.908694	4.934115	-0.396585
H	3.029670	5.651671	1.818237
H	1.647529	4.073098	3.162777
H	1.135541	1.817332	2.289830
H	0.182780	0.542466	-2.423891
H	0.622443	0.667208	-4.860306
H	2.953939	0.494192	-5.716698
H	4.836535	0.199814	-4.116231
H	4.395386	0.104799	-1.685836
H	2.110551	-2.493337	0.322969
H	3.872967	-3.952499	1.264724
H	5.979601	-2.962943	2.155576
H	6.305649	-0.496783	2.087796
H	4.554054	0.961375	1.134512
C	-2.303583	-0.189106	1.177837
C	-2.677149	0.962070	0.479956
C	-3.222545	-1.345200	1.256700
Br	-1.346785	0.177920	3.023607
C	-4.490715	-0.281479	-0.520863
H	-5.309103	-0.464461	-1.203170
H	-2.147906	1.896774	0.611525
O	-3.204119	-2.255321	2.045916
O	-4.237779	-1.341639	0.294689
C	-3.774048	0.860082	-0.423727
Br	-4.225360	2.343529	-1.546057
I	-0.625415	-2.732873	-1.095183

TS2-I

B3LYP electronic energy: -6660.75478620 a.u.
B3LYP enthalpy: -6660.388746 a.u.
B3LYP free energy: -6660.490052 a.u.
M06 SCF energy in solution: -6665.54524984 a.u.
M06 enthalpy in solution: -6665.179210 a.u.
M06 free energy in solution: -6665.280516 a.u.
Three lowest frequencies (cm-1): -144.9183 8.95 17.55
Imaginary frequency: -144.9183 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.176369	0.192958	-0.321367
P	2.127411	0.190889	0.242974
C	3.142619	-0.949337	4.649081
C	2.121354	-1.593864	3.946945
C	2.812251	4.249202	0.413880
C	1.831121	-1.230899	2.630919
C	2.733553	-1.386882	-1.979630

C	2.285228	2.967783	0.564317
C	3.595819	0.423463	2.707746
C	3.513110	-2.225221	-2.779475
C	3.992314	4.442337	-0.310782
C	3.877703	0.061518	4.027286
C	3.211833	-0.943792	-0.737417
C	4.771563	-2.641562	-2.342416
C	4.119351	2.055322	-0.709599
C	5.249139	-2.219429	-1.099145
C	2.935295	1.848806	0.012584
C	2.572117	-0.220227	1.994844
C	4.473457	-1.377329	-0.300674
C	4.639644	3.343164	-0.873929
H	1.352514	2.828615	1.105975
H	2.294267	5.099116	0.851589
H	4.397525	5.443002	-0.440241
H	5.555004	3.482351	-1.444623
H	4.639471	1.210365	-1.149406
H	1.738858	-1.093212	-2.303310
H	3.124611	-2.566666	-3.735347
H	5.373488	-3.303093	-2.961167
H	6.223090	-2.551222	-0.746545
H	4.847969	-1.064119	0.669984
H	4.170495	1.215411	2.236496
H	4.670883	0.572902	4.568269
H	3.360272	-1.228509	5.677482
H	1.538035	-2.377004	4.424477
H	1.025786	-1.727094	2.093350
C	-2.033364	0.902370	-0.687667
C	-3.252084	0.159853	-0.505800
C	-4.174152	0.622153	0.376224
H	-3.388874	-0.774741	-1.036245
C	-4.001172	1.855721	1.146052
Br	-5.784108	-0.340654	0.709982
Br	-1.250764	0.997337	-2.786242
C	-1.908613	2.116863	-0.051322
H	-1.180588	2.878177	-0.288344
O	-4.756338	2.318444	1.973357
O	-2.841415	2.559051	0.852565
I	-0.860132	-2.666937	-0.129708

CuI-pyrone
B3LYP electronic energy: -5693.79932092 a.u.
B3LYP enthalpy: -5693.724573 a.u.
B3LYP free energy: -5693.782580 a.u.
M06 SCF energy in solution: -5698.95355922 a.u.
M06 enthalpy in solution: -5698.878811 a.u.
M06 free energy in solution: -5698.936818 a.u.
Three lowest frequencies (cm-1): 24.6669 17.55 64.90

Cartesian coordinates

ATOM	X	Y	Z
Br	-0.345179	-2.865845	-1.004518
C	-0.898651	-1.368733	0.034407
C	-1.187474	-1.647719	1.459944
C	-1.325261	-0.184773	-0.569282
C	-2.007373	0.802857	0.226428
H	-1.291196	-0.070916	-1.648803
C	-2.218281	0.554661	1.539843
H	-2.724043	1.222516	2.225851
O	-0.957032	-2.655211	2.065247
O	-1.801724	-0.580589	2.138051
Br	-2.608859	2.409068	-0.568858
Cu	0.762893	-0.108480	-0.034633
I	2.890094	1.036418	0.107945

TS9

B3LYP electronic energy: -5693.77540986 a.u.
B3LYP enthalpy: -5693.701995 a.u.
B3LYP free energy: -5693.759026 a.u.
M06 SCF energy in solution: -5698.90991850 a.u.
M06 enthalpy in solution: -5698.836504 a.u.
M06 free energy in solution: -5698.893535 a.u.
Three lowest frequencies (cm-1): -57.9764 24.04 44.11
Imaginary frequency: -57.9764 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Cu	-1.434844	0.498556	-0.227344
I	-2.613835	-1.644512	-0.132148
Br	-0.762521	2.607057	-0.649113
C	0.404406	0.465204	0.374251
C	0.454660	0.598614	1.821674
C	1.457697	0.107417	-0.396997
C	2.667074	-0.293069	0.264586
H	1.406250	0.096220	-1.480010
C	2.733088	-0.211510	1.616066
H	3.603209	-0.457042	2.212424
O	-0.412358	0.967809	2.569595
O	1.696956	0.211031	2.363798
Br	4.149834	-0.903309	-0.741750

TS10

B3LYP electronic energy: -5693.77131735 a.u.
B3LYP enthalpy: -5693.697903 a.u.
B3LYP free energy: -5693.755286 a.u.
M06 SCF energy in solution: -5698.90841686 a.u.
M06 enthalpy in solution: -5698.835003 a.u.
M06 free energy in solution: -5698.892386 a.u.
Three lowest frequencies (cm-1): -54.7007 15.06 47.98

Imaginary frequency: -54.7007 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Cu	-1.665662	0.462162	-0.117245
I	-2.251361	-1.910353	0.013430
Br	-1.605229	2.672464	-0.441066
C	0.149536	0.323459	0.517010
C	0.423418	0.615026	1.802860
C	1.180710	-0.011208	-0.407759
C	2.460651	-0.066200	0.057120
H	0.959869	-0.234875	-1.444860
C	2.798448	0.202203	1.458865
O	1.690459	0.533104	2.265928
Br	3.899402	-0.525155	-1.071812
H	-0.279778	0.920404	2.566748
O	3.881242	0.170022	1.977647

TS5-cis

B3LYP electronic energy: -7003.98673413 a.u.
B3LYP enthalpy: -7003.405683 a.u.
B3LYP free energy: -7003.529680 a.u.
M06 SCF energy in solution: -7008.56042972 a.u.
M06 enthalpy in solution: -7007.979379 a.u.
M06 free energy in solution: -7008.103376 a.u.
Three lowest frequencies (cm-1): -34.0782 15.81 19.08
Imaginary frequency: -34.0782 cm-1

Cartesian coordinates

ATOM	X	Y	Z
P	-0.364917	1.690946	-0.185971
C	3.013322	2.986807	-2.224502
H	3.805174	3.715788	-2.076553
C	0.079106	2.567759	2.464475
H	0.100015	1.519701	2.742842
C	-0.122804	4.322843	0.805509
H	-0.287598	4.638768	-0.220563
C	-0.093961	2.952414	1.129047
C	0.048789	5.284076	1.798676
H	0.030632	6.338405	1.536112
C	-1.937752	2.664904	-2.387522
H	-1.099876	2.435433	-3.036108
C	-1.861466	2.412481	-1.010334
C	2.001997	2.867959	-1.268129
H	2.024495	3.502427	-0.389600
C	-4.165646	3.577775	-2.126002
H	-5.054646	4.030504	-2.556632
C	-2.957101	2.754536	-0.198390
H	-2.920884	2.568861	0.870239
C	0.976709	1.926751	-1.431864
C	0.232722	4.892614	3.129058

H	0.361146	5.644299	3.903349
C	-3.085438	3.240907	-2.940549
H	-3.124602	3.433299	-4.009304
C	2.003955	1.222843	-3.524050
H	2.002591	0.572464	-4.394434
C	0.242676	3.538657	3.458083
H	0.379218	3.223003	4.488354
C	0.999525	1.093672	-2.564359
H	0.238633	0.330094	-2.694114
C	3.014695	2.171907	-3.356262
H	3.803697	2.265741	-4.096973
C	-4.096072	3.335438	-0.751569
H	-4.931331	3.594464	-0.107002
C	1.695063	-0.314673	1.001151
C	2.025131	-0.291615	2.423461
C	2.714757	-0.413671	0.101329
C	4.080050	-0.514239	0.533310
H	2.521133	-0.431209	-0.965847
C	4.363395	-0.505670	1.852471
O	3.387138	-0.388602	2.774501
Br	5.489667	-0.676120	-0.739691
Pd	-0.374505	-0.509701	0.639508
Br	0.002297	-2.898319	1.438855
C	-2.503985	-0.734718	0.791524
C	-3.568379	-0.324391	-0.029493
C	-2.835100	-1.152232	2.101171
C	-4.894667	-0.331084	0.421252
H	-3.383506	0.017791	-1.040403
C	-4.153062	-1.133540	2.564194
H	-2.056128	-1.493446	2.774777
C	-5.193062	-0.732623	1.721521
H	-5.689136	-0.013728	-0.250720
H	-4.365438	-1.446736	3.583887
H	-6.221137	-0.737478	2.075150
Sn	-1.307174	-2.453082	-1.230270
C	-2.145846	-1.267560	-2.884928
H	-3.221608	-1.450876	-2.959159
H	-1.988278	-0.189778	-2.807324
H	-1.664893	-1.623580	-3.803882
C	-2.723829	-4.009185	-0.713984
H	-3.349728	-3.676634	0.116265
H	-3.359984	-4.228100	-1.578604
H	-2.188560	-4.913735	-0.415825
C	0.571824	-3.196896	-2.054039
H	0.916447	-4.056614	-1.475787
H	0.414704	-3.491351	-3.098590
H	1.345944	-2.426145	-2.018104
O	1.250363	-0.183750	3.356581
H	5.351188	-0.584790	2.289283

TS6-cis

B3LYP electronic energy: -7003.98264847 a.u.
B3LYP enthalpy: -7003.401597 a.u.
B3LYP free energy: -7003.526251 a.u.
M06 SCF energy in solution: -7008.56482301 a.u.
M06 enthalpy in solution: -7007.983772 a.u.
M06 free energy in solution: -7008.108426 a.u.
Three lowest frequencies (cm-1): -39.9957 15.23 18.12
Imaginary frequency: -39.9957 cm-1

Cartesian coordinates

ATOM	X	Y	Z
P	-0.509223	1.736161	-0.220994
C	3.052572	3.466729	-1.472597
H	3.720095	4.256606	-1.140078
C	-0.795462	2.416169	2.500512
H	-0.795295	1.344282	2.675925
C	-0.703494	4.295961	0.981437
H	-0.634406	4.695306	-0.026025
C	-0.656920	2.906634	1.194461
C	-0.850996	5.170415	2.057093
H	-0.878040	6.241887	1.879358
C	-1.739872	2.504855	-2.696806
H	-0.791814	2.297455	-3.179334
C	-1.883680	2.343063	-1.310725
C	1.886930	3.203809	-0.749048
H	1.671689	3.788810	0.137459
C	-4.027605	3.278528	-2.874887
H	-4.854128	3.643690	-3.478333
C	-3.120008	2.656662	-0.719576
H	-3.258721	2.536100	0.349586
C	1.019574	2.179121	-1.150136
C	-0.973059	4.670855	3.356736
H	-1.091879	5.354079	4.193072
C	-2.806855	2.966129	-3.472269
H	-2.673693	3.090769	-4.543434
C	2.515580	1.683206	-3.005309
H	2.761472	1.077267	-3.872711
C	-0.952865	3.293693	3.575936
H	-1.061641	2.897211	4.581418
C	1.358860	1.408660	-2.276329
H	0.728270	0.576143	-2.577627
C	3.365994	2.715652	-2.605077
H	4.276229	2.919167	-3.161391
C	-4.179172	3.125102	-1.494704
H	-5.125098	3.366014	-1.017729
C	1.601233	-0.064985	1.000118
C	2.088915	0.493185	2.133262
C	2.601842	-0.511275	0.067020
C	3.931546	-0.359669	0.314294
H	2.301855	-0.984467	-0.862228
C	4.431022	0.273074	1.527808
O	3.416204	0.663525	2.400281
Br	5.242974	-0.959796	-0.926854

Pd	-0.441623	-0.448308	0.652243
Br	-0.044060	-2.611432	1.891749
C	-2.566866	-0.803499	0.549649
C	-3.470830	-0.474062	-0.478088
C	-3.133607	-1.180738	1.788964
C	-4.857265	-0.520258	-0.291666
H	-3.101767	-0.167953	-1.450606
C	-4.515912	-1.201398	1.991347
H	-2.487081	-1.472511	2.610242
C	-5.386756	-0.880461	0.947237
H	-5.518425	-0.264782	-1.116797
H	-4.911834	-1.485801	2.963794
H	-6.462930	-0.915736	1.097439
Sn	-1.112061	-2.785444	-0.926995
H	1.501547	0.862231	2.965187
O	5.578277	0.488427	1.843212
C	-1.454634	-1.730290	-2.821596
H	-2.477930	-1.904174	-3.167627
H	-1.297751	-0.652959	-2.740291
H	-0.753128	-2.135831	-3.558589
C	-2.737492	-4.121014	-0.414035
H	-3.689723	-3.587155	-0.434026
H	-2.764590	-4.945368	-1.135824
H	-2.574368	-4.527910	0.585997
C	0.743390	-3.879433	-1.263129
H	0.834334	-4.683820	-0.529795
H	0.724386	-4.303908	-2.274153
H	1.617940	-3.231847	-1.169992

20a
B3LYP electronic energy: -4309.43871435 a.u.
B3LYP enthalpy: -4308.980296 a.u.
B3LYP free energy: -4309.082418 a.u.
M06 SCF energy in solution: -4311.44039647 a.u.
M06 enthalpy in solution: -4310.981978 a.u.
M06 free energy in solution: -4311.084100 a.u.
Three lowest frequencies (cm-1): 10.7525 14.24 18.23

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.426068	0.262902	-0.049967
P	-1.983160	0.268838	-0.023309
C	-2.437569	4.213197	-1.116274
C	-3.240212	-2.970563	-2.234073
C	-2.645980	-2.163738	-1.264301
C	-2.494017	-0.236461	4.016363
C	-1.921642	2.932079	-0.905488
C	-4.020017	-2.401282	-3.243855
C	-2.000694	0.109775	2.758644
C	-2.837530	-0.770198	-1.284496
C	-2.685274	-0.273727	1.593218

C	-4.206153	-1.019163	-3.276769
C	-4.355433	-1.370276	2.973244
C	-3.621215	-0.206698	-2.302614
C	-3.867221	-1.018924	1.712322
C	-2.693235	1.955201	-0.257643
C	-3.723067	4.532354	-0.678736
C	-3.672294	-0.979155	4.125785
C	-4.495631	3.567404	-0.026183
C	-3.985103	2.287162	0.184435
H	-4.590589	1.547392	0.699764
H	-5.495214	3.812821	0.322684
H	-4.121025	5.531052	-0.837871
H	-1.825952	4.961658	-1.612242
H	-0.909965	2.703921	-1.225537
H	-1.076528	0.677292	2.676599
H	-1.954145	0.066834	4.909298
H	-4.053206	-1.255567	5.105254
H	-5.270614	-1.951071	3.052328
H	-4.403054	-1.333169	0.822073
H	-2.031604	-2.619045	-0.494315
H	-3.084343	-4.045422	-2.203274
H	-4.477183	-3.032001	-4.001620
H	-4.810083	-0.567313	-4.059209
H	-3.779013	0.866107	-2.337399
C	2.432131	0.539294	-0.036710
C	3.645455	-0.079703	-0.017411
C	2.390770	1.979693	-0.050799
C	4.751342	2.079059	-0.023192
H	5.585241	2.767304	-0.018530
H	3.739117	-1.161740	-0.009048
O	1.305102	2.582197	-0.071334
O	3.548970	2.718490	-0.042757
C	4.835166	0.729318	-0.011067
Br	6.556169	-0.088571	0.016145
C	0.596126	-1.725486	-0.034775
C	0.364423	-2.465598	1.134726
C	0.960019	-2.409971	-1.205428
C	0.474993	-3.861580	1.126437
H	0.085726	-1.962577	2.056361
C	1.066182	-3.805243	-1.209299
H	1.156662	-1.859510	-2.121085
C	0.823084	-4.537144	-0.045060
H	0.288206	-4.417887	2.042546
H	1.343650	-4.317705	-2.127990
H	0.909271	-5.620711	-0.049021

21a
B3LYP electronic energy: -4309.42505524 a.u.
B3LYP enthalpy: -4308.966818 a.u.
B3LYP free energy: -4309.072922 a.u.
M06 SCF energy in solution: -4311.43886534 a.u.

M06 enthalpy in solution: -4310.980628 a.u.
M06 free energy in solution: -4311.086732 a.u.
Three lowest frequencies (cm-1): 5.6107 10.20 14.21

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.256970	-0.245835	-0.368269
P	2.110011	-0.288603	0.076154
C	3.181490	-4.808258	-0.182751
C	2.385030	-4.197374	-1.154262
C	2.006971	0.434354	4.115210
C	2.087102	-2.838095	-1.057875
C	2.979380	1.855408	-1.494524
C	1.686200	0.052705	2.812636
C	3.388692	-2.691646	0.977157
C	3.851668	2.537573	-2.343262
C	3.236339	1.041900	4.382731
C	3.681414	-4.053895	0.880234
C	3.287685	0.555314	-1.059015
C	5.032734	1.929441	-2.774310
C	3.828924	0.872914	2.040921
C	5.342228	0.635473	-2.351253
C	2.597294	0.262000	1.763586
C	2.589109	-2.068488	0.007594
C	4.476459	-0.049673	-1.496503
C	4.143836	1.261650	3.344966
H	0.722905	-0.407373	2.603938
H	1.294102	0.266127	4.917753
H	3.483283	1.347535	5.395760
H	5.099308	1.737789	3.547785
H	4.540291	1.048963	1.239988
H	2.055719	2.329864	-1.178705
H	3.601633	3.541843	-2.673949
H	5.707098	2.459972	-3.441058
H	6.258125	0.155836	-2.685891
H	4.726210	-1.055945	-1.174562
H	3.781052	-2.115893	1.809464
H	4.300827	-4.524993	1.638638
H	3.407987	-5.868541	-0.252387
H	1.989489	-4.778804	-1.982380
H	1.465825	-2.369907	-1.819120
C	-2.244417	-0.514773	-0.682479
C	-2.650705	-1.222416	-1.770604
H	-2.011296	-1.560401	-2.579644
C	-4.991789	-1.302454	-1.135779
C	-3.294580	-0.134124	0.229401
H	-3.056235	0.466957	1.101789
O	-6.095548	-1.701085	-1.420712
C	-4.585405	-0.510998	0.020235
O	-3.934811	-1.608962	-2.000145
Br	-5.970768	-0.027515	1.229771
C	-0.568697	1.720628	-0.484019
C	-0.749454	2.347540	-1.723761

C	-0.564804	2.487289	0.687903
C	-0.890336	3.738724	-1.787378
H	-0.783037	1.762857	-2.637446
C	-0.711485	3.878152	0.613199
H	-0.433239	2.018084	1.658758
C	-0.871379	4.507737	-0.622036
H	-1.027823	4.215979	-2.754898
H	-0.700651	4.464576	1.528973
H	-0.988384	5.586713	-0.675662

TS7-mono

B3LYP electronic energy: -4308.23036955 a.u.
B3LYP enthalpy: -4307.773471 a.u.
B3LYP free energy: -4307.877143 a.u.
M06 SCF energy in solution: -4311.42760921 a.u.
M06 enthalpy in solution: -4310.970711 a.u.
M06 free energy in solution: -4311.074383 a.u.
Three lowest frequencies (cm-1): -268.4120 1.36 12.94
Imaginary frequency: -268.4120 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.343445	0.028695	0.145347
P	-2.037954	0.357991	-0.072223
C	-2.030471	4.391952	-0.843627
C	-2.965289	-2.071014	-3.250852
C	-2.364267	-1.504511	-2.126346
C	-2.923942	-1.102341	3.661342
C	-1.729619	3.030838	-0.808933
C	-4.065665	-1.450536	-3.846581
C	-2.273235	-0.559367	2.552347
C	-2.867599	-0.314271	-1.576338
C	-2.960045	-0.388546	1.338914
C	-4.564121	-0.260150	-3.313708
C	-4.947090	-1.341434	2.360587
C	-3.969509	0.306782	-2.184464
C	-4.301434	-0.793300	1.250931
C	-2.516689	2.141991	-0.056474
C	-3.114345	4.887510	-0.114422
C	-4.261120	-1.493111	3.567790
C	-3.894901	4.015287	0.645612
C	-3.600298	2.649889	0.675184
H	-4.211190	1.982265	1.274738
H	-4.734763	4.395930	1.220893
H	-3.344102	5.949441	-0.133065
H	-1.413131	5.066066	-1.431249
H	-0.875584	2.652297	-1.366445
H	-1.223104	-0.284474	2.622957
H	-2.379977	-1.230125	4.593135
H	-4.764646	-1.923925	4.429178
H	-5.984700	-1.654608	2.279490

H	-4.840112	-0.691731	0.313273
H	-1.495997	-1.980584	-1.679510
H	-2.566528	-2.992647	-3.666092
H	-4.528534	-1.888857	-4.726768
H	-5.415181	0.231355	-3.777865
H	-4.359179	1.237226	-1.782190
C	2.336290	-0.158544	0.550432
C	3.293498	0.335038	-0.298173
C	2.637611	-0.270374	1.979417
C	4.855289	0.584480	1.510983
H	5.795751	0.833359	1.986677
H	3.105086	0.407544	-1.364662
O	1.896220	-0.634340	2.867007
O	3.945886	0.087449	2.372177
C	4.573649	0.735764	0.197017
Br	5.885137	1.455591	-0.980412
C	1.247525	-1.799675	-0.176704
C	1.070754	-2.809051	0.781126
C	1.543484	-2.150509	-1.504804
C	1.151605	-4.152544	0.399354
H	0.882101	-2.543613	1.814863
C	1.616068	-3.494622	-1.874873
H	1.710115	-1.381148	-2.253524
C	1.419644	-4.501764	-0.924888
H	1.003795	-4.926997	1.148297
H	1.833790	-3.753240	-2.908602
H	1.485602	-5.547141	-1.214301

TS8-bis

B3LYP electronic energy: -5345.70793605 a.u.
B3LYP enthalpy: -5344.957442 a.u.
B3LYP free energy: -5345.095394 a.u.
M06 SCF energy in solution: -5347.39220020 a.u.
M06 enthalpy in solution: -5346.641706 a.u.
M06 free energy in solution: -5346.779658 a.u.
Three lowest frequencies (cm-1): -326.5740 7.28 13.87
Imaginary frequency: -326.5740 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.063716	-0.458911	0.369159
P	-0.712081	1.881923	0.199810
P	2.461249	-0.499026	-0.223284
C	4.867752	3.435137	-0.954625
C	3.972115	3.322169	0.109909
C	-4.844632	1.876858	0.407490
C	1.698993	-2.180100	-3.905275
C	0.386038	2.720497	4.082991
C	0.251664	2.140516	2.819117
C	3.246543	2.144081	0.291089
C	1.073528	3.385102	-3.187890

C	-3.489826	1.837732	0.740758
C	3.404751	-2.747851	1.182147
C	1.597019	-1.488015	-2.697152
C	4.318335	1.178923	-1.642979
C	-0.334693	3.871717	4.402671
C	4.198410	-3.431384	2.103301
C	2.866107	-2.882714	-4.210405
C	5.034312	2.362565	-1.831990
C	0.502158	2.553318	-2.223588
C	-0.596768	2.705915	1.853396
C	3.590426	-1.372367	0.959918
C	0.095424	3.063284	-0.980034
C	-1.195571	4.435475	3.457360
C	0.879993	5.256150	-1.676842
C	-1.329028	3.856247	2.194794
C	5.180176	-2.754237	2.829243
C	3.827898	-2.190180	-2.098292
C	5.365592	-1.386603	2.623651
C	0.296617	4.426497	-0.717822
C	-2.503462	2.094821	-0.227343
C	2.661101	-1.475888	-1.781657
C	-5.238388	2.173933	-0.898716
C	3.415980	1.052468	-0.575844
C	4.579829	-0.700210	1.695068
C	1.265152	4.740311	-2.915571
C	3.928091	-2.888522	-3.303222
C	-4.268420	2.436152	-1.866586
C	-2.912490	2.394757	-1.536249
H	-2.174230	2.607926	-2.302746
H	-4.563549	2.674370	-2.885171
H	-6.292781	2.194926	-1.158854
H	-5.590165	1.655979	1.165719
H	-3.203955	1.607680	1.761880
H	0.375630	1.495279	-2.437321
H	1.378834	2.970407	-4.144792
H	1.717754	5.388811	-3.660900
H	1.031272	6.309391	-1.454413
H	0.006563	4.846535	0.239291
H	0.793632	1.228384	2.579778
H	1.045532	2.266081	4.817626
H	-0.236258	4.322075	5.386748
H	-1.770152	5.324080	3.705113
H	-2.019681	4.289995	1.477961
H	0.677830	-0.963532	-2.446608
H	0.863738	-2.179547	-4.600757
H	2.945476	-3.428937	-5.146506
H	4.837165	-3.438589	-3.531890
H	4.658172	-2.207299	-1.398848
H	2.643856	-3.291941	0.633070
H	4.037487	-4.494974	2.256645
H	5.795222	-3.287847	3.549132
H	6.129668	-0.848886	3.179301
H	4.750185	0.359572	1.538605

H	4.466467	0.353775	-2.331538
H	5.726702	2.442909	-2.666112
H	5.427874	4.354631	-1.102352
H	3.826948	4.153850	0.793928
H	2.543224	2.075132	1.115764
C	-1.781310	-1.414858	0.780147
C	-2.455849	-1.193525	1.946491
H	-1.994254	-1.003074	2.907648
C	-4.673942	-1.477713	1.005177
C	-2.627767	-1.696933	-0.359140
H	-2.174421	-1.896455	-1.324497
O	-5.864823	-1.462093	1.214995
C	-3.980877	-1.722167	-0.254772
O	-3.809617	-1.245155	2.072259
Br	-5.082760	-2.082111	-1.760691
C	-0.215855	-2.503856	0.899981
C	-0.138489	-3.505262	-0.093022
C	0.141353	-2.878832	2.217554
C	0.265114	-4.806879	0.214989
H	-0.399771	-3.274092	-1.121674
C	0.539000	-4.177122	2.522059
H	0.081617	-2.147878	3.020367
C	0.600287	-5.157519	1.524291
H	0.311085	-5.550183	-0.577845
H	0.801476	-4.426683	3.547625
H	0.895123	-6.174856	1.766142

PPh3

B3LYP electronic energy: -1036.28169971 a.u.
B3LYP enthalpy: -1035.990442 a.u.
B3LYP free energy: -1036.053657 a.u.
M06 SCF energy in solution: -1035.91706679 a.u.
M06 enthalpy in solution: -1035.625809 a.u.
M06 free energy in solution: -1035.689024 a.u.
Three lowest frequencies (cm-1): 22.2232 25.63 39.58

Cartesian coordinates

ATOM	X	Y	Z
P	0.001286	-0.001329	-1.206709
C	-1.192321	-1.168233	-0.401069
C	-1.394511	-2.406570	-1.034455
C	-1.922188	-0.884181	0.763672
C	-2.284256	-3.343285	-0.508242
H	-0.854026	-2.634265	-1.950485
C	-2.821876	-1.817373	1.284458
H	-1.791315	0.070875	1.263428
C	-3.002640	-3.049340	0.653069
H	-2.425126	-4.296740	-1.010767
H	-3.381827	-1.580076	2.185597
H	-3.704259	-3.773285	1.059099
C	-0.414063	1.616669	-0.403659

C	0.203540	2.114478	0.754379
C	-1.396351	2.402671	-1.030602
C	-0.160129	3.358469	1.275778
H	0.973720	1.530833	1.249538
C	-1.767574	3.639846	-0.503898
H	-1.869888	2.042910	-1.941325
C	-1.148154	4.121990	0.651594
H	0.329938	3.729926	2.172324
H	-2.531994	4.231508	-1.000967
H	-1.429038	5.089807	1.058618
C	1.610002	-0.450945	-0.403478
C	2.782088	0.003173	-1.032391
C	1.731470	-1.230692	0.757379
C	4.038981	-0.295092	-0.505865
H	2.707412	0.591052	-1.944424
C	2.990450	-1.539329	1.278383
H	0.839847	-1.602387	1.253298
C	4.146176	-1.070408	0.651073
H	4.934012	0.068303	-1.004170
H	3.066733	-2.147119	2.176551
H	5.124659	-1.312484	1.057555

12-trans-Cu
B3LYP electronic energy: -7894.45146470 a.u.
B3LYP enthalpy: -7893.785371 a.u.
B3LYP free energy: -7893.933154 a.u.
M06 SCF energy in solution: -7898.85484026 a.u.
M06 enthalpy in solution: -7898.188747 a.u.
M06 free energy in solution: -7898.336530 a.u.
Three lowest frequencies (cm-1): 6.8040 9.10 11.14

Cartesian coordinates

ATOM	X	Y	Z
Pd	1.208459	0.505554	-0.269919
Br	2.642572	1.584498	-2.058756
P	0.028140	2.573337	0.005546
P	2.236453	-1.597575	-0.760588
C	-1.120149	4.778550	-3.307020
H	-1.061130	5.808933	-3.646969
C	4.690722	-0.630603	0.169276
H	4.079458	0.031105	0.776809
C	4.875043	-2.325379	-1.546907
H	4.417229	-2.999251	-2.263471
C	2.408187	3.952142	0.650278
H	2.916460	3.107135	0.199058
C	0.550781	-3.545808	0.367020
H	-0.167178	-3.223326	-0.382168
C	0.358606	5.104060	1.230946
H	-0.725471	5.142144	1.273168
C	1.005759	3.982737	0.680645
C	2.744614	-3.415357	1.375364

H	3.743454	-2.993273	1.418945
C	1.101432	6.171457	1.735249
H	0.588275	7.032039	2.155754
C	-2.759645	2.530492	0.622920
H	-2.939987	2.576827	-0.445081
C	1.868427	-3.682478	-2.643109
H	2.227121	-4.350688	-1.866545
C	-1.448586	2.546802	1.120073
C	2.378204	-4.408631	2.288922
H	3.096425	-4.742663	3.032819
C	1.754065	-2.302233	-2.394559
C	1.104005	-4.972794	2.242274
H	0.822783	-5.747311	2.950443
C	-0.579482	4.430486	-2.067210
H	-0.102602	5.190981	-1.457915
C	-3.642156	2.401129	2.874730
H	-4.490369	2.344066	3.551302
C	-1.251312	2.491663	2.511770
H	-0.244761	2.518525	2.919483
C	6.080927	-0.576718	0.267732
H	6.545351	0.113431	0.966700
C	-0.640395	3.103960	-1.621907
C	2.497447	6.131278	1.703510
H	3.074850	6.961978	2.100445
C	4.074894	-1.513818	-0.730964
C	-3.848831	2.455579	1.496330
H	-4.856690	2.437431	1.091887
C	1.835572	-2.974089	0.404663
C	-1.791305	2.485297	-3.667963
H	-2.261282	1.725083	-4.285585
C	6.266496	-2.260006	-1.455420
H	6.876574	-2.887484	-2.099417
C	6.871465	-1.391116	-0.545993
H	7.954796	-1.341196	-0.478192
C	0.190474	-4.539336	1.276384
H	-0.802850	-4.977272	1.226355
C	3.146578	5.022172	1.160377
H	4.232065	4.985895	1.127824
C	-1.240972	2.129424	-2.437044
H	-1.277835	1.094299	-2.108257
C	1.506195	-4.209819	-3.882474
H	1.598748	-5.277888	-4.059508
C	1.264739	-1.465768	-3.409487
H	1.192846	-0.397497	-3.239982
C	-1.729605	3.810735	-4.106050
H	-2.151074	4.085637	-5.069047
C	-2.339300	2.423340	3.381177
H	-2.168295	2.390459	4.453873
C	0.899344	-2.000912	-4.646382
H	0.519509	-1.341144	-5.421409
C	1.017811	-3.370116	-4.886035
H	0.728120	-3.783371	-5.848332
C	0.148865	-0.322051	1.248123

C	-1.193842	-0.782819	0.998619
C	0.630998	-0.469881	2.524606
C	-0.169898	-1.042491	3.560980
H	1.637604	-0.149396	2.775657
C	-1.428467	-1.446575	3.279970
H	-2.139130	-1.887536	3.965036
O	-1.768513	-0.743384	-0.108888
O	-1.923978	-1.317689	2.026820
Br	0.514781	-1.232775	5.322416
Cu	-3.602417	-1.159227	-0.510529
I	-5.914049	-1.610523	-1.118462

13-cis-Cu
B3LYP electronic energy: -7894.43257156 a.u.
B3LYP enthalpy: -7893.766556 a.u.
B3LYP free energy: -7893.913323 a.u.
M06 SCF energy in solution: -7898.84617346 a.u.
M06 enthalpy in solution: -7898.180158 a.u.
M06 free energy in solution: -7898.326925 a.u.
Three lowest frequencies (cm-1): 6.5923 6.90 12.81

Cartesian coordinates

ATOM	X	Y	Z
Pd	1.293437	-0.682137	-0.390342
Br	1.524235	-3.122083	-0.886945
P	0.768078	1.584870	-0.010603
P	3.723963	-0.645348	0.110740
C	3.118800	4.729407	-1.384602
H	3.527887	5.660705	-1.003019
C	3.216569	-2.439271	2.232965
H	2.277938	-2.629637	1.724332
C	5.366755	-1.337566	2.337075
H	6.091064	-0.634430	1.939197
C	1.314587	1.145973	2.714339
H	1.610856	0.150122	2.398289
C	4.201745	-1.403778	-2.543523
H	3.258677	-0.904902	-2.744675
C	0.459023	3.347750	2.194169
H	0.067325	4.065109	1.479437
C	0.880623	2.077836	1.760378
C	5.860854	-2.194674	-0.974015
H	6.231388	-2.296779	0.040455
C	0.511561	3.685713	3.545950
H	0.184607	4.670767	3.866885
C	-1.214194	2.874952	-1.614813
H	-0.412607	3.154611	-2.290029
C	5.457331	1.450583	-0.738236
H	5.539981	0.906602	-1.672811
C	-0.937474	2.159005	-0.441247
C	6.571357	-2.777264	-2.024862
H	7.487282	-3.323183	-1.815619

C	4.667756	0.942402	0.304540
C	6.106104	-2.664900	-3.336025
H	6.659611	-3.121623	-4.151924
C	2.377144	3.905901	-0.535208
H	2.225525	4.204489	0.495740
C	-3.575183	2.910281	-1.067936
H	-4.596122	3.191494	-1.308775
C	-2.000896	1.830221	0.418962
H	-1.811199	1.283971	1.338317
C	3.516797	-3.126651	3.411106
H	2.792518	-3.825383	3.820734
C	1.847757	2.697944	-1.007649
C	0.962740	2.754918	4.485994
H	0.991463	3.016940	5.539973
C	4.138197	-1.534950	1.680784
C	-2.526059	3.246602	-1.923222
H	-2.722647	3.802765	-2.835698
C	4.670461	-1.498653	-1.224514
C	2.822173	3.154471	-3.190521
H	2.993623	2.855181	-4.220863
C	5.664107	-2.029307	3.511695
H	6.619148	-1.865705	4.003680
C	4.738703	-2.924221	4.053201
H	4.970639	-3.460702	4.969303
C	4.919680	-1.975621	-3.593924
H	4.540803	-1.899844	-4.609407
C	1.356219	1.482802	4.069806
H	1.689418	0.746647	4.795959
C	2.091523	2.323901	-2.340688
H	1.705664	1.378152	-2.713980
C	6.159799	2.647286	-0.581228
H	6.771325	3.018407	-1.399181
C	4.592755	1.671542	1.504358
H	3.999762	1.300822	2.333224
C	3.334948	4.362448	-2.713313
H	3.906730	5.010125	-3.372117
C	-3.308301	2.203480	0.108748
H	-4.122367	1.940375	0.778310
C	5.299692	2.863738	1.660564
H	5.237625	3.403284	2.601947
C	6.088517	3.355132	0.618474
H	6.645342	4.280034	0.742602
C	-0.678814	-1.025048	-0.801908
C	-1.243279	-0.758649	-2.005283
C	-1.548333	-1.603815	0.173437
C	-2.884068	-1.778834	-0.077575
H	-1.151779	-1.911646	1.135682
C	-3.451024	-1.393277	-1.339708
O	-2.567727	-0.954399	-2.270614
Br	-4.049803	-2.514810	1.222226
O	-4.644596	-1.429460	-1.689273
H	-0.744813	-0.368369	-2.882685
Cu	-6.141246	-0.666040	-0.736030

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I       -7.902523    0.622972    0.354722



 13-trans-Cu
B3LYP electronic energy:    -7894.44592203 a.u.
B3LYP enthalpy:    -7893.779618 a.u.
B3LYP free energy:    -7893.926576 a.u.
M06 SCF energy in solution:    -7898.85087910 a.u.
M06 enthalpy in solution:    -7898.184575 a.u.
M06 free energy in solution:    -7898.331533 a.u.
Three lowest frequencies (cm-1):       2.6687      11.28      13.51

Cartesian coordinates
ATOM       X           Y           Z
Pd      -1.993995    0.133705   -0.033826
Br      -4.419459    0.587169    0.540560
P       -2.436927   -2.225226   -0.016904
P       -1.570360    2.498293   -0.084836
C       -5.858848   -4.108864   -1.386381
H       -6.477487   -4.953723   -1.096468
C       -2.243921    2.685239    2.627933
H       -1.954925    1.638986    2.668273
C       -2.636962    4.705069    1.355389
H       -2.638564    5.244397    0.413733
C       -3.167787   -2.092672    2.698715
H       -3.428868   -1.062685    2.479029
C        0.938177    2.854373   -1.331740
H        0.435260    2.547173   -2.243784
C       -2.374018   -4.261115    1.968368
H       -1.980590   -4.914261    1.196343
C       -2.665824   -2.916484    1.677869
C        0.885622    3.395892    1.023568
H        0.344315    3.515165    1.956486
C       -2.576094   -4.766550    3.253337
H       -2.343724   -5.807064    3.463036
C       -1.278362   -3.852496   -2.040544
H       -2.199175   -3.705792   -2.595334
C       -1.751346    4.547836   -2.044852
H       -0.864169    4.973446   -1.587193
C       -1.132922   -3.305093   -0.757474
C        2.257572    3.661586    0.989155
H        2.765219    3.977265    1.896175
C       -2.300954    3.352428   -1.547596
C        2.971515    3.525931   -0.201027
H        4.038134    3.729498   -0.226358
C       -4.750659   -3.766914   -0.609251
H       -4.519377   -4.347792    0.277821
C        0.941860   -4.813502   -1.916033
H        1.743982   -5.393354   -2.363501
C        0.069456   -3.526279   -0.061851
H        0.204428   -3.118764    0.935596
C       -2.662697    3.334103    3.789464
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H	-2.679783	2.793965	4.731973
C	-3.950279	-2.672872	-0.965086
C	-3.070606	-3.939129	4.263490
H	-3.223832	-4.333567	5.264319
C	-2.217784	3.368216	1.402416
C	-0.245405	-4.599029	-2.614816
H	-0.376667	-5.016409	-3.609404
C	0.209800	2.987266	-0.135860
C	-5.379840	-2.276697	-2.887064
H	-5.626421	-1.688299	-3.766507
C	-3.067743	5.347803	2.517120
H	-3.397877	6.381761	2.467488
C	-3.077141	4.666464	3.735321
H	-3.413609	5.169110	4.637922
C	2.305602	3.125570	-1.364126
H	2.853057	3.023740	-2.297108
C	-3.368297	-2.605044	3.981613
H	-3.760097	-1.956494	4.760373
C	-4.279963	-1.924339	-2.105238
H	-3.686037	-1.053676	-2.368254
C	-2.333030	5.192325	-3.137341
H	-1.896321	6.114481	-3.510892
C	-3.443747	2.819798	-2.165461
H	-3.896681	1.916537	-1.770689
C	-6.172579	-3.368758	-2.527376
H	-7.036302	-3.636436	-3.129805
C	1.094898	-4.277839	-0.633852
H	2.014200	-4.443574	-0.078855
C	-4.020727	3.469779	-3.257930
H	-4.907122	3.047505	-3.723347
C	-3.467320	4.653402	-3.747939
H	-3.917118	5.155261	-4.600346
C	-0.029009	-0.212493	-0.430984
C	0.444314	-0.474920	-1.675259
C	0.962229	-0.175286	0.601716
C	2.289096	-0.385894	0.336526
H	0.664135	0.020592	1.627200
C	2.741423	-0.622341	-1.009101
O	1.767231	-0.668202	-1.953835
Br	3.584407	-0.360474	1.719234
O	3.898174	-0.794737	-1.421973
H	-0.140446	-0.569855	-2.581206
Cu	5.664471	-0.545943	-0.674088
I	7.985722	-0.195903	-0.013006

12-trans-I
B3LYP electronic energy: -5125.58572274 a.u.
B3LYP enthalpy: -5124.926062 a.u.
B3LYP free energy: -5125.059399 a.u.
M06 SCF energy in solution: -5127.35629716 a.u.
M06 enthalpy in solution: -5126.696636 a.u.

M06 free energy in solution: -5126.829973 a.u.
Three lowest frequencies (cm-1): 12.0875 15.52 19.18

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.032429	-0.435787	0.083846
P	2.421452	-0.363390	-0.039520
P	-2.352496	-0.576027	-0.027883
C	4.314822	-3.608960	-1.793847
H	5.056404	-4.353970	-1.518460
C	-2.570907	-0.727470	2.748497
H	-1.724543	-0.045366	2.738649
C	-4.153431	-2.122313	1.567879
H	-4.558541	-2.521944	0.644666
C	2.648862	-0.873691	2.730581
H	1.573206	-1.008282	2.707626
C	-3.174326	1.585862	-1.618921
H	-2.610630	1.089877	-2.404098
C	4.734339	-0.428997	1.586095
H	5.281996	-0.184392	0.680638
C	3.337568	-0.590251	1.543482
C	-3.997414	1.663321	0.652910
H	-4.087695	1.228959	1.642898
C	5.425223	-0.569895	2.788694
H	6.504933	-0.448252	2.806820
C	3.774382	1.298470	-1.947801
H	3.780959	0.444849	-2.615701
C	-4.328336	-1.580949	-1.786807
H	-5.013950	-0.910544	-1.277206
C	3.208381	1.192159	-0.670379
C	-4.626580	2.881643	0.378591
H	-5.193804	3.378897	1.160902
C	-2.976135	-1.635402	-1.401729
C	-4.532587	3.452046	-0.889833
H	-5.022966	4.398404	-1.101288
C	3.947684	-2.628991	-0.868942
H	4.400689	-2.627855	0.116415
C	4.346429	3.615835	-1.533282
H	4.786435	4.551637	-1.867392
C	3.219674	2.319969	0.169507
H	2.791631	2.258815	1.165860
C	-3.109186	-1.141246	3.966138
H	-2.691592	-0.764340	4.895816
C	2.985897	-1.668569	-1.206395
C	4.730181	-0.858395	3.966508
H	5.269536	-0.963969	4.904084
C	-3.095201	-1.205195	1.536314
C	4.339532	2.503828	-2.373893
H	4.774816	2.566868	-3.367540
C	-3.264780	1.003499	-0.342021
C	2.764792	-2.684397	-3.399002
H	2.298757	-2.703445	-4.380612
C	-4.681168	-2.546579	2.789420

H	-5.494290	-3.267352	2.799806
C	-4.165715	-2.054747	3.988932
H	-4.577344	-2.388624	4.937518
C	-3.804707	2.799164	-1.889108
H	-3.726161	3.234175	-2.881798
C	3.343583	-1.005256	3.935682
H	2.796225	-1.227827	4.847445
C	2.383757	-1.709378	-2.477000
H	1.620361	-0.981301	-2.741717
C	-4.797489	-2.372142	-2.834675
H	-5.845204	-2.322568	-3.118936
C	-2.103337	-2.480249	-2.101414
H	-1.058963	-2.532446	-1.816440
C	3.729098	-3.636762	-3.059816
H	4.016610	-4.401115	-3.776872
C	3.784241	3.520320	-0.257239
H	3.783812	4.380141	0.407176
C	-2.576264	-3.265196	-3.155549
H	-1.886819	-3.914059	-3.688286
C	-3.921298	-3.216637	-3.521254
H	-4.286687	-3.828628	-4.341667
C	-0.036672	1.519500	-0.457058
C	0.107154	1.810634	-1.878996
C	-0.211849	2.554089	0.415370
C	-0.243319	3.910125	-0.049890
H	-0.333131	2.374697	1.479932
C	-0.105670	4.163681	-1.368396
H	-0.113805	5.143186	-1.829519
O	0.251747	1.008603	-2.784589
O	0.062833	3.164059	-2.258944
Br	-0.471191	5.348453	1.177976
I	0.132894	-3.079034	0.939178

12-cis-I
B3LYP electronic energy: -5125.57340000 a.u.
B3LYP enthalpy: -5124.913786 a.u.
B3LYP free energy: -5125.045696 a.u.
M06 SCF energy in solution: -5127.35011449 a.u.
M06 enthalpy in solution: -5126.690500 a.u.
M06 free energy in solution: -5126.822410 a.u.
Three lowest frequencies (cm-1): 13.5799 15.05 20.41

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.186690	-0.557117	-0.179158
P	0.523063	1.760032	0.097175
P	-2.286907	-0.641041	0.048894
C	-1.456235	3.848311	3.112060
H	-2.037617	4.759858	3.219386
C	-2.281270	-1.490961	-2.640740
H	-1.209945	-1.602068	-2.511414

C	-4.464378	-0.921755	-1.767563
H	-5.095980	-0.558617	-0.962636
C	-0.701712	2.202526	-2.387057
H	-0.763586	1.120633	-2.436094
C	-2.123981	-2.045913	2.458142
H	-1.246679	-1.428568	2.628232
C	0.021468	4.213817	-1.251963
H	0.518861	4.702408	-0.419417
C	-0.128758	2.815254	-1.263885
C	-3.933098	-2.770452	1.030617
H	-4.482671	-2.717288	0.097286
C	-0.440942	4.982260	-2.319447
H	-0.323781	6.062343	-2.295986
C	2.879852	2.657855	1.448828
H	2.328161	2.551123	2.376450
C	-3.824392	0.934917	1.877185
H	-3.656332	0.143503	2.599306
C	2.262970	2.382443	0.220862
C	-4.318178	-3.700270	1.998771
H	-5.165555	-4.353156	1.807291
C	-3.300842	0.827428	0.579999
C	-3.617238	-3.796233	3.201411
H	-3.917683	-4.522104	3.952199
C	-0.973802	3.486211	1.852387
H	-1.197659	4.113968	0.998053
C	4.938558	3.240526	0.314393
H	5.972870	3.571329	0.351169
C	3.004344	2.542381	-0.963296
H	2.548324	2.330072	-1.925270
C	-2.860206	-1.798077	-3.874804
H	-2.226920	-2.134688	-4.690788
C	-0.230450	2.309836	1.690491
C	-1.034935	4.363761	-3.423431
H	-1.385194	4.963728	-4.259087
C	-3.077626	-1.054339	-1.570552
C	4.209500	3.084650	1.492859
H	4.670999	3.297525	2.453378
C	-2.834162	-1.930724	1.252533
C	-0.474073	1.863350	4.071731
H	-0.279951	1.224914	4.929426
C	-5.039545	-1.236443	-2.998473
H	-6.113070	-1.132917	-3.132792
C	-4.237929	-1.675975	-4.055236
H	-4.686823	-1.917555	-5.015102
C	-2.518784	-2.964744	3.429963
H	-1.955546	-3.044989	4.355789
C	-1.154313	2.974507	-3.460277
H	-1.587364	2.483609	-4.327215
C	-0.001611	1.492955	2.812532
H	0.547817	0.561776	2.695533
C	-4.581598	2.047756	2.250057
H	-4.984649	2.105471	3.257720
C	-3.549220	1.869613	-0.329899

H	-3.167701	1.810798	-1.343165
C	-1.200128	3.046536	4.224549
H	-1.573021	3.335221	5.203515
C	4.331047	2.968023	-0.913739
H	4.889295	3.085222	-1.838534
C	-4.306462	2.979639	0.044085
H	-4.493413	3.768110	-0.680298
C	-4.828519	3.071993	1.336076
H	-5.425858	3.932748	1.625227
C	2.175766	-0.745024	-0.589731
C	2.509789	-0.509245	-1.986938
C	3.158093	-1.099374	0.284911
C	4.509814	-1.256197	-0.167989
H	2.935975	-1.300713	1.328038
C	4.801410	-1.074878	-1.473397
H	5.778031	-1.189006	-1.926235
O	1.757924	-0.131977	-2.869233
O	3.847536	-0.720632	-2.361687
Br	5.888445	-1.741966	1.053290
I	0.223924	-3.286908	-0.308636

13-cis-I
B3LYP electronic energy: -5125.56666151 a.u.
B3LYP enthalpy: -5124.907007 a.u.
B3LYP free energy: -5125.039282 a.u.
M06 SCF energy in solution: -5127.35021828 a.u.
M06 enthalpy in solution: -5126.690564 a.u.
M06 free energy in solution: -5126.822839 a.u.
Three lowest frequencies (cm-1): 9.9368 16.40 18.62

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.129763	-0.526238	-0.361828
P	-0.437276	1.800241	-0.066387
P	2.306228	-0.686357	0.171367
C	2.281167	4.599867	-1.517866
H	2.811819	5.476646	-1.157251
C	1.593287	-2.271960	2.400073
H	0.625037	-2.352146	1.918039
C	3.877915	-1.483662	2.413816
H	4.684181	-0.910402	1.967470
C	0.014396	1.423068	2.684088
H	0.191160	0.386627	2.412529
C	2.831436	-1.479923	-2.457833
H	1.976175	-0.855730	-2.699009
C	-0.559085	3.687550	2.059489
H	-0.848649	4.417092	1.309149
C	-0.289611	2.358813	1.684952
C	4.285364	-2.501477	-0.821033
H	4.586110	-2.664880	0.208222
C	-0.483384	4.073667	3.397242

H	-0.690348	5.104324	3.672026
C	-2.236370	3.307390	-1.703582
H	-1.396081	3.507317	-2.359017
C	4.251176	1.225854	-0.679960
H	4.305025	0.658451	-1.602418
C	-2.063010	2.549070	-0.537494
C	4.963681	-3.165634	-1.844881
H	5.784972	-3.833216	-1.598542
C	3.389856	0.816425	0.348944
C	4.587261	-2.978811	-3.175720
H	5.115481	-3.498535	-3.970441
C	1.448992	3.894072	-0.646346
H	1.351502	4.226039	0.380905
C	-4.591372	3.579243	-1.207238
H	-5.570492	3.968754	-1.470700
C	-3.173578	2.319101	0.293310
H	-3.064024	1.734413	1.201265
C	1.813848	-2.922325	3.616700
H	1.004843	-3.483166	4.076610
C	0.762874	2.756380	-1.090268
C	-0.161249	3.136013	4.382561
H	-0.113355	3.437586	5.425329
C	2.622738	-1.545887	1.781230
C	-3.494486	3.819037	-2.033369
H	-3.611643	4.404927	-2.940953
C	3.213381	-1.649603	-1.118091
C	1.765771	3.043085	-3.289538
H	1.885868	2.705285	-4.315298
C	4.097014	-2.138845	3.625733
H	5.074281	-2.082503	4.097769
C	3.064644	-2.859265	4.231133
H	3.235716	-3.367431	5.176366
C	3.519710	-2.131985	-3.480688
H	3.207188	-1.995314	-4.512302
C	0.079005	1.809037	4.025577
H	0.310856	1.069321	4.786761
C	0.943432	2.329187	-2.417789
H	0.431647	1.437009	-2.771091
C	5.061808	2.352581	-0.524749
H	5.727725	2.646014	-1.331840
C	3.354731	1.574328	1.532606
H	2.708116	1.277963	2.351185
C	2.434476	4.183931	-2.840718
H	3.078160	4.740046	-3.516754
C	-4.426561	2.829076	-0.039840
H	-5.275926	2.630481	0.607324
C	4.168176	2.696745	1.687314
H	4.133504	3.258817	2.616965
C	5.028050	3.088854	0.659340
H	5.668337	3.958322	0.782615
C	-2.137925	-0.682980	-0.740391
C	-2.697196	-0.391742	-1.936809
C	-3.039968	-1.135916	0.281875

C	-4.380090	-1.212133	0.050765
H	-2.655125	-1.427180	1.254306
C	-4.972425	-0.862878	-1.234793
O	-4.031923	-0.484016	-2.192331
Br	-5.587187	-1.785257	1.404107
O	-6.140883	-0.868538	-1.545709
H	-2.166064	-0.062645	-2.822073
I	-0.153292	-3.206288	-0.872711

13-trans-I
B3LYP electronic energy: -5125.57956321 a.u.
B3LYP enthalpy: -5124.919830 a.u.
B3LYP free energy: -5125.052919 a.u.
M06 SCF energy in solution: -5127.35585711 a.u.
M06 enthalpy in solution: -5126.696124 a.u.
M06 free energy in solution: -5126.829213 a.u.
Three lowest frequencies (cm-1): 12.7950 14.68 16.83

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.000088	-0.576645	0.075999
Br	-0.000682	5.147419	-1.321926
P	-2.401133	-0.526158	0.072400
P	2.401315	-0.525800	0.072473
O	0.000063	3.109997	2.270415
O	-0.000286	5.301019	1.812712
C	-3.141014	-1.422219	-1.358471
C	-2.518118	-1.304164	-2.611027
H	-1.590458	-0.745668	-2.701223
C	-3.065695	-1.920061	-3.735514
H	-2.571659	-1.821258	-4.698148
C	-4.230330	-2.681942	-3.617600
H	-4.650365	-3.174047	-4.490555
C	-4.844732	-2.819658	-2.372472
H	-5.743903	-3.421279	-2.271101
C	-4.307312	-2.190097	-1.247748
H	-4.792306	-2.313162	-0.285248
C	-3.179381	1.149970	-0.027662
C	-3.627577	1.673892	-1.248847
H	-3.595848	1.067543	-2.147806
C	-4.130762	2.975399	-1.321454
H	-4.474765	3.363104	-2.276445
C	-4.192351	3.770877	-0.178346
H	-4.575774	4.785498	-0.237209
C	-3.753755	3.256863	1.044840
H	-3.796075	3.868839	1.941416
C	-3.250731	1.959004	1.120306
H	-2.916500	1.575524	2.078645
C	-3.161765	-1.248521	1.588342
C	-4.481306	-0.938124	1.963407
H	-5.067045	-0.243231	1.369933

C	-5.043844	-1.506934	3.106232
H	-6.064348	-1.257388	3.383851
C	-4.297299	-2.388278	3.891914
H	-4.735901	-2.827194	4.784022
C	-2.987116	-2.700926	3.528144
H	-2.400582	-3.387405	4.132458
C	-2.420968	-2.135445	2.383688
H	-1.409797	-2.398666	2.092867
C	3.141831	-1.422153	-1.357900
C	4.309016	-2.188641	-1.246778
H	4.794244	-2.310484	-0.284242
C	4.847050	-2.818310	-2.371139
H	5.746912	-3.418850	-2.269477
C	4.232378	-2.682071	-3.616306
H	4.652902	-3.174252	-4.488982
C	3.066879	-1.921587	-3.734611
H	2.572631	-1.823981	-4.697257
C	2.518686	-1.305600	-2.610463
H	1.590367	-0.748253	-2.700900
C	3.161713	-1.247633	1.588809
C	2.421177	-2.135416	2.383461
H	1.410431	-2.399479	2.091918
C	2.987067	-2.700683	3.528143
H	2.400741	-3.387846	4.131880
C	4.296722	-2.386941	3.892890
H	4.735109	-2.825667	4.785197
C	5.043000	-1.504755	3.107912
H	6.063096	-1.254358	3.386264
C	4.480733	-0.936190	1.964823
H	5.066299	-0.240687	1.371898
C	3.179132	1.150498	-0.028065
C	3.250537	1.959915	1.119622
H	2.916633	1.576653	2.078160
C	3.753190	3.257891	1.043629
H	3.795561	3.870152	1.940008
C	4.191319	3.771656	-0.179825
H	4.574435	4.786369	-0.239099
C	4.129660	2.975803	-1.322674
H	4.473302	3.363313	-2.277875
C	3.626882	1.674172	-1.249532
H	3.595117	1.067534	-2.148295
C	0.000003	1.397130	0.590293
C	0.000129	1.801151	1.882135
H	0.000331	1.150869	2.750261
C	-0.000171	4.175840	1.370155
C	-0.000333	3.756271	-0.026996
C	-0.000229	2.445882	-0.394355
H	-0.000312	2.196956	-1.451200
I	0.000047	-3.292776	-0.493700

15-Br

B3LYP electronic energy: -3265.88408559 a.u.
B3LYP enthalpy: -3265.654965 a.u.
B3LYP free energy: -3265.728214 a.u.
M06 SCF energy in solution: -3268.36057904 a.u.
M06 enthalpy in solution: -3268.131458 a.u.
M06 free energy in solution: -3268.204707 a.u.
Three lowest frequencies (cm-1): 6.7466 14.76 15.42

Cartesian coordinates

ATOM	X	Y	Z
Cu	0.000415	-0.082563	0.000174
O	1.797689	-1.129680	0.000107
C	2.810305	-0.409044	0.000072
H	2.724085	0.686595	0.000511
N	4.071554	-0.879594	-0.000028
C	4.339712	-2.311419	-0.000357
H	4.915776	-2.589107	-0.891307
H	4.915707	-2.589544	0.890503
H	3.387874	-2.841872	-0.000527
C	5.212694	0.022515	0.000265
H	5.832493	-0.140464	-0.890001
H	4.863826	1.057875	0.000456
H	5.832384	-0.140834	0.890542
O	-1.796841	-1.130328	-0.000282
C	-2.809533	-0.409806	-0.000190
H	-2.723411	0.685845	-0.000058
N	-4.070736	-0.880506	0.000067
C	-4.338734	-2.312355	0.000026
C	-5.211972	0.021477	0.000130
H	-4.915123	-2.590261	0.890696
H	-4.914340	-2.590412	-0.891112
H	-3.386831	-2.842693	0.000464
H	-5.831697	-0.141805	0.890394
H	-4.863210	1.056872	0.000192
H	-5.831711	-0.141695	-0.890147
Br	-0.001291	2.237382	-0.000120

14'
B3LYP electronic energy: -7685.53397967 a.u.
B3LYP enthalpy: -7684.875178 a.u.
B3LYP free energy: -7685.010021 a.u.
M06 SCF energy in solution: -7689.94355257 a.u.
M06 enthalpy in solution: -7689.284751 a.u.
M06 free energy in solution: -7689.419594 a.u.
Three lowest frequencies (cm-1): 10.3473 14.31 16.18

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.089791	-0.388149	-0.438625
P	1.049294	1.692967	0.127411
P	-2.419621	-0.490954	0.101745

C	-3.972003	0.892249	4.273953
C	-2.773768	1.386226	3.756699
C	4.189436	2.021930	-2.515959
C	-3.212176	-4.501944	0.563859
C	-1.618015	4.697387	-0.800772
C	-1.038462	3.462349	-0.502172
C	-2.318983	0.953407	2.509702
C	1.786253	0.535328	4.006299
C	2.920609	1.953881	-1.942822
C	-2.886499	0.655717	-2.408605
C	-2.680246	-3.218235	0.675530
C	-4.260140	-0.469472	2.292866
C	-0.820660	5.837944	-0.900254
C	-3.559363	1.422659	-3.360018
C	-4.259086	-4.753596	-0.326953
C	-4.713314	-0.037002	3.539926
C	1.585741	0.558448	2.626031
C	0.343569	3.351253	-0.292483
C	-3.372434	0.556005	-1.092831
C	1.310129	1.765660	1.959284
C	0.559056	5.739009	-0.701206
C	1.410437	2.919490	4.096276
C	1.138480	4.505691	-0.401184
C	-4.720211	2.115622	-3.007894
C	-4.245440	-2.423140	-0.987408
C	-5.205041	2.033481	-1.701332
C	1.223387	2.946728	2.711601
C	2.768292	1.839660	-0.549573
C	-3.194306	-2.161197	-0.096141
C	5.329303	1.965461	-1.708585
C	-3.058019	0.026700	1.760162
C	-4.538866	1.256441	-0.749822
C	1.695507	1.717099	4.745746
C	-4.771462	-3.713282	-1.102374
C	5.189041	1.846648	-0.325996
C	3.917431	1.787462	0.252092
H	3.826616	1.697664	1.329433
H	6.068706	1.800924	0.310529
H	6.318448	2.011201	-2.156157
H	4.287927	2.110110	-3.594625
H	2.043301	1.982520	-2.582879
H	1.638122	-0.368860	2.061614
H	2.003205	-0.407298	4.500864
H	1.842334	1.699537	5.822358
H	1.336784	3.842734	4.665375
H	1.005003	3.890067	2.221589
H	-1.663071	2.577620	-0.446747
H	-2.690052	4.759198	-0.966447
H	-1.268742	6.798947	-1.138852
H	1.186645	6.622651	-0.783124
H	2.212774	4.439554	-0.257757
H	-1.850845	-3.044305	1.354289
H	-2.797849	-5.306548	1.164833

H	-4.668183	-5.756180	-0.419044
H	-5.584720	-3.900352	-1.798902
H	-4.659385	-1.623386	-1.592871
H	-1.967513	0.141557	-2.680797
H	-3.169923	1.486883	-4.372506
H	-5.240470	2.719874	-3.746307
H	-6.105795	2.572248	-1.418678
H	-4.928510	1.201635	0.261760
H	-4.839265	-1.199539	1.735871
H	-5.643777	-0.431142	3.940246
H	-4.323805	1.221910	5.247997
H	-2.180860	2.097668	4.324809
H	-1.376322	1.326733	2.125038
C	1.339944	-1.640162	-1.508751
C	2.612033	-1.793000	-0.851132
C	2.724403	-2.622179	0.218209
H	3.463141	-1.221869	-1.205586
C	1.603357	-3.423977	0.718600
Br	4.359002	-2.772928	1.174996
Br	1.369516	-1.131187	-3.391245
C	0.246384	-2.424222	-1.062267
H	-0.531072	-2.780597	-1.727070
O	1.609313	-4.151161	1.685359
O	0.440502	-3.336794	-0.026851

16'
B3LYP electronic energy: -6649.22482978 a.u.
B3LYP enthalpy: -6648.859781 a.u.
B3LYP free energy: -6648.955339 a.u.
M06 SCF energy in solution: -6653.97826545 a.u.
M06 enthalpy in solution: -6653.613217 a.u.
M06 free energy in solution: -6653.708775 a.u.
Three lowest frequencies (cm-1): 5.8891 14.55 20.93

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.324272	-0.771112	0.144078
P	1.828121	0.142126	0.085989
C	2.115936	4.370723	2.003977
C	1.203194	3.425956	2.478236
C	2.114996	0.972372	-3.927132
C	1.126834	2.167818	1.880654
C	2.959487	-2.248425	0.983991
C	1.649395	0.794307	-2.624821
C	2.881248	2.790611	0.336795
C	3.888434	-3.055443	1.640986
C	3.442750	0.674173	-4.244662
C	2.951705	4.051842	0.932094
C	3.097194	-0.849952	0.989495
C	4.959814	-2.475089	2.323882
C	3.843853	0.032560	-1.944271

C	5.099681	-1.086100	2.343895
C	2.512504	0.329278	-1.617712
C	1.970464	1.833179	0.809297
C	4.175512	-0.276213	1.680125
C	4.303548	0.202213	-3.252892
H	0.610507	1.011314	-2.390105
H	1.436972	1.335399	-4.694662
H	3.802367	0.804204	-5.261825
H	5.336105	-0.036100	-3.494217
H	4.522972	-0.335431	-1.181360
H	2.116103	-2.701652	0.467931
H	3.768657	-4.135360	1.628410
H	5.678666	-3.102387	2.844061
H	5.927957	-0.629234	2.879001
H	4.291227	0.802989	1.706281
H	3.529581	2.556383	-0.502214
H	3.657219	4.786531	0.553287
H	2.168798	5.354748	2.461810
H	0.541142	3.671867	3.303908
H	0.399216	1.442695	2.237838
C	-2.331776	-1.449893	-0.221257
C	-3.273183	-0.598022	0.463872
C	-3.611939	0.604796	-0.067831
H	-3.700150	-0.928987	1.404590
C	-3.089586	1.077307	-1.355345
Br	-4.797984	1.775530	0.832685
Br	-2.397947	-3.352247	0.152642
C	-1.789489	-0.987745	-1.435430
H	-1.365824	-1.642029	-2.188103
O	-3.338397	2.122508	-1.902058
O	-2.233189	0.185977	-2.002212

17'

B3LYP electronic energy: -6897.74937922 a.u.
B3LYP enthalpy: -6897.271844 a.u.
B3LYP free energy: -6897.384632 a.u.
M06 SCF energy in solution: -6902.42260330 a.u.
M06 enthalpy in solution: -6901.945068 a.u.
M06 free energy in solution: -6902.057856 a.u.
Three lowest frequencies (cm-1): 9.7288 13.91 18.56

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.101626	-0.649853	0.574093
P	-2.011593	0.130791	-0.066751
C	-1.645151	4.191637	-2.318345
C	-0.842608	3.098944	-2.659586
C	-3.610602	0.896324	3.644851
C	-0.979258	1.889736	-1.978724
C	-2.877678	-2.357496	-0.991649
C	-2.732545	0.676871	2.581325

C	-2.735713	2.852237	-0.619335
C	-3.558169	-3.244739	-1.825010
C	-4.990156	0.833196	3.441356
C	-2.589096	4.065477	-1.298309
C	-2.920427	-0.974184	-1.233442
C	-4.279008	-2.762846	-2.920767
C	-4.618522	0.335001	1.101840
C	-4.319870	-1.391249	-3.174329
C	-3.229341	0.401092	1.296593
C	-1.932402	1.751416	-0.952098
C	-3.647401	-0.499500	-2.334618
C	-5.492209	0.550542	2.168689
H	-1.658664	0.708913	2.747359
H	-3.213773	1.104630	4.634981
H	-5.672402	0.995771	4.271622
H	-6.565309	0.492926	2.005940
H	-5.019073	0.106824	0.118553
H	-2.303447	-2.735930	-0.149113
H	-3.516888	-4.312135	-1.625012
H	-4.800440	-3.454421	-3.577036
H	-4.874228	-1.010804	-4.028217
H	-3.684155	0.565289	-2.543648
H	-3.476255	2.766250	0.169518
H	-3.217508	4.910353	-1.028202
H	-1.533795	5.135880	-2.844893
H	-0.101696	3.183815	-3.449632
H	-0.341555	1.053055	-2.249275
C	1.836708	-1.872247	0.164122
C	0.925778	-1.840006	-0.934358
H	0.306461	-2.688579	-1.202682
C	2.335239	-0.240832	-2.148039
Br	1.885638	-3.433672	1.317080
C	3.023423	-1.071450	0.082296
H	3.732004	-1.093661	0.903600
O	2.429804	0.468277	-3.125402
C	3.238033	-0.273083	-0.998566
O	1.285627	-1.144660	-2.093173
Br	4.729063	0.911425	-1.051789
O	0.721640	0.781338	2.428553
C	1.094479	1.858002	1.933952
N	2.303563	2.418490	2.119105
H	0.432227	2.450902	1.283860
C	2.681523	3.649757	1.439440
H	3.010646	4.401856	2.166333
H	3.495725	3.455675	0.731350
H	1.824913	4.044215	0.887157
C	3.328842	1.747653	2.908215
H	4.183109	1.492713	2.269929
H	3.672908	2.405811	3.714794
H	2.901070	0.840102	3.333913

19-DMF
B3LYP electronic energy: -8131.33149928 a.u.
B3LYP enthalpy: -8130.555077 a.u.
B3LYP free energy: -8130.711342 a.u.
M06 SCF energy in solution: -8135.70110784 a.u.
M06 enthalpy in solution: -8134.924686 a.u.
M06 free energy in solution: -8135.080951 a.u.
Three lowest frequencies (cm-1): 8.1904 11.43 15.18

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.099580	-0.173639	-0.495652
Br	-0.854281	1.465824	-2.262006
P	0.635831	-1.692002	1.192927
P	2.247642	1.081164	-0.620815
C	2.630299	-0.348335	4.578584
H	3.506560	-0.618077	5.160712
C	2.426684	0.133568	-3.273377
H	1.415970	-0.232608	-3.122428
C	4.396040	1.281886	-2.462958
H	4.932838	1.796542	-1.672005
C	2.423937	-2.889443	-0.611281
H	2.074184	-2.137476	-1.312560
C	1.035424	3.330196	0.522097
H	0.661471	2.624998	1.259370
C	2.362028	-3.903368	1.585993
H	1.951523	-3.964578	2.589265
C	1.925421	-2.901466	0.699616
C	2.308702	3.804880	-1.478486
H	2.925254	3.477677	-2.308402
C	3.307754	-4.842145	1.175834
H	3.641838	-5.606993	1.870906
C	-1.473874	-2.447801	2.955570
H	-1.281842	-1.526030	3.493076
C	3.901397	1.829523	1.584155
H	3.284439	2.716371	1.671543
C	-0.697365	-2.797404	1.841127
C	1.964383	5.154752	-1.370803
H	2.322184	5.859273	-2.116181
C	3.642973	0.882328	0.582671
C	1.166142	5.596654	-0.315634
H	0.902998	6.647328	-0.233161
C	2.311539	-1.085791	3.436217
H	2.951886	-1.908450	3.140580
C	-2.750799	-4.494618	2.736705
H	-3.540147	-5.153370	3.087155
C	-0.965518	-4.007897	1.178361
H	-0.372556	-4.303401	0.318479
C	3.052558	-0.067944	-4.505671
H	2.525717	-0.594603	-5.296346
C	1.188504	-0.746424	2.670735
C	3.810720	-4.810867	-0.128157
H	4.539882	-5.550169	-0.446843

C	3.088631	0.813936	-2.239092
C	-2.493215	-3.294173	3.398710
H	-3.078226	-3.014503	4.270315
C	1.850919	2.880602	-0.530985
C	0.718833	1.079624	4.204321
H	0.096898	1.920319	4.499567
C	5.016610	1.083430	-3.696106
H	6.025292	1.453666	-3.855850
C	4.346436	0.408241	-4.719654
H	4.832871	0.252890	-5.678406
C	0.704260	4.681029	0.634071
H	0.081821	5.016788	1.458933
C	3.361370	-3.839814	-1.023652
H	3.735044	-3.819684	-2.043372
C	0.400331	0.354386	3.055707
H	-0.465840	0.637673	2.461073
C	4.969290	1.654478	2.467360
H	5.159949	2.405000	3.229371
C	4.479254	-0.244128	0.487372
H	4.317246	-0.982045	-0.290751
C	1.833298	0.727781	4.969592
H	2.082115	1.294152	5.862505
C	-1.983191	-4.849468	1.624601
H	-2.173499	-5.783481	1.103876
C	5.544966	-0.415088	1.370322
H	6.186552	-1.286524	1.272837
C	5.793936	0.534499	2.364191
H	6.630394	0.405977	3.045465
C	-1.753785	-1.025805	-0.592918
C	-2.804007	-0.342914	0.130680
C	-2.085030	-2.097317	-1.372526
C	-3.437815	-2.563409	-1.444337
H	-1.332944	-2.622709	-1.953920
C	-4.390338	-1.933608	-0.721814
H	-5.438847	-2.196840	-0.678200
O	-2.685873	0.684209	0.805983
O	-4.087762	-0.859558	0.043564
Br	-3.889129	-4.059373	-2.519757
Cu	-2.156924	2.581085	-0.731244
O	-3.311714	3.772576	0.248221
C	-4.145462	3.398850	1.109065
H	-4.183799	2.353063	1.431275
N	-5.021173	4.222409	1.685939
C	-5.966166	3.736704	2.686723
C	-5.084565	5.640805	1.337015
H	-5.816012	4.263383	3.635655
H	-6.994251	3.907592	2.349217
H	-5.819033	2.666474	2.847264
H	-6.084160	5.884413	0.961566
H	-4.881478	6.251714	2.223389
H	-4.342960	5.850758	0.567724

19-2DMF
B3LYP electronic energy: -8379.85309037 a.u.
B3LYP enthalpy: -8378.964350 a.u.
B3LYP free energy: -8379.141973 a.u.
M06 SCF energy in solution: -8384.13434871 a.u.
M06 enthalpy in solution: -8383.245608 a.u.
M06 free energy in solution: -8383.423231 a.u.
Three lowest frequencies (cm-1): 5.5055 9.25 15.10

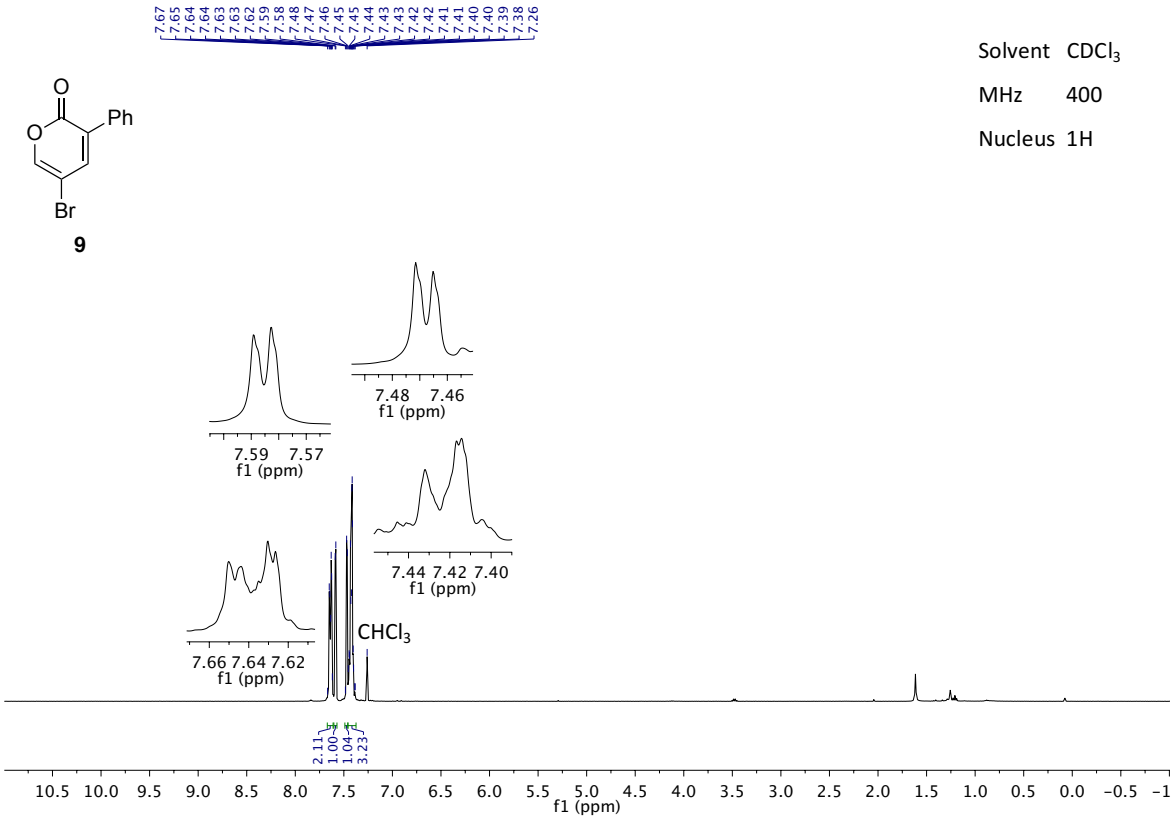
Cartesian coordinates

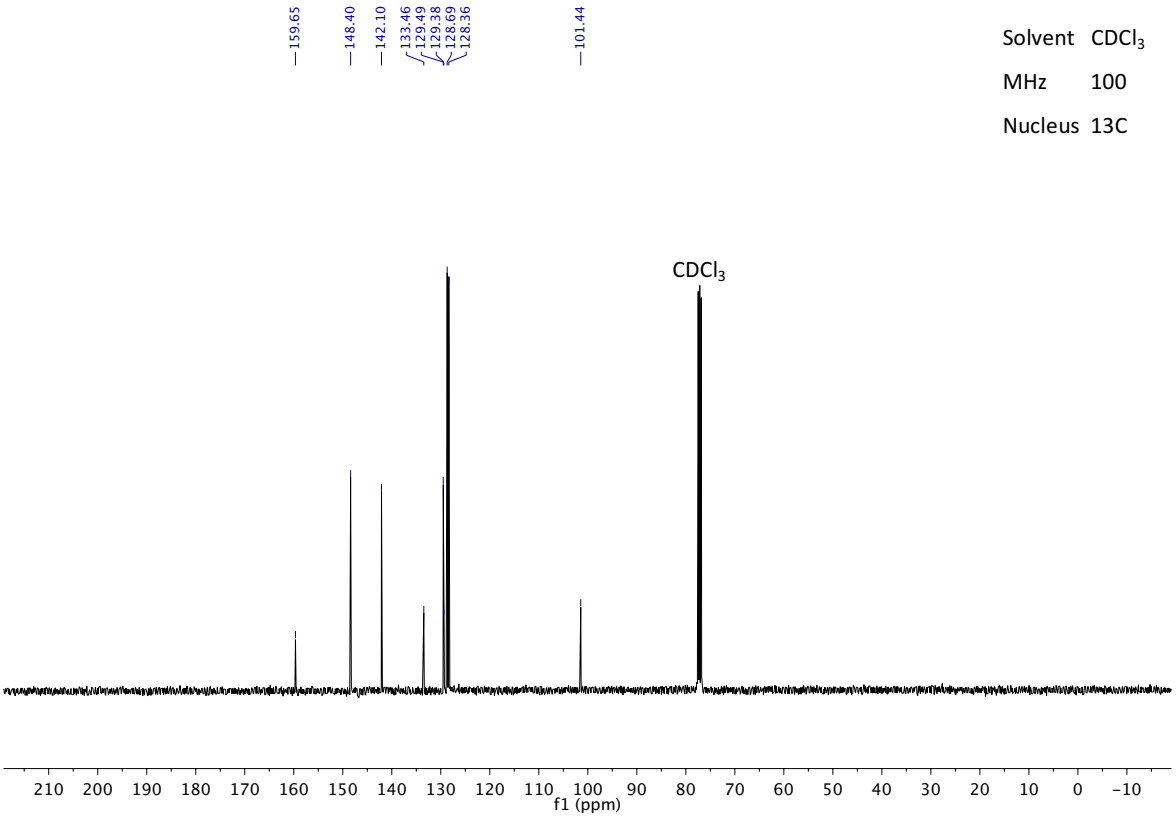
ATOM	X	Y	Z
Pd	-0.532567	-0.181287	0.115453
Br	1.325872	1.507894	0.751358
P	-2.019647	-1.889364	-0.467844
P	-2.169631	1.664090	0.481311
C	-5.193894	-1.154447	-3.035713
H	-6.270965	-1.294102	-3.047902
C	-1.350490	1.705614	3.181633
H	-0.577359	1.012155	2.867370
C	-3.260965	3.101117	2.679754
H	-4.000298	3.477128	1.979370
C	-2.951775	-1.780134	2.188659
H	-2.231266	-0.977750	2.313920
C	-1.029481	2.876892	-1.763651
H	-0.928794	1.858627	-2.128444
C	-4.000436	-3.463452	0.802925
H	-4.090056	-3.988984	-0.142944
C	-3.091079	-2.398380	0.937995
C	-1.648020	4.435653	-0.020815
H	-2.039096	4.643365	0.969368
C	-4.777653	-3.868149	1.887446
H	-5.479799	-4.688391	1.768751
C	-1.253264	-3.885646	-2.357253
H	-1.609347	-3.215863	-3.131030
C	-4.443236	2.187031	-1.157820
H	-3.768763	2.723516	-1.815936
C	-1.330182	-3.517301	-1.006902
C	-1.223659	5.496159	-0.825416
H	-1.304545	6.514738	-0.455144
C	-3.958835	1.576304	0.008393
C	-0.713183	5.251167	-2.102324
H	-0.398825	6.078780	-2.732657
C	-4.465478	-1.532703	-1.906238
H	-4.987998	-1.950530	-1.053649
C	-0.260169	-6.007708	-1.743367
H	0.148730	-6.972934	-2.028514
C	-0.860216	-4.411286	-0.028237
H	-0.916519	-4.148304	1.023838
C	-1.414256	2.102829	4.519155
H	-0.695319	1.707433	5.231302
C	-3.075718	-1.354224	-1.874472

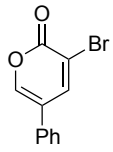
C	-4.643020	-3.233153	3.125566
H	-5.243718	-3.557226	3.970630
C	-2.268085	2.204446	2.243833
C	-0.720847	-5.125571	-2.719936
H	-0.672689	-5.398298	-3.770204
C	-1.564400	3.116613	-0.486630
C	-3.162866	-0.408086	-4.108909
H	-2.651050	0.024168	-4.964348
C	-3.318695	3.500253	4.014931
H	-4.090130	4.194908	4.335208
C	-2.395029	3.002442	4.937606
H	-2.444617	3.311067	5.978023
C	-0.613116	3.937672	-2.568703
H	-0.207873	3.735848	-3.556314
C	-3.723740	-2.194737	3.277079
H	-3.600649	-1.707302	4.240096
C	-2.427285	-0.774803	-2.981074
H	-1.348865	-0.637377	-2.966831
C	-5.801624	2.126339	-1.476881
H	-6.160083	2.613064	-2.379541
C	-4.863780	0.894957	0.841284
H	-4.519371	0.423186	1.755410
C	-4.546071	-0.599325	-4.139807
H	-5.116549	-0.313374	-5.019098
C	-0.331031	-5.647030	-0.394753
H	0.022114	-6.329180	0.373451
C	-6.219547	0.838424	0.519865
H	-6.905862	0.318127	1.182349
C	-6.693702	1.456967	-0.639258
H	-7.751638	1.421138	-0.883966
C	0.977345	-1.505162	-0.211969
C	1.366320	-1.664964	-1.607635
C	1.680674	-2.149004	0.760855
C	2.784137	-2.999124	0.413575
H	1.427303	-2.030941	1.810345
C	3.123197	-3.156449	-0.884574
H	3.922826	-3.782711	-1.260129
O	0.851470	-1.142451	-2.578508
O	2.455028	-2.516220	-1.865276
Br	3.764785	-3.907306	1.773472
Cu	3.529348	1.306182	-0.035489
O	5.192275	0.300777	-0.384344
C	5.716167	-0.657764	0.218602
H	5.184726	-1.200859	1.009195
N	6.946049	-1.116442	-0.037562
C	7.503089	-2.244700	0.701362
C	7.791626	-0.495045	-1.054103
H	7.811804	-3.032558	0.005373
H	8.377854	-1.927538	1.280495
H	6.750676	-2.652112	1.380233
H	8.716220	-0.128603	-0.594572
H	8.047965	-1.229762	-1.825355
H	7.250625	0.335860	-1.504816

O	4.196191	3.272648	-0.483746
C	3.454496	4.268607	-0.540864
N	3.882434	5.520285	-0.769015
H	2.367878	4.179554	-0.402777
C	5.298773	5.810123	-0.966035
H	5.456591	6.260400	-1.952764
H	5.649248	6.510774	-0.199532
H	5.859208	4.878747	-0.894862
C	2.954234	6.641678	-0.819353
H	3.184790	7.366454	-0.029530
H	3.024676	7.149668	-1.788413
H	1.931490	6.281853	-0.684118

7 ^{1}H and ^{13}C NMR Spectra





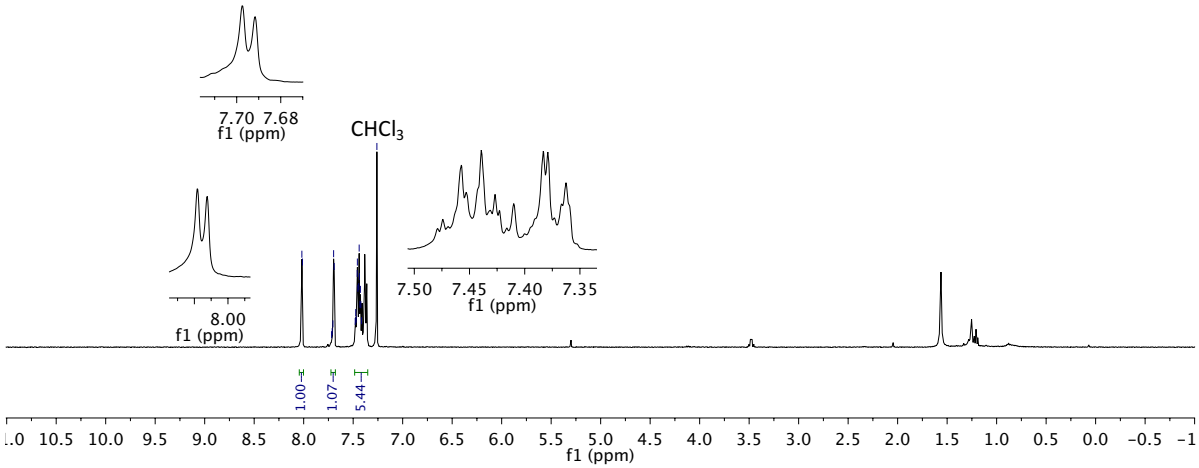


10

Solvent $CDCl_3$

MHz 400

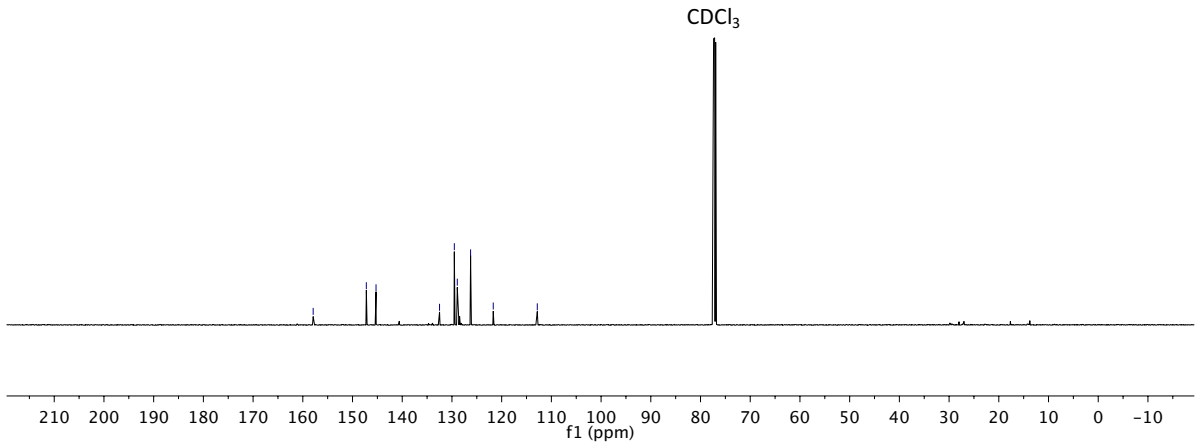
Nucleus 1H

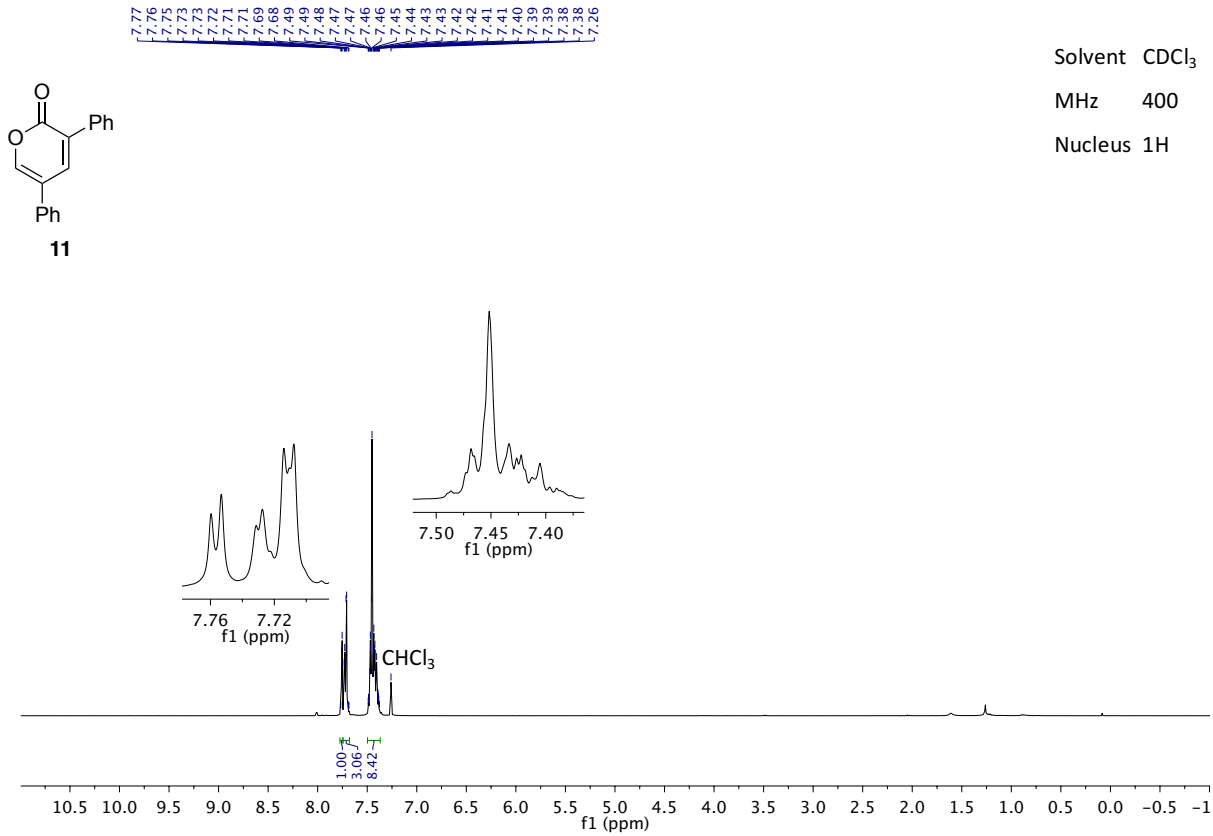


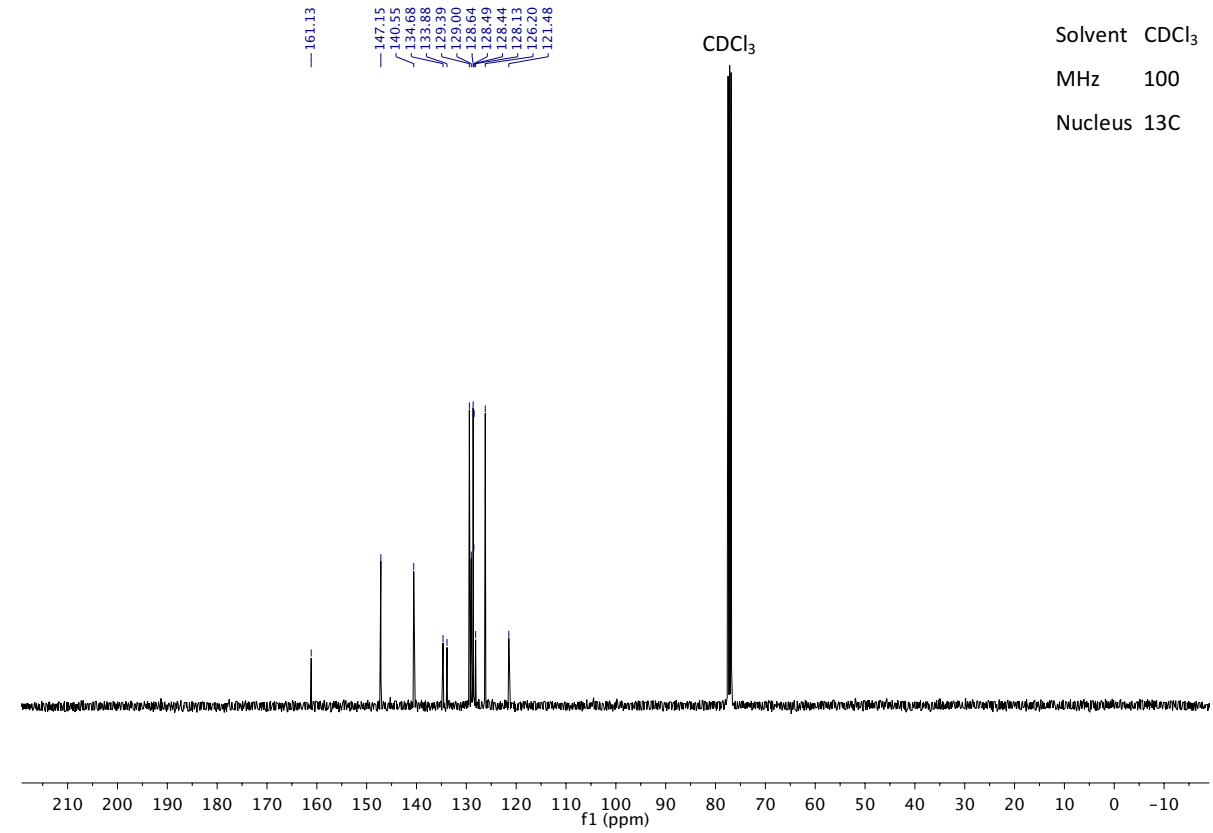
Solvent $CDCl_3$

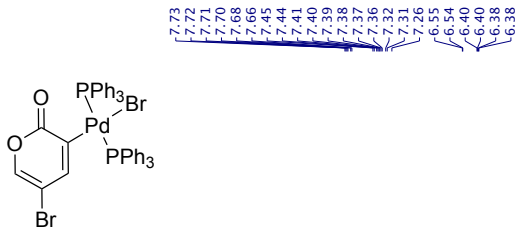
MHz 100

Nucleus 13C




7.77 7.76 7.75 7.73 7.73 7.72 7.71 7.71 7.69 7.68 7.49 7.49 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.26
O
O
Ph
Ph
11
Solvent CDCl3
MHz 400
Nucleus 1H
7.76 7.72
f1 (ppm)
7.50 7.45 7.40
f1 (ppm)
CHCl3
1.00
3.06
8.42
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


161.13
147.15
140.55
134.68
133.88
129.39
129.00
128.64
128.49
128.44
128.13
126.20
121.48
CDCl3
Solvent CDCl3
MHz 100
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

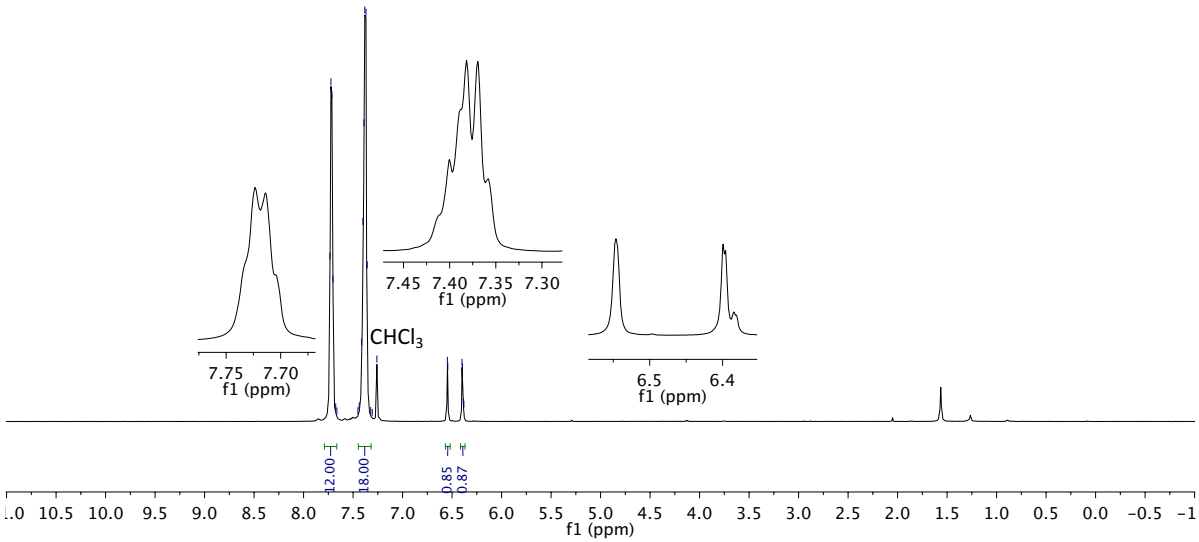


12-trans

Solvent $CDCl_3$

MHz 600

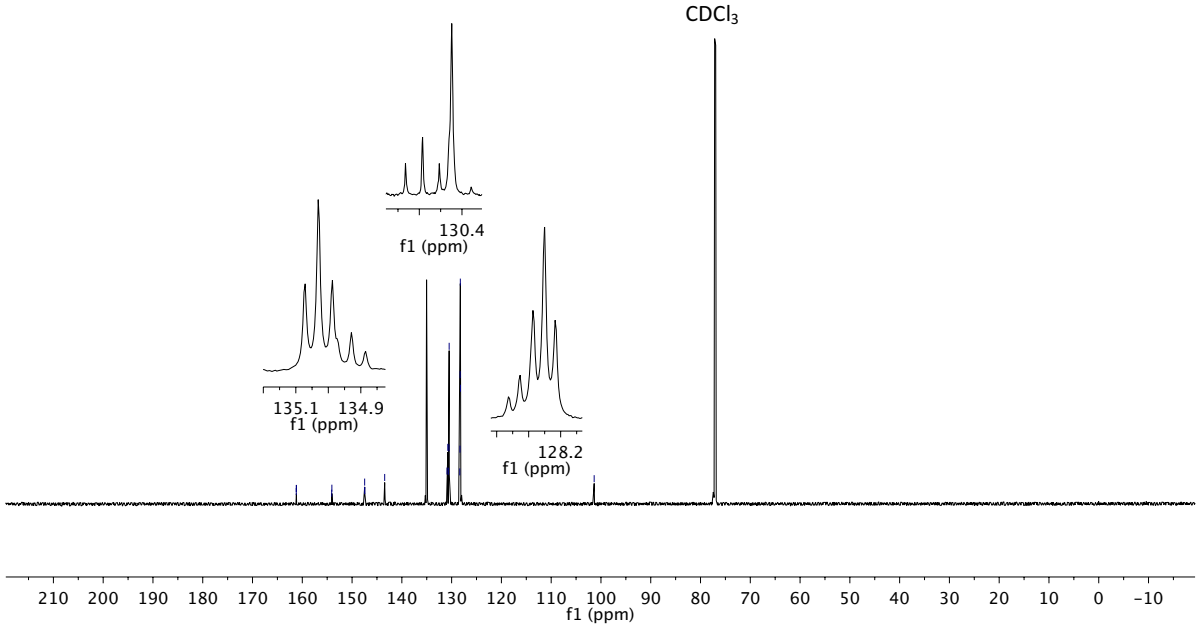
Nucleus 1H

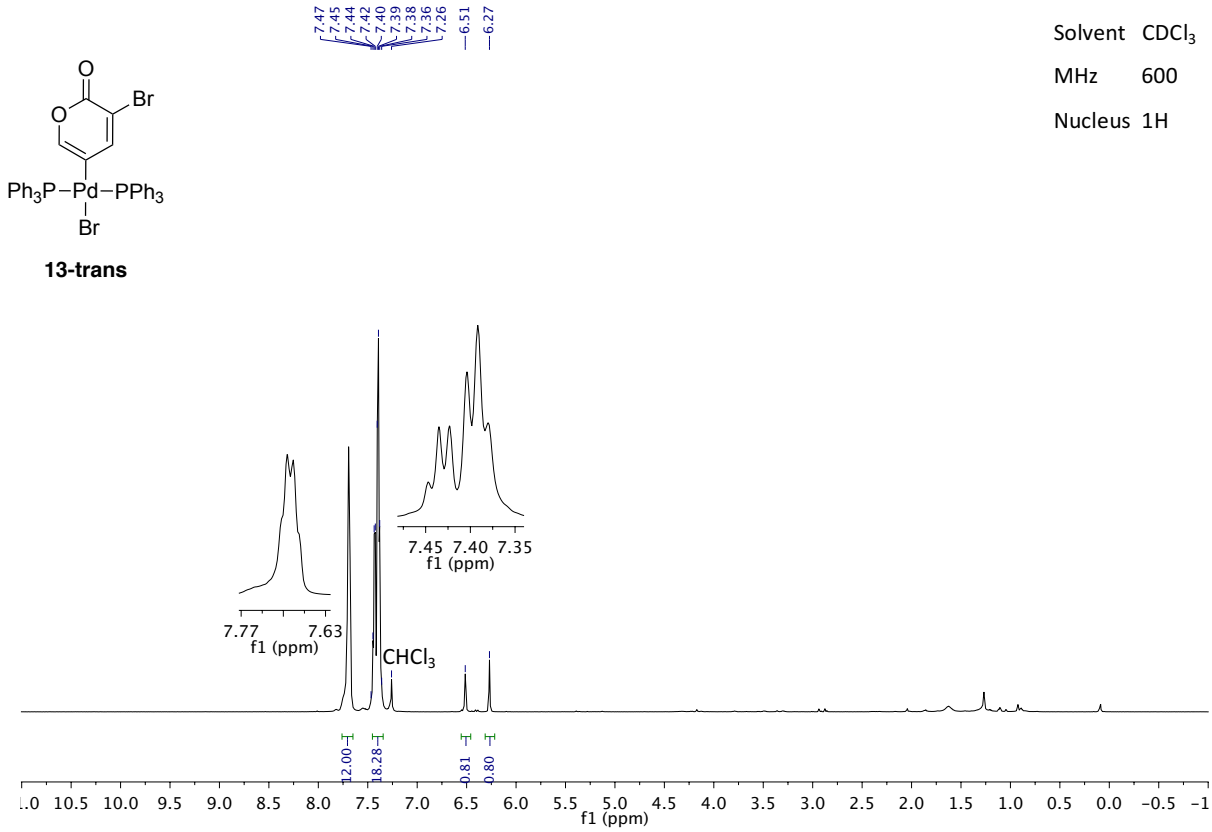


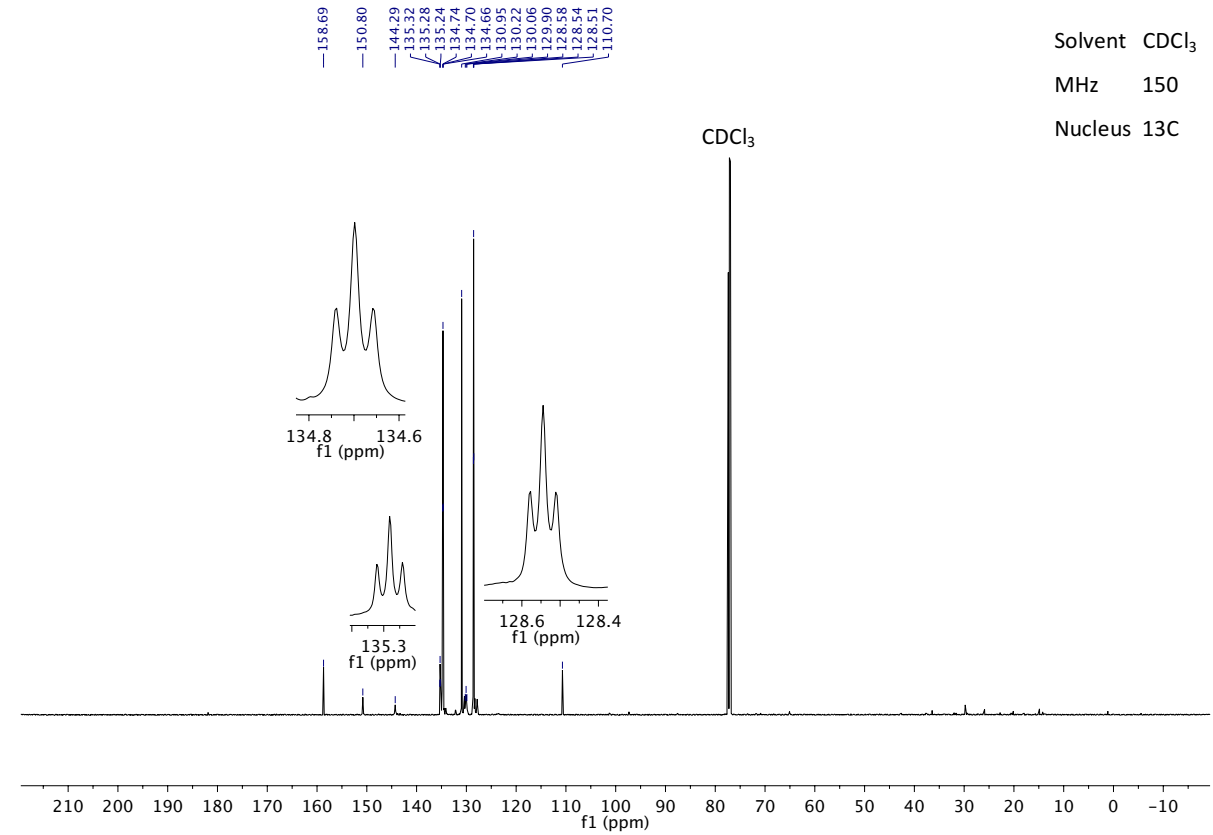
Solvent $CDCl_3$

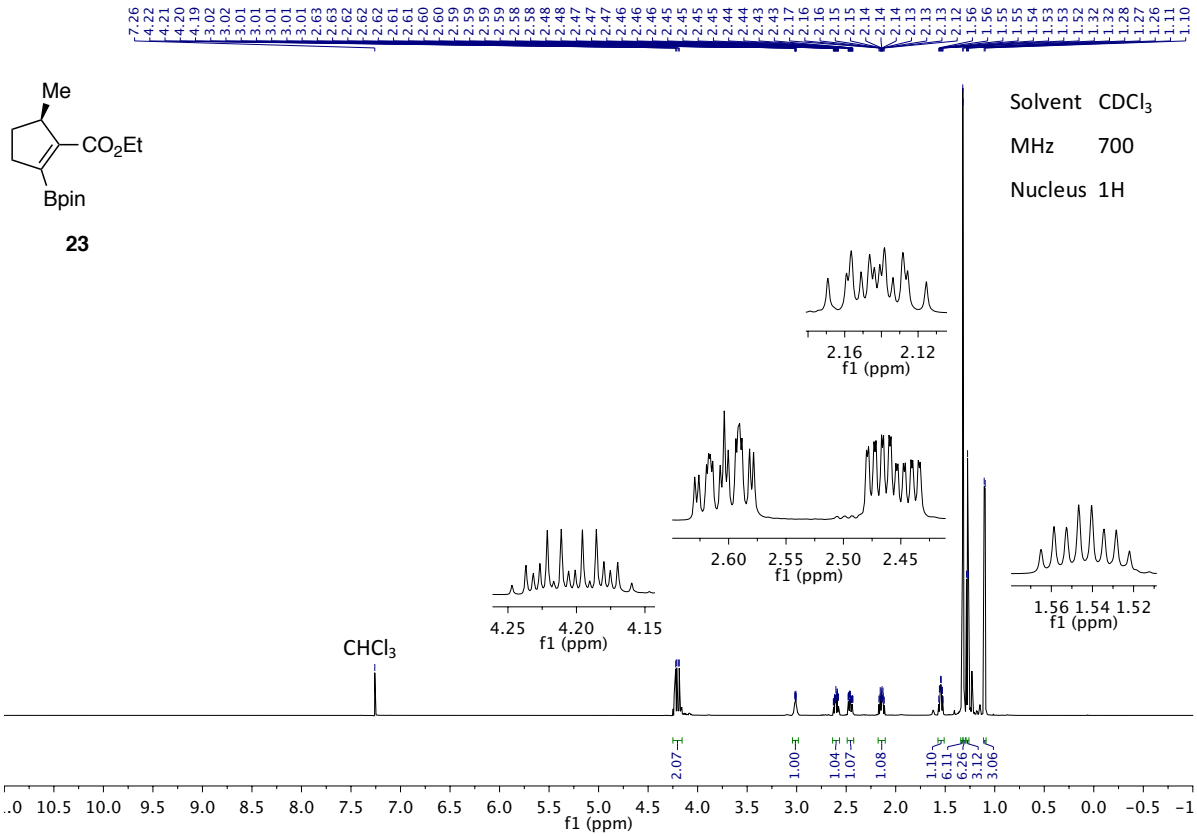
MHz 150

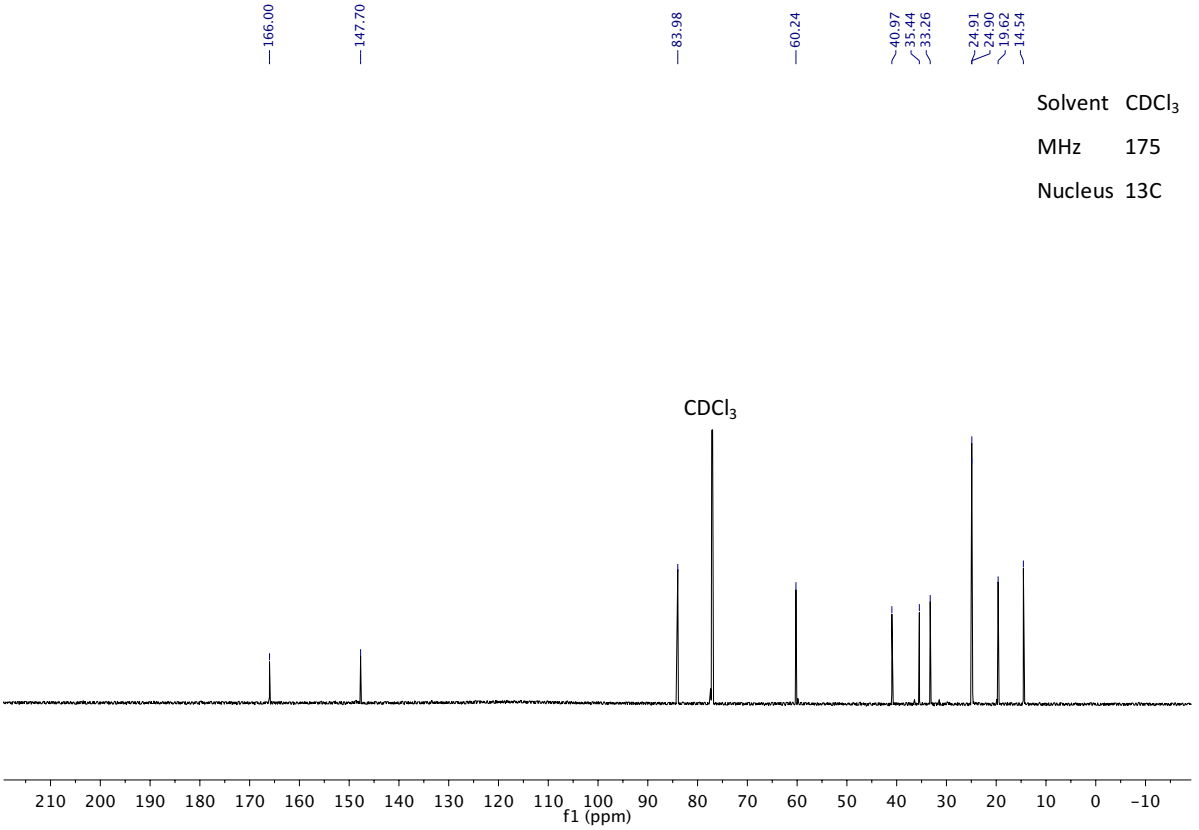
Nucleus 13C

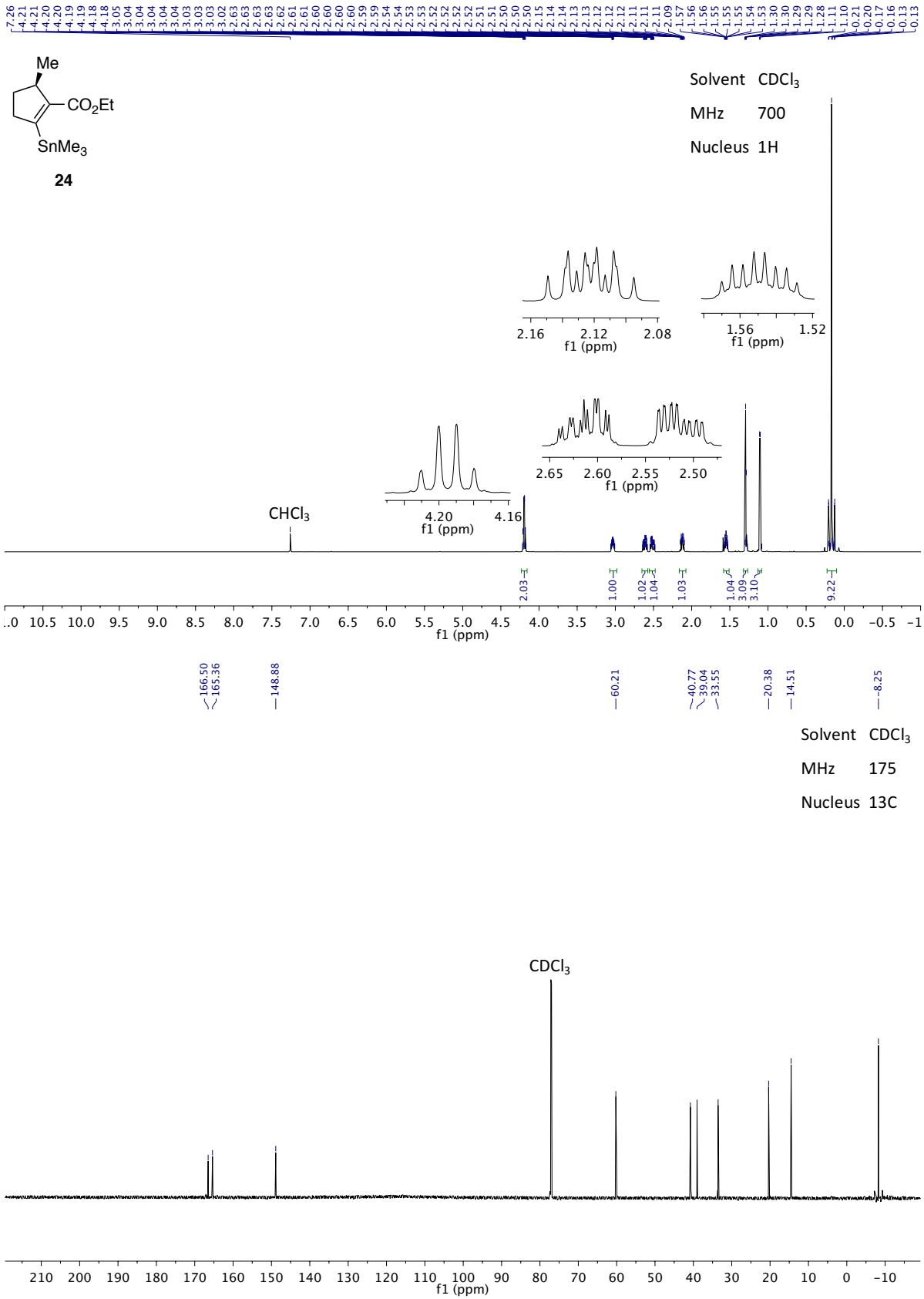


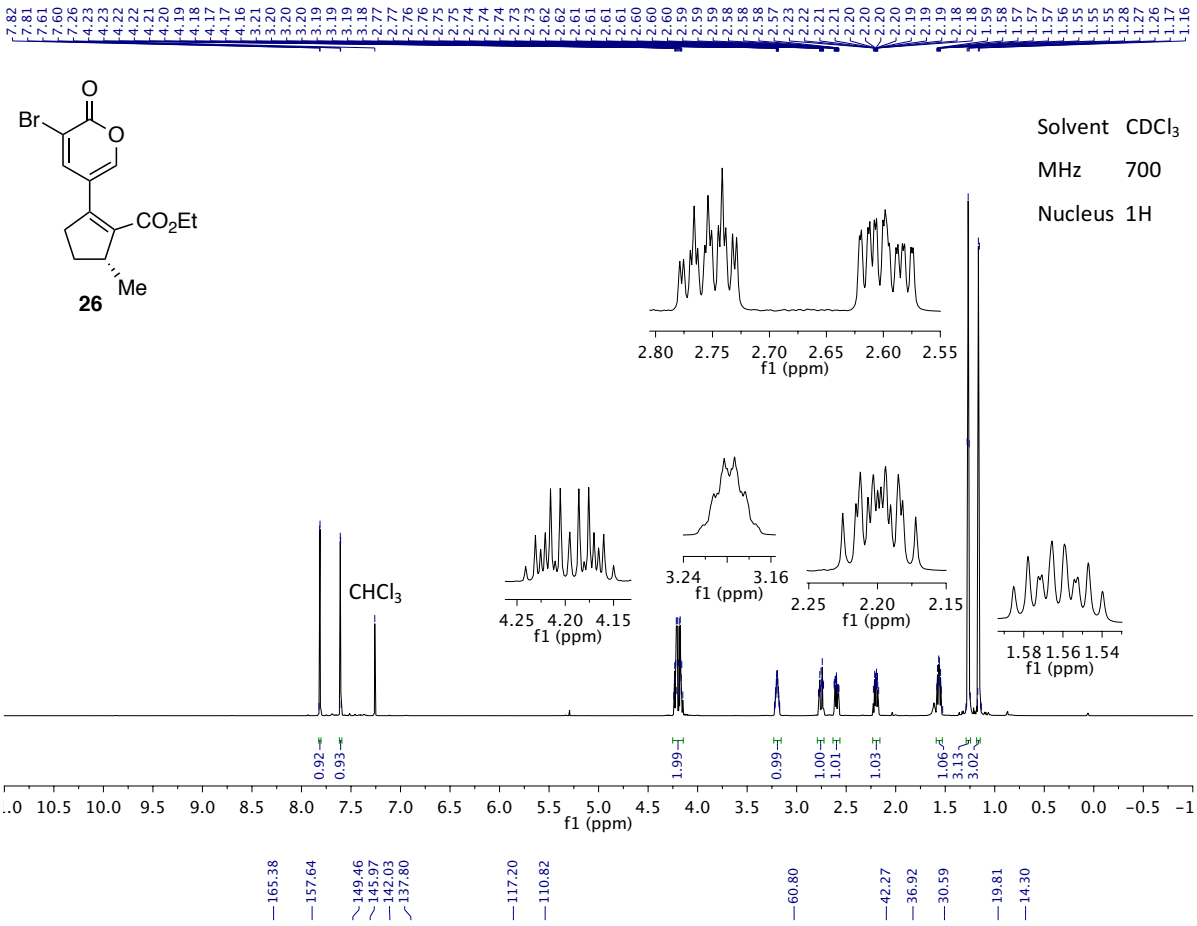

7.47
7.45
7.44
7.42
7.40
7.39
7.38
7.36
7.26
6.51
6.27
Solvent CDCl3
MHz 600
Nucleus 1H
O
O
Br
Ph3P–Pd–PPh3
Br
13-trans
7.77 7.63
f1 (ppm)
7.45 7.40 7.35
f1 (ppm)
CHCl3
12.00
1.28
0.81
0.80
f1 (ppm)

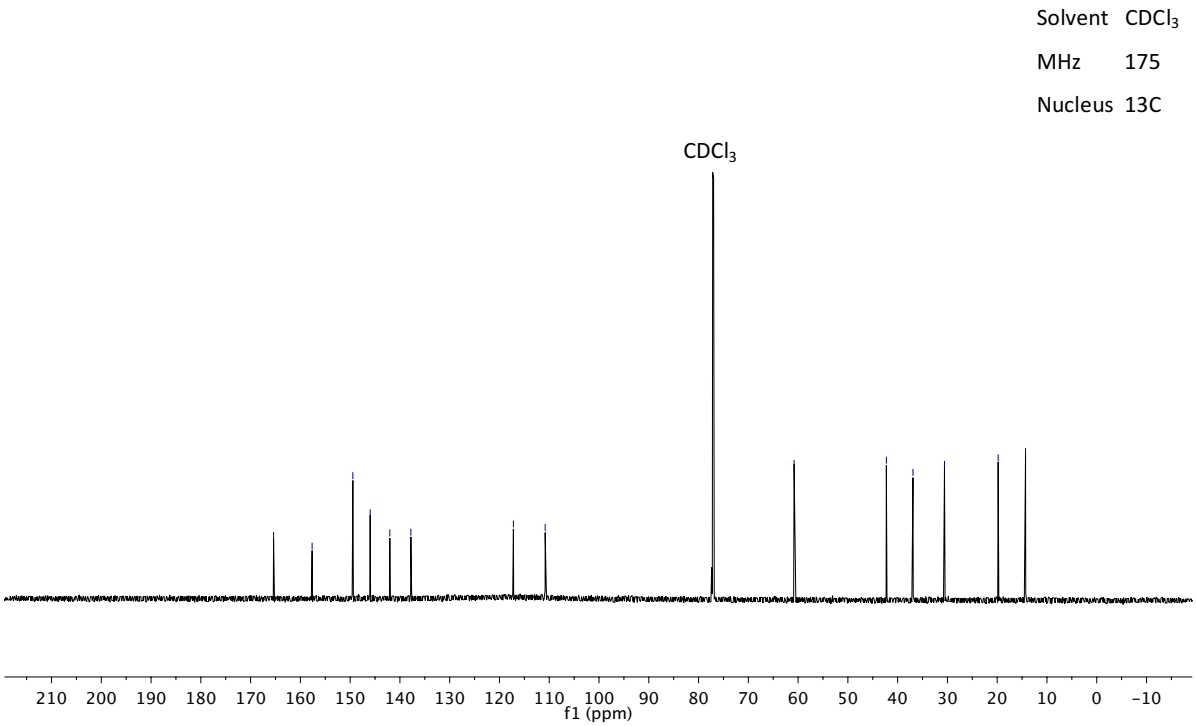

158.69
150.80
144.29
135.32
135.28
135.24
134.74
134.70
134.66
130.95
130.22
130.06
129.90
128.58
128.54
128.51
110.70
Solvent CDCl3
MHz 150
Nucleus 13C
CDCl3
134.8 134.6
f1 (ppm)
135.3
f1 (ppm)
128.6 128.4
f1 (ppm)
f1 (ppm)

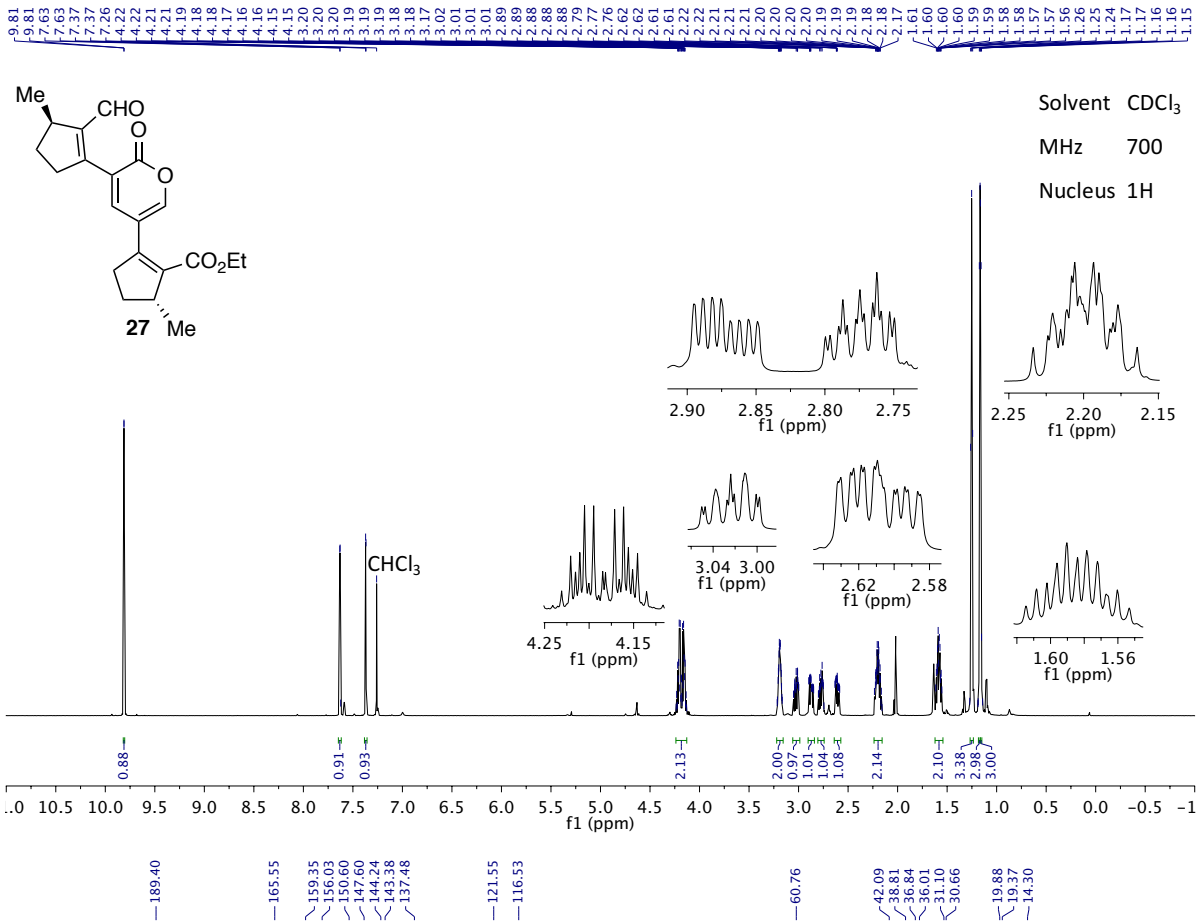

Me
CO2Et
Bpin
23
Solvent CDCl3
MHz 700
Nucleus 1H
CHCl3
f1 (ppm)


Solvent CDCl3
MHz 175
Nucleus 13C
CDCl3
f1 (ppm)

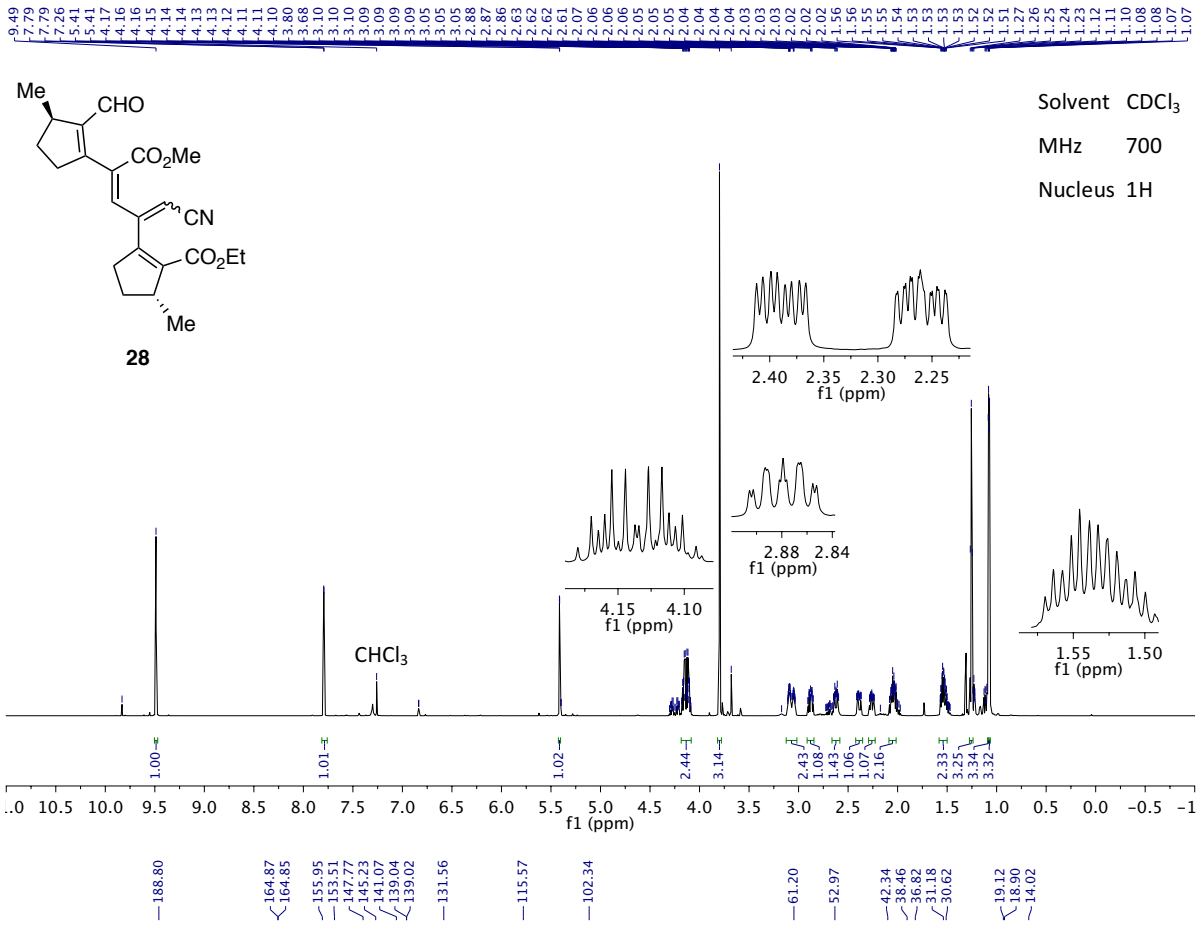

Me
CO2Et
SnMe3
24
Solvent CDCl3
MHz 700
Nucleus 1H
CHCl3
f1 (ppm)
Solvent CDCl3
MHz 175
Nucleus 13C
CDCl3
f1 (ppm)

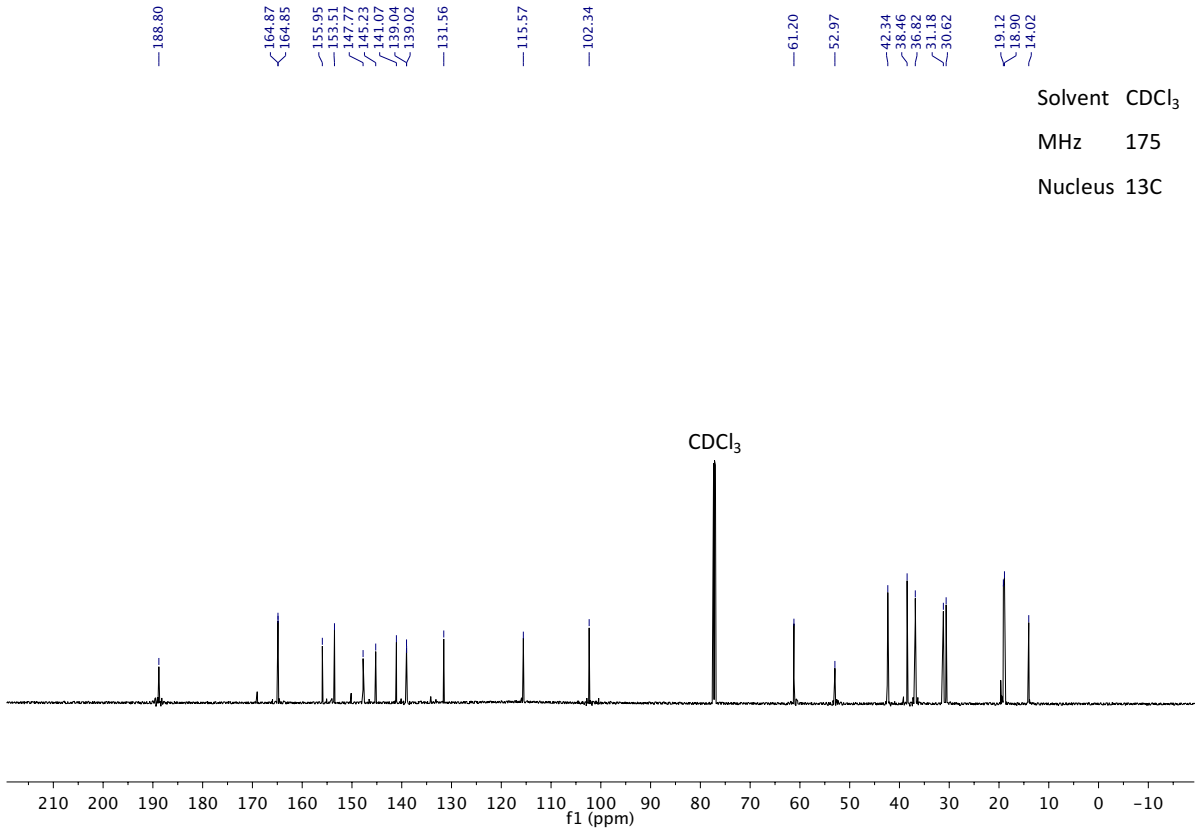

Br
O
O
CO_2Et
Me
26
Solvent $CDCl_3$
MHz 700
Nucleus 1H
$CHCl_3$
f1 (ppm)

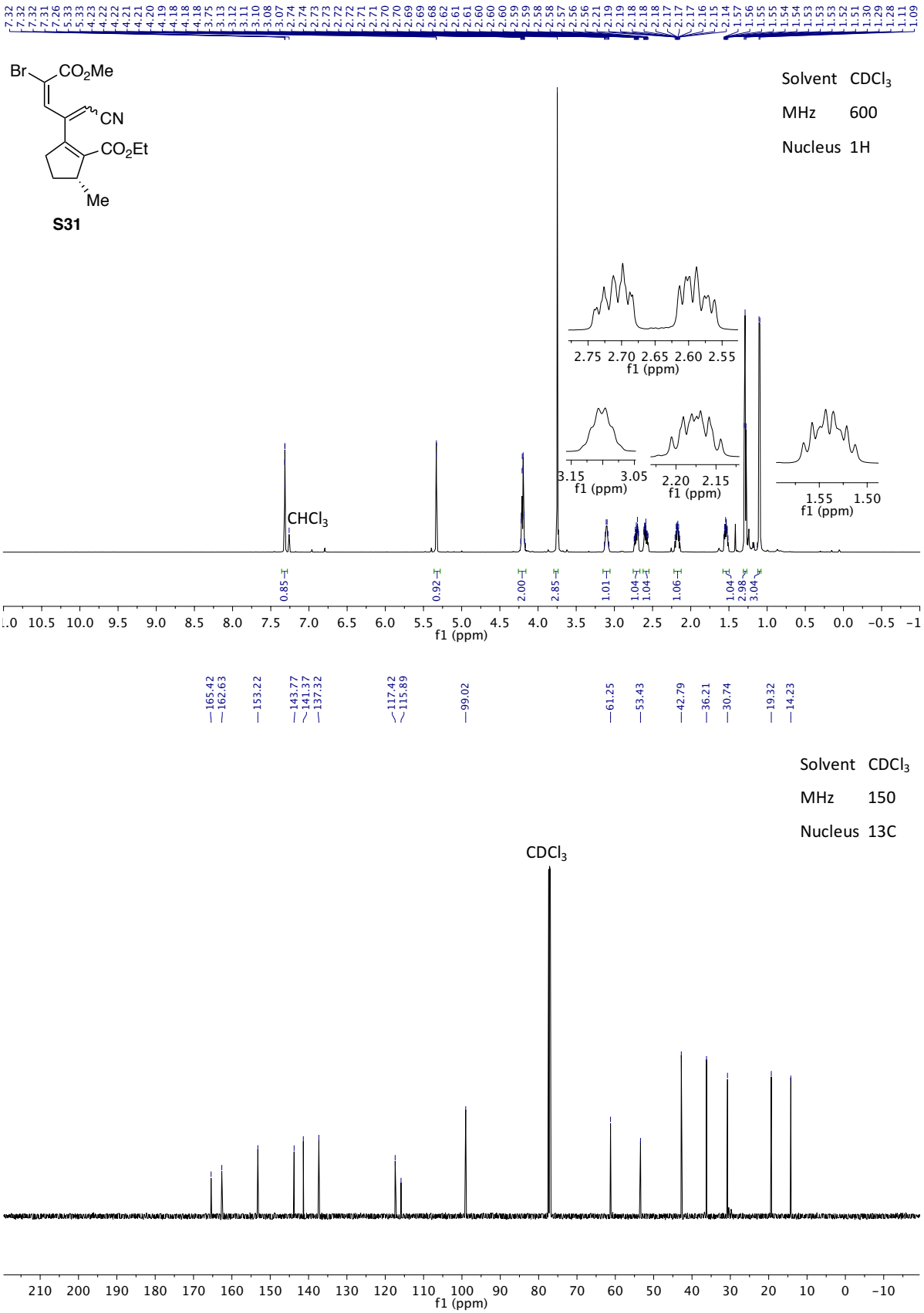

Solvent $CDCl_3$
MHz 175
Nucleus 13C
$CDCl_3$
f1 (ppm)

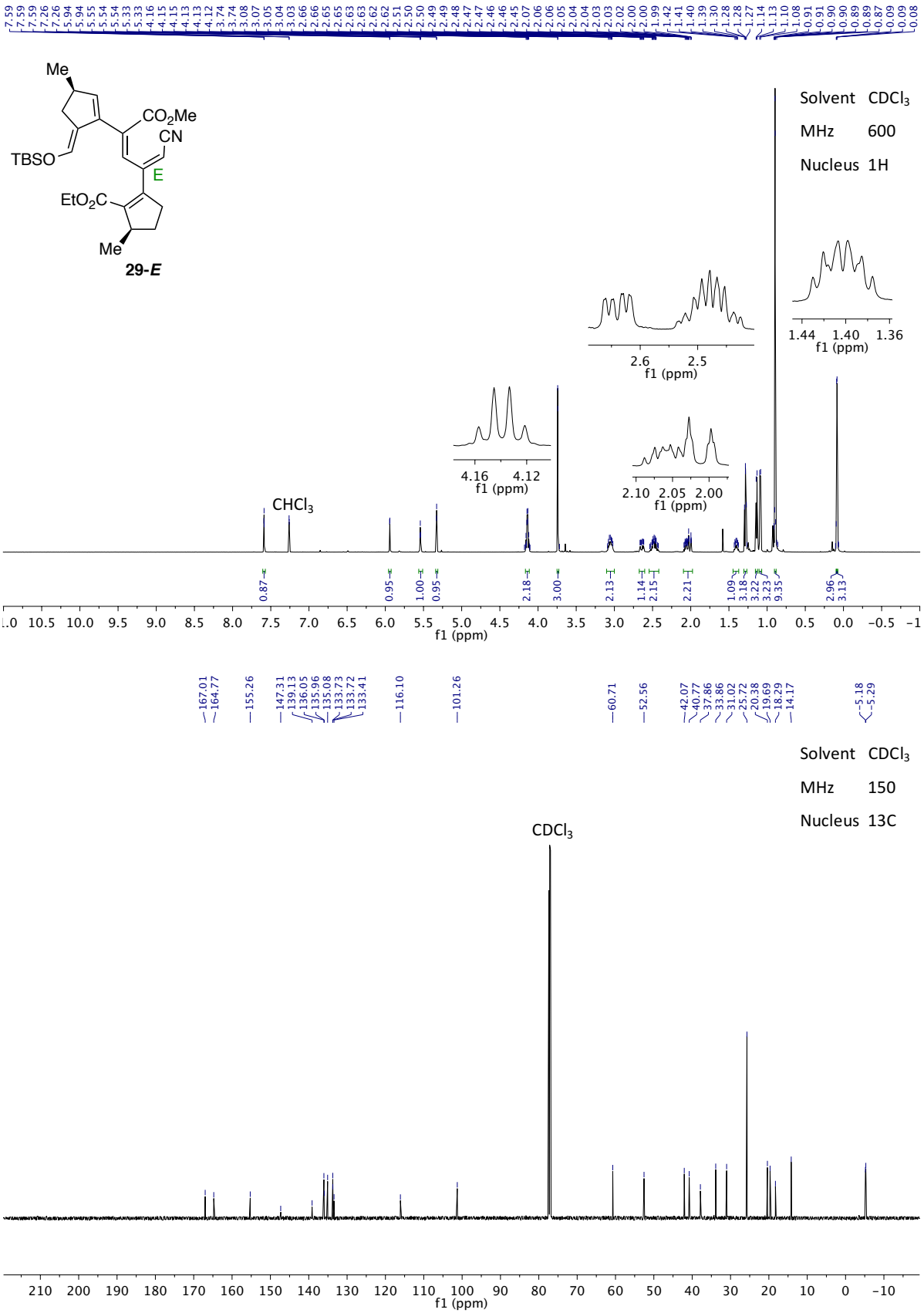

Me
CHO
O
O
CO2Et
27
Me
Solvent CDCl3
MHz 700
Nucleus 1H
CHCl3
f1 (ppm)

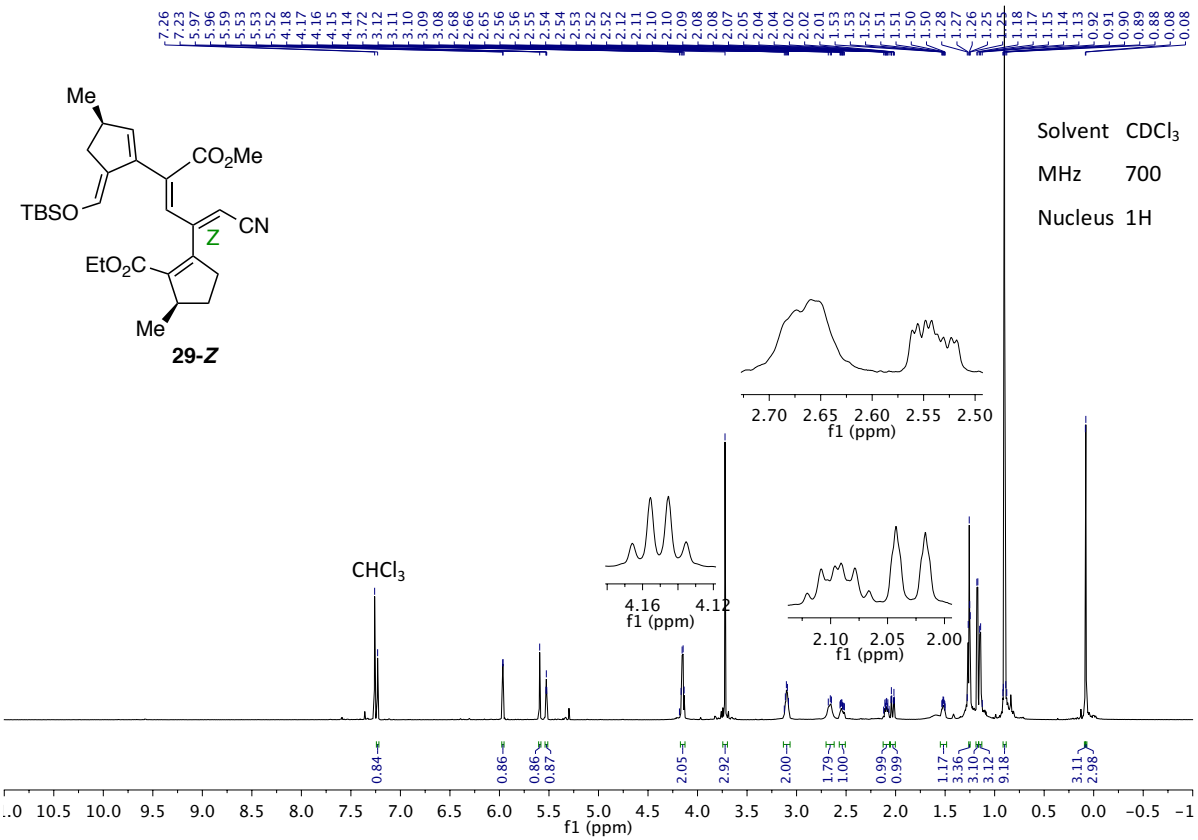
Solvent CDCl3
MHz 175
Nucleus 13C
CDCl3
f1 (ppm)

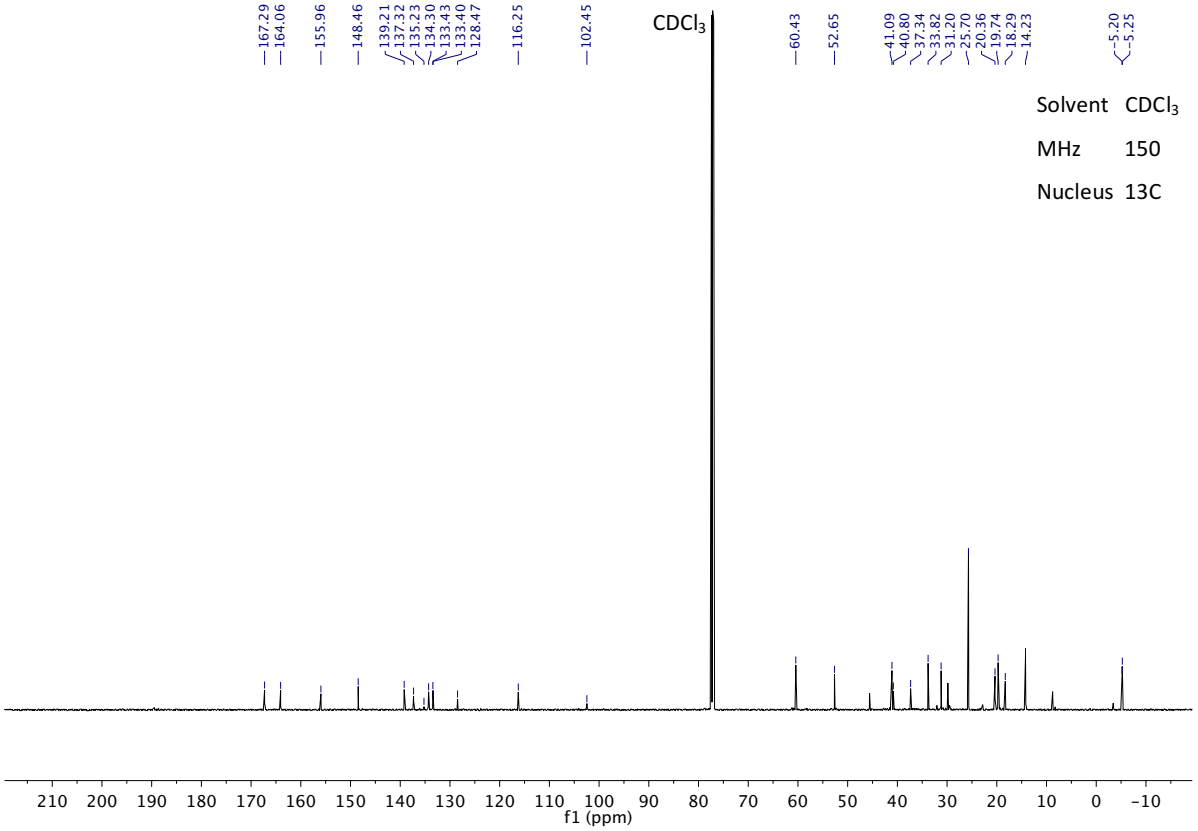

Me
CHO
CO2Me
CN
CO2Et
Me
28
Solvent CDCl3
MHz 700
Nucleus 1H
CHCl3
f1 (ppm)

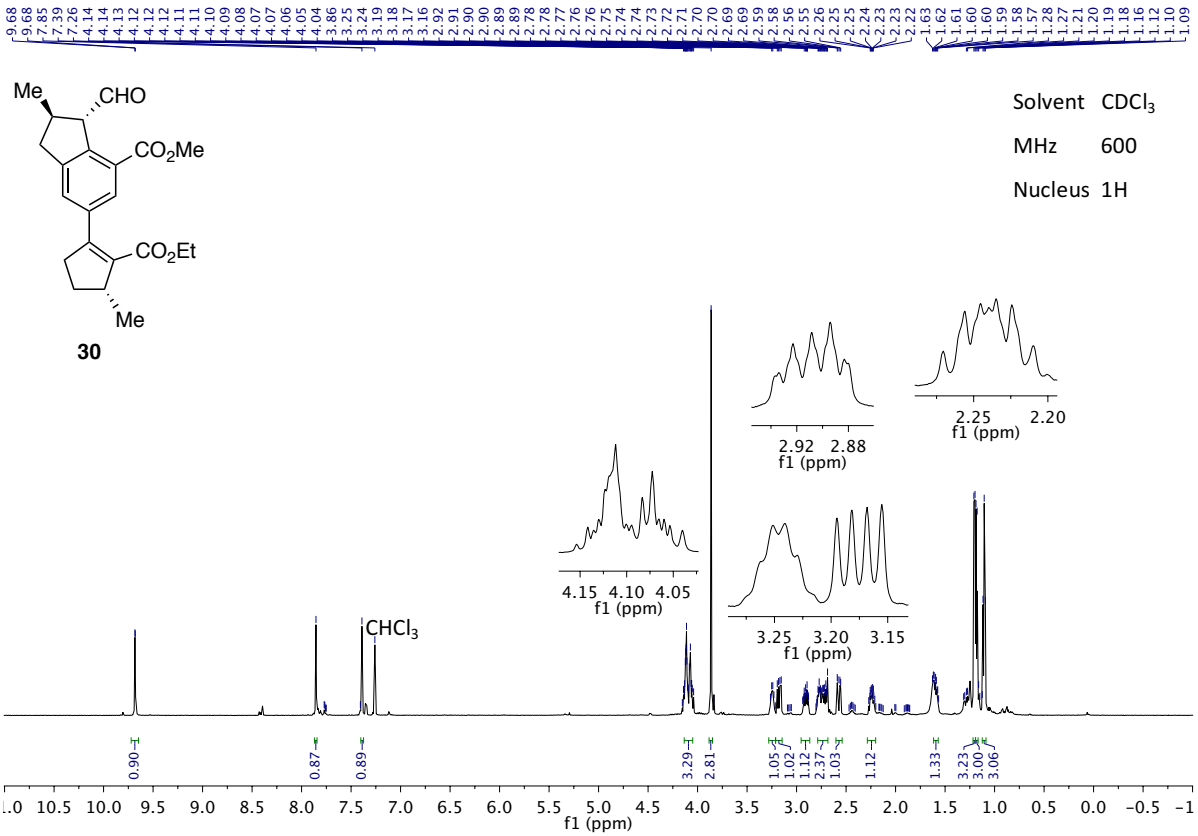

Solvent CDCl3
MHz 175
Nucleus 13C
CDCl3
f1 (ppm)

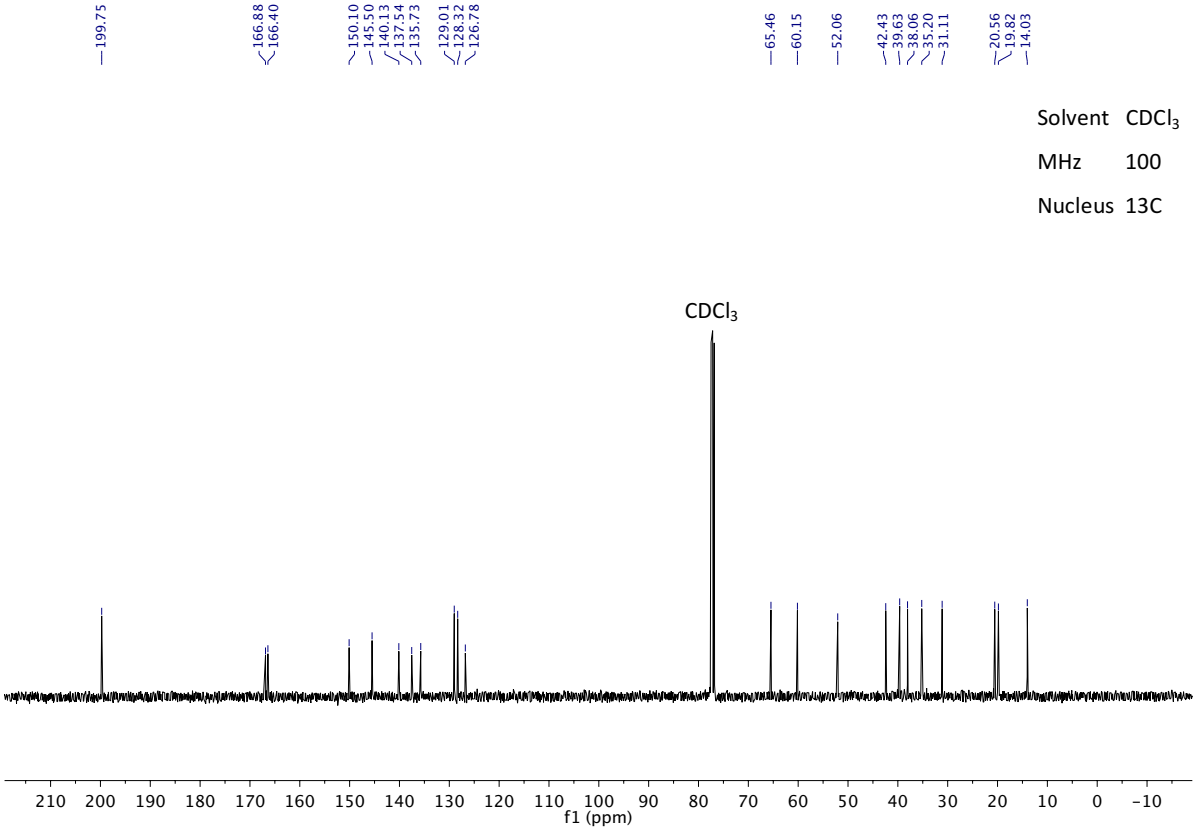

Br
CO2Me
CN
CO2Et
Me
S31
Solvent CDCl3
MHz 600
Nucleus 1H
CHCl3
f1 (ppm)
Solvent CDCl3
MHz 150
Nucleus 13C
CDCl3
f1 (ppm)

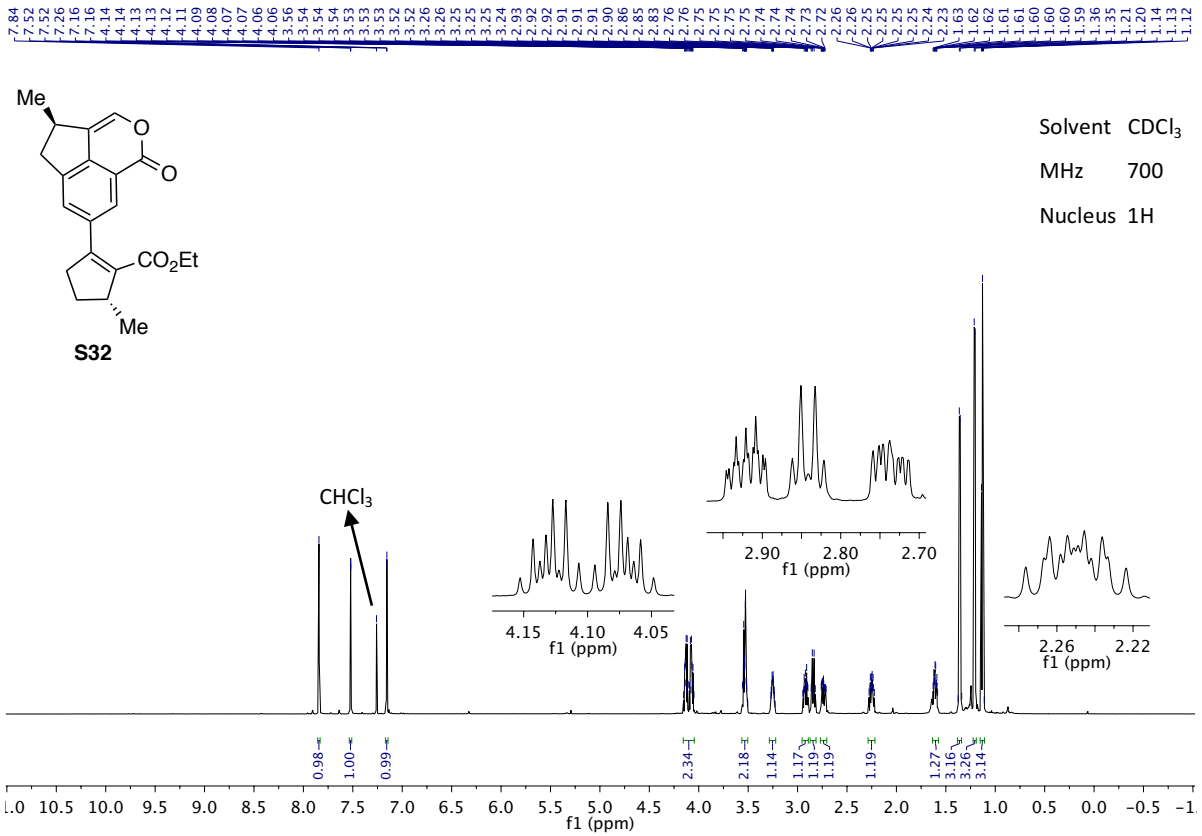

Me
CO2Me
CN
TBSO
E
EtO2C
Me
29-E
Solvent CDCl3
MHz 600
Nucleus 1H
CHCl3
f1 (ppm)
Solvent CDCl3
MHz 150
Nucleus 13C
CDCl3
f1 (ppm)

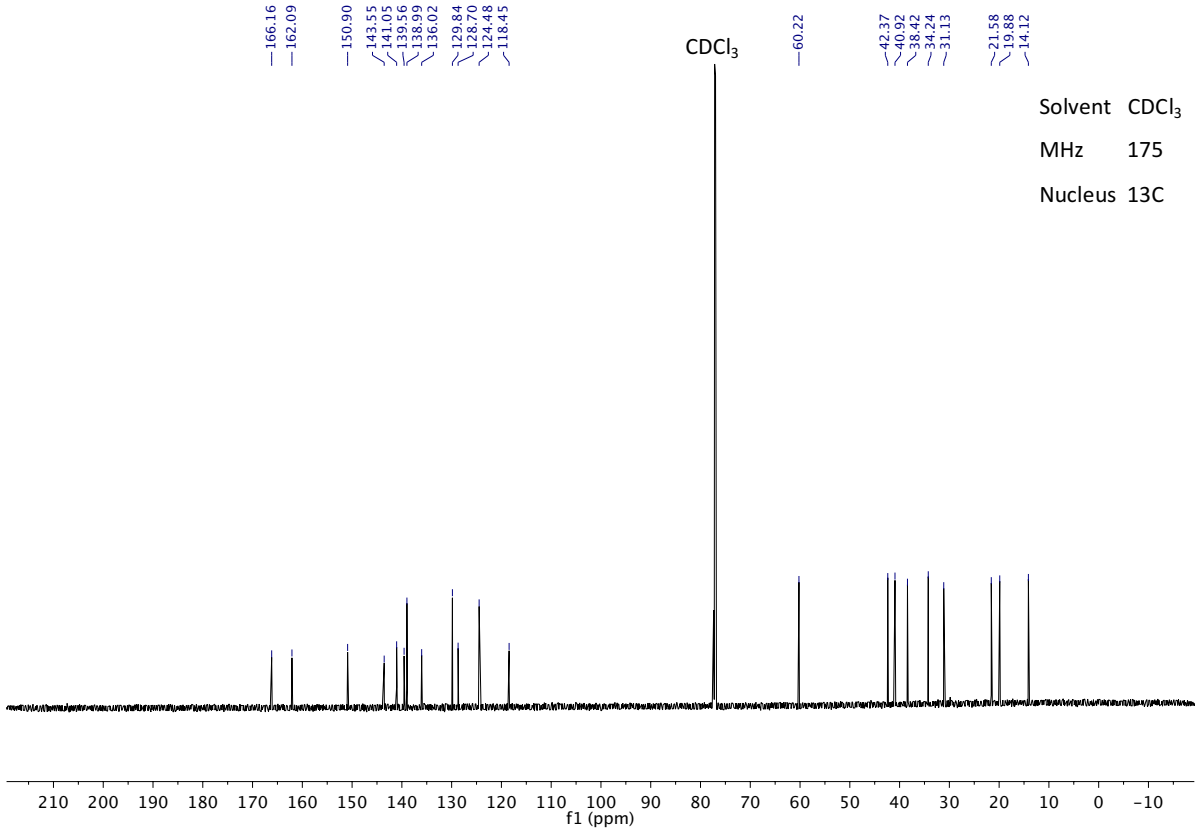

Me
CO2Me
TBSO
Z
CN
EtO2C
Me
29-Z
Solvent CDCl3
MHz 700
Nucleus 1H
CHCl3
f1 (ppm)

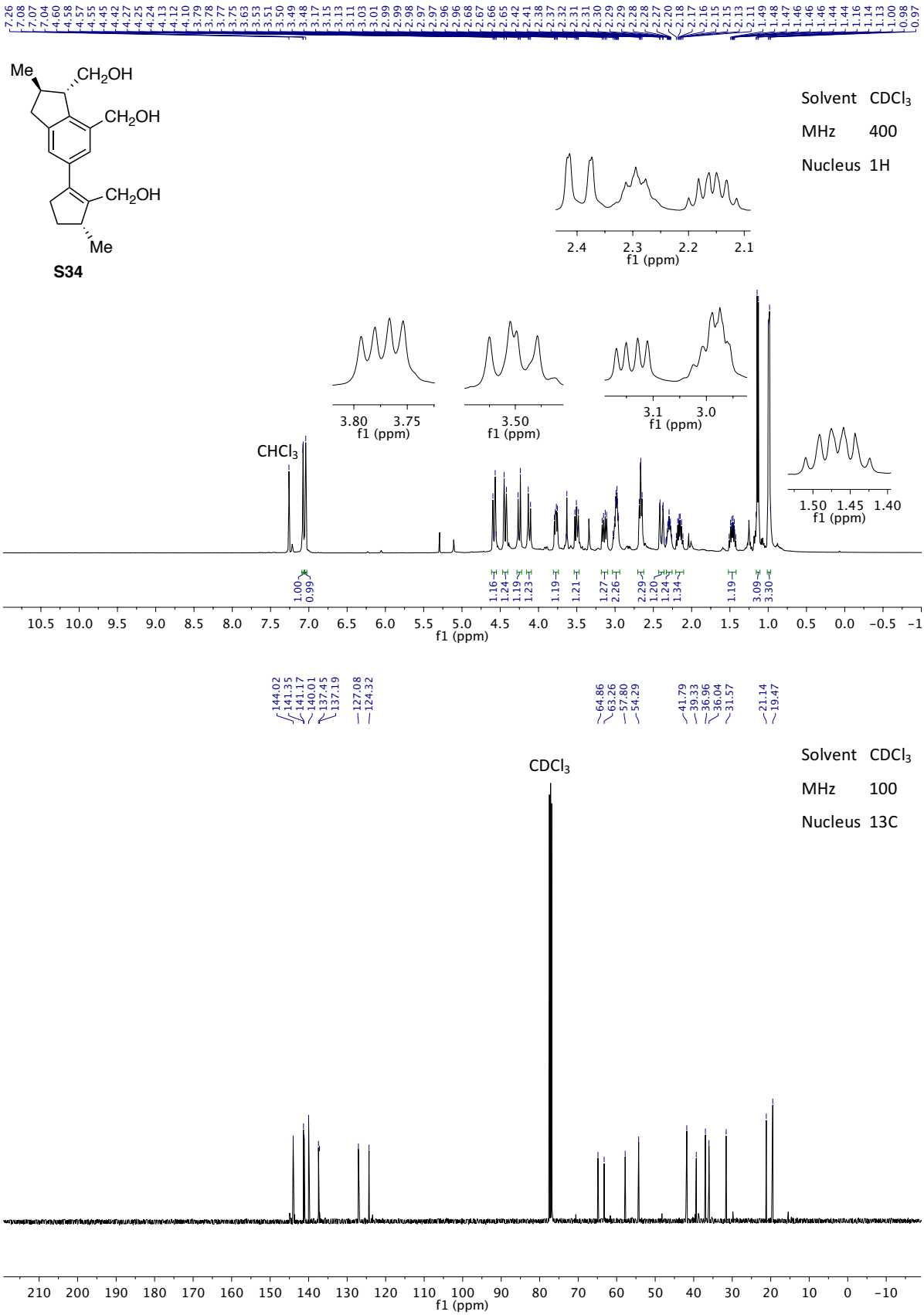

CDCl3
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

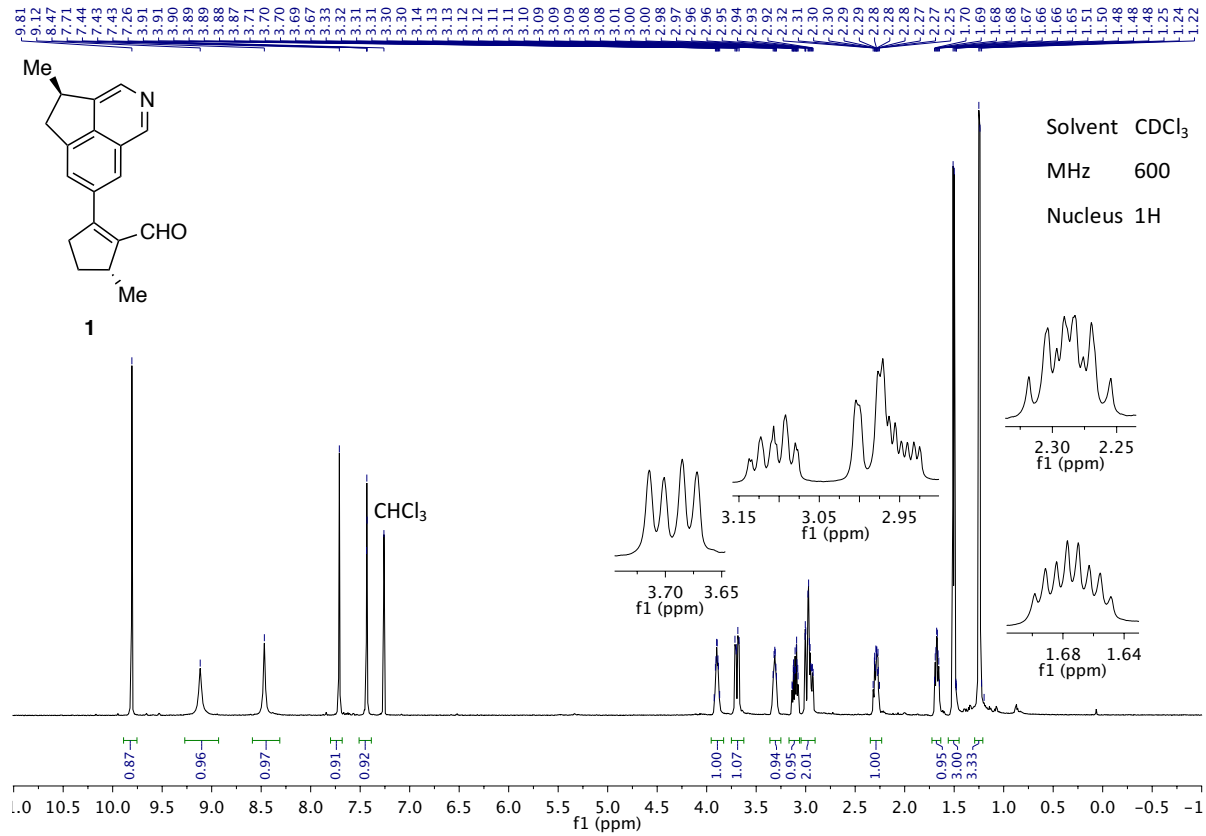

Me
CHO
CO2Me
CO2Et
Me
30
Solvent CDCl3
MHz 600
Nucleus 1H
CHCl3
f1 (ppm)

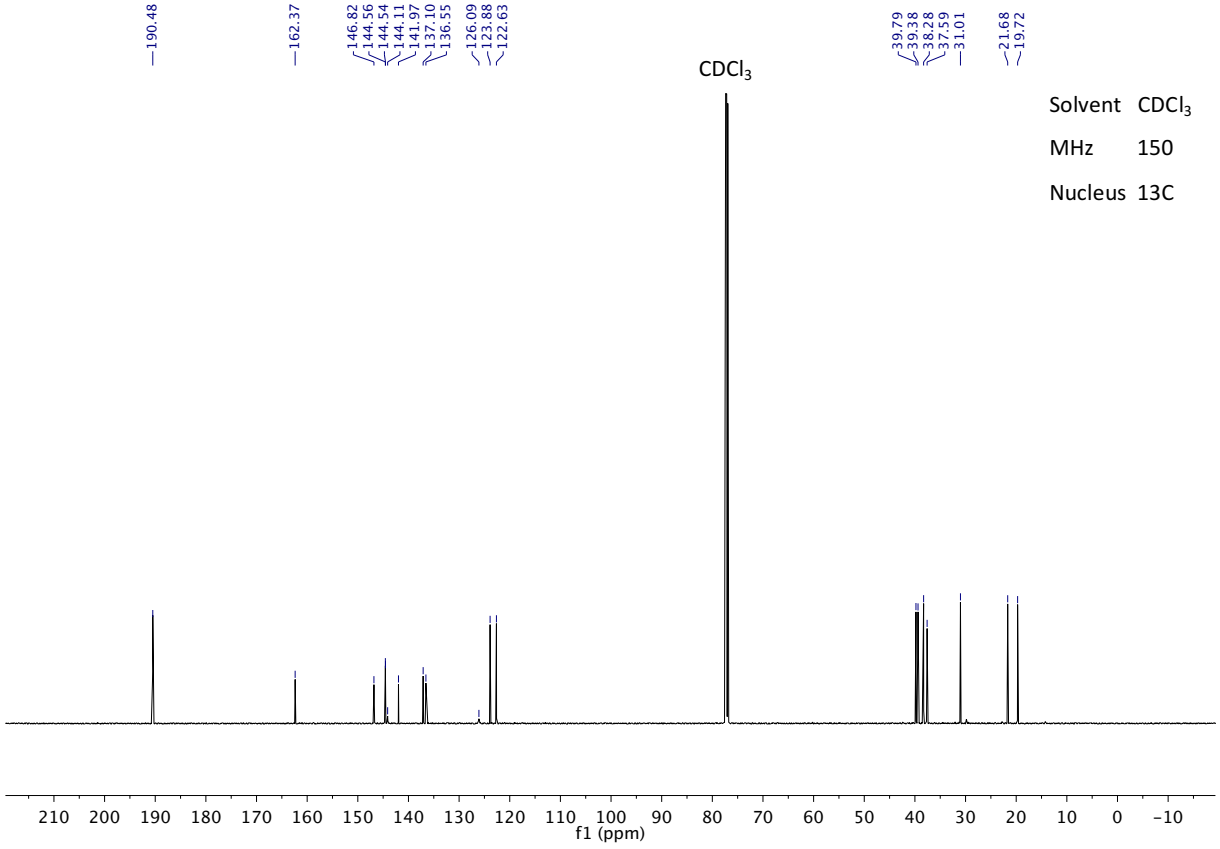

Solvent CDCl3
MHz 100
Nucleus 13C
CDCl3
f1 (ppm)


Me
O
O
CO2Et
Me
S32
Solvent CDCl3
MHz 700
Nucleus 1H
CHCl3
f1 (ppm)


CDCl3
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)


Me
CH2OH
CH2OH
CH2OH
Me
S34
Solvent CDCl3
MHz 400
Nucleus 1H
CHCl3
f1 (ppm)
Solvent CDCl3
MHz 100
Nucleus 13C
CDCl3
f1 (ppm)


Me
N
CHO
Me
1
Solvent CDCl3
MHz 600
Nucleus 1H
CHCl3
f1 (ppm)


CDCl3
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

8 References

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