Highly Enantioselective Synthesis of Indazoles with a C3-Quaternary Chiral Center Using CuH Catalysis

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I. General Information.

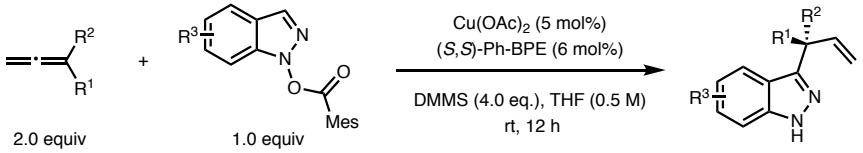
General reagent information. All reactions were performed under a nitrogen atmosphere using the indicated method in the general procedures. Tetrahydrofuran (THF) was purchased from J.T. Baker in CYCLE-TAINER® solvent delivery kegs and purified by passage under argon pressure through two packed columns of neutral alumina and copper(II) oxide. Anhydrous 1,4-dioxane was purchased from Aldrich Chemical Company in a Sure-Seal™ bottle and used as received. Copper(II) acetate was purchased from Strem and was used as received. 1,2-Bis((2*S*,5*S*)2,5-diphenylphospholano)ethane, 1,2-Bis((2*R*,5*R*)2,5-diphenylphospholano)ethane (Ph-BPE) ligands were purchased from Namena Corp. and stored in a nitrogen-filled glove box. DTBM-SEGPHOS was purchased from Takasago International Co. and used as received. Diethoxymethylsilane was purchased from TCI America. Dimethoxy(methyl)silane (DMMS) was purchased from Tokyo Chemical Industry Co. (TCI). Both silanes were stored in a nitrogen-filled glove box at −20 °C for long-term storage. (***Caution****: Dimethoxy(methyl)silane (DMMS, CAS#16881-77-9) is listed by several vendors (TCI, Alfa Aesar) SDS or MSDS as a H318, a category 1 Causes Serious Eye Damage Other vendors (Sigma-Aldrich, Gelest) list DMMS as a H319, a category II Eye Irritant. DMMS should be handled in a well-ventilated fumehood using proper precaution as outlined for the handling of hazardous materials in prudent practices in the laboratory*[1]*. At the end of the reaction either ammonium fluoride in methanol, aqueous sodium hydroxide (1 M) or aqueous hydrochloric acid (1 M) should be carefully added to the reaction mixture. This should be allowed to stir for at least 30 min or the time indicated in the detailed reaction procedure*). All other solvents and commercial reagents were used as received from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI and Combi-Blocks, unless otherwise noted. Flash column chromatography was performed using 40-63 μm silica gel (SiliaFlash® F60 from Silicycle), or with the aid of a Biotage Isolera Automated Flash Chromatography System using prepacked SNAP silica cartridges (10-100 g). Organic solutions were concentrated *in vacuo* using a Buchi rotary evaporator.

General analytical information. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, elemental analysis or high resolution mass spectrometry, optical rotation and melting point analysis (if solids). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 spectrometer. Chemical shifts for ^{1}H NMR are reported as follows: chemical shift in reference to residual $CHCl_3$ at 7.26 ppm (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, sex = sextet, sep = septet, ddd = doublet of double of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. Chemical shifts for ^{13}C NMR are reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm). Chemical shifts for ^{19}F-NMR are reported in terms of chemical shift in reference to an external standard (α,α,α-trifluorotoluene set to δ -63.7 ppm). IR spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond) and are reported in terms of frequency of absorption (cm^{-1}). Melting points were measured on a Mel-Temp capillary melting point apparatus. Optical rotations were measured using a Jasco P-1010 digital polarimeter. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. ESI- and DART-MS spectrometric data were recorded on a Bruker

Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). Enantiomeric excesses (ee's) were mostly determined by chiral SFC analysis using a Waters Acquity UPC2 instrument; specific columns and analytical methods are provided in the experimental details for individual compounds; the wavelengths of light used for chiral analyses are provided with the associated chromatograms. The enantiomeric excesss of certain compounds were determined by High pressure liquid chromatography (HPLC) performing on Agilent 1200 Series chromatographs using chiral columns (25 cm). Thin-layer chromatography (TLC) was performed on silica gel 60Å F_{254} plates (SiliaPlate from Silicycle) and visualized with UV light or potassium permanganate stain. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 x 20 cm, 1000 microns, catalog # TLG-R10011B-341 from Silicycle) and visualized with UV light. Isolated yields reported reflect the average values from two independent runs.

II. Procedures for CuH-Catalyzed Allylation Reactions

General Procedure for 0.5 mmol Scale Reaction.

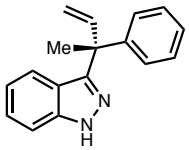


Preparation of CuH solution: In a nitrogen-filled glovebox, an oven-dried screw-top reaction tube (Fisherbrand, 13 x 100 mm, catalog no. 14-959035C) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (4.5 mg, 0.025 mmol, 5 mol %) and (*S,S*)-Ph-BPE (15.2 mg, 0.030 mmol, 6 mol %). Anhydrous THF (0.5 mL) was added via syringe and the reaction solution was stirred at room temperature (rt) for 15 min. $HSiMe(OMe)_2$ (0.25 mL, 2.0 mmol, 4.0 equiv) was added sequentially via syringe and the resulting mixture was stirred at rt to afford a pale yellow to orange solution of CuH (about 15 min).

N-Allylation: In a nitrogen-filled glovebox, a second oven-dried screw-top reaction tube (Fisherbrand, 16 x 125 mm, catalog no. 1495925C) equipped with a stir bar was charged with indazole electrophile **2** (0.50 mmol, 1.0 equiv). Allene (1.0 mmol, 2.0 equiv) and anhydrous THF (0.25 mL) were added, followed by addition of the CuH solution (0.75 mL) via syringe from the first reaction tube to the stirred reaction mixture at rt. The reaction tube was sealed with a Teflon-lined screw cap, removed from the glovebox, and stirred at rt for 12 h. After completion, the reaction cap was removed and Sat. NH_4F in MeOH (5 mL) was slowly added to the reaction tube to quench the reaction as part of the workup (*Caution*: gas evolution observed). The mixture was stirred uncapped for 30 min, transferred to a 20 mL scintillation vial (the reaction tube was rinsed with EtOAc (2 mL × 3)), and concentrated *in vacuo* with the aid of a rotary evaporator. The resulting residue was redissolved in EtOAc (10 mL), stirred at rt for 15 min, filtered through a short pad of Celite and washed with additional EtOAc (~ 5 mL). The collected EtOAc solution was concentrated *in vacuo* with the aid of a rotary evaporator, and the crude material was purified by silica gel column chromatography.

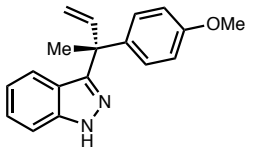
Characterization Data for Allylation Products

(*R*)-3-(2-phenylbut-3-en-2-yl)-1*H*-indazole (3a)



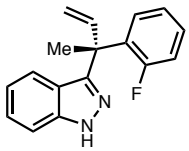
The general procedure was followed using buta-2,3-dien-2-ylbenzene (122 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 90% yield (Run 1: 108 mg, 87% yield, 99.5:0.5 er; Run 2: 115 mg, 93% yield, 99.5:0.5 ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (br, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.33 (m, 6H), 7.13 (d, J = 8.2 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.71 (dd, J = 17.4 Hz, J = 10.6 Hz, 1H), 5.24 (dd, J = 10.6 Hz, J = 1.1 Hz, 1H), 5.06 (dd, J = 17.4 Hz, J = 1.1 Hz, 1H), 2.02 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 146.3, 144.2, 141.8, 128.2, 127.3, 126.4, 126.4, 122.2, 121.0, 120.1, 113.3, 110.0, 47.9, 26.6 ppm. **EA** Calcd. for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49. Found: C, 82.48; H, 6.25. **IR** (neat): 3148, 2984, 2935, 1489, 1340, 918, 740, 698 cm^{-1}. **m.p.** 116–118 °C. **Specific rotation** $[\alpha]_D^{23}$: +32.2 (c = 1.0, $CHCl_3$). **HPLC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 7.39 (major), 7.56 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-3-(2-(4-methoxyphenyl)but-3-en-2-yl)-1*H*-indazole (3b)



The general procedure was followed using 1-(buta-2,3-dien-2-yl)-4-methoxybenzene (160 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 93% yield (Run 1: 126 mg, 91% yield, 99.5:0.5 er; Run 2: 132 mg, 95% yield, 99.5:0.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.3 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.66 (dd, J = 17.4 Hz, J = 10.6 Hz, 1H), 5.22 (dd, J = 10.6 Hz, J = 1.1 Hz, 1H), 5.02 (dd, J = 17.4 Hz, J = 1.1 Hz, 1H), 3.79 (s, 3H), 1.96 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 152.0, 144.5, 141.8, 138.3, 128.4, 126.4, 122.3, 121.0, 120.1, 113.5, 113.0, 109.8, 55.2, 47.3, 26.6 ppm. **HRMS** (DART) m/z calcd. for $C_{18}H_{19}N_2O^+$ $[M+H]^+$: 279.1492; found 279.1508. **IR** (neat): 3147, 2985, 2933, 1509, 1248, 1180, 1033, 742 cm^{-1}. **m.p.** 92–94 °C. **Specific rotation** $[\alpha]_D^{23}$: +16.0 (c = 1.0, $CHCl_3$). **HPLC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 8.71 (major), 9.07 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

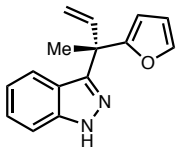
(*R*)-3-(2-(2-fluorophenyl)but-3-en-2-yl)-1*H*-indazole (3c)



The general procedure was followed using 1-(buta-2,3-dien-2-yl)-4-fluorobenzene (148 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 91% yield (Run 1: 124 mg, 93% yield, 99.5:0.5 er; Run 2: 119 mg, 89% yield, 99.5:0.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.93 (br, 1H), 7.47 (td, J = 7.8 Hz, J = 1.7 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.33–7.23 (m, 2H), 7.17 (td, J = 7.6 Hz, J =

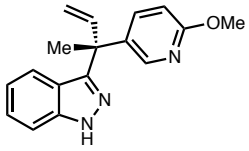
1.3 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.98–6.87 (m, 2H), 6.73 (dd, *J* = 17.4 Hz, *J* = 10.6 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 5.05 (d, *J* = 17.4 Hz, 1H), 2.03 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 161.39 (d, *J* = 249.5 Hz), 151.0, 142.7, 141.6, 133.0 (d, *J* = 11.2 Hz), 128.8 (d, *J* = 8.7 Hz), 128.5 (d, *J* = 4.2 Hz), 126.4, 123.9 (d, *J* = 3.6 Hz), 121.3, 120.8, 120.1, 116.4 (d, *J* = 22.8 Hz), 113.3, 109.8, 45.8, 25.0 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.1 ppm. **EA** Calcd. for $C_{17}H_{15}FN_2$: C, 76.67; H, 5.68. Found: C, 76.37; H, 5.78. **IR** (neat): 3149, 2983, 2934, 1487, 1445, 1341, 1226, 916, 773 cm^{-1}. **m.p.** 120–122 °C. **Specific rotation** $[\alpha]_D^{23}$: +22.1 (*c* = 1.0, $CHCl_3$). **HPLC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 7.09 (major), 7.31 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*S*)-3-(2-(furan-2-yl)but-3-en-2-yl)-1*H*-indazole (3d)



The general procedure was followed using 2-(buta-2,3-dien-2-yl)furan (120 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 78% yield (Run 1: 89 mg, 75% yield, 99:1 er; Run 2: 95 mg, 80% yield, 99:1 er). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 9.93 (br, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.40–7.28 (m, 3H), 7.02 (td, *J* = 7.4 Hz, *J* = 6.9 Hz, *J* = 1.2 Hz, 1H), 6.58 (dd, *J* = 17.4 Hz, *J* = 10.5 Hz, 1H), 6.41–6.33 (m, 1H), 6.26–6.18 (m, 1H), 5.25 (dd, *J* = 10.4 Hz, *J* = 1.2 Hz, 1H), 5.02 (dd, *J* = 17.4 Hz, *J* = 1.2 Hz, 1H), 1.97 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 158.2, 149.5, 142.0, 141.8, 141.5, 126.5, 121.8, 121.0, 120.4, 113.9, 110.0, 109.8, 106.1, 44.7, 24.8 ppm. **EA** Calcd. for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92. Found: C, 75.87; H, 6.05. **IR** (neat): 3146, 2985, 2933, 1501, 1341, 1009, 926, 772, 598 cm^{-1}. **m.p.** 64–66 °C. **Specific rotation** $[\alpha]_D^{23}$: –23.4 (*c* = 1.0, $CHCl_3$). **HPLC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 6.85 (minor), 7.05 min (major), 99:1 er. The absolute stereochemistry was assigned as (*S*) by analogy to **3g**.

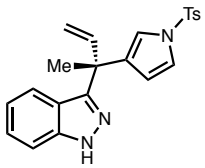
(*R*)-3-(2-(6-methoxypyridin-3-yl)but-3-en-2-yl)-1*H*-indazole (3e)



The general procedure was followed using 5-(buta-2,3-dien-2-yl)-2-methoxypyridine (161 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 3 : 1) provided the title product as an oil in 95% yield (Run 1: 134 mg, 96% yield, 99:1 er; Run 2: 131 mg, 94% yield, 99:1 er). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 9.93 (br, 1H), 8.13 (dd, *J* = 2.6 Hz, *J* = 0.7 Hz, 1H), 7.47–7.38 (m, 2H), 7.31 (ddd, *J* = 8.3 Hz, *J* = 6.9 Hz, *J* = 1.0 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.97 (ddd, *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 0.9 Hz, 1H), 6.71–6.57 (m, 2H), 5.26 (dd, *J* = 10.6 Hz, *J* = 0.9 Hz, 1H), 5.03 (dd, *J* = 17.4 Hz, *J* = 0.9 Hz, 1H), 3.92 (s, 3H), 1.97 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 162.8, 145.2, 143.5, 141.8, 138.5, 134.3, 126.6, 122.0, 120.8, 120.4, 113.8, 110.4, 109.8, 100.0, 53.4, 45.9, 26.4 ppm. **HRMS** (DART) m/z calcd. for $C_{17}H_{18}N_3O^+$ $[M+H]^+$: 280.1444; found 280.1450. **IR** (neat): 3148, 2982, 2939, 1603, 1490, 1379, 1287, 1025, 913, 731 cm^{-1}. **Specific rotation** $[\alpha]_D^{23}$: +32.0 (*c* = 1.0, $CHCl_3$). **HPLC** analysis: AS-H (5:95 MeOH: $scCO_2$ to 40:60 MeOH: $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 3.27 (minor),

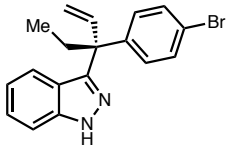
3.46 min (major), 99:1 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-3-(2-(1-tosyl-1*H*-pyrrol-3-yl)but-3-en-2-yl)-1*H*-indazole (3f)



The general procedure was followed using 3-(buta-2,3-dien-2-yl)-1-tosyl-1*H*-pyrrole (the allene was in 80% purity, 273 mg crude allene was used, ~0.80 mmol, 1.6 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 3 : 1) provided the title product as a white solid in 91% yield (Run 1: 170 mg, 87% yield, 99:1 er; Run 2: 186 mg, 95% yield, 99:1 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (br, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.41 (dt, J = 8.4 Hz, J = 0.9 Hz, 1H), 7.32–7.26 (m, 3H), 7.14–7.04 (m, 2H), 6.98 (dd, J = 2.2 Hz, J = 1.7 Hz, 1H), 6.83 (ddd, J = 8.0 Hz, J = 6.8 Hz, J = 0.9 Hz, 1H), 6.50 (dd, J = 17.3 Hz, J = 10.5 Hz, 1H), 6.10 (dd, J = 3.3 Hz, J = 1.7 Hz, 1H), 5.15 (dd, J = 10.5 Hz, J = 1.1 Hz, 1H), 4.92 (dd, J = 17.3 Hz, J = 1.0 Hz, 1H), 2.43 (s, 3H), 1.85 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 144.8, 143.5, 141.6, 136.2, 135.1, 129.9, 126.8, 126.4, 122.0, 121.3, 120.8, 120.0, 117.7, 114.3, 113.2, 109.8, 43.1, 26.5, 21.7 ppm. **EA** Calcd. for $C_{22}H_{21}N_3O_2S$: C, 67.50; H, 5.41. Found: C, 67.34; H, 5.56. **IR** (neat): 3141, 2983, 2936, 1367, 1172, 1060, 675, 595 cm^{-1}. **m.p.** 152–154 °C. **Specific rotation** $[\alpha]_D^{23}$: +8.9 (c = 1.0, $CHCl_3$). **HPLC** analysis: OJ-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 40:60 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 5.31 (minor), 5.56 min (major), 99:1 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-3-(3-(4-bromophenyl)pent-1-en-3-yl)-1*H*-indazole (3g)



The general procedure was followed using 1-bromo-4-(penta-1,2-dien-3-yl)benzene (223 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 93% yield (Run 1: 158 mg, 94% yield, 99.5:0.5 er; Run 2: 156 mg, 92% yield, 99.5:0.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.86 (br, 1H), 7.46–7.36 (m, 3H), 7.30 (ddd, J = 8.3 Hz, J = 6.8 Hz, J = 1.1 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H), 7.04 (dt, J = 8.2 Hz, J = 1.0 Hz, 1H), 6.93 (ddd, J = 8.2 Hz, J = 6.8 Hz, J = 0.9 Hz, 1H), 6.70 (dd, J = 17.5 Hz, J = 10.7 Hz, 1H), 5.26 (dd, J = 10.8 Hz, J = 1.1 Hz, 1H), 4.86 (dd, J = 17.5 Hz, J = 1.1 Hz, 1H), 2.49 (qd, J = 7.3 Hz, J = 3.6 Hz, 2H), 0.82 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 144.0, 141.9, 141.6, 131.1, 129.9, 126.5, 122.1, 121.3, 120.3, 120.3, 114.9, 109.8, 51.4, 31.7, 9.2 ppm. **HRMS** (DART) m/z calcd. for $C_{18}H_{18}N_2Br^+$ $[M+H]^+$: 341.0648; found 341.0661. **IR** (neat): 3150, 2934, 1621, 1486, 1340, 1008, 924, 907, 772, 733 cm^{-1}. **m.p.** 140–142 °C. **Specific rotation** $[\alpha]_D^{23}$: +28.1 (c = 1.0, $CHCl_3$). **HPLC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 3.89 (major), 4.14 min (minor), 99.5:0.5 er.

Single Crystal X-ray Diffraction Data for 3g (P18136)

Crystal of the complex **3g** was obtained by layering *n*-pentane upon the CH_2Cl_2 solution of **3g** at ambient conditions (room temperature, air).

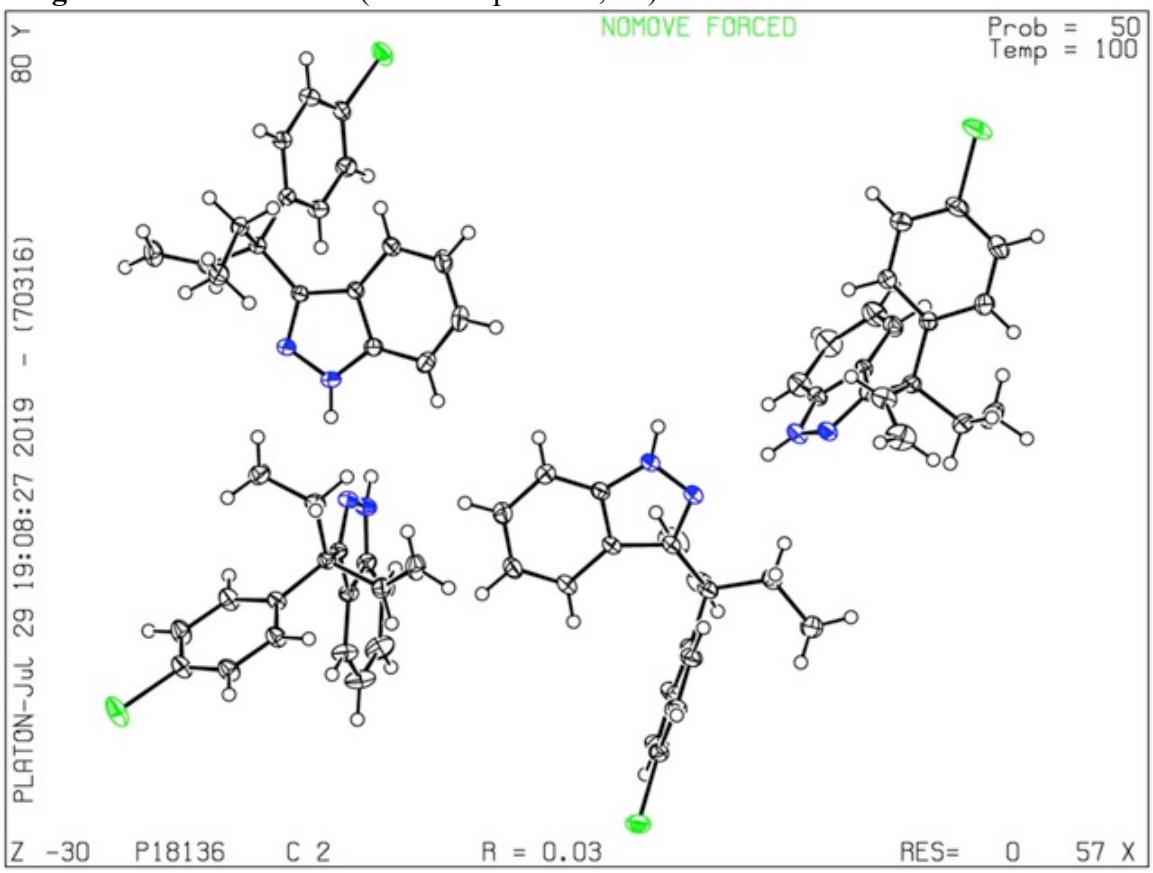


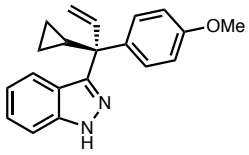
Table S1. Crystal data and structure refinement for 3g (P18136).

Identification code	P18136	
Empirical formula	C18 H17 Br N2	
Formula weight	341.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 20.5139(6) Å	a= 90°.
	b = 17.1909(5) Å	b= 116.0037(11)°.
	c = 20.0043(6) Å	g = 90°.
Volume	6340.4(3) $Å^3$	
Z	16	

Density (calculated)	1.430 Mg/m^3
Absorption coefficient	2.588 mm^{-1}
F(000)	2784
Crystal size	0.450 x 0.400 x 0.320 mm^3
Theta range for data collection	1.620 to 36.318°.
Index ranges	-34<=h<=34, -28<=k<=28, -33<=l<=33
Reflections collected	373811
Independent reflections	30718 [R(int) = 0.0532]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1101 and 0.0456
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	30718 / 5 / 773
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0711
R indices (all data)	R1 = 0.0452, wR2 = 0.0772
Absolute structure parameter	0.0149(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.849 and -1.125 $e.Å^{-3}$

The structure factors and structural output was checked using IUCr's CheckCIF routine. The routine indicated 0 A-, and 0 B-level alert in the structure.

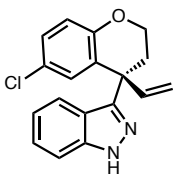
(*S*)-3-(1-cyclopropyl-1-(4-methoxyphenyl)allyl)-1*H*-indazole (3h)



The general procedure was followed using 1-(1-cyclopropylpropa-1,2-dien-1-yl)-4-methoxybenzene (186 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 4 : 1) provided the title product as a white solid in 51% yield (Run 1: 75 mg, 49% yield, 92:8 er; Run 2: 81 mg, 53% yield, 92:8 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.11 (br, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.3 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 8.7 Hz, 2H), 6.36 (dd, J = 17.3 Hz, J = 10.6 Hz, 1H), 5.02 (d, J = 10.6 Hz, 1H), 4.75 (dd, J = 17.3 Hz, 1H), 3.56 (s, 3H), 1.67 (p, J = 8.0 Hz, 1H), 0.43 (tt, J = 8.9 Hz, J = 5.5 Hz, 1H) 0.28 (tt, J = 9.1 Hz, J = 4.9 Hz, 1H), 0.09 (dq, J = 10.0 Hz, J = 5.1 Hz, 1H), -0.01 (dq, J = 10.0 Hz, J = 5.2 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.8, 148.8, 139.6, 139.4, 133.5, 127.9, 124.1, 120.3, 119.3, 117.8, 113.5, 110.9, 107.8, 53.0, 48.9, 16.7, -0.00, -0.90 ppm. **HRMS** (DART) m/z calcd. for $C_{20}H_{21}N_2O^+$ $[M+H]^+$: 305.1648; found 305.1652. **IR** (neat): 3145, 2996, 2934, 1508, 1248, 1180, 908, 826, 729 cm^{-1}. **m.p.** 70–74 °C. **Specific rotation** $[\alpha]_D^{23}$: –13.9 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 9.75 (major),

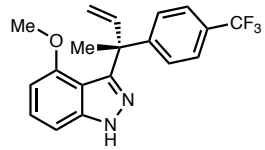
10.17 min (minor), 92:8 er. The absolute stereochemistry was assigned as (*S*) by analogy to **3g**.

(*R*)-3-(6-chloro-4-vinylchroman-4-yl)-1*H*-indazole (3i)



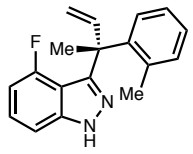
The general procedure was followed using 6-chloro-4-vinylidenechromane (193 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2a** (140 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 3 : 1) provided the title product as a white solid in 81% yield (Run 1: 119 mg, 77% yield, 99.5:0.5 er; Run 2: 132 mg, 85% yield, 99.5:0.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (br, 1H), 7.45 (dd, J = 8.3 Hz, J = 1.1 Hz, 1H), 7.38–7.30 (m, 1H), 7.28–7.23 (m, 1H), 7.13 (ddd, J = 8.7 Hz, J = 2.6 Hz, J = 1.1 Hz, 1H), 7.06–6.99 (m, 1H), 6.92–6.89 (m, 2H), 6.57 (ddd, J = 17.3 Hz, J = 10.5 Hz, J = 1.1 Hz, 1H), 5.49 (dd, J = 10.5 Hz, J = 1.1 Hz, 1H), 4.88 (dd, J = 17.3 Hz, J = 1.1 Hz, 1H), 4.32–4.09 (m, 2H), 2.77 (ddd, J = 13.9 Hz, J = 9.6 Hz, J = 3.5 Hz, 1H), 2.15 (dddd, J = 14.1 Hz, J = 5.3 Hz, J = 2.5 Hz, J = 1.0 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 150.2, 143.0, 141.8, 130.5 128.6, 126.7, 125.9, 124.9, 121.6, 120.7, 120.2, 118.4, 117.8, 110.0, 62.8, 45.0, 34.0 ppm. **EA** Calcd. for $C_{18}H_{15}ClN_2O$: C, 69.57; H, 4.87. Found: C, 69.31; H, 5.22. **IR** (neat): 3149, 2933, 2888, 1481, 1225, 905, 816, 727, 650 cm^{-1}. **m.p.** 78–83 °C. **Specific rotation** $[\alpha]_D^{23}$: +28.8 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 8.31 (major), 8.86 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-4-methoxy-3-(2-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)-1*H*-indazole (3j)



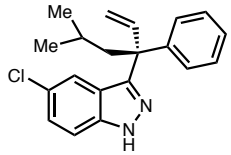
The general procedure was followed using 1-(buta-2,3-dien-2-yl)-4-(trifluoromethyl)benzene (198 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2b** (155 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 3 : 1) provided the title product as a white solid in 91% yield (Run 1: 154 mg, 89% yield, 94:6 er; Run 2: 161 mg, 93% yield, 94:6 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.71 (br, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.3 Hz, 1H), 6.81 (dd, J = 17.4 Hz, J = 10.6 Hz, 1H), 6.28 (d, J = 7.7 Hz, 1H), 5.20 (d, J = 10.5 Hz, 1H), 5.10 (d, J = 17.4 Hz, 1H), 3.35 (s, 3H), 1.96 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.5, 152.4, 144.0, 128.4, 127.6 (q, J = 32.6 Hz), 126.9, 124.5 (q, J = 3.8 Hz), 124.4 (q, J = 271.6 Hz), 113.0, 102.5, 100.2, 54.3, 48.2, 25.8 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.2 ppm. **EA** Calcd. for $C_{19}H_{17}N_2F_3O$: C, 65.89; H, 4.95. Found: C, 65.69; H, 5.11. **IR** (neat): 3160. 3129, 2938, 1323, 1261, 1112, 1077, 1015, 740 cm^{-1}. **m.p.** 111–113 °C. **Specific rotation** $[\alpha]_D^{23}$: +27.6 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 4.87 (minor), 5.37 min (major), 94:6 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-4-fluoro-3-(2-(*o*-tolyl)but-3-en-2-yl)-1*H*-indazole (3k)



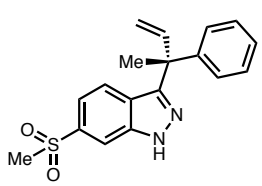
The general procedure was followed using 1-(buta-2,3-dien-2-yl)-2-methylbenzene (144 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2c** (149 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 63% yield (Run 1: 86 mg, 61% yield, 97:3 er; Run 2: 91 mg, 65% yield, 97:3 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.9 Hz, J = 1.4 Hz, 1H), 7.25–7.18 (m, 3H), 7.16 (td, J = 7.4 Hz, J = 1.4 Hz, 1H), 7.02–6.98 (m, 1H), 6.92 (dd, J = 17.5 Hz, J = 10.6 Hz, 1H), 6.58 (ddd, J = 10.6 Hz, J = 7.1 Hz, J = 1.2 Hz, 1H), 5.19 (dd, J = 10.6 Hz, J = 1.1 Hz, 1H), 4.99 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 1.99 (s, 3H), 1.74 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6 (d, J = 254.4 Hz), 151.5 (d, J = 5.4 Hz), 144.6 (d, J = 9.2 Hz), 143.8 (d, J = 254.4 Hz), 143.2 (d, J = 2.0 Hz), 136.7, 132.1, 127.9 (d, J = 8.0 Hz), 127.7 (d, J = 2.8 Hz), 126.6, 125.6, 112.6, 111.1 (d, J = 22.7 Hz), 105.7, 105.5 (d, J = 17.3 Hz), 47.9, 25.9 (d, J = 2.5 Hz), 21.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.5 ppm. **EA** Calcd. for $C_{18}H_{17}N_2F$: C, 77.12; H, 6.11. Found: C, 76.72; H, 6.32. **IR** (neat): 3173, 3135, 2949, 1633, 1344, 1240, 1034, 746, 727 cm^{-1}. **m.p.** 106–108 °C. **Specific rotation** $[\alpha]_D^{23}$: +16.3 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 6.16 (major), 6.54 min (minor), 97:3 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-5-chloro-3-(5-methyl-3-phenylhex-1-en-3-yl)-1*H*-indazole (3l)



The general procedure was followed using (5-methylhexa-1,2-dien-3-yl)benzene (172 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2d** (157 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 92% yield (Run 1: 151 mg, 93% yield, 98.5:1.5 er; Run 2: 147 mg, 91% yield, 98.5:1.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (br, 1H), 7.39–7.17 (m, 7H), 6.93 (d, J = 1.9 Hz, 1H), 6.83 (dd, J = 17.5 Hz, J = 10.7 Hz, 1H), 5.24 (dd, J = 10.7 Hz, J = 1.1 Hz, 1H), 4.79 (dd, J = 17.5 Hz, J = 1.1 Hz, 1H), 2.49–2.35 (m, 2H), 1.78–1.64 (m, 1H), 0.72 (d, J = 6.7 Hz, 3H), 0.68 (d, J = 6.7 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 144.8, 142.8, 140.1, 129.2, 128.2, 128.0, 127.1, 126.6, 125.6, 121.5, 114.9, 110.8, 51.5, 48.2, 24.9, 24.8, 24.5 ppm. **HRMS** (DART) m/z calcd. for $C_{20}H_{22}N_2Cl^+$ $[M+H]^+$: 325.1466; found 325.1475. **IR** (neat): 3137, 2953, 2915, 1985, 1273, 1049, 920, 701 cm^{-1}. **m.p.** 62–67 °C. **Specific rotation** $[\alpha]_D^{23}$: +21.7 (c = 1.0, $CHCl_3$). **SFC** analysis: OD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 20:80 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 7.71 (major), 8.36 min (minor), 98.5:1.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

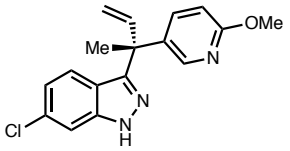
(*R*)-6-(methylsulfonyl)-3-(2-phenylbut-3-en-2-yl)-1*H*-indazole (3m)



The general procedure was followed using buta-2,3-dien-2-ylbenzene (130 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2e** (179 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 1 : 1) provided the title product as a white solid in 93% yield (Run 1: 155 mg, 95% yield, 92.5:7.5 er; Run 2: 149 mg, 91% yield, 92.5:7.5 er). **^{1}H NMR** (400

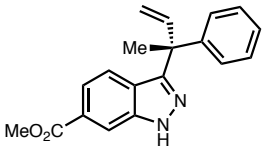
MHz, $CDCl_3$) δ 10.38 (br, 1H), 8.20–8.10 (m, 1H), 7.41 (dd, J = 8.6 Hz, J = 1.4 Hz, 1H), 7.33–7.20 (m, 6H), 6.65 (dd, J = 17.4 Hz, J = 10.6 Hz, 1H), 5.27 (dd, J = 10.6 Hz, J = 0.9 Hz, 1H), 5.01 (dd, J = 17.3 Hz, J = 0.9 Hz, 1H), 3.07 (s, 3H), 1.99 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 145.7, 143.6, 140.5, 138.4, 128.4, 127.3, 126.8, 123.9, 123.7, 117.8, 114.0, 110.7, 47.9, 44.7, 26.7 ppm. **EA** Calcd. for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56. Found: C, 66.04; H, 5.73. **IR** (neat): 3329, 2979, 2925, 1301, 1142, 1061, 961, 757, 701 cm^{-1}. **m.p.** 145–147 °C. **Specific rotation** $[\alpha]_D^{23}$: +40.4 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 10.35 (major), 10.71 min (minor), 92.5:7.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-6-chloro-3-(2-(6-methoxypyridin-3-yl)but-3-en-2-yl)-1*H*-indazole (3n)



The general procedure was followed using 5-(buta-2,3-dien-2-yl)-2-methoxypyridine (161 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2f** (157 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 3 : 1) provided the title product as a colorless oil in 81% yield (Run 1: 124 mg, 79% yield, 99.5:0.5 er; Run 2: 146 mg, 93% yield, 99.5:0.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.01 (br, 1H), 8.12 (s, 1H), 7.45–7.36 (m, 2H), 7.12 (d, J = 8.7 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 6.67 (s, 1H), 6.59 (dd, J = 17.2 Hz, J = 10.5 Hz, 1H), 5.27 (d, J = 10.1 Hz, 1H), 5.01 (d, J = 17.1 Hz, 1H), 3.93 (s, 3H), 1.95 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 150.9, 145.1, 143.2, 142.3, 138.4, 134.1, 133.0, 123.0, 121.6, 119.9, 114.2, 110.5, 109.8, 53.4, 45.9, 26.5 ppm. **HRMS** (DART) m/z calcd. for $C_{17}H_{17}N_3ClO^+$ $[M+H]^+$: 314.1055; found 314.1071. **IR** (neat): 3165, 2977, 1490, 1287, 1262, 1024, 926, 803, 735 cm^{-1}. **Specific rotation** $[\alpha]_D^{23}$: +32.0 (c = 1.0, $CHCl_3$). **SFC** analysis: AS-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 20:80 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 4.50 (major), 4.86 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

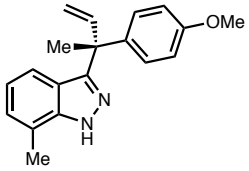
methyl (*R*)-3-(2-phenylbut-3-en-2-yl)-1*H*-indazole-6-carboxylate (3o)



The general procedure was followed using buta-2,3-dien-2-ylbenzene (130 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2g** (169 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 2 : 1) provided the title product as a white solid in 96% yield (Run 1: 148 mg, 97% yield, 99.5:0.5 er; Run 2: 148 mg, 96% yield, 99.5:0.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.54 (br, 1H), 8.20 (t, J = 1.1 Hz, 1H), 7.58 (dd, J = 8.6 Hz, J = 1.4 Hz, 1H), 7.33–7.19 (m, 5H), 7.12 (dd, J = 8.6 Hz, J = 0.8 Hz, 1H), 6.66 (dd, J = 17.4 Hz, J = 10.6 Hz, 1H), 5.26 (dd, J = 10.6 Hz, J = 1.0 Hz, 1H), 5.03 (dd, J = 17.4 Hz, J = 1.0 Hz, 1H), 3.93 (s, 3H), 2.00 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 151.9, 145.9, 143.8, 141.2, 128.3, 128.3, 127.3, 126.6, 123.7, 122.1, 120.8, 113.7, 112.5, 52.4, 47.9, 26.6 ppm. **HRMS** (DART) m/z calcd. for $C_{19}H_{19}N_2O_2^+$ $[M+H]^+$: 307.1441; found 307.1441. **IR** (neat): 3169, 3059, 2948, 1720, 1323, 1220, 1088, 761, 700 cm^{-1}. **m.p.** 141–143 °C. **Specific rotation** $[\alpha]_D^{23}$: +40.0 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 10.55

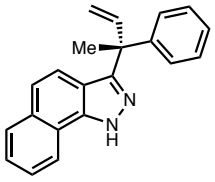
(major), 10.97 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

(*R*)-3-(2-(4-methoxyphenyl)but-3-en-2-yl)-7-methyl-1*H*-indazole (3p)



The general procedure was followed using buta-2,3-dien-2-ylbenzene (130 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2h** (147 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 82% yield (Run 1: 118 mg, 81% yield, 93.5:6.5 er; Run 2: 121 mg, 83% yield, 93.5:6.5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (br, 1H), 7.16 (d, J = 8.8 Hz, 2H), 7.06 (dt, J = 6.8 Hz, J = 1.0 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.85 (dd, J = 8.2 Hz, J = 6.9 Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 6.66 (dd, J = 17.4 Hz, J = 10.6 Hz, 1H), 5.20 (dd, J = 10.6 Hz, J = 1.1 Hz, 1H), 5.01 (dd, J = 17.4 Hz, J = 1.1 Hz, 1H), 3.78 (s, 3H), 2.52 (s, 3H), 1.96 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 152.5, 144.5, 141.9, 138.4, 128.4, 126.4, 120.7, 120.5, 119.8, 119.6, 113.5, 113.0, 55.2, 47.3, 26.6, 16.8 ppm. **HRMS** (DART) m/z calcd. for $C_{19}H_{21}N_2O^+$ $[M+H]^+$: 293.1648; found 293.1647. **IR** (neat): 3153, 2914, 1509, 1249, 1180, 1034, 829, 750 cm^{-1}. **m.p.** 154–158 °C. **Specific rotation** $[\alpha]_D^{23}$: +12.7 (c = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (0.1% Et_2NH): $scCO_2$ to 25:75 MeOH (0.1% Et_2NH): $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 8.64 (major), 8.91 min (minor), 93.5:6.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

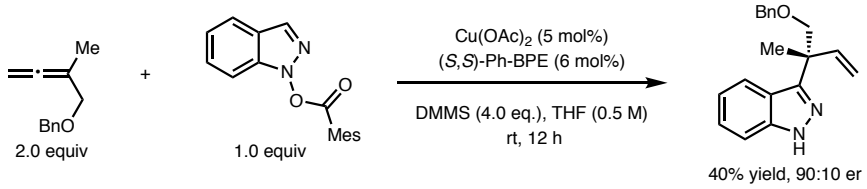
(*R*)-3-(2-phenylbut-3-en-2-yl)-1*H*-benzo[*g*]indazole (3q)



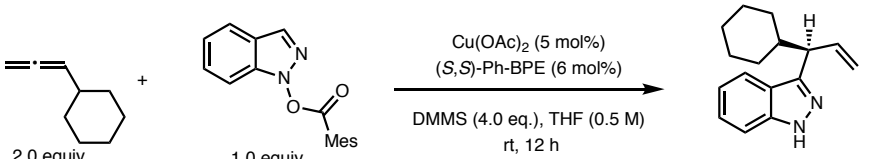
The general procedure was followed using buta-2,3-dien-2-ylbenzene (130 mg, 1.00 mmol, 2.0 equiv) and indazole electrophile **2i** (165 mg, 0.500 mmol, 1.0 equiv). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 72% yield (Run 1: 104 mg, 70% yield, 95:5 er; Run 2: 110 mg, 74% yield, 95:5 er). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.46 (m, 2H), 7.31–7.19 (m, 1H), 7.16–6.84 (m, 6H), 6.53 (dd, J = 17.6 Hz, 1H), 5.03 (m, 1H), 4.77 (m, 1H), 1.85 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 146.4, 143.9, 139.5, 132.3, 128.5, 128.2, 127.1, 126.6, 126.2, 126.1, 121.9, 121.6, 120.6, 120.0, 117.2, 113.3, 47.8, 26.6 ppm. **HRMS** (DART) m/z calcd. for $C_{21}H_{19}N_2^+$ $[M+H]^+$: 299.1543 found 299.1554. **IR** (neat): 3060, 2972, 2934, 1426, 971, 809, 749, 703 cm^{-1}. **m.p.** 200–204 °C. **Specific rotation** $[\alpha]_D^{23}$: +54.9 (c = 1.0, $CHCl_3$). **SFC** analysis: AS-H (5:95 MeOH: $scCO_2$ to 40:60 MeOH: $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 4.54 (major), 5.01 min (minor), 95:5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3g**.

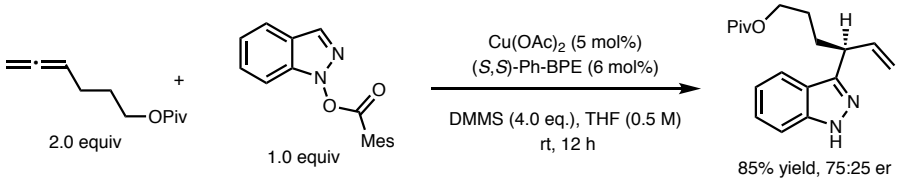
III. CuH-Catalyzed C3-Allylation of *1H*-indazoles with other Nucleophile Precursors (Scheme S1).

Dialkyl allenes:

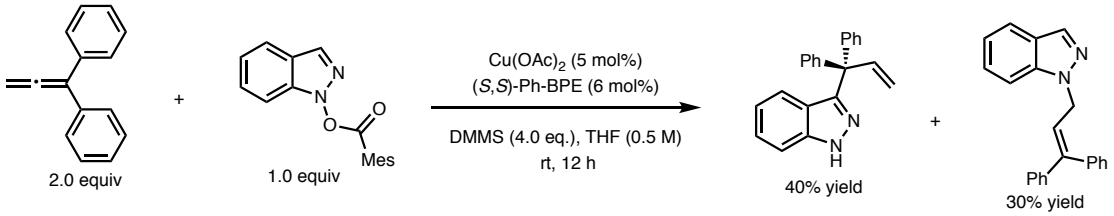


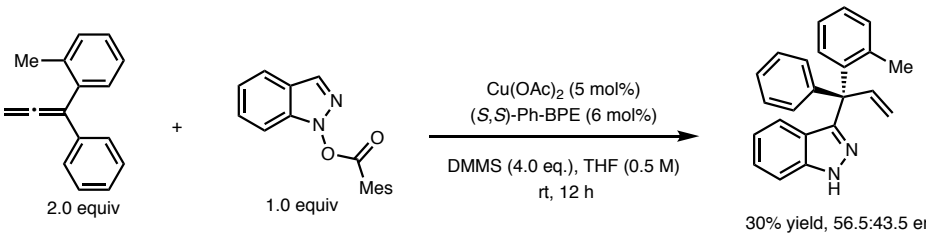
Monoalkyl allenes:



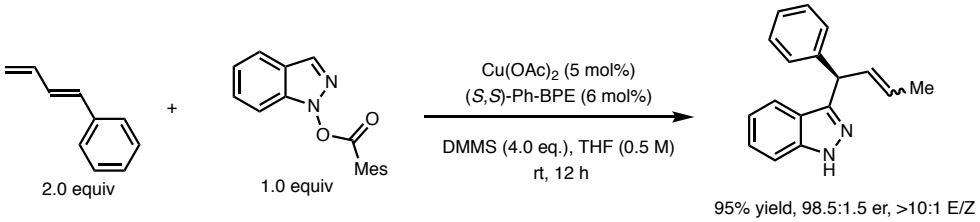


Diaryl allenes:



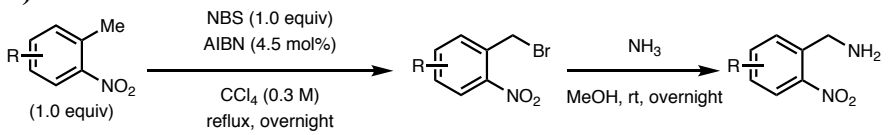


1,3-phenyldiene:



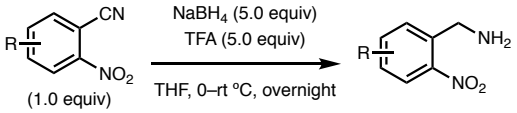
IV. Preparation of (2,4,6-trimethylbenzoyloxy) Indazoles

General Procedure A for the Synthesis of Benzyl Amines (from 2-Nitrotoluene Derivatives).



In a round bottom flask equipped with a stir bar was charged with 2-nitrotoluene derivative (25 mmol, 1.0 equiv), NBS (25 mmol, 1.0 eqiv) and AIBN (1.13 mmol, 0.045 equiv). The flask was then fitted with a reflux condenser and purged with argon for 15 min. Anhydrous carbon tetrachloride (83 ml, 0.3 M) was added via syringe. The reaction mixture was then heated to reflux overnight. After cooling to room temperature, the reaction mixture was filtered and the solid was washed with EtOAc (10 mL×3). The filtrate was concentrated with the aid of a rotary evaporator. The residue was dissolved in methanol (25 mL, 1 M) and added slowly to a 7N ammonia methanol solution (50 mL, 0.5 M). The reaction mixture was stirred overnight at room temperature. After completion as determined by TLC analysis, the reaction mixture was concentrated with the aid of a rotary evaporator. 1M NaOH aqueous solution (100 mL) and methylene chloride (CH_2Cl_2) (100 mL) were added to the residue. The mixture was transferred into a seperatory funnel and the phases were separated. The aqueous layer was rinsed with CH_2Cl_2 (20 mL x 2). The combined organic layers were washed with saturated brine (100 mL). After drying over anhydrous Na_2SO_4, and filtered, the mixture was concentrated with the aid of a rotary evaporator. The residue was purified via silica gel column chromatography, eluting with CH_2Cl_2: MeOH (10:1). The solution was concentrated with the aid of a rotary evaporator and the crude benzylamine was used directly in General Procedure C.

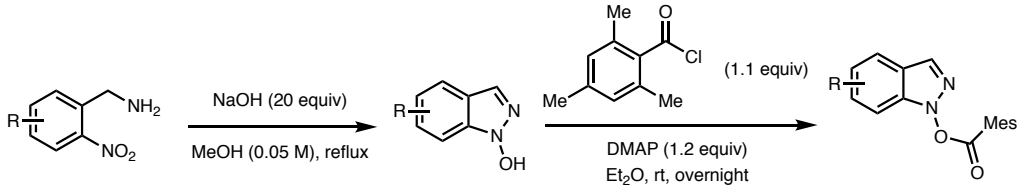
General Procedure B for the Synthesis of Benzyl Amines (from 2-Nitrotoluene Derivatives).



A round bottom flask equipped with a stir bar was charged with sodium hydroborate (5 equiv). THF (50 mL) was added via syringe. The flask was submerged into an ice/water bath and cooled to 0 ºC. To the suspension was slowly added trifluoroacetic acid (5.0 equiv) (*Caution*: gas evolution observed). A solution of nitrobenzonitrile (20 mmol) in THF (20 mL) was added. The ice bath was removed and the reaction mixture was stirred at room temperature overnight. After completion as determined by TLC analysis, the reaction mixture was poured into an aqueous solution of 1N sodium hydroxide (150 mL), then EtOAc (100 mL) was added and the biphasic mixture was stirred for 1.5 h. The layers were separated and the aqueous layer was extracted with EtOAc (50 mL×3). The combined organic layers were washed with saturated brine, and then dried over anhydrous Na_2SO_4 and filtered. The solvent was removed with the aid of a rotary evaporator, and the residue was flushed through a short silica pad, eluting with CH_2Cl_2: MeOH (10:1). The solution

was concentrated with the aid of a rotary evaporator and the crude benzylamine was used directly used in General Procedure C.

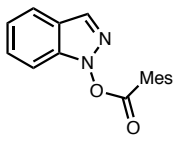
General Procedure C for Preparation of Indazole Electrophile from Corresponding Benzyl Amines.



The 1N-(hydroxyl)indazoles were prepared by previously reported procedures.[1] In a round bottom flask equipped with a stir bar was added the benzylamine derivative (5 mmol) followed by 1M methanolic solution of NaOH (0.05 M). The flask was equipped with a reflux condenser and the reaction mixture was heated to reflux and stirred overnight. After cooling to rt, the mixture was concentrated with the aid of a rotary evaporator and the residue was acidified with 1M HCl to reach pH = 1, and then extracted with EtOAc (50 mL×3). The organic phases were combined, dried over Na_2SO_4, and filtered. The solvent was then evaporated with the aid of a rotary evaporator. The residue was put under vacuum overnight to dry and subjected directly to the acylation reaction. A round bottom flask containing the residue from the previous step was charged with a stir bar and DMAP (1.2 equiv) was added. The flask was purged with argon for 15 min and ether (0.2 M) and acyl chloride (1.1 equiv) were added successively. The reaction mixture was stirred at rt overnight. After completion as determined by TLC analysis, sat Na_2CO_3 aqueous solution (50 mL) and ether (50 mL) were added. The organic phase was separated, dried over Na_2SO_4, filtered and concentrated with the aid of a rotary evaporator. The residue was purified via flash column chromatography to provide the indazole electrophile.

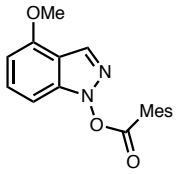
Characterization Data for Allylation Products

1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2a)



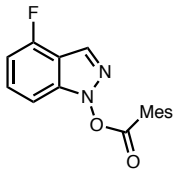
The general procedure A was followed starting from 1-(bromomethyl)-2-nitrobenzene (2.16 g, 10.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a yellow solid in 46% overall yield (three steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.49–7.33 (m, 2H), 7.28–7.17 (m, 1H), 6.95 (s, 2H), 2.54 (s, 6H), 2.31 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 141.5, 137.0, 136.8, 130.2, 128.9, 127.8, 125.9, 122.3, 122.1, 121.4, 108.4, 21.3, 20.3 ppm. **EA** Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75. Found: C, 72.89; H, 5.91. **IR** (neat): 2924, 1787, 1610, 1456, 1225, 983, 828, 740 cm^{-1}. **m.p.** 58–60 °C.

4-methoxy-1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2b)



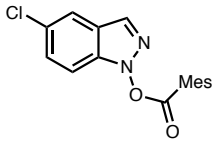
The general procedure A was followed starting from 1-methoxy-2-methyl-3-nitrobenzene (1.67 g, 10.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 4 : 1) provided the title product as a white solid in 26% overall yield (flour steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 1.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 6.98 (m, 3H), 6.56 (d, J = 7.7 Hz, 1H), 3.99 (s, 3H), 2.56 (s, 6H), 2.35 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 153.8, 141.4, 138.4, 136.8, 129.2, 128.9, 128.0, 125.9, 114.2, 101.0, 100.9, 55.6, 21.3, 20.2 ppm. **EA** Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85. Found: C, 69.65; H, 5.96. **IR** (neat): 2935, 1789, 1511, 1270, 1235, 1037, 981, 770 cm^{-1}. **m.p.** 93–96 ^{o}C.

4-fluoro-1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2c)



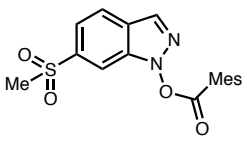
The general procedure A was followed starting from 1-fluoro-2-methyl-3-nitrobenzene (1.55 g, 10.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 68% overall yield (flour steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 1.0 Hz, 1H), 7.40 (ddd, J = 8.4 Hz, J = 7.7 Hz, J = 4.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H), 7.02–6.96 (s, 2H), 6.89 (dd, J = 9.8 Hz, J = 7.7 Hz, 1H), 2.56 (s, 6H), 2.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 155.8 (d, J = 254.5 Hz), 141.7, 138.9 (d, J = 8.7 Hz), 137.0, 129.0, 128.9 (d, J = 7.7 Hz), 126.4 (d, J = 1.7 Hz), 125.5, 112.6 (d, J = 24.3 Hz), 106.5 (d, J = 18.5 Hz), 104.4 (d, J = 4.4 Hz), 21.3, 20.3 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.5 ppm. **EA** Calcd. for $C_{17}H_{15}FN_2O_2$: C, 68.45; H, 5.07. Found: C, 68.44; H, 5.16. **IR** (neat): 2923, 1789, 1511, 1231, 1153, 981, 943, 772 cm^{-1}. **m.p.** 97–100 ^{o}C.

5-chloro-1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2d)



The general procedure B was followed starting from 5-chloro-2-nitrobenzonitrile (4.56 g, 25.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 42% overall yield (three steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.75 (d, J = 1.8 Hz, 1H), 7.42 (dd, J = 8.8 Hz, J = 1.9 Hz, 1H), 7.34 (d, J = 8.9 Hz, 1H), 6.99 (s, 2H), 2.56 (s, 6H), 2.35 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 141.7, 136.9, 135.3, 129.3, 129.0, 128.5, 127.9, 125.5, 123.0, 120.6, 109.5, 21.3, 20.3 ppm. **EA** Calcd. for $C_{17}H_{15}ClN_2O_2$: C, 64.87; H, 4.80. Found: C, 64.61; H, 4.97. **IR** (neat): 2921, 1774, 1221, 1154, 988, 951, 859, 794, 708 cm^{-1}. **m.p.** 105–108 ^{o}C.

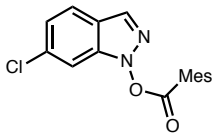
6-(methylsulfonyl)-1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2e)



The general procedure A was followed starting from 1-methyl-4-(methylsulfonyl)-2-nitrobenzene (6.46 g, 30.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 1 : 1) provided the title product as a white solid in 16% overall yield (three steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.26 (s, 1H), 7.01 (s, 2H), 3.13 (s, 3H), 2.58 (s, 6H), 2.37 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 142.1, 139.9, 137.3, 135.3, 129.9, 129.1, 124.8, 124.6, 123.0, 119.8, 109.2, 44.7, 21.4, 20.4 ppm. **EA** Calcd. for $C_{18}H_{18}SN_2O_4$:

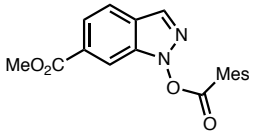
C, 60.32; H, 5.06. Found: C, 60.06; H, 5.18. **IR** (neat): 2927, 1789, 1310, 1224, 1145, 1080, 977, 770 cm^{-1}. **m.p.** 186–191 °C.

6-chloro-1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2f)



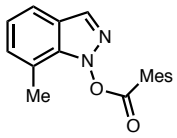
The general procedure B was followed starting from 1-methyl-4-(methylsulfonyl)-2-nitrobenzene (1.82 g, 10.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 1 : 1) provided the title product as a white solid in 45% overall yield (three steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 1.1 Hz, 1H), 7.68 (dd, J = 8.6 Hz, J = 0.7 Hz, 1H), 7.39 (dt, J = 1.8 Hz, J = 0.9 Hz, 1H), 7.22 (dd, J = 8.6 Hz, J = 1.7 Hz, 1H), 6.99 (s, 2H), 2.57 (s, 6H), 2.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 141.7, 137.1, 137.0, 134.4, 130.1, 129.0, 125.4, 123.3, 122.4, 120.8, 108.3, 21.4, 20.3 ppm. **EA** Calcd. for $C_{17}H_{16}ClN_2O_2$: C, 64.87; H, 4.80. Found: C, 64.84; H, 4.98. **IR** (neat): 2921, 1789, 1223, 1152, 977, 942, 918, 831, 611 cm^{-1}. **m.p.** 116–120 °C.

methyl 1-((2,4,6-trimethylbenzoyl)oxy)-1*H*-indazole-6-carboxylate (2g)



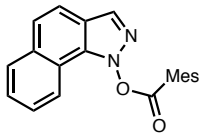
The general procedure A was followed starting from 4-methyl-3-nitrobenzoic acid (5.86 g, 30.0 mmol). 1-((2,4,6-trimethylbenzoyl)oxy)-1*H*-indazole-6-carboxylic acid was obtained as the product. An extra esterification step was carried out to prepare the methyl ester. Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 3 : 1) provided the title product as a light yellow solid in 12% overall yield (five steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 1.1 Hz, 1H), 8.02 (d, J = 1.1 Hz, 1H), 7.91 (dd, J = 8.5 Hz, J = 1.3 Hz, 1H), 7.81 (dd, J = 8.5 Hz, J = 0.9 Hz, 1H), 7.00 (s, 2H), 3.97 (s, 3H), 2.59 (s, 6H), 2.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 166.7, 141.8, 137.1, 136.2, 129.8, 129.6, 129.0, 125.4, 124.6, 122.6, 121.3, 110.7, 52.5, 21.4, 20.4 ppm. **EA** Calcd. for $C_{19}H_{18}N_2O_4$: C, 67.45; H, 5.36. Found: C, 67.17; H, 5.39. **IR** (neat): 2952, 1792, 1717, 1434, 1268, 1245, 1222, 975, 942, 734 cm^{-1}. **m.p.** 151–153 °C.

7-methyl-1*H*-indazol-1-yl 2,4,6-trimethylbenzoate (2h)



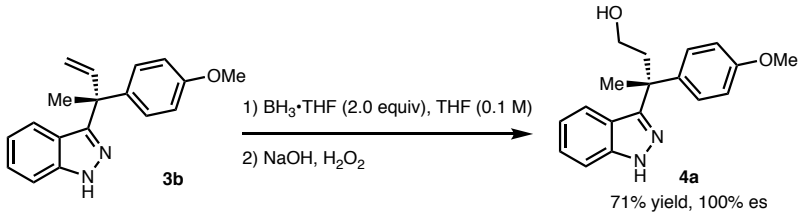
The general procedure A was followed starting from 1,3-dimethyl-2-nitrobenzene (3.02 g, 20.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a light yellow solid in 27% overall yield (four steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.58 (dt, J = 7.9 Hz, J = 1.0 Hz, 1H), 7.18 (dt, J = 6.9 Hz, J = 1.1 Hz, 1H), 7.15–7.09 (m, 1H), 6.98 (s, 2H), 2.59 (s, 3H), 2.58 (s, 6H), 2.35 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 141.8, 138.0, 137.1, 130.8, 129.3, 129.0, 125.2, 122.7, 122.5, 120.0, 118.9, 21.3, 20.6, 17.2 ppm. **EA** Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16. Found: C, 73.56; H, 6.25. **IR** (neat): 2926, 1783, 1610, 1224, 1155, 1036, 979, 738 cm^{-1}. **m.p.** 85–89 °C.

1*H*-benzo[*g*]indazol-1-yl 2,4,6-trimethylbenzoate (2i).



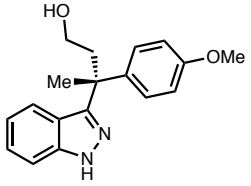
The general procedure A was followed starting from 2-(bromomethyl)-1-nitronaphthalene (2.66 g, 10.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a light solid in 38% overall yield (three steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41–8.29 (m, 1H), 8.03 (s, 1H), 8.00–7.94 (m, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.65–7.49 (m, 3H), 7.04 (s, 2H), 2.60 (s, 6H), 2.39 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 142.0, 138.0, 133.4, 132.2, 129.8, 129.3, 128.9, 127.0, 126.5, 125.1, 123.6, 121.7, 119.5, 119.0, 118.9, 21.4, 20.6 ppm. **EA** Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16. Found: C, 73.56; H, 6.25. **IR** (neat): 2926, 1783, 1610, 1224, 1155, 1036, 979, 738 cm^{-1}. **m.p.** 85–89 °C.

V. Derivatization



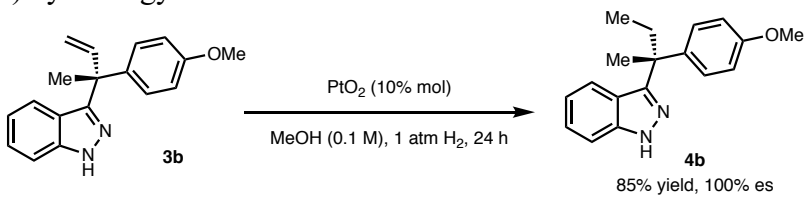
A screw-top reaction tube (Fisherbrand, 13 x 100 mm, catalog no. 14-959035C) equipped with a magnetic stir bar was charged with **3b** (55.7 mg, 0.200 mmol). Anhydrous THF (2.0 mL) was added via syringe. The reaction mixture was submerged into an ice bath and cooled to 0 ºC. BH_3·THF (0.4 mL, 1 M in THF, 2.0 equiv) was then added slowly via syringe and the reaction mixture was stirred at 0 ºC for 15 min. The ice bath was removed and the reaction mixture was stirred at room temperature (rt) for 1 h. The reaction mixture was resubmerged into an ice bath and cooled to 0 ºC. DI water (2 mL) and H_2O_2 (2 mL, 30% w/w in H_2O) were added sequentially. The ice bath was removed and the reaction mixture was vigorously stirred at rt for 1 h. Brine (5 mL) and Et_2O (5 mL) were added to quench the reaction. The layers were separated. The aqueous layer was extracted with Et_2O (3 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The residue was purified by silica gel column chromatography.

(*R*)-3-(1*H*-indazol-3-yl)-3-(4-methoxyphenyl)butan-1-ol (4a)



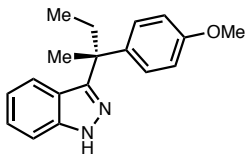
Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 2 : 1) provided the title product as a white solid in 71% yield (Run 1: 41.5 mg, 70% yield, 99.5:0.5 er, 100% es; Run 2: 43.3 mg, 73% yield, 99.5:0.5 er, 100% es). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dt, J = 8.5 Hz, J = 1.0 Hz, 1H), 7.30 (ddd, J = 8.3 Hz, J = 6.8 Hz, J = 1.1 Hz, 1H), 7.14 (d, J = 8.9 Hz, 2H), 7.02 (dt, J = 8.3 Hz, J = 1.0 Hz, 1H), 6.91 (ddd, J = 8.1 Hz, J = 6.8 Hz, J = 0.9 Hz, 1H), 6.80 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H), 3.74–3.60 (m, 2H), 2.63–2.34 (m, 2H), 1.86 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 153.2, 141.7, 139.3, 127.8, 126.8, 122.3, 120.9, 120.2, 113.6, 110.0, 59.4,

55.2, 45.5, 43.8, 27.2 ppm. **HRMS** (DART) m/z calcd. for $C_{18}H_{21}O_2N_2^+$ $[M+H]^+$: 297.1598; found 297.1612. **IR** (neat): 3224, 2932, 1511, 1464, 1252, 1184, 1045, 1030, 728 cm^{-1}. **m.p.** 166–168 °C. **Specific rotation** $[\alpha]_D^{23}$: –44.5 (*c* = 1.0, $CHCl_3$). **SFC** analysis: OJ-H (5:95 MeOH: $scCO_2$ to 40:60 MeOH: $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 4.70 (major), 4.94 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3b**.



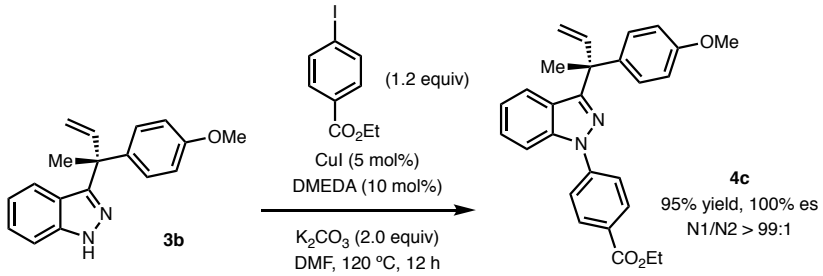
A screw-top reaction tube (Fisherbrand, 13 x 100 mm, catalog no. 14-959035C) equipped with a magnetic stir bar, was charged with **3b** (55.7 mg, 0.2 mmol). The reaction tube was sealed with a Teflon-lined screw cap, evacuated, and backfilled with dry nitrogen (this process was repeated a total of three times) by using a needle connected to a Schlenk line. Next, 10% PtO_2 (4.5 mg) was added into the reaction flask by temporarily removing the septum. Methanol (2.0 mL) was added via syringe. While the reaction mixture was stirring, the flask was briefly evacuated by using a needle connected to a Schlenk line until the solvent began to bubble. The Schlenk line was closed to vacuum, and the flask was then carefully backfilled with hydrogen using a needle connected to a hydrogen-filled balloon. This evacuation-refill cycle was repeated a total of three times. The reaction mixture was then stirred at rt for 24 h. The septum was removed slowly and carefully. Using a gentle stream of nitrogen directed into the flask, the hydrogen in the headspace was displaced. (Caution: ensure that hydrogen is fully removed by carefully bubbling nitrogen through the solution. This will reduce the risk of fire during the subsequent filtration). After 5 min, the mixture was poured onto a plug of Celite and filtered to remove PtO_2. The Celite pad was washed with additional EtOAc (ca. 10 mL). (Caution: during the filtration, solvent should be continuously added so that the Celite and other solids do not fully dry. The PtO_2 at the top of the filter cake may ignite if not continuously covered with solvent. After the filtration is complete, the wet filter cake should be carefully transferred to a properly labeled waste bottle containing water). After filtration, the solution was concentrated with the aid of a rotary evaporator and the residue was purified by flash column chromatograph.

(*R*)-3-(2-(4-methoxyphenyl)butan-2-yl)-1*H*-indazole (4b)



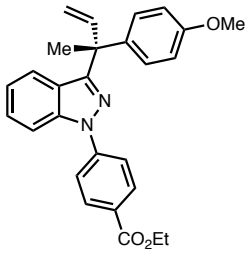
Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a white solid in 85% yield (Run 1: 50.5 mg, 90% yield, 99.5:0.5 er, 100% es; Run 2: 44.9 mg, 80% yield, 99.5:0.5 er, 100% es). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 8.4 Hz, *J* = 1.0 Hz, 1H), 7.31–7.23 (m, 1H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.04 (dt, *J* = 8.2 Hz, *J* = 1.0 Hz, 1H), 6.88 (ddd, *J* = 8.0 Hz, *J* = 6.9 Hz, *J* = 0.9 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.49–2.35 (m, 1H), 2.35–2.24 (m, 1H), 1.77 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 153.6, 141.8, 139.7, 128.0, 126.3, 122.2, 121.1, 119.9, 113.4, 109.6, 55.2, 44.1, 33.4, 26.1, 9.00 ppm. **HRMS** (DART) m/z calcd. for $C_{18}H_{21}ON_2^+$ $[M+H]^+$: 281.1648; found 281.1645. **IR** (neat): 3148, 2965, 2935, 1510, 1340, 1250, 1182, 1033, 827, 743 cm^{-1}. **m.p.** 63–68 °C. **Specific**

rotation $[\alpha]_D^{23}$: –11.0 (*c* = 1.0, $CHCl_3$). **SFC** analysis: AS-H (5:95 MeOH: $scCO_2$ to 20:80 MeOH: $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 4.51 (major), 4.70 min (minor), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3b**.



In a nitrogen-filled glovebox, an oven-dried reaction tube (Fisher 20 × 125 mm tubes – Cat. No. 1495937A) equipped with a stir bar, was charged successively with **3b** (55.7 mg, 0.2 mmol), ethyl 4-iodobenzoate (66.2 mg, 1.2 equiv), CuI (1.9 mg, 5 mol%), 1,2-dimethylethylenediamine (DMEDA, 1.8 mg, 10 mol%), K_2CO_3 (55.3 mg, 2.0 equiv) and 1 mL of DMF. The reaction tube was sealed with a screw cap (CLOSURE OT S/T 18-400TH 14, Cat. No. 033407G) containing a Teflon septa (Thermo Scientific SPTA PTFE/SIL F/18-400 10, Cat. No. 03394B), and the reaction tube was removed from the glovebox, and vigorously stirred at 120 ºC for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of silica gel, eluting with EtOAc and concentrated with the aid of a rotary evaporator. The crude material was purified by silica gel chromatography.

ethyl (*R*)-4-(3-(2-(4-methoxyphenyl)but-3-en-2-yl)-1*H*-indazol-1-yl)benzoate (4c)

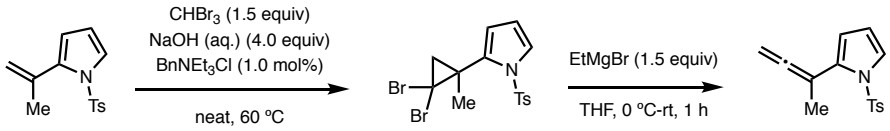


Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 10 : 1) provided the title product as a colorless oil in 95% yield (Run 1: 83.6 mg, 98% yield, 99.5:0.5 er, 100% es; Run 2: 78.5 mg, 92% yield, 99.5:0.5 er, 100% es). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.79 (dt, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H), 7.36 (ddd, *J* = 8.3 Hz, *J* = 6.9 Hz, *J* = 1.2 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.12 (dt, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H), 7.00 (ddd, *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 0.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.73 (dd, *J* = 17.4 Hz, *J* = 10.6 Hz, 1H), 5.24 (dd, *J* = 10.6 Hz, *J* = 1.1 Hz, 1H), 5.07 (dd, *J* = 17.3 Hz, *J* = 1.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.99 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 158.1, 153.5, 144.2, 144.0, 140.1, 138.2, 131.0, 128.4, 127.4, 127.1, 123.9, 123.0, 121.3, 121.2, 113.6, 113.5, 110.6, 61.1, 55.2, 47.5, 26.9, 14.4 ppm. **HRMS** (DART) m/z calcd. for $C_{27}H_{27}O_3N_2^+$ $[M+H]^+$: 428.2016; found 427.2022. **IR** (neat): 2980, 2835, 1713, 1604, 1510, 1272, 1250, 1104, 1089, 773 cm^{-1}. **Specific rotation** $[\alpha]_D^{23}$: –54.6 (*c* = 1.0, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH: $scCO_2$ to 40:60 MeOH: $scCO_2$ linear gradient over 8 min, 2.50 mL/min), 5.45 (minor), 5.83 min (major), 99.5:0.5 er. The absolute stereochemistry was assigned as (*R*) by analogy to **3b**.

VI. Preparation of Allenes

Allene synthesis: buta-2,3-dien-2-ylbenzene (**1a**),[2] 1-(buta-2,3-dien-2-yl)-4-methoxybenzene (**1b**),[2] 1-(buta-2,3-dien-2-yl)-2-fluorobenzene (**1c**),[3] 2-(buta-2,3-dien-2-yl)furan (**1d**),[4] 5-(buta-2,3-dien-2-yl)-2-methoxypyridine (**1e**),[5] 1-bromo-4-(penta-1,2-dien-3-yl)benzene (**1g**),[6] 1-(buta-2,3-dien-2-yl)-4-(trifluoromethyl)benzene (**1j**),[2] 1-(buta-2,3-dien-2-yl)-2-methylbenzene (**1k**)[4] are known compounds and were prepared by previously reported procedures. Allene 2-(buta-2,3-dien-2-yl)-1-tosyl-1*H*-pyrrole (**1f**), 1-(1-cyclopropylpropa-1,2-dien-1-yl)-4-methoxybenzene (**1h**), 6-chloro-4-vinylidenechromane (**1i**) and (5-methylhexa-1,2-dien-3-yl)benzene (**1l**) are unknown compounds and were prepared by previously reported procedures.[4]

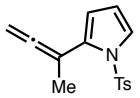
General Procedures for the Synthesis of 1,1-Disubstituted Allenes[4]



Preparation of 1,1-Dibromocyclopropanes:
1,1-Dibromocyclopropanes were prepared according to a similar procedure described for 2-(2,2-dibromo-1-methylcyclopropyl)-1-tosyl-1*H*-pyrrole. A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 2-(prop-1-en-2-yl)-1-tosyl-1*H*-pyrrole (2.61 g, 10.0 mmol), bromoform (1.3 mL, 15.0 mmol), and triethylbenzylammonium chloride (0.023 g, 0.1 mmol). A solution of NaOH (1.6 g) in water (1.6 mL) was added dropwise. The resulting mixture was submerged into a 60 ºC oil bath and stirred vigorously for 24 h. After cooled to rt, the reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL x 3). The combined organic phase was separated, dried over Na_2SO_4, filtered and concentrated with the aid of a rotary evaporator. The residue was purified via flash column chromatography to provide the indazole electrophile (Hexanes ~ Hexanes : EtOAc = 5 : 1, 2.56 g, 59% yield).

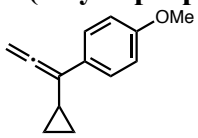
Preparation of 1,1-Disubstituted Allenes:
1,1-Disubstituted allenes were prepared according to a similar procedure described for 2-(buta-2,3-dien-2-yl)-1-tosyl-1H-pyrrole (**1f**). Under nitrogen, a 25 mL round bottom flask equipped with a magnetic stir bar was charged with 2-(2,2-dibromo-1-methylcyclopropyl)-1-tosyl-1*H*-pyrrole (2.56 g, 5.9 mmol), dry THF (6 mL). The flask was submerged into an ice/water bath and cooled to 0 ºC. To the suspension was slowly added ethylmagnesium bromide (8.85 mL, 8.85 mmol, 1.0 M in THF) over 30 min. After stirred at 0 ºC for 1 h, the reaction mixture was quenched with 3M HCl solution (2 mL) and diluted with Et_2O (20 mL). The phases were separated and the organic phase was dried over Na_2SO_4, filtered and concentrated with the aid of a rotary evaporator. The residue was purified via flash column chromatography to provide the indazole electrophile (Hexanes ~ Hexanes : EtOAc = 5 : 1, 1.31 g, 81% yield).

2-(buta-2,3-dien-2-yl)-1-tosyl-1*H*-pyrrole (1f)



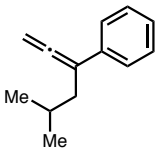
The reported procedure was followed starting from 2-(prop-1-en-2-yl)-1-tosyl-1*H*-pyrrole (2.61 g, 10.0 mmol). Silica gel column chromatography (Hexanes ~ Hexanes : EtOAc = 5 : 1) provided the title product as a light yellow solid in 48% overall yield (80% purity, two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.09 (dd, J = 3.3 Hz, J = 2.2 Hz, 1H), 7.00 (s, 1H), 6.29 (dd, J = 3.3 Hz, J = 1.7 Hz, 1H), 4.95 (qd, J = 3.1 Hz, J = 1.0 Hz, 2H), 2.40 (s, 3H), 1.93 (t, J = 3.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.6, 145.0, 143.4, 136.1, 130.0, 126.8, 121.5, 116.1, 112.6, 112.4, 107.8, 76.7, 21.6, 16.7 ppm. **HRMS** (DART) m/z calcd. for $C_{15}H_{16}NO_2S^+$ $[M+H]^+$: 274.0896; found 274.0905. **IR** (neat): 3137, 2921, 1366, 1170, 1126, 1058, 672, 602, 587 cm^{-1}. **m.p.** 68–73 °C.

1-(1-cyclopropylpropa-1,2-dien-1-yl)-4-methoxybenzene (1h)



The reported procedure was followed starting from 1-(1-cyclopropylvinyl)-4-methoxybenzene (1.74 g, 10.0 mmol). Silica gel column chromatography (Pentane ~ Pentane : Ether = 10 : 1) provided the title product as a light yellow solid in 55% overall yield (95% purity, two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.08 (d, J = 2.9 Hz, 2H), 3.82 (s, 3H), 1.57–1.50 (m, 1H), 0.92–0.82 (m, 2H), 0.57–0.50 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.5, 158.6, 129.1, 127.3, 113.8, 107.5, 79.2, 55.3, 10.5, 6.8 ppm. **HRMS** (DART) m/z calcd. for $C_{13}H_{15}O^+$ $[M+H]^+$: 187.1117; found 187.1117. **IR** (neat): 3000, 2834, 1937, 1508, 1242, 1175, 1035, 831, 604 cm^{-1}.

(5-methylhexa-1,2-dien-3-yl)benzene (1l)



The reported procedure was followed starting from (4-methylpent-1-en-2-yl)benzene (1.60 g, 10.0 mmol). Silica gel column chromatography (Pentane) provided the title product as a colorless oil in 62% overall yield (two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 5.04 (t, J = 2.9 Hz, 2H), 2.32 (dt, J = 6.5 Hz, J = 2.8 Hz, 2H), 1.87 (dp, J = 13.4 Hz, J = 6.7 Hz, 1H), 0.98 (d, J = 6.5 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.3, 136.6, 128.4, 126.5, 126.2, 103.8, 77.2, 39.4, 26.8, 22.7 ppm. **HRMS** (DART) m/z calcd. for $C_{13}H_{17}^+$ $[M+H]^+$: 173.1325; found 173.1331. **IR** (neat): 2953, 2925, 2862, 1939, 1494, 1451, 845, 762, 693 cm^{-1}.

VI. Computational Details

All calculations were performed with Gaussian 09.[16] Images of the 3D structures of molecules were generated using CYLview.[17] The geometries of all intermediates and transition states were optimized with the B3LYP functional[18] and the mixed basis set with SDD for Cu and 6-31G(d) basis set for other atoms. Vibrational frequency calculations were performed for all of the stationary points to confirm if each optimized structure is a local minimum or a transition state structure. Single-point energy calculations were performed with M06 functional[19] and the mixed basis set with SDD for Cu and 6-311+G(d,p) basis set for other atoms. Solvation effects were considered by applying the implicit SMD solvation model[20] with THF as solvent in single-point energy calculations.

VII. Additional Computational Results

Four competing hydrocupration transition states were calculated leading to the formation of allylic copper intermediates. The most stable transition state (**TS1**) requires 15.9 kcal/mol activation energy and leads to the formation of **5**. Isomer **TS1b** leading to the formation of **7** is 1.8 kcal/mol higher in energy than **TS1** and is destabilized by steric repulsions between the ligand and the bulkier phenyl group which is oriented towards the copper center. Two isomers **TS1c** and **TS1d** leading to the formation of tertiary benzylic Cu complexes also require higher activation barriers by 2.1 kcal/mol and 3.4 kcal/mol, respectively. These differences can be attributed to increased strain associated with the formation of tertiary C-Cu bonds.

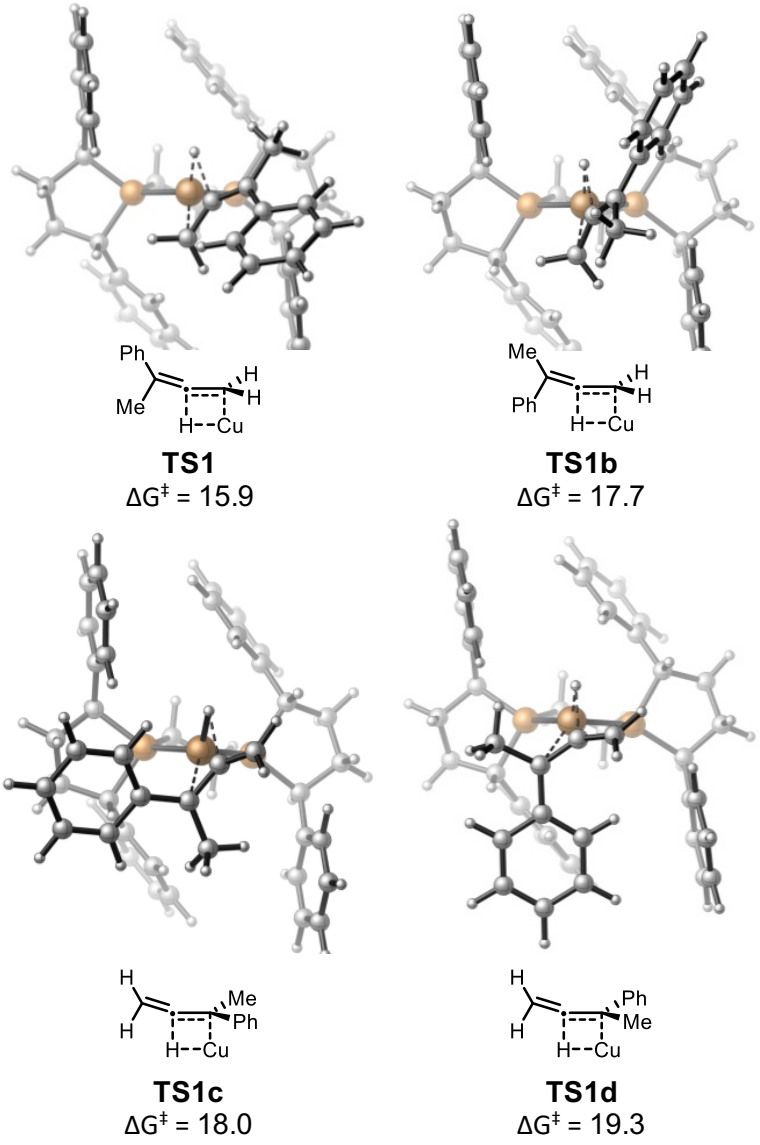
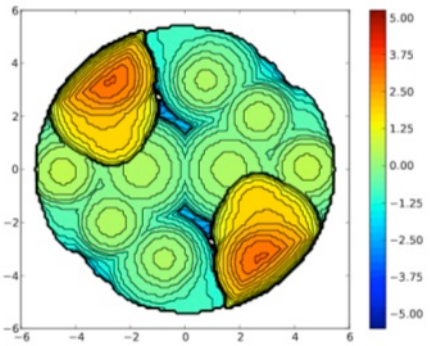


Figure S1: Calculated energies of competing hydrocupration transition states. All energies are relative to the separated LCuH catalyst **4** and allene **2a**. All energies are in kcal/mol.

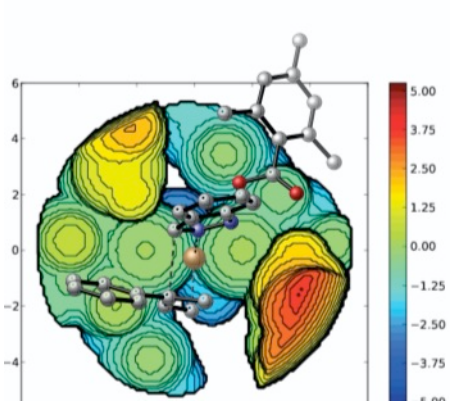
The enantioselectivity of the reaction is controlled by the unfavorable steric repulsions between the carboxylate leaving group and the proximal phenyl group on the Ph-BPE ligand in **TS2d**, which are avoided in the favorable transition state **TS2c**. To quantify these steric repulsions, we calculated the distortion energies of Ph-BPE ligand in their transition state geometries (**TS2c**, **TS2d**) relative to the Ph-BPE in CuH species **4** ($\Delta E_{\text{dist-Ph-PBE}}$). These results indicate that the ligand is significantly less distorted in **TS2c** ($\Delta E_{\text{dist-Ph-PBE}}$ = 1.4 kcal/mol) relative to that in **TS2d** ($\Delta E_{\text{dist-Ph-PBE}}$ = 5.1 kcal/mol). The difference in distortion energies ($\Delta E_{\text{dist-Ph-PBE}}$ = 3.7 kcal/mol) contributes to the relative stabilities of these two transition states ($\Delta\Delta G^{\ddagger}$ = 5.4 kcal/mol). Furthermore, the distortion of the Ph-BPE ligand can be visualized via steric contour plots,[21] which show that the ligand in **TS2c** resembles the structure in **4** more closely, when compared to the ligand in **TS2d** where

substrate is placed in an occupied quadrant (indicated by orange and yellow in the contour plots), leading to the greater distortion of the ligand.



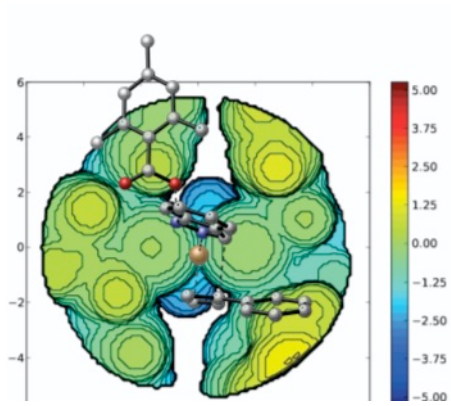
4

$E_{\text{dist-Ph-BPE}}$ = 0.0



TS2c

$E_{\text{dist-Ph-BPE}}$ = 1.4



TS2d

$E_{\text{dist-Ph-BPE}}$ = 5.1

Figure S2: Calculated ligand distortion energies ($\Delta E_{\text{dist-Ph-PBE}}$) and steric contour plots of the Ph-BPE ligand in **4**, **TS2c**, and **TS2d**. All energies are in kcal/mol.

The *Z*-allylic Cu complex **5** is less reactive than the *E*-isomer **7** in the indazole addition step. This is attributed to the unfavorable steric repulsions between the indazole and bulky phenyl group, which is placed in the pseudoaxial position in **TS2a** and **TS2b**. These unfavorable interactions lead to elongation of the forming C-C bond, which results in a later transition state, when compared to the reactions with the intermediate **7** as it can be observed both from the forming C-C bond, as well as the breaking C-Cu bonds.

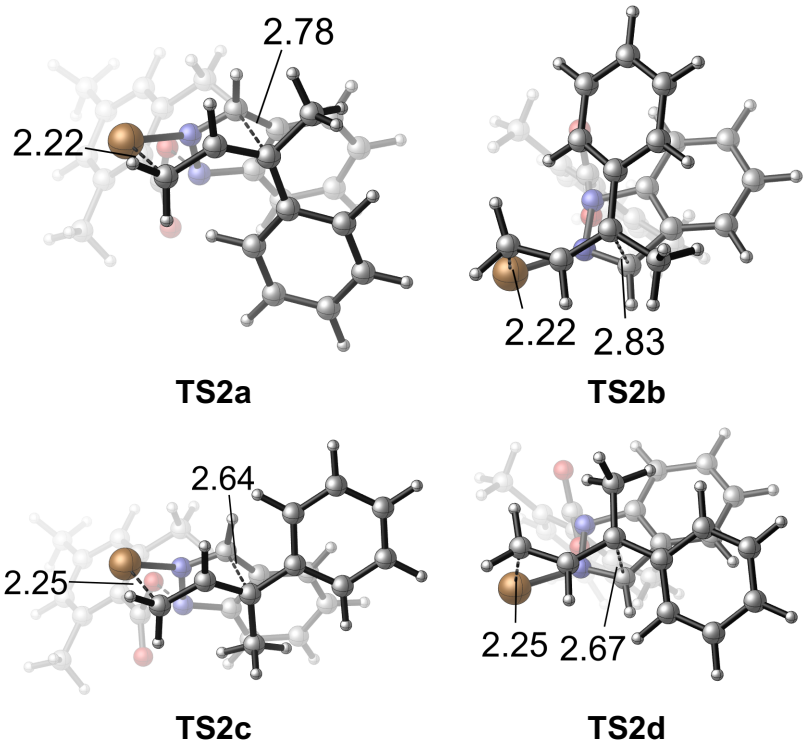


Figure S3: Calculated Zimmerman-Traxler transition state structures involving both intermediates **5** and **7**. The Ph-BPE ligand is omitted for clarity.

As oxidative addition mechanisms have been proposed to be operative in the indole alkylation reaction reported earlier,[22] we investigated this pathway from the most stable intermediate **7**, leading to the cationic Cu^{III} complex with copper bound to the either C (**9**) or N (**10**) of the indazole. Both oxidative addition transition states **TS3**, **TS4** were found to be disfavored relative to **TS2c** ($\Delta\Delta G^{\ddagger}$ = 7.0, 12.9 kcal/mol respectively). This reactivity difference is driven by thermodynamically less favorable formation of Cu^{III} intermediates (**9** and **10**).

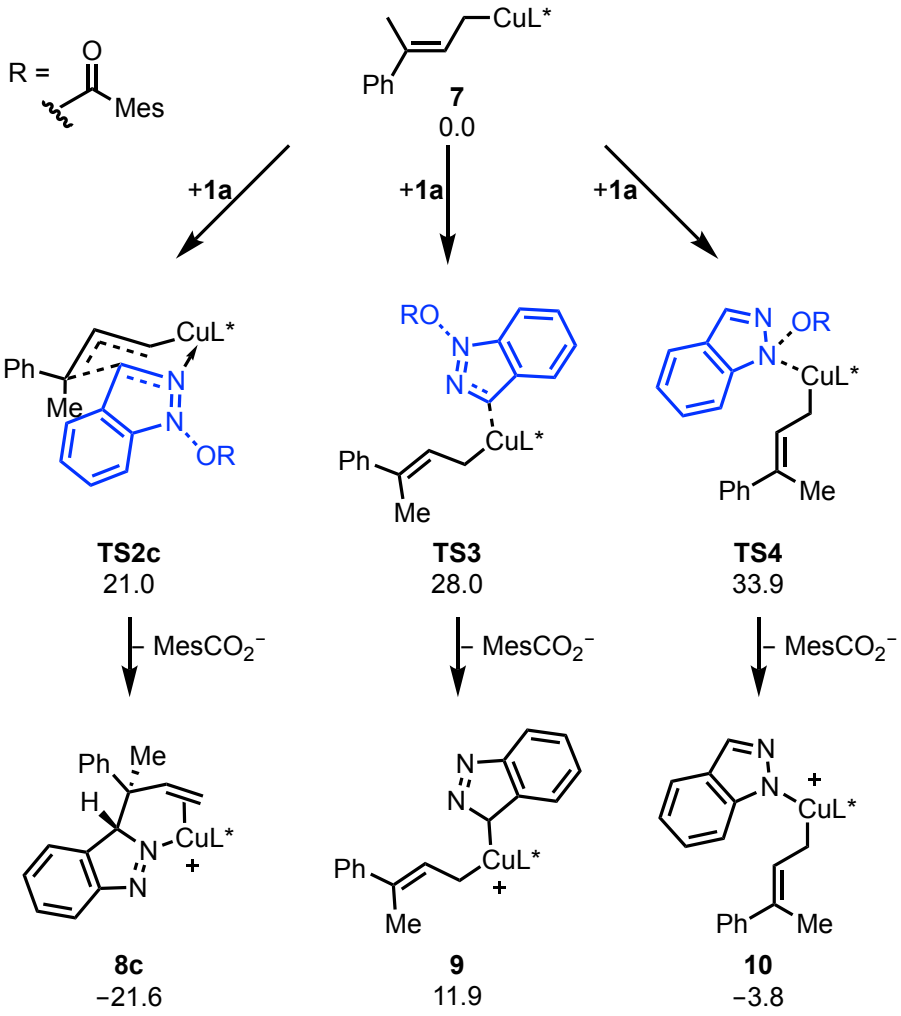


Figure S4: Calculated energies of competing oxidative addition pathways. All energies are Gibbs free energy in kcal/mol relative to **1a** and **7**.

VIII. Cartesian Coordinates (Å) and Energies of Optimized Structures.

```
2a
B3LYP SCF energy:      -387.02531234 a.u.
B3LYP enthalpy:        -386.848705 a.u.
B3LYP free energy:     -386.893183 a.u.
M06 SCF energy in solution:      -386.82076134 a.u.
M06 enthalpy in solution:        -386.644154 a.u.
M06 free energy in solution:     -386.688632 a.u.

Cartesian coordinates
ATOM       X           Y           Z
C        3.175867   -1.398669    0.000089
H        3.581087   -1.806565   -0.925915
```

H	3.581161	-1.806434	0.926115
C	2.254965	-0.471796	0.000058
C	1.337025	0.474846	-0.000017
C	-0.117603	0.156492	0.000004
C	-0.571358	-1.176417	-0.000091
C	-1.080590	1.179159	0.000055
C	-1.930326	-1.471763	-0.000079
H	0.157454	-1.981797	-0.000172
C	-2.445390	0.881894	0.000085
H	-0.769972	2.218731	0.000094
C	-2.878230	-0.442898	0.000029
H	-2.253441	-2.509686	-0.000135
H	-3.169050	1.692990	0.000149
H	-3.939886	-0.674460	0.000042
C	1.779044	1.928351	-0.000106
H	1.401374	2.456545	-0.884645
H	1.401685	2.456454	0.884617
H	2.869158	1.999034	-0.000316

4

B3LYP SCF energy: -2197.96232646 a.u.
B3LYP enthalpy: -2197.308922 a.u.
B3LYP free energy: -2197.415925 a.u.
M06 SCF energy in solution: -2197.34436935 a.u.
M06 enthalpy in solution: -2196.690965 a.u.
M06 free energy in solution: -2196.797968 a.u.

Cartesian coordinates

ATOM	X	Y	Z
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Cu	0.000156	-0.000121	-1.761683
P	-0.916768	1.339728	-0.051480
C	-0.112947	3.063585	0.136199
C	-1.246606	3.992356	0.617707
C	-2.532261	3.533908	-0.080534
C	-2.679157	2.013154	0.174982
H	-1.009436	5.041640	0.402646
H	-1.383242	3.910782	1.703311
H	-3.416471	4.071130	0.282583
H	-2.463341	3.721481	-1.159926
P	0.916942	-1.339774	-0.051292
C	0.112570	-3.063400	0.136513
C	1.246034	-3.992556	0.617736
C	2.531742	-3.534406	-0.080614
C	2.679127	-2.013763	0.175180

H	1.008531	-5.041746	0.402579
H	1.382854	-3.911163	1.703331
H	3.415826	-4.071974	0.282298
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H	0.625809	-1.123761	2.419384
H	1.519155	0.213729	1.685884
C	-0.639382	0.431163	1.569320
H	-0.115074	-3.332875	-0.902345
H	2.921542	-1.880848	1.238249
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C	-3.664882	-2.962356	2.263420
C	-2.380223	-2.741352	0.225772
C	-1.271881	-3.345218	2.276285
C	-2.496219	-3.296380	2.948397
C	-3.602148	-2.684296	0.895298
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H	-0.378883	-3.614424	2.832532
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H	-4.501207	-2.418146	0.346841
H	-4.615810	-2.924833	2.788080
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C	3.618715	-1.126585	-2.025728
C	4.948046	-0.927689	-0.024994
C	5.976877	-0.335359	-0.760954
C	4.644135	-0.532504	-2.762171
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H	5.072335	-1.079527	1.045354
H	6.893425	-0.032937	-0.260409
H	4.511339	-0.373118	-3.828869
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C	-3.618261	1.125467	-2.025984
C	-4.643657	0.531470	-2.762547
C	-5.977088	0.335440	-0.761684
H	-5.072860	1.079898	1.044655
H	-2.693549	1.400120	-2.526528
H	-4.510569	0.371686	-3.829150
H	-6.893890	0.033478	-0.261326
H	-6.624335	-0.327375	-2.711191
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C	3.664931	2.963399	2.262396

C	1.271905	3.346089	2.275625
C	2.379891	2.741753	0.225058
C	3.601953	2.684966	0.894367
C	2.496372	3.297525	2.947511
H	0.378992	3.615391	2.831963
H	2.342017	2.524680	-0.840355
H	4.500919	2.418725	0.345803
H	2.533405	3.525423	4.009839
H	4.615960	2.926092	2.786889
H	-0.625301	1.124242	2.419207
H	-1.518707	-0.213418	1.686116

1a

B3LYP SCF energy: -917.32914459 a.u.
B3LYP enthalpy: -917.013241 a.u.
B3LYP free energy: -917.082155 a.u.
M06 SCF energy in solution: -916.94783050 a.u.
M06 enthalpy in solution: -916.631927 a.u.
M06 free energy in solution: -916.700841 a.u.

Cartesian coordinates

ATOM	X	Y	Z
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C	-5.209503	-0.979940	-0.808430
C	-4.073882	-1.789635	-1.056159
C	-2.815053	-1.444814	-0.590053
C	-3.312480	1.672066	1.155368
H	-5.981840	0.815297	0.100351
H	-6.175043	-1.293879	-1.194350
H	-4.194123	-2.705821	-1.627713
H	-1.945595	-2.065756	-0.777708
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C	0.398107	0.516497	-0.284907
O	-0.099761	1.216992	-1.124460
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C	2.239708	-1.152230	0.265625
C	2.791426	1.127952	-0.477863
C	3.608809	-1.419303	0.347825
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C	4.577809	-0.455143	0.058193

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H	4.883921	1.569720	-0.592219
C	2.418684	2.517560	-0.945713
H	1.983310	2.496036	-1.949380
H	1.672938	2.986876	-0.296176
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H	6.654370	-0.164921	-0.483568
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H	6.256931	-1.822072	0.010122
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H	0.772264	-2.117274	1.544033
H	0.499099	-2.385455	-0.173279
H	1.821588	-3.226636	0.645077

TS1

B3LYP SCF energy: -2584.97447715 a.u.
B3LYP enthalpy: -2584.144519 a.u.
B3LYP free energy: -2584.273903 a.u.
M06 SCF energy in solution: -2584.16185535 a.u.
M06 enthalpy in solution: -2583.331897 a.u.
M06 free energy in solution: -2583.461281 a.u.
Imaginary frequency: -712.6835 cm-1

Cartesian coordinates

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C	-0.490567	0.262008	3.166241
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H	2.170636	0.846480	3.594324
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C	-3.319310	-0.697593	-1.860011
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C	4.057537	3.937345	0.284280
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H	4.340873	4.954708	0.025716
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C	-2.413246	-1.315568	2.779961
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H	-1.905127	2.518732	1.803553
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C	4.013280	-2.762830	-0.277333
C	4.382065	-2.754575	-1.639128
C	5.005059	-3.138137	0.652454
C	5.667109	-3.101378	-2.044906
H	3.642467	-2.479283	-2.382949
C	6.296317	-3.478331	0.245189
H	4.771346	-3.154337	1.711976
C	6.638376	-3.463990	-1.106102
H	5.911780	-3.093523	-3.104593
H	7.035754	-3.755442	0.992944
H	7.642266	-3.731543	-1.425177
C	2.234357	-2.879271	1.566897
H	2.597350	-3.893759	1.772128
H	2.627232	-2.229855	2.363501
H	1.142574	-2.867440	1.643407

5

B3LYP SCF energy: -2585.04337330 a.u.
B3LYP enthalpy: -2584.206156 a.u.
B3LYP free energy: -2584.336004 a.u.
M06 SCF energy in solution: -2584.23251208 a.u.
M06 enthalpy in solution: -2583.395295 a.u.
M06 free energy in solution: -2583.525143 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	1.044839	-0.001811	0.919518
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C	3.127900	-1.371582	2.052907
C	2.886862	0.017220	1.407991
H	1.940575	-2.723718	3.306187

H	1.857361	-1.019585	3.762037
H	4.051275	-1.358980	2.644489
H	3.255590	-2.131289	1.272054
P	-1.418084	1.769466	-0.325376
C	-1.064914	3.519156	-1.005970
C	-2.388026	4.289940	-0.838564
C	-3.517646	3.315267	-1.184310
C	-3.307512	2.031621	-0.341712
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H	-2.512730	4.628183	0.197904
H	-4.509026	3.740807	-0.988785
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H	0.680738	-2.349849	1.268902
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H	-1.290172	2.854576	1.915296
H	-1.748552	1.149867	1.980251
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H	-0.922421	3.337927	-2.079358
H	-3.577649	2.267166	0.695736
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C	2.622058	5.268134	0.458536
C	1.436894	3.785230	-1.040147
C	0.206381	5.103786	0.555318
C	1.404535	5.654273	1.019153
C	2.633971	4.328352	-0.575986
H	1.456267	3.054148	-1.845647
H	-0.728048	5.429671	1.001830
H	1.381146	6.391005	1.818161
H	3.573298	4.012560	-1.019949
H	3.552412	5.698812	0.818874
C	-4.142146	0.851032	-0.789498
C	-5.781855	-1.285057	-1.624647
C	-3.956071	0.249666	-2.044377
C	-5.161297	0.359191	0.037660
C	-5.976045	-0.698450	-0.373578
C	-4.767552	-0.806739	-2.458257
H	-3.159665	0.598021	-2.696854
H	-5.320722	0.811845	1.013970
H	-6.763373	-1.059590	0.283273
H	-4.604175	-1.259165	-3.432713
H	-6.413068	-2.108249	-1.948072
C	3.860289	0.377104	0.306164
C	5.741666	1.028986	-1.689916
C	4.781402	1.416488	0.496120
C	3.897683	-0.333568	-0.904587
C	4.828388	-0.009415	-1.891719

C	5.716591	1.740893	-0.489967
H	4.768532	1.976590	1.428848
H	3.193815	-1.142541	-1.079302
H	4.838838	-0.570433	-2.822590
H	6.425984	2.546449	-0.316756
H	6.466716	1.278111	-2.460219
C	-0.703305	-1.511057	2.640227
C	-3.307847	-1.453106	3.729334
C	-0.920907	-1.107445	3.966148
C	-1.818482	-1.892944	1.872908
C	-3.106163	-1.861462	2.407696
C	-2.210201	-1.080257	4.505601
H	-0.082687	-0.823299	4.595363
H	-1.668803	-2.211183	0.843434
H	-3.949510	-2.155233	1.789288
H	-2.352501	-0.770700	5.538060
H	-4.309168	-1.434190	4.151550
H	0.474954	1.313530	2.960194
H	1.069696	2.306403	1.626059
Cu	-0.099416	0.042637	-1.173404
C	0.099132	-1.182368	-2.753949
H	1.160043	-1.400007	-2.868742
H	-0.264486	-0.658477	-3.645034
C	-0.769007	-2.314525	-2.410531
H	-1.813740	-2.134244	-2.677782
C	-0.576573	-3.496356	-1.742747
C	-1.790506	-4.356834	-1.431281
H	-2.670850	-3.990979	-1.970568
H	-1.633956	-5.407018	-1.715650
H	-2.058033	-4.363597	-0.362693
C	0.723746	-3.997864	-1.251679
C	0.797422	-4.792118	-0.082863
C	1.943797	-3.762011	-1.926087
C	2.011472	-5.279523	0.403244
H	-0.113087	-5.028756	0.459335
C	3.156182	-4.253163	-1.444478
H	1.929246	-3.221939	-2.865345
C	3.205231	-5.007791	-0.268071
H	2.020907	-5.882467	1.308841
H	4.069630	-4.059002	-2.002573
H	4.151071	-5.392895	0.103862

6-R

B3LYP SCF energy: -2585.03296435 a.u.

B3LYP enthalpy: -2584.196059 a.u.

B3LYP free energy: -2584.325670 a.u.
M06 SCF energy in solution: -2584.22856741 a.u.
M06 enthalpy in solution: -2583.391662 a.u.
M06 free energy in solution: -2583.521273 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	1.003083	-0.496730	1.153868
C	0.197379	-1.847126	2.247254
C	1.323103	-2.356782	3.173080
C	2.629923	-2.312480	2.375642
C	2.758303	-0.886421	1.790034
H	1.093598	-3.366644	3.533860
H	1.422537	-1.715261	4.057372
H	3.502564	-2.549056	2.996136
H	2.598635	-3.051647	1.565603
P	-0.994425	1.697278	-0.282422
C	-0.225334	3.242539	-1.107988
C	-1.368239	4.276872	-1.184876
C	-2.665266	3.505870	-1.451759
C	-2.764074	2.389637	-0.384637
H	-1.162046	5.023392	-1.961458
H	-1.465905	4.820202	-0.236966
H	-3.548572	4.153937	-1.407933
H	-2.641873	3.061561	-2.454900
H	-0.020065	-2.639329	1.521108
H	2.921249	-0.198474	2.630581
C	-0.643069	1.825880	1.554695
H	-0.652766	2.871992	1.884598
H	-1.488382	1.323888	2.040503
C	0.675801	1.155204	1.986054
H	-0.027606	2.894046	-2.128954
H	-2.941799	2.875483	0.584270
C	1.092755	3.692562	-0.516604
C	3.594656	4.428678	0.566933
C	2.285910	3.123633	-0.993546
C	1.181882	4.643757	0.511612
C	2.419782	5.009088	1.046416
C	3.522808	3.481894	-0.458011
H	2.241367	2.387947	-1.793640
H	0.284101	5.116931	0.898233
H	2.462670	5.753663	1.837287
H	4.426698	3.017042	-0.840301
H	4.556785	4.715502	0.982704
C	-3.869141	1.382094	-0.615288
C	-5.991488	-0.422462	-1.041283
C	-3.892869	0.560306	-1.753713

C	-4.923465	1.280802	0.303082
C	-5.977837	0.388685	0.094027
C	-4.944397	-0.332710	-1.962456
H	-3.081885	0.600989	-2.476475
H	-4.920809	1.910237	1.190551
H	-6.788172	0.332629	0.816641
H	-4.943856	-0.960758	-2.849528
H	-6.810150	-1.117285	-1.208733
C	3.888813	-0.696862	0.803557
C	6.051030	-0.362538	-0.975230
C	4.888383	0.253436	1.054787
C	3.990881	-1.478967	-0.358029
C	5.060589	-1.312888	-1.237632
C	5.961749	0.420457	0.176169
H	4.829068	0.865526	1.952275
H	3.227552	-2.219397	-0.581005
H	5.119842	-1.928041	-2.131688
H	6.729411	1.158010	0.396938
H	6.885163	-0.237377	-1.660420
C	-1.109090	-1.451973	2.900463
C	-3.591102	-0.691424	4.014972
C	-1.176102	-0.827648	4.156448
C	-2.314904	-1.695841	2.221497
C	-3.541690	-1.316970	2.766821
C	-2.403485	-0.453160	4.708389
H	-0.268278	-0.636708	4.721444
H	-2.283953	-2.192119	1.254909
H	-4.456039	-1.508906	2.212902
H	-2.428721	0.022335	5.685731
H	-4.545207	-0.400237	4.446095
H	0.700210	1.058480	3.078138
H	1.523639	1.788066	1.696926
Cu	-0.018206	-0.286398	-0.998750
C	0.098869	-1.484177	-2.670018
C	0.100068	-2.826478	-2.002547
C	-1.041952	-3.335704	-1.328180
C	1.247543	-3.654393	-1.968196
C	-1.023980	-4.550576	-0.648775
H	-1.960284	-2.753290	-1.323346
C	1.268826	-4.867969	-1.275014
H	2.139500	-3.352619	-2.507116
C	0.138696	-5.329702	-0.600432
H	-1.928736	-4.894085	-0.150610
H	2.178188	-5.466251	-1.283484
H	0.152683	-6.277613	-0.069452
C	1.382458	-1.126117	-3.424163
H	1.346177	-0.090335	-3.780090

H	2.275749	-1.209710	-2.796824
H	1.537451	-1.761048	-4.315273
C	-1.127815	-1.186135	-3.443417
H	-2.036640	-1.659635	-3.071467
C	-1.274398	-0.428405	-4.552340
H	-0.446852	0.081898	-5.037199
H	-2.251190	-0.303525	-5.012674

6-S

B3LYP SCF energy: -2585.03353710 a.u.
B3LYP enthalpy: -2584.196841 a.u.
B3LYP free energy: -2584.326743 a.u.
M06 SCF energy in solution: -2584.22800463 a.u.
M06 enthalpy in solution: -2583.391309 a.u.
M06 free energy in solution: -2583.521211 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	0.901684	-0.324640	1.307419
C	0.180948	-1.687832	2.435227
C	1.237580	-1.906201	3.535273
C	2.609229	-1.809218	2.861558
C	2.648965	-0.481938	2.064789
H	1.088098	-2.872809	4.031862
H	1.161309	-1.132184	4.309458
H	3.431657	-1.841024	3.586031
H	2.749744	-2.656839	2.179611
P	-1.217784	1.589042	-0.338305
C	-0.549170	3.155102	-1.204492
C	-1.758105	4.104991	-1.321932
C	-2.984494	3.236276	-1.620808
C	-3.036140	2.121971	-0.546999
H	-1.584961	4.859823	-2.098692
H	-1.923117	4.645191	-0.381220
H	-3.916038	3.814516	-1.614621
H	-2.893016	2.786876	-2.618117
H	0.195843	-2.568438	1.780423
H	2.717333	0.338990	2.790401
C	-0.985687	1.838906	1.508310
H	-1.108351	2.894914	1.778456
H	-1.811028	1.286002	1.973009
C	0.358715	1.314701	2.047971
H	-0.317477	2.786690	-2.211279
H	-3.308698	2.596499	0.405044
C	0.732199	3.707235	-0.618443

C	3.168970	4.629034	0.465792
C	1.962488	3.198697	-1.070318
C	0.748788	4.692845	0.380469
C	1.955425	5.150708	0.915985
C	3.167353	3.650311	-0.531588
H	1.970827	2.439586	-1.850115
H	-0.181697	5.120812	0.742176
H	1.943557	5.920629	1.683429
H	4.103679	3.233271	-0.891001
H	4.106880	4.987295	0.881824
C	-4.039029	1.024294	-0.827680
C	-5.982318	-0.944682	-1.370326
C	-3.895987	0.155608	-1.920778
C	-5.171281	0.886161	-0.012976
C	-6.137068	-0.086872	-0.280479
C	-4.856365	-0.819813	-2.188732
H	-3.021391	0.231183	-2.560112
H	-5.300467	1.550116	0.839066
H	-7.010128	-0.170875	0.361795
H	-4.722831	-1.483414	-3.038951
H	-6.731506	-1.702799	-1.582212
C	3.814423	-0.359857	1.108271
C	6.053006	-0.155289	-0.592831
C	4.758470	0.661956	1.279938
C	4.009361	-1.278777	0.065017
C	5.117626	-1.177144	-0.775834
C	5.869013	0.765910	0.438803
H	4.624695	1.382196	2.084312
H	3.288237	-2.074462	-0.104481
H	5.247983	-1.898009	-1.578629
H	6.591444	1.563026	0.595681
H	6.916391	-0.079532	-1.248328
C	-1.251209	-1.462281	2.866815
C	-3.954241	-1.024167	3.554819
C	-1.594896	-0.834550	4.074059
C	-2.291961	-1.875887	2.017651
C	-3.627657	-1.655807	2.351907
C	-2.933021	-0.619819	4.415379
H	-0.820201	-0.516814	4.765663
H	-2.044557	-2.376759	1.084602
H	-4.411221	-1.974786	1.670875
H	-3.174224	-0.138580	5.359912
H	-4.994287	-0.856738	3.821578
H	0.321504	1.258416	3.142945
H	1.158297	2.018534	1.787061
Cu	-0.005986	-0.322801	-0.883260
C	1.641157	0.191505	-3.968234

H	0.836341	0.406189	-4.666084
H	2.571657	0.731760	-4.122535
C	1.520207	-0.707494	-2.960888
H	2.409291	-0.857384	-2.345617
C	0.332194	-1.475228	-2.545421
C	-0.816595	-1.427250	-3.560900
H	-1.116109	-0.394892	-3.780884
H	-0.525177	-1.885468	-4.522782
H	-1.706454	-1.955185	-3.204491
C	0.594303	-2.853526	-2.011393
C	-0.441742	-3.603002	-1.400977
C	1.855782	-3.486203	-2.079252
C	-0.223418	-4.865213	-0.856752
H	-1.437172	-3.167058	-1.341622
C	2.082131	-4.747053	-1.518092
H	2.669326	-2.992787	-2.602496
C	1.049926	-5.447189	-0.894683
H	-1.051650	-5.399699	-0.395373
H	3.072224	-5.192881	-1.593534
H	1.223268	-6.431402	-0.467574

7

B3LYP SCF energy: -2585.04523949 a.u.
B3LYP enthalpy: -2584.208434 a.u.
B3LYP free energy: -2584.339763 a.u.
M06 SCF energy in solution: -2584.23379347 a.u.
M06 enthalpy in solution: -2583.396988 a.u.
M06 free energy in solution: -2583.528317 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	0.933412	-1.052505	0.806553
C	-0.491501	-1.779749	1.849315
C	0.147295	-2.921570	2.665592
C	1.171553	-3.607977	1.755019
C	2.102758	-2.506590	1.188123
H	-0.620327	-3.618195	3.024162
H	0.661867	-2.527304	3.551088
H	1.758178	-4.367606	2.285348
H	0.657499	-4.118567	0.930533
P	0.833248	2.026790	-0.289595
C	2.431951	2.871193	-0.910309
C	2.178631	4.383656	-0.750412
C	0.709588	4.635625	-1.105964
C	-0.148309	3.659572	-0.263558

H	2.863868	4.963194	-1.381245
H	2.352078	4.699739	0.285676
H	0.407833	5.672092	-0.914224
H	0.544712	4.447636	-2.174537
H	-1.136005	-2.234823	1.088000
H	2.746894	-2.164343	2.008745
C	1.088180	1.706520	1.542965
H	1.701853	2.491637	2.001825
H	0.087852	1.772434	1.988206
C	1.697683	0.321422	1.835908
H	2.421314	2.647259	-1.984658
H	-0.119586	4.006701	0.777631
C	3.713938	2.304930	-0.339965
C	6.069526	1.140771	0.696228
C	4.289385	1.172268	-0.941422
C	4.350363	2.845955	0.787766
C	5.516823	2.271170	1.299018
C	5.449687	0.592217	-0.429556
H	3.817237	0.738517	-1.820351
H	3.946933	3.729706	1.272957
H	5.994418	2.713464	2.169615
H	5.863786	-0.289452	-0.909986
H	6.977300	0.695632	1.094522
C	-1.598003	3.560472	-0.687247
C	-4.306099	3.462433	-1.464408
C	-1.963840	3.099205	-1.961888
C	-2.614181	3.964728	0.189501
C	-3.956791	3.917273	-0.192686
C	-3.303532	3.052841	-2.347636
H	-1.198141	2.758576	-2.653927
H	-2.350973	4.322873	1.182494
H	-4.727091	4.238917	0.503535
H	-3.564156	2.692392	-3.339170
H	-5.349369	3.424547	-1.765636
C	2.989090	-2.953384	0.045059
C	4.668469	-3.852539	-2.034400
C	4.375417	-3.050268	0.229019
C	2.457384	-3.313916	-1.203932
C	3.288449	-3.758343	-2.232277
C	5.210072	-3.497020	-0.798439
H	4.806334	-2.775901	1.189621
H	1.388103	-3.234026	-1.379841
H	2.855509	-4.029068	-3.191671
H	6.281532	-3.570652	-0.629370
H	5.314038	-4.200205	-2.836465
C	-1.324081	-0.759000	2.594171
C	-2.896996	1.199185	3.880903

C	-1.019672	-0.331987	3.896397
C	-2.440320	-0.193520	1.954228
C	-3.216091	0.777421	2.587720
C	-1.798858	0.636797	4.533760
H	-0.176833	-0.761924	4.430311
H	-2.707798	-0.526666	0.954545
H	-4.073181	1.195618	2.067761
H	-1.548029	0.946342	5.545337
H	-3.504643	1.949709	4.379648
H	1.626911	0.103523	2.908241
H	2.762679	0.323113	1.574325
Cu	0.265210	-0.033667	-1.231168
C	-0.703695	-0.762979	-2.834396
H	-0.722186	0.024998	-3.596337
H	-0.185631	-1.644083	-3.226107
C	-2.034972	-1.017056	-2.280025
H	-2.639263	-0.115101	-2.174097
C	-2.590821	-2.176751	-1.811534
C	-3.929317	-2.200754	-1.186036
C	-4.885545	-1.172959	-1.371149
C	-4.325559	-3.279206	-0.362057
C	-6.133429	-1.212307	-0.757231
H	-4.655232	-0.339103	-2.027027
C	-5.579073	-3.320642	0.249497
H	-3.634809	-4.097853	-0.184853
C	-6.495649	-2.286488	0.062576
H	-6.838469	-0.402601	-0.933906
H	-5.836559	-4.169566	0.879331
H	-7.473800	-2.318330	0.535087
C	-1.831381	-3.483516	-1.883159
H	-1.022321	-3.426237	-2.616759
H	-1.372493	-3.771597	-0.921697
H	-2.483981	-4.316157	-2.175661

TS2a

B3LYP SCF energy: -3502.35356442 a.u.
B3LYP enthalpy: -3501.201012 a.u.
B3LYP free energy: -3501.374498 a.u.
M06 SCF energy in solution: -3501.16940526 a.u.
M06 enthalpy in solution: -3500.016853 a.u.
M06 free energy in solution: -3500.190339 a.u.
Imaginary frequency: -261.6834 cm-1

Cartesian coordinates

ATOM	X	Y	Z

C	-2.693753	1.736759	-0.408436
C	-2.373079	2.425860	-1.585625
H	-3.472229	0.982091	-0.493360
H	-2.668195	2.232036	0.555383
H	-2.670258	1.904704	-2.500477
C	2.025106	2.989822	-0.487784
C	1.572223	3.131157	-1.812984
C	2.066577	4.160474	-2.621416
C	3.004186	5.033104	-2.067977
C	3.432763	4.892215	-0.737149
C	2.944645	3.867260	0.078575
C	0.604214	2.081246	-1.964675
H	1.729373	4.285116	-3.646377
H	3.403211	5.843034	-2.672774
H	4.156963	5.594344	-0.333699
H	3.271911	3.740115	1.103445
H	0.088216	1.776326	-2.861262
N	1.352378	1.890562	0.120865
N	0.524497	1.348336	-0.849985
P	-1.106765	-1.114628	1.613495
C	0.506915	-1.785168	2.396903
C	0.211987	-1.901503	3.906923
C	-0.696463	-0.730899	4.290486
C	-1.894618	-0.742106	3.312976
H	1.145310	-1.907462	4.482833
H	-0.307520	-2.841177	4.130721
H	-1.049068	-0.801636	5.326381
H	-0.144615	0.212848	4.202743
P	-1.886109	-1.689569	-1.588780
C	-3.716874	-1.680098	-2.200649
C	-3.712260	-2.451520	-3.542365
C	-2.357691	-2.232149	-4.219209
C	-1.270403	-2.560261	-3.172898
H	-4.548582	-2.126638	-4.173313
H	-3.849409	-3.524667	-3.365087
H	-2.236205	-2.858314	-5.111160
H	-2.266387	-1.188790	-4.547539
H	1.203870	-0.952266	2.253054
H	-2.501223	-1.627473	3.546103
C	-1.762315	-3.083329	-0.344223
H	-2.413531	-3.919279	-0.623558
H	-0.728404	-3.440647	-0.413301
C	-2.065944	-2.641335	1.097923
H	-3.892262	-0.620646	-2.423747
H	-1.331565	-3.636372	-2.961924
C	-4.771306	-2.112556	-1.201564
C	-6.734389	-2.853761	0.696748

C	-5.490881	-1.144483	-0.481254
C	-5.074138	-3.463561	-0.958501
C	-6.041652	-3.829984	-0.021341
C	-6.455991	-1.506628	0.459305
H	-5.297186	-0.090961	-0.663556
H	-4.560525	-4.245835	-1.509673
H	-6.256381	-4.882823	0.142883
H	-6.992921	-0.732035	1.000094
H	-7.488730	-3.139655	1.424692
C	0.148497	-2.248707	-3.593220
C	2.796203	-1.724792	-4.415201
C	0.517432	-0.983439	-4.074482
C	1.133197	-3.244979	-3.533958
C	2.444388	-2.988597	-3.940087
C	1.825402	-0.722153	-4.480653
H	-0.226022	-0.193046	-4.132059
H	0.869658	-4.233722	-3.165369
H	3.188182	-3.779740	-3.890088
H	2.088509	0.266660	-4.846552
H	3.814937	-1.521712	-4.733514
C	-2.794494	0.470432	3.388745
C	-4.500940	2.705032	3.601854
C	-4.171200	0.309031	3.600651
C	-2.287848	1.775132	3.282596
C	-3.131330	2.881272	3.388432
C	-5.018910	1.413938	3.706464
H	-4.583158	-0.694172	3.689513
H	-1.226660	1.929316	3.104011
H	-2.718959	3.880950	3.286329
H	-6.082226	1.263360	3.875861
H	-5.156541	3.567752	3.682982
C	1.096111	-3.001942	1.713560
C	2.211602	-5.215887	0.359718
C	0.807342	-4.316022	2.116208
C	1.959997	-2.820692	0.619467
C	2.511162	-3.914047	-0.049094
C	1.358639	-5.411164	1.446734
H	0.157558	-4.498701	2.966918
H	2.203212	-1.812676	0.295910
H	3.180083	-3.741743	-0.887316
H	1.124401	-6.418166	1.783106
H	2.646490	-6.068464	-0.155557
H	-1.871586	-3.472485	1.786251
H	-3.127007	-2.381256	1.193840
Cu	-1.086502	0.214357	-0.313175
O	2.610849	0.671279	0.218778
C	3.405700	0.815935	1.273049

O	3.232099	1.592349	2.201158
C	4.586764	-0.129914	1.205979
C	5.320924	-0.306619	0.010032
C	4.980653	-0.800861	2.388469
C	6.424832	-1.166932	0.023394
C	6.076623	-1.666270	2.338353
C	6.811284	-1.868387	1.167122
H	7.001029	-1.288434	-0.891906
H	6.369742	-2.189906	3.246273
C	4.273808	-0.609442	3.712413
H	4.444137	0.396282	4.107251
H	3.188655	-0.720842	3.621330
H	4.632961	-1.341949	4.442604
C	7.978876	-2.826655	1.137742
H	8.695605	-2.561596	0.353134
H	8.511803	-2.839693	2.094920
H	7.643891	-3.854127	0.940254
C	4.995507	0.414042	-1.282478
H	4.105152	-0.002345	-1.764365
H	4.796721	1.477861	-1.123463
H	5.835847	0.326807	-1.979500
C	-1.697931	3.633479	-1.835438
C	-1.279670	4.597190	-0.812060
C	-1.677866	4.103964	-3.277637
C	-1.159724	5.973066	-1.129892
C	-0.941077	4.224280	0.511336
H	-1.843016	3.266121	-3.964561
H	-2.463741	4.845252	-3.490192
H	-0.724267	4.576639	-3.545050
C	-0.762501	6.913493	-0.184577
H	-1.399212	6.316074	-2.130680
C	-0.528736	5.168102	1.450994
H	-0.949012	3.181898	0.794574
C	-0.444958	6.520595	1.118258
H	-0.698528	7.961447	-0.468560
H	-0.251450	4.835655	2.448915
H	-0.128595	7.253826	1.855428

TS2b

B3LYP SCF energy: -3502.34307713 a.u.
B3LYP enthalpy: -3501.190601 a.u.
B3LYP free energy: -3501.366539 a.u.
M06 SCF energy in solution: -3501.15945183 a.u.
M06 enthalpy in solution: -3500.006976 a.u.
M06 free energy in solution: -3500.182914 a.u.

Imaginary frequency: -247.4754 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	2.725514	1.530890	0.298215
C	2.621523	2.478793	-0.730593
C	2.067425	3.767997	-0.802450
H	3.480266	0.759804	0.151497
H	2.583882	1.830920	1.332502
H	3.037554	2.135160	-1.678277
C	-1.758116	3.296320	-0.274029
C	-1.119148	3.551168	-1.502755
C	-1.390317	4.728179	-2.210812
C	-2.295190	5.631270	-1.652918
C	-2.907349	5.376793	-0.413122
C	-2.643495	4.204620	0.300352
C	-0.258840	2.419103	-1.685367
H	-0.913077	4.937473	-3.163900
H	-2.524646	6.553177	-2.180680
H	-3.598315	6.106656	-0.000751
H	-3.111777	3.990503	1.253199
H	0.371528	2.185342	-2.531534
N	-1.301755	2.051562	0.242389
N	-0.421060	1.535310	-0.693300
P	1.144796	-1.459147	1.488517
C	-0.105857	-2.441363	2.507336
C	-0.370885	-1.459472	3.667958
C	1.014477	-1.094368	4.234364
C	2.033211	-0.855435	3.072263
H	-0.897763	-0.570036	3.298932
H	-1.007249	-1.918284	4.433732
H	1.367656	-1.919851	4.862108
H	0.967790	-0.209559	4.878247
P	1.786739	-1.505208	-1.810477
C	3.554988	-1.844018	-2.516630
C	3.357369	-2.036166	-4.039664
C	2.016845	-2.739604	-4.262654
C	0.960856	-1.940378	-3.475768
H	3.342479	-1.064140	-4.547244
H	4.198071	-2.599213	-4.462550
H	2.078480	-3.770804	-3.893912
H	1.753573	-2.795059	-5.326278
C	1.577726	-3.046470	-0.760702
H	2.071346	-3.910087	-1.223621
H	0.507361	-3.276118	-0.708219
C	2.143946	-2.804650	0.657635
H	2.116529	-3.730424	1.243558

H	3.191454	-2.484599	0.613632
Cu	1.015551	0.188382	-0.167634
O	-2.734072	1.008564	0.033505
C	-3.601866	1.146734	1.025784
O	-3.422404	1.774932	2.059431
C	-4.900242	0.416617	0.740469
C	-5.546925	0.531421	-0.511055
C	-5.487135	-0.346054	1.778533
C	-6.765856	-0.131805	-0.700088
C	-6.694358	-1.004027	1.528475
C	-7.354089	-0.908777	0.299790
H	-7.270350	-0.032492	-1.659486
H	-7.134422	-1.604355	2.322497
C	-4.855935	-0.481806	3.146371
H	-4.837313	0.478796	3.667879
H	-3.817763	-0.824279	3.081522
H	-5.413645	-1.204647	3.750530
C	-8.679386	-1.598920	0.075509
H	-8.881729	-1.743148	-0.991134
H	-9.509213	-1.009662	0.488717
H	-8.708141	-2.579977	0.563109
C	-4.999684	1.360561	-1.654926
H	-4.116097	0.895220	-2.102876
H	-4.691256	2.358884	-1.329995
H	-5.761650	1.477968	-2.432670
H	2.131825	0.220712	2.910709
C	3.423606	-1.412147	3.300779
C	4.546427	-0.606351	3.055537
C	3.643543	-2.728454	3.741791
C	5.841152	-1.093394	3.246098
H	4.403305	0.415815	2.714245
C	4.935642	-3.218614	3.931969
H	2.797756	-3.380795	3.944508
C	6.042227	-2.402641	3.685551
H	6.691351	-0.442869	3.057842
H	5.077508	-4.239442	4.277690
H	7.048535	-2.782599	3.839871
H	0.469237	-3.280198	2.926398
C	-1.304257	-3.028355	1.800829
C	-2.153085	-2.262149	0.987658
C	-1.597167	-4.390066	1.977197
C	-3.267587	-2.844203	0.380581
H	-1.944909	-1.210714	0.814494
C	-2.711023	-4.972322	1.370937
H	-0.947663	-4.998596	2.603770
C	-3.551726	-4.198064	0.570672
H	-3.911497	-2.232173	-0.241935

H	-2.919497	-6.028132	1.525584
H	-4.421214	-4.645350	0.096280
H	0.878501	-0.956310	-3.957566
C	-0.435690	-2.518388	-3.402106
C	-0.683872	-3.899446	-3.409013
C	-1.537442	-1.648888	-3.351933
C	-1.989688	-4.393232	-3.381031
H	0.142673	-4.602712	-3.451065
C	-2.841910	-2.139657	-3.322235
H	-1.367912	-0.574864	-3.334295
C	-3.073920	-3.516467	-3.341814
H	-2.156628	-5.467142	-3.394420
H	-3.676401	-1.444737	-3.284940
H	-4.089815	-3.901449	-3.325043
H	3.819416	-2.821499	-2.095714
C	4.655686	-0.879547	-2.128813
C	4.826403	0.363897	-2.756688
C	5.569166	-1.238010	-1.125171
C	5.869549	1.216625	-2.392574
H	4.140102	0.676226	-3.539383
C	6.610026	-0.386147	-0.753363
H	5.468618	-2.202657	-0.632161
C	6.765553	0.846900	-1.388023
H	5.978739	2.174846	-2.893407
H	7.299240	-0.691321	0.029389
H	7.575998	1.512723	-1.104911
C	1.530357	4.523329	0.331517
C	0.988417	3.908472	1.486992
C	1.505820	5.940937	0.301178
C	0.479208	4.661883	2.543515
H	0.912492	2.832539	1.539606
C	1.008392	6.688645	1.362637
H	1.900483	6.466640	-0.561337
C	0.492101	6.055621	2.497427
H	0.053908	4.148410	3.402296
H	1.021932	7.774549	1.303559
H	0.099599	6.640295	3.325240
C	2.308841	4.530109	-2.091048
H	3.146656	5.239692	-2.008409
H	2.555641	3.845056	-2.909714
H	1.432241	5.116887	-2.393482

TS2c
B3LYP SCF energy: -3502.36294889 a.u.
B3LYP enthalpy: -3501.210434 a.u.

B3LYP free energy: -3501.382649 a.u.
M06 SCF energy in solution: -3501.17594046 a.u.
M06 enthalpy in solution: -3500.023426 a.u.
M06 free energy in solution: -3500.195641 a.u.
Imaginary frequency: -265.9471 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.767264	0.781545	1.284300
C	-3.139417	1.778782	0.383522
C	-2.773010	3.138908	0.412122
H	-3.325331	-0.151159	1.278661
H	-2.316309	1.033797	2.238427
H	-3.760910	1.458348	-0.453152
C	1.110660	3.451003	0.531920
C	0.213574	3.861646	-0.471845
C	0.149495	5.206316	-0.855529
C	1.002705	6.106586	-0.215684
C	1.887459	5.684960	0.792762
C	1.949209	4.346486	1.190458
C	-0.492714	2.659589	-0.828915
H	-0.553785	5.542573	-1.610413
H	0.975920	7.156795	-0.494021
H	2.533156	6.414013	1.274466
H	2.624461	4.004629	1.966229
H	-1.167685	2.517127	-1.659236
N	0.934373	2.058287	0.770038
N	-0.005984	1.615213	-0.143064
P	-0.054637	-1.823831	1.508630
C	1.769127	-2.378697	1.455516
C	1.973300	-3.156728	2.768356
C	1.278714	-2.353908	3.870831
C	-0.163860	-2.016828	3.405215
H	3.040811	-3.301582	2.976253
H	1.521145	-4.154870	2.703419
H	1.252820	-2.893589	4.824880
H	1.829352	-1.422538	4.048457
P	-1.865394	-1.719022	-1.289729
C	-3.786676	-1.870422	-1.362117
C	-4.141516	-2.011967	-2.866379
C	-3.025339	-1.377632	-3.701951
C	-1.689921	-1.942886	-3.165245
H	-5.119721	-1.560118	-3.069548
H	-4.223143	-3.071549	-3.134509
H	-3.137433	-1.597364	-4.770317
H	-3.033322	-0.283976	-3.598632
H	2.314372	-1.430934	1.537636

H	-0.796204	-2.897205	3.576216
C	-1.187398	-3.333838	-0.629926
H	-1.821949	-4.177496	-0.921601
H	-0.220245	-3.464938	-1.128144
C	-0.992233	-3.332770	0.899551
H	-4.118215	-0.881509	-1.028556
H	-1.699475	-3.026839	-3.347629
C	-4.430845	-2.893925	-0.449543
C	-5.649257	-4.756942	1.296327
C	-5.057521	-2.478023	0.736905
C	-4.442226	-4.268019	-0.745815
C	-5.041760	-5.188019	0.115557
C	-5.657158	-3.395073	1.601745
H	-5.087761	-1.418982	0.980099
H	-3.988878	-4.629962	-1.664574
H	-5.037362	-6.244250	-0.141069
H	-6.138243	-3.040604	2.509517
H	-6.118576	-5.473248	1.965039
C	-0.457338	-1.367324	-3.830565
C	1.759926	-0.305019	-5.212712
C	0.025406	-0.083829	-3.536104
C	0.197171	-2.109984	-4.824727
C	1.292731	-1.586127	-5.513002
C	1.123152	0.442074	-4.218748
H	-0.443066	0.501374	-2.751917
H	-0.159454	-3.109319	-5.065869
H	1.780040	-2.179615	-6.282429
H	1.480889	1.437293	-3.968703
H	2.612612	0.106785	-5.745974
C	-0.773606	-0.839898	4.138067
C	-1.888680	1.310201	5.576956
C	-1.927003	-1.014780	4.914452
C	-0.186011	0.435737	4.088901
C	-0.738585	1.497811	4.804885
C	-2.483523	0.049485	5.628067
H	-2.391303	-1.997733	4.966973
H	0.697355	0.615922	3.480535
H	-0.269082	2.476303	4.752974
H	-3.378046	-0.110025	6.224750
H	-2.316489	2.140764	6.132086
C	2.199783	-3.047326	0.168438
C	2.959440	-4.213110	-2.285919
C	2.280192	-4.441182	0.027860
C	2.521516	-2.247715	-0.942252
C	2.891831	-2.823204	-2.156976
C	2.657994	-5.018610	-1.187571
H	2.059092	-5.089941	0.870052

H	2.480554	-1.165854	-0.847721
H	3.123366	-2.183009	-3.002988
H	2.719492	-6.100973	-1.270433
H	3.252290	-4.662367	-3.231234
H	-0.492680	-4.259787	1.206740
H	-1.968858	-3.310962	1.399328
Cu	-0.989403	-0.108489	0.222418
O	2.400009	1.340790	0.182950
C	3.363139	1.325619	1.098443
O	3.235148	1.655589	2.270237
C	-3.308522	4.070573	-0.589117
C	-3.678300	3.649195	-1.891511
C	-3.462431	5.449393	-0.310556
C	-4.172252	4.539167	-2.839944
H	-3.561466	2.605503	-2.171137
C	-3.956611	6.339914	-1.262565
H	-3.214711	5.826415	0.675805
C	-4.315944	5.896641	-2.536649
H	-4.438567	4.171777	-3.828471
H	-4.067162	7.389812	-1.000987
H	-4.698999	6.591947	-3.278467
C	-2.137011	3.671799	1.673237
H	-1.684259	4.655526	1.529057
H	-2.863891	3.750067	2.496108
H	-1.343332	3.000137	2.020423
C	4.674175	0.830639	0.527259
C	5.106012	1.201090	-0.769358
C	5.500162	0.019139	1.344422
C	6.345081	0.734301	-1.222258
C	6.715673	-0.439240	0.829113
C	7.157802	-0.098488	-0.451330
H	6.683352	1.034169	-2.212142
H	7.340615	-1.073270	1.455053
C	5.142109	-0.364168	2.764264
H	5.206140	0.499589	3.432486
H	4.117142	-0.736361	2.852222
H	5.823530	-1.140693	3.127287
C	8.466813	-0.627300	-0.988443
H	8.877313	0.029520	-1.762704
H	9.215545	-0.727629	-0.194916
H	8.336972	-1.620951	-1.438417
C	4.315982	2.106448	-1.692855
H	3.461614	1.582807	-2.133976
H	3.912124	2.979400	-1.173082
H	4.958609	2.459838	-2.506222

TS2d
B3LYP SCF energy: -3502.35116902 a.u.
B3LYP enthalpy: -3501.198471 a.u.
B3LYP free energy: -3501.372495 a.u.
M06 SCF energy in solution: -3501.16573859 a.u.
M06 enthalpy in solution: -3500.013041 a.u.
M06 free energy in solution: -3500.187065 a.u.
Imaginary frequency: -252.7849 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.653308	0.617997	-1.419998
C	-2.931641	1.838124	-0.803403
C	-2.496048	3.118592	-1.192327
H	-3.284881	-0.229781	-1.163724
H	-2.228954	0.599312	-2.421068
H	-3.544953	1.776667	0.091157
C	1.299177	3.208013	-1.467765
C	0.484290	3.862766	-0.526268
C	0.460933	5.260881	-0.459066
C	1.266852	5.967555	-1.352821
C	2.063217	5.302251	-2.301885
C	2.085743	3.906799	-2.380291
C	-0.210029	2.793442	0.138596
H	-0.177008	5.780179	0.248481
H	1.270098	7.053974	-1.323687
H	2.670690	5.883943	-2.989720
H	2.695396	3.378545	-3.103588
H	-0.854509	2.858615	1.002608
N	1.109558	1.800020	-1.353775
N	0.216842	1.604951	-0.311437
P	-0.541137	-2.245711	-1.046142
C	0.980331	-3.275651	-1.478668
C	1.256999	-2.795394	-2.918778
C	-0.071414	-2.961138	-3.682532
C	-1.277287	-2.512253	-2.791784
H	1.587249	-1.748698	-2.915077
H	2.057440	-3.384740	-3.381328
H	-0.195046	-4.015306	-3.953396
H	-0.069420	-2.395221	-4.620145
P	-1.650121	-1.085117	1.904519
C	-3.433828	-1.474153	2.540721
C	-3.421026	-1.136050	4.054403
C	-2.015615	-1.385570	4.607337
C	-1.036974	-0.667800	3.659446
H	-3.680371	-0.081631	4.204542

H	-4.184059	-1.723637	4.578683
H	-1.811533	-2.462919	4.632828
H	-1.909816	-1.015740	5.634833
C	-1.049121	-2.842293	1.625371
H	-1.465001	-3.526384	2.375909
H	0.039618	-2.845745	1.751550
C	-1.423962	-3.320536	0.203906
H	-1.155654	-4.374970	0.072272
H	-2.504500	-3.243047	0.034538
Cu	-0.898804	-0.086495	-0.205193
O	2.630934	1.273695	-0.653589
C	3.581594	1.099524	-1.564682
O	3.424867	1.121955	-2.776787
C	-2.952343	4.304601	-0.456489
C	-3.305815	4.251047	0.915944
C	-3.045171	5.572633	-1.077000
C	-3.729475	5.379223	1.610746
H	-3.229287	3.308418	1.450718
C	-3.470184	6.702497	-0.379009
H	-2.804511	5.671813	-2.129932
C	-3.816070	6.620030	0.970666
H	-3.985076	5.292869	2.664618
H	-3.535289	7.655101	-0.899724
H	-4.144324	7.501526	1.514441
C	-1.871092	3.270637	-2.556881
H	-1.370185	4.232554	-2.685575
H	-2.617121	3.168205	-3.360053
H	-1.116706	2.492698	-2.727090
C	4.933814	0.862058	-0.922940
C	5.384367	1.653700	0.158953
C	5.770236	-0.143206	-1.466009
C	6.661867	1.413218	0.679605
C	7.027941	-0.352878	-0.894228
C	7.497230	0.414833	0.175232
H	7.013294	2.030953	1.503913
H	7.661264	-1.137856	-1.303170
C	5.353633	-1.008570	-2.634463
H	5.228161	-0.412647	-3.542074
H	4.394946	-1.504045	-2.447671
H	6.105013	-1.783540	-2.817014
C	8.879340	0.191791	0.743494
H	9.140471	-0.872420	0.758055
H	8.959964	0.575714	1.766000
H	9.643312	0.702625	0.141835
C	4.565652	2.771476	0.772245
H	3.717787	2.382004	1.344247
H	4.146458	3.439577	0.013922

H	5.191242	3.370313	1.442496
H	-1.581169	-1.507688	-3.095785
C	-2.503413	-3.400002	-2.855850
C	-3.773021	-2.824885	-3.023304
C	-2.427508	-4.797930	-2.732785
C	-4.924174	-3.613907	-3.069208
H	-3.858636	-1.745690	-3.123390
C	-3.575414	-5.589303	-2.778398
H	-1.461016	-5.278399	-2.603004
C	-4.830957	-5.001021	-2.947216
H	-5.892894	-3.141136	-3.209345
H	-3.487634	-6.668805	-2.685205
H	-5.724477	-5.618033	-2.988112
H	0.610330	-4.308966	-1.553030
C	2.136303	-3.281648	-0.507264
C	2.717524	-2.101326	-0.019580
C	2.664747	-4.511618	-0.084390
C	3.801406	-2.155724	0.858662
H	2.321411	-1.134567	-0.314671
C	3.748172	-4.566808	0.793342
H	2.225128	-5.436514	-0.453169
C	4.320398	-3.385888	1.267703
H	4.235994	-1.230469	1.222186
H	4.142373	-5.531186	1.104242
H	5.164328	-3.422294	1.951485
H	-1.247681	0.408419	3.732388
C	0.443262	-0.850311	3.914004
C	0.974127	-2.019090	4.480192
C	1.327958	0.195201	3.603004
C	2.341829	-2.133261	4.737643
H	0.319492	-2.845983	4.739019
C	2.694067	0.082763	3.857113
H	0.938553	1.107469	3.157044
C	3.206689	-1.082506	4.431261
H	2.728683	-3.045878	5.183399
H	3.356305	0.907825	3.609108
H	4.269943	-1.170074	4.637299
H	-3.509903	-2.563305	2.443026
C	-4.594580	-0.875206	1.774515
C	-4.979059	0.466731	1.920691
C	-5.349764	-1.682713	0.910108
C	-6.077021	0.982181	1.230402
H	-4.418385	1.123454	2.580957
C	-6.446484	-1.171319	0.214322
H	-5.081385	-2.729808	0.785985
C	-6.816168	0.164914	0.373124
H	-6.347307	2.026992	1.357052

H	-7.013256	-1.821529	-0.446879
H	-7.670429	0.566566	-0.164600

8a

B3LYP SCF energy: -2964.12391647 a.u.
B3LYP enthalpy: -2963.168431 a.u.
B3LYP free energy: -2963.311236 a.u.
M06 SCF energy in solution: -2963.17537316 a.u.
M06 enthalpy in solution: -2962.219888 a.u.
M06 free energy in solution: -2962.362693 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.020334	2.084354	-1.540499
C	0.988955	1.282090	-2.031984
H	-1.000168	2.014011	-1.905043
H	0.231481	2.891647	-0.848625
H	0.724333	0.547387	-2.793433
C	3.936509	-0.631197	0.930396
C	4.225745	-0.146379	-0.355240
C	5.550515	-0.005271	-0.751442
C	6.553263	-0.338077	0.168711
C	6.247742	-0.817069	1.452109
C	4.922324	-0.975638	1.854279
C	2.890476	0.038944	-1.009970
H	5.819803	0.354126	-1.739101
H	7.594041	-0.222269	-0.119235
H	7.053521	-1.066445	2.135422
H	4.659817	-1.349344	2.838716
H	2.725517	-0.782611	-1.725430
N	2.542343	-0.696026	1.131447
N	1.940819	-0.296550	0.092708
P	-1.470663	0.412636	1.580124
C	-0.926023	-0.190890	3.305890
C	-1.723098	0.687960	4.293251
C	-1.773079	2.103717	3.711413
C	-2.287913	1.998880	2.255910
H	-1.260652	0.666186	5.286738
H	-2.746233	0.311282	4.409685
H	-2.421831	2.767440	4.293590
H	-0.768951	2.543877	3.730736
P	-1.469942	-1.632980	-1.102373
C	-2.658059	-1.460113	-2.581795
C	-3.040283	-2.915424	-2.921054
C	-1.748390	-3.737253	-2.885359

C	-0.975768	-3.416824	-1.575203
H	-3.529859	-2.968290	-3.900490
H	-3.754177	-3.309144	-2.187675
H	-1.942825	-4.813069	-2.953783
H	-1.132523	-3.475415	-3.752921
H	0.126391	0.114860	3.359182
H	-3.356680	1.752783	2.300802
C	-2.587411	-1.923079	0.374696
H	-3.499337	-2.450908	0.073321
H	-2.035937	-2.594431	1.042307
C	-2.955980	-0.631023	1.126080
H	-2.007007	-1.095661	-3.388649
H	-1.381895	-4.041275	-0.770938
C	-3.786900	-0.463975	-2.422580
C	-5.841041	1.455554	-2.151651
C	-3.612695	0.854671	-2.873587
C	-5.021972	-0.805180	-1.848246
C	-6.037004	0.144838	-1.712956
C	-4.623207	1.806872	-2.738189
H	-2.679348	1.131439	-3.359647
H	-5.209847	-1.822184	-1.517757
H	-6.987604	-0.146072	-1.274472
H	-4.463480	2.817179	-3.104163
H	-6.635708	2.189694	-2.055038
C	0.518918	-3.658326	-1.645673
C	3.294202	-4.165884	-1.760425
C	1.302671	-3.151697	-2.695812
C	1.155562	-4.419240	-0.655192
C	2.528653	-4.670142	-0.708476
C	2.674246	-3.406113	-2.756625
H	0.839173	-2.567398	-3.487520
H	0.567835	-4.825434	0.164688
H	2.996348	-5.271941	0.065893
H	3.256200	-3.026753	-3.592984
H	4.359123	-4.373005	-1.812711
C	-2.134812	3.241578	1.404780
C	-1.918489	5.568051	-0.177696
C	-3.202780	3.671261	0.602711
C	-0.954309	4.000858	1.396824
C	-0.846375	5.152557	0.615727
C	-3.097598	4.821353	-0.182191
H	-4.131259	3.104636	0.598020
H	-0.104876	3.696933	2.001796
H	0.078103	5.723176	0.628841
H	-3.942703	5.139169	-0.786734
H	-1.837261	6.468523	-0.779727
C	-0.978066	-1.692390	3.507462

C	-1.007447	-4.498581	3.815355
C	-2.101359	-2.348020	4.035686
C	0.134765	-2.470222	3.143946
C	0.119877	-3.857551	3.295140
C	-2.115902	-3.736879	4.187497
H	-2.971689	-1.780481	4.350913
H	1.017456	-1.979392	2.741288
H	0.997632	-4.436532	3.019786
H	-2.993336	-4.220605	4.607861
H	-1.016668	-5.577334	3.942949
H	-3.533148	-0.879892	2.024269
H	-3.592793	0.001557	0.496762
Cu	-0.058922	0.064117	-0.234004
C	2.497991	1.365635	-1.753615
C	2.889552	2.627634	-0.961867
C	3.187874	1.318056	-3.142238
C	3.487052	3.727774	-1.596929
C	2.643180	2.733313	0.417752
H	2.967424	0.369811	-3.643766
H	2.824487	2.120906	-3.789236
H	4.273742	1.416139	-3.057882
C	3.833111	4.878692	-0.885329
H	3.695866	3.704631	-2.659886
C	2.995559	3.878591	1.133644
H	2.167369	1.918795	0.950218
C	3.593790	4.959811	0.485576
H	4.297545	5.709360	-1.409196
H	2.805912	3.920562	2.203072
H	3.872937	5.849957	1.041899

8b

B3LYP SCF energy: -2964.11677522 a.u.
B3LYP enthalpy: -2963.161906 a.u.
B3LYP free energy: -2963.308092 a.u.
M06 SCF energy in solution: -2963.16638966 a.u.
M06 enthalpy in solution: -2962.211520 a.u.
M06 free energy in solution: -2962.357706 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.553307	3.384957	-1.501359
C	1.750457	2.780050	-0.327908
C	3.048514	2.132138	0.145080
H	0.637671	3.934761	-1.699137
H	2.294725	3.375351	-2.294312

H	0.979232	2.856241	0.441284
C	3.573492	-1.253180	1.043941
C	3.842685	0.033829	1.533172
C	4.989141	0.240916	2.293762
C	5.846323	-0.845687	2.513737
C	5.571289	-2.120110	1.995510
C	4.415031	-2.345865	1.251246
C	2.698171	0.888824	1.068315
H	5.227030	1.205901	2.727490
H	6.744769	-0.696762	3.105468
H	6.260551	-2.936532	2.187038
H	4.165901	-3.324288	0.853731
H	2.097094	1.274818	1.903461
N	2.336371	-1.276222	0.380293
N	1.819702	-0.116241	0.386588
P	-1.799543	0.337694	-1.555026
C	-1.912718	-0.756271	-3.099244
C	-1.707967	0.247373	-4.261162
C	-2.517549	1.505921	-3.935151
C	-2.149895	1.958990	-2.500368
H	-0.643508	0.495215	-4.358992
H	-2.017144	-0.207211	-5.208787
H	-3.586552	1.274152	-4.001663
H	-2.323916	2.316508	-4.646538
P	-1.662295	-0.871947	1.564557
C	-2.354473	0.263514	2.928541
C	-2.502531	-0.647406	4.183475
C	-2.697408	-2.102521	3.739239
C	-1.620293	-2.402520	2.678006
H	-1.597495	-0.577249	4.796525
H	-3.330669	-0.295719	4.808063
H	-3.700502	-2.230818	3.314992
H	-2.617444	-2.795347	4.585120
C	-3.132482	-1.184506	0.447929
H	-4.047083	-1.331099	1.034434
H	-2.930456	-2.130246	-0.068801
C	-3.342797	-0.042336	-0.565606
H	-4.178055	-0.281992	-1.234089
H	-3.616373	0.884169	-0.047145
Cu	-0.122714	-0.020394	-0.019901
H	-1.163629	2.434776	-2.543251
C	-3.104268	2.926683	-1.828922
C	-2.594320	3.989118	-1.066305
C	-4.499501	2.807616	-1.940369
C	-3.442988	4.903658	-0.440367
H	-1.518189	4.108665	-0.969906
C	-5.351173	3.719805	-1.315407

H	-4.934951	2.003779	-2.526923
C	-4.827323	4.772205	-0.562138
H	-3.020779	5.727557	0.128711
H	-6.426571	3.610988	-1.425013
H	-5.490862	5.487082	-0.084352
H	-2.954885	-1.099750	-3.135924
C	-1.010796	-1.971559	-3.128923
C	0.387895	-1.852000	-3.120013
C	-1.568587	-3.254903	-3.208091
C	1.202769	-2.981600	-3.191250
H	0.846299	-0.867775	-3.065853
C	-0.755619	-4.388091	-3.280491
H	-2.650267	-3.369463	-3.227354
C	0.633220	-4.254724	-3.273872
H	2.283053	-2.865973	-3.185807
H	-1.210297	-5.372211	-3.349102
H	1.267925	-5.133964	-3.339355
H	-0.639749	-2.341187	3.171014
C	-1.686831	-3.721452	1.933396
C	-2.825849	-4.538263	1.949547
C	-0.567200	-4.151065	1.200613
C	-2.844111	-5.751865	1.256476
H	-3.702823	-4.246096	2.518524
C	-0.587619	-5.357942	0.503579
H	0.329215	-3.534368	1.177085
C	-1.727808	-6.165354	0.530385
H	-3.732955	-6.375662	1.293166
H	0.288600	-5.667909	-0.058311
H	-1.742225	-7.111147	-0.003736
H	-3.353727	0.557994	2.586049
C	-1.539418	1.524560	3.146758
C	-0.272717	1.488952	3.754267
C	-2.041827	2.769325	2.741450
C	0.458187	2.660397	3.962148
H	0.144228	0.541849	4.088498
C	-1.309273	3.942459	2.939573
H	-3.022368	2.827569	2.274650
C	-0.057202	3.894248	3.553967
H	1.422297	2.611063	4.461944
H	-1.727766	4.894925	2.626838
H	0.504338	4.807672	3.727892
C	3.969287	1.706916	-1.009781
C	3.474425	0.894435	-2.044980
C	5.317338	2.088317	-1.068596
C	4.295383	0.473618	-3.090585
H	2.430420	0.600411	-2.039102
C	6.141781	1.670805	-2.116686

H	5.744589	2.722307	-0.300261
C	5.636538	0.859623	-3.131008
H	3.883960	-0.150841	-3.879444
H	7.181106	1.986454	-2.136515
H	6.276946	0.536467	-3.946656
C	3.699020	3.194340	1.070353
H	3.948202	4.085903	0.488910
H	2.995244	3.492565	1.854707
H	4.611319	2.834694	1.551426

8c

B3LYP SCF energy: -2964.12953990 a.u.
B3LYP enthalpy: -2963.173504 a.u.
B3LYP free energy: -2963.314279 a.u.
M06 SCF energy in solution: -2963.17957382 a.u.
M06 enthalpy in solution: -2962.223538 a.u.
M06 free energy in solution: -2962.364313 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.274701	2.505347	0.142724
C	-1.390771	1.891505	0.593059
C	-2.677393	1.638529	-0.201732
H	0.544545	2.732240	0.817958
H	-0.181552	2.894809	-0.864693
H	-1.441348	1.613679	1.644246
C	-3.254731	-1.368670	-2.030804
C	-3.927547	-0.498033	-1.160159
C	-5.309071	-0.369683	-1.239899
C	-5.980931	-1.122629	-2.212898
C	-5.295342	-1.989030	-3.078734
C	-3.909468	-2.128158	-2.999103
C	-2.861555	0.080238	-0.282716
H	-5.856576	0.293356	-0.578296
H	-7.059992	-1.033592	-2.298873
H	-5.852527	-2.556777	-3.817489
H	-3.359555	-2.795269	-3.655067
H	-2.940257	-0.322238	0.735578
N	-1.864592	-1.338961	-1.779290
N	-1.620441	-0.540063	-0.830069
P	2.072723	-0.043099	-1.432976
C	2.188638	-1.371105	-2.792261
C	3.323158	-0.872723	-3.710012
C	3.140514	0.638917	-3.874374
C	3.007279	1.266152	-2.464400

H	3.300130	-1.396206	-4.672797
H	4.303273	-1.073801	-3.260636
H	3.974435	1.100391	-4.414562
H	2.236571	0.831028	-4.463362
P	1.261784	-0.812351	1.749907
C	1.878487	0.123000	3.290706
C	2.174310	-0.997925	4.308663
C	0.995615	-1.974483	4.253122
C	0.690238	-2.323536	2.769552
H	2.310548	-0.581244	5.313456
H	3.104954	-1.518242	4.052049
H	1.192461	-2.889393	4.822394
H	0.118644	-1.504046	4.711455
H	1.242605	-1.259707	-3.337655
H	4.008319	1.298816	-2.016391
C	2.817598	-1.464566	0.930016
H	3.597513	-1.658171	1.675204
H	2.547403	-2.432690	0.493838
C	3.363791	-0.532736	-0.167821
H	0.981169	0.652961	3.639554
H	1.355232	-3.137923	2.459476
C	2.959816	1.157869	3.064457
C	4.918233	3.145175	2.620856
C	2.601461	2.504414	2.887815
C	4.325542	0.832133	3.036357
C	5.293268	1.814346	2.813969
C	3.565220	3.488415	2.664735
H	1.552826	2.788182	2.950031
H	4.648145	-0.190688	3.206039
H	6.344099	1.538245	2.805113
H	3.259350	4.523794	2.542779
H	5.673374	3.908882	2.458888
C	-0.737238	-2.754129	2.496541
C	-3.381063	-3.598432	1.977808
C	-1.836227	-2.007645	2.953118
C	-0.991543	-3.928514	1.774842
C	-2.298611	-4.347399	1.515200
C	-3.144178	-2.426405	2.701542
H	-1.673896	-1.097541	3.526276
H	-0.156102	-4.523507	1.413770
H	-2.469296	-5.266906	0.961981
H	-3.979811	-1.845832	3.084464
H	-4.398228	-3.929505	1.789527
C	2.432957	2.667132	-2.413535
C	1.420490	5.299664	-2.284065
C	3.016626	3.626125	-1.571735
C	1.328230	3.053702	-3.189488

C	0.829923	4.356863	-3.129271
C	2.516148	4.927743	-1.503424
H	3.879385	3.353915	-0.967594
H	0.853054	2.340842	-3.858188
H	-0.015284	4.637742	-3.752049
H	2.992372	5.653911	-0.850386
H	1.037394	6.315229	-2.243612
C	2.263729	-2.799235	-2.291525
C	2.314902	-5.451720	-1.329344
C	3.480100	-3.474284	-2.105241
C	1.071535	-3.481895	-1.994792
C	1.096893	-4.793132	-1.518416
C	3.505183	-4.787399	-1.627967
H	4.420634	-2.989264	-2.348116
H	0.119218	-2.978441	-2.143632
H	0.161614	-5.305948	-1.309778
H	4.458384	-5.293403	-1.501642
H	2.335434	-6.476280	-0.968825
H	4.222162	-1.005519	-0.659923
H	3.722974	0.401461	0.279686
Cu	0.168835	0.145118	-0.105960
C	-3.858612	2.232899	0.600621
C	-4.140845	1.768046	1.897562
C	-4.669440	3.252456	0.082418
C	-5.191798	2.297295	2.645100
H	-3.538214	0.979540	2.341948
C	-5.723893	3.784944	0.829521
H	-4.489986	3.646426	-0.910938
C	-5.990999	3.310953	2.112612
H	-5.385436	1.917338	3.644366
H	-6.334708	4.574486	0.401024
H	-6.810484	3.725201	2.692446
C	-2.578322	2.209275	-1.625748
H	-3.498242	2.026575	-2.186738
H	-2.396360	3.287063	-1.606129
H	-1.752603	1.744491	-2.172475

8d

B3LYP SCF energy: -2964.12195931 a.u.
B3LYP enthalpy: -2963.166670 a.u.
B3LYP free energy: -2963.311966 a.u.
M06 SCF energy in solution: -2963.17378586 a.u.
M06 enthalpy in solution: -2962.218497 a.u.
M06 free energy in solution: -2962.363793 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.619709	2.124598	-1.219240
C	0.481291	2.368266	-0.478527
C	1.939153	2.292073	-0.938504
H	-1.609100	2.317709	-0.815456
H	-0.564952	1.852299	-2.268299
H	0.333121	2.726280	0.537799
C	3.945862	-0.646717	-0.529837
C	4.019806	0.741015	-0.334841
C	5.252560	1.381923	-0.373501
C	6.388553	0.598946	-0.622236
C	6.300448	-0.788224	-0.817568
C	5.066741	-1.438481	-0.772690
C	2.610759	1.172706	-0.069977
H	5.341919	2.452383	-0.221327
H	7.362173	1.078493	-0.664509
H	7.204814	-1.358843	-1.005335
H	4.968252	-2.508310	-0.922433
H	2.488963	1.443254	0.987355
N	2.605104	-1.088157	-0.454621
N	1.847965	-0.103878	-0.224001
P	-1.744983	-1.376645	-1.249223
C	-1.316779	-3.085168	-1.993154
C	-2.178173	-3.206776	-3.286311
C	-3.421090	-2.320804	-3.172025
C	-2.950715	-0.943041	-2.656723
H	-1.581797	-2.879802	-4.145199
H	-2.435421	-4.256098	-3.466795
H	-4.145423	-2.764218	-2.478770
H	-3.930736	-2.214305	-4.136640
P	-1.137914	-0.544534	1.971702
C	-2.436455	0.513786	2.893950
C	-2.058317	0.411719	4.398749
C	-1.355532	-0.925622	4.655956
C	-0.267773	-1.082538	3.572805
H	-1.380313	1.229727	4.666075
H	-2.952489	0.532476	5.019918
H	-2.080392	-1.746111	4.598330
H	-0.911831	-0.963807	5.657598
C	-2.123262	-2.060237	1.483321
H	-2.826022	-2.340132	2.277184
H	-1.409935	-2.886869	1.383587
C	-2.886724	-1.834455	0.166660
H	-3.472432	-2.726965	-0.083577
H	-3.597980	-1.007750	0.277885
Cu	-0.200484	-0.011740	-0.134331

C	2.613282	3.645461	-0.612010
C	2.674527	4.107740	0.714708
C	3.169012	4.456716	-1.611267
C	3.270769	5.327492	1.031474
H	2.253845	3.516102	1.524273
C	3.765905	5.680847	-1.297119
H	3.144952	4.145832	-2.649022
C	3.821086	6.122050	0.023725
H	3.305259	5.655864	2.066505
H	4.188192	6.287270	-2.093368
H	4.286421	7.072635	0.267074
C	2.054164	1.913034	-2.423988
H	3.101045	1.860382	-2.733894
H	1.546513	2.644346	-3.059135
H	1.601984	0.934223	-2.609494
H	-2.293369	-0.513612	-3.425238
C	-4.034172	0.073929	-2.364011
C	-3.873918	1.401219	-2.792258
C	-5.232172	-0.266861	-1.713592
C	-4.864196	2.359046	-2.571595
H	-2.969404	1.682835	-3.326678
C	-6.225775	0.688694	-1.490749
H	-5.409505	-1.290030	-1.396244
C	-6.045891	2.006164	-1.916942
H	-4.718502	3.375587	-2.926341
H	-7.149230	0.396811	-0.998111
H	-6.826473	2.744565	-1.757206
H	-1.686794	-3.805481	-1.254042
C	0.152707	-3.370973	-2.228745
C	0.896092	-2.657828	-3.182787
C	0.785029	-4.413695	-1.539699
C	2.223413	-2.989173	-3.451070
H	0.430709	-1.845518	-3.737570
C	2.114852	-4.748396	-1.803904
H	0.226588	-4.984876	-0.801301
C	2.836383	-4.041827	-2.766057
H	2.775704	-2.434461	-4.204950
H	2.578238	-5.572094	-1.267920
H	3.863570	-4.315566	-2.991700
H	0.477404	-0.292378	3.738469
C	0.471809	-2.402279	3.501798
C	-0.138475	-3.627685	3.811991
C	1.821655	-2.415181	3.116555
C	0.577892	-4.824121	3.735888
H	-1.175720	-3.657404	4.131834
C	2.538363	-3.608528	3.035595
H	2.318922	-1.475122	2.887913

C	1.917622	-4.820325	3.345307
H	0.087705	-5.759212	3.992627
H	3.583829	-3.589669	2.740810
H	2.475330	-5.750993	3.293749
H	-3.386790	-0.011193	2.738834
C	-2.594210	1.926579	2.367148
C	-1.634896	2.922937	2.613323
C	-3.723101	2.271788	1.610430
C	-1.803002	4.219824	2.125230
H	-0.751301	2.693150	3.204323
C	-3.893077	3.567323	1.116229
H	-4.485328	1.522555	1.408313
C	-2.933769	4.547622	1.372879
H	-1.053155	4.976976	2.338246
H	-4.778985	3.805652	0.535253
H	-3.067403	5.558431	0.998613

TS1b

B3LYP SCF energy: -2584.97109888 a.u.
B3LYP enthalpy: -2584.141028 a.u.
B3LYP free energy: -2584.269775 a.u.
M06 SCF energy in solution: -2584.15975637 a.u.
M06 enthalpy in solution: -2583.329685 a.u.
M06 free energy in solution: -2583.458432 a.u.
Imaginary frequency: -679.9171 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.637666	1.236781	-2.556467
H	-0.595398	0.425466	-3.282546
H	-1.583632	1.771038	-2.487594
C	0.526033	1.842673	-2.085525
H	1.598664	0.860483	-0.957675
C	1.230635	2.981876	-2.223170
Cu	0.118388	0.341202	-0.777777
P	-0.854187	0.463212	1.339943
C	0.232826	0.858576	2.863846
C	-0.729398	1.449641	3.910209
C	-1.714309	2.345392	3.150758
C	-2.315334	1.507444	1.994875
H	-0.181518	2.000837	4.684782
H	-1.289842	0.654858	4.419025
H	-2.510491	2.731268	3.798568
H	-1.186474	3.216503	2.741680
P	-0.148580	-1.936436	-0.783443

C	-1.482766	-2.704517	-1.921410
C	-0.951002	-4.099008	-2.304523
C	0.567645	-3.972559	-2.464772
C	1.115058	-3.311733	-1.176770
H	-1.435775	-4.466768	-3.217392
H	-1.163661	-4.828605	-1.513203
H	1.049985	-4.942907	-2.632100
H	0.803385	-3.344537	-3.333896
H	0.869857	1.676545	2.504063
H	-3.017868	0.789413	2.437229
C	-0.642286	-2.367450	0.971551
H	-1.170961	-3.327963	1.005059
H	0.300626	-2.490657	1.516413
C	-1.496285	-1.275299	1.642371
H	-1.422793	-2.069932	-2.814860
H	1.010840	-4.044078	-0.364817
C	-2.896182	-2.606694	-1.390342
C	-5.518227	-2.310156	-0.380179
C	-3.616447	-1.413791	-1.579333
C	-3.522204	-3.648758	-0.688589
C	-4.819740	-3.503100	-0.190930
C	-4.909234	-1.263951	-1.078028
H	-3.147378	-0.591530	-2.113100
H	-3.005748	-4.591324	-0.533561
H	-5.284452	-4.328631	0.342331
H	-5.436706	-0.326842	-1.233273
H	-6.528442	-2.199324	0.004930
C	2.567906	-2.898654	-1.250554
C	5.301407	-2.229852	-1.420425
C	3.010633	-1.901132	-2.133146
C	3.520075	-3.548812	-0.452766
C	4.875291	-3.221008	-0.535126
C	4.362853	-1.571078	-2.218096
H	2.293111	-1.362404	-2.745112
H	3.196596	-4.324759	0.238029
H	5.595663	-3.743519	0.089452
H	4.681036	-0.788659	-2.901681
H	6.354481	-1.969743	-1.486590
C	-3.061767	2.316841	0.957328
C	-4.502683	3.857108	-0.915027
C	-4.445087	2.152392	0.799936
C	-2.410998	3.267352	0.154681
C	-3.123497	4.030051	-0.770617
C	-5.162131	2.914153	-0.126015
H	-4.967022	1.420397	1.412700
H	-1.336099	3.403890	0.238754
H	-2.597927	4.758033	-1.382823

H	-6.235488	2.772593	-0.225421
H	-5.056199	4.452270	-1.636386
C	1.144492	-0.272717	3.286592
C	2.876227	-2.395865	3.966041
C	0.850556	-1.126786	4.360142
C	2.329031	-0.500428	2.562783
C	3.182909	-1.551858	2.894907
C	1.709144	-2.176519	4.698129
H	-0.046479	-0.972364	4.952210
H	2.570436	0.145348	1.721978
H	4.085025	-1.711220	2.311129
H	1.463682	-2.819609	5.539693
H	3.544012	-3.211440	4.231000
H	-1.582795	-1.477354	2.717081
H	-2.508514	-1.290088	1.222904
C	0.930230	3.843161	-3.443239
H	0.734199	4.885286	-3.158639
H	1.772964	3.858863	-4.148343
H	0.060373	3.456396	-3.978146
C	2.301460	3.455017	-1.318000
C	3.395895	4.188788	-1.818319
C	2.263828	3.219465	0.070092
C	4.415686	4.635652	-0.979891
H	3.461583	4.399840	-2.881075
C	3.282116	3.669282	0.911322
H	1.413145	2.691645	0.482527
C	4.366717	4.376987	0.392005
H	5.251849	5.189086	-1.400480
H	3.221823	3.474926	1.979901
H	5.158098	4.731344	1.047455

TS1c

B3LYP SCF energy: -2584.97119543 a.u.
B3LYP enthalpy: -2584.140362 a.u.
B3LYP free energy: -2584.267406 a.u.
M06 SCF energy in solution: -2584.16163594 a.u.
M06 enthalpy in solution: -2583.330803 a.u.
M06 free energy in solution: -2583.457847 a.u.
Imaginary frequency: -716.6716 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.669943	-2.228177	-2.043862
C	-0.378313	-1.156749	-2.898541
H	0.907788	0.012097	-2.421965

C	-0.635791	-0.732758	-4.134587
Cu	0.030628	-0.220493	-1.125617
P	-1.271580	1.628253	-0.355008
C	-0.717503	3.322361	-1.056725
C	-1.934845	4.254069	-0.907787
C	-3.181597	3.419717	-1.209395
C	-3.117538	2.153360	-0.324088
H	-1.845990	5.123465	-1.570911
H	-2.006934	4.639601	0.116715
H	-4.108758	3.973047	-1.017357
H	-3.192656	3.138079	-2.269715
P	0.976945	-0.401319	0.961205
C	0.392278	-1.885424	2.027821
C	1.664177	-2.458612	2.698681
C	2.869319	-2.132913	1.807720
C	2.787569	-0.622265	1.489481
H	1.552654	-3.537521	2.857444
H	1.820556	-2.005508	3.684793
H	3.818586	-2.368159	2.303781
H	2.832656	-2.719545	0.881549
H	-0.591704	3.105232	-2.125045
H	-3.299145	2.467669	0.711990
C	0.512218	1.177557	1.849212
H	0.584876	1.047282	2.935201
H	1.277252	1.904925	1.553772
C	-0.885465	1.705597	1.480312
H	0.071164	-2.604700	1.267592
H	2.865960	-0.088260	2.447285
C	-0.789961	-1.600104	2.928214
C	-3.058284	-1.044883	4.524567
C	-2.090260	-1.852572	2.459128
C	-0.654504	-1.064124	4.219690
C	-1.773738	-0.791675	5.009071
C	-3.211478	-1.577806	3.242836
H	-2.221991	-2.270743	1.464745
H	0.333153	-0.862288	4.624475
H	-1.638717	-0.382926	6.007294
H	-4.202992	-1.785221	2.849270
H	-3.928298	-0.835448	5.141122
C	3.869016	-0.090419	0.577058
C	5.980275	0.851533	-1.036878
C	4.003223	-0.521993	-0.751730
C	4.807810	0.823518	1.077650
C	5.856638	1.289786	0.282554
C	5.047505	-0.053936	-1.549615
H	3.283762	-1.220291	-1.165453
H	4.721011	1.168305	2.106023

H	6.576499	1.991761	0.696094
H	5.131610	-0.398880	-2.577009
H	6.796339	1.209283	-1.659403
C	-4.137696	1.092215	-0.670235
C	-6.132500	-0.805417	-1.290706
C	-5.008285	0.608764	0.317675
C	-4.280738	0.598013	-1.976542
C	-5.270253	-0.336071	-2.284553
C	-5.994629	-0.332138	0.014548
H	-4.916770	0.980551	1.335935
H	-3.608007	0.935482	-2.760619
H	-5.363619	-0.701847	-3.303719
H	-6.660999	-0.686006	0.797254
H	-6.902984	-1.532368	-1.532717
C	0.611570	3.827568	-0.535482
C	3.133382	4.682682	0.403052
C	0.714379	4.755837	0.512169
C	1.800490	3.341622	-1.107124
C	3.046846	3.758458	-0.641415
C	1.962717	5.181164	0.974836
H	-0.179853	5.167703	0.970158
H	1.742007	2.610967	-1.909792
H	3.948891	3.352751	-1.089657
H	2.015393	5.907409	1.782241
H	4.103808	5.012666	0.764261
H	-1.009901	2.726621	1.862486
H	-1.651305	1.083571	1.959274
H	-0.369038	0.260729	-4.481185
H	-1.123645	-1.398891	-4.846263
C	-2.127661	-2.557557	-1.760471
H	-2.771572	-1.724954	-2.046093
H	-2.447867	-3.445291	-2.329936
H	-2.326615	-2.775982	-0.703668
C	0.358913	-3.227582	-1.725116
C	1.663249	-3.151390	-2.273937
C	0.085956	-4.332342	-0.883266
C	2.635920	-4.101316	-1.971908
H	1.895365	-2.342023	-2.958597
C	1.062691	-5.283028	-0.587903
H	-0.907309	-4.455033	-0.462653
C	2.349156	-5.175052	-1.121971
H	3.624493	-4.011168	-2.416838
H	0.811346	-6.120540	0.059356
H	3.106881	-5.920406	-0.896195

TS1d
B3LYP SCF energy: -2584.96595907 a.u.
B3LYP enthalpy: -2584.135470 a.u.
B3LYP free energy: -2584.261949 a.u.
M06 SCF energy in solution: -2584.15985821 a.u.
M06 enthalpy in solution: -2583.329369 a.u.
M06 free energy in solution: -2583.455848 a.u.
Imaginary frequency: -745.6299 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.902050	-1.911907	-2.380598
C	-0.703841	-0.663794	-2.968919
H	0.902924	0.037415	-2.640818
C	-1.194877	0.135649	-3.917146
Cu	0.241813	-0.152524	-1.198689
P	-0.323917	1.861667	-0.004230
C	0.800029	3.324631	-0.518462
C	0.073736	4.591418	-0.030777
C	-1.418075	4.380996	-0.290760
C	-1.821403	3.017690	0.324855
H	0.460847	5.484881	-0.536394
H	0.230007	4.740438	1.044882
H	-2.032652	5.184774	0.132177
H	-1.610175	4.369916	-1.371056
P	1.188014	-0.988268	0.714062
C	0.161839	-2.345307	1.597818
C	1.189774	-3.350074	2.165754
C	2.407727	-3.357961	1.234776
C	2.835079	-1.884151	1.040872
H	0.738427	-4.344556	2.264975
H	1.516931	-3.048278	3.167880
H	3.237005	-3.946282	1.645235
H	2.148551	-3.802854	0.264839
H	0.734270	3.302797	-1.613936
H	-1.845710	3.137900	1.415523
C	1.328868	0.461368	1.885480
H	1.401373	0.109824	2.921420
H	2.282980	0.937506	1.632163
C	0.183147	1.482173	1.763373
H	-0.361676	-2.834363	0.768487
H	3.162682	-1.514685	2.022652
C	-0.893701	-1.817418	2.547410
C	-2.900603	-0.754471	4.226554
C	-2.180270	-1.542571	2.052708
C	-0.637312	-1.555430	3.902974
C	-1.629947	-1.030726	4.734081

C	-3.171448	-1.014791	2.881060
H	-2.408808	-1.745556	1.010298
H	0.340795	-1.765785	4.326323
H	-1.407629	-0.841904	5.781413
H	-4.155671	-0.812644	2.467770
H	-3.672931	-0.349111	4.875057
C	3.973033	-1.673996	0.066945
C	6.167471	-1.383905	-1.680215
C	3.826361	-1.887301	-1.311907
C	5.237888	-1.309076	0.551113
C	6.327345	-1.167547	-0.310353
C	4.911431	-1.741838	-2.176640
H	2.854607	-2.152206	-1.714002
H	5.372195	-1.139242	1.617381
H	7.299062	-0.889619	0.089974
H	4.772894	-1.906905	-3.241946
H	7.012575	-1.275602	-2.354948
C	-3.185892	2.542127	-0.121774
C	-5.793419	1.841143	-0.936484
C	-4.219399	2.395979	0.814349
C	-3.479569	2.312780	-1.475143
C	-4.769925	1.970916	-1.879419
C	-5.511420	2.047854	0.414465
H	-4.011716	2.567569	1.868318
H	-2.690974	2.386331	-2.219686
H	-4.974745	1.799722	-2.932878
H	-6.297443	1.947161	1.158536
H	-6.799686	1.580472	-1.253452
C	2.261512	3.180250	-0.146110
C	4.989370	2.834553	0.496121
C	2.819084	3.792386	0.987117
C	3.103042	2.397667	-0.956053
C	4.448959	2.221357	-0.637372
C	4.169972	3.622992	1.303889
H	2.207734	4.419258	1.629040
H	2.687475	1.903056	-1.830285
H	5.072359	1.597444	-1.271043
H	4.579254	4.114377	2.183185
H	6.039173	2.701247	0.743381
H	0.452139	2.403222	2.295865
H	-0.718432	1.080200	2.239945
H	-0.869568	1.164161	-4.038753
H	-1.942479	-0.244039	-4.612601
C	0.171098	-2.959921	-2.614168
H	1.082986	-2.486166	-2.987571
H	0.427328	-3.528012	-1.709157
H	-0.149357	-3.692071	-3.371234

C	-2.183773	-2.333718	-1.792540
C	-3.292811	-1.462740	-1.667290
C	-2.371719	-3.664121	-1.347065
C	-4.495263	-1.888319	-1.116729
H	-3.196412	-0.437556	-2.005839
C	-3.584569	-4.088438	-0.799126
H	-1.566703	-4.385429	-1.441427
C	-4.657977	-3.208447	-0.674548
H	-5.315296	-1.179150	-1.034150
H	-3.685440	-5.121281	-0.472754
H	-5.602116	-3.539940	-0.250987

TS3

B3LYP SCF energy: -3502.34726746 a.u.
B3LYP enthalpy: -3501.194734 a.u.
B3LYP free energy: -3501.370707 a.u.
M06 SCF energy in solution: -3501.16116857 a.u.
M06 enthalpy in solution: -3500.008635 a.u.
M06 free energy in solution: -3500.184608 a.u.
Imaginary frequency: -163.1985 cm-1

Cartesian coordinates

ATOM	X	Y	Z
P	-2.892017	1.458958	-0.520058
C	-1.907294	1.478855	-2.121921
C	-1.155890	0.160042	-2.393411
P	0.263823	-0.147575	-1.219572
C	1.742290	0.765851	-1.997805
C	0.885104	-1.866435	-1.755102
C	2.339296	-0.256416	-2.987393
C	2.317551	-1.619893	-2.296308
C	-3.192947	3.337270	-0.282018
C	-4.692180	1.173242	-1.143440
C	-4.728284	3.515495	-0.355640
C	-5.249219	2.577393	-1.447606
C	0.812115	-2.946998	-0.697483
C	0.075976	-4.116277	-0.930599
C	1.509583	-2.827314	0.517367
C	0.031737	-5.141676	0.018632
C	1.461647	-3.848094	1.468098
C	0.722636	-5.009470	1.223499
C	1.463275	2.155061	-2.539273
C	1.530302	3.257441	-1.668271
C	1.152822	2.393852	-3.887557
C	1.285755	4.550565	-2.132938

C	0.905918	3.688792	-4.350516
C	0.968800	4.773585	-3.475620
C	-4.831399	0.114883	-2.216162
C	-4.903282	0.418820	-3.584914
C	-4.875552	-1.239893	-1.842167
C	-5.007320	-0.592939	-4.543370
C	-4.975952	-2.251469	-2.796668
C	-5.040932	-1.932240	-4.155543
C	-2.536382	3.905379	0.958604
C	-1.466791	4.804910	0.843896
C	-2.964745	3.551118	2.249255
C	-0.845124	5.337001	1.976256
C	-2.350803	4.085035	3.382643
C	-1.286281	4.981530	3.251178
H	-1.194973	2.306748	-2.052413
H	-2.562111	1.695527	-2.973858
H	-1.836148	-0.696043	-2.310740
H	-0.768783	0.160216	-3.419879
H	2.429622	0.856264	-1.150235
H	0.242667	-2.158881	-2.595717
H	3.357804	0.034939	-3.268282
H	1.747664	-0.303233	-3.910868
H	3.030700	-1.614602	-1.466293
H	2.611182	-2.432597	-2.970721
H	-2.755812	3.835062	-1.156507
H	-5.207964	0.801488	-0.248518
H	-4.986436	4.563424	-0.550979
H	-5.186115	3.251216	0.605956
H	-4.893075	2.935175	-2.421706
H	-6.345768	2.565213	-1.494226
H	-0.461685	-4.230471	-1.869696
H	2.101103	-1.936610	0.719391
H	-0.541221	-6.042328	-0.186347
H	2.005531	-3.735156	2.402324
H	0.688811	-5.803239	1.964647
H	1.767269	3.084173	-0.621354
H	1.113171	1.571410	-4.595354
H	1.357152	5.388383	-1.443518
H	0.672125	3.847293	-5.400346
H	0.784290	5.781640	-3.837676
H	-4.894629	1.452607	-3.916903
H	-4.835201	-1.507719	-0.789636
H	-5.068265	-0.327977	-5.595981
H	-5.010852	-3.287168	-2.469896
H	-5.125517	-2.717785	-4.901736
H	-1.112090	5.085674	-0.145004
H	-3.786196	2.849593	2.371361

H	-0.015859	6.029597	1.859825
H	-2.704673	3.800789	4.370484
H	-0.806216	5.395643	4.133409
C	-1.094864	-0.819944	2.691797
H	-0.194518	-1.233399	3.148786
Cu	-0.323078	-0.002464	1.024019
N	2.941633	1.525774	1.996417
C	0.826876	0.762569	4.813988
C	1.319932	1.083762	3.547128
C	1.731087	0.285905	5.767323
H	-0.221732	0.891450	5.063775
C	2.693620	0.963228	3.273819
C	0.765800	1.594155	2.299290
C	3.097372	0.149999	5.471110
H	1.372312	0.026822	6.759886
C	3.606430	0.499216	4.217235
H	-0.165598	2.140957	2.181068
H	3.773257	-0.221159	6.236709
H	4.656503	0.419489	3.960742
O	3.662100	0.162168	0.878337
C	4.970389	0.101965	0.987878
O	5.661995	0.519689	1.906296
C	5.582066	-0.579319	-0.226453
C	5.903463	0.205116	-1.352585
C	5.872121	-1.954224	-0.197794
C	6.498094	-0.418159	-2.453246
C	6.466540	-2.536526	-1.323647
C	6.784052	-1.789226	-2.461183
H	6.756368	0.185133	-3.322109
H	6.692313	-3.601258	-1.306205
C	5.550838	-2.794356	1.017974
H	6.082908	-3.750400	0.985047
H	5.833649	-2.275640	1.939740
H	4.477863	-3.015552	1.081110
C	5.655579	1.696979	-1.352509
H	6.201778	2.180072	-0.533638
H	5.979891	2.150323	-2.294283
H	4.596384	1.936894	-1.206278
C	7.455243	-2.432075	-3.653349
H	7.076212	-2.023868	-4.597369
H	8.540061	-2.259883	-3.641242
H	7.297691	-3.515784	-3.665737
C	-2.002600	-1.822450	2.171499
C	-3.374142	-1.774845	2.112933
C	-4.134667	-0.589301	2.663166
H	-5.029622	-0.373991	2.067604
H	-4.474244	-0.762556	3.695726

H	-3.516504	0.310697	2.667007
C	-4.157070	-2.916733	1.604378
C	-5.507627	-3.093414	1.980414
C	-3.608022	-3.878651	0.724642
C	-6.259287	-4.174301	1.521262
H	-5.972625	-2.386342	2.659883
C	-4.359554	-4.957380	0.268199
H	-2.585829	-3.768194	0.378673
C	-5.692355	-5.116603	0.662399
H	-7.293177	-4.280166	1.840358
H	-3.903249	-5.676956	-0.407758
H	-6.277855	-5.957774	0.301520
H	-1.520586	-2.735006	1.825540
N	1.778380	1.852457	1.424866
H	-1.534282	-0.038312	3.310067

TS4

B3LYP SCF energy: -3502.33600930 a.u.
B3LYP enthalpy: -3501.183666 a.u.
B3LYP free energy: -3501.360397 a.u.
M06 SCF energy in solution: -3501.15067166 a.u.
M06 enthalpy in solution: -3499.998328 a.u.
M06 free energy in solution: -3500.175059 a.u.
Imaginary frequency: -356.0012 cm-1

Cartesian coordinates

ATOM	X	Y	Z
P	0.464349	2.275911	-1.047398
C	0.064261	3.038331	0.612429
C	0.606942	2.235879	1.807659
P	0.349508	0.387616	1.686821
C	-1.377612	-0.021809	2.430391
C	1.239579	-0.210634	3.245495
C	-1.093813	-0.854923	3.715537
C	0.346286	-1.388493	3.689884
C	-0.340953	3.514464	-2.244021
C	2.240047	2.861680	-1.511202
C	0.739081	3.679632	-3.338334
C	2.064852	3.933700	-2.615958
C	2.721675	-0.499828	3.172851
C	3.564935	0.028676	4.162398
C	3.288500	-1.314521	2.181156
C	4.931679	-0.253210	4.172986
C	4.656454	-1.594054	2.185792
C	5.482261	-1.068174	3.182520

C	-2.306627	1.163261	2.610410
C	-3.290057	1.419785	1.639828
C	-2.220475	2.038261	3.706548
C	-4.153271	2.510134	1.759821
C	-3.083404	3.129230	3.828139
C	-4.053832	3.371330	2.854316
C	3.133380	3.241735	-0.347254
C	3.161652	4.534682	0.200197
C	3.956859	2.265117	0.238798
C	3.985688	4.839538	1.286124
C	4.778427	2.564164	1.326202
C	4.797824	3.857027	1.854269
C	-1.716556	3.192847	-2.783642
C	-2.694429	4.198424	-2.820355
C	-2.028078	1.938335	-3.327761
C	-3.942603	3.968937	-3.401445
C	-3.274018	1.708423	-3.912592
C	-4.234350	2.722354	-3.957172
H	-1.031436	3.075398	0.655478
H	0.429370	4.070784	0.669394
H	1.692457	2.364194	1.882431
H	0.167822	2.616846	2.736075
H	-1.826315	-0.672059	1.676776
H	1.096050	0.592913	3.982244
H	-1.827710	-1.664196	3.810069
H	-1.214710	-0.225799	4.603786
H	0.452079	-2.221512	2.981736
H	0.656825	-1.764439	4.672031
H	-0.401427	4.467302	-1.698787
H	2.669535	1.968263	-1.975364
H	0.477030	4.499286	-4.018073
H	0.793270	2.765804	-3.945295
H	2.033752	4.936770	-2.176217
H	2.920568	3.917485	-3.301657
H	3.142679	0.664952	4.937640
H	2.664286	-1.715807	1.387824
H	5.562921	0.164758	4.953240
H	5.081601	-2.210443	1.400404
H	6.546197	-1.289291	3.181064
H	-3.381193	0.748725	0.791115
H	-1.477457	1.870708	4.482252
H	-4.909061	2.678891	0.997404
H	-2.996821	3.788505	4.688231
H	-4.727765	4.218399	2.951122
H	2.542472	5.321393	-0.221080
H	3.939815	1.251175	-0.150425
H	3.991768	5.850583	1.685776

H	5.394285	1.781889	1.760161
H	5.439028	4.096107	2.698436
H	-2.470530	5.176215	-2.398176
H	-1.312912	1.123529	-3.274705
H	-4.683173	4.764550	-3.421711
H	-3.493118	0.727360	-4.324878
H	-5.203330	2.539554	-4.414347
C	1.835215	-1.022300	-2.087113
H	1.402138	-2.011329	-2.232947
Cu	0.600115	-0.203035	-0.616966
C	-7.170576	-0.698044	0.079127
C	-7.405025	-1.246630	1.345005
H	-7.925114	-0.056003	-0.371500
C	-5.997395	-0.959260	-0.633415
C	-6.431797	-2.089126	1.890525
C	-5.027710	-1.795141	-0.046954
H	-6.605440	-2.542353	2.864661
C	-5.238673	-2.371563	1.218613
C	-3.771427	-2.125680	-0.825396
O	-3.714493	-2.960335	-1.704297
O	-2.766614	-1.359894	-0.378655
N	-1.186079	-1.573560	-1.100834
C	-0.270053	-4.845627	-2.355607
C	-0.656723	-3.511389	-2.215159
C	-0.101354	-5.601402	-1.194699
H	-0.105713	-5.284882	-3.335379
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H         3.955045   -3.858050   -0.253477
N        -1.333842   -1.337767   -2.485053



 9
B3LYP SCF energy:     -2964.06391870 a.u.
B3LYP enthalpy:       -2963.109734 a.u.
B3LYP free energy:    -2963.251947 a.u.
M06 SCF energy in solution:     -2963.11960594 a.u.
M06 enthalpy in solution:       -2962.165421 a.u.
M06 free energy in solution:    -2962.307634 a.u.

Cartesian coordinates
ATOM       X           Y           Z
P        -0.153205   -0.918636   -1.654311
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C	3.374871	-3.954090	0.955951
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 10
B3LYP SCF energy:     -2964.08924531 a.u.
B3LYP enthalpy:       -2963.134586 a.u.
B3LYP free energy:    -2963.279145 a.u.
M06 SCF energy in solution:     -2963.14612828 a.u.
M06 enthalpy in solution:       -2962.191469 a.u.
M06 free energy in solution:    -2962.336028 a.u.

Cartesian coordinates
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