Supporting Information

Mechanistic Studies on Au(I)-Catalyzed [3,3]-Sigmatropic Rearrangements using Cyclopropane Probes

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1. General Information

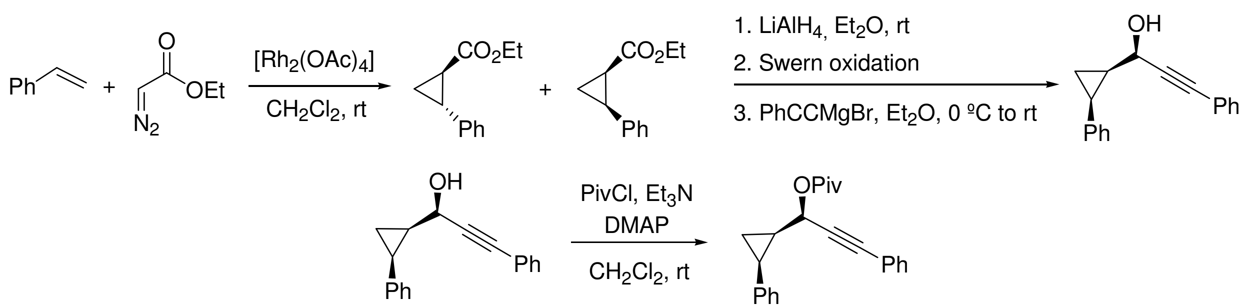
Unless otherwise noted, all reagents were obtained commercially and used without further purification. ACS grade nitromethane was obtained from Aldrich Chemical Company. Tetrahydrofuran (THF), diethyl ether and dichloromethane were dried according to a procedure by Bergman.[1] $(Ph_3P)AuCl$ was prepared according to literature procedures.[2] Extracts were dried over $MgSO_4$ or Na_2SO_4 and solvents were removed *in vacuo* via a rotary evaporator at aspirator pressure. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates. Chromatography was carried out on ICN SiliTech 32-63 D 60 Å silica gel. ^1H and ^{13}C NMR spectra were recorded with Bruker AMX-300, AVQ-400 and AVB-400 spectrometers and referenced to CD_2Cl_2, CD_3NO_2, C_6D_6 or $CDCl_3$. Mass spectral and CHN data were obtained *via* the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

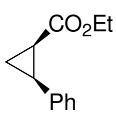
2. Selected Analytical Data and Representative Experimental Procedures

2.1. Au(I)-catalyzed vinylcyclopropane-cyclopentene rearrangements

Propargylic esters bearing aryl substituents at the cyclopyl unit.

*Representative procedure: synthesis of **9**.*

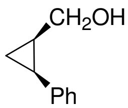




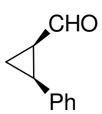
Compound previously reported.[3] To a suspension of styrene (3.0 g, 28.8 mmol) and $Rh_2(OAc)_4$ (40 mg, 0.09 mmol) in CH_2Cl_2 at room temperature was added ethyl diazoacetate (3.28 g, 28.8 mmol) via syringe pump and over the course of 12 hours. Once the addition was complete, the green mixture was stirred for another 12 hours, and then filtered through a short pad of silica gel to afford the desired cyclopropane derivative as a mixture of diastereoisomers (*trans*:*cis* = 60:40) in 88% yield. The mixture was separated by flash chromatography (typical eluent, pentane:Et_2O). The desired *cis* ethyl 2-

[1] Alaimo, P.J.; Peters, D.W.; Arnold, J.; Bergman, R.G. *J. Chem. Ed.* **2001**, *78*, 64.
[2] Bruce M. I.; Nicholson B. K.; Binshawkataly O.; Shapley Jr., Henly T. *Inorg. Syn.* **1989**, *26*, 324.
[3] Doyle, M. P.; Loh, K. L.; DeVries, K. M.; Chinn, Mi. S. *Tetrahedron Lett.* **1987**, *28*, 833.

phenylcyclopropane carboxylate was obtained as a clear oil (32% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.19 (m, 5H), 3.85 (q, *J* = 14.1 Hz, 2H), 2.55 (q, *J* = 7.8 Hz, 1H), 2.10 (m, 1H), 1.70 (m, 1H), 1.45 (m, 1H), 1.0 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 171.0, 136.5, 129.3, 127.9, 126.6, 60.2, 25.4, 21.8 14.0, 11.1.



Compound previously reported.[4] A solution of *cis* ethyl 2-phenylcyclopropane carboxylate in Et_2O was added dropwise and under vigorous stirring to a 0 ºC suspension of $LiAlH_4$ in Et_2O. The solution was stirred at room temperature until TLC showed complete consumption of the starting material (ca. 2 hours). The reaction mixture was carefully quenched with sat. aq. Na_2SO_4, stirred at room temperature for 1hour and filtered over a short pad of silica to remove the aluminum salts. Concentration afforded the desired alcohol in 94% yield, which was directly used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.17 (m, 5H), 3.48-3.44 (m, 1H), 3.27 (dd, *J* = 8.4 and 12.6 Hz, 1H), 2.32 (m, 1H), 1.51 (m, 1H), 1.29 (bs, 1H), 1.06 (dt, *J* = 5.4 and 8.4 Hz, 1H), 0.89 (q, *J* = 5.6 Hz, 1H).



Compound previously reported.[5] To a solution of oxalyl chloride (0.63 mL, 7.42 mmol) in dry CH_2Cl_2 (34 mL) was added DMSO (1.05 mL, 14.84 mmol) dropwise at -78 °C under nitrogen. The reaction mixture was stirred for 30 min, and the previously obtained alcohol (1.00 g, 6.75 mmol) was then added dropwise at -78 °C. After an additional 30 min of stirring at that temperature, dry Et_3N (4.75 mL, 33.75 mmol) was added dropwise and the reaction mixture was warmed to room temperature. Water (50 mL) was then added, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with DCM (3x10 mL). The combined organic layers were washed with brine (20 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography eluting with 5:1 hexanes/AcOEt to provide the desired aldehyde as a colorless oil (83% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, *J* = 6.7 Hz, 1H), 7.34-7.21 (m, 5H), 2.83 (q, *J* = 8.2 Hz, 1H), 2.14 (m, 1H), 1.89 (dt, *J* = 5.3 and 7.2 Hz, 1H), 1.59 (dt, *J* = 5.6 and 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 201.3, 135.7, 129.1, 128.5, 127.1, 29.6, 26.3, 11.5.

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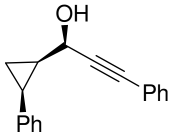
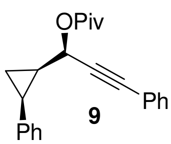
[4] Baldwin, J. E.; Patapoff, T. W.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1421.
[5] Aggarwal, V. K.; Guang Yu Fang, G. Y.; Graham Meek, G. *Org. Lett.* **2003**, *5*, 4417.



To a solution of the previously obtained phenyl cyclopropyl aldehyde (439 mg, 3.00 mmol) in ether (15 mL) was added phenylethynyl magnesium bromide (3.1 mL, 3.10 mmol) dropwise at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 2 hours. Water (10 mL) was then added to the resulting mixture, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with AcOEt (3x5 mL). The combined organic layers were washed with brine (15 mL), dried with $MgSO_4$, filtered, and concentrated to obtain the desired alcohol as a mixture of diastereoisomers about the propargylic position (87:13). The residue was purified by chromatography eluting with 10:1 hexanes/AcOEt to provide the desired product as a white solid (78% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 7.47-7.42 (m, 2H), 7.15-7.09 (m, 4H), 7.06-7.02 (m, 1H), 7.99-6.93 (m, 3H), 3.76 (d, J = 9.4 Hz, 1H), 2.02 (m, 1H), 1.59 (quint, J = 8.1 Hz, 1H), 1.37 (bs, 1H), 0.77 (m, 2H). ^{13}C NMR (75 MHz, C_6D_6): δ 137.9, 132.0, 129.7, 128.5, 128.4, 128.3, 126.6, 123.6, 91.2, 84.1, 63.0, 26.1, 22.2, 7.6. HRMS (FAB) calc. for $[C_{18}H_{16}O]^+$ ($[M]^+$) 248.1201, found 248.1204.



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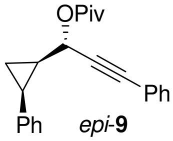
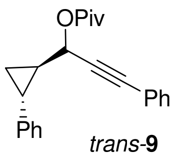
9. To a solution of the previously obtained alcohol (496 mg, 2.0 mmol) in dry CH_2Cl_2 (10 mL) were added Et_3N (0.42 mL, 3.0 mmol) and DMAP (25 mg, 0.2 mmol) at room temperature. The solution was then cooled at 0 ºC, and pivaloyl chloride (0.30 mL, 2.4 mmol) was added dropwise. The reaction mixture was then stirred overnight at room temperature. A saturated solution of $NaHCO_3$ (10 mL) was then added to the resulting mixture, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with DCM (3x5 mL). The combined organic layers were washed with brine (20 mL), dried with Na_2SO_4, filtered and concentrated. The residue was purified by chromatography eluting with AcOEt/hexanes (1:25) to provide a colorless oil (1.07 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.30-7.17 (m, 8H), 4.63 (d, J = 10.4 Hz), 2.40 (q, J = 7.6 Hz, 1H), 1.89-1.81 (m, 1H), 1.27-1.21 (m, 1H), 1.16-1.13 (m, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 136.7, 131.9, 128.9, 128.3, 128.1, 126.5, 122.6, 87.0, 84.1, 64.4, 38.4, 27.0, 23.0, 22.0, 7.7. HRMS (FAB) calc. for $[C_{23}H_{24}O_2]^+$ ($[M]^+$) 332.1776, found 332.1779.



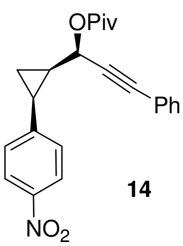
epi-9

***epi*-9.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.36-7.33 (m, 7H), 7.30-7.26 (m, 1H), 4.92 (d, *J* = 10.0 Hz), 2.47 (q, *J* = 8.4 Hz, 1H), 1.87-1.79 (m, 1H), 1.29 (s, 9H), 1.25-1.21 (m, 1H), 1.19-1.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 137.0, 131.7, 129.4, 128.3, 128.1, 126.5, 122.6, 86.5, 84.7, 65.6, 38.8, 27.0, 23.5, 21.1, 8.8. HRMS (FAB) calc. for $[C_{23}H_{24}O_2]^+$ ($[M]^+$) 332.1776, found 332.1778.



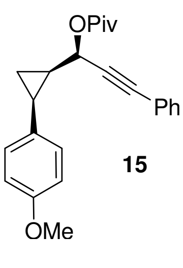
trans-9

***trans*-9.** Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 4H), 7.37-7.28 (m, 10H), 7.23-7.14 (m, 6H), 5.74 (d, *J* = 6.4 Hz, 1H), 5.64 (d, *J* = 6.8 Hz, 1H), 2.26 (quint, *J* = 4.4 Hz, 1H), 2.18 (quint, *J* = 5.2 Hz, 1H), 1.74-1.66 (m, 2H), 1.29 (s, 9H), 1.28 (s, 9H), 1.34-1.24 (m, 2H), 1.15-1.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 141.6, 141.5, 131.9, 131.8, 128.6, 128.3, 128.2, 128.1, 126.5, 126.2, 125.9, 122.2, 122.1, 85.6, 85.4, 84.8, 84.5, 66.6, 66.5, 38.8, 27.1, 25.8, 25.1, 21.6, 20.3, 12.9, 12.3. HRMS (FAB) calc. for $[C_{23}H_{24}O_2]^+$ ($[M]^+$) 332.1776, found 332.1779.



14

14. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.45-7.43 (m, 4H), 7.40-7.35 (m, 3H), 4.71 (d, *J* = 10.0 Hz, 1 Hz), 2.52 (q, *J* = 8.0 Hz, 1 Hz), 2.03 (m, 1H), 1.41 (m, 1H), 1.29, (m, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2) d 176.2, 146.2, 145.5, 131.7, 129.7, 128.7, 128.3, 123.2, 122.2, 86.3, 84.5, 63.8, 38.3, 26.7, 24.0, 22.0, 8.6. HRMS (FAB) calc. for $[C_{23}H_{23}NO_4]^+$ ($[M]^+$) 367.1627, found 367.1620.

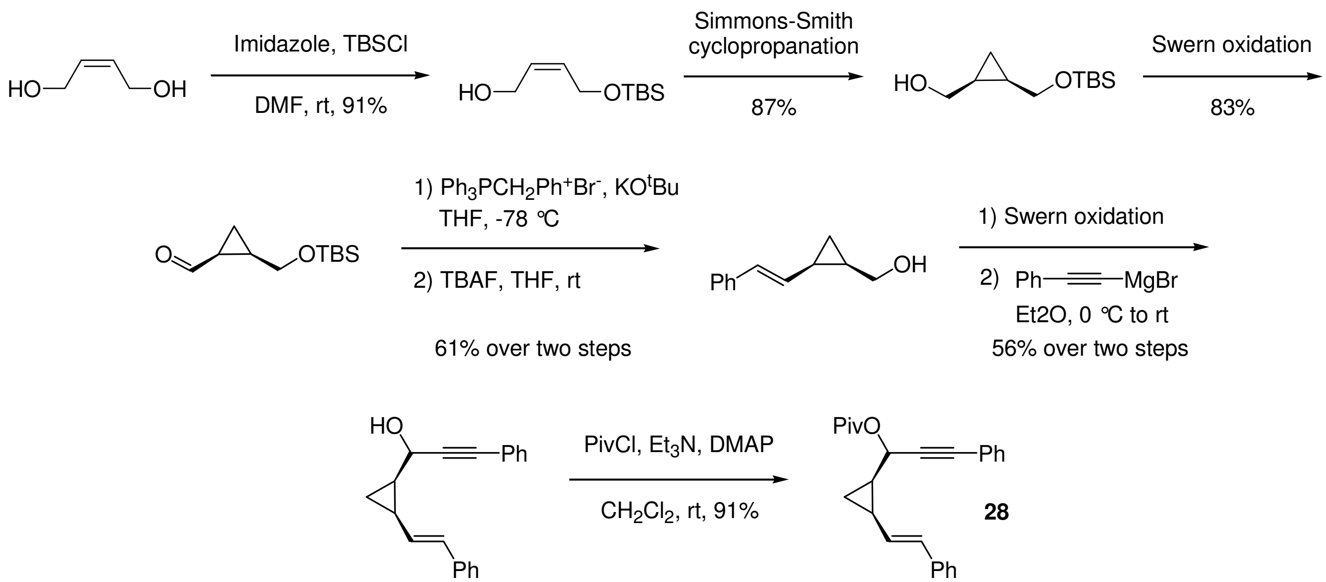


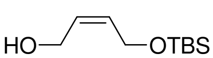
15

15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.32-7.29 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.60 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 2.36 (q, *J* = 8.0 Hz, 1H), 1.81 (m, 1H), 1.22 (m, 1H), 1.16 (s, 9H), 1.06 (q, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 158.2, 131.8, 130.0, 128.7, 128.3, 128.1, 122.6, 113.6, 87.1, 84.0, 64.6, 55.2, 38.4, 27.0, 22.6, 21.3, 7.7. HRMS (FAB) calc. for $[C_{24}H_{26}O_3]^+$ ($[M]^+$) 362.1882, found 362.1888.

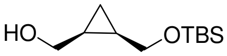
Propargylic esters bearing styrene at the cyclopropyl unit.

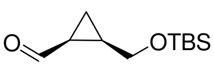
Representative procedure: synthesis of ***28****.*

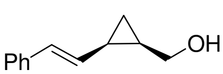




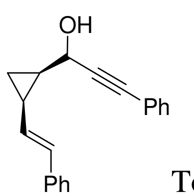
To a stirred solution of imidazole (10.2 g, 150 mmol) in dry DMF (50 mL) under a nitrogen atmosphere was added *cis*-2-butene-1,4-diol (8.2 mL, 100 mmol) dropwise. The resulting mixture was stirred at room temperature for 45 min, and then *tert*-butyldimethylsilyl chloride (16.6 g, 110 mmol) was added in one portion. The reaction mixture was stirred an additional 30 min, diluted with H_2O (100 mL), and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with ether (3x40 mL). The combined organic layers were washed with water (100 mL), brine (100 mL), dried with $MgSO_4$, filtered, and concentrated to yield a yellow residue. The residue was purified by chromatography eluting with 3:1 hexanes/EtOAc to provide a colorless oil (91% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 5.74-5.54 (m, 2H), 4.25-4.17 (dd, *J* = 6.0, 21.0 Hz, 4H), 2.44 (bs, 1H), 0.89 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.2, 130.0, 59.5, 58.7, 25.8, 25.6, 18.3, -3.6, -5.3. HRMS (FAB) calc. for $[C_{10}H_{22}O_2Si]^+$ ($[M]^+$) 202.1389, found 202.1394.

 To a solution of diiodomethane (3.18 mL, 39.6 mmol) in dry CH_2Cl_2 (100 mL) was added diethylzinc (20.0 mL, 20.0 mmol) under nitrogen at 0 °C. The resulting white suspension was stirred for 15 min at 0 °C, and then cooled to -78 °C. The previously prepared allylic alcohol (2.00 g, 9.88 mmol) was added, and the reaction mixture was stirred at -78 °C for 15 min. Approximately four drops of $TiCl_4$ were subsequently added, and the creamy white reaction mixture was warmed to -20 °C, and stirred for 3 h. The cold reaction mixture was then poured into sat. NH_4Cl (100 mL), the layers were separated, and the aqueous layer was extracted with AcOEt (3x20 mL). The combined organic layers were washed with sat. NH_4Cl, followed by brine, and then dried with $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography eluting with 10:1 hexanes/AcOEt to provide a colorless oil (5.88 g, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (dd, *J* = 5.4, 11.6 Hz, 1H), 3.97 (dd, *J* = 12.1, 5.3 Hz, 1H), 1.43-1.30 (m, 1H), 1.30-1.18 (m, 1H), 0.92 (s, 1H), 0.76 (m, 1H), 0.20 (m, 1H), 0.12 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.8, 63.0, 25.7, 18.1, 17.3, 8.3, -5.4, -5.6. HRMS (FAB) calc. for $[C_{11}H_{24}O_2Si]^+$ ($[M]^+$) 216.1546, found 216.1552.

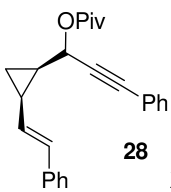
 To a solution of oxalyl chloride (0.76 mL, 8.74 mmol) in dry CH_2Cl_2 (40 mL) was added DMSO (1.24 mL, 17.5 mmol) dropwise at -78 °C under nitrogen. The reaction mixture was stirred for 30 min, and cyclopropyl alcohol (1.72 g, 7.94 mmol) was then added dropwise at -78 °C. After an additional 30 min of stirring, dry Et_3N (5.54 mL, 39.7 mmol) was added, and the reaction mixture was warmed to room temperature. Water (50 mL) was then added to the resulting mixture, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography eluting with 6:1 hexanes/Et_2O to provide a colorless oil (1.41 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 5.0 Hz, 1H), 3.97 (dd, *J* = 11.2, 5.4 Hz, 1H), 3.63 (m, 1H), 2.02-1.91 (m, 1H), 1.82-1.73 (m, 1H), 1.37-1.32 (m, 1H), 1.25-1.20 (m, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (167 MHz, $CDCl_3$) δ 201.4, 61.4, 27.9, 26.7, 26.3, 26.1, 18.7, 12.5. HRMS (FAB) calc. for $[C_{11}H_{22}O_2Si]^+$ ($[M]^+$) 214.1389, found 214.1387.

 To a solution of benzyltriphenylphosphonium bromide (3.79 g, 8.75 mmol) in dry THF (60 mL) was added potassium *tert*-butoxide (1.01 g, 9.04 mmol) in one portion at room temperature. The reaction mixture was stirred at room temperature for one hour, and then it was cooled to -78 °C before 2-(*tert*-butyl-dimethyl-silanyloxymethyl)-cyclopropanecarbaldehyde (1.6 g, 7.5 mmol)

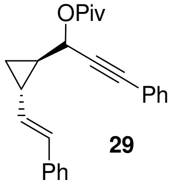
was added dropwise as a solution in THF (15 mL). The reaction mixture was subsequently warmed to room temperature, and stirred for an additional three hours. Saturated NH_4Cl (50 mL) was then added to the reaction mixture, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with AcOEt (3x10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated. The residue obtained was dissolved in THF (15 mL) and a solution of TBAF in THF (5.50 mL, 5.50 mmol) was added dropwise at 0 ºC. The reaction solution was stirred overnight at room temperature. Water (10 mL) was then added, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with AcOEt (3x10 mL). The combined organic layers were washed with brine (20 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography eluting with 1:1 hexanes/Et_2O to provide the desired product as a colorless oil (0.622 g, 61% yield over two steps). Obtained as a 2.2:1 mixture of diastereomers. ^1H NMR (400 MHz, $CDCl_3$) major diastereomer: δ 7.43-7.13 (m, 5H), 6.52 (d, J = 16.0 Hz, 1H), 5.97 (m, 1H), 3.80-3.76 (m, 1H), 3.54-3.49 (m, 1H), 1.79-1.72 (m, 1H), 1.59 (bs, 1H), 1.52-1.38 (m, 1H), 1.07-1.01 (m, 1H), 0.57-0.53 (m, 1H); minor diastereomer: δ 5.40 (m, 1H), 2.02-1.94 (m, 1H), 0.50-0.46 (m, 1H). ^{13}C NMR (167 MHz, $CDCl_3$) δ 137.3, 137.2, 130.9, 130.8, 130.7, 128.8, 128.7, 128.5, 128.3, 126.9, 126.8, 125.7, 63.8, 63.3, 22.1, 21.6, 19.1, 15.8, 13.7, 11.6. HRMS (FAB) calc. for $[C_{12}H_{14}O]^+$ ($[M]^+$) 174.1045, found 174.1050.



To a solution of oxalyl chloride (0.56 mL, 6.41 mmol) in dry CH_2Cl_2 (30 mL) was added DMSO (0.90 mL, 12.8 mmol) dropwise under nitrogen at -78 °C. The reaction mixture was stirred for 30 min, and (2-styryl-cyclopropyl)-methanol (1.01 g, 5.82 mmol) was then added dropwise at -78 °C. After an additional 30 min of stirring, dry Et_3N (4.04 mL, 29.0 mmol) was subsequently added, and the reaction mixture was warmed to room temperature. Water (20 mL) was then added to the resulting mixture, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with DCM (3x10 mL). The combined organic layers were washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated. To a solution of the obtained vinyl cyclopropyl aldehyde in ether (30 mL) at 0 ºC was added phenylethynyl magnesium bromide (7.0 mL, 7.0 mmol) dropwise. The reaction mixture was then warmed to room temperature and stirred for two hours. Water (20 mL) was then added to the resulting mixture, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with AcOEt (3x10 mL). The combined organic layers were washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography eluting with 8:1 hexanes/AcOEt to provide the desired product as a colorless oil (984 mg, 56% yield over two steps). Obtained as a 3.1:1 mixture of diastereomers. ^{1}H NMR (500 MHz, CD_2Cl_2) major diastereomer: δ 7.54-7.17 (m, 10H), 6.61-6.58 (d, J = 16.0 Hz, 1H), 6.25-6.20 (m, 1H), 4.42-4.40 (d, J = 8.5 Hz, 1H,), 2.18 (bs, 1H), 1.94-1.88 (m, 1H), 1.68-1.62 (m, 1H), 1.23-1.16 (m, 1H), 0.95-0.90 (m, 1H). Minor diastereomer: δ 6.57-6.55 (d, J = 12.0 Hz, 1H), 5.57-5.52 (m, 1H), 4.38-4.36 (d, J = 12.0 Hz, 1H), 2.12-2.06 (m, 1H), 1.74-1.69 (m, 1H), 0.81-0.78 (m, 1H). HRMS (FAB) calc. for $[C_{20}H_{28}O]^+$ ($[M]^+$) 274.1358, found 274.1362.

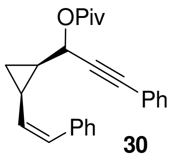


28. To a solution of the previously obtained alcohol (900 mg, 3.28 mmol) in dry CH_2Cl_2 (16.5 mL) were added Et_3N (0.69 mL, 4.92 mmol) and DMAP (41 mg, 0.33 mmol) at room temperature. The solution was then cooled at 0 ºC, and pivaloyl chloride (0.48 mL, 3.94 mmol) was added dropwise. The reaction mixture was then stirred overnight at room temperature. A saturated solution of $NaHCO_3$ (10 mL) was then added, and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with DCM (3x30 mL). The combined organic layers were washed with brine (20 mL), dried with Na_2SO_4, filtered and concentrated. The residue was purified by chromatography eluting with AcOEt/hexanes (1:25) to provide a colorless oil (1.07 g, 91% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.45 (m, 2H), 7.33 (m, 3H), 7.28 (m, 4H), 7.19 (m, 1H), 6.53 (d, J = 15.0 Hz, 1H), 5.94 (dd, J = 5.0, 15.0 Hz, 1H), 5.30 (d, J = 10.0 Hz, 1H), 1.89 (m, 1H), 1.80 (m, 1H), 1.12 (s, 9H), 0.85 (m, 1H). ^{13}C NMR (167 MHz, CD_2Cl_2) δ 177.3, 138.0, 132.3, 131.6, 129.2, 129.0, 128.9, 128.8, 127.4, 126.3, 122.9, 87.3, 84.9, 65.2, 39.0, 27.2, 24.0, 20.8, 12.14. Anal. Calc.: C, 83.76; H, 7.31, found C, 83.67; H, 7.42.

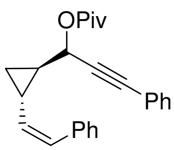


29. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 4H), 7.41-7.38 (m, 14H), 7.33-7.28 (m, 2H), 6.60 (dd, J = 12.0 and 15.6 Hz, 2H), 5.93 (dt, J = 8.4 and 15.6 Hz, 2H), 5.77 (d, J = 6.4 Hz, 1H), 5.73 (d, J = 6.8 Hz, 1H), 2.03-1.96 (m, 1H), 1.96-1.89 (m, 1H), 1.67 (m, 2H), 1.39 (s, 9H), 1.38 (s, 9H). 1.31-1.21 (m, 2H), 1.02-

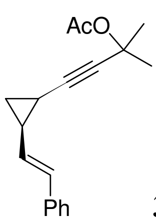
0.9 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 137.2, 137.1, 131.8, 131.7, 131.6, 131.5, 128.6, 128.5, 128.4, 128.3, 128.1, 126.7, 125.5, 122.0, 121.9, 84.5, 84.3, 66.2, 66.1, 38.6, 26.9, 23.9, 23.6, 20.4, 19.0, 12.1. 11.2. HRMS (FAB) calc. for $[C_{25}H_{26}O_2]^+$ ($[M]^+$) 358.1933, found 358.1937.



30 **30.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.37-7.28 (m, 7H), 7.26-7.21 (m, 1H), 6.49 (d, *J* = 15.2 Hz, 1H), 5.36 (dd, *J* = 12.8 and 15.2 Hz, 1H), 5.28 (d, *J* = 13.6 Hz, 1H), 2.12 (m, 1H), 1.85 (m, 1H), 1.24 (m, 1H), 1.18 (s, 9H), 0.75 (q, *J* = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 137.4, 132.0, 131.6, 131.0, 130.0, 128.9, 128.6, 128.3, 128.2, 126.9, 126.8, 122.5, 86.8, 84.5, 65.2, 38.8, 27.1, 24.0 17.3, 13.9. HRMS (FAB) calc. for $[C_{25}H_{26}O_2]^+$ ($[M]^+$) 358.1933, found 358.1936.



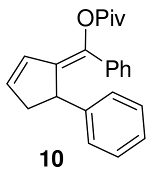
31 **31.** Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.50-7.46 (m, 6H), 7.41-7-34 (m, 8H), 7.30-7.29 (m, 2H), 6.50 (d, *J* = 11.6 Hz, 1H), 6.47 (d, *J* = 11.6 Hz, 1H), 5.72 (d, *J* = 6.4 Hz, 1H), 5.66 (d, *J* = 6.8 Hz, 1H), 5.23 (t, *J* = 10.8 Hz, 1H), 5,19 (t, *J* = 10.4 Hz, 1H), 2.33-2.25 (m, 2H), 1.65-1.56 (m, 2H), 1.32 (s, 9H), 1.30 (s, 9H), 1.16 (m, 2H), 0.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 1177.5, 137.6, 137.5, 133.9, 133.8, 132.0, 131.9, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 126.7, 122.3, 122.2, 85.8, 85.6, 84.8, 84.6, 66.3, 66.2, 38.9, 38.8, 27.2, 27.1, 24.6, 24.3, 17.5, 16.3, 13.4, 12.3. HRMS (FAB) calc. for $[C_{25}H_{26}O_2]^+$ ($[M]^+$) 358.1933, found 358.1937.



34. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 9.2 and 16.0 Hz, 1H), 1.96 (s, 3H), 1.90-1.82 (m, 1H), 1.70 (dt, *J* = 5.7 and 8.2 Hz, 1H), 1.64 (m, 3H), 1.63 (m, 3H), 1.28-1.23 (m, 1H), 0.89 (q, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 137.6, 130.4, 130.0, 128.4, 126.8, 125.8, 84.5, 79.8, 72.3, 29.3, 29.1, 22.0, 21.9, 16.4, 8.2. HRMS (FAB) calc. for $[C_{18}H_{20}O_2]^+$ ($[M]^+$) 268.1463, found 268.1465.

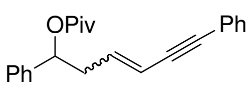
General procedure for Au(I)-catalyzed rearrangemets of propargylic esters:

A mixture of Ph_3PAuCl (1 mol%) and $AgSbF_6$ (1 mol%) in 0.3 mL of CH_2Cl_2 was stirred at room temperature for 5 minutes. Then, it was added to a 1 dram vial covered with a threaded cap containing a magnetic stir bar and the corresponding propargylic ester (100mg, 1 equiv.) in CH_2Cl_2 (0.1 M, rt). The resulting reaction mixture was then stirred at room temperature and monitored by TLC or ^{1}H NMR. Upon completion, the crude oil was purified by column chromatography to give the desired substrate.



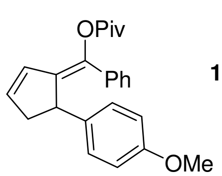
10

10. Obtained as an 87:13 mixture of olefins abot the exocyclic double bond. ^{1}H NMR (300 MHz, $CDCl_3$) major diastereomer: δ 7.42-7.11 (m, 10H), 6.50 (m, 1H), 6.15 (m, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.25 (ddt, *J* = 2.5, 8.0 and 18.0 Hz, 1H), 2.56 (d, *J* = 18.0 Hz, 1H), 1.40 (s, 9H). Minor diastereomer (diagnostic peaks): δ 6.64 (m, 1H), 6.15 (m, 1H), 4.23 (d, *J* = 8.4 Hz, 1H), 3.22 (m, 1H), 2.46 (d, *J* = 18.4 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 145.6, 145.3, 140.1, 138.7, 138.6, 138.5, 137.7, 136.1, 135.2, 131.4, 130.2, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 127.4, 127.1, 127.0, 126.9, 126.1, 125.9, 45.7, 45.2, 44.4, 44.0, 39.0, 31.6, 27.2, 26.7, 25.3, 22.6, 14.1. HRMS (FAB) calc. for $[C_{23}H_{24}O_2]^+$ ($[M]^+$) 332.1776, found 332.1773.



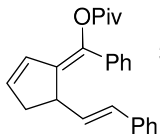
11

11. Obtained as a mixture of olefins (*E*:*Z* = 87:13). ^{1}H NMR (400 MHz, C_6D_6) major diastereomer δ 7.51-7.45 (m, 2H), 7.21-7.15 (m, 2H), 7.14-7.11 (m, 1H), 7.06-6.99 (m, 5H), 6.22 (dt, *J* = 7.2 and 15.6 Hz, 1H), 5.96 (dd, *J* = 5.2 and 7.6 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 2.47 (m, 2H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6) δ 177.0, 176.5, 141.0, 139.4, 132.2, 129.0, 128.9, 126.9, 124.4, 113.8, 90.0, 88.8, 74.5, 40.9, 39.2, 27.6. HRMS (FAB) calc. for $[C_{23}H_{24}O_2]^+$ ($[M]^+$) 332.1776, found 332.1781.



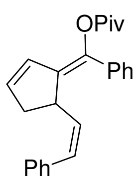
15

15. Obtained as a 75:25 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer: δ 7.44 (m, 1H), 7.26-7.21 (m, 2H), 7.19-7.13 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.46 (m, 1H), 6.13 (m, 1H), 4.27 (d, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.19 (m, 1H), 2.50 (d, *J* = 16.8 Hz, 1H), 1.38 (s, 9H). Minor diastereomer (diagnostic peaks): δ 6.84 (d, *J* = 8.6 Hz, 2H), 6.61 (m, 1H), 6.13 (m, 1H), 4.16 (dd, *J* = 2.4 and 8.4 Hz, 1H), 3.80 (s, 3H), 3.17 (m, 1H), 2.41 (dd, *J* = 2.0 and 18.0 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 176.0, 157.8, 157.7, 138.9, 138.5, 138.0, 137.7, 137.6, 136.5, 136.2, 135.2, 130.1, 128.2, 128.0, 127.9, 127.7, 127.5, 127.4, 126.8, 113.7, 55.3, 55.1, 44.9, 44.5, 44.4, 44.1, 39.0, 38.7, 27.2, 26.8. HRMS (FAB) calc. for $[C_{24}H_{26}O_3]^+$ ($[M]^+$) 362.1882, found 362.1878.



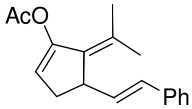
32

32. Obtained as a 70:30 mixture of olefins about the tetrasubstituted olefin. ^{1}H NMR (400 MHz, CD_2Cl_2) major diastereomer: δ 7.55-7.51 (m, 2H), 7.48-7.15 (m, 8H), 6.39 (dt, *J* = 2.1 and 5.7 Hz, 1H), 6.29 (d, *J* = 16.5 Hz, 1H), 6.15 (m, 1H), 6.08 (dd, *J* = 7.5 and 15.9 Hz, 1H), 4.05 (t, *J* = 7.5 Hz, 1H), 3.05 (ddt, *J* = 2.4, 7.8 and 18.0 Hz, 1H), 2.50 (ddt, *J* = 1.8, 3.0 and 18.0 Hz, 1H), 1.37 (s, 9H). Minor diastereomer (diagnostic peaks) δ 6.53 (m, 1H), 6.49 (*J* = 16.2 Hz, 1H), 6.27 (dd, *J* = 7.5 and 15.9 Hz, 1H), 6.18 (m, 1H), 3.84 (dt, *J* = 1.6 and 7.8 Hz, 1H), 3.05-2.97 (m, 1H), 2.50-2.43 (m, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 177.2, 177.0, 140.7, 139.0, 138.8, 138.5, 138.2, 138.1, 138.0, 137.1, 136.9, 136.2, 132.8, 132.6, 132.0, 130.1, 129.9, 129.7, 129.4, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 27.4, 16.5, 11.0. HRMS (FAB) calc. for $[C_{25}H_{26}O_2]^+$ ($[M]^+$) 358.1933, found 358.1939.



33

33. Obtained as a 85:15 mixture of diastereomers about the tetrasubstituted olefin. ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer: δ 7.39-7.24 (m, 3H), 7.18-7.14 (m, 4H), 7.12-7.08 (m, 1H), 7.04-7.01 (m, 2H), 6.30-6.27 (m, 1H), 6.25 (d, *J* = 11.6 Hz, 1H), 6.17-6.14 (m, 1H), 5.56 (dd, *J* = 10.8 and 11.6 Hz, 1H), 4.35 (t, *J* = 8.4 Hz, 1H), 3.14 (ddt. *J* = 2.6, 8.0 and 18.0 Hz, 1H), 2.58 (dd, *J* = 2.6 and 18.0 Hz, 1H), 1.33 (s, 9H). Minor diastereomer (diagnostic peaks): δ 6.45 (m, 1H), 6.37 (d, *J* = 11.2 Hz, 1H), 5.79 (dd, *J* = 9.2 and 11.2 Hz, 1H), 4.16 (t, *J* = 8.4 Hz, 1H), 2.49 (d, *J* = 17.6 Hz, 1H), 1.01 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 177.1, 139.6, 138.7, 137.6, 137.5, 135.6, 129.9, 129.3, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.8, 127.4, 127.1, 42.8, 39.4, 38.9, 27.5, 27.3. HRMS (FAB) calc. for $[C_{25}H_{26}O_2]^+$ ($[M]^+$) 358.1933, found 358.1936.

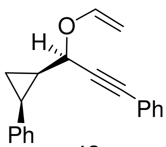


36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 1H), 7.30-7.26 (m, 7H), 7.21-7.17 (m, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.18 (dd, *J* = 8.0 and 15.6 Hz, 1H), 5.68 (bs, 1H), 3.61 (t, *J* = 8.0 Hz, 1H), 2.82 (dd, *J* = 8.0 and 17.2 Hz, 1H), 2.22 (s, 3H), 2.20-2.16 (m, 1H), 1.87 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 149.8, 137.6, 132.7, 132.4, 128.4, 128.3, 128.2, 127.9, 126.9, 126.1, 125.4, 119.3, 43.6, 33.9, 22.9, 21.3, 19.5. HRMS (FAB) calc. for $[C_{18}H_{20}O_2]^+$ ($[M]^+$) 268.1463, found 268.1465.

2.2. Au(I)-catalyzed Claisen rearrangement of propargyl vinyl ethers.

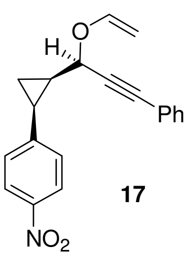
General procedure for the preparation of propargyl vinyl ethers.

The corresponding propargyl alcohol (1 equiv) was dissolved in ethyl vinyl ether (0.45 M) and mercuric acetate (66.6 mol%) was added. The resulting solution was stirred at rt for a minimum of 12 h and quenched with a 1:1 mixture of brine:5% KOH solution. The aqueous layer was extracted with hexanes, and the combined extracts washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash column chromatography.



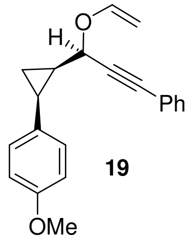
12

12. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 3H), 7.40-7.30 (m, 5H), 7.28-7.21 (m, 2H), 6.18 (dd, *J* = 6.4 and 14.0 Hz, 1H), 4.31 (d, *J* = 14.0 Hz, 1H), 4.01 (d, *J* = 6.4 Hz, 1H), 3.80 (d, *J* = 9.2 Hz, 1H), 2.49 (q, *J* = 8.0 Hz, 1H), 1.85 (m, 1H), 1.28 (m, 1H), 1.07 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 137.2, 131.8, 129.7, 128.4, 128.2, 128.0, 126.4, 122.4, 89.6, 86.9, 85.6, 69.3, 23.4, 22.2, 7.5. HRMS (FAB) calc. for $[C_{20}H_{18}O]^+$ ($[M]^+$) 274.1358, found 274.1362.



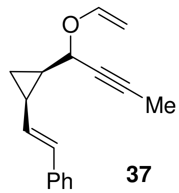
17

17. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.14 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.33 (s, 5H), 6.40 (dd, *J* = 6.8 and 14.0 Hz, 1H), 4.32 (dd, *J* = 1.6 and 14.0 Hz, 1H), 4.08 (dd, *J* = 1.6 and 6.8 Hz, 1H), 3.75 (d, *J* = 9.6 Hz, 1H), 2.50 (q, *J* = 8.4 Hz, 1H), 1.90 (ddt, *J* = 5.6, 8.8 and 17.6 Hz, 1H), 1.37-1.21 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 149.8, 147.1, 146.1, 131.9, 130.6, 129.1, 128.7, 123.5, 122.4, 90.2, 87.1, 86.3, 70.5, 24.6, 21.2, 9.9. HRMS (FAB) calc. for $[C_{20}H_{17}NO_3]^+$ ($[M]^+$) 319.1208, found 319.1211.



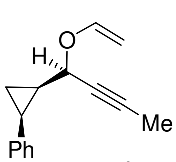
19

19. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43-7.41 (m, 2H), 7.36-7.29 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.17 (dd, *J* = 6.8 and 14.0 Hz, 1H), 4.24 (dd, *J* = 1.6 and 14.0 Hz, 1H), 4.96 (dd, *J* = 1.6 and 6.8 Hz, 1H), 3.78 (s, 3H), 3.74 (d, *J* = 9.2 Hz, 1H), 2.36 (q, *J* = 8.0 Hz, 1H), 1.72 (ddt, *J* = 5.6, 8.8 and 18.0 Hz, 1H), 1.18 (dt, *J* = 5.6 and 8.8 Hz, 1H), 0.95 (q, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 158.7, 150.0, 132.0, 131.0, 129.6, 128.9, 128.7, 122.8, 113.8, 89.6, 87.6, 85.7, 69.8, 23.6, 21.7, 7.7. HRMS (FAB) calc. for $[C_{21}H_{20}O_2]^+$ ($[M]^+$) 304.1463, found 304.1461.



37

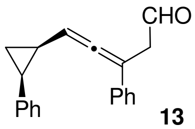
37. Obtained as a 60:40 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 4H), 7.24-7.17 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.48 (dd, *J* = 6.6 and 14.0 Hz, 1H), 6.10 (dd, *J* = 8.2 and 16.0 Hz, 1H), 4.44 (dd, *J* = 1.6 and 14.0 Hz, 1H), 4.13 (dd, *J* = 1.6 and 6.6 Hz, 1H), 4.11-4.06 (m, 1H), 1.85 (d, *J* = 2.0 Hz, 1H), 1.89-1.85 (m, 1H), 1.60 (m, 1H), 1.14 (m, 1H), 0.83 (q, *J* = 5.6 Hz, 1H). Minor diastereomer (diagnostic peaks) δ 6.51 (d, *J* = 15.6 Hz, 1H), 6.40 (dd, *J* = 6.8 and 14.4 Hz, 1H), 6.08 (dd, *J* = 7.8 and 15.6 Hz, 1H), 4.39 (dd, *J* = 2.0 and 14.4 Hz, 1H),1.89 (d, *J* = 2.0 Hz, 1H), 1.89-1.85 (m, 1H), 1.60 (m, 1H), 1.14 (m, 1H), 0.74 (q, *J* = 5.6 Hz, 1H). HRMS (FAB) calc. for $[C_{17}H_{18}O]^+$ ($[M]^+$) 238.1358, found 238.1361.



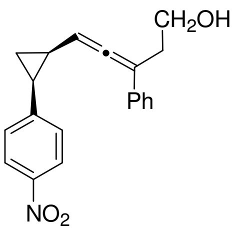
18

18. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 4H), 7.24-7.16 (m, 1H), 6.06 (dd, *J* = 6.8 and 14.0 Hz, 1H), 4.09 (dd, *J* = 1.6 and 14.0 Hz, 1H), 3.85 (dd, *J* = 1.6 and 6.8 Hz, 1H), 3.59 (m, 1H), 2.39 (q, *J* = 8.4 Hz, 1H), 1.84 (d, *J* = 2.4 Hz, 3H), 1.65 (dt, *J* = 5.6 and 8.8 Hz, 1H), 1.17 (dt, *J* = 5.6 and 8.4 Hz, 1H), 1.02 (q, *J* = 5.6 Hz, 1H). HRMS (FAB) calc. for $[C_{15}H_{16}O]^+$ ($[M]^+$) 212.1201, found 212.1204.

General Procedure for the Au(I)-Catalyzed Claisen Rearrangement of Propargyl Vinyl Ethers:
To a solution of propargyl vinyl ether (1 equiv) in CH_2Cl_2 (0.35 M) was added $[(Ph_3PAu)_3O)]BF_4$ (1 mol%) and the resulting mixture was maintained at the indicated temperature until TLC analysis indicated consumption of the starting material.



13 **13**. Obtained as a 55:45 mixture of allenes. ^{1}H NMR (400 MHz, CD_2Cl_2 δ 9.68 (bs, 1H), 9.57 (bs, 1H), 7.41-7.11 (m, 20H), 5.27 (bd, *J* = 7.6 Hz, 1H), 5.21 (bd, *J* = 8.0 Hz, 1H), 3.39 (bs, 4H), 3.16 (m, 4H), 2.49 (m, 2H), 1.92 (m, 2H), 1.40-1.24 (m, 2H), 1.18-1.05 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 206.7, 200.5, 139.2, 136.2, 130.2, 130.0, 129.0, 128.7, 128.6, 127.5, 126.8, 126.7, 126.3, 126.2, 99.4, 99.3, 95.9, 95.8, 45.5, 45.4, 24.3, 23.7, 18.6, 17.9, 11.4, 11.3. HRMS (FAB) calc. for $[C_{20}H_{18}O]^+$ ($[M]^+$) 274.1358, found 274.1362.



18. Aldehyde **18** was found to be unstable, and for characterization purpouses was reduced to the corresponding alcohol following the procedure reported in the literature.[6] The reaction mixture was diluted with MeOH (2x the volume of CH_2Cl_2) and $NaBH_4$ (1.0 equiv) was added. The resulting solution was maintained at rt for 1 h, concentrated, and purified by flash column chromatography (hexanes:AcOEt = 25:1) to yield the desired alcohol as a 81:19 mixture of allenes. ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.21-7.10 (m, 5H), 4.96 (m, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.53 (m, 2H), 2.40 (q, *J* = 8.0 Hz, 1H), 1.93 (m, 1H), 1.56 (bs, 1H), 1.36 (m, 1H), 1.12 (q, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 204.5, 147.0, 146.6, 146.3, 136.0, 135.8, 131.5, 130.1, 129.9, 129.7, 128.6, 128.4, 128.3, 127.2, 127.1, 126.1, 125.9, 123.3, 103.7, 93.6, 93.3, 63.6, 60.9, 33.4, 33.2, 26.2, 23.8, 23.3, 21.0, 19.4, 12.2, 11.5. HRMS (FAB) calc. for $[C_{20}H_{19}NO_3]^+$ ($[M]^+$) 321.1365, found 321.1369.

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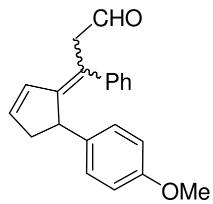
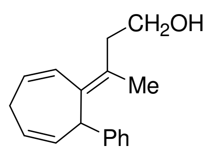
[6] Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15978.



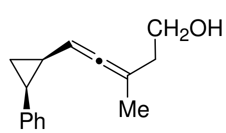
22

22. Obtained as a 77:23 mixture of diastereomers. ^{1}H NMR (400 MHz, CD_3NO_2) (major diastereomer) δ 9.63 (t, *J* = 2.0 Hz, 1H), 7.21-7.11 (m, 3H), 7.06-7.00 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.69 (dt, *J* = 2.0 and 5.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.34 (dt, *J* = 2.8 and 5.8 Hz, 1H), 4.17 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.66 (m, 2H), 3.15 (ddt, *J* = 2.0, 8.4 and 18.0 Hz, 1H), 2.41 (dd, *J* = 2.0 and 18.0 Hz, 1H), 2.10 (s, 2H). Minor diastereomer (diagnostic peaks) δ 9.11 (t, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.48 (dt, *J* = 2.0 and 5.6 Hz, 1H), 6.23 (dt, *J* = 2.8 and 5.6 Hz, 1H), 4.15 (m, 1H), 3.81 (s, 3H), 3.38 (m, 2H), 3.25 (ddt, *J* = 2.0, 8.0 and 18.0 Hz, 1H), 2.46 (m, 1H), 2.07 (s, 2H). ^{13}C NMR (100 MHz, CD_3NO_2) δ 200.2, 158.2, 157.5, 151.8, 151.5, 142.4, 139.0, 138.9, 138.3, 138.2, 138.1, 131.1, 128.7, 128.3, 128.2, 128.1, 127.9, 127.8, 126.8, 126.3, 123.6, 122.8, 113.9, 113.1, 54.5, 54.4, 50.2, 49.0, 45.3, 44.7, 43.9, 43.4. HRMS (FAB) calc. for $[C_{21}H_{20}O_2]^+$ ($[M]^+$) 304.1463, found 304.1460.



39

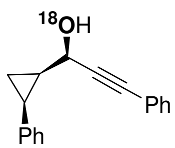
Aldehyde **39** was found to be unstable, and for characterization purpouses was reduced to the corresponding alcohol. Thus, the reaction mixture was diluted with MeOH (2x the volume of CH_2Cl_2) and $NaBH_4$ (1.0 equiv) was added. The resulting solution was maintained at rt for 1 h, concentrated, and purified by flash column chromatography (hexanes:AcOEt = 25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 3H), 7.20-7.12 /m, 2H), 6.32 (d, *J* = 12 Hz, 1H), 6.09 (m, 1H), 5.91 (dt, *J* = 5.2 and 10.4 Hz, 1H), 5.47 (dt, *J* = 4.8 and 10.8 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 3.77 (m, 2H), 2.79 (m, 2H), 2.57 (m, 1H), 2.47 (m, 1H), 1.96 (s, 3H), 1.41 (t, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 134.7, 130.7, 130.0, 128.9, 128.2, 128.0, 127.4, 127.1, 125.8, 61.1, 45.9, 38.3, 30.9, 19.1. HRMS (FAB) calc. for $[C_{17}H_{20}O]^+$ ($[M]^+$) 240.1514, found 240.1519.



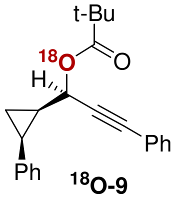
Methyl substituted allenyl aldehyde **19** was found to be unstable, and for characterization purpouses was reduced to the corresponding alcohol. Thus, the reaction mixture was diluted with MeOH (2x the volume of CH_2Cl_2) and $NaBH_4$ (1.0 equiv) was added. The resulting solution was maintained at rt for 1 h, concentrated, and purified by flash column chromatography (hexanes:AcOEt = 25:1) to yield the desired alcohol as a 60:40 mixture of allenes. ^{1}H NMR (400 MHz, CDCl$_3$) major diastereomer δ 7.37-7.29 (m, 3H), 7.26-7.18 (m, 2H), 4.75 (m, 1H), 3.69 (t, J = 6.0 Hz, 2H), 2.39 (m, 1H), 2.17 (m, 2H), 1.85 (bs, 1H), 1.81-1.71 (m, 2H), 1.57 (d, J = 2.8 Hz, 3H), 1.26 (m, 1H), 1.03 (q, J = 5.6 Hz, 1H). Minor diastereomer (diagnostic peaks) δ 4.68 (m, 1H), 3.60 (t, J = 6.0 Hz, 2H), 1.24 (ddt, J = 2.8., 6.0 and 12.0 Hz, 1H), 1.68 (d, J = 2.4 Hz, 3H), 0.99 (q, J = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.2, 201.8, 138.7, 138.5, 129.4, 129.3, 128.2, 127.9, 127.8, 125.9, 125.8, 125.5, 97.6, 97.1, 90.7, 90.5, 60.5, 60.4, 36.9, 23.4, 22.9, 19.3, 19.2, 18.3, 18.2, 10.9, 10.4. HRMS (FAB) calc. for $[C_{15}H_{18}O]^+$ ($[M]^+$) 214.1358, found 214.1262.

2.3. Other experiments

2.3.1. O^{18} labeling experiment

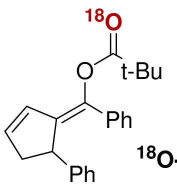


In an oven-dried round bottom flask, *cis*-2-phenyl isopropyl carbaldehyde (147 mg, 1.00 mmol) was dissolved in dry tetrahydrofuran (2 mL). Isotopically labelled water (200 mg, 0.2 mL, 10 equiv, 95-98 % $H_2{}^{18}O$) was added via syringe, and then gaseous hydrogen chloride (generated by the addition of HzS04 to solid NaCl) was bubbled through the solution for a brief period of time (ca. 10 s). The resulting solution was stirred at room temperature for 10 h, after which time the solution was canulated into a second oven-dried round bottom flask containing anhydrous magnesium sulfate to remove the excess water. Stirring of the resulting hetereogeneous mixture was continued for 30 min. The ^{18}O-labelled aldehyde solution thus obtained was filtered *via* canula to a flask containing a THF solution of 1-lithio phenylacetylene (10.0 mmol, 1.0 M) at -78 ºC**.** The resulting mixture was warmed to room temperature for 2 h. The reaction was quenched by the addition of sat. NH_4Cl solution and the biphasic mixture transferred to a separatory funnel and partitioned. The aqueous layer was extracted with AcOEt (3x5 mL), and the combined organic layers were washed with brine (10 mL) dried ($MgS0_4$), filtered and concentrated. The crude product could be purified by column chromatography 10:1 hexanes:AcOEt to afford pure, isotopically labelled alcohol as a white solid with identical spectroscopic characteristics as the non-labeled compound. GC-MS analysis of the product thus obtained indicated an isotopic composition of between 80-85% ^{18}O depending on the run.



^{18}O-9

^{18}O-9 was obtained from the previously obtained isotopically labelled alcohol by using the same procedure applied for the preparation of unlabelled **9**. This procedure affords pure, isotopically labelled **^{18}O-9** as a white solid with identical spectroscopic characteristics as the non-labeled compound.

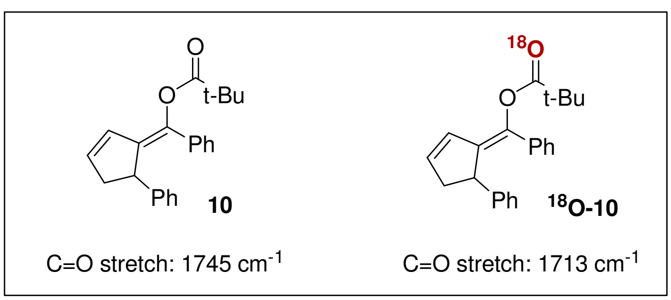


^{18}O-10

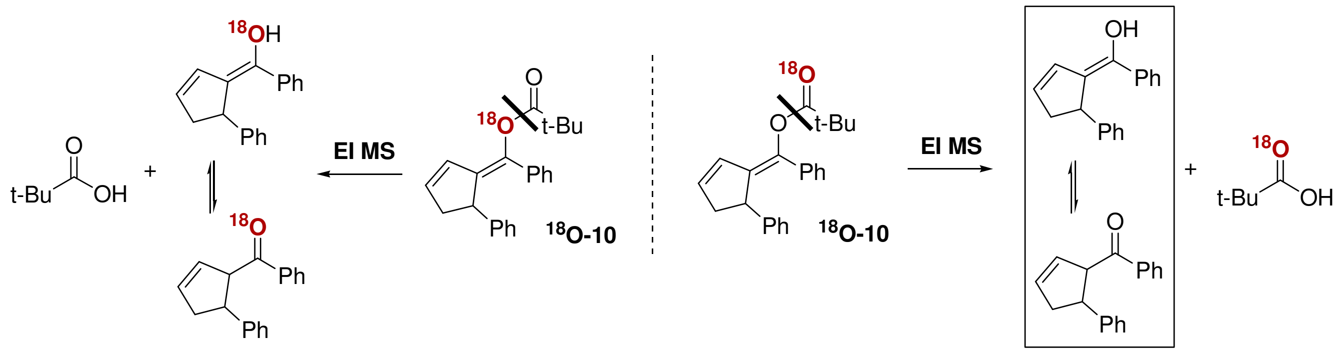
^{18}O-10 was obtained from the previously obtained isotopically labelled propargylic ester by $Ph_3PAuSbF_6$ catalyzed reaction in CH_3NO_2 using the same procedure applied for the preparation of unlabelled **10**. This protocol affords pure, isotopically labelled **^{18}O-10** as a clear oil with identical spectroscopic characteristics as the non-labeled compound.

The position of isotopically labelled oxygen in the molecule was determined by combining two different experiments:

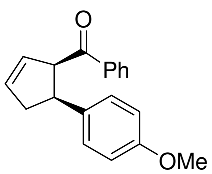
1. **IR**: Infrared spectroscopy of the unlabelled compound **10** showed a very intense peak at 1745 cm^{-1}, which corresponds to the C=O stretch. For **^{18}O-10**, IR that peak dissapeared while another one showed at 1713 cm^{-1}, which is consistent with a C=^{18}O stretch.



2. **Mass spectroscopy**: although both possible labelled compounds **^{18}O-10** must have the same mass, the fragments observed by ionization should be different. Thus, the relative intensity of the peaks observed by EI showed one main peak corresponding to the unlabeled enol-ketone (100:15). These results suggest that the labelled atom in compound **^{18}O-10** resides exclusively on the carbonyl group.



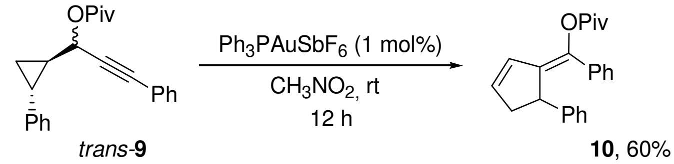
2.3.2. Cleavage of the pivaloate group



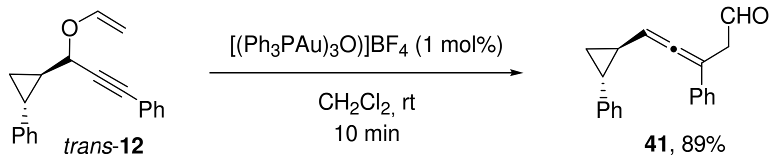
40. A solution of **16** (1 mmol, 278 mg) in Et_2O (2 mL) was added dropwise and under vigorous stirring to a 0 ºC suspension of $LiAlH_4$ (1.1 equiv.) in Et_2O (3 mL). The solution was then stirred at room temperature until TLC showed complete consumption of the starting material (2 hours). The reaction mixture was then carefully quenched with saturated aqueous Na_2SO_4 (2 mL), stirred at room temperature for 1 hour and filtered over a short pad of silica to remove the aluminum salts. After concentration, a 90:10 mixture of diastereomers was obtained which purified by flash chromatography (hexanes:AcOEt 25:1) to afford the desired ketone in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 8.7 Hz, 2H), 6.17 (m, 1H), 5.96 (m, 1H), 4.89 (m, 1H), 3.93 (dt, *J* = 5.1 and 8.7 Hz, 1H), 3.65 (s, 3H), 2.95 (m, 1H), 2.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 157.9, 137.9, 134.3, 133.5, 132.4, 129.6, 128.9, 128.1, 127.9, 113.2, 58.6, 55.1, 46.9, 41.3. HRMS (FAB) calc. for $[C_{19}H_{18}O_2]^+$ ($[M]^+$) 278.1307, found 278.1309. HPLC Chiralpak AD-H column (97:3 hexanes:isopropanol, 1 mL/min) t_R 12.5 min (major), 16.1 min (minor): 32% *ee*.

2.3.3. *trans*-Disubstituted cyclopropyl propargyl esters and vinyl ethers

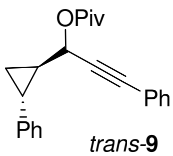
It was reasonable to predict analogous results regardless of the relative stereochemistry of cyclopropanes **9** and **12**. As expected, the reaction of *trans*-cyclopropyl substituted *trans*-**9** resulted in formation of **10** in similar yield (Supplementary Equation 1). In this case the *cis*-cyclopropyl isomer was never detected in the reaction mixture. Accordingly, the reaction of substrate *trans*-**12**, bearing a *trans* cyclopropyl group, resulted in formation of the *trans* cyclopropyl allene **41** (Supplementary Equation 2). Together these data indicate that *cis*/*trans* cyclopropyl isomerization is not kinetically feasible under these conditions.



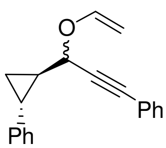
(1)



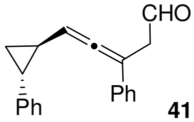
(2)



trans-**9** *trans*-**9.** Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 4H), 7.37-7.28 (m, 10H), 7.23-7.14 (m, 6H), 5.74 (d, *J* = 6.4 Hz, 1H), 5.64 (d, *J* = 6.8 Hz, 1H), 2.26 (quint, *J* = 4.4 Hz, 1H), 2.18 (quint, *J* = 5.2 Hz, 1H), 1.74-1.66 (m, 2H), 1.29 (s, 9H), 1.28 (s, 9H), 1.34-1.24 (m, 2H), 1.15-1.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 141.6, 141.5, 131.9, 131.8, 128.6, 128.3, 128.2, 128.1, 126.5, 126.2, 125.9, 122.2, 122.1, 85.6, 85.4, 84.8, 84.5, 66.6, 66.5, 38.8, 27.1, 25.8, 25.1, 21.6, 20.3, 12.9, 12.3. HRMS (FAB) calc. for $[C_{23}H_{24}O_2]^+$ ($[M]^+$) 332.1776, found 332.1779.



trans-**12** *trans*-**12**. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.54-7.48 (m, 4H), 7.44-7.37 (m, 6H), 7.34-7.30 (t, *J* = 7.3 Hz, 4H), 7.24-7.17 (m, 6H), 6.62 (dd, *J* = 6.8 and 14.0 Hz, 2H), 4.82 (d, *J* = 6.0 Hz, 1H), 4.78 (d, *J* = 6.0 Hz, 1H),4.53 (dd, *J* = 1.6 and 14.0 Hz, 2H), 4.23 (dd, *J* = 1.6 and 6.8 Hz, 2H), 2.28 (q, *J* = 5.2 Hz, 1H), 2.18 (q, *J* = 5.2 Hz, 1H), 1.77-1.68 (m, 2H), 1.35 (dt, *J* = 5.2 and 8.8 Hz, 1H), 1.28 (dt, *J* = 5.2 and 9.0 Hz, 1H), 1.16-1.10 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 150.4, 142.4, 142.3, 132.4, 132.3, 129.4, 129.3, 128.9, 128.8, 126.8, 126.6, 126.4, 122.7, 90.3, 90.2, 87.4, 87.3, 85.4, 85.3, 72.2, 72.1, 26.5, 26.3, 21.8, 20.7, 13.5, 13.0. HRMS (FAB) calc. for $[C_{20}H_{18}O]^+$ ($[M]^+$) 274.1358, found 274.1360.



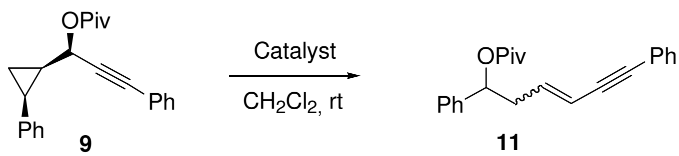
41 **41**. Obtained as a 1:1 mixture of allenes. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.81 (t, *J* = 2.4 Hz, 1H), 9.78 (t, *J* = 2.4 Hz, 1H), 7.42-7.38 (m, 8H), 7.33-7.28 (m, 6H), 7.22-7.20 (m, 2H), 7.15-7.12 (m, 4H), 5.76 (m, 2H), 3.49 (m, 4H), 2.06 (m, 2H), 1.71 (m, 2H), 1.29-1.23 (m, 2H), 1.17 (m, 2H). ^{13}C

NMR (100 MHz, CD_2Cl_2) δ 205.5, 200.3, 142.7, 136.2, 129.2, 129.1, 128.9, 127.8, 126.6, 126.3, 126.2, 126.1, 126.0, 100.6, 99.2, 45.6, 45.5, 26.2, 26.1, 22.3, 22.1, 17.4. HRMS (FAB) calc. for $[C_{20}H_{18}O]^+$ ($[M]^+$) 274.1358, found 274.1361.

2.3.4. Ionization experiments and substitution at the ester moiety

A series of experiments employing Lewis acids $AgSbF_6$ and $Zn(OTf)_2$, and Brønsted acids CF_3CO_2H and TfOH as catalysts in CH_2Cl_2 were conducted, resulting in the exclusive formation of **11**. The fact that **10** was never observed when employing catalysts other than Au(I) suggests that the pentannulation product does not originate from Lewis or Brønsted acid catalysis.

Supplementary Scheme S2. Ionization of model propargylic ester **9**.



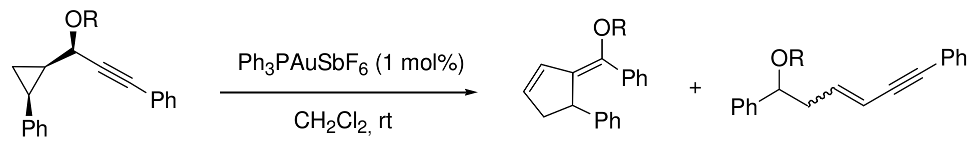
$AgSbF_6$	*92%*
$Zn(OTf)_2$	*74%*
CF_3CO_2H	*64%*
TfOH	*68%*

In trying to obtain more information on the initial [3,3]-rearrangement, we looked at the behavior of a series of esters with very different electronic properties. To that end, we investigated the $Ph_3PAuSbF_6$ catalyzed reaction of substrates **42-44**, bearing 4-$MeOC_6H_4$, Ph and 4-$NO_2C_6H_4$ groups at the carboxylic carbon (Scheme 7). Again, it was observed that in all cases the corresponding cyclopentenes were obtained in good to excellent yields (58-97%). Interestingly, a longer reaction time was required in all cases (*ca.* 1 hour), which allowed us to observe a scrambling of stereocenters similar to that observed for pivaloate protected substrate **9** (section 1.1). It was also observed that formation of the acyclic enyne is decreased or even prevented when using non-electron-rich migrating groups (4-$NO_2C_6H_4CO$ afforded the desired cyclopentene in 97% yield). These results can be easily accounted for by invoking an acid catalyzed ionization of the propargylic ester, a subsequent cyclopropyl ring opening to afford the thermodynamically more stable conjugated enyne, and a final nucleophilic attack of the carboxylate ion onto the benzylic position to afford **11**.[7] Thus, the utilization of ester partners with lower leaving group abilities reduces the participation of this competing pathway. The reaction of carbamate **45** resulted only in recovery of the unaltered starting material, indicating that in this case the initial [3,3]-rearrangement does not take place. This result suggests the possibility that the reactivity is

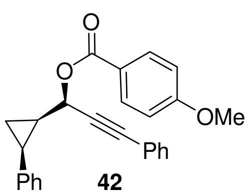
[7] Hiroi, K.; Kato, F., *Tetrahedron* **2001**, *57*, 1543.

not triggered by a Au(I)-catalyzed activation of the cyclopropane.[8] Finally, the reaction of trichloroacetimidate[9] **46** afforded a complex mixture where the corresponding enyne (63%) along with decomposition products.

Supplementary Scheme S1. Substitution at propargylic oxygen.

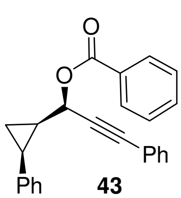


9, *R= CO^{t}Bu*	***10***, *62%*	*32%*
42, *R= COpMeOC$_6$H$_4$*	***47***, *58%*	*20%*
43, *R= COPh*	***48***, *85%*	*0%*
44, *R= COpNO$_2$C$_6$H$_4$*	***49***, *97%*	*0%*
45, *R= CONHPh*	*0%*	*0%*
46, *R= CNHCCl$_3$*	*0%*	*63%*



42

42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.45-7.43 (m, 2H), 7.32-7.27 (m, 3H), 7.23-7.21 (m, 2H), 7.14-7.12 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.85 (d, *J* = 10.4 Hz, 1H), 2.47 (q, *J* = 8.4 Hz, 1H), 1.99 (dq, *J* = 5.6 and 9.2 Hz, 1H), 1.29 (dt, *J* = 6.0 and 8.4 Hz, 1H), 1.20 (q, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.2, 136.5, 131.9, 131.7, 129.2, 128.4, 128.1, 126.5, 122.4, 122.3, 113.4, 86.9, 84.5, 65.0, 55.35, 22.8, 22.0, 7.7. HRMS (FAB) calc. for $[C_{26}H_{22}O_3]^+$ ($[M]^+$) 382.1569, found 382.1571.



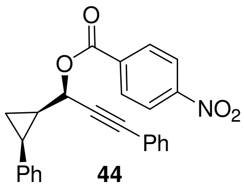
43

43. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.51-7.47 (m, 4H), 7.37-7.32 (m, 3H), 7.28-7.20 (m, 2H), 7.18-7.16 (m, 3H), 4.92 (d, *J* = 10.0 Hz, 1H),

[8] It has been shown that Pt salts like Zeise's dimmer can undergo C-C bond insertions into cyclopropanes in $CHCl_3$ at room temperature. See: Wiberg, K. B.; McCluski, J. V.; Schulte, G. K., *Tetrahedron Lett.* **1986**, *27*, 3083. For Au(I) activation of cyclopropane in the gas phase, see: Chowdhury, A. K.; Wilkins, C. L., *J. Am. Chem. Soc.* **1987**, *109*, 5536. For Au(I)-catalyzed expansion of alkynyl cyclopropanols, see: Markham, J. P.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9708.

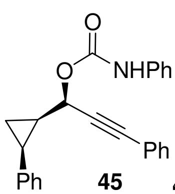
[9] (a) Overman, L. E., *J. Am. Chem. Soc.* **1974**, *96*, 597. (b) Watson, M. P.; Overman, L. E.; Bergman, R. G., *J. Am. Chem. Soc.* **2007**, *129*, 5031. (c) Kang, J.-E.; Kim, H.-K.; Lee, J.-W.; Shin, S. *Org. Lett.* **2006**, *8*, 3537.

2.53 (q, J = 8.4 Hz, 1H), 2.06 (dq, J = 5.2 and 8.4 Hz, 1H), 1.34 (dt, J = 6.0 and 8.4 Hz, 1H), 1.26 (q, J = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 136.6, 132.9, 132.0, 130.0, 129.8, 129.3, 128.6, 128.3, 128.2, 128.1, 126.3, 122.5, 86.7, 84.8, 65.5, 22.8, 22.1, 7.8. HRMS (FAB) calc. for $[C_{25}H_{20}O_2]^+$ ($[M]^+$) 352.1463, found 352.1469.



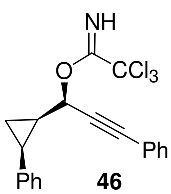
44

44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 8.12 (dd, J = 8.8 Hz, 2H), 7.49-7.44 (m, 2H), 7.37-7.30 (m, 3H), 7.22-7.19 (m, 2H), 7.15-7.13 (m, 2H), 4.94 (d, J = 10.0 Hz, 1H), 2.52 (q, J = 8.0 Hz, 1H), 2.04 (dq, J = 5.2 and 8.4 Hz, 1H), 1.35 (dt, J = 6.0 and 8.4 Hz, 1H), 1.28 (q, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 150.4, 136.3, 135.3, 131.9, 130.7, 128.9, 128.7, 128.2, 128.1, 126.6, 123.3, 122.0, 85.8, 85.3, 66.5, 22.7, 21.9, 7.8. HRMS (FAB) calc. for $[C_{25}H_{19}NO_4]^+$ ($[M]^+$) 397.1314, found 397.1316.



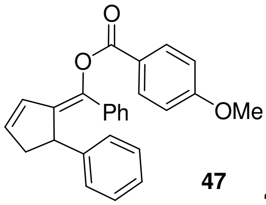
45

45. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43-7.40 (m, 2H), 7.35-7.23 (m, 11H), 7.19.7.16 (m, 1H), 7.07-7.01 (m, 1H), 6.6 (s, 1H), 4.65 (d, J = 10.0 Hz, 1H), 2.45 (q, J = 8.4 Hz, 1H), 1.85 (dq, J = 5.6 and 8.8 Hz, 1H), 1.25 (dt, J = 5.6 and 8.4 Hz, 1H), 1.18 (q, J = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 151.7, 137.8, 136.9, 131.7, 129.2, 128.9, 128.6, 128.3, 128.1, 126.5, 123.3, 122.3, 120.0, 118.7, 86.8, 84.6, 65.6, 23.0, 7.6.



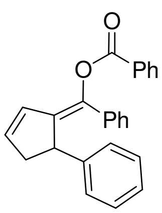
46

46. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.14 (s, 1H), 7.43-7.41 (m 2H), 6.34-7.23 (m, 5H9, 7.27-7.23 (m, 2H), 7.20-7.17 (m, 1H), 4.72 (d, J = 10.4 Hz, 1H), 2.50 (q, J = 8.0 Hz, 1H), 1.96 (m, 1H), 1.32-1.26 (m, 1H), 1.17 (q, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.5, 136.8, 131.7, 129.5, 128.7, 128.3, 128.1, 126.5, 122.2, 91.1, 85.8, 84.8, 69.6, 29.7, 22.9, 22.3, 7.5.



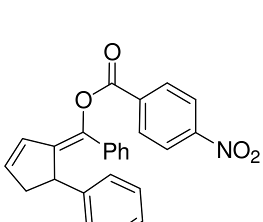
47

47. Obtained as a 70:30 mixture of olefins abot the exocyclic double bond. ^{1}H NMR (300 MHz, $CDCl_3$) major diastereomer: δ 8.17 (d, *J* = 7.2 Hz, 2H), 7.31-7.24 (m, 3H), 7.21-7.18 (m, 2H), 7.16-7.09 (m, 5H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.53 (dt, *J* = 2.0 and 5.6 Hz, 1H), 6.10 (dt, *J* = 2.4 and 5.2 Hz, 1H), 4. 38 (dd, *J* = 1.6 and 8.0 Hz, 1H), 3.89 (s, 3H), 3.24 (ddt, *J* = 2.4, 8.0 and 18.0 Hz, 1H), 2.54 (dd, *J* = 2.4 and 18.0 Hz, 1H). Minor diastereomer (diagnostic peaks): 6.69 (m, 1H), 6.23 (m, 1H), 4.14 (dd, *J* = 2.4 and 8.4 Hz, 1H), 3.85 (s, 3H), 3.17 (ddt, *J* = 2.5, 8.0 and 18.0 Hz, 1H), 2.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 163.8, 145.6, 139.2, 138.7, 136.3, 135.1, 132.2, 132.1, 131.7, 131.5, 130.7, 130.1, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 127.3, 127.2, 127.1, 127.0, 126.4, 125.9, 122.0, 113.8, 113.7, 55.5, 55.4, 46.3, 45.3, 44.6, 43.7. HRMS (FAB) calc. for $[C_{26}H_{22}O_3]^+$ ($[M]^+$) 382.1569, found 382.1574.



48

48. Obtained as a 70:30 mixture of olefins about the exocyclic double bond. ^{1}H NMR (300 MHz, $CDCl_3$) major diastereomer: δ 8.28 (d, *J* = 7.2 Hz, 2H), 7.59-7.53 (m, 2H), 7.41-7.32 (m, 4H), 7.28-7.22 (m, 2H), 7.21-7.12 (m, 5H), 6.58 (dt, *J* = 2.0 and 5.6 Hz, 1H), 6.16 (dt, *J* = 2.4 and 5.2 Hz, 1H), 4.43 (dd, *J* = 1.6 and 8.0 Hz, 1H), 3.24 (ddt, *J* = 2.4, 8.0 and 18.0 Hz, 1H), 2.54 (m, 1H). Minor diastereomer (diagnostic peaks): δ 6.74 (dt, *J* = 2.0 and 5.2 Hz, 1H), 6.29 (dt, *J* = 2.4 and 5.2 Hz, 1H), 4.20 (dd, *J* = 2.8 and 8.4 Hz, 1H), 3.21 (ddt, *J* = 2.4, 8.4 and 18.4 Hz, 1H), 2.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ165.2, 164.3, 145.5, 145.4, 140.3, 139.9, 139.3, 138.9, 138.7, 136.5, 136.1, 134.9, 133.4, 133.0, 131.5, 130.6, 130.1, 130.0, 129.9, 129.7, 129.4, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.4, 127.1, 127.0, 126.4, 126.0, 125.9, 46.4, 45.3, 44.6, 43.7. HRMS (FAB) calc. for $[C_{25}H_{20}O_2]^+$ ($[M]^+$) 352.1463, found 352.1469.



49

49. Obtained as a 67:33 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 8.36 (dd, *J* = 8.8 and 12.8 Hz, 4H), 7.28-7.23 (m, 3H), 7.17-7.08 (m, 8H), 6.48 (m, 1H), 6.18 (dt, J = 2.4 and 5.2, 1H), 4.36 (d, J = 7.6 Hz, 1H), 3.25 (ddt, J = 2.2, 8.0 and 18.0 Hz, 1H), 2.55 (m, 1H). Minor diastereomer (diagnostic peaks) δ 6.67 (m, 1H), 6.27 (dt, J = 2.8 and 6.0, 1H), 4.16 (dd, J = 2.8 and 8.4 Hz, 1H), 3.25 (m, 1H), 2.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 162.3, 150.8, 150.5, 145.2, 145.0, 140.5, 139.8, 139.6, 139.5, 138.5, 137.5, 135.5, 135.0, 134.8, 134.5, 131.2, 130.9, 130.0, 129.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.4, 127.2, 127.1, 127.0, 126.1, 126.0, 123.7, 123.2, 46.5, 45.2, 44.5, 43.9. HRMS (FAB) calc. for $[C_{25}H_{19}NO_4]^+$ ($[M]^+$) 397.1314, found 397.1316.

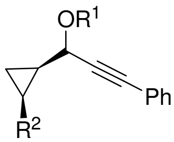
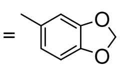
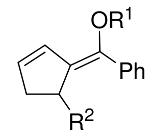
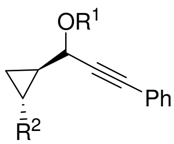
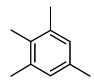
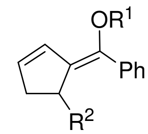
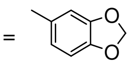
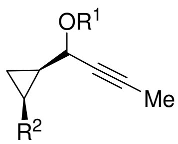
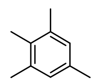
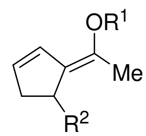
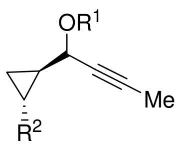
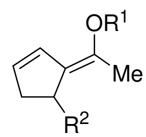
2.3.5. Cyclopentene formation: brief reaction scope

Sigmatropic rearrangements, traditionally effected under thermal conditions, usually require high reaction temperatures and often lead to complex reaction mixtures. As recently stated by Tantillo,[10] "transition metal promoted pericyclic reactions figure prominently in many complexity-creating synthetic transformations. The appeal of such reactions lies in the fact that by using appropriate metal promoters, reactions that are sluggish or even orbital-symmetry-forbidden in the absence of the metal can be achieved efficiently."

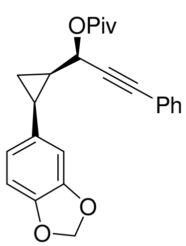
Since the first report in 1959, the vinylcyclopropane-cyclopentene rearrangement[11,12] has attracted considerable attention due to its synthetic utility and its mechanistic implications. To complete our studies, we briefly examined the scope of this interesting Au(I)-catalysed rearrangement. We observed that the $Ph_3PAuSbF_6$ catalysed the reaction of various propargylic cyclopropanes afforded cyclopentenes in excellent yields as mixtures of olefins about the exocyclic double bond (Supplementary Table 1). The use of pivaloate or acetate as the migrating group did not affect the reactivity of the system. In agreement with the results described above, yields were significantly improved by increasing the electron-donating ability of the aromatic ring directly attached to the cyclopropyl group. Turning to alkyne substitution, phenyl and methyl substituted alkynes afforded high yields, although methyl-substituted alkynes provided cleaner reaction mixtures in CH_3NO_2 solvent. Also, in all cases the cyclopentenes were obtained regardless of the relative stereochemistry at the cyclopropyl and propargylic positions.

[10] Wang, S. C. & Tantillo, D. J. *J. Organomet. Chem.* **2006**, *691*, 4386-4392.
[11] Hudlicky, T., Kutchan, T. M. & Naqvi, S. M. *Organic Reactions* vol. 33, 247-335. Paquette, L. A., Ed. (Wiley, New York, 1985).
[12] Baldwin, J. E. *Chem. Rev.* **2003**, *103*, 1197-1212.

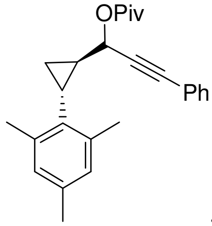
Supplementary Table 1. Au(I)-catalysed pentannulations, substrate scope.

entry[a]	substrate		product		*E*/*Z* ratio	yield[b]
1		**50** R^1 = Piv, R^2 = 		**58**	75:25	97
2		**51** R^1 = Piv, R^2 = 		**59**	90:10	95
3		**52** R^1 = Piv, R^2 = 4-MeO-C_6H_4		**15**	75:25	97
4		**53** R^1 = Piv, R^2 = 		**58**	75:25	97
5		**54** R^1 = Ac, R^2 = 		**60**	50:50	94
6		**55** R^1 = Ac, R^2 = 4-MeO-C_6H_4		**61**	50:50	95
7		**56** R^1 = Piv, R^2 = 4-MeO-C_6H_4		**62**	50:50	95
8		**57** R^1 = Ac, R^2 = 4-MeO-C_6H_4		**61**	50:50	95

[a] Conditions: 1% $AuPPh_3Cl$, 1% $AgSbF_6$, CH_2Cl_2 or CH_3NO_2, rt, 10 min. to 12 h. [b] Isolated yield.

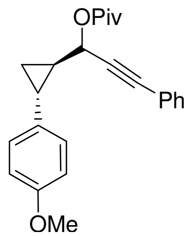


50. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44-7.41 (m, 2H), 7.34-7.30 (m, 3H), 6.75-6.68 (m, 3H), 5.92 (dd, *J* = 1.2 and 10.4 Hz, 2H), 4.57 (d, *J* = 10 Hz, 1H), 2.34 (q, *J* = 8.0 Hz, 1H), 1.79 (m, 1H), 1.21 (m, 1H), 1.16 (s, 9H), 1.03 (q, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ176.9, 148.0, 146.8, 132.3, 131.2, 129.1, 128.9, 123.0, 122.5, 110.5, 108.3, 101.7, 87.7, 84.3, 65.0, 39.0, 27.4, 23.1, 22.4, 8.2. HRMS (FAB) calc. for $[C_{24}H_{24}O_4]^+$ ($[M]^+$) 376.1675, found 376.1677.

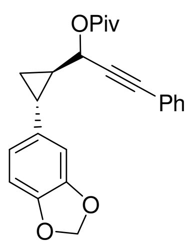


51. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 4H), 7.37-7.34 (m, 6H), 6.87 (s, 4H), 5.79 (d, *J* = 6.4 Hz, 1H), 5.76

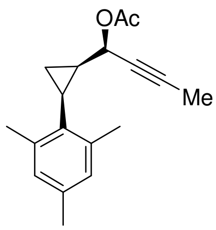
(d, J = 6.4 Hz, 1H), 2.49 (s, 6H), 2.45 (s, 6H), 2.29 (s, 6H), 2.11-2.05 (m, 1H), 2.00-1.95 (m, 1H), 1.69-1.64 (m, 2H), 1.37-1.28 (m, 1H), 1.32 (s, 9H), 1.31 (s, 9H), 1.26-1.21 (m,1H), 0.89-0.85 (m, 1H, 0.82-0.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 138.5, 138.4, 135.8, 134.0, 133.9, 131.9, 131.8, 128.8, 128.7, 128.6, 128.3, 128.2, 122.3, 122.2, 85.7, 85.0, 84.6, 67.3, 67.0, 38.9, 27.1, 23.6, 23.4, 20.9, 20.8, 20.7, 18.3, 17.5, 12.9, 12.5. HRMS (FAB) calc. for $[C_{26}H_{30}O_2]^+$ ($[M]^+$) 374.2246, found 374.2250.



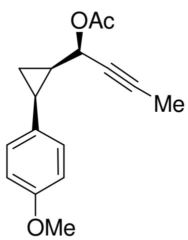
52. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 4H), 7.36-7.32 (m, 6H), 7.11 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 6.86-6.83 (m, 4H), 5.71 (d, J = 6.4 Hz, 1H), 5.59 (d, J = 7.2 Hz, 1H), 3.81 (s, 6H), 2.21 (dt, J = 5.2 and 9.6 Hz, 1H), 2.12 (dt, J = 4.8 and 9.2 Hz, 1H), 1.65-1.57 (m, 2H), 1.28 (s, 18H), 1.22 (m, 2H), 1.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 157.9, 146.1, 133.5, 133.4, 131.9, 131.8, 128.6, 128.2, 127.7, 127.4, 122.3, 122.2, 113.8, 113.7, 85.5, 85.3, 84.9, 84.6, 66.7, 66.6, 55.3, 38.8, 27.1, 26.5, 25.4, 24.7, 20.9, 19.6, 12.5, 11.9. HRMS (FAB) calc. for $[C_{24}H_{26}O_3]^+$ ($[M]^+$) 362.1882, found 362.1888.



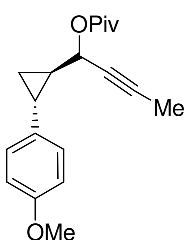
53. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 4H), 7.39-7.34 (m, 6H), 6.79-6.77 (m, 2H), 6.73-6.66 (m, 4H), 5.96 (s, 4H), 5.76 (d, J = 6.4 Hz, 1H), 5.64 (d, J = 6.8 Hz, 1H), 2.24 (dt, J = 5.2 and 9.6 Hz, 1H), 2.16 (dt, J = 4.4 and 8.8 Hz, 1H), 1.65 (m, 2H), 1.33 (s, 18H), 1.25 (m, 2H), 1.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 147.6, 147.5, 145.7, 135.3, 135.2, 131.8, 128.6, 128.4, 128.2, 122.1, 122.0, 119.7, 119.5, 108.0, 107.1, 106.8, 100.7, 85.6, 85.3, 84.8, 84.4, 66.6, 66.5, 38.7, 27.0, 26.9, 25.5, 24.7, 21.5, 20.0, 12.6, 11.9. HRMS (FAB) calc. for $[C_{24}H_{24}O_4]^+$ ($[M]^+$) 376.1675, found 376.1678.



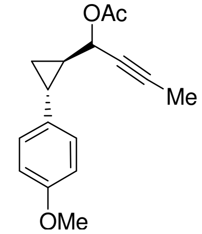
54. [1]H NMR (400 MHz, $CDCl_3$) δ 6.75 (s, 2H), 4.51 (ddt, *J* = 1.6, 4.0 and 7.6 Hz, 1H), 2.35 (s, 6H), 2.21 (s, 3H), 2.01 (q, *J* = 8.4 Hz, 1H), 1.98 (s, 3H), 1.70 (m, 1H), 1,67 (d, *J* = 2.0 Hz, 3H), 1.35 (dt, *J* = 5.6 and 8.8 Hz, 1H), 1.16 (dt, *J* = 5.6 and 7.6 Hz, 1H). [13]C NMR (100 MHz, $CDCl_3$) δ 169.4, 135.6, 130.3, 128.8, 81.6, 76.0, 65.6, 20.8, 20.7, 20.4, 19.4, 11.4, 3.5. HRMS (FAB) calc. for $[C_{18}H_{22}O_2]^+$ ($[M]^+$) 270.1620, found 270.1617.



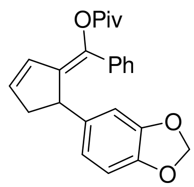
55. [1]H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 4.32 (dd, *J* = 2.0 and 10.0 Hz, 1H), 3.79 (s, 3H), 2.31 (q, *J* = 8.0 Hz, 1H), 1.93 (s, 3H), 1.85 (d, *J* = 2.0 Hz, 3H), 1.69-1.65 (m, 1H), 1.18 (dt, *J* = 5.6 and 8.4 Hz, 1H), 0.99 (q, *J* = 5.6 Hz, 1H). [13]C NMR (100 MHz, $CDCl_3$) δ 169.2, 158.2, 130.0, 128.5, 113.4, 80.9, 76.8, 64.9, 56.7, 55.1, 42.8, 34.8, 22.6, 21.0, 20.6, 7.7, 3.7. HRMS (FAB) calc. for $[C_{16}H_{18}O_3]^+$ ($[M]^+$) 258.1256, found 258.1253.



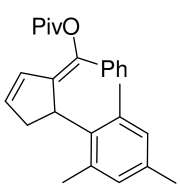
56. Obtained as a 1:1 mixture of diastereomers about the propargylic position. [1]H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.41 (m, 1H), 5.29 (m, 1H), 3.78 (d, *J* = 1.6 Hz, 6H), 2.07 (dt, *J* = 5.2 and 9.8 Hz, 1H), 1.99 (dt, *J* = 5.2 and 9.8 Hz, 1H), 1.87 (d, *J* = 2.0 Hz, 3H), 1.85 (d, *J* = 2.0 Hz, 3H), 1.47 (m, 2H), 1.22 (s, 6H), 1.08 (m, 2H), 0.93 (m, 2H). [13]C NMR (75 MHz, $CDCl_3$) δ 177.6, 157.8, 133.7, 133.6, 127.6, 127.3, 113.7, 113.6, 81.9, 81.8, 75.1, 74.7, 66.8, 66.6, 55.2, 38.8, 27.1, 26.5, 25.5, 24.8, 20.8, 19.4, 12.5, 11.8, 3.6. HRMS (FAB) calc. for $[C_{19}H_{24}O_3]^+$ ($[M]^+$) 300.1725, found 300.1728.



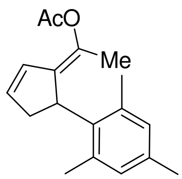
57. Obtained as a 1:1 mixture of diastereomers about the propargylic position. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.39 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.10-2.05 (m, 1H9, 2.01 (quint., *J* = 7.2 Hz, 1H), 1.52-1.48 (m, 2H), 1.16-1.04 (m, 2H), 0.98-0.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.1, 157.8, 133.6, 133.5, 127.4, 127.2, 113.8, 113.7, 82.4, 82.3, 74.5, 74.4, 67.1, 55.2, 25.2, 24.9, 21.1, 20.9, 19.5, 13.0, 12.0, 3.6. HRMS (FAB) calc. for $[C_{16}H_{18}O_3]^+$ ($[M]^+$) 258.1256, found 258.1254.



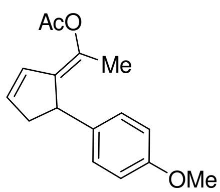
58. Obtained as a 75:25 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer: δ 7.35-7.13 (m, 5H), 6.75-6.70 (m, 1H), 6.64-6-60 (m, 2H), 6.44 (m, 1H), 6.11 (m, 1H), 5.88 (s, 2H), 4.25 (d, *J* = 7.6 Hz, 1H), 3.18 (dd, *J* = 8.0 and 17.6 Hz, 1H), 2.49 (d, *J* = 18.0 Hz, 1H), 1.38 (s, 9H). Minor diastereomer (diagnostic peaks): 4.11 (d, *J* = 6.8 Hz, 1H), 3.15 (m 1H), 2.39 (d, *J* = 18.4 Hz, 1H), 1.05 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 175.9, 147.6, 145.6, 145.5, 140.2, 139.7, 139.5, 138.7, 137.7, 136.4, 136.1, 135.2, 130.1, 128.2, 127.9, 127.8, 127.5, 127.4, 126.9, 120.2, 119.9, 107.9, 107.4, 107.3, 100.7, 45.4, 44.9, 44.5, 44.1, 39.0, 38.7, 31.6, 27.2, 26.9, 26.5, 25.3, 22.6, 14.1. HRMS (FAB) calc. for $[C_{24}H_{24}O_4]^+$ ($[M]^+$) 376.1675, found 376.11677.



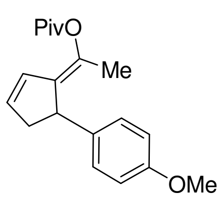
59. Obtained as a 90:10 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer: δ 7.03-6.99 (m, 5H), 6.61 (s, 1H), 6.58 (s, 1H), 6.46 (m, 1H), 6.23 (m, 1H), 4.62 (dd, *J* = 4.4 and 8.0 Hz, 1H), 3.14 (dd, *J* = 7.2 and 18.0 Hz, 1H), 4.62 (d, *J* = 18.0 Hz, 1H), 2.18 (s, 3H), 2.15 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 138.3, 137.6, 136.7, 136.6, 135.7, 134.9, 134.8, 1302, 130.1, 128.1, 128.0, 127.6, 127.4, 127.2, 127.0, 41.2, 41.0, 39.9, 38.9, 27.1, 26.5, 21.3, 20.9, 20.5, 20.1. HRMS (FAB) calc. for $[C_{26}H_{30}O_2]^+$ ($[M]^+$) 374.2246, found 374.2252.



60. Obtained as a 1:1 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87-6.80 (m, 4H), 6.32-6.29 (m, 2H), 6.11 (bs, 1H), 6.04 (bs, 1H), 4.48 (bs, 1H), 4.40 (bs, 1H), 3.06 (dd, *J* = 8.8 and 18.4 Hz, 1H), 3.00 (dd, *J* = 8.8 and 18.4 Hz, 1H), 2.51 (bs, 1H), 2.47 (bs, 1H), 2.39 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.16 (s, 6H), 2.09 (s, 3H), 1.99 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.8, 137.4, 137.3, 137.1, 136.9, 136.1, 135.9, 135.7, 135.6, 135.5, 135.4, 135.2, 134.9, 134.7, 130.7, 130.4, 129.6, 129.1, 128.7, 128.6, 128.3, 40.8, 40.4, 40.0, 39.1, 39.0, 21.3, 21.1, 20.8, 20.7, 20.6, 19.6, 19.5, 19.4, 17.2, 16.2. HRMS (FAB) calc. for $[C_{18}H_{22}O_2]^+$ ($[M]^+$) 270.1620, found 270.1618.



61. Obtained as a 1:1 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 2H), 7.08-7.05 (m, 2H), 6.86-6.82 (m, 2H), 6.81-6.79 (m, 2H), 6.32-6.29 (m, 2H), 6.05 (dt, *J* = 2.8 and 5.6 Hz, 1H), 5.93 (dt, *J* = 2.4 and 5.2 Hz, 1H), 3.98 (d, *J* = 8.0 Hz, 1H), 3.90 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.13 (dd, *J* = 8.8 and 18.0 Hz, 1H), 3.06 (dd, *J* = 8.8 and 18.0 Hz, 1H), 2.39 (d, *J* = 18.0, 2H), 2.17 (s, 3H), 2.00 (s, 3H), 1.75 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.8, 157.8, 157.7, 138.2, 138.1, 137.9, 137.6, 137.5, 137.0, 135.6, 134.5, 129.2, 128.7, 128.6, 128.0, 127.8, 113.9, 113.8, 113.6, 55.1, 44.2, 44.1, 43.9, 43.4, 20.8, 20.4, 17.2, 17.1. HRMS (FAB) calc. for $[C_{16}H_{18}O_3]^+$ ($[M]^+$) 258.1256, found 258.1259.

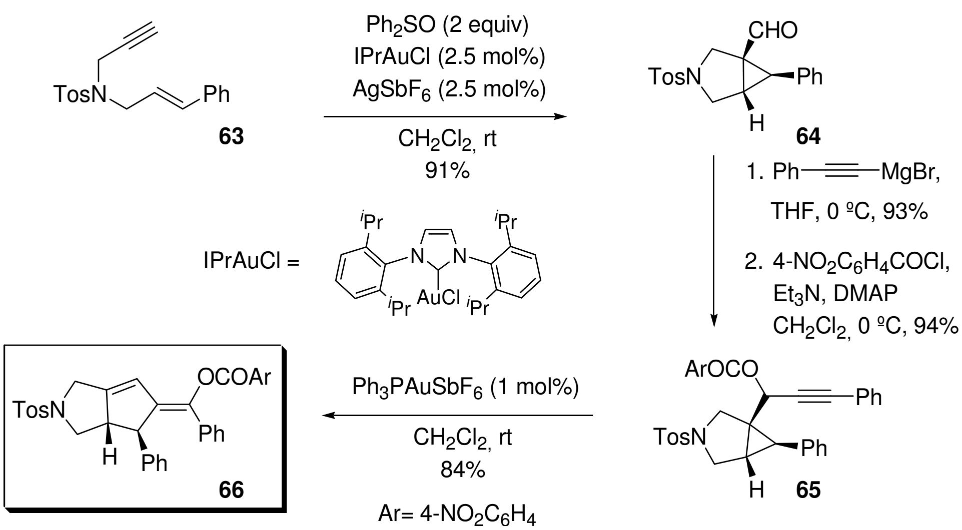


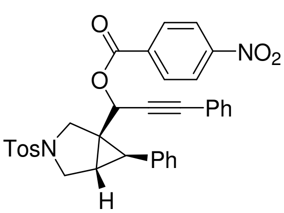
62. Obtained as a 1:1 mixture of olefins about the exocyclic double bond. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.15 (m, 2H), 7.06-7.03 (m, 2H), 6.86-6.82 (m, 2H), 6.80-6.68 (m, 2H), 6.32 (dt, *J* = 2.0 and 5.6 Hz, 1H), 6.26 (dt, *J* = 2.0 and 5.6 Hz, 1H), 5.96 (dt, *J* = 2.8 and 5.6 Hz, 1H), 5.90 (dt, *J* = 2.8 and 5.6 Hz, 1H), 3.98 (d, *J* = 9.6 Hz, 1H), 3.98 (d, *J* = 10.6 Hz, 1H), 3.78 (s, 3H), 3.76

(s, 3H), 3.12 (dd, J = 8.8 and 18.0 Hz, 1H), 3.06 (dd, J = 8.8 and 18.0 Hz, 1H), 2.38 (d, J = 18.0 Hz, 1H), 2.28 (d, J = 18.0 Hz, 1H), 2.01 (s, 3H), 1.61 (s, 3H), 1.29 (s, 9H), 0.94 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 176.1, 157.7, 157.6, 138.4, 138.0, 137.9, 137.7, 136.6, 136.4, 134.8, 134.2, 129.5, 128.8, 128.5, 128.0, 127.8, 113.9, 113.8, 113.6, 55.2, 55.1, 44.2, 44.1, 43.6, 43.5, 38.9, 38.6, 27.1, 26.8, 17.0, 16.9. HRMS (FAB) calc. for $[C_{19}H_{24}O_3]^+$ ($[M]^+$) 300.1725, found 300.1727.

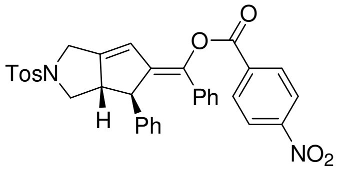
The synthetic utility of this Au(I)-catalysed cyclization is further highlighted in Supplementary Scheme 3. Starting from enyne **63**, the following four-step sequence afforded bicycle **66** as a single diastereomer in 67% overall yield: 1. Au(I)-catalysed oxidative rearrangement to furnish aldehyde **64**;[12] 2. addition of phenyl ethynyl magnesium bromide to the aldehyde; 3. 4-$NO_2C_6H_4CO$ protection of the resulting alcohol; 4. further Au(I)-catalysed pentannulation.

Supplementary Scheme 3. Four-step sequence for the formation of bicycle **66**



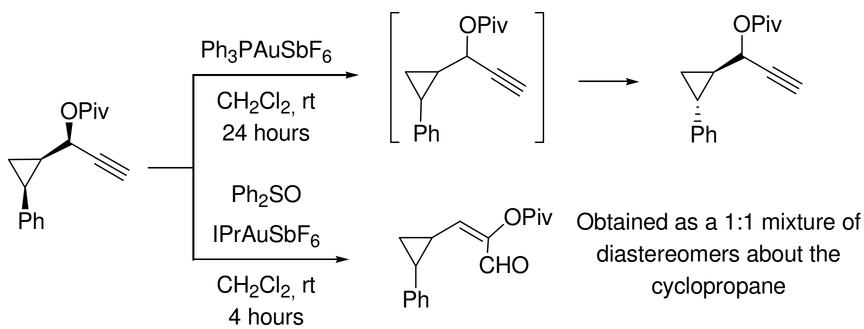


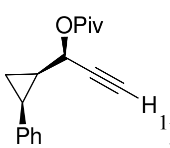
65. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.36-7.30 (m, 3H), 7.29-7.22 (m, 2H), 7.20-7.10 (m, 5H), 7.09-7.03 (m, 2H), 5.17 (s, 1H), 4.05 (d, J = 9.3 Hz, 1H), 3.78 (dd, J = 4.4 and 9.3 Hz, 2H), 3.26 (dd, J = 4.4 Hz, 1H), 2.76 (d, J = 4.4 Hz, 1H), 2.38 (s, 3H), 2.21 (t, J = 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 150.6, 143.7, 134.6, 134.2, 132.4, 131.8, 130.7, 129.7, 129.0, 128.5, 128.4, 128.1, 127.7, 127.2, 123.5, 121.2, 83.7, 83.5, 64.8, 50.9, 50.0, 37.3, 30.5, 25.3, 21.5. HRMS (FAB) calc. for $[C_{34}H_{28}N_2O_6S]^+$ ($[M]^+$) 592.1668, found 592.1673.



66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.28 (m, 4H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.10-6.94 (m, 10H), 6.15 (s, 1H), 4.14 (d, *J* = 4.3 Hz, 1H), 4.07-4.04 (s, 1H), 3.90-3.84 (s, 2H), 3.42-3.32 (m, 1H), 2.84 (dd, *J* = 8.9 and 10.1 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 150.9, 150.3, 143.8, 142.1, 141.4, 138.8, 134.7, 133.7, 133.5, 131.2, 129.9, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 126.3, 123.8, 122.5, 60.6, 52.1, 51.4, 46.5, 21.6. HRMS (FAB) calc. for $[C_{34}H_{28}N_2O_6S]^+$ ($[M]^+$) 592.1668, found 592.1673.

2.3.6. Terminal alkynes. In the case of terminal alkynes, cyclopentene products (originated from a [3,3]-rearrangement) were not observed. A reversible [2,3]-rearrangement might also account for the observed loss of relative stereochemistry.[13] In agreement with this possibility, the reaction of a model substrate bearing a terminal alkyne led only to the scrambling of the stereocenters, and eventually to the thermodynamically more stable *trans* cyclopropanes as a 1:1 mixtures of diastereomers about the propargylic position. In agreement with our previously reported observations,[14] the Au(I)-catalyzed reaction of this substrate with Ph_2SO resulted in formation of a 1:1 mixture of diastereomeric aldehydes.





^{1}H NMR (400 MHz, CH_2Cl_2) δ 7.32-7.26 (m, 2H), 7.24-7.20 (m, 3H), 4,32 (dd, *J* = 2.4 and 10.8 Hz, 1H), 2.49 (d, *J* = 2.4 Hz, 1H), 2.42 (q, *J* = 8.4 Hz, 1H), 1.80 (m, 1H), 1.24 (m, 1H), 1.12-1.07 (m, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, CH_2Cl_2) δ 176.5, 137.1, 129.4, 128.4, 126.8, 82.0, 72.4, 64.0, 38.6, 27.1, 23.0, 22.4, 7.6. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 136.4, 128.8, 128.1, 126.5, 81.5, 72.3, 63.7, 38.3, 26.9, 22.6, 22.0, 7.5. HRMS (FAB) calc. for $[C_{17}H_{20}O_2]^+$ ($[M]^+$) 256.1463, found 256.1461.

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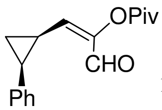
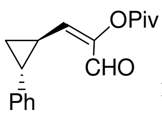
[13] Soriano, E.; Marco-Contelles, J. *Chem. Eur. J.* **2008**, *14*, 6771.
[14] Witham, C. A.; Mauleón, P.; Shapiro, N. D.; Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 5838.

Procedure for 1,6-enyne Oxidative Rearrangement Catalyzed by IPrAuCl/AgSbF$_6$:

A 0.10 mmol sample of starting material was dissolved in 1.0 mL of CH_2Cl_2 (0.1 M) in a scintillation vial. Two equivalents of diphenyl sulfoxide were added 2.5 mol % of premixed catalyst in 0.1 mL CH_2Cl_2 was added. The vial was sealed and the reaction mixture was maintained room temperature for the specified time. Crude reaction mixtures were purified by flash chromatography (5% ethyl acetate/hexanes).



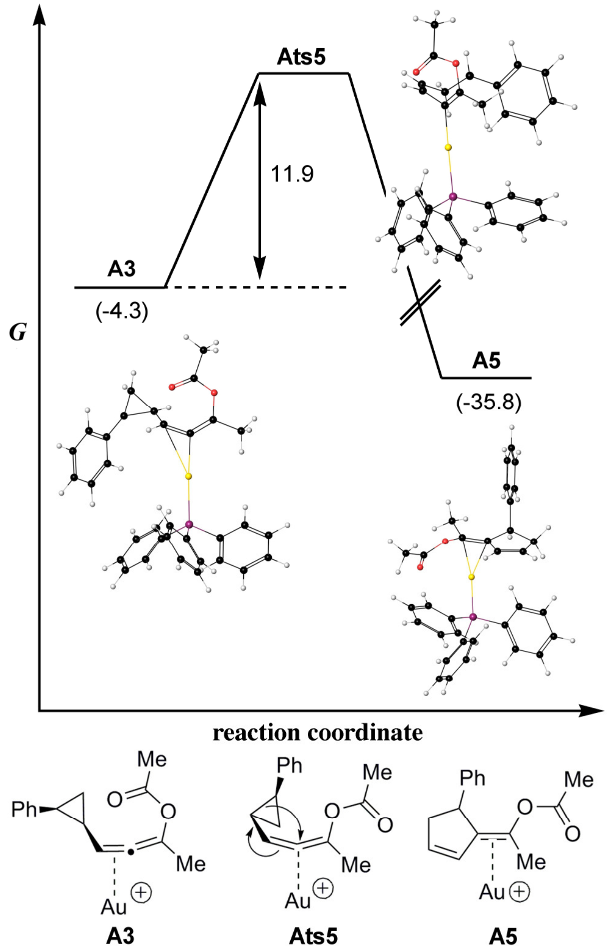
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.35-7.31 (m, 3H), 7.26-7.24 (m, 2H), 5.49 (d, *J* = 9.6 Hz, 1H), 2.76-2.66 (m, 2H), 1.62 (dt, *J* = 5.2 and 8.4 Hz, 1H), 1.30 (q, *J* = 5.6 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 176.1, 145.3, 139.6, 136.6, 129.3, 128.5, 126.9, 38.7, 27.1, 25.6, 15.9, 14.4. HRMS (FAB) calc. for $[C_{17}H_{20}O_3]^+$ ($[M]^+$) 272.1412, found 272.1414.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 5.97 (d, *J* = 10.4 Hz, 1H), 2.35 (ddd, *J* = 4.0, 6.4 and 9.6 Hz, 1H), 1.99 (m, 1H), 1.64-1.59 (m, 1H), 1.43 (dt, *J* = 7.2 and 12.8 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 175.7, 147.6, 144.8, 140.0, 128.6, 126.5, 126.1, 39.0, 27.5, 27.1, 21.9, 18.5. HRMS (FAB) calc. for $[C_{17}H_{20}O_3]^+$ ($[M]^+$) 272.1412, found 272.1415.

3. DFT calculations

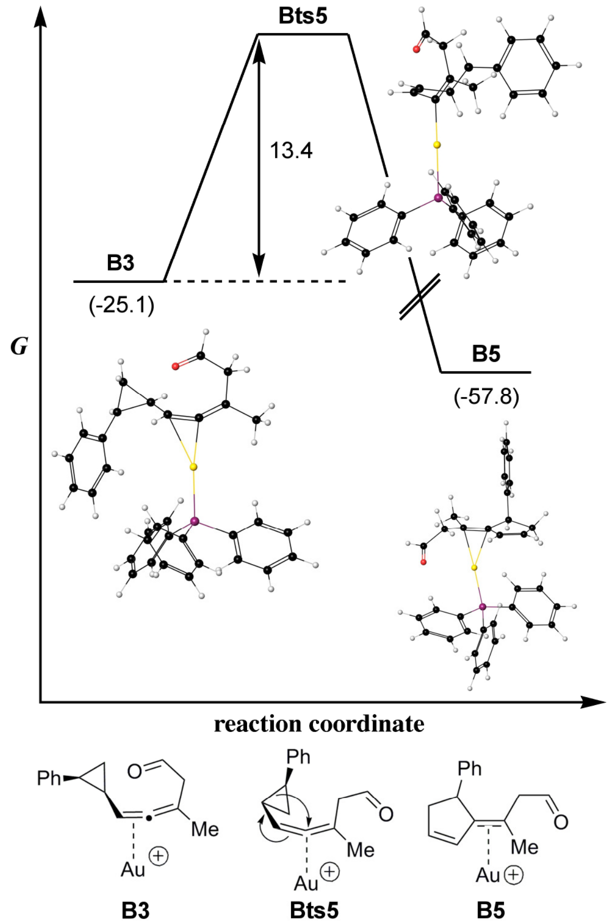
3.1. On the pentannulation process. The variability observed in the relative rates of stereochemical scrambling and pentannulation suggests that the pentannulation mechanism circumvents whatever route which is responsible for *cis*/*trans* cyclopropane isomerization. With that in mind, a pathway was explored which involves a concerted ring expansion from the cyclopropyl allene directly to the cyclopentene. For ester model system **A** the transition state **Ats5** was located, corresponding to an activation barrier of 11.9 kcal/mol and connecting **A3** with cyclopentene-gold complex **A5** (Supplementary Figure S1). The reaction coordinate consists of a simultaneous cyclopropyl ring opening and bond formation between the benzylic carbon and that bound to the gold center; the triphenylphosphine-gold fragment then migrates to an η^2 π-bonding arrangement farther along the reaction coordinate.



Supplementary Figure S1. Reaction coordinate diagram for pentannulation of acyl allene **A3** in CH_2Cl_2, Gibbs free energies (G_{STP}) in kcal/mol. Values in parentheses relative to **A1**. Color scheme: C, black; H, gray; O, red; P, purple; Au, yellow.

The concerted cyclopentene-forming transition state **Bts5** was also located (Supplementary Figure S2), with an energy corresponding to $\Delta G_{STP}{}^{\ddagger}{}_{\mathbf{Bts5}}$ = 13.4 kcal/mol. This value is too low, as formation of cyclopentene **29** was observed experimentally only at slightly elevated temperature, but higher than that in system **A**. Given the known shortcomings of hybrid DFT in dealing with transition metal chemistry it is not at all surprising that the activation barrior has significant error with respect to experiment.[15] However, because systems **A** and **B** are very similar from a computational standpoint, the comparison between $\Delta G_{STP}{}^{\ddagger}{}_{\mathbf{Ats5}}$ and $\Delta G_{STP}{}^{\ddagger}{}_{\mathbf{Bts5}}$ should be valid. Therefore, our proposed pathway successfully predicts the lower rate of cyclopentene formation associated with the propargyl vinyl ethers.

[15] Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.

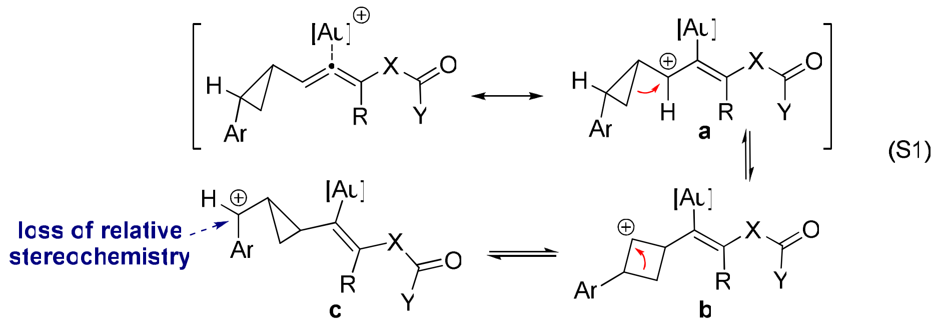


Supplementary Figure S2. Reaction coordinate diagram for pentannulation of formyl allene **B3** in CH_2Cl_2, Gibbs free energies (G_{STP}) in kcal/mol. Values in parentheses relative to **B1**. Color scheme: C, black; H, gray; O, red; P, purple; Au, yellow.

It should be noted that the free allene arising from dissociation of **A3** was predicted to be more stable than the propargyl ester substrate by almost 5 kcal/mol, and the calculated substrate dissociation energies for **A1** and **A3** (ΔG_{STP} = 6.6 and 6.0 kcal/mol, respectively) were nearly equal. Therefore, given that cyclopentene formation was empirically shown to be slower than the cyclization, the calculations predict an eventual buildup of allene in solution which was not observed experimentally. These results indicate that the model chemistry introduces a non-physical bias towards the allene-like isomers, again highlighting deficiencies in the B3LYP functional. We felt it was necessary to use this overrated functional in order to maintain comparability with previous (and probably flawed) studies of others. However, results concerning strictly isodesmic processes such as **A3/A3*trans*** isomerization should be more reliable.[16]

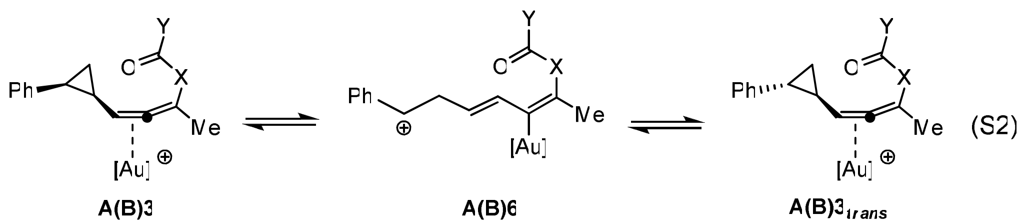
[16] Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, Jr., J. A.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570.

3.2. *Cis/trans* cyclopropyl rearrangement. As mentioned in the discussion, a plausible candidate mechanism for the *cis/trans* cyclopropyl rearrangement (shown in equation S1) was not satisfactorily modeled. The literature precedent for this process concerns carbocations that are not delocalized and so



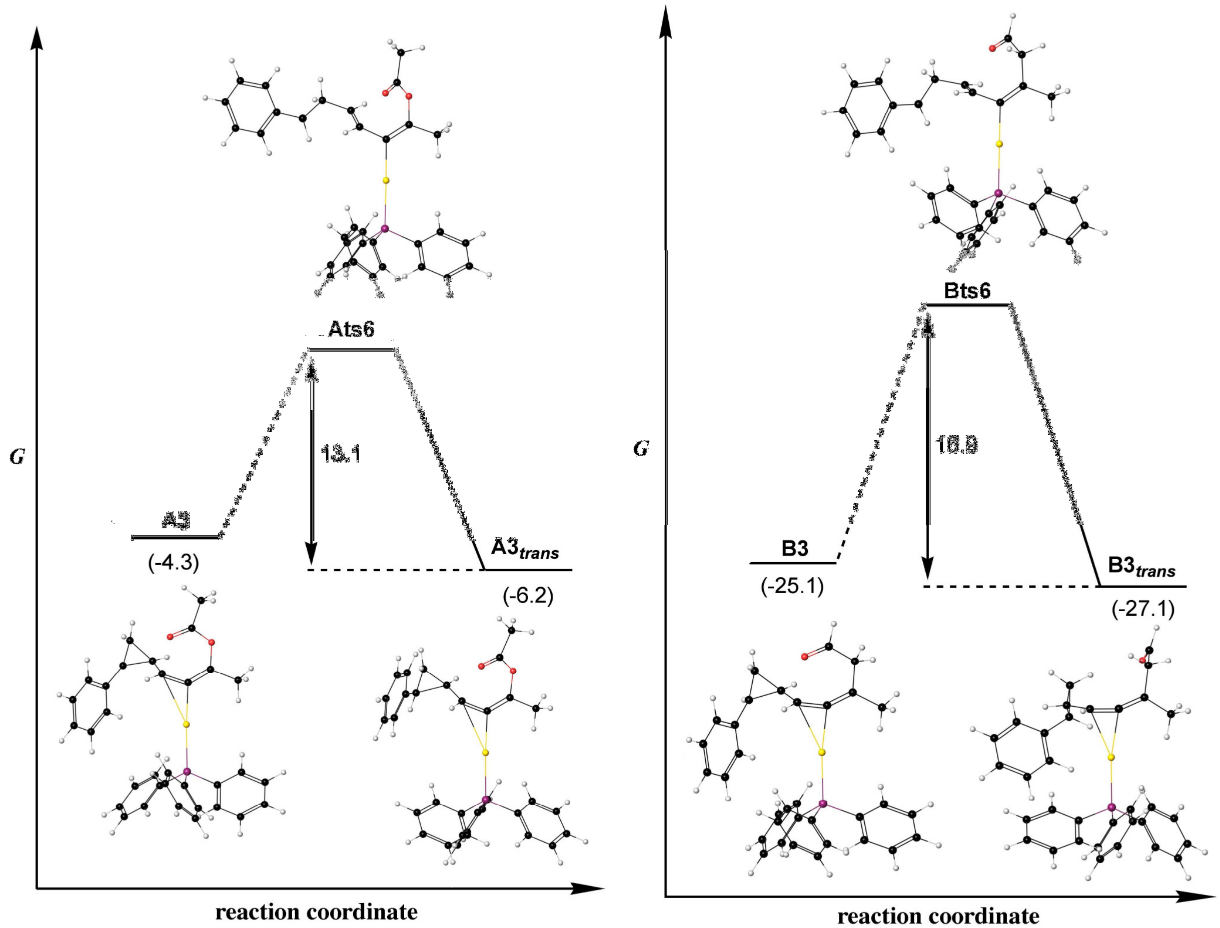
the localized, secondary carbocation in the cyclobutonium intermediate **b** is not greatly higher in energy than the cyclopropyl reactant. All attempts to locate the transition state proceeding from **a** to such a cyclobutonium species **b** in our model systems resulted in collapse to **a** or high-energy transition states with primary carbocationic character. Additionally, neither **b** nor **c** were located as minima.

An alternate mechanism was investigated which involves the heterolysis of a cyclopropyl carbon-carbon bond yielding an acyclic benzyl cation with a *trans* alkene α to the metal-bound carbon, as depicted by **A(B)6** in equation S2. Stationary points were located that appear to be either the



transition states between **A(B)3*trans*** and acyclic minima **A(B)6** or the transition states for a concerted rearrangement. These extrema exhibit imaginary modes υ = -59 cm^{-1} and υ = -125 cm^{-1} in **Ats6** and **Bts6**, respectively, and their energies correspond to activation barriers ($\Delta G_{STP}^{\ddagger}$, from the more stable *trans* cyclopropyl isomer) of 13.1 and 16.9 kcal/mol respectively. The structures of **Ats6** and **Bts6** are shown in Figure S3. Given the known tendency for DFT methods to underestimate barrier heights[14] (see above) these values are more or less reasonable and at least correctly predict that the rearrangement will be less facile for **B3*trans*** than for **A3*trans***. Furthermore, the formation of the *trans* alkene in **A(B)6** precludes the direct cyclization to cyclopentene complex **A(B)5**, a condition which is necessary because that cyclization was shown experimentally to follow a distinct pathway.

[14] Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.



Supplementary Figure S3. Reaction coordinate diagrams for cyclopropyl ring opening in CH_2Cl_2, Gibbs free energies (G_{STP}) in kcal/mol. Values in parentheses relative to **A1** (left) and **B1** (right). Color scheme: C, black; H, gray; O, red; P, purple; Au, yellow.

The problem with these structures is that while intrinsic reaction coordinate searches toward **A(B)3*trans*** resulted in the expected behavior, searches in the other direction halted at the first step (using a sufficiently large step size for the search to run) indicating that minima were reached. However, optimization of these "minima" never yielded the open configurations as stationary points and therefore it is unclear whether the potential energy wells for the acyclic cations **A(B)6** are simply very shallow or whether they do not exist. This ambiguity, taken with the lack of precedent for this mechanism of cyclopropyl rearrangement, prevents us from enthusiastically endorsing this mechanistic proposal.

3.3. Computational methods. All calculations were performed using Jaguar 6.5[17] with Maestro[18] as the graphical user interface. The popular hybrid DFT functional B3LYP[19] was used throughout. The valence double-ζ, 60-electron effective core potential LACVP[2013] basis set was employed for gold, while the remaining atoms were treated with Pople's 6-31G** (*e.g.* 6-31G(d,p)) polarized basis set.[21,22,23,24] High-accuracy cutoffs were used with the default grid sizes for all calculations. The default geometry convergence scheme gave poor results in many cases, thus all reported structures were optimized using the GDIIS method.[25] Many stationary points were located on multiple occasions, which allowed us to estimate that the precision of the optimized total energies is about ±0.3 kcal/mol. Analytic vibrational frequencies were calculated for all optimized structures, and their character as minima (0 imaginary frequencies) or transition states (1 imaginary frequency) were confirmed (imaginary modes lower than 10 cm^{-1} were ignored). Intrinsic reaction coordinate calculations were performed on all transition state structures, confirming that each connects the expected reactant and product. Solvation calculations were carried out on the gas-phase structures using the Poisson-Boltzmann method,[26,27] with a dielectric constant and probe radius of 8.93 and 2.33 Å for dichloromethane, and 37.27 and 2.20 Å for nitromethane. NBO analyses employed NBO 5.0[28] as compiled with the current Jaguar release. Molecular graphics were generated in Maestro.

[17] *Jaguar*, version 6.5; Schrodinger, LLC: New York, 2005.
[18] *Maestro*, version 7.5; Schrodinger, LLC: New York, 2005.
[19] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
[20] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
[21] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
[22] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
[23] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
[24] Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
[25] Császár, P.; Pulay, P. J.; *J. Mol. Struct.* **1984**, *114*, 31.
[26] Tannor, D. J.; Marten, B.; Murphy, R. B.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M. N.; Goddard, W. A., III; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875.
[27] Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996**, *100*, 11775.
[28] Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001); http://www.chem.wisc.edu/~nbo5.

3.4. Energies and coordinates of computed structures.

Table S1. Absolute energies and positional coordinates for **A1**.

Gas phase:
SCFE: -1903.25020387561 a.u.
ZPE: 330.435 kcal/mol
G_{STP}: -1902.802388 a.u.

Dichloromethane:
SCFE: -1903.30434340797 a.u.
G_{STP}: -1902.856527 a.u.

Nitromethane:
SCFE: -1903.31046752365 a.u.
G_{STP}: -1902.862651 a.u.

C1	11.8095216973	14.5985624484	0.7745666148
O2	12.7541971679	14.0348711138	1.5586776130
C3	12.4975191653	12.7420591686	2.1721662567
C4	12.4926281153	11.6476364329	1.1683568736
C5	12.7901502251	10.6448060251	0.5171389469
H6	13.4079559014	12.5777394224	2.7574647296
C7	13.3772270003	9.4588368910	-0.1181134927
H8	13.5245354597	9.6175536031	-1.1901604197
H9	14.3515966237	9.2603122208	0.3411160075
H10	12.7403122056	8.5808599815	0.0196046838
C11	11.3112698128	12.7352331689	3.1089665269
C12	11.4380445777	13.4676819573	4.4241970808
C13	11.4060805294	11.9641942494	4.4312170297
H14	10.3438459312	12.7421535256	2.6196881303
H15	12.3806504168	13.9676056872	4.6269750276
H16	10.5700468068	14.0044305171	4.7933881025
H17	10.4542609174	11.5248455069	4.7227579990
C18	14.7311523529	9.3802795552	5.3911271078
C19	14.8322184859	10.7487935665	5.6367787544
C20	13.7655027065	11.6010510692	5.3382334586
C21	12.5824139756	11.1003654172	4.7800051499
C22	12.4899092741	9.7177975582	4.5462867631
C23	13.5503350123	8.8659999826	4.8486025303
H24	15.5573630323	8.7178926455	5.6316836147
H25	15.7379546819	11.1580194201	6.0751644737
H26	13.8527038688	12.6582744054	5.5701141460
H27	11.5689776860	9.3088447261	4.1357508905
H28	13.4529131277	7.7985128134	4.6699799699
O29	10.7632958191	14.0494433419	0.4789136122
Au30	10.6313233623	11.2862096947	-0.2315935777
P31	8.6048602334	11.1699038287	-1.4052132841
C32	5.1457448939	12.9647229644	1.0848046080
C33	6.3816096280	13.6134403484	1.0153275774

C34	7.4266232103	13.0615035552	0.2756757634
C35	7.2310553873	11.8498202433	-0.4095297471
C36	5.9907785855	11.1984591086	-0.3379705411
C37	4.9534073636	11.7589781996	0.4092035320
H38	4.3365233642	13.3966049592	1.6661164637
H39	6.5339180303	14.5512451357	1.5414721009
H40	8.3864539257	13.5696527842	0.2310155979
H41	5.8326044362	10.2591640448	-0.8582471797
H42	3.9953991302	11.2501462305	0.4624358880
C43	7.4872212631	6.7810724156	-2.3395049619
C44	8.0181584645	7.1268593742	-1.0941311840
C45	8.3669168296	8.4488374531	-0.8275070218
C46	8.1756384468	9.4391578457	-1.8052952378
C47	7.6437187717	9.0879444486	-3.0540617843
C48	7.3024645805	7.7600572192	-3.3157675137
H49	7.2217067341	5.7489244641	-2.5483134841
H50	8.1646250939	6.3660193154	-0.3331358217
H51	8.7859147845	8.7130703091	0.1404549342
H52	7.4968396296	9.8423919980	-3.8200899113
H53	6.8931163554	7.4926045055	-4.2853474986
C54	8.7248909548	13.4177582009	-5.4454111739
C55	7.5554894244	13.4263309545	-4.6832789444
C56	7.5123161108	12.7697269134	-3.4525634758
C57	8.6486340378	12.0966744760	-2.9781752100
C58	9.8251530809	12.0975561524	-3.7440329353
C59	9.8593515697	12.7530517895	-4.9736623575
H60	8.7542047753	13.9314227093	-6.4015726800
H61	6.6732381355	13.9467495314	-5.0439308085
H62	6.5996550155	12.7858619546	-2.8649238594
H63	10.7130109708	11.5876546171	-3.3786455295
H64	10.7727316690	12.7488861734	-5.5609098320
C65	12.2284332328	15.9718839275	0.3232946072
H66	11.4593101646	16.3940114249	-0.3226133092
H67	12.3837956655	16.6177875606	1.1927225808
H68	13.1802408872	15.9148707951	-0.2132051654

Table S2. Absolute energies and positional coordinates for **Ats1**.

Gas phase:
SCFE: -1903.24013951360 a.u.
ZPE: 330.266 kcal/mol
G_{STP}: -1902.789419 a.u.
Imaginary frequencies: -144, -9 cm^{-1}

Dichloromethane:
SCFE: -1903.29523160693 a.u.
G_{STP}: -1902.844511 a.u.

Nitromethane:
SCFE: -1903.30157949274 a.u.

G_{STP}: -1902.850859 a.u.

C1	11.1039522632	14.9445934128	4.2091921166
O2	11.9026006470	14.5520592155	3.2128463497
C3	11.8088436417	13.1966510461	2.6693323152
C4	10.3728472715	12.8192573423	2.3844197014
C5	9.3421272373	12.9935231260	3.0945485202
H6	12.3739955798	13.2807620491	1.7419672532
C7	7.9907743829	13.0787255551	3.6243063434
H8	7.3348299214	12.4451007650	3.0165763597
H9	7.9596224225	12.7165852337	4.6558546464
H10	7.6171038236	14.1059372638	3.5941121771
C11	12.4628365677	12.1932037241	3.5945449312
C12	13.9304966081	12.3449249234	3.9132419306
C13	13.4932448701	11.1919016405	3.0551620521
H14	11.8145780595	11.8288337706	4.3850902054
H15	14.4560472143	13.1713357514	3.4441208812
H16	14.2531471495	12.1414703636	4.9294540770
H17	13.4417347099	10.2311911946	3.5633191973
C18	14.4763875688	10.6688066658	-1.1166936425
C19	15.0283848156	11.7355304545	-0.4090761253
C20	14.7162549833	11.9250607390	0.9391421656
C21	13.8343772759	11.0608048814	1.6009749946
C22	13.2791245960	9.9939571766	0.8735397538
C23	13.6010529572	9.7938401876	-0.4682709227
H24	14.7379369575	10.5091651697	-2.1589592516
H25	15.7223397835	12.4128846114	-0.8986436958
H26	15.1913489226	12.7374960010	1.4802564839
H27	12.6068602966	9.3008467664	1.3743376530
H28	13.1750331229	8.9502989954	-1.0041876835
O29	10.2259289838	14.2384997131	4.6996498744
Au30	9.7512140903	11.7779031371	0.6190138893
P31	9.0334530475	10.7276208212	-1.3675140350
C32	4.4149591691	10.8730150814	-1.6459898916
C33	5.1420161603	12.0106886977	-1.2864287685
C34	6.5307114584	11.9500001369	-1.1913348336
C35	7.2054679386	10.7483901902	-1.4664105798
C36	6.4718869694	9.6097318599	-1.8267467193
C37	5.0798556417	9.6766856388	-1.9137178605
H38	3.3321408275	10.9203200836	-1.7151556195
H39	4.6267552183	12.9439110126	-1.0788552619
H40	7.0921694893	12.8377418117	-0.9108243206
H41	6.9797633199	8.6746905791	-2.0385296854
H42	4.5167238993	8.7909908245	-2.1918205181
C43	10.2360899135	6.2728432718	-1.6345693922
C44	9.8833276068	6.8373706712	-0.4064465181
C45	9.5463359299	8.1874145976	-0.3304294990
C46	9.5508776218	8.9799937741	-1.4892928430
C47	9.9076232622	8.4102542400	-2.7204297688
C48	10.2502129137	7.0590403422	-2.7874922947

H49	10.5029590222	5.2217003158	-1.6915528142
H50	9.8747313052	6.2273179015	0.4919148779
H51	9.2782054822	8.6260929242	0.6275495498
H52	9.9211447504	9.0160577388	-3.6211209568
H53	10.5273350477	6.6219251793	-3.7421955848
C54	10.6644114001	12.8772491542	-5.1216317437
C55	9.3342931547	12.4577981864	-5.0952617923
C56	8.8236523051	11.8142421340	-3.9672841374
C57	9.6506997861	11.5886013141	-2.8572539057
C58	10.9884728243	12.0156817228	-2.8849450430
C59	11.4904898253	12.6541730982	-4.0173942932
H60	11.0568563967	13.3810533283	-6.0002292510
H61	8.6899325848	12.6324761437	-5.9518212939
H62	7.7866487673	11.4944889528	-3.9527844072
H63	11.6371530207	11.8455748096	-2.0290068974
H64	12.5251689282	12.9834599535	-4.0354020370
C65	11.3887111304	16.3552597411	4.6439395906
H66	10.7641156517	16.6074053605	5.5000757801
H67	12.4458484012	16.4642054767	4.9008316810
H68	11.1807681137	17.0415474313	3.8166555448

Table S3. Absolute energies and positional coordinates for **A2**.

Gas phase:
SCFE: -1903.25903932863 a.u.
ZPE: 331.707 kcal/mol
G_{STP}: -1902.806915 a.u.

Dichloromethane:
SCFE: -1903.31544268368 a.u.
G_{STP}: -1902.863319 a.u.

Nitromethane:
SCFE: -1903.32175927098 a.u.
G_{STP}: -1902.869635 a.u.

C1	11.8095216973	14.5985624484	0.7745666148
O2	12.7541971679	14.0348711138	1.5586776130
C3	12.4975191653	12.7420591686	2.1721662567
C4	12.4926281153	11.6476364329	1.1683568736
C5	12.7901502251	10.6448060251	0.5171389469
H6	13.4079559014	12.5777394224	2.7574647296
C7	13.3772270003	9.4588368910	-0.1181134927
H8	13.5245354597	9.6175536031	-1.1901604197
H9	14.3515966237	9.2603122208	0.3411160075
H10	12.7403122056	8.5808599815	0.0196046838
C11	11.3112698128	12.7352331689	3.1089665269
C12	11.4380445777	13.4676819573	4.4241970808
C13	11.4060805294	11.9641942494	4.4312170297
H14	10.3438459312	12.7421535256	2.6196881303

H15	12.3806504168	13.9676056872	4.6269750276
H16	10.5700468068	14.0044305171	4.7933881025
H17	10.4542609174	11.5248455069	4.7227579990
C18	14.7311523529	9.3802795552	5.3911271078
C19	14.8322184859	10.7487935665	5.6367787544
C20	13.7655027065	11.6010510692	5.3382334586
C21	12.5824139756	11.1003654172	4.7800051499
C22	12.4899092741	9.7177975582	4.5462867631
C23	13.5503350123	8.8659999826	4.8486025303
H24	15.5573630323	8.7178926455	5.6316836147
H25	15.7379546819	11.1580194201	6.0751644737
H26	13.8527038688	12.6582744054	5.5701141460
H27	11.5689776860	9.3088447261	4.1357508905
H28	13.4529131277	7.7985128134	4.6699799699
O29	10.7632958191	14.0494433419	0.4789136122
Au30	10.6313233623	11.2862096947	-0.2315935777
P31	8.6048602334	11.1699038287	-1.4052132841
C32	5.1457448939	12.9647229644	1.0848046080
C33	6.3816096280	13.6134403484	1.0153275774
C34	7.4266232103	13.0615035552	0.2756757634
C35	7.2310553873	11.8498202433	-0.4095297471
C36	5.9907785855	11.1984591086	-0.3379705411
C37	4.9534073636	11.7589781996	0.4092035320
H38	4.3365233642	13.3966049592	1.6661164637
H39	6.5339180303	14.5512451357	1.5414721009
H40	8.3864539257	13.5696527842	0.2310155979
H41	5.8326044362	10.2591640448	-0.8582471797
H42	3.9953991302	11.2501462305	0.4624358880
C43	7.4872212631	6.7810724156	-2.3395049619
C44	8.0181584645	7.1268593742	-1.0941311840
C45	8.3669168296	8.4488374531	-0.8275070218
C46	8.1756384468	9.4391578457	-1.8052952378
C47	7.6437187717	9.0879444486	-3.0540617843
C48	7.3024645805	7.7600572192	-3.3157675137
H49	7.2217067341	5.7489244641	-2.5483134841
H50	8.1646250939	6.3660193154	-0.3331358217
H51	8.7859147845	8.7130703091	0.1404549342
H52	7.4968396296	9.8423919980	-3.8200899113
H53	6.8931163554	7.4926045055	-4.2853474986
C54	8.7248909548	13.4177582009	-5.4454111739
C55	7.5554894244	13.4263309545	-4.6832789444
C56	7.5123161108	12.7697269134	-3.4525634758
C57	8.6486340378	12.0966744760	-2.9781752100
C58	9.8251530809	12.0975561524	-3.7440329353
C59	9.8593515697	12.7530517895	-4.9736623575
H60	8.7542047753	13.9314227093	-6.4015726800
H61	6.6732381355	13.9467495314	-5.0439308085
H62	6.5996550155	12.7858619546	-2.8649238594
H63	10.7130109708	11.5876546171	-3.3786455295
H64	10.7727316690	12.7488861734	-5.5609098320

C65	12.2284332328	15.9718839275	0.3232946072
H66	11.4593101646	16.3940114249	-0.3226133092
H67	12.3837956655	16.6177875606	1.1927225808
H68	13.1802408872	15.9148707951	-0.2132051654

Table S4. Absolute energies and positional coordinates for **Ats2**.

Gas phase:
SCFE: -1903.25456429383 a.u.
ZPE: 330.479 kcal/mol
G_{STP}: -1902.804403 a.u.
Imaginary frequencies: -130 cm^{-1}

Dichloromethane:
SCFE: -1903.30896264203 a.u.
G_{STP}: -1902.858802 a.u.

Nitromethane:
SCFE: -1903.31542828759 a.u.
G_{STP}: -1902.865267 a.u.

C1	11.2658082791	15.0101334546	4.2045548512
O2	12.1610642348	14.3322012464	3.6930162275
C3	11.5345589987	12.6775882020	2.7075669128
C4	10.1964040978	13.0437126356	2.3522984436
C5	9.4599806269	13.9905580638	2.9399388196
H6	12.3106691242	12.8522375265	1.9650643378
C7	8.0416481374	14.3848625822	2.6763759162
H8	7.5901405234	13.7015474575	1.9556569206
H9	7.4579497896	14.3556840049	3.6032965927
H10	7.9830242781	15.4067073811	2.2837423977
C11	11.8070033013	11.6326317718	3.6717553115
C12	13.2210624200	11.4660917853	4.2323219064
C13	12.7740338313	10.4539935709	3.2534533428
H14	10.9777397417	11.3506606577	4.3126112789
H15	13.9450327945	12.2149765033	3.9299803143
H16	13.2771340813	11.1902557232	5.2804445613
H17	12.4088300323	9.5190291111	3.6725009257
C18	14.2696491940	9.9851505989	-0.7572102212
C19	13.1405471726	9.2835126644	-0.3268640970
C20	12.6690357224	9.4518449921	0.9735354613
C21	13.3166461366	10.3207201422	1.8667353086
C22	14.4537733797	11.0113707225	1.4271113585
C23	14.9239342837	10.8471368578	0.1226454405
H24	14.6442237204	9.8504539742	-1.7678643023
H25	12.6292658977	8.6016583365	-1.0002181411
H26	11.7919087547	8.9003280441	1.3025316646
H27	14.9953166238	11.6633612863	2.1061003777
H28	15.8114618299	11.3841444233	-0.1993120165
O29	9.9672936615	14.8461962203	3.9611835262

Au30	9.5457391901	11.9508163013	0.6722921494
P31	8.7419963883	10.9188135850	-1.3181151714
C32	4.1290244253	11.1886250139	-1.5997130304
C33	4.8766400519	12.2643014894	-1.1152645841
C34	6.2628465543	12.1638760344	-1.0204659408
C35	6.9152817685	10.9857456628	-1.4199827259
C36	6.1597786840	9.9090705012	-1.9060983580
C37	4.7707466873	10.0145039991	-1.9926770691
H38	3.0480606592	11.2658893617	-1.6682942575
H39	4.3794199510	13.1796211257	-0.8082588963
H40	6.8411268167	13.0040209714	-0.6435954977
H41	6.6497548822	8.9914875417	-2.2154197173
H42	4.1915860565	9.1763092700	-2.3684875838
C43	9.8121564767	6.4337541422	-1.7724737684
C44	9.4032879471	6.9464768815	-0.5381153010
C45	9.1034706980	8.3017642382	-0.4077135683
C46	9.2000620904	9.1562481933	-1.5183615755
C47	9.6106633451	8.6380070908	-2.7551161185
C48	9.9164310209	7.2807206279	-2.8768014941
H49	10.0490327602	5.3787906036	-1.8718118604
H50	9.3197892211	6.2906441680	0.3234486941
H51	8.7891472990	8.6966244975	0.5554852474
H52	9.6929933175	9.2884523360	-3.6202938161
H53	10.2337337532	6.8870258185	-3.8380102683
C54	10.3949379529	13.1507708274	-5.0222757831
C55	9.0594504138	12.7492284540	-5.0041916066
C56	8.5436809434	12.0748054973	-3.8967151855
C57	9.3694783381	11.8004882499	-2.7963491346
C58	10.7129006065	12.2108733322	-2.8177136514
C59	11.2215450159	12.8785435830	-3.9300082201
H60	10.7911234767	13.6796123937	-5.8840751242
H61	8.4141235847	12.9628108821	-5.8510748597
H62	7.5018656145	11.7702007465	-3.8891058711
H63	11.3582400211	12.0074312908	-1.9665689194
H64	12.2606116867	13.1940183620	-3.9409892645
C65	11.5378261274	16.1170613312	5.1784778122
H66	11.1467188154	17.0597682829	4.7841341217
H67	11.0138441597	15.9131490586	6.1177386954
H68	12.6092327147	16.1989301324	5.3568382343

Table S5. Absolute energies and positional coordinates for **A3**.

Gas phase:
SCFE: -1903.25533874023 a.u.
ZPE: 330.065 kcal/mol
G_{STP}: -1902.808021 a.u.

Dichloromethane:
SCFE: -1903.31076447770 a.u.

G_{STP}: -1902.863447 a.u.

Nitromethane:
SCFE: -1903.31707108853 a.u.
G_{STP}: -1902.869753 a.u.

C1	11.3938371205	15.1972088823	3.8328096604
O2	12.2824044936	14.7087291703	3.1667923694
C3	11.4599547572	12.5108952508	2.3938149937
C4	10.2081530236	13.0709993568	2.1115999930
C5	9.5308450334	14.0651772074	2.7018316838
H6	12.2516834094	12.6204809349	1.6527981015
C7	8.1289178375	14.5095470778	2.4182032213
H8	7.6297284300	13.8067575221	1.7487044618
H9	7.5612914473	14.5761617327	3.3526810345
H10	8.1198963828	15.5048804888	1.9588692356
C11	11.7313526877	11.6476924605	3.5002562250
C12	13.1587866907	11.6863853360	4.1105285441
C13	12.8013996164	10.4849407485	3.3474848253
H14	10.9128957211	11.4515831238	4.1845552514
H15	13.8315900772	12.4199304023	3.6799998772
H16	13.1722800997	11.6440459482	5.1951179431
H17	12.4743519519	9.6278799653	3.9330320651
C18	14.4492755346	9.4254488871	-0.4823000703
C19	13.2420562346	8.8702471332	-0.0494166427
C20	12.7188542666	9.2233266682	1.1919224578
C21	13.3896910931	10.1399948566	2.0174436259
C22	14.6035921662	10.6831818429	1.5787645575
C23	15.1289877961	10.3281060598	0.3347171608
H24	14.8617140822	9.1471232179	-1.4477260325
H25	12.7091731949	8.1612027321	-0.6764747406
H26	11.7815748138	8.7855384110	1.5265513958
H27	15.1567783380	11.3682714351	2.2146897974
H28	16.0750884569	10.7516194226	0.0108704864
O29	10.0677016350	14.8879210742	3.7012186719
Au30	9.4817083847	12.0490614633	0.3910363661
P31	8.5891364828	11.0322067394	-1.5660711352
C32	3.9696727514	10.7144310109	-1.4137715158
C33	4.6209616705	11.8404288172	-0.9043034488
C34	6.0120048717	11.9215812810	-0.9433095810
C35	6.7660889255	10.8767702141	-1.5010467590
C36	6.1072705955	9.7480223758	-2.0118194841
C37	4.7143853054	9.6715680167	-1.9660275702
H38	2.8864053578	10.6490335171	-1.3765455414
H39	4.0455627137	12.6530575151	-0.4709770212
H40	6.5128383338	12.7995574907	-0.5432906801
H41	6.6763193047	8.9286257464	-2.4390232623
H42	4.2129413141	8.7929533680	-2.3608295413
C43	10.0990667106	6.6948981349	-2.1515334009
C44	9.6388907645	7.1270213770	-0.9038270450

C45	9.2113847304	8.4427665646	-0.7350645933
C46	9.2269402338	9.3338026214	-1.8210952770
C47	9.6912969650	8.8975151815	-3.0694368095
C48	10.1280910897	7.5804925269	-3.2290882577
H49	10.4335151473	5.6695832593	-2.2815514679
H50	9.6136231452	6.4385761423	-0.0640278122
H51	8.8559987648	8.7758878450	0.2371336301
H52	9.7107078143	9.5777503886	-3.9147773712
H53	10.4864177571	7.2473148155	-4.1987209863
C54	9.7046592959	13.4100898488	-5.3796401195
C55	8.4480350921	12.8103056647	-5.2856513485
C56	8.0906564291	12.1000252465	-4.1386566931
C57	8.9960428254	11.9879982114	-3.0733371302
C58	10.2557975215	12.6003976472	-3.1684543798
C59	10.6077999271	13.3035396811	-4.3197520168
H60	9.9774378718	13.9637009135	-6.2730099112
H61	7.7410654825	12.8956530215	-6.1051689714
H62	7.1101405621	11.6394813289	-4.0743483695
H63	10.9589048806	12.5293950855	-2.3426621745
H64	11.5838599247	13.7740491803	-4.3861025001
C65	11.5795084421	16.2402495166	4.8993254848
H66	10.9055085775	16.0602086044	5.7399690322
H67	12.6190898175	16.2459392474	5.2268658372
H68	11.3338443038	17.2245096109	4.4841282823

Table S6. Absolute energies and positional coordinates for **A3*trans***.

Gas phase:
SCFE: -1903.25670156081 a.u.
ZPE: 330.017 kcal/mol
G_{STP}: -1902.809704 a.u.

Dichloromethane:
SCFE: -1903.31335376907 a.u.
G_{STP}: -1902.866357 a.u.

Nitromethane:
SCFE: -1903.32012549938 a.u.
G_{STP}: -1902.873129 a.u.

C1	1.7345556704	5.2963522591	0.5934062952
O2	1.1478188912	4.7898984864	1.5231825288
C3	-0.2833428143	3.0184641952	0.5185387029
C4	0.7960789516	2.5840430912	-0.2660740312
C5	1.7561135950	3.3150290674	-0.8630223894
H6	-0.3783759674	2.6072294613	1.5245241494
C7	2.7873547375	2.8366085283	-1.8377013383
H8	2.5708554520	1.8182916671	-2.1649947628
H9	2.8105719782	3.4993216000	-2.7096764595
H10	3.7872029650	2.8575589390	-1.3883378170

C11	-1.3690406535	3.8131199755	0.0513695018
C12	-2.2450705423	4.5767741086	1.0545425504
C13	-2.8517840748	3.3624588737	0.4913904588
H14	-1.3112657668	4.2018870286	-0.9598463715
H15	-1.9137409618	4.5642559807	2.0877469889
H16	-2.5838728553	5.5469884080	0.7062025030
H17	-2.8433108796	2.4870146326	1.1349062330
O18	1.9745940247	4.6711989562	-0.6076022452
Au19	0.7490280683	0.4697820316	-0.3856097770
P20	0.7987501681	-1.9001484854	-0.5531471753
C21	5.1074006440	-3.4988039574	-1.1202664467
C22	4.8568503151	-2.4129689386	-0.2774369453
C23	3.5585768427	-1.9278534776	-0.1281512289
C24	2.4949469209	-2.5341588802	-0.8164967395
C25	2.7513285846	-3.6223843431	-1.6641335287
C26	4.0547605795	-4.0990910809	-1.8128409647
H27	6.1200484677	-3.8722365291	-1.2395781502
H28	5.6732812691	-1.9405949022	0.2607724104
H29	3.3709003643	-1.0790185074	0.5248789603
H30	1.9405253933	-4.0952312079	-2.2092857759
H31	4.2458538871	-4.9404103983	-2.4724830269
C32	-1.7080864465	-3.4535339139	-4.1175250322
C33	-0.9824403068	-2.2649506407	-4.2248379535
C34	-0.2453605331	-1.7970324764	-3.1387796490
C35	-0.2208174628	-2.5230386471	-1.9373827895
C36	-0.9545366651	-3.7142047848	-1.8328796151
C37	-1.6950459111	-4.1741563394	-2.9226450542
H38	-2.2865694659	-3.8145099338	-4.9628543938
H39	-0.9953856686	-1.6993273442	-5.1517798955
H40	0.3096362927	-0.8660293606	-3.2228819509
H41	-0.9524471367	-4.2791261471	-0.9059002893
H42	-2.2625564389	-5.0960316876	-2.8354587361
C43	-0.8977880192	-3.8946478959	3.2626719844
C44	0.2638299931	-4.4050404318	2.6833001738
C45	0.7967797723	-3.8135739268	1.5364503546
C46	0.1639163005	-2.7008847607	0.9646379551
C47	-1.0010384872	-2.1862517813	1.5568415439
C48	-1.5308995733	-2.7851379818	2.6972032888
H49	-1.3078664268	-4.3569228784	4.1556659830
H50	0.7597574983	-5.2651829614	3.1231877086
H51	1.7019138927	-4.2165610812	1.0933523198
H52	-1.4930905232	-1.3196510317	1.1219997312
H53	-2.4337605553	-2.3842847146	3.1484981349
C54	2.3140958239	6.6830662087	0.5701226508
H55	1.9849995230	7.2137169068	-0.3279371680
H56	2.0067780210	7.2223242788	1.4654596627
H57	3.4065691395	6.6249841442	0.5313425309
C58	-5.8521683096	3.1465957504	-2.5714737894
C59	-5.5425108763	2.0308485536	-1.7931259033
C60	-4.5656597913	2.1205451952	-0.8037072485

C61	-3.8885930006	3.3276813785	-0.5715925876
C62	-4.2100846548	4.4446218729	-1.3584799119
C63	-5.1829707944	4.3527001308	-2.3507970850
H64	-6.6129101259	3.0796600118	-3.3434946041
H65	-6.0621701517	1.0911522390	-1.9548310385
H66	-4.3292527416	1.2488157441	-0.1982813416
H67	-3.7097367557	5.3957138227	-1.1985615968
H68	-5.4240753689	5.2259420515	-2.9497344390

Table S7. Absolute energies and positional coordinates for **Ats4**.

Gas phase:
SCFE: -1903.249364 a.u.
ZPE: 329.663 kcal/mol
G_{STP}: -1902.801501 a.u.
Imaginary frequencies: -40 cm^{-1}

Dichloromethane:
SCFE: -1903.308158 a.u.
G_{STP}: -1902.860295 a.u.

C1	0.2789586818	-0.1832312048	-0.4619410715
O2	0.4756202327	0.3299674480	0.6092629050
C3	3.8673964990	0.0311535024	-1.8876576578
C4	3.5213758602	-0.7101964618	-0.7631482378
C5	2.3825926256	-1.2980306099	-0.3687025880
H6	3.8944005802	-0.4881017114	-2.8513416378
C7	2.1735818196	-2.2535178528	0.7633404976
H8	3.1250390417	-2.6204714584	1.1533119762
H9	1.6206321597	-1.7678574630	1.5731572362
H10	1.5798604964	-3.1057197583	0.4160349481
C11	4.2475670759	1.4083927140	-1.9037260158
C12	3.8746869885	2.2190446172	-3.1769014919
C13	5.3033413791	1.9667208060	-2.9500876558
H14	4.2074642999	1.9369387998	-0.9569550720
H15	3.3555241349	1.6726571606	-3.9578392018
H16	3.4657693547	3.2034759491	-2.9719057654
H17	5.8503171700	2.7806682040	-2.4783790823
C18	7.8716535151	-0.5488608337	-5.3108857091
C19	8.2727689230	-0.0955013436	-4.0515880723
C20	7.4224237804	0.7076665962	-3.2959641448
C21	6.1564905417	1.0693970498	-3.7849847645
C22	5.7651924199	0.6145435725	-5.0509958983
C23	6.6186483440	-0.1911207490	-5.8076854936
H24	8.5359592719	-1.1699565264	-5.9044993446
H25	9.2506158134	-0.3615439976	-3.6606156641
H26	7.7439068208	1.0636430964	-2.3202333325
H27	4.8065740765	0.9101473901	-5.4678799598
H28	6.3064969349	-0.5286620306	-6.7916263390
O29	1.2246591132	-0.9823441329	-1.0894262847

Au30	5.3208430402	-0.9227177292	0.3802531009
P31	7.2327803843	-1.2143348668	1.7551182398
C32	6.8014703515	0.5774651298	5.9939892847
C33	5.6930991248	0.0276786951	5.3465491129
C34	5.8192364179	-0.4807034490	4.0546563269
C35	7.0623192425	-0.4465987472	3.4049944055
C36	8.1725193031	0.1140056287	4.0564660061
C37	8.0378523286	0.6226553280	5.3480699580
H38	6.7001771885	0.9750058557	6.9995138184
H39	4.7290945353	-0.0013251532	5.8453299640
H40	4.9526194007	-0.9021228497	3.5517069252
H41	9.1370002170	0.1549478006	3.5600652210
H42	8.8996174384	1.0546620386	5.8482017562
C43	10.8744659038	0.9116489666	-0.1507123092
C44	9.6762504150	1.6000257199	0.0654231480
C45	8.5845458202	0.9392990004	0.6234854476
C46	8.6891268358	-0.4146310931	0.9854879893
C47	9.8903415599	-1.1009323797	0.7674297477
C48	10.9778848918	-0.4349192975	0.1971129784
H49	11.7248885878	1.4266496386	-0.5876734504
H50	9.5960151606	2.6509007906	-0.1981278333
H51	7.6546422170	1.4775897911	0.7928621926
H52	9.9821924274	-2.1471739656	1.0419705898
H53	11.9079340055	-0.9713087723	0.0314226689
C54	8.3839494741	-5.6462486486	2.4163805953
C55	8.6394461636	-4.7077639491	3.4173892962
C56	8.2810221355	-3.3725772767	3.2348348027
C57	7.6624024055	-2.9681102604	2.0405746089
C58	7.3995716165	-3.9178419235	1.0405593707
C59	7.7640299655	-5.2506480084	1.2293126884
H60	8.6616571660	-6.6858989567	2.5632687258
H61	9.1150652869	-5.0142474573	4.3443137237
H62	8.4780531221	-2.6525990275	4.0223896023
H63	6.9111546641	-3.6160786282	0.1173513923
H64	7.5584068488	-5.9806145251	0.4520972182
C65	-0.9580589186	-0.0678347184	-1.3091069360
H66	-1.4324408472	-1.0500625387	-1.4080186087
H67	-1.6503562373	0.6304575342	-0.8379711642
H68	-0.7013552969	0.2736034884	-2.3167579498

Table S8. Absolute energies and positional coordinates for **A4**.

Gas phase:
SCFE: -1903.259784 a.u.
ZPE: 330.062 kcal/mol
G_{STP}: -1902.812793 a.u.

Dichloromethane:
SCFE: -1903.316418 a.u.
G_{STP}: -1902.869427 a.u.

C1	0.0000000000000	0.0000000000000	0.0000000000000
O2	0.0000000000000	0.0000000000000	1.1957427644470
C3	3.4199571848922	0.0000000000000	-2.2432524958896
C4	3.4959374886221	-0.5020779049355	-0.9489407598997
C5	2.3134170928225	-0.7834281808199	-0.2613628182233
H6	2.4757553118977	-0.0973837026901	-2.7829864144365
C7	2.2424453568056	-1.6368028873316	0.9614698149737
H8	3.1514004919522	-2.2347330472744	1.0390161057710
H9	2.1399882430752	-1.0199594885044	1.8605748643811
H10	1.3626954974331	-2.2870437778983	0.9312773666558
C11	4.4958318427963	0.5932537006609	-2.9749784823360
C12	4.1693032764638	1.6046859069221	-4.0950867836388
C13	4.6765181666590	0.2949866815240	-4.5315745933057
H14	5.4301873560233	0.7305098021477	-2.4404842177487
H15	3.1178348738908	1.8331147590677	-4.2363819529661
H16	4.8238218419708	2.4696719521532	-4.1373400084756
H17	5.7425324153949	0.2521000388954	-4.7458801721050
C18	2.4786725202204	-2.7457618277163	-6.6300414795697
C19	3.7000037044312	-3.0390532854681	-6.0179475771676
C20	4.3919827952348	-2.0439387826422	-5.3340230675700
C21	3.8755435005677	-0.7407607230434	-5.2464015278661
C22	2.6549497154367	-0.4539800665176	-5.8704325447066
C23	1.9606981759666	-1.4525859201062	-6.5561969146919
H24	1.9394855299399	-3.5192239366396	-7.1690621066381
H25	4.1136751081515	-4.0414587774825	-6.0790997944297
H26	5.3463787295521	-2.2728000976752	-4.8655146273796
H27	2.2531029704443	0.5552012389129	-5.8484678863287
H28	1.0195687731854	-1.2148087790435	-7.0434581054972
O29	1.1716214941126	-0.2550212258898	-0.7606626214609
Au30	5.3384610433437	-0.8355283294014	-0.0130105741883
P31	7.4688488098420	-1.1349904448856	1.0052809321587
C32	7.7566151275358	0.9511013362156	5.1319651686449
C33	6.6241987140592	0.2100640320664	4.7845028405994
C34	6.5456492331185	-0.4030847101912	3.5357410256664
C35	7.6076567539912	-0.2892752893330	2.6237292991095
C36	8.7419019262951	0.4567882943924	2.9759453128349
C37	8.8114025817094	1.0737650492174	4.2266021478961
H38	7.8133815144544	1.4343102121643	6.1027346136895
H39	5.7990307466303	0.1152924873218	5.4841666150743
H40	5.6574702409757	-0.9696927361373	3.2676291714880
H41	9.5675150269451	0.5597832025900	2.2789450155855
H42	9.6920780099981	1.6518637105722	4.4905885921441
C43	10.6379380036466	0.8375278585989	-1.7351103605584
C44	9.4215548946664	1.4712224713038	-1.4703394713687
C45	8.4810120069618	0.8560681020979	-0.6474996952844
C46	8.7534037801747	-0.3967708224874	-0.0719815707040
C47	9.9765281719713	-1.0256236510962	-0.3370821786649
C48	10.9124790551502	-0.4075077315301	-1.1692853579192
H49	11.3689396907989	1.3140193522222	-2.3817567298416

H50	9.2064996019189	2.4430724044857	-1.9052889386619
H51	7.5347483874767	1.3514454164445	-0.4420341999895
H52	10.1989713710248	-1.9950455470363	0.0978344793539
H53	11.8575895152428	-0.9017907068841	-1.3737582764206
C54	8.6068347077490	-5.5780505118924	1.6592448579838
C55	9.0465547538154	-4.6135535328271	2.5676071090196
C56	8.7083201092555	-3.2717177865136	2.3878231151037
C57	7.9232905599426	-2.8860854157331	1.2897320671856
C58	7.4757798103938	-3.8620639048617	0.3841011100641
C59	7.8216950834498	-5.2002104219510	0.5672145153619
H60	8.8691817086304	-6.6215785381624	1.8054096688056
H61	9.6511949978871	-4.9045673256122	3.4214775866919
H62	9.0488537593677	-2.5302188503663	3.1040460066227
H63	6.8534792024314	-3.5743003980682	-0.4596497597349
H64	7.4715878565260	-5.9487646521622	-0.1374374874017
C65	-1.1344924943571	0.3128407965869	-0.9271362292284
H66	-1.2274620728994	-0.4577020887888	-1.6970576530700
H67	-2.0546264596595	0.3905757313563	-0.3489363971324
H68	-0.9404054887175	1.2640432532418	-1.4337242243136

Table S9. Absolute energies and positional coordinates for **Ats5**.

Gas phase:
SCFE: -1903.22997745206 a.u.
ZPE: 329.254 kcal/mol
G_{STP}: -1902.780678 a.u.
Imaginary frequencies: -100 cm^{-1}

Dichloromethane:
SCFE: -1903.29367075726 a.u.
G_{STP}: -1902.844372 a.u.

Nitromethane:
SCFE: -1903.30170682964 a.u.
G_{STP}: -1902.852408 a.u.

C1	9.9657250053	16.0600829676	4.3227070289
O2	9.7773063976	16.5962173224	3.2578831370
C3	11.5513105960	14.0107131284	2.3794411846
C4	10.1652268007	13.5433045950	2.4466958675
C5	9.3491484919	13.9234960290	3.4413432882
H6	11.6845561039	15.0747875076	2.1697431151
C7	7.8993105069	13.6062712787	3.6436768711
H8	7.5354507268	12.9130560800	2.8829499487
H9	7.7317089242	13.1715125039	4.6367250022
H10	7.3013767967	14.5248565315	3.5890868989
C11	12.6775195891	13.2702061929	2.4737234663
C12	12.6900168743	11.7564633242	2.6693633797
C13	12.0981795902	11.5113957330	3.9937209185
H14	13.6465688309	13.7577048404	2.4251692341

H15	12.1767671631	11.2243613746	1.8638228748
H16	13.7361455990	11.4185673317	2.6928995921
H17	12.5726496871	12.0568873419	4.8091083623
C18	9.0683809797	8.8750394263	5.2259133368
C19	9.7301171297	9.6757846748	6.1656725159
C20	10.6996387136	10.5661115114	5.7379232704
C21	11.0324099729	10.6670620862	4.3546571944
C22	10.3337628443	9.8495710646	3.4178437481
C23	9.3706042113	8.9626326799	3.8556075812
H24	8.3030996194	8.1801402676	5.5608366953
H25	9.4823666947	9.5986643363	7.2191439940
H26	11.2232557095	11.1927805407	6.4538221060
H27	10.5364009839	9.9450466258	2.3575318047
H28	8.8332345470	8.3485493553	3.1402027503
O29	9.8447836854	14.7049581516	4.5186736034
Au30	9.4819990490	12.4795955129	0.7944770897
P31	8.6488200270	11.2394368169	-1.0781633899
C32	5.0829938100	13.3617566053	-3.1287210428
C33	6.1170698453	14.1031876329	-2.5541395030
C34	7.1770648436	13.4527505260	-1.9237972173
C35	7.2123637495	12.0501624623	-1.8706283220
C36	6.1671002725	11.3098095983	-2.4451673233
C37	5.1084706603	11.9671476258	-3.0722313070
H38	4.2554533500	13.8700054207	-3.6151213332
H39	6.0962400091	15.1883436780	-2.5902252826
H40	7.9743456491	14.0352115440	-1.4692250474
H41	6.1735794873	10.2249572456	-2.3994325924
H42	4.3023591517	11.3885860898	-3.5140612061
C43	7.0348696801	7.0968851574	0.2739384902
C44	6.6161565491	8.2745420636	0.9022981131
C45	7.1226063999	9.5066296458	0.4903432047
C46	8.0423120945	9.5784571323	-0.5706207350
C47	8.4573258361	8.3953280017	-1.1964075170
C48	7.9569294082	7.1616146368	-0.7707949467
H49	6.6386108467	6.1374518322	0.5935763722
H50	5.8873122985	8.2339768680	1.7073820552
H51	6.7915262301	10.4170027756	0.9842976802
H52	9.1652261048	8.4320623720	-2.0183122345
H53	8.2841696329	6.2515906117	-1.2653906469
C54	11.8209617007	10.4618464051	-4.3682932844
C55	10.4730678773	10.5584896136	-4.7203579837
C56	9.5061414058	10.8035079167	-3.7449091953
C57	9.8834946164	10.9532509002	-2.4011371740
C58	11.2414252469	10.8686884618	-2.0564108013
C59	12.2034823459	10.6185992967	-3.0345765447
H60	12.5705680729	10.2742437530	-5.1312629621
H61	10.1719970794	10.4473401694	-5.7579376553
H62	8.4626733745	10.8850658583	-4.0327425854
H63	11.5446153725	11.0095512019	-1.0221668066
H64	13.2518618026	10.5561127653	-2.7574148232

C65	10.3536796601	16.7444883753	5.6088531342
H66	11.2298681953	16.2627291443	6.0515775520
H67	10.5612267778	17.7956777965	5.4112580484
H68	9.5350341109	16.6624328633	6.3310492712

Table S10. Absolute energies and positional coordinates for **A5**.

Gas phase:
SCFE: -1903.31194307830 a.u.
ZPE: 331.321 kcal/mol
G_{STP}: -1902.859512 a.u.

Dichloromethane:
SCFE: -1903.36608004516 a.u.
G_{STP}: -1902.913649 a.u.

Nitromethane:
SCFE: -1903.37220293173 a.u.
G_{STP}: -1902.919772 a.u.

C1	4.3800564177	0.9347844097	2.7789910253
C2	3.2098821351	0.2730488509	2.6996143068
C3	2.4990414094	0.6426600929	1.4770601727
H4	5.0883715797	0.8352121558	3.5955637519
H5	2.8227367593	-0.4373017700	3.4192608708
C6	1.2525200294	0.1723359396	1.0860686497
O7	0.5591621177	-0.5684407331	2.0659082774
C8	-0.0453193743	-1.7479029835	1.7168387978
O9	0.1322216539	-2.2806366701	0.6430144591
C10	0.3668622314	0.7841988905	0.0311419574
H11	0.9489777600	1.3259766046	-0.7150636138
H12	-0.2263842330	0.0187711910	-0.4725151828
H13	-0.3151019773	1.4966306789	0.5108080154
C14	4.6233782525	1.8243581667	1.5944595978
H15	5.4443247510	1.4289581377	0.9796722107
H16	4.9105466896	2.8400330203	1.8857050476
C17	3.2649007482	1.8094084377	0.8218067550
H18	3.4386638837	1.6164761078	-0.2397611964
C19	1.1473932369	5.5810026674	1.0983199583
C20	1.2631632511	4.7648179490	2.2251148083
C21	1.9363919653	3.5468729989	2.1449924951
C22	2.5011811071	3.1252873229	0.9330779793
C23	2.3803458188	3.9507048979	-0.1917838773
C24	1.7098386687	5.1724353223	-0.1106250155
H25	0.6217019044	6.5289354982	1.1632530046
H26	0.8274594399	5.0768223624	3.1698938376
H27	2.0199935915	2.9245229228	3.0316465337
H28	2.8170610172	3.6388225602	-1.1385007946
H29	1.6267972851	5.8015379111	-0.9921465059
Au30	2.7493278033	-1.2867045349	-0.0441694029

P31	3.8897346835	-2.9381122374	-1.2623725533
C32	1.5593727789	-4.2040463037	-5.0410762994
C33	0.8744282422	-3.8431058138	-3.8787511086
C34	1.5807246386	-3.4424651531	-2.7457958767
C35	2.9854326823	-3.4122470762	-2.7743124886
C36	3.6710044654	-3.7704615020	-3.9448832260
C37	2.9540568352	-4.1662299854	-5.0736172513
H38	1.0055005344	-4.5107848852	-5.9233223026
H39	-0.2110033844	-3.8685239759	-3.8548911817
H40	1.0428885350	-3.1602403464	-1.8437084293
H41	4.7558125472	-3.7391932339	-3.9776018096
H42	3.4866653204	-4.4425210231	-5.9785503065
C43	4.3718603187	-6.7072365053	1.3724666316
C44	4.6357716550	-5.4389470599	1.8955698141
C45	4.4845363071	-4.3091716204	1.0964051527
C46	4.0785098036	-4.4414140754	-0.2418072171
C47	3.8104822673	-5.7157392991	-0.7623115863
C48	3.9595265353	-6.8436202720	0.0470924115
H49	4.4829020242	-7.5866708816	1.9998118462
H50	4.9523522740	-5.3306971186	2.9284996126
H51	4.6816075774	-3.3239569894	1.5113404461
H52	3.4874692225	-5.8307506264	-1.7921985995
H53	3.7488699670	-7.8279088148	-0.3606290765
C54	8.1063349006	-1.5372790929	-2.5529419641
C55	7.9421982281	-2.8089141650	-2.0047013595
C56	6.6775468890	-3.2473164243	-1.6080508978
C57	5.5660498550	-2.4046850345	-1.7585928511
C58	5.7372480726	-1.1215943825	-2.3045215898
C59	7.0013030978	-0.6956771621	-2.7049297535
H60	9.0919053856	-1.1999404072	-2.8581130161
H61	8.7985297050	-3.4651519500	-1.8820158292
H62	6.5602973169	-4.2385255411	-1.1812131457
H63	4.8820256951	-0.4597501307	-2.4180238066
H64	7.1254923712	0.2953206710	-3.1309561225
C65	-0.9268387566	-2.2657941017	2.8185135082
H66	-0.7212110551	-1.7745289240	3.7694017141
H67	-1.9716060743	-2.0812519897	2.5447369357
H68	-0.7957423870	-3.3465113208	2.9035156603

Table S11. Absolute energies and positional coordinates for **Ats6**.

Gas phase:
SCFE: -1903.218397 a.u.
ZPE: 328.627 kcal/mol
G_{STP}: -1902.773380 a.u.
Imaginary frequencies: -59 cm^{-1}

Dichloromethane:
SCFE: -1903.290575 a.u.

G_{STP}: -1902.845558 a.u.

Nitromethane:
SCFE: -1903.299390 a.u.
G_{STP}: -1902.854373 a.u.

C1	0.3297348561	20.7695193684	15.5082913526
O2	1.3990136182	20.2766387927	15.7706856350
C3	0.0824908128	17.6889469445	15.1003583183
C4	0.3128328312	18.2370800142	13.7641065223
C5	0.0522126085	19.5234846521	13.4522254654
H6	0.9479502448	17.2280749158	15.5838352539
C7	0.1826264207	20.1954145666	12.1206109171
H8	0.4043641820	19.4717675980	11.3345042870
H9	-0.7439178139	20.7245014736	11.8681849853
H10	0.9838526186	20.9456361437	12.1465122810
C11	-1.1034482009	17.6445211797	15.7341949708
C12	-1.2863759815	16.9530934990	17.0643349803
C13	-1.5437492090	15.4963961770	17.0171689386
H14	-1.9837413440	18.1031504777	15.2894160374
H15	-0.3028416468	17.0075723250	17.5831631055
H16	-1.9877111253	17.4646562683	17.7348323671
H17	-1.2749946978	15.0079659834	16.0792017202
C18	-3.0122089821	12.9216575297	19.9860478797
C19	-2.6314628216	12.4088814350	18.7373714094
C20	-2.1290208684	13.2655702351	17.7763507548
C21	-2.0063700424	14.6657048349	18.0439320989
C22	-2.3973058480	15.1606094671	19.3280215237
C23	-2.8930749004	14.2927652911	20.2794337940
H24	-3.4056430336	12.2482174585	20.7423430969
H25	-2.7293088502	11.3481789768	18.5316214550
H26	-1.8271102915	12.8873842535	16.8036005149
H27	-2.3031138821	16.2171752080	19.5522994564
H28	-3.1927063830	14.6629145084	21.2542965845
O29	-0.4208526784	20.4486788921	14.4072585382
Au30	1.1019825936	16.8898288601	12.3993694162
P31	2.0115173443	15.2975089529	10.8542821504
C32	1.9481969098	16.8701180522	6.4979442040
C33	2.2815326459	17.7136610101	7.5600057296
C34	2.2768640296	17.2272956359	8.8656711294
C35	1.9489224085	15.8854728594	9.1185828654
C36	1.6117763975	15.0435679392	8.0493703561
C37	1.6116023326	15.5388535834	6.7441693200
H38	1.9474111097	17.2515638336	5.4809916047
H39	2.5406188412	18.7514988432	7.3720306999
H40	2.5317197002	17.8882028193	9.6904449290
H41	1.3480199124	14.0064232694	8.2313817289
H42	1.3480815145	14.8819475016	5.9202339627
C43	-0.3326648156	11.2907225086	10.8295981960
C44	-1.0013023613	12.5129858845	10.9362733174

C45	-0.2807925307	13.7063980151	10.9627165750
C46	1.1207352787	13.6908154615	10.8677382728
C47	1.7867476347	12.4606662128	10.7663782631
C48	1.0602768669	11.2680127255	10.7493172790
H49	-0.8947213022	10.3615273866	10.8091065311
H50	-2.0857294097	12.5376624958	10.9975592945
H51	-0.8061729791	14.6541257393	11.0517534129
H52	2.8697262477	12.4302642741	10.6995521971
H53	1.5865280960	10.3210963404	10.6688829247
C54	6.4373883533	14.2593214472	11.7512246669
C55	5.9850450045	14.2484149408	10.4307811057
C56	4.6584580871	14.5684141290	10.1405063302
C57	3.7718268617	14.9016422585	11.1762744531
C58	4.2370542154	14.9225158420	12.5002547490
C59	5.5623974574	14.5973565839	12.7850311052
H60	7.4718551680	14.0134098470	11.9730033464
H61	6.6659912383	13.9949701874	9.6234066098
H62	4.3180184051	14.5657967287	9.1095368319
H63	3.5625302430	15.2033597243	13.3049714813
H64	5.9144941280	14.6184846605	13.8122739814
C65	-0.3811543840	21.8262790119	16.3177625053
H66	-1.4022440060	21.5069072281	16.5463787078
H67	0.1725971935	22.0136052118	17.2374036346
H68	-0.4538577877	22.7516838547	15.7380676298

Table S12. Absolute energies and positional coordinates for **$AuPPh_3^+$**.

Gas phase:
SCFE: -1171.580886 a.u.
ZPE: 166.388 kcal/mol
G_{STP}: -1171.366728 a.u.

Dichloromethane:
SCFE: -1171.651073 a.u.
G_{STP}: -1171.436915 a.u.

Au1	0.0000000000000	0.0000000000000	0.0000000000000
P2	0.0000000000000	0.0000000000000	2.3065962124770
C3	4.3448668821942	0.0000000000000	3.8233884009027
C4	3.9502424605462	0.8920682567028	2.8208179080358
C5	2.6409572535377	0.8762282108502	2.3488865677413
C6	1.7154433201475	-0.0347531048172	2.8882315245755
C7	2.1120014810498	-0.9325236555415	3.8924920661234
C8	3.4278288572476	-0.9073676370505	4.3559324961002
H9	5.3684740428932	0.0110767356769	4.1848519546734
H10	4.6644038556252	1.5946719660589	2.4030403706729
H11	2.3394925065812	1.5646266133446	1.5635208368864
H12	1.4053738246635	-1.6416348582173	4.3105037647581
H13	3.7344079833176	-1.6003186789873	5.1332762760845
C14	-2.1678342500281	-3.7493339838544	3.8544873125296

C15	-1.2209475959107	-3.8600760125453	2.8313564651235
C16	-0.5818404701715	-2.7223723606109	2.3479307372007
C17	-0.8878764677621	-1.4647467267480	2.8967307794088
C18	-1.8414306581113	-1.3531634071560	3.9215626695155
C19	-2.4754272990061	-2.5010278158422	4.3967979991043
H20	-2.6689632367289	-4.6383876640440	4.2251059015991
H21	-0.9867041356130	-4.8313333327606	2.4071434301368
H22	0.1481989025168	-2.8089855865720	1.5472843367017
H23	-2.0863647819726	-0.3854683012316	4.3461749387089
H24	-3.2117924827505	-2.4169113444834	5.1899831846116
C25	-2.1796026642520	3.7418075393346	3.8545961018248
C26	-0.9356662519897	3.3999805585620	4.3861929629734
C27	-0.2514189781678	2.2816495717385	3.9099357693293
C28	-0.8264953876110	1.5008247747704	2.8948700550469
C29	-2.0781149226745	1.8483684405290	2.3567482934285
C30	-2.7509874716894	2.9659742159865	2.8409621333649
H31	-2.7050337839475	4.6162216212203	4.2263899398173
H32	-0.4934012060899	4.0039296387269	5.1723210782782
H33	0.7158763385956	2.0215891895542	4.3265558788337
H34	-2.5200101820034	1.2502821989119	1.5639368760138
H35	-3.7167065729123	3.2359588071572	2.4253974121386

Table S13. Absolute energies and positional coordinates for **A1 - $AuPPh_3^+$**.

Gas phase:
SCFE: -731.607253 a.u.
ZPE: 163.515 kcal/mol
G_{STP}: -731.395550 a.u.

Dichloromethane:
SCFE: -731.620846 a.u.
G_{STP}: -731.409144 a.u.

C1	0.0146435160	0.1562706703	0.1438709402
O2	0.0258754104	0.0833279335	1.4959061264
C3	1.3176816398	0.1306239130	2.1855897322
C4	1.9753917118	1.4283277379	2.0107326459
C5	2.5209203990	2.5020086494	1.9054912237
H6	1.0103678078	0.0318644714	3.2311726512
C7	3.1747288447	3.7985219639	1.7529989751
H8	3.1469818746	4.1308874801	0.7091681790
H9	2.6880411528	4.5664523578	2.3645832303
H10	4.2264823326	3.7469678304	2.0565776721
C11	2.2130790292	-1.0414994642	1.8280658524
C12	1.7904758990	-2.4349243067	2.2247643232
C13	2.9587475586	-1.7919550636	2.9259887462
H14	2.7278564886	-0.9285233579	0.8817688741
H15	0.8595572468	-2.5300165570	2.7765050761
H16	1.9768309265	-3.2464586841	1.5283143727
H17	3.9424987625	-2.1414559722	2.6154014624

C18	2.8694415216	-0.6166069868	7.0783102474
C19	2.1302192557	-1.7196247538	6.6533011723
C20	2.1471035282	-2.1005930848	5.3099198515
C21	2.8991922316	-1.3851417731	4.3699200552
C22	3.6411778441	-0.2778578527	4.8115163192
C23	3.6271292463	0.1032313632	6.1517037319
H24	2.8553296368	-0.3179118877	8.1227834906
H25	1.5396130894	-2.2874401038	7.3671105500
H26	1.5760764258	-2.9668865213	4.9881784292
H27	4.2201323428	0.2930078439	4.0906025423
H28	4.2035178190	0.9663715882	6.4734675213
O29	1.0035505577	0.2289210883	-0.5507780532
C30	-1.4084821793	0.1415711530	-0.3680427006
H31	-1.3998522698	0.0966565624	-1.4568775908
H32	-1.9526486838	-0.7135923265	0.0421780558
H33	-1.9278327973	1.0476058560	-0.0404866666

Table S14. Absolute energies and positional coordinates for **A3 - $AuPPh_3^+$**.

Gas phase:
SCFE: -731.613267 a.u.
ZPE: 163.089 kcal/mol
G_{STP}: -731.403310 a.u.

Dichloromethane:
SCFE: -731.626897 a.u.
G_{STP}: -731.416940 a.u.

C1	0.0000000000000	0.0000000000000	0.0000000000000
O2	0.0000000000000	0.0000000000000	1.2055328620410
C3	3.4830505915885	0.0000000000000	1.7578742112289
C4	2.8060624386975	0.5412333239057	0.7745084603941
C5	2.1346776695184	1.1134330306686	-0.1920689089658
H6	3.2012532685249	0.2466892145521	2.7832351825897
C7	2.4692078030375	2.4188762667425	-0.8546694092924
H8	3.3968949170985	2.8269872547871	-0.4490288411712
H9	2.5836418555758	2.2857587574186	-1.9368122664155
H10	1.6648552778754	3.1473229156473	-0.6961145383784
C11	4.6144299144008	-0.9453375261954	1.5895864035989
C12	4.7765188234444	-2.1044582558597	2.5568931873158
C13	5.7675248214411	-0.9779390747356	2.6045070421399
H14	4.8954827621620	-1.1330853226065	0.5571902657656
H15	4.0429358621926	-2.1786618618820	3.3539605988673
H16	5.0945232660205	-3.0632224913354	2.1588438556448
H17	6.7307945227278	-1.1859681360715	2.1410031227556
C18	6.0843675800025	1.8488937037089	5.8495664737695
C19	6.5406027983778	2.1744147744318	4.5699793644966
C20	6.4254504421672	1.2536887294338	3.5312958222996
C21	5.8546468110879	-0.0108889262228	3.7463251936123
C22	5.4087389781363	-0.3268402143162	5.0351362546949

C23	5.5194545629060	0.5953885530526	6.0780811765295
H24	6.1709287655500	2.5667099933961	6.6603899068555
H25	6.9834088438179	3.1486928577628	4.3815958713253
H26	6.7760119971422	1.5144418347480	2.5356795531718
H27	4.9818203023073	-1.3059987200788	5.2295563291235
H28	5.1669347635595	0.3294294627351	7.0709104658667
O29	0.9916075722997	0.5275051551280	-0.7828651437918
C30	-1.0864829175563	-0.5712158534614	-0.8816780382074
H31	-0.6753526351460	-1.3637864452190	-1.5141143493781
H32	-1.8841487767183	-0.9714781759069	-0.2564307951696
H33	-1.4828565414692	0.2033973644066	-1.5445732456367

Table S15. Absolute energies and positional coordinates for **B1**.

Gas phase:
SCFE: -1827.96984604720 a.u.
ZPE: 327.615 kcal/mol
G_{STP}: -1827.522465 a.u.

Dichloromethane:
SCFE: -1828.02632138945 a.u.
G_{STP}: -1827.578941 a.u.

Nitromethane:
SCFE: -1828.03223929557 a.u.
G_{STP}: -1827.584858 a.u.

C1	7.0668226506	10.9972306748	3.8708480469
O2	7.2240737626	12.2730283478	3.3992363298
C3	8.3188242466	13.0968381129	3.8231483031
C4	9.6340920015	12.5972612343	3.3240927237
C5	10.8176216343	12.3316864874	3.1085488604
H6	6.0863544210	10.6388018755	3.5692703002
H7	8.1233328304	14.0401049619	3.3022951857
C8	12.2632430300	12.0822349468	3.0766752183
H9	12.4765156948	11.0116738462	3.0049564181
H10	12.7369072848	12.5914481023	2.2329906654
H11	12.7075138279	12.4599885076	4.0037050209
C12	8.3596473871	13.3763039142	5.3145879173
C13	7.1710414295	14.0853359031	5.9208974581
C14	8.4724094597	14.8260254869	5.8019810918
H15	8.8519157882	12.6265994557	5.9240277394
H16	6.3614179441	14.3473790509	5.2467612172
H17	6.8397429002	13.7645848536	6.9028848796
H18	9.0444779667	14.9169251290	6.7231653016
C19	9.1850137557	18.0947841383	3.0762291817
C20	7.8756106794	17.7207804084	3.3732049918
C21	7.6267751895	16.6667327283	4.2566209546
C22	8.6846959321	15.9677897578	4.8520690200
C23	9.9992792159	16.3615523240	4.5507556618

C24	10.2488368057	17.4131854530	3.6725242559
H25	9.3777125286	18.9185819042	2.3952008615
H26	7.0417640895	18.2561156509	2.9278983485
H27	6.6007926853	16.4052922657	4.4984697568
H28	10.8309921276	15.8414495025	5.0206860072
H29	11.2723631940	17.7072632162	3.4580203920
C30	7.9077860524	10.2303158591	4.5694268226
H31	7.5863917640	9.2340685778	4.8492019536
H32	8.8922342957	10.5412646588	4.8938378696
Au33	9.5528919790	11.6110699509	1.2047510373
P34	8.7613281649	10.7894317886	-0.8409819937
C35	12.0460780163	10.6567536570	-4.0876406101
C36	12.3056647025	10.1839952143	-2.7984150079
C37	11.3159172077	10.2456992551	-1.8206345486
C38	10.0533734166	10.7757656339	-2.1315597745
C39	9.7960554707	11.2511051838	-3.4252702786
C40	10.7950935609	11.1896316299	-4.3982496720
H41	12.8205966920	10.6119172141	-4.8474853434
H42	13.2798237844	9.7705723336	-2.5551203629
H43	11.5220474135	9.8773777748	-0.8185423169
H44	8.8258341788	11.6685681062	-3.6742813590
H45	10.5930382461	11.5599279965	-5.3988646089
C46	5.4167675381	13.5829678112	-2.3825190255
C47	6.5782840910	14.1140342939	-1.8155003998
C48	7.5730878756	13.2635045846	-1.3380083139
C49	7.4141292836	11.8704970917	-1.4341678088
C50	6.2455925644	11.3415494581	-2.0003923254
C51	5.2520223003	12.2007391254	-2.4719173580
H52	4.6400118832	14.2470989334	-2.7499408387
H53	6.7076688728	15.1897359080	-1.7414036901
H54	8.4727098436	13.6827535287	-0.8935107972
H55	6.1076766123	10.2676505736	-2.0733298870
H56	4.3480981406	11.7866799657	-2.9083903311
C57	6.9790725244	6.5348631605	-0.5379862072
C58	7.5628772370	6.9610811620	-1.7326814843
C59	8.1265440846	8.2336062626	-1.8245152290
C60	8.1043444365	9.0917002784	-0.7130628270
C61	7.5274238968	8.6561112571	0.4904060379
C62	6.9648586888	7.3824720054	0.5720154878
H63	6.5428253332	5.5428096922	-0.4702685857
H64	7.5831412800	6.3019936507	-2.5954296782
H65	8.5835718903	8.5532516501	-2.7559722836
H66	7.5226874507	9.3040025608	1.3634145798
H67	6.5204495900	7.0500933003	1.5054419753

Table S16. Absolute energies and positional coordinates for **Bts1**.

Gas phase:
SCFE: -1827.96441811422 a.u.
ZPE: 327.798 kcal/mol

G_{STP}: -1827.517128 a.u.
Imaginary frequencies: -171 cm^{-1}

Dichloromethane:
SCFE: -1828.01976630163 a.u.
G_{STP}: -1827.572477 a.u.

Nitromethane:
SCFE: -1828.02581125372 a.u.
G_{STP}: -1827.578522 a.u.

C1	11.2521835208	14.9327421733	4.1189164941
O2	12.0406129469	14.4210219651	3.1712756833
C3	11.8420454289	13.0693172505	2.6839252741
C4	10.3647295267	12.8472295996	2.4218340984
C5	9.3323887387	13.2489439213	3.0345057082
H6	11.2644851217	16.0200659101	4.0830312076
H7	12.3889185562	13.0857754555	1.7403743916
C8	7.9370265878	13.4964883180	3.3942639544
H9	7.2906547735	12.9886974910	2.6680582174
H10	7.7018467221	13.1040391746	4.3881604187
H11	7.7037895502	14.5650180358	3.3695023124
C12	12.4282316737	11.9966295244	3.5820525112
C13	13.8880489494	12.0816104994	3.9578437399
C14	13.4488702060	10.9905838533	3.0237678885
H15	11.7496996262	11.5912191353	4.3265396252
H16	14.4509099520	12.9173694463	3.5539289123
H17	14.1693588103	11.8138336168	4.9711907337
H18	13.3481778127	10.0071225984	3.4775382853
C19	14.5154725289	10.6643104226	-1.1461401478
C20	15.0373739580	11.7093210957	-0.3840831044
C21	14.7018860744	11.8342964282	0.9661339569
C22	13.8306225780	10.9220098189	1.5767541092
C23	13.3079752113	9.8770832327	0.7953512135
C24	13.6489289370	9.7445274630	-0.5495889553
H25	14.7927613449	10.5571408743	-2.1910382606
H26	15.7242427673	12.4212067292	-0.8332239236
H27	15.1506480290	12.6340021500	1.5477158321
H28	12.6419139277	9.1503325122	1.2545947983
H29	13.2438246191	8.9196147016	-1.1291370613
C30	10.4645672735	14.2684859849	4.9978361320
H31	9.8497989292	14.8496604388	5.6761170117
H32	10.5510963471	13.2088325483	5.1935566767
Au33	9.7278451745	11.7648643942	0.6729268160
P34	9.0126826402	10.7535185033	-1.3346496622
C35	4.3910787722	10.7882203489	-1.6381058337
C36	5.0867393742	11.9267303504	-1.2214897584
C37	6.4758200962	11.8984126779	-1.1177046353
C38	7.1851015408	10.7292828267	-1.4412913505
C39	6.4838571205	9.5894481938	-1.8589118785

C40	5.0908865603	9.6235825979	-1.9539990591
H41	3.3081818630	10.8104363745	-1.7148607327
H42	4.5464838778	12.8367382236	-0.9772179402
H43	7.0115086643	12.7885323972	-0.7962124918
H44	7.0176702548	8.6789814284	-2.1110181626
H45	4.5548493200	8.7364167866	-2.2779791003
C46	10.3659291238	6.3580225015	-1.8000162148
C47	9.9618251866	6.8454426104	-0.5544653574
C48	9.5754528391	8.1774962512	-0.4183516760
C49	9.5808916135	9.0289265106	-1.5349183311
C50	9.9890298432	8.5367854985	-2.7831039017
C51	10.3811930056	7.2034380081	-2.9102584534
H52	10.6718107427	5.3210952786	-1.9035200121
H53	9.9521391876	6.1893240018	0.3107998923
H54	9.2691427600	8.5562876850	0.5535787177
H55	10.0043421407	9.1885926848	-3.6508649701
H56	10.6978885820	6.8267469444	-3.8784077582
C57	10.6054493535	13.0889680250	-4.9927461366
C58	9.2936663301	12.6138858913	-5.0008471531
C59	8.7929898795	11.9163144327	-3.9009457101
C60	9.6111359842	11.6934770308	-2.7835182651
C61	10.9300724839	12.1758669527	-2.7775343661
C62	11.4230999919	12.8674710973	-3.8820191820
H63	10.9898341674	13.6343413404	-5.8497380104
H64	8.6561166338	12.7868989843	-5.8628129192
H65	7.7701163481	11.5532858621	-3.9132378037
H66	11.5724180122	12.0053165108	-1.9171366148
H67	12.4436220914	13.2385691704	-3.8733227564

Table S17. Absolute energies and positional coordinates for **B3**.

Gas phase:
SCFE: -1828.00924997341 a.u.
ZPE: 327.330 kcal/mol
G_{STP}: -1827.563110 a.u.

Dichloromethane:
SCFE: -1828.06503606221 a.u.
G_{STP}: -1827.618896 a.u.

Nitromethane:
SCFE: -1828.07153580274 a.u.
G_{STP}: -1827.625396 a.u.

C1	10.5913398113	14.6812722494	4.9429243603
O2	11.4259525485	14.8003579857	4.0720831908
C3	11.2836644546	12.6754084471	2.4359734220
C4	9.9599401614	12.6127390747	2.7945381120
C5	9.0379810558	12.9467837813	3.6932950470
H6	10.6826441706	15.2605832714	5.8865837283

H7	11.5854274393	13.4431815641	1.7225645954
C8	7.5940576577	12.5124528795	3.6147762252
H9	7.4264358850	11.7983745555	2.8050424862
H10	7.2799017355	12.0425752275	4.5547841637
H11	6.9376749795	13.3776259152	3.4563394728
C12	12.3278290334	11.7827773951	2.9107531360
C13	13.6964268760	12.4359096683	3.1912178102
C14	13.5860020142	11.5013484655	2.0462539950
H15	12.0113768053	10.9907866963	3.5815823166
H16	13.7640660734	13.5028204133	3.0061711557
H17	14.1922389381	12.1072817654	4.0989143816
H18	13.9613279986	10.4956914411	2.2255929984
C19	13.9084833939	12.6336451032	-2.0998800179
C20	13.2551375428	11.4534938129	-1.7321868691
C21	13.1367155708	11.1091797990	-0.3861655154
C22	13.6763340724	11.9344915444	0.6147062238
C23	14.3314048467	13.1123580084	0.2342400927
C24	14.4435960266	13.4617601641	-1.1139467562
H25	14.0108808035	12.8973709513	-3.1487549719
H26	12.8470148668	10.7952867606	-2.4938592859
H27	12.6392813087	10.1830531386	-0.1105389260
H28	14.7813823273	13.7506371978	0.9891006858
H29	14.9639586444	14.3740906659	-1.3911619576
C30	9.3575668420	13.8001799889	4.9088636872
H31	8.5078264635	14.4707278778	5.1130009655
H32	9.4038759002	13.1635440307	5.8077831127
Au33	9.5289811040	11.5885487945	0.8860148196
P34	8.7143554605	10.7108711382	-1.1707030341
C35	8.6881574392	14.0871163443	-4.3328516592
C36	9.7863170649	13.9142550835	-3.4866686122
C37	9.7798925274	12.9009221449	-2.5306595663
C38	8.6717229217	12.0435745176	-2.4227132753
C39	7.5712881547	12.2195138745	-3.2739909759
C40	7.5841912107	13.2412677049	-4.2251051502
H41	8.6924640325	14.8825359675	-5.0724158409
H42	10.6462257843	14.5728099495	-3.5666769203
H43	10.6386195016	12.7725638350	-1.8768382810
H44	6.7072335707	11.5674242320	-3.1960840101
H45	6.7286156542	13.3753511072	-4.8803606049
C46	4.3686163335	9.1669335345	-0.7890268426
C47	4.7717680178	10.3275798470	-0.1235566055
C48	6.0878456600	10.7730732283	-0.2305434458
C49	7.0122183196	10.0632907615	-1.0147870185
C50	6.6039373580	8.8983554687	-1.6805266957
C51	5.2852043284	8.4553890554	-1.5640706325
H52	3.3442131168	8.8181214944	-0.7011414566
H53	4.0620297019	10.8841221533	0.4812057517
H54	6.3948079939	11.6784984410	0.2874020072
H55	7.3082484219	8.3374582819	-2.2864654719
H56	4.9763451307	7.5520358895	-2.0814658734

C57	11.2508986523	7.2402564972	-2.8940084814
C58	10.7730027400	8.2368748422	-3.7464465150
C59	10.0188426476	9.2965628838	-3.2378999342
C60	9.7392693612	9.3632975025	-1.8642476364
C61	10.2271633145	8.3615526583	-1.0090450641
C62	10.9754177948	7.3039618870	-1.5252170042
H63	11.8386182889	6.4191802699	-3.2932423479
H64	10.9853160733	8.1929247069	-4.8107229565
H65	9.6524158167	10.0668941805	-3.9091211416
H66	10.0209443026	8.4078800080	0.0576418361
H67	11.3474607262	6.5317160018	-0.8585724579

Table S18. Absolute energies and positional coordinates for **B3***trans*.

Gas phase:
SCFE: -1828.00922919473 a.u.
ZPE: 327.262 kcal/mol
G_{STP}: -1827.564281 a.u.

Dichloromethane:
SCFE: -1828.06713255665 a.u.
G_{STP}: -1827.622184 a.u.

Nitromethane:
SCFE: -1828.07396749401 a.u.
G_{STP}: -1827.629019 a.u.

C1	-4.1824925589	6.2285287007	6.9976461800
O2	-4.1158402960	6.0653771709	5.8000393333
C3	-7.1221690756	4.4981762867	6.7990694181
C4	-5.8844905879	4.3486984071	7.2428921093
H5	-3.5115905606	6.9438954227	7.5189453631
C6	-5.0762936647	3.0790934129	7.1375418376
H7	-5.6244232017	2.2793255121	6.6349664206
H8	-4.1565795909	3.2752869230	6.5746785862
H9	-4.7833340915	2.7238704459	8.1326156230
C10	-5.1827619294	5.5226559616	7.9056474207
H11	-5.8954630438	6.2864435963	8.2438282748
H12	-4.6503553080	5.1896067421	8.8076558407
Au13	-8.3817552631	2.7499783596	6.0221170261
P14	-9.3731181445	0.7233204191	5.3068817892
C15	-8.6146871185	-2.7634072181	8.2502703836
C16	-8.7738952224	-1.4593708642	8.7259173486
C17	-8.9815918333	-0.4096512655	7.8325844488
C18	-9.0401432265	-0.6609489517	6.4520318645
C19	-8.8770016658	-1.9715915859	5.9775726207
C20	-8.6647380666	-3.0159976389	6.8783220680
H21	-8.4473577467	-3.5791586562	8.9470496801
H22	-8.7314553717	-1.2584093235	9.7921904667
H23	-9.0995494774	0.6035432236	8.2087140518

H24	-8.9113361540	-2.1785677942	4.9125855058
H25	-8.5365448887	-4.0276580150	6.5050983694
C26	-7.8334837997	-0.6073133137	1.1507323861
C27	-6.9634326447	-0.0145720336	2.0697611874
C28	-7.4372317660	0.4027645367	3.3127934615
C29	-8.7890402592	0.2231666533	3.6491725208
C30	-9.6605962949	-0.3685206723	2.7218391036
C31	-9.1792569920	-0.7812396099	1.4782877994
H32	-7.4638718199	-0.9279944743	0.1813895630
H33	-5.9169742098	0.1272030067	1.8168314058
H34	-6.7559362735	0.8689292933	4.0203907777
H35	-10.7099795463	-0.5032972483	2.9645871131
H36	-9.8594363681	-1.2378678252	0.7653619119
C37	-13.9472855740	1.3140690536	4.9483899696
C38	-13.4512125589	0.2181724201	5.6549446774
C39	-12.0735329568	0.0238048757	5.7787460703
C40	-11.1852094237	0.9350417319	5.1912321188
C41	-11.6869411632	2.0422632226	4.4847488338
C42	-13.0627212959	2.2242744356	4.3618533556
H43	-15.0191538281	1.4610425993	4.8554472619
H44	-14.1349274286	-0.4906940245	6.1124796753
H45	-11.6976300635	-0.8326967440	6.3291381629
H46	-11.0068475825	2.7538512102	4.0220121066
H47	-13.4444029136	3.0782012246	3.8101520510
C48	-8.2675777049	5.1686210431	6.4885176776
H49	-9.0682070162	5.1680427317	7.2329932490
C50	-8.5352277220	5.9590770661	5.2716442022
C51	-7.4396986122	6.7690640405	4.5791285119
C52	-7.9645931299	5.5584051728	3.8891389017
H53	-9.5361325828	6.3778156243	5.2342323196
H54	-7.7232746481	7.7525329396	4.2175457984
H55	-6.4375071200	6.7005654336	4.9892132928
H56	-7.3076225492	4.6918071218	3.9444019358
C57	-10.5505668627	5.4564189640	0.4487381516
C58	-10.4432568178	6.6320859191	1.1940861309
C59	-9.6023283895	6.6882261082	2.3046849235
C60	-8.8556840500	5.5666365912	2.6927538651
C61	-8.9691000595	4.3909302691	1.9344664736
C62	-9.8081955390	4.3355848027	0.8215118608
H63	-11.2020573991	5.4178011342	-0.4193776752
H64	-11.0114437440	7.5119000348	0.9060689579
H65	-9.5285797225	7.6173879473	2.8631616778
H66	-8.3864142389	3.5157032040	2.2139778612
H67	-9.8761259240	3.4183171057	0.2432485222

Table S19. Absolute energies and positional coordinates for **Bts4**.

Gas phase:
SCFE: -1828.000389 a.u.
ZPE: 326.744 kcal/mol

G_{STP}: -1827.552886 a.u.
Imaginary frequencies: -54 cm^{-1}

Dichloromethane:
SCFE: -1828.059882 a.u.
G_{STP}: -1827.612380 a.u.

C1	0.0000000000000	0.0000000000000	0.0000000000000
O2	0.0000000000000	0.0000000000000	1.2075371811640
C3	3.9254855000828	0.0000000000000	-0.2024968171219
C4	3.1739577688206	-1.0544065592166	0.2902816733327
C5	1.9869492965607	-1.5927224607296	-0.0760127646431
H6	-0.7521075640435	0.5770208145406	-0.5794580525692
H7	4.1841079064247	-0.0144729374953	-1.2670869121354
C8	1.4748012557091	-2.9295569789308	0.3780109392049
H9	2.2464772545663	-3.5264035173824	0.8674273917752
H10	0.6492868126615	-2.7894758451856	1.0872498882858
H11	1.0752596823716	-3.4920047545027	-0.4745960906042
C12	4.4910764177352	1.0881968600406	0.5456312703781
C13	4.5953510545974	2.4571285878494	-0.1689799535561
C14	5.8564285074183	1.7389067082767	0.0867554036084
H15	4.2913235997712	1.1090358250023	1.6120796673932
H16	4.2097142397835	2.5110210995961	-1.1818551522541
H17	4.3359752582965	3.3090242405249	0.4516184716924
H18	6.4159503845420	2.0636352155466	0.9617004477626
C19	8.3173529867075	-0.1343546580743	-2.9087171256711
C20	8.5110079417635	-0.4025182560286	-1.5510335766846
C21	7.7064924290462	0.2133857697532	-0.5953371008722
C22	6.6947353107385	1.1092230887278	-0.9790042941445
C23	6.5192393528791	1.3824984760914	-2.3419391110133
C24	7.3238417445873	0.7617149604066	-3.3000216328660
H25	8.9459826613489	-0.6118083186980	-3.6545057361740
H26	9.2963945382855	-1.0850222449879	-1.2384815326732
H27	7.8672591532366	0.0108734765301	0.4612815502204
H28	5.7723759454470	2.1023643175778	-2.6640736123916
H29	7.1798318154982	0.9896005464914	-4.3520728402496
C30	1.0039578547270	-0.7620736307482	-0.8672437348201
H31	1.5148741787696	-0.0131852927289	-1.4899386423534
H32	0.4196953762179	-1.3918116524312	-1.5538925232029
Au33	4.3849357667594	-2.0115955766814	1.7994853643909
P34	5.4874354206805	-3.3430654074733	3.4256084848944
C35	8.8366723969195	-5.9233346124642	1.5456724303375
C36	8.5749645022131	-4.6420928131692	1.0564834673837
C37	7.5577082343246	-3.8733256695385	1.6194645163451
C38	6.7985345079372	-4.3816831859988	2.6851660458915
C39	7.0629689537165	-5.6717830627800	3.1714891110206
C40	8.0806982133871	-6.4362490894354	2.6007847964890
H41	9.6238725823521	-6.5244268464142	1.1000984694142
H42	9.1564592283287	-4.2460704813396	0.2292061210916
H43	7.3456570579178	-2.8831427988368	1.2240708037670

H44	6.4723687226188	-6.0824974622144	3.9845116787510
H45	8.2782348552819	-7.4352021843233	2.9782191696599
C46	2.4449856743421	-6.3201847218312	5.2540906457825
C47	2.5684318845877	-6.1835161888711	3.8684279658848
C48	3.4817809659273	-5.2775423023492	3.3345921135229
C49	4.2893292451751	-4.5025206560248	4.1844929040800
C50	4.1651622667553	-4.6447647965633	5.5731429369459
C51	3.2429770322586	-5.5515123928865	6.1013221478505
H52	1.7289421232262	-7.0227629136000	5.6695323000326
H53	1.9514164409480	-6.7815494836867	3.2042631273759
H54	3.5768732240959	-5.1815147702470	2.2557379986140
H55	4.7810735256494	-4.0529003492112	6.2424020615940
H56	3.1515877418124	-5.6550979574080	7.1784543057747
C57	7.2872891423185	-0.9234489643534	6.9362400914260
C58	7.9837062604650	-2.0215469066421	6.4290527621107
C59	7.4641922798400	-2.7520184855846	5.3591328266743
C60	6.2373462795671	-2.3811234554346	4.7885773122835
C61	5.5449427374693	-1.2682752762741	5.2939949315311
C62	6.0673648947632	-0.5482100094085	6.3672959160430
H63	7.6950949097101	-0.3591630603672	7.7694896250323
H64	8.9343173681945	-2.3135944442784	6.8654980575012
H65	8.0131085818818	-3.6053966005814	4.9736131324679
H66	4.5966746669206	-0.9704701314490	4.8530622781456
H67	5.5239667730026	0.3071953565749	6.7574498837195

Table S20. Absolute energies and positional coordinates for **B4**.

Gas phase:
SCFE: -1828.003239 a.u.
ZPE: 327.071 kcal/mol
G_{STP}: -1827.556732 a.u.

Dichloromethane:
SCFE: -1828.062668 a.u.
G_{STP}: -1827.616160 a.u.

C1	0.0000000000000	0.0000000000000	0.0000000000000
O2	0.0000000000000	0.0000000000000	1.2061268337290
C3	3.7664464980192	0.0000000000000	-0.2126178913200
C4	3.1496490329062	-1.0920785209697	0.3954284040431
C5	1.9534301492612	-1.6136396588058	-0.0733324053737
H6	-0.7398553996419	0.5867095350856	-0.5838267617139
H7	3.5771267365912	0.1809603753607	-1.2742825160135
C8	1.4377669225089	-2.9543724030248	0.3403986176707
H9	2.2160160930617	-3.5773865426902	0.7852227155588
H10	0.6400218036578	-2.8185380212743	1.0853949066195
H11	0.9847582726437	-3.4746823196438	-0.5118768019081
C12	4.7403162129284	0.8615731691046	0.3759114880874
C13	4.9157640810525	2.2957551110673	-0.1710698403220
C14	5.9828596725370	1.3460313132556	-0.5136464571422

H15	4.9661667068431	0.7053121265830	1.4255163205238
H16	4.2187012449752	2.6060030539919	-0.9424717784334
H17	5.0979818320112	3.0455917716499	0.5926187448016
H18	6.8691267068168	1.3742774549155	0.1168643082879
C19	6.6489660989392	-0.3411173797312	-4.4104142610360
C20	7.1956872164092	-0.9388546724015	-3.2711585572180
C21	6.9779145863480	-0.3758308854254	-2.0168824320049
C22	6.2064542663492	0.7896979299855	-1.8792700301970
C23	5.6740524654876	1.3889615310914	-3.0277407225960
C24	5.8942201254793	0.8251472951312	-4.2859670841372
H25	6.8195996464155	-0.7783066158153	-5.3899449532032
H26	7.7923744261043	-1.8418497904735	-3.3627819077712
H27	7.4039650415043	-0.8441830922229	-1.1326701822632
H28	5.1061317475342	2.3116005857061	-2.9497429881986
H29	5.4825904637221	1.3040523100011	-5.1696073653419
C30	0.9927441680483	-0.7823768686061	-0.8766447787680
H31	1.5045796756476	-0.0315976756229	-1.4952684271683
H32	0.3931793104490	-1.4021279759093	-1.5574542188999
Au33	4.0105942735854	-1.8755628478161	2.1544389927777
P34	4.7406056369161	-2.5948108790224	4.3019174396081
C35	9.3040672479378	-3.0121537620340	4.9780485237898
C36	8.8084117066346	-2.0837188678084	4.0602459683387
C37	7.4348497448277	-1.9754802979907	3.8458320233901
C38	6.5420774970676	-2.7919218776415	4.5570182842738
C39	7.0463465041517	-3.7296615448187	5.4729982390839
C40	8.4218669874138	-3.8347525736469	5.6805471248746
H41	10.3740889840354	-3.0994024994235	5.1397532630043
H42	9.4925100587373	-1.4481449924535	3.5058827936934
H43	7.0526954790487	-1.2591175892947	3.1230496154709
H44	6.3692927048378	-4.3803075237694	6.0181474026132
H45	8.8030032749504	-4.5639119928528	6.3893762773122
C46	2.9479865767626	-6.7341516389239	5.3232766849859
C47	3.5504964416219	-6.5029755848973	4.0841240541390
C48	4.0683851429981	-5.2451426567147	3.7851032848950
C49	3.9970689650801	-4.2096403745920	4.7319747937859
C50	3.3882353368027	-4.4438674309198	5.9723339634282
C51	2.8651057350077	-5.7056554847879	6.2622889194022
H52	2.5400704558725	-7.7137276724156	5.5543112252758
H53	3.6130839828668	-7.3014050669086	3.3506768435512
H54	4.5327724378438	-5.0672547940836	2.8179358126202
H55	3.3203238547631	-3.6480622772453	6.7077304460401
H56	2.3931039945006	-5.8823354663166	7.2243063701164
C57	3.1669874567412	0.5134509339950	7.3592358984852
C58	4.4337041543136	-0.0424295156151	7.5410334424244
C59	4.9273777283300	-0.9852519110270	6.6372115816485
C60	4.1495099336843	-1.3773088946689	5.5379621258622
C61	2.8758436931172	-0.8095938109659	5.3565577627460
C62	2.3876100691169	0.1259975139824	6.2667088004757
H63	2.7895546724841	1.2484933744086	8.0634810652628
H64	5.0441768047946	0.2577144265842	8.3875071210784

H65	5.9159890295544	-1.4077433705466	6.7871648565278
H66	2.2678172198761	-1.0959600378959	4.5018437688555
H67	1.4020001884608	0.5566080262693	6.1173789415290

Table S21. Absolute energies and positional coordinates for **Bts5**.

Gas phase:
SCFE: -1827.97892136479 a.u.
ZPE: 326.503 kcal/mol
G_{STP}: -1827.533699 a.u.
Imaginary frequencies: -76 cm^{-1}

Dichloromethane:
SCFE: -1828.04282606346 a.u.
G_{STP}: -1827.597604 a.u.

Nitromethane:
SCFE: -1828.05103804151 a.u.
G_{STP}: -1827.605816 a.u.

C1	8.9532028717	16.0395697791	3.8452830736
O2	8.5266658111	16.4887505342	2.8079742275
C3	11.1224470606	13.0835278946	2.3461436345
C4	9.6765846124	13.0419759077	2.1785911693
C5	8.7786279690	13.6379190690	2.9984847316
H6	11.6526273367	13.8556855208	1.7814698555
C7	7.2866026546	13.5146828874	2.8242066420
H8	7.0275320445	12.8134043287	2.0274014239
H9	6.8128064081	13.1784008614	3.7573823835
H10	6.8512051373	14.4904352610	2.5785557615
C11	11.9013127777	12.1945631063	3.0062354914
C12	11.3647858612	10.9409943810	3.6862123429
C13	10.5370355614	11.3872167970	4.8191386036
H14	12.9766890005	12.3438026606	3.0370323716
H15	10.8297810975	10.2898879653	2.9889805072
H16	12.2162013544	10.3749621215	4.0917091625
H17	11.0462331077	12.0628963840	5.5058306356
C18	6.7292118110	10.1781080473	6.1400009489
C19	7.4824010304	11.0863320004	6.8932785783
C20	8.7146145647	11.5092632151	6.4215116374
C21	9.2245699217	11.0226354883	5.1816803486
C22	8.4307490524	10.1117845069	4.4265021168
C23	7.2062643784	9.6935106335	4.9095345536
H24	5.7607579828	9.8491092187	6.5058076662
H25	7.1033558950	11.4550555137	7.8408298909
H26	9.3158800939	12.2011935869	7.0048333607
H27	8.7824008292	9.7647944324	3.4619383415
H28	6.6030820675	8.9975886321	4.3353817447
Au29	9.1921885499	12.0998658459	0.3778207537
P30	8.6747527004	11.0016170029	-1.6967713149

C31	4.4983689560	12.1558136259	-3.3428583176
C32	5.3037231617	13.1036290936	-2.7067835729
C33	6.5481066967	12.7362350389	-2.1962754646
C34	7.0042900621	11.4143274718	-2.3281902299
C35	6.1894493047	10.4646158675	-2.9633613302
C36	4.9417883551	10.8380464094	-3.4664571751
H37	3.5278403948	12.4425686738	-3.7369493076
H38	4.9617605951	14.1293187844	-2.6040464554
H39	7.1661498648	13.4776307460	-1.6958292080
H40	6.5239284948	9.4368532725	-3.0654828760
H41	4.3172688150	10.0965374216	-3.9563912328
C42	8.6935656360	6.3877377771	-1.1968606299
C43	8.1072383535	7.2108329499	-0.2317231891
C44	8.1226955997	8.5952128255	-0.3895663778
C45	8.7130098998	9.1735383758	-1.5252635954
C46	9.2998671698	8.3435801109	-2.4904045562
C47	9.2901542022	6.9569324263	-2.3220080656
H48	8.6861754045	5.3092173745	-1.0705843823
H49	7.6392126062	6.7715332844	0.6448430780
H50	7.6676554475	9.2331957464	0.3645556114
H51	9.7664754853	8.7751374385	-3.3703587655
H52	9.7494841005	6.3227081743	-3.0746229102
C53	11.7104183080	11.9887605554	-5.0589899763
C54	10.3620205030	11.8201686133	-5.3784685132
C55	9.4317764116	11.5343044819	-4.3777796370
C56	9.8492598877	11.4142395729	-3.0430777520
C57	11.2050815939	11.5965280616	-2.7266863968
C58	12.1296996840	11.8767471853	-3.7314073290
H59	12.4305834489	12.2135660953	-5.8400574905
H60	10.0299610744	11.9133313449	-6.4084053050
H61	8.3850405616	11.4097337421	-4.6372010990
H62	11.5352344647	11.5211381463	-1.6937164719
H63	13.1762792086	12.0154765181	-3.4766634350
H64	9.2157234725	16.7094662531	4.6946849248
C65	9.1967372436	14.5600608090	4.1257246588
H66	10.2640838980	14.4651794897	4.3658272116
H67	8.6525511797	14.3276540262	5.0567106791

Table S22. Absolute energies and positional coordinates for **B5**.

Gas phase:
SCFE: -1828.06470862792 a.u.
ZPE: 328.813 kcal/mol
G_{STP}: -1827.614581 a.u.

Dichloromethane:
SCFE: -1828.12111494222 a.u.
G_{STP}: -1827.670987 a.u.

Nitromethane:
SCFE: -1828.12769417307 a.u.
G_{STP}: -1827.677566 a.u.

C1	1.7416772306	-1.4155645166	3.4731494421
C2	0.9539243098	-1.0966235213	2.4288376190
C3	1.5815251344	-0.0632479997	1.5972874966
H4	1.4944873540	-2.1596502250	4.2241379276
H5	-0.0043218269	-1.5556112636	2.2148964158
C6	1.0812429896	0.5129177416	0.4281577766
C7	-0.3609154911	0.2899375540	-0.0054862578
H8	-0.8684881012	-0.4872729899	0.5799609000
H9	-0.9347784050	1.2099828862	0.1875017241
C10	-0.5712163206	-0.0803045146	-1.4610930245
O11	0.3012980932	-0.4868876314	-2.2014768665
H12	-1.6135439200	0.0200744648	-1.8250069751
C13	1.7197706417	1.7451689031	-0.1887974921
H14	2.7903858643	1.8143716655	0.0068951494
H15	1.5693800073	1.7600265218	-1.2710623020
H16	1.2524860840	2.6458102397	0.2301957870
C17	3.0311577363	-0.6492117816	3.4773324878
H18	3.8733367503	-1.3183237989	3.2495871574
H19	3.2461456141	-0.1939401686	4.4494646435
C20	2.8305894021	0.4250647045	2.3637056369
H21	3.7027294988	0.4532636067	1.7063049544
C22	2.3516805307	4.4042206381	4.0236741119
C23	1.3383887605	3.4576938965	4.1835500085
C24	1.4788267197	2.1794768483	3.6440425554
C25	2.6352057560	1.8284752259	2.9318890234
C26	3.6452233477	2.7856661487	2.7777692730
C27	3.5072121342	4.0640349050	3.3210461551
H28	2.2409068093	5.3989375546	4.4447944128
H29	0.4359798023	3.7137048227	4.7313866650
H30	0.6836746200	1.4526041473	3.7852764705
H31	4.5512379188	2.5294738270	2.2323795842
H32	4.3029325964	4.7922862220	3.1934098402
Au33	2.3964320578	-1.3003786232	-0.3691479927
P34	3.7914242688	-2.9358238134	-1.3250749625
C35	1.8678980729	-7.1455452955	-1.3443207556
C36	1.6401383259	-6.2691697375	-0.2801605010
C37	2.2054389586	-4.9949632309	-0.2896974260
C38	3.0142622604	-4.5906148048	-1.3643368760
C39	3.2363027929	-5.4715280356	-2.4336511113
C40	2.6626436995	-6.7439290323	-2.4188752854
H41	1.4225070968	-8.1357704301	-1.3378914877
H42	1.0174547631	-6.5763735987	0.5548307277
H43	2.0197124827	-4.3142707775	0.5375620795
H44	3.8507635306	-5.1682686261	-3.2754172374
H45	2.8371055055	-7.4195511540	-3.2509092904
C46	7.7203507043	-3.2358450882	1.1134420721

C47	7.2187665373	-1.9918960087	0.7184668858
C48	6.0311243964	-1.9149648599	-0.0055444632
C49	5.3365865497	-3.0866228326	-0.3519679948
C50	5.8429373116	-4.3316612850	0.0449890049
C51	7.0311538589	-4.4006923226	0.7767808910
H52	8.6433886091	-3.2942093665	1.6823685252
H53	7.7526681821	-1.0819998247	0.9768812476
H54	5.6454984374	-0.9440898459	-0.3079716171
H55	5.3166622687	-5.2449944995	-0.2132548016
H56	7.4163682906	-5.3692044004	1.0816887409
C57	4.9813033087	-1.8969003981	-5.6706974780
C58	5.8965979384	-2.5449166102	-4.8389270887
C59	5.5540563194	-2.8503299358	-3.5214590561
C60	4.2843322110	-2.5062956306	-3.0298492377
C61	3.3678593150	-1.8476443598	-3.8660320359
C62	3.7194523325	-1.5496917560	-5.1825131187
H63	5.2530646761	-1.6575938614	-6.6944399306
H64	6.8811260962	-2.8104416186	-5.2125659659
H65	6.2753799994	-3.3467022612	-2.8795159710
H66	2.3875541746	-1.5639300975	-3.4918447331
H67	3.0078520825	-1.0395231560	-5.8247898296

Table S23. Absolute energies and positional coordinates for **Bts6**.

Gas phase:
SCFE: -1827.96552955780 a.u.
ZPE: 325.707 kcal/mol
G_{STP}: -1827.523503 a.u.
Imaginary frequencies: -125 cm^{-1}

Dichloromethane:
SCFE: -1828.03720047530 a.u.
G_{STP}: -1827.595174 a.u.

Nitromethane:
SCFE: -1828.04564961212 a.u.
G_{STP}: -1827.603623 a.u.

C1	10.0259208282	14.5049240375	5.2055625345
O2	10.1650951468	15.1702949964	4.2054082022
C3	11.5809921372	12.5999466753	2.8421003741
C4	10.1517863908	12.2652286181	2.8481184392
C5	9.3530516488	12.3814926798	3.9363246725
H6	10.0704719302	14.9779265364	6.2127640791
H7	11.8598761972	13.4652473924	2.2324634216
C8	7.8872915230	12.0287406607	3.9340488865
H9	7.5752815856	11.5932936402	2.9818237159
H10	7.6503505553	11.3160955085	4.7355002709
H11	7.2731558016	12.9213397338	4.1198739269
C12	12.5639655057	11.8898307900	3.4247313984

C13	14.0303279175	12.1768038761	3.1871759015
C14	14.6181688725	11.5111000116	2.0011654197
H15	12.3287596002	11.0176647732	4.0323593118
H16	14.1081075911	13.2578453994	2.9349520934
H17	14.6604615369	12.0480369915	4.0756544530
H18	13.8916378680	11.1672282901	1.2634965672
C19	18.6221979491	10.7883277840	0.9688157289
C20	17.5898893305	10.3994659777	0.1014958751
C21	16.2776124109	10.6665241099	0.4437170913
C22	15.9667320306	11.3238860764	1.6768798186
C23	17.0395369995	11.7147155955	2.5386937201
C24	18.3453838761	11.4464428292	2.1820267093
H25	19.6537505142	10.5788674114	0.7001906412
H26	17.8232109390	9.8946973524	-0.8300201287
H27	15.4651242239	10.3721093726	-0.2148220159
H28	16.8241506701	12.2236593773	3.4717264346
H29	19.1611690957	11.7397757949	2.8342820322
C30	9.8399954185	12.9911979655	5.2370888973
H31	9.1700365534	12.7514298385	6.0719550444
H32	10.8270391682	12.6004718771	5.5253378052
Au33	9.5184115325	11.6210424506	0.9781275021
P34	8.8205417876	10.8017332181	-1.1743753255
C35	9.4857338018	13.7912626410	-4.6534947495
C36	10.3073405957	13.8207380556	-3.5254408188
C37	10.0904623567	12.9237818975	-2.4798579146
C38	9.0532454167	11.9822876240	-2.5588343292
C39	8.2241265121	11.9650554694	-3.6916170692
C40	8.4437797191	12.8653915784	-4.7335208246
H41	9.6502181109	14.4948930800	-5.4645384217
H42	11.1092769421	14.5501847093	-3.4545456515
H43	10.7173281850	12.9607355754	-1.5924631152
H44	7.4034077254	11.2573618908	-3.7567930746
H45	7.7963230285	12.8476003778	-5.6054629242
C46	4.2825966428	9.8771207823	-1.2472555965
C47	4.7733794107	11.0152397137	-0.6033180830
C48	6.1441670192	11.2647065353	-0.5739209415
C49	7.0368877780	10.3803166081	-1.2009467623
C50	6.5395068890	9.2366539985	-1.8414395613
C51	5.1658250465	8.9888833883	-1.8615666418
H52	3.2142902105	9.6815958725	-1.2659974747
H53	4.0890960481	11.7065847620	-0.1201069504
H54	6.5226194410	12.1483803088	-0.0660657262
H55	7.2187038979	8.5390314367	-2.3213297461
H56	4.7869929530	8.1006760188	-2.3589961956
C57	10.9805154062	6.8470115498	-2.2939710167
C58	10.7577441603	7.8048818347	-3.2841833174
C59	10.1201022474	9.0076945339	-2.9710913471
C60	9.7020492715	9.2621764980	-1.6569371488
C61	9.9421958275	8.2998729155	-0.6616335042

C62	10.5709456081	7.0975532568	-0.9816769217
H63	11.4696910167	5.9096706252	-2.5426941243
H64	11.0748491186	7.6164718885	-4.3060682267
H65	9.9478526417	9.7424596815	-3.7514228984
H66	9.6318522098	8.4921447720	0.3624864408
H67	10.7402272066	6.3557685013	-0.2062634386