Cycloisomerization of Dienes with Carbophilic Lewis Acids: Mimicking Terpene Biosynthesis with Pt(II) Catalysts

Supporting Information

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1. Experimental Procedures

1.1 Synthesis of Dienes

General. Synthetic procedures were performed under dinitrogen using standard Schlenk techniques. CH_2Cl_2 and THF were sparged with dry argon and passed through a column of activated alumina. DMSO was distilled from CaH_2. Acetone was distilled from $CaSO_4$. Cycloisomerization substrates **2** and **4** were

commercially available. Hept-6-enyl-triphenylphosphonium bromide,[1] and [(PPP)PtMe]BF_4,[2] were prepared according to literature procedures. All other chemicals were used as received. NMR spectra were recorded on either a Bruker 500 MHz DRX, Bruker 400 MHz DRX, or Bruker 300 MHz AMX spectrometer; chemical shifts are given in ppm and are referenced to residual solvent resonances (^{1}H) or an external 85% H_3PO_4 standard (^{31}P). GC was performed on a HP 6890 with a DB-1 column. Low-resolution EI mass spectrometry was performed on an Agilent 5973 GC/MS with an HP-5 column. Low-resolution ESI mass spectrometry was performed on a Quattro II triple quadrapole mass spectrometer. Low-resolution CI was performed in the labs of Gary Glish at the University of North Carolina.

2-Allyl-2-(3-methyl-but-2-enyl)-malonic acid dimethyl ester (6): To a suspension of 137 mg NaH (5.71 mmol) in 9.0 mL THF at 0°C was added 480 mg dimethyl allylmalonate (2.79 mmol) in 3.5 mL THF *via* cannula. The mixture was raised to 23°C, stirred for 1 hour, then cooled again to 0°C, at which point 1.71 g 4-bromo-2-methyl-2-butene (11.5 mmol) was added dropwise. The reaction was warmed to 23°C and stirred overnight. The cloudy white suspension was quenched with 2 N HCl at 0°C, extracted with ether, and the combined organic extracts washed with 2 N HCl, saturated $NaHCO_3$, and brine. The solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography in 16:1 hexanes/EtOAc to yield 670 mg (60%) of colorless oil.; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.63 (m, 1H), 5.07 (m, 2H), 4.92 (t, 1H, J = 7.6 Hz), 3.69 (s, 6H), 2.60 (t, 4H, J = 6.8 Hz), 1.68 (s, 3H), 1.59 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 171.5, 135.7, 132.6, 118.9, 117.4, 57.9, 52.3, 36.9, 31.1, 26.0, 17.9; LR ESI m/z = 241.1 (calculated 241.14 for $C_{13}H_{21}O_4^+$).

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[1] Douat, C.; Heitz, A.; Paris, M.; Martinez, J.; Fehrentz, J.-A. *J. Pep. Sci.* **2002**, *8*, 601.

[2] Annibale, G.; Bergamini, P.; Bertolasi, V.; Cattabriga, M.; Ferretti, V. *Inorg. Chem. Comm.* **2000**, *3*, 303.

8-Methyl-nona-1,7-diene (8): To a solution of 5.88 g (12.7 mmol) hept-6-enyl-triphenylphosphonium bromide in 32 mL DMSO at 0°C was added 5.30 mL n-butyllithium (12.7 mmol, 2.4 M in hexanes). After 15 min, the red solution was raised to 23°C and stirred for an additional 30 min before 1.1 mL (15 mmol) acetone was added. The solution was stirred for 16 h then cooled to 0°C and quenched with 40 mL sat. NH_4Cl, then extracted with n-pentane and the combined organic fractions washed with brine. The combined organic fractions were dried over MgSO4 and filtered through a plug of silica, eluting with n-pentane. The solvent was removed by fractional distillation and the product was dried at 0°C/150 mmHg to yield 1.31 g (74%) of a colorless liquid; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.13 (m, 1H), 4.96 (m, 2H), 2.02 (m, 4H), 1.70 (s, 3H), 1.61 (s, 3H), 1.38 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.1, 131.2, 124.7, 114.1, 33.8, 29.4, 28.6, 27.9, 25.7, 17.6; LR CI *m/z* = 138.1 (calculated 138.14 from $C_{10}H_{18}^+$).

***Rac*-benzyl linalool (10):** To a suspension of 66.1 mg NaH (2.62 mmol) in 5.0 mL THF was added 0.440 mL *rac*-linalool (2.48 mmol) dropwise at 23°C. The solution was stirred for 1 h then cooled to 0°C and transferred *via* cannula to a solution of 0.355 ml BnBr (2.99 mmol) and 45.8 mg nBu_4NI (0.147 mmol) in 2.0 mL THF at 0°C. After addition, the temperature was raised to 23°C. After 4 hours, the solution was quenched with H_2O and extracted 3x with diethyl ether. The combined organic extracts were washed once with saturated $NaHCO_3$ and twice with brine. The extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography in 50:1 hexanes/EtOAc to yield 0.473 g (78%) of a colorless oil; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.24 (m, 1H), 5.88 (dd, 1H, *J* = 18.0, 10.8 Hz), 5.21 (m, 2H), 5.13 (tt, 1H, *J* = 7.0, 1.2 Hz), 4.39 (s, 2H), 2.07 (q, 2H, *J* = 8.0 Hz), 1.68 (s, 3H), 1.65 (m, 2H), 1.61 (s, 3H), 1.34 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.2, 139.8, 131.4, 128.2, 127.2, 127.0, 124.5, 114.7, 64.4, 39.9, 25.7, 22.4, 22.3, 17.6 (not all carbons were observed); LR EI *m/z* = 244.2 (calculated 244.18 from $C_{17}H_{24}O^+$).

1.2 Catalytic Cycloisomerizations

General: Reactions were set up in a dinitrogen-filled drybox then sealed in a Kontes tube to prevent loss of volatile cycloisomerization products. CD_3NO_2,[3] and Ph_2NMe were distilled from CaH_2 and freeze-pump-thaw degassed. Acetone was distilled from $CaSO_4$ and freeze-pump-thaw degassed. $HNTf_2$ was sublimed under vacuum. $AgNO_3$-impregnated silica gel was prepared according to a literature procedure.[4,5]

Typical Procedure: To a 0.25 M solution of $[(PPP)PtMe]BF_4$ (typically 80 μmol) in CD_3NO_2 was added 1.5 equiv. acetone and 0.95 equiv. $HNTf_2$. After 15 min at 23°C, 0.2 equiv. Ph_2NMe and 20 equiv. diene was added. This resulted in the formation of a hydrocarbon/$MeNO_2$ biphase. The tube was then sealed and heated to 40°C, stirring until the reaction was complete by GC. The reaction was quenched by addition of commercial CH_3NO_2, (containing traces of propionitrile) and the $MeNO_2$/hydrocarbon biphase was then extracted with three small portions of n-pentane. The combined extracts were loaded directly onto a Ag^+-silica column for chromatography.

1-Isopropyl-bicyclo[3.1.0]hexane (3): Prepared from **2** as above with the crude material purified by flash chromatography on Ag^+-impregnated silica in n-pentane. The solvent was removed by fractional distillation to yield 114 mg (58%) of a 48% w/w solution in n-pentane. An analytically pure sample could be obtained by drying at 0°C/150 mmHg but with a substantial reduction in yield; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 1.64 (m, 2H), 1.55 (m, 3H), 1.38 (h, 1H, J = 6.8 Hz), 1.15 (m, 1H), 0.95 (m, 1H), 0.91 (d, 3H, J = 6.8 Hz), 0.85

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[3] Commercial CH_3NO_2 contains traces of propionitrile that poison the Pt catalyst and must be removed, see: Olah, G. A.; Ramaiah, P.; Rao, C. B.; Sandford, G.; Golam, R.; Trivedi, N. J.; Olah, J. A. *J. Am. Chem. Soc*. **1993**, *115*, 7246. Commercial CD_3NO_2 (Cambridge), however, is free of nitriles and its use was cost effective because of the small solvent volume of a typical cycloisomerization reaction (c.a. 0.30 mL CD_3NO_2).

[4] Tong-Shuang, L.; Ji-Tai, L.; Hui-Zhang, L. *J. Chrom. A*. **1995**, *715*, 372.

[5] Ag^+ silica was developed for separation of alkenes however it proved effective for purification of fully-saturated cyclopropane products because the impurities present (presumably alkene-containing) were strongly adsorbed to the column.

(d, 3H, *J* = 6.8 Hz), 0.24 (t, 1H, *J* = 4.0 Hz), 0.17 (dd, 1H, *J* = 8.0, 4.8 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 34.0, 32.7, 27.8, 27.6, 22.4, 21.1, 20.2, 20.0, 11.2; LR CI *m/z* = 124.1 (calculated 124.13 for $C_9H_{16}^+$).

***Cis*-1-isopropyl-4-methyl-bicyclo[3.1.0]hexane (*cis*-thujane, 5):** Prepared from **4** as above with the crude material purified by flash chromatography on Ag^+-impregnated silica in n-pentane. The solvent was removed by fractional distillation to yield 137 mg (64%) of a 56% w/w solution in n-pentane, d.r. = 46:1 (GC). An analytically pure sample could be obtained by drying at 0°C/150 mmHg but with a substantial reduction in yield; ^{1}H NMR: (600 MHz, $CDCl_3$) δ 1.99 (sep., 1H, *J* = 7.2 Hz), 1.66 (m, 1H), 1.45 (dd, 1H, *J* = 12.0, 8.4 Hz), 1.33 (m, 2H), 1.16 (dd, 1H, *J* = 13.2, 8.4 Hz), 0.94 (d, 3H, *J* = 6.6 Hz), 0.91 (d, 3H, *J* = 7.2 Hz), 0.89 (d, 3H, *J* = 6.6 Hz), 0.75 (dd, 1H, *J* = 8.4, 3.6 Hz), 0.26 (t, 1H, *J* = 4.2 Hz), 0.21 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 34.4, 33.7, 32.7, 29.9, 28.6, 24.6, 21.4, 20.4, 19.8, 12.9; LR CI *m/z* = 138.1 (calculated 138.14 for $C_{10}H_{18}^+$).

1-Isopropyl-bicyclo[3.1.0]hexane-3,3-dicarboxylic acid dimethyl ester (7): Prepared from **6** as above with the crude material purified by flash chromatography on Ag^+-impregnated silica in 33:1 hexanes/EtOAc to yield 105 mg (58%) of a colorless oil; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.69 (s, 3H), 2.47 (m, 3H), 2.33 (dd, 1H, *J* = 13.6, 1.6 Hz), 1.42 (h, 1H, *J* = 6.8 Hz), 1.12 (p, 1H, *J* = 4.4 Hz), 0.95 (d, 3H, *J* = 6.8 Hz), 0.85 (d, 3H, *J* = 6.8 Hz), 0.36 (t, 1H, *J* = 6.8 Hz), 0.08 (dd, 1H, *J* = 5.6, 4.0 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 173.5, 172.7, 59.7, 52.9, 52.8, 37.1, 36.6, 34.5, 32.5, 22.3, 20.0, 19.9, 14.2; LR ESI *m/z* = 241.0 (calculated 241.14 for $C_{13}H_{21}O_4^+$).

1-Isopropyl-bicyclo[4.1.0]heptane (9): Prepared from **8** as above with the crude material purified by flash chromatography on Ag^+-impregnated silica in n-pentane. Solvent removed by fractional distillation to yield 131 mg (66%) of a 45% w/w solution in n-pentane. An analytically pure sample could be obtained by drying at 0°C/100 mmHg but with a substantial reduction in yield; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 1.81 (m, 1H), 1.63 (m, 2H), 1.42 (m, 1H), 1.18 (m, 4H), 0.89 (d, 3H, *J* = 6.0 Hz), 0.88 (d, 3H, *J* = 6.0 Hz), 0.80 (m, 1H), 0.62 (m, 1H), 0.29 (dd, 1H, *J* = 9.0, 4.2 Hz); 0.12 (t, 1H, *J* = 4.8 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 38.6, 24.4, 24.2, 23.9, 22.4, 21.7, 19.0, 18.4, 18.1, 17.5; LR CI *m/z* = 138.1 (calculated 138.14 for $C_{10}H_{18}^+$).

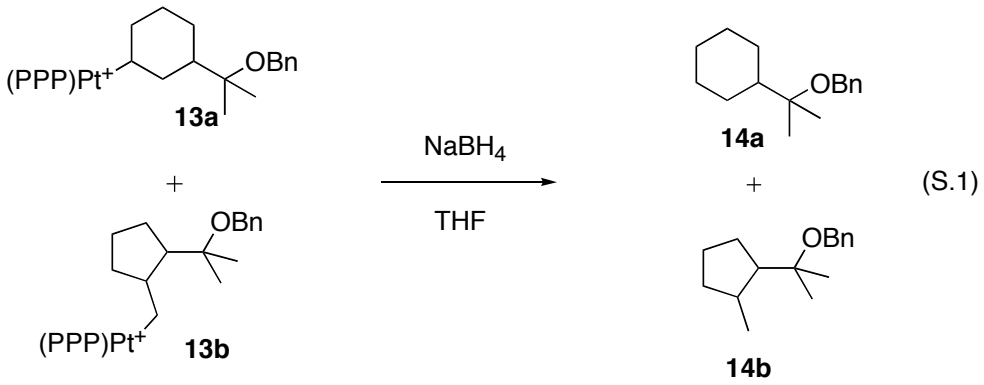
***Cis*-4-(1-benzyloxy-1-methyl-ethyl)-1-methyl-bicyclo[3.1.0]hexane (11):** Prepared from **10** as above with the crude material purified by sequential flash chromatography; first on Ag^+-impregnated silica in 99:1 hexanes:EtOAc then on normal silica in 99:1 hexanes:EtOAc to yield 5 mg (5%) of a colorless oil; ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.36 (m, 4H), 7.28 (m, 1H), 4.50 (d, 1H, J = 11.0 Hz), 4.45 (d, 1H, J = 11.0 Hz), 2.29 (d, 1H, J = 8.50 Hz), 1.68 (m, 3H), 1.40 (m, 1H), 1.26 (s, 3H), 1.22 (s, 3H), 1.22 (s, 3H), 1.05 (dd, 1H, J = 8.5, 4.0 Hz), 0.41 (dd, 1H, J = 7.0, 3.5 Hz), 0.27 (t, 1H, J = 4.0 Hz); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 140.0, 128.2, 127.4, 127.0, 77.7, 63.3, 50.3, 33.7, 26.9, 25.5, 24.7, 23.6, 23.3, 21.3, 15.5; LR EI m/z = 244.2 (calculated 244.18 for $C_{17}H_{25}O^+$).

1.3 Cation Trapping Experiments

Thermodynamic products, [(PPP)Pt(*endo*-alkyl)]NTf_2 (13a): To a solution of 212 mg [(PPP)PtMe]BF_4 (0.255 mmol) in 0.64 mL CD_3NO_2 at 23°C was added 28 μL acetone (0.38 mmol) and 75.1 mg $HNTf_2$ (0.267 mmol), which was accompanied by vigorous release of methane. After 15 min, 933 mg Ph_2NMe (5.09 mmol), 633 mg 7-methyl-1,6-octadiene **2** (5.10 mmol), and 1.65 g benzyl alcohol (15.2 mmol) was added. The reaction was monitored by ^{31}P NMR until equilibrium had been reached (24 hours), then diluted with 25 mL CH_2Cl_2 and washed three times with distilled water. The organic fraction was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was dissolved in CH_2Cl_2 and layered with n-pentane to produce a yellow oil. This process was repeated five times until no benzyl alcohol remained by ^{1}H NMR. The oil was dried under vacuum, at which point it solidified to yield 294 mg (93%) of an off-white foam. The product was a mixture of **13a** (85%), **13b** (4%), and two other uncharacterized Pt-alkyls in 7% and 4% respectively. Attempts to purify by recrystallization were unsuccessful; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70-7.25 (m, 25H), 4.21 (s, 2H), 3.30 (m, 2H), 2.79 (m, 2H), 2.29 (m, 4H), 1.50-0.49 (m, 10H), 0.75 (s, 3H), 0.69 (s, 3H); ^{31}P NMR: (162 MHz, $CDCl_3$) δ 89.3 (s, 1P, $J_{P\text{-}Pt}$ = 1280 Hz), 41.9 (s, 2P, $J_{P\text{-}Pt}$ = 3050 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -79.1 (s, 6F).

Kinetic products, [(PPP)Pt(*endo*-alkyl)]NTf_2 (9a) and [(PPP)Pt(*exo*-alkyl)]NTf_2 (13b): To a solution of 305 mg [(PPP)PtMe]BF_4 (0.366 mmol) in 0.90 mL CD_3NO_2 at 23°C was added 40 μL acetone (0.54 mmol) and 106 mg $HNTf_2$ (0.376 mmol), which was accompanied by vigorous release of methane. After 15 min, 1.34 g Ph_2NMe (7.31 mmol), 0.910 g 7-methyl-1,6-octadiene **2** (7.33 mmol), and 2.30 mL benzyl alcohol (22.2 mmol) was added. The reaction was stirred for 30 min, then diluted with 25 mL CH_2Cl_2 and washed three times with distilled water. The organic fraction was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was dissolved in CH_2Cl_2 and layered with n-pentane to produce a yellow oil. This process was repeated five times until no benzyl alcohol remained by ^{1}H NMR. The oil was dried under vacuum, at which point it solidified to yield 385 mg (93%) of an off-white foam. The product was a 1.29:1 mixture of **13a**:**13b** (88%), and two other uncharacterized Pt-alkyls in 7% and 5% respectively. Attempts to purify by recrystallization were unsuccessful; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70-7.25 (m, 25H major, 25H minor), 4.19 (s, 2H major), 4.17 (s, 2H minor), 3.30 (m, 2H major, 2H minor), 2.79 (m, 2H major, 2H minor), 2.29 (m, 4H major, 4H minor), 1.50-0.49 (m, 10H major, 10H minor), 0.75 (s, 3H major), 0.74 (s, 3H minor), 0.70 (s, 2H minor), 0.69 (s, 3H major); ^{31}P NMR: (162 MHz, $CDCl_3$) δ 91.9 (s, 1P minor, $J_{P\text{-}Pt}$ = 1380 Hz) 89.3 (s, 1P major, $J_{P\text{-}Pt}$ = 1280 Hz), 41.8 (s, 2P major, 2P minor, $J_{P\text{-}Pt}$ = 3050 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -79.1 (s, 6F major, 6F minor).

13a and **13b** could not be fully characterized because they were obtained as intractable oils (meaningful ^{13}C NMR and elemental analysis were impossible). To determine the identity of the organic fragment, the kinetic product mixture **13a**:**13b** was treated with $NaBH_4$ to reductively cleave the Pt-alkyl and the organic products were separated and isolated (eq. S.1). **14a** and **14b** were characterized by 2D NMR (HMQC, HMBC) and the data is summarized in Tables S.2 and S.3 respectively.



(1-Cyclohexyl-1-methyl-ethoxymethyl)-benzene (14a): To 375 mg of a 1.29:1 mixture of **13a**/**13b** (0.302 mmol) in 20 mL THF was added 117 mg $NaBH_4$ (3.09 mmol) at 0°C. The reaction was warmed to ambient temperature and stirred for 2 hours. It was then quenched by the slow addition of water, diluted with brine, and extracted three times with diethyl ether. The combined organic extracts were washed two times with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. To remove the Pt-containing byproducts, the crude material was dissolved in CH_2Cl_2 and c.a. 1 g silica gel was added. The slurry was dried under vacuum and loaded atop a short column of silica, eluting with 4:1 n-pentane/CH_2Cl_2. The eluent was concentrated *in vacuo* to give a mixture of **14a** and **14b** as a colorless oil which was separated by flash chromatography in 9:1 n-pentane/CH_2Cl_2 to yield 14 mg **14a** (35%) as a colorless oil; ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.23 (m, 1H), 4.42 (s, 2H), 1.80 (m, 4H), 1.67 (m, 1H), 1.55 (m, 1H), 1.22 (m, 2H), 1.18 (s, 6H), 1.13 (m, 1H), 1.04 (m, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 140.2, 128.2, 127.2, 126.9, 77.4, 63.0, 46.4, 27.6, 26.9, 26.7, 22.9; LR EI *m*/*z* = 232.2 (calculated 232.18 for $C_{16}H_{24}O^+$).

[1-Methyl-1-(2-methyl-cyclopentyl)-ethoxymethyl]-benzene (14b): The **14b** isomer was isolated from the above column (14 mg (46%)) as a colorless oil; ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.23 (m, 1H), 4.46 (s, 2H), 1.98 (m, 1H), 1.74 (m, 3H), 1.55 (m, 3H), 1.25 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H), 1.05 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 140.4, 128.1, 126.9, 126.8, 77.7, 63.2, 55.8, 36.2, 35.0, 29.1, 25.3, 23.6, 23.3, 22.9; LR EI *m*/*z* = 232.2 (calculated 232.18 for $C_{16}H_{24}O^+$).

Lewis acid activation of 13a: To a solution of 5.6 mg **13a** (4.5 μmol) in 0.60 mL CD_3NO_2 was added 1.8 mg *tris*-(pentafluorophenyl)boron (3.5 μmol) at 23°C. The reaction was sealed in an NMR tube under dinitrogen. Catalyst speciation was monitored by ^{31}P NMR and conversion of **2** to **3** was monitored by ^{1}H NMR.

2. 2D NMR Experiments

2.1 Structural and Stereochemical Determination of 11

The structure of the cyclopropane-containing product of the reaction of O-Bn linalool with $(PPP)Pt^{+2}$ was determined by 2D $^{1}H/^{13}C$ correlation experiments (HMQC, HMBC). These data are summarized in Table S.1. Once the identity of the product was known, relative stereochemistry was detemined by a 2D NOESY experiment. Monte Carlo geometry minimization of the 10 lowest energy conformers (MacSpartan 04, AM1 semi-empirical) at 3-21G* led to the structure shown in Figure S.1. This *trans* relative stereochemistry is consistent with the strong nOe observed between the cyclopropane methylene and the adjacent methine. The *cis* stereoisomer is significantly higher in energy and is spatially inconsistent with the observed nOe.

Figure S.1. Monte Carlo minimization (3-21G*) of *trans*-**11**.

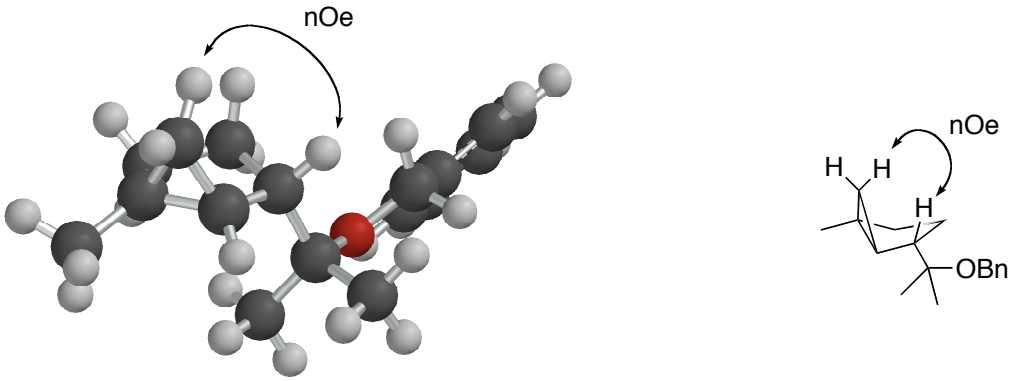


Table S.1 2D NMR data for **11**.

^{1}H NMR Chemical Shifts (ppm) for 11

Position	δ ^{1}H
H1	0.27
H2	0.41
H3	1.05
H4	1.22
H5	1.22
H6	1.26
H7[a]	1.4
H8[a]	1.59
H9[a]	1.64
H10[a]	1.7
H11	2.29
H12[a]	4.45
H13[a]	4.5

[a]diastereotopic methylene

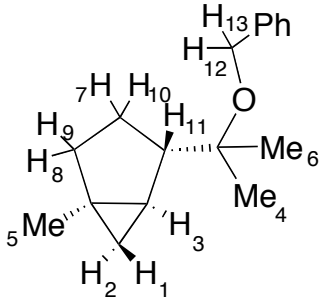
^{1}H/^{1}H Correlations (COSY) for 11

Proton	Cross Peaks
H1	H2, H3[a]
H2	H1, H3
H3	H1[a], H2
H4	--
H5	--
H6	--
H7	H8, H9, H10
H8	H7, H8, H10
H9	H7, H8, H10
H10	H7, H8, H9
H11	H7
H12	H13
H13	H12

[a]weak

Selected NOESY Correlations for 11

Proton	Cross Peaks
H1	H2, H7, **H11**
H2	H1, H3, H5
H3	H4, H5, H6, H11
H11	**H1**, H3, H4, H6, H7, H12, H13
H12	H4, H6, H11, H13
H13	H4, H6, H11, H12



proton assignments for **11**

selected ^{13}C NMR shifts (ppm) for **11**

Position	δ ^{13}C (APT)
C1	15.5 (up)
C2	21.3 (down)
C3	23.3 (down)
C4	23.6 (down)
C5	24.7 (up)
C6	25.5 (up)
C7	26.9 (down)
C8	33.8 (up)
C9	50.3 (down)
C10	63.3 (up)
C11	77.7 (up)

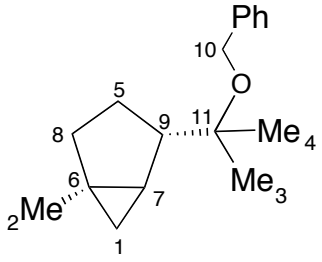
Long-range (Mainly Three-bond) $^{13}C/^{1}H$ Correlations (HMBC) for **11**

Carbon	Cross Peaks
C1	H3, H5, H8, H9, H11
C2	H1, H2, H3, H8
C3	H6, H11
C4	H4, H11
C5	H3, H8, H9, H11
C6	H1, H2, H5, H8, H9, H10, H11
C7	H1, H2, H5, H9, H10, H11
C8	H1, H2, H3, H5, H7, H10, H11
C9	H3, H4, H6, H7, H9, H10
C10	H4, H6
C11	H3, H4, H6, H7, H11, H12

One-Bond 13C/1H Correlations (HMQC) for **11**

Carbon	Cross Peak
C1[a]	H1, H2
C2	H5
C3	H4
C4	H6
C5	H7, H10
C6	none
C7	H3
C8[a]	H8, H9
C9	H11
C10	H12
C11	none

[a]diastereotopic methylene



carbon assignments for **11**

2.2 Structural Determination of 14a

The identity of **14a** was determined by $^{1}H/^{13}C$ heteronuclear correlation experiments (HMQC, HMBC) and the results are summarized in Table S.2.

Table S.2. 2D NMR data for **14a**.

^{1}H and ^{13}C NMR shifts (ppm) for **14a**

Position	δ ^{1}H	δ ^{13}C (APT)
1	1.67, 1.13[a]	26.7 (up)
2	1.80, 1.22[a]	26.9 (up)
3	1.80, 1.04[a]	27.6 (up)
4	1.55	46.4 (down)
5	--	77.4 (up)
6	1.18	22.9 (down)
7	4.42	63.0 (up)
8	--	140.2 (up)
9	7.33	127.2 (down)
10	7.33	128.2 (down)
11	7.23	126.9 (down)

[a]diastereotopic methylene

Long-range (Mainly Three-bond) $^{13}C/^{1}H$ Correlations (HMBC) for **14a**

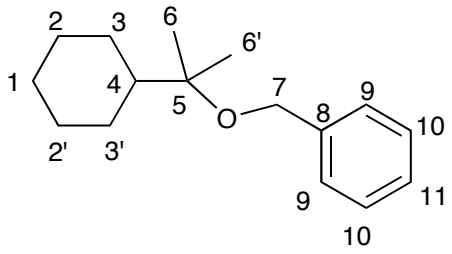
Carbon	Cross Peaks
C1	1.80, 1.22, 1.04
C2	1.80, 1.55,[a] 1.04
C3	1.80, 1.55, 1.22, 1.04[a]
C4	1.80[a], 1.18, 1.04
C5	4.42, 1.55,[a] 1.18
C6	1.55, 1.18
C7	7.33, 1.18
C8	7.33, 4.42
C9	7.33, 7.23, 4.42
C10	7.33
C11	7.33

[a]weak

One-Bond $^{13}C/^{1}H$ Correlations (HMQC) for **14a**

Carbon	Cross Peak
C1	1.67, 1.13[a]
C2	1.80, 1.22[a]
C3	1.80, 1.04[a]
C4	1.55
C5	--
C6	1.18
C7	4.42
C8	--
C9	7.33
C10	7.33
C11	7.23

[a]diastereotopic methylene



2.2 Structural Determination of 14b

The identity of **14b** was determined by $^{1}H/^{13}C$ heteronuclear correlation experiments (HMQC, HMBC) and the results are summarized in Table S.3. While a single diastereomer was obtained, the relative stereochemistry is unknown.

Table S.3. 2D NMR data for **14b**.

^{1}H and ^{13}C NMR shifts (ppm) for **14b**

Position	δ ^{1}H	δ ^{13}C (APT)
1	1.05	22.9 (up)
2	1.98	35.0 (down)
3	1.74, 1.25[a]	36.2 (up)
4	1.55[a]	25.3 (up)
5	1.74, 1.55[a]	29.1 (up)
6	1.74	55.8 (down)
7	--	77.7 (up)
8	1.23	23.3 (down)
9	1.21	23.6 (down)
10	4.46	63.2 (up)
11	--	140.4 (up)
12	7.33	126.9 (down)
13	7.33	128.1 (down)
14	7.23	126.8 (down)

[a]diastereotopic methylene

Long-range (Mainly Three-bond) $^{13}C/^{1}H$ Correlations (HMBC) for **14b**

Carbon	Cross Peaks
C1	1.98,[a] 1.74,[a] 1.25[a]
C2	1.74, 1.55,[a] 1.25, 1.05
C3	1.98, 1.74,[a] 1.55,[a] 1.05
C4	1.98,[a] 1.74, 1.55, 1.25
C5	1.74, 1.55, 1.25
C6	1.98, 1.74, 1.55,[a] 1.23, 1.21, 1.05
C7	4.46, 1.98, 1.74,[a] 1.55,[a] 1.23, 1.21
C8	1.21
C9	1.23
C10	7.33, 1.23,[a] 1.21[a]
C11	7.33, 4.46
C12	7.33, 7.23, 4.46
C13	7.33
C14	7.33

[a]weak

One-Bond $^{13}C/^{1}H$ Correlations (HMQC) for **14b**

Carbon	Cross Peak
C1	1.05
C2	1.98
C3	1.74, 1.25[a]
C4	1.55[a]
C5	1.74, 1.55[a]
C6	1.74
C7	--
C8	1.23
C9	1.21
C10	4.46
C11	--
C12	7.33
C13	7.33
C14	7.23

[a]diastereotopic methylene