Supporting Information for

Palladium-Catalyzed Ring-Expansion Reaction of (Z)-1-(1,3-Butadienyl)cyclobutanols with Aryl Iodides. Stereospecific Synthesis of (Z)-2-(3-Aryl-1-propenyl)cyclopentanones

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General. All nonaqueous reactions were carried out under a positive atmosphere of argon or nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocols. The phrase ‘residue upon workup’ refers to the residue obtained when the organic layer was separated and dried over anhydrous MgSO_4 and the solvent was evaporated under reduced pressure.

Scheme S1. Synthesis of 1,3-dienylcyclobutanols (*Z*)- and (*E*)-**1a** and (*Z*)-**1b**.

Spiro[3.5]nonan-1-one (S1a): To a stirred suspension of NaH (2.69 g, 60% of oil suspension, 67.3 mmol) in THF (100 mL) was added cyclopropyltriphenylphosphonium bromide (25.8 g, 67.3 mmol) at rt. After the mixture had been stirred for 10 h at 62 °C, a solution of cyclohexanone (6.00 g, 61.1 mmol) in THF (20 mL) was added dropwise, and the stirring was continued for 3 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O . The combined extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (99:1 v/v) as eluent to give the cyclopropylidene derivative (7.47 g, 61.1 mmol) as a colorless oil. To a stirred solution of the obtained cyclopropylidene derivative, NMO (14.3 g, 122.2 mmol) in $\text{MeCN-H}_2\text{O-}t\text{-BuOH}$ (6:1:2 v/v, 90 mL) was added a catalytic amount of OsO_4 at rt and stirring was continued for 20 h. The reaction mixture was added aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and further stirring was continued for 1 h, the

mixture was extracted with AcOEt. The combined extracts were washed with 1 N HCl, saturated aqueous NaHCO₃ and NaCl. To a solution of the workup in AcOEt (120 mL) was added a catalytic amount of AMBERLYST 15 and stirring was continued for 3 h. The reaction mixture was filtered through Celite and the residue upon evaporation was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluent to give the cyclobutanone **S1a** (5.45 g, 2 steps 65%) as a colorless oil. The spectral data of **S1a** is completely agreement with the reported data.¹

1-[(2-Trimethylsilyl)ethynyl]spiro[3.5]nonan-1-ol (S2a): To a stirred solution of (trimethylsilyl)acetylene (4.30 g, 43.4 mmol) and TMEDA (5.04 g, 43.4 mmol) in THF (100 mL) was added 1.57 M solution of BuLi in hexane (27.6 mL, 43.4 mmol) at –78 °C. After stirring was continued for 1 h at the same temperature, a solution of spiro[3.5]nonan-1-one **S1a** (2.00 g, 14.5 mmol) in THF (10 mL) was added dropwise to this solution, and stirring was continued for 3 h at the same temperature. The reaction mixture was quenched with water and extracted with Et₂O. The combined extracts were washed with aqueous saturated NH₄Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (92:8 v/v) as eluent to give the acetylenylalcohol **S2a** (3.43 g, quant.) as a colorless oil: IR (neat) 3364, 2162 cm^{–1}; ¹H NMR (400 MHz, CDCl₃) δ 0.17 (9H, s), 1.16–1.54 (8H, m), 1.59–1.71 (4H, m), 1.98 (1H, br s), 2.11 (1H, ddd, *J* = 11.7, 10.0 and 8.3 Hz), 2.30 (1H, ddd, *J* = 11.7, 9.0 and 4.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ –0.16, 22.4, 22.8, 25.5, 25.9, 30.7, 33.4, 35.2, 47.6, 73.1, 90.2, 107.5; MS *m/z* 235 (*M*⁺–1); HRMS calcd for C₁₄H₂₃OSi (*M*⁺–1) 235.1519, found 235.1515.

1-(2-Bromoethynyl)spiro[3.5]nonan-1-ol (S3a): To a stirred solution of acetylenylcyclobutanol **S2a** (974 mg, 4.12 mmol) and NEt₃ (1.25 g, 12.4 mmol) in CH₂Cl₂ (25 mL) was added TESOTf (1.63 g, 6.18 mmol) at 0 °C. After stirring was continued for 1 h at the same temperature, the reaction mixture was diluted with water and extracted with hexane. The combined extracts were washed with saturated aqueous NH₄Cl and saturated aqueous NaCl. The residue upon workup was filtered through a short column of silica gel and the solvent was removed under reduced pressure. To a stirred solution of the obtained crude silyl ether in acetone (20 mL) were added NBS (806 mg, 4.53 mmol), H₂O (148 mg, 8.24 mmol) and AgNO₃ (70.0 mg, 0.412 mmol). After stirring was continued for 4 h at rt in the dark, the reaction mixture was filtered through a Celite. The combined organic filtrates were washed with saturated aqueous NaCl, and the residue upon workup was used without further purification. To a stirred solution of the above bromoacetylene in THF (12 mL) was added 1.0 M solution of TBAF in THF (6.18 mL, 6.18 mmol), and stirring was continued for 15 min at room temperature. The reaction mixture was quenched with water and extracted with ether, and the combined extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (95:5 v/v) as

eluent to give the bromoacetylene **S3a** (938 mg, 94% for 3 steps) as a colorless oil: IR (neat) 3350 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.18–1.75 (12H, m), 2.03 (1H, br s), 2.11 (1H, ddd, $J = 12.0, 9.6$ and 7.6 Hz), 2.33 (1H, ddd, $J = 11.6, 8.8$ and 4.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 22.2, 22.7, 25.5, 25.9, 30.6, 33.2, 35.2, 45.5, 48.0, 73.9, 81.8; MS m/z 216 ($\text{M}^+ - 28$); HRMS calcd for $\text{C}_9\text{H}_{11}^{81}\text{BrO}$ ($\text{M}^+ - 28$) 215.9973, found 215.9967.

1-(3-Buten-1-ynyl)spiro[3.5]nonan-1-ol (S4a): To a stirred solution of bromoacetylene **S3a** (938 mg, 3.87 mmol) in DMF (20 mL) were added tributyl(vinyl)tin (1.29 g, 4.07 mmol), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (30.1 mg, 0.116 mmol) and hydroquinone (21.3 mg, 0.194 mmol). After stirring was continued for 3 h at room temperature, the reaction mixture was filtered through Celite. The organic layer was washed with water and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (85:15 v/v) as eluent to give the enylalcohol **S4a** (629 mg, 85%) as a colorless oil: IR (neat) 3358 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.18–1.76 (12H, m), 1.99 (1H, br s), 2.15 (1H, ddd, $J = 12.0, 9.6$ and 8.4 Hz), 2.33 (1H, ddd, $J = 12.0, 9.3$ and 5.4 Hz), 5.47 (1H, dd, $J = 11.1$ and 2.1 Hz), 5.63 (1H, dd, $J = 17.7$ and 2.1 Hz), 5.86 (1H, dd, $J = 17.7$ and 11.1 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 22.3, 22.7, 25.5, 25.9, 30.7, 33.4, 35.2, 48.0, 73.2, 84.6, 91.5, 116.9, 126.9; MS m/z 162 ($\text{M}^+ - 28$); HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}$ ($\text{M}^+ - 28$) 162.1044, found 162.1039.

1-[(Z)-1,3-Butadienyl]spiro[3.5]nonan-1-ol [(Z)-1a]: To a stirred suspension of zinc powder (4.10 g, 62.9 mmol) in EtOH (6 mL) was added dibromoethane (0.15 mL) at room temperature, and heated at 80 °C. When the release of ethylene gas ceased, an additional dibromoethane (0.15 mL) was added. After the reaction mixture was stirred for 20 min at the same temperature, a solution of LiBr (1.46 g, 16.8 mmol) and CuBr (960 mg, 6.70 mmol) in THF (6 mL) was added at 50 °C. To the suspension of activated zinc was added a solution of enylcyclobutanol **S4a** (79.8 mg, 0.419 mmol) in EtOH (2 mL) at 50 °C, and stirring was continued at 80 °C for 2 h. The reaction mixture was filtered through Celite, and removed the solvent under reduced pressure. The residue was dissolved in AcOEt, washed with saturated aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (90:10 v/v) to give the dienylcyclobutanol (Z)-**1a** (51.5 mg, 64%) as a colorless oil: IR (neat) 3449, 1587 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.14–1.55 (9H, m), 1.63–1.67 (1H, m), 1.73–1.80 (3H, m), 2.03–2.10 (1H, m), 2.17–2.24 (1H, m), 5.14 (1H, d, $J = 12.8$ Hz), 5.18 (1H, d, $J = 18.8$ Hz), 5.65 (1H, d, $J = 11.6$ Hz), 6.07 (1H, dd, $J = 11.6$ and 11.6 Hz), 7.05 (1H, ddd, $J = 18.8, 12.8$ and 11.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 22.5, 22.9, 25.6, 26.2, 31.3, 34.7, 34.8, 48.9, 79.0, 118.5, 131.2, 134.0, 134.2; MS m/z 192 (M^+); HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}$ (M^+) 192.1514, found 192.1518.

1-[(*E*)-1,3-Butadienyl]spiro[3.5]nonan-1-ol [(*E*)-1a]: To a solution of enylcyclobutanol **S4a** (58.1 mg, 0.305 mmol) in THF (6 mL) were added LiAlH₄ (23.2 mg, 0.611 mmol) and NaOMe (66.6 mg, 1.22 mmol) at 0 °C. After the reaction mixture was reflux for 1 h, the solution was quenched with water and extracted with AcOEt. The combined extracts were washed with saturated aqueous NaHCO₃ and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (90:10 v/v) to give the dienylcyclobutanol (*E*)-**1a** (44.3 mg, 76%) as a colorless oil: IR (neat) 3364, 1651, 1603 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.13–1.28 (3H, m), 1.33–1.53 (6H, m), 1.62–1.64 (1H, m), 1.70–1.76 (2H, m), 1.83 (1H, br s), 1.99 (1H, ddd, *J* = 12.0, 9.6 and 8.0 Hz), 2.17 (1H, ddd, *J* = 12.0, 8.8 and 4.8 Hz), 5.06 (1H, *J* = 10.0 Hz), 5.20 (1H, d, *J* = 15.8 Hz), 5.91 (1H, d, *J* = 15.2 Hz), 6.26 (1H, dd, *J* = 15.2 and 10.4 Hz), 6.38 (1H, ddd, *J* = 15.8, 10.4 and 10.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 22.6, 22.9, 25.3, 26.2, 31.7, 34.5, 48.5, 78.1, 116.6, 128.2, 136.6, 136.8; MS *m/z* 192 (M⁺); HRMS calcd for C₁₃H₂₀O (M⁺) 192.1514, found 192.1507.

2,2-Dipentylcyclobutan-1-one (S1b): According to the same procedure described for **S1a**, the cyclobutanone **S1b** was prepared from 6-undecanone; 74% for two steps; colorless oil; IR (neat) 1774 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (6H, t, *J* = 7.2 Hz), 1.17–1.37 (12H, m), 1.48–1.56 (4H, m), 1.82 (2H, t, *J* = 8.4 Hz), 2.90 (2H, t, *J* = 8.4 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 21.8, 22.3, 23.8, 32.2, 33.9, 42.2, 68.3, 216.5; MS *m/z* 210 (M⁺); Anal. calcd for C₁₄H₂₆O C, 79.94; H, 12.46. Found: C, 79.70; H, 12.33.

1-[(2-Trimethylsilyl)ethynyl]-2,2-dipentylcyclobutan-1-ol (S2b): THF (16 mL) was added to anhyd. CeCl₃ (2.17 g, 8.82 mmol) and the suspension was stirred for 2 h at room temperature. In another flask, to a solution of trimethylsilylacetylene (816 mg, 8.31 mmol) in THF (16 mL) was added BuLi (1.56 M in hexane solution, 4.83 mL, 7.53 mmol) at –78 °C. The mixture was stirred at the same temperature for 30 min to give a solution of 2-trimethylsilylethynyllithium. To a suspension of CeCl₃ in THF was added dropwise the solution of 2-trimethylsilylethynyllithium at –78 °C. After the stirring was continued for 30 min, the cyclobutanone **S1b** (530 mg, 2.52 mmol) in THF (4 mL) was added to the suspension at –78 °C. The reaction mixture was stirred for 3 h at the same temperature, then the reaction was quenched with water at –78 °C. The reaction mixture was extracted with AcOEt and the organic layer was washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (95:5 v/v) as eluent to give the acetylenylcyclobutanol **S2b** (777 mg, quant.) as a colorless oil: IR (neat) 3317, 2164 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.13 (9H, s), 0.87 (6H, t, *J* = 6.9 Hz), 1.13–1.43 (16H, m), 1.50–1.71 (2H, m), 2.01 (1H, br s), 2.02–2.12 (1H, m), 2.19–2.27 (1H, m); ¹³C NMR (75 MHz, CDCl₃) δ –0.2, 13.9, 14.0, 22.5, 22.6, 23.2, 23.5, 25.7, 30.3, 32.6, 33.6, 35.7, 50.1, 73.0, 89.6, 108.3; MS *m/z* 307 (M⁺–1); Anal. calcd for C₁₉H₃₆OSi C, 73.95; H, 11.76. Found: C, 73.94; H, 11.74.

1-(2-Bromoethynyl)-2,2-dipentylcyclobutan-1-ol (S3b): By following the same procedure described for **S3a**, the bromoacetylene **S3b** was prepared from **S2b**; 70% for three steps; colorless oil; IR (neat) 3389, 2203 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.86–0.93 (6H, m), 1.20–1.48 (15H, m), 1.60–1.68 (3H, m), 1.97 (1H, br s), 2.10 (1H, ddd, $J = 12.0, 10.0$ and 8.0 Hz), 2.30 (1H, ddd, $J = 12.0, 9.2$ and 4.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 14.0, 22.4, 22.5, 23.3, 23.4, 25.9, 30.4, 32.5, 32.6, 33.4, 35.4, 45.1, 50.4, 73.9, 82.3; MS m/z 288 ($\text{M}^+ - 28$); Anal. calcd for $\text{C}_{16}\text{H}_{27}\text{OBr}$ C, 60.95; H, 8.63. Found: C, 60.89; H, 8.41.

1-(3-Buten-1-ynyl)-2,2-dipentylcyclobutan-1-ol (S4b): By following the same procedure described for **S4a**, the enylcyclobutanol **S4b** was prepared from **S3b**; yield 66%; colorless oil; IR (neat) 3418, 1609 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.84–0.92 (6H, m), 1.14–1.47 (15H, m), 1.58–1.68 (3H, m), 1.97 (1H, br s), 2.09–2.19 (1H, m), 2.26–2.33 (1H, m), 5.46 (1H, dd, $J = 8.7$ and 2.4 Hz), 5.62 (1H, dd, $J = 17.4$ and 2.4 Hz), 5.86 (1H, dd, $J = 17.4$ and 8.7 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 14.0, 22.5, 22.6, 23.3, 23.5, 25.9, 30.5, 32.5, 32.6, 33.6, 35.5, 50.6, 73.2, 84.2, 92.2, 117.0, 126.8; MS m/z 262 (M^+); HRMS calcd for $\text{C}_{18}\text{H}_{30}\text{O}$ (M^+) 262.2296, found 262.2303.

1-[(Z)-1,3-Butadienyl]-2,2-dipentylcyclobutan-1-ol [(Z)-1b]: By following the same procedure described for (Z)-**1a**, the dienylcyclobutanol (Z)-**1b** was prepared from **S4b**; yield 57%; colorless oil; IR (neat) 3470, 1587 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.2$ Hz), 0.91 (3H, t, $J = 7.2$ Hz), 1.12–1.50 (16H, m), 1.62–1.75 (2H, m), 1.78 (1H, br s), 2.06 (1H, ddd, $J = 11.6, 9.6$ and 7.6 Hz), 2.18 (1H, ddd, $J = 11.6, 9.2$ and 5.6 Hz), 5.13 (1H, dd, $J = 10.4$ and 1.2 Hz), 5.17 (1H, dd, $J = 17.2$ and 1.2 Hz), 5.70 (1H, d, $J = 11.6$ Hz), 6.03 (1H, dd, $J = 11.6$ and 11.6 Hz), 7.09 (1H, ddd, $J = 17.2, 11.6$ and 10.4 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.5, 22.6, 23.3, 23.5, 26.3, 31.6, 32.5, 32.7, 34.3, 34.7, 50.7, 79.5, 118.6, 130.6, 134.1, 134.2; MS m/z 264 (M^+); Anal. calcd for $\text{C}_{18}\text{H}_{32}\text{O}$ C, 81.75; H, 12.20. Found: C, 81.74; H, 12.13.

Scheme S2. Synthesis of 1,3-dienylcyclobutanols *trans*- and *cis*-(*Z*)-**1c** and (*Z*)-**1d**, and determination of the stereochemistry by NOESY correlation of *cis*-(*Z*)-**1c**.

2-(1-*t*-Butyldiphenylsiloxyethyl)-2-methylcyclobutan-1-one (S1c): By following the same procedure described for **S1a**, the cyclobutanone **S1c** was prepared from 1-*t*-butyldiphenylsiloxypropan-2-one³; yield 83% for two steps; colorless oil; IR (neat) 1778 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.04 (9H, s), 1.11 (3H, s), 1.79 (1H, ddd, *J* = 11.2, 10.0 and 7.6 Hz), 2.43 (1H, ddd, *J* = 10.8, 10.0 and 6.8 Hz), 3.02 (1H, ddd, *J* = 18.8, 10.8 and 6.8 Hz), 3.09 (1H, dd, *J* = 18.8, 10.8 and 7.6 Hz), 3.48 (1H, d, *J* = 10.0 Hz), 3.79 (1H, d, *J* = 10.0 Hz), 7.40–7.49 (6H, m), 7.64–7.70 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 17.7, 19.4, 21.8, 26.8, 43.8, 66.1, 66.7, 127.7, 129.7, 135.5, 135.5, 214.9; MS *m/z* 295 (M⁺-57); HRMS calcd for C₁₈H₁₉O₂Si (M⁺-57) 295.1155, found 295.1153.

[(1*S,2*S**) and (1*R**,2*S**)]-2-(*t*-Butyldiphenylsiloxyethyl)-2-methyl-1-[(2-trimethylsilyl)ethynyl]cyclobutan-1-ol (*trans*-**S2c** and *cis*-**S2c**):** By following the same procedure described for **S2a**, the cyclobutanols *trans*-**S2c** and *cis*-**S2c** were prepared from **S1c**. *trans*-**S2c**: 47% yield; colorless oil; IR (neat) 3418, 2162 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.07 (9H, s), 1.08 (9H, s), 1.24 (3H, s), 1.49–1.55 (1H, m), 1.60–1.68 (1H, m), 2.03 (1H, br s), 2.13–2.21 (1H, m), 2.24–2.31 (1H, m), 3.66 (1H, d, *J* = 10.0 Hz), 3.78 (1H, d, *J* = 10.0 Hz), 7.35–7.43 (6H, m), 7.65–7.68 (4H, m); ¹³C NMR

(100 MHz, CDCl₃) δ -0.04, 17.7, 19.6, 24.6, 27.0, 34.0, 48.6, 69.9, 70.9, 89.9, 106.8, 127.5, 129.4, 133.9, 133.9, 135.6, 135.6; MS m/z 393 (M^+ -57); Anal. calcd for C₂₇H₃₈O₂Si₂ C, 71.94; H, 8.50. Found: C, 71.84; H, 8.51. *cis*-**S2c**: 47% yield; colorless oil; IR (neat) 3458, 2162 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.20 (9H, s), 1.09 (9H, s), 1.18 (3H, s), 1.45–1.52 (1H, m), 1.81–1.88 (1H, m), 2.19–2.26 (1H, m), 2.38–2.44 (1H, m), 3.64 (1H, d, J = 10.4 Hz), 3.67 (1H, br s), 3.82 (1H, d, J = 10.4 Hz), 7.37–7.46 (6H, m), 7.66–7.69 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 0.10, 19.3, 21.7, 24.5, 26.9, 34.4, 47.4, 68.9, 73.4, 89.9, 107.1, 127.7, 127.7, 129.8, 129.8, 132.5, 132.6, 135.5, 135.6; MS m/z 393 (M^+ -57); Anal. calcd for C₂₇H₃₈O₂Si₂ C, 71.94; H, 8.50. Found: C, 71.63; H, 8.56.

(1*S,2*S**)-1-(2-Bromoethynyl)-2-(*t*-butyldiphenylsiloxymethyl)-2-methylcyclo-butan-1-ol** (*trans*-**S3c**): By following the same procedure described for **S3a**, the bromoacetylene *trans*-**S3c** was prepared from *trans*-**S2c**; yield 72% for three steps; colorless oil; IR (neat) 3418, 2203 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.07 (9H, s), 1.25 (3H, s), 1.44–1.50 (1H, m), 1.53–1.60 (1H, m), 2.11 (1H, br s), 2.15–2.22 (1H, m), 2.28–2.34 (1H, m), 3.49 (1H, d, J = 10.0 Hz), 3.82 (1H, d, J = 10.0 Hz), 7.36–7.41 (6H, m), 7.67–7.72 (4H, m); ¹³C NMR (150 MHz, CDCl₃) δ 17.8, 19.4, 19.4, 23.9, 26.9, 33.4, 45.4, 49.1, 69.6, 72.1, 82.0, 127.6, 127.7, 129.5, 129.6, 133.6, 133.6, 135.7, 135.7; MS m/z 401 (M^+ -57); Anal. calcd for C₂₄H₂₉O₂BrSi C, 63.01; H, 6.39. Found: C, 62.96; H, 6.42.

(1*R,2*S**)-1-(3-Buten-1-ynyl)-2-(*t*-butyldiphenylsiloxymethyl)-2-methylcyclobutan-1-ol** (*trans*-**S4c**): By following the same procedure described for **S4a**, the enylcyclobutanol *trans*-**S4c** was prepared from *trans*-**S3c**; yield 58%; colorless oil; IR (neat) 3391, 2341, 1589 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 1.06 (9H, s), 1.28 (3H, s), 1.47–1.51 (1H, m), 1.57–1.63 (1H, m), 2.08 (1H, br s), 2.20–2.25 (1H, m), 2.29–2.32 (1H, m), 3.54 (1H, d, J = 10.2 Hz), 3.83 (1H, d, J = 10.2 Hz), 5.43 (1H, dd, J = 12.0 and 2.4 Hz), 5.52 (1H, dd, J = 16.8 and 2.4 Hz), 5.76 (1H, dd, J = 16.8 and 12.0 Hz), 7.36–7.43 (6H, m), 7.67–7.71 (4H, m); ¹³C NMR (150 MHz, CDCl₃) δ 14.2, 17.8, 19.4, 21.0, 24.1, 26.9, 33.7, 49.2, 60.4, 69.8, 71.2, 84.1, 91.6, 116.7, 126.9, 127.6, 129.5, 133.7, 133.8, 135.7, 135.7; MS m/z 403 (M^+ -1); HRMS calcd for C₂₆H₃₁O₂Si (M^+ -1) 403.2093, found 403.2082.

(1*R,2*S**)-1-[(*Z*)-1,3-Butadienyl]-2-(*t*-butyldiphenylsilyloxymethyl)-2-methylcyclo-butan-1-ol** [*trans*-(*Z*)-**1c**]: By following the same procedure described for (*Z*)-**1a**, the dienylcyclobutanol *trans*-(*Z*)-**1c** was prepared from *trans*-**S4c**; yield 69%; colorless oil; IR (neat) 3445, 1589 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 1.06 (9H, s), 1.21 (3H, s), 1.61–1.67 (2H, m), 1.75 (1H, brs), 2.10 (1H, ddd, J = 12.0, 9.2 and 7.2 Hz), 2.23 (1H, ddd, J = 12.0, 8.8 and 6.8 Hz), 3.49 (1H, d, J = 10.0 Hz), 3.55 (1H, d, J = 10.0 Hz), 5.11 (1H, d, J = 10.4 Hz), 5.16 (1H, d, J = 16.8 Hz), 5.77 (1H, d, J = 11.2 Hz), 6.00 (1H, dd, J =

11.6 and 11.2 Hz), 6.96 (1H, ddd, $J = 16.8$, 11.6 and 10.4 Hz), 7.36–7.43 (6H, m), 7.64–7.67 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 18.5, 19.4, 24.9, 27.0, 34.7, 49.6, 68.8, 77.7, 118.7, 127.5, 129.5, 131.4, 133.6, 133.9, 134.0, 135.6; MS m/z 406 (M^+); HRMS calcd for $\text{C}_{26}\text{H}_{34}\text{O}_2\text{Si}$ (M^+) 406.2328, found 406.2356.

(1R*,2S*)-1-(2-Bromoethynyl)-2-(*t*-butyldiphenylsiloxymethyl)-2-methylcyclo-butan-1-ol (*cis*-S3c):

By following the same procedure described for **S3a**, the bromoacetylene *cis*-**S3c** was prepared from *cis*-**S2c**; yield 73% for three steps; colorless oil; IR (neat) 3418, 2196 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.09 (9H, s), 1.18 (3H, s), 1.45–1.52 (1H, m), 1.79–1.86 (1H, m), 2.18–2.25 (1H, m), 2.37–2.44 (1H, m), 3.63 (1H, d, $J = 10.4$ Hz), 3.83 (1H, d, $J = 10.4$ Hz), 3.87 (1H, br s), 7.37–7.44 (6H, m), 7.65–7.67 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 19.1, 21.6, 24.2, 26.8, 33.9, 45.6, 47.7, 68.8, 74.3, 81.8, 127.9, 128.0, 130.0, 132.7, 135.8; MS m/z 401 ($\text{M}^+ - 57$); HRMS calcd for $\text{C}_{20}\text{H}_{20}^{81}\text{BrO}_2\text{Si}$ ($\text{M}^+ - 57$) 401.0396, found 401.0409.

(1S*,2S*)-1-(3-Buten-1-ynyl)-2-(*t*-butyldiphenylsiloxymethyl)-2-methylcyclobutan-1-ol (*cis*-S4c):

By following the same procedure described for **S4a**, the enylcyclobutanol *cis*-**S4c** was prepared from *cis*-**S3c**; yield 57%; colorless oil; IR (neat) 3443, 2361, 1589 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.09 (9H, s), 1.18 (3H, s), 1.50 (1H, ddd, $J = 11.2$, 9.2 and 7.2 Hz), 1.85 (1H, ddd, $J = 11.2$, 10.0 and 5.6 Hz), 2.26 (1H, ddd, $J = 12.0$, 10.4 and 7.2 Hz), 2.41 (1H, ddd, $J = 12.0$, 9.2 and 5.6 Hz), 3.66 (1H, d, $J = 10.4$ Hz), 3.83 (1H, d, $J = 10.4$ Hz), 5.47 (1H, dd, $J = 10.8$ and 2.4 Hz), 5.65 (1H, dd, $J = 17.6$ and 2.4 Hz), 5.88 (1H, dd, $J = 17.6$ and 10.8 Hz), 7.37–7.46 (6H, m), 7.66–7.69 (4H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 19.2, 21.7, 24.3, 26.9, 34.4, 47.9, 69.0, 73.6, 84.5, 91.4, 116.9, 126.7, 127.8, 127.8, 129.9, 129.9, 132.6, 132.7, 135.7, 135.7; MS m/z 347 ($\text{M}^+ - 57$); HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{O}_2\text{Si}$ ($\text{M}^+ - 57$) 347.1467, found 347.1456.

(1S*,2S*)-1-[(*Z*)-1,3-Butadienyl]-2-(*t*-butyldiphenylsilyloxymethyl)-2-methylcyclo-butan-1-ol [*cis*-(*Z*)-1c]:

By following the same procedure described for (*Z*)-**1a**, the dienylcyclobutanol *cis*-(*Z*)-**1c** was prepared from *cis*-**S4c**; yield 57%; colorless oil; IR (neat) 3499, 1589 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 0.95 (3H, s), 1.10 (9H, s), 1.37–1.44 (1H, m), 1.90–1.96 (1H, m), 2.25–2.29 (2H, m), 3.70 (1H, d, $J = 10.4$ Hz), 3.78 (1H, d, $J = 10.4$ Hz), 3.96 (1H, br s), 5.13 (1H, dd, $J = 11.4$ and 2.4 Hz), 5.18 (1H, dd, $J = 16.8$ and 2.4 Hz), 5.63 (1H, d, $J = 11.4$ Hz), 6.09 (1H, dd, $J = 11.4$ and 11.4 Hz), 7.13 (1H, ddd, $J = 16.8$, 11.4 and 2.4 Hz), 7.40–7.47 (6H, m), 7.68–7.70 (4H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 19.2, 21.0, 24.4, 26.9, 35.7, 48.4, 69.7, 79.4, 118.4, 127.8, 127.8, 129.9, 129.9, 131.1, 132.6, 133.9, 134.4, 135.7, 135.7; MS m/z 349 ($\text{M}^+ - 57$); HRMS calcd for $\text{C}_{22}\text{H}_{25}\text{O}_2\text{Si}$ ($\text{M}^+ - 57$) 349.1624, found 349.1610.

1-(3-Methylbut-3-en-1-ynyl)spiro[3.5]nonan-1-ol (S5): By following the same procedure described for **S2a**, the enylcyclobutanol **S5** was prepared from spiro[3.5]nonan-1-one **S1a** and 2-methyl-1-buten-3-yne; yield 68%; colorless oil; IR (neat) 3360, 1614 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.17–1.75 (12H, m), 1.90 (3H, s), 2.08–2.20 (2H, m), 2.32 (1H, ddd, $J = 12.0, 9.3$ and 5.1 Hz), 5.22 (1H, s), 5.28 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 22.3, 22.8, 23.4, 25.5, 25.9, 30.8, 33.4, 35.2, 48.0, 73.0, 87.1, 89.9, 121.6, 126.6; MS m/z 204 (M^+); Anal. calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ C, 82.30; H, 9.87. Found: C, 82.18; H, 9.92.

1-[3-Methyl-(Z)-1,3-butadienyl]spiro[3.5]nonan-1-ol [(Z)-1d]: By following the same procedure described for (Z)-**1d**, the dienylcyclobutanol (Z)-**1d** was prepared from **S5**; yield 38%; colorless oil; IR (neat) 3458, 1624 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.11–1.64 (10H, m), 1.71–1.78 (2H, m), 1.87 (3H, s), 2.03–2.14 (2H, m), 3.07 (1H, br s), 4.95 (1H, d, $J = 1.2$ Hz), 4.96 (1H, d, $J = 1.2$ Hz), 5.66 (1H, d, $J = 12.0$ Hz), 5.87 (1H d, $J = 12.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 22.2, 22.8, 23.4, 25.0, 26.1, 30.9, 32.6, 35.0, 48.7, 79.1, 113.5, 129.7, 133.8, 145.4; MS m/z 206 (M^+); HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ (M^+) 206.1670, found 206.1669.

General procedure for the Palladium-Catalyzed Insertion–Ring expansion reaction.

Reaction of (Z)-1a with 2a (entry 6 in Table 1). To a stirred solution of the 1,3-dienylcyclobutanol (Z)-1a (35.7 mg, 186 μmol) in toluene (0.74 mL) were added iodobenzene 2a (56.8 mg, 278 μmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (9.6 mg, 9.3 μmol), $\text{P}(o\text{-tolyl})_3$ (11.3 mg, 37.2 μmol) and Ag_2CO_3 (103 mg, 372 μmol) at rt, and stirring was continued for 4 h at 45 °C. After filtration of the reaction mixture using AcOEt with small amount mixture of silica gel and Celite followed by evaporation of the eluate, the residue was chromatographed on silica gel with hexane-AcOEt (98:2 v/v) as eluent to give the cyclopentanone 3aa (41.3 mg, 83%) and the α -arylated cyclopentanone 4aa (9.5 mg, 15%) as a colorless oil, respectively.

1-[3-Phenyl-(Z)-1-propenyl]spiro[4.5]decan-2-one (3aa): Colorless oil; IR (neat) 1738, 1601 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.15–1.31 (3H, m), 1.40–1.60 (8H, m), 2.18–2.34 (3H, m), 3.02 (1H, d, J = 10.0 Hz), 3.34 (1H, dd, J = 15.5 and 7.0 Hz), 3.47 (1H, dd, J = 15.5 and 7.0 Hz), 5.36 (1H, dd, J = 10.0 and 10.0 Hz), 5.90 (1H, ddd, J = 10.0, 7.0 and 7.0 Hz), 7.14–7.18 (3H, m), 7.21–7.27 (2H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 22.2, 22.4, 25.8, 29.4, 29.9, 33.8, 34.9, 37.8, 44.7, 60.0, 123.0, 126.0, 128.4, 128.4, 133.6, 140.2, 218.6; MS m/z 268 (M^+); HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{O}$ (M^+) 268.1827, found 268.1848.

1-Phenyl-1-[3-phenyl-(Z)-1-propenyl]spiro[4.5]decan-2-one (4aa): Colorless oil; IR (KBr) 1703, 1616 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.17–1.26 (3H, m), 1.35–1.42 (4H, m), 1.54–1.74 (5H, m), 2.11 (1H, ddd, J = 18.5, 9.0 and 7.0 Hz), 2.17 (1H, ddd, J = 18.5, 9.0 and 7.0 Hz), 2.90 (1H, dd, J = 13.5 and 8.5 Hz), 3.07 (1H, dd, J = 13.5 and 7.0 Hz), 5.28 (1H, ddd, J = 10.0, 8.5 and 7.0 Hz), 5.92 (1H, d, J = 10.0 Hz), 7.08–7.12 (3H, m), 7.15–7.20 (3H, m), 7.22–7.30 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 22.3, 22.5, 25.7, 28.4, 36.3, 37.1, 37.4, 42.9, 43.1, 44.0, 125.9, 126.4, 127.8, 127.9, 128.5, 129.4, 139.5, 141.1, 143.7, 144.8, 209.5; MS m/z 344 (M^+); Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{O}$: C, 87.16; H, 8.19. Found: C, 86.93; H, 8.20.

1-[3-(2-Methoxyphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ab): Colorless oil; IR (neat) 1738, 1599, 1242 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.15–1.34 (4H, m), 1.41–1.64 (7H, m), 2.21–2.29 (2H, m), 2.32–2.36 (1H, m), 3.11 (1H, d, J = 9.6 Hz), 3.37 (1H, dd, J = 15.6 and 7.2 Hz), 3.41 (1H, dd, J = 15.6 and 7.2 Hz), 3.81 (3H, s), 5.35 (1H, dd, J = 10.8 and 9.6 Hz), 5.91 (1H, ddd, J = 10.8, 7.2 and 7.2 Hz), 6.84 (1H, d, J = 7.8 Hz), 6.89 (1H, dd, J = 7.8 and 7.2 Hz), 7.12–7.20 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 22.2, 22.5, 26.0, 28.1, 29.4, 29.9, 35.0, 37.8, 44.8, 55.3, 60.1, 110.1, 120.4, 122.6, 127.2, 128.5, 129.4, 133.4, 157.1, 218.8; MS m/z 298 (M^+); HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2$ (M^+) 298.1933, found 298.1909.

1-[3-(4-Methoxyphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ac): Colorless oil; IR (neat) 1738, 1610, 1246 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.18–1.35 (4H, m), 1.42–1.64 (7H, m), 2.22–2.37 (3H, m), 3.05 (1H, d, J = 10.2 Hz), 3.31 (1H, dd, J = 16.2 and 7.2 Hz), 3.42 (1H, dd, J = 16.2 and 7.2 Hz), 3.78

(3H, s), 5.36 (1H, dd, $J = 10.8$ and 10.2 Hz), 5.90 (1H, ddd, $J = 10.8$, 7.2 and 7.2 Hz), 6.74 (2H, d, $J = 8.4$ Hz), 7.12 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 22.2, 22.4, 25.9, 29.5, 29.9, 32.9, 34.9, 37.8, 44.7, 55.3, 60.0, 113.9, 122.7, 129.3, 132.2, 134.1, 158.0, 218.7; MS m/z 298 (M^+); HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2$ (M^+) 298.1933, found 298.1909.

1-(4-Methoxyphenyl)-1-[3-(4-methoxyphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (4ac): Colorless oil; IR (neat) 1709, 1630, 1611, 1246 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.14–1.27 (3H, m), 1.33–1.44 (4H, m), 1.54–1.77 (5H, m), 2.14–2.20 (2H, m), 2.82 (1H, dd, $J = 13.4$ and 8.3 Hz), 2.97 (1H, dd, $J = 13.4$ and 8.3 Hz), 3.75 (3H, s), 3.77 (3H, s), 5.17 (1H, ddd, $J = 10.3$, 8.3 and 8.3 Hz), 5.90 (1H, d, $J = 10.3$ Hz), 6.72 (2H, d, $J = 8.5$ Hz), 6.81 (2H, d, $J = 8.5$ Hz), 6.99 (2H, d, $J = 8.5$ Hz), 7.16 (2H, d, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 22.4, 22.5, 22.6, 25.7, 28.4, 29.6, 36.4, 37.2, 37.5, 42.3, 42.3, 44.0, 55.1, 113.3, 113.9, 128.7, 130.3, 131.7, 135.9, 141.8, 144.4, 158.1, 209.6; MS m/z 404 (M^+); HRMS calcd for $\text{C}_{27}\text{H}_{32}\text{O}_3$ (M^+) 404.2351, found 404.2370.

1-[3-(2-Methylphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ad): Colorless oil; IR (neat) 1736 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.15–1.22 (1H, m), 1.32–1.34 (2H, m), 1.43–1.63 (8H, m), 2.22–2.37 (6H, m), 3.04 (1H, d, $J = 9.6$ Hz), 3.34 (1H, dd, $J = 16.2$ and 7.2 Hz), 3.42 (1H, dd, $J = 16.2$ and 7.2 Hz), 5.39 (1H, dd, $J = 10.2$ and 9.6 Hz), 5.87 (1H, ddd, $J = 10.2$, 7.2 and 7.2 Hz), 7.10–7.25 (4H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 19.5, 22.2, 22.4, 25.9, 29.5, 29.9, 31.4, 34.9, 37.8, 44.7, 60.1, 123.1, 126.1, 126.2, 128.6, 130.1, 133.2, 136.1, 138.5, 218.5; MS m/z 282 (M^+); Anal. calcd for $\text{C}_{20}\text{H}_{26}\text{O}$ C, 85.06; H, 9.28. Found: C, 84.93; H, 9.33.

1-(2-Methylphenyl)-1-[3-(2-methylphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (4ad): Colorless oil; IR (neat) 1711, 1634 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.17–1.45 (7H, m), 1.53–1.73 (5H, m), 1.99 (1H, ddd, $J = 18.6$, 9.6 and 6.6 Hz), 2.09 (1H, ddd, $J = 18.6$, 9.0 and 7.2 Hz), 2.25 (3H, s), 2.31 (3H, s), 2.85 (1H, dd, $J = 13.2$ and 9.0 Hz), 3.02 (1H, dd, $J = 13.2$ and 6.0 Hz), 5.55 (1H, ddd, $J = 10.2$, 9.0 and 6.0 Hz), 5.92 (1H, d, $J = 10.2$ Hz), 6.92 (1H, d, $J = 7.2$ Hz), 6.98 (1H, dd, $J = 7.2$ and 7.2 Hz), 7.03 (1H, ddd, $J = 7.2$, 7.2 and 1.2 Hz), 7.06 (1H, dd, $J = 7.2$ and 7.2 Hz), 7.08–7.11 (2H, m), 7.19–7.22 (1H, m), 7.36 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 19.4, 19.6, 22.5, 22.6, 25.8, 36.2, 36.9, 37.2, 37.4, 40.5, 44.1, 125.0, 126.0, 126.1, 126.1, 126.1, 130.0, 130.5, 130.6, 136.7, 137.1, 137.4, 137.4, 140.1, 142.4, 144.8, 208.9; MS m/z 372 (M^+); HRMS calcd for $\text{C}_{27}\text{H}_{32}\text{O}$ (M^+) 372.2453, found 372.2439.

1-[3-(4-Methylphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ae): Colorless oil; IR (neat) 1736 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.17–1.33 (3H, m), 1.43–1.63 (8H, m), 2.22–2.35 (6H, m), 3.04 (1H, d, $J = 9.6$ Hz), 3.33 (1H, dd, $J = 16.0$ and 7.2 Hz), 3.44 (1H, dd, $J = 16.0$ and 7.2 Hz), 5.36 (1H, dd, $J = 10.8$

and 9.6 Hz), 5.76 (1H, ddd, $J = 10.8, 7.2$ and 7.2 Hz), 7.09 (4H, s); ^{13}C NMR (100M Hz, CDCl_3) δ 21.0, 22.2, 22.5, 25.9, 29.5, 30.0, 33.4, 34.9, 37.8, 44.7, 60.0, 122.7, 128.2, 128.2, 129.0, 133.9, 135.4, 137.0, 218.6; MS m/z 282 (M^+); HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{O}$ (M^+) 282.1983, found 282.1969.

1-(4-Methylphenyl)-1-[3-(4-methylphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (4ae): Colorless oil; IR (neat) 1711, 1632 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.17–1.27 (3H, m), 1.33–1.46 (3H, m), 1.56–1.75 (6H, m), 2.13–2.19 (2H, m), 2.27 (3H, s), 2.31 (3H, s), 2.85 (1H, dd, $J = 13.2$ and 8.4 Hz), 3.02 (1H, dd, $J = 13.2$ and 6.8 Hz), 5.21 (1H, ddd, $J = 10.0, 8.4$ and 6.8 Hz), 5.91 (1H, d, $J = 10.0$ Hz), 6.98 (4H, s), 7.08 (2H, d, $J = 8.0$ Hz), 7.16 (2H, d, $J = 8.0$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 21.0, 21.0, 22.5, 22.6, 25.8, 28.5, 36.4, 37.2, 37.3, 37.5, 42.6, 42.7, 44.1, 127.5, 128.5, 129.1, 129.2, 135.2, 135.7, 136.4, 140.7, 141.6, 144.3, 209.3; MS m/z 372 (M^+); HRMS calcd for $\text{C}_{27}\text{H}_{32}\text{O}$ (M^+) 372.2453, found 372.2432.

1-[3-(1-Naphthyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3af): Colorless oil; IR (neat) 1738, 1597 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.20–1.25 (2H, m), 1.33–1.38 (2H, m), 1.45–1.65 (7H, m), 2.25–2.39 (3H, m), 3.15 (1H, d, $J = 10.2$ Hz), 3.82 (1H, dd, $J = 16.2$ and 7.2 Hz), 3.91 (1H, dd, $J = 16.2$ and 7.2 Hz), 5.46 (1H, dd, $J = 10.8$ and 10.2 Hz), 6.04 (1H, ddd, $J = 10.8, 7.2$ and 7.2 Hz), 7.37 (1H, d, $J = 6.6$ Hz), 7.41 (1H, dd, $J = 8.4$ and 6.6 Hz), 7.48 (1H, dd, $J = 9.0$ and 7.8 Hz), 7.52 (1H, dd, $J = 9.0$ and 8.4 Hz), 7.73 (1H, d, $J = 8.4$ Hz), 7.86 (1H, d, $J = 7.8$ Hz), 8.03 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 22.3, 22.5, 26.0, 29.6, 30.0, 31.0, 35.0, 37.9, 44.8, 123.4, 123.7, 125.5, 125.5, 125.8, 126.8, 128.6, 131.8, 133.4, 133.7, 136.2, 218.4; MS m/z 318 (M^+); HRMS calcd for $\text{C}_{23}\text{H}_{26}\text{O}$ (M^+) 318.1984, found 318.1972.

1-(1-Naphthyl)-1-[3-(1-naphthyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (4af): Colorless oil; IR (neat) 1709, 1632 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.06–1.38 (3H, m), 1.44–1.49 (2H, m), 1.61–1.67 (2H, m), 1.86 (1H, ddd, $J = 18.6, 9.0$ and 6.0 Hz), 2.02 (1H, ddd, $J = 18.6, 9.0$ and 7.2 Hz), 3.49 (1H, dd, $J = 14.4$ and 9.6 Hz), 3.72 (1H, dd, $J = 14.4$ and 5.4 Hz), 6.00 (1H, d, $J = 10.8$ Hz), 6.39 (1H, ddd, $J = 10.8, 9.6$ and 5.4 Hz), 7.21 (1H, d, $J = 6.6$ Hz), 7.25–7.28 (1H, m), 7.44–7.53 (5H, m), 7.60 (1H, d, $J = 7.2$ Hz), 7.65 (1H, d, $J = 8.4$ Hz), 7.74 (1H, d, $J = 8.4$ Hz), 7.80 (1H, d, $J = 7.2$ Hz), 7.82–7.84 (1H, m), 8.15 (1H, d, $J = 8.4$ Hz), 8.29–8.30 (1H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 22.4, 22.6, 25.7, 28.3, 36.0, 36.8, 36.9, 37.1, 39.5, 44.1, 123.6, 124.0, 124.2, 124.8, 125.4, 125.5, 125.6, 125.8, 126.1, 126.8, 126.9, 127.5, 128.5, 128.6, 132.2, 132.4, 133.7, 134.0, 135.3, 140.3, 140.8, 145.0, 208.9; MS m/z 444 (M^+); HRMS calcd for $\text{C}_{33}\text{H}_{32}\text{O}$ (M^+) 444.2453, found 444.2460.

1-[3-(4-Nitrophenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ag): Colorless oil; IR (neat) 1738, 1597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.19–1.25 (1H, m), 1.32–1.35 (2H, m), 1.42–1.66 (8H, m), 2.23–2.40 (3H, m), 3.01 (1H, d, $J = 9.6$ Hz), 3.46 (1H, dd, $J = 16.4$ and 7.0 Hz), 3.60 (1H, dd, $J = 16.4$ and 7.0 Hz), 5.48 (1H, dd, $J = 10.8$ and 9.6 Hz), 5.89 (1H, ddd, $J = 10.8$, 7.0 and 7.0 Hz), 7.38 (2H, d, $J = 8.4$ Hz), 8.15 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 22.2, 22.4, 25.9, 29.7, 30.1, 33.7, 35.0, 37.9, 44.7, 60.0, 123.7, 124.6, 129.2, 131.4, 146.5, 147.8, 217.9; MS m/z 313 (M^+); HRMS calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ (M^+) 313.1618, found 313.1648.

1-[3-(4-Acetylphenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ah): Colorless oil; IR (neat) 1736, 1682, 1605 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.18–1.26 (2H, m), 1.32–1.34 (2H, m), 1.43–1.66 (7H, m), 2.22–2.40 (3H, m), 2.58 (3H, s), 3.03 (1H, d, $J = 9.9$ Hz), 3.42 (1H, dd, $J = 15.9$ and 7.2 Hz), 3.55 (1H, dd, $J = 15.9$ and 7.2 Hz), 5.44 (1H, dd, $J = 10.8$ and 9.9 Hz), 5.91 (1H, ddd, $J = 10.8$, 7.2 and 7.2 Hz), 7.31 (2H, d, $J = 8.4$ Hz), 7.90 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 22.0, 22.3, 25.7, 26.4, 29.4, 29.9, 33.7, 34.8, 37.7, 44.6, 60.0, 124.0, 128.7, 132.5, 135.4, 146.0, 198.0, 218.6; MS m/z 310 (M^+); HRMS calcd for $\text{C}_{21}\text{H}_{26}\text{O}_2$ (M^+) 310.1933, found 310.1960.

1-[3-(2-Bromophenyl)-(Z)-1-propenyl]spiro[4.5]decan-2-one (3ai): Colorless oil; IR (neat) 1732, 1620 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.15–1.26 (3H, m), 1.41–1.66 (9H, m), 2.21–2.39 (3H, m), 3.08 (1H, d, $J = 10.0$ Hz), 3.53 (2H, d, $J = 7.6$ Hz), 5.45 (1H, dd, $J = 11.2$ and 10.0 Hz), 5.90 (1H, dt, $J = 11.2$ and 7.6 Hz), 7.07 (1H, ddd, $J = 8.0$, 8.0 and 2.4 Hz), 7.23–7.29 (2H, m), 7.53 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 22.2, 22.4, 25.9, 29.4, 29.9, 34.1, 34.9, 37.8, 44.7, 60.2, 124.0, 124.5, 127.6, 127.8, 130.1, 132.1, 132.6, 139.6, 218.4; MS m/z 348 (M^+); HRMS calcd for $\text{C}_{19}\text{H}_{23}^{81}\text{BrO}$ (M^+) 348.0912, found 348.0923.

3,3-Dipentyl-2-[3-phenyl-(Z)-1-propenyl]cyclopentan-1-one (3ba): Colorless oil; IR (neat) 1740, 1601 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 0.86–0.89 (6H, m), 1.23–1.47 (16H, m), 1.73–1.78 (1H, m), 1.90–1.93 (1H, m), 2.23–2.35 (2H, m), 3.11 (1H, d, $J = 9.6$ Hz), 3.38 (1H, dd, $J = 15.6$ and 7.8 Hz), 3.47 (1H, dd, $J = 15.6$ and 7.8 Hz), 5.40 (1H, dd, $J = 9.6$ and 9.6 Hz), 5.89 (1H, dd, $J = 9.6$ and 7.8 Hz), 7.18–7.21 (3H, m), 7.26–7.30 (2H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 14.0, 22.5, 23.6, 23.9, 30.1, 32.6, 32.7, 33.5, 33.8, 35.2, 38.7, 46.1, 58.9, 123.5, 126.0, 128.4, 133.2, 140.2, 218.7; MS m/z 340 (M^+); HRMS calcd for $\text{C}_{24}\text{H}_{36}\text{O}$ (M^+) 340.2751, found 340.2766.

(2R*,3S*)-3-(*t*-Butyldiphenylsiloxy)methyl-3-methyl-2-[3-phenyl-(Z)-1-propenyl]-cyclopentan-1-one [*trans*-(Z)-3ca]: Colorless oil; IR (neat) 1738, 1600 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.86 (3H, m), 1.06 (9H, s), 1.57–1.62 (1H, m), 2.20–2.42 (3H, m), 3.26 (1H, dd, $J = 16.0$ and 6.0 Hz), 3.44–3.54 (4H,

m), 5.30 (1H, dd, $J = 10.8$ and 9.2 Hz), 5.90 (1H, ddd, $J = 10.8$, 6.0 and 6.0 Hz), 7.11–7.27 (5H, m), 7.32–7.45 (6H, m), 7.59–7.62 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 17.9, 19.2, 26.9, 29.9, 33.9, 46.0, 54.2, 68.8, 77.4, 123.0, 126.0, 127.8, 128.5, 129.8, 133.3, 133.4, 134.5, 135.7, 135.8, 140.3, 218.5; MS m/z 425 ($\text{M}^+ - 57$); HRMS calcd for $\text{C}_{28}\text{H}_{29}\text{O}_2\text{Si}$ ($\text{M}^+ - 57$) 425.1937, found 425.1919.

(2*S,3*S**)-3-(*t*-Butyldiphenylsiloxy)methyl-3-methyl-2-[3-phenyl-(*Z*)-1-propenyl]-cyclopentan-1-one [*cis*-(*Z*)-3ca]:** Colorless oil; IR (neat) 1738, 1620 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.02 (3H, s), 1.05 (9H, s), 1.76–1.85 (1H, m), 2.15–2.21 (1H, m), 2.31–2.38 (1H, m), 2.48–2.58 (1H, m), 3.07 (1H, d, $J = 9.6$ Hz), 3.34 (1H, dd, $J = 15.6$ and 7.6 Hz), 3.41–3.50 (3H, m), 5.45 (1H, dd, $J = 10.8$ and 9.6 Hz), 5.92 (1H, ddd, $J = 10.8$, 7.6 and 7.6 Hz), 7.17–7.20 (3H, m), 7.24–7.28 (2H, m), 7.36–7.46 (6H, m), 7.61–7.66 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 19.2, 24.0, 26.9, 32.9, 33.9, 36.6, 45.9, 57.5, 69.5, 123.2, 126.0, 127.6, 128.3, 128.4, 129.6, 129.8, 132.7, 133.0, 134.0, 135.5, 135.7, 140.0, 217.4; MS m/z 425 ($\text{M}^+ - 57$); HRMS calcd for $\text{C}_{28}\text{H}_{29}\text{O}_2\text{Si}$ ($\text{M}^+ - 57$) 425.1937, found 425.1926.

1-[2-Methyl-3-phenyl-(*Z*)-1-propenyl]spiro[4.5]decan-2-one [(*Z*)-3da]: Colorless oil; IR (neat) 1740, 1601 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 1.15–1.22 (1H, m), 1.28–1.36 (2H, m), 1.40–1.49 (3H, m), 1.50–1.59 (4H, m), 1.60–1.63 (1H, m), 1.68 (3H, d, $J = 1.2$ Hz), 2.19–2.33 (3H, m), 2.97 (1H, d, $J = 9.6$ Hz), 3.22 (1H, d, $J = 15.0$ Hz), 3.52 (1H, d, $J = 15.0$ Hz), 5.18 (1H, dd, $J = 9.6$ and 1.2 Hz), 7.16–7.19 (3H, m), 7.25–7.27 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 22.1, 22.3, 23.7, 25.8, 29.3, 29.7, 34.8, 37.7, 38.0, 44.6, 60.9, 119.2, 126.1, 128.5, 128.7, 139.3, 139.7, 219.5; MS m/z 282 (M^+); Anal. calcd for $\text{C}_{20}\text{H}_{26}\text{O}$ C, 85.06; H, 9.28. Found: C, 84.70; H, 9.42.

1-[2-Methyl-3-phenyl-(*E*)-1-propenyl]spiro[4.5]decan-2-one [(*E*)-3da]: Colorless oil; IR (neat) 1738 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.17–1.35 (4H, m), 1.37–1.64 (10H, m), 2.17–2.34 (3H, m), 2.88 (1H, d, $J = 10.0$ Hz), 3.35 (1H, d, $J = 14.0$ Hz), 3.45 (1H, d, $J = 14.0$ Hz), 5.12 (1H, dd, $J = 10.0$ and 1.2 Hz), 7.18–7.22 (3H, m), 7.27–7.30 (2H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 16.4, 22.3, 22.4, 26.0, 29.6, 30.0, 34.9, 37.8, 45.1, 46.7, 60.8, 119.5, 126.1, 128.3, 128.8, 129.3, 139.9, 140.3, 219.5; MS m/z 282; HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{O}$ (M^+) 282.1984, found 282.1985.

Scheme S3. Determination of the Stereochemistries of *trans*- and *cis*-**3ca**, (*Z*)- and (*E*)-**3da** in Table 3.

[(1*R,2*R**,3*S**) and (1*S**,2*R**,3*S**)-3-(*t*-Butyldiphenylsiloxy)methyl-3-methyl-2-[3-phenyl-(*Z*)-1-propenyl]cyclopentan-1-ol (β -*trans*-S6 and α -*trans*-S6):** To a stirred solution of *trans*-**3ca** (18.2 mg, 37.7 μmol) in CH_2Cl_2 was added DIBAL (1.0 M in hexane solution, 57 μL , 57 μmol) at $-78\text{ }^\circ\text{C}$. After stirring was continued for 2 h at the same temperature, the reaction mixture was diluted with Et_2O and added MeOH. After stirring was continued for 0.5 h at the same temperature, the suspension was filtered through Celite and removed the solvent under the reduced pressure. The residue was chromatographed on silica gel with hexane-AcOEt (96:4 v/v) as eluent to give alcohols β -*trans*-S6 (9.0 mg, 49%, colorless oil) and α -*trans*-S6 (4.2 mg, 23%, colorless oil); β -*trans*-S6: IR (neat) 3439, 1601 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.97 (3H, s), 1.06 (9H, s), 1.51 (1H br s), 1.57–1.64 (1H, m), 1.71–7.86 (2H, m), 1.97–2.04 (1H, m), 3.03 (1H, dd, $J = 10.4$ and 5.6 Hz), 3.29–3.38 (3H, m), 3.46 (1H, dd, $J = 15.6$ and 7.6 Hz), 4.27–4.30 (1H, m), 5.62 (1H, dd, $J = 10.8$ and 10.4 Hz), 5.82 (1H, ddd, $J = 10.8$, 7.6 and 7.6 Hz), 7.12–7.19 (3H, m), 7.23–7.26 (2H, m), 7.31–7.43 (6H, m), 7.62–7.64 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 19.2, 21.4, 26.8, 33.3, 34.0, 34.0, 46.4, 46.8, 70.7, 76.8, 126.0, 126.6, 127.7, 128.4, 128.6, 129.7, 132.2, 133.8, 135.8, 140.9; MS m/z 427 ($\text{M}^+ - 57$); HRMS calcd for $\text{C}_{28}\text{H}_{31}\text{O}_2\text{Si}$ ($\text{M}^+ - 57$) 427.2093, found 427.2077; α -*trans*-S6: IR (neat) 3391, 1600 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 0.83 (3H, s), 1.07 (9H, s), 1.32–1.37 (1H, m), 1.61–1.67 (1H, s), 1.72 (1H, br s), 2.06–2.14 (2H, m), 2.86 (1H, dd, $J = 10.8$ and 8.4 Hz), 3.26 (1H, dd, $J = 15.6$ and 6.6 Hz), 3.35 (1H, d, $J = 9.6$ Hz), 3.40 (1H, d, $J = 9.6$ Hz), 3.49 (1H, dd, $J = 15.6$ and 7.8 Hz), 4.02–4.06 (1H, m), 5.42 (1H, dd, $J = 10.8$ and 10.8 Hz), 5.76 (1H, ddd, $J = 10.8$, 7.8 and 6.6 Hz), 7.11–7.16 (3H, m), 7.22–7.24 (2H, m), 7.32–7.43 (6H, m), 7.62–7.64 (4H, m); ^{13}C NMR (150 MHz,

CDCl₃) δ 20.7, 27.0, 32.4, 33.1, 33.9, 46.4, 50.9, 70.6, 78.5, 125.9, 127.6, 128.3, 128.4, 129.2, 129.6, 132.1, 133.6, 135.7, 135.8; MS m/z 427 ($M^+ - 57$); HRMS calcd for C₂₈H₃₁O₂Si ($M^+ - 57$) 427.2093, found 427.2075.

(1*R,2*S**,3*S**)-3-(*t*-Butyldiphenylsiloxy)methyl-3-methyl-2-[3-phenyl-(*Z*)-propenyl]cyclopentan-1-ol (α -*cis*-**S6**):** By following the same procedure described for β -*trans*-**S6** and α -*trans*-**S6**, the cyclopentanol α -*cis*-**S6** was prepared from *cis*-**3ca**; yield 75%; Colorless oil; IR (neat) 3439, 1601 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 0.90 (3H, s), 1.12 (9H, s), 1.45 (1H, ddd, J = 13.2, 9.0 and 3.6 Hz), 1.86–1.90 (2H, m), 2.23 (1H, ddd, J = 13.2, 9.6 and 9.6 Hz), 2.75 (1H, dd, J = 10.8 and 4.2 Hz), 3.24 (1H, d, J = 10.2 Hz), 3.38 (1H, dd, J = 16.2 and 7.2 Hz), 3.49–3.52 (2H, m), 3.92 (1H, d, J = 10.2 Hz), 4.09–4.12 (1H, m), 5.82 (1H, ddd, J = 10.8, 7.2 and 7.2 Hz), 5.88 (1H, dd, J = 10.8 and 10.8 Hz), 7.16–7.20 (3H, m), 7.27 (2H, dd, J = 7.8 and 7.8 Hz), 7.40–7.47 (6H, m), 7.70–7.75 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 19.2, 26.1, 26.9, 32.7, 33.9, 34.5, 46.6, 52.9, 69.3, 76.9, 125.8, 126.8, 127.7, 128.2, 129.8, 129.8, 130.8, 132.3, 132.3, 135.7, 135.7, 140.7; MS m/z 427 ($M^+ - 57$); HRMS calcd for C₂₈H₃₁O₂Si ($M^+ - 57$) 427.2093, found 427.2075.

Scheme S4. Synthesis of Saturated Cyclopentanone **11**.

1-(3-Phenylpropyl)spiro[4.5]decan-2-one (11): A mixture of cyclopentanone **3aa** (57.9 mg, 216 μ mol) and 10% Pd/C (30 mg) in AcOEt (10 mL) was stirred for 10 h at rt under H₂ atmosphere. After filtration of the reaction mixture through Celite using AcOEt followed by evaporation, the residue was chromatographed on silica gel with hexane-AcOEt (98:2 v/v) as eluent to give the saturated cyclopentanone **11** (55.9 mg, 96 %) as a colorless oil; IR (neat) 1732 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 1.13–1.21 (3H, m), 1.30–1.39 (2H, m), 1.42–1.67 (9H, m), 1.80 (1H, dd, J = 8.4 and 3.0 Hz), 1.96 (1H, m), 2.07–2.18 (2H, m), 2.22–2.27 (1H, m), 2.63 (2H, t, J = 7.2 Hz), 7.15–7.20 (3H, m), 7.26–7.28 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 22.2, 22.5, 24.0, 26.0, 28.9, 29.5, 30.4, 34.6, 36.2, 37.8, 43.0, 60.1, 125.6, 128.2, 128.3, 142.2, 220.7; MS m/z 270 (M^+); HRMS calcd for C₁₉H₂₆O (M^+) 270.1984, found 270.1963.

Reaction of 3aa with 2a for the Synthesis of 4aa (Scheme 4). To a stirred solution of the cyclopentanone **3aa** (34.6 mg, 129 μ mol) in toluene (0.52 mL) were added iodobenzene **2a** (39.4 mg, 193

μmol), $\text{Pd}(\text{PPh}_3)_4$ (14.9 mg, 12.9 μmol) and Cs_2CO_3 (84.1 mg, 258 μmol) at rt, and stirring was continued for 24 h at 60 °C. After filtration of the reaction mixture using AcOEt with small amount mixture of silica gel and Celite followed by evaporation of the eluate, the residue was chromatographed on silica gel with hexane-AcOEt (97:3 v/v) as eluent to give the α -arylated cyclopentanone **4aa** (35.8 mg, 81 %) as a colorless oil.

Reaction of 1a with 2a for the One-Pot Synthesis of 4aa (Scheme 4). To a stirred solution of the 1,3-dienylcyclobutanol (*Z*)-**1a** (33.2 mg, 173 μmol) in toluene (0.69 mL) were added iodobenzene **2a** (42.3 mg, 207 μmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (9.0 mg, 8.65 μmol), $\text{P}(o\text{-tolyl})_3$ (10.5 mg, 34.6 μmol) and Ag_2CO_3 (57.2 mg, 207 μmol) at rt, and stirring was continued for 8 h at 45 °C. To the reaction mixture were added toluene (0.69 mL), iodobenzene **2a** (35.3 mg, 173 μmol), $\text{Pd}(\text{PPh}_3)_4$ (20.0 mg, 17.3 μmol) and Cs_2CO_3 (67.4 mg, 207 μmol) at rt, and stirring was continued for 24 h at 60 °C. After filtration of the reaction mixture using AcOEt with small amount mixture of silica gel and Celite followed by evaporation of the eluate, the residue was chromatographed on silica gel with hexane-AcOEt (97:3 v/v) as eluent to give the α -arylated cyclopentnaone **4aa** (37.0 mg, 62 %) as a colorless oil.

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 date Feb 27 04 dfrq 299.954
 solvent CDCl3 dn H1
 file ACQUISITION exp dnp 0
 sfrq 75.431 dm yyy
 tn 0.973 dnm w
 at 32768 9720
 np 18761.7 1b PROCESSING 1.00
 sw 9500 wft1e ft
 bs 16 pproc 32758
 pw 8.4 fn
 d1 1.127
 tof 0 wexp
 nt 900 wft
 ct 500 wft
 alock n
 gain not used
 flags
 11 n
 1n n
 dp y
 DISPLAY
 sp -1897.8
 wp 18761.7
 vs 214
 sc 0
 wc 400
 hzmm 1.48
 is 500.00
 rfi 7706.0
 rfp 5808.2
 th 14
 ins 1.000
 nm no ph

FILE D:\AL400 NMR\data\m03f111 bromoethylethnol
 CONTINUED
 DATE Tue Nov 11 13:09:02 2003
 NAME NON
 EXMNO
 OBSFREQ 399.65 MHz
 OBSSET 124.00 kHz
 PULPROG zgpg30
 FREQ 793.80 Hz
 SCANS 8
 ACQTIME 4.0983 sec
 F2 - 2.0000 Hz
 PULP 5.70 usec
 INJUG 1H
 RTMPC 22.1 e
 STVAT
 CDCL3
 BF 0.12 Hz
 RGAIN 14

S-3a

13C OBSERVE

expi std13c

SAMPLE DEC. 6 VT
 date Nov 11 03 dfreq 299.954
 solvent CDCl3 dn H4
 file exp dhp 1
 ACQUISITION
 sfrq 75.431 dm yyy 0
 tn C13 dmm w
 at 0.873 dmf 9720
 np 32768 1b PROCESSING 1.00
 sw 18761.7
 fd 9500 wfile
 bs 16 proc ft
 pw 8.4 fn 32768
 d1 1.127
 tof 0 warr
 nt 400 wexd wft
 ct 400 wds wft
 alock n wnt
 gsin not used
 FLAGS
 j1 n
 jn n
 dp y
 DISPLAY
 sp -1899.0
 wp 18761.7
 vs 214
 sc 0
 wc 400
 hzmm 2.54
 js 500.00
 rfj 7707.2
 rfp 5808.2
 th 20
 ns 1.000
 nm no ph

STANDARD 1H OBSERVE

exp1 std1n

SAMPLE
date Nov 12 03
solvent CDCl3
file exp
ACQUISITION
sfrq 299.955
tn H1
at 3.641
np 32768
sw 4500.5
fb 2250
bs 16
pw 11.3
d1 1.359
tof 600.0
nt 16
ct 16
ajock n
gain not used
FLAG n
j1 n
jn y
dp y
DISPLAY
sp -24.7
wp 2999.5
vs 203
sc 0
wc 400
hzmm 11173.67
j3 7.89
rf1 566.4
th 0
jns 20
nm cdc ph 11.840

STANDARD 1H OBSERVE

Wed Nov 12 23:05:33 JST 2003

INDEX	FREQUENCY (PPM)	H _z	HEIGHT	FREQUENCY (PPM)	H _z	HEIGHT
1	7.268	2180.0385	1.3	458.4784	1.2	1.2
2	7.268	2179.4891	1.3	456.2807	1.6	1.6
3	5.907	1771.8307	1.5	453.5337	2.0	2.0
4	5.870	1760.8426	1.5	451.0514	1.7	1.7
5	5.848	1754.2498	1.8	448.3144	2.0	2.0
6	5.812	1743.2617	2.5	445.5674	1.5	1.5
7	5.667	1699.8567	3.1	443.4034	1.7	1.7
8	5.660	1697.8611	2.9	440.8126	0.8	0.8
9	5.658	1697.1117	3.2	401.3403	0.9	0.9
10	5.608	1682.2777	1.9	399.4173	1.0	1.0
11	5.601	1680.0801	1.9	396.3956	1.1	1.1
12	5.493	1647.6652	1.8	392.8245	0.6	0.6
13	5.491	1647.1158	2.8	386.7810	0.9	0.9
14	5.485	1645.1929	2.6	384.3087	0.9	0.9
15	5.448	1635.1277	2.3	375.2435	1.1	1.1
16	5.448	1634.2048	2.2	366.7278	0.7	0.7
17	2.375	712.3034	0.8	352.9807	0.9	0.9
18	2.357	707.0841	0.9	352.9926	0.6	0.6
19	2.344	703.2382	0.9	0.0000	2.1	2.1
20	2.344	700.2165	1.3	-0.5494	2.0	2.0
21	2.338	698.2936	1.0			
22	2.318	695.2719	1.3			
23	2.305	691.4260	1.4			
24	2.289	686.4814	1.4			
25	2.172	659.8953	1.1			
26	2.168	651.9342	1.4			
27	2.160	650.2607	1.5			
28	2.160	648.0231	0.9			
29	2.140	641.9795	1.5			
30	2.138	640.0657	1.0			
31	2.128	638.4085	1.0			
32	2.111	630.1074	5.6			
33	1.983	598.3780	1.0			
34	1.787	529.3783	0.9			
35	1.720	511.6535	1.3			
36	1.720	511.8912	2.4			
37	1.703	510.9465	2.1			
38	1.687	506.0018	2.7			
39	1.670	501.0572	2.1			
40	1.657	496.9367	1.5			
41	1.641	492.8668	1.2			
42	1.623	486.7727	1.5			
43	1.609	482.6622	3.0			
44	1.594	477.9822	1.3			
45	1.578	473.3123	1.9			
46	1.550	464.7965	2.4			
47	1.541	462.3242	2.3

13C OBSERVE

exp1 std13c

SAMPLE		DEC. & VT	
date	NOV 12 03	dfrq	299.994
solvent	CDCl3	dn	H1
file	exp	dm	1
ACQUISITION	exp	dot	0
tn	75.431	dm	yyy
at	0.873	dm	w
nd	32768	dm	9720
sw	18761.7	lb	1.00
fb	9500	wtfile	ft
bs	16	proc	32768
pw	8.4	fn	
d1	1.127	wt	
to	0	wt	
nt	500	wt	
ct	500	wt	
clock	n	wt	
gain	not used	wt	
11	n	wt	
1n	n	wt	
dp	y	wt	
DISPLAY			
sd	-1897.8		
wd	18761.7		
vs	214		
sc	0		
wc	400		
hzmm	0.71		
is	500.00		
rfl	7706.0		
rtp	5808.2		
th	20		
ins	1.000		
nm	no		
ph

DPFILE
 CDHNT
 1H
 CDHNT
 EXMOD
 NON
 399.65 MHz
 OBSFQ
 124.00 KHz
 OBSFQ
 100.620 Hz
 POINT
 32768
 FREQU
 7993.60 Hz
 SCANS
 8
 PCOLM
 4.000 sec
 PULP
 2.000 sec
 5.70 usec
 INJULC
 29.9 e
 STAMP
 0.00 ppm
 EXREF
 0.12 Hz
 RGAIN
 10

(Z)-1a

FILE
 COM1
 DATIM
 ENUC
 13C
 BOM
 100.40 MHz
 OBSF1
 125.00 kHz
 OBSF1
 10500.00 Hz
 POINT
 32798
 SCANS
 27180 Hz
 600
 ACQIM
 1.2059 sec
 PD
 1.7940 sec
 F1
 6.10 usec
 F2
 25.3 e
 CTMP
 77.00 ppm
 SLWT
 0.2 Hz
 EXREF
 22
 RGAIN

(Z)-1a

FILE: D:\AL400 NMR\data\219 E dienhydrochalcone.a
 COUNT: 1
 DATE: Fri Dec 19 09:25:27 2003
 NAME: 219 E dienhydrochalcone.a
 INSTR: 400
 OBSERVE: 399.65 MHz
 OBSERVE: 124.00 KHz
 OBSERVE: 10500.00 Hz
 F2: 327.88 MHz
 F3: 754.80 Hz
 SCANS: 8
 ACQTIME: 4.0993 sec
 PD: 2.9010 sec
 RF: 5.70 usec
 RNUC: 23.3 c
 CTMP: 0.00 ppm
 SLVT: 0.7 Hz
 RGAIN: 7

D:\AL400 NMR\spgimoc\1223 13C a dema.als
 Tue Dec 23 10:11:03 2003
 13C
 ENUC
 BOM
 126.00 MHz
 126.00 MHz
 10600.00 Hz
 32758
 2773.90 Hz
 12089 sec
 1.7940 sec
 6.10 usec
 24.0 c
 77.00 ppm
 0.12 Hz
 ZZ
 ROBIN

(E)-1a

```

enyne 2,2-dipentyl cyclobutanol
exp1 std1h
SAMPLE Aug 29 03 299.954
date Aug 29 03 299.954
solvent CDCl3 dn H1
file exp dof 0
ACQUISITION 299.955 dm
sfrq 299.955 dm
tn H1 dm
at 3.641 PROCESSING
np 32768 wftjle ft
sw 4500.5 proc 32768
fb 2250 fn
bs 16 react
pw 5.7 wepr
d1 1.358 wepd
tof 600.0 wbs
nt 16 wnt
ct 16
ajock n
gain not used
flags not used
j1 n
jn n
dp y
DISPLAY -28.3
sp -28.3
wp 2999.5
vs 203
sc 0
wc 400
hzmm 7.89
is 17932.74
rfi 571.9
rfd 0
th 10
jns 1.000
nm cdc ph

```

INDEX	FREQUENCY (PPM)	HZ	HEIGHT
1	7.269	2180.3133	0.5
2	5.905	1771.2813	0.6
3	5.869	1760.2932	0.7
4	5.847	1753.9751	1.0
5	5.836	1750.5766	0.3
6	5.810	1742.7123	1.2
7	5.800	1739.6905	0.3
8	5.651	1695.1887	1.1
9	5.644	1692.9911	1.5
10	5.633	1689.6947	0.5
11	5.593	1677.6078	0.7
12	5.586	1675.4102	0.9
13	5.576	1672.1157	0.3
14	5.490	1646.8411	1.1
15	5.483	1644.6435	1.2
16	5.472	1641.3471	0.4
17	5.454	1635.8520	1.0
18	5.446	1633.6554	0.9
19	5.435	1630.3589	1.0
20	5.352	1590.0189	0.3
21	5.315	1570.8984	0.3
22	5.303	1567.8956	0.3
23	5.298	1565.2057	0.4
24	5.288	1562.0882	0.5
25	5.274	1557.4182	0.3
26	5.256	1548.8241	0.2
27	5.188	1526.2641	0.3
28	5.150	1508.0231	0.2
29	5.156	1510.6485	0.5
30	5.149	1508.1338	0.5
31	5.127	1496.1338	0.4
32	5.121	1493.8373	0.5
33	5.116	1491.5408	0.5
34	5.099	1482.5963	0.3
35	5.089	1480.0608	2.0
36	5.057	1459.6837	0.3
37	5.057	1459.6837	0.8
38	5.057	1459.6837	0.8
39	5.057	1459.6837	0.8
40	5.057	1459.6837	0.8
41	5.057	1459.6837	0.8
42	5.057	1459.6837	0.8
43	5.057	1459.6837	0.8
44	5.057	1459.6837	0.8
45	5.057	1459.6837	0.8
46	5.057	1459.6837	0.8
47	5.057	1459.6837	0.8

13C OBSERVE

exp1 std13c

SAMPLE DEC. 8 VT
 date AUG 29 03 dfrq 299.954
 solvent CDCl3 on HI
 file ACQUISITION 1
 sfrq 75.431 dm yyy
 tn 0.133 dm w
 ac 0.873 dm
 mp 32.768
 sw 18761.7 1b 1.00
 fd 9500 wcf1le ft
 bs 16 proc 32768
 pw 8.4 tn
 d1 1.127
 tof 0 werr
 nt 1024 wbsd wft
 ct 1024 wbs wft
 alock not used
 gain n wnt
 flags not used
 j1 n
 jn n
 dp y
 DISPLAY
 sp -1896.7
 wp 18761.7
 vs 214
 sc 0
 wc 400
 hzmm 0.65
 is 500.00
 rf1 7704.9
 rfp 5808.2
 th 20
 ins 1.000
 nm no ph

DLE		Sun Feb 22 19:06:03 2004
CONNT		
1H		
OBNUC		
EMMOD		
OFFREQ	398.65 MHz	
CORR	-0.00 Hz	
OBSRV	10560.00 Hz	
POINT	32768	
FREQSU	7953.50 Hz	
SS		
ACQTIM	4.4093 sec	
PD	2.5010 sec	
PWID	5.70 usec	
PHI		
HPRF		
CTEMP	25.5 c	
SLVINT	7.15 ppm	
EXREF	0.12 Hz	
RGAIN	18

S-1c

FILE D:\AL400 NMR\data\002 24 13C methyl OSI
 COUNT 13C
 DATE Tue Feb 24 08:28:46 2004
 NAME BOM
 ORIGIN 12500.00 Hz
 OBSERV 10500.00 Hz
 POINT 32768
 F2 2710000 Hz
 SCANS 12059 sec
 ACQTM 1.7940 sec
 PD 6.10 usec
 PULP 21.7 e
 INJULC 21.7 e
 CTEMP 77.00 ppm
 SILVNT 77.00 Hz
 EXREF 77.00 Hz
 ROAIN 23

S-1c

FILE D:\ECA600\No.24\ugmactb\KS.2-methyl-2-OTB
 T 19-06-2003 16:59:14
 DATIN 1H
 OBNUC 1H
 EXMOD single pulse ex2
 OBRFO 600.17 MHz
 OBRIN 5.47 Hz
 OBRIN 5.47 Hz
 POINT 13107
 FREQU 9008.87 Hz
 ACQTM 1.45 sec
 PD 5.0000 sec
 PW 6.95 usec
 OBNUC 1H
 STNUF 23.3 s
 CDOL3 0.00 ppm
 SLVNT EXREF 0.12 Hz
 BF 42
 K0AIN

trans-S-4c

FILE D:\ECS\ADN02\24\mgmt\13C\13C-2-methyl-2-OTBDPSmethyl-1-ene
 COUNT 19-08-2003 23:27:10
 DATE 13C
 ORIGIN single-pulse data
 ORFREQ 125.761 MHz
 OBSREV 3.52 kHz
 OBSREV 1.74 Hz
 POINT 32708 Hz
 F2 471000 Hz
 SCANS 471000
 ACQTM 0.6921 sec
 PD 2.0000 sec
 FID 5.45 usec
 IRNUC 1H
 CTEMP 24.4 c
 SILVIT CDOL3
 EXREF 77.00 ppm
 ROAIN 0.02 Hz
 60

FILE D:\ECA600N\24summon\K1228.diene.OTBDPS.methyl.cis.1
 COUNT 2
 D 200.13
 ORNUC 1H
 ENMOD single pulse ex2
 OFFSET 600.17 MHz
 O1 0.00 sec
 O2 0.00 sec
 POINT 5.47 Hz
 POINT 32768
 FREQ 11261.26 Hz
 SCANS 2
 ACQTM 2.408 sec
 PD 5.0000 sec
 PW 6.45 usec
 IRNUC 1H
 F2 23.9 c
 SAMP CDCL3
 SOLVT CDCL3
 EXREF 0.00 ppm
 BR 0.12 Hz
 ROIAN 48

D4AL400 NMR spectrum 13C@820 Zn reduction
 COUNT 13C
 DATE Thu Aug 21 11:55:29 2003
 OBS 13C
 OBS 100.40 MHz
 OBS 125.00 kHz
 OBS 10500.00 Hz
 OBS 127.08
 OBS 27.600 Hz
 OBS 1.2039 sec
 OBS 1.7940 sec
 OBS 6.10 msec
 OBS 235 e
 OBS 77.00 ppm
 OBS 75.00 Hz
 OBS 24
 OBS 24

FILE DYAL400 NMR spectrum 20 Bracetylene alk
 COMMENT F1 Feb 20 18:42:36 2004
 NAME
 DATA
 EXMOD NON
 OBSERVED 399.65 MHz
 OBSSET 124.00 kHz
 POINT 1032768 Hz
 FREQU 7393.68 Hz
 SCANS 8
 ACQTIME 4.089 sec
 F2 2.250 sec
 PUL 5.70 msec
 INJULC 22.5 e
 CTEMP 0.000 ppm
 EXREF 0.12 Hz
 BF 8
 RGAIN

cis-S-3c

13C OBSERVE

exp1 std13c

SAMPLE DEC. 8 VT
 date Aug 27 03 dfrq 299.954
 solvent CDCl3 dn H1
 file ACQUISITION
 exp 0
 dnt 0
 sfrq 75.431 dm
 tn C13 dnm
 at 0.873 dmf 9720
 np 32768
 sw 18761.7 1b
 ds 9500 wft11e 1.00
 dw 16 proc ft
 d1 1.127 32758
 tof 0 werr
 nt 1024 wexp wft
 ct 1024 wds
 alock n wft
 gain not used
 flags
 i1 n
 in n
 dp y
 DISPLAY
 sp -1899.0
 wp 18761.7
 vs 214
 sc 0
 wc 400
 hzmm 0.59
 ls 500.00
 rfi 7707.2
 rfp 5806.2
 th 9
 ins 1.000
 nm no ph

DFILE
 COUNT 11
 ORNUC 1H
 EXNOID NON
 OBFTED 399.65 MHz
 OBSER 126.00 KHz
 ORSET 100000.0 Hz
 POINT 32768 Hz
 FREQ 7393.60 Hz
 SCANS 16
 ACQTIME 4.000 sec
 PULPROG zgpg30
 PWD 2.00 Hz
 PWR 5.70 usec
 IRNUC 1H
 STAMP 24.5 e
 CDOL 0.00 ppm
 EXREF 0.12 Hz
 BF 12
 RGAIN 12

DFILE
 CONT
 CONT
 CONT
 EXMOD
 OFFREQ
 OFFSET
 GPCIN
 POINT
 FREQU
 SCANS
 DO
 PVI
 IRNUC
 OTMPP
 EXREF
 BF
 RGAIN

1663

30 mg
COMENT NON
EXMOD single_pulse.ex
SLVNT CDCL3
BF 0.00 Hz
XE 5347.61 Hz
XS -6.24 Hz
Start 8.8 ppm
End -0.2 ppm
ZFE
R.T. : () °C
OPERATOR: K. MUSHIAKE

FILE D:\ECA600N_28augmotor\130KKS_13C_diene.O
 COUNT 1
 DATE 04-09-2003 13:55:28
 NAME single pulse dec
 EXMOD 150.92 MHz
 OBSFREQ 8.32 kHz
 OBS 1.74 Hz
 POINT 32768
 FREQU 47346.49 Hz
 SOLANS 800
 ACQTIME 0.021 sec
 PULPROG zgpg30
 INTRPULC 22.000 usec
 SFO 125.761 MHz
 T1 24.1 c
 T2 2.000 usec
 T2RHO 0.000 usec
 EXREF 0.12 Hz
 RGAIN 60

FILE D:\AL400 NMR\run\mgm023 Zn reduction upp
 COUNT 11
 DATE Fri Oct 24 14:00:43 2003
 NAME NO1
 INSTR NO1
 OBSFREQ 399.66 MHz
 OBSSET 124.00 KHz
 P1 10.000000 Hz
 P2 10.000000 Hz
 FREQ 7353.66 Hz
 SCANS 16
 ACQTIME 4.0393 sec
 F2 2.3910 sec
 P1 5.170 usec
 INJULC 28.7 e
 SLVNT CDCL3
 SAMP 100 ppm
 REF 0.12 Hz
 RGAIN 9

13C OBSERVE

exp1 std13c

SAMPLE DEC. 6 VT
 date Oct 24 03 dfreq 299.954
 solvent CDCl3 dn H1
 file exp dnp 1
 ACQUISITION exp dot 0
 sfreq 75.431 dm
 tn 0.873 dmf
 at 32768 9720
 np 18761.7 lb 1.00
 SW 9500 wtfile ft
 fb 16 proc 32768
 bs 8.4 ft
 pw d1 1.127
 tof 0 wefr
 nt 800 wep
 ct 800 wbs
 alock n wft
 gain not used
 flags
 11 n
 1n n
 dp y
 DISPLAY
 SP -1899.0
 WD 18761.7
 VS 214
 SC 0
 WC 400
 hzmm 2.01
 is 500.00
 rfi 7707.2
 rfp 5908.2
 th 20
 jns 1.000
 nm no ph

FILE D:\AL400 NMR\data\1217 o-methoxy proal
 NAME 1217 o-methoxy proal
 DATE 17 Oct 2003
 TIME 17:08:36
 INSTR 13C
 PULPROG zgpg30
 EXMOD 100.40 MHz
 ORNUC 13C
 ORF1 160.000 Hz
 POINT 32768
 FREQ 2717330 Hz
 SCANS 400
 ACQTIME 1.200 sec
 PD 1.7940 sec
 PULPROG 6.10 usec
 PVI 23.1 o
 RNUC CDCl3
 ORF2 77.00 ppm
 EXREF 0.12 Hz
 BF 22
 ROAIN

3ab

FILE D:\EQA000\6-24-ug\motok\KS.1203.p-iodantiole
 NAME 6-24-ug\motok\KS.1203.p-iodantiole
 DATE 06-24-2003 12:32:56
 INSTR single.pulse.a2
 EXM00 800.17 MHz
 OBNUC 1H
 OBR00 500.13 MHz
 OBR01 5.47 Hz
 PONT 282.14
 FREQ0 9008.87 Hz
 FREQ1 500.13 MHz
 ACQ00 2.9098 sec
 PD 5.0000 sec
 PUL 6.45 usec
 INJ00 34.0 e
 CDCL3 0.00 ppm
 SOLNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 42

13C OBSERVE

exp1 std13c

SAMPLE DEC. S VT
 date Mar 5 03 dfreq 299.954
 solvent CDCl3 dn H1
 file exp dhp 1
 ACQUISITION 1
 tn 75.431 dm yyy 0
 at 0.873 dmf 9720
 np 32768
 SW 18761.7 lb PROCESSING 1.00
 fb 9500 wtfile ft
 bs 15 pproc 32768
 pw 8.4 fn
 d1 1.127
 tof 0 werr
 nt 1024 wexp wft
 ct 1024 wds wft
 alock n
 gain not used
 FLAOS n
 j1 n
 jn n
 dp y
 DISPLAY y
 SP -1899.0
 WP 18761.7
 VS 214
 SC 0
 WC 400
 Hzmm 1.12
 IS 500.00
 FFI 7707.2
 FFI 5808.2
 TH 20
 INS 1.000
 nm no ph

NAME D:\ECA\ADONIS-25491000XQS.1127.13C.2addad1
 DATE 27-11-2003 10:42:31
 DATA 13C
 ENUC single pulse dec
 FREQ 101.62 MHz
 OBSF 1.74 Hz
 POINT 32768
 FREQ 47348.49 Hz
 SFO 101.62 MHz
 ACQTM 0.692 sec
 PD 20000 sec
 PULP 5.12 usec
 FWH 26.3 o
 CDCL3 77.00 ppm
 EXREF 0.12 Hz
 RFAM 80

FILE D:\AL400 NMR\Sugimoto\124 from p-toi 1 added
 DATE Mon Nov 24 17:55:29 2003
 1H NMR
 ORNUC NON
 EXMOD 300.85 MHz
 OBSST 144.0 MHz
 ORFNI 10500.00 Hz
 POINT 32768
 FREQU 798380 Hz
 SPROS 5.000000
 ACQIN 4.0893 sec
 PD 2.9010 sec
 PVI 5.70 usec
 NMRUC 1H
 ORNUC 24.6 c
 CDCL3 0.00 ppm
 SLANT EXREF 0.12 Hz
 BR 15
 ROAN

FILE D:\AL400 NMR\data\gm04\124 13C from p-tol 1
 COUNT 13C
 DATE Mon Nov 24 18:32:27 2003
 PROC B01
 OBSF0 00.40 MHz
 OBSF1 125.00 MHz
 OBSF2 105500.00 Hz
 FREQ1 127.06 MHz
 FREQ2 271.454 Hz
 SCANS 271
 ACQTM 1.2059 sec
 PD 1.7940 sec
 INJ1 61.0 usec
 INJ2 23.5 c
 CTMP 77.00 ppm
 CDCL3
 SILVIT 0.2 Hz
 EXREF 22
 RGAIN

FILE
 COMMENT
 DATE
 DATIM
 EBNOC
 EBNOC
 ORSET
 ORSET
 POINT
 POINT
 SCANS
 SCANS
 ACQTM
 PD
 PMIC
 PMIC
 CTENP
 CTENP
 SLVNT
 SLVNT
 EXREF
 EXREF
 RGAN
 RGAN

DKAL400 NMRsugimotol 123 2added from p-tol
 Sun Nov 23 20:05:42 2003
 1H
 99.65 MHz
 124.00 MHz
 10500.00 Hz
 32/768
 793.90 Hz
 32
 4.0993 sec
 2.9010 sec
 5.70 usec
 1H
 23.5 c
 CDCl3
 0.00 ppm
 0.1 Hz
 21

FILE DJEC6000h-2kugimnKYS.130.1122.1
CONT 22-11-2003 17:08:20
DATE 130
NAME single pulse dec
EXPNO 150.92 MHz
PROCNO 1
PROBHD 5 mm
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
F2 101.25 MHz
F1 500.13 MHz
AQ 0.6921 sec
RG 327.5
WDW EM
SSB 0
LB 3.0 Hz
GB 0
PC 1.00
GC 0.00
DC 0.00
BF 0.12 Hz
RGAIN 60

3af

FILE D:\AL400 NMR\data\moco\1227 13C 1-mph 1 ad
 COUNT Sat Dec 27 15:28:55 2003
 DATE
 NAME
 OBNUC 13C
 OBSO BOM 00.40 MHz
 OBSO 125.00 KHz
 OBSO 10500.00 Hz
 POINT 32789 Hz
 POINT 27220 Hz
 SCANS 1200
 ACQTM 1.2069 sec
 PD 1.7940 sec
 INU 6.10 usec
 FNUC 21.8 c
 CDCL3 77.00 ppm
 EXREF 0.50 Hz
 RGAIN 24

DJECAR000-24ugimochKS.1217.2.mph2.1
 COMNT
 single-pulse
 17-12-2003 18:59:11
 NAME
 single-pulse-2
 PMO
 600.17 MHz
 OFRQ
 5.30 kHz
 OBSSET
 5.30 Hz
 ORN
 5.30 Hz
 SCANS
 11261.28 Hz
 FREQ
 16
 ACQTM
 2.5008 sec
 PMV
 5.40 uarc
 IRNUC
 IH
 CTMPC
 23.9 c
 SLVNT
 CDCl3
 EXPRT
 0.12 Hz
 RFAN
 44

D:\ECA000\26\mpm000\K1217.13C.mpf2.1
 COUNT 17
 DATE 17-12-2003 22:41:10
 single pulse decoupled gated NOE
 DNAME
 DBNAME
 DBUSER
 DBPASS
 DBHOST
 OBSERVE 13C
 OBSERVE 101.25 MHz
 OBSERVE 8.32 kHz
 PULPROG zgpg30
 PCOUNT 32768
 FIDRES 4.73389 Hz
 AQC 2.000
 SCANS 2000
 ACQTM 0.6921 sec
 PD 2.0000 sec
 PDI 5.12 usec
 RFNUC 1H
 CTENP 25.3 e
 CDCL3
 SLVNT CDCL3
 EXREF 77.00 ppm
 EXREF 0.12 Hz
 RGAIN 50

DFILE D:\AL400 NMR\data\102 pic from lido nit
 CONTIN Sun Nov 02 17:45:08 2003
 DATE
 NAME
 EXMOD NON
 OBSFRO 399.65 MHz
 OBSSET 124.00 kHz
 PULPROG zgpg30
 FREQU 798.30 Hz
 SCANS 8
 ACQTM 4.0983 sec
 PUL 2.50 sec
 PW 5.70 sec
 IRNUC 1H
 CTMP 23.9 e
 STVNT CDCl₃
 SLSOLV 0.00 ppm
 REF 012 Hz
 RGAIN 14

3ag

DITLE DKAL400 NMRsugimotok13C41102 after pile iodo
 Sun Nov 02 19:57:54 2003
 NAME 3ag
 DATE 02/11/2003
 ERMOD BCM
 P1 125.00 MHz
 OBSER 125.00 MHz
 OBSF1 10600.00 Hz
 POINT 32758
 PRENU 277320 Hz
 SCAUS 125.00 MHz
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PULP 6.10 usec
 PM1C 25.4 e
 PM1O 0.12 Hz
 STANK 77.00 ppm
 SLANT 0.12 Hz
 EXREF ZZ
 BE ROAIN

exp1 std13c

DATE	SAMPLE	14 03	dfreq	DEC. & VT
solvent	CCCC13	dn	239.954	
file	exp	dnp	1	
ACQUISITION		dof	41	
sfreq	75.431	dm	0	
tm	C13	dmm	yy	
at	0.873	dmf	yy	
bt	32768			
wp	18781.7		9720	
nd				
fb	9500	1b	PROCESSING	1.00
bs	16	prec		
dw	1.127			
dm	8.4	fn		32768
tof	0			
nt	1024	WERR		
rt	1024	WEXP		
ct	1024	WOS		
block	n	WMC		
gain	not used			
FLAGS

FILE D:\ECA\ADONIS-28491904XYS_1202_13C_1B.pro.
 NAME 3ai
 CONT 1
 DATE 02-12-2009 21:17:28
 INSTR Bruker Avance 400
 PULPROG zgpg30
 PROCNO 1
 F2 - 100.626 MHz
 F1 - 400.146 MHz
 AQCNT 1
 PD 0.0021 sec
 P1 5.12 usec
 PM 25.2 c
 CTEMP 77.00 ppm
 SLEW 0.12 Hz
 EXREF 60
 RGAIN 80

FILE D:\ECA600\0\24suplmo\KKS_product from 2,2'-
 NAME 3ba
 ORNUC 1H
 0 99-2000 224.427
 single pulse ex2
 EMOD 6001.7 MHz
 QRES 320
 OBRN 5.30 kHz
 POINT 2621.4
 FREQ 9008.97 Hz
 SCANS 16
 AQT 2.5000 sec
 PD 5.0000 sec
 PVI 6.95 usec
 RNUC 1H
 CTAMP 23.4 °
 CDCL 0.00 ppm
 EXREF 0.12 Hz
 BF 38
 RGAIN 38

FILE: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 DATA: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 NAME: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 DATE: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 TIME: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 USER: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 INSTR: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 PROG: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 METHOD: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 ACQTM: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 PD: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 PM: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 FID: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 CTMP: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 SILNT: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 EXRF: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1
 RAIN: 2010-01-13 10:05:13, 13C, pro, from 2,2-diphenyl, 5, 1

FILE: D:\AL400 NMR\ugmno-c821 a added pro purif
 COUNT 1
 DATIM Mon Aug 25 16:52:47 2003
 ORBUC 1H
 ORBRO 399.65 MHz
 OSSET 124.00 kHz
 OSFTN 10500.00 Hz
 POFIT 327.68
 PRSNU 399.650 Hz
 SCANS 8
 ACQTM 4.00993 sec
 PD 2.0010 sec
 INJIC 5.00 usec
 RMUC 1H
 CTWMP 24.5 c
 SILWT 0.00 ppm
 EXREF 0.00 Hz
 RGAIN 12

13C OBSERVE

exp1 sctd13c

SAMPLE DEC. & VT
 date Aug 25 03 dfrq 299.954
 solvent CDCl3 dn H1
 file ACQUISITION exp dmp 1
 sfrq 75.431 dm 0
 tn C13 dmf yyy
 at 0.873 dmf w
 np 32768 1.00
 sw 18761.7 lb PROCESSING
 fb 9500 wffile ft
 bs 16 Proc 32768
 dv 8.4 fm
 d1 1.127
 tot 0 weff
 nt 1024 wekd wff
 ct 1024 wds wff
 alock n mnt
 gain not used
 flags
 11 n
 1n n
 dp y
 DISPLAY
 sp -1897.8
 wp 18761.7
 vs 214
 sc 0
 wc 400
 hzmm 1.24
 is 500.00
 rf1 7706.0
 rfp 5808.2
 th 10
 fns 1.000
 nm no ph

D:\AL400 NMR\supino\1005 key cyclopentanone.al
 DATE: Tue Oct 07 16:55:53 2003
 CONCENT: 1H
 NAME: NON
 EXMOTO: 399.65 MHz
 OBSERV: 125.00 MHz
 OBSERV: 10500.00 Hz
 POINT: 32738
 FREQU: 7993.50 Hz
 SCANS: 8
 SCANTIME: 4.000 sec
 PD: 2.0010 sec
 PULPROG: zgpg30
 PW: 5.70 usec
 INJULC: 1H
 SFO: 231.0
 CDCL3: 0.00 ppm
 EXREF: 0.12 Hz
 BF: 9
 RGAIN: 9

D:\AL400 NMR\data\13C\13C 1005 key cy
 FILE D:\AL400 NMR\data\13C\13C 1005 key cy
 NAME 13C
 TMS 0.12 Hz
 INJ 100.40 MHz
 OBS 125.00 MHz
 POINT 125.00 MHz
 FREQ 271.7390 Hz
 SCANS 300
 SQT 1289 sec
 PD 1.1500 sec
 PUL 6.10 usec
 INJ 23.9 c
 CDCl3 77.00 ppm
 EXPT 0.12 Hz
 RGAIN 22

PPM E
 COUNT
 DATIM
 1H
 ERMUC
 124.00 MHz
 10500.00 Hz
 32768
 7981.800 Hz
 4.0993 sec
 2.9010 sec
 5.70 usec
 23.4 c
 CDCl₃
 0.00 ppm
 0.12 Hz
 19

FILE DJECAR000u_24augmonovs_1209.130c_2.pro.1
 COUNT 100
 DATE 09-12-2003 23:20:41
 INSTR spect
 OBSRO 13C
 OBSSET 125.002 MHz
 OBSFREQ 125.002 MHz
 FREQ 125.002 MHz
 SCANS 1600
 ACQTIME 0.6921 sec
 PULPROG zgpg30
 INSTRUM spect
 TEMPERATURE 25.2 c
 SOLVENT CDCl3
 EXREF 77.000 ppm
 FIDRES 0.17 Hz
 RGAIN 60

D:\AL400 NMR\Sample\mcs2 27 upper of 1212 dls
 FILE D:\AL400 NMR\Sample\mcs2 27 upper of 1212 dls
 DATE Feb 27 10:15:35 2004
 NAME NON
 EXMOD 399.88 MHz
 OBFRQ 399.88 MHz
 OBSCT 1056000 Hz
 OBENT 1056000 Hz
 POINT 32768
 FREQ 7983.60 Hz
 SCANS 8
 SOLVM 4.000 sec
 PD 2.8010 sec
 PUL 5.770 usec
 PRNUC 1H
 INSTR 21.3 c
 CDOL 0.00 ppm
 SLMNT EXREF
 BF 1.00 Hz
 RGAIN 11

SAMPLE		date		Feb 26 04		DEC. 6 VI	
solvent				CDCl3	dn	dfreq	299,954
file				exp	dmf	dn	1
ACQUISITION							
sfreq				75,431	dm	dmf	0
tn				0.813	dm	dmf	0
at				0.673	dm	dmf	0
mp				32768	dmf	dmf	0
sw				18761.7	dmf	dmf	0
fb				9500	dmf	dmf	0
bs				16	dmf	dmf	0
dv				8.4	dmf	dmf	0
d1				1.127	dmf	dmf	0
tof					dmf	dmf	0
nt				1024	dmf	dmf	0
ct				1024	dmf	dmf	0
alock					dmf	dmf	0
gain					dmf	dmf	0
PROCESSING							
11				1.00	dmf	dmf	0
11				1.00	dmf	dmf	0
11				1.00	dmf	dmf	0
dp				1.00	dmf	dmf	0
DISPLAY							
sp				1889.0	dmf	dmf	0
wp				18761.7	dmf	dmf	0
sc				214	dmf	dmf	0
tc				0	dmf	dmf	0
hzmm				1.34	dmf	dmf	0
1s				500.00	dmf	dmf	0
1f1				7707.2	dmf	dmf	0
1f2				5608.2	dmf	dmf	0
1f3				20	dmf	dmf	0
1f4				1.000	dmf	dmf	0
1f5					dmf	dmf	0
1f6					dmf	dmf	0
1f7					dmf	dmf	0
1f8					dmf	dmf	0
1f9					dmf	dmf	0
1f10					dmf	dmf	0
1f11					dmf	dmf	0
1f12					dmf	dmf	0
1f13					dmf	dmf	0
1f14					dmf	dmf	0
1f15					dmf	dmf	0
1f16					dmf	dmf	0
1f17					dmf	dmf	0
1f18					dmf	dmf	0
1f19					dmf	dmf	0
1f20					dmf	dmf	0
1f21					dmf	dmf	0
1f22					dmf	dmf	0
1f23					dmf	dmf	0
1f24					dmf	dmf	0
1f25					dmf	dmf	0
1f26					dmf	dmf	0
1f27					dmf	dmf	0
1f28					dmf	dmf	0
1f29					dmf	dmf	0
1f30					dmf	dmf	0
1f31					dmf	dmf	0
1f32					dmf	dmf	0
1f33					dmf	dmf	0
1f34					dmf	dmf	0
1f35					dmf	dmf	0
1f36					dmf	dmf	0
1f37					dmf	dmf	0
1f38					dmf	dmf	0
1f39					dmf	dmf	0

FILE D:\ECA600N\24sup\mets\KS_1215_dilal_red.pro
 COUNT 16
 DATE 12-2009 10:11:21
 NAME single pulse ex2
 INSTR 600.17 MHz
 P1 13.00
 POINT 5.47 Hz
 FREQ 13107
 ACQ 9008.87 Hz
 XN 1.455 sec
 PD 5.0000 sec
 PW 6.45 usec
 PRNU 24.1 g
 DMSO CDCl3
 SLVMT 0.00 ppm
 EXREF 1.20 Hz
 BF 44
 RGAIN

D:\ECHO\600N\25aug\mz\13C_difal_bottom.1
 single pulse decoupled gated NDE
 13C
 11-2003 1435227
 single pulse, dec
 150.92 MHz
 8.32 KHz
 32768
 47348.49 Hz
 400
 9.8000 sec
 2.0000 sec
 5.12 usec
 26.3 o
 77.00 ppm
 0.12 Hz
 60
 ROAIN

OPERATOR: K. MUSHIAKE

56 mg
COMPT NON
EXMOD single_pulse.ex
SLVNT CDCL3
BF 0.00 Hz
XE 5941.89 Hz
XS -302.97 Hz
Start 7.8 ppm
End 0.2 ppm
ZF: 0.2 ppm
RT: () 'c

医薬製造化学

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D:\AL400 NMR\data\mol41007.dlbt 13C.h5
 Mon Dec 01 16:02:23 2003
 NAME: 6
 EXPNO: 1
 PROCNO: 1
 F2 - 125.00 MHz
 OBSF2: 125.00 MHz
 OBSF1: 100.000 MHz
 PULPROG: zgpg30
 POINT: 32768
 PRENUC: 13C
 ACQTIME: 271.230 Hz
 ACQTIME: 1.2059 sec
 PD: 1.7940 sec
 P1: 6.10 usec
 P1 DELTA: 25.6 c
 CDECO: 77.00 ppm
 EXREF: 0.12 Hz
 ROAN: ZZ

----- PROCESSING PARAMETERS -----
 seq : 51Hz
 xresol : 0 [%] : 80 [%] : 100 [%]
 yresol : 1
 file : 1 : TRUE

[transpose]
 seq : 51Hz
 xresol : 0 [%] : 80 [%] : 100 [%]
 yresol : 2
 file : 1 : TRUE
 phase correct : TRUE : TRUE
 machinephase
 transpose
 [transpose]

----- ACQUISITION PARAMETERS -----

File Name = chuoct065.2
 Author ID =
 Sample ID =
 Date = 9-OCT-2003 06:08:42
 Creation Date = 9-OCT-2003 08:25:33
 Revision Date = ECA600
 Spec Site =
 Spec Type =
 Data Format = 2D COMPLEX COMPLEX
 Dimensions =
 Dim 1 = 1H
 Dim 2 = 1H
 Dim 3 = 1H
 Dim 4 = 1H
 Experiment =
 Probe ID = 2632
 Temp_get = 24.7 [C]
 Spin_get = 13 [Hz]
 Solvent = CHLOROFORM-D
 Scan_rate = 108
 X_prescan = 4
 Digital Filter = TRUE
 Filter Factor = 4.024
 X_domain = 1H
 X_offset = 4.2 [ppm]
 X_freq = 594.1705168 [MHz]
 X_sweep = 8.91583452 [kHz]
 X_acq_time = 0.11682184 [s]
 X_resolution = 27.85403594 [Hz]
 Y_points = 256
 Y_domain = 1H
 Y_offset = 4.2 [ppm]
 Y_freq = 594.1705168 [MHz]
 Y_sweep = 3.9024 [kHz]
 Y_acq_time = 27.85403594 [Hz]
 Y_resolution = 180
 Relaxation_time = 1.61485184 [s]
 Repetition_time = 1.61485184 [s]
 X_atn = 3.5 [dB]
 Mix_time = 1.9 [s]
 T1_time = 45.8 [s]
 T1 = FALSE
 Dante_presat =
 T1_presat =
 T1_freq = 594.1705168 [MHz]
 T1_offset = 5 [ppm]
 T1_width = 76 [us]
 T1_delay = 0 [us]
 T1_domain = 1H
 T1_freq = 594.1705168 [MHz]
 T1_offset = 5 [ppm]
 T1_width = 76 [us]
 T1_delay = 0 [us]
 T1_domain = 1H
 T1_freq = 594.1705168 [MHz]
 T1_offset = 5 [ppm]
 T1_width = 76 [us]
 T1_delay = 0 [us]
 T1_domain = 1H
 T1_freq = 594.1705168 [MHz]
 T1_offset = 5 [ppm]
 T1_width = 76 [us]
 T1_delay = 0 [us]
 T1_domain = 1H

NOESY spectrum of α -trans-S6

transposed

```
Non_pwidth = 1[us]
```

CC(=C(C1CCCCC1)C2CCCCC2)C(=O)C3CCCCC3

D:\E
 COUNT 26-12-2003 12:12:22
 DATUM 26-12-2003 12:12:22
 OBNUC 1H
 EXMOD single pulse
 EXMOD 2
 OBNUC 1H
 OBSET 5.30 kHz
 POINT 32768
 SCANS 11281.26 Hz
 ACQTM 2.9098 sec
 PD 5.0000 sec
 FID 6.45 usec
 T1 23.9 s
 CTENP 0.00 ppm
 COL3 0.12 Hz
 EXREF 40
 RGAIN

FILE: D:\AL400 NMR\data\mgm05\1228 hydrogenated po
 COUNT: 1000
 DATE: Fri Dec 26 16:26:49 2003
 NAME: 11
 EXPNO: 1
 PROCNO: 1
 F2: 100.62 MHz
 OBSRV: 100.62 MHz
 OBSRV: 100.62 MHz
 FREQ1: 100.62 MHz
 FREQ2: 100.62 MHz
 ACQTM: 1.2059 sec
 PUL: 6.10 usec
 INVC: 22.3 c
 CTEMP: 22.3 c
 SOLVT: CDCl3
 SREF: 77.00 ppm
 BE: 0.03 Hz
 RGAIN: 22