Supporting Information

Highly Enantioselective and Regioselective Copper-Catalyzed 1,4 Addition of Grignard Reagents to Cyclic Enynones

Matthieu Tissot,^a Alexandra Pérez Hernandez,^a Daniel Müller,^a Marc Mauduit^b and Alexandre Alexakis*^a

^a *Department of Organic Chemistry, University of Geneva, 30, quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland*

^b *Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France*

E-mail: Alexandre.Alexakis@unige.ch

1. GENERAL REMARKS	2
2. SYNTHESIS OF ENYNONES	3
3. GENERAL PROCEDURE FOR THE ENANTIOSELECTIVE 1,4 ADDITION OF GRIGNARD REAGENTS.	4
4. TYPICAL PROCEDURE FOR APPLICATIONS	13
5. SPECTRA	14

1. GENERAL REMARKS

All reactions were carried out under argon atmosphere with flame-dried glassware. Solvents were dried over alumina previously activated at 350°C during 12 hours under nitrogen before use. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker 400FTNMR in CDCl_3 and chemical shift (δ) are given in ppm relative to residual CHCl_3 . Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), qd (quartet of doublet), brs (broad singlet). Coupling constants J are reported in Hertz (Hz). Evolution of reaction was followed by GC-MS (EI mode) on an HP6890. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 25°C in a 10 cm cell in the stated solvent; $[\alpha]_D$ values are given in $10^{-1} \text{ deg.cm}^2 \text{ g}^{-1}$ (concentration c given as g/100 mL). Enantiomeric excesses were determined by chiral GC measurement either on a HP6890 (H_2 as vector gas) or HP6850 (H_2 as vector gas) with the stated column. Temperature programs are described as follows: initial temperature (°C) – initial time (min) – temperature gradient (°C/min) – final temperature (°C); retention times (R_T) are given in min. Enantiomeric excesses were in some cases determined by chiral SFC measurement on a Berger SFC with the stated column. Gradient programs are described as follows: initial methanol concentration (%) – initial time (min) – percent gradient of methanol (%/min) – final methanol concentration (%); retention times (R_T) are given in min. Flash chromatography was performed using silicagel 32-63 μm , 60 Å.

2. Synthesis of enynones

Typical procedure : The appropriate alkyne (1.2 eq) was dissolved in dry cold THF (0.7M) and *n*-BuLi (1.2 eq) was slowly added. After stirring for 60 min, the corresponding cyclic enones was added over 5 min. The reaction mixture was stirred at -78 °C for 1h after which time, brine was poured into the cold solution. The aqueous phase was separated, extracted with ether, the combined organic phases were washed with brine, dried over magnesium sulfate, filtered, concentrated in *vacuo*. The crude alcohol can be used without purification depending of the purity¹. Then to a solution of the tertiary alcohol (1eq) in CH₂Cl₂ (0.15M) was added TEMPO (0.02 eq) and NaIO₄ on silicagel (2 eq). After stirring overnight, the filtrate was concentrated in *vacuo* and the residue was purified by flash column chromatography to give the desired enynone².

3-(hex-1-ynyl)cycloheptanone (5)

From cycloheptenone according to General Procedure. The crude product was purified by column chromatography (cyclohexane/ethylacetate 85:15) to afford 40 % yield over 2 steps of **5** as a yellow pale oil.

¹H-NMR: (400 MHz, CDCl₃): δ 0.92 (t, 3H, *J* = 7.1 Hz), 1.39-1.44 (m, 2H), 1.49-1.54 (m, 2H), 1.77-1.84 (m, 4H), 2.34-2.37 (t, 3H, *J* = 6.8 Hz), 2.55-2.60 (m, 4H), 6.22 (s, 1H). ¹³C-NMR: (100 MHz, CDCl₃): 13.6, 19.4, 21.2, 22.0, 25.3, 30.5, 34.6, 42.5, 83.0, 98.8, 135.7, 141.4, 203.2. HRMS (ESI) calcd for C₁₃H₁₈O [M+H]⁺ 191.43, found 191.429.

¹ Spino C.; Beaulieu C. *J. Am. Chem. Soc.* **1998**, *120*, 11832

² Shibuya, M.; Tomizawa, M.; Iwabuchi, Y. *Org. Lett.* **2008**, *10*, 4715

3-(4-(tetrahydro-2H-pyran-2-yloxy)but-1-ynyl)cyclohex-2-enone (1e)

From the corresponding alcohol according to the general protection procedure. The crude product was purified by column chromatography (cyclohexane/ethylacetate 85:15) to afford 60 % yield of **1e** as a yellow pale oil.

¹H-NMR: (400 MHz, CDCl₃): δ 1.49-1.61 (m, 4H), 1.67-1.83 (m, 2H), 1.96-2.02 (m, 2H), 2.36-2.41 (m, 4H), 2.69 (t, 2H, *J* = 8 Hz), 3.48-3.61 (m, 2H), 3.82-3.89 (m, 2H), 4.64 (t, 1H, *J* = 4 Hz), 6.12 (s, 1H). **¹³C-NMR:** (100 MHz, CDCl₃): 19.4, 21.4, 22.6, 25.4, 30.5, 30.7, 37.3, 62.2, 65.2, 81.1, 98.8, 98.9, 132.2, 144.2, 199.0. HRMS (ESI) calcd for C₁₅H₂₀O₃ [M+H]⁺ 249.1485, found 249.1491.

3. General procedure for the enantioselective 1,4 addition of Grignard reagents.

In a dried Schlenk fitted out with stirring bar and septum under nitrogen, Cu(OTf)₂ (5.42 mg, 0.015 mmol, 0.06 eq) and **L1** (7.3 mg, 0.0225 mmol, 0.09 eq) were dissolved in dry CH₂Cl₂ (0.75 mL). The mixture was cooled to -10°C and after few minutes, the Grignard reagent (2eq) was added. After stirring for 5 minutes, a solution of enynone (substrate) (44.05 mg, 0.25 mmol, 1 eq) in dry CH₂Cl₂ (2.5 mL) was added with a syringe pump over 15 minutes. The reaction mixture was stirred 1 h at -10°C and NH₄Cl-solution (0.5 mL, 1M) were added. The mixture was warmed at room temperature and 5 mL of CH₂Cl₂ were added. The layers were separated. After extraction with CH₂Cl₂ (2 x 5 mL), the combined organic extracts were dried over MgSO₄, filtered and evaporated. The crude mixture was purified.

In some case, the conditions change, therefore to get more information see below.

3-ethyl-3-(hex-1-yn-1-yl)cyclohexanone (**2a**)

The solution of $\text{Cu}(\text{OTf})_2$ and **L1** was more diluted. In fact, 1.5 mL and 5 mL of dry CH_2Cl_2 were added. Moreover, the substrate was added over 30 minutes.

The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.037g (72%) of **2a** as a yellow pale oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 78.24, 78.98. $[\alpha]_D^{25} = +50.08$ (c 1, CHCl_3) for 82% of ee.

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 0.87 (t, $J = 7.08$ Hz, 3H), δ 1.00 (t, $J = 7.36$ Hz, 3H), δ 1.3-1.5 (m, 7H), δ 1.8-1.99 (m, 2H), δ 2-2.2 (m, 5H), δ 2.23-2.4 (m, 1H), δ 2.4-2.55 (d, $J = 2.04$ Hz, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): δ 8.8, 13.6, 18.3, 21.8, 22.8, 31.1, 35.1, 35.9, 40.8, 41, 52.8, 82.2, 85, 210.1.

HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ $[\text{M}+\text{Na}]^+$ 229.1564, found 229.1564.

3-(but-3-en-1-yl)-3-(hex-1-yn-1-yl)cyclohexanone (**2b**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.052g (90%) of **2b** as a yellow pale oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 95.99, 96.41. $[\alpha]_D^{25} = +32.8$ (c 1, CHCl_3) for 95% of ee.

$^1\text{H-NMR}$: (500 MHz, CDCl_3): δ 0.88 (t, $J = 7.25$ Hz, 3H), δ 1.3-1.45 (m, 4H), δ 1.5-1.65 (m, 3H), δ 1.8-2.0 (m, 2H), δ 2.02-2.2 (m, 7H), δ 2.35 (m, 1H), δ 2.45 (d, $J = 13.55$ Hz, 1H), δ 5 (m, 2H), δ 5.8 (m, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): δ 13.6, 18.3, 21.8, 22.7, 28.9, 31.1, 36.3, 40.2, 41.0, 41.6, 53.1, 82.0, 85.4, 114.6, 138.5, 209.7. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{24}\text{O}$ $[\text{M}+\text{Na}]^+$ 255.1719, found 255.1719.

3-(hex-1-yn-1-yl)-3-isopropylcyclohexanone (**2c**)

The ether of the Grignard reagent was substituted by CH_2Cl_2 . The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.033g (60%) of **2c** as a colorless oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 85.48, 86.85. $[\alpha]_D^{25} = +56.8$ (*c* 1, CHCl_3) for 92% of ee.

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 0.87 (t, $J = 1.52$ Hz, 3H), 1 (m, 6H), 1.3-1.45 (m, 4H), 1.5-1.6 (m, 2H), 1.89-2 (m, 2H), 2.05-2.2 (m, 5H), 2.3 (m, 1H), 2.5 (d, $J = 2.04$ Hz, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): δ 13.6, 17.7, 18.1, 18.3, 21.8, 22.8, 31.2, 33.9, 37.3, 40.9, 44.5, 51.0, 80.8, 85.8, 210.5. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}$ $[\text{M}+\text{Na}]^+$ 243.3402, found 243.3400.

3-(hex-1-yn-1-yl)-3-isobutylcyclohexanone (**2d**)

The ether of the Grignard reagent was substituted by CH_2Cl_2 . The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.051g (88%) of **2d** as a yellow pale oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 90.44, 90.74. $[\alpha]_D^{25} = +48.3$ (*c* 1, CHCl_3) for 95% of ee.

$^1\text{H-NMR}$: (500 MHz, CDCl_3): 0.87 (t, $J = 7.25$ Hz, 3H), 0.97 (m, 6H), 1.3-1.48 (m, 6H), 1.5-1.65 (m, 1H), 1.8-1.99 (m, 3H), 2.03-2.2 (m, 5H), 2.21-2.4 (m, 1H), 2.5 (d, $J = 1.9$ Hz, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): 13.6, 18.3, 21.8, 22.6, 24.62, 24.66, 24.9, 31.0, 37.0, 39.9, 40.9, 51.1, 53.8, 82.7, 85.1, 210. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{26}\text{O}$ $[\text{M}+\text{Na}]^+$ 257.1876, found 247.1876.

3-(3,3-dimethylbut-1-yn-1-yl)-3-methylcyclohexanone (**2f**)

The solution of $\text{Cu}(\text{OTf})_2$ and **L1** was more diluted. In fact, 1.5 mL and 5 mL of dry CH_2Cl_2 were added. Moreover, the substrate was added over 30 minutes and 13 mol. % of **L1** were added. The crude mixture was purified by column chromatographic (ethylacetate/cyclohexane 0.5:9.5) to afford 0.014g (29%) of **2f** an colorless oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 41.53, 43.00. $[\alpha]_D^{25} = +27.3$ (c 1, CHCl_3) for 83% of ee.

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 1.1 (s, 9H), 1.2 (s, 3H), 1.55-1.7 (m, 2H), 1.79-1.99 (m, 2H), 2.02-2.2 (m, 2H), 2.3 (m, 1H), 2.4 (m, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): 22.9, 29.7, 30.3, 31.3, 35.9, 38.0, 40.6, 54.7, 82.0, 92.6, 209.7. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{20}\text{O}$ $[\text{M}+\text{Na}]^+$ 215.2870, found 215.2870.

3-(3,3-dimethylbut-1-yn-1-yl)-3-ethylcyclohexanone (**2g**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.046g (82%) of **2g** as a colorless oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 116.03, 116.50. $[\alpha]_D^{25} = +36.5$ (c 1, CHCl_3) for 79% of ee.

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 0.9 (t, $J = 7.32$ Hz, 3H), 1.1 (s, 9H), 1.2-1.28 (m, 1H), 1.4-1.55 (m, 2H), 1.8-1.95 (m, 2H), 2-2.2 (m, 3H), 2.3 (m, 1H), 2.4 (m, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): δ 8.8, 22.8, 27.3, 31.3, 35.0, 35.9, 40.5, 41.0, 52.8, 80.4, 94.1, 210.0. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ $[\text{M}+\text{Na}]^+$ 229.1563, found 229.1561.

3-(3,3-dimethylbut-1-yn-1-yl)-3-isopropylcyclohexanone (**2h**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.031g (57%) of **2h** as a yellow pale oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 60.76, 63.41. $[\alpha]_D^{25} = +45.2$ (c 1, CH_3Cl) for 87% of ee.

$^1\text{H-NMR}$: (500 MHz, CDCl_3): δ 0.96 (q, $J = 6.65$ Hz, 6H), 1.1 (s, 9H), 1.48-1.52 (m, 1H), 1.55-1.65 (m, 1H), 1.85-1.98 (m, 2H), 2-2.1 (m, 1H), 2.1-2.2 (m, 2H), 2.3 (m, 1H), 2.4 (m, 1H). **$^{13}\text{C-NMR}$** : (400 MHz, CDCl_3): 17.6, 18.0, 22.7, 27.4, 31.3, 33.9, 37.1, 40.9, 44.1, 51.0, 79.1, 94.8, 210.4. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}$ $[\text{M}]^-$ 220.1827, found 220.1830.

3-(3,3-dimethylbut-1-yn-1-yl)-3-isobutylcyclohexanone (**2i**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.051g (87%) of **2i** as a yellow pale oil/solid. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 68.92, 69.95. $[\alpha]_D^{25} = +39.4$ (c 1, CH_2Cl_2) for 93% of ee.

$^1\text{H-NMR}$: (500 MHz, CDCl_3): δ 0.96 (t, $J = 6.3$ Hz, 6H), 1.1 (s, 9H), 1.3-1.4 (m, 2H), 1.45-1.55 (m, 1H), 1.8-1.95 (m, 3H), 2-2.1 (m, 1H), 2.1-2.23 (m, 2H), 2.3 (m, 1H), 2.4 (d, $J = 13.25$ Hz, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): δ 22.6, 24.56, 24.57, 24.9, 27.3, 31.0, 31.1, 37.0, 39.5, 40.9, 51.0, 53.8, 81.1, 93.9, 209.9. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{26}\text{O}$ $[\text{M}+\text{Na}]^+$ 257.1876, found 257.1879.

3-isobutyl-3-((trimethylsilyl)ethynyl)cyclohexanone (**2j**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.061g (98%) of **2j** as a yellow oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 72.12, 72.80. $[\alpha]_D^{25} = +40.4$ (c 1, CH_3Cl) for 95% of ee.

¹H-NMR: (400 MHz, CDCl₃): δ 0.08 (s, 9H), 0.9 (m, 6H), 1.35-1.45 (m, 2H), 1.5-1.6 (m, 1H), 1.8-1.95 (m, 3H), 2.0-2.1 (m, 1H), 2.1-2.2 (m, 2H), 2.3 (m, 1H), 2.4 (m, 1H). **¹³C-NMR:** (100 MHz, CDCl₃): 0.04, 22.4, 24.50, 24.53, 24.9, 36.6, 40.4, 40.8, 50.3, 53.2, 88.9, 109.6, 209.2. HRMS (EI) calcd for C₁₅H₂₆OSi [M+Na]⁺ 273.1645, found 273.1648.

3-(but-3-enyl)-3-(2-(trimethylsilyl)ethynyl)cyclohexanone (2k)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.045g (72%) of **2k** as a colorless oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T: 76.32, 76.97. [α]_D²⁰ = +34.9 (*c* 1, CH₃Cl) for 91% of ee.

¹H-NMR: (400 MHz, CDCl₃): δ 0.10 (s, 9H), 1.54-1.63 (m, 3H), 1.90-1.97 (m, 2H), 2.02-2.24 (m, 5H), 2.35-2.38 (d, 1H, *J* = 12 Hz), 2.50 (d, 1H, *J* = 12 Hz), 5.95-5.06 (m, 2H), 5.78-5.88 (m, 1H). **¹³C-NMR:** (100 MHz, CDCl₃): 0.14, 22.53, 28.9, 35.9, 40.7, 40.9, 52.6, 89.2, 108.6, 114.7, 138.3, 209.0. HRMS (EI) calcd for C₁₅H₂₄OSi [M-H] 247.1518, found 247.1517.

(S)-3-cyclohexyl-3-(2-(trimethylsilyl)ethynyl)cyclohexanone (2l)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.045g (72%) of **2k** as a white solid. The enantiomeric excess was determined by GC on a chiral stationary phase (Hydrodex B-3P, method: 60-0-1-170-5, 45 cm/s), R_T: 96.05, 96.62. [α]_D²⁰ = +19.1 (*c* 1, CH₃Cl) for 96% of ee.

¹H-NMR: (400 MHz, CDCl₃): δ 0.11 (s, 9H), 1.10-1.27 (m, 6H), 1.53-1.67 (m, 3H), 1.77-1.86 (m, 4H), 1.91-1.96 (m, 2H), 2.05-2.09 (m, 2H), 2.21 (d, 1H, *J* = 16 Hz), 2.36 (d, 1H, *J* = 16 Hz), 2.47 (d, 1H, *J* = 12 Hz). **¹³C-NMR:** (100 MHz, CDCl₃): 0.2, 22.5, 26.4, 26.6, 26.6, 27.4, 27.7, 35.9, 33.3, 41.0, 44.7, 46.6, 50.4, 89.7, 108.5, 210.0. HRMS (ESI) calcd for C₁₅H₂₄OSi [M-H] 277.1982, found 277.1985.

3-isobutyl-3-(2-phenylethynyl)cyclohexanone(2m)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.051g (81%) of **2m** as a yellow pale oil. The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 111.10, 111.74. $[\alpha]_D^{20} = +51.7$ (*c* 1, CH₃Cl) for 94% of ee.

¹H-NMR: (400 MHz, CDCl₃): 1.02-1.05 (m, 6H), 1.53 (m, 1H), 1.68 (m, 1H), 1.95-2.05 (m, 2H), 2.16-2.31 (m, 3H), 2.42 (d, *J* = 13.8 Hz, 1H), 2.63 (d, *J* = 13.8 Hz, 1H), 7.25-7.41 (m, 5H). **¹³C-NMR**: (100 MHz, CDCl₃): 22.7, 24.5, 24.6, 25.1, 26.7, 36.9, 40.4, 41.0, 50.7, 53.4, 85.1, 92.6, 123.4, 127.9, 128.2, 131.6. HRMS (EI) calcd for C₁₈H₂₂O [M]⁺ 254.1671, found 254.1673.

3-(but-3-enyl)-3-(2-phenylethynyl)cyclohexanone (**2n**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.055g (87%) of **2n** as a yellow pale oil. The enantiomeric excess was determined

by SFC on a chiral stationary phase (Chiralcel OD column, method: MeOH 0%-2-1-15, 5°C), R_T : 05.15, 05.67. $[\alpha]_D^{20} = +50.4$ (c 1, CH_3Cl) for 95% of ee.

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 1.67-1.73 (m, 3H), 1.97-2.44 (m, 7H), 2.60-2.64 (d, $J = 13.6$ Hz, 1H), 4.98-5.10 (dd, 1H, $J = 13.6$ Hz), 5.82-5.81 (m, 1H), 7.27-7.28 (m, 3H), 7.35-7.38 (m, 2H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): 22.8, 27.0, 29.0, 36.2, 40.8, 41.0, 41.3, 52.8, 85.3, 91.7, 114.9, 123.2, 128.2, 128.3, 131.6, 138.3. HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ $[\text{M-H}]$ 251.1436, found 251.1433.

(3R)-3-(but-3-enyl)-3-(4-(tetrahydro-2H-pyran-2-yloxy)but-1-ynyl)cyclohexanone. (**2o**)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.055g (79%) of **2n** as a yellow pale oil. The enantiomeric excess was determined on the

deprotected alcohol (see below). $[\alpha]_D^{20} = +50.4$ (c 1, CH_3Cl) for 96% of ee

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 1.47-1.73 (m, 9H), 1.78-1.85 (m, 1H), 1.90-1.95 (m, 2H), 2.04-2.24 (m, 5H), 2.35-2.48 (m, 3H), 3.44-3.52 (m, 2H), 3.72-3.78 (m, 1H), 3.83-3.88 (m, 1H), 4.61 (s, 1H), 4.94-5.05 (m, 2H), 5.77-5.87 (m, 1H). **$^{13}\text{C-NMR}$** : (100 MHz, CDCl_3): 19.4, 20.2, 22.7, 25.5, 28.9, 30.6, 36.2, 40.2, 41.0, 41.5, 53.0, 62.1, 66.1, 82.0, 83.1, 98.8, 114.6, 138.4, 209.5. HRMS (EI) calcd for $\text{C}_{19}\text{H}_{28}\text{O}_3$ $[\text{M}+\text{Na}]^+$ 324.4136, found 324.4138.

(R)-3-(but-3-enyl)-3-ethynylcyclohexanone (2p)

¹H-NMR: (400 MHz, CDCl₃): δ 1.56-1.64 (m, 3H), 1.92-1.98 (m, 2H), 2.05-2.13 (m, 1H), 2.18-2.26 (m, 5H), 2.34-2.39 (m, 1H), 2.50 (d, 1H, *J* = 12.0 Hz), 4.93-5.05 (m, 2H), 5.75-5.85 (m, 1H). **¹³C-NMR:** (100 MHz, CDCl₃): 22.5, 28.7, 35.8, 40.0, 40.9, 41.0, 52.6, 72.9, 86.3, 114.9, 138.0, 209.0. HRMS (EI) calcd for C₁₂H₁₆O [M]⁺ 176.1201, found 176.1189. [α]_D²⁰ = +26.4 (*c* 1, CH₃Cl)

3-(but-3-enyl)-3-(hex-1-ynyl)cycloheptanone (6)

The reaction was performed in the standard conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 3:7) to afford 0.041g (67%) of **6** an colorless oil . The enantiomeric excess was determined by GC on a chiral stationary phase (HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), *R*_T: 96.45, 96.76. [α]_D²⁰ = +84.0 (*c* 1, CH₃Cl) for 97% of ee.

¹H-NMR: (400 MHz, CDCl₃): δ 0.89 (t, 3H, *J* = 7.3 Hz), 1.34-1.51 (m, 8H), 1.82-1.96 (m, 4H), 2.14-2.23 (m, 4H), 2.58-2.63 (m, 4H), 4.93-5.04 (m, 2H), 5.76-5.86 (m, 1H). **¹³C-NMR:** (100 MHz, CDCl₃): 13.6, 18.4, 22.0, 24.1, 26.5, 29.2, 31.2, 36.7, 42.6, 43.1, 43.8, 55.0, 82.4, 85.8, 114.5, 138.5, 212.4. HRMS (EI) calcd for C₁₇H₂₆O [M-H] 245.1905, found 245.1907.

3-(but-3-enyl)-3-(4-hydroxybut-1-ynyl)cyclohexanone.

The deprotection was performed in the classical conditions. The crude mixture was purified by quick filtration on a silica pad (ethylacetate/cyclohexane 5:5) to afford 0.041g (67%) of **6** an colorless oil .

¹H-NMR: (400 MHz, CDCl₃): δ 1.48-1.58 (m, 3H), 1.85-2.18 (m, 3H), 2.20-2.24 (m, 4H), 2.30-2.42 (m, 4H), 2.56 (brs, 1H), 3.60 (t, 2H, *J* = 8.0 Hz), 4.91-5.01 (m, 2H), 5.73-5.82 (m, 1H). **¹³C-NMR:** (100 MHz, CDCl₃): 23.10, 23.13, 28.9, 36.1, 40.8, 41.1, 41.3, 53.3, 61.3, 82.5, 83.9, 114.7, 138.2, 210.6. HRMS (EI) calcd for C₁₅H₂₀O₂ [M-H] 219.1385, found 219.1386. The enantiomeric excess was determined by GC on a chiral stationary phase

(HYDRODEX B-6-TBDM column, method: 60-0-1-170-5, 45 cm/s), R_T : 39.67, 40.39. $[\alpha]_D^{20} = +38.7$ (c 1, CH_3Cl) for 96% of ee.

4. Typical procedure for application

Substrate (6a-b) was dissolved in degassed CH_2Cl_2 (5 mL) and Grubbs 1st generation catalyst (1.0 mol% per hour during 5 h) was added to the solution. The mixture was refluxed under an ethylene atmosphere (1 atm, balloon) until full conversion was reached, as judged by TLC. The mixture was concentrated under reduced pressure and purified by column chromatography to yield the desired products 8a-b as a colourless oils.

1-vinylspiro[4.5]dec-1-en-7-one (7)

Substrate **2p** (0.25 mmol) was dissolved in degassed CH_2Cl_2 (5 mL) and Grubbs 1st generation catalyst (1.0 mol% per hour during 5 h) was added to the solution. The mixture was stirred at rt under an ethylene atmosphere (1 atm, balloon) during 2 hours. The mixture was concentrated under reduced pressure and purified by column chromatography to yield (65%) the desired product as a colorless oil.

$^1\text{H-NMR}$: (400 MHz, CDCl_3): δ 1.53 (m, 1H), 1.62-1.69 (m, 1H), 1.72-1.84 (m, 2H), 1.99-2.12 (m, 3H), 2.24-2.37 (m, 4H), 2.56 (d, 1H, $J = 16.0$ Hz), 5.09 (d, 1H, $J = 12.0$ Hz), 5.44 (d, 1H, $J = 16.0$ Hz), 5.79 (s, 1H), 6.18-6.25 (dd, 1H, $J_1 = 12.0$ Hz, $J_2 = 16.0$ Hz). $^{13}\text{C-NMR}$: (100 MHz, CDCl_3): 23.3, 29.4, 34.4, 35.4, 41.3, 50.3, 53.8, 115.1, 128.2, 130.5, 146.9, 211.7. HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 176.1201, found 176.1200. $[\alpha]_D^{20} = -43.8$ (c 1, CH_3Cl)

(1R)dimethyl 3-oxo-2',3',3a',6'-tetrahydrospiro[cyclohexane-1,1'-indene]-4',5'-dicarboxylate (8)

7 (0.25 mmol) was dissolved in degassed CH_2Cl_2 (5 mL) and

DMAD was added to the solution. The mixture was stirred at rt overnight. The mixture was concentrated under reduced pressure and purified by column chromatography (ethylacetate/cyclohexane 7:3) to yield the desired product as a yellow pale oil (67%).

NMR: The NMR are not detailed (see spectrum below). HRMS (EI) calcd for $C_{12}H_{16}O$ $[M+Na]^+$ 341.3540, found 341.3542. $[\alpha]_D^{20} = -25.2$ (c 1, CH_3Cl)

dimethyl 3-oxo-2',3'-dihydrospiro[cyclohexane-1,1'- indene]-4',5'-dicarboxylate (9)

Substrate **8p** (0.25 mmol) was dissolved in degassed CH_2Cl_2 (2 mL) and DDQ was added to the solution. The mixture was stirred at rt overnight. The mixture was concentrated under reduced pressure and purified by column chromatography to yield the desired product as a red oil (95%).

1H -NMR: (400 MHz, $CDCl_3$): δ 1.73-1.77 (m, 1H), 1.86-1.91 (m, 1H), 1.97 (q, 2H, $J_1 = 13.8$ Hz, $J_2 = 6.8$ Hz), 2.03-2.10 (m, 2H), 2.36 (d, 1H, $J = 13.8$ Hz), 2.44 (m, 2H), 2.50 (d, 1H, $J = 13.8$ Hz), 2.95 (t, 2H, $J = 7.3$ Hz), 3.87 (s, 3H), 3.91 (s, 3H), 7.26 (d, 1H, $J = 8.0$ Hz), 7.79 (d, 1H, $J = 8.0$ Hz). **^{13}C -NMR:** (100 MHz, $CDCl_3$): 22.9, 28.5, 35.5, 36.5, 41.2, 51.8, 52.2, 52.3, 52.6, 123.8, 127.9, 128.9, 131.32, 141.7, 154.3, 166.7, 169.0, 210.1. HRMS (EI) calcd for $C_{12}H_{16}O$ $[M+Na]^+$ 339.12029, found 339.12010. $[\alpha]_D^{20} = -25.2$ (c 1, CH_3Cl)

5. Spectra

2a

2a

13C CPD-Spectrum

File : C:\MSDCHEM\2\DATA\mt557b.D
 Operator : JB
 Acquired : 28.10.2010 11:35:15 AM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: mt557b
 Misc Info :
 Vial Number: 3

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : mt557b.D
 Signal(s) : FID1A.CH
 Acq On : 28.10.2010 11:35:15 AM
 Sample : mt557b
 Misc :
 ALS Vial : 3 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	78.240	78.032	78.649	M	142724	14381431	10.03%	9.115%
2	78.976	78.750	80.245	M	957119	143396976	100.00%	90.885%
Sum of corrected areas:						157778407		

F60-1.M Fri Dec 10 08:19:50 2010

2b

209.7404

138.5355

114.5855

85.4178

82.0219

53.1603

41.6462

41.0231

40.2142

36.3446

31.1050

28.9771

22.7646

21.8756

18.3485

13.6226

```

*** Current Data Parameters ***
NAME      : ap055p2
EXPNO     : 2
PROCNO    : 1
*** Processing Parameters ***
SF        : 125.757890 MHz

```

2b

File : C:\MSDCHEM\2\DATA\MT491P.D
 Operator : GL
 Acquired : 30.06.2010 11:37:50 AM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: MT491P
 Misc Info :
 Vial Number: 1

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : MT491P.D
 Signal(s) : FID1A.CH
 Acq On : 30.06.2010 11:37:50 AM
 Sample : MT491P
 Misc :
 ALS Vial : 1 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	95.996	95.804	96.176	M	44740	4420965	3.28%	3.174%
2	96.414	96.188	97.689	M	960213	134876145	100.00%	96.826%
Sum of corrected areas:						139297110		

F60-1.M Fri Dec 10 08:21:26 2010

2c

¹³C CPD-Spectrum

```

*** Current Data Parameters ***
NAME      :  ap035p2
EXPNO     :  2
PROCNO    :  1
*** Processing Parameters ***
SF         :  100.6127690 MHz
  
```

2c

File : C:\MSDCHEM\2\DATA\AP035.D
 Operator : JB
 Acquired : 19.04.2010 01:49:37 PM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name : AP035
 Misc Info :
 Vial Number: 1

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : AP035.D
 Signal(s) : FID1A.CH
 Acq On : 19.04.2010 01:49:37 PM
 Sample : AP035
 Misc :
 ALS Vial : 1 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	85.481	85.273	85.696	M	32897	3260969	3.96%	3.810%
2	86.846	86.653	88.178	M	688607	82321487	100.00%	96.190%
Sum of corrected areas:						85582456		

F60-1.M Fri Dec 10 07:35:55 2010

2d

C13CPD

```

*** Current Data Parameters ***
NAME      : ap034p2
EXPNO     : 2
PROCNO    : 1
*** Processing Parameters ***
SF         : 125.757890 MHz
  
```

File : C:\MSDCHEM\2\DATA\AP034P.D
 Operator : JB
 Acquired : 16.04.2010 02:23:02 PM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: AP034P
 Misc Info :
 Vial Number: 2

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : AP034P.D
 Signal(s) : FID1A.CH
 Acq On : 16.04.2010 02:23:02 PM
 Sample : AP034P
 Misc :
 ALS Vial : 2 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	90.439	90.277	90.552	M	45852	4001498	2.71%	2.641%
2	90.745	90.562	92.147	M	1052472	147522488	100.00%	97.359%
Sum of corrected areas:						151523986		

F60-1.M Fri Dec 10 07:34:19 2010

*** Current Data Parameters ***
 NAME : ap043pp
 EXPNO : 1
 PROCNO : 1
 *** Processing Parameters ***
 SF : 400.1300220 MHz

2.4326
 2.4275
 2.4042
 2.3991
 2.3941
 2.3739
 2.3707
 2.3656
 2.3461
 2.3417
 2.3385
 2.3341
 2.3303
 2.3271
 2.2267
 2.2135
 2.2110
 2.1990
 2.1971
 2.1832
 2.1807
 2.1604
 2.1579
 2.1478
 2.1270
 2.1245
 2.0897
 2.0809
 2.0721
 2.0594
 2.0506
 2.0386
 1.9439
 1.9344
 1.9275
 1.9186
 1.9098
 1.9010
 1.8940
 1.8852
 1.8770
 1.8725
 1.8637
 1.8397
 1.8353
 1.8309
 1.5449
 1.5360
 1.5158
 1.5127
 1.5064
 1.4969
 1.4887
 1.4824
 1.4779
 1.4704
 1.4590
 1.4521
 1.2626
 1.2437
 1.2260
 1.2140
 1.2033
 1.1976
 1.1907
 1.1774
 1.1692
 1.1484
 1.1351
 1.1338
 1.1218
 0.9918
 0.9735
 0.9545

2g

¹³C CPD-Spectrum

```

*** Current Data Parameters ***
NAME      : ap045pp
EXPNO     : 2
PROCNO    : 1
*** Processing Parameters ***
SF        : 100.6127690 MHz
  
```

2g

File : C:\MSDCHEM\2\DATA\MT559-2.D
 Operator : JB
 Acquired : 01.11.2010 08:32:20 AM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: MT559-2
 Misc Info :
 Vial Number: 1

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : MT559-2.D
 Signal(s) : FID1A.CH
 Acq On : 01.11.2010 08:32:20 AM
 Sample : MT559-2
 Misc :
 ALS Vial : 1 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1116.027	115.672	116.199		M	151559	21171253	11.90%	10.637%
2116.505	116.220	117.219		M	1071454	177856975	100.00%	89.363%
Sum of corrected areas:						199028228		

F60-1.M Fri Dec 10 08:23:17 2010

2h

1H Spectrum

*** Current Data Parameters ***
 NAME : ap050p
 EXPNO : 1
 PROCNO : 1
 *** Processing Parameters ***
 SF : 500.1300290 MHz

*** Current Data Parameters ***
NAME : ap050p
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 125.757890 MHz

2h

File :C:\MSDCHEM\2\DATA\AP050.D
 Operator : JB
 Acquired : 04.05.2010 11:57:07 AM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: AP050
 Misc Info :
 Vial Number: 2

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : AP050.D
 Signal(s) : FID1A.CH
 Acq On : 04.05.2010 11:57:07 AM
 Sample : AP050
 Misc :
 ALS Vial : 2 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	60.762	60.555	61.013	M	55603	6005183	6.91%	6.464%
2	63.407	63.181	63.830	M	769638	86900775	100.00%	93.536%
Sum of corrected areas:						92905958		

F60-1.M Fri Dec 10 07:39:28 2010

2i

¹H Spectrum

209.9444

93.9732

81.1511

53.8526

51.0068

40.9758

39.5511

37.0515

31.1852

31.0613

27.3630

24.9472

24.5792

24.5683

22.6480

*** Current Data Parameters ***

NAME : ap049p

EXPNO : 2

PROCNO : 1

*** Processing Parameters ***

SF : 125.757890 MHz

File :C:\MSDCHEM\2\DATA\AP049P.D
 Operator : JB
 Acquired : 03.05.2010 01:35:58 PM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: AP049P
 Misc Info :
 Vial Number: 2

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : AP049P.D
 Signal(s) : FID1A.CH
 Acq On : 03.05.2010 01:35:58 PM
 Sample : AP049P
 Misc :
 ALS Vial : 2 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	68.916	68.746	69.098	M	20859	2016071	3.71%	3.573%
2	69.951	69.738	70.323	M	544572	54408763	100.00%	96.427%
Sum of corrected areas:						56424834		

F60-1.M Fri Dec 10 07:37:36 2010

2j

2j

File :C:\MSDCHEM\2\DATA\AP064.D
 Operator : DM
 Acquired : 18.05.2010 02:59:54 PM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: AP064
 Misc Info :
 Vial Number: 6

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : AP064.D
 Signal(s) : FID1A.CH
 Acq On : 18.05.2010 02:59:54 PM
 Sample : AP064
 Misc :
 ALS Vial : 6 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	72.116	71.950	72.284	M	18477	1652410	2.90%	2.819%
2	72.796	72.567	73.225	M	575274	56959432	100.00%	97.181%
Sum of corrected areas:						58611842		

F60-1.M Fri Dec 10 07:41:02 2010

2k

2k

File :C:\MSDCHEM\2\DATA\MT533B.D
 Operator : JB
 Acquired : 21.09.2010 03:21:31 PM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: MT533B
 Misc Info :
 Vial Number: 2

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : MT533B.D
 Signal(s) : FID1A.CH
 Acq On : 21.09.2010 03:21:31 PM
 Sample : MT533B
 Misc :
 ALS Vial : 2 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	76.316	76.147	76.506	M	11530	1176104	4.82%	4.595%
2	76.969	76.730	77.447	M	246584	24417187	100.00%	95.405%
Sum of corrected areas:						25593291		

F60-1.M Fri Dec 10 08:26:43 2010

21

21

HYDRODEX B-3P 60-1 45cm/s

```
=====
Injection Date   : 21-Dec-10 5:50:53 PM
Sample Name      : MT617
Acq. Operator    : MT
Location         : Vial 2
Inj              : 1
Inj Volume       : 1 µl

Acq. Method      : C:\HPCHEM\3\METHODS\60-1.M
Last changed     : 20-Feb-09 8:38:58 AM by DM
Analysis Method  : C:\HPCHEM\3\METHODS\60-1.M
Last changed     : 22-Dec-10 9:34:24 AM by MT
                  (modified after loading)
=====
```

```
=====
Area Percent Report
=====
```

```
Sorted By      : Signal
Calib. Data Modified : Wednesday, October 24, 2007 10:23:09 AM
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	23.349		0.0000	0.00000	0.00000	
2	24.031		0.0000	0.00000	0.00000	
3	96.049	MM	0.1806	135.43921	1.84503 ?	
4	96.622	MM	0.3498	7205.30664	98.15497 ?	

Totals : 7340.74585

Results obtained with enhanced integrator!
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found

2m

¹³C CPD-Spectrum

*** Current Data Parameters ***
 NAME : m490p
 EXPNO : 2
 PROCNO : 1
 *** Processing Parameters ***
 SF : 100.6127690 MHz

File : C:\MSDCHEM\2\DATA\MT490P2.D
 Operator : JB
 Acquired : 28.06.2010 01:12:55 PM using AcqMethod F60-1.M
 Instrument : GC CHIRAL
 Sample Name: MT490P2
 Misc Info :
 Vial Number: 1

94 %

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : MT490P2.D
 Signal(s) : FID1A.CH
 Acq On : 28.06.2010 01:12:55 PM
 Sample : MT490P2
 Misc :
 ALS Vial : 1 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M

Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max	% of total
1111.103	110.777	111.270		M	5651	1007916	3.16%	3.066%
2111.738	111.296	112.588		M	139785	31867372	100.00%	96.934%
Sum of corrected areas:						32875289		

F60-1.M Mon Jun 28 17:34:54 2010

2n

$$2n$$

Chromatogram : mt489-21_channel1

System : SFC
Method : S2-OD
User : SFC Admin

Acquired : 6/30/2010 11:56:14 AM
Processed : 6/30/2010 12:50:02 PM
Printed : 6/30/2010 12:50:15 PM

Peak results :

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	5.15	5.34	5.67	0.00	96.56	380.5	71.2	96.555
2	UNKNOWN	5.67	5.87	6.06	0.00	3.44	17.8	2.5	3.445
Total						100.00	398.3	73.8	100.000

2o

2o

6

6

¹³C CPD-Spectrum

— 212.4328

*** Current Data Parameters ***
 NAME : m500p2
 EXPNO : 2
 PROCNO : 1
 *** Processing Parameters ***
 SF : 100.6127690 MHz

CHIRASIL DEX-CB 60-1-170-5.M

```

=====
Injection Date   : 08-Jul-10 9:42:36 AM
Sample Name      : MT500B
Acq. Operator    : MT
Location         : Vial 1
Inj              : 1
Inj Volume       : 1 µl

Acq. Method      : C:\HPCHEM\1\METHODS\60-1.M
Last changed     : 02-Jul-09 3:36:37 PM by OJ
Analysis Method  : C:\HPCHEM\1\METHODS\60-1.M
Last changed     : 08-Jul-10 12:41:23 PM by MT
                  (modified after loading)
=====

```

```

=====
Area Percent Report
=====

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	96.455	MM	0.1272	37.06460	4.85547	1.72735
2	96.764	MM	0.2310	2108.68481	152.13057	98.27265

Totals : 2145.74941 156.98604

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

2p

2p

File : C:\MSDCHEM\2\DATA\mt523P.D
 Operator : JB
 Acquired : 07.09.2010 02:30:42 PM using AcqMethod F140-1-170-12.M
 Instrument : GC CHIRAL
 Sample Name: mt523P
 Misc Info :
 Vial Number: 1

Area Percent Report

Data Path : C:\MSDCHEM\2\DATA\
 Data File : mt523P.D
 Signal(s) : FID1A.CH
 Acq On : 07.09.2010 02:30:42 PM
 Sample : mt523P
 Misc :
 ALS Vial : 1 Sample Multiplier: 1

Integration File: events.e

Method : C:\MSDCHEM\2\METHODS\F60-1.M
 Title :

Signal : FID1A.CH

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	39.673	39.205	39.860	M	3734	879140	2.02%	1.980%
2	40.385	39.881	42.585	M	93491	43521555	100.00%	98.020%
Sum of corrected areas:							44400695	

F60-1.M Fri Dec 10 08:28:59 2010

7

7

8

9

9

9