SUPPORTING INFORMATION

**Title:** Interaction of Dihydropyridines and Nucleophiles with Carbene Complexes of Chromium: Diastereo- and Enantioselective Synthesis of Polycyclic Butenolides

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I- PREPARATION OF THE CARBENE COMPLEXES

A- CARBENE COMPLEXES BEARING THE TRIPLE BOND IN THE ALKYL CHAIN

1- Preparation of the carbene complexes 37 and 48 ab

General procedure

To a solution of the corresponding iodide (1.0 eq) under Argon at –78°C in diethyl ether (7 mL/mmol of iodide) and pentane (10 mL/mmol of iodide) was added by syringe t-butylithium (2.1 eq of a 1.7 M hexane solution) over a period of 10 mn. This solution was stirred at –78°C for a period of 15 mn and then transferred by cannula to a suspension of chromium hexacarbonyl (or tungsten hexacarbonyl) (1.0 eq) in diethyl ether (15 mL/mmol) at –78°C. This mixture was warmed to room temperature and was allowed to stir 2.5h. The solvent was removed on a rotary evaporator and the reaction mixture was cooled to 0°C. Water (15 mL/mmol), petroleum ether (15 mL/mmol), then triethyl oxonium tetrafluoroborate (1.1 eq) were added. The reaction mixture was warmed to room temperature and was extracted with petroleum ether. The organic layer was washed with sodium bicarbonate solution, water, brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and final purification was achieved through chromatography on silica gel using pure petroleum ether as eluent.

Complex 37

The general procedure was followed using (5-iodo-pent-1-ynyl)-benzene (6.00 g; 22.2 mmol), tertiobutyllithium (27.4 mL), chromium hexacarbonyl (4.89 g, 22.22 mmol) and triethyloxonium tetrafluoroborate (4.62 g, 24.4 mmol) after chromatography on silica gel an brownish oil identified as complex 37 was obtained (5.22 g, 13.33 mmol, 60.0%).

$^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.41-7.24 (m, 5H, arom H); 5.08 (q, 2H, $J = 7.0$ Hz, $H^7$); 3.49 (t, 2H, $J = 7.5$ Hz, $H^2$); 2.43 (t, 2H, $J = 7.5$ Hz, $H^4$); 1.77 (qn, 2H, $J = 7.5$ Hz, $H^3$); 1.64 (t, 3H, $J = 7.0$ Hz, $H^8$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 359.0 (C$_1$); 223.3 (trans CO); 216.5 (cis CO); 131.6-127.8 (arom HC); 123.7 (qC); 88.8, 81.8 (C$_6$ or C$_5$); 78.1 (C$_7$); 62.2 (C$_2$); 25.2 (C$_4$); 19.1 (C$_3$); 15.0 (C$_8$). Anal. calcd. for C$_{19}$H$_{16}$O$_6$Cr: C, 58.17; H, 4.11. Found: C, 58.21; H, 4.07.
The general procedure was followed using (5-iodo-4-phenyl-pent-1-ynyl)-benzene (4.83 g; 13.96 mmol), terbutyllithium (17.2 mL, 29.3 mmol), chromium hexacarbonyl (3.07 g, 13.95 mmol) and triethyl oxonium tetrafluoroborate (2.92 g, 15.33 mmol). After chromatography on silica gel a reddish oil identified as complex 48a was obtained (2.28 g, 4.87 mmol, 34.9%). 1H NMR (200 MHz, CDCl3) δ: 7.38-7.18 (m, 10H, arom H); 4.92 (q, 2H, J = 7.0 Hz, H7); 3.96 (d, 2H, J = 7.3 Hz, H2); 3.44 (m, 1H, H3); 2.66 (m, 2H, H4); 1.40 (t, 3H, J = 7.0 Hz, H8). 13C NMR (100 MHz, CDCl3) δ: 357.5 (C1); 223.2 (trans CO); 216.4 (cis CO); 142.9 (qC); 131.7 (qC); 128.6-127.3 (arom HC); 123.6 (qC); 87.6, 83.1 (C5 or C6); 78.2 (C3); 42.3 (C2); 27.2 (C4); 14.8 (C9). HRMS (M+NH4) calcd. for C25H24O6NCr: 486.1069. Found: 486.1071.

Complex 48b

The general procedure was followed using 1-iodo-hex-3-yne (4.16 g, 20.00 mmol), terbutyllithium (24.7 mL), chromium hexacarbonyl (4.40 g, 20.00 mmol) and triethyl oxonium tetrafluoroborate (4.20 g, 22.00 mmol). After chromatography on silica gel an orange oil identified as complex 48b was obtained (3.50 g, 10.60 mmol, 53.0%). 1H NMR (200 MHz, CDCl3) δ: 5.11 (q, 2H, J = 7.0 Hz, H8); 3.50 (t, 2H, J = 6.0 Hz, H2); 2.30 (t, 2H, J = 6.0 Hz, H3); 2.11 (q, 2H, J = 8.0 Hz, H6); 1.64 (t, 3H, J = 7.0 Hz, H7); 1.07 (t, 3H, J = 8.0 Hz, H8). Anal. Calcd for C14H14O6Cr: C, 50.90; H, 4.24. Found: C, 50.97; H, 4.50.

2- Preparation of the carbene complexes 48c, 48d

General procedure

These compounds were prepared by phase transfer catalysed alkylation of complex 37 with alkylbromides or iodides. The carbene complex (n mmol) and tetrabutylammonium bromide (0.1 n mmol) in dichloromethane (15 n mL) was treated with 50% aqueous NaOH and the halide (2-n mmol). The mixture was stirred at room temperature under argon until the starting material was consumed. The reaction mixture was diluted with water, extracted with
dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by chromatography on silica gel by elution with petroleum ether.

**Complex 48c**

\[
\text{(OC)}_5\text{Cr} \quad 8 
\quad 1
\quad 2
\quad 3 
\quad 4 
\quad 5 
\quad 6 \quad \text{Ph}
\]

The general procedure was followed using carbene complex 37 (4.24 g, 10.82 mmol), and methyl iodide (3.18 mL, 51 mmol), as starting material. After chromatography on silica gel a deep red oil identified as complex 48c was obtained (2.83 g, 6.97 mmol, 64.4%). \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.40-7.24 (m, 5H, arom H); 5.08 (q, 2H, J = 7.0 Hz, H\(_8\)); 4.17 (m, 1H, H\(_2\)); 2.41 (m, 2H, H\(_4\)); 1.88 (m, 1H, H\(_3\)); 1.60 (t, 3H, J = 7.0 Hz, H\(_9\)); 1.46 (m, 1H, H\(_3\)); 1.06 (d, 3H, J = 6.6 Hz, H\(_7\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 363.3 (C\(_1\)); 223.1 (trans CO); 216.4 (cis CO); 131.6-127.8 (arom HC); 123.81 (qC); 89.1, 81.5 (C\(_5\) or C\(_6\)); 78.1 (C\(_8\)); 64.5 (C\(_2\)); 31.9 (C\(_4\)); 17.6 (C\(_3\)); 16.1 (C\(_7\)); 14.9 (C\(_9\)). HRMS (EI\(^+\)), calcd. for C\(_{20}\)H\(_{18}\)O\(_6\)Cr: 406.0508. Found: 406.0486.

**Complex 48d**

\[
\text{(OC)}_5\text{Cr} \quad 8 
\quad 1
\quad 2
\quad 3 
\quad 4 
\quad 5 
\quad 6 \quad \text{Ph}
\]

The general procedure was followed using carbene complex 37 (2.50 g, 6.37 mmol), and benzyl bromide (1.50 mL, 12.74 mmol), as starting material. After chromatography on silica gel, a brownish oil identified as complex 48d was obtained (2.28 g, 4.73 mmol, 74.3%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.42-7.21 (m, 10H, arom H); 5.16 (q, 2H, J = 7.0 Hz, H\(_8\)); 4.41 (m, 1H, H\(_2\)); 2.99 (dd, 1H, J = 5.6-13.4 Hz, H\(_4\)); 2.50-2.32 (m, 3H, H\(_4\) and H\(_7\)); 1.92 (m, 1H, H\(_3\)); 1.70 (t, 3H, J = 7.0 Hz, H\(_9\)); 1.58 (m, 1H, H\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 364.0 (C\(_1\)); 223.1 (trans CO); 216.2 (cis CO); 138.7 (qC); 131.6 (qC); 129.3-127.8 (arom HC); 123.7 (qC); 89.2, 81.5 (C\(_5\) and C\(_6\)); 78.0 (C\(_8\)); 71.8 (C\(_3\)); 37.8 (C\(_7\)); 30.6 (C\(_6\)); 17.8 (C\(_3\)); 15.0 (C\(_9\)). Anal calcd. for C\(_{22}\)H\(_{22}\)O\(_6\)Cr: C, 64.72; H, 4.60. Found: 64.75; H, 4.67.

**3- Preparation of the chromium carbonyl acylate salts: A, B, C**

pentacarbonyl[(methyl-tetramethylammonio)carbene]chromium salt : A

\[
\text{(OC)}_5\text{Cr} \quad + \quad \text{Me}
\quad \text{O NMe}_4
\]
To a suspension of Cr(CO)$_6$ (4.4 g, 20 mmol) in Et$_2$O (95 mL) was added methyllithium (15.05 mL, 1.33 M, 20 mmol). After 10 minutes at room temperature, the solvent was evaporated in vacuo. Addition of water (100 mL) followed by filtration through celite and treatment with a saturated solution of tetramethylammonium bromide (6.16 g, 40 mmol) in water (10 mL) led to immediate formation of the ammonium salt. Dissolution with CH$_2$Cl$_2$ and addition of pentane gave the salt A as a yellow solid (5.19 g, 16.80 mmol, 84.0%).

**pentacarbonyl [(phenyl-tetramethylammonio)carbene] chromium salt : B**

\[
(OC)_5Cr\equiv\text{Ph}^+\text{O NMe}_4
\]

To a suspension of Cr(CO)$_6$ (4.4 g, 20 mmol) in Et$_2$O (95 mL) was added phenyllithium (30.5 mL, 0.65 M, 20 mmol). After 10 minutes at room temperature, the solvent was evaporated in vacuo. Addition of water (100 mL) followed by filtration through celite and treatment with a saturated solution of tetramethylammonium bromide (6.16 g, 40 mmol) in water (10 mL) led to the formation of the ammonium salt. The salt B was extracted with CH$_2$Cl$_2$ and dried over sodium sulfate. The solvent was removed on a rotary evaporator to give a red solid (6.83 g, 18.40 mmol, 92.0%).

**pentacarbonyl [(cyclopropyl-tetramethylammonio)carbene] chromium salt : C**

\[
(OC)_5Cr\equiv\text{O NMe}_4
\]

To a solution of bromocyclopropane (2.42 g, 20 mmol) in Et$_2$O (100 mL) at -78°C, was added slowly a solution of tBuLi (24.7 mL, 1.7 M) in hexane. After 10 minutes at -78°C, the resulting mixture was transferred to a flask containing a suspension of Cr(CO)$_6$ (4.4 g, 20 mmol) in Et$_2$O (200 mL) at -78°C. After two hours at room temperature, the solvent was evaporated in vacuo. The crude product was dissolved in water (100 mL), filtered through celite and treated with a saturated aqueous solution of tetramethylammonium bromide (8.00 g/10 mL) to cause formation of a yellow precipitate. This material was dissolved in CH$_2$Cl$_2$ and crystallisation was induced by addition of pentane. A 70.0% yield (4.69 g, 14.00 mmol) of salt C was obtained as a yellow solid.

4- Preparation of the carbene complexes 48e-f

Complex 48e
To a solution of salt A (4.13 g, 13.38 mmol) dissolved in CH$_2$Cl$_2$ (25 mL) at -40°C was added pivaloyl chloride (2.48 mL, 13.38 mmol) by syringe. The reaction mixture was stirred at -40 °C for one hour, then a solution of cyclopropyl-methanol (963 mg, 13.38 mmol) in CH$_2$Cl$_2$ (5 mL) was added. The reaction was stirred 2 hours at this temperature before being allowed to reach room temperature. The resulting orange solution was evaporated and the crude product was purified by flash chromatography using PE as eluent giving a carbene complex as a orange oil (2.60 g, 8.96 mmol, 67%). To a solution of this complex (2.50 g, 8.62 mmol) in THF (100 mL) at -78°C was added butyllithium (5.38 mL, 8.62 mmol). After 10 minutes, a solution of triflate derivated from 4-phenyl-but-3-yn-1-ol (2.86 g, 10.29 mmol) in THF (15 mL) was added and the reaction was allowed to warm to -20°C and stirred for two hours at this temperature. Column chromatography on silica gel gave the complex 48e as a red oil (620 mg, 1.44 mmol, 16.7%).

**Complex 48f**

To a solution of (5-iodo-pent-1-ynyl)-benzene (5.40 g, 20 mmol) under argon at –78°C in diethyl ether (140 mL) and pentane (200 mL) was added by syringe tbutyllithium (24.7 mL, 42.00 mmol, 1.7 M) over a period of 10 mn. This solution was stirred at –78°C for a period of 15 mn and then transferred by cannula to a suspension of chromium hexacarbonyl (4.40 g, 20 mmol) in diethyl ether (300 mL) at –78°C. This mixture was warmed to room temperature and was allowed to stir for 2.5h. The solvent was removed on a rotary evaporator and water was added (100 mL ) and the resultant solution was filtered over celite and added to a solution of tetramethylammonium bromide (6.16 g, 40 mmol) in water (10 mL). The reaction mixture was extracted with CH$_2$Cl$_2$ (3x100 mL ) and dried over sodium sulfate. The solvent was removed on a rotary evaporator giving the ammonium salt as a brownish oil (5.16 g, 11.82 mmol, 59.1%). To a solution of this salt (1.80 g, 4.12 mmol) in CH$_2$Cl$_2$ (100 mL) at -20°C was added triflate derivated from benzylic alcohol (1.18 g, 4.92 mmol) and the reaction mixture was stirred for two hours before being allowed to reach room temperature. After column chromatography, the complex 48f was obtained as a yellow solid (800 mg, 1.76 mmol, 42.8%) mp = 35°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.50-7.28 (m, 10H, arom H); 6.06 (s, 2H, H$^7$); 3.61 (t, 2H, J = 7.0
Hz, H$^3$; 2.45 (t, 2H, J = 7.0 Hz, H$^3$); 1.77 (qn, 2H, J = 7.0 Hz, H$^3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 360.2 (C$^1$); 223.1 (trans CO); 216.4 (cis CO); 131.6 (qC); 129.4-128.4 (arom HC); 123.7 (qC); 88.7, 81.9 (C$^5$ or C$^6$); 83.7 (C$^7$); 62.3 (C$^2$); 25.3 (C$^4$); 19.1 (C$^3$). Anal. calcd. for C$_{24}$H$_{18}$O$_6$Cr: C, 63.44; H, 3.99. Found: C, 63.34; H, 4.39.

**B- CARBENE COMPLEXES BEARING THE TRIPLE BOND IN THE OXYGEN CHAIN**

1- Preparation of the carbene complexes 49a-l and 56a-b.

**General procedure 1**

The pentacarbonyl [(tetramethylammonio)carbene] chromium salt (A or B or C) (1.0 mol equivalent) was dissolved in CH$_2$Cl$_2$ (20 mL/mmol) under Ar. The flask was covered with aluminium foil, cooled to −20°C and acetyl chloride (1.1 mol equivalent) was added dropwise over 5mn by syringe to give a red solution. After addition, the mixture was warmed to −10°C and stirred for 10mn. The alkynol (1.0 mol equivalent) was added as a solution in CH$_2$Cl$_2$ (1 mL/mmol) and the solution was stirred at room temperature for 30mn. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography to give the carbene complex.

**General procedure 2**

A solution of pentacarbonyl [(tetramethylammonio)carbene] chromium salt (A or B or C) (1 mmol) dissolved in CH$_2$Cl$_2$ (15 mL/mmol) in an oven dried flask was put under argon atmosphere and cooled to −40°C with an acetone/dry ice bath. To the red solution was added pivaloyl chloride (1.1 mol equivalent) by syringe. The reaction mixture was stirred at −40 °C for one hour and the solution changed slowly to deep red brown. Then, a solution of alcohol (1.1 mol equivalent) in CH$_2$Cl$_2$ (5 mL/mmol) was added. The reaction was stirred for about 3 hours at this temperature before being allowed to reach room temperature. The resulting red solution was evaporated and the crude product was purified by flash chromatography using mixtures of PE/ CH$_2$Cl$_2$ as eluent giving after evaporation, the pure carbene complex.

Complex 49a

![Complex 49a](image)
Salt B (5.08 g, 13.70 mmol), acetyl chloride (1.17 g, 15.0 mmol) and 4-phenyl-but-3-yn-1-ol (2.00 g, 13.70 mmol) were combined following the **general procedure 1**. Complex 49a was obtained as a deep red solid (3.90 g, 9.15 mmol, 66.8%). mp: 55 °C. ¹H NMR (200 MHz, CDCl₃) δ: 7.42-7.24 (m, 10H, arom H); 4.99 (t, 2H, J = 6.0 Hz, H³); 3.14 (t, 2H, J = 6.0 Hz, H⁴). ¹³C NMR (50 MHz, CDCl₃) δ: 349.8 (C¹); 224.3 (trans CO); 216.1 (cis CO); 131.7-121.2 (arom HC and qC); 84.4 (C⁵ or C⁶); 77.9 (C³); 71.5 (C⁵ or C⁶); 21.0 (C⁴). Anal. calcd. for C₂₂H₁₄O₆Cr: C, 61.98; H, 3.31. Found: C, 61.80; H, 3.35.

**Complex 49b**

![Diagram of Complex 49b](image)

Salt A (1.00 g, 3.23 mmol), pivaloyl chloride (480 µL, 3.88 mmol) and 4-phenyl-but-3-yn-1-ol (570 mg, 3.88 mmol) were combined following the **general procedure 2**. Complex 49b was obtained as a yellow solid (753 mg, 2.07 mmol, 64.0%), mp = 47°C. ¹H NMR (200 MHz, CDCl₃) δ: 7.42-7.25 (m, 5H, arom H); 5.06 (m, 2H, H³); 3.12 (t, 2H, J = 6.5 Hz, H⁴); 2.99 (s, 3H, H⁷). Anal. calcd. for C₁₇H₁₂O₆Cr: C, 56.05; H, 3.32. Found: C, 56.00; H, 3.49.

**Complex 49c**

![Diagram of Complex 49c](image)

Salt C (1.70 g, 5.07 mmol), acetyl chloride (380 µL, 5.32 mmol) and 4-phenyl-but-3-yn-1-ol (1.11 g, 7.61 mmol) were combined following the **general procedure 1**. Complex 49c was obtained as a yellow solid (1.40 g, 3.58 mmol, 71.0%). mp : 55 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.39-7.25 (m, 5H, arom H); 5.07 (t, 2H, J = 6.1 Hz, H³); 3.47 (m, 1H, H⁷); 3.01 (t, 2H, J = 6.1 Hz, H³); 1.57-1.11 (m, 4H, H⁸ and H⁹). ¹³C NMR (100 MHz, CDCl₃) δ: 344.4 (C²); 223.8 (trans CO); 216.7 (cis CO); 131.9-123.0 (arom HC); 123.1 (qC); 84.8, 82.9 (C⁵ or C⁶); 77.2 (C³); 41.9 (C³); 20.8 (C⁴); 18.5 (C⁸ and C⁹). Anal. calcd. for C₁₉H₁₆O₆Cr: C, 58.46; H, 3.59. Found: C, 58.31; H, 3.81.

**Complex 49d**

![Diagram of Complex 49d](image)
Salt B (2.25 g, 6.07 mmol), pivaloyl chloride (900 µL, 7.28 mmol) and but-3-yn-1-ol (0.511 g, 7.30 mmol) were combined following the general procedure 2. Complex 49d was obtained as a red solid (1.26 g, 3.58 mmol, 59.0%). $^1$H NMR (200 MHz, CDCl$_3$): 7.39-7.25 (m, 5H, arom H); 4.92 (t, 2H, J = 6.0 Hz, H$^1$); 2.92 (dt, 2H, J = 2.5-6.0 Hz, H$^4$); 2.10 (t, 1H, J = 2.5 Hz, H$^6$). $^{13}$C NMR (CDCl$_3$, 50 MHz): 349.9 (C$^1$); 224.2 (trans CO); 216.1 (cis CO); 153.5 (qC); 130.5-128.3 (arom HC); 123.3 (qC); 79.0 (C$^5$); 77.7 (C$^3$); 71.2 (C$^6$); 20.1 (C$^4$).

Complex 49e

Salt A (1.88 g, 6.08 mmol), pivaloyl chloride (900 µL, 7.29 mmol) and but-3-yn-1-ol (510 mg, 7.29 mmol) were combined following the general procedure 2. Complex 49e was obtained as a orange liquid (1.16 g, 4.01 mmol, 66.0%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 5.02 (bs, 2H, H$^3$); 3.00 (bs, 2H, H$^4$); 2.92 (s, 3H, H$^7$); 2.12 (s, 1H, H$^6$). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 359.7(C$^1$); 223.3 (trans CO); 215.5 (cis CO); 78.9 (C$^5$); 71.2(C$^3$); 64.3 (C$^6$); 19.9 (C$^7$). Anal. calcd. for C$_{11}$H$_8$O$_6$Cr: C, 45.85; H, 2.80. Found: C, 45.68; H, 2.99.

Complex 49f

Salt C (1.60 g, 4.77 mmol), acetyl chloride (358 µL, 5.01 mmol) and but-3-yn-1-ol (351 mg, 5.01 mmol) were combined following the general procedure 1. Complex 49f was obtained as a yellow liquid (886 mg, 2.82 mmol, 59.1%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.39-7.25 (m, 5H, arom H); 5.07 (t, 2H, J = 6.1 Hz, H$^1$); 3.51-3.45 (1H, H$^7$); 3.01 (t, 2H, J = 6.1 Hz, H$^4$); 1.57-1.11 (m, 4H, H$^8$ and H$^9$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 344.4 (C$^2$); 223.8 (trans CO); 216.7 (cis CO); 131.9-123.0 (arom HC); 123.1 (qC); 84.8-82.9 (C$^6$ or C$^5$); 77.2 (C$^3$); 41.9 (C$^7$); 20.8 (C$^6$); 18.5 (C$^8$ and C$^9$). Anal. calcd. for C$_{13}$H$_{10}$O$_6$Cr: C, 49.69; H, 3.21 Found: C, 49.34; H, 3.42.

Complex 49g
Salt B (1.52 g, 4.11 mmol), pivaloyl chloride (556 µL, 4.52 mmol) and (R)2,4-diphenyl-but-3-yn-1-ol (1.00 g, 4.52 mmol) were combined following the general procedure 2. Complex 49g was obtained as a deep red oil (932 mg, 1.86 mmol, 45.2%).

$\left(\text{CO}\right)_5\text{Cr} = \begin{array}{cccccc}
\text{Ph} & & & & \\
1 & & & & \\
2 & & & & \text{O} \\
3 & & & & \text{H} \\
4 & & & & \text{Ph} \\
5 & & & & 6
\end{array}$

$^1$H NMR (200 MHz, CDCl$_3$) δ: 7.49-7.11 (m, 15H, arom H); 4.98 (br s, 1H, H$_3$); 4.58 (br s, 1H, H$_4$). $^{13}$C NMR (50 MHz, CDCl$_3$) δ: 350.0 (C$_1$); 224.5 (trans CO); 216.0 (cis CO); 153.1 (qC); 136.7 (qC); 131.8-128.3 (arom HC); 122.7 (qC); 86.7, 85.4 (C$_5$ or C$_6$); 82.9 (C$_3$); 39.3 (C$_4$). HRMS calcd. for C$_{28}$H$_{18}$O$_6$Cr: 502.0509. Found: 502.0499.

Complex 49h

Salt B (3.20 g, 8.62 mmol), pivaloyl chloride (1.06 mL, 8.62 mmol) and 3-methyl-5-phenyl-pent-4-yn-2-ol (1.00 g, 5.75 mmol) were combined following the general procedure 2. Complex 49h was obtained as a red solid (1.85 g, 4.08 mmol, 71.0%). $^1$H NMR (200 MHz, CDCl$_3$) δ: 7.40-7.25 (m, 10H, arom H); 5.28 (m, 1H, H$_3$); 3.14 (m, 1H, H$_4$); 1.60 (d, 3H, J = 5.9 Hz, H$_7$); 1.40 (d, 3H, J = 6.9 Hz, H$_8$). $^{13}$C NMR (50 MHz, CDCl$_3$) δ: 348.7 (C$_1$); 224.6 (trans CO); 216.2 (cis CO); 131.7-122.1 (arom HC and qC); 89.7 (C$_3$); 89.2, 83.6 (C$_5$ or C$_6$); 33.2 (C$_4$); 19.1 (C$_7$); 17.0 (C$_8$). Anal. calcd. for C$_{24}$H$_{18}$O$_6$Cr: C, 63.44; H, 3.99. Found: C, 62.95; H, 4.48.

Complex 49i

Salt A (2.96 g, 9.59 mmol), pivaloyl chloride (1.18 mL, 9.59 mmol) and 3-methyl-5-phenyl-pent-4-yn-2-ol (1.11 g, 6.39 mmol) were combined following the general procedure 2. Complex 49i was obtained as a red oil (1.30 g, 3.31 mmol, 51.8%). $^1$H NMR (200 MHz, CDCl$_3$) δ: 7.41-7.25 (m, 5H, arom H); 5.62 (m, 1H, H$_3$); 3.15 (m, 1H, H$_4$); 2.98 (s, 3H, H$_9$); 1.63 (d, 3H, J = 6.4 Hz, H$_7$); 1.40 (d, 3H, J = 6.9 Hz, H$_8$). $^{13}$C NMR (50 MHz, CDCl$_3$) δ: 355.2 (C$_1$); 223.5 (trans CO); 216.5 (cis CO); 131.6-128.2 (arom HC and qC); 91.3 (C$_3$); 89.0, 83.7 (C$_5$ or C$_6$); 33.1 (C$_4$); 29.8 (C$_9$); 18.3 (C$_7$); 16.4 (C$_8$). Anal. calcd. for C$_{19}$H$_{16}$O$_6$Cr: C, 58.17; H, 4.11. Found: C, 59.12; H, 4.60.
Complex 49j

Salt C (2.86 g, 8.54 mmol), acetyl chloride (1.18 mL, 8.96 mmol) and 3-methyl-5-phenyl-pent-4-yn-2-ol (2.00 g, 11.50 mmol) were combined following the general procedure 1. Complex 49j was obtained as a yellow solid (749 mg, 1.79 mmol, 21.0%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.61-7.03 (m, 5H, arom H); 5.56 (m, 1H, H$_3$); 3.15 (m, 1H, H$_4$); 2.98 (s, 1H, H$_9$); 1.63 (d, 3H, J = 6.4 Hz, H$_7$); 1.40 (d, 3H, J = 6.9 Hz, H$_8$); 1.37-1.11 (m, 4H, H$_{10}$ and H$_{11}$).

$^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 348.5 (C$_1$); 223.7 (trans CO); 216.7 (cis CO); 131.6-128.1 (arom HC and qC); 89.3 (C$_3$); 89.1, 83.6 (C$_5$ or C$_6$); 41.6 (C$_9$); 33.1 (C$_{10}$); 29.8 (C$_{11}$); 18.9 (C$^i$); 18.3 (C$^i$); 17.7 (C$^{10}$ and C$^{11}$). Anal. calcd. for C$_{19}$H$_{16}$O$_6$Cr: C, 58.17; H, 4.11. Found: C, 59.12; H, 4.60

Complex 49k

Salt B (2.20 g, 5.93 mmol), pivaloyl chloride (875 µL, 7.11 mmol) and 2-phenylethynyl-cyclohexanol (1.42 g, 7.11 mmol) were combined following the general procedure 2. Complex 49k was obtained as a deep red oil (823 mg, 1.71 mmol, 28.9%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.38-7.28 (m, 10H, arom H); 3.15 (br s, 1H, H$_1$); 2.27-1.27 (br s, 9H, H$_2$, H$_3$, H$_4$, H$_5$, H$_6$, H$_7$, and H$_8$). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 350.0 (C$_1$); 224.6 (trans CO); 216.2 (cis CO); 131.8-128.3 (arom HC and qC); 122.7 (qC); 92.0 (C$_3$); 89.1, 82.4 (C$_5$ or C$_6$); 36.4 (C$_8$); 32.0 (C$_9$); 31.1 (C$^i$); 24.2, 23.6 (C$^i$ or C$^6$). HRMS (M+NH$_4$) calcd. for C$_{26}$H$_{24}$O$_6$NCr: 498.1009. Found: 498.0991.

Complex 49l
Salt C (1.80 g, 5.37 mmol), acetyl chloride (460 µL, 6.44 mmol) and 2-phenylethynyl-cyclohexanol (1.29 g, 6.44 mmol) were combined following the general procedure 1. Complex 49l was obtained as a deep red oil (430 mg, 0.97 mmol, 18.1%). \(^{1}\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.36-7.29 (m, 5H, arom H); 3.48 (br s, 1H, H\(_3\)); 2.94-1.02 (br s, 14 H, H\(_4\), H\(_5\), H\(_6\), H\(_7\), H\(_8\), H\(_11\), H\(_12\) and H\(_13\)). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 348.4 (C\(_1\)); 223.9 (trans CO); 216.8 (cis CO); 131.5-123.2 (arom HC and qC); 91.6 (C\(_3\)); 88.7, 83.4 (C\(_9\) or C\(_10\)); 41.5-5.4 (C\(_4\), C\(_5\), C\(_6\), C\(_7\), C\(_8\), C\(_11\), C\(_12\) and C\(_13\)). HRMS (M+NH\(_4\)) calcd. for C\(_{23}\)H\(_{24}\)O\(_6\)NCr: 462.1009. Found: 462.1000.

Complex 56b

Salt B (4.00 g, 10.78 mmol), acetyl chloride (894 µL, 11.88 mmol) and 5-phenyl-pent-4-yn-1-ol (1.73 g, 10.80 mmol) were combined following the general procedure 1. Complex 56b was obtained as a deep red oil (2.09 g, 4.75 mmol, 44.1%). \(^{1}\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.45-7.10 (m, 10H, arom H); 4.96 (t, 2H, J = 6.0 Hz, H\(_3\)) 2.70 (t, 2H, J = 6.0 Hz, H\(_5\)); 2.30 (q, 2H, J = 6.0 Hz, H\(_4\)). HMRS (EI\(^{-}\)-CO), calcd. for C\(_{22}\)H\(_{17}\)O\(_5\)Cr: 413.0481. Found: 413.0486.

Complex 56a

Salt C (2.09 g, 6.24 mmol), acetyl chloride (470 µL, 6.25 mmol) and 5-phenyl-pent-4-yn-1-ol (1.10 g, 6.88 mmol) were combined following the general procedure 1. Complex 56a was obtained as a yellow solid (1.92 g, 4.75 mmol, 76.2%). \(^{1}\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.45-7.28 (m, 5H, arom H); 5.06 (t, 2H, J = 6.0 Hz, H\(_3\)); 3.47 (m, 1H, H\(_8\)); 2.61 (t, 2H, J = 6.7 Hz, H\(_7\)); 2.20 (dt, 2H, J = 6.0-6.7 Hz, H\(_2\)); 1.48-1.18 (m, 4H, H\(_4\) et H\(_5\)). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 352.0 (C\(_1\)); 223.7 (trans CO); 216.8 (cis CO); 131.7-127.9 (arom HC and qC); 85.7, 82.5 (C\(_7\) or C\(_8\)); 78.9 (C\(_3\)); 41.6 (C\(_9\)); 28.4 (C\(_4\)); 18.1 (C\(_5\) or C\(_10\)); 16.4 (C\(_6\)). Anal. calcd. for C\(_{20}\)H\(_{16}\)O\(_2\)Cr: C, 59.41; H, 3.99. Found: C, 59.33; H, 4.02.
II- REACTION OF N-METHYLDIHYDROPYRIDINE WITH CARBENE COMPLEXES

N-methyl dihydropyridine 19 was prepared following the literature procedure.

General procedure

To a solution of carbene complex (1 mol eq) in CH$_2$Cl$_2$ (25 mL/mmol of carbene) at –10°C, under argon was added dropwise from an addition funnel a solution of N-methyl dihydropyridine (3 mol eq) in CH$_2$Cl$_2$ (0.5 mL/mmol of amine). After 15mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixture of PE/Et$_2$O as eluent.

A- WITH COMPLEXES BEARING THE TRIPLE BOND IN THE ALKYL CHAIN

Obtention of butenolides 38, 39, 50a-f, and 51a-f.

With complex 37: 7-ethoxy-3-phenyl 3, 6, 7a-tetrahydro-4H-benzofuran-2-one 38 and 39.

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{3} & \quad 1 \\
\text{2} & \quad \text{O} \\
\text{3a} & \quad \text{H} \\
\text{7a} & \quad \text{O} \\
\text{6} & \quad 8 \\
\text{5} & \quad 9 \\
\text{4} & \quad \text{O}
\end{align*}
\]

The general procedure was followed using carbene complex 37 (1.30 g, 3.29 mmol). Elution with PE/Et$_2$O (20/80) gave the butenolide 38 as as a colorless liquid (484 mg, 1.87 mmol, 57.0%). $^1$H NMR (200 MHz, CDCl$_3$) δ: 7.47-7.34 (m, 5H, arom H); 4.70 (d, 1H, J = 8.4 Hz, H$_7$); 3.88 (m, 1H, H$_8$); 3.66 (m, 1H, H$_8$); 3.23 (m, 1H, H$_7$); 3.03 (m, 1H, H$_7$); 2.33-2.11 (m, 2H, H$_4$ and H$_6$); 2.00 (m, 1H, H$_5$); 1.53 (m, 1H, H$_6$); 1.37 (m, 1H, H$_5$); 1.23 (t, 3H, J = 7.1 Hz, H$_9$). $^{13}$C NMR (100MHz, CDCl$_3$) δ: 172.7 (C$_2$); 160.9 (C$_{3a}$); 129.7 (qC); 129.0-128.6 (arom HC); 125.0 (qC); 85.7 (C$_{7a}$); 82.8 (C$_7$); 66.3 (C$_8$); 29.9 (C$_9$); 26.3 (C$_5$); 23.6 (C$_5$); 15.7 (C$_9$). Then 39 as a white solid (51 mg, 0.20 mmol, 6.0%) mp 90°C. $^1$H NMR (400MHz, CDCl$_3$) δ: 7.50-7.30 (m, 5H, arom H) 4.78 (d, 1H, J = 3.5 Hz, H$_{7a}$); 4.10 (m, 1H, H$_7$); 3.56 (dq, 2H, J = 7.1-8.0 Hz, H$_8$); 3.03 (m, 1H, H$_8$); 2.27 (m, 1H, H$_6$); 2.05 (m, 1H, H$_5$); 1.71(m, 2H, H$_5$); 1.57 (m, 1H, H$_7$); 1.09 (t, 3H, J = 7.1 Hz, H$_9$). $^{13}$C NMR (100MHz, CDCl$_3$) δ: 173.3 (C$_2$); 161.0 (C$_{3a}$); 130.5 (qC); 129.2-128.6 (arom HC); 125.4 (qC); 82.0 (C$_{7a}$); 76.0 (C$_7$); 67.1(C$_8$); 28.4 (C$_9$); 26.8 (C$_5$); 20.8 (C$_5$); 15.9 (C$_9$). Anal. calcd. for C$_{16}$H$_{18}$O$_3$: C, 74.40; H, 7.02. Found: C, 73.99; H, 7.06.

With complex 48e: 7-Cyclopropylmethoxy-3-phenyl-5,6,7a-tetrahydro-4H-benzofuran-2-one 50e and 51e.
The general procedure was followed using carbene complex 48f (600 mg, 1.43 mmol). Elution with PE/Et$_2$O (60/40) gave the butenolide. 50e: (202 mg, 0.71 mmol, 49.7%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.50-7.33 (m, 5H, arom H); 4.73 (d, 1H, J = 8.7 Hz, H$_7^a$); 3.66 (dd, 1H, J = 7.1 -10.2 Hz, H$_8$); 3.51 (dd, 1H, J = 7.1-10.2 Hz, H$_8^a$); 3.26 (ddd, 1H, J = 4.6-8.7-13.2 Hz, H$_7$); 3.04 (m, 1H, H$_4$); 2.26(ddd, 1H, J = 6.1-13.7-13.7 Hz, H$_7^a$); 2.17 (m, 1H, H$_5$); 2.01 (m, 1H, H$_5^a$); 1.60 (m, 1H, H$_6$); 1.31 (m, 1H, H$_6^a$); 1.10 (m, 1H, H$_7$); 0.59-0.21 (m, 4H, H$_8^b$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 172.7 (C$_2$); 160.9 (C$_3a$); 129.7 (Cq); 129.0 -128.5 (arom HC); 125.0 (qC); 85.7 (C$_7a$); 82.8 (C$_7$); 75.9 (C$_8$); 30.0 (C$_6$); 26.3 (C$_4$); 23.7 (C$_5$); 11.0 (C$_5^a$); 3.2 (C$_10^b$ and C$_11^b$). Anal. calcd. for C$_{18}$H$_{20}$O$_3$: C, 76.03; H, 7.09. Found: C, 76.05; H, 7.19.

Then 51e: (51 mg, 0.18 mmol, 12.4%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.49-7.29 (m, 5H, arom H); 4.79 (d, 1H, J = 11.8 Hz, H$_8$); 4.86 (d, 1H, J = 8.4 Hz, H$_7^a$); 4.76 (d, 1H, J = 11.8 Hz, H$_7^b$); 3.41 (ddd, 1H, J = 4.6-8.4-15.3 Hz, H$_7$); 3.06 (dd, 1H, J = 1.8-14.3 Hz, H$_4$); 2.30 (dt, 1H, J = 7.5-14.3 Hz, H$_4$); 2.22 (m, 1H, H$_5$); 2.03 (m, 1H, H$_5^a$); 1.65 (m, 1H, H$_6$); 1.36 (m, 1H, H$_8$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 173.2 (C$_2$); 160.9 (C$_3a$); 138.0-128.9 (qC); 128.6-128.4 (arom HC); 127.8 (qC); 85.7 (C$_7a$); 82.2 (C$_7$); 72.4 (C$_8$); 29.8 (C$_6$); 26.1 (C$_5$); 23.5 (C$_5^a$). Anal. calcd. for C$_{19}$H$_{20}$O$_3$: C, 78.73; H, 6.29. Found: C, 79.20; H, 6.54. Further elution with PE/Et$_2$O (70/30) gave the cis isomer 51f (70 mg, 0.22 mmol, 12.8%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.53-7.28 (m, 10H, arom H); 4.88 (d, 1H, J = 3.5 Hz, H$_7^a$); 4.77 (d, 1H, J = 12.2 Hz, H$_7^b$); 4.77 (d, 1H, J = 12.2 Hz, H$_7^b$); 4.28 (m, 1H, H$_5$); 3.11 (m, 1H, H$_5^a$); 2.36 (m, 1H, H$_5^b$); 2.10 (m, 1H, H$_5^a$); 1.79 (m, 2H, H$_5^b$ et H$_5^b$); 1.63 (m, 1H, H$^6$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 173.2 (C$_2$); 161.0 (C$_3a$); 138.7 (qC); 129.3 (qC); 128.9-127.7 (arom HC); 125.4 (qC); 82.1 (C$_5^a$); 75.6 (C$_5$); 73.3 (C$_8$); 28.3 (C$_6$); 26.9 (C$_5$); 20.8 (C$_5^a$).
With complex 48d: 6-benzyl-7-ethoxy-3-phenyl 5, 6, 7, 7a-tetrahydro-4H-benzofuran-2-one 50d and 51d.

The general procedure was followed using carbene complex 48d (2.02 g, 4.19 mmol). The butenolide was obtained as two isomers: Elution with PE/Et₂O (30/70) gave 50d as white solid (219 mg, 0.63 mmol, 15.0%) mp 153°C. 

**1H NMR (400MHz, CDCl₃)**: δ: 7.36-7.07 (m, 10H, arom H); 4.74 (d, 1H, H = 8.2 Hz, H₇); 4.10 (m, 1H, H₉); 3.59 (m, 1H, H₉); 3.25 (dd, 1H, J = 8.0-13.5 Hz, H₈); 2.91 (dd, 1H, J = 8.2-10.2 Hz, H₇); 2.88 (m, 1H, H₈); 2.25(dd, 1H, J = 9.6-13.5 Hz, H₈); 2.11 (dt, 1H, J = 5.0-13.7 Hz, H₄); 1.91-1.76 (m, 2H, H₅ and H₆); 1.23 (t, 3H, J = 7.1 Hz, H₁₀); 0.98 (m, 1H, H₅).

**13C NMR (100 MHz, CDCl₃)**: δ: 172.9 (C₂); 161.2 (C₃a); 140.1 (qC); 129.9 (qC); 129.7-126.6 (arom HC); 124.9 (qC); 86.5(C₇a); 86.4 (C₇); 68.3 (C₉); 43.2 (C₆); 37.9 (C₅); 29.4 (C₅); 25.9 (C₄); 16.0 (C₁₀). Anal. Calcd. for C₂₃H₂₄O₃: C, 79.28; H, 6.94. Found: C, 79.24; H, 7.00.

Elution with PE/Et₂O (20/80) gave 51d as a yellow oil (729 mg, 2.09 mmol, 50.0%).

**1H NMR (400 MHz, CDCl₃)**: δ: 7.76-7.42 (m, 10H, arom H); 4.96 (d, 1H, J = 3.0 Hz, H₇); 4.06-3.96 (m, 2H, H₇ and H₈); 3.80 (m, 1H, H₈); 3.18 (m, 1H, H₈); 2.98 (m, 1H, H₈); 2.89 (m, 1H, H₈); 2.50 (m, 1H, H₈); 2.21 (m, 1H, H₈); 1.84-1.78 (m, 2H, H₄); 1.41 (t, 3H, J = 7.0 Hz, H₁₀). **13C NMR (100 MHz, CDCl₃)**: δ: 173.2 (C₂); 161.6 (C₃a); 140.5 (qC); 130.6 (qC); 125.6 (qC); 83.2 (C₇a); 78.8 (C₇); 69.6 (C₉); 41.7 (C₆); 38.6 (C₅); 27.0 (C₅); 26.0 (C₄); 16.3 (C₁₀).

With complex 48c: 6-methyl-7 ethoxy-3-phenyl 5, 6, 7, 7a-tetrahydro-4H-furan-2-one 50c and 51c.

The general procedure was followed using carbene complex 48c (2.03 g, 5.00 mmol). Elution with PE/Et₂O (70/30) gave the butenolide as a 4/3 mixture of two isomers (952 mg, 3.50 mmol 70.0%).

**50c**: white solid, mp = 58°C, 534 mg, 1.96 mmol, 39.3%: **1H NMR (400 MHz, CDCl₃)**: δ: 7.49-7.24 (m, 5H, arom H); 4.96 (d, 1H, J = 3.0 Hz, H₇); 4.06-3.96 (m, 2H, H₇ and H₈); 3.80 (m, 1H, H₈); 3.18 (m, 1H, H₈); 2.98 (m, 1H, H₈); 2.89 (m, 1H, H₈); 2.50 (m, 1H, H₈); 2.21 (m, 1H, H₈); 1.84-1.78 (m, 2H, H₄); 1.41 (t, 3H, J = 7.0 Hz, H₁₀). **13C NMR (100 MHz, CDCl₃)**: δ: 172.6 (C₂); 161.2 (C₃a); 129.6 (qC); 128.8-128.2 (arom HC); 124.45 (qC); 87.8 (C₇); 85.9 (C₇a); 68.0 (C₅); 36.0 (C₅); 25.7 (C₄); 17.4 (C₃); 15.5 (C₁₀). **51c**: 418 mg, 1.54 mmol, 30.7%: **1H NMR (400 MHz, CDCl₃)**: δ: 7.49-7.24 (m, 5H, arom H); 4.82 (d, 1H, J
= 3.4 Hz, Hδ); 3.82 (b, 1H, Hδ); 3.72 (m, d, 1H, J = 7.0-9.4 Hz, Hδ); 3.57 (d, 1H, J = 7.0-9.4 Hz, Hδ); 3.01 (m, 1H, Hδ); 2.30 (m, 1H, Hδ); 1.80 (m, 1H, Hδ); 1.58 (m, 2H, Hδ); 1.13 (t, 3H, J = 9.0 Hz, H6); 1.08 (d, 3H, J = 6.3 Hz, H8).

$^{13}$C NMR (100 MHz, CDCl3) δ: 173.0 (C2); 160.7 (C4b); 130.3 (qC); 129.0-128.3 (arom HC); 125.5 (qC); 82.7 (C5a); 80.7 (C7); 69.6 (C8); 34.2 (C6); 26.4 (C5); 25.9 (C4); 17.6 (C3); 15.7 (C10). HRMS calcd. for C12H12O3: 273.1491. Found: 273.1495.

With complex 48a: 7-ethoxy-3,5-diphenyl-5,6,7,7a-tetrahydro-4H-benzofuran-2-one 50a and 51a.

The general procedure was followed using carbene complex 48a (1.15 g, 2.46 mmol). The butenolide was obtained as two isomers: Elution with PE/EtO (70/30) gave the trans isomer 50a as white solid (227 mg, 0.68 mmol, 27.6%) mp 120°C. $^1$H NMR (400 MHz, CDCl3) δ: 7.42-7.14 (m, 10H, arom H); 4.79 (d, 1H, J = 8.1 Hz, H7a); 3.83 (d, 1H, J = 6.9-9.1 Hz, Hδ); 3.62 (d, 1H, J = 6.9-9.1 Hz, Hδ); 3.35 (dd, 1H, J = 4.0-8.1-12.7 Hz, H6); 3.15 (m, 1H, Hδ); 2.65 (m, 1H, Hδ); 2.45 (m, 1H, Hδ); 2.28 (m, 1H, Hδ); 1.82 (m, 1H, Hδ); 1.18 (t, 3H, J = 6.9 Hz, H8). $^{13}$C NMR (100 MHz, CDCl3) δ: 172.5 (C3); 159.5 (C5b); 142.7 (qC); 129.2 (qC); 129.0-127.0 (arom HC); 126.4 (qC); 85.3 (C6); 81.6 (C5a). HRMS (M+1) calcd. for C12H12O3: 335.1647. Found: 335.1647. Further elution with PE/EtO (60/40) gave the cis isomer 51a as a white solid (118 mg, 0.35 mmol, 14.4%). mp = 92°C. $^1$H NMR (400 MHz, CDCl3) δ: 7.45-7.18 (m, 10H, arom H); 4.89 (d, 1H, J = 4.0 Hz, H7a); 4.15 (m, 1H, Hδ); 3.58 (m, 2H, Hδ); 3.19 (m, 1H, Hδ); 3.10 (m, 1H, Hδ); 2.48 (m, 1H, Hδ); 2.26 (m, 1H, Hδ); 2.17 (m, 1H, Hδ); 1.84 (m, 1H, Hδ); 1.09 (t, 3H, J = 7.0 Hz, Hδ). $^{13}$C NMR (100MHz, CDCl3) δ: 173.0 (C3); 159.6 (C5b); 143.7 (qC); 129.9 (qC); 128.9-127.0 (arom HC); 125.7 (qC); 81.4 (C7a); 75.3 (C5); 67.3 (C6); 38.4 (C5); 35.9 (C6); 34.3 (C4); 15.7 (C9). HRMS (M+1) calcd. for C12H12O3: 335.1647. Found: 335.1652.

With complex 48b: 6-ethoxy-3 ethyl 4, 5, 6, 6a-tetrahydro-cyclopenta [b] furan-2-one 50b, 51b and 2-ethoxy-5-propylidene-cyclopentanone 52.

The general procedure was followed using carbene complex 48b (2.50 g, 7.58 mmol). Elution with PE/EtO (90/10) gave the cyclopentanone 52 as an oil (142 mg, 0.85 mmol, 11.1%). $^1$H NMR (400 MHz, CDCl3) δ: 6.65 (m, 1H, H8); 3.91 (t, 1H, J = 8.0 Hz, H6); 3.83 (m, 1H, Hδ); 3.63 (m, 1H, Hδ); 2.65 (m, 1H, Hδ); 2.34 (m, 2H, Hδ and H6); 2.17 (m, 2H, Hδ); 1.77 (m, 1H, Hδ); 1.25 (t, 3H, J = 8.0 Hz, H10); 1.05 (t, 3H, J = 8.0 Hz, H8). $^{13}$C NMR (100 MHz, CDCl3) δ: 203.7 (C3); 140.1 (C6); 133.7 (C7); 81.6 (C5); 65.8 (C8); 27.2 (C3); 22.8 (C5); 22.4 (C4); 15.4 (C10); 12.9 (C6). HRMS calcd. for C10H17O2: 169.1229. Found: 169.1230. The butenolide was obtained as two isomers in 1/1 ratio (863 mg, 4.40 mmol, 58.1%). Elution with PE/EtO (85/15) gave 50b (trans) as a yellow oil. $^1$H NMR (200 MHz, CDCl3) δ: 4.66 (d, 1H, J = 8.0 Hz, H8); 3.77 (m, 1H, Hδ); 3.56 (m, 2H, Hδ and H6); 2.75-2.00 (m, 6H, Hδ, Hδ and H6); 1.20 (t, 3H, J = 7.0 Hz, Hδ).
Hz, H<sup>10</sup>); 1.06 (t, 3H, J = 7.4 Hz, H<sup>9</sup>). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ: 176.0 (C<sup>2</sup>); 164.7 (C<sup>3b</sup>); 127.8 (C<sup>3</sup>); 88.4 (C<sup>6a</sup>); 80.7 (C<sup>6</sup>); 66.2 (C<sup>9</sup>); 31.3 (C<sup>5</sup>); 20.9 (C<sup>4</sup>); 18.1 (C<sup>3</sup>); 15.6 (C<sup>10</sup>); 12.6 (C<sup>8</sup>). Further elution with PE/Et<sub>2</sub>O (80/20) gave 51b (cis) as a yellow oil. <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ: 4.89 (bs, 1H, H<sup>6a</sup>); 3.95 (m, 1H, H<sup>6</sup>); 3.57 (m, 2H, H<sup>9</sup>); 2.62-2.14 (m, 6H, H<sup>4</sup>, H<sup>5</sup> and H<sup>7</sup>); 1.18 (t, 3H, J = 7.4 Hz, H<sup>10</sup>); 1.05 (t, 3H, J = 7.0 Hz, H<sup>8</sup>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 177.1 (C<sup>2</sup>); 166.5 (C<sup>3a</sup>); 133.9 (C<sup>3</sup>); 86.0 (C<sup>6a</sup>); 75.5 (C<sup>6</sup>); 67.1 (C<sup>9</sup>); 32.7 (C<sup>5</sup>); 20.4 (C<sup>4</sup>); 18.4 (C<sup>3</sup>); 15.8 (C<sup>10</sup>); 12.6 (C<sup>8</sup>). HRMS calcd. for C<sub>11</sub>H<sub>17</sub>O<sub>3</sub>: 197.1178. Found: 197.1181.

**B- WITH COMPLEXES BEARING THE TRIPLE BOND IN THE OXYGEN CHAIN**

Obtention of butenolides 53a-l, 54c, 55g, 57a,b, 58a.

With complex 49a: 3,7-diphenyl-4,5,7,7a-tetrahydro-furo [2,3-c] pyran-2-one 53a.

The general procedure was followed using carbene complex 49a (600 mg, 1.4 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave 53a as a white solid (299 mg, 1.02 mmol, 75%) mp: 59°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.58-7.35 (m, 10H, arom H); 4.75 (d, 1H, J = 8.8 Hz, H<sup>7a</sup>); 4.38 (dd, 1H, J = 6.5 -11.7 Hz, H<sup>5</sup>); 4.15 (d, 1H, J = 8.8Hz, H<sup>7</sup>); 3.52 (ddd, 1H, J = 2.7-11.7-11.7 Hz, H<sup>5'</sup>); 3.15 (dd, 1H, J = 2.7 -13.9 Hz, H<sup>4</sup>); 2.91 (ddd, 1H, J = 6.5 -11.7-13.9 Hz, H<sup>4'</sup>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 171.9 (C<sup>2</sup>); 159.4 (C<sup>3a</sup>); 138.0 (qC); 129.4 -128.7 (arom HC); 126.4 -124.9 (qC); 85.2 (C<sup>7</sup>); 85.0 (C<sup>7a</sup>); 67.8 (C<sup>5</sup>); 29.4 (C<sup>4</sup>). HRMS calcd. for C<sub>19</sub>H<sub>17</sub>O<sub>3</sub>: 293.1178. Found: 293.1174. Anal. calcd. for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>: C, 78.06; H, 5.52. Found: C, 77.93; H, 5.49.

With complex 49b: 7-methyl-3-phenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53b.

The general procedure was followed using carbene complex 49b (1.30 g, 3.58 mmol). Elution with PE/Et<sub>2</sub>O (70/30) gave the butenolide 53b as a white solid (390 mg, 1.70 mmol, 47.5%). mp = 81°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.43-7.36 (m, 5H, arom H); 4.42 (d, 1H, J = 8.9 Hz, H<sup>7a</sup>); 4.38 (dd, 1H, J = 6.5-11.7 Hz, H<sup>5</sup>); 4.15 (d, 1H, J = 8.8Hz, H<sup>7</sup>); 3.52 (ddd, 1H, J = 2.7-11.5-13.9 Hz, H<sup>5</sup>); 3.15 (dd, 1H, J = 2.7-11.5-13.9 Hz, H<sup>7</sup>); 2.91 (ddd, 1H, J = 6.5-11.5-13.7 Hz, H<sup>4</sup>); 1.49 (d, 3H, J = 6.1 Hz, H<sup>8</sup>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 171.9 (C<sup>5</sup>); 159.4 (C<sup>3a</sup>); 129.4-128.7 (arom HC); 126.4-124.9 (qC); 85.2 (C<sup>7</sup>); 85.0 (C<sup>7a</sup>); 67.8 (C<sup>5</sup>); 29.4 (C<sup>4</sup>). HRMS calcd. for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>: 293.1178. Found: 293.1174. Anal. calcd. for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>: C, 78.06; H, 5.52. Found: C, 77.93; H, 5.49.

With complex 49c: 7-Cyclopropyl-3-phenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53c and 54c.
The general procedure was followed using carbene complex 49c (1.32 g, 3.38 mmol). The butenolide was obtained as two isomers: Elution with PE/Et\(_2\)O (70/30) gave 53c the trans isomer as white solid (521 mg, 1.95 mmol, 57.6%) mp 89°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.51-7.35 (m, 5H, arom H); 4.66 (d, 1H, \(J = 8.7\) Hz, H\(_7\)); 4.20 (dd, 1H, \(J = 6.6-11.5\) Hz, H\(_5\)); 3.28 (ddd, 1H, \(J = 2.0-11.5-11.5\) Hz, H\(_5'\)); 3.02 (dd, 1H, \(J = 7.5-8.7\) Hz, H\(_4\)); 2.78 (ddd, 1H, \(J = 6.6-11.5-13.5\) Hz, H\(_4'\)); 2.63 (dd, 1H, \(J = 7.5-8.7\) Hz, H\(_7\)); 1.21 (m, 1H, H\(_8\)); 0.72-0.40 (m, 4H, H\(_9\) and H\(_{10}\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 171.2 (C\(_2\)); 159.9 (C\(_{3a}\)); 133.0 (qC); 129.4 -128.7 (arom HC); 124.0 (qC); 86.7 (C\(_7\)); 80.9 (C\(_7a\)); 67.4 (C\(_5\)); 29.3 (C\(_4\)); 14.2 (C\(_8\)); 2.2 -2.0 (C\(_9\) or C\(_{10}\)). HRMS M+1 calcd. for C\(_{16}\)H\(_{17}\)O\(_3\): 257.1178. Found: 257.1182.

Further elution with PE/Et\(_2\)O (80/20) gave the cis isomer (31 mg, 0.21 mmol, 6.1%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.53-7.25 (m, 5H, H arom); 5.09 (d, 1H, \(J = 7.1\) Hz, H\(_3\)); 3.94 (dd, 1H, \(J = 7.6 -11.7\) Hz, H\(_5\)); 3.77 (ddd, 1H, \(J = 2.8-11.7-11.7\) Hz, H\(_5'\)); 3.62 (dd, 1H, \(J = 7.1-9.7\) Hz, H\(_7\)); 3.04 (dd, 1H, \(J = 2.8-13.5\) Hz, H\(_4\)); 2.81 (m, 1H, H\(_8\)); 1.18 (m, 1H, H\(_9\)); 0.80-0.28 (m, 4H, H\(_9\) or H\(_{10}\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 175.5 (C\(_2\)); 157.8 (C\(_{3a}\)); 136.7 (qC); 129.4-128.7 (arom HC); 125.3 (qC); 82.7 (C\(_7\)); 78.1 (C\(_7a\)); 59.5 (C\(_5\)); 28.9 (C\(_5\)); 14.3 (C\(_8\)); 6.0, 5.6 (C\(_9\) or C\(_{10}\))

With complex 49d: 7-phenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53d.

The general procedure was followed using carbene complex 49d (940 mg, 2.68 mmol). Elution with PE/Et\(_2\)O (80/20) gave the butenolide 53d as white solid (365 mg, 1.69 mmol, 63.1%) mp 48°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.48-7.25 (m, 5H, arom H); 5.93 (s, 1H, H\(_1\)); 4.66 (d, 1H, \(J = 8.7\) Hz, H\(_7\)); 4.42 (ddd, 1H, \(J = 6.5-11.1-11.1\) Hz, H\(_8\)); 4.05 (d, 1H, \(J = 8.7\) Hz, H\(_3\)); 3.51 (ddd, 1H, \(J = 2.7-11.1-11.1\) Hz, H\(_5\)); 2.86 (dd, 1H, \(J = 2.7-13.7\) Hz, H\(_4\)); 2.77 (ddd, 1H, \(J = 6.5-11.1-13.7\) Hz, H\(_7\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 169.7 (C\(_2\)); 167.6 (C\(_{3a}\)); 137.8 (qC); 128.7-128.3 (arom HC); 126.5 (qC); 113.6 (C\(_7\)); 85.3 (C\(_7\)); 82.9 (C\(_7a\)); 68.1 (C\(_5\)); 30.4 (C\(_4\)). HRMS (M+1) calcd. for C\(_{13}\)H\(_{13}\)O; 217.0865. Found: 217.0869.

With complex 49e: 7-Methyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53e.
The general procedure was followed using carbene complex 49e (1.40 g, 4.86 mmol). Elution with PE/Et₂O (85/15) gave the butenolide 53e as colorless liquid (285 mg, 1.85 mmol, 38.1%). ¹H NMR (400 MHz, CDCl₃) δ: 5.81 (s, 1H, H₃); 4.30 (d, 1H, J = 8.6 Hz, H₇a); 4.21 (dd, 1H, J = 6.7-11.3 Hz, H₅); 3.31 (ddd, 1H, J = 2.6-11.3 Hz, H₅'); 3.11 (dq, 1H, J = 6.1-8.6 Hz, H₇); 2.78 (dd, 1H, J = 2.9-13.6 Hz, H₄); 2.65 (m, 1H, H₄'). ¹³C NMR (100 MHz, CDCl₃) δ: 169.9 (C₂); 168.0 (C₃a); 112.7 (C₃); 83.2 (C₇); 80.1 (C₇a); 67.6 (C₅); 30.2 (C₄); 19.3 (C₆). Anal. calcd. for C₈H₁₀O₃: C, 62.33; H, 6.54. Found: C, 62.42; H, 6.56.

With complex 49f: 7-Cyclopropyl-4,5,7a-tetrahydro-furo[2,3-c]pyran-2-one 53f.

The general procedure was followed using carbene complex 49f (784 mg, 2.50 mmol). Elution with PE/Et₂O (85/15) gave the butenolide 53f as white solid (214 mg, 1.19 mmol, 47.5%) mp 23°C. ¹H NMR (400 MHz, CDCl₃) δ: 5.76 (s, 1H, H₃); 4.52 (d, 1H, J = 8.7 Hz, H₇a); 4.20 (dd, 1H, J = 6.8-11.3 Hz, H₅); 3.23 (ddd, 1H, J = 2.7-11.3-11.3 Hz, H₅'); 2.77 (dd, 1H, J = 2.7-13.5 Hz, H₄); 2.65 (dd, 1H, J = 6.8-11.3-13.5 Hz, H₄'); 2.50 (dd, 1H, J = 7.5-8.7 Hz, H₇); 1.10 (m, 1H, H₈); 0.61-0.35 ( m, 4H, H₉, H₁₀). ¹³C NMR (100 MHz, CDCl₃) δ: 173.0 (C₂); 167.9 (C₃a); 112.7 (C₃); 86.7 (C₇); 82.5 (C₇a); 67.6 (C₅); 30.2 (C₄); 14.1 (C₆); 2.0-1.9 (C₉, C₁₀). Anal. calcd. for C₁₀H₁₂O₃: C, 66.65; H, 6.71 Found: C, 66.55; H, 6.87.

With complex 49g: (4R,7R,7aS) 3,4,7-triphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53g and (4R,7S,7aR) 3,4,7-triphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 55g.
The general procedure was followed using carbene complex 49g (820 mg, 1.63 mmol). The butenolide was obtained as two isomers: Elution with PE/Et₂O (80/20) gave the trans-trans isomer 53g as a fluorescent solid (293 mg, 0.80 mmol, 48.9%) mp 97°C. \([\alpha]_D^{20} = 171.43\) (c = 2.1, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 7.58-7.25 (m, 15H, arom H); 4.96 (d, 1H, J = 9.0 Hz, H\(^7a\)); 4.46 (d, 1H, J = 3.1 Hz, H\(^4\)); 4.26 (d, 1H, J = 9.0 Hz, H\(^8\)); 3.87 (dd, 1H, J = 3.1 -11.7 Hz, H\(^5\)). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\): 172.2 (C\(^2\)); 161.2 (C\(^3a\)); 139.2 (qC); 138.3 (qC); 132.5 -129.0 (arom HC); 126.9 (qC); 86.0 (C\(^7\)); 80.1 (C\(^7a\)); 72.7 (C\(^5\)); 44.5 (C\(^4\)). Anal. calcd. for C\(_{25}\)H\(_{20}\)O\(_3\): C, 81.50; H, 5.47. Found: C, 81.33; H, 5.36. Further elution with PE/Et₂O (70/30) gave the trans-cis isomer 55g as a yellow solid (515 mg, 0.14 mmol, 8.60%), mp = 174°C, \([\alpha]_D^{20} = 90.93\) (c = 2.0, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 7.56-6.80 (m, 15H, arom H); 4.84 (d, 1H, J = 9.4 Hz, H\(^7a\)); 4.39 (d, 1H, J = 9.4 Hz, H\(^7\)); 4.33 (dd, 1H, J = 6.4-11.0 Hz, H\(^5\)); 4.22 (dd, 1H, J = 6.4 -11.0 Hz, H\(^4\)); 3.69 (dd, 1H, J = 11.0 -11.0 Hz, H\(^5\)). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\): 172.8 (C\(^2\)); 160.0 (C\(^3a\)); 138.1 (qC); 134.0 (qC); 129.7 -126.6 (arom HC); 122.2 (qC); 84.3 (C\(^7\)); 81.7 (C\(^7a\)); 74.3 (C\(^5\)); 48.2 (C\(^4\)). HRMS (M+1) calcd. for C\(_{25}\)H\(_{21}\)O\(_3\): 369.1491. Found: 369.1485.

With complex 49h: 4,5-dimethyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53h.

The general procedure was followed using carbene complex 49h (830 mg, 1.83 mmol). Elution with PE/Et₂O (60/40) gave the butenolide 53h as a white solid (310 mg, 0.97 mmol, 52.9%). mp = 168°C. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 7.51 -7.25 (m, 10H, arom H); 4.68 (d, 1H, J = 9.2 Hz, H\(^7a\)); 4.23 (d, 1H, J = 9.2 Hz, H\(^7\)); 3.41 (dq, 1H, J = 6.1-9.7 Hz, H\(^5\)); 2.64 (dq, 1H, J = 6.8-9.7 Hz, H\(^5\)); 1.41 (d, 3H, J = 6.1 Hz, H\(^9\)); 0.90 (d, 3H, J = 6.8 Hz, H\(^8\)). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\): 173.1 (C\(^2\)); 163.1 (C\(^3a\)); 138.2 (qC); 130.7 (qC); 130.2-126.7 (arom HC); 126.0 (qC); 83.9 (C\(^7\)); 82.0 (C\(^5\)); 80.7 (C\(^3\)); 42.8 (C\(^4\)); 19.5 (C\(^9\)); 14.1 (C\(^8\)). Anal. calcd. for C\(_{21}\)H\(_{20}\)O\(_3\): C, 78.73; H, 6.29. Found: C, 78.57; H, 6.45.

With complex 49i: 4,5,7-trimethyl-3-phenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53i.

The general procedure was followed using carbene complex 49i (700 mg, 1.78 mmol). Elution with PE/Et₂O (60/40) gave the butenolide 53i as a white solid (139 mg, 0.54 mmol, 30.4%). mp = 108 °C. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 7.32-7.16 (m, 5H, arom H); 4.29 (d, 1H, J = 9.2 Hz, H\(^7a\)); 3.25 (dq, 1H, J = 6.1-9.2 Hz, H\(^5\)); 3.14 (dq, 1H, J =
6.1-9.2 Hz, H\textsuperscript{3}; 2.43 (dq, 1H, J = 6.6-9.2 Hz, H\textsuperscript{4}); 1.43 (d, 3H, J = 6.1 Hz, H\textsuperscript{5}); 1.25 (d, 3H, J = 6.1 Hz, H\textsuperscript{6}); 0.78 (d, 3H, J = 6.6 Hz, H\textsuperscript{8}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 173.4 (C\textsuperscript{2}); 163.4 (C\textsuperscript{3}); 130.2-128.0 (arom HC and qC); 125.2 (qC); 82.4 (C\textsuperscript{5}); 80.2 (C\textsuperscript{7}); 78.7 (C\textsuperscript{5}); 42.7 (C\textsuperscript{4}); 19.4 (C\textsuperscript{6}); 19.3 (C\textsuperscript{8}); 14.0 (C\textsuperscript{9}). Anal. calcd. for C\textsubscript{16}H\textsubscript{18}O\textsubscript{3}: C, 74.39; H, 7.02. Found: C, 74.27; H, 7.19.

With complex 49j: 7-Cyclopropyl-4,5-dimethyl-3-phenyl-5,6,7,7a-tetrahydro-4H-benzofuran-2-one 53j.

The general procedure was followed using carbene complex 49j (691 mg, 1.80 mmol). Elution with PE/Et\textsubscript{2}O (70/30) gave the butenolide 53j as a white solid (195 mg, 0.68 mmol, 39.0%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.39-7.15 (m, 5H, arom H); 4.54 (d, 1H, J = 8.9 Hz, H\textsuperscript{7a}); 3.10 (dq, 1H, J = 6.1-9.7 Hz, H\textsuperscript{5}); 2.60 (m, 1H, H\textsuperscript{7}); 2.41 (dq, 1H, J = 7.0-9.7 Hz, H\textsuperscript{4}); 1.25 (d, 3H, J = 6.1 Hz, H\textsuperscript{9}); 1.15 (m, 1H, H\textsuperscript{10}); 0.78 (d, 3H, J = 6.6 Hz, H\textsuperscript{8}); 0.70-0.50 (m, 4H, H\textsuperscript{11} and H\textsuperscript{12}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 173.5 (C\textsuperscript{2}); 163.5 (C\textsuperscript{3}); 132.7-128.4 (arom HC and qC); 85.7 (C\textsuperscript{7}); 81.8 (C\textsuperscript{7a}); 80.1 (C\textsuperscript{5}); 42.7 (C\textsuperscript{4}); 19.4 (C\textsuperscript{6}); 14.1 (C\textsuperscript{10}); 14.0 (C\textsuperscript{8}); 2.3, 2.2 (C\textsuperscript{11} or C\textsuperscript{12}).

With complex 49k: 1,4-diphenyl-3a,4,5a,6,7,8,9,9a-octahydro-3,5-dioxa-cyclopenta[a] naphthalen-2-one 53k.

The general procedure was followed using carbene complex 49k (730 mg, 1.52 mmol). Elution with PE/Et\textsubscript{2}O (60/30) gave the butenolide 53k as a white solid (386 mg, 1.12 mmol, 73.9%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.53-7.28 (m, 10H, arom H); 4.70 (d, 1H, J = 9.0 Hz, H\textsuperscript{3a}); 4.25 (d, 1H, J = 9.0 Hz, H\textsuperscript{4}); 4.41 (ddd, 1H, J = 4.0-9.6-13.5 Hz, H\textsuperscript{5a}); 2.53 (ddd, 1H, J = 3.1-9.6-12.4 Hz, H\textsuperscript{9a}); 2.16 (m, 1H, H\textsuperscript{6}); 1.89-1.78 (m, 2H, H\textsuperscript{7} and H\textsuperscript{9}); 1.62-1.52 (m, 2H, H\textsuperscript{8} and H\textsuperscript{6}); 1.30-1.12 (m, 2H, H\textsuperscript{7} and H\textsuperscript{8}); 0.96 (m, 1H, H\textsuperscript{10}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 173.2 (C\textsuperscript{2}); 162.3 (C\textsuperscript{10}); 138.2 (qC); 130.2 (qC); 129.6-126.7 (arom HC); 125.4 (qC); 84.6 (C\textsuperscript{4}); 82.6 (C\textsuperscript{8a}); 82.0 (C\textsuperscript{7}); 46.8 (C\textsuperscript{9a}); 32.6 (C\textsuperscript{8}); 27.6 (C\textsuperscript{6}); 25.2 (C\textsuperscript{5}); 24.3 (C\textsuperscript{3}). Anal. calcd. for C\textsubscript{23}H\textsubscript{22}O\textsubscript{3}: C, 79.74; H, 6.40. Found: C, 79.88; H, 6.43.

With complex 49l: 4-Cyclopropyl-1-phenyl-3a,4,5a,6,7,8,9a-octahydro-3,5-dioxa-cyclopenta[a] naphthalen-2-one 53l.
The general procedure was followed using carbene complex 49l (204 mg, 0.46 mmol). Elution with PE/Et₂O (60/30) gave the butenolide 53l as a white solid (75 mg, 0.25 mmol, 53.2 %). ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.16 (m, 5H, arom H); 4.54 (d, 1H, J =7.8-8.7 Hz, H₃a); 2.89 (ddd, 1H, J = 4.0-10.8-13.7 Hz, H₅a); 2.32 (ddd, 1H, J = 2.9-10.8-12.3 Hz, H₉a); 1.89-0.36 (m, 13H, H₆', H₇', H₈', H₉', H₁₁, H₁² and H₁³). ¹³C NMR (100 MHz, CDCl₃) δ: 173.9 (C₂); 163.1 (C₃a); 132.9 -125.4 (arom HC and qC); 86.6 (C₄); 82.4 (C₅a); 82.1 (C₃a); 47.0 (C₈a); 32.9 (C₆'); 27.8 (C₆); 25.5 (C₅'); 14.6 (C₁²); 2.7, 2.6 (C₁² or C₁³). Anal. calcd. for C₂₀H₂₂O₃: C, 77.39; H, 7.14. Found: C, 76.43; H, 7.39.

With complex 56b: 3,8-diphenyl-5, 6, 8, 8a-tetrahydro 4H-furo [2,3-c] oxepin-2-one 57b.

The general procedure was followed using carbene complex 56b (2.10 g, 4.77 mmol). Elution with PE/Et₂O (85/15) gave 57b as an oil (112 mg, 0.37 mmol, 7.7%). ¹H NMR (400MHz, CDCl₃) δ: 7.44-7.27 (m, 10H, arom H); 4.94 (d, 1H, J = 9.2 Hz, H₈a); 4.21 (dt, 1H, J = 6.0 -12.0 Hz, H₆); 4.10 (d, 1H, J = 9.2 Hz, H₈); 3.64 (ddd, 1H, J = 4.0-7.6-15.8 Hz, H₄); 2.79 (ddd, 1H, J = 5.3-7.6-15.8 Hz, H₄); 2.15 (m, 1H, H₅); 1.90 ( m, 1H, H₅). ¹³C NMR (100 MHz, CDCl₃) δ: 172.4 (C₂); 163.8 (C₃a); 129.3-128.9 (arom HC) ; 127.3 (qC); 85.7 (C₈); 84.3 (C₈a); 71.0 (C₆); 26.7 (C₄); 24.9 (C₅). HRMS (MH⁺), calcd. for C₂₀H₁₉O₃: 307.1334. Found: 307.1336.

With complex 56a: 8-Cyclopropyl-3-phenyl-5,6,8,8a-tetrahydro-4H-furo[2,3-c]oxepin-2-one 57a.

The general procedure was followed using carbene complex 56a (3.30 g, 8.17 mmol). The butenolide was obtained as two isomers: Elution with PE/Et₂O (70/30) gave 57a the trans isomer as white solid (780 mg, 2.89 mmol, 35.4%) mp = 73°C. ¹H NMR (400 MHz, CDCl₃) δ: 7.52-7.25 (m, 5H, arom H); 4.82 (d, 1H, J = 8.6 Hz, H₈a); 4.12 (ddd, 1H, J = 5.6-5.6-12.5 Hz, H₈); 3.48 (ddd, 1H, J = 4.6-7.7-12.5 Hz, H₈); 2.96 (ddd, 1H, J = 5.1-7.1-15.0 Hz, H₈); 2.85 (dd, 1H, J = 2.5-8.6 Hz, H₈); 2.69 (ddd, 1H, J = 4.6-8.7-15.0 Hz, H₈); 2.05 (m, 1H, H₅); 1.83 (m, 1H, H₅); 1.25 (m, 1H, H₅);
0.68-0.42 (m, 4H, H10, H11). 13C NMR (100 MHz, CDCl3) δ: 172.5 (C2); 163.7 (C3a); 129.8 (qC); 129.0-128.6 (arom HC); 127.0 (qC); 85.5 (C8a); 83.3 (C8); 70.2 (C6); 26.3 (C4); 24.3 (C5); 14.6 (C9); 2.6-1.3 (C10 or C11). Anal. calcd. for C17H18O3: C, 75.53; H, 6.71. Found: C, 75.35; H, 6.79. Further elution with PE/Et2O (80/20) gave 58a the cis isomer as a colorless liquid (357 mg, 1.32 mmol, 16.2%).

1H NMR (400 MHz, CDCl3) δ: 7.54-7.25 (m, 5H, H arom); 5.23 (d, 1H, J = 4.0 Hz, H8a); 4.04 (ddd, 1H, J = 3.6-6.6-13.0 Hz, H6); 3.71 (ddd, 1H, J = 2.5-7.6-13.0 Hz, H6'; 3.25 (dd, 1H, J = 4.0-9.7 Hz, H8); 3.00 (ddd, 1H, J = 3.6-8.1-16.5 Hz, H4'; 2.76 (ddd, 1H, J = 3.6-8.1-16.5 Hz, H4); 1.86 (m, 2H, H5, H5'); 0.99 (m, 1H, H9); 0.70-0.35 (m, 4H, H10 and H11). 13C NMR (CDCl3, 100 MHz) δ: 172.7 (C2); 162.9 (C3a); 132.6 (qC); 130.1-128.5 (arom HC); 127.2 (qC); 85.0 (C8a); 84.0 (C8); 69.7 (C6); 29.2 (C5); 26.7 (C4); 9.3 (C9); 3.8-2.5 (C10 or C11). HRMS (M+1) calcd. for C17H19O3: 271.1334. Found: 271.1336.

C- OTHER EXPERIMENTAL CONDITIONS, REACTION OF N-METHYLDIHYDROPYRIDINE WITH COMPLEXES 49d AND 49e IN VARIOUS SOLVENTS

General procedure

To a solution of carbene complex 49d or 49e (1 mol eq) in the appropriate solvent (25 mL/mmol of carbene) at –10°C, under argon was added dropwise a solution of N-methyl dihydropyridine (3 mol eq) by syringe. After 15mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixtures of PE/Et2O as eluent.

With complex 49d: 7-phenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53d.

In CH2Cl2 : The general procedure was followed using carbene complex 49d (940 mg, 2.68 mmol). Elution with PE/Et2O (80/20) gave the butenolide 53d (365 mg, 1.69 mmol, 63.1%, de = 100%).

In DMF : The general procedure was followed using carbene complex 49d (450 mg, 1.29 mmol). Elution with PE/Et2O (80/20) gave the butenolide 53d (117 mg, 0.54 mmol, 42.1%, de = 100%).

In MeCN : The general procedure was followed using carbene complex 49d (450 mg, 1.29 mmol). Elution with PE/Et2O (80/20) gave the butenolide 53d (156 mg, 0.72 mmol, 56.0%, de = 100%).

In MeOH : The general procedure was followed using carbene complex 49d (463 mg, 1.60 mmol). No formation of butenolide 53d was observed.

With complex 49e: 7-Methyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53e.

In CH2Cl2 : The general procedure was followed using carbene complex 49e (1.40 g, 4.86 mmol). Elution with PE/Et2O (85/15) gave the butenolide 53e (285 mg, 1.85 mmol, 38.1%, de = 100%).

In THF : The general procedure was followed using carbene complex 49e (454 mg, 1.58 mmol). Elution with PE/Et2O (85/15) gave the butenolide 53e (74 mg, 0.48 mmol, 30.3%, de = 60%).
In MeCN : The general procedure was followed using carbene complex 49e (463 mg, 1.60 mmol). Elution with PE/Et₂O (85/15) gave the butenolide 53e (139 mg, 0.90 mmol, 56.0%, de = 82%).

III- BEHAVIOUR OF OTHER DIHYDROPYRIDINES WITH CARBENE COMPLEXES

A- REACTION OF N-BENZYL DIHYDROPYRIDINE 59 WITH COMPLEXES 37, 48a AND 48d

1,4-N-benzyl dihydropyridine 59 was synthetized following the literature procedure.⁴⁴

General procedure

To a solution of carbene complex (1 mol eq) in CH₂Cl₂ (25 mL/mmol of carbene) at –10°C, under argon was added dropwise from an additional funnel a solution of N-benzyl dihydropyridine (3 mol eq) in CH₂Cl₂ (0.5 mL/mmol of amine). After 15mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixtures of PE/Et₂O as eluent.

With complex 37: 7-ethoxy-3-phenyl 3, 6, 7, 7a-tetrahydro-4H-benzofuran-2-one 38 and 39

The general procedure was followed using carbene complex 7 (1.74 g, 4.44 mmol). Elution with PE/Et₂O (20/80) gave the butenolide as two isomers in 43.0% global yield: trans isomer 38 (394 mg, 1.53 mmol, 34.4%), cis isomer 39 (98 mg, 0.38 mmol, 8.6%), de = 60%.

With complex 48d: 6-benzyl-7-ethoxy-3-phenyl 5, 6, 7, 7a-tetrahydro-4H-benzofuran-2-one 50d and 51d.

The general procedure was followed using carbene complex 48d (1.50 g, 3.11 mmol). Elution with PE/Et₂O (30/70) gave the butenolide as two isomers in 45.0% global yield: trans isomer 50d (205 mg, 0.59 mmol, 21.0%), cis isomer 51d (283 mg, 0.81 mmol, 24.0%), de = 16%.

With complex 48a: 7-ethoxy-3,5-diphenyl-5,6,7,7a-tetrahydro-4H-benzofuran-2-one 50a and 51a.

The general procedure was followed using carbene complex 48a (1.05 g, 2.24 mmol). Elution with PE/Et₂O (30/70) gave the butenolide as two isomers in 42.0% global yield: trans isomer 50a (157 mg, 0.47 mmol, 21.0%), cis isomer 51a (157 mg, 0.47 mmol, 21.0%), de = 0%. 
B- REACTION OF N-METHYL-N,N-DIETHYLDIHYDRONICOTINAMIDE 60 WITH COMPLEX 49a

Dihydronicotinamide 60 was prepared following the literature procedure.

To a solution of carbene complexes 49a (360 mg, 0.84 mmol) in CH₂Cl₂ (20 mL) at –10°C, under argon was added dropwise a solution of nicotinamide 6 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solvent was evaporated under vacuum and the butenolide 53a was obtained after silica gel chromatography as a white solid (91 mg, 0.31 mmol, 37.0%, de = 100%).

C-REACTIVITY OF THE CHIRAL NICOTINAMIDES

Dihydronicotamides 61, 62, 63 were prepared following the literature procedures.

Reaction with chiral nicotinamides

General procedure

To a solution of carbene complexes 49e or 49d (1 mol eq) in CH₂Cl₂ (25 mL/mmol of carbene) at –40°C, under argon was added dropwise a solution of the appropriate nicotinamide (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolides 53d and 53e were obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

With nicotinamide 61

The general procedure was followed using the complex 49d (350 mg, 1.00 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53d (65 mg, 0.30 mmol, 30.1%, de = 100%, ee = 20%).

The general procedure was followed using the complex 49e (734 mg, 2.55 mmol). Elution with PE/Et₂O (70/30) gave the butenolide 53e (216 mg, 1.40 mmol, 55.0%, de = 100%, ee = 1%).

With nicotinamide 62

The general procedure was followed using the complex 49d (402 mg, 1.15 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53d (32 mg, 0.15 mmol, 13.1%, de = 100%, ee = 2%).

With nicotinamide 63

The general procedure was followed using the complex 49e (402 mg, 1.15 mmol). Elution with PE/Et₂O (70/30) gave the butenolide 53e (20 mg, 0.13 mmol, 15.0%, de = 49%, ee = 11%).

Reaction of nicotinamide 61 with complex 49d in various solvents

General procedure
To a solution of carbene complex 49d (1 mol eq) in the appropriate solvent (25 mL/mmol of carbene) at –40°C, under argon was added dropwise a solution of the nicotinamide 61 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolide 53d was obtained after silica gel chromatography using mixtures of PE/Et<sub>2</sub>O as eluent.

In CH<sub>2</sub>Cl<sub>2</sub>: The general procedure was followed using complex 49d (350 mg, 1.00 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave the butenolide 53d (65 mg, 0.30 mmol, 30.1%, de = 100%, ee = 20%).

In MeCN: The general procedure was followed using complex 49d (400 mg, 1.14 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave the butenolide 53d (71 mg, 0.33 mmol, 28.9%, de = 100%, ee = 1%).

In toluol: The general procedure was followed using complex 49d (450 mg, 1.28 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave the butenolide 53d (78 mg, 0.36 mmol, 28.0%, de = 100%, ee = 6%).

D- REACTIVITY OF N- ALKYLDIHYDROPYRIDINES

When the chiral center is linked to the pyridinium nitrogen

Dihydropyridines 64<sup>30b</sup>, 65<sup>50b</sup>, 66<sup>67</sup>, 67<sup>50c</sup> and 68<sup>50</sup> were prepared following the literature procedures.

**General procedure**

To a solution of carbene complexes 49e or 49d or 49f (1 mol eq) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL/mmol of carbene) at -40°C, under argon was added dropwise a solution of the appropriate N-alkyldihydropyridine (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolides 53e, 53d or 53f were obtained after silica gel chromatography using mixtures of PE/Et<sub>2</sub>O as eluent.

**With dihydropyridine 64**

The general procedure was followed using complex 49d (410 mg, 1.17 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave the butenolide 53d (151 mg, 0.70 mmol, 59.7%, de = 100%, ee = 4.3%).

The general procedure was followed using complex 49e (746 mg, 2.57 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave the butenolide 53e (247 mg, 1.60 mmol, 62.5%, de = 100%, ee = 1.2%).

The general procedure was followed using complex 49f (1.00 g, 3.18 mmol). Elution with PE/Et<sub>2</sub>O (80/20) gave the butenolide 53f (332 mg, 1.84 mmol, 58.0%, de = 100%, ee = 1.8%).

**With dihydropyridine 65**

The general procedure was followed using complex 49d (1 mol eq) in the appropriate solvent (25 mL/mmol of carbene) at –40°C, under argon was added dropwise a solution of the nicotinamide 61 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolide 53d was obtained after silica gel chromatography using mixtures of PE/Et<sub>2</sub>O as eluent.
The general procedure was followed using complex 49d (380 mg, 1.08 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53d (167 mg, 0.77 mmol, 71.6%, de = 100%, ee = 27%).

The general procedure was followed using complex 49e (480 mg, 1.67 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (171 mg, 1.11 mmol, 66.7%, de = 100%, ee = 11.5%).

The general procedure was followed using complex 49f (500 mg, 1.59 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53f (172 mg, 0.95 mmol, 60.0%, de = 100%, ee = 1%).

**Reaction of N-alkyldihydropyridine 65 with complex 49e in various solvents**

**General procedure**

To a solution of carbene complex 49e (1 mol eq) in the appropriate solvent (25 mL/mmol of carbene) at -40°C, under argon was added dropwise a solution of N-alkyldihydropyridine 65 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolide 53e was obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

In CH₂Cl₂: The general procedure was followed using complex 49e (480 mg, 1.67 mmol). Elution with PE/Et₂O (80/20) gave the butenolides 53e (171 mg, 1.11 mmol, 66.7%, de = 100%, ee = 11.5%).

In pentane: The general procedure was followed using complex 49e (320 mg, 1.11 mmol). Elution with PE/Et₂O (80/20) gave the butenolides 53e and 53e' (86 mg, 0.56 mmol, 50.0%, de = 94%, ee = 25.8%).

In toluol: The general procedure was followed using complex 49e (400 mg, 1.39 mmol). Elution with PE/Et₂O (80/20) gave the butenolides 53e and 53e' (116 mg, 0.75 mmol, 54.0%, de = 92%, ee = 20.0%).

In hexane: The general procedure was followed using complex 49e (370 mg, 1.29 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e and 53e' (105 mg, 0.68 mmol, 53.0%, de = 94%, ee = 25.0%).

In MeCN: The general procedure was followed using complex 49e (370 mg, 1.29 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e and 53e' (160 mg, 1.04 mmol, 81.0%, de = 80%, ee = 3.5%).

**Reaction of N-alkyldihydropyridine 65 (various equivalents) with complex 49e**

To a solution of carbene complex 65 (1 mol eq) in CH₂Cl₂ (25 mL/mmol of carbene) at -40°C, under argon was added dropwise a solution of N-alkyldihydropyridine (various equivalents) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolide 53e was obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

With 1 equivalent: The general procedure was followed using complex 49e (425 mg, 1.47 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (115 mg, 0.75 mmol, 50.6%, de = 100%, ee = 9.2%).

With 1 equivalent + 2 equivalents of pyridine: The general procedure was followed using complex 49e (438 mg, 1.52 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (135 mg, 0.88 mmol, 57.6%, de = 100%, ee = 11.2%).
With 2 equivalents: The general procedure was followed using complex 49e (425 mg, 1.47 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (140 mg, 0.91 mmol, 61.6%, de = 100%, ee = 8.9%).

With 3 equivalents: The general procedure was followed using complex 49e (480 mg, 1.67 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (171 mg, 1.11 mmol, 66.7%, de = 100%, ee = 11.5%).

With 5 equivalents: The general procedure was followed using complex 49e (435 mg, 1.51 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (145 mg, 0.94 mmol, 62.5%, de = 100%, ee = 14.2%).

**Reaction of N-alkyldihydropyridines 66 and 67 with complex 49d and 68 with complex 49e**

**General procedure**

To a solution of carbene complexes 49d or 49e (1 mol eq) in CH₂Cl₂ (25 mL/mmol of carbene) at –40°C, under argon were added dropwise solutions of N-alkyldihydropyridines 66 or 67 or 68 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolides 53d or 53e was obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

With dihydropyridine 66

The general procedure was followed using complex 49d (396 mg, 1.13 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53d (165 mg, 0.76 mmol, 67.5%, de = 100%, ee = 18.0%).

With dihydropyridine 67

The general procedure was followed using complex 49d (600 mg, 1.71 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53d (94 mg, 0.43 mmol, 25.3%, de = 100%, ee = 11.0%).

With dihydropyridine 68

The general procedure was followed using complex 49e (443 mg, 1.54 mmol). Elution with PE/Et₂O (70/30) gave the butenolide 53e (118 mg, 0.77 mmol, 50.0%, de = 100%, ee = 7.6%).

When the chiral center is carried by a substituent linked to the cycle

*N*-benzynicotinium bromide 70,⁵³ was prepared following the literature procedure.

**Synthesis of N-benzylidihydronicotine 71**
To a suspension of sodium dithionite (15.66 g, 99 mmol) and potassium carbonate (12.43 g, 90 mmol) in toluol (80 mL) and water (90 mL), was added by a dropping funnel an aqueous solution (25 mL) of N-benzylnicotinium bromide 70 (5 g, 15 mmol). The resulting mixture was refluxed during 12 mn. The organic phase was separated, washed with sodium bicarbonate solution, water and dried over sodium sulfate. After removal of the solvent, the N-benzyl-1,4-dihydronicotine 71 was obtained as a yellow oil in 24% yield (1.04 g, 4.1 mmol).

\[ \text{Synthesis of N-methyldihydronicotine 73} \]

\[
\text{Formation of 3-(1-methyl-pyrrolidin-2-yl)-2H-pyridine-1-carboxylic acid methyl ester 72}
\]

To a mixture of S(-)-nicotine 69 (8.00 g, 49.40 mmol) and sodium borohydride (1.88 g, 49.40 mmol) in absolute ethanol (60 mL), cooled to -78°C, a solution of methylchloroformate (3.80 mL, 49.40 mmol) in Et₂O (16 mL) was added. The temperature did not exceed -70°C. The reaction mixture was allowed to warm to -40°C and stirred for an additional 1.5 hours, then poured into ice water before being extracted 3 times with Et₂O (200 mL). The organic layers were combined, washed with brine and finally dried over sodium sulfate. The crude oil was purified by flash chromatography on silica gel using a mixture of PE/AcOEt (65/35) as eluent. After solvent removal, the 1,2-N-carbomethoxydihydropyridine 72 was obtained as a yellow oil in 76% yield (8.36 g, 37.64 mmol).

\[ \text{Reduction with LiAlH}_4: 1\text{-methyl-3-(1-methyl-pyrrolidin-2-yl)-1,2-dihydropyridine 73} \]
To a suspension of lithium aluminium hydride (2.44 g, 1.7 eq) in Et₂O (120 mL) at 0°C, was added a Et₂O solution (25 mL) of 3-(1-methyl-pyrrolidin-2-yl)-2H-pyridine-1-carboxylic acid methyl ester (8.35 g, 37.60 mmol). After addition, the mixture was refluxed 24 hours. A 10% solution of sodium hydroxide (50 mL) was added slowly at 0 °C. The mixture was extracted 3 times with Et₂O (250 mL), washed with water and brine, dried over sodium sulfate. After removal of the solvent, the N-methyl-1,2-dihydropyridine 73 was obtained as a yellow oil in 90% yield (6.02 g, 33.82 mmol).

\[ \text{1H NMR (200 MHz, CDCl}_3 \text{)} \delta: 5.93 (dd, 1H, } J = 0.7 -7.0 \text{ Hz, } H^6; 5.77 \text{ (d, 1H, } J = 5.5 \text{ Hz, } H^4; 4.68 \text{ (dd, 1H, } J = 5.5 -7.0 \text{Hz, } H^5; 3.66 \text{ (s, 2H, } H^2; 2.63 \text{ (s, 3H, NMe); 2.58 \text{ (m, 1H, } H^3; 2.17-2.0 \text{ (m, 5H, } H^3 \text{ and NMe); 1.77 \text{ (m, 2H, } H^4. \text{ 13C NMR (50 MHz, CDCl}_3 \text{)} \delta: 138.5 (C^6); 124.3 (qC); 121.6 (C^5); 95.2 (C^5); 72.0 (C^7); 56.9 (C^5); 49.2 (C^5); 42.5 (NMe); 40.6 (NMe); 29.0 (C^3); 22.6 (C^3). } [\alpha]_{D}^{20} = -92.6 \text{ (c = 2.42, CHCl}_3). \]

**REACTIVITY OF N-ALKYLDIHYDRONICOTINES**

**Reaction of N-benzylidihydronicotine 71 with complex 49e: 7-Methyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53e.**

To a solution of carbene complex 49e (576 mg, 2 mmol) in CH₂Cl₂ (40 mL) at -40°C, under argon was added dropwise a solution of N-benzylidihydronicotine 71 (720 mg, 3 mmol) in CH₂Cl₂ (4 mL) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solvent was evaporated and after silica gel chromatography, the butenolide 53e was obtained as a colorless oil (157 mg, 1.02 mmol, 51.1%, ee = 4.3%).

**Reaction of N-methyldihydronicotine 73 with complexes 49a-f**

**General procedure**

To a solution of the appropriate carbene complex (1 mol eq) in CH₂Cl₂ solvent (25 mL/mmol of carbene) at -40°C, under argon was added dropwise a solution of N-methylidihydronicotine 73 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the expected butenolide was obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

The general procedure was followed using complex 49a (500 mg, 1.17 mmol). Elution with PE/Et₂O (85/15) gave the butenolide 53a (129 mg, 0.44 mmol, 37.7%, de = 100%, ee = 30%, [α]D²⁰ = 54.0 (c = 2.0, CHCl₃)).
The general procedure was followed using complex 49b (710 mg, 1.95 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53b (44 mg, 0.19 mmol, 9.8%, de = 100%, ee = 37%, [α]D20 = -30.4 (c = 2.0, CHCl₃)).

The general procedure was followed using complex 49c (420 mg, 1.07 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53c (118 mg, 0.46 mmol, 43.0%, de = 100%, ee = 12.5%, [α]D20 = 5.5 (c = 2.1, CHCl₃)).

The general procedure was followed using complex 49d (500 mg, 1.43 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53d (194 mg, 0.90 mmol, 62.9%, de = 100%, ee = 12.5%, [α]D20 = 9.3 (c = 2.1, CHCl₃)).

The general procedure was followed using complex 49e (800 mg, 2.55 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (146 mg, 0.81 mmol, 31.8%, de = 100%, ee = 14%, [α]D20 = 9.3 (c = 2.1, CHCl₃)).

Reaction of N-methyldihydronicotine 73 with complex 49e in various solvents

General procedure

To a solution of carbene complex 49e (1 mol eq) in the appropriate solvent (25 mL/mmol of carbene) at –40°C, under argon was added dropwise a solution of the nicotinamide 73 (3 mol eq) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolide 53e was obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

In CH₂Cl₂: The general procedure was followed using complex 49e (375 mg, 1.30 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (68 mg, 0.44 mmol, 34.0%, de = 100%, ee = 55%).

In THF: The general procedure was followed using complex 49e (375 mg, 1.30 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (20 mg, 0.13 mmol, 10.1%, de = 80%, ee = 55%).

In MeCN: The general procedure was followed using complex 49e (502 mg, 1.74 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (98 mg, 0.63 mmol, 37.0%, de = 96%, ee = 46%).

In pentane: The general procedure was followed using complex 49e (390 mg, 1.36 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (79 mg, 0.52 mmol, 38.0%, de = 96%, ee = 54%).

In C₆F₁₄: The general procedure was followed using complex 49e (390 mg, 1.36 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (16 mg, 0.10 mmol, 8.0%, de = 100%, ee = 44%).

Reaction of N-methyldihydronicotine 73 (various equivalents) with complex 49e

To a solution of carbene complex 49e (1 mol eq) in CH₂Cl₂ (25 mL/mmol of carbene) at –40°C, under argon was added dropwise a solution of N-alkyldihydronicotine 35 (various equivalents) by syringe. After 20mn, the ice bath was taken off and the mixture allowed to stir at room temperature during 24h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the butenolide 53e was obtained after silica gel chromatography using mixtures of PE/Et₂O as eluent.

With 0.9 equivalent: The general procedure was followed using complex 49e (400 mg, 1.38 mmol). Elution with PE/Et₂O (80/20) gave the butenolide 53e (69 mg, 0.45 mmol, 36.0%, de = 100%, ee = 54.6%).
With 3 equivalents: The general procedure was followed using complex 49e (400 mg, 1.38 mmol). Elution with PE/Et$_2$O (80/20) gave the butenolide 53e (64 mg, 0.42 mmol, 30.1%, $de = 100\%, ee = 54.4\%$).

With 6 equivalents: The general procedure was followed using complex 49e (400 mg, 1.38 mmol). Elution with PE/Et$_2$O (80/20) gave the butenolide 53e (66 mg, 0.43 mmol, 31.0%, $de = 100\%, ee = 47.5\%$).
E-OTHER NUCLEOPHILES

A- INORGANIC HYDRIDES

Reaction of complex 4b with KHB(OiPr)$_3$ and 1-methyl-pyridinium iodide 74: tungstenate complex 75

\[
\begin{align*}
&\text{(OC)}_5W^1H^2\text{Ph}^3N^4Me^5 \\
&\text{At } 0°C, 4 \text{ mL of potassium triisopropoxyborohydride (0.83M in THF) was added to a solution of the carbene complex 4b (1.00 g, 2.67 mmol) in 30 mL of THF. The reaction turned immediately from red to yellow and, after five minutes, 2 mL of a 10% sodium hydroxide solution in water were added in order to destroy the excess of hydride. Then 1.18 g (5.34 mmol) of 1-methyl-pyridinium iodide were added leading to the formation of the tungstenate complex 75 as a red oil (1.31 g, 2.38 mmol, 89.0%).} \\
&\text{H NMR (CDCl$_3$, 400 MHz) } \delta: 9.12 (d, 2H, J = 6.0 Hz, H$_o$py.); 8.72 (t, 1H, J = 7.0 Hz, H$_p$py.); 8.27 (m, 2H, H$_m$py.); 8.00-7.01 (m, 5H, arom H); 5.05 (s, 1H, H$_1$); 4.65 (s, 3H, H$_4$); 3.42 (m, 1H, H$_2$); 3.06 (m, 1H, H$_2'$); 1.15 (t, 3H, J = 7.0 Hz, H$_3$). \\
&\text{C NMR (CDCl$_3$, 100 MHz) } \delta: 205.1 (\text{trans CO}); 192.4 (\text{cis CO}); 146.5-120.3 (\text{arom HC and qC}); 97.4 (C$_1$); 67.2 (C$_2$); 49.7 (C$_4$); 16.6 (C$_3$).
\end{align*}
\]

Reaction of complex 4b with N-methyldihydropyridine 19: tungstenate complex 75

A solution of the N-methyl-dihydropyridine 19 (650 mg, 6.80 mmol) in Et$_2$O (20 mL) was added to a solution of complex 4b (1.00 g, 2.30 mmol) in CH$_2$Cl$_2$ (10 mL) at -78°C. The solution turned immediately to dark red. After warming at 0°C, the solvent was evaporated under vacuum to give the tungstenate complex 75 (1.09 g, 1.98 mmol, 86.0% yield).

Reaction of complex 49a with KHB(OiPr)$_3$: 3-benzylidene-2-phenyl-tetrahydro-furan 79 and 80, 3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53a and 4-phenyl-but-3-yn-1-ol.

\[
\begin{align*}
&\text{At } -10°C, 845 \mu\text{L of potassium triisopropoxyborohydride (0.83 M in THF) was added to a solution of the carbene complex 49a (300 mg, 0.70 mmol) in 15 mL of THF. After 10 minutes at 0°C the reaction was allowed to warm to room temperature and then stirred for 15 hours. After cooling at 0°C, the unreacted hydride was destroyed by addition of ice and then the THF was removed on a rotary evaporator. After extraction with CH$_2$Cl$_2$ (3x 10 mL) the combined extracts were washed with water and brine and dried over anhydrous Na$_2$SO$_4$.
\end{align*}
\]
Chromatography on silica gel with mixtures of PE/EtO as eluent gave first 3-benzyldiene-2-phenyl-tetrahydro-furan \(79\) and \(80\) as a clear oil (50 mg, 0.21 mmol, 30.2 %) as a mixture of two isomers in a 6/4 ratio: one isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.28-6.99\) (m, 10H, arom H); \(6.60\) (d, 1H, \(J = 1.5\) Hz, H\(^8\)); \(5.68\) (s, 1H, H\(^7\)); \(3.83\) (t, 2H, \(J = 6.8\) Hz, H\(^1\)); \(2.95-2.76\) (m, 2H, H\(^3\)). \(^1^3^C\) (100 MHz, CDCl\(_3\)) \(\delta: 142.4\) (C\(^3\)); 141.0 (qC); 137.1 (qC); 129.8-127.0 (arom HC); 124.1 (C\(^6\)); 80.8 (C\(^5\)); 65.5 (C\(^4\)); 35.9 (C\(^2\)). HMRs (M+1) calcd for C\(_{17}\)H\(_{20}\)O 237.1279. Found 237.1273. Other isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.34-6.99\) (m, 10H, arom H); \(6.02\) (d, 1H, \(J = 2.3\) Hz, H\(^8\)); \(5.68\) (d, 1H, \(J = 1.5\) Hz, H\(^3\)); \(4.23\) (m, 1H, H\(^7\)); \(3.87\) (m, 1H, H\(^8\)); \(2.96-2.92\) (m, 2H, H\(^3\)). \(^1^3^C\) (100 MHz, CDCl\(_3\)) \(\delta: 144.7\) (C\(^3\)); 141.9 (qC); 137.9 (qC); 128.8-127.1 (arom HC); 123.2 (C\(^6\)); 85.3 (C\(^5\)); 68.4 (C\(^4\)); 32.2 (C\(^2\)).

Further elution gave the butenolide \(53a\) in 20.9 % yield as a single \(trans\) isomer.

Finally, the alcohol 4-phenyl-but-3-yn-1-ol was obtained as a colorless oil (33 mg, 0.22 mmol, 32.1%).

**Reaction of carbene complex 49e with NaBH\(_4\): 7-methyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53e**

To a solution of carbene complex 49e (199 mg; 0.69 mmol) in THF (10 mL) at \(-20^\circ\)C was added sodium borohydride (7 mg; 0.25 equiv.) in portions. The reaction mixture was slowly warmed to room temperature and stirred for 12 hours. The starting material was completely reduced after 5 minutes (TLC monitoring). Addition of 2 mL of water followed by extraction with CH\(_2\)Cl\(_2\) (3x15 mL) drying over anhydrous sodium sulfate and evaporation gave a brown residue. Silica gel chromatography gave the butenolide 53a as a yellow oil and as two isomers in 7/3 ratio in 22.4 % global yield (23.8 mg, 0.15 mmol).

**Reaction of carbene complex 49e with KHB(O\(_i\)Pr\(_3\)): 7-methyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53e**

At \(-10^\circ\)C, 1.46 mL of potassium triisopropoxyborohydride (0.83M in THF) was added to a solution of the carbene complex 49e (349 mg, 1.21 mmol) in 15 mL of THF. After 10 minutes at \(0^\circ\)C the reaction was allowed to warm to room temperature and then stirred for 15 hours. After cooling to \(0^\circ\)C, the unreacted hydride was destroyed by addition of ice and then THF was removed on a rotatory evaporator. After extraction with CH\(_2\)Cl\(_2\) (3x 10 mL) the combined extracts were washed with water and brine and dried over anhydrous Na\(_2\)SO\(_4\). Chromatography on silica gel gave the butenolide 53e as a mixture of two isomers (\(trans/cis\): 90/10) in 12.5 % yield (23 mg, 0.15 mmol).

**Reaction of carbene complex 49e with 9-BBN and S(-) nicotine: 7-methyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 53e**

To a mixture of S(-)nicotine 69 (243 mg, 1.5 mmol) and 9-BBN (3.00 mL; 1.50 mmol, 0.5 M) in THF (3 mL), cooled at -20 °C, a solution of complex 49e (425 mg, 1.47 mmol) in THF (5 mL) was added. The yellow solution turned immediately red. The mixture was allowed to reach room temperature and stirred for 24 hours. The expected butenolide...
53e was obtained after silica gel chromatography as a mixture of two isomers in 6/4 ratio in 12.8% yield (29 mg, 0.19 mmol).

**B- ALCOHOLATES**

Reaction of complex 49a with sodium methylate: 3,7-diphenyl-4,5-dihydro-furo[2,3-c]pyran-2-one 83 and 7-methoxy-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 82

At 0°C, 66 µl of a 30% MeO-\text{Na}^+/\text{MeOH} solution was added by syringe to a solution of carbene complex 49a (153 mg ; 0.36 mmol) in 15 mL of THF. The solution turned from red to yellow. The resulting mixture was stirred 10 minutes at 0°C and then allowed to warm to room temperature and stirred for 15 hours. Removal of the solvent left a brownish residue that was purified by silica gel chromatography with various mixtures of PE/EtO as eluent. Two butenolides 83 and 82 were obtained. 83: (8 mg, 0.03 mmol, 7.7%), white solid, mp = 119°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.05-7.34 (m, 10H, arom H); 4.42 (t, 2H, J = 6.3 Hz, H$_5$); 3.19 (t, 2H, J = 6.3 Hz, H$_4$). $^{13}$C NMR (100 MHz, CDCl$_3$)δ: 169.0 (C$_2$); 143.4 (C$_{7a}$); 141.5 (qC); 135.2 (C$_7$), 130.9-127.9 (arom HC and qC); 116.6 (C$_3$); 67.1 (C$_5$); 24.7 (C$_4$). HMRS (M+1) calcd for C$_{19}$H$_{15}$O$_2$ 291.1021. Found 291.1013. 82: (25 mg, 0.08 mmol, 21.6%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.71-7.37 (m, 10H, arom H); 4.88 (s, 1H, H$_{7a}$); 4.11 (dd, 1H, J = 6.6-7.4 Hz, H$_5$); 3.76 (dd, 1H, J = 3.4-11.7 Hz, H$_8$); 3.13-2.78 (m, 2H, H$_4$), 2.96 (s, 3H, H$_8$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 172.5 (C$_2$); 156.3 (C$_{3a}$); 137.5 (C$_3$); 130.8-125.0 (arom CH and qC); 101.1 (C$_1$); 82.8 (C$_{7a}$); 59.8 (C$_5$); 49.8 (C$_8$); 28.3 (C$_4$).

Reaction of complex 11b with sodium phenylbutynolate: 3,7-diphenyl-4,5-dihydro-furo[2,3-c]pyran-2-one 83 and 7-ethoxy-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 84

To a suspension of NaH (210 mg, 60% oil, 5.25 mmol, 3.3 equiv.) in THF (15 mL) was added a solution of 4-phenyl-but-3-yn-1-ol (255 mg, 1.75 mmol, 1.1 equiv.) in THF (10mL) and the mixture was stirred for 1 hour at room temperature. The resulting solution was cannulated to a solution of carbene complex 11b (518 mg, 1.59 mmol, 1 equiv.) in THF (15 mL) at -40 °C. The mixture was stirred 20 minutes at this temperature then allowed to warm to room temperature and stirred for 15 hours. Removal of the solvent left a brownish residue that was purified by silica gel
chromatography. 83 (116 mg, 0.397 mmol, 25%) and 84 (134 mg, 0.397 mmol, 25%) were obtained. 84 as a white solid, Mp = 150 °C. 1H NMR (200 MHz, CDCl3) δ: 7.72-7.36 (m, 10H, arom H); 4.66 (s, 1H, H7a); 4.11 (dd, 1H, J = 5.5-11.7 Hz, H5); 3.78 (dd, 1H, J = 2.9-11.8 Hz, H5); 3.28-3.06 (m, 3H, H4 and H8); 2.81 (m, 1H, H4); 1.06 (t, 3H, H9).

13C NMR (50 MHz, CDCl3) δ: 172.6 (C2), 156.3 (C3a), 138.6 (C3), 129.7-125.5 (arom HC and qC), 100.8 (C7), 82.8 (C7a), 59.7 (C5), 57.6 (C8), 28.3 (C4), 14.7(C9). HMRS (M+1) calcd for C21H21O3 337.1440. Found 337.1437.

To a suspension of NaH (154 mg, 60% oil, 3.9 mmol, 3.3 equiv.) in THF (15 mL) was added a solution of 4-phenyl-but-3-yn-1-ol (188 mg, 1.29 mmol, 1.1 equiv.) in THF (10 mL) and the mixture was stirred for 1 hour at room temperature. The resulting solution was cannulated to a solution of carbene complex 49a (500 mg, 1.17 mmol, 1 equiv.) in THF (15 mL) at -40 °C. The mixture was stirred 20 minutes at this temperature then allowed to warm to room temperature and stirred for 15 hours. Removal of the solvent left a brownish residue that was purified by silica gel chromatography. Two butenolides were obtained: 83 (100 mg, 0.345 mmol, 29%) and 85 (44 mg, 0.101 mmol, 9%) as a white solid, Mp = 142 °C. 1H NMR (400 MHz, CDCl3) δ: 7.7-7.1 (m, 15H, arom H); 4.7 (s, 1H, H7a); 4.1 (m, 2H, H5); 3.4 (ddd, 1H, J = 6-9-9 Hz, H1'); 3.2 (dq, 1H, J = 5-6.5-9 Hz H1'); 3.0 (dd, 1H, J = 2.8-13.5 Hz H4); 2.8 (ddd, 1H, J = 7.5-11.5-13.5 Hz H4); 2.6 (m, 1H, H2'). 13C NMR (100 MHz, CDCl3) δ: 172.7 (C2), 156.2 (C3a), 138 (Cq), 131.5-123.4 (arom and qC), 100.6 (C7), 86.9(C7a); 82.7(C7b), 81.6(C1'), 60.3 (C1'), 60.0 (C7), 28.3 (C4), 20.4(C2'). Anal. calcd. for C29H25O4: C, 79.8; H, 5.54. Found: C,79.4; H, 5.73.

**C- ORGANOLITHIUMS**

**Reaction of MeLi with carbene complex 49a : 7-Methyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one : 86a and 87a.**

To a solution of carbene complex 49a (350mg, 0.82 mmol) in THF (20 mL) cooled to -40°C was added methyllithium (520 µl, 1.6M, 0.82 mmol) by syringe and the resulting mixture was stirred 30 minutes at this temperature before being allowed to reach room temperature. After 12 hours, the solution was hydrolysed with aqueous
10% HCl and then extracted 3 times with CH₂Cl₂. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The residue was purified by thin layer chromatography (elution with 10% AcOEt/Cyclohexane) and the butenolide was obtained as two isomers (de = 22%). 86a (100 mg, 0.33 mmol, 40.2%) as a white solid, mp = 132°C. 1H NMR (400 MHz, CDCl₃) δ: 7.74-7.35 (m, 10H, arom H); 4.96 (s, 1H, H⁷); 4.21 (dd, 1H, J = 7.6-11.7 Hz, H⁴); 3.82 (dd, 1H, J = 3.5-11.7 Hz, H⁵); 3.12 (dd, 1H, J = 3.5-14.2 Hz, H⁴); 1.40 (s, 3H, H⁸). 13C NMR (100 MHz, CDCl₃) δ: 172.4 (C₂); 158.2 (C₃a); 145.5 (qC); 129.4 -124.9 (arom HC and qC); 83.2 (C⁷); 80.5 (C⁷'); 60.1 (C⁵); 28.7 (C₄); 17.5 (C₈). Anal. calcd. for C₂₀H₁₈O₃: C, 78.41; H, 5.92. Found: C, 78.44; H, 5.89.

87a (65 mg, 0.21 mmol, 25.6%) as a white solid, mp = 119°C. 1H NMR (400 MHz, CDCl₃) δ: 7.72-7.23 (m, 10H, arom H); 5.08 (s, 1H, H⁷); 4.00 (ddd, 1H, J =2.5 -6.2-11.7 Hz, H⁵); 3.64 (ddd, 1H, J = 5.5 -9.7-11.7Hz, H⁵'); 2.98-2.88 (m, 2H, H₄); 1.81 (s, 3H, H₈). 13C (50 MHz, CDCl₃) δ: 172.4 (C²); 158.3 (C₃a); 139.6 (qC); 129.3 -124.8 (arom HC and qC); 85.1 (C⁷); 80.7 (C⁷'); 60.8 (C⁵); 32.6 (C₈); 28.1 (C₄). Anal. calcd. for C₂₀H₁₈O₃: C, 78.41; H, 5.92. Found: C, 78.51; H, 6.05.

MeLi with carbene complex 49a: 7-Methyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 86a and 7a-Hydroxy-7-methyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 88.

To a solution of carbene complex 49a (800mg, 1.87 mmol) in THF (30 mL) at -40°C, under argon atmosphere was added methyllithium (1.6M, 1.23 mL, 1.97 mmol, 1.05 eq) by syringe. After 30 minutes, the ice bath was taken off and the mixture was allowed to stir at room temperature during 24 hours. The solvent was evaporated under vacuum and the residue was purified by chromatography on silicagel with mixture of EP/Et₂O as eluent. The butenolide 86a (107 mg, 0.35 mmol, 19%), then 88 (120 mg, 0.37 mmol, 20%) as a white solid, mp = 119°C. 1H NMR (400 MHz, CDCl₃) δ: 7.8-7.4 (m, 10H, arom H); 4.2 (ddd, 1H, J = 11.3-6.5-1.8Hz H⁵); 3.9 (dt, 1H, J = 11.3-4 Hz, H⁵'); 3.1-3 (m, 2H, H₄); 1.6 (s, 3H, Me). 13C NMR (100 MHz, CDCl₃) δ: 170.2 (C²); 158.3 (C³); 139.6 (qC); 129.3-126.6 (arom HC and qC); 102.1 (C⁵); 82.7 (C⁵'); 60.6 (C⁵); 26.9 (C₄'); 19.8 (Me) ; HRMS (M+1) calcd for C₂₀H₁₉O₄ : 323.1283 . Found : 323.1279.

MeLi with carbene complex 49a under O₂ atmosphere: 7a-Hydroxy-7-methyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 88.

To a solution of carbene complex 49a (804 mg, 1.89 mmol) in THF (30 mL) cooled to -40°C was added methyllithium (1.6M, 1.23 mL, 1.97 mmol, 1.05 eq) by syringe and the resulting mixture was stirred 30 minutes at this temperature before being allowed to reach room temperature. The flask was purged with O₂ and the solution stirred during 12 hours. Silicagel
was introduced and the solvent was evaporated under reduce pressure. The residue was purified by chromatography (elution EP/Et₂O). The lactonol 88 (89 mg, 0.28 mmol, 14.5%) was obtained.

**MeLi with carbene complex 49h**

4,5,7-Trimethyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 89 and 90. 7a-Hydroxy-4,5,7-trimethyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 91 and 92.

![Chemical structures of compounds 89, 90, 91, and 92](image)

To a solution of carbene complex 49h (839 mg, 1.82 mmol) in THF (30 mL) at -40°C was added methyllithium (1.4 L, 1.6 M, 2.22 mmol) by syringe. After 30 minutes the ice bath was taken off and the mixture allowed to stir at room temperature. After 24 hours, silicagel was introduced in the flask and the solvent was evaporated under reduce pressure. The residue was purified by chromatography (elution EP/Et₂O) and the butenolide was obtained as two isomers (de = 8%).

**89** (136 mg, 0.41 mmol, 22%) as a white solid, mp = 168°C.

**1H NMR (400 MHz, CDCl₃)**: δ: 7.6-7.2 (m, 10H, arom H); 5.3 (d, 1H, J = 6-9.6 Hz, H⁷ᵃ); 3.5 (dq, 1H, J = 6-9.6 Hz, H⁵); 3.1 (dq, 1H, J = 7-9.6 Hz, H⁴); 1.4 (d, 3H, J=6Hz, Me⁵); 1.3 (s, 3H, J=6Hz, Me⁷); 1.1 (d, 3H, J=7Hz, Me⁴).

**13C NMR (100 MHz, CDCl₃)**: δ: 173.4 (C²); 164.8 (C³a); 146.4 (C³); 133.9-124.7 (arom HC and qC); 82.0 (C⁷ᵃ); 81.5 (C⁷); 73.1 (C⁵); 40.6 (C⁴); 25.6 (Me⁵); 19.4 (Me⁷); 15.7 (Me⁴). HRMS (M+1) calcd for C₂₂H₂₃O₃: 335.1647, Found: 335.1643.

**90** (159 mg, 0.48 mmol, 26%) as a white solid, mp = 146°C. 

**1H NMR (400 MHz, CDCl₃)**: δ: 7.7-7.3 (m, 10H, H arom); 4.8 (s, 1H, H⁷ᵃ); 3.6 (dq, 1H, J =9.4-5.8 Hz, H⁵); 2.5 (dq, 1H, J = 9.4-6.8Hz, H⁴); 1.42 (s, 3H, Me⁷); 1.40 (d, 3H, J=5.8Hz, Me⁵); 0.90 (d, 3H, J=6.8Hz, Me⁴).

**13C NMR (50 MHz, CDCl₃)**: δ: 173.6 (C²); 161.7 (C³a); 145.5 (qC); 130.2-125.0 (arom HC and qC); 84.0 (C⁷ᵃ); 79.7 (C⁷); 72.6 (C⁵); 42.5 (C⁴); 19.8 (Me⁵); 17.9 (Me⁷). 14.1 (Me⁴).

Further elution furnished lactonol as two isomers (de =20%).

**91** (24 mg, 0.068 mmol, 3.7%) as a white solid, mp=140°C. 

**1H NMR (400 MHz, CDCl₃)**: 7.7-7.3 (m, 10H, H arom); 4.1 (dq, 1H, J=9.5-6Hz, H⁴); 3.4 (s, 1H, , OH); 3.0 (dq, 1H, J=9.5-7Hz, H⁵); 1.46 (s, 3H, , Me³); 1.42 (d, 3H, J=6Hz, Me⁵); 1.2 (d, 3H, J=7Hz, Me⁴).

**13C NMR (50 MHz, CDCl₃)**: δ: 170.8 (C²); 161.0 (C³a); 140.0 (qC); 129.5-125.0 (arom HC and qC); 84.0 (C⁷ᵃ); 82.0 (C⁷); 72.5 (C⁵); 40.1 (C⁴); 27.9 (Me³); 19.5 (Me⁵); 16.2 (Me⁷). 16 (mg, 0.046 mmol, 2.5%) as an oil. 

**92** (16 mg, 0.046 mmol, 2.5%) as an oil. 

Further elution furnished lactonol as two isomers (de =20%).
BuLi with carbene complex 49a: 7-Butyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 86c and 87c

To a solution of carbene complex 49a (500 mg, 1.17 mmol) in THF (30 mL) cooled to -40°C was added butyllithium (470 µL, 2.5 M, 1.17 mmol) by syringe and the resulting mixture was stirred 30 minutes at this temperature before being allowed to reach room temperature. After 24 hours, the solution was hydrolysed with aqueous 10% HCl and then extracted 3 times with CH$_2$Cl$_2$. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under reduced pressure, the residue was purified by chromatography (elution EP/Et$_2$O). The butenolide was obtained as two isomers 86c and 87c (de > 90%).

86c trans isomer, viscous oil (173 mg, 0.5 mmol, 43%).

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.61–7.16 (m, 10H, H arom), 4.73 (s, 1H, H$^{7a}$); 4.08 (dd, 1H, J = 7.6–11.7 Hz, H$^5$); 3.54 (dt, 1H, J = 3.0–11.7 Hz, H$^{5'}$); 3.01 (dd, 1H, J = 3.0–14.2 Hz, H$^4$); 2.76 (ddd, 1H, J = 7.6–11.7–14.2 Hz, H$^{4'}$); 1.72 (m, 1H, H$^8$); 1.6 (m, 1H, H$^{8'}$); 1.02 (m, 3H, H$^9$); 0.78 (m, 1H, H$^{9'}$); 0.67 (t, 3H, J = 7.5 Hz, CH$_3$).

$^{13}$C (50 MHz, CDCl$_3$) δ: 172.5 (C$^2$); 158.2 (C$^{3a}$); 143.7 (qC); 129.5–125.2 (arom HC and qC); 84.1 (C$^7$); 82.3 (C$^7$); 58.8 (C$^5$); 28.7 (C$^4$); 27.1 (C$^8$); 23.3 (C$^{10}$); 14.1 (CH$_3$). HRMS (M+1) calcd for C$_{23}$H$_{25}$O$_3$: 349.1804, Found: 349.1801.

Trimethylsilylmethyl lithium with carbene complex 49a: 7-(trimethyl-silylanylmethyl)-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 86d and 87d

To a solution of carbene complex 49a (500 mg, 1.17 mmol) in THF (30 mL) at -40°C was added butyllithium (2.34 µL, 1 M, 4.4 mmol) by syringe. After 30 min, the ice bath was taken off and the mixture allowed to stir at room temperature during 24 hours. The solution was hydrolysed with aqueous 10% HCl and extracted 3 times with CH$_2$Cl$_2$. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixture of EP/Et$_2$O as eluent. The butenolide was obtained as a mixture of isomers 86d and 87d (de > 90%).

86d trans isomer, yellow solid Mp = 97°C.

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.70–7.29 (m, 10H, H arom), 4.69 (s, 1H, H$^{7a}$); 4.14 (dd, 1H, J = 7.0–11.7 Hz, H$^5$); 3.54 (dt, 1H, J = 3.0–11.7 Hz, H$^{5'}$); 3.01 (dd, 1H, J = 3.0–14.2 Hz, H$^4$); 2.76 (ddd, 1H, J = 7.0–11.7–13.5 Hz, H$^{4'}$); 1.27 (d, 1H, J = 16Hz, H$^8$); 1.1 (d, 1H, J = 16Hz, H$^{8'}$); 0.3 (s, 9H, 3CH$_3$).

$^{13}$C (50 MHz, CDCl$_3$) δ: 172.6 (C$^2$); 157.9 (C$^{3a}$); 145.2 (qC); 129.6–125.1 (arom HC and qC); 84.7 (C$^7$); 83.1 (C$^7$); 60.1 (C$^{10}$); 28.7 (C$^4$); 16.5 (C$^8$); -0.34 (3CH$_3$). HRMS (M+1) calcd for C$_{23}$H$_{27}$O$_3$Si: 379.1716, Found: 379.1718.

Ethyllithium with carbene complex 49a: 7-ethyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 86b, 87b and 53a.
To a solution of carbene complex 49a (600 mg, 1.4 mmol) in THF (25 mL) at -40°C, under argon was added ethyllithium (282 µl, 0.5M, 2.8 mmol, 2 equiv.) by syringe. After 30 min, the ice bath was taken off and the mixture allowed to stir at room temperature during 24 hours. The solvent was evaporated under vacuum and the mixture was purified by chromatography on silica gel with mixtures of EtO/PrOH as eluent. Two butenolides 86b and 87b (de>90%) were obtained. 86b (113 mg, 0.35 mmol, 25%) as a white solid, mp = 127°C. 1H NMR (200 MHz, CDCl3) δ: 7.7-7.3 (m, 10H, arom H); 4.8 (s, 1H, H1); 4.15 (ddd, 1H, J = 0.9-6.5-11.5 Hz, H2); 3.6 (dt, 1H, J = 3-11.5 Hz, H3); 3.1 (dd, 1H, J = 3-14 Hz, H4); 2.85 (m, 1H, H4); 1.8 (m, 2H, H7); 0.6 (t, 3H, J=7Hz,H9). 13C NMR (50 MHz, CDCl3) δ: 172.5 (C2); 158.2 (C3a); 143.3 (qC); 129.5-124.4 (arom HC and qC); 84 (C7a); 82.5 (C7); 59.7 (C5); 28.7 (C4); 20.3 (C9); 5.5 (C9). HRMS (M+1) calcd for C21H21O3: 321.1491. Found : 321.1486. And 53a (40 mg, 0.14 mmol, 10%).

Phenylpentynyllithium with carbene complex 95:3-Phenyl-7-o-tolyl-5,6-dihydro-4H-benzofuran-2-one 96

at -78°C, 2.6 ml of t-Butyllithium (1.6N, 4.4 mmol, 3 eq.) was added to a solution of (5-iodo-pent-1-ynyl) benzene (600 mg, 2.2 mmol, 1.5 eq) in pentane (19ml) and ether (10ml). The mixture was stirred 15 mn and was cannulated to a solution of carbene complex (500mg, 1.47 mmol) in ether (20ml) at -78°C. The mixture first became clear red then gradually deep purple. After 1/2 h, the mixture was allowed to reach room temperature and stirred 12 hours. After hydrolysis and extraction with dichloromethane, the residue was purified on thin layer chromatography (elution with 10% AcOEt/ Cyclohexane): the UV fluorescent stripe under the unreactive carbene complex furnished 96 (70mg, 0.231 mmol, 16%) as an oil. 1H NMR(200 MHz, CDCl3) δ: 7.69-7.20 (m, 10H, H arom), 2.93 (t, 2H, J=6Hz, H4 or H6); 2.61 (t, 2H, J=6 Hz, H4 or H6); 2.23 (s, 3H, CH3); 1.97 (qt, 2H, J=6Hz, H5). 13C NMR (50 MHz, CDCl3) δ: 169.3 (C2); 148.0 (C7a); 145.1 (qC); 136.4-125.7 (arom HC and qC); 124.5 (C3); 121.2 (C7); 30.6 (C4); 24.6 (C6); 23.4 (C5); 20.3 (CH3). HRMS (M+1) calex for C21H19O2 : 303.1385, Found : 303.1384 .

D. ORGANOMAGNESIUMS

Ethylmagnesium bromide with carbene complex 49a

General procedure

To a solution of carbene complex 49a (1 mol eq) in THF (25 mL/mmol) at -40°C, under argon was added ethylmagnesium bromide (3 M in ether, x mol equiv.) by syringe. After 20 mn, the ice bath was taken off and the
mixture allowed to stir at room temperature during 24 hours. The solution was hydrolysed with a saturated solution of NH₄Cl and extracted 3 times with CH₂Cl₂. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixture of EP/Et₂O as eluent.

**Obtention of butenolides 93: 7-ethyl7a-hydroxy-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one and 53a**

The general procedure was followed using carbene 49a (300mg, 0.704 mmol) and 1.2 equivalent of ethylmagnesium bromide (0.845mmol, 282 µL). butenolide 53a was obtained (5 mg, 0.017 mmol, 2%) then 93 (21 mg, 0.062mmol, 9%) as a white solid, mp = 138°C. ¹H NMR (200 MHz, CDCl₃) δ : 2.9 (m, 1H, J = 3-11 Hz, H³); 2.5 (m, 1H, H⁴); 2.9 (m, 1H, J = 3-12.4 Hz, H⁴); 2.2 (m, 1H, H⁵ or H¹⁰); 2.1 (m, 1H, H⁸ or H¹⁰); 1.4 (m, 1H, H⁸ or H¹⁰); 1.2 (m, 1H, H⁸ or H¹⁰); 1.0 (t, 3H, J=7.5 Hz, H⁹ or H¹¹); 0.4 (t, 3H, J=7.5 Hz, H⁹ or H¹¹). ¹³C NMR (100 MHz, CDCl₃) δ : 177.6 (C²); 155.2 (C³); 133.9 (qC); 130.0-125.5 (arom HC and qC); 113.9 (C¹); 90.3 (C⁵); 64.5 (C⁷); 33.0 (C⁴); 29.7 (C¹⁰) 19.7 (C⁸); 11.5 (C¹¹); 7.4 (C⁶). HRMS (M+1) calcd for C₂₁H₂₁O₄: 337.1440. Found : 337.1442.

**Obtention of butenolides 93 and 7,7a-diethyl-3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-c]pyran-2-one 94.**

The general procedure was followed using carbene 49a (655mg, 1.54 mmol) and 2 equivalents of ethylmagnesium bromide (3.08 mmol, 1.03mL). butenolide 94 was obtained (79 mg, 0.23mmol, 15%) was obtained as an oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.5-7.2 (m, 10H, arom H); 4.5 (q, 1H, J = 8 Hz, H⁵); 2.9 (m, 1H, H³); 2.4 (dd, 1H, J = 3-8.12 Hz, H⁴); 2.2 (m, 1H, H⁸ or H¹⁰); 2.1 (m, 1H, H⁸ or H¹⁰); 1.4 (m, 1H, H⁸ or H¹⁰); 1.2 (m, 1H, H⁸ or H¹⁰); 1.0 (t, 3H, J=7.5 Hz, H⁹ or H¹¹); 0.4 (t, 3H, J=7.5 Hz, H⁹ or H¹¹). ¹³C NMR (100 MHz, CDCl₃) δ : 177.6 (C²); 155.2 (C³); 133.9 (qC); 130.0-125.5 (arom HC and qC); 113.9 (C¹); 90.3 (C⁵); 64.5 (C⁷); 33.0 (C⁴); 29.7 (C¹⁰) 19.7 (C⁸); 11.5 (C¹¹); 7.4 (C⁶). HRMS (M+1) calcd for C₂₃H₂₅O₃: 349.1804. Found : 349.1800. then 93 (23 mg, 0.07mmol, 5%).

**Methylmagnesium bromide with complexe 49a**
To a solution of carbene complex 49a (600 mg, 1.4 mmol) in THF (25 mL) at -40°C, under argon was added methylmagnesium bromide (3 M in ether, 2.8 mmol, 950 µL) by syringe. After 20 min, the ice bath was taken off and the mixture allowed to stir at room temperature during 24 hours. The solution was hydrolysed with a saturated solution of NH₄Cl and extracted 3 times with CH₂Cl₂. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixture of EP/Et₂O as eluent and the butenolide was obtained as two isomers (de=46%) 86a (93 mg, 0.3 mmol, 22%) and 87a (33 mg, 0.10 mmol, 8%).

**E- PECULIAR CASES**

**Sodium Phenylthiolate with complex 49a: [4-(1-Methyl sulfanyl-benzyloxy) but-1-ynyl] benzene 98a**

To a suspension of sodium hydride (80 mg, 60% oil, 1.64 mmol, 2 equiv.) in THF (25 ml) was added thiophenol by syringe (0.2 ml, 2 equiv.), the mixture was stirred at room temperature during 15 min. A solution of carbene complex 49a (350 mg, 0.82 mmol) in THF (5 ml) was canulated to the resulting mixture cooled to – 40°C then stirred 30 mn at this temperature and allowed to reach room temperature. After one hour, the mixture was heated to reflux and stirred at this temperature during 12 hours. After hydrolysis and extraction with dichloromethane, the residue was purified by thin layer chromatography (elution with 5% AcOEt/ Cyclohexane). The first stripe at the top of the plate gave PhSSPh (168 mg, 0.77 mmol). The second one furnished 98a as an oil (129 mg, 0.37 mmol, 46%). 

**1H NMR (200 MHz, CDCl₃)**:
- 7.53-7.12 (m, 15H, H arom), 5.89 (s, 1H, H'₂)
- 4.01 (q, 1H, J =7- 8.8 Hz, H₁)
- 3.73 (q, 1H, J = 7-8.8 Hz, H₁')
- 2.76 (t, 2H, J = 7Hz, H²)

**13C NMR (50 MHz, CDCl₃)**:
- 139.1-126.4 (arom)
- 89.5 (C²')
- 86.7-83.57 (C³, C⁴')
- 67.0 (C¹)
- 20.7 (C²)

**HRMS (M+1) calcd for C₂₃H₂₁O₃S : 345.1313, Found : 345.1309**.

**Tetramethylammoniumcyanide with carbene complex 11b: ethoxy-phenyl-acetonitrile 100.**

Tetramethylammonium cyanide (156 mg, 1 mmol) was added at room temperature to a solution of carbene complex 11b (326 mg, 1 mmol) in THF (20 mL). The red solution became slowly greenish. After 12 hours, the solution was hydrolysed with aqueous NH₄Cl then extracted 3 times with CH₂Cl₂. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue purified by chromatography (elution EP/AcOEt). The first product eluted was ethylbenzoate (66 mg, 0.44 mmol, 44%). Further elution furnished 100b as an oil (31 mg, 0.19 mmol, 19%).

**Tetramethylammoniumcyanide with carbene complex 11b and 2-cyclopentenone: Ethoxy-(3-oxo-cyclopentyl)-phenyl-acetonitrile 101.**
Tetramethylammonium cyanide (312mg, 2mmol) was added at room temperature to a solution of carbene complex 11b (652mg, 2mmol) and 2-cyclopentenone (300µL, 4eq) in THF (50mL) the resulting mixture was refluxed during 12 hours. The solution was hydrolysed with aqueous NH₄Cl then extracted 3 times with CH₂Cl₂. The organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue purified by chromatography (elution EP/AcOEt). 101 was obtained as a colorless liquid, a mixture of diastereoisomers (de=30%) (228mg, 0.94mmol, 47%). ¹H NMR (400 MHz, CDCl₃) δ: 7.48-7.37 (m, 5H, arom H); 3.61 (m, 1H, H⁷); 3.32 (m, 1H, H⁷'); 2.72 (m, 1H, H⁵); 2.50-1.73 (m, 6H, H⁵, H⁴, H²); 1.22 and 1.20 (t, 3H, H⁸); ¹³C NMR (100 MHz, CDCl₃) δ: 216.3 and 215.8 (C¹); 136.2(qC); 129.4-125.7(arom HC); 117.6 (CN); 84.4 and 83.7 (C⁶); 62.8(C⁷); 48.5 (C³); 40.9 and 40.6,38.2 and 38.1, 24.7 (C³, C¹² and C⁶); 14.9 (C³). HRMS (EI⁺), calcd. for C₁₅H₁₅O₂N: 244.1338. Found: 244.1315.

Tetramethylammonium cyanide with complex 49a: Phenyl-(4-phenyl-but-3-ynyloxy) acetonitrile 98b.

Tetramethylammonium cyanide (128mg, 0.82mmol) was added at 0°C to a solution of carbene complex 49a (350mg, 0.82mmol) in anhydrous CH₂Cl₂ (10mL). The solution turned from red to yellow. 15 mn later, the solution was allowed to reach room temperature and stirred for 24 hours. Water was added. After extraction 3 times with CH₂Cl₂, the organic layers were combined, washed with brine and finally dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue purified by chromatography (elution EP/EtO). 98b was obtained as an oil (50mg, 0.19mmol, 23%). IR: ν CN : 1947 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ: 7.53-7.29 (m, 10H, H arom), 5.40 (s, 1H, H²); 3.85 (m, 2H, H¹); 2.77 (t, 2H, J = 6.5 Hz, H²'); 1.83-1.14 (m, 8H, H³, H⁴, H⁵, H⁶); 1.03 (t, 3H, H⁸). ¹³C NMR (50 MHz, CDCl₃) δ: 133.2-123.3 (arom); 117.1 (CN); 85.7 (C³); 82.1 (C¹); 70.9 (C²); 67.9 (C¹'); 20.7 (C²'). HRMS (M+1) calcd for C₁₈H₁₄O₂N : 262.1232, Found : 262.1230.
Crystal Structure Determinations of 53g, 53h, 53k, 57a, 83, 84, 86a, 88, and 91. Diffraction experiments were performed on an Enraf-Nonius CAD-4 (53g, 84, 86a, and 88), Enraf-Nonius MACH-3 (53h, 53k, 83, and 91) and Enraf-Nonius Kappa-CCD (57a) at room temperature (293K) with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS*) and refined with CRYSTALS** (on F) by full-matrix least-squares. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and introduced as fixed contributors in the last refinements with an overall isotropic displacement parameter. Details of the crystal determinations, data collections and refinements are summarized in table....Further informations are available from the cif-files.


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Table S1. (continued) Crystal structure data for 83, 84, 86a, 88 and 91.

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